Asymmetric Synthesis of 3-(1-Phenylethylamion)-1-propanol from 3-[(1-Phenylethylidene) amino] propene by a Sequence of Hydroboration/Imine Reduction

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Asymmetric Synthesis of 3-(1-Phenylethylamion)-1-propanol from 3-[(1-Phenylethylidene)amino]propene by a Sequence of Hydroboration/Imine Reduction

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A new synthetic method consisting of a hydroboration/imine reduction sequence is described. Hydroboration of 3-[(1-phenylethylidene)amino]-propene with optically pure isopinocanpheylborane is followed by the reac tion with diethylzinc and then the oxidation with hydrogen peroxide to produce 3-(1-phenylethylamino)-1-propanol with a moderate enantioselectivity. The alkylborane produced in the hydroboration step forms a chiral five-membered complex structure which induces the new chirality in the imine reduction step.

Chiral organoboron reagents have long played an important role in asymmestric organic synthesis.[1] Among them, monoisopinocanpheylborane ($IPCBH_2$) and diisopinocanpheylborane (IPC_2BH), which have been first introduced by H. C. Brown,[2] are especially useful for asymmetric synthesis of alcohols since they are readily available in situ through a stereoselective hydroboration process using optically pure (1*S*)-(−)α-pienene.

Hydroborations of IPC_2BH with alkenes often proceed in high optical yields and this reaction has been widely applied to the synthesis of optically active alcohols.[3] On the other hand, asymmetric reductions of ketones with these chiral organoboranes are much less stereoselective. For example, reduction of 3-methyl-2-butanone with IPC_2BH gives the corresponding alcohol only in 46.3 % optical yeild.[4] This makes a striking contrast with the highly stereoselective ketone reduction with borane in the presence of a chiral oxazaborolidine.[5] Only limited examples are known for the asymmetric reduction of imines with chiral boranes, and chiral inductions in the reported reactions are far from satisfactory levels.[6] For example, the reduction of 6-methyl-2,3,4,5-tetrahydropyridine with lithium butyldiisopinocanpheylborate provides an optical yield of 24 % ee.[7]

It is well known that nitogen compounds, such as amines and imines, form stable complexes by coordination to boranes throuh the ready donation of the unshared electron pair of nitrogen to the vacant *p*-orbital of boron.[8] When these two functionalities are arranged in the same molecules, tight intramolecular coordination should be achieved between them to give the complexes of cyclic structure. In the case that an imine group is involved as nitrogen function, such intramolecular coordination of borane should secure both the conformational stabilization of the resulting cyclic structures and the activation of the imine moiety toward the addition by a nucleophilic reagent. Accordingly, some chiral induction is expected in the imine addition step when the chiral complexes are employed. Use

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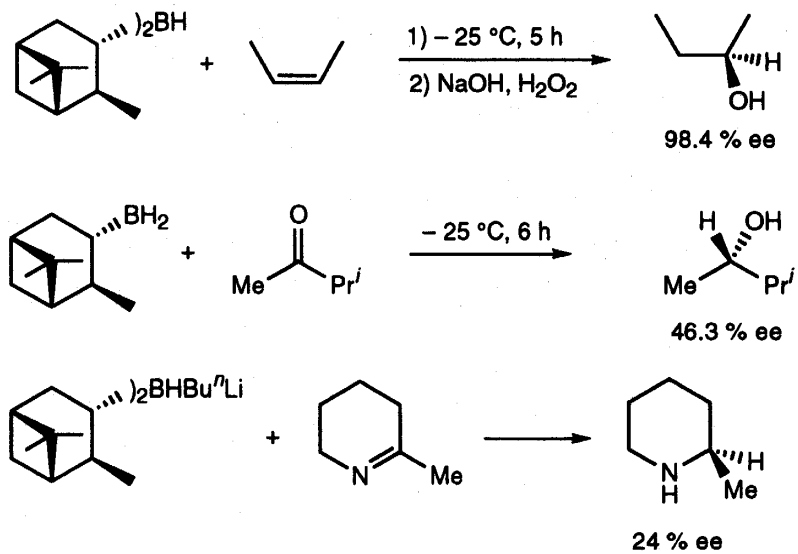
Dedicated to Professor Tetsu Fujii on the occasion of his retirement



of either chiral amines and imines or chiral boranes in this process would lead to the formation of an additional chiral center(s).

