Catalytic Asymmetric Addition of Diethylzinc to Benzaldehyde Using α-Pinene-Derived Ligands

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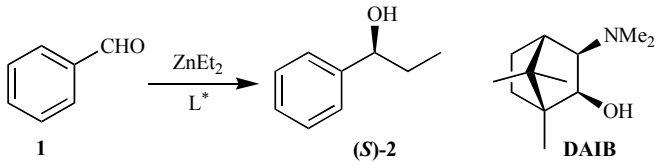
Abstract: The amines obtained from α-pinene and containing a phenol or pyridine fragment can be used as ligands in the asymmetric addition of diethylzinc to aromatic aldehydes; the enantiomeric excess (*ee*) was up to 80%. The enantioselectivity of the reaction is not very sensitive to the nature of substituents in the aromatic ring of aldehydes.

Keywords: Diethylzinc, benzaldehyde, asymmetric addition, α-pinene, ligand.

INTRODUCTION

The enantioselective addition of organozinc reagents to aldehydes is one of the most effective methods for the synthesis of optically active secondary alcohols [1, 2]. The first highly enantioselective ligand for the addition of diethylzinc to aromatic aldehydes was (−)-3-*exo*-(dimethylamino)isoborneol (DAIB) obtained from camphor. The interaction of diethylzinc with benzaldehyde **1** in the presence of DAIB led to the formation of (*S*)-1-phenyl-1-propanol **2** with high *ee* up to 99% (Scheme **1**) [3]. A search for other ligands for the catalytic addition of diethylzinc to aldehydes was stimulated by the necessity to find new accessible ligands and the far lower accessibility of the second DAIB enantiomer because (-)-camphor is over 150 times more expensive than naturally occurring (+)-camphor [4].



Scheme 1.

The ligands synthesized from monoterpenoids of the *para*-menthane [5-7] and carane series [6, 8] were also successfully used for the addition of diethylzinc to aromatic aldehydes. In recent decades, the attention of chemists engaged in the synthesis of chiral ligands was attracted by compounds with a pinane framework, namely, α- (**3**) and β-(**4**)-pinenes (Fig. **1**) and their derivatives [4, 9-13]. This was due to the significant steric hindrances created by the gem-dimethyl group of the cyclobutane ring of pinenes and comparable accessibility of the two enantiomers of α-pinene, which makes it possible to obtain both optical isomers of the desired secondary alcohols. Compounds **5**-**7** synthesized from (-)-α-pinene (-)-**3** proved to be quite effective ligands for the addition of $ZnEt_2$ to benzaldehyde, which yielded compound **2** with *ee* from 40 to 62% [10]. Curiously, the major product was the (*R*)-**2** when amino alcohols **5** and **6** were used, but the (*S*)-enantiomer was formed when **7** was used.

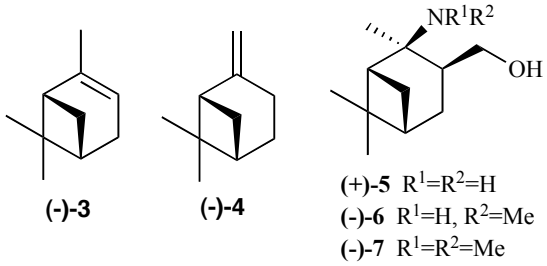


Fig. (1).

Recently, we showed that Schiff bases **8a**, **b** obtained from amino alcohol (-)-**5** and amino alcohols **9a**, **b** synthesized from **8a**, **b** (Fig. **2**) could be used as ligands in the vanadium-catalyzed asymmetric oxidation of sulfides into optically active sulfoxides [14-17].

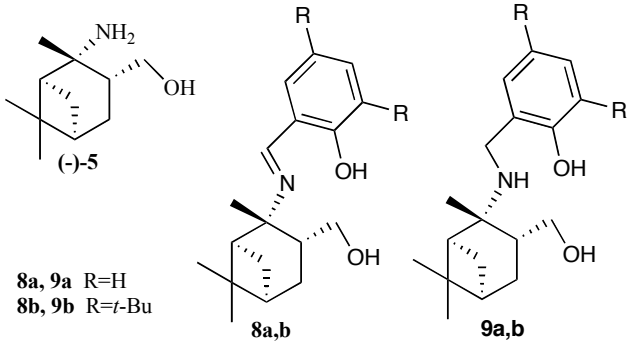


Fig. (2).

