Tetrahedron 68 (2012) 1581–1589

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Phosphites and diamidophosphites based on mono-ethers of BINOL: a comparison of enantioselectivity in asymmetric catalytic reactions

Konstantin N. Gavrilov [a,*], Sergey V. Zheglov [a], Mariya N. Gavrilova [a], Ivan M. Novikov [a], Marina G. Maksimova [a], Nikolay N. Groshkin [a], Eugenie A. Rastorguev [b], Vadim A. Davankov [b]

[a] Department of Chemistry, Ryazan State University, 46 Svoboda Street, 390000 Ryazan, Russian Federation
[b] Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Street, 119991 Moscow, Russian Federation

ARTICLE INFO

Article history:
Received 27 September 2011
Received in revised form 8 November 2011
Accepted 28 November 2011
Available online 6 December 2011

Keywords:
Asymmetric allylic substitution
Palladium
Asymmetric addition
Rhodium
Phosphites
Diamidophosphites

ABSTRACT

Novel *P*-monodentate phosphite-type ligands have been synthesized in one step from BINOL monotosylate and BINOL mono-(−)-menthylcarbonate. The use of these ligands provides up to 96% ee in Pd-catalyzed asymmetric allylic substitution of (*E*)-1,3-diphenylallyl acetate and up to 99% ee in Rh-catalyzed asymmetric addition of phenylboronic acid to cyclohex-2-enone. The influence of the structural modules such as the nature of phosphorus-containing ring or exocyclic substituent on the enantioselectivity is discussed.

1. Introduction

Asymmetric metal complex catalysis is one of the most effective and environmentally safe methods for the synthesis of enantiopure organic and heteroorganic compounds, as reflected by the many publications in this field and the award of the Nobel Prize in 2001 to W. S. Knowles, R. Noyori, and K. B. Sharpless. In addition to the well-known application in pharmaceutical chemistry, this method is successfully used in the synthesis of enantiopure fragrance compounds, plant protection chemicals, polymers, and liquid crystals.[1] To achieve the highest levels of reactivity and selectivity in catalytic enantioselective reactions, several reaction parameters must be optimized, the most crucial of which is perhaps the design of appropriate chiral ligands, among which phosphorus-containing compounds are worth noting.[1f,2] Since the early 1970s, an impressive number of chiral phosphorus-based ligands have been applied in many asymmetric catalytic reactions.[1–3] Nevertheless, only a handful of them (so-called privileged ligands), rooted in a few core structures, can be regarded a truly successful in demonstrating proficiency in various mechanistically unrelated reactions.[4] Therefore, the tuning of existing ligands and/or the development of novel chiral ligands with improved performance continue to attract the interest of synthetic chemists.[1b,5]

From a practical point of view, air-stable, inexpensive, and easily accessible ligands are highly desirable.[6] Optically active phosphite-type compounds completely satisfy these criteria. Indeed, various P–O and/or P–N bond containing phosphorus ligands may be constructed in large quantities through the use of relatively simple condensation processes, and from inexpensive starting materials. Another advantage of phosphite-type ligands is that they are less sensitive to air and other oxidizing agents than phosphines. Hence, this makes it possible to develop protocols for the whole process, including the ligand synthesis, that do not necessitate the use of a glove box. Furthermore, they are amenable to parallel synthesis, even in solid phase synthesis. Such key advantages allow synthesis and screening of extensive libraries of chiral ligands aiming at high activities and selectivities for each particular reaction. In addition, phosphite-type ligands are characterized by pronounced π-acidity and low cost. It should be noted, that phosphites are rather prone to decomposition reactions such as hydrolysis or alcoholysis but, in many instances, these side reactions can be suppressed when bulky ligands (especially with aryl substituents) are used.[1f,2,7]

Herein, we report the synthesis of a small series of novel phosphite-type ligands containing dissymmetric monoprotected BINOL fragments and their evaluation in Pd-catalyzed asymmetric allylation and Rh-catalyzed asymmetric addition. Note, that

* Corresponding author. Tel.: +7 4912 280580; fax: +7 4912 281435; e-mail address: k.gavrilov@rsu.edu.ru (K.N. Gavrilov).

0040-4020/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2011.11.092

enantioselective Pd-catalyzed allylic substitution has emerged as a powerful synthetic tool, which is tolerant of various functional groups in the substrate and operates with a wide range of *C*-, *N*-, *O*-, *S*- and *P*-nucleophiles. As consequence, Pd-catalyzed allylic substitution is a novel and highly efficient strategy in the total synthesis of enantiopure natural and unnatural products.[1c,8] The asymmetric conjugate addition of arylboronic acids to α,β-unsaturated carbonyl compounds constitutes nowadays a very efficient method for the stereoselective construction of C–C bonds.[9] On the other hand, both catalytic processes are a common benchmark tests for initial ligand screening. From a functional point of view, the reached ees are the simplest indexes for evaluating new chiral ligands.[6,8g,h]

The steric and electronic properties of the chiral ligands have a tremendous effect on the performance of asymmetric metal catalysts. A well-conceived stereoselector should possess one or more structural features that may be varied readily in a systematic fashion, in order to optimize the design for a given purpose. A design is informative to the extent that variations in the ligand features can be correlated to changes in the reactivity or selectivity of the catalyst. In particular, the nature of phosphocycle and the stereochemistry of coordinating atom are crucial features for obtaining satisfactory asymmetric induction.[1b,3,4,5c,d] Our novel phosphite-type ligands **4**, **5** give some new examples in this field.

2. Results and discussion

The preparation of each ligand **4**, **5** was a convenient single-step operation (Scheme 1).

The appropriate enantiomer of monoacylated BINOL derivatives **1a** or **1b** reacted smoothly in toluene in the presence of Et_3N as a HCl scavenger and DMAP as catalyst with phosphorylating reagents **2** or **3**, whose syntheses have been described in the literature.[10,11] In turn, (S_a)- and (R_a)-2-hydroxy-2′-(−)-menthyl-1,1′-binaphthyl carbonate (S_a)-**1a** and (R_a)-**1a**, (S_a)- and (R_a)-2-hydroxy-2′-tosyloxy-1,1′-binaphthyl (S_a)-**1b** and (R_a)-**1b** were easily obtained by direct interaction between the corresponding enantiomer of BINOL and (−)-menthyl chloroformate or tosyl chloride.[12,13] Compounds **4** and **5** were obtained in moderate to good yields (66–82%), reflecting their stability during the workup and subsequent chromatographic purification. They also can be stored in the solid form under dry conditions at room temperature over several months without any degradation. Ligands **4** and **5** were fully characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, MALDI TOF/TOF mass spectrometry as well as by elemental analysis.

All ligands are readily available and can be prepared on a gram scale. Indeed, the phosphorylating agent **2** can easily be synthesized in high yield from readily accessible (*S*)-glutamic acid anilide.[14] Furthermore, BINOL is commercially available in both enantiomeric forms and is one of the cheapest chiral auxiliaries currently on the market. As stated above, its transformation into derivatives **1a** and **1b** (as well as into phosphorylating agent **3**) requires only one step.

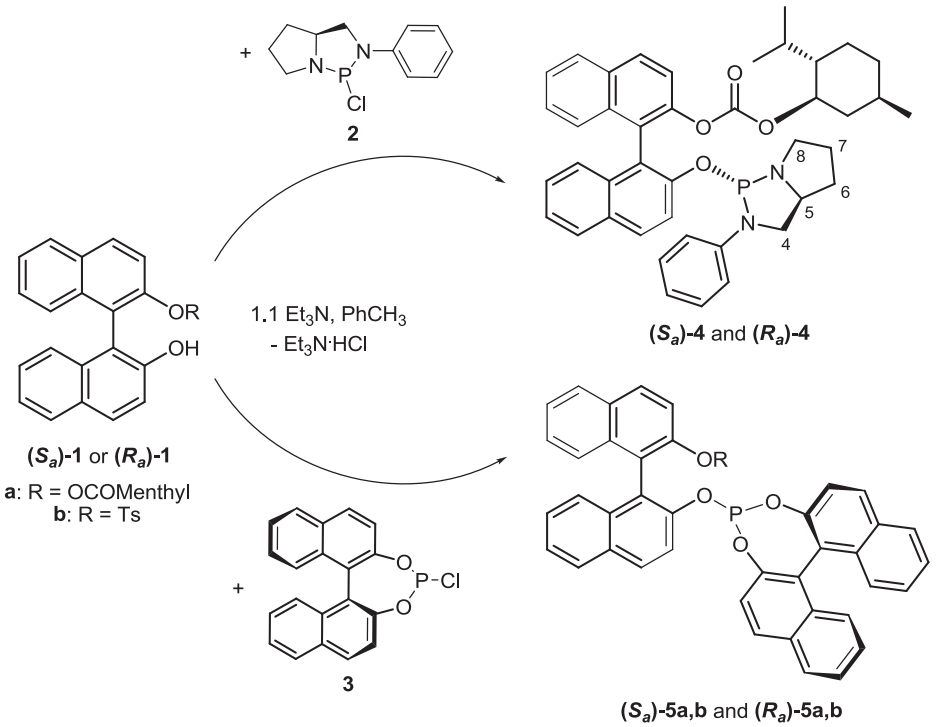
The ^{31}P NMR spectroscopic data for compounds **4** and **5** are summarized in Table 1.

Table 1
^{31}P NMR chemical shifts ($CDCl_3$) and cone angles θ (deg.) of ligands (S_a)-**4**, (R_a)-**4**, (S_a)-**5a**,**b**, and (R_a)-**5a**,**b**

Ligand		δ_P	θ
(S_a)-**4**	(76%)[a]	127.1	153
	(24%)	118.9	
(R_a)-**4**	(78%)	125.1	165
	(22%)	118.2	
(S_a)-**5a**		143.6	152
(R_a)-**5a**		145.7	149
(S_a)-**5b**		146.3	171
(R_a)-**5b**		145.5	142

[a] Percentage of P*-epimers.