This new synthetic method would be realized by utilization of *N*-alkylideneallylamines. Hydroboration using a scaremic borane at the allylic double bond would occur regioselectively to provide the chiral five-membered internal omplexes **A**. The activated imines of **A** can be then employed for the subsequent nucleophilic additions by an external or internal nucleophile (Figure 1), where some chiral induction by the chirality introduced from the borane reagent is expected. After the imine addition step (**A** to **B**), the boron-carbon bond is cleaved by oxidation to produce chiral γ-amino alcohol derivatives **C**.

In this work, we present the enantio-controlled synthesis of 3-(1-phenylethylamino)-1-propanol (**4a**) from 3-[(1-phenylethylidene)amino]propene (**1**) by a sequence of hydroboration/imine reduction. Optically active $IPCBH_2$, is used for the first step of hydroboration. The second step consists of the nucleophilic addition of diethylzinc to the boron atom of the resulting complex to form a borate complex, and the third step the intramolecular hydride

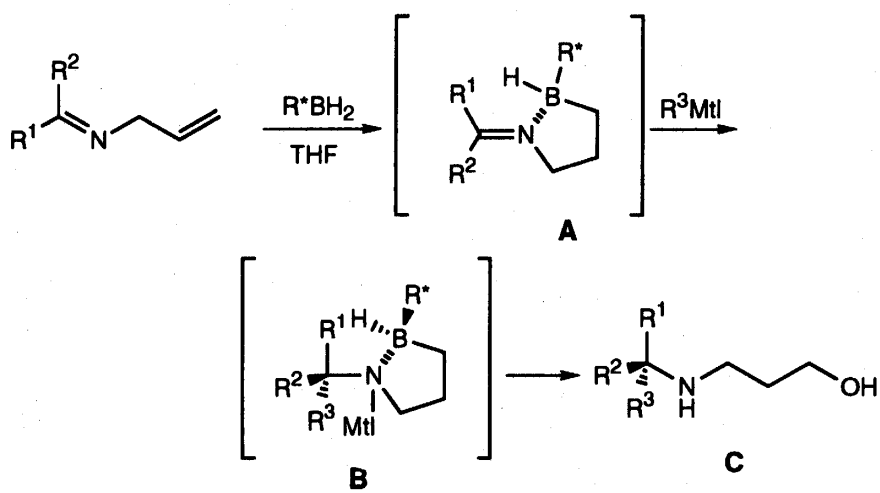
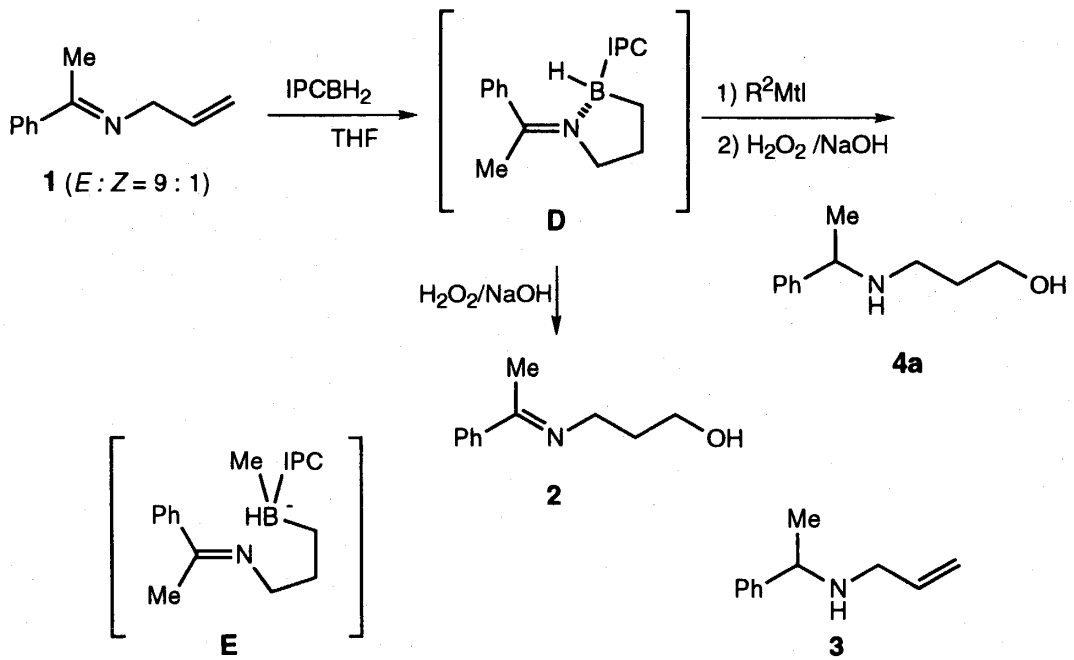


