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When C–H bond functionalization meets visible-light photoredox catalysis

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ABSTRACT

In recent years, visible-light-mediated C–H bond functionalization has become an emerging field at the forefront of organic synthesis. It is of considerable interest to academic and industrial chemists owing to the atom/step economical features as well as the overall sustainability. In this Letter, we mainly discussed the recent typical examples in sp^2 and sp^3 C–H bond functionalization by means of visible-light photoredox catalysis.

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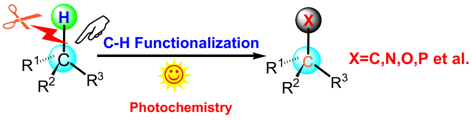
Introduction

The C–H bonds are ubiquitous in organic compounds, but they do not seem to be operative functional groups owing to the low relativities and high thermodynamic stabilities.[1] It is a great challenging task to accomplish highly selective C–H bond functionalization in laboratory.[2] Meanwhile, this strategy represents an atom and step economical process. In the past decade, with the efforts of synthetic chemists, transition-metal, such as Pd,[3–5] Rh,[6,7] Ru,[8,9] Au,[10,11] and Cu[12] catalyzed C–H bond functionalization has become an unparalleled platform to construct target molecules. Despite the great achievements, they usually require high reaction temperature. It indicates that the use of exhaustive and nonrenewal fossil fuels is usually necessary in chemical industry behind this kind of chemistry. Therefore, the development a mild and effective organic transformation with clean and renewable energy is of high interest (Scheme 1).

Solar energy is a unique and renewable resource in nature.[13] In the 20th century, some pioneering researchers have dedicated to converting solar energy into chemical energy for chemical transformations.[14–19] However, organic molecules generally cannot absorb visible-light efficiently, thereby, visible-light-induced organic reactions were not popular until 2008 when a milestone made by MacMillan[20] and Yoon[21] demonstrated the utility of visible light to drive organic transformations for the formation of new chemical bonds (C–C and C–hetero). In the past five years, owing to its significant advances in energy-saving and environmentally benign features, visible-light photoredox catalysis has witnessed rapid development and attracted considerable attention in both academia and industry. Up to date, several important reviews have summarized the fundamental organic transformations.[22–28] In this Letter, we will highlight the recent development of visible-light photocatalytic sp^2 and sp^3 C–H bond functionalization (Scheme 2).



Scheme 1. Photochemical C–H bond functionalization.

Visible-light-mediated sp^3 C–H bond functionalization

Iminium-ions-forming

At the beginning of 2010, Stephenson and co-workers reported the first visible-light-induced sp^3 C–H bond functionalization adjacent to nitrogen atom.[29] Compared with transition-metal-catalyzed this transformation, it can occur without any synthetic oxidants (such as TBHP, H_2O_2). Moreover, the visible-light-promoted sp^3 C–H functionalization of nonbenzylic amine is more favorable than the known oxidative aza-Henry reaction (CuBr/

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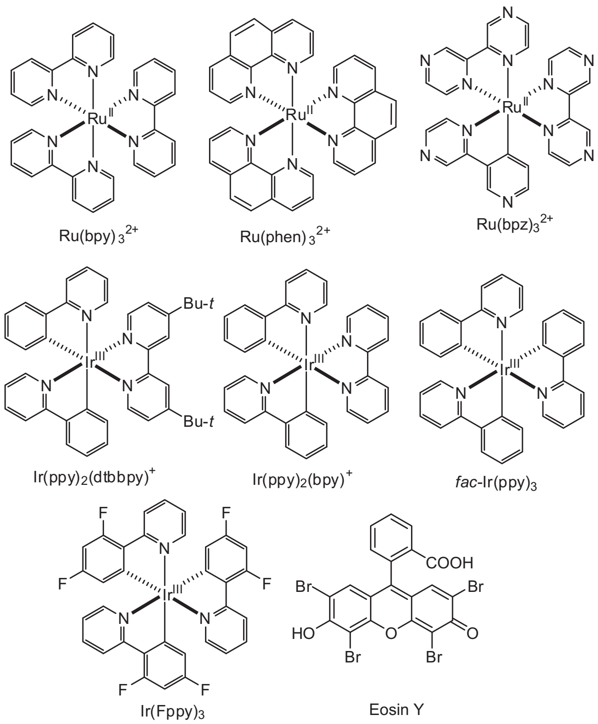
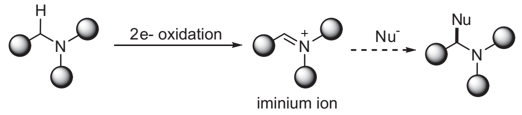
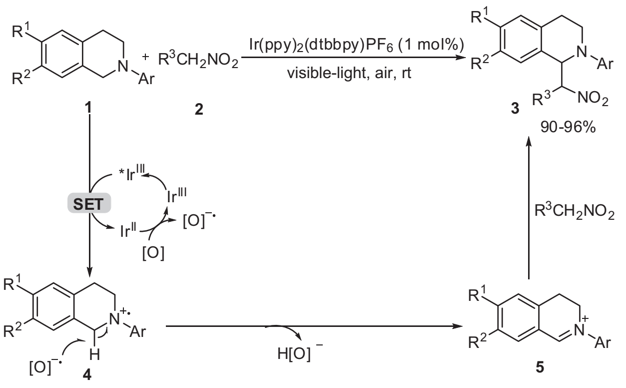


