

# NHCs and Visible Light-mediated Photoredox Co-catalyzed Radical 1,2-Dicarbonylation of Alkenes for 1,4-Diketones

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## Abstract

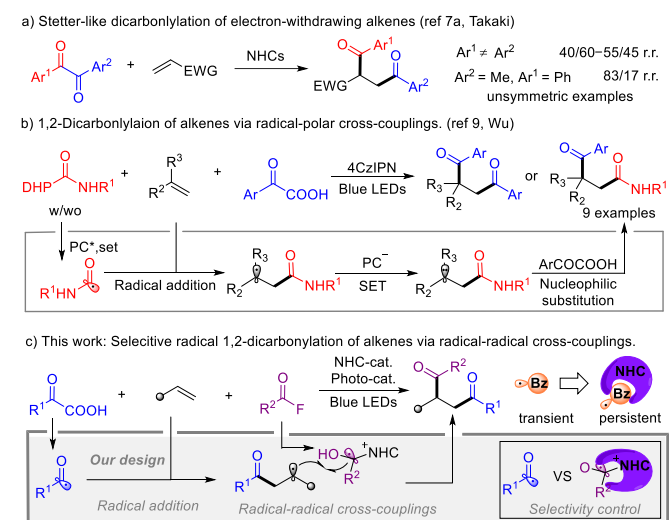
Alkenes are ubiquitous, and radical difunctionalization of alkenes represents one of the most practical approaches to constructing value-added compounds. Dicarbonylation of alkenes provides direct access to value-added 1,4-dicarbonyl compounds. However, selectivity control for unsymmetric 1,2-dicarbonylation is an unclosed challenge. We herein describe NHCs and photocatalysis co-catalyzed three competent radical 1,2-dicarbonylation of alkenes by distinguishing two carbonyl groups, providing structurally diversified 1,4-diketones. Mechanistic studies indicated that NHCs-stabilized ketyl-type radicals originate from aroyl fluorides via oxidative quenching process of excited photocatalysis, and acyl radicals are generated from single-electron-oxidation of  $\alpha$ -keto acids. Distinct properties of acyl radical and NHCs-stabilized ketyl radical contributed to selectivity control. Transient acyl radicals are rapidly added to alkenes delivering alkyl radicals, which undergo subsequent radical-radical cross-coupling with ketyl-type radicals, affording 1,2-dicarbonylation products. This transformation features mild reaction conditions, broad substrate scope, and excellent selectivity, providing a general and practical approach for the dicarbonylation of olefins.

## Introduction

Alkenes are ubiquitous and fundamental motifs in organic molecules. Radical difunctionalization of alkenes<sup>1</sup> is one of the most practical approaches to constructing value-added compounds in the atom- and step-economic manner and with significant synthetic potential. Since the radical-radical cross-couplings preceded nearly diffusion-controlled processes,<sup>2</sup> steric hindrance and electron effects were insensitive, representing an attractive approach for the difunctionalization of C=C bonds. However, selectivity control for radical-radical cross-coupling pathways was a formidable challenge. The research was limited to two radicals with apparent differences in properties, such as transient radicals and persistent radicals.<sup>2-3</sup> Reactivity is the natural property of the radical species depending on the structure; distinguishing the reactivity for two radicals with a similar structure is a significantly attractive but challenging task in radical chemistry. Turning the radical reactivity<sup>4</sup> might be essential to achieve selectivity control.

1,4-Dicarbonyl compounds found widespread applications in pharmaceutical molecules, bioactive natural compounds, and materials science.<sup>5</sup> Direct dicarbonylation of alkenes might provide straightforward access to 1,4-dicarbonyl compounds.<sup>6-10</sup> Symmetric 1,2-dicarbonylations have been achieved by employing a stoichiometric reducing agent,<sup>6</sup> or NHCs-catalyzed Stetter reaction for activated Michael acceptor (Scheme 1b).<sup>7</sup> Recently, Xia et al. developed symmetric 1,2-dicarbonylations of olefins, in which the second C-acyl bond was formed via Ni-participated reductive eliminations.<sup>8</sup> For unsymmetric 1,2-dicarbonylation, selectivity is an unclosed problem (Scheme 1b).<sup>7a</sup> Wu and co-workers achieved the

major breakthrough in this domain by employing a visible light-mediated radical-polar cross-coupling strategy (Scheme 1c).<sup>9</sup> Efficient distinguishment of amide acyl and arylformyl groups was developed for the first time by tuning the reductive and electrophilic ability of acyl precursors. Despite the significance, the development of general unsymmetric 1,2-dicarbonylation of olefins, especially for the selective installation of two similar acyl groups, was highly attractive and largely underdeveloped.<sup>9-10</sup>

