Phosphorylated (*S*)-*tert*-leucinol isophthalic diamide as a ligand for Pd-catalyzed asymmetric allylic substitution

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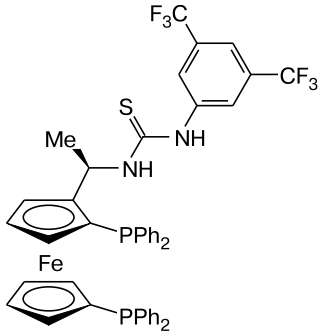
O-Phosphorylation of *N*,*N*′-(isophthaloyl)di-(*S*)-*tert*-leucinol with (5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane afforded bidentate phosphite-type ligand. This ligand provided 93% *ee* in Pd-catalyzed enantioselective allylation of (*E*)-1,3-diphenylallyl acetate, and 55% *ee* in alkylation of cinnamyl acetate with ethyl 2-oxocyclohexane-1-carboxylate.

Key words: amino alcohols, diamines, diamidophosphites, palladium catalysts, asymmetric allylation.

Activity and stereoselectivity of metal complex catalysts are mainly determined by the success in design and synthesis of the corresponding chiral ligands. Phosphorus-containing chiral ligands repeatedly used in various asymmetric transformations are of special interest.[1—7] The metal complexes comprising the vast majority of chiral phosphorus ligands have proven to afford the excellent enantiomeric control only in certain chemical transformations. Only few ligands have a general scope (so called privileged ligands); moreover, a high cost of these ligands limited their wide applications. Consequently, the design of novel effective phosphorus-containing chiral inductors readily accessible from enantiomerically pure building blocks is still urgent.[8—12]

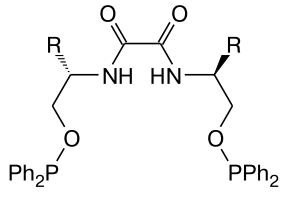
One of the promising strategies to achieve this goal is the synthesis of ligands combining the advantages of organic and phosphorus chiral inductors.[13—15] The synthetic approaches towards these ligands may involve either introduction of organocatalytic functional groups into the molecules of chiral phosphines or direct phosphorylation of different organocatalysts. For instance, thiourea *P*,*P*-bidentate ligand $\mathbf{L_A}$ obtained *via* reaction of ferrocenyl aminobisphosphine with substituted phenyl isothiocyanate shows excellent enantioselectivity in Rh-catalyzed hydrogenation of nitroalkenes.[16]

Amides derived from enantiomerically pure amino alcohols (these compounds are efficient organocatalysts for asymmetric reduction of ketimines with trichlorosilane and ketones with borane[17—20]) can be regarded as suitable



$\mathbf{L_A}$

starting material for the introduction of the phosphorus chiral centers. Thus, phosphinite derivatives of diamides of oxalic acid with available chiral amino alcohols $\mathbf{L_B}$ have been found to be effective in Ru-catalyzed asymmetric transfer hydrogenation of aromatic ketones.[21—23] However, the significant disadvantage of these compounds is their high sensitivity to oxidation and hydrolysis.[21]



$\mathbf{L_B}$

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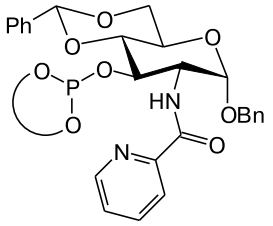
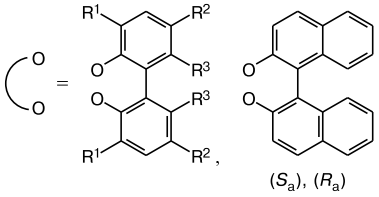
In this regard, inexpensive phosphite ligands stable to oxidation and exhibiting pronounced acidity are more promising. Accessibility of phosphite ligands *via* condensation reactions including parallel and solid-phase syntheses[11,24–29] are also of note. At the same time, the known asymmetric phosphite inductors derived from amides of carboxylic acids with chiral amino alcohols are limited only to compounds $\mathbf{L_C}$.[30–32]

