Heteroatom Chemistry
Volume 18, Number 7, 2007

Effect of Borane Source on the Enantioselectivity in the Enantiopure Oxazaborolidine-Catalyzed Asymmetric Borane Reduction of Ketones

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Received 18 September 2006; revised 29 January 2007

ABSTRACT: *The effect of borane source on enantioselectivity in the enantiopure oxazaborolidine-catalyzed asymmetric borane reduction of ketones has been investigated by using (S)-3,1,2-oxazaborobicyclo[3.3.0]octane and (S)-7,3,1,2-thiaxazaborobicyclo[3.3.0]octane as catalysts. The results indicate that the enantioselective order of different borane sources is borane–dimethyl sulfide < borane–N,N-diethylaniline < borane–THF for the asymmetric reduction of a ketone under the same conditions.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:740–746, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20370

INTRODUCTION

Enantiopure oxazaborolidine-catalyzed borane reduction of prochiral ketones is one of the most important methods to prepare highly optically active secondary alcohols [1]. During the past two decades, numerous efficient catalysts and their applications have been reported [1]. Investigations into the mechanism of the catalytic asymmetric reduction were also conducted [2,3]. Some researchers have paid much attention to the factors that affect the enantioselectivity in the asymmetric reduction, such as the structure [1,2,4], the stability [2a,5] and the loading amount [2a,5a,6] of catalysts, the type [7] and amount [2a,6c] of borane sources, the order and rate of the addition of a ketone or a borane complex into a reductive system [1d,6c], the reduction temperature [5d,6c,8], the solvent [5a,6c,7a,d], the additive [8g,9,10], the secondary reduction [9a,11], the stabilizer in borane [12], the electronic effects of both ketones [4a,5a,10,13,14] and catalysts [4a,10,14], the kinetics of the asymmetric reduction [15], etc. Although some investigators have referred that different enantioselectivities could be observed with different borane sources [7], all of them evaluated the effect at about room temperature. The effect of borane source on the enantioselectivity in the asymmetric reduction of ketones at different temperatures is not clear, as well as the order of different borane sources on the enantioselectivity is not completely clear. Herein, we present our experimental results.

RESULTS AND DISCUSSION

After investigations into the effect of the temperature [5d,6c], the electronic effects of substrate ketones

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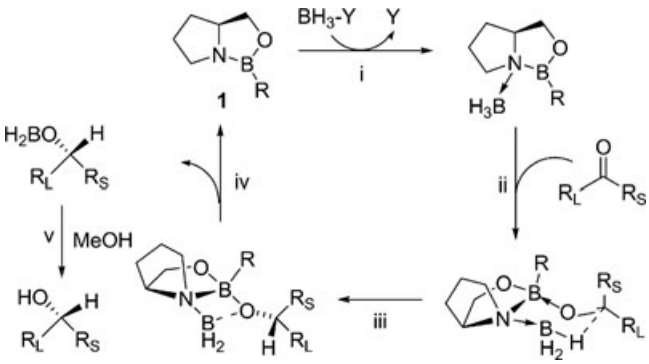
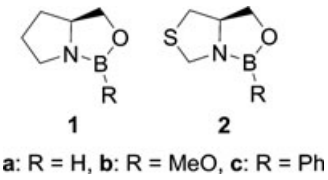
Contract grant sponsor: National Natural Science Foundation of China.
Contract grant number: 20472005.



SCHEME 1 Reasonable reaction mechanism of the asymmetric borane reduction of ketones.



SCHEME 2 Structures of catalysts **1** and **2**.

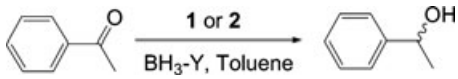
[10] and catalysts [14], anions [10], the secondary reduction [11b], and the function of additives [11b] on the enantioselectivity, we wish to study the effect of borane sources on the enantioselectivity in the asymmetric reduction of ketones to understand all factors that affect the enantioselectivity and to use the asymmetric reaction efficiently. In the reasonable reaction mechanism of the asymmetric borane reduction of ketones [1–3], borane–catalyst complexes formed from the reaction of borane sources and catalysts serve as efficient reagents in the catalytic cycle for the reduction that occurs by the coordination of the electrophilic boron atom of catalysts with the carbonyl oxyatom of ketones and subsequent intramolecular hydrogen transfers from the N-BH_3 moiety of borane–catalyst complexes to the carbon atom of the activiated carbonyl group via a six-membered ring transition state, followed by regeneration of the borane–catalyst complexes via the subsequent ligand exchange with borane sources to produce the alkoxyboranes, which give rise to optically active secondary alcohols after workup (Scheme 1). Accordingly, it is expected that the nature of borane sources should play an important role and affect the enantioselectivity in the asymmetric reduction.

