Received: 17 August 2020 | Revised: 29 September 2020 | Accepted: 5 October 2020

DOI: 10.1002/aoc.6073

Applied Organometallic Chemistry WILEY

FULL PAPER

Copper-mediated simple and direct aerobic oxidative esterification of arylacetonitriles with alcohols/phenols

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Funding information
National Natural Science Foundation of China, Grant/Award Numbers: 21706058, 21878072, 21573065; Hunan Provincial Natural Science Foundation of China, Grant/Award Number: 2020JJ2011; Research Foundation of Education Bureau of Hunan Province, Grant/Award Number: 16B054

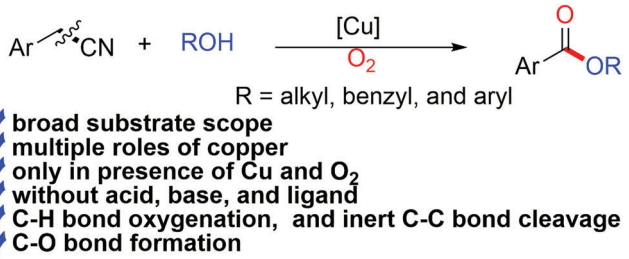
A simple and direct aerobic oxidative esterification reaction of arylacetonitriles with alcohols/phenols is achieved in the presence of a copper salt and molecular oxygen, which produces a broad range of aryl carboxylic acid esters in good to high yields. Copper salt plays multiple roles in the transformation, which allows the oxygenation of C—H bond, cleavage of inert C—C bond, and formation of C—O bond in one pot without the assistance of any of the acids, bases, ligands, and so on. The reaction provides a simple, direct, and efficient protocol towards functionalized esters, especially aryl benzoates, from readily available starting materials.

KEYWORDS
aerobic oxidative esterification, alcohols/phenols, arylacetonitriles, copper salt, esters

1 | INTRODUCTION

Esters are very common chemicals that are widely used as precursors for various functional group transformations in organic synthesis. Ester groups, especially aryl ester, are also versatile functional units in numerous pharmaceuticals, agrochemicals, fragrances, and polymers.[1,2] Traditional synthetic procedures for the preparation of esters rely on the transformations of carboxylic acids and acid anhydrides,[3,4] Over the past decades, alternative methods have been developed, such as transformations of amides,[5] transesterifications of esters,[6] the direct oxidative esterifications of aldehydes[7] and hydrocarbons,[2b,8] and carbonylation reactions of arene derivatives.[9] Due to their extreme significance and extensive applications in chemistry and chemical industry, it still necessitates diverse methods for preparing esters with facile operations, simple conditions, readily available starting materials, broad substrate scope, and/or step economy.

Herein, as a part of our ongoing research in copper catalysis,[10] we report a simple and direct aerobic oxidative esterification of easily available arylacetonitriles with alcohols/phenols mediated by simple copper salt (Scheme 1). This procedure successfully combines inert C—C bond cleavage,[11,12] C—H bond oxygenation, and C—O bond formation in one pot from readily available starting materials without the need for any of the acids,



SCHEME 1 Simple and direct approach to aryl esters

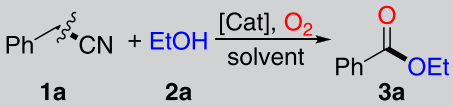
bases, ligands, and so on and produces a broad range of aryl carboxylic acid esters in good to high yields. Copper salt acts as multiple roles in this reaction, that is, catalyzing the Ritter-type oxidation of sp^3C—H bonds of arylacetonitriles, activating the carbonyl groups of aryl formyl cyanide intermediates, and improving the nucleophilicity of phenols.

Multiple roles of a metal catalyst, especially palladium catalysts, have attracted extensive attention in chemistry,[13] because diverse individual transformations and chemical bond cleavage/formation can occur in a one pot with the assistance of such a catalyst, which makes a reaction simpler and consuming less. Over past decades, copper salts have received great attention as earth-abundant metal catalysts, readily available and effective alternatives to noble metals due to their excellent catalytic efficiency in diverse types of reactions.[14] However, it is rare in copper chemistry that copper catalysts play multiple roles in one-pot reaction.[15] Undoubtedly, the multiple roles of copper salt promotes the esterification reaction in a very simple and efficient manner and avoids the employment of exotic additives and reagents, which is interesting and attractive.

