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C_2-Symmetric Bisphosphine Ligands Derived from 1,1′-Binaphthyldiamines and Diphenylphosphinobenzoic Acid for Palladium Catalyzed Desymmetrizations

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Abstract—A series of novel C_2-symmetric bisphosphine ligands derived from DPPBA and C_2-symmetric 1,1′-binaphthyldiamines has been synthesized. In palladium catalyzed desymmetrization of *meso* cyclic carbamates, the enantioselectivity and the stereochemistry of the major enantiomers are largely affected by the substitution position of DPPBA moiety on the 1,1′-binaphthyl chiral scaffold.

Introduction

Increased hindrance to rotation at the pivotal 1,1′-bond can make the 2,2′-substituted 1,1′-binaphthyls resolvable as optically active enantiomers. Because of their highly stable chiral configuration, they have been extensively used to control many asymmetric processes and have demonstrated outstanding chiral discrimination properties. For example, bidentate diphosphine, BINAP, has been utilized as a chiral ligand in Rh(I)- or Ru(II)-catalyzed asymmetric hydrogenations, double bond isomerizations, and numerous other asymmetric catalytic reactions.[1] Despite the great success that the bisphosphine ligands possessing a 1,1′-binaphthyl chiral scaffold have enjoyed over the years, less satisfactory results have been reported for their application in Pd(0)-catalyzed allylic substitutions, especially, desymmetrization of *meso*-compounds.[2–4]

Recently, for Pd(0)-catalyzed allylic substitutions and desymmetrization of cyclic *meso*-compounds, Trost developed highly efficient bisphosphine ligands derived from 2-(diphenylphosphino)benzoic acid (DPPBA) and various chiral diamines or their amide linker invertomers from 2-(diphenylphosphino)aniline (DPPA) and chiral dicarboxylic acids.[5,6] However, in Pd(0)-catalyzed desymmetrization of *meso*-cyclopenten-1,3-diol bis(carbamate) **16a** (Scheme 2), the 2,2′-substituted 1,1′-binaphthyl ligands such as BINAPO (55% ee),[4a] **1** (40% ee)[4b] and **2** (30% ee)[4c] afforded low to moderate enantioselectivities. It has been found that the enantiodiscrimination abilities of the ligands are highly sensitive to small structural change of the ligands. For example, simply inverting of the amide linker of the DPPBA derived ligands but keeping everything else the same inverts the sense of chiral recognition and increases enantioselectivity which may be due to the change of the P–Pd–P bite-angles of the Pd-complexes formed with bisphosphine ligands.[5] Therefore, we expected that changing the substitution positions of DPPBA moiety on 1,1′-binaphthyl scaffold from 2,2′- to 6,6′- or 7,7′-positions may have effects on the enantioselectivity in palladium-catalyzed desymmetrization of *meso*-compounds. In ongoing efforts to develop C_2-symmetric chiral ligands for asymmetric catalysis,[7] we decided to examine the differential ionization ability of the ligands in which the DPPBA moiety placed at different positions on 1,1′-binaphthyl chiral scaffold. Herein, we report on the preparation of bisphosphine ligands **3**–**6** and their catalytic acitvities in Pd-catalyzed desymmetrization of *meso*-cyclic biscarbamates **16a**–**c** (Fig. 1).

Results and Discussion

The ligand **3** was prepared from commercially available (*R*)-1,1′-binaphthyl-2,2′-diamine and 2-(diphenylphosphino)benzoic acid (DPPBA) using DCC in 59% yield. For the synthesis of (*R*)-7,7′-disubstituted-2,2′-dimethoxy-1,1′-binaphthyl ligands **4** and **5**, optically pure 7,7′-bis-(benzyloxy)-2,2′-dihydroxy-1,1′-binaphthyl, (*R*)-**7**, has been chosen as a key intermediate. The (*R*)-**7** could be synthesized from 7-benzyloxy-2-naphthol[8] via oxidative coupling followed by resolution. Initially, the 7-benzyloxy-2-naphthol was oxidatively coupled using $Mn(acac)_3$[8a] or *t*-$BuNH_2$–$CuCl_2$[8b,9c] to obtain *rac*-**7**, but the coupling yields were low (35–60%).[9] However, when the coupling

