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Enantioselective addition of diethylzinc to aldehydes catalyzed by optically active 1,4-aminoalcohols

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Abstract

Enantioselective addition reactions of diethylzinc to aldehydes were performed by catalytic reactions with chiral 1,4-aminoalcohols. Optically active 1,4-aminoalcohols were synthesized from (+)-camphor and (–)-fenchone through four steps involving iodine-mediated lactonization of 3-hydroxy acids.

1. Introduction

Enantioselective addition reactions of diethylzinc to aldehydes using a chiral catalyst are very useful for the synthesis of optically active secondary alcohols, and many chiral catalysts have been synthesized for the application to this asymmetric reaction.[1] It is known that chiral 1,2-aminoalcohols show high catalytic activity for this enantioselective alkylation;[2] however, only a few examples using chiral 1,4-aminoalcohols have been reported.[3] Recently, we reported that a 1,4-aminoalcohol prepared from (+)-camphor was an efficient chiral catalyst for the ethylation of aldehydes by diethylzinc.[4] In this paper, we report the details of iodine-mediated lactonization of bicyclic 3-hydroxy acids and the synthesis of new optically active 1,4-aminoalcohols which can catalyze enantioselective addition reactions of diethylzinc to aldehydes.

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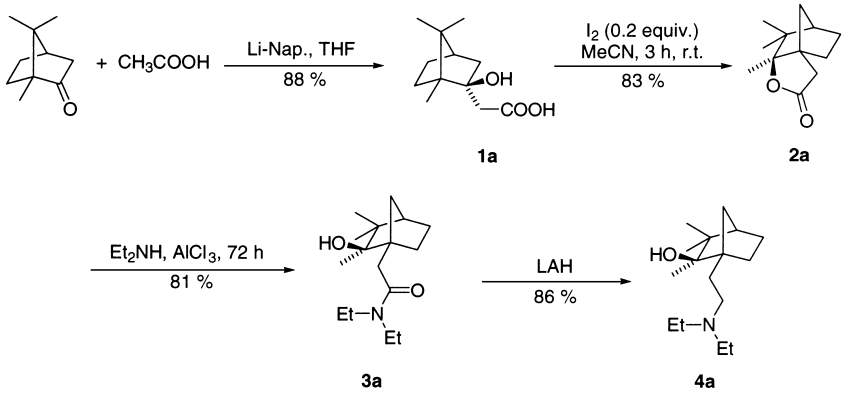
2. Results and discussion

2.1. Synthesis of optically active 1,4-aminoalcohols via iodine-mediated lactonization of bicyclic 3-hydroxy acids

1,4-Aminoalcohol **4a** was prepared from (+)-camphor through four steps (Scheme 1). A nucleophilic attack of an acetic acid dianion, generated by the reaction of acetic acid with lithium naphthalenide,[5] and (+)-camphor gave *exo*-hydroxy acid **1a** in 88% chemical yield (*endo*:*exo* = 8:92). The reaction is reasonably explained in terms of the nucleophilic addition that takes place from the *endo*-side of the carbonyl face due to the steric hindrance of the methyl group. The lactonization of **1a** was performed by the use of a catalytic amount of iodine. When **1a** was reacted with 0.2 equiv. of iodine in acetonitrile, lactone **2a** was obtained in 83% yield. The configuration of **2a** was determined by NMR techniques; specifically, NOEs were observed between H_a and Me_a but not between H_b and Me_a. Accordingly, we deduced the 5*S*-configuration (Fig. 1). A plausible mechanism is shown in Scheme 2, which is based on the report by Kim.[6] Namely, hydrogen iodide generated by the reaction of iodine with free carboxylic acid reacts as a catalyst to form cation **I**, and the reaction was subsequently followed by Wagner[7a] and Meerwein[7b] type rearrangement to give intermediate **II**. Then, the attack of carbonyl oxygen resulted in the formation of the lactone **2a** and iodine, which will be recycled. The reaction of **2a** with diethylamine in the presence of aluminum chloride[8] gave hydroxyamide **3a** in 81% yield, which was easily reduced by lithium aluminum hydride to 1,4-aminoalcohol **4a** in 86% yield.