2 | RESULTS AND DISCUSSION

Initially, phenylacetonitrile (**1a**) and ethanol (**2a**) were chosen as model substrates to examine the reaction parameters, and the results were summarized in Table 1. The reaction of **1a** and **2a** gave ethyl benzoate (**3a**) in GC 40% yield in the presence of 50 mol% CuCl in CH_3CN at 120°C under the oxygen atmosphere (Table 1, Entry 1). Then, copper salts were screened (Table 1, Entries 2–8), $Cu(OAc)_2$ showed the best catalytic efficiency, producing **3a** in 89% yield (Table 1, Entry 8). A lower loading (20 mol%) of $Cu(OAc)_2$ resulted in a low yield of the product (32%; Table 1, Entry 9). In contrast, $FeBr_3$ that is an efficient catalyst in an oxidative esterification reaciton[12f] was ineffective for the reaction (Table 1, Entry 10). Other transition metal catalysts such as Mn, Ag, and Ni salts did not work either (Table 1, Entries 11–13). The effect of solvents was also investigated (Table 1, Entries 14–18), and CH_3CN was found to be the best choice. The reaction proceeded neither in the absence of the catalyst (Table 1, Entry 19) nor under

TABLE 1 Optimization of the reaction conditions



Entry	Catalyst	T (°C)	Solvent	Yield (%)[a]
1	CuCl	120	CH_3CN	43
2	$CuCl_2$	120	CH_3CN	16
3	CuBr	120	CH_3CN	4
4	$CuBr_2$	120	CH_3CN	Trace
5	CuI	120	CH_3CN	8
6	Cu^0	120	CH_3CN	40
7	$Cu(NO_3)_2$	120	CH_3CN	32
8	$Cu(OAc)_2$	120	CH_3CN	89
9[b]	$Cu(OAc)_2$	120	CH_3CN	32
10	$FeBr_3$	120	CH_3CN	None
11	$Mn(OAc)_2$	120	CH_3CN	None
12	$AgNO_3$	120	CH_3CN	None
13	$NiCl_2$	120	CH_3CN	None
14	$Cu(OAc)_2$	120	DCE	Trace
15	$Cu(OAc)_2$	120	Dioxane	22
16	$Cu(OAc)_2$	120	Toluene	21
17	$Cu(OAc)_2$	120	THF	18
18	$Cu(OAc)_2$	120	EA	4
19	—	120	CH_3CN	None
20[c]	$Cu(OAc)_2$	120	CH_3CN	None
21[c,d]	$Cu(OAc)_2$	120	CH_3CN	None
22[c,e]	$Cu(OAc)_2$	120	CH_3CN	None
23	$Cu(OAc)_2$	100	CH_3CN	Trace
24	$Cu(OAc)_2$	130	CH_3CN	60
25	$Cu(OAc)_2$	120	EtOH	91 (83)[f]
26[g]	CuCl	120	EtOH	94 (85)[f]

Note: Reaction conditions: phenylacetonitrile (**1a**, 0.2 mmol), ethanol (**2a**, 0.24 mmol), catalyst (50 mol%) based on **1a**, solvent (1.0 ml), O_2 (1 atm), and sealed Schlenck tube of 25 ml.

[a]GC yield using dodecane as an internal standard.

[b]20 mol% $Cu(OAc)_2$.

[c]N_2 (1 atm).

[d]0.5 mmol H_2O_2 was employed as oxidant.

[e]0.5 mmol TBHP (*tert*-butylhydroperoxide) as oxidant.

[f]Isolated yields.

[g]100 mol% CuCl.

the inert atmosphere (Table 1, Entry 20). By the replacement of the oxidant with H_2O_2 or TBHP, the reaction did not take place either (Table 1, Entries 21 and 22). The reaction was sensitive to the temperature, it did not work (Table 1, Entry 23) by lowering the temperature to 100°C. Meanwhile, the yield of **3a** was sharply reduced (60%; Table 1, Entry 24) at 130°C. Notably, excellent yield (91%; Table 1, Entry 25) of **3a** was achieved by the conduction of the reaction in **2a** (1.0 ml) or by the replacement of $Cu(OAc)_2$ with CuCl (100 mol%, 94% yield; Table 1, Entry 26).