Diamidophosphites (S_a)-**4** and (R_a)-**4** are mixtures of epimers with respect to the phosphorus stereocentre and contain 76% and 78% of the major P*-epimers, respectively. The major epimers of (S_a)-**4** and (R_a)-**4** have the *P**-stereocentres with the (*R*) configuration. Indeed, the ^{13}C NMR spectra of these compounds are characterized



Scheme 1. Synthesis of diamidophosphites (S_a)-**4**, (R_a)-**4**, and phosphites (S_a)-**5a**,**b**; (R_a)-**5a**,**b**.

by large spin–spin coupling constants ^2JC(8),P (34.7 and 36.9 Hz, see Experimental section). These values suggest the *anti*-orientation of the pseudoequatorial exocyclic substituent at the phosphorus atom and the $-(CH_2)_3-$ part of the pyrrolidine fragment of the phosphabicyclic skeleton and, consequently, the *syn*-orientation of the phosphorus lone pair with respect to the C(8) atom (Fig. 1).

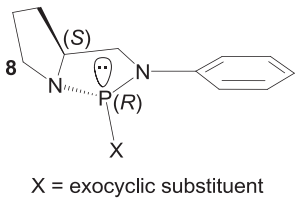


Fig. 1. Stereochemistry of the phosphabicyclic part in major epimers of diamidophosphites (S_a)-**4** and (R_a)-**4**.

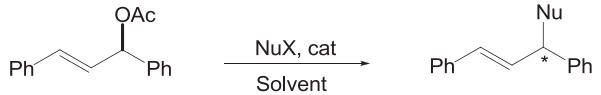
On the contrary, the minor epimers of (S_a)-**4** and (R_a)-**4** contain asymmetric phosphorus atoms with the (*S*) configuration, as evidenced by the fact that their ^{13}C NMR spectra have the small constants ^2JC(8),P (3.8 and 3.9 Hz, see Experimental section).[10,14,15]

In order to have an estimation of the steric demands of ligands **4** and **5**, we calculated their Tolman cone angles[16] by the reported method using semi-empirical quantum-mechanical AM1 techniques with full optimization of geometrical parameters.[17] The obtained results (Table 1) show that the steric parameters (θ) of **4** and **5** vary within the interval of 142°–171°, peaking at compounds (R_a)-**4** and (S_a)-**5b**. Compounds (S_a)-**4**, (S_a)-**5a**, (R_a)-**5a**, and (R_a)-**5b** are characterized by moderate steric demands (θ=142°–153°), while (R_a)-**4** and (S_a)-**5b** appear to be rather bulky ligands (θ=165° and 171°, respectively).[16,18]

With a view to examine the influence of the nature of phosphocycle, exocyclic substituent at the phosphorus atom, as well as the stereochemistry of coordinating atom, we investigated the ability of ligands **4** and **5** as stereoselectors for Pd-catalyzed asymmetric allylic substitution of (*E*)-1,3-diphenylallyl acetate **6** as a benchmark catalytic process (Tables 2–4). The reactions were run in THF or CH_2Cl_2. Palladium complexes were prepared in situ with [Pd(allyl)Cl]$_2$ as the precatalyst and L/Pd molar ratio 1 or 2. In general, the obtained results showed that the efficiency of novel phosphite-type ligands differs dramatically. Beyond doubt, diamidophosphites (S_a)-**4** and (R_a)-**4** are most efficient chiral inductors. Thus, the allylic sulfonylation of **6** with *p*-TolSO_2Na as the *S*-nucleophile proceeded smoothly to afford sulfone **7a** in very good yields and enantioselectivity (up to 95% ee for the *S*-enantiomer, Table 2, entry 2). When the reaction was carried out using (S_a)-**4** as the ligand, the enantioselectivity was higher than in the case of diastereomeric compound (R_a)-**4** (Table 2, entries 1,2 and 3,4).

In the next step, diamidophosphites (S_a)-**4** and (R_a)-**4** were studied in the Pd-catalyzed asymmetric allylic alkylation of substrate **6** with dimethyl malonate. Again, the best result (quantitative conversion and 96% ee) was obtained with ligand (S_a)-**4** (Table 2, entry 6). Like the Pd-catalyzed allylic sulfonylation, the experiments with the use of (S_a)-**4** afforded the reaction product **7b** having the (*S*) configuration. It is clear that CH_2Cl_2 is the solvent of choice; using THF led to a considerably decrease in conversion (Table 2, entries 5–8). The molar ratio L/Pd=2 was optimal in both solvents. With ligand (R_a)-**4**, a diastereoisomer of (S_a)-**4** with respect to the axis of chirality, the degrees of asymmetric induction and conversion were greatly reduced (43% ee, Table 2, entries 9–12). It is also noteworthy that the alkylation product **7b** has the opposite (*R*) configuration in contrast to the one observed with (S_a)-**4**. It is possible to assume that the mismatched combination of the (2*R*,5*S*)-stereocentres of the phosphabicyclic core with (R_a)-BINOL fragment takes place.

Table 2
Pd-catalyzed allylic sulfonylation and alkylation of (*E*)-1,3-diphenylallyl acetate (**6**)[a]



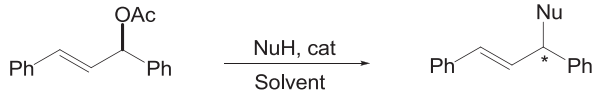
6 **7a,b**

Nu = SO_2pTol, X = Na, **7a**
Nu = $CH(CO_2Me)_2$ X = H, **7b**

Entry	Ligand	L/Pd	Solvent	Conversion (%) [b]	ee (%)
Allylic sulfonylation with sodium p-toluenesulfinate[c]					
1	(S_a)-**4**	1	THF	85	95 (*S*)
2	*(S_a)-**4***	*2*	*THF*	*87*	*95 (S)*
3	(R_a)-**4**	1	THF	96	35 (*S*)
4	(R_a)-**4**	2	THF	85	82 (*S*)
Allylic alkylation with dimethyl malonate (BSA, KOAc)[d]					
5	(S_a)-**4**	1	CH_2Cl_2	97	83 (*S*)
6	*(S_a)-**4***	*2*	*CH_2Cl_2*	*100*	*96 (S)*
7	(S_a)-**4**	1	THF	46	94 (*S*)
8	(S_a)-**4**	2	THF	63	95 (*S*)
9	(R_a)-**4**	1	CH_2Cl_2	—	—
10	(R_a)-**4**	2	CH_2Cl_2	44	14 (*R*)
11	(R_a)-**4**	1	THF	—	—
12	(R_a)-**4**	2	THF	23	43 (*R*)

[a] All reactions were carried out with 2 mol % of [Pd(allyl)Cl]$_2$ at room temperature for 48 h.
[b] Isolated yield of **7a**.
[c] The ee of **7a** was determined by HPLC (Daicel Chiralcel OJ, C_6H_{14}/*i*-PrOH=4:1, 0.5 mL/min, 254 nm).
[d] The conversion of substrate **6** and ee of **7b** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH=99:1, 0.6 mL/min, 254 nm).

Table 3
Pd-catalyzed allylic amination of (*E*)-1,3-diphenylallyl acetate (**6**)[a]



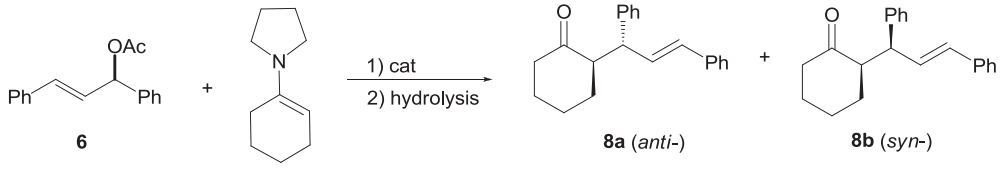
6 **7c,d**

Nu = $N(Pr)_2$, **7c**
Nu = $N(CH_2)_4$, **7d**

Entry	Ligand	L/Pd	Solvent	Conversion (%)	ee (%)
Allylic amination with dipropylamine[b]					
1	(S_a)-**4**	1	CH_2Cl_2	100	91 (+)
2	(S_a)-**4**	2	CH_2Cl_2	100	87 (+)
3	(S_a)-**4**	1	THF	48	93 (+)
4	*(S_a)-**4***	*2*	*THF*	*100*	*95 (+)*
5	(R_a)-**4**	1	CH_2Cl_2	98	91 (+)
6	(R_a)-**4**	2	CH_2Cl_2	100	84 (+)
7	(R_a)-**4**	1	THF	31	91 (+)
8	(R_a)-**4**	2	THF	73	95 (+)
Allylic amination with pyrrolidine[c]					
9	(S_a)-**4**	1	CH_2Cl_2	100	47 (*R*)
10	(S_a)-**4**	2	CH_2Cl_2	100	21 (*R*)
11	(S_a)-**4**	1	THF	100	39 (*R*)
12	(S_a)-**4**	2	THF	100	57 (*R*)
13	*(R_a)-**4***	*1*	*CH_2Cl_2*	*100*	*70 (R)*
14	(R_a)-**4**	2	CH_2Cl_2	100	50 (*R*)
15	(R_a)-**4**	1	THF	44	5 (*R*)
16	(R_a)-**4**	2	THF	46	31 (*R*)

[a] All reactions were carried out with 2 mol % of [Pd(allyl)Cl]$_2$ at room temperature for 48 h.
[b] The conversion of substrate **6** and ee of **7c** 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, $t_R(+)$= 8.2 min, $t_R(-)$=9.1 min).
[c] The conversion of substrate **6** and ee of **7d** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH/HN(Et)$_2$=200:1:0.1, 0.9 mL/min, 254 nm).

