Diastereomeric *P*,*N*-bidentate amidophosphites based on (*S*,*S*)- and (*R*,*R*)-hydrobenzoin as ligands in the Pd-catalyzed asymmetric allylation

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New *P*,*N*-bidentate diastereomeric amidophosphite ligands were obtained by phosphorylation of (*S*)-2-[(phenylamino)methyl]pyrrolidine involving (4*S*,5*S*)- and (4*R*,5*R*)-2-chloro-4,5-diphenyl-1,3,2-dioxaphospholanes. Their efficiency in the Pd-catalyzed enantioselective allylic substitution was compared, it was found that the reaction involving (*E*)-1,3-diphenylallyl acetate and pyrrolidine gives up to 75% *ee*.

Key words: amidophosphites, 1,3,2-dioxaphospholanes, palladium catalysts, asymmetric allylation.

A fast progress in the asymmetric metal complex catalysis is of fundamental and practical importance. From the one hand, this implies obtaining new knowledge on the nature of molecular chiral identification and asymmetric induction. From the other hand, this means development of highly efficient methods for the preparation of enantiopure drugs, pheromones, agrochemicals, food additives, fragrances, and stereoindividual polymers. In addition, the use of highly selective catalytic systems is one of the basic principles of "green chemistry".[1—5] Activity and stereoselectivity of the metal complex catalysts is largely defined by successful strategy of the design and synthesis of the corresponding chiral ligands, in the first place, phosphorus-containing ones.[6,7]. Virtually all the arsenal of available natural compounds, as well as binaphthyl, biphenyl, and ferrocene derivatives, were used in the preparation of large libraries of different phosphorus-containing chiral ligands. Nevertheless, the overwhelming majority of such ligands in the composition of the corresponding metal complexes are able to catalyze with different enantioselectivity either a certain type of chemical transformations, or one certain reaction. The versatile enough (the so-called "privileged") ligands are very rare, and their expensiveness significantly restrains their wide practical use. In this connection, development of simple and efficient methods for the preparation of inexpensive ligands based on available optically pure synthons is still a relevant problem.[8—11]

Ligands of the phosphite nature are of the first and foremost interest, since they advantageously differ in synthetic availability, stability to oxidation, pronounced π-acidity, and are inexpensive. This allows one to easy enough obtain wide series of ligands, including application of parallel and solid-phase syntheses.[11—17]

Introduction of additional donor atom, for example, a nitrogen atom, into the structure of the phosphorus-containing chiral ligand creates new possibilities. In this case, enantioselectivity of the catalyst is contributed not only by stereochemistry of the ligand, but also by its electron asymmetry due to the presence of the donor atoms of different nature. Electron asymmetry greatly affects the mechanism of the catalytic cycle, and, as a consequence, efficiency of the chirality transfer in its key step. Thus, the π-acceptor character of the phosphorus atom in the *P*,*N*-bidentate ligands allows one to stabilize the low oxidation states of the complexation metals and increase their electrophilicity, whereas the σ-donor ability of the nitrogen atom make them more susceptible to the processes of oxidative addition. Different trans-effects of the phosphorus and nitrogen donor centers are also significant factors.[18—20]

In the present work, we report on obtaining and application in enantioselective catalysis of new *P*,*N*-bidentate amidophosphites (*S*,*S*,*S*)-**3** and (*R*,*R*,*S*)-**3** containing 1,3,2-dioxaphospholane rings based on the (*S*,*S*)- and (*R*,*R*)-hydrobenzoin. Note that this synthon is one of the most available C_2-symmetric enantiopure diols.[21] It should

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2026—2030, October, 2011.

