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Synthesis of Novel Monodentate Phosphoramidites and Their Application in Iridium-Catalyzed Asymmetric Hydrogenations

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Abstract: New monodentate H_8-binaphthol based phosphoramidites **6b–i** have been prepared. Starting from (*S*)-3,3′-dibromo-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol **3**, a general protocol for the synthesis of ligands **6** is presented. A small ligand library bearing aryl substituents in the 3,3′-position of the binaphthol core was synthesized and successfully tested in the iridium-catalyzed asymmetric hydrogenation of 2-amidocinnamates to obtain different α-amino acid derivatives in up to 99% *ee*.

Keywords: asymmetric catalysis · homogeneous catalysis · hydrogenation · iridium · P ligands

Introduction

Enantioselective hydrogenation is the most important catalytic asymmetric method with respect to industrial applications. Nevertheless, the development of improved and more general hydrogenation catalysts is a quest for both academia as well as the pharmaceutical industry. Until now, several hundred transition-metal-based catalysts have been applied for such reactions, for example, Rh, Ru, and Ir complexes, the latter being the most rarely used metal in asymmetric hydrogenation of α-amino acid precursors.

From chemical and economical points of view, one of the major factors that influence the asymmetric reaction is the choice of chiral ligand coordinated to the transition metal; therefore, the design of new ligands for asymmetric hydrogenation is an important research goal. In general, phosphorus ligands have been effectively employed in catalytic hydrogenation reactions.[1] Recently, in particular monodentate phosphoramidites (e.g. the MonoPhos family) have attracted significant attention owing to their convenient synthesis and wide applicability.[2] The MonoPhos-type ligands were first applied in asymmetric hydrogenations by Feringa, de Vries, and co-workers[3] and are now commercially available. The catalytic potential of this ligand class has been investigated in detail during the last decade.[4] Various types of olefins like α- or β-dehydroamino acid ester,[5] enamides, α,β-disubstituted unsaturated acids,[6,7] and β^2-amino acids[8] are hydrogenated highly selectively in the presence of phosphoramidites or mixtures of them with other chiral or achiral ligands. Most recently, these ligands have also found application in the iridium-catalyzed hydrogenation of methyl α-acetamidocinnamate.[9]

Although several MonoPhos derivatives have been synthesized and tested, only a limited number of sterically hindered derivatives with substitution in the 3,3′-position of the binaphthol backbone is known.[10,11] Catalytic applications of bulky 3,3′-disubstituted phosphoramidites include a range of addition reactions to C=C double bonds, for example, the copper-catalyzed conjugated 1,4-addition of diethylzinc, the [2+2+2] cycloaddition of alkenyl isocyanates and terminal alkynes,[12] and others.[13] Hydrogenation of the binaphthyl backbone leads to another class of active phosphoramidite ligands, such as the H_8-MonoPhos **6a**.[14] These partially hydrogenated phosphoramidites have also been mainly investigated in asymmetric hydrogenations[5,15,16] and addition reactions.[13,17,18] However, to the best of our knowledge, there is no example known on the synthesis of bulky phosphoramidites with partially hydrogenated H_8-binaphthol backbone and 3,3′-substitution.

Our interest in this class of ligands resulted from the recent development of an improved procedure for the preparation of H_8-binaphthyl-substituted phosphates **5**, which are chiral Brønsted acids.[19] Partially hydrogenated binaphthol underwent selective bromination in the 3,3′-position

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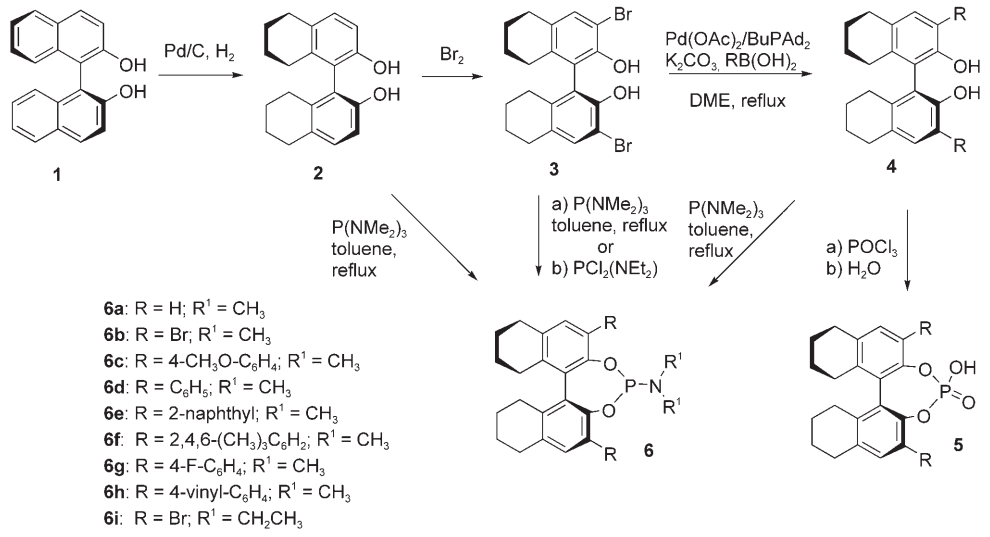

Scheme 1. Synthesis of H_8-binaphthol based phosphoramidites **6**.

without protection and deprotection of the phenolic groups, which resulted in a straightforward, multi-gram scale synthesis of a number of new H_8-binaphthyl-substituted diols. Because of the availability of 3′-aryl substituted binaphthols **4** and our work in the area of asymmetric hydrogenation with monodentate ligands,[20] we became interested in using these intermediates for the preparation of novel H_8-binaphthol based phosphoramidites **6**.

Herein, we report on the synthesis of these new ligands and their application in the iridium-catalyzed asymmetric hydrogenation of different α-amino acid derivatives.

Results and Discussion

Preparation of Ligands

The overall synthesis of phosphoramidites **6** proceeds in four steps and starts with the selective hydrogenation of enantiomerically pure 2,2′-binaphthol **1**[21] in the presence of catalytic amounts of Pd/C (Scheme 1).[22,23] The corresponding 5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol **2** is obtained in excellent yield, which allows for subsequent bromination in the 3,3′-position with Br_2 at −30 °C in a selective manner. Subsequent Suzuki coupling with arylboronic acids in the presence of $Pd(OAc)_2$/$BuPAd_2$ (*n*-butyl-di-1-adamantylphosphine) gave the corresponding 3,3′-disubstituted binaphthols **4a–i** in good to excellent yield.[24,25] The resulting diols **4a–i** are treated with $P(NMe_2)_3$ or Et_2NPCl_2/NEt_3 in refluxing toluene to obtain **6a–i** in moderate to good yields.[3]

The ligands were purified by crystallization in diethyl ether or by column flash chromatography in a mixture of *n*-hexane/ethyl acetate. The reaction sequence is shown in Scheme 1 and has several advantages compared with the synthesis of known 3,3′-disubstituted phosphoramidites. Owing to the partial hydrogenation of the binaphthol core, an extremely regioselective bromination is possible, which does not require protection (and later deprotection) of the hydroxy groups. Thus, a variety of 3,3′-disubstituted binaphthols are more easily accessible, which can be utilized as versatile chiral building blocks. The molecular structures of compounds **6b** and **6g** were confirmed by X-ray crystallography and are depicted in Figure 1.

Catalytic Applications

Preliminary catalytic experiments showed that hydrogenation of α-amino acid derivatives in the presence of rhodium complexes had impaired catalytic activity with these novel ligands. Therefore, we directed our efforts to iridium-catalyzed hydrogenation reactions. Following the excellent recent work of de Vries,[9] we started out with a catalyst in situ formed by mixing $[\{Ir(cod)Cl\}_2]$ and one equivalent of phosphoramidite **6g** per metal in dichloromethane at 5 bar. Under these conditions methyl α-acetamidocinnamate **7b** is hydrogenated with particularly high enantioselectivities (94–95 % *ee*), whereas methyl acetamidoacrylate **7a** and itaconic acid dimethylester **7c** produced only low to moderate results (Table 1, entries 1–3).

