Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron
Tetrahedron 63 (2007) 598–601

Enantioselective diethylzinc addition to aldehydes catalyzed by Ti(IV) complex of unsymmetrical chiral bis(sulfonamide) ligands of *trans*-cyclohexane 1,2-diamine

Alakesh Bisai, Pradeep K. Singh and Vinod K. Singh*

Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, U.P., India

Received 3 September 2006; revised 20 October 2006; accepted 9 November 2006
Available online 27 November 2006

Abstract—Titanium(IV) complexes of bidentate *trans*-cyclohexane 1,2-diamine-based unsymmetrical chiral bis(sulfonamide) ligands were evaluated as catalysts for the asymmetric addition of diethylzinc to aldehydes. The reaction provided secondary alcohols in quantitative yields and very good enantioselectivity (up to 96% ee).

1. Introduction

The enantioselective addition of organozinc reagents to carbonyl compounds catalyzed by a metal–chiral ligand complex has attracted attention for a long time.[1] Since the reaction is very useful for the synthesis of optically active secondary alcohols, several excellent chiral ligands have been evaluated for dialkylzinc addition to carbonyls.[2] In catalytic asymmetric systems, small changes in the donating ability of a ligand or the size of a substituent can have a dramatic effect on the catalytic efficiency and enantioselectivity. Thus, there is a need for developing new types of chiral ligands. Cyclohexanediamine based C_2-symmetric bis(sulfonamide) chiral ligands of type **1**, which bind well with early transition metals and main group elements, have been used for enantioselective addition of organozinc to carbonyl compounds.[3–5]

The use of C_2-symmetric ligands has an advantage of restricting the number of possible competing diastereomeric transition states.[6] To the best of our knowledge, there is only one report disclosed by Walsh and co-workers where application of a pseudo C_2-symmetric bis(sulfonamide) ligand **2** has been reported for the enantioselective diethylzinc addition to benzaldehyde.[5c] However, the enantiomeric excess was 91% using ligand **2**, which is lower than the ee obtained from C_2-symmetric ligand **1a** (97% ee).

Recently, we developed a very good method for the synthesis of unsymmetrical bis(sulfonamide) ligands of type **3** through the desymmetrization of cyclohexyl-*N*-tosyl aziridines with chiral amines (Fig. 1).[7]

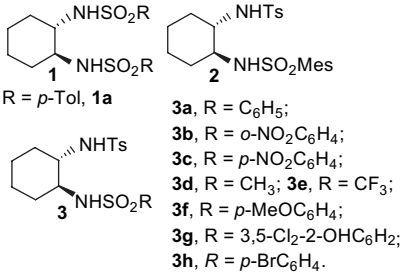


Figure 1. Symmetrical and unsymmetrical chiral ligands based on *trans*-1,2-cyclohexane diamine.

In this paper, we report that these unsymmetrical bis(sulfonamide) ligands are as efficient as C_2-symmetric bis(sulfonamide) ligands in the enantioselective addition of diethylzinc to aldehydes.

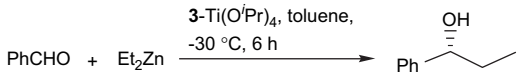
2. Results and discussion

At the outset, the addition of diethylzinc to benzaldehyde was studied in the presence of 2–20 mol % catalyst prepared from a chiral ligand **3a** and Ti(O^iPr)$_4$ at −30 °C (Table 1). The reaction completed in 6 h and the product was obtained in very good yields (81–87%) and high enantioselectivities (88–96% ee). It is obvious from the results that 4–6 mol % catalyst is optimum for high asymmetric induction (96% ee) in the reaction. Under these optimized conditions, other chiral ligands **3b**–**3h** were evaluated for the same reaction

* Corresponding author. Tel.: +91 512 2597291; fax: +91 512 2597436; e-mail: vinodks@iitk.ac.in

0040–4020/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2006.11.022

Table 1. Enantioselective diethylzinc addition to benzaldehyde in the presence of different chiral ligands **3a**–**3h**



