CHIRALITY 22:844–848 (2010)

(*S*)-6-Bromo-BINOL-Based Phosphoramidite Ligand with C_1 Symmetry for Enantioselective Hydrogenation and Allylic Substitution

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ABSTRACT (*S*)-6-Br-BINOL-derived phosphoramidite, a **s**imple monodentate ligand with a stereogenic center at the phosphorus atom, was synthesized for the first time. This stereoselector generated a high level of enantioselectivity (80–95% *ee*) in the rhodium-catalyzed hydrogenation of α-dehydrocarboxylic acid esters and was also successfully employed in the asymmetric palladium-catalyzed allylic substitution of (*E*)-1,3-diphenylallyl acetate. The optical yield also showed significant dependence with reaction type: up to 70% *ee* for allylic amination, up to 75% *ee* for allylic sulfonylation, and up to 90% *ee* for allylic alkylation. *Chirality 22:844–848, 2010.*

KEY WORDS: asymmetric reactions; phosphorus ligands; hydrogenation; allylation

INTRODUCTION

The preparation of new enantiopure ligands, which offer chiral environment to coordinated metal atoms, is one of the most straightforward challenges for organic chemists.[1] Main families of successful phosphorus-containing stereoselectors belong to C_2-symmetric chelates (usually chiral diphosphine) or C_2-symmetric monodentate ligands (notably, chiral phosphites and phosphoramidites).[2–4] However, to date, there has not been a substantial reason why a C_2-symmetric ligand should necessarily be superior to a nonsymmetric counterpart. In contrast, good arguments have recently surfaced suggesting that nonsymmetrical ligands provide a more effective enantiocontrol than C_2-symmetric ligands for certain reactions.[5] Also noteworthy, the idea that C_1-symmetric phosphite-type compounds with P^*-stereocenters still remain as relatively rare class of chiral inductors.[6–13] This is rather surprising, as phosphites and phosphoramidites are easy to prepare from readily available starting materials and are also less sensitive to air than phosphines. Hence, this creates a challenge to develop a new protocol for the whole process, including the ligand synthesis, which does not necessitate the use of a glove box. In addition, phosphites are characterized by pronounced π-acidity and low-cost. As a whole, phosphites provide broad opportunities for fine tuning of their donor-acceptor and steric properties by incorporating oxygen and nitrogen into the first coordination sphere of phosphorus and varying the O- and/or N-containing building blocks.[14–23]

It is important to note that all nonsymmetrical phosphite-type ligands are obtained on the basis of optically active amino alcohols, diamines or diols with C_1 symmetry.

To the best of our knowledge, there are only few examples of P^*-chiral phosphites and phosphoramidites, based on C_1-symmetric BINOL derivatives.[24] In particular, phosphoramidites $\mathbf{L_A}$ and $\mathbf{L_B}$ (Fig. 1) showed excellent activities and enantioselectivities in Rh-catalyzed olefin hydrogenation.

Herein, we describe an independent approach to the synthesis of new C_1-symmetric phosphoramidite from readily available monosubstituted BINOL as a convenient optically active auxiliary and its application in catalytic asymmetric transformations.

MATERIALS AND METHODS

General

NMR spectra of ^{31}P, ^{13}C, and ^{1}H were recorded with a Bruker AMX 400 instrument (162.0 MHz for ^{31}P, 100.6 MHz for ^{13}C, and 400.13 MHz for ^{1}H). Complete assignment of all the resonances in ^{13}C NMR spectra was achieved by the use of distortionless enhancement by polarization transfer (DEPT) techniques. Chemical shifts (usually expressed in ppm) are given relative to Me_4Si (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P NMR). Mass spectra electron ionization (EI) were recorded with a Varian MAT 311 spectrometer. Optical rotations were measured on a Perkin-Elmer 341 polarimeter. Elemental analyses were

Contract grant sponsor: INTAS Open Call 2005-2006, Russian Science Support Foundation; Contract grant number: INTAS Ref. No. 05-1000008-8064; Contract grant sponsor: RFBR; Contract grant number: 08-03-00416-a

