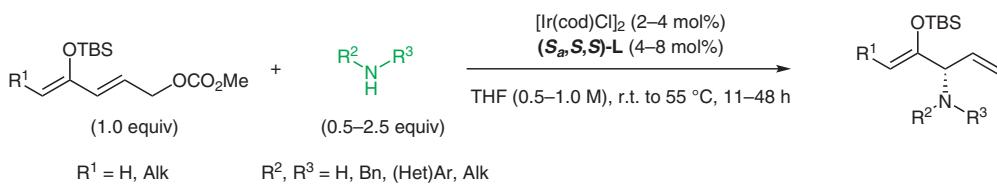
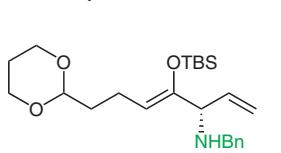


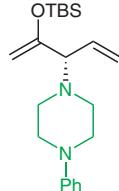
Enantioselective α -Functionalization of Ketones



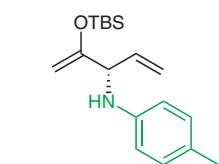
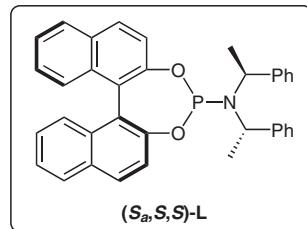
Selected examples:



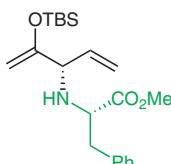
b/l = 19:1
90% yield, 95% ee



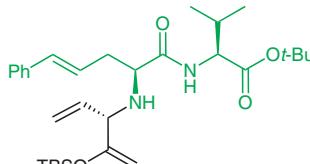
b/l > 20:1
92% yield, 97% ee



b/l > 20:1
87% yield, 96% ee
DABCO (20 mol% was added)

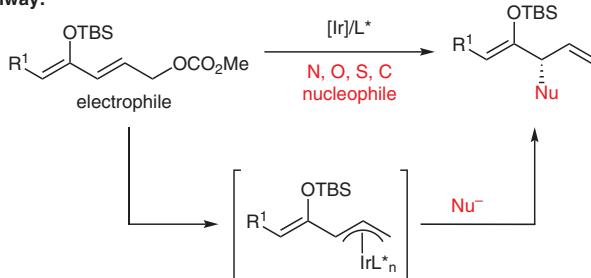


b/l > 20:1
87% yield, dr > 99:1



b/l = 15:1
77% yield, dr > 96:4

Proposed reaction pathway:



Significance: Hartwig and He developed an efficient and enantioselective method for the α -functionalization of ketones by performing iridium-catalyzed allylic substitutions on silyl enol ethers.

Comment: The yields and enantio- or diastereoselectivities of this method are exceptionally high, making this protocol extremely useful for the synthesis of enantiomerically pure α -substituted ketones. Additionally, not only N-, but also S-, O-, or C-nucleophiles were applicable to this method.