Figure 1 Asymmetric imine addition of a nucleophile to the five-membered internal complex **A**.

migration giving the title product in a moderate optical yield.

Reaction of 3-aminopropene with acetophenone gives 3-[(1-phenylethylidene)amino]-propene (**1**) as a 9 : 1 π-diastereomeric mixture (the intensity ratio of signals at δ 4.17 and 3.85=9 : 1 by ^{1}H NMR). Since the higher field signal (δ 3.85 for NCH_2 moiety) is assigned as that of the Z-isomer and the lower one for the *E*-isomer, then the *E:Z* isomer ratio of **1** was 9 : 1. These isomers could be neiter separated from each other, by vacuum distillation or column chromatography on silica gel, nor the ratio could be equilibrated in favor of one of the isomers. Distillation of **1** did not affect the isomer ratio and chromatography on silca gel caused decompsition of **1**. Accordingly, the 9 : 1 mixture of *E:Z*-isomers was used for the following reactions.

A pentane solution of $IPCBH_2$ was prepared in situ from the pure enantiomer of (1*S*)-(−)-α-pinene and 2,3-dimethyl-2-butylborane ($ThexBH_2$)/triethylamine complex according to the following procedure:[9] $ThexBH_2$ was synthesized by the reaction of borane/dimethylsulfide with 2,3-dimethyl-2-butene in the presence of triethylamine. The resulting borane was treated with (1*S*)-(−)-α-pinene and the whole volatile materials were removed in vacuo. Pentane was added to the residue and the mixture was treated with boron trifluoride/ether complex. The pentane souluble material consists of $IPCBH_2$ and its concentration was determined on the basis of the amount of hydrogen evolved on hydrolysis.



Scheme 1

The regioselective hydroboration of 3-[(1-phenylethylidene)amino]propene (**1**, *E:Z* = 9 : 1) with the aforementioned $IPCBH_2$ solution was performed at 0 °C for 3 h (Scheme 1). The ^{1}H NMR spectral analysis of the crude hydroboration product failed because of the signal broadening caused by some impurities and the spin couplings between ^{11}B and ^{1}H nuclei. Crystallization of the product was also unsuccessful.

