Tetrahedron: *Asymmetry* 19 (2008) 1862–1866

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

Novel chiral phosphine-phosphoramidite ligands derived from 1-naphthylamine for highly efficient Rh-catalyzed asymmetric hydrogenation

Sai-Bo Yu [a,b], Jia-Di Huang [a,b], Dao-Yong Wang [a,b], Xiang-Ping Hu [a,*], Jun Deng [a,b], Zheng-Chao Duan [a,b], Zhuo Zheng [a,*]

[a] *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*
[b] *Graduate School of Chinese Academy of Sciences, Beijing 100039, China*

ARTICLE INFO

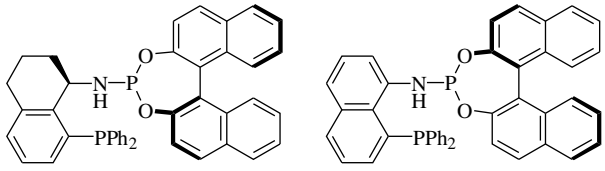
Article history:
Received 24 June 2008
Accepted 15 July 2008
Available online 8 August 2008

ABSTRACT

A new chiral phosphine-phosphoramidite ligand (*S*)-HY-Phos **1** has been prepared from 1-naphthylamine via a two-step transformation, and successfully applied in the Rh-catalyzed asymmetric hydrogenation of various functionalized olefins, including α-(acetamido)cinnamates, enamides and α-enol ester phosphonates, in which up to 98% ee, 99% ee and 99% ee were achieved, respectively.

1. Introduction

Unsymmetrical hybrid phosphine-phosphoramidite compounds have recently emerged as a new class of chiral ligands for highly efficient asymmetric catalysis.[1] Due to the two different phosphorus binding sites, this kind of ligands can offer a unique electronic environment around the central metal, which results in significantly improved enantioselectivities in some cases. The first successful phosphine-phosphoramidite ligand was known as QUINAPHOS, reported by Leitner et al. in 2000, which exhibited good enantioselectivities in the Rh-catalyzed asymmetric hydrogenation of dimethyl itaconate and methyl 2-acetamidoacrylate.[2] Since then, a few examples of chiral phosphine-phosphoramidite species (e.g., ferrocene-based derivatives,[3] PEAPhos,[4] Me-AnilaPhos,[5] IndolPhos[6] and others[7]) have been found to be highly efficient ligands for various asymmetric catalyses including Rh-catalyzed asymmetric hydrogenation, Rh-catalyzed asymmetric hydroformylation and Cu-catalyzed asymmetric conjugate addition of diethylzinc to enones. In spite of these advances, the development of new chiral phosphine-phosphoramidite ligands in terms of easy preparation and wide substrate scope remains an interesting and important goal. As part of our ongoing efforts toward the development of new and efficient unsymmetrical hybrid ligands for asymmetric catalysis,[4,8,9] in our recent research, we have reported a highly efficient 1,2,3,4-tetrahydro-1-naphthylamine-derived phosphine-phosphoramidite ligand, (R_c,R_a)-THNAPhos, for the Rh-catalyzed asymmetric hydrogenation of various functionalized olefins.[8] Due to the high cost of chiral 1,2,3,4-tetrahydro-1-naphthylamine, the search for an inexpensive alternative for the synthesis of new phosphine-phosphoramidite ligands is highly desirable. Due to the structural similarity, we therefore surmised that 1-naphthylamine should be a good candidate. Furthermore, the increased rigidity from 1,2,3,4-tetrahydro-1-naphthylamine to 1-naphthylamine may also result in the significantly different results in the catalytic asymmetric hydrogenation. As a result, we herein report our study on the development of this new chiral phosphine-phosphoramidite ligand [(*S*)-HY-Phos] from commercially available and inexpensive starting materials, 1-naphthylamine. The results disclose that this newly developed phosphine-phosphoramidite ligand, despite the absence of the central chirality in comparison with (R_c,R_a)-THNAPhos, displayed excellent enantioselectivities in the Rh-catalyzed asymmetric hydrogenation of various functionalized olefins including α-(acetamido)cinnamates, enamides and α-enol ester phosphonates, in which up to 98% ee, 99% ee and 99% ee were achieved, respectively (see Fig. 1).



