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Tetrahedron: *Asymmetry* 17 (2006) 468–473
Tetrahedron: *Asymmetry*

Synthesis of a novel spiro bisphosphinite ligand and its application in Rh-catalyzed asymmetric hydrogenation

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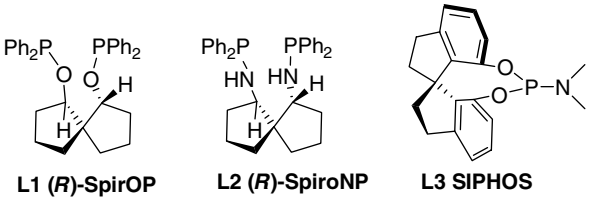
Received 21 December 2005; accepted 23 January 2006

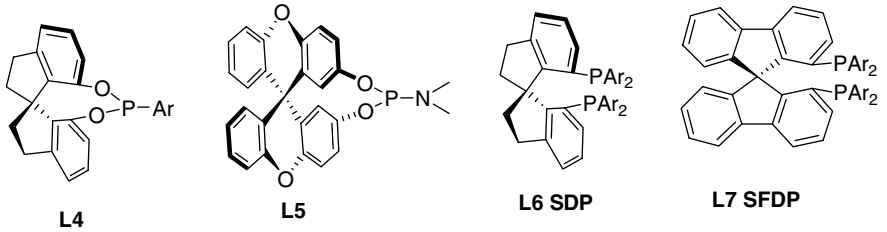
Abstract—A novel, chiral bisphosphinite ligand (*R*)-SpiroBIP has been synthesized. The rhodium complex of the ligand was found to be highly enantioselective in the asymmetric hydrogenation of α-dehydroamino acid derivatives.

1. Introduction

Asymmetric hydrogenation based on transition metal catalyzed processes has attracted a great deal of interest because of its large success for the preparation of enantiomerically pure compounds. Lots of bidentate ligands, with their various frameworks, such as biaryl chirality with BINAP and bisphosphanes with Duphos and BPE, have been developed for highly efficient asymmetric hydrogenation of various olefins, ketones and imines.[1] Since 1997, ligands with another type of axial chirality, namely a spiro framework, have attracted much attention. Notable reports include the application of (*R*)-SpirOP **L1**[2] and *R*-SpiroNP **L2**[3] in the hydrogenation of enamides and α-dehydroamino acid derivatives; SIPHOS **L3**,[4] **L4**[5] and **L5**[6] in the hydrogenation of enamides and α- and β-dehydroamino acid derivatives; SDP **L6**[7] and SFDP **L7**[8] in the hydrogenation of unsymmetrical ketones and unsaturated acids.

The success of these ligands in asymmetric hydrogenation arises from the highly skewed and rigid conformation, which is also considered important to the effectiveness of biaryl type ligands, such as BINAP.[9]





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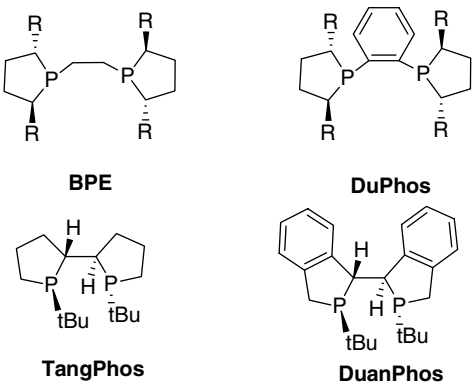
0957-4166/$ - see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.tetasy.2006.01.021

However, the syntheses of the spiro based ligands is difficult in most cases. In our recent pursuit of the design and synthesis of novel chiral ligands, we noticed that *cis*,*cis*-2,2′-spirobiindane-1,1′-diol **4** can be easily synthesized.[10] The resolution of **4** into the enantiomerically pure forms (⩾95% ee) was reported by Keay,[11] but no further attempts had been made for further application of the corresponding ligands in asymmetric catalysis. It was reported that by introducing fused benzenes to some old ligands, the corresponding ligands with new structures showed the same or even better performances, in term of both enantioselectivity and reactivity, for example, BPE[12a] versus DuPhos,[12b] TangPhos[13] versus DuanPhos,[14] SDP[7] versus SFDP.[8] In view of the successful examples described above, we were interested in the synthesis of (1*R*,2*R*,1′*R*)-1,1′-bis(diphenylphosphinoxy)-2,2′-spirobiindane **7** [abbreviated (*R*)-SpiroBIP] and its applications in the asymmetric hydrogenation of (*Z*)-acetamidocinnamic acid derivatives as a testing ground for its effectiveness.