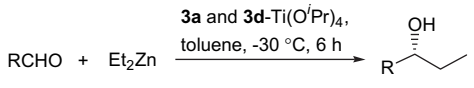
Entry	Ligand	Mol %	% Yield[a]	% ee[b]
1	**3a**	2	83	94
2	**3a**	4	87	96
3	**3a**	6	81	96
4	**3a**	10	83	93
5	**3a**	20	82	88
6	**3b**	4	82	88
7	**3c**	4	81	94
8	**3d**	4	75	94
9	**3e**	4	82	93
10	**3f**	4	85	81
11	**3g**	4	53	76
12	**3h**	4	88	91

[a] Isolated yields after purification.
[b] The ees were determined by HPLC using chiralcel OD-H column.

and the results are summarized in Table 1. The ligand **3a** (R=Ph) gave the highest enantioselectivity (96% ee) in the reaction. The ligands **3c**, **3d**, and **3e** showed comparable asymmetric inductions (93–94% ee). Tridentate ligand **3g** having a hydroxyl group on the phenyl ring gave only 76% ee in the reaction.

The ligands **3a** and **3d** were selected for evaluation on other substrates. Most of the aromatic aldehydes gave high asymmetric induction in the diethylzinc addition reaction (Table 2). However, **3a** gave better results than **3d** in the addition of diethylzinc to cyclohexyl carboxaldehyde (Table 2, entry 12). The reactions were carried out on other aliphatic aldehydes, but we could not determine ee due to lack of base line separation of products on chiral columns we had in our laboratory. The mechanism of the reaction can be explained based on the literature work with C_2-symmetric ligands.[5]

Table 2. Enantioselective diethylzinc addition to aldehydes in the presence of different chiral ligands **3a** and **3d**



Entry	R	% Yield[a]		% ee[b]	
		3a	**3d**	**3a**	**3d**
1	Ph	87	75	96	94
2	4-Cl–C_6H_4	97	98	96	96
3	4-OMe–C_6H_4	81	84	82	79
4	3-Br–C_6H_4	92	84	95	93
5	4-^{i}Pr–C_6H_4	98	99	93	90
6	3-Cl–C_6H_4	94	93	92	94
7	3-F–C_6H_4	84	74	92	92
8	3-Cl-4-F–C_6H_3	91	94	93	93
9	2,3-F_2–C_6H_3	74	74	76	83
10	3,5-Me_2–C_6H_3	83	87	93	92
11	3-Me–C_6H_4	85	94	95	95
12	*c*-C_6H_{11}[c]	56	57	96	82

[a] Isolated yields were reported here after purification.
[b] The ees were determined by HPLC using chiralcel OD-H or chiralpak AD-H column.
[c] Reaction time was 10–12 h and ees were determined using its 4-methoxybenzoate.

3. Conclusion

In conclusion, the chiral Ti(IV)–**3** complex prepared from Ti(O^{i}Pr)$_4$ and unsymmetric bis(sulfonamide) ligands **3** was found to be an effective catalyst for the enantioselective diethylzinc addition to aldehydes. The reaction can furnish a variety of secondary alcohols in good to excellent yields (up to 99%) with excellent enantioselectivities (up to 96% ee). These results provide a new way to design and synthesize new chiral ligands for enantioselective reactions.

4. Experimental

4.1. General

All the chemicals were purchased either from Aldrich or Alfa–Aesar and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-LA 400 spectrometer. All chemical shifts are quoted on the δ scale, with TMS as internal standard, and coupling constants are reported in hertz. Routine monitoring of reactions was performed by TLC using 0.2 mm Kieselgel 60 F_{254} precoated aluminum sheets, commercially available from Merck. Visualization was done by fluorescence quenching at 254 nm or by exposure to iodine vapor. All the column chromatographic separations were done by using silica gel (Acme's, 100–200 mesh). HPLC was done on Daicel chiral column having 0.46 cm I.D.×25 cm L. Petroleum ether used was of boiling range 60–80 °C. Reactions that needed anhydrous conditions were run under the atmosphere of nitrogen using flame-dried glassware. The organic extracts were dried over *anhydrous* sodium sulfate. Evaporations of solvents were performed at reduced pressure. Toluene and diethyl ether were both distilled from sodium benzophenone-ketyl. Dichloromethane was distilled from calcium hydride. Acetonitrile was distilled from anhydrous phosphorus pentoxide under nitrogen.

