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Synthesis of atropisomeric 5,5′-linked biphenyl bisaminophosphine ligands and their applications in asymmetric catalysis

Yong Jian Zhang [a], Hao Wei [b], Wanbin Zhang [a,*]

[a] School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, PR China
[b] Institute of Micro/Nano Science and Technology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, PR China

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ABSTRACT

Atropisomeric 5,5′-linked biphenyl bisaminophosphine ligands **2** has been synthesized. The axial chirality of this type of ligands can be retained by macro-ring strain produced from 5,5′-linkage of biphenyl even without 6,6′-substituents on biphenyls. The Rh complex of bisaminophosphine **2a** as a catalyst is effectively working in the asymmetric hydrogenation of methyl (*Z*)-2-acetamido-3-arylacrylates, however, for hydrogenation of arylenamide, the low enantioselectivity was observed. When the ligands applied to Pd-catalyzed allylic alkylation, it is found that ligand **2b** having a longer backbone linkage is a better ligand for enantioselection in the reaction.

1. Introduction

Chiral ligands have played a dominant role in the development of efficient transition metal-catalyzed asymmetric reactions. Thousands of chiral ligands have been developed and applied in various catalytic asymmetric reactions to produce enantiomerically pure compounds.[1] Among them, atropisomeric biaryl ligands, such as BINAP,[2] BINOL,[3] and boxax,[4] have been explored as effective skeletons for many transition metal-catalyzed asymmetric reactions.[5] Encouraged by great success of axially chiral bisphosphine ligand BINAP in asymmetric hydrogenation reactions, many bisphosphine ligands supported by an atropisomeric scaffold have been developed.[5] It was found that modulation of the steric and electronic properties of atropisomeric scaffold of the ligand could remarkably influence on their efficiency in asymmetric catalytic reactions. Recently, the steric design of the biaryl core has been extensively explored such as BIPHEMP,[6] MeO-BIPHEP,[6] TunePhos,[7] SEGPHOS,[8] SYNPHOS,[9] and DIFLUORPHOS.[10] In Ru-catalyzed asymmetric hydrogenation of β-keto esters, it was demonstrated that the ligand displayed a narrow dihedral angel of biaryl backbone showed better enantioselectivity.[11] However, the better enantioselectivity was obtained with increasing dihedral angel of biaryl core in Pd-catalyzed asymmetric allylic alkylation.[12] It is obvious that subtle changes in steric property of chiral ligands can lead to dramatic variations in efficiency for different asymmetric reactions. Most recently, we developed novel atropisomeric framework **1** (Fig. 1),[13] in which the biphenyl has only two coordinating groups next to the axis, and the axial chirality of the ligand can be retained by steric hindrance of two bulky coordinating groups and macro-ring strain produced from 5,5′-linkage of biphenyls even without 6,6′-substituents. The modulation of the length of the backbone carbon chain could control the conformational flexibility of the metal chelate rings formed with atropisomeric ligands to provide more suitable chiral environment for asymmetric catalysis. In our initial study, we found that the bisoxazolines[13a] and bismethylenephosphines[13b] with atropisomeric framework **1** are provided with stable axial chirality at appropriate temperature, and they can be effectively applied in Pd(II)-catalyzed asymmetric Wacker-type cyclization of 2-allylphenols and Rh(I)-catalyzed asymmetric hydrogenation of dehydroamino acids, respectively.

Most effort on asymmetric catalysis has been focused on the use of transition-metal catalysts containing chiral phosphine ligands over the last three decades.[1] Recently, it has been shown that some of the results obtained with chiral phosphinite,[14] phosphite,[15] phosphonite[16] or phosphoramidite[17] ligand can match those

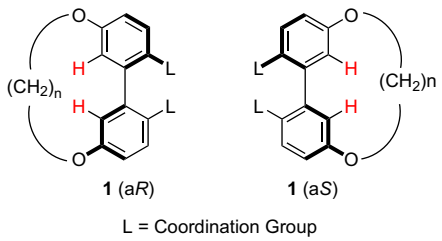

Figure 1. Atropisomeric ligands with a 5,5′-linkage of biphenyl.

* Corresponding author. Tel./fax: +86 21 5474 3265.
E-mail address: wanbin@sjtu.edu.cn (W. Zhang).

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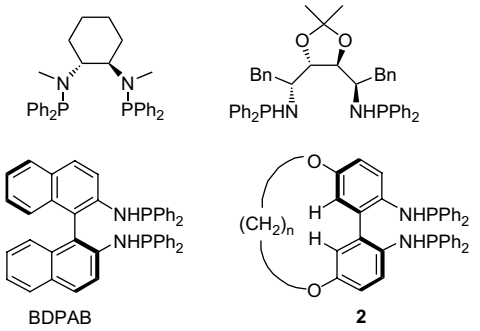
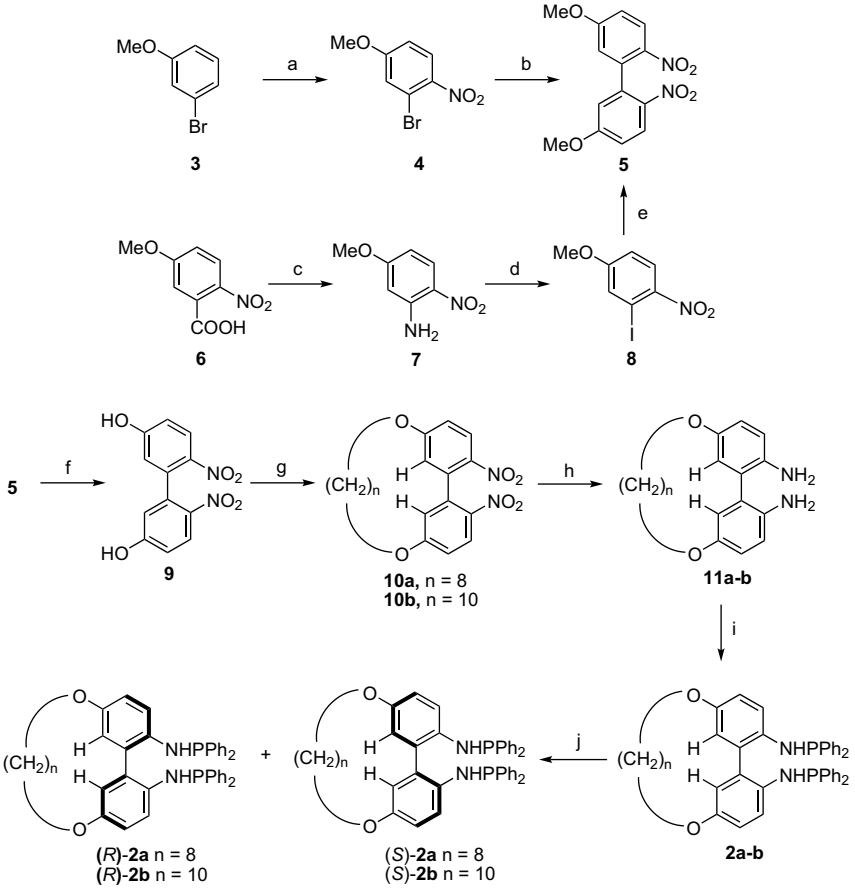


