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Enantioselective Synthesis of Optically Active Secondary Amines *via* Asymmetric Reduction

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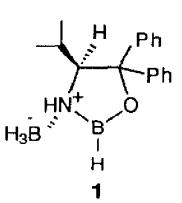
Abstract : The enantioselective synthesis of optically active secondary amines via the asymmetric reduction of N-substituted ketimines with various chiral hydride reagents, such as Itsuno's reagent (**1**), Corey's reagent (**2**), K glucoride (**3**), Sharpless' reagent (**4**), and Mosher's reagent (**5**) has been investigated. Among the hydride reagents examined, **1** gave the best results in terms of asymmetric induction. Thus, the reduction of N-phenylimine derivatives of aromatic ketones with **1** provided the corresponding amines in 96 - 98 % yields with high optical induction, such as 73 % ee for acetophenone N-phenylimine (**6a**), 87 % ee for propiophenone N-phenylimine (**6b**), 88 % ee for butyrophenone N-phenylimine (**6c**), and 71 % ee for isobutyrophenone N-phenylimine (**6d**). In the case of N-alkyl ketimine derivatives, the reduction afforded somewhat lower optical inductions as compared to those of N-phenyl derivatives, giving 46 % ee for acetophenone N-benzylimine (**6f**), 52 % ee for acetophnone N-*n*-heptylimine (**6g**) and 43 % ee for acetophenone N-cyclohexylimine (**6h**). However, the substitution of a bulky alkyl group on nitrogen of the ketimines increases remarkably the optical induction of product amine, such as 80 % ee for acetophenone N-*tert*-butylimine (**6e**). The reduction of N-substituted aliphatic ketimines gave very low optical inductions (7.4 - 24 % ee). The catalytic effects of oxazaborolidines (**1a** and **2a**) in the reduction of ketimines with **1** and **2** were also examined.

Introduction

Optically active amines are important compounds utilized extensively in organic synthesis as resolving agents[1], intermediates for biologically active substances[2], and chiral auxiliaries[3] for asymmetric synthesis. One of the most convenient methods for the preparation of optically active amines involves the asymmetric hydrogenation of ketimines with various chiral catalysts.[4]

In recent years, a wide variety of highly effective chiral hydride reagents which achieve excellent asymmetric reductions of ketones, have been reported.[5] However, the potentially useful enantioselective conversion of ketimines into the corresponding amines with chiral hydride reagents has been relatively neglected and only limited success has been achieved.[6] Therefore, it appeared desirable to develop synthetic methods for the preparation of optically active amines via the asymmetric reduction of ketimines with chiral hydrides.

Very recently, we reported the enantioselective conversion of N-substituted ketimines into the corresponding amines using chiral hydride reagents, such as Itsuno's reagent (**1**),[7] Corey's reagent (**2**),[8] K glucoride (**3**),[9] Sharpless' reagent (**4**),[10] and Mosher's reagent (**5**)[11] in the form of communications.[12] In this paper, details of the enantioselective conversions of ketimines into amines via asymmetric reductions are described.



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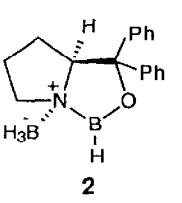

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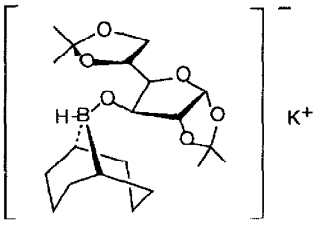

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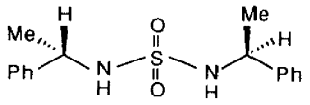
$LiAlH_4$ / Xc

Xc =



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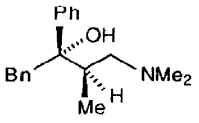

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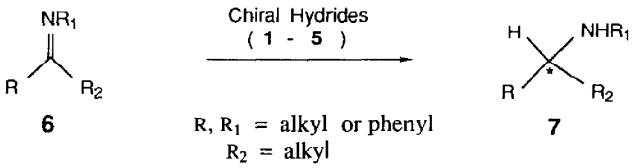
Results and Discussion

