Catalytic enantioselective reactions. Part 9.[1] 1,2-*O*-Isopropylidene-5-deoxy-5-*N*,*N*-dialkyl (or -*N*-monoalkyl)amino-α-D-xylofuranose derivatives as highly effective chiral catalysts for enantioselective addition of diethylzinc to aliphatic and aromatic aldehydes

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A series of new 1,2-*O*-isopropylidene-5-deoxy-5-*N*,*N*-dialkyl (or -*N*-monoalkyl)amino-α-D-xylofuranose derivatives have been prepared from α-D-xylose and their enantioselectivities as chiral catalysts for the addition of diethylzinc to aldehydes have been examined. Of the chiral catalysts examined, 5-deoxy-1,2-*O*-isopropylidene-5-morpholino-α-D-xylofuranose provides high enantioselectivity for aromatic and relatively hindered aliphatic aldehydes, and 5-deoxy-5-hexahydroazepinyl-1,2-*O*-isopropylidene-α-D-xylofuranose is highly effective for unhindered aliphatic aldehydes.

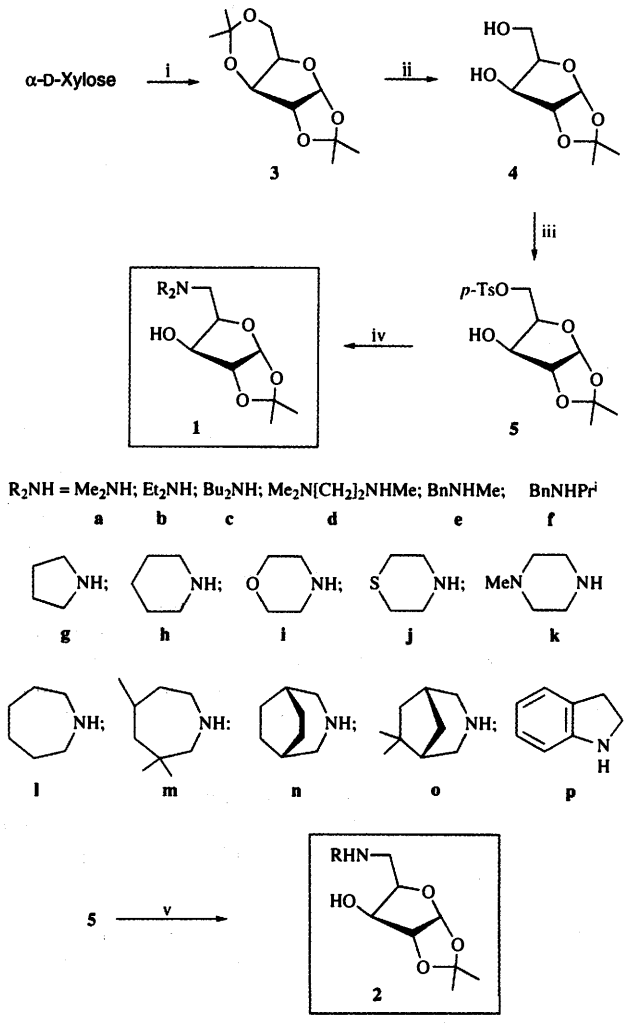
Introduction

Enantioselective addition of diethylzinc to aldehydes using chiral ligands as catalysts is a convenient method for the preparation of optically active secondary alcohols.[2] Accordingly, a wide variety of chiral ligands for the catalytic enantioselective addition have been extensively developed.[2a] Among them, effective chiral ligands for the reaction are β-amino alcohols derived from natural products, such as camphor, α-amino acids, norephedrine and cinchona alkaloids. Also, several kinds of synthetic chiral amino alcohol derivatives proved to be potentially chiral catalysts and may afford high asymmetric induction for such a reaction. However, no report on the use of chiral catalysts derived from inexpensive monosaccharides for the reaction has appeared in the literature, although they are widely used chiral auxiliaries for asymmetric syntheses.[3] Therefore, we undertook to synthesize some β- and γ-amino alcohols from α-D-glucose and α-D-xylose, respectively, and we examined their enantioselectivities for such a reaction.[4] In the course of this study, we found that a γ-dialkylamino alcohol, 5-deoxy-1,2-*O*-isopropylidene-5-morpholino-α-D-xylofuranose prepared from α-D-xylose, was highly effective as a chiral catalyst for the enantioselective addition of diethylzinc to aromatic and relatively hindered aliphatic aldehydes, leading to the corresponding optically active secondary alcohols with high enantioselectivity.[4a] In order to gain a better understanding of the catalytic effects and with the hope of developing improved chiral catalysts for the enantioselective alkylation of aldehydes, we prepared a series of new 1,2-*O*-isopropylidene-5-deoxy-5-*N*,*N*-dialkyl (or -*N*-monoalkyl)amino-α-D-xylofuranose derivatives **1** or **2** possessing a variety of amine substituents at the 5-position of the xylofuranose ring and compared their enantioselectivities as chiral catalysts for such reactions. In this paper, we describe details of our preliminary reports,[4a–d] and the scope and limits of these reactions.

Results and discussion

Synthesis of 1,2-*O*-isopropylidene-5-deoxy-5-*N*,*N*-dialkyl (or -*N*-monoalkyl)amino-α-D-xylofuranose derivatives (1 and 2)

In order to examine effects of the substituents on the nitrogen atom of compounds **1** and **2** for asymmetric induction, we chose a variety of dialkylamines (**a–f**) and heterocyclic amines (**g–p**) as shown in Scheme 1. 1,2-*O*-Isopropylidene-α-D-xylofuranose **4**[5] was prepared by partial hydrolysis of 1,2:3,5-di-*O*-isopropylidene-α-D-xylofuranose **3**, obtained from α-D-xylose,



Scheme 1 *Reagents and conditions:* i, acetone, H_2SO_4, $CuSO_4$ (80%); ii, 0.2% HCl (90%); iii, *p*-TsCl, pyridine, $CHCl_3$ (94%); iv, R_2NH (40–80%); v, RNH_2 (45–88%)

Table 1 Synthesis and physical properties of 1,2-*O*-isopropylidene-5-deoxy-5-*N*,*N*-dialkyl and -*N*-monoalkylamino-α-D-xylofuranose derivatives **1** and **2**[a]

