Palladium and rhodium-catalyzed enantioselective reactions mediated by pseudodipeptide-based phosphite-type ligand

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*P**-Chiral diamidophosphite ligand of a 1,3,2-diazaphopholidine series bearing the exocyclic pseudodipeptide fragment was synthesized. The possibility of its application in the palladium- and rhodium-catalyzed asymmetric transformations was demonstrated. This ligand provided up to 84% *ee* in the Pd-catalyzed alkylation of (*E*)-1,3-diphenylallyl acetate with dimethyl malonate, up to 56% *ee* in amination of this substrate with pyrrolidine, and up to 68% *ee* in alkylation of cinnamyl acetate with ethyl 2-oxocyclohexane-1-carboxylate. In the Rh-catalyzed hydrogenation of (*Z*)-methyl 2-acetamido-3-phenylacrylate mediated by this ligand, up to 53% *ee* was achieved.

Key words: chiral diamidophosphites, asymmetric allylation, palladium catalysts, asymmetric hydrogenation, rhodium catalysts.

Among chiral inductors, asymmetric phosphorus ligands have emerged as one of the most efficient class of ligands in metal-catalyzed enantioselective reactions.[1—11] At the same time, the majority of metal complexes containing these ligands are capable of promoting with some enantioselectivity only a specific type of the reactions or even only one particular reaction. Chiral ligands affecting a wide variety of transformations are known as privileged ligands but they are few in number and their high price significantly limits their wide applications in organic synthesis. These facts prompted the design and synthesis of new efficient phosphorus chiral inductors from readily available and inexpensive enantiopure precursors. Moreover, application of newly synthesized chiral inductors provides the experimental data necessary for the better understanding of the mechanisms of asymmetric induction and for overcoming patent restriction requirements on the use of some ligand series.[3,12—16]

Phosphite-type ligands are of considerable interest. These ligands can be efficiently synthesized in high yields by the simple condensation reactions from readily available enantiomerically pure precursors without any preliminary modifications. A one-step phosphorylation (including parallel and solid-phase approaches) gives excess to the phosphite ligand libraries. Besides phosphite-type ligands are inexpensive and favorably distinguished by their oxidation-resistance because of the lack of the P—C bond in their structure and good solubility of metal complexes derived from them in a wide variety of solvents suitable for catalytic reactions (common organic solvents, ionic liquids, and super-critical carbon dioxide). Due to the pronounced π acceptor ability, phosphites are capable of stabilizing the low oxidation states of the metals and increasing their electrophilicity upon complexation.[10,11,14,16—26]

Hydroxamide derivatives of phosphite-type ligands $\mathbf{L_A}$—$\mathbf{L_C}$ comprise an interesting chiral ligand series successfully applied in Rh- and Ir-catalyzed hydrogenation and Cu-catalyzed conjugate addition.[27—31] Design and synthesis of phosphite-type ligands based on amino alcohol amides and *N*-protected amino acids (pseudodipeptides) seem promising. Pseudodipeptides have proved to be the efficient chiral inductors in Ru- and Rh-catalyzed enantioselective transfer hydrogenation.[32—38]

In the present work, we describe the synthesis of diamidophosphite derivative of pseudodipeptide bearing a stereogenic phosphorus atom in the 1,3,2-diazaphospholidine cycle and its application in asymmetric catalysis. Note that diamidophosphites have balanced electronic properties and involvement of the amidophosphite phosphorus atom into the phospholidine cycle increases oxidation and hydrolytic stability of the ligand; while the possibility to widely vary the phosphorus and/or nitrogen substituents allows the fine-tuning of its steric and electronic properties.[39—44] The presence of an asymmetric donor phosphorus atom significantly facilitates the chirality transfer from the chiral catalyst to the product.[2,15,45,46] The asymmetrizing activity of the newly synthesized diamidophosphite was estimated on the enantioselective Pd-catalyzed allylic substitution and Rh-catalyzed hydro-

