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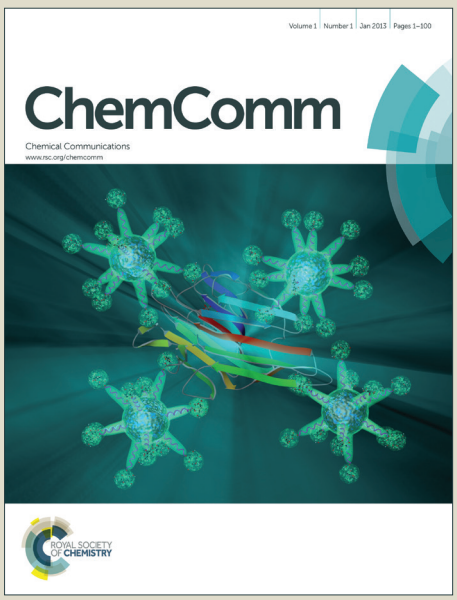

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Copper-catalyzed direct α-ketoesterification of propiophenones with acetophenones via C(sp^3)–H oxidative cross-coupling

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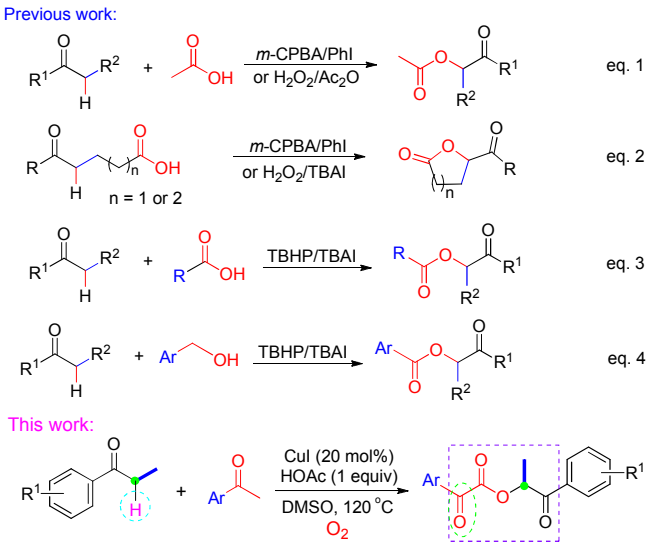
A novel copper-catalyzed direct *α*-ketoesterification of propiophenones with acetophenones via C(sp^3)–H oxidative cross-coupling was developed. The reaction utilized O_2 as a clean oxidant with high atom economy and the starting materials are facile and commercial available.

α-Functionalization of ketones is a significant and fundamental organic reaction.[1] The direct cross-coupling at α-C(sp^3)–H of arylketons is one of the most concise and effective route to them. Among the cross-coupling reactions, α-allylation,[2] α-alkylation,[3] α-amination,[4] α-arylation,[5] α-halogenation,[6] α-hydroxylation,[7] α-oximation,[8] α-azidation,[9] α-imidation,[10] α-vinylation[11] of arylketones have received much more attentions, and the transition-metal as a catalyst is essential in the most of cases. The transition metal used in the reactions was found to be Pd,[2a,2b,5c-5i,7b] Cu,[3a,4,11a,11c] Rh,[3b,3c] Ru,[3d,3e] Ni,[5b] or Ir.[3f] On the other hand, the oxidative cross-couplings of arylketons have been developed in recent years. For example, the synthesis of α-ketoamides from acetophenones with secondary amines[12] and dialkylformamides[13] in the presence of TBHP as an oxidant was reported.

α-Acyloxycarbonyl compounds play an essential role in biological processes, serve as the backbones in some natural products, and are used as significant building blocks in organic synthesis. Traditionally, they can be prepared by the reaction of α-halocarbonyl compounds with carboxylates[14] or the direct oxidative coupling of carbonyl compounds with $Pb(OAc)_4$, $Tl(OAc)_3$, and $Hg(OAc)_2$.[15] Most recently, hypervalent iodine compounds as effective oxidants to promoted esterification were investigatived.[16] For example, the intra- and intermolecular oxidative couplings of ketones with carboxylic acid catalyzed by hypervalent (diacyloxyiodo)benzene generated in situ from iodobenzene and *meta*-chloroperbenzoic acid (*m*-CPBA) were demonstrated (Scheme 1, Eq. 1 and 2).[16b,16d] The same reaction was also mediated by H_2O_2 and Ac_2O as oxidant (Eq. 1),[17] as well as by H_2O_2/Bu_4NI and TBHP/Bu_4NI (Eq. 2 and 3).[18] Moreover, α-acyloxycarbonyl compounds could be prepared by the Bu_4NI-catalyzed reaction of ketones with benzylic alcohols in the presence of TBHP (Scheme 1, Eq. 4).[19]