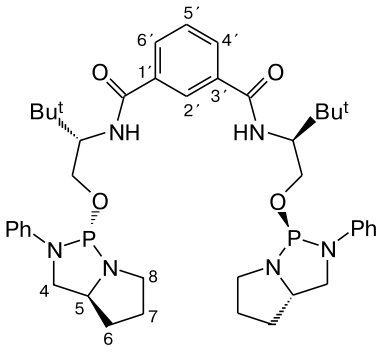


L_C



(S_a), (R_a)

In the present work, we describe the synthesis and application in asymmetric catalysis of *P**,*P**-bidentate diamidophosphite **1** bearing 1,3,2-diazaphospholidine cycles and fragments of diamide of isophthalic acid with (*S*)-*tert*-leucinol.



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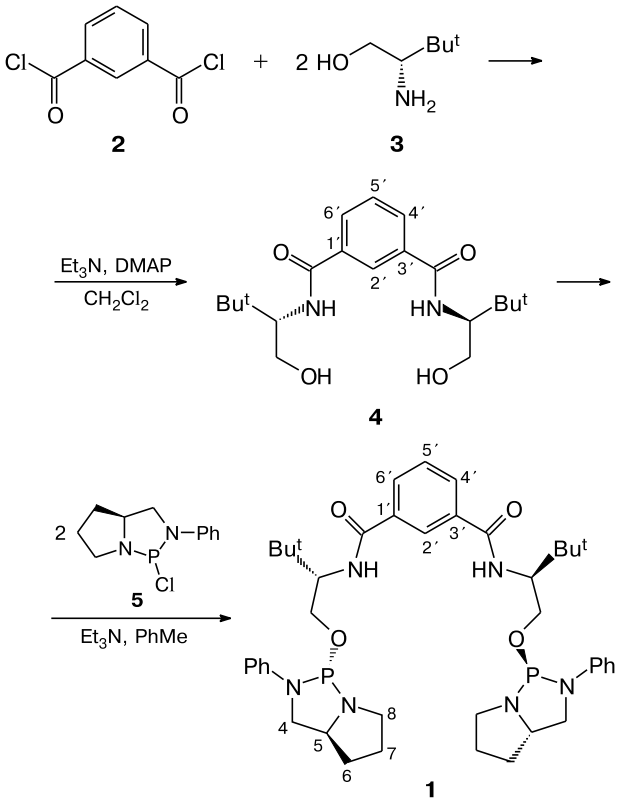
It should be noted that these diamides provide good results in asymmetric Ti- and Zn-catalyzed conjugate addition of terminal alkynes.[33,34] Moreover, *P**-chiral 1,3,2-diazaphospholidines are very interesting family of chirogenic diamidophosphite ligands. In particular, these compounds owing to the finely balanced electronic properties are able to act as both good π acceptors (due to the availability of the low energy π^*_{PN} orbitals) and good σ donors. Phosphorus atom of the phospholidine increases the stability of the ligand towards oxidation and hydrolysis; while, the possibility to widely vary the substituents at the phosphorus and/or nitrogen atoms allows the turning of its steric and electronic properties.[35,36] A stereogenic donor phosphorus atom is directly bonded to a central chelating atom (ion) and is in closest proximity to the chelated substrate thus promoting the effective asymmetric induction on the key stage of the catalytic cycle.[2,12,37]

The enantioselectivity of a novel diamidophosphite **1** was examined on the examples of the asymmetric Pd-catalyzed allylic substitutions. On the one hand, these reactions are the reliable models to evaluate the efficiency of the novel chiral ligands. On the other hand, the Pd-catalyzed allylic substitution is tolerated to different functional groups in allylic substrates and is widely used for the asymmetric synthesis of valuable organic and natural compounds.[4,37–40] For example, the products of alkylation with dimethyl malonate readily underwent transformations to give the esters and amides of chiral unsaturated carboxylic acids under mild conditions and in the absence of a *C**-chiral center.[41]

