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Cooperative photoredox and N-heterocyclic carbene-catalyzed formal C–H acylation of cyclopropanes via a deconstruction–reconstruction strategy†

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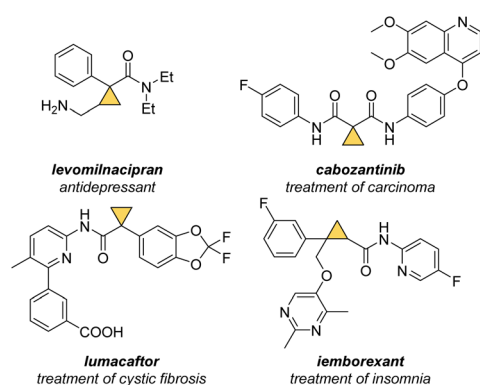
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Cyclopropanes are ubiquitous and key structural motifs in commercially available drugs and bioactive molecules. Herein, we present regio-selective acylation of aryl cyclopropanes with cooperative photoredox and N-heterocyclic carbene catalysis. This approach involves a deconstruction–reconstruction strategy via γ -chloro-ketones as intermediates and fulfills the formal C(sp³)–H functionalization of cyclopropanes.

Cyclopropanes, as strained cycloalkanes, have gained significant attention due to their ubiquitous and key structural motif in commercially available pharmaceutical candidates and drugs as well as their promising bioactivities (Scheme 1).¹ Additionally, compared with *gem*-dimethyl, isopropyl and phenyl groups, cyclopropane derivatives exhibit enhanced metabolic stability and reduced lipophilicity because of their structural characteristics involving high coplanarity of the ring-carbon atoms, enhanced π -character, relatively shorter C–C bonds, and shorter and stronger C–H bonds.² However, the functionalization of strained cyclopropane frameworks represents an important challenge for chemical synthesis.

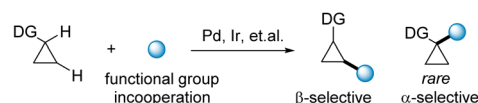


Scheme 1 Selected application examples of bioactive cyclopropane.

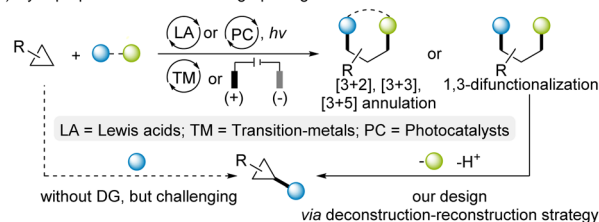
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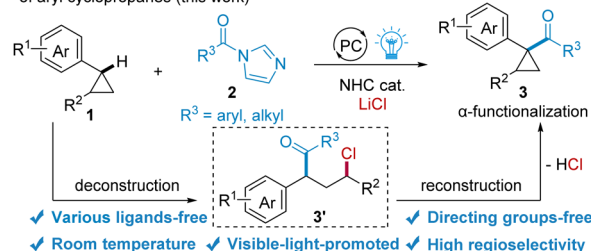
Direct C(sp³)–H functionalization of strain cyclopropane frameworks has been recognized as an economic and simple strategy to access various cyclopropane scaffolds. Yu, Gaunt, Xu and others have reported powerful strategies to synthesize monofunctionalized cyclopropane derivatives³ via the coordination interaction of transition-metals (Pd or Ir) and various directing groups (DGs) such as carboxylic acids,^{3f} primary amines,^{3g} *N*-aryl carboxamides,³ⁱ *N*-triflamides,^{3e} *N*-aryl-amino-methyl,^{3h} carboxamide,^{3c,d} and ether^{3j} (Scheme 2a).

a) Selective C(sp³)–H functionalization of cyclopropane with directing groups

b) Cyclopropane as C3 unit for ring-opening reactions



c) Construct tertiary cyclopropane via deconstruction–reconstruction strategy of aryl cyclopropanes (this work)



Scheme 2 Functionalization of strained cyclopropanes.