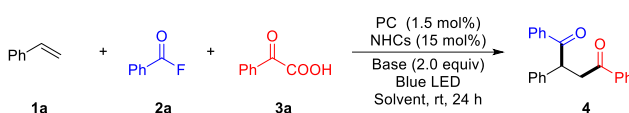


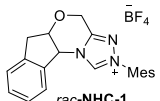
**Scheme 1** Unsymmetric 1,2-dicarbonylation of Alkenes

As distinctive radical species, acyl radicals play an essential role in the construction of carbonyl compounds. Most frequently, acyl radicals undergo addition to unsaturated bonds.<sup>11</sup> NHCs inhibit predominant activity<sup>12</sup> in constructing the carbon-acyl bond via the polar pathway. Recently, NHCs-catalyzed radical transformation opened a new avenue for radical acylation chemistry that enables NHCs-stabilized ketyl-type radicals<sup>13</sup> to undergo radical-radical cross-coupling.<sup>14</sup> Pioneered by Omiya et al.,<sup>15a</sup> numerous elegant progress has been developed for direct coupling<sup>15,16,20a-c</sup> or difunctionalization strategy,<sup>17-19,20d-f</sup> providing alternative methods for synthesizing functionalized ketone units.<sup>14-20</sup> Cooperation of NHCs with photocatalysis is attractive that realizes novel transformation under very mild reaction conditions.<sup>16,18,20,21</sup> In this domain, Studer,<sup>20c-f</sup> Scheidt,<sup>16a-c,18b</sup> and Chi<sup>16d</sup> et al. made significant contributions for the radical transformation of acylazolum intermediate. Studer et al. developed new properties of aroyl fluorides,<sup>20c-f</sup> which could act as efficient ketyl-type radical precursors *via* photo-induced single-electron transfer. Motivated by that elegant progress<sup>20c-f</sup> and acyl radical formation from  $\alpha$ -keto acids,<sup>22</sup> we envisaged that cooperation of NHCs and photocatalysis<sup>16,18,20,21</sup> enables the generation of acyl radicals and NHCs-stabilized ketyl radicals under extremely mild conditions, which may provide a solution for challenging distinguishment for similar acyl radicals (Scheme 1c). As our longstanding interests in radical chemistry,<sup>23</sup> we now describe our findings in three-component unsymmetric radical 1,2-dicarbonylation of alkenes by turning reactivity of one acyl radicals, providing direct access to structurally diversified 1,4-diketones (Scheme 1c).

