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Convenient Synthesis of a New Class of Chiral Hydroxymethyl-dihydrooxazole Ligands and Their Application in Asymmetric Addition of Diethylzinc to Aromatic Aldehydes*

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Abstract—A number of chiral hydroxymethyl-substituted dihydrooxazoles were synthesized from D- or L-mandelic acid and amino alcohols. The chiral ligands thus obtained were tested as catalyst in the asymmetric addition of diethylzinc to aromatic aldehydes, and the structure–activity relationship was studied. The addition products were characterized by an enantiomeric excess of up to 91%.

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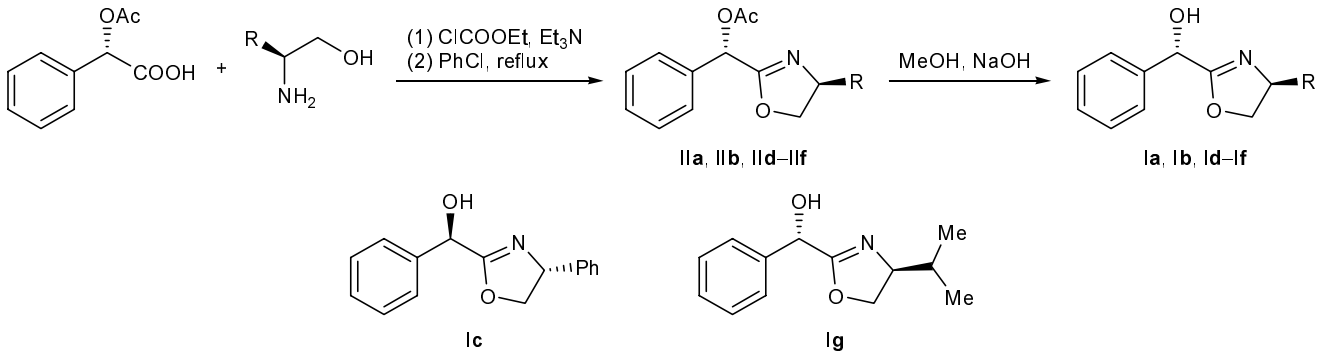
Enantioselective addition of organic reagents to aldehydes in the presence of a catalytic amount of a chiral ligand provides an excellent procedure for the preparation of secondary alcohols with a high enantiomeric purity [1]. Various compounds, such as amno alcohols, amino phenols [2–4], diols [5–7], sulfonamides [8], amides [9], and thiazolidine derivatives [10], were reported to catalyze this reaction with excellent asymmetric induction. Dihydrooxazoles were also widely used as chiral ligands in asymmetric reactions; in particular hydroxymethyl-substituted dihydrooxazoles were proposed as chiral ligands for enantioselective addition of dialkylzinc to aldehydes [11–13] and imines [14], as well as for asymmetric hydrogenation of olefins having no functional groups [15, 16]; as a result, products with an enantiomeric excess from moderate to excellent were obtained. As far as we know, there are no published data on the use of hydroxy-containing dihydrooxazoles possessing two chiral centers as ligands in enantioselective addition of diethylzinc.

The present communication reports on the results of our study on hydroxymethyl-substituted dihydrooxazoles **Ia**–**Ig** as chiral ligands in the enantioselective addition of diethylzinc to aromatic aldehydes. Compounds **Ia**–**Ig** were synthesized as follows. The hydroxy group in L- or D-mandelic acid molecule was protected by acetylation (Scheme 1); the corresponding 2-acetoxy-2-phenylacetic acid was thus obtained in 95% yield. Its condensation with an appropriate L- or

Scheme 1.



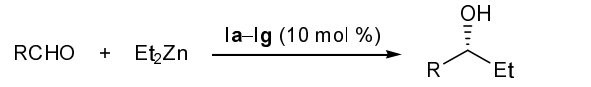
R = Me (**a**), *i*-Bu (**b**), $PhCH_2$ (**d**), *i*-Pr (**e**), *t*-Bu (**f**).

* The text was submitted by the authors in English.

