Phosphorodiamidite derivatives of 1,1′-bi-2-naphthol containing stereogenic phosphorus atoms as ligands in enantioselective catalysis

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*P**-Mono- and *P**,*P**-bidentate phosphorodiamidites containing the (S_a)-1,1′-binaphthyl core and 1,3,2-diazaphospholidine rings were synthesized. The use of these compounds in the rhodium-catalyzed asymmetric hydrogenation, as well as in the palladium- and platinum-catalyzed asymmetric alkylation and amination, resulted in the formation of the products with *ee* of up to 99%.

Key words: *P**-chiral phosphorodiamidites, rhodium complexes, palladium complexes, platinum complexes, catalysts, asymmetric allylation, asymmetric hydrogenation.

The modern asymmetric metal complex catalysis is one of the most effective and environmentally safe methods for the synthesis of optically pure organic and heteroorganic compounds. In addition to the well-known application in pharmaceutical chemistry, this method is successfully used in the synthesis of fragrance compounds, plant protection chemicals, individual stereoisomeric polymers, and liquid crystals.[1—4] To achieve virtually quantitative chemical and optical yields in enantioselective catalytic transformations, it is necessary to carefully optimize various reaction parameters, primarily, to correctly choose the corresponding ligand group and to rationally design each representative of this group.[5] *P*,*P*-Bidentate phosphines belong to a class of effective phosphorus-containing stereoselectors. At the same time, recent studies have shown[6—11] that phosphite-type *P*,*P*-bidentate ligands are highly competitive with the above-mentioned compounds and have advantages in that they can easily be synthesized from readily accessible precursors, are resistant to oxidation, have a pronounced π-acidity, and are less expensive. In particular, bis-phosphite derivatives of the known chiral agent 1,1′-bi-2-naphthol (BINOL) can be considered as promising stereoinducers.[12] Thus, phosphite ligands $L_{A—C}$ containing the 1,3,2-dioxaphosphepine rings based on BINOL, its octahydrogenated derivative (H_8-BINOL), or various 2,2′-dihydroxy-1,1′-biphenyls were successfully used in the Cu-catalyzed conjugated addition,[13—17] the Co-catalyzed Pauson—Khand reaction,[18] and the Rh-catalyzed hydroformylation.[19,20] Phosphites $L_{D—F}$ containing the 1,3,2-dioxaphosphorinane and 1,3,2-dioxaphospholane rings based on chiral 1,3- and 1,2-diols appeared to be ineffective stereoselectors. Thus, the *ee* of no higher than 40% was achieved with their use in the Rh-catalyzed hydroformylation of styrene.[21—23]

Hence, the synthesis of new effective phosphite-type BINOL-based *P*,*P*-bidentate ligands remains an important problem. Previously,[24,25] we have described the synthesis of diastereomeric *P**,*P**-bidentate phosphorodiamidites containing 1,3,2-diazaphospholidine rings based on 1,4:3,6-dianhydro-D-mannite and reported on the use of these compounds in catalytic asymmetric reactions. It should be noted that *P**-chiral 1,3,2-diazaphospholidines belong to an attractive group of optically active phosphorodiamidite ligands. In particular, these ligands have balanced electronic characteristics because they are both good π-acceptors (due to the accessibility of low-lying π^*_{PN} orbitals) and good σ-donors. The inclusion of the phosphorus atom in the five-membered ring enhances the resistance of the ligands to oxidation and hydrolysis, and the

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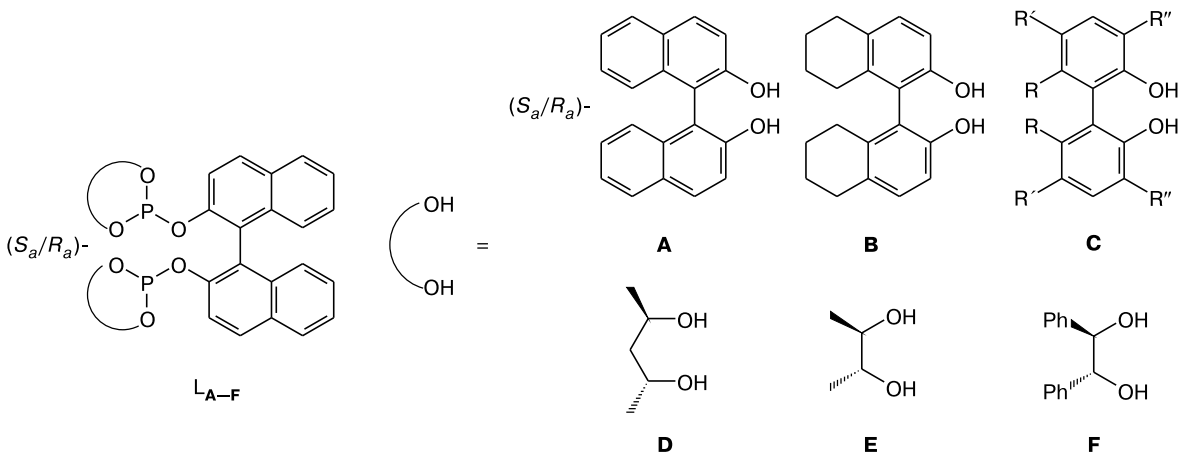