Compound	Yield[b] (%)	Bp (°C/mmHg) or mp (°C)	$[\alpha]_D^{24}$ (*c* 1, $CHCl_3$)	Compound	Yield (%)	Bp (°C/mmHg) or mp (°C)	$[\alpha]_D^{24}$ (*c* 1, $CHCl_3$)
1a[c]	70	(78/0.2)	2.54	**1m**	45	(134–136/0.15)	−4.82
1b[c]	74	(80/0.15)	17.10	**1n**	49	106–107	−3.60
1c[c]	61	(146–149/0.2)	10.66	**1o**	64	70–71	5.47
1d[c]	58	(132/0.01)	−58.67	**1p**	40	78–79	3.70
1e[c]	77	(164–165/0.15)	11.57	**2a'**	88	104–105	18.76
1f	48	54–55	12.00	**2b'**	54	32–33	9.11
1g[c]	80	94–95	7.06	**2c'**	54	(152–153/0.15)	14.00
1h	78	73–74[d]	16.90	**2d'**	45	66–67	17.40
1i	61	63–64[d]	13.20	**2e'**	88	68–69	15.17
1j	86	102–103	12.10	**2f'**	61	62–63	11.86
1k	88	152–153[d]	11.84	**2g'**	51	112–113	16.69
1l	64	40–41[e]	−13.60	**2h'**	88	64–65	11.62

[a] Obtained from the reaction of compound **5** (1 mol equiv.) with dialkylamines (4 mol equiv.) in propan-2-ol at reflux temperature, unless otherwise indicated. [b] Isolated yields. [c] Ref. 4*c*. [d] Ref. 4*a*. [e] Ref. 4*d*.

Table 2 Catalytic and temperature effects on asymmetric inductions for enantioselective addition of diethylzinc to benzaldehyde using catalyst **1i** as a chiral catalyst[a]

				1-Phenylpropan-1-ol		
Entry	**1i** (mol%)	Time (*t*/h)	Temp. (*T*/°C)	Yield (%)[b]	% ee[c]	Confg.[d]
1	2	10	25	87	89	*R*
2	5	10	25	90	96	*R*
3	10	10	25	91	96	*R*
4	25	10	25	92	96	*R*
5	5	48	−25	41	20	*R*
6	5	24	0	88	96	*R*
7	5	2	70	90	75	*R*

[a] [Benzaldehyde]:[Et_2Zn] = 1 : 2. [b] GLC yields. [c] Determined by capillary GLC analyses of (*R*)-(+)-MTPA esters [MTPA = α-methoxy-α-(trifluoromethyl)phenylacetic acid].[7] [d] Based on the sign of optical rotations and elution orders of peaks in GLC analyses.

with 0.2% HCl at room temperature in 90% yield. Tosylation of diol **4** in the usual manner afforded 1,2-*O*-isopropylidene-5-*O*-(*p*-tolylsufonyl)-α-D-xylofuranose **5**[6] in 94% yield. Finally, compound **5** was treated with an excess of the amines (**a–p**) (4 mol equiv.) in propan-2-ol. The reaction mixture was heated to reflux for 24 h. The reactions proceeded smoothly to produce the corresponding γ-dialkylamino alcohols **1** in 40–80% yield. Using the same procedure, 5-deoxy-1,2-*O*-isopropylidene-5-*N*-monoalkylamino-α-D-xylofuranose derivatives **2** were prepared from the reaction of compound **5** with monoalkylamines (**a'–h'**) in 45–88% yield. The results are summarized in Scheme 1 and Table 1.

Effects of amount of catalyst and temperature

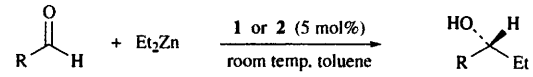
To find the optimum conditions to provide high asymmetric induction in the enantioselective addition of diethylzinc to aldehydes using compounds **1** or **2** as chiral catalysts, we initially investigated the effects of the amount of catalyst and the reaction temperature on enantioselectivity. Benzaldehyde and 5-deoxy-1,2-*O*-isopropylidene-5-morpholino-α-D-xylofuranose **1i** were selected as representative. First, the reactions were carried out by addition of 2 mol equiv. of diethylzinc in toluene to the aldehyde in the presence of different amounts of the catalyst at room temperature (~ 25 °C). As shown in Table 2, the use of 5 mol% of compound **1i** provided the best results, to give 1-phenylpropan-1-ol of 96% enantiomeric excess (ee). Increasing the amount of catalyst from 5 to 25 mol% did not significantly affect the enantioselectivity, which was 89% ee with 2 mol% **1i**, 96% ee with 10 mol% and 96% ee with 25 mol%. Next, we examined temperature effects by carrying out the same reaction with 5 mol% of catalyst **1i** at various temperatures. The maximum optical induction (96% ee) was observed when the reaction was performed at 25 °C or 0 °C, although the same reaction at 0 °C was somewhat slower than at 25 °C. The reaction at lower temperature (−25 °C) was very slow to give the product alcohol with very low enantioselectivity (20% ee) in 41% yield after 48 h. At 70 °C, the reaction proceeded rapidly to give the product alcohol in 90% yield within 2 h; however, lower enantioselectivity (75% ee) was observed.

Effects of the structure of the chiral catalysts (1 and 2)

We examined the effects of the structure of the chiral catalysts **1** and **2** on asymmetric induction by comparing their enantioselectivities under standard reaction conditions (2 mol equiv. diethylzinc; 5 mol% of catalysts; at room temperature). As shown in Table 3, it was found that the enantioselectivities were very sensitive to the structure of the chiral catalysts. For benzaldehyde chosen as a representative aromatic aldehyde, when the R group in dialkylamino moieties (R_2N) of chiral catalysts **1** changed from methyl to ethyl and butyl, their enantioselectivities decreased: 86% ee with **1a**, 81% with **1b** and 64% ee with **1c**. The catalyst **1e** with the *N*-methylbenzylamino group provided 75% ee, whereas **1f** with *N*-isopropylbenzylamino group moiety gave only 7% ee. The catalysts **1g–j** in which R_2N = pyrrolidino, piperidino, morpholino, and thiomorpholino afforded high enantioselectivities (entries 7-12). Among them, compounds **1i** and **1j** provided the best results, and gave 1-phenylpropan-1-ol of 96% ee and 94% ee, respectively. Enantioselectivities of compounds **1l–o** bearing 7-membered heterocyclic rings (entries 14 and 15) are inferior to those obtained by the catalysts (**1g–j**) with 5- or 6-membered heterocyclic amine moieties. For heptanal, chosen as a representative aliphatic aldehyde, compounds **1j** and **1l** having a thiomorpholino and a hexahydroazepinyl group, respectively, afforded the best results to give 82% ee and 83% ee, respectively, although all the catalysts examined provided somewhat lower enantioselectivities (49–83% ee) than those attained with benzaldehyde. We also examined the substituent effect of adding a second ligand site to the dialkylamino substituents, such as with compounds **1d** and **1k** bearing *N*,*N*,*N'*-trimethylethylenediamino and 4-methylpiperidino moieties, respectively. However, these catalysts are much less reactive at room temperature for both benzaldehyde and heptanal, although the reaction is complete within 2 h at 70 °C to provide the desired alcohols with low enantioselectivity (entries 4 and 13). Compound **1p** with an indolinyl moiety gave low asymmetric inductions for both benzaldehyde and heptanal: 50% ee and 69% ee, respectively (entry 18).