D-amino alcohol in the presence of ethyl chloroformate and triethylamine gave intermediate amide which was subjected to cyclodehydration in boiling chlorobenzene with formation of dihydrooxazole **IIa**–**IIg** in good yield. Mild hydrolysis of the acetoxy group in **IIa**–**IIg** afforded enantiomerically pure ligands **Ia**–**Ig**.

Compounds **Ia**–**Ig** were tested for their ability for asymmetric induction in the addition of diethylzinc to benzaldehyde. The results are given in table. In the presence of chiral ligands **Ia**–**Ig** 1-phenylpropanol was formed in a high yield (up to 89%) with an enantiomeric excess from poor to moderate (*ee* 24–66%). The low enantioselectivity was observed with the use of ligands **Ie** and **Ig** (see table, run nos. 5, 7). Increase in the size of the substituent in the amino alcohol fragment of the ligand improves the enantioselectivity (cf. run nos. 1, 2, 3, and 6). The largest *ee* value was obtained in the reaction with ligand **If** possessing a *tert*-butyl group (run no. 6). Probable reasons for the relatively low enantioselectivity in the addition of diethylzinc to benzaldehyde in the presence of ligands **Ia**–**Ig** may be decomposition of the ligand by the action of Lewis acid and epimerization at the benzylic carbon atom under strongly basic conditions.

Addition of diethylzinc to aromatic aldehydes in the presence of ligands **Ia**–**Ig**



Run no.	Ligand no.	Aldehyde	Yield[a]	*ee*[b]	Configuration[c]
1	**Ia**	PhCHO	86	24	*S*
2	**Ib**	PhCHO	85.9	25	*S*
3	**Ic**	PhCHO	89	51	*R*
4	**Id**	PhCHO	84.8	35	*S*
5	**Ie**	PhCHO	84.2	58	*S*
6	**If**	PhCHO	87	66	*S*
7	**Ig**	PhCHO	85.7	28	*R*
8	**If**	*p*-MeC_6H_4	80	77.5	*S*
9	**If**	*p*-$MeOC_6H_4$	83	76	*S*
10	**If**	*p*-ClC_6H_4	94	91	*S*
11	**If**	*o*-ClC_6H_4	86	53	*S*
12	**If**	*o*-BrC_6H_4	84	39	*S*
13	**If**	2-$C_{10}H_7CHO$	96	56	*S*
14	**If**	PhCH=CHCHO	84	53	*S*

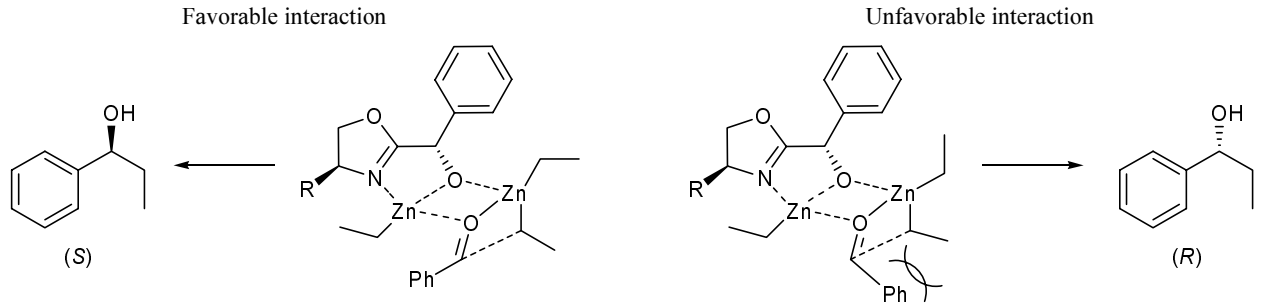
[a] Isolated product.
[b] According to the HPLC and NMR data.
[c] The configuration was assigned on the basis of the sign of specific optical rotation.