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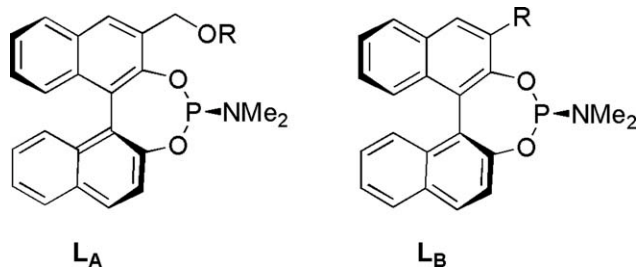
Received for publication 17 March 2009; Accepted 6 January 2010
DOI: 10.1002/chir.20845
Published online 21 April 2010 in Wiley InterScience (www.interscience.wiley.com).



L_A L_B

Fig. 1. Examples of BINOL-derived P^*-chiral monodentate phosphoramidites.

performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow).

All reactions were carried out under a dry argon atmosphere in freshly dried and distilled solvents; benzylamine, pyrrolidine, and dipropylamine. Distillation was done successively over KOH and then over a small amount of $LiAlH_4$ before use. (*S*)-6-Bromo-2,2′-dihydroxy-1,1′-binaphthyl [(*S*)-Br-BINOL **4**] was synthesized using literature procedures,[25] except for the modified technique for the preparation of intermediate product **3**. $[Rh(cod)_2]BF_4$[26] and $[Pd(allyl)Cl]_2$[27] were prepared as described earlier. Rh-catalyzed hydrogenation of α-dehydrocarboxylic acid esters **6a-d** was performed in accordance to known procedures.[28,29] Furthermore, the Pd-catalyzed allylic substitution: amination of substrate **8** with benzylamine, dipropylamine, and pyrrolidine; sulfonylation with sodium *para*-toluene sulfinate and alkylation with dimethyl malonate were all carried out using the appropriate procedures.[8,30–32]

The starting substrates **6b** and **8** were synthesized as published.[27,33] (*S*)-2,2′-Dihydroxy-1,1′-binaphthyl [(*S*)-BINOL **1**], $P(NEt_2)_3$, $Pd(CF_3CO_2)_2$, dimethyl itaconate, methyl 2-acetamidoacrylate, ethyl 2-acetoxyacrylate, dimethyl malonate, BSA [N,O-bis(trimethylsilyl) acetamide], and sodium *para*-toluene sulfinate were purchased from Aldrich and Acros Organics and used without further purification.

(S)-6-Bromo-2-Hydroxy-2′-Pivaloyloxy-1,1′-Binaphthyl (3)

A solution of bromine (1.96 ml, 38.3 mmol) in 1,4-dioxane (20 ml) was slowly added to a solution of (*S*)-2-hydroxy-2′-pivaloyloxy-1,1′-binaphthyl **2** (3.55 g, 9.6 mmol) in 1,4-dioxane (170 ml) at 0°C. The reaction mixture was then stirred at 20°C for 2 h and quenched with aqueous Na_2SO_3. After addition of 200 ml of CH_2Cl_2, the organic phase was washed with saturated aqueous $NaHCO_3$ and brine, and dried over $MgSO_4$. After removal of the solvent, **3** (4.31 g, 100%) was obtained as a white solid. Optical rotation and all spectroscopic data pertaining to compound **3** are consistent with published data.[25]

(S)-6′-Bromo-2-(Diethylamino)-Dinaphtho[2′,1′-d:1″,2″-f][1,3,2]Dioxaphosphepine (5)

