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Copper-Catalyzed Oxidative α-Alkylation of α-Amino Carbonyl Compounds with Ethers *via* Dual C(sp^3)-H Oxidative Cross-Coupling

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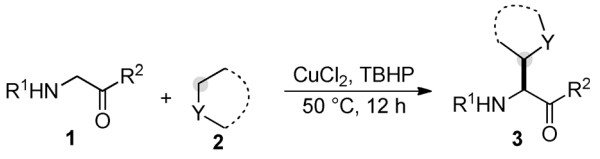
Abstract: A novel copper-catalyzed oxidative alkylation of α-amino carbonyl compounds with ethers has been established for the selective synthesis of α-etherized α-amino carbonyl compounds. This oxidative alkylation is achieved by dual C(sp^3)–H bond oxidative cross-coupling, and its scope is expanded to α-amino ketones, α-amino esters and α-amino amides.

Keywords: alkylation; α-amino carbonyl compounds; *tert*-butyl hydrogen peroxide (TBHP); copper; C(sp^3)–H functionalization; ethers

α-Amino carbonyl compounds are ubiquitous subunits in biologically active natural products, biomolecules and therapeutic agents.[1] The development of efficient strategies for their assembly has been a long-standing hot topic in organic and bioorganic synthesis. In this context, α-C–H functionalization of the preexisting α-amino carbonyl structures has attracted considerable efforts due to its direction and site-specificity.[2–5] Despite impressive progress in the field, there remains a great need for new strategies. In particular, the traditional α-C–H alkylation[3] is more limited: the reaction usually requires expensive organohalides with the aid of a strong base leading to a mass of unwanted wastes; moreover, any NH_2 group should be pre-protected to avoid free N–H bond functionalization side-reactions.

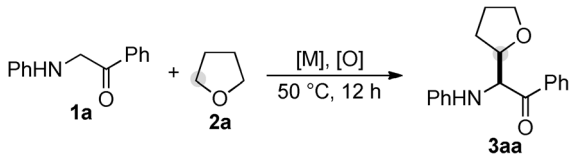
Recently, a fascinating transition metal-catalyzed cross dehydrogenative coupling strategy was established for α-C–H alkylation of α-amino esters, wherein a carbon-hydrogen bond at the α-position of ketones is used to replace the traditional carbon-halogen bond, and free N–H bonds are tolerated.[4,5] In 2008, Li and Zhao firstly reported that α-amino esters could be alkylated with malonates by Cu-catalyzed dual C–H functionalization.[4] However, the reaction was carried out under rather harsh conditions [20 mol% $Cu(OAc)_2$ at 150 °C]; moreover, a catalytic amount of bases combined with a ligand was still needed to facilitate the reaction. Subsequently, Huang and Xie have illustrated a new, mild cross dehydrogenative coupling strategy for α-alkylation of α-amino esters with ketones through a Cu/aminocatalyst-catalyzed oxidative dual C–H functionalization process under neutral conditions.[5] To the best of our knowledge, however, oxidative α-alkylation of α-amino carbonyl compounds with ethers using the dual C–H functionalization strategy has not been exploited. The reason may be that in the cross dehydrogenative coupling reactions both α-amino carbonyl compounds[2l–o,4,5] and ethers[6] are utilized as electrophilies to react with a wide range of nucleophiles.[7]

Herein we report a novel and mild Cu-catalyzed oxidative alkylation of α-amino carbonyl compounds with ethers for selective synthesis of α-etherized α-amino carbonyl compounds[8,9] in the presence of *tert*-butyl hydrogen peroxide (TBHP; Scheme 1); this oxidative alkylation is achieved by dual C(sp^3)–H bonds oxidative cross-coupling, and its scope is extended to α-amino ketones, α-amino esters and α-amino amides. To the best of our knowledge, this work represents the first example of metal-catalyzed oxidative α-C–H



Scheme 1. Cu-catalyzed oxidative α-alkylation.

