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NEW CHIRAL PYRROLIDINYL- AND 2-AZANORBORNYL-OXAZOLIDINE LIGANDS FOR ENANTIOSELECTIVE ADDITION OF DIETHYLZINC TO ALDEHYDES

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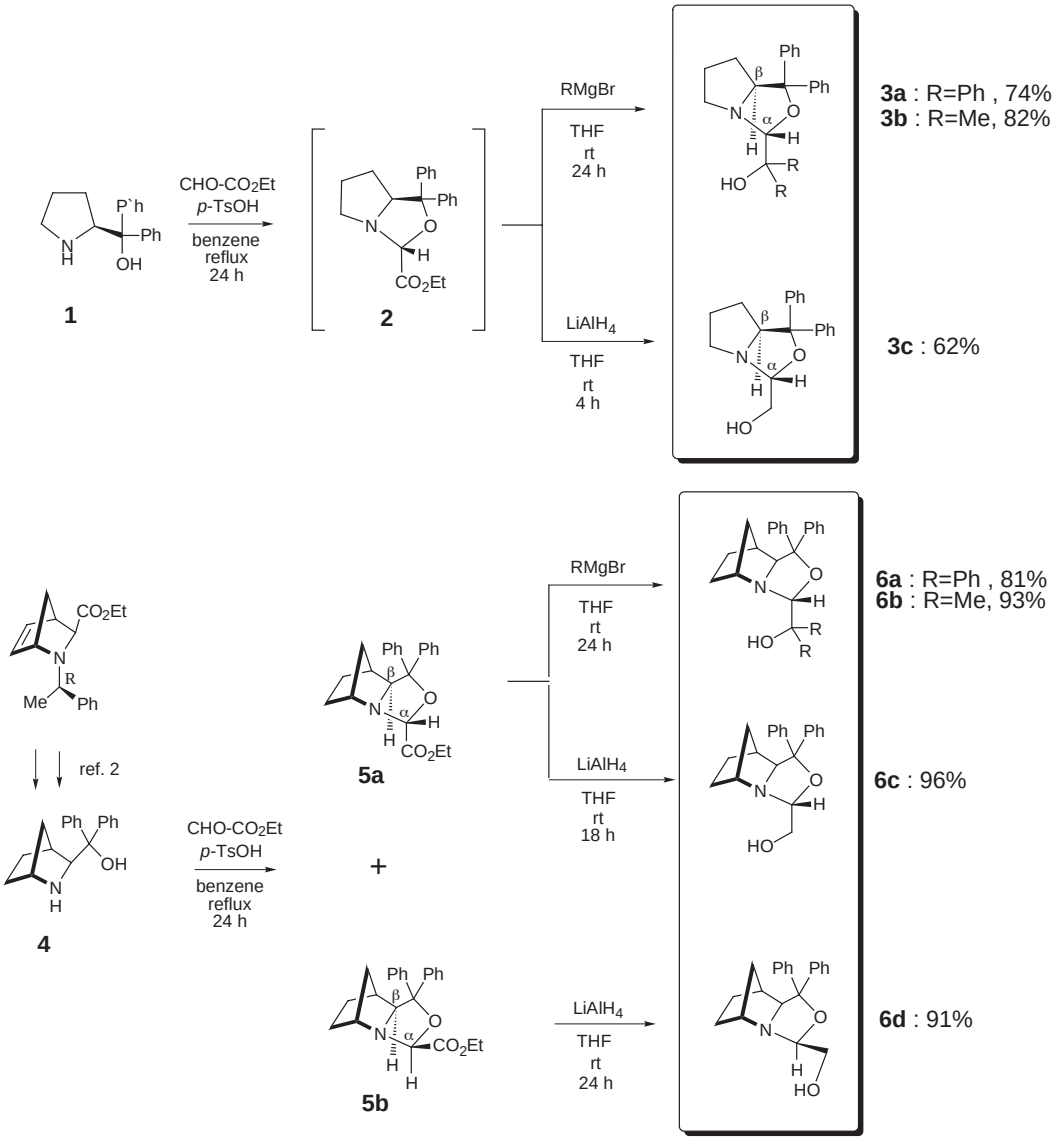
Abstract - A new type of optically active ligands, pyrrolidinyl- (**3a-c**) and 2-azanorbornyloxazolidines (**6a-d**) were synthesized and their abilities as ligands were examined in the enantioselective addition of diethylzinc to aromatic and aliphatic aldehydes to give optically active secondary alcohols of up to 83% ee.

