Palladium-catalyzed allylic substitution assisted by 1,3,2-diazaphospholidine derivatives of (*R*,*R*)-*N*-naphthyltartarimide

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P,*P*-Bidentate diamidophosphite ligands containing the (3*R*,4*R*)-3,4-dioxy-1-(1-naphthyl)pyrrolidine-2,5-dione framework and 1,3,2-diazaphospholidine rings with the stereogenic P atoms were obtained. The use of these ligands provides up to 85% *ee* in Pd-catalyzed asymmetric amination of (*E*)-1,3-diphenylallyl acetate and up to 95% *ee* in its asymmetric alkylation with dimethyl malonate.

Key words: ligands, diamidophosphites, 1,3,2-diazaphospholidines, palladium catalysts, asymmetric amination, asymmetric alkylation.

The preparation of drugs, chemical agents for plant protection, food additives, flavors, and stereoindividual polymers is based on modern approaches to the synthesis of optically pure compounds. One of the leading approaches is asymmetric metal complex catalysis.[1—5] In turn, the activity and stereoselectivity of metal complex catalysts largely depend on the successful strategy of design and synthesis of appropriate chiral ligands, among which phosphorus-containing compounds are worth noting.[6,7] Along with classic *P*,*P*-bidentate phosphines, *P*,*P*-bidentate phosphite ligands are successfully used because they can simply be prepared from accessible precursors, are inert to oxidants, exhibit pronounced π-acidity, and are less expensive.[8—14] The main attention of researchers is focused on *P*,*P*-bidentate phosphites containing 1,3,2-dioxaphosphepine rings based on BINOL, H_8-BINOL, and various 2,2′-dihydroxy-1,1′-biphenyls.[13—22]

Our investigations deal with the synthesis of various diamidophosphites containing stereogenic P atoms and 1,3,2-diazaphospholidine rings and their use in asymmetric catalytic reactions.[23—28] It should be noted that 1,3,2-diazaphospholidines, including *P**-chiral ones, are an attractive group of optically active diamidophosphite ligands. For instance, they have balanced electron characteristics: they are both good π-acceptors (because of the accessibility of the low-energy π^*_{PN}-orbitals) and good σ-donors. Inclusion of a phosphorus atom into the five-membered ring makes the ligand more resistant to oxidation and hydrolysis; by widely varying the substituents at the N atoms, one can control its steric and electronic parameters.[29,30] If the electron-donating P atom is asymmetric, this substantially promotes chirality transfer in the key step of the catalytic cycle.[2]

In the present work, we report on the synthesis of *P*,*P*-bidentate diamidophosphites **1** and **2** and their use for enantioselective catalysis (Scheme 1). The 1,3,2-diazaphospholidine rings in these ligands are linked to the sterically rigid tartarimide (3,4-dioxypyrrolidine-2,5-dione) ring. Note that known ligands with the pyrrolidine-2,5-dione fragment $\mathbf{L_{A—C}}$ are efficient stereoselectors in Pd-catalyzed allylic substitution and Rh-catalyzed hydrogenation.[31—33]

We tested compounds **1** and **2** in Pd-catalyzed asymmetric allylation, which is an effective tool for (1) estimation of the efficiency of novel chiral ligands and (2) stereoselective synthesis of valuable natural compounds.[14,34—37] We also compared the asymmetry-inducing activity of both ligands **1** and **2** themselves and their known analogs $\mathbf{L_B}$ and $\mathbf{L_C}$.

