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BINOL-derived diphosphoramidites bearing unsymmetrical 1,2-diamine link and their application in asymmetric catalysis

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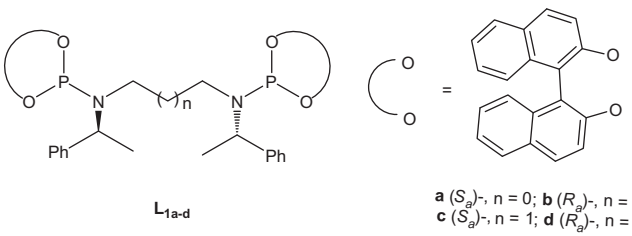
ABSTRACT

New *P,P*-bidentate diastereomeric diphosphoramidite chiral ligands with mixed stereogenic elements and a C_1 backbone symmetry have been prepared from (S_a)- and (R_a)-1,1′-binaphthyl-2,2′-diol (BINOL) and (*S*)-*N*-benzyl-1-(pyrrolidin-2-yl)methanamine and are fully characterized. The use of these ligands provides up to 84% ee in the Pd-catalyzed asymmetric allylic substitution of (*E*)-1,3-diphenylallyl acetate and up to 95% ee in the Rh-catalyzed asymmetric hydrogenation of α-dehydrocarboxylic acid esters. The results indicate that the catalytic performance is highly affected by the axial chirality of the binaphthyl moieties of the ligand and the nature of the solvent.

1. Introduction

The preparation of drugs, agrochemicals, pheromones, food additives, fragrances, stereoindividual polymers and other fine chemicals and natural compounds is based on modern approaches to the synthesis of enantiomerically pure substances. One of the leading approaches is asymmetric metal complex catalysis, because it can provide very high reactivity and stereoselectivity, and is environmentally friendly. Indeed, the use of highly selective catalytic systems is one of the basic principles of 'green chemistry'.[1–8] In turn, 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, among which phosphorus-containing compounds are worth noting.[6,9–12] Since the early 1970s, an impressive number of chiral phosphorus-based ligands have been applied in many asymmetric catalytic reactions.[1–13] Nevertheless, only a handful of them (so-called privileged ligands), rooted in a few core structures, can be regarded as truly successful in demonstrating proficiency in various mechanistically unrelated reactions.[14] Among the phosphite-type chiral ligands phosphoramidites, those with a BINOL-backbone completely satisfy this definition.[15] Phosphoramidites are highly versatile, readily accessible and efficient stereoselectors. Their modular structure enables the formation of extensive ligand libraries and easy fine-tuning for a specific catalytic reaction.[15,16]

It should be noted that much attention has been focused on *P*-monodentate BINOL-based phosphoramidites.[15–18] In contrast, only a limited number of *P,P*-bidentate diphosphoramidites, in particular those derived from chiral diamines, have been reported to date, despite their easy accessibility. Thus, a small series of C_2-symmetric diphosphoramidites **L$_{1a–d}$** (Fig. 1) has been successfully applied in the Rh-catalyzed enantioselective hydrogenation of (*Z*)-methyl 2-acetamido-3-phenylacrylate and in the Cu-catalyzed enantioselective conjugate addition of diethylzinc to 2-cyclohexenone with good enantioselectivities.[16,19] Diastereomeric diphosphoramidites with C_1 symmetry from D-(+)-xylose **L$_{2a,b}$** (Fig. 2) have been used productively in asymmetric Cu-catalyzed 1,4-addition and allylic substitution reactions, and especially in Pd-catalyzed allylic substitution processes.[20–22]



L$_{1a-d}$

a (S_a)-, n = 0; **b** (R_a)-, n = 0;
c (S_a)-, n = 1; **d** (R_a)-, n = 1

Figure 1. The *P,P*-bidentate diphosphoramidites based on symmetrical chiral diamines.

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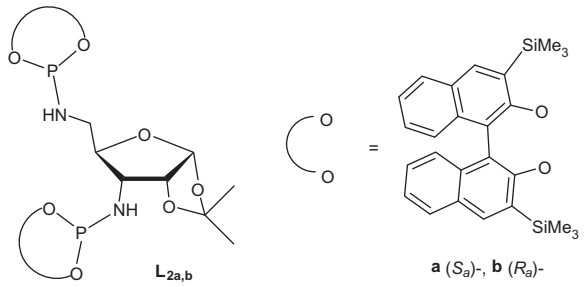


Figure 2. The *P,P*-bidentate diphosphoramidites based on 3,5-dideoxy-3,5-diamino-1,2-*O*-isopropylidene-ribofuranose as an unsymmetrical chiral diamine.