The development of efficient enantioselective catalysts applicable to a wide range of carbon-carbon bond forming reactions represents a pivotal challenge to the synthetic community. Among the ligands, chiral β-amino alcohols have proved to be extremely efficient ligands in some catalytic reactions.[1] Most recently, oxazolidine ligands derived easily by the condensation of β-amino alcohols and aldehydes have been shown to be effective ligands to some catalytic asymmetric reactions by our group and others. [2] In this report, we wish to demonstrate the synthesis of seven kinds of new chiral pyrrolidinyl- and 2-azanorbornane[3]-based oxazolidine type ligands (**3a-c** and **6a-d**) derived from pyrrolidinylmethanol and 2-azanorbornylmethanol, respectively, followed by the application to the enantioselective addition of diethylzinc to aldehydes.[4,5]

The chiral ligands (**3a-c**) were synthesized in two steps as shown in Scheme 1. Thus, a mixture of commercially available **1** and ethyl glyoxylaldehyde in benzene was heated to reflux with azeotropic removal of water. After removal of benzene, resulting oxazolidine ester (**2**) was directly treated with phenylmagnesium bromide, methylmagnesium bromide, or lithium aluminum hydride, respectively, to

* Dedicated to Professor James P. Kutney on the occasion of his 70th birthday.

give the corresponding chiral ligands (**3a-c**) in 74, 82, and 62% yields. The products of the corresponding diastereomers at the α-position of **3a-c** could not be confirmed in these reactions. The chiral ligands (**6a-d**) also were prepared efficiently as follows. The precursors (**5a** and **5b**) of the chiral ligands (**6a-d**) were readily synthesized in almost quantitative yields as a diastereomeric mixture (**5a** :



Scheme 1

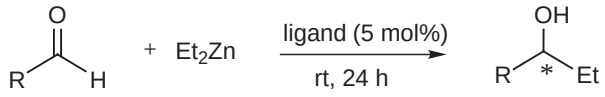
48%, **5b** : 52%) by the condensation of 2-azanorbornylmethanol (**4**) with ethyl glyoxylaldehyde in refluxing benzene using a Dean-Stark apparatus. Diastereomerically pure compounds (**5a** and **5b**) were isolated from the mixture by column chromatography easily. The treatments of **5a** with phenylmagnesium bromide or methylmagnesium bromide gave the corresponding chiral ligands (**6a**) and (**6b**), respectively, in 81 and 93% yields. In addition, the chiral ligand (**6c**) having a hydroxymethyl

substituent was obtained by the reduction of **5a** with lithium aluminum hydride in 96% yield. Furthermore, the diastereomeric ligand (**6d**) of **6c** was also made from **5b** using the above same manner in 91% yield. The stereochemistry of the newly stereogenic center at the α-position of the oxazolidine ring in **3a-c** and **6a-d** was determined by the NOE measurement of ^{1}H-NMR spectra for **3a-c**, **5a,** and **5b**. Thus, the NOE experiment for **5b** confirmed an interaction between the hydrogen at the α-position and the hydrogen at the β-position. However, both **5a** and **3c** did not have the interaction between the hydrogens at the same positions (α- and β-positions).

