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ARTICLE

*n*Bu$_4$NI-mediated oxidation of methyl ketones to α-ketoamides: using ammonium, primary and secondary amine -salt as amine moiety

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Presented here is the first example of synthesizing an array of primary-, secondary-, and tertiary- α-ketoamides with a non-metal catalyst *n*Bu$_4$NI from methyl ketones and inexpensive readily available amine/ammonium salts, the reactions proceeded smoothly under mild conditions, TBHP was used as oxidant and the corresponding α-ketoamides were afforded in moderate to excellent yields.

Introduction

α-Ketoamides and their derivatives are key constituents in natural products and biologically relevant molecules, especially as useful precursors for functional group transformations.[1-3] Due to their wide utilities, the synthesis of α-ketoamides has attracted considerable focuses in recent years. There has developed a plethora of synthetic routes for the preparation of α-ketoamides with varied reaction conditions and different starting materials (**Fig 1**). Some used oxidative double carbonylation reactions of monoalkylpalladium complexes or halide in the presence of a Pd catalyst under a carbon monoxide (CO) atmosphere, resulting in good yields and selectivities, [4-5] some use terminal alkynes, terminal alkenes or ethylarenes in the presence of Cu or I_2 catalyst,[6-8] some employed α-ketoaldehydes or α-keto acids along with amines catalysed by silver, Cu, gold or Fe -catalyst to give their corresponding α-ketoamides, [9-10] and some others used aryl methyl ketone, or 1-arylethanols, or α-hydroxy ketones with Cu, Fe or I_2 to provide α-ketoamides.[11-13] We has recently developed a one-pot procedure using catalyst CuI with ethylarene and amines to provide secondary, tertiary α-ketoamides,[14] nevertheless, our attempt for preparing primary α-ketoamides failed with the same protocol. In most reactions, heavy or noble metal catalysts are involved and pollutions caused by heavy metals to environment are associated, in addition, harsh conditions were usually required for reactions proceed smoothly. Therefore, developing mental-free procedures for efficient preparations of α-ketoamides under mild conditions is highly desirable and therefore is promising for sustainable developments and potential for industrial purposes. Wang Z.Y. *etal.*[15] developed a novel approach using excess (2 equiv) catalyst *n*Bu$_4$NI or KI, aryl methyl ketones and primary amines and NH_4OAc were as the starting materials *via* anodic oxidation assisted by electric current to provide primary/secondary α-ketoamides with yields varying from 5% to 90%. Qu L. B. *etal.*[12b] presented a procedure using aryl methyl ketones and dialkylformamides catalysed by *n*Bu$_4$NI (20%mol) to provide tertiary α-ketoamides, however, harsh reaction conditions are involved. Despite all the achievements in α-ketoamides synthesis, there has been rare examples that with a metal-free catalyst capable of providing all primary-, secondary-, and tertiary- α-ketoamides.

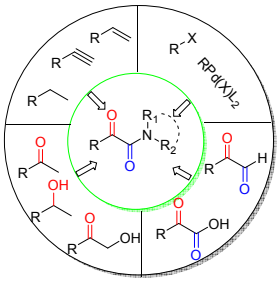

Fig 1 Selected examples for α-ketoamides synthesis with varied starting materials

Herein, we present an nBu$_4$NI-mediated synthesis of α-ketoamides via C-H activation using *t*butylhydroperoxide (TBHP) as the oxidant, aryl methyl ketones and amine- or

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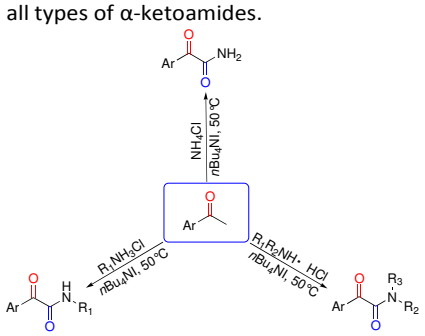
ammonium- salts are as the starting materials under mild conditions (**Scheme 1**) to yield the desired product primary-, secondary-, and tertiary- α-ketoamides with yields of up to 96%. Representing the first example using metal-free catalyst to provide all types of α-ketoamides.



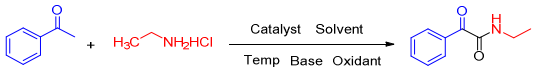
Scheme 1 Synthesis of primary, secondary, and tertiary α-ketoamides using catalyst nBu$_4$NI

