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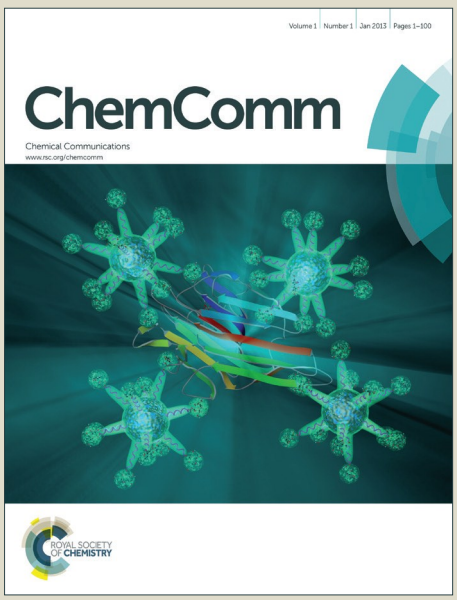

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ARTICLE TYPE

Visible-light-induced photocatalytic oxytrifluoromethylations of *N*-allylamides for the synthesis of CF_3-containing oxazolines and benzoxazines

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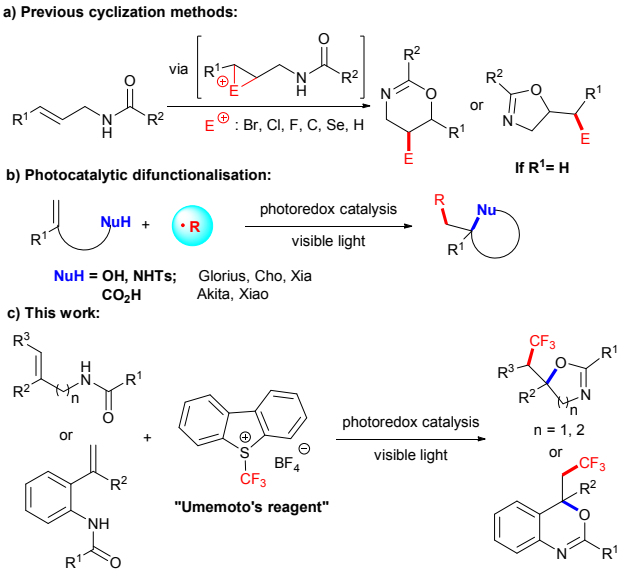
A visible-light-induced photocatalytic oxytrifluoromethylation of *N*-allylamides has been developed for the efficient synthesis of CF_3-containing oxazolines and benzoxazines under mild reaction conditions.

Oxazolines and benzoxazines respresent a class of common core structures of numerous natural products,[1] many of which exhibit remarkable biological activities (e.g. anti-inflammatory,[2] anticonvulsant,[1j] antiobiotic,[3] and anti-fungal[4] activities). For example, the 2,5-substituted oxazole and 2,4-substituted-4*H*-1,3-benzoxazine scaffolds frequently occur in many pharmaceutically active molecules, and they are also useful synthetic intermediates in organic synthesis.[5] As a result, many elegant methodologies have been developed by many research groups for their synthesis.[5,6] However, some traditional methods usually require harsh reaction conditions or are limited to specific substrates. Recently, the cyclization of *N*-allylamides have emerged as an attractive platform to efficiently construct functionalised oxazolines and benzoxazines.[7] The transformation is based on the mode of electrophilic cyclization, wherein the carbon-carbon double bond is activated by electrophiles, such as Br^+, Cl^+, F^+ sources, followed by the attack of oxygen atom of the amide carbonyl group to produce the corresponding five or six-membered heterocycles (Scheme 1a).[8] Despite advances, the exploration of other suitable electrophiles and analogs still remains an area of intensive research.

It has been well known that the incorporation of fluorinated moieties, particularly the CF_3 group, into carbocycles and heterocycles can significantly alter their lipophilicity, metabolic stability and bioavailability.[9] As a result, developing more efficient and practical approaches for incorporation of CF_3 motif into the heterocyclic compounds has attracted considerable research interest over the past decades.[10] Typically, trifluoromethylation reactions can be divided into three categories: electrophilic, nucleophilic, and radical processes. However, the use of these protocols to make CF_3-containing oxazolines and benzoxazines remain a dark side in this area. Quite recently, the Fu group has reported a transition metal-free trifluoromethylation of *N*-allylamides using readily available CF_3SO_2Na as the CF_3 source, giving the corresponding CF_3-containing oxazolines with satisfactory yields.[6g] The success of this reaction requires the stoichiometric use of $PhI(OAc)_2$ as oxidant at elevated temperature.