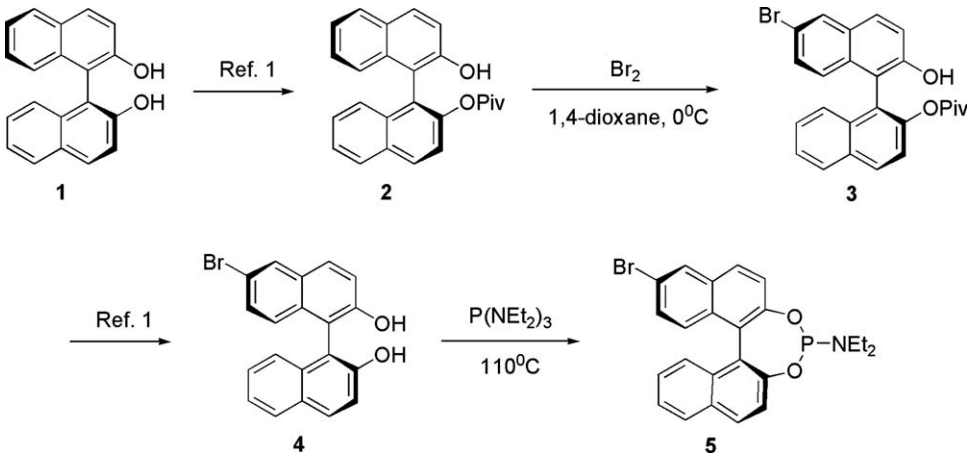
A mixture of (*S*)-6-bromo-2,2′-dihydroxy-1,1′-binaphthyl **4** (1.83 g, 5 mmol) and $P(NEt_2)_3$ (1.37 ml, 5 mmol) was stirred at 110°C for 45 min. Then the mixture was stirred in vacuum (10 Torr, 90°C) for 30 min to remove $HNEt_2$ and cooled down to 20°C. The residue was washed with hexane (7 ml) and dried in vacuum (1 Torr) for 1 h to yield **5** as yellowish amorphous solid in analytically pure form (2.22 g, 95%). $[\alpha]_D^{20} = -366.7$ (*c* 1.0, CH_2Cl_2); ^{13}C NMR ($CDCl_3$): δ 14.7 (d, J = 7.3 Hz, 2x CH_3), 38.3 (d, J = 21.2 Hz, 2x CH_2), 120.9 (Cq), 121.9 (CH), 122.9 (Cq), 123.3 (d, J = 1.3 Hz, CH), 124.4 (d, J = 5.1 Hz, Cq), 124.8 (CH), 126.3 (CH), 126.7 (CH), 128.4 (CH), 128.7 (CH), 129.2 (CH), 130.1 (CH), 130.3 (CH), 130.5 (CH), 130.7 (Cq), 131.4 (Cq), 131.8 (Cq), 132.5 (Cq), 149.8 (Cq), 150.4 (d, J = 5.1 Hz, Cq); MS (EI, *m/z* (I%): 466 (52) $[M]^+$, 452 (74) $[M\text{-}Me+H]^+$, 395 (100) $[M\text{-}NEt_2+H]^+$; Anal. Calcd for $C_{24}H_{21}BrNO_2P$: C, 61.82; H, 4.54; N, 3.00; Found: C, 61.98; H, 4.72; N, 2.95.

RESULTS AND DISCUSSION

The synthetic route for (*S*)-6-Br-BINOL **4**, the precursor of structurally unusual phosphoramidite **5**, is outlined in Scheme 1 (as patterned from a modified literature method[25]).

According to this procedure, the commercial (*S*)-BINOL **1** was treated with pivaloyl chloride in the presence of triethylamine in acetonitrile at 0°C to give monoester **2** as the single product with a 94% yield. Compound **2** was treated with 4 equivalent of bromine in 1,4-dioxane at 20°C for 2 h. After quenching with aqueous Na_2SO_3, the analytically pure substance **3** was obtained by simple extraction with CH_2Cl_2 in quantitative yield without further purification. In contrast to the literature[25] the monobromination step to obtain **3** was only successful with using of acetonitrile instead of 1,4-dioxane. Deprotection of the OH group by saponification of **3** with potassium hydroxide in a mixture of THF/H_2O at 25°C gave the resulting **4** in quantitative yield. It is rather important, that this synthesis of **4** is much easier than the preparation of precursors of ligands $\mathbf{L_A}$ and $\mathbf{L_B}$, which involved more steps, including *ortho*-metallation by butyllithium.[24]

