Chiral Catalyst Optimization Using Both Solid-Phase and Liquid-Phase Methods in Asymmetric Aza Diels-Alder Reactions

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Supporting Information

General: Melting points were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA300, JNM-LA400, or JNM-LA500 spectrometer in $CDCl_3$ unless otherwise noted. SR-MAS NMR spectra[1] were measured on a JEOL JNM-LA-400 FT-NMR system. Tetramethylsilane (TMS) served as internal standard ($\delta = 0$) for ^{1}H NMR, and $CDCl_3$ was used as internal standard ($\delta = 77.0$) for ^{13}C NMR. Nitromethane served as external standard ($\delta = 0$) for ^{15}N NMR. IR spectra were measured with JASCO FT/IR-610 spectrometers. High-performance liquid chromatography was carried out using following apparatuses; SHIMADZU LC-10AT (liquid chromatograph), SHIMADZU SPD-10A (UV detector), and SHIMADZU C-R6A Chromatopac. Column chromatoghapy was conducted on Silica gel 60 (Merck) and preparative thin-layer chromatography was carried out using Wakogel B-5F. All chemical compounds were purified based on standard procedures.

Preparation of Polymer-Supported BINOLs: (*R*)-Ethyl-4-(2,2'-dimethoxy-1,1'-binaphth-6-yl)butanoate was prepared according to the literature.[2]

(*R*)-Ethyl-4-[2,2'-bis(methoxymethyloxy)-1,1'-binaphth-6-yl]butanoate (3). To a suspension of NaH (60% dispersion in mineral oil, 367 mg, 11.0 mmol) in DMF (10 ml) was added (*R*)-ethyl-4-(2,2'-dimethoxy-1,1'-binaphth-6-yl)butanoate (1.47 g, 3.67 mmol) in DMF (5 ml) and

the mixture was stirred at rt for 1 h. The mixture was then cooled to 0 °C, and MOMCl (886 mg, 11.0 mmol) was added. After stirred at rt for 1 h, water was added to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. After a usual work-up, the crude adduct was chromatographed on silica gel (hexane/AcOEt = 9/1) to afford **3** (1.71 g, 95%). ^{1}H NMR ($CDCl_3$) δ 1.24 (t, 2H, *J* = 7.0 Hz), 1.97-2.03 (m, 2H), 2.33 (t, 2H, *J* = 7.5 Hz), 2.76 (t, 2H, *J* = 7.5 Hz), 3.13 (s, 3H), 3.15 (s, 3H), 4.12 (q, 2H, *J* = 7.0 Hz), 4.95 (d, 1H, *J* = 6.8 Hz), 4.98 (d, 1H, *J* = 6.8 Hz), 5.06 (d, 1H, *J* = 6.8 Hz), 5.07 (d, 1H, *J* = 6.8 Hz), 7.05-7.09 (m, 2H), 7.15 (d, 1H, *J* = 7.9 Hz), 7.23 (ddd, 1H, *J* = 1.2, 7.3, 7.9 Hz), 7.34 (ddd, 1H, *J* = 1.2, 7.3, 7.6 Hz), 7.54 (d, 1H, *J* = 8.8 Hz), 7.57 (d, 1H, *J* = 9.1 Hz), 7.64 (s, 1H), 7.86 (d, 1H, *J* = 7.6 Hz), 7.87 (d, 1H, *J* = 9.1 Hz), 7.94 (d, 1H, *J* = 9.1 Hz); ^{13}C NMR ($CDCl_3$) δ 14.2, 26.3, 33.7, 35.0, 55.77, 55.82, 60.3, 95.2, 95.3, 117.3, 117.5, 121.2, 121.4, 124.0, 125.5, 125.6, 126.3, 126.6, 127.7, 127.8, 128.8, 129.3, 129.8, 130.0, 132.6, 134.0, 137.0, 152.2, 152.6, 173.5.

(*R*)-4-[2,2'-Bis(methoxymethyloxy)-1,1'-binaphth-6-yl]-1-butanol (4). To $LiAlH_4$ (80 mg, 2.1 mmol) in Et_2O/THF (5 ml each) was added **3** (1.65 g, 3.38 mmol) in THF (5 ml) at rt. After stirred for 45 min, H_2O (0,16 ml) and 1N NaOH (0.33 ml) were added. The mixture was filtered and the filtrate was dried (Na_2SO_4). After a usual work-up, the crude adduct was chromatographed on silica gel (hexane/AcOEt = 2/1) to afford **4** (1.51 g, quant). ^{1}H NMR ($CDCl_3$) δ 1.37 (brs, 1H), 1.59-1.65 (m, 2H), 1.71-1.78 (m, 2H), 2.75 (t, 2H, *J* = 7.6 Hz), 3.13 (s, 3H), 3.15 (s, 3H), 3.65 (t, 2H, *J* = 6.6 Hz), 4.94 (d, 1H, *J* = 7.0 Hz), 4.97 (d, 1H, *J* = 6.7 Hz), 5.05 (d, 1H, *J* = 7.0 Hz), 5.06 (d, 1H, *J* = 6.7 Hz), 7.07 (m, 2H), 7.16 (d, 1H, *J* = 8.5 Hz), 7.22 (ddd, 1H, *J* = 1.2, 6.7, 8.5 Hz), 7.33 (ddd, 1H, *J* = 1.2, 6.7, 8.2 Hz), 7.53 (d, 1H, *J* = 9.1 Hz), 7.56 (d, 1H, *J* = 9.1 Hz), 7.64 (s, 1H), 7.86 (d, 1H, *J* = 8.2 Hz), 7.87 (d, 1H, *J* = 8.8 Hz), 7.94 (d, 1H, *J* = 9.1 Hz); ^{13}C NMR ($CDCl_3$) δ 27.3, 32.3, 35.5, 55.77, 55.81, 62.8, 95.26, 95.31, 117.4, 117.5, 121.2, 121.5, 124.0, 125.5, 125.6, 126.2, 126.3, 127.78, 127.81, 128.8, 129.3, 129.9, 130.0, 132.5, 134.0, 137.9, 152.1, 152.6.

