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Photoinduced iron-catalyzed direct coupling of cycloalkanes and *N*-sulfonyl ketimines using air as oxidant

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Abstract

An iron-catalyzed direct coupling of cycloalkanes and *N*-sulfonyl ketimines enabled by photoinduced ligand-to-metal charge transfer (LMCT) and energy transfer has been developed. This reaction demonstrates high atom economy and operates under eco-friendly, mild conditions with a good substrate scope. A notable aspect of this study is the proposal of a potential radical-radical coupling mechanism, involving a cycloalkyl radical and a cation radical intermediate, which may lead to C–C bond formation. This discovery significantly enhances our comprehension of reaction mechanisms in this domain.

Keywords: Radical coupling, iron photocatalysis, *N*-sulfonyl ketimines, LMCT

INTRODUCTION

Carbon-centered radicals are fascinating and highly active neutral intermediates that have been extensively used in organic chemistry and medical chemistry^[1]. Particularly, mild conditions for the generation of unstable alkyl radicals and the precise control for ensuing reaction are highly sought in organic synthesis. Over the last few decades, advances in photocatalysis have enabled novel radical synthetic methodologies for molecular skeleton construction. Among these excellent transformations, diverse alkyl radicals can be



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efficiently generated upon visible light irradiation. For instance, alkyl carboxylic acids and their derivatives^[2-5], alkyl halides^[6], alkyl silicates^[7], alkyltrifluoroborates^[8,9], α -silyl amines^[10], cycloketone oxime esters^[11], Katritzky pyridinium salts^[12,13] could serve as effective alkyl radical precursors to give the alkyl radicals under single-electron-transfer by photocatalysis [Figure 1A]. Though significant progress has been made in this area, hydrocarbons were regarded as the most appealing and economical alkyl source for alkylation reactions. However, challenges remain due to the inert nature of C(sp³)–H of alkanes and unpredictable chemoselectivity of alkyl radicals, necessitating the development of greener and more efficient catalytic systems.

Alkylated heteroarenes are commonly found in pharmaceuticals, natural products, and ligand scaffolds. They are widely distributed in various bioactive compounds, drugs, and molecular frameworks, making them a prevalent and essential motif in the field of chemistry and drug discovery^[14,15]. Significant attention has been devoted to the alkylation of valuable heteroarenes, reflecting its importance in various synthetic and pharmaceutical applications^[16-27]. In particular, *N*-sulfonyl ketimines are widely found in bioactive molecules and pharmaceuticals [Figure 1B]^[28,29]. Owing to their unique properties, C4-alkylation of sulfonyl ketimines has attracted widespread attention. In 2021, Wang *et al.* carried out groundbreaking work on the first silver-catalyzed *N*-sulfonyl ketimine alkylation reaction using carboxylic acid as an alkyl radical precursor^[30]. Subsequently, methods for alkylating *N*-sulfonyl ketimines with cycloalkanol^[31], alkylaldehydes^[32], and alkylboronic acids^[33] were successfully developed [Figure 1C]. However, these methods have limitations, such as the necessity for noble metal catalysis, excessive oxidants, high temperatures, and pre-activated substrates, which restrict the widespread application of this reaction. The cross-dehydrogenative coupling (CDC) reaction has proven to be a powerful tool for constructing a variety of structures, including those accessed via Csp²–Csp³ cross-coupling. However, the research on the direct CDC reaction of *N*-sulfonyl ketimines with alkanes has been limited. In 2023, Song *et al.* reported the visible light-induced alkylation of *N*-sulfonyl ketimine with alkanes as an alkyl precursor in the presence of H₂O₂ as the oxidant^[34]. Therefore, developing a sustainable and practical methodology for the synthesis of 4-alkylated *N*-sulfonyl ketimines using simple alkanes as an alkyl source is highly desired.