Herein we report on the synthesis and characterization of novel C_1-symmetric *P,P*-bidentate diastereomeric BINOL-based diphosphoramidite ligands containing an unsymmetrical 1,2-diamine core and on their evaluation in Pd-catalyzed asymmetric allylations and Rh-catalyzed asymmetric hydrogenations. It should be noted that 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 *C*-, *N*-, O-, *S*- and *P*-nucleophiles. As a result, Pd-catalyzed allylic substitution is a novel and highly efficient strategy in the total synthesis of enantiopure natural and unnatural products.[3,23–31] The enantioselective hydrogenation, using inexpensive molecular hydrogen and a small amount of a catalyst, is one of the most mature and dependable types of catalytic asymmetric transformations, and this technology has become widely used in the pharmaceutical and agrochemical industries.[32,33] On the other hand, both catalytic processes are common benchmark tests for initial ligand screening. From a functional point of view, the enantiomeric excesses obtained are the simplest indexes for evaluating new chiral ligands.[29,30,34]

2. Results and discussion

Diastereomeric diphosphoramidite ligands **3a,b** were synthesized very efficiently from 1,2-diamine **1** via reaction with 2 equiv of the appropriate enantiomer of phosphorylating reagent **2a** or **2b** in toluene in the presence of Et_3N as an HCl scavenger and DMAP as a catalyst (Scheme 1). The new ligands were stable during purification on basic aluminum oxide and isolated in good yields as white solids. They can also be stored in the solid form under dry conditions at room temperature over several months without any degradation. Diphosphoramidites **3a,b** were fully characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, MALDI TOF/TOF mass spectrometry as well as by elemental analysis. The ^{31}P, ^1H, and ^{13}C NMR spectra were as expected for these C_1 ligands. In particular, for each compound two signals with equal intensity were observed in the ^{31}P NMR spectrum. Two different phosphoramidite phosphorus atoms displayed two distinct singlets in the ^{31}P NMR spectrum of **3a** (δ_P 148.6 and 146.4) and **3b** (δ_P 150.4 and 145.3). Both ligands are readily available and can be prepared on a gram scale. In fact, (*S*)-*N*-benzyl-1-(pyrrolidin-2-yl)methanamine **1** can be easily synthesized in three steps from inexpensive (*S*)-pyroglutamic acid.[35] Furthermore, BINOL is commercially available in both enantiomeric forms and is one of the least expensive chiral auxiliaries currently on the market. It should be noted that ligands **3a,b** have in their structures, the skeletons of two famous kinds of *P*-monodentate BINOL-based phosphoramidites $\mathbf{L_A}$ and $\mathbf{L_B}$ (Fig. 3).[15–18]

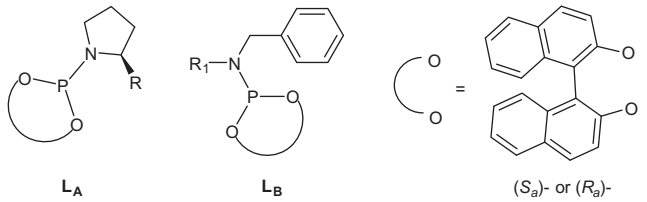
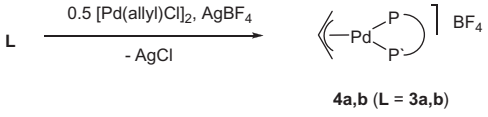


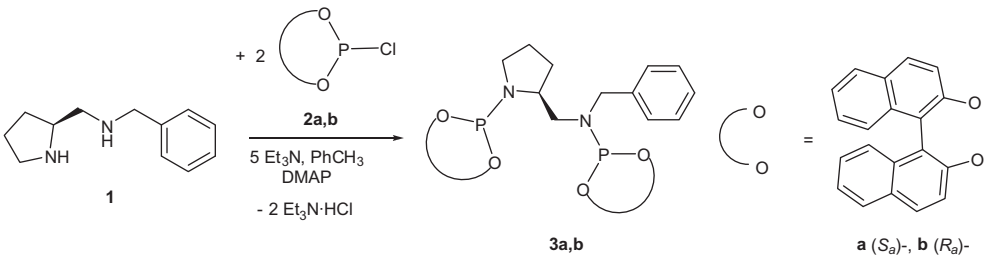
Figure 3. Two very efficient types of *P*-monodentate BINOL-based phosphoramidite.

