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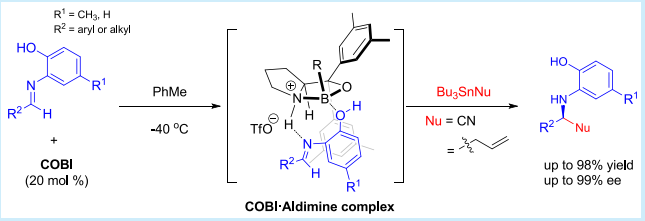
Enantioselective Strecker and Allylation Reactions with Aldimines Catalyzed by Chiral Oxazaborolidinium Ions

Ki-Tae Kang, Sang Hyun Park, and Do Hyun Ryu*

Department of Chemistry, Sungkyunkwan University, Suwon 16419, Korea

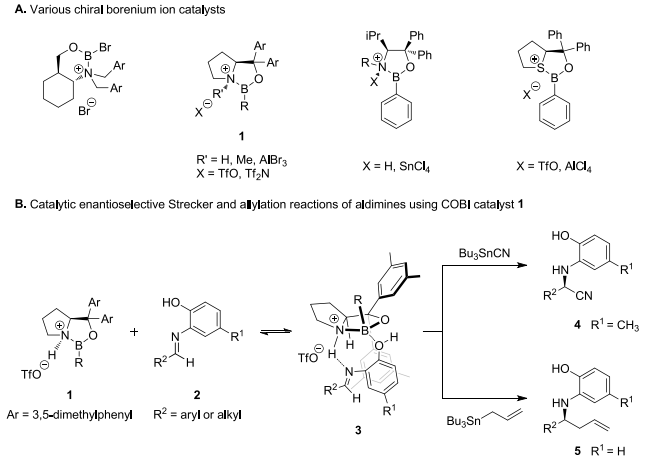
Supporting Information

ABSTRACT: Chiral oxazaborolidinium ion (COBI)-catalyzed enantioselective nucleophilic addition reactions of aldimines using tributyltin cyanide and allyltributylstannane have been developed. Various α-aminonitriles and homoallylic amines were synthesized in high yield (up to 98%) with high to excellent enantioselectivity (up to 99% ee). A rational mechanistic model for the complex of COBI and aldimine is provided to account for these enantioselective reactions.



Enantioselective carbon−carbon bond-forming reactions catalyzed by chiral boron Lewis acids are useful and versatile synthetic methods for stereoselective generation of chiral centers.[1] Among them, chiral borenium ions[2] (Scheme 1A), boron cations in the form of a three-coordinate boron center with a net positive charge, are powerful Lewis acids that have been widely utilized as oxophilic activating agents for carbonyl compounds.[3] As a representative example, chiral oxazaborolidinium ion (COBI)[4] catalyst **1**, which is generated from the corresponding oxazaborolidine by activation with strong Brønsted or Lewis acid, has been demonstrated to be an effective catalyst for various enantioselective carbon−carbon bond-forming reactions of carbonyl compounds, such as cycloaddition reactions,[4,5] nucleophilic 1,2-[6] or 1,4-addition,[7] and corresponding tandem reactions,[8] leading to a family of useful chiral building blocks containing carbonyl compounds. However, despite the potential for practical syntheses of chiral amine compounds, highly enantioselective borenium ion-catalyzed carbon−carbon bond formations with imines have not been reported to date.[9] Herein, we describe the first successful development of highly enantioselective nucleophilic addition reactions such as Strecker and allylation reactions of aldimines using a COBI catalyst to obtain highly optically active α-aminonitriles **4** and homoallylic amines **5** (Scheme 1B). A possible pretransition state assembly **3** of COBI and *o*-hydroxyphenyl aldimine[10] **2e** is also suggested (Scheme 1B).

Scheme 1. Catalytic Enantioselective Strecker and Allylation Reactions of Aldimines



Since COBI catalyst **1** has proven to be an effective catalyst for enantioselective cyanosilylation of aldehydes and ketones with TMSCN,[6d,e] we first decided to investigate **1** for the catalytic enantioselective Strecker reaction[11] with aldimine **2**. Initially, the enantioselective Strecker reaction between trimethylsilyl cyanide and benzaldimines with various protecting groups such as Bn, Boc, and Ph was examined in the presence of 20 mol % COBI catalyst **1a** activated by triflic acid. However, the obtained α-aminonitriles **4a**−**4c** were racemic (Table 1, entries 1−3). Gratifyingly, when the protecting group of the aldimine was changed to an *o*-hydroxy *p*-methyl phenyl group,[12] α-aminonitrile **4e** was obtained in 94% yield and 81% ee (Table 1, entry 5). Since *o*-methoxy-substituted phenyl aldimine **2d** did not provide any enantioselectivity (Table 1, entry 4), we assumed that bidentate binding of the imine nitrogen and *o*-hydroxy group to COBI catalyst **1a** is necessary to achieve high enantioselectivity as shown in complex **3** (Scheme 1B). In complex **3**, hydrogen-bonding between the aldimine and ammonium of COBI **1a** is essential. To support this hypothesis, we tested Strecker reactions with oxazaborolidine **1b** and methylammonium type[13] COBI **1c**, which does not have a proton for hydrogen-bonding to give chirally inverted or racemic product **4e** (Table 1, entries 6 and 7). Intermolecular hydrogen-bonding[14,15] between COBI and aldimine was further supported by low-temperature (−40 °C)