Running the hydrogenation experiments with **7b** at atmospheric hydrogen pressure (Table 1, entry 4) resulted in

Abstract in German: Die Synthese und die katalytische Anwendung neuartiger monodentater Phosphoramidite (**6b–i**) basierend auf einem H_8-Binaphthol-Gerüst wird vorgestellt. Ausgehend von (*S*)-3,3′-Dibromo-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol (**3**) konnte eine allgemeine Syntheseroute für die Darstellung der Ligandenklasse **6** entwickelt werden. Die 3,3′-diaryl-substituierten Liganden wurden erfolgreich in der Iridium-katalysierten asymmetrischen Hydrierung verschiedener 2-Amidozimtsäureester eingesetzt, wobei Enantioselektivitäten von bis zu 99 % *ee* erzielt wurden.

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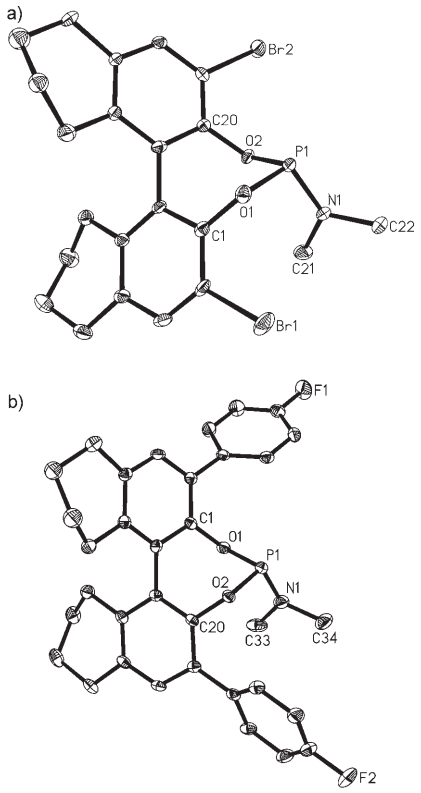
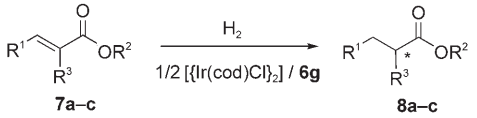


Figure 1. Molecular structures of H_8-binaphthol based phosphoramidites **6b** (a) and **6g** (b). The thermal ellipsoids correspond to 30% probability. Hydrogen atoms and one position of the disordered parts are omitted for clarity.

Table 1. Asymmetric hydrogenation of α-amino acid derivatives **7a** and **7b** and itaconic acid dimethylester **7c**.[a]



7a–c **8a–c**

7a: R^1= H; R^2= Me; R^3= NHAc
7b: R^1= Ph; R^2= Me; R^3= NHAc
7c: R^1= H; R^2= Me; R^3= CH_2COOMe

Entry	Substrate	Sub./Cat.	$p(H_2)$	TOF $[h^{-1}]$[c]	t [h]	Conv. [%]	ee [%]
1	**7a**	25:1	5 bar	–	16	>99	40 (*R*)
2	**7b**	25:1	5 bar	–	16	>99	94 (*R*)
3	**7c**	25:1	5 bar	–	16	>99	13 (*S*)
4[b]	**7b**	25:1	1 atm	14	6	>99	95 (*R*)
5[b]	**7b**	50:1	1 atm	22	6	>99	95 (*R*)
6[b]	**7b**	100:1	1 atm	14	24	>99	95 (*R*)
7[b]	**7b**	1000:1	1 atm	27	72	>99	94 (*R*)

[a] Reaction conditions: substrate **7** (0.25 mmol); $[\{Ir(cod)Cl\}_2]$ (5×10^{-3} mmol); Ir/L(**6g**) = 1:1; CH_2Cl_2 (2 mL); 25 °C. Conversion and enantioselectivity were determined by GC (for **8a:** Chirasil Val, 120 °C isotherm; for **8b:** Lipodex E, 150 °C isotherm; for **8c:** Lipodex E, 80 °C isotherm). [b] Substrate **7b** (1 mmol); $[\{Ir(cod)Cl\}_2]$ (2×10^{-2} mmol); Ir/L (**6g**) = 1:1; CH_2Cl_2 (10 mL); 25 °C. [c] Average time of flight (TOF) estimated from H_2 consumption curve.

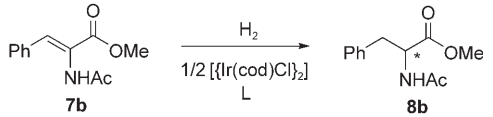
an improvement in the *ee* value to 95% and the reaction showed complete conversion within six hours. Advantageously, a decrease in the catalyst concentration had no negative influence on the enantioselectivity (Table 1, entries 5–7). Still at a substrate/catalyst ratio of 1000:1, the phosphoramidite **6g** produced 94% enantioselectivity, albeit the required reaction time for a complete conversion is significantly longer.

Next, we set out to study the influence of various substituents attached to the aryl groups in the 3,3′-position of the H_8-binaphthol backbone on the asymmetric hydrogenation of methyl α-acetamidocinnamate **7b**. For this purpose, a number of ligands bearing different aryl substitutions were tested, but also those derived directly from the bromide precursors **3**.

With respect to structure–activity relationships and finally a more rational ligand design, we were looking for a simple test to assess the electronic properties of the new ligands and similar phosphoramidites.[26] In this case, the measure of the first-order coupling constant between the phosphorus and selenium atoms of the corresponding selenides seemed to be suitable to us.[27] The corresponding selenides are easily prepared by mixing the ligands with elemental selenium in refluxing chloroform. The readily measured $J_{P\text{-}Se}$ values are summarized in Table 2 together with their ^{31}P NMR spectroscopy chemical shifts. In general, the greater the coupling constant between ^{31}P and ^{77}Se becomes, the stronger the σ bond between the two, which in turn indicates a low electron density of the phosphorus lone-pair orbital.

As shown in Table 2, it is apparent that disubstitution at the 3,3′-position of the binaphthol backbone is essential to achieve high catalyst activity and enantioselectivity (Table 2, entry 1). The bromide-substituted ligands **6b** and **6i** showed a marked acidic character of the phosphorus and this is accompanied by a slight decrease in the enantioselection (Table 2, entries 2 and 9). Many aryl-substituted ligands

Table 2. Asymmetric hydrogenation of methyl α-acetamidocinnamate **7b**.[a]



7b **8b**

Entry	Ligand	Sub./Cat.	TOF $[h^{-1}]$[d]	Conv. [%]	ee [%]	^{31}P [ppm][c]	$J_{P\text{-}Se}$ [Hz][c]
1	**6a**	25:1	–	15	37 (*R*)	85.3	958.4
2	**6b**	25:1	11	>99	91 (*R*)	81.3	990.0
3	**6c**	25:1	17	>99	94 (*R*)	79.9	965.4
4	**6d**	25:1	25	>99	96 (*R*)	80.1	968.9
5	**6e**	25:1	22	>99	95 (*R*)	80.4	969.7
6	**6f**	25:1	24	>99	98 (*R*)	84.6	952.9
7	**6g**	25:1	14	>99	95 (*R*)	80.1	971.0
8	**6h**	25:1	20	>99	94 (*R*)	80.0	968.9
9	**6i**	25:1	16	>99	89 (*R*)	80.4	981.0
10	**6f**	50:1	37	>99	98 (*R*)	–	–
11[b]	**6f**	50:1	37	>99	99 (*R*)	–	–

[a] Reaction conditions: substrate **7b** (1 mmol); $[\{Ir(cod)Cl\}_2]$ (2×10^{-2} mmol); Ir/L = 1:1; CH_2Cl_2 (10 mL); 25 °C, 1 atm H_2. [b] L/Ir = 2:1. Conversion and enantioselectivity were determined by GC (Lipodex E, 150 °C isotherm). [c] Values pertain to selenides of the corresponding ligands. [d] Average TOF estimated from H_2 consumption curve.

scored similar electronic values and stereoselection in spite of electron-donating or -withdrawing substitution (**6c–d** and **6g–h**, Table 2, entries 3–5, and 7–8). Notably, ligand **6d** attained comparable results with those reported by de Vries et al.[9] and its parental ligand had an aromatized backbone (>99% conv., 93% *ee*). The only exception is the mesityl-substituted aryl ligand **6f**, which had a distinct basic character and induced a noticeable improvement of enantioselection (Table 2, entry 6). A correlation graph between coupling constants of the 3,3′-disubstituted phosphoramidite selenides and the enantioselectivity of the related ligands is illustrated in Figure 2. Notably, a rough relationship between catalyst activity and the respective coupling constant seems to be possible. It can be seen that basic character of the ligand favors rapid hydrogenation (compare ligands **6f** and **6b**).