Scheme 1 Direct *α*-ketoesterification of ketones

In this paper, an efficient Cu-catalyzed C(sp^3)–H oxidative cross-coupling of propiophenones with acetophenones was developed. The reaction underwent smoothly in one-pot with good regioselectivity, and molecular oxygen as oxidant is inexpensive,[20] abundant and environmentally friendly (Scheme 1).

At the investigation of the reaction conditions, propiophenone (**1a**) and acetophenone (**2a**) were chosen as the model substrates. The results were shown in Table 1. Firstly, the effect of oxidant on the model reaction was examined. When the reaction was performed

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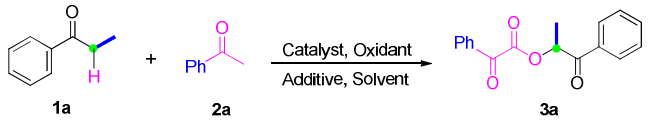
Table 1 Optimization of the reaction conditions[a]



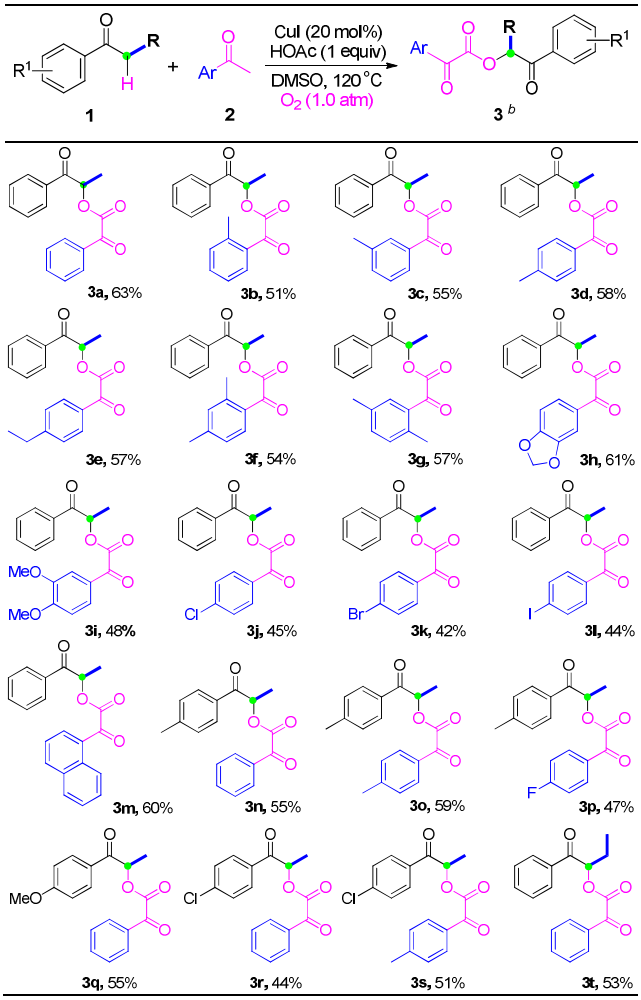
1a 2a 3a

Entry	Catalyst	Oxidant	Additive	Solvent	Yield[b](%)
1	CuI	O_2	-	DMSO	20
2	CuI	TBHP	-	DMSO	trace
3	CuI	H_2O_2	-	DMSO	11
4	CuI	DTBP	-	DMSO	N.R.
5	CuBr	O_2	-	DMSO	18
6	CuCl	O_2	-	DMSO	N.R.
7	$CuBr_2$	O_2	-	DMSO	N.R.
8	$CuCl_2$	O_2	-	DMSO	trace
9	CuO	O_2	-	DMSO	N.R.
10	$Cu(OAc)_2$	O_2	-	DMSO	N.R.
11	$Cu(OTf)_2$	O_2	-	DMSO	N.R.
12	CuI	O_2	-	NMP	trace
13	CuI	O_2	-	DMF	N.R.
14	CuI	O_2	-	THF	N.R.
15	CuI	O_2	-	toluene	N.R.
16	CuI	O_2	-	CH_3CN	N.R.
17	CuI	O_2	-	DCE	N.R.
18	CuI	O_2	HOAc	DMSO	40
19	CuI	O_2	PivOH	DMSO	37
20	CuI	O_2	TFA	DMSO	39
21	CuI	O_2	CF_3SO_3H	DMSO	31
22	CuI	O_2	$PhCO_2H$	DMSO	36
23	***CuI***	***O_2***	***HOAc***	***DMSO***	***63[c]***
24	CuI	O_2	Cs_2CO_3	DMSO	N.R.
25	CuI	O_2	Et_3N	DMSO	N.R.
26	CuI	O_2	Pyridine	DMSO	N.R.

[a] Reaction conditions: propiophenone (**1a**, 0.375 mmol) and acetophenone (**2a**, 0.25 mmol), catalyst (0.05 mmol, 20 mol%), oxidant (4.0 equiv, 1.0 mmol), additive (1.0 equiv, 0.25 mmol), solvent (2.0 mL), at 120 °C for 12 h. [b] Isolated yields. [c] DMSO (0.3 mL). N.R. = No reaction.

