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Cobalt-Catalyzed Asymmetric Allylation of Cyclic Ketimines

Liang Wu, Qihang Shao, Guoqiang Yang,* and Wanbin Zhang*

Abstract: A Co^{II}/Box-catalyzed enantioselective addition of potassium allyltrifluoroborate to cyclic ketimines was developed, providing the corresponding chiral α-tertiary amines in high yields and with good enantioselectivities. Alkoxycarbonyl and alkyl substituted saccharin-derived ketimines are suitable substrates for this allylation reaction. The product can be converted to complex molecules over several simple steps, including a precursor of MK-0371, which is a kinesin spindle protein inhibitor. In addition, this catalytic system showed a strong positive non-linear effect.

Optically active homoallylic amines, especially α-tertiary homoallylamines, are important chiral building blocks for a wide variety of medicinally important agents and natural products (Figure 1).[1] The asymmetric addition of organometallic reagents

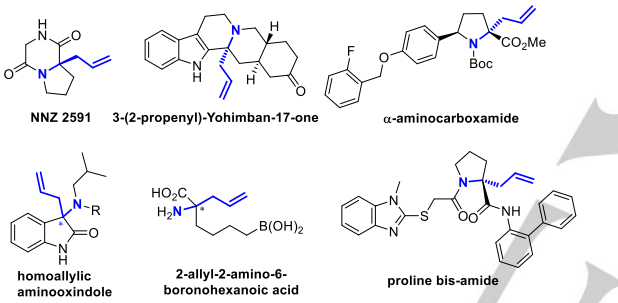

Figure 1. α-Trisubstituted Homoallylamines-containing Natural Products and Drugs.

to ketimines is the most attractive and effective methodology for the preparation of α-trisubstituted homoallylamines due to the simultaneous construction of the carbon-skeleton and stereocenter. Although the allylation of carbonyls and imines has been developed into one of the most powerful C-C bond-forming reactions,[2] the asymmetric allylation of ketimines is not often reported because of the steric and electronic factors of this type of substrate.[3-5] Recently, a significant advance has been made in catalytic allylation using allylboronates.[6] The reactions possess several advantages: they only require relatively mild experimental conditions, and have high functional group tolerance; allylboronates are readily available, stable, and possess relatively low toxicity. Although significant achievements have been made in the allylation of aldimines for direct access to chiral homoallylic amines using allylboron reagents,[7] the enantioselective allylation of ketimines is not a trivial task due to their low reactivity. Pioneering work on the catalytic enantioselective allylation of ketimines has been reported by Shibasaki and co-workers in which the reaction of acyclic ketimines with allylboronate using a Duphos-CuF catalyst gave the corresponding products in high yields with high enantioselectivities.[8] In 2012, Lam and co-workers reported a chiral diene-ligated rhodium complex-catalyzed enantioselective addition of potassium allyltrifluoroborates to cyclic ketimines.[9]

In recent decades, a strong tendency has emerged to utilize the more economical and abundant late first-row transition-metal-catalysts for sustainable chemical synthesis.[10] Cobalt, as a relatively harmless first-row transition metal, has attracted much attention. A number of successful examples have been reported for the application of this metal in catalytic organometallic reactions, such as for use in hydrogenations,[11] hydroborations,[12] hydroacylations[13] and C-H functionalizations.[14] Rh-catalyzed asymmetric addition of organoboron reagents to imines has been well studied by several groups, initiated by Hayashi.[15] However, the using of other metals, especially earth abundant late first row transition metals, have not been widely studied in this reaction. The use of cobalt in such reactions is attractive to synthetic chemists and the pharmaceutical industry. Indeed, several reports concerning the Co^{II}-catalyzed addition of arylboronic acids to unsaturated double bonds have recently been divulged by the Cheng and Zhao groups.[16] In a continuation of our studies on the late first-row transition-metal-catalyzed asymmetric addition of organoboron reagents to cyclic imines,[17] herein we report an allylation reaction of potassium allyltrifluoroborates with cyclic *N*-sulfonyl ketimines that yields α-tertiary cyclic homoallylamines with excellent enantioselectivities using a cobalt-bisoxazoline complex as a chiral catalyst. More interestingly, a significant positive nonlinear effect was observed and a dimetal-catalytic mechanism has been proposed for this catalysis.[18]

