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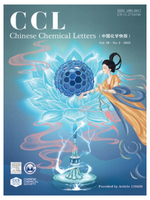

Homogeneous catalysis and heterogeneous separation: Ionic liquids as recyclable photocatalysts for hydroacylation of olefins

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ABSTRACT

The photoinduced ligand-to-metal charge transfer (LMCT) process has been extensively investigated, however, the recovery of photocatalysts has remained a persistent challenge in the field. In light of this issue, a novel approach involving the development of iron-based ionic liquids as photocatalysts has been pursued for the first time, with the goal of simultaneously facilitating the LMCT process and addressing the issue of photocatalyst recovery. Remarkably, the iron-based ionic liquid 1–butyl–3-methylimidazolium tetrachloroferrate (C_4mim-$FeCl_4$) demonstrates exceptional recyclability and stability for the photocatalytic hydroacylation of olefins. This study will pave the way for new approaches to photocatalytic organic synthesis using ionic liquids as recyclable photocatalysts.

Photoredox catalysis has been considered a highly effective strategy for generating active radical intermediates under mild conditions over the past few decades, causing widespread attention from synthetic chemists [1-7]. Currently, precious transition-metal catalysts such as iridium and ruthenium play important roles in photocatalytic organic reactions [8-13]. However, these precious transition-metal catalysts have some boundedness, such as high cost and sensitivity to oxygen, which might limit their application in organic synthesis. In this context, the advancement of cost-effective photocatalytic systems has been an enduring objective within the field of photocatalytic organic chemistry.

Recently, photoinduced ligand-to-metal charge transfer (LMCT), an electronic transition from the filling orbit of the ligand to the empty orbit of the metal center, has been a powerful photocatalytic platform to achieve the construction of organic compounds [14-19]. Compared to classical iridium and ruthenium complexes, LMCT employed inexpensive and readily available metal complexes (Cu, Fe, Ce, *etc.*) as photocatalysts, the high-valent metal complexes were excited with the irradiation of light to obtain active radicals, further participating in the relevant transformation (Scheme 1A) [20-25]. While many research groups have made significant contributions in this field [26-32], the recycling and reutilization of homogeneous photocatalysts still face significant challenges.

Indeed, over the past few years, our group has developed several heterogeneous photocatalytic systems for organic reactions based on semiconductor catalysis [33-35]. However, in these processes, photocatalytic reactions occur on the surface of heterogeneous photocatalysts, often resulting in relatively low efficiency. Therefore, we aim to develop a novel photocatalytic system that combines the high efficiency of homogeneous catalysis with the recyclability characteristic of heterogeneous catalysts.

Ionic liquids (ILs) are one of the most promising green solvents and catalysts of the 21st century due to their potential advantages including non-volatile, good chemical and thermal stability, recyclable, and environmentally friendly [36-42]. The designability of ILs, changing the combination of anions and cations to synthesize the required functionalized ILs, provides us with ideas for designing the required photocatalysts [43-47]. Based on the mechanism of photocatalysts in the LMCT process, the high-valent metal halides could be regarded as the anionic portion of ILs. Additionally, iron, as the most abundant transition metal element in the earth's crust, has become one of the most concerned transition metal catalysts due to its inexpensiveness, easy availability, good biocompatibility, and environmental friendliness [15,48-50]. Consequently, we herein report the first example of ionic liquids as recyclable photocatalysts for organic reactions. By using the iron(III)-based IL photocatalyst, a light-induced hydroacylation of alkenes with various aldehydes was realized via the LMCT process (Scheme 1B). Notably, the IL photocatalyst exhibits outstanding recyclability without notable decomposition after reaction, suggesting its great potential for the sustainable development of organic

