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.