



## Digest Paper

## Olefin difunctionalizations via visible light photocatalysis



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## ABSTRACT

Due to unique redox property, visible light photoredox catalysis is emerging as a powerful tool in synthetic organic chemistry. This review summarizes the previous researches employing visible light photoredox catalysts for difunctionalization of alkenes.

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## Introduction

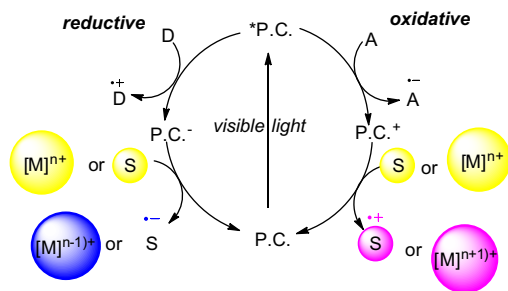
Functionalized organic compounds play a crucial role in many aspects in daily life, such as pharmaceuticals, agrochemicals, and material science. With the development of organic chemistry, a lot of protocols aiming at synthesizing these compounds have been explored. Among these, difunctionalization of alkenes is a rapid and straightforward strategy for synthesizing functionalized compounds,<sup>1</sup> furthermore, different functional groups are capable to be further transferred into diverse organic skeletons. On the other hand, irreversible sources such as coal, oil, and gas are in an increasing consumption with the development of society. Energy crisis is getting more and more serious all over the world, consequently sustainable organic transformation has been a direct target for scientists. As a renewable and simple accessible energy, solar

energy is an ideal kind of energy without any pollution or toxicity, and can be applied to generate electric energy,<sup>2</sup> split water,<sup>3</sup> or reduce carbon dioxide.<sup>4</sup> Since 2008, due to its unique redox property<sup>5</sup> (Table 1), visible light photoredox catalysis has been widely applied into organic transformations,<sup>6</sup> such as synthetic methodologies, synthesis of natural products,<sup>7</sup> enantioselective catalysis,<sup>8</sup> and polymerization.<sup>9</sup> The ground state photocatalyst could absorb visible light to convert to photoexcited state (\*P.C.) which could undergo redox pathway or energy transfer pathway. In the reductive quench pathway, the \*P.C. could trap an electron from the electron donor to generate P.C.<sup>-</sup> which is a good reductant for one-electron reducing the substrate (S) or transition metal (M<sup>n+</sup>). Meanwhile, the photocatalyst was regenerated and reduced species radical anion S<sup>-</sup> or M<sup>(n-1)+</sup> could undergo further transformations. In oxidative quench pathway, the \*P.C. could lose an electron to the electron acceptor to generate P.C.<sup>+</sup> which is a good oxidant for one-electron oxidizing the substrate (S) or transition metal

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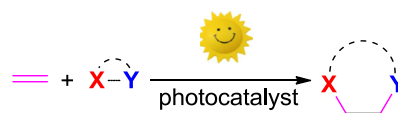
**Table 1**  
Redox potentials of some visible light photocatalysts

Entry	Photocatalyst	$E_{1/2}$ ( $M^+/M^*$ )	$E_{1/2}$ ( $M^+/M^-$ )	$E_{1/2}$ ( $M^+/M$ )	$E_{1/2}$ ( $M/M^-$ )
1	Ru(bpy) $_3^{2+}$	-0.81	+0.77	+1.29	-1.33
2	Ru(phen) $_3^{2+}$	-0.87	+0.82	+1.26	-1.36
3	Ir[dF(CF $_3$ )ppy] $_2$ (dtbbpy) $^+$	-0.89	+1.21	+1.69	-1.37
4	Ir(ppy) $_2$ (dtbbpy) $^+$	-0.96	+0.66	+1.21	-1.51
5	fac-Ir(ppy) $_3$	-1.73	+0.31	+0.77	-2.19
6	Cu(dap) $_2^+$	-1.43		+0.62	

**Scheme 1.** Redox photocatalysts via reductive or oxidative pathway.

( $M^{n+}$ ). Simultaneously, the photocatalyst was generated and oxidative species radical cation  $S^+$  or  $M^{(n+1)+}$  could undergo further transformations. Additionally, the protocol is operationally simple under mild conditions with low photocatalyst loading. This review focuses on difunctionalization of carbon–carbon double bonds using visible light photoredox catalysts (Schemes 1 and 2). This kind of reaction can be described as Scheme 3.

