

Complimentary and personal copy

[www.thieme.com](http://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.

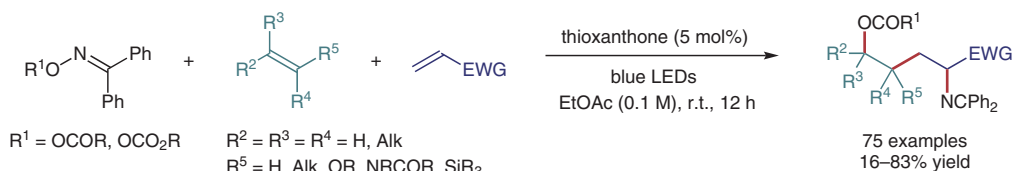
Publishing House and Copyright:  
© 2023 by  
Georg Thieme Verlag KG  
Rüdigerstraße 14  
70469 Stuttgart  
ISSN 1861-1958

Any further use  
only by permission  
of the Publishing House

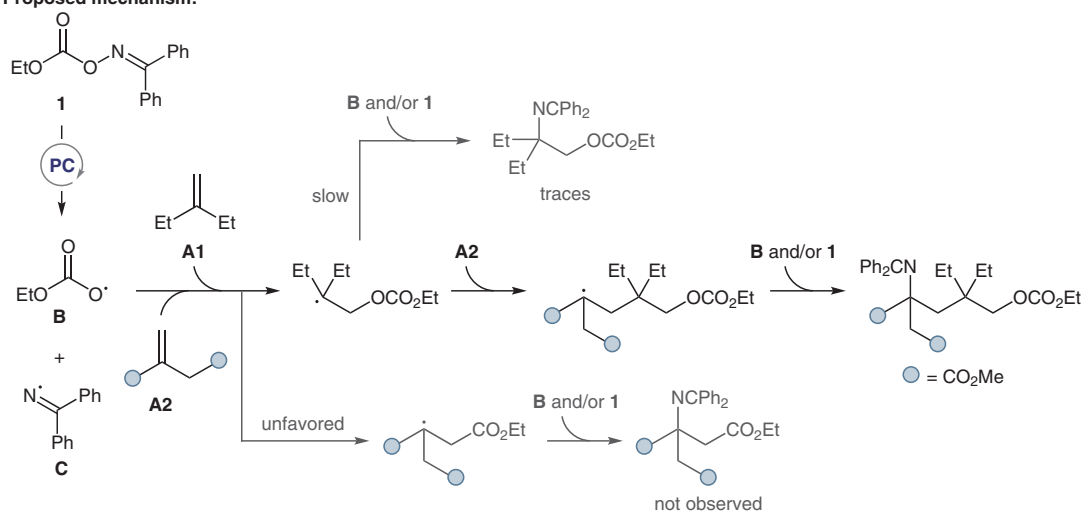
 **Thieme**

G. TAN, F. PAULUS, Á. RENTERÍA-GÓMEZ, R. F. LALISSE, C. G. DANILIUC, O. GUTIERREZ\*, F. GLORIUS\* (TEXAS A&M UNIVERSITY, COLLEGE STATION, USA AND WESTFÄLISCHE WILHELMS-UNIVERSITÄT MÜNSTER, GERMANY)  
Highly Selective Radical Relay 1,4-Oxyimination of Two Electronically Differentiated Olefins  
*J. Am. Chem. Soc.* **2022**, *144*, 21664–21673, DOI: 10.1021/jacs.2c09244.

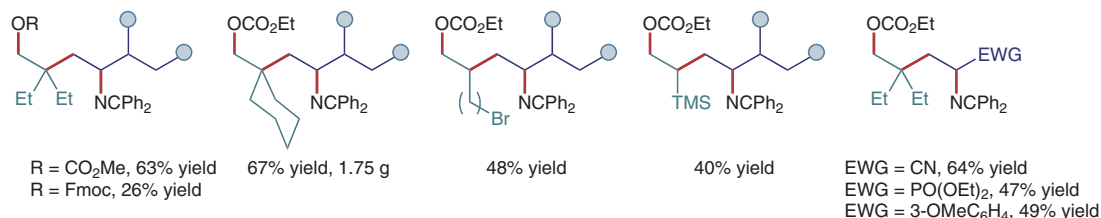
## Radical-Based 1,4-Difunctionalization of Two Electronically Differentiated Olefins



### Proposed mechanism:



### Selected examples:



**Significance:** Gutierrez, Glorius, and co-workers disclose an unprecedented 1,4-oxyimination of two electronically differentiated olefins with a class of bifunctional oxime carbonate reagents via an energy transfer strategy. The process enables the formation of three different chemical bonds (C–C, C–O, and C–N) in an orchestrated single operation. A wide scope of 1,4-oxyimination products was obtained in fair to good yields and with excellent functional group tolerance. Furthermore, the products were easily converted into biologically relevant  $\delta$ -hydroxy- $\alpha$ -amino acids.

**Comment:** Mechanistic studies suggest an energy transfer step to promote the homolytic N–O bond cleavage of the oxime carbonate reagent to form O-centered alkoxy carbonyloxy and N-centered iminyl radicals, which are of ambiphilic and electrophilic properties, respectively. In turn, the alkoxy carbonyloxy radical undergoes a chemoselective double Giese-type addition to the olefin, followed by C–N bond formation with an oxime carbonate reagent that functions as a radical chain mediator.

SYNFACTS Contributors: Benjamin List, Marian Guillén  
Synfacts 2023, 19(03), 0292 Published online: 13.02.2023  
DOI: 10.1055/s-0042-1753373; Reg-No.: B02123SF