Results and Discussion

Isophthaloyl dichloride **2** smoothly reacts with (*S*)-*tert*-leucinol (**3**) in CH_2Cl_2 in the presence of a catalytic amount of DMAP and a triethylamine excess to give isophthaloyl diamido diol **4** (Scheme 1). Further direct phos-

Scheme 1

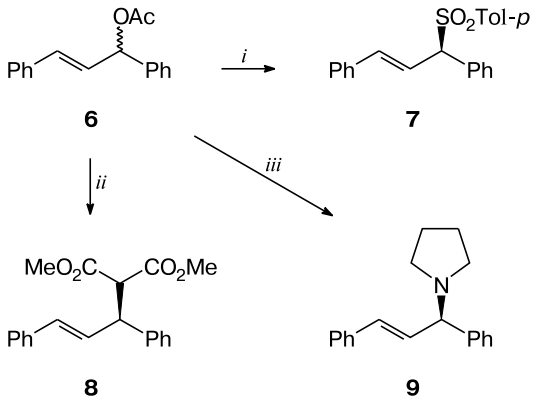


phorylation of compound **4** in toluene affords *P**,*P**-bidentate diamidophosphite **1**. Note that phosphorylating reagent **5** is readily available[42] in good yield from (*S*)-glutamic acid anilide.[43,44]

Ligand **1** is enantiomerically pure. The presence of the sharp singlet signal at δ_P 125.7 in the ^{31}P NMR spectrum ($CDCl_3$) of ligand **1** indicates the (*R*)-configuration of the *P**-chiral centers. The large spin-spin coupling constant value $^2J_{C(8),P} = 37.6$ Hz in the ^{13}C NMR spectrum reveals that the exocyclic substituent at the P atom occupies a pseudo-equatorial position and is *anti* with respect to the $-(CH_2)_3-$ moiety of the pyrrolidine cycle of phosphabicyclo[3.3.0]octane core and, consequently, the lone electron pair at the P atom and the C(8) atom are in the *syn* conformation (Fig. 1).[42–47]

Diamidophosphite **1** can be easily purified by flash column chromatography; it is relatively stable in air and can be stored for a long time under dry conditions. Taking into account the availability of the starting compounds, ligand **1** can be synthesized in gram-scale amounts. First, we evaluated the catalytic performance of diamidophosphite **1** in three model reactions of asymmetric Pd-catalyzed allylation using (*E*)-1,3-diphenylallyl acetate (**6**). As a precatalyst, $[Pd(allyl)Cl]_2$ was applied (Scheme 2, Tables 1—3). Allylic sulfonylation of compound **6** with sodium *p*-toluenesulfinate (S nucleophile) results in sulfone (*R*)-**7** with good enantioselectivity (up to 86% *ee*); the optimum L/Pd molar ratio is 1 (see Table 1).

Scheme 2



i. *p*-$TolSO_2Na$, Cat.; *ii*. $CH_2(CO_2Me)_2$, BSA, Cat.; *iii*. $(CH_2)_4NH$, Cat.

Cat is $[Pd(allyl)Cl]_2$—**1** (1 : 2 molar ratio), BSA is *N*,*O*-bis(trimethylsilyl)acetamide.

In allylic alkylation of substrate **6** with dimethyl malonate (C nucleophile), *P**,*P**-bidentate ligand **1** provides the high enantioselectivity (*ee* 88—93%) regardless of both the solvent nature and the L/Rh molar ratio (Table 2).

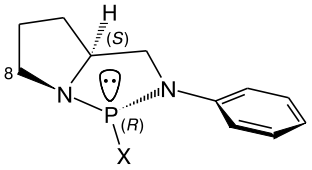


Fig. 1. Schematic representation of the fragment of the structure of ligand **1** (X is an exocyclic substituent).

The highest conversions were achieved in CH_2Cl_2. In all cases, (*S*) enantiomer of product **8** predominates.

The use of pyrrolidine as an *N* nucleophile produces 90% *ee* with enantiomer (*R*)-**9** being the major product (see Table 3). The highest asymmetric induction was observed in CH_2Cl_2 at a molar ratio of L/Pd = 2. In the vast majority of cases, the conversion of the starting substrate **6** was quantitative.