Compounds **3a,b** readily reacted with $[Pd(allyl)Cl]_2$ (CH_2Cl_2/THF, $AgBF_4$ as a chloride scavenger, room temperature, 3 h) to give cationic metallochelates **4a,b** of the type $[Pd(allyl)(L)]BF_4$ (Scheme 2). Duplication of the AX systems in the ^{31}P NMR spectra (in $CDCl_3$) of complexes **4a** [δ_P 146.3, d and δ_P 135.6, d, $^2J_{P,P}$ = 114.8 Hz (64%); δ_P 144.7,d and δ_P 135.1, d, $^2J_{P,P}$ = 119.8 Hz (36%)] and **4b** [δ_P 148.4, d and δ_P 133.4, d, $^2J_{P,P}$ = 118.3 Hz (72%); δ_P 145.7, d and δ_P 133.2, d, $^2J_{P,P}$ = 123.1 Hz (28%)] indicated the presence of their *exo*- and *endo*-isomers.[36] The AX systems were observed in the ^{31}P NMR spectra of complexes **4a,b** due to the presence of the two different phosphoramidite phosphorus atoms in the coordination sphere of the palladium. The MALDI TOF/TOF mass spectrometry and elemental analysis data (see Section 4) were also in good agreement with the proposed structures of **4a,b**.



Scheme 2. Synthesis of cationic palladium complexes **4a,b**.

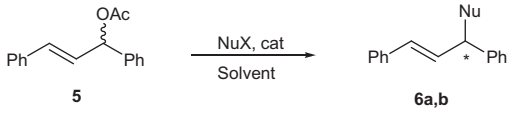
Our initial studies on the application of new diastereomeric diphosphoramidites **3a,b** and their cationic palladium complexes **4a,b** in catalysis focused on the Pd-catalyzed asymmetric allylic substitution of racemic (*E*)-1,3-diphenylallyl acetate **5**. We first tested the new stereoselectors in the allylic sulfonylation of **5** with *p*-$TolSO_2Na$ as the *S*-nucleophile, using standard conditions (Table 1). The reaction proceeded smoothly to afford sulfone **6a** in good yields and with moderate to good enantioselectivity [up to



Scheme 1. Synthesis of the diastereomeric diphosphoramidites **3a,b**.

82% ee for the (*S*)-enantiomer, Table 1, entry 6]. The L/Pd molar ratio did not have a profound influence on the enantioselectivity. The configuration of the BINOL-based phosphacycles determined the absolute configuration of the desired sulfone: ligand **3a** led to the formation of (*R*)-**6a**, while ligand **3b** led to the formation of (*S*)-**6a**. It should be noted that diastereomer **3b** is slightly more efficient (Table 1, entries 1–3 and 4–6).

Table 1
Pd-catalyzed allylic sulfonylation and alkylation of (*E*)-1,3-diphenylallyl acetate **5** [a]



5 **6a,b**

Nu = SO_2pTol, X = Na, **6a**
Nu = $CH(CO_2Me)_2$ X = H, **6b**

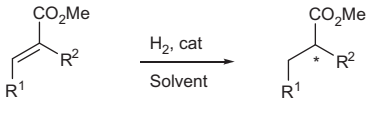
Entry	Ligand	L/Pd	Solvent	Conversion[b] (%)	ee (%)
Allylic sulfonylation with sodium p-toluenesulfinate[c]					
1	**3a**	1	THF	75	70 (*R*)
2	**3a**	2	THF	96	60 (*R*)
3	**3a**	1	THF	64	73 (*R*)[d]
4	**3b**	1	THF	93	77 (*S*)
5	**3b**	2	THF	89	75 (*S*)
6	**3b**	**1**	**THF**	**75**	**82 (*S*)**[e]
Allylic alkylation with dimethyl malonate (BSA, KOAc)[f]					
7	**3a**	1	CH_2Cl_2	100	62 (*R*)
8	**3a**	2	CH_2Cl_2	98	59 (*R*)
9	**3a**	1	THF	37	57 (*R*)
10	**3a**	2	THF	38	65 (*R*)
11	**3a**	1	CH_2Cl_2	95	65 (*R*)[d]
12	**3a**	1	THF	44	64 (*R*)[d]
13	**3b**	1	CH_2Cl_2	20	17 (*S*)
14	**3b**	2	CH_2Cl_2	18	13 (*S*)
15	**3b**	1	THF	32	49 (*S*)
16	**3b**	2	THF	29	65 (*S*)
17	**3b**	1	CH_2Cl_2	98	17 (*S*)[e]
18	**3b**	**1**	**THF**	**94**	**84 (*S*)**[e]

