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Copper-catalysed *ortho*-selective C–H bond functionalization of phenols and naphthols with α-aryl-α-diazoesters†

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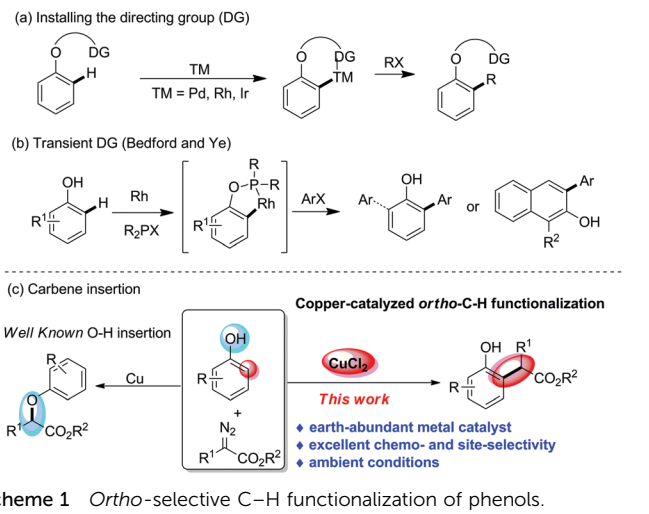
Herein, we reported the first copper-catalyzed highly efficient C(sp^2)–H functionalization of unprotected naphthols and phenols with α-aryl-α-diazoesters. In this transformation, $CuCl_2$ efficiently promoted the highly chemo- and site-selective C–H bond functionalization under mild conditions, furnishing diverse phenol derivatives in moderate to excellent yields from readily available starting materials.

Phenol and naphthol motifs are prevalent in natural products, dyes, medicines, bioactive compounds, functional materials, and privileged chiral ligands, and they also represent the most readily available chemical feedstocks and versatile building blocks for diverse transformations in chemical science.[1] Thus, the development of straightforward strategies to synthesize phenol derivatives *via* the direct site-selective C–H bond functionalization of free phenols is highly attractive to the synthetic community. However, chemo- and site-selective C–H functionalization of unprotected phenols poses considerable challenges, because there are four possible reaction sites, including the chemoselectivity of oxygen or carbon and the site-selectivity of the *ortho*-, *meta*- or *para*-position.[2]

In the past decade, with the advance of transition-metal-catalysed directed C–H bond functionalization,[3] many strategies have been developed to achieve *ortho*-selective functionalization of phenols. In this regard, a directing-group-assisted approach, which requires directing groups to be installed on the oxygen atom to ensure *ortho* selectivity, as well as to protect the hydroxyl group, has emerged as one of the most efficient and popular solutions to address the *ortho*-selectivity problem (Scheme 1a).[4] However, this extra operation of installing and removing such directing groups limits the utilization of this approach in organic synthesis. Recently, Bedford and Ye *et al.* realized an alternative way for direct *ortho*-selective C–H bond arylation of phenols and naphthols by using P-containing ligands R_2PX as transient directing groups (Scheme 1b).[5] Unfortunately, this strategy is still limited to a few examples.

Recently, the catalytic carbene transfer reaction, typically using diazo compounds,[6] has emerged as one of the most powerful strategies for aromatic C(sp^2)–H bond functionalization.[7] Nonetheless, most of the commonly used catalysts are based on noble metals, including rhodium, gold, palladium and iridium, which are becoming more and more expensive and scarce because they are derived from dwindling resources.[8] The development of effective and abundant catalysts to replace the rare and toxic transition metals is a long-term need. Copper, which is an earth abundant, readily available, inexpensive, environmentally benign, and less toxic metal, represents an ideal catalyst in organic synthesis.[9] Although Cu-catalysed carbene transfer reactions have



Scheme 1 *Ortho*-selective C–H functionalization of phenols.

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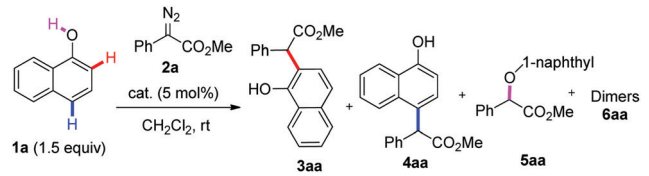
been in use for over half a century, compared with the well-established O–H bond insertion of phenols with copper–carbene,[10] the analogous C(sp^2)–H bond functionalization is still unknown.[11] Very recently, Nemoto and we have reported the *ortho*-C–H functionalization of naphthols and phenols with diazoesters.[12] However, these methods require the use of expensive catalysts, gold complexes or $B(C_6F_5)_3$. In addition, gold catalysts[12b,c] were suitable for naphthols, but were not compatible with phenols, and $B(C_6F_5)_3$[12a] showed the opposite trend. A general approach to achieve *ortho*-alkylation of both phenols and naphthols has not been developed so far. Herein, we reported the unprecedented $CuCl_2$-catalysed highly chemo- and ortho-selective C–H bond functionalization of phenols and naphthols with diazoesters (Scheme 1c).