General. According to the literature methods,[6e, 13] N-substituted ketimines (**6**) were prepared by condensation of the corresponding ketones and amines. The chiral hydride reagents (**1**-**5**) were prepared by the known procedures.[7-11] The asymmetric reductions of ketimines with these hydrides were carried out under the same conditions as those found most successful for the reduction of ketones with the hydride reagents, such as 30 °C with **1**, 0 °C with **2**, - 78 °C with **3**, - 20 °C with **4**, and 0 °C with **5** (Scheme 1). Optical purities of the product amines (**7**) were determined by capillary Gc analysis of diastereoisomeric ratios of the corresponding MTPA amides.[14]



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Scheme 1

Comparison of the Asymmetric Reductions of N-Substituted Ketimines with Various Chiral Hydride Reagents. In order to compare the asymmetric reducing characteristics of the selected hydrides (**1**-**5**) for N-substituted ketimines, asymmetric reductions of the representative ketimines, such as propiophenone N-phenylimine (**6b**) and 2-butanone N-benzylimines (**6k**) with the chiral hydride reagents were carried out. Thus, **6b** was smoothly reduced by both **1** and **2** to the corresponding amine (**7b**) in high yields with 87 % ee and 78 % ee, respectively. Ketimine **4** afforded **7b** of 66 % ee, although the reduction is somewhat slow as compared to those by **1** and **2**. In contrast, **3** and **5** did not reduce **6b**. On the other hand, an aliphatic ketimine, **6k**, was also reduced readily by **1** and **2** to the corresponding amine (**7k**) in high yields, however, the optical inductions of the product amine (**7k**) are low, such as 24 % ee with **1** and 3.3 % ee with **2**. Unlike **6b**, **3** could reduce **6k** to **7k** , although the reduction was slow and gave low

optical induction (5.1 % ee). The reduction of **6k** with **4** was very slow, giving a low yield (< 10 %) even after 2 days at 0 °C, and **5** did not reduce **6k**. The results are summarized in Table1.

Table 1. Asymmetric Reduction of Propiophenone N-phenylimine (6b) and 2-Butanone N-Benzylimine (6k) with Various Chiral Hydrides (1-5).[a]

compounds	chiral hydride	Temp. (°C)	Time (h)	amines Yield[b] (%)	amines % ee[d]
Propiophenone N-phenylimine (**6b**)	**1**	30	20	98(87)[c]	87
	2	25	15	96	78
	3	-78 - 0		no reaction	
	4	- 20	36	60	66
	5	0		no reaction	
2-Butanone N-benzylimine (**6k**)	**1**	30	18	95	24
	2	25	6	90	3.3
	3	-78 - 0	30	55	5.1
	4	- 20		very slow	
	5	0		no reaction	

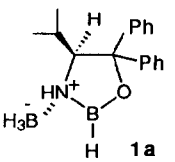
[a] [chiral hydride / compound] = 1.0, [compounds] = 0.3 M. [b] Gc yields. [c] Isolated yield after column chromatography. [d] Determined by capillary Gc analysis of their MTPA amides.

Catalytic Effects of Oxazaborolidines (1a and 2a) in the Reduction of N-Substituted Ketimines with 1 and 2. In the reduction of ketones[8] and oxime ethers[15] with **1** and **2**, it was found that the asymmetric induction in the products was enhanced by a catalytic amount of oxazaborolidines, **1a** and **2a**. Therefore, we examined the catalytic effects of the oxazaborolidines in the reduction of the ketimines with **1** and **2**. **6b** was chosen as a representative ketimine and reacted with 1.0 equiv of BH_3.THF in the presence of 0.1, 0.2 and 1.0 equiv of **1a** in THF at 30 °C. As shown in Table 2, **6b** was reduced smoothly to the corresponding amine (**7b**) with 66 % ee, 68 % ee and 87 % ee, respectively. The results indicated that the presence of even 10 mole % of **1a** was highly effective for enhancing the optical induction. In this case, a

