

# Enantioselective Synthesis of Trisubstituted Allenes via Cu(I)-Catalyzed Coupling of Diazoalkanes with Terminal Alkynes

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**S** Supporting Information

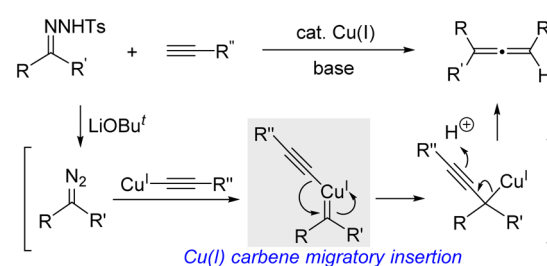
**ABSTRACT:** A highly enantioselective synthesis of trisubstituted allenes has been achieved through Cu(I)-catalyzed cross-coupling of aryldiazoalkanes and terminal alkynes with chiral bisoxazoline ligands. Alkynyl migratory insertion of Cu(I) carbene is proposed as the key step for the construction of axial chirality.

Because of their unique structure feature and reactivities, allenes have attracted significant attention in the fields of organic synthesis, natural product chemistry, and materials science.<sup>1,2</sup> In particular, chiral allenes are a type of fascinating molecules possessing axial chirality and have found many applications as useful building blocks in organic synthesis.<sup>2</sup> Accordingly, substantial efforts have been made toward the stereoselective synthesis of axially chiral allenes.<sup>3</sup> Early successful examples relied on the resolution of racemic allenes,<sup>4</sup> and the reactions involving chirality transfer from enantiomerically enriched propargylic derivatives.<sup>5</sup> The construction of axial chirality of allenes through asymmetric catalysis remains a substantially challenging problem. Recently, some progress has been made in catalytic asymmetric synthesis of chiral allenes, which include nucleophilic addition to enynes,<sup>6</sup>  $\beta$ -hydride elimination of enol triflates,<sup>7</sup> enantioselective functionalization of racemic allenes,<sup>8</sup> sigmatropic rearrangements of alkynes,<sup>9</sup> isomerization of 3-alkynes,<sup>10</sup> and Mukaiyama aldol reactions.<sup>11</sup> Despite all these successful catalytic systems, there are still limitations with the existing methods such as the need to use expensive metals, complex substrates, limited scopes, and the possible formation of homopropargylic alcohols as the byproducts in some cases.

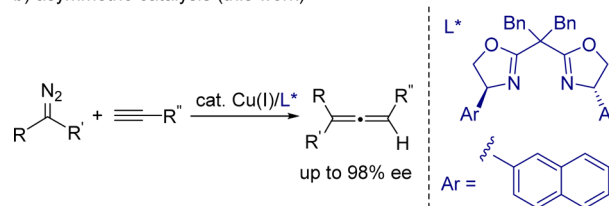
As a part of our research program on carbene-based coupling reaction,<sup>12</sup> we have previously developed a straightforward method for the synthesis of substituted allenes through Cu(I)-catalyzed cross-coupling of terminal alkynes and *N*-tosylhydrazones (Scheme 1a).<sup>13</sup> The related Cu(I)-catalyzed cross-coupling of terminal alkynes and diazo compounds has also been documented.<sup>14</sup> These coupling reactions may follow a common reaction pathway involving alkynyl migratory insertion of Cu(I) carbene species. In terms of efficiency and versatility, these direct coupling methods are attractive because they can construct the core structure of allenes from two readily available fragments. Thus, the development of a catalytic asymmetric version of these reactions is highly desirable. However, such direct buildup of axial chirality under catalytic

## Scheme 1. Allene Synthesis through Cu(I)-Catalyzed Carbene Coupling with Terminal Alkynes

a) our previous work (ref. 13)



b) asymmetric catalysis (this work)