Scheme 1.

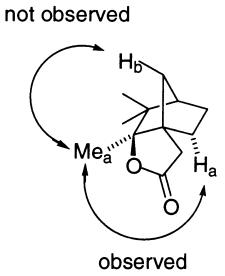
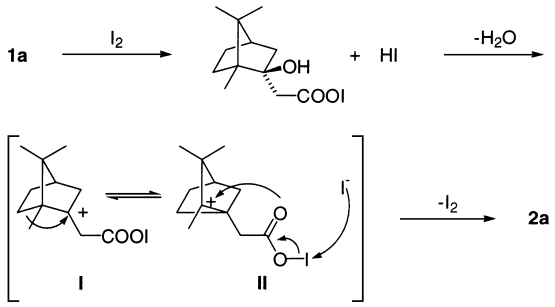
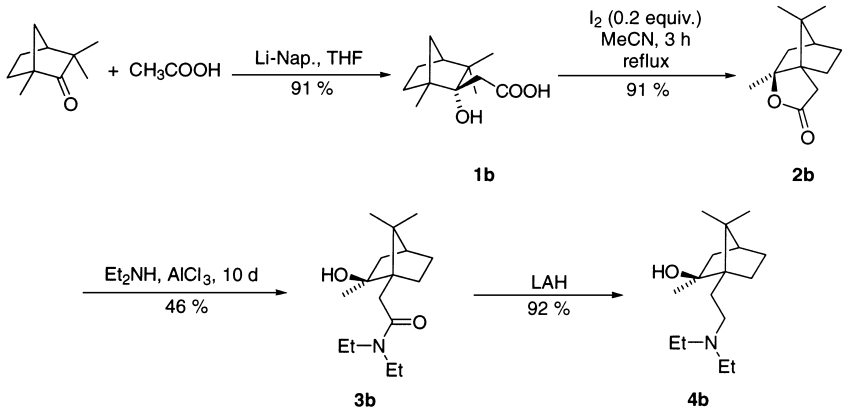


Figure 1.



Scheme 2.

1,4-Aminoalcohol **4b** was prepared from (–)-fenchone by the same protocol (Scheme 3). When (–)-fenchone reacted with the acetic acid dianion, the less hindered *exo*-side of the carbonyl face was preferentially attacked by the dianion, and the *endo*-hydroxy acid **1b** was obtained in 91% yield (*endo*:*exo* = 89:11). The 3-hydroxy acid **1b** was treated in the same manner as **1a**; however, the lactone **2b** was obtained in only 19% yield. When the reaction mixture was refluxed for 3 hours, the lactone **2b** was obtained in 91% yield. In the case of lactone **2b**, though the addition of amine was relatively slow and 10 days were needed to complete the reaction, **3b** was obtained in 46% yield. Decrease of reactivity may be due to the steric hindrance of the geminal methyl groups. Amide **3b** was also easily reduced by lithium aluminum hydride to **4b** in 92% yield.

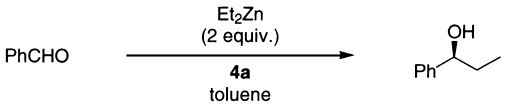


Scheme 3.

2.2. Enantioselective addition of diethylzinc to aldehydes using 1,4-aminoalcohols

Ethylation of benzaldehyde by diethylzinc using chiral catalyst **4a** was carried out under various conditions (Table 1). When a toluene solution of benzaldehyde was reacted with 2.0 equiv. of diethylzinc in the presence of 5 mol% of **4a** for 3 hours at room temperature, (*S*)-1-phenyl-1-propanol was obtained in 99% chemical yield (93% ee). Many successive enantiomeric syntheses were performed at low temperature. However, in this case, lowering the temperature did not give any better enantioselectivity. Furthermore, the reaction under reflux conditions resulted in a fast reaction, but slightly lower enantioselectivity. Reducing the amount of catalyst to 1 mol% or 0.5 mol% based on the amount of aldehyde was still efficient for the catalytic reaction, and 91% ee

