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Electronic and steric effects of ligands as control elements for rhodium-catalyzed asymmetric hydroformylation. Part 3: Highly active hydroformylation of styrene☆

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Abstract—The electronic and steric effects in the rhodium diphosphinite catalyzed asymmetric hydroformylation were investigated. Phosphinite basicity was varied by using 4-CH_3, 4-CF_3, 3,5-$(CH_3)_2$ and 3,5-$(CF_3)_2$ substituents on the diphenylphosphine moieties. Two series of ligands based on (*S*)-BINOL and (*S*)-H_8-BINOL were synthesized. In the hydroformylation of styrene an increase in *l*:*b* ratio, in activity and in enantioselectivity was observed with decreasing phosphinite basicity.

1. Introduction

Asymmetric catalytic hydroformylation is one of the most efficient functionalizations of the C=C-double bond and a convenient method for preparing a wide range of enantiomerically pure compounds.[2] The precise control of molecular chirality plays an increasing role in chemistry, life science and material science. High activity, selectivity and stability, readily accessible ligands and enzyme-like stereocontrol are among the characteristic features of an ideal catalyst for practical asymmetric synthesis.[2] Two important factors control the activity and selectivity of transition metal catalyst modified by phosphorus containing ligands: steric and electronic effects.

We and others have recently reported that the performance of enantioselective catalysts in hydrogenation,[1,3] hydrocyanation,[4] diethyl zinc addition,[5] epoxidation[6] and hydroformylation,[7] can be boosted by appropriate electronic tuning of the chiral ligand. Electronic and steric effects in the rhodium diphosphinite catalyzed asymmetric hydrogenation were investigated. A series of electronically and sterically modified (*S*)-BINOL and (*S*)-H_8-BINOL ligands was synthesized and the effects on the catalytic performance studied. Phosphinite basicity was varied by using *p*-CH_3O, *p*-CH_3, *p*-H, *p*-CF_3, 3,5-$(CH_3)_2$ and 3,5-$(CF_3)_2$ substituents on the diphenylphosphine moieties.[1] In the hydrogenation of dimethyl itaconate and methyl (*Z*)-α-acetamidocinnamate, an increase in enantioselectivity and activity was observed with increasing phosphinite basicity. Thus, electronic tuning of the ligands offers a unique chance to improve the selectivity of such reactions.

Moser et al. investigated the electronic effect by the modification of *p*-substituents in triphenylphosphine.[8] Bidentate phosphines of different basicities were studied by Unruh and Christenson.[9] Both studies showed that decreasing phosphine basicity gives an increase both in *l*:*b* ratio and in activity. Chan et al. reported a highly regioselective system based on the use of a rhodium catalyst modified by a perfluoro analogue of dppe (1,2-bis(diphenylphosphino)ethane).[10] This catalyst gave much higher branched/linear product ratios in hydroformylation than the catalyst modified by dppe. Recently, RajanBabu and Ayers studied the electronic

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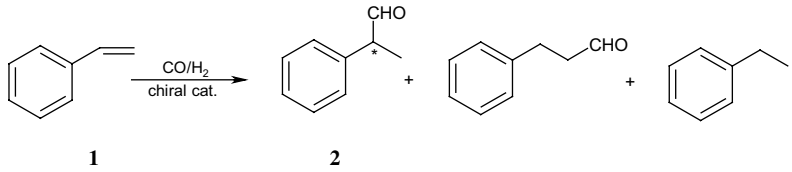


Scheme 1. Asymmetric catalytic hydroformylation of styrene.

effects of rhodium diphosphinites on the enantioselectivity of the hydroformylation of vinylarenes and found that substitution of electron-withdrawing aryl groups on phosphorus increased enantioselectivity for the rhodium catalyst.[7] Casey et al. developed the concept of a natural bite angle[11] and demonstrated its pronounced effect on the selectivity of hydroformylation. Leeuwen et al. reconsidered the mechanistic explanations of the effect of the natural bite angle on regioselectivity.[12]

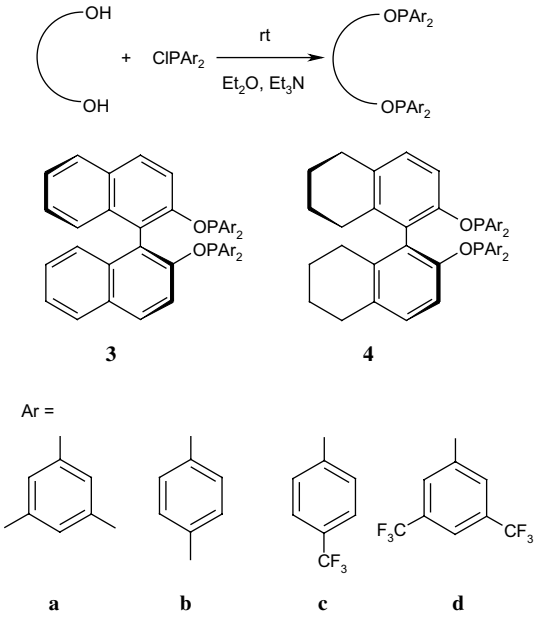
Herein we report bidentate phosphinites as new ligands for the enantioselective hydroformylation of styrene with unprecedented high activity (Scheme 1). The electron-donating property of the diphosphinites is modulated by substituents at the aryl *para* or *meta* position.

2. Results and discussion

Novel ligands **3** and **4** were readily prepared by the reaction of enantiomerically pure (*S*)-BINOL (BINOL = 1,1′-bi-2-naphthol) or (*S*)-H_8-BINOL (H_8-BINOL = 5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-bi-2-naphthol) with the corresponding chlorodiarylphosphine in the presence of triethylamine (Scheme 2). (*S*)-H_8-BINOL can be readily derived from BINOL using the protocol of Cram et al.[13] Chan et al. prepared chiral diphosphinites **3**, **4** (Ar = Ph), **3a** and **4a**. Rhodium complexes of these ligands were investigated in the asymmetric hydrogenation of α-dehydroamino acid derivatives.[14] Parent diphosphinite **3** (Ar = Ph) has previously been used for the copolymerization of ethylene and carbon monoxide.[14]

The precatalysts were prepared by the reaction of phosphinites with $[Rh(acac)_2(CO)_2]$ in toluene (ligand to Rh molar ratio was generally 2:1). The catalysis was carried out under typical hydroformylation conditions, 30 bar of *syn* gas (CO/H_2 = 1:1). In order to obtain comparable results 1 h reaction time was chosen. Phosphinites **3** and **4** were tested in the Rh-catalyzed hydroformylation of styrene.