Using the same methodology, we also compared the enantioselectivities of γ-monoalkylamino alcohol derivatives **2** as chiral catalysts (entries 19–25 and 30). For both benzaldehyde

Table 3 Comparison of enantioselective addition of diethylzinc to benzaldehyde and heptanal in the presence of 5 mol% of compounds **1** and **2** in toluene at room temperature[a]



		1-Phenylpropan-1-ol				3-Nonanol			
Entry	Cat.	Time (*t*/h)	Yield[b]	% ee[c]	Confg.[d]	Time (*t*/h)	Yield[b]	% ee[c]	Confg.[d]
1	**1a**	24	88	86[g]	*R*	12	90	70	*R*
2	**1b**	10	90	81[g]	*R*	10	96	67	*R*
3	**1c**	10	85	64[g]	*R*	10	84	74	*R*
4	**1d**	2[f]	98	30[g]	*R*	2	38	54	*R*
5	**1e**	10	86	75[g]	*R*	10	85	74	*R*
6	**1f**	10	66	7	*R*	10	65	54	*R*
7	**1g**	10	90	90[g]	*R*	10	95	70	*R*
8	**1h**	10	92	87[h]	*R*	10	96	76[h]	*R*
9	**1h-Li**[k]	10	57	83	*R*	*e*			
10	**1i**	10	90	96[h]	*R*	10	95	75[h]	*R*
11	**1i-Li**[k]	10	91	92	*R*	*e*			
12	**1j**	10	88	94	*R*	10	78	82	*R*
13	**1k**	2[f]	99	78[h]	*R*	2	70	49	*R*
14	**1l**	10	98	76[i]	*R*	10	75	83[i]	*R*
15	**1m**	10	98	62	*R*	10	77	76	*R*
16	**1n**	10	90	76	*R*	10	61	78	*R*
17	**1o**	10	90	80	*R*	10	76	76	*R*
18	**1p**	10	88	50	*R*	10	70	69	*R*
19	**2a'**	48	50	7[j]	*R*	48	50	19	*R*
20	**2b'**	10	78	69[j]	*R*	48	36	17	*R*
21	**2c'**	10	78	58	*R*	12	49	54	*R*
22	**2d'**	10	83	77[j]	*R*	12	66	57	*R*
23	**2e'**	10	83	77	*R*	10	54	65	*R*
24	**2f'**	10	95	72	*R*	10	66	70	*R*
25	**2g'**	10	95	82[j]	*R*	10	67	68[j]	*R*
26	**2g'-Li**[k]	10	98	70	*R*	*e*			
27	**2g'-B**[k]	10	94	68	*R*	*e*			
28	**2g'-Ti**[k]	10	83	67	*R*	*e*			
29	**2g'-Al**[k]	10	87	41	*R*	*e*			
30	**2h'**	10	71	69[j]	*R*	12	43	8	*R*

[a] [Aldehyde]:[catalysts]:[Et_2Zn] = 1:0.05:2. [b–d] See the corresponding footnotes in Table 2. [e] The reaction was not carried out. [f] At 70 °C. [g] Ref. 4*c*. [h] Ref. 4*a*. [i] Ref. 4*d*. [j] Ref. 4*b*. [k] [Aldehyde]:[**1h, 1i,** or **2g'**]:[BuLi, BH_3, $Ti(OPr^i)_4$, or $AlMe_3$] = 1:0.05:0.05:2.

and heptanal, the enantioselective preparation of the product alcohols increased as the steric size of the R in the chiral catalysts **2** increased.

On the other hand, it has already been realized that the actual catalysts of these reactions are not the amino alcohols themselves, but zinc chelates formed *in situ* from dialkylzincs and amino alcohols.[2] Therefore, we examined the effect of central metals in the catalysts on their enantioselectivities by introducing other metals into the catalyst. First, compounds **1h** and **1i** were treated with an equimolar amount of BuLi to generate *in situ* the corresponding Li-based catalysts (**1h–Li** and **1i–Li**). We also prepared catalysts based on Li, B, Al and Ti by treating the ligand **2g** with BuLi, BH_3, $AlMe_3$ and $Ti(OPr^i)_4$, respectively and compared their enantioselectivities for benzaldehyde.† However, as shown in entries 9, 11 and 26–29 in Table 3, the ees of the product alcohol obtained with these metal-chelated catalysts are clearly inferior to those obtained with zinc chelates.

Enantioselective addition of diethyl- and dimethyl-zinc to some other aldehydes

Since compounds **1i** and **1l** provided the best enantioselectivities for benzaldehyde and heptanal, respectively, as shown in Table 3, we examined the usefulness of the catalysts towards other aldehydes. As shown in Table 4, compound **1l** again provided the best results for the ethylation of unhindered aliphatic aldehydes to give 78–92% ee (entries 1, 3 and 5). For relatively hindered aliphatic aldehydes, compound **1i** afforded higher enantioselectivities (93–96% ee) than those with compound **1l** (entries 6, 8 and 10). In the case of the α,β-unsaturated aldehyde, (*E*)-cinnamaldehyde, the reactions proceeded more slowly to produce the desired alcohols with low enantioselectivities (18–49% ee), compared with other aldehydes examined. For aromatic aldehydes, such as *o*-tolualdehyde, *p*-tolualdehyde, *p*-chlorobenzaldehyde and 1-naphthaldehyde, compound **1i** provided high enantioselectivities (86–89% ee) (entries 16, 18, 19 and 23). The catalysts **1g**, **1h** and **1j** bearing other 5- or 6-membered heterocyclic rings also showed high enantioselectivities (86–90% ee) for aromatic aldehydes examined (entries 20–22).

On the other hand, the catalytic enantioselective addition of dimethylzinc instead of diethylzinc was also examined. Thus, 2 mol equiv. of dimethylzinc was treated with benzaldehyde in the presence of 5 mol% of **1h** or **1i** under standard reaction conditions. The reaction proceeded much more slowly to give the desired alcohol in 84% and 81% yield within 48 h in contrast to 92% and 90% yield with diethylzinc within 10 h, respectively. In this reaction, enantioselectivities of the product alcohol obtained were 77% ee with **1h** and 92% ee with **1i**, which showed somewhat lower enantioselectivities than the figures of 87% ee and 96% ee obtained by diethylzinc under the same reaction conditions. Again, no significant effect of the central metal of a catalyst on enantioselectivity was observed (entry 27).

