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MOP-Type Binaphthyl Phosphite and Diamidophosphite Ligands and Their Application in Catalytic Asymmetric Transformations

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Abstract: Monodentate phosphite and diamidophosphite ligands have been developed based on *O*-methyl-BINOL. These chiral ligands are easy to prepare from readily accessible phosphorylating reagents – (S_a or R_a)-2-chlorodinaphtho[2,1-*d*:1′,2′-*f*]-[1,3,2]dioxaphosphepine and (*2R,5S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane. The new ligands have demonstrated excellent enantioselectivity in the palladium-catalysed allylic substitution reactions of (*E*)-1,3-diphenylallyl acetate with sodium *p*-toluenesulfinate (up to 99% *ee*), pyrrolidine (up to 97% *ee*), dipropylamine (up to 95% *ee*) and dimethyl malonate (up to 99% *ee*). In the palladium-catalysed deracemization of ethyl (*E*)-1,3-diphenylallyl carbonate, up to 96% enantioselectivity has been achieved. The diamidophosphite ligands have exhibited very good enantioselectivity in the Rh-catalysed asymmetric hydrogenation of dimethyl itaconate (up to 90% *ee*).

Keywords: allylic substitution; asymmetric catalysis; hydrogenation; P ligands

Introduction

In the last few years significant achievements have taken place in the application of chiral P monodentate phosphite-type ligands for asymmetric reactions. Such compounds showed excellent results in enantioselective rhodium-catalysed hydrogenation and addition of arylboronic acids, copper-catalysed addition of organozinc and organoaluminium reagents, iridium-catalysed allylic substitution, palladium-catalysed hydrosilylation-oxidation and diboration-allylation, nickel-catalysed hydrovinylation and cycloisomerisation, ruthenium-catalysed hydrogenation of ketones and cyclopropanation.[1–18] Nevertheless, the number of chiral P monodentate phosphites that have been studied in Pd-catalysed asymmetric allylic transformations is rather limited. Meanwhile, catalytic asymmetric allylic substitution serves as one of the most powerful methods for the regio- and stereoselective formation of C–C, C–N, C–O and C–S bonds. The high synthetic utility of this catalytic process is now well established through numerous efficient syntheses of enantiopure natural and unnatural products.[19,20] Compounds $\mathbf{L_a}$–$\mathbf{L_e}$ (Figure 1) represent leading P monodentate phosphite-type ligands for Pd-catalysed enantioselective allylic transformations. In the standard benchmark test, namely allylic alkylation of (*E*)-1,3-diphenylallyl acetate with dimethyl malonate, they afforded up to 97% ($\mathbf{L_a}$), 93% ($\mathbf{L_b}$), 95% ($\mathbf{L_c}$) and 77% *ee* ($\mathbf{L_d}$).[21–24] Other Pd-catalysed reactions with chiral monodentate phosphites have been explored fragmentarily. For example, the palladium complex of $\mathbf{L_e}$ promotes the key step of enantioselective synthesis of alkaloid (+)-γ-lycorane.[19,25]

We describe here the applications of the novel phosphite and diamidophosphite analogues of the well-known phosphine MOP[26,27] (Figure 2) in various asymmetric transformations, first of all to Pd-catalysed allylation and to Rh-catalysed hydrogenation.

It is of note that, in comparison with traditional phosphines, optically active phosphites and amidophosphites seem to be more versatile ligands.[1,2,8] In general, the main advantages of phosphites include high π-acidity of the phosphorus atom, high resistance to oxidative destruction, synthetic availability and their low cost. For example, BINOL-based monophosphites, which are very efficient in asymmetric hydrogenation, are only 2% of the price of the well-known diphosphine BINAP.[28] Moreover, electronic properties of the – traditional for phosphines – PPh_2-

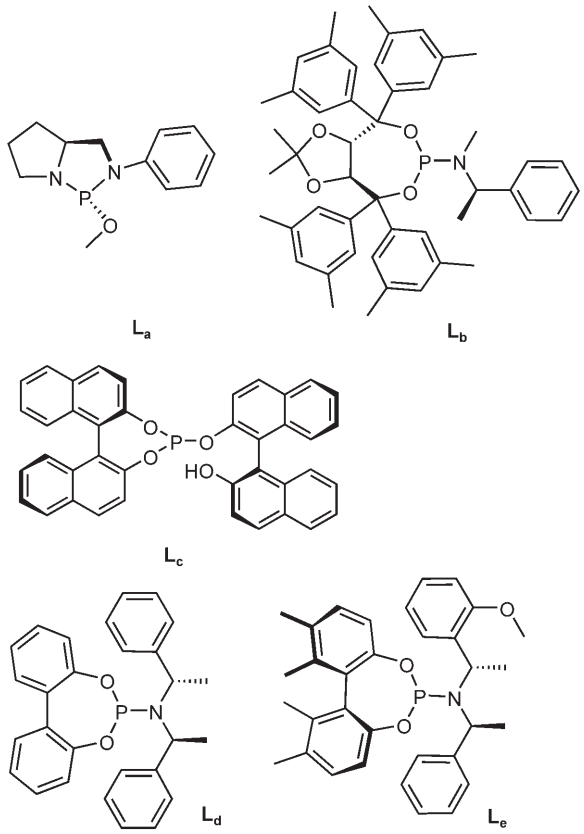


Figure 1. P Monodentate phosphite-type ligands for Pd-catalysed asymmetric allylation.

fragment can be regulated basically only by introduction of electron-donor or electron-acceptor substituents into the phenyl rings. In contrast, phosphites provide broad opportunities for fine tuning of their donor-acceptor and steric properties by incorporation of oxygen and nitrogen into the first coordination sphere of phosphorus and wide variation of the O- and N-containing building blocks.[1] This approach is now considered most practical in developing one universal ligand for different types of asymmetric catalytic reactions. As an original framework for the new ligands, we chose phosphite and diamidophosphite derivatives of rigid, axially chiral, monomethylated BINOL.

