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(1*S*, 3*R*, 4*R*)-2-Azanorbornyl-3-methanol Oxazaborolidines in the Asymmetric Reduction of Ketones

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Abstract:

Synthesis of new rigid (1*S*, 3*R*, 4*R*)-2-azanorbornyl-3-methanols and its application in the asymmetric borane reduction of ketones are described. The influence of temperature, solvent and concentration on the reaction outcome were also studied and enantiomeric excess up to 89% could be obtained.

Keywords: Asymmetric reactions; Reduction; Ketones; Amino alcohols.

Introduction

Enantioselective reduction of prochiral ketones has received large attention in the last decade, since the resulting secondary alcohols are of extreme importance in organic synthesis[1]. Different procedures to prepare these enantiomerically enriched alcohols from those starting materials are currently available, and the use of borane chiral complexes is among one of the most useful methods. Since its introduction in 1981[2] and later developments[3] by Itsuno *et al.* many improvements have been made and very high enantioselectivities have been reported for this reaction[4], [5], [6]. Excellent reviews on the use of oxazaborolidines[7] in asymmetric synthesis[8],[9] are also available.

During our most recent work we found 2-azanorbornyl derivatives as very efficient chiral ligands for a variety of asymmetric transformations[10], [11], [12]. At the same time it has been suggested[8] that a rigid analogue of the widely used CBS catalyst[7] could match the structural requirements for a highly efficient catalytic system. For these reasons we decided to investigate the usefulness of this kind of structure in the enantioselective borane reduction of unsymmetric ketones.

The highest enantioselectivities for this reaction have been reported using compounds derived from natural amino acids. This restricts the availability of both enantiomeric forms of the resulting secondary alcohol, since unnatural analogues are much more expensive. This is obviously not the case of the 2-azanorbornyl structures, since the chiral precursor

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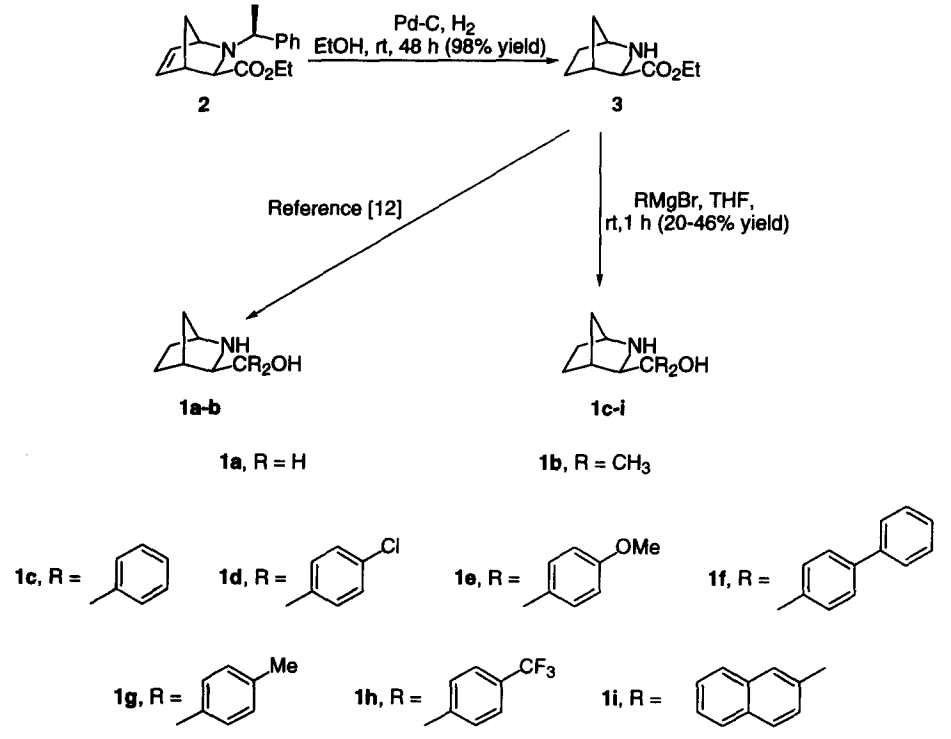
for their preparation is 1-phenylethylamine which is inexpensive and available in both enantiomeric forms.

Herein we present our results on the application of 2-azanorbornyl-3-methanol oxazaborolidines in the reduction of prochiral ketones.