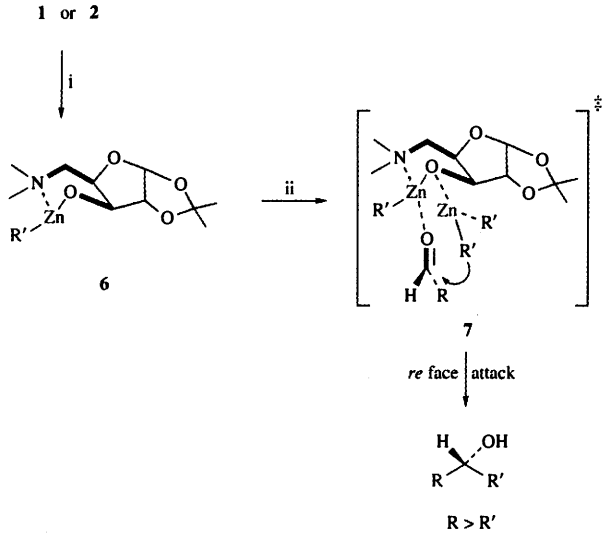
The absolute configurations of all the product alcohols obtained are consistently enriched in *R* enantiomers. We have not performed a detailed mechanistic study. However, a plausible mechanism which explains the stereochemical course of the reaction is shown in Scheme 2: dialkylzinc reacts initially with

† These catalysts presumably contain Li, B, Al or Ti. However, the exact structure of these catalysts in solution is unclear.

Table 4 Catalytic enantioselective addition of diethyl- and dimethyl-zincs to aldehydes using some representative γ-amino-alcohols (**1**) in toluene at room temperature[a]

				Product alcohols			
Entry	Aldehyde	Cat.	R_2Zn	Time (*t*/h)	Yield[b] (%)	% ee[c]	Confg.[d]
1	Hexanal	**1l**	Et_2Zn	16	90	78[f]	*R*
2	Hydrocinnamaldehyde[k]	**1i**	Et_2Zn	12	96	79	*R*
3	Hydrocinnamaldehyde[k]	**1l**	Et_2Zn	16	87	83[f]	*R*
4	3-Methylbutanal	**1i**	Et_2Zn	12	90	88	*R*
5	3-Methylbutanal	**1l**	Et_2Zn	18	92	92[f]	*R*
6	2-Methylpropanal	**1i**	Et_2Zn	12	93	93	*R*
7	2-Methylpropanal	**1l**	Et_2Zn	16	92	92[f]	*R*
8	2,2-Dimethylpropanal	**1i**	Et_2Zn	24	86	93[g,h]	*R*
9	2,2-Dimethylpropanal	**1l**	Et_2Zn	16	85	76[f]	*R*
10	Cyclohexanecarbaldehyde	**1i**	Et_2Zn	12	88	96[g,h]	*R*
11	Cyclohexanecarbaldehyde	**1l**	Et_2Zn	16	85	85[h]	*R*
12	(*E*)-Cinnamaldehyde	**1g**	Et_2Zn	30	87	49[i]	*R*
13	(*E*)-Cinnamaldehyde	**1h**	Et_2Zn	30	88	45[i]	*R*
14	(*E*)-Cinnamaldehyde	**1i**	Et_2Zn	30	85	42[i]	*R*
15	(*E*)-Cinnamaldehyde	**1l**	Et_2Zn	30	75	18[i]	*R*
16	*o*-Tolualdehyde	**1i**	Et_2Zn	10	88	89[g,h]	*R*
17	*o*-Tolualdehyde	**1j**	Et_2Zn	10	91	90	*R*
18	*p*-Tolualdehyde	**1i**	Et_2Zn	10	84	88[g]	*R*
19	*p*-Chlorobenzaldehyde	**1i**	Et_2Zn	10	91	88[g,j]	*R*
20	*p*-Chlorobenzaldehyde	**1j**	Et_2Zn	10	91	87	*R*
21	1-Naphthaldehyde	**1g**	Et_2Zn	10	90	86	*R*
22	1-Naphthaldehyde	**1h**	Et_2Zn	10	91	89	*R*
23	1-Naphthaldehyde	**1i**	Et_2Zn	10	90	86[g,i]	*R*
24	1-Naphthaldehyde	**1l**	Et_2Zn	12	92	61[f,i]	*R*
25	Benzaldehyde	**1h**	Me_2Zn	48	84	77	*R*
26	Benzaldehyde	**1i**	Me_2Zn	48	81	92	*R*
27	Benzaldehyde	**1i-Li**	Me_2Zn	48	56	90	*R*

[a–d] See the corresponding footnotes in Table 3. [e] Ref. 4*b*. [f] Ref. 4*d*. [g] Ref. 4*a*. [h] Determined by capillary GLC analyses using a Chiraldex GTA column (Astec Inc.). [i] Determined by HPLC analysis using a Chiralcel OD column. [j] Determined by a capillary GLC analysis of (−)-menthyl carbonate.[8] [k] 3-Phenylpropanal.



Scheme 2 *Reagents:* i, R'_2Zn; ii, RCHO, R'_2Zn

chiral γ-amino alcohols (**1** and **2**) to form zinc chelates **6** which are presumably the real chiral catalysts in this reaction. Oxygen from the aldehydes and dialkylzincs (R'_2Zn) may be simultaneously coordinated with Zn of species **6** in the *anti* direction and with the oxygen of the zinc alkoxides **6** to form a 6-membered bimetallic transition state **7**, where R′ is transferred to aldehyde on the *re* side to give the alcohols with *R* configurations.[9] The results from Tables 3 and 4 suggest that the steric size of the substituents on the nitrogen atom of the chiral catalyst may affect the formation and stability of the six-centre transition state **7**. For benzaldehyde, there is a large difference between the optical purities (87–96% ee) of the alcohols obtained by catalysts **1g–j** with 5- or 6-membered heterocyclic amine moieties and those (62–80% ee) obtained by catalysts **1l–o** bearing 7-membered heterocyclic rings (entries 7, 8, 10, 12 and 14–17 in Table 3). It may be assumed that the more rigid conformation of catalysts **1g–j** acts effectively as a face blocker to form the stable transition state **7** for the ensuing reaction. The steric effect of the catalysts on asymmetric induction is apparent between catalysts **1e** (75% ee) and **1f** (7% ee) or **2a′** (7% ee) and **2d′** (77% ee). In Scheme 2, the larger steric size of substituents on the nitrogen atom may act as a better face blocker. However, when substituents on the nitrogen atom of the catalysts **1** are too large, the formation of intermediates **7** may be inhibited, resulting in a decrease in enantioselectivity. In contrast, an increase in enantioselectivity of product alcohols upon increasing the steric size of R in the catalysts **2** may be attributable to the smaller steric size of monoalkylamino groups of compounds **2** compared with those of the dialkylamino groups of compounds **1**.