Results and discussion

Initial investigations for optimized reaction conditions were carried out by employing acetophenone and ethylamine hydrochloride as the model substrates, reaction parameters such as catalysts, reaction temperatures, oxidants and their loadings, and co-solvents were evaluated, and the results were summarized in **Table 1**. In most reactions, the desired product **3ab** could be obtained in moderate to excellent yields. After that, an array of iodide-containing reagents was investigated for a possibly suitable catalyst, to our disappointed, the oxidative coupling product **3ab** was obtained in an unexpected low yield of 59% when using CuI as the catalyst (Entry 1, **Table 1**), as to KI and I_2, similar results were afforded as those reactions from using CuI under the same conditions (Entry 2, 3, **Table 1**), among of them, nBu$_4$NI proved itself the most efficient catalyst (Entry 4, **Table 1**). The temperature had much affection on product yields (Entry 4-8, **Table 1**) as when temperature increased to 50°C, the yield of desired product **3ab** significantly increased to 96% (Entry 4, **Table 2**). Control experiments (Entry 9-11, **Table 1**) revealed that an oxidant (Entry 9, **Table 1**), an iodide-containing catalyst (Entry 10, **Table 1**) and a base (Entry 11, **Table 1**) are all necessary for the formation of α-ketoamidates. Simply increasing the loading of catalyst and/or oxidant could not result in improved yields (Entry 12, 13, **Table 1**). The effect of solvent also evaluated, results indicated that when reactions were proceeded in tetrahydrofuran (THF), *N, N*-Dimethylformamide (DMF), and Acetonitrile (ACN) (Entry 14-16, **Table 1**), low product yields were resulted. After evaluation of a range of bases, the results disclosed that K_2CO_3 performed the best over other bases, $CaCO_3$, Na_2CO_3 and $NaHCO_3$. Meanwhile, TBHP could provide higher yield compared with those using O_2 or H_2O_2(Entry 4, Entry 20, 21, **Table 1**).

With the optimized conditions, we wish to possibly extend the substrate scope for oxidative coupling of various substituted aryl methyl ketones with different primary amine hydrochloride listed in **Table 3**. All reactions were proceeded smoothly to afford the desired products, results indicated that in most

Table 1 Optimization of reaction conditions of synthesis of secondary/ tertiary α-ketoamides with catalyst nBu$_4$NI from aryl methyl ketone and primary/ secondary amine hydrochloride[a]

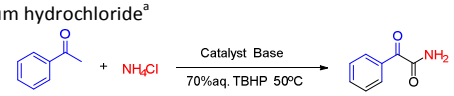


1a 2b 3ab

Entry	Catalyst	T (°C)	Solvent	Base	Oxidant	Yield[b](%)
1	CuI	50	DMSO	K_2CO_3	TBHP	59
2	KI	50	DMSO	K_2CO_3	TBHP	82
3	I_2	50	DMSO	K_2CO_3	TBHP	76
4	nBu$_4$NI	50	DMSO	K_2CO_3	TBHP	96
5	nBu$_4$NI	60	DMSO	K_2CO_3	TBHP	88
6	nBu$_4$NI	70	DMSO	K_2CO_3	TBHP	83
7	nBu$_4$NI	80	DMSO	K_2CO_3	TBHP	79
8	nBu$_4$NI	40	DMSO	K_2CO_3	TBHP	85
9	nBu$_4$NI	50	DMSO	K_2CO_3	--	Trace
10	--	50	DMSO	K_2CO_3	TBHP	0
11	nBu$_4$NI	50	DMSO	--	TBHP	Trace
12[c]	nBu$_4$NI	50	DMSO	K_2CO_3	TBHP	95
13[d]	nBu$_4$NI	50	DMSO	K_2CO_3	TBHP	92
14	nBu$_4$NI	50	THF	K_2CO_3	TBHP	79
15	nBu$_4$NI	50	DMF	K_2CO_3	TBHP	82
16	nBu$_4$NI	50	ACN	K_2CO_3	TBHP	68
17	nBu$_4$NI	50	DMSO	$CaCO_3$	TBHP	26
18	nBu$_4$NI	50	DMSO	Na_2CO_3	TBHP	65
19	nBu$_4$NI	50	DMSO	$NaHCO_3$	TBHP	74
20	nBu$_4$NI	50	DMSO	K_2CO_3	O_2	42
21	nBu$_4$NI	50	DMSO	$CaCO_3$	H_2O_2	23

[a]Conditions: Aryl methyl ketone **1a**, 1.0 mmol; Ethylamine hydrochloride **2a**, 1.2 mmol; Base, 1.1 mmol; Catalyst, 10mol%; Oxidant, 5 mmol (70 wt% TBHP in H_2O); Solvent, 0.2mL. [b]Yields were determined by HPLC analysis equipped with a Vertex C18 column at the wavelength of 254 nm. [c]Reaction was carried out with 10 equivalents of TBHP. [d]With nBu$_4$NI of 20%.

Table2. Optimization of reaction conditions of synthesis of Primary α-ketoamides with catalyst nBu$_4$NI from aryl methyl ketone and ammonium hydrochloride[a]



1a 5a

Entry	Catalyst	Solvent. Loading (mL)	Base(mmol)	Yield[b](%)
1	nBu$_4$NI	0.2	K_2CO_3(1.1)	38
2	nBu$_4$NI	0.2	$CaCO_3$(1.1)	25
3	nBu$_4$NI	0.2	$NaHCO_3$(1.1)	41
4	I_2	0.2	$NaHCO_3$(1.1)	19
5	KI	0.2	$NaHCO_3$(1.1)	27
6	nBu$_4$NI	0.3	$NaHCO_3$(1.1)	56
7	nBu$_4$NI	0.4	$NaHCO_3$(1.1)	62
8	nBu$_4$NI	0.4	$NaHCO_3$(1.3)	75
9	nBu$_4$NI	0.4	$NaHCO_3$(1.5)	89
10	nBu$_4$NI	0.4	$NaHCO_3$(2.0)	64
11[c]	nBu$_4$NI	0.4	$NaHCO_3$(1.5)	Trace
12[d]	nBu$_4$NI	0.4	$NaHCO_3$(1.5)	31
13[e]	nBu$_4$NI	0.4	$NaHCO_3$(1.5)	37

[a]Conditions: Aryl methyl ketone **1a**, 1.0 mmol; ammonium chloride, 2.0 mmol; catalyst, 0.1mmol (10%mmol); Base; Oxidant 5 mmol (70 wt% TBHP in water); Solvent, DMSO; Temperature, 50°C. [b]Yields were determined by HPLC analysis at the wavelength of 254 nm. [c]NH_4CO_3 was used instead. [d]NH_4SO_4 was used. [e]NH_4OAc was used here.