Failure of purification of the expected hydroboration product **D** led us to give up the direct structural assignment of **D**. The crude complex **D** was accordingly oxidized with alkaline hydrogen peroxide. The major products obtained were 3-(alkylideneamino)-1-propanol **2** and acetophenone which was presumably produced by hydrolysis of **2** or the

Table 1 Asymmetric Sequence of Hydroboration/Imine Reduction

Entry	R_1BH_2 (equiv) Temp. (°C)		R_2Mtl (equiv) Temp. (°C)		Yield (%) **4a**	% ee[a] (Config)
1	$IPCBH_2$[b] (1.5)	0	MeLi (1.0)	0	45	19 (*R*)
2	$IPCBH_2$ (1.5)	0	EtMgBr (1.0)	0	19	10 (*R*)
3	$IPCBH_2$ (1.5)	0	Et_2Zn (1.0)	0	46	49 (*S*)
4	$IPCBH_2$ (1.0)	0	Et_2Zn (1.0)	0	15	0
5	$IPCBH_2$ (2.0)	0	Et_2Zn (1.0)	0	56	30 (*S*)
6	$IPCBH_2$ (1.5)	-10	Et_2Zn (1.0)	0	44	38 (*S*)
7	$IPCBH_2$ (1.5)	55	Et_2Zn (1.0)	rt	32	30 (*S*)
8	$IPCBH_2$ (1.5)	0	Et_2Zn (1.0)	-23	24	0
9	$IPCBH_2$ (1.5)	0	Et_2Zn (1.0)	55	54	43 (*S*)
10	$IPCBH_2$ (1.0)	0	$IPCBH_2+Et_2Zn$ (1.0)	0	46	37 (*S*)
11	$ThexBH_2$ [c] (1.0)	0	$IPCBH_2+Et_2Zn$ (1.0)	0	34	0
12	$IPCBH_2$ (1.0)	0	$ThexBH_2+Et_2Zn$ (1.0)	0	28	27 (*S*)
13	$IPCBH_2$ (1.0)	0	$BH_3 \cdot Sce_2+Et_2Zn$ (1.0)	0	46	31 (*S*)
14	$IPCBH_2$ (1.0)	0	$Zn(BH_4)2$ (1.0)	0	34	0
15	$IPCBH_2$ (1.0)	0	$LiBHEt_3$ (1.0)	0	11	0

a) Determined by HPLC (DAICEL Chiral OD with hexane : 2-propanol : diethylamine=50 : 1 : 0.05). b) $IPCBH_2$: isopinocanpheylborane. c) $ThexBH_2$: 2, 3-dimethyl-2-butylborane.

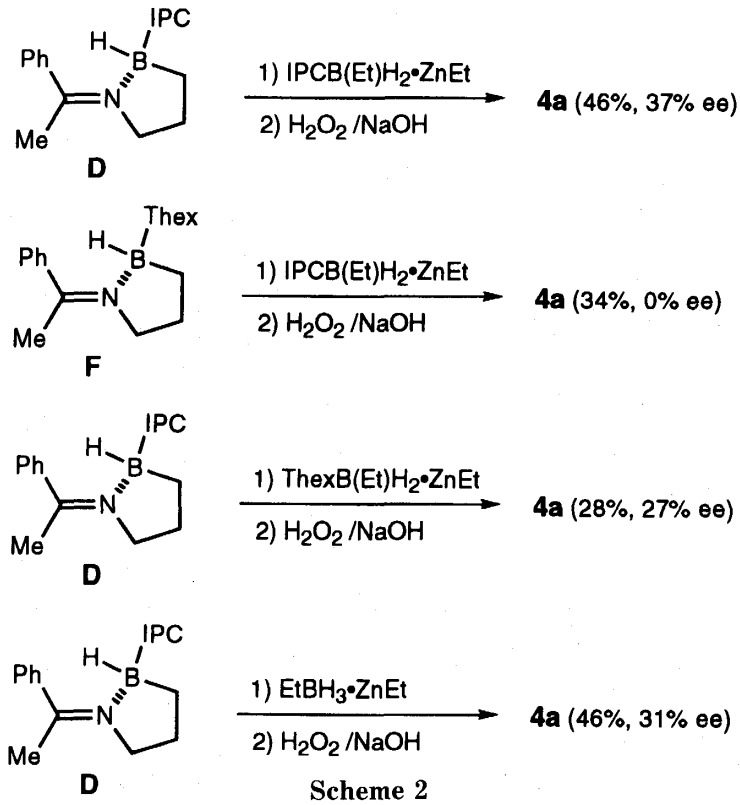
unchanged starting mateial **1**. Indeed, chromatography on silica gel caused the decomposition of **2**. The third product was 3-[(1-phenylethyl)amino]propene (**3**) wihch corresponds to the reduction product at the imine part of **1**. Products derived from a hydroboration/imine reduction were never detected, indicating the imine moiety of **D** is safe aginst reduction under the reaction conditions.