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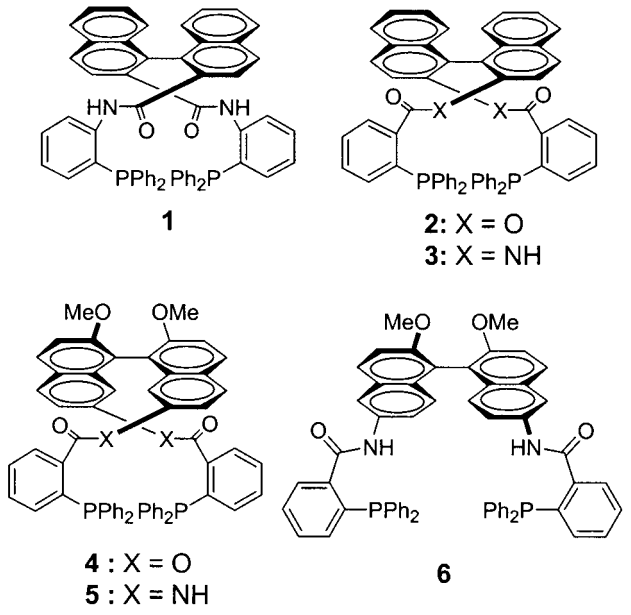
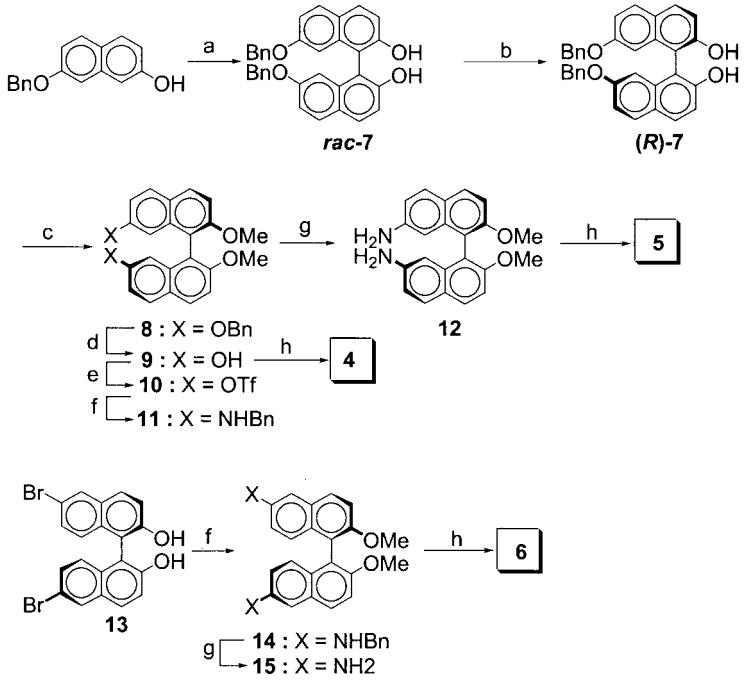


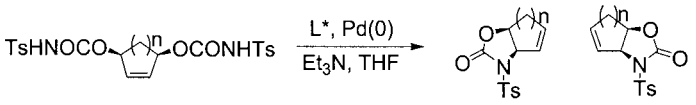
Figure 1.

reaction was carried out under the reaction conditions reported by Nakajima,[10] i.e. using 1 mol% of CuCl(OH)·TMEDA catalyst and O_2, the oxidative coupling occurred efficiently to give *rac*-**7** in 92% yield. Among the numerous efficient methods for the optical resolution of *rac*-1,1′-bi-2-naphthol to optically pure enantiomer,[11] the *rac*-**7** was resolved to optically pure (*R*)-(−)-**7** through clathrate formation with quinine.[12] Methylation of (*R*)-(−)-**7** with excess methyl iodide in the presence of K_2CO_3 in DMF afforded (*R*)-(−)-7,7-bis(benzyloxy)-2,2′-dimethoxy-1,1′-binaphthyl **8** almost quantitatively.[8d] Debenzylation of **8** performed with $Pd(OH)_2/H_2$ to give (*R*)-(−)-7,7′-dihydroxy-2,2′-dimethoxy-1,1′-binaphthyl **9** in 91% yield. DCC coupling of **9** with DPPBA afforded ligand **4** in 68% yield. To introduce the amine functional group of the 7,7′-diamine **12**, the dihydroxy compound **9** was converted to the corresponding bis(triflate) **10** using Tf_2O.[8d,13] For the Buchward[14,15] and Hartwig[16] aryl amination of bis(triflate) **10** with benzylamine, initially, we employed bis[2-(diphenylphosphino)phenyl]ether (DPEphos)[14] and $Pd(OAc)_2$ catalyst. However, the monoaminated product was formed as a major product. Fortunately, reaction of **10** with benzylamine in the presence of NaO-*t*-Bu and a combination of $Pd_2(dba)_3$ (dba=dibenzylideneacetone) and DPPF (DPPF=1,1′-bis(diphenylphosphino)ferrocene) in toluene afforded the desired diaminated product **11** in 92% yield without any loss of optical purity. Debenzylation of **11** using Pd–C/H_2 in methanol afforded the diamine **12**, which was used for the next reactions without further purification. DCC coupling of the diamine **12** with DPPBA afforded bisphosphine ligand **5** in 68% yield. As shown in Scheme 1, optically pure 6,6′-disubstituted-2,2′-dimethoxy-1,1′-binaphthyl ligand (*R*)-**6** was easily prepared starting from an optically pure (*R*)-6,6′-dibromide **13**, which was prepared by bromination of commercially available (*R*)-1,1′-bi-2-naphthylol according to the reported procedure.[17]