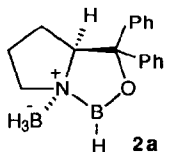
Table 2. Catalytic Effects of Oxazaborolidines(1a and 2a) in the Reduction of Propiophenone N-Phenylimine (6b) with 1 and 2

Oxazaborlidine	Equiv of **1a** or **2a**	Equiv of BH_3.THF	Temp. (°C)	Time (h)	**7b** yield[a]	**7b** % ee[b]
1a	0.1	1.0	30	24	95	66
1a	0.2	1.0	30	22	93	68
1a	1.0	1.0	30	22	97	87
2a	0.1	1.0	25	20	92	70
2a	0.2	1.0	25	24	95	72
2a	1.0	1.0	25	15	96	78

[a] Gc yields [b] Determined by capillary Gc analysis of their MTPA amides



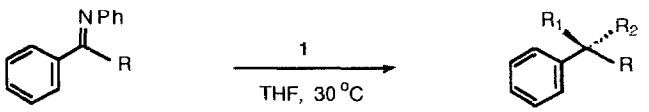
1a



2a

somewhat lower optical induction as compared to that given by the presence of 1.0 equiv of **1a** is probably attributable to competing noncatalyzed reduction by BH_3.THF. Similarly, the catalytic effect of **2a** in the reduction of **6b** with **2** was also observed.

Asymmetric Reduction of N-Substituted Ketimines (6) with 1. From Table 1 and Table 2, we realized that **1** gave the best results for obtaining optically active secondary amines by the reduction of the representative N-substituted ketimines, such as **6b** and **6k**, with the selected chiral hydride reagents (**1-5**). The results led us to extend the asymmetric reduction of the other ketimines (**6**) with **1**. Thus, asymmetric reductions of N-substituted aromatic ketimines, such as acetophenone N-phenylimine (**6a**), propiophenone N-phenylimine (**6b**), butyrophenone N-phenylimine (**6c**), isobutyrophenone N-phenylimine (**6d**), acetophnone N-*tert*-butylimine (**6e**), acetophenone N-benzylimine (**6f**), acetophenone N-n-heptylimine (**6g**) and acetophenone N-cyclohexylimine (**6h**) with 1 equiv of **1** in THF at 30 °C were carried out. The reductions proceeded smoothly to give the corresponding amines (**7a-7h**) in high yields. Of the aromatic ketimines examined, N-phenylimine derivatives were converted into the N-phenyl secondary amines with high optical inductions showing the increase of the optical induction by the variation of the steric size of R in PhCR=NPh from Me ⟶ Et ⟶ Pr, such as 73 % ee for **6a**, 87 % ee for **6b**, 88 % ee for **6c**. In contrast, in the case of isobutyrophenone N-phenylimine (R = *i*-pr, **6d**), the optical induction was decreased remarkably. The reason for the decrease of optical induction is not fully understood, but it seems to be attributable to the steric effect of isopropyl group of the ketimine in the transition state during the reaction with **1**. Indeed, the absolute configuration of the product amine (**7d**) was S enantiomer in contrast with R enantiomers of **7a-7c** (eq 1).

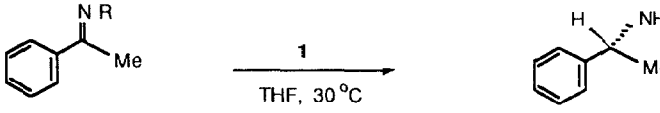


(eq 1)

R = Me (**6a**), Et (**6b**)
n-Pr (**6c**), *i*-Pr (**6d**)

7a (73 % ee, R) R = Me ; R_1 = H ; R_2 = NHPh
7b (87 % ee, R) . R = Et , R_1 = H ; R_2 = NHPh
7c (88 % ee, R) : R = *n*-Pr , R_1 = H ; R_2 = NHPh
7d (71 % ee, S) · R = *i*-Pr ; R_1 = NHPh ; R_2 = H