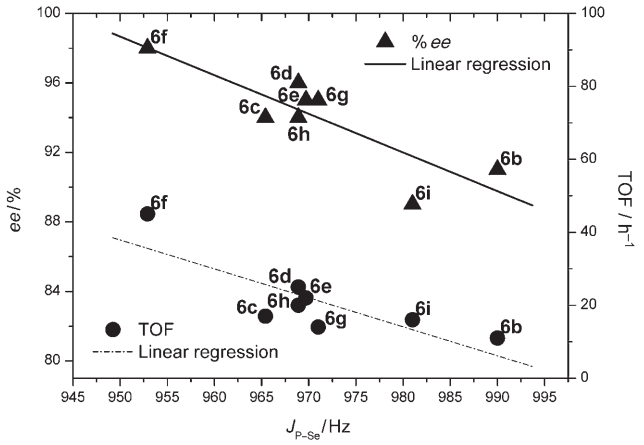


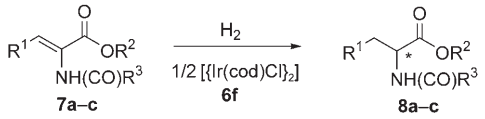
Figure 2. Enantioselectivity and catalyst activity versus coupling constants $J_{P\text{-}Se}$ for selenides of ligands **6b–i.**

The most selective ligand **6f** was also tested by applying a lower catalyst loading, which yielded similar results (Table 2, entry 10). Remarkably, the addition of two equivalents of the ligand did not affect the outcome of the reaction significantly (Table 2, entry 11), which is a strong indication for monosubstitution of the iridium complex.

Finally, after optimization, we demonstrated the generality of our ligands with several α-amino acid derivatives (Table 3). Various amidocinnamates were synthesized following literature procedures,[28] and they were hydrogenated under 5 bar of H_2 for 4 h at room temperature in the presence of ligand **6f**. Enantioselectivities greater than 97% and full conversion within 4 h are observed for different esters, amido, and aryl-substituted derivatives. For example, when the ethyl ester of **7b** is employed, enantioselectivity up to 99% is achieved. The catalyst system is rather stable even at a lower hydrogen pressure (Table 3, entry 9) and lower catalyst loading (Table 3, entry 10).

Hydrogenation of the precursor of L-Dopa **7e** confirmed the high selectivity of the catalyst. With respect to functional-group tolerance, it is noteworthy that benzamidocinnamates are tolerated without problems. Again, different aryl amino acid esters, either with electron-withdrawing (**7h** and **7i**, Table 3, entries 6–7) or electron-donating substituents (**7k**, Table 3, entry 8), gave high enantioselectivity values (97–99%) under those hydrogenation conditions.

Table 3. Asymmetric hydrogenation of different α-aminoacid derivatives **7** with ligand **6f**.[a]



7b: R^1= Ph; R^2= Me; R^3= Me
7d: R^1= Ph; R^2= Et; R^3= Me
7e: R^1= 3,4-OCH_2O-C_6H_3; R^2= Me; R^3= Me
7f: R^1= Ph; R^2= Et; R^3= Ph
7g: R^1= Ph; R^2= Me; R^3= Ph
7h: R^1= 4-Cl-C_6H_4; R^2= Me; R^3= Ph
7i: R^1= 4-F-C_6H_4; R^2= Me; R^3= Ph
7k: R^1= 4-MeO-C_6H_4; R^2= Me; R^3= Ph

Entry	Substrate	Sub./Cat.	$p(H_2)$	Conv. [%]	*ee* [%]
1	**7b**	25:1	5 bar	>99	98.0 (*R*)
2	**7d**	25:1	5 bar	>99	99.0 (*R*)
3	**7e**	25:1	5 bar	>99	97.0 (*R*)
4	**7f**	25:1	5 bar	>99	97.0 (*R*)
5	**7g**	25:1	5 bar	>99	97.5 (*R*)
6	**7h**	25:1	5 bar	>99	97.0 (*R*)
7	**7i**	25:1	5 bar	>99	97.5 (*R*)
8	**7k**	25:1	5 bar	>99	97.0 (*R*)
9	**7d**	25:1	1 atm	>99	99.0 (*R*)
10	**7d**	50:1	1 atm	>99	98.5 (*R*)

[a] Reaction conditions: substrate **7** (0.125 mmol); $[\{Ir(cod)Cl\}_2]$ (2.5×10^{-3} mmol); Ir/L (**6f**) = 1:1; CH_2Cl_2 (1.5 mL); 25 °C, 1 atm H_2, 4 h. Conversion and enantioselectivity were determined by HPLC (Chiralcel OD-H, heptane/ethanol 95:5, 1 mL min^{-1} or heptane/ethanol 90:10, 1 mL min^{-1}).

Conclusions

In summary, eight H_8-binaphthol based phosphoramidites with substituents in the 3,3′-position have been easily prepared in high yields. Owing to the partially hydrogenated binaphthol core, selective bromination in the 3,3′-position is possible without protection and deprotection of the phenolic groups. Hence, these ligands are available on a multi-gram scale from inexpensive starting materials. The novel ligands have been successfully used in iridium-catalyzed hydrogenation of different acetamido- and benzamido-cinnamates. Reduction took place at low H_2 pressure and in less than 4 hours, and all substrates were hydrogenated with high enantioselectivity (97–99%). Substitution in the 3,3′-position of the binaphthyl core was proven to be essential to obtain high enantioselectivity. The effect of different types of functionalization in this position was studied in detail, and a rough correlation with the catalyst activity was observed. In selected cases, a higher selectivity is obtained compared with similar known iridium-catalyzed hydrogenations. We

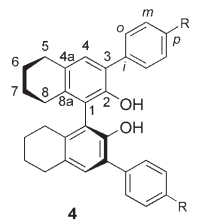
believe that the presented ligand and catalyst systems might also serve as a promising tool for other catalytic transformations.

Experimental Section

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker spectrometers AVANCE 300 (^{1}H: 300.13 MHz, ^{13}C: 75.5 MHz, ^{31}P: 121.5 MHz) and AVANCE 500 (compounds **4f**, **4g** and **6f**, **6g**; ^{1}H: 500.13 MHz, ^{13}C: 125.8 MHz, ^{31}P: 202.5 MHz). The calibration of ^{1}H and ^{13}C spectra was carried out based on solvent signals (δ ($CDCl_3$) = 7.25 and 77.0). The ^{31}P NMR chemical shifts are referenced to 85% H_3PO_4. The multiplicity of ^{13}C NMR signals was determined by DEPT spectra. Furthermore, for compounds **4f**, **4g** and **6f**, **6g** two-dimensional NMR spectra (COSY, NOESY, HMBC, and HSQC) were recorded, which confirmed the assignment of NMR signals. The numbering of atoms corresponds to the given formula. Mass spectra were recorded on an AMD 402 spectrometer. Chemical shifts are given in ppm, and coupling constants are reported in Hz. Elemental analyses were performed at a Leco CHNS-932. Optical rotations were measured on a Gyromat-HP polarimeter. IR spectra were recorded as KBr pellets or Nujol mulls on a Nicolet Magna 550. All manipulations were performed under argon atmosphere by using standard Schlenk techniques. The octahydro binaphthol **2** and (*S*)-3,3′-dibromo-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol **3** were prepared according to literature procedures.[22,23]

3′-Diaryl-substituted H_8-binaphthols 4

General procedure: (*S*)-3,3′-Dibromo-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol **3** (2 g, 4.4 mmol), an appropriate boronic acid (13.1 mmol), K_2CO_3 (1.8 g, 13.1 mmol), palladium(II) acetate (20 mg, 0.09 mmol), and diadamantyl-*n*-butylphosphine (40 mg, 0.1 mmol) were dissolved in 1,2-dimethoxyethane (20 mL) and refluxed for 24 h or longer. After the reaction mixture was cooled to room temperature, a saturated solution of NH_4Cl was added and extracted with dichloromethane (2× 100 mL). The organic phase was washed with water and dried over Na_2SO_4. The solvent was removed and the residue was purified by column chromatography (eluent: CH_2Cl_2/*n*-hexane).



