Pergamon

SCIENCE DIRECT®

Tetrahedron: *Asymmetry* 14 (2003) 1285–1289

TETRAHEDRON: *ASYMMETRY*

Readily available new pyridyl alcohols derived from D-glucose as ligands for the enantioselective addition of diethylzinc to aldehydes

Hanmin Huang, Zhuo Zheng,* Huilin Chen,* Changmin Bai and Junwei Wang

Dalian Institute of Chemical Physics, The Chinese Academy of Sciences, Dalian 116023, PR China

Received 14 January 2003; revised 27 February 2003; accepted 28 February 2003

Abstract—A series of new chiral ligands derived from D-glucose has been synthesized and applied in the enantioselective addition of diethylzinc to aldehydes. Up to 94.1% e.e. was obtained in the ethylation reactions. In contrast to the ligands derived from D-fructose, ligands derived from D-glucose gave the opposite asymmetric induction.

1. Introduction

The enantioselective addition of diethylzinc to aldehydes is one of the most important synthetic procedures for obtaining enantiopure secondary alcohols,[1] which are key intermediates in the preparation of many biologically active compounds. Since the first report on the asymmetric reaction in 1984 by Oguni and Omi, who used certain β-amino alcohols as catalysts,[2] numerous efforts have been made to search for new effective ligands in the reaction and to elucidate the reaction mechanism.[3]

As analogs of β-amino alcohols, pyridyl alcohols have been proved to be effective ligands for this reaction and although a variety of pyridyl alcohols derived from natural products such as camphor and nopinone have been synthesized,[4] reports on the design and development of cheap and effective pyridyl alcohols derived from carbohydrates are scarce.[5] Moreover, it is difficult to obtain two antipodal ligands derived from the natural products, because both enantiomers of the natural product are not always readily available.

Recently, we synthesized a series of novel pyridyl alcohols derived from D-fructose as catalysts to explore the structure–activity relationship of pyridyl alcohol ligands in the enantioselective addition of diethylzinc to aldehydes.[6] Some relevant observations from that study are that the appropriate backbone length between the coordinating nitrogen and oxygen is crucial for a highly effective catalysis with these ligands. As might be expected, all ligands derived from the D-fructose gave the products with the same absolute (*R*)-configuration. This led to the proposal that it is necessary to develop effectively antipodal ligands to give the products with (*S*)-configuration. However, from a synthetic viewpoint, it is difficult to obtain the other enantiomers of the pyridyl alcohols derived from the D-fructose, the reason is that the L-fructose is not easy to obtain. Conformational analysis of the chiral ketones derived from D-fructose and D-glucose, allowed us to propose that the chiral pyridyl alcohols derived from these two chiral ketones might function as pseudo-enantiomers (Fig. 1), i.e. they should give the reverse asymmetric induction in the diethylzinc addition to aldehydes. In addition, in contrast to the D-fructose-derived pyridyl alcohols, the framework of the D-glucose-derived ligands is a five-membered furanose-ring which is more rigid than the six-membered pyranose-ring of the D-fructose derived ligands and this might lead to higher asymmetric induction for the ethylation reaction. Herein, we report the synthesis of the pyridyl alcohols derived from D-glucose with an appropriate backbone length and their application in the enantioselective addition of diethylzinc to aldehydes.

* Corresponding authors. Tel.: +86+411-4379276; fax: +86+411-4684746; e-mail: zhengz@ms.dicp.ac.cn

