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Axial [6,6′-(2,4-pentadioxy)]-1,1′-biphenyl-2,2′-diamine (PD-BIPHAM): practical synthesis and applications in asymmetric hydrogenation

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ABSTRACT

A rapid, reliable, and atom-economical procedure for the novel axially biphenyl diamine, (*R*,*R*,S_{ax})-PD-BIPHAM **1**, has been developed successfully by using highly efficient central-to-axial transformation strategy. The attractive feature of this methodology is that no tedious resolution was needed. The effectiveness of this new chiral skeleton was initially demonstrated by highly enantioselective hydrogenation of α-dehydroamino acid esters.

1. Introduction

Catalytic asymmetric reaction is one of the most powerful methods for the synthesis of enantiomerically enriched products, and ligand design based on chiral backbone plays a crucial role in this area.[1] Among many successful chiral skeletons, atropisomeric biaryl backbones, most notably 1,1′-binaphthalene derivatives (e.g., BINOL, BINAP, BINAM, and NOBIN),[2] occupy a prominent position in asymmetric synthesis (Fig. 1). 1,1′-Binaphthyl-2,2′-diamine (abbreviated to BINAM), the commercially available but restrictively expensive chiral binaphthalene diamine, and has found widespread uses in many metal-catalyzed[2d,3] or organo-catalyzed[4] asymmetric reactions in the past decades. Comparing to the widely used binaphthalene counterpart, much less attention has been paid to the similarly atropisomeric biphenyl backbond although the steric and electronic properties of such skeleton are more easily modified.[5] One biphenyl diamine, 6,6′-dimethyl-biphenyl-2,2′-diamine (abbreviated to BIPHAM) was synthesized early in 1927,[6] however, only limited applications in asymmetric catalysis have been reported probably due to its unpractical and exhaustive fractional resolution procedures.[7] Although BIPHAM has also been commercialized, the higher cost prevents it from being investigated sufficiently as an axial scaffold. Therefore, the development of a new and practical atropisomeric biphenyl diamine is in high demand.

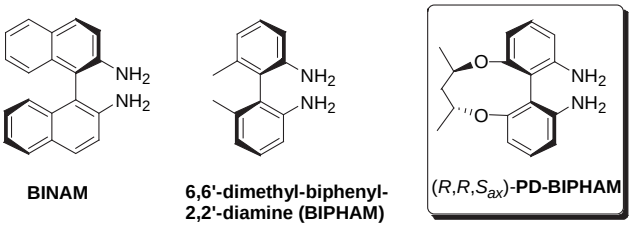

Figure 1. Atropisomeric biaryl diamine: BINAM, 6,6′-dimethyl-biphenyl-2,2′ diamine and the newly designed (*R*,*R*,S_{ax})-PD-BIPHAM.

Herein, we reported the concise synthesis of a new type of atropisomeric biphenyl diamine: (S_{ax})-[6,6′-(2*R*,4*R*-pentadioxy)]-1,1′-biphenyl-2,2′-diamine (abbreviated to (*R*,*R*,S_{ax})-PD-BIPHAM) through central-to-axial chirality transformation strategy, and the asymmetric inductive efficiency of the new chiral biphenyl diamine backbone was demonstrated through highly efficient asymmetric hydrogenation with bis(aminophosphine) ligands derived from (*R*,*R*,S_{ax})-PD-BIPHAM.[8]

2. Results and discussion

The conceptual diastereoselective intramolecular Ullmann coupling of two aryl units, pre-fixed through chiral tether,[9] is