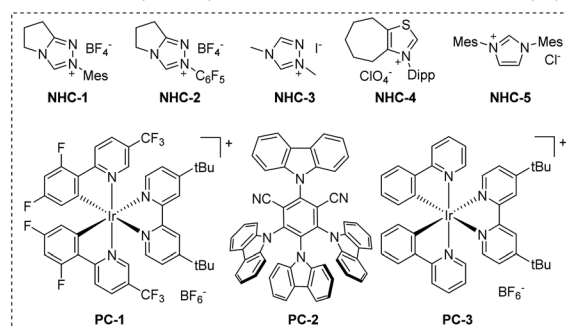
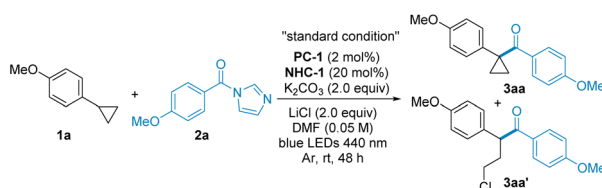
Those available protocols show good regioselectivity, introducing various functional groups to the β -position of DGs, while few directed $C(sp^3)$ -H functionalized examples at the α -position^{3f} have been achieved. Besides requiring tedious processes to introduce appropriate directing groups (DGs) and costly transition-metals as catalysts, those aforesaid methodologies usually require harsh reaction conditions, like heating to keep high regio- and stereoselectivity.

Due to their high ring strain energies (*ca.* 27.5 kcal mol⁻¹), cyclopropane derivatives easily undergo deconstruction of the coplanarity ring, and have been identified as versatile and powerful C3 units in synthesis. Diverse strategies catalyzed by Lewis acids,⁴ transition-metals (Rh, Ni, Pd, Fe),⁵ visible light⁶ and electricity⁷ have been developed to produce [3 + *n*]

annulation products (Scheme 2b). Meanwhile, 1,3-difunctionalization of cyclopropanes has also been achieved, generating acyclic products with introduction of two distinct functional groups.⁸ We envisioned that, with suitable functional groups as leaving groups, 1,3-elimination reactions are viable, which will reconstruct the cyclopropane skeleton. The two-step strategy of deconstructive 1,3-difunctionalization and 1,3-elimination would fulfill the formal $C(sp^3)$ -H functionalization of cyclopropanes and avoid the preinstallation of directing groups. With the rapid development of radical N-heterocyclic carbene (NHC) catalysis⁹ and our contribution in this area,^{9,10} herein, we disclose a cooperative NHC and photoredox^{9h,11} catalyzed acylation of aryl cyclopropanes, which involves formal C-H functionalization that has been achieved *via* a deconstruction-

Table 1 Reaction optimization^a

Entry	Variation from "standard conditions"	Yield ^b 3aa [%]	Yield ^b 3aa' [%]
1	None	78	0
2	K ₂ CO ₃ (0.2 equiv.) instead of K ₂ CO ₃ (2.0 equiv.)	50	26
3	NHC-2 instead of NHC-1	11	12
4	NHC-3 instead of NHC-1	8	26
5	NHC-4 instead of NHC-1	24	0
6	NHC-5 instead of NHC-1	0	0
7	PC-2 (5 mol%) instead of PC-1	32	0
8	PC-3 instead of PC-1	11	0
9	MeCN instead of DMF	21	20
10	DMSO instead of DMF	42	0
11	Cs ₂ CO ₃ instead of K ₂ CO ₃	57	0
12	K ₃ PO ₄ instead of K ₂ CO ₃	29	22
13	Na ₂ CO ₃ instead of K ₂ CO ₃	37	0
14	Me ₄ NCl instead of LiCl	50	0
15	KCl instead of LiCl	15	0
16	Without NHC-1	0	0
17	Without PC-1	0	0
18	In the dark	0	0
19	DMF (0.1 M) instead of DMF (0.05 M)	85(79) ^c	0



^a All reactions were performed by using **1a** (0.1 mmol), **2a** (2.0 equiv.), **PC-1** (2 mol%), **NHC-1** (20 mol%), K₂CO₃ (2.0 equiv.), LiCl (2.0 equiv.), and anhydrous DMF (0.05 M) under blue LEDs (440 nm, 20 W), stirred at room temperature and in Ar for 48 h. ^b Yield was determined by ¹H NMR.