We first examined the enantioselective addition of diethylzinc to benzaldehyde as a substrate with 5 mol% of the chiral ligands (**3a-c** and **6a-d**). The results were summarized in Table 1. The chiral ligand (**3a**) having the bulky *gem*-diphenyl groups afforded a low chemical yield (37%) and an

Table 1

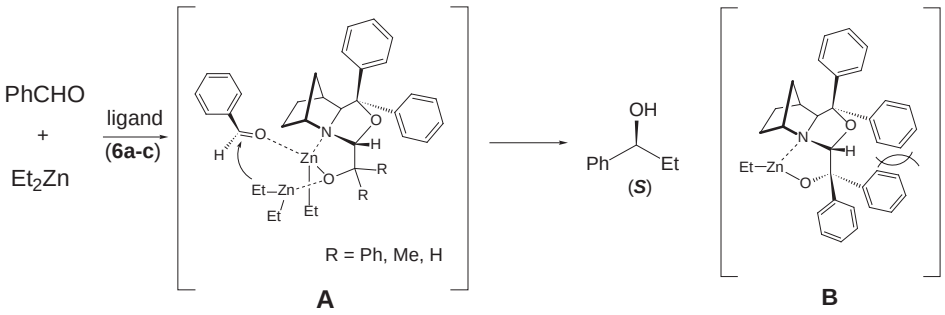
Enantioselective addition of diethylzinc to aldehydes using chiral ligans (**3a-c** and **6a-d**)



entry[a]	aldehyde/R	ligand	yield (%)[b]	ee (%)	config.
1	benzaldehyde	**3a**	37	14	*S*[f]
2	benzaldehyde	**3b**	69	15	*S*
3	benzaldehyde	**3c**	84	40	*S*
4	benzaldehyde	**6a**	50	18	*S*
5	benzaldehyde	**6b**	63	44	*S*
6	benzaldehyde	**6c**	89	83	*S*
7	benzaldehyde	**6d**	50	7	*S*
8	2-naphthylaldehyde	**6c**	89	56[c]	*S*[g]
9	2-Ethoxybenzaldehyde	**6c**	70	63[d]	*S*[h]
10	2-Bromobenzaldehyde	**6c**	60	64[d]	*S*[g]
11	(*E*)-cinnamaldehyde	**6c**	32	24[c]	*S*[f]
12	octylaldehyde	**6c**	40	36[e]	*S*[e]

[a]All reactions were carried out in toluene-hexane (1:1) at room temperature. [b]Isolated yield. [c]Determined by HPLC analysis using Chiralcel OD. [d]Determined by HPLC analysis using Chiralcel OB. [e]Determined by the specific rotation value. Ref. 5f. [f]Ref. 5a. [g]Ref. 5c. [h]Ref. 5b.

enantiomeric excess (14% ee)(entry 1). Furthermore, the chiral ligand (**3b**) did not also afford a good result (69%, 15% ee)(entry 2). Although the chiral ligand (**3c**), less sterically crowded, gave a good chemical yield (84%), the enantiomeric excess was low (40% ee)(entry 3). Next, we examined the same reaction using 2-azanorbornane-based chiral ligands (**6a-d**). As the results, the chiral ligand (**6a**) gave a moderate chemical yield (50%) and a low enantiomeric excess (18% ee) similarly to the result of **3a** (entry 4). Although the chiral ligand (**6b**) afforded a little bit better result than **6a**, that was not a satisfactory result (63%, 44% ee)(entry 5). However, the chiral ligand (**6c**), less sterically crowded, worked as an effective ligand to this reaction in comparison with the chiral ligands (**6a**) and (**6b**) to give the desired alcohol in 89% yield and 83% ee (entry 6). Considering this result using **6c**, we tested the effectiveness of the chiral ligand (**6d**). Unfortunately, a good result was not obtained by using this ligand (**6d**) (entry 7). Next, this enantioselective addition of diethylzinc to some kinds of aromatic and aliphatic aldehydes using the chiral ligand (**6c**) was examined. These results are summarized in Table 1. The reaction of *β*-naphthylaldehyde with diethylzinc using the chiral ligand (**6c**) under the above same reaction conditions (entries 1-7) was performed to give optically active 1-(2-naphthyl)-1-propanol in 89% yield and 56% ee (entry 8). Furthermore, when 2-ethoxybenzaldehyde was used as a substrate, a good chemical yield and moderate enantioselectivity (70%, 63% ee) were obtained to give (*S*)-1-(2-ethoxyphenyl)-1-propanol (entry 9). In addition, the ethylation of 2-bromobenzaldehyde also afforded a moderate result (60%, 64% ee)(entry 10). However, the reactions of cinnamaldehyde and octylaldehyde, respectiveiy, did not give the satisfactory results (32%, 24% ee and 40%, 36% ee)(entries 11 and 12). From these results, this reaction may proceed assuming that **A** is a possible transition state involved in the addition reaction using the chiral ligands (**6a-c**) as shown in Scheme 2. Furthermore, the less activity of catalysts (**6a** and **6b**) may be explained using the chiral ligand (**6a**) and Et_2Zn (**B**). Thus, when R is a