Enantioselective catalytic synthesis of compounds bearing the quaternary asymmetric atoms is a relatively complex task. One of the approaches to access these type of compounds is the Pd-catalyzed allylic substitution generating the *C**-chiral center at the carbon atom of the nucleophile. Stereoselectivity of such allylation is difficult to control, since the nucleophile approaches the allylic fragment of a η^3-allylpalladium(II) intermediate from the

Table 1. Pd-catalyzed sulfonylation of substrate **6** with sodium *p*-toluenesulfinate[a]

Entry	L/Pd	Yield (%)	*ee* (%)[b]
1	1	71	86 (*R*)
2	2	55	78 (*R*)

[a] All reactions were carried out in THF at 20 °C, 48 h, 2 mol.% $[Pd(allyl)Cl]_2$.
[b] Enantiomeric excesses of product **7** were measured by HPLC (Daicel Chiralcel OD-H, $C_6H_{14}/Pr^iOH = 4 : 1$, 0.5 mL min^{-1}, 254 nm, $t(R) = 16.3$ min, $t(S) = 18.5$ min).

Table 2. Pd-catalyzed alkylation of substrate **6** with dimethyl malonate[a]

Entry	L/Pd	Solvent	Conversion (%)	*ee* (%)[b]
1	1	THF	60	93 (*S*)
2	2	THF	41	91 (*S*)
3	1	CH_2Cl_2	68	88 (*S*)
4	2	CH_2Cl_2	100	91 (*S*)

[a] All reactions were carried out at 20 °C, 48 h, 2 mol.% $[Pd(allyl)Cl]_2$.
[b] Conversion of substrate **6** and enantiomeric excesses of product **8** 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).

Table 3. Pd-catalyzed amination of substrate **6** with pyrrolidine[a]

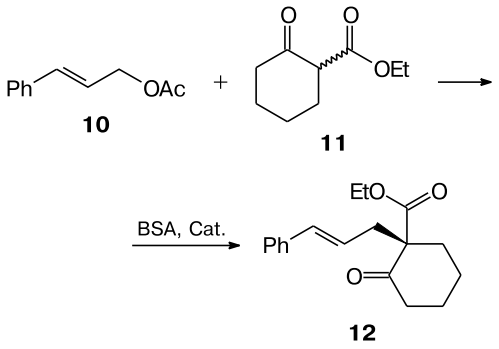
Entry	L/Pd	Solvent	Conversion (%)	*ee* (%)[b]
1	1	THF	100	84 (*R*)
2	2	THF	90	71 (*R*)
3	1	CH_2Cl_2	100	81 (*R*)
4	2	CH_2Cl_2	100	90 (*R*)

[a] All reactions were carried out at 20 °C, 48 h, 2 mol.% $[Pd(allyl)Cl]_2$.

[b] Conversion of substrate **6** and enantiomeric excesses of product **9** 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).

side opposite to a central chelating atom and coordinated to it chiral ligand.[42,48—50] The example of this reaction, asymmetric alkylation of cinnamyl acetate (**10**) with ethyl 2-oxocyclohexanecarboxylate (**11**), is given in Scheme 3. When diamidophosphite **1** was used as a chiral inductor, 55% *ee* was achieved (Table 4).

Scheme 3



Cat is $[Pd(allyl)Cl]_2$—**1** (1 : 2 molar ratio).

Table 4. Pd-catalyzed alkylation of substrate **10** with ethyl 2-oxocyclohexanecarboxylate[a]

Entry	L/Pd	Solvent	Conversion (%)	*ee* (%)[b]
1	1	Toluene	87	55 (*S*)
2	2	Toluene	99	34 (*S*)
3	1	CH_2Cl_2	100	42 (*S*)
4	2	CH_2Cl_2	100	44 (*S*)

[a] All reactions were carried out at 20 °C, 48 h, 2 mol.% $[Pd(allyl)Cl]_2$.

[b] Conversion of substrate **10** and enantiomeric excesses of product **12** 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).