in the presence of CuI in DMSO (dimethyl sulfoxide) under oxygen atmosphere at 120 °C for 12 h, the product **3a** was obtained in 20% yield (Table 1, entry 1), which was characterized by HRMS, ^{1}H and ^{13}C NMR, and confirmed by single crystal X-ray crystallography.[21] However, additional peroxide, such as TBHP (*tert*-butyl hydroperoxide, 70% aqueous solution), H_2O_2 (30% aqueous solution) or DTBP (di-*tert*-butyl peroxide) was added to the reaction, providing less yields of **3a** (Table 1, entries 2–4). Next, the effect of Cu-catalyst was examined. CuBr gave the comparable result with CuI, and other Cu-catalysts including CuCl, $CuBr_2$, $CuCl_2$, CuO, $Cu(OAc)_2$, and $Cu(OTf)_2$ shut down the reaction completely (Table 1, entries 5–11). The solvent also plays an important role in the reaction. When the reaction was carried out in NMP (*N*-methylpyrrolidone), only trace amount of the desired product was

Table 2 Scope of the substrates[a]



[a] Reaction conditions: **1** (0.375 mmol) and **2** (0.25 mmol), CuI (0.05 mmol, 0.20 equiv), HOAc (0.25 mmol, 1.0 equiv), O_2 (1.0 atm), DMSO (0.30 mL), at 120 °C for 12 h. [b] Isolated yields.

detected (Table 1, entry 12), and the reaction failed in DMF (*N,N*-dimethylformamide), THF, toluene, CH_3CN, or DCE (1,2-dichloroethane) (Table 1, entries 13–17). To our delight, additional an organic acid, such as HOAc, PivOH, TFA (trifluoroacetic acid), CF_3SO_3H, or $PhCO_2H$ enhanced the reaction, and HOAc was found to be most effective one (Table 1, entries 18–22). However, inorganic and organic base including Cs_2CO_3, Et_3N, pyridine, completely failed (Table 1, entries 24–26).