(*R*,*R*)-THNAPhos (*S*)-HY-Phos **1**

Figure 1. The structure of phosphine-phosphoramidite ligands (*R*,*R*)-THNAPhos and (*S*)-HY-Phos **1**.

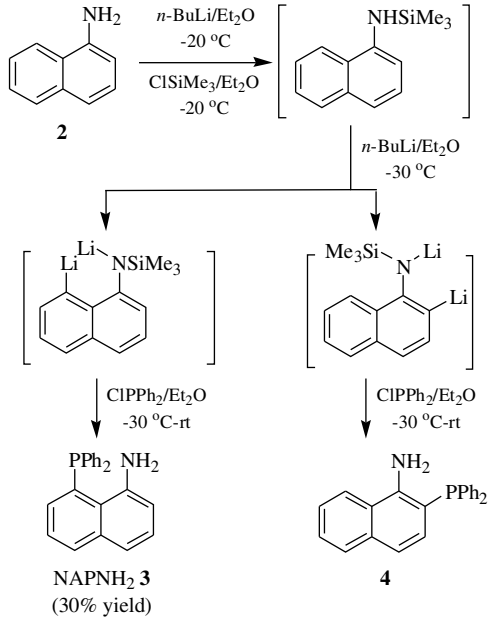
* Corresponding authors. Tel.: +86 411 84379206; fax: +86 411 84684746.
E-mail addresses: xiangping@dicp.ac.cn (X.-P. Hu), zhengz@dicp.ac.cn (Z. Zheng).

0957-4166/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetasy.2008.07.022

2. Results and discussion

2.1. Synthesis of chiral phosphine-phosphoramidite ligand 1 from 1-naphthylamine

The key to the synthesis of the target phosphine-phosphoramidite ligand is the preparation of an amino-phosphine intermediate, which can be obtained by the direct *ortho*-lithiation of 1-naphthylamine followed by the introduction of a diphenylphosphino group as the method described by us recently.[4] Thus, commercially available 1-naphthylamine **2** was treated with *n*-BuLi at −20 °C, followed by the slow addition of neat $ClSiMe_3$, which in situ generated a monosilyated product, *N*-(trimethylsilyl)-1-naphthylamine. The compound was further dilithiated by the addition of 3 equiv of *n*-BuLi at −30 °C, and then *ortho*-phosphinated with $ClPPh_2$. Since 1-naphthylamine can undergo lithiation at either the 8-position or the 2-position, the subsequent reaction with $ClPPh_2$ gives rise to 1-(8-diphenylphosphino)naphthylamine **3** ($NAPNH_2$) and 1-(2-diphenylphosphino)naphthylamine **4**, respectively, as shown in Scheme 1.



Scheme 1. Synthesis of amino-phosphine intermediate via direct *ortho*-lithiation of 1-naphthylamine followed by the introduction of a diphenylphosphino group.

Fortunately, after work-up and crystallization from *n*-hexane, 1-(8-diphenylphosphino)naphthylamine **3** ($NAPNH_2$) was obtained in 30% yield exclusively, and no 1-(2-diphenylphosphino)naphthylamine **4** was separated. The structure of 1-(8-diphenylphosphino)naphthylamine **3** was confirmed by X-ray diffraction analysis of its acetylated derivative (Fig. 2).

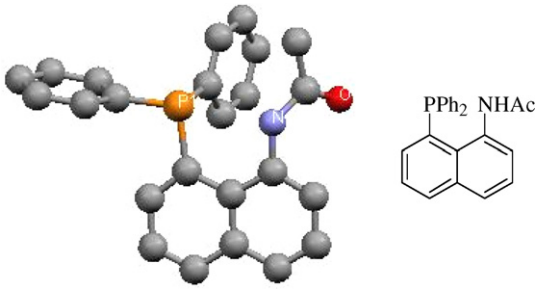
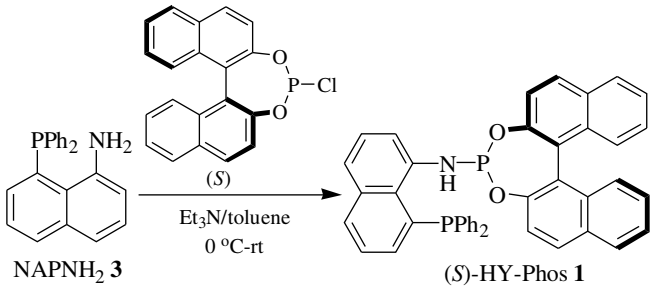


Figure 2. Crystal structure of *N*-acetyl-1-(8-diphenylphosphinon)naphthylamine. Hydrogen atoms are omitted for clarity (CCDC 697094).

