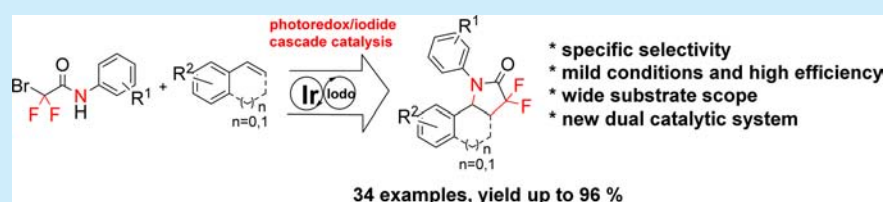


Cascade Photoredox/Iodide Catalysis: Access to Difluoro- γ -lactams via Aminodifluoroalkylation of AlkenesMuliang Zhang,[†] Weipeng Li,[†] Yingqian Duan,[†] Pan Xu,[†] Songlin Zhang,[†] and Chengjian Zhu^{*,†,‡}[†]State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China[‡]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai 200032, China

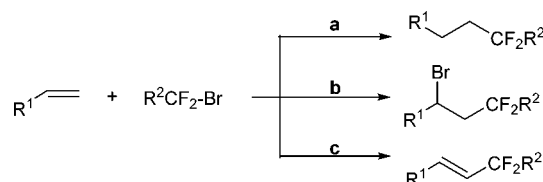
S Supporting Information



ABSTRACT: The novel cascade photoredox/iodide catalytic system enables the alkene to serve as a radical acceptor capable of achieving aminodifluoroalkylation of alkenes. Cheap iodide salts play a vital role in this reaction, which could tune carbocation reactivity through reversible C–I bond formation for controlling reaction selectivity, and a series of competitive reactions are completely eliminated in the presence of multiple reactivity pathways. The present dual catalytic protocol affords a very convenient method for direct synthesis of various difluoro- γ -lactams from simple and readily available starting materials under mild reaction conditions.

Given the great significance of the difluoromethylene group (CF_2) in drug discovery, medicinal chemistry, and life science,¹ the development of a new synthetic approach for the assembly of fluorinated small compounds has become a hot area of chemical research, and increasingly general and practical methods are now accessible for these transformations.² Among the various developed routes thus far, the addition of a CF_2 radical to a π acceptor (alkene, alkyne, arene, isocyanides, imines) is considered a useful and economical synthesis strategy.^{3,4} However, most difunctionalization-type difluoroalkylation of alkenes with bromodifluoro reagents is still limited to the modes of hydrogen atom abstraction, halogen atom attack, and deprotonation (Scheme 1).⁵ This is due mainly to

Scheme 1. Developed Difunctionalization-Type Difluoroalkylation of Alkenes with Bromodifluoro Reagents



the fact that the highly reactive and unstable radical or carbocation intermediates make controlling reaction selectivity very challenging in organic transformations.⁶ Consequently, it is a desirable, yet difficult, task to continue to explore new catalytic strategy to tune the reactive intermediates for achieving the target reaction, in particular, of which the

reaction energy barrier is higher than others in the presence of multiple reaction paths. As a proof of concept, we herein describe photoredox/iodide cascade catalysis reaction that comprises aminodifluoroalkylation of alkenes to difluoro- γ -lactams, which are commonly present in natural products and pharmacological compounds and largely improve a broad range of biological activities.⁷