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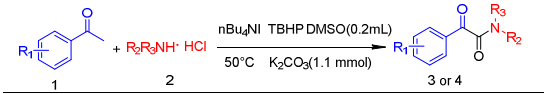
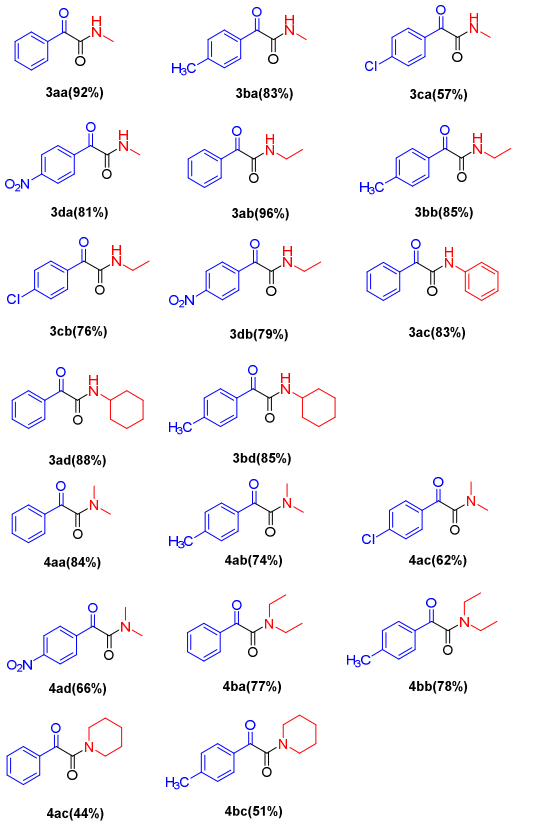
conditions, when aryl methyl ketones bearing an electron-rich or electron-deficient substituent, their corresponding secondary α-ketoamides could be afforded in moderate to excellent yields of up to 96%. It is noteworthy that when employing substrate with a chloride substituent on aromatic ring, the generated product was provided in poorer yields compared with those without chloride substituent (**3ca** and **3cb**). In addition, more steric hindered amine salts could also react well with aryl methyl ketones to afford products in good yields (**3ac, 3ad** and **3bd**).

Table 3 Synthesis of secondary/tertiary α-ketoamides catalysed by *n*Bu_4NI using aryl methyl ketone and primary/secondary amine hydrochloride[a]



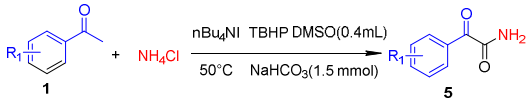


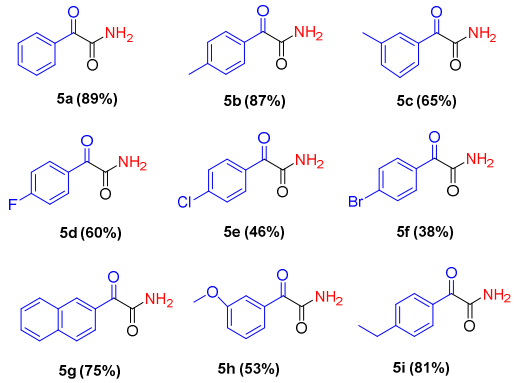
[a]Reactions were performed on at a 1mL scale, conditions: Aryl methyl ketone **1**, 1.0mmol; primary/secondary amine hydrochloride **2,** 1.2 mmol; *n*Bu_4NI, 0.1mmol (10%mol); K_2CO_3, 1.1 mmol; TBHP, 5 mmol (70 wt% in water), DMSO, 0.2mL, temperature, 50°C**.** Yields were determined by HPLC analysis equipped with a C18 column.

Encouraged by efficient synthesis of secondary α-ketoamides from primary amine salts, the scope of the reaction was further extended to more challenging tertiary α-ketoamides synthesis using secondary amines salts (**Table 3**). As expected, most of the products could be provided in good to excellent yields. However, the reaction of acetophenone and *p*-methyl acetophenone with more steric hindered piperidine hydrochloride gave the desired α-ketoamides **4ca** and **4cb** in yields of 44% and 51%, respectively at 50°C. We thought that low conversions may possibly due to the increased steric hindrance of amine moieties. When ketones bearing an electron-withdrawing or electron-donating substituent, better yields were resulted (**4ab-4ad, 4bb**).

