Design and Synthesis of 1,4-Amino Alcohol Ligands with a Chiral Cyclopropane Backbone for Asymmetric Diethylzinc Addition to Aromatic Aldehydes

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Abstract: A new type of *cis*-1,4-amino alcohols with a cyclopropane backbone have been developed in three simple steps, from a cheap industrial intermediate for enantioselective asymmetric diethylzinc addition to aromatic aldehydes, under mild conditions to afford corresponding secondary alcohols in high yield with excellent enantioselectivity.

Key words: amino alcohols, cyclopropane backbone, organozinc addition, diethylzinc, aromatic aldehydes

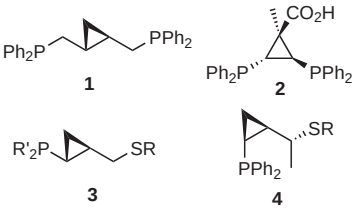

Figure 1 Chiral cyclopropane-based ligand

Optically active amino alcohols are not only versatile chiral building blocks in asymmetric synthesis,[1] but also important chiral ligands developed for enantioselective addition of dialkylzinc to aldehydes, which is one of the most widely studied areas in asymmetric C–C bond formation.[2] Thus, design and synthesis of chiral amino alcohols is an area of intense research. Among various chiral ligands, such as diols,[3] amino alcohols,[4] amino thiols,[5] and amino sulfides,[6] amino alcohols are the most investigated ligands and prominent for asymmetric dialkylzinc addition to aldehydes.[2] Usually, 1,2-amino alcohols are highly efficient and the most popular. There are only a few 1,4-amino alcohols ever used in this reaction.[1c,7] Recently, Tanyeli and co-workers synthesized a chiral 1,4-amino alcohol ligand with a rigid norbornene backbone and demonstrated its successful application in diethylzinc addition with an 88% ee.[7b] These results inspired us to assume that those ligands **9**, which incorporate chiral cyclopropane structural features, might afford higher enantiomeric excesses for diethylzinc addition to aldehydes.

Although the cyclopropane ring with an advantageous combination of structural rigidity, low molecular weight on a well-defined and highly variable platform, and unusual bond angles provides an attractive chiral backbone, only a few chiral cyclopropane-based ligands **1**–**4** have been reported.[8] In 1979, Colleuille and co-workers developed the first chiral cyclopropane-based ligand **1**.[8a] With the cyclopropyl-based diphosphine **1** as chiral ligand in the rhodium-catalyzed hydrogenation of dehydroamino acids, the corresponding reduction product can be obtained in 23% ee. Until 1992, another chiral ligand (**2**) with a cyclopropane ring as chiral backbone was reported by Minami and co-workers.[8b] In the presence of catalyst Pd-**2** asymmetric allylic alkylation was carried out with 61% ee. Most recently, Molander and coworkers developed chiral ligands **3** and **4**, and used them in the palladium-catalyzed allylic alkylation of 1,3-diphenylpropenyl acetate with dimethyl malonate, the corresponding product can be obtained in high yield and with good enantioselectivity (up to 93% ee).[8c] The authors also found that the ligands based on the *trans*-cyclopropane ring and metal would form a dimeric complex with a bridging ligand, which has been proven by obtaining the X-ray crystal structure of the complex from ligand **1** and $PdCl_2$. Dimeric or a mixture of monomeric non-chelate catalyst has a high fluxional environment that subsequently leads to lower enantioselectivity. But *cis*-ligands did chelate without forming dimers. The results showed that a *cis*-cyclopropane-based ligand should have a better chelating capability. Based on these results, we designed and synthesized a new type of 1,4-aminoalcohol ligands **9** with *cis*-cyclopropane as the chiral backbone. Their application to the diethylzinc addition to aldehydes was also carried out.

In the synthesis of target ligands, (1*R*,5*S*)-4-hydroxy-6,6-dimethyl-3-oxa-bicyclo[3.1.0]hexan-2-one (**5**; 98% ee) was used as starting material (Scheme 1), which is a key intermediate in the synthesis of pyrethroid insecticides. Treatment of compound **5** with diazomethane in diethyl ether gave the aldehydoester **6** quantitatively. Subsequent reductive amination of **6** by $NaBH_3CN$ and secondary amines in methanol afforded a series of *cis*-cyclopropane aminoesters **7a**–**d** in 90–95% yield. Reduction of **7a** with $LiAlH_4$ resulted in ligand **8**. Ligands **9a**–**d**[9] were obtained from the reaction of PhMgCl with **7a**–**d** at low temperature. Since all the reactions did not involve the chiral carbons of cyclopropane, the absolute configurations of **8** and **9a**–**d** were determined as (1*R*,3*S*) by comparison with the starting material **5**. The enantiomeric excesses of **8** and **9a**–**d** are 98–99%, and those of compounds **9a**–**d** can be slightly improved by recrystallization, but are always nearly the same as observed for **5**.

