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Catalytic Enantioselective Allylation of Ketoimines

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Abstract: A general catalytic allylation of simple ketoimines was developed using 1 mol % of $CuF\cdot 3PPh_3$ as catalyst, 1.5 mol % of $La(O^iPr)_3$ as the cocatalyst, and stable and nontoxic allylboronic acid pinacol ester as the nucleophile. This reaction constituted a good template for developing the first catalytic enantioselective allylation of ketoimines. In this case, using LiO^iPr as the cocatalyst produced higher enantioselectivity and reactivity than $La(O^iPr)_3$. Thus, using the CuF−cyclopentyl−DuPHOS complex (10 mol %) and LiO^iPr (30 mol %) in the presence of ^{t}BuOH (1 equiv) produced high enantioselectivity up to 93% ee from a range of aromatic ketoimines. Mechanistic studies indicated that LiO^iPr accelerates the reaction by increasing the concentration of an active nucleophile, allylcopper.

Introduction

The asymmetric allylation of simple ketoimines to afford enantiomerically enriched α-trisubstituted homoallylamines is among the most useful transformations in organic synthesis.[1] Two main methods have been reported for this type of reaction: (1) the addition of an allyl Grignard reagent to chiral *N*-sulfinyl ketoimines reported by Hua[2] and Ellman[3] and (2) the addition of a chiral allylsilane to ketone-derived acyl hydrazones reported by Leighton.[4] Although these reactions are practical and offer excellent stereoselectivity and substrate generality, stoichiometric amounts of a chiral controller are required. The catalytic enantioselective allylation of ketoimines is an important challenge that has never been achieved so far.[5] Indeed, there is not even a general *racemic* catalytic method for ketoimine allylation that can be extended to an asymmetric version because of the low reactivity of ketoimines. Marginally successful catalytic allylation reactions of ketoimines without enantiocontrol were reported by our group[6] and Yoshida's group[7] using allylsilanes as nucleophiles; however, both groups studied only one substrate, and the allylation products were obtained in only moderate yields. Thus, a new concept was needed to achieve the desired reaction.

Meanwhile, we previously developed a catalytic enantioselective allylation of ketones using a CuF−(*R*,*R*)-^{i}Pr−DuPHOS (**8**) complex as the catalyst and allylboronate as the nucleophile.[8,9] The addition of $La(O^iPr)_3$ as a cocatalyst was essential for the high reactivity of this system. We proposed that highly nucleophilic allylcopper, the actual nucleophile, is generated from allylboronate via transmetalation. Kinetic studies indicated that $La(O^iPr)_3$ facilitates the catalytic cycle by accelerating the rate-determining catalyst turnover step without affecting the enantioselectivity; however, the precise mechanism of rate acceleration by $La(O^iPr)_3$ remained unclear.

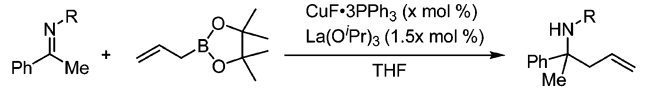
Taking advantage of the high catalyst activity of CuF in the allylboration reaction, we launched a project to develop a catalytic enantioselective allylation of ketoimines. In this paper, we describe (1) a general catalytic allylation of ketoimines, (2) an extension to the catalytic enantioselective allylation of ketoimines, and (3) a proposed mechanism for rate acceleration by the cocatalyst (LiO^iPr in this case) based on NMR studies.

Results and Discussion

Catalytic Allylation of Ketoimines. To realize a synthetically useful catalytic allylation of ketoimines, we first studied the effect of different protecting groups for the substrate nitrogen atom. $CuF\cdot 3PPh_3$ was used as the catalyst (10 mol %), and allylboronate **4** was used as the nucleophile, in the presence of 15 mol % of $La(O^iPr)_3$[8] (Table 1, entries 1−3). Although

