

Synthesis of Aminophosphine Ligands with Binaphthyl Backbones for Silver(I)-catalyzed Enantioselective Allylation of Benzaldehyde[†]

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A series of aminophosphine ligands was synthesized from 2-amino-2'-hydroxy-1,1'-binaphthyl (NOBIN). Their asymmetric induction efficiency was examined for silver(I) catalyzed enantioselective allylation reaction of benzaldehyde with allyltributyltin. Under the optimized reaction conditions, quantitative yield as well as moderate *ee* value (54.5% *ee*) of product was achieved by the catalysis with silver(I)/3 complex. The effects of the binaphthyl backbone and the substitutes situated at chelating N, P atoms on enantioselectivity of the reaction were also discussed.

Keywords silver, aminophosphine ligand, asymmetric catalysis, allylation

Introduction

Enantioselective allylation of carbonyl compounds is one of the useful and convenient method for the preparation of optically active secondary homoallylic alcohols.¹ Although numerous work on the reaction using a stoichiometric amount of chiral Lewis acids has been reported,² there are only few methods available for a catalytic process including chiral acyloxyborane (CAB) complex/allylic silanes³ or allylic stannanes⁴ and binaphthol-derived chiral titanium complexes/allylic stannanes.⁵ Yamamoto *et al.*⁶ has reported that BINAP·silver(I) complex was an efficient catalyst for enantioselective allylation reaction of aldehydes with allyltributyltin. More recently, a novel

kind of S, N ligand was synthesized by Shi and its silver(I) complex exhibited moderate enantioselectivity in the same reaction.⁷ These interesting results demonstrated that both N and P atoms could coordinate to silver(I) atom, and an N, P chiral ligand should be a potential chiral inducer for this reaction. In our laboratory, a variety of aminophosphine ligands 1—5 (Fig. 1) with binaphthyl backbones have been synthesized and were found to be efficient chiral inducers for Pd(0)-catalyzed allylic substitution.⁸ In this article, we describe the details for the preparation of these ligands and their application to silver(I) complex-catalyzed enantioselective allylation of benzaldehyde with allyltributyltin.

Results and discussion

Synthesis of chiral aminophosphine ligands 1—5

Chiral ligands (*R*)-1a and (*R*)-2a—2e were prepared according to our reported methods.^{8a,9} In order to demonstrate the substituent effect of diarylphosphino group on the enantioselectivity of the reaction, the analogous ligands (*R*)-1b—1f of (*R*)-1a were synthesized following a similar procedure as described in the literature from (*R*)-2-amino-2'-hydroxy-1,1'-binaphthyl (NOBIN) (Scheme 1).⁹ The substituted diphenylphosphine oxides

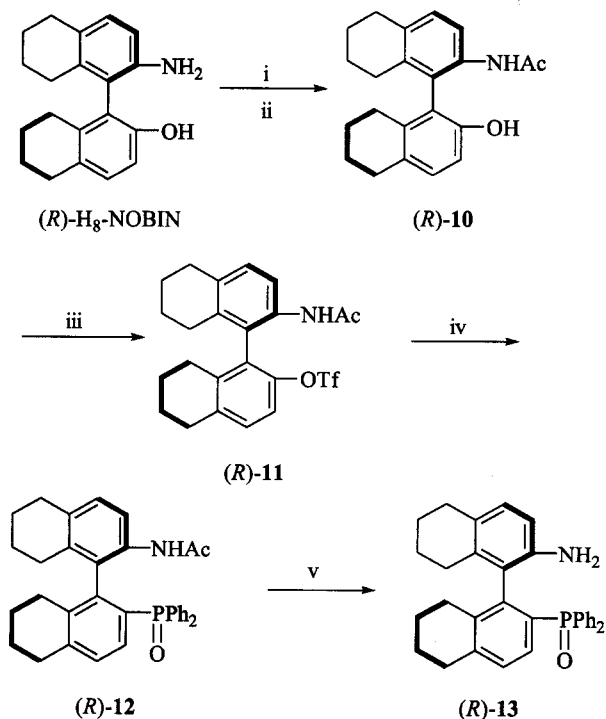
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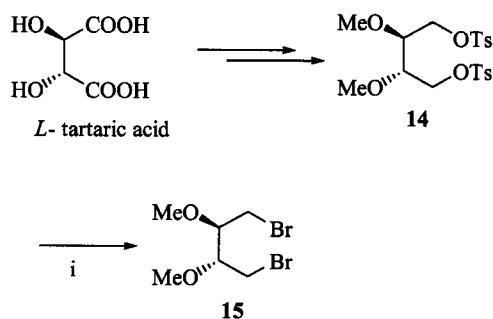
[†]Dedicated to Professor HUANG Yao-Zeng on the occasion of his 90th birthday.

Scheme 2



Reagents and conditions: (i) AcCl, Et₃N, CH₂Cl₂, 0 °C – r.t.; (ii) NaOH, CH₃OH/H₂O, r.t.; (iii) (TfO)₂O, Et₃N, CH₂Cl₂, –78 °C; (iv) 10 mol% Pd(OAc)₂, 15 mol% dppp, (*i*-Pr)₂NEt, HP(O)Ph₂, DMSO, 100 °C; (v) 5% aqueous HCl, EtOH, reflux.

Scheme 3

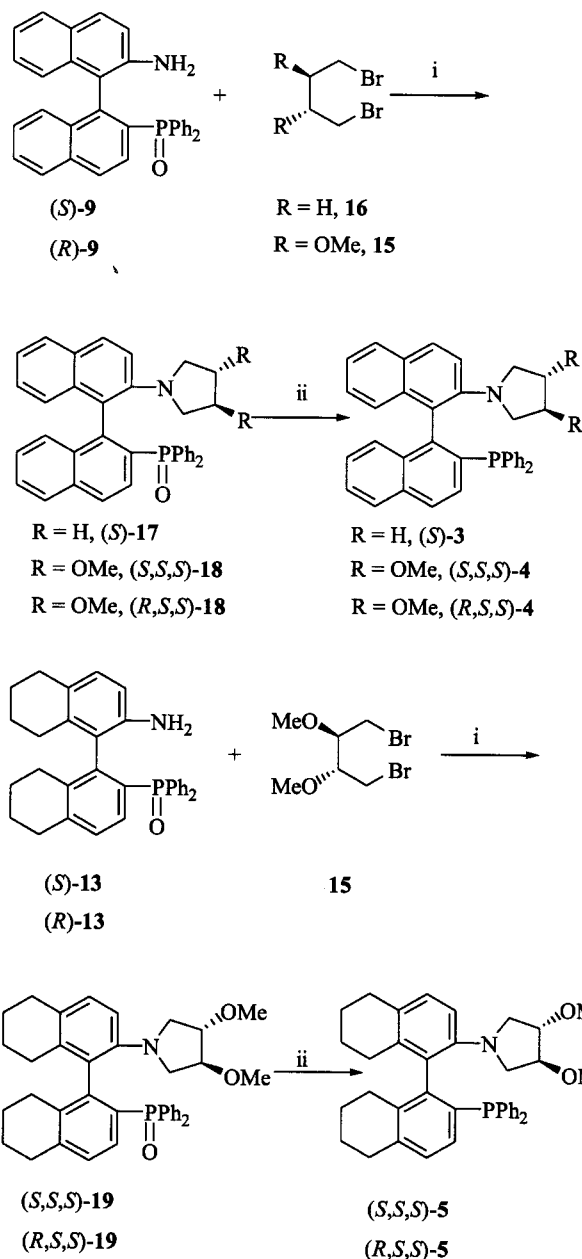


Reagents and conditions: (i) LiBr·H₂O, acetone, reflux.