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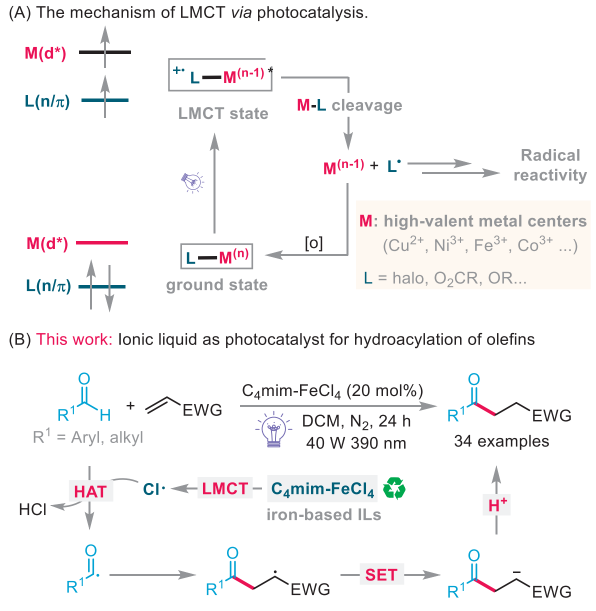
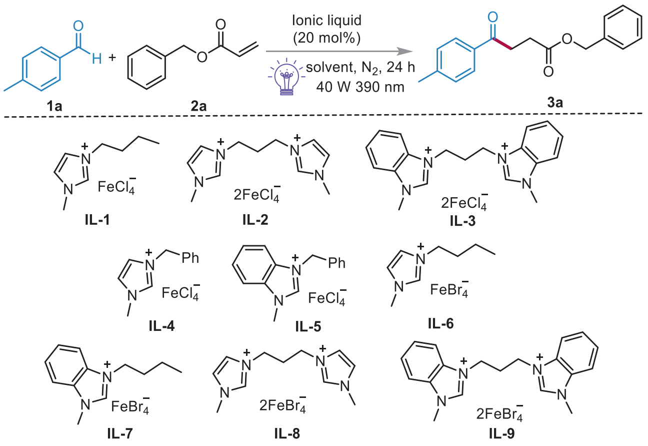


Scheme 1. Photoinduced ligand-to-metal charge transfer (LMCT) process.

Table 1
Optimization of reaction conditions.[a]



Entry	Ionic liquid	Solvent	Yield (%)[b]
1	**IL-1**	DCM	78
2	**IL-1**	DCE	65
3	**IL-1**	CH_3CN	23
4	**IL-1**	EtOAc	56
5	**IL-1**	acetone	33
6	**IL-1**	PhCl	59
7	**IL-2**	DCM	61
8	**IL-3**	DCM	47
9	**IL-4**	DCM	51
10	**IL-5**	DCM	55
11	**IL-6**	DCM	N.D.
12	**IL-7**	DCM	trace
13	**IL-8**	DCM	19
14	**IL-9**	DCM	trace
15[c]	**IL-1**	DCM	37
16[d]	**IL-1**	DCM	58
17	–-	DCM	N.D.
18[e]	**IL-1**	DCM	N.D.

[a] Reaction conditions: **1a** (0.6 mmol), **2a** (0.2 mmol), ionic liquid (20 mol%), solvent (2 mL), 40 W purple Kessil LED lamp (390 nm), under N_2 atmosphere for 24 h. N.D. = not detection.

[b] Isolated yields were given.

[c] 10 W purple Kessil LED lamp (390 nm).

[d] 20 W purple Kessil LED lamp (390 nm).

[e] In dark.

