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Development of *P**-monodentate diamidophosphites with a C_1-symmetric 1,2-diamine backbone: the effects of substituents in the 1,3,2-diazaphospholidine cycle on Pd-catalyzed asymmetric allylations

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ABSTRACT

We have designed and synthesized a small library of modular monodentate diamidophosphite ligands with stereogenic phosphorus atoms. The library was prepared efficiently from the commercially available and inexpensive (*S*)-*N*-Boc-amino acids. These novel ligands were screened in the Pd-catalyzed asymmetric allylations of (*E*)-1,3-diphenylallyl acetate with dimethyl malonate as the *C*-nucleophile with up to 93% ee being obtained. The results showed that the different substituents in the 1,3,2-diazaphospholidine cycle had remarkable effects on the enantioselectivity.

1. Introduction

The successful development of transition metal catalyzed asymmetric processes over the last few decades has been largely steered by the introduction of new chiral ligands. A chiral ligand is used to both influence the reactivity of the metal and to direct the stereochemical course of the catalyzed reaction. Due to the special metal ligation properties of phosphorus derivatives, phosphorus-containing ligands play a major role as metal binders in asymmetric organometallic catalysis.[1,2] Since the early 1970s, a large number of such stereoselectors have been applied in many asymmetric catalytic transformations. Virtually all available natural compounds, as well as binaphthyl, biphenyl, and ferrocene derivatives, have been used in the preparation of large libraries of different phosphorus-based chiral ligands.[3–16] The overwhelming majority of such ligands in the composition of the corresponding metal complexes is able to catalyze with different enantioselectivities either a certain type of chemical transformation, or one certain reaction. Only so-called privileged ligands, rooted in a few core structures, can be regarded as being truly successful in demonstrating proficiency in various mechanistically unrelated reactions. These ligands are very rare, and their cost significantly restrains their wide practical use.[16,17] As a result, the development of simple and efficient methods for the preparation of inexpensive ligands based on available enantiopure synthons is still a relevant subject.[16,18,19]

In recent years, phosphite-type chiral compounds have emerged as extremely attractive ligands for many metal-catalyzed asymmetric processes. First, they are easy to prepare from inexpensive feedstocks in large quantities through the use of relatively simple condensation processes. Second, phosphite-type ligands are less sensitive to air and other oxidizing agents than typical phosphanes. Hence, this makes it possible to develop protocols for the whole process, including 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 the synthesis and screening of extensive libraries of structurally diverse chiral ligands with the aim of obtaining high activities and selectivities for each particular reaction. In addition, phosphite-type ligands are characterized by a highly modular structure and pronounced π-acceptor capacity.[8,12,19–33]

It should be noted that among the phosphite-type chiral ligands, much attention has been focused on phosphites (three P–O bonds) and phosphoramidites (two P–O bonds and one P–N bond).[8,12,17,19,20,24–26,34–36] Less research has been reported on the synthesis and catalytic application of chiral diamidophosphite ligands (one P–O bond and two P–N bonds).[1,37–43] It is rather important that these compounds have different properties from phosphites or phosphoramidites. For example, nitrogen substituents create more steric bulk around the phosphorus than oxygen, since nitrogen substitution may be greater. Furthermore, the replacement of the oxygen atom in the first coordination sphere of the phosphorus by a nitrogen atom increases the electron density on the phosphorus center.[1,43]

Diamidophosphites with phospholidine rings and asymmetric phosphorus atoms can be considered as very promising

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stereoinducers. In particular, these compounds display balanced electronic characteristics since they are both good π-acceptors (due to the accessibility of low-lying π^{ast}_{PN} orbitals) as well as good σ-donors. The inclusion of the phosphorus atom in the five-membered ring enhances the resistance of the ligands to oxidation and hydrolysis, while the possibility of varying the nature of the substituents on the nitrogen and phosphorus atoms allows control over the steric and electronic parameters. Moreover, their modular nature allows a facile systematic variation of the configuration of the *P**- and *C**-stereocenters in the phospholidine rings.[1,39,44,45] If in this case the donor phosphorus atom is asymmetric, this significantly assists in the transfer of chirality in the key step of the catalytic cycle. In the appropriate complexes, the asymmetric phosphorus atom binds directly to the metal atom. This factor provides a more efficient chiral environment at the site where the enantioselection originates.[4,17,46,47] The efficiency of these ligands strongly depends on their framework. Thus, *P**-mono and *P**,*N*-bidentate diamidophosphites with a phosphabicyclic skeleton **L$_{A–D}$** (Fig. 1)
were used successfully in Pd- and Ir-catalyzed asymmetric allylations, Rh-catalyzed asymmetric additions, and hydrogenations.[33,38,44,45,47–53] At the same time, monocyclic ligands **L$_E$** and **L$_F$** appeared to be ineffective stereoselectors. Thus, practically racemic products were obtained with their use in Pd- and Ir-catalyzed allylic alkylations with the participation of dimethyl malonate.[54,55]

Herein, we report the synthesis of a small series of *P**-monodentate diamidophosphites containing 1,3,2-diazaphospholidine rings and based on C_1-symmetric 1,2-diamines as advantageous precursors. We also report the results of a direct comparison of these stereoselectors in Pd-catalyzed asymmetric allylations of (*E*)-1,3-diphenylallyl acetate. On the one hand, the enantioselective Pd-catalyzed allylic substitution has emerged as a powerful synthetic tool, which is tolerant of various functional groups in the substrate and which operates with a wide range of nucleophiles. As a result, the Pd-catalyzed allylic substitution is a versatile process that is widely used in the total synthesis of enantiopure natural and unnatural products.[2,5,46,56–62] On the other hand, this is a common benchmark test for initial ligand screening. From a functional point of view, the enantiomeric excesses obtained are the simplest indexes for evaluating new chiral ligands.[2,61,63]

2. Results and discussion

The *P**-chiral diamidophosphite ligands **5a–e** and **6a**,**b** were prepared in two steps, starting from the corresponding 1,2-diamines **3a–e**, which are easily prepared from the commercially available (*S*)-*N*-Boc-amino acids **1a–e** (Schemes 1 and 2). It should be noted that these synthons are highly versatile and inexpensive enantiopure raw materials. In the design of novel diamidophosphites, we pursued ligand structures that contained a Ph-substituent at one of the nitrogen atoms. It is known that the proximity of the aryl group to the phosphorus atom is important in enhancing the chiral space around the metal center.[43] Treatment of **1a–e** with aniline in the presence of DCC (1,3-dicyclohexylcarbodiimide) as a coupling agent allowed isolation of the corresponding carbamates **2a–e**.[64] Next, $LiAlH_4$ reduction of **2a–e** leads to (*S*)-N^2-methyl-N^1-phenyl-1,2-diamines **3a–e** with C_1 symmetry. In turn, **3a–e** were used as simple and convenient starting materials for the substituted 2-chloro-3-methyl-1-phenyl-1,3,2-diazaphospholidines **4a–e** as phosphorylating reagents (Scheme 1). Compounds **4a–e** containing the stereogenic phosphorus atoms were obtained by reaction of the corresponding 1,2-diamine **3a–e** and PCl_3 in benzene in the presence of Et_3N as a base because of the concomitant formation of HCl. Reagents **4a–e** are stable on storage under a dry atmosphere, can be easily purified by vacuum distillation, and can be prepared on a gram scale. Compounds **4a–e** are stereoindividual, since the ^{31}P NMR spectra of their solutions in $CDCl_3$ exhibited narrow singlets at δ_P between 154.8 and 161.9. The ^1H and ^{13}C NMR spectra were in agreement with those expected for these C_1 compounds (see Section 4).

Reagents **4a–e** readily and efficiently perform the phosphorylation. Compounds **4a–e** reacted smoothly in toluene in the presence of Et_3N as a HCl scavenger with adamantan-1-ol or methanol (Scheme 2). Diamidophosphites **5a–e** and **6a**,**b** were obtained in rather good yields (77–90%), reflecting their stability during the work-up and purification by distillation under vacuum or by flash chromatography. Compounds **5a–e** and **6a**,**b** are either oils, waxy solids, or liquids, which are readily soluble in common organic solvents. They can also be stored under dry conditions at room temperature over several months without any degradation. The diamidophosphites **5a–e** and **6a**,**b** possess a 1,3,2-diazaphospholidine ring, *P**- and *C**-stereocenters, and various substituents on these chirogenic atoms. They were fully characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, MALDI TOF/TOF or EI mass spectrometry as well as by elemental analysis. The ^{31}P NMR spectroscopic data for **5a–e** and **6a**,**b** are summarized in Table 1. These diamidophosphites are mixtures of epimers with respect to the phosphorus stereocenter and contain 52–77% of the major epimers. Ligands **5a–e** with a bulky adamantyloxy exocyclic substituent at the phosphorus atom contain smaller amounts of the minor epimers. We did not establish the absolute configuration of the *P**-stereocenters in the structure of ligands **5a–e** and **6a**,**b**. Nevertheless, considering the data presented in the literature on the related compounds **L$_A$** (Fig. 1).[33,45,48] it can be assumed that the