Conclusions

A series of new chiral γ-amino alcohols, 5-deoxy-1,2-*O*-isopropylidene-5-*N*,*N*-dialkyl (or -*N*-monoalkyl)amino-α-D-xylofuranose derivatives (**1** and **2**) was prepared from α-D-xylose, and enantioselective additions of diethylzinc to aldehydes, which used them as chiral catalysts, were examined. It was found that carrying out the reaction in the presence of 5 mol% of catalyst **1** and **2** at ~ 25 °C is best for obtaining high enantioselectivity. Of the chiral catalysts examined, 5-deoxy-1,2-*O*-isopropylidene-5-morpholino-α-D-xylofuranose **1i** provides high enantioselectivities for aromatic and relatively hindered aliphatic aldehydes, and 5-deoxy-5-hexahydroazepinyl-1,2-*O*-isopropylidene-α-D-xylofuranose **1l** is highly effective for unhindered aliphatic aldehydes. The reaction with dimethylzinc under the same reaction conditions proceeded much more slowly to give the product alcohol with somewhat lower optical purity compared with those obtained with diethylzinc.

Experimental

General

All reactions with air-sensitive materials were carried out under static pressure of nitrogen. Liquid materials were transferred with a double-ended needle. ^1H and ^{13}C NMR spectra were conducted on a Varian Gemini 300 (300 MHz) spectrometer with Me_4Si as internal standard in $CDCl_3$, and *J*-values are given in Hz. IR measurements were recorded on a Shimadzu IR-435 ratio-recording spectrophotometer equipped with a Shimadzu data recorder. Optical rotations were measured with a Rudolph polarimeter Autopol III, and $[\alpha]_D$-values are given in units of 10^{-1} deg cm^2 g^{-1}. Mps were determined with a Fisher-Johns melting point apparatus and are uncorrected. All GLC analyses were carried out with Shimadzu GC-7A and Hewlett-Packard 5890 gas chromatographs, the latter equipped with a Hewlett-Packard 3390A intergrater/plotter. Enantiomeric excesses (% ee) were determined by capillary GLC analyses of the corresponding MTPA esters[7] of product alcohols using a Hewlett-Packard 5890 gas chromatograph equipped with a 50 m methyl silicon capillary column, by capillary GLC analyses using a chiral column (Chiraldex GTA, Astec, Inc.), or by HPLC analysis using a Chiralcel OD column (Daicel Co. Ltd.).

Materials

Most of the organic compounds utilized in this study were commercial products of the highest purity. They were further purified by distillation when necessary. Diethylzinc, dimethylzinc and commercially available dialkylamines were purchased from Aldrich Chemical Company. 1,2-*O*-Isopropylidene-5-*O*-(*p*-tolylsulfonyl)-α-D-xyofuranose **5**[6] was prepared by tosylation of 1,2-*O*-isopropylidene-α-D-xylofuranose **4**,[5] itself obtained by a partial hydroysis of 1,2:3,5-di-*O*-isopropylidene-α-D-xyofuranose **3**, with toluene-*p*-sulfonyl chloride in the usual manner. (*R*)-MTPA was purchased from Aldrich Chemical Company and was converted into the acid chloride.[7]

Preparation of 5-deoxy-1,2-*O*-isopropylidene-5-*N*,*N*-dialkyl (or -*N*-monoalkyl)amino-α-D-xylofuranoses, 1 and 2

General method.[4c] A mixture of ester **5** (10 mmol) and di(or mono)alkylamine (40 mmol) in propan-2-ol (20 cm^3) was heated to reflux for 24 h. After evaporation of solvent and excess of amine *in vacuo*, the residue was treated with saturated aq. $NaHCO_3$ and extracted with diethyl ether. The extracts were concentrated to dryness and the product γ-amino alcohols (**1** and **2**) were obtained by crystallization from hexane or by fractional distillation *in vacuo*. The results are summarized in Table 1. Spectroscopic and analytical data of the products (**1** and **2**) are as follows. The data for compounds **1a–e**, **1g–i** and **1k–l** are reported in our previous papers.[4a,c,d]

5-(N-*Benzyl*-N-*isopropylamino*)-5-*deoxy*-1,2-O-*isopropylidene*-α-D-*xylofuranose* **1f**: 48% yield; mp 54–55 °C (Found: C, 67.6; H, 8.5; N, 4.4. $C_{18}H_{27}NO_4$ requires C, 67.26; H, 8.47; N, 4.36%); $[\alpha]_D^{24}$ 12.00 (*c* 1, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3436, 3075, 2957, 1493, 1452 and 1380; δ_H 0.98 (3 H, d, *J* 6.56, CH_3), 1.09 (3 H, d, *J* 6.62, CH_3), 1.31 (3 H, s, CH_3), 1.46 (3 H, s, CH_3), 3.04–3.06 (3 H, m, CHN, H_a-5 and CH_aH_bPh), 3.38 (1 H, d, *J* 13.34, H_b-5), 4.12–4.20 (3 H, m, H-3, H-4 and CH_aH_bPh), 4.49 (1 H, d, *J* 3.6, H-2), 5.96 (1 H, d, *J* 3.6, H-1) and 7.26–7.33 (5 H, m, ArH); δ_C(75.46 MHz; $CDCl_3$) 139.1 (arom C-*i*), 129.6 (arom C-*m*), 129.0 (arom C-*o*), 127.8 (arom C-*p*), 111.7 (CMe_2), 105.3 (C-1), 85.8 (C-2), 77.9 (C-3), 77.6 (C-4), 56.1 (NCH_2Ph), 48.8 (C-5), 47.8 ($NCMe_2$), 28.8 and 26.2 [$(CH_3)_2C$] and 19.8 and 14.1 [$(CH_3)_2$ CN].