On the other hand, the reduction of N-alkyl aromatic ketimines provided somewhat low optical inductions, such as 46 % ee for **6f**, 52 % ee for **6g** and 43 % ee for **6h**. However, the substitution of the bulky alkyl group on nitrogen of the same ketimine enhanced remarkably the optical yield of the product amine, such as



(eq 2)

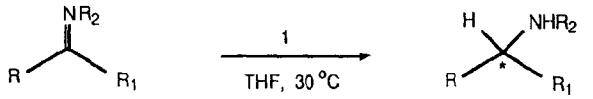
R = *tert*-Bu (**6e**), Bn (**6f**)
n-Hept (**6g**), Cyclohexyl (**6h**)

7e (80 % ee, R) : R = *tert*-Bu
7f (46 % ee, R) : R = Bn
7g (52 % ee, R) : R = *n*-Hept
7h (43 % ee, R) : R = Cyclohexyl

80 % ee for **6e** (eq 2). Unfortunately, the reduction of N-substituted aliphatic ketimines, such as 2-butanone

N-phenylimine (**6i**), 2-heptanone N-phenylimine (**6j**), 2-butanone N-benzylimine (**6k**), 2-heptanone N-benzylimine (**6l**) and 3-methyl-2-butanone N-benzylimine (**6m**) provided the corresponding amines with very low optical yields which were 9.4 % ee, 18.4 % ee, 24 % ee, 7.4 % ee and 14 % ee, respectively. The results are summarized in Table 3 .

Table 3. Asymmetric Reduction of N-Substituted Ketimines with 1 in THF at 30 °C[a]



6 **7**

	6			Time	7			
	R	R_1	R_2	(h)	Yield[b]	% ee[d]	$[\alpha]_D^{22}$ [f]	abs. confg.
a	Ph	Me	Ph	20	98 (87)[c]	73	- 4.27 (0.81)	R[16]
b	Ph	Et	Ph	22	97 (89)	87	- 6.79 (1.06)	R[i]
c	Ph	*n*-Pr	Ph	24	97	88	- 7 08 (0.88)	R[i]
d	Ph	*i*-Pr	Ph	24	96 (90)	71	11.15 (0.17)	S[i]
e	Ph	Me	*tert*-Bu	18	90	80	- 19.51 (1.02)[g]	R[i]
f	Ph	Me	Bn	20	98	46	5.53 (0.98)[h]	R[17]
g	Ph	Me	*n*-C_7H_{15}	20	96	52	- 33.9 (1.05)	R[i]
h	Ph	Me	*c*-C_6H_{11}	24	93	43	- 18.48 (0.85)	R[i]
i	Et	Me	Ph	18	86	9.4	e	j
j	Me	*n*-C_5H_{11}	Ph	24	87	18.4	- 6.36 (0.81)	j
k	Et	Me	Bn	18	88	24	- 6.03 (0.69)	j
l	Me	*n*-C_5H_{11}	Bn	24	90	7.4	e	j
m	Me	*i*-Pr	Bn	18	89	14	e	j

[a-d] See corresponding footnotes in Table 1. [e] Not measured. [f] The figures in parentheses indicated the concentration (%) in metha nol, unless otherwise mentioned. [g] In chloroform. [h] In cyclopentane. [i] Based on the order of elution of MTPA amides and the sign of rotation. [j] The absolute configurations are unknown.

Conclusion

The enantioselective synthesis of optically active secondary amines via asymmetric reductions of N-substituted ketimine derivatives with chiral hydride reagents, such as Itsuno's reagent (**1**), Corey's reagent (**2**), K glucoride (**3**), Sharpless' reagent (**4**) and Mosher's reagent (**5**) were examined. Among the hydride reagents examined, **1** provided the best results to give high optical inductions for aromatic ketone N-phenylketimine derivatives. The present study provides a convenient and simple synthesis of optically active secondary amines.

