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Communication

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Cobalt-Catalyzed Regio- and Enantioselective Allylic Amination

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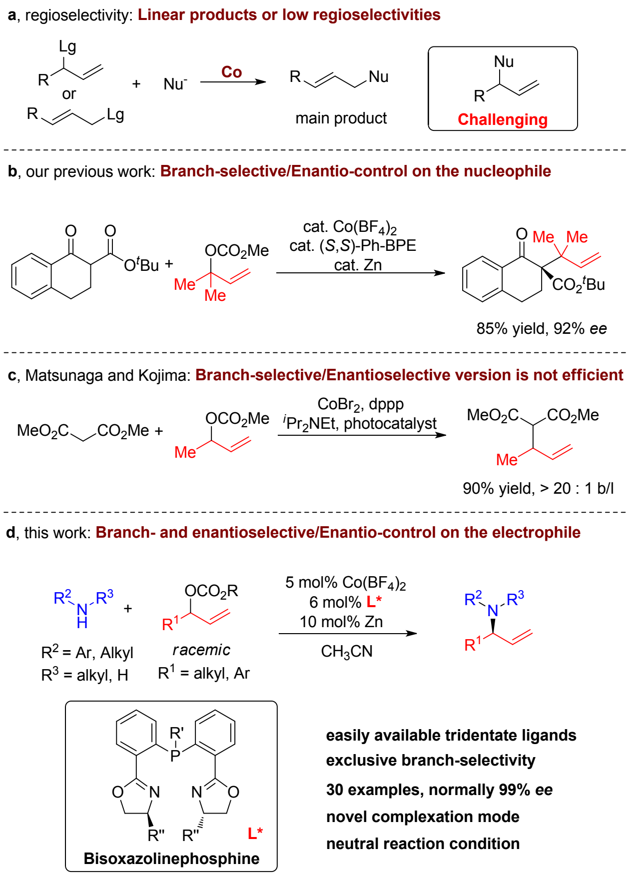
Supporting Information Placeholder

ABSTRACT: The first earth-abundant cobalt-catalyzed highly branched- and enantioselective allylic amination of racemic branched allylic carbonates bearing alkyl groups with both aromatic and aliphatic amines have been developed. The process allows rapid access of allylic amines in high yields with exclusively branched selectivity and excellent enantioselectivities (normally 99% *ee*) under mild reaction conditions.

Transition-metal-catalyzed asymmetric allylic substitution reaction provides powerful methods for the enantioselective construction of carbon-carbon and carbon-heteroatom bonds.[1] However, several issues, such as regio/enantioseletive control and substrate scope, are still challenging for this transformation. For unsymmetrical allylic substrates, it is well known that Pd-catalyzed allylic substitutions mostly give the products at the less-hindered positions. Different from Pd, Ir-catalyzed asymmetric allylic substitution of linear allylic substrates could afford branched products with high regio- and enantioselectivities.[2] Nevertheless, the Ir-catalyzed reactions for the more readily accessible racemic branched allylic substrates remain challenging. Although regio- and enantioselective allylic substitution for certain substrates[3,4] or by other transition metals[5] have been achieved in some cases, the reaction of simple alkyl-substituted allylic donors is largely unexplored. Highly regio- and enantioselective allylations of aliphatic amines and indoles have only been recently reported by Krische with their π-allyliridium C,O-benzoate catalysts.[4a,c] Therefore, the development of new efficient catalytic system to achieve asymmetric allylic substitution of simple alkyl-substituted allylic substrates is still highly desired.