Table 1
Enantioselective addition reaction of diethylzinc to benzaldehyde with chiral catalyst **4a** under various conditions

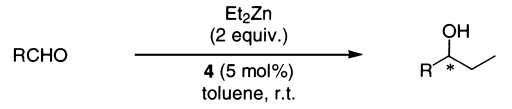


5a (*S*)-**6a**

Amount of **4a** (mol%)[a]	Temp. (°C)	Time (h)[b]	Yield of **6a** (%)[c]	ee of **6a** (%)[d]
5	r.t.	3	99	93
5	0	20	98	88
5	-20	168	46	73
5	reflux	1	98	86
1	r.t.	14	99	91
0.5	r.t.	24	94	90
0.2	r.t.	24	72	84

[a]Based on the amount of benzaldehyde. [b]The reaction was followed by GC. [c]Determined by GC. [d]Determined by HPLC using a Chiralcel OD-H column.

Table 2
Enantioselective addition reaction of diethylzinc to aldehydes with chiral catalyst **4**



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a: R=Ph
b: R=2-MeOPh
c: R=4-MeOPh
d: R=2-MePh
e: R=4-MePh
f: R=α-Naphthyl
g: R=*E*-Cinnamyl
h: R=$PhCH_2CH_2$

6

Entry	Aldehyde	Catalyst	Time (h)[a]	Yield (%)[b]	ee (%)	Config. of **6**[c]
1	**5a**	**4a**	3	99	93[d]	*S*
2	**5a**	**4b**	2	99	60[d]	*R*
3	**5a**	**4b**[f]	36	40	11[d]	*R*
4	**5b**	**4a**	2	99	86[d]	*S*
5	**5c**	**4a**	2	99	87[d]	*S*
6	**5c**	**4a**[f]	14	92	63[d]	*S*
7	**5c**	**4b**	2.5	97	44[d]	*R*
8	**5c**	**4b**[f]	36	75	33[d]	*R*
9	**5d**	**4a**	6	96	93[d]	*S*
10	**5e**	**4a**	3	99	95[e]	*S*
11	**5e**	**4b**	3	98	62[e]	*R*
12	**5e**	**4b**[f]	24	50	49[e]	*R*
13	**5f**	**4a**	5.5	96	82[e]	*S*
14	**5g**	**4a**	6	97	60[e]	*S*
15	**5g**	**4b**	3.5	99	50[e]	*R*
16	**5h**	**4a**	24	80	54[e]	*S*

[a]The reaction was followed by GC. [b]Determined by GC. [c]Determined by the sign of the specific rotation. [d]Determined by HPLC using a Chiralcel OD-H column. [e]Determined by HPLC using a Chiralcel OJ column. [f]1 mol% of catalyst was used.

and 90% ee of **6a** was obtained, respectively. However, the reaction with 0.2 mol% of catalyst resulted in a lower chemical and ee value.

The enantioselective addition reaction of diethylzinc to various aldehydes using chiral catalyst **4** is summarized in Table 2. With the use of 5 mol% of chiral ligand **4a**, the addition reaction proceeded in high yield and the corresponding *sec*-alcohols were obtained in 80–99% yield and 54–95% ee with *S*-configuration (entries 1, 4, 5, 9, 10, 13, 14 and 16). When substituted benzaldehydes or 1-naphthaldehyde were used as substrates, high ee values of the products were obtained almost quantitatively (entries 1–12); however, the reaction of *E*-cinnamaldehyde or 3-phenylpropanal resulted in low ee values of the products in 60 and 54% ee, respectively (entries 14 and 16). When 1 mol% of **4a** was used, the product was obtained quantitatively, but the ee value was slightly decreased (entries 6). For the chiral ligand **4b**, the *sec*-alcohols were obtained in 97–99% yield and 44–62% ee with *R*-configuration (entries 2, 7, 11 and 15). Reducing the amount of catalyst to 1 mol% affected both the reaction rate and the enantioselectivity. The reaction needed 24 or 36 hours to complete and 40–75% of alcohols **6** were obtained in lower ee values (entries 3, 8 and 12).

