Polymer-bound *N*-Alkylnorephedrines as Efficient Chiral Catalysts for the Enantioselective Addition of Dialkylzincs to both Aromatic and Aliphatic Aldehydes

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Polymer-bound *N*-alkylnorephedrines are recyclable catalysts of the enantioselective addition of dialkylzincs to both aromatic and aliphatic aldehydes. Optically active aromatic and aliphatic *secondary* alcohols are obtained in high enantiomeric excess. The catalyst derived from *N*-methylnorephedrine (ephedrine) affords aliphatic alcohols of up to 89% e.e. in the alkylation of *aromatic* aldehydes. On the other hand, the catalyst derived from *N*-ethylnorephedrine affords up to 80% e.e. in the alkylation of *aliphatic* aldehydes.

Increasing interest has been directed to catalytic asymmetric reactions.[1a,b] Among these reactions, a carbon–carbon bond-forming reaction is one of the most important. On the other hand, polymer-bound reagents have been widely utilized in organic chemistry because of the easy product isolation and work-up.[1c,d] In many cases, they can be easily recovered and recycled. Enzymes are considered to be naturally occurring polymer-bound catalysts which have high selectivities. Design of synthetic polymer-bound catalysts is interesting because these catalysts can be considered to be analogous to enzymes (biologically active macromolecules).

In spite of many efforts to use chiral polymer-bound catalysts in asymmetric syntheses, optical yields have been low to moderate in catalytic asymmetric carbon–carbon bond-forming reactions such as Michael addition[2] and hydrocyanation.[3] Stille very recently reported a highly selective asymmetric hydroformylation using polymer-bound catalyst,[4] although the yield of the product was low. Thus, it is a challenging problem to find a polymer-bound catalyst which performs highly stereoselective asymmetric reactions.

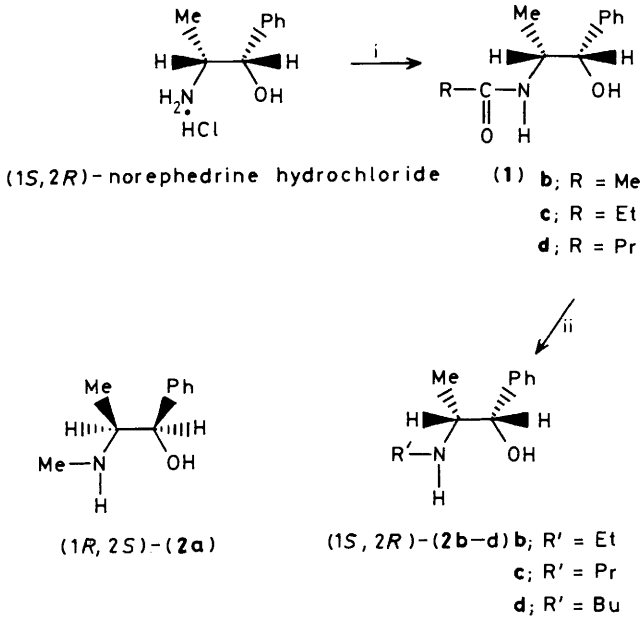
On the other hand, enantioselective addition of dialkylzincs to aldehydes has been reported to occur in the presence of monomeric chiral amino alcohols as catalysts.[5,6] We have already reported an enantioselective addition of dialkylzincs to aldehydes, using *N*,*N*-dibutylnorephedrine as a monomeric catalyst.[7]

In this paper, we describe the enantioselective addition of dialkylzincs to both aromatic and aliphatic aldehydes, using polymer-bound *N*-alkylnorephedrines as *polymeric* catalysts.[8]

Results and Discussion

Preparation of Polymer-bound N-*Alkylnorephedrines.*—*N*-Methylnorephedrine, *i.e.* ephedrine (**2a**), is commercially available in either enantiomeric form. On the other hand, *N*-alkylnorephedrines (**2b**—**d**) were easily prepared from norephedrine which is also inexpensive and readily available in either enantiomeric form. (1*S*,2*R*)-Norephedrine hydrochloride was treated with various acid chlorides under alkaline (Schotten–Baumann) reaction conditions. The corresponding amides (**1b**—**d**) were obtained in 56—90% yield. Subsequent reduction of amides (**1b**—**d**) with borane–tetrahydrofuran (THF) complex afforded (1*S*,2*R*)-N-alkylnorephedrines (**2b**—**d**) in 49—66% yield (Scheme 1). Results are summarized in Table 1.