$NAPNH_2$ **3** was then converted into the corresponding phosphine-phosphoramidite ligand [(*S*)-HY-Phos **1**] by the reaction with 1 equiv of (*S*)-4-chloro-3,5-dioxa-4-phosphacyclohepta[2,1-α;3,4-α′]dinaphthalene in toluene at 0 °C in the presence of Et_3N as a scavenger for the HCl eliminated (Scheme 2). This new phosphine-phosphoramidite ligand is air-stable and can be used in the open air, which makes this ligand practical for general laboratory preparations, as well as scale-up operations.

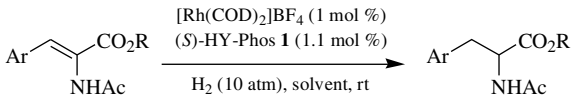


Scheme 2. Synthesis of chiral phosphine-phosphoramidite ligand (*S*)-HY-Phos **1**.

2.2. Rh-catalyzed asymmetric hydrogenation of various functionalized olefins with phosphine-phosphoramidite ligand 1

With this newly developed phosphine-phosphoramidite ligand in hand, we then examined its efficiency in the Rh-catalyzed asymmetric hydrogenation of α-(acetamido)cinnamates **5**. The hydrogenation was performed at room temperature under an H_2 pressure of 10 atm in the presence of 1 mol % of the Rh-catalyst prepared in situ from $[Rh(COD)_2]BF_4$ and 1.1 equiv of chiral ligand. As shown in Table 1, this new phosphine-phosphoramidite ligand displayed excellent enantioselectivity for the hydrogenation of methyl (*Z*)-acetamidocinnamate **5a**, affording the hydrogenation product in an ee-value of up to 98% ee (entry 2). This result is comparable to that obtained with (*R*,*R*)-THNAPhos, although only axial chirality

Table 1
Rh-catalyzed asymmetric hydrogenation of α-(acetamido)cinnamates **5** with phosphine-phosphoramidite ligand **1**[a]



5 **6**

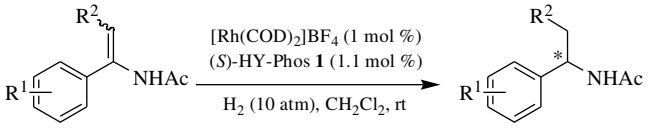
Entry	Substrate (Ar, R)	Solvent	Conv.[b] (%)	ee[c] (%) (config.)
1	**5a** (Ph, Me)	CH_2Cl_2	100	99 (*S*)[d]
2	**5a** (Ph, Me)	CH_2Cl_2	100 (98)	98 (*R*)
3	**5a** (Ph, Me)	toluene	100	97 (*R*)
4	**5a** (Ph, Me)	MeOH	100	95 (*R*)
5	**5a** (Ph, Me)	*i*-PrOH	100	92 (*R*)
6	**5b** (Ph, Et)	CH_2Cl_2	100 (98)	97 (*R*)
7	**5c** (2-$MeOC_6H_4$, Me)	CH_2Cl_2	100 (98)	97 (*R*)
8	**5d** (4-$MeOC_6H_4$, Me)	CH_2Cl_2	100 (97)	98 (*R*)
9	**5e** (2-ClC_6H_4, Me)	CH_2Cl_2	100 (97)	97 (*R*)
10	**5f** (4-ClC_6H_4, Me)	CH_2Cl_2	100 (98)	98 (*R*)
11	**5g** (4-ClC_6H_4, Et)	CH_2Cl_2	100 (98)	97 (*R*)

