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Photoinduced radical-initiated carboxylative cyclization of allyl amines with carbon dioxide[†]

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Visible light-promoted CO_2 upgrading: A highly efficient and metal-free photochemical method for the carboxylative cyclization of allyl amines with CO_2 is reported to prepare perfluoroalkylated oxazolidinones with high efficiency at ambient conditions by using perfluoroalkyl iodides as radical sources.

The development of sustainable strategies for organic synthesis has received increasing attention. In this context, utilizing CO2 as a synthon for the synthesis of heterocycles is attractive, because CO2 is a ubiquitous nontoxic and renewable C1building block. Commonly, CO₂ conversion requires energy input due to its thermodynamically stable and kinetically inert. Solar energy as an initiator or promoter for CO₂ transformation is undoubtedly appealing because of its natural abundance, ease of use and potential applications on an industrial scale.² In recent years, much attention has been paid to photocatalytic reduction of CO₂ to produce energy-related products such as formic acid, methanol, methane or hydrocarbons.³ To the best of our knowledge, the work towards the light-driven incorporation of CO₂ into value-added heterocycles has rarely been reported.⁴ Excitingly, Murakami group developed the solar-driven/UV light-driven strategy for chemical fixation of CO₂ into organic componnds e.g. amino-substituted cyclic carbonates and carboxylic acids from a-methylamino ketones and o-alkylphenyl ketones, seperately.⁵ To extend the application of photochemical synthesis to CO₂ fixation is urgently required, and represents a promising field.

On the other hand, the carboxylative cyclization of allyl amines with CO_2 is a promising example for CO_2 utilization,⁶ because the products i.e. 2-oxazolidones are of significant pharmaceutical scaffolds that widely exist in drugs and organic synthesis.⁷ In 2012, Minakata group demonstrated that

equivalent tert-butyl hypoiodite (^{*t*}BuOI) could efficiently promote the carboxylative cyclization of CO₂ with allyl amines.^{6b} As a result, the active iodine reagent (electrophilic I⁺ as key species) as promoter is crucial for this reaction. To date, the development of this kind of carboxylative cyclization is still limited with using active iodine reagents (i.e. I₂, ^{*t*}BuOI, *N*iodosuccinimide) at a low temperature (-20 – 0 °C), presumably going through activation of the C=C bond of allyl amines by electrophilic monovalent iodine (I⁺). Accordingly, the development of effective strategies for the carboxylative cyclization of allyl amines with CO₂ at ambient conditions remains attractive and challenging.

As well-known, the C=C bond easily reacts with a radical generated through photocatalysis. In this aspect, photoinduced perfluoroalkylation of alkenes is attractive,⁸ because the introduction of a perfluoroalkyl substituent into the organic motifs can significantly alter physical, chemical and biological properties of the resultant molecules.⁹ In this context, we hypothesized that a photoinduced perfluoroalkyl radical could react with the C=C bond of allyl amines, thus in situ generating an active intermediate, which subsequently reacts with CO₂. Herein, we presented an efficient photoinduced radical-initiated protocol for the carboxylative cyclization of allyl amines with CO₂ under mild conditions using perfluoroalkyl iodides as radical and fluorine sources, which simultaneously achieves the incorporation of perfluoroalkyl moiety into 2-oxazolidinones as shown in Scheme 1.

We began our study by examining the reaction of *N*-benzylprop-2-en-1-amine (**1a**) and CO₂, with perfluorobutyl iodide (${}^{n}C_{4}F_{9}I$) as the ${}^{n}C_{4}F_{9}$ radical source, in acetonitrile under a 300 W xenon lamp (420-700 nm). Delightedly, the

Photoinduced radical-initiated reaction strategy

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Visible-light-driven; Metal-free; High efficiency; Ambient conditions

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Scheme 1 Photoinduced radical-initiated carboxylative cyclization of allyl amines with $\mathrm{CO}_{2^{*}}$

Table 1 Visible-light induced carboxylative cyclization of allyl amines with CO₂^a

yields under the identical conditions, with ${}^{n}C_{3}F_{7}I_{\text{view}}C_{6}F_{\text{id}}I_{0}$ and CF₃I as radical source respectively. Interestingly, this protocopA **Table 2** Scope of allyl amines and perfluoroalkyl iodides^a

