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Development of a new class of C_1-symmetric bisphosphine ligands for rhodium-catalyzed asymmetric hydrogenation

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ABSTRACT

A new class of C_1-symmetric bisphosphine ligands with three hindered quadrants have been obtained through facile synthesis from chiral BINOL derivatives. Their rhodium complexes have exhibited high enantioselectivities (up to 98% ee) in the asymmetric hydrogenation of various unsaturated prochiral olefins, providing an efficient catalytic system for the enantioselective synthesis of chiral amino acids and amines.

1. Introduction

The development of the pharmaceutical and fine chemical industry requires the large scale production of enantiomerically pure organic molecules as chiral building blocks.[1] Among the catalytic asymmetric methods that have been explored, Rh-catalyzed asymmetric hydrogenation of prochiral olefins has become one of the most efficient and powerful strategies.[2] The transition metal catalyzed hydrogenation reaction is environmentally friendly and cost effective, hence it is among the most widely investigated areas in modern organometallic chemistry.[2]

Since the first *P*-chiral ligand DIPAMP was reported by Knowles in the 1970s, the development of this type of ligands has been relatively slow due to the difficulties in ligand synthesis.[3] It was not until BisP* reported by Imamoto in 1998 that *P*-chiral ligands regained significant attention.[4] Other representative *P*-chiral ligands, such as TangPhos[5] and BINAPINE[6] by Zhang, have shown good enantioselectivities in asymmetric hydrogenation of a wide range of functionalized olefins. More recently, C_1-symmetric bisphosphine ligand trichickenfootPhos, which has three hindered quadrants, was reported by Hoge and co-workers from Pfizer.[7] It affords extremely high selectivity and reactivity in Rh-catalyzed hydrogenation of α-dehydroamino acids under mild conditions (ee up to 99%).

It is notable that most of the highly enantioselective chiral phosphorus ligands for asymmetric hydrogenation have inherent backbone chirality. There are few examples of efficient *P*-chiral phosphorus ligands. The synthetic difficulties in the construction of stereogenic phosphorus centers have slowed the development of *P*-chiral ligands for nearly two decades after the first report of DIPAMP by Knowles.[8] Moreover, a major drawback of many *P*-chiral phosphine synthetic methods developed by Imamoto,[8a] Juge,[8b] Corey,[8c] Evans,[8e] and Livinghouse[8g] is that either only one enantiomer of the ligand is readily accessible due to the nature of the chiral auxiliaries that were used for chiral induction, or a tedious diastereomeric derivatization sequence is needed. On the other hand, the success of C_2-symmetry design for potentially high enantioselectivities has also delayed the widespread development of useful C_1-symmetric bisphosphine ligands. Recently, Hoge reported the synthesis of a bisphosphine ligand (trichickenfootPhos) with three hindered quadrants.[7] However, one major drawback of the synthetic approach for this ligand is the requirement for chiral HPLC separation to obtain both enantiomeric forms of the ligand, which limits its large scale production and application in industry. Our ligand design involves a modification, which puts a linkage between the two phosphorus atoms. With this variation, alternative chiral separation methods can be used in the ligand synthesis to circumvent the present limitation of trichickenfootPhos.

In this article, the development of a new series of C_1-symmetric bisphosphine ligands will be discussed. Their application in Rh-catalyzed asymmetric hydrogenation of various functionalized olefins will be covered as well. The hydrogenation results have shown that the ligand performance is highly substrate dependent and different phosphino substituent groups on the ligands have a great impact on the reactivity and selectivity of the reaction.

2. Results and discussion

2.1. Ligand synthesis

Starting from commercially available (*S*)-BINOL **2**, cyclic monophosphine sulfide **5** could be obtained in three steps in good overall

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yield (Scheme 1).[6] Subsequent *ortho*-lithiation by ^{t}BuLi/HMPA/TMEDA at −78 °C, followed by electrophilic attack by various phosphine chlorides, afforded **6a–d** as intermediates. When the R group on the phosphine is *o*-tolyl (**6b**) or ^{t}Bu (**6d**), direct purification by flash column chromatography can be performed. Once purified, **6b** and **6d** can be reduced with hexachlorodisilane to provide the desired products **1b** and **1d**. On the other hand, when R=Ph (**6a**) or Cy (**6c**), the intermediates are quite air sensitive and large amounts of oxidation occurred when subjected to flash column purification. To circumvent this problem, the intermediates were further reduced with Si_2Cl_6 and protected with BH_3·THF to generate **7** or directly protected with BH_3·THF to generate **8**. These protected phosphines could be easily purified by flash column chromatography without being subjected to rapid oxidation. Removal of BH_3 with DABCO (1,4-diazabicyclo[2,2,2]octane) and reduction of the P═S bond with hexachlorodisilane afforded **1a** and **1c** in moderate yields.

2.2. Rh-catalyzed asymmetric hydrogenation

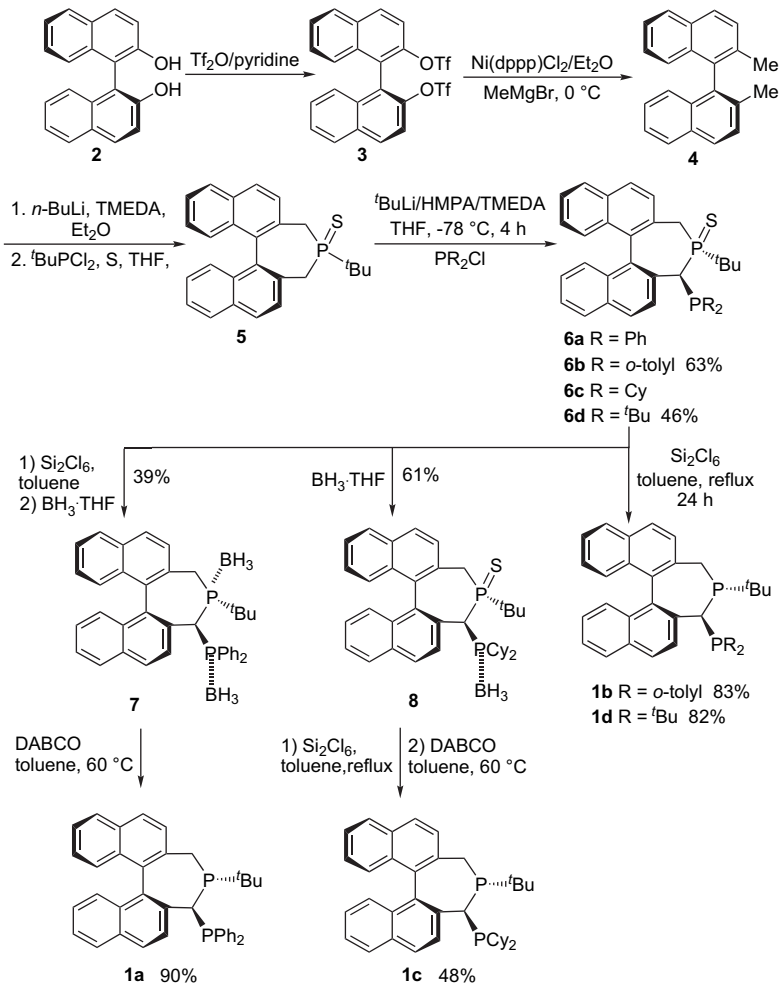
In order to examine the catalytic efficiency of **1a–d**, cationic Rh complexes [Rh(cod)**1**]BF_4 (cod=1,5-cyclooctadiene) (**9a–d**) were prepared following a standard procedure (cf. Section 4). The use of these complexes as precatalysts for the hydrogenation of various prochiral olefins was also investigated.

