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Photoredox Mediated Alkylation of Imines with Potassium Organotrifluoroborates in the Presence of an Organic Photocatalyst

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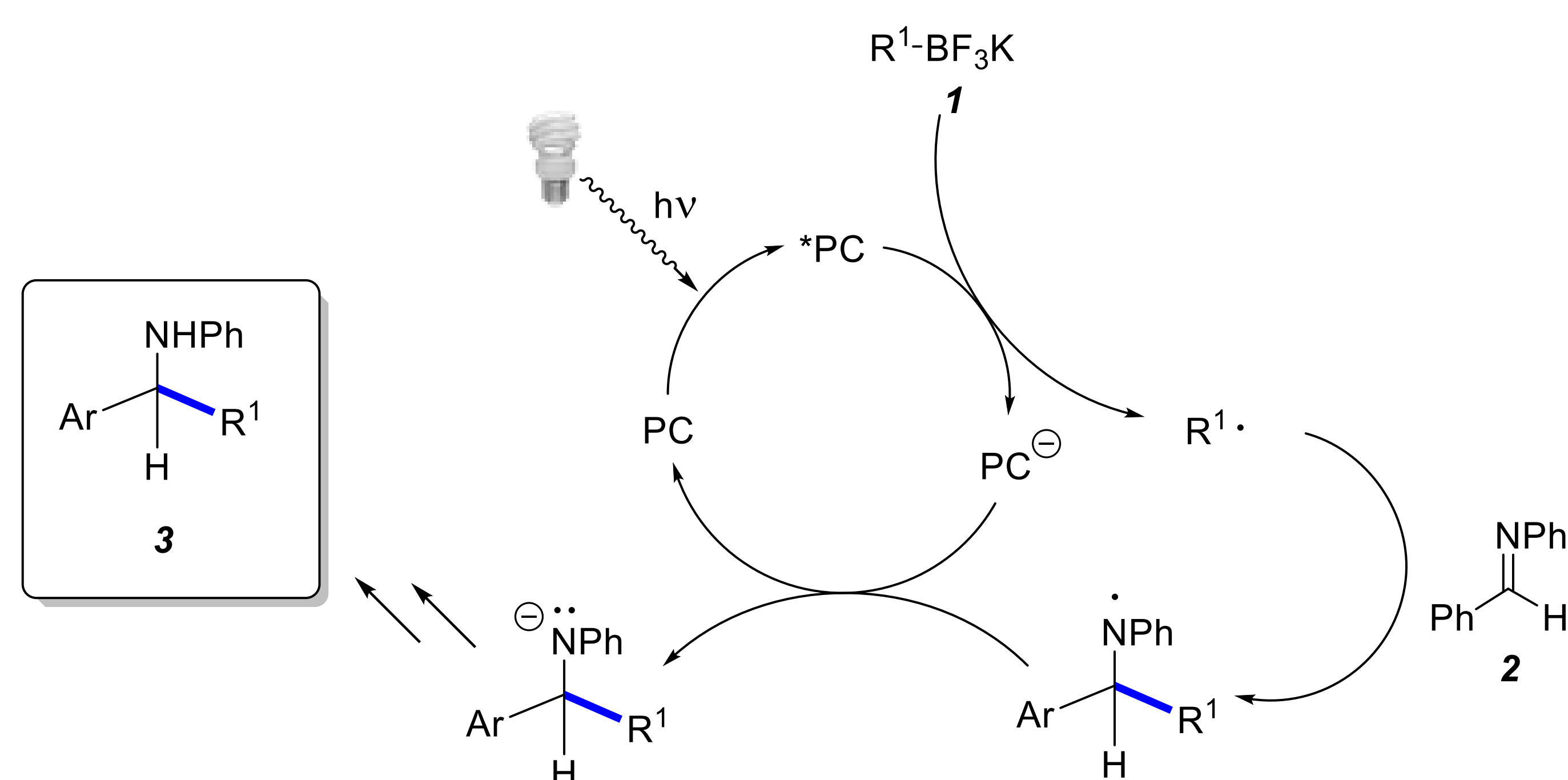
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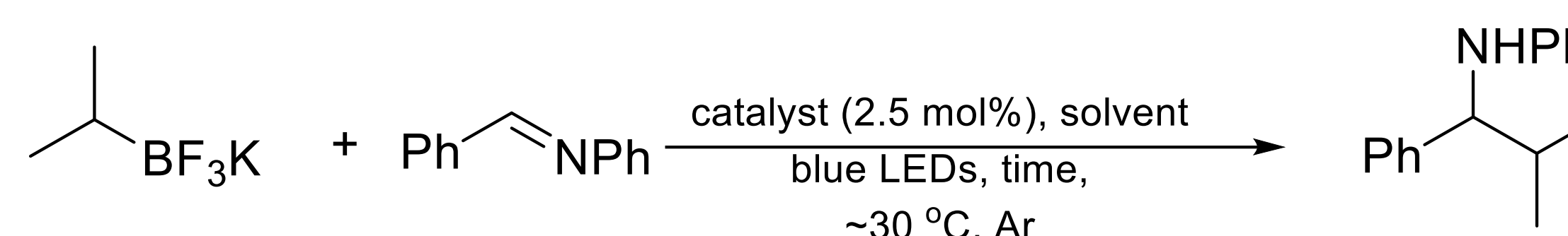
Introduction