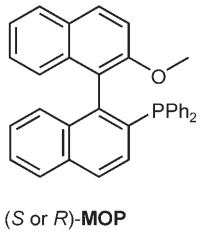
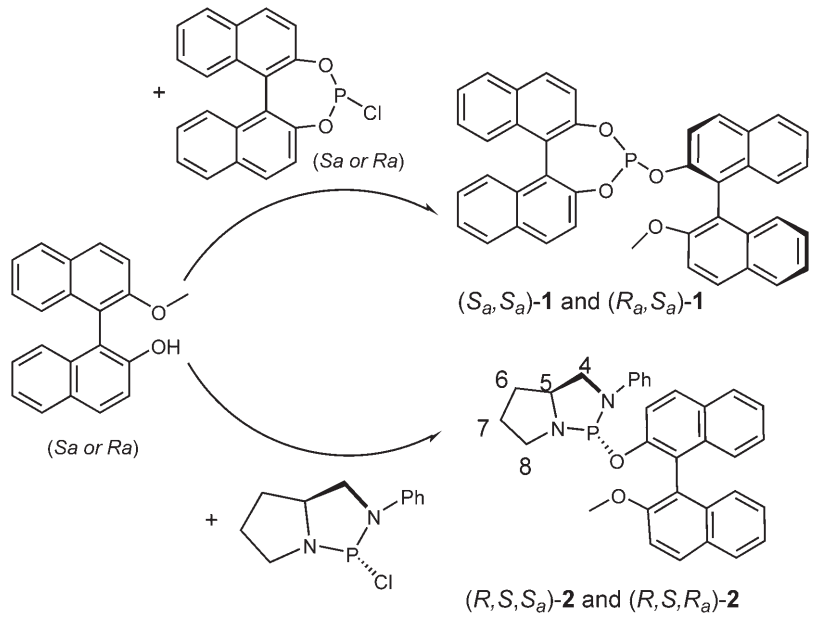


Figure 2. Structure of the phosphine ligand MOP.

Results and Discussion

Synthesis of P Monodentate Phosphite-Type Ligands and their Palladium and Rhodium Complexes

The novel MOP-type phosphites and diamidophosphites were easily obtained by direct phosphorylation of (S_a)- or (R_a)-1-(2-methoxynaphthalen-1-yl)naphthalen-2-ol (*O*-methyl-BINOL) in the presence of Et_3N in C_6H_6 (Scheme 1).



Scheme 1. Synthesis of phosphite-type ligands (S_a,S_a)-**1**, (R_a,S_a)-**1** and (*R*,*S*,S_a)-**2**, (*R*,*S*,R_a)-**2**.

All compounds are white solids, which are stable on prolonged storage. Since appropriate phosphorylating reagents are readily available, new ligands can be prepared on a gram scale. It is worthy of note that structures (*R,S,S*$_a$)-**2** and (*R,S,R*$_a$)-**2** combine together two famous chiral auxiliaries: (*S*)-2-(anilinomethyl)-pyrrolidine and BINOL.

Although the crude *P**-chiral ligands contain minor epimers with an (*S*) configuration of the *P**-stereocentre [diastereoselectivity 94:6, $\delta = 128.9$ and 119.6 for (*R,S,S*$_a$)-**2**; 97:3, $\delta = 125.7$ and 118.4 for (*R,S,R*$_a$)-**2**], simple reprecipitation from $CHCl_3$/hexane yields stereoindividual (*R,S,S*$_a$)-**2** and (*R,S,R*$_a$)-**2**. Therefore, purified (*R,S,S*$_a$)-**2** and (*R,S,R*$_a$)-**2** represent single epimers with a pseudo-equatorial orientation of the exocyclic substituents at the phosphorus atom. The *P**-stereocentre has an (*R*) absolute configuration, which is proved by the characteristic $^2J_{C\text{-}8,P}$ (33.5 and 35.7 Hz) coupling in the ^{13}C NMR spectra of (*R,S,S*$_a$)-**2** and (*R,S,R*$_a$)-**2** (see Experimental Section). The magnitude of $^2J_{C\text{-}8,P}$ seems to be strongly controlled by the dihedral angle associated with the lone-pair orbital of the phosphorus atom and C-8.[21,29–32] The pseudo-equatorial location of exocyclic functions was previously established for ligands $\mathbf{L_a}$.[21]

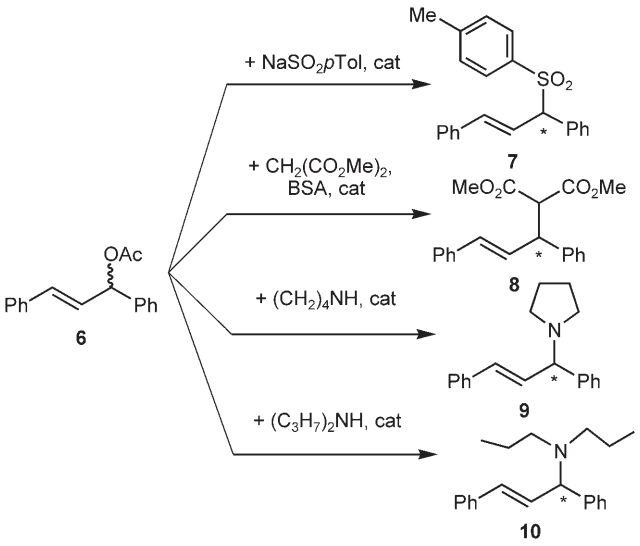
To estimate the steric demands of the new compounds, we calculated their Tolman's angles[33] by the previously reported method using semi-empirical quantum mechanical AM1 techniques with full optimisation of geometrical parameters.[34] The obtained results show that (*S*$_a$,*S*$_a$)-**1** and (*R*$_a$,*S*$_a$)-**1** are characterised by moderate steric demands ($\theta = 141°$), while (*R,S,S*$_a$)-**2** and (*R,S,R*$_a$)-**2** are very bulky ligands ($\theta = 193°$). For comparison, Tolman's angle for $P(C_6F_5)_3$ is 184°, for P(*o*-Tol)$_3$ it is 194°.[34,35]

Complexation of the novel phosphites and diamidophosphites with $[Pd(allyl)Cl]_2$ (in the presence of $AgBF_4$) and $[Rh(COD)_2]BF_4$ produced cationic Pd(II) complexes (Scheme 2).

These compounds are stable in air and well soluble in common organic media. According to the ^{31}P NMR data (see Experimental Section), **3a,b** and **4a,b** demonstrate fast interconversion of the *exo* and *endo* isomers or the absence of one of them.[21] AB spin systems in the spectra of **3a,b** indicate non-equivalence of two P monodentate ligands in the coordination sphere of the palladium atom.[36] It is interesting that the ^{31}P NMR spectra of rhodium complexes **5a,b** contain two doublets with close chemical shifts and $J_{P,Rh}$ coupling constants (see Experimental Section).