(*R*)-1-(*tert*-Butyldimethylsiloxy)-4-[2,2'-bis(methoxymethyloxy)-1,1'-binaphth-6-yl]-butane (5). To a mixture of **4** (1.39 g, 3.11 mmol) and imidazole (529 mg, 7.78 mmol) in DMF (4.7 ml) was added TBSCl (563 mg, 3.73 mmol) at rt. After stirred for 2 h, water was added to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. After a usual work-up, the crude adduct was chromatographed on silica gel

(hexane/AcOEt = 30/1) to afford **5** (1.73 g, quant). ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 6H), 0.88 (s, 9H), 1.54-1.60 (m, 2H), 1.68-1.75 (m, 2H), 2.73 (t, 2H, *J* = 7.8 Hz), 3.12 (s, 3H), 3.14 (s, 3H), 3.63 (t, 2H, *J* = 6.4 Hz), 4.94 (d, 1H, *J* = 6.7 Hz), 4.97 (d, 1H, *J* = 6.7 Hz), 5.04 (d, 1H, *J* = 6.7 Hz), 5.06 (d, 1H, *J* = 6.7 Hz), 7.07 (m, 2H), 7.16 (d, 1H, *J* = 8.5 Hz), 7.21 (ddd, 1H, *J* = 1.2, 6.7, 8.5 Hz), 7.33 (ddd, 1H, *J* = 1.2, 6.7, 8.2 Hz), 7.53 (d, 1H, *J* = 9.1 Hz), 7.56 (d, 1H, *J* = 9.1 Hz), 7.63 (s, 1H), 7.85 (d, 1H, *J* = 8.2 Hz), 7.86 (d, 1H, *J* = 9.1 Hz), 7.93 (d, 1H, *J* = 9.1 Hz); ^{13}C NMR ($CDCl_3$) δ -5.3, 18.3, 26.0, 27.4, 32.5, 35.5, 55.75, 55.79, 63.0, 95.3, 95.4, 117.40, 117.44, 121.3, 121.6, 124.0, 125.5, 125.6, 126.2, 126.3, 127.8, 127.9, 128.8, 129.3, 129.9, 130.1, 132.5, 134.0, 138.2, 152.1, 152.7.

(*R*)-1-(*tert*-Butyldimethylsiloxy)-4-[3,3'-dibromo-2,2'-bis(methoxymethyloxy)-1,1'-binaphth-6-yl]butane (6). To **5** (1.5 g, 2.67 mmol) in Et_2O (45 ml) was added *n*-BuLi (1.57M, 5.1 ml, 8.0 mmol) at rt, and the mixture was stirred for 3 h. The mixture was cooled to 0 °C, and to this mixture was added BrF_2CCF_2Br (2.43 g, 9.35 mmol) in THF (15 ml). After stirred at rt for 4 h, sat. NH_4Cl aq. was added to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. After a usual work-up, the crude adduct was chromatographed on silica gel (hexane/AcOEt = 30/1) to afford **6** (1.70 g, 90%). ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 6H), 0.88 (s, 9H), 1.54-1.60 (m, 2H), 1.67-1.77 (m, 2H), 2.55 (s, 3H), 2.75 (t, 2H, *J* = 7.7 Hz), 3.64 (t, 2H, *J* = 6.5 Hz), 4.79-4.83 (m, 4H), 7.09 (d, 2H, *J* = 8.5 Hz), 7.15 (dd, 1H, *J* = 1.5, 8.5 Hz), 7.20 (d, 1H, *J* = 8.3 Hz), 7.30 (ddd, 1H, *J* = 0.7, 7.1, 8.3 Hz), 7.44 (ddd, 1H, *J* = 0.7, 7.1, 8.1 Hz), 7.56 (brs, 1H), 7.80 (d, 1H, *J* = 8.1 Hz), 8.19 (s, 1H), 8.26 (s, 1H); ^{13}C NMR $CDCl_3$) δ -5.3, 18.3, 26.0, 26.2, 27.2, 32.4, 35.5, 56.2, 56.3, 62.9, 99.1, 117.2, 117.3, 125.3, 126.0, 126.4, 126.6, 126.8, 127.1, 127.5, 128.5, 131.4, 131.7, 132.4, 132.9, 133.1, 140.5, 149.4, 150.0.

(*R*)-4-[3,3'-Dibromo-2,2'-bis(methoxymethyloxy)-1,1'-binaphth-6-yl]-1-butanol (7). To **6** (1.53 g, 2.10 mmol) in THF (12 ml) was added Bu_4NF (4.2 ml (1M solution in THF), 4.2 mmol) at 0 °C. After stirred for 4 h at rt, water was added to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. After a usual work-up, the crude adduct was chromatographed on silica gel (hexane/AcOEt = 30/1) to afford **7** (1.20 g, 95%). ^{1}H NMR ($CDCl_3$) δ 1.45 (brs, 1H), 1.58-1.65 (m, 2H), 1.72-1.79 (m, 2H), 2.55 (s, 3H), 2.59 (s, 3H), 2.76 (t, 2H, *J* = 7.6 Hz), 3.66 (t, 2H, *J* = 6.6 Hz), 4.79-4.83 (m, 4H), 7.09 (d, 1H, *J* = 8.5 Hz), 7.15

(dd, 1H, *J* = 1.5, 8.5 Hz), 7.19 (d, 1H, *J* = 8.3 Hz), 7.30 (ddd, 1H, *J* = 1.2, 7.1, 8.3 Hz), 7.43 (ddd, 1H, *J* = 1.0, 7.1, 8.1 Hz), 7.57 (brs, 1H), 7.80 (d, 1H, *J* = 8.1 Hz), 8.17 (s, 1H), 8.26 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 27.2, 32.3, 35.5, 56.2, 56.3, 62.7, 99.1, 117.26, 117.29, 125.3, 126.0, 126.45, 126.53, 126.8, 127.1, 127.5, 128.4, 131.4, 131.5, 131.7, 131.9, 132.4, 132.9, 133.0, 140.2, 149.5, 150.0.

(*R*)-4-[3,3'-Dibromo-2,2'-bis(methoxymethyloxy)-1,1'-binaphth-6-yl]butoxymethyl polystyrene (8).[3] To a suspension of NaH (60% dispersion in mineral oil, 79.0 mg, 1.97 mmol) in DMF (10 ml) was added **7** (1.19g, 1.97 mmol) in DMF (6 ml) at rt. After stirred at the same temperature for 1.5 h, Merrifield resin (1.19 g, 1.97 mmol) and Bu_4NI (24.5 mg, 0.066 mmol) were added, and the mixture was stirred at rt for 24 h. A water/THF solution was added and afetr stirred for 10 min, the mixture was filtrated. The resin was washed with H_2O (20 ml x 3), THF (20 ml x 3), CH_2Cl_2 (20 ml x 3), and Et_2O (20 ml x 3). The resulting resin was dried under reduced pressure (1 mmHg) at 60 °C. The loading of **8** (0.375 mmol/g) was determined by the elementary analysis of bromine. ^{1}H SR-MAS NMR ($CDCl_3$) δ 1.41 (brs, polystyrene), 1.76 (brs, polystyrene), 2.55 (brs, 6H), 2.72 (brs, 2H), 3.45 (brs, 2H), 4.81 (brs, 4H), 6.55 (brs, polystyrene), 7.03 (brs, polystyrene), 7.36 (brs, 1H), 7.54 (brs, 1H), 7.74 (brs, 1H), 8.16 (brs, 1H), 8.24 (brs, 1H); ^{13}C SR-MAS NMR ($CDCl_3$) δ 27.7, 29.4, 35.5, 40.8 (polystyrene), 56.2, 69.9, 72.7, 99.1, 117.3, 125.3, 125.6 (polystyrene), 126.0, 126.4, 126.5, 126.8, 127.6 (polystyrene), 127.9 (polystyrene), 128.4, 131.4, 131.6, 132.4, 132.8, 133.1, 140.2, 145.2 (polystyrene), 149.4, 150.0.

