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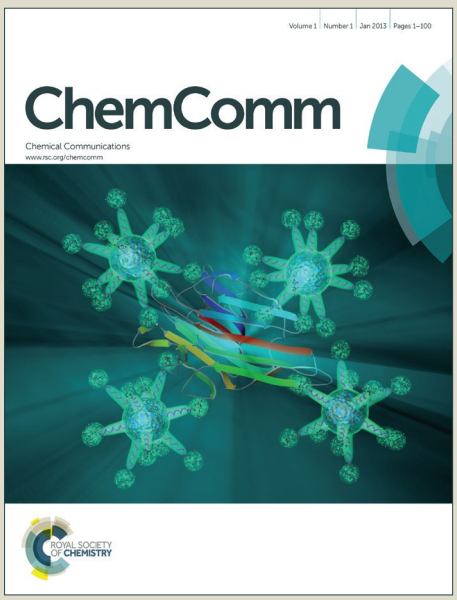

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COMMUNICATION

Photocatalyst-free hypervalent iodine reagent catalyzed decarboxylative acylarylation of acrylamides with α-oxocarboxylic acids driven by visible-light irradiation

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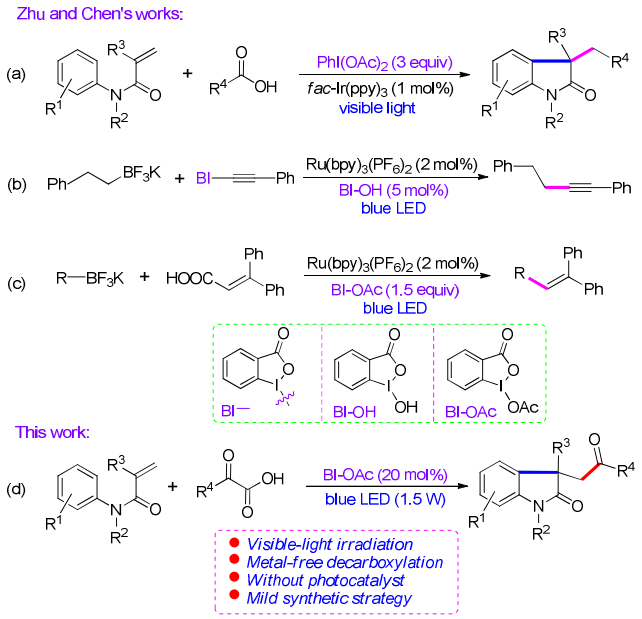
A hypervalent iodine (III) reagent catalyzed carbonylarylation of acrylamides with α-oxocarboxylic acids driven by visible-light without photoredox catalyst has been developed. The reactions generate the corresponding products in good yields at room temperature. Experiments indicate that blue LED (450–455 nm) is the most effective energy to cleavage of oxygen-iodine bond to initiate the reaction. Mechanistic study further demonstrates that the reaction undergoes a cascade decarboxylative radical addition/cyclization process along with releasing CO_2 and H_2.

Oxindoles, an important class of nitrogen-containing heterocycles with remarkable biological and medicinal properties, are the key structural motifs in numerous natural products and biologically active compounds.[1] Moreover, oxindoles are valuable intermediates in asymmetric synthesis, library design and drug discovery.[2] Therefore, the development of straightforward and highly efficient methods for their preparation have received much more attention. Recently, the difunctionalizations of activated alkenes have been developed.[3] In particular, oxidative 1,2-difunctionalization of C=C bonds in arylacrylamides has attracted the interest of synthetic chemists and is a fascinating approach to 3,3-disubstituted 2-oxindoles. These reactions can be initiated by the addition of either carbon radical or heteroatom radical to C=C bonds followed by intramolecular radical cyclization. According to the radical species, these transformations are divided into 1,2-alkylarylation,[4-6] 1,2-carbonylarylation,[7] 1,2-azidoarylation,[8] 1,2-nitroarylation,[9] 1,2-sulfonylarylation,[10] 1,2-phosphorylarylation,[11] and others,[12] which allow the rapid access to diverse 3,3-disubstituted 2-oxindole scaffolds by simultaneous formation of two C–C bonds or C–C/C–hetero bonds.