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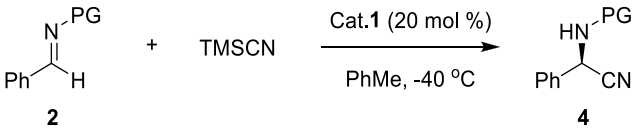
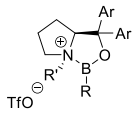
Org. Lett. XXXX, XXX, XXX−XXX

Table 1. Optimization of the Enantioselective Strecker Reaction[a]





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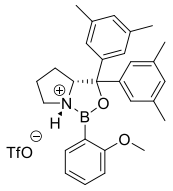
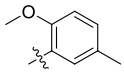
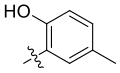


ent-**1f**

1a: Ar = Phenyl, R = Phenyl, R' = H
1b: Ar = Phenyl, R = Phenyl, R' = None
1c: Ar = Phenyl, R = Phenyl, R' = Me
1d: Ar = Phenyl, R = *o*-tolyl, R' = H
1e: Ar = 3,5-dimethylphenyl, R = Phenyl, R' = H
1f: Ar = 3,5-dimethylphenyl, R = *o*-methoxy, R' = H

entry	cat.	2	PG	4	time (h)	yield[b] (%)	ee[c] (%)
1	**1a**	**2a**	Bn	**4a**	24	47	0
2	**1a**	**2b**	Boc	**4b**	12	98	0
3	**1a**	**2c**	Ph	**4c**	16	66	0
4	**1a**	**2d**		**4d**	12	76	0
5	**1a**	**2e**		**4e**	8	94	81
6	**1b**	**2e**		**4e**	16	34	-63
7	**1c**	**2e**		**4e**	8	95	0
8	**1d**	**2e**		**4e**	8	76	9
9	**1e**	**2e**		**4e**	4	87	88
10	**1f**	**2e**		**4e**	4	91	95
11[d]	**1f**	**2e**		**4e**	2	98	95

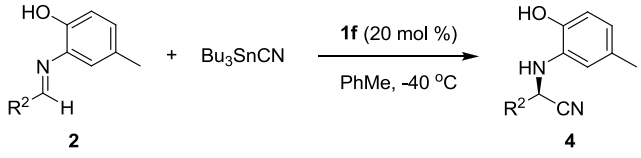
[a]The reaction of aldimines (0.2 mmol) with TMSCN (0.3 mmol) was performed in the presence of catalyst (20 mol %) in 1.4 mL of toluene at −40 °C. [b]Isolated yield of **4**. [c]The ee of **4** was determined by chiral HPLC. [d]The reaction was performed with Bu_3SnCN.

^{1}H NMR analysis.[16] The aldimine proton (N=C−H) peak was downfield shifted from δ = 7.95 to 8.41 ppm and the doublet splitting from $^+$N−H···N of **3** observed at δ = 11.36 ppm had the same coupling constant (d, J = 15 Hz) as N = C−H (δ = 8.41 ppm, d, J = 15 Hz).[14]

Next, we screened the catalyst structure and found that the catalyst system with a 3,5-dimethylphenyl Ar substituent and 2-methoxyphenyl R substituent, activated by triflic acid, gave the best result of 91% yield and 95% ee (Table 1, entry 9). Next, we applied Bu_3SnCN[17] as a safer cyanide source[17b] instead of TMSCN to afford **4e** in higher yield (Table 1, entry 10).