Over the past several years, visible-light-induced photoredox catalysis has been established as a versatile activation mode for reactivity engineering and reaction design.[11] In this context, the visible-light-induced photocatalytic difunctionalisation of alkenes provides a useful approach to various diversely functionalized molecules (Scheme 1b).[12] For example, the Glorius group has reported an interesting oxy- and aminoarylation of alkenes using aryldiazonium salts as aryl radical sources by the combination of gold and photoredox catalysis.[12a] Our group has also recently developed a photocatalytic arylation/lactonization of alkenes for efficient preparation of γ,γ-disubstituted butyrolactones.[12c] The photocatalytic difunctionalisation of alkenes with suitable CF_3 sources also enable facile incorporation of CF_3 moiety into valuable organic compounds.[13] However, the application of such photocatalytic strategy to achieve highly functionalised CF_3-containing heterocycles is still quite limited.[12b,d,13j,p]

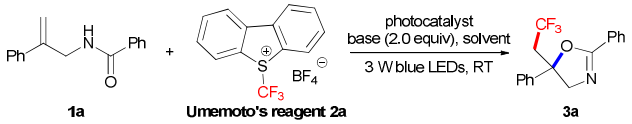


Scheme 1 Difunctionalisation of alkenes for heterocycle synthesis.

As part of our ongoing research program on construction of

biologically potential heterocycles by visible-light-induced photoredox catalysis,[14] we recently achieved an efficient and practical visible-light-induced oxytrifluoromethylation of *N*-allylamides to synthesize CF_3-containing oxazoline and benzoxazine derivatives (Scheme 1c). In this communication, we describe the preliminary results.

Table 1 Optimization studies[a]



1a Umemoto's reagent 2a **3a**

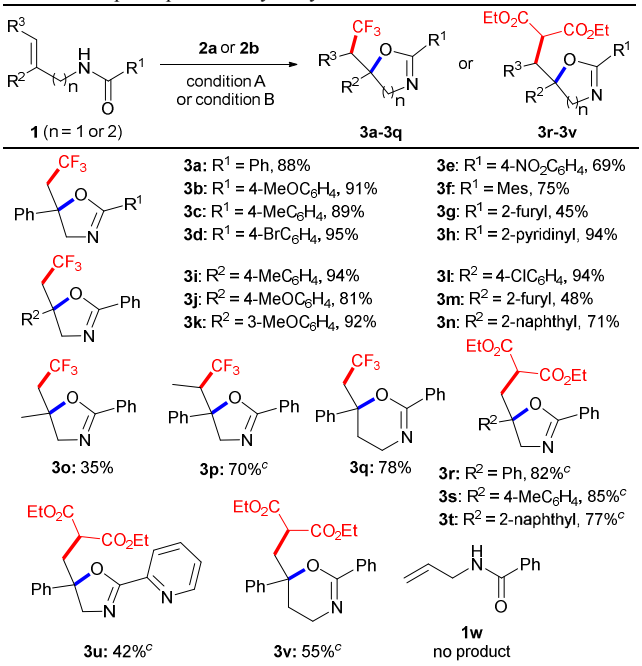
Entry	Catalyst	Base	Solvent	Time/h	Yield[b] (%)
1	$Ru(bpy)_3(PF_6)_2$	no	CH_3CN	5	87
2	$Ru(bpy)_3(PF_6)_2$	Na_2HPO_4	CH_3CN	5	93
3	$Ir(ppy)_2(dtbbpy)PF_6$	Na_2HPO_4	CH_3CN	5	88
4	EosinY	Na_2HPO_4	CH_3CN	5	0
5	$Ru(bpy)_3(PF_6)_2$	Na_2HPO_4	DMF	5	59
6	$Ru(bpy)_3(PF_6)_2$	Na_2HPO_4	DCM	5	85
7	$Ru(bpy)_3(PF_6)_2$	NaOH	CH_3CN	5	29
8	$Ru(bpy)_3(PF_6)_2$	$NaHCO_3$	CH_3CN	5	95
9[c]	**$Ru(bpy)_3(PF_6)_2$**	**$NaHCO_3$**	**CH_3CN**	**5**	**92(89[d])**
10[e]	none	$NaHCO_3$	CH_3CN	5	0
11[f]	$Ru(bpy)_3(PF_6)_2$	$NaHCO_3$	CH_3CN	5	0

[a] Unless noted, reactions were performed with **1a** (0.1 mmol), **2a** (0.11 mmol), catalyst (5 mol%), base (0.2 mmol) in the solvent (1.0 mL) under Ar with 3 W blue LEDs irradiation at room temperature. [b] GC yield using biphenyl as an internal standard. [c] Using 0.5 mol% photocatalyst loading. [d] Isolated yield. [e] Without photocatalyst. [f] Without visible-light irradiation.