(*S*)-6-Br-BINOL **4** was used as the starting material for the nonsymmetrical phosphoramidite **5**. Reaction of **4** with hexaethylphosphorous triamide $P(NEt_2)_3$ (Scheme 1) in solvent-free conditions followed by simple washing of the residue with hexane gave analytically pure **5** in 95% yield without further chromatographic purification or recrystallization. It should be noted that this convenient method does not require additional base and that the volatile $HNEt_2$ is formed only as a by-product. The newly synthesized monodentate ligand is stable on prolonged storage and can be obtained on a gram scale. Moreover, the monosubstitution at the 6-position of the 1,1′-binaphthyl skeleton not only reduced C_2 to C_1 symmetry, but also led to the creation of a stereogenic center at the phosphorus atom. The phosphorylation of **4** proceeded with complete diastereoselectivity. Thus, the ^{31}P NMR spectrum of **5** (in $CDCl_3$) shows a narrow singlet δ 150.1. We did not establish configuration of the P^*-stereo center in the structure of ligand **5**. Nevertheless, on the basis of data presented



Scheme 1. Synthesis of Br-substituted phosphoramidite ligand.

in article,[24] it is possible to assume, that we deal with (S_a,S_P)-epimer of **5**.

The products of catalytic hydrogenation of olefins substituted by both an amido and a carboxylic acid (or ester) group are important chiral building-blocks for the industrial synthesis of peptides and for numerous biomedical and medicinal applications.[4] Accordingly, we describe here results of the Rh-catalyzed hydrogenation of α-dehydrocarboxylic acid esters, as well-known benchmark substrates, with ligand **5** (Table 1).

The reactions were performed in propylene carbonate or CH_2Cl_2 at room temperature (with $[Rh(cod)_2]BF_4$, L/Rh = 2). In the transformation of dimethyl itaconate **6a** to succinate **7a**, phosphoramidite **5** has shown good enantioselectivity (80–81% *ee*), irrespective of the nature of the solvent (Table 1, entries 1, 2). A very good optical yield (93%, Table 1, entry 3) has been obtained in the hydrogenation of substrate **6b**, but only in propylene carbonate; in CH_2Cl_2, product **7b** was formed with a slightly smaller optical purity (85%). With its high polarity propylene carbonate offers great possibilities to recycle catalysts successfully. [34] In the Rh-catalyzed hydrogenation of esters **6c,d** excellent enantioselectivities were achieved in both solvents (up to 93 and 95% *ee*, respectively, Table 1, entries 5–8). Interestingly, the Rh-catalyzed hydrogenation of substrates **6a,d** phosphoramidites $\mathbf{L_A}$ and $\mathbf{L_B}$ caused a considerable dispersion of the asymmetric induction (0–97% *ee* for **6a** and 34–99% *ee* for **6d**).[24] Thus, being much easier available, ligand **5** reliably provides enantioselectivities that are rather close to the best results for $\mathbf{L_A}$ and $\mathbf{L_B}$.

Metal-catalyzed enantioselective allylation led to the formation of C—H, —C, —O, —N, —S, and other bonds with very high levels of asymmetric induction and tolerates a broad range of functional groups. This method, therefore, has been applied successfully to the synthesis of many natural products and new chiral compounds.[35] In this connection, we turned our attention to the application of **5** in the Pd-catalyzed allylic substitution of (*E*)-1,3-diphenylallyl acetate **8** as a widely used model substrate with N-, S- and C-containing nucleophiles (Table 2).