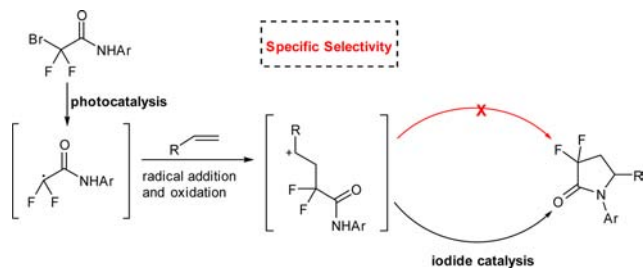
The greatest challenge that requires circumvention for the validation of the concept is how to overcome these developed reaction pathways as shown in Scheme 1. Recently, dual catalysis realized by merging visible-light-induced photoredox catalysis with other catalytic modes has been found to be attractive, and it garners great interest and concern from chemists.⁸ These dual-catalytic strategies have been widely used to develop various valuable chemical transformations, which are not easily available, if not impossible, by a single catalytic system. In spite of these impressive advances, further exploration of combination of photoredox catalysis with other catalytic forms to search for other useful chemical reactions, especially in carbon–heteroatom bond formation, remains a great challenge. It is well-known that iodide salts are an inexpensive and readily available reagents and could be usually applied as the nucleophilic catalyst in carbon–heteroatom bond formation reactions for iodide ion properties of nucleophilic and leaving performance.⁹ We envisaged that reversible C–I bond formation might represent another promising approach for tuning reactivity of carbocation produced by a CF_2 radical

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added to an olefinic substrate under visible-light photoredox catalysis conditions, and other alternative reaction ways were suppressed throughout the course of the reaction (Scheme 2).

Scheme 2. Cascade Photoredox/Iodide Catalysis for Aminodifluoroalkylation of Alkenes



To validate the feasibility of a photoredox/iodide cascade catalytic system, the readily accessible bromodifluoroacetamide **1a** was chosen as the model substrate. As a preliminary experiment, **1a** was reacted with 2 equiv of styrene (**2b**) in the presence of 2 equiv of sodium carbonate, the photocatalyst *fac*-[Ir(ppy)₃], and iodide catalyst sodium iodide at room temperature, we observed the formation of the desired in degassed CH₃CN (0.1 M) under irradiation with visible light from blue LEDs (5 W, λ_{max} = 455 nm). Delightfully, after 36 h, product **3ab**, with a moderate yield of 52% (Table 1, entry 1), showed that the novel catalytic strategy worked well. Solvent screening showed that strong polar solvents such as DMF provided better results for this reaction and the reaction could not occur with a nonpolar solvent (entries 2 and 3). The catalysts [Ir(ppy)₂(dtbpy)]PF₆ and [Ru(bpy)₃]PF₆ showed inferior reactivity toward the conversion of **1a** (entries 4 and 5). It was observed that the use of inorganic bases such as NaHCO₃, K₂CO₃, and Na₂HPO₄ promoted the reactions, NaOAc gave the best result, and the use of organic base (Et₃N) completely inhibited the reaction (entries 6–10). In this system, the amount of styrene (**2b**) employed could be further reduced to 1.5 equiv without lowering the yield (86%, entry 11). Importantly, when sodium iodide was not added to the reaction system or sodium bromide was added, the reaction occurred in a state of complete confusion and the desired product **3ab** was not detected (entries 12–14). It can be seen that added iodine anion exerts a powerful catalytic effect on the reaction. Finally, control experiments demonstrated that the photocatalyst *fac*-[Ir(ppy)₃], and visible light were all important (entries 15 and 16).

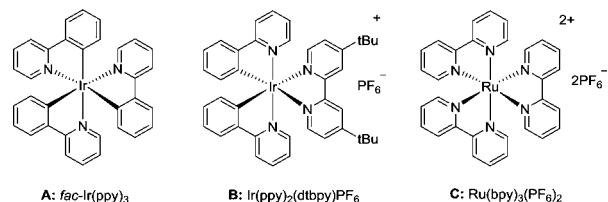
With the optimized conditions in hand, we explored the scope of the bromodifluoroacetamide, and the representative examples are shown in Scheme 3. This cascade catalytic strategy has good substrate compatibility and showed excellent chemoselectivity. Bromodifluoroacetamide bearing either electron-donating (methyl, methoxy) or electron-withdrawing groups such as halide substituents furnished the corresponding products in moderate to good yields (**3aa**–**fa**). The position of the substituents on the phenyl ring has no obvious influence on this reaction. *Ortho*-substituted (methyl, phenyl) derivatives also worked well, providing the desired products with good yields, which seems to have a lower steric effect (**3ma**–**oa**). Substrates with more substituents on the phenyl ring were used, and they all underwent the aminodifluoroalkylation reaction to yield difluoro- γ -lactam products in 50–65% yield (**3pa**–**ta**). However, when we used the bromodifluoroaceta-