Initially, we chose potassium allyltrifluoroborate **2a** and cyclic *N*-sulfonyl α-ketiminoester **1a** as the model substrate to study the allylation reaction. As shown in Table 1, the reaction proceeded smoothly to afford the desired adduct **3a** in 66% yield and with a low *ee* when the complex of $Co(OTf)_2$·2MeCN/bisoxazoline **L1** was used as a catalyst (entry 1). Ligand examination revealed that substituents on the oxazoline rings were critical for the enantioselectivity. Good *ee* was obtained with **L4** (entry 4), while **L2** and **L3** provided very poor enantioselectivities (entries 2 and 3). Seemingly, the phenyl groups on the oxazoline ring are required for obtaining high enantioselectivity. One of the possible explanations for this observation is the presence of π-x (x = H, π…) interaction in the catalytic cycle. Other ligands were also examined, including **L5**-**L9** which possess different linkers between the two oxazoline rings. However, they all gave **3a** in lower *ee*s compared to **L4** (entries 5-9). Thus, (*S*)-Ph-Box **L4** provided the best results

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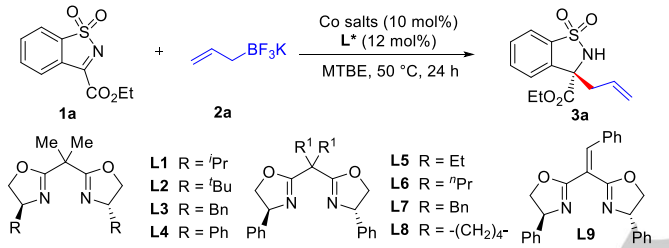
giving product **3a** in 92% isolated yield and 90% *ee* (entry 4). Solvent screening showed that MTBE (methyl *tert*-butyl ether) was the best solvent (for more detail information of condition screening, see SI). Subsequently, a variety of cobalt salts were evaluated. The product **3a** was obtained in good yields and with higher enantioselectivities in the presence of $Co(BF_4)_2{\cdot}6H_2O$ or $Co(ClO_4)_2{\cdot}6H_2O$ (entries 10 and 11), with $Co(ClO_4)_2{\cdot}6H_2O$ proving to be the best Co^{II} source giving the desired product with excellent *ee* (97%) (entry 11). Moreover, the reaction could be conducted at 40 °C to furnish **3a** in a slightly lower yield but with 98% *ee* (entry 12). Notably, a low yield of product was obtained when the temperature was reduced to 30 °C (entry 13). The catalyst loading can be reduced to 3 mol% by extending the reaction time to 48 h, giving the desired product in good yield and *ee* (entries 14 and 15).

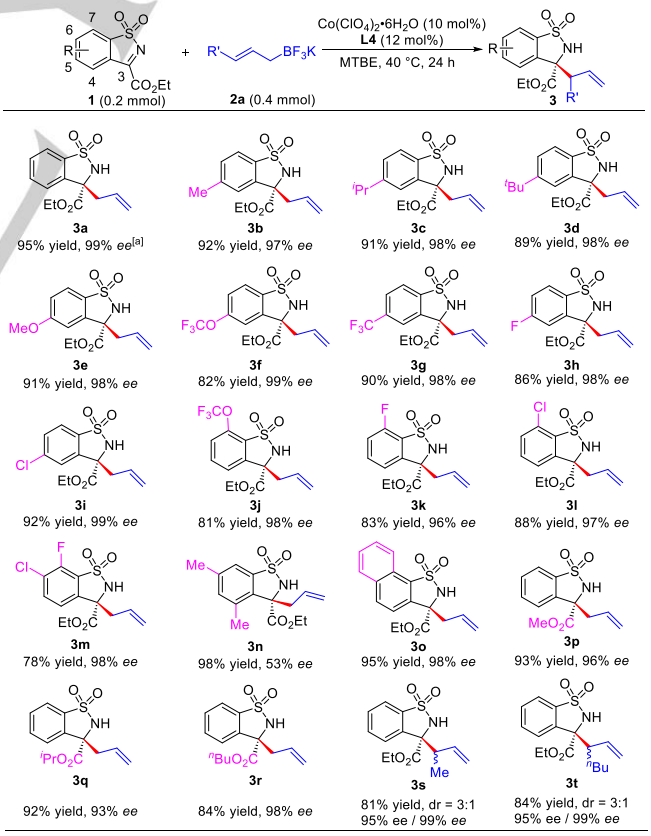
Table 1. Reaction optimization.[a]



