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Asymmetric Catalytic Reactions Using *P**-Mono-, *P**,*N*- and *P**,*P**-Bidentate Diamidophosphites with BINOL Backbones and 1,3,2-Diazaphospholidine Moieties: Differences in the Enantioselectivity

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Abstract: A new series of *P**-chiral diamidophosphites with 1,3,2-diazaphospholidine rings, based on (S_a)- or (R_a)-BINOL and their easily accessible derivatives, has been synthesized for the first time and tested in asymmetric transition metal catalysis. Up to 99% *ee* was achieved in the rhodium-catalyzed asymmetric hydrogenation of functionalized olefins and in the palladium-catalyzed allylic substitution. The influence of the nature of the donor atoms and denticity on the asymmetric induction is discussed. In addition, the first example of a successful platinum-catalyzed asymmetric allylic amination (up to 86% *ee*) with participation of organophosphorus ligands is considered.

Keywords: asymmetric catalysis; palladium; platinum; P ligands; rhodium

Introduction

Asymmetric catalysis is now regarded as one of the most cost-effective and environmentally viable methods for the production of a truly vast array of structurally diverse, enantiomerically pure compounds. In addition to the well-known applications in pharmaceutical chemistry, this method is successfully used in the synthesis of fragrance compounds, plant protection chemicals, individual stereoisomeric polymers, and liquid crystals.[1] One of the core research activities in the field of asymmetric catalysis is the ongoing development of new ligands to achieve higher levels of efficiency and selectivity to meet the increasing demands of both academic and industrial sectors. Although the use of numerous chiral ligands has been reported, the design and synthesis of new types of ligands with improved performance continue to attract the interest of synthetic chemists. A well-conceived ligand class should possess one or more structural and/or electronic features (modules) 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 modules can be correlated to changes in the reactivity or selectivity of the catalyst.[1c,2] The set of such powerful modules includes the nature of the donor atoms and denticity. The majority of very important and widely used chiral ligands bear phosphorus and/or nitrogen donor atoms. The π-acceptor character of phosphorus can stabilize a metal centre in a low oxidation state, while the nitrogen σ-donor ability makes the metal more susceptible to oxidative addition reactions. This can help to stabilize intermediate oxidation states or geometries during a catalytic cycle.[3] The most efficient of such ligands are *P*-mono, *P,N*- and *P,P*-bidentate compounds. Chelation is a general characteristic of *P,N*- and *P,P*-ligands. As a rule, chelation reduces the degree of rotational freedom around the metal-phosphorus bond, leading to a certain degree of ri-

gidity necessary for efficient transfer of chirality in the catalytic process. Moreover, *P,N*-bidentate compounds are able to generate electronic asymmetry on the metal. This asymmetry can be transmitted to reacting molecules bonded to the metal (for instance, through the *trans*-effect) and has the potential to control both the stability and reactivity of metal-substrate intermediates.[1–3] *P*-monodentate ligands represent a class of widespread stereoselectors in asymmetric catalysis, and their coordination mode allows the development of new strategies in combinatorial asymmetric catalysis, which are impossible with bidentate ligands.[4]

To embark on the synthesis of any modern ligands, it is necessary to select carefully the optimal backbone. Ligands embodying the binaphthyl framework have earned a prominent status as shown by their versatility in many catalytic asymmetric reactions over the last three decades.[1,2a] Standard BINOL-derived monophosphites[4a] and monophosphoramidites[4b] are considered to be priviledged ligands. However, structural variations lead to further interesting perspectives. Examples of some phosphite-type compounds with different coordination modes and binaphthyl backbone are shown in Figure 1.

Note that the use of the phosphite-type ligands has become an established tool in asymmetric catalysis.[4a] The most important advantages of such ligands include their pronounced π-acidity, oxidation stability, as well as their synthetic availability and low cost. This often enables 'fine-tuning' towards desired properties, such as high selectivity and rate in homogeneous catalytic reactions.[5] Thus, *P,P*-bidentate phosphites $\mathbf{L_{A–C}}$ were successfully used in the Cu-catalyzed conjugated addition, Co-catalyzed Pauson–Khand reaction and Rh-catalyzed hydroformylation,[6–8] but phosphites $\mathbf{L_{D–F}}$ containing phosphocycles based on chiral aliphatic diols appeared to be rather ineffective stereoselectors.[9] NOBIN-based *P,N*-bidentate phosphites $\mathbf{L_{G,H}}$ are highly efficient in the Cu-catalyzed enantioselective conjugate additions, and *P*-monodentate MOP-type compounds $\mathbf{L_{I,J}}$ were shown to have good to excellent enantioselectivity in the Pd-catalyzed allylation and in the Rh-catalyzed hydrogenation.[10,11]

In the last few years, we have developed a new class of highly modular diamidophosphite ligands with 1,3,2-diazaphospholidine rings that promote a wide range of catalytic asymmetric reactions.[12] It should be noted that these *P**-chiral 1,3,2-diazaphos-

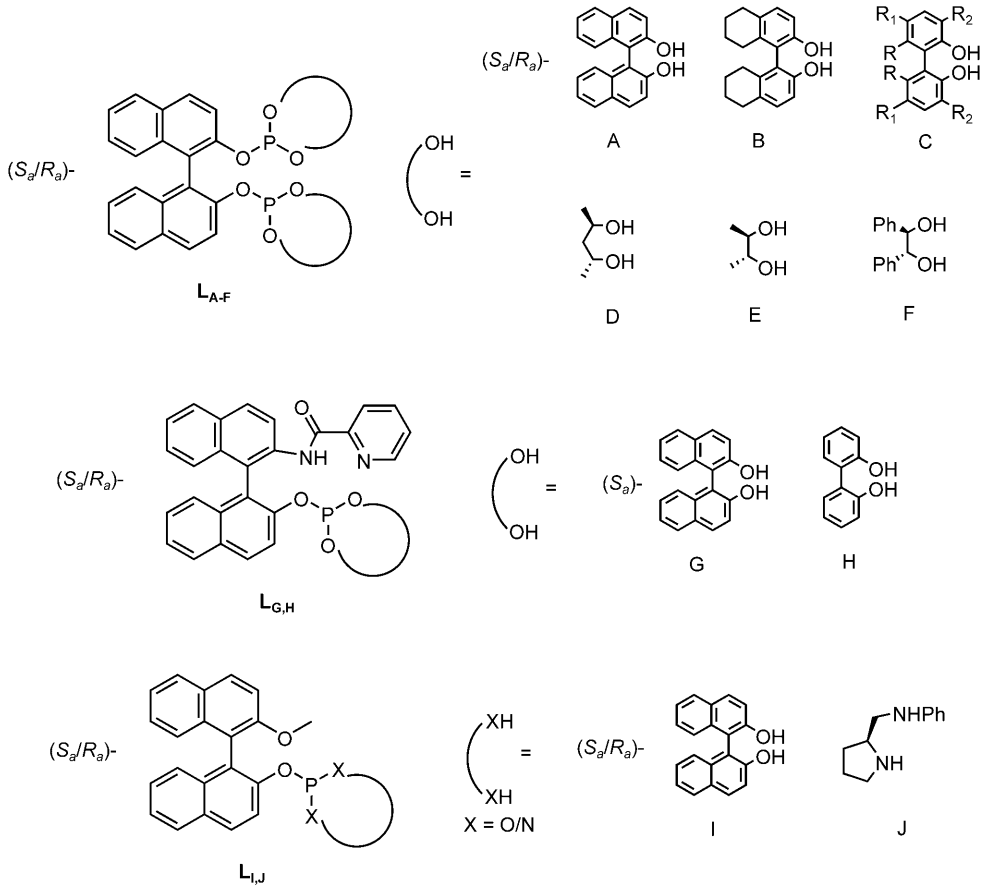


Figure 1. *P*-Mono-, *P,N*- and *P,P*-bidentate phosphite-type ligands for asymmetric metal complex catalysis.

pholidines belong to an attractive group of optically active diamidophosphite ligands. In particular, these 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. The inclusion of the phosphorus atom in the five-membered ring enhances the resistance of the ligands to oxidation and hydrolysis, and the possibility of varying the nature of the substituents at the nitrogen and phosphorus atoms allows the control over the steric and electronic parameters. Also, their modular nature allows a facile systematic variation at the configuration of the *P**- and *C**-stereocenters in the 1,3,2-diazaphospholidine rings. As a whole, the stability of these ligands and their straightforward syntheses provide easy fine tuning of their catalytic properties.[12,13]

As stated above, in enantioselective catalysis ligands induce asymmetry in a reaction, not just through steric factors, but also through the nature of donor atoms and coordination mode. However, a systematic evaluation of the effectiveness of phosphite-type ligands within the framework of this concept is hampered by the lack of specially-designed series of them having the same backbone, but different donor atoms and denticity. In this connection, we report the synthesis of a small library of *P**-mono, *P**,*N*- and *P**,*P**-bidentate diamidophosphites **5–7** containing the (S_a)- or (R_a)-1,1′-binaphthyl core and 1,3,2-diazaphospholidine rings. We also present the results of direct comparison of these stereoselectors in asymmetric catalysis.

