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ARTICLE TYPE

Iron-Catalyzed Aerobic Oxidative Functionalization of sp^3C-H Bonds: a Versatile Strategy for the Construction of *N*-Heterocycles

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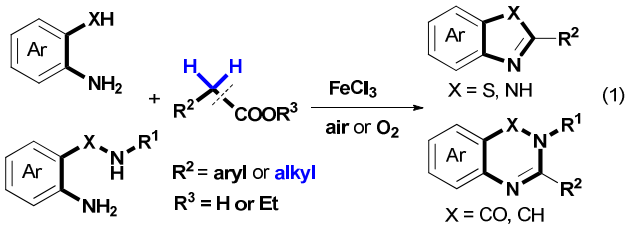
An iron-catalyzed aerobic oxidative functionalization of sp^3C-H bonds has been developed for the construction of *N*-heterocycles from easily available carboxylic acid derivatives and *o*-substituted anilines. This transformation represents a widely applicable protocol to *N*-heterocycles using biofriendly iron as catalyst in combination with molecular oxygen or air as the sole oxidant.

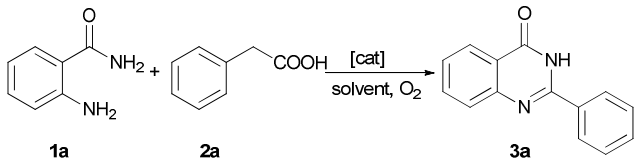
The application of iron salts as catalysts in organic synthesis has attracted much attention due to their abundance, low price, less toxic and biofriendly properties.[1] For example, iron salts have been utilized extensively to promote the traditional cross-coupling,[2] Friedel–Crafts benzylation,[3] carbonylation[4] and other processes.[5-8] Iron-catalyzed oxidations for C-H bonds have also been extensively developed[6-8] with Gif chemistry[6] and Fenton chemistry being the most famous.[7] However, these oxidations have commonly depended on hazardous peroxides. Nowadays, the improvement emphasizes on the development of synthetic models, using a "green" oxidant such as readily available and nontoxic O_2 or air.[9] Therefore, the iron-catalyzed aerobic oxidation of C-H bonds is highly desired. In 2012, Maes et al realized iron-catalyzed aerobic oxidation of benzylic C-H bonds in diarylmethanes for the preparation of diarylketones.[10] Subsequently, Kappe et al developed gas-liquid continuous-flow technology to improve Maes' iron-catalyzed aerobic oxidation system.[11] Despite these advances, further Iron-catalyzed aerobic oxidative functionalization of sp^3C-H bonds is rare.[12] Currently, the decarboxylation reactions are also emerging as the powerful methodology for the construction of carbon-carbon bonds and carbon-heteroatom bonds in organic synthesis due to the readily available substrates, simple operation and clean byproduct (only CO_2 as the byproduct).[13,14] Herein, we communicate an efficient strategy of iron-catalyzed aerobic oxidative functionalization of sp^3C-H bonds to construct *N*-heterocycles from easily accessible carboxylic acid derivatives and *o*-substituted anilines (eq 1). In the present catalytic system, we achieved aerobic oxidation of sp^3C-H bonds, decarboxylation and oxidative cyclization in one pot. Compared to conventional methods, this procedure is distinguished by using biofriendly iron catalyst in combination of clean dioxygen oxidant. This new method provides a general and environmentally friendly access to *N*-heterocyclic compounds which are ubiquitous core units of various biologically active drugs and natural products.[15,16]



(1)

o-Aminobenzamide **1a** and phenylacetic acid **2a** were chosen as the model substrates for optimization of the present iron-catalyzed aerobic oxidative functionalization of sp^3C-H bonds to construct *N*-heterocycles and the results are compiled in Table 1. Preliminary screening shows that various iron catalysts can catalyze the reaction alone without any ligands, bases or additives, and $FeCl_3$ shows the highest catalytic efficiency among the examined iron catalysts (Table 1, entries 1-7). In the presence of 10 mol% $FeCl_3$, this tandem reaction takes place smoothly at 100 °C in DMF to produce the corresponding 2-phenyl quinazolin-4(3*H*)-one compound **3a** in 92% yield (Table 1, entry 7). Worth noting is that iron catalyst is essential for the current catalytic system. In the absence of iron complex, this reaction cannot work and no product is detectable at all (Table 1, entry 8). Other metal complexes such as $PdCl_2$, $NiCl_2.6H_2O$ and $CuCl_2$ (Note: Cu salts are used as good catalyst for the oxidative decarboxylation of the sp^3C-H bonds[9e-9g]) cannot mediate the present reaction (Table 1, entries 9-11). The solvents also play an important role, and only DMF serves as the good solvent (Table 1, entries 12-15). Under the similar reaction conditions, replacement of dioxygen with other oxidants such as TBHP, DTBP, *m*CPBA and $K_2S_2O_8$ results in no yield of the desired product (Table 1, entries 16-17). This transformation also depends on the reaction temperature. For example, catalyzed by 10 mol% $FeCl_3$, the reaction doesn't occur at 80 °C (Table 1, entry 18), while the yield dramatically increases to 92% at 100 °C (Table 1, entry 7). However, further increase of reaction temperature to 120 °C leads to no evident improvement on product yield (Table 1, entry 19).