At optimized reaction conditions for the catalytic enantioselective Strecker reaction, we evaluated this methodology with various aldimines (Table 2). Regardless of the electronic or steric properties of substituents on the aldimines, highly optically active α-aminonitriles **4** were obtained (Table 2, entries 2−10). This catalytic system was also successfully applied to reactions of various aromatic aldimines such as naphthyl, furyl, and thienyl (Table 2, entries 11−14). While

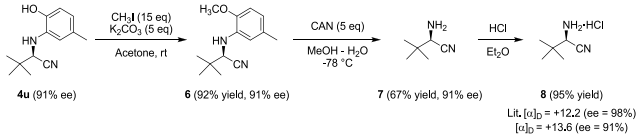
Table 2. Substrate Scope for Enantioselective Strecker Reaction[a]



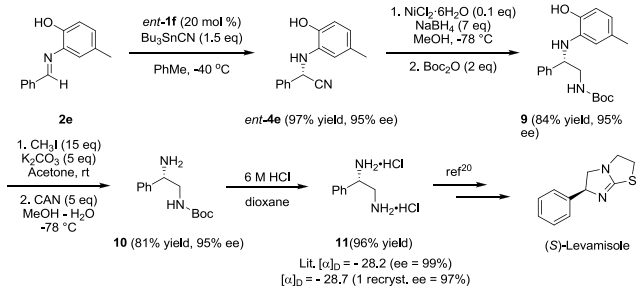
entry	4	R^2	time (h)	yield[b] (%)	ee[c] (%)
1[d]	**4e**	Ph	2	98	95
2	**4f**	4-MeC_6H_4	2	93	97
3	**4g**	2-MeC_6H_4	2	96	91
4	**4h**	4-$MeOC_6H_4$	2	96	94
5	**4i**	2-$MeOC_6H_4$	2	94	91
6	**4j**	4-FC_6H_4	2	91	92
7	**4k**	2-FC_6H_4	2	93	94
8	**4l**	4-ClC_6H_4	12	94	82
9	**4m**	4-BrC_6H_4	12	92	83
10	**4n**	4-$CF_3C_6H_4$	24	91	87
11	**4o**	1-naphth	4	95	99
12	**4p**	2-naphth	4	91	93
13	**4q**	2-furyl	2	94	92
14	**4r**	2-thienyl	2	96	91
15[e]	**4s**	Et	72	85	67
16[e]	**4t**	*i*-Pr	12	82	77
17[e]	**4u**	*t*-Bu	18	91	91

[a]The reaction of aldimines (0.2 mmol) with Bu_3SnCN (0.3 mmol) was performed in the presence of catalyst (20 mol %) in 1.4 mL of toluene at −40 °C. [b]Isolated yield of **4**. [c]The ee of **4** was determined by chiral HPLC. [d]1 mmol scale reaction was also performed to give 98% yield and 94% ee value. The one-pot reaction was also performed to give 97% yield and 95% ee.[17a] [e]One-pot reaction of aldehyde and 2-aminocresol.

Scheme 2. Transformation of a Chiral α-Aminonitrile



Scheme 3. Formal Synthesis of (*S*)-Levamisole



primary and secondary alkyl-substituted aldimines provided products with moderate enantioselectivities, tertiary butyl aldimine provided the desired α-aminonitrile **4** with high yield and enantioselectivity (Table 2, entries 15−17).

Further chemical transformation of the resulting optically active α-aminonitrile **4u** to confirm the absolute structure is illustrated in Scheme 2. Oxidative cleavage of **6** with cerium ammonium nitrate (CAN)[18] after methylation led to highly optically enriched α-aminonitrile **7** with a free amine group.

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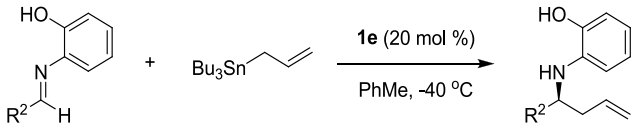
Table 3. Substrate Scope for Enantioselective Allylation[a]



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entry	5	R^2	time (h)	yield[b] (%)	ee[c] (%)
1[d]	**5a**	Ph	3	88	93[e]
2[f]	**5b**	4-MeC_6H_4	1	87	94
3[f]	**5c**	3-MeC_6H_4	3	83	92
4[f]	**5d**	2-MeC_6H_4	3	82	96
5[f]	**5e**	4-$MeOC_6H_4$	1	85	90
6	**5f**	4-FC_6H_4	3	91	95
7	**5g**	2-FC_6H_4	3	87	93
8	**5h**	4-ClC_6H_4	4	89	92
9	**5i**	4-BrC_6H_4	3	84	92
10	**5j**	4-$CF_3C_6H_4$	3	91	93
11	**5k**	1-naphth	3	86	90
12	**5l**	2-furyl	4	78	94
13	**5m**	2-thienyl	3	80	93
14[g]	**5n**	*i*-Pr	6	77	94
15[g]	**5o**	*t*-Bu	3	91	90

[a]The reaction of aldimines (0.2 mmol) with allyltributylstannane (0.22 mmol) was performed in the presence of catalyst (20 mol %) in 1.4 mL of toluene at −40 °C. [b]Isolated yield of **5**. [c]The ee of **5** was determined by chiral HPLC. [d]1 mmol scale reaction was also performed to give 84% yield and 93% ee. The one-pot reaction was also performed to give 87% yield and 93% ee.[21c] [e]The absolute configurations of **5a** shown in Table 3 were assigned by measurement of optical rotation and comparison with known substances.[21c,22] For details, see the Supporting Information. [f]The reaction was performed at 0 °C. [g]One-pot reaction of aldehyde and 2-aminophenol.