of NaHCO₃ to give (*S*)-17 in 63% yield. Reduction of (*S*)-17 with HSiCl₃ in the presence of *N,N*-dimethylaniline afforded (*S*)-3 in 90% yield. The reaction of both enantiomers of 9 with 15 needed much harsher reaction conditions (at 150 °C in 1,3,5-trimethylbenzene), and addition of catalytic amount of NaI was found to be critical

to achieve practical transformation. The resulted phosphine oxide derivatives (*S,S,S*)-18 and (*R,S,S*)-18 were reduced smoothly by HSiCl₃/Et₃N in toluene, giving the corresponding ligands 4 in good yield. The octahydroanalogue of 4, ligands 5, were also synthesized by the similar procedure (Scheme 4).

Scheme 4



Reagents and conditions: (i) R = H: NaHCO₃, toluene, 100 °C; R = OMe: NaI, NaHCO₃, 1,3,5-trimethylbenzene, 150 °C; (ii) HSiCl₃, PhNMe₂, Et₃N, toluene, 100 °C.

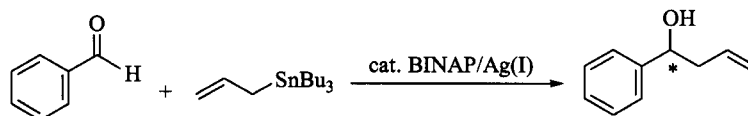
The application of chiral aminophosphine ligands to silver(I)-catalyzed enantioselective allylation of benzaldehyde with allyltributyltin

With the MAP ligands **1**—**5** in hand, we then investigated their asymmetric inductive ability in silver(I)-catalyzed allylation reaction. The details of the results obtained by using ligands **1** and **2** are summarized in Table 1.

As shown in Table 1, the reaction was first carried out in the presence of silver(I)/**1a** complex at room temperature in THF (Entry 1). Quantitative yield and 30.8% *ee* value of the product were obtained. Switching the reaction in CH₂Cl₂ and toluene showed that enantioselectivity could be improved slightly, but the yield was dramatically dropped, particularly in CH₂Cl₂. The reac-

tion in DMF was inferior to that in THF in terms of both yield and *ee* value (Table 1, Entries 2—4 vs. 1). AgOTf was the better silver source than AgBF₄ and AgPF₆ (Table 1, Entries 4 vs. 5, 6). Then the silver(I) complexes of **1b**—**1f** and **2a**—**2e** were utilized in this reaction by using THF as the solvent. It was found that silver(I) complexes of **1** usually exhibited better enantioselectivities than those of **2** (Entries 1, 7—11 vs. 12—16). The best enantioselectivity of the reaction was obtained by using silver(I) complex of ligand **1a** when the reaction temperature was decreased to -20 °C (Entry 17). Moreover, the inferior activity and enantioselectivity of the reaction with the catalysis of silver(I)/**1f** complex demonstrated the importance of the aromatic substituents at P atom (Entries 11 vs. 1, 7—10).

Table 1 Enantioselective addition of allyltributyltin to benzaldehyde with the catalysis of silver(I)/MAP and silver(I)/H₈-MAP complexes ^a



Entry	Catalyst	Solvent	Time (h) ^b	Temp. (°C)	Yield (%) ^c	<i>ee</i> (%) ^d	Config. ^e
1	AgOTf/ 1a	THF	36	20	100	30.8	<i>R</i>
2	AgOTf/ 1a	CH ₂ Cl ₂	36	20	Trace	31.3	<i>R</i>
3	AgOTf/ 1a	DMF	36	20	86	21.7	<i>R</i>
4	AgOTf/ 1a	Toluene	36	20	74	34.8	<i>R</i>
5	AgBF ₄ / 1a	Toluene	36	20	100	< 5	<i>R</i>
6	AgPF ₆ / 1a	Toluene	36	20	100	33.3	<i>R</i>
7	AgOTf/ 1b	THF	18	20	100	22.5	<i>R</i>
8	AgOTf/ 1c	THF	18	20	100	25.0	<i>R</i>
9	AgOTf/ 1d	THF	18	20	100	22.8	<i>R</i>
10	AgOTf/ 1e	THF	18	20	100	29.5	<i>R</i>
11	AgOTf/ 1f	THF	18	20	100	14.9	<i>R</i>
12	AgOTf/ 2a	THF	18	20	90	5	<i>R</i>
13	AgOTf/ 2b	THF	18	20	92	5.2	<i>R</i>
14	AgOTf/ 2c	THF	18	20	67	5.2	<i>R</i>
15	AgOTf/ 2d	THF	18	20	86	10.6	<i>R</i>
16	AgOTf/ 2e	THF	18	20	100	9.1	<i>R</i>
17	AgOTf/ 1a	THF	36	-20	100	39.1	<i>R</i>

^a Reactions were carried out at 20 °C with a ratio of AgOTf:ligand:PhCHO:allyltributyltin = 0.1:0.1:1:1.2 in THF. ^b Reaction time was not optimized. ^c Isolated yield. ^d Determined by HPLC on Chiralcel OD column (hexane: *iso*-propanol = 98:2, flow rate = 0.6 mL/min). ^e Determined by comparison with the reported results.^{6a}

In our previous work, the application of aminophosphine ligands **3**–**5** in Pd(0)-catalyzed reaction of 1,3-diphenylallylic acetate with dimethyl malonate showed that better *ee* of the product could be obtained when the two chiral elements of the ligands were matched with each other.^{8b} This finding prompted us to employ ligands **3**–**5** in the reaction of silver(I) complex-catalyzed allylic addition of allyltributyltin to benzaldehyde. The results are summarized in Table 2. It was found that the enantioselectivity of the reaction with the catalysis of Ag(I)/**3** complex at 20 °C in toluene was higher than that obtained with silver(I)/**1a** complexes (Entry 1 in Table 2 vs. Entry 4 in Table 1). However, the reaction did not take place at a lower temperature in toluene. Again, the reaction was carried out in the presence of silver(I)/**3** complex in THF at –20 °C. Quantitative yield and up to 54.5% *ee* of the product could be obtained (Entry 2). When the reaction temperature was further decreased to –40 °C, the enantioselectivity of the reaction slightly dropped (Entries 3 vs. 2). Then the silver(I) complexes of **4** and **5** were submitted for promoting the reaction in THF at –20 °C, but no reaction occurred at all. When the temperature was enhanced to 0 °C, the reaction proceeded smoothly to give the desired product in good yields (Entries 4–7). It is obvious that absolute configuration of the major enantiomer of the product was predominantly controlled by the sense of backbone chirality. Although the *ee* of the product was not so high as that obtained with silver(I)/**3**, it was clearly demonstrated that mutual match of axial chirality of the scaffold and the central chirality of the modification group was important for achieving higher enantioselectivity in the reaction.