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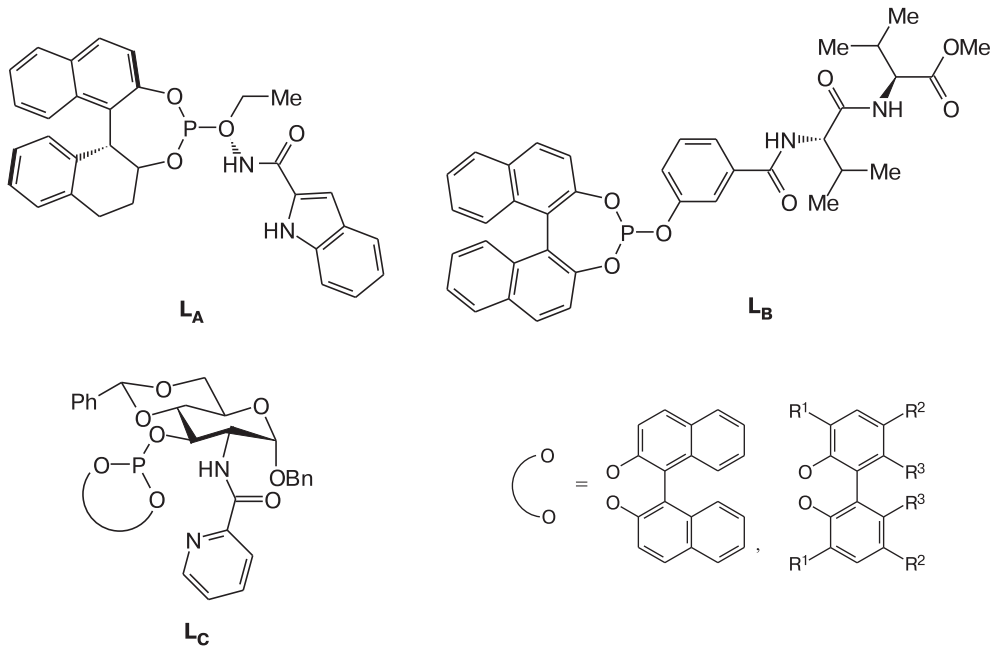
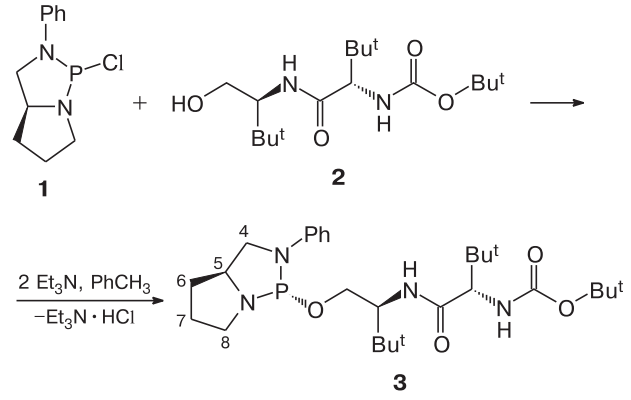


genation reactions. These reactions are widely used for estimating the catalytic performance of new chiral inductors and for asymmetric synthesis of valuable organic and natural compounds.[8,10,14,15,45,47—56]

Results and Discussion

The reaction of phosphorylating agent **1** with pseudodipeptide **2** in toluene in the presence of the Et_3N excess gave new diamidophosphite ligand **3** (Scheme 1). The starting chlorodiamidophosphite **1** can be easily synthesized[57] in high yield from readily available (*S*)-glutamic acid anilide.[58,59] In turn, compound **2** can be easily prepared by condensation of *N*-Boc-*tert*-leucine with *tert*-leucinol.[60]