With the optimized conditions in hand, the scope of the reaction concerning for alcohols was investigated (Table 2). All of the three kinds of alcohols reacted smoothly with phenylacetonitrile (**1a**) to produce the corresponding benzoates in good to high yields. The aerobic oxidative esterification of phenylacetonitrile with alkyl alcohols such as ethanol (**2a**), propyl alcohol (**2b**), octanol (**2c**), and isoamyl alcohol (**2d**) produced the corresponding alkyl benzoates in high yields (78–83%; Table 2, Entries 1–4). When sterically hindered tertiary alcohol *t*-butanol (**2e**) was used as a substrate, the desired product (**3e**) was obtained in 69% yield (Table 2, Entry 5). Benzyl alcohols were also good substrates for the reaction, giving the corresponding benzyl benzoates in good yields (71–74%; Table 2, Entries 6–10). The electronic variation of substituents was not significantly influential on the reaction efficiency. Comparable yields were observed for the products bearing electron-donating (OMe, 74%) and electron-withdrawing groups (NO_2, 71%; CF_3, 71%) on the phenyl ring. Notably, the transformation of other types of arylmethyl alcohols, such as sterically hindered naphthyl methanols (naphthalen-1-ylmethanol and naphthalen-2-ylmethanol) and heteroaryl methanols (furan-3-ylmethanol and thiophen-3-ylmethanol) proceeded more efficiently than benzyl alcohols, giving the corresponding esters in high yields (80–83%; Table 2, Entries 11–14).

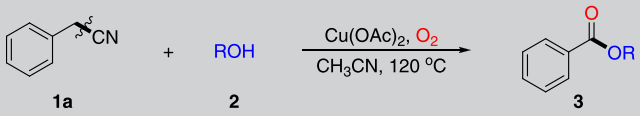
Next, the substrate scope of nitriles was investigated (Table 3). 2-Phenylacetonitriles substituted with electron-rich as well as those with electron-deficient groups could undergo aerobic oxidative esterification with ethanol, giving the corresponding esters in good to high yields (71–80%). 2-Phenylacetonitriles substituted by methyl (**1b**) and methoxyl (**1c**) groups work well as substrates to give ester derivatives **3o** and **3p** in 72 and 71% yields, respectively (Table 4, Entries 2 and 3). Slightly better results were observed in the reaction of 2-phenylacetonitriles bearing electron-deficient groups such as chloro (**1d**), bromo (**1e**), trifluoromethyl (**1f**), and nitro (**1g**) groups with ethanol, and the corresponding products **3q**–**3t** were produced in 77–80% yields (Table 3, Entries 4–7). Notably, there were different performances of the substituent groups in the steps of Ritter-type oxidation of benzyl C—H bonds[16] and subsequent nucleophilic attack of ethanol at benzoyl cyanides in the reaction. The electron-donating (electron-withdrawing) groups facilitate (disfavor) oxidation of benzyl C—H bonds but disfavor (facilitate) the subsequent nucleophilic attack (vide infra). All of the substituted 2-phenylacetonitriles (electron-rich and electron-deficient groups) shown slightly lower efficiency than that of phenylacetonitrile (**1a**, 85% yield; Table 3, Entry 1). This result indicated that the overall-electronic effect of substituent groups is detrimental to the reaction. 2-(Naphthalen-2-yl) acetonitrile (**1h**) also served as a good substrate, furnishing the desired ester (**3u**) in 76% yield (Table 3, Entry 8). To our delight, a heteroaryl ester **3v** was obtained (70% yield) by the treatment of 2-(thiophen-2-yl)acetonitrile **1i** with **2a** under the present reaction system, indicating that this method will be an efficient approach to introduce an aromatic heterocycle into functional molecules (Table 3, Entry 9). Unfortunately, when 2-(pyridin-3-yl)acetonitrile **1k** was used as substrate, the oxidative esterification reaction did not take place, which was probably due to the strong coordination between N atom and Cu cation (Table 3, Entry 11).

It was noted that Song's group had pioneered a Fe-catalyzed oxidative C—CN bond cleavage of phenylacetonitriles for the synthesis of esters.[12f] Although it is very elegant, the toxic additive pyridine is indispensable. By the replacement of copper salt with $FeBr_3$ that was used in Song's reaction system, the reaction did not proceed. Therefore, this protocol is quite different from Song's method.