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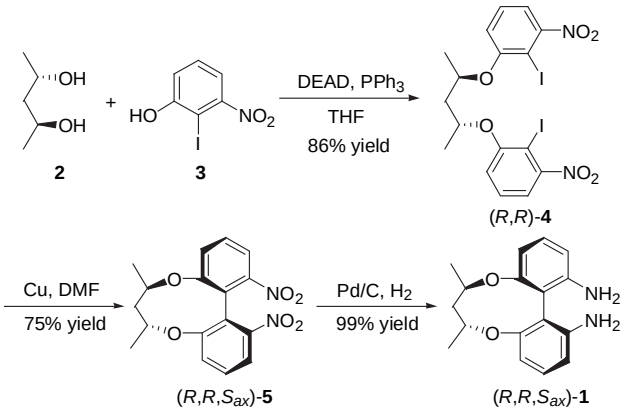
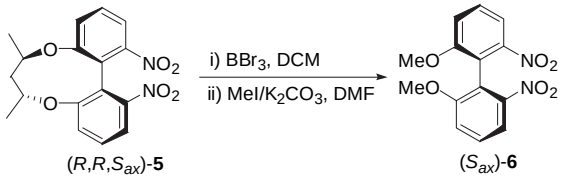
a popular and appealing strategy in the synthesis of atropisomeric biaryl compounds since it avoids the time-consuming and tedious resolution for obtaining the enantiomerically pure compounds. Highly efficient central-to-axial chirality transformation (up to 99% de) has been realized through various chiral diols and 1,2-amino alcohols,[9a] and it has also been successfully demonstrated for constructing several atropisomeric diphosphine ligands, such as NAPhenPhos,[10] PQ-Phos,[11] and C_3*-tunephos,[12] in which the commercially available chiral (*S*,*S*)- or (*R*,*R*)-2,4-pentanediol was used as the central chiral bridge and remarkably high diaselectivities were achieved. Inspired by the aforementioned research works, we envisioned that the central-to-axial chirality transformation strategy would facilitate synthesizing atropisomeric diamine without extra resolution, and thereby present more efficient and practical synthetic method for the biphenyl diamine. To the best of our knowledge, this strategy has not been reported for the synthesis of atropisomeric diamine so far.[8]

The concise synthetic route of atropisomeric (R,R,S_{ax})-PD-BIPHAM **1** is depicted in Scheme 1. The chiral dinitro compound **4** containing central stereogenic linkage was prepared by Mitsunobu reaction with (2*S*,4*S*)-pentanediol **2** and 3-nitro-2-iodophenol **3**.[13] Both enantiomers of (2*S*,4*S*) and (2*R*,4*R*)-pentanediol are commercially available or easily obtained through Ru-BINAP-catalyzed asymmetric hydrogenation of inexpensive starting material 2,4-pentandione.[14] The double Mitsunobu reaction proceeded smoothly and afforded (2*R*,4*R*)-**4** in 86% yield within 2 h as a single diastereoisomer.[15] Alternatively, the linked (2*R*,4*R*)-**4** could be also achieved in little lower yield through reaction (2*S*,4*S*)-pentanediol di-*p*-tosylate with 3-nitro-2-iodophenol in the presence of K_2CO_3 in DMF (see Experimental section). The linked central stereogenic (2*R*,4*R*)-**4** underwent copper-mediate intramolecular Ullmann coupling to generate the corresponding atropisomeric dinitro compound (R,R,S_{ax})-**5** in 75% yield.



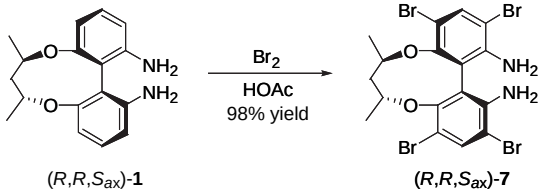
Scheme 1. Synthesis of atropisomeric diamine (R,R,S_{ax})-**PD-BIPHAM 1** through central-to-axial chirality transformation strategy.

