Organic & Biomolecular Chemistry

PAPER

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Cite this: *Org. Biomol. Chem.*, 2016, **14**, 8570

Copper–TEMPO-catalyzed synthesis of α-ketoamides *via* tandem sp^3C–H aerobic oxidation and amination of phenethyl alcohol derivatives†

Chengkou Liu,[a] Zhao Yang,[b] Shiyu Guo,[a] Yu Zeng,[a] Ning Zhu,[a] Xin Li,[a] Zheng Fang*[a] and Kai Guo*[a,c]

Received 27th June 2016,
Accepted 17th August 2016

DOI: 10.1039/c6ob01387b

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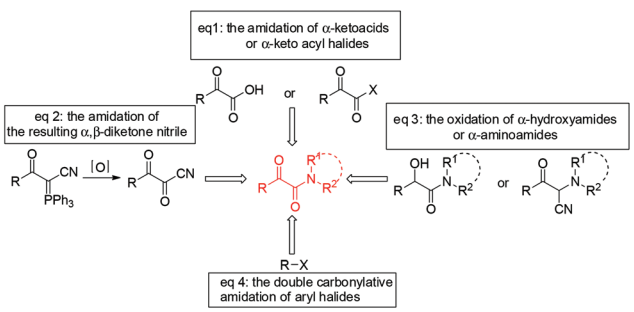
An efficient copper–TEMPO-catalyzed one-pot synthesis of α-ketoamides from phenethyl alcohol derivatives was developed firstly. Moreover, molecular oxygen in open air was employed as the oxidant with a broad substrate scope, which makes this methodology more practical. Based on some control experiments, a plausible mechanism was proposed.

Introduction

The α-keto amide moiety is a prevalent structural unit in drug candidates and a variety of biologically active natural products.[1] Moreover, it can serve as a useful precursor for further transformations, especially the synthesis of heterocycles.[2] Accordingly, developing practical and economical methodologies to synthesize α-ketoamides remains a hot research topic and immense work has been done. A series of traditional methods[3] have been developed as shown in Scheme 1. However, their application was limited by the use of hazardous reagents, harsh reaction conditions or multi-step processes. So, developing a more practical and economical methodology has attracted considerable interest.

Over the past decade, direct functionalization of the C–H bond has become a field of intense interest.[4] It offers substantial benefits because it is atom-economical. However, it is also a fundamental challenge in organic chemistry. With the development of C–H activation, C–C and C-heteroatom bonds were built successfully *via* tandem C–H/heteroatom-H cleavages. In parallel, α-ketoamides were generated effectively *via* oxidative cross-dehydrogenative couplings between the C–H center and the N–H center as shown in Fig. 1.[5]

Firstly, Jiao reported the one-pot preparation of α-ketoamides from aryl acetaldehydes[5a] involving two C_{sp^3}–H cleavages, one C_{sp^2}–H cleavage, and one N–H bond cleavage. About the same time, aryl methyl ketones were proved to be



Scheme 1 Traditional methods for the synthesis of α-ketoamides.

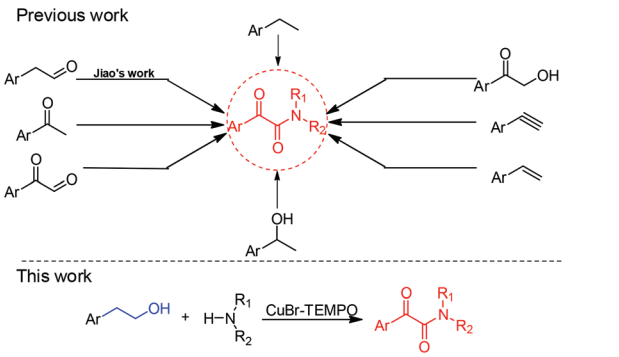


Fig. 1 One-pot preparation of α-ketoamides from a series of starting materials.