Phenols have low nucleophilicity and are easily oxidized to diverse compounds such as coupling products, *ortho*-oxidation products, and polymers[14b–e]; aerobic oxidative esterification of precursors with phenols cannot be easily achieved. To address this issue, an over-stoichiometric amount of phenols are generally required, and an additional additive base is also used to form phenolic salts for facilitating the esterification.[12b,f] Gratifyingly, phenols were suited for the present aerobic oxidative esterification reaction using nearly equimolar quantities of phenols (1.2 equiv). Phenols bearing both electron-donating (methyl and OMe) and electron-withdrawing (Cl^-, Br^-, and —NO_2) groups worked well, a variety of functionalized phenyl benzoates were produced in good to high isolated yields (67–77%, Table 4, Entries 1–6). Naphthol (**2u**) was also suited for the transformation, and naphthyl benzoate (**3ze**) was furnished in a 60% yield (Table 4, Entry 7).

To explore the reaction mechanism, several control experiments were performed. By the replacement of $^{16}O_2$

TABLE 2 Substrate scope of alcohols **2**

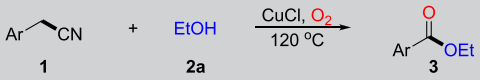


Entry	R	Product	Yield (%)
1	Et	**2a**	**3a**, 83
2	*n*-Propyl	**2b**	**3b**, 82
3	*n*-Octoyl	**2c**	**3c**, 79
4	*tert*-Amyl	**2d**	**3d**, 78
5	*t*-Bu	**2e**	**3e**, 69
6	Benzyl	**2f**	**3f**, 71
7	*p*-OMe-benzyl	**2g**	**3g**, 74
8	*p*-CF_3-benzyl	**2h**	**3h**, 71
9	*p*-NO_2-benzyl	**2i**	**3i**, 71
10	1-Phenylethyl	**2j**	**3j**, 72
11	Naphthalen-1-ylmethyl	**2k**	**3k**, 80
12	Naphthalen-2-ylmethyl	**2l**	**3l**, 81
13	Furan-3-ylmethyl X = O	**2m**	**3m**, 83
14	Thiophen-3-ylmethyl X = S	**2n**	**3n**, 80

Note: Reaction conditions: phenylacetonitrile (**1a**, 0.2 mmol), alcohol **2** (0.24 mmol), $Cu(OAc)_2$ (50 mol%) based on **1a**, CH_3CN (1.0 ml), O_2 (1 atm), 120°C, 24 h, sealed Schlenck tube of 25 ml, and isolated yields.

with $^{18}O_2$ (97 atom%), the $^{18}O_2$ labeled product (**3ze′**) in 58% yield with quantitative incorporation of $^{18}O_2$ (94.4 atom%) (Scheme 2, Equation 1; for details, see Scheme S1 and Figure S1). These results suggested that the O atom of the product came from the molecular oxygen. The addition of butylated hydroxytoluene (BHT) could restrain the reaction (Scheme 2, Equation 2); only a 27% yield of **3a** was observed, suggesting that a free

TABLE 3 Substrate scope of nitriles **1**



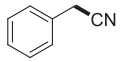
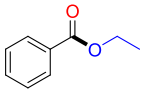
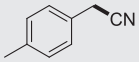
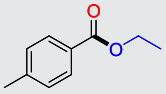
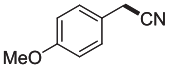
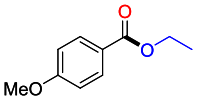
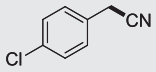
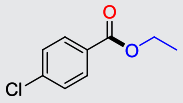
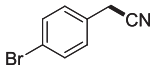
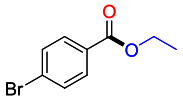
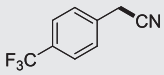
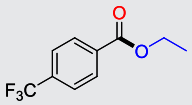
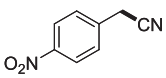
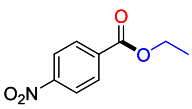
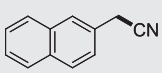
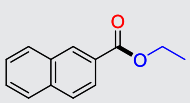
Entry	1		Product	Yield (%)
1		**1a**		**3a**, 85(80)[a]
2		**1b**		**3o**, 72
3		**1c**		**3p**, 71
4		**1d**		**3q**, 80
5		**1e**		**3r**, 78
6		**1f**		**3s**, 79
7		**1g**		**3t**, 77
8		**1h**		**3u**, 76

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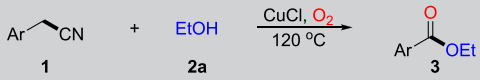
TABLE 3 (Continued)



Entry	1	Product	Yield (%)
9[b]	**1i**		**3v**, 70
10[b]	**1j**		**3w**, 69
11	**1k**		**3x**, n.d.

