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A Novel Chiral Niobium Complex for Lewis Acid-catalyzed Enanioselective Reactions; Design of a Tridentate Chiral Ligand and Elucidation of the Catalyst Structure

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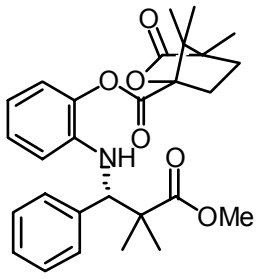
I. Determination of the absolute configuration of the (–)-camphanic ester of 3a

For the absolute configuration and the optical rotation of Mannich-type adduct **3a**, there are confusions in literature.[1] The absolute configuration of **3a** was determined by converting to the corresponding (–)-camphanic ester. Thus, **3a** (98% ee) was treated with (–)-camphanic chloride, pyridine, and DMAP in CH_2Cl_2 at 0 ˚C, and the desired product was purified by recrystallization (ether-hexane). The obtained crystal was employed in X-ray crystal structure analysis (Figure S-1). Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-251939. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033, e-mail: deposit@ccdc.cam.ac.uk).

Figure S-1.



II. Experimental Section

General

^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA300, JNM-LA400, or JNM-LA500 spectrometer in $CDCl_3$, unless otherwise noted. Tetramethylsilane (TMS) served as internal standard (0 ppm) for ^1H NMR, and $CDCl_3$ was used as internal standard (77.0 ppm) for ^{13}C NMR, and dichloromethane served as internal standard (5.32 ppm) for ^1H NMR, and (53.8 ppm) for ^{13}C

NMR. IR spectra were measured with a JASCO FT/IR-610 spectrometer. Optical rotations were measured with a JASCO P-1010 polarimeter. High-performance liquid chromatography was carried out using following apparatuses; SHIMADZU LC-10AT (liquid chrmatograph), SHIMADZU SPD-10A (UV detecter), and SHIMADZU C-R6A Chromatopac. EI high-resolution mass spectra (EI-HRMS) were measured with JEOL JMX-SX-102 Mass Spectrometer. Column chromatography was conducted on Silica gel 60 (Merck) and preparative thin-layer chromatography was carried out using Wakogel B-5F. All solvents were distilled and dried over MS 4A. Niobium ethoxide was purchased from Sigma-Aldrich Co. Other niobium alkoxides were purchased from Kojundo Chemical Laboratory Co., Ltd. Ketene silyl acetals were synthesized according to the literature's method.[2] All imines were prepared by mixing appropriate aldehydes and 2-aminophenol in dichloromethane and DMF at room temperature in the presence of a small amount of MS4A, and were purified by silica gel chromatography and recrystallization. All reactions were carried out under argon atmosphere in well-dried glassware.

Typical Experimental Procedure for Asymmetric Reaction Using a Chiral Niobium Catalyst. A typical experimental procedure is described for the reaction of imine **1a** with ketene silyl acetal **2a**. To a solution of ligand **4c** (0.072 mmol) in toluene (0.30 mL) was added *N*-methylimidazole (NMI, 0.060 mmol) in toluene (0.60 mL) at room temperature. The mixture was stirred for 10 min at the same temperature. $Nb(OMe)_5$ (0.060 mmol) in toluene (0.60 mL) was added to the mixture, and then the reaction temperature was raised to 60 ^{o}C. The mixture was stirred for 3 h at the same temperature, and then cooled to room temperature. MS3A (100 mg) was prepared in the other flask. The mixture was transferred to another vessel in which MS3A was placed by using a cannnula (rinsed with dichloromethane (0.50 mL)), and then was stirred for 30 min at the same temperature. The mixture was cooled to -20 ^{o}C, and **1a** (0.60 mmol) in dichloromethane (0.70 mL) and **2a** (0.72

mmol) in dichloromethane (0.30 mL) were added successively. The reaction mixture was stirred for 48 h, and saturated aqueous $NaHCO_3$ was added to quench the reaction. The aqueous layer was extracted with dichloromethane, and the organic layer was dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, and the crude product was treated with THF-1*N* HCl (10:1) at 0 ^oC for 1 h. Then the solution was basified with saturated $NaHCO_3$ and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the crude product was purified by preparative thin layer chromatography (Benzene-ethyl acetate = 15:1) to afford the product **3a**. The optical purity was determined by HPLC analysis using a chiral column.