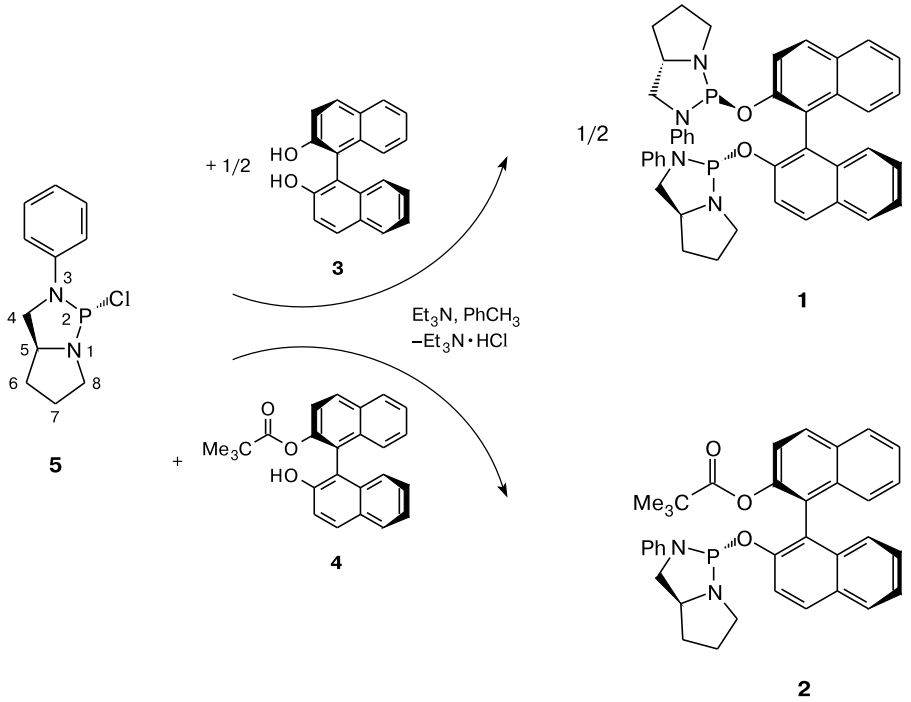
possibility of varying the nature of the substituents at the nitrogen atoms allows the control over the steric and electronic parameters.[26,27]

In the present study, we report the synthesis of the first *P**,*P**-bidentate phosphorodiamidite **1** containing the (S_a)-1,1′-binaphthyl core and 1,3,2-diazaphospholidine rings and the application of this compound in the enantioselective catalysis. We also compared the performance characteristics of phosphorodiamidite **1** with those of the specially synthesized related *P**-monodentate ligand **2** containing the pivalate moiety (*S*)-BINOL as the exocyclic substituent. We investigated the asymmetric hydrogenation and allylation as catalytic reactions. The enantioselective hydrogenation with the use of inexpensive molecular hydrogen and a small amount of a catalyst holds considerable promise for the industrial use. The allylic substitution, which is tolerant to various functional groups in the substrate and operates with a wide range of C-, N-, O-, S-, and P-nucleophiles, is successfully used in the key steps of the synthesis of various natural compounds.[28–31]

Results and Discussion

New *P**-chiral phosphorodiamidites **1** and **2** were synthesized by the one-step phosphorylation of (*S*)-BINOL **3** or its pivalate **4** by reagent **5** in toluene (Scheme 1).