2. Results and discussion

2.1. Ligand preparation

The overall synthesis for (*R*)-SpiroBIP is illustrated in Scheme 1. *cis*,*cis*-2,2′-Spirobiindane-1,1′-dione **3** was prepared according to a literature method[12] from diethylmalonate and benzyl chloride. The reduction of dione **3** with lithium *tert*-butyldiisobutylaluminium hydride provided only (±)-*cis*,*cis*-2,2′-spirobiindane-1,1′-diol **4**, without an appreciate amount of *cis*,*trans* and *trans*, *trans* diol isomers. We then attempted to resolve diol **4** according to Keay's experimental steps[11] using (2*S*)-2-(*tert*-butyldimethylsilyl)-mandeloyl chloride as a chiral auxiliary. In our hands, the esterification did not proceed well and most of the unreacted diol **4** was recovered under the literature conditions (1.1 equiv *n*-BuLi, THF, −78 °C, 5 min then 2.5 equiv **9**, THF, −78 °C to rt, overnight). We therefore modified the reaction conditions and mono esters (1*R*,2*R*,1′*R*)-2,2′-spirobiidan-1-((2*S*)-(*O*-*tert*-butyldimethylsilyl)mandeloxy)-1′-ol **5A** and (1*S*,2*S*,1′*S*)-2,2′-spirobiidan-1-((2*S*)-(*O*-*tert*-butyldimethylsilyl)mandeloxy)-1′-ol **5B** were prepared (1.5 equiv *n*-BuLi, THF, 50 °C, 20 min then 3 equiv **9**, THF, rt, 30 min). Column chromatography of the crude reaction mixture gave **5A** and **5B** in good yield. The hydrolysis of mono esters **5A** and **5B** with 10% aqueous NaOH in EtOH provided (−)-diol **6A** (82%, ⩾99% ee) and (+)-diol **6B** (85%, ⩾99% ee), respectively. Subsequent ligand **7** was conveniently prepared through the reaction of (−)-diol **6A** with chlorodiphenylphosphine in 48% yield.