4.1.1. 4-Methyl-*N*-(2-trifluoromethanesulfonylamino-cyclohexyl)-benzene sulfonamide. This was prepared as per the general procedure[7b] from *N*-tosyl cyclohexyl aziridines; 70% yield (0.516 g); white solid; mp 123–126 °C; $[\alpha]_D^{25}$ −34.0 (*c* 1.0, $CHCl_3$); R_f 0.36 (30% EtOAc in petroleum ether); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.77 (d, *J*=8.3 Hz, 2H), 7.33 (d, *J*=8.3 Hz, 2H), 5.97 (d, *J*=7.1 Hz, 1H, NH), 4.97 (d, *J*=8.8 Hz, 1H, NH), 3.16–3.25 (m, 1H), 2.92–3.00 (m, 1H), 2.44 (s, 3H), 2.17–2.23 (m, 1H), 1.42–1.71 (m, 3H), 1.08–1.39 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 143.9, 137.3, 129.9, 126.9, 59.3, 56.4, 33.9, 33.0, 24.5, 24.2, 21.6. Anal. Calcd for $C_{14}H_{19}F_3N_2O_4S_2$: C, 41.99; H, 4.78; N, 7.00. Found: C, 42.19; H, 4.83; N, 7.02.

4.1.2. *N*-(2-*p*-Toluenesulfonylamino-cyclohexyl)-3,5-dichloro-2-hydroxy-benzene sulfonamide. This was prepared as per the general procedure[7b] from *N*-tosyl cyclohexyl aziridines; 66% yield (0.554 g); light yellow solid; mp 81–84 °C; $[\alpha]_D^{25}$ +3.70 (*c* 1.0, $CHCl_3$); R_f 0.42 (50% EtOAc in petroleum ether); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.65–7.78 (m, 3H), 7.55 (s, 1H), 7.30 (d, *J*=7.8 Hz, 2H), 5.87 (br s, 1H, NH), 4.55 (br s, 1H, NH), 2.75–2.95 (m, 2H), 2.43 (s, 3H), 2.03–2.15 (m, 1H), 1.50–1.70 (m, 3H), 1.09–1.24 (m, 4H). Anal. Calcd for $C_{19}H_{22}Cl_2N_2O_5S_2$: C, 46.25; H, 4.49; N, 5.68. Found: C, 46.39; H, 4.51; N, 5.71.

4.2. General procedure for the enantioselective diethylzinc addition to aldehydes

Diethylzinc (1.2 mL, 1 M solution in *n*-hexane) was added to a solution of ligand **3** (4 mol %) in dry toluene (2 mL) at rt. It was stirred for 15 min and then the flask was cooled to −30 °C. $Ti(O^iPr)_4$ (0.36 mL) solution in 0.5 mL toluene was added dropwise to the reaction mixture. After stirring the orange color solution for 5 min at the same temperature, an aldehyde (1 mmol) was added and stirred for 6 h. The reaction was quenched with 2 mL of 2 N HCl and extracted with diethyl ether. The organic layer was washed with brine and dried over *anhydrous* Na_2SO_4. The solvent was evaporated and the crude mixture was chromatographed over silica gel using EtOAc and petroleum ether as eluents (5–10%). Enantiomeric excess was determined using Chiralcel OD-H or Chiralpak AD-H column.

4.2.1. (*R*)-1-Phenyl-1-propanol (Table 2, entry 1). 96% ee; 87% yield (0.118 g); colorless liquid; $[\alpha]_D^{25}$ +45.5 (*c* 1.14, $CHCl_3$) (lit.[8a] $[\alpha]_D^{16}$ −40.7 (*c* 1.95, $CHCl_3$, 91% ee)); R_f 0.37 (10% EtOAc in petroleum ether); spectroscopic data identical to that reported;[8a] HPLC conditions: Diacel chiralcel OD-H (4.6 cm I.D.×25 cm), 98:2 hexane/*i*-PrOH, 0.5 mL/min flow rate, λ=254 nm, t_R (major)=28.86 min and t_R (minor)=35.70 min.