The radical-radical coupling reaction, in contrast to the classical radical addition pathway restricted to unsaturated bonds and requiring high activation energy, has an activation energy close to zero^[35]. This enables the reaction to occur under mild conditions. Therefore, we hypothesized that, under photoredox conditions, alkanes could generate alkyl radicals via a ligand-to-metal charge transfer (LMCT) process. Additionally, the single-electron transfer (SET) process could generate *N*-sulfonyl ketimine cation radicals, which could facilitate the direct radical-radical coupling to construct alkylated *N*-sulfonyl ketimines. Building upon the principles of sustainable chemistry, we report a photoinduced Fe-catalyzed C–H alkylation of *N*-sulfonyl ketimines with simple alkanes by using air as an oxidant via a novel radical-radical coupling process. This reaction is simple to operate, conducted at ambient temperature, and relies solely on atmospheric oxygen as the oxidizing agent. Furthermore, Fe is an abundant metal and much cheaper than traditional metal photocatalysts such as Ir and Ru, making it a practical and cost-effective choice for large-scale synthesis^[36]. Meanwhile, photoinduced Fe catalysis has been proven to be a powerful tool in radical chemistry; generally, the types of reactions undergo a process of radical addition^[37-46]. However, in this work, we proposed a novel pathway for radical-radical coupling between cycloalkyl radical and cation radical intermediate of heteroarene, which complemented the classic reaction mechanism well [Figure 1D].

EXPERIMENTAL

A 10 mL oven-dried Schlenk tube, fitted with a magnetic stirring bar, was charged with **1** (0.2 mmol, 1.0 equiv.), **2** (4.0 mmol, 20.0 equiv.), FeCl₃ (3.2 mg, 0.02 mmol), tetrabutylammonium chloride (TBACl,