Results and Discussion

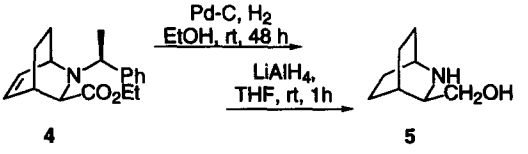
With the objective of investigating different oxazaborolidines, amino alcohols **1a-i** were prepared from the common Diels-Alder adduct **2** (Scheme 1). Obtained via a highly diastereoselective aza-Diels-Alder reaction between cyclopentadiene and the protonated imine derived from ethyl glyoxylate and (*S*)-1-phenylethylamine using a literature procedure[13], [14], compound **2** was further submitted to hydrogenation/hydrogenolysis in the presence of 5% Pd-C leading to amino ester **3** (Scheme 1). HPLC analysis of the *N*-benzoyl derivative of **3** indicated an optical purity of 98%.



Scheme 1. Synthesis of ligands **1a-i**

Compounds **1a** and **1b** were prepared from **3** according to a literature procedure[12] and amino alcohols **1c-i** were prepared by simple addition of the same amino ester to the

corresponding Grignard reagent generated from magnesium and the required halide in the classical fashion. Unlike proline methyl ester[15], epimerization at C-3 of compound **3** was not observed, therefore Grignard reactions were possible without the need of cyclic protection. We also tried to study the influence of the backbone flexibility and for that purpose compound **5** was prepared. Using a similar procedure by simply employing cyclohexadiene in the aza-Diels-Alder reaction, **4** was obtained. When submit to the same treatment as compound **2**, adduct **4** yielded the desired amino alcohol **5** (Scheme 2).



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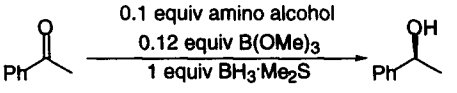
Sheme 2. Synthesis of ligand **5**

All borane reductions were performed using a literature procedure[16], [17] outlined for acetophenone in Scheme 3. The catalytically active oxazaborolidine is generated *in situ* using $B(OMe)_3$ and the corresponding chiral amino alcohol. This simple procedure allows reproductible results to be obtained in an easier way, once isolation of the very air and moisture sensitive oxazaborolidine species is not required.



Scheme 3. Borane reduction of acetophenone

To study the influence of different reaction conditions on the enantiomeric excess **1c** and acetophenone were chosen. We decided to first investigate the effect of the amino alcohol concentration on the asymmetric induction at rt and in THF (Table 1).

Table 1.
Amino alcohol concentration effect on the reduction of acetophenone

Entry	Initial amino alcohol concentration / M[a]	% *ee*[b]
1	0.05	83
2	0.1	84
3	0.2	87
4	0.9	87

[a]Initial concentration means the **1c** concentration in THF before any other addition. The ketone is then added as a solution in equal volume of solvent (see experimental). The total amount of catalyst employed is in any case 10 mol%.
[b]Isolated yields of the corresponding secondary alcohol were in all cases > 95%.

The results show a dependence of the enantiomeric excess on the concentration of **1c**, having a maximum at 87% *ee*. We found an optimum relation % *ee*/concentration for 0.2 M initial amino alcohol concentration.

Using this concentration of 0.2 M, we decide to explore the influence of solvent and temperature on the enantiomeric excess of the resulting alcohol (Table 2). Its known from the literature that these reactions are extremely dependent on the temperature[18] and solvent.

Table 2.
Solvent and temperature effects

Entry	Solvent	Temperature / °C	Total time / h	% *ee*[a]
1	THF	rt (23-26)	2	87
2	CH_2Cl_2	rt	6	*rac.*[b]
3	CH_3CN	rt	4	23
4	Toluene	rt	2	67
5	THF	6-7	8	49
6	THF	40	2	79

[a]Isolated yields of the corresponding secondary alcohol were in all cases > 95%.
[b]3% *ee*.

Confirming the need for a donor type of solvent[2], [3], THF turned out to be the solvent of choice. Reactions in solvents other than THF were much slower and led to lower enantioselectivities. Temperature dependence of this type of reaction is related to the catalytic system used, and in the case of our 2-azanorbornyl-3-methanols it appears to have an optimum value at rt. The use of lower temperature led to poor results and very slow reactions, and the use of higher temperature also resulted in lower enantiomeric excess.