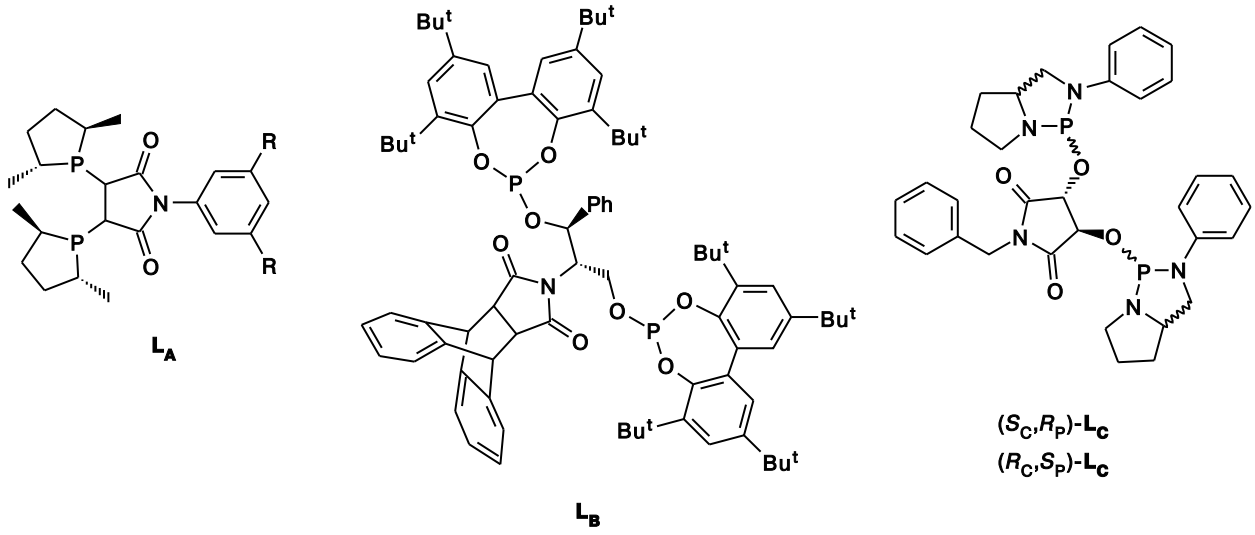
Results and Discussion

Novel *P*,*P*-bidentate diamidophosphites **1** and **2** were obtained by direct phosphorylation of (*R*,*R*)-*N*-naphthyltartarimide **3** with reagents **4** and **5** in THF (see Scheme 1).

Note that the starting chiral diol **3** is easily accessible through high-yielding condensation of (*R*,*R*)-tartaric acid with 1-naphthylamine.[38] Ligand **1** is stereochemically in-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1216—1222, June, 2010.