With an expectation that a nucleophile could be introduced at the imine carbon, the complex **D** was treated with methyllithium (R^2Mtl=MeLi, 1 equiv) followed by oxidation with alkaline hydrogen peroxide to give 3-[(1-phenylethyl)amino]-1-propanol (**4a**) in 45% yield. Its optical purity was determined to be 19% ee by HPLC using a chiral column (Table 1, entry 1). Determination of its absolute configuration will be discussed below.

Formation of the unexpected reduction product **4a** is certainly based on the nucleophilic attack of methyllithium not at the imine carbon but at the boron atom. The resulting borate anion **E** would have undergone an intramolecular imine reduction. Since no trace of **4a** is produced in the absence of methyllithium as mentioned above, use of some other organometallic reagents was examined. Although employment of ethylmagnesium bromide gave lower chemical and optical yields (entry 2), reaction with diethylzinc gave satisfactory chemical and optical yields (46% and 49% ee, entry 3). It was our great surprise that the mode of chirality induced in the reactions with ethylmagnesium bromide and diethylzinc was opposite, indicating that the counterion of borate intermediate **E** is an important factor to determine the sence of chiral induction.

The absolute configuration of **4a** was determined to be the *S*-enantiomer by comparison of its optical rotation with the reported value:[10] The optical rotaion of **4a** (49% ee) was $-23.0°$ and the *R*-**4a** has $+52°$. Based on the fact that the starting imine **1** was a 9:1 *E*/*Z* isomeric mixture, the observed optical yield of 49% ee is acceptable.

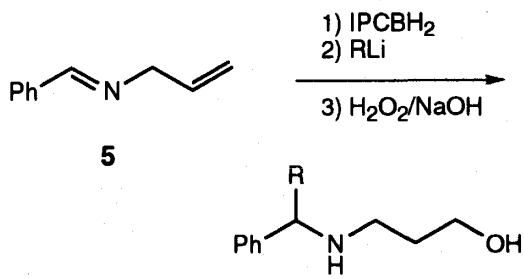
When an equimolar amount of $IPCBH_2$ was employed, chemical yield of **4a** was reduced down to 15% and no optical induction was observed (entry 4). On the other hand, use of two



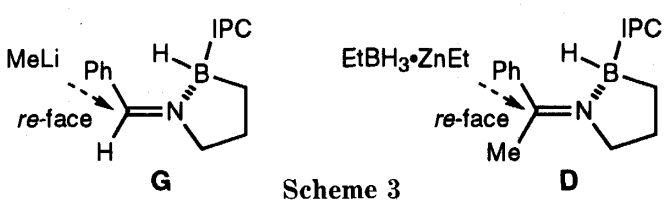
Scheme 2

equimolar amounts of $IPCBH_2$ led to the increase of chemical yield but with a lower selectivity (entry 5). Reaction temperature at the hydroboration step was not so sensitive to the optical yields of **4a** that a little lower optical yields were obtained either −10 °C or at 55 °C (entries 6 and 7). However, temperature at the addtion step of diethylzinc is critical: A higher temperature gave a better optical yield (entries 8 and 9).