2.2.1. Asymmetric hydrogenation of dehydroamino acid derivatives

α-Dehydroamino acid derivatives are a typical class of substrates for the evaluation of asymmetric hydrogenation catalysts. Initially, rhodium complex **9c** was used in the solvent screening for the hydrogenation of methyl α-(acetamido)acrylate (**10a**) under very mild conditions (rt, 50 psi of H_2 pressure, Table 1). After 12 h, quantitative yields and high ee of the products were observed regardless of the solvent polarity. The highest enantioselectivity of 97.5% was achieved when methanol was used (Table 1, entry 1).

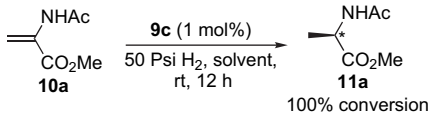
Using the optimized conditions, we have investigated asymmetric hydrogenation of several α-dehydroamino acid derivatives using rhodium complexes **9a–d** as catalysts (Table 2). In most cases, complete conversions were observed with the exception of substrate **10c**, a tetra-substituted α-dehydroamino ester (Table 2, entries 9 and 10). Complex **9d**, while providing moderate enantioselectivity in the hydrogenation of the simple substrate **10a**, afforded the highest enantioselectivity in the hydrogenation of **10c** (Table 2, entries 4 and 11). The relationship between steric hindrance of the ligands **1a–d** around the metal center and catalytic efficiency is under investigation. This relationship may provide an explanation for the high substrate-dependent properties of complex **9d**.

Asymmetric hydrogenation of β-(acetamido)acrylate derivatives, one of the most efficient and practical ways to obtain unnatural enantiomerically enriched β-amino acids, remains much



Scheme 1. Ligand synthesis.

Table 1
Screening of solvents for asymmetric hydrogenation of **10a**



Entry[a]	Solvent	ee[b] (%) (Configuration)
1	MeOH	97.5 (*R*)
2	EtOH	95.0 (*R*)
3	^{i}PrOH	95.5 (*R*)
4	THF	96.0 (*R*)
5	DCM	94.7 (*R*)
6	EtOAc	96.8 (*R*)
7	Acetone	95.1 (*R*)
8	Toluene	97.1 (*R*)

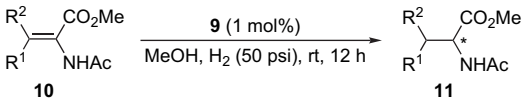
[a] See Section 4 for general procedure.
[b] The enantiomeric excess was determined by chiral GC (Chirasil-VAL III FSOT). The *R* absolute configuration was assigned by comparison of optical rotations with reported data.

less successful compared to the hydrogenation of their α-analogues.[9] As shown in Table 3, several β-dehydroamino acid derivatives were hydrogenated with Rh complexes **9** as the catalyst precursor using two different solvent systems. For (*Z*)-ethyl 3-acetamido-2-butenoate (**12a**), both **9a** and **9c** gave good enantioselectivities of up to 90% (Table 3, entries 1 and 3) when methanol was used. Changing the solvent to THF in the hydrogenation reaction with complexes **9b** and **9c** gave slightly better enantioselectivities although complete conversions were not obtained (Table 3, entries 5 and 6). For more challenging β-aryl substituted substrates **12b** and **12c**, high ee values (90 and 93%) were also obtained with **9a** and **9c**, respectively (Table 3, entries 7 and 9). While still under investigation, we currently do not have a viable hypothesis regarding the variable enantioselectivities with this series of ligands.

2.2.2. Asymmetric hydrogenation of dehydroamino acid derivatives

Hydrogenation of α-arylenamides was also investigated with Rh complexes **9** as the catalyst precursor. As shown in Table 4, both acyclic enamide **14a** and cyclic enamide **14b** were employed in the hydrogenation reactions. When **9c** was used in the hydrogenation of **14a**, the highest enantioselectivity of 80% ee was achieved (Table 4, entry 3). In contrast, complex **9c** only afforded a poor ee of 32%

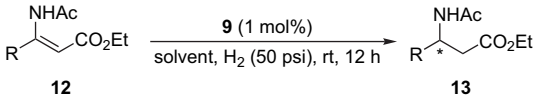
Table 2
Asymmetric hydrogenation of several α-dehydroamino acid derivatives



Entry[a]	Substrate		Complex	Conversion[b] (%)	ee[c] (%) (Configuration)
1	**10a**	R^1, R^2=H	**9a**	100	97.0 (*R*)
2	**10a**		**9b**	100	91.1 (*R*)
3	**10a**		**9c**	100	97.5 (*R*)
4	**10a**		**9d**	100	77.5 (*S*)
5	**10a**		**9a**	100	92.0 (*R*)
6	**10b**	R^1=4-MeO–Ph, R^2=H	**9b**	100	47.0 (*R*)
7	**10b**		**9c**	100	89.7 (*R*)
8	**10b**		**9d**	72	41.4 (*S*)
9	**10c**	R^1, R^2=C_4H_8	**9a**	64	38.7 (*R*)
10	**10c**		**9c**	55	8.5 (*R*)
11	**10c**		**9d**	100	49.6 (*R*)

[a] See Section 4 for general procedure.
[b] The conversions were based on GC detection.
[c] The enantiomeric excess was determined by chiral GC (Chirasil-VAL III FSOT) and HPLC. The absolute configurations were assigned by comparison of optical rotations with reported data.