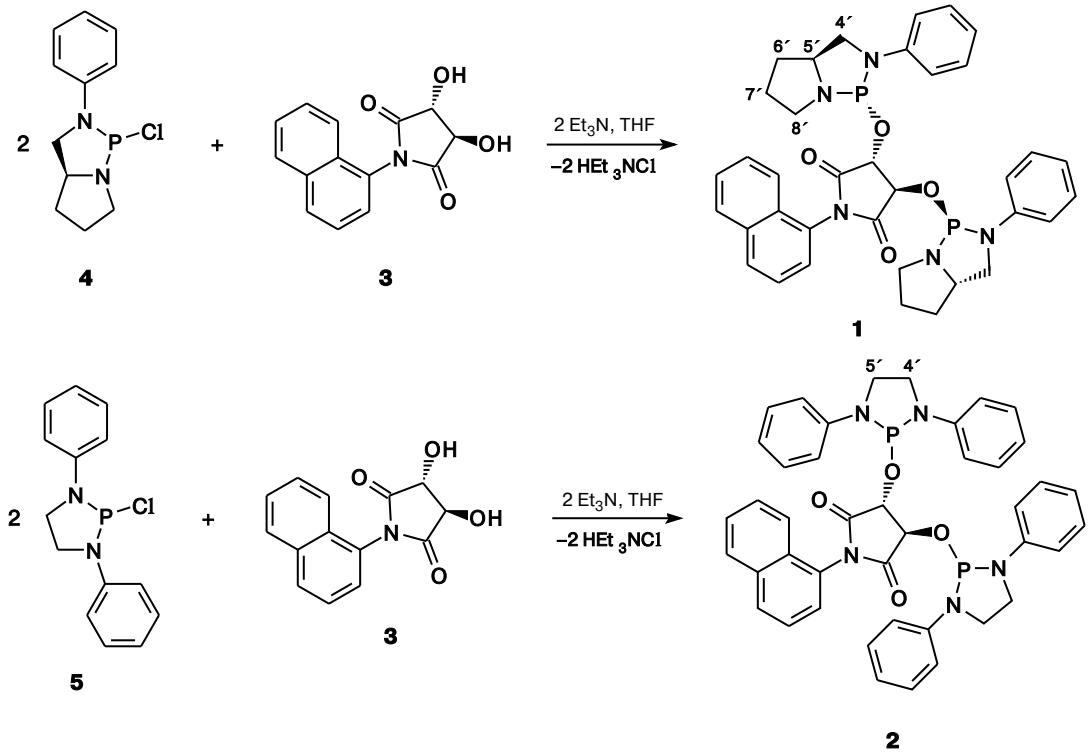
1066-5285/10/5906-1242



dividual; its *P**-stereocenters have (*R*)-configuration, which is evident from the presence of narrow singlets at δ_P 130.5 and 130.3 in the ^{31}P NMR spectrum of its solution in $CDCl_3$ and from the high coupling constant $^2J_{C(8'),P}$ = = 35.5 Hz in the ^{13}C NMR spectrum (see Experimental). This value suggests the *anti*-orientation of the pseudoequatorial exocyclic substituent at the P atom and the fragment $-(CH_2)_3-$ of the pyrrolidine ring of the diazaphosphabicyclo[3.3.0]octane framework and, consequently, the *cis*-orientation of the lone electron pair of the P atom and the C(8′) atom (Fig. 1).[23,33,39–44]

The ^{31}P NMR spectrum of ligand **2** in $CDCl_3$ also exhibits two narrow singlets of equal intensities at δ_P 112.4 and 112.1. The presence of two signals in the ^{31}P NMR spectra of diamidophosphites **1** and **2** is due to the nonequivalence of their phosphorus centers. Such a nonequivalence is confirmed by different Tolman conical angles θ of the phosphorus centers: according to semiempirical

Scheme 1



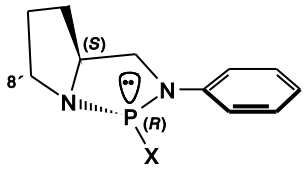


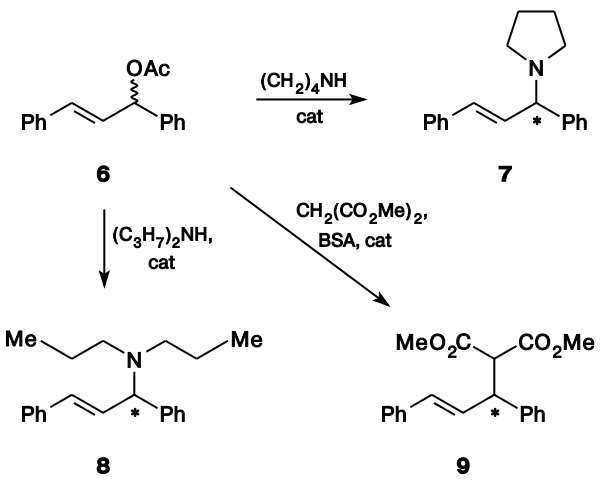
Fig. 1. Fragment of structure **1** (X is an exocyclic substituent).

AM1 calculations with full optimization of the geometrical parameters, θ = 159° and 147° in ligand **1** and θ = 205° and 186° in ligand **2**.[45,46]

Compounds **1** and **2** can easily be purified by flash chromatography, are fairly stable in air, and can be stored in a dry atmosphere for a long period of time. Since the starting synthons are accessible, ligands **1** and **2** can be prepared in amounts of multigrams.

Diamidophosphites **1** and **2** were tested in Pd-catalyzed asymmetric amination and alkylation of (*E*)-1,3-diphenylallyl acetate (**6**) using $[Pd(allyl)Cl]_2$ as a palladium source (Scheme 2, Tables 1—3).

