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

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Asymmetric Cyclization of Ene-Allenes by Nickel Catalysis

Category

Metal-Catalyzed
Asymmetric
Synthesis and
Stereoselective
Reactions

Key words

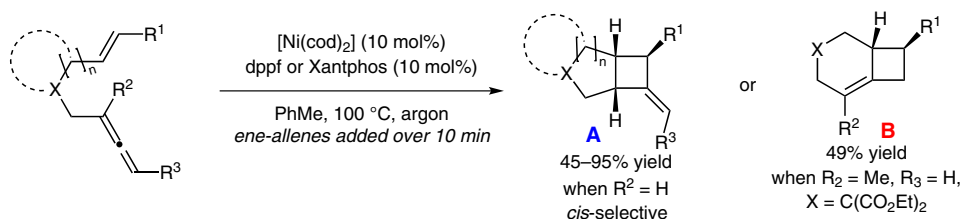
nickel

ene-allenes

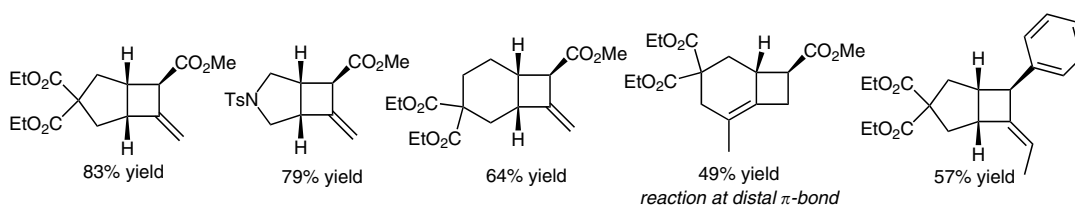
[2+2] cycloaddition

Synfact
of the month

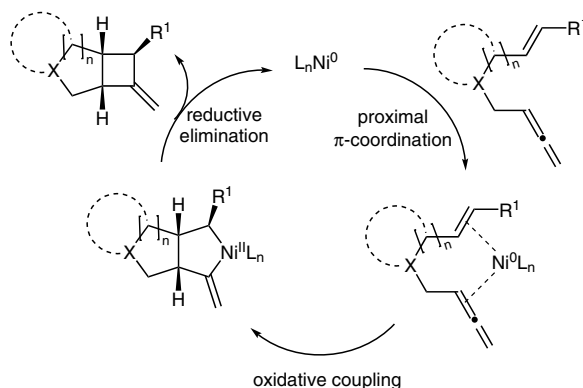
General reaction:



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**.

SYNFACTS Contributors: Mark Lautens, Charles C. J. Loh
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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 R² 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.