First *P*,*P**-bidentate phosphine-phosphite-type ligand with a *P**-stereocenter in the phosphite moiety: synthesis and application in the Pd-catalyzed asymmetric allylic alkylation*

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A new *P*,*P**-bidentate phosphine-diamidophosphite bearing an asymmetric phosphorus atom in the 1,3,2-diazaphospholidine ring was obtained. A possibility of its application in the palladium-catalyzed enantioselective allylic substitution was demonstrated. A 70% *ee* was reached in the alkylation of (*E*)-1,3-diphenylallyl acetate with dimethyl malonate.

Key words: phosphine-phosphites, phosphine-diamidophosphites, palladium catalysts, asymmetric alkylation.

Asymmetric metal complex catalysis is an extremely powerful means for the preparation of enantiopure or, in general case, enantioenriched organic and organoelement compounds. Such compounds are widely used as the main components of drugs, chemical protection of agricultural and forest plantations, perfume compositions, food additives, and fragrances.[1—6]

Besides the central complexation atom (ion), coordinated molecules of a substrate, a reagent, and a chiral ligand are included in the key catalytic intermediate. The metal center provides a low-energy pathway for the reaction, while the ligand controls the reactivity and secures an asymmetric environment. In this way a predominant discrimination of one of the enantiotopic elements (an atom, a substituent, or a molecule side) in the structure of the substrate is achieved.[7] Therefore, activity and stereoselectivity of the metal complex catalysts are to a great extent determined by a proper design and synthesis strategy of the corresponding chiral ligands, first of all, phosphorus-containing ligands, thousands representatives of which were used in various asymmetric transformations.[1,2,4,7—10] Nonetheless, the overwhelming majority of such ligands in the corresponding metal complexes are capable of catalyzing only a certain type of chemical transformations or even a certain reaction showing a specific enantioselectivity. There are very few versatile (the so-called "privileged") ligands, and the high cost significantly limits their wide practical application. In this connection, a search for the new efficient phosphorus-containing inductors of chirality easily synthesized from available enantiopure synthons is still an actual problem.[11—15]

Researchers direct much attention to the hybrid *P*,*P*-bidentate phosphine-phosphite-type ligands represented by phosphine-phosphites (C_2PC/OPO_2) and phosphine-amidophosphites (C_2PC/NPO_2).[7,16] First, they combine advantages of both classes of phosphorus-containing ligands, for example, a considerable π-acidity of the phosphite center and unique steric parameters of the phosphine center. Second, irrespective of the substrate type of coordination, such compounds possess the C_1-symmetry, that favors the asymmetric induction in the key catalytic intermediate step, as well as they have unsymmetric electron pattern due to the presence in their structure of phosphorus centers with different electron demands. The π-accepting power of the phosphite center makes it possible to stabilize the metal complex intermediates in the low oxidation states of the central complexation ions, while the σ-donating ability of the phosphine center facilitates the processes of oxidative addition. The different *trans*-effect of the various phosphorus centers and the essential asymmetry of the metal center environment also considerably contribute to the activity and stereoselectivity of the metal complex catalysts based on the phosphine-phosphite-type ligands.[7,14—25]

Phosphine-phosphite ligands bearing *P**-stereocenters are of special interest. The presence of a stereogenic donor phosphorus atom significantly promotes the successful