Experimental

General. All glassware was dried at 140 °C overnight, assembled hot, and cooled to room temperature in a stream of nitrogen. All reactions involving air sensitive materials were carried out under static pressure of

nitrogen. The liquids were transferred with a double-ended needles.[18]

Spectra. ^{1}H NMR spectra were conducted on Varian Gemini 300 (300 MHz) and Varian T-60 (60 MHz) spectrometers with Me_4Si as an internal standard. 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. Melting points were determined with a Fisher- Johns melting point apparatus.

Gc analysis. All Gc analyses were carried out with Shimadzu Gc-7A gas chromatograph and Hewlett-Packard 5890 gas chromatographs equipped with a Hewlett-Packard 3390A intergrater / plotter. Optical purities (% ee) were determined by capillary Gc analysis of the corresponding MTPA amides of products amines using a Hewlett-Packard 5890 gas chromatograph equipped with a 50 m methyl silicon capillary column.

Materials. 9-Boratabicyclo[3.3.1]nonane (9-BBN), borane-THF, potassium hydride, 1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose, Darvon alcohol, (S)-valine methyl ester, (S)-proline, and the other commercially available chemical reagents were purchased from the Aldrich Chemical Company. Tetrahydrofuran and ethyl ether were distilled over sodium benzophenone ketyl and stored in ampules under nitrogen pressure. N-substituted ketimine derivatives were prepared by the literature procedures:[6c,13] **6a**, mp 37 - 39 °C (lit.[6c] mp 38 -39 °C); **6b**, mp 47 - 49 °C (lit.[6c] mp 49 - 51 °C); **6c**, syrup (lit.[6c] mp 26 - 28 °C); **6d**, syrup (lit.[6c] mp 28 - 29 °C); **6e**, oil, 100 °C/12 mmHg; **6f**, mp 44 -45 °C (lit.[13e] mp 44 - 46°C); **6g**, oil, 124 - 126 °C/0.3 mmHg; **6h**, oil, 103 - 105 °C/0.3 mmHg; **6i**, oil, 104 - 106 °C/25 mmHg (lit[13b] 106 - 108 °C/25 mmHg; **6j**, oil, 122 °C/0.5 mmHg; **6k**, oil, 82 - 84 °C/0.3 mmHg; **6l**, oil, 117 - 119 °C/0.5 mmHg; **6m**, oil, 108 - 110 °C/4 mmHg. The chiral hydride reagents, **1**[7], **2**[8], **3**[9], **4**[10] and **5**[11], were prepared by the known methods.

Asymmetric Reduction of N-Substituted Ketimines (6) with Various Chiral Hydride Reagents (1-5). **6b** was chosen as a representative N-substituted ketimine and reacted with the chiral hydride reagents, such as **1**, **2**, **3**, **4**, and **5** with the following procedures. The results are summarized in Table 1.

Asymmetric Reduction with 1. An oven-dried 25 m*l*, long necked, round-bottom flask equipped with a septum capped-side arm, a magnetic stirring bar, and a stopcock adaptor was cooled to room temperature under a stream of nitrogen. The flask was charged with **1** (3 mmol, 0.5 M, 6 m*l*) in THF. To this, **6b** (627 mg, 3 mmol) in 4 m*l* of THF was added at room temperature. The reaction mixture was stirred at 30 °C for 22 h and then excess hydride was decomposed by the addition of 1 M HCl solution. After THF was removed in *vacuo*, the reaction mixture was filtered and the filter cake was washed with water. The filtrate was cooled to 0 °C, basified with 3 M NaOH, and extracted with ether. The extract was washed with brine, dried over anhydrous K_2CO_3, and evaporated to give an oily residue. Column chromatography on silica gel (eluent: chloroform) provided **7b** (564 mg, 89 % yield) of a pale yellow syrup: $[\alpha]_D^{22}$ - 7.61 (*c* 1.06, methanol). This was converted into its MTPA amide by treatment of MTPA chloride[19]. Capillary Gc analysis of the diastereoisomeric ratio of the amide shows 87 % ee.