Note: Reaction conditions: arylacetonitrile **1** (0.2 mmol), ethanol **2a** (1.0 ml), CuCl (100 mol%) based on arylacetonitrile, O_2 (1 atm), 120°C, 24 h, sealed Schlenck tube of 25 ml, and isolated yield.

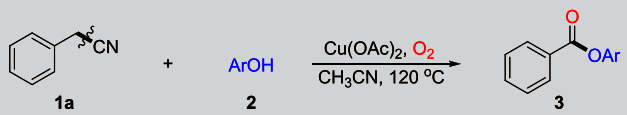
[a]2-mmol scale.

[b]1.0-ml propyl alcohol instead of ethanol.

radical process might be involved in the present reaction. The reaction of benzoic acid **4** with ethanol **2a** did not give **3a** under the standard reaction conditions (Scheme 2, Equation 3). Only a small amount of **3a** (13%) was observed from benzaldehyde **5** and ethanol **2a** under similar conditions (Scheme 2, Equation 4). These results demonstrated that neither benzoic acid nor benzaldehyde was the efficient intermediate for this transformation. In the absence of the catalyst, benzoyl cyanide (**6**) reacted with ethanol to produce **3a** in 45% yield (Scheme 2, Equation 5). Indeed, by the treatment of phenylacetonitrile with 10 mol% $Cu(OAc)_2$ in the absence of ethanol, compound **6** was observed in 38% yield (Scheme 2, Equation 6). These results suggested that benzoyl cyanide was an efficient intermediate for this transformation, and copper salt catalyzed the step of Ritter-type oxidation of benzyl C—H bonds to benzoyl cyanides (Table 1, Entry 19). Expectedly, the addition of a catalytic amount of $Cu(OAc)_2$ (10 mol%) could remarkably improve the reaction efficiency (86% vs. 45% yield). This result suggested that copper salt activated the carbonyl group of benzoyl cyanides and facilitated the addition-elimination of benzoyl cyanides with alcohols.[17] However, the stoichometric copper salt gave a lower yield (61% vs. 86%) of the product, which was probably due to the interaction between the copper salt and the oxygen atom of ethanol, and it decreased the nucleophilicity of ethanol. Similar results (28% and 55% yields of **3y**) were observed by the treatment of benzoyl cyanides with phenol in absence and in the presence of 10 mol% of copper salt, respectively (Scheme 2, Equation 7). In a sharp contrast (vs. 61% yield of **3a**), much more yield (83%) of **3y** was observed in the presence of stoichiometric $Cu(OAc)_2$ (100 mol%). This result suggested that phenolic anion (phenolic copper salt) was produced, which increased the nucleophilicity of phenol and facilitated its addition to benzoyl cyanide.