The goal of this work was to study the possibility of using compounds of the type of **9** as ligands for the asymmetric addition of $ZnEt_2$ to benzaldehyde.

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EXPERIMENTAL SECTION

Reagents and solvents were purchased from commercial suppliers and used as received. Dry solvents were obtained according to the standard procedures. GC: *7820A* gas chromatograph (Agilent Tech., USA); flame-ionization detector; HP-5 capillary column (0.25 mm Ø × 30 m × 0.25 μm), He as carrier gas (flow rate 2 ml/min, flow division 99 : 1). Chirospecific GC-MS: *6890N* gas chromatograph (Agilent Tech., USA); *5973 INERT* mass-selective detector (Agilent Tech., USA); Cyclosil-B capillary column (0.32 mm Ø × 30 m × 0.25 μm, Agilent Tech., USA); the temperature of the column thermostat was 50 ºC / 2 min; temperature gradient from 2 ºC/min to 220 ºC/5 min; evaporator and interface temperature 250 ºC; He as carrier gas (flow rate 2 mL/min, flow division 99 : 1); sweep from m/z 29 to m/z 500; 1 μl sample. Optical rotation: *polAAr 3005* spectrometer; $CHCl_3$ soln. ^{1}H- and ^{13}C-NMR Spectra: *Bruker DRX-500* apparatus at 500.13 MHz (^{1}H) and 125.76 MHz (^{13}C) in $CCl_4/CDCl_3$ 1:1 (v/v); chemical shifts δ in ppm rel. to residual $CHCl_3$ [δ(H) 7.24 ppm] and $CDCl_3$ [δ(C) 76.90 ppm], *J* in Hz. The structure of the products was determined by analyzing the ^{1}H- and ^{13}C-NMR spectra, ^{1}H,^{1}H double-resonance spectra and ^{13}C,^{1}H-type 2D-COSY (*J*(C,H) = 160 Hz). HR-MS: *DFS Thermo Scientific* spectrometer in a full scan mode (0-500 *m/z*, 70 eV electron impact ionization, direct sample administration). Column chromatography (CC) was performed on silica gel (60-200 μ, Macherey-Nagel).

The geometrical parameters of the conformers of compound **12** were optimized by DFT (PBE functional [18], L1 basis (Λ01 [19], cc-pVDZ analog) using the PRIRODA program [20, 21]). The chemical shifts were calculated by GIAO/DFT/PBE in the L22 basis (Λ22, cc-pCVTZ analog) using the PRIRODA program. For quantum chemical calculations, we used the cluster of the Information Computation Center, Novosibirsk State University.

((1*S*,2*S*,3*R*,5*S*)-2-Amino-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)methanol (-)-**5** was obtained from (+)-α-pinene (+)-**3** (Aldrich) according to previously described methods [14].