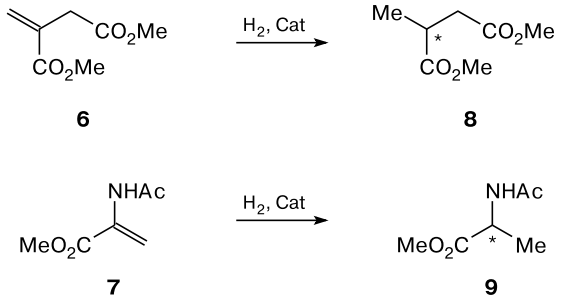
Scheme 1



It should be noted that phosphorylating agent **5** can easily be synthesized[32] in high yield from readily accessible (*S*)-glutamic acid anilide.[33,34] Compound **1** is an individual stereoisomer, whereas compound **2** is a mixture of epimers with respect to the phosphorus stereocenter. This is evident from the fact that the ^{31}P NMR spectra of these compounds in $CDCl_3$ show one singlet at δ_P 128.7 and two singlets at δ_P 129.7 (73%) and 119.6 (27%), respectively. Ligand **1** and the major epimer of ligand **2** have the *P** stereocenters in the (*R*) configuration. The ^{13}C NMR spectra of these ligands are characterized by large spin-spin coupling constants $^2J_{C(8'),P}$ (36.5 and 32.7 Hz), which are indicative of the *cis* orientation of the phosphorus lone pair with respect to the C(8′) atom. The pseudoequatorially oriented exocyclic substituent at the phosphorus atom and the pyrrolidine ring of the phosphabicyclo[3.3.0]-octane core are in the *trans* arrangement. On the contrary, the minor epimer of ligand **2** contains the asymmetric phosphorus atom in the (*S*) configuration, as evidenced by the fact that the ^{13}C NMR spectrum of **2** has the small constant $^2J_{C(8'),P}$ = 3.8 Hz.[32,34–38] Compounds **1** and **2** are rather stable in air, can be stored over a long period of time under a dry atmosphere, and are readily soluble in usual organic media.

In the first step of the catalytic experiments, phosphorodiamidites **1** and **2** were used in the Rh-catalyzed asymmetric hydrogenation of prochiral methyl esters of unsaturated acids, *viz.*, dimethyl itaconate (**6**) and methyl *N*-acetylaminoacrylate (**7**) (Scheme 2, Table 1). The complex $[Rh(COD)_2]BF_4$ (COD is 1,5-cyclooctadiene) was used as the precatalyst.

Scheme 2



6 **8** **7** **9**

Cat is a catalyst

*P**,*P**-Bidentate ligand **1** provides the virtually quantitative enantioselectivity (*ee* 97—99%) regardless of the nature of the starting substrate and the L/Rh molar ratio (see Table 1, runs *1*, *2*, *4*, and *5*). At the same time, *P**-monodentate stereoselector **2** allows the synthesis of products **8** and **9** having the same absolute configuration as in the reactions with the involvement of ligand **1** but with a substantially lower optical purity (*ee* 49 and 35%, respectively) (see Table 1, runs *3* and *6*). *P**-Mono- and

Table 1. Results of the Rh-catalyzed hydrogenation of substrates **6** and **7**[a]

Run	Ligand (L)	L/Rh	Substrate	*ee* (%)[b,c] (configuration)
1	**1**	1	**6**	>99 (*R*)
2	**1**	2	**6**	98 (*R*)
3	**2**	2	**6**	49 (*R*)
4	**1**	1	**7**	99 (*S*)
5	**1**	2	**7**	97 (*S*)
6	**2**	2	**7**	35 (*S*)

[a] The reaction conditions: 25 °C, CH_2Cl_2, 20 h, 0.5 mol.% $[Rh(COD)_2]BF_4$, P_{H_2} = 1.3 atm; in all cases, the conversion was 100%.

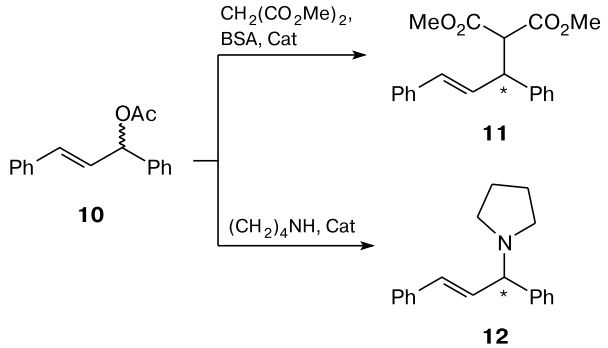
[b] The conversion of substrate **6** and the enantiomeric excesses of product **8** were determined by GC (Lipodex E, 25 m × 0.25 mm, 80 °C, 1 mL min^{-1}) or HPLC (Daicel Chiralcel OD-H, C_6H_{14} : Pr^iOH = 98 : 2, 0.8 mL min^{-1}, 220 nm, $t(R)$ = 9.1 min, $t(S)$ = 16.1 min).