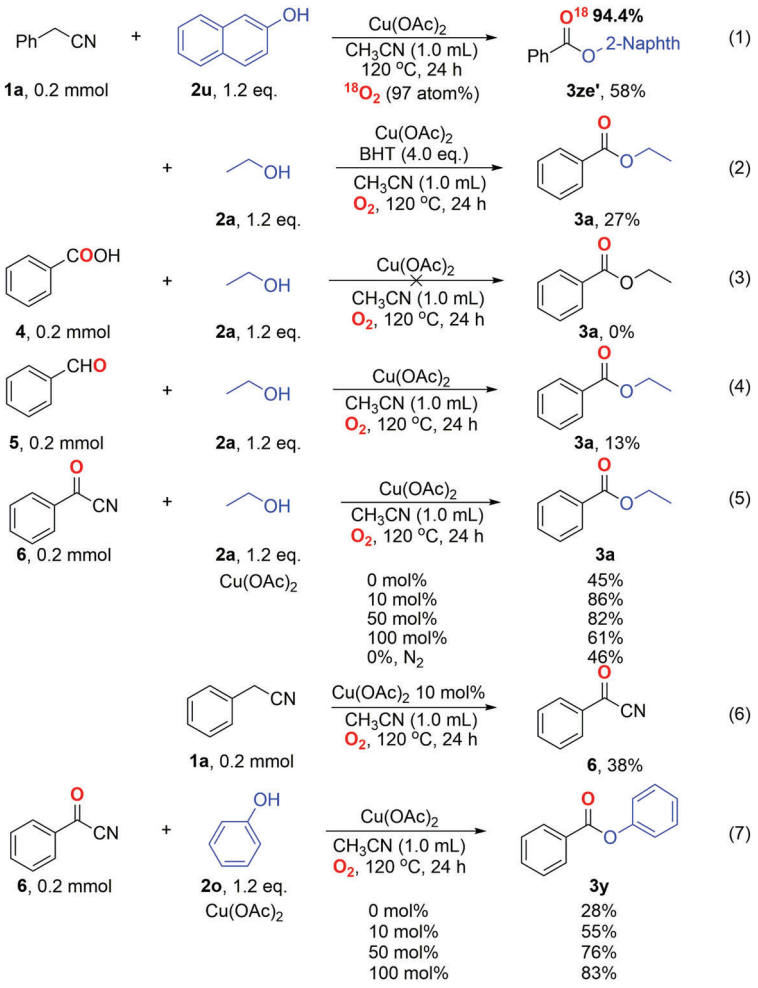
Based on the present results and the previous literature,[12f,16a,17,18] a plausible reaction mechanism is proposed for the copper-catalyzed oxidative synthesis of ester (Scheme 3). Initially, in the presence of Cu/O_2, Ritter-type oxidation (free radical processes) of phenylacetonitrile **1** takes place, giving aryl formyl cyanide **III** via aryl methyl radical **I** and aryl methyl peroxy radical **II**. The interaction between the carbonyl group of **III** and cooper salt forms intermediate **IV**.[17] Then, the nucleophilic attack of the oxygen atom of alcohol/phenol at the carbonyl group of **IV** forms intermediate **V**. Elimination

TABLE 4 Substrate scope of phenols

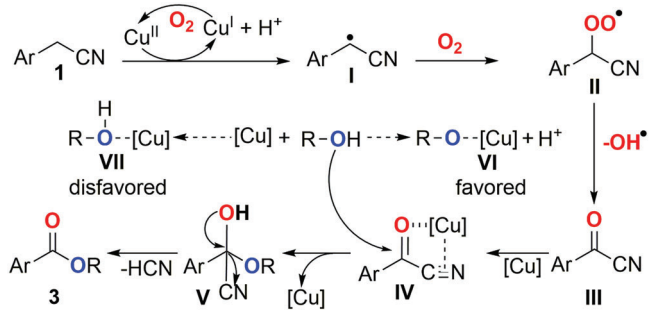


Entry	2	Product	Yield (%)
1	**2o**		**3y**, 77
2	**2p**		**3z**, 71
3	**2q**		**3za**, 70
4	**2r**		**3zb**, 69
5	**2s**		**3zc**, 67
6	**2t**		**3zd**, 68
7	**2u**		**3ze**, 60

Note: Reaction conditions: phenylacetonitrile (**1a**, 0.2 mmol), phenols **2o**–**2r** (0.24 mmol), $Cu(OAc)_2$ (50 mol%) based on **1a**, CH_3CN (1.0 ml), O_2 (1 atm), 120°C, 24 h, sealed Schlenck tube of 25 ml, and isolated yield.



SCHEME 2 Experimental probes of the reaction mechanism



SCHEME 3 Possible reaction mechanism

of cyano group from **V** gives the desired ester **3**. H—Cu exchange between alchohol/phenol and cooper salt that forms intermediate **VI** promotes the reaction, whereas the interaction between the copper salt and the oxygen atom of the substrate that forms intermediate **VII** hinders the reaction.

It is known that alcohols are more nucleophilic than phenols but have lower acidity than phenols. The interaction between the oxygen atom of alcohol with copper salt (**VII**) that decreases the nucleophilicity of alcohol hampers the reaction, whereas the H—Cu exchange between phenol and copper salt (**VI**) that improves the nucleophilicity of phenols facilitates the reaction. Therefore, the lower loadings of the copper salt are used for alcohols, and the higher loadings of copper salt are required for phenols in the reaction.