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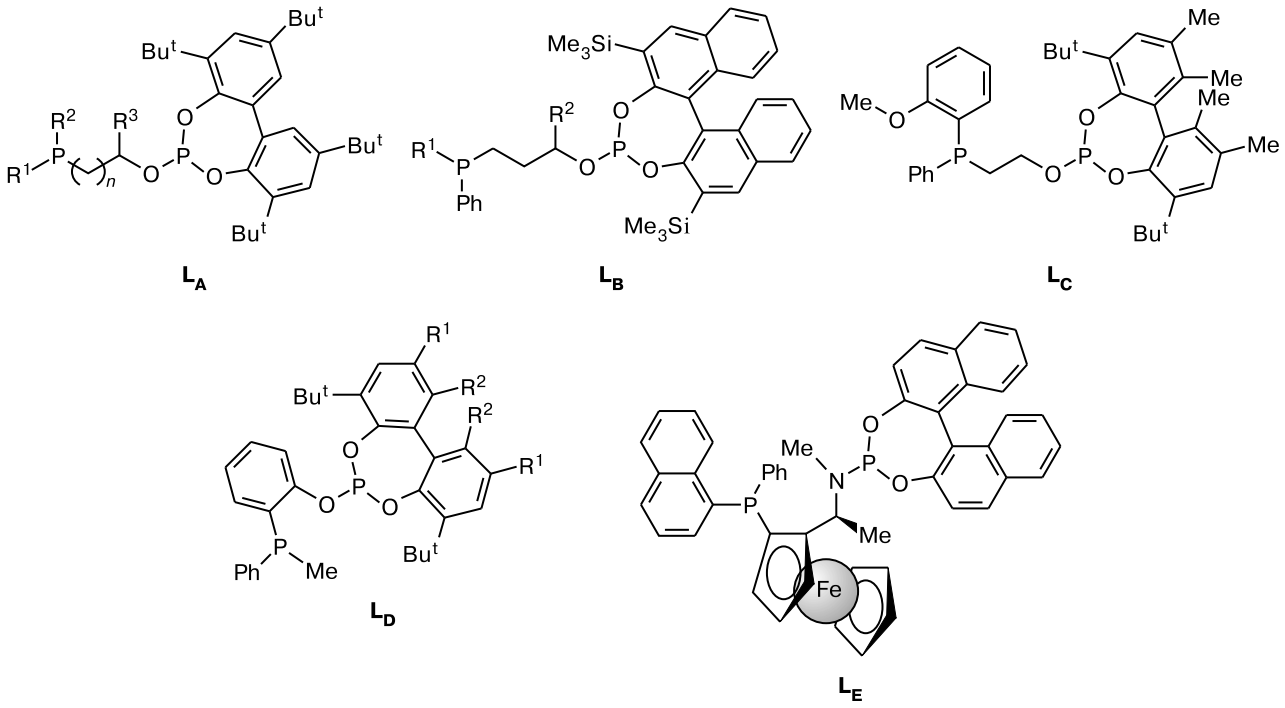


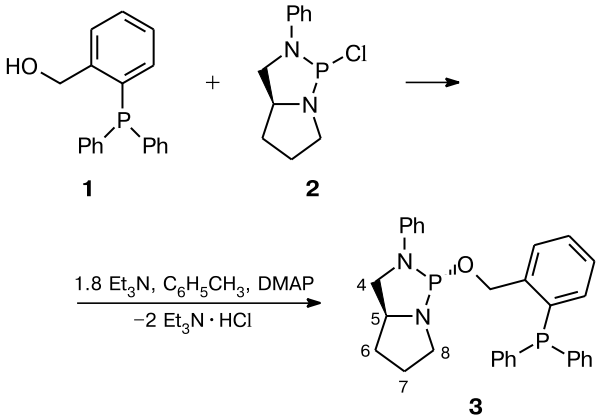
asymmetric induction in the key step of the catalytic cycle. Since this atom is directly bonded to the central complexation atom (ion), it is positioned very close to the coordinated substrate, that interferes with a potentially inefficient secondary transfer of chirality from the ligand framework.[2,15,26] Thus, phosphine-phosphites $\mathbf{L_{A–D}}$ are successfully used in the asymmetric reactions of Pd-catalyzed allylation, Rh-catalyzed hydroformylation, and Rh- and Ir-catalyzed hydration, while the epimeric phosphine-amidophosphites $\mathbf{L_E}$ are used in Ag-catalyzed cycloaddition and Cu-catalyzed conjugate reduction.[27–34] All these ligands have phosphine *P**-stereocenters, whereas *P*,*P**-bidentate stereoselectors of the phosphine-phosphite-type with asymmetric phosphorus atoms in the phosphite moiety are not yet described. There is no literature data on phosphine-diamidophosphites (C_2PC/OPN_2), either.

In the present work, we report the synthesis of the first *P*,*P**-bidentate phosphine-diamidophosphite bearing an asymmetric phosphorus atom in the 1,3,2-diazaphosphaolidine ring and its application in the enantioselective catalysis. The Pd-catalyzed asymmetric allylic alkylation was chosen as a test catalytic reaction. On the one hand, this reaction is a reliable method to evaluate the efficiency of new chiral ligands. On the other hand, since this reaction is not very sensitive to different functional groups in the structure of allylic substrates, it is actively used in asymmetric synthesis of valuable organic and natural compounds.[7,26,35–37] In particular, the products of alkylation with dimethyl malonate under mild conditions and without involvement of the *C**-stereocenter can be easily converted to esters and amides of chiral unsaturated carboxylic acids.[38]

Results and Discussion

A one-step phosphorylation of 2-(diphenylphosphino)-phenylmethanol (**1**) with (5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**2**) in toluene in the presence of a DMAP catalyst and Et_3N as the hydrogen chloride acceptor yielded *P*,*P**-bidentate phosphine-diamidophosphite **3** (Scheme 1).

