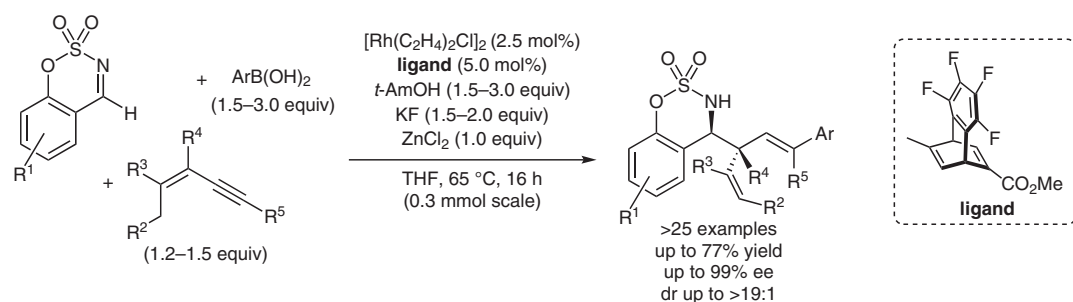


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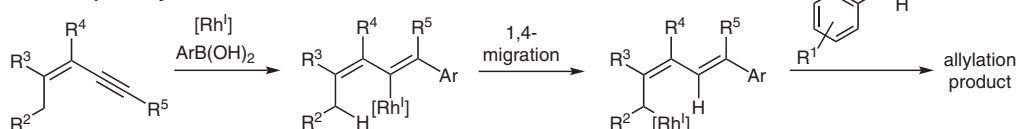
Enantioselective Rhodium-Catalyzed Coupling of Arylboronic Acids, 1,3-Enynes, and Imines by Alkenyl-to-Allyl 1,4-Rhodium(I) Migration

Angew. Chem. Int. Ed. **2017**, *56*, 16352–16356.

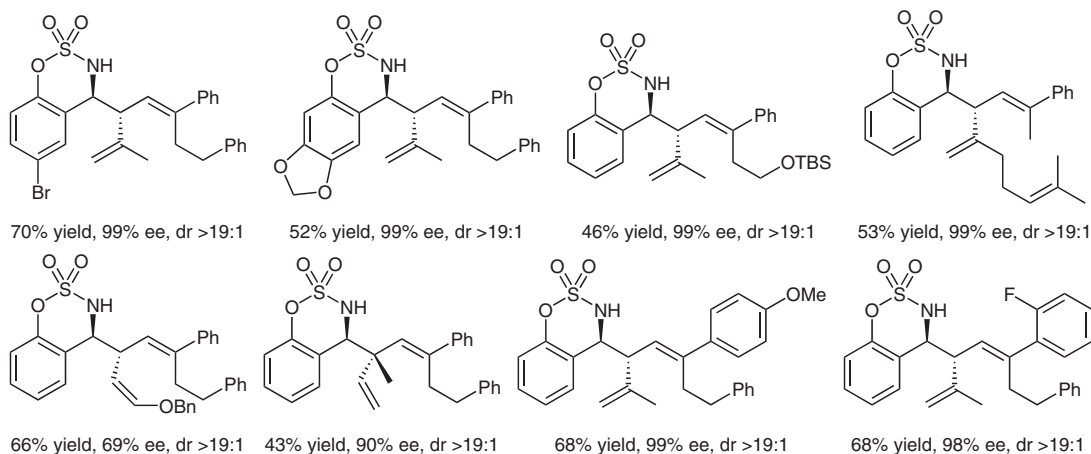
Coupling of Boronic Acids, 1,3-Enynes and Cyclic Imines



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.

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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.