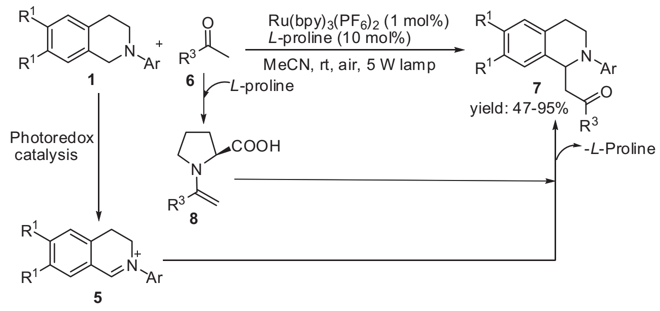
Scheme 2. Typical photocatalysts.



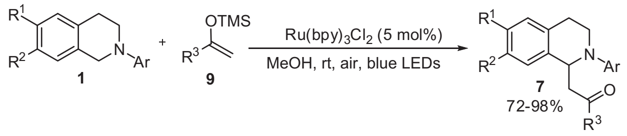
Scheme 3. Visible-light-mediated sp^3 C–H bond functionalization via iminium-ions-forming.



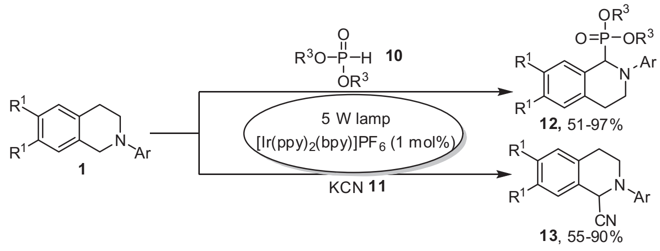
Scheme 4. The first visible-light-mediated sp^3 C–H functionalization adjacent to nitrogen atom.



Scheme 5. Photocatalytic oxidative Mannich reaction with ketones.



Scheme 6. Photocatalytic oxidative Mannich reaction with enol silanes.



Scheme 7. Photoredox catalytic cyanation and phospholation of sp^3 C–H bonds.

TBHP) (Scheme 3).[30] The control experiments suggest that both light and photocatalyst are essential for the successful conversion of aza-Henry reaction. The fluorescence quenching experiments demonstrate that *N*-ph-1,2,3,4-tetrahydroisoquinoline is a reductive quencher of the excited state photoredox catalyst. A possible mechanism is listed in Scheme 4. Firstly, a radical cation **4** can be formed via SET (single electron transfer) process from tertiary amines **1** to the excited-state $^{*}Ir(ppy)_2(dtbbpy)PF_6$. Then, the reactive iminium ions **5** are generated through hydrogen atom abstraction, which can be easily trapped by nucleophilic nitroalkanes to give the desired aza-Henry reaction product **3**. The photoredox catalytic cycle is accomplished by oxidizing Ir^{II} to ground state Ir^{III} in the presence of suitable electron acceptors (e.g., CH_3NO_2, O_2).

Subsequently, Rueping et al. finished visible-light-promoted oxidative Mannich reactions of tertiary amines by combining photoredox and organocatalysis under mild reaction conditions.[31] In this reaction, a dual activation system was adopted. The photoredox catalysis can convert tertiary amines **1** to the corresponding iminium ion **5**, and L-proline is a well-known aminocatalyst for the generation of highly nucleophilic enamine intermediate **8**. Finally, the enamine **8** can rapidly attack **5**, producing the β-amino ketone **7**. After this publication, Rueping et al. have developed visible-light-induced alkynylation of tetrahydroisoquinoline derivatives by combining photoredox catalysis and copper catalysis (Scheme 5).[32]

Alternatively, Xia and colleagues have also contributed an elegant access to β-amino ketones with silyl enol ether by means of visible-light photoredox catalysis (Scheme 6).[33] Unlike Rueping's design, they firstly converted methyl ketones to silyl enol ether, and most C–C coupling products can be obtained in good to excellent yields (up to 98%). A fly in the ointment for the oxidative Mannich reaction is that other ketones except methyl ketones give unsatisfactory results and an asymmetric version is highly desirable.

In 2011, Rueping et al. continued to report other examples by means of photoredox catalysis. They developed photocatalytic oxidative α-cyanation[34] and α-phospholation[35] of tertiary amines **1** under mild reaction conditions (Scheme 7). Furthermore, they found that non-benylic amines can also undergo visible-light-mediated Strecker reaction smoothly under the optimal reaction conditions, which compares much favorably with the known methods.

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