Scheme 1

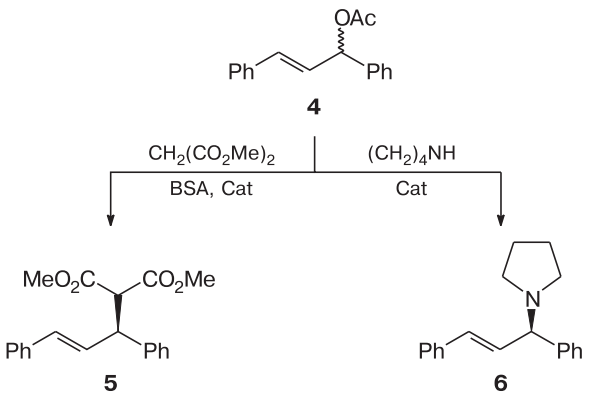


Diamidophosphite **3** is easily purifiable by crystallization, it is readily soluble in common organic solvents, stable upon long term storage under dry atmosphere, and can be synthesized in multi-gram amounts. Structure of compound **3** was established by ^1H, ^{13}C, and ^{31}P NMR spectroscopy (including 2D $^1H—^1H$ COSY and $^1H—^{13}C$ HSQC experiments) and confirmed by elemental analysis. Ligand **3** is enantiomerically pure with the (*R*)-configuration of the *P**-stereogenic center. The configuration of ligand **3** was confirmed by the presence of a narrow singlet signal at δ_P 125.5 in the ^{31}P NMR ($CDCl_3$) spectrum and a large spin-spin coupling constant value $^2J_{C(8),P} = 37.6$ Hz in the ^{13}C NMR spectrum. This spin-spin coupling constant value is indicative of the *anti*-orientation of the pseudo-equatorial exocyclic substituent at the P atom and the $—(CH_2)_3—$ pyrrolidine moiety of phosphabicyclo[3.3.0]octane framework and, consequently, of the *syn*-orientation of the lone electron pair of the P atom and the C(8) atom.[57—59,61,62]

Catalytic performance of diamidophosphite **3** was first tested on the model reactions of the enantioselective Pd-catalyzed allylation of (*E*)-1,3-diphenylallyl acetate (**4**) (Scheme 2, Tables 1 and 2).

Table 1 shows that both conversion and asymmetric induction achieved by the allylic alkylation of compound **4** with dimethyl malonate (C-nucleophile) depend on the solvent nature, the L : Pd molar ratio, and the base and precatalyst used. In all cases, the (*S*)-enantiomer of product **5** predominates; enantiomeric excess of compound **5** varies in the range of 34—84% *ee*. By carrying out the reactions in THF and CH_2Cl_2, it was revealed that the molar ratio L : Pd = 2 is the most preferable (see Table 1,

Scheme 2



entries *1*—*4*) and, therefore, was used in further experiments. The highest asymmetric induction was achieved in CH_2Cl_2 and $CHCl_3$; while it was noticeably lower in toluene and THF. In addition, THF provided low conversion of substrate **4** (see Table 1, entries *2* and *4*—*6*). When Cs_2CO_3 was used as a base instead of BSA/KOAc, the enantioselectivity was somewhat lower. The same effect was observed by changing precatalyst $[Pd(allyl)Cl]_2$ on $[Pd(cod)Cl_2]$, and, especially, on $[Pd_2(dba)_3]\cdot CHCl_3$ (see Table 1, entries *7* and *9*, *10*). In general, the highest enantioselectivity (84% *ee*) was achieved at molar ratio L : Pd = 2 in the presence of the $[Pd(allyl)Cl]_2$ as a precatalyst and BSA/KOAc as a base in CH_2Cl_2 at 0 °C (see Table 1, entry *8*).

Table 1. Pd-Catalyzed alkylation of substrate **4** with dimethyl malonate[a]

Entry	L : Pd	Solvent	Conversion (%)	*ee* (%)[b]
1	1	THF	10	34 (*S*)
2	2	THF	15	54 (*S*)
3	1	CH_2Cl_2	98	68 (*S*)
4	2	CH_2Cl_2	100	80 (*S*)
5	2	$CHCl_3$	99	78 (*S*)
6	2	Toluene	100	46 (*S*)
7	2	CH_2Cl_2	100	76 (*S*)[c]
8	2	CH_2Cl_2	100	84 (*S*)[d]
9	2	CH_2Cl_2	96	74 (*S*)[e]
10	2	CH_2Cl_2	75	60 (*S*)[f]

[a] Reaction conditions: 2 mol.% $[Pd(allyl)Cl]_2$, bis(trimethylsilyl) acetamide (BSA), KOAc, 20 °C, 48 h.
[b] Conversion of substrate **4** and enantiomeric excess of product **5** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}—Pr^iOH (99 : 1), 0.3 mL min^{-1}, 254 nm, $t(R)$ = 28.0 min, $t(S)$ = 29.3 min).
[c] In the presence of Cs_2CO_3 as a base.
[d] At 0 °C.
[e] 4 mol.% $[Pd(cod)Cl_2]$ (cod is cycloocta-1,5-diene).
[f] 2 mol.% $[Pd_2(dba)_3]\cdot CHCl_3$ (H_4dba is dibenzylideneacetone).