Enantiopure L-prolinol shows moderate enantioselectivity in the asymmetric reduction of ketones [5d]. It was reported that different borane sources show different enantioselectivities in the asymmetric reduction [7]. To observe the obvious effect of the borane sources on the enantioselectivity in the asymmetric reduction, we chose L-prolinol as the chiral source to prepare enantiopure oxazaborolidine catalysts. The representative borane sources [borane–dimethyl sulfide (BH_3–SMe_2), borane-*N*,*N*-diethylaniline (BH_3–$PhNMe_2$), and borane–tetrahydrofuran (BH_3–THF) complexes] were selected as reducing reagents. Initially, (*S*)-3,1,2-oxazaborobicyclo[3.3.0]octane (**1a**) (Scheme 2) was prepared *in situ* to evaluate the enantioselectivity in the asymmetric reduction of acetophenone with different borane sources. Then the reductions were conducted in toluene at two representative temperatures 25°C and 110°C, respectively [6c]. The results indicate that (*R*)-1-phenylethanol was obtained as a major enantiomer under the catalysis of **1a** in all cases, and the enantioselectivities at 110°C were higher than those at 25°C for each reactions (Table 1, entries 1–6). This phenomenon could be attributed to inhibition of dimerization of the catalyst **1a** at 110°C [5d]. On the other hand, equilibria between the borane source complexes and the borane–catalyst complexes could move predominantly to the latter side at higher temperature because such a borane–transfer reaction is endothermic in nature [16]. Borane sources BH_3–SMe_2 and BH_3–$PhNMe_2$ show similar enantioselectivity at 25°C (Table 1, entries 1 and 2). BH_3–$PhNMe_2$ and BH_3–THF complexes give almost the same enantioselectivity at 110°C (Table 1, entries 5 and 6).

The enantioselective order of the borane sources is BH_3–SMe_2 < BH_3–$PhNMe_2$ < BH_3–THF on the basis of our experiments. The BH_3–THF complex shows the best enantioselectivity at both temperatures (Table 1, entries 3 and 6). Such an order indicates that the coordinating stability of the borane sources is BH_3–SMe_2 > BH_3–$PhNMe_2$ > BH_3–THF. Unstable BH_3–THF complex favors the transfer of its borane to the catalyst to undergo fast asymmetric reduction to inhibit the competitive noncatalytic reduction, resulting in the higher enantioselectivity, because the noncatalytic reduction is a nonneglectable factor in the asymmetric synthesis [6c]. However, the stable BH_3–SMe_2 complex does not favor this transfer, leading to relatively lower enantioselectivity.

During our work, we observed that the rates of the asymmetric reductions are very different for different borane sources. BH_3–$PhNMe_2$ showed the slowest reduction rate. Such a phenomenon, which seemed not in accordance with the order of coordinating stability of borane sources, can be attributed

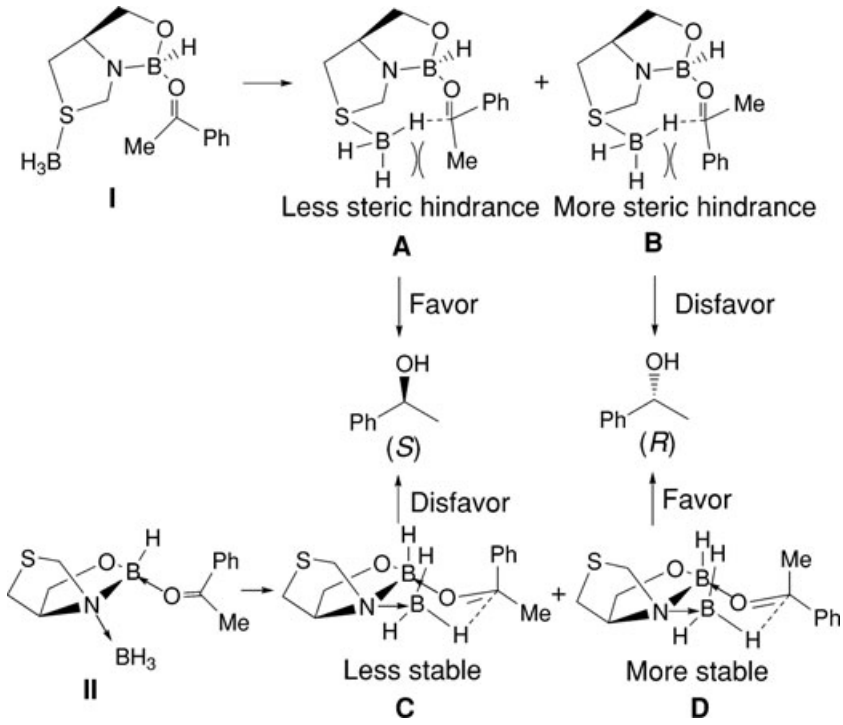
TABLE 1 Catalytic Asymmetric Borane Reduction of Acetophenone With Different Catalysts and Borane Sources