Given the prevalence of the primary α-ketoamides in biological pharmaceutical, there have been very limited examples for primary α-ketoamides synthesis, we would like to further extend our approach to prepare primary α-ketoamides. Initially, we use the same conditions developed for secondary and tertiary α-ketoamides to check the possibility for primary α-ketoamide **5a** synthesis, the yield is provided in 38% (Entry 1 **Table 2**) after reaction. Base may possibly be considered to have some effects on such reactions to improve the product yields, therefore, several bases such as $CaCO_3$, K_2CO_3, $NaHCO_3$, $SeCO_3$, Na_2CO_3, NaOH, and KOH (not all of them in **Table 2**) were then

Table 4 Synthesis of primary α-ketoamides catalysed by nBu4NI from aryl methyl ketone and ammonium hydrochloride[a]





[a]Reaction were performed on at a 1mL scale, conditions: Aryl methyl ketone **1a**, 1.0 mmol; ammonium hydrochloride, 2.0 mmol; nBu_4NI, 0.1mmol (10% mol); $NaHCO_3$, 1.5mmol; Oxidant 5 mmol (70 wt% TBHP in water,); Solvent, 0.4mL. Yields were determined by HPLC analysis equipped with a C18 column.

evaluated, and finally $NaHCO_3$ proved itself the best among of all tested bases (Entry 3 **Table 2**). Also, catalysts such as *n*Bu_4NI, I_2, KI and CuI were investigated again for more suitable one. To our delight, *n*Bu_4NI performed better than all, the yield was slightly increased to 41% (Entry3 **Table 2**) with $NaHCO_3$, no obvious improvement was observed, we think possibly this may due to the low solubility of **5a** in DMSO(0.2mL), more solvent was applied to check whether improved yield could be provided, and the results were listed in **Table 2**, results indicated that the loading of solvent played an important role in **5a** synthesis (Entry 5,6 **Table 2).** Varied ratios of base: aryl methyl ketone were investigated for more suitable conditions to improve the yield of **5a**, and the ratio 1:1.5 proved to be the best (Entry 9 **Table 2**) and will be chosen in future evaluations. Several ammonium salts, such as ammonium carbonate (Entry 11 **Table 2**), ammonium sulfate (Entry 12 **Table 2**), and ammonium acetate

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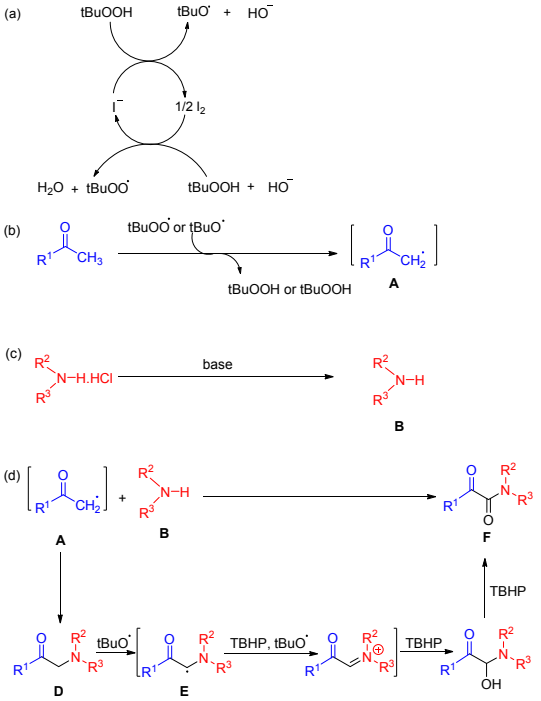
(Entry 13 **Table 2**) were also explored as suitable amine source. Finally ammonium chloride we initially used gave better yield in **5a** synthesis.

With the optimized reaction conditions in hand, an array of primary α-ketoamides were obtained in moderate to good yields (**Table 4**). Generally, ketone with electron-neutral or -rich group (**5a, 5b, 5c, 5g**) provided better yields than ketone bearing electron-deficient group (**5d, 5e, 5f**). Substituent at different positions on phenyl ring could also affect the yields of products to some extent. When a substituted group is at the para position (**5b**), substrate displayed more reactive than that with a substituent at the meta position (**5c**), the reason for this may possible be attributed to weak electron supplies. We did not observe any negative effects on product yield when using more steric hindered substrate (**5g**).

To further explore the substrate scope, heteroaromatic substrates were also employed with the reported conditions, however, heteroaromatic substrates do not provide adequate yields.



Scheme 2. Possible mechanism for radical oxidative coupling reactions

A plausible mechanism for radical oxidative coupling is proposed in **Scheme 2**. The catalytic cycle was proposed as shown in **Scheme 2** (**a**): In the first step, the *tert*-butoxyl and *tert*-butylperoxyl radical formed catalytically assisted with I^- released from catalyst nBu$_4$NI.[16] The resulted *tert*-butoxyl or *tert*-butylperoxyl radical trap a hydrogen atom from the aryl methyl ketone to generate radical **A** (**Scheme 4** (**b**)).[17] To verify the formation of a free amine, several control experiments were performed under the same conditions described in the foot note of **Table 1** (**Fig. 2**). Free amine released from amine salt with the assistance of base[18] was introduced, and the free amine was lively which can be combined with a lot of reactants.[19] Firstly, it was considered that aryl methyl ketones may be demethylated under the oxidative conditions.

