Metal-Free sp^2 and sp^3 C-H Functionalization/C-O Bond Forming Reaction

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INTRODUCTION

Hypervalent iodine (III) reagents have been employed as mild oxidants in a variety of C-X bond-forming reactions. However, superstoichiometric amounts of iodine (III) reagents are typically employed, thus generating equimolar amounts of undesired aryl iodides. In 2005, the Ochiai[1] and Kita[2] groups independently reported a catalytic process involving in situ oxidation of iodoarenes by using meta-chloroperbenzoic acid (*m*-CPBA). Since then, this concept has been extensively used for the synthesis of a variety of organic molecules[3]. We herein report our preliminary results on an economical approach to benzolactones from simple benzoic acids via metal-free, aryl iodide-catalized C-O bond formation initiated by Csp^2-H and Csp^3-H functionalization.

RESULTS AND DISCUSSION

After a considerable screening of the experimental variables, we found conditions to effect an intramolecular Csp^2-H functionalization of 2-phenyl substituted benzoic acid derivatives by using aryl iodide as catalyst in the presence of oxidant at room temperature in good to excellent yields. A wide number of functional groups such as nitro, ester, acetoxyl, trifluoromethyl were tolerated under optimized reaction conditions. We also found that 2-pyrrolidinonyl substituted benzoic acids trigger a Csp^3-H bond functionalization by using aryl iodide as catalyst under similar reaction condition in moderate to good yields. Interestingly, Chloro- and bromo-substituted benzoic acids were perfactly tolerated under these reaction conditions.

Figure 1. Iodoarene catalyzed Csp^2-H and Csp^3-H functionalization/C-O bond-formation.

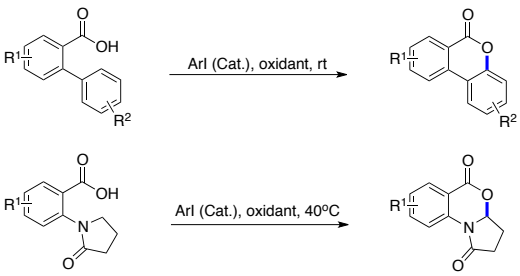
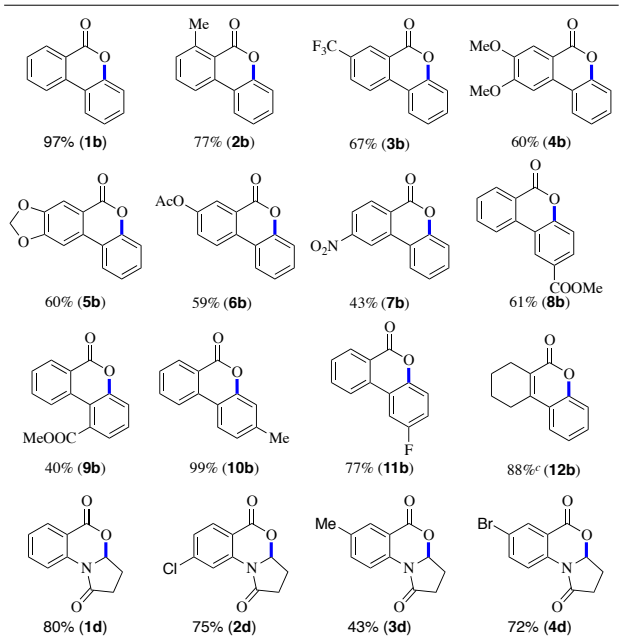


Table 1. Substrate scope of iodoarene catalyzed Csp^2-H and Csp^3-H functionalization/C-O bond-formation.



CONCLUSION

In conclusion, we have disclosed a highly efficient, enviromently-benign method for a metal-free C-O bond-formation via Csp^2-H and Csp^3-H functionaliz-ation. The method is distinguished by its wide scope and mild reaction conditions without the need of metal complexes.

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