Consistent with the literature,[15] both the catalytic activity and selectivity to 3-phenylpropanal increased when increasing the temperature. The temperature dependency of the catalytic systems with **3d** and **4d** provided an extraordinary variation in the enantioselectivity (Table 1). When the reaction temperature was increased from 24 to 60 °C, the enantiomeric excess was increased markedly from 27% to 50% (entries 5 and 2). Increasing the temperature further, decreased the ee. The best



Scheme 2. Synthesis of diphosphinite ligands.

results are achieved at an optimum temperature of around 60 °C without olefin hydrogenation and alcohol formation. This variation in enantioselectivity may be related with equilibrium between species before the rate determining step and attributed to the conformational change of the nine-membered chelate ring and strongly related to the chirality of the whole molecular framework. A less sensitive change was observed with **4**, which indicates that the dihedral angle in this structure having an H_8-BINOL based backbone possesses a more hindered axial flexibility. As expected, the formation of a linear aldehyde was enhanced by using a higher temperature.[16]

Under other wise identical conditions, both catalytic systems **3** and **4** gave excellent activities and moderate ee values (Table 2). An increase in the ee value was achieved by using a small excess of diphosphinite (P/Rh 4). The H_8-BINOL-based catalysts generally gave higher catalytic activities than the corresponding BINOL-based systems. Consistent with the literature,[15] the best results were achieved in solvents of medium polarity such as toluene.

A direct influence of the basicity of the ligand on the activity of the corresponding catalyst was observed. The activity was improved from a TOF 114 to 358 h^{-1} or from 380 to 566 h^{-1} when the methyl group at the *para* position was replaced by CF_3. On the other hand

Table 1. Enantioselective Rh-catalyzed hydroformylation of styrene **1**[a]

Entry	Ligand	Reaction temperature (°C)	Conv. (%)[b]	TOF[c]	*b*/*n* Ratio[b]	Ee[d] (%)
1	**3d**	80	85	1708 (2320)[e]	34/66	30 (*S*)
2	**3d**	60	62	1236	41/59	50 (*S*)
3	**3d**	50	38	760	48/52	42 (*S*)
4	**3d**	40	20	400	54/46	39 (*S*)
5[f]	**3d**	24	6	64	63/37	27 (*S*)
6	**4d**	80	84	1686 (2360)[e]	36/64	13 (*S*)
7	**4d**	60	66	1310	37/63	30 (*S*)
8	**4d**	50	42	840	49/51	21 (*S*)
9	**4d**	40	24	480	53/47	17 (*S*)
10[f]	**4d**	24	12	123	57/43	16 (*S*)

[a] Reaction conditions: H_2 and CO (1:1) at 30 bar initial total pressure, reaction time 1 h. Catalyst: 0.0125 mmol [Rh(acac)$(CO)_2$], and 0.025 chiral ligand in 4 mL toluene, substr/catalyst molar ratio is 2000.
[b] For determination see Section 4.
[c] Amount of RCHO in mol (mol Rh)$^{-1}$ h^{-1} determined at 1 h.
[d] Determined by GC analysis of the distilled product (β-DEX 225, 30 m, id 0.25 mm, 0.25 μm film).
[e] Amount of RCHO in mol (mol Rh)$^{-1}$ h^{-1} determined at 0.5 h.
[f] Reaction time 2 h and amount of RCHO in mol (mol Rh)$^{-1}$ h^{-1} determined at 2 h.

Table 2. Enantioselective Rh-catalyzed hydroformylation of styrene **1**[a]

Entry	Ligand	Solvent	Conv. (%)[b]	TOF[c]	*b*/*n* Ratio[b]	Ee[d] (%)
1	**3a**	Toluene	10	212	82/18	2 (*S*)
2	**3b**	Toluene	6	114	86/14	1 (*S*)
3[e]	**3b**	Toluene	1	20	77/23	2 (*S*)
4	**3c**	Toluene	18	358	79/21	3 (*S*)
5	**3d**	Toluene	62	1236 (1556)[f]	41/59	50 (*S*)
6[e]	**3d**	Toluene	59	1190	43/57	36 (*S*)
7	**4a**	Toluene	7	134	78/22	9 (*S*)
8	**4b**	Toluene	19	380	86/14	1 (*S*)
9[e]	**4b**	Toluene	7	131	78/22	4 (*S*)
10	**4c**	Toluene	28	566	73/27	3 (*S*)
11	**4d**	Toluene	66	1310 (1640)[f]	37/63	30 (*S*)
12	**4d**	Hexane	39	786	45/55	20 (*S*)
13	**4d**	EtOAc	51	1015	50/50	16 (*S*)
14[e]	**4d**	Toluene	60	1200	43/57	26 (*S*)
15	—	Toluene	4	88	82/18	—

[a] Reaction conditions: H_2 and CO (1:1) at 30 bar initial total pressure, $T = 60$ °C, reaction time 1 h. Catalyst: 0.0125 mmol [Rh(acac)$(CO)_2$] and 0.025 chiral ligand in 4 mL of solvent, substr/catalyst molar ratio is 2000.
[b] For determination see Section 4.
[c] Amount of RCHO in mol (mol Rh)$^{-1}$ h^{-1} determined at 1 h.
[d] Determined by GC analysis of the distilled product (β-DEX 225, 30 m, id 0.25 mm, 0.25 μm film).
[e] P/Rh 12.
[f] Amount of RCHO in mol (mol Rh)$^{-1}$ h^{-1} determined at 0.5 h.