In order to determine the diastereoselectivity of the key intramolecular Ullmann coupling step, the crude dinitro compound **5**, after removing the copper salts, were treated with BBr_3 followed by methylation with MeI/K_2CO_3 in DMF to generate the known compound **6**[16] (Scheme 2). Note that upon cleavage of the chiral linkage embedded in the crude compound **5**, any mixture of diastereomers with respect to the assured central chirality (2*R*,4*R*) and the axial chirality formed in the intramolecular Ullmann coupling reaction would now become a mixture of enantiomers with respect to the axial chirality. According to HPLC analysis, up to 97% ee was determined for the derived compound **6** and therefore 98.5:1.5 diastereoselectivity was generated in the key Ullmann coupling reaction, that is, the diastereoselective differentiation was highly controlled for this copper-mediate intramolecular Ullmann coupling even at 120 °C. To our delight, the enantiopure dinitro compound **5** (>99% de) can be easily achieved by simple crystallization of the crude product. Finally, reductive hydrogenation of enantiomerically pure **5** in the presence of catalytic amount of Pd/C afforded the desired atropisomeric (R,R,S_{ax})-PD-BIPHAM **1** in quantitative yield (Scheme 1). Finally, reductive hydrogenation of enantiomerically pure **5** in the presence of catalytic amount of Pd/C afforded the desired atropisomeric (R,R,S_{ax})-PD-BIPHAM **1** in quantitative yield.



Scheme 2. Diastereoselectivity determination of intramolecular Ullmann Coupling through HPLC analysis of the known compound (S_{ax})-**6**.

To determine the absolute axial chirality of the biaryl moiety of **5** and **1**, 3,3′,5,5′-tetrakis-bromo-PD-BIPHAM **7** was synthesized from PD-BIPHAM through highly efficient and simple bromination protocol, which also verifies the easily modification property of biphenyl backbones mentioned before (Scheme 3). A X-ray analysis of crystal of **7** revealed S_{ax} configuration for axial biphenyl moiety and (2*R*,4*R*) configuration for the two central chirality therefore also for the corresponding moiety in **5** and **1** (Fig. 2).[17]



Scheme 3. Synthesis of (R,R,S_{ax})-3′,3′,5,5′-tetrakis-bromo-PD-BIPHAM **7**.

With enantiopure (R,R,S_{ax})-PD-BIPHAM **1** in hand, we extended its application to the synthesis of bis(aminophosphine) ligands **8**.

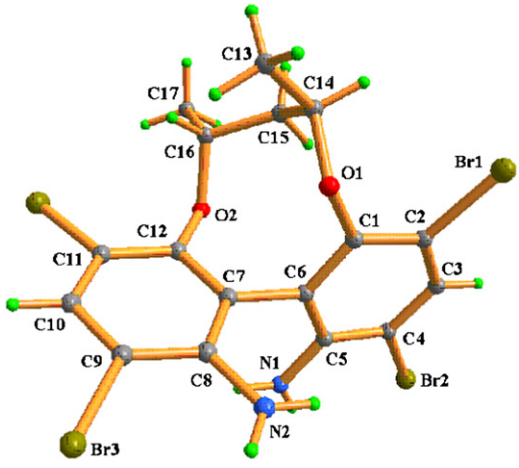


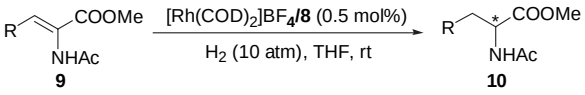
Figure 2. X-ray crystal structure of (R,R,S_{ax})-**7**.

As shown in Scheme 4, the chiral ligand was conveniently obtained in good yield by the reaction of (*R*,*R*,S_{ax})-PD-BIPHAM **1** with PPh_2Cl in the presence of Et_3N and catalytic amount of DMAP.

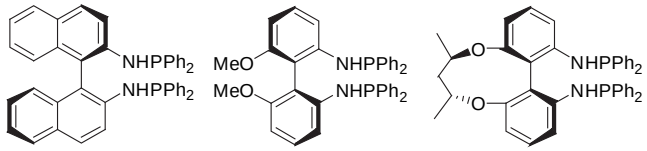
Scheme 4. Synthesis of the bis(aminophosphine) (*R*,*R*,S_{ax})-**8**.