Table 1. Screening for optimal conditions.[a]



Entry	[M] [mol%]	[O] [equiv.]	T [°C]	Yield [%][b]
1	$CuCl_2$ (5)	air (1 atm)	50	40
2	$CuCl_2$ (5)	O_2 (1 atm)	50	10
3[c]	$CuCl_2$ (5)	–	50	trace
4	$CuCl_2$ (5)	TBHP (1.2)	50	76
5	$CuCl_2$ (5)	DTBP (1.2)	50	61
6	$CuCl_2$ (5)	*m*-CPBA (1.2)	50	25
7	$CuCl_2$ (5)	DDQ (1.2)	50	10
8	$CuCl_2$ (5)	oxone (1.2)	50	36
9	$CuBr_2$ (5)	TBHP (1.2)	50	53
10	$Cu(OTf)_2$ (5)	TBHP (1.2)	50	24
11	$Cu(OAc)_2$ (5)	TBHP (1.2)	50	48
12	CuCl (5)	TBHP (1.2)	50	53
13	$FeCl_3$ (5)	TBHP (1.2)	50	11
14	–	TBHP (1.2)	50	0
15	$CuCl_2$ (2)	TBHP (1.2)	50	76
16	$CuCl_2$ (1)	TBHP (1.2)	50	41
17	$CuCl_2$ (2)	TBHP (2)	50	74
18	$CuCl_2$ (2)	TBHP (1.2)	25	30
19	$CuCl_2$ (2)	TBHP (1.2)	70	65
20[d]	$CuCl_2$ (2)	TBHP (1.2)	50	75
21[e]	$CuCl_2$ (2)	TBHP (1.2)	50	78

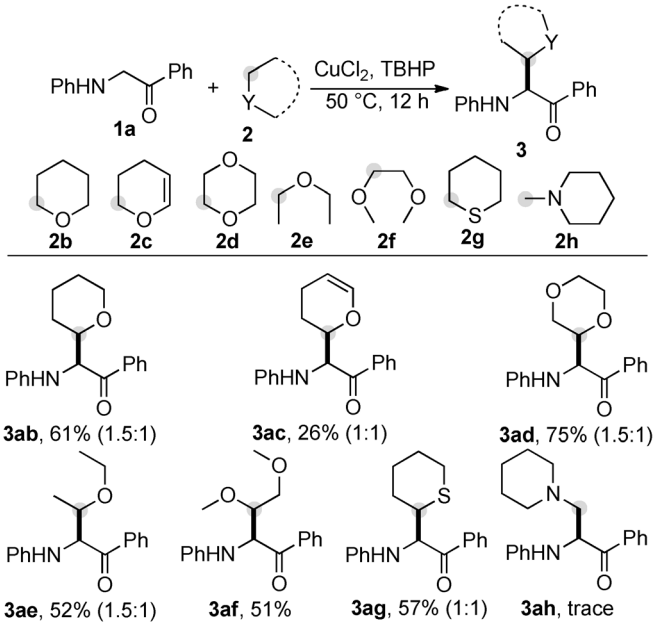
[a] *Reaction conditions:* **1a** (0.5 mmol), **2a** (7.5 mmol), [M] and [O] at 50 °C under air atmosphere for 12 h. TBHP = *tert*-butyl hydrogen peroxide (anhydrous, 5 M in decane), DTBP = di-*tert*-butyl peroxide.
[b] Yield of **3aa** (*dr* is about 1.5:1).
[c] Under an argon atmosphere.
[d] In toluene (0.5 mL).
[e] **1a** (10 mmol, 2.11 g).

alkylation of α-amino carbonyl compounds with a C(sp^3)–H bond adjacent to a heteroatom (an oxygen or a sulfur atom).

We initiated our investigation on the reaction between 1-phenyl-2-(phenylamino)ethanone (**1a**) and tetrahydrofuran (THF; **2a**), and the results are summarized in Table 1. Interestingly, substrate **1a** could react with THF **2a** in the presence of $CuCl_2$ and air, providing the desired product **3aa** in 40% yield (entry 1). However, the use of O_2 instead of air resulted in a poor yield (entry 2), and no product **3aa** was detectable in argon (entry 3). The results suggest that the reaction is highly dependent on the oxidant. A number of other oxidants were subsequently screened (entries 4–8): they effected the reaction, among which TBHP proved to be superior (76% yield; entry 4). Encouraged by the results, the reactions between substrate **1a** and THF **2a** were examined with respect to metal catalysts (entries 9–13): metal salts, such as $CuBr_2$, $Cu(OTf)_2$ $Cu(OAc)_2$, CuCl or $FeCl_3$, have catalytic activity for the reaction, but they were inferior to $CuCl_2$. However, the reaction cannot take place without metal catalysts (entry 14). Among the amounts of both $CuCl_2$ and TBHP examined, it turned out that the reaction at 2 mol% $CuCl_2$ and 1.2 equiv. TBHP provided the best results (entry 15 *vs.* entries 4, 16 and 17). Extensive screening revealed that the reaction temperature affected the reaction, and the yield was lowered at either 25 °C or 70 °C (entries 18 and 19 *vs.* entry 15). It is noteworthy that a good yield is still achieved using toluene as the medium (entry 20). Gratifyingly, a large scale reaction, 10 mmol of 1-phenyl-2-(phenylamino)ethanone (**1a**), proceeded smoothly, furnishing product **3aa** in good yield (entry 21).