Table 1. Optimizing Reaction Conditions^a

Reaction scheme showing the synthesis of **3ab** from **1a** and **2b** under photoredox conditions.

entry	photocat ^c	halide	base	solvent ^c	yield ^b (%)
1	A	NaI	Na ₂ CO ₃	CH ₃ CN	52
2	A	NaI	Na ₂ CO ₃	CH ₂ Cl ₂	trace
3	A	NaI	Na ₂ CO ₃	DMF	73
4	B	NaI	Na ₂ CO ₃	DMF	45
5	C	NaI	Na ₂ CO ₃	DMF	36
6	A	NaI	NaHCO ₃	DMF	79
7	A	NaI	k ₂ CO ₃	DMF	60
8	A	NaI	Na ₂ HPO ₄	DMF	40
9	A	NaI	NaOAc	DMF	87
10	A	NaI	Et ₃ N	DMF	
11 ^c	A	NaI	NaOAc	DMF	86
12	A	NaBr	NaOAc	DMF	trace
13	A	nBu ₄ NI	NaOAc	DMF	73
14	A		NaOAc	DMF	
15		NaI	NaOAc	DMF	
16 ^d	A	NaI	NaOAc	DMF	

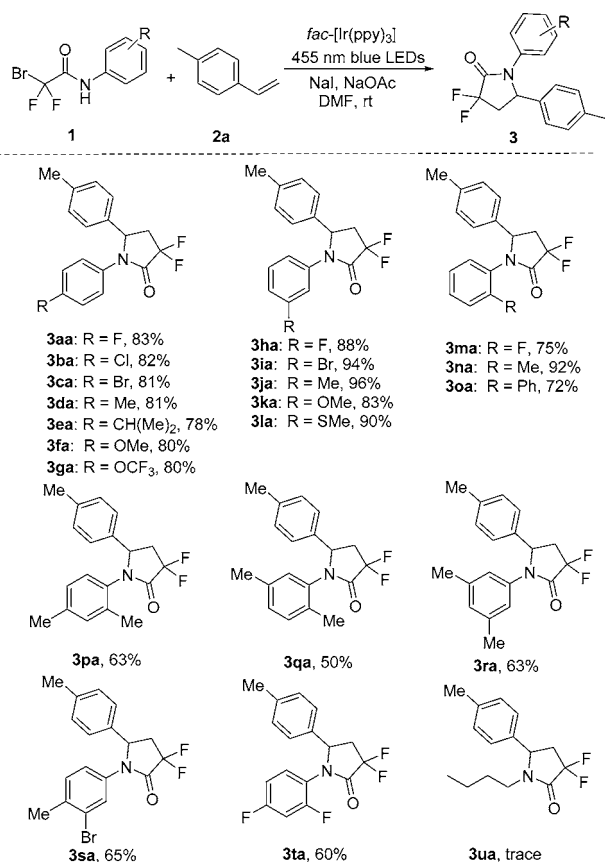
^aThe reactions were carried out with **1a** (0.2 mmol), **2b** (0.4 mmol, 2.0 equiv), base (0.4 mmol, 2.0 equiv), photocatalyst (0.004 mmol, 2 mol %), halidecatalyst (0.04 mmol, 20 mol %), solvent (2 mL), at room temperature, 5 W LEDs, 36 h. ^bisolated yields. ^c1.5 equiv **2b** was used. ^dIn dark. ^eDMF = *N,N*-dimethylformamide, CH₃CN = acetonitrile, CH₂Cl₂ = dichloromethane.



mid of an aliphatic substituent with replacement of the phenyl ring, the desired product could not be obtained (**3ua**), presumably owing to the reduced nucleophilicity of nitrogen.