5-*Deoxy*-1,2-O-*isopropylidene*-5-*thiomorpholino*-α-D-*xylofuranose* **1j**: 86% yield; mp 102–103 °C (Found: C, 52.5; H, 8.1; N, 5.1; S, 11.0. $C_{12}H_{21}NO_4S$ requires C, 52.34; H, 7.69; N, 5.09; S, 11.65%); $[\alpha]_D^{24}$ 12.10 (*c* 1, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3363, 3091, 2961, 2839, 1455, 1418, 1391, 1234, 1101, 1076 and 1001; δ_H 1.32 (3 H, s, CH_3), 1.47 (3 H, s, CH_3), 2.17 (1 H, s, OH), 2.65–2.75 (4 H, m, CH_2SCH_2), 2.81 (2 H, dd, *J* 2.75 and 14.83, H-5), 3.12–3.14 (4 H, m, CH_2NCH_2), 4.11 (1 H, m, H-4), 4.28 (1 H, d, *J* 2.32, H-3), 4.49 (1 H, d, *J* 3.58, H-2) and 5.95 (1 H, d, *J* 3.58, H-1); δ_C(75.46 MHz; $CDCl_3$) 111.4 (CMe_2), 104.8 (C-1), 85.5 (C-2), 77.7 (C-3), 77.4 (C-4), 57.8 (C-5), 56.4 (CH_2NCH_2), 27.7 and 26.4 [$(CH_3)_2C$] and 25.8 (CH_2SCH_2).

5-*Deoxy*-1,2-O-*isopropylidene*-5-(3,3,5-*trimethylhexahydroazepino*)-α-D-*xylofuranose* **1m**: 45% yield; bp 134–136 °C/0.15 mmHg (Found: C, 65.6; H, 10.5; N, 4.6. $C_{17}H_{31}NO_4$ requires C, 65.15; H, 9.97; N, 4.47%); $[\alpha]_D^{24}$ −4.82 (*c* 1, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3442, 3096, 2942, 1457 and 1379; δ_H 0.83–0.96 (9 H, m), 1.32 (3 H, s, CH_3), 1.47 (3 H, s, CH_3), 1.21–1.55 (4 H, m), 1.80–1.87 (1 H, m), 2.14–3.29 (6 H, m), 4.06–4.09 (1 H, m, H-4), 4.31 (1 H, d, *J* 2.54, H-3), 4.49 (1 H, d, *J* 2.70, H-2) and 5.96 (1 H, d, *J* 2.40, H-1); δ_C(75.46 MHz; $CDCl_3$) 111.7 (CMe_2), 105.4 (C-1), 86.0 (C-2), 78.2 (C-3), 77.3 (C-4), 67.9, 66.4, 58.5, 57.7, 53.2, 52.7, 49.9, 41.5, 32.5, 32.1, 29.0, 26.9 and 26.3 [$(CH_3)_2C$] and 22.7.

5-(3-*Azabicyclo*[3.2.2]*nonan*-3-*yl*)-5-*deoxy*-1,2-O-*isopropylidene*-α-D-*xylofuranose* **1n**: 49% yield; mp 106–107 °C (Found: C, 64.6; H, 9.2; N, 4.3. $C_{16}H_{27}NO_4$ requires C, 64.62; H, 9.15; N, 4.71%); $[\alpha]_D^{24}$ −3.60 (*c* 1, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3090, 2930, 2810, 1454 and 1380; δ_H 1.31 (3 H, s, CH_3), 1.46 (3 H, s, CH_3), 1.35–1.72 (8 H, m, 4 × CH_2), 1.88 (2 H, br s), 2.58–2.64 (2 H, m), 2.89–3.08 (4 H, m), 4.12–4.15 (1 H, m, H-4), 4.32 (1 H, d, *J* 2.75, H-3), 4.51 (1 H, d, *J* 3.64, H-2) and 5.97 (1 H, d, *J* 3.63, H-1); δ_C(75.46 MHz; $CDCl_3$) 111.7 (CMe_2), 105.5 (C-1), 86.1 (C-2), 78.4 (C-3), 77.3 (C-4), 65.6 (C-5), 57.8 (CH_2NCH_2), 30.0 [$C(CH_2)_3$], 26.9 and 26.2 [$(CH_3)_2C$] and 25.6 (CH_2).

5-*Deoxy*-1,2-O-*isopropylidene*-5-(1,6,6-*trimethyl*-3-*azabicyclo*[3.2.1]*octan*-3-*yl*)-α-D-*xylofuranose* **1o**: 64% yield; mp 70–71 °C (Found: C, 66.4; H, 9.75; N, 4.0. $C_{18}H_{31}NO_4$ requires C, 66.43; H, 9.60; N, 4.30%); $[\alpha]_D^{24}$ 5.47 (*c* 1, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3184, 2986, 1483 and 1382; δ_H 0.90 (3 H, s, CH_3), 1.04 (3 H, s, CH_3), 1.03–1.76 (7 H, m), 1.32 (3 H, s, CH_3), 1.47 (3 H, s, CH_3), 2.04–2.94 (2 H, m), 3.20–3.57 (5 H, m), 4.05–4.14 (1 H, m, H-4), 4.32 (1 H, d, *J* 2.0, H-3), 4.50 (1 H, d, *J* 3.1, H-2) and 5.98 (1 H, d, *J* 3.3, H-1); δ_C(75.46 MHz; $CDCl_3$) 111.7 (CMe_2), 105.4 (C-1), 86.0 (C-2), 78.3 (C-3), 77.3 (C-4), 66.5, 58.0, 51.7, 44.5, 41.6, 40.6, 37.0, 30.0 and 26.3 [$(CH_3)_2C$].

5-*Deoxy*-5-(*indolin*-1-*yl*)-1,2-O-*isopropylidene*-α-D-*xylofuranose* **1p**: 40% yield; mp 78–79 °C (Found: C, 66.85; H, 7.4; N, 5.05. $C_{16}H_{21}NO_4$ requires C, 65.96; H, 7.27; N, 4.81%); $[\alpha]_D^{24}$ 3.70 (*c* 1, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3401, 3045, 2902, 1605, 1493, 1383, 1273, 1219, 1066, 1018 and 858; δ_H 1.34 (3 H, s, CH_3), 1.52 (3 H, s, CH_3), 2.97 (2 H, t, *J* 7.55, CH_2CH_2N), 3.29–3.37 (1 H, m, H_a-5), 3.53–3.63 (3 H, m, NCH_2CH_2 and H_b-5), 4.33–4.35 (2 H, m, H-3 and -4), 4.54 (1 H, d, *J* 3.66, H-2), 6.00 (1 H, d, *J* 3.78, H-1), 6.74–6.82 (2 H, m, ArH) and 7.10–7.27 (2 H, m, ArH); δ_C(75.45 MHz; $CDCl_3$) 152.2, 130.4, 127.5, 124.7 and 119.6 (arom. C), 111.7 (CMe_2), 109.6 (arom. C), 104.9 (C-1), 85.5 (C-2), 78.3 (C-3), 77.3 (C-4), 56.2 (C-5), 50.5 (NCH_2CH_2), 28.9 (NCH_2CH_2), 26.7 and 26.2 [$(CH_3)_2C$].