H N`Bn + 1a	$n^{n}C_{4}F_{9}I + CO_{2} -$	Base Visible light	0 0 N−Bn ⁿ C ₄ F ₉ 2a
Entry	Base (equiv.)	Solvent	$\operatorname{Yield}^{b}(\%)$
1	_	MeCN	21
2^c	K ₂ CO ₃ (2.0)	MeCN	0
3	K ₂ CO ₃ (2.0)	MeCN	70
4	Li ₂ CO ₃ (2.0)	MeCN	12
5	Cs ₂ CO ₃ (2.0)	MeCN	72
6	DBU (2.0)	MeCN	85
7	TBD (2.0)	MeCN	89
8	TBD (2.5)	MeCN	85
9	TBD (1.5)	MeCN	92
10	TBD (1.2)	MeCN	84
11^{d}	TBD (1.5)	MeCN	91
12^{e}	TBD (1.5)	MeCN	83
13	TBD (1.5)	THF	47
14	TBD (1.5)	DMF	65
15	TBD (1.5)	DMSO	90
16	TBD (1.5)	CH ₃ Cl	trace

^{*a*} Reaction conditions: **1a** (73.2 mg, 0.5 mmol), ${}^{n}C_{4}F_{9}I$ (172 μ L, 1.0 mmol), MeCN (2 mL), CO₂ (1 bar), room temperature. ^{*b*} Isolated yield. ^{*c*} No light. ^{*d*} {}^{n}C_{4}F_{9}I (1.25 mmol). ^{*e*} {}^{n}C_{4}F_{9}I (0.75 mmol).

product i.e. 3-benzyl-5-nonafluoropentyl oxazolidin-2-one (2a) of the carboxylative cyclization was obtained in 21% yield after 12 h (Table 1, entry 1) which demonstrated that our hypothesis is feasible. Notably, control experiment showed that visible light was required (entry 2). These results inspired us to further optimize the reaction conditions. We speculated that the addition of a base could stabilize the carbamate anion generated from **1a** and CO₂.¹⁰ Gratifyingly, the target product **2a** was produced in 70% yield by adding two equivalents of K₂CO₃ (entry 3). Then several other bases were tested (entries 4-7), and 1,5,7-triazabicyclo[4,4,0]dec-5-ene (TBD) was identified as the best choice, thus providing 2a in 89% yield (entry 7). Next, we investigated the effects of the stoichiometry of reagents including perfluorobutyl iodide and TBD on the reaction outcome (entries 8-12). An excess amount of TBD (1.5 equiv.) and ${}^{n}C_{4}F_{9}I$ (2 equiv.) was needed for obtaining the maximum yield (92%) (entry 9). In addition, among the solvents we investigated (entries 13-16), besides MeCN, DMSO could also give a comparable yield of product 2a (entry 15 vs 9).

Having established the method of radical-initiated carboxylative cyclization of allyl amines with CO_2 , we then examined the reactivity of various allyl amines to further explore the utility of this protocol as listed in Table 2. Both *N*-benzyl- and *N*-alkyl-allyl amines gave the corresponding products (**2a**-**2d**) in excellent yields. Functional groups like fluoro, chloro, bromo, methoxyl and methylal on the aromatic ring were tolerated with the present protocol (**2e**-**2i**). Heptafluorobutyl, tridecafluoroheptyl and trifluoroethyl 2-oxazolidinones (**2j**-**2l**) were also successfully attained in good