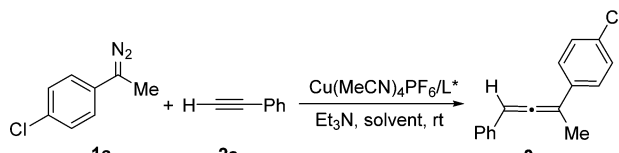


asymmetric conditions was not known until very recently. In 2015, the group of Liu and Feng reported the first catalytic asymmetric coupling for the highly enantioselective synthesis of allenates with chiral cationic guanidinium salts/Cu(I) as the catalyst.<sup>15</sup> Although the work represents a significant breakthrough, the reaction is limited to  $\alpha$ -diazoesters, which leads to the formation of 2,4-disubstituted allenates. Thus, further development of catalytic asymmetric coupling for allene synthesis with nonstabilized diazo alkanes is highly demanded. Herein, we report a Cu(I)-catalyzed coupling of nonstabilized diazo compounds for the highly enantioselective synthesis of trisubstituted allenes with a newly designed chiral bisoxazoline ligand (Scheme 1b).

We began our investigation by examining the Cu(I)-catalyzed cross coupling reaction between 1-(*p*-chlorophenyl)-1-diazoethane **1a** and phenylacetylene **2a** (Table 1). Gratifyingly, the initial experiment with Cu(MeCN)<sub>4</sub>PF<sub>6</sub> and commercially available chiral bisoxazoline ligand **4a** in toluene afforded the desired allene product **3aa** in 69% yield and 71% ee (entry 1). Encouraged by this result, we then proceeded to

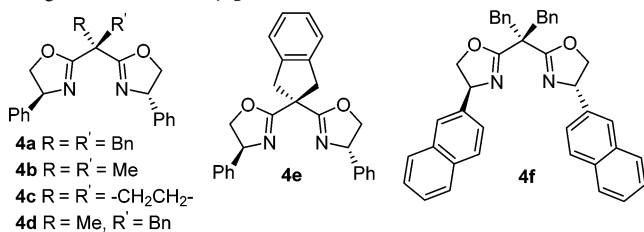
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Table 1. Optimization of the Reaction Conditions<sup>a</sup>


entry	L*	solvent	yield, % <sup>b</sup>	ee, % <sup>c</sup>
1	4a	toluene	69	71
2	4a	CHCl <sub>3</sub>	90	75
3	4a	CH <sub>2</sub> Cl <sub>2</sub>	30	83
4	4a	ClCH <sub>2</sub> CH <sub>2</sub> Cl	18	81
5	4a	THF	40	80
6	4a	MeCN	trace	—
7	4a	1,4-dioxane	20	73
8	4b	CHCl <sub>3</sub>	85	34
9	4c	CHCl <sub>3</sub>	60	61
10	4d	CHCl <sub>3</sub>	90	39
11	4e	CHCl <sub>3</sub>	50	18
12	4f	CHCl <sub>3</sub>	98	88
13	4f	CH <sub>2</sub> Cl <sub>2</sub> :CHCl <sub>3</sub> (1:1)	93	90

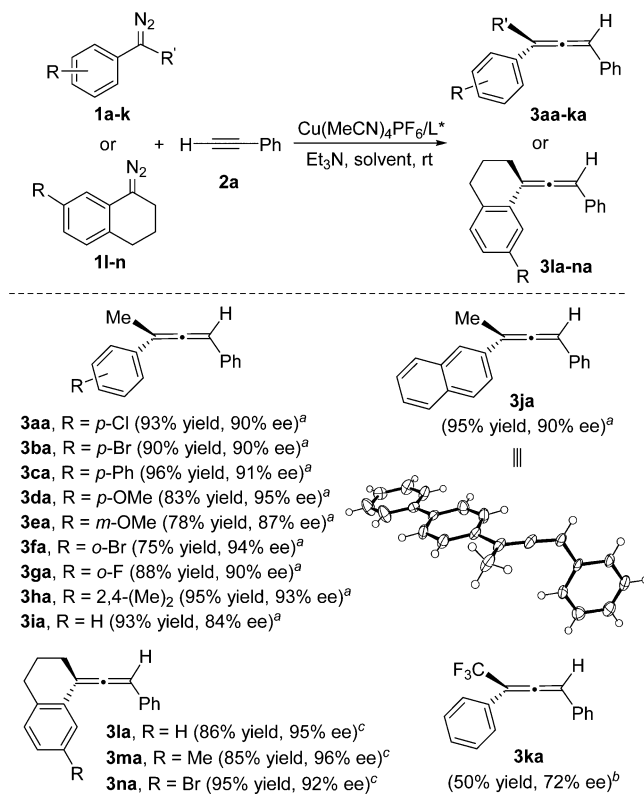
<sup>a</sup>Reaction was run under the following conditions: a solution of **1a** (0.2 mmol), **2a** (0.1 mmol), Et<sub>3</sub>N (0.1 mmol), Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (10 mol %), and chiral ligand (11 mol %) in anhydrous solvent (1 mL) was stirred at 25 °C under nitrogen atmosphere for 60 min. <sup>b</sup>Yields refer to isolated products. <sup>c</sup>Determined by HPLC analysis using a chiral stationary phase.



