# Sn-Mediated Catalytic Asymmetric Reduction of Carbonyl Groups by Sodium Borohydride (or Sodium Borodeuteride)†

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**Two remarkable reducing agents $NaBH_4$ (or $NaBD_4$)/$SnCl_2$(or $SnCl_4 \cdot 2Et_2O$) with chiral ligands are applied to the asymmetric reduction of carbonyl compounds with excellent chemical yields and enantioselective excesses.**

**Keywords** asymmetric reduction, chiral ligand, carbonyl compound

## Introduction

Asymmetric reduction of carbonyl compounds to the corresponding optically active alcohols is one of the most useful reactions in organic synthesis.[1] Many methods have been developed for the reduction, including enantioselective hydrogenation,[2] transfer hydrogenation[3] and hydride reduction.[4] The later has been studied extensively since Brown first reported the reduction by diborane more than half a century ago.[5] In the extensive family of hydride donors, sodium borohydride has received much attention as a mild, convenient and economical reducing agent for the reduction of carbonyl group.[6] For the asymmetric reduction, sodium borohydride is always modified by chiral amino alcohols,[7] carbohydrates,[8] carboxylic acids[9] or amino acids.[10] However, these chirally modified sodium borohydrides as reducing agents often are used in excess to obtain good chemical yields. Furthermore, very few of them have achieved success in terms of enantioselectivity.

It has been reported that new complex reducing systems can be formed by combining sodium borohydride with various Lewis acids such as aluminum(III),[11] copper(I),[12] iron(III),[13] tin(II or IV),[14] titanium(IV)[15] and zirconium (IV)[16] halides. Some papers about the asymmetric reduction of ketones by combining sodium borohydride with $AlCl_3$,[17] $ZnCl_2$[17b,18] or $ZrCl_4$[17a,19] have been reported. But these methods are far away from ideal because they suffer from poor to moderate enantioselectivity and the use of stiochiometric of chiral ligands or catalysts, hence limiting the application of them.

In 1995, Mukaiyama *et al.*[20] reported that optically active aldiminato cobalt(II) can catalyze the reduction of chromanone derivatives with high optical yields, but the *ee* value was only moderate for the simple aromatic ketone such as acetophenone. So the development of an efficient methodology in this area is still desirable.

## Results and discussion

During our ongoing research in asymmetric reduction of ketones,[21] we wish to report herein that $SnCl_2$ or $SnCl_4 \cdot 2Et_2O$ promoted a catalytic asymmetric reduction of ketones by sodium borohydride in the presence of chiral ligands **1**—**7** (Fig. 1).