In conclusion, we have described the synthesis of a

series of aminophosphine ligands from 2-amino-2'-hydroxy-1,1'-binaphthyl (NOBIN). Their asymmetric induction efficiency was examined for silver(I) catalyzed enantioselective allylation reaction of benzaldehyde and allyltributyltin. Under the optimized reaction conditions, quantitative yield and moderate *ee* value (54.5% *ee*) of product were achieved by the catalysis with silver(I)/**3** complex. It was again confirmed that correct assembly of axial chirality of the scaffold and the central chirality of the modification group was important for achieving higher enantioselectivity in the reaction.

Experimental

General consideration.

¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ on Bruker AM300 and Bruker DRX400 spectrometers at 25 °C, respectively. Chemical shifts were expressed in δ with TMS as an internal standard (δ 0) for ¹H NMR and with residual signal of CDCl₃ as an internal standard (δ 77.0) for ¹³C NMR. The ³¹P NMR spectra were recorded on Bruker DRX400 and Bruker AM300 instruments in CDCl₃ with 85% H₃PO₄ as an external reference. Optical rotation was measured with a PE-341 automatic polarimeter. Liquid chromatographic analyses were conducted on a JASCO 1580 system. The IR spectra were recorded on a Rio-Rad FTS-185 spectrometer in KBr pellets. EI mass spectra and ESI mass spectra were obtained on HP5989A and Mariner LC-TOF spectrometer respectively. HRMS was determined on a Kratos Concept 1H instrument. Elemental analysis was performed with an Elemental VARIO EL apparatus. All the experiments which

Table 2 Enantioselective addition of allyltributyltin to benzaldehyde with the catalysis of silver(I) complexes of **3**, **4** and **5**^a

Entry	Ligand	Temp. (°C)	Solvent	Time (h)	Yield (%)	<i>ee</i> (%)	Config.
1	(<i>S</i>)- 3	20	Toluene	27	96	40.4	<i>S</i>
2	(<i>S</i>)- 3	–20	THF	36	100	54.5	<i>S</i>
3	(<i>S</i>)- 3	–40	THF	60	100	41.5	<i>S</i>
4	(<i>R,S,S</i>)- 4	0	THF	24	99	44.2	<i>R</i>
5	(<i>S,S,S</i>)- 4	0	THF	24	90	33.0	<i>S</i>
6	(<i>R,S,S</i>)- 5	0	THF	24	100	<5	<i>R</i>
7	(<i>S,S,S</i>)- 5	0	THF	24	89	27.1	<i>S</i>

^a Other reaction and analytic conditions were the same as those of Table 1.

are sensitive to moisture or air were carried out under argon atmosphere using standard Schlenk techniques. Commercial reagents were used as received without further purification unless otherwise noted. Dichloromethane and DMF were freshly distilled from calcium hydride and THF, toluene from sodium benzophenone ketyl. Optically pure NOBIN, H₈-NOBIN, compounds **6**, **7a**, **1a**, **8a**—**8f**, **14**, **15**, both enantiomers of **9** and ligands **2a**—**2e** were prepared according to reported procedure.⁸⁻¹⁵

(R)-2-Dimethylamino-2'-di(4-tolyl)phosphinyl-1,1'-binaphthyl [(*R*)-**7b**]

To a mixture of (*R*)-**6** (445 mg, 1 mmol), HP(O)(*p*-Tol)₂ (472 mg, 2 mmol), palladium acetate (22 mg, 0.1 mmol), and 1,3-bis(diphenylphosphino)propane (dppp, 62 mg, 0.15 mmol) were added dimethyl sulfoxide (5 mL) and diisopropylethylamine (0.87 mL, 5 mmol), and the reaction mixture was stirred at 100 °C for 5 h. After the removal of the solvent under reduced pressure, the resulting red residue was dissolved in 50 mL of EtOAc, washed with water and brine, dried over anhydrous MgSO₄, and concentrated again under reduced pressure. Chromatography of the crude product on silica gel with a 1:1:0.1 hexane/EtOAc/Et₃N mixed solvent as eluent gave (*R*)-**7b** as a yellow amorphous solid (522 mg, 99%), [α]_D²⁰ - 45.6 (*c* 0.55, THF); ¹H NMR (300 MHz, CDCl₃) δ: 2.23 (s, 3H), 2.27 (s, 3H), 2.37 (s, 6H), 6.71 (d, *J* = 8.5 Hz, 1H), 6.76—6.78 (m, 2H), 6.94—6.97 (m, 3H), 7.12—7.40 (m, 8H), 7.50—7.94 (m, 3H), 8.13—8.27 (m, 3H); ¹³C NMR (100.6 MHz, CDCl₃) δ: 21.41, 43.57, 119.40, 122.90, 125.67, 126.68, 127.05, 127.21, 127.40, 127.64, 127.91, 128.00, 128.08, 128.28, 128.45, 129.03, 129.31, 129.72, 129.88, 130.98, 131.12, 131.57, 131.70, 134.24, 134.62, 140.51, 140.98, 150.41; ³¹P NMR (161.9 MHz, CDCl₃) δ: 28.9; IR (KBr pellet) ν: 3294 (m), 1598 (m), 1498 (m), 1449 (m), 1116 (s), 813 (s), 751 (s) cm⁻¹; EIMS *m/z* (%): 525 (M⁺, 24); HRMS (EI) calcd for C₃₆H₃₂NOP 525.2222, found 525.2203.

(R)-2-Dimethylamino-2'-di(3-tolyl)phosphinyl-1,1'-binaphthyl [(*R*)-**7c**]

Following the same procedure for the preparation of (*R*)-**7b**, (*R*)-**7c** was obtained as a yellow amorphous

solid (yield, 96%), [α]_D²⁰ - 24.2 (*c* 0.50, THF); ¹H NMR (300 MHz, CDCl₃) δ: 2.10 (s, 3H), 2.19 (s, 3H), 2.39 (s, 6H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.88—7.56 (m, 15H), 7.85—7.96 (m, 4H); ³¹P NMR (161.9 MHz, CDCl₃) δ: 29.0; IR (KBr pellet) ν: 3050 (w), 1616 (m), 1497 (s), 1199 (m), 702 (m) cm⁻¹; EIMS *m/z* (%): 525 (M⁺, 38); HRMS (EI) calcd for C₃₆H₃₂NOP 525.2222, found 525.2219.