Table 4
Pd-catalyzed allylic alkylation of (*E*)-1,3-diphenylallyl acetate (**6**) with 1-cyclohexenylpyrrolidine[a,b]



Entry	Ligand	L/Pd	Solvent	Conversion (%)	*anti*/*syn*[c,d]	ee (%)
1	(S_a)-**4**	1	CH_2Cl_2	100	56:44	84:84
2	(S_a)-**4**	2	CH_2Cl_2	100	52:48	59:56
3	(S_a)-**4**	1	THF	30	55:45	43:40
4	(S_a)-**4**	2	THF	100	52:48	49:51
5	(R_a)-**4**	1	CH_2Cl_2	98	59:41	81:84
6	(R_a)-**4**	2	CH_2Cl_2	98	52:48	76:77
7	(R_a)-**4**	1	THF	25	61:39	71:70
8	(R_a)-**4**	*2*	*THF*	*96*	*62:38*	*92:94*

[a] All reactions were carried out with 2 mol % of $[Pd(allyl)Cl]_2$ at room temperature for 48 h.
[b] The conversion of substrate **6** and ee of **8a** and **8b** were determined by HPLC (Kromasil 5-CelluCoat, C_6H_{14}/*i*-PrOH=96:4, 0.5 mL/min, 254 nm, t_R(*S*,*R*)-**8b**=14.0 min, t_R(*R*,*S*)-**8b**=15.1 min; t_R(*S*,*S*)-**8a**=16.9 min, t_R(*R*,*R*)-**8a**=19.0 min).
[c] Determined by ^1H NMR.
[d] The absolute configuration of the predominant enantiomers of *anti*- and *syn*-products was determined according to Ref. 19.

Ligands (S_a)-**4** and (R_a)-**4** were next evaluated in the Pd-catalyzed allylic amination of (*E*)-1,3-diphenylallyl acetate **6** with dipropylamine and pyrrolidine as *N*-nucleophiles. The asymmetric amination with dipropylamine gives product (+)-**7c** in high enantioselectivities (84–95%) (Table 3, entries 1–8) regardless of the absolute configuration of monoacylated BINOL fragment, the L/Pd molar ratio and the nature of the solvent. As a rule, the highest conversion was observed in CH_2Cl_2. The asymmetric amination of **6** with pyrrolidine showed a considerably smaller enantioselectivity (ee is no higher than 70%, Table 3, entries 9–16). The resulting product **7d** proved to have the same (*R*) configuration in all cases. In contrast to the substitution reactions stated above, diamidophosphite (R_a)-**4** has been found to be more efficient stereoselector (Table 3, entry 13). With participation of ligand (R_a)-**4**, the higher enantioselectivity was observed in CH_2Cl_2 at the molar ratio L/Pd=1, with participation of its diastereomer (S_a)-**4**—in THF at the molar ratio L/Pd=2 (Table 3, entries 12 and 13).

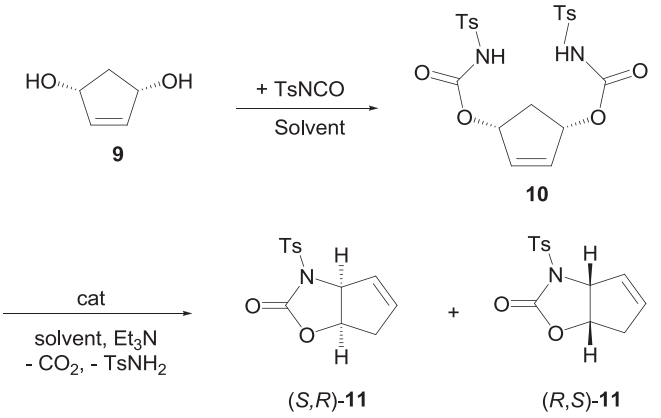
We also screened diamidophosphites (S_a)-**4** and (R_a)-**4** in the Pd-catalyzed allylic alkylation of (*E*)-1,3-diphenylallyl acetate **6** with a pyrrolidine enamine of cyclohexanone as the *C*-nucleophile (Table 4). Enamines can serve as good nucleophiles for Pd-catalyzed asymmetric allylic alkylation, avoiding the use of unstablilized ketone enolates formed by strong bases. Nevertheless, successful examples of Pd-catalyzed asymmetric allylic substitution with enamines are very scarce,[19] and this process remains a challenge for synthetic chemists. As a whole, the new catalytic systems based on (S_a)-**4** and (R_a)-**4** led to the expected product as a mixture of diastereomers **8a** and **8b** with excellent conversion, moderate to very good enantioselectivity with both *anti*- and *syn*-configuration (up to 94% ee, Table 4, entry 8) and moderate diastereomeric ratio. Both (S_a)-**4** and (R_a)-**4** gave virtually equal conversion. However, diamidophosphite (R_a)-**4** demonstrated higher *anti*/*syn*-ratio and enantioselectivity than its diastereomer (S_a)-**4** (70–94% and 40–84% ee, respectively; Table 4, entries 1–4 and 5–8). When the reaction was carried out using (S_a)-**4** as the ligand, the enantioselectivity was higher in CH_2Cl_2 than in THF. At the same time, at the molar ratio L/Pd=1 (L=(R_a)-**4**) the highest asymmetric induction being observed in CH_2Cl_2, at the molar ratio L/Pd=2—in THF. To the best of our knowledge, this is the first example of the use of phosphite-type ligands in Pd-catalyzed asymmetric allylic alkylation with enamine nucleophiles.

Unfortunately, phosphites (S_a)-**5a**,**b** and (R_a)-**5a**,**b** are practically inefficient in Pd-catalyzed asymmetric allylic substitution of (*E*)-1,3-diphenylallyl acetate **6**. Indeed, these ligands gave no conversion or enantioselectivity in the allylic sulfonylation of substrate **6** (Table S1 in Supplementary data, entries 1–8). Catalytic performance in the allylic alkylation of **6** with dimethyl malonate followed the same trend, excluding compounds (S_a)-**5b** and (R_a)-**5b**. Nevertheless, these ligands afforded product (*S*)-**7b** with mediocre enantiomeric purity (up to 57% ee, Table S1, entries 17–22). Besides, in the allylic amination of **6** with pyrrolidine in the presence of phosphites (S_a)-**5a**,**b** and (R_a)-**5a**,**b** the asymmetric induction was poor (no more than 37% ee, Table S1, entries 25–40).

We evaluated the small phosphite-type ligands library **4** and **5** in the Pd-catalyzed desymmetrization of *N*,*N*′-ditosyl-*meso*-cyclopent-4-ene-1,3-diol biscarbamate **10** (Table 5). Note that this process has been successfully used in key steps during the synthesis of mannostatin A and (−)-swainsonine.[1c,8c] The reaction was performed in THF or CH_2Cl_2, in the presence of $[Pd_2(dba)_3]\cdot CHCl_3$ as the catalytic precursor. In contrast to the Pd-catalyzed asymmetric allylic substitution of (*E*)-1,3-diphenylallyl acetate **6**, phosphites (S_a)-**5b** and (R_a)-**5b** have been found to be the most efficient stereoselectors (up to 67% and 65% *ee*, respectively; Table 5, entries 19 and 23). The use of both diastereomers of ligand **5b** made it possible to obtain product **11** with opposite absolute configurations (Table 5, entries 17–20 and 21–24). We found that there was no obvious trend in the influence of the nature of the solvent and the L/Pd molar ratio on the chemical yield and asymmetric induction. When the reaction was carried out using related phosphites (S_a)-**5a** and (R_a)-**5a**, the chemical yields and enantioselectivities were considerably lower (no more than 45% *ee*, Table 5, entries 9–16). Interestingly, an increase of the L/Pd molar ratio led to a significant increase in chemical yield and enantioselectivity. Diamidophosphites (S_a)-**4** and (R_a)-**4** allowed the synthesis of product **11** with moderate enantioselectivity, and (S_a)-**4** was shown to be a better stereoselector than its diastereomer (R_a)-**4** (57% and 38% ee, respectively, Table 5, entries 4 and 8). The best chemical yields and ee values were observed in THF.