Table 1. Optimization of the reaction conditions[a]



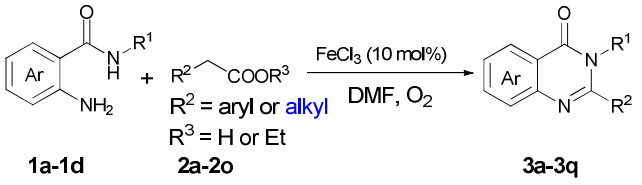
1a 2a 3a

Entry	Catalyst	Solvent	Yield[b] (%)
1	Fe_2O_3	DMF	60
2	$FeCl_2.H_2O$	DMF	88
3	$FeSO_4.7H_2O$	DMF	30
4	ferrocene	DMF	50
5	Ferrous acetylacetonate	DMF	53
6	$FeBr_3$	DMF	86
7	$FeCl_3$	DMF	92
8	-	DMF	-
9	$PdCl_2$	DMF	-
10	$NiCl_2.6H_2O$	DMF	-
11	$CuCl_2$	DMF	-
12	$FeCl_3$	DMSO	-
13	$FeCl_3$	dioxane	-
14	$FeCl_3$	CH_3CN	-
15	$FeCl_3$	toluene	-
16[c]	$FeCl_3$	DMF	-
17[d]	$FeCl_3$	DMF	-
18[e]	$FeCl_3$	DMF	-
19[f]	$FeCl_3$	DMF	93

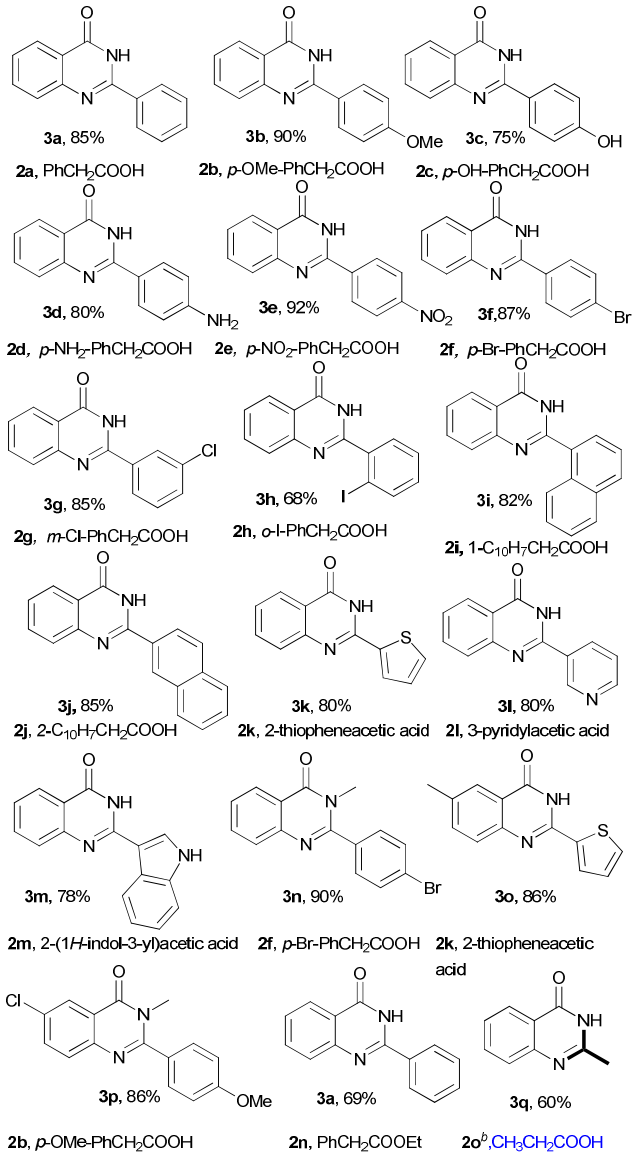
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.22 mmol), catalyst (0.02 mmol), sovent (1 mL), O_2 (1 atm) in a Schlenk tube (10 mL) at 100 °C, 12 h, recharging dioxygen after 6 h. [b]GC yields based on **1a** using dodecane as an internal standard. [c]0.5 mmol *m*-CPBA (*m*-chloroperbenzoic acid) or $K_2S_2O_8$ was employed as oxidant under N_2 (1 atm) atmosphere. [d]0.5 mmol TBHP (*tert*-butylhydroperoxide) or DTBP (di-*tert*-butyl peroxide) was used as oxidant under N_2 (1 atm) atmosphere. [e]80 °C. [f]120 °C.

