Enantioselective Coupling of Diazooalkanes 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.

**Selected examples:**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
<th>Yield (%)</th>
<th>Enantiomeric Excess (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>93%</td>
<td>90% ee</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>85%</td>
<td>96% ee</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>50%</td>
<td>94% ee</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>92%</td>
<td>98% ee</td>
</tr>
</tbody>
</table>

**Conditions:**

- **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)