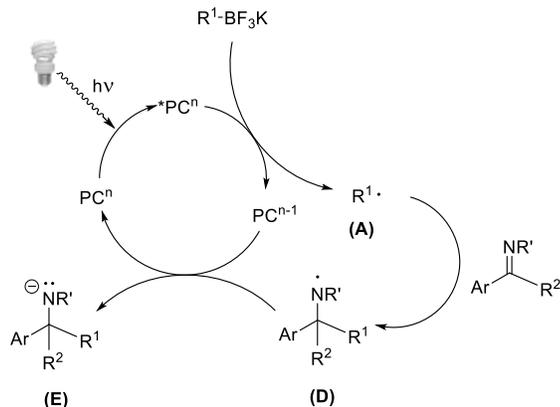
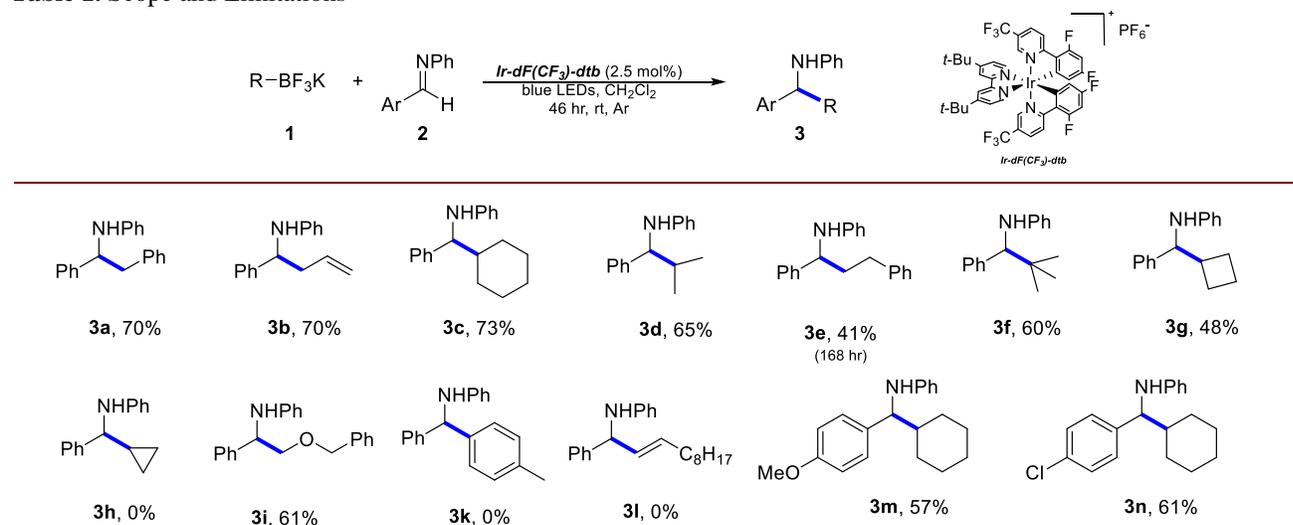


Overview

The goal of this work is to develop the visible light-promoted reaction of potassium organoborates ($R-BX_3K$, $X = F$ or OR') with imines ($R_2C=NR'$). If successful, this would extend the applicability of visible light photoredox catalysis and represent a novel approach to the formal addition of potassium organoborates to imines, a desirable goal given the properties of organoborates, such as their stability, availability, ease of preparation, and functional group tolerance. The mechanistic hypothesis is shown in Figure 1 (PC = photocatalyst).

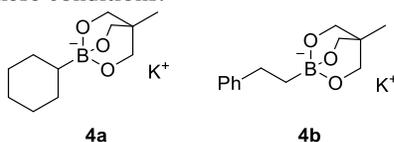
Figure 1. Mechanistic Hypothesis for the Addition of RBF_3K to Imines using Visible Light Photoredox Catalysis.**Year 1 Results****Scope and Limitations**

In our preliminary work, we had found that irradiation of an argon-sparged dichloromethane solution of potassium benzyltrifluoroborate (**1a**), benzaldehyde (**2a**), and *Ir-dF(CF₃)-dtb* (structure shown in Table 1), mounted between 2 16 W 450-nm LED floodlights, resulted in a 70% (isolated) yield of **3a** (Table 1). GC/MS of the reaction mixture showed that **2a** was completely consumed, and only a small amount of bibenzyl, resulting from homocoupling of the benzyl radical generated from **1a**, was detected. During this grant year, we examined the reaction of several potassium organotrifluoroborates with aryl aldimines under these conditions, and the results are shown in Table 1. A wide range of potassium alkyltrifluoroborates were shown to be competent radical sources. Significantly, potassium phenethyltrifluoroborate ($E_{red} = +1.83$ V) was found to be a viable substrate in this protocol, giving **3e** in 41% yield.