0957-4166/03/$ - see front matter
doi:10.1016/S0957-4166(03)00212-X

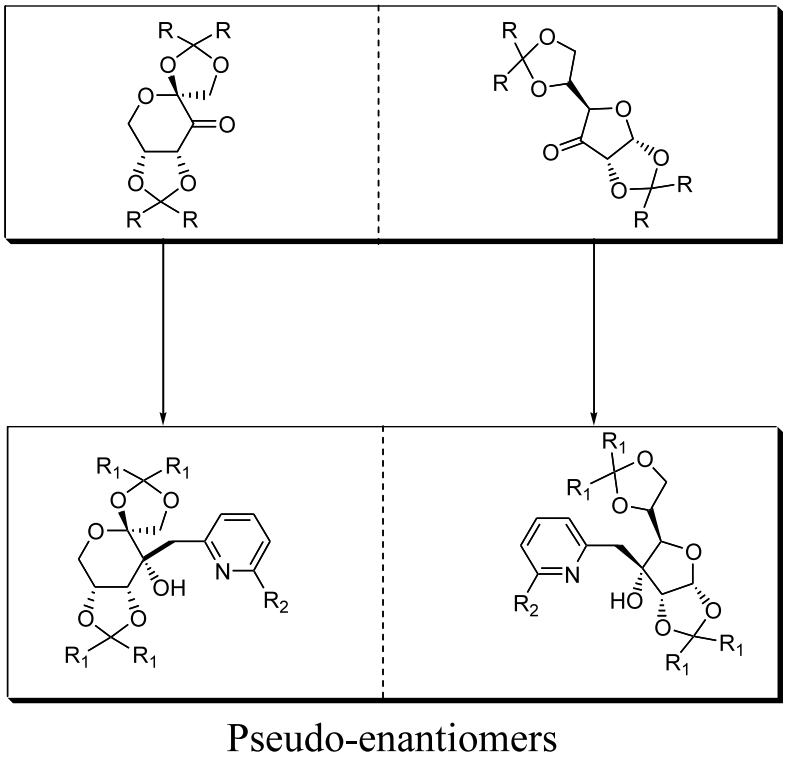


Figure 1.

2. Results and discussion

2.1. Synthesis of ligands derived from D-glucose

The routes for the synthesis of the D-glucose derivatives **1**–**6** are shown in Scheme 1. 2-Picoline, 2,6-lutidine and 2-methylquinoline were first lithiated with *n*-BuLi in ether at 0°C to give the corresponding organolithium, followed by trapping with chiral ketone **7** or **8**, which can be readily synthesized from the commercially available D-glucose,[7] produced compounds **1**–**6** in 51–78% yields. The relative configurations of the products were determined by two-dimensional NOESY experiments. As far as **2** is concerned, the relative configuration is confirmed by the existence of strong NOE interaction between C(2)H and benzylic hydrogen H (Fig. 2), which indicates that the benzylic group is *cis* to the C(2)H. Accordingly, the (1*R*,2*R*,3*R*,4*R*,5*R*)-configurations of furanose ring were deduced unambiguously.

