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High Site- and Enantioselective Cu-Catalyzed Allylic Alkylation Reactions with Easily Accessible Vinylaluminum Reagents

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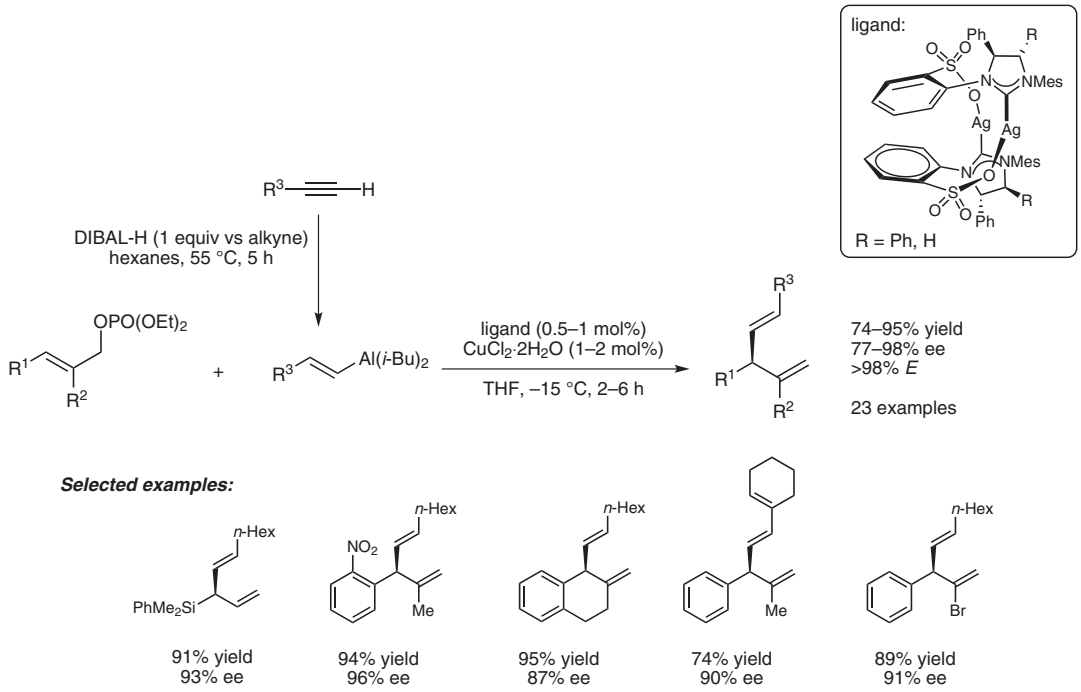
Catalytic Asymmetric Allylic Alkylation with Vinylaluminum Reagents



Significance: A new efficient method for catalytic asymmetric allylic alkylation of allylic phosphates with vinylaluminum reagents is reported. The desired products are obtained in good yields and with enantioselectivities up to 98% ee.

Comment: The vinylaluminum reagents are prepared and used in situ by reaction of commercially available DIBAL-H with terminal alkynes. The asymmetric allylic alkylations are promoted in the presence of a readily available chiral N-heterocyclic carbene complex and a commercially available and air-stable copper salt. The desired products are obtained in relative short time (2–12 h) in 74–95% isolated yields, 77% to >98% ee, and with >98% *E*-selectivities. Various allylic phosphates can be used, including trisubstituted and disubstituted olefines. Vinyl bromides and cyclic alkenes are also suitable substrates for the allylic alkylation. A variety of terminal alkynes can be employed, including conjugated enynes. The hydroalumination/catalytic AAA sequence can be performed in a single vessel, on gram scale.

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Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

allylic alkylation

vinylaluminum

DIBAL-H

SYNFACT of the month

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