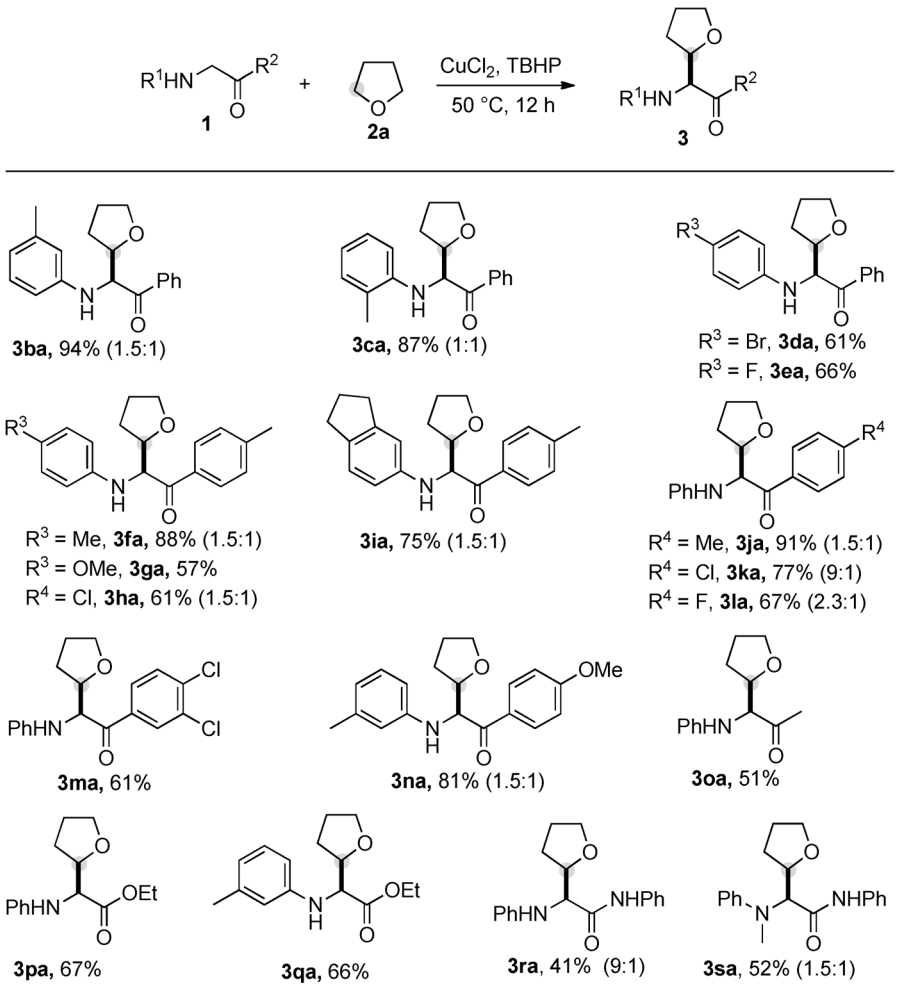
With the optimal conditions in hand, the scope of both α-amino carbonyl compounds **1** and ethers **2** in the α-etherized α-amino carbonyl compound synthesis was examined (Table 2 and Table 3). As shown in Table 2, all of the tested ethers and a thioether acted as excellent substrates to react with 1-phenyl-2-(phenylamino)ethanone (**1a**), $CuCl_2$ and TBHP, furnishing the corresponding products **3ab**–**ag** in moderate to good yields. Tetrahydro-2*H*-pyran (**2b**), for instance, could successfully undergo the oxidative cross-coupling reaction with substrate **1a** in 61% yield (product **3ab**). However, 3,4-dihydro-2*H*-pyran (**2c**) selectively gave the desired product **3ac** in low yield. Using 1,4-dioxane (**2d**), diethyl ether (**2e**) or 1,2-dimethoxyethane (**2f**), the corresponding products **3ad**–**af** were isolated in 75%, 52% and 51% yields, respectively.

Table 2. Scope of substrates **2**.[a]



[a] *Reaction conditions:* **1a** (0.5 mmol), **2** (7.5 mmol), $CuCl_2$ (2 mol%), and TBHP (1.2 equiv.) at 50 °C under air atmosphere for 12 h. The *dr* value is given in parenthesis.