the activity was improved dramatically from a TOF 212 to 1236 h^{-1} or from 134 to 1310 h^{-1} when the methyl groups at the *meta* positions were replaced by CF_3 groups. For comparison, additional information on the activity and selectivity of the catalyst formed was provided without using phosphinite (entry 15). The rate of hydroformylation increased in the order of **3b** < **3a** < **3c** < **3d** and **4a** < **4b** < **4c** < **4d**. With respect to the ligand effect, the most active catalysts proved to be **3d** and **4d**. In contrast, the lowest activity was provided by the unmodified catalyst. Table 2 shows that with the exception of ligand **3a**, the rate of the reaction increases with decreasing phosphinite basicity. The deviant behaviour of **3a** is still not clear. Comparison of the performances of ligands **4b** and **4c** is particularly revealing as the structural difference between these two compounds is minimal so that the electronic effect of the *para* substituents can be clearly identified. When **4a**–**d** (partially hydrogenated analogues of **3a**–**d**) were used as bisphosphinite ligands for the catalyst precursor, the activity and linearity of the catalysts were distinctly higher with **4** than with **3** (Table 2). This is consistent with previously observed trends in hydroformylation, which show that catalytic activity and linearity of the catalyst increases with the increase of the bite angle.[17]

To ascertain the electronic properties of ligands **3** and **4**, we prepared a series of compounds [Rh(**3** or **4**)(CO)Cl], as summarized in Table 3. The *cis*-[LRh(CO)Cl] complexes were readily formed from $[Rh(CO)_2Cl]_2$ and an excess of ligand (Fig. 1). The position of the *ν*CO in the IR spectrum of the *trans*-[P_2Rh(CO)Cl] complexes is known for a large variety of phosphines (and always in agreement with the expected σ-donor strength of

Table 3. IR data for (diphosphinite)Rh(CO)CL complexes

Entry	L	*v*CO *cis*-LRh(CO)Cl (cm^{-1})
1	**3a**	1990.5
2	**3b**	1988.9
3	**3c**	2001.8
4	**3d**	2003.8
5	**4a**	1987.5
6	**4b**	1988.7
7	**4c**	1999.5
8	**4d**	2003.6

IR spectra recorded as KBr discs.

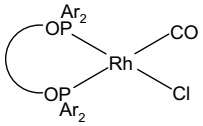


Figure 1. Structure of *cis*-LRh(CO)Cl complexes.

the phosphine).[18] A regular shift towards higher wave numbers with decreasing diphosphinite basicity is exhibited. The lower electron density on metal leads to a decrease in back-bonding from rhodium to the carbonyl ligand, and hence, higher CO stretching frequencies being observed.

As can be seen from Table 3, the position of *v*CO for the eight ligands exhibits the expected donor ability trend, and are ordered on a decreasing basicity **3a** > **3c** > **3d**; **4a** > **4b** > **4c** > **4d**, respectively. The measured stretching frequencies span a range of 13.3 and 16.1 cm^{-1} for (*S*)-BINOL and (*S*)-H_8-BINOL, respectively. Another trend observed by comparison of the two series is a slight but regular shift to lower wave numbers for (*S*)-H_8-BINOL based system [1990.5 (**3a**) vs 1987.5 cm^{-1} (**4a**), 1988.7 (**4b**) vs 1988.9 cm^{-1} (**3b**), 1999.5 (**4c**) vs 2001.8 cm^{-1} (**3c**), 2003.6 (**4d**) vs 2003.8 cm^{-1} (**3d**)].

It is noteworthy that for all diphosphinite ligands, the formation of the (diphosphinite)Rh(COD)]BF_4 complexes was evidenced by the appearance of a doublet in their ^{31}P NMR spectra. NMR spectroscopic analysis showed that complexes with two coordinated phosphorus at the *cis* positions were formed. We found that decreasing the phosphinite basicity gave an increase in the rhodium/phosphorus ^1J(Rh,P) coupling constants and an increase in the coordination shifts (δP for complex−δP for free ligand).[1] Unlike the other parameters, the chemical shift values for the [(diphosphinite)-Rh(COD)]BF_4 complexes were very similar.

Decreasing the phosphinite basicity enhanced the electrophilicity of the rhodium centre and the CO dissociation rate from (diphosphinite)$Rh(CO)_2H$ and as a consequence, facilitated alkene coordination to form a (diphosphinite)Rh(CO)H(alkene) complex. The second consequence is the higher reactivity of the rhodium alkyl species toward CO dissociation and β-elimination leading to an increase in *l*:*b* ratio (**3a** vs **3d**, **3b** vs **3c**; **4a** vs **4d**, **4b** vs **4c**). In this context it should be noted that electron-withdrawing groups have a negative impact on the regioselectivity of the asymmetric hydroformylation.

The partially hydrogenated (*S*)-H_8-BINOL based phosphinites **4** are slightly better σ-donors than the corresponding (*S*)-BINOL analogous. Surprisingly, an unexpected electronic effect of (*S*)-H_8-BINOL based phosphinites was observed for the linearity of the catalytic system.[8,9,11] The selectivities for linear aldehydes were higher (in one case equal) with (*S*)-H_8-BINOL based phosphinites, than with the corresponding (*S*)-BINOL analogous. This can be attributed to the larger bite angle of the (*S*)-H_8-BINOL based phosphinites **4**.

Detailed reasoning for the correlation between enantioselectivity and electron-withdrawing aryl substituents (Table 2) remains speculative because the relative rates of many of the fundamental steps and the structures of the intermediates still remain largely unknown.

It has been reported that Ir(I)- and Ru(II)-complexes of H_8-BINAP served as more effective catalyst precursors for the asymmetric hydrogenation of some substrates, than the analogous complexes of BINAP.[19] Furthermore, the Pd(II) complex of (*R*,*S*)-H_8-BINAPHOS was a more active catalyst when compared to that of (*R*,*S*)-BINAPHOS for alternating copolymerization of propene with carbon monoxide.[20] The dihedral angles in these structures suggest that ligands having an H_8-BINOL based backbone possess a quite different axial flexibility. Unfortunately, suitable crystals of the free ligands or its rhodium complexes for X-ray analysis could not be obtained.