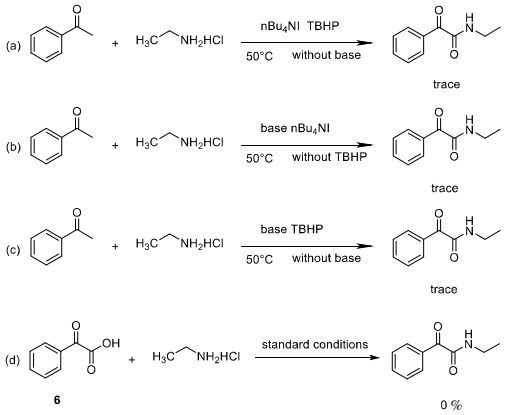


Fig 2 Control experiments to test the proposed mechanism

To verify this, control reaction using acid **6** coupled with ethylamine hydrochloride under the conditions in the foot note of **Table 1** was investigated. However, product **3ba** was not detected, indicating that **6** was not the intermediate for nBu$_4$NI-catalyzed radical oxidative transformations (**Fig. 2 d**). And next, radical **A** and free amine coupled to form the intermediate **D**, a hydrogen atom (C-H) from intermediate **D** is trapped by a *tert*-butoxyl radical to from radical **E**. which is further oxidized by TBHP to finally form the desired product. Based on the above observations and some researches on the '*n*Bu4NI-TBHP'' system,[12b, 17a] a plausible mechanism for radical oxidative coupling reaction is proposed and illustrated in **Scheme 2**.

Conclusions

In summary, we have developed an efficient and environmentally friendly approach to prepare a range of aromatic α-ketoamides using a non-metal catalyst nBu$_4$NI in moderate to excellent yields, which are important structural units in a plethora of biological compounds or drugs. Easily commercial obtainable ketones and amine salts are used as the starting materials, and reactions were proceeded smoothly well under mild conditions. To the best of our knowledge, we have, for the first time, successfully achieved the formation of primary-, secondary-, and tertiary- α-ketoamidions by oxidative amidation of ketones with inexpensive amine/ammonium salts and a non-metal catalyst nBu4NI. This α-ketoamides synthetic approach is believed to provide us an alternative for the synthesis of α-ketoamides, and therefore it is potential for practical and sustainably industrial applications. Further optimisation of the conditions for heteroaromatic substrates so that these substrates can be utilized is underway.

Experimental section

General Methods

All chemicals were commercially available and purchased from Aladdin (Shanghai, China) and were used as received without any further purification. All chemicals used were of analytical

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grade. ^{1}H NMR and ^{13}C NMR spectrum were recorded on a Bruker Avance 400 instrument, 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. All chemical shifts (δ) were quoted in parts per million (ppm) and reported relative to an internal tetramethylsilane (TMS, δ 0.00) standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t =triplet, q =quartet, m = multiplet. Yields of products were measured by HPLC analysis using SHIMADZU instrument equipped with a column Wonda Sil C18-WR 5μm. HRMS spectrum were recorded on a Shimadzu LCMS-IT-TOF instrument.

General procedures for the synthesis of secondary /tertiary α-Ketoamides.

A mixture of Aryl methyl ketone 1.0mmol and ethylamine hydrochloride 1.2 mmol; nBu_4NI 0.1 mmol (10%mmol); TBHP 5mmol (70 wt% in water); K_2CO_3 1.1mmol; in DMSO 0.2 mL was stirred at 50^{o}C till almost completed conversion of the substrates by TLC analysis, the action mixture was cooled to room temperature, and then extracted with ethyl acetate (50 mL × 3). The combined organic layers were washed with brine solution and dried over anhydrous $MgSO_4$. And the yields were determined by HPLC analysis equipped with a C18 column. The solvent was removed, and the residue was purified with chromatography column on silica gel using hexane/ethyl acetate (5:1) as eluent to give the corresponding product.

General procedures for the synthesis of primary α-Ketoamides.

A mixture of Aryl methyl ketone 1.0 mmol; Ammonium chloride 2.0 mmol; nBu_4NI 0.1 mmol (10%mmol); TBHP 5mmol (70 wt% in water); $NaHCO_3$ 1.5mmol; in DMSO 0.4 mL was stirred at 50^{o}C till almost completed conversion of the substrates by TLC analysis, the action mixture was cooled to room temperature, and then extracted with ethyl acetate (50 mL × 3). The combined organic layers were washed with brine solution and dried over anhydrous $MgSO_4$. And the yields were determined by HPLC analysis equipped with a C18 column. The solvent was removed, and the residue was purified with chromatography column on silica gel using hexane/ethyl acetate (5:1) as eluent to give the corresponding product.

N-methyl-2-oxo-2-phenylacetamide **(3aa)**[20] Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ =8.27 (d, *J* = 4.0Hz, 2H), δ =7.57 (d, *J* = 4.0Hz, 1H), δ = 7.43 (t, *J* = 4.0Hz 2H), δ = 2.91(d, *J* = 8.0Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.31, δ = 162.25, δ = 134.26, δ = 133.33, δ = 130.96, δ = 128.41, δ = 34.31, δ = 14.36.

N-methyl-2-oxo-2-(p-tolyl)acetamide **(3ba)**[20] Yellow solid ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 8.0Hz, 2H), δ =7.22 (d, *J* = 8.0Hz, 2H), δ = 2.915 (d, *J* = 4.0Hz, 3H), δ = 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.49, δ = 163.12, δ = 145.52, δ = 131.22, δ = 130.83, δ = 129.21, δ = 25.94, δ = 21.81.