Initially, we performed the reaction of 1-naphthol **1a** with α-phenyl-α-diazoacetate **2a** in the presence of 5 mol% $Cu(ClO_4)_2\cdot 6H_2O$ in DCM at room temperature. To our delight, the desired *ortho*-C–H functionalization products, including **3aa** and the corresponding lactone **11** from **3aa**, were obtained in 60% yield with 30 : 1 C–H/O–H selectivity and regio-specific *ortho*-selectivity (Table 1, entry 1). Encouraged by this result, various copper salts were then screened, and finally $CuCl_2$ was observed to be the best catalyst, affording the *ortho*-selective C–H bond alkylation product in 85% yield with excellent chemo- and site-selectivity after 6 h at room temperature (Table 1, entries 2–7). Solvent screening showed that DCE, toluene and THF could not improve the yield (Table 1, entries 10–12).

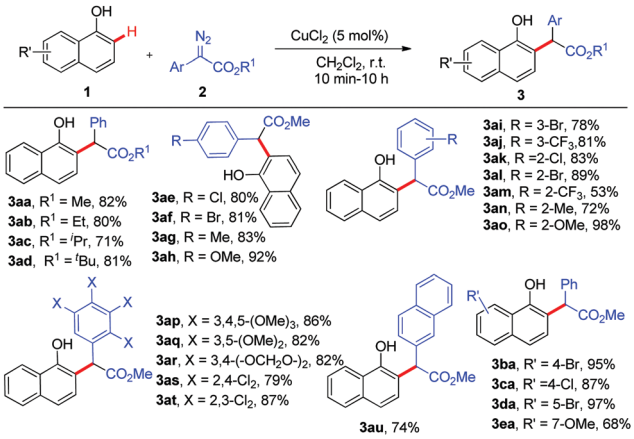
Next, the scope of the copper-catalysed *ortho*-selective C–H functionalization of 1-naphthol with various α-aryl-α-diazoacetates was explored using $CuCl_2$ (5 mol%) in DCM at room temperature. As shown in Scheme 2, this reaction proved to be applicable to a wide range of α-aryl-α-diazoacetates and the desired 2-alkylated

Table 1 Optimization of reaction conditions[a]



Entry	Cat. (5 mol%)	Yield[a] (%) 3/4/5/6
1	$Cu(ClO_4)_2\cdot 6H_2O$	60 (12)[b]/0/2/38
2	$Cu(CH_3CN)_4PF_6$	60 (18)[b]/0/2/38
3	CuOAc	68 (10)[b]/0/1/31
4	CuOTf	54 (24)[b]/0/0/46
5	CuCl	72(4)[b]/0/0/22
6	**$CuCl_2$**	**85 (2)[b]/0/2/3**
7	CuF_2	70(12)[b]/0/2/24
8[c]	$CuCl_2$	76 (2)[b]/0/5/5
9[d]	$CuCl_2$	53/0/3/35
10[e]	$CuCl_2$	25/0/5/31

Reaction conditions: a solution of **2a** (0.4 mmol) in 1 mL of solvent was introduced into **1a** (0.6 mmol) and the catalyst (5 mol%) in solvent (1 mL) at room temperature *via* a syringe over a period of 15 min. [a] NMR yield. [b] The corresponding lactone **11** from **3aa** was detected. [c] DCE instead of DCM. [d] Toluene instead of DCM. [e] THF instead of DCM.