[a] All reactions were carried out with 2 mol % $[Pd(allyl)Cl]_2$ at room temperature for 48 h.
[b] Isolated yield of **6a**.
[c] Enantiomeric excess of **6a** 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].
[d] With complex **4a** as the catalyst.
[e] With complex **4b** as the catalyst.
[f] The conversion of substrate **5** and the enantiomeric excess of **6b** 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].

Next we turned our attention to the use of **3a,b** and **4a,b** in the alkylation of **5** with dimethyl malonate as the *C*-nucleophile (in THF and CH_2Cl_2) (Table 1), the enantiomeric excesses were generally moderate to good with up to 65% (*R*) and 84% (*S*), respectively. Similar to the Pd-catalyzed allylic sulfonylation, the use of **3a** afforded the reaction product **6b** with an (*R*)-configuration, while the use of **3b** gave the (*S*)-configuration. Ligand **3a** gave (*R*)-**6b** with modest enantiomeric purity (57–65% ee) (Table 1, entries 7–12) regardless of the L/Pd molar ratio and the nature of the solvent; the highest conversion was observed in CH_2Cl_2. On the contrary, with ligand **3b** (a diastereoisomer of **3a** with respect to the axis of chirality) the degree of asymmetric induction was very sensitive to the solvent. It was thus clear that THF was the solvent of choice; using CH_2Cl_2 led to a considerable decrease in enantioselectivity (Table 1, entries 13, 14, 17 and 15, 16, 18). It is also noteworthy that in a THF medium, complex **4b** was the best stereoselector among the catalytic systems based on ligand **3b**.

In order to further investigate the potential of the new readily available diphosphoramidite ligands **3a,b**, they were tested in the Rh-catalyzed enantioselective hydrogenation of prochiral methyl esters of unsaturated acids, dimethyl itaconate **7a** and (*Z*)-methyl 2-acetamido-3-phenylacrylate **7b** (Table 2). 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 the appropriate solvent. Unfortunately, negligible conversion and enantioselectivity were observed in the hydrogenation of substrate **7a** in CH_2Cl_2 or CH_3OH (Table 2, entries 1, 3 and 4). In strong contrast, in a CF_3CH_2OH medium, both diastereomeric ligands **3a** and **3b** provided quantitative conversion of **7a**, and essentially equally very good levels of asymmetric induction (94% and 95% ee) with the (*R*)- and (*S*)-configuration of **8a**, respectively (Table 2, entries 2 and 5). The results achieved with **3a** and substrate **7b** show that the enantioselectictivity and conversion increased in the consistent order: CH_2Cl_2 < CH_3OH < CF_3CH_2OH and that product (*R*)-**8b** was formed with 71% ee (Table 2, entries 6–8). At the same time, ligand **3b** afforded **8b** with opposite absolute configuration but with superior enantioselectivity [up to 95% ee for the (*S*)-enantiomer, Table 2, entry 9], probably due to the matched combination of the (2*S*)-stereocenter of the 1,2-diamine core with the (R_a)-BINOL fragments. High enantioselectivity was observed for both solvents CH_2Cl_2 and CF_3CH_2OH (95% and 93% ee, respectively), but quantitative conversion of **7b**, only for CF_3CH_2OH (Table 2, entries 9–11). As a whole, the data obtained using substrates **7a,b** and CF_3CH_2OH as the reaction medium are in good agreement with the well-known positive influence of fluorinated alcohols on activity and stereoselectivity in Rh-catalyzed asymmetric hydrogenations.[37,38]

Table 2
Rh-catalyzed hydrogenation of α-dehydrocarboxylic acid esters **7a,b**[a]