optimize the reaction by first evaluating the effect of solvents (entries 2–7). It was found that the reaction in CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, ClCH<sub>2</sub>CH<sub>2</sub>Cl, THF and dioxane all afforded the product **3aa** in comparatively high ee (entries 2–7), but the yields varied significantly and the reaction in CHCl<sub>3</sub> afforded the highest yield. A subsequent investigation of ligands confirmed that **4a** provided higher ee than other bisoxazoline ligands **4b–e** (entries 8–11). Subsequently, a substantial increase in both yield and enantioselectivity was observed by replacing bisoxazoline ligand **4a** with **4f**, in which the phenyl substituents are replaced by 2-naphthyl groups (entry 12). To improve further the enantioselectivity, a mixed solvent of CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> (1:1) was employed. Under the optimized conditions, the reaction could afford the allene product with 90% ee and 93% yield (entry 13).

With the optimized reaction conditions, the reaction scope was then evaluated. A series of aryldiazoalkanes **1a–j** (R' = Me) bearing electron-neutral, -deficient or -rich aromatic substituents were smoothly reacted with phenylacetylene **2a** to give the corresponding trisubstituted allenes **3aa–ja** in 84–95% ee and 75–96% yield (Table 2). The absolute configuration (*R*) of **3ia** was established by the comparison of its optical rotation with the same compound of known configuration reported in the literature.<sup>16</sup> The absolute configuration (*R*) was further confirmed by X-ray crystallographic analysis of a single crystal of **3ja**. The assignment was extended to other allene products based on the assumption that all the reactions followed the same reaction pathway. It is worth mentioning that when the R'

Table 2. Substrate Scope for Aryldiazoalkanes



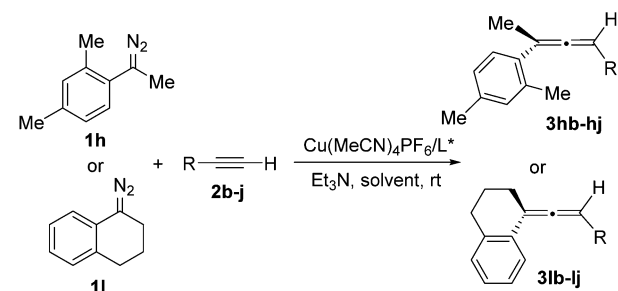
<sup>a</sup>Reaction conditions: a solution of **1a–j** (0.2 mmol), **2a** (0.1 mmol), Et<sub>3</sub>N (0.1 mmol), Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (10 mol %), and **4f** (11 mol %) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) and CHCl<sub>3</sub> (0.5 mL) was stirred at 25 °C under N<sub>2</sub> atmosphere for 70 min. <sup>b</sup>20 mol % Cu(MeCN)<sub>4</sub>PF<sub>6</sub> and 22 mol % of **4a** were used. <sup>c</sup>Reaction conditions: a solution of **1l–n** (0.2 mmol), **2a** (0.1 mmol), Et<sub>3</sub>N (0.1 mmol), Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (20 mol %), and **4a** (22 mol %) in CHCl<sub>3</sub> (1.0 mL) was stirred at 25 °C under N<sub>2</sub> atmosphere for 70 min. The yields refer to isolated products, and the ee values were determined by chiral HPLC analysis.

group was changed to CF<sub>3</sub>, ligand **4a** was proved to be the most efficient one, albeit affording the desired product **3ka** in only 50% yield and 72% ee. To expand further the scope of the reaction, tetralone-derived diazo compounds **1l–n** were then examined. For these diazo substrates, the best results were obtained with 20 mol % of **4a** as the ligand, affording the corresponding allene products **3la–na** in 92–96% ee and 85–95% yield.