Asymmetric Reduction with 2. The experimental set-up and work-up procedure were the same as described above. **6b** (3 mmol) was treated with **2** (3 mmol) in THF at 25 °C for 15 h. After work-up, the product **7b** was obtained in 96 % yield (Gc): 78 % ee.

Asymmetric Reduction with 4. To a THF solution of **4** prepared from 3 mmol of $LiAlH_4$ was added **6b** at - 20 °C. The reaction mixture was stirred at - 20 °C for 36 h. Excess hydride was destroyed by the addition of water (66 % yield by Gc). The precipitate was filtered and filtrate was concentrated in *vacuo*. The residue was purified by column chromatograph, followed by determination of optical purity by capillary Gc analysis of MTPA amide of **7b**: 66 % ee. The asymmetric reduction of **6b** with **3** and **5** was also carried out, but the reaction did not occur.

Catalytic Effect of Oxazaborolidines (1a and 2a) in the reduction of 6 with 1 and 2. To a

mixture of **1a** (0.3 mmol) and BH_3.THF (3 mmol) was added **6b** (3 mmol) in THF. The reaction mixture was stirred at 30 °C for 24 h. After work-up, Gc analysis indicated the formation of **7b** in 95 % yield. Optical purity of **7b** determined by capillary Gc analysis of the MTPA amide as described above was 66 % ee. With the same procedure, the presence of 0.6 mmol (0.2 equiv) of **1a** provided 68 % ee. Similarly, the catalytic effect of **2a** was also investigated. The results are summarized in Table 2.