Then polymer-bound *N*-alkylnorephedrines (**3a**—**d**) were prepared in 84—93% yield from the reaction of (1*R*,2*S*)-(**2a**) or (1*S*,2*R*)-(**2b**—**d**) and chloromethylated polystyrene (1% divinylbenzene; chlorine content 0.8 mmol g^{-1}; 100—200 mesh) in the presence of potassium carbonate according to the literature procedure (Scheme 2).†



Scheme 1. *Reagents:* i, RCOCl, 2M aq. NaOH; ii, BH_3–THF

Enantioselective Addition of Dialkylzincs to Aldehydes using Compound (**3**) *as a Catalyst.*—We first examined the enantioselective addition of dialkylzincs to various aldehydes at room temperature in the presence of 10 mol% of compound (**3a**) as a catalyst (Scheme 3, Table 2). Reaction of benzaldehyde and diethylzinc in hexane for 45 h afforded (*R*)-(+)-1-phenylpropan-1-ol (**6a**) in 83% yield and in 89% e.e. (entry 1). As to the effect of solvents, the reaction in hexane was faster than in toluene. The same reaction in toluene for 93 h afforded (*R*)-(+)-(**6a**) of 80% e.e.; however, synthetic yield was only 58% even after prolonged reaction time (93 h). Catalyst (**3a**) swelled in toluene; in contrast

† The complex of the polymer-bound ephedrine and lithium aluminium hydride has been used in non-catalytic asymmetric reduction of acetophenone: J. M. J. Frèchet, E. Bald, and P. Lecavalier, *J. Org. Chem.*, 1986, **51**, 3462.

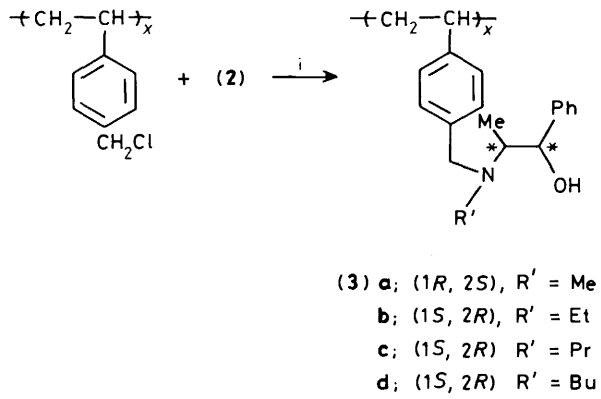
Table 1. Synthesis of *N*-alkylnorephedrines (**2b—d**)

(**1**)		(1*S*,2*R*)-(**2b—d**) hydrochloride				
R	Yield (%)		R′	Yield (%)	$[\alpha]_D$ (*c* in H_2O)	M.p. (°C)
Me	56	(**2b**)	Et	66	$[\alpha]^{22}$ +26.8° (1.98)	215.0—215.8 (decomp.)
Et	66	(**2c**)	Pr	49	$[\alpha]^{22}$ +21.5° (2.01)	224.8—225.5 (decomp.)
Pr	49	(**2d**)	Bu	60	$[\alpha]^{20}$ +19.0° (2.00)	228.8—229.2 (decomp.)