Figure 2. Bisaminophosphine ligands.

obtained by using phosphine ligands in catalytic asymmetric hydrogenation. Chiral aminophosphines, which can easily synthesize from chiral amines, have been widely used as ligands in the preparation of metallic complexes and application in catalytic asymmetric reactions.[18] Among them, the easily prepared C_2-symmetric bisaminophosphine ligands (Fig. 2) were also found to be effective ligands for transition metal-catalyzed asymmetric reactions.[19] For example, bisaminophosphines (BDPAB) with binaphthyl have effectively been applied in asymmetric hydrogenation of dehydroamino acid derivatives[19b] and enamides.[19d] Herein we wish to report synthesis of novel bisaminophosphine ligands with our atropisomeric framework **1**, 2,2′-bis(diphenylphosphinoamino)-5,5′-(polymethylenedioxy)-1,1′-biphenyls **2**,[20] and their application in Rh-catalyzed asymmetric hydrogenation of dehydroamino acid derivatives and arylenamide, and Pd-catalyzed asymmetric allylic alkylation.

2. Results and discussion

Bisaminophosphine ligands **2** could be readily prepared from 2,2′-dinitro-5,5′-dimethoxybiphenyl (**5**) as illustrated in Scheme 1. For synthesis of biphenyl compound **5**, 3-bromoanisole (**3**) was initially chosen as a starting material. Nitration of 3-bromoanisole afforded a mixture of desired 3-bromo-4-nitroanisole (**4**) and byproduct 5-bromo-2-nitroansole. Compound **4** can be isolated by column chromatography in only 32% yield. Ullman coupling of **4** with activated copper powder furnished the biphenyl skeleton **5** in 78% yield. To more effectively prepare compound **5**, the synthetic route was modified from commercially available compound, 4-methoxy-2-nitrobenzoic acid (**6**) as a starting material. Curtius rearrangement of benzoic acid **6** furnished 5-methoxy-2-nitroaniline (**7**) in 97% yield. Diazotization of compound **7** followed by iodination with potassium iodide gave 3-iodo-4-nitroanisole (**8**) (93% yield), which was then converted to biphenyl compound **5** by Ullman coupling in 90% yield. Demethylation of **5** with aluminum chloride and 1-dodecanethiol afforded biphenol compound **9** in 79% yield. Cyclization of biphenol **9** with 1,8-dibromooctane and 1,10-dibromodecane in the presence of potassium carbonate in DMF led to the key intermediates **10a** and **10b** in 58% and 55% yields, respectively. Straightforward reduction of **10a** with Pd–C under 5 atm of hydrogen gave quantitatively biphenyldiamine **11a**. Then, we tried optical resolution of biphenyldiamine **11a** to obtain optically pure diamine compound, however, all attempts in



Scheme 1. Reagents and conditions: (a) HNO_3–H_2SO_4, 32%; (b) Cu, 78%; (c) (i) $SOCl_2$, (ii) NaN_3, (iii) AcOH, 97%; (d) 50% H_2SO_4, $NaNO_2$, then KI, 93%; (e) Cu, 90%; (f) $AlCl_3$, 1-dodecanethiol, CH_2Cl_2, 79%; (g) $Br(CH_2)_nBr$, K_2CO_3, DMF; for **10a**, 58%; for **10b**, 55%; (h) H_2, Pd–C, EtOAc; for **11a**, 100%; for **11b**, 99%; (i) $ClPPh_2$, Et_3N, CH_2Cl_2; for **2a**, 81%; for **2b**, 79%; (j) chiral preparative HPLC, a Daicel Chiralcel AD-H column, for **2a**, 42%; for **2b**, 39%.

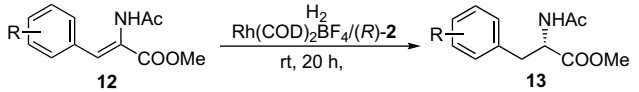
resolution of **11a** failed. The reaction of racemic biphenyldiamine **11a** with chlorodiphenylphosphine in the presence of triethylamine furnished racemic bisaminophosphine **2a** in 81% yield. The optical separation of racemic **2a** by chiral preparative HPLC using a Daicel Chiralcel AD-H column afforded, respectively, enantiomerically pure (>99% ee) (+)-**2a** and (−)-**2a** in 42% yield. In the same way, the optically pure aminophosphine ligand **2b** was prepared from 5,5′-decamethylenedioxy-biphenyl-2,2′-dinitrate (**10b**) in 31% overall yield. The sense of axial chirality of **2a** was determined by the major *Cotton* effects (CEs) in the CD spectra. The CD curve of (−)-**2a** displayed negative CE at 237.0 nm. This signed feature is the characteristic of (*R*)-configuration at chiral axis, which was in contrast with the spectra in the literature of axially chiral biphenyl compounds.[21]