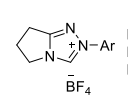
## Results and discussion

**Table 1** Condition optimizations.<sup>a,b</sup>

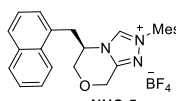
					
Entry	NHC Cat. (15 mol%)	PC (1.5 mol%)	Solvent (2 mL)	Base (2.0 eq.)	Yields (%)
1	<b>NHC-1</b>	<b>PC-1</b>	DCM	Cs <sub>2</sub> CO <sub>3</sub>	34
2	<b>NHC-1</b>	<b>PC-1</b>	DCM	K <sub>2</sub> PO <sub>4</sub>	20
3	<b>NHC-1</b>	<b>PC-1</b>	DCM	DBU	28
4	<b>NHC-1</b>	<b>PC-1</b>	Dioxane	Cs <sub>2</sub> CO <sub>3</sub>	44
5	<b>NHC-1</b>	<b>PC-1</b>	THF	Cs <sub>2</sub> CO <sub>3</sub>	45
6	<b>NHC-1</b>	<b>PC-1</b>	<sup>t</sup> BuOMe	Cs <sub>2</sub> CO <sub>3</sub>	42
7	<b>NHC-1</b>	<b>PC-1</b>	CH <sub>3</sub> CN	Cs <sub>2</sub> CO <sub>3</sub>	28
8	<b>NHC-1</b>	<b>PC-1</b>	Tolune	Cs <sub>2</sub> CO <sub>3</sub>	74
9	<b>NHC-2</b>	<b>PC-1</b>	Tolune	Cs <sub>2</sub> CO <sub>3</sub>	56
10	<b>NHC-3</b>	<b>PC-1</b>	Tolune	Cs <sub>2</sub> CO <sub>3</sub>	trace
11	<b>NHC-4</b>	<b>PC-1</b>	Tolune	Cs <sub>2</sub> CO <sub>3</sub>	12
12	<b>NHC-5</b>	<b>PC-1</b>	Tolune	Cs <sub>2</sub> CO <sub>3</sub>	62
13	<b>NHC-1</b>	<b>PC-2</b>	Tolune	Cs <sub>2</sub> CO <sub>3</sub>	69
14	<b>NHC-1</b>	<b>PC-3</b>	Tolune	Cs <sub>2</sub> CO <sub>3</sub>	n.d.
15	<b>NHC-1</b>	<b>PC-4</b>	Tolune	Cs <sub>2</sub> CO <sub>3</sub>	40
16	<b>NHC-1</b>	<b>PC-5</b>	Tolune	Cs <sub>2</sub> CO <sub>3</sub>	n.d.
17 <sup>c</sup>	<b>NHC-1</b>	<b>PC-1</b>	<b>Tolune</b>	<b>Cs<sub>2</sub>CO<sub>3</sub></b>	<b>72</b>



**PC-1:** [Ir(ppy)<sub>2</sub>(dtbbpy)]PF<sub>6</sub>  
**PC-3:** Ir(ppy)<sub>3</sub>



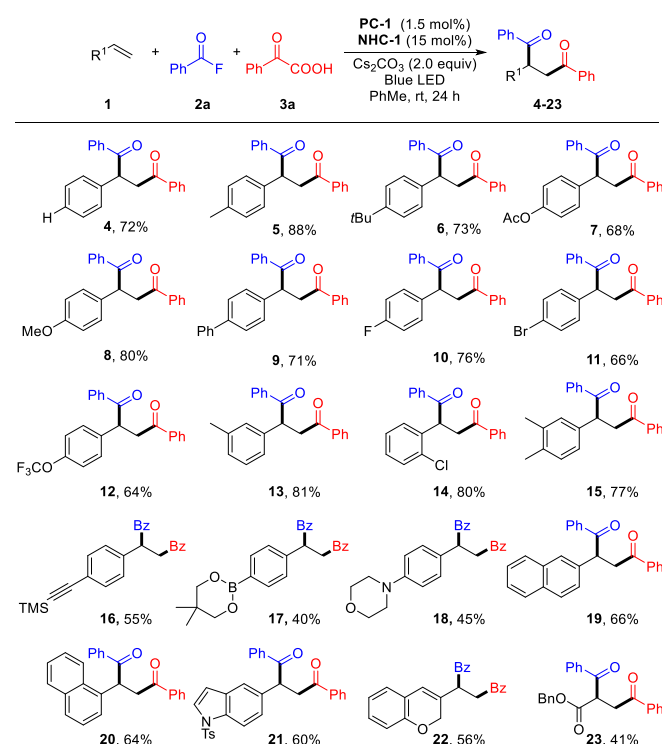
**NHC-2:** Ar = Mes  
**NHC-3:** Ar = C<sub>6</sub>F<sub>5</sub>  
**NHC-4:** Ar = Ph



**PC-2:** [Ir(dF(CF<sub>3</sub>))ppy]<sub>2</sub>(dtbbpy)]PF<sub>6</sub>  
**PC-4:** 4CZIPN  
**PC-5:** Ru(bpy)<sub>3</sub>(BF<sub>4</sub>)<sub>2</sub>

