**Category**
Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

**Key words**
allylic alkylation
copper
regioselectivity

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**Copper-Catalyzed Stereospecific Allylic Alkylation of Ketene Silyl Acetals**

**Significance:** Allylic alkylation of enolates is an important transformation in organic synthesis. The copper-catalyzed method described employs unsymmetrical internal allylic phosphates as electrophiles, which react with excellent γ-regioselectivity and excellent Z-diastereoselectivity.

**Comment:** The γ-selective allylic alkylation of chiral allylic phosphates proceeds with efficient 1,3-anti α-to-γ chirality transfer. The stereochemical outcome of the product is dependent on the E/Z geometry of the allylic phosphate. The authors propose the reaction pathway shown above, invoking an allyl copper(III) intermediate.

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**Selected examples:**

- **82% yield**
  - γ/α = 95:5
  - E/Z > 99:1
  - 96% ee

- **85% yield**
  - γ/α = 98:2
  - E/Z > 99:1
  - 96% ee

- **88% yield**
  - γ/α = 98:2
  - E/Z > 99:1
  - 97% ee

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**Proposed reaction pathway:**