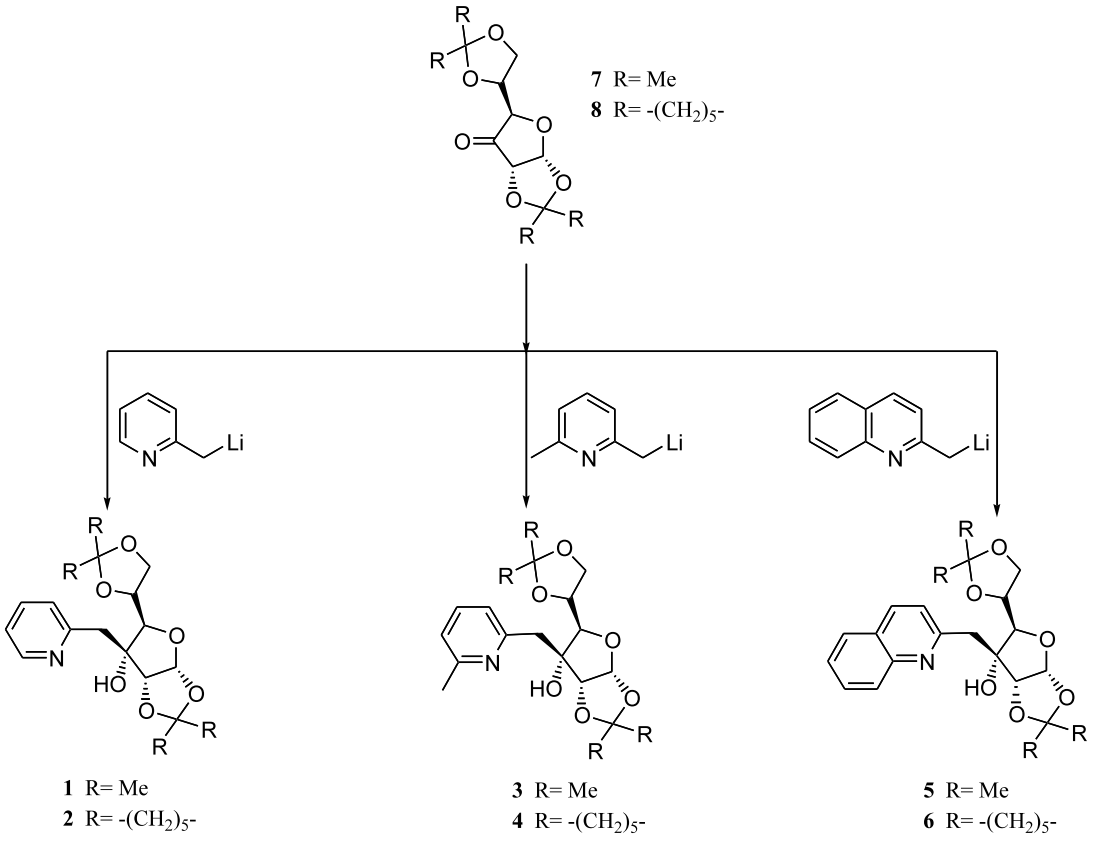
2.2. Enantioselective addition of diethylzinc to aldehydes catalyzed by ligands 1–6

According to the general procedure (see Section 4), the catalysts **1**–**6** were tested in the enantioselective addition reaction by the addition of 2.2 equiv. of diethylzinc to benzaldehyde in the presence of a catalytic amount (5 mol%) of the catalyst in toluene at 0°C to compare their efficiency. The results are summarized in Table 1.

As can be seen from the Table 1, all the reactions proceeded smoothly to give (*S*)-1-phenyl-1-propanol in good yields and with enantiomeric excesses ranging from 73.2 to 89.1%. Furthermore, the enantioselectivities of this reaction were very sensitive to the substituents of the pyridine ring and the protecting groups on the D-glucose skeleton in the chiral catalysts. Enhancement of the bulk of the protecting group on the D-glucose skeleton induced an increase in the enantioselectivity (entries 1 versus 2, or 3 versus 4, 5 versus 6). Comparison of entries 2, 4 and 6 clearly shows that the enantiomeric excesses were also dependent on the pyridine ring: It is noteworthy that the methyl-group on the 6-position of pyridine ring is key to obtaining high e.e., which indicated that the presence of a methyl-group on the 6-position of pyridine ring may play a screening role to push the Zn closer to the stereogenic center in the transition state or that it can prevent the approach of the substrate from the pyridine side. The results suggest that **4** is the most effective chiral ligand in this asymmetric reaction.

The effect of the reaction temperature on activity and enantioselectivity was also studied using ligand **4** as the catalyst. As expected, the yields of the ethylation product were better at high temperature but the best enantioselectivity was found at –10°C, the enantiomeric excess dropped when the temperature was either raised or lowered (entries 4, 7–9). In addition, the solvents of the diethylzinc reagent have marginal effect on the reaction (entries 7 versus 10).

In view of the above results, chiral ligands **4** was used in catalysts for the enantioselective addition of diethylzinc to a family of aldehydes comprising both aromatic and aliphatic aldehydes and the results are shown in



Scheme 1.

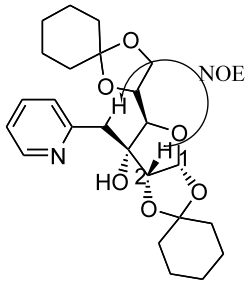


Figure 2.