The reactions were performed in THF, propylene carbonate, or CH_2Cl_2 at room temperature (with $[Pd(allyl)Cl]_2$ or $Pd(CF_3CO_2)_2$, L/Pd = 1 or 2). In the allylic amination of **8** with benzylamine, dipropylamine, and pyrroli-

TABLE 1. Rh-catalysed hydrogenation of α-dehydrocarboxylic acid esters (25°C, 1 bar H_2)[a]

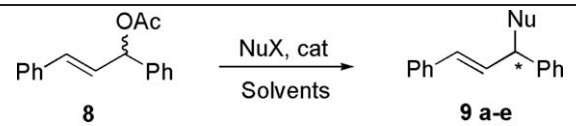
6 a-d **7 a-d**

R_1 = H, R_2 = CH_2CO_2Me, R_3 = Me, **6a** and **7a**
R_1 = Ph, R_2 = NHAc, R_3 = Me, **6b** and **7b**
R_1 = H, R_2 = OAc, R_3 = Et, **6c** and **7c**
R_1 = H, R_2 = NHAc, R_3 = Me, **6d** and **7d**

Entry	Substrate	Solvent	Time (min)	*ee* (%)[c,d,e,f]
1	**6a**	PC[b]	200	80 (*S*)
2	**6a**	CH_2Cl_2	60	**81 (*S*)**
3	**6b**	PC	1470	**93 (*R*)**
4	**6b**	CH_2Cl_2	1440	85 (*R*)
5	**6c**	PC	540	**93 (*R*)**
6	**6c**	CH_2Cl_2	500	90 (*R*)
7	**6d**	PC	120	95 (*R*)
8	**6d**	CH_2Cl_2	90	**95 (*R*)**

[a]100% conversion in all cases.
[b]Propylene carbonate.
[c]The conversion of substrate **6a** and enantiomeric excess of **7a** were determined by GC (Lipodex E, 25 m × 0.25 mm, 80°C, 1 ml/min) or HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH = 98/2, 0.8 ml/min, 220 nm, $t(R)$ = 9.1 min, $t(S)$ = 16.1 min).
[d]The conversion of the substrate **6b** and enantiomeric excess of **7b** were determined by GC (Lipodex E, 25m × 0.25 mm, 145°C, 1 ml/min).
[e]The conversion of substrate **6c** and enantiomeric excess of **7c** were determined by GC (50m Chiraldex ß-pm; Astec).
[f]The conversion of substrate **6d** and enantiomeric excess of **7d** were determined by GC (XE-valin(*tert*-butylamide) 4 × 0.25 mm, 85°C, 1 ml/min).

TABLE 2. Pd-catalysed allylic substitution of (*E*)-1,3-diphenylallyl acetate 8 (20°C)



8 9 a-e

Nu = $NHCH_2Ph$, X = H, **9a**
Nu = $N(Pr)_2$, X = H, **9b**
Nu = $N(CH_2)_4$, X = H, **9c**
Nu = SO_2pTol, X = Na, **9d**
Nu = $CH(CO_2Me)_2$ X = H, **9e**

Entry	Precatalyst	L/Pd	Solvent	Time (h)	Conv. (%)[a]	*ee* (%)
Allylic amination with benzylamine[b]						
1	$[Pd(allyl)Cl]_2$	1/1	PC	12	91	60 (*R*)
2	$[Pd(allyl)Cl]_2$	1/1	CH_2Cl_2	12	99	**60 (*R*)**
Allylic amination with dipropylamine[c]						
3	$[Pd(allyl)Cl]_2$	1/1	CH_2Cl_2	48	97	60 (−)
4	$[Pd(allyl)Cl]_2$	2/1	CH_2Cl_2	48	100	**65 (−)**
5	$[Pd(allyl)Cl]_2$	1/1	THF	48	15	60 (−)
6	$Pd(allyl)Cl]_2$	2/1	THF	48	19	64 (−)
Allylic amination with pyrrolidine[d]						
7	$[Pd(allyl)Cl]_2$	1/1	CH_2Cl_2	48	100	**70 (*S*)**
8	$[Pd(allyl)Cl]_2$	2/1	CH_2Cl_2	48	100	60 (*S*)
9	$[Pd(allyl)Cl]_2$	1/1	THF	48	41	57 (*S*)
10	$[Pd(allyl)Cl]_2$	2/1	THF	48	52	53 (*S*)
Allylic sulfonylation with sodium *para*-toluene sulfinate[e]						
11	$[Pd(allyl)Cl]_2$	1/1	THF	48	69	**75 (*R*)**
12	$[Pd(allyl)Cl]_2$	2/1	THF	48	61	72 (*R*)
Allylic alkylation with dimethyl malonate (BSA, KOAc)[f]						
13	$Pd(CF_3CO_2)_2$	1/1	PC	14	80	54 (*R*)
14	$Pd(CF_3CO_2)_2$	1/1	CH_2Cl_2	14	99	65 (*R*)
15	$[Pd(allyl)Cl]_2$	1/1	CH_2Cl_2	48	99	88 (*R*)
16	$[Pd(allyl)Cl]_2$	2/1	CH_2Cl_2	48	100	80 (*R*)
17	$[Pd(allyl)Cl]_2$	1/1	THF	48	94	**90 (*R*)**
18	$[Pd(allyl)Cl]_2$	2/1	THF	48	85	87 (*R*)