[a] All reactions were carried out with 0.5 mmol of substrates, 1 mol % of catalyst prepared from $[Rh(COD)_2]BF_4$ and 1.1 equiv of ligand for 12 h under the conditions given in the equation.
[b] Conversions were determined by GC, and the isolated yields were provided in parentheses.
[c] Enantiomeric excesses were determined by GC, using a CP-Chiralsil-L-Val capillary (0.25 mm × 30 m) column. The absolute configurations were determined by comparing the GC retention times with the GC data in the literature.
[d] The data were obtained with (*R*,*R*)-THNAPhos.

is present in (*S*)-HY-Phos (entry 2 vs entry 1). A solvent screening experiment revealed that the nature of solvent had some effect on the enantioselectivity; however, no result surpassed that obtained in CH_2Cl_2 (entries 2–5). Hydrogenation of a series of substituted α-(acetamido)cinnamates **5b–g** was then performed in CH_2Cl_2. The results revealed that there was no major effect on the substitution pattern or electronic properties of the α-(acetamido)cinnamates, while all of the tested substrates were hydrogenated in excellent enantioselectivities with full conversions (entries 6–11).

We next investigated the application of this newly developed phosphine-phosphoramidite ligand in the Rh-catalyzed asymmetric hydrogenation of enamide substrates **7**, and the results are summarized in Table 2. Under the optimized hydrogenation conditions as used in the hydrogenation of α-(acetamido)cinnamates, a series of substituted *N*-(phenylethenyl)acetamides **7a–f** were hydrogenated in good to excellent enantioselectivities, with the best enantioselectivity (99% ee) being achieved in the hydrogenation of substrate **7b** with a 4-Cl group (entries 1–6). In particular, with the hydrogenation of trisubstituted enamides **7g–i**, this ligand also displayed good enantioselectivities, providing ee-values of 93–96% (entries 7–9). In comparison with the corresponding (*R*,*R*)-THNAPhos, (*S*)-HY-Phos displayed somewhat lower enantioselectivity in the hydrogenation of disubstituted substrate **7a** (entry 1 vs entry 10). However, for the hydrogenation of trisubstituted substrates, (*S*)-HY-Phos **1** showed significantly higher enantioselectivities (entries 7 and 8 vs entries 11 and 12).

Table 2
Rh-catalyzed asymmetric hydrogenation of enamides **7** with phosphine-phosphoramidite ligand **1**[a]



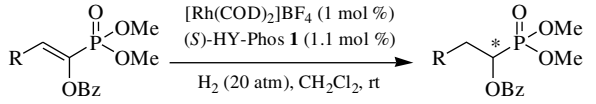
7 **8**

Entry	Substrate (R^1, R^2)	Ligand	Conv.[b] (%)	ee[c] (%) (config.)
1	**7a** (H, H)	HY-Phos	100 (96)	96 (*R*)
2	**7b** (4-Cl, H)	HY-Phos	100 (99)	99 (*R*)
3	**7c** (4-Br, H)	HY-Phos	100 (96)	98 (*R*)
4	**7d** (4-Me, H)	HY-Phos	100 (97)	96 (*R*)
5	**7e** (4-CF_3, H)	HY-Phos	100 (98)	98 (*R*)
6	**7f** (3-OMe, H)	HY-Phos	100 (98)	96 (*R*)
7	**7g** (H, Me) (*E*/*Z*, 75/25)	HY-Phos	100 (98)	96 (*R*)
8	**7h** (4-Cl, Me) (E/Z, 63/37)	HY-Phos	100 (99)	93 (*R*)
9	**7i** (4-OMe, Me) (*E*/*Z*, 73/27)	HY-Phos	100 (95)	94 (*R*)
10	**7a** (H, H)	THNAPhos	100	>99 (*S*)
11	**7g** (H, Me) (*E*/*Z*, 75/25)	THNAPhos	100	91 (*S*)
12	**7h** (4-Cl, Me) (*E*/*Z*, 63/37)	THNAPhos	100	78 (*S*)

[a] All reactions were carried out with 0.5 mmol of substrates, 1 mol % of catalyst prepared from $[Rh(COD)_2]BF_4$ and 1.1 equiv of ligand for 12 h under the conditions given in the equation.
[b] Conversions were determined by GC, and the isolated yields were provided in parentheses.
[c] Enantiomeric excesses were determined by GC, using a Chiral Select 1000 capillary (0.25 mm × 30 m) column. The absolute configurations were determined by comparing the GC retention times with the GC data in the literature.

