Intermolecular Reductive C−N Cross-Coupling of Nitro Compounds and Boronic Acids by P^{III}/P^{V}=O Catalysis

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Intermolecular C–N cross coupling has emerged as a powerful technology for the preparation of aromatic amines in both academia and industry. The prevailing strategy for the C–N bond construction is currently shaped by transition metal-catalyzed methods (e.g., Buchwald-Hartwig, Ullmann, and Chan-Lam couplings) from parent amines. Orthogonal to current strategies, new methods that transform readily available nitro compounds into value-added products by organophosphorus-catalyzed reductive C–N bond formation will be described in this presentation.

Though nitro compounds are frequently reduced to the amine coupling-partner, utilizing nitro compounds as an amine surrogate in C–N cross-coupling proves challenging with current methods due to poor compatibility between reducing reagents and coupling catalysts. In our work, a simple organophosphorus catalyst is shown to catalyze the deoxygenative coupling of nitro compounds with boronic acids to form secondary amines. This strategy has been further extended to various heteroarenes syntheses; starting with *ortho*-functionalized nitroarenes, organophosphorus-catalyzed reductive C–N cross coupling with boronic acids, followed by intramolecular cyclization provides a regiospecific approach to *N*-substituted benzimidazoles and quinoxalinediones.