This iron-catalyzed aerobic oxidative functionalization of sp^3C-H bonds can be successfully applied to other substrates, showing that this reaction is a general method for the preparation of *N*-heterocyclic compounds, i.e. quinazolin-4(3*H*)-ones (Table 2), quinazolines (Table 3), benzimidazoles and benzothiazoles (Table 4). As shown in Table 2, *o*-aminobenzamide **1a** reacts readily with different kinds of arylacetic acids bearing both electron-donating groups and electron-withdrawing groups on the aromatic cycles to give the corresponding quinazolin-4(3*H*)-ones. Various valuable functional groups such as OMe **2b**, OH **2c**, NH_2 **2d**, NO_2 **2e**, Br **2f** and Cl **2g** all survive in the present catalytic system and the expected products are produced in high yields. Especially, the iodine substituted phenylacetic acid also reacts readily with *o*-aminobenzamide **1a** under similar reaction conditions, generating the desired product **3h** in 68% yield. Catalyzed by 10 mol% $FeCl_3$, both 1-naphthylacetic acid and 2-naphthylacetic acid undergo aerobic oxidation tandem reaction with **1a** and the corresponding products **3i** and **3j** are afforded in 82% and 85% yields, respectively. Furthermore, different kinds of heterocycles can be introduced into

Table 2. Synthesis of 2-substituted quinazolin-4(3*H*)-ones[a]



1a-1d 2a-2o 3a-3q

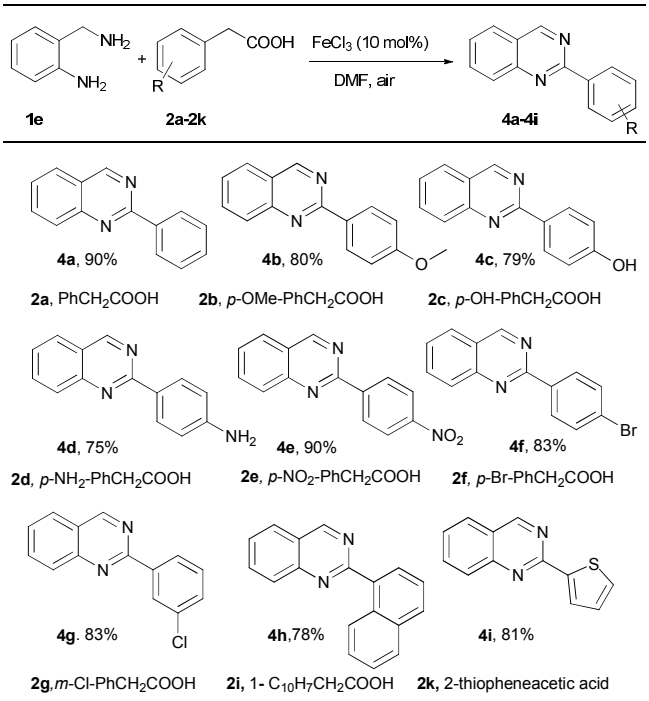


[a] Reaction conditions: **1a**-**1d** (0.2 mmol), **2a**-**2o** (0.22 mmol), $FeCl_3$ (0.02 mmol, 10 mol%), DMF (1 mL), O_2 (1 atm) in a Schlenk tube (10 mL) at 100 °C, 12 h, recharging dioxygen after 6 h. [b]Chlorobenzene as solvent, 3 equivs propionic acid, 140 °C, 12 h, recharging dioxygen after 6 h.