The novel phosphite-type ligands **4** and **5** were applied in Rh-catalyzed asymmetric addition of phenylboronic acid to cyclohex-2-enone **12** using published mild highly practical protocol.[20] The reaction was performed in 1,4-dioxane/water medium in the presence of Et_3N at room temperature. In all cases the rhodium catalysts were prepared in situ by treating $[Rh(C_2H_4)_2Cl]_2$ with 2 or 4 equiv of the corresponding monodentate ligand; the results are summarized in Table 6. Overall, ligands **4**–**5** displayed mediocre to

Table 5
Pd-catalyzed desymmetrization of *N*,*N*′-ditosyl-*meso*-cyclopent-4-ene-1,3-diol biscarbamate (**10**)[a]

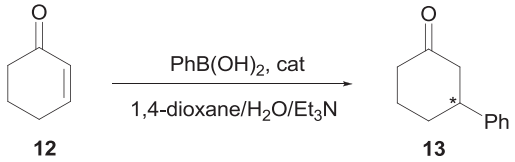


Entry	Ligand	L/Pd	Solvent	Yield (%)	ee (%)[b,c]
1	(S_a)-**4**	1	CH_2Cl_2	53	20 (II)
2	(S_a)-**4**	2	CH_2Cl_2	57	35 (II)
3	(S_a)-**4**	1	THF	69	47 (II)
4	(S_a)-**4**	2	THF	73	57 (II)
5	(R_a)-**4**	1	CH_2Cl_2	29	4 (II)
6	(R_a)-**4**	2	CH_2Cl_2	34	3 (II)
7	(R_a)-**4**	1	THF	46	30 (II)
8	(R_a)-**4**	2	THF	42	38 (II)
9	(S_a)-**5a**	1	CH_2Cl_2	59	2 (II)
10	(S_a)-**5a**	2	CH_2Cl_2	78	35 (II)
11	(S_a)-**5a**	1	THF	38	8 (I)
12	(S_a)-**5a**	2	THF	42	10 (I)
13	(R_a)-**5a**	1	CH_2Cl_2	59	2 (II)
14	(R_a)-**5a**	2	CH_2Cl_2	70	17 (II)
15	(R_a)-**5a**	1	THF	59	10 (II)
16	(R_a)-**5a**	2	THF	64	45 (II)
17	(S_a)-**5b**	1	CH_2Cl_2	83	53 (I)
18	(S_a)-**5b**	2	CH_2Cl_2	92	64 (I)
19	*(S_a)-**5b***	*1*	*THF*	*89*	*67 (I)*
20	(S_a)-**5b**	2	THF	75	50 (I)
21	(R_a)-**5b**	1	CH_2Cl_2	88	63 (II)
22	(R_a)-**5b**	2	CH_2Cl_2	85	52 (II)
23	(R_a)-**5b**	1	THF	91	65 (II)
24	(R_a)-**5b**	2	THF	83	61 (II)

[a] All reactions were carried out with 5 mol% of $[Pd_2(dba)_3]\cdot CHCl_3$ at 35 °C for 24 h.
[b] The ee of **11** was determined by HPLC (Kromasil 5-CelluCoat, C_6H_{14}/*i*-PrOH=9:1, 2 mL/min, 219 nm, t_R(I)=15 min, t_R(II)=18 min).
[c] The absolute configuration of the product **11** was not assigned.

good yields and moderate to high enantioselectivities. In particular, diamidophosphite (R_a)-**4** provided an excellent enantioselectivity (98–99% ee, Table 6, entries 3 and 4) irrespective of the L/Rh molar ratio. It should be noted that in the pair of diastereoisomers (S_a)-**4** and (R_a)-**4**, (R_a)-**4** is more efficient (Table 6, entries 1,2 and 3,4). It is possible that this is a consequence of a matched (2*R*,5*S*) phosphorus centre/(R_a)-BINOL combination and the much greater value of the Tolman cone angle for (R_a)-**4** (Table 1). With participation of phosphites (S_a)-**5a** and (R_a)-**5a**, the medium enantioselectivity was achieved (43–65% ee, Table 6, entries 5–8). In this diastereomeric pair, phosphite (R_a)-**5a** is the best stereoselector: up to 65% ee at the molar ratio L/Rh=1. Among (S_a)-**5b** and (R_a)-**5b**, diastereoisomer (R_a)-**5b** bearing a monoacylated (R_a)-BINOL fragment also produced a significantly better asymmetric induction (Table 6, entries 9–12). It is interesting, that in the case of (R_a)-**5b** the decrease of the L/Rh molar ratio gave rise the dramatically growth of the enantioselectivity (88% versus 23% ee, Table 6, entries 11 and 12). In all cases the diastereomeric ligands **4** or **5a**,**b** caused the formation of product **13** with opposite absolute configurations, as a consequence of the determining influence of the monoacylated BINOL fragment.

Table 6
Rh-catalyzed asymmetric addition of phenylboronic acid to cyclohex-2-enone (**12**)[a]



Entry	Ligand	L/Rh	Yield (%)	ee (%)[b,c]
1	(S_a)-**4**	1	56	70 (II)
2	(S_a)-**4**	2	46	55 (II)
3	*(R_a)-**4***	*1*	*65*	*99 (I)*
4	(R_a)-**4**	2	77	98 (I)
5	(S_a)-**5a**	1	84	44 (I)
6	(S_a)-**5a**	2	73	46 (I)
7	(R_a)-**5a**	1	64	65 (II)
8	**(R_a)-5a**	2	25	43 (II)
9	(S_a)-**5b**	1	26	40 (II)
10	(S_a)-**5b**	2	25	51 (II)
11	(R_a)-**5b**	1	70	88 (I)
12	(R_a)-**5b**	2	53	23 (I)

[a] All reactions were carried out with 1.8 mol% of $[Rh(C_2H_4)_2Cl]_2$ at room temperature for 72 h.
[b] The ee of **13** was determined by HPLC (Kromasil 5-CelluCoat, C_6H_{14}/*i*-PrOH=99:1, 0.8 mL/min, 219 nm, t_R(I)=22 min, t_R(II)=24 min).
[c] The absolute configuration of the product **13** was not assigned.

3. Conclusion

We have successfully designed and synthesized a small series of readily available phosphite-type ligands prepared from monoethers of BINOL. The catalytic performance is highly affected by the nature of phosphocycle and the stereochemistry of coordinating atom. Indeed, novel *P**-chiral diamidophosphites (S_a)-**4** and (R_a)-**4** with 1,3,2-diazaphospholidine rings, as well as the previously described[15d,21] analogous ligands with Ts–BINOL and Piv–BINOL exocyclic moieties, yielded much higher conversion and enantioselectivities in the Pd-catalyzed asymmetric allylic substitution of (*E*)-1,3-diphenylallyl acetate with various nucleophiles than phosphites (S_a)-**5a**,**b** and (R_a)-**5a**,**b** with 1,3,2-dioxaphosphepine rings. In addition, the first example of successful Pd-catalyzed asymmetric allylic alkylation with enamine nucleophiles (up to 94% ee) with participation of phosphite-type ligands was found. Furthermore, (S_a)-**4** and (R_a)-**4** are better stereoselectors than (S_a)-**5a**,**b** and (R_a)-**5a**,**b** in the Rh-catalyzed asymmetric addition of phenylboronic acid to cyclohex-2-enone. Hence, introducing the 1,3,2-diazaphospholidine rings with *P**-stereocentres into ligands (S_a)-**4** and (R_a)-**4** is advantageous. Such compounds display balanced electronic characteristics since they are both good π-acceptors (due to the accessibility of low-lying π^*_{PN} orbitals) as well as good σ-donors.[22] In their complexes, the asymmetric phosphorus atom bind directly to the metal atom and, as consequence, it is as close as possible to the coordinated substrate. This factor eliminates potentially inefficient secondary transfer of chirality from the ligand backbone and, thus provides a more efficient chiral environment at the site where the enantioselection originates.[4,8b] At the same time, in the Pd-catalyzed intramolecular allylic substitution reaction such as desymmetrization of *N*,*N*′-ditosyl-*meso*-cyclopent-4-ene-1,3-diol biscarbamate BINOL-based phosphites (S_a)-**5b** and (R_a)-**5b** are preferable. In most cases there is no direct correlation between the values of Tolman cone angles of diastereomeric ligands **4** or **5a**,**b** and the values of the asymmetric induction. Thus, a less sterically demanding diastereomer may be a substantially better stereoselector. To sum up the results obtained here in and published earlier,[15d,21] we can conclude that the presence of the (−)-menthyl substituent with an additional *C**-stereocentres in the exocyclic BINOL fragment has no

positive effect on the stereochemical outcome of the catalytic reactions. Therefore, more accessible and cheap ligands with Ts-BINOL and Piv-BINOL moieties should be widely used. Such investigations are currently in progress in our laboratories.

4. Experimental section

4.1. General comments

^{31}P, ^{13}C, and ^{1}H NMR spectra 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 DEPT techniques. Chemical shifts (ppm) were given relative to Me_4Si (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P NMR). IR spectra were recorded on a Specord M80 instrument. Mass spectra were recorded with a Bruker Daltonics Ultraflex spectrometer (MALDI TOF/TOF). HPLC analyses were performed on an Agilent 1100 and Stayer instruments using Chiralcel® and Kromasil® columns. Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow).

All manipulations were carried out under a dry argon atmosphere in flame-dried glassware and in freshly dried and distilled solvents. For example, toluene and tetrahydrofuran were freshly distilled from sodium benzophenone ketyl before use; dichloromethane was distilled from NaH. Triethylamine, pyrrolidine, and dipropylamine were distilled over KOH and then over a small amount of $LiAlH_4$ before use. Column chromatography was performed using silica gel MN Kieselgel 60 (230–400 mesh) and MN-Aluminum oxide, basic, Brockmann Activity 1. $Pd(allyl)Cl]_2$, starting substrate **6**, and $[Pd_2(dba)_3]\cdot CHCl_3$ were prepared as published.[23,24] Pd-catalyzed allylic substitution: sulfonylation of substrate **6** with sodium *para*-toluene sulfinate, alkylation with dimethyl malonate, amination with dipropylamine and pyrrolidine, alkylation with 1-cyclohexenylpyrrolidine were performed according to the appropriate procedures.[10,25,26,19] Pd-catalyzed desymmetrization of *N,N′*-ditosyl-*meso*-cyclopent-4-ene-1,3-diol biscarbamate and Rh-catalyzed asymmetric addition of phenylboronic acid to cyclohex-2-enone **12** were performed as published.[27,20] DMAP (4-eimethylamino-pyridine), dimethyl malonate, BSA (*N,O*-bis(trimethylsilyl) acetamide), sodium *para*-toluene sulfinate, 1-cyclohexenylpyrrolidine, *meso*-cyclopent-4-ene-1,3-diol **9**, tosyl isocyanate, cyclohex-2-enone **12**, phenylboronic acid, and $[Rh(C_2H_4)_2Cl]_2$ were purchased from Aldrich and Acros Organics and used without further purification.