Typical Experimental Procedure for Non-Linear Effect Using a Chiral Niobium Catalyst. Optically pure (*R*)- and (*S*)- niobium catalysts were prepared respectively according to the typical experimental procedure. These catalyst solutions were mixed in appropriate ratios, and stirred for 18 h at room temperature, and then cooled to -20 ^oC. Imine **1a** (0.40 mmol) in dichloromethane (0.70 mL) and silicon enolate **2a** in dichloromethane (0.30 mL) were successively added. The reaction mixture was stirred for 48 h, and saturated aqueous $NaHCO_3$ was added to quench the reaction. After acidic work up, the crude product and recovered BINOL were purified by preparative thin layer chromatography (benzene-ethyl acetate = 15:1) to afford the product **3a**. The optical purity of the product and BINOL were determined by HPLC analysis using a chiral column.

Experimental procedure for the Mannich-type reaction using niobium-low ee ligand complexes. Preparation of low ee BINOL is following; optically pure (*R*)- and (*S*)- BINOL were mixed in dichloromethane in proper ratio, and stirred for 5 h at room temperature, and then, solvent was removed under reduced pressure for 2 h at the same temperature. The optical purity was determined by HPLC analysis using a chiral column. The asymmetric reaction was performed according to the typical experimental procedure.

Typical Experimental Procedure for NMR experiments of the catalyst. To ligand **4c** (0.144 mmol) in deuteriated dichloromethane (0.20 mL) was added *N*-methylimidazole (NMI, 0.144 mmol) in deuteriated dichloromethane (0.40 mL) at room temperature. The mixture was stirred for 10 min at the same temperature. $Nb(OEt)_5$ (0.120 mmol) in deuteriated dichloromethane (0.40 mL) was added to the mixture and stirred for 3 h at the same temperature. This sample was analyzed with NMR.

(*S*)-Methyl 2,2'-dimethyl-3-(2-hydroxyphenyl)amino-3-phenylpropionate (3a): $[\alpha]_D^{23}$ +29.9 (c 0.52, 1N HCl) (95% ee). IR (KBr) 3401, 1709, 1611, 1514, 1453, 1391 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.21 (s, 3H), 1.24 (s, 3H) 3.68 (s, 3H), 4.57 (s, 1H), 6.36-6.76 (m, 4H), 7.21-7.28 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 19.9, 24.2, 47.3, 52.1, 64.3, 113.2, 114.1, 117.6, 120.8, 127.3, 127.9, 128.3, 135.6, 138.9, 144.0, 178.0. HPLC: Daicel Chiralpak AD, hexane/^{i}PrOH = 9/1, flow rate =1.0 mL/min: t_R=9.3 min (3*R*), t_R=16.0 min (3*S*). Anal. Calcd for $C_{18}H_{21}NO_3$: C, 72.22; H, 7.07; N, 4.68. found: C, 72.28; H, 7.20; N, 4.62. HRMS: Calcd for $C_{18}H_{21}NO_3$ (M^+) 299.1522, found 299.1497. The absolute configuration of (*S*)- **3a** was determined by X-ray crystal structure analysis after conversion to the corresponding (-)-camphanic ester.

(*S*)-Methyl 3-(4-chlorophenyl)-2,2'-dimethyl-(2-hydroxyphenyl)amino propionate (3b): IR (KBr) 3359, 1709, 1610, 1513, 1490, 1450, 738 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.19 (s, 3H), 1.24 (s, 3H) 3.67 (s, 3H), 4.55 (s, 1H), 6.31-6.90 (m, 4H), 7.22 (s, 2H), 7.35 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 20.2, 24.7, 47.3, 52.4, 64.0, 113.3, 114.3, 117.9, 121.1, 128.2, 128.3, 129.7, 133.2, 135.4, 137.7, 144.0, 177.5. HPLC: Daicel Chiralpak AD, hexane/^{i}PrOH = 9/1, flow rate =1.0 mL/min: t_R =8.3 min (3*R*), t_R=16.7 min (3*S*). Anal. Calcd for $C_{18}H_{20}NO_3Cl$: C, 64.77; H, 6.04; N, 4.20. found: C, 64.47; H, 6.18; N, 4.01. HRMS: Calcd for $C_{18}H_{20}NO_3Cl$ (M^+) 333.1133, found 333.1109.