Table 2. It can be seen from the results that high enantioselectivities were generally obtained for all the aldehydes except for *trans*-cinnamaldehyde (entry 9), which gave much lower enantioselectivity. The best asymmetric induction (94.1%, entry 7 in Table 2) was obtained by using electron-donating and bulky *o*-anisaldehyde as substrate.

As expected, all ligands derived from D-glucose produced (*S*)-secondary alcohols, which is opposite to the (*R*)-products promoted by the D-fructose-derived pyridyl alcohols. From a synthetic viewpoint, it is of interest to note that with both D-fructose and D-glucose-derived pyridyl alcohols in hand, it is possible to obtain both enantiomers of the chiral products.

3. Conclusions

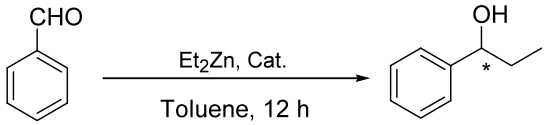
In conclusion, as pseudo-antipodal ligands of D-fructose-derived pyridyl alcohols, a new series of chiral ligands based on D-glucose have been readily synthesized and applied as catalysts in the asymmetric addition diethylzinc to aldehydes with good e.e. Further studies are now in progress to use these new ligands in other catalytic asymmetric reactions.

4. Experimental

4.1. General methods

All reactions were carried out under an N_2 atmosphere. Melting points were measured on a Metter FP5 melting apparatus and are uncorrected. NMR spectra were measured in $CDCl_3$ on a Bruker DRX-400 NMR spectrometer with TMS as an internal reference. Optical rotations were measured with a JASCO P-1020 automatic polarimeter. High resolution mass spectra were recorded on Applied Biosystems Mariner System 5303. Elemental analyses were performed on Elemental Analyzer-MOD 1106. Enantiomeric excess (e.e.) determination was carried out using GC with a β-DEX 120 capillary column on an Agilent HP-4890 GC instrument with FID as detector or using HPLC with a Chiralcel OD-H column on an Agilent 1100 Series. All

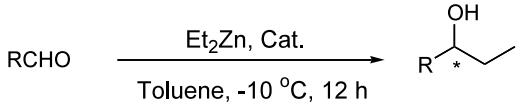
Table 1. Enantioselective addition of diethylzinc to benzaldehyde promoted by chiral ligands **1**–**6**[a]



Entry	Ligand	Temperature (°C)	Yield (%)[b]	E.e. (%) (config.)[c]
1	**1**	0	92	73.2 (*S*)
2	**2**	0	99	81.0 (*S*)
3	**3**	0	99	86.7 (*S*)
4	**4**	0	99	89.1 (*S*)
5	**5**	0	99	76.5 (*S*)
6	**6**	0	99	79.3 (*S*)
7	**4**	−10	99	**90.1** (*S*)
8	**4**	−20	92	87.5 (*S*)
9	**4**	20	99	85.5 (*S*)
10	**4**	−10	99	**92.4** (*S*)[d]

[a] The reactions were carried out in toluene for 12 h, benzaldehyde/Et_2Zn/ligand = 1.0/2.2/0.05, unless otherwise specified, diethylzinc reagent is 1 M diethylzinc in hexane.
[b] Isolated yields based on the benzaldehyde.
[c] Determined by GC with β-DEX 120 capillary column and the absolute configuration was determined by comparing the sign of specific rotation.[8]
[d] 1.1 M diethylzinc in toluene was used.