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(*S*)-3,3′-Di(4-methoxyphenyl)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol (**4c**): Yield: 98% (colorless foam); R_f = 0.1 (CH_2Cl_2/*n*-hexane 4:1); $[\alpha]_D^{22}$ = 804.7 (*c* = 0.5, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.50 (m, 4H; *o*-C_6H_4), 7.11 (brs, 2H; 4-H), 6.98–6.93 (m, 4H; *m*-C_6H_4), 4.88 (s, 2H; OH), 3.83 (s, 6H; CH_3O), 2.79 (t, 4H; 5-H), 2.44–2.18 (m, 4H; 8-H), 1.80–1.65 ppm (m, 8H; 6-H, 7-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.7 (*p*-C_6H_4), 148.0 (C2), 136.0 (C8a), 131.4 (C4), 130.3 (*o*-C_6H_4), 130.2, 130.0 (C4a, *i*-C_6H_4), 125.6 (C3), 120.1 (C1), 113.8 (*m*-C_6H_4), 55.3 (CH_3O), 29.2 (C5), 27.1 (C8), 23.1, 23.0 ppm (C6, C7); IR (KBr): $\tilde{\nu}$ = 3505 m, 2925 m, 2835 m, 1724 w, 1663 w, 1608 m, 1514 s, 1458 m, 1398 m, 1289 m, 1245 s, 1178 s, 1132 m, 1111 m, 1034 m, 945 w, 915 w, 833 m, 813 m, 785 w, 757 w, 733 w, 633 w, 553 cm^{-1} w; MS (EI): *m*/*z* (%): 506 (100) [M^+], 253 (12), 57 (10), 44 (21); HRMS calcd for $C_{34}H_{34}NO_4$: 506.24516; found: 506.245369.

(*S*)-3,3′-Diphenyl-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol (**4d**): Yield: 85% (off-white solid); R_f = 0.28 (CH_2Cl_2:*n*-hexane 1:1); m.p.: 186–190 °C. $[\alpha]_D^{22}$ = 27.8 (*c* = 0.122, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.57 (m, 4H; *o*-C_6H_4), 7.47–7.41 (m, 4H; *m*-C_6H_4), 7.35–7.29 (m, 2H; *p*-C_6H_4), 7.15 (brs, 2H; 4-H), 4.90 (s, 2H; OH), 2.80 (t, 4H; 5-H), 2.46–2.20 (m, 4H; 8-H), 1.81–1.67 ppm (m, 8H; 6-H, 7-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 148.1 (C2), 137.9 (*i*-C_6H_4), 136.6 (C8a), 131.7 (C4), 130.2 (C4a), 129.2, 128.4 (*o*-, *m*-C_6H_4), 127.1 (*p*-C_6H_4), 126.0 (C3), 120.1 (C1), 29.2 (C5), 27.1 (C8), 23.1, 23.0 ppm (C6, C7); IR (KBr): $\tilde{\nu}$ = 3450 s, 3387 s, 3058 w, 3034 w, 2926 s, 2857 m, 2831 m, 1718 w, 1607 m, 1498 w, 1461 s, 1432 m, 1409 m, 1353 w, 1316 m, 1278 m, 1236 s, 1186 m, 1133 s, 1073 w, 1033 w, 1008 w, 946 w, 911 w, 894 w, 880 w, 823 w, 805 w, 775 s, 739 m, 696 s, 669 w, 654 w, 625 w, 591 w, 560 m, 435 cm^{-1} w; MS (EI): *m*/*z* (%): 446 (100) [M^+], 400 (6), 356 (3), 289 (3), 181 (11), 119 (6), 77 (4); HRMS calcd for $C_{32}H_{30}O_2$: 446.22403; found: 446.224120.

(*S*)-3,3′-Dinaphthyl-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol (**4e**): Yield: 50% (colorless needles); m.p.: 207–212 °C; $[\alpha]_D^{22}$ = 154.9 (*c* = 0.324, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 1.8 Hz, 2H), 7.91–7.83 (m, 6H), 7.76 (dd, *J* = 8.5 Hz, 1.8 Hz, 2H), 7.51–7.44 (m, 4H; 2$C_{10}H_7$), 7.27 (brs, 2H; 4-H), 5.02 (s, 2H; 2OH), 2.84 (t, 4H; 5-H), 2.52–2.26 (m, 4H; 8-H), 1.84–1.71 ppm (m, 8H; 6-H, 7-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 148.3 (C2), 136.8 (C8a), 135.4, 133.5, 132.5 (C_q, $C_{10}H_7$), 132.0 (C4), 130.4 (C4a), 128.1, 127.9, 127.8, 127.6 (2), 126.1, 125.9 (CH, $C_{10}H_7$), 126.0 (C3), 120.1 (C1), 29.3 (C5), 27.2 (C8), 23.1, 23.0 ppm (C6, C7); IR (KBr): $\tilde{\nu}$ = 3504 w, 3360 w, 3051 w, 3014 w, 2920 m, 2854 w, 2834 w, 1724 w, 1628 w, 1602 w, 1505 w, 1473 w, 1454 m, 1431 w, 1409 w, 1353 w, 1316 w, 1297 w, 1242 m, 1232 m, 1187 m, 1135 m, 1117 m, 1065 w, 1015 w, 951 w, 937 w, 905 w, 858 m, 821 s, 785 w, 754 s, 738 s, 675 m, 659 cm^{-1} m; MS (EI): *m*/*z* (%): 546 (100) [M^+], 500 (2), 436 (2), 403 (2), 355 (1), 300 (2), 273 (11), 231 (6), 148 (2), 121 (6), 91 (6), 57 (5), 44 (23); HRMS calcd for $C_{40}H_{34}O_2$: 546.25533; found: 546.255376.

(*S*)-3,3′-Di(2,4,6-trimethylphenyl)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol (**4f**)**:** Yield: 60% (colorless foam); R_f = 0.48 (CH_2Cl_2/*n*-hexane 1:1); m.p.: 141–143 °C; $[\alpha]_D^{22}$ = 24.1 (*c* = 0.26, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.98 (brs, 2H), 6.96 (brs, 2H; *m*-C_6H_2), 6.84 (s, 2H; 4-H), 4.50 (s, 2H; OH), 2.80 (t, 4H; 5-H), 2.39 (m, 4H; 8-H), 2.33 (s, 6H; *p*-Me), 2.12 (s, 6H), 2.05 (s, 6H; *o*-Me), 1.84–1.73 ppm (m, 8H; 6-H, 7-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 147.9 (C2), 137.0 (2), 136.9 (*o*-, *p*-C_6H_2), 135.9 (C8a), 133.6 (C9), 131.1 (C4), 129.7 (C4a), 128.3, 128.1 (*m*-C_6H_2), 124.6 (C3), 120.3 (C1), 29.2 (C5), 27.1 (C8), 23.2, 23.1 (C6, C7), 21.1 (*p*-Me), 20.5, 20.4 ppm (*o*-Me); IR (KBr): $\tilde{\nu}$ = 3527 m, 2997 w, 2921 m, 2855 m, 1609 m, 1570 w, 1447 s, 1376 w, 1315 w, 1276 m, 1230 s, 1173 m, 1123 m, 1070 w, 1058 w, 1032 w, 1012 w, 938 w, 913 w, 878 w, 846 s, 823 w, 797 m, 765 w, 736 w, 653 cm^{-1} w; MS (EI): *m*/*z* (%): 530 (100) [M^+], 490 (6), 410 (2), 367 (2), 292 (2), 265 (10), 223 (4), 184 (3), 133 (2), 91 (2), 69 (2), 44 (5)); HRMS calcd for $C_{38}H_{42}O_2$: 530.31793; found: 530.317323.