Ligand **If** was also examined in the addition of diethylzinc to other aromatic aldehydes (see table). It is seen that this compound is fairly effective with respect to both *para*- and *ortho*-substituted benzaldehydes, as well as to cinnamaldehyde and 2-naphthaldehyde. The presence of electron-donor substituents and bulky substituents in the *ortho* position appreciably reduces the enantioselectivity (run nos. 11, 12), whereas electron-withdrawing groups increase *ee* value. The best result was obtained in the reaction with *p*-chlorobenzaldehyde: the yield of the corresponding secondary alcohol was 94%, and *ee* value reached 91% (run no. 10). Figure shows unfavorable interaction between the *ortho*-substituent and ethyl group on the zinc atom in the transition state. This interaction may be responsible for the observed loss in the enantioselectivity.

EXPERIMENTAL

The melting points were determined on a Yanagimoto micro apparatus and are uncorrected. The specific optical rotations were measured on an Autopol IV polarimeter. The *ee* values were determined by HPLC (Chiralcel™ OD-H column, eluent propan-2-ol–hexane) or ^{1}H NMR spectroscopy. The NMR spectra were recorded on a Bruker AV-400 spectrometer at 400 MHz for ^{1}H and 100 MHz for ^{13}C using $CDCl_3$ as solvent and tetramethylsilane as internal reference. The IR spectra were obtained on a Nicolet-670 FT-IR spectrometer. The elemental compositions were determined on a Foss analyzer. All asymmetric addition reactions were carried out in dry glassware under nitrogen.

General procedure for the preparation of dihydrooxazoles IIa–IIg. A solution of 1.08 g (10 mmol) of ethyl chloroformate was added dropwise under stirring and cooling to –10°C to a solution of 1.94 g (10 mmol) of (*R*)- or (*S*)-2-acetoxy-2-phenylacetic acid and 1.21 g (12 mmol) of triethylamine in 10 ml of methylene chloride. After 10 min, 10 mmol of the corresponding (*R*)- or (*S*)-amino alcohol was added, maintaining the mixture at the same temperature. The mixture was stirred for 5 h at room temperature, 10 ml of methylene chloride and 5 ml of water were added, the organic phase was separated, washed in succession with a 5% solution of sodium hydrogen carbonate, 5% hydrochloric acid, and a saturated solution of sodium chloride, and dried over anhydrous sodium sulfate, and



Models of transition states in the addition of diethylzinc to benzaldehyde.

the solvent was removed under reduced pressure. The residue was a fairly pure colorless solid which was dissolved in 25 ml of chlorobenzene, and the solution was heated under reflux in a flask equipped with a Dean–Stark trap until water no longer separated (15 h). The solvent was removed, and the residue (a brown oily substance) was purified by column chromatography on silica gel using hexane–ethyl acetate as eluent. Compounds **IIa**–**IIg** were isolated as pale yellow oils.

(*S*)-[(4*S*)-4-Methyl-4,5-dihydrooxazol-2-yl]-(phenyl)methyl acetate (IIa). Yield 86.3%, $[\alpha]_D^{20}$ = –21.8 (*c* = 2.8, EtOH). ^{1}H NMR spectrum, δ, ppm: 1.25 d (3H, CH_3, *J* = 6.6 Hz), 2.17 s (3H, CH_3CO), 3.85 t (1H, OCH_2, *J* = 7.8 Hz), 4.21–4.25 m (1H, NCH), 3.85 t (1H, OCH_2, *J* = 9.2 Hz), 6.28 s (1H, OCH), 7.26–7.40 m (2H, H_{arom}), 7.47–7.49 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 20.9, 21.2, 61.6, 70.8, 74.5, 127.6, 128.6, 129.0, 135.3, 163.8, 169.8. IR spectrum (film), ν, cm^{-1}: 3035, 2969, 1746, 1676, 1203, 1046, 792, 761. Found, %: C 66.89; H 6.45; N 5.97. $C_{13}H_{15}NO_3$. Calculated, %: C 66.94; H 6.48; N 6.00.