Furthermore, various alkenes were studied in Scheme 4. The presence of an electron-donating (methyl or *tert*-butyl) electron-withdrawing (halide or methyl formate) substituent on the benzene ring was well tolerated (**3ab**–**ah**). Nonterminal olefins including β -methylstyrene, indene, and 1,2-dialin could react smoothly, delivering the corresponding products **3al**–**an**, respectively. The vinyl ether compound can also be applied to the catalytic system (**3ao**).

To gain mechanistic insight into the cascade photoredox/iodide catalysis for aminodifluoroalkylation of alkenes, the radical scavenger TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) was introduced into the photochemical system, and the reaction was completely restrained under these conditions, indicating that a single-electron-transfer radical process is operating (Scheme 5a). When we did not add base to this photoredox/iodide cascade catalytic system, interestingly, the adduct **5a** was formed as estimated by ESI-HRMS analysis (SI), which implied **5a** may be the reaction intermediate (Scheme 5b). Additionally, we also prepared 2,2-difluoro-2-iodo-*N*-phenylacetamide **4a** and replaced 2-bromo-2,2-difluoro-*N*-phenylacetamide **1a** as a CF₂ radical source. The desired

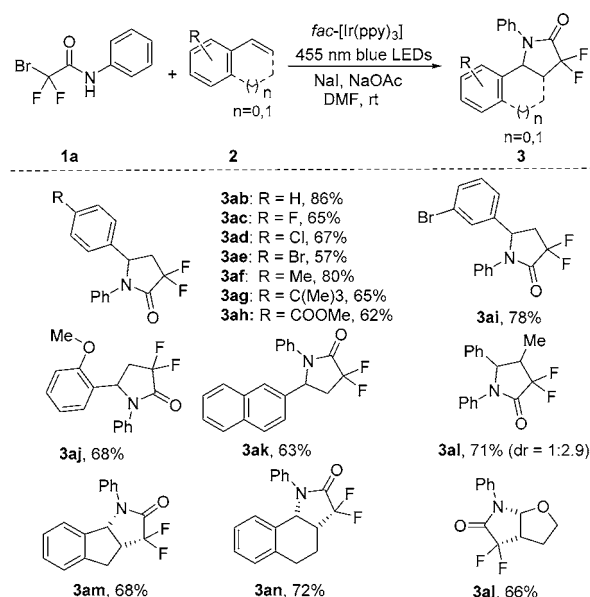
Scheme 3. Scope of Bromodifluoroacetamides in the Aminodifluoroalkylation reaction.^a

^aReaction conditions: 1 (0.2 mmol), 2a (0.3 mmol, 1.5 equiv), NaOAc (0.4 mmol, 2 equiv), $\text{fac-Ir}(\text{ppy})_3$ (0.004 mmol, 2 mol %), NaI (0.04 mmol, 20 mol %), DMF (2 mL), at room temperature, 5 W LEDs, 30–48 h.

product **3ab** was obtained in the absence of iodide catalyst in 78% yield (Scheme 5c). This provided straightforward evidence of the reaction process through the intermediate **5a**.