2.2. Asymmetric hydrogenation of α-dehydroamino acid derivatives with Rh/(*R*)-SpiroBIP

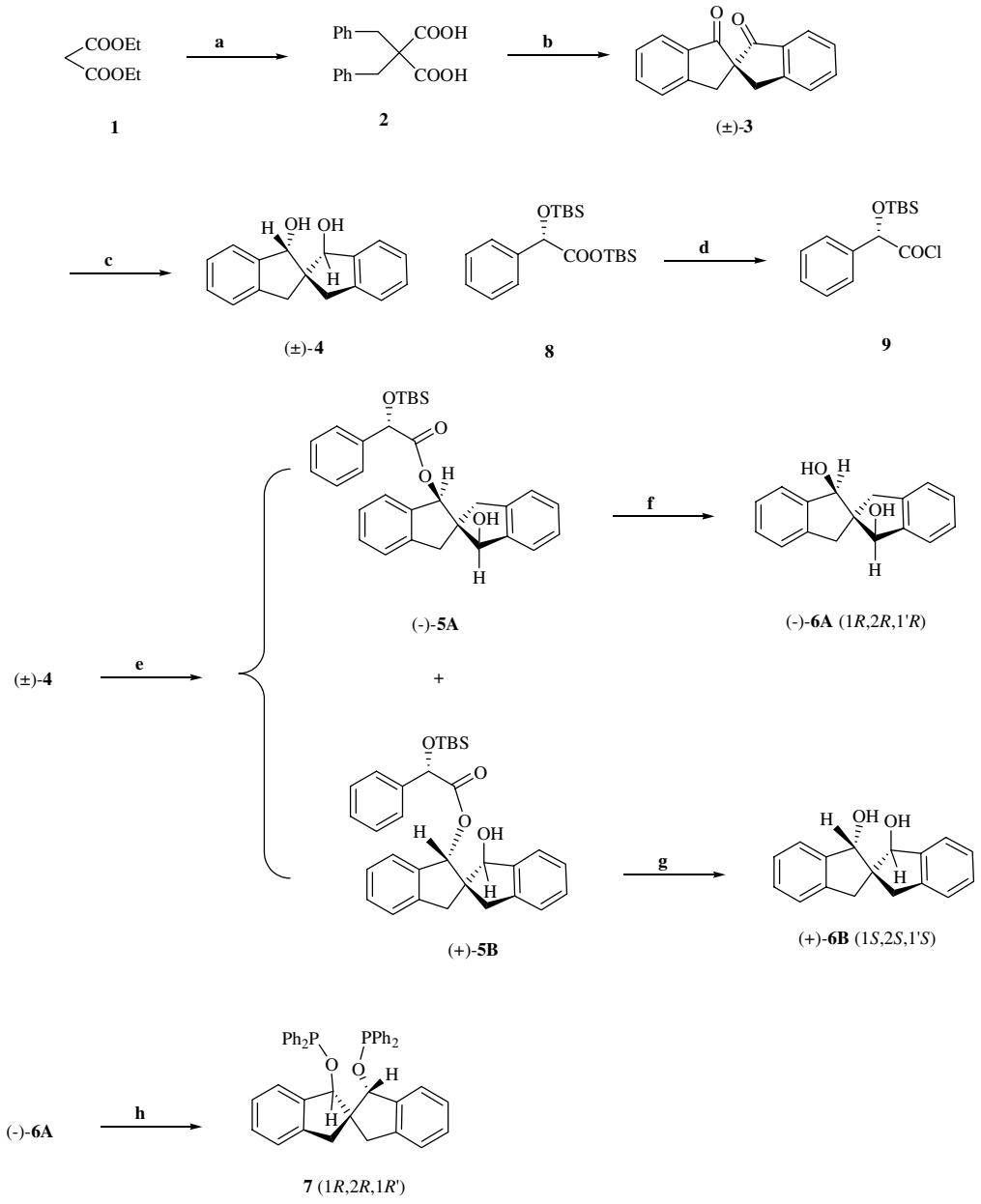
The cationic Rh(I) complex [Rh(COD)(*R*-SpiroBIP)]BF_4 was prepared in situ by mixing $[Rh(COD)_2]BF_4$ with 1.2 M equiv of (*R*)-SpiroBIP under an inert atmosphere. Asymmetric hydrogenation of the α-dehydroamino acid derivatives has been extensively studied and afforded a model reaction to test the effectiveness of the new spiro ligand. Routine screening of reaction conditions for the hydrogenation of methyl (*Z*)-acetamidocinnamate revealed that both the hydrogen pressure and solvents had significant effects on the enantioselectivity of the reaction (Table 1). It was found that by lowering the hydrogen pressure the ee value of the products increased (entries 1–3). The hydrogenation reaction could not be performed under 1 atm H_2 at room temperature and only the starting material was recovered (entry 4). In MeOH, acetone and CH_2Cl_2, the hydrogenation products were obtained in high ee (entries 3, 5 and 6). However, products of much lower ee and conversion were obtained in toluene, THF and EtOAc (entry 8–10).

Having established the preferred conditions, a number of methyl esters of (*Z*)-2-acetamidoacrylic acid and (*Z*)-acetamidocinnamic acid derivatives were hydrogenated in quantitative yield with moderate to good enantioselectivities (Table 2). The electronic properties of the substituents on the phenyl ring has a certain degree of influence on the ee. Electron-donating groups increased the enantioselectivity of products (entries 2, 3 and 4).

Direct catalytic asymmetric conversion of (*Z*)-2-acetamidoacrylic acid and (*Z*)-2-acetamido-3-arylacrylic acids into their corresponding amino acids is also feasible with [Rh(COD)(*R*-SpiroBIP)]BF_4 (Table 3). In general, the hydrogenation of α-dehydroamino acids gave higher ee values than the corresponding methyl esters, bar a few exceptions (Table 2, entries 1, 4 and 6 vs Table 3 entries 1, 4 and 6). The substituents on the aryl ring had an almost negligible effect on the resulting enantioselectivity.