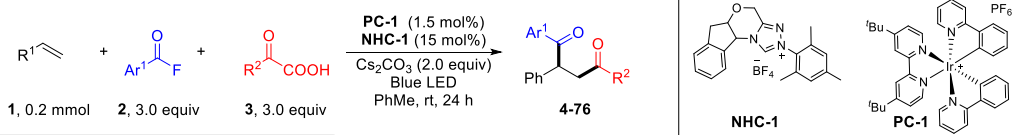
<sup>a</sup> Unless otherwise noted, all the reactions were carried out with **1a** (0.1 mmol), **2a** (0.2 mmol), **3a** (0.2 mmol), **NHCs** (0.015 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.2 mmol), and **PC** (0.0015 mmol) in anhydrous solvent, irradiation with Blue LEDs at room temperature for 4 h. <sup>b</sup> isolated yields. <sup>c</sup> 0.2 mmol scale reaction was conducted.

Our initial study of the 1,2-dicarbonylation of alkenes commenced with the dicarbonylation of styrene (**1a**) with benzoyl fluoride (**2a**) and benzoic acid (**3a**). Fortunately, by employing **NHC-1** (15 mol%) and [Ir(ppy)<sub>2</sub>(dtbbpy)]PF<sub>6</sub> (1.5 mol%) as catalyst, Cs<sub>2</sub>CO<sub>3</sub> (2.0 equiv) as base under Blue LED irradiation in DCM afforded desired 1,4-diketone **4** in 34% yields (Table 1, entry 1). Other bases, such as K<sub>2</sub>PO<sub>4</sub> and DBU, were also effective with slightly lower yields. Dioxane, THF, <sup>t</sup>BuOMe, and CH<sub>3</sub>CN could promote the transformation effectively with moderate yields (entries 4–7). The yields could improve to 74% when switching the solvent to PhMe (entry 8). An NHCs screen indicated that **NHC-1** is the most effective catalyst compared with other NHCs (entries 8–12); steric hindrance NHCs seem to be more suitable for this cascade reaction. Replacing the photocatalysts to Ir[dF(CF<sub>3</sub>))ppy]<sub>2</sub>(dtbbpy)]PF<sub>6</sub> and 4CZIPN provided **4** in 69 and 40% yields. However, no product was observed for **PC-4** and **PC-5**. When the reaction was carried out at 0.2 mmol scales, the desired 1,4-diketone **4** could be separated in 72% yield.

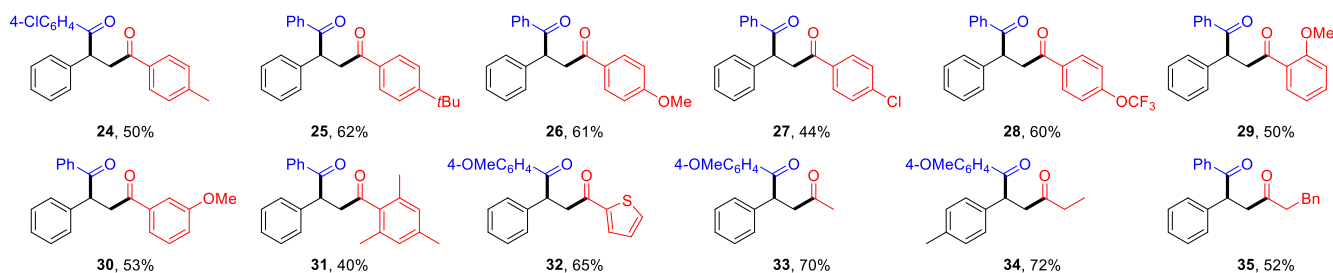


**Scheme 2** Substrate scope for symmetric 1,2-dicarbonylation of Alkenes.<sup>a,b</sup> Conditions A: Unless otherwise noted, all the reactions were carried out with **1** (0.2 mmol), **2a** (0.4 mmol), **3a** (0.4 mmol), **NHC-1** (0.03 mmol), **PC-1** (0.003 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (0.4 mmol) in PhMe (4 mL) at rt under N<sub>2</sub>, irradiation with Blue LED (453.5 nm, 5 W) for 24 h. <sup>b</sup> Isolated yield.