(1) For a general review of asymmetric addition of organometallic reagents to imines, see: (a) Bloch, R. *Chem. Rev.* **1998**, *98*, 1407. (b) Enders, D.; Reinhold, U. *Tetrahedron: Asymmetry* **1997**, *8*, 1895.
(2) Hua, D. H.; Miao, S. W.; Chan, J. S.; Iguchi, S. *J. Org. Chem*. **1991**, *56*, 4.
(3) (a) Cogan, D. A.; Liu, G.; Ellman, J. *Tetrahedron* **1999**, *55*, 8883. (b) Ellman, J. A.; Owens, T. D.; Tang, T. P. *Acc. Chem. Res.* **2002**, *35*, 984.
(4) Berger, R.; Duff, K.; Leighton, J. L. *J. Am. Chem. Soc.* **2004**, *126*, 5686.
(5) For examples of catalytic enantioselective allylation of aldimines or *N*-acylhydrazones derived from aldehydes, see: (a) Nakamura, H.; Nakamura, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4242. (b) Nakamura, K.; Nakamura, H.; Yamamoto, Y. *J. Org. Chem.* **1999**, *64*, 2614. (c) Fernandes, R. A.; Stimac, A.; Yamamoto, Y. *J. Am. Chem. Soc.* **2003**, 125, 14133. (d) Fernandes, R. A.; Yamamoto, Y. *J. Org. Chem.* **2004**, *69*, 735. (e) Gastner, T.; Ishitani, H.; Akiyama, R.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 1896. (f) Hamada, T.; Manabe, K.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 3927.
(6) Yamasaki, S.; Fujii, K.; Wada, R.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc*. **2002**, *124*, 6536.
(7) Kamei, T.; Fujita, K.; Itami, K.; Yoshida, J. *Org. Lett*. **2005**, *7*, 4725.
(8) Wada, R.; Oisaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc*. **2004**, *126*, 8910.
(9) For the pioneering CuF-catalyzed enantioselective aldol reaction, see: (a) Krüger, J.; Carreira, E. M. *J. Am. Chem. Soc.* **1998**, *120*, 867. (b) Pagenkopf, B. L.; Krüger, J.; Stojanovic, A.; Carreira, E. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 3124. For AgF-catalyzed enantioselective allylation reactions, see: (c) Yanagisawa, A.; Kageyama, H.; Nakatsuka, Y.; Asakawa, K.; Matsumoto, Y.; Yamamoto, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 3701. (d) Wadamoto, M.; Yamamoto, H. *J. Am. Chem. Soc*. **2005**, *127*, 14556.

Table 1. Optimization of Reaction Conditions for Catalytic Allylation of Ketoimines



1: R = NHBz
2: R = P(O)Ph_2
3a: R = Bn

4 (2.5 equiv)

5: R = NHBz
6: R = P(O)Ph_2
7a: R = Bn

entry	substrate	catalyst (*x* mol %)	additive	time (h)	yield (%)[a]
1	**1**	10	none	27	0
2	**2**	10	none	4	73
3	**3a**	10	none	3	85
4[b]	**3a**	1	none	24	32
5[b]	**3a**	1	^{t}BuOH[c]	2	94

[a] Isolated yield. [b] Reactions were performed at 45 °C. [c] 1.0 equiv of ^{t}BuOH was added.

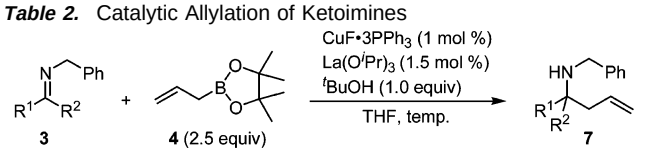
N-benzoylhydrazone **1** did not afford any allylated product, both *N*-phosphinoylimine **2** and *N*-benzylimine **3a** gave the corresponding products in high yield (entries 2 and 3). The less electrophilic **3a** produced a higher reaction rate and a greater product yield than **2**. This apparent contradiction can be partially understood by analogy to the previous allylation of ketones, in which regeneration of allylcopper, rather than allyl addition, was found to be the turnover-limiting step.[8] On the basis of these initial observations, we selected *N*-benzylketoimine **3** as the substrate for further optimization.

Next, we attempted to reduce the catalyst loading to 1 mol %. Under those conditions, however, even increasing the reaction temperature to 45 °C did not lead to complete conversion (entry 4). Thus, we sought other means by which to increase reactivity, particularly through the use of an additive proton source.[10] A beneficial effect of added ^{t}BuOH in the catalytic allylsilylation of imines was previously recognized by our group.[6] ^{t}BuOH is expected to facilitate catalysis through protonolysis of the intermediate copper amide that is generated by the addition of allylcopper to an imine (see Scheme 2, **15**). As expected, we observed a significantly increased reaction rate in the presence of 1 equiv of ^{t}BuOH, and product **7** was obtained in 94% yield after 2 h (entry 5).

