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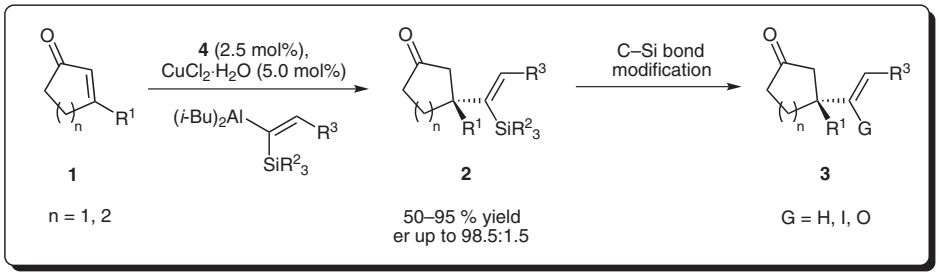
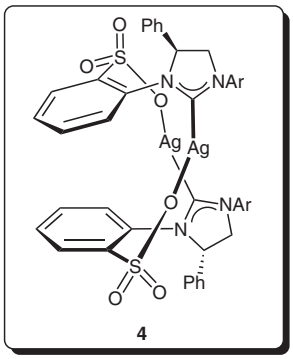
Formation of Vinyl-, Vinylhalide- or Acyl-Substituted Quaternary Carbon Stereogenic Centers through NHC–Cu-Catalyzed Enantioselective Conjugate Additions of Si-Containing Vinylaluminums to β-Substituted Cyclic Enones
J. Am. Chem. Soc. **2011**, *133*, 736-739.

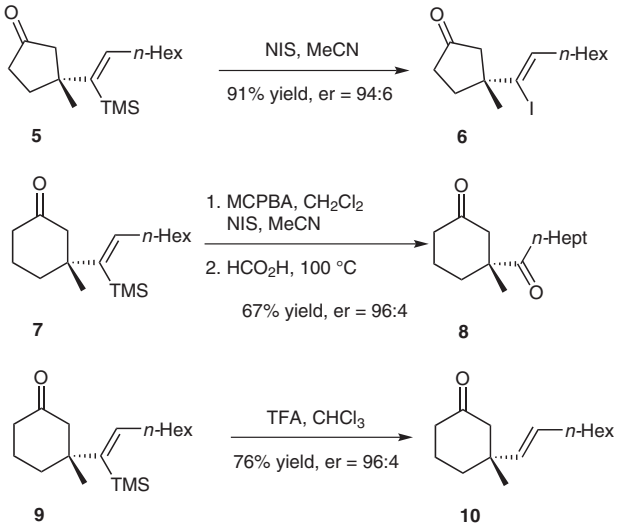
Enantioselective Conjugated Addition of Vinylaluminums to Cyclic Enones





Ar = 2,6-$Et_3C_6H_3$

C–Si bond functionalization:



Significance: The development of transition-metal-catalyzed enantioselective reactions allowing the formation of quaternary stereogenic centers is a challenging task. Herein, the authors report a highly enantioselective conjugated addition of Si-substituted vinylaluminum reagents to five- and six-membered cyclic β-substituted enones of type **1**. A chiral bidentate NHC–copper complex has been identified to facilitate the desired transformation of **1** into **2** with good to excellent yields and enantioselectivities.

Comment: The active catalyst for the enantioselective addition is easily formed in situ starting from air-stable $CuCl_2·H_2O$ and complex **4**. The reaction (**1** → **2**) is typically finished within 15–20 minutes and the required Si-containing vinylaluminum reagents are readily available from silylacetylenes though a stereoselective hydroalumination using DIBAL-H. Furthermore, it has been shown that the enantiomerically enriched vinylsilane products can be easily protodesilylated (**7** → **8**), oxidized (**9** → **10**) or transformed into the corresponding vinyl iodides (**5** → **6**) with good to excellent yields.

SYNFACTS Contributors: Mark Lautens, Norman Nicolaus
Synfacts 2011, 4, 0395-0395 Published online: 18.03.2011
DOI: 10.1055/s-0030-1259649; **Reg-No.:** L02111SF