Typically, once novel ligands have been prepared, their metal complexes are tested for their catalytic activity and enantiodifferentiating ability in standard transformations. These benchmark reactions include (among others) asymmetric hydrogenation and allylic substitution. The enantioselective hydrogenation, using inexpensive molecular hydrogen and a small amount of a catalyst, holds a considerable promise for industrial use. The allylic substitution, which is tolerant to various functional groups in the substrate and operates with a wide range of C-, N-, O-, S-, and P-nucleophiles, has been successfully used in key steps of the synthesis of various natural compounds.[14]

Results and Discussion

Ligand Design and Synthesis

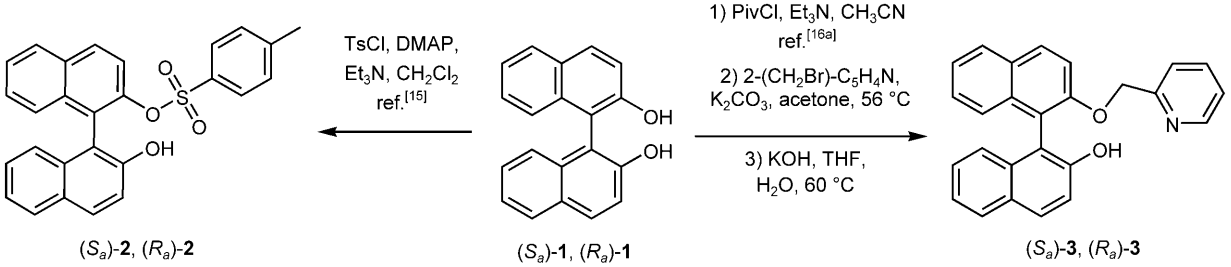
The general strategy for the synthesis of the starting synthons **2** and **3** with the binaphthyl framework is presented in Scheme 1.

Thus, (S_a)- and (R_a)-2-hydroxy-2′-tosyloxy-1,1′-binaphthyls (S_a)-**2** and (R_a)-**2** were conveniently obtained by direct interaction between the appropriate enantiomer of BINOL and TsCl.[15] (S_a)- and (R_a)-2-hydroxy-2′-[(pyridin-2-yl)methoxy]-1,1′-binaphthyls (S_a)-**3** and (R_a)-**3** were easily synthesized according to a modified procedure from literature.[16]

*P**-Chiral diamidophosphites **5–7** were synthesized efficiently by the one-step phosphorylation of BINOL **1** or its derivatives **2** and **3** by reagent **4** in toluene (Scheme 2). The reactions require the presence of Et_3N as HCl scavenger. The target ligands **5–7** were obtained with overall yields ranging from 78% to 89% after purification by chromatography on silica gel (see Experimental Section).

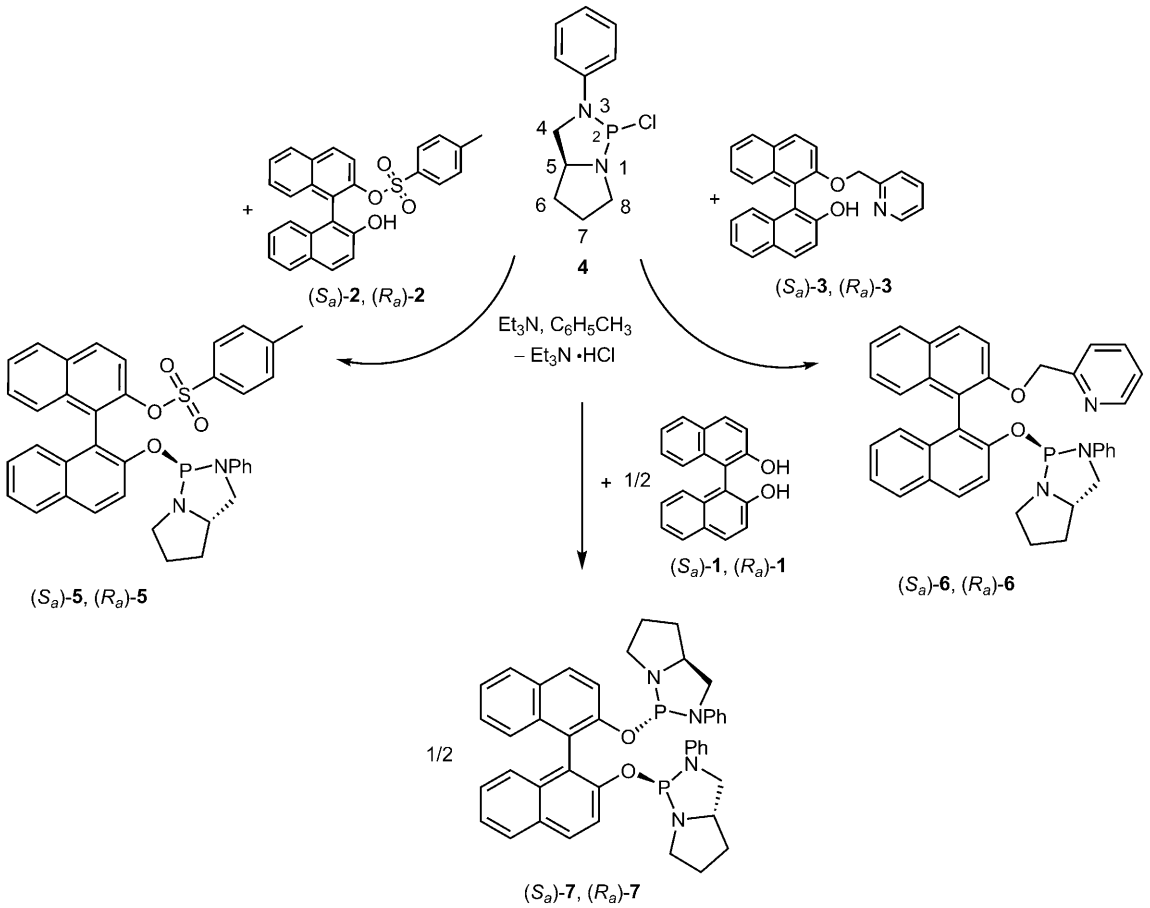
All ligands are readily available and can be prepared on a gram scale. Furthermore, the phosphorylating agent **4** can easily be synthesized[12a] in high yield from readily accessible (*S*)-glutamic acid anilide.[17] Moreover, BINOL **1** is commercially available in both enantiomeric forms and is one of the cheapest chiral auxiliaries currently on the market. As stated above, its transformation into derivatives **2** and **3** requires only one or three simple steps, respectively.

The novel ligands are white solids, which are stable enough to allow manipulation in open air and can be stored under dry conditions at room temperature over several months without any degradation. In addition, they are fairly stable in solutions in common organic solvents. They were fully characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, EI and/or MALDI TOF/TOF mass spectrometry as well as by elemental analysis. These stereoselectors possess: (i) chirogenic phosphorus donor atoms, (ii) a rigid structure imposed by the atropoisomeric binaphthyl backbone and (iii) *P**-mono, *P**,*N*- and *P**,*P**-bidentate coordination modes. The ^{31}P NMR spectroscopic data for diamidophosphites **5–7** are summarized in Table 1.



(S_a)-**2**, (R_a)-**2** (S_a)-**1**, (R_a)-**1** (S_a)-**3**, (R_a)-**3**

Scheme 1. Synthesis of BINOL-based compounds (S_a)-**2**, (R_a)-**2** and (S_a)-**3**, (R_a)-**3**.



Scheme 2. Synthesis of epimeric diamidophosphite ligands (S_a)-**5**, (R_a)-**5**; (S_a)-**6**, (R_a)-**6** and (S_a)-**7**, (R_a)-**7**

Table 1. ^{31}P NMR chemical shifts ($CDCl_3$) and cone angles θ (deg.) of the phosphocenters of ligands (S_a)-**5**, (R_a)-**5**; (S_a)-**6**, (R_a)-**6** and (S_a)-**7**, (R_a)-**7**.

Ligand	δ_P	θ
(R_P)-(S_a)-**5** (91%)[a]	128.9	135
(S_P)-(S_a)-**5** (9%)	118.2	
(R_P)-(R_a)-**5** (88%)	125.5	129
(S_P)-(***R_a***)-**5** (12%)	118.6	
(R_P)-(S_a)-**6** (92%)	129.6	128
(S_P)-(S_a)-**6** (8%)	119.4	
(R_P)-(R_a)-**6** (96%)	125.8	133
(S_P)-(R_a)-**6** (4%)	118.5	
(S_a)-**7**	128.7	174[b]
(R_a)-**7**	124.5	168[b]

[a] Percentage of *P**-epimers.
[b] The average value for both phosphocenters.

Compounds **5** and **6** are mixtures of epimers with respect to the phosphorus stereocentre and contain 88-96% of the major *P** epimers, while ligands **7** are formed as single stereoisomers (Table 1). Ligands **7** and the major epimers of ligands **5, 6** have the *P** stereocentres with the (*R*) configuration. The ^{13}C NMR spectra of these compounds are characterized by large spin-spin coupling constants $^2J_{C8",P}$ (33.4–37.5 Hz, see Experimental Section), which are indicative of the *cis* orientation of the phosphorus lone pair with respect to the C-8" atom. Correspondingly, the pseudoequatorially oriented exocyclic substituent at the phosphorus atom and the $-(CH_2)_3-$ part of the pyrrolidine fragment of phosphabicyclic skeleton are in the *trans* arrangement (Figure 2).