Methyl 2,2'-dimethyl-3-(2'-hydroxyphenylamino)-3-(4'-methoxyphenyl)propionate (3c): IR

(neat) 3420, 2979, 1715, 1612, 1510, 1252 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.20 (s, 3H), 1.22 (s, 3H), 3.68 (s, 3H), 3.76 (s, 3H), 4.50 (s, 1H), 6.39 (d, 1H, *J* = 7.9 Hz), 6.35 (dd, 1H, *J* = 7.6, 7.6 Hz), 6.62 (dd, 1H, *J* = 7.6, 7.6 Hz), 6.68 (d, 1H, *J* = 7.9 Hz), 6.81 (d, 1H, *J* = 8.5 Hz), 7.19 (d, 1H, *J* = 8.5 Hz). ^{13}C NMR ($CDCl_3$): δ 20.1, 24.4, 47.5, 52.2, 55.2, 64.2, 113.4, 114.3, 115.3, 117.2, 118.1, 119.7, 121.1, 129.4, 131.0, 135.6, 144.4, 158.8, 177.8. HPLC Daicel Chiralpak AD, hexane/^{i}PrOH = 9/1, flow rate = 1.0 mL/min: t_R = 11.1 min (3*R*), t_R = 28.0 min (3*S*). HRMS: Calcd for $C_{19}H_{23}NO_4$ (M^+) 329.1627, found 329.1638.

(*S*)-Methyl 2,2'-dimethyl-3-(2-hydroxyphenyl)amino 3-(1'-naphthyl)-propionate (3d): ^1H NMR ($CDCl_3$): δ 1.18 (s, 3H), 1.25 (s, 3H) 3.66 (s, 3H), 5.62 (s, 3H), 6.28-6.62 (m, 4H), 7.22-8.00 (m, 7H). ^{13}C NMR ($CDCl_3$): δ 19.9, 25.1, 48.4, 52.4, 57.8, 113.4, 114.2, 117.9, 121.2, 122.1, 123.2, 125.2, 125.3, 125.4, 126.1, 128.1, 129.1, 133.6, 135.3, 144.1, 177.9. HPLC: Daicel Chiralcel AD, hexane/^{i}PrOH = 9/1, flow rate =1.0 mL/min: t_R =10.6 min (3*R*), t_R=14.6 min (3*S*). Anal. Calcd for $C_{22}H_{23}NO_3$: C, 75.62; H, 6.63; N, 4.01. found: C, 75.48; H, 6.49; N, 3.94. HRMS: Calcd for $C_{18}H_{20}NO_3Cl$ (M^+) 349.1678, found 349.1668.

Methyl 2,2'-dimethyl-3-(2'-hydroxyphenylamino)-3-(2'-naphtyl)propionate (3e): IR (KBr) 3418, 1710, 1610, 1510, 1270, 736 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.26 (s, 3H), 1.29 (s, 3H), 3.70 (s, 3H), 4.71 (s, 1H), 6.40-6.70 (m, 4H) 7.41-7.46 (m, 3H), 7.75-7.81 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 20.2, 24.5, 47.6, 52.3, 64.8, 114.0, 114.3, 118.0, 121.1, 125.8, 126.2, 127.5, 127.6, 127.6, 127.9, 132.9, 133.0, 135.5, 136.7, 144.3, 177.7. HPLC Daicel Chiralpak AD, hexane/^{i}PrOH = 9/1, flow rate = 0.8 mL/min: t_R = 12.2 min (3*R*), t_R = 26.0 min (3*S*). HRMS: Calcd for $C_{22}H_{23}NO_3$ (M^+) 349.1678, found 349.1671.

