Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

allenes

organocuprates

cyclopropane-diesters

1,7-addition

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Synthesis of Enantioenriched Allenes from 1,1-Cyclopropanediesters

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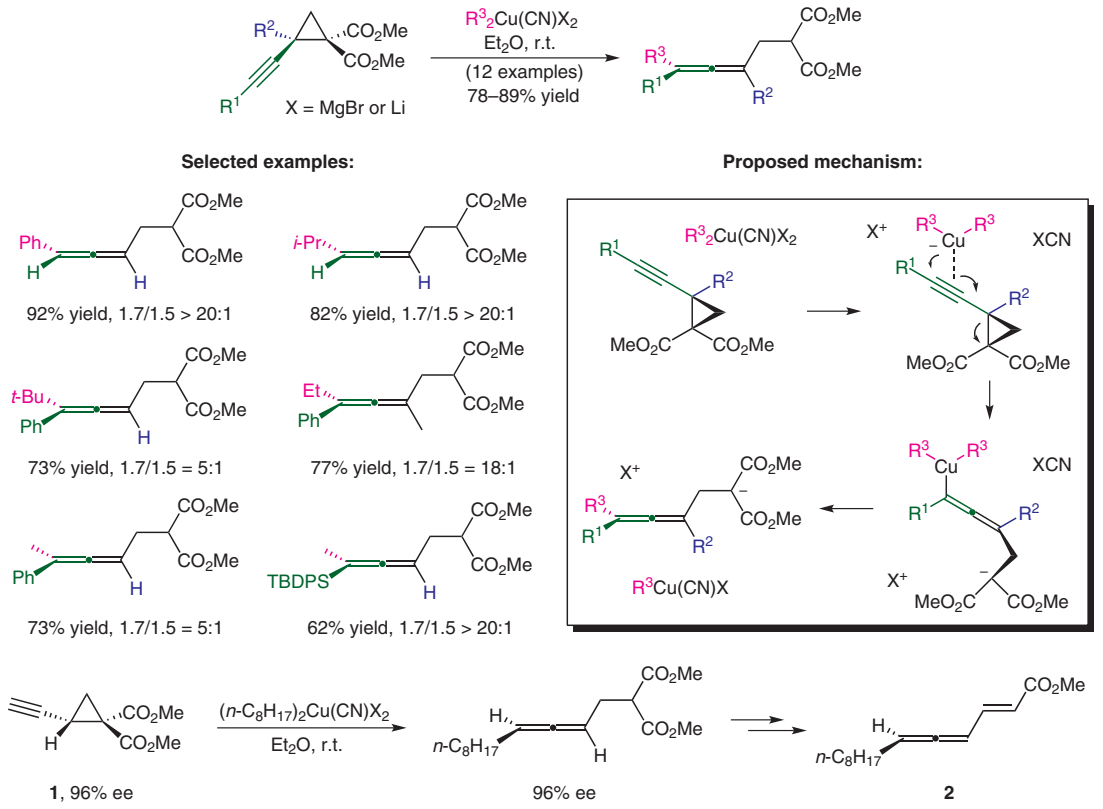

Significance: In this paper the authors report a protocol allowing the formation of chiral allenes via S_N2' addition of organocuprates to enantioenriched propargylcyclopropanes. Development of such a method is important in light of high synthetic utility of chiral allenes, which lacked an expedient synthetic approach thus far despite a number of reports. Under optimized conditions, a range of 1,7-addition products was obtained with 78–89% yields. Complete preservation of enantiomeric purity was observed for an enantioenriched substrate **1**, leading to a synthetic precursor of a pheromone **2** of *Acanthoscelides obtectus*.

Comment: A ratio of 2:1 of a Grignard reagent to CuCN demonstrated optimum results; a 1:1 mixture led to inferior yields. Lithiated species were shown to be as suitable for the protocol as organomanganese compounds. Primary, secondary, and tertiary alkyl cuprates were tolerated. Alkyl- and aryl-substituted alkynes also furnished corresponding products (73–89% yield). Tetrasubstituted allenes were also accessible through the developed methodology with good yields. The observed enantiospecificity of the reaction is impressive.

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