Table 2. Enantioselective addition of diethylzinc to aldehydes catalyzed by **4**[a]



Entry	R	Yield (%)[b]	E.e. (%) (config.)[c]
1	C_6H_5	99	**90.1** (*S*)
2	*p*-ClC_6H_4	99	**91.8** (*S*)
3	*p*-BrC_6H_4	99	**90.0** (*S*)
4	*p*-$CH_3C_6H_4$	93	**92.4** (*S*)
5	*p*-$CH_3OC_6H_4$	81	87.7 (*S*)
6	*p*-FC_6H_4	92	**91.4** (*S*)
7	*o*-$CH_3OC_6H_4$	99	**94.1** (*S*)
8	*o*-ClC_6H_4	95	85.1 (*S*)
9	2-Thiophene-	46	70.2 (*S*)
10	E-PhCH=CH	87	35.0 (*S*)[d]
11	*c*-C_6H_{11}	78	**90.2** (*S*)[e]
12	$CH_3(CH_2)_7$	52	77.3 (*S*)[e]

[a] The reactions were carried out in toluene at −10°C for 12 h, aldehyde/Et_2Zn/**4** = 1.0/2.2/0.05, the diethylzinc reagent is 1 M in hexane.
[b] Isolated yields based on the aldehydes.
[c] Determined by GC with β-DEX 120 capillary column and the absolute configuration was determined by comparing the sign of specific rotation.[8]
[d] Determined by HPLC on a Chiralcel OD-H column.
[e] Determined by analyzing the acetate derivative of the product on the β-DEX 120 capillary column.

solvents were dried and degassed by standard methods and all other chemicals obtained commercially.

4.2. General procedures for the synthesis of *N,O* ligands 1–6

To a solution of pyridine or quinoline derivatives (10 mmol) in 30 mL diethyl ether under N_2 was added a 1.6 M solution of *n*-BuLi in hexane (11 mmol) at 0°C over 30 min. This solution was allowed to warm to rt and stirred for 1 h. A solution of ketone (10 mmol) in 30 mL diethyl ether was added dropwise over 15 min with vigorous stirring while the temperature cooled back to 0°C. The mixture was stirred overnight and hydrolyzed with a saturated aqueous NH_4Cl solution. The layers were separated and the aqueous layer was extracted with ether (3×50 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and crude product was purified by silica gel column chromatography to give white solid, which recrystallized from ethyl acetate and hexane.

4.2.1. Synthesis of *N,O* ligand 1. The above procedure was followed using 2-picoline and chiral ketone **7**. After work-up, it gave 1.8 g (51%) of **1**: mp 129–130°C; $[\alpha]_D^{12} = +34.7$ (*c* 0.48, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.26 (s, 3H), 1.38 (s, 3H), 1.48 (s, 3H), 1.59 (s, 3H), 2.79 (d, 1H, $J = 14.4$ Hz), 3.36 (d, 1H, $J = 14.4$ Hz), 3.97–4.03 (m, 2H), 4.12–4.22 (m, 1H), 4.24–4.26 (m, 2H), 5.28 (br, 1H), 5.79 (d, 1H, $J = 3.6$ Hz), 7.22 (m, 1H), 7.29 (t, 1H, $J = 7.6$ Hz), 7.66 (m, 1H), 8.51 (d, 1H, $J = 4.4$ Hz); ^{13}C NMR ($CDCl_3$): δ 25.36, 26.36, 26.62, 26.77, 38.56, 67.76, 73.39, 79.88, 81.46, 82.07, 103.56, 109.65, 112.54, 121.89, 125.15, 136.78, 148.65, 157.61; HRMS (ESI) calcd for $C_{18}H_{25}NO_6$ (M^++1): 352.1754, found: 352.1737.

4.2.2. Synthesis of *N,O* ligand 2. The above procedure was followed using 2-picoline and chiral ketone **8**. After work-up, it gave 3.2 g (74%) of **2**: mp 104–105°C; $[\alpha]_D^{12} = +42.0$ (*c* 0.67, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.30–1.79 (m, 20H), 2.80 (d, 1H, $J = 14.4$ Hz), 3.36 (d, 1H, $J = 14.4$ Hz), 3.94–4.00 (m, 2H), 4.12 (t, 1H, $J = 7.6$ Hz), 4.20–4.30 (m, 2H), 4.81 (br, 1H), 5.80 (d, 1H, $J = 3.6$ Hz), 7.18–7.21 (m, 1H), 7.31 (t, 1H, $J = 7.6$ Hz), 7.63–7.67 (m, 1H), 8.52 (d, 1H, $J = 4.4$ Hz); ^{13}C NMR ($CDCl_3$): δ 23.25, 23.68, 23.83, 24.66, 24.93, 34.69, 35.78, 36.01, 36.06, 38.62, 67.38, 72.92, 79.57, 80.65, 81.69, 103.06, 109.90, 112.93, 121.73, 125.36, 136.69, 148.19, 157.28; HRMS (ESI) calcd for $C_{24}H_{33}NO_6$ (M^+ +1): 432.2380, found: 432.2382.