To evaluate the effectiveness of our atropisomeric bisaminophophine ligands **2** in catalytic asymmetric reactions, we first chose Rh-catalyzed asymmetric hydrogenation of methyl (*Z*)-α-acetamidocinnamate (**12a**) as standard test reaction. The hydrogenation reaction was catalyzed by 1 mol % of the Rh(I)–(*R*)-**2a** complex generated in situ by mixing $Rh(COD)_2BF_4$ with bisaminophosphine (*R*)-**2a** in methanol at room temperature. It was found that the catalytic efficiency largely depended on the hydrogen pressure. As shown in Table 1, the hydrogenation reaction showed higher catalytic activity with enhancement of the hydrogen pressure (entries 1–4). The enantioselectivity also enhanced with the hydrogen pressure increasing from 1 to 3 atm (from 91.4% to 92.1% ee, entries 1 and 2). However, further raising the hydrogen pressure, the enantioselectivity remarkably decreased (entries 3 and 4). With (*R*)-**2b** as a ligand, which had decamethylenedioxy bridge, the enantioselectivity decreased to 87.1% ee under 3 atm of hydrogen pressure (entry 5). It may demonstrate that the shorter 5,5′-linkage of the ligand backbone could improve conformational rigidity, which may be beneficial to enantioselection for the hydrogenation reaction. The reaction medium also affects the catalytic activity and enantioselectivity in the hydrogenation reaction (entries 6–9). The highest enantioselectivity (94.4% ee) was obtained in methylene chloride under 3 atm of hydrogen pressure (entry 7). With optimization reaction conditions in hands, we have performed asymmetric hydrogenations of various methyl (*Z*)-2-acetamido-3-arylacrylates **12** catalyzed by Rh(I)–(*R*)-**2a** complex. A variety of substrates **12** can be hydrogenated to produce the corresponding α-amino ester derivatives **13** in quantitative conversions with high enantioselectivities (entries 10–16). The electronic and steric nature of the phenyl ring of the substrate had a little influence on the catalytic activity and enantioselectivity in the hydrogenation reactions (91.3–95.3% ee).

Inspired by initial success in hydrogenation reaction, our next goal was to extend the scope of atropisomeric bisaminophosphine ligands to arylenamide as a hydrogenated substrate.[23] The hydrogenation reaction of *N*-acetyl-α-phenylenamide (**14**) was catalyzed by 1 mol % of the Rh(I)–(*S*)-**2a** complex generated in situ by mixing $Rh(COD)_2BF_4$ with bisaminophosphine (*S*)-**2a** in methylene chloride at room temperature for 24 h. As shown in Table 2, it was found that the reaction required correspondingly high hydrogen press to accomplish well (entries 1–4), and low enatioselectivity (45.3% ee) was obtained. Using decamethylenedioxy linked bisaminophosphine **2b** as a ligand, the enantioselectivity was slightly decreased (entry 4). Further optimization with varying reaction solvent, the enantioselectivity could not be improved significantly (entries 6–9).

Finally, the atropisomeric bisaminophosphine ligands **2** were applied in Pd-catalyzed asymmetric allylic alkylation, which is one of the most important asymmetric C–C bond forming reactions.[24] We chose the reaction of 1,3-diphenylpropenyl acetate **16** with dimethyl malonate, the standard test reaction for asymmetric allylic alkylation. Under the standard reaction conditions: catalyst generated in situ by mixing 2.5 mol % of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and 6.0 mol % of ligand (*S*)-**2**; a mixture of *N*,*O*-bis(trimethylsilyl)-acetamide (BSA) and LiOAc in methylene chloride, the alkylated product **17** was afforded in high yields (>95%). As shown in Table 3, in contrast with hydrogenation reaction, the better enantioselectivity was observed using ligand (*S*)-**2b**, which has longer backbone linkage (entries 1 and 2). Indeed, it was found by Trost and Van Vranken that Pd–bisphosphine catalyst having the larger P–Pd–P bite angle lead to better enantioselectivity in asymmetric allylic alkylation.[25] It could be rationalized that, therefore, the catalyst Pd–(*S*)-**2b**, which having a larger P–Pd–P bite angle comparing with that of Pd–(*S*)-**2a** due to its longer backbone linkage, is conducive to enantioselection in alkylation reaction. The reaction solvent also affects the enantioselectivity in the reaction (entries 2–

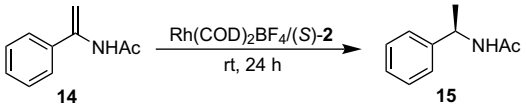
Table 1
Rh-catalyzed asymmetric hydrogenation of methyl (*Z*)-α-acetamidocinnamate using bisaminophosphines (*R*)-**2** as ligands[a]



Entry	Ligand	**12**, R	H_2 press (atm)	Solvent	Conv.[b] (%)	ee[c] (%)
1	**2a**	**12a**, H	1	MeOH	85	91.4
2	**2a**	**12a**, H	3	MeOH	99	92.1
3	**2a**	**12a**, H	5	MeOH	100	83.8
4	**2a**	**12a**, H	10	MeOH	100	84.3
5	**2b**	**12a**, H	3	MeOH	100	87.1
6	**2a**	**12a**, H	3	IPA	100	92.4
7	**2a**	**12a**, H	3	THF	100	94.1
8	**2a**	**12a**, H	3	CH_2Cl_2	100	94.4
9	**2a**	**12a**, H	3	Acetone	91.7	84.0
10	**2a**	**12b**, *p*-Me	3	CH_2Cl_2	100	94.4
11	**2a**	**12c**, *p*-OMe	3	CH_2Cl_2	100	95.3
12	**2a**	**12d**, *p*-Cl	3	CH_2Cl_2	100	95.1
13	**2a**	**12e**, *p*-F	3	CH_2Cl_2	100	94.3
14	**2a**	**12f**, *p*-Br	3	CH_2Cl_2	100	93.4
15	**2a**	**12g**, *o*-Cl	3	CH_2Cl_2	100	92.1
16	**2a**	**12h**, *m*-Cl	3	CH_2Cl_2	100	91.3

[a] All reactions were carried out at room temperature for 20 h. The catalyst was prepared in situ from $Rh(COD)_2BF_4$ and ligand (substrate/Rh/ligand=100:1:1.1).
[b] Determined by ^1H NMR analysis.
[c] The enantiomeric excesses were determined by chiral HPLC using a Daicel Chiralcel OD-H column. The *S* absolute configurations were assigned by comparison of optical rotations with the known reported data.[22]

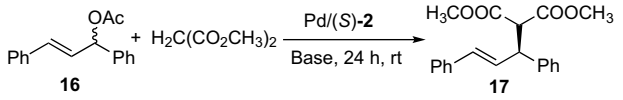
Table 2
Rh-catalyzed asymmetric hydrogenation of *N*-acetyl-α-phenylamide using bisaminophosphines (*S*)-**2** as ligands[a]