(*Z*)-Acetamidocinnamic acid methyl ester gave higher enantioselectivities than (*Z*)-benzamidocinnamic acid methyl ester (Table 2 entry 4 vs entry 5), but the reverse is true for corresponding free acid substrates, when (*Z*)-benzamidocinnamic acid gave higher ee than the corresponding (*Z*)-acetamidocinnamic acid (Table 3 entry 5 vs entry 4).

Compared to (*R*)-SpirOP as reported by Chan et al.,[2] (*R*)-SpiroBIP is considered to have a more rigid conformation due to the fused benzene rings on the spiro backbone. Although comparable enantioselectivities were observed in some cases, the increasing conformational



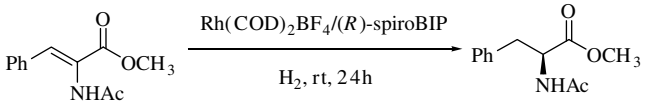
Scheme 1. Reagents and conditions: (a) (i) NaOEt (2 equiv), EtOH, reflux, 2 h; (ii) $PhCH_2Cl$ (2 equiv), 85°C, 6 h; (iii) 50% aq NaOH, 100 °C, 6 h, 55%; (b) P_2O_5, toluene, rt, overnight, 35%; (c) lithium *tert*-butyldiisobutylaluminium hydride (3 equiv), THF, −78 °C, overnight, 95%; (d) $SOCl_2$ (1.5 equiv), $CHCl_3$, reflux, 30 min; (e) (i) *n*-BuLi (1.5 equiv), THF, 50 °C, 20 min; (ii) **9** (3 equiv), THF, rt, 30 min, 52%; (f) 10% aq NaOH, EtOH, rt, 82%; (g) 10% aq NaOH, EtOH, rt, 85%; (h) Ph_2PCl (2.25 equiv), DMAP, TEA, THF, rt, 30 min, 48%.

rigidity of SpiroBIP exhibited less catalytic activity in the asymmetric hydrogenation of dehydroamino acid derivatives. To our opinion, the possible reason for the decreased activity is due to much weaker coordination of SpiroBIP to the rhodium metal because of increased steric hindrance of the ligand. The weak coordination was evidenced by ^{31}P NMR of the rhodium complex. Weak and broad ^{31}P signals of the complex was observed and no improvement with elevated temperature. Nevertheless, the current ligand did show some advantages. The SpiroBIP can be easily prepared in both enantiomers from inexpensive raw materials.[15] Preliminary study shows that SpiroBIP is not particularly air sensitive, which makes its preparation and handling more practical. And the ligand can be further modified by introducing functional group on the fused aromatic ring. Ready availability and easy modification of spiroBIP would make it feasible to look at other metal complexes and to explore other catalytic asymmetric reactions.

3. Conclusions

A new chiral bisphosphinite ligand, (*R*)-SpiroBIP, based on a spiro backbone has been developed. The cationic rhodium complex of (*R*)-SpiroBIP was found to be an excellent catalyst for the asymmetric hydrogenation of

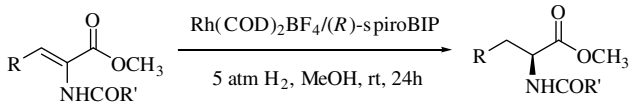
Table 1. Optimization of the asymmetric hydrogenation of methyl (*Z*)-acetamidocinnamate catalyzed by Rh/(*R*)-SpiroBIP complex[a]



Entry	Solvent	*P* (atm)	Conv.[b] (%)	ee[b] (%)
1	MeOH	50	100	80
2	MeOH	20	100	91
3	MeOH	5	97	94
4	MeOH	1	—[c]	—[c]
5	Acetone	5	97	86
6	CH_2Cl_2	5	100	87
7	Toluene	5	57	74
8	THF	5	80	37
9	EtOAc	5	80	42

[a] The reaction was carried out in 4 mL of solvent [substrate: $Rh(COD)_2BF_4$:ligand = 100:1:1.2].
[b] Determined by GC. The (*R*) configuration of the products was observed in all cases.
[c] No reaction and the starting material was recovered.