Cobalt is an earth-abundant, lower-cost first-row transition metal. The development of Co-catalyzed allylic substitution is undoubtedly one of the ways to meet the criteria of sustainable and green chemistry.[6] Although Co-catalyzed allylic substitution has sporadically been reported, the transformations normally produce the linear products (Scheme 1, **a**).[7] To the best of our knowledge, highly branched- and enantioselective Co-catalyzed allylic substitutions were unknown before our recent report on Co-catalyzed enantioselective reverse prenylation of β-ketoesters, in which the enantioselectivity on the nucleophiles can be controlled (Scheme 1, **b**). During we are preparing this manuscript, Matsunaga and Kojima developed a Co-catalyzed allylation of malonates and other derivatives with high branch-selectivity in non-asymmetric variant (Scheme 1, **c**).[9] Herein, we report the first Co-catalyzed highly regio- and enantioselective allylic amination with aniline and aliphatic amine derivatives, which allows rapid access allylic amines[10] in high yields with complete branch-selectivities and excellent enantioselectivities. In addition, the protocol is effective for both racemic branched and linear (*Z* and *E*) allylic substrates under neutral conditions (Scheme 1, **d**).

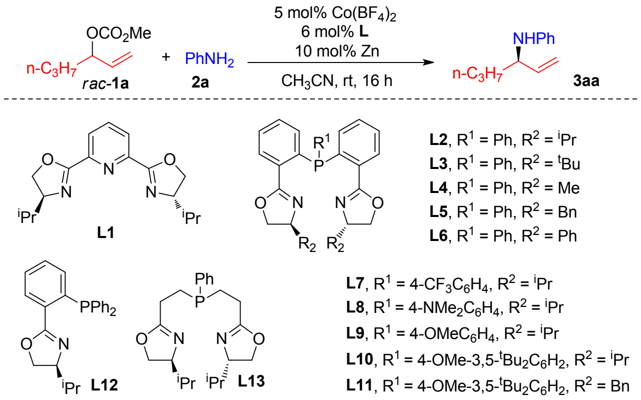
Scheme 1. Earth-abundant Cobalt-Catalyzed Allylic Substitutions



Inspired by the high stability and reactivity of base-metal/pincer complexes,[11] we initially conducted the reaction of racemic *n*-propyl allylic carbonate **1a** and aniline **2a** as the model substrates in the presence of Co-catalyst in situ formed by $Co(BF_4)_2$ and tridentate chiral ligand (Table 1). However, the reaction with Pybox ligand **L1** barely took place (entry 1). To our delight, when the reaction with bisoxazolinephosphine[12] **L2** in the presence of zinc dust as a reductant was conducted at room temperature, the desired allylic amine **3aa** was obtained with exclusively branched regioselectivity and excellent enantioselectivity (>99% *ee*), whereas in moderate yield (entry 2). To further optimize the catalytic reactivity, several NPN-type ligands with variations on the oxazoline rings and the phosphine atom were synthesized (see

Supporting Information). It was found that the substitution on the oxazoline rings for the ligand played important roles for the reaction (entries 2-6). The reaction with ligand **L3** bearing tert-butyl group almost did not proceed (entry 3). It was delightedly found that the reaction with ligand **L6** with phenyl on the oxazoline rings proceeded smoothly to give product **3aa** in almost quantitative yield with complete branch- and enantioselectivity (entry 6). Next, the ligand with several different R^1-substituents were examined to evaluate the electronic and steric properties on the phosphorus atom. The electronic and steric properties of P-atom of the ligand also affected for the reaction efficiency (entries 7-11). The ligand with the electron-rich and more bulky group is beneficial for the reactivity, thus the reaction could be improved to give **3aa** in high yield when using the ligand **L10** and **L11** with 4-MeO-3,5-^{t}Bu$_2$C$_6$H$_2$ group (entries 10 and 11). Notably, although the NPN-type ligands showed different reactivity for the reaction, above 99% *ee*s could be observed for all cases (entries 2-11). Next, we examined the allylic amination reaction by using PN-type ligand **L12** and NPN-type ligand **L13** without rigid phenyl ring. However, the ligands are not effective for the reaction (entries 12 and 13). Full conversion of **2a** was also obtained with 1 mol% cobalt catalyst, although longer time (33 hours) is needed (entry 14).

