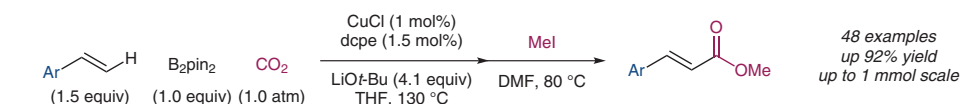


H. SAHOO, L. ZHANG, J. CHENG, M. NISHIURA, Z. HOU* (RIKEN CENTER FOR SUSTAINABLE RESOURCE SCIENCE, WAKO, JAPAN)

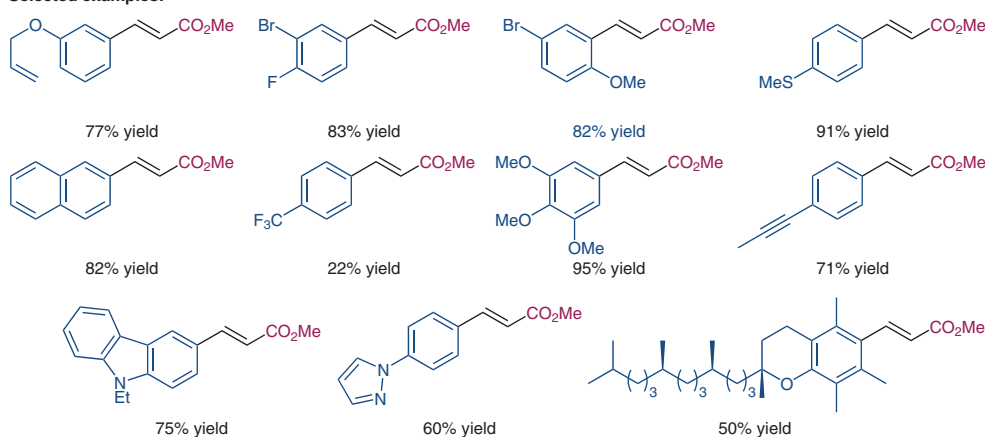
Auto-Tandem Copper-Catalyzed Carboxylation of Undirected Alkenyl C–H Bonds with CO₂ by Harnessing β-Hydride Elimination

J. Am. Chem. Soc. **2022**, *144*, 23585–23594, DOI: 10.1021/jacs.2c10754.

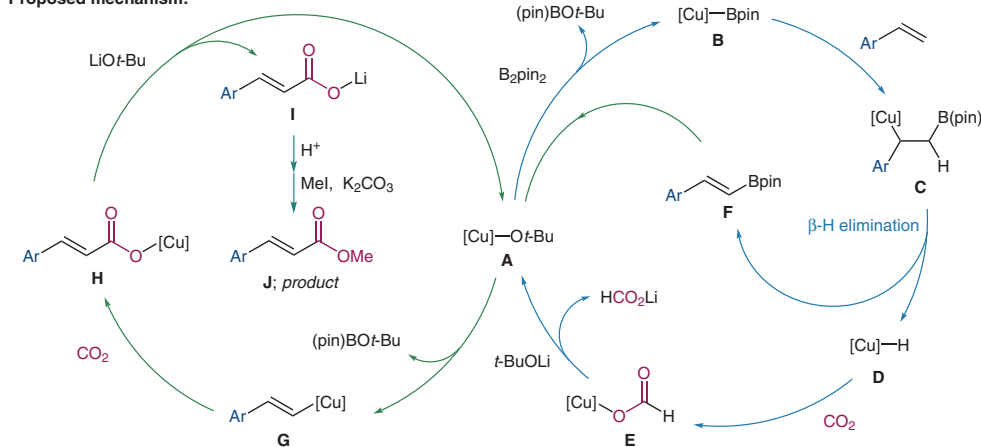
Copper-Catalyzed Selective C–H Carboxylation of Alkenes with CO₂



Selected examples:



Proposed mechanism:



Significance: Zhang and Hou report the highly selective C–H carboxylation of styrene derivatives to access α,β -unsaturated esters using copper catalysis. In-depth mechanistic studies reveal novel catalytic activity and a potential pathway involving two catalytic cycles linked by an in situ generated copper-alkoxide species (A). Notably, the authors propose CO₂ acts as a multitasking carboxylation reagent.

Comment: Compound A enables borylcupration of the alkene to generate intermediate C. The β -H elimination generates vinyl boronate F and a copper hydride species, which instantly reacts with CO₂ to form copper formate E. Formation of E enables regeneration of A and initiates the tandem catalytic cycle. Transmetalation of A and F forms the nucleophilic organocopper G. CO₂ insertion and metathesis with the alkoxide base regenerates A, while product J is obtained following protolysis and methylation.

SYNFACTS Contributors: Mark Lautens, Alexa Torelli
Synfacts 2023, 19(03), 0247 Published online: 13.02.2023
DOI: 10.1055/s-0042-1753383; Reg-No.: L03323SF

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

Category

Metals in Synthesis

Key words

copper catalysis

borylation

carbonylation

tandem reaction

Synfact
of the
Month