With these preliminary results we decided to investigate the influence of different amino alcohols on the reaction. For this purpose compounds **1a** and **1b**, **1c-h** and **5** were prepared (Scheme 1) and tested in the reduction of acetophenone using 0.2 M as initial concentration in THF at rt (Table 3).

The best results were obtained with **1c** and **1i** having phenyl and 2-naphtyl substituents, respectively. As expected the use of a primary alcohol system as well as the use of an alkyl substituent decreased the *ee* (entries 1, and 2, Table 3). Unfortunately the introduction of different aryl groups by varying the substituent on the *p*-position of the aromatic ring did not improve the obtained enantiomeric excess, independently of their electronic effects (entries 4-8, Table 3). Also as expected the change on the amino alcohol backbone, using the less rigid compound **5** did not improve the *ee* (entry 10, Table 3).

A similar result to the one obtained with **1c** could only be achieved when using a 2-naphtyl system (entry 9, Table 3) as the aryl substituent on the amino alcohol structure.

Table 3.
Reduction of acetophenone with amino alcohols **1a-i** and **5**

Entry	Amino alcohol	% *ee*[a]
1	1a	55
2	1b	13[b]
3	1c	87
4	1d	63
5	1e	45
6	1f	77
7	1g	60
8	1h	77
9	1i	87
10	5	45

[a]Isolated yields of the corresponding secondary alcohol were in all cases > 95%.
[b]Result using a initial concentration of 0.1M.

To the extension of this catalytic system to other prochiral ketones we chose amino alcohol **1c**, and the obtained results are summarized in Table 4. One should note that the inversion observed in the absolute configuration of the resulting alcohol when using α-halogenated ketones[19] is only a consequence of the Cahn-Ingold-Prelog convention and do not reflect any difference in the preferred approach of these type of ketones to the active catalytic species.

Table 4.
Reduction of different ketones with amino alcohol **1c**

Entry	Ketone	% *ee*[a]	Alcohol's abs. config.[b]
1	Acetophenone	87	(*S*)
2	Propiophenone	70[c]	(*S*)
3	Valerophenone	58	(*S*)
4	1-Indanone	83[d]	(*S*)
5	1-Tetralone	77[d]	(*S*)
6	1-Acetonaphtone	47	(*S*)
7	α-Chloroacetophenone	82	(*R*)
8	α-Bromoacetophenone	89	(*R*)

[a]Isolated yields of the corresponding secondary alcohol were in all cases > 95%.
[b]Absolute configurations were assigned by comparison of the optical rotation sign with the ones available for commercial products or reported in the literature.
[c]Reduction with ligand **1i** gave the corresponding secondary alcohol in 81% *ee*.
[d]Result using a initial concentration of 0.1M.

Conclusion

The work demonstrates the usefulness of (1*S*, 3*R*, 4*R*)-2-azanorbornyl-3-methanols in the borane reduction of prochiral ketones and also the concentration, temperature and solvent dependence of this reaction. We showed that in the case of this catalytic system a initial concentration of 0.2 M at rt in THF are the optimum conditions for the title reaction.

Experimental

General experimental information[20]: When mentioned, deactivated silica gel means that it was treated with 5% Et_3N in pentane and the column was eluted with the same solvent mixture until the coming eluent was basic according to pH paper. When mentioned, deactivated TLC plates means that the plates were eluted with 5% Et_3N in pentane and dried before applying the sample. HPLC analysis were carried out using a chiral column (Chiral Cel OD-H), a 254 nm UV detector and a 0.5 mL/min flow rate of hexane/2-propanol: 95/5. Absolute configurations were assigned by comparison of the optical rotation sign with the ones available for commercial products or reported in the literature. All ^1H NMR and ^{13}C NMR were recorded for $CDCl_3$ solutions.

Ethyl(1*S*, 3*R*, 4*R*)-2-[(*S*)-1-phenylethylamino]-2-azabicyclo[2.2.1]hept-5-ene -3-carboxylate (2). Compound **2** was prepared following a literature procedure[13], [14]. All the physical and spectroscopic data for this compound were in complete agreement with the reported data for its enantiomer[14], [21], except for the sign of the optical rotation.

Ethyl(1*S*, 3*R*, 4*R*)-2-azabicyclo[2.2.1]heptane-3-carboxylate (3). Compound **3** was prepared according to a literature procedure[11], and all physical and spectroscopic data were in complete agreement with the reported one.