Table 2. Pd-Catalyzed amination of substrate **4** with pyrrolidine[a]

Entry	L : Pd	Solvent	Conversion (%)	*ee* (%)[b]
1	1	CH_2Cl_2	67	52 (*R*)
2	2	CH_2Cl_2	100	54 (*R*)
3	2	CH_2Cl_2	100	56 (*R*)[c]
4	2	$CHCl_3$	100	52 (*R*)
5	2	THF	37	44 (*R*)
6	2	Toluene	45	14 (*R*)

[a] Reaction conditions: 2 mol.% $[Pd(allyl)Cl]_2$, 20 °C, 48 h.
[b] Conversion of substrate **4** and enantiomeric excesses of product **6** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}—Pr^iOH—$HNEt_2$ (200 : 1 : 0.1), 0.9 mL min^{-1}, 254 nm, $t(R)$ = 5.0 min, $t(S)$ = 6.1 min).
[c] At 0 °C.

Similar dependencies were found for the reactions catalyzed by the catalysts based on ligand **3** and pyrrolidine as the N-nucleophile (see Scheme 2 and Table 2).

Thus, the optimum molar ratio L : Pd is equal to 2 (see Table 2, entries *1* and *2*). The highest enantioselectivity (52—56% *ee*) was reached in CH_2Cl_2 and $CHCl_3$ but the change of the solvent on either THF or toluene resulted in lowering of both the conversion and asymmetric induction (see Table 2, entries *1*—*6*). The selected conditions led predominantly to amine **6** with the (*R*)-configuration.

Asymmetric catalytic synthesis of compounds with the *C**-stereogenic centers presents an ongoing problem in chemistry. One of the efficient approaches to overcome this problem is the Pd-catalyzed allylic substitution producing the chiral quaternary center at the carbon atom of nucleophile. It is difficult to control the enantioselectivity of the Pd-catalyzed allylation since the nucleophile approaches the allylic moiety of η^3-allylpalladium(II) intermediate from the side opposite to the central complex-forming ion and the chiral ligand bonded to it.[43,53,57,63,64] This case can be exemplified by the asymmetric alkylation of cinnamyl acetate (**7**) with ethyl 2-oxocyclohexanecarboxylate (**8**) (Scheme 3).

The use of diamidophosphite **3** as a chiral inductor in the reaction shown on Scheme 3 provided up to 68% (Table 3). An increase in the L : Pd molar ratio up to 2 noticeably increased the conversion and only slightly increased the asymmetric induction. (*S*)-Enantiomer of product **9** was the major enantiomer in both cases.

Ligand **3** was also used in Rh-catalyzed asymmetric hydrogenation of (*Z*)-methyl 2-acetamido-3-phenyl-

Scheme 3

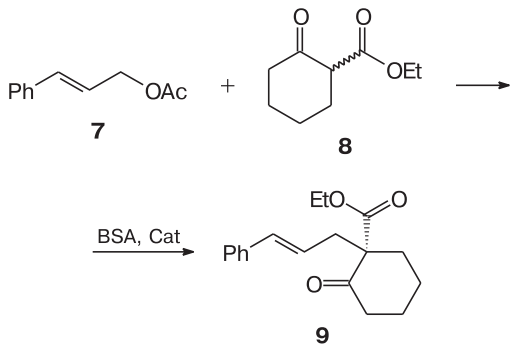


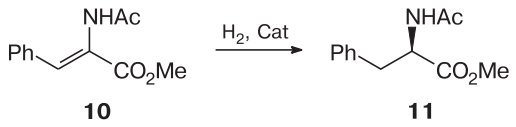
Table 3. Pd-Catalyzed alkylation of substrate **7** with ethyl 2-oxocyclohexanecarboxylate[a]

Entry	L : Pd	Conversion (%)	*ee* (%)[b]
1	1	19	62 (*S*)
2	2	60	68 (*S*)

[a] Reaction conditions: 2 mol.% $[Pd(allyl)Cl]_2$, toluene, BSA, $Zn(OAc)_2$, 20 °C, 48 h.
[b] Conversion of substrate **7** and enantiomeric excesses of product **9** were determined by HPLC (Kromasil 5-CelluCoat, C_6H_{14}—Pr^iOH (95 : 5), 0.4 mL min^{-1}, 254 nm, $t(R)$ = 14.3 min, $t(S)$ = 16.4 min).

acrylate (**10**) in the presence of $[Rh(cod)_2]BF_4$ as a precatalyst (Scheme 4).