- Recently, the use of visible light to promote key bond-forming steps in organic synthesis has emerged as a viable strategy to achieve a number of important synthetic transformations (MacMillan et al. *Chem. Rev.* **2013**, *113*, 5322).
- Most synthetic applications employing visible light involve single-electron transfer (SET) between photoexcited catalyst and one or more organic substrates.
 - Catalysts are typically Ru- or Ir-polypyridyl complexes.
 - Cost: ~\$1,000/mmol for Ir-based catalysts (e. g., *Ir-dF(CF₃)-dtb*)
 - Absorption of visible light, such as sunlight or household light bulbs (LEDs or CFLs) produces an excited singlet state, which undergoes rapid intersystem crossing (ISC) to the more stable long-lived triplet state.
 - These excited-state photocatalysts engage with organic substrates in downstream single electron transfer (SET) events, ultimately leading to the final product(s).
- Our research group recently reported the alkylation of aryl aldimines with RBF₃K using an Ir-based photocatalyst (Plasko et al. *Photochem. Photobiol. Sci.* **2018**, *17*, 534).
- Due to the significantly lower cost of organic photocatalysts, we desired to explore their use in this transformation.
 - Cost: ~\$50/mmol for acridinium-based catalysts (e. g., *Mes-Acr-Me*)

Hypothesis

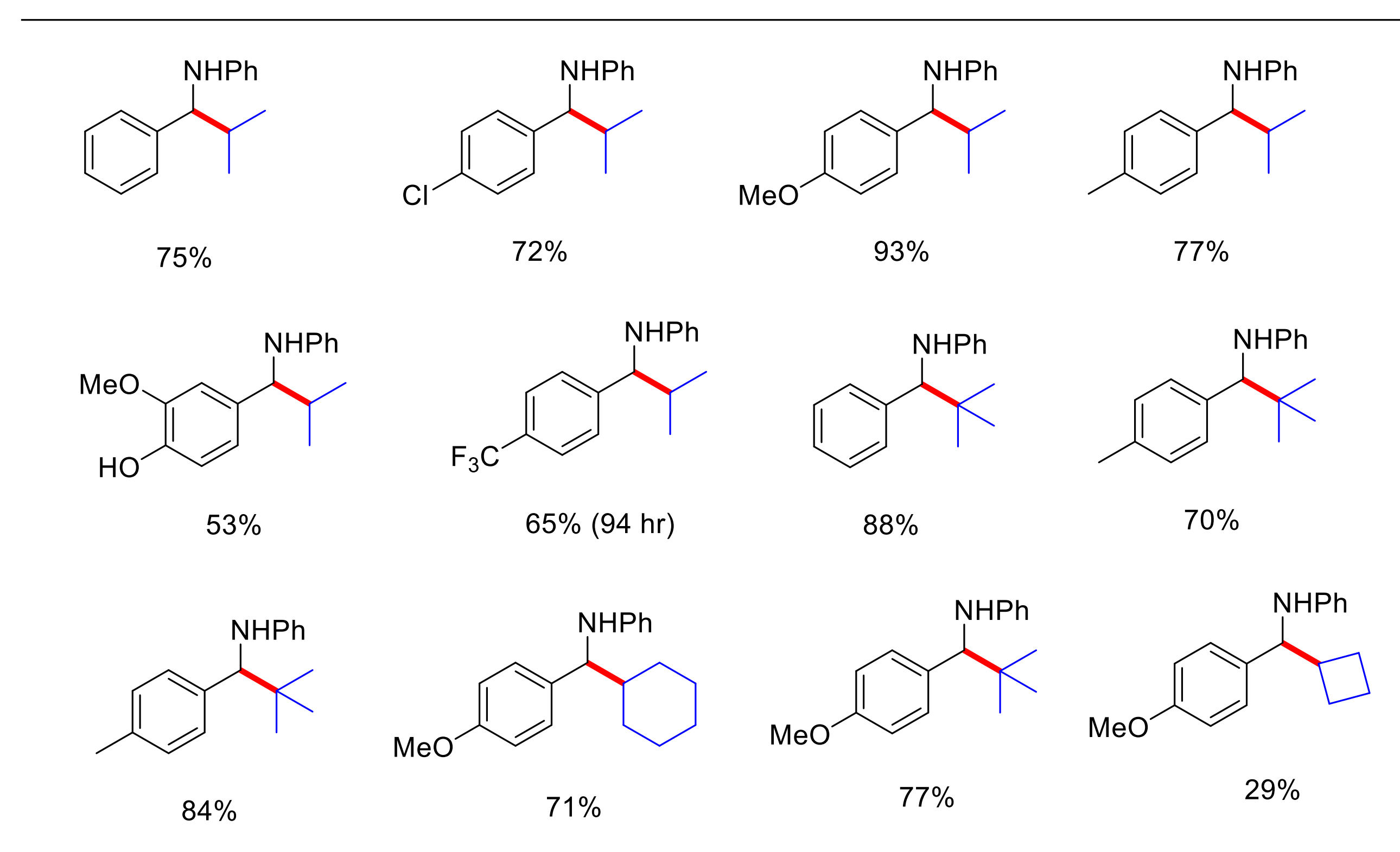


Previous Optimization Studies



- Using the above reaction of potassium isopropyltrifluoroborate with benzaldehyde, evaluation of several alternative catalysts (organic and inorganic) and solvents (CH₂Cl₂, dioxane, THF, CH₃CN, DMF, DMSO) was carried out. Results indicated that, in CH₂Cl₂ solvent, the organic photocatalysts 9-mesityl-10-methylacridinium tetrafluoroborate (*Mes-Acr-Me*) and 9-mesityl-10-phenylacridinium tetrafluoroborate (*Mes-Acr-Ph*) performed equally well in this protocol, and since *Mes-Acr-Me* was much easier for us to obtain commercially, it was chosen for further scope and limitations work.