The catalytic efficiencies of these DPPBA-derived 1,1′-binaphthyl bisphosphine ligands **3**,**4**,**5** and **6** have been examined in Pd(0)-catalyzed desymmetrizations of *meso*-cyclic carbamates **16a**–**c**[18] (Scheme 2). The desymmetrization reactions have been carried out with the molar ratios of $Pd_2(dba)_3{\cdot}CHCl_3$: ligand:substrate=2.5:7.5:100 in THF solvent at 20°C in the presence of Et_3N. The results are summarized in Table 1. Desymmetrization of five-membered *meso*-carbamate **16a** using ligand **3** afforded **17a** as a major isomer with 14% ee (entry 1). When the ligand was changed to **4**, which has ester linker, the



Scheme 1. (a) CuCl(OH)·TMEDA (1 mol%), O_2, CH_2Cl_2; (b) resolution using quinine; (c) NaH, MeI, DMF; (d) $Pd(OH)_2$–C/H_2, MeOH; (e) Tf_2O, pyridine, CH_2Cl_2; (f) $Pd_2(diba)_3$, DPPF, $PhCH_2NH_2$, toluene; (g) Pd–C/H_2, CH_3OH; (h) DPPBA, DCC, DMAP, CH_2Cl_2.



16a : n = 1 **17a** ***ent*-17a**
16b : n = 2 **17b** ***ent*-17b**
16c : n = 3 **17c** ***ent*-17c**

Scheme 2.

enantioselectivity was slightly increased to 24% ee, but the major isomer was *ent*-**17a** (entry 2). The more dramatically increased enantioselectivity (76% ee) has been observed using ligand **5** (entry 4). The effects of reaction temperatures and bases on the enantioselectivity have been examined using 7,7′-derived ligand **5**. Comparing entries 3,4 and 5 indicate that the enantioselectivities were not dependent on the reaction temperature, but largely on the base.[3h] Thus, the same reactions without Et_3N (54% ee, entry 6) or with BSA/KOAc (34% ee, entry 7) caused decreasing of the enantioselectivities. Desymmetrization of **16a** using 6,6′-derived ligand **6** afforded **17a** as a major isomer with 30% ee (entry 8). Interesting is the absolute configuration of the product **17a**. Comparing entries 1, 2, 4 and 8 show that maintaining the same axial chirality of the chiral scaffold and only changing the substitution position of the DPPBA moiety reverses the sense of chirality in the product. However, at present time, the origin of the reverse chirality of the product cannot be explained simply. It has been also found that as increasing the ring size of the substrates, the enantioselectivities and reactivities were decreased. The superiority of the 7,7′-derived ligands **4** and **5** was maintained in the desymmetrization of the 6- and 7-membered substrates, **16b** (compare entries 9–12) and **16c** (compare entries 13–16). In palladium catalyzed allylic substitutions, since bond breaking and bond making occur distal to palladium, the chiral ligands forcing the chiral environment to embrace the substrate by opening the bite-angle are necessary for high chiral recognition. Unfortunately, we do not have solid evidences that the real bite-angle of ligand **5** is increased compared with **3**. Nevertheless, the observed results indicate that changing the substitution positions of the DPPBA moiety from 2,2′- to 7,7′-positions on binaphthyl scaffold enhanced the depth of the chiral pocket in which the substrate must reside, thus, more effectively creating a chiral space to control the enantioselectivity. Therefore, the lower enantiodiscrimination ability of the 2,2′-derived 1,1′-binaphthyl bisphosphine chiral ligands may be related with small P–Pd–P bite-angles.