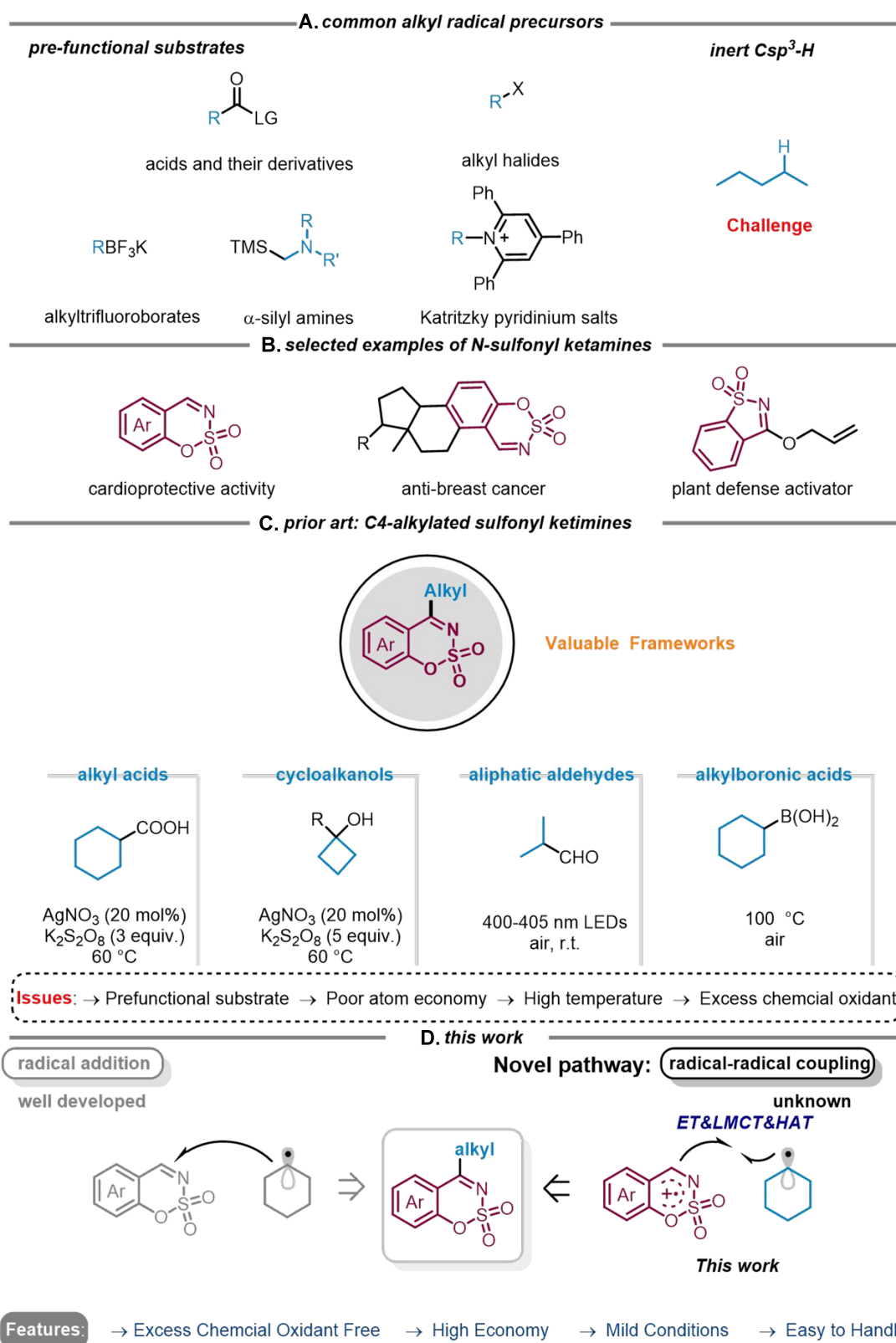


Figure 1. (A) Common alkyl radical precursors; (B) Selected examples of N-sulfonyl ketimines; (C) Prior art; (D) This work.

0.4 mmol, 2.0 equiv.), and dichloromethane (DCM, 2.0 mL). The vessel was positioned 2 cm from a 385 nm light-emitting diode (LED, 6 W), and the reaction mixture was exposed to light for 13 h under an air atmosphere. Following irradiation, the mixture was transferred to a 50 mL round-bottom flask, and the solvent was removed under reduced pressure. The desired product **3** was isolated using flash column chromatography on silica gel.

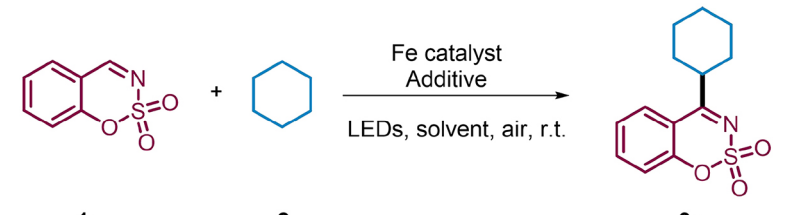
RESULTS AND DISCUSSION

The initial optimization of the reaction was performed using *N*-sulfonyl ketimine **1a** and cyclohexane **2a** as model substrates [Table 1]. Various Fe(III) and Fe(II) salts were screened under irradiation with a 6 W, 395 nm LED in an acetonitrile (MeCN) solvent under an air atmosphere (entries 1-4), though the results showed no significant difference in efficiency. Control experiments using Fe(NO₃)₃·9H₂O and FeSO₄ without a halide source showed only trace amounts of product **3a**, underscoring the essential role of halide radicals in facilitating the hydrogen atom transfer (HAT) process and enabling product formation. When the additive was changed from TBACl to LiCl, the yield dropped markedly to 9% (entry 5). The effect of TBACl equivalents was also examined, with 2.0 equivalents yielding 23% (entry 6), while 3.0 equivalents led to a slightly lower yield of 18% (entry 7). Next, we evaluated the impact of different solvents, including MeCN, DCM, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and dioxane. Among these, DCM proved to be the most effective, delivering the highest yield (entries 6, 8-11). Gratifyingly, the yield increased to 60% when 20 equivalents of cyclohexane **2a** were used (entry 13). However, further increasing the amount of **2a** led to a decrease in yield (entry 14). Switching the light source to a 385 nm LED significantly enhanced the C(sp³)-H activation efficiency, resulting in an improved yield of 73% (entries 15-17). Based on this optimization, the optimal conditions were identified as follows: **1a** (0.2 mmol), **2a** (20.0 mmol), 2.0 equivalents of TBACl, and 10 mol% FeCl₃ as a photocatalyst in DCM under 385 nm LED irradiation for 13 h in an air atmosphere.

With the optimized reaction conditions in hand, the scope of *N*-sulfonyl ketimines **1** and alkanes **2** was explored [Figure 2]. Various *N*-sulfonyl ketimines bearing different substituents were compatible with the reaction system, affording the corresponding products in moderate to good yields. Reaction progress was monitored by thin-layer chromatography (TLC), which confirmed near-complete consumption of the starting materials. Both electron-donating (-Me) and electron-withdrawing groups (EWGs) (-F, -Cl, -Br, -CO₂Me, -NO₂) on the aromatic ring were well-tolerated. The reactivity of substrates bearing electron-donating groups (EDGs) and EWGs exhibited relatively modest variations, except for the nitro group (-NO₂), which resulted in a substantial reduction in yield (**3a-3o**). Moreover, the position of the substituent on the benzene ring had no significant impact on the reaction outcome. Next, the scope of cycloalkanes in the reaction was examined. Regardless of ring size, *N*-sulfonyl imines were smoothly converted into their corresponding 4-alkylated sulfonyl ketimines (**3p** and **3q**).