7a,b **8a,b**

R^1 = H, R^2 = CH_2CO_2Me, **7a** and **8a**
R^1 = Ph, R^2 = NHAc, **7b** and **8b**

Entry	Ligand	Solvent	Conversion (%)	ee (%)
Hydrogenation of dimethyl itaconate ***7a***[b]				
1	**3a**	CH_2Cl_2	0	—
2	**3a**	CF_3CH_2OH	100	94 (*R*)
3	**3b**	CH_2Cl_2	0.4	3 (*S*)
4	**3b**	CH_3OH	24	2 (*S*)
5	**3b**	**CF_3CH_2OH**	**100**	**95 (*S*)**
Hydrogenation of (Z)-methyl 2-acetamido-3-phenylacrylate ***7b***[c]				
6	**3a**	CH_2Cl_2	0	—
7	**3a**	CH_3OH	30	16 (*R*)
8	**3a**	CF_3CH_2OH	93	71 (*R*)
9	**3b**	**CH_2Cl_2**	**19**	**95 (*S*)**
10	**3b**	CH_3OH	97	66 (*S*)
11	**3b**	CF_3CH_2OH	100	93 (*S*)

[a] All reactions were carried out with 1 mol % $[Rh(cod)_2]BF_4$ at 25 °C, L/Rh = 1 and 1 bar H_2 for 24 h.
[b] The conversion of substrate **7a** and enantiomeric excess of **8a** were determined by GC (Lipodex E, 25 m × 0.25 mm, 80 °C, 1 mL/min).
[c] The conversion of substrate **7b** and enantiomeric excess of **8b** were determined by GC (Lipodex E, 25 m × 0.25 mm, 145 °C, 1 mL/min).

3. Conclusion

In conclusion, we have described the successful application of novel C_1-symmetric *P,P*-bidentate diastereomeric diphosphoramidites in Pd-catalyzed asymmetric allylations and in Rh-catalyzed asymmetric hydrogenations. These ligands have the advantage of being readily prepared in a few steps from commercial (*S*)-pyroglutamic acid and (S_a)- or (R_a)-BINOL, low-cost chiral precursors. For all of the investigated catalytic reactions we found that the absolute configuration of the binaphthyl moieties unequivocally determines the absolute configuration of the products obtained. In some cases, the asymmetric induction was very sensitive to the solvent nature. In particular, in the Rh-catalyzed hydrogenations of α-dehydrocarboxylic acid esters, the strongly polar CF_3CH_2OH was the solvent of choice. A comparison of the results obtained with the novel diphosphoramidites **3a,b** and well-known $\mathbf{L_{1a-d}}$ [up to 95% and 80% ee in Rh-catalyzed hydrogenation of (*Z*)-methyl 2-acetamido-3-phenylacrylate, respectively][16] and $\mathbf{L_{2a,b}}$ [up to 84% and 75% ee in Pd-catalyzed alkylation of (*E*)-1,3-diphenylallyl acetate with dimethyl malonate, respectively][20] showed that **3a,b** are comparable or even more efficient stereoselectors. As a result, additional studies highlighting the potential of these new ligands in other asymmetric reactions are currently in progress in our laboratories.

4. Experimental

4.1. General

^{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 of the resonances in the ^{13}C NMR spectra was achieved by the use of DEPT techniques and published data.[35] Chemical shifts (ppm) were given relative to Me_4Si (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P NMR). Mass spectra are recorded with a Bruker Daltonics Ultraflex spectrometer (MALDI TOF/TOF). HPLC analyses were performed on an Agilent 1100 and Stayer instruments using Chiralcel® columns. GC was performed on an Agilent 6890 chromatograph with a Lipodex E column. 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, toluene and tetrahydrofuran were freshly distilled from sodium benzophenone ketyl before use; dichloromethane was distilled from NaH. Triethylamine was distilled over KOH and then over a small amount of $LiAlH_4$ before use. Column chromatography was performed using silica gel MN Kieselgel 60 (230–400 mesh) and MN-Aluminum oxide, basic, Brockmann Activity 1. Enantiomeric phosphorylating reagents—(S_a)-2-chlorodinaphtho[2,1-*d*:1′,2′-*f*][1,3,2] dioxaphosphepine **2a** and (R_a)-2-chlorodinaphtho[2,1-*d*:1′,2′-*f*][1,3,2] dioxaphosphepine **2b** were prepared according to the literature.[39] Pd(allyl)Cl]$_2$ and starting substrate **5** were prepared analogously to the known procedures.[40] Pd-catalyzed allylic substitution: sulfonylation of substrate **5** with sodium *p*-toluenesulfinate and alkylation with dimethyl malonate were performed according to the appropriate procedures.[36] [Rh(cod)$_2$]BF_4 and starting substrate **7b** were prepared as published.[41,42] Rh-catalyzed hydrogenation of α-dehydrocarboxylic acid esters **7a,b** was performed as published.[43] (S_a)- and (R_a)-BINOL, DMAP (4-dimethylamino-pyridine), dimethyl malonate, BSA (*N,O*-bis(trimethylsilyl) acetamide), sodium *p*-toluenesulfinate and dimethyl itaconate **7a** were purchased from Aldrich and Acros Organics and used without further purification.