It is recognized that the actual catalyst is in situ formed ethylzinc aminoalkoxide.[9] When the ethylzinc aminoalkoxide **A** is formed from **4a** and diethylzinc, the O–Zn linkage should be arranged to the *syn*-position of the norbornane skeleton due to the steric repulsion between the methyl group of carbinol carbon and the aminoethyl group (Fig. 2). Hence, less hindered *Si*-face

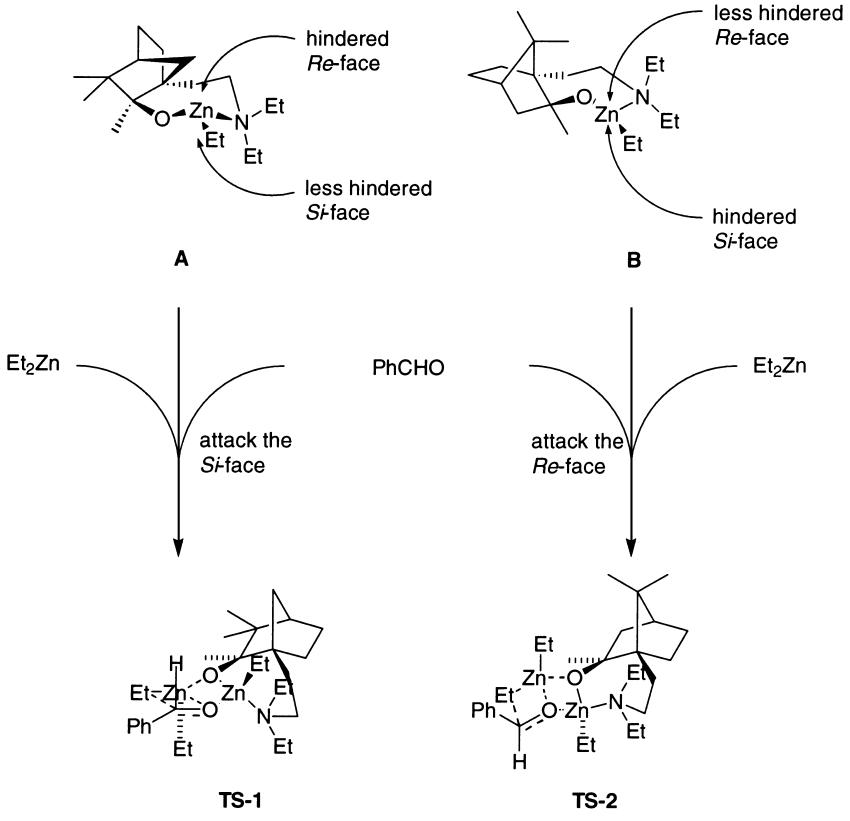

Figure 2.

of the zinc atom might be more reactive towards the aldehyde oxygen leading to **Ts-1**. The *anti*-configured 7/4/4 transition state was favored because of the electrostatic repulsion between the two non-reacting ethyl groups on the zinc atom[10] and (*S*)-enriched product was obtained from the reaction. On the other hand, the O–Zn linkage arranged to the *anti*-position of the norbornane skeleton in the aminoalkoxide **B** because of the steric hindrance between the geminal methyl groups of norbornane and the ethyl group on the zinc atom, and the less hindered side was changed to *Re*-face of the zinc atom. **TS-2** was also configured *anti* 7/4/4 transition state due to the repulsion between the two ethyl groups on the zinc atom, and (*R*)-enriched product was obtained from the reaction. In the aminoalkoxide **A**, the remarkable difference of the reactivity between *Re*-and *Si*-face resulted in the high enantioselective formation of alcohols.

In conclusion, we have demonstrated that 1,4-aminoalcohols **4a** and **4b** could be easily prepared from (+)-camphor and (–)-fenchone in four steps via iodine-mediated lactonization of 3-hydroxy acids, and that they are effective catalysts for the enantioselective addition of diethylzinc to aldehydes.

