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Catalytic Metal-Free Allylic C–H Amination of Terpenoids

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A Selenium-Catalyzed Oxidative Allylic Sulfonamidation

Category

Organo- and Biocatalysis

Key words

allylic amination

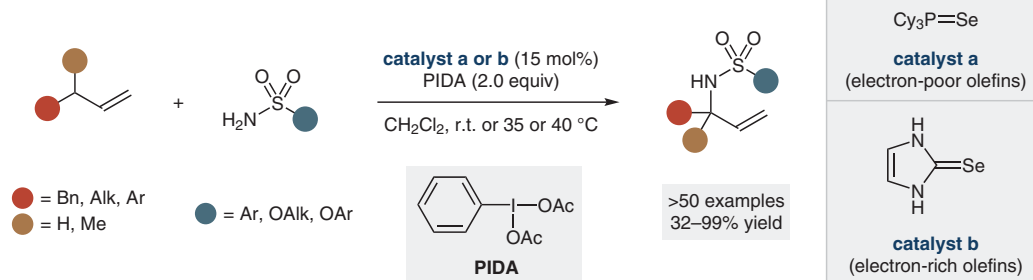
sulfonimidation

late-stage functionalization

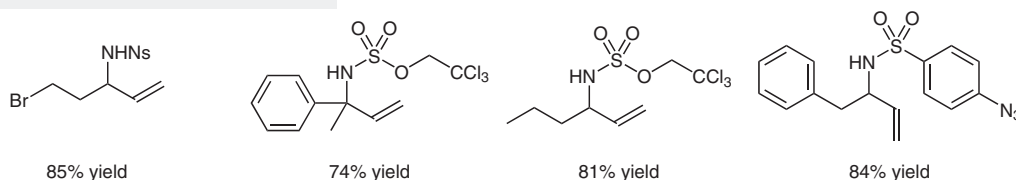
selenium catalysis

terpenoids

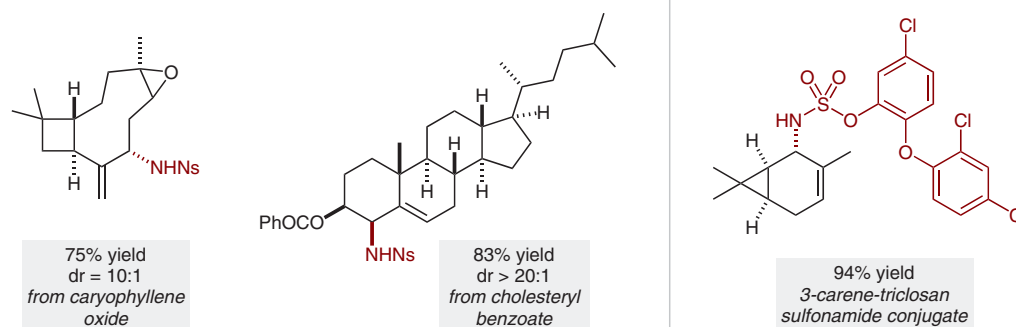
Synfact
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Month



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.

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