Scheme 2



BSA is *N*,*O*-bis(trimethylsilyl)acetamide

Allylic amination of compound **6** with pyrrolidine in the presence of ligand **1** gives product (*R*)-**7** with up to 73% *ee*. The reaction in THF is more enantioselective, while the higher conversion was achieved in CH_2Cl_2 (see Table 1, entries *1*—*4*), with the optimum molar ratio L/Pd = 1. An increase in this ratio to two lowers the asymmetric induction in both THF and CH_2Cl_2. Ligand **2** provides the 100% conversion of substrate **6**, although this reaction is less enantioselective (at most 20% *ee*) and the resulting amine **7** has (*S*)-configuration (Table 1, entries *5*—*8*).

With diamidophosphite **1** as a ligand and with dipropylamine as a N-nucleophile, the highest enantioselectivity is 85% *ee* (Table 2). As in the amination with pyrrolidine, the better asymmetric induction is achieved in THF but for L/Pd = 2. The conversions of substrate **6** are comparable in both solvents.

Table 1. Data for the Pd-catalyzed allylic amination of compound **6** with pyrrolidine[a]

Entry	Catalyst	Solvent	Conversion (%)	*ee* (%)[b]
1	$[Pd(allyl)Cl]_2$—2[**1**]	THF	87	73 (*R*)
2	$[Pd(allyl)Cl]_2$—4[**1**]	THF	59	30 (*R*)
3	$[Pd(allyl)Cl]_2$—2[**1**]	CH_2Cl_2	67	65 (*R*)
4	$[Pd(allyl)Cl]_2$—4[**1**]	CH_2Cl_2	100	45 (*R*)
5	$[Pd(allyl)Cl]_2$—2[**2**]	THF	100	11 (*S*)
6	$[Pd(allyl)Cl]_2$—4[**2**]	THF	100	9 (*S*)
7	$[Pd(allyl)Cl]_2$—2[**2**]	CH_2Cl_2	100	20 (*S*)
8	$[Pd(allyl)Cl]_2$—4[**2**]	CH_2Cl_2	100	7 (*S*)

[a] All reactions were carried out at 20 °C for 48 h in the presence of $[Pd(allyl)Cl]_2$ (2 mol.%).
[b] The conversion of substrate **6** and the enantiomer excesses of product **7** 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).

Allylic alkylation of compound **6** with dimethyl malonate in the presence of *P**,*P**-bidentate ligand **1** gives product (*S*)-**9** with 91—95% *ee* (Scheme 2, Table 3, entries *3*, *4*); the starting substrate is fully converted, regardless of the molar ratio L/Pd. In contrast to the allylic amination, the optimum solvent for this reaction is CH_2Cl_2 (see Table 3, *cf.* entries *1*, *2* and *3*, *4*). Palladium complexes with ligand **2** favor the formation of product (*R*)-**9**; the highest enantioselectivity is 31% *ee* (see Table 3, entries *5*—*8*).

Compounds **1** and **2** were also used in Pd-catalyzed asymmetric alkylation of a cyclic substrate, namely, cyclohex-2-en-1-yl ethyl carbonate (**10**), with dimethyl malonate (Scheme 3, Table 4). Diamidophosphite **1** provides up to 46% *ee* and the 90% conversion of substrate **10** (CH_2Cl_2, L/Pd = 1; see Table 4, entry *3*).

Table 2. Data for the Pd-catalyzed allylic amination of compound **6** with dipropylamine[a]

Entry	Catalyst	Solvent	Conversion (%)	*ee* (%)[b]
1	$[Pd(allyl)Cl]_2$—2[**1**]	THF	90	49 (+)
2	$[Pd(allyl)Cl]_2$—4[**1**]	THF	78	85 (+)
3	$[Pd(allyl)Cl]_2$—2[**1**]	CH_2Cl_2	98	47 (+)
4	$[Pd(allyl)Cl]_2$—4[**1**]	CH_2Cl_2	64	41 (+)

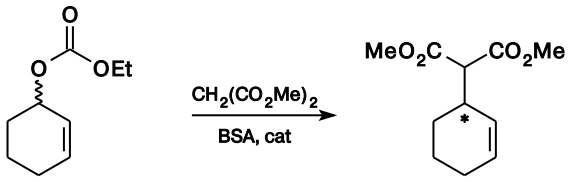
[a] All reactions were carried out at 20 °C for 48 h in the presence of $[Pd(allyl)Cl]_2$ (2 mol.%).
[b] The conversion of substrate **6** and the enantiomer excesses of product **8** were determined by HPLC (Daicel Chiralcel OD—H, $C_6H_{14}/Pr^iOH/HNEt_2$ = 1000 : 1 : 1, 0.4 mL min^{-1}, 254 nm, *t*(+) = 8.2 min, *t*(−) = 9.1 min).

