

Complimentary and personal copy

www.thieme.com

SYNFACTS Highlights in Chemical Synthesis

This electronic reprint is provided for non-commercial and personal use only: this reprint may be forwarded to individual colleagues or may be used on the author's homepage. This reprint is not provided for distribution in repositories, including social and scientific networks and platforms.

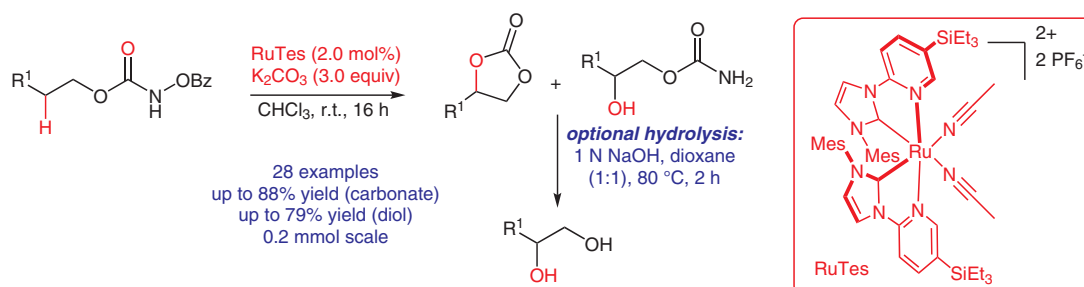
Publishing House and Copyright:
© 2021 by
Georg Thieme Verlag KG
Rüdigerstraße 14
70469 Stuttgart
ISSN 1861-1958

Any further use
only by permission
of the Publishing House

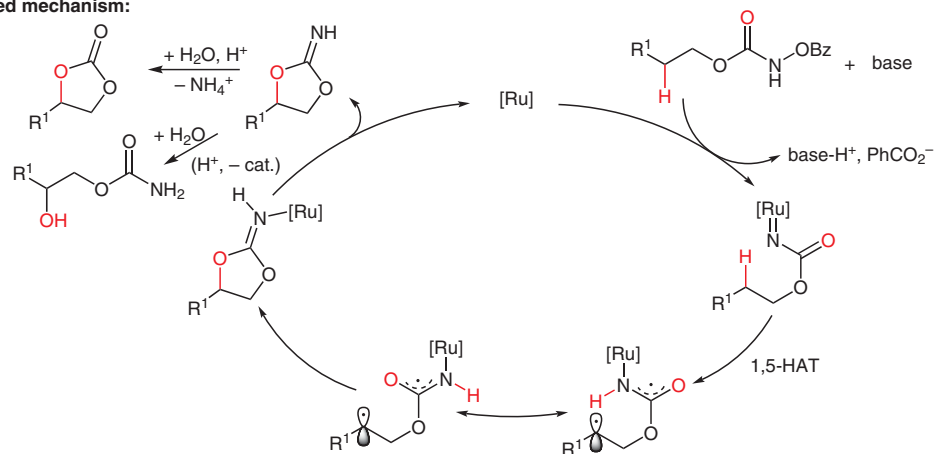
 **Thieme**

Y. TAN, S. CHEN, Z. ZHOU, Y. HONG, S. IVLEV, K. N. HOUK*, E. MEGGERS* (UNIVERSITY OF CALIFORNIA, LOS ANGELES, USA AND PHILIPPS-UNIVERSITÄT MARBURG, GERMANY)
Intramolecular C(sp³)-H Bond Oxygenation by Transition-Metal Acylnitrenoids
Angew. Chem. Int. Ed. 2020, DOI: 10.1002/anie.202009335.

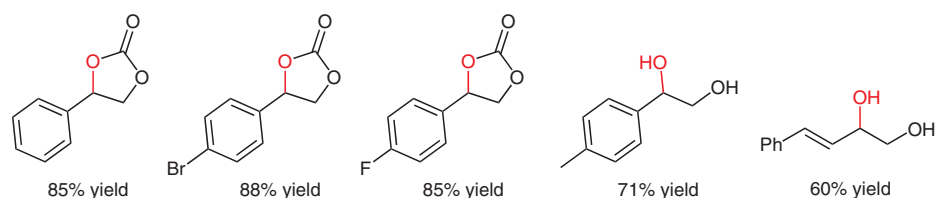
Ruthenium-Catalyzed C(sp³)-H Bond Oxygenation of *N*-Benzoyloxycarbamates



Proposed mechanism:



Selected examples:



Significance: Houk, Meggers, and co-workers report the use of transition-metal acylnitrenoids to direct C(sp³)-H oxygenations. This ruthenium-catalyzed intramolecular C–H oxygenation affords access to carbonates, hydroxylated carbamates or 1,2-diols in good to excellent yields. In addition to being chemoselective, the reaction can be made enantioselective by using enantiomerically pure catalyst.

Comment: The ruthenium catalyst features a stereogenic metal center with a right/left-handed helical twist of the bidentate ligand. Chemoselectivity can be switched to favor C–H oxygenation or C–H amination starting from the same nitrene precursor, by changing a single functional group on the catalyst.