Entry	Ligand	H_2 press (atm)	Solvent	Conv.[b] (%)	ee[c] (%)
1	**2a**	1	CH_2Cl_2	69.4	44.7
2	**2a**	5	CH_2Cl_2	86.9	43.2
3	**2a**	10	CH_2Cl_2	97.1	45.3
4	**2a**	40	CH_2Cl_2	100	39.1
5	**2b**	10	CH_2Cl_2	100	43.9
6	**2a**	10	MeOH	100	41.7
7	**2a**	10	IPA	100	43.1
8	**2a**	10	THF	100	48.7
9	**2a**	10	Acetone	100	33.2

[a] All reactions were carried out at room temperature for 24 h. The catalyst was prepared in situ from $Rh(COD)_2BF_4$ and ligand (substrate/Rh/ligand=100:1:1.1).
[b] Determined by ^1H NMR analysis.
[c] The enantiomeric excesses were determined by chiral HPLC using a Daicel Chiralcel AD-H column. The *R* absolute configurations were assigned by comparison of optical rotations with the known reported data.[23]

Table 3
Pd-catalyzed asymmetric allylic alkylation of 1,3-diphenylpropenyl acetate with dimethyl malonate[a]



Entry	Ligand	Solvent	Base/additive	ee[b] (%)
1	**2a**	CH_2Cl_2	BSA/LiOAc	54.1
2	**2b**	CH_2Cl_2	BSA/LiOAc	58.4
3	**2b**	THF	BSA/LiOAc	61.7
4	**2b**	Toluene	BSA/LiOAc	34.7
5	**2b**	DMF	BSA/LiOAc	51.9
6	**2b**	Et_2O	BSA/LiOAc	52.8
7	**2b**	THF	BSA/NaOAc	53.3
8	**2b**	THF	BSA/KOAc	55.6
9	**2b**	THF	NaH	51.4

[a] Molecular ratio: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/ligand/substrate/BSA/$H_2C(CO_2Me)_2$=2.5:6.0:100:300:300. Reactions were conducted at room temperature. The catalyst was prepared by mixing $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with ligands in solvent at room temperature for 1 h before use. All reactions gave above 95% isolated yields.

[b] The enantiomeric excesses were determined by chiral HPLC using a Daicel Chiralcel OD-H column. The *S* absolute configurations were assigned by comparison of optical rotations with the known reported data.[26]

6). Highest enantioselectivity (61.7% ee) was obtained in THF (entry 3). The reaction enantioselectivities could not be improved by altering other reaction parameters such as base or additive (entries 7–9).

3. Conclusion

In summary, a new type of atropisomeric 5,5′-linked biphenyl bisaminophosphine ligands **2** has been synthesized. It was demonstrated that the axial chirality of this type of ligands can be retained by macro-ring strain produced from 5,5′-linkage of biphenyl. The Rh complex of bisaminophosphine **2a** as a catalyst is effectively working in the asymmetric hydrogenation of methyl (*Z*)-2-acetamido-3-arylacrylates **12**, however, for hydrogenation of arylenamide, the low enantioselectivity was observed. When the ligands applied to Pd-catalyzed allylic alkylation, it is found that ligand **2b** having a longer backbone linkage is a better ligand for enantioselection in the reaction. Further study of development and application of this type of atropisomeric ligands are in progress.

4. Experimental

4.1. General experimental conditions

All air- and moisture-sensitive manipulations were carried out with standard Schelenk techniques under nitrogen. The reaction solvents were distilled prior to use (toluene and dichloromethane were distilled from CaH_2, THF was distilled from Na). The commercially available reagents were used without further purification. Column chromatography was run on silica gel (100–200 mesh). Melting points are uncorrected. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Varian MERCURY plus-400 spectrometer. The ee values were determined by HPLC using a Daicel Chiralcel OD-H column and a Daicel Chiralpak AD-H column. Optical rotation (concentration *c* given as g/100 mL) and CD spectrum were measured at the Shanghai Institute of Organic Chemistry, Chinese Academic of Science. Elemental analysis was performed at the Instrumental Analysis Center of Shanghai Jiao Tong University. HRMS was performed on a Micromass LCTTM at the Analysis and Research Center of East China University of Science and Technology.

4.2. 3-Bromo-4-nitroanisole (4)

Concentrated sulfuric acid (4 mL) was added dropwise to nitric acid (70%, 5 mL) at 0 °C. To this cooled solution, 3-bromoanisole (4.1 g, 21.8 mmol) was added dropwise. The reaction mixture was then stirred at 40 °C for 5 h. After cooling, the mixture was poured into 100 mL of cooled water and extracted with ethyl acetate (50 mL×3). The organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography to give white solid **4**[26] (1.6 g, 32%). Mp 43–45 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.89 (3H, s), 6.91 (1H, dd, *J*=9.1, 2.7 Hz), 7.21 (1H, d, *J*=2.7 Hz), 7.98 (1H, d, *J*=9.1 Hz).

4.3. 5,5′-Dimethoxy-2,2′-dinitrobiphenyl (5)

The mixture of compound **4** (13.2 g, 56.9 mmol) and activated copper powder (18.2 g, 284.4 mmol) was stirred at 170 °C for 12 h. The residue was cooled, and CH_2Cl_2 (250 mL) was added. Filtered and washed with CH_2Cl_2 (50 mL×4) and the filtrate was concentrated. The obtained residue was recrystallized with acetonitrile to give yellow solid **5** (6.8 g, 78%). Mp 142–144 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.28 (d, *J*=8.8 Hz, 2H), 7.00 (dd, *J*=8.8, 2.8 Hz, 2H), 6.70 (d, *J*=2.8 Hz, 2H), 3.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.46, 140.17, 137.57, 127.60, 115.87, 113.45, 56.17. HRMS (Micromass LCT) calcd for $C_{14}H_{13}N_2O_6$ $(M+H)^+$: 305.0774; found: 305.0779.