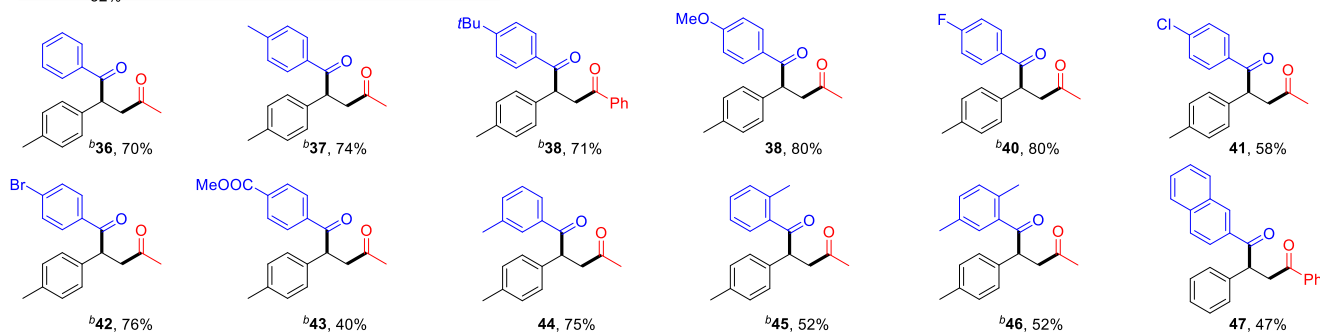
With the optimized conditions in hand, we next explored the substrate scope for this 1,2-dicarbonylation. As shown in Scheme 2, styrene derivatives bearing electron-donating (methyl, *t*-butyl, methoxycarbonyl, methoxyl), phenyl, halogen (fluorine, bromine), or strong electron-withdrawing trifluoromethoxy group at the para position were all well tolerated and affording 1,4-diketone **4-12** in 66–80% yields, indicating the intensity of electron effect. This transformation shows well tolerances to steric hindrance as identified by *meta*-(**13**, 81%), or *ortho*-(**14**, 82%) substituted styrenes. Disubstituted styrenes were also applicable for this



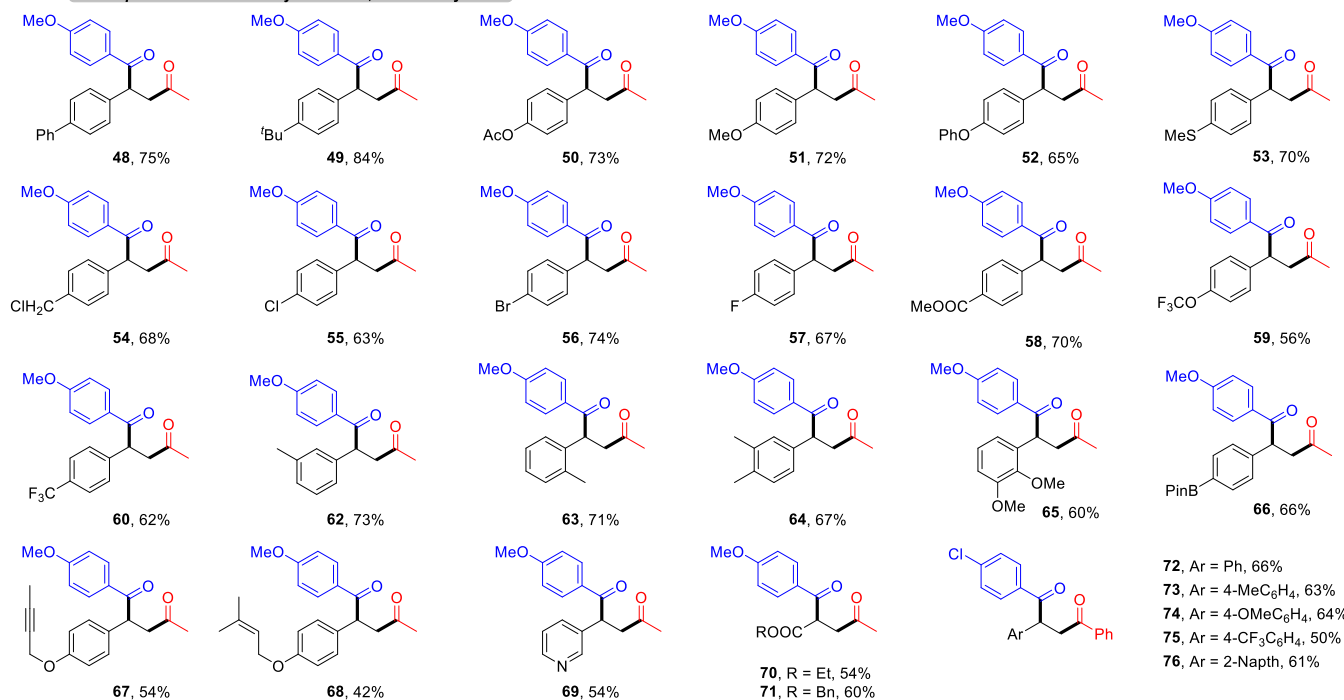
**A Scope of  $\alpha$ -keto acids for unsymmetric 1,2-dicarbonylation**