*Reaction of compound (-)-**5** with picolinealdehyde **11***. Compound (-)-**5** (80 mg, 0.44 mmol) was dissolved in absolute methanol (4 ml), and picolinealdehyde **11** (42 mg, 0.39 mmol) in methanol (5 ml) was added while stirring. The reaction mixture was stirred at r.t. for 2 days. The solvent was distilled off and the residue was recrystallized from diethyl ether. This gave (2*S*,4a*R*,6*S*,8*S*,8a*S*)-7,7,8a-trimethyl-2-pyridin-2-yloctahydro-2*H*-6,8-methano-3,1-benzoxazine **12** (104 mg, 97%), $[\alpha]_D^{24}$ = -31.25 (*c* 0.16, $CHCl_3$). ^{1}H NMR, δ, ppm (*J*, Hz): 1.03 (s, 3H, C(9)Me), 1.23 (s, 3H, C(10)Me), 1.27-1.33 (m, 1H, H(5an)), 1.33 (d, 1H, H(7an), $J_{7an,7syn}$ = 10.5), 1.38 (s, 3H, C(8)Me), 1.87 (m, 1H, H(6)), 1.90 (d.d, 1H, H(2), $J_{2,7syn}$ = 6.0, $J_{2,6}$ = 5.5), 1.90-1.96 (m, 1H, H(5syn)), 1.98-2.05 (m, 1H, H(4)), 2.23 (d.d.d.d, 1H, H(7syn), $J_{7syn,7an}$ = 10.5, $J_{7syn,2}$ = $J_{7syn,6}$ = 6.0, $J_{7syn,5syn}$ = 2.2), 3.53 (d.d, 1H, H(11), $J_{11,11'}$ = 10.3, $J_{11,4}$ = 8.8), 3.66 (d.d, 1H, H(11'), $J_{11',11}$ = 10.3, $J_{11',4}$ = 6.2), 5.49 (s, 1H, H(12)), 7.14 (d.d.d, 1H, H(16), $J_{16,17}$ = 7.6, $J_{16,15}$ = 4.7, $J_{16,18}$ = 0.5), 7.28 (d.d.d, 1H, H(18), $J_{18,17}$ = 7.6, $J_{18,15}$ = 0.8, $J_{18,16}$ = 0.5), 7.59 (d.d.d, 1H, H(17), $J_{17,16}$ = $J_{17,18}$ = 7.6, $J_{17,15}$ = 1.8), 8.48 (d.d.d, 1H, H(15), $J_{15,16}$ = 4.7, $J_{15,17}$ = 1.8, $J_{15,18}$ = 0.8). ^{13}C NMR, δ, ppm: 38.95 (s, C(1)), 53.85 (d, C(2)), 53.88 (s, C(3)), 35.12 (d, C(4)), 30.40 (t, C(5)), 40.28 (d, C(6)), 27.72 (t, C(7)), 27.02 (q, C(8)), 23.89 (q, C(9)), 28.07 (q, C(10)), 66.10 (t, C(11)), 82.46 (d, C(12)), 158.56 (s, C(13)), 148.72 (d, C(15)), 123.05 (d, C(16)), 136.36 (d, C(17)), 121.95 (d, C(18)). Found: *m/z* 271.1806 $[M-H]^+$. $C_{17}H_{23}N_2O$. Calculated: M = 271.1805.

The absolute configuration at the C^{12} atom of **12** as (*S*) was determined by a comparison of the experimental proton chemical shifts in the ^{1}H NMR spectrum of this compound with the chemical shifts of diastereomers (12*R*)-**12** and (12*S*)-**12** calculated by the GIAO technique. The conformation analysis of these diastereomers, carried out by a procedure described in [22], showed that the most stable conformer was dominant (87 and 76%, respectively according to Boltzmann distribution at 298 K based on calculated energies) for each of them; therefore only these conformers were taken for comparison (Fig. **3**).[1]

A comparison of the spectra (Fig. **3**) shows that the best agreement between the calculated and experimental chemical shifts is observed for diastereomer (12*S*)-**12**. In the case of (12*R*)-**12**, the considerable difference between the experimental and calculated shifts shows itself for one of the C^{7}H$_2$ protons and one proton of the C^{11}H$_2$ group, experiencing the deshielding effect of the heteroaromatic ring. One of the characteristic signals is the signal of the C^{8}H$_3$ group, which is considerably shifted upfield for (12*R*)-**12**. This is not observed in the experimental or calculated spectrum of (12*S*)-**12**.

The calculated formation energy of diastereomer (12*S*)-**12** is much (3.4 kcal/mol) lower than the energy of the (12*R*)-isomer, which probably explains its formation as the sole reaction product if the reaction way is determined by thermodynamic control.

