N. N. NOUCTI, E. J. ALEXANIAN* (THE UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL, USA)

Stereoselective Nickel-Catalyzed [2+2] Cycloadditions of Ene-Allenes
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Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

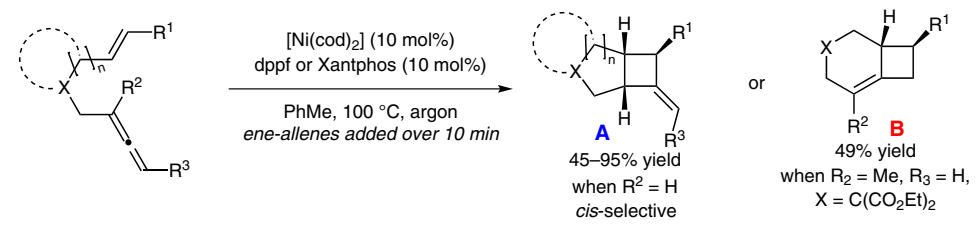
nickel

ene-allenes

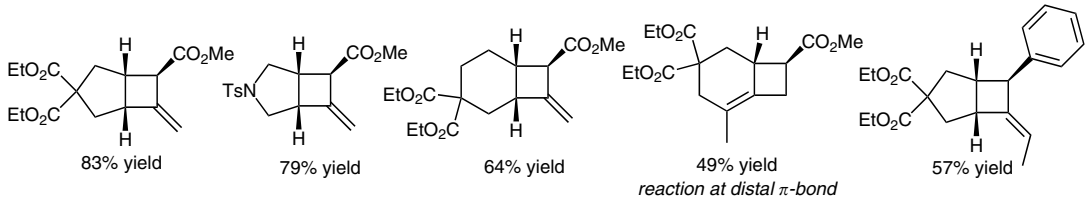
[2+2] cycloaddition

Asymmetric Cyclization of Ene-Allenes by Nickel Catalysis

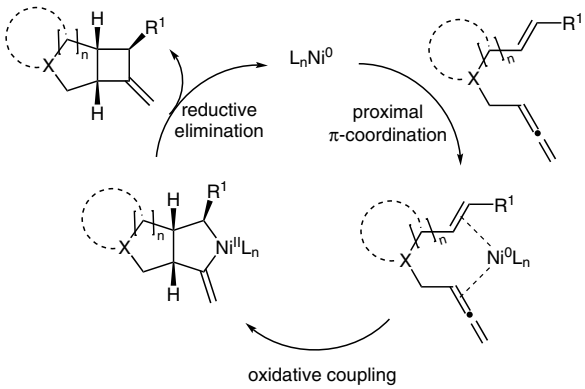
General reaction:



Selected examples:



Mechanism of the [2+2]-cyclization pathway:



Significance: The [2+2] cycloaddition of ene-allenes is a powerful methodology in the construction of fused cyclobutanes. However, one of the challenges of known protocols is the limited substrate scope, tolerating only styrene or diene π-components. Alexanian and Noucti demonstrate the utility of nickel catalysis in a stereoselective [2+2]-cycloaddition to generate diverse carbocyclic frameworks **A**.

Comment: It is noteworthy to point out the effectiveness of this protocol to cyclize terminal allenes which are not tolerated in other known methods. Moreover, an interesting observation was discovered where methyl substitution at R^2 changes the [2+2] cycloaddition from the proximal to the distal π-bond of the allene, generating the bicyclo[4.2.2] scaffold **B** instead.

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