Scheme 4



The reaction provided up to 53% *ee* and a quantitative conversion of substrate **10** with the major enantiomer being (*R*)-enantiomer of methyl *N*-Ac-phenylalaninate **11** (Table 4, entries *1*—*3*). The solvent of choice was CH_2Cl_2 as in the case of the Pd-catalyzed allylation of (*E*)-1,3-diphenylallyl acetate.

In summary, in the present work diamidophosphite **3**, a pseudodipeptide-based phosphite-type ligand, was synthesized. This ligand was found to be very sensitive to the nature of nucleophile and conditions of enantioselective Pd- and Rh-catalyzed allylation and hydrogenation. Ligand **3** in Pd-catalyzed alkylation of (*E*)-1,3-diphenylallyl acetate with dimethyl malonate provided up to 84 % *ee*

Table 4. Rh-Catalyzed hydrogenation of substrate **10**[a]

Entry	Solvent	Conversion (%)	*ee* (%)[b]
1	CF_3CH_2OH	100	27 (*R*)
2	Toluene	100	32 (*R*)
3	CH_2Cl_2	100	53 (*R*)

[a] Reaction conditions: 2 mol.% $[Rh(cod)_2]BF_4$, 1.5 atm H_2, L : Rh = 2, 20 °C, 24 h.
[b] Conversion of substrate **10** and enantiomeric excesses of product **11** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}—Pr^iOH (90 : 10), 1 mL min^{-1}, 215 nm, $t(R)$ = 9.5 min, $t(S)$ = 12.7 min).

in contrast to the palladium complexes with the known phosphites $\mathbf{L_C}$ giving almost racemic product.[31] Diamidophosphite **3** is very promising chiral inductor and studies of the performance of this ligand (and other similar ligands) in metal complex catalysis are already in progress in our working group.

Experimental

^{31}P, ^1H, and ^{13}C NMR spectra were recorded with Bruker Avance 400 (working frequencies of 161.98, 400.13, and 100.61 MHz, respectively) and Bruker Avance III 600 (working frequencies of 242.94, 600.13, and 150.9 MHz, respectively) instruments; the chemical shifts are given in the δ scale relative to 85% H_3PO_4 in D_2O and Me_4Si, respectively. ^1H and ^{13}C NMR signals were attributed using APT, ^1H—^1H COSY, and ^1H—^{13}C HSQC experiments and taking into accounts the published data.[11,43,57—60] Optical rotation was measured with an Atago AP-300 polarimeter. Specific rotation values are quoted in (deg mL) $(g\ dm)^{-1}$, the concentrations of the working solutions are given in g $(100\ mL)^{-1}$. Enantiomeric analysis of ligand **3** and products of catalytic reactions was performed with a Staier HPLC system. Elemental analysis was carried out on a Carlo Erba EA1108 CHNS-O CHN analyzer.

All reactions were carried out in anhydrous solvents under dry argon. The starting substrates, (*E*)-1,3-diphenylallyl acetate (**4**) and (*Z*)-methyl 2-acetamido-3-phenylacrylate (**10**), and the catalysts, $[Pd(allyl)Cl]_2$, $[Pd_2(dba)_3]\cdot CHCl_3$, $[Pd(cod)Cl_2]$, and $[Rh(cod)_2]BF_4$, were synthesized following the known procedures.[65—69] Catalytic studies of asymmetric alkylation of substrate **4** with dimethyl malonate and its amination with pyrrolidine, alkylation of substrate **7** with nucleophile **8**, asymmetric hydrogenation of substrate **10**, determination of the conversion of compounds **4**, **7**, and **10** and enantiomeric excesses of products **5**, **6**, **9**, and **11** were performed as earlier described.[57,63,64,70—72]

Dimethyl malonate, BSA, pyrrolidine, triethylamine, cinnamyl acetate (**7**), and ethyl 2-oxocyclohexanecarboxylate (**8**) were purchased from Fluka and Aldrich.