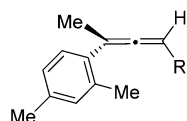
Next, the scope of the reaction was extended by conducting the reaction with various terminal alkynes. To facilitate the determination of ee values by HPLC, **1h** was selected as the representative aryldiazoalkanes (Table 3). When the standard condition was employed for the reactions between **1h** and **2b–j**, moderate ee values were observed. We speculated that the background reactions were more severe when these alkynes were used. Further optimization of the reaction parameters showed that by changing the ratio of **1h** and alkynes from 2 to 0.5, the reactions provided excellent ee values, albeit with lower yields. A series of terminal alkynes could react smoothly with **1h**, affording the corresponding trisubstituted allenes **3hb–hi** in moderate yields and excellent enantioselectivities, regardless of the electronic nature of the substituents on the aromatic ring of the alkyne substrates **2b–i**.

It is also noteworthy that the reaction with benzyl-substituted alkyne **2j** also gave the coupling product **3hj** in 46% yield and

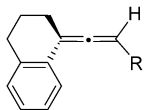
Table 3. Substrate Scope for Terminal Alkynes



**3hb**, R = *p*-FC<sub>6</sub>H<sub>4</sub> (55% yield, 93% ee)<sup>a</sup>  
**3hc**, R = *m*-FC<sub>6</sub>H<sub>4</sub> (50% yield, 90% ee)<sup>a</sup>  
**3hd**, R = *m*-ClC<sub>6</sub>H<sub>4</sub> (53% yield, 95% ee)<sup>a</sup>  
**3he**, R = *m*-BrC<sub>6</sub>H<sub>4</sub> (54% yield, 90% ee)<sup>a</sup>  
**3hf**, R = *m*-OMeC<sub>6</sub>H<sub>4</sub> (52% yield, 85% ee)<sup>a</sup>  
**3hg**, R = *m*-MeC<sub>6</sub>H<sub>4</sub> (60% yield, 95% ee)<sup>a</sup>  
**3hh**, R = *o*-ClC<sub>6</sub>H<sub>4</sub> (50% yield, 94% ee)<sup>a</sup>  
**3hi**, R = *o*-MeC<sub>6</sub>H<sub>4</sub> (43% yield, 93% ee)<sup>a</sup>  
**3hj**, R = CH<sub>2</sub>Ph (46% yield, 92% ee)<sup>a</sup>



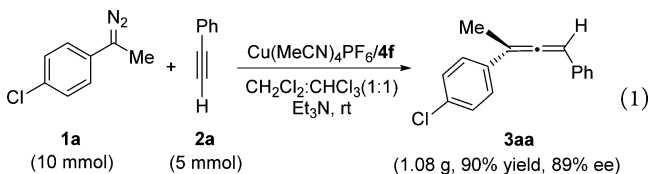
**3lb**, R = *p*-FC<sub>6</sub>H<sub>4</sub> (92% yield, 98% ee)<sup>b</sup>  
**3lc**, R = *m*-FC<sub>6</sub>H<sub>4</sub> (95% yield, 98% ee)<sup>b</sup>  
**3le**, R = *m*-BrC<sub>6</sub>H<sub>4</sub> (86% yield, 97% ee)<sup>b</sup>  
**3lg**, R = *m*-MeC<sub>6</sub>H<sub>4</sub> (81% yield, 96% ee)<sup>b</sup>  
**3lh**, R = *o*-ClC<sub>6</sub>H<sub>4</sub> (90% yield, 97% ee)<sup>b</sup>  
**3li**, R = *o*-MeC<sub>6</sub>H<sub>4</sub> (85% yield, 94% ee)<sup>b</sup>  
**3lj**, R = CH<sub>2</sub>Ph (93% yield, 96% ee)<sup>b</sup>