Table 2. Enantioselective addition of dialkylzincs (**5**) to aldehydes (**4**) using compound (**3a**) as catalyst

			(*R*)-(**6**)			
Entry	R	R′		Yield (%)	$[\alpha]_D$ (*c*, solvent)	E.e. (%)[a]
1	Ph	Et	(**6a**)	83	$[\alpha]^{24}$ +40.5° (5.21, $CHCl_3$)	89
2	Ph	Pr	(**6b**)	57	$[\alpha]^{23}$ +37.6° (1.17, PhH)	86
3	Ph	Me	(**6c**)	43	$[\alpha]^{26}$ +14.3° (1.12, c-C_5H_{11})	33
4	*p*-ClC_6H_4	Et	(**6d**)	78	$[\alpha]^{27}$ +20.1° (5.03, PhH)	83
5[b]	*p*-ClC_6H_4	Et	(**6d**)	77	$[\alpha]^{24}$ +18.7° (5.01, PhH)	77
6[c]	*p*-ClC_6H_4	Et	(**6d**)	69	$[\alpha]^{22}$ +18.4° (5.01, PhH)	76
7	*p*-$MeOC_6H_4$	Et	(**6e**)	75	$[\alpha]^{26}$ +18.1° (5.07, PhH)	54
8	*o*-$MeOC_6H_4$	Et	(**6f**)	79	$[\alpha]^{26}$ +27.6° (2.03, PhMe)	51[d]
9	2-Naphthyl	Et	(**6g**)	78	$[\alpha]^{26}$ +23.7° (5.35, PhH)	56
10	$Me[CH_2]_5$	Et	(**6h**)	64	$[\alpha]^{23}$ −3.56° (4.39, $CHCl_3$)	37
11	$Me[CH_2]_7$	Me	(**6i**)	47	$[\alpha]^{23}$ −2.39° (3.01, EtOH)	27

[a] Based on the reported values of $[\alpha]_D$ +45.45° (*c* 5.15 in $CHCl_3$) for (*R*)-(**6a**);[9] $[\alpha]_D^{20}$ +43.6° (*c* 4.18 in PhH) for (*R*)-(**6b**);[10] $[\alpha]_D^{20}$ −43.1° (*c* 7.19 in cyclo-C_5H_{10}) for (*S*)-(**6c**);[11] $[\alpha]_D$ −10.4° (*c* 5 in PhH) for (*S*)-(**6d**) in 43% e.e.;[12] $[\alpha]_D$ −17.2° (*c* 5 in PhH) for (*S*)-(**6e**) in 51% e.e.;[12] $[\alpha]_D^{20}$ + 47.0° (*c* 1 in PhMe) for (**6f**) in 87% e.e.;[13] $[\alpha]_D^{20}$ −18.81° (PhH) for (*S*)-(**6g**) for 44.7% e.e.;[14] $[\alpha]_D^{24}$ +9.6° (*c* 8.3 in $CHCl_3$) for (*S*)-(**6h**);[15] $[\alpha]_D^{20}$ + 8.89° (EtOH) for (*S*)-(**6i**).[16] [b] First recycle. [c] 2nd recycle. [d] Configuration is tentatively assumed.