With optimized reaction conditions in hand, a variety of propiophenones and acetophenones were examined to illustrate the efficiency and scope of the oxidative cross-coupling (Table 2). Acetophenones with an electron-donating group (Me, Et) and two methyl groups on the benzene rings reacted with propiophenone to generate the desired products in 51–58% yields (Table 2, **3b–3g**). It should be noted that acetophenone with acetal group generated **3h**in 61% yield, and acetophenone with two methoxy groups afforded **3i** in 48% yield. On the other hand, acetophenones with an electron-withdrawing group (Cl, Br, I) on the benzene rings reacted with propiophenone to generate the desired products (**3j–3l**) in 42–45% yields. When acetophenones with more electron-deficient groups

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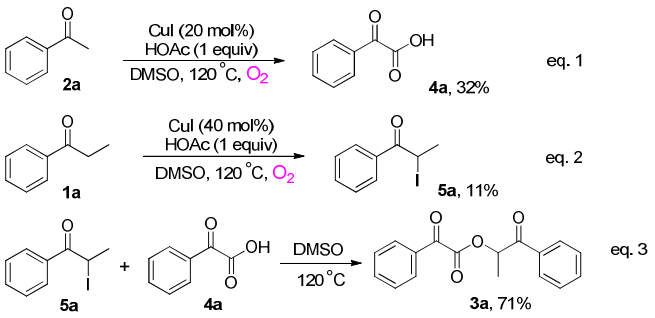
(CO_2CH_3 and CF_3) reacted with propiophenone, no desired products were detected. Under the optimized conditions, 1-acetyl naphthalene gave the desired product (**3m**) in 60% yield. A slight steric effect was observed during the formation of **3b** and **3f**. A variety of propiophenones were also examined and the results were shown in Table 2. Propiophenones with an electron-rich (Me, MeO) or electron-deficient group (Cl) on the phenyl rings reacted with 4-methylacetophenone and 4-fluoroacetophenone to give the desired products (**3n–3s**) in 44–59% yields. It should be noted that butyrophenone underwent the reaction with acetophenone to afford the corresponding products **3t** in 53% yield.

In order to gain insight into the mechanism, several control experiments were performed. When a radical scavenger (2,2,6,6-tetramethylpiperidyl-1-oxyl, TEMPO, 1.0 equiv) was added to the system, the reaction was completely shut down. It indicated a radical pathway may be involved in the reaction. In the presence of CuI/HOAc/O_2, the reaction of acetophenone (**2a**) generated 2-oxo-2-phenylacetic acid (**4a**) in 32% yield (Scheme 2, Eq. 1), and propiophenone (**1a**) afforded α-iodo-propiophenone (**5a**) in 11% yield (Scheme 2, Eq. 2). The prepared **5a** reacted with **4a** in DMSO at 120 °C to afford **3a** in 71% yield (Scheme 2, Eq. 3).

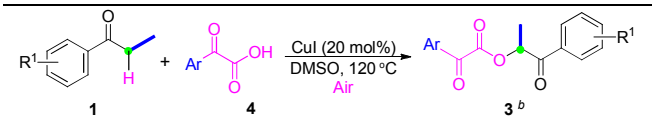
In order to confirm the activity of α-ketoacids, the reaction of 2-oxo-2-arylacetic acids (**4**) with propiophenones (**1**) was investigated, shown in Table 3. As anticipated, all of the corresponding compounds were obtained in good to excellent yields. Electron-donating groups (Me, MeO, Et, acetal) or electron-withdrawing groups (F, Cl, Br, I) on benzyl rings of ketoacids gave the superior yields to the corresponding acetophenones (**3a–3l** and **3n–3s**, Table 3 *vs* Table 2). 2-(Naphthalen-1-yl)-2-oxoacetic acid reacted with **1a** to generate the corresponding product **3m** in 76% yield (Table 3). It is important to note that the reactions of 2-(furan-2-yl)-2-oxoacetic acid with 1-(4-methylphenyl)propan-1-one, 1-(4-methoxyphenyl)propan-1-one and 1-(4-chlorophenyl)propan-1-one afforded the desired products (**3u**, **3v** and **3w**, Table 3) in 92, 90 and 91% yields, respectively. However, no desired product was found for the reactions of 2-acetylfuran with propiophenone.