To further demonstrate the efficiency of this new phosphine-phosphoramidite ligand in the catalytic asymmetric hydrogenation, we applied it to the Rh-catalyzed asymmetric hydrogenation of various α-enol ester phosphonates **9** (Table 3). The catalytic asymmetric hydrogenation of α-enol ester phosphonates remains a rarely explored area.[10] It is only very recently that some unsymmetrical hybrid bidentate phosphorus ligands have been found to show good to excellent enantioselectivities in this transformation.[8,11] We found that this newly developed phosphine-phosphoramidite ligand was also highly efficient for the hydrogenation of this substrate class, providing an ee-value of 99% in the rhodium-catalyzed asymmetric hydrogenation of dimethyl α-benzoyloxyethenephosphonate **9a**, comparable to that obtained with (*R*,*R*)-THNAPhos (entries 1 and 2). The hydrogenation of various β-alkyl substituted α-benzoyloxyethenephosphonates **9b–d** was then examined. The results indicated that the β-alkyl substituent in the substrate had little effect in the enantioselectivity, and all substrates were hydrogenated in excellent enantioselectivities (entries 3–5). We next examined the Rh-catalyzed hydrogenation of a set of structurally diverse β-aryl substituted substrates **9e–l** with this new ligand. It was found that all β-aryl substituted substrates **9e–l** were hydrogenated in excellent enantioselectivity (95–99% ee), regardless of the substitution pattern and electronic property of the substituent in the phenyl ring of the substrates (entries 6–13). High enantioselectivity was also observed in the hydrogenation of β-alkoxy substituted substrates **9m–n**, in which 96% ee and 98% ee were obtained, respectively (entries 14 and 15).

Table 3
Rh-catalyzed asymmetric hydrogenation of α-enol ester phosphonates **9** with phosphine-phosphoramidite ligand **1**[a]



9 **10**

Entry	Substrate	Conv.[b] (%)	ee[c] (%) (config.)
1	**9a**: R = H	100	99 (*S*)[d]
2	**9a**: R = H	100 (99)	99 (*R*)[e]
3	**9b**: R = Me	100 (98)	99 (*R*)
4	**9c**: R = Et	100 (99)	98 (*R*)[e]
5	**9d**: R = $CH_2(CH_2)_8CH_3$	100 (98)	98[e]
6	**9e**: R = Ph	100 (98)	98 (*R*)
7	**9f**: R = 4-FC_6H_4	100 (97)	98
8	**9g**: R = 4-ClC_6H_4	100 (97)	99
9	**9h**: R = 4-$NO_2C_6H_4$	100 (99)	98
10	**9i**: R = 4-$MeOC_6H_4$	100 (95)	95
11	**9j**: R = 3-$MeOC_6H_4$	100 (98)	99
12	**9k**: R = 3-ClC_6H_4	100 (97)	>99
13	**9l**: R = 2-ClC_6H_4	100 (98)	98
14	**9m**: R = OEt	100 (98)	96
15	**9n**: R = O^{i}Pr	100 (98)	98

[a] All reactions were carried out with 0.5 mmol of substrate, 1 mol % of catalyst prepared from $[Rh(COD)_2]BF_4$ and 1.1 equiv of ligand for 24 h under the conditions given in the equation unless otherwise specified.
[b] Conversions were determined by NMR, and the isolated yields were provided in parentheses.
[c] Enantiomeric excesses were determined by HPLC on a chiral column (Chiralpak AD, Chiralcel OD-H, or Chiralcel OJ-H, 0.46 mm × 25 cm). The absolute configurations were determined by comparing the HPLC retention times with the reported data.
[d] The data were obtained with (*R*,*R*)-THNAPhos.
[e] Hydrogenation was performed under 10 atm of H_2 pressure for 12 h.