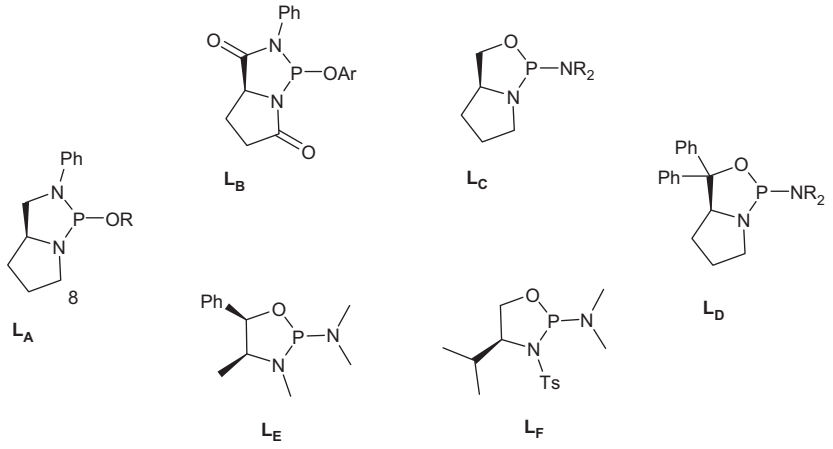
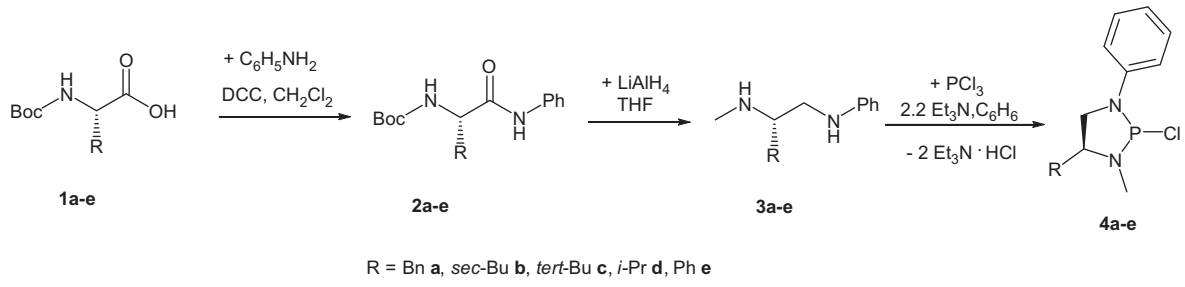
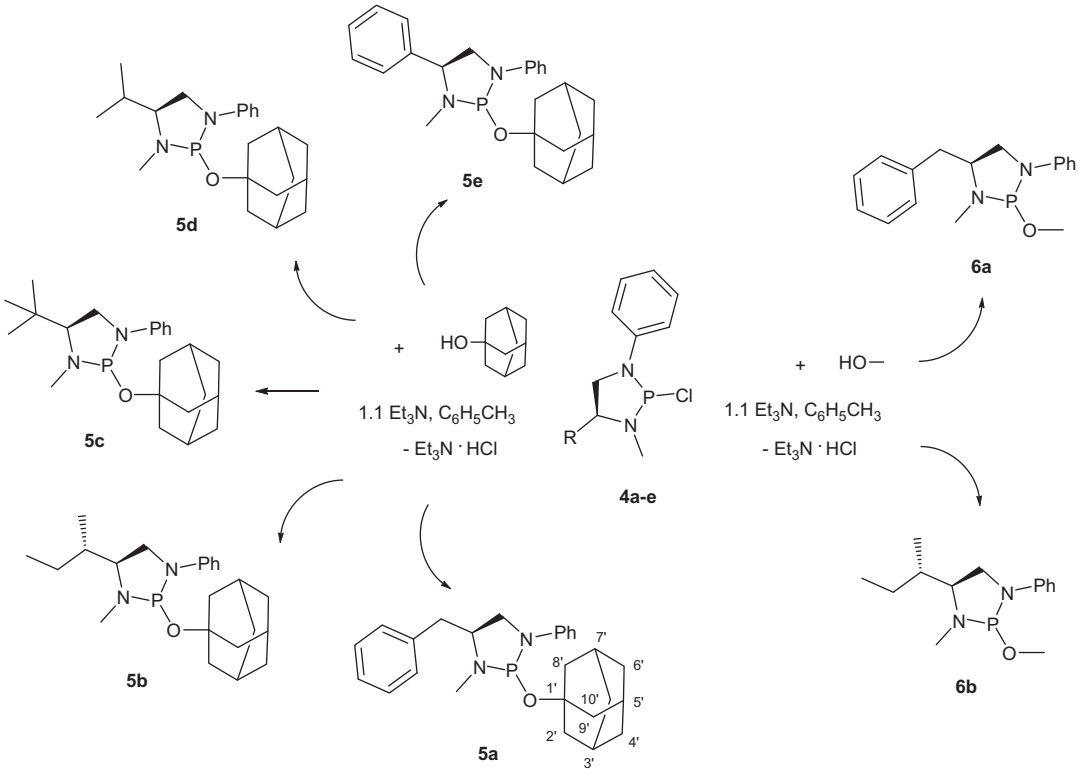


Figure 1. *P**-Chiral 1,3,2-diazaphospholidine and 1,3,2-oxazaphospholidine ligands.



Scheme 1. Synthesis of 1,2-diamines **3a**–**e** and phosphorylating reagents **4a**–**e**.



Scheme 2. Synthesis of *P**-monodentate diamidophosphites **5a**–**e** and **6a**,**b**.

major epimers of **5a**,**b**,**d**,**e** and **6a**,**b** have asymmetric phosphorus atoms with an (*S*)-configuration. The ^{13}C NMR spectra of (2*S*,5*S*)-epimers of diamidophosphites $\mathbf{L_A}$ are characterized by essentially lower spin–spin coupling constants $^{2}J_{C(8),P}$ than the ^{13}C NMR spectra of (2*R*,5*S*)-epimers. Analogously, the $^{2}J_{N\text{-}CH3}$ values (13.6–20.4 Hz) in the ^{13}C NMR spectra of major epimers of **5a**,**b**,**d**,**e** and **6a**,**b** are considerably smaller than in the case of minor epimers (29.5–41.0 Hz) (see Section 4). In the ^{31}P NMR spectra of **5a**,**b**,**d**,**e** and **6a**,**b**, their major epimers have the up-field resonances δ_P 115.1–117.6 (Table 1). On the contrary, the major epimer (59%) of ligand **5c** has a low-field signal δ_P 130.2, high coupling constant $^{2}J_{N\text{-}CH3}$ = 45.3 Hz and, as a result, presumably an (*R*)-configuration for the *P**-stereocenter. In order to estimate the steric demands of ligands **5a**–**e** and **6a**,**b**, we calculated their Tolman's angles[65] by the reported method, by using semi-empirical quantum-mechanical AM1 techniques with full optimization of the geometrical parameters.[66] The results obtained (Table 1) show that the steric demands (θ) of **5a**–**e** and **6a**,**b** vary over a wide range between 134° and 193°, peaking at diamidophosphites **5a** and **5e**. Phosphacyclanes **6a** and **6b** with P-OMe fragments are characterized by moderate steric demands (θ = 140° and 134°, respectively), while **5b** (θ = 151°) and especially **5a** and **5c**–**e** (θ = 166°–193°), bearing adamantyl groups, appear to be substantially more bulky ligands.[65,67]

Table 1
^{31}P NMR chemical shifts ($CDCl_3$) and cone angles θ (deg.) of ligands **5a**–**e** and **6a**,**b**

Ligand	δ_P	θ
5a (38%)[a]	117.5	185
(62%)	116.2	
5b (32%)	120.3	151
(68%)	115.1	
5c (59%)	130.2	174
(41%)	115.6	
5d (23%)	121.0	166
(77%)	115.6	
5e (25%)	117.1	193
(75%)	115.1	
6a (43%)	126.1	140
(57%)	117.6	
6b (48%)	127.8	134
(52%)	116.0	

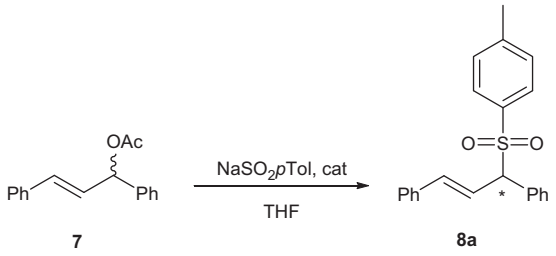
[a] Percentage of *P**-epimers.

With these ligands with pronounced structural diversity in hand, we studied their reactivities and enantioselectivities in the Pd-catalyzed asymmetric allylations of (*E*)-1,3-diphenylallyl acetate **7**. As stated above, the latter was chosen as a substrate because this model process is very convenient for the direct comparison of the efficiency of the different stereoselectors. The catalysts were generated in situ from $[Pd(allyl)Cl]_2$ and the ligands at 1:1 and 2:1 L/Pd molar ratios. In a first set of experiments, we tested the new diamidophosphites in the allylic sulfonylation of **7** with sodium *para*-toluene sulfinate as an *S*-nucleophile, under standard conditions and in THF as the solvent (Table 2). The results obtained showed that the efficiency of these ligands differs dramatically. In particular, sulfone (*R*)-**8a** was obtained in 98% yield and 75% ee when diamidophosphite **5e** with a Ph-substituent at the *C**-stereocenter was employed as the chiral auxiliary (Table 2, entry 9). For **5e**, the L/Pd molar ratio had no effect on the reactivity or enantioselectivity (see Table 2, entries 9 and 10). Compounds **5b**, **5d**, **6a,** and **6b** displayed moderate asymmetric induction (up to 48%, 59%, 42%, and 55% ee, respectively). The palladium catalysts derived from ligands **5a** and **5c** showed excellent activity, but poor enantioselectivity (no more than 19% ee, Table 2, entries 1, 2, 5, and 6). It should be noted that in all cases, the catalytic systems based on novel diamidophosphites led to product **8a** with an (*R*)-configuration.

On the contrary, in the Pd-catalyzed allylic alkylation of **7** with dimethyl malonate as the *C*-nucleophile, diamidophosphites **5a** and **5c** were found to be the most efficient stereoinducers, providing up to 93% and 70% ee, respectively. The enantiomeric excess does not depend on the molar ratio of L/Pd. It is clear that CH_2Cl_2 is the solvent of choice in both cases (Table 3, entries 1–4 and 9–12). At the same time, ligand **5e** afforded product (*R*)-**8b** with low enantiomeric purity (up to 27% ee, Table 3, entries 17–20). As in the case of the allylic sulfonylation, **5b** and **5d** are moderate stereoselectors: enantioselectivities of up to 40% and 69% ee were observed for these ligands. The best asymmetric induction was achieved with L/Pd = 2. The reaction in THF was more enantioselective, while a higher conversion was achieved in CH_2Cl_2 (Table 3, entries 5–8 and 13–16). The effect of the substituent at the *C**-stereocenter was also studied with a pair of less bulky diamidophosphite ligands **6a** and **6b**. The best activities and enantioselectivities were obtained using phosphacyclane **6b**, which contains a *sec*-Bu-substituent (Table 3, 21–24 and 25–28). This behavior is in contrast with the substituent effect observed for the related pair of **5a** and **5b**, for which the enantioselectivity was higher when a Bn-substituent was present. Remarkably, all ligands **5a**–**e** and **6a**,**b** promoted formation of the (*R*)-enantiomer of malonate **8b**.

