Copper(I)-Mediated Asymmetric Boryl Substitution of Allyl Acetals

Significance: The authors describe a novel Cu-mediated enantioselective and γ-selective boryl substitution of allyl acetals for the synthesis of enantioenriched α-chiral linear or carbocyclic (E)-(γ-Alkoxyallyl)boronates under mild conditions. The derived chiral boronates were used in aldehyde allylation reactions rendering the respective 1,2-diol products in good yields and excellent enantioselectivity.

Comment: Z-Substituted allyl acetates gave superior results over the analogous E-substrates. This versatile strategy was highlighted by an impressive example within the modular synthesis of 3,3-disubstituted cyclopentene. In this system the strategy was used twice, formally replacing both alkoxy groups of the acetal by two subsequent boryl substitution/aldehyde allylation reactions. Exceptional enantiocontrol and high yields were obtained.

General reaction:

Selected examples (boryl substitution):

3,3-Disubstituted cyclopentenes via a double boryl substitution/allylation strategy:

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