To demonstrate the scalability and potential practicality of this Fe-catalyzed photoredox C(sp³)-H functionalization protocol, a gram-scale reaction was conducted to produce **3a** in a 54% yield [Figure 3A]. Despite the use of excess alkanes, both the solvent and reagent (alkanes) can be easily recovered for subsequent use, highlighting the potential of this protocol for industrial applications.

To further elucidate the reaction mechanism, several control experiments were conducted [Supplementary Materials]. A light/dark experiment demonstrated that the reaction was completely halted in the absence of light, confirming that light is crucial for the transformation [Figure 3B]. Additionally, when 2,2,6,6-tetramethylpiperidinyloxy (TEMPO), a well-known radical quencher, was introduced into the reaction, product formation was significantly suppressed. Notably, a radical adduct was detected by electrospray

Table 1. Reaction optimization^a


Entry	Fe catalyst	2a (equiv.)	Solvent	Light	Yield [%] ^b
1 ^c	FeCl ₃ ·6H ₂ O	5	MeCN	395 nm	16
2 ^c	FeCl ₃	5	MeCN	395 nm	17
3 ^c	Fe(NO ₃) ₃ ·9H ₂ O	5	MeCN	395 nm	15
4 ^c	FeSO ₄ ·7H ₂ O	5	MeCN	395 nm	16
5 ^d	FeCl ₃	5	MeCN	395 nm	9
6	FeCl ₃	5	MeCN	395 nm	23
7 ^e	FeCl ₃	5	MeCN	395 nm	18
8	FeCl ₃	5	DCM	395 nm	45
9	FeCl ₃	5	DMF	395 nm	ND
10	FeCl ₃	5	DMSO	395 nm	ND
11	FeCl ₃	5	1,4-Dioxane	395 nm	ND
12	FeCl ₃	10	DCM	395 nm	46
13	FeCl ₃	20	DCM	395 nm	60
14	FeCl ₃	30	DCM	395 nm	55
15	FeCl ₃	20	DCM	Blue LEDs	ND
16	FeCl ₃	20	DCM	385 nm	73
17	FeCl ₃	20	DCM	410-420 nm	60

^aGeneral conditions: **1a** (0.2 mmol), **2** (X equiv.), TBACl (2.0 equiv.) and FeCl₃ (10 mol%) in 2.0 mL of solvent and irradiated under 6 W LEDs at room temperature for 13 h under air atmosphere. ^bIsolated yield. ^c1.0 equiv. TBACl was added. ^d1.0 equiv. LiCl instead of TBACl. ^e3.0 equiv. TBACl was added. MeCN: Acetonitrile; DCM: dichloromethane; DMF: N,N-dimethylformamide; ND: not detected; DMSO: dimethyl sulfoxide; LEDs: light-emitting diodes; TBACl: tetrabutylammonium chloride.

ionization high-resolution mass spectrometry (ESI-HRMS), providing further evidence for the involvement of cyclohexane radicals [Figure 3C]. On performing the template reaction with 5 equiv. 1,4-diazabicyclo[2.2.2]octane (DABCO) or benzoquinone, the reaction was completely inhibited, which indicated that singlet oxygen and superoxide radicals might be formed in the reaction [Figure 3D and E]. We assumed that singlet oxygen and superoxide radicals may both be generated by compound **1a**. To investigate the origin of ¹O₂ and O₂^{•−}, electron paramagnetic resonance (EPR) test was also conducted to verify our hypothesis [Supplementary Materials]. The EPR spectrum of a mixture of **1a** and 2,2,6,6-tetramethylpiperidine (TEMPO) in DCM under irradiation showed strong signal of TEMPO (αN = 15.91 and g = 2.006), which could verify the source of ¹O₂ [Figure 4A left]. Besides, a strong signal peak of an O₂^{•−} adduct with 5,5-dimethylpyrroline N-oxide (DMPO) was detected (αN = 12.78, αH = 7.9 and g = 2.006), when the solution of **1a** was irradiated with 385 nm LEDs [Figure 4A right], which further implies the generation of an N-sulfonyl ketimine radical cation intermediate. The results suggest that both singlet oxygen (¹O₂) and superoxide radicals (O₂^{•−}) play critical roles in the transformation. To gain deeper insights into the reaction mechanism, fluorescence quenching experiments were conducted between excited Fe(III) and various components of the reaction system [Supplementary Materials], including TBACl, cyclohexane, and N-sulfonyl ketimine [Figure 4B]. Of the reagents present in the reaction, only Cl[−] was able to quench the fluorescence of Fe(III) excited at 385 nm, indicating that a LMCT process occurs between Fe(III) and Cl[−].

