W. WANG, Y. YU, B. CHENG, H. FANG, X. ZHANG*, H. QIAN*, S. MA* (FUDAN UNIVERSITY AND SHANGHAI INSTITUTE OF ORGANIC CHEMISTRY, P. R. OF CHINA)
Stereodefined Rhodium-Catalysed 1,4-H/D Delivery for Modular Syntheses and Deuterium Integration
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Rhodium-Catalyzed Stereoselective Synthesis of Enones and Enals from 2,3-Allenols and Organoboronic Acids

Proposed mechanism:

Selected examples:

Significance: Zhang, Qiang, Ma, and co-workers report a rhodium–copper co-catalyzed synthesis of enones and enals from organoboronic acids and 2,3-allenols under mild reaction conditions. The transformation involves a highly selective 1,4-hydride transfer that, when employing deuterated allenols, allows for the stereoselective synthesis of deuterated enones/enals.

Comment: The broad functional group tolerance of the reaction allowed for the modular incorporation of pharmacologically relevant scaffolds. Detailed DFT studies were conducted and the findings indicate that the carboration step is rate-limiting.

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