Reduction of **12**. Compound **12** (75 mg, 0.28 mmol) was dissolved in absolute methanol (20 ml), and $NaBH_4$ (85 mg, 2.24 mmol) was added with stirring. The reaction mixture was stirred for 1 h. The solvent was distilled off. Diethyl ether and then water were added. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organic extracts were dried over $MgSO_4$. This procedure gave ((1*S*,2*S*,3*R*,5*S*)-2,6,6-trimethyl-2-(pyridin-2-ylmethylamino)bicyclo[3.1.1]heptan-3-yl)methanol **10** (77 mg, 47%), $[\alpha]_D^{24}$ = -9.02 (*c* 1.21, $CHCl_3$). ^{1}H NMR, δ, ppm (*J*, Hz): 1.05 (s, 3H, C(9)Me), 1.19 (d, 1H, H(7an), $J_{7an,7syn}$ = 10.2), 1.26 (s, 3H, C(10)Me), 1.35 (s, 3H, C(8)Me), 1.45-1.51 (m, 1H, H(5an)), 1.88-1.96 (m, 2H, H(5syn), H(6)), 2.10 (d.d, 1H, H(2), $J_{2,7syn}$ = 6.0, $J_{2,6}$ = 5.1), 2.15 (d.d.d.d, 1H, H(7syn), $J_{7syn,7an}$ = 10.2, $J_{7syn,2}$ = $J_{7syn,6}$ = 6.0, $J_{7syn,5syn}$ = 2.3), 2.19-2.26 (m, 1H, H(4syn)), 3.52 (d.d, 1H, H(11), $J_{11,11'}$ = 11.7, $J_{11,4}$ = 8.9), 3.65 (d.d, 1H, H(11'), $J_{11',11}$ = 11.7, $J_{11',4}$ = 4.6), 3.66 (d, 1H, H(12), $J_{12,12'}$ = 13.2) and 3.77 (d, 1H, H(12'), $J_{12',12}$ = 13.2) - AB system, 7.10 (d.d.d, 1H, H(16), $J_{16,17}$ = 7.7, $J_{16,15}$ = 4.8, $J_{16,18}$ = 0.6), 7.20 (br.d, 1H, H(18), $J_{18,17}$ = 7.7), 7.58 (d.d.d, 1H, H(17), $J_{17,16}$ =

[1]The spatial structures of all the conformers are given at http://limor1.nioch.nsc.ru/quant/conformers/Zn.

$J_{17,18}$ = 7.7, $J_{17,15}$ = 1.8), 8.48 (d.d.d, 1H, H(15), $J_{15,16}$ = 4.8, $J_{15,17}$ = 1.8, $J_{15,18}$ = 0.9). ^{13}C NMR, δ, ppm: 38.39 (s, C(1)), 50.62 (d, C(2)), 59.29 (s, C(3)), 41.02 (d, C(4)), 29.88 (t, C(5)), 40.24 (d, C(6)), 27.85 (t, C(7)), 27.71 (q, C(8)), 23.85 (q, C(9)), 28.43 (q, C(10)), 65.47 (t, C(11)), 47.28 (t, C(12)), 159.51 (s, C(13)), 149.13 (d, C(15)), 121.83 (d, C(16)), 136.29 (d, C(17)), 122.08 (d, C(18)). Found: *m/z* 274.2024 $[M]^+$. $C_{17}H_{26}N_2O$. Calculated: M = 274.2040.

General procedure for addition of diethylzinc to benzaldehyde. A 1 M solution of $ZnEt_2$ (3.33 ml, 3.33 mmol) in hexane (Acros) was added slowly to a solution of the ligand (0.3 mmol) in dry hexane (20 ml). The resulting solution was stirred at r.t. for 20 min. The solution was then cooled to 0 ºC, and benzaldehyde **1** (320 mg, 3 mmol) was added dropwise. The reaction mixture was kept at 0 ºC for 20 h. Then a saturated solution of NH_4Cl was added, and the mixture was stirred for 15 min. The organic layer was separated, and the aqueous phase was extracted with Et_2O. The combined organic layers were dried over Na_2SO_4. The solvent was distilled off, and the residue was purified by column chromatography on SiO_2 (EtOAc gradient in hexane from 10 to 50% as eluent). The enantiomeric excess (*ee*) in 1-phenylpropan-1-ol **2** was determined by GLC-MS on a column with a chiral stationary phase. The results are listed in the Table **1**.

Addition of diethylzinc to benzaldehyde in the presence of Ti(Oi-Pr)$_4$. Ti(O*i*-Pr)$_4$ (0.64 ml, 2.1 mmol) was added to a solution of **9b** (85 mg, 0.21 mmol) in dry hexane (15 ml) at r.t. The mixture was stirred for 25 min. Then a 1 M solution of $ZnEt_2$ in hexane (2.34 ml, 2.34 mmol) was added. The resulting solution was stirred at r.t. for 15 min. and cooled to 0 ºC. Then benzaldehyde (244 mg, 2.13 mmol) was added dropwise. The reaction mixture was kept at 0 ºC for 20 h. Then 1 M HCl (5 ml) was added slowly, and the solution was extracted with Et_2O. The combined organic layers were dried over Na_2SO_4. The solvent was distilled off, and the residue was purified by column chromatography on SiO_2 (an EtOAc gradient in hexane from 10 to 50% as eluent was used). This gave 97 mg of benzaldehyde **1** (conversion 59%) and 180 mg (95% based on changed aldehyde **1**) of (*R*)-**2** (*ee* 3%).