(*R*)-4-[3,3'-Diphenyl-2,2'-bis(methoxymethyloxy)-1,1'-binaphth-6-yl]butoxymethyl polystyrene (9).[4] To a mixture of **8** (500.0 mg, 0.375 mmol/g) and $Pd(PPh_3)_4$ (43.0 mg, 0.037 mmol) in DMF (5 ml) were added phenylboronic acid (91.7 mg, 0.75 mmol) and aqueous sodium carbonate (2M; 0.46 ml). The mixture was stirred for 24 h under reflux conditions. After adding NH_4COOH aq., the mixture was filtered. The resulting resin was washed with H_2O (20 ml x 3), THF (20 ml x 3), CH_2Cl_2 (20 ml x 3), and Et_2O (20 ml x 3) to afford MOM ether **9**. ^{1}H SR-MAS NMR ($CDCl_3$) δ 1.44 (brs, polystyrene), 1.82 (brs, polystyrene), 2.34 (brs, 6H), 2.76 (brs, 2H), 3.46 (brs, 2H), 4.40 (brs, 4H), 6.55 (brs, polystyrene), 7.05 (brs, polystyrene), 7.34-7.42 (m, 7H), 7.75-7.92 (m, 6H); ^{13}C SR-MAS NMR ($CDCl_3$) δ 27.8, 29.5, 35.7, 40.3 (polystyrene), 55.8, 70.1, 72.8,

98.5, 125.1, 125.6 (polystyrene), 126.3, 126.6, 127.6 (polystyrene), 127.9 (polystyrene), 128.2, 129.6, 130.1, 130.4, 130.8, 131.0, 132.1, 133.6, 135.4, 139.2, 145.3 (polystyrene), 150.7, 151.3.

(*R*)-4-(3,3'-Diphenyl-2,2'-dihydroxy-1,1'-binaphth-6-yl)butoxymethyl polystyrene (10). A mixture of **9** and conc HCl/MeOH (1/25, 11 ml) was stirred at 60 °C for 6 h. After filtration, the resin was washed with H_2O (20 ml x 3), THF (20 ml x 3), CH_2Cl_2 (20 ml x 3), and Et_2O (20 ml x 3) to afford **10** (478 mg). ^{1}H SR-MAS NMR ($CDCl_3$) δ 1.44 (brs, polystyrene), 1.79 (brs, polystyrene), 2.74 (brs, 2H), 3.48 (brs, 2H), 5.34 (s, 1H), 5.38 (s, 1H), 6.57 (brs, polystyrene), 7.05 (brs, polystyrene), 7.26-7.44 (m, 4H), 7.72 (brs, 4H), 7.93 (m, 2H); ^{13}C SR-MAS NMR ($CDCl_3$) δ 27.9, 29.4, 35.6, 40.4 (polystyrene), 70.0, 72.8, 112.3, 112.7, 124.3, 125.6 (polystyrene), 127.0, 127.7 (polystyrene), 128.0 (polystyrene), 128.4, 128.9, 129.4, 129.6, 130.6, 130.9, 131.3, 131.4, 133.0, 137.5, 138.4, 145.2 (polystyrene), 149.6, 150.1.

Similarly, other polymer-supported BINOLs were prepared.

(*R*)-4-[3,3'-Bis(3-trifluoromethylphenyl)-2,2'-bis(methoxymethyloxy)-1,1'-binaphth-6-yl] butoxymethyl polystyrene. ^{1}H SR-MAS NMR ($CDCl_3$) δ 1.44 (brs, polystyrene), 1.83 (brs, polystyrene), 2.40 (brs, 6H), 2.77 (brs, 2H), 4.39 (brs, 4H), 6.66 (brs, polystyrene), 7.05 (brs, polystyrene), 7.61 (m, 4H), 7.94 (m, 4H); ^{13}C SR-MAS NMR ($CDCl_3$) δ 28.0, 29.8, 36.0, 40.7 (polystyrene), 56.3, 70.4, 73.1, 99.1, 124.3, 125.9 (polystyrene), 126.6, 127.1, 128.2 (polystyrene), 128.8, 129.0, 130.6, 131.0, 131.3, 131.6, 132.6, 133.5, 134.2, 134.4, 140.0, 140.2, 145.5 (polystyrene), 150.9, 151.5.

(*R*)-4-[3,3'-Bis(3-trifluoromethylphenyl)-2,2'-dihydroxy-1,1'-binaphth-6-yl] butoxymethyl polystyrene. ^{1}H SR-MAS NMR ($CDCl_3$) δ 1.42 (brs, polystyrene), 1.80 (brs, polystyrene), 2.73 (brs, 2H), 5.29 (s, 1H), 5.34 (s, 1H), 6.55 (brs, polystyrene), 7.05 (brs, polystyrene), 7.53 (m, 4H), 7.98 (4H): ^{13}C SR-MAS NMR ($CDCl_3$) δ 27.9, 29.4, 35.5, 40.3 (polystyrene), 70.0, 72.8, 111.8, 112.1, 122.9, 124.1, 124.3, 124.7, 125.6 (polystyrene), 126.5, 127.9 (polystyrene), 128.6, 129.1, 129.5, 130.1, 130.5, 130.8, 131.1, 131.4, 131.7, 132.9, 138.3, 138.4, 138.9, 145.2 (polystyrene), 149.4, 150.0.