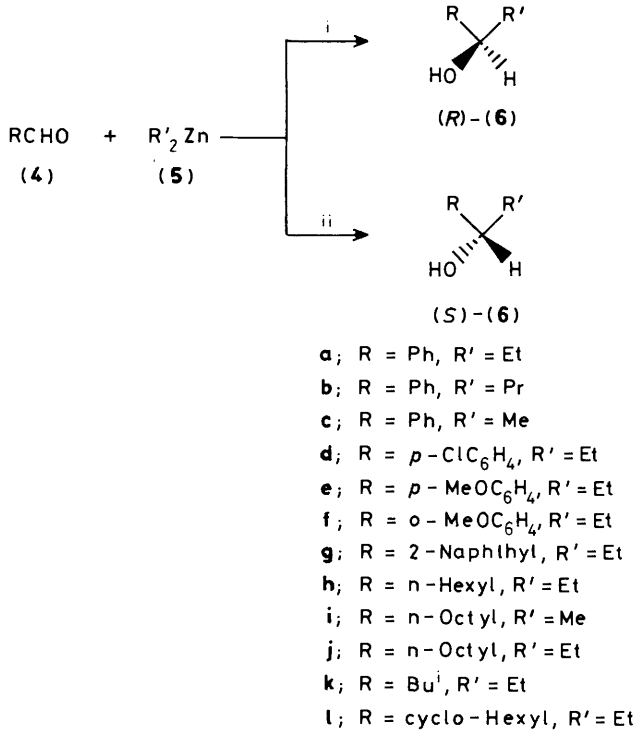


Scheme 2. *Reagent:* i, K_2CO_3, toluene

very little swelling was observed in hexane. Catalyst (**3a**) was easily removed from the reaction mixture by a simple filtration in 95% recovery. Other aromatic aldehydes were also ethylated enantioselectively in moderate to high e.e.s. Recovered catalyst (**3a**), dried after alkaline treatment, was used repeatedly without considerable change in enantioselectivity (entries 5 and 6).

As to the effect of the structure of dialkylzinc reagents, reaction of dipropylzinc with benzaldehyde afforded (*R*)-(+)-1-phenylbutan-1-ol (**6b**) in 86% e.e. (entry 2). On the other hand, reaction of dimethylzinc was slow and enantioselectivity was low (entry 3).

As described above, polymer-bound ephedrine (**3a**) catalysed the enantioselective alkylation of aromatic aldehydes to afford the corresponding optically active *secondary* alcohols in high e.e.s. However, attempted reactions with aliphatic aldehydes using (**3a**) as catalyst gave disappointing results (entries 10 and 11).



Scheme 3. *Reagents:* i, 10 mol % catalyst (**3a**); ii, 10 mol % catalyst (**3b—d**)

Enantioselective Addition of Diethylzinc to (Aliphatic) Aldehydes using Polymer-bound N-*Alkylnorephedrines* (**3b—d**).—In order to find a catalyst which is effective for enantioselective addition to aliphatic aldehydes, we investigated

Table 3. Enantioselective addition of diethylzinc to aldehydes (**4**) using compounds (**3a—d**) as catalysts