4.4. 5-Methoxy-2-nitroaniline (7)

A solution of 5-methoxy-2-nitrobenzoic acid (5.0 g, 25.4 mmol) and thionyl chloride (10 mL) in benzene (20 mL) was refluxed for 5 h. The solution was concentrated and then dissolved in acetone (50 mL). A solution of NaN_3 (10.0 g, 154.0 mmol) in water (30 mL) was added dropwise at 0 °C. The mixture was stirred at the same temperature for 2 h, and poured into cooled water (300 mL) and extracted with CH_2Cl_2 (100 mL×4). The solvent was concentrated and the obtained residue was dissolved in acetic acid (30 mL) and water (10 mL). The reaction mixture was refluxed overnight. To this mixture, saturated aqueous $NaHCO_3$ (80 mL) was added dropwise at room temperature and stirred for 1 h. The obtained precipitate was filtered, and washed with water and dried under vacuum to give **7**[27] (4.1 g, 97%) as a yellow solid. Mp 128–130 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07 (d, *J*=9.5 Hz, 1H), 6.28 (dd, *J*=9.5, 2.6 Hz, 1H), 6.21 (br s, 2H), 6.15 (d, *J*=2.6 Hz, 1H), 3.83 (s, 3H).

4.5. 3-Iodo-4-nitroanisole (8)

To a solution of 5-methoxy-2-nitroaniline (0.3 g, 1.8 mmol) in sulfuric acid (50%, 10 mL), a solution of $NaNO_2$ in concentrated sulfuric acid (4 mL) was added at 0 °C and stirred at the same temperature for 2 h. The diazonium salt solution was added dropwise to an ice-water solution of KI (0.45 g, 2.7 mmol) at 0 °C, and the resulting mixture was stirred overnight. The solution was made basic with NaOH (aq, 10%), and extracted with CH_2Cl_2 (30 mL×3) and washed with brine (50 mL). The organic layer was dried over $MgSO_4$, filtered, and the solvent was removed at reduced pressure to give 8[28] (0.47 g, 93%) as a yellow solid. Mp 65 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 (d, *J*=9.0 Hz, 1H), 7.52 (d, *J*=2.5 Hz, 1H), 6.97 (dd, *J*=9.0, 2.5 Hz, 1H), 3.85 (s, 3H).

4.6. 5,5′-Dihydroxy-2,2′-dinitrobiphenyl (9)

A solution of compound **5** (6.8 g, 22.4 mmol) in CH_2Cl_2 (150 mL) was added dropwise to the mixture prepared from 1-dodecanethiol (54.3 g, 268.2 mmol) and aluminum trichloride (17.9 g, 134.1 mmol) in CH_2Cl_2 (150 mL) at room temperature. The mixture was stirred overnight at room temperature, and then poured into

ice-water, extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. Finally, the obtained residue was purified by column chromatography (eluent: ethyl acetate and petroleum ether) to give brown solid **9** (4.9 g, 79%). Mp 214–215 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.10 (s, 2H), 8.12 (d, J=8.8 Hz, 2H), 6.93 (dd, J=8.8, 2.4 Hz, 2H), 6.61 (d, J=2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.25, 138.96, 138.20, 128.28, 117.53, 115.88. HRMS (Micromass LCT) calcd for $C_{12}H_9N_2O_6$ $(M+H)^+$: 277.0461; found: 277.0470.

4.7. 2,2′-Dinitro-5,5′-(octamethylenedioxy)-1,1′-biphenyl (10a)

To a suspension of anhydrous potassium carbonate (12.3 g, 88.7 mmol) in DMF (100 mL), a solution of compound **9** (4.9 g, 17.7 mmol) and 1,8-dibromooctane (4.8 g, 17.7 mmol) in DMF (50 mL) was added dropwise at 80 °C for 5 h. The mixture was stirred further at 80 °C for 24 h. The reaction mixture was filtered, and the filtrate was concentrated in vacuo. The resulting residue was dissolved in CH_2Cl_2 (50 mL), washed with water and brine, dried over $MgSO_4$, concentrated in vacuo, then purified by chromatography on silica gel to give product **10a** as a brown solid (4.0 g, 58%). Mp 192–196 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.22 (d, J=9.2 Hz, 2H), 7.00 (dd, J=9.2, 2.8 Hz, 2H), 6.75 (d, J=2.8 Hz, 2H), 4.39 (m, 2H), 4.20 (m, 2H), 1.95 (m, 2H), 1.64 (m, 2H), 1.42–1.30 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.10, 139.73, 138.16, 127.53, 118.05, 113.36, 66.73, 28.78, 28.62, 24.76. HRMS (Micromass LCT) calcd for $C_{20}H_{23}N_2O_6$ $(M+H)^+$: 387.1556; found: 387.1558.

4.8. 2,2′-Dinitro-5,5′-(decamethylenedioxy)-1,1′-biphenyl (10b)

Product **10b** was obtained as a brown solid in 55% yield following the procedure for synthesis of **10a**. Mp 153–156 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.19 (d, J=9.6 Hz, 2H), 6.96 (dd, J=9.6, 2.0 Hz, 2H), 6.71 (d, J=2.0 Hz, 2H), 4.23 (m, 2H), 4.13 (m, 2H), 1.81 (m, 2H), 1.66 (m, 2H), 1.36–1.24 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.74, 139.50, 137.91, 127.28, 115.69, 115.55, 68.71, 28.48, 28.36, 27.32, 24.91. HRMS (Micromass LCT) calcd for $C_{22}H_{27}N_2O_6$ $(M+H)^+$: 415.1869; found: 415.1870.

4.9. 2,2′-Diamino-5,5′-(octamethylenedioxy)-1,1′-biphenyl (11a)

The mixture of compound **10a** (3.4 g, 8.8 mmol) and Pd (10% on carbon, 0.4 g) was suspended in ethyl acetate (50 mL), and was stirred at room temperature under H_2 (5 atm) for 12 h. The solution was filtered through a bed of Celite to remove the catalyst and the filtrate was evaporated to dryness to afford product **11a** (2.9 g, 100%). Mp 161–163 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.82–6.75 (m, 6H), 4.20 (m, 2H), 4.00 (m, 2H), 1.89 (m, 2H), 1.62 (m, 2H), 1.52–1.32 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.81, 137.12, 126.51, 118.99, 118.09, 116.69, 67.72, 28.77, 27.85, 24.90. HRMS (Micromass LCT) calcd for $C_{20}H_{27}N_2O_2$ $(M+H)^+$: 327.2073; found: 327.2074.

4.10. 2,2′-Diamino-5,5′-(decamethylenedioxy)-1,1′-biphenyl (11b)

Product **11b** was obtained in 99% yield following the procedure for synthesis of **11a**. Mp 138–139 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.81–6.69 (m, 6H), 4.14 (m, 2H), 3.97 (m, 2H), 1.82 (m, 2H), 1.63 (m, 2H), 1.43–1.24 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.89, 137.53, 126.37, 117.94, 117.76, 117.44, 69.22, 28.65, 28.44, 28.01, 25.18. HRMS (Micromass LCT) calcd for $C_{22}H_{30}N_2O_2$: 354.2307; found: 354.2307.