Entry	*Catalyst*	*Borane Source*	*Reduction Temperature (°)*	*Yield (%)*[a]	*e.e.(%)*[b]	*Configuration*[b]
1	**1a**	BH_3–Me_2S	25	94	30	*R*
2	**1a**	BH_3–Et_2NPh	25	67	37	*R*
3	**1a**	BH_3–THF	25	92	77	*R*
4	**1a**	BH_3–Me_2S	110	93	45	*R*
5	**1a**	BH_3–Et_2NPh	110	62	85	*R*
6	**1a**	BH_3–THF	110	88	86	*R*
7	**1b**	BH_3–Me_2S	25	95	53	*R*
8	**1b**	BH_3–Et_2NPh	25	95	53	*R*
9	**1b**	BH_3–Me_2S	110	95	42	*R*
10	**1b**	BH_3–Et_2NPh	110	70	38	*R*
11	**1c**	BH_3–Me_2S	25	63	8	*R*
12	**1c**	BH_3–Et_2NPh	25	65	16	*R*
13	**1c**	BH_3–Me_2S	110	94	81	*R*
14	**1c**	BH_3–Et_2NPh	110	70	78	*R*
15	**1c**	BH_3–Me_2S (MeSPh)	110	70	73	*R*
16	**1a**	BH_3–Me_2S	50	93	32	*R*
17	**1a**	BH_3–THF	50	83	80	*R*
18	**1b**	BH_3–Me_2S	50		60	*R*
19	**1c**	BH_3–Et_2NPh	50		37	*R*
20	**2a**	BH_3–THF	50		−32	*S*
21	**2a**	BH_3–Me_2S	25	83	−21	*S*
22	**2a**	BH_3–Et_2NPh	25	65	31	*R*
23	**2a**	BH_3–THF	25	94	15	*R*
24	**2a**	BH_3–Me_2S	110	66	−55	*S*
25	**2a**	BH_3–Et_2NPh	110	47	−52	*S*
26	**2a**	BH_3–THF	110	66	−51	*S*
27	**2b**	BH_3–Et_2NPh	25	81	12	*R*
28	**2b**	BH_3–Et_2NPh	110	72	45	*R*
29	**2c**	BH_3–Et_2NPh	25	58	11	*R*
30	**2c**	BH_3–Et_2NPh	110	58	9	*R*

[a]Isolated yields after the column chromatography.
[b]Determined by HPLC analysis using an OD chiral column (4.6 mm × 250 mm, Chiralcel) and a mixture of *n*-hexane and 2-propanol (98.5:1.5, v/v) as an eluent at a rate of 0.8 mL/min at monitoring wave of 220 nm. Configuration was assigned according to the rotation value [6c].
[c]Equimolar amount of thioanisole was added.