The optimized allylation conditions were applied to various ketoimines (Table 2). Allylated products were obtained in excellent yields from a variety of substrates, including heteroaromatic and enolizable aliphatic ketoimines. Therefore, this catalytic allylation seemed to be a good template for the further development of a catalytic enantioselective allylation of ketoimines.

Catalytic Enantioselective Allylation of Ketoimines. Having established a general *racemic* catalytic allylation of ketoimines, we hoped to develop a corresponding enantioselective variant through the use of a chiral ligand for copper. The initial trials were conducted using **3a** as a substrate and ^{i}Pr-DuPHOS (**8**) as a chiral ligand (Table 3, entries 1−5).[11] Toluene was chosen as a solvent because it gave slightly better reaction rates than THF. The chiral Cu^{I}F complex was reductively generated in situ by combining CuF_2•$2H_2O$ and **8** in a 1:2 ratio.[12] Other catalyst preparation methods, including those employing an achiral reductant (e.g., PPh_3), led to inferior levels of enantioselectivity, probably due to unselective catalysis by achiral Cu^{I}F complexes.[13] The rate acceleration effect of La(O^{i}Pr)$_3$ was once again observed in this case (entry 1 vs entry 2).

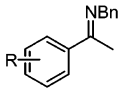
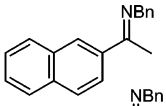
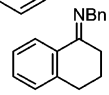
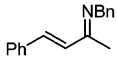
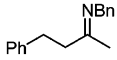
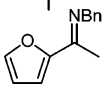
Table 2. Catalytic Allylation of Ketoimines



3

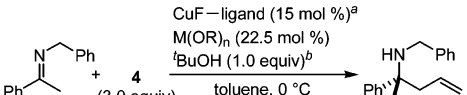
4 (2.5 equiv)

7

entry	substrate		temp. (°C)	time (h)	yield (%)[a]
1		**3a**: R = H	45	2	94
2		**3b**: R = 3-Me	45	1.5	88
3		**3c**: R = 3-OMe	45	1	94
4		**3d**: R = 3-F	45	1	92
5		**3e**: R = 4-OMe	45	5	93
6		**3f**: R = 4-Cl	45	1.5	96
7		**3g**	45	0.5	98
8[b]		**3h**	45	4	92
9		**3i**	rt	1	85
10		**3j**	rt	1	96
11		**3k**	rt	1	96
12		**3l**	45	1	94

[a] Isolated yield. [b] 5 mol % of CuF•$3PPh_3$ and 7.5 mol % of La(O^{i}Pr)$_3$ were used.

Table 3. Optimization of Catalytic Enantioselective Allylation of Ketoimine **3a**

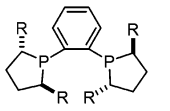


3a

4 (3.0 equiv)

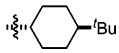
7a

entry	ligand	$M(OR)_n$	time (h)	yield (%)[c]	ee (%)[d]
1	**8**	none	24	57	78
2	**8**	La(O^{i}Pr)$_3$	24	63-87[e]	17-80[e]
3	**8**	KO^{t}Bu	14	87	75
4	**8**	Al(O^{t}Bu)$_3$	22	28	43
5	**8**	LiO^{i}Pr	24	99	84
6	**9**	LiO^{i}Pr	2	89	89
7[f]	**9**	LiO^{i}Pr	0.5	92	89
8	**10**	LiO^{i}Pr	14	85	73



8: (*R*,*R*)-^{i}Pr-DuPHOS (R = ^{i}Pr)

9: R = 

10: R = 

[a] Catalyst was prepared by reducing CuF_2•$2H_2O$ with 2 equiv of chiral phosphine to Cu in situ. See Experimental Section for details. [b] ^{t}BuOH was slowly added over 2 h. [c] Isolated yield. [d] Determined by chiral HPLC. [e] Yield and enantioselectivity were not constant in each run. [f] 10 mol % of chiral Cu catalyst and 30 mol % of LiO^{i}Pr were used.

