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The Isomerization of Allylrhodium Intermediates in the Rhodium-Catalyzed Nucleophilic Allylation of Cyclic Imines
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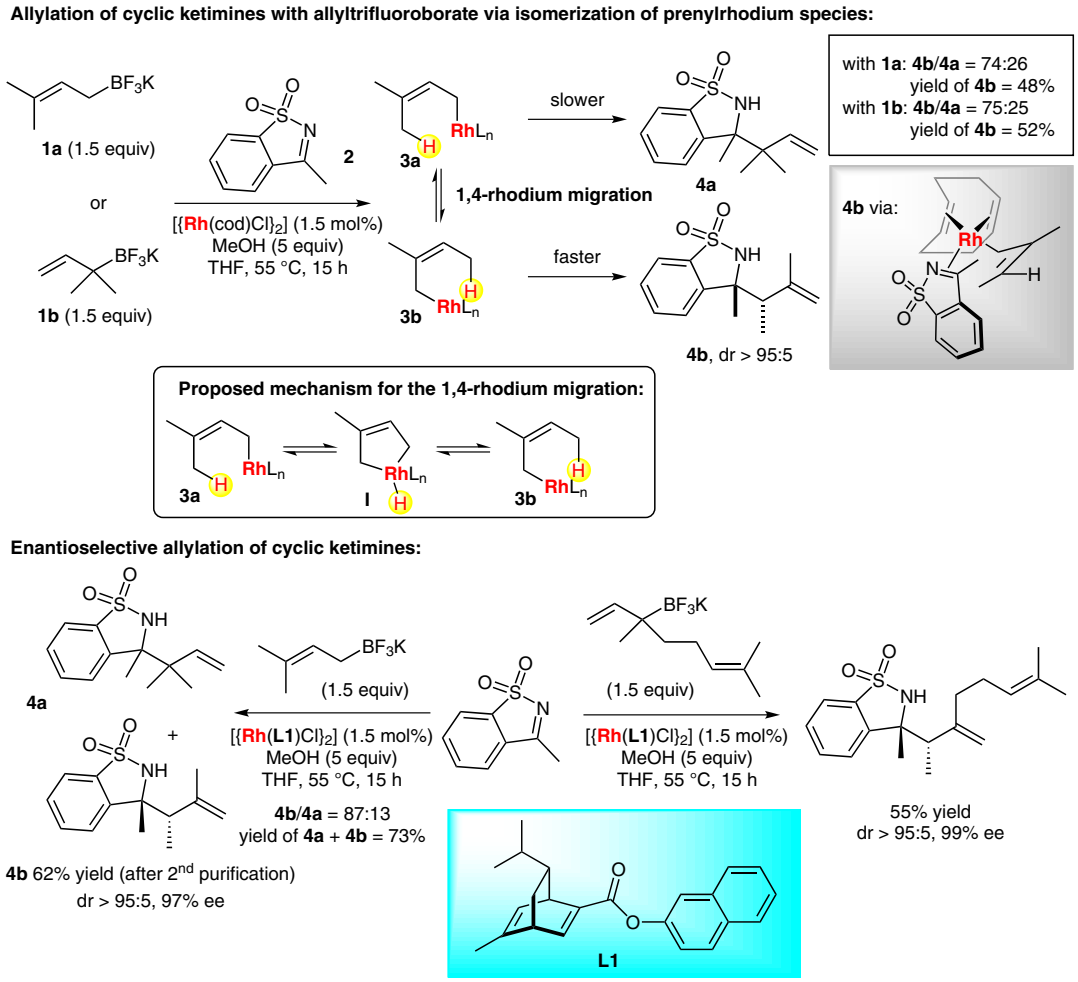
Isomerization of Allylrhodium Intermediates During Allylations of Imines



Significance: The authors present a 1,4-rhodium(I) migration of allylrhodium intermediates which then react with cyclic imines to yield the allylation product with three stereochemical elements with high selectivity. Using a chiral diene–rhodium catalyst the reaction can be performed enantioselectively. The significance of this work is the generation of stereochemically more complex products from simple starting material through rhodium(I)-catalyzed isomerization processes.

Comment: The reaction is favored in combination of two factors: 1) the steric hindrance of the initially formed allylrhodium species, and 2) the reactivity of the imine such that normal allylation is disfavored. Through the deuterium-labeling experiments it is proposed that the 1,4-rhodium(I) migration (**3a** → **3b**) occurs by a C–H oxidative addition–reductive elimination sequence via intermediate **I**.

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Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

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