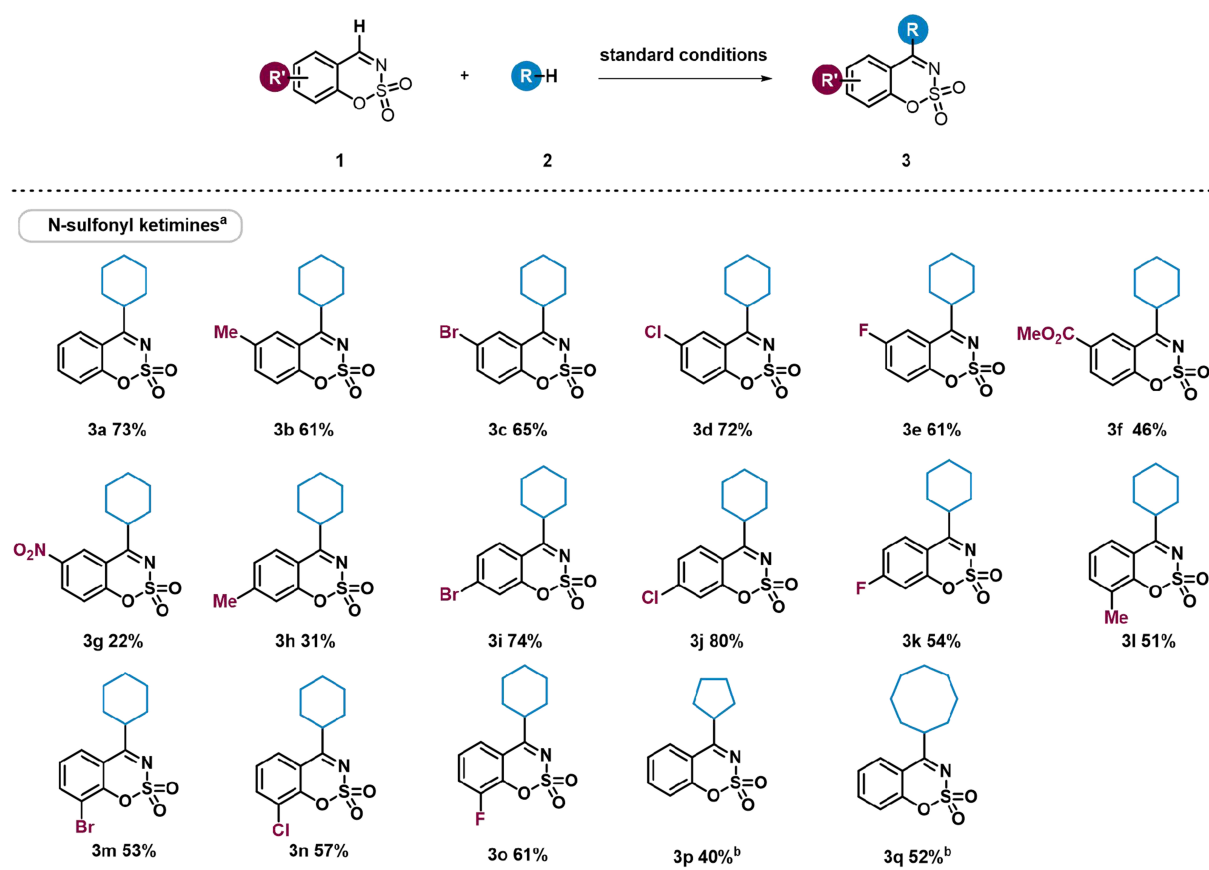


Figure 2. Scope of reaction. ^aReaction conditions: **1** (0.2 mmol), **2** (4.0 mmol), TBACl (2.0 equiv.) and FeCl₃ (10 mol%) in 2.0 mL of DCM and irradiated under 6 W 385 nm LEDs at room temperature for 13 h under air atmosphere. ^b1 equiv. TFA was added. TBACl: Tetrabutylammonium chloride; DCM: dichloromethane; LEDs: light-emitting diodes; TFA: trifluoroacetic acid.