[c] The conversion of substrate **7** and the enantiomeric excesses of product **9** were determined by GC (XE-valine(*tert*-butylamide), 4×0.25 mm, 85 °C, 1 mL min^{-1}).

*P**,*P**-bidentate phosphorodiamidites based on 1,4:3,6-dianhydro-D-mannite show an analogous behavior. These compounds also provide the much higher asymmetric induction.[25] In this respect, *P**-chiral 1,3,2-diazaphospholidines substantially differ from known BINOL-based axially chiral 1,3,2-dioxa- and 1,3,2-oxazaphosphepines, where *P*-mono- and *P,P*-bidentate ligands are equally effective in most cases.[39,40]

In the next step, stereoselectors **1** and **2** were studied in the Pd- and Pt-catalyzed asymmetric allylation of (*E*)-1,3-diphenylallyl acetate (**10**) (Scheme 3, Tables 2 and 3).

Scheme 3



10 **11** **12**

The Pd-catalyzed allylic alkylation of substrate **10** with dimethyl malonate with the use of ligand **1** affords product (*S*)-**11** (*ee* up to 99%). The higher enantioselectivity is observed in THF; the highest conversions is achieved in CH_2Cl_2 (see Table 2, runs *1*—*4*). The optimal L/Pd molar ratio is 1, whereas an increase in this ratio to 2 leads to

Table 2. Results of the Pd- and Pt-catalyzed allylic alkylation of substrate **10** with dimethyl malonate[a]

Run	Source of Pd or Pt	Ligand (L)	L/Pd (L/Pt)	Solvent	Conversion (%)	*ee* (%)[b] (configuration)
1	$[Pd(All)Cl]_2$	**1**	1	THF	57	99 (*S*)
2	$[Pd(All)Cl]_2$	**1**	2	THF	65	92 (*S*)
3	$[Pd(All)Cl]_2$	**1**	1	CH_2Cl_2	94	94 (*S*)
4	$[Pd(All)Cl]_2$	**1**	2	CH_2Cl_2	93	65 (*S*)
5	$[Pt(All)Cl]_4$	**1**	1	THF	56	60 (*R*)
6	$[Pt(All)Cl]_4$	**1**	2	THF	54	72 (*R*)
7	$[Pt(All)Cl]_4$	**1**	1	CH_2Cl_2	73	87 (*R*)
8	$[Pt(All)Cl]_4$	**1**	2	CH_2Cl_2	61	85 (*R*)
9	$[Pd(All)Cl]_2$	**2**	1	THF	90	29 (*S*)
10	$[Pd(All)Cl]_2$	**2**	2	THF	83	40 (*S*)
11	$[Pd(All)Cl]_2$	**2**	1	CH_2Cl_2	72	41 (*S*)
12	$[Pd(All)Cl]_2$	**2**	2	CH_2Cl_2	100	20 (*S*)

[a] The reaction conditions: 20 °C, 48 h, 2 mol.% $[Pd(All)Cl]_2$ or 1 mol.% $[Pt(All)Cl]_4$.
[b] The conversion of substrate **10** and the enantiomeric excesses of product **11** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14} : Pr^iOH = 99 : 1, 0.6 mL min^{-1}, 254 nm).

a decrease in the asymmetric induction, particularly, in the reaction performed in CH_2Cl_2. Like the asymmetric hydrogenation, the experiments with the use of *P**-monodentate ligand **2** afforded the reaction product having the same absolute configuration and low optical purity (*ee* is at most 41%) (see Table 2, runs *9—12*). In the presence of the platinum catalyst, phosphorodiamidite **1** provides a somewhat lower enantioselectivity (*ee* is no higher than 87%) (see Table 2, runs *5—8*), but it is comparable to that of the effective *P*,*N*- and *P*,*P*-bidentate phosphine stereoselectors PHOX and CHIRAPHOS.[41,42] It should be noted that the Pt-catalyzed alkylation of substrate **10** results in the higher conversion and enantioselectivity in CH_2Cl_2, and product **11** has the (*R*) configuration.