(R)-2-Dimethylamino-2'-(di(3,5-dimethyl)phenyl)phosphinyl-1,1'-binaphthyl [(*R*)-**7d**]

Following the same procedure for the preparation of (*R*)-**7b**, (*R*)-**7d** was obtained as a yellow amorphous solid (yield, 100%), [α]_D²⁰ - 38.4 (*c* 0.52, THF); ¹H NMR (300 MHz, CDCl₃) δ: 2.05 (s, 6H), 2.16 (s, 6H), 2.41 (s, 6H), 6.70—6.73 (m, 2H), 6.84—6.89 (m, 3H), 6.99—7.29 (m, 7H), 7.50—7.56 (m, 3H), 7.89—7.94 (m, 3H); ³¹P NMR (161.9 MHz, CDCl₃) δ: 29.1; IR (KBr pellet) ν: 2916 (s), 1616 (s), 1597 (s), 1498 (m), 1424 (m), 1194 (vs), 1131 (vs), 854 (s), 696 (vs) cm⁻¹; EIMS *m/z* (%): 553 (M⁺, 38); HRMS (EI) calcd for C₃₈H₃₆NOP 553.2535, found 553.2550.

(R)-2-Dimethylamino-2'-(di(4-tert-butyl)phenyl)phosphinyl-1,1'-binaphthyl [(*R*)-**7e**]

Following the same procedure for the preparation of (*R*)-**7b**, (*R*)-**7e** was obtained as a yellow amorphous solid (yield, 100%), [α]_D²⁰ - 50.0 (*c* 0.52, THF); ¹H NMR (300 MHz, CDCl₃) δ: 1.23 (s, 9H), 1.26 (s, 9H), 2.38 (s, 6H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.96—7.54 (m, 15H), 7.87—7.96 (m, 4H); ³¹P NMR (161.9 MHz, CDCl₃) δ: 28.9; IR (KBr pellet) ν: 3055 (m), 2958 (s), 1596 (s), 1497 (m), 1425 (m), 1201 (s), 1094 (vs), 819 (s), 749 (s), 644 (s), 613 (s) cm⁻¹; EIMS *m/z* (%): 609 (M⁺, 29); HRMS (EI) calcd for C₄₂H₄₄NOP 609.3161, found 609.3169.

(R)-2-Dimethylamino-2'-(dicyclohexyl)phosphinyl-1,1'-binaphthyl [(*R*)-**7f**]

Following the same procedure for the preparation of

(*R*)-**7b**, (*R*)-**7f** was obtained as a yellow amorphous solid (yield, 58%), $[\alpha]_D^{20} - 5.7$ (*c* 0.54, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ : 0.8–1.41 (m, br, 14H), 1.57–1.67 (m, br, 6H), 1.86–1.97 (m, br, 1H), 2.10 (br, 1H), 2.50 (s, 6H), 6.68 (d, $J = 8.6$ Hz, 1H), 7.02–7.04 (m, 1H), 7.05–7.38 (m, 3H), 7.46–7.51 (m, 2H), 7.80 (d, $J = 8.1$ Hz, 1H), 7.91–8.10 (m, 4H); ^{31}P NMR (161.9 MHz, CDCl_3) δ : 47.9; IR (KBr pellet) ν : 3056 (w), 2928 (vs), 2849 (s), 1620 (m), 1595 (m), 1506 (m), 1444 (m), 1216 (m), 1183 (vs), 985 (m), 814 (s), 758 (s), 747 (s) cm^{-1} ; EIMS m/z (%): 509 (M^+ , 54); HRMS (EI) calcd for $\text{C}_{34}\text{H}_{40}\text{NOP}$ 509.2848, found 509.2855.

Synthesis of (R)-2-dimethylamino-2'-(4-tolyl)phosphino-1,1'-binaphthyl [(R)-1b]

THF (4 mL) was added to anhydrous CeCl_3 (282 mg, 1.14 mmol) in a Schlenk tube and the mixture was stirred at room temperature for 1 h. Then LiAlH_4 (58 mg, 1.5 mmol) and (*R*)-**7b** (200 mg, 0.38 mmol) were added, and the mixture was stirred for 12 h at 40 °C. After cooling to room temperature, the reaction was quenched with water, diluted with diethyl ether, filtered through celite. The filtrate was washed with water and brine, dried over anhydrous MgSO_4 , and then concentrated under reduced pressure. The residue was chromatographed on silica gel (10:1 hexane/EtOAc as eluent) to afford (*R*)-**1b** as a light yellow amorphous solid (165 mg, 85%), $[\alpha]_D^{20} - 54.0$ (*c* 0.49, THF); ^1H NMR (300 MHz, CDCl_3) δ : 2.21 (s, 3H), 2.24 (s, 6H), 2.34 (s, 3H), 6.75 (d, $J = 8.4$ Hz, 1H), 6.77–7.51 (m, 15H), 7.46–7.85 (m, 3H), 7.93 (d, $J = 8.9$ Hz, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ : 23.86, 23.96, 45.91, 121.89, 128.47, 128.52, 128.90, 129.14, 130.09, 130.14, 130.43, 130.68, 131.41, 131.46, 131.50, 131.54, 131.84, 135.49, 135.73, 135.79, 136.06, 139.88, 153.00; ^{31}P NMR (161.9 MHz, CDCl_3) δ : -14.2; IR (KBr pellet) ν : 2777 (m), 1618 (m), 1594 (m), 1496 (s), 1450 (m), 1350 (m), 1186 (m), 1088 (m), 1091 (m), 985 (s), 819 (s), 807 (vs) cm^{-1} ; EIMS m/z (%): 509 (M^+ , 11); HRMS (EI) calcd for $\text{C}_{36}\text{H}_{32}\text{NP}$ 509.2272, found 509.2244.

(R)-2-Dimethylamino-2'-(3-tolyl)phosphino-1,1'-binaphthyl [(R)-1c]

Following the same procedure for the preparation of (*R*)-**1b**, (*R*)-**1c** was obtained as a light yellow amorphous solid (yield, 89%), $[\alpha]_D^{20} - 15.5$ (*c* 0.53, THF); ^1H NMR (300 MHz, CDCl_3) δ : 2.11 (s, 3H), 2.25 (s, 6H), 2.30 (s, 3H), 6.75–6.95 (m, 3H), 7.00–7.28 (m, 9H), 7.38–7.54 (m, 4H), 7.81–7.88 (m, 3H), 7.96 (d, $J = 8.9$ Hz, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ : 21.29, 21.56, 43.28, 119.25, 123.38, 125.72, 125.84, 126.24, 126.50, 127.47, 128.02, 128.29, 128.69, 129.18, 129.48, 129.87, 130.08, 130.29, 131.60, 133.45, 133.73, 134.10, 134.21, 134.42, 137.35, 151.00; ^{31}P NMR (161.9 MHz, CDCl_3) δ : -12.2; IR (KBr pellet) ν : 3046 (w), 2934 (w), 1619 (m), 1592 (s), 1505 (s), 1477 (s), 1450 (m), 1350 (m), 1332 (m), 1140 (m), 987 (s), 814 (s), 776 (s), 745 (s), 695 (s) cm^{-1} ; EIMS m/z (%): 509 (M^+ , 16); HRMS (EI) calcd for $\text{C}_{36}\text{H}_{32}\text{NP}$ 509.2272, found 509.2262.