4.2. General procedure for the preparation of ligands

A solution of the appropriate enantiomer of **1a** or **1b** (2 mmol) in toluene (10 mL) was added dropwise to a vigorously stirred solution of the appropriate phosphorylating reagent (2 mmol), Et_3N (0.31 mL, 2.2 mmol), and DMAP (0.025 g, 0.2 mmol) in toluene (10 mL). The mixture was then heated to the boiling point, stirred for 20 min, and cooled to 20 °C. Solid $Et_3N\cdot HCl$ was removed by filtration. The resulting solution was filtered through a short plug of aluminum oxide, the solvent evaporated under reduced pressure (40 Torr), and the residue was purified by careful trituration with $CHCl_3$/hexane (1:20) and then by flash chromatography on silica gel (EtOAc/hexane, 1:1). The product was dried in vacuum (1 Torr) for 1 h.

*4.2.1. (S_a)-2-[(2R,5S)-3-Phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]oct-2-yloxy]-1,1′-binaphthyl-2′-yl (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl carbonate ((S_a)-**4**).* Yield: 0.93 g (69%) as white solid, mp 103–104 °C. ^{1}H NMR ($CDCl_3$, 25 °C): δ=0.33 (d, J=6.1 Hz, 3H, menthyl), 0.59 (d, J=6.1 Hz, 3H, menthyl), 0.70–0.79 (m, 2H, menthyl), 0.84 (d, J=6.5 Hz, 3H, menthyl), 0.90–0.98 (m, 2H, menthyl), 1.11–1.18 (m, 2H, menthyl), 1.26–1.39 (m, 3H, C(6)H_2C(7)H_2), 1.45–1.56 (m, 2H, menthyl), 1.64–1.71 (m, 1H, C(6)H_2C(7)H_2), 1.84–1.93 (m, 1H, menthyl); 2.51–2.59 (m, 1H), 2.81–2.88 (m, 1H), 2.99–3.08 (m, 1H), 3.27–3.39 (m, 2H, C(4)H_2, C(5)H, C(8)H_2), 4.21–4.30 (m, 1H, menthyl), 6.77 (br d, J=7.0 Hz, 2H, CH, aryl), 7.09–7.25 (m, 6H, CH, aryl), 7.30–7.53 (m, 5H, CH, aryl), 7.82–7.93 (m, 4H, CH, aryl). $^{13}C\{H\}$ NMR ($CDCl_3$, 25 °C): δ_C=16.3, 20.3, 22.0 (s, CH_3, menthyl), 23.6 (s, CH_2, menthyl), 26.1 (s, CH, menthyl), 26.2 (d, ^{3}J=4.5 Hz, C(7)), 31.3 (s, CH, menthyl), 31.4 (s, C(6)), 34.1, 40.5 (s, CH_2, menthyl), 46.9 (s, CH, menthyl), 47.4 (d, ^{2}J=34.7 Hz, C(8)), 53.6 (d, ^{2}J=7.0 Hz, C(4)), 62.4 (d, ^{2}J=9.1 Hz, C(5)), 78.7 (s, CHO, menthyl), 115.1 (d, ^{3}J=12.8 Hz, CH, phenyl), 118.9 (s, CH, phenyl), 121.4 (s, CH, binaphthyl), 122.7 (d, ^{3}J=3.0 Hz, C, binaphthyl), 123.0 (d, ^{3}J=5.3 Hz, CH, binaphthyl), 124.3, 125.3 (s, CH, binaphthyl), 125.4 (s, C, binaphthyl), 126.1, 126.2, 126.3, 126.9, 127.8, 127.9, 128.8, 128.9 (s, CH, binaphthyl), 129.4 (s, CH, phenyl), 131.7, 133.6, 133.8, 133.9 (s, C, binaphthyl), 145.1 (d, ^{2}J=16.5 Hz, C, phenyl), 147.1 (s, CO, binaphthyl), 150.2 (d, ^{2}J=5.6 Hz, CO, binaphthyl), 153.0 (s, CO_3) (major epimer) and 16.4, 20.4, 21.9 (s, CH_3, menthyl), 23.5 (s, CH_2, menthyl), 26.0 (s, CH, menthyl), 27.5 (s, C(7)); 31.2 (s, CH, menthyl), 31.7 (s, C(6)), 34.0, 40.4 (s, CH_2, menthyl), 43.4 (d, ^{2}J=3.8 Hz, C(8)), 46.8 (s, CH, menthyl), 51.2 (d, ^{2}J=6.0 Hz, C(4)), 65.5 (d, ^{2}J=10.6 Hz, C(5)), 79.0 (s, CHO, menthyl), 117.1 (d, ^{3}J=13.6 Hz, CH, phenyl), 118.3 (s, CH, phenyl), 120.2 (d, ^{3}J=1.5 Hz, CH, binaphthyl), 121.5 (s, CH, binaphthyl), 122.5 (s, C, binaphthyl), 123.9, 125.4, 125.6 (s, CH, binaphthyl), 125.7 (s, C, binaphthyl), 126.5, 126.6, 126.8, 127.7, 128.0, 128.9, 129.1 (s, CH, binaphthyl), 129.7 (s, CH, phenyl), 131.9, 133.7, 133.9, 134.0 (s, C, binaphthyl), 145.3 (d, ^{2}J=15.7 Hz, C, phenyl), 146.7 (s, CO, binaphthyl), 150.5 (d, ^{2}J=5.2 Hz, CO, binaphthyl), 152.6 (s, CO_3) (minor epimer). IR, cm^{-1}: ν(CO) 1752 (KBr). MS (MALDI TOF/TOF): m/z (%)=711 (12) $[M+K]^+$, 673 (100) $[M+H]^+$, 534 (9) $[M-menthyl+H]^+$, 490 (13) $[M-menthylO_2C+H]^+$, 474 (48) $[M-menthylO_3C+H]^+$. Anal. Calcd for $C_{42}H_{45}N_2O_4P$: C, 74.98; H, 6.74; N, 4.16. Found: C, 75.26; H, 6.64; N, 4.21.

*4.2.2. (R_a)-2-[(2R,5S)-3-Phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]oct-2-yloxy]-1,1′-binaphthyl-2′-yl (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl carbonate ((R_a)-**4**).* Yield: 0.89 g (66%) as off-white solid, mp 129–130 °C. ^{1}H NMR ($CDCl_3$, 25 °C): δ=0.41–0.49 (m, 1H, menthyl), 0.59–0.67 (m, 1H, menthyl), 0.68 (d, J=6.6 Hz, 3H, menthyl), 0.72 (d, J=7.5 Hz, 3H, menthyl), 0.79 (d, J=7.5 Hz, 3H, menthyl), 1.14–1.22 (m, 3H, menthyl), 1.29–1.39 (m, 3H, C(6)H_2C(7)H_2), 1.48–1.57 (m, 1H, menthyl), 1.61–1.75 (m, 2H, menthyl and 1H, C(6)H_2C(7)H_2), 1.79–1.89 (m, 1H, menthyl); 2.84–2.95 (m, 2H), 3.24–3.31 (m, 2H), 3.36–3.48 (m, 1H, C(4)H_2, C(5)H, C(8)H_2); 4.15–4.25 (m, 1H, menthyl), 6.82 (br d, J=6.1 Hz, 2H, CH, aryl), 7.08–7.24 (m, 7H, CH, aryl), 7.26–7.35 (m, 2H, CH, aryl), 7.38–7.47 (m, 1H, CH, aryl), 7.48 (d, J=8.9 Hz, 1H, CH, aryl), 7.75 (d, J=9.0 Hz, 1H, CH, aryl), 7.79 (d, J=9.0 Hz, 1H, CH, aryl), 7.88–7.96 (m, 2H, CH, aryl). $^{13}C\{H\}$ NMR ($CDCl_3$, 25 °C): δ_C=16.4, 20.6, 21.8 (s, CH_3, menthyl), 23.4 (s, CH_2, menthyl), 25.8 (d, ^{3}J=4.5 Hz, C(7)), 26.0, 31.1 (s, CH, menthyl), 31.5 (s, C(6)), 34.0, 39.6 (s, CH_2, menthyl), 46.4 (s, CH, menthyl), 47.2 (d, ^{2}J=36.9 Hz, C(8)), 53.8 (d, ^{2}J=7.6 Hz, C(4)), 62.6 (d, ^{2}J=8.3 Hz, C(5)), 78.9 (s, CHO, menthyl), 115.1 (d, ^{3}J=12.8 Hz, CH, phenyl), 119.0 (s, CH, phenyl), 121.7 (s, CH, binaphthyl), 122.5 (s, C, binaphthyl), 122.8 (d, ^{3}J=5.3 Hz, CH, binaphthyl), 124.3, 125.2 (s, CH, binaphthyl), 125.3 (s, C, binaphthyl), 126.0, 126.1, 126.5, 127.2, 127.7, 128.0, 128.9, 129.1 (s, CH, binaphthyl), 129.4 (s, CH, phenyl), 130.4, 131.6, 133.7, 133.8 (s, C, binaphthyl), 145.2 (d, ^{2}J=16.1 Hz, C, phenyl), 147.4 (s, CO, binaphthyl), 150.2 (d, ^{2}J=5.5 Hz, CO, binaphthyl), 152.9 (s, CO_3) (major epimer) and 16.5, 20.4, 21.7 (s, CH_3, menthyl), 23.5 (s, CH_2, menthyl), 25.9 (s, CH, menthyl), 27.8 (s, C(7)), 31.2 (s, CH, menthyl), 31.7 (s, C(6)), 34.1, 39.8 (s, CH_2, menthyl), 42.7 (d, ^{2}J=3.9 Hz, C(8)), 46.5 (s, CH, menthyl), 51.4 (d, ^{2}J=5.3 Hz, C(4)), 65.5 (d, ^{2}J=10.6 Hz, C(5)), 78.8 (s, CHO, menthyl), 117.5 (d, ^{3}J=12.8 Hz, CH, phenyl), 118.9