The Pd-catalyzed allylic amination of (*E*)-1,3-diphenylallyl acetate (**10**) with pyrrolidine with the use of *P**,*P**-bidentate ligand **1** gives product (*R*)-**12** in high optical yields (96—99%) (see Scheme 3 and Table 3, runs *1—4*) regardless of the L/Pd molar ratio and the nature of the solvent, the highest conversion being observed in CH_2Cl_2. It is interesting that *P**-monodentate ligand **2** is also an excellent stereoinducer. Thus, the *ee* of up to 99% was achieved in the reactions with this ligand (see Table 3, runs *9—12*). It should be noted that *P**-monodentate ligands based on 1,4:3,6-dianhydro-D-mannite are virtu-

Table 3. Results of the Pd- and Pt-catalyzed allylic amination of substrate **10** with pyrrolidine[a]

Run	Source of Pd or Pt	Ligand (L)	L/Pd (L/Pt)	Solvent	Conversion(%)	*ee* (%)[b] (configuration)
1	$[Pd(All)Cl]_2$	**1**	1	THF	48	96 (*R*)
2	$[Pd(All)Cl]_2$	**1**	2	THF	68	98 (*R*)
3	$[Pd(All)Cl]_2$	**1**	1	CH_2Cl_2	100	98 (*R*)
4	$[Pd(All)Cl]_2$	**1**	2	CH_2Cl_2	90	99 (*R*)
5	$[Pt(All)Cl]_4$	**1**	1	THF	100	83 (*S*)
6	$[Pt(All)Cl]_4$	**1**	2	THF	100	50 (*S*)
7	$[Pt(All)Cl]_4$	**1**	1	CH_2Cl_2	100	86 (*S*)
8	$[Pt(All)Cl]_4$	**1**	2	CH_2Cl_2	100	84 (*S*)
9	$[Pd(All)Cl]_2$	**2**	1	THF	98	89 (*R*)
10	$[Pd(All)Cl]_2$	**2**	2	THF	32	88 (*R*)
11	$[Pd(All)Cl]_2$	**2**	1	CH_2Cl_2	96	99 (*R*)
12	$[Pd(All)Cl]_2$	**2**	2	CH_2Cl_2	100	73 (*R*)

[a] The reaction conditions: 20 °C, 48 h, 2 mol.% $[Pd(All)Cl]_2$ or 1 mol.% $[Pt(All)Cl]_4$.
[b] The conversion of substrate **10** and the enantiomeric excesses of product **12** were determined by HPLC (Daicel Chiralcel OD-H, OD-H, C_6H_{14} : Pr^iOH : $HNEt_2$ = 200 : 1 : 0.1, 0.9 mL min^{-1}, 254 nm).

ally as effective in this reaction as *P**,*P**-bidentate analogs.[25] The Pt-catalyzed amination of compound **10** with pyrrolidine is characterized by the quantitative conversion of the starting substrate and the good enantioselectivity of the formation of product (*S*)-**12** (up to 86%). The nature of the solvent has virtually no effect on the asymmetric induction, and the optimal L/Pt molar ratio is 1 (see Table 3, runs *5*—*8*).

To sum up all the above-considered data, the following conclusions can be drawn. *P**,*P**-Bidentate phosphorodiamidite **1** is a substantially better stereoselector than *P**-monodentate ligand **2** in the Rh-catalyzed asymmetric hydrogenation and the Pd-catalyzed allylic alkylation, whereas these ligands are equally effective in the Pd-catalyzed allylic amination. In addition to the studies,[41,42] we describes the third example of the successful use of phosphorus-containing ligands in the Pt-catalyzed asymmetric allylic alkylation. We also report the first example of the use of this ligands in the Pt-catalyzed asymmetric allylic amination.[31] The allylic substitution in the presence of palladium and platinum catalysts affords products having the opposite absolute configurations, all other conditions being the same.

Experimental

The ^{31}P, ^{1}H, and ^{13}C NMR spectra were measured on a Bruker AMX-400 instrument (161.98, 400.13, and 100.61 MHz, respectively) with respect to 85% H_3PO_4 in D_2O (^{31}P) and Me_4Si (^{1}H and ^{13}C). The assignment of the signals in the ^{13}C NMR spectra was made with the use of the DEPT technique. The EI mass spectra (70 eV) were measured on a Varian MAT-311 instrument. The matrix-assisted laser desorption ionization time-of-flight (MALDI TOF/TOF) mass spectra were obtained on a Bruker Daltonics Ultraflex instrument. The IR spectra were recorded on a Specord M-80 instrument in $CHCl_3$ in polyethylene cells. The enantiomeric analysis of the catalytic reaction products was performed by HPLC on an HP Agilent 1100 chromatograph. The optical rotation was measured on a SM-3 polarimeter. The specific rotation is expressed in (deg mL) (g dm)$^{-1}$; the concentrations of the solutions are expressed in g (100 mL)$^{-1}$. The elemental analysis was performed at the Laboratory of Organic Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