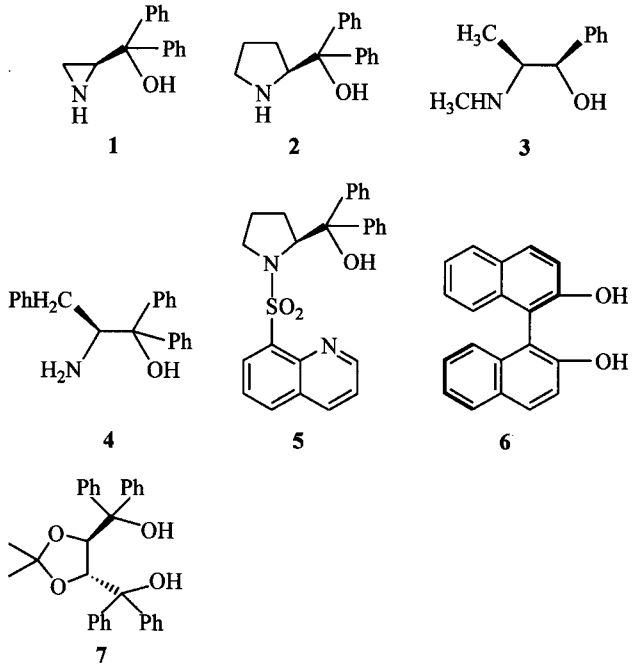


**Fig. 1** Chiral ligands **1**—**7**.

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Firstly, a variety of Lewis acids were screened for the asymmetric reduction of acetophenone with chiral ligand **2**. All the reactions were carried out in tetrahydrofuran (THF) and sodium borohydride/Lewis acid system [the molar ratio of sodium borohydride to Lewis acid ($MX_n$) was $n:1$]. In the absence of Lewis acids full conversion would occur within 43 h with 0% *ee*. Nine Lewis acids were found to promote the reductions to complete within 10 min: LiCl (96%, 0% *ee*), LiBr (97%, 0% *ee*), $CaCl_2$ (95%, 0% *ee*), $ZnCl_2$ (97%, 5% *ee*), $TiCl_4$ (94%, 73% *ee*), $ZrCl_4$ (95%, 60% *ee*), $AlCl_3$ (92%, 58% *ee*), $SnCl_4 \cdot 2Et_2O$ (95%, 95% *ee*) and $SnCl_2$ (96%, 97% *ee*).

Having established the superiority of $SnCl_4 \cdot 2Et_2O$ and $SnCl_2$ as reduction promoters, a variety of chiral ligands, including chiral diols **6** and **7**, β-amino alcohols **1**—**4** and chiral sulfonamide **5** were evaluated under the same reaction conditions as those for ligand **2** (Table 1). The results showed that chiral diols almost had no optical induction for the reductions, while amino alcohols and chiral sulfonamide could give the corresponding alcohols with moderate to excellent enantiomeric excesses. Best enantioselectivities were observed when **2** was employed as a chiral ligand. Under the same reaction conditions, no significant difference was observed between the two reducing systems.

**Table 1** Effects of chiral ligands **1**—**7**[a]

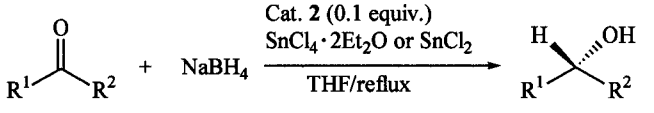
| Entry | Catalyst | $NaBH_4/SnCl_4 \cdot 2Et_2O$ | | $NaBH_4/SnCl_2$ | |
|---|---|---|---|---|---|
| | | Yield[b] (%) | *ee*[c] (%) | Yield[b] (%) | *ee*[c] (%) |
| 1 | **1** | 91 | 64 | 94 | 71 |
| 2 | **2** | 95 | 95 | 96 | 97 |
| 3 | **3** | 94 | 61 | 96 | 57 |
| 4 | **4** | 89 | 80 | 92 | 82 |
| 5 | **5** | 93 | 87 | 95 | 90 |
| 6 | **6** | 96 | 0 | 96 | 0 |
| 7 | **7** | 94 | 3 | 95 | 8 |

[a] All reactions were completed within 10 min and offered the corresponding alcohols riched with *R* enantiomers. The molar ratio of $NaBH_4/SnCl_4 \cdot 2Et_2O$ or $NaBH_4/SnCl_2$ was 4:1 or 2:1, respectively. [b] Isolated yields. [c] Determined by chiral HPLC.

To explore the generality of the two reducing systems, the application of $NaBH_4/SnCl_4 \cdot 2Et_2O$ (or $SnCl_2$) was extended to various ketones and the results are shown in Table 2.