4.11. 2,2′-Bis(diphenylphosphinoamino)-5,5′-(octamethylenedioxy)-1,1′-biphenyl (2a)

Chlorodiphenylphosphine (3.0 mL, 16.8 mmol) and Et_3N (8.9 mL, 61.6 mmol) were added to a solution of compound **11a** (2.5 g, 7.7 mmol) in anhydrous CH_2Cl_2 (50 mL), and the mixture was stirred for 24 h under reflux. The solution was cooled, concentrated under reduced pressure, and EtOAc (50 mL) was added. The precipitate was filtered and washed with EtOAc (50 mL). The solvent was removed in vacuo and the crude residue was purified by chromatography on silica gel to give product **2a** as a white solid (4.3 g, 81%). Mp 217–218 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.23 (m, 22H), 6.86 (dd, J=8.8, 2.8 Hz, 2H), 6.75 (d, J=9.2, 2.8 Hz, 2H), 4.55 (d, J_{P-H}=6 Hz, 2H), 4.20 (m, 2H), 4.05 (m, 2H), 1.89 (m, 2H), 1.62 (m, 2H), 1.48–1.29 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.33, 137.55, 137.40, 131.34, 131.13, 130.88, 130.67, 128.91, 128.89, 128.54, 128.49, 128.47, 128.43, 119.08, 118.74, 118.55, 116.15, 67.16, 28.32, 27.99, 24.95; ^{31}P NMR ($CDCl_3$, 161 MHz) δ 34.27. HRMS (Micromass LCT) calcd for $C_{44}H_{43}N_2O_2P_2$ $(M+H)^+$: 693.2800; found: 693.2808.

4.12. (*R*)-(−)-2,2′-Bis(diphenylphosphinoamino)-5,5′-(octamethylenedioxy)-1,1′-biphenyl [(*R*)-(−)-2a]

$[\alpha]_D^{25}$ −32.8 (c 1, $CHCl_3$); all other analytical data were identical to those of **2a**.

4.13. (*S*)-(+)-2,2′-Bis(diphenylphosphinoamino)-5,5′-(octamethylenedioxy)-1,1′-biphenyl [(*S*)-(+)-2a]

$[\alpha]_D^{25}$ +31.9 (c 1, $CHCl_3$); all other analytical data were identical to those of **2a**.

4.14. 2,2′-Bis(diphenylphosphinoamino)-5,5′-(decamethylenedioxy)-1,1′-biphenyl (2b)

Product **2b** was obtained as a white solid in 79% yield following the procedure for synthesis of **2a**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25 (m, 22H), 6.87 (dd, J=8.8, 2.8 Hz, 2H), 6.73 (d, J=9.2, 2.8 Hz, 2H), 4.44 (d, J_{P-H}=6.4 Hz, 2H), 4.12 (m, 2H), 4.00 (m, 2H), 1.85 (m, 2H), 1.61 (m, 2H), 1.41–1.29 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.44, 137.98, 137.80, 131.14, 130.93, 130.91, 130.71, 128.93, 128.85, 128.52, 128.45, 118.36, 118.07, 117.87, 117.10, 68.96, 28.71, 28.65, 28.02, 25.10; ^{31}P NMR ($CDCl_3$, 161 MHz): δ 32.86. HRMS (Micromass LCT) calcd for $C_{46}H_{47}N_2O_2P_2$ $(M+H)^+$: 721.3113; found: 721.3152.

4.15. (*R*)-(−)-2,2′-Bis(diphenylphosphinoamino)-5,5′-(decamethylenedioxy)-1,1′-biphenyl [(*R*)-(−)-2b]

$[\alpha]_D^{25}$ −37.5 (c 1, $CHCl_3$); all other analytical data were identical to those of **2b**.

4.16. (*S*)-(+)-2,2′-Bis(diphenylphosphinoamino)-5,5′-(decamethylenedioxy)-1,1′-biphenyl [(*S*)-(+)-2b]

$[\alpha]_D^{25}$ +39.7 (c 1, $CHCl_3$); all other analytical data were identical to those of **2b**.

4.17. General procedure for Rh(I)-catalyzed asymmetric hydrogenation (*Z*)-acetamido-3-arylacrylic acid derivatives

$[Rh(COD)_2]BF_4$ (0.01 mmol) and (*R*)-**2a** (0.012 mmol) were dissolved in degassed MeOH (2 mL) and stirred for 30 min to form a solution of [Rh(COD)(*R*)-**2a**]BF_4 catalyst for the asymmetric hydrogenation. Then a solution of substrate (1 mmol) in MeOH (2 mL) was added to a catalyst solution prepared above. The

hydrogenation was performed in stainless steel autoclave at room temperature under 3 atm of hydrogen for 20 h. The resulting solution was passed through a short silica gel column to remove the catalyst. The ee value and conversion of the product were measured by chiral HPLC and ^{1}H NMR spectroscopy without any further purification. The products of (*Z*)-acetamido-3-arylacrylic acid were converted to corresponding methyl ester for the determination of their ee value using chiral HPLC (a Daicel Chiralcel OD-H column, flow rate=0.5 mL/min, hexane/2-propanol (75:25), UV detector, 254 nm: t_R (*R*)=10.45 min, t_R (*S*)=12.31 min).

4.18. General procedure for Rh(I)-catalyzed asymmetric hydrogenation arylenamides

[Rh(COD)$_2$]BF$_4$ (0.01 mmol) and (*R*)-**2a** (0.012 mmol) were dissolved in degassed MeOH (2 mL) and stirred for 30 min to form a solution of [Rh(COD)(*R*)-**2a**]BF$_4$ catalyst for the asymmetric hydrogenation. Then a solution of substrate (1 mmol) in MeOH (2 mL) was added to a catalyst solution prepared above. The hydrogenation was performed in stainless steel autoclave at room temperature under 3 atm of hydrogen for 24 h. The resulting solution was passed through a short silica gel column to remove the catalyst. The ee value and conversion of the product were measured by chiral HPLC and ^{1}H NMR spectroscopy without any further purification. The products ee value using chiral HPLC (a Daicel Chiralcel AD-H column, flow rate=0.5 mL/min, hexane/2-propanol (90:10), UV detector, 254 nm: t_R (*S*)=10.45 min, t_R (*R*)=12.91 min).