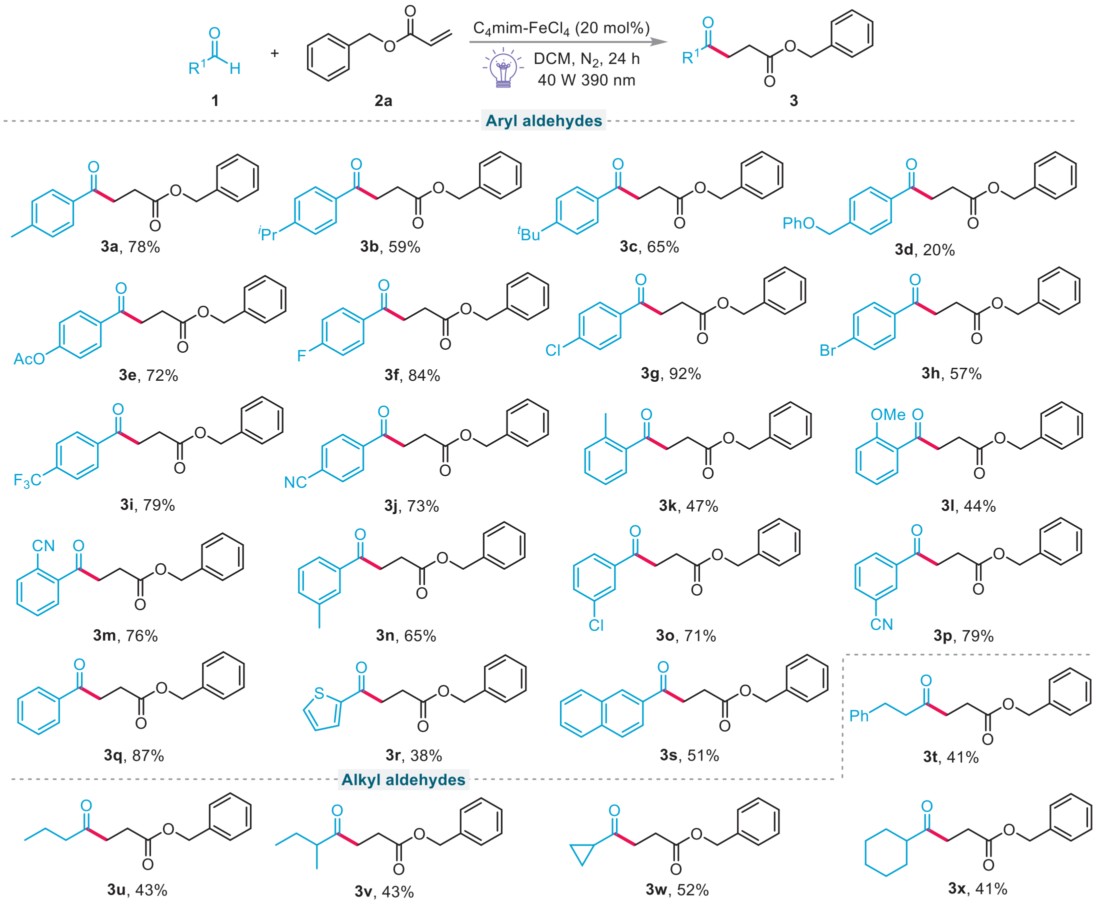
synthetic chemistry. Additionally, the remarkable advantages of our developed universal methodology are broad substrate scope, mild reaction conditions, and easy scale-up.

The experiments were started using *p*-tolualdehyde **1a**, and benzyl acrylate **2a** as the model substrates, as summarized in Table 1. The model reaction was carried out by employing 1–butyl–3-methylimidazolium tetrachloroferrate (C_4mim-$FeCl_4$) (**IL-1**) as a photocatalyst, and DCM as reaction solvent under N_2 atmosphere with the irradiation of 40 W purple LED (390 nm) for 24 h. Fortunately, the desired product **3a** was obtained in a 78% isolated yield (entry 1). Subsequently, various solvents including DCE, CH_3CN, EtOAc, acetone, and PhCl were screened, and the results indicated that the best solvent was DCM (entries 2–6). To further enhance the reaction efficiency, a series of ILs were evaluated, it is regrettable that the yield of the target product did not further increase (entries 7–14). As the light intensity decreases, the yield of the target product also further decreases (entries 15 and 16). The results of the control experiments revealed that when there was an absence of light or IL in the photocatalytic reaction, the reaction could not proceed smoothly (entries 17 and 18), suggesting that light or IL played a vital role in this photocatalytic transformation. Consequently, the optimal reaction conditions were illustrated as follows: **1a** (0.6 mmol), **2a** (0.2 mmol), C_4mim-$FeCl_4$ (20 mol%), and DCM (2 mL) were stirred under N_2 atmosphere with the irradiation of 40 W purple LED (390 nm) for 24 h.