Table 1. Optimization for Co-catalyzed Asymmetric Allylic Amination[a]

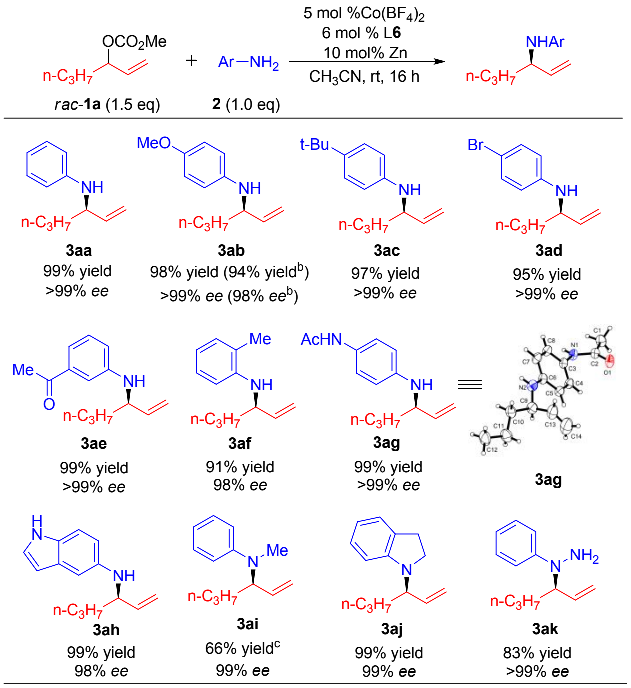


entry	catalyst	yield (**3aa**, %)[b]	*ee* (%)[c]
1	Co(BF$_4$)$_2$/**L1**	< 5	--
2	Co(BF$_4$)$_2$/**L2**	57	> 99
3	Co(BF$_4$)$_2$/**L3**	< 5	> 99
4	Co(BF$_4$)$_2$/**L4**	84	> 99
5	Co(BF$_4$)$_2$/**L5**	68	> 99
6	**Co(BF$_4$)$_2$/L6**	**99**	**> 99**
7	Co(BF$_4$)$_2$/**L7**	38	> 99
8	Co(BF$_4$)$_2$/**L8**	70	--
9	Co(BF$_4$)$_2$/**L9**	63	> 99
10	Co(BF$_4$)$_2$/**L10**	89	> 99
11	Co(BF$_4$)$_2$/**L11**	96	> 99
12	Co(BF$_4$)$_2$/**L12**	< 5	--
13	Co(BF$_4$)$_2$/**L13**	< 5	--
14[d]	Co(BF$_4$)$_2$/**L6**	99	99

[a]Conditions: **1a** (0.38 mmol, 1.5 equiv), **2a** (0.25 mmol, 1.0 equiv), Co(BF$_4$)$_2$ (0.0125 mmol, 0.05 eq), ligand (0.015 mmol, 0.06 eq), Zn dust (0.025 mmol, 0.1 eq) and CH$_3$CN (2 mL). [b]Isolate yield. [c]The enantiomeric excess of **3aa** was determined by HPLC with a chiral column. [d]Co(BF$_4$)$_2$ (0.01 eq), **L6** (0.0125 eq), Zn dust (0.02 eq) were used in 1.25 mmol scale and the reaction time is 33 hours.

Under the optimized condition (Table 1, entry 6), the reaction scope was evaluated by using different substituted anilines (Scheme 2). Various anilines with different electronic and steric nature were tolerated under the reaction conditions to afford allylic amines **3aa-3af** in high yields with complete regioselectivities and very high levels of enantioselectivities. In a 6 mmol scale reaction with 2 mol % catalyst, **3ab** could be obtained in 94% yield and 98% *ee*, which indicates this transformation could be conducted in a larger scale. High chemoselectivity was also observed with N-(4-aminophenyl)acetamide and 5-aminoindole, thus allylic amines **3ag** and **3ah** as the only products were obtained with almost quantitative yields and high enantioselectivities. Secondary amines such as N-methylaniline and indoline were also suitable reaction partners to give corresponding allylic amines **3ai** and **3aj** with high selectivities. The phenylhydrazine **2k** was also involved in this reaction to afford the product **3ak**, which could be transformed into the N-allyl indole.[10d] The absolute configuration of **3ag** was assigned to be *R* by the single crystal X-ray diffraction analysis.