1066-5285/11/6010-2063

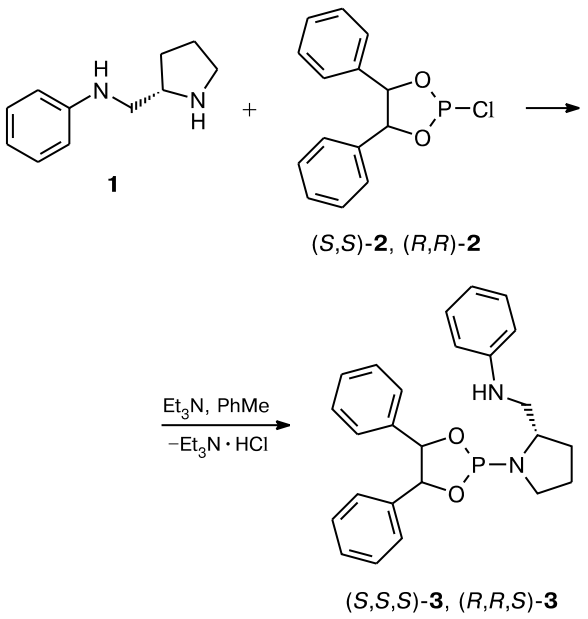
be noted that several *P*-monodentate and *P*,*P*-bidentate phosphites of the 1,3,2-dioxaphospholane series based on hydrobenzoin were used in the Cu-catalyzed conjugated addition, Rh-catalyzed hydroformylation, and Ni-catalyzed hydrovinylation with low or moderate enantioselectivity (no more than 60% *ee*).[22—25] We have chosen Pd-catalyzed asymmetric allylation as a catalytic process for the testing the amidophosphites (*S*,*S*,*S*)-**3** and (*R*,*R*,*S*)-**3**, which is used for both the evaluation of efficiency of new chiral ligands and stereoselective synthesis of valuable natural compounds.[26—29] It should be noted that earlier we have suggested several efficient *P**,*N*-bidentate ligands of the phosphite nature bearing asymmetric phosphorus atoms for a number of Pd-catalyzed asymmetric allylation reactions.[30—32]

Results and Discussion

The new *P*,*N*-bidentate amidophosphites (*S*,*S*,*S*)-**3** and (*R*,*R*,*S*)-**3** were synthesized by phosphorylation of (*S*)-2-[(phenylamino)methyl]pyrrolidine (**1**) with the reactants (*S*,*S*)-**2** and (*R*,*R*)-**2** in toluene (Scheme 1). It is very important that the starting enantiopure diamine **1** is easy available, since it can be obtained by the condensation of (*S*)-glutamic acid and aniline with subsequent hydride reduction of the (*S*)-pyroglutamic acid anilide that formed.[33,34] It is necessary to note that the known method for the preparation of enantiomeric phosphorylating agents (*S*,*S*)-**2** and (*R*,*R*)-**2** consists in the reflux of a suspension of (*S*,*S*)- or (*R*,*R*)-hydrobenzoin in excess PCl_3 for a long time (about 10—12 h).[35] We improved this method and carried out the reaction in the presence of *N*-methylpyrrolidone in catalytic amount, which was used earlier for the preparation of chlorophosphite based on BINOL (see Ref. 36). This allowed us to reduce the reaction time to 20 min, thus developing an efficient procedure for the synthesis of amidophosphites (*S*,*S*)-**2** and (*R*,*R*)-**2**.

It should be emphasized that a direct phosphorylation of **1** upon the action of (*S*,*S*)-**2** or (*R*,*R*)-**2** occurs exclusively at the pyrrolidine amino group. The ^{31}P, ^{1}H, and ^{13}C NMR spectroscopic data for compounds (*S*,*S*,*S*)-**3** and (*R*,*R*,*S*)-**3** completely agree with the structure suggested for them (see Experimental). Note, in particular, the presence of signals characteristic of the protons of the peripheral aniline NH group as broad singlets at δ_H 4.25 and 4.22, respectively,[33,37] in their ^{1}H NMR spectra. The IR spectra of solutions of amidophosphites (*S*,*S*,*S*)-**3** and (*R*,*R*,*S*)-**3** in $CHCl_3$ exhibit symmetric absorption bands of medium intensity ν(N—H) 3368 and 3381 cm^{-1} also corresponding to the secondary NH(Ph) amino group.[38] In addition, unlike the signals for the carbon atoms in the phenyl substituent at the aniline nitrogen atom, the signals for the carbon atoms of the pyrrolidine fragment in the molecules of (*S*,*S*,*S*)-**3** and (*R*,*R*,*S*)-**3** are characterized by the spin-spin coupling constants $^{2}J_{C,P}$ and $^{3}J_{C,P}$ in the ^{13}C NMR spectra. Besides, treatment of compound **1** with two equivalents of (*S*,*S*)-**2** under conditions similar to those in the synthesis of ligand (*S*,*S*,*S*)-**3** (see Experimental) does not lead to phosphorylation of this diamine at both amino groups with the formation of the corresponding *P*,*P*-bidentate derivative. Instead, the ^{31}P NMR spectrum of the residue after filtration and concentration of the reaction solution exhibits the signals for the phosphorylating reactant (*S*,*S*)-**2** present in excess at δ_P 174.2 and for the product (*S*,*S*,*S*)-**3** at δ_P 144.4 ($CDCl_3$).