The catalytic performance of bis(aminophosphine) **8** was tested in the Rh(I)-catalyzed asymmetric hydrogenation[18] of α-dehydroamino acid esters **9**, and the results are summarized in Table 1. A wide array of ring substituted phenylalanine derivatives **10** were formed with excellent enantioselectivities, regardless of the position and the electronic property of the substituents on the phenyl ring, which demonstrates the asymmetric inductive efficiency of the new chiral biphenyl diamine backbone. Compared with the results achieved by (*R*)-BDPAB (**L1**) derived from (*R*)-1,1′-binaphthyl-2,2′-diamine[19] and similar ligand (**L2**) derived from (*S*)-6,6′-dimethoxyl-1,1′-biphenyl-2,2′-diamine, our catalyst system shows much higher enantioselectivities.[20]

Table 1
Rh-catalyzed asymmetric hydrogenation of (*Z*)-acetamido-3-arylacrylic acid methyl esters[a]



Entry	Substrate	R	ee (%)		
			(*R*)-**L1**[b]	(*S*)-**L2**[c]	(*R*,*R*,S_{ax})-**8**[d]
1	**9a**	Ph	90	74	96
2	**9b**	*o*-Me–Ph	—	—	96
3	**9c**	*p*-Me–Ph	95	71	96
4	**9d**	*o*-Cl–Ph	90	72	97
5	**9e**	*m*-Cl–Ph	90	72	94
6	**9f**	*p*-Cl–Ph	88	74	93
7	**9g**	*o*-MeO–Ph	—	—	96
8	**9h**	*p*-MeO–Ph	—	73	96
9	**9i**	*p*-F–Ph	—	73	95
10	**9j**	2-Naphthyl	—	—	94
11	**9k**	H	93	—	95



[a] In all cases, full conversion was achieved with (*R*,*R*,S_{ax})-**8** as chiral ligand.
[b] The data were reported by Chan under 30 psi hydrogenation in THF using (*R*)-BDPAB (**L1**) as chiral ligand, see: Ref. 19a.
[c] The date were reported by Chen under 0.68 MPa in acetone using (*S*)-DMBDPPABD (**L2**) as chiral ligand, see: Ref. 20.
[d] Enantiomeric excesses were determined by GC. The absolute configuration of the products was determined as *S* by comparing the retention times with the reported data in the literatures.

3. Conclusions

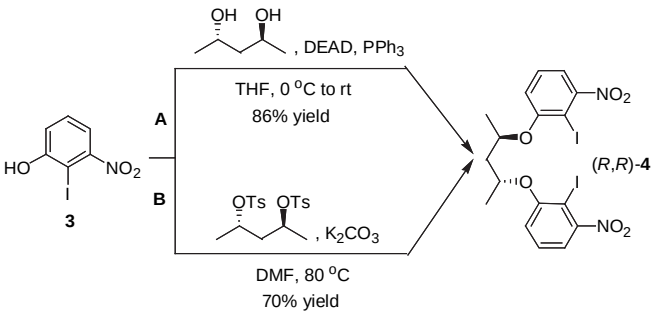
In summary, the atropisomeric PD-BIPHAM is designed and prepared successfully for the first time by using central-to-axial transformation strategy, which presents a rapid, reliable and atom-economical procedure for axially biphenyl diamine without tedious resolution and diversifies the family of chiral axially chiral biphenyl backbones. The effectiveness of this new chiral skeleton was demonstrated by highly efficient asymmetric hydrogenation of α-dehydroamino acid esters with the chiral bis(aminophosphine) ligand derived from (*R*,*R*,S_{ax})-PD-BIPHAM. Further investigations of this new axially biphenyl diamine in asymmetric catalysis are underway in our laboratory and will be reported in due course.