On the contrary, the minor epimers of ligands **5** and **6** contain the asymmetric phosphorus atoms with the (*S*) configuration.[11,12,17b,18]

In order to have an estimation of the steric demands of diamidophosphites **5**–**7**, we calculated their Tolman cone angles[19] by the reported method using a semi-empirical quantum-mechanical AM1 method

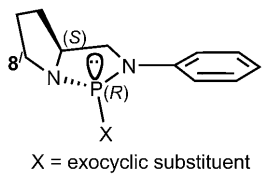


Figure 2. Stereochemistry of the phosphabicyclic part in ligands **7** and in major epimers of ligands **5**, **6**.

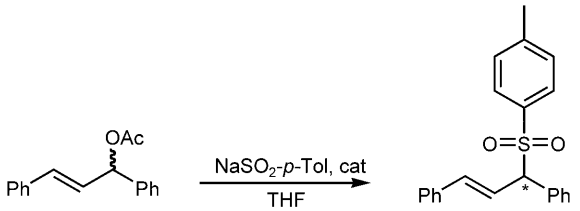
with full optimization of geometrical parameters.[20] The obtained results showed that *P**-mono, *P**,*N*-bidentate ligands **5** and **6** have moderate steric demands and their steric parameters (θ) vary within the narrow interval of 128°–135° (Table 1). In contrast, *P**,*P**-bidentate diamidophosphites (S_a)-**7** and (R_a)-**7** appear to be rather bulky ligands ($\theta = 174°$ and 168°, respectively).[19,21]

Palladium- and Platinum-Catalyzed Asymmetric Allylic Substitution

Diamidophosphites **5–7** were first applied in the Pd-catalyzed allylic sulfonylation of (*E*)-1,3-diphenylallyl acetate **8** with *p*-TolSO_2Na as the S-nucleophile (Table 2).

Compound **8** was chosen as a substrate because the reaction itself was performed with a wide range of ligands, allowing the efficiency of the various ligand systems to be compared directly.[1b,d,14e] In all cases, **5–7** provided the formation of the (*S*)-enantiomer of sulfone **9a**. *P**,*N**-bidentate ligand (S_a)-**6** was the most efficient, and (*S*)-**9a** was formed with 89% yield and 99% *ee* (Table 2, entry 5). It should be noted that chiral allylic sulfones are exceptionally versatile intermediates in organic synthesis.[14c] Diastereomeric ligand (R_a)-**6** showed a considerably smaller enantioselectivity (Table 2, entries 7, 8). *P**-Monodentate diamidophosphite (S_a)-**5** afforded product (*S*)-**9a** with good enantiomeric purity (up to 86% *ee*), but the analogous catalysts based on diastereomer (R_a)-**5** proved to be much less efficient: only 58% yield and 30% *ee* for (*S*)-**9a** were achieved in this case (Table 2, entries 1–4). *P**,*P**-Bidentate ligands **7** are mediocre stereoselectors: enantioselectivity varies from 30% to 67% *ee* (Table 2, entries 9–12).

Table 2. Pd-catalyzed allylic sulfonylation of (*E*)-1,3-diphenylallyl acetate **8** with sodium *para*-toluenesulfinate.[a]



8 **9a**

Entry	Ligand	L/Pd	Yield [%]	*ee*[b] [%]
1	(S_a)-**5**	1/1	88	86 (*S*)
2	(S_a)-**5**	2/1	47	77 (*S*)
3	(R_a)-**5**	1/1	49	30 (*S*)
4	(R_a)-**5**	2/1	58	5 (*S*)
5	(S_a)-**6**	**1/1**	**89**	**99 (*S*)**
6	(S_a)-**6**	2/1	67	97 (*S*)
7	(R_a)-**6**	1/1	62	86 (*S*)
8	(R_a)-**6**	2/1	90	75 (*S*)
9	(S_a)-**7**	1/1	63	55 (*S*)
10	(S_a)-**7**	2/1	90	30 (*S*)
11	(R_a)-**7**	1/1	40	67 (*S*)
12	(R_a)-**7**	2/1	53	59 (*S*)

[a] All reactions were carried out with 2 mol% of [Pd(allyl)Cl]$_2$ in THF at room temperature for 48 h.

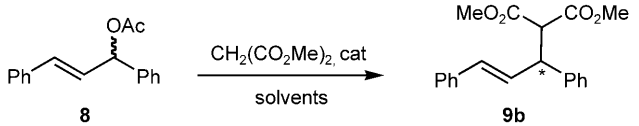
[b] Enantiomeric excess of **9a** was determined by HPLC (Daicel Chiralcel OJ, C_6H_{14}/*i*-PrOH = 4/1, 0.5 mL min^{-1}, 254 nm).

In the next step, stereoselectors **5–7** were studied in the Pd- and Pt-catalyzed asymmetric allylic alkylation of substrate **8** (Table 3). In the Pd-catalyzed process, diamidophosphites **5–7** provided an excellent enantioselectivity irrespective of their denticity and absolute configuration of the binaphthyl backbone (95–99% *ee*, Table 3, entries 4, 7, 11, 13, 17 and 25). Like the Pd-catalyzed allylic sulfonylation, the experiments with the use of ligands **5–7** afforded the reaction product **9b** having the (*S*) configuration. In general, both the conversion of **8** and asymmetric induction were poorly sensitive to the L/Pd molar ratio and solvent nature. Nevertheless, it is possible to specify some correlations. In particular, for *P**-monodentate diamidophosphites **5** the molar ratio L/Pd = 2 is undoubtedly preferable (Table 3, entries 1–8). In most cases, with participation of *P**-mono- and *P**,*N*-bidentate ligands **5** and **6**, the higher enantioselectivity was observed in CH_2Cl_2, with participation of *P**,*P**-bidentate ligands **7** – in THF. In the presence of [Pt(allyl)Cl]$_4$ as the metal precursor, diamidophosphite (S_a)-**7** provided a somewhat lower enantioselectivity (*ee* is no higher than 87%) (Table 3, entries 21–24), but it was comparable to that of the effective *P,N*- and *P,P*-bidentate phosphine stereoselectors PHOX and CHIRAPHOS.[22] It should be noted that the Pt-catalyzed alkylation of substrate **8** with participation of (S_a)-**7** resulted in higher conversion and enantioselectivity in CH_2Cl_2, and the resulting product **9b** also showed the (*R*) configuration. At the same time, diastereomeric ligand (R_a)-**7** afforded product (*S*)-**9b** with lower enantiomeric purity (up to 76% *ee*, Table 3, entries 29, 30).

Ligands **5–7** were next evaluated in the Pd-catalyzed allylic amination of (*E*)-1,3-diphenylallyl acetate **8** with dipropylamine as an N-nucleophile. As in the case of the allylic sulfonylation, positive influence on the enantioselectivity was observed for *P**,*N*-bidentate coordination mode, (+)-**9c** was obtained in 90% and 98% *ee* with (S_a)-**6** and (R_a)-**6**, respectively (Table 4, entries 10 and 13).

For comparison, the corresponding ligands with a different denticity (**5** and **7**, Scheme 2) afforded the amination product (+)-**9c** with 84% and 89% *ee*, respectively. As clearly shown in Table 4, very high enantioselectivity was observed for both diastereomers of *P**,*N*-bidentate diamidophosphite **6** (en-

Table 3. Pd- and Pt-catalyzed allylic alkylation of (*E*)-1,3-diphenylallyl acetate **8** with dimethyl malonate.[a]



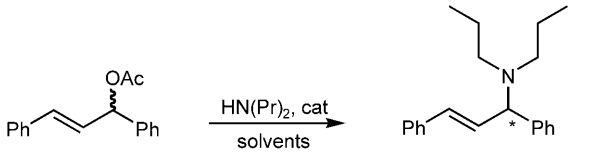
Entry	Ligand	L/Pd or L/Pt	Solvent	Conv.[b] [%]	*ee*[b] [%]
1	(S_a)-**5**	1/1	THF	23	51 (*S*)
2	(S_a)-**5**	2/1	THF	58	87 (*S*)
3	(S_a)-**5**	1/1	CH_2Cl_2	78	92 (*S*)
4	(S_a)-**5**	2/1	CH_2Cl_2	100	96 (*S*)
5	(R_a)-**5**	1/1	THF	91	55 (*S*)
6	(R_a)-**5**	2/1	THF	99	97 (*S*)
7	(R_a)-**5**	1/1	CH_2Cl_2	67	98 (*S*)
8	(R_a)-**5**	2/1	CH_2Cl_2	96	97 (*S*)
9	(S_a)-**6**	1/1	THF	52	92 (*S*)
10	(S_a)-**6**	2/1	THF	66	94 (*S*)
11	(S_a)-**6**	1/1	CH_2Cl_2	99	95 (*S*)
12	(S_a)-**6**	2/1	CH_2Cl_2	99	88 (*S*)
13	(R_a)-**6**	1/1	THF	85	97 (*S*)
14	(R_a)-**6**	2/1	THF	45	72 (*S*)
15	(R_a)-**6**	1/1	CH_2Cl_2	38	95 (*S*)
16	(R_a)-**6**	2/1	CH_2Cl_2	72	97 (*S*)
17	(S_a)-**7**	**1/1**	**THF**	**57**	**99 (*S*)**
18	(S_a)-**7**	2/1	THF	65	92 (*S*)
19	(S_a)-**7**	1/1	CH_2Cl_2	94	94 (*S*)
20	(S_a)-**7**	2/1	CH_2Cl_2	93	65 (*S*)
21	(S_a)-**7**	1/1	THF	56	60 (*R*)[c]
22	(S_a)-**7**	2/1	THF	54	72 (*R*)[c]
23	(S_a)-**7**	1/1	CH_2Cl_2	73	87 (*R*)[c]
24	(S_a)-**7**	2/1	CH_2Cl_2	61	85 (*R*)[c]
25	(R_a)-**7**	1/1	THF	59	98 (*S*)
26	(R_a)-**7**	2/1	THF	57	93 (*S*)
27	(R_a)-**7**	1/1	CH_2Cl_2	46	73 (*S*)
28	(R_a)-**7**	2/1	CH_2Cl_2	56	95 (*S*)
29	(R_a)-**7**	1/1	CH_2Cl_2	98	76 (*S*)[c]
30	(R_a)-**7**	2/1	CH_2Cl_2	99	59 (*S*)[c]

[a] All reactions were carried out with 2 mol% of $[Pd(allyl)Cl]_2$ or 1 mol% $[Pt(allyl)Cl]_4$ at room temperature for 48 h (BSA, KOAc).