3. Conclusion

A pronounced effect of diphosphinite basicity on the activity, regioselectivity and enantioselectivity in the rhodium-diphosphinite catalyzed asymmetric hydroformylation of styrene was observed. Increases in the enantioselectivity, activity and *l*:*b* ratio were observed when the aryl groups at the phosphorus were changed from electron-donating 4-tolyl to electron-deficient 4-trifluoromethylphenyl or from 3,5-dimethylphenyl to the more electron-deficient 3,5-bis(trifluoromethyl)phenyl.

4. Experimental

4.1. General techniques

All the reactions were carried out in oven-dried glasswork using Schlenk techniques under an argon atmosphere. $^{31}P\{^1H\}$ NMR spectra were recorded on either a VARIAN UNITY 300 spectrometer operating at 121.42 MHz or a Bruker DRX-500 spectrometer operating at 202.45 MHz. Chemical shifts are relative to external 85% H_3PO_4 with downfield values reported as positive. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 300.15 and at 75.43 MHz, respectively, on a VARIAN UNITY 300 spectrometer or at 500.13 and 125.76 MHz, respectively, on a Bruker DRX-500 spectrometer.

Chemical shifts are relative to tetramethylsilane as the external reference or calibrated against solvent resonances. ^{19}F–^{1}H NMR spectra were recorded on a VARIAN UNITY 300 spectrometer operating at 282.21 MHz. Chemical shifts are relative to CF_3Cl as the external reference. Infrared (IR) spectra were recorded on an AVATAR 330 FT-IR spectrometer. Optical rotations were measured on a Schmidt Haensch 21245 polarimeter using 10 cm cells. Gas chromatographic analyses were performed on a Hewlett–Packard 5830A gas chromatograph equipped with a flame ionization detector and an SPB-1 column (30 m, film thickness 0.1 μm, carrier gas 2 mL/min).

4.2. Materials and methods

Diethyl ether (Et_2O), tetrahydrofuran (THF), toluene and hexane were distilled from sodium benzophenone ketyl under argon. Methylene chloride (CH_2Cl_2) and triethylamine (Et_3N) were distilled from CaH_2. Deuterated chloroform and methylene chloride ($CDCl_3$ and CD_2Cl_2) were deoxygenated by distillation under argon. Chlorodiarylphosphines were prepared from dichloro (diethylamino)phosphine and a Grignard reagent followed by treatment of the resulting diarylaminophosphine with anhydrous HCl.[21] All the other chemicals were commercial products and were used as received without further purification.

4.2.1. (*S*)-2,2′-Bis{[di((3,5-dimethyl)phenyl)phosphinyl]-oxy}-1,1′-binaphthyl 3a. This compound has already been described by Chan and co-workers.[14] Yield: 0.5 g (10%), mp 140–142 °C; $[\alpha]_D^{20} = -6$ (*c* 1, CH_2Cl_2). $^{31}P\{^{1}H\}$ NMR (121.42 MHz, $CDCl_3$): $\delta = 111.26$ (s), ^{1}H NMR (300.15 MHz, $CDCl_3$): $\delta = 2.03$ (s, 12H, diast. CH_3), 2.05 (s, 12H, diast. CH_3), 6.63–6.75 (m, 8H) 7.13–7.50 (m, 12H), 7.71–7.82 (m, 4H); $^{13}C\{^{1}H\}$ NMR (125.76 MHz, $CDCl_3$): $\delta = 19.60$ (s, CH_3), 117.13 (s, C_3), 117.26 (s, C_3'), 120.23 (s, C_1, C_1'), 122.06 (s), 123.97 (s), 124.39 (s), 125.32 (d, $^{2}J(P,C) = 21.8$ Hz, diast. C_o), 125.72 (d, $^{2}J(P,C) = 24.2$ Hz, diast. C_o), 125.93 (s), 127.45 (s), 128.01 (s, C_5, C_5'), 128.80 (s, diast. C_p), 129.07 (s, diast. C_p), 132.27 (s, C_{10}, C_{10}'), 135.39 (br s, CH_3C), 139.29 (d, $^{1}J(P,C) = 16.9$ Hz, diast. C_i), 139.55 (d, $^{1}J(P,C) = 19.4$ Hz, diast. C_i), 150.96 (d, $^{2}J(P,C) = 7.2$ Hz, C_2), 151.00 (d, $^{2}J(P,C) = 4.8$ Hz, C_2'). Anal. Calcd for $C_{52}H_{48}O_2P_2$: C 81.44, H 6.30%. Found: C 81.15, H 6.30.