Based on the previous reports and the above results, a possible reaction mechanism was proposed in Scheme 3. Initially, iodide anion was oxidized by molecular oxygen or Cu^I/O_2 to iodine radical, which reacted with propiophenone (**1a**) to generate α-carbonyl radical **I**.[4] The obtained **I** lost an electron in the presence of Cu^{II} from Cu^I/O_2 to generate α-carbonyl cation **II**,[4,22] which reacted with iodide ion to form intermediate **5a**. On the other hand, acetophenone (**2a**) reacted with molecular iodine, which produced from the reaction of iodide anion and O_2 or Cu^I/O_2, to afford 2-iodo-1-phenylethanone, as an intermediate **III**.[22a] The formed **III** was oxidized with DMSO to phenylglyoxal **IV**, and was further oxidized by O_2 to intermediate 2-oxo-2-phenylacetic acid (**4a**).[23] Finally, the reaction of **4a** with **II** or **5a** provided the desired product **3a**. In order to further investigate the mechanism, the trapping of free radical intermediate with TEMPO by HPLC-HRMS probe was carried out. The coupling product of α-carbonyl radical **I** with TEMPO was confirmed by HRMS (ESI for detail). The good regioselectivity in the reaction is considered as the more stable of α-carbonyl radical **I** from propiophenone (**1a**) compared with the corresponding α-carbonyl radical from acetophenone (**2a**).



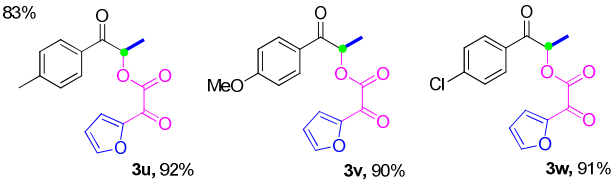
Scheme 2 The control experiments

Table 3 The reaction of 2-oxo-2-arylacetic acids (**4**) with propiophenones (**1**)[a]



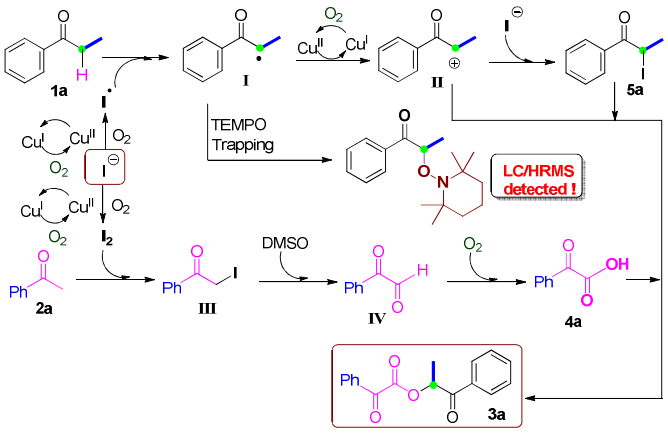
3a, 80%	**3b,** 76%	**3c,** 79%	**3d,** 78%	**3e,** 81%	**3f,** 64%
3g, 68%	**3h,** 76%	**3i,** 73%	**3j,** 48%	**3k,** 50%	**3l,** 47%
3m, 76%	**3n,** 74%	**3o,** 75%	**3p,** 67%	**3q,** 78%	**3r,** 49%

3s, 83%



3u, 92% **3v,** 90% **3w,** 91%

[a] Reaction conditions: **1** (0.375 mmol) and **4** (0.25 mmol), CuI (0.05 mmol, 0.20 equiv), DMSO (0.30 mL), open flask at 120 °C for 12 h. [b] Isolated yields.



Scheme 3 The proposed mechanism

In summary, we have developed a novel and efficient CuI-catalyzed direct α-ketoesterification of propiophenones with acetophenones via C(sp^3)–H oxidative cross-coupling reactions. The reactions underwent smoothly in one-pot with good regioselectivity. The molecular oxygen is employed as an oxidant. Meanwhile, the desired products were obtained in superior yields from the reactions of propiophenones with 2-oxo-2-arylacetic acids, which were from

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the oxidation of acetophenones. Further investigations on reaction mechanism are underway currently.

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Notes and references

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† Electronic Supplementary Information (ESI) available: CCDC 1035327. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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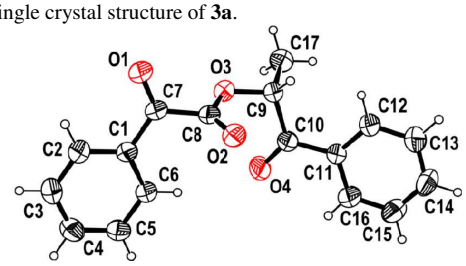
21. X-ray single crystal structure of **3a**.



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