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Copper-Catalysed Selective Hydroamination Reactions of Alkynes
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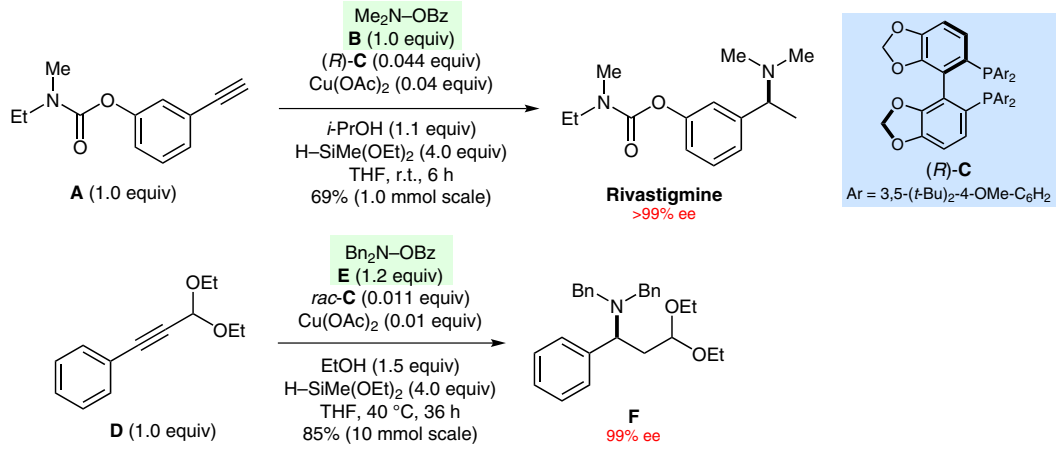
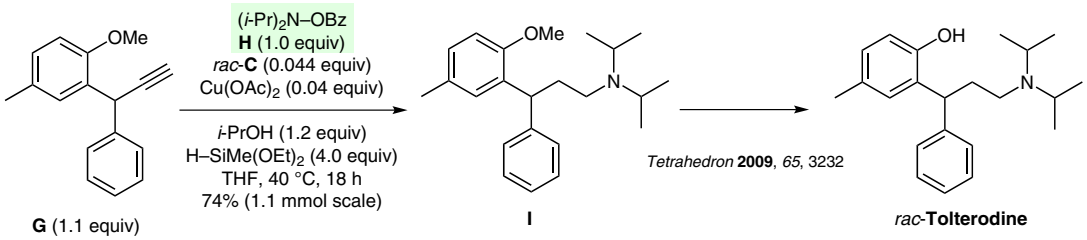
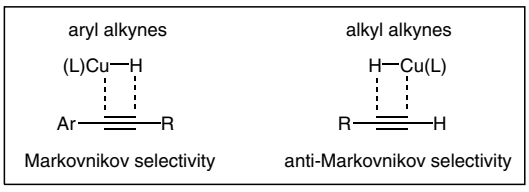
Asymmetric Copper-Catalyzed Hydroamination of Aryl Alkynes

Reductive hydroamination of aryl alkynes (14 examples): Markovnikov selectivity



Reductive hydroaminaton of alkyl alkynes (9 examples): anti-Markovnikov selectivity





Significance: A new asymmetric synthesis of alkyl amines from readily available alkynes and electrophilic amine sources proceeds under mild conditions with high levels of regio- and stereocontrol. The regiochemistry of the initial hydrocupration reaction depends on the structure of the alkynes. Aryl alkynes display Markovnikov addition, whereas alkyl alkynes give anti-Markovnikov addition.

Comment: When the hydroamination reaction is performed in the absence of a proton source such as *i*-PrOH or EtOH, enamine intermediates (not shown) are isolated in good yield (5 examples). Catalytic cycles for the enamine formation (direct hydroamination) and the reductive hydroamination reactions are proposed. A synthesis of rivastigmine exemplifies the value of the method.

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Key words

asymmetric reductive hydroamination

copper catalysis

enamines

hydrocupration

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