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Asymmetric Reduction of Oxime Ethers Promoted by Chiral Spiroborate Esters with an O_3BN Framework†

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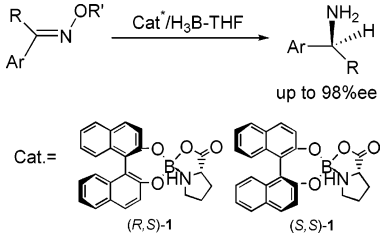
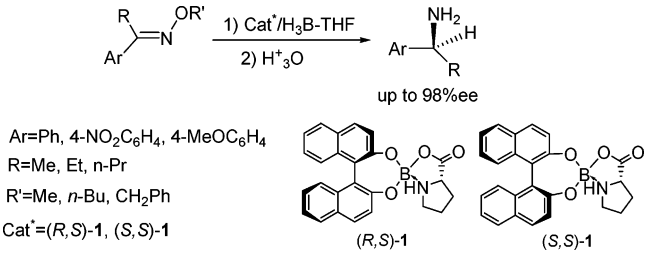


Enatioselective reduction of oxime ethers promoted by chiral spiroborate esters with an O_3BN framework is reported for the first time. In the presence of (*R*,*S*)-**1**, 11 aralkyloxime ethers are reduced by borane−THF at 0−5 °C to give (*S*)-1-aralkylamine in high yield and excellent enatiomeric excess (up to 98% ee). Influence of reaction conditions on the enantioselectivity of the reduction is investigated, and a possible mechanism of the catalytic reduction is suggested.

Asymmetric reduction of C═N bond by hydride is one of the most attractive protocols to chiral amines. Unfortunately, the asymmetric reduction has been much less studied than that of C═O bond. The presence of *Z*- and *E*-isomers of the C═N double bond makes the steric chemistry of the reaction difficult to control. As far as the asymmetric reduction of prochiral oxime ethers is concerned,[1] several classes of chiral compounds, including aluminates,[2] hydroborates,[3] and transition-metal complexes[4] modified by using chiral amino acid or amino alcohol and oxazaborolidines,[5] were used as chiral reagents or chiral catalysts. However, most of the reductions, except the reductions of some phenone *O*-methyl or *O*-benzyl oximes catalyzed by the oxazaborolidines (up to 2.5 equiv) formed from (*S*)-diphenylvalinol[6a,b] or polymer-supported 2-piperazinemethanol,[6c] show low to moderate enantioselectivity even though high ratio of chiral inducers were used. Therefore, development of highly efficient asymmetric reduction system of C═N double bond is significant. In this paper, we report a new class of boron-containing chiral catalysts, chiral spiroborate esters with three B−O bonds and one N−B coordination bond[7] that enantioselectively promote reduction of prochiral oxime ethers to give chiral amines of up to 98% ee in high yield (Scheme 1).

SCHEME 1. Asymmetric Borane Reduction of Aralkyl Ketone Oxime Ethers Promoted by Chiral Spiroborate Ester (*R*,*S*)-1 or (*S*,*S*)-1



The chiral spiroborate esters within the O_3BN framework were previously synthesized by our group in the investigation of preparative methodology of enantiopure 1,1′-bi-2-naphthols.[8] This type of boron compounds is highly stable to hydrolysis, thermolysis, oxidation, and racemization due to the existence of a N−B coordination bond.[9] Recently, we observed that some chiral spiroborate esters showed high asymmetric catalytic activity toward reductions of prochiral ketones[10] and imines[11] and direct aldol addition of methyl ketone to aromatic aldehydes. To further expand the scope of application of the chiral spiroborate esters in asymmetric synthesis, asymmetric reduction of prochiral aralkyl ketone oxime ethers with borane in the presence of (*R*,*S*)-**1** or (*S*,*S*)-**1** is examined.

Chiral inductors (*R*,*S*)-**1** and (*S*,*S*)-**1** can be conveniently prepared from racemic 1,1′-bi-2-naphthol, boric acid, and (*S*)-

† Chiral Borate Esters in Asymmetric Synthesis. 5.