Scheme 1



Note that the phosphorylating agent **2** was easily obtained[39] in good yield starting from available (*S*)-glutamic

acid anilide,[40,41] whereas alcohol **1** was obtained by the reduction of commercial 2-(diphenylphosphino)benzaldehyde with $NaBH_4$ (see Ref. 42). Ligand **3** is a stereoindividual compound, its ^{31}P NMR spectrum in solution in $CDCl_3$ exhibits two singlets of equal intensity at δ_P 120.0 and −15.7 related to the diamidophosphite and the phosphine phosphorus atoms, respectively. Phosphine-diamidophosphite **3** has (*R*)-configuration of the *P**-stereocenter as evidenced by a large spin-spin coupling constant $^2J_{C(8),P}$ (37.6 Hz) in the ^{13}C NMR spectrum of its solution in $CDCl_3$ (see Experimental). Such a value indicates an *anti*-orientation of the pseudoequatorial exocyclic substituent at the diamidophosphite phosphorus atom and the fragment $-(CH_2)_3-$ of the pyrrolidine ring in the phosphabicyclo[3.3.0]octane skeleton and, therefore, a *syn*-orientation between the lone pair of electrons on the phosphorus atom and atom C(8) (Fig. 1).[39—41,43—45]

Compound **3** was easily purified by flash-chromatography, it is stable enough in air and can be stored for a long time under dry atmosphere.

The reaction of ligand **3** with $[Pd(allyl)Cl]_2$ (in the presence of $AgSbF_6$) leads to the formation of the cationic metal chelate **4** with *cis*-orientation[46,47] of the phosphorus atoms (Scheme 2).

Scheme 2

4

In the ^{31}P NMR spectrum of the solution of complex **4** in $CDCl_3$ one can see doublets for two AX systems (δ_P 127.2 and 14.9, $^2J_{P,P*}$ = 64.0 Hz, 58%; δ_P 127.3 and 13.1, $^2J_{P,P*}$ = 62.3 Hz, 42%) indicating that **4** exists as an equilibrium mixture of interconversible *exo*- and *endo*-isomers.[7,39,46—48]

Phosphine-diamidophosphite **3** and its complex **4** were studied in the Pd-catalyzed asymmetric allylic alkylation of (*E*)-1,3-diphenylallyl acetate (**5**) with dimethyl malonate (Scheme 3, Table 1).

The data in Table 1 show that the values of conversion and the asymmetric induction depend on the nature of pre-catalyst, solvent, and base and the molar ratio L/Pd. In all the cases, the (*S*)-enantiomer of the reaction product **6** predominates, with the enantiomeric purity of **6** varying within 30—70% *ee*.

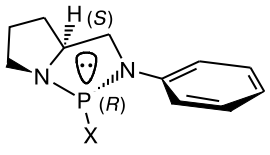
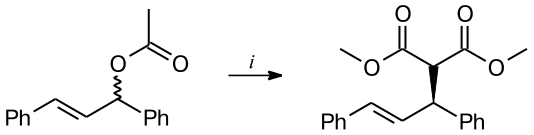


Fig. 1. The structural fragment of ligand **3** (X is the exocyclic substituent).

Scheme 3



5 **6**

i. $CH_2(CO_2Me)_2$, Pd-cat.

When $[Pd(allyl)Cl]_2$ was used as a pre-catalyst (see Table 1, entries *1—14*), a higher enantioselectivity was observed in the reactions in THF and CH_2Cl_2 compared to those in toluene and 1,4-dioxane. The influence of bases (BSA or Cs_2CO_3) on the stereoinduction varied, however, with Cs_2CO_3 almost always considerably higher conversion was recorded. Similarly, the influence of the molar ratio L/Pd on enantioselectivity was not straightforward, with the highest conversion being observed for L/Pd = 1 in almost all the cases. The maximal enantioselectivity was reached in THF in the presence of BSA with the molar ratio L/Pd = 1 (70% *ee*, see Table 1, entry *7*).