All reactions were carried out under dry argon in anhydrous solvents. (2*R*,5*S*)-2-Chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**5**), (*S*)-2-pivaloyloxy-2′-hydroxy-1,1′-binaphthyl (**4**), and the complexes $[Rh(COD)_2]BF_4$, $[Pd(All)Cl]_2$, and $[Pt(All)Cl]_4$ were synthesized according to known procedures.[32,43—46]

The starting substrate, *viz.*, (*E*)-1,3-diphenylallyl acetate (**10**), was synthesized according to a procedure described previously.[45] The catalytic experiments on the asymmetric hydrogenation of substrates **6** and **7** were carried out, and the conversions and the optical yields of products **8** and **9** were determined according to known procedures.[47] The catalytic experiments on the asymmetric alkylation of substrate **10** with dimethyl malonate and the amination of **10** with pyrrolidine were performed, and the conversions and the optical yields of products **11** and **12** were determined according to procedures described in the literature.[32,48]

(*S*)-BINOL (**3**), dimethyl itaconate (**6**), methyl 2-(*N*-acetylamino)acrylate (**7**), dimethyl malonate, and *N*,*O*-bis(trimethylsilyl)acetamide (BSA) are commercial products (Fluka and Aldrich).

2,2′-Bis[(2*R*,5*S*)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]oct-2-yloxy]-(S_a)-1,1′-binaphthyl (1). A solution of (*S*)-BINOL (1.43 g, 5 mmol) in toluene (17 mL) was added dropwise with vigorous stirring to a solution of (2*R*,5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**5**) (2.41 g, 10 mmol) and Et_3N (1.45 mL, 10.4 mmol) in toluene (26 mL) at 20 °C for 30 min. The reaction solution was stirred at 20 °C for 24 h, and then $Et_3N \cdot HCl$ was removed by filtration. The filtrate was concentrated *in vacuo* (40 Torr). The product was purified by column chromatography on silica gel using a 1 : 1 hexane—AcOEt mixture as the eluent. The yield was 2.92 g (84%), white powder, m.p. 144—145 °C, $[\alpha]^{20}_D$ +171.4 (*c* 1.0, CH_2Cl_2). Found (%): C, 72.88; H, 5.86; N, 7.93. $C_{42}H_{40}N_4O_2P_2$. Calculated (%): C, 72.61; H, 5.80; N, 8.06. ^{13}C NMR ($CDCl_3$), δ: 25.6 (d, C(7″), ^3J = 4.4 Hz), 31.3 (s, C(6″)), 47.1 (d, C(8″), ^2J = 36.5 Hz), 53.8 (d, C(4″), ^2J = 8.0 Hz), 62.3 (d, C(5″), ^2J = 8.8 Hz), 114.9 (d, CH_{Ph}, ^3J = 12.4 Hz), 118.7 (s, CH_{Ph}), 123.1 (d, CH_{Ar}, ^3J = 5.1 Hz), 123.6 (s, CH_{Ar}), 124.5 (s, C_{Ar}), 125.3 (s, CH_{Ar}), 127.0 (s, CH_{Ar}), 127.6 (s, CH_{Ar}), 128.4 (s, CH_{Ar}), 128.8 (s, CH_{Ph}), 130.1 (s, C_{Ar}), 134.1 (s, C_{Ar}), 145.2 (d, C_{Ph}, ^2J = = 16.1 Hz), 150.1 (d, C_{Ar}, ^2J = 8.0 Hz). ^1H NMR ($CDCl_3$), δ: 1.37 (dq, 2 H, *J* = 11.8 Hz); 1.50 (m, 4 H); 1.68 (dq, 2 H, *J* = 11.8 Hz); 2.53 (ddd, 2 H, *J* = 8.2 Hz, *J* = 7.1 Hz, *J* = 5.9 Hz); 2.90 and 3.40 (both m, 4 H each); 6.65 (d, 4 H, *J* = 7.8 Hz); 6.71 (t, 4 H, *J* = 7.9 Hz); 7.02 (t, 4 H, *J* = 8.5 Hz); 7.16 (m, 4 H); 7.36 (d, 2 H, *J* = 7.7 Hz, *J* = 7.3 Hz; 7.74 (d, 4 H, *J* = 8.3 Hz). EI MS, *m*/*z* (I_{rel} (%)): 695 $[M]^+$ (2). MALDI TOF/TOF MS, *m*/*z* (I_{rel} (%)): 718 $[M + Na]^+$ (100), 696 $[M + H]^+$ (28).