[a]Isolated yield of **9d** in allylic sulfonylation.
[b]The conversion of substrate **8** and enantiomeric excess of **9a** were determined by HPLC (Daicel Chiralcel OJ, C_6H_{14}/*i*-PrOH = 80/20, 0,5 ml/min, 254 nm).
[c]The conversion of the substrate **8** and enantiomeric excess of **9b** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH/$HN(Et)_2$ = 1000/1/1, 0.4 ml/min, 254 nm, $t(+)$ = 8.2 min, $t(-)$ = 9.1 min).
[d]The conversion of the substrate **8** and enantiomeric excess of **9c** were determined by HPLC (Daicel Chiralcel OD-H, OD-H, C_6H_{14}/*i*-PrOH/$HN(Et)_2$ = 200/1/0,1 0.9 ml/min, 254 nm).
[e]Enantiomeric excess of **9d** were determined by HPLC ((Daicel Chiralcel OJ, C_6H_{14}/*i*-PrOH = 4/1, 0.5 ml/min, 254 nm).
[f]The conversion of substrate **8** and enantiomeric excess of **9e** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH = 99/1, 0.6 ml/min, 254 nm).

dine, the use of phosphoramidite **5** resulted in moderate enantioselectivities (53–70%) in all cases. Propylene carbonate and CH_2Cl_2 provided much better conversion, than THF. In the allylic sulfonylation of **8** with $NaSO_2p$Tol as the *S*-nucleophile, ligand **5** showed a slightly higher enantioselectivity (up to 75%, Table 2, entries 11, 12). Similar to the case of allylic amination, L/Pd molar ratio has basically shown no effect on the optical yields. The best asymmetric induction (up to 90% *ee*) with the participation of phosphoramidite **5** was achieved in the allylic alkylation of **8** with dimethyl malonate as the *C*-nucleophile (Table 2, entries 13–18). Interestingly, the precatalyst $Pd(CF_3CO_2)_2$ provides a comparable conversion but considerably smaller asymmetric induction in comparison with $[Pd(allyl)Cl]_2$. At the same time, with the participation of $[Pd(allyl)Cl]_2$, fairly good levels of conversion (85–100%) and enantioselectivity (80–90%) were achieved, almost irrespective of both the L/Pd molar ratio and the nature of the solvent.

CONCLUSION

In summary, we have prepared and characterized an original (*S*)-6-Br-BINOL-derived C_1-symmetric phosphoramidite ligand that exposes a phosphorus stereocenter. It is a very efficient ligand in the Rh-catalyzed hydrogenation and Pd-catalyzed allylic alkylation. Moreover, the concept of ligands design presented above looks very promising. Indeed, there exist convenient approaches to the synthesis of a whole set of 6-monofunctionalized 2,2′-dihydroxy-1,1′-binaphthyl compounds (including those with ionic fragments), starting from (*S*)- or (*R*)-6-Br-BINOL.[36] Accordingly, the new route opens access to variable and highly prospective P^*-chiral phosphite-type stereoselectors for transition metal-catalyzed asymmetric reactions.