Scheme 1

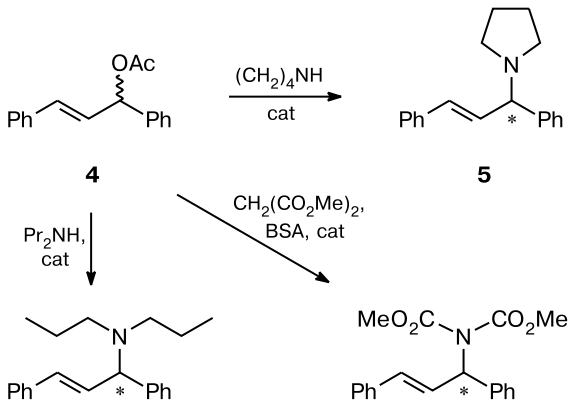


Amidophosphites (*S*,*S*,*S*)-**3** and (*R*,*R*,*S*)-**3** were isolated by flash-chromatography, they are well soluble in most organic solvents and are stable enough in air and on prolonged storage under dry atmosphere.

The ligands (*S*,*S*,*S*)-**3** and (*R*,*R*,*S*)-**3** (L) were studied in the Pd-catalyzed asymmetric allylation with (*E*)-1,3-diphenylallyl acetate (**4**), $[Pd(allyl)Cl]_2$ was chosen as a precatalyst (Scheme 2, Table 1—3). In the allylation of pyrrolidine with compound **4**, palladium complexes of both diastereomeric ligands provide the quantitative conversion, but diverse asymmetric induction. Amidophosphite (*S*,*S*,*S*)-**3** virtually irrespective of the solvent nature and the molar ratio L : Pd leads to the product (*R*)-**5** with low enantioselectivity (no more than 29% *ee*, see Table 1, entries *1—4*). Conversely, when the ligand (*R*,*R*,*S*)-**3** is involved the amine (*R*)-**5** is formed with the enantiomeric excess up to 75% (see Table 1, entries *5—8*). Consequently, in the case of (*R*,*R*,*S*)-**3**, a concerted stereoselective action of its (*R*,*R*)-hydrobenzoin and (*S*)-2-[(phenylamino)methyl]pyrrolidine fragments takes place. The highest enantioselectivity is observed when the reaction is carried out in THF with the molar ratio L : Pd = 2 (see

Table 1, entry *6*). Note that an increase in the molar ratio L : Pd leads to the increase in enantioselectivity in THF and to its decrease in CH_2Cl_2 (see Table 1, *cf.* pairs of entries *5*, *6* and *7*, *8*).

Scheme 2



BSA is the bis-trimethylsilylacetamide, cat is the catalyst.

When dipropylamine is used as the N-nucleophile, amidophosphite (*R*,*R*,*S*)-**3** is also more efficient ligand allowing us to reach the complete conversion of the substrate **4** and enantioselectivity up to 65% *ee* (Table 2).

As in the allylation of pyrrolidine, the higher asymmetric induction is reached in THF, but at the molar ratio L : Pd = 1 (see Table 2, entry *5*). The diastereomeric ligand (*S*,*S*,*S*)-**3** allows one to obtain the opposite enantiomer of amine **6**, but with low (7—13% *ee*) enantioselectivity (see Table 2, entries *1*—*4*).

The *P*,*N*-bidentate ligands (*S*,*S*,*S*)-**3** and ((*R*,*R*,*S*)-**3** were also used in the allylation of dimethyl malonate with

Table 2. The Pd-catalyzed allylation of dipropylamine with diphenylallyl acetate **4**[a]

Entry	Ligand	L/Pd	Solvent	Conversion (%)	*ee* (%)[b]
1	(*S*,*S*,*S*)-**3**	1	THF	82	11 (–)
2	(*S*,*S*,*S*)-**3**	2	THF	89	9 (–)
3	(*S*,*S*,*S*)-**3**	1	CH_2Cl_2	100	7 (–)
4	(*S*,*S*,*S*)-**3**	2	CH_2Cl_2	100	13 (–)
5	(*R*,*R*,*S*)-**3**	1	THF	100	65 (+)
6	(*R*,*R*,*S*)-**3**	2	THF	100	55 (+)
7	(*R*,*R*,*S*)-**3**	1	CH_2Cl_2	100	23 (+)
8	(*R*,*R*,*S*)-**3**	2	CH_2Cl_2	100	15 (+)

[a] Reaction conditions: $[Pd(allyl)Cl]_2$ (2 mol.%), 20 °C, 48 h.
[b] Conversion of **4** and enantiomeric excess of product **6** were determined by HPLC (a Daicel Chiralcel OD—H chiral stationary phase, the eluent C_6H_{14} : Pr^iOH : $HNEt_2$ = 1000 : 1 : 1 was used at the rate 0.4 mL min^{-1}, detection at 254 nm, the retention times: for (+)-isomer 8.2 min, for (–)-isomer 9.1 min). The sign of the optical rotation angle is shown in parentheses.