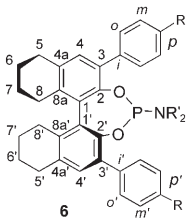
(*S*)-3,3′-Di(4-fluorophenyl)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol (**4g**): Yield: 99% (colorless needles); R_f = 0.22 (CH_2Cl_2/*n*-hexane 1:1); m.p.: 176–178 °C; $[\alpha]_D^{22}$ = 21.4 (*c* = 0.13, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.58–7.54 (m, 4H; *o*-C_6H_4), 7.12 (br s, 2H; 4-H), 7.12–7.07 (m, 4H; *m*-C_6H_4), 4.85 (s, 2H; OH), 2.79 (t, 4H; 5-H), 2.41–2.34 (m, 2H), 2.27–2.20 (m, 2H; 8-H), 1.80–1.68 ppm (m, 8H; 6-H, 7-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 162.0 (d, $J_{F,C}$ = 246 Hz, *p*-C_6H_4), 148.1 (C2), 136.6 (C8a), 133.8 (d, $J_{F,C}$ = 3.2 Hz, *i*-C_6H_4), 131.8 (C4), 130.8 (d, $J_{F,C}$ = 8.2 Hz, *o*-C_6H_4), 130.4 (C4a), 125.1 (C3), 119.8 (C1), 115.2 (d, $J_{F,C}$ = 21.5 Hz, *m*-C_6H_4), 29.2 (C5), 27.1 (C8), 23.0 ppm (2) (C6, C7); IR (KBr): $\tilde{\nu}$ = 3501 m, 3378 m, 2929 m, 2859 m, 2836 m, 1601 m, 1510 s, 1456 s, 1437 m, 1393 m, 1319 m, 1277 m, 1219 m, 1188 w, 1158 m, 1132 m, 1095 w, 1016 w, 946 w, 915 w, 836 s, 793 w, 753 w, 659 w, 631 w, 544 cm^{-1} m; MS (EI): *m*/*z* (%): 482 (100) [M^+], 462 (4), 436 (5), 292 (4), 241 (13), 220 (5), 199 (9), 149 (9), 57 (9), 44 (8); HRMS calcd for $C_{32}H_{28}O_2F_2$: 482.204906; found: 482.20519.

(*S*)-3,3′-Di(4-vinylphenyl)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol (**4h**): Yield: 59% (colorless solid); R_f = 0.17 (CH_2Cl_2/*n*-hexane 1:1); m.p.: 155–157 °C; $[\alpha]_D^{22}$ = 167.4 (*c* = 0.25, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59–7.44 (m, 8H; C_6H_4), 7.15 (br s, 2H; 4-H), 6.75 (dd, ^3J = 17.7 Hz, 11.0 Hz, 2H; C*H*=CH$_2$), 5.77 (dd, ^3J = 17.7 Hz, ^2J = 1.0 Hz, 2H), 5.25 (dd, ^3J = 11.0 Hz, ^2J = 1.0 Hz, 2H), (CH=C*H*$_2$), 4.90 (s, 2H; OH), 2.80 (t, 4H; 5-H), 2.45–2.19 (m, 4H; 8-H), 1.81–1.66 ppm (m, 8H; 6-H, 7-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 148.1 (C2), 137.4 (*i*-C_6H_4), 136.7, 136.3 (C8a, *p*-C_6H_4), 136.5 (*C*H=CH$_2$), 131.6 (C4), 130.3 (C4a), 129.3, 126.2 (*o*-, *m*-C_6H_4), 125.6 (C3), 120.0 (C1), 113.8 (CH=*C*H$_2$), 29.2 (C5), 27.2 (C8), 23.0 ppm (C6, C7); IR (KBr): $\tilde{\nu}$ = 3501 s, 3085 w, 3011 w, 2925 s, 2852 m, 2369 w, 1683 w, 1628 m, 1607 m, 1576 w, 1512 m, 1456 m, 1436 m, 1395 m, 1320 m, 1291 m, 1237 m, 1181 m, 1133 m, 1070 w, 1017 w, 989 m, 946 w, 901 m, 843 s, 764 w, 668 w, 653 w, 635 w, 550 w, 460 cm^{-1} w; MS

(EI): *m/z* (%): 498 (3) [M^+], 457 (63), 313 (13), 283 (14), 172 (46), 143 (18), 115 (15), 77 (14), 60 (11), 57 (15), 44 (100); HRMS calcd for $C_{36}H_{34}O_2$: 498.25533; found: 498.255415.

H_8-binaphthol based phosphoramidites 6

General procedure: Diol **3** or **4** (2.1 mmol) and $(Me_2N)_3P$ (0.6 mL, 3.2 mmol) were dissolved in toluene (20 mL) and refluxed for 16 h (for ligand **6c** and **6h** a catalytic amount of NH_4Cl was added). The solvent was removed and the residue was purified by crystallization in diethyl ether or by column chromatography (eluent: ethyl acetate/*n*-hexane).



6

6b: Yield: 95%; m.p.: 191–194°C; $[\alpha]_D^{22}=433.9$ ($c=0.14$, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.32$ (brs, 1H), 7.27 (brs, 1H; 4-H, 4′-H), 2.85–2.68 (m, 4H; 5-H, 5′-H), 2.61–2.44 (m, 2H), 2.29–2.12 (m, 2H; 8-H, 8′-H), 2.50 (d, $^3J_{P,H}=9.4$ Hz, 6H; N-$(CH_3)_2$), 1.81–1.67 (m, 6H), 1.60–1.45 ppm (m, 2H; 6-H, 6′-H, 7-H, 7′-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=145.3$, 145.2 (d, $J_{P,C}=2.8$ Hz, C2, C2′), 137.3 (d, $J_{P,C}=1.8$ Hz), 136.9, 135.5 (d, $J_{P,C}=1.3$ Hz), 134.5 (C4a, C4a′, C8a, C8a′), 132.6 (2) (C4, C4′), 130.7 (d, $J_{P,C}=4.5$ Hz), 129.5 (d, $J_{P,C}=1.8$ Hz, C1, C1′), 113.0 (d, $J_{P,C}=3.0$ Hz), 112.6 (C3, C3′), 35.3 (d, $J_{P,C}=21.0$ Hz, $N(CH_3)_2$), 28.9, 28.8 (C5, C5′), 27.6, 27.4 (C8, C8′), 22.5, 22.4, 22.4, 22.2 ppm (C6, C6′, C7, C7′); ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta=141.4$ ppm; IR (KBr): $\tilde{\nu}=2926$ m, 2857 w, 2838 w, 2803 w, 1479 w, 1419 s, 1387 m, 1353 w, 1292 m, 1245 m, 1233 m, 1188 m, 1061 m, 1015 m, 979 m, 970 m, 944 s, 910 w, 877 w, 863 m, 810 s, 717 w, 693 m, 667 m, 657 cm^{-1} 1; MS (ESI): *m/z* (%): 525 (100) [M^+], 482 (77), 446 (25), 401 (45), 383 (5), 322 (10), 298 (5), 247 (7), 202 (10), 189 (6), 82 (6), 60 (4), 44 (7); HRMS calcd for $C_{22}H_{24}Br_2NO_2P$: 522.99114; found: 522.99059.

6c: Yield: 47% (off-white foam); $R_f=0.81$ (ethyl acetate/*n*-hexane 1:2); $[\alpha]_D^{22}=322.2$ ($c=0.46$, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.59$–7.48 (m, 4H; *m*-,*m*′-C_6H_4), 7.12 (brs, 1H), 7.09 (brs, 1H; 4-H, 4′-H), 6.94–6.87 (m, 4H; *o*-C_6H_4, *o*′-C_6H_4), 3.82 (s, 3H; CH_3O), 3.81 (s, 3H; CH_3O), 2.89–2.81 (t, 4H; 5-H, 5′-H), 2.73–2.61 (m, 2H), 2.42–2.30 (m, 2H; 8-H, 8′-H), 1.91 (d, $J_{P,H}=9.4$ Hz, 6H; $N(CH_3)_2$), 1.87–1.77 (m, 6H), 1.72–1.56 ppm (m, 2H; 6-H, 6′-H, 7-H, 7′-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=158.5$, 158.4 (*p*-C_6H_4, *p*′-C_6H_4), 145.4, 144.7 (d, $J_{P,C}=1.3$ Hz, C2, C2′), 136.6 (d, $J_{P,C}=1.5$ Hz), 136.4 (C8a, C8a′), 133.6 (d, $J_{P,C}=1.2$ Hz), 133.1 (C4a, 4a′), 131.3 (d, $J_{P,C}=2.5$ Hz), 130.9 (C3, C3′), 130.7, 130.7 (*i*-C_6H_4, *i*′-C_6H_4), 130.7, 129.4 (C4, C4′), 130.6, 130.4 (*o*- C_6H_4, *o*′-C_6H_4), 130.4 (d, $J_{P,C}=4.5$ Hz), 129.9 (d, $J_{P,C}=1.3$ Hz, C1, C1′), 113.4, 113.3 (*m*-C_6H_4, *m*′-C_6H_4), 55.3, 55.2 (OCH_3), 34.3 (d, $J_{P,C}=20.0$ Hz, $N(CH_3)_2$), 29.3, 29.2 (C5, C5′), 27.8, 27.7 (C8, C8′), 23.0, 22.9, 22.9, 22.8 ppm (C6, C6′, C7, C7′); ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta=140.1$ ppm; IR (KBr): $\tilde{\nu}=2990$ w, 2930 m, 2837 m, 2799 w, 1609 m, 1578 w, 1515 s, 1450 m, 1434 m, 1399 m, 1287 m, 1247 s, 1197 m, 1179 s, 1135 m, 1111 w, 1065 w, 1035 m, 1001 w, 982 m, 943 m, 914 w, 877 w, 831 s, 777 m, 733 m, 733 m, 688 m, 598 w, 559 w, 527 cm^{-1} w; MS (ESI): *m/z* (%): 579 (68) [M^+], 536 (20), 457 (39), 422 (41), 283 (12), 262 (18), 246 (14), 172 (27), 83 (12), 77 (11), 71 (10), 57 (20), 44 (100); HRMS calcd for $C_{36}H_{38}NO_4P$: 579.25330; found: 579.253043.