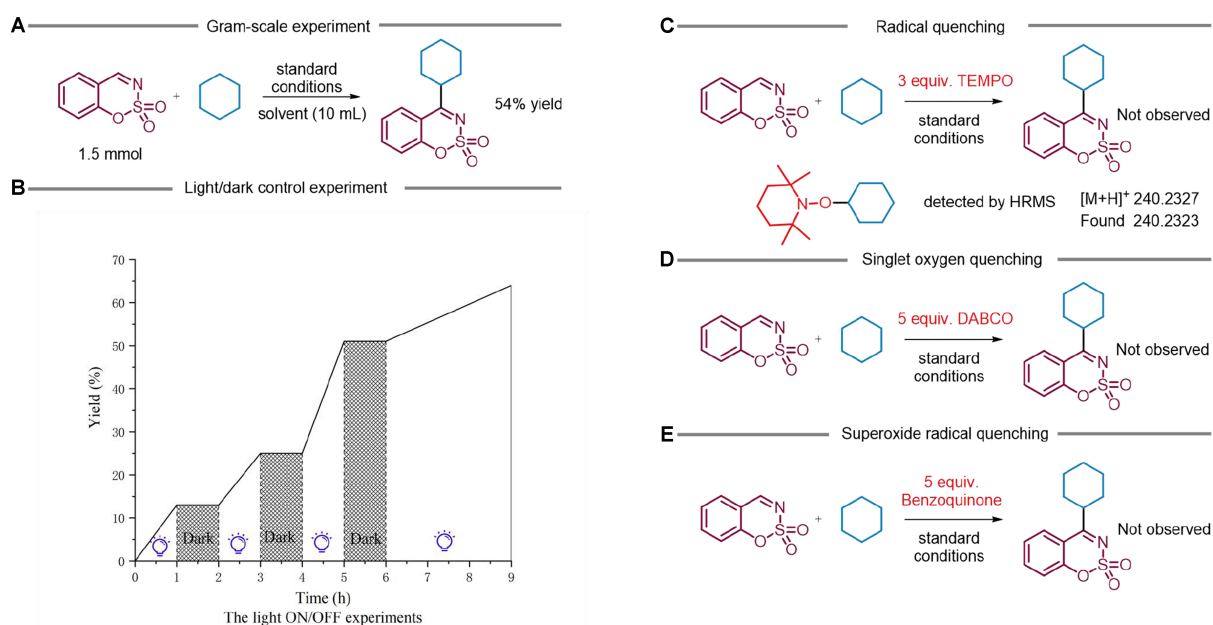


Figure 3. Gram-scale experiment and control experiments.

