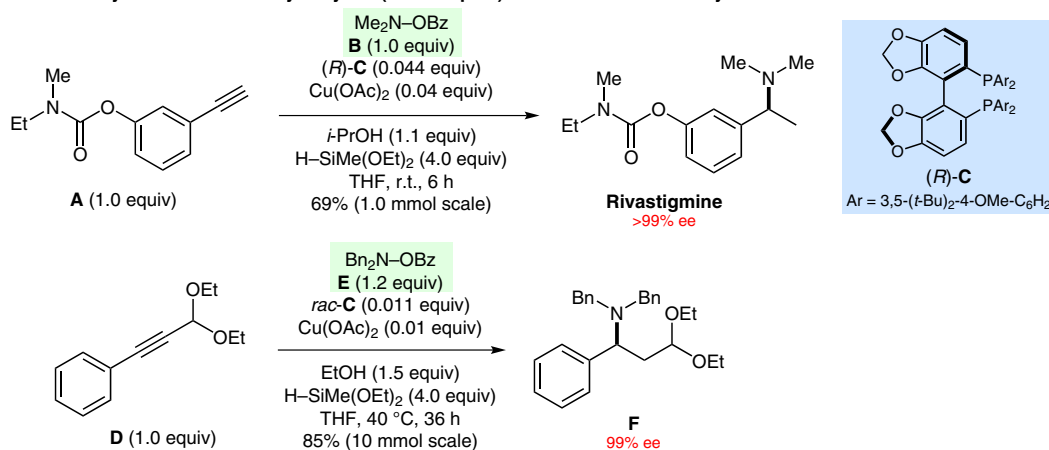
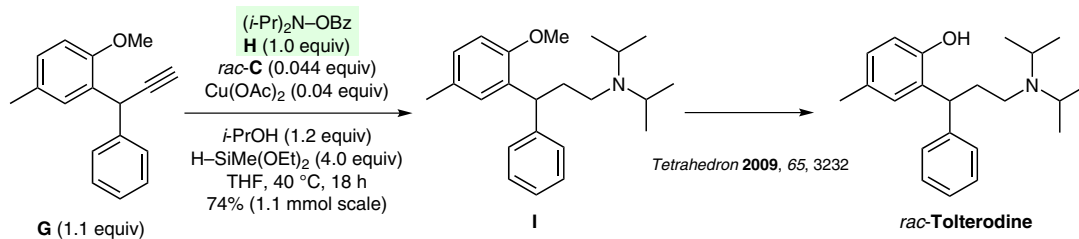


Asymmetric Copper-Catalyzed Hydroamination of Aryl Alkynes

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



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



Significance: A new asymmetric synthesis of aryl 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.