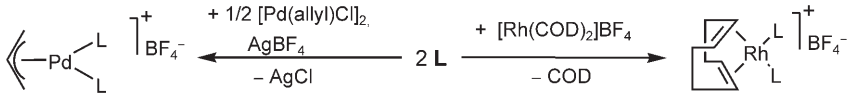
Palladium-Catalysed Asymmetric Allylic Substitution

Next we turned our attention to the applications of (*S*$_a$,*S*$_a$)-**1**, (*R*$_a$,*S*$_a$)-**1** and (*R,S,S*$_a$)-**2**, (*R,S,R*$_a$)-**2** in the palladium complex-catalysed allylation (Scheme 3).



Scheme 3. Enantioselective palladium-catalysed allylic substitution of (*E*)-1,3-diphenylallyl acetate **6**.

In allylic sulfonylation of (*E*)-1,3-diphenylallyl acetate **6** with *p*-TolSO_2Na as the S-nucleophile diamidophosphite (*R,S,R*$_a$)-**2** showed excellent activity and enantioselectivity (Table 1, entries 4–6). It should be noted that chiral allylic sulfones are exceptionally versatile intermediates in organic synthesis[20] and that the 99% enantioselectivity achieved with (*R,S,R*$_a$)-**2** (Table 1, entry 4) is superior to the highest previously known result (97% *ee*) for allylic sulfonylation obtained with other *P**-chiral diamidophosphites.[21] (*R,S,S*$_a$)-**2** afforded product **7** in opposite absolute configuration but with lower enantioselectivity



3a L = (*S*$_a$,*S*$_a$)-**1**
3b L = (*R*$_a$,*S*$_a$)-**1**
4a L = (*R,S,Sa*)-**2**
4b L = (*R,S,R*$_a$)-**2**

5a L = (*R,S,S*$_a$)-**2**
5b L = (*R,S,R*$_a$)-**2**

Scheme 2. Synthesis of complexes **3a**,**b**, **4a**,**b** and **5a**,**b**.

Table 1. Palladium-catalysed allylic sulfonylation of **7** with *p*-$TolSO_2Na$ (20 °C, 48 h) and allylic alkylation of **6** with dimethyl malonate (BSA, KOAc, 20 °C, 48 h).

Entry	Catalyst	L/Pd	Solvent	Conv. [%][a]	*ee* [%]
		allylic sulfonylation			
1	$[Pd(allyl)Cl]_2$/(R,S,S_a)-**2**	1/1	THF	71	65 (*S*)
2	$[Pd(allyl)Cl]_2$/(R,S,S_{ax})-**2**	2/1	THF	63	73 (*S*)
3	**4a**	2/1	THF	90	86 (*S*)
4	**$[Pd(allyl)Cl]_2$/(R,S,R_{ax})-2**	**1/1**	**THF**	**95**	**99 (*R*)**
5	$[Pd(allyl)Cl]_2$/(R,S,R_{ax})-**2**	2/1	THF	91	95 (*R*)
6	**4b**	2/1	THF	95	92 (*R*)
		allylic alkylation			
7	$[Pd(allyl)Cl]_2$/(S_a,S_a)-**1**	1/1	CH_2Cl_2	53	67 (*S*)
8	$[Pd(allyl)Cl]_2$/(S_a,S_a)-**1**	2/1	CH_2Cl_2	32	61 (*S*)
9	**3a**	2/1	CH_2Cl_2	71	56 (*S*)
10	$[Pd(allyl)Cl]_2$/(R_a,S_a)-**1**	1/1	CH_2Cl_2	40	52 (*S*)
11	$[Pd(allyl)Cl]_2$/(R_a,S_a)-**1**	2/1	CH_2Cl_2	60	30 (*S*)
12	**3b**	2/1	CH_2Cl_2	59	56 (*S*)
13	**3b**	2/1	THF	38	72 (*S*)
14	$[Pd(allyl)Cl]_2$/(R,S,S_{ax})-**2**	1/1	THF	75	94 (*R*)
15	$[Pd(allyl)Cl]_2$/(R,S,S_{ax})-**2**	1/1	CH_2Cl_2	49	15 (*R*)
16	$[Pd(allyl)Cl]_2$/(R,S,S_{ax})-**2**	2/1	THF	77	95 (*R*)
17	$[Pd(allyl)Cl]_2$/(R,S,S_{ax})-**2**	2/1	CH_2Cl_2	54	13 (*R*)
18	**4a**	2/1	THF	79	94 (*S*)
19	**4a**	2/1	CH_2Cl_2	97	91 (S)
20	**$[Pd(allyl)Cl]_2$/(R,S,R_{ax})-2**	**1/1**	**THF**	**71**	**99 (*R*)**
21	$[Pd(allyl)Cl]_2$/(R,S,R_{ax})-**2**	1/1	CH_2Cl_2	76	85 (*S*)
22	$[Pd(allyl)Cl]_2$/(R,S,R_{ax})-**2**	2/1	THF	66	95 (*R*)
23	$[Pd(allyl)Cl]_2$/(R,S,R_{ax})-**2**	2/1	CH_2Cl_2	76	91 (*S*)
24	**4b**	2/1	THF	77	84 (*S*)
25	**4b**	2/1	CH_2Cl_2	99	98 (*S*)

[a] Isolated yield of **7** in allylic sulfonylation.

(Table 1, entries 1–3), probably because of the mismatched combination of the (2*R*,5*S*)-phosphocentre with (S_{ax})-*O*-methyl-BINOL fragment. Rather unexpectedly, phosphites (S_a,S_a)-**1** and (R_a,S_a)-**1** {with $[Pd(allyl)Cl]_2$, L/Pd = 1 or 2} and their palladium complexes **3a,b** gave no conversion in the synthesis of **7**.

On the contrary, in the allylic alkylation of **6** with dimethyl malonate as the C-nucleophile (S_a,S_a)-**1** and (R_a,S_a)-**1** showed good conversion (up to 71 %) and *ee* (up to 72 %, Table 1, entries 7–13). Since (*S*)-**8** was isolated in all trials, one can conclude that absolute configuration of the product is determined by the peripheral (S_a)-*O*-methyl-BINOL group. (R,S,S_a)-**2** and (R,S,R_a)-**2** were found to be highly efficient stereoselectors, as up to 95 and 99 % *ee*, respectively, were obtained (Table 1, entries 16 and 20). The enantiomeric excess depends significantly on the solvent used: practically in all cases THF is the optimal solvent. On the contrary, the L/Pd molar ratio has basically no effect on enantioselectivity. The absolute configuration of product **8** depends not only on the applied ligand, but also on the solvent used and counterion in the catalytic complex (Table 1, entries 16 and 18, 20 and 21, 22 and 24). The excellent enantioselectivity (99 %) achieved in this reaction is the best result for all known chiral P monodentate phosphite-type ligands, as it exceeds the previously reported enantiomeric excess (up to 97 %) shown by the compounds $\mathbf{L_a}$–$\mathbf{L_d}$.