(*R*)-Methyl 3-(2-hydroxyphenyl)amino-2,2'-dimethyl-3-(3'-thienyl)propionate (3f): IR (neat) 3413, 2978, 1708, 1608, 1513, 1446, 1267, 1192, 1140, 741 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.25(s, 3H), 1.28(s, 3H), 3.69(s, 3H), 4.66(s, 1H), 6.46-6.71 (m, 4H), 6.98(d, 1H, *J* = 5.6 Hz), 7.06(s, 1H), 7.21(s,

1H). ^{13}C NMR ($CDCl_3$): δ 20.4, 24.1, 47.2, 52.2, 61.2, 114.5, 115.1, 118.9, 121.1, 122.9, 125.2, 127.3, 135.3, 140.7, 145.0, 177.7. HPLC Daicel Chiralpak AD, hexane/^{i}PrOH = 9/1, flow rate = 1.0 mL/min, t_R = 9.2 min (3*S*), t_R = 14.3 min (3*R*).

(*S*)-Methyl 3-(2-hydroxy-5-trifluoromethylphenyl)amino-2,2'-dimethyl-3-phenylpropionate (3g): IR (neat) 1707, 1612, 1531, 1442, 1336, 1277, 1115 cm^{-}1. ^{1}H NMR ($CDCl_3$): δ 1.22 (s, 3H), 1.26 (s, 3H), 3.70 (s, 3H), 4.54 (s, 1H), 6.58 (s, 1H), 6.75 (d, 2H, *J* = 7.6 Hz), 7.23-7.32 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 20.2, 24.7, 47.3, 52.4, 64.5, 109.9, 113.6, 115.0, 123.2, 123.5, 127.8, 128.2, 135.7, 138.3, 137.0, 146.6, 177.9. HPLC Daicel Chiralpak AD, hexane/^{i}PrOH = 9/1, flow rate = 1.0 mL/min, t_R = 5.4min (3*R*), t_R = 7.3 min (3*S*).

***(S)-S*-Ethyl 3-(2-hydroxyphenyl)amino-3-phenylpropanethioate (3h):** IR (KBr) 3396, 1647, 1608, 1520, 1449, 1362 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.67 (t, 3H, *J* = 7.3 Hz), 2.83 (q, 2H, *J* = 7.3 Hz), 2.97 (dd, 1H, *J* = 5.4, 14.9 Hz), 3.07 (dd, 1H, *J* = 8.1, 14.9 Hz), 4.81 (dd, 1H, *J* = 5.4, 8.1 Hz), 6.44-6.71 (m, 4H), 7.20-7.33 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 14.4, 23.6, 51.4, 56.1, 114.4, 114.6, 118.8, 121.1, 126.3, 127.4, 128.6, 134.9, 141.7, 144.7, 198.4. HPLC: Daicel Chiralpak AS, hexane/^{i}PrOH = 19/1, flow rate =1.0 mL/min: t_R=26.6 min (3*S*), t_R=38.2 min (3*R*). Anal. Calcd for $C_{17}H_{19}NO_2S$: C, 67.74; H, 6.35; N, 4.65. found: C, 68.00; H, 6.54; N, 4.54. HRMS: Calcd for $C_{17}H_{19}NO_2S$ (M^+) 301.1138, found 301.1102.

***(S)-S*-Ethyl 3-(4'-chlorophenyl)-3-(2-hydroxyphenyl)amino-propanethioate (3i):** IR (neat) 3412, 1665, 1516, 1447, 742 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.21 (t, 2H, *J* = 7.4 Hz), 2.83 (q, 2H, *J* = 7.4 Hz), 2.96 (dd, 1H, *J* = 5.1, 14.9 Hz), 3.05 (dd, 1H, *J* = 8.3, 14.9 Hz), 4.78 (dd, 1H, *J* = 5.1, 8.3 Hz), 6.39-6.78 (m, 4H), 7.22-7.28 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 14.5, 23.7, 51.2, 55.6, 114.5, 115.0, 119.3, 121.2, 127.8, 128.9, 133.2, 134.6, 140.3, 144.7, 197.8. HPLC: Daicel Chiralpak AD, hexane/^{i}PrOH = 9/1, flow rate =1.0 mL/min: t_R=19.5 min (3*S*), t_R=24.3 min (3*R*). Anal. Calcd for $C_{17}H_{18}NO_2ClS$: C, 60.80; H, 5.40; N, 4.17. found: C, 60.85; H, 5.60; N, 3.99. HRMS: Calcd for $C_{17}H_{18}NO_2ClS$