4.19. General procedure for the palladium-catalyzed allylic alkylation of 1,3-diphenyl-2-propen-1-yl acetate

[Pd(η^3-C$_3$H$_5$)Cl]$_2$ (25.0 μmol) and (*S*)-**2** (60 μmol) were dissolved in degassed CH_2Cl_2 (2 mL) and stirred for 60 min to form a solution of [Pd–(*S*)-**2**] catalyst for allylic alkylation. Then a solution of substrate (1 mmol) and LiOAc (20 μmol) in CH_2Cl_2 (2 mL) added a catalyst solution prepared above. Then added 1,3-diphenyl-2-propen-1-yl acetate (3.00 mmol) and BSA (3.00 mmol). The reaction was conducted under nitrogen in solvent at room temperature for 24 h. The resulting solution was passed through a silica gel column to calculate yield. The ee value of the product was measured by chiral HPLC (a Daicel Chiralcel OD-H column, flow rate=0.5 mL/min, hexane/2-propanol (98:2), UV detector, 254 nm: t_R (*R*)=20.31 min, t_R (*S*)=21.78 min).

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References and notes

1. (a) Ojima, I. *Catalytic Asymmetric Synthesis*, 2nd ed.; Wiley-VCH: New York, NY, 2000; (b) Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H. *Comprehensive Asymmetric Catalysis*; Springer: Berlin, 1999; Vol. I–III; (c) Zhang, X. *Chem. Rev.* **2003**, *103*, 3029.
2. (a) Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932; (b) For review, see: Noyori, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2008.
3. For recent reviews, see: (a) Chen, Y.; Yekta, S.; Yudin, A. K. *Chem. Rev.* **2003**, *103*, 3155; (b) Brunel, J. M. *Chem. Rev.* **2005**, *105*, 857.
4. Uozumi, Y.; Kyota, H.; Kishi, E.; Kitayama, K.; Hayashi, T. *Tetrahedron: Asymmetry* **1996**, *7*, 1603.
5. For recent reviews, see: (a) McCarthy, M.; Guiry, P. J. *Tetrahedron* **2001**, *57*, 3809; (b) Che, C.-M.; Huang, J.-S. *Coord. Chem. Rev.* **2003**, *242*, 97; (c) Au-Yeung, T. T.-L.; Chan, S.-S.; Chan, A. S. C. *Adv. Synth. Catal.* **2003**, *345*, 537; (d) Shimizu, H.; Nagasaki, I.; Saito, T. *Tetrahedron* **2005**, *61*, 5405.
6. (a) Schmid, R.; Cereghetti, M.; Heiser, B.; Schönholzer, P.; Hansen, H.-J. *Helv. Chim. Acta* **1988**, *71*, 897; (b) Schmid, R.; Foricher, J.; Cereghetti, M.; Schönholzer, P. *Helv. Chim. Acta* **1991**, *74*, 370; (c) Schmid, R.; Broger, E. A.; Cereghetti, M.; Crameri, Y.; Foricher, J.; Lalonde, M.; Müller, R. K.; Scalone, M.; Schoettel, G.; Zutter, U. *Pure Appl. Chem.* **1996**, *68*, 131.
7. Zhang, Z.; Qian, H.; Longmire, J.; Zhang, X. *J. Org. Chem.* **2000**, *65*, 6223.
8. Saito, T.; Yokozawa, T.; Ishizaki, T.; Moroi, T.; Sayo, N.; Miura, T.; Kumobayashi, H. *Adv. Synth. Catal.* **2001**, *343*, 264.
9. (a) Pai, C. C.; Li, Y. M.; Zhou, Z. Y.; Chan, A. S. C. *Tetrahedron Lett.* **2002**, *43*, 2789; (b) Paule, S.; Jeulin, S.; Ratovelomanana-Vidal, V.; Genêt, J. P.; Champion, N.; Dellis, P. *Eur. J. Org. Chem.* **2003**, 1931.
10. Jeulin, S.; Paule, S.; Ratovelomanana-Vidal, V.; Genêt, J. P.; Champion, N.; Dellis, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 320.
11. Genêt, J.-P. *Acc. Chem. Res.* **2003**, *36*, 908.
12. Raghunath, M.; Zhang, X. *Tetrahedron Lett.* **2005**, *46*, 8213.
13. (a) Wang, F.; Zhang, Y. J.; Wei, H.; Zhang, J.; Zhang, W. *Tetrahedron Lett.* **2007**, *48*, 4083; (b) Wei, H.; Zhang, Y. J.; Wang, F.; Zhang, W. *Tetrahedron: Asymmetry* **2008**, *19*, 482.
14. (a) For review, see: Agbossou-Niedercorn, F.; Suisse, I. *Coord. Chem. Rev.* **2003**, *242*, 145; For recent examples, see: (b) Lam, K. H.; Xu, L.; Feng, L.; Fan, Q.-H.; Lam, F. L.; Lo, W.-H.; Chan, A. S. C. *Adv. Synth. Catal.* **2005**, *347*, 1755; (c) Zhou, Y.-G.; Tang, W.; Wang, W.-B.; Li, W.; Zhang, X. *J. Am. Chem. Soc.* **2002**, *124*, 4953; (d) Chan, A. S. C.; Hu, W. H.; Pai, C. C.; Lau, C. P.; Jiang, Y. Y.; Mi, A. Q.; Yan, M.; Sun, J.; Lou, R. L.; Deng, J. G. *J. Am. Chem. Soc.* **1997**, *119*, 9570.
15. For recent examples, see: (a) Huang, H.; Liu, X.; Chen, H.; Zheng, Z. *Tetrahedron: Asymmetry* **2005**, *16*, 693; (b) Hua, Z.; Vassar, V. C.; Ojima, I. *Org. Lett.* **2003**, *5*, 3831; (c) Hannen, P.; Militzer, H.-C.; Vogl, E. M.; Rampf, F. A. *Chem. Commun.* **2003**, 2210; (d) Reetz, M. T.; Mehler, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 3889; (e) Reetz, M. T.; Neugebauer, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 179.