Monodentate phosphites (S_a,S_a)-**1** and (R_a,S_a)-**1** {with $[Pd(allyl)Cl]_2$, L/Pd = 1 or 2} and their palladium complexes **3a,b** were tested in Pd-catalysed allylic amination of **6** with pyrrolidine as the N-nucleophile (in THF and CH_2Cl_2), the *ee*s generally being moderate to poor: up to 57 % (*S*) and 39 % (*R*), respectively. The configuration of the BINOL-based phosphocycle determines the absolute configuration of product **9**. *P**-Chiral diamidophosphites (R,S,S_a)-**2** and (R,S,R_a)-**2** gave better *ee*s of up to 83 and 97 % (Table 2, entries 4 and 9). The (2*R*,5*S*)-phosphocentre/(R_a)-*O*-methyl-BINOL represents the matched case. Here again the stereochemistry of the phosphocentre dictates the stereochemistry of product **9**. Although the ratio of ligand to Pd does not have a profound influence on the enantioselectivity, the highest results were obtained at L/Pd = 2. In general, CH_2Cl_2 proved to be the solvent of choice for (R,S,S_a)-**2**, while for (R,S,R_a)-**2** THF gave better results.

In a closely related Pd-catalysed allylic amination of **6** with dipropylamine (S_a,S_a)-**1** and (R_a,S_a)-**1** demonstrated somewhat higher enantioselectivity of up to

Table 2. Palladium-catalysed allylic amination of **6** with pyrrolidine and di-*n*-propylamine (20 °C, 48 h).

Entry	Catalyst	L/Pd	Solvent	Conv. [%]	*ee* [%]
		with pyrrolidine			
1	$[Pd(allyl)Cl]_2$/(R,S,S_a)-**2**	1/1	THF	95	57 (*R*)
2	$[Pd(allyl)Cl]_2$/(R,S,S_a)-**2**	1/1	CH_2Cl_2	100	60 (*R*)
3	$[Pd(allyl)Cl]_2$/(R,S,S_a)-**2**	2/1	THF	97	35 (*R*)
4	$[Pd(allyl)Cl]_2$/(R,S,S_a)-**2**	2/1	CH_2Cl_2	100	83 (*R*)
5	**4a**	2/1	THF	48	71 (*R*)
6	**4a**	2/1	CH_2Cl_2	97	65 (*R*)
7	$[Pd(allyl)Cl]_2$/(R,S,R_a)-**2**	1/1	THF	81	94 (*R*)
8	$[Pd(allyl)Cl]_2$/(R,S,R_a)-**2**	1/1	CH_2Cl_2	42	88 (*R*)
9	**$[Pd(allyl)Cl]_2$/(R,S,R_a)-2**	**2/1**	**THF**	**100**	**97 (*R*)**
10	$[Pd(allyl)Cl]_2$/(R,S,R_a)-**2**	2/1	CH_2Cl_2	100	86 (*R*)
11	**4b**	2/1	THF	94	83 (*R*)
12	**4b**	2/1	CH_2Cl_2	95	45 (*R*)
		with dipropylamine			
13	$[Pd(allyl)Cl]_2$/(S_a,S_a)-**1**	1/1	CH_2Cl_2	26	4 (−)
14	$[Pd(allyl)Cl]_2$/(S_a,S_a)-**1**	2/1	CH_2Cl_2	21	2 (−)
15	**3a**	2/1	CH_2Cl_2	100	44 (−)
16	$[Pd(allyl)Cl]_2$/(R_a,S_a)-**1**	1/1	CH_2Cl_2	40	50 (+)
17	$[Pd(allyl)Cl]_2$/(R_a,S_a)-**1**	2/1	CH_2Cl_2	39	74 (+)
18	**3b**	2/1	CH_2Cl_2	100	6 (+)
19	$[Pd(allyl)Cl]_2$/(R,S,S_a)-**2**	1/1	THF	95	95 (+)
20	**$[Pd(allyl)Cl]_2$/(R,S,S_a)-2**	**1/1**	**CH_2Cl_2**	**100**	**95 (+)**
21	$[Pd(allyl)Cl]_2$/(R,S,S_a)-**2**	2/1	THF	65	93 (+)
22	$[Pd(allyl)Cl]_2$/(R,S,S_a)-**2**	2/1	CH_2Cl_2	100	94 (+)
23	**4a**	2/1	THF	64	74 (+)
24	**4a**	2/1	CH_2Cl_2	77	30 (+)
25	$[Pd(allyl)Cl]_2$/(R,S,R_a)-**2**	1/1	THF	65	37 (+)
26	$[Pd(allyl)Cl]_2$/(R,S,R_a)-**2**	1/1	CH_2Cl_2	100	23 (+)
27	$[Pd(allyl)Cl]_2$/(R,S,R_a)-**2**	2/1	THF	100	51 (+)
28	$[Pd(allyl)Cl]_2$/(R,S,R_a)-**2**	2/1	CH_2Cl_2	92	50 (+)
29	**4b**	2/1	THF	68	92 (+)
30	**4b**	2/1	CH_2Cl_2	90	66 (+)

74 % *ee* (Table 2, entries 13–18). (R_a)-BINOL/(S_a)-*O*-methyl-BINOL is the matched case (74 % *ee*) in contrast to the mismatched combination (S_a)-BINOL/(S_a)-*O*-methyl-BINOL (44 % *ee*, Table 2, entries 15 and 17). Both ligands (R,S,S_a)-**2** and (R,S,R_a)-**2** gave **10** with close optical purity 95 and 92 % *ee* (Table 3, entries 20 and 29) at quantitative conversion in the case of (R,S,S_a)-**2**. This is the best result ever achieved in the discussed reaction.[37] The molar ratio L/Pd = 1 and CH_2Cl_2 as reaction medium are crucial for high asymmetric induction in the case of diamidophosphite (R,S,S_a)-**2**, while for (R,S,R_a)-**2** optimal conditions in-

Table 3. Palladium-catalysed deracemisation of **11** (CH_2Cl_2, $NaHCO_3$, $(Bu)_4NHSO_4$, 20 °C, 48 h).