LITERATURE CITED

1. Mellah M, Voituriez A, Schulz E. Chiral sulfur ligands for asymmetric catalysis. Chem Rev 2007;107:5133–5209.
2. Ojima I. Catalytic asymmetric synthesis, 2nd ed. New York: Wiley-VCH; 2000.
3. Beller M, Bolm C. Transition metals for organic synthesis: building blocks and fine chemicals, 2nd ed. Weinheim: Wiley-VCH; 2004.
4. Eberhardt L, Armspach D, Harrowfield J, Dominique DM. BINOL-derived phosphoramidites in asymmetric hydrogenation: can the presence of a functionality in the amino group influence the catalytic outcome? Chem Soc Rev 2008;37:839–864.
5. Pavlov VA. C_2 and C_1 symmetry of chiral auxiliaries in catalytic reactions on metal complexes. Tetrahedron 2008;64:1147–1179.
6. Arzoumanian H, Buono G, Choukrad M, Petrignani J-F. Asymmetric carbonylation of alpha-methylbenzyl bromide catalyzed by oxazaphospholane-palladium complexes under phase-transfer conditions. Organometallics 1988;7:59–62.
7. Bartels B, Garcia-Yerba C, Helmchen G. Asymmetric Ir^I-catalysed allylic alkylation of monosubstituted allylic acetates with phosphorus amidites as ligands. Eur J Org Chem 2003;6:1097–1103.
8. Tsarev VN, Lyubimov SE, Shiryaev AA, Zheglov SV, Bondarev OG, Davankov VA, Kabro AA, Moiseev SK, Kalinin VN, Gavrilov KN. P*-chiral monodentate diamidophosphites - new and efficient ligands for palladium-catalysed asymmetric allylic substitution. Eur J Org Chem 2004;10:2214–2222.
9. Pfretzschner T, Kleemann L, Janza B, Harms K, Schrader T. On the role of PIII ligands in the conjugate addition of diorganozinc derivatives to enones. Chem Eur J 2004;10:6048–6057.
10. Bondarev OG, Goddard R. Tetrahedron Lett 2006;47:9013–9015.
11. Mikhel IS, Bernardinelli G, Alexakis A. Inorg Chim Acta 2006;359:1826–1836.
12. Kimura M, Uozumi Y. Development of new P-chiral phosphorodiamidite ligands having a pyrrolo[1,2-*c*]diazaphosphol-1-one unit and their application to regio- and enantioselective iridium-catalyzed allylic etherification. J Org Chem 2007;72:707–714.
13. Benetsky EB, Zheglov SV, Grishina TB, Macaev FZ, Bet LP, Davankov VA, Gavrilov KN. Various P*-chiral phosphite-type ligands: their synthesis, stereochemistry and use in Pd-catalysed allylation. Tetrahedron Lett 2007;48:8326–8330.