4.2.3. Synthesis of *N,O* ligand 3. The above procedure was followed using 2,6-lutidine and chiral ketone **7**. After work-up, it gave 2.0 g (54%) **3c**: mp 85–86°C; $[\alpha]_D^{12} = +22.4$ (*c* 0.61, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.26 (s, 3H), 1.34 (s, 3H), 1.48 (s, 3H), 1.60 (s, 3H), 2.53 (s, 3H), 2.75 (d, 1H, $J = 14.8$ Hz), 3.29 (d, 1H, $J = 14.8$ Hz), 3.98–4.00 (m, 2H), 4.12 (t, 1H, $J = 7.6$ Hz), 4.21–4.36 (m, 2H), 5.73 (d, 1H, $J = 3.6$ Hz), 7.03–7.09 (m, 2H), 7.55 (t, 1H, $J = 7.8$ Hz); ^{13}C NMR ($CDCl_3$): δ 24.23, 25.35, 26.35, 26.59, 26.86, 38.00, 67.59, 73.41,

80.00, 81.20, 82.01, 103.38, 104.85, 109.56, 112.59, 121.62, 137.22, 156.95, 157.67; HRMS (ESI) calcd for $C_{19}H_{27}NO_6$ (M^++1): 366.1911, found: 366.1897.

4.2.4. Synthesis of *N,O* ligand 4. The above procedure was followed using 2,6-lutidine and chiral ketone **8**. After work-up, it gave 3.5 g (78%) of **4**: mp 103–104°C; $[\alpha]_D^{12}$ = + 29.4 (*c* 0.64, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.31–1.82 (m, 20H), 2.52 (s, 3H), 2.82 (d, 1H, J = 14.8 Hz), 3.29 (d, 1H, J = 14.8 Hz), 3.94–4.02 (m, 2H), 4.09 (t, 1H, J = 7.6 Hz), 4.10–4.20 (m, 2H), 5.75 (d, 1H, J = 3.6 Hz), 5.79 (br, 1H), 7.03–7.06 (m, 2H), 7.53 (t, 1H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$): δ 23.38, 23.77, 23.90, 24.79, 25.03, 34.79, 35.91, 36.07, 36.21, 38.04, 67.36, 73.05, 79.73, 81.41, 81.52, 103.04, 109.95, 113.09, 121.64, 137.29, 156.68, 157.21; HRMS (ESI) calcd for $C_{25}H_{35}NO_6$ (M^++1): 446.2537, found: 446.2511. Anal. calcd for $C_{25}H_{35}NO_6$: C, 67.39; H, 7.92; N, 3.14. found: C, 67.37; H, 7.56; N, 3.21%.

4.2.5. Synthesis of *N,O* ligand 5. The above procedure was followed using 2-methylquinoline and chiral ketone **7**. After work-up, it gave 2.3 g (57%) **5**: mp 151–152°C; $[\alpha]_D^{12}$ = +53.3 (*c* 0.41, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.24 (s, 3H), 1.31 (s, 3H), 1.49 (s, 3H), 1.59 (s, 3H), 3.17 (d, 1H, J = 14.8 Hz), 3.57 (d, 1H, J = 14.8 Hz), 4.00–4.05 (m, 2H), 4.15 (t, 1H, J = 7.6 Hz), 4.24–4.30 (m, 2H), 5.88 (d, 1H, J = 3.6 Hz), 7.52 (d, 1H, J = 8.4 Hz), 7.60 (t, 1H, J = 8.0 Hz), 7.75 (t, 1H, J = 8.0 Hz), 7.86 (d, 1H, J = 8.0 Hz), 8.14 (d, 1H, J = 8.4 Hz), 8.20 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$): δ 25.29, 26.38, 26.66, 26.76, 38.47, 67.88, 73.46, 80.14, 81.67, 81.77, 103.67, 109.70, 112.61, 123.43, 126.94, 127.59, 130.49, 137.86, 158.17; HRMS (ESI) calcd for $C_{22}H_{27}NO_6$ (M^++1): 402.1911, found: 402.1900.