[b] Both the conversion of substrate **8** and enantiomeric excess of **9b** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH = 99/1, 0.6 mL min^{-1}, 254 nm).

[c] With $[Pt(allyl)Cl]_4$ as a precatalyst.

Table 4. Pd-catalyzed allylic amination of (*E*)-1,3-diphenylallyl acetate **8** with dipropylamine.[a]



Entry	Ligand	L/Pd	Solvent	Conv.[b] [%]	*ee*[b] [%]
1	(S_a)-**5**	1/1	THF	100	80 (+)
2	(S_a)-**5**	2/1	THF	97	84 (+)
3	(S_a)-**5**	1/1	CH_2Cl_2	100	67 (+)
4	(S_a)-**5**	2/1	CH_2Cl_2	100	57 (+)
5	(R_a)-**5**	1/1	THF	25	15 (+)
6	(R_a)-**5**	2/1	THF	46	20 (+)
7	(R_a)-**5**	1/1	CH_2Cl_2	64	20 (+)
8	(R_a)-**5**	2/1	CH_2Cl_2	70	25 (+)
9	(S_a)-**6**	1/1	THF	32	89 (+)
10	(S_a)-**6**	2/1	THF	20	90 (+)
11	(S_a)-**6**	1/1	CH_2Cl_2	72	88 (+)
12	(S_a)-**6**	2/1	CH_2Cl_2	100	88 (+)
13	(R_a)-**6**	**1/1**	**THF**	**71**	**98 (+)**
14	(R_a)-**6**	2/1	THF	31	90 (+)
15	(R_a)-**6**	1/1	CH_2Cl_2	96	80 (+)
16	(R_a)-**6**	2/1	CH_2Cl_2	100	87 (+)
17	(S_a)-**7**	1/1	THF	38	4 (−)
18	(S_a)-**7**	2/1	THF	37	2 (−)
19	(S_a)-**7**	1/1	CH_2Cl_2	100	19 (−)
20	(S_a)-**7**	2/1	CH_2Cl_2	100	34 (−)
21	(R_a)-**7**	1/1	THF	50	88 (+)
22	(R_a)-**7**	2/1	THF	58	89 (+)
23	(R_a)-**7**	1/1	CH_2Cl_2	91	65 (+)
24	(R_a)-**7**	2/1	CH_2Cl_2	100	53 (+)

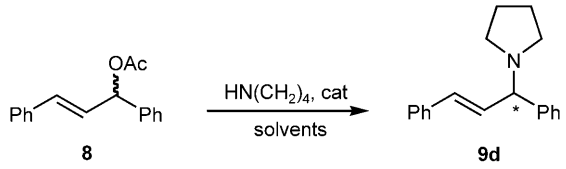
[a] All reactions were carried out with 2 mol% of $[Pd(allyl)Cl]_2$ at room temperature for 48 h.

[b] Both the conversion of substrate **8** and enantiomeric excess of **9c** were determined by HPLC [Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH/$HNEt_2$ = 1000/1/1, 0.4 mL min^{-1}, 254 nm, $t(+) = 8.2$ min, $t(-) = 9.1$ min].

tries 9–16), while efficiency of *P**-monodentate (S_a)-**5** and (R_a)-**5** was quite different (entries 1–4 and 5–8). Similarly, *P**,*P**-bidentate (R_a)-**7** is a rather good stereoselector, but (S_a)-**7** provided much lower asymmetric induction. The reaction product (<M>)-**9c** also showed opposite absolute configuration (Table 4, entries 17–24), probably due to the mismatched combination of the (2″*R*,5″*S*)-stereocentres of the phosphabicyclic cores with the (S_a)-BINOL framework. For most efficient ligands **6**, the nature of the solvent and the L/Pd molar ratio were not found to have a significant effect on the reaction rate or asymmetric induction (Table 4, entries 9–16).

Table 5 shows the results obtained when pyrrolidine was used as an alternative N-nucleophile. Catalytic performance in the Pd-catalyzed allylic amination of **8** with pyrrolidine followed the same trend as for the allylic alkylation of **8**. From good to excellent enantioselectivity (81–99% *ee*) was observed when employing diamidophosphites **5–7** with different coordination modes and absolute configuration of the binaphthyl backbone. The resulting product **9d** proved to have the same (*R*) configuration in all cases. In contrast to the allylic amination of **8** with dipropylamine, diamidophosphite (S_a)-**7** has been found to be an especially efficient stereoselector. This *P**,*P**-bidentate ligand gave amine (*R*)-**9d** with high enantiomeric purity (96–99% *ee*) (Table 5, entries 17–20) re-

Table 5. Pd- and Pt-catalyzed allylic amination of (*E*)-1,3-diphenylallyl acetate **8** with pyrrolidine.[a]



8 **9d**

Entry	Ligand	L/Pd or L/Pt	Solvent	Conv.[b] [%]	*ee*[b] [%]
1	(S_a)-**5**	1/1	THF	31	83 (*R*)
2	(S_a)-**5**	2/1	THF	60	84 (*R*)
3	(S_a)-**5**	1/1	CH_2Cl_2	100	20 (*R*)
4	(S_a)-**5**	2/1	CH_2Cl_2	100	47 (*R*)
5	(R_a)-**5**	1/1	THF	35	53 (*R*)
6	(R_a)-**5**	2/1	THF	80	71 (*R*)
7	(R_a)-**5**	1/1	CH_2Cl_2	80	75 (*R*)
8	(R_a)-**5**	2/1	CH_2Cl_2	78	81 (*R*)
9	(S_a)-**6**	1/1	THF	100	68 (*R*)
10	(S_a)-**6**	2/1	THF	65	84 (*R*)
11	(S_a)-**6**	1/1	CH_2Cl_2	99	73 (*R*)
12	(S_a)-**6**	2/1	CH_2Cl_2	100	75 (*R*)
13	(R_a)-**6**	1/1	THF	63	89 (*R*)
14	(R_a)-**6**	2/1	THF	65	87 (*R*)
15	(R_a)-**6**	1/1	CH_2Cl_2	100	57 (*R*)
16	(R_a)-**6**	2/1	CH_2Cl_2	100	78 (*R*)
17	(S_a)-**7**	1/1	THF	48	96 (*R*)
18	(S_a)-**7**	2/1	THF	68	98 (*R*)
19	(S_a)-**7**	1/1	CH_2Cl_2	100	98 (*R*)
20	(S_a)-**7**	**2/1**	**CH_2Cl_2**	**90**	**99 (*R*)**
21	(S_a)-**7**	1/1	THF	100	83 (*S*)[c]
22	(S_a)-**7**	2/1	THF	100	50 (*S*)[c]
23	(S_a)-**7**	1/1	CH_2Cl_2	100	86 (*S*)[c]
24	(S_a)-**7**	2/1	CH_2Cl_2	100	84 (*S*)[c]
25	(R_a)-**7**	1/1	THF	74	80 (*R*)
26	(R_a)-**7**	2/1	THF	48	69 (*R*)
27	(R_a)-**7**	1/1	CH_2Cl_2	100	81 (*R*)
28	(R_a)-**7**	2/1	CH_2Cl_2	100	50 (*R*)

[a] All reactions were carried out with 2 mol% of $[Pd(allyl)Cl]_2$ or 1 mol% $[Pt(allyl)Cl]_4$ at room temperature for 48 h.

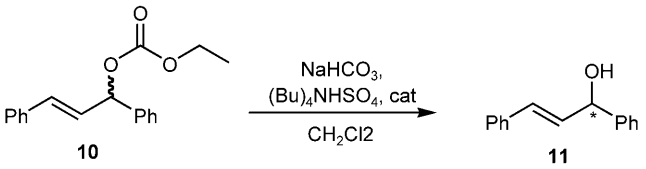
[b] Both the conversion of substrate **8** and enantiomeric excess of **9d** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH/$HNEt_2$ = 200/1/0.1, 0.9 mL min^{-1}, 254 nm).

[c] With $[Pt(allyl)Cl]_4$ as a precatalyst

gardless of the L/Pd molar ratio and the nature of the solvent, and with the highest conversion being observed in CH_2Cl_2. The Pt-catalyzed amination of (*E*)-1,3-diphenylallyl acetate **8** with pyrrolidine was characterized by the quantitative conversion of the starting substrate and the good enantioselectivity of the resulting product (*S*)-**9d**, with opposite absolute configuration (up to 86% *ee*). The nature of the solvent did not influence the asymmetric induction, and the optimal L/Pt molar ratio is 1 (see Table 5, entries 21–24). To the best of our knowledge, this is the first example of the use of organophosphorus ligands in the Pt-catalyzed asymmetric allylic amination.[14e]

*P**,*P**-Bidentate diamidophosphites (S_a)-**7** and (R_a)-**7** were also involved in the deracemization reaction that provides valuable optically active allylic alcohols, such as chalcol **11**,[23] which is of considerable practical significance. Ethyl (*E*)-1,3-diphenylallyl carbonate **10** was chosen as a substrate (Table 6).