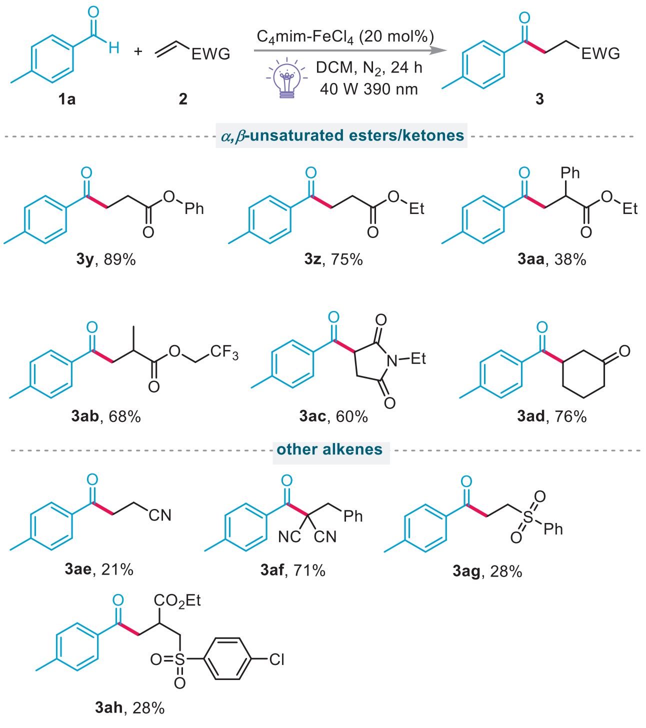
With the optimal reaction conditions in hand, the scope of aldehydes was investigated (Scheme 2). Benzaldehydes bearing electron-donating groups (–Me, –iPr, –^{t}Bu, –CH_2OPh, –OAc) and electron-withdrawing substituents (–F, –Cl, –Br, –CF_3, –CN) at the *para*-position all reacted smoothly with **2a**, leading to the corresponding products **3a**-**3j** in 20%–92% yields. Additionally, the *meta*- and *ortho*-substituted benzaldehydes were suitable for this photocatalytic system to afford the target products **3k**-**3p** in moderate to good yields (44%–79%). When benzaldehyde without any substituents was employed as a reaction substrate, the product **3q** could be generated in an isolated yield of 87%. It was worth mentioning that 2-thiophenecarboxaldehyde and 2-naphthaldehyde were compatible with the reaction system, obtaining the target products **3r** and **3s** in 38% and 51% yield, respectively. More importantly, various alkyl aldehydes including linear chains and rings could be also considered as feasible substrates to generate the products **3t**-**3x** in 41%–52% yields.

Afterward, the scope of alkenes was also explored. As shown in Scheme 3, the reactivity of diverse substituted alkenes derived from acrylate was surveyed, both aryl acrylates and alkyl acrylates could react smoothly with **1a** to deliver the products **3y**-**3ab** in 38%–89% yields. Then, the products **3ac**-**3ad** were successfully prepared in moderate to good yields (60%–76%), suggesting α,β-unsaturated ketones could also be applied to this photocatalytic methodology. To further highlight the diversity and efficiency of our strategy, other alkenes including alkenylnitriles and alkenylsulfones were also amenable, obtaining the desired products **3ae**-**3ah** in 21%–71% yields. However, some unactivated alkenes, including styrene, and 1-pentene, were not suitable for the reaction system (Fig. S2 in Supporting information).

Additionally, a scale-up reaction between **1a** and **2a** was carried out under standard conditions (Fig. S3 in Supporting information). The desired product **3a** could be isolated in 66% yield (372.2 mg) (Scheme 4A), exhibiting great potential in practical applications. Considering the synthetic versatility of 1,4-dicarbonyl compounds, the transformations of **3a** were further performed (Scheme 4B). Condensation of **3a** with hydrazine hydrate led to obtaining the target 4,5-dihydropyridazin-3(2*H*)-one product **4** in 80%



Scheme 2. Substrate scope of aldehydes.



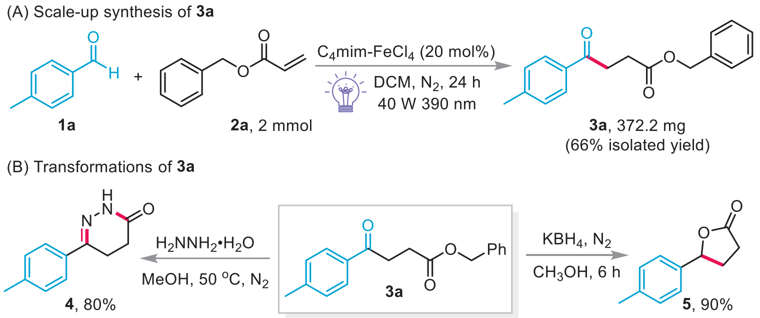
Scheme 3. Substrate the scope of alkenes.

isolated yield. **3a** could also undergo reduction by KBH_4, followed by condensation to form five-membered cyclic lactone **5** in 90% yield.

To evaluate the sensitivity of this photocatalytic system, a series of parameters including concentration, water level, reaction time, light intensity, air atmosphere, and scale were tested based on standard conditions (Table S5 in Supporting information). It can be seen from Fig. 1 that the N_2 atmosphere and light intensity were a vital point for the smooth progress of the photoreaction.