4.2. General procedure for the preparation of ligands 3a,b

A solution of diamine **1** (0.19 g, 1 mmol) in toluene (7 mL) was added dropwise to a vigorously stirred solution of the appropriate enantiomer **2a** or **2b** (0.7 g, 2 mmol), Et_3N (0.7 mL, 5 mmol), and DMAP (0.024 g, 0.2 mmol) in toluene (10 mL). The mixture was then heated to boiling point, stirred for 30 min, and then cooled to 20 °C. The resulting suspension was filtered through a short plug of aluminum oxide, the column was washed twice with toluene (8 mL) and the solvent evaporated under reduced pressure (40 Torr). The product was dried in vacuo (1 Torr, 1 h).

4.2.1. (S_a,S_a)-*N*-Benzyl-*N*-(((2*S*)-1-(dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-4-yl)pyrrolidin-2-yl)methyl)dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-4-amine 3a

White powder (0.68 g, yield 83%). $[\alpha]_D^{20} = +168.7$ (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.62–1.75 (m, 4H, CH_2CH_2), 2.60–2.68 (m, 1H, 2(CH_2N)), 2.78–2.92 (m, 3H, 2(CH_2N)), 3.86 (dd, $^{2}J_{H,H}$ = 14.7 Hz, $^{3}J_{H,P}$ = 8.3 Hz, 1H, CH_2, Bn), 4.11–4.19 (m, 1H, CHN), 4.26 (dd, $J_{H,H}$ = 14.7 Hz, $J_{H,P}$ = 5.4 Hz, 1H, CH_2, Bn), 7.21–7.28 (m, 3H, CH, aryl), 7.36–7.52 (m, 16H, CH, aryl), 7.69 (d, $^{3}J_{H,H}$ = 9.0 Hz, 1H, CH, aryl), 7.91–8.08 (m, 9H, CH, aryl). $^{13}C\{H\}$ NMR ($CDCl_3$, 25 °C): δ_C = 24.0 (s, CH_2); 29.6 (d, ^{3}J = 3.9 Hz, CH_2); 44.8 (d, ^{2}J = 5.5 Hz, CH_2N); 49.0 (d, ^{2}J = 9.9 Hz, CH_2N); 49.9 (dd, ^{2}J = 27.6 Hz, ^{3}J = 6.0 Hz, CH_2N); 55.7 (d, ^{2}J = 28.1 Hz, CHN); 121.8, 121.9 (s, CH, binaphthyl); 122.1 (d, ^{3}J = 1.7 Hz, CH, binaphthyl); 122.3 (s, CH, binaphthyl); 122.5 (d, ^{3}J = 2.2 Hz, C, binaphthyl); 122.6 (d, ^{3}J = 2.2 Hz, C, binaphthyl); 124.1, 124.2 (s, C, binaphthyl); 124.6, 124.7, 124.8, 124.9, 125.4, 126.1 (s, CH, binaphthyl); 126.2 (br s, 2 × CH, binaphthyl); 126.9 (s, CH, phenyl); 127.1 (br s, 2 × CH, phenyl); 127.4 (s, CH, binaphthyl); 128.2 (br s, 2 × CH, phenyl); 128.3 (s, CH, binaphthyl); 128.4 (br s, 3 × CH, binaphthyl); 129.0 (br s, 2 × CH, binaphthyl); 129.1, 129.8, 130.2, 130.3, 130.4 (s, CH, binaphthyl); 130.7, 130.8, 131.4, 131.5, 132.6, 132.8, 132.9, 133.0 (s, C, binaphthyl); 137.7 (s, C, phenyl); 149.4 (s, CO, binaphthyl); 149.8 (d, ^{2}J = 3.3 Hz, CO, binaphthyl); 149.9 (d, ^{2}J = 2.2 Hz, CO, binaphthyl); 150.6 (d, ^{2}J = 4.4 Hz, CO, binaphthyl). MS (MALDI TOF/TOF), *m/z* (I, %): = 819 (18) $[M+H]^+$, 505 (100) $[M-C_{20}H_{12}O_2P+2H]^+$, 316 (47) $[C_{20}H_{12}O_2PH]^+$. Anal. Calcd for $C_{52}H_{40}N_2O_4P_2$: C, 76.27; H, 4.92; N, 3.42. Found: C, 76.51; H, 4.87; N, 3.61.