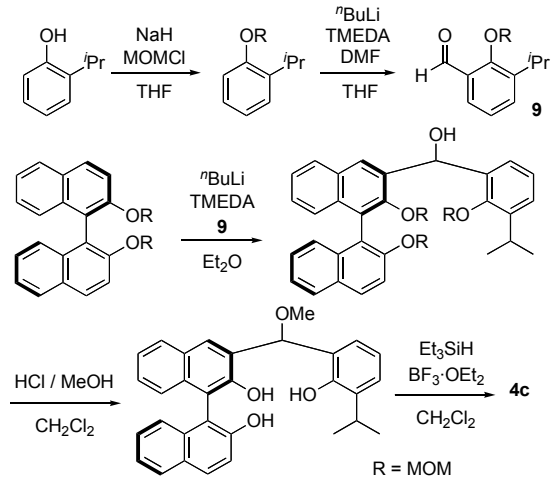
(M^+) 335.0747, found 335.9758.

***(S)-S*-Ethyl 3-(2'-furyl)-3-(2-hydroxyphenyl)amino-propanethioate (3j):** IR (neat) 3414, 1674, 1608, 1513, 1448, 1349, 740 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.32 (t, 3H, *J* = 7.3 Hz), 2.90 (q, 2H, *J* = 7.3 Hz), 3.06 (dd, 1H, *J* = 5.4, 15.6 Hz), 3.19 (dd, 1H, *J* = 8.3, 15.6 Hz), 4.81 (dd, 1H, *J* = 5.4, 8.3 Hz), 6.11 (d, 1H, *J* = 3.2 Hz), 6.26 (dd, 1H, *J* = 2.0, 3.2 Hz), 6.60-6.81 (m, 4H), 7.35 (d, 1H, *J* = 2.0 Hz). ^{13}C NMR ($CDCl_3$): δ 14.5, 23.6, 48.0, 50.8, 106.8, 110.2, 115.0, 118.0, 120.7, 121.5, 133.8, 142.0, 147.1, 153.8, 198.2. HPLC: Daicel Chiralcel AD, hexane/^{i}PrOH = 9/1, flow rate =1.0 mL/min: t_R= 8.9 min (3*R*), t_R= 15.4 min (3*S*). Anal. Calcd for $C_{15}H_{17}NO_3S$: C, 61.83; H, 5.88; N, 4.81. found: C, 61.86; H, 5.72; N, 4.80. HRMS: Calcd for $C_{15}H_{17}NO_3S$ (M^+) 291.0932, found 291.0931.

Syntheses of tridentate BINOL derivative (4)

A typical experimental procedure is described for the synthesis of **4c** (Sheme S-1).

Scheme S-1.



3-Isopropyl-2-methoxymethoxybenzaldehyde (9): 2-isoprorylphenol (15.1 g, 111 mmol) in THF (30 mL) was added to a suspension of sodium hydride (60%; 11.0 g, 275 mmol) in THF (120 mL)

at 0 °C. After stirring for 30 min at the same temperature, chloromethyl methyl ether (16.6 mL, 221 mmol) was added to the reaction mixture. The mixture was allowed to warm to room temperature, and was carefully quenched with MeOH and water. The aqueous layer was extracted with Et_2O, and the combined organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography to give 1-isopropyl-2-methoxymethoxybenzene (17.5 g, 87 % yield). A hexane solution of *n*-butyllithium (*n*-BuLi, 1.57 M; 64 mL, 100 mmol) was added to 1-isopropyl-2-methoxymethoxybenzene (15.0 g, 83.2 mmol) and TMEDA (100 mL, 53 mmol) in THF (200 mL) at –78 °C. After stirring for 30 min at –78 °C and for 1 h at 0 °C, the mixture was then cooled to –78 °C again. Dimethylformamide (15.9 mL) was added to the reaction mixture at –78 °C. The reaction mixture was allowed to warm to room temperature slowly, and then poured into a saturated aqueous NH_4Cl solution and extracted with Et_2O. The combined organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified with silica gel column chromatography to give 3-isopropyl-2-methoxymethoxybenz-aldehyde (12.88 g, 74% yield). ^{1}H NMR ($CDCl_3$): δ 1.25 (d, 6H, J = 7.1 Hz), 3.40 (sept, 1H, J = 7.1 Hz), 3.60 (s, 3H), 5.06 (s, 1H), 7.25 (dd, 1H, J = 7.6, 7.6 Hz), 7.55 (dd, J = 1.7, 7.6 Hz), 7.70 (dd, 2H, J = 1.7, 7.6 Hz), 10.3 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 23.5, 26.2, 57.8, 101.7, 125.0, 126.7, 129.7, 133.0, 143.0, 157.6, 191.0.