Table 1. Pd(0)-catalyzed desymmetrization of *meso*-bis(carbamates) using bisphosphine ligands **3**–**6**

Entry[a]	Ligand	Substrate	Yield (%)[b]	**17**/*ent*-**17** (% ee)[c]
1	**3**	**16a**	72	57/43 (14)
2	**4**	**16a**	72	38/62 (24)
3[d]	**5**	**16a**	84	12/88 (76)
4	**5**	**16a**	87	12/88 (76)
5[e]	**5**	**16a**	93	13/87 (74)
6[f]	**5**	**16a**	71	23/77 (54)
7[g]	**5**	**16a**	64	33/67 (34)
8	**6**	**16a**	64	65/35 (30)
9	**3**	**16b**	70	55/45 (10)
10	**4**	**16b**	88	24/76 (52)
11	**5**	**16b**	74	19/81 (62)
12	**6**	**16b**	68	47/53 (6)
13	**3**	**16c**	64	Racemic
14	**4**	**16c**	91	30/70 (40)
15	**5**	**16c**	72	29/71 (42)
16	**6**	**16c**	58	44/56 (12)

[a] The reactions were carried out in THF with the molar ratios of $Pd_2(dba)_3{\cdot}CHCl_3$:ligand:substrate=2.5:7.5:100 in the presence of Et_3N at 20°C unless otherwise noted.
[b] Isolated yields.
[c] Determined by chiral HPLC using Chiralpak AD column.[5h]
[d] Reaction carried out at 0°C.
[e] Reaction carried out at 40°C.
[f] Reaction carried out without Et_3N.
[g] Reaction carried out using BSA/KOAc (BSA=*N*,*N*-bis(trimethylsilyl)acetamide) instead of Et_3N.

Conclusion

In summary, we have synthesized a series of C_2-symmetric chiral binaphthyl-bisphosphine ligands **3**–**6** having apparently different bite-angles. In Pd(0)-catalyzed desymmetrization of *meso*-cyclic carbamates **16a**–**c**, the enantioselectivities are dramatically increased by changing the substitution position of the DPPBA moiety on the 1,1′-binaphthyl chiral scaffold from 2,2′- (**3**) to 7,7′-positions (**5**). However, the 6,6′-derived ligand **6** showed the lower enantiodiscrimination ability than the ligand **5**. Moreover, it has been found that only changing the substitution position of the DPPBA moiety reverses the sense of chirality in the product.

Experimental

General

^1H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on a Bruker 300 MHz spectrometer, IR spectra were recorded on a MIDAC 101025 FT-IR spectrometer and optical rotation was measured with Autopol® polarimeter. Chemical analyses were carried out by the Advanced Analysis Center at KIST. HRMS (FAB) analysis has been carried out by the Mass Spectrometry Analysis Group at Korea Basic Science Institute. Melting points taken on a Thomas–Hoover capillary melting point apparatus are uncorrected. The reactions were carried out using standard Schlenk techniques under nitrogen atmosphere. Commercially available (*R*)-2,2′-diamino-1,1′-binaphthyl and 2-(diphenylphosphino)benzoic acid were used without purification. Optically pure (*R*)-6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthyl **13** was prepared by bromination of commercially available (*R*)-1,1′-bi-2-naphthylol.[18] 7-Benzyloxy-2-naphthol was prepared from

2,7-dihydroxynaphthalene according to the reported procedure.[8b]

***rac*-7,7-Bis(benzyloxy)-2,2′-dihydroxy-1,1′-binaphthyl (*rac*-7).** To a solution of 7-benzyloxy-2-naphthol (18 g, 72 mmol) in dichloromethane (100 mL) was added CuCl(OH)·TMEDA (3.3 g, 14.2 mmol), and stirred under the oxygen atmosphere until the reaction was complete. The reaction mixture was washed with water and brine, dried over $MgSO_4$. After filtration, the volatile materials were removed to give yellowish solids which were purified by passing on short-silica gel column (EtOAc/*n*-Hexane=1:4) to give pure *rac*-**7** (16.3 g, 92%). Mp 105–107°C (lit.[8a] 104–106°C). All the spectral data were consistent with the reported data.[8a]

