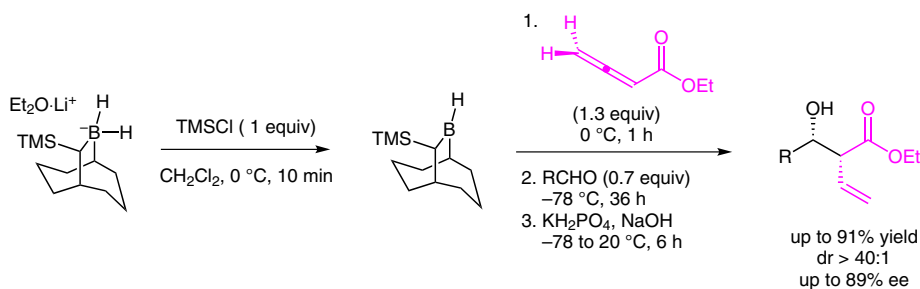


J. KISTER, D. H. ESS, W. R. ROUSH* (SCRIPPS FLORIDA, JUPITER AND BRIGHAM YOUNG UNIVERSITY, PROVO, USA)

Enantio- and Diastereoselective Synthesis of *syn*- β -Hydroxy- α -vinyl Carboxylic Esters via Reductive Aldol Reactions of Ethyl Allenecarboxylate with 10-TMS-9-Borabicyclo[3.3.2]decane and DFT Analysis of the Hydroboration Pathway

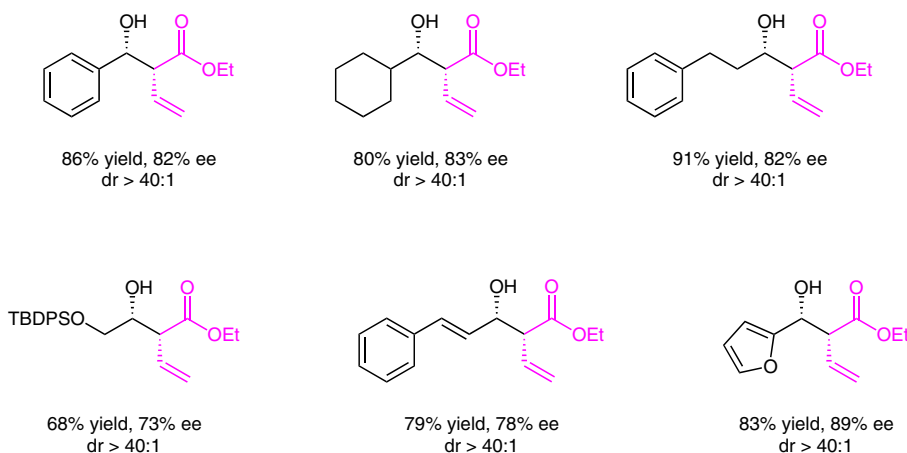
Org. Lett. **2013**, *15*, 5436–5439.

Stereoselective Synthesis of *syn*- β -Hydroxy- α -vinyl Carboxylate Esters



R = Ph, Cy, $(\text{CH}_2)_2\text{Ph}$, CH_2OTBDPS , CHCHPh , 3-pyridyl, 2-furyl

Selected examples:



Significance: The authors report a novel enantio- and diastereoselective synthesis of *syn*- β -hydroxy- α -vinyl carboxylate esters. The reaction proceeds via a reductive aldol reaction of an ethyl allene carboxylate with 10-TMS-9-borabicyclo[3.3.2]decane.

Comment: The exclusive formation of *syn*- β -hydroxy- α -vinyl carboxylate esters can be explained by an aldol reaction via a chair-like transition state. DFT calculations suggest that the allene hydroboration involves a 1,4-reduction of the ethyl allene carboxylate with 10-TMS-9-borabicyclo[3.3.2]decane.

SYNFACTS Contributors: Paul Knochel, Andreas K. Steib
Synfacts 2014, 10(1), 0079 Published online: 13.12.2013

DOI: 10.1055/s-0033-1340369; Reg-No.: P15913SF