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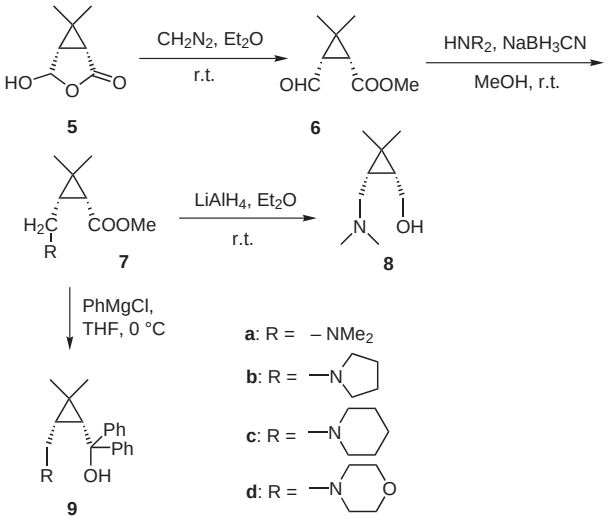
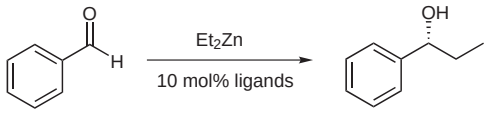


Scheme 1 Synthesis of chiral cyclopropane-based ligands **9a–d**

The efficiency of these new ligands was examined in the diethylzinc addition to benzaldehydes.[10] Initially, the reaction was carried out in toluene with 10 mol% amino alcohol ligand. As shown in Table 1, the diethylzinc addition to benzaldehyde proceeded smoothly at 20 °C with **9a** as the chiral ligand to give (*R*)-1-phenylpropanol in 90% yield and 80% ee (Table 1, entry 2). Lowering the reaction temperature to 0 °C or –15 °C only resulted in a slight decrease in the reactivity with a slight improvement in the enantioselectivity (Table 1, entry 2 vs 3 and 4). When the reaction temperature continued to be lowered to –25 °C, the reactivity obviously decreased and the ee remained unchanged (Table 1, entry 4 vs 5). The solvent effect was also examined. Changing the solvent from toluene to hexane gave the product in similar yield with slightly higher enantioselectivity (Table 1, entry 6 vs 4). With dichloromethane as solvent, both yield and enantiomeric excess dropped (Table 1, entry 6 vs 7). When THF was used, no reaction took place. Obviously, hexane was the best solvent for this addition reaction. Under the optimized conditions, we also examined the ligands **9b–d** in the same reaction, and found that **9c** and **9d** promoted the diethylzinc addition to benzaldehyde to give the corresponding secondary alcohol in 87% and 90% yields with a uniform 96% ee (Table 1, entries 10 and 11), respectively.

After establishing the optimized reaction conditions, the diethylzinc addition to other aldehydes was carried out (Table 2). We carefully examined the utility of ligands **9c** and **9d** for the diethylzinc addition to aromatic aldehydes. In all cases, the aldehydes were completely consumed after 48 hours under the reaction conditions described in Table 2. Addition of diethylzinc to aromatic aldehydes proceeded in high yields with enantioselectivities in the range 90–97% ee (Table 2, entries 1–12). There was almost no difference in enantioselectivites observed for ligands **9c** and **9d** in the addition reaction. Moreover, the electron-deficient and electron-rich aromatic aldehydes demonstrated nearly the same reactivity and enantioselectivity for this reaction. Generally, the position of substituents relative to the CHO group on the aromatic ring has no influence on the reactivity and enantioselectivity.

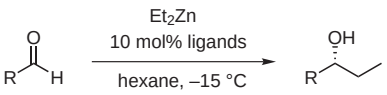
Table 1 Asymmetric Diethylzinc Addition to Benzaldehyde by Using *cis*-Cyclopropane-Based 1,4-Amino Alcohol Ligands



Entry	Catalyst	Temp (°C)	Time	Solvent	Yields (%)[a]	ee (%)[b]
1	**8**	20	20 h	toluene	70	78
2	**9a**	20	20 h	toluene	90	80
3	**9a**	0	20 h	toluene	88	82
4	**9a**	–15	48 h	toluene	87	84
5	**9a**	–25	72 h	toluene	77	84
6	**9a**	–15	48 h	hexane	90	85
7	**9a**	–15	48 h	CH_2Cl_2	70	79
8[c]	**9a**	–15	48 h	THF	–	–
9	**9b**	–15	48 h	hexane	85	86
10	**9c**	–15	48 h	hexane	87	96
11	**9d**	–15	48 h	hexane	90	96

[a] Isolated yield after flash chromatography.
[b] Determined by HPLC analysis on a Chiralcel Daicel OD-H column. The major enantiomer has an *R* configuration.
[c] No reaction.