We initially tested the feasibility of the photocatalytic oxytrifluoromethylative cyclization of *N*-(2-phenylallyl)benzamide **1a** with Umemoto's reagent[15] **2a** in the present of $Ru(bpy)_3(PF_6)_2$ (5 mol%) in CH_3CN under 3 W blue LEDs irradiation for 5 h at room temperature. To our delight, the oxytrifluoromethylative cyclization proceed smoothly to give 2,5-diphenyl-5-(2,2,2-trifluoroethyl)-4,5-dihydrooxazole **3a** in 87% GC yield (entry 1). The addition of Na_2HPO_4 as the base made the reaction cleaner and increased the GC yield to 93% (Table 1, entry 2). Encouraged by these results, other reaction parameters such as photocatalysts, solvents and bases were then examined to further improve the reaction efficiency.[16] Among the photocatalyst examined, $Ru(bpy)_3(PF_6)_2$ displayed the best catalytic performances (Table 1, entries 2-4). A brief screen of reaction media and bases showed that the combination of CH_3CN and $NaHCO_3$ gave the best results with **3a** being formed in 95% GC yield (entry 8). Remarkably, the reaction can proceed smoothly even with 0.5 mol% of $Ru(bpy)_3(PF_6)_2$ to furnish the desired product **3a** in 89% isolated yield (entry 9). Control experiments disclosed that there was no reaction occurred either in absence of photocatalyst or in the dark, strongly supporting that both photocatalyst and visible light are critical to this transformation (entries 10 and 11). Surprisingly, the use of togni reagent as CF_3 source under the standard conditions led to no formation of the desired product.

With the optimal reaction conditions in hand, the scope of this process was next investigated. As shown in Table 2, this visible-light-induced photocatalytic oxytrifluoromethylative cyclization tolerated a wide range of substrates **1** with various substitution patterns. As for the amide moiety, the substrates

Table 2 Scope of photocatalytic synthesis of oxazolines[a, b]



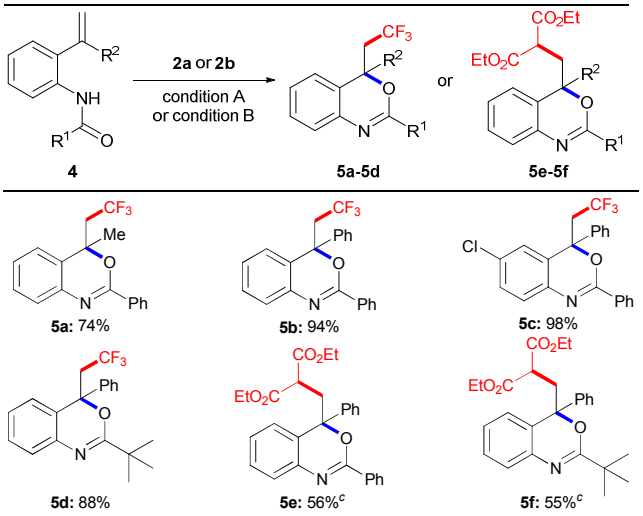
[a] Unless noted, reactions were performed under condition A: **1** (0.3 mmol), Umemoto's reagent **2a** (0.33 mmol), $Ru(bpy)_3(PF_6)_2$ (0.5 mol%), $NaHCO_3$ (0.6 mmol) in CH_3CN (3.0 mL) under Ar with 3 W blue LEDs irradiation at room temperature for 5 h. [b] Isolated yield. [c] dr = 1.1:1. [d] Reactions were performed under conditions B: **1** (0.3 mmol), $BrCH(CO_2Et)_2$ **2b** (0.6 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (1 mol%), 4-methoxy-*N*,*N*-diphenylaniline (0.6 mmol), 4 Å MS (100 mg), Na_2HPO_4 (0.6 mmol) in CH_3CN (3.0 mL) under Ar with 3 W blue LEDs irradiation at room temperature for 12 h.

with various electron-donating or electron-withdrawing groups at the phenyl ring participated in the reaction very well to afford the desired CF_3-containing oxazolines **3a-3f** in generally good yields (69-95%). Note that the heteroaryl-substituted substrates also proved to be suitable for this transformation to give **3g** and **3h** in 45% and 94% yields, respectively. Siginificantly, a variety of aryl and heteroaryl groups could be well tolerated at the β-position of alkene moiety, providing the desired products **3i-3n** with satisfactory yields (48-94%). The reaction also worked very well with internal alkene **1p** to produce **3p** in 70% yield, albeit with only 1.1:1 dr. In contrast to Fu's studies,[6g] this methodology could be extended to the synthesis of six-membered ring oxazines, further highlighting the synthetic potential of this reaction. For example, the oxazine **3q** can be obtained in 78% yield. To our delight, the reaction also proceeded very well to give the corresponding cyclized products **3r-3u** with good yields when diethyl 2-bromomalonate **2b** was used as a radical precursor. Under the standard conditions, oxazine **3v** was also obtained in 55% yield. The *N*-allylbenzamide **1w** (R^2

= H) proved to be unsuitable for the current catalytic system.

