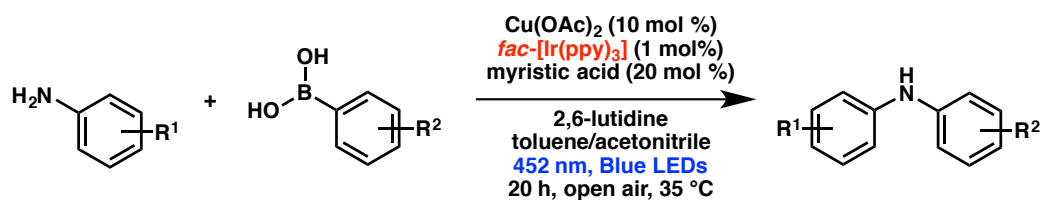


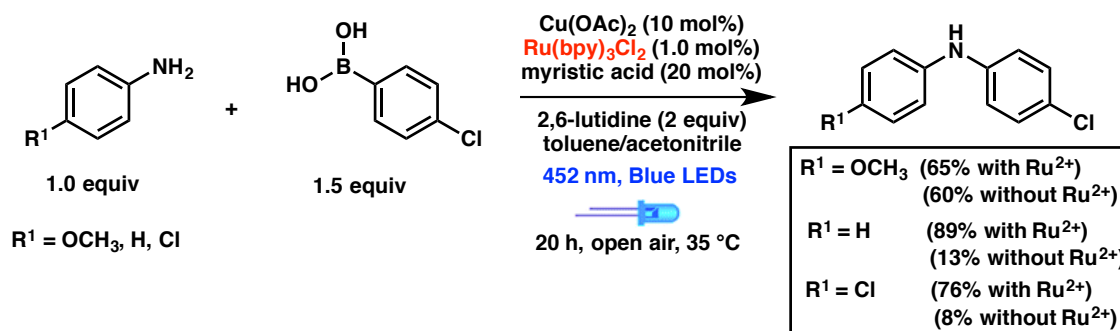
The current project funded by the ACS PRF UNI Program has facilitated the continued cultivation of undergraduate scientific culture, physical infrastructure, advancement of meaningful data acquisition at High Point University. As the undergraduate sciences are being actively supported by the administration at HPU, the current ACS PRF award has added further excitement and motivation for continued university investment. This is most profoundly evidenced by the construction of a \$65 million, 128,000-square-foot facility, which will open in Fall 2019, to support the undergraduate sciences at HPU. Prior to this ACS PRF award, efforts to affect significant impacts on student outcomes were admirably supported by the Summer Research Program in the Sciences (SuRPS) at HPU. This 8-week program provides an atmosphere of scholarly research activity to enable continued student growth, replicate the requirements of graduate-level research, and generate original data for communication in seminars, poster presentations, and manuscript preparation/submission. The current ACS PRF award has brought external validation for this summer research program and in-semester research efforts, as both faculty, staff, students, and administrators see how the data acquired during these experiences are validated by scientific experts.

During the first budget period of the current ACS PRF UNI Award, progress has been found in extending preliminary results to publishable outcomes, in both a fundamental research capacity and also as a mechanism for leading undergraduate students in novel teaching lab activities. One long-standing problem with the Chan-Lam coupling reaction was low and variable yields when using coupling partners of electron-poor character, which was significantly advanced under the mild inclusion of an iridium-based photocatalyst described by Koybayashi and coworkers (Scheme 1).¹



Scheme 1. The C–N bond forming Chan-Lam coupling reaction showing conditions from the Kobayashi and Lab. Although R^1 and R^2 are typically electron-rich substituents, the incorporation of the iridium(III) photoredox catalyst facilitates an expanded substrate scope with aryl coupling partners.

The exchange of the expensive iridium(III) catalyst for the more economical option of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ was found to provide comparable yields under equally mild reaction conditions. This was initially investigated as a means to provide our undergraduate science students with exposure to an increasingly important reaction paradigm in synthetic organic chemistry; photoredox methodologies have and are continuing to have a dramatic effect on how the synthetic chemist designs and constructs molecular architectures.² Indeed, this lab has shown a dramatic example of how transition-metal catalysis can be altered by photoredox co-catalysis. As seen in Scheme 2, our undergraduates are given the opportunity to study when a photocatalyst is needed for oxidative copper catalyst turnover and when the substrate choice allows productive union without the ruthenium(II) additive.



Scheme 2. Using alternative aniline derivatives, undergraduates observe a stark contrast in yields with and without ruthenium(II) photocatalyst, which provides clear data as to how putative intermediates in the catalytic cycle could be affected by electron-donating or electron-withdrawing substituents.

Further investigation into the substrate scope was probed during in-semester and summer research opportunities for four talented undergraduate students. The data obtained during our studies into the ruthenium(II) photocatalytic contribution to extending the oxidative copper coupling reaction is shown in abbreviated form in Figure 1, where aryl amines and aryl boronic acids were productively joined in the C–N bond-forming process.