Carbonyl-containing oxindoles are considered to be privileged frameworks in pharmaceutical agents, natural compounds, as well as versatile intermediates in synthetic chemistry.[13] As we known, α-oxocarboxylic acids have been used as acylating reagents due to their stability, easily preparation and high reactivity.[14] In general, α-oxocarboxylic acids are considered to undergo a decarboxylative process to form acyl radicals along with extrusion of CO_2, and Duan developed a $AgNO_3/K_2S_2O_8$ promoted 1,2-carbonylarylation of arylacrylamides using α-oxocarboxylic acids.[7b] Despite these achievements obtained in this area, the current methods require excessive oxidants, expensive metals, or higher reaction temperature. To develop the mild and environmentally-begin route to carbonyl-containing oxindoles is highly desirable.



Scheme 1 The applications of hypervalent iodine reagents and visible-light photoredox catalysts in organic transformations

Recently, organic photochemical reactions, especially visible-light induced organic transformations have emerged as one of the most attractive research area due to its intrinsic characteristics of mild, environmentally benign, operationally simple, infinitely available source.[15] Meanwhile, hypervalent iodine reagents (HIRs) were found to be the effective reagents in organic synthesis,[16] and HIRs used for organic transformation by visible-light photoredox catalysis have received considerable attention recently.[16d-g] For example, Zhu described the formation of 3,3-disubstituted oxindoles by visible-light photoredox catalysis in the presence of *fac*-$Ir(ppy)_3$ and $PhI(OAc)_2$ (Scheme 1a).[16d] Subsequently,

Table 1. Optimization of the reaction conditions[a]

Entry	HIR (equiv)	Yield[b](%)	Entry	HIR (equiv)	Yield[b](%)
1	$PhI(OAc)_2$ (1.0)	46[c]	9	BI-C≡CPh (0.25)	0
2	$PhI(OAc)_2$ (1.0)	45[d]	10	BI-OAc (0.35)	78
3	$PhI(OAc)_2$ (1.0)	60	***11***	***BI-OAc (0.20)***	***78***
4	$PhI(OAc)_2$ (0.5)	47	12	BI-OAc (0.15)	71
5	$PhI(OAc)_2$ (0.25)	32	13	$PhI(OAc)_2$ (0.25)	0[e]
6	BI-OAc (0.25)	78	14	BI-OAc (0.20)	0[f]
7	BI-OH (0.25)	61	15	BI-OAc (0.20)	15[g]
8	BI-OTf (0.25)	15	16	–	0

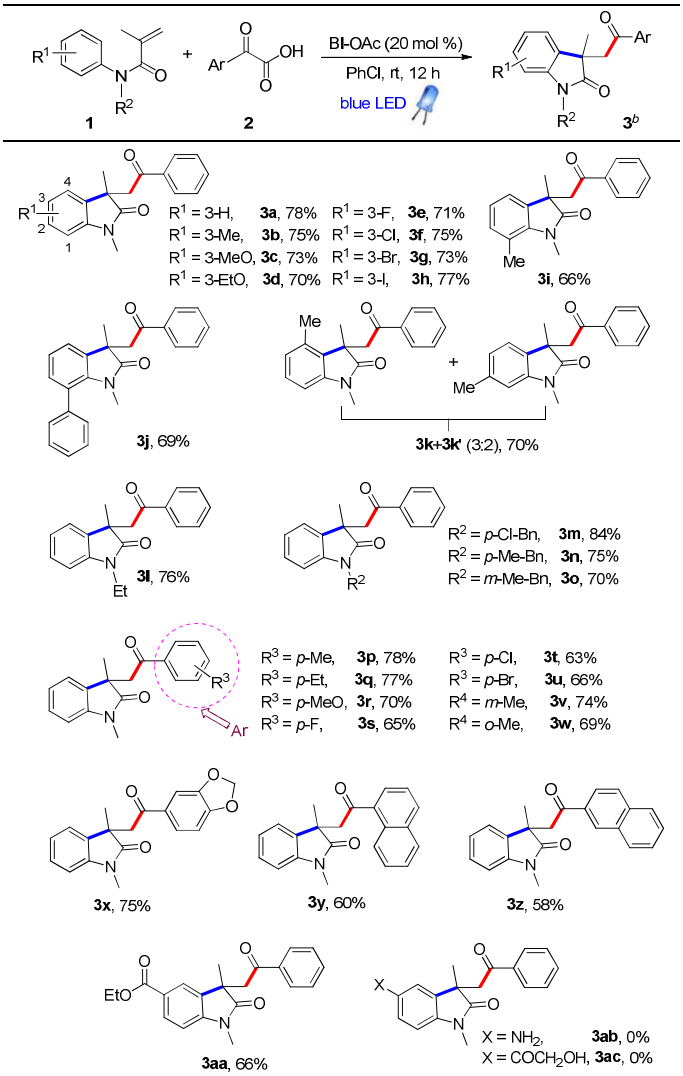
[a]Reaction conditions: *N*-methyl-*N*-phenyl-methacrylamide (**1a**, 0.20 mmol), 2-oxo-2-phenylacetic acid (**2a**, 0.30 mmol), HIR (amount indicated in Table 1), PhCl (1.0 mL) at room temperature under blue LED (450–455 nm, 1.5 W) irradiation in air for 12 h. [b]Isolated yield. [c]With $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ (2.0 mol%). [d]With Eosin Y (2.0 mol%). [e]In dark. [f]70 °C in dark. [g]100 °C in dark.