This review summarizes the previous researches employing visible light photoredox catalysts to the difunctionalization of alkenes, not including the cycloadditions via visible light photocatalysis, which has already been summarized by Yoon.<sup>10</sup> The hydroelementation of alkenes is not included in this review. This review is divided

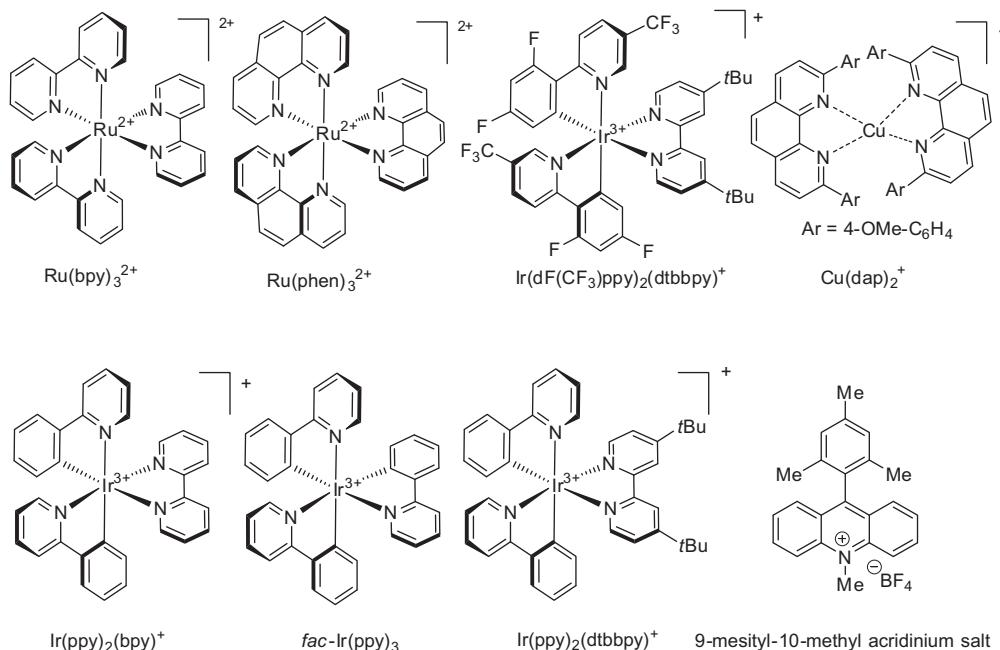
**Scheme 3.** Photo-difunctionalization of alkenes.

into four categories according to initiated radicals generating from different sources such as activated alkyl halides, electrophilic  $CF_3$  reagents, diazonium salts and active amides. It is hoped that the collective presentation of reaction discovery will provide a class of methodologies for difunctionalization of alkenes in the presence of photoredox catalysts. Basic information about the topic is disclosed in detail, however, an in-depth discussion in these field is outside the range of this review.

### Activated alkyl halides

Atom transfer radical addition (ATRA) haloalkanes onto alkenes offers an extremely direct method to simultaneously form a new carbon–carbon bond and a new carbon–halogen bond. The development of ATRA has made great contributions to synthetic chemistry, especially alkene difunctionalizations.<sup>11</sup> In typical ATRA, the initiators including toxic and hazardous reagents, or the protocols employing harsh conditions could not tolerate broad functional groups. Due to its unique redox property, visible light photocatalysis has a great potential to promote the ATRA reaction (Scheme 4).

Stephenson demonstrated that visible light could perform ATRA between activated halides and alkenes utilizing visible light photosensitizer to afford haloalkylation products in 65–99% yields.<sup>12</sup> The reaction is operationally simple under mild reaction conditions, which is capable of tolerating a variety of functional groups such as free alcohols, esters, ethers, silyl ethers, halides, enones, and carbamates. Additionally, perfluoroalkyl halides are good partners and could react with olefins to afford fluorinated compounds which have particular value in medicinal chemistry, agrochemicals, and material science.<sup>13</sup> Later, the same lab studied this reaction in terms of photocatalysts, solvents and substrates,<sup>14</sup> then a much

**Scheme 2.** Commonly used photocatalysts for difunctionalization of alkenes.

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