Interestingly, in comparison to traditional heterogeneous catalysts, the homogeneous C_4mim-$FeCl_4$ exhibits superior solubility within the reaction system and can be easily recovered after the reaction. As illustrated in Fig. 2A, the C_4mim-$FeCl_4$ and the target product **3a** could be easily separated by removing the reaction solvent (DCM) and washing with diethyl ether from the homogeneous catalytic system. Additionally, the recycling experiments of C_4mim-$FeCl_4$ were performed to verify the stability and reusability of the photocatalytic system. The catalytic reactivity of C_4mim-$FeCl_4$ could still be maintained after 5 runs (Fig. 2B). Meanwhile, the UV–vis of fresh C_4mim-$FeCl_4$ and recovered C_4mim-$FeCl_4$ was displayed in Fig. 2C, the recovered C_4mim-$FeCl_4$ remains almost unchanged. These results indicated that C_4mim-$FeCl_4$ was an effective and stable photocatalyst for transformation.

Subsequently, a series of radical trapping experiments were performed. When the radical scavengers 2,2,6,6-tetramethylpiperidin-1-yl-oxidanyl (TEMPO) or 2,6-di–*tert*–butyl–4-methylphenol (BHT) were respectively added to the model reaction, the photoreaction was significantly suppressed, suggesting that this may involve a radical pathway (Fig. 3A). Additionally, the radical adducts **A** and **B** were detected by high-resolution mass spectroscopy (HRMS), sug-



Scheme 4. Synthetic applications.

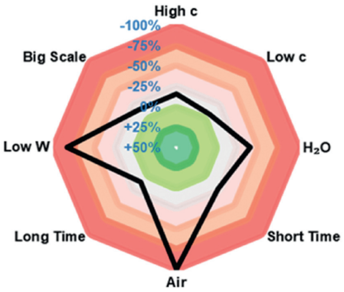


Fig. 1. Sensitivity assessment.

gesting the generation of acyl radicals. Chlorine radicals were confirmed by observing the radical adducts **C** (Fig. S10 in Supporting information).

To further explore the mechanism of photoreaction, we proceed with the UV–vis absorbance experiments by controlling the irradiation time of C_4mim-$FeCl_4$. We found that $[Fe^{III}Cl_4]^-$ could be converted into $[Fe^{II}Cl_4]^{2-}$ under the irradiation of the purple light (390 nm), indicating the generation of chlorine radicals in the photoreaction (Fig. 3B).

Based on the above detailed experimental results and relevant literature reports [51], a possible mechanism was proposed (Fig. 3C). Initially, the high-valent metal complex $[Fe^{III}Cl_4]^-$ was excited to $^*[Fe^{III}Cl_4]^-$ under the irradiation of purple light, undergoing a LMCT process to form $[Fe^{II}Cl_3]^-$ and key chlorine radical. Then, the chlorine radical could react with aldehydes **1** *via* hydrogen atom transfer (HAT), leading to the acyl radical **4**. The radical **4** was added to alkenes to obtain the radical intermediate **5**, which was further reduced by $[Fe^{II}Cl_3]^-$ *via* a single-electron transfer (SET) process to form the anion **6** and $[Fe^{III}Cl_4]^-$. Finally, **6** was protonated to generate the desired products **3**.

In conclusion, our study presents an unprecedented example of utilizing an ionic liquid as a recyclable photocatalyst for the light-induced hydroacylation of alkenes through the photoinduced LMCT process. Building upon the principles of homogeneous catalysis and heterogeneous separation, the ionic liquid photocatalyst demonstrates excellent catalytic efficiency and functional group compatibility, enabling easy separation and recycling through phase behavior. Various target products including ketones, 1,3-dicarbonyl compounds, and 1,4-dicarbonyl compounds could be synthesized under mild conditions, wherein 1,4-dicarbonyl compounds could serve as significant intermediates in organic transformation. Notably, the iron-based ionic liquid exhibits good recyclability and stability without obvious decomposition in this photoreaction. Our discovery will pave the way for new approaches to photocatalytic organic synthesis using ionic liquids as recyclable and versatile photocatalysts.