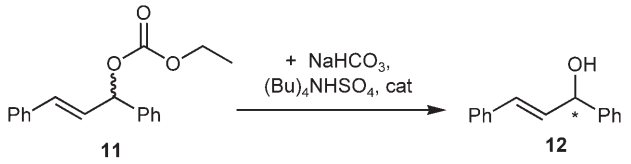
Entry	Catalyst	L/Pd	Conv. [%]	*ee* [%]
1	$[Pd(allyl)Cl]_2$/(R,S,S_a)-**2**	1/1	30	20 (*R*)
2	$[Pd(allyl)Cl]_2$/(R,S,S_a)-**2**	2/1	97	94 (*R*)
3	$[Pd(allyl)Cl]_2$/(R,S,S_a)-**2**[a]	2/1	68	81 (*R*)
4	$[Pd_2(dba)_3]\cdot CHCl_3$/($R,S,S_a$)-**2**	1/1	72	79 (*R*)
5	$[Pd_2(dba)_3]\cdot CHCl_3$/($R,S,S_a$)-**2**	2/1	67	73 (*R*)
6	$[Pd_2(dba)_3]\cdot CHCl_3$/**($R,S,S_a$)-2**[b]	1/1	74	14 (*R*)
7	**4a**	2/1	98	95 (*R*)
8	$[Pd(allyl)Cl]_2$/(R,S,R_a)-**2**	1/1	77	46 (*R*)
9	**$[Pd(allyl)Cl]_2$/(R,S,R_a)-2**	**2/1**	**97**	**96 (*R*)**
10	$[Pd_2(dba)_3]\cdot CHCl_3$/($R,S,R_a$)-**2**	1/1	70	30 (*R*)

[a] With substrate **6**.
[b] In THF.

clude L/Pd = 2 and THF as solvent. Analogously to **9**, the stereochemistry of **10** is determined by the (2*R*,5*S*)-phosphocentre of ligands (*R,S,S*$_a$)-**2** and (*R,S,R*$_a$)-**2**.

Palladium-Catalysed Deracemisation

The complete conversion of a racemate to one enantiomer without intermediate separation of materials (deracemisation) is one of the current challenges in asymmetric synthesis. Allylic alcohols are targets of high synthetic importance because of their many applications (see[38] and the references cited therein). Their deracemisation can be achieved by Pd-catalysed substitution of allylic esters with carboxylate ions in the presence of a chiral ligand for the palladium atom. The deracemisation of allylic esters is usually carried out in CH_2Cl_2/H_2O (9:1),[38] but we chose water-free conditions with formation of the $(Bu)_4NHCO_3$ salt *in situ* directly in organic media (Scheme 4).



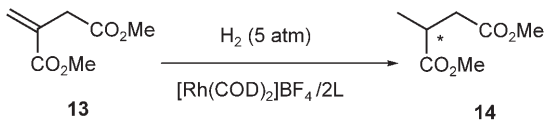
Scheme 4. Enantioselective palladium-catalysed deracemisation of ethyl (*E*)-1,3-diphenylallyl carbonate **11**.

This approach excludes an ester hydrolysis step from the catalytic cycle[38] and makes it possible to apply the hydrogen carbonate ion as an external nucleophile. What is even more important, use of water-sensitive organophosphorus ligands becomes possible.

*P**-Chiral diamidophosphites (*R,S,S*$_a$)-**2** and (*R,S,R*$_a$)-**2** resulted in 95–96 % *ee* and 97–98 % conversion (Table 3), which stands in contrast to the mediocre results obtained with phosphites (*S*$_a$,*S*$_a$)-**1** and (*R*$_a$,*S*$_a$)-**1** (not more than 47 % *ee* and 50 % of conversion). Table 3 shows some remarkable trends. Both ligands (*R,S,S*$_a$)-**2** and (*R,S,R*$_a$)-**2** provided practically equally high levels of asymmetric induction and the (*R*)-configuration of **12** (Table 3, entries 2, 7 and 9). The use of $[Pd(allyl)Cl]_2$ instead of $[Pd_2(dba)_3]\cdot CHCl_3$ as the palladium precursor gave better results (see entries 2, 5, 8 and 10 in Table 3), the molar ratio L/Pd = 2 being optimal in the case of π-allyl palladium complexes. When allyl acetate **6** was used as a substrate instead of allyl carbonate **11**, the conversion and *ee* decreased significantly (Table 3, entries 2 and 3). It is necessary to note that known methods of synthesis can provide an important chiral alcohol chalcol **12** only in 75–92 % *ee*.[39–45] Accordingly, Pd-catalysed deracemisation of ethyl (*E*)-1,3-diphenylallyl carbonate **11** with participation of inexpensive diamidophosphites (*R,S,S*$_a$)-**2** and (*R,S,R*$_a$)-**2** is a highly efficient method of preparation of **12** with a record high enantioselectivity.

Rhodium-Catalysed Asymmetric Hydrogenation

The efficacy of the MOP-type phosphite and diamidophosphite ligands was also evaluated in the Rh-catalysed asymmetric hydrogenation of dimethyl itaconate **13** (Scheme 5). Some results are summarised in Table 4.



Scheme 5. Enantioselective rhodium-catalysed hydrogenation of dimethyl itaconate **13**.

Ligands (*R,S,S*$_a$)-**2** and (*R,S,R*$_a$)-**2** exhibited moderate to good enantioselectivity and low to moderate conversion. Using *P*-chirogenic ligand (*R,S,R*$_a$)-**2** gave 90 % *ee* (Table 4, entry 3), while the asymmetric induction and activity of its diastereoisomer (*R,S,S*$_a$)-**2** was rather low. Focusing on ligand (*R,S,R*$_a$)-**2**, the enantioselectivities were increased when the reactions were carried out in CH_2Cl_2 (90 % *ee*) instead of ethyl acetate (62 % *ee*) (Table 4, entries 3 and 4). Unfortunately, phosphite (*S*$_a$,*S*$_a$)-**1** did not show any activity under the same conditions, but (*R*$_a$,*S*$_a$)-**1** exhibited very low conversion and enantioselectivity (in CH_2Cl_2 18 % and 8 %, respectively). The results achieved with *P**-chiral diamidophosphite (*R,S,R*$_a$)-**2** are rather remarkable, as there are only a few examples in asym-

Table 4. Rhodium-catalysed hydrogenation of **13** (5 bar H_2, 20 °C, 20 h, $[Rh(COD)_2]BF_4$ as precatalyst).