quinazolin-4(3*H*)-one molecule using the current aerobic oxidative functionalization of sp^3C-H bonds. Under dioxygen atmosphere, the reaction of 2-thiopheneacetic acid and **1a** takes place smoothly in the presence of 10 mol% $FeCl_3$ at 100 °C in DMF, furnishing the expected product **3k** in 80% yield. 3-Pyridylacetic acid **2l** is also an efficient

substrate and can be converted to **3l** in 80% yield. 2-(1H-indol-3-yl)quinazolin-4(3*H*)-one **3m** bearing indolyl has been synthesized from the reaction of 2-(1H-indol-3yl)acetic acid and **1a**. In addition to *o*-aminobenzamide **1a**, substituted *o*-aminobenzamides also serve as good substrates and react with arylacetic acids to afford the corresponding quinazolin-4(3*H*)-one derivatives **3n**-**3p**. Using ethyl 2-phenylacetate **2n** instead of 2-phenylacetic acid, the tandem reaction proceeds smoothly, giving the desired product **3a** in 69% yield. In addition, 2-methylquinazolin-4(3*H*)-one **3q** is obtained in 60% yield from propionic acid **2o** and *o*-aminobenzamide.

Table 3. Synthesis of 2-substituted quinazolines[a]

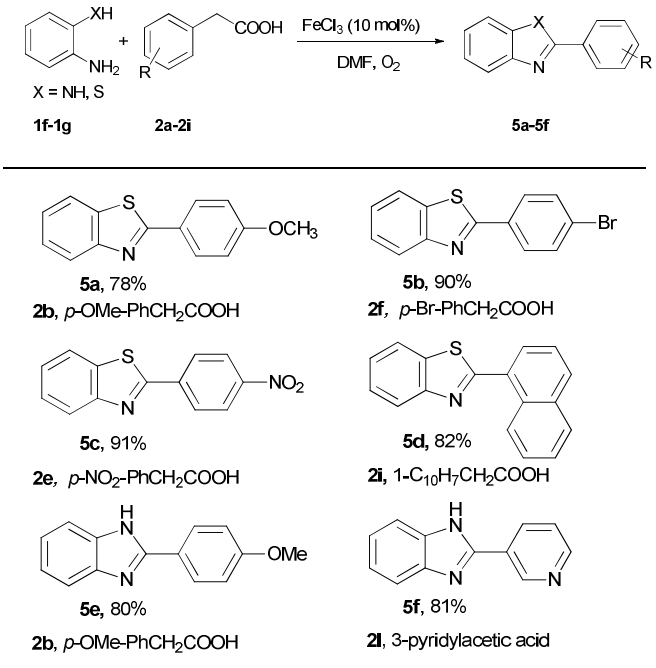


[a]Reaction conditions: **1e** (0.2 mmol), **2a**-**2k** (0.22 mmol), $FeCl_3$ (0.02 mmol, 10 mol%), DMF (1 mL), air (1 atm) in a Schlenk tube (25 mL) at 100 °C, 18 h, recharging air after 6 h.

To our delight, quinazoline derivatives **4** have been efficiently synthesized using the current aerobic oxidative functionalization of sp^3C-H bonds (Table 3). It is noted that the reaction of 2-aminobenzylamine with arylacetic acid can occur smoothly under air atmosphere catalyzed by 10 mol% $FeCl_3$ at 100 °C in DMF to give the expected product **4a** in 90% yield. As shown in Table 3, similar to the substrate scope for the synthesis of quinazolin-4(3*H*)-one derivatives, arylacetic acids holding both electron-donating groups and electron-withdrawing groups on the aromatic cycles work well and react readily with 2-aminobenzylamine to give the corresponding quinazolines in high yields. Noteworthy, valuable functional groups such as OMe, OH, NH_2, NO_2, Br and Cl all are compatible under the present reaction conditions. The heterocycle exemplified by **4i** having thiophenyl has also been introduced into quinazoline framework by this strategy.

Under the optimal reaction conditions, the protocol can be applied to preparation of the bioactive five-membered compounds like benzimidazoles and benzothiazoles (Table 4). Benzothiazole **5a** is obtained from similar reaction of *o*-aminothiophenol **1f** with **2b**. Other substituted phenylacetic acid also serves as good substrates, affording the corresponding benzothiazoles **5b**-**5d** in high yields. Besides, bioactive benzimidazoles **5e** and **5f** have been prepared from the reaction of *o*-phenylenediamine **1g** with phenylacetic acid and 2-(thiophen-2-yl)aceticacid under similar reaction conditions and the yields are 80% and 81%, respectively.