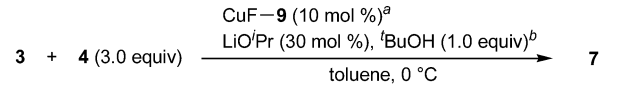
(10) For examples of beneficial effects of protic additives in facilitation of the catalytic cycle, see: (a) Kitajima, H.; Ito, K.; Katsuki, T. *Tetrahedron* **1979**, *101*, 17015. (b) Evans, D. A.; Rovis, T.; Kozlowski, M. C.; Tedrow, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 1994. (c) Krueger, C. A.; Kuntz, K. W.; Dzierba, C. D.; Wirschun, W. G.; Gleason, J. D.; Snapper, M. L.; Hoveyda, A. H. *J. Am. Chem. Soc*. **1999**, *121*, 4284. (d) Takamura, M.; Hamashima, Y.; Usuda, H.; Kanai, M.; Shibasaki, M. *Angew. Chem., Int. Ed*. **2000**, *39*, 1650. (e) Majima, K.; Takita, R.; Okada, A.; Ohshima, T.; Shibasaki, M. *J. Am. Chem. Soc*. **2003**, *125*, 15837.

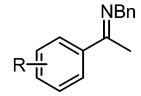
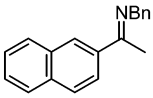
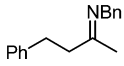
(11) Other chiral bisphosphine ligands such as BINAP and DTBM-SEGPHOS gave less satisfactory enantiomeric excesses than ^{i}Pr-DuPHOS. See Supporting Information.

(12) Phosphines can reduce Cu(II)F_2 to Cu(I)F−phosphine complexes. See: Gulliver, D. J.; Levason, W.; Webster, M. *Inorg. Chim. Acta* **1981**, *52*, 153.

(13) Cu(I)F itself is unstable and cannot be isolated in the absence of phosphine ligands. See: Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*; Wiley-Interscience: New York, 1999.

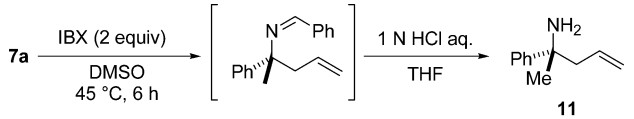
Table 4. Scope of Catalytic Enantioselective Allylation of Ketoimines



entry	substrate		time (h)	yield (%)[c]	ee (%)[d]
1		**3a**: R = H	0.5	92	89[e]
2		**3b**: R = 3-Me	1	96	91
3		**3c**: R = 3-OMe	1	97	93
4		**3d**: R = 3-F	1	89	87
5		**3e**: R = 4-OMe	24	76	85
6		**3f**: R = 4-Cl	24	82	81
7[f]		**3g**	12	88	92
8[g]		**3j**	2	98	23

[a] Catalyst was prepared by reducing 10 mol % of $CuF_2 \cdot H_2O$ with 20 mol % of **5**. [b] ^{t}BuOH was slowly added over 2 h. [c] Isolated yield. [d] Determined by chiral HPLC. [e] The absolute configuration was determined to be (*R*). [f] THF was used as solvent. [g] **8** was used as the chiral ligand.

Scheme 1. Removal of the *N*-Benzyl Group



Unfortunately, yields and enantioselectivities were variable. We hypothesized that metal salt contaminents present in commercial $La(O^iPr)_3$ might be to blame. Therefore, we examined several alternate metal alkoxide additives (entries 2−5). LiO^iPr exhibited an additive effect similar to that of $La(O^iPr)_3$ but gave more reproducible yields and slightly improved enantiomeric excesses (84% ee; entry 5).

To further improve the enantioselectivity, extensive tuning of the DuPHOS structure was conducted next (entries 5−8). Using a novel ligand (**9**), having cyclopentyl groups,[14] product **7a** was obtained with increased enantioselectivity (89% ee; entry 6). The amount of copper catalyst could be reduced to 10 mol % without affecting the enantioselectivity, provided that 30 mol % of LiO^iPr was used (entry 7).

Having determined the optimum reaction conditions, we then examined substrate generality. Aromatic ketoimines were converted to corresponding homoallylamines in good to excellent yield and enantioselectivity (Table 4, entries 1−7). When aliphatic ketoimines were used as substrates, however, enantioselectivity was not satisfactory (see entry 8 for typical results using an aliphatic ketoimine). Enantiomerically enriched primary homoallylamines (e.g., **11**) can be obtained by removal of the *N*-benzyl group from **7** (Scheme 1). Nicolaou's IBX chemistry[15] proved ideal in this case because benzyl deprotection could be carried out while leaving the allyl moiety intact. Although there is still room to improve substrate generality and enantioselectivity, this is the first catalytic enantioselective allylation of ketoimines.