Scheme 2

large group (phenyl), the formation from the ligand (**6a**) and Et_2Zn to **6a**-Et_2Zn could be hard due to the steric interaction between the phenyl group at the side chain of oxazolidine ring and the phenyl group at oxazolidine ring. From the reason, the chiral ligands (**6a**) and **6b**) sterically crowded may not give the satisfactory chemical yield and enantiomeric excess in comparison with less sterically crowded **6c**.

As the conclusion, we have prepared seven kinds of new chiral ligands (**3a-c** and **6a-d**). These worked as the ligand for the enantioselective addition of diethylzinc to aromatic and aliphatic aldehydes. Particularly, the chiral ligand (**6c**) was a good and effective ligand for the reaction.

EXPERIMENTAL

General. IR spectra were measured with a PERKIN ELMER 1725X spectrophotometer. ^{1}H-NMR spectra were recorded on a JEOL JNM-GSX 270, a JEOL JNM-LA 400 and 600 spectrometers with TMS as an internal standard. MS were taken on a Hitachi RMG-6MG and a JEOL-JNM-DX 303 spectrometers. Optical rotations were measured with a JASCO-DIP-370 digital polarimeter. Diethylzinc in hexane was obtained from Kanto Chemical Co.

(2*R*,5*S*)-2-Diphenylhydroxymethyl-4,4-diphenyl-3-oxa-1-azabicyclo[3.3.0]octane (3a)

Compound (**1**)(100 mg, 0.39 mmol), ethyl glyoxylaldehyde (56 mg, 0.47 mmol), benzene (10 mL), and *p*-toluenesulfonic acid (10 mg) were placed in a flask equipped with a Dean-Stark trap. The mixture was refluxed for 24 h. The solution was cooled and the solvent was removed. The residue was used for the next steps without further purifications Thus, the obtained crude product (**2**) [(2*R*, 5*S*)-2-ethoxycarbonyl-4,4-diphenyl-3-oxa-1-azabicyclo[3.3.0]octane] decomposed on chromatography using sillica gel or alumina. Phenylmagnesium bromide (0.35 g, 1.19 mmol) in THF (1.1 mL) was added to a THF (5 mL) solution of the crude product (**2**) (135 mg). The mixture was stirred at rt for 24 h. Saturated aqueous ammonium chloride was added to quench the reaction. After extraction with chloroform, the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*, and the residue was chromatographed on a silica gel column eluted with ether-hexane (1:4) to give **3a** (134 mg, 74%) as an oil, $[\alpha]_D^{23}$= -144.3° (c=2.0, $CHCl_3$), IR (KBr) cm^{-1} : 3162. ^{1}H-NMR($CDCl_3$) δ : 7.58 (m, 2H), 7.51 (m,

2H), 7.35-7.10 (m, 16H), 5.73 (s, 1H), 3.88 (dd, J=5.28, 7.09 Hz, 1H), 3.63 (br s, 1H), 2.71 (m, 1H), 2.40 (m, 1H), 1.88 (m, 1H), 1.68 (m, 1H), 1.50 (m, 1H), 1.13 (m, 1H). *Anal.* Calcd for $C_{31}H_{29}NO_2$: C, 83.19; H, 6.53; N, 3.13. Found: C, 83.25, H, 6.34, N, 2.98. MS m/z: 447 (M^+).

