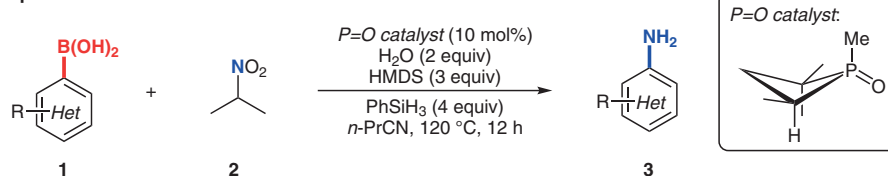
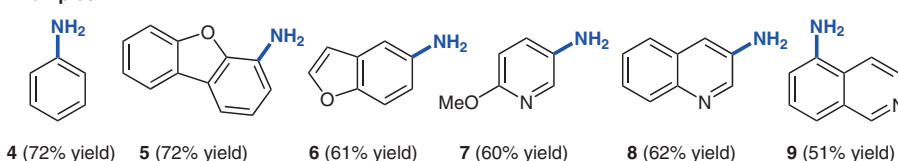


Synthesis of Anilines from Boronic Acids

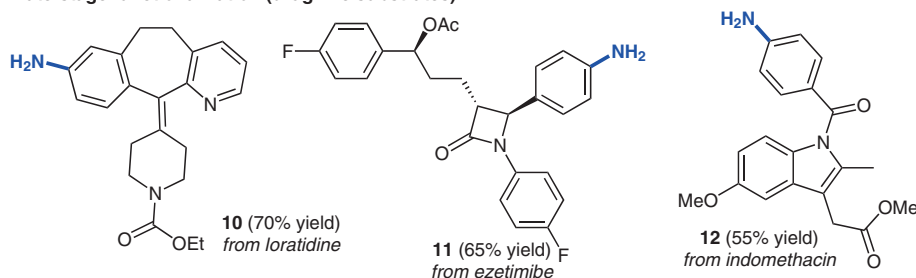
Optimized conditions:



Examples:



Late-stage functionalization (drug-like substrates):



Significance: Primary amination of aryl nucleophiles represents a valuable transformation though is limited to some degree by the documented safety concerns and/or availability of suitable H_2N^+ synthons. The current report exploits the Nef decomposition of 2-nitropropane (2) to form in situ the nitroxyl intermediate HNO, which is captured by a phosphetane-based catalyst generating an oxazaphosphirane that reacts with the boronic acid to provide the desired C–N coupled product through ring opening followed by a 1,2-metalate rearrangement.

Comment: Model studies demonstrated that not only was judicious selection of the catalyst and solvent important for the optimal outcome of the reaction but inclusion of HMDS as an additive significantly enhanced the yield through base-promoted activation of 2-nitropropane. The methodology was shown to be relatively insensitive to both the electronic and steric constraints of the substrates and was demonstrated for a range of heterocyclic boronic acids including N-basic heterocyclic systems (7–9) that would be incompatible with electrophilic NH_2 -aminating reagents. The new protocol was shown to be complementary in scope and chemoselectivity to transition-metal-catalyzed methods of aryl amination and was further applied for the late-stage functionalization of drug-like molecules (10–12).