4.2.2. (*S*)-2,2′-Bis{[di((3,5-dimethyl)-phenyl)phosphinyl]-oxy}-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl 4a. This compound has already been described by Chan and co-workers.[14] Yield: 2.8 g (72%), mp 172 °C; $[\alpha]_D^{20} = -41$ (*c* 1, CH_2Cl_2). $^{31}P\{^{1}H\}$ NMR (121.42 MHz, $CDCl_3$): $\delta = 109.24$ (s), ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.60$ (m, 6H; CH_2), 1.72 (m, 2H, CH_2), 2.16 (s, 12H, diast. CH_3), 2.22 (m, 2H, ArCH_2, overlapped by the signal of CH_3), 2.24 (s, 12H, diast. CH_3), 2.45 (m, 2H, ArCH_2), 2.67 (m, 2H, ArCH_2), 2.78 (m, 2H, ArCH_2), 6.88 (s, 2H, diast. H_p), 6.93 (m, 12H, H_3, H_3', diast. H_o, diast. H_p), 7.01 (d, $^{3}J(H,H) = 8.8$ Hz, 2H, H_4, H_4'), $^{13}C\{^{1}H\}$ NMR (125.76 MHz, $CDCl_3$): $\delta = 21.92$ (s, diast. CH_3), 22.00 (s, diast. CH_3), 23.75 (s, CH_2), 23.84 (s, CH_2), 28.31 (s, ArCH_2), 30.27 (s, ArCH_2), 115.54 (br s, C_3), 115.66 (d, $^{3}J(P,C) = 2.4$ Hz, C_3'), 127.68 (d, $^{2}J(P,C) = 23.0$ Hz, diast. C_o), 127.97 (d, $^{2}J(P,C) = 24.2$ Hz, diast. C_o), 128.73 (s, C_1, C_1'), 129.30 (s, C_4, C_4'), 131.05 (s, diast. C_p), 131.22 (s, diast. C_p), 131.53 (s, C_5, C_5'), 137.22 (s, C_{10}, C_{10}'), 137.74 (d, $^{3}J(P,C) = 4.8$ Hz, diast. CH_3C), 137.80 (d, $^{3}J(P,C) = 4.8$ Hz, diast. CH_3C), 142.30 (br s, diast. C_i), 142.45 (br s, diast. C_i), 152.82 (br s, C_2), 152.88 (d, $^{2}J(P,C) = 4.9$ Hz, C_2'). Anal. Calcd for $C_{52}H_{56}O_2P_2$: C 80.59, H 7.28%. Found: C 80.78, H 7.59.

4.2.3. (*S*)-2,2′-Bis{[di(4-methylphenyl)phosphinyl]oxy}-1,1′-binaphthyl 3b. (*S*)-BINOL (5.2 mmol, 1.5 g) was dried azeotropically with toluene (3 × 30 mL), and the solvent then evaporated. To a solution of (*S*)-BINOL (5.2 mmol, 1.5 g) and Et_3N (11.8 mmol, 1.2 g, 1.6 mL) in Et_2O (40 mL) was added slowly a solution of bis(4-methylphenyl)chlorophosphine (11.5 mmol, 2.9 g) in Et_2O (20 mL) at ambient temperature. The reaction mixture was stirred for 1 h at ambient temperature. The suspension was filtered through a pad of Al_2O_3 and the pad washed with Et_2O (2 × 20 mL). The solvent was removed under reduced pressure to give the product as a white solid. Yield: 3.0 g (81%), mp 54–57 °C; $[\alpha]_D^{20} = -32.6$ (*c* 1, CH_2Cl_2). $^{31}P\{^{1}H\}$ NMR (121.42 MHz, $CDCl_3$): $\delta = 111.9$ (s), ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 2.20$ (s, 6H, diast. CH_3), 2.24 (s, 6H, diast. CH_3), 6.78–7.86 (m, 28H, aromatic protons), $^{13}C\{^{1}H\}$ NMR (125.76 MHz, $CDCl_3$): $\delta = 21.66$ (s, diast. CH_3), 21.70 (s, diast. CH_3), 119.28 (s, C_3), 119.40 (s, C_3'), 122.31 (s, C_1, C_1'), 124.00 (s), 125.98 (s), 126.31 (s), 127.78 (s), 128.73 (d, $^{3}J(P,C) = 7.3$ Hz, diast. C_m), 128.85 (d, $^{3}J(P,C) = 7.3$ Hz, diast. C_m), 129.26 (s), 129.82 (d, $^{2}J(P,C) = 24.2$ Hz, diast. C_o), 130.03 (s, C_5, C_5'), 130.21 (d, $^{2}J(P,C) = 24.2$ Hz, diast. C_o), 134.23 (s, C_{10}, C_{10}'), 138.23 (d, $^{1}J(P,C) = 9.7$ Hz, diast. C_i), 138.38 (d, $^{1}J(P,C) = 7.3$ Hz, diast. C_i), 138.72 (s, diast. CH_3C), 139.01 (s, diast. CH_3C), 152.89 (d, $^{2}J(P,C) = 14.5$ Hz, C_2), 152.96 (d, $^{2}J(P,C) = 12.1$ Hz, C_2'). Anal. Calcd for $C_{48}H_{40}O_2P_2$: C 81.11, H 5.67%. Found: C 80.86, H 5.41.

4.2.4. (*S*)-2,2′-Bis{[di(4-methylphenyl)phosphinyl]oxy}-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl 4b. This compound was prepared similar to **3b**. Yield: 2.4 g (65%), mp 53–55 °C; $[\alpha]_D^{20} = -43.5$ (*c* 1, CH_2Cl_2). $^{31}P\{^{1}H\}$ NMR (121.42 MHz, $CDCl_3$): $\delta = 108.48$ (s), ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.54$ (m, 4H, CH_2), 1.61 (m, 2H, CH_2), 1.70 (m, 2H, CH_2), 2.22 (td, $^{2}J(H,H) = 16.9$ Hz, $^{3}J(H,H) = 5.9$ Hz, 2H, ArCH_2), 2.31 (s, 6H, diast. CH_3), 2.34 (s, 6H, diast. CH_3), 2.38 (td, $^{2}J(H,H) = 16.9$ Hz, $^{3}J(H,H) = 6.6$ Hz, 2H, ArCH_2, overlapped by the signal of CH_3), 2.68 (td, $^{2}J(H,H) = 16.3$ Hz, $^{3}J(H,H) = 6.3$ Hz, 2H, ArCH_2), 2.78 (td, $^{2}J(H,H) = 16.3$ Hz, $^{3}J(H,H) = 6.6$ Hz, 2H, ArCH_2), 6.98 (d, $^{3}J(H,H) = 8.8$ Hz, 2H, H_3, H_3'), 7.00 (d, $^{3}J(H,H) = 7.5$ Hz, 4H, diast. H_m, overlapped by the signals of H_3, and H_3'), 7.04 (d, $^{3}J(H,H) = 7.5$ Hz, 4H, diast H_m, overlapped by the signals of H_4, and H_4'), 7.05 (d, $^{3}J(H,H) = 8.8$ Hz, 2H, H_4, H_4'), 7.14 (t, $^{3}J(H,H) \sim {}^{3}J(P,H) = 7.5$ Hz, 4H, diast. H_o), 7.17 (t, $^{3}J(H,H) \sim {}^{3}J(P,H) = 7.5$ Hz, 4H, diast. H_o), $^{13}C\{^{1}H\}$