Table 3
Asymmetric hydrogenation of several β-dehydroamino acid derivatives



Entry[a]	Substrate		Solvent	Complex	Conversion[b] (%)	ee[c] (%) (Configuration)
1	**12a**	R=Me	MeOH	**9a**	100	89.8 (*R*)
2	**12a**		MeOH	**9b**	100	22.4 (*R*)
3	**12a**		MeOH	**9c**	100	88.5 (*R*)
4	**12a**		MeOH	**9d**	100	17.7 (*R*)
5	**12a**		THF	**9b**	100	34.8 (*R*)
6	**12a**		THF	**9c**	93	92.6 (*R*)
7	**12b**	R=H	THF	**9a**	80	89.6 (*S*)
8	**12b**		THF	**9b**	100	16.1 (*S*)
9	**12c**	R=4-OMe-Ph	MeOH	**9c**	100	92.5 (*R*)

[a] See Section 4 for general procedure.
[b] The conversions were based on GC detection.
[c] The enantiomeric excess was determined by chiral GC (Chirasil-VAL III FSOT). The absolute configurations were assigned by comparison of optical rotations with reported data.

when cyclic substrate **14b** was used (Table 4, entry 7). Complex **9d**, which gave the best results in the hydrogenation of tetra-substituted dehydroamino acid derivatives, again proved to be the complex of choice for the tetra-substituted enamide (Table 4, entry 8).

3. Conclusion

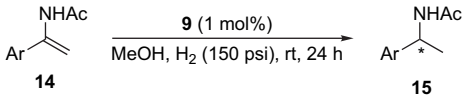
In conclusion, we have developed a series of C_1-symmetric bisphosphine ligands **1a**–**d** with three hindered quadrants from enantiomerically pure (*S*)-BINOL. Several slightly different synthetic routes were used in the ligand syntheses based on different chemical properties of the reaction intermediates **6a**–**d**. The hydrogenation of various functionalized prochiral olefins was performed with the rhodium complexes of these ligands. In most cases, good to excellent enantioselectivities were achieved with some substrate-dependence noted.

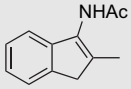
4. Experimental section

4.1. General methods

All reactions and manipulations were performed in a nitrogen-filled glove box or under nitrogen using standard Schlenk

Table 4
Asymmetric hydrogenation of α-arylenamides



Entry[a]	Substrate		Complex	Conversion[b] (%)	ee[c] (%) (Configuration)
1	**14a**	Ar=3-Me–Ph	**9a**	100	53.5 (*R*)
2	**14a**		**9b**	100	53.7 (*S*)
3	**14a**		**9c**	100	79.7 (*R*)
4	**14a**		**9d**	100	71.8 (*S*)
5	**14b**		**9a**	100	37.1 (*S*)
6	**14b**		**9b**	60	69.7 (*R*)
7	**14b**		**9c**	100	31.5 (*S*)
8	**14b**		**9d**	100	84.5 (*R*)

[a] See Section 4 for general procedure.
[b] The conversions were based on GC detection.
[c] The enantiomeric excess was determined by chiral GC (Chirasil-VAL III FSOT). The absolute configurations were assigned by comparison of optical rotations with reported data.

techniques. All the solvents are dried and deoxygenated by solvent purification system. Column chromatography was performed using EM silica gel 60 Å (230~400 mesh). ^{1}H, ^{13}C, and ^{31}P NMR spectral data were recorded on Bruker DPX-300, CDPX-300, AMX-360, and DRX-400 MHz spectrometers. Chemical shifts are reported in parts per million upfield to tetramethylsilane with the solvent resonance as the internal standard. Mass spectra were recorded on a KRATOS MS 9/50 mass spectrometer for LR-ESI and HR-ESI. GC analyses were carried out on a Hewlett-Packard 6890 gas chromatograph, using chiral capillary columns. HPLC analyses were carried out on a Waters™ 600 chromatograph.

4.2. Synthetic procedures for preparation of intermediates 6a–d, 7, and 8

*4.2.1. 4-tert-Butyl-3-diphenylphosphanyl-3,5-dihydro-4-phosphacyclohepta[2,1-α;3,4-α′]dinaphthalene-4-sulfide (**6a**)*

At −78 °C, to a solution of **5** (0.40 g, 1 mmol), TMEDA (182 μL, 1.2 mmol) in THF (10 mL) was added dropwise ^{t}BuLi (0.88 mL, 1.7 M in pentane, 1.5 mmol). The reaction mixture was stirred at −78 °C for 4 h, followed by slow addition of a solution of PPh_2Cl (0.204 mL, 1.1 mmol) in 3 mL of THF at the same temperature. The resulting mixture was allowed to slowly warm to rt and stirred overnight before quenching with NH_4Cl (aq). The organic layer was extracted with ether (3×10 mL) and washed with brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was directly used in the next step without further purification.

*4.2.2. 4-tert-Butyl-3-(di-o-tolylphosphanyl)-3,5-dihydro-4-phosphacyclohepta[2,1-α;3,4-α′]dinaphthalene-4-sulfide (**6b**)*

At −78 °C, to a solution of **5** (2.00 g, 5 mmol), TMEDA (0.91 mL, 6 mmol) in THF (25 mL) was added dropwise ^{t}BuLi (4.4 mL, 1.7 M in pentane, 7.5 mmol). The reaction mixture was stirred at −78 °C for 4 h, followed by slow addition of a solution of $P(o\text{-tolyl})_2Cl$ (1.37 g, 5.5 mmol) in 8 mL of THF at the same temperature. The resulting mixture was allowed to slowly warm to rt and stirred overnight before quenching with NH_4Cl (aq). The organic layer was extracted with ether (3×15 mL) and washed with brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexenes/EtOAc, 95:5) to afford **6b** as a white solid (1.93 g, 63%). ^{1}H NMR ($CDCl_3$, 360 MHz) δ 8.08 (d, J=8.4 Hz, 1H), 7.97 (d, J=8.2 Hz, 1H), 7.89 (s, 2H), 7.85 (d, J=8.1 Hz, 1H), 7.80 (d, J=7.7 Hz, 1H), 7.77 (dd, J=1.4, 7.6 Hz, 1H), 7.65–7.67 (m, 1H), 7.37–7.44 (m, 2H), 7.01–7.16 (m, 4H), 6.88–6.98 (m, 2H), 6.80–6.83 (m, 2H), 6.56–6.60 (m, 1H), 6.24 (d, J=8.5 Hz, 1H), 4.81 (dd, J=5.4, 9.1 Hz, 1H), 3.62 (dd, J=10.0, 12.7 Hz, 1H), 2.90–2.96 (m, 1H), 2.43 (s, 3H), 1.19 (d, J=15.7 Hz, 9H), 1.14 (d, J=2.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.0, 143.6, 140.5, 140.2, 136.6, 136.3, 135.5, 135.4, 135.0, 134.1, 133.9, 132.8 (d, J=2.5 Hz), 132.7 (d, J=5.2 Hz), 132.5, 132.4, 131.0 (d, J=2.7 Hz), 130.2 (d, J=6.0 Hz), 129.7 (d, J=3.3 Hz), 129.6 (d, J=5.6 Hz), 128.4 (d, J=2.0 Hz), 127.9, 127.8, 127.6, 127.4, 127.3, 127.2, 126.0, 125.9, 125.7, 125.3, 125.2, 124.2, 44.0 (t, J=39.7 Hz), 36.6 (d, J=41.4 Hz), 34.8 (d, J=41.5 Hz), 25.8, 22.0 (d, J=24.1 Hz), 20.5 (d, J=29.0 Hz); ^{31}P NMR ($CDCl_3$, 145 MHz) δ 86.85 (d, J_{P-P}=69.9 Hz), −40.69 (d, J_{P-P}=69.8 Hz); HRMS (ESI^+) calcd for $C_{40}H_{39}P_2S$ (MH^+) 613.2248, found 613.2227.