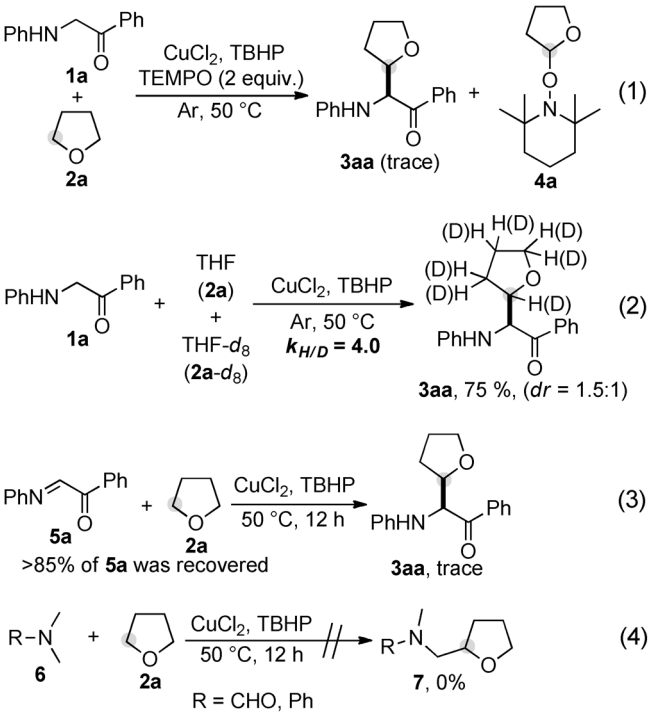
Table 3. Scope of the α-amino carbonyl compounds **1**.[a]



[a] *Reaction conditions:* **1** (0.5 mmol), **2a** (7.5 mmol), $CuCl_2$ (2 mol%), and TBHP (1.2 equiv.) at 50 °C under an air atmosphere for 12 h. The *dr* value is given in parenthesis.

Gratifyingly, tetrahydro-2*H*-thiopyran (**2g**) was also compatible with the oxidative cross-coupling reaction with substrate **1a** (product **3ag**). Unfortunately, tertiary amine **2h** cannot react with substrate **1a** under the optimal conditions.

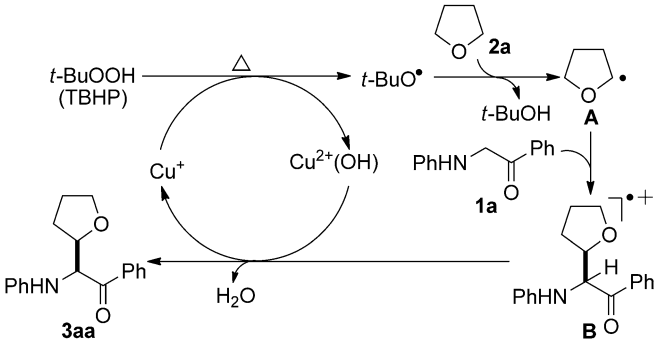
The reaction was found to be applicable to a wide range of α-amino carbonyl compounds **1** (Table 3). Steric and electronic variations in the *N*-aryl moiety of α-amino ketones **1** were initially tested in the presence of THF **2a**, $CuCl_2$ and TBHP (products **3ba–ia**). Extensive screening revealed that several substituents, including Me, MeO, Br, Cl and F groups, on the *N*-aryl ring were perfectly tolerated under the optimal conditions. For example, substrates bearing an Me group at the *para*-, *ortho*- or *meta*-position had high reactivity to couple with THF **2a** in excellent yields (products **3ba**, **3ca** and **3fa**). Gratifyingly, Br, Cl and F groups could be tolerated well, thereby facilitating additional modifications at the halogenated position (products **3da**, **3ea** and **3ha**). An *N*-1*H*-inden-5-yl-containing substrate was also found to be viable for the reaction (product **3ia**). We next set out to exploit the substitution effect on the aryl group of the 1-arylethanone moiety: a number of substituents, such as Me, Cl, F or MeO, are consistent with the optimal conditions, and the electron-donating groups are superior to the electron-withdrawing groups (products **3ja–na**). The reaction was readily expanded to an aliphatic substrate, 1-(phenylamino)propan-2-one, albeit with a diminished yield (product **3oa**). To our delight, both α-amino esters and α-amino amides were compatible with the oxidative cross-coupling reaction (products **3pa–sa**). For example, ethyl 2-(phenylamino)acetate was alkylated with THF **2a** smoothly to construct product **3pa** in 67% yield. When α-amino amides were employed under the optimal conditions, moderate yields were still obtained (products **3ra–sa**).



