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One-pot Suzuki coupling of aromatic amines via visible light photocatalyzed metal free borylation using *t*-BuONO at room temperature

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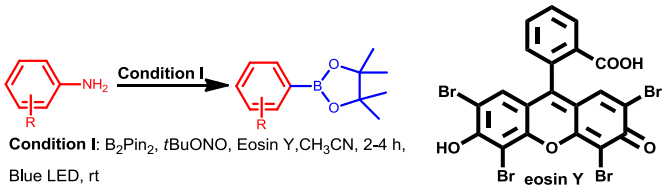
ABSTRACT

A convenient and efficient metal free borylation of aromatic amines has been achieved using tertiary butyl nitrite and B_2Pin_2 (bis(pinacolato) diborane) under irradiation with blue LED light at room temperature. This protocol has been successfully extended to subsequent Suzuki coupling in the same pot. Thus a series of functionalized aryl boronates and biaryls are obtained in high yields in a shorter reaction period starting from relatively cheap aryl amines in one-pot avoiding isolation of potentially unstable and hazardous intermediates.

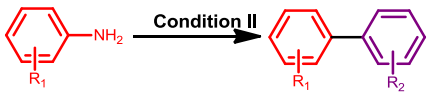
Introduction

Boronates and boronic acids are of much importance in organic synthesis, pharmaceutical research and material science.[1] Suzuki-Miyaura reaction is a landmark in involving aryl boronates and boronic acids in cross coupling reaction.[2] Thus the synthesis of functionalized aryl boron compounds has received much attention in recent years. Traditionally, aryl boronic compounds were prepared by the reaction of aryl Grignard or aryl lithium reagents with trialkyl boronates.[3] However, these reactions are associated with the limitation of substrate scope and tedious reaction procedure. Several transition metal catalyzed borylation have been developed in last decades. In 1995, Miyaura et al. reported palladium catalyzed borylation of aryl halide with HBPin or B_2Pin_2.[4] An alternative Cu catalyzed borylation of aryl halide was also developed.[5] Hartwig and co-workers reported borylation *via* C-H activation by using iridium catalyst,[6] whereas Pucheault and co-workers demonstrated borylation of aryl diazonium salt using iron and Gr-IV metallocene under mild conditions.[7] However, use of expensive ligand, catalyst and the chance of metal contamination in the final product has prompted the necessity of transition metal free less expensive protocols. Wang and co-workers developed a milder metal free one pot borylation with aryl amine and B_2Pin_2 using t-BuONO as a diazotizing agent and benzoyl peroxide as an additive at room temperature.[8a] They have also observed that heating may be used to perform the reaction in absence of BPO.[8b]

In recent times, visible light photocatalysis has emerged as a powerful green tool in organic transformations. Various C-C,[9] C-N,[10] C-P,[11] C-S[12] bond formations have been accomplished by this protocol. The generation of aryl radical from aryl diazonium salt using a photocatalyst in presence of visible light through a single electron transfer process is the key concept in this protocol.[13] Very recently, Yan and co-workers reported a metal free borylation using aryl diazonium tetrafluoroborates, prepared from aryl amine separately, under visible light.[14] Being encouraged by our recent results on one-pot C-H heteroarylation and heteroaryl selenylation from aromatic amine using t-BuONO *via* an aryl/heteroaryl radical,[15] we report here a direct one pot borylation of aryl amines with B_2Pin_2 under visible light (blue LED) using eosin Y as a photocatalyst at room temperature (Scheme 1A) and subsequent same-pot Suzuki coupling leading to the synthesis of biaryls from aryl amines directly (Scheme 1B).



Scheme 1A. Visible light photocatalyzed borylation of aryl amines.



Scheme 1B. One pot visible light photocatalyzed borylation and subsequent Suzuki coupling.

Anilines are attractive starting materials as many of them are commercially available and cheap. They can be also prepared