*4.2.3. 4-tert-Butyl-3-dicyclohexylphosphanyl-3,5-dihydro-4-phosphacyclohepta-[2,1-α;3,4-α′]dinaphthalene-4-sulfide (**6c**)*

At −78 °C, to a solution of **5** (0.60 g, 1.5 mmol), TMEDA (0.27 mL, 1.8 mmol) in THF (15 mL) was added dropwise ^{t}BuLi (1.32 mL, 1.7 M in pentane, 2.25 mmol). The reaction mixture was stirred at −78 °C for 4 h, followed by slow addition of a solution of PCy_2Cl (0.364 mL, 1.65 mmol) in 5 mL of THF at the same temperature. The resulting mixture was allowed to slowly warm to rt and stirred overnight before quenching with NH_4Cl (aq). The organic layer was extracted with ether (3×10 mL) and washed with brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was directly used in the next step without further purification.

*4.2.4. 4-tert-Butyl-3-(di-tert-butylphosphanyl)-3,5-dihydro-4-phosphacyclohepta-[2,1-α;3,4-α′]dinaphthalene-4-sulfide (**6d**)*

At −78 °C, to a solution of **5** (1.20 g, 3 mmol), TMEDA (0.55 mL, 3.6 mmol), HMPA (0.62 mL, 3.6 mmol) in THF (35 mL) was added dropwise ^{t}BuLi (2.1 mL, 1.7 M in pentane, 3.6 mmol). The reaction mixture was stirred at −78 °C for 4 h, followed by slow addition of a solution of $P^{t}Bu_2Cl$ (0.59 mL, 3.1 mmol) in 10 mL of THF at the same temperature in 10 min. The resulting mixture was stirred at −78 °C for another 30 min, then allowed to slowly warm to rt and refluxed overnight before quenching with NH_4Cl (aq). The organic layer was extracted with ether (3×15 mL) and washed with brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexenes/EtOAc, 95:5) to afford **6d** as a white solid (0.75 g, 46%). ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.86 (q, J=4.3 Hz, 3H), 7.81 (s, 1H), 7.57 (t, J=8.8 Hz, 2H), 7.36–7.43 (m, 3H), 7.18 (ddd, J=1.3, 7.9, 9.6 Hz, 1H), 7.09–7.13 (m, 2H), 4.16 (dd, J=3.6, 18.7 Hz, 1H), 2.68–2.82 (m, 2H), 1.21 (d, J=15.0 Hz, 9H), 1.12 (d, J=11.1 Hz, 9H), 1.00 (d, J=15.0 Hz, 9H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 136.6, 136.0 (d, J=5.4 Hz), 134.7, 133.8, 133.7, 133.6, 133.2, 133.1, 133.0, 132.9, 132.6, 129.7, 129.3, 127.8, 127.7, 127.6, 127.5, 125.8, 125.7, 125.0, 42.3, 41.9, 41.5, 32.9 (d, J=7.4 Hz), 32.6 (d, J=7.1 Hz), 29.7(d, J=24.6 Hz), 29.3, 28.7(d, J=10.3 Hz); ^{31}P NMR ($CDCl_3$, 145 MHz) δ 93.52 (d, J_{P-P}=69.4 Hz), 37.63 (d, J_{P-P}=69.2 Hz); HRMS (ESI^+) calcd for $C_{34}H_{43}P_2S$ (MH^+) 545.2561, found 545.2526.

*4.2.5. 4-tert-Butyl-3-diphenylphosphanyl-3,5-dihydro-4-phospha-cyclohepta[2,1-α;3,4-α′]dinaphthalene bisborane complex (**7**)*

To the solution of crude product **6a** in 12 mL of toluene was slowly added Si_2Cl_6 (1.72 mL, 10 mmol). The reaction mixture was heated to reflux and stirred for 20 h before being quenched with 15 mL of NaOH solution (30% w/w). The resulting mixture was heated at 60 °C for 1 h until both layers became clear. The organic layer was extracted with ether (3×5 mL), washed with brine (5 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was redissolved in 10 mL of THF and cooled to 0 °C followed by addition of 6 mL of $BH_3\cdot$THF (1 M). The resulting mixture was allowed to warm to rt and stirred overnight. Methanol was added to quench excess of $BH_3\cdot$THF. After removal of solvents, the residue was purified by flash column chromatography on silica gel (hexenes/EtOAc, 97:3) to afford **7** as a white solid (0.23 g, 39%). ^{1}H NMR ($CDCl_3$, 360 MHz) δ 7.82–7.89 (m, 3H), 7.59–7.71 (m, 5H), 7.22–7.44 (m, 8H), 7.06–7.11 (m, 1H), 6.94–7.09 (m, 2H), 6.80–6.85 (m, 2H), 6.69 (d, J=8.5 Hz, 1H), 4.35 (dd, J=12.9, 18.5 Hz, 1H), 3.21 (dd, J=12.9, 16.8 Hz, 1H), 2.84 (d, J=12.8 Hz, 1H), 1.26–1.42 (m, 3H), 1.12 (d, J=13.2 Hz, 9H), 0.83–0.97 (m, 3H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 135.6 (d, J=4.7 Hz), 135.0 (d, J=10.3 Hz), 134.0, 133.6, 133.1 (d, J=5.2 Hz), 133.0 (dd, J=5.4, 12.4 Hz), 132.8 (d, J=12.1 Hz), 132.5 (d, J=2.6 Hz), 131.6, 130.8 (d, J=11.2 Hz), 129.6, 129.5, 129.4, 129.0, 128.5, 128.4, 128.0 (d, J=9.9 Hz), 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 125.8, 125.1, 122.5, 121.9, 41.5 (d, J=15.3 Hz), 33.1 (dd, J=3.5, 23.2 Hz), 28.3 (d, J=29.8 Hz), 26.3; ^{31}P NMR ($CDCl_3$, 145 MHz) δ 67.12 (br s), 31.20 (br s); MS (ESI^+) m/z 603.2 (MNa^+).