(*R*)-7,7-Bis(benzyloxy)-2,2′-dihydroxy-1,1′-binaphthyl ((*R*)-7). A mixture of quinine (18.1 g, 0.057 mol) and *rac*-**7** (24.6 g, 0.049 mol) in ethanol (600 mL) was refluxed for 3 h. On cooling, precipitates were collected and dried to give the (*R*)-**7**·quinine complex (15 g). Recrystallization twice from ethanol (500 mL) yielded the pure complex (14.9 g) which was dissolved in chloroform (300 mL) and washed with 2 N HCl (3×250 mL). The aqueous layer was extracted with chloroform. The combined organic layers were washed with water, brine, dried with $MgSO_4$. Evaporation of the solvent afforded 9.8 g (40% based on *rac*-**7**) of (*R*)-**7**. $[\alpha]_D^{25}=-232.8$ (*c* 1.06, $CHCl_3$) (lit.[12] $[\alpha]_D^{21}=-232.0$ (*c* 1.0, $CHCl_3$)). To determine the optical purity, to a solution of (*R*)-**7** (20 mg, 0.04 mmol) and MTPA (44 mg, 0.19 mmol) in dry CH_2Cl_2 (10 mL) were added DMAP (20 mg, 0.164 mmol) and DCC (80 mg, 0.4 mmol). After refluxing for 2 h, the mixture was cooled and the formed dicyclohexylurea was removed by filtration. The solution was diluted with CH_2Cl_2 and washed with H_2O, 5% CH_3CO_2H, and brine. The ^1H NMR (300 MHz, $CDCl_3$) spectrum of the crude Mosher's ester showed only one α-OCH_3 resonance signal at 2.97 ppm indicating that the optical purity is of >99% ee.

(*R*)-7,7-Bis(benzyloxy)-2,2′-dimethoxy-1,1′-binaphthyl (8). To a solution of the diol **7** (4.28 g, 8.6 mmol) in DMF (40 mL) was added NaH (1.1 g, 21.5 mmol, 60% dispersed in oil) at 0°C, and the mixture was stirred for 1 h at room temperature. After the reaction temperature was allowed to cooled to 0°C, iodomethane (4.9 g, 34.5 mmol) was added slowly, and then stirred for overnight at room temperature. The reaction mixture was diluted with CH_2Cl_2. After careful addition of water at 0°C, the organic layer was separated and washed with 2% aqueous HCl solution, water and brine. After evaporation of the solvent, the residue was purified by recrystallization from methanol to give pure **8** (4.52 g, 99%) as a white solid. Mp 129–131°C; $[\alpha]_D^{25}=-130.5$ (*c* 0.2, $CHCl_3$) (lit.[8d] Mp 126.5–127°C, $[\alpha]_D^{23}=-132$ (*c* 1.28, $CHCl_3$)); ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J*=8.9 Hz, 2H), 7.67 (d, *J*=7.7 Hz, 2H), 7.29 (d, *J*=8.9 Hz, 2H)), 7.24–7.14 (m, 10H), 7.10 (dd, *J*=8.9, 2.5 Hz, 2H), 6.47 (d, *J*=2.5 Hz, 2H), 4.73 (bs, 4H), 3.69 (s, 6H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 157.48, 155.86, 137.26, 135.52, 129.90, 129.40, 128.79, 128.10, 127.95, 125.30, 119.40, 117.07, 112.09, 105.49, 69.99, 57.13 ppm.

(*R*)-7,7′-Dihydroxy-2,2′-dimethoxy)-1,1′-binaphthyl (9). A mixture of **8** (4.52 g, 8.6 mmol) and catalytic amount of $Pd(OH)_2/C$ in methanol (100 mL) was stirred under the hydrogen atmosphere (1 atm) for overnight. After filtration of the catalyst through Celite, the filtrate was concentrated to give pure **9** (2.73 g, 91%) as a white solid. Mp 219–220°C; $[\alpha]_D^{25}=-53.5$ (*c* 0.28, CH_3OH); ^1H NMR (300 MHz, DMSO-d_6) δ 9.36 (bs, 2H), 7.89 (d, *J*=8.9 Hz, 2H), 7.78 (d, *J*=8.8 Hz, 2H), 7.33 (d, *J*=8.9 Hz, 2H), 6.89 (*J*=8.8 Hz, 2H), 5.77 (bs, 2H), 3.68 (s, 6H) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6) δ 156.50, 155.80, 136.08, 130.42, 129.68, 124.60, 128.21, 117.03, 111.72, 106.72, 56.89 ppm; IR(KBr) 3384(OH); HRMS(FAB^+) Calcd for $C_{22}H_{18}O_4$: 346.1205. Found: 346.1208.