Table 2. Asymmetric hydrogenation of α-dehydroamino acid methyl esters[a]



Entry	Substrate	ee[b] (%)	Config.[c]
1	R = H, R′ = CH_3	80	*R*
2	R = *p*-MeOPh, R′ = CH_3	93	*R*
3	R = *p*-MePh, R′ = CH_3	89	*R*
4	R = Ph, R′ = CH_3	94[d]	*R*
5	R = Ph, R′ = Ph	85	*R*
6	R = *p*-FPh, R′ = CH_3	86	*R*
7	R = *p*-ClPh, R′ = CH_3	67	*R*
8	R = *m*-ClPh, R′ = CH_3	84	*R*
9	R = *o*-ClPh, R′ = CH_3	73	*R*
10	R = *p*-BrPh, R′ = CH_3	88	*R*
11	R = 3,4-(Methylenedioxy)-Ph, R′ = CH_3	86	*R*

[a] The reaction was carried out in 4 mL of MeOH [substrate: $Rh(COD)_2BF_4$:ligand = 100:1:1.2].
[b] Determined by GC. Conversions (100%) and quantitative yields were obtained unless mentioned otherwise.
[c] The configuration was determined by comparison with authentic examples.
[d] The reaction conversion is 97%.

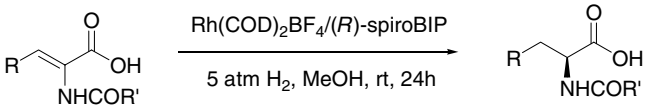
α-dehydroamino acid derivatives under mild conditions. A further study of other applications of this new ligand is in progress.

4. Experimental

4.1. General procedures

^1H NMR, ^{13}C and ^{31}P NMR spectra were recorded on a Brucker-300 (300/75 MHz) spectrometer. Optical rotations were measured with a Perkin–Elmer 341 Polarimeter in a 10 cm cell. Melting points were measured on an electro thermal digital melting point apparatus. Mass spectra were recorded on a Brucker BioTOF Q. Chiral GC analyses were performed on a VARIAN CP-3380 using a Chirasil-L-Val column. HPLC analysis was performed on Waters-Breeze (2487 Dual 1 Absorbance Detector and 1525 Binary HPLC Pump) with a Chiralpak AS column.

Table 3. Asymmetric hydrogenation of α-dehydroamino acid[a]



Entry	Substrate	ee[b] (%)	Config.[c]
1	R = H, R′ = CH_3	74	*R*
2	R = *p*-MeOPh, R′ = CH_3	94	*R*
3	R = *p*-MePh, R′ = CH_3	91	*R*
4	R = Ph, R′ = CH_3	90	*R*
5	R = Ph, R′ = Ph	91	*R*
6	R = *p*-FPh, R′ = CH_3	82	*R*
7	R = *p*-ClPh, R′ = CH_3	97	*R*
8	R = *m*-ClPh, R′ = CH_3	94	*R*
9	R = *o*-ClPh, R′ = CH_3	93	*R*
10	R = *p*-BrPh, R′ = CH_3	90	*R*
11	R = 3,4-(Methylenedioxy)-Ph, R′ = CH_3	96	*R*

[a] The reaction was carried out in 4 mL of MeOH [substrate: $Rh(COD)_2BF_4$:ligand = 100:1:1.2].
[b] Determined by GC on the corresponding methyl ester. Conversions (100%) and quantitative yields were obtained unless mentioned otherwise.
[c] The configuration was determined by comparison with authentic examples.

All reactions were carried out under a dry argon atmosphere using standard Schlenk line techniques unless otherwise mentioned. THF, toluene and triethylamine were distilled from sodium benzophenone ketyl. Solvents for hydrogenation were degassed by three freeze–thaw cycles prior to use. Racemic spiro diketone **3** and the corresponding *cis*,*cis*-diol **4** were prepared according to literature procedure.[11,16]

4.2. Preparation of mono esters (1*R*,2*R*,1′*R*)-2,2′-spirobiidan-1-((2*S*)-(*O*-*tert*-butyldimethylsilyl)mandeloxy)-1′-ol 5A and (1*S*,2*S*,1′*S*)-2,2′-spirobiidan-1-((2*S*)-(*O*-*tert*-butyldimethylsilyl)mandeloxy)-1′-ol 5B

$SOCl_2$ (0.74 mL, 9.0 mmol) was added dropwise into a solution of *tert*-butyldimethylsilyl (2*S*)-(*O*-*tert*-butyldimethysilyl)mandelate **8**[11] (2.30 g, 6.0 mmol) in $CHCl_3$ (20 mL) at room temperature, after the addition of the solution was at heated reflux and stirred for 30 min. The solvent and excess $SOCl_2$ was removed in vacuo to provide compound **9**. THF (10 mL) was added to make a solution.