4.2.2. (*R*)-1-(4-Chlorophenyl)-1-propanol (Table 2, entry 2). 96% ee; 98% yield (0.115 g); colorless liquid; $[\alpha]_D^{25}$ +37.3 (*c* 1.57, $CHCl_3$) (lit.[8b] $[\alpha]_D^{20}$ +26.4 (*c* 5.27, benzene, 97% ee)); R_f 0.28 (10% EtOAc in petroleum ether); spectroscopic data identical to that reported;[8a] HPLC conditions: Diacel chiralpak AD-H (4.6 cm I.D.×25 cm), 95:5 hexane/*i*-PrOH, 0.5 mL/min flow rate, λ=254 nm, t_R (major)=16.89 min and t_R (minor)=17.62 min.

4.2.3. (*R*)-1-(4-Methoxyphenyl)-1-propanol (Table 2, entry 3). 82% ee; 81% yield (0.135 g); colorless liquid; $[\alpha]_D^{25}$ +35.0 (*c* 1.68, $CHCl_3$) (lit.[8a] $[\alpha]_D^{16}$ −31.5 (*c* 2.1, $CHCl_3$, 91% ee)); R_f 0.20 (10% EtOAc in petroleum ether); spectroscopic data identical to that reported;[8a] HPLC conditions: Diacel chiralpak AD-H (4.6 cm I.D.×25 cm), 95:5 hexane/*i*-PrOH, 0.5 mL/min flow rate, λ=254 nm, t_R (major)=24.78 min and t_R (minor)=27.73 min.

4.2.4. (*R*)-1-(3-Bromophenyl)-1-propanol (Table 2, entry 4). 95% ee; 92% yield (0.202 g); colorless liquid; $[\alpha]_D^{25}$ +26.9 (*c* 1.79, $CHCl_3$); R_f 0.31 (10% EtOAc in petroleum ether); IR (thin film): 3348, 3062, 2967, 2930, 2875, 1593, 1569, 1467, 1425, 1342, 1195, 1076, 1016, 911, 840, 781, 670 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.49–7.51 (m, 1H), 7.40 (dt, *J*=7.6, 1.7 Hz, 1H), 7.19–7.27 (m, 2H), 4.58 (t, *J*=6.6 Hz, 1H), 1.68–1.85 (m, 2H), 0.92 (t, *J*=7.3 Hz, 3H). Anal. Calcd for $C_9H_{11}BrO$: C, 50.26; H, 5.15. Found: C, 50.41; H, 5.13; HPLC conditions: Diacel chiralpak AD-H (4.6 cm I.D.×25 cm), 95:5 hexane/*i*-PrOH, 0.5 mL/min flow rate, λ=254 nm, t_R (major)=16.88 min and t_R (minor)=17.66 min.

4.2.5. (*R*)-1-(4-Isopropylphenyl)-1-propanol (Table 2, entry 5). 93% ee; 98% yield (0.174 g); colorless liquid; $[\alpha]_D^{25}$ +35.4 (*c* 1.68, $CHCl_3$); R_f 0.34 (10% EtOAc in petroleum ether); IR (thin film): 3362, 2962, 2930, 2873, 1661, 1613, 1511, 1460, 1418, 1330, 1208, 1094, 1047, 1013, 973, 832 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.25 (d, *J*=8.0 Hz, 2H), 7.20 (d, *J*=8.0 Hz, 2H), 4.54 (t, *J*=6.6 Hz, 1H), 2.90 (h, *J*=7.1 Hz, 1H), 1.92 (br s, 1H, OH), 1.69–1.84 (m, 2H), 1.23 (d, *J*=6.8 Hz, 6H), 0.91 (t, *J*=7.3 Hz, 3H). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.90; H, 10.21; HPLC conditions: Diacel chiralpak AD-H (4.6 cm I.D.×25 cm), 95:5 hexane/*i*-PrOH, 0.5 mL/min flow rate, λ=254 nm, t_R (major)=15.80 min and t_R (minor)=16.89 min.