2-[(2*R*,5*S*)-3-Phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]oct-2-yloxy]-2′-pivaloyloxy-(S_a)-1,1′-binaphthyl (2). A solution of (*S*)-2-pivaloyloxy-2′-hydroxy-1,1′-binaphthyl (**4**) (1.85 g, 5 mmol) and Et_3N (0.73 mL, 5.2 mmol) in toluene (15 mL) was added dropwise with vigorous stirring to a solution of (2*R*,5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**5**) (1.2 g, 5 mmol) in toluene (15 mL) at 20 °C for 20 min. The reaction mixture was heated to reflux and then cooled to 20 °C, $Et_3N \cdot HCl$ was removed by filtration, and the filtrate was concentrated *in vacuo* (40 Torr). The product was purified by column chromatography on silica gel using a 1 : 1 hexane—AcOEt mixture as the eluent. The yield was 2.04 g (71%), white powder, m.p. 59—60 °C, $[\alpha]^{20}_D$ +83.8 (*c* 1.0, CH_2Cl_2). Found (%): C, 75.45; H, 6.08; N, 4.99. $C_{36}H_{35}N_2O_3P$. Calculated (%): C, 75.24; H, 6.14; N, 4.87. ^{13}C NMR ($CDCl_3$), δ: 26.0 (d, C(7″), ^3J = = 3.8 Hz), 26.2, 26.3 (s, CH_3), 31.0 (s, C(6″)), 38.5 (s, C), 47.1 (d, C(8″), ^2J = 32.7 Hz), 53.1 (d, C(4″), ^2J = 6.8 Hz), 62.0 (d, C(5″), ^2J = 8.0 Hz), 115.0 (d, CH_{Ph}, ^3J = 12.4 Hz), 118.2 (s, CH_{Ph}), 120.5 (s, CH_{Ar}), 122.7 (s, CH_{Ar}), 122.9 (s, CH_{Ar}), 123.6 (s, CH_{Ar}), 123.9 (s, C_{Ar}), 124.0 (s, CH_{Ar}), 124.9 (s, CH_{Ar}), 125.7 (s, CH_{Ar}), 125.8 (s, CH_{Ar}), 126.2 (s, CH_{Ar}), 127.4 (s, CH_{Ar}), 127.7 (s, CH_{Ar}), 128.3 (s, CH_{Ar}), 128.7 (s, CH_{Ph}), 128.9 (s, C_{Ar}), 129.2 (s, C_{Ar}), 130.9 (s, C_{Ar}), 133.5 (s, C_{Ar}), 133.9 (s, C_{Ar}), 146.0 (d, C_{Ph}, ^2J = 17.7 Hz), 151.0 (d, C_{Ar}, ^2J = 5.1 Hz), 154.6 (s, C_{Ar}), 176.1 (s, C=O) (major epimer) and 26.4, 26.5 (s, CH_3),

27.3 (s, C(7″)), 31.6 (s, C(6″)), 38.3 (s, C), 43.0 (d, C(8″), ^2J = = 3.8 Hz), 51.0 (d, C(4″), ^2J = 6.5 Hz), 65.2 (d, C(5″), ^2J = 10.7 Hz), 117.2 (d, CH_{Ph}, ^3J = 13.1 Hz), 118.0 (s, CH_{Ph}), 120.6 (s, CH_{Ar}), 122.7 (s, CH_{Ar}), 122.9 (s, CH_{Ar}), 123.3 (s, CH_{Ar}), 123.9 (s, C_{Ar}), 124.7 (s, CH_{Ar}), 124.9 (s, CH_{Ar}), 125.1 (s, CH_{Ar}), 125.9 (s, CH_{Ar}), 126.0 (s, CH_{Ar}), 127.5 (s, CH_{Ar}), 127.7 (s, CH_{Ar}), 128.4 (s, CH_{Ar}), 128.6 (s, CH_{Ph}), 128.9 (s, C_{Ar}), 129.5 (s, C_{Ar}), 130.8 (s, C_{Ar}), 133.7 (s, C_{Ar}), 133.9 (s, C_{Ar}), 146.8 (d, C_{Ph}, ^2J = 16.7 Hz), 151.5 (d, C_{Ar}, ^2J = 3.1 Hz), 155.6 (s, C_{Ar}), 176.0 (s, C=O) (minor epimer). ^{1}H NMR ($CDCl_3$), δ: 0.67 (s, 9 H); 1.39 (dq, 1 H, J = 11.3 Hz); 1.58 (m, 2 H, J = 7.4 Hz, J = 7.3 Hz, J = 6.6 Hz); 1.71 (dq, 1 H, J = 11.3 Hz); 2.53 (m, 1 H, J = 7.3 Hz, J = 6.5 Hz); 2.90 (m, 2 H); 3.40 (m, 2 H); 6.70 (t, 1 H, J = 7.5 Hz); 7.00 (d, 2 H, J = 7.5 Hz); 7.10 (d, 2 H, J = 8.2 Hz); 7.15 (d, 1 H, J = 7.3 Hz); 7.20 (dd, 1 H, J = 7.5 Hz, J = 7.1 Hz); 7.31 (ddd, 2 H, J = 8.5 Hz, J = 7.0 Hz, J = 1.3 Hz); 7.38 (ddd, 2 H, J = = 8.6 Hz, J = 7.1 Hz, J = 1.2 Hz); 7.41 (d, 2 H, J = 8.7 Hz); 7.61 (d, 2 H, J = 8.3 Hz); 7.82 (d, 2 H, J = 8.8 Hz). IR ($CHCl_3$), ν/cm^{-1}: 1742 (C=O). EI MS, m/z (I_{rel} (%)): 575 $[M]^+$ (5). MALDI TOF/TOF MS, m/z (I_{rel} (%)): 576 $[M + H]^+$ (100).

