

Stereoselective Synthesis Using Olefins and Acetylenes: Inter and Intramolecular Reactions

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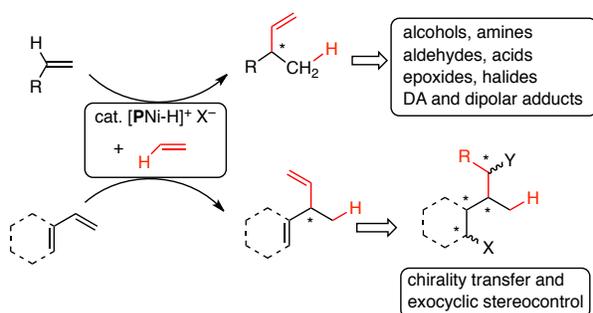
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Abstract

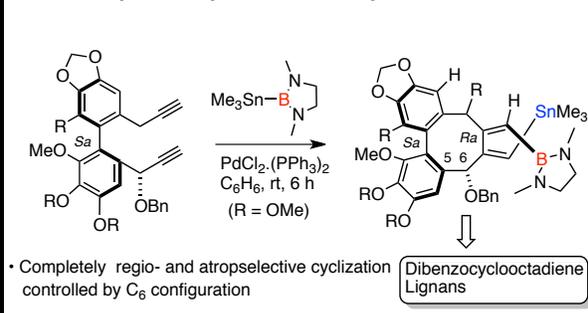
One of the major challenges facing organic synthesis in the 21st century is the utilization of abundantly available carbon sources for fine chemical synthesis. The dual problems of activation of thermodynamically stable precursors and their stereoselective incorporation pose new challenges, solutions of which may have broader implications in homogeneous catalysis, and, at a practical level, how we synthesize/manufacture chemical intermediates. In this context, we have discovered new protocols for a nearly quantitative and highly selective codimerization of ethylene (and propylene), and various functionalized vinylarenes, 1,3-dienes and strained alkenes. This talk will deal with the development of various strategies for stereochemical control in an enantioselective version of this reaction. These include design and synthesis of new ligands and applications of the 'hemi-labile ligand concept'. The products of this reaction are potentially useful for the synthesis of several classes of compounds, especially with intricately placed methyl-bearing chiral centers. Examples include 2-arylpropionic acids, amphiletanes like bisabolanes, pseudopterosins, cyclopenta[G]indoles, pyrrolidinoindolines with all-carbon quaternary centers, and steroid D-ring derivatives with unnatural side-chains.

One of the major problems with many cyclization reactions is that functional groups are depleted in the ring-forming event. Recently we have been interested in reactions in which the annulation reaction is accompanied by formation of vinyl-X bonds, which in turn can be used for subsequent stereoselective operations. Applications of such reactions for a general synthesis of dibenzocyclooctadiene lignans will be illustrated.

Asymmetric Hydrovinylation Reactions



Multi-Component Cyclizations for Synthesis



[For leading references: *J. Am. Chem. Soc.* **2012**, *134*, 5496.; *J. Am. Chem. Soc.* **2012**, *134*, 6556.; *Chem. Sci.* **2012**, *3*, 1221.]

Stereoselectivity in Ring-Opening Reactions. Regiodivergent Parallel Kinetic Resolution

A bimetallic Y-catalyst, designed on the basis of a tentative mechanistic proposal, was found to effect highly enantioselective desymmetrization of meso aziridines. The same catalyst also brings about a regio-divergent parallel kinetic resolution of racemic aziridines with exceptional selectivity. [*Science* **2009**, *326*, 1662.]