Entry	Ligand	Solvent	Conv. [%]	*ee* [%]
1	(*R,S,S*$_a$)-**2**	CH_2Cl_2	0	-
2	(*R,S,S*$_a$)-**2**	EtOAc	27	38 (*S*)
3	**(*R,S,R*$_a$)-2**	**CH_2Cl_2**	**63**	**90 (*S*)**
4	(*R,S,R*$_a$)-**2**	EtOAc	53	62 (*S*)

metric hydrogenation when P monodentate phosphite-type ligands without BINOL and biphenol moieties showed satisfactory enantioselectivity.[46–49]

Conclusions

In summary, stereoindividual MOP-type binaphthyl monodentate phosphite and diamidophosphite ligands have been prepared for the first time by applying the cheap and readily accessible *O*-methyl-BINOL as common precursor. Bulky *P**-chiral diamidophosphites based on inexpensive (*S*)-2-(anilinomethyl)pyrrolidine can successfully be applied in the Pd-catalysed allylic substitution reactions of (*E*)-1,3-diphenylallyl acetate with S-, C- and N-nucleophiles and in the Rh-catalysed hydrogenation of dimethyl itaconate. On the whole, epimer (*R,S,R*$_a$)-**2** provides higher enantioselectivity in both processes thanks to the matched combination of the (2*R*,5*S*)-phosphocentre with the (*R*$_a$)-*O*-methyl-BINOL fragment. In the Pd-catalysed deracemisation of ethyl (*E*)-1,3-diphenylallyl carbonate, both (*R,S,R*$_a$)-**2** and (*R,S,S*$_a$)-**2** show high asymmetric induction. In general, record high optical yields were obtained in all three tested asymmetric reactions: allylic substitution of (*E*)-1,3-diphenylallyl acetate with sodium *p*-toluenesulfinate (99% *ee*) and with dipropylamine (95% *ee*), and in the deracemisation of ethyl (*E*)-1,3-diphenylallyl carbonate (96% *ee*). BINOL-based phosphites (*S*$_a$,*S*$_a$)-**1** and (*R*$_a$,*S*$_a$)-**1** demonstrated moderate enantioselectivity only in the Pd-catalysed allylation of (*E*)-1,3-diphenylallyl acetate with dimethyl malonate (72% *ee*) and dipropylamine (74% *ee*). Presumably, other types of asymmetric transformations might be more suitable for these ligands. Thus, Pd-catalysed hydrosilylation-oxidation and Rh-catalysed addition of arylboronic acids are currently under investigation in our laboratory, as is the expansion of our MOP-type chiral phosphite ligand library.

Experimental Section

General Remarks

^{31}P and ^{13}C spectra were recorded on a Bruker AMX-400 instrument (162.0 MHz for ^{31}P and 100.6 MHz for ^{13}C). The complete assignment of all the resonances in ^{13}C NMR spectra was achieved using DEPT techniques. Chemical shifts (ppm) are given relative to Me_4Si (^{13}C NMR) and 85% H_3PO_4 in D_2O (^{31}P NMR). Mass spectra were recorded with a Varian MAT 311 spectrometer (EI) and a Finnigan LCQ Advantage spectrometer (electrospray ionisation technique, ESI). Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow).

Enantiomeric excesses of product **7** were determined using HPLC [(*R,R*)-WHELK-01 column] according to the literature.[50] Conversion of substrate **6**[51] and optical purity of products **8**[51], **9**[52] and **10**[53] were determined using HPLC (Daicel Chiralcel OD-H column) as described previously. Conversion of substrate **11** and *ee* of product **12** were determined using HPLC (Daicel Chiralcel OD-H column) according to the literature.[41] The *ee* values of product **14** were determined using HPLC (Daicel Chiralcel OD-H column) according to the literature.[54]

All reactions were carried out under a dry argon atmosphere 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. 1-(2-Methoxynaphthalen-1-yl)naphthalen-2-ol was synthesised using literature procedures.[55] Phosphorylating reagents (*S*$_a$ or *R*$_a$)-2-chlorodinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine and (2*R,5S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo-[3.3.0]octane were prepared as published.[21,56] [Rh-(COD)$_2$]BF$_4$[57], [Pd(allyl)Cl]$_2$[58] and [Pd$_2$(dba)$_3$]·CHCl$_3$[59] were prepared as described earlier. Cationic palladium complexes **3a**,**b** and **4a,b** were synthesised analogously to the known procedures.[21] Catalytic experiments: allylic sulfonylation of substrate **6** with sodium *p*-toluenesulfinate, allylic alkylation with dimethyl malonate, allylic amination with pyrrolidine, and allylic amination with dipropylamine were performed according to the appropriate procedures.[21,36,37]

Starting substrates **6** and **11** were synthesised as published.[58,60] Dimethyl itaconate, dimethyl malonate, BSA [*N,O*-bis(trimethylsilyl)acetamide] and sodium *p*-toluenesulfinate were purchased from Aldrich and Acros Organics and used without further purification.

General Procedure for the Synthesis of Ligands (*S*$_a$,*S*$_a$)-1, (*R*$_a$,*S*$_a$)-1, (*R,S,S*$_a$)-2 and (*R,S,R*$_a$)-2

A solution of Et_3N (1.9 mmol) and 1-(2-methoxynaphthalen-1-yl)naphthalen-2-ol (1.8 mmol) in benzene (10 mL) was added to a vigorously stirred solution of the appropriate phosphorylating reagent (1.8 mmol) in benzene (20 mL).The mixture was heated with stirring to boiling and then cooled down to 20 °C. Solid Et_3N·HCl was filtered off; benzene was removed under reduced pressure (40 Torr). The residue was dissolved in 1 mL of $CHCl_3$ and precipitated with hexane (12 mL), filtered and dried under vacuum (1 Torr) for 2 h.