In a separate round bottom flask, racemic diol **4** (500 mg, 2.0 mmol) was dissolved into 70 mL of THF under an argon atmosphere and heated to 50 °C whereupon *n*-butyllithium (1.90 mL, 1.6 M in hexane, 3.0 mmol) was added to the above solution. After stirring for 20 min, the solution was cooled to room temperature.

The acid chloride **9** THF solution was added dropwise to this solution. The resulting solution was stirred at rt for 30 min. Saturated sodium bicarbonate was added and the aqueous layer extracted three times with $CHCl_3$. The combined organic layer was dried over Na_2SO_4 and solvent removed in vacuo. The diastereomers were separated from other impurities by column chromatography (petroleum ether/EtOAc = 20:1). This procedure provided an oil mixture of **5A** and **5B** (520 mg, 1.0 mmol, 52% yield), which partially solidified on standing. The mixture of diastereomers **5A** and **5B** was separated by silica gel column chromatography (petroleum ether/CH_2Cl_2 from 1:5 to 0:100) to give diastereomer **5A** (234 mg, 0.47 mmol, 45% yield) and **5B** (244 mg, 0.49 mmol, 47% yield). All spectroscopic and physical data were in accordance with previous literature.[11]

Diastereomer **5A**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.51–7.17 (m, 13H), 6.10 (s, 1H), 5.19 (s, 1H), 5.06 (d, 1H, $J = 3.2$ Hz), 3.16 (d, 1H, $J = 10.2$ Hz), 3.10 (d, 1H, $J = 10.2$ Hz), 2.50 (d, 1H, $J = 12.0$ Hz), 2.44 (d, 1H, $J = 12.0$ Hz), 2.03 (d, 1H, $J = 3.2$ Hz), 0.82 (s, 9H), −0.06 (s, 3H), −0.14 (s, 3H). $[\alpha]_D^{20} = -84.5$ (*c* 10.6, chloroform).

Diastereomer **5B**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.65 (dd, 1H, $J = 7.3$ and 1.3 Hz), 7.51–7.17 (m, 12H), 6.13 (s, 1H), 5.16 (s, 1H), 4.78 (d, 1H, $J = 3.8$ Hz), 3.14 (d, 1H, $J = 11.2$ Hz), 3.09 (d, 1H, $J = 11.2$ Hz), 2.43 (d, 1H, $J = 9.8$ Hz), 2.38 (d, 1H, $J = 9.8$ Hz), 1.55 (d, 1H, $J = 3.4$ Hz), 0.90 (s, 9H), 0.10 (s, 3H), −0.03 (s, 3H). $[\alpha]_D^{20} = +114.0$ (*c* 8.4, chloroform).

Mono esters' de values were determined by HPLC ((Chiralpak AS column, ^{i}PrOH/Hex(3/97), 0.25 mL/min at 254 nm) $t_{5A} = 3.12$ min, $t_{5B} = 6.03$ min). $De_{5A} \geqslant 99\%$ and $De_{5B} \geqslant 99\%$.

