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## Visible Light Mediated Chemo-selective Oxidation of Benzylic Alcohols

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### ABSTRACT

A highly chemoselective visible light mediated strategy has been developed for oxidation of benzylic alcohols. The method circumvents the use of toxic metal catalysts, high energy light source and operates at room temperature. Furthermore reaction is easily scalable to gram levels.

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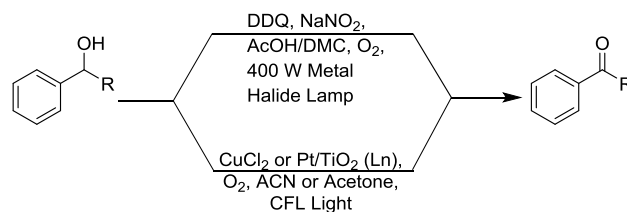
### 1. Introduction

Unarguably the synthesis of carbonyl compounds from alcohols represents one of the most addressed problems in organic synthesis as well as in process and medicinal chemistry. They serve as fundamental intermediates to the construction of a wide variety natural products as well as bioactive molecules.<sup>1</sup> Owing to their importance myriad methods have appeared for their synthesis particularly via oxidation of alcohols.<sup>2</sup> Though, the oxidation of alcohols in general is a very well addressed problem, however chemo-selective oxidation of alcohols,<sup>3</sup> particularly benzyl and allyl alcohol still represents an interesting challenge. Though methods like DDQ/NaNO<sub>2</sub>,<sup>4</sup> DDQ/(MnOAc)<sub>3</sub>,<sup>5</sup> NBS/thiourea,<sup>6</sup> vanadium complexes,<sup>7</sup> K<sub>2</sub>[OsO<sub>2</sub>(OH)<sub>4</sub>]/chloramine-T<sup>8</sup> have been developed in recent years, however, most of these processes employ toxic metal catalysts and require higher temperatures.

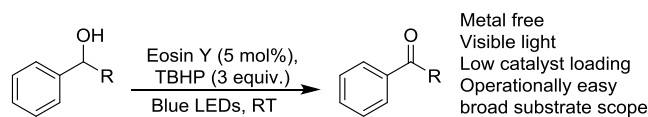
Recently, considerable attention has been focussed towards visible light mediated strategies for the oxidation of alcohols.<sup>9</sup> However, the disadvantage with most of these methods is lack of chemo-selectivity, use of complex or toxic catalytic system and high energy light source, that is, either 400 W metal halide, halide lamp or mercury lamp making them non-ideal for upscaling and industrial applications. For example to evade the use of high energy source, a LED/CFL mediated oxidation of alcohol was reported, which required a rather complex catalytic system comprising of riboflavin tetraacetate and non-heme iron catalyst<sup>10</sup> and lacked selectivity. To overcome the issue of selectivity a well known DDQ/NaNO<sub>2</sub><sup>11</sup> catalytic system was used for chemo-selective oxidation of allyl/benzyl alcohol.

However, the limiting factor of this work is use of 400W metal halide lamp or solar light and use of DDQ, which has a LD50 of 82mg/Kg,<sup>12</sup> release of HCN as a by-product and requires molecular oxygen as well. This limitation to some extent were overcome in a recent visible light mediated report for selective oxidation of benzyl alcohols into benzaldehyde, wherein, the reaction is catalysed by use of CuCl<sub>2</sub> or Pt/TiO<sub>2</sub> in presence of molecular oxygen as an oxidant leading to the formation of visible light responsive complex of Cu(II) with solvent (acetonitrile or acetone).

#### Chemo-selective photocatalytic approaches



#### This Work



**Scheme 1.** Chemo-selective oxidation of benzyl alcohols

The preceding discussion makes it clear that development of a chemo-selective, metal free protocol employing use of a simple visible light source viz., LED or CFL is highly challenging and desirable. In this regard, Eosin Y, a commercially friendly

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