N-(4-chloride)-2-oxo-2-(p-tolyl)acetamide **(3ca)**[20] Yellow solid 1H NMR (400 MHz, CDCl3): δ =8.29 (d, *J* = 8.0Hz, 2H), δ = 7.425 (d, *J* = 12.0Hz, 2H), δ = 2.915 (d, *J* = 4.0Hz, 3H). ^{13}C NMR (100 MHz, CDCl3): δ = 186.38, δ = 162.26, δ = 141.10, δ = 132.62, δ = 131.65, δ = 128.85, δ = 26.04.

N-methyl-2-(4-nitrophenyl)-2-oxoacetamide **(3da)**[20] Yellow solid ^{1}H NMR (400 MHz, $CDCl_3$):, δ = 8.57 (d, *J* = 8.0Hz, 2H), δ = 8.34 (d, *J* = 8.0Hz, 2H).δ = 3.03 (d, *J* = 4.0Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.01, δ = 161.18, δ = 150.84, δ = 137.93, δ = 132.37, δ = 123.48, δ = 26.19.

N-ethyl-2-oxo-2-phenylacetamide **(3ab)**[21] Yellow oil ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 4.0Hz, 2H), δ = 7.52 (d, *J* = 4.0Hz, 1H), δ = 7.38 (t, *J* = 4.0Hz 2H), δ = 3.36-3.31 (m, 2H). δ = 1.15(t, *J* = 4.0Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.31, δ = 162.25, δ = 134.26, δ = 133.33, δ = 130.96, δ = 128.41, δ = 34.31, δ = 14.36.

N-ethyl-2-oxo-2-(p-tolyl)acetamide (3bb) Yellow solid ^{1}H NMR (400 MHz, $CDCl_3$), δ = 8.24 (d, *J* = 8.0Hz, 2H), δ = 7.26 (d, *J* = 8.0Hz, 2H). δ = 3.46-3.39 (m, 2H), δ = 2.41(s, 3H)δ = 1.23 (t, *J* = 4.0Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.57, δ = 162.14, δ = 145.52, δ = 131.31, δ = 130.89, δ = 129.21, δ = 34.32, δ = 21.32, δ = 14.47. HRMS m/z (APCI) Calcd for $C_{11}H_{13}NO_2$ $(M + H)^+$ 192.1019, found 192.1001.

2-(4-chlorophenyl)-N-ethyl-2-oxoacetamide **(3cb)** Yellow solid ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.265 (d, *J* = 8.0Hz, 2H), δ =7.40 (d, *J* = 8.0Hz, 2H), δ = 3.43-3.36 (m, 2H), δ = 1.21 (t, *J* = 8.0Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.59, δ = 161.48, δ = 141.00, δ = 132.59, δ = 131.68, δ = 128.79, δ = 34.40, δ = 14.40. HRMS m/z (APCI) Calcd for $C_{10}H_{10}ClNO_2$ $(M + H)^+$ 212.0473, found 212.0429.

N-ethyl-2-(4-nitrophenyl)-2-oxoacetamide **(3db)** Yellow solid ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (d, *J* = 8.0Hz, 2H), δ = 8.33 (d, *J* = 8.0Hz, 2H), δ = 3.49 (q, *J* = 8.0Hz 2H), δ = 3.09(t, *J* = 8.0Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.25, δ = 160.41, δ = 150.81, δ = 138.00, δ = 132.41, δ = 123.45, δ = 34.60, δ = 14.44. HRMS m/z (ESI) Calcd for $C_{10}H_{10}N_2O_4$ $(M - H)^-$ 221.0568, found 221.0548.

2-oxo-N,2-diphenylacetamide **(3ac)**[22] Yellow oil ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.07 (s, 3H), δ = 8.44 (d, *J* = 8.0Hz, 2H), δ = 7.75 (d, *J* = 8.0Hz, 2H), δ = 7.69 (t, *J* = 4.0Hz, 1H), δ = 7.54 (t, *J* = 8.0Hz, 2H), δ = 7.43 (t, *J* = 8.0Hz, 2H), δ = 7.23 (t, *J* = 4.0Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.52, δ = 159.05, δ = 136.71, δ = 134.65, δ = 131.48, δ = 129.24, δ = 128.59, δ = 125.32, δ = 120.02.

N-cyclohexyl-2-oxo-2-phenylacetamide **(3ad)**[23] light Yellow solid ^{1}H NMR (400 MHz, $CDCl_3$):, δ = 8.35 (d, *J* = 8.0Hz, 2H), δ = 7.64 (t, *J* = 8.0Hz, 1H), δ = 7.49 (t, *J* = 8.0Hz, 2H), δ = 3.88 (d, *J* = 8.0Hz, 1H), δ =2.01 (d, *J* = 12.0Hz, 2H), δ = 1.80-1.77 (m, 2H), δ = 169-166 (m, 1H), δ = 3.03 (dd, *J* = 12.0Hz, 2H), δ = 1.35-1.23 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$), δ = 188.19, δ = 160.93, δ = 134.30, δ = 133.48, δ = 131.22, δ = 128.46, δ = 48.49, δ =32.72, δ = 25.44, δ = 24.77.