(2*R*, 5*S*)-2-Dimethylhydroxymethyl-4,4-diphenyl-3-oxa-1-azabicyclo[3.3.0]octane (3b)

Methylmagnesium bromide (0.14 g, 1.19 mmol) in THF (1.2 mL) was added to a THF (5 mL) solution of the crude product (**2**) (135 mg). The mixture was stirred at rt for 24 h. Saturated aqueous ammonium chloride was added to quench the reaction. After extraction with chloroform, the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed on a silica gel column eluted with ether-hexane (1:4) to give **3b** (106 mg, 82%) as an oil, $[\alpha]_D^{23}$= -165.5°(c=2.0, $CHCl_3$). IR (KBr) cm^{-1} : 3160. ^{1}H-NMR ($CDCl_3$) δ : 7.41 (m, 2H), 7.34-7.13 (m, 8H), 4.75 (s, 1H), 4.28 (dd, J=7.40, 4.30 Hz, 1H), 3.13-3.04 (m, 1H), 2.73 (m, 1H), 2.04 (m, 1H), 1.87 (m, 1H), 1.67 (m, 1H), 1.19 (s, 3H). 1.18 (m, 1H), 1.17 (m, 1H). *Anal.* Calcd for $C_{21}H_{25}NO_2$: C, 77.98; H, 7.79; N, 4.33. Found: C, 78.11, H, 7.55, N, 4.16. MS m/z : 323(M^+).

(2*R*, 5*S*)-2-Hydroxymethyl-4,4-diphenyl-3-oxa-1-azabicyclo[3.3.0]octane (3c)

To a solution of **2** (135 mg) in dry THF (5 mL) at 0 °C, lithium aluminum hydride (27 mg, 0.7 mmol) in dry THF (5 mL) was added. The mixture was stirred at rt for 4 h, quenched by addition to water, and filterated through celite 545. The filtrate was dried ($MgSO_4$) and concentrated *in vacuo* to afford the residue. The residue was chromatographed on a silica gel column (ether) to give **3c** (74 mg, 62%) as colorless prisms (ether). mp 109-110 °C, $[\alpha]_D^{23}$= -227.0° (c=2.0, $CHCl_3$). IR (film) cm^{-1}: 3611. ^{1}H-NMR ($CDCl_3$) δ: 7.48 (br s, 2H), 7.36-7.15 (m, 8H), 4.87 (t, J=5.12 Hz, 1H), 4.39 (t, J=6.59 Hz, 1H), 3.34 (d, J=5.37, 2H), 3.14 (m, 1H), 2.86 (m, 1H), 1.83 (m, 1H), 1.76-1.42 (m, 3H). *Anal.* Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.52, H, 6.97, N, 4.48. MS m/z: 295 (M^+).

(1*R*,3*R*,6*S*,7*S*)-3-Ethoxycarbonyl-5,5-diphenyl-4-oxa-2-azatricyclo[5.2.1.0^{2,6}]decane (5a) and (1*R*,3*S*,6*S*,7*S*)-3-Ethoxycarbonyl-5,5-diphenyl-4-oxa-2-azatricyclo[5.2.1.0^{2,6}]decane (5b)

Compound (**4**) (100 mg, 0.36 mmol), ethyl glyoxylaldehyde (44 mg, 0.43 mmol) and benzene (15 mL) were placed in a flask equipped with a Dean-Stark trap. The mixture was refluxed for 24 h. The solution was cooled and the solvent was removed. The residue was purified by preparative TLC (ether : hexane = 1:2) to give the desired products (**5a** and **5b**). **5a** : 63 mg (48%). Colorless prisms, mp 118-120 °C (ether), $[\alpha]_D^{23}$= -208.3° (c=2.0, $CHCl_3$). IR (film) cm^{-1}: 3615. ^{1}H-NMR ($CDCl_3$) δ : 7.46 (m, 2H), 7.36-7.15 (m, 8H), 5.01 (s, 1H), 3.83-3.61(m, 2H), 3.46 (br s, 1H), 1.82-1.56 (m, 2H), 1.50-1.39 (m, 4H), 0.98 (t, J=7.0 Hz, 3H), 0.88 (d, J=10.1 Hz, 1H), *Anal.* Calcd for $C_{23}H_{25}NO_3$: C, 76.00; H, 6.93; N, 3.85. Found: C, 76.27, H, 6.67, N, 3.59. MS m/z: 363 (M^+).