The novel diamidophosphites were next evaluated in the Pd-catalyzed allylic amination of **7** with pyrrolidine as the *N*-nucleophile. In most experiments, **5a**–**e** and **6a**,**b** demonstrated excellent conversion, but mediocre levels of asymmetric induction (up to 50% ee, Table 4). With regards to the enantioselectivity, the influence of the nature of the substituent at the *C**-stereocenter follows the following trend: *tert*-Bu **5c** (up to 50% ee, entry 10) > *i*-Pr **5d** (up to 47% ee, entry 16) > Bn **5a** (up to 40% ee, entry 4) > Ph **5e** (up to 37% ee, entry 20) > *sec*-Bu **5b** (up to 31% ee, entry 8) and *sec*-Bu **6b** (up to 39% ee, entry 28) > Bn **6a** (up to 19% ee, entry 23). In most cases THF as the reaction medium and a molar ratio L/Pd = 2 are undoubtedly preferable, but the catalytic process with

Table 2
Pd-catalyzed allylic sulfonylation of (*E*)-1,3-diphenylallyl acetate **7** with sodium *para*-toluene sulfinate[a]

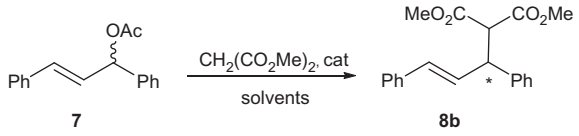


7 **8a**

Entry	Ligand	L/Pd	Yield (%)	ee[b] (%)
1	**5a**	1	98	9 (*R*)
2	**5a**	2	97	19 (*R*)
3	**5b**	1	25	14 (*R*)
4	**5b**	2	40	48 (*R*)
5	**5c**	1	94	2 (*R*)
6	**5c**	2	95	3 (*R*)
7	**5d**	1	70	55 (*R*)
8	**5d**	2	98	59 (*R*)
9	**5e**	**1**	**98**	**75 (*R*)**
10	**5e**	2	95	74 (*R*)
11	**6a**	1	53	42 (*R*)
12	**6a**	2	90	7 (*R*)
13	**6b**	1	98	55 (*R*)
14	**6b**	2	82	15 (*R*)

[a] All reactions were carried out with 2 mol % of $[Pd(allyl)Cl]_2$ in THF at room temperature for 48 h.
[b] Enantiomeric excess of **8a** was determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH = 4/1, 0.5 mL/min, 254 nm, *t*(*R*) = 16.3 min, *t*(*S*) = 18.5 min).

Table 3
Pd-catalyzed allylic alkylation of (*E*)-1,3-diphenylallyl acetate **7** with dimethyl malonate[a]

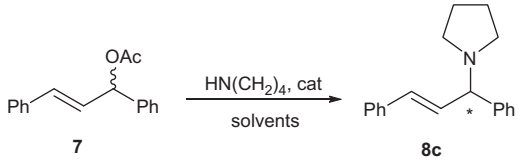


7 **8b**

Entry	Ligand	L/Pd	Solvent	Conversion (%)	ee[b] (%)
1	**5a**	1	CH_2Cl_2	100	90 (*R*)
2	**5a**	**2**	**CH_2Cl_2**	**99**	**93 (*R*)**
3	**5a**	1	THF	34	7 (*R*)
4	**5a**	2	THF	100	46 (*R*)
5	**5b**	1	CH_2Cl_2	52	9 (*R*)
6	**5b**	2	CH_2Cl_2	100	30 (*R*)
7	**5b**	1	THF	20	11 (*R*)
8	**5b**	2	THF	47	40 (*R*)
9	**5c**	1	CH_2Cl_2	35	65 (*R*)
10	**5c**	2	CH_2Cl_2	86	70 (*R*)
11	**5c**	1	THF	0	–
12	**5c**	2	THF	0	–
13	**5d**	1	CH_2Cl_2	100	29 (*R*)
14	**5d**	2	CH_2Cl_2	100	63 (*R*)
15	**5d**	1	THF	0	–
16	**5d**	2	THF	50	69 (*R*)
17	**5e**	1	CH_2Cl_2	78	20 (*R*)
18	**5e**	2	CH_2Cl_2	91	27 (*R*)
19	**5e**	1	THF	34	20 (*R*)
20	**5e**	2	THF	33	25 (*R*)
21	**6a**	1	CH_2Cl_2	100	11 (*R*)
22	**6a**	2	CH_2Cl_2	100	26 (*R*)
23	**6a**	1	THF	25	0
24	**6a**	2	THF	60	2 (*R*)
25	**6b**	1	CH_2Cl_2	100	54 (*R*)
26	**6b**	2	CH_2Cl_2	100	47 (*R*)
27	**6b**	1	THF	100	6 (*R*)
28	**6b**	2	THF	100	50 (*R*)

[a] All reactions were carried out with 2 mol % of $[Pd(allyl)Cl]_2$ at room temperature for 48 h (BSA, KOAc).
[b] The conversion of substrate **7** and enantiomeric excess of **8b** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH = 99/1, 0.3 mL/min, 254 nm, *t*(*R*) = 28.0 min, *t*(*S*) = 29.3 min).

Table 4
Pd-catalyzed allylic amination of (*E*)-1,3-diphenylallyl acetate **7** with pyrrolidine[a]



7 **8c**

Entry	Ligand	L/Pd	Solvent	Conversion (%)	ee[b] (%)
1	**5a**	1	CH_2Cl_2	100	2 (*S*)
2	**5a**	2	CH_2Cl_2	100	4 (*S*)
3	**5a**	1	THF	100	20 (*S*)
4	**5a**	2	THF	100	40 (*S*)
5	**5b**	1	CH_2Cl_2	100	2 (*R*)
6	**5b**	2	CH_2Cl_2	100	3 (*R*)
7	**5b**	1	THF	32	13 (*R*)
8	**5b**	2	THF	61	31 (*R*)
9	**5c**	1	CH_2Cl_2	83	40 (*S*)
10	**5c**	**2**	**CH_2Cl_2**	**100**	**50 (*S*)**
11	**5c**	1	THF	82	17 (*S*)
12	**5c**	2	THF	61	49 (*S*)
13	**5d**	1	CH_2Cl_2	100	0
14	**5d**	2	CH_2Cl_2	100	2 (*S*)
15	**5d**	1	THF	100	33 (*S*)
16	**5d**	2	THF	100	47 (*S*)
17	**5e**	1	CH_2Cl_2	100	35 (*R*)
18	**5e**	2	CH_2Cl_2	100	25 (*R*)
19	**5e**	1	THF	77	29 (*S*)
20	**5e**	2	THF	100	37 (*S*)
21	**6a**	1	CH_2Cl_2	100	5 (*R*)
22	**6a**	2	CH_2Cl_2	100	6 (*R*)
23	**6a**	1	THF	50	19 (*R*)
24	**6a**	2	THF	100	11 (*R*)
25	**6b**	1	CH_2Cl_2	100	19 (*S*)
26	**6b**	2	CH_2Cl_2	100	33 (*S*)
27	**6b**	1	THF	100	19 (*S*)
28	**6b**	2	THF	100	39 (*S*)

[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 **7** and enantiomeric excess of **8c** 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, *t*(*R*) = 5.0 min, *t*(*S*) = 6.1 min).

participation of **5c** resulted in higher conversion and enantioselectivity in CH_2Cl_2. In the allylic amination of substrate **7**, not only different stereoinducers, but even different solvents caused the formation of the opposite enantiomers of amine **8c** (Table 4, see, together with others, entries 17–20).

3. Conclusion

In summary, our results have led us to the following conclusions: (i) we have developed a small family of easily accessible monodentate *P**-chirogenic diamidophosphites **5a**–**e** and **6a**,**b**. The advantage of these ligands is that their modular nature enables the substituents in the 1,3,2-diazaphospholidine ring and the steric demands to be easily and systematically varied, so their influence on the effectiveness at transferring the chiral information can be studied; (ii) moderate to good enantioselectivity (up to 93% ee) was obtained in the Pd-catalyzed asymmetric allylations of (*E*)-1,3-diphenylallyl acetate as a benchmark substrate. Furthermore, **5a**–**e** and **6a**,**b** are substantially more successful stereoselectors, than the known similar monocyclic diamidophosphites $\mathbf{L_E}$ and $\mathbf{L_F}$, despite the fact that the latter have a higher diastereomeric purity;[54,55,68] (iii) the results showed that the different substituents at the *C**-stereocenter have very marked effects on the activity and enantioselectivity. However, the concrete substituent outcome depends strongly on the nature of the nucleophile; (iv) as a whole, the most sterically demanding phosphacyclanes **5e**, **5a,** and **5c** (θ = 193°, 185° and 174°), bearing the adamantyl group, are the best stereoselectors in the Pd-catalyzed allylic sulfonylations, alkylations, and aminations, respectively. The enantioselectivity obtained with the less bulky diamidophosphites **6a** and **6b** was poor or mediocre. Nevertheless, in some cases these ligands were more efficient than the related compounds **5a** and **5b**. It is clear that the asymmetric induction is powerfully affected by the substituents at the *C**- and *P**-stereocenters, the steric properties of the ligands, and the nature of the nucleophile.

In general, *P**-chiral monocyclic diamidophosphites with a 1,3,2-diazaphospholidine ring are very attractive for further research due to their easy accessibility, stability, facile modular construction, and because they are inexpensive. The availability of many C_1-symmetric 1,2-diamines makes ligand-tuning possible, which allows the synthesis of many series of diamidophosphite ligands that can be screened in transition metal catalyzed asymmetric reactions for high activity and enantioselectivity. As a result, such investigations are currently in progress in our laboratories.

4. Experimental

4.1. General

The ^{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). The 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). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants in Hertz (Hz) integration. Mass spectra were recorded with a Varian MAT 311 spectrometer (EI) and a Bruker Daltonics Ultraflex spectrometer (MALDI TOF/TOF). HPLC analyses were performed on Agilent 1100 and Stayer instruments using Chiralcel® columns. Optical rotations were measured on a Perkin–Elmer 341 polarimeter. 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, benzene, toluene, and tetrahydrofuran were freshly distilled from sodium benzophenone ketyl before use; dichloromethane was distilled from NaH. Triethylamine and pyrrolidine were distilled over KOH and then over a small amount of $LiAlH_4$ before use. Thin-layer chromatography was performed on E. Merck pre-coated silica gel 60 F254 and Macherey-Nagel Alugram Alox N/UV_{254} plates. Column chromatography was performed using silica gel MN Kieselgel 60 (230–400 mesh) and MN-Aluminum oxide, basic, Brockmann Activity 1. Carbamates **2a**–**e** were synthesized using a modified literature procedure.[64] All spectroscopic data for compounds **2a**, **2d**, **3d,** and **3e** were in good agreement with the literature.[64,69,70] Phosphorylating reagents **4a**–**e** and ligands **5a**–**e**, **6a**,**b** were prepared analogously to known procedures.[45,49,71] $[Pd(allyl)Cl]_2$ and starting substrate **7** were obtained as published.[72] Pd-catalyzed allylic substitution: sulfonylation of substrate **7** with sodium *para*-toluene sulfinate, alkylation with dimethyl malonate, and amination with pyrrolidine were performed according to the appropriate procedures.[49,73] (*S*)-*N*-Boc-amino acids **1a**–**e**, DCC (1,3-dicyclohexylcarbodiimide), aniline, adamantan-1-ol, 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.

4.2. General procedure for the preparation of carbamates 2a–e

To a vigorously stirred solution of the relevant (*S*)-*N*-Boc-amino acid **1a–e** (15.1 mmol) and aniline (1.93 mL, 21.1 mmol) in CH_2Cl_2 (25 mL) was added DCC (3.43 g, 16.6 mmol) in small portions. The solution was stirred at room temperature for 16 h, filtered on Celite, and then concentrated under vacuum (40 Torr). The crude product was purified by flash chromatography on silica gel (EtOAc/hexane, 4:1) and then by crystallization from heptane, to afford the relevant compounds **2a–e** in good yield.