3. Experimental

3.1. General

NMR spectra were recorded on a JEOL GSX-400 system or a Bruker DPX-300 system with TMS as an internal standard. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. Mass spectra were recorded on a JEOL JMS-HX110. Optical rotations were measured on a JASCO DIP-370 or a HORIBA SEPA-300. Elemental analyses were performed on an Elementar vario EL. Tetrahydrofuran (THF) was distilled from calcium hydride and stored under sodium wire. Toluene was distilled from phosphorus pentoxide. Diethylzinc was purchased from KANTO as 1.02 M solution in hexane and used as received. Other materials were obtained commercially.

3.2. Preparation of 3-hydroxy acid *1*

A mixture of naphthalene (12.8 g, 100 mmol), metallic lithium cuttings (1.4 g, 200 mmol), diethylamine (14.6 g, 200 mmol) and THF (150 mL) was stirred at room temperature under a nitrogen atmosphere. After 2 hours, acetic acid (6.0 g, 100 mmol) in 50 mL of THF was added dropwise for 1 hour and stirred for an additional hour. To the reaction solution, ketone (80 mmol) in 50 mL of THF was added dropwise for 1 hour and the mixture was stirred for 24 hours. The acid was separated as reported previously.[5]

Compound **1a**: 88% yield (14.8 g, 70 mmol); viscous oil: ^{1}H NMR (δ, ppm): 0.87 (3H, s), 0.88 (3H, s), 0.96–1.07 (1H, m), 1.12 (3H, s), 1.25–1.36 (1H, m), 1.41–1.49 (1H, m), 1.52 (1H, d, J = 13.5 Hz), 1.68–1.77 (2H, m), 2.14 (1H, dt, J = 13.5 and 3.6 Hz), 2.57 (1H, d, J = 15.5 Hz), 2.63 (1H, d, J = 15.5 Hz); ^{13}C NMR (δ, ppm): 10.44, 21.02, 21.36, 26.82, 30.67, 42.97, 44.95, 46.52, 49.15, 52.51, 79.62, 178.32; IR: 1700 cm^{-1}; $[\alpha]_D^{25}$: –22.3 (*c* 1.04, $CHCl_3$); HRMS (FAB) calcd for $C_{12}H_{19}O_3$ $[M–H]^+$: 211.1334; found: *m*/*z* 211.1325.

Compound **1b**: 91% yield (15.6 g, 73 mmol); colorless crystal: ^{1}H NMR (δ, ppm): 1.00 (3H, s), 1.02 (3H, s), 1.02 (3H, s), 0.97–1.06 (1H, m), 1.14 (1H, dd, J = 10.6 and 1.5 Hz), 1.42 (1H, ddt,

J = 4.6, 5.1 and 12.5 Hz), 1.52–1.56 (1H, m), 1.64–1.67 (1H, m), 1.69–1.77 (1H, m), 2.02–2.11 (1H, m), 2.54 (1H, d, J = 17.2 Hz), 2.61 (1H, d, J = 17.2 Hz); ^{13}C NMR (δ, ppm): 17.42, 22.22, 25.24, 27.28, 29.14, 39.72, 40.65, 44.35, 49.76, 52.23, 80.43, 180.03; IR: 1690 cm^{-1}; $[\alpha]_D^{25}$: 1.9 (*c* 1.55, $CHCl_3$); m.p.: 134.5–135.5 °C; anal. calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50; found: C, 67.94; H, 9.53.

3.3. Iodine-mediated lactonization of 3-hydroxy acid

Iodine (0.24 g, 0.94 mmol), 3-hydroxy acid (4.7 mmol), and acetonitrile (60 mL) were placed in a 100 mL flask and stirred at an appropriate temperature for 3 hours. After stirring, the solution was quenched with a 5% aqueous solution of sodium thiosulfate to remove iodine. After the usual extractive work-up, the crude product was purified by silica gel column chromatography using hexane and ethyl acetate (8:1) as an eluent to give the corresponding lactone.