4. Experimental section

4.1. General remarks

All reactions were carried out using standard Schlenk techniques unless specified other otherwise. The degassed dry solvents are used throughout each experiment. ^{1}H NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer in chloroform-*d*. Chemical shifts are reported in parts per million with the internal TMS signal at 0.0 ppm as a standard. The data are reported as (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet or unresolved, br s=broad singlet, coupling constant(s) in Hz, integration). ^{13}C NMR spectra were recorded on a VARIAN Mercury 75 MHz spectrometer in chloroform-*d*. Chemical shifts are reported in parts per million with the internal chloroform signal at 77.0 ppm as a standard. ^{31}P NMR spectra were recorded on a VARIAN Inova-600 MHz spectrometer in chloroform-*d*, chemical shifts are reported in parts per million with the external 85% H_3PO_4 signal at 0.0 ppm as a standard. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel-coated plates. Enantiomeric ratios were determined by chiral HPLC using a chiralpak AD-H column with hexane and *i*-PrOH as solvents, or determined by chiral GC using a Supelco chiral Select 1000 or a Chirasil-L-Val column. The absoluted configurations of the known products were determined by comparing the GC or HPLC retention times with the reported data. 3-Nitro-2-iodophenol[13] and (2*S*,4*S*)-pentanediol[14] was prepared by the reported synthetic methods.

4.1.1. *Synthesis of (R,R)-**4***.



Method A: To a solution of 2-iodo-3-nitrophenol (1.65 g, 6.24 mmol), (2*S*,4*S*)-pentane-2,4-diol (0.31 g, 3.0 mmol), and triphenylphosphine (1.63 g, 6.24 mmol) in 10 mL THF, a solution of diethyl azodicarboxylate (1.09 g, 62.4 mmol) in 5 mL THF was added at 0 °C. The mixture was gradually warmed up to room temperature. The reaction was completed in additional 6 h. The solvent was removed in vacuum, and the residue was subjected to flash silica gel chromatography to afford **4** in 86% yield. Mp 80 °C; $[\alpha]_D^{25}$ −192.8 (*c* 0.98, $CHCl_3$); IR (KBr) *ν* 2978, 2092, 1642, 1583, 1450, 1355, 1272, 1144, 1109, 1019, 844, 790, 734 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) *δ* 7.23 (dd, *J*=7.2, 7.8 Hz, 2H), 7.09 (d, *J*=7.2 Hz, 2H), 6.83 (d, *J*=7.8 Hz, 2H), 4.89–4.82 (m, 2H), 2.15 (m, 2H), 1.45 (d, *J*=6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) *δ* 158.16, 155.59,

130.33, 116.89, 115.97, 81.36, 73.98, 44.78, 20.34; HRMS calcd for $C_{17}H_{16}I_2N_2O_6$: 597.9098, found: 597.9099.

Method B: To a solution of 2-iodo-3-nitrophenol (1.06 g, 4 mmol) in dry 10 mL DMF, K_2CO_3 (1.1 g, 8 mmol) was added. The mixture was stirred for 4 h. A solution of (2*S*,4*S*)-2,4-pentanediol di-*p*-toluenesulfonate (0.91 g, 2.2 mmol) in 10 mL dry DMF was added. The mixture was stirred at 80 °C for 4 h. The reaction mixture was poured into ice-water, and then extracted with ether. The combined organic layers were dried over Na_2SO_4. The solvent was removed in vacuum, and the residue was subjected to flash silica gel chromatography to afford **4** in 70% yield.

*4.1.2. Synthesis of **5**.* To a solution of **4** (3.60 g, 6.0 mmol) in 35 mL dry DMF was added copper powder (1.52 g, 24.0 mmol). The mixture was heated at 120 °C until the reaction was completed. After DMF was removed in vacuum, the residue was dissolved in DCM, and then washed with water and brine. The organic layer was dried over Na_2SO_4. The solvent was removed in vacuum, and the residue was subjected to flash silica gel chromatography to afford **5** in 75% yield and 97% diastereoselectivity. The enantiopure dinitro compound **5** (>99% de) can be easily achieved by simple crystallization of the crude product in $CHCl_3$. Mp 264 °C; $[\alpha]_D^{25}$ +567.2 (*c* 1.17, $CHCl_3$); IR (KBr) ν 2933, 1633, 1528, 1444, 1344, 1270, 1194, 1159, 1086, 979, 892, 813, 743 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.91 (d, *J*=7.5 Hz, 2H), 7.52 (dd, *J*=7.5, 7.8 Hz, 2H), 7.41 (d, *J*=7.8 Hz, 2H), 4.61 (m, 2H), 1.80 (m, 2H), 1.34 (d, *J*=6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 157.82, 148.76, 129.56, 123.50, 119.15, 77.03, 39.98, 21.90; HRMS calcd for $C_{17}H_{16}N_2O_6$: 344.1008, found: 344.1012.