4.2.1. *tert*-Butyl (2*S*,3*S*)-3-methyl-1-oxo-1-(phenylamino)pentan-2-ylcarbamate 2b

White powder (3.52 g, yield 76%). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 0.91 (t, J = 7.4 Hz, 3H), 0.99 (d, J = 6.8 Hz, 3H), 1.12–1.26 (m, 2H), 1.43 (s, 9H), 1.92–2.0 (br m, 1H), 4.05–4.13 (br m, 1H), 5.24 (br d, J ~8.8 Hz, 1H), 7.06 (t, J = 7.4 Hz, 1H), 7.24 (t, J = 7.5 Hz, 2H), 7.48 (d, J = 7.8 Hz, 2H), 8.28 (br s, 1H). Anal. Calcd for $C_{17}H_{26}N_2O_3$: C, 66.64; H, 8.55; N, 9.14. Found: C, 66.78; H, 8.61; N, 9.07.

4.2.2. (*S*)-*tert*-Butyl 3,3-dimethyl-1-oxo-1-(phenylamino)butan-2-ylcarbamate 2c

White powder (3.33 g, yield 72%). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.06 (s, 9H), 1.42 (s, 9H), 4.03 (br d, J ~9.4 Hz, 1H), 5.40 (br d, J ~9.1 Hz, 1H), 7.07 (t, J = 7.8 Hz, 1H), 7.27 (t, J = 8.0 Hz, 2H), 7.46 (d, J = 8.8 Hz, 2H), 7.88 (br s, 1H). Anal. Calcd for $C_{17}H_{26}N_2O_3$: C, 66.64; H, 8.55; N, 9.14. Found: C, 66.74; H, 8.43; N, 9.01.

4.2.3. (*S*)-*tert*-Butyl 2-oxo-1-phenyl-2-(phenylamino)ethylcarbamate 2e

White powder (4.19 g, yield 85%). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.42 (s, 9H), 5.35 (br s, 1H), 5.81 (br s, 1H), 7.07 (t, J = 7.4 Hz, 1H), 7.23–7.30 (m, 2H), 7.31–7.39 (m, 3H), 7.41–7.48 (m, 4H), 7.79 (br s, 1H). Anal. Calcd for $C_{19}H_{22}N_2O_3$: C, 69.92; H, 6.79; N, 8.58. Found: C, 69.72; H, 6.63; N, 8.62.

4.3. General procedure for the preparation of 1,2-diamines 3a–e

To a vigorously stirred cold suspension of $LiAlH_4$ (1.02 g, 27 mmol) in THF (50 mL), 10.8 mmol of the relevant carbamates **2a–e** was added portionwise. The reaction mixture was then heated up to boiling point, refluxed for 8 h, and hydrolyzed with 2 mL of 15% aqueous KOH solution at 0 °C. The reaction mixture was then quickly heated up to boiling point, cooled down to room temperature, and filtered. The filter cake was washed with THF (2 × 20 mL) and CH_2Cl_2 (2 × 20 mL) and the combined filtrates were concentrated under vacuum (40 Torr). All volatiles were removed under vacuum and the crude product was purified by bulb-to-bulb distillation under vacuum (1 Torr).

4.3.1. (*S*)-N^2-Methyl-N^1,3-diphenylpropane-1,2-diamine 3a

Colorless oil (2.13 g, yield 82%). Bp 152–153 °C (1 Torr). $[\alpha]_D^{25}$ = +28.7 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.78 (br s, 1H), 2.49 (s, 3H), 2.80–2.88 (m, 1H), 2.90–2.97 (m, 1H), 3.01–3.12 (m, 2H), 3.18–3.26 (m, 1H), 4.28 (br s, 1H), 6.65 (d, J = 8.1 Hz, 2H), 6.75 (t, J = 7.8 Hz, 1H), 7.19–7.42 (m, 7H). Anal. Calcd for $C_{16}H_{20}N_2$: C, 79.96; H, 8.39; N, 11.66. Found: C, 79.88; H, 8.18; N, 11.59.

4.3.2. (2*S*,3*S*)-N^2,3-Dimethyl-N^1-phenylpentane-1,2-diamine 3b

Slightly yellow oil (1.58 g, yield 71%). Bp 110–111 °C (1 Torr). $[\alpha]_D^{25}$ = +9.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 0.88 (d, J = 6.8 Hz, 3H), 0.94 (t, J = 7.4 Hz, 3H), 1.23–1.31 (m, 1H), 1.43–1.51 (m, 1H), 1.66–1.73 (m, 1H), 1.75 (br s, 1H), 2.39 (s, 3H), 2.51–2.59 (m, 1H), 2.82–2.90 (m, 1H), 3.12–3.20 (m, 1H), 4.20 (br s, 1H), 6.63 (d, J = 7.6 Hz, 2H), 6.68 (t, J = 7.5 Hz, 1H), 7.17 (t, J = 7.6 Hz, 2H). Anal. Calcd for $C_{13}H_{22}N_2$: C, 75.68; H, 10.75; N, 13.58. Found: C, 75.93; H, 10.89; N, 13.67.

4.3.3. (*S*)-N^2,3,3-Trimethyl-N^1-phenylbutane-1,2-diamine 3c

Slightly yellow oil (1.72 g, yield 77%). Bp 118–119 °C (1 Torr). $[\alpha]_D^{25}$ = +16.7 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.0 (s, 9H), 1.82 (br s, 1H), 2.25–2.33 (m, 1H), 2.51 (s, 3H), 2.91–2.99 (m, 1H), 3.23–3.31 (m, 1H), 4.21 (br s, 1H), 6.64 (d, J = 7.8 Hz, 2H), 6.70 (t, J = 7.4 Hz, 1H), 7.19 (t, J = 8.0 Hz, 2H). Anal. Calcd for $C_{13}H_{22}N_2$: C, 75.68; H, 10.75; N, 13.58. Found: C, 75.89; H, 10.79; N, 13.39.

4.4. General procedure for the preparation of phosphorylating reagents 4a–e

To a vigorously stirred solution of PCl_3 (0.88 mL, 10 mmol) and Et_3N (3.06 mL, 22 mmol) in benzene (100 mL) was added dropwise a solution of the relevant 1,2-diamine **3a–e** (10 mmol) in benzene (50 mL) at 0 °C over 30 min. The reaction mixture was then heated up to boiling point, refluxed for 5 min, and cooled down to 20 °C. Solid $Et_3N{\cdot}HCl$ was filtered off, and the filtrate was concentrated under vacuum (40 Torr). The residue was dried for 30 min at 10 Torr and purified by bulb-to-bulb distillation under vacuum (1 Torr).

4.4.1. (4*S*)-4-Benzyl-2-chloro-3-methyl-1-phenyl-1,3,2-diazaphospholidine 4a

Light yellow resin, solidifying on storage (2.41 g, yield 79%). T_{bath} 232–235 °C (1 Torr). $[\alpha]_D^{20}$ = −127.1 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 2.81 (d, J = 18.1 Hz, 3H), 3.17–3.25 (m, 1H), 3.26–3.35 (m, 1H), 3.36–3.44 (m, 1H), 3.51–3.59 (m, 1H), 3.79–3.88 (m, 1H), 6.89–6.97 (m, 3H), 7.09–7.32 (m, 7H). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 31.5 (d, ^2J = 18.1 Hz, CH_3N), 38.3 (d, ^3J = 3.8 Hz, CH_2Ph), 53.6 (d, ^2J = 9.1 Hz, CH_2N), 64.1 (d, ^2J = 11.3 Hz, CHN), 116.4 (d, ^3J = 14.3 Hz, CH_{PhN}), 121.5 (d, ^4J = 2.2 Hz, CH_{PhN}), 126.8 (s, CH_{Ph}), 128.8 (s, CH_{Ph}), 129.0 (s, CH_{Ph}), 129.3 (s, CH_{PhN}), 137.4 (s, C_{Ph}), 142.7 (d, ^2J = 15.1 Hz, C_{PhN}). ^{31}P NMR ($CDCl_3$, 25 °C): δ = 156.7. MS (EI, 70 eV): m/z (%) = 304 (28) $[M]^+$, 269 (100) $[M-Cl]^+$. Anal. Calcd for $C_{16}H_{18}ClN_2P$: C, 63.06; H, 5.95; N, 9.19. Found: C, 63.36; H, 6.07; N, 9.38.

4.4.2. (4*S*)-4-*sec*-Butyl-2-chloro-3-methyl-1-phenyl-1,3,2-diazaphospholidine 4b

Slightly yellow viscous oil (1.87 g, yield 69%). T_{bath} 204–207 °C (1 Torr). $[\alpha]_D^{21}$ = −109.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 0.87 (d, J = 6.8 Hz, 3H), 1.0 (t, J = 7.8 Hz, 3H), 1.21–1.29 (m, 1H), 1.34–1.42 (m, 1H), 1.84–1.92 (m, 1H), 2.72 (d, J = 16.1 Hz, 3H), 3.42–3.49 (m, 1H), 3.57–3.65 (m, 1H), 3.65–3.73 (m, 1H), 6.97 (t, J = 7.2 Hz, 1H), 7.04–7.10 (m, 2H), 7.30 (t, J = 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 11.5 (s, CH_3), 12.2 (s, CH_3), 27.2 (s, CH_2), 30.8 (d, ^2J = 19.6 Hz, CH_3N), 33.5 (d, ^3J = 3.8 Hz, CH), 48.2 (d, ^2J = 9.1 Hz, CH_2N), 65.8 (d, ^2J = 10.6 Hz, CHN), 116.3 (d, ^3J = 15.9 Hz, CH_{Ph}), 121.3 (d, ^4J = 2.3 Hz, CH_{Ph}), 129.2 (s, CH_{Ph}), 142.8 (d, ^2J = 15.0 Hz, C_{Ph}). ^{31}P NMR ($CDCl_3$, 25 °C): δ = 158.2. MS (EI, 70 eV): m/z (%) = 270 (57) $[M]^+$, 235 (100) $[M-Cl]^+$. Anal. Calcd for $C_{13}H_{20}ClN_2P$: C, 57.67; H, 7.45; N, 10.35. Found: C, 58.02; H, 7.25; N, 10.58.