**B Scope of acyl fluorides for unsymmetric 1,2-dicarbonylation**



**C Scope of alkenes for unsymmetric 1,2-dicarbonylation**

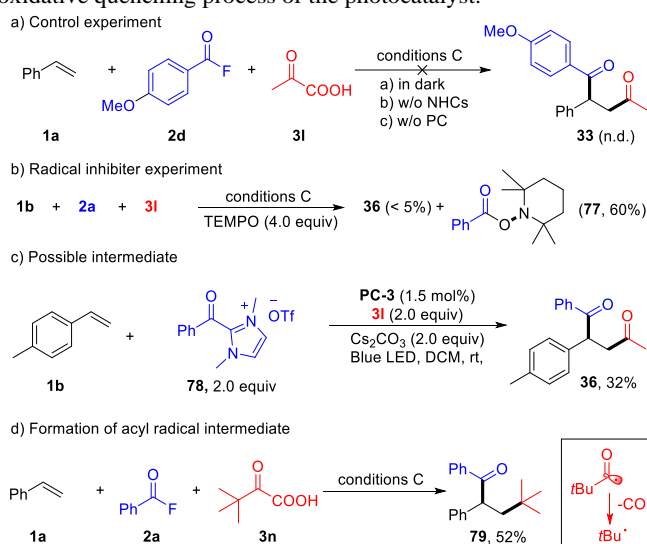


**Scheme 3** Substrate scope for symmetric 1,2-dicarbonylation of Alkenes.<sup>a</sup> Conditions B: For aryl-substituted  $\alpha$ -keto acids, the reactions were carried out with **1** (0.2 mmol), **2** (0.6 mmol), **3** (0.6 mmol), **NHC-1** (0.03 mmol), **PC-1** (0.003 mmol) and  $Cs_2CO_3$  (0.4 mmol) in PhMe (4 mL) at rt under  $N_2$ , irradiation with Blue LED (453.5 nm, 5 W) for 24 h. isolated yields. Conditions C: For alkyl-substituted  $\alpha$ -keto acids, DCM was employed as the solvent instead of PhMe. Isolated yields. <sup>b</sup> **2** (0.8 mmol), **3** (0.8 mmol) was employed.

dicarbonylation. Furthermore, vulnerable trimethylsilyl ethynyl (**16**), boric ester (**17**) and morpholino (**18**) groups were left intact under reaction conditions, providing an opportunity for further transformation. Naphthalene (**19**, **20**), indole (**21**), 2H-chromene (**22**) substituted styrenes could also deliver the desired product in 56-66% yields. This 1,2-dicarbonylation system could be extended to Michael acceptor (**23**).