*4.2.6. 4-tert-Butyl-3-dicyclohexylphosphanyl-3,5-dihydro-4-phosphacyclohepta-[2,1-α;3,4-α′]dinaphthalene-4-sulfide monoborane complex (**8**)*

To the solution of crude product **6c** in 15 mL of THF was added 9 mL of $BH_3\cdot$THF (1 M) dropwise at 0 °C. The resulting mixture was allowed to warm to rt and stirred overnight. Methanol was added to quench excess of $BH_3\cdot$THF. After removal of solvents, the residue

was purified by flash column chromatography on silica gel (hexenes/EtOAc, 97:3) to afford **8** as a white solid (0.55 g, 61%). ^{1}H NMR ($CDCl_3$, 360 MHz) δ 8.01 (d, J=8.4 Hz, 1H), 7.86–7.93 (m, 3H), 7.68 (dd, J=1.3, 8.4 Hz, 1H), 7.41–7.51 (m, 3H), 7.10–7.27 (m, 3H), 6.93 (d, J=8.5 Hz, 1H), 4.22 (t, J=16.2 Hz, 1H), 3.75 (dd, J=10.4, 13.0 Hz, 1H), 3.03 (dd, J=10.3, 13.1 Hz, 1H), 2.89 (d, J=13.5 Hz, 1H), 2.47 (d, J=12.3 Hz, 1H), 2.04 (d, J=8.5 Hz, 1H), 1.85 (d, J=11.2 Hz, 1H), 1.16–1.71 (m, 7H), 0.98 (d, J=6.6 Hz, 9H), 0.96–1.16 (m, 5H), 0.83–0.91 (m, 4H), 0.38–0.65 (m, 5H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 135.1, 134.5, 134.2 (d, J=4.1 Hz), 133.8 (d, J=2.4 Hz), 133.7, 133.6, 133.3 (d, J=2.0 Hz), 133.0, 132.7, 129.4, 128.9, 128.8 (d, J=9.6 Hz), 128.3, 128.1, 128.0, 127.7, 127.4, 126.6, 126.2 (d, J=13.0 Hz), 126.0, 42.5 (d, J=34.0 Hz), 39.4 (d, J=40.6 Hz), 36.6 (d, J=44.3 Hz), 33.0 (d, J=25.9 Hz), 31.7 (d, J=21.0 Hz), 29.6 (d, J=26.8 Hz), 28.5 (d, J=6.0 Hz), 27.5, 26.6 (dd, J=17.7, 28.0 Hz), 26.1, 26.0, 25.7 (d, J=45.4 Hz); ^{31}P NMR ($CDCl_3$, 145 MHz) δ 89.15 (d, J_{P-P}=22.2 Hz), 55.76 (br s); HRMS (ESI$^+$) calcd for $C_{38}H_{49}BP_2SNa$ (MNa^+) 633.3021, found 633.2997.

4.3. Synthetic procedures for preparation of ligands 1a–d

*4.3.1. 4-tert-Butyl-3-diphenylphosphanyl-3,5-dihydro-4-phosphacyclohepta[2,1-α;3,4-α′]dinaphthalene (**1a**)*

To a solution of **7** (150 mg, 0.26 mmol) in 10 mL of toluene was added DABCO (0.234 g, 2.08 mmol) in one portion. The reaction mixture was stirred at 50 °C for 4 h. After removal of the solvent, the residue was purified by flash column chromatography on silica gel under nitrogen (hexanes/ether, 50:50) to afford **1a** as a white solid (128 mg, 90%). ^{1}H NMR (CD_2Cl_2, 360 MHz) δ 8.04 (d, J=8.4 Hz, 1H), 7.99 (d, J=8.1 Hz, 1H), 7.84 (d, J=8.1 Hz, 1H), 7.77 (d, J=8.4 Hz, 1H), 7.69 (d, J=8.4 Hz, 1H), 7.42–7.52 (m, 4H), 7.36–7.40 (m, 1H), 7.07–7.27 (m, 11H), 6.72 (d, J=8.5 Hz, 1H), 4.00 (s, 1H), 2.74–2.90 (m, 2H), 0.94 (d, J=11.4 Hz, 9H); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 138.3 (d, J=20.1 Hz), 136.6 (d, J=5.2 Hz), 134.5 (d, J=22.4 Hz), 134.2, 134.1, 133.9, 133.1, 132.8, 132.7, 132.3, 132.1, 129.3, 129.1, 128.9, 128.8, 128.5, 128.2, 128.0, 127.9, 127.8, 127.6, 127.5, 127.1, 126.7, 126.0 (d, J=25.4 Hz), 125.7, 125.4, 125.2 (d, J=26.1 Hz), 41.1 (d, J=15.7 Hz), 30.9 (dd, J=11.3, 24.6 Hz), 28.0 (dd, J=8.9, 13.5 Hz), 26.9; ^{31}P NMR (CD_2Cl_2, 145 MHz) δ 29.86 (d, J_{P-P}=161.7 Hz), −9.55 (d, J_{P-P}=161.2 Hz); HRMS (ESI$^+$) calcd for $C_{38}H_{35}P_2$ (MH^+) 553.2214, found 553.2250.