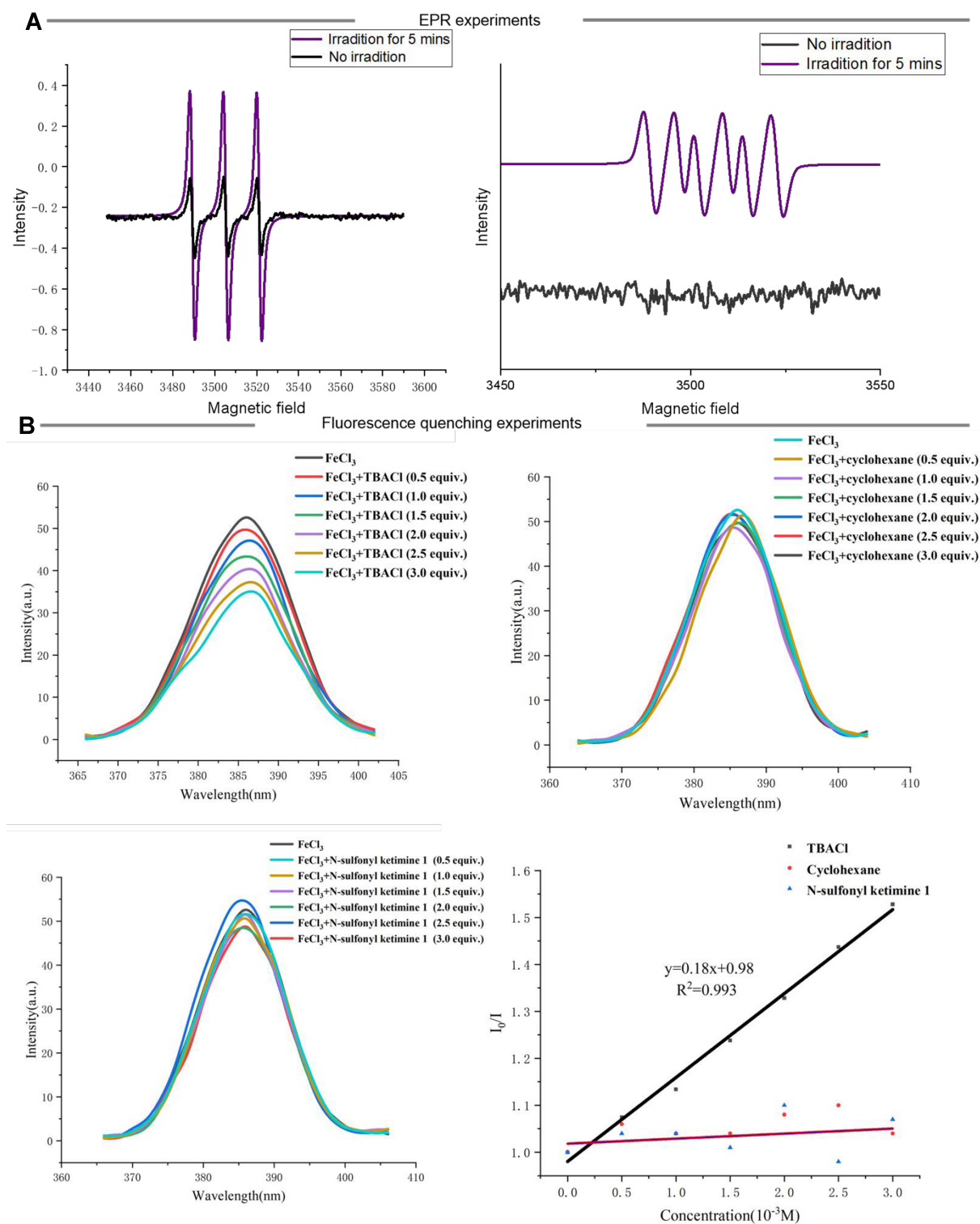


Figure 4. Mechanistic studies.

Based on the abovementioned studies and previous work, a detailed description of our proposed catalytic mechanism is outlined in Figure 5. Under light irradiation, the Fe(III) complex turns into its excited state and subsequently the process of LMCT generates Fe(II) complex with a highly active chlorine radical (Cl^\bullet).