4.4.3. (4*S*)-4-*tert*-Butyl-2-chloro-3-methyl-1-phenyl-1,3,2-diazaphospholidine 4c

Slightly yellow viscous oil (2.0 g, yield 74%). T_{bath} 215–218 °C (1 Torr). $[\alpha]_D^{20}$ = −124.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 0.98 (s, 9H), 2.92 (d, J = 16.0 Hz, 3H), 3.24–3.32 (m, 1H), 3.53–3.61 (m, 1H), 3.82–3.91 (m, 1H), 7.0 (t, J = 8.0 Hz, 1H), 7.05–7.11 (m, 2H), 7.30 (t, J = 7.9 Hz, 2H). ^{13}C NMR ($CDCl_3$, 25 °C):

δ = 27.7 (s, CH_3), 36.7 (d, ^2J = 17.1 Hz, CH_3N), 46.6 (s, C), 51.9 (d, ^2J = 8.1 Hz, CH_2N), 73.4 (d, ^2J = 11.1 Hz, CHN), 118.2 (d, ^3J = 14.1 Hz, CH_{Ph}), 121.8 (d, ^4J = 2.0 Hz, CH_{Ph}), 130.2 (s, CH_{Ph}), 143.2 (d, ^2J = 13.1 Hz, C_{Ph}). ^{31}P NMR ($CDCl_3$, 25 °C): δ = 161.9. MS (EI, 70 eV): *m*/*z* (%) = 270 (68) $[M]^+$, 235 (100) $[M-Cl]^+$. Anal. Calcd for $C_{13}H_{20}ClN_2P$: C, 57.67; H, 7.45; N, 10.35. Found: C, 57.46; H, 7.55; N, 10.39.

4.4.4. (4*S*)-2-Chloro-4-isopropyl-3-methyl-1-phenyl-1,3,2-diazaphospholidine 4d

White viscous oil (1.72 g, yield 67%). T_{bath} 210–214 °C (1 Torr). $[\alpha]_D^{20}$ = +93.5 (*c* 1.0, C_6H_6). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 0.89 (d, *J* = 4.1 Hz, 3H), 1.0 (d, *J* = 7.9 Hz, 3H), 2.11–2.19 (m, 1H), 2.73 (d, *J* = 16.4 Hz, 3H), 3.45–3.53 (m, 1H), 3.56–3.67 (m, 2H), 6.97 (t, *J* = 8.1 Hz, 1H), 7.07 (br d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 14.2 (s, CH_3), 19.5 (s, CH_3), 26.7 (d, ^3J = 3.8 Hz, CH), 31.1 (d, ^2J = 18.9 Hz, CH_3N), 48.4 (d, ^2J = 9.1 Hz, CH_2N), 67.1 (d, ^2J = 11.3 Hz, CHN), 116.4 (d, ^3J = 14.3 Hz, CH_{Ph}), 121.4 (d, ^4J = 2.3 Hz, CH_{Ph}), 129.3 (s, CH_{Ph}), 142.8 (d, ^2J = 15.1 Hz, C_{Ph}). ^{31}P NMR ($CDCl_3$, 25 °C): δ = 158.6. MS (EI, 70 eV): *m*/*z* (%) = 256 (33) $[M]^+$, 221 (100) $[M-Cl]^+$. Anal. Calcd for $C_{12}H_{18}ClN_2P$: C, 56.14; H, 7.07; N, 10.91. Found: C, 55.86; H, 7.25; N, 10.69.

4.4.5. (4*S*)-2-Chloro-3-methyl-1,4-diphenyl-1,3,2-diazaphospholidine 4e

Slightly yellow resin (2.06 g, yield 71%). T_{bath} 241–244 °C (1 Torr). $[\alpha]_D^{20}$ = −154.4 (*c* 0.9, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 2.57 (d, *J* = 16.6 Hz, 3H), 3.62–3.70 (m, 1H), 4.06 (br t, *J* = 11.9 Hz, 1H), 4.60–4.68 (m, 1H), 6.99 (t, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.34–7.45 (m, 5H). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 31.5 (d, ^2J = 17.4 Hz, CH_3N), 57.2 (d, ^2J = 9.2 Hz, CH_2N), 67.7 (d, ^2J = 10.6 Hz, CHN), 116.2 (d, ^3J = 15.1 Hz, CH_{PhN}), 121.5 (d, ^4J = 1.9 Hz, CH_{PhN}), 127.8 (s, CH_{Ph}), 128.6 (s, CH_{Ph}), 129.0 (s, CH_{PhN}), 129.4 (s, CH_{Ph}), 137.9 (d, ^3J = 4.5 Hz, C_{Ph}), 142.6 (d, ^2J = 15.2 Hz, C_{PhN}). ^{31}P NMR ($CDCl_3$, 25 °C): δ = 154.8. MS (EI, 70 eV): *m*/*z* (%) = 290 (14) $[M]^+$, 255 (100) $[M-Cl]^+$. Anal. Calcd for $C_{15}H_{16}ClN_2P$: C, 61.97; H, 5.55; N, 9.64. Found: C, 62.11; H, 5.61; N, 9.34.

4.5. General procedure for the preparation of ligands 5a–e and 6a,b

To a vigorously stirred solution of the relevant phosphorylating reagents **4a**–**e** (4 mmol) and Et_3N (0.61 mL, 4.4 mmol) in toluene (10 mL) was added dropwise a solution of adamantan-1-ol or methanol (4 mmol) in toluene (10 mL) at 0 °C over 20 min. The reaction mixture was then heated up to boiling point, refluxed for 10 min, and cooled down to 20 °C. Solid $Et_3N{\cdot}HCl$ was then removed by filtration. The resulting solution was filtered through a short plug of aluminum oxide, and the solvent evaporated under reduced pressure (40 Torr). The residue was purified by bulb-to-bulb distillation under vacuum (1 Torr, **5b**, **5c**, **5d**, **6a,** and **6b**) or by flash chromatography on aluminum oxide (EtOAc/hexane, 1:1, **5a** and 1:3, **5e**).

4.5.1. (4*S*)-4-Benzyl-3-methyl-1-phenyl-2-(tricyclo[3.3.1.1.$^{3',7'}$]dec-1′-yloxy)-1,3,2-diazaphospholidine 5a

Colorless viscous oil (1.36 g, yield 81%). $[\alpha]_D^{22}$ = +254.4 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.63 (br s, 6H), 1.91 (br s, 4H), 1.93–2.05 (br m, 2H), 2.15 (br s, 3H), 2.72 (d, *J* = 15.0 Hz, 3H), 3.07–3.15 (m, 1H), 3.45–3.55 (m, 2H), 3.57–3.65 (m, 1H), 3.77–3.85 (m, 1H), 6.80 (t, *J* = 8.2 Hz, 1H), 6.95 (br d, *J* ~8.1 Hz, 2H), 7.17–7.38 (m, 7H) (major epimer) and 1.65 (br s, 6H), 1.91 (br s, 4H), 1.93–2.05 (br m, 2H), 2.15 (br s, 3H), 2.53 (t, *J* = 9.3 Hz, 1H), 2.84 (d, *J* = 12.0 Hz, 3H), 3.19–3.30 (m, 2H), 3.57–3.65 (m, 1H), 3.77–3.85 (m, 1H), 6.80 (t, *J* = 8.2 Hz, 1H), 6.95 (br d, *J* ~8.1 Hz, 2H), 7.17–7.38 (m, 7H) (minor epimer). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 31.0 (s, C(3′), C(5′), C(7′)), 31.7 (d, ^2J = 17.4 Hz, CH_3N), 36.1 (s, C(4′), C(6′), C(10′)), 39.2 (d, ^3J = 4.5 Hz, CH_2Ph), 45.2 (d, ^3J = 8.3 Hz, C(2′), C(8′), C(9′)), 52.8 (d, ^2J = 7.6 Hz, CH_2N), 61.9 (d, ^2J = 9.1 Hz, CHN), 73.1 (d, ^2J = 6.8 Hz, C(1′)), 115.0 (d, ^3J = 14.3 Hz, CH_{PhN}), 118.4 (d, ^4J = 2.3 Hz, CH_{PhN}), 126.3 (s, CH_{Ph}), 128.5 (s, CH_{Ph}), 128.9 (s, CH_{Ph}), 129.1 (s, CH_{PhN}), 138.9 (s, C_{Ph}), 145.8 (d, ^2J = 17.4 Hz, C_{PhN}) (major epimer) and 31.0 (s, C(3′), C(5′), C(7′)), 33.1 (d, ^2J = 31.7 Hz, CH_3N), 36.2 (s, C(4′), C(6′), C(10′)), 40.3 (s, CH_2Ph), 45.3 (d, ^3J = 8.2 Hz, C(2′), C(8′), C(9′)), 52.1 (d, ^2J = 9.1 Hz, CH_2N), 65.3 (d, ^2J = 10.6 Hz, CHN), 68.1 (s, C(1′)), 115.1 (d, ^3J = 14.3 Hz, CH_{PhN}), 118.3 (d, ^4J = 1.5 Hz, CH_{PhN}), 126.1 (s, CH_{Ph}), 128.5 (s, CH_{Ph}), 128.9 (s, CH_{Ph}), 129.3 (s, CH_{PhN}), 139.8 (s, C_{Ph}), 146.3 (d, ^2J = 15.7 Hz, C_{PhN}) (minor epimer). MS (MALDI TOF/TOF): *m*/*z* (%) = 439 (82) $[M+H_2O+H]^+$, 421 (80) $[M+H]^+$, 287 (100) $[(PhNCH_2CH(Bn)NMe)POH+H]^+$, 241 (38) $[PhNHCH_2CH(Bn)NHMe+H]^+$, 136 (10) $[C_{10}H_{16}]^+$. Anal. Calcd for $C_{26}H_{33}N_2OP$: C, 74.26; H, 7.91; N, 6.66. Found: C, 74.39; H, 7.83; N, 6.51.