(s, CH, phenyl), 120.4 (d, ^3J=1.9 Hz, CH, binaphthyl), 121.8 (s, CH, binaphthyl), 122.6 (s, C, binaphthyl), 123.9 (s, CH, binaphthyl), 125.4 (s, C, binaphthyl), 125.5, 125.8, 126.4, 126.6, 126.7, 127.9, 128.3, 129.2, 129.3 (s, CH, binaphthyl), 129.5 (s, CH, phenyl), 130.2, 131.9, 133.6, 133.9 (s, C, binaphthyl), 144.3 (d, ^2J=15.1 Hz, C, phenyl), 147.1 (s, CO, binaphthyl), 150.4 (d, ^2J=5.3 Hz, CO, binaphthyl), 153.0 (s, CO_3) (minor epimer). IR, cm^{-1}: ν(CO) 1751 (KBr). MS (MALDI TOF/TOF): *m/z* (%)=711 (27) $[M+K]^+$, 673 (100) $[M+H]^+$, 534 (19) $[M-menthyl+H]^+$, 490 (7) $[M-menthylO_2C+H]^+$, 474 (33) $[M-menthylO_3C+H]^+$. Anal. Calcd for $C_{42}H_{45}N_2O_4P$: C, 74.98; H, 6.74; N, 4.16. Found: C, 75.13; H, 6.82; N, 4.19.

*4.2.3. (S_a)-2-[(S_a)-Dinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphosphepin-4-yloxy]-1,1′-binaphthyl-2′-yl (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl carbonate ((S_a)-**5a**).* Yield: 1.28 g (82%) as white solid, mp 172–173 °C. ^{1}H NMR ($CDCl_3$, 25 °C): δ=0.18 (d, *J*=7.2 Hz, 3H, menthyl), 0.50 (d, *J*=7.2 Hz, 3H, menthyl), 0.66–0.75 (m, 1H, menthyl), 0.79 (d, *J*=6.5 Hz, 3H, menthyl), 0.80–0.88 (m, 1H, menthyl), 0.91–1.0 (m, 1H, menthyl), 1.02–1.11 (m, 1H, menthyl), 1.21–1.29 (m, 2H, menthyl), 1.43–1.52 (m, 2H, menthyl), 1.79–1.87 (m, 1H, menthyl), 4.16–4.25 (m, 1H, menthyl), 7.16–7.24 (m, 6H, CH, aryl), 7.24–7.32 (m, 4H, CH, aryl), 7.35–7.43 (m, 3H, CH, aryl), 7.44–7.51 (m, 2H, CH, aryl), 7.58 (d, *J*=12.0 Hz, 1H, CH, aryl), 7.66 (d, *J*=12.0 Hz, 1H, CH, aryl), 7.83–7.91 (m, 5H, CH, aryl), 7.97 (d, *J*=8.0 Hz, 1H, CH, aryl), 8.09 (d, *J*=8.1 Hz, 1H, CH, aryl). ^{13}C{H} NMR ($CDCl_3$, 25 °C): δ_C=16.0, 20.3, 21.9 (s, CH_3, menthyl), 23.4 (s, CH_2, menthyl)m 25.8, 31.3 (s, CH, menthyl), 33.9, 40.5 (s, CH_2, menthyl), 46.7 (s, CH, menthyl), 79.0 (s, CHO, menthyl), 121.0, 121.1 (s, C, aryl), 121.6, 121.7, 121.8, 121.9 (s, CH, aryl), 122.5, 122.6 (s, C, aryl), 124.3, 124.8, 125.1, 125.2, 125.9, 126.1, 126.2, 126.3, 126.9, 127.0, 127.9, 128.2, 128.3, 128.4, 129.5, 129.8, 130.1, 130.2 (s, CH, aryl), 130.9, 131.1, 131.5, 131.8, 132.4, 132.8, 133.7(s, C, aryl), 147.0, 147.5 (s, CO, aryl), 147.7 (d, ^2J=6.0 Hz, CO, aryl), 147.9 (d, ^2J=8.0 Hz, CO, aryl), 152.9 (s, CO_3). IR, cm^{-1}: ν(CO) 1752 (KBr). MS (MALDI TOF/TOF): *m/z* (%)=805 (4) $[M+Na]^+$, 783 (14) $[M+H]^+$, 644 (100) $[M-menthyl+H]^+$, 600 (52) $[M-menthylO_2C+H]^+$. Anal. Calcd for $C_{51}H_{43}O_6P$: C, 78.24; H, 5.54; P, 3.96. Found: C, 78.49; H, 5.64; P, 3.88.

*4.2.4. (R_a)-2-[(S_a)-Dinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphosphepin-4-yloxy]-1,1′-binaphthyl-2′-yl (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl carbonate ((R_a)-**5a**).* Yield: 1.19 g (76%) as white solid, mp149–150 °C. ^{1}H NMR ($CDCl_3$, 25 °C): δ=0.25 (d, *J*=7.3 Hz, 3H, menthyl), 0.53 (d, *J*=6.5 Hz, 3H, menthyl), 0.68–0.79 (m, 2H, menthyl), 0.82 (d, *J*=7.3 Hz, 3H, menthyl), 1.01–1.15 (m, 2H, menthyl), 1.23–1.33 (m, 2H, menthyl), 1.43–1.55 (m, 2H, menthyl), 1.81 (br d, *J*=12.0 Hz, 1H, menthyl), 4.20–4.28 (m, 1H, menthyl), 7.15–7.25 (m, 6H, CH, aryl), 7.25–7.32 (m, 4H, CH, aryl), 7.33–7.43 (m, 4H, CH, aryl), 7.46–7.60 (m, 3H, CH, aryl), 7.74 (d, *J*=8.0 Hz, 1H, CH, aryl), 7.83–7.91 (m, 3H, CH, aryl), 7.95 (d, *J*=8.0 Hz, 1H, CH, aryl), 8.04 (d, *J*=8.1 Hz, 1H, CH, aryl), 8.11 (d, *J*=8.1 Hz, 1H, CH, aryl). ^{13}C{H} NMR ($CDCl_3$, 25 °C): δ_C=15.9, 20.2, 21.8 (s, CH_3, menthyl), 23.1 (s, CH_2, menthyl), 25.6, 31.1 (s, CH, menthyl), 33.8, 40.2 (s, CH_2, menthyl), 46.4 (s, CH, menthyl), 78.9 (s, CHO, menthyl), 120.9 (d, ^3J=7.0 Hz, CH, aryl), 121.4, 121.5, 121.6 (s, CH, aryl), 122.3 (d, ^3J=2.1 Hz, C, aryl), 124.1, 124.2, 124.3 (s, C, aryl), 124.6, 124.9, 125.0, 125.7, 125.8, 125.9, 126.0, 126.4, 126.7, 126.8, 126.9, 127.8, 127.9, 128.0, 128.1, 129.1, 129.8, 130.0, 130.1 (s, CH, aryl), 131.3, 131.7, 132.0, 132.6, 133.4, 133.5 (s, C, aryl), 146.9 (d, ^2J=3.0 Hz, CO, aryl), 147.2, 147.3 (s, CO, aryl), 147.6 (d, ^2J=8.1 Hz, CO, aryl), 152.8 (s, CO_3). IR, cm^{-1}: ν(CO) 1755 (KBr). MS (MALDI TOF/TOF): *m/z* (%)=783 (37) $[M+H]^+$, 644 (100) $[M-menthyl+H]^+$, 600 (49) $[M-menthylO_2C+H]^+$. Anal. Calcd for $C_{51}H_{43}O_6P$: C, 78.24; H, 5.54; P, 3.96. Found: C, 78.36; H, 5.49; P, 4.21.

*4.2.5. (S_a)-2-[(S_a)-Dinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphosphepin-4-yloxy]-1,1′-binaphthyl-2′-yl 4-methylbenzenesulfonate ((S_a)-**5b**).* Yield: 1.12 g (74%) as white solid, mp 155–156 °C. ^{1}H NMR ($CDCl_3$, 25 °C): δ=2.04 (s, 3H, CH_3), 6.30 (d, *J*=8.1 Hz, 2H, CH), 6.72 (d, *J*=8.0 Hz, 2H, CH), 7.07 (d, *J*=7.9 Hz, 1H, CH), 7.13–7.24 (m, 6H, CH), 7.25–7.32 (m, 2H, CH), 7.34–7.45 (m, 5H, CH), 7.69 (d, *J*=8.0 Hz, 1H, CH), 7.81–7.90 (m, 5H, CH), 7.92–7.99 (m, 3H, CH), 8.12 (d, *J*=8.1 Hz, 1H, CH). ^{13}C{H} NMR ($CDCl_3$, 26 °C): δ_C=21.3 (s, CH_3), 120.8 (d, ^3J=6.0 Hz, CH, aryl), 121.3, 121.7, 122.3 (s, CH, aryl), 123.3 123.8, 124.2, 124.5 (s, C, aryl), 124.9, 125.0, 125.2, 125.7, 125.8, 126.0, 126.1, 126.4, 126.7, 127.0 (s, CH, aryl), 127.1 (s, CH, tosyl), 127.4, 127.7, 127.9, 128.3, 128.5, 129.2 (s, CH, aryl), 129.4 (s, CH, tosyl), 129.6, 129.9, 130.0 (s, CH, aryl), 131.3, 131.7, 132.0, 132.6, 133.4, 133.5, 134.2 (s, C, aryl), 143.8, 146.3 (s, C, tosyl), 146.9 (s, CO, aryl), 147.4 (d, ^2J=4.3 Hz, CO, aryl), 147.6 (d, ^2J=7.5 Hz, CO, aryl), 148.8 (s, CO, aryl). MS (MALDI TOF/TOF): *m/z* (%)=793 (21) $[M+K]^+$, 777 (17) $[M+Na]^+$, 755 (81) $[M+H]^+$, 600 (100) $[M-Ts+H]^+$. Anal. Calcd for $C_{47}H_{31}O_6PS$: C, 74.79; H, 4.14; P, 4.10. Found: C, 75.02; H, 4.18; P, 3.89.