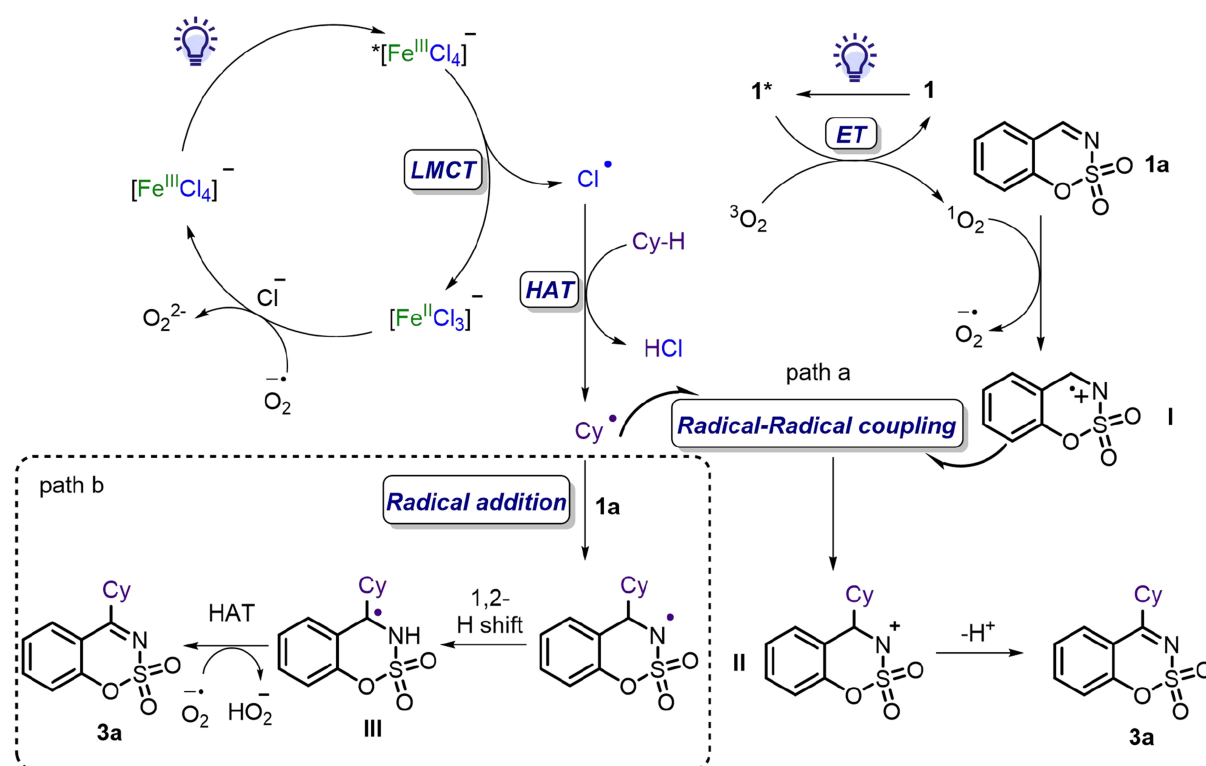


Figure 5. Mechanistic proposal.

Then, a HAT from cyclohexane to Cl^\bullet leads to the formation of cyclohexyl radical (Cy^\bullet) and aerobic oxidation of the Fe(II) complex regenerates the Fe(III) complex. In the meantime, the excited-state species of substrate **1** is produced by irradiation, which undergoes an energy-transfer process with $^3\text{O}_2$ to deliver $^1\text{O}_2$. The $^1\text{O}_2$ with high oxidation potential ($E = 2.2 \text{ V}$)^[47] could oxidize N-sulfonyl ketimines ($E = 1.76 \text{ V}$)^[48] to give N-sulfonyl ketimine cation radical intermediate **I**, which is also confirmed by EPR experiments. Finally, a radical-radical coupling between the cyclohexyl radical (Cy^\bullet) and radical intermediate **I** occurs, followed by a deprotonation process facilitated by superoxide radicals or superoxide anions abstracting a hydrogen atom, leading to the formation of the target product **3a** (path a). Despite the proposed radical coupling mechanism outlined above, we cannot exclude the possibility of a radical addition process. In this alternative pathway (path b), the cyclohexyl radical could directly attack the C4 position of the sulfonyl ketimine **1a** to generate an N-centered radical. This intermediate then undergoes a 1,2-hydrogen shift to form radical intermediate **III**, which is subsequently converted into the desired product **3a** through a HAT process with superoxide ($\text{O}_2^{\cdot-}$).

CONCLUSIONS

In conclusion, this study presents an efficient and direct system for C-H alkylation by iron photocatalysis using hydrocarbons as an alkyl source. The detailed mechanistic studies support that Fe(III)–Cl LMCT process and energy transfer process are involved in this transformation. Notably, a novel pathway of radical-radical coupling was proposed, a process not previously reported for photoinduced C-C formation between cycloalkyl radical and cation radical intermediate of heteroarene. This sustainable method offers a new synthetic strategy for functionalizing sulfonyl ketimines, and it is expected to have wide utility in both medicinal and synthetic chemistry. We are currently working on developing additional photochemical transformations in our laboratory by utilizing this approach.

DECLARATIONS

Authors' contributions

Conceptualized and directed the project: Xia, Z. H.

Supervised the project: Xia, Z. H.; Zhao, H. Q.

Designed the experiments: Xia, Z. H.; Liu, W. H.; Sun, X. Y.

Performed the experiments and analyzed the data: Xia, Z. H.; Liu, W. H.; Sun, X. Y.; Liu, X. Y.; Liu, M. Q.

All authors discussed the results and commented on the manuscript.

Availability of data and materials

Experimental procedures and characterization of new compounds are available in the [Supplementary Materials](#).

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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