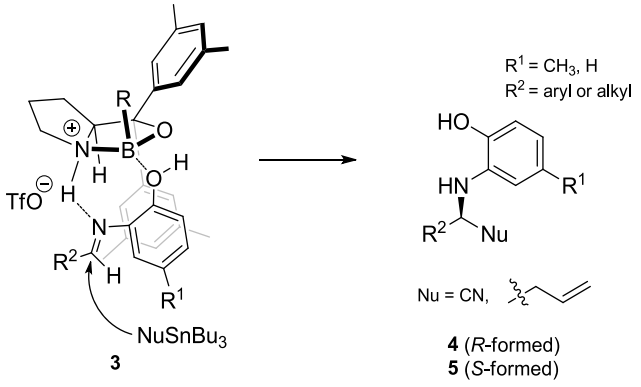

Figure 1. Transition-state model for enantioselective nucleophilic addition reactions with aldimine.

Recrystallization of the hydrochloride salt gave optically enriched (*R*)-aminonitrile hydrochloride **8**. Comparison of the optical rotation data of **8** confirmed the absolute (*R*) stereochemistry of **4u**.[19]

The synthetic utility of the present reaction and absolute structure of *ent*-**4e** were further demonstrated by formal synthesis of levamisole (Scheme 3). Enantioselective Strecker reaction of benzaldimine **2e** with the enantiomeric catalyst of **1f**, *ent*-**1f**, provided *ent*-**4e** in 97% yield and 95% ee. Reduction of *ent*-**4e** was followed by Boc protection to furnish protected diamine **9** without loss of optical purity. Subsequent deprotection of *o*-hydroxyphenyl and Boc groups produced diamine HCl salt **11** in 78% overall yield with 97% ee after one recrystallization. Comparison of the optical rotation data of **11** confirmed the absolute (*S*) stereochemistry of *ent*-**4e**.[20b] A two-step transformation was reported to the known anthelmintic levamisole.[20]

Encouraged by the good results exhibited in Table 2, we applied our new catalytic method to allylation reactions with a range of aldimines and allyltributylstannane to obtain chiral homoallylic amines **5**. Performing a screen of COBI catalysts with the *o*-hydroxyphenyl aldimine **2** identified COBI catalyst **1e** as the optimal catalyst (see the Supporting Information for details). The synthesis of chiral homoallylic amines is important because they have been used as versatile building blocks, after transformation to other functional groups, in syntheses of biologically active natural products.[21] As summarized in Table 3, the reactions produced the corresponding chiral homoallylic amines in good yields and high enantioselectivities regardless of the electronic or steric properties of substituents on the aldimines (Table 3, entries 1−14).

Based on catalyst structures, aldimine protecting groups (vide supra, Table 1) and ^{1}H NMR analysis, the observed stereochemistry for the enantioselective nucleophilic addition reactions using COBI catalyst **1e** can be rationalized using the transition-state model shown in Figure 1. In the pretransition state assembly **3**, shown in Figure 1, the aldimine group is situated above the 3,5-dimethylphenyl group, which effectively shields the *re* face (back) from attack by the nucleophiles. Nucleophilic addition from the *si* face (front) of the aldimine leads to the major enantiomers shown in Figure 1.

In summary, we report the first example of highly enantioselective borenium ion-catalyzed carbon−carbon bond formation of imines in Strecker and allylation reactions of aldimines. In the presence of COBI catalyst, various α-aminonitriles and homoallylic amines were obtained in good yields and high to excellent enantioselectivities. The absolute configuration of the products was the same as predicted by the transition-state model in Figure 1. We believe that the mechanistic model implied by complex **3** has useful predictive power, and there are many potential uses for complex **3** in catalytic enantioselective syntheses of various nitrogen-containing compounds beyond those outlined here. Other applications of **3** and further mechanistic studies are underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02280.

Experimental procedures and full analytical data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dhryu@skku.edu.

ORCID

Do Hyun Ryu: 0000-0001-7615-4661

Notes

The authors declare no competing financial interest.

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