Table 6. Pd-catalyzed deracemization of ethyl (*E*)-1,3-diphenylallyl carbonate **10**.[a]



10 **11**

Entry	Ligand	L/Pd	Conv.[b] [%]	*ee*[b] [%]
1	(S_a)-**7**	**1/1**	**65**	**90 (*S*)**
2	(S_a)-**7**	2/1	90	86 (*R*)
3	(R_a)-**7**	1/1	56	87 (*R*)
4	(R_a)-**7**	2/1	93	29 (*S*)

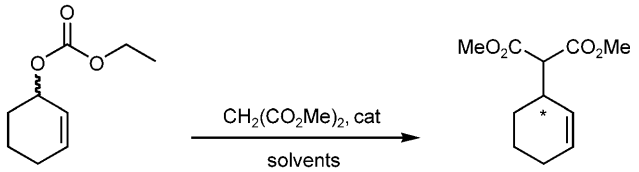
[a] All reactions were carried out with 2 mol% of $[Pd(allyl)Cl]_2$ in CH_2Cl_2 at room temperature for 48 h.

[b] Both the conversion of substrate **10** and enantiomeric excess of **11** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH = 9/1, 0.7 mL min^{-1}, 254 nm).

Note that the complete conversion of a racemate to one enantiomer without intermediate separation of materials (deracemization) is one of the current challenges in asymmetric synthesis. Traditionally, the Pd-catalyzed deracemization of allylic esters was carried out in CH_2Cl_2-H_2O (9:1) medium.[23] However, we used a unique procedure carried out in anhydrous CH_2Cl_2 with the formation of $(Bu)_4NHCO_3$ salt directly (*in situ*) in organic media.[11] Under these conditions and at the molar ratio L/Pd = 1, both ligands (S_a)-**7** and (R_a)-**7** provided moderate conversion of **10**, and essentially equally good levels of asymmetric induction (90% and 87% *ee*) with (*S*) and (*R*) configuration of **11**, respectively (Table 6, entries 1 and 3). It is interesting, that the increase of the L/Pd molar ratio gave rise to product **11** having opposite absolute configuration (Table 6, entries 1,2 and 3,4).

We also screened ligands **5–7** in the Pd-catalyzed allylic alkylation of the cyclic substrate, cyclohex-2-enyl ethyl carbonate **12**, with dimethyl malonate as the C-nucleophile (Table 7). The enantioselectivity for the cyclic substrate **12** is usually more difficult to control than for the hindered acyclic substrate **8**.[24] The stereochemistry of the alkylation of **12** revealed some remarkable trends. It is clear that *P**-monodentate diamidophosphite (S_a)-**5** demonstrated higher catalytic

Table 7. Pd-catalyzed allylic alkylation of cyclohex-2-enyl ethyl carbonate **12** with dimethyl malonate.[a]



12 **13**

Entry	Ligand	L/Pd	Solvent	Conv.[b] [%]	*ee*[b] [%]
1	(S_a)-**5**	1/1	THF	85	47 (*R*)
2	(S_a)-**5**	2/1	THF	90	50 (*R*)
3	(S_a)-**5**	**1/1**	**CH_2Cl_2**	**100**	**70 (*R*)**
4	(S_a)-**5**	2/1	CH_2Cl_2	100	50 (*R*)
5	(R_a)-**5**	1/1	THF	61	40 (*R*)
6	(R_a)-**5**	2/1	THF	30	12 (*R*)
7	(R_a)-**5**	1/1	CH_2Cl_2	89	33 (*R*)
8	(R_a)-**5**	2/1	CH_2Cl_2	90	54 (*R*)
9	(S_a)-**6**	1/1	CH_2Cl_2	92	40 (*R*)
10	(S_a)-**6**	2/1	CH_2Cl_2	100	43 (*R*)
11	(R_a)-**6**	1/1	CH_2Cl_2	82	30 (*R*)
12	(R_a)-**6**	2/1	CH_2Cl_2	100	32 (*R*)
13	(S_a)-**7**	1/1	THF	28	21 (*S*)
14	(S_a)-**7**	2/1	THF	42	60 (*S*)
15	(S_a)-**7**	1/1	CH_2Cl_2	100	26 (*S*)
16	(S_a)-**7**	2/1	CH_2Cl_2	100	44 (*S*)
17	(R_a)-**7**	1/1	THF	74	58 (*R*)
18	(R_a)-**7**	2/1	THF	87	15 (*R*)
19	(R_a)-**7**	1/1	CH_2Cl_2	97	46 (*R*)
20	(R_a)-**7**	2/1	CH_2Cl_2	99	30 (*R*)

[a] All reactions were carried out with 2 mol% of $[Pd(allyl)Cl]_2$ at room temperature for 48 h (BSA, KOAc).

[b] Both the conversion of substrate **12** and enantiomeric excess of **13** were determined by HPLC [Daicel Chiralcel AD, C_6H_{14}/*i*-PrOH = 200/1, 1 mL min^{-1}, 219 nm, *t*(R) = 11.3 min, *t*(S) = 12.1 min].

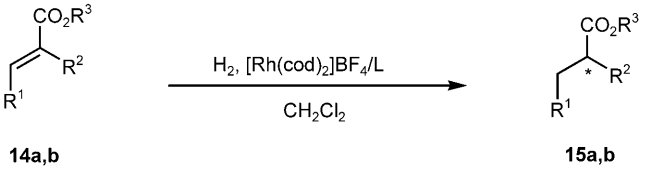
activity and enantioselectivity (up to 70% *ee*) than its diastereomer (R_a)-**5** and bidentate ligands **6** and **7** (*ee* is no higher than 54%, 43% and 60%, respectively; Table 7, entries 1–4 and 5–20).

With the participation of diamidophosphites **5** and **6**, (*R*)-enantiomer of product **13** is formed. At the same time, like the Pd-catalyzed amination of **8** with dipropylamine, the use of both isomers of ligand **7** made it possible to obtain product **13** with opposite absolute configurations. (Table 7, entries 13–16 and 17–20). In general, diamidophosphite (S_a)-**5** showed enantioselectivities of up to 70% in the asymmetric synthesis of dimethyl 2-(cyclohex-2-enyl)malonate **13**, which is a rather good result for the sterically undemanding substrate **12** (see Ref.[24] and references cited therein).

Rhodium-Catalyzed Asymmetric Hydrogenation

In this section, we report the use of the diamidophosphites **5–7** in the Rh-catalyzed enantioselective hydrogenation of prochiral methyl esters of unsaturated acids, *viz.*, dimethyl itaconate **14a** and methyl 2-acetamidoacrylate **14b** (Table 8).

Table 8. Rh-catalyzed hydrogenation of α-dehydrocarboxylic acid esters.[a]



14a,b **15a,b**

R^1 = H, R^2 = CH_2CO_2Me, R^3 = Me, **14a** and **15a**
R^1 = H, R^2 = NHAc, R^3 = Me, **14b** and **15b**

Entry	Substrate	Ligand	L/Rh	Conv.[b,c] [%]	*ee*[b,c] [%]
1	**14a**	(S_a)-**5**	2/1	70	60 (*S*)
2	**14a**	(R_a)-**5**	2/1	100	45 (*S*)
3	**14a**	(S_a)-**6**	1/1	20	0
4	**14a**	(R_a)-**6**	1/1	100	4 (*R*)
5	**14a**	(S_a)-**7**	**1/1**	**100**	**> 99 (*R*)**
6	**14a**	(S_a)-**7**	2/1	100	98 (*R*)
7	**14b**	(S_a)-**5**	2/1	100	72 (*R*)
8	**14b**	(R_a)-**5**	2/1	100	11 (*R*)
9	**14b**	(S_a)-**6**	1/1	100	0
10	**14b**	(R_a)-**6**	1/1	35	30 (*S*)
11	**14b**	(S_a)-**7**	**1/1**	**100**	**99 (*S*)**
12	**14b**	(S_a)-**7**	2/1	100	97 (*S*)

[a] All reactions were carried out with 0.5 mol% of $[Rh(COD)_2]BF_4$ in CH_2Cl_2 at 25 °C and 1.3 bar H_2 for 20 h.

[b] Both the conversion of substrate **14a** and enantiomeric excess of **15a** were determined by GC (Lipodex E, 25 m × 0.25 mm, 80 °C, 1 mL min^{-1}) or HPLC [Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH = 98/2, 0.8 mL min^{-1}, 220 nm, *t*(R) = 9.1 min, *t*(S) = 16.1 min].

[c] Both the conversion of substrate **14b** and enantiomeric excess of **15b** were determined by GC [XE-valine(*tert*-butylamide) 4 × 0.25 mm, 85 °C, 1 mL min^{-1}].

These benchmark substrates have been already investigated with a wide variety of ligands characterized by various donor groups.[1b,d] We can, therefore, compare directly the efficacy of different ligand systems. In all cases, the catalysts were generated *in situ* from the complex $[Rh(COD)_2]BF_4$ (COD is 1,5-cyclooctadiene) and the corresponding ligand in CH_2Cl_2 medium.