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SCHEME 2. Preparation of Chiral Spiroborate Esters (*R*,*S*)-1 and (*S*,*S*)-1

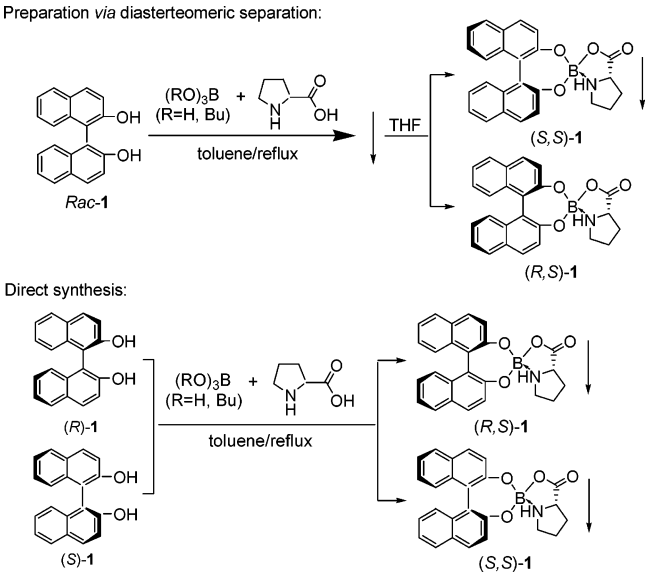


TABLE 1. Effect of the Amount of (*R*,*S*)-1 on the Reduction of Acetophenone *O*-Methyloxime with Borane[a]

entry	(*R*,*S*)-**1**/sub/BH_3	*T*/°C	time/h	yield/%	ee/%	config
1	0.1:1:2	rt	48	58	42	*S*
2	0.2:1:2	rt	48	60	48	*S*
3	0.5:1:2	rt	48	69	81	*S*
4	0.8:1:2	rt	48	80	84	*S*
5	1.0:1:2	rt	48	84	84	*S*

[a] Sub represents acetophenone *O*-methyloxime. The yields were obtained after distillation under reduced pressure.

proline via diastereomeric separation[8] or alternatively synthesized from enantiopure (*R*)- or (*S*)-1,1′-bi-2-naphthol, boric acid, and (*S*)-proline via a one-pot reaction (Scheme 2).[9] However, (*R*)-proline analogues of (*R*,*S*)-**1** and (*S*,*S*)-**1** were not synthesized due to the greater expense of (*R*)-proline.

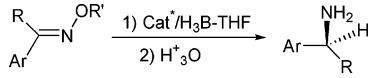
As a model of the reduction, the reaction of acetophenone *O*-methyloxime with borane was investigated. In the presence of (*R*,*S*)-**1**, acetophenone *O*-methyloxime was reduced to the corresponding primary amine in THF with 2 equiv of borane at ambient temperature within 48 h. The results are shown in Table 1. The enantiomeric excess of the reduction product was increased with the increase of the amount of the spiroborate. When the amount of (*R*,*S*)-**1** increased from 0.1 equiv to 0.5 equiv, the ee of the desired product was upgraded from 42% to 81%; further enhancement of the ratio of the (*R*,*S*)-**1** simply led to an increase of the yield of the product, but not the enantioselectivity. Taking into account the enantioselectivity and the yield, it is preferable to utilize 0.8−1.0 equiv of the chiral spiroborate ester for the reduction. Thereupon, the reduction was further examined in the presence of one equivalent of (*R*,*S*)-**1**. The result indicates that the efficiency of the asymmetric reduction is in close relationship with the reactant ratio, reaction temperature, and the configuration of the diol ligand in the spiroborates (Table 2). It indicated that the asymmetric induction ability of (*R*,*S*)-**1** was higher than that of (*S*,*S*)-**1** in the reduction (entries 4−7); in the presence of 1.0 equiv of (*R*,*S*)-**1**, the utilization of 1.5 equiv of borane could furnish the product in excellent ee (entry 1); and lowering the reaction temperature from 65 °C to 0 °C, the ee of the product was upgraded from

TABLE 2. Effect of the Reaction Condition on the Reduction of Acetophenone *O*-Methyloxime[a]

entry	borates	BH_3/sub/borates	*T*/°C	time/h	yield/%	ee/%	config
1	(*R*,*S*)-**1**	1.5:1:1	0−5	48	76	98	*S*
2	(*R*,*S*)-**1**	1.5:1:1	rt	48	78	91	*S*
3	(*R*,*S*)-**1**	1.5:1:1	reflux	48	82	59	*S*
4	(*R*,*S*)-**1**	2.0:1:1	rt	48	84	84	*S*
5	(*S*,*S*)-**1**	2.0:1:1	rt	48	95	71	*S*
6	(*R*,*S*)-**1**	2.4:1:1	rt	48	97	79	*S*
7	(*S*,*S*)-**1**	2.4:1:1	rt	48	97	61	*S*

[a] Sub represents acetophenone *O*-methyloxime. The yields were obtained after distillation under reduced pressure.