Table 2 Diethylzinc Addition to Aromatic Aldehydes Using the Ligands **9c** and **9d**[a]



Entry	R	Ligand	Yield (%)[b]	ee (%)[c]
1	2-$MeOC_6H_4$	**9c**	90	95
2		**9d**	88	95
3	3-$MeOC_6H_4$	**9c**	93	95
4		**9d**	92	96
5	4-$MeOC_6H_4$	**9c**	89	96
6		**9d**	90	96
7	2-ClC_6H_4	**9c**	65	90
8		**9d**	60	94
9	4-ClC_6H_4	**9c**	77	96
10		**9d**	80	96
11	1-naphthyl	**9c**	94	96
12		**9d**	93	97

[a] Reaction conditions: Et_2Zn (220 mol%), ligand (10 mol%), hexane, –15 °C, 48 h.
[b] Isolated yield after flash chromatography.
[c] Determined by HPLC analysis on Chiral Daicel OD-H column or by GC analysis on Chiral cyclodextrin capillary column, and the absolute configuration of the major enantiomer was assigned as *R* by comparison with the literature data.

In conclusion, we have developed a new type of *cis*-cyclopropane-based 1,4-amino alcohol ligands, which were synthesized in three steps from the cheap intermediate of pyrethroid insecticide and promoted the enantioselective diethylzinc addition to aromatic aldehydes under mild conditions to afford the corresponding secondary alcohols in high yield with excellent enantioselectivity. These results showed that a cyclopropane-based ligand is promising in asymmetric catalysis. Research on the synthesis of other chiral cyclopropane-based ligands and their application in other types of asymmetric reactions is being carried out in this laboratory and will be reported in due course.

Acknowledgment

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(9) ***cis*-Cyclopropane Aminoester 7a–d; Typical Procedure**
To a solution of secondary amine (60 mmol) in MeOH (50 mL) was added 5 N HCl–MeOH (4 mL, 20 mmol), followed by **6** (3.12 g, 20 mmol) and $NaBH_3CN$ (1 g, 16 mmol). The resulting solution was stirred at r.t. for 16 h, then

concentrated HCl was added until pH <2, and the MeOH was removed in vacuo. The residue was taken up in H_2O (15 mL) and extracted with Et_2O (3 × 20 mL). The aqueous solution was brought to pH >10 with 20% aq NaOH and extracted with Et_2O (5 × 15 mL). The combined extracts were dried over $MgSO_4$ and concentrated under reduced pressure to give **7a**–**d** in 90–95% yields.

***cis*-Cyclopropane Aminoalcohol 9a–9d; Typical Procedure**

Mg (0.6 g, 25.0 mmol) and a very small amount of I_2 were added to anhyd THF (20 mL). A solution of chlorobenzene (3.14 g, 20 mmol) in THF (10 mL) was added slowly dropwise. Once the reaction began, the rest of the chlorobenzene solution was added at a rate that maintained a gentle reflux. After the addition was complete, the mixture was refluxed for 20 min then cooled to –15 °C. Compound **7** (5 mmol) was dissolved in anhyd THF (5 mL) and added to the prepared Grignard mixture. The resulting solution was stirred at r.t. for 12 h. The reaction was quenched with a sat. solution of NH_4Cl, and the mixture was extracted several times with Et_2O. The combined organic phases was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography (hexane–EtOAc, 1:2) to afford **9a** and **9b** as white crystals.

8: Oil; $[\alpha]_D^{18}$ +49.25 (*c* 0.00201, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85–0.87 (m, 1 H), 1.06 (s, 3 H), 1.06 (s, 3 H), 2.28 (s, 6 H), 2.33–2.35 (m, 2 H), 3.30–3.34 (m, 1 H), 3.83–3.85 (m, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.5, 20.4, 25.5, 29.3, 29.6, 45.0, 55.0, 59.3. HRMS (ESI): *m*/*z* calcd for $C_9H_{20}NO$ [M^+]: 158.1539; found: 158.1543.