Scheme 2. The scope of anilines[a]

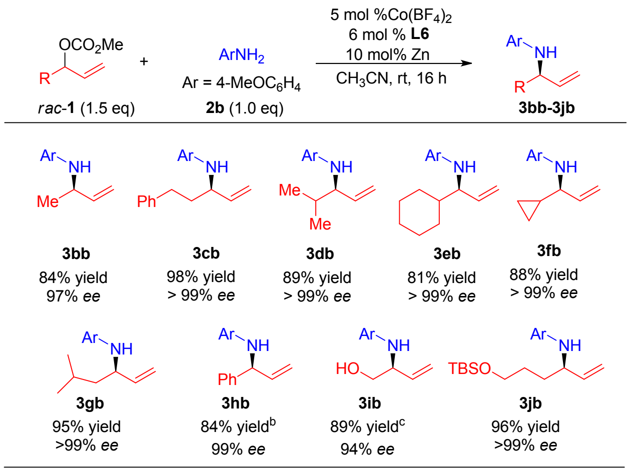


[a]Conditions: **1a** (0.38 mmol, 1.5 equiv), **2** (0.25 mmol, 1.0 equiv), Co(BF$_4$)$_2$ (0.0125 mmol, 0.05 eq), **L6** (0.015 mmol, 0.06 eq), Zn dust (0.025 mmol, 0.1 eq) and CH$_3$CN (2 mL). [b]2 mol% catalyst in a 6 mmol scale. [c]10 mol% catalyst

The reaction scope was next examined by using various allylic carbonates with p-anisidine **2b** as model substrate (Scheme 3). Importantly, the reaction is also effective for the allylic carbonate derivatized from but-3-en-2-ol to afford allylic amine **3bb** in 84% yield with high enantioselectivity (97% *ee*). The allylic amine **3cb** with phenylethyl group could be synthesized in high yield and above 99% *ee*. Sterically more hindered isopropyl, isobutyl and cyclohexyl groups could be introduced by the allylic amination to give corresponding allylic amines in high yields with excellent enantioselectivities. Significantly, versatile cyclopropyl group, free and protected hydroxyl groups could also be installed to afford corresponding allylic amines with high yields with high levels of enantioselectivities. Not only aliphatic racemic allylic carbonates, phenyl substituted allylic carbonate **1h** also participated in this reaction to produce allylic amine **3hb** in 84% yield with 99% of *ee* value when electron-rich **L11** was used as a ligand under otherwise identical conditions.

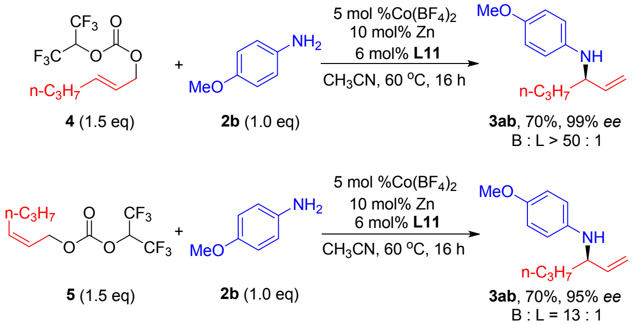
We next examined the Co-catalyzed allylic amination of linear allylic carbonates. However, both *Z*- and *E*-linear allylic methyl carbonates are not active under the optimal conditions. To accelerate the oxidative addition step, electron-withdrawing hexafluoroisopropyl carbonates[13] **4** and **5** were synthesized. As shown in Scheme 4, when using electron-riched **L11** as a ligand at 60 °C, the allylic aminations of both E/Z isomers **4** and **5** proceeded smoothly to afford same allylic product **3ab** in acceptably high yields with excellent enantioselectivities, albeit slightly less regio- and enantioselectivity were observed for the reaction of Z-isomer **5**.