^c Isolated yield was given in parentheses.

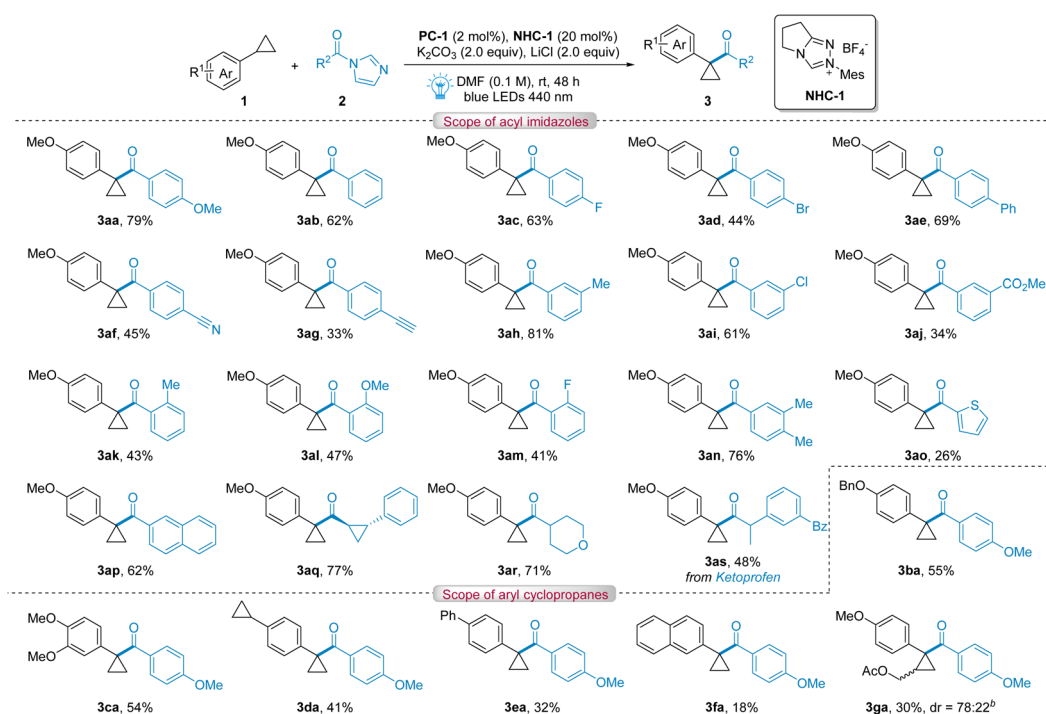
reconstruction strategy with γ -chloro-ketones as intermediates. Either aromatic or aliphatic acyl groups can be selectively introduced to the α -position of aryl groups. Meanwhile, this method could be extended to esterification of cyclopropanes with carbonate esters.