(*E*)-1,3-diphenylallyl acetate (**4**) (Table 3). In contrast to the reactions involving amines, the better results were shown by the diastereomer (*S*,*S*,*S*)-**3**: the product (*R*)-**7** is formed with the enantioselectivity up to 60% *ee* at high conversions of the starting substrate **4** (see Table 3, entries *1*—*4*). The optimum solvent is THF at the molar ratio L : Pd = 2 (see Table 3, entry *2*). The allylic substitution involving allyl acetate **4** and amidophosphite (*R*,*R*,*S*)-**3** proceeds with lower conversion and enantioselectivity (to 45% *ee*, see Table 3, entries *5*—*8*), with the product **7** having the (*S*)-configuration.

In conclusion, in the present work we obtained the first representatives of *P*,*N*-bidentate ligands of the phosphite nature based on the known C_2-symmetric enantiopure 1,2-diol, *viz.*, hydrobenzoin. A convenient method

Table 1. The Pd-catalyzed allylation of pyrrolidine with diphenylallyl acetate **4**[a]

Entry	Ligand	L/Pd	Solvent	Conversion (%)	*ee* (%)[b] (configuration)
1	(*S*,*S*,*S*)-**3**	1	THF	100	19 (*R*)
2	(*S*,*S*,*S*)-**3**	2	THF	95	21 (*R*)
3	(*S*,*S*,*S*)-**3**	1	CH_2Cl_2	100	29 (*R*)
4	(*S*,*S*,*S*)-**3**	2	CH_2Cl_2	100	23 (*R*)
5	(*R*,*R*,*S*)-**3**	1	THF	100	63 (*R*)
6	(*R*,*R*,*S*)-**3**	2	THF	100	75 (*R*)
7	(*R*,*R*,*S*)-**3**	1	CH_2Cl_2	100	65 (*R*)
8	(*R*,*R*,*S*)-**3**	2	CH_2Cl_2	100	57 (*R*)

[a] Reaction conditions: $[Pd(allyl)Cl]_2$ (2 mol.%), 20 °C, 48 h.
[b] Conversion of **4** and enantiomeric excess of product **5** were determined by HPLC (a Daicel Chiralcel OD—H chiral stationary phase, the eluent C_6H_{14} : Pr^iOH : $HNEt_2$ = 200 : 1 : 0.1 was used at the rate 0.9 mL min^{-1}, detection at 254 nm).

Table 3. The Pd-catalyzed allylation of dimethyl malonate with diphenylallyl acetate **4**[a]

Entry	Ligand	L/Pd	Solvent	Conversion (%)	*ee* (%)[b] (configuration)
1	(*S*,*S*,*S*)-**3**	1	THF	89	30 (*R*)
2	(*S*,*S*,*S*)-**3**	2	THF	100	60 (*R*)
3	(*S*,*S*,*S*)-**3**	1	CH_2Cl_2	100	20 (*R*)
4	(*S*,*S*,*S*)-**3**	2	CH_2Cl_2	97	19 (*R*)
5	(*R*,*R*,*S*)-**3**	1	THF	62	11 (*S*)
6	(*R*,*R*,*S*)-**3**	2	THF	66	10 (*S*)
7	(*R*,*R*,*S*)-**3**	1	CH_2Cl_2	100	13 (*S*)
8	(*R*,*R*,*S*)-**3**	2	CH_2Cl_2	100	45 (*S*)

[a] Reaction conditions: $[Pd(allyl)Cl]_2$ (2 mol.%), 20 °C, 48 h.
[b] Conversion of **4** and enantiomeric excess of product **7** were determined by HPLC (a Daicel Chiralcel OD—H chiral stationary phase, the eluent C_6H_{14} : Pr^iOH = 99 : 1 was used at the rate 0.6 mL min^{-1}, detection at 254 nm).

was used for the synthesis of available diastereomeric amidophosphites (*S*,*S*,*S*)-**3** and (*R*,*R*,*S*)-**3** with the secondary peripheral amino group, which is based on the efficient procedure for the preparation of chlorophosphites from (*S*,*S*)- and (*R*,*R*)-hydrobenzoins as necessary phosphorylating agents. A model reactions of the Pd-catalyzed asymmetric allylation using (*E*)-1,3-diphenylallyl acetate (**4**) demonstrated that (*S*,*S*,*S*)-**3** and (*R*,*R*,*S*)-**3** are the complementary chiral ligands. Allylation of pyrrolidine showed a good level of enantioselectivity up to 75% *ee*.