In the transformation of **14a** to succinate (*S*)-**15a**, ligands **5** showed good conversion and mediocre enantioselectivity (up to 60% *ee*, Table 8, entries 1 and 2). Unfortunately, the use of both diastereomers of *P**,*N*-

bidentate diamidophosphite **6** generated an almost racemic product **15a**. On the contrary, *P*,P**-bidentate ligand (S_a)-**7** resulted in virtually quantitative enantioselectivity (98 to >99% *ee*) regardless of the L/Rh molar ratio. The asymmetric hydrogenation of **14b** was characterized by similar trends. In particular, *P**-monodentate diamidophosphites **5** allowed the synthesis of product (*R*)-**15b** with moderate enantioselectivity, and (S_a)-**5** was shown to be a better stereoselector than its diastereomer (R_a)-**5** (*ee* 72 and 11%, respectively, Table 8, entries 7 and 8). *P*,N*-Bidentate diamidophosphites **6** were again practically inefficient (*ee* is no higher than 30%). As in the case of hydrogenation of dimethyl itaconate **14a**, *P*,P**-bidentate ligand (S_a)-**7** is an excellent stereoselector: the product (*S*)-**15b** was formed with the enantioselectivity up to 99%.

In order to throw light on the nature of the catalytic species, we carried out MALDI TOF/TOF and ^{31}P NMR investigations of the rhodium complexes obtained from stereoselectors **5–7**. The appropriate measurements were performed in dichloromethane solutions of 1:2 mixtures of $[Rh(COD)_2]BF_4$/**5** and 1:1 mixtures of $[Rh(COD)_2]BF_4$/**6** or (S_a)-**7** because hydrogenation reactions were carried out using these ratios. It was shown that *P**-monodentate diamidophosphites **5** are capable of forming cationic complexes $[Rh(COD)(\mathbf{5})_2]BF_4$ bearing two phosphorus ligands which are *cis*-arranged at Rh(I). *P*,N*- and *P*,P**-bidentate ligands **6** and (S_a)-**7** are chelating agents and form cationic metal chelates $[Rh(COD)(\mathbf{6})]BF_4$ and $\{Rh(COD)[(S_a)\text{-}\mathbf{7}]\}BF_4$ with *cis*-orientation of the *P*,N*- or *P*,P**- donor atoms. MALDI TOF/TOF mass spectral examination of the resulting solutions revealed the mononuclear nature of the complexes $\{Rh(COD)[(S_a)\text{-}\mathbf{5}]_2\}BF_4$ {*m/z* (I, %) = 1501 (18) $[M-BF_4]^+$, 1393 (100) $[M-BF_4-COD]^+$}, $[Rh(COD)(\mathbf{6})]BF_4$ {*m/z* (I, %) = 793 (54) $[M-BF_4]^+$, 685 (100) $[M-BF_4-COD]^+$) and $\{Rh(COD)[(S_a)\text{-}\mathbf{7}]\}BF_4$ {*m/z* (I, %) = 906 (54) $[M-BF_4]^+$, 798 (100) $[M-BF_4-COD]^+$}. The ^{31}P NMR spectrum of the $[Rh(COD)_2]BF_4$/(S_a)-**5** 1:2 mixture showed the presence of a doublet signal of complex $\{Rh(COD)[(R_P)\text{-}(S_a)\text{-}\mathbf{5}]_2\}BF_4$ based on major (R_P)-(S_a)-**5** *P**-epimer at 108.4 ppm with the typical coupling constant $^1J_{P,Rh}$ = 228.9 Hz (81%) and AX spin system of mixed complex $\{Rh(COD)[(R_P)\text{-}(S_a)\text{-}\mathbf{5}][(S_P)\text{-}(S_a)\text{-}\mathbf{5}]\}BF_4$ δ_P = 105.9, $^1J_{P,Rh}$ = 226.7 Hz, $^2J_{P,P}$ = 38.2 Hz; δ_P = 92.6, $^1J_{P,Rh}$ = 227.4 Hz, $^2J_{P,P}$ = 38.2 Hz (19%). In contrast, the ^{31}P NMR spectrum of the $[Rh(COD)_2]BF_4$/(R_a)-**5** 1:2 mixture proved to be more complicated and contained two dominant doublets δ_P = 107.2, $^1J_{P,Rh}$ = 230.1 Hz (22%) and δ_P = 101.9, $^1J_{P,Rh}$ = 213.8 Hz (53%) alongside with a number of additional spectral signals in the interval 106.1–97.6 ppm with coupling constants $^1J_{P,Rh}$ = 188.3–225.5 Hz. As the ^{31}P NMR data clearly showed the presence in solution of several Rh(I) catalytic precursors based on (R_a)-**5**, it is possible to understand the fact that this diamidophosphite is a less efficient stereoselector than (S_a)-**5** (Table 8, entries 1, 2 and 7, 8). It should be further noted that in the case of the excellent *P*,P**-bidentate stereoselector (S_a)-**7**, only a sharp doublet at δ_P = 108.5, $^1J_{P,Rh}$ = 227.2 Hz of the individual cationic complex $\{Rh(COD)[(S_a)\text{-}\mathbf{7}]\}BF_4$ was observed in the ^{31}P NMR spectrum of the reaction solution. At the same time, the situation with *P*,N*-bidentate diamidophosphites **6** is rather ambiguous. On the one hand, complex $\{Rh(COD)[(R_a)\text{-}\mathbf{6}]\}BF_4$ showed in the ^{31}P NMR spectrum a broad signal with maximum at 102.4 ppm and upfield shift relative to the free ligand. Such spectral behaviour can be rationalized by taking into account the flexible nature of the eleven-membered *P*,N*-chelate ring. On the other hand, the ^{31}P NMR spectrum of $[Rh(COD)_2]BF_4$/(S_a)-**6** 1:1 mixture contained two doublet signals of complexes $\{Rh(COD)[(S_P)\text{-}(S_a)\text{-}\mathbf{6}]_2\}BF_4$ at δ_P = 111.6, $^1J_{P,Rh}$ = 220.3 Hz (9%) and $\{Rh(COD)[(R_P)\text{-}(S_a)\text{-}\mathbf{6}]_2\}BF_4$ at δ_P = 101.6, $^1J_{P,Rh}$ = 228.4 Hz (91%). Nevertheless, in the asymmetric hydrogenation both (S_a)-**6** and (R_a)-**6** were almost equally inefficient. Thus, the reason behind this finding remains unclear. However, there are some other examples of low conversion and/or asymmetric induction in the Rh-catalyzed hydrogenation with participation of the BINOL-based *P,N*-bidentate ligands.[5d,25]

Conclusions

In summary, the present paper has led to the following conclusions: i) novel *P**-chiral diamidophosphites **5–7** with 1,3,2-diazaphospholidine rings and (S_a)- or (R_a)-binaphthyl backbone have been successfully synthesized; ii) in asymmetric Pd-catalyzed allylation, *P**-mono, *P*,N*- and *P*,P**-bidentate diamidophosphites are very efficient and complementary groups of stereoselectors; iii) in asymmetric Rh-catalyzed hydrogenation, *P**-monodentate diamidophosphites **5** and especially *P*,N*-bidentate diamidophosphites **6** are less efficient stereoselectors than *P*,P**-bidentate ligand (S_a)-**7**, whereas in Pd-catalyzed allylation they can demonstrate similar and even high productivity. The combination of high enantioselectivity (*ee*s up to 99%), low cost, and easy synthesis of the ligands makes them very attractive for further catalytic applications. As a consequence, additional studies highlighting the potential of these new stereoselectors in other asymmetric reactions are now in progress in our laboratories.

Experimental Section

General Remarks

^{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). Mass spectra were recorded with a Varian MAT 311 spectrometer (EI) and a Bruker Daltonics Ultraflex spectrometer (MALDI TOF/TOF). Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow).

All reactions were carried out under argon in freshly dried and distilled solvents; Et_3N, pyrrolidine and dipropylamine were twice distilled over KOH and then over a small amount of $LiAlH_4$ before use. The phosphorylating reagent – (5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]-octane **4** – was prepared as published.[12a] $[Pd(allyl)Cl]_2$, $[Pt(allyl)Cl]_4$ and $[Rh(COD)_2]BF_4$ were prepared as described earlier.[26–28] Starting substrates (*E*)-1,3-diphenylallyl acetate **8**, ethyl (*E*)-1,3-diphenylallyl carbonate **10** and cyclohex-2-enyl ethyl carbonate **12** were synthesized as published.[26,29,30] (S_a)- and (R_a)-2,2′-dihydroxy-1,1′-binaphthyls (S_a)-**1** and (R_a)-**1**, sodium *para*-toluenesulfinate, dimethyl malonate, BSA [*N,O*-bis(trimethylsilyl)acetamide] and starting substrates dimethyl itaconate **14a** and methyl 2-acetamidoacrylate **14b** were purchased from Aldrich and Acros Organics and used without further purification.