RESULTS AND DISCUSSION

It was recently discovered [23] that using Schiff bases obtained from aldehydes for the catalytic addition of diethylzinc to benzaldehyde led to the formation of compound **2** with a moderate yield (36-53%) and low enantioselectivity (*ee* 18-21%). Therefore here we used amines **9**, but not Schiff bases **8** as ligands.

In addition to the previously obtained ligands **9a**, **b**, we synthesized a new compound **10** containing a pyridine ring (Scheme **2**).

The reaction of (-)-**5** and **11** formed tricyclic compound **12**. The reaction evidently starts with the formation of a Schiff base **13**, which undergoes heterocyclization to oxazinane **12** under the reaction conditions (methanol, r.t.). Indeed, previously we showed that some of the Schiff bases, obtained from α-pinene and 3-carene, could be partially in a tricyclic oxazinane form [14, 24]. Curiously, in the case of **12**, we found only the traces of the acyclic compound **13**. The reduction of **12** with $NaBH_4$ led to the formation of the desired compound **10**.

The results of the enantioselective addition of $ZnEt_2$ to aldehydes **1**, **14** and **15** (Scheme **3**) in the presence of ligands **9a**, **b** and **10** are presented in Table **1**. The ligands were used in amounts of 10 mol %.

Using ligand **9a** led to the formation of product **2** with a small excess of the (*S*)-enantiomer and a moderate yield may be due to side reactions. For the sterically more hindered ligand **9b**, the yield and the enantioselectivity of the reaction increased dramatically (from 5 to 69% *ee*), the major product being the (*R*)-enantiomer of **2**. Application of ligand **10** for asymmetric addition diethylzinc to benzaldehyde was more effective than using its analog with a phenyl group **9a**; the

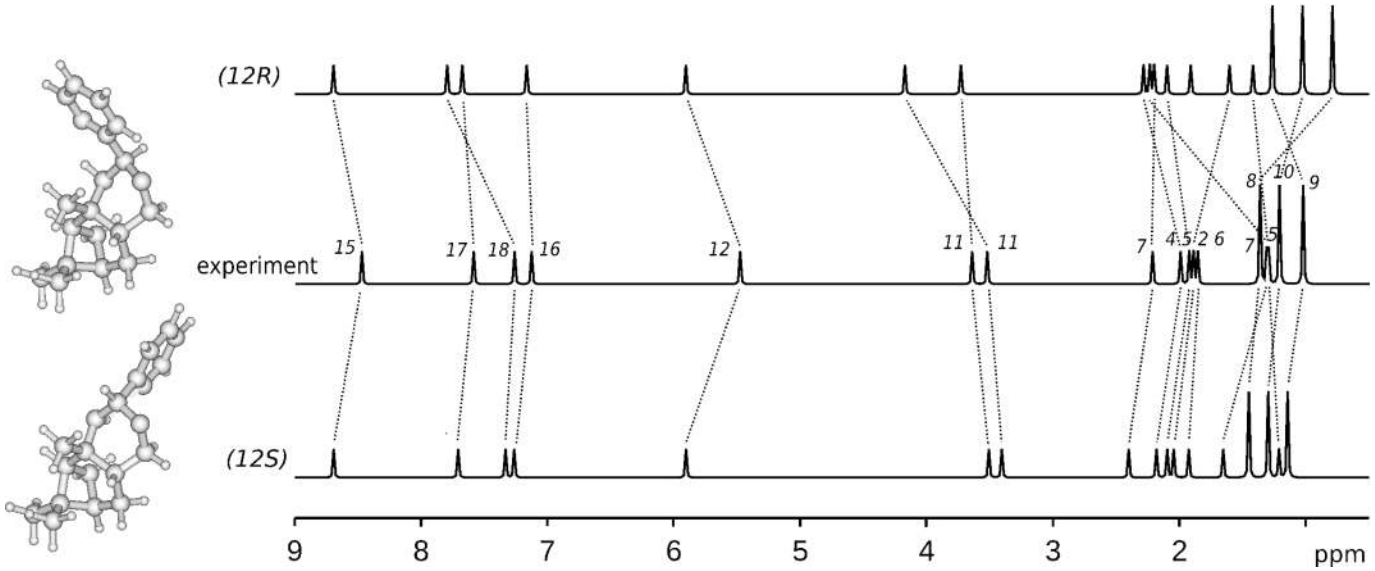
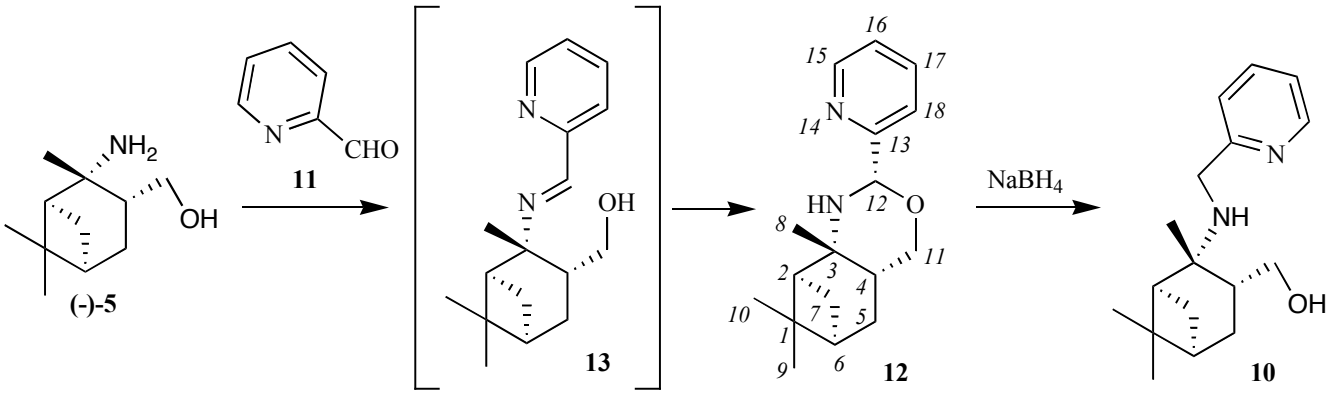