After defining the scope of symmetric 1,2-dicarbonylation, we turned attention to the more challenging unsymmetric 1,2-dicarbonylations, which could reflect the advantages of designed tricomponent cascade reaction. First, we attempted the scope of acyl radical source, and the results were summarized in Scheme 3a. Different benzoylformic acids bearing a range of functional groups were well tolerated, including alkyl (**24**, **25**), strong electron-donating methoxyl (**26**), halogen (**27**), and strong electron-withdrawing trifluoromethoxy (**28**) group. *Meta*- (**30**), *ortho*- (**29**), and sterically encumbered 2,4,6-*tri*- (**31**) substituted benzoylformic acids were competent to afford the products in acceptable yield. Thiophene substituted benzoylformic acid was proved to be an efficient acylation source and provided **32** in 65% yield. It should be noted that our 1,2-dicarbonylation system could be further extended to pyruvic acid and its derivatives, affording **33-35** in 52-72% yield with slightly modified conditions. To the best of our knowledge, this is the first practical selective acetylative carbonylation. We next explore the scope of aryl fluorides by employing pyruvic acid as an acetylation source (Scheme 3b). To our delight, this acetylative carbonylation strategy was tolerated with various electron-donating (alkyl, methoxyl), halogen (fluorine, chlorine, bromine), electron-withdrawing (ester carbonyl), and phenyl substituents at para (**36-43**), meta (**44**), or ortho (**45**) positions of the phenyl rings, affording **36-45** in 40-80% yields. Electron-withdrawing aryl fluoride exhibited slightly lower activity (**43**, 40%). 2,4-*di*Me-substituted aryl fluoride (**45**, 52%) was proved to be an effective ketyl-type radical precursor the acetylative carbonylation. Naphthyl fluoride was also tolerated in this cascade reaction, delivering **47** in 47% yield. While this method demonstrates the considerable scope for benzoylformic acids and aryl fluorides, we next investigate the substrates scope of olefins for unsymmetric 1,2-dicarbonylations. As summarized in Scheme 3c, various styrenes and Michael acceptors were tolerated and afforded **48-76** in moderate to high yields. For styrenes, the electron-donating group at the para position of phenyl rings provides excellent reactivity, providing **48-54** 65-84% yields. Acetoxy (**50**, 73%), benzyl chloride (**54**, 68%), and methylthio (**53**, 70%) groups were tolerated, indicating broad application scope. Halogen (fluorine, chlorine, bromine) groups were applicable (**55-57**), which might provide the opportunity for cross-coupling. Methoxycarbonyl substituted aryl olefin could be converted to **58** in 70% yield. Strong electron-withdrawing trifluoromethoxy and trifluoromethyl groups were also compatible with this cascade reaction, and corresponding product **59** and **60** was isolated in 56 and 62% yield, respectively. 2-Me (**63**, 71%), 3,4-*di*Me (**64**, 67%) and 2,3-*di*OMe (**65**, 60%) substituted aryl olefins were also effective. Furthermore, some potentially reactive functional groups, such as Bpin (**66**, 66%), insular alkyne (**67**, 54%), and olefin (**68**, 42%) units have been preserved in our system. Notably, heterocycle substrates were suitable for this chemistry, such as pyridine (**69**, 54%). This strategy was also applicable for acetylation carbonylation of acrylate, affording **70** and **71** in 54 and 60% yield, respectively. Finally, we also tested the substrate scope of unsymmetric 1,2-dicarbonylations by installing benzoyl and 4-chlorobenzoyl groups. Preliminary attempts show electron-donating (**72-74**) and -withdrawing group (**75**) substituted phenyl ring, and naphthalene ring (**76**) were competent, delivering 1,4-diketone in 50-66% yields. The scope and selectivity of this NHCs and PC co-catalyzed system are quite broad and practical, addressing the important unsolved problem of classical methods for 1,2-dicarbonylation of olefins.

To get further information for 1,2-dicarbonylation, we performed a series of mechanism investigations (Scheme 4). Control experiments indicate NHCs, photocatalysis, and visible lights were indispensable for 1,2-dicarbonylation of olefins (Scheme 4a). The yield of **36** was dropped to 20% when the radical scavenger 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) was added, and TEMPO-trapping product **77** was isolated in 55% yield (Scheme 4b). This result indicates that the reaction might proceed via a radical mechanism involving ketyl radical originating from aryl fluorides. We synthesized acyl azolium ion **78** and applied it in the dicarbonylation reaction without NHCs. Desired product **36** was isolated in 32% yields (Scheme 4c), supporting acyl azolium ion might be the efficient intermediate. Furthermore, when employing 3,3-dimethyl-2-oxobutanoic acid **3n** as a radical precursor, alkylative acylation product **79** was identified, which might proceed via decarbonylation of *t*-Bu carbonyl radical species (Scheme 4d). Stern-Volmer quenching studies indicate the excited state of [Ir(ppy)<sub>2</sub>(dtbbpy)]PF<sub>6</sub> was preferred to be quenched by acyl azolium ion **78**, instead of pyruvic acid or olefins (Figure S1-4), which has a significant difference with Wu's<sup>9</sup> system. This result indicates the oxidative quenching process of the photocatalyst.