(*R*)-4-[3,3'-Bis(3,5-bistrifluoromethylphenyl)-2,2'-dihydroxy-1,1'-binaphth-

6-yl] butoxymethyl polystyrene. ^{13}C SR-MAS NMR ($CDCl_3$) δ 27.8, 29.4, 35.5, 40.4 (polystyrene), 69.9, 72.8, 111.7, 112.0, 122.1, 124.0, 124.8, 125.1, 125.6 (polystyrene), 127.9 (polystyrene), 128.5, 128.8, 129.4, 129.6, 129.9, 130.1, 131.0, 131.4, 131.7, 132.1, 133.3, 139.4, 139.6, 139.7, 145.3 (polystyrene), 149.2, 149.8.

(*R*)-4-[3,3'-Bis(4-fluorophenyl)-2,2'-dihydroxy-1,1'-binaphth-6-yl] butoxymethyl polystyrene. ^{13}C SR-MAS NMR ($CDCl_3$) δ 27.9, 29.4, 35.6, 43.8 (polystyrene), 112.0, 112.3, 115.1, 115.4, 124.2, 124.5, 125.6 (polystyrene), 127.0, 128.0 (polystyrene), 128.4, 129.0, 129.4, 129.6, 131.0, 131.3, 132.9, 133.5, 138.6, 145.3 (polystyrene), 149.5, 150.1, 161.2, 163.7.

(*R*)-4-[3,3'-Bis(3,4-difluorophenyl)-2,2'-dihydroxy-1,1'-binaphth-6-yl] butoxymethyl polystyrene. ^{13}C SR-MAS NMR ($CDCl_3$) δ 27.9, 29.4, 35.5, 40.4 (polystyrene), 69.9, 72.8, 111.5, 111.9, 116.6, 116.7, 123.8, 124.2, 124.6, 125.6 (polystyrene), 126.6, 128.0 (polystyrene), 128.5, 129.1, 129.3, 129.6, 131.7, 132.2, 132.5, 133.3, 138.8, 145.3 (polystyrene), 147.1, 149.7, 150.4, 152.1.

(*R*)-4-[3,3'-Bis(3-tolyl)-2,2'-dihydroxy-1,1'-binaphth-6-yl] butoxymethyl polystyrene. ^{13}C SR-MAS NMR (100 MHz, $CDCl_3$) δ 21.5, 27.9, 29.4, 35.6, 40.3 (polystyrene), 70.0, 72.7, 112.4, 112.8, 124.1, 124.3, 125.6 (polystyrene), 126.6, 126.9, 127.9 (polystyrene), 128.3, 128.7, 129.3, 129.5, 130.2, 130.7, 131.1, 131.4, 132.9, 137.4, 138.0, 138.3, 145.2 (polystyrene), 149.4, 150.0.

(*R*)-4-[3,3'-Bis(4-tolyl)-2,2'-dihydroxy-1,1'-binaphth-6-yl] butoxymethyl polystyrene. ^{13}C SR-MAS NMR ($CDCl_3$) δ 21.2, 27.9, 29.4, 35.5, 40.3, 70.0, 72.7, 112.3, 112.7, 124.1, 124.3, 125.6 (polystyrene), 126.9, 127.9 (polystyrene), 128.6, 129.1, 129.4, 130.6, 131.0, 131.3, 132.8, 134.6, 137.4, 138.3, 145.2 (polystyrene), 149.6, 150.1.

(*R*)-4-[3,3'-Bis(4-*tert*-butylphenyl)-2,2'-dihydroxy-1,1'-binaphth-6-yl] butoxymethyl polystyrene. ^{13}C SR-MAS NMR ($CDCl_3$) δ 27.9, 29.4, 31.3, 34.6, 35.6, 40.3 (polystyrene), 70.0, 72.7, 112.2, 112.6, 124.1, 124.3, 125.4, 125.6 (polystyrene), 126.9, 127.9 (polystyrene), 128.6, 129.2, 129.4, 129.6, 130.4, 130.6, 131.0, 131.3, 132.8, 134.5, 138.3, 145.2 (polystyrene), 149.6, 150.2, 150.4.

(*R*)-4-[3,3'-Bis(3,5-xylyl)-2,2'-dihydroxy-1,1'-binaphth-6-yl] butoxymethyl polystyrene. ^{13}C SR-MAS NMR ($CDCl_3$) δ 21.3, 27.9, 29.4, 35.6, 40.3 (polystyrene), 70.0, 72.7, 112.6, 112.9,

124.0, 124.4, 125.6 (polystyrene), 126.9, 127.0, 127.9 (polystyrene), 128.2, 128.5, 129.4, 130.4, 130.8, 131.4, 133.0, 137.3, 138.0, 138.1, 145.2, 149.4, 149.9.

(*R*)-4-[3,3'-Bis(4-biphenyl)-2,2'-dihydroxy-1,1'-binaphth-6-yl] butoxymethyl polystyrene. ^{13}C SR-MAS NMR ($CDCl_3$) δ 27.9, 29.4, 35.6, 40.3, 70.0, 72.7, 112.2, 112.5, 124.3, 125.6 (polystyrene), 127.9 (polystyrene), 128.7, 129.6, 129.9, 130.8, 131.3, 132.9, 136.5, 138.4, 140.4, 140.7, 145.2 (polystyrene), 149.6, 150.2.

(*R*)-4-[3,3'-Bis(3-methoxyphenyl)-2,2'-dihydroxy-1,1'-binaphth-6-yl] butoxymethyl polystyrene. ^{13}C SR-MAS NMR ($CDCl_3$) δ 27.9, 29.5, 35.6, 40.4 (polystyrene), 55.3, 70.1, 72.8 112.5, 112.9, 113.5, 115.2, 121.9, 124.3, 124.4, 125.6 (polystyrene), 127.0, 128.0 (polystyrene), 128.9, 129.3, 129.5, 130.5, 130.7, 131.1, 138.4, 138.9, 145.3 (polystyrene), 149.4 150.0, 159.6.

(*R*)-4-[3,3'-Bis(4-methoxyphenyl)-2,2'-dihydroxy-1,1'-binaphth-6-yl] butoxymethyl polystyrene. ^{13}C SR-MAS NMR ($CDCl_3$) δ 27.9, 29.5, 35.6, 40.4 (polystyrene), 55.2, 70.1, 72.8, 112.3, 112.7, 113.9, 124.2, 124.3, 125.6 (polystyrene), 128.0 (polystyrene), 128.6, 129.5, 129.7, 129.9, 130.3, 130.4, 130.7, 131.2, 132.8, 138.3, 145.3 (polystyrene), 149.7, 150.2, 159.2.