*4.3.2. 4-tert-Butyl-3-(di-o-tolylphosphanyl)-3,5-dihydro-4-phosphacyclohepta[2,1-α;3,4-α′]dinaphthalene (**1b**)*

To the solution of **6b** (1.72 g, 2.8 mmol) in 20 mL of toluene was added Si_2Cl_6 (2.89 mL, 16.8 mmol) slowly. The reaction mixture was heated to reflux and stirred for 24 h before being quenched with 20 mL of NaOH solution (30% w/w). The resulting mixture was heated at 60 °C for 1 h until both layers became clear. The organic layer was extracted with ethyl ether (3×15 mL), washed with brine (15 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel under nitrogen (hexanes/ether, 50:50) to afford **1b** as a white solid (1.35 g, 83%). ^{1}H NMR (CD_2Cl_2, 360 MHz) δ 8.01 (d, J=8.4 Hz, 1H), 7.96 (d, J=8.2 Hz, 1H), 7.85–7.92 (m, 3H), 7.78 (d, J=8.5 Hz, 1H), 7.68 (dd, J=1.0, 8.4 Hz, 1H), 7.35–7.40 (m, 3H), 7.21–7.23 (m, 1H), 7.07–7.16 (m, 3H), 6.94–7.05 (m, 4H), 6.75–6.78 (m, 1H), 6.62 (d, J=8.5 Hz, 1H), 3.98 (d, J=1.5 Hz, 1H), 2.71–2.84 (m, 2H), 2.21 (s, 3H), 1.29 (d, J=2.6 Hz, 3H), 0.87 (d, J=11.6 Hz, 9H); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 145.7 (d, J=31.3 Hz), 143.2 (d, J=29.9 Hz), 137.8 (d, J=17.3 Hz), 137.5, 137.0 (d, J=7.6 Hz), 136.8, 136.6, 134.6, 134.5, 134.4, 134.1, 133.0 (d, J=6.7 Hz), 132.5, 132.4, 131.9, 130.1 (d, J=4.2 Hz), 129.6 (d, J=5.8 Hz), 129.4, 129.0 (d, J=5.9 Hz), 128.6, 128.3, 128.2, 128.1, 127.7, 127.3, 127.0, 126.1, 126.0, 125.8, 25.5, 125.2, 124.9, 41.4 (dd, J=24.3, 36.1 Hz), 30.8 (dd, J=11.3, 25.4 Hz), 28.3 (d, J=23.9 Hz), 28.0 (d, J=14.1 Hz), 22.5 (dd, J=7.1, 24.5 Hz), 20.3 (d, J=27.1 Hz); ^{31}P NMR (CD_2Cl_2, 145 MHz) δ 28.41 (d, J_{P-P}=157.1 Hz), −40.76 (d, J_{P-P}=157.1 Hz); HRMS (ESI$^+$) calcd for $C_{40}H_{39}P_2$ (MH^+) 581.2527, found 581.2470.

*4.3.3. 4-tert-Butyl-3-dicyclohexylphosphanyl-3,5-dihydro-4-phosphacyclohepta-[2,1-α;3,4-α′]dinaphthalene (**1c**)*

To the solution of **8** (0.495 g, 0.83 mmol) in 15 mL of toluene was added Si_2Cl_6 (1.14 mL, 6.64 mmol) slowly. The reaction mixture was heated at reflux and stirred for 24 h before being quenched with 15 mL of NaOH solution (30% w/w). The resulting mixture was heated at 60 °C for 1 h until both layers became clear. The organic layer was extracted with ether (3×5 mL), washed with brine (5 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude compound was redissolved in 10 mL of toluene and DABCO (0.372 g, 3.32 mmol) was added in one portion. The resulting mixture was stirred at 50 °C for 4 h. After the reaction was completed, solvent was removed under vacuum. The residue was purified by flash column chromatography on silica gel under nitrogen (hexanes/ether, 50:50) to afford **1c** as a white solid (0.225 g, 48%). ^{1}H NMR (CD_2Cl_2, 360 MHz) δ 7.84–7.93 (m, 4H), 7.60 (d, J=8.3 Hz, 1H), 7.33–7.47 (m, 3H), 7.13–7.25 (m, 3H), 7.02 (d, J=8.5 Hz, 1H), 3.52 (s, 1H), 2.87 (d, J=11.5 Hz, 1H), 2.74 (dd, J=11.9, 15.6 Hz, 1H), 1.63–1.82 (m, 6H), 1.29–1.57 (m, 6H), 1.15–1.23 (m, 4H), 1.05 (d, J=11.1 Hz, 9H), 0.67–0.88 (m, 5H), 0.52 (s, 1H); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ 138.3 (d, J=4.2 Hz), 134.7 (d, J=3.3 Hz), 134.0, 133.8, 133.6, 133.1, 132.8, 132.5, 131.6, 128.8, 128.5, 128.3, 127.8 (d, J=2.0 Hz), 127.7, 127.3, 127.0, 125.9, 125.6, 125.3, 124.7, 36.0 (d, J=3.2 Hz), 35.8 (d, J=13.1 Hz), 35.5, 35.1, 34.8 (d, J=4.5 Hz), 34.4 (d, J=4.3 Hz), 33.1 (dd, J=7.6, 13.5 Hz), 31.9 (dd, J=3.6, 13.0 Hz), 31.8, 31.6, 31.4, 31.3, 29.2, 28.5 (d, J=13.3 Hz), 28.2 (dd, J=2.2, 16.8 Hz), 28.1 (d, J=13.8 Hz), 27.0, 26.7; ^{31}P NMR (CD_2Cl_2, 145 MHz) δ 34.70 (d, J_{P-P}=133.8 Hz), 10.38 (d, J_{P-P}=133.6 Hz).

*4.3.4. 4-tert-Butyl-3-(di-tert-butylphosphanyl)-3,5-dihydro-4-phosphacyclohepta-[2,1-α;3,4-α′]dinaphthalene (**1d**)*

To the solution of **6d** (0.40 g, 0.73 mmol) in 10 mL of toluene was added Si_2Cl_6 (1.22 mL, 7.1 mmol) slowly. The reaction mixture was heated at reflux and stirred for 24 h before being quenched with 12 mL of NaOH solution (30% w/w). The resulting mixture was heated at 60 °C for 1 h until both layers became clear. The organic layer was extracted with ethyl ether (3×15 mL), washed with brine (15 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel under nitrogen (hexanes/ether, 50:50) to afford **1d** as a white solid (0.31 g, 82%). ^{1}H NMR (CD_2Cl_2, 360 MHz) δ 7.83–7.92 (m, 4H), 7.59 (d, J=8.2 Hz, 1H), 7.34–7.47 (m, 3H), 7.11–7.22 (m, 3H), 7.00 (d, J=8.5 Hz, 1H), 3.34 (s, 1H), 2.69–2.86 (m, 2H), 1.23 (d, J=15.0 Hz, 9H), 1.12 (d, J=11.1 Hz, 9H), 1.02 (d, J=15.0 Hz, 9H); ^{31}P NMR (CD_2Cl_2, 145 MHz) δ 56.61 (d, J_{P-P}=32.9 Hz), 35.23 (d, J_{P-P}=32.3 Hz); HRMS (ESI$^+$) calcd for $C_{34}H_{43}P_2$ (MH^+) 513.2840, found 513.2812.