(1*S*, 3*R*, 4*R*)-2-azabicyclo[2.2.1]heptane-3-methanol (1a). Compound **1a** was prepared according to a literature procedure[12], and all physical and spectroscopic data were in complete agreement with the reported one.

(1*S*, 3*R*, 4*R*)-2-azabicyclo[2.2.1]heptane-3-*bis*(methyl)methanol (1b). Compound **1b** was prepared according to a literature procedure[12], and all physical and spectroscopic data were in complete agreement with the reported one.

Ethyl(1*S*, 3*R*, 4*R*)-2-[(*S*)-1-phenylethylamino]-2-azabicyclo[2.2.2]oct-5-ene -3-carboxylate (4). Compound **4** was prepared in a analogous way to the one used for preparation of **2**. All the physical and spectroscopic data for this compound were in

complete agreement with the reported in the literature for its enantiomer[13], except for the sign of the optical rotation.

(1*S*, 3*R*, 4*R*)-2-azabicyclo[2.2.2]octane-3-methanol (5). This compound was prepared as compound **1a**, using **4** as starting material, in 90% yield. mp = 67-68 °C; R_f 0.23 (methanol; deactivated silica gel); $[\alpha]^{24}_D$ = -37.6 (0.63, CH_2Cl_2); IR (KBr, cm^{-1}) 3277 and 2940; ^{1}H NMR δ 1.30-2.00 (10 H, m), 2.92 (1 H, br s), 3.15 (1 H, br t, J = 6.0 Hz), 3.46-3.70 (2 H, m) and 4.02 (1 H, m); ^{13}C NMR δ 20.2, 25.9, 26.3, 27.1, 44.0, 56.6, 64.8 and 76.6; MS (EI) *m/z* (rel. intensity) 123 (M^+-$H_2$0, 4%), 110 (100), 82 (65), 67 (44) and 54 (44); HRMS: calcd for $C_8H_{15}NO$ (M^+) *m/z* 141.2148, found 141.1155.

General procedure for the Grignard additions: A solution of compound **3** in dry THF was added at 0 °C to a previously prepared RMgBr solution in dry THF (ratio ester/Grignard = 1/3.2). After addition the reaction was stirred at rt until completion according to TLC (usually 1 h). The reaction was then cooled to 0 °C and quenched with NH_4Cl saturated solution, CH_2Cl_2 was added and the phases were separated. After extraction with CH_2Cl_2 the combined organic layers were dried over $MgSO_4$. Filtration and evaporation of the solvent afforded a residue that was purified by flash chromatography on deactivated silica gel using pentane/EtOAc: 90/10 to 50/50, unless otherwise noted. With the exception of **1h** all compounds were recrystallized from hexane.

(1*S*, 3*R*, 4*R*)-2-azabicyclo[2.2.1]heptane-3-*bis*(phenyl)methanol (1c). This compound was obtained in 45% yield and all the physical and spectroscopic data were in complete agreement with the reported data for its enantiomer[22], except for the sign of the optical rotation.

(1*S*, 3*R*, 4*R*)-2-azabicyclo[2.2.1]heptane-3-*bis*(*p*-chlorophenyl)methanol (1d). This compound was obtained in 43% yield. mp = 192-193 °C; R_f 0.54 (pentane/EtOAc: 60/40, deactivated silica); $[\alpha]^{24}_D$ = +69.8 (c = 0.43, CH_2Cl_2); IR (KBr, cm^{-1}) 3402, 2900, 1487 and 1.090; ^{1}H NMR δ 1.00 (1 H, br d, J = 10.1 Hz), 1.31-1.70 (5 H, m), 1.82 (1 H, br d, J = 10.1 Hz), 2.07 (1 H, br s), 3.52 (1 H, br s), 3.60 (1 H, br s), 4.54 (1 H, m) and 7.22-7.42 (8 H, m); ^{13}C NMR δ 30.1, 32.5, 34.9, 38.5, 55.5, 66.1, 76.4, 127.0, 127.4, 128.0, 132.1, 132.3, 143.3 and 146.2; MS (EI) *m/z* (rel. intensity) 330 (M^+-$H_2$0, 1%), 139 (25), 111 (17), 96 (100) and 68 (75). Anal. Calcd for $C_{19}H_{19}Cl_2NO$: C, 65.52; H, 5.50; N, 4.02. Found: C, 65.32; H, 5.60; N, 3.94.