Compound **2a**: 84% yield (0.76 g, 3.9 mmol); colorless crystal: ^{1}H NMR (δ, ppm): 1.03 (3H, s), 1.07 (3H, s), 1.17 (3H, s), 1.28 (1H, dd, J = 10.2 and 1.5 Hz), 1.39–1.48 (1H, m), 1.51–1.63 (2H, m), 1.66–1.76 (1H, m), 1.79–1.82 (1H, m), 1.87–1.92 (1H, m), 2.46 (1H, d, J = 17.3 Hz), 2.59 (1H, d, J = 17.3 Hz); ^{13}C NMR (δ, ppm): 17.81, 22.37, 23.84, 24.45, 24.73, 34.53, 39.69, 44.88, 48.48, 55.64, 95.21, 176.48; IR: 1765 cm^{-1}; $[\alpha]_D^{25}$: –95.8 (*c* 1.24, $CHCl_3$); m.p.: 125.5–126.5°C; HRMS (FAB) calcd for $C_{12}H_{19}O_2$ $[M+H]^+$: 195.1385; found: *m*/*z* 195.1371.

Compound **2b**: 91% yield (0.83 g, 4.3 mmol); colorless crystal: ^{1}H NMR (δ, ppm): 0.95 (3H, s), 1.03 (3H, s), 1.20–1.26 (1H, m), 1.34 (3H, s), 1.46 (1H, d, J = 13.7 Hz), 1.45–1.51 (1H, m), 1.75–1.81 (1H, m), 1.84–1.90 (2H, m), 2.27 (1H, d, J = 17.7 Hz), 2.47 (1H, d, J = 17.7 Hz), 2.50 (1H, dt, J = 13.7 and 3.4 Hz); ^{13}C NMR (δ, ppm): 20.43, 20.79, 24.47, 24.68, 26.43, 30.49, 43.22, 45.00, 49.06, 56.34, 92.76, 177.00; IR: 1755 cm^{-1}; $[\alpha]_D^{25}$: –8.1 (*c* 1.50, $CHCl_3$); m.p.: 183–184 °C; HRMS (FAB) calcd for $C_{12}H_{19}O_2$ $[M+H]^+$: 195.1385; found: *m*/*z* 195.1371.

3.4. Preparation of hydroxyamide **3**

A solution of diethylamine (2.2 g, 30 mmol) in 15 mL of THF was added dropwise to aluminum chloride (1.3 g, 10 mmol) in 30 mL of THF at 0°C and agitated for 20 min. The reaction mixture was maintained at the same temperature during the addition. After an additional 30 min, the cooling bath was removed and a solution of lactone (5.2 mmol) in 15 mL of THF was added dropwise for 15 min and stirred for the appropriate hours. The reaction mixture was quenched with water (50 mL) under external cooling, stirred for 30 min and the aqueous layer extracted three times with diisopropyl ether. The combined organic layers were washed twice with water and dried over sodium sulfate. After filtration and evaporation, the crude product was purified by silica gel column chromatography using hexane and ethyl acetate (8:1) as an eluent to give the corresponding hydroxyamide **3**.

Compound **3a**: 81% yield (1.1 g, 4.2 mmol); colorless crystal: ^{1}H NMR (δ, ppm): 0.93 (3H, s), 1.01 (3H, s), 1.07 (3H, s), 1.12 (3H, t, J = 7.1 Hz), 1.19 (3H, t, J = 7.1 Hz), 1.08–1.14 (1H, m), 1.34–1.43 (2H, m), 1.50–1.64 (2H, m), 1.66–1.71 (1H, m), 2.13–2.21 (1H, m), 2.45 (1H, d, J = 14.8 Hz), 2.63 (1H, d, J = 14.8 Hz), 3.24–3.47 (4H, m), 3.80 (1H, br-s); ^{13}C NMR (δ, ppm): 13.06, 14.42, 19.49, 23.75, 24.73, 25.47, 31.87, 33.96, 38.31, 40.46, 42.81, 45.16, 48.33, 54.36, 80.56, 172.97; IR: 3367, 2964, 1620 cm^{-1}; $[\alpha]_D^{25}$: –19.1 (*c* 1.00, CH_3CN); m.p.: 122–123°C; anal. calcd for $C_{16}H_{29}NO_2$: C, 71.86; H, 10.93; N, 5.24; found: C, 71.92; H, 11.08; N, 5.18.