For Pd- and Pt-catalyzed allylic substitution reactions, sulfonylation of substrate **8** with sodium *para*-toluenesulfinate, alkylation with dimethyl malonate, amination with dipropylamine and pyrrolidine; and alkylation of substrate **12** with dimethyl malonate were performed according to the appropriate procedures.[12a,b,31,32,12c] Pd-catalyzed deracemization of substrate **10** was performed according to the known procedure.[11] Rh-catalyzed hydrogenation of α-dehydrocarboxylic acid esters **14a, b** was performed as published.[12c,33]

General Procedure for the Synthesis of Ligands (S_a)-5, (R_a)-5 and (S_a)-6, (R_a)-6

A solution of compounds **2** or **3** (5 mmol) in toluene (15 mL) was added dropwise to a vigorously stirred solution of phosphorylating reagent **4** (1.21 g, 5 mmol) and Et_3N (0.73 mL, 5.2 mmol) in toluene (15 mL). The mixture was then heated to the boiling point, stirred for 15 min and cooled to 20 °C. Solid $Et_3N{\cdot}HCl$ was filtered off; toluene was removed under reduced pressure (40 Torr). Products (S_a)-**5**, (R_a)-**5** and (S_a)-**6**, (R_a)-**6** were purified by flash chromatography on silica gel using undegassed eluents (EtOAc/hexane 1/2 and 1/1, respectively) and dried in vacuum (1 Torr) for 2 h.

2-[(2″*R*,5″*S*)-3″-Phenyl-1″,3″-diaza-2″-phosphabicyclo-[3.3.0]octyloxy]-2′-tosyloxy-(*Sa*)-1,1′-binaphthyl [(S_a)-5]: White solid; yield: 2.51 g (78%); mp 149–150 °C. ^{1}H NMR ($CDCl_3$): $\delta = 1.33$ (dq, $J = 11.4$ Hz, 1H), 1.43 (m, 2H), 1.65 (dq, $J = 11.4$ Hz, 1H), 2.21 (s, 3H), 2.94 (m, $J = 7.3$, 6.6 Hz, 2H), 3.08 (m, 1H), 3.35 (m, 2H), 6.65 (d, $J = 9.1$ Hz, 2H), 6.83 (d, $J = 9.1$ Hz, 1H), 6.94 (m, 3H), 7.04 (d, $J = 8.9$ Hz, 2H), 7.13–7.26 (m, 6H), 7.47 (m, 1H), 7.72–7.91 (m, 4H), 7.99 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 21.3$ (s, CH_3), 25.9 (d, $^{3}J = 4.2$ Hz, C-7″), 31.0 (s, C-6″), 47.1 (d, $^{2}J = 33.4$ Hz, C-8″), 53.0 (d, $^{2}J = 7.3$ Hz, C-4″), 62.1 (d, $^{2}J = 8.4$ Hz, C-5″), 114.9 (d, $^{3}J = 13.2$ Hz, CH_{Ph}), 118.8 (s, CH_{Ph}), 121.1 (s, CH_{Ar}), 121.6 (s, C_{Ar}), 122.5 (d, $^{3}J = 7.0$ Hz, CH_{Ar}), 123.7 (s, CH_{Ar}), 125.1 (s, C_{Ar}), 125.3 (s, CH_{Ar}), 125.8 (s, CH_{Ar}), 126.0 (s, CH_{Ar}), 126.8 (s, CH_{Ar}), 127.0 (s, CH_{Ts}), 127.3 (s, CH_{Ar}), 127.7 (s, CH_{Ar}), 128.8 (s, CH_{Ph}), 129.0 (s, CH_{Ar}), 129.1 (s, CH_{Ts}), 129.7 (s, C_{Ar}), 130.1 (s, CH_{Ar}), 130.6 (s, CH_{Ar}), 131.4 (s, C_{Ar}), 133.5 (s, C_{Ar}), 133.7 (s, C_{Ar}), 143.7 (s, C_{Ts}), 144.6 (d, $^{2}J = 15.7$ Hz, C_{Ph}), 145.9 (s, C_{Ts}), 150.1 (s, C_{Ar}), 151.8 (d, $^{2}J = 5.5$ Hz, C_{Ar}); MS (EI): *m/z* (I, %) = 645 (3) $[M]^+$; MS (MALDI TOF/TOF): *m/z* (I, %) = 646 (10) $[M+H]^+$, 491 (100) $[M-Ts+H]^+$; anal. calcd. for $C_{38}H_{33}N_2O_4PS$: C 70.79, H 5.16, N, 4.35; found: C 70.97, H 5.22, N 4.25.

2-[(2″*R*,5″*S*)-3″-Phenyl-1″,3″-diaza-2″-phosphabicyclo-[3.3.0]octyloxy]-2′-tosyloxy-(*Ra*)-1,1′-binaphthyl [(R_a)-5]: White solid; yield: 2.58 g (80%); mp 109–110 °C. ^{1}H NMR ($CDCl_3$): $\delta = 1.40$ (m, $J = 11.5$ Hz, 2H), 1.66 (m, $J = 11.5$ Hz, 2H), 2.25 (s, 3H), 2.95 (m, $J = 7.2$, 6.6 Hz, 2H), 3.1 (m, 1H), 3.37 (m, 2H), 6.64 (d, $J = 9.0$ Hz, 2H), 6.83 (d, $J = 9.0$ Hz, 1H), 6.92 (m, 3H), 7.05 (d, $J = 8.9$ Hz, 2H), 7.12–7.26 (m, 6H), 7.44 (m, 1H), 7.72–7.93 (m, 4H), 8.03 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 21.1$ (s, CH_3), 26.1 (d, $^{3}J = 4.2$ Hz, C-7″), 31.1 (s, C-6″), 47.5 (d, $^{2}J = 35.4$ Hz, C-8″), 53.4 (d, $^{2}J = 7.1$ Hz, C-4″), 63.0 (d, $^{2}J = 8.2$ Hz, C-5″), 115.1 (d, $^{3}J = 13.2$ Hz, CH_{Ph}), 118.9 (s, CH_{Ph}), 121.1 (s, CH_{Ar}), 122.8 (s, C_{Ar}), 123.1 (d, $^{3}J = 7.3$ Hz, CH_{Ar}), 123.4 (s, CH_{Ar}), 125.1 (s, C_{Ar}), 125.5 (s, CH_{Ar}), 125.7 (s, CH_{Ar}), 126.1 (s, CH_{Ar}), 126.5 (s, CH_{Ar}), 127.0 (s, CH_{Ts}), 127.2 (s, CH_{Ar}), 127.9 (s, CH_{Ar}), 128.7 (s, CH_{Ph}), 129.0 (s, CH_{Ar}), 129.3 (s, CH_{Ts}), 129.8 (s, C_{Ar}), 130.4 (s, CH_{Ar}), 130.9 (s, CH_{Ar}), 131.4 (s, C_{Ar}), 133.2 (s, C_{Ar}), 133.7 (s, C_{Ar}), 143.8 (s, C_{Ts}), 144.3 (d, $^{2}J = 16.1$ Hz, C_{Ph}), 146.3 (s, C_{Ts}), 150.0 (s, C_{Ar}), 153.5 (d, $^{2}J = 5.2$ Hz, C_{Ar}); MS (MALDI TOF/TOF): *m/z* (I, %) = 646 (21) $[M+H]^+$, 491 (100) $[M-Ts+H]^+$; anal. calcd. for $C_{38}H_{33}N_2O_4PS$: C 70.79, H 5.16, N, 4.35; found: C 70.91, H 5.02, N 4.41.

2-[(2″*R*,5″*S*)-3″-Phenyl-1″,3″-diaza-2″-phosphabicyclo-[3.3.0]octyloxy]-2′-[(pyridin-2-yl)methoxy]-(*Sa*)-1,1′-binaphthyl [(S_a)-6]: White solid; yield: 2.38 g (82%); mp 84–85 °C. ^{1}H NMR ($CDCl_3$): $\delta = 1.38$ (m, $J = 11.2$ Hz, 1H), 1.53 (m, $J = 11.2$ Hz, 3H), 2.60 (m, $J = 7.5$, 6.4 Hz, 1H), 2.88 (m, 1H), 2.98 (m, 1H), 3.29 (m, 2H), 5.23 (s, 2H), 6.65 (d, $J = 6.1$ Hz, 2H), 6.83 (m 2H), 7.09 (m, 3H), 7.19 (m, 2H), 7.25 (m, 2H), 7.35–7.46 (m, 4H), 7.51 (d, $J = 9.0$ Hz, 1H), 7.88 (d, $J = 9.0$ Hz, 1H), 7.95 (m, 3H), 8.48 (m, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 25.8$ (d, $^{3}J = 3.7$ Hz, C-7″), 30.7 (s, C-6″), 47.2 (d, $^{2}J = 33.5$ Hz, C-8″), 53.3 (d, $^{2}J = 6.9$ Hz, C-4″), 61.9 (d, $^{2}J = 8.4$ Hz, C-5″), 70.0 (s, OCH_2), 114.2 (s, CH_{Py}), 114.7 (d, $^{3}J = 12.8$ Hz, CH_{Ph}), 118.7 (s, CH_{Ph}), 119.9 (s, C_{Ar}), 120.8 (s, CH_{Ar}), 121.8 (s, CH_{Ar}), 122.9 (d, $^{3}J = 6.6$ Hz, CH_{Ar}), 123.3 (s, CH_{Ar}), 124.0 (s, CH_{Ar}), 124.3 (d, $^{3}J = 2.9$ Hz, C_{Ar}), 125.8 (s, CH_{Ar}), 125.9 (s, CH_{Ar}), 127.5 (s, CH_{Ar}), 127.7 (s, CH_{Ar}), 127.5 (s, CH_{Ar}), 127.7 (s, CH_{Ar}), 128.6 (s, CH_{Ph}), 128.7 (s, CH_{Py}), 128.9 (s, C_{Ar}), 129.8 (s, CH_{Ar}), 130.2 (s, C_{Ar}), 133.9 (s, C_{Ar}), 134.1 (s, C_{Ar}), 136.3 (s, CH_{Py}), 144.8 (d, $^{2}J = 15.7$ Hz, C_{Ph}), 148.2 (s, CH_{Py}), 149.7 (s, C_{Ar}), 153.7 (s, C_{Ar}), 157.6 (s, C_{Py}); MS (EI): *m/z* (I, %) = 582 (2) $[M]^+$; MS (MALDI TOF/TOF): *m/z* (I, %) = 583 (15) $[M+H]^+$, 475 (100) $[M-OCH_2Py+H]^+$; anal. calcd. for $C_{37}H_{32}N_3O_2P$: C 76.40, H 5.55, N, 7.22; found: C 76.67, H 5.60, N 7.04.