to the different volatilities of *N*,*N*-diethylaniline and dimethyl sulfide. When the reaction was conducted in toluene at higher temperature than 25°C, *N*,*N*-diethylaniline was retained in the liquid phase, while part of the dimethyl sulfide would evaporate to the gaseous phase after borane transfers from BH_3–SMe_2 to the catalyst owing to its low boiling point and high vapor pressure. Thus, it is more easy for borane in the BH_3–SMe_2 complex to get transferred to the catalysts in the reduction system than that in the BH_3–$PhNMe_2$ complex. To get further evidence for this assumption, we conducted the reduction under another two widely used catalysts, (*S*)-2-methoxy-3,1,2-oxazaborobicyclo[3.3.0]octane (**1b**) and (*S*)-2-phenyl-3,1,2-oxazaborobicyclo[3.3.0]octane (**1c**) (Scheme 2), in toluene at 25°C and 110°C, respectively. The results indicate that (*R*)-1-phenylethanol was obtained as a major enantiomer under the catalysis of **1b** and **1c** in all cases. BH_3–SMe_2 and BH_3–$PhNMe_2$ complexes show similar enantioselectivity under the same reaction conditions (Table 1, entries 7–14). Catalyst **1c** shows higher enantioselectivity than catalyst **1b** at 110°C and lower enantioselectivity than catalyst **1b** at 25°C with BH_3–SMe_2 and BH_3–$PhNMe_2$ complexes as reducing reagents. The difference between these two borane sources is caused by the different coordinating ability of dimethyl sulfide and *N*,*N*-diethylaniline and their different volatilities. To further verify this explanation, we conducted the asymmetric reduction of acetophenone under the catalysis of **1c** with BH_3–SMe_2 as the reducing reagent in the presence of equimolar amount of thioanisole. In this reaction system, even while dimethyl sulfide evaporates into gaseous



SCHEME 3 Proposed transition states under the catalysis of **2a**.

phase, borane can still coordinate with thioanisole, and serve as a reducing reagent in the form of the borane sulfide complex. The reduction would show lower enantioselectivity (Table 1, entry 15) than that in the absence of thioanisole (Table 1, entry 13), as well as lower than that with BH_3–$PhNMe_2$ as reducing reagent (Table 1, entry 14). The experimental result supports our explanation.

Moreover, the effect of temperature on the enantioselectivity in the asymmetric borane reduction has been well investigated till now [5d,6c,8]. The results indicate that the enantioselectivity increases with increasing reaction temperature under the catalytic reduction of B-H catalysts [5d,8c] because the amount of dimers of the B-H catalysts decreases with increasing temperature [5d], while reactions catalyzed with B-substituted catalysts show protruding-shaped plots of the enantioselectivity with temperature [6c,8b,14]. That is, the enantioselectivity at first increases over the lower temperature range and then decreases over the higher temperature range with increasing temperature. For the most cases of B-substituted catalyst systems, the highest enantioselectivities were obtained over the temperature range 25°C to 60°C on the basis of the reported results [6c,8b,14]. We also conducted several asymmetric reductions at 50°C (Table 1, entries 16–20). The results are in good agreement with the previous results [6c,8b,14].

It was previously observed that (*S*)-7,3,1,2-thiaxazaborobicyclo[3.3.0]octane (**2a**) (Scheme 2), the sulfur analogue of **1a**, prepared *in situ* from (*R*)-1,3-thiazacyclopent-2-ylmethanol (L-thiaprolinol), shows the opposite enantiofacial selectivity to **1a** in the asymmetric reduction of ketones with BH_3–THF complex as the reducing agent [17] as well as shows different enantiofacial selectivity in different solvents at different temperatures [18]. Previously, it was assumed that the borane coordinated to sulfur atom in catalyst **2a**, result in different enantiofacial selectivity in the asymmetric reduction [17]. Thus, we consider that catalyst **2a** can be used as a probe to determine the coordinating order of borane with heteroatoms by analyzing the configuration of the reduction product to confirm partly the above obtained order of borane sources on the enantioselectivity.

For catalysts **2**, if borane coordinates with its N atom, it undergoes a six-membered ring chair transition state to give rise predominantly to (*R*)-1-phenylethanol as catalysts **1** [2,6c], whereas if borane coordinates with it S atom, it undergoes an eight-membered ring double-chair-like transition state to give rise predominantly to (*S*)-1-phenylethanol (Scheme 3) [18].