Table 1. Scope and Limitations

This is somewhat unexpected, since the much higher reduction potential of primary alkyltrifluoroborates should render the oxidation by *Ir-dF(CF₃)-dtb* ($E_{*Ir(III)/Ir(II)} = +1.21$ V) quite endergonic. The reaction did proceed much more slowly than those with more easily oxidized organotrifluoroborates, however, requiring 168 h, instead of the usual 46 h. Aryl, vinyl, and cyclopropyl trifluoroborates failed to react, presumably due to their much higher bond strengths. Preliminarily, the reaction appears to be insensitive to electronic effects, with aryl aldimines containing electron-donating and -withdrawing

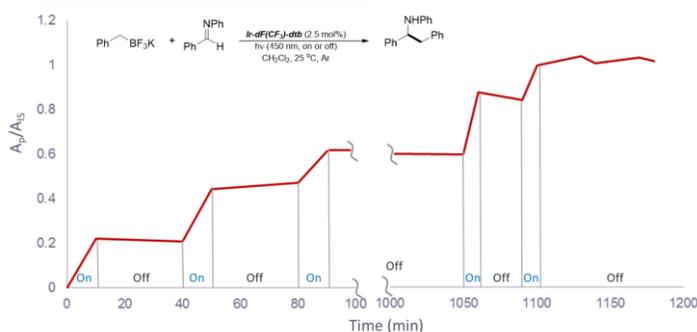
groups giving similar yields (**3m**, **3n**). Surprisingly, use of the cyclic triolborates **4a** and **4b**, which have reduction potentials about 0.4 V lower than their corresponding trifluoroborates, and thus should be more easily oxidized, failed to give appreciable yields of product under these conditions.



Mechanistic Studies

To distinguish between the proposed closed-cycle mechanism and a potential radical chain mechanism, we also carried out a “light-dark” experiment; the results are shown in Figure 2. Product formation appeared to stop during the “dark” periods in which the light was off; this is a preliminary indication that a radical chain mechanism is probably not operative. In future work, we intend to validate this conclusion using quantum yield studies.

Figure 2. “Light-Dark” Experiment Results



Evaluation of Catalysts/Solvents

Using the reaction of potassium isopropyltrifluoroborate (**1d**) with benzalaniline (**2a**), we evaluated several alternative catalysts (organic and inorganic) and solvents (CH_2Cl_2 , dioxane, THF, CH_3CN , DMF, DMSO) in the protocol, including several organic photocatalysts. Our results indicate that the organic photocatalyst 9-mesityl-10-methylacridinium tetrafluoroborate (*[Mes-Acr-Me]BF₄*) in CH_2Cl_2 performs best for this reaction, giving complete consumption of starting material and resulting in an 88% yield (by NMR) of product **3d** (Table 1) after 46 h. We intend to examine the scope and limitations of the protocol with respect to both organotrifluoroborate and imine in the future using this catalyst/solvent combination.

Career Impact

During this grant year, ACS-PRF funds have been used to support two undergraduate students during the 2017-18 academic year and the summer of 2018. One presented her preliminary results at the Southeastern Regional Meeting of the American Chemical Society (SERMACS) in 2017, and will present her updated results at SERMACS 2018. The other made an oral presentation of her work at our Summer Undergraduate Research Experience (SURE) Summer Symposium, and will also present these results in poster form at the SURE poster session this fall. The PI presented the latest results of this project at the 2017 North Carolina Photochemistry meeting (NC Photochem 2017), held in conjunction with SERMACS 2018. Also in 2018, we also described our preliminary results in a manuscript published in *Photochemical and Photobiological Sciences*.