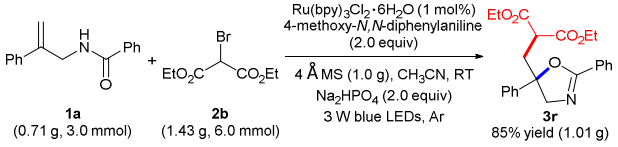
It is worthy that this photocatalytic oxytrifluoromethylation can be also successfully applied to the synthesis of biologically significant CF_3-containing benzoxazines. As shown in Table 3, incorporation of methyl or phenyl group into the β-position of akene was well accomodated to provide the benzoxazines **5a-5c** with 74%-98% yields. Moreover, aliphatic groups, such as ^{t}Bu could be successfully introduced into the 2-position of benzoxazine with **5d** being formed in 88% yield. Under this catalytic system, the diethyl 2-bromomalonate **2b** can also react smoothly to produce benzoxazines **5e** and **5f** with fair yields. The structure of **5f** was ambiguously confirmed by X-ray analysis.[17]

Table 3 Scope of photocatalytic synthesis of benzoxazines[a, b]



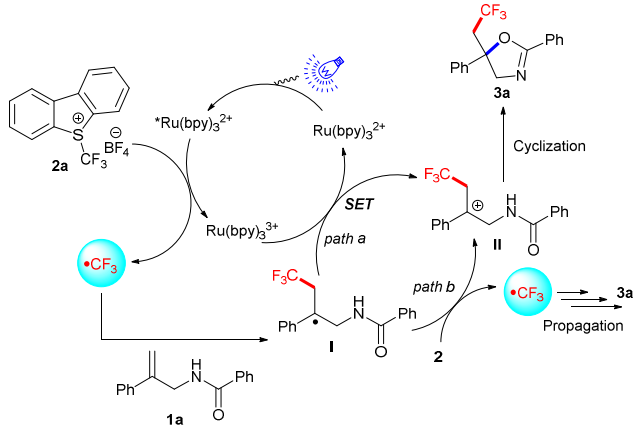
[a] Unless noted, reactions were performed under condition A: **1** (0.3 mmol), Umemoto's reagent **2a** (0.33 mmol), $Ru(bpy)_3(PF_6)_2$ (0.5 mol%), $NaHCO_3$ (0.6 mmol) in CH_3CN (3.0 mL) under Ar with 3 W blue LEDs irradiation at room temperature for 5 h. [b] Isolated yield. [c] Reactions were performed under condition B: **1** (0.3 mmol), $BrCH(CO_2Et)_2$ **2b** (0.6 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (1 mol%), 4-methoxy-*N*,*N*-diphenylaniline (0.6 mmol), 4 Å MS (100 mg), Na_2HPO_4 (0.6 mmol) in CH_3CN (3.0 mL) under Ar with 3 W blue LEDs irradiation at room temperature for 12 h.

To further demonstrate the synthetic potential of this methodology, a gram-scale reaction with **1a** and **2b** was performed under the standard conditions (Scheme 2). Pleasingly, the desired product **3r** was obtained in 85% yield, suggesting that this protocol proved to be suitable for large-scale synthesis.



Scheme 2 Synthesis of **3r** on a gram-scale.

On the basis of the control experimental results and previous studies,[13h-l] a possible mechanism was also proposed for this visible-light-induced photocatalytic cyclization of *N*-allylamides (Scheme 3). First, the $[Ru(bpy)_3]^{2+}$ was excited into $^*[Ru(bpy)_3]^{2+}$ under the irradiation by visible light, which reduced the Umemoto's reagent **2a** to generate the CF_3 radical through a SET process. Then, the CF_3 radical underwent an addition to *N*-allylamide **1a** to provide the radical intermediate **I**, which can be oxidized by $[Ru(bpy)_3]^{3+}$ to give the cation intermediate **II** (path a). A further cyclization reaction of intermediate **II** led to the formation of the final product **3a**. Another possible pathway (path b) for the conversion of intermediate **I** into **II** can not be rule out at the current stage. However, the control experiments showed that continuous irradiation by visible-light was required for this reaction (see Figure S1 in the ESI), revealing that the radical chain propagation may not be the main mechanistic pathway.



Scheme 3 Proposed mechanism.

In summary, we have developed an efficient and practical visible-light-induced photocatalytic cyclization of *N*-allylamides for the first time. The reaction provides a facile access to diversely functionalised oxazoline and benzoxazine derivatives with generally high yields. Further exploration of this methodology as well as the biological evaluation of the products are currently underway in our laboratory.

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Notes and references

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17 CCDC 1039093 (**5f**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.