(*R*)-3-(2-Hydroxy-3-isopropylbenzyl)-[1,1']binaphthalene-2,2'-diol (4c) : A hexane solution of n-BuLi (1.57 M, 28.9 mL, 45.4 mmol) was added dropwise to (*R*)-2,2'-bis(methoxy-methyloxy)-1,1'-binaphthalene (14.2 g, 37.9 mmol) and tetramethylethylenediamine (6.8 mL, 45.1 mmol) in Et_2O (450 mL) at room temperature. The reaction mixture was stirred for 1.5 h at the same temperature, and then cooled to -78 ^{o}C. To this mixture was added 3-isopropyl-2-methoxymethoxybenzaldehyde (**9**, 4.77 g, 22.9 mmol) in Et_2O (50 mL) dropwise at the same

temperature. The reaction mixture was allowed to warm to room temperature slowly, and then poured into saturated aqueous NH_4Cl solution. The organic layer was separated, and the aqueous layer was extracted with Et_2O. The combined organic layer was washed with water and brine, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography to give (*R*)-(2,2'-dimethoxy-methoxy-[1,1']binaphthyl-3-yl)-(3-isopropyl-2-methoxymethoxyphenyl)methanol as ca. 1:1 diastereomer mixture (12.23 g, 92 % yield). Saturated methanolic HCl (35 mL) was added to this alcohol (12.23 g, 21.0 mmol) in dichloromethane (35 mL) at 0 ^oC. The reaction mixture was stirred for 2 h, and then neutralized with a saturated aqueous $NaHCO_3$ solution. The organic layer was separated, and then the aqueous layer was extracted with dichloromethane. The combined organic layer was washed with water, dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure to give the crude product, the residue was used for the subsequent reaction without purification. To this alcohol in dichloromethane (100 mL) was added triethylsilane (7.81 g, 67.2 mmol) at 0 ^oC, and then trifluoroborane etherate (9.24 g, 65.1 mmol) was added dropwise at the same temperature. The reaction mixture was stirred for overnight, and then neutralized with a saturated aqueous $NaHCO_3$ solution. The organic layer was separated, and then the aqueous layer was extracted with dichloromethane. The combined organic layer was washed with water and brine, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography to give (*R*)-3-(2-hydroxy-3-isopropylbenzyl)-[1,1']binaphthalene-2,2'-diol (6.18 g, 14.2 mmol, 68 % yield in 2 steps).

(*R*)-3-(2-Hydroxy-3-isopropylbenzyl)-[1,1']binaphthalene-2,2'-diol (4c): $[\alpha]_D^{30}$ +63.6 (c 1.03, THF). Mp 205-206 °C. IR (KBr) 3505, 3425, 1592, 1463, 820, 751 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.20 (d, 3H, *J* = 6.8 Hz), 1.21 (d, 3H, *J* = 6.8 Hz), 3.25 (sept, 1H, *J* = 6.8 Hz), 4.17 (d, 1H, *J* = 14.9 Hz),