Scheme 3. The scope of allylic carbonates[a]



[a]Conditions: **1** (0.38 mmol, 1.5 equiv) and **2b** (0.25 mmol, 1.0 equiv) $Co(BF_4)_2$ (0.0125 mmol, 0.05 eq), **L6** (0.015 mmol, 0.06 eq), Zn dust (0.025 mmol, 0.1 eq) in CH_3CN (2mL). [b]**L11** was used. [c]10 mol% of catalyst was used.

Scheme 4. The reactions of *Z*- and *E*-linear allylic carbonates.

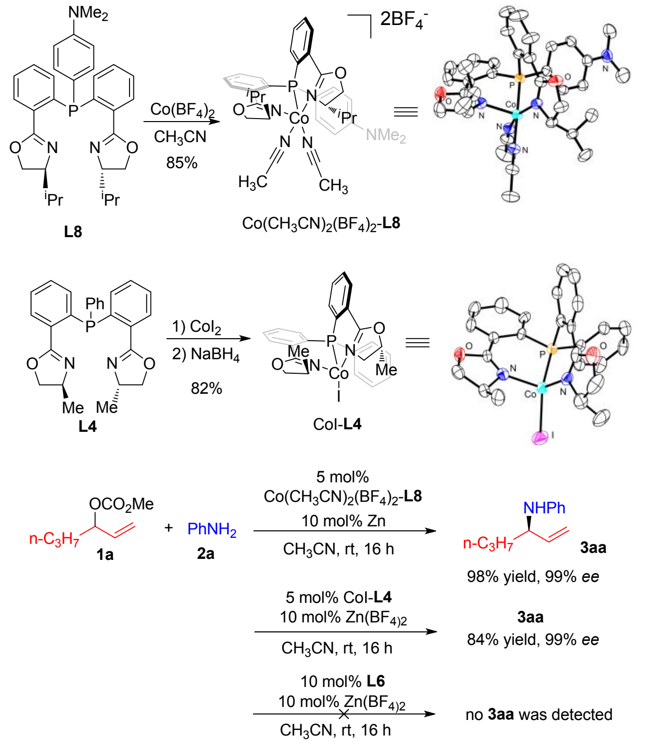


To further expand the reaction scope of the Co-catalyzed asymmetric allylic amination, we investigated the allylic amination with aliphatic amines. Unfortunately, the reaction did not proceed under the optimal conditions (Table 1, entry 6). More basic aliphatic amines may lead to the deactivation of catalysts because of the relative hard nature of cobalt metal. After further optimization, we found that with 20 mol% Lewis acid $La(OTf)_3$ under otherwise identical conditions, the allylic product **7ka** could be obtained in moderate yield. Inspired by the linear allylic carbonates, when branched allyl hexafluoroisopropyl carbonate **1k** was used in the presence of electron-rich **L11** as ligand at 60 °C, full conversion of morpholine was realized to afford allylic amine **7ka** with 99% *ee* (Scheme 5). With this optimal conditions in hand, the reaction with different aliphatic amines was examined. The reactions with other cyclic secondary amines **6b**, **6c** and **6d** gave corresponding allylic amines with good yields and excellent enantioselectivities. Primary aliphatic amines were also suitable reaction partners to produce allylic amines **7ke** to **7kg** in good yields with high levels of enantioselectivities. The reactions of both enantiomers of 1-phenylethanamine could also give the corresponding **7kh** and **7ki** with high diastereoselectivities, which supports an excellent catalyst control. As predicted, primary aliphatic amines with electron-withdrawing CF_3 group is more reactive, thus the allylic amine **7kj** bearing CF_3 group was isolated in 84% yield.