(*S*)-[(4*S*)-4-Isobutyl-4,5-dihydrooxazol-2-yl]-(phenyl)methyl acetate (IIb). Yield 79.7%, $[\alpha]_D^{20}$ = 6.68 (*c* = 5.8, EtOH). ^{1}H NMR spectrum, δ, ppm: 0.91–0.95 m (6H, CH_3), 1.25–1.31 m (1H, CH_2), 1.57–1.65 m (1H, CH_2), 1.69–1.75 m (1H, CH), 2.19 s (3H, CH_3CO), 3.89–3.93 m (1H, OCH_2), 4.18–4.21 m (1H, NCH), 4.30–4.35 m (1H, OCH_2), 6.29 s (1H, OCH, *J* = 2.6 Hz), 7.29–7.51 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 20.9, 22.5, 22.8, 25.2, 45.1, 64.6, 70.8, 73.6, 127.5, 128.6, 129.0, 135.2, 163.7, 169.7. IR spectrum (film), ν, cm^{-1}: 3343, 2957, 1747, 1673, 1229, 1046, 734. Found, %: C 69.77; H 7.70; N 5.08. $C_{16}H_{21}NO_3$. Calculated, %: C 69.79; H 7.69; N 5.09.

(*R*)-(Phenyl)[(4*R*)-4-phenyl-4,5-dihydrooxazol-2-yl]methyl acetate (IIc). Yield 80%, $[\alpha]_D^{20}$ = 6.68 (*c* = 5.8, EtOH). ^{1}H NMR spectrum, δ, ppm: 2.20 s (3H, CH_3CO), 4.12–4.16 m (1H, OCH_2), 4.58–4.63 m (1H, OCH_2), 5.22 t (1H, NCH, *J* = 8.1 Hz), 6.36 s (1H, OCH, *J* = 2.6 Hz), 7.14–7.56 m (10H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 20.9, 69.5, 70.9, 75.6, 126.5, 127.6, 128.7, 128.7, 129.2, 135.1, 141.8, 165.5, 169.9. IR spectrum (film), ν, cm^{-1}: 3065, 2903, 1751, 1673, 1229, 1046, 793. Found, %: C 73.12; H 5.79; N 4.67. $C_{18}H_{17}NO_3$. Calculated, %: C 73.20; H 5.80; N 4.74.

(*S*)-[(4*S*)-4-Benzyl-4,5-dihydrooxazol-2-yl]-(phenyl)methyl acetate (IId). Yield 80.2%, $[\alpha]_D^{20}$ = 18.7 (*c* = 2.0, EtOH). ^{1}H NMR spectrum, δ, ppm: 2.18 s (s, 3H, CH_3CO), 2.62 d.d (1H, OCH_2, *J* = 16.8, 8.4 Hz), 3.05 d (1H, PhC**H**$_2$, *J* 5.2 Hz), 3.09 d (1H, PhC**H**$_2$, *J* = 5.2 Hz), 4.02 d.d (1H, OCH_2, *J* = 7.0, 14.0 Hz), 4.14 t (1H, OCH_2, *J* = 9 Hz), 4.42–4.45 m (1H, NCH), 6.27 s (1H, OCH), 7.14–7.46 m (10H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 20.9, 41.3, 67.2, 70.8, 72.3, 126.5, 127.5, 128.5, 128.7, 129.0, 129.2, 135.1, 137.5, 164.5, 169.8. IR spectrum (film), ν, cm^{-1}: 3064, 3030, 2930, 1746, 1672, 1229, 1044, 791, 761. Found, %: C 73.71; H 6.12; N 4.47. $C_{19}H_{19}NO_3$. Calculated, %: C 73.77; H 6.19; N 4.53.