Compound **3b**: 46% yield (0.64 g, 2.4 mmol); colorless crystal: ^{1}H NMR (δ, ppm): 0.87 (3H, s), 1.15 (3H, t, $J=7.1$ Hz), 1.21 (3H, t, $J=7.1$ Hz), 1.22 (3H, s), 1.24 (3H, s), 1.20–1.34 (1H, m), 1.46–1.89 (5H, m), 2.11–2.23 (1H, m), 2.34 (1H, d, $J=13.2$ Hz), 2.56 (1H, d, $J=13.2$ Hz), 3.10–3.37 (2H, m), 3.54–3.73 (2H, m), 4.89 (1H, br-s); ^{13}C NMR (δ, ppm): 13.04, 14.31, 21.26, 21.44, 27.07, 28.66, 29.77, 31.42, 40.22, 42.87, 44.83, 47.55, 50.77, 55.49, 78.55, 173.63; IR: 3373, 2937, 1624 cm^{-1}; $[\alpha]_D^{25}$: –26.5 (*c* 1.00, $CHCl_3$); m.p.: 99.5–100.5°C; anal. calcd for $C_{16}H_{29}NO_2$: C, 71.86; H, 10.93; N, 5.24; found: C, 71.73; H, 11.04; N, 5.29.

3.5. Preparation of 1,4-aminoalcohol *4*

A solution of **3** (1.9 mmol) in 15 mL of THF was added dropwise to a suspension of lithium aluminum hydride (0.22 g, 5.7 mmol) in 20 mL of THF at 0°C for 30 min. The reaction mixture was refluxed for 12 hours, then cooled and quenched with water (30 mL). A 10% aqueous solution of sodium hydroxide was added and the mixture was stirred for 30 min. The aqueous layer was extracted three times with diisopropyl ether and the combined organic layers were washed twice with water and dried over sodium sulfate. After filtration and evaporation, the crude product was purified by alumina column chromatography using hexane and ethyl acetate (3:1) as an eluent to give the corresponding 1,4-aminoalcohol **4**.

Compound **4a**: 86% yield (0.41 g, 1.6 mmol); viscous oil: ^{1}H NMR (δ, ppm): 0.88 (3H, s), 0.99 (3H, s), 1.03 (6H, t, $J=7.2$ Hz), 1.05 (3H, s), 1.01–1.08 (1H, m), 1.12–1.18 (1H, m), 1.23–1.68 (5H, m), 1.87–1.96 (1H, m), 2.10–2.16 (1H, m), 2.24–2.35 (1H, m), 2.37 (1H, dq, $J=7.2$ and 14.4 Hz), 2.51–2.61 (1H, m), 2.68 (2H, dq, $J=7.2$ and 14.4 Hz), 6.52 (1H, br-s); ^{13}C NMR (δ, ppm): 10.63, 19.59, 24.16, 25.58, 25.95, 29.88, 33.70, 37.29, 44.36, 45.74, 48.70, 50.59, 57.04, 78.62; IR: 3195, 3095, 2965 cm^{-1}; $[\alpha]_D^{25}$: –11.4 (*c* 0.20, CH_3CN); HRMS (FAB) calcd for $C_{16}H_{32}NO$ $[M+H]^+$: 254.2484; found: *m*/*z* 254.2472.