Scheme 5. The scope of aliphatic amines[a]

[a]Conditions: **1k** (0.38 mmol, 1.5 equiv) and **6** (0.25 mmol, 1.0 equiv) $Co(BF_4)_2$ (0.0125 mmol, 0.05 eq), **L6** (0.015 mmol, 0.06 eq), Zn dust (0.025 mmol, 0.1 eq) in CH_3CN (2 mL). [b]**1k** (1.0 eq) and **6j** (2.0 eq).

Scheme 6. The synthesis of $Co(CH_3CN)_2(BF_4)_2$-L8, Co(I)I-L4 and their reactivities



To gain mechanistic insight of the Co-catalyzed asymmetric allylic amination, the complex of $Co(CH_3CN)_2(BF_4)_2$-**L8** was synthesized by mixing **L8** with $Co(BF_4)_2$ in acetonitrile (Scheme 6). In the solid state, the complex adopts a distorted square pyramidal geometry, with all of the three NPN atoms in ligand coordinated to cobalt center. However, the complex of $Co(CH_3CN)_2(BF_4)_2$-**L8** is not able to catalyze the reaction. Upon reduction by 10 mol% Zn, full conversion of aniline **2a** was observed. These results indicated that a low oxidative state Co is the active species.[14] To demonstrate whether the Co(I) is real active species, a complex of Co(I)-**L4** was synthesized. The complex of CoI-**L4** adopts a distorted tetrahedral geometry, and again the three NPN atoms in **L4** coordinate with cobalt center.[15] Although CoI-**L4** itself is not active for the reaction, after the addition of 10 mol% $Zn(BF_4)_2$, the reaction proceeded smoothly to afford **3aa** in 84% yield with 99% *ee*. Control experiment with 10 mol% $Zn(BF_4)_2$ and **L6** excludes the possibility of zinc-catalyzed allylation reaction. These results implied that a cationic Co(I)/NPN complex is likely the active catalytic species in this allylic amination reaction, and Zn(II) species may works as Lewis acid to active allylic carbonate (see SI).

In conclusion, we have developed a cobalt/bisoxazolinephosphine catalyst system for the exclusively branch-selective allylic substitutions. Chiral allylic amines were prepared in excellent enantioselectivities (normally 99% *ee*) from readily accessible racemic allylic carbonates bearing aliphatic groups under mild reaction conditions. Bisoxazolinephosphine was found to be unique in this transformation. Investigations on reaction intermediate isolation, nucleophiles scope and more challenging chiral quaternary carbon construction with this catalyst system are on-going in our group.

ASSOCIATED CONTENT

Supporting Information. Detailed experimental procedures, characterization data, copies of ^1H, ^{13}C NMR spectra, HPLC spectra and X-ray crystal structure of $Co(CH_3CN)_2(BF_4)_2$-**L8**, CoI-**L4** and compound **3ag**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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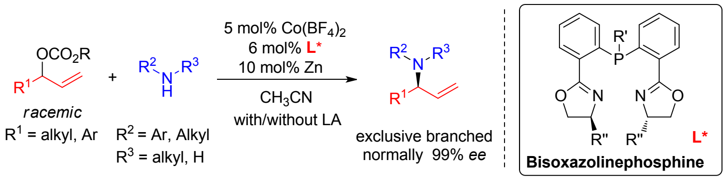
OCO$_2$R
R^1
racemic
R^1 = alkyl, Ar
+
R^2 N R^3 H
R^2 = Ar, Alkyl
R^3 = alkyl, H
5 mol% Co(BF$_4$)$_2$
6 mol% L*
10 mol% Zn
CH$_3$CN
with/without LA
R^2 N R^3
R^1
exclusive branched
normally 99% ee
R'
P
O N N O
R'' R''
L*
Bisoxazolinephosphine