14. Ansel J, Wills M. Enantioselective catalysis using phosphorus-donor ligands containing two or three P–N or P–O bonds. Chem Soc Rev 2002;31:259–268.
15. Alexakis A, Benhaim C. Enantioselective copper-catalysed conjugate addition. Eur J Org Chem 2002;19:3221–3236.
16. Molt O, Schrader T. Asymmetric synthesis with chiral cyclic phosphorus auxiliaries. Synthesis 2002;18:2633–2670.
17. Reetz MT, Mehler G, Meiswinkel A, Sell T. Enantioselective hydrogenation of enamides catalyzed by chiral rhodium–monodentate phosphite complexes. Tetrahedron Lett 2002;43:7941–7943.
18. Dieguez M, Pamies O, Claver C. Recent advances in Rh-catalyzed asymmetric hydroformylation using phosphite ligands. Tetrahedron: Asymmetry 2004;15:2113–2122.
19. Gavrilov KN, Bondarev OG, Polosukhin AI. Chiral phosphites as ligands in asymmetric metal complex catalysis and synthesis of coordination compounds. Russ Chem Rev 2004;73:671–699.
20. Jerphagnon T, Renaud J-L, Bruneau C. Chiral monodentate phosphorus ligands for rhodium-catalyzed asymmetric hydrogenation. Tetrahedron: Asymmetry 2004;15:2101–2111.
21. Reetz MT, Mehler G, Bondarev O. Chiral diphosphites and diphosphoramidites as cheap and efficient ligands in Rh-catalyzed asymmetric olefin hydrogenation. Chem Comm 2006:2292–2294.
22. de Vries JG, Lefort L. The combinatorial approach to asymmetric hydrogenation: phosphoramidite libraries, ruthenacycles, and artificial enzymes. Chem Eur J 2006;12:4722–4734.
23. Jagt RBC, Toullec PY, Geerdink D, de Vries JG, Feringa BL, Minnaard AJ. A ligand-library approach to the highly efficient rhodium/phosphoramidite-catalyzed asymmetric arylation of N,N-dimethylsulfamoyl-protected aldimines. Angew Chem Int Ed Engl 2006;45:2789–2791.
24. Reetz MT, Ma J-An, Goddard R. Binol-derived monodentate phosphites and phosphoramidites with phosphorus stereogenic centers: novel ligands for transition-metal catalysis. Angew Chem Int Ed Engl 2005;44:412–415.
25. Hocke H, Uozumi Y. A simple synthetic approach to homochiral 6- and 6′-substituted 1,1′-binaphthyl derivatives. Tetrahedron 2003;59:619–630.
26. RajanBabu TV, Ayers TA, Halliday GA, You KK, Calabrese JC. Carbohydrate phosphinites as practical ligands in asymmetric catalysis: electronic effects and dependence of backbone chirality in Rh-catalyzed asymmetric hydrogenations. Synthesis of *R*- or *S*-amino acids using natural sugars as ligand precursors. J Org Chem 1997;62:6012–6028.
27. Auburn PR, McKenzie PB, Bosnich B. Asymmetric synthesis. Asymmetric catalytic allylation using palladium chiral phosphine complexes. J Am Chem Soc 1985;107:2033–2046.
28. Korostylev A, Monsees A, Fischera C, Börner A. BINOL derived monodentate acylphosphite ligands for homogeneously catalyzed enantioselective hydrogenation. Tetrahedron: Asymmetry 2004;15:1001–1005.
29. Vallianatou KA, Kostas ID, Holz J, Börner A. Me-AnilaPhos: a new chiral phosphine-phosphoramidite ligand for a highly efficient Rh-catalyzed asymmetric olefin hydrogenation. Tetrahedron Lett 2006;47:7947–7950.
30. Birkholz M-N, Dubrovina NV, Shuklov IA, Holz J, Paciello R, Waloch C, Breit B, Börner A. Enantioselective Pd-catalyzed allylic amination with self-assembling and non-assembling monodentate phosphine ligands. Tetrahedron: Asymmetry 2007;18:2055–2060.
31. Lyubimov SE, Davankov VA, Gavrilov KN. The use of an ionic liquid in asymmetric catalytic allylic amination. Tetrahedron Lett 2006;47:2721–2723.
32. Gavrilov KN, Lyubimov SE, Zheglov SV, Benetsky EB, Davankov VA. Enantioselective Pd-catalysed allylation with BINOL-derived monodentate phosphite and phosphoramidite ligands. J Mol Catal A 2005;231:255–260.
33. Gladiali S, Pinna L. Asymmetric hydroformylation of N-acyl 1-aminoacrylic acid derivatives by rhodium/chiral diphosphine catalysts. Tetrahedron: Asymmetry 1991;2:623–632.
34. Bayardon J, Holz J, Schäffner B, Andrushko V, Verevkin S, Preetz A, Börner A. Propylene carbonate as a solvent for asymmetric hydrogenations. Angew Chem Int Ed Engl 2007;46:5971–5974.
35. Lu Z, Ma S. Metal-catalyzed enantioselective allylation in asymmetric synthesis. Angew Chem Int Ed Engl 2008;47:258–297.
36. Gadenne B, Hesemann P, Moreau JJE. Easily recoverable BINOL ligand with ionic tag for asymmetric catalysis. Tetrahedron: Asymmetry 2005;16:2001–2006.