Some experiments to confirm the reaction mechanism were performed as follows (Scheme 2): Complex **D** was prepared from **1** and $IPCBH_2$ (1 equiv) and allowed to react with the zinc borate, $IPCB(Et)H_2 \cdot ZnEt$ prepared from $IPCBH_2$ and diethylzinc, to give comparable results with respect to the chemical and optical yields (entry 10). This indicates



4a: R = Me (12 %, 26 % ee) + **4c**: R = H (24%)
4b: R = *n*-Bu (8 %, 33 % ee) + **4c**: R = H (32%)



Scheme 3

that the intermololecular reduction by an external borate is the more favored reaction path. The intermediary complex must be chiral since reaction of the achiral complex **F** with the same chiral borate IPCB(Et)H_2•ZnEt produded only racemic **4a** (entry 11). On the other hand, the external reducing reagent can be achiral: The reactions of chiral complex **D** with achiral borates, such as ThexB(Et)H_2•ZnEt or $EtBH_3$•ZnEt, prepared from $ThexBH_2$ or BH_3 and diethylzinc, respectively, gave optically enriched **4a** (entries 12 and 13).

Thus, it is now clear that the chirality of product **4a** was induced from the chiral ligand involved in the intermediary complex **D**. The tight coordination structure of **D** is stable even at 55 °C. However, the correct choice of reducing reagent is important. Use of $Zn(BH_4)_2$ or $LiBHEt_3$ as reducting reagents produced racemic mixtures of **4a** (entries 14 and 15). Employment of bulky borates containing zinc counterion is useful as asymmetric reduction of the imine moiety.

The observed high thermodynamic stability of the intermediary chiral complex **D** suggests a possibility of the initially proposed pattern of asymmetric reactions (Scheme 3). That involves the addition of an external nucleophile other than hydride to a chiral internal complex such as **D**. A less hindered imine alkene should be much more favored for the substrate for hydroboration. We accordingly selected 3-(benzylideneamino)propene (**5**) and performed the reaction with equimolar amount of $IPCBH_2$. Treatment with an alkyllithium such as methyllithium or butyllithium was followed. Subsequent oxidation with alkaline hydrogen peroxide produced the methylated product **4a** (12%, 26% ee) together with 3-benzylamino-1-propanol (**4c**), the latter being the major product. Similarly, the butylated product **4b** (8%, 33% ee) was obtained again as minor product.

The absolute configuration of **4a** was assigned ot be *R*-enantiomer, indicating the predominant attack of methyllithium to the *re*-face of imine moiety of the intermediary complex **G** as shown in Scheme 3. Since hydride reduction of the chiral complex **D** also occurred at the *re*-face as described above, the same enantiofaces were shielded by the chiral five-membered cyclic structures of **D** and **G**. The low chemical yields of these reactions were due to the competitive nucleophilic attack of lithium reagents onto the boron atom. The reduction product **4c** was obtained in two or four times of the yield of **4a** or **4b**. In this case, an external reducting reagent should be absent since just equimolar amount of $IPCBH_2$ was used in this reactions. The internal reduction of **G** may have occurred in this reaction.

When a more appropriate nucleophile is employed, which favors the attack onto the imine carbon rather than the boron atom, more satisfactory reactions might be realized. The research along this line is now under progress.

Experimental

The IR spectra were taken with a JASCO A-702 spectrometer. The ^1H and ^{13}C NMR spectra were recorded on a JEOL EX-90 (90 MHz for ^1H NMR) and a GSX-270 (270 MHz for ^1H MNR and 67.94 MHz for ^{13}C NMR) instruments. Chemical shifts are expressed in ppm downfield from tetramethylsilane as an internal standard.