[a]College of Biotechnology and Pharmaceutical Engineering Nanjing Tech University 30 Puzhu South Road, Nanjing, 211816, China. E-mail: guok@njtech.edu.cn, fzcpu@163.com; Tel: +862558139935
[b]College of Engineering China Pharmaceutical University, 24 Tongjiaxiang, NanJing, 210003, China
[c]State Key Laboratory of Materials-Oriented Chemical Engineering Nanjing Tech, University, 30 Puzhu South Road, Nanjing, 211816, China

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ob01387b

effective starting materials in a similar reaction system by Ji.[5b] Immediately, many synthetic methods were developed to prepare α-ketoamides from different starting materials, such as acetophenone, ethylbenzene, styrene, phenylacetylene, 1-arylethanol, phenylglyoxal and 2-hydroxy-1-phenyl-ethanone. Among these starting materials, acetophenone and phenylglyoxal have been widely used. As for phenylglyoxal, one C_{sp^2}–H cleavage and one N–H bond cleavage were involved, which were relatively easy compared with the C_{sp^3}–H cleavage. Similarly, the sequential C–O and C–N bond formation to synthesize α-ketoamides from styrene or phenylacetylene was based on tandem C_{sp^2}–H or C_{sp}–H/N–H bond cleavages. Although C_{sp^3}–H cleavage was involved when acetophenone was used, activated methyl compounds (carbonyl compounds) were necessary. Herein, a copper-catalyzed one-pot aerobic oxidative coupling of phenethyl alcohol derivatives with amines *via* four C_{sp^3}–H cleavages and one N–H bond cleavage is presented. As far as we know, there has been no report on the synthesis of α-ketoamides from aryl ethanols. β-Phenylethyl alcohol can be obtained by a Friedel–Crafts reaction between benzene and ethylene oxide easily.[6] Thus, the preparation of α-ketoamides from phenethyl alcohol derivatives was meaningful.

Results and discussion

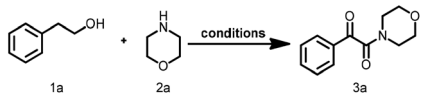
Recently, two metal-free oxidation systems were reported for the direct preparation of α-ketoamides from aryl methyl ketones and 1-arylethanols by our group.[5o,p] During the work above, some transition metals were involved and various substrates were tested to extend starting materials. It was found that CuBr/TEMPO promoted the direct oxidation coupling of phenethyl alcohol derivatives with many aliphatic amines and aromatic amines.

The direct coupling between phenethyl alcohol and 1-oxa-4-azacyclohexane was chosen as the model reaction as shown in Table 1. Initially, various transition metal complexes, especially copper salts, were studied in the presence of 20 mmol% TEMPO and 2.0 equiv. of pyridine in toluene at 90 °C under an oxygen atmosphere (Table 1, entries 1–6).

Delightedly, a good yield (88%) was produced when CuBr was involved (Table 1, entry 4). However, only a trace amount or almost no product was detected when other metal complexes were used (Table 1, entries 1, 2, 5, and 6). Interestingly, the reaction gave a satisfactory yield (76%) when $CuBr_2$ and CuI were added together (Table 1, entry 3). This was likely because $CuBr_2$ and CuI promoted part of the process separately. An obvious decrease of yield (52%) was observed in the absence of TEMPO (Table 1, entry 7). It was likely indispensable in the oxidation of alcohols. Then, the reaction was performed under N_2. As expected, the reaction failed to produce the desired product, which revealed that O_2 was the terminal oxidant (Table 1, entry 8). Only a little desired product (5%) was observed in the absence of a base, which indicated that it can promote this process smoothly. The addition of pyridine, K_2CO_3, trimethylamine or *N*,*N*-diisopropylethylamine could improve this transformation obviously (Table 1, entries 4 and 9–13). Relatively, pyridine and K_2CO_3 were better choices than trimethylamine and *N*,*N*-diisopropylethylamine. However, an obvious lower yield (34%) was obtained when Cs_2CO_3 was involved. K_2CO_3 was chosen finally because of its low toxicity. Afterwards, the solvents were examined. Toluene was found to be the best choice among toluene, dimethyl sulfoxide, *N*,*N*-dimethylformamide and 1,4-dioxane (Table 1, entries 4 and 14–16). DMSO showed a similar reactivity to toluene. Considering the toxicity, DMSO was chosen for the following research. The screening of temperatures indicated that 70 °C should be the right choice (Table 1, entries 4 and 17–19). An obvious lower yield was obtained when the temperature was decreased further. To our delight, the decrease of the yield could be ignored when the reaction was performed under air instead of O_2 (Table 1, entry 20). Furthermore, the equiv. of TEMPO, CuBr, K_2CO_3 and amine were screened as shown in Tables S2, S3, S4 and S5.† Loading fewer TEMPO, CuBr or K_2CO_3 resulted in a negligible decrease of the yield when the reaction time was prolonged. And, 1.5 equivalents of amines were proved to be effective (ESI, Table S5†). After screening of the reaction parameters above, the optimized reaction conditions were obtained: **1a** (1 mmol), **2a** (1.5 mmol), CuBr (8 mmol%), TEMPO (15 mmol%), and K_2CO_3 (1 mmol) in DMSO (3 mL) at 70 °C under air for 12 h.