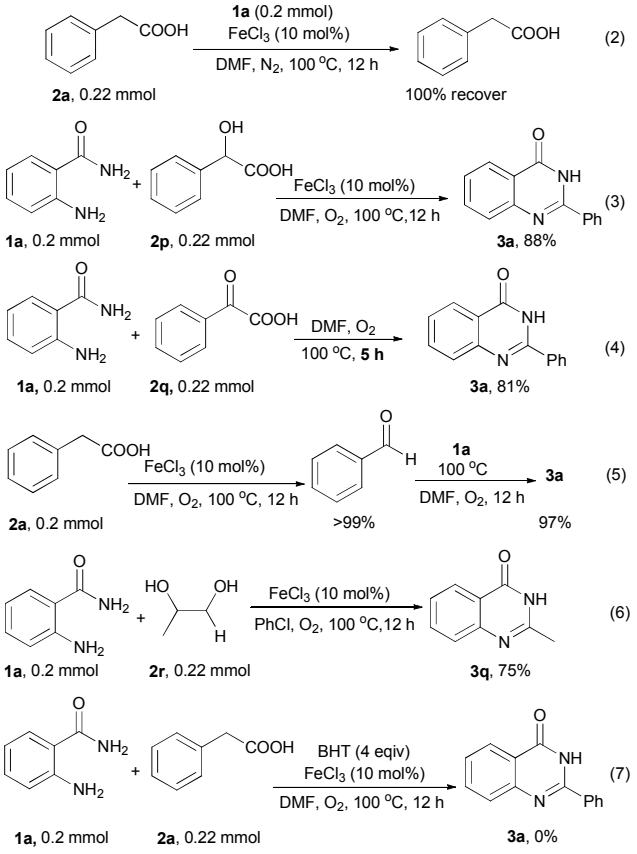
Table 4. Fe-catalyzed aerobic oxidative amidation of sp^3C-H bonds for the synthesis benzimidazoles and benzothiazoles[a]



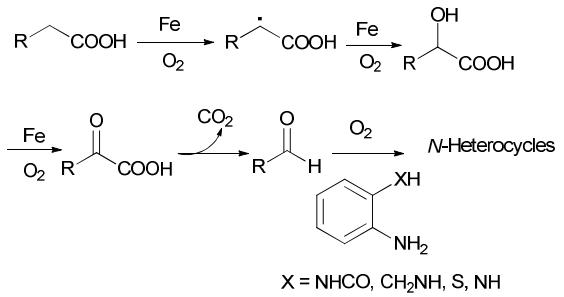
[a]Reaction conditions: **1f**-**1g** (0.2 mmol), **2a**-**2i** (0.22 mmol), $FeCl_3$ (0.02 mmol, 10 mol%), DMF (1 mL), O_2 (1 atm) in a Schlenk tube (10 mL) at 100 °C, 12 h, recharging dioxygen after 6 h.

To clarify the reaction mechanism, several control experiments were performed. In the nitrogen atmosphere, phenylacetic acid **2a** is recovered completely and no decarboxylative products are detectable under similar condition (eq 2). Thus it is reasonable that the aerobic oxidation of sp^3C-H bonds takes place prior to decarboxylation.[17] In addition, α-hydroxyphenylacetic acid **2p** reacts with *o*-aminobenzamide **1a** smoothly under the optimal condition to give the corresponding product **3a** in 88% yield (eq 3). When 2-oxo-2-phenylacetic acid **2q** is used as substrate without the aid of anhydrous $FeCl_3$, the reaction with **1a** takes place to give **3a** in 81% yield (eq 4). While in the absence of **1a**, benzaldehyde is generated in 99% yield from the iron-catalyzed aerobic oxidation of phenylacetic acid, and the resulting benzaldehyde can further react with **1a** to furnish **3a** in 97% yield (eq 5). Therefore, it is speculated that α-hydroxyphenylacetic acid, 2-oxo-2-phenylacetic acid and benzaldehyde probably serve as the efficient intermediates in the current iron-catalyzed aerobic oxidation-decarboxylation-cyclization system. When phenylacetic acid **2a** was replaced

by 1,2-propanediol **2r**, the 2-methylquinazolin-4(3*H*)-one **3q** was obtained in 75% yield (eq 6). Moreover, when the radical trapper BHT (2,6-di-tert-butyl-4-methylphenol) is loaded, the reaction of **1a** with **2a** does not occur and no product **3a** or benzaldehyde can be detected, indicating that this iron-catalyzed sp^3C-H bonds aerobic oxidation and decarboxylation of arylacetic acids proceeds via a radical process (eq 7).