Origin of Rate Acceleration by LiO^iPr. To gain insight into the acceleration mechanism of LiO^iPr, NMR studies were conducted (Figure 1). Although the NMR experiments were performed using PPh_3 as a ligand, the obtained mechanistic insight should also apply to the catalytic enantioselective reaction. Consistent with previous observations,[8] the ^{11}B NMR spectrum of a mixture of $CuF \cdot 3PPh_3$ and **4** (1:3) in THF in the absence of LiO^iPr showed two peaks corresponding to copper fluoroborate **12b** (−13.4 ppm) and fluoroboronate **13b** (4.2 ppm) (**4**/**12b**/**13b** = 56:33:11, Figure 1a).[16] The observation of **13b** indicates the formation of allylcopper **14**; the peak intensity of **13b** should directly correlate with the concentration of **14** (see eq 1 in Figure 1a).[17] In the presence of LiO^iPr ($CuF \cdot 3PPh_3$/**4**/LiO^iPr = 1:3:1.5), the concentration of allylcopper **14**, which corresponds to the combined peak intensities of boronates **13a** and **13b** (overlapping), is increased significantly (**4**/**12b**/**13a** + **13b** = 29:13:58, Figure 1b). These results indicate that LiO^iPr promotes formation of the active nucleophile (**14**).

The following results suggested that this LiO^iPr effect is likely due to the generation of transient electron-rich copper alkoxyborate **12c**, which apparently has higher transmetalation ability than fluoroborate **12b**. First, when LiO^iPr was mixed with **4** (1:1) in the absence of $CuF \cdot 3PPh_3$, the clean formation of lithium alkoxyborate **12a** (−10.1 ppm) was observed (Figure 1c; **4**/**12a** = 3:97). Similarly, when $CuF \cdot 3PPh_3$ was mixed with **4** (1:1), the Lewis acid/Lewis base adduct (copper fluoroborate **12b**: −13.4 ppm) was observed to be the predominant species in solution (data not shown, similar to Figure 1a). In neither of these experiments were peaks corresponding to **13a** or **13b** observed, indicating that transmetalation to allylmetal species is not favorable under these conditions.[18] On the other hand, when **12a** and **12b** were separately generated and then combined in a 1:1 ratio, the peak of alkoxyborate **12a** selectively disappeared, yet no peak assignable to **12c** was apparent, presumably because it was converted to **13a** and **13b** (both observed at 4.2 ppm) and allylcopper **14**. A small peak of fluoroborate **12b** (and **12d**) also remained (Figure 1d, **12b** + **12d**/**13a** + **13b** = 25:75).[19] These results suggest that the alkoxyborate **12c** was produced via facile cation exchange between **12a** and **12b** and that this reactive precursor (**12c**), rather than fluoroborate **12b**, is the major species that is transformed to allylcopper **14** (eq 4).

On the basis of this information, implicating LiO^iPr as an effective generator of active nucleophile **14**, we propose the following catalytic cycle (Scheme 2). The thus-generated allylcopper **14** reacts with **3** to produce copper amide **15**. ^{t}BuOH acts as a proton source to dissociate the product **7** from the copper catalyst with concomitant production of CuO^tBu. CuO^tBu then reacts with **4** to regenerate **14**, possibly via a copper *t*-butoxyborate corresponding to **12c**. Indeed, the catalytic cycle can be efficiently initiated by CuO^tBu; using 10 mol %

(14) See Supporting Information for the synthesis of **9**. Ligand **9** generally produced higher enantioselectivity than **8** for the substrates shown in Table 4.

(15) Nicolaou, K. C.; Mathison, C. J. N.; Montagnon, T. *J. Am. Chem. Soc.* **2004**, *126*, 5192.

(16) The structures of **12** and **13** were assigned by correlation of their ^{11}B NMR chemical shift values to those of separately synthesized related compounds. See ref 8 for details.

(17) Allylcopper **14** was not detected by ^{1}H and ^{13}C NMR, possibly because of the dynamic allylic rearrangement of copper. Similarly, allylsilver is not detected by NMR (see ref 9c).

(18) Lithium allylborate **12a** did not react with ketoimine **3a** in the absence of $CuF \cdot 3PPh_3$.