5-*Deoxy*-1,2-O-*isopropylidene*-5-*methylamino*-α-D-*xylofuranose* **2a'**: 88% yield; mp 104–105 °C (Found: C, 53.6; H, 8.45; N, 6.8. $C_9H_{17}NO_4$ requires C, 53.19; H, 8.43; N, 6.89%); $[\alpha]_D^{24}$ 18.76 (*c* 1, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3247, 3069, 2935, 1494, 1461 and 1379; δ_H 1.32 (3 H, s, CH_3), 1.48 (3 H, s, CH_3), 2.41 (3 H, s, CH_3N), 2.92 (1 H, dd, *J* 1.4 and 13.0, H_a-5), 3.37 (1 H, dd, *J* 1.4 and 13.0, H_b-5), 4.20 (1 H, m, H-4), 4.21 (1 H, d, *J* 3.0, H-3), 4.50 (1 H, d, *J* 3.7, H-2) and 5.95 (1 H, d, *J* 3.6, H-1); δ_C(75.46 MHz; $CDCl_3$) 111.9 (CMe_2), 105.5 (C-1), 86.4 (C-2), 78.7 (C-3), 77.3 (C-4), 50.9 (C-5), 36.2 (NCH_3) and 27.6 and 26.3 [$(CH_3)_2C$].

5-*Deoxy*-1,2-O-*isopropylidene*-5-*propylamino*-α-D-*xylofuranose* **2b'**: 54% yield; mp 32–33 °C (Found: C, 57.6; H, 9.3; N, 6.05. $C_{11}H_{21}NO_4$ requires C, 57.12; H, 9.15; N, 6.06%); $[\alpha]_D^{24}$ 9.11 (*c* 1, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3445, 3298, 3142, 2953, 1456 and 1380; δ_H 1.32 (3 H, s, CH_3), 1.48 (3 H, s, CH_3), 1.43–1.53 (2 H, m, CH_2), 2.52 (1 H, dt, *J* 7.1 and 11.6, CH_aH_bN), 2.63

(1 H, dt, J 6.9 and 11.6, CH_aH_bN), 2.95 (1 H, dd, J 1.43 and 13.1, H_a-5), 3.40 (1 H, dd, J 3.6 and 12.9, H_b-5), 4.20 (1 H, m, H-4), 4.29 (1 H, d, J 2.8, H-3), 4.49 (1 H, d, J 3.6, H-2) and 5.96 (1 H, d, J 3.6, H-1); δ_C (75.46 MHz; $CDCl_3$) 111.8 (CMe_2), 105.5 (C-1), 86.5 (C-2), 78.6 (C-3), 77.3 (C-4), 51.6 (C-5), 48.7 (NCH_2), 26.9 and 26.3 [$(CH_3)_2C$], 22.8 (CH_2CH_3) and 11.7 (CH_3).

5-Deoxy-5-isopropylamino-1,2-O-*isopropylidene*-α-D-*xylofuranose* **2c'**: 54% yield; bp 152–153 °C/0.15 mmHg (Found: C, 56.9; H, 9.2; N, 6.2%); $[\alpha]_D^{24}$ 14.00 (*c* 1, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3289, 3183, 2956 and 1380; δ_H 1.06 (3 H, d, J 6.4, CH_3), 1.08 (3 H, d, J 6.3, CH_3), 1.32 (3 H, s, CH_3), 1.48 (3 H, s, CH_3), 2.77 (hept, J 6.3, NCH), 2.97 (1 H, dd, J 2.3 and 12.9, H_a-5), 3.38 (1 H, dd, J 3.5 and 12.8, H_b-5), 4.22–4.23 (1 H, m, H-4), 4.29 (1 H, d, J 3.0, H-3), 4.49 (1 H, d, J 3.7, H-2) and 5.96 (1 H, d, J 3.7, H-1); δ_C(75.46 MHz; $CDCl_3$) 111.8 (CMe_2), 105.5 (C-1), 86.5 (C-2), 78.6 (C-3), 77.3 (C-4), 48.9 (C-5), 46.1 (NCH_2), 27.0 and 26.3 [$(CH_3)_2C$] and 22.8 and 22.5 (CH_3).

5-(tert-*Butylamino*)-5-*deoxy*-1,2-O-*isopropylidene*-α-D-*xylofuranose* **2d'**: 45% yield; mp 67–58 °C (Found: C, 58.5; H, 9.45; N, 5.5. $C_{12}H_{23}NO_4$ requires C, 58.75; H, 9.45; N, 5.71%); $[\alpha]_D^{24}$ 17.40 (*c* 1, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3364, 3051, 2927, 1492 and 1384; δ_H 1.10 (9 H, s, CH_3), 1.32 (3 H, s, CH_3), 1.48 (3 H, s, CH_3), 2.97 (1 H, dd, J 1.31 and 12.8, H_a-5), 3.36 (1 H, dd, J 3.57 and 12.8, H_b-5), 4.23–4.29 (1 H, m, H-4), 4.29 (1 H, d, J 3.03, H-3), 4.48 (1 H, d, J 3.7, H-2) and 5.96 (1 H, d, J 3.8, H-1); δ_C (75.46 MHz; $CDCl_3$) 111.8 (CMe_2), 105.5 (C-1), 86.5 (C-2), 77.7 (C-3), 77.3 (C-4), 50.4 (C-5), 41.6 [$NCMe_3$], 28.5 (CH_3), 27.0 and 26.3 [$(CH_3)_2C$].

5-Cyclohexylamino-5-deoxy-1,2-O-*isopropylidene*-α-D-*xylofuranose* **2e'**: 88% yield; mp 68–69 °C (Found: C, 62.2; H, 9.6; N, 5.1. $C_{14}H_{25}NO_4$ requires C, 61.97; H, 9.29; N, 5.16%); $[\alpha]_D^{24}$ 15.17 (*c* 1, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3223, 3219, 2971, 1453 and 1381; δ_H 1.04–1.29 (5 H, m), 1.32 (3 H, s, CH_3), 1.48 (3 H, s, CH_3), 1.57–1.69 (1 H, m), 1.70–1.75 (2 H, m), 1.83–1.92 (2 H, m), 2.38–2.44 (1 H, m, NCH), 3.01 (1 H, dd, J 1.3 and 12.9, H_a-5), 3.42 (1 H, dd, J 3.5 and 12.9, H_b-5), 4.20–4.22 (1 H, m, H-4), 4.28 (1 H, d, J 3.0, H-3), 4.49 (1 H, d, J 3.6, H-2) and 5.96 (1 H, d, J 3.8, H-1); δ_C(75.46 MHz; $CDCl_3$) 111.8 (CMe_2), 105.5 (C-1), 86.5 (C-2), 78.6 (C-3), 77.3 (C-4), 56.5 (C-5), 45.7 (NCH), 33.3 (CH_2), 33.0 (CH_2), 27.0 and 26.3 [$(CH_3)_2C$], 26.0, 24.9 and 24.8 (CH_2).