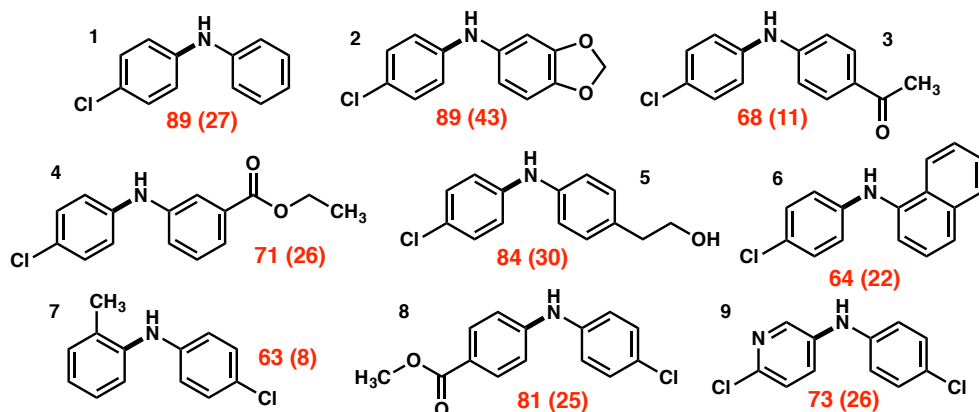


Figure 1. Select data illustrating substrate scope investigations of aryl-aryl coupling products. The bolded bond represents the new C–N union. Yields are shown in red, where yield without photocatalyst are shown in parentheses.

As shown in Figure 1 above, our data suggests substantial increases in yield of electron-poor substrates when in the presence of the ruthenium(II) co-catalyst to form products under additional stresses of steric hindrance (6 & 7), chemoselectivity (5), and metal coordinating motifs (9). Furthermore, our studies have also been extended into coupling of aryl boronic acids with alkyl amines, which was also previously underexplored in the Chan-Lam reaction.

Figure 2, shows the outcome of select coupling alkyl amine coupling partners with 4-chlorophenylboronic acid. Within this data set is seen how electron-rich olefins (12) and unhindered alkenes (13) are preserved during the oxidative reactions conditions. Also noteworthy is the tolerance of sterically hindered primary amine coupling partners (11, 14, & 19) as well as secondary amines (16 & 17).

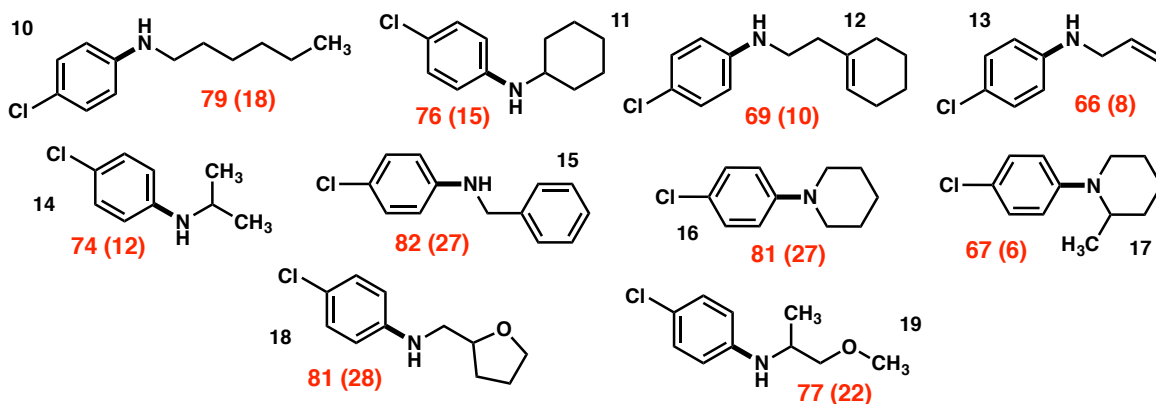


Figure 2. Coupling of alkyl amines with 4-chlorophenylboronic acid allows general access to secondary and tertiary amines products in moderate to high yields. The bolded bond shows the site of the new C–N connection. Yields with photocatalyst are shown in red, where yield without photocatalyst are shown in parentheses.

While preliminary fluorescence quenching studies have shown both copper(II) and copper(I) to powerfully quench the photoexcited state of Ru(bpy)₃Cl₂ in Ar-degassed solution, studies to probe the impact of atmospheric composition on reaction efficiency are ongoing, whereby complementary oxidative turnover of copper-based intermediates may be plausibly facilitated by both photocatalyst and aerobic conditions.

The ACS PRF UNI Program has greatly impacted my professional development, but more importantly, the effect of this external award has encouraged my students and provided further momentum to the administration to proudly support undergraduate sciences at HPU.

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