Studer's group has achieved the 1,3-difunctionalization of aryl cyclopropanes catalyzed by a cooperative NHC and organophotoredox catalyst, generating various γ -aryloxy ketones.^{11d} To facilitate reconstruction of cyclopropanes, we used acyl imidazole as the acyl source to avoid introducing the poor-leaving ester group. Hence, we first started our investigation by using 1-anisoylcyclopropane (**1a**) and *N*-anisoylimidazole (**2a**) as the model substrates in the presence of the triazolium-type NHC-1 as the organo-catalyst, [Ir(dF(CF₃)ppy)₂(dtbbpy)]PF₆ (**PC-1**) as the photocatalyst, LiCl as an additive, K₂CO₃ as the base and anhydrous DMF as the solvent at room temperature under an Ar atmosphere and the irradiation of 20 W blue LEDs. After 48 h of reaction, the desired tertiary cyclopropane product **3aa** was obtained in 78% yield (Table 1, entry 1). When we reduced 2.0 equivalents of K₂CO₃ to 0.2 equivalents, a 50% yield of **3aa** was obtained, accompanied by the 1,3-difunctionalization product **3aa'** in 26% yield (entry 2). This indicates that product **3aa'** was transformed into product **3aa** after increasing the equivalent of base and that product **3aa'** was the key intermediate. Screening different organo-catalysts (entries 3–6) showed that the yields of **3aa** decreased with other NHCs. Other photocatalysts (entries 7 and 8) like 4CzIPN also showed

decreased yields. Lower yields were obtained in CH₃CN and DMSO (entries 9 and 10). Subsequently, several bases and additives were explored (entries 11–15), and the results showed that LiCl and K₂CO₃ were the most suitable additive and base in this reaction system. Control experiments indicated that the NHC catalyst, photocatalyst and visible light were critical for this reaction (entries 16–18). Finally, a higher concentration for substrates gave a better yield of 85% (entry 19).

With the optimized reaction conditions in hand, we explored a series of acyl imidazoles **2** (Table 2). Benzoyl imidazoles with different substituents bearing electron-donating or electron-withdrawing groups at the *para*- or *meta*-position proceeded smoothly to afford the desired tertiary cyclopropanes **3aa–3aj** in moderate to good yields (33–81%). In general, higher yields were obtained for benzoyl imidazoles with electron-donating groups while lower yields were obtained for benzoyl imidazoles with strong electron-withdrawing groups. A low yield was obtained for **3ad**, which is due to dehalogenation. For benzoyl imidazoles with *ortho*-substituents, corresponding products were obtained in 41–47% yields due to the effect of steric hindrance. Different aromatic substituted acyl imidazoles like 2-thienyl and 2-naphthyl were also found to be suitable in this reaction, affording corresponding products **3ao** and **3ap** in 26% and 62% yields, respectively. We speculate that the oxidation of thienyl under reaction conditions results in the low yield for **3ao**. NHC-catalyzed radical acylations were usually limited to aryl acyl substrates, while aliphatic substrates were

Table 2 Scope of substrates acyl imidazoles and aryl cyclopropanes^a



^a All reactions were performed by using **1a** (0.1 mmol), **2** (2.0 equiv.), **PC-1** (2 mol%), **NHC-1** (20 mol%), K₂CO₃ (2.0 equiv.), LiCl (2.0 equiv.), and anhydrous DMF (0.1 M) under blue LEDs (440 nm, 20 W), stirred at room temperature and in Ar for 48 h, isolated yields were given. ^b dr was determined by ¹H NMR.