Entry	Aldehyde (**4**) R	Catalyst	Time (h)	(**6**)	Yield (%)	$[\alpha]_D$ (*c*, solvent)	E.e. (%)[a]
1	$Me[CH_2]_5$	(**3a**)	97	(**6h**)	64	$[\alpha]^{23}$ −3.56° (4.39, $CHCl_3$)	37 (*R*)
2	$Me[CH_2]_5$	(**3b**)	137	(**6h**)	67	$[\alpha]^{23}$ +5.88° (6.57, $CHCl_3$)	61 (*S*)
3	$Me[CH_2]_5$	(**3c**)	156	(**6h**)	65	$[\alpha]^{24}$ +3.62° (6.14, $CHCl_3$)	38 (*S*)
4	$Me[CH_2]_5$	(**3d**)	71	(**6h**)	49	$[\alpha]^{25}$ +3.71° (2.59, $CHCl_3$)	39 (*S*)
5	$Me[CH_2]_7$	(**3a**)	137	(**6j**)	63	$[\alpha]^{23}$ −2.99° (5.69, EtOH)	48 (*R*)
6	$Me[CH_2]_7$	(**3b**)	137	(**6j**)	88	$[\alpha]^{25}$ +4.99° (7.57, EtOH)	80 (*S*)
7	$Me[CH_2]_7$	(**3c**)	162	(**6j**)	65	$[\alpha]^{24}$ +3.08° (4.67, EtOH)	50 (*S*)
8	$Me[CH_2]_7$	(**3d**)	113	(**6j**)	65	$[\alpha]^{22}$ +3.16° (4.12, EtOH)	51 (*S*)
9	Me_2CHCH_2	(**3a**)	87	(**6k**)	43	$[\alpha]^{25}$ −7.17° (2.93, EtOH)	35 (*R*)
10	Me_2CHCH_2	(**3b**)	89	(**6k**)	49	$[\alpha]^{24}$ +11.1° (2.57, EtOH)	54 (*S*)
11	Me_2CHCH_2	(**3c**)	61	(**6k**)	49	$[\alpha]^{23}$ +11.6° (2.21, EtOH)	57 (*S*)
12	Me_2CHCH_2	(**3d**)	42	(**6k**)	84	$[\alpha]^{25}$ +8.01° (1.56, EtOH)	40 (*S*)
13	cycio-C_6H_{11}	(**3a**)	43	(**6l**)	49	$[\alpha]^{25}$ +2.67° (2.45, Et_2O)	42 (*R*)
14	cyclo-C_6H_{11}	(**3b**)	43	(**6l**)	55	$[\alpha]^{25}$ −3.20° (2.75, Et_2O)	50 (*S*)
15	cyclo-C_6H_{11}	(**3c**)	63	(**6l**)	59	$[\alpha]^{23}$ −2.05° (4.39, Et_2O)	33 (*S*)
16	cyclo-C_6H_{11}	(**3d**)	46	(**6l**)	49	$[\alpha]^{23}$ −3.33° (2.40, Et_2O)	52 (*S*)
17	Ph	(**3a**)	45	(**6a**)	83	$[\alpha]^{24}$ −40.5° (5.21, $CHCl_3$)	89 (*R*)
18	Ph	(**3b**)	117	(**6a**)	72	$[\alpha]^{23}$ −18.4° (4.53, $CHCl_3$)	41 (*S*)
19	Ph	(**3c**)	157	(**6a**)	70	$[\alpha]^{24}$ −13.0° (4.10, $CHCl_3$)	29 (*S*)
20	Ph	(**3d**)	115	(**6a**)	64	$[\alpha]^{25}$ −7.88° (4.44, $CHCl_3$)	17 (*S*)

[a] Based on the reported values of $[\alpha]_D^{24}$ +9.6° (*c* 8.3 in $CHCl_3$) for (*S*)-(**6h**);[15] $[\alpha]_D^{20}$ −6.22° (EtOH) for (*R*)-(**6j**);[15] $[\alpha]_D^{21}$ −20.3° (*c* 5.25 in EtOH) for (*R*)-(**6k**);[15] $[\alpha]_D^{21.5}$ −6.4 (Et_2O) for (*S*)-(**6l**);[17] $[\alpha]_D$ +45.45° (*c* 5.15 in $CHCl_3$) for (*R*)-(**6a**).[9]

the structure of the amino alcohol moiety of the catalyst. We thought that the catalyst would be effective with aliphatic aldehydes if it has a more bulky substituent than methyl on the nitrogen atom of norephedrine. Therefore we synthesized some *N*-alkylnorephedrines from (1*S*,2*R*)-norephedrine. These were attached to chloromethylated polystyrene by the method described above. We examined the enantioselective ethylation of various aliphatic aldehydes and benzaldehyde using polymer-bound catalysts (**3b—d**) having ethyl (**3b**), propyl (**3c**), and butyl (**3d**) groups as *N*-substituents (Scheme 3). The results are shown in Table 3 and the Figure. The following conclusions can be drawn from a quick survey of the Figure. (1) For the alkylation of benzaldehyde (aromatic aldehyde), catalyst (**3a**) was the most enantioselective. (2) For the alkylation of aliphatic aldehydes, catalyst (**3b**) was the most enantioselective.

Enantioselective addition of diethylzinc to aliphatic aldehydes such as heptanal and nonanal with straight carbon chains was examined. E.e.s of the obtained secondary alcohols were relatively high when catalyst (**3b**) with an *N*-ethyl substituent was used (Table 3, entries 2, 6, and 10). (*S*)-(+)-Undecan-3-ol (**6j**) was obtained in 80% e.e. from the ethylation of nonanal (entry 6). On the other hand, moderate e.e.s were observed using (**3a**), (**3c**), or (**3d**) as catalysts. Configuration of the alcohols obtained from the reaction using catalysts (**3b—d**) was opposite to that from the reaction using (**3a**). This is due to the difference in the absolute configuration of (1*R*,2*S*)-ephedrine and (1*S*,2*R*)-norephedrine which were utilized in the synthesis of catalysts (**3a**) and (**3b—d**) respectively.