Chen developed a series of visible-light-induced organic transformations with $Ru(bpy)_3(PF_6)_2$/HIR photoredox catalytic system (Scheme 1b and 1c).[16e-g] However, there is rare example of the organic transformation driven by visible-light in the presence of HIR catalyst without photoredox catalyst for saving precious metal, such as Ru or Ir.[16h] Based on this understanding and our recent works,[17] herein, we report a remarkably mild HIR-catalyzed direct decarboxylative carbonylarylation of acrylamides with α-oxocarboxylic acids under visible-light photolysis without visible-light photoredox catalyst, which represents a novel and energy-efficient approach to carbonyl-containing oxindoles (Scheme 1d).

Our initial investigation focused on the effect of photo-catalyst on the decarboxylative acylarylation of acrylamide with α-oxocarboxylic acid. The representative $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ (2.0 mol%) and Eosin Y (2.0 mol%) were screened in a model reaction of *N*-methyl-*N*-phenylmethacrylamide (**1a**) with 2-oxo-2-phenylacetic acid (**2a**) performed with $PhI(OAc)_2$ (1.0 equiv) and blue LED (450–455 nm, 1.5 W) irradiation at room temperature for 12 h in PhCl, providing the product **3a** in 46% and 45% yields, respectively (Table 1, entries 1 and 2). When the model reaction was carried out in the absence of photocatalyst, a significant improved yield of **3a** was obtained (entry 3). The yield of **3a** is decreased along with the less loading of $PhI(OAc)_2$ (entries 4 and 5). Next, a variety of HIRs, including BI-OAc, BI-OTf, BI-OH and BI-C≡CPh, were examined. It is evident that BI-OAc was the most effective one, **3a** was isolated in 78% yield (entries 6–9). BI-OH and BI-OTf gave **3a** in 61% and 15% yields, and BI-C≡CPh was no effect. It was also found that the amount of BI-OAc up to 35 mol% did not enhance the transformation, and less than 20 mol% of BI-OAc resulted in less yield of the product (entries 10–12). Specifically, no **3a** was formed when the reaction was performed at either room temperature or 70 °C in dark, and 15% yield of **3a** was obtained at 100 °C in the absence of light (entries 13–15). It is important to note that the addition of BI-OAc is essential to realize the reaction (entry 16). The further optimization indicated that the reaction was generally completed within 12 h at room temperature using 20 mol % of BI-OAc under blue LED irradiation in chlorobenzene (Table S1 in Supporting Information).