(19) Theoretically, the relative abundance of **13a** + **13b** (corresponding to the concentration of allylcopper **14**) cannot exceed 50% under these conditions. The observed ratio (75%) might be attributed to the existence of side-reaction pathways generating boron species undetectable by NMR (such as polyboron aggregates) and/or species giving the same chemical shift as **13a** and **13b**.

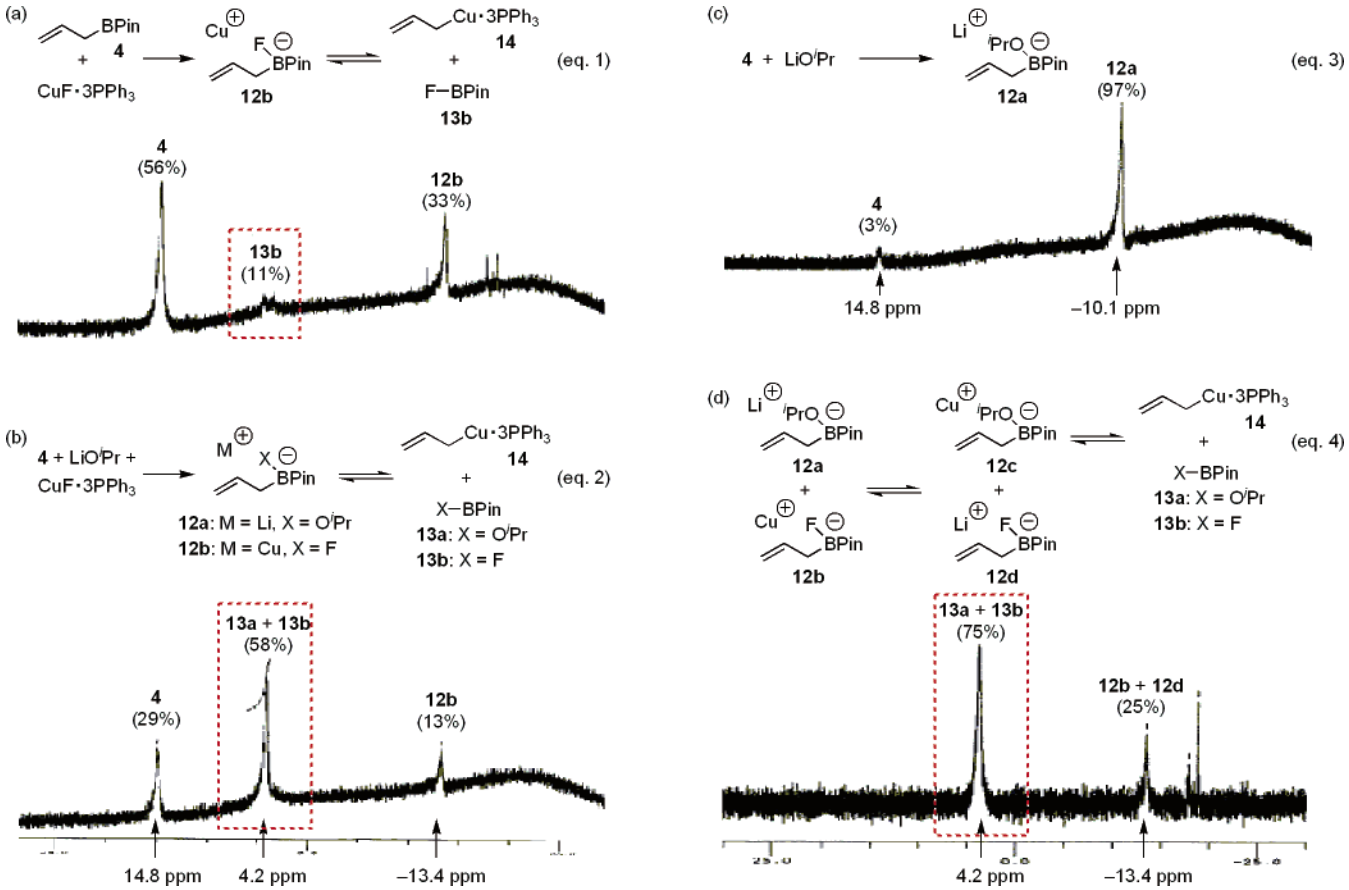
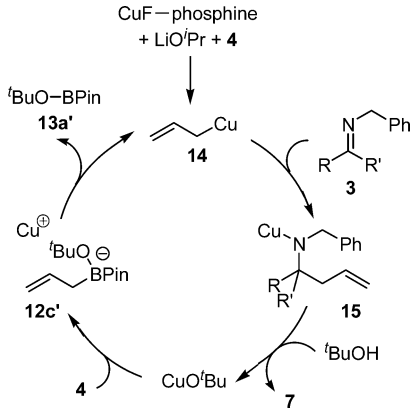