4.23 (d, 1H, *J* = 14.9 Hz), 4.99 (s, 1H), 5.63 (s, 1H), 6.51 (s, 1H), 6.90 (ddd, 1H, *J* = 1.5, 7.5, 7.5 Hz), 7.08-7.11 (m, 3H), 7.22-7.39 (m, 6H), 7.82 (d, 1H, *J* = 7.9 Hz), 7.88 (d, 1H, *J* = 8.1 Hz), 7.93 (s, 1H), 7.97 (d, 1H, *J* = 9.0 Hz). ^{13}C NMR ($CDCl_3$): δ 22.5, 22.8, 27.1, 31.5, 108.9, 110.6, 111.5, 117.8, 120.6, 124.1, 124.2, 124.5, 124.9, 125.9, 127.1, 127.6, 128.0, 128.1, 128.5, 128.8, 129.5, 129.9, 131.2, 131.7, 132.2, 133.2, 135.8, 149.8, 151.1, 152.8. HPLC Daicel Chiralpak AD, hexane/2-PrOH = 9/1, flow rate = 1.0 mL/min: t_R = 10.8 min (*R*), t_R = 15.7 min (*S*). HRMS: Calcd for $C_{30}H_{26}O_3$ (M^+) 434.1882, found 434.1882.

(*R*)-3-(3-Ethyl-2-hydroxybenzyl)-[1,1']binaphthalene-2,2'-diol (4b): $[\alpha]_D^{30}$ +60.7 (c 1.05, THF). Mp 157-158 °C. IR (KBr) 3433, 1618, 1593, 1505, 1466, 752 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.20 (t, 3H, *J* = 7.5 Hz), 2.62 (q, 2H, *J* = 7.5 Hz), 4.16 (d, 1H, *J* = 15 Hz), 4.22 (d, 1H, *J* = 15 Hz), 4.99 (s, 1H), 5.62 (s, 1H), 6.41 (s, 1H), 6.87 (dd, 1H, *J* = 7.5, 7.5 Hz), 7.04-7.11 (m, 3H), 7.25-7.38 (m, 6H) 7.82 (d, 1H, *J* = 7.9 Hz), 7.89 (d, 1H, *J* = 7.9 Hz), 7.92 (s, 1H), 7.97 (d, 1H, *J* = 8.99 Hz). ^{13}C NMR ($CDCl_3$): δ 14.0, 23.3, 31.3, 110.6, 111.5, 117.8, 120.6, 124.1, 124.5, 125.8, 127.0, 127.6, 127.8, 128.0, 128.4, 128.4, 128.8, 129.5, 129.8, 131.1, 131.3, 131.6, 132.2, 133.2, 149.8, 151.7, 152.8. MS m/z 420 (M^+). Anal. Calcd for $C_{29}H_{24}O_3$: C, 82.83; H, 5.75. found: C, 82.61; H, 5.92.

(*R*)-3-(3-*tert*-Butyl-2-hydroxybenzyl)-[1,1']binaphthalene-2,2'-diol (4d): $[\alpha]_D^{30}$ +73.2 (c 1.20, THF). Mp 248-250 °C. IR (KBr) 3478, 1620, 1595, 1439, 1226, 751 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.38 (s, 9H), 4.17 (d, 1H, *J* = 15 Hz), 4.22 (d, 1H, *J* = 15 Hz), 4.99 (s, 1H), 5.59 (s, 1H), 6.71 (s, 1H), 6.87 (dd, 1H, *J* = 7.5, 7.7 Hz), 7.09-7.12 (m, 2H), 7.18-7.41 (m, 7H), 7.81 (d, 1H, *J* = 7.7 Hz), 7.90 (d, 1H, *J* = 8.1 Hz), 7.92 (s, 1H), 7.99 (d, 1H, *J* = 8.8 Hz). ^{13}C NMR ($CDCl_3$): δ 29.7, 31.4, 34.8, 110.4, 111.5, 117.8, 120.1, 124.0, 124.1, 124.2, 124.5, 125.7, 126.7, 127.1, 127.7, 128.1, 128.5, 128.6, 128.6, 129.5, 129.9, 131.2, 131.7, 132.1, 133.1, 137.2, 149.6, 152.9, 152.9. MS m/z 448 (M^+). Anal. Calcd for $C_{31}H_{28}O_3$: C, 83.01; H, 6.29. found: C, 82.87; H, 6.44.

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