2-{(2″*R*,5″*S*)-3″-phenyl-1″,3″-diaza-2″-phosphabicyclo-[3.3.0]octyloxy}-2′-[(pyridin-2-yl)methoxy]-(*Ra*)-1,1′-binaphthyl [(R_a)-6]: White solid; yield: 2.33 g (80%); mp 90–91 °C. ^{1}H NMR ($CDCl_3$): δ = 1.39 (m, J = 11.4 Hz, 1H), 1.56 (m, J = 11.4 Hz, 3H), 2.63 (m, J = 7.5, 6.5 Hz, 1H), 2.88 (m, 1H), 3.0 (m, 1H), 3.31 (m, 2H), 5.21 (s, 2H), 6.66 (d, J = 7.3 Hz, 2H), 6.83 (m 2H), 7.11 (m, 3H), 7.17 (m, 2H), 7.24 (m, 2H), 7.35–7.44 (m, 4H), 7.52 (d, J = 8.8 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.93 (m, 3H), 8.51 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 25.8 (d, ^3J = 4.0 Hz, C-7″), 31.2 (s, C-6″), 47.2 (d, ^2J = 35.4 Hz, C-8″), 53.7 (d, ^2J = 7.3 Hz, C-4″), 62.3 (d, ^2J = 8.8 Hz, C-5″), 71.3 (s, OCH_2), 114.7 (d, ^3J = 13.1 Hz, CH_{Ph}), 114.8 (s, CH_{Py}), 118.8 (s, CH_{Ph}), 119.9 (s, C_{Ar}), 121.0 (s, CH_{Ar}), 121.9 (s, CH_{Ar}), 122.8 (d, ^3J = 5.5 Hz, CH_{Ar}), 123.3 (s, CH_{Ar}), 124.1 (s, CH_{Ar}), 124.2 (d, ^3J = 2.9 Hz, C_{Ar}), 125.8 (s, CH_{Ar}), 125.9 (s, CH_{Ar}), 126.0 (s, CH_{Ar}), 126.1 (s, CH_{Ar}), 127.6 (s, CH_{Ar}), 127.7 (s, CH_{Ar}), 128.7 (s, CH_{Ph}), 128.8 (s, CH_{Py}), 129.1 (s, C_{Ar}), 129.3 (s, CH_{Ar}), 130.3 (s, C_{Ar}), 133.9 (s, C_{Ar}), 134.0 (s, C_{Ar}), 136.3 (s, CH_{Py}), 145.0 (d, ^2J = 16.4 Hz, C_{Ph}), 148.3 (s, CH_{Py}), 150.0 (d, ^2J = 6.2 Hz, C_{Ar}), 153.9 (s, C_{Ar}), 157.8 (s, C_{Py}); MS (MALDI TOF/TOF): *m/z* (I, %) = 583 (11) $[M+H]^+$, 475 (100) $[M-OCH_2Py+H]^+$; anal. calcd. for $C_{37}H_{32}N_3O_2P$: C 76.40, H 5.55, N, 7.22; found: C 76.22, H 5.67, N 7.26.

General Procedure for the Synthesis of Ligands (S_a)-7, (R_a)-7

A solution of compound **1** (1.43 g, 5 mmol) in toluene (17 mL) was added dropwise to a vigorously stirred solution of phosphorylating reagent **4** (2.41 g, 10 mmol) and Et_3N (1.45 mL, 10.4 mmol) in toluene (26 mL) within 30 min. The reaction mixture was stirred 24 h at room temperature. Solid Et_3N·HCl was filtered off; toluene was removed under reduced pressure (40 Torr). Products (S_a)-**7**, (R_a)-**7** were purified by column chromatography on silica gel using undegassed eluents (EtOAc/hexane 1/1) and dried in vacuum (1 Torr) for 2 h.

2,2′-Bis{(2″*R*,5″*S*)-3″-phenyl-1″,3″-diaza-2″-phosphabicyclo[3.3.0]octyloxy}-(*Sa*)-1,1′-binaphthyl [(S_a)-7]: White solid; yield: 2.92 g (84%); mp 144–145 °C. ^{1}H NMR ($CDCl_3$): δ = 1.37 (dq, J = 11.8 Hz, 2H), 1.5 (m, 4H), 1.68 (dq, J = 11.8 Hz, 2H), 2.53 (ddd, J = 8.2, 7.1, 5.9 Hz, 2H), 2.9 (m, 4H), 3.4 (m, 4H), 6.65 (d, J = 7.8 Hz, 4H), 6.71 (t, J = 7.9 Hz, 4H), 7.02 (t, J = 8.5 Hz, 4H), 7.16 (m, 4H), 7.36 (d, J = 7.7, 7.3 Hz, 2H), 7.74 (d, J = 8.3 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ = 25.6 (d, ^3J = 4.4 Hz, C-7″), 31.3 (s, C-6″), 47.1 (d, ^2J = 36.5 Hz, C-8″), 53.8 (d, ^2J = 8.0 Hz, C-4″), 62.3 (d, ^2J = 8.8 Hz, C-5″), 114.9 (d, ^3J = 12.4 Hz, CH_{Ph}), 118.7 (s, CH_{Ph}), 123.1 (d, ^3J = 5.1 Hz, CH_{Ar}), 123.6 (s, CH_{Ar}), 124.5 (s, C_{Ar}), 125.3 (s, CH_{Ar}), 127.0 (s, CH_{Ar}), 127.6 (s, CH_{Ar}), 128.4 (s, CH_{Ar}), 128.8 (s, CH_{Ph}), 130.1 (s, C_{Ar}), 134.1 (s, C_{Ar}), 145.2 (d, ^2J = 16.1 Hz, C_{Ph}), 150.1 (d, ^2J = 8.0 Hz, C_{Ar}); MS (EI): *m/z* (I, %) = 695 (2) $[M]^+$; MS (MALDI TOF/TOF): *m/z* (I, %) = 718 (100) $[M+Na]^+$, 696 (28) $[M+H]^+$; anal. calcd. for $C_{42}H_{40}N_4O_2P_2$: C 72.61, H 5.80, N, 8.06; found: C 72.88, H 5.86, N 7.93.

2,2′-Bis{(2″*R*,5″*S*)-3″-phenyl-1″,3″-diaza-2″-phosphabicyclo[3.3.0]octyloxy}-(*Ra*)-1,1′-binaphthyl [(R_a)-7]: White solid; yield: 3.09 g (89%); mp 126–127 °C. ^{1}H NMR ($CDCl_3$): δ = 1.35 (dq, J = 11.8 Hz, 2H), 1.5 (m, 4H), 1.69 (dq, J = 11.8 Hz, 2H), 2.55 (ddd, J = 8.1, 7.2, 6.0 Hz, 2H), 3.0 (m, 4H), 3.4 (m, 4H), 6.65 (d, J = 7.7 Hz, 4H), 6.70 (t, J = 8.0 Hz, 4H), 7.05 (t, J = 8.4 Hz, 4H), 7.16 (m, 4H), 7.33 (d, J = 7.8, 7.1 Hz, 2H), 7.75 (d, J = 8.3 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ = 25.9 (d, ^3J = 4.4 Hz, C-7″), 31.1 (s, C-6″), 47.1 (d, ^2J = 37.5 Hz, C-8″), 53.6 (d, ^2J = 8.2 Hz, C-4″), 62.6 (d, ^2J = 8.9 Hz, C-5″), 115.1 (d, ^3J = 12.3 Hz, CH_{Ph}), 118.7 (s, CH_{Ph}), 123.1 (d, ^3J = 5.2 Hz, CH_{Ar}), 123.5 (s, CH_{Ar}), 124.5 (s, C_{Ar}), 125.1 (s, CH_{Ar}), 127.0 (s, CH_{Ar}), 127.8 (s, CH_{Ar}), 128.6 (s, CH_{Ar}), 128.9 (s, CH_{Ph}), 130.1 (s, C_{Ar}), 134.3 (s, C_{Ar}), 145.4 (d, ^2J = 16.1 Hz, C_{Ph}), 150.3 (d, ^2J = 8.1 Hz, C_{Ar}); MS (MALDI TOF/TOF): *m/z* (I, %) = 718 (100) $[M+Na]^+$, 696 (54) $[M+H]^+$; anal. calcd. for $C_{42}H_{40}N_4O_2P_2$: C 72.61, H 5.80, N, 8.06; found: C 72.91, H 5.92, N 8.23.

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