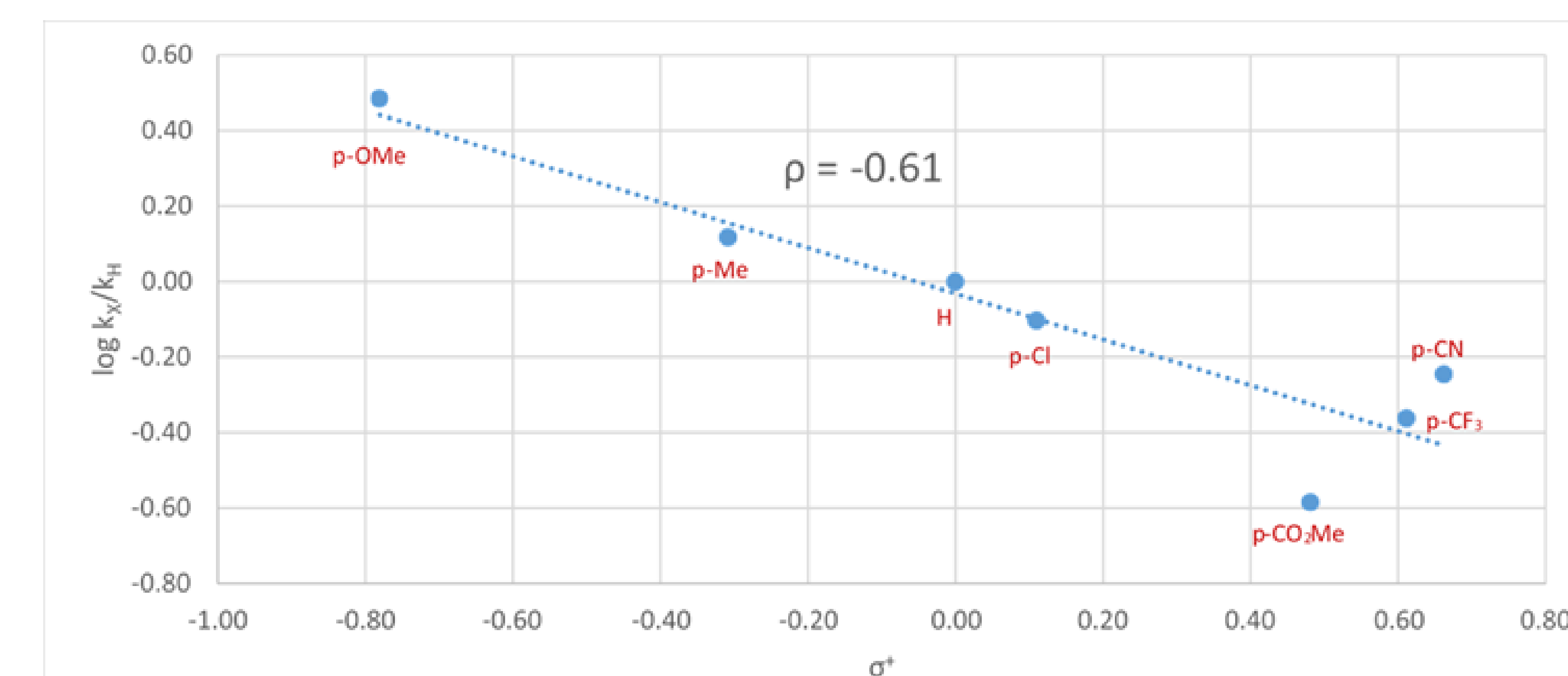
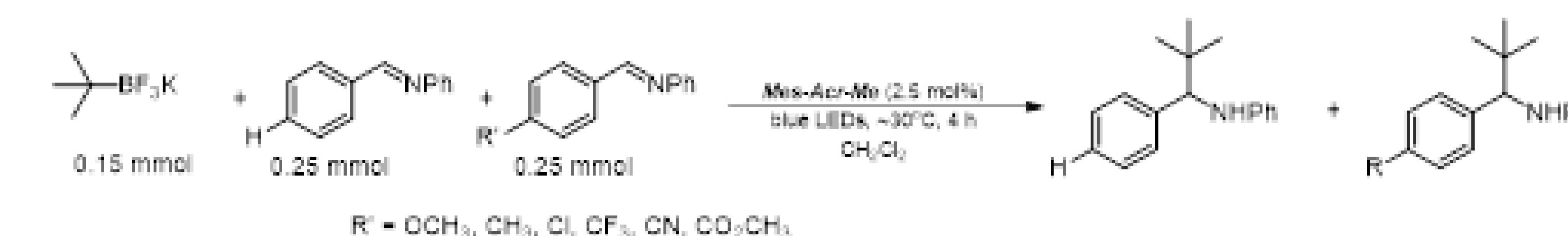
Scope & Limitations



- The protocol appears to be applicable to broad range of substituted aldimines, including those substituted with both electron donating and electron withdrawing groups, although extended reaction time was necessary to complete the reaction with highly electron withdrawing substituents (e. g. CF₃). Secondary, and tertiary potassium alkyltrifluoroborates were also shown to be competent reaction partners. Potassium cyclobutyltrifluoroborate gave a low yield compared to other secondary alkyltrifluoroborates, presumably because it required formation of the less stable cyclobutyl radical.

Substituent Effects (Competition Studies)

- A series of competition experiments, designed to assess the electronic effect of various substituents on the reaction was performed. Equimolar amounts benzaldehyde and a substituted benzaldehyde were reacted with a limited molar amount of potassium *t*-butyltrifluoroborate. The relative rates of product formation were determined by measuring GC product area % ratios.
- Hammett plots were constructed using several substituent constant scales (including σ^+ values developed for free radical reactions; see for example Dust and Arnold *JACS* **1983**, *105*, 1221)
- The best fit (shown in the figure below) was obtained when σ^+ values were used, suggesting that polar effects are more important than radical stabilization effects.
- The small negative value of ρ seems to indicate that the *t*-butyl radical exhibits weakly electrophilic behavior in this reaction.



Acknowledgments

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