With the optimized reaction conditions in hand, the scope of BI-OAc catalyzed decarboxylative acylarylation of acrylamides with 2-oxo-2-phenylacetic acid (**2a**) under visible-light irradiation

Table 2. The scope of acrylamides and α-oxocarboxylic acids[a]



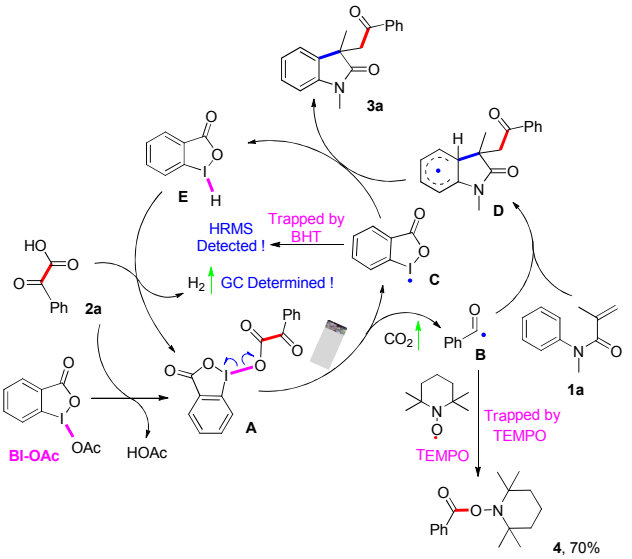
[a]Reaction conditions: acrylamide (**1**, 0.20 mmol), α-oxocarboxylic acid (**2**, 0.30 mmol), BI-OAc (0.040 mmol, 20 mol%), PhCl (1.0 mL) under blue LED (1.5 W) irradiation at room temperature for 12 h in air. [b]Isolated yield.

in the absence of photocatalyst was investigated with a variety of acrylamides. The results were listed in Table 2. As can be seen from Table 2, *N*-methyl-*N*-arylmethacrylamides (**1**) with both electron-donating and electron-withdrawing groups, such as methyl, methoxy, ethoxy, fluoro, chloro, bromo, iodo, phenyl, and ester on the benzene rings reacted with **2a** to afford the corresponding products in good yields (Table 2, **3b**–**k**, **3aa**). The reactions of **2a** with *N*-methyl-*N*-aryl-methacrylamides (**1**) containing a Me, MeO, or EtO group at the *para*-position of the phenyl ring generated 70–75% yields of the products (**3b**–**d**). *N*-Methyl-*N*-aryl- methacrylamides (**1**) with a F, Cl, Br, I or EtOCO group at the *para*-position of the benzene ring gave 66–77% yields of the products (**3e**–**h**, **3aa**). In addition, *N*-methyl-*N*-aryl-methacrylamide (**1**) with a Ph group at the *ortho*-position of the aromatic ring afforded the product **3j** in 69% yield. However, *N*-methyl-*N*-arylmethacrylamides attached amino or alcohol group on the benzene rings could not react with **2a** to generate the desired products (**3ab** and **3ac**). It should be noted that substrate **1** with an electron-donating group (Me) at the *meta*-position of

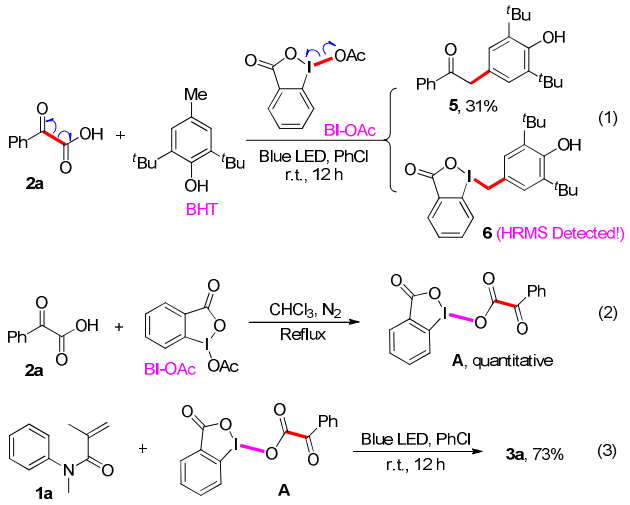
the phenyl ring delivered a mixture of isomers **3k** and **3k'** in 3:2 ratio with 70% yield. Moreover, *N*-ethyl-*N*-phenymethacrylamide, *N*-(*p*-chlorobenzyl)-*N*-phenyl methacrylamide, *N*-(*p*-methylbenzyl)-*N*-phenyl-methacrylamide and *N*-(*m*-methylbenzyl)-*N*-phenyl-methacrylamide underwent the reaction with **2a** to generate the anticipated products **3l**–**o** in 70–84% yields. However, no desired product was isolated when *N*-phenylmethacrylamide reacted with **2a**.