*4.2.6. (R_a)-2-[(S_a)-Dinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphosphepin-4-yloxy]-1,1′-binaphthyl-2′-yl 4-methylbenzenesulfonate ((R_a)-**5b**).* Yield: 1.19 g (79%) as white solid, mp 182–183 °C. ^{1}H NMR ($CDCl_3$, 25 °C): δ=2.20 (s, 3H, CH_3), 6.32 (d, *J*=8.1 Hz, 1H, CH), 6.71 (d, *J*=8.0 Hz, 2H, CH), 6.93 (d, *J*=12.0 Hz, 1H, CH), 7.06 (d, *J*=7.8 Hz, 2H, CH), 7.12–7.23 (m, 5H, CH), 7.33–7.43 (m, 5H, CH), 7.74–7.90 (m, 10H, CH), 7.93 (d, *J*=8.0 Hz, 1H, CH), 8.0 (d, *J*=8.1 Hz, 1H, CH). ^{13}C{H} NMR ($CDCl_3$, 26 °C): δ_C=21.4 (s, CH_3), 121.2 (d, ^3J=6.2 Hz, CH, aryl), 121.3, 121.6, 122.3 (s, CH, aryl), 123.5 123.9, 124.1, 124.5 (s, C, aryl), 124.9, 125.2, 125.4, 125.5, 126.0, 126.2, 126.3, 126.4, 127.0, 127.2 (s, CH, aryl), 127.5 (s, CH, tosyl), 127.6, 127.7, 127.9, 128.2, 128.5, 129.3 (s, CH, aryl), 129.5 (s, CH, tosyl), 129.7, 130.1, 130.3, 130.5 (s, CH, aryl), 131.4, 131.7, 132.0, 132.5, 133.1, 133.5, 134.4 (s, C, aryl), 143.5, 146.4 (s, C, tosyl), 147.2 (s, CO, aryl), 147.5 (d, ^2J=4.5 Hz, CO, aryl), 147.9 (d, ^2J=7.1 Hz, CO, aryl), 148.7 (s, CO, aryl). MS (MALDI TOF/TOF): *m/z* (%)=793 (43) $[M+K]^+$, 777 (3) $[M+Na]^+$, 755 (92) $[M+H]^+$, 600 (100) $[M-Ts+H]^+$. Anal. Calcd for $C_{47}H_{31}O_6PS$: C, 74.79; H, 4.14; P, 4.10. Found: C, 74.95; H, 4.22; P, 4.14.

4.3. Catalytic reactions

*4.3.1. Pd-catalyzed allylic sulfonylation of (E)-1,3-diphenylallyl acetate **6** with sodium para-toluene sulfinate.* A solution of $[Pd(allyl)Cl]_2$ (0.0019 g, 0.005 mmol) and the appropriate ligand (0.01 mmol or 0.02 mmol) in THF (1.5 mL) was stirred for 40 min. (*E*)-1,3-Diphenylallyl acetate (0.05 mL, 0.25 mmol) was added and the solution stirred for 15 min, then sodium *para*-toluene sulfinate (0.089 g, 0.5 mmol) was added and the reaction mixture stirred for further 48 h, quenched with brine (3 mL), and extracted with THF (3×2 mL). The organic layer was washed with brine (2×2 mL) and dried over $MgSO_4$. The solvent was evaporated at reduced pressure (40 Torr). Crystallization of the residue from EtOH, followed by desiccation in vacuum (10 Torr, 12 h), gave (*E*)-1,3-diphenyl-3-tosylprop-1-ene **7a** as white crystals. The ee of **7a** was determined by HPLC.

*4.3.2. Pd-catalyzed allylic alkylation of (E)-1,3-diphenylallyl acetate **6** with dimethyl malonate.* A solution of $[Pd(allyl)Cl]_2$ (0.0019 g, 0.005 mmol) and appropriate ligand (0.01 mmol or 0.02 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min. (*E*)-1,3-Diphenylallyl acetate (0.05 mL, 0.25 mmol) was added and the solution stirred for 15 min. Dimethyl malonate (0.05 mL, 0.44 mmol), BSA (0.11 mL, 0.44 mmol), and potassium acetate (0.002 g) were added. The reaction mixture was stirred for 48 h, diluted with CH_2Cl_2 or THF (2 mL), and filtered through Celite. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10 Torr, 12 h) affording a residue containing (*E*)-dimethyl 2-(1,3-diphenylallyl)malonate **7b**. In order to evaluate ee and

conversion, the obtained residue was dissolved in an appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis.

*4.3.3. Pd-catalyzed allylic amination of (E)-1,3-diphenylallyl acetate **6** with dipropylamine or pyrrolidine.* A solution of $[Pd(allyl)Cl]_2$ (0.0019 g, 0.005 mmol) and appropriate ligand (0.01 mmol or 0.02 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min. (*E*)-1,3-Diphenylallyl acetate (0.05 mL, 0.25 mmol) was added and the solution stirred for 15 min, then freshly distilled dipropylamine or pyrrolidine (0.75 mmol) was added and the reaction mixture was stirred for further 48 h. The resulting solution was filtered through Celite. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10 Torr, 12 h) affording a residue containing (*E*)-1,3-diphenyl-*N*,*N*-dipropylprop-2-en-1-amine **7c** or (*E*)-1-(1,3-diphenylallyl)pyrrolidine **7d**. In order to evaluate ee and conversion, the obtained residue was dissolved in an appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis.

*4.3.4. Pd-catalyzed allylic alkylation of (E)-1,3-diphenylallyl acetate **6** with 1-cyclohexenylpyrrolidine.* A solution of $[Pd(allyl)Cl]_2$ (0.0019 g, 0.005 mmol) and appropriate ligand (0.01 mmol or 0.02 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min. (*E*)-1,3-Diphenylallyl acetate (0.05 mL, 0.25 mmol) was added and the solution stirred for 15 min, then 1-cyclohexenylpyrrolidine (0.115 g, 0.75 mmol) was added and the reaction mixture was stirred for further 48 h, quenched with saturated NH_4Cl solution (5 mL) for 2 h, and extracted with CH_2Cl_2 (3×3 mL). The combined organic extracts were washed with water (3 mL), brine (3 mL), dried over Na_2SO_4, and concentrated under reduced pressure (40 Torr) after filtration. The residue was dissolved in EtOAc/hexane (1:10) and filtered through a short plug of silica gel. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10 Torr, 12 h) affording a residue containing (*E*)-2-(1,3-diphenylallyl)cyclohexanone of *anti*-configuration (**8a**) and *syn*-configuration (**8b**). The ratio of *anti*- and *syn*-configuration was determined by ^1H NMR. In order to evaluate ee and conversion, the obtained residue was dissolved in an appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis.

*4.3.5. Pd-catalyzed desymmetrization of N,N′-ditosyl-meso-cyclopent-4-ene-1,3-diol biscarbamate **10**.* A solution of $[Pd_2(dba)_3]\cdot CHCl_3$ (0.005 g, 0.005 mmol) and appropriate ligand (0.01 mmol or 0.02 mmol) in the appropriate solvent (1 mL) was stirred for 40 min. The resulting solution was brought to 35 °C and a solution of *N*,*N*′-ditosyl-*meso*-cyclopent-4-ene-1,3-diol biscarbamate **10** and Et_3N (14 μL, 0.099 mmol) in the appropriate solvent (0.5 mL) was added (compound **10** was prepared in situ as follows: to a solution of the *meso*-cyclopent-4-ene-1,3-diol **9** (0.01 g, 0.099 mmol) in the appropriate solvent (0.5 mL), tosyl isocyanate (35 μL, 0.232 mmol) was added; the mixture was stirred at room temperature for 15 min, heated to 55 °C for 1 h and cooled down to room temperature). The reaction mixture was stirred for 24 h. The solvent was removed at reduced pressure (40 Torr) and the residue was purified by flash chromatography on a short pad of silica gel (EtOAc/hexane, 1:4) and dried in vacuum (1 Torr) for 2 h gave the desired product **11** as a slightly brown solid. The ee of **11** was determined by HPLC.

*4.3.6. Rh-catalyzed asymmetric addition of phenylboronic acid to cyclohex-2-enone **12**.* A solution of $[Rh_2(C_2H_4)_2Cl]_2$ (0.0037 g, 0.0094 mmol) and appropriate ligand (0.0188 mmol or 0.0376 mmol) in 1,4-dioxane (1 mL) was stirred for 1 h. Phenylboronic acid (0.065 g, 0.535 mmol) was added and the solution stirred for 2 h. Cyclohex-2-enone (0.05 mL, 0.51 mmol), water (0.125 mL), and Et_3N (0.071 mL, 0.51 mmol) were added. The reaction mixture was stirred for 72 h and diluted with heptane (1.5 mL), MTBE (0.5 mL), and water (2 mL). The organic layer was separated and washed with water (2 mL). The aqueous layers were combined and extracted with MTBE/heptane (1:2, 2 mL). Combined organic layers were filtered through Celite and concentrated in vacuum (40 Torr). The residue was dissolved in heptane, filtered through Celite, concentrated in vacuum (40 Torr), purified by flash chromatography on a short plug of silica gel ($CHCl_3$), and dried in vacuum (1 Torr) for 1 h gave the desired product **13** as a colorless oil. The ee of **13** was determined by HPLC.