Entry	Solvent	Ligand[b]	Yield [%][b]	*ee* [%][c]
1	$Co(OTf)_2{\cdot}2MeCN$	**L1**	66	5
2	$Co(OTf)_2{\cdot}2MeCN$	**L2**	85	9
3	$Co(OTf)_2{\cdot}2MeCN$	**L3**	53	5
4	$Co(OTf)_2{\cdot}2MeCN$	**L4**	92	90
5	$Co(OTf)_2{\cdot}2MeCN$	**L5**	86	40
6	$Co(OTf)_2{\cdot}2MeCN$	**L6**	78	43
7	$Co(OTf)_2{\cdot}2MeCN$	**L7**	95	45
8	$Co(OTf)_2{\cdot}2MeCN$	**L8**	87	85
9	$Co(OTf)_2{\cdot}2MeCN$	**L9**	96	80
10	$Co(BF_4)_2{\cdot}6H_2O$	**L4**	94	94
11	$Co(ClO_4)_2{\cdot}6H_2O$	**L4**	95	97
12[d]	**$Co(ClO_4)_2{\cdot}6H_2O$**	**L4**	**94**	**98**
13[e]	$Co(ClO_4)_2{\cdot}6H_2O$	**L4**	80	98
14[d,f,g]	$Co(ClO_4)_2{\cdot}6H_2O$	**L4**	84	95
15[d,f,h]	$Co(ClO_4)_2{\cdot}6H_2O$	**L4**	78	93

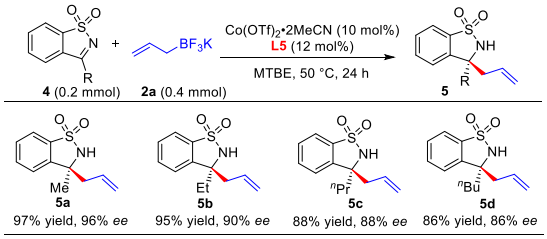
[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equiv), **2a** (0.2 mmol, 2.0 equiv), MTBE (1.5 ml), Co salts (10 mol%), **L1**−**L9** (12 mol%), 50 °C, 24 h. [b] Isolated yields. [c] Enantioselectivity was determined by HPLC using a chiral column. [d] 40 °C. [e] 30 °C. [f] 48 h. [g] Co^{II} (5 mol%) and **L4** (6 mol%). [h] Co^{II} (3 mol%) and **L4** (3.6 mol%).