4.2. Diastereoselectivity determination of the intramolecular Ullmann Coupling step

To a solution of (*R*,*R*,S_{ax})-**5** (69 mg, 0.2 mmol) in 5 mL dry dichloromethane was added BBr_3 (50 mL, 0.5 mmol) at −78 °C, and the solution was stirred for 1 h. The mixture was quenched with 2 N HCl. The water layer was extracted with ether. The combined organic layers were dried over Na_2SO_4 and evaporated to afford a yellow solid. The yellow solid was dissolved in 3 mL DMF, K_2CO_3 (212 mg, 2.0 mmol) and CH_3I (170 mg, 1.2 mmol) were added, and then the mixture was heated at 80 °C for 48 h. The reaction mixture was poured into ice-water, and then extracted with ether. The combined organic layers were dried over Na_2SO_4. The solvent was removed in vacuum, and the residue was subjected to flash silica gel chromatography to afford the known compound **6** in 97% yield. The product **6** was analyzed by HPLC to determine the diastereoselectivity of the intramolecular Ullmann Coupling reaction (Chiralcel AD-H, *i*-propanol/hexane=3:97, flow rate 1.0 mL/min, λ=254 nm): 99.8% ee, t_{major}=32.2 min, t_{minor}=48.9 min. ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.75 (d, *J*=7.2 Hz, 2H), 7.50 (dd, *J*=7.2, 8.1 Hz, 2H), 7.19 (d, *J*=8.1 Hz, 2H), 3.72 (s, 6H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 156.56, 149.03, 29.28, 118.32, 116.33, 115.33, 56.33.

*4.2.1. Synthesis of (R,R,S$_{ax}$)-**1**.* To a solution of **5** (5.0 g, 14.5 mmol) in 80 mL methanol was added Pd/C (0.5 g) in autoclave, into which hydrogen gas was charged at the desired pressure (60 bar). The mixture was stirred overnight at 50 °C, and then the hydrogen was released carefully. The mixture was filtered and the solvent was removed under reduced pressure. The residue was subjected to flash silica gel chromatography to give (*R*,*R*,S_{ax})-**1** in 99% yield. Mp 100 °C; $[\alpha]_D^{25}$ +298.5 (*c* 1.02, $CHCl_3$); IR (KBr) ν 3363, 2973, 2933, 2100, 1623, 1455, 1376, 1004, 1250, 1113, 1091, 1005, 900, 784, 744, 721 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.11 (dd, *J*=7.2, 7.8 Hz, 2H), 6.55 (d, *J*=7.8 Hz, 2H), 6.48 (d, *J*=7.2 Hz, 2H), 4.57–4.51(m, 2H), 1.80 (m, 2H), 1.32(d, *J*=6.3 Hz, 6H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 159.10, 145.55, 129.24, 113.37, 110.29, 108.11, 75.21, 41.18, 22.54; HRMS calcd for $C_{17}H_{20}N_2O_2$: 284.1525, found: 284.1522.