In all cases, the reductions afforded the corresponding alcohols in excellent chemical yields and the absolute configurations of all products were in agreement with those obtained with Corey reagent.[4] The results showed that aromatic ketones could give well to excellent enantiomeric excesses and the electron density of the aromatic ring

**Table 2** Asymmetric reductions of ketones




| Run | Ketone | $NaBH_4/SnCl_4 \cdot 2Et_2O$ | | $NaBH_4/SnCl_2$ | | |
|---|---|---|---|---|---|---|
| | | Yield[a] (%) | *ee*[b] (%) | Yield[a] (%) | *ee*[b] (%) | Config.[c] |
| 1 | Propiophenone | 96 | 84 | 95 | 85 | *R* |
| 2 | *p*-Bromoacetophenone | 96 | 98 | 96 | 98 | *R* |
| 3 | *p*-Methoxyacetophenone | 94 | 75 | 95 | 78 | *R* |
| 4 | β-Acetonaphenone | 98 | 94 | 98 | 96 | *R* |
| 5 | α-Chloroacetophenone | 95 | 97 | 96 | 95 | *S* |
| 6 | α-Bromoacetophenone | 96 | 92 | 95 | 96 | *S* |
| 7 | α-Tetralone | 95 | 94 | 96 | 95 | *R* |
| 8 | Methyl isobutyl ketone | 91 | 92[d] | 93 | 94[d] | *R* |
| 9 | 3-Methyl-2-butanone | 92 | 72[d] | 91 | 68[d] | *R* |
| 10 | Methyl 3-benzoylpropionate | 91 | 84 | 94 | 82 | *R* |
| 11 | Ethyl benzoylacetate | 90 | 96 | 89 | 97 | *R* |
| 12 | Benzil | 93 | 96[e] | 95 | 96[f] | *S*,*S* |

[a] Isolated yields after column purification or distillation. [b] Determined by chiral HPLC. [c] Determined by comparison of specific rotation with the reported. [d] Analytical samples were converted to 3,5-dinitrobenzoates. [e] The diastereomeric excess (*dl*/*meso*) was determined by $^1H$ NMR analysis and was 5.02/1.00.[22] [f] The *dl*/*meso* was 5.40/1.00.

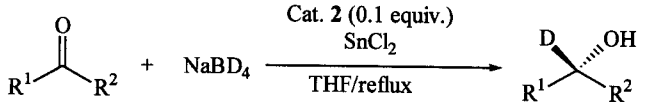
appeared to have a significant effect on the enantioselectivity. Asymmetric reduction of *p*-methoxyacetophenone gave the corresponding alcohols only in 75% and 78% *ee*, respectively, for the two reducing systems. From the results it is suggested that the electron-donating group such as methoxy group lowered enantiomeric excess (Run 3).

The reduction of aliphatic ketones showed that the more steric substutient group often offered better enantioselectivity. For example, with $NaBH_4/SnCl_2$ as reducing system the methyl isobutyl ketone could be reduced with 94% *ee* (Run 8), while only 68% *ee* could be obtained from the reduction of 3-methyl-2-butanone (Run 9). The reduction of *β*- or *γ*-keto ester provided similar optical induction to that for acetophenone or propiophenone, giving the corresponding alcohols in 96% *ee* and 84% *ee*, respectively (Runs 10 and 11 for the reducing system of $NaBH_4/SnCl_4 \cdot 2Et_2O$). Diols could be obtained from the reduction of benzil by the two reducing systems in excellent enantiomeric excesses (96% *ee* for both reducing systems, Run 12) and similar diastereoselectivity.

Having developed a highly efficient and practical process for the asymmetric synthesis of optically secondary alcohols, we focused our attention to the synthetic utility of this method. As we know, optically active deuterated alcohols are useful compounds for the mechanistic studies of chemical and biochemical transformations,[23] as well as chiral auxiliaries or ligands for asymmetric synthesis.[24] Previous efforts in this research have focused on the preparation of enantiomerically pure primary 1-deuterio alcohols by means of asymmetric biological and chemical reduction,[25] while there has been only one report, to the best of our knowledge, about the asymmetric synthesis of deuterated secondary alcohols. Soai *et al*.[26] described the first asymmetric synthesis of deuterated secondary alcohols by the enantioselective addition of dialkylzinc compounds to aldehyde-formal-d used as chiral ligand. Although the asymmetric catalytic reduction of ketones would be a promising approach to deuterated secondary alcohols, no practical reducing systems were available for this transformation. Our reducing systems [$NaBD_4/SnCl_2$ (or $SnCl_4 \cdot 2Et_2O$)] may make this transformation probably.