Experimental

^{31}P, ^{1}H, and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer (161.98, 400.13, and 100.61 MHz, respectively) relatively to 85% H_3PO_4 in D_2O (^{31}P) and Me_4Si (^{1}H and ^{13}C). Signals in the ^{13}C NMR spectra were assigned using the DEPT procedure. Mass spectra with the laser desorption ionization (MALDI TOF/TOF) were recorded on a Bruker Daltonics Ultraflex instrument. IR spectra were recorded on a Specord M-80 spectrometer in $CHCl_3$ in polyethylene cuvettes. Optical rotation was measured on a Perkin—Elmer 341 polarimeter. Enantiomeric analysis of products of the catalytic reactions was performed on a HP Agilent 1100 HPL-chromatograph. Elemental analysis was performed in the Laboratory of Organic Microanalysis of INEOS RAS.

All the reactions were carried out under dry argon in anhydrous solvents. The starting compounds, *i.e.*, the $[Pd(allyl)Cl]_2$ complex and (*E*)-1,3-diphenylallyl acetate (**4**), were synthesized according to the known procedures.[39] Catalytic experiments on asymmetric allylation of pyrrolidine, dipropylamine, and dimethyl malonate upon the action of **4**, determination of conversion of **4** and enantiomeric excess of products **5**, **6**, and **7** were carried out according to the published procedures.[40—42]

(*S*)-Glutamic acid, (*S*,*S*)-hydrobenzoin, (*R*,*R*)-hydrobenzoin, *N*-methylpyrrolidone, pyrrolidine, dipropylamine, as well as dimethyl malonate and bis-trimethylsilylacetamide (BSA) were commercially available reactants from Fluka and Aldrich.

Synthesis of enantiomeric phosphorylating agents (*S*,*S*)-2 and (*R*,*R*)-2 (general procedure). *N*-Methylpyrrolidone (0.01 g, 0.1 mmol) was added to a suspension of (*S*,*S*)-hydrobenzoin or (*R*,*R*)-hydrobenzoin (0.75 g, 3.5 mmol) in PCl_3 (4 mL, 45.5 mmol) and the mixture was refluxed for 20 min until the complete homogenization was reached. Then the excess of PCl_3 was removed *in vacuo* (40 Torr), the residue was dried *in vacuo* (30 min, 1 Torr) to remove the PCl_3 traces. The yield was 0.96 g (98%), pale yellow solid compound. Spectral and physicochemical characteristics of enantiomeric products (*S*,*S*)-**2** and (*R*,*R*)-**2** completely agree with the data published earlier.[35]

Synthesis of *P*,*N*-bidentate ligands (*S*,*S*,*S*)-3 and (*R*,*R*,*S*)-3 (general procedure). A solution of (*S*)-2-[(phenylamino)methyl]-pyrrolidine (**1**) (0.6 g, 3.4 mmol) in toluene (5 mL) was added dropwise to a solution of (4*S*,5*S*)-2-chloro-4,5-diphenyl-1,3,2-dioxaphospholane ((*S*,*S*)-**2**) or (4*R*,5*R*)-2-chloro-4,5-diphenyl-1,3,2-dioxaphospholane ((*R*,*R*)-**2**) (0.95 g, 3.4 mmol) and Et_3N (1.22 mL, 8.8 mmol) in toluene (15 mL) over 20 min at 20 °C with vigorous stirring. The mixture that obtained was stirred for 24 h at 20 °C, then heated to 40 °C, stirred at this temperature for 1 h, and cooled to 20 °C. A precipitate of $Et_3N \cdot HCl$ was removed by filtration, the filtrate was concentrated *in vacuo* (40 Torr). The products (*S*,*S*,*S*)-**3** and (*R*,*R*,*S*)-**3** were purified by flash-chromatography on alumina using hexane—ethyl acetate (1 : 1) as an eluent.