(1*S*, 3*R*, 4*R*)-2-azabicyclo[2.2.1]heptane-3-*bis*(*p*-methoxyphenyl)methanol (1e). This compound was obtained, after flash chromatography on deactivated silica gel (pentane/EtOAc: 95/5 to 20/80), in 45% yield. mp = 119-120 °C; R_f 0.26 (pentane/EtOAc: 40/60, deactivated silica); $[\alpha]^{24}_D$ = +67.8 (c = 0.51, CH_2Cl_2); IR (KBr, cm-1) 3362, 2951,

1608, 1509 and 1248; ^{1}H NMR δ 0.98 (1 H, br d, J = 9.4 Hz), 1.33-1.68 (6 H, m), 1.84 (1 H, br d, J = 9.4 Hz), 2.14 (1 H, br s), 3.50 (1 H, br s), 3.61 (1 H, br s), 3.76 (6 H, d, J = 5.4 Hz), 6.77-6.85 (4 H, m) and 7.33-7.41 (4 H, m); ^{13}C NMR δ 30.1, 32.5, 34.9, 38.5, 54.9, 55.4, 76.4, 113.0, 113.1, 126.7, 127.0, 137.7 and 157.6; MS (EI) *m/z* (rel. intensity) 321 (M^+-H_20, 7%), 135 (33), 123 (25), 108 (27), 96 (100), 77 (11) and 68 (34). Anal. Calcd. for $C_{21}H_{25}NO_3$: C, 74.31; H, 7.42; N, 4.13. Found: C, 74.24; H, 7.55; N, 4.15.

(1*S*, 3*R*, 4*R*)-2-azabicyclo[2.2.1]heptane-3-[4,4'-*bis*(biphenyl)]methanol (1f). This compound was obtained in 46% yield. mp = 155-156 °C; R_f 0.16 (pentane/EtOAc: 60/40, deactivated silica); $[\alpha]^{24}_D$ = +55.5 (c = 0.51, CH_2Cl_2); IR (KBr, cm^{-1}) 3340, 2959 and 1487; ^{1}H NMR δ 1.05 (1 H, br d, J = 9.7 Hz), 1.41-1.74 (5 H, m), 1.94 (1 H, br d, J = 9.7 Hz), 2.26 (1 H, br s), 3.56 (1 H, br s), 3.80 (1 H, br s), 4.49 (1 H, m) and 7.31-7.66 (18 H, m); ^{13}C NMR δ 30.4, 32.7, 35.2, 38.8, 55.7, 66.7, 77.8, 126.2, 126.5, 126.7, 126.8, 126.99, 127.05, 127.1, 128.7, 139.1, 139.2, 140.76, 140.84, 144.3 and 147.3; MS (EI) *m/z* (rel. intensity) 413 (M^+-H_20, 2%), 181 (14), 152 (12), 96 (100) and 68 (28). Anal. Calcd. for $C_{31}H_{29}NO$: C, 86.27; H, 6.77; N, 3.25. Found: C, 86.08; H, 6.86; N, 3.26.

(1*S*, 3*R*, 4*R*)-2-azabicyclo[2.2.1]heptane-3-*bis*(*p*-tolyl)methanol (1g). This compound was obtained in 45% yield. mp = 119-120 °C; R_f 0.46 (pentane/EtOAc: 60/40, deactivated silica); $[\alpha]^{24}_D$ = +69.5 (c = 0.50, CH_2Cl_2); IR (KBr, cm^{-1}) 3340, 2959, 1487 and 1404; ^{1}H NMR δ 0.98 (1 H, br d, J = 9.7 Hz), 1.34-1.69 (5 H, m), 1.86 (1 H, br d, J = 9.7 Hz), 2.15 (1 H, br s), 2.29 (6 H, d, J = 6.6 Hz), 3.50 (1 H, br s), 3.66 (1 H, br s), 4.36 (1 H, m), and 7.05-7.40 (8 H, m); ^{13}C NMR δ 20.9, 21.0, 30.4, 32.8, 35.2, 38.8, 55.6, 66.6, 77.8, 125.6, 126.0, 128.6, 128.7, 135.6, 135.7, 142.6 and 145.6; MS (EI) *m/z* (rel. intensity) 289 (M^+-H_20, 3%), 119 (24), 96 (100), 91 (16) and 68 (39). Anal. Calcd. for $C_{21}H_{25}NO$: C, 82.04; H, 8.20; N, 4.56. Found: C, 81.86; H, 8.28; N 4.51.