4.2.6. (*R*)-1-(3-Chlorophenyl)-1-propanol (Table 2, entry 6). 94% ee; 93% yield (0.160 g); colorless liquid; $[\alpha]_D^{25}$ +32.1 (*c* 1.30, $CHCl_3$) (lit.[8a] $[\alpha]_D^{16}$ −28.4 (*c* 3.74, $CHCl_3$, 98% ee)); R_f 0.34 (10% EtOAc in petroleum ether); spectroscopic data identical to that reported;[8a] HPLC conditions: Diacel chiralpak AD-H (4.6 cm I.D.×25 cm), 95:5 hexane/*i*-PrOH, 0.5 mL/min flow rate, λ=254 nm, t_R (major)=15.92 min and t_R (minor)=16.69 min.

4.2.7. (*R*)-1-(3-Fluorophenyl)-1-propanol (Table 2, entry 7). 92% ee; 84% yield (0.129 g); colorless liquid; $[\alpha]_D^{25}$ +32.7 (*c* 1.61, $CHCl_3$); R_f 0.37 (10% EtOAc in petroleum ether); IR (thin film): 3362, 2969, 2932, 2877, 1591, 1486, 1451, 1248, 1142, 1100, 1044, 1016, 979, 872, 787, 751, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.26–7.32 (m, 1H), 7.05–7.10 (m, 2H), 6.95 (td, *J*=8.6, 2.7 Hz, 1H), 4.60 (t, *J*=6.4 Hz, 1H), 1.97 (br s, 1H, OH), 1.69–1.83 (m, 2H), 0.91 (t, *J*=7.3 Hz, 3H). Anal. Calcd for $C_9H_{11}FO$: C, 70.11; H, 7.19. Found: C, 70.24; H, 7.09; HPLC conditions: Diacel chiralpak AD-H (4.6 cm I.D.×25 cm), 95:5 hexane/*i*-PrOH, 0.5 mL/min flow rate, λ=254 nm, t_R (major)=15.32 min and t_R (minor)=16.28 min.

4.2.8. (*R*)-1-(3-Chloro-4-fluorophenyl)-1-propanol (Table 2, entry 8). 93% ee; 93% yield (0.174 g); colorless liquid; $[\alpha]_D^{25}$ +30.2 (*c* 1.37, $CHCl_3$); R_f 0.29 (10% EtOAc in petroleum ether); IR (thin film): 3346, 2969, 2932, 2878, 1599, 1499, 1460, 1409, 1338, 1253, 1096, 1054, 1016, 978, 885, 824, 793, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.39 (dd, *J*=7.1, 2.0 Hz, 1H), 7.16–7.21 (m, 1H), 7.10 (t, *J*=8.6 Hz, 1H), 4.57 (t, *J*=6.4 Hz, 1H), 1.93 (br s, 1H, OH), 1.67–1.83 (m, 2H), 0.90 (t, *J*=7.6 Hz, 3H). Anal. Calcd for $C_9H_{10}ClFO$: C, 57.31; H, 5.34. Found: C, 57.46; H, 5.39; HPLC conditions: Diacel chiralpak AD-H (4.6 cm I.D.×25 cm), 95:5 hexane/*i*-PrOH, 0.5 mL/min flow rate, λ=254 nm, t_R (major)=13.40 min and t_R (minor)=14.28 min.

4.2.9. (*R*)-1-(2,3-Difluorophenyl)-1-propanol (Table 2, entry 9). 83% ee; 74% yield (0.128 g); colorless liquid; $[\alpha]_D^{25}$ +20.6 (*c* 1.59, $CHCl_3$); R_f 0.37 (10% EtOAc in petroleum ether); IR (thin film): 3350, 2971, 2935, 2880, 1626, 1595, 1485, 1277, 1203, 1095, 1043, 958, 878, 824, 786, 749, 725 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.21–7.23 (m, 1H), 7.04–7.11 (m, 2H), 4.97 (t, *J*=6.3 Hz, 1H), 1.98 (br s, 1H, OH), 1.75–1.87 (m, 2H), 0.96 (t, *J*=7.3 Hz, 3H). Anal. Calcd for $C_9H_{10}F_2O$: C, 62.78; H, 5.85. Found: C, 62.93; H, 5.91; HPLC conditions: Diacel chiralcel OD-H (4.6 cm I.D.×25 cm), 99:1 hexane/*i*-PrOH, 0.5 mL/min flow rate, λ=254 nm, t_R (major)=20.44 min and t_R (minor)=22.74 min.