On the basis of results described above and in literatures,[9,10,16,18] a plausible reaction process for the present iron-catalyzed aerobic oxidative functionalization of sp^3C-H bonds is proposed as shown in Scheme 1. In the Fe/O_2 system, the C-H bonds are first oxidized to form α-hydroxycarboxylic acid via a radical path, followed by dehydrogenation to give 2-oxo-2-carboxylic acid.[9,10,18] Subsequently, the resulting 2-oxo-2-carboxylicacetic acid undergoes decarboxylation generating aldehyde, which is captured by *o*-substituted anilines to produce *N*-heterocyclic compounds under oxygen atmosphere.[16]



Scheme 1. Plausible reaction process for the construction of *N*-heterocycles from arylacetic acid and *o*-substituted anilines

In summary, we have developed an efficient strategy of iron-catalyzed sp^3C-H bonds aerobic oxidative functionalization to construct *N*-heterocycles. The transformation occurs via a tandem sequence involving iron-catalyzed sp^3C-H bonds aerobic oxidation, decarboxylation and subsequent oxidation cyclization. This method also provides an environmentally friendly protocol to *N*-heterocyclic compounds from easily accessible carboxylic acid derivatives and *o*-substituted anilines with wide substrate scope.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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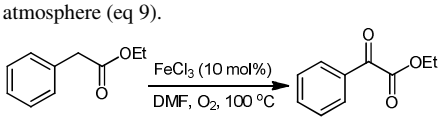
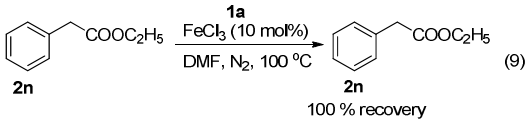
16 ***There are several methods to prepare N-heterocyclic compounds, in which the coupling of 2-substituted aniline with aldehydes was the popular choice. Although aldehydes can serve as the efficient starting material for the preparation of N-heterocyclic compounds, the aldehydes are chemically unstable for preparation and suffer from difficult storage. Thus, efficient alternative methods are still desired***. For selected examples using aldehyde as starting material see: a) G. Wang, C. Miao, H. Kang and *Bull. Chem. Soc. Jpn*. 2006, **79**, 1426-1430; b) C. Balakumar, P. Lamba, D. P.Kishore, B. L. Narayana, K. V. Rao, K. Rajwinder, A. R. Rao, B. Shireesha and B. Narsaiah, *Eur. J. Med. Chem*. 2010**,** **45**, 4904-4913; c) C. Balakumar, P. Lamba, D. P. Kishore, B. L. Narayana, K. V. Rao, K. Rajwinder, A. R. Rao, B. Shireesha and B. Narsaiah, *Eur. J. Med. Chem*. 2010, **45**, 4904-4913; For selected examples of Ullmann-type *N*-arylation, see: d) D. S. Yang, Y. Y. Wang, H. J. Yang, T. Liu and H. Fu, *Adv. Synth. Catal*. 2012, **354**, 477-482; for selected examples using alcohol as starting material, see: e) M. Heidary, M. Khoobi, S. Ghasemi, Z. Habibi and M. Ali Faramarzi, *Adv. Synth. Catal*. 2014, 1789-1794; for CO insertion and intramolecular cyclization, see: f) B. Ma, Y. Wang, J. L. Peng and Q. Zhu, *J. Org. Chem*. 2011, **76**, 6362-6366; for selected examples using amines as starting material, see: g) T. B. Nguyen, L. Ermolenko and A. Al-Mourabit, *Green Chem*. 2013, **15**, 2713-2717.

17 When ethyl 2-phenylacetate **2n** (efficient substrate for the current catalytic system, see Table 2) was loaded in the absence of **1a** under similar condition, ethyl 2-oxo-2-phenylacetate was produced in 31% yield after 12 hours (eq 8). It should be noted that the hydrolysis of ethyl 2-phenylacetate does not occur during the reaction process, because 100% **2n** was recovered from the reaction system under N_2 atmosphere (eq 9).



(8)

2n, 0.2 mmol **2n-1**, 31%



(9)

2n **2n**

100 % recovery

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