Photo-Redox Functionalization of Aryl Bromide Derivatives by N-Heterocyclic Carbene (NHC) Catalysis

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Aryl Bromides are significant compounds having great potential in cross-coupling reactions and interconversions of functional groups. To functionalize these groups into boronates (high-value molecules used in a variety of drugs) however, the most current approaches are with metal catalysts, which can be costly, scarce, and environmentally toxic. Few alternative techniques exist for direct activation of the C(sp2)-Br bond in aryl bromides because of their limiting negative reduction potential. Therefore, it becomes imperative to evaluate NHCs' (N-heterocyclic carbenes) validity as a photocatalyst for the functionalization of aryl bromides because of their highly capable ability in single electron transfer when excited under light. Thus, a novel, mild method for the oxidative coupling of aryl bromides with boronic esters is presented, catalyzed by self-supported NHCs. A general procedure of putting reactant and catalyst species under light for 24 hours was developed, along with an optimization framework with independent variables of NHC type, light wavelength, type of solvent, and type of base to generate the highest yield of product (55%-65% yield for most boronates tested). Analysis occurred via product characterization by NMR, TLC, and GC-MS. Additionally, UV-Vis Spectrometry, Radical Trapping, and Stern-Volmer Studies were done for confirmation of in-lab results and mechanism development. Compared to the status quo, this method is transition metal-free and does not rely on external photocatalysts, ligands, and/or thermal activation, displaying a cleaner alternative pathway in photo-redox chemistry for boronate production. Further studies can investigate other high-value boronate molecules that can be produced with this process.

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