(1*S*, 3*R*, 4*R*)-2-azabicyclo[2.2.1]heptane-3-*bis*[*p*-(triflouromethyl)phenyl] methanol (1h). CAUTION (Preparation of the needed Grignard reagent can be extremely hazardous[23]). This compound was obtained, after flash chromatography on deactivated silica gel (pentane/EtOAc: 95/5 to 80/20), as a yellow oil in 20% yield. R_f 0.68 (pentane/EtOAc: 60/40, dectivated silica); $[\alpha]^{24}_D$ = +50.0 (c = 0.68, CH_2Cl_2); IR (neat, cm^{-1}) 2962, 1325, 1166 and 1128; ^{1}H NMR δ 1.02 (1 H, br d, J = 9.4 Hz), 1.35-1.80 (5 H, m), 1.85 (1 H, br d, J = 9.4 Hz), 2.06 (1 H, br s), 3.54 (1 H, br s), 3.73 (1 H, br s), 4.62 (1 H, m) and 7.50-7.66 (8 H, m); ^{13}C NMR δ 30.2, 32.6, 35.1, 55.7, 66.4, 77.8, 125.18, 125.23, 125.5, 125.58, 125.63, 126.1, 126.5, 126.7, 148.4 and 151.5; MS (EI) *m/z* (rel. intensity) 397 (M^+-H_20, < 1%), 173 (16), 145 (18), 108 (13), 96 (100) and 68 (83); HRMS: calcd for $C_{21}H_{19}F_6NO$ (M^+) *m/z* 415.3821, found 415.1373.

(1*S*, 3*R*, 4*R*)-2-azabicyclo[2.2.1]heptane-3-*bis*(2-naphtyl)methanol (1i). This compound was obtained in 44% yield. mp = 163-164 °C; R_f 0.22 (pentane/EtOAc:

60/40, deactivated silica); $[\alpha]^{24}_D$ = +186 (c = 0.50, CH_2Cl_2); IR (KBr, cm^{-1}) 3336, 2938 and 1506; ^1H NMR δ 1.02 (1 H, br d, *J* = 9.8 Hz), 1.40-1.73 (5 H, m), 1.97 (1 H, br d, 9.8 Hz), 2.18 (1 H, br s), 3.56 (1 H, br s), 3.97 (1 H, br s), 4.82 (1 H, m) and 7.40-8.10 (14 H, m); ^{13}C NMR δ 30.3, 32.8, 35.3, 38.9, 55.7, 66.0, 78.3, 123.8, 124.3, 124.6, 125.6, 125.68, 125.73, 125.87, 125.94, 127.38, 127.44, 127.6, 128.0, 128.2, 128.3, 132.1, 132.9, 133.1, 142.6 and 145.4; MS (EI) *m/z* (rel. intensity) 361 (M^+-H_20, 2%), 282 (12), 155 (42), 127 (44), 123 (68), 108 (34), 96 (100) and 68 (34). Anal. Calcd. for $C_{27}H_{25}NO$: C, 85.45; H, 6.64; N, 3.69. Found: C, 85.64; H, 6.58; N, 3.52.

General procedure for the borane reductions[16], [17]: A dry 10 mL round bottom flask loaded with a magnetic bar was charged with amino alcohol **1c** (140 mg, 0.5 mmol) that was dissolved in dry THF (2.5 mL) under argon. To this solution was added $B(OMe)_3$ (68 μL, 0.60 mmol). After stirring at rt for 1 h, BH_3•Me_2S (474 μL, 5.0 mmol) was added and the mixture was allowed to stir for 10 min before starting the addition of acetophenone (583 μL, 5.0 mmol) as a solution in dry THF (2.5 mL) via syringe pump over a period of 1 h.