$NaBD_4/SnCl_2$ was chosen here as the reducing system for the asymmetric synthesis of deuterated secondary and primary alcohols. It should be pointed out that $NaBD_4/Me_3SiCl$ (or $BF_3 \cdot Et_2O$) system could not get the deuterated secondary alcohols in good yield and enantioselectivity although the reaction was carried out for a long time. The results are summarized in Table 3. The results showed that all the reductions afforded excellent chemical yields. The HPLC behavior of the deuterated secondary alcohols was the same as that of the non-deuterated secondary alcohols, although the absolute configurations of some deuterated secondary alcohols could not be assigned. In view of these observations, we assume the absolute configurations of the deuterated secondary alcohols in the same configurations with the non-deuterated secondary alcohols. Excellent enantioselectivities were observed when ketones were reduced. But under the same reaction conditions, the synthesis of optically active deuterated primary alcohols could be achieved only in moderate enantioselectivities.

**Table 3** Asymmetric synthesis of deuterated secondary alcohols




| Run | $R^1COR^2$ | Yield[a] (%) | *ee*[b] (%) | Config.[c] |
|---|---|---|---|---|
| 1 | Acetophenone | 96 | 90 | *R* |
| 2 | *p*-Bromoacetophenone | 97 | 96 | — |
| 3 | Propiophenone | 98 | 83 | *R* |
| 4 | *β*-Acetonaphenone | 98 | 91 | — |
| 5 | *α*-Chloroacetophenone | 96 | 95 | — |
| 6 | *α*-Bromoacetophenone | 96 | 96 | — |
| 7 | Methyl isobutyl ketone | 91 | 98 | *R*[d] |
| 8 | 3-Methyl-butanone | 89 | 68 | *R*[d] |
| 9 | *p*-Bromobenzaldehyde | 96 | 55 | *S*[e] |
| 10 | *p*-Chlorobenzaldehyde | 96 | 48 | *S*[e] |
| 11 | Benzaldehyde | 97 | 42 | *S*[e] |

[a] Isolated yields. [b] Determined by chiral HPLC. [c] Determined by comparison of specific rotation with literature data. [d] Analytical samples were converted to 3,5-dinitrobenzoates. [e] Determined by $^1H$ NMR (500 MHz) analysis of its ester of (*S*)-MTPA.

It was reported that diborane could be generated by heating sodium borohydride and tin chloride, while Tsuda[14a] reported that the reduction of iodolactone by $NaBH_4/SnCl_4 \cdot 2Et_2O$ led to different products. To explore the intriguing mechanism of this reaction, we studied the asymmetric reduction of acetophenone by the two different reducing agents under different reaction temperatures (Table 4). It was observed that temperature has a profound effect on the reducing system of $NaBH_4/SnCl_4 \cdot 2Et_2O$, while $BH_3 \cdot SMe_2$ received little effect from the temperature, especially between room temperature and 66 ℃ (THF, b.p.). From the results, we could conclude that diborane could be generated *in situ* by heating $NaBH_4/SnCl_4 \cdot 2Et_2O$ or $NaBH_4/SnCl_2$ at higher temperature. The reducing mechanism of $NaBH_4/SnCl_4 \cdot 2Et_2O$ or $NaBH_4/SnCl_2$ is not just like that of $BH_3 \cdot SMe_2$ reagent.

**Table 4** Reduction of acetophenone at different temperatures

| Run | *T* (℃) | $NaBH_4/SnCl_4 \cdot 2Et_2O$ | | $BH_3 \cdot SMe_2$ | |
|---|---|---|---|---|---|
| | | Yield (%) | *ee* (%) | Yield (%) | *ee* (%) |
| 1 | 0 | 91 | 0 | 91 | 67 |
| 2 | 23 | 94 | 22 | 96 | 93 |
| 3 | 45 | 96 | 91 | 97 | 96 |
| 4 | Reflux | 95 | 95 | 97 | 98 |

In summary, we have disclosed that $SnCl_4 \cdot 2Et_2O$ and $SnCl_2$ are two excellent promoters for the asymmetric reduction of carbonyl compounds by sodium borohydride.