*4.2.2. Synthesis of **7**.* To a solution of (*R*,*R*,S_{ax})-**1** (0.568 g, 2.0 mol) in 15 mL AcOH was added Br_2 (1.41 g, 8.8 mol) in 10 mL AcOH dropwise, and then the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was poured into ice-water, and then extracted with DCM. The combined organic layers were dried over Na_2SO_4. The solvent was removed in vacuum, and the residue was subjected to flash silica gel chromatography to obtain **7** in 98% yield. $[\alpha]_D^{25}$ +215.4 (*c* 1.48, $CHCl_3$); IR (KBr) ν 3363, 2973, 2933.5, 2100.1, 1623, 1455, 1376, 1004, 1250, 1113, 1091, 1005, 900, 784, 744, 721 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.64 (s, 2H), 4.92 (m, 2H), 1.73 (m, 2H), 1.28 (d, *J*=5.7 Hz, 6H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 153.50, 142.46, 136.07, 116.88, 104.38, 103.33, 74.38, 40.80, 21.57; HRMS calcd for $C_{17}H_{16}Br_4N_2O_2$: 595.7945, found: 595.7947.

4.3. Procedure for the preparation of (*R*,*R*,S_{ax})-8

To a solution of (*R*,*R*,S_{ax})-**1** (0.10 g, 0.352 mmol), Et_3N (0.28 g, 0.40 mL, 2.77 mmol), and DMAP (12 mg, 0.098 mmol) in 3 mL DCM was added Ph_2PCl (0.186 g, 0.85 mmol) at 0 °C. The reaction mixture was then allowed to warm to ambient temperature and stirred overnight. The solvent was removed under vacuum, and the crude product was purified through a basic alumina column to afford (*R*,*R*,S_{ax})-**8** as white solid in 85% yield. $[\alpha]_D^{25}$ +88.9 (*c* 0.94, $CHCl_3$); IR (KBr) ν 3366, 2676, 2927, 2095, 1644, 1592, 1575, 1453, 1433, 1375, 1289, 1250, 1089, 1032, 739, 695 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz, phosphorous decoupled) δ 7.25–7.13 (m, 22H), 7.03 (d, *J*=6.6 Hz, 2H), 6.64 (d, *J*=7.8 Hz, 2H), 4.61 (m, *J*=6.9 Hz, 2H), 1.79 (m, 2H), 1.33 (d, *J*=6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz, phosphorous decoupled) δ 153.63, 140.29, 135.68, 134.17, 126.14, 125.22, 124.25, 123.65, 123.09, 110.26, 104.89, 104.41, 69.99, 35.70, 17.11; ^{31}P NMR ($CDCl_3$, 85% H_3PO_4, 242.86 MHz) δ 32.257; HRMS calcd for $C_{41}H_{38}N_2O_2P_2$: 652.2409, found: 652.2411.

4.4. Procedure for the preparation of [Rh(8)(COD)]BF_4

[Rh(COD)$_2$]BF_4 (32.6 mg, 0.080 mmol) and chiral bisaminophosphine ligand (*R*,*R*,S_{ax})-**8** (54.9 mg, 0.084 mmol) was dissolved in 2 mL degassed CH_2Cl_2 in a Schlenk tube under N_2 at room temperature. The resulting mixture was stirred at ambient temperature for 2 h. The solvent was removed under vacuum to afford [Rh(**8**)(COD)]BF_4 as an orange solid, which was used as the catalyst without further purification. ^{31}P NMR ($CDCl_3$, 85% H_3PO_4, 242.86 MHz) δ 68.645 (d, J_{Rh-P}=249.2 Hz).

4.5. Representative experimental procedure for the asymmetric hydrogenation

[Rh(**8**)(COD)]BF_4 (10.0 mg, 0.01 mmol) was dissolved in degassed THF (8 mL) in a glovebox, and distributed equally to four vials. To the catalyst solution was added substrate (0.5 mmol). All the vials were placed together in a steel autoclave into which hydrogen gas was charged at the desired pressure. After stirring at room temperature for 2 h, the hydrogen was released carefully and the solution was concentrated. The residue was purified by column chromatography to give the corresponding hydrogenation product,

which was then directly analyzed by chiral GC to determine the enantiomeric excess.

Acknowledgements

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Supplementary data

Spectroscopic data of compounds **1**–**8**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2010.03.073.

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