4.5.2. (4*S*)-4-*sec*-Butyl-3-methyl-1-phenyl-2-(tricyclo[3.3.1.1.$^{3',7'}$]dec-1′-yloxy)-1,3,2-diazaphospholidine 5b

Colorless oil (1.31 g, yield 85%). T_{bath} 262–265 °C (1 Torr). $[\alpha]_D^{22}$ = −203.9 (*c* 0.8, C_6H_6). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 0.81 (d, *J* = 6.9 Hz, 3H), 0.97 (t, *J* = 7.8 Hz, 3H), 1.19–1.28 (m, 1H), 1.36–1.46 (m, 1H), 1.63 (br s, 6H), 1.72–1.85 (br m, 2H), 1.92 (br s, 4H), 2.05–2.12 (m, 1H), 2.13 (br s, 3H), 2.55 (d, *J* = 16.2 Hz, 3H), 3.07–3.15 (m, 1H), 3.35–3.65 (m, 2H), 6.81 (t, *J* = 7.5 Hz, 1H), 7.02 (br d, *J* = 8.1 Hz, 2H), 7.16–7.26 (m, 2H) (major epimer) and 0.94 (d, *J* = 7.0 Hz, 3H), 1.01 (t, *J* = 7.7 Hz, 3H), 1.19–1.28 (m, 1H), 1.36–1.46 (m, 1H), 1.63 (br s, 6H), 1.72–1.85 (br m, 2H), 1.92 (br s, 4H), 2.05–2.12 (m, 1H), 2.13 (br s, 3H), 2.77 (d, *J* = 13.2 Hz, 3H), 3.35–3.65 (m, 3H), 6.66 (t, *J* = 7.8 Hz, 1H), 7.00 (br d, *J* = 8.0 Hz, 2H), 7.16–7.26 (m, 2H) (minor epimer). ^{13}C NMR ($CDCl_3$, 26 °C): δ = 11.4 (s, CH_3), 12.6 (s, CH_3), 27.5 (s, CH_2), 31.0 (s, C(3′), C(5′), C(7′)), 31.1 (d, ^2J = 13.6 Hz, CH_3N), 34.1 (d, ^3J = 3.8 Hz, CH), 36.2 (s, C(4′), C(6′), C(10′)), 45.3 (d, ^3J = 7.5 Hz, C(2′), C(8′), C(9′)), 47.3 (d, ^2J = 8.3 Hz, CH_2N), 63.5 (d, ^2J = 9.8 Hz, CHN), 73.5 (d, ^2J = 6.8 Hz, C(1′)), 114.8 (d, ^3J = 15.8 Hz, CH_{Ph}), 118.2 (d, ^4J = 2.3 Hz, CH_{Ph}), 128.9 (s, CH_{Ph}), 145.6 (d, ^2J = 17.1 Hz, C_{Ph}) (major epimer) and 12.5 (s, CH_3), 13.2 (s, CH_3), 27.1 (s, CH_2), 30.8 (s, C(3′), C(5′), C(7′)), 31.3 (d, ^2J = 29.5 Hz, CH_3N), 33.5 (d, ^3J = 6.0 Hz, CH), 36.3 (s, C(4′), C(6′), C(10′)), 45.2 (d, ^3J = 7.5 Hz, C(2′), C(8′), C(9′)), 47.7 (d, ^2J = 8.3 Hz, CH_2N), 67.9 (d, ^2J = 10.6 Hz, CHN), 73.7 (d, ^2J = 5.3 Hz, C(1′)), 116.0 (d, ^3J = 13.6 Hz, CH_{Ph}), 118.4 (d, ^4J = 2.3 Hz, CH_{Ph}), 129.3 (s, CH_{Ph}), 144.9 (d, ^2J = 15.5 Hz, C_{Ph}) (minor epimer). MS (MALDI TOF/TOF): *m*/*z* (%) = 387 (100) $[M+H]^+$, 207 (42) $[PhNHCH_2CH(sec\text{-}Bu)NHMe+H]^+$, 136 (11) $[C_{10}H_{16}]^+$. Anal. Calcd for $C_{23}H_{35}N_2OP$: C, 71.47; H, 9.13; N, 7.25. Found: C, 71.62; H, 9.23; N, 7.19.

4.5.3. (4*S*)-4-*tert*-Butyl-3-methyl-1-phenyl-2-(tricyclo[3.3.1.1.$^{3',7'}$]dec-1′-yloxy)-1,3,2-diazaphospholidine 5c

Colorless oil (1.27 g, yield 82%). T_{bath} 276–279 °C (1 Torr). $[\alpha]_D^{25}$ = +238.1 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 0.99 (s, 9H), 1.59 (br s, 6H), 1.84 (br s, 4H), 1.87–2.95 (br m, 2H), 2.10 (br s, 3H), 2.90 (d, *J* = 16.1 Hz, 3H), 3.06–3.14 (m, 1H), 3.56–3.64 (m, 1H), 3.69–3.76 (m, 1H), 6.77 (t, *J* = 8.0 Hz, 1H), 6.95 (br d, *J* = 7.9 Hz, 2H), 7.18–7.26 (m, 2H) (major epimer) and 0.90 (s, 9H), 1.61 (br s, 6H), 1.83 (br s, 4H), 1.87–2.95 (br m, 2H), 2.10 (br s, 3H), 2.70 (d, *J* = 12.2 Hz, 3H), 3.06–3.14 (m, 1H), 3.56–3.64 (m, 1H), 3.69–3.76 (m, 1H), 6.79 (t, *J* = 7.8 Hz, 1H), 6.99 (br d, *J* = 8.0 Hz, 2H), 7.18–7.26 (m, 2H) (minor epimer). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 27.4 (s, CH_3), 30.9 (s, C(3′), C(5′), C(7′)), 36.3 (s, C(4′), C(6′), C(10′)), 39.7 (d, ^2J = 45.3 Hz, CH_3N), 43.9 (d, ^3J = 3.8 Hz, C),

45.1 (d, ^3J = 8.3 Hz, C(2′), C(8′), C(9′)), 49.8 (d, ^2J = 7.6 Hz, CH_2N), 73.1 (d, ^2J = 6.6 Hz, C(1′)), 75.6 (d, ^2J = 10.6 Hz, CHN), 115.7 (d, ^3J = 13.6 Hz, CH_{Ph}), 118.3 (d, ^4J = 2.3 Hz, CH_{Ph}), 128.9 (s, CH_{Ph}), 145.7 (d, ^2J = 16.0 Hz, C_{Ph}) (major epimer) and 27.0 (s, CH_3), 31.1 (s, C(3′), C(5′), C(7′)), 35.7 (d, ^2J = 14.3 Hz, CH_3N), 36.1 (s, C(4′), C(6′), C(10′)), 43.6 (d, ^3J = 4.5 Hz, C), 45.2 (d, ^3J = 8.3 Hz, C(2′), C(8′), C(9′)), 48.6 (d, ^2J = 6.8 Hz, CH_2N), 71.6 (d, ^2J = 10.6 Hz, CHN), 73.3 (d, ^2J = 6.7 Hz, C(1′)), 116.3 (d, ^3J = 14.3 Hz, CH_{Ph}), 118.7 (d, ^4J = 2.3 Hz, CH_{Ph}), 128.8 (s, CH_{Ph}), 143.7 (d, ^2J = 15.1 Hz, C_{Ph}) (minor epimer). MS (EI, 70 eV): *m*/*z* (%) = 386 (7) $[M]^+$, 329 (100) $[M-t\text{-}Bu]^+$. Anal. Calcd for $C_{23}H_{35}N_2OP$: C, 71.47; H, 9.13; N, 7.25. Found: C, 71.77; H, 8.97; N, 7.36.

4.5.4. (4*S*)-4-Isopropyl-3-methyl-1-phenyl-2-(tricyclo[3.3.1.1.$^{3',7'}$]-dec-1′-yloxy)-1,3,2-diazaphospholidine 5d

Colorless oil (1.34 g, yield 90%). T_{bath} 249–253 °C (1 Torr). $[\alpha]_D^{20}$ = +221.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 26 °C): δ = 0.80 (d, *J* = 4.1 Hz, 3H), 0.97 (d, *J* = 8.0 Hz, 3H), 1.60 (br s, 6H), 1.70–1.82 (br m, 2H), 1.88 (br s, 4H), 2.0–2.08 (m, 1H), 2.12 (br s, 3H), 2.53 (d, *J* = 16.1 Hz, 3H), 3.07–3.15 (m, 1H), 3.37–3.53 (m, 2H), 6.78 (t, *J* = 8.1 Hz, 1H), 7.01 (br d, *J* = 7.9 Hz, 2H), 7.22 (t, *J* = 7.9 Hz, 2H) (major epimer) and 0.94 (d, *J* = 4.0 Hz, 3H), 0.99 (d, *J* = 8.1 Hz, 3H), 1.60 (br s, 6H), 1.70–1.82 (br m, 2H), 1.89 (br s, 4H), 2.0–2.08 (m, 1H), 2.12 (br s, 3H), 2.78 (d, *J* = 12.2 Hz, 3H), 3.19–3.27 (m, 1H), 3.37–3.53 (m, 2H), 6.78 (t, *J* = 8.1 Hz, 1H), 6.96 (br d, *J* = 8.2 Hz, 2H), 7.22 (t, *J* = 7.9 Hz, 2H) (minor epimer). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 13.9 (s, CH_3), 19.6 (s, CH_3), 26.7 (d, ^3J = 4.0 Hz, CH), 30.8 (s, C(3′), C(5′), C(7′)), 31.0 (d, ^2J = 17.1 Hz, CH_3N), 35.9 (s, C(4′), C(6′), C(10′)), 45.0 (d, ^3J = 8.1 Hz, C(2′), C(8′), C(9′)), 47.0 (d, ^2J = 8.1 Hz, CH_2N), 64.4 (d, ^2J = 10.1 Hz, CHN), 72.7 (d, ^2J = 6.0 Hz, C(1′)), 114.6 (d, ^3J = 16.1 Hz, CH_{Ph}), 117.9 (d, ^4J = 1.5 Hz, CH_{Ph}), 128.7 (s, CH_{Ph}), 145.8 (d, ^2J = 18.1 Hz, C_{Ph}) (major epimer) and 16.6 (s, CH_3), 19.6 (s, CH_3), 29.5 (s, CH), 30.7 (s, C(3′), C(5′), C(7′)), 34.2 (d, ^2J = 40.2 Hz, CH_3N), 36.0 (s, C(4′), C(6′), C(10′)), 44.9 (d, ^3J = 9.1 Hz, C(2′), C(8′), C(9′)), 48.1 (d, ^2J = 8.1 Hz, CH_2N), 69.1 (d, ^2J = 10.2 Hz, CHN), 72.5 (d, ^2J = 7.0 Hz, C(1′)), 115.5 (d, ^3J = 14.1 Hz, CH_{Ph}), 118.1 (d, ^4J = 2.3 Hz, CH_{Ph}), 128.6 (s, CH_{Ph}), 145.6 (d, ^2J = 16.2 Hz, C_{Ph}) (minor epimer). MS (MALDI TOF/TOF): *m*/*z* (%) = 411 (18) $[M+K]^+$, 373 (36) $[M+H]^+$, 239 (100) $[(PhNCH_2CH(i\text{-}Pr)NMe)POH+H]^+$, 193 (53) $[PhNHCH_2CH(i\text{-}Pr)NHMe+H]^+$, 136 (13) $[C_{10}H_{16}]^+$. Anal. Calcd for $C_{22}H_{33}N_2OP$: C, 70.94; H, 8.93; N, 7.52. Found: C, 71.21; H, 8.75; N, 7.29.