<sup>a</sup>Reaction conditions: a solution of **1h** (0.1 mmol), **2b–j** (0.2 mmol), Et<sub>3</sub>N (0.2 mmol), Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (10 mol %), and **4f** (11 mol %) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) and CHCl<sub>3</sub> (0.5 mL) was stirred at 25 °C under N<sub>2</sub> atmosphere for 70 min. <sup>b</sup>Reaction conditions: a solution of **1i** (0.2 mmol), **2b–j** (0.1 mmol), Et<sub>3</sub>N (0.1 mmol), Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (20 mol %), and **4a** (22 mol %) in CHCl<sub>3</sub> (1.0 mL) was stirred at 25 °C under N<sub>2</sub> atmosphere for 70 min. All the yields refer to isolated products. The ee values were determined by chiral HPLC analysis.

92% ee. Furthermore, tetralone-derived diazoalkane **1i** was also chosen as the model diazo substrate to study the scope of terminal alkynes. The reaction with alkyne substrates bearing various substituents on the aromatic ring all proceeded smoothly to afford the corresponding allene products **3lb–li** in excellent yields and enantioselectivities. Finally, the reaction could also be extended to benzyl substituent, the corresponding trisubstituted allenes **3lj** could be obtained in 96% ee and 93% yield.

To show the synthetic potential of this strategy, we have carried out a gram scale synthesis of **3aa** (eq 1). Under the optimized reaction conditions, the reaction with 5 mmol of **2a** proceeded smoothly with 2 equiv of **1a**, affording 1.08 g of **3aa** (90% yield) with 89% ee.



A stereocontrol model was tentatively proposed to explain the enantioselection in the present reaction (Figure 1). Based on previous studies,<sup>13,14</sup> the Cu(I)-catalyzed coupling reaction follows a pathway involving Cu(I) carbene formation, alkynyl migratory insertion and protonation (Scheme 1a). In this

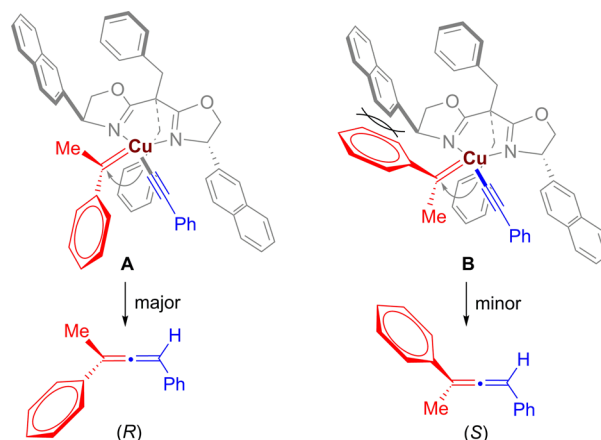


Figure 1. Rationale for enantioselection.

mechanism, the alkynyl migratory insertion generates the C(sp)–C(sp<sup>3</sup>) bond and this step is enantio-determining. Therefore, for this step two competing structures **A** and **B** are proposed to lead to the allene products with (*R*) and (*S*) configurations, respectively. Because of the steric repulsion existed in **B** between the phenyl group of the carbene and the naphthyl group of the chiral skeleton of the bisoxazoline, **A** is energetically more favored than **B**, leading to the formation of (*R*)-configured allene as the major product.

In summary, we have developed a highly enantioselective Cu(I)-catalyzed coupling reaction between aryldiazoalkanes and terminal alkynes with chiral bisoxazoline as the ligand. A series of trisubstituted allenes were obtained with moderate to high yields (up to 96%) and excellent enantioselectivities (up to 98% ee). Further investigations on the related Cu(I)-catalyzed enantioselective carbene coupling reaction is current under way in our laboratory.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b09674.

Experimental procedure, characterization data, copies of <sup>1</sup>H and <sup>13</sup>C NMR spectra (PDF)

Data for **3ja** (CIF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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