4.2.2. (R_a,R_a)-*N*-Benzyl-*N*-(((2*S*)-1-(dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-4-yl)pyrrolidin-2-yl)methyl)dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-4-amine 3b

White powder (0.71 g, yield 87%). $[\alpha]_D^{20} = +122.3$ (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.36–1.44 (m, 1H, CH_2CH_2), 1.46–1.56 (m, 2H, CH_2CH_2), 1.69–1.77 (m, 1H, CH_2CH_2), 2.63–2.72 (m, 1H, 2(CH_2N)), 3.03–3.15 (m, 3H, 2(CH_2N)), 3.78 (br d, $^{2}J_{H,H}$ = 15.0 Hz, 1H, CH_2, Bn), 3.86–3.94 (m, 1H, CHN), 4.20 (br d, $^{2}J_{H,H}$ = 15.0 Hz, 1H, CH_2, Bn), 7.14–7.25 (m, 6H, CH, aryl), 7.32–7.45 (m, 10 H, CH, aryl), 7.49 (d, $^{3}J_{H,H}$ = 8.9 Hz, 1H, CH, aryl), 7.55–7.66 (m, 3H, CH, aryl), 7.78–8.03 (m, 9H, CH, aryl). $^{13}C\{H\}$ NMR ($CDCl_3$, 25 °C): δ_C = 24.7 (s, CH_2); 28.8 (d, ^{3}J = 4.0 Hz, CH_2); 43.2 (s, CH_2N); 48.8 (br s, CH_2N); 50.4 (dd, ^{2}J = 32.7 Hz, ^{3}J = 4.1 Hz, CH_2N); 56.6 (dd, ^{2}J = 31.4 Hz, ^{3}J = 3.4 Hz, CHN); 121.9, 122.1 (s, CH, binaphthyl); 122.2 (d, ^{3}J = 3.4 Hz, CH, binaphthyl); 122.3 (s, CH, binaphthyl); 122.9, 123.0 (s, C, binaphthyl); 123.8 (d, ^{3}J = 4.7 Hz, C, binaphthyl); 124.1 (d, ^{3}J = 5.4 Hz, C, binaphthyl); 124.4 (br s, 2 × CH, binaphthyl); 124.5, 124.7, 125.7, 125.8, 125.9, 126.0, 126.7, 126.8, 126.9, 127.0, 127.1 (s, CH, binaphthyl); 128.1 (s, CH, phenyl); 128.2 (br s, 2 × CH, phenyl); 128.3 (br s, 3 × CH, binaphthyl); 128.7 (br s, 2 × CH, phenyl); 129.7, 129.9, 130.0, 130.1, (s, CH, binaphthyl);

130.5, 130.7, 131.1, 131.3, 132.3, 132.4, 132.7, 132.8 (s, C, binaphthyl); 137.5 (s, C, phenyl); 149.1 (s, CO, binaphthyl); 149.6 (d, ^2J = 1.4 Hz, CO, binaphthyl); 149.9 (d, ^2J = 6.1 Hz, CO, binaphthyl); 150.0 (d, ^2J = 6.7 Hz, CO, binaphthyl). MS (MALDI TOF/TOF), *m/z* (I, %): = 819 (23) $[M+H]^+$, 505 (100) $[M-C_{20}H_{12}O_2P+2H]^+$, 316 (64) $[C_{20}H_{12}O_2PH]^+$. Anal. Calcd for $C_{52}H_{40}N_2O_4P_2$: C, 76.27; H, 4.92; N, 3.42. Found: C, 76.40; H, 5.03; N, 3.15.