TABLE 3. (*R*,*S*)-1-Promoted Asymmetric Reduction of Aralkyl Ketoxime Ethers[a]



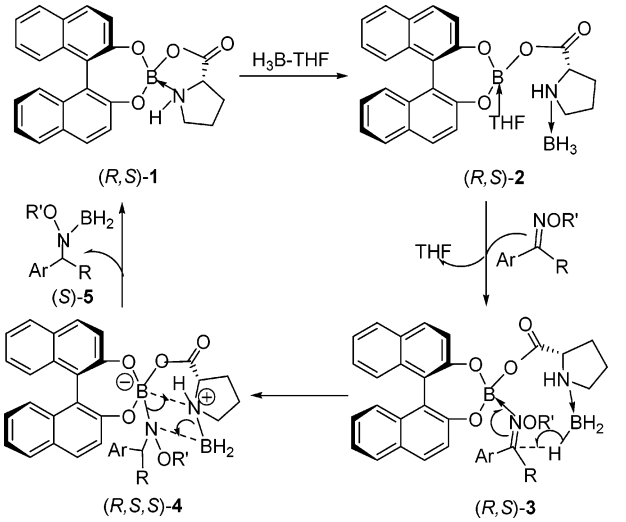
	Ar(R)C=NOR′					
entry	Ar	R	R′	isolated yield/%	ee[b]/%	config[c]
1	Ph	Me		76	98	*S*
2	Ph	Me	Bn	74	89	*S*
3	Ph	Et	Me	78	92	*S*
4	Ph	Et	*n*-Bu	76	80	*S*
5	Ph	Et	Bn	80	81	*S*
6	4-NO_2-C_6H_4	Me	Me	86	96	*S*
7	4-NO_2-C_6H_4	Me	*n*-Bu	78	75	*S*
8	4-NO_2-C_6H_4	Me	Bn	84	90	*S*
9	4-MeO-C_6H_4	Me	Me	83	90	*S*
10	4-MeO-C_6H_4	Et	Me	87	89	*S*
11	4-MeO-C_6H_4	Pr	Me	85	88	*S*

[a] All of the reductions were performed in a 1:1.5:1 molar ratio of the oxime ether, borane, and (*R*,*S*)-**1** in THF at 0 °C for 48 h. [b] Enantiomeric excesses of chiral amines were determined as their acetylated derivatives by HPLC analysis with a chiral column. [c] Configuration was established by comparing the sign of the optical rotation with literature reports.

59% to 98% (entries 1−3). Thus, the reduction condition of prochiral oxime ethers promoted by the chiral spiroborates is optimized as 1.0:1.5:1.0 molar ratio of the substrate, borane, and (*R*,*S*)-**1** at 0−5 °C for 48 h.

The above optimized reaction conditions were applied to reduction of other prochiral aralkyl ketone oxime ethers, including acetophenone *O*-benzyl oxime, acetophenone *O*-methyl oxime, propionophenone *O*-*n*-butyl oxime, propionophenone *O*-methyl oxime, propionophenone *O*-benzyl oxime, 1-(4-methoxyphenyl)butan-1-one *O*-methyl oxime, 1-(4-methoxyphenyl)ethanone *O*-methyl oxime, 1-(4-methoxyphenyl)-propan-1-one *O*-methyl oxime, 1-(4-nitrophenyl)ethanone *O*-benzyl oxime, 1-(4-nitrophenyl)ethanone *O*-*n*-butyl oxime, and 1-(4-nitrophenyl)ethanone *O*-methyl oxime. The results are summarized in Table 3. This asymmetric reduction offers good to excellent enantioselectivity in general. The electronic property of the substituent in aromatic ring of the aralkyl ketone slightly affects the sterioselectivity of the reaction (entries 6 and 9). The reduction of the ketoximes bearing an electron-withdrawing group in the aromatic ring gives the desired product in higher ee (entries 6−8). On the other hand, the enantioselectivity of the reduction appears to decrease with the increase of alkyl chain in OR′ (entries 1, 2, 3−5, and 6−8, OMe > OBn > OBu). The reduction of all of the *O*-methyloximes gives better enantioselectivity than that of *O*-benzyloximes and *O*-butyloximes. For 4-methoxyphenylketoximes, the reduction is insensitive to the

SCHEME 3. Possible Mechanism for the Asymmetric Borane Reduction of Prochiral Oxime Ethers Promoted by a Chiral Spiroborate Ester



size of the alkyl group in the aralkyl ketone in terms of enantioselectivity and yield (entries 9−11).