In order to expand the scope of α-oxocarboxylic acids (**2**) diverse array of 2-oxo-2-(substituted-phenyl)acetic acids were surveyed, also shown in Table 2. 2-Oxo-2-arylacetic acids with either electron-donating or electron-withdrawing groups on the phenyl rings of **2** could be applied to react with **1a**, providing the desired products **3p**–**z** in moderate to good yields. The reactions of substituted 2-oxo-2-phenylacetic acids with an electron-donating group, such as methyl, ethyl or methoxy group at the *para*-position of the benzene ring gave the desired products (**3p**–**r**) in 70–78% yields. On the other hand, substituted 2-oxo-2-phenylacetic acids with an electron-withdrawing group including fluoro, chloro or bromo group on the *para*-position of the phenyl ring generated the corresponding products **3s**–**u** in 63–66% yields. At same time, 2-oxo-2-arylacetic acids attached a methyl group on the *meta*-position or *ortho*-position of the benzene ring afforded the desired products **3v** and **3w** in 74% and 69% yields, respectively. It is important to note that the substrate introduced two strong electron-donating groups (RO) on the aromatic ring of 2-oxo-2-arylacetic acid (for example, 2-(benzo[d][1,3]dioxol-5-yl)-2-oxoacetic acid) reacted with **1a** to provide the corresponding product **3x** in 75% yield. 2-(Naphthalen-1-yl)-2-oxoacetic acid and 2-(naphthalen-2-yl)-2-oxoacetic acid were used to react with **1a** to generate the products **3y** and **3z** in 60% and 58% yields, respectively. However, the reactions were limited to furoylformic acid and 2-thienylglyoxylic acid under the optimal reaction conditions. Furthermore, 2-oxo-2-aliphatic acetic acid and its derivatives, such as 4-methyl-2-oxopentanoic acid and oxalic acid 1-ethyl ester failed under the recommended reaction conditions owing to the less stable of aliphatic acyl radicals compared with aromatic ones.

A plausible mechanism of BI-OAc catalyzed and visible-light driven decarboxylative acylarylation of acrylamides with α-oxocarboxylic acids was depicted in Scheme 2. The reaction processes probably proceed as follows; (i) the formation of an intermediate **A**,[18] by a transesterification of BI-OAc with 2-oxo-2-phenylacetic acid (**2a**); (ii) the generation of iodanyl radical **C**[16h,19] and benzoyl radical **B** from the homolytic cleavage of **A** under blue LED irradiation along with releasing CO_2 (FT-IR analysis of the resulting CO_2 gas, Supporting Information);[17a,b] (iii) the formation of an intermediate **D** through a free radical addition[16d,17c] of formed **B** to the C=C bond of **1a** and followed by intramolecular radical cyclization; (ix) the generation of the product **3a** by a hydrogen atom abstraction of **D** along with forming intermediate **E**, which reacts with **2a** to afford **A** for next cycle run and H_2 (GC analysis of the forming H_2 gas, Supporting Information). It is important to note that benzoyl radical **B** derived from the formed **A** in situ was trapped by TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy), affording the corresponding adduct **4** in 70% yield under the standard reaction conditions.[20] On the other hand, the in situ generated iodanyl radical **C** was trapped by BHT (2,6-di-*tert*-butyl-4-methylphenol)[21] as in Scheme 3, providing the anticipated product **5** in 31% yield and **6** (HRMS analysis, SI). In order to further support the proposed mechanism, the related control experiments were conducted (SI). These results imply that **A**, as an important intermediate may involve in the reaction.



Scheme 2. The Proposed Mechanism



Scheme 3. The control experiments

In summary, an efficient approach for the direct decarboxylative acylarylation of acrylamides with α-oxocarboxylic acids has been developed. The reaction was based on a BI-OAc catalyzed process and was driven by visible-light in the absence of photocatalyst. This acylarylation tolerates a series of substituted groups and affords the desired carbonyl-containing oxindoles in good yields. Experiments showed that blue LED is the most effective energy source to initiate the reaction. The reaction mechanism investigation indicated that the reaction undergoes a cascade decarboxylative radical addition/cyclization process along with releasing CO_2 and H_2. Further study on the detail reaction mechanism and application of HIRs are underway.

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Notes and reference

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