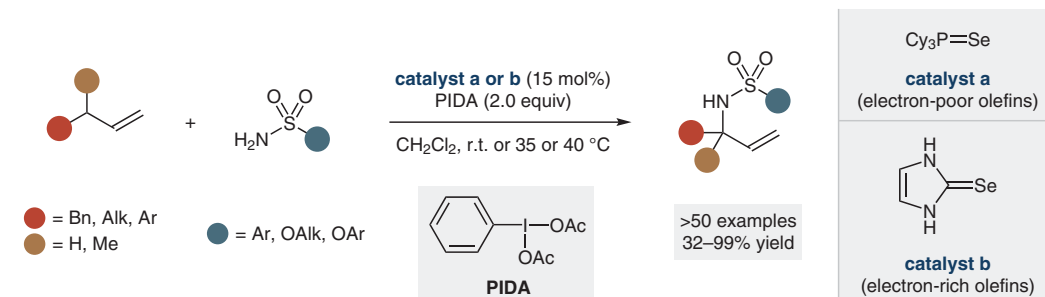


W. P. THE, D. C. OBENSCHAIN, B. M. BLACK, F. E. MICHAEL* (UNIVERSITY OF WASHINGTON, SEATTLE, USA)

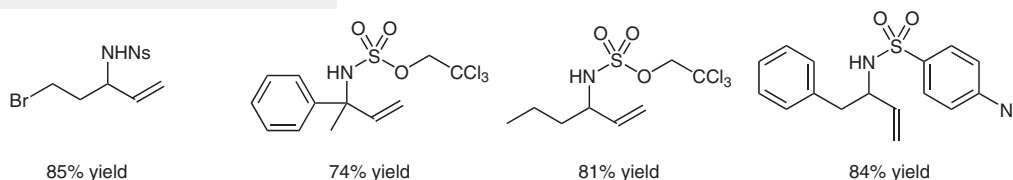
Catalytic Metal-Free Allylic C–H Amination of Terpenoids

J. Am. Chem. Soc. **2020**, *142*, 16716–16722, DOI: 10.1021/jacs.0c06997.

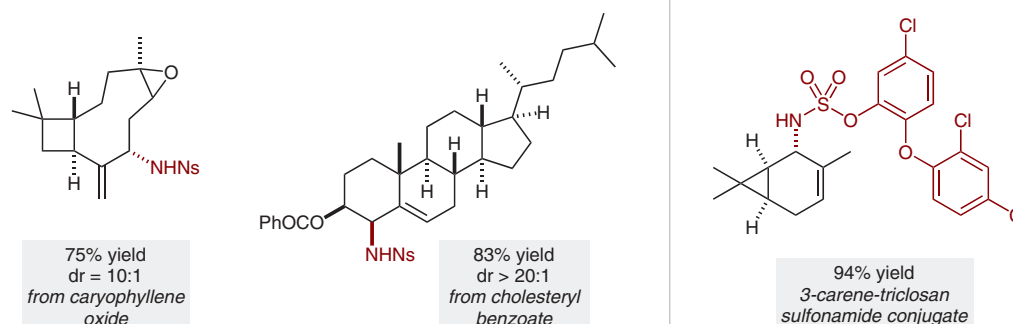
A Selenium-Catalyzed Oxidative Allylic Sulfonamidation



Sulfonamidation of feedstock olefins:



Late-stage functionalization and oxidative amination using drug-derived sulfonamides:



Significance: Michael and co-workers report a general catalytic metal-free allylic C–H sulfonamidation of olefins. By analogy to selenium dioxide-mediated transformations, this reaction is proposed to proceed via an imido selenium intermediate that undergoes a classical ene/[2,3]-sigmatropic shift to provide a broad variety of allylic amines in moderate to excellent yields and mostly with high regioselectivity.

Comment: Although the aza-variant of the allylic oxidation of olefins could be expected to be in no way inferior to the selenium dioxide-mediated transformation, the major limitation in the past has been the involvement of highly explosive anhydrous chloramine T. By introducing phosphine selenides (**catalyst a**) or selenoureas (**catalyst b**) as precursors for the relevant catalytic imido selenium intermediate in combination with (diacetoxyiodo)benzene (PIDA) as a readily available oxidant, this work could lead to a renaissance in direct oxidative allylic amination reactions.

SYNFACTS Contributors: Benjamin List, Benjamin Mitschke
Synfacts 2020, 16(12), 1463 Published online: 17.11.2020
DOI: 10.1055/s-0040-1719577; Reg-No.: B10220SF

© 2020, Thieme. All rights reserved.
Georg Thieme Verlag KG, Rüdigerstraße 14, 70469 Stuttgart, Germany

Category

Organo- and Biocatalysis

Key words

allylic amination

sulfonimidation

late-stage functionalization

selenium catalysis

terpenoids

Synfact
of the
Month

This document was downloaded for personal use only. Unauthorized distribution is strictly prohibited.