(R)-2-Dimethylamino-2'-(di(3,5-dimethyl)phenyl)phosphino-1,1'-binaphthyl [(R)-1d]

Following the same procedure for the preparation of (*R*)-**1b**, (*R*)-**1d** was obtained as a light yellow amorphous solid (yield, 48%), $[\alpha]_D^{20} - 20.0$ (*c* 0.43, THF); ^1H NMR (300 MHz, CDCl_3) δ : 2.06 (s, 6H), 2.24 (s, 6H), 2.32 (s, 6H), 6.56 (d, $J = 7.8$ Hz, 1H), 6.70–6.72 (m, 1H), 6.90–7.07 (m, 3H), 7.23–7.45 (m, 9H), 7.81–7.94 (m, 4H); ^{13}C NMR (100.6 MHz, CDCl_3) δ : 21.12, 21.39, 43.34, 119.25, 123.30, 125.49, 125.60, 125.65, 125.89, 126.07, 126.32, 126.54, 127.33, 127.59, 127.94, 128.18, 128.91, 129.06, 129.14, 129.64, 130.43, 130.67, 131.04, 131.30, 131.53, 133.48, 133.65, 137.00, 137.09; ^{31}P NMR (161.9 MHz, CDCl_3) δ : -11.8; IR (KBr pellet) ν : 2916 (w), 1618 (m), 1595 (s), 1514 (s), 1333 (m), 1125 (m), 987 (s), 846 (s), 815 (vs), 747 (vs), 693 (vs) cm^{-1} ; EIMS m/z (%): 537 (M^+ , 13); HRMS (EI) calcd for $\text{C}_{38}\text{H}_{36}\text{NP}$ 537.2585, found 537.2583.

(R)-2-Dimethylamino-2'-(di(4-*tert*-butyl) phenyl)-phosphino-1,1'-binaphthyl [(*R*)-1e]

Following the same procedure for the preparation of (*R*)-1b, (*R*)-1e was obtained as a light yellow amorphous solid (yield, 86%), $[\alpha]_D^{20} - 48.3$ (*c* 0.51, THF); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 1.21 (s, 9H), 1.31 (s, 9H), 2.27 (s, 6H), 6.68 (d, $J = 8.5$ Hz, 1H), 6.84—6.92 (m, 3H), 7.07 (d, $J = 7.7$ Hz, 2H), 7.17—7.53 (m, 10 H), 7.77—7.94 (m, 4H); $^{13}\text{C NMR}$ (100.6 MHz, CDCl_3) δ : 31.08, 31.23, 31.32, 34.43, 34.55, 43.22, 119.31, 123.25, 124.82, 124.92, 125.00, 125.64, 125.08, 126.15, 126.35, 127.26, 127.40, 127.60, 127.97, 129.08, 129.41, 131.49, 132.62, 132.87, 133.06, 133.34, 133.60, 133.69, 134.16, 135.13, 150.44, 150.69; $^{31}\text{P NMR}$ (161.9 MHz, CDCl_3) δ : -14.7; IR (KBr pellet) ν : 3052 (w), 2961 (s), 1619 (m), 1595 (s), 1504 (s), 1493 (s), 1361 (s), 1268 (s), 1082 (s), 987 (s), 815 (vs), 746 (vs) cm^{-1} ; EIMS m/z (%): 593 (M^+ , 12); HRMS (EI) calcd for $\text{C}_{42}\text{H}_{44}\text{NP}$ 593.3211, found 593.3201.

Synthesis of (R)-2-dimethylamino-2'-(dicyclohexyl)-phosphino-1,1'-binaphthyl [(*R*)-1f]

Toluene (6 mL) was added to (*R*)-7f (200 mg, 0.4 mmol) in a Schlenk tube, then Et_3N (1.1 mL) was injected. After the mixture was cooled to 0 °C, HSiCl_3 (0.2 mL, 2 mmol) was added dropwise. Then the mixture was kept stirring at 0 °C for 0.5 h, and then was heated to 110 °C, stirred for 24 h. After being cooled to room temperature, the reaction was quenched with 1 mol/L aqueous NaOH, diluted with EtOAc, filtered through celite. The filtrate was washed with water and brine, dried over anhydrous MgSO_4 , and then concentrated under reduced pressure. The residue was chromatographed on silica gel (10:1 hexane/EtOAc as eluent) to afford (*R*)-1f as a light yellow amorphous solid (95 mg, 49%), $[\alpha]_D^{20} - 107.4$ (*c* 0.42, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 0.57—0.76 (m, 2H), 0.85—0.93 (m, 3H), 1.12—1.52 (m, 12H), 1.68—1.74 (m, 4H), 1.98—2.09 (m, 1H), 2.46 (s, 6H), 6.79 (d, $J = 8.4$ Hz, 1H), 7.01—7.06 (m, 1H), 7.19—7.27

(m, 2H), 7.35 (d, $J = 8.1$ Hz, 1H), 7.43—7.48 (m, 2H), 7.78 (d, $J = 8.7$ Hz, 2H), 7.88—7.93 (m, 3H); $^{31}\text{P NMR}$ (161.9 MHz, CDCl_3) δ : -7.6; IR (KBr pellet) ν : 3054 (w), 2920 (vs), 2847 (s), 1618 (m), 1594 (m), 1506 (m), 1446 (m), 1349 (m), 1140 (w), 987 (m), 814 (s), 748 (s) cm^{-1} ; EIMS m/z (%): 493 (M^+ , 6); HRMS (EI) calcd for $\text{C}_{34}\text{H}_{40}\text{NP}$ 493.2898; found 493.2913.

Synthesis of (R)-2-(acetamido)-2'-hydroxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl [(*R*)-10]

Acetyl chloride (0.5 mL, 7.0 mmol) in CH_2Cl_2 (3 mL) was added slowly to a solution of (*R*)-H₈-NOBIN (884 mg, 3.0 mmol) in CH_2Cl_2 (10 mL) at 0 °C in the presence of Et_3N (1.3 mL). After the mixture was kept at room temperature for 3 h, the reaction mixture was filtered through celite. The filtrate was diluted with ethyl acetate, washed with water and brine respectively, and then dried over anhydrous Na_2SO_4 . The solvent was evaporated under reduced pressure, then the residue was dissolved in CH_3OH (78 mL) to which NaOH (0.52 g, 13 mmol) and H_2O (5.2 mL) were added. The reaction mixture was stirred at room temperature for 1 h. After the completion of the hydrolysis, the solvent was removed under the reduced pressure again. The residue was diluted with H_2O (13 mL), neutralized with saturated aqueous NH_4Cl , extracted with ethyl acetate. The extracts were washed with brine, and then dried over anhydrous Na_2SO_4 . After the removal of the solvent under reduced pressure, the resulting residue was submitted to chromatographic separation on silica gel with hexane/EtOAc (1:1, *V*:*V*) as eluent to give (*R*)-10 as a white solid (871 mg, 87%), m.p. 147—149 °C, $[\alpha]_D^{25} + 51.4$ (*c* 0.5, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 1.26—1.78 (m, 8H), 1.92 (s, 3H), 2.05—2.30 (m, 4H), 2.74—2.81 (m, 4H), 4.80 (s, 1H), 6.70 (s, 1H), 6.84 (d, $J = 8.6$ Hz, 1H), 7.07 (d, $J = 8.6$ Hz, 1H), 7.15 (d, $J = 8.6$ Hz, 1H), 8.06 (d, $J = 7.9$ Hz, 1H); IR (KBr pellet) ν : 3379, 3223, 2926, 1652, 1596, 1521, 1421, 1413, 807, 532 cm^{-1} ; EIMS m/z (%): 335 (M^+ , 79). Anal. calcd for $\text{C}_{22}\text{H}_{25}\text{NO}_2$: C 78.77, H 7.51, N 4.18; found C 78.75, H 7.70, N 4.00.