Sythesis of 3-[(1-phenylethylidene)amino]propene (1). 3-Aminopropene (5 ml, 67 mmol) was added at 0 °C to a benzene solution (30 ml) of acetophenone (3.5 ml, 30 mmole) and *6*-poluenesulfenic acid (0.57 g, 3 mmole). The mixture was refluxed for 10 h. After cooling, the reaction mixturre was diluted with ether, washed with brine, and then with water. The organic layer was dried over anhydrous sodium sulfate and evapolated in vacuo. A vacuum distillation of the residue gave **1** as a 9 : 1 *E*/*Z* mixture (bp 55-65 °C/0.3 mmHg). Pale yellow oil; IR (neat) 3110, 2870, 1690, 1640, 1580, 1500, 1450, 1370, 1290, 1190, 1090, 1000, 920, 760, 700, and 570 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.22 (3H×9/10, s, Me (*E*)), 2.32 (3H×

1/10, s, Me (*Z*)), 3.85 (2H×1/10, dt, J=1.5 and 4.4 Hz, H-1 (*Z*)), 4.17 (2H×9/10, ddd, J= 1.8, 2.6, and 5.5 Hz, H-1 (*E*)), 5.08-5.18 (2H×1/10, m, H-3 (*Z*)), 5.14 (1H×9/10, ddt, J=1. 5, 2.6, and 17.2 Hz H-3 (*E*)), 5.25 (1H×9/10, ddt, J=1.5, 1.8, and 10.3 Hz, H-3 (*E*)), 5.82-6.10 (1H×1/10, m, H-2 (*Z*)) 6.11 (1H×9/10, ddt, J=5.5, 10.3, and 17.2 Hz, H-2 (*E*)), 7.35 -7.39 (3H, m, Ph), and 7.77-7.81 (2H, m, Ph); ^{13}C NMR ($CDOCl_3$) δ=15.57, 54.57, 115.12, 126. 62, 128,17, 129,51, 136.02, 141.10, and 166.21 (for *E*-isomer). δ=29.17, 55.97, 128.27, 128.47, 133. 06, 136.53, 138.72, and 169.68 (for *Z*-isomer).

Reaction of 1 with Isopinocanphylborane. To a soution of **1** (0.159 g, 1.0 mmole) in tetrahydrofuran (THF, 5 ml) was added at 0 °C a solution of isopinocanphylborane in pentane (0.5 M solution, 3 ml, 1.5 mmole). After stirring for 3 h, 2 N sodium hydroxide soution (2 ml) and 30 % hydrogen peroxide (2 ml) were added in this order and stirring was continued for 3 h. The mixture was extracted with dichrolomethane. The combined organic layers were dried over anhydrous sodium sulfate and the solvent was evapolated in vacuo. The residue contained **2**, acetophenone, and **3** with the ratio of 54:24:18 which was determined by GLC analysis. Chromatography of the residue on silica gel with ethyl acetate-methanol (1 : 2 v/v) as an eluent gave **3** (0.018 g, 11%). Pale yellow oil; IR (neat) 3320, 2980, 2960, 1645, 1495, 1455, 11370, 1130, 990, 920, 760, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.35 (3H, d, J=6.6 Hz, Me), 1.58 (1H, brs, NH), 3.10 (2H, ddd, J=1.5, 2.9, and 5.9 Hz, H-1), 3.79 (1H, q, J=6.6 Hz, PhCH), 5.06 (1H, ddt, J=1.8, 2.9, and 5.9 Hz, one of H-3), 5.12 (1H, J=1.5, 1.8, and 17.2 Hz, the other of H-3), 5.88 (1H, ddt, J=5.9, 10.3, and 17.2 Hz, H-2), and 7.19-7.36 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=24.20, 50.22, 57.51, 115.71, 126.61, 126.91, 128.43, 136.94, and 145.47.

Also, the major peaks of **2** were picked up from ^{1}H MNR spectrum of crude mixture. ^{1}H NMR ($CDCl_3$) δ=2.21 (3H, s, Me) and 3.73 (2H, 0, J=7.0 Hz, H-1).