Following the optimized conditions, the investigation into the scope of various substituents was carried out as shown in

Table 1 Optimization of the reaction conditions[a]



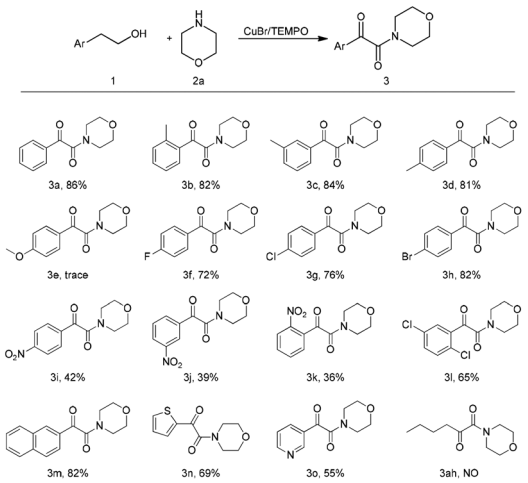
1a 2a 3a

Entry	Catalyst	Additive	Solvent	*T* (°C)	Yield[b] (%)
1	$CuBr_2$	Pyridine	Toluene	90	8
2	CuI	Pyridine	Toluene	90	Trace
3	$CuBr_2$/CuI	Pyridine	Toluene	90	76
4	CuBr	Pyridine	Toluene	90	88
5	CuO	Pyridine	Toluene	90	NO
6	$NiBr_2$	Pyridine	Toluene	90	NO
7[c]	CuBr	Pyridine	Toluene	90	52
8[d]	CuBr	Pyridine	Toluene	90	NO
9	CuBr		Toluene	90	4
10	CuBr	TEA	Toluene	90	70
11	CuBr	DIPEA	Toluene	90	73
12	CuBr	K_2CO_3	Toluene	90	86
13	CuBr	Cs_2CO_3	Toluene	90	34
14	CuBr	K_2CO_3	DMSO	90	85
15	CuBr	K_2CO_3	DMF	90	72
16	CuBr	K_2CO_3	Dioxane	90	62
17	CuBr	K_2CO_3	DMSO	80	85
18	CuBr	K_2CO_3	DMSO	70	86
19	CuBr	K_2CO_3	DMSO	60	72
20[e]	CuBr	K_2CO_3	DMSO	70	84

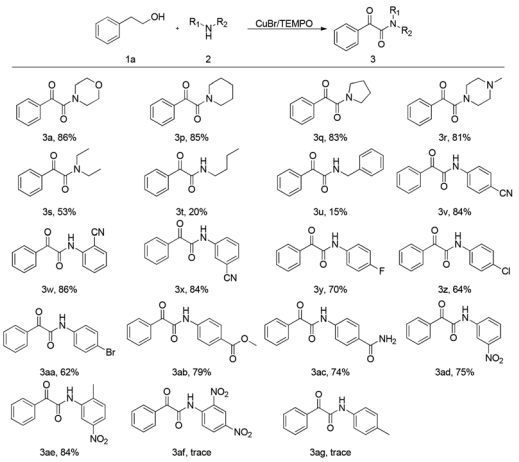
[a] Reaction conditions: **1a** (1 mmol), **2a** (3 mmol), catalyst (0.1 mmol), additive (2 mmol), TEMPO (0.2 mmol) and solvent (3 mL) were heated under O_2 (O_2 balloon) for 12 h. [b] Yields of the isolated product. [c] In the absence of TEMPO. [d] Under N_2. [e] Under air.