Table 3. Data for the Pd-catalyzed allylic alkylation of compound **6** with dimethyl malonate[a]

Entry	Catalyst	Solvent	Conversion (%)	*ee* (%)[b]
1	$[Pd(allyl)Cl]_2$—2[**1**]	THF	58	33 (*S*)
2	$[Pd(allyl)Cl]_2$—4[**1**]	THF	42	70 (*S*)
3	$[Pd(allyl)Cl]_2$—2[**1**]	CH_2Cl_2	100	91 (*S*)
4	$[Pd(allyl)Cl]_2$—4[**1**]	CH_2Cl_2	100	95 (*S*)
5	$[Pd(allyl)Cl]_2$—2[**2**]	THF	62	31 (*R*)
6	$[Pd(allyl)Cl]_2$—4[**2**]	THF	91	11 (*R*)
7	$[Pd(allyl)Cl]_2$—2[**2**]	CH_2Cl_2	95	20 (*R*)
8	$[Pd(allyl)Cl]_2$—4[**2**]	CH_2Cl_2	100	5 (*R*)

[a] All reactions were carried out at 20 °C for 48 h in the presence of $[Pd(allyl)Cl]_2$ (2 mol.%).
[b] The conversion of substrate **6** and the enantiomer excesses of product **9** were determined by HPLC (Daicel Chiralcel OD—H, C_6H_{14}/Pr^iOH = 99 : 1, 0.6 mL min^{-1}, 254 nm).

Scheme 3



10 **11**

This result is acceptable since a high enantioselectivity is difficult to achieve for cyclic substrate **10**.[14,37,47] The asymmetric induction in the presence of ligand **2** is low (7—11% *ee*; see Table 4, entries *5*—*8*). Interestingly, in this reaction, as in the above allylic substitution of (*E*)-1,3-diphenylallyl acetate, diamidophosphites **1** and **2** favor the formation of the opposite enantiomers of product **11**.

Table 4. Data for the Pd-catalyzed allylic alkylation of compound **10** with dimethyl malonate[a]

Entry	Catalyst	Solvent	Conversion (%)	*ee* (%)[b]
1	$[Pd(allyl)Cl]_2$—2[**1**]	THF	56	33 (*R*)
2	$[Pd(allyl)Cl]_2$—4[**1**]	THF	59	25 (*R*)
3	$[Pd(allyl)Cl]_2$—2[**1**]	CH_2Cl_2	90	46 (*R*)
4	$[Pd(allyl)Cl]_2$—4[**1**]	CH_2Cl_2	74	15 (*R*)
5	$[Pd(allyl)Cl]_2$—2[**2**]	THF	39	7 (*S*)
6	$[Pd(allyl)Cl]_2$—4[**2**]	THF	54	11 (*S*)
7	$[Pd(allyl)Cl]_2$—2[**2**]	CH_2Cl_2	25	9 (*S*)
8	$[Pd(allyl)Cl]_2$—4[**2**]	CH_2Cl_2	54	10 (*S*)

[a] All reactions were carried out at 20 °C for 48 h in the presence of $[Pd(allyl)Cl]_2$ (2 mol.%).
[b] The conversion of substrate **10** and the enantiomer excesses of product **11** were determined by HPLC (Daicel Chiralcel AD, C_6H_{14}/Pr^iOH = 200 : 1, 1 mL min^{-1}, 219 nm).