5-Deoxy-1,2-O-*isopropylidene*-5-(1,1,3,3-*tetramethylbutylamino*)-α-D-*xylofuranose* **2f'**: 61% yield; mp 62–63 °C (Found: C, 63.7; H, 10.6; N, 4.6. $C_{16}H_{31}NO_4$ requires C, 63.76; H, 10.37; N, 4.65%); $[\alpha]_D^{24}$ 11.86 (*c* 1, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3299, 3184, 2943, 1480 and 1381; δ_H 1.00 (9 H, s, CH_3), 1.13 (3 H, s, CH_3), 1.17 (3 H, s, CH_3), 1.32 (3 H, s, CH_3), 1.42 (2 H, d, J 10.73, CH_2), 1.48 (3 H, s, CH_3), 2.96 (1 H, d, J 12.57, H_a-5), 3.35 (1 H, dd, J 3.51 and 12.57, H_b-5), 4.25–4.28 (2 H, m, H-3 and -4), 4.48 (1 H, d, J 3.56, H-2) and 5.95 (1 H, d, J 3.57, H-1); δ_C(75.46 MHz; $CDCl_3$) 111.9 (CMe_2), 105.5 (C-1), 86.5 (C-2), 8.6 (C-3), 77.4 (C-4), 54.4 (C-5), 53.6 (CMe_2), 41.1, 31.8, 31.7, 28.2 and 28.1 (CMe_3, CH_2 and CH_3) and 27.0 and 26.3 [$(CH_3)_2C$].

5-(1-*Adamantylamino*)-5-*deoxy*-1,2-O-*isopropylidene*-α-D-*xylofuranose* **2g'**: 51% yield; mp 112–113 °C (Found: C, 66.4; H, 9.1; N, 4.3. $C_{18}H_{29}NO_4$ requires C, 66.85; H, 9.04; N, 4.33%); $[\alpha]_D^{24}$ 16.69 (*c* 1, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3284, 3059, 2905, 1461 and 1346; δ_H 1.32 (3 H, s, CH_3), 1.48 (3 H, s, CH_3), 1.48–1.69 (12 H, m), 2.08 (3 H, br s), 3.03 (1 H, d, J 12.8, H_a-5), 3.37 (1 H, dd, J 3.45 and 12.8, H_b-5), 4.21–4.23 (1 H, m, H-4), 4.28 (1 H, d, J 3.02, H-3), 4.48 (1 H, d, J 3.79, H-2) and 5.96 (1 H, d, J 3.79, H-1); δ_C(75.46 MHz; $CDCl_3$) 111.5 (CMe_2), 105.2 (C-1), 86.2 (C-2), 78.3 (C-3), 76.9 (C-4), 50.2 (C-5), 41.9 [$C(CH_2)_3N$], 39.2, 36.3 and 29.1 (adamantyl C) and 26.6 and 26.3 [$(CH_3)_2C$].

5-Benzylamino-5-deoxy-1,2-O-*isopropylidene*-α-D-*xylofuranose* **2h'**: 88% yield; mp 64–65 °C (Found: C, 65.0; H, 7.7; N, 5.1. $C_{15}H_{21}NO_4$ requires C, 64.50; H, 7.58; N, 5.01%); $[\alpha]_D^{24}$ 11.62 (*c* 1, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3103, 2859, 2983, 1473, 1493 and 1370; δ_H 1.32 (3 H, s, CH_3), 1.47 (3 H, s, CH_3), 3.00 (1 H, dd, J 1.4 and 13.0, H_a-5), 3.40 (1 H, dd, J 3.6 and 12.9, H_b-5), 3.78 (2 H, d, J 3.2, NCH_2Ph), 4.21–4.23 (1 H, m, H-4), 4.29 (1 H, d, J 2.2, H-3), 4.50 (1 H, d, J 3.6, H-2), 5.95 (1 H, d, J 3.6, H-1) and 7.26–7.37 (5 H, m, ArH); δ_C(75.46 MHz; $CDCl_3$) 139.0 (arom C-*i*), 129.1 (arom C-*m*), 128.7 (arom C-*o*), 128.0 (arom C-*p*), 111.9 (CMe_2), 105.5 (C-1), 86.3 (C-2), 78.5 (C-3), 77.3 (C-4), 54.0 (NCH_2Ph), 48.1 (C-5) and 27.0 and 26.3 [$(CH_3)_2C$].

Enantioselective addition of dialkylzincs to aldehydes in the presence of 5 mol% of catalyst 1 or 2

The following procedure is representative. Under nitrogen a toluene solution (3.6 cm^3) of diethylzinc (4 mmol) was added to a solution of catalyst **1i** (25.9 mg, 0.1 mmol) in toluene (0.4 cm^3) at 0 °C; the mixture was warmed to room temperature (~ 25 °C) and stirred for 30 min. After benzaldehyde (212 mg, 2 mmol) was added to this, the mixture was stirred at the same temperature for 10 h and then diluted with diethyl ether (15 cm^3). The excess of diethylzinc was destroyed by addition of 1.5 M HCl (10 cm^3). The mixture was then extracted with diethyl ether (3 × 15 cm^3). GLC analysis indicated the formation of 1-phenylpropan-1-ol in 90% yield. The extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The product alcohol was isolated by bulb-to-bulb distillation and was further purified with silica gel column chromatography. Ee was measured by GLC analysis of the diastereoisomeric (*R*)-(+)-MTPA ester of the product alcohol using a 50 m methyl silicon capillary column. The diastereoisomeric ratio by GLC analysis showed a composition of 98% (*R*) and 2% (*S*) (*i.e.*, 96% ee) (Table 4). Similarly, using 2, 10 and 25 mol% of catalyst **1i** in the same reaction, the product alcohols with 89, 96 and 96% ee, respectively, were obtained. When the same reaction in the presence of 5 mol% of catalyst **1i** was carried out at −25, 0 and 70 °C, the product alcohols were obtained as follows: at −25 °C, 41% yield (48 h), 20% ee; at 0 °C, 88% yield (24 h), 96% ee; at 70 °C, 90% yield (2 h), 75% ee (Table 2).

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