6d: Yield: 99%; $R_f=0.8$ (ethyl acetate/*n*-hexane 1:4); $[\alpha]_D^{22}=376.4$ ($c=0.14$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.66$–7.56 (m, 4H; *o*-C_6H_5, *o*′-C_6H_5), 7.41–7.33 (m, 4H; *m*-C_6H_5, *m*′-C_6H_5), 7.31–7.23 (m, 2H; *p*-C_6H_5, *p*′-C_6H_5), 7.17 (brs, 1H), 7.13 (brs, 1H; 4-H, 4′-H), 2.90–2.85 ('t', 4H; 5-H, 5′-H), 2.78–2.64 (m, 2H), 2.46–2.34 (m, 2H; 8-H, 8′-H), 1.89 (d, $J_{P,H}=9.2$ Hz, 6H; $N(CH_3)_2$), 1.86–1.78 (m, 6H), 1.73–1.61 ppm (m, 2H; 6-H, 6′-H, 7-H, 7′-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=145.4$, 144.8 (d, $J_{P,C}=1.8$ Hz, C2, C2′), 138.3 (2) (*i*-C_6H_5, *i*′-C_6H_5), 137.0 (d, $J_{P,C}=1.3$ Hz), 137.0 (C8a, C8a′), 133.7 (d, $J_{P,C}=1.2$ Hz), 133.2 (C4a, C4a′), 131.8 (d, $J_{P,C}=2.5$ Hz), 130.9 (C3, C3′), 130.7, 129.6 (C4, C4′), 130.3 (d, $J_{P,C}=4.5$ Hz), 129.9 (d, $J_{P,C}=1.8$ Hz, C1, C1′), 129.7, 129.5, 127.9, 127.8 (*o*-C_6H_5, *o*′-C_6H_5, *m*-C_6H_5, *m*′-C_6H_5), 126.7, 126.6 (*p*-C_6H_5, *p*′-C_6H_5), 34.2 (d, $J_{P,C}=20.0$ Hz, $N(CH_3)_2$), 29.3, 29.2 (C5, C5′), 27.8, 27.7 (C8, C8′), 23.0, 22.9, 22.9, 22.7 ppm (C6, C6′, C7, C7′); ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta=140.6$ ppm; IR (KBr): $\tilde{\nu}=3428$ w, 3056 w, 3019 w, 2921 s, 2856 m, 2794 w, 1602 w, 1579 w, 1559 w, 1499 m, 1481 w, 1449 s, 1412 s, 1396 m, 1349 w, 1289 m, 1230 s, 1198 s, 1156 m, 1135 w, 1066 m, 1006 m, 981 s, 943 s, 911 w, 877 w, 830 s, 783 s, 757 s, 744 m, 698 s, 676 m, 642 w, 629 w, 599 m, 560 w, 511 w, 486 cm^{-1} w; MS (EI): *m/z* (%): 519 (100) [M^+], 475 (28), 399 (2), 371 (2), 279 (5), 216 (11), 193 (2), 167 (8), 149 (21), 113 (2), 91 (1), 57 (2); HRMS calcd for $C_{34}H_{34}NO_2P$: 519.23217; found: 519.232218.

6e: Yield: 82%; $[\alpha]_D^{22}=343.3$ ($c=0.14$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=8.09$ (d, $J=1.3$ Hz, 1H), 8.02 (d, $J=1.5$ Hz, 1H), 7.87–7.81 (m, 7H), 7.74 (dd, $J=8.5$ Hz, 1.8 Hz, 1H), 7.48–7.41 (m, 4H; $C_{10}H_7$), 7.30 (brs, 1H), 7.25 (brs, 1H; 4-H, 4′-H), 2.97–2.86 (m, 4H; 5-H, 5′-H), 2.80–2.71 (m, 2H), 2.51–2.43 (m, 2H; 8-H, 8′-H), 1.91–1.84 (m, 6H), 1.75–1.66 (m, 2H; 6-H, 6′-H, 7-H, 7′-H), 1.81 ppm (d, $J_{P,H}=9.2$ Hz, 6H; $N(CH_3)_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=145.7$, 145.0 (d, $J_{P,C}=1.3$ Hz, C2, C2′), 137.3 (d, $J_{P,C}=1.3$ Hz), 137.2 (C8a, C8a′), 136.0, 136.0, 133.4 (2), 132.3, 132.2 (C_q, $C_{10}H_7$), 133.8 (d, $J_{P,C}=1.5$ Hz), 133.3 (C4a, C4a′), 131.8 (d, $J_{P,C}=2.5$ Hz), 130.8 (C3, C3′), 130.8, 130.0 (C4, C4′), 130.4 (d, $J_{P,C}=4.5$ Hz), 130.1 (d, $J_{P,C}=1.5$ Hz, C1, C1′), 128.3 (d, $J_{P,C}=2.7$ Hz), 128.3 (d, $J_{P,C}=3.7$ Hz), 128.2, 128.2, 128.1, 127.9, 127.5, 127.5, 127.2, 127.1, 125.8, 125.7, 125.6, 125.6 (CH, $C_{10}H_7$), 34.3 (d, $J_{P,C}=20.2$ Hz, $N(CH_3)_2$), 29.3, 29.3 (C5, C5′), 27.8, 27.0 (C8, C8′), 23.0, 22.9, 22.9, 22.8 ppm (C6, C6′, C7, C7′); ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta=140.6$ ppm; IR (KBr): $\tilde{\nu}=3432$ s, 3052 m, 2929 s, 2856 m, 2798 w, 2284 w, 1630 m, 1600 w, 1559 w, 1506 m, 1479 w, 1448 m, 1414 m, 1337 w, 1290 m, 1270 w, 1230 s, 1190 m, 1148 m, 1119 m, 1065 m, 1020 w, 984 m, 975 s, 959 m, 938 s, 907 m, 887 m, 856 m, 844 m, 818 s, 807 s, 779 s, 745 s, 695 s, 677 m, 592 m, 501 w, 477 s, 418 cm^{-1} w; MS (EI): *m/z* (%): 619 (100) [M^+], 576 (44), 499 (3), 439 (3), 346 (3), 266 (20), 228 (4), 141 (4), 84 (3), 44 (6); HRMS calcd for $C_{42}H_{38}NO_2P$: 619.26347; found: 619.263289.

