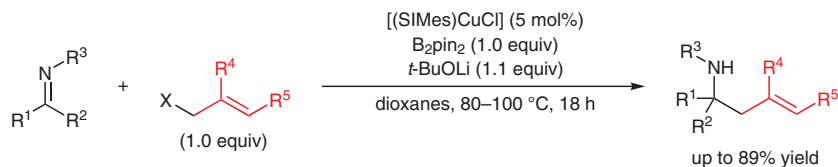


Z. LI, L. ZHANG*, M. NISHIURA, Z. HOU* (RIKEN CENTER FOR SUSTAINABLE RESOURCE SCIENCE AND RIKEN CLUSTER FOR PIONEERING RESEARCH, WAKO, JAPAN)

Copper-Catalyzed Umpolung of Imines through Carbon-to-Nitrogen Boryl Migration

ACS Catal. 2019, 9, 4388–4393.

Copper-Catalyzed Allylation of Imines via Umpolung



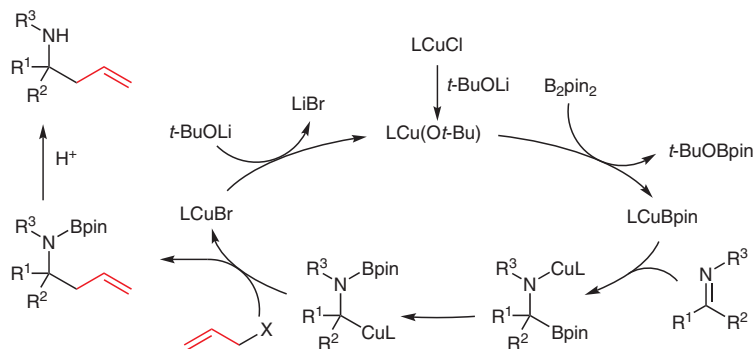
$R^1, R^2, R^3 = \text{H, Alk, (Het)Ar}$

$R^4 = \text{H, Me}$

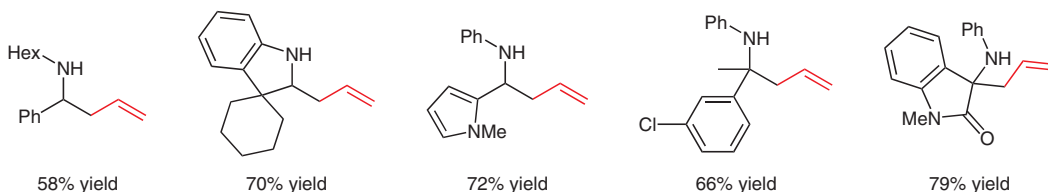
$R^5 = \text{H, Ph}$

$X = \text{Cl, Br, MeOCO}_2, (\text{EtO})_2\text{PO}_2$

Proposed mechanism:



Selected examples:



Significance: The authors developed a copper-catalyzed allylation of various functionalized aldehydes and ketimines using allyl halides, carbonates or phosphates. A combination of B_2pin_2 and $t\text{-BuOLi}$ was crucial to obtain the corresponding allylated amines in high yields.

Comment: The reaction proceeds through an unprecedented copper-boron rearrangement. The 1,2-boryl migration from nitrogen to carbon leads to an α -borylaminoalkylcopper species, which subsequently reacts with an allylic electrophile leading, after hydrolysis, to the functionalized amine.

SYNFACTS Contributors: Paul Knochel, Ferdinand H. Lutter
Synfacts 2019, 15(07), 0764 Published online: 17.06.2019
DOI: 10.1055/s-0039-1689939; Reg-No.: P06519SF

© 2019, Thieme. All rights reserved.
Georg Thieme Verlag KG, Rüdigerstraße 14, 70469 Stuttgart, Germany