For the enantioselective ethylation of 3-methylbutanal, with a branched carbon chain, catalysts (**3b**) and (**3c**) afforded (*S*)-(+)-5-methylhexan-3-ol (**6k**) of good e.e. (entries 10, 11). For the ethylation of cyclohexanecarbaldehyde, a cyclic aliphatic aldehyde, no particular tendency was observed in the relation of e.e.s of the alcohol and the catalysts used. (*S*)-(−)-1-Cyclohexylpropan-1-ol (**6l**) of moderate e.e. was obtained using catalysts (**3b**) and (**3d**) (entries 14 and 16).

On the other hand, when enantioselective addition of Et_2Zn to benzaldehyde (aromatic aldehyde) was examined using

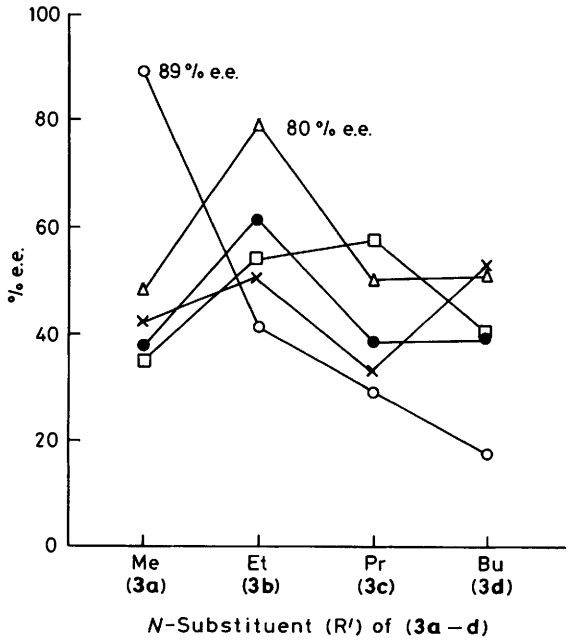


Figure 1. Relation between *N*-alkyl groups (R′) of the catalyst (**3a—d**) and e.e.s of the alcohols obtained from the enantioselective ethylation of aldehydes (**2**; RCHO): R = ●, $Me(CH_2)_5$; △, $Me(CH_2)_7$; □, Me_2CHCH_2; x, c-C_6H_{11}; ○, Ph.

catalysts (**3a—d**) (entries 17—20) it was found that the enantioselectivities of the reactions with benzaldehyde decreased according to the increasing number of carbon atoms in the *N*-alkyl group of the catalyst. The highest e.e. being observed on using compound (**3a**) with the shortest *N*-alkyl group (methyl group). Thus in the case of aromatic aldehydes, unlike the case of aliphatic aldehydes, catalyst (**3a**) with a small *N*-alkyl (methyl) group was the most effective.

As described above, polymer-bound norephedrine derivatives (**3b—d**) catalysed highly enantioselective addition of dialkylzincs to both aromatic and aliphatic aldehydes.

Enantioselective ethylation to *aromatic* aldehydes has been very recently reported, in a preliminary communication, using chiral polymer-bound catalysts.[18] However, addition to *aliphatic* aldehydes has not been described.

Conclusions.—Polymer-bound ephedrine was an efficient catalyst for the enantioselective addition of dialkylzincs to aromatic aldehydes. Optically active aromatic *secondary* alcohols were obtained in high e.e. On the other hand, polymer-bound *N*-ethylnorephedrine catalysed the enantioselective addition to aliphatic aldehydes to afford optically active aliphatic alcohols in moderate to high e.e.