Fig. (3). The spatial structure of the most stable conformers of the (12*R*)- and (12*S*)-isomers of **12** and schematic representation of their ^{1}H NMR spectra in comparison with the experimental spectrum (the atomic numbering is shown in Scheme **2**).



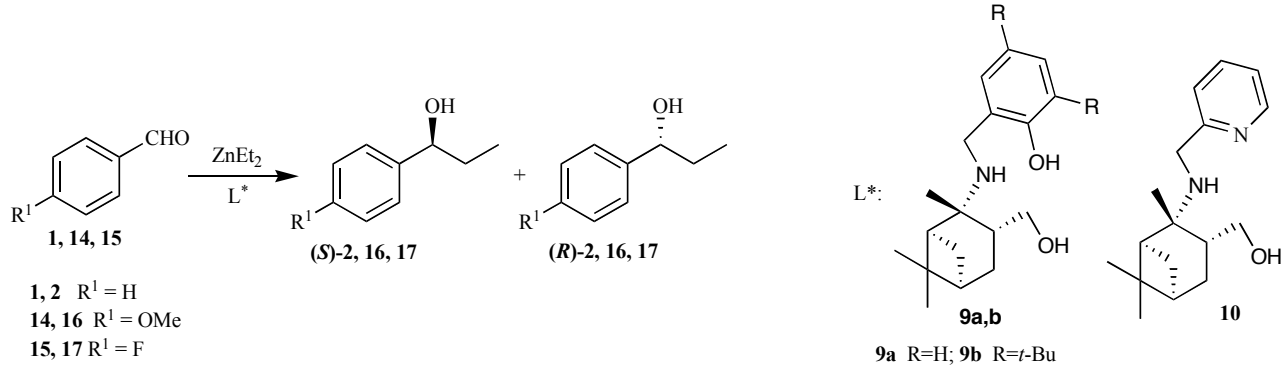
Scheme 2.

enantiomeric excess in the product was 49%, and the major product was the (*R*)-enantiomer.