Asymmetric hydrogenation of dimethyl itaconate (6) and methyl 2-(*N*-acetylamino)acrylate (7). A solution of $[Rh(COD)_2]BF_4$ (0.001 g, 0.0025 mmol) and the corresponding ligand (0.0025 or 0.005 mmol) in CH_2Cl_2 (5 mL) was stirred for 40 min. Then the corresponding substrate (0.5 mmol) was added, and the mixture was placed in an autoclave. The catalytic apparatus was purged with argon and then with hydrogen (three times), and then the mixture was stirred at 25 °C for 20 h at a hydrogen pressure of 1.3 atm. The reaction mixture was diluted with pentane (10 mL) and filtered through a thin layer of silica gel. The solvents were removed under reduced pressure (40 Torr), and the residue was dried *in vacuo* (10 Torr). The conversions of substrates **6** and **7** and the optical yields of products **8** and **9** were determined by GC and/or HPLC on chiral stationary phases.

Asymmetric allylic alkylation of (*E*)-1,3-diphenylallyl acetate (10) with dimethyl malonate. A solution of $[Pd(All)Cl]_2$ (0.0037 g, 0.01 mmol) and the corresponding ligand (0.02 or 0.04 mmol) (or a solution of $[Pt(All)Cl]_4$ (0.005 g, 0.005 mmol) and the corresponding ligand (0.02 or 0.04 mmol)) in the corresponding solvent (5 mL) was stirred for 40 min. (*E*)-1,3-Diphenylallyl acetate (**10**) (0.1 mL, 0.5 mmol) was added, and the reaction solution was stirred for 15 min. Then dimethyl malonate (0.10 mL, 0.87 mmol), BSA (0.22 mL, 0.87 mmol), and potassium acetate (0.002 g) were added. The reaction mixture was stirred for 48 h, diluted with hexane (5 mL), and filtered through Celite. The solvents were removed under reduced pressure (40 Torr), and the residue was dried *in vacuo* (10 Torr). The conversion of substrate **10** and the optical yields of product **11** were determined by HPLC on chiral stationary phases.

Asymmetric allylic amination of (*E*)-1,3-diphenylallyl acetate (10) with pyrrolidine. A solution of $[Pd(All)Cl]_2$ (0.0037 g, 0.01 mmol) and the corresponding ligand (0.02 or 0.04 mmol) (or a solution of $[Pt(All)Cl]_4$ (0.005 g, 0.005 mmol) and the corresponding ligand (0.02 or 0.04 mmol)) in the corresponding solvent (5 mL) was stirred for 40 min. (*E*)-1,3-Diphenylallyl acetate (**10**) (0.1 mL, 0.5 mmol) was added, and the reaction solution was stirred for 15 min. Then freshly distilled pyrrolidine (0.12 mL, 1.5 mmol) was added. The reaction mixture was stirred for 48 h, diluted with hexane (5 mL), and filtered through Celite. The solvents were removed under reduced pressure (40 Torr), and the residue was dried *in vacuo* (10 Torr). The conversion of substrate **10** and the optical yields of product **12** were determined by HPLC on chiral stationary phases.

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