Reaction of 1 with Isopinocanphylborane and Diethylzinc. To a solution of **1** (0.159 g, 1.0 mmole) in THF (5 ml) was added at 0 °C a solution of isopinocanpheylborane in pentane (0.5 M solution, 3 ml, 1.5 mmole). After stirring for 3h, diethylzinc (1.0 M solution in hexane, 1 ml, 1.0 mmole) was added and the mixture was stirred for additional 3 h at 0 °C. Then, 2 N sodium hydroxide soution (2 ml) and 30 % hydrogen peroxide (2 ml) were added in this order and stirring was continued for 3 h. The mixture was extracted with dichrolomethane. The combined organic layers were dried over anhydrous sodium sulfate. The residue obtained by evaporation of the solvent in vacuo was chromatographed on silca gel with ethyl acetate - methanol (1 : 2 v/v) as an eluent to give **4a** (0.097 g, 46 %). Colorless prisms; mp 49-51 °C; IR (neat) 3300, 2920, 1600, 1500, 1450, 1370, 1200, 1120, 1080, 760, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.37 (3H, d, J=6.6 Hz, Me), 1.66 (2H, m, H-2), 2.63 (1H, ddd, J=4.4, 7. 7, and 11.7 Hz, one of H-3), 2.75 (1H, ddd, J=4.8, 6.6, and 11.7 Hz, the other of H-3), 3.39 (2H, br s, NH and OH), 3.70 (1H, ddd, J=4.0, 6.6, and 16.5 Hz, one of H-ff), 3.73 (1H, q, J= 6.6 Hz, PhCH), 3.77 (1H, ddd, J=4.8, 7.7, and 165 Hz, the other of H-1), and 7.21-7.62 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=24.6, 31.23, 47.47, 58.59, 63.87, 126.50, 127.14, 128.58, and 144.63.

Reaction of 5 with Isopinocanpheylborane and Alkyllithum. To a solution of **5** (0.145 g, 1.0 mmole) in THF (5.0 ml) was added a solution of monoisopinocanphyl-boran in pentane (0.5 M solution, 2 ml, 1.0 mmole) at 0 °C. After stirring for 3h, methyllithium (1.1 M soution in ether, 0.91 ml, 1.0 mmole) or butylithum (1.6 M solution in hexane, 0.63 ml, 1.0 mmole) was added and stirring was continued for additonal 3 h at 0 °C. Then, 2 N sodium hydroxide soution (2.0 ml) and 30% hydrogen peroxide (2.0 ml) were added and stirring was continued for 3 h. The mixture was extracted with dichrolomenthane. The combined organic layers were dried over anhydrous sodium sulfate. The residue was chromatographed on silca gel with ethyl acetate - methanol (1 : 2 v/v) as an eluent to give **4a** (0.022g, 24%) and **4c** (0.049 g, 24%) in the case of using methyllithum or **4b** (0.013 g, 8%) and **4c** (0.053 , 32%) in the case of using butyllithum.

4b: Yellow oil; IR (neat) 3300, 2930, 1590, 1450, 1370, 1200, 1070, 750, 194 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.76-0.90 (3H, t, J=6.8 Hz, Bu), 1.12-1.34 (4H m, Bu), 1.59-1.89 (4H, m, Bu and H-2), 2.65-2.80 (2H, m, H-3), 3.59-3.82 (5H, m, PhCH, H-1, NH, and OH), and 7.23 -7.64 (5H, m, Ph).

4c: Pale yellow oil; IR (neat) 3300, 2930, 1550, 1450, 1070, 1030, 740, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.71 (2H, tt, J=5.5 and 5.9 Hz, 2-H), 2.86 (2H, t, J=5.9 Hz, H-3), 3.38 (2H, s, NH and OH), 3.77 (2H, t, J=5.5 Hz, H-1), and 7.22-7.35 (5H, m, Ph).

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