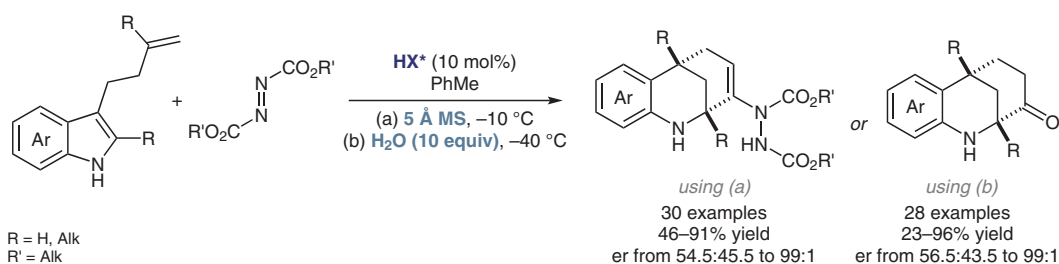


X.-Y. HUANG, P.-P. XIE, L.-M. ZOU, C. ZHENG*, S.-L. YOU* (SHANGHAI INSTITUTE OF ORGANIC CHEMISTRY AND EAST CHINA UNIVERSITY OF SCIENCE AND TECHNOLOGY, SHANGHAI, P. R. OF CHINA)

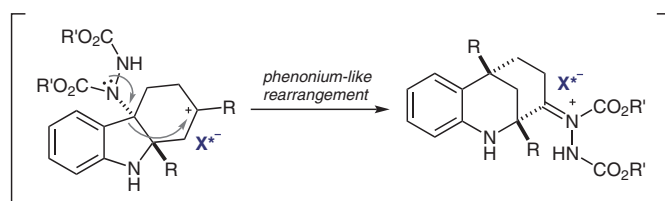
Asymmetric Dearomatization of Indoles with Azodicarboxylates via Cascade Electrophilic Amination/Aza-Prins Cyclization/Phenonium-like Rearrangement

J. Am. Chem. Soc. **2023**, *145*, 11745–11753, DOI: 10.1021/jacs.3c02773.

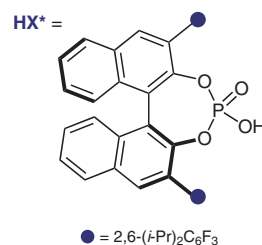
Chiral-Phosphoric-Acid-Catalyzed Asymmetric Dearomatization of Indole Derivatives



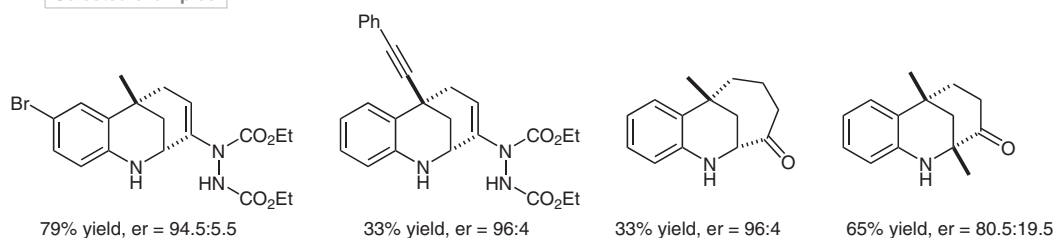
Cascade aza-Prins cyclization and rearrangement



Catalyst structure



Selected examples



Significance: Zheng, You and co-workers report the chiral-phosphoric-acid-catalyzed synthesis of enantioenriched aza-[3.3.1]-bicyclic enamines and ketones via asymmetric dearomatization of indoles with azodicarboxylates. The presence or absence of water as the additive in the reaction determines whether the enamine or ketone products are obtained. In both cases, the products were obtained in moderate to excellent yields and good to excellent enantioselectivities.

Comment: According to the control experiments and DFT calculations, reaction proceeds via an electrophilic amination (which was recognized as the enantiodetermining step) followed by an aza-Prins cyclization and a phenonium-like rearrangement. The enamine products remained intact when exposed to the catalyst and water, which suggests that ketone products are not generated via hydrolysis of the corresponding enamine products, but via an alternative pathway.

SYNFACTS Contributors: Benjamin List, Marian Guillén
Synfacts 2023, 19(08), 0813 Published online: 14.07.2023
DOI: 10.1055/s-0042-1751970; Reg-No.: B06923SF

© 2023, Thieme. All rights reserved.
Georg Thieme Verlag KG, Rüdigerstraße 14, 70469 Stuttgart, Germany

Category

Organo- and Biocatalysis

Key words

asymmetric dearomatization

indoles

rearrangement

azodicarboxylates

Synfact
of the Month

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