(4*S*,5*S*)-Diphenyl-2-[(*S*)-(2′-[(phenylamino)methyl]pyrrolidin-1′-yl)]-1,3,2-dioxaphospholane ((*S*,*S*,*S*)-3). The yield was 1.11 g (78%), colorless viscous oil. Found (%): C, 72.0; H, 6.59; N, 6.65. $C_{25}H_{27}N_2O_2P$. Calculated (%): C, 71.75; H, 6.50; N, 6.69. ^{31}P NMR ($CDCl_3$), δ: 144.4. ^{13}C NMR ($CDCl_3$), δ ($J_{C,P}$): 24.9 (s, CH_2), 29.9 (d, CH_2, ^3J = 4.0 Hz); 44.5 (d, CH_2N, ^2J = 9.0 Hz); 48.4 (d, CH_2N, ^3J = 4.8 Hz); 56.9 (d, CHN, ^2J = 24.9 Hz); 83.4 (d, CHO, ^2J = 10.0 Hz); 85.2 (d, CHO, ^2J = 8.9 Hz); 113.0 (s, CH_{PhNH}); 117.3 (s, CH_{PhNH}); 126.5 (s, CH_{Ph}); 127.1 (s, CH_{Ph}); 128.4 (s, CH_{Ph}); 128.5 (s, CH_{Ph}); 128.6 (s, CH_{Ph} Hz); 129.2 (s, CH_{PhNH}); 136.7 (d, C_{Ph}, ^3J = 5.0 Hz); 137.6 (d, C_{Ph}, ^3J = 10.1 Hz); 148.1 (s, C_{PhNH}). ^1H NMR ($CDCl_3$), δ: 1.78 (m, 1 H); 1.94 (m, 2 H); 2.04 (m, 1 H); 3.07 (m, 1 H); 3.14 (m, 1 H); 3.39 (m, 1 H); 3.55 (m, 1 H); 4.15 (m, 1 H); 4.25 (br.s, 1 H); 4.89(dd, 2 H, ^3J = 8.0 Hz); 6.62 (d, 2 H, ^3J = 7.9 Hz); 6.68 (t, 1 H, ^3J = 7.9 Hz); 7.15 (t, 2 H, ^3J = 7.9 Hz); 7.25 (m, 10 H). MS (MALDI TOF/TOF), *m*/*z* (I_{rel} (%)): 419 $[M + H]^+$ (21), 283 $[OCHPhCHPhOPH + K]^+$ (100).

(4*R*,5*R*)-Diphenyl-2-[(*S*)-(2′-[(phenylamino)methyl]pyrrolidin-1′-yl)]-1,3,2-dioxaphospholane ((*R*,*R*,*S*)-3). The yield was 1.02 g (72%), colorless viscous oil. Found (%): C, 71.89; H, 6.47; N, 6.75. $C_{25}H_{27}N_2O_2P$. Calculated (%): C, 71.75; H, 6.50; N, 6.69. ^{31}P NMR ($CDCl_3$), δ: 142.8. ^{13}C NMR ($CDCl_3$), δ, ($J_{C,P}$): 24.7 (s, CH_2); 29.5 (d, CH_2, ^3J = 3.0 Hz); 44.1 (d, CH_2N, ^2J = 3.9 Hz), 48.3 (d, CH_2N, ^3J = 3.1 Hz); 57.1 (d, CHN, ^2J = 20.2 Hz); 82.7 (d, CHO, ^2J = 7.0 Hz); 85.1 (d, CHO, ^2J = 4.9 Hz); 112.7 (s, CH_{PhNH}); 117.1 (s, CH_{PhNH}); 126.5 (s, CH_{Ph}); 127.0 (s, CH_{Ph}); 128.2 (s, CH_{Ph}); 128.3 (s, CH_{Ph}); 128.4 (s, CH_{Ph}); 129.0 (s, CH_{PhNH}); 135.8 (d, C_{Ph}); 137.1 (d, C_{Ph}, ^3J = 7.1 Hz); 147.8 (s, C_{PhNH}). ^1H NMR ($CDCl_3$), δ: 1.77 (m, 1 H); 1.94 (m, 2 H); 2.05 (m, 1 H); 3.13 (m, 2 H); 3.24 (m, 1 H); 3.76 (m, 1 H); 4.12 (m, 1 H); 4.22 (br.s, 1 H); 4.87(dd, 2 H, ^3J = 8.0 Hz); 6.62 (d, 2 H, ^3J = 8.0 Hz); 6.70 (t, 1 H, ^3J = 8.0 Hz); 7.17 (t, 2 H, ^3J = 8.0 Hz); 7.28 (m, 10 H). MS (MALDI TOF/TOF), *m*/*z* (I_{rel} (%)): 419 $[M + H]^+$ (31), 283 $[OCHPhCHPhOPH + K]^+$ (100).

Asymmetric allylation of pyrrolidine with (*E*)-1,3-diphenylallyl acetate (4) (general procedure). A solution of $[Pd(allyl)Cl]_2$ (0.0037 g, 0.01 mmol) and the corresponding ligand (0.02 mmol or 0.04 mmol) in the corresponding solvent (5 mL) was stirred for 40 min (see Table 1). Then, (*E*)-1,3-diphenylallyl acetate (0.1 mL, 0.5 mmol) was added and the solution was stirred for another 15 min, followed by addition of freshly distilled pyrrolidine (0.12 mL, 1.5 mmol). The reaction mixture was stirred for 48 h, diluted with hexane (5 mL), and filtered through the layer of celite. The solvents were evaporated at reduced pressure (40 Torr), the residue was dried *in vacuo* (10 Torr). Conversion of the substrate **4** and enantiomeric excess of the product **5** were determined by HPLC on a chiral stationary phase.