Synthesis of (R)-2-(acetamido)-2'-(trifluoromethanesulfonyloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl [(R)-11]

Trifluoromethanesulfonic anhydride (0.6 mL, 6.76 mmol) in CH₂Cl₂ 5 mL was slowly added to a solution of (R)-10 (823 mg, 2.46 mmol) and Et₃N (0.68 mL) in dichloromethane (15 mL) at -78 °C. The reaction mixture was stirred for 1 h, and then warmed to room temperature. After the removal of the solvent under reduced pressure, the resulting residue was submitted to chromatographic separation on silica gel with hexane/EtOAc (2:1, V:V) as eluent to give (R)-11 as a white solid (906 mg, 79%), m.p. 115–117 °C, $[\alpha]_D^{25} - 3.8$ (c 0.5, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ: 1.58–2.36 (m, 12H), 1.93 (s, 3H), 2.79–2.87 (m, 4H), 6.71 (br, 1H), 7.12–7.27 (m, 3H), 7.77 (d, J = 8.6 Hz, 1H); IR (KBr pellet) ν: 3425, 2935, 1701, 1591, 1505, 1403, 1219, 1133, 1124, 927, 854, 808 cm⁻¹; EIMS m/z (%): 467 (M⁺, 100). Anal. calcd for C₂₃H₂₄FNO₄S: C 59.09, H 5.17, N 3.00; found C 59.23, H 5.01, N 2.88.

Synthesis of (R)-2-(acetamido)-2'-(diphenylphosphinyl)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl [(R)-12]

To a mixture of (R)-11 (566 mg, 1.21 mmol), diphenylphosphine oxide (489 mg, 2.42 mmol), palladium acetate (27 mg, 0.12 mmol), and 1,3-bis-(diphenylphosphino) propane (dppp, 75 mg, 0.18 mmol) were added dimethyl sulfoxide (6 mL) and diisopropylethylamine (1.1 mL, 6.05 mmol), and the reaction mixture was stirred at 100 °C for 15 h. After the removal of the solvent under reduced pressure, the resulting residue was dissolved in EtOAc, washed with water and saturated brine, dried over anhydrous Na₂SO₄, and then concentrated again under reduced pressure. Chromatography of the crude product on silica gel (1:1:0.06 of hexane/EtOAc/Et₃N as eluent) gave (R)-12 as a white solid (622 mg, 99%), m.p. 256–258 °C, $[\alpha]_D^{25} - 111.2$ (c 0.5, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ: 1.42–1.74 (m, 10H), 1.95 (s, 3H), 2.01–2.04 (m, 1H), 2.22–2.26 (m, 2H), 2.49–2.58 (m, 1H), 2.80–2.84 (m, 2H), 6.90 (d, J = 8.6 Hz, 1H), 7.07–7.66 (m, 11H), 7.89–8.96

(m, 2H), 9.22 (s, 1H); ³¹P NMR (121.46 MHz, CDCl₃) δ: 27.8; IR (KBr pellet) ν: 3052, 2930, 1676, 1590, 1521, 1438, 1162, 705, 532 cm⁻¹; EIMS m/z (%): 519 (M⁺, 100). Anal. calcd for C₃₄H₃₄NO₂P: C 78.59, H 6.60, N 2.70; found C 78.27, H 6.63, N 2.51.

Synthesis of (R)-2-(amino)-2'-(diphenylphosphinyl)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl [(R)-13]

(R)-12 (568 mg, 1.1 mmol) was dissolved in absolute EtOH (20 mL). After the addition of 5% aqueous HCl (4 mL), the reaction mixture was kept refluxing for 18 h. Then the solvent was evaporated under reduced pressure. The residue was diluted with water, neutralized with 25% aqueous ammonia solution, extracted with CH₂Cl₂. The organic phase was washed with water and brine, dried over anhydrous Na₂SO₄, and then concentrated again under reduced pressure to afford crude 13 (531 mg, 100%) as a white solid. The crude product could be used directly in the next step without further purification.

Synthesis of (R,R)-1,4-dibromo-2,3-dimethoxybutane [(R,R)-15]

14 (4.41 g, 9.6 mmol) and LiBr · H₂O (10.07 g, 96 mmol) were dissolved in acetone (100 mL). The mixture was refluxed for 24 h before the solvent was removed under reduced pressure. The resulting residue was diluted with water, extracted with diethyl ether. The extracts were washed with brine, dried over anhydrous Na₂SO₄, and then concentrated again under reduced pressure. Chromatography of the crude product on silica gel with hexane/EtOAc (100:1–100:5) as eluent gave (R,R)-15 as a colorless liquid (2.18 g, 82%), $[\alpha]_D^{25} + 12.3$ (c 6.4, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ: 3.48–3.58 (m, 10H), 3.74–3.80 (m, 2H); IR (neat) ν: 2934, 2830, 1116, 1090, 892, 675 cm⁻¹. Anal. calcd for C₆H₁₂Br₂O₂: C 26.11, H 4.38; found C 25.99, H 4.37.

Synthesis of (S)-2-(pyrrolidino)-2'-(diphenylphosphinyl)-1,1'-binaphthyl [(S)-17]

A mixture of (S)-9 (469 mg, 1 mmol), 1,4-

dibromobutane (0.14 mL, 1.2 mmol), and NaHCO_3 (403 mg, 4.8 mmol) in toluene (4 mL) was refluxed for 20 h. Then the mixture was diluted with water, extracted with CH_2Cl_2 . The organic phase was washed with brine, dried over anhydrous Na_2SO_4 , and then concentrated under reduced pressure. Chromatography of the crude product on silica gel with a 1:2:0.09 (V:V:V) of hexane/EtOAc/ Et_3N mixture as eluent gave (*S*)-**17** as a yellow solid (329 mg, 63%), m. p. 259–261 °C, $[\alpha]_{\text{D}}^{25} + 278.9$ (c 0.5, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ : 1.62–1.67 (m, 4H), 2.76–2.80 (m, 2H), 2.96–2.99 (m, 2H), 6.62 (d, $J = 8.6$ Hz, 1H), 6.79–7.87 (m, 3H), 6.92–7.12 (m, 5H), 7.27–7.42 (m, 6H), 7.50–7.65 (m, 4H), 7.72–7.79 (m, 1H), 7.90–7.96 (m, 2H); ^{31}P NMR (121.46 MHz, CDCl_3) δ : 27.8; IR (KBr pellet) ν : 3035, 2977, 1616, 1598, 1504, 1459, 1187, 1109, 699, 524; EIMS m/z (%): 523 (M^+ , 100). HRMS (EI) calcd for $\text{C}_{36}\text{H}_{30}\text{NOP}$ 523.2065, found 523.2107.

