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

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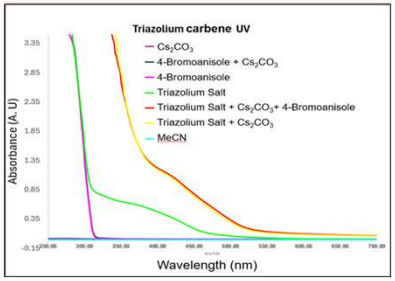
Research Question

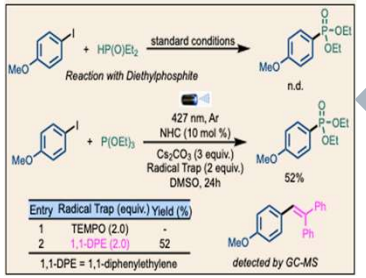
To what extent can N-Heterocyclic Carbenes (NHCs) sufficiently activate the C(sp2)-Br bond in Aryl Bromides and be used as a photocatalyst for the functionalization of these compounds via Borylation to produce high value Boronate chemicals?

- Metal catalysts cause serious problems like being more costly, energy-soaking, and toxic for the environment
- Few techniques have been developed because of the negative reduction potential (hard to get electrons) of the C(sp2)-Br bond in Aryl Bromides (reactants in borylation)
- NHCs have potential to avoid the negative consequences of metal catalysts and overcome negative reduction potential since it is a good electron donor under light

Data Analysis and Results

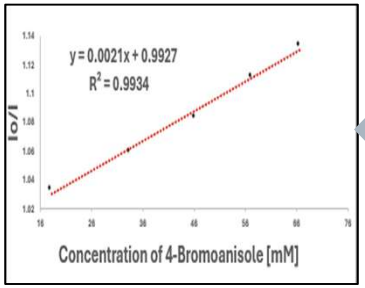


UV-Vis Analysis to confirm NHC is absorbing light shined



Radical Trap Test to confirm electron transfer and radical formation

Result: Highest yield was with 425 nm light, Triazolium NHC, DMSO, Cs2CO3



Stern-Volmer Studies to analyze quenching constant (slope) for efficiency of quenching (or how well the Aryle Bromides can absorb the electrons

Methodology

Reaction Outline:

10 mL microwave vial charged with aryl bromide, NHC, Cs2CO3, B2pin2 → Vial was brought into argon-filled glovebox → Once outside glovebox, DMSO (1.0 mL) were added via syringe → Vial was capped with 20 mm 107 microwave crimp caps with septa → Vial was placed ~3 cm from the LED dual lamp setup and stirred at 1000 RPM for 24hrs → Organic-water workup performed + solvent was removed in Rotovap

Process was then used for optimization framework with variations of wavelength of light shined, NHC type, base type, and solvent type

Interpretation and Conclusions

The hypothesis is supported by the data because:

- 65% Boronate molecule yields were reached → showing how high and effective Boronate yields were established with the optimized conditions
- Theoretical analysis supports NHC is donating electrons and the Aryl Bromides are properly receiving them and culminates in final mechanism
- Optimized condition at 425 nm (blue light) also means this procedure is mild and not very energy intensive
- **In summary**, a mild method for functionalization of aryl bromides was effectively developed to improve upon the weaknesses of metal catalysts and make the borylation process more environmentally friendly, energy, and cost efficient