9a: Mp 102–103 °C; $[\alpha]_D^{18}$ +63.5 (*c* 0.01021, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (s, 3 H), 0.93–0.99 (m, 1 H), 1.22 (s, 3 H), 1.75 (d, 1 H, *J* = 9.5 Hz), 2.14 (s, 6 H), 2.41–2.45 (m, 1 H), 2.62–2.66 (m, 1 H), 7.09–7.11 (m, 2 H), 7.12–7.16 (m, 4 H), 7.22–7.27 (m, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.6, 20.2, 25.9, 30.2, 38.4, 44.2, 55.0, 125.5, 125.7, 125.9, 126.0, 127.6, 127.7, 149.0, 152.0. HRMS (EI): *m*/*z* calcd for $C_{21}H_{28}NO$ [M + H^+]: 310.2165; found: 310.2164.

9b: Mp 112–113 °C; $[\alpha]_D^{18}$ +14.1 (*c* 0.01508, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (s, 1 H), 0.92–1.02 (m, 1 H), 1.22 (s, 3 H), 1.61–1.64 (m, 3 H), 1.65–1.74 (m, 3 H), 2.40–2.91 (m, 5 H), 2.93–2.95 (m, 1 H), 7.09–7.16 (m, 2 H), 7.22–7.28 (m, 4 H), 7.50–7.56 (m, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.5, 20.1, 23.3, 26.5, 30.1, 38.3, 51.3, 52.9, 125.3, 125.7, 125.9, 127.6, 127.7, 149.1, 152.1. HRMS (ESI): *m*/*z* calcd for $C_{23}H_{30}NO$ [M + H^+]: 336.2321; found: 336.2322.

9c: Crystals; mp 162–163 °C; $[\alpha]_D^{18}$ +167.6 (*c* 0.00816, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (s, 1 H), 1.00–1.05 (m, 1 H), 1.16 (s, 3 H), 1.20–1.37 (m, 4 H), 1.84 (d, 1 H, *J* = 9.0 Hz), 2.46–2.50 (m, 1 H), 2.56–2.61 (m, 1 H), 7.09–7.14 (m, 2 H), 7.23–7.27 (m, 4 H), 7.52–7.60 (m, 4 H), 7.78 (br, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.4, 20.0, 24.1, 25.1, 25.3, 30.3, 37.3, 53.5, 54.7, 125.63, 125.66, 125.74, 125.9, 127.5, 127.7 149.3, 152.0. HRMS (ESI): *m*/*z* calcd for $C_{24}H_{32}NO$ [M + H^+]: 350.2478; found: 350.2479.

9d: Crystals; mp 156–157 °C; $[\alpha]_D^{18}$ +158.5 (c 0.00928, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.94 (s, 1 H), 0.93–1.05 (m, 1 H), 1.17 (s, 3 H), 1.88 (d, 1 H, *J* = 9.0 Hz), 2.35 (br, 2 H), 2.52 (br, 2 H), 2.56–2.60 (m, 1 H), 2.65–2.69 (m, 2 H), 3.30 (br, 2 H), 3.48–3.52 (m, 2 H), 7.11–7.15 (m, 2 H), 7.24–7.27 (m, 4 H), 7.51–7.61 (m, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.3, 20.1, 24.5, 30.3, 37.1, 52.64, 54.55, 66.2, 125.5, 125.6, 125.8, 126.2, 127.7, 127.9, 148.9, 151.6. HRMS (ESI): *m*/*z* calcd for $C_{23}H_{30}NO_2$ [M + H^+]: 352.2271; found: 352.2272.

(10) **Diethylzinc Addition to Aldehydes; General Procedure**

The chiral ligand (0.1 mmol) was dissolved in hexane (3 mL), cooled to –15 °C, and diethylzinc (1.5 M toluene solution; 1.5 mL, 2.2 mmol) was injected. After the mixture was stirred for 20 min, benzaldehyde (0.1 g, 1 mmol) was added dropwise via syringe, and the mixture was stirred for the corresponding reaction time under N_2. The reaction was quenched by the addition of a sat. solution of NH_4Cl (10 mL).The mixture was then extracted with Et_2O (3 × 15 mL), the combined organic extracts were dried, concentrated in vacuo, and the crude products were purified by flash column chromatography (hexane–EtOAc). The ee values of the alcohol products were determined by HPLC on a Chiralcel OD-H column (*i*-PrOH–hexane) or by GC analysis on a chiral cyclodextrin capillary column. The absolute configuration of the major enantiomer was assigned by comparison of retention time of HPLC or GC with literature data. For literature related to HPLC or GC analysis, please see: (a) Huang, W. S.; Hu, Q. S.; Pu, L. *J. Org. Chem.* **1998**, *63*, 1364. (b) Bolm, C.; Muñiz-Fernández, K.; Seger, A.; Raabe, G.; Günther, K. *J. Org. Chem.* **1998**, *63*, 7860. (c) Nakamura, Y.; Takeuchi, S.; Okumura, K.; Ohgo, Y. *Tetrahedron* **2001**, *57*, 5565.