The L/Pd molar ratio does not virtually affect the conversion and enantioselectivity of the reaction carried out in CH_2Cl_2; however, in toluene the increase in the L/Pd molar ratio to 2 results in an insignificant increase in the conversion and noticeable decrease in the asymmetric induction. In all cases, (*S*)-enantiomer of product **12** predominates.

In summary, in the present work we described the synthesis of ligand **1**, the first representative of *P*,*P*-bidentate phosphite ligands bearing the fragment of amide derived from chiral amino alcohol. Ligand **1** provides 93% *ee* in asymmetric Pd-catalyzed allylation of sodium *p*-toluenesulfinate with (*E*)-1,3-diphenylallyl acetate (**6**) and 55% *ee* in alkylation of cinnamyl acetate (**10**) with ethyl 2-oxocyclohexanecarboxylate (**11**). Thus, ligand **1** can be regarded as a promising chiral inductor.

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 (242.94, 600.13, and 150.9 MHz) instruments, the chemical shifts are given in the δ scale relative to 85% H_3PO_4 in D_2O and Me_4Si, respectively. The signals in ^1H and ^{13}C NMR spectra were attributed using COSY, DEPT, and HSQC NMR techniques taking into account the published data.[42—44] Matrix-assisted laser desorption/ionization mass spectrometry (MALDI TOF/TOF) was performed with a Bruker Daltonics Ultraflex instrument. Enantiomeric excesses of the products were measured with a Staier HPLC system. Elemental analyses were carried out with a Carlo Erba EA1108 CHNS-O analyzer.

All reactions were carried out under dry argon in anhydrous solvents. N^1,N^3-Bis((*S*)-1-hydroxy-3,3-dimethylbut-2-yl)isophthalamide (**4**)[33], (*E*)-1,3-diphenylallyl acetate (**6**),[51] and $[Pd(allyl)Cl]_2$[51] were synthesized by the known procedures. Asymmetric allylation of substrate **6** with sodium *p*-toluenesulfinate, dimethyl malonate, and pyrrolidine, alkylation of substrate **10** with nucleophile **11**, as well as the measurements of conversion of substrates **6** and **10** and enantiomeric excesses of products **7**,[42] **8**,[52] **9**,[49] and **12**[50] were performed following the described procedures.

Isophthaloyl dichloride (**2**), (*S*)-*tert*-leucinol (**3**), 4-dimethylaminopyridine (DMAP), sodium *p*-toluenesulfinate, dimethyl malonate, bis(trimethylsilyl)acetamide (BSA), pyrrolidine, cinnamyl acetate (**10**), and ethyl 2-oxocyclohexanecarboxylate (**11**) are commercially available from Fluka and Aldrich.

N^1,N^3-Bis((*S*)-1-hydroxy-3,3-dimethylbut-2-yl)isophthalamide (4). To a vigorously stirred solution of (*S*)-*tert*-leucinol (**3**) (1.17 g, 10 mmol), Et_3N (4.17 mL, 30, mmol), and DMAP (0.12 g, 1 mmol) in CH_2Cl_2 (20 mL), a solution of isophthaloyl dichloride (**2**) (1.02 g, 5 mmol) in CH_2Cl_2 (10 mL) was added dropwise over a period of 30 min at 0 °C. Then the reaction mixture was stirred at 20 °C for 24 h, diluted with CH_2Cl_2 (10 mL), washed with 1 *M* HCl (2×10 mL), saturated aqueous $NaHCO_3$ (3×10 mL), and brine (3×10 mL). The organic layer was dried with $MgSO_4$, filtered, and the solvent was removed *in vacuo* (40 Torr). The obtained yellow solid was washed with hexane (2×10 mL) to give target product **4** in the yield of 1.35 g