(*R*)-7,7-Bis(trifluoromethanesulfonyloxy)-2,2′-dimethoxy-1,1′-binaphthyl (10). To a solution of the diol **9** (4 g, 11.5 mmol) in anhydrous CH_2Cl_2 (40 mL) was added Tf_2O (8.2 g, 28.9 mmol) and pyridine (2.7 g, 34.6 mmol) at 0°C. The reaction mixture was stirred at 0°C until all of the diol **9** was consumed in TLC. After evaporation of the solvent, the crude residue was purified by column chromatography on silica gel with 50% CH_2Cl_2 in ether to give **10** (6.14 g, 92%) as a white solid. Mp 136°C (sharply); $[\alpha]_D^{25}=+55.6$ (*c* 1.02, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J*=9.1 Hz, 2H), 7.95 (d, *J*=9.0 Hz, 2H), 7.52 (d, *J*=9.1 Hz, 2H), 7.23 (dd, *J*=2.2, 9.0 Hz, 2H), 6.98 (d, *J*=2.2 Hz, 2H), 3.78 (s, 6H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 156.38, 148.63, 134.53, 131.25, 130.59, 128.34, 121.20, 118.51, 117.52, 116.9, 114.90, 56.75 ppm; HRMS(FAB^+) Calcd for $C_{24}H_{16}F_6O_8S_2$:610.0191. Found: 610.0186.

(*R*)-7,7-Bis(aminobenzyl)-2,2′-dimethoxy-1,1′-binaphthyl (11). To a mixture of $Pd_2(dba)_3$ (47 mg, 52 μmol), diphenylphosphinoferrocene (94 mg, 0.17 mmol) and *t*-BuONa (500 mg, 5.2 mmol) in toluene (50 mL) was added the bis(triflate) **10** (1 g, 1.73 mmol) and benzylamine (0.57 mL, 5.2 mmol) at 0°C. The reaction mixture was stirred for 14 h at 90°C and the reaction temperature was allowed to cooled to 0°C. After dilution with EtOAc (100 mL), the organic layer was washed with 2% aqueous HCl solution, water and brine, and dried over anhydrous $MgSO_4$, filtered and concentrated. The resulting residue was purified by column chromatography on silica-gel (EtOAc/*n*-Hexane=1:3) to give **11** (690 mg, 76% yield) as a pale yellowish solid. Mp 78–80°C; $[\alpha]_D^{25}=-385.5$ (*c* 0.2, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J*=8.9 Hz, 2H), 7.67 (d, *J*=7.7 Hz, 2H), 7.07–7.10 (m, 12H), 6.65 (dd, *J*=2.2, 9.0 Hz, 2H), 6.02 (d, *J*=2.2 Hz, 2H), 3.99 (m, 4H), 3.59 (s, 6H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 155.88, 146.34, 139.78, 135.99, 129.38, 129.10, 128.83, 128.03, 127.33, 124.06, 118.61, 115.54, 110.75, 103.72, 57.18, 48.58 ppm; IR(KBr) 3412 (NH); HRMS(FAB^+) Calcd for $C_{36}H_{32}N_2O_2$: 524.2464. Found: 524.2463.

(*R*)-2,2′-Bis[(*N*,*N*′-bis(*o*-diphenylphosphinobenzoyl))-amino]-1,1′-binaphthyl (3). A mixture of (*R*)-(+)-1,1-binaphthyl-2,2-diamine (100 mg, 0.35 mmol), 2-(diphenylphosphino)benzoic acid (270 mg, 0.88 mmol), DCC (220 mg, 1.06 mmol) and DMAP (43 mg, 0.35 mmol) in anhydrous CH_2Cl_2 (10 mL) was stirred until the starting was completely consumed in TLC. The precipitates were removed by filtration through the Celite, the filtrate was

washed with 2% HCl solution and water. After concentration, the residue was purified by silica-gel column chromatography to give **3** (180 mg, 59 %) as a white solid. Mp 134–135°C; $[\alpha]_D$=+26.0 (*c* 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (d, *J*=9.0 Hz, 2H), 7.96 (dd, *J*=9.0, 8.1 Hz, 4H), 7.70 (bs, 2H), 7.47 (t, *J*=7.7 Hz, 2H), 7.04–7.36 (m, 28H), 6.81–6.88 (m, 4H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 167.01, 140.52, 140.21, 137.49, 137.30, 137.25, 137.20, 137.15, 137.10, 135.23, 134.39, 133.89, 133.84, 133.63, 133.56, 132.37, 131.35, 130.45, 129.85, 128.73, 128.55, 128.39, 128.30, 127.37, 127.10, 127.04, 125.52, 125.33, 121.75, 120.90 ppm; ^{31}P NMR (121 MHz, $CDCl_3$) −4.56 ppm (triphenylphosphine as an external standard); HRMS(FAB$^+$) Calcd for $C_{58}H_{43}N_2O_2P_2$ [(M+H)$^+$]: 861.2800. Found: 861.2791.