NMR (125.76 MHz, $CDCl_3$): δ = 22.07 (s, diast. CH_3), 22.09 (s, diast. CH_3), 23.67 (s, CH_2), 23.71 (s, CH_2), 28.31 (s, ArCH_2), 30.21 (s, ArCH_2), 115.66 (s, C_3), 115.80 (s, C'_3), 128.77 (s, C_1, C'_1), 129.10 (s, C_4, C'_4), 129.25 (br s, diast. C_m), 129.30 (d, ^3J(P,C) = 2.4 Hz, diast. C_m), 130.23 (d, ^2J(P,C) = 23.0 Hz, diast. C_o), 130.47 (d, ^2J(P,C) = 23.0 Hz, diast. C_o), 131.78 (s, C_5, C'_5), 137.30 (s, diast. CH_3C), 138.98 (s, C_{10}, C'_{10}), 139.25 (s, diast. CH_3C), 139.37 (d, ^1J(P,C) = 6.0 Hz, diast. C_i), 139.51 (d, ^1J(P,C) = 7.3 Hz, diast. C_i), 152.85 (d, ^2J(P,C) = 4.8 Hz, C_2), 152.87 (d, ^2J(P,C) = 9.7 Hz, C'_2). Anal. Calcd for $C_{48}H_{48}O_2P_2$: C 80.20, H 6.73%. Found: C 80.42, H 6.87.

4.2.5. (*S*)-2,2′-Bis{[di(4-trifluoromethyl-phenyl)phosphinyl]oxy}-1,1′-binaphthyl 3c. This compound was prepared similar to **3b**. Yield: 3.4 g (71%), mp 51–53 °C; $[\alpha]_D^{20} = -11.0$ (*c* 1, CH_2Cl_2). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$): δ = 106.31 (s), ^1H NMR (300.15 MHz, $CDCl_3$): δ = 7.05–7.11 (m, 8H, H_o), 7.23–7.39 (m, 16H, H_3, H'_3, H_7, H'_7, H_8, H'_8, H_9, H'_9, H_m), 7.80–7.87 (m, 4H, H_4, H'_4, H_6, H'_6); $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): δ = 119.05 (d, ^3J(P,C) = 4.8 Hz, C_3), 119.15 (d, ^3J(P,C) = 4.8 Hz, C'_3), 122.33 (s, C_1, C'_1), 123.84 (q, ^1J(F,C) = 271.3 Hz, CF_3), 124.90 (s) 124.98 (m, C_m) 125.74 (s), 127.00 (s), 128.13 (s), 129.64 (m, C_o), 130.17 (s), 130.40 (s, C_5, C'_5), 131.34 (m, CF_3C), 133.92 (s, C_{10}, C'_{10}), 145.08 (d, ^1J(P,C) = 7.2 Hz, C_i), 145.21 (d, ^1J(P,C) = 9.7 Hz, C_i), 152.42 (d, ^2J(P,C) = 7.3 Hz, C_2), 152.47 (d, ^2J(P,C) = 4.8 Hz, C'_2); ^{19}F–^1H NMR (282.21 MHz, $CDCl_3$): δ = 63.07 (s), 63.12 (s). Anal. Calcd for $C_{48}H_{28}F_{12}O_2P_2$: C 62.21, H 3.04%. Found: C 62.01, H 3.07.

4.2.6. (*S*)-2,2′-Bis{[di(4-trifluoromethyl-phenyl)phosphinyl]oxy}-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl 4c. This compound was prepared similar to **3b**. Yield: 3.4 g (72%), mp 55–57 °C; $[\alpha]_D^{20} = -8.0$ (*c* 1, CH_2Cl_2). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$): δ = 104.04 (s), ^1H NMR (500.13 MHz, $CDCl_3$): δ = 1.53 (m, 4H, CH_2), 1.64 (m, 2H, CH_2), 1.72 (m, 2H, CH_2), 2.23 (td, ^2J(H,H) = 17.6 Hz, ^3J(H,H) = 5.9 Hz, 2H, ArCH_2), 2.35 (td, ^2J(H,H) = 17.6 Hz, ^3J(H,H) = 6.6 Hz, 2H, ArCH_2), 2.64 (td, ^2J(H,H) = 16.3 Hz, ^3J(H,H) = 6.0 Hz, 2H, ArCH_2), 2.78 (td, ^2J(H,H) = 16.3 Hz, ^3J(H,H) = 6.3 Hz, 2H, ArCH_2), 6.89 (d, ^3J(H,H) = 8.2 Hz, 2H, H_3, H'_3), 7.05 (d, ^3J(H,H) = 8.2 Hz, 2H, H_4, H'_4), 7.28 (t, ^3J(H,H) ~ ^3J(P,H) = 6.6 Hz, 4H, diast. H_o), 7.35 (t, ^3J(H,H) ~ ^3J(P,H) = 6.6 Hz, 4H, diast. H_o), 7.43 (d, ^3J(H,H) = 7.5 Hz, 4H, diast. H_m), 7.52 (d, ^3J(H,H) = 8.2 Hz, 4H, diast. H_m); $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): δ = 23.49 (s, CH_2), 23.55 (s, CH_2), 28.38 (s, ArCH_2), 30.02 (s, ArCH_2), 116.14 (d, ^3J(P,C) = 7.3 Hz, C_3), 116.20 (d, ^3J(P,C) = 6.0 Hz, C'_3), 124.23 (q, ^1J(F,C) = 272.5 Hz, CF_3), 125.48 (m, C_m), 128.51 (s, C_1, C'_1), 129.79 (s, C_4, C'_4), 130.07 (m, C_o), 131.59 (m, CF_3C), 133.26 (s, C_5, C'_5), 137.67 (s, C_{10}, C'_{10}), 146.23 (m, C_i), 152.30 (d, ^2J(P,C) = 6.0 Hz, C_2), 152.35 (d, ^2J(P,C) = 6.0 Hz, C'_2); ^{19}F–^1H NMR (282.21 MHz, $CDCl_3$): δ = 63.12 (s), 63.15 (s). Anal. Calcd for $C_{48}H_{36}F_{12}O_2P_2$: C 61.67, H 3.88%. Found: C 61.46, H 3.66.

