Benzimidazolines as New Acyl Donors for Photocatalytic Transformations of Unactivated Alkenes: Intermolecular Hydroacylation and 3-Component Acylcarboxylation *via* CO_2 Insertion

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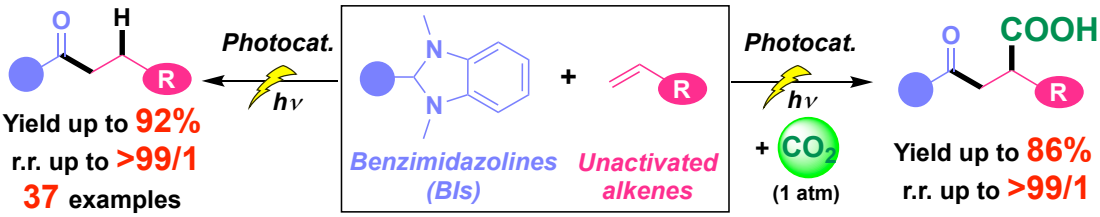
Ketones are versatile and ubiquitous structural motifs found in many biologically active natural products and pharmaceuticals. In recent years, photocatalytic hydroacylation of alkenes received considerable attentions as an attractive method for accessing ketones from abundant and cheap feedstocks under mild conditions[1]. However, there have been only few examples to accomplish the reaction with unactivated alkenes, and the substrates in previous reports were strictly limited to activated alkenes, such as Michael radical acceptors (e.g. acrylates, malonitriles and so on) or 1,1'-disubstituted ethylene derivatives. In this regard, the versatile synthetic methodology enabling hydroacylation of unactivated alkenes is strongly demanded.

Herein, we achieve the first photocatalytic hydroacylation of unactivated alkenes without using acyl radical species, which is the conventional and dominant acyl donors for this kind of reaction[2]. A key to our success was to employ benzimidazolines (BIs) as new acyl donor precursors. We demonstrated that BI radicals, formed by one-electron oxidation of BIs, can function as unprecedented acyl donors for photocatalytic hydroacylation of unactivated alkenes. Moreover, our mild, general and simple system enabled the excellent compatibility with highly sensitive functional groups (i.e. carboxylic acid, boronic acid, phosphine etc.) as well as the broad substrate scopes (37 examples).

Furthermore, we also achieved the first 3-component acylcarboxylation of alkenes with BIs as acyl donors *via* CO_2 insertion. Detailed reaction development, investigations on substrate generalities as well as mechanistic studies will be given in the presentation.



1) M. Zhang, J. Xie, C. Zhu, *Nat. Commun.*, **2018**, *9*, 3517. 2) Y. Saga, Y. Nakayama, M. Kondo, S. Masaoka, *manuscript in preparation.*