(*S*)-2-{(*S*)-[1-(2-Methoxynaphthalen-1-yl)]naphthalen-2-oxy}dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine [(*S*$_a$,*S*$_a$)-1]: White solid; yield: 1.042 g (94%); mp 151–153 °C; $[\alpha]_D^{20}$: +72.6 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 3.72 (3H, s), 7.14–7.55 (17H, m), 7.68–8.09 (7H, m); ^{13}C NMR ($CDCl_3$): δ = 155.3, 147.6 (d, $^2J_{C,P}$ = 7.3 Hz), 147.5 (d, $^2J_{C,P}$ = 4.4 Hz), 146.9, 134.2, 132.6, 132.2, 131.3, 130.9, 130.8, 130.0, 129.9, 129.4, 129.2, 128.9, 128.2, 128.1, 127.9, 127.8, 126.8, 126.6, 126.5, 126.1, 125.9, 125.8, 125.1, 124.9, 124.8, 124.7, 124.6, 123.9, 123.6, 122.4, 121.7, 121.5, 120.9, 120.8, 117.9, 56.2 (OCH_3); ^{31}P NMR ($CDCl_3$): δ = 144.7; MS (EI): *m*/*z* (%) = 614 (18, [M]$^+$), 583 (100, [M−MeO]$^+$), 268 (81, [$C_{20}H_{12}O$]$^+$); anal. calcd. for $C_{41}H_{27}O_4P$: C 80.12, H 4.43, P 5.04; found: C 80.33, H 4.68, P 4.92.

(*R*)-2-{(*S*)-[1-(2-Methoxynaphthalen-1-yl)]naphthalen-2-oxy}dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine [(*R*$_a$,*S*$_a$)-1]: White solid; yield: 1.064 g (96%); mp 196–

198 °C; $[\alpha]_D^{20}$: −84.55 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 3.79 (3H, s), 7.13–7.53 (17H, m), 7.72–8.15 (7H, m); ^{13}C NMR ($CDCl_3$): δ = 155.3, 147.7 (d, $^2J_{C,P}$ = 8.8 Hz), 147.2 (d, $^2J_{C,P}$ = 4.4 Hz), 147.0, 134.1, 133.8, 132.5, 132.0, 131.3, 131.0, 130.9, 130.1, 130.0, 129.5, 129.1, 128.5, 128.1, 128.0, 127.8, 126.7, 126.6, 126.5, 126.2, 126.0, 125.9, 125.7, 125.4, 124.9, 124.8, 124.5, 124.2, 124.1, 124.0, 123.9, 123.6, 122.4, 121.6, 121.5, 117.8, 55.9 (OCH_3); ^{31}P NMR ($CDCl_3$): δ = 146.1; MS (EI): *m*/*z* (%) = 614 (25, $[M]^+$), 583 (100, $[M-MeO]^+$), 268 (90, $[C_{20}H_{12}O]^+$); anal. calcd. for $C_{41}H_{27}O_4P$: C 80.12, H 4.43, P 5.04; found: C 80.24, H 4.33, P 5.29.

(2*R*,5*S*,*S*$_a$)-2-[1-(2-Methoxynaphthalen-1-yl)naphthalen-2-oxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane [(*R*,*S*,*S*$_a$)-2]: White solid; yield: 0.735 g (81%); mp 156–158 °C; $[\alpha]_D^{20}$: +129.8 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 1.49 (1H, m), 1.74 (2H, m), 2.08 (1H, m), 2.94–3.28 (2H, m), 3.35–3.62 (3H, m), 3.73 (3H, s), 6.79 (1H, t, *J* = 7.2 Hz), 7.07–7.93 (16H, m); ^{13}C NMR ($CDCl_3$): δ = 155.1, 149.6, 144.8 (d, $^2J_{C,P}$ = 16.1 Hz), 134.0, 133.9, 130.2, 129.3, 128.7, 128.6, 128.5, 127.7, 127.5, 126.1, 125.7, 125.6, 125.5, 124.2, 124.0, 123.1, 123.0, 122.9, 119.4, 118.6, 114.7 (d, $^3J_{C,P}$ = 13.1), 62.0 (d, $^2J_{C,P}$ = 8.0 Hz, C-5), 56.4 (OCH_3), 53.3 (d, $^2J_{C,P}$ = 6.6 Hz, C-4), 47.2 (d, $^2J_{C,P}$ = 33.5 Hz, C-8), 30.9 (C-6), 25.8 (d, $^3J_{C,P}$ = 3.7 Hz, C-7); ^{31}P NMR ($CDCl_3$): δ = 128.9; MS (EI): *m*/*z* (%) = 504 (8, $[M]^+$), 473 (39, $[M-MeO]^+$), 300 (14, $[C_{21}H_{16}O_2]^+$), [268 (11, $[C_{20}H_{12}O]^+$), 205 (100, $[M-C_{21}H_{15}O_2]^+$); anal. calcd. for $C_{32}H_{29}N_2O_2P$: C 76.17, H 5.79, N 5.55; found: C 76.42, H 6.0, N 5.49.

(2*R*,5*S*,*R*$_a$)-2-[1-(2-Methoxynaphthalen-1-yl)naphthalen-2-oxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane [(*R*,*S*,*R*$_a$)-2]: White solid; yield: 0.762 g (84%); mp 130–134 °C; $[\alpha]_D^{20}$: −198.25 (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 1.53 (1H, m), 1.82 (2H, m), 1.98 (1H, m), 3.09–3.32 (2H, m), 3.41–3.68 (3H, m), 3.72 (3H, s), 6.81 (1H, t, *J* = 7.3 Hz), 7.18–7.90 (16H, m); ^{13}C NMR ($CDCl_3$): δ = 155.2, 149.8 (d, $^2J_{C,P}$ = 6.6 Hz), 145.0 (d, $^2J_{C,P}$ = 16.8 Hz), 133.9, 133.8, 130.2, 129.2, 128.8, 128.7, 128.5, 127.7, 127.5, 125.9, 125.8, 125.7, 125.6, 124.1, 123.9, 123.1, 122.9, 122.8, 119.3, 118.6, 114.7 (d, $^3J_{C,P}$ = 12.4 Hz), 62.2 (d, $^2J_{C,P}$ = 9.5 Hz, C-5), 56.6 (OCH_3), 53.6 (d, $^2J_{C,P}$ = 7.3 Hz, C-4), 47.0 (d, $^2J_{C,P}$ = 35.7 Hz, C-8), 31.4 (C-6), 25.7 (d, $^3J_{C,P}$ = 4.4 Hz, C-7); ^{31}P NMR ($CDCl_3$): δ = 125.7; MS (EI): *m*/*z* (%) = 504 (6, $[M]^+$), 473 (50, $[M-MeO]^+$), 300 (9, $[C_{21}H_{16}O_2]^+$), [268 (15, $[C_{20}H_{12}O]^+$), 205 (100, $[M-C_{21}H_{15}O_2]^+$); anal. calcd. for $C_{32}H_{29}N_2O_2P$: C 76.17, H 5.79, N 5.55; found: C 76.31, H 5.88, N 5.81.