(*R*)-4-[3,3'-Bis(3,4-dimethoxyphenyl)-2,2'-dihydroxy-1,1'-binaphth-6-yl]butoxymethyl polystyrene. ^{13}C SR-MAS NMR ($CDCl_3$) δ 27.9, 29.5, 35.6, 40.4 (polystyrene), 56.0, 70.0, 72.8, 111.3, 112.5, 113.0, 122.0, 124.4, 125.6 (polystyrene), 127.9 (polystyrene), 128.6, 129.4, 129.6, 130.3, 130.7, 131.3, 132.9, 138.4, 145.2, 148.9, 149.5, 150.1.

(*R*)-4-[3,3'-Bis(4-ethoxyphenyl)-2,2'-dihydroxy-1,1'-binaphth-6-yl] butoxymethyl polystyrene. ^{13}C SR-MAS NMR ($CDCl_3$) δ 14.9, 27.9, 29.5, 35.6, 40.4 (polystyrene), 63.5, 70.0, 72.8, 112.3, 112.7, 114.5, 124.2, 124.3, 125.6 (polystyrene), 127.0, 127.9 (polystyrene), 129.5, 129.7, 130.3, 130.7, 131.2, 132.8, 138.3, 145.3 (polystyrene), 149.7, 150.2, 158.7.

(*R*)-4-(3,3'-Di-2-naphthyl-2,2'-dihydroxy-1,1'-binaphth-6-yl) butoxymethyl polystyrene. ^{13}C SR-MAS NMR (100 MHz, $CDCl_3$) δ 27.9, 29.4, 35.6, 40.4 (polystyrene), 70.0, 72.8, 112.4, 112.8, 124.3, 125.6 (polystyrene), 126.2, 127.9 (polystyrene), 128.2, 128.5, 128.9, 129.5, 129.7, 130.6, 131.2, 131.5, 131.6, 132.7, 133.1, 133.4, 135.1, 138.4, 145.3 (polystyrene), 149.7, 150.3.

(*R*)-4-[3,3'-Bis(6-methoxy-2-naphthyl)-2,2'-dihydroxy-1,1'-binaphth-6-yl]

butoxymethyl polystyrene. ^{13}C SR-MAS NMR ($CDCl_3$) δ 27.9, 29.4, 35.6, 40.3 (polystyrene), 55.2, 70.0, 72.7, 105.6, 112.4, 112.8, 119.0, 124.2, 124.3, 125.6 (polystyrene), 126.7, 126.9, 127.9 (polystyrene), 128.2, 128.7, 128.9, 129.5, 129.7, 130.6, 130.9, 131.3, 131.4, 132.8, 132.9, 133.9, 138.3, 145.2 (polystyrene), 149.7, 150.3, 157.9.

(*R*)-4-(3,3'-Di-2-thienyl-2,2'-dihydroxy-1,1'-binaphth-6-yl) butoxymethyl polystyrene. ^{13}C SR-MAS NMR ($CDCl_3$) δ 27.8, 29.4, 35.5, 40.4 (polystyrene), 70.0, 72.8, 112.0, 112.3, 123.4, 124.1, 124.6, 125.6 (polystyrene), 126.1, 127.0, 128.0 (polystyrene), 129.1, 129.3, 129.5, 131.0, 132.5, 135.5, 138.7, 139.0, 139.1, 145.3 (polystyrene), 149.0, 149.6.

Preparation of 3,3'-Diaryl-BINOLs.[5] To a suspension of NaH (60 % dispersion in mineral oil; 1.15 g, 29.0 mmol) in DMF (30ml) was added (*R*)-(+)-1,1'-bi-2-naphthol ((*R*)-BINOL; 3.62 g, 12.6 mmol) in DMF (30 ml) at 0 °C. The mixture was stirred at the same temperature for 20 min, and MOMCl (2.0 ml, 12.6 mmol) was then added. The resulting mixture was gradually allowed to warm to rt over 1 h, and water was added to quench the reaction. The organic layer was separated and the aqueous layer was extracted with Et_2O. The combined organic layers were dried, and after evaporation, (*R*)-1,1'-bi-2-methoxymethyloxynaphthalene was obtained in a quantitative yield.

To a solution of (*R*)-1,1'-bi-2-methoxymethyloxynaphthalene (4.71 g, 12.6 mmol) in Et_2O (200 ml) was added *n*-BuLi in hexane (1.5M; 25.2 ml, 37.8 mmol) at rt. After 3 h, the solution was cooled to 0 °C. A THF (50 ml) solution of 1,2-dibromo-1,1',2,2'-tetrafluoroethane (11.5 g, 44.1 mmol) was added to the above mixture, and the resulting mixture was allowed to warm to rt over 4 h. Saturated NH_4Cl aq. was then added to quench the reaction, and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried, and after evaporation, the crude product was purified by column chromatography on silica gel (hexane-AcOEt = 5/1) to afford (*R*)-1,1'-bi-3-bromo-2-methoxymethyl-naphthalene (6.44 g, 96% yield).

To $Pd(PPh_3)_4$ (728 mg, 0.63 mmol) in DME (30 ml) was added (*R*)-1,1'-bi-3-bromo-2-methoxymethyl-naphthalene (6.44 g 12.1 mmol) in DME (40 ml) at rt. After 10 min, an arylboronic acid[6] (36.3 mmol) in ethanol and aqueous sodium carbonate (2 M; 12.1 ml) were added successively, and the resulting mixture was heated under reflux. After 18 h, insoluble materials

were removed by filtration, and DME was distilled off. Dichloromethane (100 ml) was added to the crude mixture and the dichloromethane solution was washed with water and brine. The solution was concentrated *in vacuo* to afford crude (*R*)-1,1'-bi-3-aryl-2-methoxymethyloxynaphthalene. To a THF solution (50ml) of crude (*R*)-1,1'-bi-3-aryl-2-methoxymethyloxynaphthalene was added conc. HCl (1.5 ml), and the acidic solution was warmed to 50 °C and stirred for 2 h. After a usual work-up, the crude mixuture was chromatographed on silica gel (hexane-AcOEt = 4/1) and then recrystalyzed from dichloromethane to afford 3,3'-diaryl-1,1'-bi-2-naphthol in a quantitative yield.

(*R*)-3,3'-Bis(4-fluorophenyl)-2,2'-dihydroxy-1,1'-binaphthyl. $[\alpha]_D^{28}$ +83.5 (*c* = 1.0, THF); IR (KBr) 514, 751, 832, 1127, 1164, 1230, 1359, 1402, 1443, 1512, 1594, 2926, 2954, 3055, 3506 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.31 (s, 2H), 7.12-7.17 (m, 4H), 7.20 (d, 2H, *J* = 8.2 Hz), 7.30 (ddd, 2H, *J* = 1.2, 7.0, 8.2 Hz), 7.38 (ddd, 2H, *J* = 0.9, 7.0, 7.9 Hz), 7.67-7.71 (m, 4H), 7.90 (d, 2H, *J* = 7.9 Hz), 7.98 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 112.1, 115.3 (d, J_{CF} = 20.7 Hz), 124.1, 124.5, 127.5, 128.4, 129.4, 129.7, 131.3 (d, J_{CF} = 8.3 Hz), 131.5, 132.9, 133.4 (d, J_{CF} = 4.1 Hz), 150.1, 162.5 (d, J_{CF} = 247.2 Hz).