3 | CONCLUSION

We have successfully developed a simple, direct, and efficient aerobic oxidative functionalization of inert C—C bond for the synthesis of esters from readily available arylacetonitrile derivatives and alcohol/phenols promoted by simple copper salt without any additives. This method successfully realizes C—H bond oxygenation, C—C bond activation, and C—O bond formation in one pot. A variety of alcohols and phenols are suitable substrates for this transformation, providing a wide range of functionalized esters. The copper salt was found to play the multiple roles of the copper, such as catalyzing the Ritter-type oxidation of sp^3C—H bonds of arylacetonitriles, activating the carbonyl groups of aryl

formyl cyanide intermediates, and forming phenolic salts, which enable the high efficiency of the reaction without the assistance of any of the acids, bases, and ligands, which are rarely reported and attractive in copper chemistry.

4 | EXPERIMENTAL

4.1 | General information

The reactions were carried out in Schlenk tubes of 25 ml under the O_2 atmosphere. Reagents were used as received unless otherwise noted, and solvents were purified according to standard operating procedure. Column chromatography was performed using Silica Gel 60 (300–400 mesh). The reactions were monitored by GC and GC–MS, GC–MS results were recorded on GC–MS QP2010, and GC analysis was performed on GC 2014 plus. The ^1H and ^{13}C NMR spectra were recorded on a Brucker ADVANCE III spectrometer at 400 and 101 MHz, respectively, and chemical shifts were reported in parts per million (ppm). All solvents and reagents were purchased from Energy Chemical, Alfa Aesar, and Aladdin.

4.2 | General procedure for the synthesis of esters 3

An oven-dried 25-ml Schlenk tube, equipped with a magnetic stir bar and charged with Cu catalyst, was evacuated and backfilled with O_2 three times. Under an oxygen atmosphere, nitrile **1** (0.2 mmol), alcohol or phenol **2** (0.24 mmol), and CH_3CN (1.0 ml) were added at room temperature. Then, the Schlenck tube was sealed, and the reaction mixture was stirred at 120°C for 24 h. The reaction was monitored by GC or GC–MS. After completion of the reaction, the resulting solution was cooled to room temperature and neutralized with saturated NH_4Cl solution. The product was extracted with EtOAc, dried with anhydrous Na_2SO_4, subject to filtration, and concentrated in vacuo. The residue was purified by column chromatography on silica gel and eluted with petroleum/ethyl acetate to afford the desired product **3**.

4.3 | Preparation of ethyl benzoate 3a at 2-mmol scale

An oven-dried 100-ml Schlenk tube, equipped with a magnetic stir bar and charged with CuCl (2 mmol, 198 mg), was evacuated and backfilled with O_2 three times. Under oxygen atmosphere, arylacetonitrile **1a** (2.0 mmol, 234 mg) and alcohol **2a** (10 ml) was added at room temperature. Then, the Schlenk tube was sealed, and the reaction mixture was stirred at 120°C for 24 h. After completion of the reaction, the resulting solution was cooled to room temperature and neutralized with saturated NH_4Cl solution. The product was extracted with EtOAc, dried with anhydrous Na_2SO_4, subject to filtration, and concentrated in vacuo. The residue was purified by column chromatography on silica gel and eluted with petroleum ether to afford the desired colorless oil product ethyl benzoate **3a** (240 mg, 80%).

ACKNOWLEDGMENTS

Financial support from the National Natural Science Foundation of China (Grant Nos. 21706058, 21878072, and 21573065), the Hunan Provincial Natural Science Foundation of China (Grant No. 2020JJ2011), and the Research Foundation of Education Bureau of Hunan Province (16B054) is much appreciated. We also thank Prof. Shuanglin Qu (Hunan University) for his kind help.

AUTHOR CONTRIBUTIONS

Jianyu Dong: Conceptualization; data curation; formal analysis; funding acquisition; methodology; project administration; resources; supervision. **Xiuling Chen:** Data curation; formal analysis; methodology. **Fangyan Ji:** Data curation; formal analysis; methodology. **Lixin Liu:** Data curation; methodology. **Lebin Su:** Data curation; methodology. **Min Mo:** Data curation; formal analysis; funding acquisition. **Jian-Sheng Tang:** Formal analysis; methodology. **Yongbo Zhou:** Data curation; formal analysis; funding acquisition; investigation; project administration; resources; supervision.

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Dong J, Chen X, Ji F, et al. Copper-mediated simple and direct aerobic oxidative esterification of arylacetonitriles with alcohols/phenols. *Appl Organomet Chem*. 2020; e6073. https://doi.org/10.1002/aoc.6073