4.4. General procedure for preparation of Rh complexes 9a–d

A solution of ligand **1** (0.25 mmol) in 5 mL of THF was added dropwise to a solution of $[Rh(cod)_2]BF_4$ (0.25 mmol) in 8 mL of methanol at rt while stirring. After addition, the reaction mixture was stirred for 1 h and solvents were removed in vacuo to provide an orange solid.

*4.4.1. [Rh(cod)**1a**]BF_4 (**9a**)*

^{1}H NMR (CD_2Cl_2, 360 MHz) δ 8.12 (d, J=8.2 Hz, 1H), 7.82–8.04 (m, 3H), 7.78 (d, J=8.1 Hz, 1H), 7.42–7.59 (m, 8H), 7.23 (t, J=7.1 Hz, 1H), 7.06–7.10 (m, 1H), 6.82–6.86 (m, 2H), 6.62–6.67 (m, 3H), 6.48–6.54 (m, 2H), 5.98 (m, 2H), 5.78 (br s, 1H), 5.54 (s, 2H), 5.14 (br s, 1H), 4.96 (br s, 1H), 3.42 (d, J=12.9 Hz, 1H), 3.24 (t, J=14.9 Hz, 1H), 2.83–

2.92 (m, 1H), 2.51–2.54 (m, 3H), 2.24–2.31 (m, 2H), 1.24 (d, J=15.0 Hz, 9H); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 134.9 (d, J=7.4 Hz), 134.2 (d, J=7.4 Hz), 133.3 (d, J=12.8 Hz), 132.6, 132.5, 132.4, 132.3, 131.7, 131.6, 131.2, 131.1, 130.3, 129.7, 129.6, 129.3, 128.8, 128.7, 128.6, 128.3, 128.1, 128.0, 127.7, 127.4, 127.3, 127.0, 126.8, 126.5, 125.3, 102.8 (d, J=6.7 Hz), 99.0, 96.4, 68.1 (d, J=23.9 Hz), 59.3, 50.5, 29.9, 29.4, 28.6, 27.4, 26.9 (dd, J=2.3, 4.5 Hz), 25.7 (d, J=14.8 Hz); ^{31}P NMR (CD_2Cl_2, 145 MHz) δ 22.92 (dd, J=72.1, 127.1 Hz), −23.11 (dd, J=72.1, 134.2 Hz); HRMS (ESI^+) calcd for $C_{46}H_{46}P_2Rh$ (cation) 763.2130, found 763.2094; HRMS (ESI^-) calcd for BF_4 (anion) 87.0029, found 87.0023.

*4.4.2. [Rh(cod)**1b**]BF_4 (**9b**)*

^{1}H NMR (CD_2Cl_2, 360 MHz) δ 8.18–8.23 (m, 1H), 8.07 (d, J=8.4 Hz, 1H), 7.96 (d, J=8.5 Hz, 1H), 7.86 (d, J=8.1 Hz, 1H), 7.80 (d, J=8.4 Hz, 1H), 7.76 (d, J=8.1 Hz, 1H), 7.70 (d, J=8.4 Hz, 1H), 7.62 (t, J=7.6 Hz, 1H), 7.37–7.42 (m, 2H), 7.24 (t, J=7.7 Hz, 1H), 6.99–7.11 (m, 3H), 6.66–6.69 (m, 2H), 6.50 (t, J=7.5 Hz, 1H), 6.35 (dd, J=3.3, 7.3 Hz, 1H), 6.09–6.20 (m, 3H), 6.02 (d, J=8.6 Hz, 1H), 5.53 (s, 2H), 5.40 (br s, 1H), 5.10 (br s, 1H), 3.22–3.29 (m, 2H), 2.85 (d, J=3.8 Hz, 2H), 2.27 (s, 3H), 2.14–2.25 (m, 5H), 1.30 (d, J=14.8 Hz, 9H), 1.10 (s, 3H); ^{31}P NMR (CD_2Cl_2, 145 MHz) δ 26.52 (dd, J=62.3, 131.3 Hz), −17.52 (dd, J=63.5, 131.2 Hz); HRMS (ESI^+) calcd for $C_{48}H_{50}P_2Rh$ (cation) 791.2413, found 791.2443; HRMS (ESI^-) calcd for BF_4 (anion) 87.0029, found 87.0021.

*4.4.3. [Rh(cod)**1c**]BF_4 (**9c**)*

^{1}H NMR (CD_2Cl_2, 360 MHz) δ 8.18 (d, J=8.3 Hz, 1H), 7.95–8.05 (m, 4H), 7.52 (t, J=7.2 Hz, 2H), 7.41 (d, J=8.4 Hz, 1H), 7.21–7.29 (m, 2H), 7.14 (d, J=8.5 Hz, 1H), 7.00 (d, J=8.5 Hz, 1H), 5.71 (s, 1H), 5.39 (s, 1H), 5.32 (s, 1H), 5.08–5.15 (m, 2H), 3.66–3.69 (m, 3H), 3.40–3.43 (m, 1H), 3.22–3.30 (m, 1H), 2.61 (q, J=7.1 Hz, 2H), 2.31–2.34 (m, 5H), 2.14–2.20 (m, 4H), 1.74–2.03 (m, 9H), 1.32–1.51 (m, 4H), 1.14 (d, J=14.7 Hz, 9H), 1.02–1.06 (m, 3H); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 134.9, 134.1, 133.7, 133.6, 133.4, 131.9, 131.8, 130.6, 130.1, 129.4, 129.3, 129.0, 128.6, 128.5, 128.1, 127.9, 127.8, 127.1, 127.0, 126.5, 103.7 (t, J=8.0 Hz), 97.4 (t, J=8.0 Hz), 96.3 (t, J=7.7 Hz), 91.2, 68.1, 52.2 (t, J=17.0 Hz), 38.8 (d, J=9.6 Hz), 36.5, 35.5, 33.2, 32.8, 31.6, 31.4, 29.7, 28.8, 28.5 (d, J=9.0 Hz), 28.3 (d, J=4.6 Hz), 28.2 (d, J=6.0 Hz), 28.0 (d, J=8.5 Hz), 27.5 (d, J=8.7 Hz), 27.2 (d, J=3.9 Hz), 26.3, 26.0, 25.9 (d, J=15.1 Hz), 25.2, 25.1; ^{31}P NMR (CD_2Cl_2, 145 MHz) δ 21.72 (dd, J=59.8, 129.5 Hz), −6.09 (dd, J=59.9, 125.4 Hz); HRMS (ESI^+) calcd for $C_{46}H_{58}P_2Rh$ (cation) 775.3069, found 775.3003; HRMS (ESI^-) calcd for BF_4 (anion) 87.0029, found 87.0023.