6f: Yield: 80%; $R_f=0.88$ (ethyl acetate/*n*-hexane 1:4); m.p.: 205–207°C; $[\alpha]_D^{22}=219.9$ ($c=0.1$, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=6.90$ (brs, 2H), 6.87 (brs, 3H), 6.80 (s, 1H; 4-H, 4′-H, 2-C_6H_2), 2.85–2.61 (m, 6H), 2.40–2.20 (m, 2H; 5-H, 5′-H, 8-H, 8′-H), 2.30 (s, 3H), 2.28 (s, 6H), 2.15 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H; 6-CH_3), 2.11 (d, $J_{P,H}=9.0$ Hz, 6H; N-$(CH_3)_2$), 1.88–1.62 ppm (m, 8H; 6-H, 6′-H, 7-H, 7′-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta=146.1$ (d, $J_{P,C}=1.0$ Hz), 145.4 (d, $J_{P,C}=4.0$ Hz) (C2, C2′), 138.0, 137.0, 136.5, 136.0, 135.9 (*o*-C_6H_2, *o*′-C_6H_2, *p*-C_6H_2, *p*′-C_6H_2), 136.1 (d, $J_{P,C}=1.5$ Hz), 135.7 (d, $J_{P,C}=0.8$ Hz, C8a, C8a′), 135.1, 135.0 (C9, C9′), 134.5, 133.3 (d, $J_{P,C}=1.0$ Hz, C4a, C4a′), 131.3, 130.3 (C4, C4′), 130.4 (d, $J_{P,C}=2.5$ Hz), 130.1 (d, $J_{P,C}=5.0$ Hz), 128.8 (d, $J_{P,C}=2.3$ Hz), 128.8 (C1, C1′, C3, C3′), 128.1, 128.0 (2), 127.5 (*m*-C_6H_2, *m*′-C_6H_2), 35.1 (d, $J_{P,C}=19.7$ Hz, $N(CH_3)_2$), 29.3, 29.2 (C5, C5′), 27.9, 27.5 (C8, C8′), 23.2, 23.1, 23.0, 22.9 (C6, C6′, C7, C7′), 21.4 (*p*-CH_3, *p*′-CH_3), 21.1, 20.9, 20.6, 20.3 ppm (*o*-CH_3, *o*′-CH_3); ^{31}P NMR (202.5 MHz, $CDCl_3$): $\delta=138.7$; IR (KBr): $\tilde{\nu}=3530$ w, 2998 w, 2922 m, 2856 w, 1611 w, 1572 w, 1448 m, 1435 m, 1418 m, 1375 w, 1354 w, 1283 w, 1230 m, 1198 m, 1132 w, 1064 w, 1002 w, 980 m, 957 w, 937 s, 914 w, 879 w, 848 m, 829 s, 784 s, 741 m, 700 s, 685 cm^{-1} s; MS (EI): *m/z* (%): 603 (21) [M^+], 558 (9), 530 (19), 512 (100), 455 (2), 349 (1), 302 (5), 247 (2), 149 (6), 83 (2), 44 (3); HRMS calcd for $C_{40}H_{46}NO_2P$: 603.325887; found: 603.32607.

6g: Yield: 80%; m.p.: 185–188°C; $[\alpha]_D^{22}=323.9$ ($c=0.14$, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.63$–7.58 (m, 2H), 7.55–7.51 (m, 2H; *o*-C_6H_4, *o*′-C_6H_4), 7.13 (brs, 1H), 7.10 (brs, 1H; 4-H, 4′-H), 7.10–7.03 (m, 4H; *m*-C_6H_4, *m*′-C_6H_4), 2.92–2.81 (m, 4H; 5-H, 5′-H), 2.74–2.64 (m, 2H), 2.43–2.33 (m, 2H; 8-H, 8′-H), 1.93 (d, $J_{P,H}=9.1$ Hz, 6H; $N(CH_3)_2$), 1.88–1.78 (m, 6H), 1.70–1.62 ppm (m, 2H; 6-H, 6′-H, 7-H, 7′-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta=162.0$ (d, $J_{F,C}=246$ Hz), 161.9 (d, $J_{F,C}=246$ Hz, *p*-C_6H_4, *p*′-C_6H_4), 145.4, 144.7 (d, $J_{P,C}=2.0$ Hz, C2, C2′), 137.2 (d, $J_{P,C}=1.5$ Hz), 137.1 (C8a, C8a′), 134.4 (d, $J_{P,C}=3.2$ Hz), 134.2 (d, $J_{P,C}=3.2$ Hz, *i*-C_6H_4, *i*′-C_6H_4), 133.8 (d, $J_{P,C}=1.0$ Hz), 133.3 (C4a, C4a′), 131.2 (dd, $J_{F,C}=7.8$ Hz, $J_{P,C}=3.2$ Hz), 131.0 (d, $J_{F,C}=7.8$ Hz, *o*-C_6H_4, *o*′-C_6H_4), 130.8 (d, $J_{P,C}=2.5$ Hz), 129.8 (C3, C3′), 130.5, 129.5 (C4, C4′), 130.3 (d, $J_{P,C}=4.5$ Hz), 129.9 (d, $J_{P,C}=1.5$ Hz, C1, C1′), 114.9 (d, $J_{F,C}=21.1$ Hz), 114.7 (d, $J_{F,C}=21.1$ Hz, *m*-C_6H_4, *m*′-C_6H_4), 34.3 (d, $J_{P,C}=20.2$ Hz, $N(CH_3)_2$), 29.3, 29.2 (C5, C5′), 27.8, 27.7 (C8, C8′), 22.9, 22.8, 22.8, 22.7 ppm (C6, C6′, C7, C7′); ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta=140.2$ ppm; IR (KBr): $\tilde{\nu}=3041$

w, 3002 w, 2929 m, 2884 w, 2855 w, 2839 w, 2796 w, 1906 w, 1883 w, 1782 w, 1666 w, 1601 w, 1511 s, 1448 m, 1432 m, 1394 m, 1347 w, 1289 m, 1226 s, 1195 m, 1155 m, 1095 w, 1065 w, 1005 w, 977 m, 943 s, 913 w, 897 w, 871 w, 843 m, 822 s, 798 m, 776 s, 746 w, 735 m, 726 w, 690 cm^{-1} s; MS (EI): *m*/*z* (%): 555 (100) [M^+], 512 (56), 494 (8), 464 (5), 436 (3), 407 (3), 314 (2), 257 (5), 234 (13), 211 (2), 149 (6), 109 (2), 44 (6); HRMS calcd for $C_{34}H_{32}O_2F_2PN$: 555.21387; found: 555.21332; Anal.: calcd (%) for $C_{34}H_{32}O_2F_2PN$: C 73.50, H 5.81, N 2.52, found: C 73.29, H 5.81, N 2.39.

6h: Yield: 27%; R_f=0.83 (ethyl acetate/*n*-hexane 1:4); $[\alpha]_D^{22}$=369.9 (*c*=0.1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.61–7.59 (m, 2H), 7.56–7.53 (m, 2H), 7.42 (m, 4H; 2-C_6H_4), 7.16 (br s, 1H), 7.13 (br s, 1H; 4-H, 4′-H), 6.72 (dd, ^3J=17.7 Hz, 11.0 Hz, 2H; 2C*H*=CH_2), 5.76 (dd, ^3J=17.7 Hz, ^2J=1.0 Hz, 1H), 5.75 (dd, ^3J=17.7 Hz, ^2J=1.0 Hz, 1H), 5.23 (dd, ^3J=11.0 Hz, ^2J=1.0 Hz, 1H), 5.22 (dd, ^3J=11.0 Hz, ^2J=1.0 Hz, 1H; 2-CH=CH_2), 2.92–2.80 (m, 4H; 5-H, 5′-H), 2.73–2.64 (m, 2H), 2.43–2.36 (m, 2H; 8-H, 8′-H), 1.90 (d, $J_{P,H}$=9.5 Hz, 6H; $N(CH_3)_2$), 1.86–1.77 (m, 6H), 1.70–1.61 ppm (m, 2H; 6-H, 6′-H, 7-H, 7′-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=145.5, 144.8 (d, $J_{P,C}$=1.3 Hz, C2, C2′), 137.9, 137.9 (*i*- C_6H_4, *i*′-C_6H_4), 137.1 (d, $J_{P,C}$=1.9 Hz), 137.1 (C8a, C8a′), 136.7, 136.7 (2*C*H=CH_2), 135.9, 135.8 (*p*-C_6H_4, *p*′-C_6H_4), 133.7 (d, $J_{P,C}$=1.3 Hz), 133.3 (C4a, C4a′), 131.4 (d, $J_{P,C}$=2.5 Hz), 130.5 (C3, C3′), 130.4 (d, $J_{P,C}$=5.0 Hz), 130.0 (d, $J_{P,C}$=1.5 Hz) (C1, C1′), 130.4, 129.5 (C4, C4′), 129.8 (d, $J_{P,C}$=3.2 Hz), 129.6 (*o*-C_6H_4, *o*′-C_6H_4), 125.9, 125.8 (*m*-C_6H_4,*m*′-C_6H_4), 113.5, 113.4 (2CH=CH_2), 34.3 (d, $J_{P,C}$=20.0 Hz, $N(CH_3)_2$), 29.3, 29.2 (C5, C5′), 27.8, 27.7 (C8, C8′), 23.0, 22.9, 22.8, 22.7 ppm (C6, C6′, C7, C7′); ^{31}P NMR (121.5 MHz, $CDCl_3$): δ=140.1 ppm; IR (KBr): $\tilde{\nu}$=3440 w, 3080 w, 3007 w, 2925 s, 2852 m, 2790 w, 1908 w, 1628 m, 1607 w, 1551 w, 1513 m, 1495 m, 1481 w, 1448 m, 1433 w, 1391 m, 1350 w, 1312 w, 1290 m, 1253 w, 1229 m, 1198 m, 1186 m, 1156 m, 1135 w, 1116 w, 1065 m, 1030 w, 1017 w, 1003 m, 983 s, 943 s, 907 m, 879 w, 843 s, 831 s, 776 s, 755 m, 730 m, 689 s, 596 w, 556 w, 504 w, 482 w, 451 w, 401 cm^{-1} w; MS (EI): *m*/*z* (%): 571 (100) [M^+], 528 (38), 510 (13), 263 (17), 242 (17), 97 (11), 83 (12), 69 (15), 55 (17); HRMS calcd for $C_{38}H_{38}NO_2P$: 571.26347; found: 571.263825.