The two reducing systems formed by combining sodium borohydride and $SnCl_4 \cdot 2Et_2O$ or $SnCl_2$, proved efficient to the asymmetric reduction of carbonyl groups.

## Experimental

*General*

All the reactions were carried out under a dry Ar atmosphere with freshly distilled THF from sodium. Acetophenone, propiophenone, α-tetralone, methyl isobutyl ketone and 3-methyl-butanone were dried and distilled over calcium hydride. Other ketones were further purified by recrystallization before use. $SnCl_4 \cdot 2Et_2O$ was prepared according to the protocol of Tsuda *et al*.[14a]

*Typical procedure for the asymmetric reduction of prochiral ketones*

To a suspension of sodium borohydride (46 mg, 1.2 mmol) in THF (8 mL) was added $SnCl_4 \cdot 2Et_2O$ [102 mg, 0.3 mmol (or 115 mg $SnCl_2$, 0.6 mmol)] at room temperature. Black precipitates appeared along with generated gas. After the resultant mixture was stirred at room temperature for 1 h, catalyst **2** (25 mg, 0.1 mmol) was added and the reaction mixture was refluxed and stirred for another 0.5 h. Then a solution of acetophenone (0.121 g, 1.0 mmol) in THF (8 mL) was added over 1.6 h. After the addition was completed, the mixture was treated with water, filtered and washed by EtOAc (3 × 10 mL). The resulting aqueous solution was extracted with EtOAc (3 × 10 mL) and dried with $MgSO_4$. The solution was evaporated and purified by silica gel chromatography to give pure product in 95% yield and the recovered catalyst **2** (22 mg, 87% yield). 1-Phenyl-ethanol: colorless liquid, $[\alpha]_D^{20} + 52.0$ (*c* 1.01, $CHCl_3$). The optical yield was determined to be 95% by a chiralcel OJ column. $^1H$ NMR ($CDCl_3$, 300 MHz) δ: 1.39 (d, *J* = 6.4 Hz, 3H, $CH_3$), 2.92 (s, 1H, OH), 4.74 (q, *J* = 6.4 Hz, 1H, CHOH), 7.20—7.30 (m, 5H, Ph).

*Typical procedure for the asymmetric synthesis of optically active deuterated alcohols*

To a suspension of sodium borodeuteride (50.2 mg, 1.2 mmol) in THF (8 mL) was added $SnCl_4 \cdot 2Et_2O$ [102 mg, 0.3 mmol (or 115 mg $SnCl_2$, 0.6 mmol)] at room temperature. Black precipitates appeared along with generated gas. After the resultant mixture was stirred at room temperature for 1 h, catalyst **2** (25 mg, 0.1 mmol) was added and the reaction mixture was refluxed and stirred for another 0.5 h. Then a solution of acetophenone (0.121 g, 1.0 mmol) in THF (8 mL) was added over 1.6 h. After the addition was completed, the mixture was treated with water, filtered and washed by EtOAc (3 × 10 mL). The resulting aqueous solution was extracted with EtOAc (3 × 10 mL) and dried with $MgSO_4$. The solution was evaporated and purified by silica gel chromatography to give pure product in 96% yield and the recovered catalyst **2** (22 mg, 87% yield). 1-Deuterio-1-phenyl-ethanol: colorless liquid, $[\alpha]_D^{20} + 52.0$ (*c* 1.01, $CHCl_3$). The optical yield was determined to be 95% by a chiralcel OJ column. $^1H$ NMR ($CDCl_3$, 300 MHz) δ: 0.89 (s, 3H, $CH_3$), 1.86 (s, 1H, OH), 7.11—7.40 (m, 5H, Ph).

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