(*R*)-7,7′-Bis[(*O*,*O*′-bis(*o*-diphenylphosphinobenzoyl))hydroxy]-2,2′-dimethoxy-1,1′-binaphthyl (4). A solution of 2-(diphenylphosphino)benzoic acid (500 mg, 2 mmol), DCC (530 mg, 2.6 mmol) and DMAP (100 mg, 0.78 mmol) in anhydrous CH_2Cl_2 (20 mL) was stirred for 1 h, and then the diol **9** (300 mg, 0.87 mmol) was added at room temperature. After stirring until all of the diol **9** was consumed, the precipitates were removed through the Celite, the filtrate was washed with 2% aqueous HCl solution and water. After concentration, the residue was purified by silica-gel column chromatography to give **4** (540 mg, 68%) as a white solid. Mp 202–203°C; $[\alpha]_D^{25}$=−81.6 (*c* 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (m, 2H), 7.85 (d, *J*=9.1 Hz, 2H), 7.77 (d, *J*=9.0 Hz, 2H), 7.17–7.38 (m, 26H), 6.92–6.95 (m, 4H), 6.74 (bs, 2H), 3.64 (s, 6H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 165.58, 155.77, 141.55, 138.01, 135.01, 134.62, 134.54, 134.50, 134.26, 134.22, 132.73, 131.78, 129.76, 129.61, 129.04, 129.00, 128.88, 128.78, 128.56, 127.62, 119.46, 116.37, 114.11, 57.06 ppm; ^{31}P NMR (121 MHz, $CDCl_3$) −1.17 ppm (triphenylphosphine as an external standard); IR(KBr) 1732 (C=O) cm^{-1}; HRMS(FAB$^+$) Calcd for $C_{60}H_{45}O_6P_2$ [(M+H)$^+$]: 923.2691. Found: 923.2694.

(*R*)-7,7′-Bis[(*N*,*N*′-bis(*o*-diphenylphosphinobenzoyl))amino]-2,2′-dimethoxy-1,1′-binaphthyl (5). A mixture of *N*,*N*′-dibenzylamine **11** (4.52 g, 8.6 mmol) and catalytic amount of Pd/C in methanol (100 mL) was stirred under the hydrogen atmosphere (1 atm) during overnight and filtered through Celite to removed the catalyst, and then concentrated to give (*R*)-(−)-7,7-bis(amino)-2,2′-dimethoxy-1,1′-binaphthyl **12** (2.73 g, 91%) as a yellowish solid which used for the next reaction without further purification. DCC coupling of the diamine **12** (300 mg, 0.87 mmol) with 2-(diphenylphosphino)benzoic acid (500 mg, 2 mmol) under the same reaction conditions as **3** afforded **5** (540 mg, 68%) as a white solid. Mp 157–158°C; $[\alpha]_D^{25}$=−161.5 (*c* 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J*=8.99 Hz, 2H), 7.76–7.82 (m, 4H), 7.60 (m, 2H), 7.50 (bs, 2H), 7.13–7.38 (m, 28H), 6.92–6.96 (m, 2H), 6.65 (bs, 2H), 3.74 (s, 6H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 167.46, 155.77, 141.99, 141.65, 136.95, 136.81, 136.72, 136.51, 134.66, 134.45, 134.28, 134.18, 130.77, 129.67, 129.30, 129.23, 129.02, 128.93, 128.66, 127.24, 119.03, 118.80, 114.45, 113.70, 57.23 ppm; ^{31}P NMR (121 MHz, $CDCl_3$) −4.93 ppm (triphenylphosphine as an external standard); HRMS(FAB$^+$) Calcd for $C_{60}H_{47}N_2O_4P_2$ [(M+H)$^+$]: 921.3031. Found: 921.3005.