As is known, the addition of Ti(O*i*-Pr)$_4$ to the $ZnEt_2$/ligand complex can substantially affect the enantioselectivity of the reaction [26, 27] and even the absolute configuration of the product [28]. We performed an experiment with ligand **9b**, adding Ti(O*i*-Pr)$_4$ under the conditions suggested in [28]. Compound **2** was formed with a very good yield, but proved to be practically a racemate with a very small excess of the (*S*)-isomer.

Application of the catalytic system with ligand **9b** to the addition of diethylzinc to 4-methoxybenzaldehyde **14** having electron donating group led to a sharp decrease of conversion following with minor *ee* decreasing. At the same time the alcohol (*R*)-**17** with electron withdrawing nitro group was obtained with *ee* 80%, conversion of compound **15** was almost 100%.

Based on the proposed transition state for the asymmetric addition of dialkylzinc with chiral Schiff bases [23], we propose a transition state model for our ligand-catalyzed asymmetric diethylzinc ethylation reaction (Fig. **4**). This model reasonably predicts the facial selectivity observed in our system.



Scheme 3.

Table 1. Asymmetric Addition of $ZnEt_2$ to Aldehydes 1, 14 and 15[a]

Entry	Ligand	Aldehydes	Conversion, %	Yield, %[b]	*ee*, %[c]
1	**9a**	**1**	66	40	5 (*S*)
2	**9b**	**1**	52	80	69 (*R*)
3	**10**	**1**	68	77	49 (*R*)
4	**9b**[d]	**1**	60	95	3 (*S*)
5	**9b**	**14**	27	26	59 (*R*)
6	**9b**	**15**	99	77	80 (*R*)

[a]The **1**/$ZnEt_2$/ligand molar ratio was 1/1.1/0.1, the temperature 0°C.
[b]Isolated yield after a column chromatography, based on changed benzaldehyde **1**.
[c]The optical purity of compound **2** was determined by GLC-MS on a chiral phase. The absolute configuration of the major enantiomer was determined by comparison of the specific rotation with the one reported in the literature [25].
[d]The reaction was carried out in the presence of Ti(O*i*-Pr)$_4$. The **1**/$ZnEt_2$/Ti(O*i*-Pr)$_4$/ligand molar ratio was 1/1.1/1/0.1, the temperature 0°C.

Thus it was shown that compounds **9a**, **b** and **10** synthesized from α-pinene (+)-**3** can be used as ligands in the asymmetric addition of diethylzinc to aromatic aldehydes, the enantiomeric excess was up to 80%.

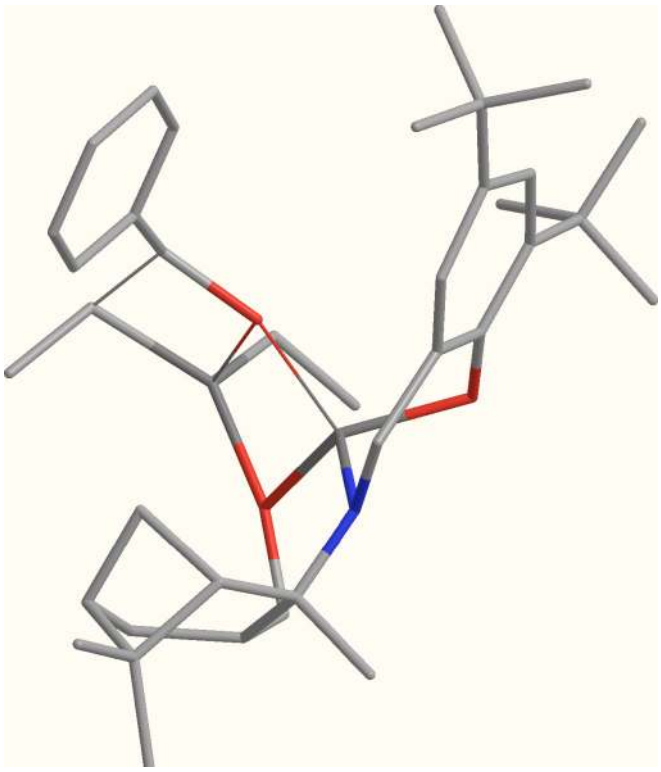


Fig. (4). Proposed transition state for the asymmetric addition of dialkylzinc to benzaldehyde with ligand **9b**. The bonds of the aldehyde with zinc atoms and ethyl are depicted as thin lines.

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CONFLICT OF INTEREST

None declared.

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