(2*R*,5*S*)-2-[(*S*)-2-{(*S*)-2-[(*tert*-butoxycarbonyl)amino]-3,3-dimethylbutanamido}-3,3-dimethylbutyl]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (3). To a vigorously stirred solution

of phosphorylating agent **1** (0.48 g, 2 mmol) and Et_3N (0.56 mL, 4 mmol) in toluene (15 mL), compound **2** (0.66 g, 2 mmol) was added in one portion at 20 °C. The reaction mixture was stirred at 20 °C for 24 h and passed through a short column filled with SiO_2/Al_2O_3. The filtrate was concentrated *in vacuo* (40 Torr). The residue was dried *in vacuo* (1 Torr) and crystallized from heptane to afford compound **3**. Yield 0.82 g (77%), white powder, m.p. 137—138 °C, $[\alpha]^{20}_D$ −93.4 (*c* 1.0, THF). Found (%): C, 63.11; H, 8.92; N, 10.32. $C_{28}H_{47}N_4O_4P$. Calculated (%): C, 62.90; H, 8.86; N, 10.48. HPLC (Daicel Chiralcel OD—H, C_6H_{14}/Pr^iOH = 200 : 1, 1.5 mL min^{-1}, 254 nm), t_{ret}: 16.6 min. ^{13}C NMR ($CDCl_3$), δ: 26.2 (d, C(7), $^3J_{C,P}$ = 4.4 Hz); 26.5 (s, C($\underline{C}H_3)_3$); 27.1 (s, C($\underline{C}H_3)_3$); 28.3 (s, OC($\underline{C}H_3)_3$); 32.3 (s, C(6)); 34.2 (s, $\underline{C}(CH_3)_3$); 34.6 (s, $\underline{C}(CH_3)_3$); 48.7 (d, C(8), $^2J_{C,P}$ = 37.6 Hz); 54.9 (d, C(4), $^2J_{C,P}$ = 7.5 Hz); 56.1 (s, CHN); 61.4 (s, CH_2O), $^2J_{C,P}$ = 5.7 Hz); 62.7 (s, CHN); 63.7 (s, C(5), $^2J_{C,P}$ = 8.6 Hz); 79.5 (s, O$\underline{C}(CH_3)_3$); 114.8 (d, *o*-CH_{Ph}, $^3J_{C,P}$ = 13.3 Hz); 119.1 (s, *p*-CH_{Ph}); 129.2 (s, *m*-CH_{Ph}); 145.5 (d, C_{Ph}, $^2J_{C,P}$ = 15.5 Hz); 155.9 (s, C=O); 170.8 (s, C=O). ^1H NMR ($CDCl_3$), δ: 0.91 (s, 9 H, $C(CH_3)_3$); 0.92 (s, 9 H, $C(CH_3)_3$); 1.42 (s, 9 H, $OC(CH_3)_3$); 1.59—1.64 (m, 1 H, C(6)H); 1.74—1.79 (m, 1 H, C(7)H); 1.83—1.88 (m, 1 H, C(7)H); 2.02—2.08 (m, 1 H, C(6)H); 3.13—3.21 (m, 2 H, C(4)H and C(8)H); 3.44—3.49 (m, 1 H, CH_2O); 3.53—3.59 (m, 1 H, C(8)H); 3.69—3.75 (m, 2 H, C(4) H and CHN); 3.79—3.84 (m, 1 H, CHN); 3.85—3.89 (m, 1 H, CH_2O); 4.09—4.13 (m, 1 H, C(5)H)); 5.23 (d, 1 H, NH, ^3J = = 9.6 Hz); 5.96 (d, 1 H, NH, ^3J = 9.4 Hz); 6.83 (t, 1 H, *p*-CH_{Ph}, ^3J = 7.3 Hz); 6.97 (d, 2 H, *o*-CH_{Ph}, ^3J = 7.2 Hz); 7.21 (t, 2 H, *m*-CH_{Ph}, ^3J = 7.3 Hz). ^{31}P NMR ($CDCl_3$), δ: 125.5.