(74%), white powder, m.p. 123—124 °C. Found (%): C, 66.17; H, 8.96; N, 7.50. $C_{20}H_{32}N_2O_4$. Calculated (%): C, 65.91; H, 8.85; N, 7.69. ^{13}C NMR (DMSO-d_6), δ: 27.4 (s, CH_3); 34.4 (s, C); 59.9 (s, CHN); 60.6 (s, CH_2O); 127.0 (s, C(2′)); 128.1 (s, C(5′)), 130.0 (s, C(4′), C(6′)); 135.7 (s, C(1′), C(3′)); 167.1 (s, C=O). ^{1}H NMR (DMSO-d_6), δ: 0.91 (s, 18 H, CH_3); 3.44—3.53 (m, 2 H); 3.61—3.69 (m, 2 H); 3.85—3.94 (m, 2 H); 4.45 (br.s, 2 H, OH); 7.52 (t, 1 H, C(5′)H, ^3J = 7.6 Hz); 7.96 (dd, 2 H, C(4′)H, C(6′)H, ^3J = 7.6 Hz, ^4J = 1.6 Hz); 8.03 (d, 2 H, NH, ^3J = 9.2 Hz); 8.28 (br.s, 1 H, C(2′)H).

***N*^{1},*N*^{3}-Bis[(*S*)-1-((2*R*,5*S*)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]oct-2-yloxy)-3,3-dimethylbut-2-yl]isophthalamide (1).** To a vigorously stirred solution of phosphorylating reagent **5** (0.48 g, 2 mmol) and Et_3N (0.56 mL, 4 mmol) in toluene (20 mL), compound **4** (0.36 g, 1 mmol) was added in one portion at 20 °C. The mixture was stirred for 24 h, precipitated $Et_3N \cdot HCl$ was filtered off, and the filtrate was concentrated *in vacuo* (40 Torr). The flash alumina chromatography (elution with toluene) afforded the target product **1** in the yield of 0.67 g (86%), white powder, m.p. 88—89 °C. Found (%): C, 65.49; H, 7.61; N, 10.75. $C_{42}H_{58}N_6O_4P_2$. Calculated (%): C, 65.27; H, 7.56; N, 10.87. ^{13}C NMR ($CDCl_3$), δ: 26.1 (d, C(7), $^3J_{C,P}$ = 3.8 Hz); 27.4 (s, CH_3); 32.2 (s, C(6)); 35.0 (s, C); 48.7 (d, C(8), $^2J_{C,P}$ = 37.6 Hz); 54.8 (d, C(4), $^2J_{C,P}$ = 7.2 Hz); 56.7 (s, CHN); 62.1 (s, CH_2O); 63.6 (d, C(5), $^2J_{C,P}$ = 8.4 Hz); 114.8 (d, *o*-CH_{Ph}, $^3J_{C,P}$ = 12.1 Hz); 119.2 (s, *p*-CH_{Ph}); 125.7 (s, C(2′)); 128.7 (s, C(5′)); 129.1 (s, *m*-CH_{Ph}); 129.6 (s, C(4′), C(6′)); 135.5 (s, C(1′), C(3′)); 145.3 (d, C_{Ph}, $^2J_{C,P}$ = 15.6); 166.6 (s, C=O). ^{1}H NMR ($CDCl_3$), δ: 1.05 (s, 18 H, CH_3); 1.59—1.66 (m, 2 H, C(6)H); 1.68—1.75 (m, 2 H, C(7)H); 1.76—1.83 (m, 2 H, C(7)H); 2.02—2.09 (m, 2 H, C(6)H); 2.94—3.0 (m, 2 H, C(8)H); 3.17—3.22 (m, 2 H, C(4)H); 3.42—3.48 (m, 2 H, C(8)H); 3.70—3.78 (m, 4 H, C(4)H, CH_2O); 4.02—4.08 (m, 2 H, CH_2O); 4.09—4.14 (m, 2 H, CHN); 4.16—4.22 (m, 2 H, C(5)H); 6.72 (d, 2 H, NH, ^3J = 9.7 Hz); 6.76 (t, 2 H, (*p*-C_{Ph})H, ^3J = 7.5 Hz); 6.97 (br.d, 4 H, (*o*-C_{Ph})H, ^3J = 7.8 Hz); 7.13 (br.t, 4 H, (*m*-C_{Ph})H, ^3J = 7.9 Hz); 7.46 (t, 1 H, C(5′)H, ^3J = 7.7 Hz); 7.83 (dd, 2 H, C(4′)H, C(6′)H, ^3J = 7.7 Hz, ^4J = 1.6 Hz); 8.13 (br.s, 1 H, C(2′)H). MS (MALDI TOF/TOF), *m*/*z* (I_{rel} (%)): 773 $[M + H]^+$ (100), 715 $[M - Bu^t]^+$ (82).