Scheme 2, **3**. Firstly, a range of phenethyl alcohol derivatives were tested with 1-oxa-4-azacyclohexane (Scheme 2). To our delight, a moderate to good yield (72%–84%, Scheme 2, **3a–3d**, **3f–3h**, **3l**) was obtained when phenethyl alcohol with substitution at the phenyl ring of electron donating as well as electron withdrawing groups such as methyl, fluorine, chlorine, and bromine was involved. Furthermore, no obvious effect on the reaction efficiency was observed by the substituents at different positions (*p*-, *m*- and *o*-positions, Scheme 2, **3b–3d**, **3i–3k**). Delightedly, both benzene fused ring and aryl heterocyclic substituents could be transformed into the desired products with acceptable yields (Scheme 2, **3m–3o**). However, phenethyl alcohol with a strong electron withdrawing group such as the nitro-group failed to give full conversion and a lower yield (36%–42%, Scheme 2, **3i–3k**) was observed. The instability of the radical intermediate discussed in the mechanism may be the main reason. Unfortunately, only a trace amount of the desired product was detected when 4-methoxyphenethyl alcohol was involved. The methoxy group was likely to be unstable under the optimized conditions. The desired product was not obtained when hexyl alcohol, *trans*-2-hexen-1-ol or 2-hexyn-1-ol was employed (Scheme 2, **3ah**). Actually, the oxidation of aliphatic alcohols was successful under the optimized conditions. The failure of the oxidation of the α-position of the alcohol might be the main nodus.

Then, a range of amines were examined. To our delight, both aliphatic amines and substituted anilines could be transformed into the corresponding products (Scheme 3, **3a**, **3p–3ae**). As for the aliphatic amines, good yield was obtained when a secondary amine was involved (Scheme 3, **3a**, **3p–3s**). Unfortunately, primary amines reacted with **1a** to produce an obvious lower yield (Scheme 3, **3t**, **3u**). Interestingly, cyclic secondary amines gave a better yield than acyclic secondary amines (Scheme 3, **3a**, **3p–3s**). Substituted anilines with a



Scheme 2 Scope of phenethyl alcohol derivatives. Reaction conditions: **1** (1 mmol), **2a** (1.5 mmol), CuBr (0.08 mmol), TEMPO (0.15 mmol), K_2CO_3 (1 mmol) and DMSO (3 mL) were heated under air for 12 h. Yields given were isolated products.

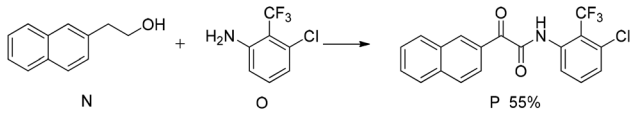


Scheme 3 Scope of amines. Reaction conditions: aliphatic amines used as the substrates: **1a** (1 mmol), **2** (1.5 mmol), CuBr (0.08 mmol), TEMPO (0.15 mmol), K_2CO_3 (1 mmol) and DMSO (3 mL) were heated under air for 12 h. Substituted anilines used as the substrates: **1a** (1 mmol), **2** (1.5 mmol), CuBr (0.08 mmol), TEMPO (0.15 mmol), pyridine (2 mmol) and toluene (3 mL) were heated under air for 12 h. Yields given were isolated products.

range of functional groups were examined. The oxidative coupling of phenethyl alcohol and anilines with electron-withdrawing groups proceeded smoothly to afford the desired products with moderate to good yields (Scheme 3, **3v–3ae**). Moreover, the effect of substituents at different positions could be ignored (Scheme 3, **3v–3x**). Notably, this methodology has broad functional group tolerance, including cyano, fluorine, chlorine, bromine, ester, amide, nitro and methyl. So, it provides a potential method to prepare pharmaceuticals and natural products. It is noteworthy that an obvious lower yield was obtained when anilines bearing electron-donating substituents were involved (Scheme 3, **3ag**). Two possible reasons are given. On the one hand, electron-rich amines could be smoothly transformed into azo compounds,[7] which were confirmed by NMR. On the other hand, the instability of Schiff bases (intermediate) bearing electron-rich amines resulted in a decrease of the yield. In general, electron-poor amines could be converted into the corresponding products with good yields. However, 2,4-dinitroaniline failed to give the desired product. It is likely that the weak nucleophiles and the instability of the amine radical cation resulted in poor conversion.

Now, a variety of simple structures of α-keto amines were prepared. Many bioactive natural products contain α-keto amines as discussed before. **P**, a cytokine inhibitor,[8] was produced in 55% isolated yield from readily available starting materials 2-naphthaleneethanol and 2-amino-6-chlorobenzotrifluoride as shown in Scheme 4. This indicated that the present method provides another choice of starting materials to prepare α-ketoamides.