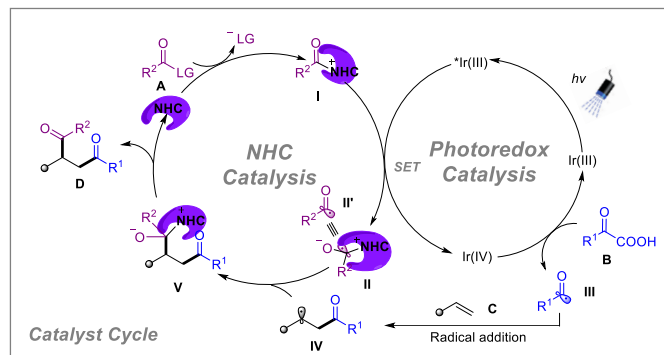


**Scheme 4** Mechanism investigation

Based on a series of experimental studies and insights from previous reports, we propose a mechanistic picture for the 1,2-dicarbonylation in Scheme 5. Acylazolium intermediate **I** is generated from the reaction of the aryl fluoride, or its analogs **A** react with NHCs. In situ generated excited state of [Ir(ppy)<sub>2</sub>(dtbbpy)]PF<sub>6</sub> undergo oxidative quenching by Acylazolium intermediate **I** afford the Ir<sup>IV</sup>-complex, and NHCs stabilized persistent ketyl-type radical species **II**. Ir<sup>IV</sup>-complex could oxidate pyruvic acid **B** to yield transient acyl radical **III** and regenerate the ground-state photocatalyst for the next photocatalyst cycle. Distinct properties of acyl and NHCs-stabilized ketyl radical show different reactivity regard with olefins. Transient acyl radical **III** undergoes radical addition to the double bond of olefin **C** delivering alkyl radical **IV**, which is specifically trapped by persistent ketyl-type radical **II** providing NHCs-linked intermediate **V**. Persistent radical effect<sup>2d</sup> made critical contributions to selectivity control towards acyl and ketyl-type radical in radical-radical coupling strategy.



Dissociation of NHCs from VI affording the 1,4-diketone **D**, completes the NHCs catalytic cycle. Additionally, the above evidence for free radical intermediates originated from aroyl fluoride (Scheme 4b) and pyruvic acid (Scheme 4d), and photochemical experiments are consistent with this catalytic cycle.



**Scheme 5** Proposed catalytic cycle

## Conclusions

In summary, we have developed an efficient NHCs Photoredox Co-catalyzed three-component unsymmetric radical 1,2-dicarbonylation of alkenes by turning reactivity of one acyl radicals. Mechanistic studies indicated that the reaction proceeded via radical-radical cross-couplings. Ketyl radicals originate from aroyl fluorides via the oxidative quenching process of excited photocatalysis, while the acyl radicals are formed from single-electron-oxidation of  $\alpha$ -keto acids. Distinct properties of acyl radical and NHCs-stabilized ketyl radical contributed to selectivity control. Different from Wu's strategy,<sup>9</sup> we realized selective 1,2-dicarbonylation for two aroyl groups or aroyl and alkanoyl groups. To the best of our knowledge, this strategy represents the first selective three-component dicarbonylation of olefins installing aroyl and alkanoyl groups.<sup>9,10</sup> The transformation proceeds under extremely mild conditions with good functional group tolerance and broad scope (73 examples, up to 84% yield), providing a general and practical approach for unsymmetric 1,2-dicarbonylation of olefins.

## Data availability

Data for all compounds in this manuscript are available in the ESI,<sup>†</sup> which includes experimental details, characterization and copies of <sup>1</sup>H and <sup>13</sup>C NMR spectra.

## Author Contributions

L. W., J. S., J. X., R. M., and M. L. performed the experiments and analyzed data. L. Z. participated in writing the paper. G. Z., and Q. Z. conceived the concept, directed the project and wrote the paper.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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