Palladium Complexes

{Pd(allyl)[(*S*$_a$,*S*$_a$)-1]$_2$}BF$_4$ (3a): White solid; yield: 94%; mp 160–162 °C (dec.); ^{31}P NMR ($CDCl_3$): δ = 138.6 and 137.2 (AB system, each d, $^2J_{P,P'}$ = 111.5 Hz); MS (ESI): *m*/*z* (%) = 1377 (16, $[M-BF_4]^+$), 706 (100, $[Pd(L)-Me]^+$); anal. calcd. for $C_{85}H_{59}BF_4O_8P_2Pd$: C 69.76, H 4.06, P 4.23; found: C 70.09, H 4.2, P 4.03.

{Pd(allyl)[(*R*$_a$,*S*$_a$)-1]$_2$}BF$_4$ (3b): White solid; yield: 96%; mp 168–170 °C (dec.); ^{31}P NMR ($CDCl_3$): δ = 141.1, d and 140.0 (AB system, each d , $^2J_{P,P'}$ = 108.2 Hz); MS (ESI): *m*/*z* (%) = 1377 (23, $[M-BF_4]^+$), 706 (100, $[Pd(L)-Me]^+$); anal. calcd. for $C_{85}H_{59}BF_4O_8P_2Pd$: C 69.76, H 4.06, P 4.23; found: C 69.92, H 3.97, P 4.08.

{Pd(allyl)[(*R*,*S*,*S*$_a$)-2]$_2$}BF$_4$ (4a): White solid; yield: 92%; mp 178–180 °C (dec.); ^{31}P NMR ($CDCl_3$): δ = 112.1 (broad); MS (ESI): *m*/*z* (%) = 1156 (100, $[M-BF_4]^+$); anal. calcd. for $C_{67}H_{63}BF_4N_4O_4P_2Pd$: C 64.72, H 5.11, N 4.51; found: C 64.47, H 5.01, N 4.38.

{Pd(allyl)[(*R*,*S*,*R*$_a$)-2]$_2$}BF$_4$ (4b): White solid; yield: 94%; mp 180–182 °C (dec.); ^{31}P NMR ($CDCl_3$): δ = 115.1; MS (ESI): *m*/*z* (%) = 1156 (100, $[M-BF_4]^+$); anal. calcd. for $C_{67}H_{63}BF_4N_4O_4P_2Pd$: C 64.72, H 5.11, N 4.51; found: C 64.83, H 5.22, N 4.41.

General Procedure for the Synthesis of Rhodium Complexes

A solution of the relevant ligand (*R*,*S*,*S*$_a$)-**2** or (*R*,*S*,*R*$_a$)-**2** (0.101 g, 0.2 mmol) in CH_2Cl_2 (10 mL) was added dropwise during 40 min to a vigorously stirred solution of [Rh(COD)$_2$]BF$_4$ (0.041 g, 0.10 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for additional 1 h and concentrated at reduced pressure to a volume of *ca.* 0.5 mL and ether (15 mL) was added. The precipitated solid was separated by centrifugation, washed with ether (2×10 mL) and dried under vacuum (1 Torr) for 1 h.

{Rh(COD)[(*R*,*S*,*S*$_a$)-2]$_2$}BF$_4$ (5a): Yellow solid; yield: 0.251 g (96%); mp 143–147 °C (dec.); ^{31}P NMR ($CDCl_3$): δ = 106.1 (d, $^1J_{P,Rh}$ = 229.7 Hz, 21%), 99.9 (d, $^1J_{P,Rh}$ = 213.0 Hz, 79%); MS (ESI): *m*/*z* (%) = 1112 (100, $[M-BF_4-COD]^+$), 1194 (96, $[Rh(CH_3CN)_2(L)_2]^+$); anal. calcd. for $C_{72}H_{70}BF_4N_4O_4P_2Rh$: C 66.16, H 5.40; found: C 66.37, H 5.27.

{Rh(COD)[(*R*,*S*,*R*$_a$)-2]$_2$}BF$_4$ (5b): Yellow solid; yield: 0.245 g (94%); mp 149–154 °C (dec.); ^{31}P NMR ($CDCl_3$): δ = 106.4 (d, $^1J_{P,Rh}$ = 228.3 Hz, 70%), 100.7 (d, $^1J_{P,Rh}$ = 214.1 Hz, 30%); MS (ESI): *m*/*z* (%) = 1112 (100, $[M-BF_4-COD]^+$), 1194 (82, $[Rh(CH_3CN)_2(L)_2]^+$); anal. calcd. for $C_{72}H_{70}BF_4N_4O_4P_2Rh$: C 66.16, H 5.40; found: C 66.41, H 5.49.

General Procedure for the Hydrogenation of Dimethyl Itaconate

[Rh(COD)$_2$]BF$_4$ (2.4 mg; 0.006 mmol), the appropriate ligand (0.012 mmol), dimethyl itaconate (0.1 g, 0.6 mmol) and the appropriate solvent (3 mL) were placed in a 25-mL autoclave under an atmosphere of argon. The autoclave was closed and flushed three times with hydrogen, and then the hydrogenation was performed at room temperature under an H_2 pressure of 5 bar during 20 h. The reaction mixture was diluted with hexane (5 mL), passed through a short silica gel plug using hexane as the eluent and analysed by HPLC and ^{1}H NMR.

General Procedure for the Deracemisation of Ethyl (*E*)-1,3-Diphenylallyl Carbonate

A solution of [Pd(allyl)Cl]$_2$ (0.0037 g, 0.01 mmol) or [Pd$_2$(dba)$_3$]·$CHCl_3$ (0.0103 g, 0.01 mmol) and the appropriate ligand (0.02 mmol, 0.04 mmol) in 5 mL of the appropriate solvent was stirred for 40 min [alternatively, the presynthesised complex **4a** (0.02 mmol) was dissolved in appropriate solvent (5 mL)]. Then ethyl (*E*)-1,3-diphenylallyl carbonate (0.141 g, 0.5 mmol) was added and the solution stirred for 15 min, then $NaHCO_3$ (0.73 g, 8.7 mmol) and $(Bu)_4NHSO_4$

(0.289 g, 0.85 mmol) were added. The reaction mixture was stirred for 48 h. After that, the resulting solution was passed through a short Celite plug using CH_2Cl_2 (10 mL) as the eluent and analysed by HPLC.

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