When the pre-catalyst $[Pd_2(dba)_3]\cdot CHCl_3$ was used, ligand **3** provided a somewhat lower enantioselectivity (to 60% *ee*), with CH_2Cl_2 being the optimal solvent (see Table 1, entries *15—18*). In the catalytic experiment which used a pre-synthesized complex **4** (see Table 1, entries *19—24*), the *ee* reached 56%, with the highest asymmetric induction being observed for the reaction in CH_2Cl_2. The use of Cs_2CO_3 as the base provided virtually quantitative conversion (see Table 1, entries *20*, *22*, and *24*).

In conclusion, in the present work we described the synthesis of the first representative **3** of the phosphine-phosphite-type *P*,*P**-bidentate ligands with a stereogenic phosphorus atom in the phosphite moiety. Its involvement in the model Pd-catalyzed asymmetric allylic alkylation reaction of (*E*)-1,3-diphenylallyl acetate (**5**) with dimethyl malonate provided a good level of enantioselectivity, up to 70% *ee*. Therefore, phosphine-diamidophosphite **3** is a promising stereoselector, whose application (as well as of other similar *P*,*P**-bidentate ligands with *P**-stereocenters in the 1,3,2-diazaphosphaolidine rings) in the practically useful catalytic processes of the C—C bond formation[37,49] is studied in our laboratories.

Experimental

^{31}P, ^1H, and ^{13}C NMR spectra were recorded on Bruker Avance 400 (161.98, 400.13, and 100.61 MHz) and Bruker Avance III 600 spectrometers (242.94, 600.13, and 150.9 MHz) relative to 85% H_3PO_4 in D_2O and Me_4Si, respectively. The signals in the ^1H and ^{13}C NMR spectra were assigned using

Table 1. Pd-catalyzed alkylation of **5** with dimethyl malonate[a]

Entry	Palladium complex	L/Pd	Solvent	Base	Conversion	*ee* (%)[b]
1	$[Pd(allyl)Cl]_2$	1	Toluene	BSA	80	45 (*S*)
2	$[Pd(allyl)Cl]_2$	2	Toluene	BSA	21	47 (*S*)
3	$[Pd(allyl)Cl]_2$	1	CH_2Cl_2	BSA	100	47 (*S*)
4	$[Pd(allyl)Cl]_2$	2	CH_2Cl_2	BSA	60	54 (*S*)
5	$[Pd(allyl)Cl]_2$	1	CH_2Cl_2	Cs_2CO_3	100	57 (*S*)
6	$[Pd(allyl)Cl]_2$	2	CH_2Cl_2	Cs_2CO_3	100	53 (*S*)
7	$[Pd(allyl)Cl]_2$	1	THF	BSA	62	70 (*S*)
8	$[Pd(allyl)Cl]_2$	2	THF	BSA	10	47 (*S*)
9	$[Pd(allyl)Cl]_2$	1	THF	Cs_2CO_3	78	36 (*S*)
10	$[Pd(allyl)Cl]_2$	2	THF	Cs_2CO_3	22	46 (*S*)
11	$[Pd(allyl)Cl]_2$	1	1,4-Dioxane	BSA	60	40 (*S*)
12	$[Pd(allyl)Cl]_2$	2	1,4-Dioxane	BSA	5	50 (*S*)
13	$[Pd(allyl)Cl]_2$	1	1,4-Dioxane	Cs_2CO_3	75	44 (*S*)
14	$[Pd(allyl)Cl]_2$	2	1,4-Dioxane	Cs_2CO_3	9	44 (*S*)
15	$[Pd_2(dba)_3]\cdot CHCl_3$	1	CH_2Cl_2	BSA	73	51 (*S*)
16	$[Pd_2(dba)_3]\cdot CHCl_3$	2	CH_2Cl_2	BSA	49	60 (*S*)
17	$[Pd_2(dba)_3]\cdot CHCl_3$	1	THF	BSA	0	—
18	$[Pd_2(dba)_3]\cdot CHCl_3$	2	THF	BSA	28	53 (*S*)
19	4	1	CH_2Cl_2	BSA	62	56 (*S*)
20	4	1	CH_2Cl_2	Cs_2CO_3	100	54 (*S*)
21	4	1	THF	BSA	37	30 (*S*)
22	4	1	THF	Cs_2CO_3	100	52 (*S*)
23	4	1	1,4-Dioxane	BSA	98	46 (*S*)
24	4	1	1,4-Dioxane	Cs_2CO_3	99	40 (*S*)

[a] All the reactions were carried out at 20 °C, for 48 h, with 2 mol.% $[Pd(allyl)Cl]_2$ or $[Pd_2(dba)_3]\cdot CHCl_3$.
[b] Conversion of substrate **5** and enantiomeric excess of product **6** were determined by HPLC (Daicel Chiralcel OD—H, C_6H_{14}/Pr^iOH = 99 : 1, 0.6 mL min^{-1}, 254 nm).