N-cyclohexyl-2-oxo-2-(p-tolyl)acetamide **(3bd)**[23] light Yellow solid ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 8.0Hz, 2H), δ = 7.25 (d, *J* = 8.0Hz, 2H), δ =3.84 (dd, *J* = 8.0Hz, J = 4.0Hz 1H), δ = 2.40 (s, 3H), δ = 1.97 (d, *J* = 12.0Hz, 2H), δ = 1.76-1.73 (m, 2H), δ = 1.63 (d, J = 12.0Hz, 1H), δ = 1.40 (dd, *J* = 8.0Hz, *J* = 4.0Hz 2H), δ = 1.26-1.18 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.74, δ = 161.34, δ = 145.41, δ = 131.33, δ = 130.97, δ = 1229.17, δ = 48.43, δ =32.67, δ = 25.43, δ = 24.79 δ = 24.79, δ = 21.83.

N,N-dimethyl-2-oxo-2-phenylacetamide **(4aa)**[21] Yellow oil ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.80 (d, *J* = 4.0Hz, 2H), δ = 7.28 (d, *J* = 8.0Hz, 2H), δ = 3.07 (s, 2H), δ = 2.92(s, 3H), δ = 2.87(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.60, δ = 167.28, δ = 146.03, δ = 130.58, δ = 129.75, δ = 129.71, δ = 37.02, δ = 33.90, δ = 21.87.

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N,N-dimethyl-2-oxo-2-(p-tolyl)acetamide **(4ba)**[21] Yellow solid ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.92 (d, *J* = 4.0Hz, 2H), δ = 7.62 (t, *J* = 4.0Hz, 1H), δ = 7.49 (t, *J* = 8.0Hz 2H), δ = 3.09(s, 3H), δ = 2.93(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.86, δ = 167.07, δ = 134.77, δ = 133.02, δ = 129.61, δ = 129.04, δ = 37.02, δ = 33.95.

2-(4-chlorophenyl)-N,N-dimethyl-2-oxoacetamide **(4ca)**[21] Yellow solid ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.0Hz, 2H), δ = 7.44 (d, *J* = 8.0Hz, 2H), δ = 3.07 (s, 3H), δ = 2.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.35, δ = 166.49, δ = 141.25, δ = 131.45, δ = 130.99, δ = 129.38, δ = 37.00, δ = 34.02.

N,N-dimethyl-2-(4-nitrophenyl)-2-oxoacetamide **(4da)**[21] Yellow solid ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, *J* = 8.0Hz, 2H), δ = 8.15 (d, *J* = 8.0Hz, 2H), δ = 3.10 (s, 3H), δ = 3.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$), δ = 189.32, δ = 165.63, δ = 151.56, δ = 137.56, δ = 130.81, δ = 124.10, δ = 37.09, δ = 34.30.

N,N-diethyl-2-oxo-2-phenylacetamide **(4ab)**[23] Yellow oil ^{1}H NMR (400 MHz, $CDCl_3$):, δ = 7.92 (d, *J* = 8.0Hz, 1H), δ = 7.62 (t, *J* = 8.0Hz, 2H), δ = 7.49 (t, *J* = 8.0Hz, 2H),δ = 3.55(q, *J* = 8.0Hz,2H), δ = 3.23(q, *J* = 8.0Hz,2H), δ = 1.27 (t, *J* = 4.0Hz, 3H), δ = 1.13 (t, *J* = 4.0Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.64, δ = 166.76, δ = 134.61, δ = 133.22, δ = 129.57, δ = 128.98, δ = 42.12, δ = 38.80, δ = 14.08, δ = 12.83.

N,N-diethyl-2-oxo-2-(p-tolyl)acetamide **(4bb)**[23] Yellow solid ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.68 (d, *J* = 8.0Hz, 2H), δ = 7.15 (d, *J* = 8.0Hz, 2H), δ = 3.40 (q, *J* = 8.0Hz, 2H), δ = 3.08 (q, *J* = 8.0Hz, 2H), δ = 2.26(s, 3H), δ = 1.13(t, *J* = 8.0Hz, 3H), δ = 0.98(t, *J* = 8.0Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$), δ = 191.27, δ = 166.82, δ = 145.69, δ = 130.69, δ = 129.59, δ = 129.49, δ = 42.99, δ = 38.63, δ = 21.66, δ = 13.95, δ = 12.69.

1-phenyl-2-(piperidin-1-yl)ethane-1,2-dione **(4ca)**[24] Yellow solid ^{1}H NMR (400 MHz, $CDCl_3$):, δ = 7.95 (d, *J* = 8.0Hz, 2H), δ = 7.66-7,62 (m, 1H), δ = 7.52 (t, *J* = 4.0Hz, 2H), δ = 3.71(s, , 2H), δ = 3.31-3.28 (m, 2H), δ = 1.71-1.68 (m, 4H), δ = 1.55 (d, *J* = 4.0, 2H). ^{13}C NMR (100 MHz, $CDCl_3$), δ = 191.97, δ = 165.47, δ = 134.65, δ = 133.29, δ = 129.54, δ = 129.01, δ = 47.03, δ =42.15, δ = 26.19, δ = 25.44, δ = 24.36.

1-(piperidin-1-yl)-2-(p-tolyl)ethane-1,2-dione **(4cb)**[25] Yellow solid ^{1}H NMR (400 MHz, $CDCl_3$):, δ = 7.32 (d, *J* = 8.0Hz, 2H), δ = 7.29 (t, *J* = 8.0Hz, 2H), δ = 3.63 (s, 2H), δ = 3.27-3.24 (m, , 2H), δ = 2.41 (s, 3H), δ = 1.67 (s, 4H), δ = 1.53 (d, *J* = 12.0, 3H) δ = 1.24-1.20 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$), δ = 191.73, δ = 165.66, δ = 145.91, δ = 130.29, δ = 129.73, δ = 129.65, δ = 47.01, δ =42.07, δ = 26.18, δ = 25.44, δ = 24.36, δ = 21.87.

