B. FAN,* S. LI, H. CHEN, Z. LU, S. LIU, Q. YANG, L. YU, J. XU, Y. ZHOU, J. WANG* (YUNNAN UNIVERSITY OF NATIONALITIES, KUNMING AND SOUTH UNIVERSITY OF SCIENCE AND TECHNOLOGY OF CHINA, SHENZHEN, P. R. OF CHINA)
Palladium/Copper Complexes Co-Catalyzed Highly Enantioselective Ring Opening Reaction of

Azabenzonorbornadienes with Terminal Alkynes

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Ring Opening of Azabicyclic Alkenes Co-Catalyzed by Palladium and Copper

Significance: The ring opening of strained *meso*-heterobicyclic alkenes with different nucleophiles serves as a useful strategy for setting multiple stereocenters in a single transformation. Previous methods for this particular ring opening were limited to the use of bulky terminal acetylenes. Here, the authors report the development of a palladium and copper co-catalyzed system that exhibits broad substrate scope.

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Comment: The authors propose that the copper(I) catalyst plays two distinct roles in the mechanism: (1) Copper facilitates transmetalation of the acetylene to palladium via the copper acetylide; (2) Copper behaves as a Lewis acid to activate the azabicyclic alkene. In addition to demonstrating wide functional group tolerance, the yields and enantioselectivities observed are excellent across the series of substrates tested.

Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

copper

desymmetrization
asymmetric ring
opening
palladium