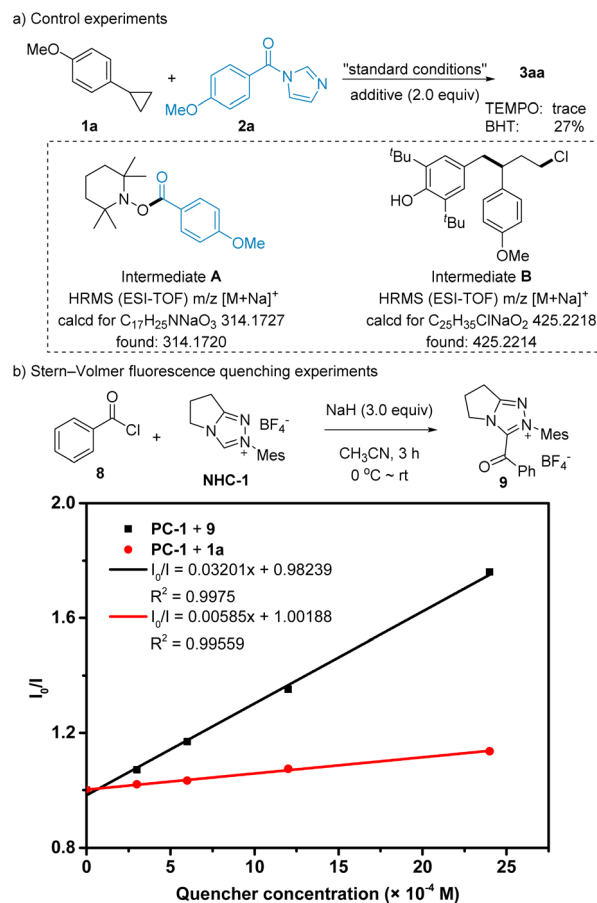
challenged.^{11e} Gratifyingly, we found that aliphatic acyl imidazoles could also react smoothly with cyclopropane **1a**, leading to the formation of desired products **3aq–3ar** in high yields (71–77%). To demonstrate the high functional group tolerance and broad substrate scope of acyl imidazoles, late-stage functionalization of a bioactive molecule derived from ketoprofen was explored, generating the corresponding α -acylated cyclopropane derivative **3as** in moderate yield (48%).

The scope of aryl cyclopropanes was also investigated (Table 2). For aryl cyclopropanes bearing various substituents at the *para*-positions of the aryl moiety such as benzyloxy, disubstituted methoxy, cyclopropyl and phenyl, the corresponding products **3ba–3ea** were obtained in moderate yields (32–55%). Notably, it could selectively afford mono-acylated cyclopropane derivatives **3da** from a substrate bearing two cyclopropyl groups at 1,4-positions of the benzene ring. A low yield was obtained for **3fa**, which is due to acylation at the naphthalene ring.¹² Finally, to address the limitation of regioselectivity and diastereoselectivity, an unsymmetric cyclopropane, 1-ethoxy-2-phenylcyclopropane was explored to produce **3ga** in 30% yield, showing excellent regioselectivity albeit moderate diastereoselectivity (*dr* = 78 : 22).

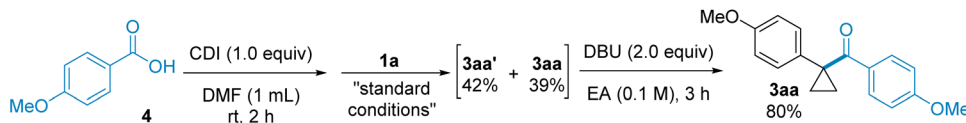
To demonstrate the ease and practicality of this method, a “one-pot, two-step” process was performed starting from carboxylic acid **4**, generating **3aa** in 80% yield (compared to 79% when starting from *N*-anisoylimidazole **2a**) (Scheme 3). NHC-catalyzed radical esterification reactions have been developed recently.^{11g} We also extended this deconstruction–reconstruction strategy for the formal esterification of cyclopropanes. With diethyl dicarbonate **5** as the esterification reagent, **1a** was converted to α -esterified cyclopropanes **6** in 74% yield. Furthermore, **6** can be easily converted to amide product **7**, which has the skeleton of lumacaftor (Scheme 4).

To gain a deep insight into the mechanism for this transformation, several control experiments were subsequently conducted. Initially, radical scavengers (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO) and 2,6-di-*tert*-butyl-4-methylphenol (BHT) were employed respectively, which clearly inhibited the reaction (Scheme 5a). These results indicated that a radical process might be involved. Moreover, the intermediates **A** and **B** were successfully detected by high-

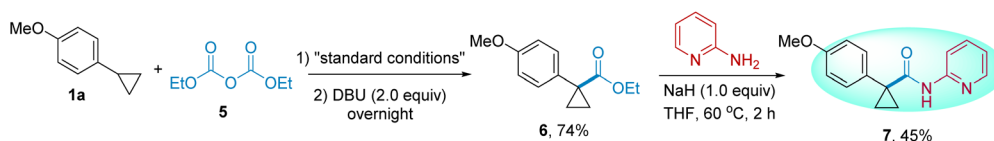
resolution mass spectrometry (HRMS), implying that the NHC-derived ketyl radical and alkyl radical were generated in this transformation. Subsequently, Stern–Volmer fluorescence quenching experiments were carried out (for details see ESI†). As shown in Scheme 5b, the obvious linear relationships and different slopes between the fluorescence intensities and the concentrations of **1a** and **9** suggested that the excited photocatalyst was more favorable to be quenched by acyl azolium **9**.