(*S*)-7,3,1,2-Thiaxazaborobicyclo[3.3.0]octane (**2a**) was prepared *in situ* to evaluate the enantioselectivity in the asymmetric reduction of acetophenone

with different borane sources. To compare with the catalyst **1a**, reductions were conducted in toluene at 25°C and 110°C, respectively (Table 1, entries 21–26). The results indicate that (*S*)-1-phenylethanol was obtained as a major enantiomer at 110°C under the catalysis of **2a** in all cases (Table 1, entries 24–26). However, at 25°C, BH_3–SMe_2 shows *S*-enantioselectivity, while BH_3–$PhNMe_2$ and BH_3–THF show *R*-enantioselectivity (Table 1, entries 21–23). All reductions conducted at higher temperature show the *S*-enantioselectivity. This indicates that the energy of the six-membered ring transition state is lower than that of the eight-membered ring transition state. The asymmetric reduction produces kinetically (*R*)-1-phenylethanol at low temperatures, while the asymmetric reduction undergoes the eight-membered ring transition state to give rise thermodynamically to (*S*)-1-phenylethanol at high temperatures.

Because borane–sulfide complex is more stable than borane–amine complex and the coordination becomes weaker at higher temperatures than that at lower temperatures, most of borane coordinates favorably with the S atom in catalysts **2** at 110°C. This is the possible reason that all borane sources show the *S*-enantioselectivity at 110°C. It also supports this assumption that different borane sources show similar enantioselectivities at 110°C. Although borane can coordinate with both N and S atoms at 25°C, the sixmembered ring reaction process is faster than the eight-membered ring process, producing (*R*)-1-phenylethanol as the major enantiomer at 25°C because the energy of the sixmembered ring transition state is lower than that of the eight-membered ring one. BH_3–SMe_2 complex shows *S*-enantioselectivity at 25°C, possibly because borane in the BH_3–SMe_2 complex exchanges to the S atom of **2a** faster than that to the nitrogen atom of **2a** owing to the stability order of the borane coordination (S > N).

According to the result of quantum calculation published previously [16], the conversion from intermediates **I** or **II** to (*S*)- or (*R*)-1-phenylethanol is the rate-determining step, and the difference in rates is the dominant factor in the reduction system. According to the Arrhenius equation, the rate of the former conversion is more sensitive to the variation of temperature. When the temperature changes from 25°C to 110°C, the rate of the conversion leading to (*S*)-1-phenylethanol is enhanced more significantly than that leading to (*R*)-1-phenylethanol.

Incidentally, the proposed transition states in our model herein are different from those proposed by Li et al. [19]. In their model, they presumed that borane coordinated only to the nitrogen atom in catalyst **2a**. After the quantum calculation of the intermediates, they concluded that the introduction of a sulfur atom into the skeleton of the catalyst let the intermediate from which (*S*)-1-phenylethanol could be formed became more favorable. Since they only considered the interaction among borane, ketone, and sulfur-containing catalyst, the configuration of the product should not be affected by different borane sources. This is not in accordance with our experimental results. Thus, our model is more reasonable.

For the reduction of acetophenone, the enantiofacial selectivity changed under the influence of **2a**, with BH_3–$PhNEt_2$ and BH_3–THF as borane sources at different temperatures. To evaluate the enantiofacial selectivity of BH_3–$PhNEt_2$ complex under the catalysis of different catalysts **2** at different temperatures, the asymmetric reduction of acetophenone was carried out under the catalysis of **2b** and **2c** (Scheme 2), with the BH_3–$PhNEt_2$ complex as the reducing reagent at 25°C and 110°C, respectively. The results indicate that *R*-enantioselectivity was obtained in all cases. This indicates that different combinations of catalyst, and borane source will show different enantiofacial selectivity at different temperatures for (*S*)-7,3,1,2-thiaxazaborobicyclo[3.3.0]-octane catalysts **2** because they could undergo the catalytic cycles via either a six-membered ring transition state (borane coordinates to their N atom) or an eight-membered ring transition state (borane coordinates to their S atom), as well as different B-substituents in catalysts **2** and different reduction temperatures affect the borane coordinating position.