(*R*)-3,3'-Bis(3-trifluoromethylphenyl)-2,2'-dihydroxy-1,1'-binaphthyl. $[\alpha]_D^{28}$ +39.4 (*c* = 1.0, THF); IR (KBr) 700, 751, 804, 896, 1127, 1167, 1235, 1333, 1422, 1502, 1621, 2928, 3059, 3510 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.35 (s, 2H), 7.22 (d, 2H, *J* = 7.9 Hz), 7.36 (ddd, 2H, *J* = 1.2, 7.0, 7.9 Hz), 7.42 (ddd, 2H, *J* = 1.2, 7.0, 7.9 Hz), 7.57-7.60 (m, 2H),), 7.66 (d, 2H, *J* = 7.9 Hz), 7.94 (t, 4H, *J* = 7.6 Hz), 8.03 (s, 2H), 8.06 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 111.9, 124.1, 124.2 (q, J_{CF} = 272.1 Hz), 124.4 (q, J_{CF} = 4.1 Hz), 124.8, 126.5 (q, J_{CF} = 4.1 Hz), 128.0, 128.66, 128.73, 129.3, 129.5, 130.8 (q, J_{CF} = 32.1 Hz), 132.0, 133.0, 133.1, 138.3, 150.1.

(*R*)-3,3'-Diphenyl-1,1'-bi-2-naphthol is a literature known compound.[5]

Preparation of 6,6'-Dibromo-3,3'-diphenyl-1,1'-bi-2-naphthol (3).[7] A solution of 3,3'-diphenyl-BINOL (11.0 mmol) in dichloromethane (60 ml) was cooled to -50 °C. Bromine (3.68 g, 23.0 mmol) in dichloromethane (5 ml) was slowly added to the solution over 30 min. After the addition was completed, the reaction mixture was allowed to warm to rt over 2.5 h, and then stirred for additional 30 min. Aqueous sodium bicarbonate (10 %) was added to quench the reaction. After a usual work-up and recrystallization from dichlorometane, (*R*)-6,6'-dibromo-3,3'-diphenyl-

1,1'-bi-2-naphthol (**3**) was obtained in a 98% yield. IR (KBr): 3406, 3505 cm^{-1}. $[\alpha]_D^{26}$ +96.6 ° (c 1.0, THF). Mp: 262-264 °C. ^1H NMR ($CDCl_3$): δ 5.40 (s, 2H), 7.05 (d, 2H, *J* = 8.9 Hz), 7.37 (dd, 2H,*J* = 2.1, 8.9 Hz), 7.43 (d, 2H, *J* = 7.3 Hz), 7.50 (t, 4H, *J* = 7.3 Hz), 7.68 (d, 4H, *J* = 7.3 Hz), 7.90 (s, 2H), 8.06 (d, 2H, *J* = 2.1 Hz); ^{13}C NMR ($CDCl_3$): δ 112.6, 118.1, 126.0, 128.2, 128.7, 129.5, 130.3, 130.4, 130.5, 130.6, 131.5, 131.8, 136.7, 150.2.

(*R*)-6,6'-Dibromo-3,3'-bis(4-fluorophenyl)-2,2'-dihydroxy-1,1'-binaphthyl. $[\alpha]_D^{28}$ +79.0 (*c* = 1.0, THF); IR (KBr) 835, 1132, 1159, 1228, 1488, 1510, 1586, 2924, 3038, 3512 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.30 (s, 2H), 7.02 (d, 2H, *J* = 8.8 Hz), 7.15-7.20 (m, 4H), 7.38 (dd, 2H, *J* = 2.1, 8.8 Hz), 7.64-7.69 (m, 4H), 7.89 (s, 2H), 8.07 (d, 1H, *J* = 2.1 Hz); ^{13}C NMR ($CDCl_3$) δ 112.2, 115.6 (d, J_{CF} = 21.7 Hz), 118.4, 125.9, 130.4, 130.48, 130.53, 130.8, 130.9, 131.28 (d, J_{CF} = 8.3 Hz), 131.34, 132.7 (d, J_{CF} = 3.1 Hz), 150.3, 162.7 (d, *J* = 248.3 Hz).

(*R*)-6,6'-Dibromo-3,3'-bis(3-trifluoromethylphenyl)-2,2'-dihydroxy-1,1'-binaphthyl. $[\alpha]_D^{28}$ +45.1 (*c* = 1.0, THF); IR (KBr) 701, 804, 901, 1127, 1163, 1235, 1331, 1416, 1491, 1588, 2927, 3059, 3513 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.34 (s, 2H), 7.04 (d, 2H, *J* = 9.0 Hz), 7.42 (dd, 2H, *J* = 2.0, 9.0 Hz), 7.59-7.63 (m, 2H), 7.68 (d, 2H, *J* = 7.8 Hz), 7.90 (d, 2H, *J* = 7.8 Hz), 7.96 (s, 2H), 7.99 (s, 2H), 8.11 (d, 2H, *J* = 2.0 Hz); ^{13}C NMR ($CDCl_3$) δ 111.9, 118.7, 124.0 (q, J_{CF} = 272.9 Hz), 124.8 (q, J_{CF} = 3.3 Hz), 125.8, 126.5 (q, J_{CF} = 3.3 Hz), 129.0, 130.45, 130.53, 130.62, 130.9 (q, J_{CF} = 32.2 Hz), 131.0, 131.4, 131.5, 132.9, 137.6, 150.3.