(*R*)-6,6-Bis(benzylamino)-2,2′-dimethoxy-1,1′-binaphthyl (14). To a mixture of $Pd_2(dba)_3$ (97 mg, 0.11 mmol), diphenylphosphinoferrocene (120 mg, 0.21 mmol) and NaO*t*-Bu (610 mg, 6.35 mmol) in toluene (50 mL) was added (*R*)-6,6′-dibromo-1,1′-naphth-2-ol (1 g, 2.12 mmol) and benzylamine (910 mg, 8.47 mmol) at 0°C followed by stirred for 14 h at 90°C. After the same workup as **11**, the crude product was purified by column chromatography on silica-gel (EtOAc/*n*-Hexane=1:4) to give **14** (980 mg, 88%) as a pale yellowish solid. Mp 85–87°C; $[\alpha]_D^{25}$=−62.5 (*c* 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J*=9.0 Hz, 2H), 7.23–7.41 (m, 12H), 6.95 (d, *J*=9.0 Hz, 2H), 6.86 (d, *J*=2.3 Hz, 2H), 6.60 (dd, *J*=9.0, 2.3 Hz, 2H), 4.37 (s, 4H), 3.96 (bs, 2H), 3.67 (s, 6H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 153.02, 144.56, 139.86, 131.23, 129.06, 128.50, 128.08, 127.66, 127.51, 127.03, 121.00, 119.01, 115.74, 105.23, 57.78, 48.98 ppm; HRMS(FAB$^+$) Calcd for $C_{36}H_{32}N_2O_2$: 524.2464. Found: 524.2462.

(*R*)-(−)-6,6′-Bis[(*N*,*N*′-bis(*o*-diphenylphosphinobenzoyl))amino]-2,2′-dimethoxy-1,1′-binaphthyl (6). A mixture of 900 mg (1.72 mmol) dibenzyl **14** and catalytic amount of Pd/C in methanol (20 mL) was stirred under the hydrogen atmosphere (1 atm) for overnight afforded diamine **15** (620 mg, 95%) as a yellowish solid which used for the next reaction without purification. A solution of 2-(diphenylphosphino)benzoic acid (500 mg, 2mmol), DCC (530 mg, 2.6 mmol) and DMAP (100 mg, 0.78 mmol) in anhydrous CH_2Cl_2 (20 mL) was stirred for 1 h. To this solution was added diamine **15** (300 mg, 0.87 mmol) at room temperature. The reaction mixture was further stirred during overnight. After filtration of the precipitate formed, the volitiles were removed under reduced pressure and the residue was purified by column chromatography to give **6** (600 mg, 75%) as a pale yellowish solid. Mp 181–183°C; $[\alpha]_D^{25}$−60 (*c* 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (bs, 2H), 7,86 (d, *J*=9.0 Hz, 2H), 7.73–7.74 (m, 4H), 7.68 (d, *J*=2.1 Hz, 2H), 7.23–7.43 (m, 26H), 6.98–7.02 (m, 2H), 6.92 (d, *J*=9.0 Hz, 2H), 6.66 (dd, *J*=9.0, 2.1 Hz, 2H), 3.73 (s, 6H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 167.61, 154.90, 142.55, 142.19, 136.90, 136.76, 134,53, 134.27, 133.36, 131.73, 130.87, 129.79, 129.72, 129.54, 129.48, 129.24, 129.17, 128.95, 128.88, 126.36, 120.87, 117.78, 115.24, 57.31 ppm; ^{31}P NMR (121 MHz, $CDCl_3$) −5.92 ppm (triphenylphosphine as an external standard); HRMS(FAB$^+$) Calcd for $C_{60}H_{47}N_2O_4P_2$ [(M+H)$^+$]: 921.3031. Found: 921.3005.

General procedure for Pd(0)-catalyzed desymmetrization of bis(carbamate) 16

To a solution of bis(carbamate) **16** (0.5 mmol) in THF (0.5 mL) was added a solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (12.5 μmol) and bisphosphine ligand (37.4 μmol) in THF (0.8 mL) at 0°C. The reaction mixture was degassed and stirred at 20°C for 14 h. After evaporation of the solvent, the residue was purified by preparative TLC (EtOAc/petroleum ether=1:2) to give a mixture of oxazolidinones **17** and *ent*-**17**. Enantiomeric excess has been determined by HPLC using Chiralpak AD chiral column (eluent: for **17a** and **17b**,

heptane:isopropanol=85:15, for **17c** heptane:isopropanol=30:70, flow rate: 1 mL/min).[5h] Retention time (min): **17a** (33.95), *ent*-**17a** (29.79); **17b** (45.28), *ent*-**17b** (36.94); **17c** (19.40), *ent*-**17c** (15.79). The results are listed in Table 1.

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