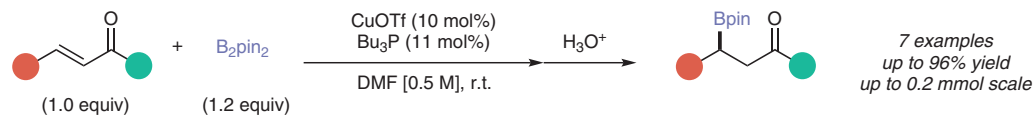
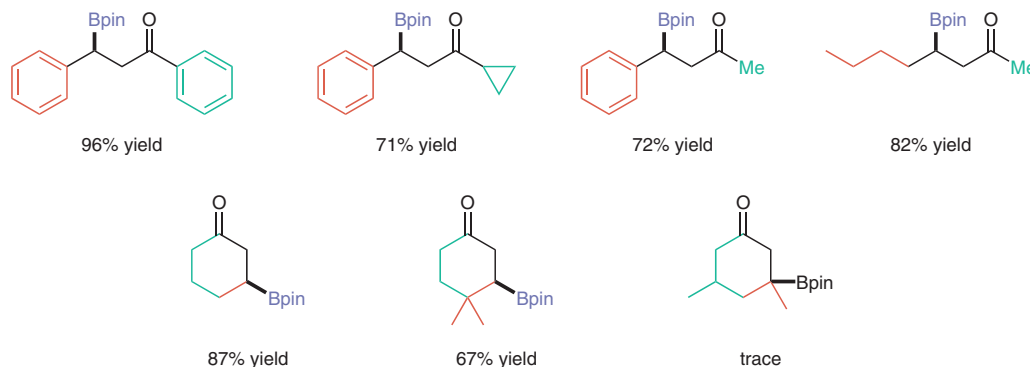


H. ITO, H. YAMANAKA, J. TATEIWA, A. HOSOMI* (UNIVERSITY OF TSUKUBA, JAPAN)
Boration of an α,β -Enone using a Diboron Promoted by a Copper(I)-Phosphine Mixture Catalyst
Tetrahedron Lett. **2000**, *41*, 6821–6825, DOI: 10.1016/S0040-4039(00)01161-8.

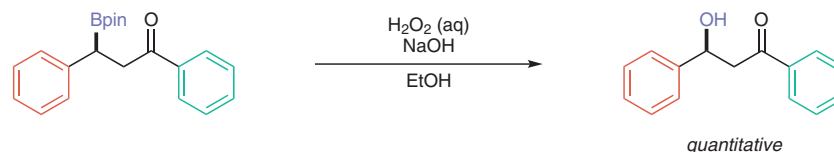
Copper-Catalyzed Conjugate Borylation of Enones



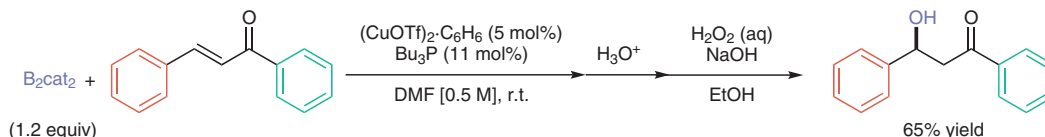
Selected examples:



Oxidation protocol:



2-Step-1-pot oxidation:



Significance: The value of boron-containing compounds in organic synthesis has been appreciated for decades. In 2000, the Hosomi group disclosed the first copper-catalyzed borylation reaction utilizing a simple monodentate phosphine as the ligand and B_2pin_2 as the boron source. Michael acceptors, in particular enones, were used as the accepting π -system to afford the borylated products. This field has seen unceasing developments, particularly enantioselective variants, in the past two decades.

Review: Hemming et al. *Chem. Soc. Rev.* **2018**, *47*, 7477–7494.

Comment: Notably, linear and cyclic enones were tolerated, but tetrasubstituted olefins were unreactive in the transformation, an unmet challenge in the field. The authors reasoned that the role of the phosphine was to ligate the copper complex and not to activate the diboron reagent. Using excess phosphine led to inhibition of the reaction, and ^{31}P NMR analysis of the phosphine with B_2pin_2 showed negligible change in the chemical shift compared to the free phosphine. Conversely, the ^{31}P NMR signal of the phosphine and copper resulted in a downfield shift, suggesting coordination.