4.2.10. (*R*)-1-(3,5-Dimethylphenyl)-1-propanol (Table 2, entry 10). 93% ee; 83% yield (0.136 g); colorless liquid;

$[\alpha]_D^{25}$ +31.8 (*c* 0.85, $CHCl_3$); R_f 0.31 (10% EtOAc in petroleum ether); IR (thin film): 3357, 3012, 2965, 2926, 2872, 1606, 1460, 1348, 1161, 1094, 1044, 1022, 976, 897, 847, 708 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 6.94 (s, 2H), 6.91 (s, 1H), 4.51 (t, J=6.6 Hz, 1H), 2.31 (s, 6H), 1.67–1.85 (m, 2H), 0.91 (t, J=7.3 Hz, 3H). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.60; H, 9.80; HPLC conditions: Diacel chiralcel OD-H (4.6 cm I.D.× 25 cm), 99.5:0.5 hexane/*i*-PrOH, 0.5 mL/min flow rate, λ=254 nm, t_R (major)=20.33 min and t_R (minor)= 22.15 min.

4.2.11. (*R*)-1-(3-Methylphenyl)-1-propanol (Table 2, entry 11). 95% ee; 94% yield (0.141 g); colorless liquid; $[\alpha]_D^{25}$ +37.9 (*c* 1.76, $CHCl_3$) (lit.[8a] $[\alpha]_D^{16}$ −12.1 (*c* 2.43, $CHCl_3$, 44% ee)); R_f 0.31 (10% EtOAc in petroleum ether); spectroscopic data identical to that reported;[8a] HPLC conditions: Diacel chiralcel OD-H (4.6 cm I.D.×25 cm), 98:2 hexane/*i*-PrOH, 0.5 mL/min flow rate, λ=254 nm, t_R (major)= 15.34 min and t_R (minor)=18.45 min.

4.2.12. (*R*)-1-Cyclohexyl-propanol (Table 2, entry 12). 96% ee; 56% yield (0.085 g); colorless liquid; $[\alpha]_D^{25}$ +7.0 (*c* 1.04, $CHCl_3$) (lit.[8b] $[\alpha]_D^{20}$ +6.35 (*c* 3.0, $CHCl_3$, 95% ee)); ^1H NMR ($CDCl_3$, 400 MHz) δ: 3.27–3.28 (m, 1H), 1.73–1.79 (m, 2H), 1.63–1.68 (m, 1H), 1.52–1.54 (m, 1H), 0.99–1.43 (m, 9H), 0.95 (t, J=7.4 Hz, 3H). Anal. Calcd for $C_9H_{18}O$: C, 76.00; H, 12.76. Found: C, 76.19; H, 12.80.

4.2.13. 4-Methoxybenzoate derivative of (*R*)-1-cyclohexyl-propanol. Yield 65% (0.046 g); colorless liquid; $[\alpha]_D^{25}$ +13.6 (*c* 1.02, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ: 8.02 (d, J=8.8 Hz, 2H), 6.92 (d, J=9.0 Hz, 2H), 4.90–4.92 (m, 1H), 3.86 (s, 3H), 1.59–1.80 (m, 8H), 1.06–1.33 (m, 5H), 0.91 (t, J=7.3 Hz, 3H). Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 74.01; H, 8.80; HPLC conditions: Diacel chiralpak AD-H (4.6 cm I.D.×25 cm), 99.8:0.2 hexane/*i*-PrOH, 0.5 mL/min flow rate, λ=254 nm, t_R (major)=24.40 min and t_R (minor)=30.81 min.

Acknowledgements

V.K.S. thanks the Department of Science and Technology, Government of India for a research grant. A.B. and P.K.S. thank the Council of Scientific and Industrial Research, New Delhi, for research fellowships.

