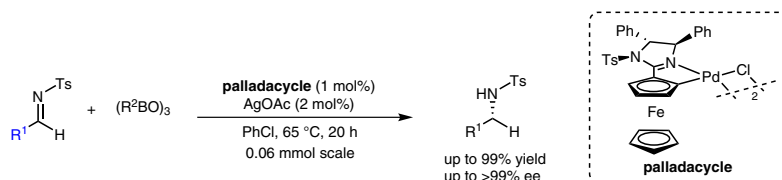
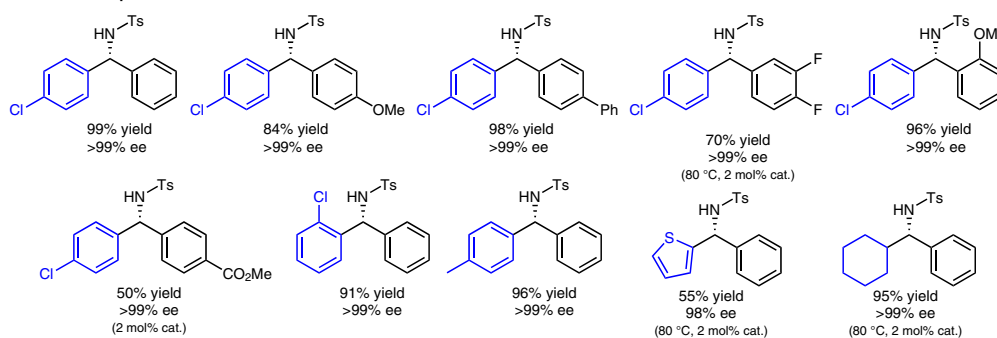


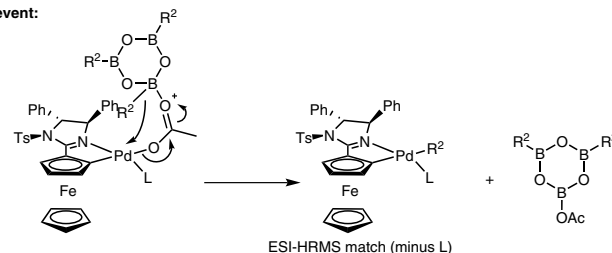
Palladacycle-Catalyzed Highly Enantioselective Arylation of Sulfonylimines



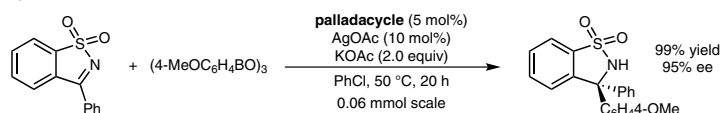
Selected examples:



Possible transmetalation event:



Formation of a quaternary stereocenter:



Significance: The rhodium- or palladium-catalyzed 1,2-addition of arylboron reagents to activated imines is a useful reaction for the synthesis of chiral amines. The palladium-catalyzed version is often affected by diminished yields due to competitive hydrolysis of the starting imine and/or homocoupling of the boronic acid. Peters and Schrapel address these issues with an efficient protocol using a chiral palladacycle catalyst that was developed in their group.

Comment: Virtually perfect enantioselectivity and high yields are achieved with a range of imine/boroxine combinations, with electron-poor boroxines giving lower yields. Boronic acids were found to be more reactive than boroxines, but the latter were chosen for this study to enable a reproducible protocol. The authors propose that an anionic acetate ligand on palladium facilitates transmetalation with the boroxine. The use of less coordinative anions (OTf^- , TFA^-) led to low or no reactivity. Preliminary results with cyclic ketimines show that the formation of a quaternary center is also possible.

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