Compared with the two oxidation systems[5o,p] discussed before, phenethyl alcohol derivatives, simpler and readily available substrates, were employed firstly instead of acetophenone



Scheme 4 The synthesis of cytokine inhibitor **P**. Reaction conditions: 2-naphthaleneethanol (1 mmol), 2-amino-6-chlorobenzotrifluoride (1.5 mmol), CuBr (0.08 mmol), TEMPO (0.15 mmol), pyridine (2 mmol) and toluene (3 mL) were heated under air for 12 h. Yields given were isolated products.

or 1-arylethanol. And, two-step processes were necessary when 1-arylethanol was employed.[5j,p] Moreover, this reaction is applicable to a wider variety of amines, such as aliphatic amines and substituted anilines. It is noteworthy that O_2 in open air is employed as the oxidant instead of I_2 or H_2O_2.

A phenomenon was observed. On the one hand, the substituted anilines failed to afford the desired products under the optimized conditions of CuBr/DMSO/K_2CO_3/TEMPO/O_2 throughout the preparation of various α-ketoamides. Comparatively, good yields could be obtained under CuBr/toluene/pyridine/TEMPO/O_2. Moreover, phenylacetaldehyde was obtained and detected under CuBr/toluene/pyridine/TEMPO/O_2, which indicated that the reaction process was similar to Jiao's report[5a] (aryl acetaldehydes were used as the starting material). The detailed mechanism is shown in the ESI.† On the other hand, aliphatic amines could be transformed into the corresponding α-ketoamides with good yields under CuBr/DMSO/K_2CO_3/TEMPO/O_2. Furthermore, phenylacetaldehyde was not detected obviously. Besides, low yields were obtained when DMSO was used as the solvent or K_2CO_3 was used as the base under Jiao's reaction conditions. On the basis of the results above, we believe that another reaction process different from Jiao's report exists under CuBr/DMSO/K_2CO_3/TEMPO/O_2. In order to catch some clues of this process, a series of control experiments were performed as shown in Fig. 2. Excellent yield was obtained when 2-hydroxyacetophenone or phenylglyoxal was involved, which indicated that 2-hydroxyacetophenone and phenylglyoxal might be the intermediate in the process (Fig. 2, eqn (1) and (2)). Interestingly, ethylbenzene could be smoothly transformed into the product in moderate yield (Fig. 2, eqn (3)). In addition, acetophenone was detected in this process. These results revealed that the oxidation of benzyl was likely to occur. Furthermore, good yield was obtained in the absence of TEMPO (Fig. 2, eqn (4)). However, only a trace amount of the product was detected when O_2 or CuBr was removed (Fig. 2, eqn (5) and (6)). This indicated that O_2 and CuBr were necessary in the oxidation of benzyl. Then an isotope labeling experiment was performed ($^{16}O_2$, anhydrous DMSO, H_2O^{18} (2 equiv.)). An obvious $^{16}O/^{18}O$-labeled product (53%) was detected (HRMS spectrum, Fig. 2, eqn (7)), which indicated that the generation of intermediate **H** and the transformation between **H** and **L** might have occurred (Fig. 3).

Based on the results above, a plausible mechanism was provided. Initially, particularly active intermediate **H** was generated through step a and step b. Step a and step b involved the oxidation of alcohol and the oxidation of benzyl, respectively. The plausible mechanism of steps a and b is shown in Fig. 3. Which occurred first between step a and step b is not certain. It is likely that the two processes occurred almost at the same time.

As for the oxidation of alcohol, LCu^{I} was oxidized to LCu^{II} salt firstly. And, copper(II) alkoxide complex **A** was produced in the presence of a base, which contributed to the deprotonation of alcohols. Connecting **A** to TEMPO produced a six-membered radical intermediate **B** by Cu–N coordination bonding and O–H hydrogen bonding, followed by an abstraction of hydrogen with TEMPO to give radical intermediate **C**. At the same time, the hydroxylamine **D** was produced, which could be oxidized to TEMPO to catalyze this process. Finally, the intramolecular electron transfer (O to Cu) and O–Cu bond cleavage led to carbonyl compounds and Cu^{I}. Thus, Cu^{I} was continuously regenerated to promote this reaction. As for the oxidation of benzyl,