4.2.7. (*S*)-2,2′-Bis{[di(3,5-bis(trifluoromethyl)phenyl)-phosphinyl]oxy}-1,1′-binaphthyl 3d. This compound was prepared similar to **3b**. Yield: 4.7 g (75%), mp 43–44 °C; $[\alpha]_D^{20} = -19.1$ (*c* 1, CH_2Cl_2). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$): δ = 104.00 (s), ^1H NMR (300.15 MHz, $CDCl_3$): δ = 7.10–7.33 (m, 8H, H_3, H'_3, H_7, H'_7, H_8, H'_8, H_9, H'_9), 7.49–7.66 (m, 10H, H_o, H_4, H'_4), 7.68–7.74 (m, 6H, H_p, H_6, H'_6), $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): δ = 119.48 (d, ^3J(P,C) = 4.8 Hz), 119.55 (d, ^3J(P,C) = 3.6 Hz,), 122.29 (d, ^3J(P,C) = 3.6 Hz, C_1, C'_1), 123.20 (q, ^1J(F,C) = 272.5 Hz, CF_3), 124.42 (m, C_p) 125.77 (s), 125.90 (s), 127.79 (s), 128.48 (s), 129.30 (m, C_o) 130.84 (s, C_5, C'_5), 131.38 (s), 132.25 (m, CF_3C), 133.73 (s, C_{10}, C'_{10}), 143.60 (m, C_i), 152.65 (d, ^2J(P,C) = 2.4 Hz, C_2), 152.69 (d, ^2J(P,C) = 4.8 Hz, C'_2), ^{19}F–^1H NMR (282.21 MHz, $CDCl_3$): δ = 63.03 (s), 63.09 (s). Anal. Calcd for $C_{52}H_{24}F_{24}O_2P_2$: C 52.10, H 2.01%. Found: C 52.04, H 1.91.

4.2.8. (*S*)-2,2′-Bis{[di(3,5-bis(trifluoromethyl)phenyl)-phosphinyl]oxy}-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl 4d. This compound was prepared similar to **3b**. Yield: 4.8 g (78%), mp 99–101 °C; $[\alpha]_D^{20} = +16.4$ (*c* 1, CH_2Cl_2). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$): δ = 101.84 (s), ^1H NMR (300.15 MHz, $CDCl_3$): δ = 1.57 (m, 8H, CH_2), 2.11 (td, ^2J(H,H) = 17.1 Hz, ^3J(H,H) = 6.1 Hz, 2H, ArCH_2), 2.29 (td, ^2J(H,H) = 17.1 Hz, ^3J(H,H) = 6.3 Hz, 2H, ArCH_2), 2.48 (td, ^2J(H,H) = 16.6 Hz, ^3J(H,H) = 5.8 Hz, 2H, ArCH_2), 2.64 (td, ^2J(H,H) = 16.6 Hz, ^3J(H,H) = 5.8 Hz, 2H, ArCH_2), 6.56 (d, ^3J(H,H) = 8.3 Hz, 2H, H_3, H'_3), 6.82 (d, ^3J(H,H) = 8.3 Hz, 2H, H_4, H'_4), 7.70 (m, 8H, H_o), 7.80 (s, 4H, H_p); $^{13}C\{^1H\}$ NMR (75.42 MHz, $CDCl_3$): δ = 22.55 (s, CH_2), 22.61 (s, CH_2), 27.76 (s, ArCH_2), 29.00 (s, ArCH_2), 116.26 (d, ^3J(P,C) = 5.5 Hz, C_3), 116.33 (d, ^3J(P,C) = 4.4 Hz, C'_3), 122.85 (q, ^1J(F,C) = 273.5 Hz, CF_3), 123.88 (m, C_p), 127.37 (m, C_1, C'_1), 129.10 (m, C_o), 130.24 (s, C_4, C'_4), 131.92 (m, CF_3C), 133.90 (s, C_5, C'_5), 137.45 (s, C_{10}, C'_{10}), 143.86 (m, C_i), 151.13 (d, ^2J(P,C) = 5.5 Hz, C_2), 151.21 (d, ^2J(P,C) = 5.5 Hz, C'_2). ^{19}F–^1H NMR (282.21 MHz, $CDCl_3$): δ = 63.05 (s). Anal. Calcd for $C_{52}H_{32}F_{24}O_2P_2$: C 51.72, H 2.65%. Found: C 51.88, H 2.81.

4.3. Catalytic experiments

In a typical experiment, 0.0125 mmol of $Rh(acac)(CO)_2$ and 0.025 mmol of ligand, 4 mL of toluene, and then 25 mmol of styrene with 5 mmol of decane as an internal standard were placed under argon into a Schlenk-tube. The stainless-steel autoclave (280 mL) was filled with this solution, purged with *syn* gas [CO–H_2 (1:1)] and then pressurized to the appropriate initial pressure with this gas mixture. The autoclave was then heated to 60 °C and stirred magnetically at an agitation speed of 650 rpm using a Brand magnetic stirring bar (diam. = 4.5 mm, *L* = 12 mm). At the end of the reaction, the autoclave was cooled and depressurized. The reaction mixture was directly vacuum distilled to remove the catalyst. The reaction mixture and the distilled products were analyzed by gas chromatography. The enantiomeric excess of the aldehyde was determined by GC analysis of the

distilled product on a Hewlett–Packard HP 4890 gas chromatograph equipped with a split/spitless injector and a β-DEX 225 column [30 m, internal diameter 0.25 mm, film thickness 0.25 μm, carrier gas: 100 kPa nitrogen, F.I.D. detector; the retention times of the enantiomers are 30.4 min (*R*), 31.4 min (*S*)]. The configuration of the prevailing enantiomer in the product was determined by the sign of specific rotation of the corresponding aldehyde. Conversions and composition of the reaction mixture (branched–linear–hydrogenated) were determined by GC (SPB-1) using decane as an internal standard.