6i: (*S*)-3,3′-Dibromo-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol **3** (2 g, 4.4 mmol), NEt_3 (7 mL, 4.8 mmol) and $(Et_2N)PCl_2$ (0.65 mL, 4.4 mmol) were dissolved in toluene (20 mL) and refluxed for 16 h. The solvent was removed and the sticky residue was purified by flash column chromatography (eluent: ethyl acetate: *n*-hexane 1:4). Yield: 60%; R_f=0.78 (ethyl acetate/*n*-hexane 1:4); m.p.: 153–157°C; $[\alpha]_D^{22}$=−363.9 (*c*=0.15, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.33 (br s, 1H), 7.28 (br s, 1H; 4-H, 4′-H), 3.06–2.83 (m, 4H; 2NCH_2), 2.78–2.68 (m, 4H; 5-H, 5′-H), 2.59–2.42 (m, 2H), 2.27–2.07 (m, 2H; 8-H, 8′-H), 1.78–1.66 (m, 6H), 1.58–1.41 (m, 2H; 6-H, 6′-H, 7-H, 7′-H), 1.06 ppm (t, *J*=7.1 Hz, 6H; 2CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=145.5 (d, $J_{P,C}$=3.2 Hz), 145.2 (C2, C2′), 137.1 (d, $J_{P,C}$=1.6 Hz), 136.7, 135.2 (d, $J_{P,C}$=1.5 Hz), 133.9 (C4a, C4a′, C8a, C8a′), 132.4 (2) (C4, C4′), 130.6 (d, $J_{P,C}$=5.0 Hz), 128.9 (d, $J_{P,C}$=2.0 Hz, C1, C1′), 113.1 (d, $J_{P,C}$=2.8 Hz), 112.6 (C3, C3′), 38.8 (d, $J_{P,C}$=22.0 Hz, NCH_2), 28.8, 28.7 (C5, C5′), 27.6, 27.3 (C8, C8′), 22.5, 22.4, 22.4, 22.2 (C6, C6′, C7, C7′), 14.9 ppm (d, $J_{P,C}$=3.5 Hz, CH_3); ^{31}P NMR (121.5 MHz, $CDCl_3$): δ=142.3 ppm; IR (KBr): $\tilde{\nu}$=2976 w, 2928 m, 2865 w, 1685 w, 1575 w, 1419 m, 1379 m, 1353 w, 1245 m, 1205 m, 1172 m, 1065 w, 1015 m, 940 m, 921 w, 864 m, 808 s, 784 m, 746 s, 718 w, 659 cm^{-1} m; MS (EI): *m*/*z* (%): 553 (17) [M^+], 538 (50), 510 (5), 481 (64), 401 (11), 371 (5), 282 (12), 274 (11), 255 (7), 246 (8), 231 (10), 215 ′(15), 202 (14), 189 (12), 104 (11), 86 (33), 72 (100), 58 (72), 44 (32); HRMS calcd for $C_{24}H_{28}Br_2O_2PN$: 551.02244; found: 551.02189; Anal.: calcd (%) for $C_{24}H_{28}Br_2O_2PN$: C 52.10, H 5.10, Br 28.88, N 2.53; found: C 51.88, H 5.10, Br 30.1, N 2.36.

Hydrogenation experiments

In a typical experiment, a solution of the α-dehydroamino acid precursors **7** (0.25 mmol) in 1.0 mL solvent was transferred through a syringe into an autoclave charged with argon. The catalyst was generated in situ by stirring $[\{Ir(cod)Cl\}_2]$ (5 μmol) and the corresponding ligand (10 μmol) in solvent (1.0 mL) for a period of 10 min and afterwards transferring the solution through a syringe into the autoclave. Then, the autoclave was charged with hydrogen at the required pressure and stirred at 25°C. After the predetermined time, the hydrogen was released and the reaction mixture was analysed.

Hydrogenation experiments were performed at normal pressure at 25°C as follows: A mixture of $[\{Ir(cod)Cl\}_2]$ (0.02 mmol), ligand **6** (0.04 mmol), and methyl α-acetamidocinnamate **7** (1 mmol) was stirred for 10 min in solvent (10 mL). The hydrogenation flask was flushed several times with hydrogen. The solution was transferred to the reaction vessel and the progress was followed by a volumetric measurement at 25°C ±0.5°C.

Crystal structure analysis

Diffraction data were collected on a STOE-IPDS diffractometer. The structures were solved by direct methods (G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997) and refined by full-matrix least-squares techniques on F^2 (G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997). XP (BRUKER AXS) was used for graphical representations. All non-hydrogen atoms except the atoms of the disordered parts were refined anisotropically. H atoms were included at calculated positions and refined by using the riding model.

X-ray crystal structure analysis of **6b**: crystal dimensions 0.50×0.35×0.10 mm^3, monoclinic, space group $P2_1$, *a*=9.4482(6), *b*=7.7201(3), *c*=15.4135(9) Å, β=107.769(5)°,*V*=1070.6(1) $Å^3$, *Z*=2, ρ_{calcd}=1.629 $g\,cm^{-3}$, $Mo_{K\alpha}$ radiation λ=0.71073 Å, *T*=200(2) K, 2θ_{max}=52.00°, 15333 reflections measured, 4120 were independent of symmetry of which 3623 were observed, absorption correction: numerical (μ=3.879 mm^{-1}, min/max transmission=0.2706/0.7779, *R*1(*I*> 2σ(*I*))=0.0292, *wR*2 (all data)=0.0555, min/max residual electron density −0.280/0.452 e $Å^{-3}$, 252 parameters. The absolute configuration was determined by the Flack parameter *x*=0.006(7).

X-ray crystal structure analysis of **6g**: crystal dimensions 0.40×0.35×0.20 mm^3, orthorhombic, space group $P2_12_12_1$, *a*=10.246(2), *b*=14.635(3), *c*=18.655(4) Å, *V*=2797.5(10) $Å^3$, *Z*=4, ρ_{calcd}=1.319 $g\,cm^{-3}$, $Mo_{K\alpha}$ radiation λ=0.71073 Å, *T*=200(2) K, 2θ_{max}=52.00°, 39768 reflections measured, 5495 were independent of symmetry, of which 3657 were observed, μ=0.144 mm^{-1}, *R*1(I> 2σ(*I*))=0.0386, *wR*2 (all data)=0.0707, min/max residual electron density −0.255/0.225 e $Å^{-3}$, 360 parameters, Flack parameter, *x*=−0.01(10). The absolute configuration corresponds to the known chirality of the starting compound.

CCDC 670284 and 670285 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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