Compound **4b**: 92% yield (0.43 g, 1.7 mmol); viscous oil: ^{1}H NMR (δ, ppm): 0.87 (3H s), 1.01 (6H, t, $J=7.2$ Hz), 1.01–1.08 (1H, m), 1.22–1.36 (2H, m), 1.28 (6H, s), 1.47–1.58 (2H, m), 1.60–1.75 (3H, m), 2.01–2.11 (1H, m), 2.36–2.72 (6H, m); ^{13}C NMR (δ, ppm): 10.33, 21.35, 22.70, 26.03, 26.80, 29.07, 31.90, 45.26, 46.60, 47.81, 49.89, 55.06, 77.71; IR: 3386, 3132, 2964 cm^{-1}; $[\alpha]_D^{25}$: 18.1 (*c* 1.02, $CHCl_3$); HRMS (FAB) calcd for $C_{16}H_{32}NO$ $[M+H]^+$: 254.2484; found: *m*/*z* 254.2476.

3.6. Typical procedure for addition reaction of diethylzinc to aldehydes

A well-dried Schlenk flask was charged with **4** (0.05 mmol). The Schlenk flask was evacuated twice and flushed with argon. Toluene (2.0 mL) was added and the solution is cooled to 0°C followed by addition of diethylzinc (1.02 M solution in hexane, 2.0 ml, 2.0 mmol). The reaction mixture was stirred at room temperature for 30 min and the reaction temperature was changed to the appropriate degree. Then aldehyde (1.0 mmol) was added directly via a syringe and stirred for the appropriate hours. The reaction was quenched by addition of 2.0 M aqueous solution of HCl (10 mL) and the resulting mixture was extracted three times with diisopropyl ether. The combined organic layers were washed twice with water and dried over sodium sulfate. After filtration and evaporation, the crude product was purified by silica gel column chromatography using hexane and ethyl acetate as an eluent to give the corresponding alcohols. The enantiomeric excess of the product was determined by analytical HPLC using *n*-hexane and 2-propanol (95:5) as an eluent, and the flow rate was 0.5 mL/min.

References

1. (a) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; John Wiley & Sons: New York, 1994; Chapter 5. (b) Noyori, R.; Kitamura, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 49. (c) Soai, K.; Niwa, S. *Chem. Rev.* **1992**, *92*, 833.
2. (a) Cho, B. T.; Chun, Y. S. *Tetrahedron: Asymmetry* **1998**, *9*, 1489. (b) Beliczey, J.; Giffels, G.; Kragl, U.; Wandrey, C. *Tetrahedron: Asymmetry* **1997**, *8*, 1529. (c) Solà, L.; Vidal-Ferran, A.; Moyano, A.; Pericàs, M. A.; Riera, A. *Tetrahedron: Asymmetry* **1997**, *8*, 1559. (d) Nugent, A. W. *J. Chem. Soc., Chem. Commun.* **1999**, 1369.
3. (a) Genov, M.; Kostova, K.; Dimitrov, V. *Tetrahedron: Asymmetry* **1997**, *8*, 1607. (b) Genov, M.; Dimitrov, V.; Ivanova, V. *Tetrahedron: Asymmetry* **1997**, *8*, 3703. (c) Knollmüller, M.; Ferencic, M.; Gärtner, P. *Tetrahedron: Asymmetry* **1999**, *10*, 3969.
4. Hanyu, N.; Mino, T.; Sakamoto, M.; Fujita, T. *Tetrahedron Lett.* **2000**, *41*, 4587.
5. Watanabe, S.; Suga, K.; Fujita, T.; Fujiyoshi, K. *Israel J. Chem.* **1970**, *8,* 731.
6. Kim, K. M.; Ryu, E. K. *Tetrahedron Lett.* **1996**, *37*, 1441.
7. (a) Wagner, R. *J. Russ. Phys. Chem. Soc.* **1899**, *31*, 690. (b) Meerwein, H. *Ann.* **1914**, *405,* 129.
8. Lesimple, P.; Bigg, D. C. H. *Synthesis* **1991**, 306.
9. (a) Kitamura, M.; Okada, S.; Suga, S.; Noyori, R. *J. Am. Chem. Soc.* **1989**, *111*, 4028. (b) Kitamura, M.; Suga, S.; Niwa, M.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 4832. (c) Yamakawa, M.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 6327.
10. Yamakawa, N.; Noyori, R. *Organometallics* **1999**, *18*, 128.