4.5.5. (4*S*)-3-Methyl-1,4-diphenyl-2-(tricyclo[3.3.1.1.$^{3',7'}$]dec-1′-yloxy)-1,3,2-diazaphospholidine 5e

White waxy solid (1.25 g, yield 77%). $[\alpha]_D^{20}$ = +276.0 (*c* 0.9, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.65 (br s, 6H), 1.82–1.94 (br m, 2H), 1.99 (br s, 4H), 2.17 (br s, 3H), 2.40 (d, *J* = 16.1 Hz, 3H), 3.24–3.32 (m, 1H), 3.90–3.99 (m, 1H), 4.52–4.59 (m, 1H), 6.81 (t, *J* = 7.9 Hz, 1H), 7.0 (br t, *J* = 7.9 Hz, 2H), 7.24 (t, *J* = 8.0 Hz, 2H), 7.27–7.43 (m, 5H) (major epimer) and 1.61 (br s, 6H), 1.82–1.94 (br m, 2H), 1.99 (br s, 4H), 2.11 (br s, 3H), 2.60 (d, *J* = 12.4 Hz, 3H), 3.61 (t, *J* = 8.0 Hz, 1H), 3.90–3.99 (m, 1H), 4.38–4.46 (m, 1H), 6.81 (t, *J* = 7.9 Hz, 1H), 7.0 (br t, *J* = 7.9 Hz, 2H), 7.24 (t, *J* = 8.0 Hz, 2H), 7.27–7.43 (m, 3H), 7.54 (d, *J* = 8.0 Hz, 2H) (minor epimer). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 31.1 (s, C(3′), C(5′), C(7′)), 31.8 (d, ^2J = 15.9 Hz, CH_3N), 36.2 (s, C(4′), C(6′), C(10′)), 45.3 (d, ^3J = 8.3 Hz, C(2′), C(8′), C(9′)), 56.8 (d, ^2J = 8.3 Hz, CH_2N), 65.8 (d, ^2J = 9.1 Hz, CHN), 73.5 (d, ^2J = 6.8 Hz, C(1′)), 114.8 (d, ^3J = 15.1 Hz, CH_{PhN}), 118.5 (d, ^4J = 1.8 Hz, CH_{PhN}), 127.8 (s, CH_{PhN}), 128.1 (s, CH_{Ph}), 128.9 (s, CH_{Ph}), 129.0 (s, CH_{Ph}), 140.7 (d, ^3J = 4.5 Hz, C_{Ph}), 145.9 (d, ^2J = 17.4 Hz, C_{PhN}) (major epimer) and 31.0 (s, C(3′), C(5′), C(7′)), 32.7 (d, ^2J = 34.7 Hz, CH_3N), 36.3 (s, C(4′), C(6′), C(10′)), 45.4 (d, ^3J = 6.8 Hz, C(2′), C(8′), C(9′)), 56.2 (d, ^2J = 8.1 Hz, CH_2N), 68.7 (d, ^2J = 10.6 Hz, CHN), 72.8 (d, ^2J = 6.7 Hz, C(1′)), 116.5 (d, ^3J = 13.6 Hz, CH_{PhN}), 118.9 (d, ^4J = 3.0 Hz, CH_{PhN}), 127.4 (s, CH_{Ph}), 128.5 (s, CH_{Ph}), 128.6 (s, CH_{PhN}), 129.0 (s, CH_{Ph}), 141.9 (s, C_{Ph}), 145.4 (d, ^2J = 16.2 Hz, C_{PhN}) (minor epimer). MS (MALDI TOF/TOF): *m*/*z* (%) = 425 (100) $[M+H_2O+H]^+$, 273 (94) $[(PhNCH_2CH(Ph)NMe)POH+H]^+$, 227 (76) $[PhNHCH_2CH(Ph)NHMe+H]^+$, 136 (15) $[C_{10}H_{16}]^+$. Anal. Calcd for $C_{25}H_{31}N_2OP$: C, 73.87; H, 7.69; N, 6.89. Found: C, 74.01; H, 7.74; N, 7.08.

4.5.6. (4*S*)-4-Benzyl-2-methoxy-3-methyl-1-phenyl-1,3,2-diazaphospholidine 6a

Colorless oil (1.07 g, yield 89%). T_{bath} 213–216 °C (1 Torr). $[\alpha]_D^{22}$ = −117.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 2.42–2.51 (m, 1H), 2.71–2.78 (m, 1H), 2.82 (d, *J* = 13.6 Hz, 3H), 3.36 (d, *J* = 8.4 Hz, 3H), 3.38–3.64 (m, 2H), 3.87–3.95 (m, 1H), 6.83 (br t, *J* ~8.1 Hz, 1H), 6.97 (br t, *J* ~8.0 Hz, 2H), 7.17–7.28 (m, 5H), 7.29–7.36 (m, 2H) (major epimer) and 2.42–2.51 (m, 1H), 2.71–2.78 (m, 1H), 2.87 (d, *J* = 13.2 Hz, 3H), 3.28 (d, *J* = 8.8 Hz, 3H), 3.38–3.64 (m, 2H), 3.87–3.95 (m, 1H), 6.83 (br t, *J* ~8.1 Hz, 1H), 6.97 (br t, *J* ~8.0 Hz, 2H), 7.17–7.28 (m, 5H), 7.29–7.36 (m, 2H) (minor epimer). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 25.3 (d, ^2J = 18.2 Hz, CH_3N), 35.9 (d, ^3J = 2.8 Hz, CH_2Ph), 50.0 (d, ^2J = 2.2 Hz, CH_3O), 52.5 (d, ^2J = 7.7 Hz, CH_2N), 64.3 (d, ^2J = 10.5 Hz, CHN), 125.5 (d, ^3J = 19.9 Hz, CH_{PhN}), 130.8 (d, ^4J = 1.4 Hz, CH_{PhN}), 139.6 (s, CH_{Ph}), 142.1 (s, CH_{Ph}), 142.6 (s, CH_{Ph}), 142.7 (s, CH_{PhN}), 153.5 (s, C_{Ph}), 162.2 (d, ^2J = 15.4 Hz, C_{PhN}) (major epimer) and 28.9 (d, ^2J = 34.1 Hz, CH_3N), 36.0 (s, CH_2Ph), 47.8 (d, ^2J = 2.8 Hz, CH_3O), 52.7 (d, ^2J = 7.7 Hz, CH_2N), 65.7 (d, ^2J = 9.4 Hz, CHN), 125.7 (d, ^3J = 19.8 Hz, CH_{PhN}), 130.9 (s, CH_{PhN}), 139.5 (s, CH_{Ph}), 142.1 (s, CH_{Ph}), 142.6 (s, CH_{Ph}), 142.6 (s, CH_{PhN}), 153.9 (s, C_{Ph}), 161.8 (d, ^2J = 13.8 Hz, C_{PhN}) (minor epimer). MS (EI, 70 eV): *m*/*z* (%) = 301 (9) $[M+H]^+$, 269 (22) $[M-OMe]^+$, 209 (100) $[M-Bn]^+$, 179 (87) $[M-OMe-Bn+H]^+$. Anal. Calcd for $C_{17}H_{21}N_2OP$: C, 67.98; H, 7.05; N, 9.33. Found: C, 67.68; H, 6.90; N, 9.46.

4.5.7. (4*S*)-4-*sec*-Butyl-2-methoxy-3-methyl-1-phenyl-1,3,2-diazaphospholidine 6b

Colorless liquid (0.91 g, yield 85%). T_{bath} 182–185 °C (1 Torr). $[\alpha]_D^{22}$ = −105.0° (*c* 1.0, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 0.76 (d, *J* = 6.8 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H), 1.18–1.27 (m, 1H), 1.33–1.44 (m, 1H), 1.81–1.89 (m, 1H), 2.73 (d, *J* = 13.2 Hz, 3H), 3.34 (d, *J* = 8.0 Hz, 3H), 3.45–3.56 (m, 2H), 3.69–3.77 (m, 1H), 6.81–6.87 (m, 1H), 7.05 (br t, *J* ~8.5 Hz, 2H), 7.20–7.29 (m, 2H) and 0.97 (d, *J* = 6.8 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H), 1.18–1.27 (m, 1H), 1.33–1.44 (m, 1H), 1.81–1.89 (m, 1H), 2.65 (d, *J* = 13.6 Hz, 3H), 3.24 (d, *J* = 8.8 Hz, 3H), 3.25–3.33 (m, 2H), 3.41 (t, *J* = 9.4 Hz, 1H), 6.81–6.87 (m, 1H), 7.05 (br t, *J* ~8.5 Hz, 2H), 7.20–7.29 (m, 2H) (mixture of epimers). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 10.9 (s, CH_3), 12.4 (s, CH_3), 26.8 (s, CH_2), 29.8 (d, ^2J = 20.4 Hz, CH_3N), 34.0 (d, ^3J = 3.4 Hz, CH), 47.9 (d, ^2J = 8.7 Hz, CH_2N), 51.2 (d, ^2J = 1.9 Hz, CH_3O), 65.2 (d, ^2J = 11.7 Hz, CHN), 114.4 (d, ^3J = 14.4 Hz, CH_{Ph}), 119.0 (d, ^4J = 2.3 Hz, CH_{Ph}), 129.0 (s, CH_{Ph}), 144.2 (d, ^2J = 16.8 Hz, C_{Ph}) and 10.9 (s, CH_3), 12.0 (s, CH_3), 27.2 (s, CH_2), 33.5 (d, ^2J = 41.0 Hz, CH_3N), 35.2 (s, CH), 48.2 (d, ^2J = 8.8 Hz, CH_2N), 48.9 (s, CH_3O), 66.1 (d, ^2J = 9.1 Hz, CHN), 114.9 (d, ^3J = 13.3 Hz, CH_{Ph}), 118.9 (s, CH_{Ph}), 128.9 (s, CH_{Ph}), 143.5 (d, ^2J = 15.2 Hz, C_{Ph}) (mixture of epimers). MS (EI, 70 eV): *m*/*z* (%) = 266 (11) $[M]^+$, 235 (39) $[M-OMe]^+$, 209 (100) $[M-sec\text{-}Bu]^+$. Anal. Calcd for $C_{14}H_{23}N_2OP$: C, 63.14; H, 8.70; N, 10.52. Found: C, 63.28; H, 8.76; N, 10.25.

4.6. Catalytic reactions

4.6.1. Pd-catalyzed allylic sulfonylation of (*E*)-1,3-diphenylallyl acetate 7 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. Next, (*E*)-1,3-diphenylallyl acetate (0.05 mL, 0.25 mmol) was added and the solution stirred for 15 min, after which sodium *para*-toluene sulfinate (0.089 g, 0.5 mmol) was added and the reaction mixture stirred for a 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 **8a** as white crystals. The enantiomeric excess of **8a** was determined by HPLC.

4.6.2. Pd-catalyzed allylic alkylation of (*E*)-1,3-diphenylallyl acetate 7 with dimethyl malonate

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 the appropriate solvent (1.5 mL) was stirred for 40 min. Next, (*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 then stirred for 48 h, diluted with CH_2Cl_2 or THF (2 mL), and filtered through a thin layer 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*)-dimethyl 2-(1,3-diphenylallyl)malonate **8b**. In order to evaluate the ee and conversion, the residue obtained was dissolved in an appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis.