2-oxo-2-phenylacetamide **(5a)**[26] Yellow solid ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.37 (s,1H), δ = 8.01 (d, *J* = 4.0Hz, 3H), δ = 7.74 (t, *J* = 4.0Hz, 1H), δ = 7.62 (s, *J* = 4.0Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6), δ = 191.31, δ = 167.67, δ = 134.94, δ = 133.24, δ = 130.23, δ = 129.42.

2-oxo-2-(p-tolyl)acetamide **(5b)**[15] Yellow solid ^{1}H NMR (400 MHz, DMSO-d_6):, δ = 8.32 (s, 1H), δ = 7.97 (s, 1H), δ = 7.91 (d, *J* = 8.0Hz, 2H), δ = 7.41 (d, *J* = 8.0Hz, 2H) δ = 2.42 (s, 3H) ^{13}C NMR (100 MHz, DMSO-d_6), δ = 190.91, δ = 167.83, δ = 145.67, δ = 130.78, δ = 130.26, δ = 129.98, δ = 21.82.

2-oxo-2-(m-tolyl)acetamide **(5c)**[15] Yellow solid ^{1}H NMR (400 MHz, DMSO-d_6): δ =8.35 (s, 1H), δ =8.00 (s, 1H), δ =7.80 (s, 2H) δ = 7.56 (d, *J*=8.0Hz, 1H), δ =7.49 (t, *J*=8.0Hz, 1H) δ =2.96 (s, 3H) ^{13}C NMR (100 MHz, DMSO-d_6): δ =191.48, δ = 167.80, δ = 138.86, δ = 135.60, δ = 133.30, δ = 130.30, δ = 129.33. δ = 127.45, δ = 21. 28.

2-(4-fluorophenyl)-2-oxoacetamide **(5d)**[15] Yellow solid ^{1}H NMR (400 MHz, DMSO-d_6):, δ = 8.37 (s, 1H), δ = 8.11 (t, *J* = 8.0Hz, 2H), δ = 8.05 (s, 1H), δ = 7.43 (t, *J* = 8.0Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 189.51, δ = 167.17, δ = 164.88, δ = 133.38, δ = 130.02, δ = 116.72.

2-(4-chlorophenyl)-2-oxoacetamide **(5e)**[26] Yellow solid ^{1}H NMR (400 MHz, DMSO-d_6):, δ = 8.37 (s, 1H), δ = 8.07 (s, 1H), δ = 8.04-8.008 (m, 2H), δ = 7.69-7.66 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 189.82, δ = 166.93, δ = 139.90, δ = 132.04, δ = 132.01, δ = 129.60.

2-(4-bromophenyl)-2-oxoacetamide **(5f)**[27] Yellow solid ^{1}H NMR (400 MHz, DMSO-d_6):, δ =8.37 (s, 1H), δ = 8.06 (s, 1H).δ = 7.94 (m, 2H), δ = 7.82 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 190.08, δ = 166.95, δ = 132.59, δ = 132.31, δ = 132.09, δ = 129.22.

2-(naphthalen-2-yl)-2-oxoacetamide **(5g)**[15] Yellow solid ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.88 (d, *J* = 8.0Hz 1H), δ = 8.53 (s, 1H).δ = 8.14 (d, *J* = 8.0Hz, 2H), δ = 8.09 (d, *J* = 8.0Hz, 1H), δ = 7.76-7.64 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6), δ = 194.16, δ = 168.08, δ = 135.19, δ = 133.98, δ = 133.70, δ = 130.77, δ = 129.36, δ =129.17δ =127.24, δ = 125.41, δ = 125.29.

2-(3-methoxyphenyl)-2-oxoacetamide **(5h)**[26] Yellow solid ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.03 (s, 1H), δ = 7.52-7.48 (m, 1H).δ = 7.44 (s, 1H), δ = 7.33 (t, *J* = 8.0Hz, 2H), δ = 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$), δ = 168.22, δ = 159.62, δ = 136.19, δ = 129.79, δ = 120.18, δ = 117.52, δ = 113.15, δ = 55.66. ^{13}C NMR (100 MHz, DMSO-d_6): δ =187.74, δ = 161.34, δ = 145.41, δ = 131.33, δ = 130.97, δ = 129.17, δ = 48.43, δ =32.67, δ = 25.43, δ = 24.79, δ = 21.83.

2-(4-ethylphenyl)-2-oxoacetamide **(5i)** Yellow solid ^{1}H NMR (400 MHz, DMSO-d_6):, δ = 8.31 (s, 1H), δ = 7.96 (s, 1H).δ = 7.91 (m, 2H), δ = 7.43 (d, *J* = 8.0Hz, 2H), δ = 2.70 (q, *J* = 8.0Hz, 2H).δ = 1.21 (t, J=8.0Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ =190.97, δ = 167.89, δ = 151.74, δ = 130.96, δ = 130.37, δ = 128.86, δ = 28.81, δ = 15.57. HRMS m/z (ESI) Calcd for $C_{10}H_{11}NO_2$ (M + Na)$^+$ 200.0682, found 200.0648.

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