Asymmetric sulfonylation of (*E*)-1,3-diphenylallyl acetate (6) with sodium *p*-toluenesulfinate. A solution of $[Pd(allyl)Cl]_2$ (0.0037 g, 0.01 mmol) and ligand **1** (0.0155 g, 0.02 mmol or 0.0309 g, 0.04 mmol) in THF (5 mL) was stirred for 40 min, then, (*E*)-1,3-diphenylallyl acetate (0.1 mL, 0.5 mmol) was added. After 15 min stirring, sodium *p*-toluenesulfinate (0.178 g, 1 mmol) was added and stirring was continued for 48 h. The reaction was quenched with brine (5 mL), stirred for 1 h, and extracted with THF (3×2 mL). The organic layer was washed with brine (2×2 mL), dried with $MgSO_4$, and filtered through a Celite pad. The solvent was removed *in vacuo* (40 Torr), the residue was recrystallized from 95% EtOH, and the target product **7** was dried *in vacuo* (10 Torr), milk-white crystals. ^{1}H NMR and IR spectra of the obtained product **7** are in complete agreement with the previously published data.[53] Enantiomeric excesses for product **7** were measured by HPLC using chiral stationary phase.

Asymmetric 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 ligand **1** (0.0155 g, 0.02 mmol or 0.0309 g, 0.04 mmol) in the corresponding solvent (5 mL) was stirred for 40 min and (*E*)-1,3-diphenylallyl acetate (0.1 mL, 0.5 mmol) was added. After 15 min stirring, dimethyl malonate (0.1 mL, 0.87 mmol), BSA (0.22 mL, 0.87 mmol), and AcOK (2 mg) were added. The reaction mixture was stirred for 48 h, diluted with hexane (5 mL), and filtered through a Celite pad. The solvents were removed *in vacuo* (40 Torr) and residue was dried *in vacuo* (10 Torr). Conversion of substrate **6** and enantiomeric excesses of product **8** were measured by HPLC using chiral stationary phase.

Asymmetric amination of (*E*)-1,3-diphenylallyl acetate (6) with pyrrolidine. A solution of $[Pd(allyl)Cl]_2$ (0.0037 g, 0.01 mmol) and ligand **1** (0.0155 g, 0.02 mmol or 0.0309 g, 0.04 mmol) in the corresponding solvent (5 mL) was stirred for 40 min and (*E*)-1,3-diphenylallyl acetate (0.1 mL, 0.5 mmol) was added. After 15 min stirring, 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 a Celite pad. The solvents were removed *in vacuo* (40 Torr), the residue was dried *in vacuo* (10 Torr). Conversion of substrate **6** and enantiomeric excesses for product **9** were measured by HPLC using chiral stationary phase.

Asymmetric alkylation of cinnamyl acetate 10 with ethyl 2-oxocyclohexanecarboxylate (11). A solution of $[Pd(allyl)Cl]_2$ (0.0037 g 0.01 mmol) and ligand **1** (0.0155 g, 0.02 mmol or 0.0309 g, 0.04 mmol) in the corresponding solvent (5 mL) was stirred for 40 min and cinnamyl acetate (0.08 mL, 0.5 mmol) was added. After 15 min stirring, ethyl 2-oxocyclohexanecarboxylate (0.12 mL, 0.75 mmol), BSA (0.5 mL, 2 mmol) and $Zn(AcO)_2$ (0.01 g) were added. The reaction mixture was stirred for 48 h, diluted with hexane (5 mL), and filtered through a Celite pad. The volatiles were removed *in vacuo* (40 Torr) and the residue was dried *in vacuo* (10 Torr). Conversion of substrate **10** and enantiomeric excesses for product **12** were measured by HPLC using chiral stationary phase.

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