4.6.3. Pd-catalyzed allylic amination of (*E*)-1,3-diphenylallyl acetate 7 with pyrrolidine

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 the appropriate solvent (1.5 mL) was stirred for 40 min. Next, (*E*)-1,3-diphenylallyl acetate (0.05 mL, 0.25 mmol) was added and the solution stirred for 15 min, then freshly distilled pyrrolidine (0.06 mL, 0.75 mmol) was added. The reaction mixture was stirred for 48 h, diluted with CH_2Cl_2 or THF (2 mL) and filtered through a thin layer 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*)-1-(1,3-diphenylallyl)pyrrolidine **8c**. In order to evaluate the ee and conversion, the residue obtained was dissolved in an appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis.

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References

1. Ayora, I.; Ceder, R. M.; Espinel, M.; Muller, G.; Rocamora, M.; Serrano, M. *Organometallics* **2011**, *30*, 115–128.
2. Fernandez-Perez, H.; Etayo, P.; Panossian, A.; Vidal-Ferran, A. *Chem. Rev.* **2011**, *111*, 2119–2176.
3. Brown, J. M. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 1999; Vol. I, pp 121–182.
4. Ohkuma, T.; Kitamura, M.; Noyori, R. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley-VCH: New York, 2000; pp 1–110.
5. Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921–2943.
6. Blaser, H.-U.; Schmidt, E. *Asymmetric Catalysis on Industrial Scale*; Wiley-VCH: Weinheim, 2004.
7. Burk, M. J. *Acc. Chem. Res.* **2000**, *33*, 363–372.
8. van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Claver, C.; Pamies, O.; Dieguez, M. *Chem. Rev.* **2011**, *111*, 2077–2118.
9. Beletskaya, I. P.; Kustov, L. M. *Russ. Chem. Rev.* **2010**, *79*, 441–461.
10. Coll, M.; Ahlford, K.; Pamies, O.; Adolfsson, H.; Dieguez, M. *Adv. Synth. Catal.* **2012**, *354*, 415–427.
11. Hammerer, T.; Weisgerber, L.; Schenk, S.; Stelzer, O.; Englert, U.; Leitner, W.; Francio, G. *Tetrahedron: Asymmetry* **2012**, *23*, 53–59.
12. Claver, C.; Pamies, O.; Dieguez, M. In *Phosphorus Ligands in Asymmetric Catalysis*; Börner, A., Ed.; Wiley-VCH: Weinheim, 2008; Vol. II, pp 507–528.
13. Falciola, C. A.; Alexakis, A. *Eur. J. Org. Chem.* **2008**, 3765–3780.
14. Hargaden, G. C.; Guiry, P. J. *Chem. Rev.* **2009**, *109*, 2505–2550.
15. Bini, L.; Muller, C.; Vogt, D. *Chem. Commun.* **2010**, 8325–8334.
16. Tolstikov, A. G.; Khlebnikova, T. B.; Tolstikova, O. V.; Tolstikov, G. A. *Russ. Chem. Rev.* **2003**, *72*, 803–822.
17. Zhou, Q.-L. *Privileged Chiral Ligands and Catalysts*; Wiley-VCH: Weinheim, 2011.
18. Dieguez, M.; Ruiz, A.; Claver, C. *Dalton Trans.* **2003**, 2957–2963.
19. Teichert, J. F.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2010**, *49*, 2486–2528.
20. Ansell, J.; Wills, M. *Chem. Soc. Rev.* **2002**, *31*, 259–268.
21. Alexakis, A.; Benhaim, C. *Eur. J. Org. Chem.* **2002**, *19*, 3221–3236.
22. Molt, O.; Schrader, T. *Synthesis* **2002**, 2633–2670.
23. Reetz, M. T.; Mehler, G.; Meiswinkel, A.; Sell, T. *Tetrahedron Lett.* **2002**, *43*, 7941–7943.
24. Dieguez, M.; Pamies, O.; Claver, C. *Tetrahedron: Asymmetry* **2004**, *15*, 2113–2122.
25. Gavrilov, K. N.; Bondarev, O. G.; Polosukhin, A. I. *Russ. Chem. Rev.* **2004**, *73*, 671–699.
26. Jerphagnon, T.; Renaud, J.-L.; Bruneau, C. *Tetrahedron: Asymmetry* **2004**, *15*, 2101–2111.
27. Reetz, M. T.; Mehler, G.; Bondarev, O. *Chem. Commun.* **2006**, 2292–2294.
28. deVries, J. G.; Lefort, L. *Chem. Eur. J.* **2006**, *12*, 4722–4734.
29. 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.
30. Mata, Y.; Pamies, O.; Dieguez, M. *Chem. Eur. J.* **2007**, *13*, 3296–3304.
31. 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.
32. Qiao, X.-C.; Zhu, S.-F.; Zhou, Q.-L. *Tetrahedron: Asymmetry* **2009**, *20*, 1254–1261.
33. Gavrilov, K. N.; Zheglov, S. V.; Gavrilova, M. N.; Novikov, I. M.; Maksimova, M. G.; Groshkin, N. N.; Rastorguev, E. A.; Davankov, V. A. *Tetrahedron* **2012**, *68*, 1581–1589.
34. Reetz, M. T.; Ma, J.-An.; Goddard, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 412–415.
35. Chapsal, B. D.; Hua, Z.; Ojima, I. *Tetrahedron: Asymmetry* **2006**, *17*, 642–657.
36. Eberhardt, L.; Armspach, D.; Harrowfield, J.; Matta, D. *Chem. Soc. Rev.* **2008**, *37*, 839–864.
37. Hilgraf, R.; Pfaltz, A. *Synlett* **1999**, 1814–1816.
38. Delapierre, G.; Brunel, J. M.; Constantieux, T.; Buono, G. *Tetrahedron: Asymmetry* **2001**, *12*, 1345–1352.
39. Reetz, M. T.; Oka, H.; Goddard, R. *Synthesis* **2003**, 1809–1814.
40. Hilgraf, R.; Pfaltz, A. *Adv. Synth. Catal.* **2005**, *347*, 61–77.
41. Schonleber, M.; Hilgraf, R.; Pfaltz, A. *Adv. Synth. Catal.* **2008**, *350*, 2033–2038.
42. Markert, C.; Rosel, P.; Pfaltz, A. *J. Am. Chem. Soc.* **2008**, *130*, 3234–3235.
43. Trost, B. M.; Lam, T. M. *J. Am. Chem. Soc.* **2012**, *134*, 11319–11321.
44. Buono, G.; Toselli, N.; Martin, D. In *Phosphorus Ligands in Asymmetric Catalysis*; Börner, A., Ed.; Wiley-VCH: Weinheim, 2008; Vol. II, pp 529–546.
45. 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.
46. Crepy, K. V. L.; Imamoto, T. *Adv. Synth. Catal.* **2003**, *345*, 79–101.
47. Gavrilov, K. N.; Zheglov, S. V.; Shiryaev, A. A.; Groshkin, N. N.; Rastorguev, E. A.; Benetsky, E. B.; Davankov, V. A. *Tetrahedron Lett.* **2011**, *52*, 964–968.
48. Brunel, J. M.; Constantieux, T.; Buono, G. *J. Org. Chem.* **1999**, *64*, 8940–8942.
49. 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.
50. Kimura, M.; Uozumi, Y. *J. Org. Chem.* **2007**, *72*, 707–714.
51. Benetsky, E. B.; Bolm, C. *Tetrahedron: Asymmetry* **2011**, *22*, 373–378.
52. Bondarev, O. G.; Goddard, R. *Tetrahedron Lett.* **2006**, *47*, 9013–9015.
53. Mariz, R.; Briceno, A.; Dorta, Reto.; Dorta, R. *Organometallics* **2008**, *27*, 6605–6613.
54. Mikhel, I. S.; Bernardinelli, G.; Alexakis, A. *Inorg. Chim. Acta* **2006**, *359*, 1826–1836.
55. Bartets, B.; Garcia-Yebra, C.; Helmchen, G. *Eur. J. Org. Chem.* **2003**, 1097–1103.
56. McCarthy, M.; Guiry, P. J. *Tetrahedron* **2001**, *57*, 3809–3844.
57. Graening, T.; Schmalz, H.-G. *Angew. Chem., Int. Ed.* **2003**, *42*, 2580–2584.
58. Chapsal, B. D.; Ojima, I. *Org. Lett.* **2006**, *8*, 1395–1398.
59. Lu, Z.; Ma, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 258–297.
60. Dieguez, M.; Pamies, O. *Acc. Chem. Res.* **2010**, *43*, 312–322.
61. Lam, F. L.; Kwong, F. Y.; Chan, A. S. C. *Chem. Commun.* **2010**, 4649–4667.
62. Lafrance, D.; Bowles, P.; Leeman, K.; Rafka, R. *Org. Lett.* **2011**, *13*, 2322–2325.
63. Nemoto, T.; Hamada, Y. *Tetrahedron* **2011**, *67*, 667–687.
64. Pelagatti, P.; Carcelli, M.; Calbiani, F.; Cassi, C.; Elviri, L.; Pelizzi, C.; Rizzotti, U.; Rogolino, D. *Organometallics* **2005**, *24*, 5836–5844.
65. Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.
66. Polosukhin, A. I.; Kovalevskii, A. I.; Gavrilov, K. N. *Russ. J. Coord. Chem.* **1999**, *25*, 758–761.
67. Bunten, K. A.; Chen, L.; Fernandez, A. L.; Poe, A. *J. Coord. Chem. Rev.* **2002**, *233–234*, 41–51.
68. Alexakis, A.; Mutti, S.; Normant, J. F. *J. Am. Chem. Soc.* **1991**, *113*, 6332–6334.
69. Falorni, M.; Lardicci, L.; Giacomelli, G. *Gazz. Chim. Ital.* **1988**, *118*, 573–576.
70. Cortes, S.; Kohn, H. *J. Org. Chem.* **1983**, *48*, 2246–2254.
71. Gavrilov, K. N.; Chuchelkin, I. V.; Zheglov, S. V.; Shiryaev, A. A.; Potapova, O. V.; Novikov, I. M.; Rastorguev, E. A.; Petrovskii, P. V.; Davankov, V. A. *Izv. Akad. Nauk. Ser. Khim.* **2012**, 1910–1917.
72. Auburn, P. R.; McKenzie, P. B.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2033–2046.
73. Gavrilov, K. N.; Lyubimov, S. E.; Zheglov, S. V.; Benetsky, E. B.; Davankov, V. A. *J. Mol. Catal. A: Chem.* **2005**, *231*, 255–260.