<i>ا</i> للہ ا	NHR + ⁿ C _n F _{2n+1} I +	CO ₂ TBI MeC	D (1.5 equiv) N, visible light ⁿ F _{2n+1} C _r	
Entry	Allyl amine 1	${}^{n}C_{n}F_{2n+1}I$	Product 2	Yield ^b (%)
	^H N ^N R	$^{n}C_{4}F_{9}I$	°C4F9	
1	R = Bn, 1a		R = Bn, 2a	91
2	$\mathbf{R} = \mathbf{C}\mathbf{y}, 1\mathbf{b}$		$\mathbf{R} = \mathbf{C}\mathbf{y}, \mathbf{2b}$	80
3	R = Me, 1c		R = Me, 2c	99
4	$\mathbf{R} = {}^{t}\mathbf{B}\mathbf{u}, \mathbf{1d}$		$\mathbf{R} = {}^{t}\mathbf{B}\mathbf{u}, \mathbf{2d}$	88
		ⁿ C ₄ F ₉ I	°C4F9	
5	X = F, 1e		$\mathbf{X}=\mathbf{F},\mathbf{2e}$	82
6	X = Cl, 1f		X = Cl, 2f	90
7	X = Br, 1g		X = Br, 2g	90
8	$X = OCH_3$, 1h		$X = OCH_3, 2h$	82
9		ⁿ C ₄ F ₉ I		87
	H N 1a		21 0 N-Bn	
10		$^{n}C_{3}F_{7}I$	n = 3, 2j	94
11		$^{n}C_{6}F_{13}I$	n = 6, 2k	73
12		CF ₃ I	n = 1, 2l	96

^{*a*} Reaction conditions: allyl amine **1** (0.5 mmol), ${}^{n}C_{n}F_{2n+1}I$ (1.0 mmol), TBD (0.75 mmol), MeCN (2 mL), CO₂ (1 bar, closed), visible light (420-700 nm), r.t., 12 h. ^{*b*} Isolated yield. Cy = cyclohexyl.



Scheme 2 Carboxylative cyclization of allyl alcohols with CO2

is also applicable to the allyl alcohol (Scheme 2), producing the perfluoroalkylated cyclic carbonates (**2m** and **2n**), of which, **2m** is a promising co-solvent of lithium battery electrolytes.¹¹

As an attractive set of this work, the mechanism of this visible light-driven carboxylative cyclization was strictly explored. In the course of initial study on the reaction of *N*-benzylprop-2-en-1-amine **1a**, CO₂ and perfluorobutyl iodide in the absence of base, besides the product **2a**, an aziridine i.e. 1-benzyl-2-nonafluoropentyl-aziridine **3a** was isolated with a 35% yield (Table S1, entry 1, ESI[†]). When a base like TBD existed, most of reactants were converted into **2a** (Table S1, entry 2, ESI[†]). These results corroborated our initial hypothesis that the base is vital to efficient generation of a carbamate intermediate with subsequent formation of C–O bond rather than C–N bond formation. Indeed, treatment of the allyl amine **1a** and perfluorobutyl iodide with two equivalents of TBD under argon and visible light, the aziridine **3a** was obtained as the sole product in excellent yield (Table S1, entry 3, ESI[†]). When

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the resultant in above experiment was further treated with CO_2 , only **3a** recovered (Scheme 3a). In addition, when **3a** was subjected to the



Scheme 3 Exclusion experiment of the aziridine intermediate.

standard reaction conditions or treated with [TBDH]⁺I, the carboxylative cyclization was not observed (Scheme 3b). On the basis of these observations and previous reports about the iodo-perfluoroalkylation of alkene,⁸ it is strongly suggested that **2a** is not generated from **3a** but may be from an iodo-perfluoroalkylated intermediate **A**, which can be converted into **2a** facilely under basic conditions through intramolecular nucleophilic cyclization due to the good leaving ability of iodide ion (Scheme 4). In contrary, the intermediate **A** under neutral conditions tends to release CO₂, leading to afford β -halogenated amine species **B**, further the formation of byproduct **3a**.



Scheme 4 Competitive reactions between the formation of oxazolidinone 2a and aziridine 3a.