To sum up, one can conclude that diamidophosphite **1** containing the asymmetric P atoms is an efficient stereoselector and successfully supplements similar diastereomeric ligands $\mathbf{L_C}$ (see Ref. 33). In particular, being not less enantioselective than $\mathbf{L_C}$ in the Pd-catalyzed amination of (*E*)-1,3-diphenylallyl acetate (**6**) with pyrrolidine (73 and 73% *ee*) and in its Pd-catalyzed alkylation with dimethyl malonate (96 and 95% *ee*), ligand **1** is superior to them in the amination of compound **6** with dipropylamine (73 and 85% *ee*) but somewhat inferior in the Pd-catalyzed alkylation of cyclohex-2-en-1-yl ethyl carbonate (**10**) with dimethyl malonate (65 and 46% *ee*). In the Pd-catalyzed alkylation of (*E*)-1,3-diphenylallyl acetate with dimethyl malonate, ligand **1** is slightly superior to *P*,*P*-bidentate phosphite $\mathbf{L_B}$ in asymmetric induction (see Ref. 32) (95 and 90% *ee*, respectively). At the same time, diamidophosphite **2** with the *C**-stereocenters only in the pyrrolidine-2,5-dione ring is an inefficient stereoselector, although its steric demands are higher than those of ligand **1** (for the Tolman conical angles of the phosphorus centers in **1** and **2**, see above). Thus, the pyrrolidine-2,5-dione fragment in efficient ligands **1** and $\mathbf{L_{A—C}}$ forms a sterically rigid basis and additional *P**- and/or *C**-stereocenters should be present in their structures for achieving high catalytic enantioselectivity.

Experimental

^{31}P, ^1H, and ^{13}C NMR spectra were recorded on a Bruker AMX-400 instrument (161.98, 400.13, and 100.61 MHz, respectively) with reference to 85% H_3PO_4 in D_2O (^{31}P) and Me_4Si (^1H, ^{13}C). The signals in the ^{13}C NMR spectra were assigned using the DEPT procedure. Mass spectra (MALDI TOF/TOF) were measured on a Bruker Daltonics Ultraflex instrument. IR spectra were recorded on a Specord M-80 instrument ($CHCl_3$, polyethylene cell). Enantiomer analysis of the products was performed on an HP Agilent 1100 chromatograph. Elemental analysis was carried out at the Organic Microanalysis Laboratory of the A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences.

All reactions were carried out under dry argon in dry solvents. The starting complex $[Pd(allyl)Cl]_2$, (3*R*,4*R*)-3,4-dihydroxy-1-(1-naphthyl)pyrrolidine-2,5-dione (**3**), and the phosphorylating reagents (5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**4**) and 2-chloro-1,3-diphenyl-1,3,2-diazaphospholidine (**5**) were prepared according to known procedures.[23,38,48,49]

The starting substrates (*E*)-1,3-diphenylallyl acetate (**6**) and cyclohex-2-en-1-yl ethyl carbonate (**10**) were prepared as described earlier.[49,50] Palladium-catalyzed asymmetric amination of substrate **6** with pyrrolidine and dipropylamine and alkylation of substrate **6** with dimethyl malonate, as well as determination of its conversion and the enantiomer excesses of products **7**—**9**, were carried out according to published procedures.[51,52,23] Catalytic asymmetric alkylation of substrate **10** with dimethyl mal-

onate and determination of its conversion and the enantiomer excesses of product **11** were carried out as described earlier.[53,54]

(*R*,*R*)-Tartaric acid, 1-naphthylamine, pyrrolidine, dipropylamine, dimethyl malonate, and *N*,*O*-bis(trimethylsilyl)acetamide (BSA) were the Fluka and Aldrich chemicals.

Synthesis of *P*,*P*-bidentate ligands 1 and 2 (general procedure). A solution of (3*R*,4*R*)-3,4-dihydroxy-1-(1-naphthyl)-pyrrolidine-2,5-dione (**3**) (1.29 g, 5 mmol) in THF (15 mL) was added dropwise at 20 °C for 20 min to a vigorously stirred solution of (5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo-[3.3.0]octane (**4**) (2.41 g, 10 mmol) or 2-chloro-1,3-diphenyl-1,3,2-diazaphospholidine (**5**) (2.77 g, 10 mmol) and Et_3N (1.45 mL, 10.4 mmol) in THF (25 mL). The reaction mixture was refluxed with stirring for 1.5 h and cooled to 20 °C. The salt $Et_3N \cdot HCl$ was filtered off and the filtrate was concentrated *in vacuo* (40 Torr). Products **1** and **2** were purified by flash chromatography on silica gel with hexane—ethyl acetate (1 : 1) (**1**) and hexane—CH_2Cl_2 (1 : 1) (**2**) as eluents.