With the optimal reaction conditions in hand, we investigated the scope of this reaction as shown in Scheme 1. All the reactions of cyclic *N*-sulfonyl α-ketiminoesters bearing either electron-donating or electron-withdrawing substituents on the phenyl ring occurred smoothly to afford the desired products with excellent enantioselectivities and in modest to excellent yields (**3a**-**3l**). Halides, CF_3, OCF_3, OMe, and alkyl groups attached at the C5-C7 position of the *N*-sulfonyl α-ketimines were found to be tolerant to the reaction conditions (**3b**-**3m**). Naphthofused sultam **3o** was also isolated in good yield and excellent enantioselectivity. An exception to these excellent results was substrate **1n** bearing 4,6-diMe groups, which gave a significantly lower *ee*, showing that the enantioselectivities were also influenced by the sterics of the substrate. Moreover, good yields and good to excellent enantioselectivities were obtained for substrates bearing a variety of ester groups (Me, ^{i}Pr, or ^{n}Bu) (**3p**-**3r**). The allylation of cyclic *N*-sulfonyl-ketiminoesters with substituted potassium allyltrifluoroborates was also carried out. In these reactions, a clean allylic transposition took place to form a new carbon-carbon bond at the more substituted carbon atom of the allyltrifluoroborate; high enantioselectivities were obtained but the diastereomeric ratios were only modest (**3s** and **3t**). To confirm the scalability of the present protocol, a larger scale reaction of *N*-sulfonyl α-ketiminoester **1a** (4 mmol) with potassium allyltrifluoroborate **2a** was carried out, and product **3a** (1.07 g) was readily isolated in 95% yield and 99% *ee*.

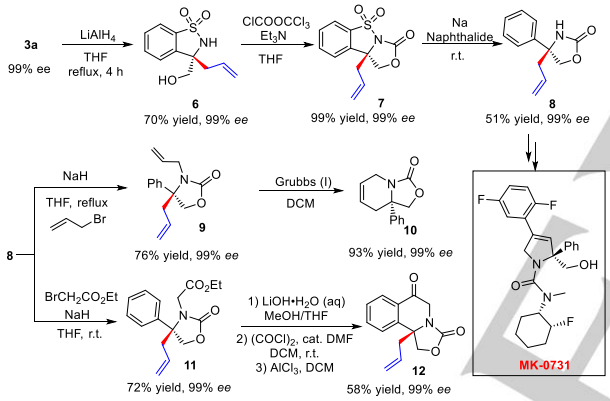


Scheme 1. Substrate scope of *N*-sulfonyl α-ketiminoesters. [a] 4 mmol scale, 1.07 g of product was obtained.

A range of *N*-sulfonyl ketimines possessing alkyl substituents were also tolerable to the enantioselective cobalt-catalyzed allylation reaction (Scheme 2). Excellent yields and high *ee*s were obtained when the reaction was carried out in MTBE at 50 °C using $Co(OTf)_2$·2MeCN/bisoxazoline **L5** as a catalyst. All of the substrates gave good yields and good enantioselectivities of the desired products (**5a**-**5d**). Acyclic aldimine and ketimine are unreactive for our Co^{II}-catalytic system.



Scheme 2. Substrate scope of *N*-sulfonyl ketimines possessing alkyl substituents.



Scheme 3. Transformations of product **3a**.

To highlight the synthetic utility, we have applied this methodology to the synthesis of a series of biologically interesting compounds (Scheme 3). For example, treatment of amino ester **3a** (99% *ee*) with $LiAlH_4$ in refluxing THF afforded the corresponding cyclic *N*-sulfonamido alcohol **6** in 70% yield and without loss of enantiopurity. **6** was readily converted into **7** in equivalent yield. This product could be further transformed in moderate yield to the oxazolidinone structure **8** bearing a chiral α-tertiary amine motif (99% *ee*) via removal of the SO_2 group. Oxazolidinone **8** is an important intermediate for the total synthesis of MK-0731.[19] In another example, reaction of **8** with allyl bromide and sodium hydride in THF and under reflux conditions furnished the *N*-allylated derivative **9** in 76% yield. Subsequent ring-closing metathesis using the Grubbs' first-generation RCM catalyst in DCM afforded the bicycle **10** in excellent yield after flash-filtration with no loss in optical purity. To this end, treatment of oxazolidinone **8** with ethyl bromoacetate followed by Friedel-Crafts cyclization furnished the tricyclic compound **12** bearing a tetrasubstituted carbon stereogenic center on the ring system.