4.2.6. Synthesis of *N,O* ligand 6. The above procedure was followed using 2-methylquinoline and chiral ketone **8**. After work-up, it gave 3.1 g (64%) **6**: mp 153–154°C; $[\alpha]_D^{12}$ = +61.6 (*c* 0.57, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.30–1.82 (m, 20H), 3.02 (d, 1H, J = 14.8 Hz), 3.54 (d, 1H, J = 14.8 Hz), 3.97–4.00 (m, 2H), 4.08 (t, 1H, J = 7.6 Hz), 4.22–4.27 (m, 1H), 4.33 (d, 1H,, J = 3.6 Hz), 5.25 (br, 1H), 5.82 (d, 1H, J = 3.6 Hz), 7.46 (d, 1H, J = 8.4 Hz), 7.53 (t, 1H, J = 8.0 Hz), 7.71 (t, 1H, J = 8.0 Hz), 7.81 (d, 1H, J = 8.0 Hz), 8.03 (d, 1H, J = 8.8 Hz), 8.12 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$): δ 23.40, 23.72, 23.85, 23.98, 24.80, 25.06, 34.78, 35.93, 36.21, 38.80, 67.68, 73.16, 80.00, 81.14, 82.07, 103.31, 110.18, 113.23, 123.68, 126.83, 126.96, 127.57, 130.37, 137.59, 158.23; HRMS (ESI) calcd for $C_{28}H_{35}NO_6$ (M^++1): 482.2537, found: 482.2555.

4.3. General procedures for the asymmetric addition of diethylzinc to aldehydes

Chiral ligand (0.05 mmol, 5 mol%) in dry toluene (3 mL) was cooled to 0°C and 1 M diethylzinc in hexane (2.2 mmol, 2.2 mL) was added slowly. After stirring for 30 min at 0°C, freshly distilled aldehyde (1 mmol) was added and the reaction was monitored by TLC. When the reaction was completed, 1N HCl (5 mL) was added. The layers were separated and the aqueous layer was extracted with diethylether (3×15 mL). The combined organic phases were washed with brine, dried by Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatography, the enantiomeric excess was determined by GC or HPLC.

Acknowledgements

Financial support from the National Science Foundation of China (29933050) is gratefully acknowledged. The authors thank Dr. Yonggui Zhou and Dr. Xinquan Hu for helpful discussions.