Enantioselective Synthesis of Optically Active amines (7) via Asymmetric Reduction of N-Substituted Ketimines (6) with 1. The experimental set-up was the same as described above. The reaction was performed with similar procedure as described in asymmetric reduction of **6b** with **1**. The optical purities of products amines were determined by capillary Gc analyses of their MTPA amides. The yields (Gc), optical rotation ($[\alpha]_D^{22}$ in MeOH), optical purities and spectra [^{1}H NMR (300 MHz, $CDCl_3$, δ), IR (neat or KBr, υ cm^{-1})] of the products are as follows: **7a** : 98 % (oil); - 4.27 (*c* 0.81), 73 % ee; 7.03 - 7.35 (m, 7 H), 6.46 - 6.65 (m, 3 H), 4.45 (q, J = 6.59, 1 H), 1.46 (d, J = 6.74, 3 H); 3491, 3132, 2917, 1336, 1600, 1503, 747, 696; **7b**: 97 % (oil); - 6.79 (*c* 1.06); 87 % ee; 7.03 - 7.34 (m, 7 H), 6.45 - 6.64 (m, 3 H), 4.21 (t, J = 6.59, 1 H), 1.75 - 1.86 (m, 2 H), 0.93 (t, J = 7.42, 3 H); 3510, 3202, 2959, 1315, 1601, 1503, 747, 690; **7c** : 97 % (mp 50 - 52°C ; lit.[6c] 51 -52 °C); - 7.08 (*c* 0.88); 88 % ee; 7.04 - 7.35 (m, 7 H), 6.49 - 6.64 (m, 3 H), 4.30 (t, J = 6.87, 1 H), 1.68 - 1.80 (m, 2 H), 1.26 - 1.44 (m, 2 H), 0.92 (t, J = 7.42, 3 H); 3402, 3044, 2918, 1600, 1501, 744, 688; **7d** : 96 % (mp 53 -55°C ; lit.[6c] 54 -55 °C); 11.15 (*c* 0.17); 71 % ee; 7.04 - 7.32 (m, 7 H), 6.49 - 6.64 (m, 3 H), 4.12 (d, J = 6.05 Hz, 1 H), 4.11 (s, 1 H), 2.03 (m, 1 H), 0.98 (d, J = 6.79 Hz, 3 H), 0.92 (d, J = 6.82 Hz, 3 H); 3432, 3072, 2947, 1599, 1501, 1320, 735, 687; **7e** : 90 % (oil); - 19.51 (*c* 1.02, $CHCl_3$); 80 % ee; 7.16 - 7.73 (m, 5 H), 3.92 (m, 1 H), 1.32 (d, J = 6.74 Hz, 3 H), 1.02 (s, 9 H); 3372, 3055, 2921, 1600, 1490, 1449, 1363, 759, 697; **7f** : 98 % (oil); 5.53 (*c* 0.98, cyclopentane); 46 % ee; 7.18 - 7.36 (m, 10 H), 3.78 (q, J = 6.60, 1 H), 3.56, 3.64 (AB, J = 13.1 Hz, 1 H), 1.56 (br s, 1 H), 1.33 (d, J = 6.59 Hz, 3 H); 3306, 3073, 2957, 1600, 1491, 1449, 758, 695; **7g** : 96 % (oil); - 33.9 (*c* 1.05); 52 % ee; 7.14 - 7.39 (m, 5 H), 3.74 (m, 1 H), 2.35 - 2.61 (m, 2 H), 1.34 (d, J = 6.65 Hz, 3 H), 1.17 - 1.25 (m, 10 H), 0.86 (t, J = 6.80 Hz, 3 H); 3381, 3055, 2952, 1511, 1463, 757, 696; **7h** : 93 % (oil); - 18.48 (*c* 0.85); 43 % ee; 7.19 - 7.32 (m, 5 H); 3.93 (m, 1 H), 2.23 - 2.27 (m, 1 H), 1.42 - 1.69 (m, 4 H), 1.31 (d, J = 6.65 Hz, 3 H), 0.99 - 1.20 (m, 4 H), 0.89 (m, 2 H); **7i** : 86 % (oil); 9.4 % ee; 7.12 - 7.73 (m, 3 H), 6.55 - 6.68 (m, 2 H), 3.39 (m, 1 H), 1.27 - 1.32 (m, 2 H), 1.16 (d, J = 6.65 Hz, 3 H), 0.92 (t, J = 6.86 Hz, 3 H); 3361, 3028, 2866, 1601, 1498, 1315, 731, 687; **7j** : 87 % (oil); - 6.36 (*c* 0.81); 18.4 % ee; 7.11 - 7.17 (m, 2 H), 6.55 - 6.67 (m, 3 H), 3.43 (m, 1 H), 1.20 - 1.57 (m, 8 H), 1.15 (d, J = 7.32 Hz, 3 H), 0.89 (m, 3 H); 3395, 3042, 2923, 1600, 1501, 1316, 747, 672; **7k** : 88 % (oil); - 6.03 (*c* 0.69); 24 % ee; 7.21 - 7.33 (m, 5 H), 3.80, 3.72 (AB, J = 12.51, 1 H), 2.60 (m, 1 H), 1.30 - 1.55 (m, 2 H), 1.06 (d, j = 6.30 Hz, 3 H), 0.89 (t, J = 7.41, 3 H); 3354, 3055, 2915, 1492, 1460, 1372, 720, 691; **7l** : 90 % (oil); 7.4 % ee; 7.20 - 7.33 (m, 5 H), 3.82, 3.72 (AB, J = 13.0 Hz, 1 H), 2.65 (m, 1 H), 1.22 - 1.49 (m, 8 H), 1.07 (d, J = 6.23 Hz, 3 H), 0.87 (m, 3 H); 3463, 3053, 2950, 1491, 1450, 1373, 717, 693; **7m** : 89 5 (oil); 14 % ee; 7.20 - 7.34 (m, 5 H), 3.83, 3.76 (AB, J = 13.10 Hz, 1 H), 2.51 (m, 1 H), 1.72 (m, 1 H), 0.99 (d, J = 6.44 Hz, 3 H), 0.89 (m, 6 H); 3478, 3055, 2815, 1492, 1451, 1381, 730, 694. The results are summarized in Table 3.

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