

Enantioselective Coupling of Diazalkanes with Terminal Alkynes

Significance: An enantioselective coupling reaction of aryldiazoalkanes with terminal alkynes is described. A copper complex promotes this transformation to afford trisubstituted allenes with high enantioselectivities. A rational stereocontrol model is proposed.

Comment: This reaction involves copper(I) carbene formation, alkynyl migratory insertion, and protonation. The authors suggest that migratory insertion of the copper(I) carbene species is the enantiodetermining step.

Possible stereocontrol model:

**Selected examples:**

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
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<tbody>
<tr>
<td>R(^2) (\text{N}_2) R(^1) or N(^2) R(^1)</td>
<td>H = 1 equiv</td>
<td>H = 1 equiv</td>
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<tr>
<td>93% yield 90% ee (conditions A)</td>
<td>85% yield 96% ee (conditions B)</td>
<td>50% yield 94% ee (conditions C)</td>
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**Conditions A:**

1 (2 equiv), 2 (1 equiv)  
Cu (10 mol%), ligand (11 mol%), Et\(_3\)N (1 equiv) in CH\(_2\)Cl\(_2\)–CHCl\(_3\) (1:1)

**Conditions B:**

1 (2 equiv), 2 (1 equiv)  
Cu (20 mol%), ligand (22 mol%), Et\(_3\)N (1 equiv) in CHCl\(_3\)

**Conditions C:**

1 (1 equiv), 2 (2 equiv)  
Cu (10 mol%), ligand (11 mol%)  
Et\(_3\)N (2 equiv) in CH\(_2\)Cl\(_2\)–CHCl\(_3\) (1:1)