Catalytic Asymmetric Aza Diels-Alder Reactions. A typical experimental procedure is described for the reaction of an aldimine with 1-methoxy-3-trimethylsiloxy-1,3-butadiene (**13**, Danishefsky's diene):[8] To a mixture of (*R*)-3,3'-bis(3-trifluoromethylphenyl)-2,2'-dihydroxy-1,1'-binaphthyl (22.5 mg, 0.039 mmol), *N*-methylimidazole (3.2 mg, 0.039 mmol), and MS 3A (160 mg) in benzene (0.75 ml) was added a benzene (0.25 ml) solution of $Zr(O^tBu)_4$ (5.0 mg, 0.013 mmol), and the mixture was stirred at 80 °C for 2.5 h. To this mixture was added Me_3SiCN (2.7 mg, 0.027 mmol) in toluene (0.2 ml), and the mixture was stirred for 30 min at rt. A benzene solution (1.25 ml each) of an aldimine (0.65 mmol) and **13** (168.0 mg, 0.98 mmol) was added to this mixture over 1 h at the same temperature, and the mixture was further stirred for 1h. Saturated $NaHCO_3$ aq. was then added to quench the reaction. The aqueous layer was extracted with dichloromethane, and the

crude adduct was treated with THF-1N HCl (20:1) at 0 °C for 30 min. After a usual work up, the crude product was chromatographed on silica gel ($CHCl_3$-MeOH=9/1) to give the corresponding cycloaddition adduct.

The determination of enantioselectivities (HPLC analyses) and full charactalerlization of the products were performed after converting to the corresponding *o*-methylated compounds. The aldimine adduct was treated with 5 ml of 20 % MeI-acetone and 200 mg of K_2CO_3. After the mixture was stirred at rt for 6 h, saturated aqueous NH_4Cl was added to quench the reaction. After extraction of the aqueous layer with dichloromethane, the crude product was chromatographed on silica gel ($CHCl_3$-MeOH=19/1) to afford the corresponding methylated product.

For the product obtained from the imine derive from benzaldehyde and **2**, the enantiomeric excess wa detremined by HPLC analysis after converting to the corresponding benzoate.

Physical data of the aldimine adducts are as follows.

1-(2-Benzoyloxyphenyl)-2-phenyl-1,2,3,4-tetrahydropyridin-4-one.[7] ^{1}H NMR ($CDCl_3$): δ 2.71 (dd, 1H, *J* = 5.9, 16.4 Hz), 2.98 (dd, 1H, *J* = 6.6, 16.4 Hz), 5.07 (dd, 1H, J = 5.9, 6.6 Hz), 5.13 (d, 1H, *J* = 7.8 Hz), 7.06 (d, 1H, *J* = 7.8 Hz), 7.13-7.30 (m, 9H), 7.53 (t, 2H, *J* = 7.6 Hz), 7.67 (t, 1H, *J* = 7.3 Hz), 8.16 (d, 2H, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$): δ 43.6, 63.5, 101.2, 123.9, 126.5, 126.87, 126.90, 127.9, 128.1, 128.2, 128.3, 128.4, 128.5, 128.7, 128.8, 130.0, 130.1, 134.2, 137.6, 138.5, 145.6, 152.1, 164.6, 190.7. HPLC: Daicel Chiralcel OD, hexane/^{i}PrOH = 9/1, flow rate = 1.0 ml/mim: ^tR = 42.3 min (*S*), ^tR = 45.6 min (*R*).

1-(2-Methoxyphenyl)-5-methyl-2-phenyl-1,2,3,4-tetrahydropyridin-4-one.[7] ^{1}H NMR ($CDCl_3$): δ 1.77 (s, 3H), 2.85 (dd, 1H, *J* = 8.9, 16.5 Hz), 3.03 (dd, 1H, *J* = 6.1, 16.5 Hz), 3.81 (s, 3H), 5.18 (dd, 1H, *J* = 6.1, 8.9 Hz), 6.80-6.83 (m, 2H), 6.97 (dd, 1H, *J* = 1.5, 7.6 Hz), 7.09-7.29 (m, 7H); ^{13}C NMR ($CDCl_3$): δ 12.8, 44.1, 55.5, 63.1, 106.9, 111.8, 120.8, 126.8, 127.1, 127.2, 127.5, 128.3, 133.7, 139.3, 151.5, 191.0. HPLC: Daicel Chiralcel AD, hexane/^{i}PrOH = 19/1, flow rate = 1.0 ml/mim: ^tR = 19.3 min (*S*), ^tR = 20.3 min (*R*).

1-(2-Methoxyphenyl)-2-(2-methylphenyl)-1,2,3,4-tetrahydrpridin-4-one.[7] ^{1}H NMR ($CDCl_3$): δ 2.24 (s, 3H), 2.75 (dd, 1H, *J* = 7.8 Hz), 2.96 (dd, 1H, *J* = 6.6, 16.3 Hz), 3.81 (s, 3H), 5.20 (d, 1H, *J* = 7.9 Hz), 5.52 (dd, 1H, *J* = 6.6, 9.2 Hz), 6.76-7.15 (m, 7H), 7.32 (d, 1H, *J* = 7.9 Hz),

7.41-7.44 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 18.9, 43.1, 55.2, 59.2, 99.6, 111.8, 120.8, 126.0, 126.6, 126.9, 127.4, 127.9, 130.7, 133.4, 134.6, 137.2, 153.9, 154.6, 191.1. HPLC: Daicel Chiralcel OD, hexane/^{i}PrOH = 24/1, flow rate = 1.0 ml/mim: $^{t}_{R}$ = 44.1 min (*S*), $^{t}_{R}$ = 50.3 min (*R*).

1-(2-Methoxyphenyl)-5-methyl-2-(2-methylphenyl)-1,2,3,4-tetrahydropri-din-4-one.[7] ^{1}H NMR ($CDCl_3$): δ 1.79 (s, 3H), 2.24 (s, 3H), 2.76 (dd, 1H, *J* = 10.1, 16.5 Hz), 2.91 (dd, 1H, *J* = 6.4, 10.1 Hz), 6.77-6.79 (m, 2H), 6.94-7.09 (m, 5H), 7.35-7.38 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 12.7, 18.9, 43.3, 55.4, 59.4, 106.5, 111.6, 120.6, 125.9, 126.4, 126.8, 127.2, 127.4, 130.5, 133.7, 134.5, 137.4, 152.5, 153.8, 190.9. HPLC: Daicel Chiralcel OD, hexane/^{i}PrOH = 9/1, flow rate = 1.0 ml/mim: $^{t}_{R}$ = 10.4 min (*S*), $^{t}_{R}$ = 12.7 min (*R*).

1-(2-Methoxyphenyl)-2-(1'naphthyl)-1,2,3,4-tetrahydropyridin-4-one.[7] ^{1}H NMR ($CDCl_3$): δ 1.80 (s, 3H), 2.96-3.27 (m, 2H), 3.81 (s, 3H), 6.05 (t, 1H, *J* = 7.6 Hz), 6.78-7.00 (m, 2H), 7.25-8.02 (m, 8H); ^{13}C NMR ($CDCl_3$): δ 12.8, 43.3, 55.5, 106.6, 111.8, 120.7, 122.5, 125.0, 125.4, 125.9, 126.0, 127.2, 128.2, 128.3, 129.1, 130.1, 133.8, 134.0, 134.1, 152.2, 153.7, 190.8. HPLC: Daicel Chiralcel OD, hexane/^{i}PrOH = 9/1, flow rate = 1.0 ml/mim: $^{t}_{R}$ = 35.8 min (*S*), $^{t}_{R}$ = 43.7 min (*R*).