To confirm that an iodo-perfluoroalkylated intermediate is involved in the overall reaction, we monitored the carboxylative cyclization reaction of allyl alcohol 1m, CO₂ and ⁿC₄F₉I in deuterated acetonitrile by ¹H NMR technique in consideration of the relative stability of β -halogenated alcohol to β -halogenated amine. Within 1 h, the solubility of the allyl carbonate precipitated from allyl alcohol, CO2 and TBD is increasing, probably due to a little increase in reaction temperature caused by light input. Thus, an enhancement in the intensity of signal centred at 4.36 ppm was observed (Fig. 1). Meanwhile, a group of weak signals corresponding to 4nonafluoropentyl-ethylene carbonate 2m (diamonds in Fig. 1) appeared, indicating the start of this carboxylative cyclization reaction. As the reaction progressed at 4 h, a new set of signals emerged at $\delta = 4.31$, 3.82, 3.67 ppm (triangles in Fig. 1), assigned to the iodo-perfluoroalkylated carbonate D, which was indirectly corroborated by GC-MS (see Fig. S1, ESI[†]). From 6 h to 6.2 h, the carbonate **D** was fully converted into $2\mathbf{m}$. The ¹H NMR study confirms that the iodo-perfluoroalkylated carbonate



D is an intermediate in the carboxylative cyclization of allyl

Fig. 1 ¹H NMR spectra for the visible light-driven carboxylative cyclization of allyl alcohol **1m** (14.5 mg, 0.25 mmol), TBD (52.2 mg, 0.375 mmol), CO_2 (1 bar, closed) and ^{*n*}C₄F₉I (86 μ L, 0.5 mmol) in CD₃CN.

carbamate species A could presumably be involved in the carboxylative cyclization of allyl amines with CO_2 .

Since the visible light is indispensable to smooth conversion of **1a**, we speculated that the formation of iodoperfluoroalkylated carbamate intermediate **A** may go through the visible light-driven radical addition of ${}^{n}C_{4}F_{9}I$ to allyl amines. To further gain insight into the reaction mechanism, the radicaltrapping experiment was carried out by employing two equivalents of 4-OH-TEMPO under the standard conditions (Scheme 5a). As expected, **1a** was completely recovered, hinting that this carboxylative cyclization proceeded via a radical path. Furthermore, the reaction of ${}^{n}C_{4}F_{9}I$ with allyl ether **4** under standard conditions gave the cyclic product **5** in 61% yield (dr = 50:11), also implicating the involvement of the radical propagation (Scheme 5b).



On the basis of above observations, a plausible mechanism for the present metal-free and visible light-driven carboxylative cyclization of allyl amines **1** with CO₂ is depicted in Scheme 6, taking **1a** for an example. Initially, the carbamate **E** (Detailed characterizations of carbamate **E**, see ESI†) is formed readily from **1a** and CO₂ promoted by TBD.¹² Initiated by visible light, ${}^{n}C_{4}F_{9}I$ occurs to homolytic cleavage of carbon-iodine bond, generating $\bullet {}^{n}C_{4}F_{9}$ and I \bullet radical species. Addition of $\bullet {}^{n}C_{4}F_{9}$ radical to the π -bond of carbamate **E** furnishes the perfluoroalkylated secondary carbon radical species **F**, which is trapped by I \bullet radical to produce the iodo-perfluoroalkylated

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carbamate intermediate A-1 (Path I). Alternatively, the intermediate A-1 might be formed via a radical propagation of F with ${}^{n}C_{4}F_{9}I$ (Path II). Finally, intramolecular nucleophilic cyclization of A-1 gives the perfluoroalkylated 2-oxazolidinone 2a with release of [TBDH]⁺I⁻.



Conclusions

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In summary, we have developed an unprecedented radical protocol for carboxylative cyclization of allyl amines with CO_2 promoted by visible light irradiation with high efficiency under ambient conditions. By using perfluoroalkyl iodides as radical and fluorine sources, this strategy achieves concurrent and direct incorporation of both CO_2 and perfluoroalkyl moiety into oxazolidinones in excellent yields. Control experiments and ¹H NMR study show that the iodo-perfluoroalkylated carbamate generated through the visible light-driven radical addition of ${}^{n}C_{4}F_{9}I$ to allyl amines could be the intermediate of this reaction. Notably, the perfluoroalkylated cyclic carbonate is also obtained successfully via this protocol from allyl alcohol and CO_2 . This protocol also offers a sustainable and promising approach for incorporating CO_2 into heterocycles through efficient usage of solar energy.

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