(3*R*,4*R*)-1-(1-Naphthyl)-3,4-bis[(2*R*,5*S*)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]oct-2-yloxy]pyrrolidine-2,5-dione (1). Yield 2.73 g (82%), yellow powder. Found (%): C, 65.14; H, 5.66; N, 10.31. $C_{36}H_{37}N_5O_4P_2$. Calculated (%): C, 64.96; H, 5.60; N, 10.52. ^{13}C NMR ($CDCl_3$), δ: 26.4 (d, C(7′), ^3J = = 4.4 Hz); 32.0 (s, C(6′)); 48.1 (d, C(8′), ^2J = 35.5 Hz); 53.7 (d, C(4′), ^2J = 7.8 Hz); 62.7 (d, C(5′), ^2J = 8.1 Hz); 74.9 (s, CHO); 75.7 (s, CHO); 115.3 (d, CH_{Ph}, ^3J = 13.0 Hz); 119.7 (s, CH_{Ph}); 121.6 (s, $CH_{Naphthyl}$); 124.8 (s, $CH_{Naphthyl}$); 125.9 (s, $CH_{Naphthyl}$); 126.8 (s, $C_{Naphthyl}$); 127.0 (s, $CH_{Naphthyl}$); 127.9 (s, $CH_{Naphthyl}$); 128.1 (s, $CH_{Naphthyl}$); 128.9 (s, CH_{Ph}); 129.8 (s, $CH_{Naphthyl}$); 131.4 (s, $C_{Naphthyl}$); 136.4 (s, $C_{Naphthyl}$); 145.1 (d, C_{Ph}, ^2J = 16.1 Hz); 174.6 (s, C=O); 175.1 (s, C=O). ^1H NMR ($CDCl_3$), δ: 1.47 (dq, 2 H, J = 10.8 Hz); 1.7 (m, 4 H); 1.88 (dq, 2 H, J = 10.9 Hz); 2.93 (ddd, 2 H, J = 8.0 Hz, J = 7.1 Hz, J = 5.9 Hz); 3.22 (m, 2 H); 3.64 (m, 4 H); 3.89 (m, 2 H); 4.77 (s, 1 H); 4.84 (s, 1 H); 6.83 (t, 2 H, J = 7.8 Hz); 7.08 (d, 4 H, J = 8.0 Hz); 7.16 (m, 5 H); 7.33 (m, 2 H); 7.50 (m, 2 H); 7.82 (t, 1 H, J = 8.3 Hz); 7.91 (m, 1 H). IR ($CHCl_3$), ν/cm^{-1}: 1737 (C=O). MS (MALDI TOF/TOF), m/z (I_{rel} (%)): 689 (100) $[M + Na]^+$, 667 (89) $[M + H]^+$.