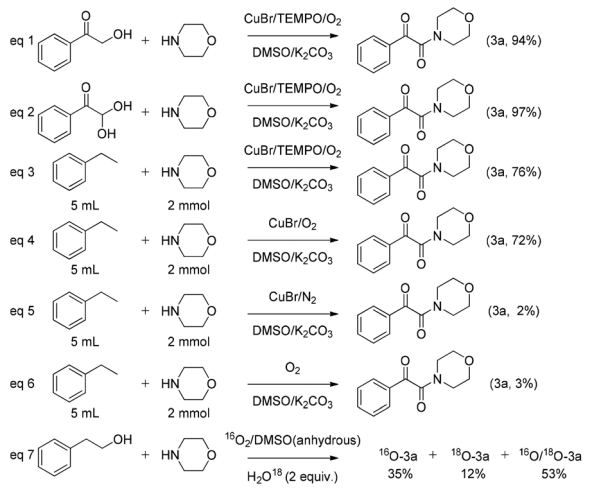


Fig. 2 Control experiments.

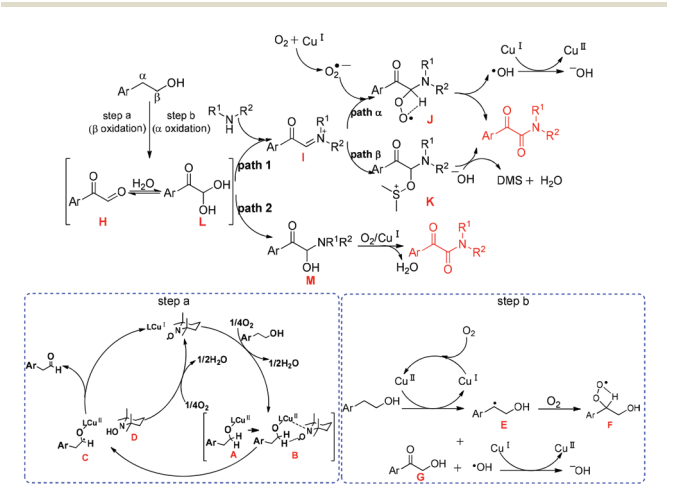


Fig. 3 Proposed mechanism.

radical intermediate **E** was reacted in the presence of more-active Cu^{II} salt, which was obtained from the oxidation of Cu^{I} by O_2. Subsequently, a four-membered intermediate **F** was formed. Then, the oxidation product **G** was produced from intramolecular ring opening. Afterwards, two processes occurred probably as shown in paths **1** and **2**. On the one hand, amines reacted with **H** quickly to form imine I in path 1.[5i,9] So it is too hard to detect **H**. Two possible paths were supplied for the following steps. In path α, a superoxide radical ($O_2^{\bullet-}$) was generated in the presence of O_2 and Cu^{I}, which reacted with **I** to give intermediate **J**. The intramolecular ring opened to give the desired product. In path β, nucleophilic attack of DMSO on **I** gave intermediate **K**. The corresponding product was produced through elimination of DMS and H_2O. On the other hand, hemiaminal intermediate **M** could be obtained from the addition of amine to aryl glyoxal in path **2**.[5b,j] The desired product was obtained from the oxidation of **M** by O_2 catalysed by copper salt.

Conclusions

In conclusion, a convenient and efficient copper-catalyzed methodology for the one-pot preparation of α-ketoamides was demonstrated. It is noteworthy that phenethyl alcohol derivatives, simple and readily available substrates, were used as the starting materials firstly. Four C_{sp^3}–H and one N–H bond cleavages were involved. Moreover, O_2 in open air was employed as the oxygen source. On the one hand, both phenethyl alcohol derivatives containing electron-withdrawing and electron-donating substituents and aryl heterocyclic substituents could be transformed into the desired products. On the other hand, both aliphatic amines and substituted anilines could be transformed into the corresponding α-ketoamides. So, this methodology has a broad substrate scope and holds great potential in constructing the α-keto amide moiety. Furthermore, some control experiments were performed. And, a plausible mechanism was proposed.

Acknowledgements

The research has been supported by the National Key Basic Research Program of China (973 Program) 2012CB721104 and 2012CB725204, the National Natural Science Foundation of China (Grant No. U1463201 and 21402240), and the Jiangsu Province Natural Science Fund (Grant No. BK20150031 and BK20130913).

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