Synthesis of (S)-2-(pyrrolidino)-2'-(diphenylphosphino)-1,1'-binaphthyl [(S)-3]

To a solution of (*S*)-**17** (262 mg, 0.5 mmol) in toluene (4 mL) were added *N,N*-dimethylaniline (0.45 mL, 3.5 mmol) and HSiCl_3 (0.38 mL, 3.5 mmol). After the reaction mixture was refluxed for 12 h, it was quenched with 1 mol/L aqueous NaOH, diluted and extracted with ethyl acetate. The extracts were washed with 5% aqueous HCl, water, saturated aqueous NaHCO_3 and brine, and then dried over anhydrous MgSO_4 . After the removal of the solvent under reduced pressure, the resulting residue was submitted to chromatographic separation on silica gel with hexane/EtOAc (10:1, V:V) as eluent to give (*S*)-**3** as light yellow solid (177 mg, 70%), m. p. 156–158 °C, $[\alpha]_{\text{D}}^{25} + 205.2$ (c 0.5, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ : 1.18–1.24 (m, 2H), 1.44–1.46 (m, 2H), 2.68–2.72 (m, 4H), 6.74 (d, $J = 8.6$ Hz, 1H), 6.83–6.89 (m, 2H), 6.94–6.99 (m, 1H), 7.04–7.12 (m, 4H), 7.23–7.52 (m, 9H), 7.68–7.75 (m, 2H), 7.84–7.89 (m, 3H); ^{31}P NMR (121.46 MHz, CDCl_3) δ : -13.4; IR (KBr pellet) ν : 3049, 1616, 1597, 1506, 1473, 1433, 1382, 805, 743, 692 cm^{-1} ; EIMS m/z (%): 507 (M^+ , 15); HRMS (EI) calcd for $\text{C}_{36}\text{H}_{30}\text{NP}$ 507.2116, found 507.2114.

Synthesis of (R)-2-((3S,4S)-dimethoxypyrrolidino)-2'-(diphenylphosphinyl)-1,1'-binaphthyl [(R,S,S)-18]

The mixture of (*R*)-**9** (469 mg, 1 mmol), **15** (662 mg, 2.4 mmol), NaHCO_3 (840 mg, 10 mmol), and NaI (30 mg, 0.2 mmol) in 1,3,5-trimethylbenzene (6 mL) was kept at 150 °C over 30 h. Then the reaction mixture was diluted with water, extracted with CH_2Cl_2 . The extracts were washed with brine, dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure. Chromatography of the crude product on silica gel with 1:3:0.12 hexane/EtOAc/ Et_3N (V:V:V) mixed solvent as eluent gave (*R,S,S*)-**18** as a yellow amorphous solid (393 mg, 67%), $[\alpha]_{\text{D}}^{25} - 97.9$ (c 0.5, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ : 2.72 (d, $J = 11.2$ Hz, 2H), 3.14 (s, 6H), 3.25–3.30 (m, 2H), 3.57–3.59 (m, 2H), 6.62–6.69 (m, 2H), 6.91–7.01 (m, 4H), 7.11–7.52 (m, 12H), 7.64–7.71 (m, 1H), 7.78–7.83 (m, 1H), 7.88–7.98 (m, 2H); ^{31}P NMR (121.46 MHz, CDCl_3) δ : 28.9; IR (KBr pellet) ν : 3053, 2926, 1617, 1598, 1508, 1436, 1183, 1110, 699, 539 cm^{-1} ; ESIMS m/z (%): 584.4 ($[\text{M}+1]^+$, 100).

Synthesis of (R)-2-((3S,4S)-dimethoxypyrrolidino)-2'-(diphenylphosphino)-1,1'-binaphthyl [(R,S,S)-4]

To a solution of (*R,S,S*)-**18** (318 mg, 0.54 mmol) in toluene (4 mL) was added Et_3N (0.53 mL) and Cl_3SiH (0.42 mL, 3.78 mmol). After the reaction mixture was kept at 100 °C for 12 h, it was quenched with 1 mol/L aqueous NaOH, diluted and extracted with ethyl acetate. The extracts were washed with 5% aqueous HCl, water, saturated aqueous NaHCO_3 , and brine, dried over anhydrous Na_2SO_4 . After the removal of the solvent under reduced pressure, the resulting residue was submitted to chromatographic separation on silica gel with hexane/EtOAc (4:1, V:V) as eluent to give (*R,S,S*)-**4** as light yellow amorphous solid (235 mg, 76%), $[\alpha]_{\text{D}}^{25} - 167.4$ (c 0.5, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ : 3.00 (d, $J = 10.9$ Hz, 2H), 3.12–3.16 (m, 8H), 3.54–3.56 (m, 2H), 6.37 (d, $J = 8.6$ Hz, 1H), 6.66–6.70 (m, 1H), 6.84–7.04 (m, 5H), 7.25–7.60 (m, 10H), 7.62–7.64 (m, 2H), 7.84 (t, $J = 8.9$ Hz, 3H); ^{31}P NMR (121.46 MHz, CDCl_3) δ : -12.2; IR (KBr pellet) ν : 3048, 2926,

1616, 1597, 1508, 1458, 1429, 1106, 806, 741, 694 cm^{-1} ; EIMS m/z (%): 567 (M^+ , 29). Anal. calcd for $\text{C}_{38}\text{H}_{34}\text{NO}_2\text{P}$: C 80.04, H 6.04, N 2.47; found C 79.92, H 6.30, N 2.19.

Synthesis of (S)-2-((3S,4S)-dimethoxyppyrolidino)-2'-(diphenylphosphinyl)-1,1'-binaphthyl [(S,S,S)-18]

Following the same procedure for the preparation of (*R,S,S*)-**18**, (*S,S,S*)-**18** was obtained as a yellow amorphous solid (yield, 67%), $[\alpha]_{\text{D}}^{25} + 175.4$ (*c* 0.5, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ : 2.89—2.94 (m, 2H), 3.07—3.12 (m, 2H), 3.16 (s, 6H), 3.62—3.65 (m, 2H), 6.63 (d, $J = 8.4$ Hz, 1H), 6.85—7.17 (m, 7H), 7.26—7.70 (m, 11H), 7.89—7.91 (m, 3H); ^{31}P NMR (121.46 MHz, CDCl_3) δ : 28.1; IR (KBr pellet) ν : 3053, 2928, 1617, 1598, 1507, 1437, 1184, 1111, 700, 539, 524 cm^{-1} ; ESIMS m/z (%): 584.4 ($[M+1]^+$, 100).