3. Conclusion

In conclusion, a new chiral phosphine-phosphoramidite ligand (*S*)-HY-Phos **1** has been prepared from commercially available and inexpensive 1-naphthylamine through a two-step transformation and successfully applied in the Rh-catalyzed asymmetric hydrogenation of various functionalized C=C double bonds including α-(acetamido)cinnamates, enamides and α-enol ester phosphonates. Despite the absence of the central chirality, this newly developed phosphine-phosphoramidite ligand showed excellent enantioselectivities in the hydrogenation of α-(acetamido)cinnamates and α-enol ester phosphonates, comparable to those ob-

tained with the corresponding (*R*,*R*)-THNAPhos derived from chiral 1,2,3,4-tetrahydro-1-naphthylamine. In the hydrogenation of disubstituted enamides, (*S*)-HY-Phos gave somewhat lower enantioselectivity than (*R*,*R*)-THNAPhos. However, higher enantioselectivities were observed in the hydrogenation of trisubstituted enamides by the use of (*S*)-HY-Phos instead of (*R*,*R*)-THNAPhos. Further investigations on other catalytic asymmetric reactions with this ligand are underway, and progress will be reported in due time.

4. Experimental

4.1. General

All synthetic reactions and manipulations were performed in a nitrogen or argon atmosphere using standard Schlenk techniques. Hydrogenations were carried out in a stainless steel autoclave. Solvents were reagent grade, dried and distilled before use, following the standard procedures. (*S*)-4-Chloro-3,5-dioxa-4-phosphacyclohepta[2,1-α;3,4-α′]din-aphthalene was synthesized according to the literature procedure.[12] α-(Acetamido)cinnamates **5**,[13] enamides **7**[14] and α-enol ester phosphonates **9**[10] are known compounds, which were prepared according to the literature methods. All other chemicals were obtained commercially.

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on BRUKER DEX-400 spectrometer. Chemical shift values (δ) are denoted in ppm and are referenced to residue protons in deuterated solvents for ^{1}H NMR ($CDCl_3$: 7.27 ppm), to $CDCl_3$ (77.0 ppm) for ^{13}C NMR and to external H_3PO_4 (85% solution in D_2O, 0 ppm) for ^{31}P NMR. Optical rotations were recorded using a JASCO P-1020 high sensitive polarimeter. Enantiomeric excesses were determined by capillary GC analysis with a CP-Chiralsil-L-Val column (0.25 mm × 30 m) for **6**, a chiral Select 1000 column (0.25 mm × 30 m) for **8** and by HPLC analysis with a chiral column (Chiralpak AD, Chiralcel OD-H, and Chiralcel OJ-H, 0.46 mm × 25 cm) for **10**.

4.2. Preparation of 1-(8-diphenylphosphino)naphthylamine 3 [$NAPNH_2$]

To a solution of 1-naphthylamine (1.43 g, 10 mmol) in 10 mL of ether at −20 °C was dropwise added 5.8 mL (1.7 M in *n*-hexane) of *n*-BuLi. The resulting solution was stirred at −20 °C for 30 min, and then 1.4 mL (1.1 equiv) of Me_3SiCl was added slowly at the same temperature. The reaction mixture was stirred for another 1 h, and then 17.6 mL (1.7 M in hexane) of *n*-BuLi was dropwise at −30 °C. After the addition was completed, the reaction mixture was stirred at −30 °C for 3 h. The reaction mixture was slowly warmed to room temperature and stirred overnight. The reaction mixture was cooled to −30 °C again, and a solution of chlorodiphenylphosphine (2.2 g, 10 mmol) in 10 mL of ether was added dropwise. After holding at the same temperature for 3 h, the reaction mixture was warmed to room temperature for another 4 h. A solution of 1 M of aqueous HCl was added slowly until the reaction mixture became clear in both phases. The aqueous phase was extracted with ether (3 × 30 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexanes/acetate, 20/1) to give 0.98 g (30% yields) of 1-(8-diphenylphosphino)naphthylamine **3** as a pale-yellow solid. Mp 92–94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.42 (br, 2H), 6.69–6.71 (m, 1H), 7.01–7.03 (m, 1H), 7.22–7.28 (m, 7H), 7.30–7.34 (m, 6H), 7.75–7.77 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 113.1, 119.8, 125.0, 126.4, 128.5, 128.6, 128.7, 128.9, 130.9, 133.8, 134.0, 134.1, 136.1, 136.2, 137.0, 137.1, 145.4; ^{31}P NMR (162 MHz, $CDCl_3$): δ −4.0.