5b : as an oil, 68 mg (52 %), $[\alpha]_D^{23}$= -156.4° (c=2.0, $CHCl_3$). IR (film) cm^{-1}: 3615. ^{1}H-NMR ($CDCl_3$) δ : 7.52-7.43 (m, 4H), 7.34-7.18 (m, 6H), 4.81(s, 1H), 4.43-4.24 (m, 2H), 4.04 (s, 1H), 3.29 (br s, 1H), 1.80 (m, 2H), 1.64-1.26 (m, 3H), 0.82 (d, J=9.1 Hz, 1H), MS m/z: 363 (M^+). HRMS found :363.1794; Calcd for $C_{23}H_{25}NO_3$: 363.1834.

(1*R*,3*R*,6*S*,7*S*)-3-Diphenylhydroxymethyl-5,5-diphenyl-4-oxa-2-azatricyclo[5.2.1.0^{2,6}]decane (6a)

Phenylmagnesium bromide (108 mg, 0.55 mmol) in THF (0.5 mL) was added to a THF (0.8 mL) solution of **5a** (100 mg, 0.28 mmol) and the mixture was stirred at rt for 24 h. Saturated aqueous ammonium chloride was added to quench the reaction. After extraction with chloroform, the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*, and the residue was chromatographed on a silica gel column eluted with ether-hexane (1:4) to give **6a,** 105 mg (81%), as colorless prisms (ether). mp 59-60 °C, $[\alpha]_D^{23}$= -143.4°(c=2.2, $CHCl_3$). IR (film) cm^{-1}: 3611. ^{1}H-NMR ($CDCl_3$) δ: 7.73 (d, J=8.5 Hz, 2H), 7.55 (d, J=8.5, 2H), 7.44 (d, J=7.25, 2H), 7.38-7.09 (m, 14H), 5.43 (s, 1H), 4.19 (br s, 1H), 3.86 (s, 1H), 2.52 (d, J=3.6 Hz, 1H), 2.10 (br s, 1H), 1.54-1.16 (m, 4H), 0.70 (d, J=10.4 Hz, 1H), 0.56 (d, J=10.4, 1H). *Anal.* Calcd for $C_{33}H_{31}NO_2$: C, 83.69; H, 6.60; N, 2.96. Found: C, 83.97, H, 6.42, N, 2.69. MS m/z: 290 [M^+(473)-183].

(1*R*,3*R*,6*S*,7*S*)-3-Dimethylhydroxymethyl-5,5-diphenyl-4-oxa-2-azatricyclo[5.2.1.0^{2,6}]decane (6b)

Methylmagnesium bromide (75 mg, 0.6 mmol) in THF (0.6 mL) was added to a THF (0.8 mL) solution of **5a** (100 mg, 0.28 mmol) and the mixture was stirred at rt for 24 h. Saturated aqueous ammonium

chloride was added to quench the reaction. After extraction with chloroform, the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*, and the residue was chromatographed on a silica gel column eluted with ether-hexane (1:4) to give **6b,** 96 mg (93%) as colorless prisms (ether - hexane). mp 122-124 °C, $[\alpha]_D^{23}$= -127.5° (c=2.1,$CHCl_3$). IR (film)cm^{-1}: 3611. ^{1}H-NMR ($CDCl_3$) δ: 7.46 (m, 2H), 7.35 (m, 2H), 7.30-7.12 (m, 6H), 4.43 (s, 1H), 3.88 (s, 1H), 3.12 (br s, 1H), 2.49 (br s, 2H), 1.60-1.39 (m, 4H), 1.26 (s, 3H), 1.23 (s, 3H), 1.13 (d, J=7.1 Hz, 1H), 0.75 (d, J=7.1, 1H). *Anal.* Calcd for $C_{23}H_{27}NO_2$: C, 79.05; H, 7.79; N, 4.01. Found: C, 79.31, H, 7.57, N, 3.87. MS m/z: 290 [M^+(349)-59].