Scheme 2. Control experiments.

To understand the mechanism, some control experiments were carried out (Scheme 2). Two radical inhibitors, TEMPO [Eq. (1)] and 2,6-di-*tert*-butylphenol, were added to the α-alkylation reaction: a stoichiometric amount of radical inhibitor (2 equiv.) results in no conversion of substrate **1a**; however, THF was transferred by TEMPO into 2,2,6,6-tetramethyl-1-(tetrahydrofuran-2-yloxy)piperidine (**4a**). The results imply that an alkyl radical from diethyl ether is formed. Notably, there is a high kinetic isotope effect ($k_H/k_D = 4.0$) in the deuterated experiment between THF and THF-d_8 [Eq. (2)], suggesting that this C–H oxidative functionalization of ether is an irreversible step.[7] The results in Eq. (3) demonstrate that the reaction does not include the direct formation of imine intermediates from α-amino carbonyl compounds **1**: an imine, 1-phenyl-2-(phenylimino)ethanone (**5a**), could not react with THF (**2a**) under the optimal conditions. Moreover, both an amide and a tertiary amine are also inert [Eq. (4)].

Consequently, a possible mechanism as outlined in Scheme 3 is proposed.[2l–o,4–8] Initially, TBHP is split by Cu^+ into a *tert*-butoxy radical and $Cu^{2+}(OH)$ under heating conditions. Subsequently, a C(sp^3)–H bond adjacent to an oxygen atom in THF **2a** can be readily cleaved by a *tert*-butoxy radical, and transfers into an alkyl radical intermediate **A**. Finally, radical intermediate **A** adds to α-carbon of 1-phenyl-2-(phenylamino)ethanone (**1a**) leading to the cation radical intermediate **B**, followed by hydrogen atom abstraction from intermediate **B** with $Cu^{2+}(OH)$



Scheme 3. Possible mechanism.

which takes place to afford the desired product **3aa** and regenerate the active Cu species.

In summary, we have illustrated a highly effective synthesis of α-etherized α-amino carbonyl compounds from the copper-catalyzed oxidative α-alkylation of α-amino carbonyl compounds with ethers. The reaction features a dual C(sp^3)–H bonds oxidative cross-coupling across both the ether C(sp^3)–H bond adjacent to an oxygen atom and the α-amino carbonyl compound α-C(sp^3)–H bond to generate a new α-amino carbonyl nucleus. Studies are currently underway to apply this oxidative alkylation to the synthesis of other bioactive molecules in our laboratory.

Experimental Section

Typical Experimental Procedure for the Cu-Catalyzed Oxidative α-Alkylation of α-Amino Carbonyl Compounds (1) with Ethers (2)

To a Schlenk tube were added α-amino carbonyl compound **1** (0.5 mmol), ether **2** (7.5 mmol), $CuCl_2$ (2 mol%) and TBHP (anhydrous, 1.2 equiv.). Then the tube was charged with air, and was stirred at 50 °C (oil bath temperature) for the indicated time until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the reaction mixture was cooled to room temperature, diluted with diethyl ether, and washed with brine. The aqueous phase was re-extracted with diethyl ether. The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate = 30:1) to afford the desired product **3**.

1-Phenyl-2-(phenylamino)-2-(tetrahydrofuran-2-yl)ethanone (3aa): Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.03–8.01 (m, 2H), 7.60–7.56 (m, 1H), 7.50–7.46 (m, 2H), 7.17–7.14 (m, 2H), 6.83 (d, J = 8.0 Hz, 1H), 6.73–6.69 (m, 2H), 5.21 (d, J = 4.5 Hz, 0.6H), 5.11 (d, J = 2.5 Hz, 0.4H), 4.86 (brs, 1H), 4.37–4.33 (m, 1H), 3.83–3.80 (m, 1H), 3.78–3.66 (m, 1H), 2.01–1.98 (m, 1H), 1.92–1.84 (m, 1H), 1.83–1.79 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.6, 199.3, 147.7, 147.5, 135.7, 135.6, 133.7, 133.4, 129.3, 129.2, 128.8, 128.6 (2), 118.2, 114.2, 113.7, 80.5, 79.2, 69.0, 68.7, 62.4, 61.3,

28.1, 26.8, 25.9, 25.8; IR (KBr): $\nu = 1681$ cm^{-1}; LR-MS (EI, 70 eV): m/z (%) = 281 (M^+, 3), 211 (100), 77 (37); HR-MS (ESI): $m/z = 282.1504$, calcd. for $C_{18}H_{20}NO_2$ ($[M+H]^+$): 282.1489.

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