COSY, DEPT, and HSQC procedures, as well as taking into account the data in the works.[30,31,39—41] Mass spectra of laser desorption ionization (MALDI TOF/TOF) were recorded on a Bruker Daltonics Ultraflex instrument. Enantiomeric composition of the catalytic reaction products was analyzed on a Staier HPL-chromatograph. Elemental analysis was performed in the Laboratory of organic microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

All the reactions were carried out under dry argon in anhydrous solvents. The starting substrate (*E*)-1,3-diphenylallyl acetate (**5**), as well as complexes $[Pd(allyl)Cl]_2$ and $[Pd_2(dba)_3]\cdot CHCl_3$ were obtained according to the known procedures.[50,51] Catalytic experiments of the asymmetric alkylation of substrate **5** with dimethyl malonate, determination of conversion of **5** and enantiomeric excesses of product **6** were carried out following by the procedure published earlier.[39]

2-(Diphenylphosphino)benzaldehyde, dimethyl malonate, *bis*-trimethylsilylacetamide (BSA), 4-dimethylaminopyridine (DMAP), and $AgSbF_6$ were commercially available from Fluka and Aldrich.

(2*R*,5*S*)-2-[2-(Diphenylphosphino)phenylmethoxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (3). A solution of 2-(diphenylphosphino)phenylmethanol **2** (0.59 g, 2 mmol) in toluene (5 mL) was added was added dropwise during 20 min at 20 °C to a vigorously stirred solution of phosphorylating agent **1** (0.48 g, 2 mmol), Et_3N (0.5 mL, 3.6 mmol), and catalyst DMAP (0.024 g, 0.2 mmol) in toluene (10 mL). The mixture obtained was refluxed for 15 min and cooled to 20 °C, a precipitate of $Et_3N\cdot HCl$ was filtered off. The filtrate was concentrated *in vacuo* (40 Torr). The product obtained was purified by flash-chromatography on alumina, eluent toluene. The yield was 0.83 g (84%), colorless dense oil. Found (%): C, 72.85; H, 6.16; N, 5.44. $C_{30}H_{30}N_2OP_2$. Calculated (%): C, 72.57; H, 6.09; N, 5.64. ^{13}C NMR ($CDCl_3$), δ: 26.3 (d, C(7), $^3J_{C,P}$ = 4.1 Hz); 32.1 (s, C(6)); 48.4 (d, C(8), $^2J_{C,P}$ = 37.6 Hz); 54.9 (d, C(4), $^2J_{C,P}$ = = 7.6 Hz); 61.8 (dd, CH_2O, $^2J_{C,P}$ = 27.5 Hz, $^3J_{C,P}$ = 4.8 Hz); 63.2 (d, C(5), $^2J_{C,P}$ = 8.8 Hz); 114.9 (d, CH_{PhN}, $^3J_{C,P}$ = 12.2 Hz); 118.8 (s, CH_{PhN}); 127.0 (d, CH_{PhP}, $^3J_{C,P}$ = 5.3 Hz); 127.1 (s, CH_{PhP}); 128.6 (d, CH_{PhP}, $^3J_{C,P}$ = 6.9 Hz); 128.7 (s, CH_{PhP}); 128.8 (s, CH_{PhP}); 128.9 (s, CH_{PhP}); 129.0 (s, CH_{PhN}); 132.6 (s, CH_{PhP}); 133.8 (s, CH_{PhP}); 134.0 (s, CH_{PhP}); 134.2 (s, CH_{PhP}); 136.1 (d, C_{PhP}, $^1J_{C,P}$ = 9.8 Hz); 136.2 (d, C_{PhP}, $^1J_{C,P}$ = 10.1 Hz); 143.0 (dd, C_{PhP}, $^2J_{C,P}$ = 21.7 Hz, $^3J_{C,P}$ = 2.6 Hz); 145.7 (d, C_{PhN}, $^2J_{C,P}$ = 16.3 Hz). ^1H NMR ($CDCl_3$), δ: 1.54—1.60 (m, 1 H, C(6)H); 1.71—1.82 (m, 2 H, $C(7)H_2$); 1.94—2.0 (m, 1 H, C(6)H); 3.05—3.14 (m, 2 H, C(8)H and C(4)H); 3.50—3.57 (m, 2 H, C(8)H and C(4)H); 3.88—3.92 (m, 1 H, C(5)H); 4.72 (dd, 1 H, CHO, $^2J_{H,H}$ = 13.4 Hz, $^3J_{H,P}$ = 5.4 Hz); 4.99 (ddd, 1 H, CHO, $^2J_{H,H}$ = 13.4 Hz, $^3J_{H,P}$ = 6.0 Hz, $^4J_{H,P}$ = = 2.1 Hz); 6.82 (t, 1 H, CH_{PhP}, ^3J = 6.4 Hz); 6.85 (t, 1 H, CH_{PhN}, ^3J = 7.2 Hz); 7.0 (d, 2 H, CH_{PhN}, ^3J = 8.4 Hz); 7.15 (t, 1 H, CH_{PhP}, ^3J = 7.2 Hz); 7.21—7.26 (m, 2 H, CH_{PhN} and 1 H, CH_{PhP}); 7.28—7.39 (m, 10 H, CH_{PhP}); 7.6—7.62 (m, 1 H,