4.3. General procedure for the preparation of complexes 4a,b

A solution of the appropriate ligand **3a** or **3b** (0.164 g, 0.2 mmol) in CH_2Cl_2 (3 mL) was added dropwise over 30 min to a vigorously stirred solution of $[Pd(allyl)Cl]_2$ (0.037 g, 0.1 mmol) in CH_2Cl_2 (2 mL). The mixture was stirred for an additional 1 h, followed by the dropwise addition of $AgBF_4$ (0.039 g, 0.2 mmol) in THF (3 mL) over 30 min. The mixture was then stirred for 1 h, and the precipitated AgCl was filtered off. The filtrate was concentrated at reduced pressure to a volume of approximately 0.5 mL, and then diethyl ether (10 mL) was added. The precipitated solid was separated by centrifugation, washed twice with diethyl ether (7 mL) and dried in vacuo (1 Torr, 1 h).

4.3.1. $[Pd(allyl)(3a)]BF_4$ 4a

Sand-colored powder (0.192 g, yield 91%). MS (MALDI TOF/TOF), *m/z* (I,%): = 965 (100) $[M-BF_4]^+$. Anal. Calcd for $C_{55}H_{45}BF_4N_2O_4P_2Pd$: C, 62.73; H, 4.31; N, 2.66. Found: C, 63.02; H, 4.44; N, 2.75.

4.3.2. $[Pd(allyl)(3b)]BF_4$ 4b

Sand-colored powder (0.196 g, yield 93%). MS (MALDI TOF/TOF), *m/z* (I,%): = 965 (100) $[M-BF_4]^+$. Anal. Calcd for $C_{55}H_{45}BF_4N_2O_4P_2Pd$: C, 62.73; H, 4.31; N, 2.66. Found: C, 63.04; H, 4.25; N, 2.88.

4.4. Catalytic reactions

4.4.1. General procedure for the Pd-catalyzed allylic sulfonylation of (*E*)-1,3-diphenylallyl acetate 5 with sodium *p*-toluenesulfinate

A solution of $[Pd(allyl)Cl]_2$ (0.0019 g, 0.005 mmol) and the appropriate ligand (0.008 g or 0.016 g, 0.01 mmol or 0.02 mmol) in THF (1.5 mL) was stirred for 40 min. ((*E*)-1,3-Diphenylallyl acetate (0.05 mL, 0.25 mmol) was added and the solution was stirred for 15 min. Next, sodium *p*-toluenesulfinate (0.089 g, 0.5 mmol) was added and the reaction mixture was 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 vacuo (10 Torr, 12 h), gave (*E*)-1,3-diphenyl-3-tosylprop-1-ene **6a** as white crystals. The ee of **6a** was determined by HPLC.

4.4.2. General procedure for the Pd-catalyzed allylic alkylation of (*E*)-1,3-diphenylallyl acetate 5 with dimethyl malonate

A solution of $[Pd(allyl)Cl]_2$ (0.0019 g, 0.005 mmol) and the appropriate ligand (0.008 g or 0.016 g, 0.01 mmol or 0.02 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min. (*E*)-1,3-Diphenylallyl acetate (0.05 mL, 0.25 mmol) was then 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 then added. The reaction mixture was stirred for 48 h, then 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 vacuo (10 Torr, 12 h) to afford a residue containing (*E*)-dimethyl 2-(1,3-diphenylallyl)malonate **6b**. 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.

4.4.3. General procedure for the Rh-catalyzed hydrogenation of α-dehydrocarboxylic acid esters 7a,b

A solution of $[Rh(cod)_2]BF_4$ (0.002 g, 0.005 mmol) and the appropriate ligand (0.004 g, 0.005 mmol) in the appropriate solvent (8 mL) was stirred for 40 min. Next, the resulting solution and the prochiral olefin (0.5 mmol) were transferred to the hydrogenation device (a standard device for hydrogenation under 1 bar hydrogen pressure) under a hydrogen atmosphere. The reaction mixture was stirred at 25 °C for 24 h. The conversions of substrates **7a,b** were determined by GC simultaneously with the determination of the ee values of products **8a,b**. In some cases, conversions were also determined by ^1H NMR.

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