4.3. Preparation of *N*-[1-(8-diphenylphosphino)naphthyl]-(*S*)-1,10-bi-2-naphthylphosphoramidite [(*S*)-HY-Phos 1]

(*S*)-4-Chloro-3,5-dioxa-4-phosphacyclohepta[2,1-α;3,4-α′]dinaphthalene (350.5 mg, 1.0 mmol) was dissolved in 2.0 mL of dried toluene, which was cooled to 0 °C. A solution of 1-(8-diphenylphosphino)naphthylamine **3** (327 mg, 1.0 mmol) and Et_3N (303 mg, 3.0 mmol) in 4.0 mL of toluene was added to the above solution for 30 min. The resulting mixture was left standing at room temperature overnight. The precipitate was filtered, and the filtrate collected, and concentrated under reduced pressure. The residue was purified by column chromatography to give the target phosphine-phosphoramidite ligand, (*S*)-HY-Phos **1** (280 mg, 44% yields). Mp 94–96 °C; $[\alpha]_D^{20} = +53.7$ (*c* 0.56, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00–7.16 (m, 8H), 7.26–7.32 (m, 10 H), 7.40–7.44 (m, 4H), 7.53–7.63 (m, 2H), 7.76–7.93 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 119.2, 124.9, 125.1, 126.2, 126.4, 127.3, 127.3, 128.5, 128.6, 128.7, 128.8, 128.9, 129.1, 133.9, 134.1, 134.7, 134.8, 134.9; ^{31}P NMR (162 MHz, $CDCl_3$): δ −4.7, 145.5; HRMS (EI) calcd for $C_{42}H_{30}NO_2P_2$ [M+H]: 642.1752, found 642.1771.

4.4. General procedure for asymmetric hydrogenation

In a nitrogen-filled glovebox, a stainless steel autoclave was charged with $[Rh(COD)_2]BF_4$ (2.0 mg, 0.5×10^{-2} mmol) and (*S*)-HY-Phos **1** (3.5 mg, 0.55×10^{-2} mmol) in 1.5 mL of a degassed CH_2Cl_2. After stirring for 10 min at room temperature, the substrate (0.5 mmol) in 1.5 mL of the same solvents was added to the reaction mixture. The hydrogenation was performed at room temperature under an H_2 pressure of 10 atm for 12 h. The reaction mixture was passed through a short silica gel column to remove the catalyst. After evaporating the solvent, the crude product was subjected to determine the conversions by GC or ^{1}H NMR and the enantiomeric excesses by GC or HPLC.

Acknowledgement

We are grateful for financial support from the National Natural Science Foundation of China (20472083).