CH_{PhP}). MS (MALDI TOF/TOF), m/z (I_{rel} (%)): 535 $[M + K]^+$ (100), 497 $[M + H]^+$ (17).

{(2*R*,5*S*)-2-[2-(Diphenylphosphino)phenylmethoxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane-*P*,*P}(π-allyl)-palladium(2+) hexafluoroantimonate (4).** A solution of *P*,*P**-bidentate ligand **3** (0.1 g, 0.2 mmol) in CH_2Cl_2 (2 mL) was added dropwise during 30 min to a stirred solution of $[Pd(All)Cl]_2$ (0.037 g, 0.1 mmol) in CH_2Cl_2 (1 mL) at 20 °C. The reaction mixture was stirred for another 1 h at 20 °C. Then, a solution of $AgSbF_6$ (0.069 g, 0.2 mmol) in CH_2Cl_2 (2 mL) was added dropwise during 30 min to the solution obtained and the reaction mixture was stirred for 1.5 h at 20 °C. A precipitate of AgCl was filtered off. Excessive solvent was evaporated at reduced pressure (40 Torr) to the volume of ~0.5 mL) and diethyl ether (7 mL) was added. A precipitate formed was separated by centrifugation, washed with diethyl ether (2×5 mL) and hexane (2×5 mL), dried in air and *in vacuo* (1 Torr). The yield was 0.162 g (92%), a powder light yellow, m.p. 180—183 °C (with decomp.). Found (%): C, 45.31; H, 3.82; N, 3.24. $C_{33}H_{35}F_6N_2OP_2PdSb$. Calculated (%): C, 45.05; H, 4.01; N, 3.18. MS (MALDI TOF/TOF), m/z (I_{rel} (%)): 643 $[M - SbF_6]^+$ (44), 602 $[M - All - SbF_6]^+$ (100).

Asymmetric alkylation of (*E*)-1,3-diphenylallyl acetate (5) with dimethyl malonate. A solution of $[Pd(allyl)Cl]_2$ (0.0037 g, 0.01 mmol) or $[Pd_2(dba)_3]\cdot CHCl_3$ (0.01 g, 0.01 mmol) and the corresponding ligand (0.01 g, 0.02 mmol or 0.02 g, 0.04 mmol) in the corresponding solvent (5 mL) were stirred for 40 min or complex **4** (0.0176 g, 0.02 mmol) was dissolved in the corresponding (5 mL) solvent, followed by the addition of (*E*)-1,3-diphenylallyl acetate (0.1 mL, 0.5 mmol), and the solution was stirred for another 15 min. Then, dimethyl malonate (0.1 mL, 0.87 mmol), BSA (0.22 mL, 0.87 mmol), and potassium acetate (0.002 g) or dimethyl malonate (0.1 mL, 0.87 mmol) and cesium carbonate (0.163 g, 0.5 mmol) were added. The reaction mixture was stirred for 48 h, diluted with hexane (5 mL) and filtered through Celite. The solvents were evaporated at reduced pressure (40 Torr), the residue was dried *in vacuo* (10 Torr). Conversion of substrate **5** and enantiomeric excess of products **6** were determined by HPLC on a chiral stationary phase.

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