(1*R*,3*R*,6*S*,7*S*)-3-Hydroxymethyl-5,5-diphenyl-4-oxa-2-azatricyclo[5.2.1.$0^{2,6}$]decane (6c)

To a stirred suspension of lithium aluminum hydride (10 mg, 0.26 mmol) in dry THF (15 mL) was added a solution of **5a** (80 mg, 0.22 mmol) in dry THF (15 mL) at 0 °C. The mixture was stirred at rt for 18 h, quenched by addition to water, and filtrated through celite 545. The filtrate was dried ($MgSO_4$) and concentrated *in vacuo* to afford the residue. The residue was chromatographed on a silica gel column (ether : hexane = 2:1) to give **6c** (68 mg, 96%) as colorless prisms, mp 166-168 °C (ether), $[\alpha]_D^{23}$= -165.2° (c=1.6, $CHCl_3$). IR (film) cm^{-1}: 3617. ^{1}H-NMR ($CDCl_3$) δ: 7.51-7.46 (m, 2H), 7.36-7.12 (m, 8H), 4.79 (t, J=6.3 Hz, 1H), 4.03 (s, 1H), 3.28 (br s, 1H), 3.13 (dd, J=11.1, 5.94 Hz, 1H), 2.98 (dd, J=11.1, 6.6 Hz, 1H), 1.95 (br s, 1H), 1.65-1.21 (m, 5H), 0.83 (d, J=8.7 Hz, 1H). *Anal.* Calcd for $C_{21}H_{23}NO_2$: C, 78.47; H, 7.21; N, 4.36. Found: C, 78.65, H, 6.99, N, 4.11. MS m/z: 321 (M^+).

(1*R*,3*S*,6*S*,7*S*)-3-Hydroxymethyl-5,5-diphenyl-4-oxa-2-azatricyclo[5.2.1.$0^{2,6}$]decane (6d)

To a stirred suspension of lithium aluminum hydride (10 mg, 0.26 mmol) in dry THF (15 mL) was added a solution of **5b** (80 mg, 0.22 mmol) in dry THF (15 mL) at 0 °C. The mixture was stirred at rt for 24 h, quenched by addition to water, and filterated through celite 545. The filtrate was dried ($MgSO_4$) and concentrated *in vacuo* to afford the residue. The residue was chromatographed on a silica gel column (ether : hexane = 2:1) to give **6d** (62 mg, 91%) as colorless prisms. mp 168-170 °C (ether), $[\alpha]_D^{23}$= -243.6° (c=2.2, $CHCl_3$). IR (film) cm^{-1}: 3614. ^{1}H-NMR ($CDCl_3$) δ: 7.49 (m, 2H), 7.36-7.26 (m, 8H), 4.49 (br s, 1H), 4.03 (m, 3H), 3.57 (br s, 3H), 1.94-1.84 (m, 2H), 1.58-1.26 (m, 5H), 0.83 (d, J=9.0 Hz, 1H). *Anal.* Calcd for $C_{21}H_{23}NO_2$: C, 78.47; H, 7.21; N, 4.36. Found: C, 78.68, H, 7.03, N,

4.19. MS m/z: 321 (M^+).

General procedure for the enantioselective alkylation of aldehydes with Et_2Zn

To a solution of chiral ligands [**3a-c, 6a-d** (0.0175 mmol)] in toluene (0.7 mL), diethylzinc (0.7 mmol, 0.7 mL of 1 M solution in hexane) was added at rt. After the mixture had been stirred at rt for 30 min, aldehydes (0.35 mmol) were introduced. The homogeneous solution was stirred for 7 h at rt and quenched with 10% HCl. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layers were dried ($MgSO_4$) and then evaporated under reduced pressure. The residue was purified by preparative TLC over silica gel to afford the corresponding chiral alcohols, respectively.

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