Synthesis of (S)-2-((3S,4S)-dimethoxyppyrolidino)-2'-(diphenylphosphino)-1,1'-binaphthyl [(S,S,S)-4]

Following the same procedure for the preparation of (*R,S,S*)-**4**, (*S,S,S*)-**4** was obtained as a light yellow amorphous solid (yield, 72%), $[\alpha]_{\text{D}}^{25} + 207.4$ (*c* 0.5, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ : 2.59—2.64 (m, 2H), 2.94—2.99 (m, 2H), 3.02 (s, 6H), 3.23—3.27 (m, 2H), 6.69 (d, $J = 8.6$ Hz, 1H), 6.84—6.86 (m, 2H), 6.97—7.57 (m, 14H), 7.58 (d, $J = 8.4$ Hz, 1H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.84—7.89 (m, 3H); ^{31}P NMR (121.46 MHz, CDCl_3) δ : -13.1; IR (KBr pellet) ν : 3035, 2930, 1616, 1596, 1459, 1431, 1109, 813, 742, 694 cm^{-1} ; EIMS m/z (%): 567 (M^+ , 34). Anal. calcd for $\text{C}_{38}\text{H}_{34}\text{NO}_2\text{P}$: C 80.04, H 6.04, N 2.47; found C 80.31, H 6.38, N 2.28.

Synthesis of (R)-2-((3S,4S)-dimethoxyppyrolidino)-2'-(diphenylphosphinyl)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl [(R,S,S)-19]

Following the same procedure for the preparation of (*R,S,S*)-**18**, (*R,S,S*)-**19** was obtained as a white amorphous solid (yield, 83%), $[\alpha]_{\text{D}}^{25} + 63.0$ (*c* 0.5,

CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ : 1.24—2.18 (m, 11H), 2.31—2.38 (m, 1H), 2.52—2.62 (m, 2H), 2.76—2.86 (m, 4H), 3.14—3.20 (m, 2H), 3.28 (s, 6H), 3.64—3.66 (m, 2H), 6.22 (d, $J = 8.6$ Hz, 1H), 6.86 (d, $J = 7.9$ Hz, 1H), 7.09—7.11 (m, 1H), 7.23—7.65 (m, 11H); ^{31}P NMR (121.46 MHz, CDCl_3) δ : 28.4; IR (KBr pellet) ν : 3053, 2927, 1595, 1483, 1459, 1436, 1185, 1110, 699, 528 cm^{-1} ; ESIMS m/z (%): 592.3 ($[M+1]^+$, 100).

Synthesis of (R)-2-((3S,4S)-dimethoxyppyrolidino)-2'-(diphenylphosphino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl [(R,S,S)-5]

Following the same procedure for the preparation of (*R,S,S*)-**4**, (*S,S,S*)-**5** was obtained as a white amorphous solid (yield, 89%), $[\alpha]_{\text{D}}^{25} + 4.5$ (*c* 0.5, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ : 1.25—1.91 (m, 10H), 2.31—2.68 (m, 4H), 2.76—2.83 (m, 2H), 2.89—2.95 (m, 2H), 3.09—3.18 (m, 2H), 3.25 (s, 6H), 3.63—3.64 (m, 2H), 6.87 (d, $J = 8.6$ Hz, 1H), 7.01—7.03 (m, 3H), 7.25—7.34 (m, 10H); ^{31}P NMR (121.46 MHz, CDCl_3) δ : -14.3; IR (KBr pellet) ν : 3049, 2926, 4593, 1481, 1458, 1433, 1108, 806, 742, 696 cm^{-1} ; EIMS m/z (%): 575 (M^+ , 25). Anal. calcd for $\text{C}_{38}\text{H}_{42}\text{NO}_2\text{P}$: C 79.28, H 7.35, N 2.43; found C 78.83, H 7.35, N 2.24.

Synthesis of (S)-2-((3S,4S)-dimethoxyppyrolidino)-2'-(diphenylphosphinyl)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl [(S,S,S)-19]

Following the same procedure for the preparation of (*R,S,S*)-**18**, (*S,S,S*)-**19** was obtained as a white amorphous solid (yield, 89%), $[\alpha]_{\text{D}}^{25} + 20.5$ (*c* 0.5, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ : 1.26—1.93 (m, 10H), 2.10—2.31 (m, 4H), 2.54—2.60 (m, 2H), 2.74—2.91 (m, 4H), 3.21 (s, 6H), 3.54—3.57 (m, 2H), 6.29 (d, $J = 7.9$ Hz, 1H), 6.75 (d, $J = 7.9$ Hz, 1H), 7.08—7.12 (m, 1H), 7.24—7.60 (m, 11H); ^{31}P NMR (121.46 MHz, CDCl_3) δ : 28.8; IR (KBr pellet) ν : 3035, 2927, 1594, 1483, 1459, 1436, 1187, 1110, 699, 528 cm^{-1} ; ESIMS m/z (%): 592.4 ($[M+1]^+$, 100).

Synthesis of (S)-2-((3S,4S)-dimethoxy pyrrolidino)-2'-(diphenylphosphino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl [(S,S,S)-5]

Following the same procedure for the preparation of (*R,S,S*)-**4**, (*S,S,S*)-**5** was obtained as a white amorphous solid (yield, 84%), $[\alpha]_D^{25} + 101.8$ (*c* 0.5, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 1.17—1.22 (m, 1H), 1.44—1.76 (m, 8H), 1.97—2.05 (m, 1H), 2.40—2.51 (m, 2H), 2.71—2.75 (m, 4H), 2.81—2.83 (m, 2H), 2.97—3.02 (m, 2H), 3.15 (s, 6H), 3.43—3.46 (m, 2H), 6.69 (d, $J = 7.9$ Hz, 1H), 7.04—7.29 (m, 13H); $^{31}\text{P NMR}$ (121.46 MHz, CDCl_3) δ : -14.2; IR (KBr pellet) ν : 3049, 2930, 1592, 1471, 1433, 1104, 807, 741, 695 cm^{-1} ; EIMS m/z (%): 575 (M^+ , 29.8). Anal. calcd for $\text{C}_{38}\text{H}_{42}\text{NO}_2\text{P}$: C 79.28, H 7.35, N 2.43; found C 79.61, H 7.71, N 2.22.

Typical procedure for Ag(I) complexes catalyzed allylation of benzaldehyde with allyltributyltin

To a Schlenk tube containing AgOTf (3 mg, 0.013 mmol, 10 mol%) and ligand (*S*)-**3** (6 mg, 0.01 mmol, 10 mol%) was added THF (1 mL), the mixture was stirred at room temperature (20 °C) for 10 min. Benzaldehyde (12.5 mg, 0.125 mmol) was then added, and the mixture was stirred for an additional 10 min before cooling to -20 °C. At this temperature, allyltributyltin (46.5 μL , 0.15 mmol) was added. After 36 h, the reaction mixture was quenched with saturated aqueous KF, diluted and extracted with EtOAc. The organic phase was then washed with water and brine respectively, dried over anhydrous MgSO_4 , and then concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with hexane/EtOAc (6:1, *V:V*) as eluent to give allylation product (17.2 mg, 100%) as colorless oil with 54.5% *ee*. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 2.40 (br, 1H), 2.45—2.50 (m, 2H), 4.66—4.70 (m, 1H), 5.09—5.16 (m, 2H), 5.73—5.82 (m, 1H), 7.24—7.33 (m, 5H). The enantiomeric excess was determined by HPLC (Chiralcel OD, flow rate = 0.6 mL/min, hexane : *iso*-propanol = 98:2, *V:V*).

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