After complete addition of the acetophenone the reaction was monitored by TLC and when completed (usually shortly after addition) was cooled down to 0 °C and quenched with 2 M HCl, diluted with ether and stirred for 30 min at rt. The two phase system was then poured into a extraction funnel and the ether phase was washed with brine, saturated $NaHCO_3$ solution and brine. After drying over $MgSO_4$ solvent evaporation afforded pure (*S*)-1-phenylethanol in > 95% yield and 87% *ee*. The same procedure was used in the test of the different ligands and different ketones and in all cases similar yields were obtained. The optical purity of the products was determined by HPLC analysis as decribed in general experimental information, under this conditions the secondary alcohols showed the following retention times: 1-phenylethanol 16.7 (*R*) and 20.8min (*S*), 1-phenyl-1-propanol 15.3 (*R*) and 18.9min (*S*), 1-phenyl-1-pentanol 14.4 (*R*) and 16.5min (*S*), 1-indanol 18.5 (*S*) and 20.9min (*R*), 1,2,3,4-tetrahydro-1-naphthol 16.3 (*S*) and 18.3min (*R*), 1-naphthyl-1-ethanol 32.8 (*S*) and 51.0min (*R*), 2-chloro-1-phenylethanol 23.6 (*S*) and 28.4min (*R*) and 2-bromo-1-phenylethanol 22.5 (*S*) and 30.8min (*R*).

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References

[1] See for example: Corey, E.J.; Helal, C.J. *Tetrahedron Lett.* **1997**, *38*, 7511.
[2] Hirao, A.; Itsuno, S.; Nakahama, S.; Yamazaki, N. *J. Chem. Soc. Chem. Comm.* **1981**, 315.
[3] Itsuno, S.; Hirao, A.; Nakahama, S.; Yamazaki, N. *J. Chem. Soc. Perkin Trans. I* **1983**, 1673.
[4] Corey, E.J.; Bakshi, R.K.; Shibata, S. *J. Am. Chem. Soc.* **1987**, *109*, 5551.
[5] Corey, E.J.; Bakshi, R.K.; Shibata, S. *J. Am. Chem. Soc.* **1987**, *109*, 7925.
[6] Mathre, D.J.; Jones, T.K.; Xavier, L.C.; Blacklock, T.J.; Reamer, R.A.; Mohan, J.J; Jones, E.T.T.; Hoogsteen, K.; Baum, M.W.; Grabowski, E.J.J. *J. Org. Chem.* **1991**, *56*, 751.
[7] Corey, E.J.; Azimioara, M.; Sarshar, S. *Tetrahedron Lett.* **1992**, *33*, 3429.
[8] Wallbaun, S.; Martens, J. *Tetrahedron: Asymmetry* **1992**, *3*, 1475.
[9] Katritzky, A.R.; Meth-Cohn, O.; Rees, C.W. *Comprehensive Organic Functional Group Transformations*, Volume 2. Oxford: Pergamon Press, **1986**: 64-67.
[10] Södergren, M.J.; Andersson, P.G. *Tetrahedron Lett.* **1996**, *37*, 7577.
[11] Guijarro, D.; Pinho, P.; Andersson, P.G. *J. Org. Chem.* **1998**, *8*, 2530.
[12] Alonso, D.A.; Guijarro, D.; Pinho, P.; Temme, O.; Andersson, P.G. *J. Org. Chem.* **1998**, *8*, 2749.
[13] Stella, L.; Abraham, H.; Feneu-Dupont, J.; Tinant, B.; Declercq, J.P. *Tetrahedron Lett.* **1990**, *31*, 2603.
[14] Abraham, H.; Stella, L. *Tetrahedron* **1992**, *48*, 9707.
[15] Xavier, L.C.; Mohan, J.J.; Mathre, D.J.; Thompson, A.S.; Carroll, J.D.; Corley, E.G.; Desmond, R. *Org. Synth.* **1996**, *74*, 50.
[16] Masui, M.; Shioiri, T. *Synlett* **1996**, 49.
[17] Masui, M.; Shioiri, T. *Synlett* **1997**, 273.
[18] Stone, G.B. *Tetrahedron: Asymmetry* **1994**, *5*, 465.
[19] See for example: Shen, Z-X.; Lu, J.; Zhang, Q.; Zhang, Y-W. *Tetrahedron: Asymmetry* **1997**, *8*, 2287.
[20] Bedeker, A.V.; Koroleva, E.B.; Andersson, P.G. *J. Org. Chem.* **1997**, *62*, 2518.
[21] Waldmann, H.; Braun, M. *Liebigs Ann. Chem.* **1991**, 1045.
[22] Nakano, H.; Kumagai, N.; Matsuzaki, H.; Kabuto, C.; Hongo, H. *Tetrahedron: Asymmetry* **1997**, *8*, 1391.
[23] Ashby, E.C.; Al-Fekri, D.M. *J. Organomet. Chem.* **1990**, *390*, 275.