Asymmetric allylation of dipropylamine with (*E*)-1,3-diphenylallyl acetate (4) (general procedure). A solution of $[Pd(allyl)Cl]_2$ (0.0037 g, 0.01 mmol) and the corresponding ligand (0.02 mmol or 0.04 mmol) in the corresponding solvent (5 mL) was stirred for 40 min (see Table 2), followed by addition of (*E*)-1,3-diphenylallyl acetate (0.1 mL, 0.5 mmol). After the solution was stirred for another 15 min, 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 the layer of celite. The solvents were evaporated at reduced pressure (40 Torr), the residue was dried *in vacuo* (10 Torr). Conversion of the substrate **4** and enantiomeric excess of the product **6** were determined by HPLC on a chiral stationary phase.

Asymmetric allylation of dimethyl malonate with (*E*)-1,3-diphenylallyl acetate (4) (general procedure). A solution of $[Pd(allyl)Cl]_2$ (0.0037 g, 0.01 mmol) and the corresponding ligand (0.02 mmol or 0.04 mmol) in the corresponding solvent (5 mL) was stirred for 40 min (see Table 3), followed by addition of (*E*)-1,3-diphenylallyl acetate (0.1 mL, 0.5 mmol). After the solution was stirred for another 15 min, 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 the layer of celite. The solvents were evaporated at reduced pressure (40 Torr), the residue was dried *in vacuo* (10 Torr). Conversion of the substrate **4** and enantiomeric excess of the product **7** were determined by HPLC on a chiral stationary phase.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 11-03-00347-a) and the Council on Grants at the President of the Russian Federation (Program of State Support for Young Russian Scientists-Candidates of Science (PhD), Grant MK-3889.2010.3).