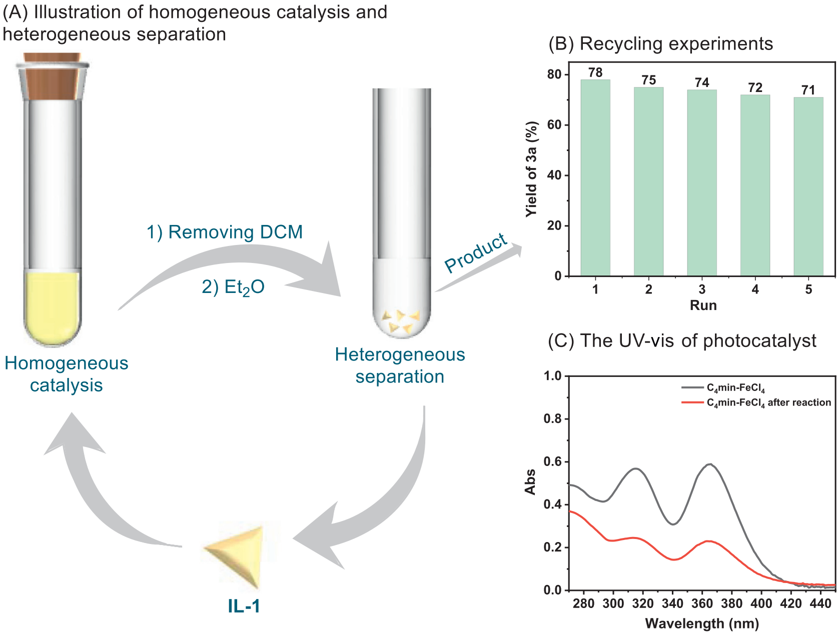


Fig. 2. Recovery of photocatalyst C_4mim-$FeCl_4$ (**IL-1**).

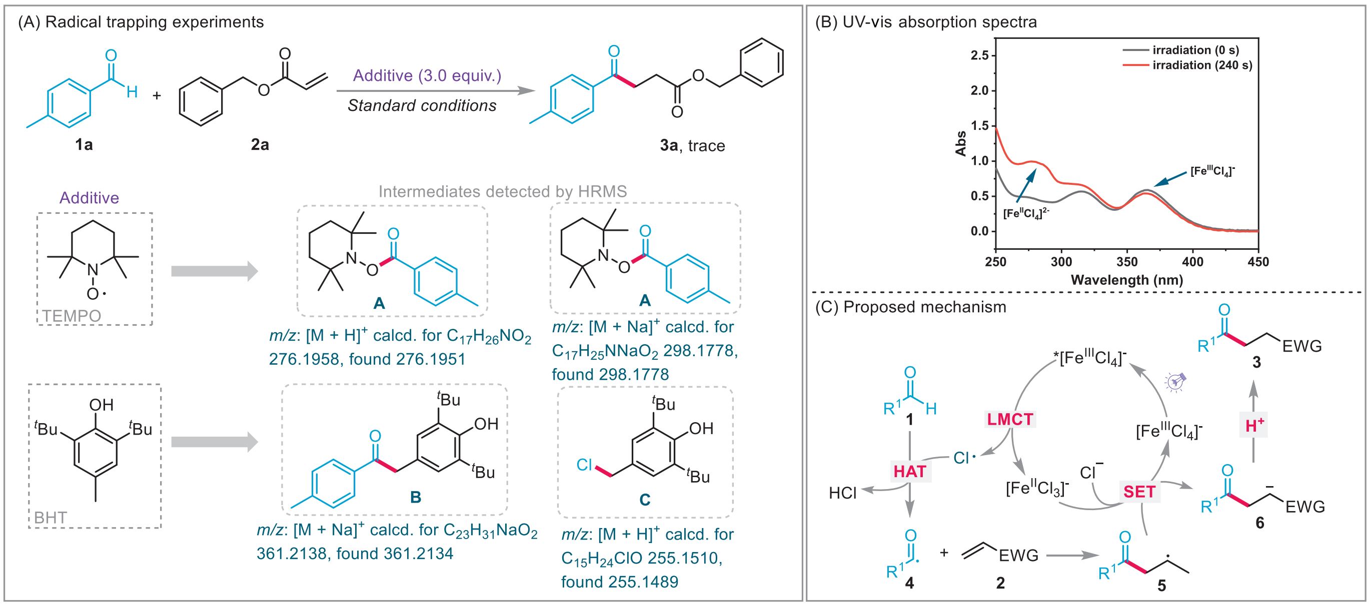


Fig. 3. Mechanistic studies.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Hao-Cong Li: Writing – original draft, Methodology, Investigation. **Ming Zhang:** Methodology, Investigation. **Qiyan Lv:** Writing – review & editing, Supervision, Data curation. **Kai Sun:** Methodology. **Xiao-Lan Chen:** Writing – review & editing, Supervision, Investigation. **Lingbo Qu:** Data curation. **Bing Yu:** Writing – review & editing, Supervision, Investigation, Data curation.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2024.110579.

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