Figure 1. ^{11}B NMR studies for the rate acceleration mechanism of LiO^{i}Pr. (a) CuF·3PPh$_3$ + allylboronate **4** (1:3). (b) CuF·3PPh$_3$ + **4** + LiO^{i}Pr (1:3:1.5). (c) LiO^{i}Pr + **4** (1:1). (d) {LiO^{i}Pr + **4** (1:1)} + {CuF·3PPh$_3$ + **4** (1:1)} (1:1). The intensity of **13a** and **13b** (the peak in dashed squares) corresponds to the concentration of the active allylcopper.

Scheme 2. Proposed Catalytic Cycle



of CuO^{t}Bu, allylation of **3a** proceeded in 3 h, giving product **7a** in 76% yield even in the absence of LiO^{i}Pr.[20]

Conclusions

In this paper, we describe the first possible solution to a long-standing problem: a catalytic enantioselective allylation of ketoimines. First, the general basic methodology for allylation of ketoimines was developed using a Cu^{I}F catalyst combined with a La(O^{i}Pr)$_3$ cocatalyst and allylboronate as a nucleophile. This reaction can be applied to a wide range of ketoimines including heteroaromatic and enolizable ketoimines, using 1 mol % of catalyst. Second, this catalytic reaction was extended to an enantioselective variant. In that case, LiO^{i}Pr rather than La(O^{i}Pr)$_3$ was the best cocatalyst, leading to significantly improved reaction rates. Sterically tuned cyclopentyl-DuPHOS (**9**) was identified as the optimum chiral ligand, and high enantioselectivity (up to 93% ee) was produced from aromatic *N*-benzylketoimines. Aliphatic ketoimines, however, gave unsatisfactory enantioselectivity under the present conditions. Third, the role of LiO^{i}Pr was elucidated. Intensive NMR studies demonstrated that the addition of LiO^{i}Pr increases the concentration of the active nucleophile, allylcopper, by generating an electron-rich precursor, copper alkoxyallylborate **12c**. Studies toward improving the substrate generality of the asymmetric reaction are ongoing in our laboratory.

Experimental Section

Typical Procedure for Catalytic Enantioselective Allylation of Ketoimines. CuF$_2$·2H$_2$O (4.1 mg, 0.03 mmol) and (*R,R*)-cyclopentyl-DuPHOS (31.4 mg, 0.06 mmol) were refluxed in MeOH (1.0 mL) for 2 h. The solvent was evaporated, and the resulting amorphous was coevaporated with toluene (0.1 mL) twice. LiO^{i}Pr (5.9 mg, 0.09 mmol) and ketoimine **3a** (62.8 mg, 0.3 mmol) were added. Toluene (0.3 mL) was added at 0 °C, followed by the addition of allylboronate **4** (171 μL, 0.9 mmol). ^{t}BuOH (5.3 M in toluene (^{t}BuOH/toluene = 1:1 v/v), 0.3 mmol, 54.6 μL) was slowly added over 2 h using a syringe pump. After the addition of ^{t}BuOH was completed, the reaction mixture was stirred for 0.5 h, and then H$_2$O was added to

(20) On the basis of the proposed mechanism in Scheme 2, CuO^{t}Bu is expected to be a more atom-economical catalyst for the catalytic enantioselective allylation of ketoimines. CuO^{t}Bu is, however, unstable and difficult to handle. Therefore, the use of the catalyst combination of Cu^{I}F and LiO^{i}Pr is more convenient than the use of CuO^{t}Bu.

quench the reaction. The product was extracted with AcOEt, and the combined organic layer was washed with saturated aqueous NaCl. After drying over Na_2SO_4, filtration, evaporation, and purification through silica gel column chromatography gave the allylated product **7a** in 92% yield. The enantiomeric excess of the product was determined by chiral HPLC analysis. HPLC (DAICEL CHIRALPAK OD-H, hexane/2-propanol 1000:1, 1.0 mL/min) t_R: 12.1 min (major) and 16.1 min (minor).

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Supporting Information Available: Experimental procedures and characterization of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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