It should be pointed out that all oxime ethers used in the experiment are *E* isomers. The *E* and *Z* isomers can be efficiently separated by chromatography on silicon gel column, though a mixture of both the isomers was obtained in the preparative course. Only the major E isomer was collected and examined because the Z isomer was minor.

The mechanism for asymmetric reduction of prochiral oxime ethers promoted by the chiral spiroborate ester is suggested (Scheme 3). The structure of the intermediate (*R*,*S*)-**2** has previously been proved.[10a] In the mixed system consisting of (*R*,*S*)-**1**, borane, and the ketoxime ether in THF, the oxime ether replaces THF in (*R*,*S*)-**2** to form the complex (*R*,*S*)-**3** which undergoes hydrogen transfer and rearrangement and (*S*)-aminoborane **5** is liberated as the spiroborate is reformed. Compound **5** will yield the corresponding amine at aqueous workup. Thus, a catalytic cycle is accomplished.

In summary, a class of new and effective chiral promoter for borane reduction of prochiral aralkylketoxime ethers has been discovered. They are readily prepared as stable solids and can be stored on shelf.

Experimental Section

General Procedure for the Borane Reduction of the Aralkylketoxime Ethers Promoted by Chiral Spiroborate Ester. An oven-dried, two-necked, round-bottom flask charged with a septum, argon inlet, and magnetic stirring bar was cooled to room temperature under a continuous flow of dry Ar gas, and a THF solution (50 mL) of (*R*,*S*)-**1** (5 mmol) dried with 4 Å molecular sieves and BH_3·THF (1 M, 7.5 mmol) were added in sequence. After being stirred for 30 min, the contents were cooled to 0−5 °C, followed by addition of an aralkylketoxime (5 mmol) via syringe within 15 min. The resulting mixture was stirred at the same temperature for 48 h and then decomposed with 2 M HCl to give a homogeneous solution. The solution was evaporated under reduced pressure to remove THF, and a white solid was isolated, filtered, washed with water, and then recrystallized in toluene (recovery of enantiopure BINOL). The water phase was basified with ammonium hydroxide and extracted with diethyl ether (3 × 15 mL). The ether layer was dried over anhydrous Na_2SO_4 and evaporated to give a colorless oil, which upon distillation under reduced pressure and purification via chromatography on silicon gel column furnished (*S*)-1-aralkylamine.

(*S*)-1-Phenylethylamine (A): colorless liquid, 76% yield 98% ee, $[\alpha]^{20}_D$ −28.3 (*c* 0.92, MeOH) for the reduction of acetophenone *O*-methyloxime; 74% yield, 89% ee, $[\alpha]^{20}_D$ −25.7 (*c* 0.98, MeOH) [lit.[12] $[\alpha]^{20}_D$ −29 (MeOH)] for the reduction of acetophenone *O*-benzyloxime. IR (neat, cm^{-1}): ν 3363, 3286, 3061, 3026, 2963, 2924, 2865, 1604, 1492, 1451, 1367, 764, 701. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (d, J = 6.6 Hz, 3H), 1.62 (s, 2H), 4.13 (q, J = 6.6 Hz, 1H), 7.23−7.35 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.6, 52.0, 125.8, 126.9, 128.5, 147.6. Anal. Calcd for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.03; H, 9.25; N, 11.42.

(*S*)-1-phenylpropy1amine (B): colorless liquid, 78% yield, 92% ee, $[\alpha]^{27}_D$ −7.82 (*c* 0.92, EtOH) for the reduction of propionophenone *O*-methyloxime; 80% yield, 81% ee, $[\alpha]^{27}_D$ −6.87 (*c* 0.96, EtOH) for the reduction of propionophenone *O*-benzyloxime; 76% yield, 80% ee, $[\alpha]^{27}_D$ −6.38 (*c* 0.89, EtOH) [lit.[13] $[\alpha]^{27}_D$ +8.1 (*c* 7.9, EtOH)] for the reduction of propionophenone *O*-*n*-butyloxime. IR (neat, cm^{-1}): ν 3363, 3296, 3061, 3027, 2962, 2930, 2874, 1603, 1492, 1453, 1373, 762, 701. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.92 (t, J = 7.2 Hz, 3H), 1.63 (s, 2H), 1.75 (m, J = 7.2 Hz, 2H), 3.84 (t, J = 7.2 Hz, 1H), 7.27−7.34 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.1, 33.2, 58.5, 126.5, 126.9, 128.4, 146.2. Anal. Calcd for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.36. Found: C, 79.76; H, 9.48; N, 10.52.

