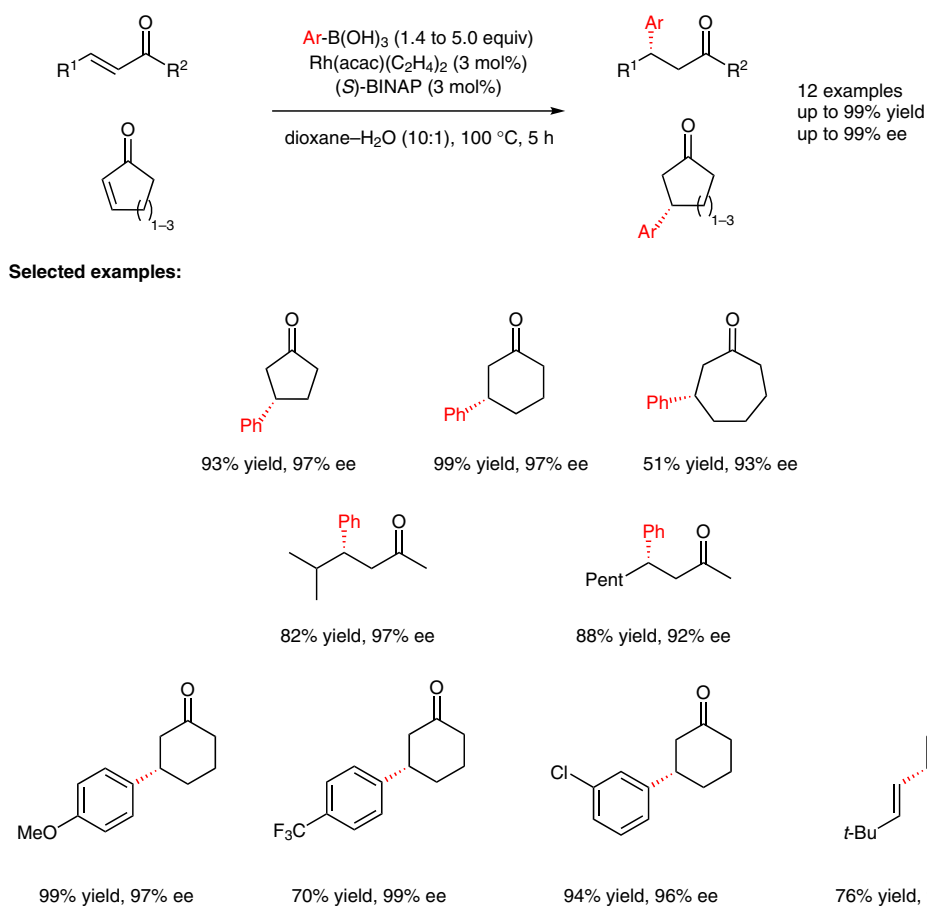


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Rhodium-Catalyzed Asymmetric 1,4-Addition of Aryl- and Alkenylboronic Acids to Enones
J. Am. Chem. Soc. **1998**, *120*, 5579–5580.

The First Enantioselective Rhodium-Catalyzed 1,4-Addition



Significance: Although Miyaura was the first to report rhodium-catalyzed conjugate addition of boronic acid reagents (M. Sakai, H. Hayashi, N. Miyaura *Organometallics* **1997**, *16*, 4229), it was the combined effort of Hayashi and Miyaura that, in the present work, demonstrated that this process can be done with a high level of enantioselectivity. This reaction, now often referred to as the Hayashi–Miyaura reaction, has become highly popular because: 1) it proceeds under neutral reaction conditions, 2) no background uncatalyzed 1,4-addition occurs, 3) no 1,2-addition in the presence or absence of catalyst takes place, and 4) it has a high functional group tolerance.

Comment: The authors noted that the reaction works best with [Rh(acac)(C₂H₄)₂] as opposed to the racemic version, which proceeded with [Rh(acac)(CO)₂]. The ethylene complex enables facile formation of the active [Rh(acac)(BINAP)] species. Another modification from the original work is the higher reaction temperature. This work represented the first time that high yields and enantioselectivities could be achieved in an aryl group 1,4-addition using a chiral BINAP ligand. Since this seminal report, other ligand classes have been elucidated, and this venerable methodology has been expanded to include domino reaction systems.

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