*4.4.4. [Rh(cod)**1d**]BF_4 (**9d**)*

^{1}H NMR (CD_2Cl_2, 360 MHz) δ 8.10 (d, J=8.4 Hz, 1H), 7.91–7.99 (m, 3H), 7.70 (d, J=8.4 Hz, 1H), 7.43–7.50 (m, 3H), 7.14 (p, J=7.5 Hz, 2H), 7.02 (d, J=8.7 Hz, 1H), 6.71 (d, J=8.7 Hz, 1H), 5.92 (t, J=8.1 Hz, 2H), 5.47 (t, J=14.7 Hz, 1H), 5.43 (s, 1H), 5.04 (s, 1H), 3.29–3.40 (m, 2H), 2.43–2.52 (m, 4H), 2.11–2.27 (m, 4H), 1.56 (d, J=13.3 Hz, 9H), 1.19 (d, J=14.2 Hz, 9H), 0.46 (s, 9H); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ 135.9, 135.8, 134.4 (d, J=2.0 Hz), 134.3, 134.2, 133.3, 131.4, 130.6, 130.5, 130.4, 130.3, 128.9, 128.5, 128.4, 128.2 (d, J=3.6 Hz), 127.9, 127.3, 127.0, 126.6, 126.5, 104.0 (t, J=7.0 Hz), 98.9 (dd, J=6.5, 10.1 Hz), 96.5 (t, J=7.4 Hz), 91.7 (dd, J=6.8, 11.0 Hz), 56.8 (d, J=13.9 Hz), 41.7 (d, J=4.1 Hz), 39.3, 37.9, 32.6, 32.1, 31.9 (d, J=4.3 Hz), 30.9, 28.7 (d, J=3.9 Hz), 28.4, 28.0; ^{31}P NMR (CD_2Cl_2, 145 MHz) δ 36.26 (dd, J=36.5, 127.3 Hz), 26.32 (dd, J=36.3, 133.4 Hz); HRMS (ESI^+) calcd for $C_{42}H_{54}P_2Rh$ (cation) 723.2697, found 723.2756; HRMS (ESI^-) calcd for BF_4 (anion) 87.0029, found 87.0019.

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References and notes

1. (a) Izumi, Y.; Tai, A. *Stereo-differentiating Reactions: The Nature of Asymmetric Reactions*; Academic: New York, NY, 1977; (b) *Asymmetric Catalysis*; Bosnich, B., Ed.; Martinus Nijhoff: New York, NY, 1986; (c) *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, NY, 1993; (d) Brunner, H.; Zettlmeier, W. *Handbook of Enantioselective Catalysis*; VCH: Weinheim, 1993; (e) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, NY, 1994; (f) *Chiral Reactions in Heterogeneous Catalysis*; Jannes, G., Dubois, V., Eds.; Plenum: New York, NY, 1995; (g) *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, 1996; Vols. 1 and 2; (h) *Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, 1998; Vols. 1 and 2; (i) *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 1999; Vols. 1–3; (j) *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley-VCH: New York, NY, 2000.
2. (a) Noyori, R.; Kitamura, M. *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer: Berlin, 1989; Vol. 5, p 115; (b) Takaya, H.; Ohta, T.; Noyori, R. *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, NY, 1993; p 1; (c) Ohkuma, T.; Noyori, R. *Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 2, p 25.
3. (a) Knowles, W. S.; Sabacky, M. J. *J. Chem. Soc., Chem. Commun.* **1968**, 1445; (b) Horner, L.; Siegel, H.; Büthe, H. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 941.
4. (a) Imamoto, T.; Watanabe, J.; Wada, Y.; Masuda, H.; Yamada, H.; Tsuruta, H.; Matsukawa, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **1998**, *120*, 1635; (b) Gridnev, I. D.; Yamanoi, Y.; Higashi, N.; Tsuruta, H.; Yasutake, M.; Imamoto, T. *Adv. Synth. Catal.* **2001**, *343*, 118.
5. (a) Tang, W.; Zhang, X. *Angew. Chem., Int. Ed.* **2002**, *41*, 1612; (b) Tang, W.; Zhang, X. *Org. Lett.* **2002**, *4*, 4159; (c) Tang, W.; Liu, D.; Zhang, X. *Org. Lett.* **2003**, *5*, 205.
6. Tang, W.; Wang, W.; Chi, Y.; Zhang, X. *Angew. Chem., Int. Ed.* **2003**, *42*, 3509.
7. Hoge, G.; Wu, H.-P.; Kissel, W. S.; Pflum, D. A.; Greene, D. J.; Bao, J. *J. Am. Chem. Soc.* **2004**, *126*, 5966.
8. (a) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Kazuhiko, S. *J. Am. Chem. Soc.* **1990**, *112*, 5244; (b) Juge, S.; Stephan, M.; Laffitte, J. A.; Genet, J. P. *Tetrahedron Lett.* **1990**, *31*, 6357; (c) Corey, E. J.; Chen, Z.; Tanoury, G. J. *J. Am. Chem. Soc.* **1993**, *115*, 11000; (d) Pietrusiewicz, K. M.; Zablocka, M. *Chem. Rev.* **1994**, *94*, 1375; (e) Muci, A. R.; Campos, K. R.; Evans, D. A. *J. Am. Chem. Soc.* **1995**, *117*, 9075; (f) Ohff, M.; Holz, J.; Quirmbach, M.; Borner, A. *Synthesis* **1998**, 1391; (g) Wolfe, B.; Livinghouse, T. *J. Am. Chem. Soc.* **1998**, *120*, 5116; (h) Al-Masum, M.; Kumaraswamy, G.; Livinghouse, T. *J. Org. Chem.* **2000**, *65*, 4776; (i) Moncarz, J. R.; Laritcheva, N. F.; Glueck, D. S. *J. Am. Chem. Soc.* **2002**, *124*, 13356; (j) Leung, P.-H. *Acc. Chem. Res.* **2004**, *37*, 169.
9. Drexler, H.-J.; You, J.; Zhang, S.; Fischer, C.; Baumann, W.; Spannenberg, A.; Heller, D. *Org. Process Res. Dev.* **2003**, *7*, 355 and references cited therein.