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References

1. (a) Gergely, I.; Hegedüs, C.; Szöllősy, Á.; Monsees, A.; Riermeier, T.; Bakos, J. *Tetrahedron Lett.* **2003**, *44*, 9025; (b) Herseczki, Z.; Gergely, I.; Hegedüs, C.; Szöllősy, Á.; Bakos, J. *Tetrahedron: Asymmetry* **2004**, *15*, 1673.
2. (a) Botteghi, C.; Paganelli, S.; Schionato, A.; Marchetti, M. *Chirality* **1991**, *3*, 355; (b) Brunner, H.; Zettlmeier, W. In *Handbook of Enantioselective Catalysis with Transition Metal Compounds*; VCH: Weinheim, 1993; Vol. 1–2; (c) Agbossou, F.; Carpentier, J.-F.; Mortreux, A. *Chem. Rev.* **1995**, *95*, 2485; (d) Gladiali, S.; Bayón, J. C.; Claver, C. *Tetrahedron: Asymmetry* **1995**, *6*, 1453; (e) *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 1999; Vol. 1–3.
3. (a) Morimoto, T.; Chiba, M.; Achiwa, K. *Tetrahedron Lett.* **1989**, *30*, 735; Morimoto, T.; Chiba, M.; Achiwa, K. *Chem. Pharm. Bull.* **1992**, *40*, 2894; (b) Morimoto, T.; Nakajima, N.; Achiwa, K. *Tetrahedron: Asymmetry* **1995**, *6*, 23; (c) RajanBabu, T. V.; Ayers, T. A.; Casalnuovo, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 4101.
4. Casalnuovo, A. L.; RajanBabu, T. V.; Ayers, T. A.; Warren, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 9869.
5. Casey, M.; Smyth, M. P. *Synlett* **2003**, *1*, 102.
6. Jacobsen, E. N.; Zhang, W.; Güler, M. L. *J. Am. Chem. Soc.* **1991**, *113*, 6703.
7. RajanBabu, T. V.; Ayers, T. A. *Tetrahedron Lett.* **1994**, *35*, 4295.
8. Moser, W. R.; Papile, C. J.; Brannon, D. A.; Duwell, R. A.; Weininger, S. J. J. *J. Mol. Catal.* **1987**, *41*, 271.
9. Unruh, J.; Christenson, J. R. *J. Mol. Catal.* **1982**, *14*, 19.
10. Chan, A. S. C.; Pai, C.-C.; Yang, T.-K.; Chen, S.-M. *J. Chem. Soc., Chem. Commun.* **1995**, 2031.
11. (a) Casey, C. P.; Paulsen, E. L.; Beuttenmueller, E. W.; Proft, B. R.; Petrovich, L. M.; Matter, B. A.; Powell, D. R. *J. Am. Chem. Soc.* **1997**, *119*, 11817; (b) Casey, C. P.; Paulsen, E. L.; Beuttenmueller, E. W.; Proft, B. R.; Petrovich, L. M.; Matter, B. A.; Powell, D. R. *J. Am. Chem. Soc.* **1999**, *121*, 63.
12. van der Veen, L. A.; Boele, M. D. K.; Bregman, F. R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K.; Fraanje, J.; Schenk, H.; Bo, C. *J. Am. Chem. Soc.* **1998**, *120*, 11616.
13. Cram, D. J.; Helgeson, R. C.; Peacock, S. C.; Kaplan, L. J.; Domeier, L. A.; Moreau, P.; Koga, K.; Mayer, J. M.; Chao, Y.; Siegel, M.; Hoffman, D. H.; Sogah, G. D. Y. *J. Org. Chem.* **1978**, *43*, 1930.
14. (a) Zhang, F.-Y.; Pai, F. Y.; Chan, A. S. C. *J. Am. Chem. Soc.* **1998**, *120*, 5808; (b) Au-Yeung, T. T.-L.; Chan, S. S.; Chan, A. S. *Adv. Synth. Catal.* **2003**, *345*, 537, and references cited therein; (c) Keim, W.; Maas, H. *J. Organomet. Chem.* **1996**, *514*, 271.
15. (a) Consiglio, G.; Pino, P. *Top. Curr. Chem.* **1982**, *105*, 77; (b) Tóth, I.; Guo, I.; Hanson, B. E. *Organometallics* **1993**, *12*, 848.
16. Lazzaroni, R.; Raffaelli, A.; Settambolo, R.; Bertozzi, S.; Vittuli, G. *J. Mol. Catal.* **1989**, *50*, 1.
17. Leeuwen, P. W. N. M.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. *Chem. Rev.* **2000**, *100*, 2741.
18. For recent application see: Sermon, S.; Huang, J.; Nolan, S. P. *Organometallics* **1998**, *17*, 534.
19. (a) Yhang, X.; Mashima, K.; Kozano, K.; Sazo, N.; Kumobayashi, H.; Akutagawa, S.; Takaya, H. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2309; (b) Yhang, X.; Mashima, K.; Kozano, K.; Sazo, N.; Kumobayashi, H.; Akutagawa, S.; Takaya, H. *J. Am. Chem. Soc* **1993**, *115*, 3318.
20. (a) Nozaki, K.; Yasutomi, M.; Nakamoto, K.; Hiyama, T. *Polyhedron* **1998**, *17*, 1159; (b) Ling, R.; Yoshida, M.; Mariano, P. S. *J. Org. Chem.* **1996**, *61*, 4439.
21. RajanBabu, T. V.; Ayers, T. A.; Holliday, G. A.; You, K. K.; Calabrese, J. C. *J. Org. Chem.* **1997**, *62*, 6012.