Considering the mechanism of the reaction, on one hand Co^{II} is a good Lewis acid so that it may activate the ketimine (Figure 2, A).[20] On the other hand, the transmetalation of allylboron with Co^{II} to form an allyl-Co^{II} species has also been reported (corresponding to models B or C).[21] To shed some light on the mechanism of this reaction, several other Lewis acids were also tested by replacement of the Co^{II} salt with other metal salts using the same reaction conditions. $Cu(ClO_4)_2·6H_2O$, $Cu(OTf)_2$, $Mg(OTf)_2$, $Sc(OTf)_3$ and $Fe(OTf)_3$ could also catalyze this reaction to give the allylation product **3a** in 54-92% yield, but the enantiomeric excess of the product was very poor (0-7% *ee*, see SI). We thus hypothesize that the allylation reaction of potassium allyltrifluoroborate with cyclic *N*-sulfonyl α-ketiminoesters can be catalyzed by metal Lewis acids (A), but Co^{II} may also play other roles in the asymmetric catalysis to give the product in high *ee* (B, D). Interestingly, significant positive nonlinear effects of the catalyst's enantiomeric composition on reaction enantioselectivity are observed in this reaction (Figure 2).[22] Although we cannot exclude the formation of unreactive catalytic oligomers of heterochiral complexes ($[Co_nL^S_xL^R_y](ClO_4)_{2n}$) which may be one possible explanation for non-linear effect, we propose a dimetal catalysis model (D) for this reaction based on the aforementioned results.[23,24] The two Co catalytic center may or may not ligates with each other.

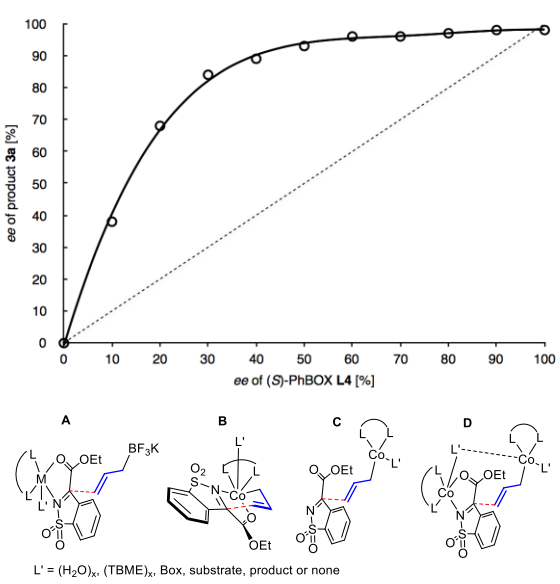


Figure 2. Nonlinear Effect Experiment Using **1a** as Substrate and **L4** as Ligand (10 mol% Co, 12 mol% **L4**), and Proposal of Catalysis Models.

In summary, we have developed an efficient and enantioselective cobalt-catalyzed addition of potassium allyltrifluoroborates to *N*-sulfonyl ketimines. A wide scope of optically active α-trisubstituted homoallylamines can be obtained, which are anticipated to be potential bioactive compounds or drug precursors for medical applications. Further studies of the synthetic utilities of this protocol reveal it to be a promising

method for the synthesis of many other valuable homoallylamine derivatives.

Acknowledgements

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Keywords: cobalt • allylation • asymmetric catalysis • ketimine • α-tertiary amine

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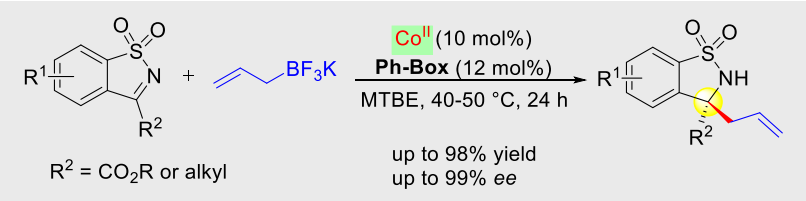

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Cobalt-Catalyzed Asymmetric Allylation of Cyclic Ketimines

Co^{2+}operation: A Co^{II}/Box-catalyzed asymmetric allylation of cyclic ketimines was developed using potassium allyltrifluoroborate. The desired homoallylic amines were obtained in excellent yields and enantioselectivities.