(*S*)-1-(4-Nitrophenyl)ethylamine (C): yellow liquid, 86% yield, 96% ee, $[\alpha]^{24}_D$ −16.0 (*c* 0.76, $CHCl_3$) for the reduction of 1-(4-nitrophenyl)ethanone *O*-methyloxime; 84% yield, 90% ee, $[\alpha]^{24}_D$ −14.8 (*c* 0.82, $CHCl_3$) for the reduction of 1-(4-nitrophenyl)-ethanone *O*-benzyloxime; 78% yield, 75% ee, $[\alpha]^{24}_D$ −12.5 (*c* 0.68, $CHCl_3$) [lit.[14] $[\alpha]^{24}_D$ +16.9 ($CHCl_3$)] for the reduction of 1-(4-nitrophenyl)ethanone *O*-*n*-butyloxime. IR (neat, cm^{-1}): ν 3376, 3311, 3108, 3076, 2968, 2927, 2869, 1603, 1517, 1345, 1108, 855, 755, 700. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40 (d, J = 6.6 Hz 3H), 1.57 (s, 2H), 4.26 (q, J = 6.6 Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 8.19 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.0, 51.1, 124.0, 126.9, 147.1, 155.3. Anal. Calcd for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.64; H, 6.15; N, 16.72.

(*S*)-1-(4-Methoxyphenyl)ethylamine (D): colorless liquid, 83% yield, 90% ee, $[\alpha]^{24}_D$ −23.0 (*c* 0.88, $CHCl_3$) [lit.[15] $[\alpha]^{24}_D$ +24.6 (*c* 1.0, $CHCl_3$)] for the reduction of 1-(4-methoxyphenyl)ethanone *O*-methyloxime. IR (neat, cm^{-1}): ν 3364, 3291, 3060, 3029, 998, 2960, 2926, 2836, 1611, 1585, 1512, 1463, 1370, 1247, 1177, 1034, 921, 832, 808, 733, 700. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.35 (d, J = 6.6 Hz, 3H), 1.52 (s, 2H), 3.78 (s, 3H), 4.07 (q, J = 6.6 Hz, 1H), 6.85 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.1, 51.0, 55.6, 114.0, 127.0, 140.1, 158.5. Anal. Calcd for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.28; H, 8.72; N, 9.42.

(*S*)-1-(4-Methoxyphenyl)propylamine (E): colorless liquid, 87% yield, 89% ee, $[\alpha]^{24}_D$ −14.2 (*c* 0.92, EtOH) [lit[16] $[\alpha]^{24}_D$ +13 (*c* 0.8, EtOH)] for the reduction of 1-(4-methoxyphenyl)propan-1-one *O*-methyloxime. IR (neat, cm^{-1}): ν 3364, 3297, 3060, 3029, 2998, 2960, 2931, 2874, 2836, 1611, 1585, 1512, 1463, 1302, 1247, 1177, 1036, 832, 736, 693. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84 (t, J = 7.2 Hz, 3H), 1.53 (s, 2H), 1.62 (m, J = 7.2 Hz, 2H), 3.74 (t, J = 7.2 Hz, 1H), 3.78 (s, 3H), 6.85 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.2, 32.7, 55.5, 57.4, 113.9, 127.6, 138.8, 158.7. Anal. Calcd for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.42; H, 9.21; N, 8.36.

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(*S*)-1-(4-Methoxyphenyl)butylamine (F): colorless liquid, 85% yield, 88% ee, $[\alpha]^{24}_D$ −11.2 (*c* 0.82, $CHCl_3$) [lit.[17] $[\alpha]^{25}_D$ +12.57 (*c* 7.39, $CHCl_3$)] for the reduction of 1-(4-methoxyphenyl)butan-1-one *O*-methyloxime. IR (neat, cm^{-1}): ν 3371, 3297, 3065, 3029, 2998, 2956, 2931, 2871, 2836, 1610, 1585, 1512, 1464, 1301, 1247, 1176, 1036, 830. ^1H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, $J = 7.2$ Hz, 3H), 1.24 (m, $J = 7.2$ Hz, 2H), 1.52 (s, 2H), 1.62 (m, $J = 7.2$ Hz, 2H), 3.78 (s, 3H), 3.83 (t, $J = 7.2$ Hz, 1H), 6.85 (d, $J = 8.4$ Hz, 2H), 7.21 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 20.0, 42.1, 55.5, 55.6, 114.0, 127.6, 139.1, 158.7. Anal. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.48; H, 9.64; N, 7.72.

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Supporting Information Available: Preparative procedures and characterization data for all of the oxime ethers and the chiral amines. This material is available free of charge via the Internet at http://pubs.acs.org.

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