References

1. J. M. Brown, in *Comprehensive Asymmetric Catalysis*, Eds E. N. Jacobsen, A. Pfaltz, Y. Yamamoto, Springer, Berlin, 1999, Vol. **1**, p. 121.
2. T. Ohkuma, M. Kitamura, R. Noyori, in *Catalytic Asymmetric Synthesis*, Ed. I. Ojima, Wiley-VCH, New York, 2000, p. 1.
3. *Asymmetric Catalysis on Industrial Scale*, Eds H.-U. Blaser, E. Schmidt, Wiley-VCH, Weinheim, 2004, 450 pp.
4. V. A. Pavlov, T. N. Pavlova, *Usp. Khim.*, 2010, **79**, 961 [*Russ. Chem. Rev.* (*Engl. Transl.*), 2010, **79**, 881].
5. I. P. Beletskaya, L. M. Kustov, *Usp. Khim.*, 2010, **79**, 493 [*Russ. Chem. Rev.* (*Engl. Transl.*), 2010, **79**, 441].
6. C. A. Falciola, A. Alexakis, *Eur. J. Org. Chem.*, 2008, 3765.
7. G. C. Hargaden, P. J. Guiry, *Chem. Rev.*, 2009, **109**, 2505.
8. M. Diéguez, A. Ruiz, C. Claver, *Dalton Trans.*, 2003, 2957.
9. A. G. Tolstikov, T. B. Khlebnikova, G. A. Tolstikov, *Butlerov Soobshch.*, 2002, **2**, № 8, 27 [*Butlerov Commun.* (*Engl. Transl.*), 2002, **2**].
10. A. G. Tolstikov, T. B. Khlebnikova, O. V. Tolstikova, G. A. Tolstikov, *Usp. Khim.*, 2003, **72**, 902 [*Russ. Chem. Rev.* (*Engl. Transl.*), 2003, **72**, 803].
11. J. F. Teichert, B. L. Feringa, *Angew. Chem., Int. Ed.*, 2010, **49**, 2486.
12. J. Ansel, M. Wills, *Chem. Soc. Rev.*, 2002, **31**, 259.
13. A. Alexakis, C. Benhaim, *Eur. J. Org. Chem.*, 2002, 3221.
14. O. Molt, T. Shrader, *Synthesis*, 2002, 2633.
15. K. N. Gavrilov, O. G. Bondarev, A. I. Polosukhin, *Usp. Khim.*, 2004, **73**, 726 [*Russ. Chem. Rev.* (*Engl. Transl.*), 2004, **73**, 671].
16. M. T. Reetz, G. Mehler, A. Meiswinkel, T. Sell, *Tetrahedron Lett.*, 2002, **43**, 7941.
17. B. H. G. Swennenhuis, R. Chen, P. W. N. M. van Leeuwen, J. G. de Vries, P. C. J. Kamer, *Eur. J. Org. Chem.*, 2009, 5796.
18. K. N. Gavrilov, A. I. Polosukhin, *Usp. Khim.*, 2000, **69**, 721 [*Russ. Chem. Rev.* (*Engl. Transl.*), 2000, **69**, 661].
19. G. Chelucci, G. Orru, G. A. Pinna, *Tetrahedron*, 2003, **59**, 9471.
20. P. J. Guiry, C. P. Saunders, *Adv. Synth. Catal.*, 2004, **346**, 497.
21. K. C. Bhowmick, N. N. Joshi, *Tetrahedron: Asymmetry*, 2006, **17**, 1901.
22. A. Alexakis, J. Vastra, J. Burton, P. Mangeney, *Tetrahedron: Asymmetry*, 1997, **8**, 3193.
23. R. Kadyrov, D. Heller, R. Selke, *Tetrahedron: Asymmetry*, 1998, **9**, 329.
24. V. Beghetto, A. Scrivanti, U. Matteoli, *Catal. Commun.*, 2001, 139.
25. H. Park, R. Kumareswaran, T. V. RajanBabu, *Tetrahedron*, 2005, **61**, 6352.
26. K. V. L. Crepy, T. Imamoto, *Adv. Synth. Catal.*, 2003, **345**, 79.
27. B. M. Trost, M. L. Crawley, *Chem. Rev.*, 2003, **103**, 2921.
28. T. Graening, H.-G. Schmalz, *Angew. Chem.*, *Int. Ed.*, 2003, **42**, 2580.
29. Z. Lu, S. Ma, *Angew. Chem., Int. Ed.*, 2008, **47**, 258.
30. K. N. Gavrilov, O. G. Bondarev, R. V. Lebedev, A. A. Shiryaev, S. E. Lyubimov, A. I. Polosukhin, G. V. Grintselev-Knyazev, K. A. Lyssenko, S. K. Moiseev, N. S. Ikonnikov, V. N. Kalinin, V. A. Davankov, A. V. Korostylev, H.-J. Gais, *Eur. J. Inorg. Chem.*, 2002, 1367.
31. V. N. Tsarev, S. E. Lyubimov, O. G. Bondarev, A. A. Korlyukov, M. Yu. Antipin, P. V. Petrovskii, V. A. Davankov, A. A. Shiryaev, E. B. Benetsky, P. A. Vologzhanin, K. N. Gavrilov, *Eur. J. Org. Chem.*, 2005, 2097.
32. K. N. Gavrilov, M. G. Maksimova, S. V. Zheglov, O. G. Bondarev, E. B. Benetsky, S. E. Lyubimov, P. V. Petrovskii, A. A. Kabro, E. Hey-Hawkins, S. K. Moiseev, V. N. Kalinin, V. A. Davankov, *Eur. J. Org. Chem.*, 2007, 4940.
33. J. M. Brunel, T. Constantieux, G. Buono, *J. Org. Chem.*, 1999, **64**, 8940.
34. K. Barta, M. Holscher, G. Francio, W. Leitner, *Eur. J. Org. Chem.*, 2009, 4102.
35. H. Park, T. V. RajanBabu, *J. Am. Chem. Soc.*, 2002, **124**, 734.
36. G. Francio, C. G. Arena, F. Faraone, C. Graiff, M. Lanfranchi, A. Tiripicchio, *Eur. J. Inorg. Chem.*, 1999, **8**, 1219.
37. C. W. Edwards, M. R. Shipton, N. W. Alcock, H. Clasea, M. Wills, *Tetrahedron*, 2003, **59**, 6473.
38. *Comprehensive Organic Chemistry*, Eds D. Barton, W. D. Ollis, Vol. **2**, *Nitrogen Compounds*, Ed. I. O. Sutherland, Pergamon Press, Oxford, 1979, 917 pp.
39. P. R. Auburn, P. B. McKenzie, B. Bosnich, *J. Am. Chem. Soc.*, 1985, **107**, 2033.
40. K. N. Gavrilov, S. E. Lyubimov, S. V. Zheglov, E. B. Benetsky, V. A. Davankov, *J. Mol. Catal. A*, 2005, **231**, 255.
41. S. E. Lyubimov, V. A. Davankov, K. N. Gavrilov, *Tetrahedron Lett.*, 2006, **47**, 2721.
42. V. N. Tsarev, S. E. Lyubimov, A. A. Shiryaev, S. V. Zheglov, O. G. Bondarev, V. A. Davankov, A. A. Kabro, S. K. Moiseev, V. N. Kalinin, K. N. Gavrilov, *Eur. J. Org. Chem.*, 2004, 2214.

Received February 8, 2011;
in revised form April 5, 2011