CONCLUSION

In summary, we investigated the effect of borane source on the enantioselectivity in the asymmetric reduction of acetophenone. The results indicate that the enantioselective order of different borane sources is BH_3–SMe_2 < BH_3–$PhNEt_2$ < BH_3–THF for the asymmetric reduction of a ketone under the same conditions because the coordinating stability of borane sources is BH_3–SMe_2 > BH_3–$PhNEt_2$ > BH_3–THF. The different enantiofacial selectivities of the sulfur-containing catalysts with different borane sources and/or at different reduction temperatures were evaluated and interpreted. We hope that these results are beneficial to chemists in both laboratory and industry for selecting a suitable system (catalyst and borane source) to asymmetrically reduce a ketone with high enantioselectivity.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 300 (300 MHz) spectrometer in

$CDCl_3$ solution with TMS as an internal standard and chemical shifts are reported in ppm. HPLC analyses were performed on an HP1100 HPLC equipment with a Chiralcel OD column (4.6 mm × 250 mm). Borane–THF and borane–dimethyl sulfide complexes, trimethyl borate, and phenylboric acid were purchased from Acros Chemicals Co. Borane-*N*,*N*-diethylaniline complex was purchased from TCI Chemicals Co. Toluene was heated under reflux over sodium and distilled prior to use.

Catalytic Asymmetric Reduction of Acetophenone Using (S)-3,1,2-Oxazaborabicyclo[3.3.0]octane **1a**, *(R)-7,3,1,2-Thiaxazaborabicyclo[3.3.0]octane* **2a**

General Procedure. To a solution of (*S*)-prolinol (5.1 mg, 0.05 mmol) [or (*R*)-1,3-thiazalidine-4-methanol (6.0 mg, 0.05 mmol)] in dry toluene (2.5 mL) was added the desired borane complex (0.075 mmol), and the mixture was stirred under nitrogen atmosphere at 110°C for 30 min. After the mixture was adjusted to the desired temperature followed by the addition of the borane complex (0.5 mmol), a solution of acetophenone (60 mg, 0.5 mmol) in dry toluene (2.5 mL) was added dropwise within 0.5 h. After the mixture was stirred at the same temperature for 4 h, the resulting mixture was quenched with methanol in an ice water bath and concentrated under reduced pressure. The residue was purified on a silica gel column with a mixture of petroleum ether (60–90°) and ethyl acetate (5:1, v/v) as an eluent to give chiral 1-phenylethanol.

Catalytic Asymmetric Reduction of Acetophenone Using (S)-2-Methoxy-3,1,2-oxazaborabicyclo[3.3.0]octane **1b**, *or (R)-2-Methoxy-7,3,1,2-thiaxazaborabicyclo-[3.3.0]octane* **2b**

General Procedure. To a solution of (*S*)-prolinol (5.1 mg, 0.05 mmol) [or (*R*)-1,3-thiazalidine-4-methanol (6.0 mg, 0.05 mmol)] in dry toluene (2.5 mL) was added trimethyl borate (6.0 mg, 0.06 mmol), and the mixture was stirred under nitrogen atmosphere at room temperature for 2 h. After the addition of the desired borane complex (0.5 mmol), a solution of acetophenone (60 mg, 0.5 mmol) in dry toluene (2.5 mL) was added dropwise at the desired temperature within 0.5 h. After the mixture was stirred at the same temperature for 4 h, the same workup was conducted as mentioned above.

Preparation of (S)-2-Phenyl-3,1,2-oxazaborabicyclo[3.3.0]octane **1c**, *or (R)-2-Phenyl-7,3,1,2-thiaxazaborabicyclo[3.3.0]octane* **2c**

A 25-mL one-necked, round-bottomed flask was equipped with a stirring bar and a 10-mL pressure-equalizing addition funnel (containing a cotton plug and ca. 10 g of 5 Å molecular sieves, and functioning as a Soxhlet extractor). A mixture of (*S*)-prolinol (5.1 mg, 0.05 mmol) [or (*R*)-1,3-thiazalidine-4-methanol (6.0 mg, 0.05 mmol)] and phenylboronic acid (6.1mg, 0.05 mmol) was dissolved in 15 mL of dry toluene. The resulting solution was heated under reflux for 12 h. Then most of the solvent was distilled and the residue (ca. 3 mL) was cooled to room temperature. The addition funnel was removed and the flask was airproofed quickly to avoid moisture.

General Procedure for the Catalytic Asymmetric Reduction of Acetophenone with Catalysts **1c** *and* **2c**

To a solution of catalyst **1c** (or **2c**) (0.05 mmol, 10% mol) freshly prepared in dry toluene was added the desired borane complex (0.5 mmol) under a nitrogen atmosphere at the desired temperature. A solution of acetophenone (60 mg, 0.5 mmol) in 4 mL of toluene was added dropwise at the desired temperature within 0.5 h. After the mixture was stirred at the same temperature for 4 h, the same workup was conducted as mentioned above.

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