(*S*)-[(4*S*)-4-Isopropyl-4,5-dihydrooxazol-2-yl]-(phenyl)methyl acetate (IIe). Yield 79.7%, $[\alpha]_D^{20}$ = 4.65 (*c* = 2.1, EtOH). ^{1}H NMR spectrum, δ, ppm: 0.82 d (3H, CH_3, *J* = 6.8 Hz), 0.89 d (3H, CH_3, *J* = 6.8 Hz), 1.74–1.77 m (1H, CH), 2.17 s (3H, CH_3CO), 3.97–4.01 m (1H, NCH), 4.02 t (1H, OCH_2, *J* = 8.3 Hz), 4.19 t (1H, OCH_2, *J* = 8.3 Hz), 6.28 s (1H, OCH), 7.26–7.50 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 17.8, 18.4, 20.9, 32.3, 70.6, 70.9, 71.8, 127.5, 128.6, 129.0, 135.2, 163.7, 169.8. IR spectrum (film), ν, cm^{-1}: 3036, 2964, 1747, 1678, 1043, 794. Found, %: C 68.90; H 7.31; N 5.31. $C_{15}H_{19}NO_3$. Calculated, %: C 68.94; H 7.33; N 5.36.

(*S*)-[(4*S*)-4-*tert*-Butyl-4,5-dihydrooxazol-2-yl]-(phenyl)methyl acetate (IIf). Yield 65.2%, $[\alpha]_D^{20}$ = –0.5 (*c* = 4.2, EtOH). ^{1}H NMR spectrum, δ, ppm: 0.85 s [9H, $(CH_3)_3$], 2.19 s (3H, CH_3CO), 3.90–3.92 m (1H, NCH), 4.14–4.17 m (2H, OCH_2), 6.28 s (1H,

OCH), 7.36–7.50 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 20.9, 25.6, 33.9, 69.5, 71.0, 75.5, 127.5, 128.6, 128.7, 129.0, 135.2, 163.7, 169.8. IR spectrum (film), ν, cm^{-1}: 3035, 2955, 1750, 1678, 1046, 698. Found, %: C 69.76; H 7.69; N 5.08. $C_{16}H_{21}NO_3$. Calculated, %: C 69.79; H 7.69; N 5.09.

(*R*)-[(4*S*)-4-Isopropyl-4,5-dihydrooxazol-2-yl]-(phenyl)methyl acetate (IIg). Yield 83.7%, $[\alpha]_D^{20}$ = –94.5 (*c* = 2, EtOH). ^1H NMR spectrum, δ, ppm: 0.82 d (3H, CH_3, *J* = 6.8 Hz), 0.92 d (3H, CH_3, *J* = 6.8 Hz), 1.84–1.85 m (1H, CH), 2.17 s (3H, CH_3CO), 3.94–3.99 m (2H, OCH_2), 4.24 t (1H, NCH, *J* = 8.0 Hz), 6.29 s (1H, OCH), 7.35–7.51 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 17.8, 18.4, 20.9, 32.3, 70.6, 70.9, 71.8, 127.5, 128.6, 129.0, 135.2, 163.7, 169.8. IR spectrum (film), ν, cm^{-1}: 3036, 2961, 1747, 1678, 1043, 794. Found, %: C 68.91; H 7.33; N 5.34. $C_{15}H_{19}NO_3$. Calculated, %: C 68.94; H 7.33; N 5.36.

General procedure for the preparation of dihydrooxazoles Ia–Ig. Compound **IIa**–**IIg**, 5 mmol, was dissolved in 15 ml of ethanol, the solution was cooled to 0°C, and 10 ml of 20% aqueous sodium hydroxide was added. The mixture was stirred for 2 h at 0°C and treated with diethyl ether (3 × 10 ml), the organic extracts were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure, and the residue (a white solid) was recrystallized from diethyl ether–hexane.

(*S*)-[(4*S*)-4-Methyl-4,5-dihydrooxazol-2-yl]-(phenyl)methanol (Ia). Yield 80%, mp 96–98°C, $[\alpha]_D^{20}$ = –65.25 (*c* = 1.2, EtOH). ^1H NMR spectrum, δ, ppm: 1.26–1.29 m (3H, CH_3), 3.87–3.92 m (1H, OCH_2), 4.13–4.19 m (1H, NCH), 4.34–4.40 m (1H, OCH_2), 5.29 s (1H, OCH), 7.26–7.46 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 21.2, 60.8, 69.7, 75.5, 75.6, 126.6, 128.3, 128.4, 128.5, 139.1, 168.3. IR spectrum (KBr), ν, cm^{-1}: 3459, 2974, 1670, 1187, 1066, 737. Found, %: C 69.03; H 6.80; N 7.28. $C_{11}H_{13}NO_2$. Calculated, %: C 69.09; H 6.85; N 7.32.