4.3. Preparation of diol (1*R*,2*R*,1′*R*)-2,2′-spirobiindane-1,1′-diol (−)-6A and (1*S*,2*S*,1′*S*)-2,2′-spirobiindane-1,1′-diol (+)-6B

To a solution of compound **5A** or **5B** (1.0 g, 2.0 mmol) in EtOH (200 mL) was added 10% sodium hydroxide (100 mL) at room temperature. Slow formation of a white precipitate was observed. After stirring for 20 min, the reaction mixture was extracted with $CHCl_3$ (250 mL). The organic layer was dried over Na_2SO_4 and solvent was removed in vacuo. The residue was recrystallization from $CHCl_3$ to provided a white solid **6A** (410 mg, 1.6 mmol, 82% yield, ⩾99% ee) or **6B** (425 mg, 1.7 mmol, 85% yield, ⩾99% ee). Diols' ee values were determined by HPLC ((Chiralpak AS column, ^{i}PrOH/Hex(15/85), 0.50 mL/min at 254 nm) $t_{6A} = 7.57$ min, $t_{6B} = 9.90$ min). All the spectroscopic and physical data were identical to that in the literature.[11] ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.49–7.45 (m, 2H), 7.32–7.21 (m, 6H), 5.18 (s, 2H), 3.16 (d, 2H, $J = 15.5$ Hz), 2.95 (br s, 2H), 2.55 (d, 2H, $J = 15.5$ Hz). (−)-**6A**: mp 243–244 °C (dec). $[\alpha]_D^{20} = -50.3$ (*c* 0.056, Sure/Seal TM acetone). (+)-**6B**: mp 236–237 °C (dec). $[\alpha]_D^{20} = +42.5$ (*c* 0.084, 1 dm, Sure/Seal TM acetone).

4.4. Synthesis of (1*R*,2*R*,1′*R*)-1,1′-bis(diphenylphosphinoxy)-2,2′-spirobiindane 7 [(*R*)-SpiroBIP]

Diol **6A** (100 mg, 0.4 mmol) and DMAP (36 mg, 0.3 mmol) were dissolved into 20 mL of THF under an argon atmosphere and cooled to 0 °C with an ice bath. A solution of chlorodiphenylphosphine (0.16 mL, 0.9 mmol) in THF (1 mL) was added dropwise and followed by the addition of triethylamine (0.50 mL, 3.6 mmol). The reaction mixture was allowed to warm to ambient temperature and stirred for 30 min. Filtration of triethylammonium chloride followed by flash column chromatography on basic silica gel (toluene as eluent) to give a white solid **7** (120 mg, 0.2 mmol, 48% yield). mp 113–114 °C; $[\alpha]_D^{20} = +8.4$ (*c* 0.154, $CHCl_3$); ^{31}P NMR ($CDCl_3$, 75 MHz) δ (ppm) 103.1 (s); ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.37–7.08 (m, 14H), 5.52 (d, 1H, $J = 5.4$ Hz), 3.20 (d, 1H, $J = 14.7$ Hz), 2.28 (d, 1H, $J = 14.7$ Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 144.2, 143.3 (d, $J = 81.9$ Hz), 142.6 (d, $J = 58.2$ Hz), 142.1, 131.1 (d, $J = 39.6$ Hz), 130.2, 130.0, 129.9, 129.7, 128.7, 128.4, 127.9, 127.8, 127.6, 127.5, 126.4, 125.9, 125.2, 85.5 (d, $J = 67.7$ Hz), 63.4, 41.6. HRESI-MS (positive ion) $C_{41}H_{34}NaO_2P_2$ ($[M+Na]^+$) requires 643.1920. Found 643.1926.

4.5. Typical procedures for the preparation of the catalyst and for an asymmetric catalytic hydrogenation

$[Rh(COD)_2]BF_4$ (2.5 mg, 6.2 μmol) and (*R*)-SpiroBIP **7** (4.6 mg, 7.4 μmol) were dissolved in degassed toluene (0.30 mL) and degassed MeOH (0.30 mL) and stirred for 20 min to form a solution of [Rh(COD)(*R*-SpiroBIP)]BF_4 catalyst for the asymmetric hydrogenation. Then 0.6 mmol of substrate, the catalyst solution prepared above and 4 mL of degassed MeOH under argon atmosphere was added into a 50 mL stainless steel autoclave. The vessel was charged with H_2 with a final pressure of 5 atm. The reaction was carried out at room temperature 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 determined from the crude reaction mixture. Free amino acids were converted to corresponding methyl ester for the determination of ee by chiral GC (CP-Chirasil-DXE column for the analysis of 2-acetamidopropionic acid methyl ester and Chirasil-L-Val column for other products).

Acknowledgement

We are grateful for financial support from National Natural Science Foundation of China (Project 20502025).

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