Acknowledgements

We acknowledge the financial support from the Russian Foundation for Basic Research (Grant No. 11-03-00347-a) and a grant from the President of the Russian Federation for Young Candidates of Sciences (No. MK-3889.2010.3).

Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.11.092.

References and notes

1. (a) Brown, J. M. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 1999; Vol. I, pp 121–182; (b) Ohkuma, T.; Kitamura, M.; Noyori, R. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley-VCH: New York, NY, 2000; pp 1–110; (c) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921–2943; (d) Blaser, H.-U.; Schmidt, E. *Asymmetric Catalysis on Industrial Scale*; Wiley-VCH: Weinheim, 2004; (e) Burk, M. J. *Acc. Chem. Res.* **2000**, *33*, 363–372; (f) van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Claver, C.; Pamies, O.; Dieguez, M. *Chem. Rev.* **2011**, *111*, 2077–2118.
2. Claver, C.; Pamies, O.; Dieguez, M. In *Phosphorus Ligands in Asymmetric Catalysis*; Börner, A., Ed.; Wiley-VCH: Weinheim, 2008; Vol. II, pp 507–528.
3. Bini, L.; Muller, C.; Vogt, D. *Chem. Commun.* **2010**, 8325–8334.
4. Zhou, Q.-L. *Privileged Chiral Ligands and Catalysts*; Wiley-VCH: Weinheim, 2011.
5. (a) Falciola, C. A.; Alexakis, A. *Eur. J. Org. Chem.* **2008**, 3765–3780; (b) Hargaden, G. C.; Guiry, P. J. *Chem. Rev.* **2009**, *109*, 2505–2550; (c) Au-Yeung, TT.-L.; Chan, S.-S.; Chan, A. S. C. *Adv. Synth. Catal.* **2003**, *345*, 537–555; (d) Caldentey, X.; Pericas, M. A. *J. Org. Chem.* **2010**, *75*, 2628–2644.
6. Nemoto, T.; Hamada, Y. *Tetrahedron* **2011**, *67*, 667–687.
7. (a) Ansell, J.; Wills, M. *Chem. Soc. Rev.* **2002**, *31*, 259–268; (b) Alexakis, A.; Benhaim, C. *Eur. J. Org. Chem.* **2002**, *19*, 3221–3236; (c) Molt, O.; Schrader, T. *Synthesis* **2002**, 2633–2670; (d) Reetz, M. T.; Mehler, G.; Meiswinkel, A.; Sell, T. *Tetrahedron Lett.* **2002**, *43*, 7941–7943; (e) Dieguez, M.; Pamies, O.; Claver, C. *Tetrahedron: Asymmetry* **2004**, *15*, 2113–2122; (f) Gavrilov, K. N.; Bondarev, O. G.; Polosukhin, A. I. *Russ. Chem. Rev.* **2004**, *73*, 671–699; (g) Jerphagnon, T.; Renaud, J.-L.; Bruneau, C. *Tetrahedron: Asymmetry* **2004**, *15*, 2101–2111; (h) Reetz, M. T.; Mehler, G.; Bondarev, O. *Chem. Commun.* **2006**, 2292–2294; (i) de Vries, J. G.; Lefort, L. *Chem.—Eur. J.* **2006**, *12*, 4722–4734; (j) Jagt, R. B. C.; Toullec, P. Y.; Geerdink, D.; de Vries, J. G.; Feringa, B. L.; Minnaard, A. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 2789–2791; (k) Swennenhuis, B. H. G.; Chen, R.; van Leeuwen, P. W. N. M.; de Vries, J. G.; Kamer, P. C. J. *Org. Lett.* **2008**, *10*, 989–992; (l) Qiao, X.-C.; Zhu, S.-F.; Zhou, Q.-L. *Tetrahedron: Asymmetry* **2009**, *20*, 1254–1261; (m) Teichert, J. F.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2010**, *49*, 2486–2528.
8. (a) McCarthy, M.; Guiry, P. J. *Tetrahedron* **2001**, *57*, 3809–3844; (b) Crepy, K. V. L.; Imamoto, T. *Adv. Synth. Catal.* **2003**, *345*, 79–101; (c) Graening, T.; Schmalz, H.-G. *Angew. Chem., Int. Ed.* **2003**, *42*, 2580–2584; (d) Chapsal, B. D.; Ojima, I. *Org. Lett.* **2006**, *8*, 1395–1398; (e) Lu, Z.; Ma, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 258–297; (f) Dieguez, M.; Pamies, O. *Acc. Chem. Res.* **2010**, *43*, 312–322; (g) Lam, F. L.; Kwong, F. Y.; Chan, A. S. C. *Chem. Commun.* **2010**, 4649–4667; (h) Fernandez-Perez, H.; Etayo, P.; Panossian, A.; Vidal-Ferran, A. *Chem. Rev.* **2011**, *111*, 2119–2176; (i) Lafrance, D.; Bowles, P.; Leeman, K.; Rafka, R. *Org. Lett.* **2011**, *13*, 2322–2325.
9. (a) Scafato, P.; Caprioli, F.; Rosini, C. *Tetrahedron: Asymmetry* **2011**, *22*, 558–561; (b) Naeemi, Q.; Robert, T.; Kranz, D. P.; Velder, J.; Schmalz, H.-G. *Tetrahedron: Asymmetry* **2011**, *22*, 887–892.
10. Tsarev, V. N.; Lyubimov, S. E.; Shiryaev, A. A.; Zheglov, S. V.; Bondarev, O. G.; Davankov, V. A.; Kabro, A. A.; Moiseev, S. K.; Kalinin, V. N.; Gavrilov, K. N. *Eur. J. Org. Chem.* **2004**, 2214–2222.
11. Francio, G.; Arena, C. G.; Faraone, F.; Graiff, C.; Lanfranchi, M.; Tiripicchio, A. *Eur. J. Inorg. Chem.* **1999**, 1219–1227.
12. Trotta, F.; Costa, L.; Cravotto, G. *J. Incl. Phenom. Macrocycl. Chem.* **2002**, *44*, 341–343.
13. Solinas, M.; Meadows, R. E.; Wilson, C.; Blake, A. J.; Woodward, S. *Eur. J. Org. Chem.* **2007**, 1613–1623.
14. (a) Brunel, J. M.; Constantieux, T.; Buono, G. *J. Org. Chem.* **1999**, *64*, 8940–8942; (b) Barta, K.; Holscher, M.; Francio, G.; Leitner, W. *Eur. J. Org. Chem.* **2009**, 4102–4116.

15. (a) Arzoumanian, H.; Buono, G.; Choukrad, M.; Petrignani, J.-F. *Organometallics* **1988**, *7*, 59–62; (b) Ngono, C. J.; Constantieux, T.; Buono, G. *Eur. J. Org. Chem.* **2006**, 1499–1507; (c) Kimura, M.; Uozumi, Y. *J. Org. Chem.* **2007**, *72*, 707–714; (d) Gavrilov, K. N.; Zheglov, S. V.; Rastorguev, E. A.; Groshkin, N. N.; Maksimova, M. G.; Benetsky, E. B.; Davankov, V. A.; Reetz, M. T. *Adv. Synth. Catal.* **2010**, *352*, 2599–2610.
16. Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.
17. Polosukhin, A. I.; Kovalevskii, A. I.; Gavrilov, K. N. *Russ. J. Coord. Chem.* **1999**, *25*, 758–761.
18. Bunten, K. A.; Chen, L.; Fernandez, A. L.; Poe, A. J. *Coord. Chem. Rev.* **2002**, *233–234*, 41–51.
19. (a) Liu, D.; Xie, F.; Zhang, W. *Tetrahedron Lett.* **2007**, *48*, 7591–7594; (b) Zhao, X.; Liu, D.; Xie, F.; Zhang, W. *Tetrahedron* **2009**, *65*, 512–517; (c) Zhao, X.; Liu, D.; Xie, F.; Liu, Y.; Zhang, W. *Org. Biomol. Chem.* **2011**, *9*, 1871–1875.
20. Lukin, K.; Zhang, Q.; Leanna, M. R. *J. Org. Chem.* **2009**, *74*, 929–931.
21. Gavrilov, K. N.; Benetskiy, E. B.; Grishina, T. B.; Rastorguev, E. A.; Maksimova, M. G.; Zheglov, S. V.; Davankov, V. A.; Schaffner, B.; Borner, A.; Rosset, S.; Bailat, G.; Alexakis, A. *Eur. J. Org. Chem.* **2009**, 3923–3929.
22. Buono, G.; Toselli, N.; Martin, D. In *Phosphorus Ligands in Asymmetric Catalysis*; Börner, A., Ed.; Wiley-VCH: Weinheim, 2008; Vol. II, pp 529–546.
23. Auburn, P. R.; McKenzie, P. B.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2033–2046.
24. Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253–266.
25. Lyubimov, S. E.; Davankov, V. A.; Gavrilov, K. N. *Tetrahedron Lett.* **2006**, *47*, 2721–2723.
26. Gavrilov, K. N.; Lyubimov, S. E.; Zheglov, S. V.; Benetsky, E. B.; Davankov, V. A. *J. Mol. Catal. A: Chem.* **2005**, *231*, 255–260.
27. Gavrilov, K. N.; Zheglov, S. V.; Shiryaev, A. A.; Groshkin, N. N.; Rastorguev, E. A.; Benetskiy, E. B.; Davankov, V. A. *Tetrahedron Lett.* **2011**, *52*, 964–968.