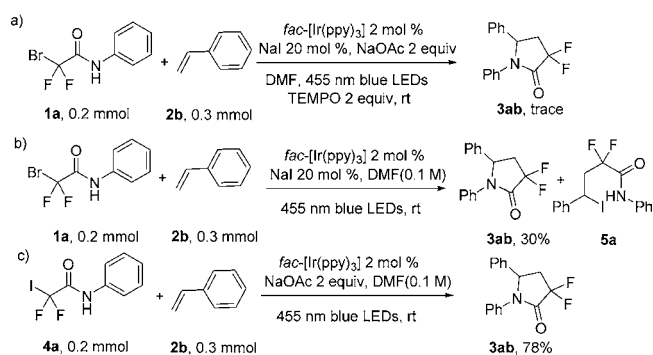
On the basis of the experimental results and literature,^{3j,4d} a possible mechanism is shown in Scheme 6. The photocatalyst $\text{fac-Ir}^{3+}(\text{ppy})_3$ **1** undergoes a metal-to-ligand charge-transfer (MLCT) process under visible-light irradiation to transfer from this Ir species to **3** to generate the CF₂ radical precursor **4** and the Ir intermediate Ir^{4+} (+0.77 V vs SCE in CH₃CN). The electrophilic radical added to alkenes to form intermediate **6**, which was oxidized to the β -difluoroalkylated carbocation intermediate **7** by the Ir intermediate **5** followed by rapid iodide ion nucleophilic trapping. The nitrogen of the amide as a nucleophile performs intramolecular nucleophilic attack to form the intermediate **9**, and the iodide anion could be regenerated. Finally, difluoro- γ -lactam **10** was produced by deprotonation of the nitrogen in the presence of base.

In conclusion, we have developed a novel photoredox/iodide cascade catalytic system for achieving aminodifluoroalkylation of alkenes. The use of iodide catalyst is the key to achieve specific selectivity for obtaining various α,α -difluorinated γ -lactams in the presence of multiple reaction pathways. We anticipate that this dual-catalytic protocol will be applied to the development of other reactions to achieve more valuable transformations. Further exploration of this photoredox/iodide

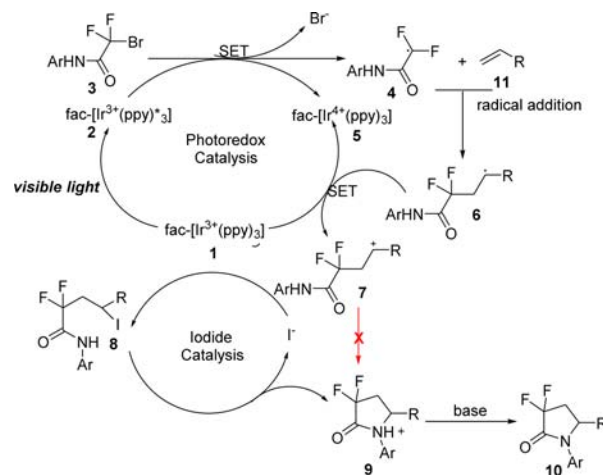
Scheme 4. Scope of Alkenes in the Aminodifluoroalkylation Reaction^a

^aReaction conditions: 1a (0.2 mmol), 2 (0.3 mmol, 1.5 equiv), NaOAc (0.4 mmol, 2 equiv), $\text{fac-Ir}(\text{ppy})_3$ (0.004 mmol, 2 mol %), NaI (0.04 mmol, 20 mol %), DMF (2 mL), at room temperature, 5 W LEDs, 36–48 h.

Scheme 5. Mechanistic Investigations of Aminodifluoroalkylation of Alkenes



Scheme 6. Proposed Mechanism



cascade catalytic system will continue to be a focus of research in our group.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental procedures, characterization data. The Supporting Information is available free of charge on the ACS Publications Web site. The Supporting Information is available free of charge on the [ACS Publications website](https://doi.org/10.1021/acs.orglett.6b01515) at DOI: [10.1021/acs.orglett.6b01515](https://doi.org/10.1021/acs.orglett.6b01515).

Experimental procedures (PDF)

^1H , ^{13}C , and ^{19}F NMR spectra (PDF)

Additional ^1H , ^{13}C , and ^{19}F NMR spectra and ESI-
HRMS spectra (PDF)

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Notes

The authors declare no competing financial interest.

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