(*S*)-[(4*S*)-4-Isobutyl-4,5-dihydrooxazol-2-yl]-(phenyl)methanol (Ib). Yield 90%, mp 101–102°C, $[\alpha]_D^{20}$ = –71.17 (*c* = 1.2, EtOH). ^1H NMR spectrum, δ, ppm: 0.91–0.95 m (6H, CH_3), 1.24 m (1H, CH_2), 1.59–1.64 m (1H, CH_2), 1.76–1.77 m (1H, CH), 3.90–3.95 m (1H, OCH_2), 4.10–4.14 m (1H, NCH), 4.34–4.39 m (1H, OCH_2), 5.26 d (1H, OCH, *J* = 4.3 Hz), 7.25–7.45 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 22.6, 22.7, 25.3, 45.3, 63.8, 69.7, 74.8, 126.6, 128.3, 128.5, 139.1, 163.7, 168.4. IR spectrum (KBr), ν, cm^{-1}: 3401, 2907, 1663, 1177, 761. Found, %: C 72.01; H 8.18; N 5.95. $C_{14}H_{19}NO_2$. Calculated, %: C 72.07; H 8.21; N 6.00.

(*R*)-(Phenyl)[(4*R*)-4-phenyl-4,5-dihydrooxazol-2-yl]methanol (Ic). Yield 87%, mp 110–112°C, $[\alpha]_D^{20}$ = 21.29 (*c* = 1.0, CH_2Cl_2). ^1H NMR spectrum, δ, ppm: 4.19 s (1H, OH), 4.21–4.26 m (1H, OCH_2), 4.63–4.68 m (1H, OCH_2), 5.16–5.20 t (1H, NCH, *J* = 8.4 Hz), 5.29 s (1H, OCH), 7.24–7.49 m (10H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 68.7, 69.6, 76.3, 126.5, 126.6, 126.6, 127.8, 128.4, 128.5, 128.8, 139.0, 141.5, 168.8. IR spectrum (KBr), ν, cm^{-1}: 3410, 2908, 1644, 1455, 1177, 1080, 760. Found, %: C 75.83; H 5.96; N 5.51. $C_{16}H_{15}NO_2$. Calculated, %: C 75.87; H 5.97; N 5.53.

(*S*)-[(4*S*)-4-Benzyl-4,5-dihydrooxazol-2-yl]-(phenyl)methanol (Id). Yield 92%, mp 107–108.5°C, $[\alpha]_D^{20}$ = –48.31 (*c* = 1.0, EtOH). ^1H NMR spectrum, δ, ppm: 2.69 d.d (1H, OCH_2, *J* = 16.0, 8.0 Hz), 3.06 d (1H, PhC**H**$_2$, *J* = 5.6 Hz), 3.09 d (1H, PhC**H**$_2$, *J* = 5.6 Hz), 3.83 s (1H, OH), 4.08 t (1H, OCH_2, *J* = 8.4 Hz), 4.21 t (1H, OCH_2, *J* = 8.4 Hz), 4.26–4.40 m (1H, NCH), 5.26 s (1H, OCH), 7.18–7.42 m (10H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 40.8, 65.8, 69.1, 72.8, 125.9, 126.3, 127.7, 127.9, 128.2, 128.6, 128.9, 129.2, 136.8, 137.1, 163.5. IR spectrum (KBr), ν, cm^{-1}: 3397, 2923, 1667, 1492, 1191, 1068, 738. Found, %: C 76.35; H 6.45; N 5.20. $C_{17}H_{17}NO_2$. Calculated, %: C 76.38; H 6.41; N 5.24.

