

Copper-Catalyzed Stereospecific Allylic Alkylation of Ketene Silyl Acetals

Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

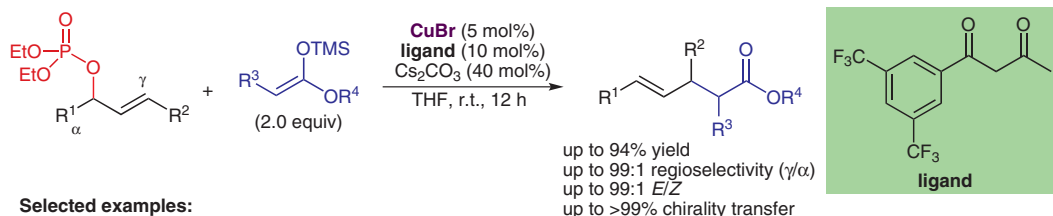
Key words

allylic alkylation

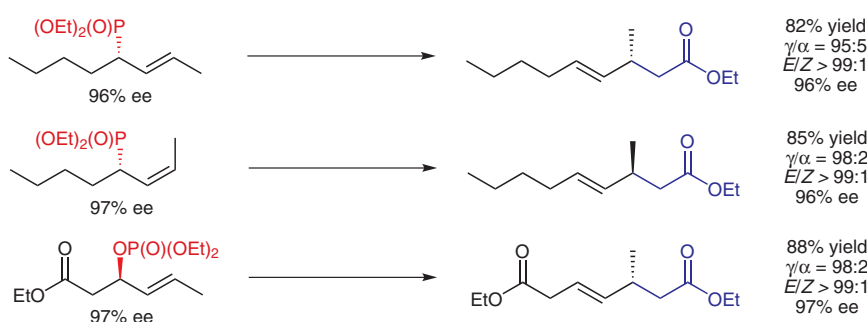
copper

regioselectivity

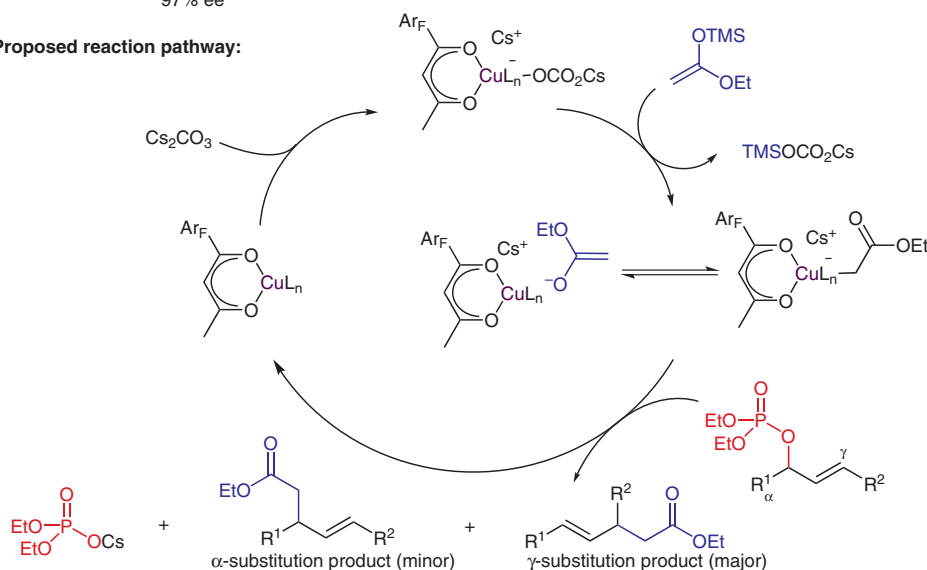
SYNFACT
of the month



Selected examples:



Proposed reaction pathway:



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.