16. For recent examples, see: (a) Gridnev, I. D.; Fan, C.; Pringle, P. G. *Chem. Commun.* **2007**, 1319; (b) Hou, G.-H.; Xie, J.-H.; Wang, L.-X.; Zhou, Q.-L. *J. Am. Chem. Soc.* **2006**, *128*, 11774; (c) Fu, Y.; Hou, G.-H.; Xie, J.-H.; Xing, L.; Wang, L.-X.; Zhou, Q.-L. *J. Org. Chem.* **2004**, *69*, 8157; (d) Reetz, M. T.; Mehler, G.; Meiswinkel, A. *Tetrahedron: Asymmetry* **2004**, *15*, 2165; (e) Zanotti-Gerosa, A.; Malan, C.; Herzberg, D. *Org. Lett.* **2001**, *3*, 3687.
17. (a) For review, see: Minnaard, A. J.; Feringa, B. L.; Lefort, L.; de Vries, J. G. *Acc. Chem. Res.* **2007**, *40*, 1267; For recent examples, see: (b) Huo, X.-H.; Xie, J.-H.; Wang, Q.-S.; Zhou, Q.-L. *Adv. Synth. Catal.* **2007**, *349*, 2477; (c) Giacomina, F.; Meetsma, A.; Panella, L.; Lefort, L.; de Vries, A. H. M.; de Vries, J. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 1497; (d) Liu, Y.; Ding, K. *J. Am. Chem. Soc.* **2005**, *127*, 10488; (e) Wu, S.; Zhang, W.; Zhang, Z.; Zhang, X. *Org. Lett.* **2004**, *6*, 3565; (f) Li, X.; Jia, X.; Lu, G.; Au-Yeung, T. T.-L.; Lam, K.-H.; Lo, T. W. H.; Chan, A. S. C. *Tetrahedron: Asymmetry* **2003**, *14*, 2687; (g) Pena, D.; Minnaard, A. J.; de Vries, J. G.; Feringa, B. L. *J. Am. Chem. Soc.* **2002**, *124*, 14552; (h) Hu, A.-G.; Fu, Y.; Xie, J.-H.; Zhou, H.; Wang, L.-X.; Zhou, Q.-L. *Angew. Chem., Int. Ed.* **2002**, *41*, 2348.
18. For recent reviews, see: (a) Bento-Garagorri, D.; Kirchner, K. *Acc. Chem. Res.* **2008**, *41*, 201; (b) Alajarín, M.; López-Leonardo, C.; Llamas-Lorente, P. *Top. Curr. Chem.* **2005**, *250*, 77.
19. For selected examples: (a) Chen, X.; Guo, R.; Li, Y.; Chen, G.; Yeung, C.-H.; Chan, A. S. C. *Tetrahedron: Asymmetry* **2004**, *15*, 213; (b) Guo, R.; Li, X.; Wu, J.; Kwok, W. H.; Chen, J.; Choi, M. C. K.; Chan, A. S. C. *Tetrahedron Lett.* **2002**, *43*, 6803; (c) Zhang, F.-Y.; Kowk, W. H.; Chan, A. S. C. *Tetrahedron: Asymmetry* **2001**, *12*, 2337; (d) Zhang, F.-Y.; Pai, C. C.; Chan, A. S. C. *J. Am. Chem. Soc.* **1998**, *120*, 5808; (e) Zhang, A.; Jiang, B. *Tetrahedron Lett.* **2001**, *42*, 1761; (f) Zhang, A.; Feng, Y.; Jiang, B. *Tetrahedron: Asymmetry* **2000**, *11*, 3123; (g) Miyano, S.; Nawa, M.; Mori, A.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1984**, 2171; (h) Onuma, K.; Ito, T.; Nakamura, A. *Bull Chem. Soc. Jpn.* **1980**, *53*, 2012; (i) Miyano, S.; Nawa, M.; Hashimoto, H. *Chem. Lett.* **1980**, 729; (j) Fiorini, M.; Giongo, G. M. *J. Mol. Catal.* **1980**, *7*, 411.
20. Part of this work has been communicated, see: Wei, H.; Zhang, Y. J.; Dai, Y.; Zhang, J.; Zhang, W. *Tetrahedron Lett.* **2008**, *49*, 4106.
21. Mislow, B. K.; Bunnenberg, E.; Records, R. *J. Am. Chem. Soc.* **1963**, *85*, 1342.
22. (a) Lee, S.-g.; Zhang, Y. J. *Tetrahedron: Asymmetry* **2002**, *13*, 1039; (b) Zhang, Y. J.; Kim, K. Y.; Park, J. H.; Song, C. E.; Lee, K.; Lah, M. S.; Lee, S.-g. *Adv. Synth. Catal.* **2005**, *347*, 563.
23. Recent examples for asymmetric hydrogenation of arylenamides: (a) Xie, J.-H.; Zhou, Q.-L. *Acc. Chem. Res.* **2008**, *41*, 581 and references therein; (b) Zhang, W.; Chi, Y.; Zhang, X. *Acc. Chem. Res.* **2007**, *40*, 1278 and references therein; (c) Hu, X.-P.; Zheng, Z. *Org. Lett.* **2004**, *6*, 3585; (d) Lee, S.-g.; Zhang, Y. J.; Song, C. E.; Lee, J. K.; Choi, J. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 847; (e) Gridnew, I. D.; Yasutake, M.; Higashi, N.; Imamoto, T. *J. Am. Chem. Soc.* **2001**, *123*, 5268; (f) Burk, M. J.; Wang, Y. M.; Lee, J. R. *J. Am. Chem. Soc.* **1996**, *118*, 5142.
24. For reviews, see: (a) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921; (b) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395; (c) Refs. 1a,b.
25. Trost, B. M.; Van Vranken, D. L. *J. Am. Chem. Soc.* **1993**, *115*, 444.
26. Younong, Y.; Sudhir, K. S.; Angela, L.; Tsai, K. L.; Leroy, F. L.; Edmond, J. L. *Bioorg. Med. Chem.* **2003**, *11*, 1475.
27. Hay, M. P.; Gamage, S. A.; Kovacs, M. S.; Pruijn, F. B.; Anderson, R. F.; Patterson, A. V.; Wilson, W. R.; Brown, J. M.; Denny, W. A. *J. Med. Chem.* **2003**, *46*, 169.
28. Dantale, S. W.; Soderberg, B. C. G. *Tetrahedron* **2003**, *59*, 5507.