1-(2-Methoxyphenyl)-5-methyl-2-(1'naphthyl)-1,2,3,4-tetrahydropyridin-4-one.[7] ^{1}H NMR ($CDCl_3$): δ 1.80 (s,3H), 2.96-3.27 (m,2H), 3.81 (s, 3H), 6.05 (t, 1H, *J* = 7.6 Hz), 6.70 (t, 1H, *J* = 7.6 Hz),6.78-7.00 (m, 2H), 7.25-8.02 (m, 8H); ^{13}C NMR ($CDCl_3$): δ 12.8, 43.3, 55.5, 106.6, 111.8, 120.7, 122.5, 125.0, 125.4, 125.9, 126.0, 127.2, 128.2, 128.3, 129.1, 130.1, 133.8, 134.0, 134.1, 152.2, 153.7, 190.8. HPLC: Daicel Chiralcel OD, hexane/^{i}PrOH = 9/1, flow rate = 1.0 ml/mim: $^{t}_{R}$ = 19.3 min (*S*), $^{t}_{R}$ = 29.7 min (*R*).

1-(2-Methoxyphenyl)-2-(3,4-methylenedioxyphenyl)-1,2,3,4-tetrahydrop-yridin-4-one.[7] ^{1}H NMR ($CDCl_3$): δ 2.79 (dd, 1H, *J* = 8.1, 16.3 Hz), 3.03 (dd, 1H, *J* = 6.3, 16.3 Hz), 3.84 (s, 3H), 5.11 (dd, 1H, *J* = 6.3, 8.1 Hz), 5.17 (d, 1H, *J* = 7.8 Hz), 5.88 (s, 2H), 6.62-6.67 (m, 2H), 6.77 (s, 1H), 6.81-6.88 (m, 2H), 6.98 (d, 1H, *J* = 7.6 Hz), 7.15-7.18 (m, 1H), 7.23 (d, 1H, *J* = 7.7 Hz); ^{13}C NMR ($CDCl_3$): δ 44.0, 55.6, 62.7, 99.7, 101.0, 107.4, 108.0, 111.9,, 120.7, 120.8, 127.0, 128.2, 133.0, 133.3, 147.1, 147.6, 153.6, 154.0, 191.1. HPLC: Daicel Chiralcel OD, hexane/^{i}PrOH = 9/1, flow rate = 1.0 ml/mim: $^{t}_{R}$ = 30.0 min (*S*), $^{t}_{R}$ = 31.9 min (*R*).

1-(2-Methoxyphenyl)-5-methyl-2-(3,4-methylenedioxyphenyl)-1,2,3,4-tetrahydropyridin-4-one.[7] ^{1}H NMR ($CDCl_3$): δ 1.76 (s, 3H), 2.79 (dd, 1H, *J* = 8.9, 16.5 Hz), 2.98 (dd, 1H, *J* = 6.3, 16.5 Hz), 3.83 (s, 3H), 5.09 (dd, 1H, *J* = 6.3, 8.9 Hz), 5.87 (s, 2H), 6.62-7.27 (m, 7H), 7.13 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 12.7, 44.2, 55.6, 62.9. 101.0, 106.8, 107.4, 107.9, 111.8, 120.7, 120.8, 127.0, 127.6, 133.3, 133.7, 146.9, 147.5, 151.5, 154.1, 191.0. HPLC: Daicel Chiral AD, hexane/^{i}PrOH = 9/1, flow rate = 1.0 ml/mim: ^tR = 15.9 min (*S*), ^tR = 17.6 min (*R*).

1-(2-Methoxyphenyl)-2-(2-thienyl)-1,2,3,4-tetrahydropyridin-4-one.[7] ^{1}H NMR ($CDCl_3$): δ 2.72 (dd, 1H, *J* = 5.5, 16.2 Hz), 3.12 (dd, 1H, *J* = 6.5, 16.2 Hz), 3.87 (s, 3H), 5.13 (t, 1H, *J* = 6.2 Hz), 5.17 (d, 1H, *J* = 7.7 Hz), 6.87-7.02 (m, 3H), 7.15 (d, 1H, *J* = 7.7 Hz), 7.21-7.26 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 42.0, 54.6, 55.7, 99.8, 109.4, 111.9, 121.0, 122.9, 127.1, 128.4, 133.3, 140.3, 143.1, 152.2, 153.9, 191.3. HPLC: Daicel Chiralcel AD, hexane/^{i}PrOH = 19/1, flow rate = 1.0 ml/mim: ^tR = 36.9 min (*S*), ^tR = 40.2 min (*R*).

2-Cyclohexyl-1-(2-methoxy-6-methylphenyl)-5-methyl-1,2,3,4-tetrahydr-opyridin-4-one.[7] This material was appeared as a pair of conformational isomers. ^{1}H NMR ($CDCl_3$): δ 0.93-1.75 (m, 11H), 1.69 (s, 1.5H), 1.70 (s, 1.5H), 2.32 (s, 1.5H), 2.33 (s, 1.5H), 2.53 (dd, 0.5H, J = 8.2, 16.2 Hz), 2.60 (dd, 0.5H, J = 3.4, 16.8 Hz), 2.78 (dd, 0.5H, J = 6.7, 16.2 Hz), 2.91 (dd, 0.5H, J = 8.5, 16.8 Hz), 3.47 (dt, 0.5H, J = 3.4, 8.5 Hz), 3.81-3.86 (m, 0.5+1.5H), 3.83 (s, 1.5H), 6.77-6.89 (m, 3H), 7.19 (d, 1H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$): δ 12.7, 17.8, 18.2, 26.1, 26.2, 26.3, 26.5, 26.6, 27.6, 27.9, 29.5, 30.0, 36.4, 36.8, 40.9, 55.5, 55.6, 55.7, 63.4, 64.0, 105.2, 109.0, 109.2, 122.9, 123.2, 127.9, 128.1, 136.3, 137.1, 137.2, 152.4, 153.0, 155.9, 156.0, 192.3. HPLC: Daicel Chiralcel OD, hexane/^{i}PrOH =24/1, flow rate = 1.0 ml/mim: ^tR = 11.6 min (*S*), ^tR = 13.7 min (*R*).

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