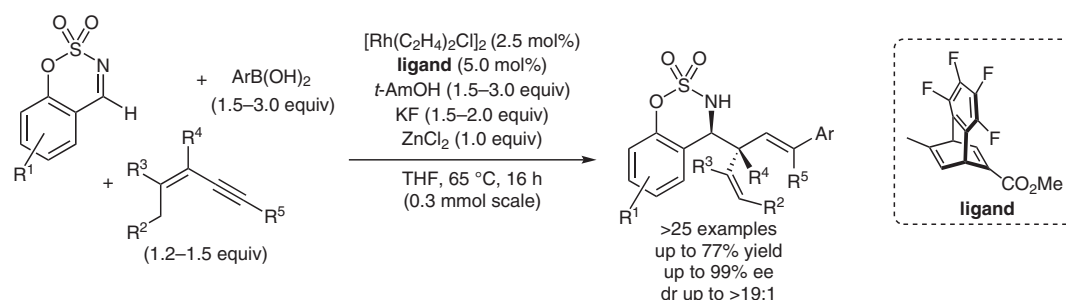
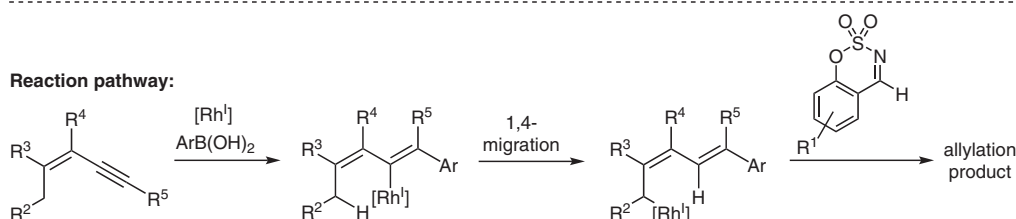


M. CALLINGHAM, B. M. PARTRIDGE, W. LEWIS, H. W. LAM* (UNIVERSITY OF NOTTINGHAM AND UNIVERSITY OF SHEFFIELD, UK)
 Enantioselective Rhodium-Catalyzed Coupling of Arylboronic Acids, 1,3-Enynes, and Imines by Alkenyl-to-Allyl 1,4-Rhodium(I) Migration
Angew. Chem. Int. Ed. **2017**, *56*, 16352–16356.

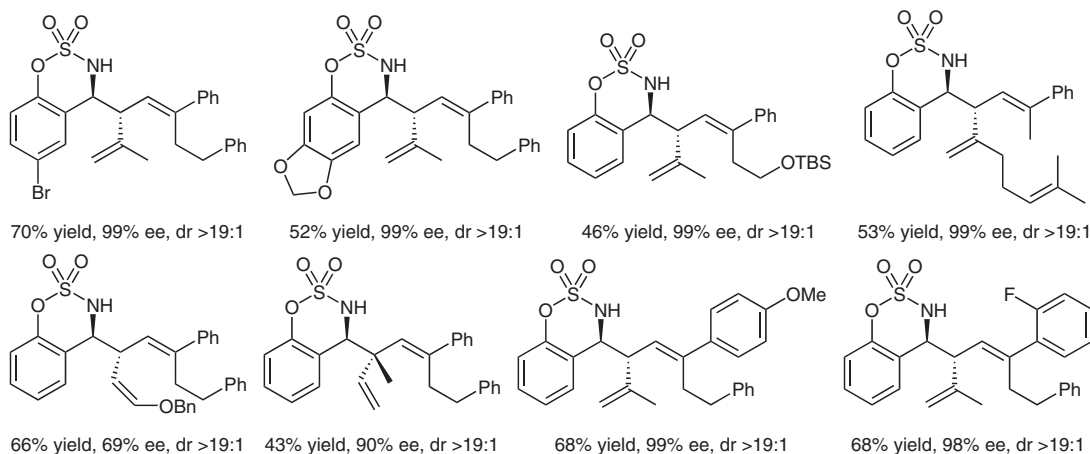
Coupling of Boronic Acids, 1,3-Enynes and Cyclic Imines



Reaction pathway:



Selected examples:



Significance: The authors describe a rhodium-catalyzed highly stereoselective coupling of arylboronic acids, 1,3-enynes and cyclic imines. The key step is an alkenyl-to-allyl 1,4-Rh(I) migration, which leads to enantioselective allylation with the cyclic imine. Given the number of alternative pathways, the chemoselectivity of this method is notable.

SYNFACTS Contributors: Mark Lautens, Tamara Beisel
 Synfacts 2018, 14(02), 0149 Published online: 18.01.2018
 DOI: 10.1055/s-0036-1591015; Reg-No.: L16917SF

Comment: Deuterium-labeling experiments suggest that the 1,4-Rh(I) migration occurs by C–H oxidative addition to give a Rh(III) hydride, followed by C–H reductive elimination. Use of ZnCl₂ gave more consistent results. The authors suggest an acceleration of the allylation by Lewis acid activation or improvement of catalyst turnover.

Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

rhodium catalysis

enantioselective nucleophilic allylation

1,4-rhodium(I) migration

three-component coupling