References

1. (a) Kok, S. H. L.; Au-Yeung, T. T.-L.; Cheung, H.-Y.; Lam, W. S.; Chan, S. S.; Chan, A. S. C. In *The Handbook of Homogeneous Hydrogenation*; de Vries, J. C., Elsevier, C. J., Eds.; Wiley-VCH: Weinheim, 2007. Part IV, Chapter 27; (b) Amoroso, D.; Graham, T. W.; Guo, R.; Tsang, C.-W.; Abdur-Rashid, K. *Aldrichim. Acta* **2008**, *41*, 15.
2. (a) Franciò, G.; Faraone, F.; Leitner, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 1428; (b) Burk, S.; Franciò, G.; Leitner, W. *Chem. Commun.* **2005**, 3460.
3. (a) Jia, X.; Li, X.; Lam, W. S.; Kok, S. H. L.; Xu, L.; Lu, G.; Yeung, C.-H.; Chan, A. S. C. *Tetrahedron: Asymmetry* **2004**, *15*, 2273; (b) Hu, X.-P.; Zheng, Z. *Org. Lett.* **2004**, *6*, 3585; (c) Zeng, Q.-H.; Hu, X.-P.; Duan, Z.-C.; Liang, X.-M.; Zheng, Z. *Tetrahedron: Asymmetry* **2005**, *16*, 1233; (d) Hu, X.-P.; Zheng, Z. *Org. Lett.* **2005**, *7*, 419.
4. Huang, J.-D.; Hu, X.-P.; Duan, Z.-C.; Zeng, Q.-H.; Yu, S.-B.; Deng, J.; Wang, D.-Y.; Zheng, Z. *Org. Lett.* **2006**, *8*, 4367.
5. Vallianatou, K. A.; Kostas, I. D.; Holz, J.; Börner, A. *Tetrahedron Lett.* **2006**, *47*, 7947.
6. (a) Wassenaar, J.; Reek, J. N. H. *Dalton Trans.* **2007**, 3750; (b) Wassenaar, J.; Kuil, M.; Reek, J. N. H. *Adv. Synth. Catal.* **2008**, *350*, 1610.
7. (a) Zhang, W.; Zhang, X. *Angew. Chem., Int. Ed.* **2006**, *45*, 5515; (b) Zhang, W.; Zhang, X. *J. Org. Chem.* **2007**, *72*, 1020; (c) Yan, Y.; Zhang, X. *J. Am. Chem. Soc.* **2006**, *128*, 7198; (d) Boeda, F.; Rix, D.; Clavier, H.; Crévisy, C.; Mauduit, M. *Tetrahedron: Asymmetry* **2006**, *17*, 2726.
8. (a) Wang, D.-Y.; Hu, X.-P.; Huang, J.-D.; Deng, J.; Yu, S.-B.; Duan, Z.-C.; Xu, X.-F.; Zheng, Z. *Angew. Chem., Int. Ed.* **2007**, *46*, 7810; (b) Qiu, M.; Hu, X.-P.; Wang, D.-Y.; Deng, J.; Huang, J.-D.; Yu, S.-B.; Duan, Z.-C.; Zheng, Z. *Adv. Synth. Catal.* **2008**, *350*, 1413.
9. (a) Hu, X.-P.; Chen, H.-L.; Zheng, Z. *Adv. Synth. Catal.* **2005**, *347*, 541; (b) Deng, J.; Duan, Z.-C.; Huang, J.-D.; Hu, X.-P.; Wang, D.-Y.; Yu, S.-B.; Xu, X.-F.; Zheng, Z. *Org. Lett.* **2007**, *9*, 4825; (c) Deng, J.; Hu, X.-P.; Huang, J.-D.; Yu, S.-B.; Wang, D.-Y.; Duan, Z.-C.; Zheng, Z. *J. Org. Chem.* **2008**, *73*, 2015; (d) Wang, D.-Y.; Huang, J.-

D.; Hu, X.-P.; Deng, J.; Yu, S.-B.; Duan, Z.-C.; Zheng, Z. *J. Org. Chem.* **2008**, *73*, 2011.
10. (a) Burk, M. J.; Stammers, T. A.; Straub, J. A. *Org. Lett.* **1999**, *1*, 387; (b) Gridnev, I. D.; Higashi, N.; Imamoto, T. *J. Am. Chem. Soc.* **2001**, *123*, 4631; (c) Gridnev, I. D.; Yasutake, M.; Imamoto, T.; Beletskaya, I. P. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 5385; (d) Liu, H.; Zhou, Y.-G.; Yu, Z.-K.; Xiao, W.-J.; Liu, S.-H.; He, H.-W. *Tetrahedron* **2006**, *62*, 11207.
11. (a) Rubio, M.; Suárez, A.; Álvarez, E.; Pizzano, A. *Chem. Commun.* **2005**, 628; (b) Rubio, M.; Vargas, S.; Suárez, A.; Álvarez, E.; Pizzano, A. *Chem. Eur. J.* **2007**, *13*, 1821.
12. Franciò, G.; Arena, C. G.; Faraone, F.; Graiff, C.; Lanfranchi, M.; Tiripicchio, A. *Eur. J. Inorg. Chem.* **1999**, *23*, 1219.
13. Vineyard, B. D.; Knowles, W. S.; Sabacky, M. J.; Bachman, G. L.; Weinkauff, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5946.
14. (a) van den Berg, M.; Minnaard, A. J.; Schudde, E. P.; van Esch, J.; de Vries, A. H. M.; de Vries, J. G.; Feringa, B. L. *J. Am. Chem. Soc.* **2000**, *122*, 11539; (b) Burk, M. J.; Casy, G.; Johnson, N. B. *J. Org. Chem.* **1998**, *63*, 6084.