Asymmetric alkylation of (*E*)-1,3-diphenylallyl acetate (4) with dimethyl malonate. A solution of either $[Pd(allyl)Cl]_2$ (0.0037 g, 0.01 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (0.01 g, 0.01 mmol), or [Pd(cod)-Cl_2] (0.0057 h, 0.02 mmol) and ligand **3** (0.0107 g, 0.02 mmol or 0.0214 g, 0.04 mmol) in the corresponding solvent (5 mL) was stirred for 40 min. Then (*E*)-1,3-diphenylallyl acetate (0.1 mL, 0.5 mmol) was added, the mixture was stirred for 15 min, and treated with (1) dimethyl malonate (0.1 mL, 0.87 mmol), BSA (0.22 mL, 0.87 mmol), and KOAc (0.002 g) or (2) dimethyl malonate (0.1 mL, 0.87 mmol) and $CsCO_3$ (0.163 g 0.5 mmol). The reaction mixture was stirred for 48 h, diluted with hexane (5 mL), and filtered through a short SiO_2 layer. The solvents were removed *in vacuo* (40 Torr) and the residue was dried *in vacuo* (10 Torr). Conversion of substrate **4** and enantiomeric excesses of products **5** were determined by HPLC on a Daicel Chiralcel OD-H chiral column (elution with C_6H_{14}—Pr^iOH (99 : 1), 0.3 mL min^{-1}, 254 nm, *t*(*R*) = 28.0 min, *t*(*S*) = = 29.3 min).

Asymmetric amination of (*E*)-1,3-diphenylallyl acetate (4) with pyrrolidine. A solution of $[Pd(allyl)Cl]_2$ (0.0037 g, 0.01 mmol) and ligand **3** (0.0107 g, 0.02 mmol or 0.0214 g, 0.04 mmol) in the corresponding solvent (5 mL) was stirred for 40 min. Then (*E*)-1,3-diphenylallyl acetate (0.1 mL, 0.5 mmol) was added followed by addition of freshly distilled pyrrolidine (0.12 mL, 1.5 mmol) after 15 min stirring. The reaction mixture was stirred for 48 h, diluted with hexane (5 mL), and filtered through a short SiO_2 layer. The solvents were removed *in vacuo* (40 Torr) and the residue was dried *in vacuo* (10 Torr). Conversion of substrate **4** and enantiomeric excesses of products **6** were determined by HPLC on a Daicel Chiralcel OD-H chiral column (elution with C_6H_{14}—Pr^iOH—$HNEt_2$ (200 : 1 : 0.1), 0.9 mL min^{-1}, 254 nm, *t*(*R*) = 5.0 min, *t*(*S*) = 6.1 min).

Asymmetric alkylation of cinnamyl acetate (7) with ethyl 2-oxocyclohexanecarboxylate (8). A solution of $[Pd(allyl)Cl]_2$ (0.0037 g, 0.01 mmol) and ligand **3** (0.0107 g, 0.02 mmol or 0.0214 g, 0.04 mmol) in toluene (5 mL) was stirred for 40 min. Then cinnamyl acetate (0.08 mL, 0.5 mmol) was added and after 15 min stirring the mixture was treated with ethyl 2-oxocyclohexanecarboxylate (0.12 mL, 0.75 mmol), BSA (0.5 mL, 2 mmol), and ZnOAc (0.01 g). The reaction mixture was stirred for 48 h, diluted with hexane (5 mL), and filtered through a short SiO_2 layer. The volatiles were removed *in vacuo* (40 Torr) and the residue was dried *in vacuo* (10 Torr). Conversion of substrate **7** and enantiomeric excesses of products **9** were determined by HPLC on a Kromasil 5-CelluCoat chiral column (elution with C_6H_{14}—Pr^iOH (95 : 5), 0.4 mL min^{-1}, 254 nm, *t*(*R*) = 14.3 min, *t*(*S*) = 16.4 min).

Asymmetric hydrogenation of (*Z*)-methyl 2-acetamido-3-phenylacrylate (10). A solution of $[Rh(cod)_2]BF_4$ (0.001 g, 0.0025 mmol) and ligand **3** (0.0027 g, 0.005 mmol) in the corresponding solvent (2 mL) was stirred for 40 min. Then (*Z*)-methyl 2-acetamido-3-phenylacrylate (0.027 g, 0.125 mmol) was added. Catalytic vessel containing the resulting solution was filled with hydrogen to a pressure of 1.5 atm and the reaction mixture was stirred for 24 h. The volatiles were removed *in vacuo* (40 Torr), the residue was dissolved in diethyl ether (2 mL), filtered through a short SiO_2 layer, concentrated *in vacuo* (40 Torr), and the residue was dried *in vacuo* (10 Torr). Conversion of substrate **10** and enantiomeric excesses of products **11** were determined by HPLC on a Daicel Chiralcel OD-H chiral column (elution with C_6H_{14}—Pr^iOH (90 : 10), 1 mL min^{-1}, 215 nm, *t*(*R*) = 9.5 min, *t*(*S*) = 12.7 min).

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