(3*R*,4*R*)-3,4-Bis(1,3-diphenyl-1,3,2-diazaphospholidin-2-yloxy)-1-(1-naphthyl)pyrrolidine-2,5-dione (2). Yield 2.88 g (78%), white powder. Found (%): C, 68.62; H, 5.19; N, 9.58. $C_{42}H_{37}N_5O_4P_2$. Calculated (%): C, 68.38; H, 5.06; N, 9.49. ^{13}C NMR ($CDCl_3$), δ: 47.6 (d, C(4′), ^2J = 10.1 Hz); 47.8 (d, C(5′), ^2J = 9.9 Hz); 73.4 (s, CHO); 74.1 (s, CHO); 116.5 (d, CH_{Ph}, ^3J = 12.0 Hz); 120.2 (s, CH_{Ph}); 121.6 (s, $CH_{Naphthyl}$); 125.0 (s, $CH_{Naphthyl}$); 125.7 (s, $CH_{Naphthyl}$); 126.9 (s, $C_{Naphthyl}$); 127.2 (s, $CH_{Naphthyl}$); 127.7 (s, $CH_{Naphthyl}$); 128.4 (s, $CH_{Naphthyl}$); 129.2 (s, CH_{Ph}); 129.8 (s, $CH_{Naphthyl}$); 132.0 (s, $C_{Naphthyl}$); 136.8 (s, $C_{Naphthyl}$); 147.3 (d, C_{Ph}, ^2J = 16.0 Hz); 174.8 (s, C=O); 175.2 (s, C=O). ^1H NMR ($CDCl_3$), δ: 3.67 (m, 4 H); 3.82 (m, 4 H); 4.74 (m, 1 H); 4.78 (m, 1 H); 6.94 (m, 4 H); 7.06 (t, 1 H, J = 8.0 Hz); 7.14 (m, 6 H); 7.21 (m, 3 H); 7.23—7.41 (m, 9 H); 7.48 (m, 2 H); 7.84 (t, 1 H, J = 8.4 Hz); 7.90 (m, 1 H). IR ($CHCl_3$), ν/cm^{-1}: 1732 (C=O). MS (MALDI TOF/TOF), m/z (I_{rel} (%)): 761 (23) $[M + Na]^+$, 739 (100) $[M + H]^+$.

Asymmetric allylic amination of (*E*)-1,3-diphenylallyl acetate (6) with pyrrolidine. A solution of $[Pd(allyl)Cl]_2$ (0.0037 g, 0.01 mmol) and an appropriate ligand (0.02 or 0.04 mmol) in an appropriate solvent (5 mL) was stirred for 40 min. Then (*E*)-1,3-diphenylallyl acetate (0.1 mL, 0.5 mmol) was added. The resulting solution was stirred for 15 min, whereupon 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 **6** and the enantiomer excesses of product **7** were determined by HPLC on a chiral stationary phase.

Asymmetric allylic amination of (*E*)-1,3-diphenylallyl acetate (6) with dipropylamine. A solution of $[Pd(allyl)Cl]_2$ (0.0037 g, 0.01 mmol) and an appropriate ligand (0.02 or 0.04 mmol) in an appropriate solvent (5 mL) was stirred for 40 min. Then (*E*)-1,3-diphenylallyl acetate (0.1 mL, 0.5 mmol) was added. The resulting solution was stirred for 15 min, whereupon freshly distilled dipropylamine (0.15 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 **6** and the enantiomer excesses of product **8** were determined by HPLC on a chiral stationary phase.

Asymmetric allylic alkylation of (*E*)-1,3-diphenylallyl acetate (6) with dimethyl malonate. A solution of $[Pd(allyl)Cl]_2$ (0.0037 g, 0.01 mmol) and an appropriate ligand (0.02 or 0.04 mmol) in an appropriate solvent (5 mL) was stirred for 40 min. Then (*E*)-1,3-diphenylallyl acetate (0.1 mL, 0.5 mmol) was added. The resulting solution was stirred for 15 min, whereupon 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 **6** and the enantiomer excesses of product **9** were determined by HPLC on a chiral stationary phase.

Asymmetric allylic alkylation of cyclohex-2-en-1-yl ethyl carbonate (10) with dimethyl malonate. A solution of $[Pd(allyl)Cl]_2$ (0.0037 g, 0.01 mmol) and an appropriate ligand (0.02 or 0.04 mmol) in an appropriate solvent (5 mL) was stirred for 40 min. Then cyclohex-2-en-1-yl ethyl carbonate (0.085 g, 0.5 mmol) was added. The resulting solution was stirred for 15 min, whereupon dimethyl malonate (0.10 mL, 0.87 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (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 enantiomer excesses of product **11** were determined by HPLC on a chiral stationary phase.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 08-03-00416-a) and the Council on Grants at the President of the Russian Federation (State Support Program for young Russian Ph.D. scientists, Grant MK-3889.2010.3).

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Received December 24, 2009;
in revised form March 30, 2010