References

1. For reviews, see: (a) Noyori, R.; Kitamura, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 49; (b) Soai, K.; Niwa, S. *Chem. Rev.* **1992**, *92*, 833; (c) Blaser, H. U. *Chem. Rev.* **1992**, *29*, 359; (d) Pu, L.; Yu, H. B. *Chem. Rev.* **2001**, *101*, 757.
2. Oguni, N.; Omi, T. *Tetrahedron Lett.* **1984**, *25*, 2823.
3. Corey, E. J.; Yuen, P. W.; Hammon, F. J. D.; Wierda, A. *J. Org. Chem.* **1990**, *55*, 784.
4. (a) Bolm, C.; Zehnder, M.; Bur, D. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 205; (b) Bolm, C.; Ewald, M.; Felder, M.; Schlingloff, G. *Chem. Ber.* **1992**, *125*, 1169; (c) Bolm, C.; Schlingloff, G.; Harms, K. *Chem. Ber.* **1992**, *125*, 1191; (d) Chelucci, G.; Soccolini, F. *Tetrahedron: Asymmetry* **1992**, *3*, 1235; (e) Collomb, P.; Von Zelewsky, A. *Tetrahedron: Asymmetry* **1998**, *9*, 3911; (f) Kwong, H. L.; Lee, W. S. *Tetrahedron: Asymmetry* **1999**, *10*, 3791; (g) Ishizaki, M.; Fujita, K.; Shimamoto, M.; Hoshino, O. *Tetrahedron: Asymmetry* **1994**, *5*, 411; (h) Ishizaki, M.; Hoshino, O. *Chem. Lett* **1994**, 337; (i) Williams, D.; Fromhold, M. G. *Synlett* **1997**, 523; (j) Macedo, E.; Moberg, C. *Tetrahedron: Asymmetry* **1995**, *6*, 549; (k) Kang, J.; Kim, H.-Y.; Kim, J.-H. *Tetrahedron: Asymmetry* **1999**, *10*, 2523; (l) Kotsuki, H.; Nakagawa, Y.; Moriya, N.; Tateishi, H.; Ochi, M.; Suzuki, T.; Isobe, K. *Tetrahedron: Asymmetry* **1995**, *6*, 1165; (m) Kotsuki, H.; Hayakawa, H.; Tateishi, H.; Wakao, M.; Shiro, M. *Tetrahedron: Asymmetry* **1998**, *9*, 3203; (n) Wu, Y.; Yun, H.; Wu, Y.; Ding, K.; Zhou, Y. *Tetrahedron: Asymmetry* **2000**, *11*, 3543; (o) Yun, H.; Wu, Y.; Wu, Y.; Ding, K.; Zhou, Y. *Tetrahedron Lett.* **2000**, *41*, 10263; (p) Zhang, H.; Xue, F.; Mak, T. C. W.; Chan, K. S. *J. Org. Chem.* **1996**, *61*, 8002; (q) Zhang, H.; Chan, K. S. *J. Chem. Soc., Perkin. Trans. 1* **1999**, 381; (r) Soai, K.; Shibata, T.; Sato, I. *Acc. Chem. Res.* **2000**, *33*, 382; (s) Goanvic, D. L.; Holler, M.; Pale, P. *Tetrahedron: Asymmetry* **2002**, *13*, 119; (t) Zhong, Y. W.; Lei, X. S.; Lin, G. Q. *Tetrahedron: Asymmetry* **2002**, *13*, 2251.
5. Zhou, Y. G.; Dai, L. X.; Hou, X. L. *Chin. J. Chem.* **2000**, *18*, 121.
6. Huang, H.; Chen, H.; Hu, X.; Bai, C.; Zheng, Z. *Tetrahedron: Asymmetry* **2003**, *14*, 297.
7. (a) Hockett, R. C.; Miller, R. E.; Scattergood, A. *J. Am. Chem. Soc.* **1949**, *71*, 3072; (b) James, K.; Tatchell, A. R.; Ray, P. K. *J. Chem. Soc. (C)* **1967**, 2681; (c) Singh, P. P.; Gharia, M. M.; Dasgupta, F.; Srivastava, H. C. *Tetrahedron Lett.* **1977**, 439.
8. (a) Asami, M.; Watanabe, H.; Honda, K.; Inoue, S. *Tetrahedron: Asymmetry* **1998**, *9*, 4165; (b) Kang, J.; Lee, J. W.; Kim, J. I. *J. Chem. Soc., Chem. Commun.* **1994**, 2009; (c) Watanabe, M.; Araki, S.; Butsugan, Y.; Uemura, M. *J. Org. Chem.* **1991**, *56*, 2218; (d) Kitamura, M.; Suga, S.; Kawai, K.; Noyori, R. *J. Am. Chem. Soc.* **1986**, *108*, 6071; (e) Kang, S. K.; Jenon, J. H.; Yamaguchi, T.; Kim, J. S.; Ko, B. S. *Tetrahedron: Asymmetry* **1995**, *6*, 2139.