References and notes

1. Reviews: (a) Yus, M.; Ramon, D. J. *Pure Appl. Chem.* **2005**, *77*, 2111–2119; (b) Ramon, D. J.; Yus, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 284–287; (c) Soai, K.; Niwa, S. *Chem. Rev.* **1992**, *92*, 833–856; (d) Pu, L.; Yu, H.-B. *Chem. Rev.* **2001**, *101*, 757–824.
2. For some recent selected papers in this area, see: (a) Cozzi, P. G.; Kotrusz, P. *J. Am. Chem. Soc.* **2006**, *128*, 4940–4941; (b) Huang, J.; Ianni, J. C.; Antoline, J. E.; Hsung, R. P.; Kozlowski, M. C. *Org. Lett.* **2006**, *8*, 1565–1568; (c) Roudeau, R.; Pardo, D. G.; Cossy, J. *Tetrahedron* **2006**, *62*, 2388–2394; (d) Richmond, M. L.; Seto, C. T. *J. Org. Chem.* **2003**, *68*, 7505–7508; (e) DiMauro, E. F.; Kozlowski, M. C. *Org. Lett.* **2002**, *4*, 3781–3784; (f) Nugent, W. A. *Org. Lett.* **2002**, *4*, 2133–2136; (g) DiMauro, E. F.; Kozlowski, M. C. *Org. Lett.* **2001**, *3*, 3053–3056.
3. Review: Walsh, P. J. *Acc. Chem. Res.* **2003**, *36*, 739–749.
4. (a) Yoshioka, M.; Kawakita, T.; Ohno, M. *Tetrahedron Lett.* **1989**, *30*, 1657–1660; (b) Takahashi, H.; Kawakita, T.; Yoshioka, M.; Kobayashi, S.; Ohno, M. *Tetrahedron Lett.* **1989**, *30*, 7095–7098; (c) Takahashi, H.; Kawakita, T.; Ohno, M.; Yoshioka, M.; Kobayashi, S. *Tetrahedron* **1992**, *48*, 5691–5700; (d) Rozema, M. J.; Sidduri, A.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 1956–1958; (e) Brieden, W.; Ostwald, R.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 582–584; (f) Nowotny, S.; Vettel, S.; Knochel, P. *Tetrahedron Lett.* **1994**, *35*, 4539–4540; (g) Ostwald, R.; Chavant, P.; Stadtmuller, H.; Knochel, P. *J. Org. Chem.* **1994**, *59*, 4143–4153; (h) Lutz, C.; Knochel, P. *J. Org. Chem.* **1997**, *62*, 7895–7898; (i) Ho, D. E.; Betancort, J. M.; Woodmansee, D. H.; Larter, M. L.; Walsh, P. J. *Tetrahedron Lett.* **1997**, *38*, 3867–3870; (j) Pritchett, S.; Woodmansee, D. H.; Davis, T. J.; Walsh, P. J. *Tetrahedron Lett.* **1998**, *39*, 5941–5942.
5. For structure and mechanistic aspect, see: (a) Pritchett, S.; Woodmansee, D. H.; Gantzel, P.; Walsh, P. J. *J. Am. Chem. Soc.* **1998**, *120*, 6423–6424; (b) Royo, E.; Betancort, J. M.; Davis, T. J.; Caroll, P.; Walsh, P. J. *Organometallics* **2000**, *19*, 4840–4851; (c) Balsells, J.; Betancort, J. M.; Walsh, P. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3428–3429.
6. Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581–1590.
7. (a) Bisai, A.; Prasad, B. A. B.; Singh, V. K. *Tetrahedron Lett.* **2005**, *46*, 7935–7939; (b) Bisai, A.; Prasad, B. A. B.; Singh, V. K. *ARKIVOC* **2007**, (Part v), 20–37.
8. (a) Chen, Y.-J.; Lin, R.-X.; Chen, C. *Tetrahedron: Asymmetry* **2004**, *15*, 3561–3571; (b) Dai, W.-M.; Zhu, H.-J.; Hao, X.-J. *Tetrahedron: Asymmetry* **2000**, *11*, 2315–2337.