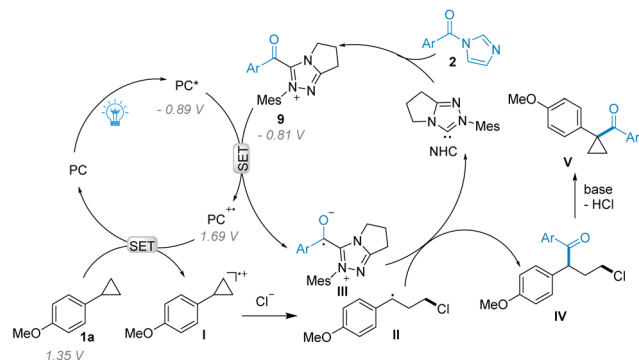
Scheme 5 Control experiments and linear relationship between I_0/I and the concentration of **1a** and **9**.



Scheme 3 “One-pot, two-step” acylation reaction from carboxylic acid.



Scheme 4 Esterification of cyclopropane **1a** and further transformation.



Scheme 6 Plausible reaction mechanism.

Based on these results of control experiments and previous investigations, we proposed the following mechanism (Scheme 6). The excited photocatalyst $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (PC^*) ($E_{\text{ox}} = -0.89$ V vs. SCE)¹³ was oxidatively quenched by acyl azolium **9** ($E_{1/2} = -0.81$ V vs. SCE)¹⁴ to generate NHC-derived ketyl radical intermediate **III** and $\text{PC}^{+\bullet}$. Then, the substrate **1a** ($E_{1/2} = +1.35$ V vs. SCE) was oxidized by $\text{PC}^{+\bullet}$ ($E_{\text{PC}^{+\bullet}/\text{PC}} = +1.69$ V vs. SCE) to regenerate ground photocatalyst **PC** and intermediate **I**. Subsequently, chloride ions reacted with intermediate **I** to produce alkyl radical intermediate **II**, which coupled with the NHC-derived ketyl radical intermediate **III** to produce γ -chloro ketones as intermediates **IV**. Finally, the targeted product **V** was afforded *via* nucleophilic substitution in the presence of a base.

Conclusions

Directed $\text{C}(\text{sp}^3)\text{-H}$ functionalization of strained cyclopropanes usually requires the coordination of transition-metals (Pd or Ir), ligands and various directing groups (DGs) to obtain high regio- and stereoselectivity cyclopropane scaffolds. In this paper, we present a deconstruction–reconstruction strategy for the regio-selective acylation of aryl cyclopropanes with cooperative photoredox and N-heterocyclic carbene catalysis, fulfilling the formal $\text{C}(\text{sp}^3)\text{-H}$ acylation of cyclopropanes. Besides that aromatic and aliphatic acyl groups can be selectively introduced to the α -position of aryl groups, this method could be extended to esterification of cyclopropanes with carbonate esters. α -Esterified cyclopropanes subsequently transformed into amide products, undoubtedly providing a far superior alternative for the preparation of analogous derivatives of commercially available pharmaceutical candidates and available drugs. Further studies on the applications of this deconstruction–reconstruction strategy will be reported in due course.

Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

F. G. and X. Y. conceived and designed the study. F. G. and T. W. performed the synthetic experiments with input from X. Y. The

mechanistic investigations were performed by F. G. The manuscript was prepared by F. G. and X. Y. All authors discussed the experimental results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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