(*S*)-[(4*S*)-4-Isopropyl-4,5-dihydrooxazol-2-yl]-(phenyl)methanol (Ie). Yield 85%, mp 94.5–96°C, $[\alpha]_D^{20}$ = –73.54 (*c* = 1.1, EtOH). ^1H NMR spectrum, δ, ppm: 0.87 d (3H, CH_3, *J* = 6.8 Hz), 0.96 d (3H, CH_3, *J* = 6.8 Hz), 1.71–1.78 m (1H, CH), 3.84–3.90 m (1H, NCH), 3.99 s (1H, OH), 4.05 t (1H, OCH_2, *J* = 8.3 Hz), 4.25 t (1H, OCH_2, *J* = 8.3 Hz), 5.29 s (1H, OCH), 7.25–7.46 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 18.2, 18.6, 32.6, 69.6, 71.3, 72.0, 126.6, 128.3, 128.5, 139.2, 168.3. IR spectrum (KBr), ν, cm^{-1}: 3416, 2959, 1670, 1643, 1264, 1193, 1087, 749. Found, %: C 71.18; H 7.82; N 6.35. $C_{13}H_{17}NO_2$. Calculated, %: C 71.21; H 7.81; N 6.39.

(*S*)-[(4*S*)-4-*tert*-Butyl-4,5-dihydrooxazol-2-yl]-(phenyl)methanol (If). Yield 88%, mp 132°C, $[\alpha]_D^{20}$ = –68.5 (*c* = 1, EtOH). ^1H NMR spectrum, δ, ppm: 0.91 s [9H, $(CH_3)_3$], 3.70 s (1H, OH), 3.84 d.d (1H, NCH, *J* = 8.0, 12 Hz), 4.17–4.21 m (2H, OCH_2), 5.29 s (1H, OCH), 7.33–7.47 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 25.7, 33.6, 69.6, 70.6, 74.8, 123.5,

128.3, 128.5, 139.2, 168.2. IR spectrum (KBr), ν, cm^{-1}: 3395, 2959, 1671, 1366, 1162, 699. Found, %: C 72.06; H 8.22; N 5.98. $C_{14}H_{19}NO_2$. Calculated, %: C 72.07; H 8.21; N 6.00.

(*R*)-[(4*S*)-4-Isopropyl-4,5-dihydrooxazol-2-yl]-(phenyl)methanol (Ig). Yield 87%, mp 69–71°C, $[\alpha]_D^{20}$ = –67 (*c* = 1.2, EtOH). ^{1}H NMR spectrum, δ, ppm: 0.84 d (3H, CH_3, *J* = 6.8 Hz Hz), 0.94 d (3H, CH_3, *J* = 6.8 Hz), 1.72–1.77 m (1H, CH), 3.78 s (1H, OH), 3.95–3.98 m (1H, NCH), 4.00 t (1H, OCH_2, *J* = 8.0 Hz), 4.36 t (1H, OCH_2, *J* = 8.0 Hz), 5.25 s (1H, OCH), 7.26–7.46 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 18.1, 18.7, 32.6, 69.8, 71.2, 71.9, 126.7, 128.4, 128.5, 139.2, 168.2. IR spectrum (KBr), ν, cm^{-1}: 3416, 2959, 1670, 1643, 1087, 698. Found, %: C 71.20; H 7.81; N 6.38. $C_{13}H_{17}NO_2$. Calculated, %: C 71.21; H 7.81; N 6.39.

Addition of diethylzinc to aromatic aldehydes in the presence of ligands Ia–Ig (*general procedure*). A solution of 0.1 mmol of ligand **Ia**–**Ig** in 10 ml of anhydrous toluene was cooled to 0°C, and 2.4 mmol of diethylzinc was added with stirring under nitrogen. The mixture was stirred for 30 min, and 1 mmol of the corresponding aldehyde was added. The mixture was allowed to warm up to room temperature, stirred for 20 h, cooled to 0°C, and treated with 10 ml of 10% hydrochloric acid. The organic phase was separated, and the aqueous phase was extracted with diethyl ether. The extracts were combined with the organic phase, washed with a 10% solution of $NaHCO_3$ and a saturated solution of NaCl, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel.

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