Because both enantiomers of ephedrine and norephedrine are commercially available, either configuration of the optically active *secondary* alcohols should be obtained by using the polymer-bound catalysts of appropriate configurations.

Experimental

General.—M.p.s were measured with a Yamato MP-21 melting point apparatus and are uncorrected. I.r. spectra, ^{1}H n.m.r. spectra, and optical rotations were recorded respectively with a Hitachi 260-10 spectrophotometer, a JEOL JNM-PMX-60 spectrometer, and a JASCO DIP-181 polarimeter. Bulb-to-bulb distillation was carried out with a Shibata Glass Tube Oven GTO-250. Toluene and hexane were distilled over lithium aluminium hydride. All the reactions were performed under argon except for Schotten–Baumann reaction. Diethylzinc in hexane was purchased from Kanto Chemical Co., and chloromethylated polystyrene (1% divinylbenzene; chlorine content 0.8 mmol g^{-1}; 100—200 mesh) was purchased from Wako Pure Chemical Industries.

Synthesis of (1S,2R)-2-*Ethylamino*-1-*phenylpropan*-1-*ol* (**2b**).—To a solution of (1*S*,2*R*)-norephedrine hydrochloride (5.64 g, 30 mmol) in 2M aq. NaOH (15 ml) and ether (5 ml) in an ice-bath were added acetyl chloride (2.5 ml, 35.2 mmol) and 2M aq. NaOH (15 ml) simultaneously during 10 min with vigorous stirring of the mixture. THF (20 ml) was added to dissolve the precipitative and the mixture was stirred 30 min at 0 °C. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (5 × 50 ml). The combined organic layer was washed with 5% aq. $NaHCO_3$ (2 × 100 ml) and dried (Na_2SO_4). The solvent was evaporated off under reduced pressure and the residual solid was washed with ether (50 ml) to give the amide (**1b**) (3.27 g, 56%).

To a solution of amide (**1b**) (2.94 g, 15.2 mmol) in THF (15 ml) in an ice-bath was added 1M BH_3–THF (38 ml, 38 mmol) during 20 min. The reaction mixture was stirred for 2.5 h at room temperature and quenched by addition of 6M HCl (20 ml). The solvent was evaporated off under reduced pressure and the aqueous layer was washed with ether (2 × 15 ml), then made alkaline (pH 9) by addition of 10M NaOH and extracted with AcOEt (6 × 50 ml). The combined organic layer was dried (Na_2SO_4), and evaporated under reduced pressure. The residue was treated with dry HCl (2M solution in AcOEt; 8 ml). *Compound* (**2b**) was obtained as its *hydrochloride* (2.48 g, 66%), m.p. 215.0—215.8 °C (decomp.); $[\alpha]_D^{22}$ +26.8° (*c* 1.98 in H_2O); $\nu_{max.}$ 3 300, 2 980, 2 870, 1 610, 1 500, and 1 460 cm^{-1}; δ ($CDCl_3$) 0.90 (3 H, d), 1.12 (3 H, t), 2.23—3.07 (5 H, m), 4.67 (1 H, d), and 7.23 (5 H, s) (for hydrochloride: Found: C, 61.3; H, 8.3; N, 6.5. $C_{11}H_{18}ClNO$ requires C, 61.25; H, 8.41; N, 6.49%).

Synthesis of (1S,2R)-1-*Phenyl*-2-*propylaminopropan*-1-*ol* (**2c**).—This was synthesized from (1*S*,2*R*)-norephedrine hydrochloride and propionyl chloride according to the same procedure described in the synthesis of (**2b**). Yield of amide (**1c**) was 66%. Yield of *title compound*, (**2c**) was 49%, m.p. 224.8—225.5 °C (decomp.) as its *hydrochloride;* $[\alpha]_D^{22}$ +21.5° (*c* 2.01 in H_2O); $\nu_{max.}$ 3 300, 2 960, 2 860, 1 600, 1 500, and 1 450 cm^{-1}; δ ($CDCl_3$) 0.73—1.17 (6 H, m), 1.23—1.80 (2 H, m), 2.17—3.00 (5 H, m), 4.70 (1 H, d), and 7.23 (5 H, s) (for hydrochloride: Found: C, 62.8; H, 9.05; N, 6.1. $C_{12}H_{20}ClNO$ requires C, 62.74; H, 8.77; N, 6.10%).

Synthesis of (1S,2R)-2-*Butylamino*-1-*phenylpropan*-1-*ol* (**2d**).—This was synthesized from (1*S*,2*R*)-norephedrine hydrochloride and butyryl chloride according to the same procedure described in the synthesis of (**2b**). Yield of amide (**1d**) was 90%. *Compound* (**2d**) was obtained as its *hydrochloride* in 60% yield, m.p. 228.8—229.2 °C (decomp.); $[\alpha]_D^{20}$ +19.0° (*c* 2.00 in H_2O); $\nu_{max.}$ 3 350, 3 100, 2 960, 2 860, 1 600, 1 500, and 1 450 cm^{-1}; δ ($CDCl_3$) 0.73—1.67 (10 H, m), 1.97—3.07 (5 H, m), 4.70 (1 H, d), and 7.27 (5 H, s) (for hydrochloride: Found: C, 64.3; H, 9.4; N, 5.7. $C_{13}H_{22}ClNO$ requires C, 64.05; H, 9.10; N, 5.75%).

General Procedure for the Preparation of Polymer-bound N-*Alkylnorephedrines* (**3a—d**).—A mixture of (1*R*,2*S*)-ephedrine (**2a**) (5.97 mmol) or (1*S*,2*R*)-*N*-alkylnorephedrine (**2b-d**) (5.97 (mmol), anhydrous potassium carbonate (1.55 g, 11.2 mmol), and chloromethylated polystyrene (2.97 g, 2.13 mmol of chlorine) in toluene (25 ml) was refluxed for 30 h. The polymer was then filtered off and washed successively with water, MeOH, THF, aq. THF, THF, and MeOH (each 50 ml). After being dried *in vacuo* at 40 °C for 5 h, polymers (**3a—d**) were obtained respedtively in 91 (**3a**), 84 (**3b**), 89 (**3c**), and 93% (**3d**) yield.

General Procedure for the Enantioselective Alkylation of Aldehydes using Compounds (**3a—d**) *as Catalysts. Synthesis of Optically Active Secondary Alcohols* (**6a—l**).—An aldehyde (**4**) (0.12 ml, 1.18 mmol) was added to a suspension of catalyst (**3a—d**) (10 mol % of *N*-alkylnorephedrine to aldehyde) in hexane (3 ml) in an ice-bath. After 10 min, a dialkylzinc (**5**) (2.55 mmol, 2.55 ml of 1M hexane solution) was added during 10 min. The reaction mixture was stirred at room temperature and quenched by addition of 1M HCl (5 ml). The catalyst was removed by filtration and was washed several times with dichloromethane. The aqueous layer was extracted with dichloromethane (3 × 15 ml). The combined organic solvent was dried over anhydrous sodium sulphate and evaporated under reduced pressure. The residue was purified by silica gel t.l.c. [hexane–AcOEt (5:1) as developing solvent]. Optically active secondary alcohols (**6a—l**) were obtained.

Recovery of Polymer-bound Catalyst (**1**).—The recovered polymer (**1**) from the filtration was stirred for 4 h in a 4:1 mixture of THF–2M HCl (1.3 ml). The polymer was filtered off and washed successively with water and a 4:1 mixture of THF–2M HCl. Then the polymer was stirred again for 4 h in a 4:1 mixture of THF–2M NaOH (1.3 ml), filtered off, and washed successively with water, MeOH, THF, aq. THF, THF, and MeOH. After being dried *in vacuo* at 40 °C, the polymer-bound catalyst was used in the enantioselective addition of dialkylzinc to aldehyde.

Acknowledgements

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