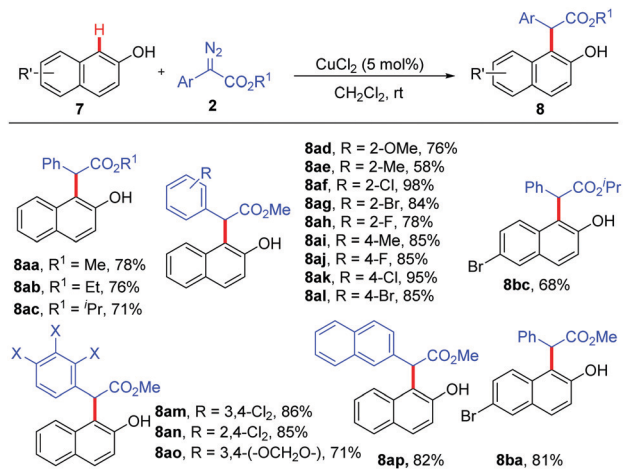


Scheme 2 *Ortho* C–H bond functionalization of 1-naphthols.

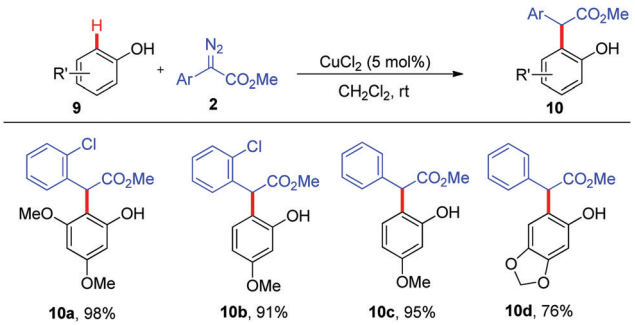
1-naphthols were obtained in good to excellent yields with excellent chemo- and site-selectivity. The steric hindrance of the ester group had no effect on this reaction (**3ab–3ad**). Various commonly encountered functional groups such as chloro, bromo, methyl, methoxyl, and CF_3 at various positions of the phenyl rings of α-aryl-α-diazoacetates were well tolerated (**3ae–3at**). Strong electron-donating groups (OMe) could facilitate this reaction (**3ah** and **3ao**), while strong electron-withdrawing groups (CF_3) would slow down this reaction (**3am**). Furthermore, several substituted 1-naphthols **1b–1e** were tested in this transformation, delivering the corresponding *ortho*-selective C–H functionalization products **3ba–3ea** in moderate to excellent yields (68% to 97%). It must be noted that all the reactions exhibited 100% *ortho*-selectivity.

Subsequently, we investigated the substrate scope of the $CuCl_2$-catalyzed *ortho*-selective C–H bond functionalization of 2-naphthols. All the reactions of 2-naphthols **7** with various diazoacetates **2** proceeded smoothly under standard conditions, affording the corresponding *ortho*-selective products in 58% to 98% yields with excellent chemo- and site-selectivity (Scheme 3).

Furthermore, we wondered whether phenols were applicable to this copper-catalysed *ortho*-C–H functionalization, which was



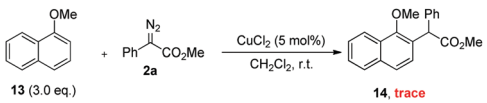
Scheme 3 *Ortho* C–H bond functionalization of 2-naphthols.



Scheme 4 *Ortho* C–H bond functionalization of phenols.

more challenging because the nucleophilicity of phenols was much lower than that of naphthols. Indeed, all attempts to realize the *ortho*-C–H alkylation of unsubstituted phenol failed. To our delight, $CuCl_2$ could enable the *ortho*-C–H bond functionalization of alkoxyl-substituted phenols **9** with α-aryl-α-diazoacetates **2** to give the corresponding products **10a–10d** in good to excellent yields with excellent site-selectivity (Scheme 4).

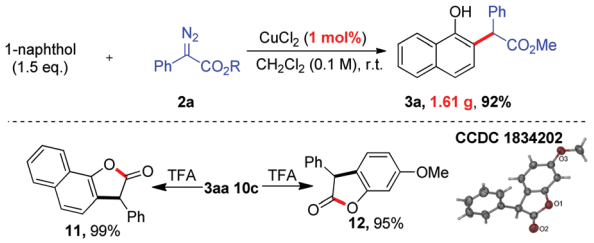
To demonstrate the practicality of this transformation, a gram-scale reaction was carried out (Scheme 5). To our delight, the *ortho*-selective alkylation was easy to scale up to a gram-scale with only 1 mol% catalyst loading, affording the desired product **3aa** (1.61 g, 92%). To demonstrate the utility of this method further, transformations of the products were also performed. As shown in Scheme 5, TFA-catalyzed lactonization of **3aa** and **10c** could afford the corresponding cyclized products **11** and **12** in 99% and 95% yields, respectively. The structure of **12** was further confirmed by single-crystal X-ray analysis.[13]



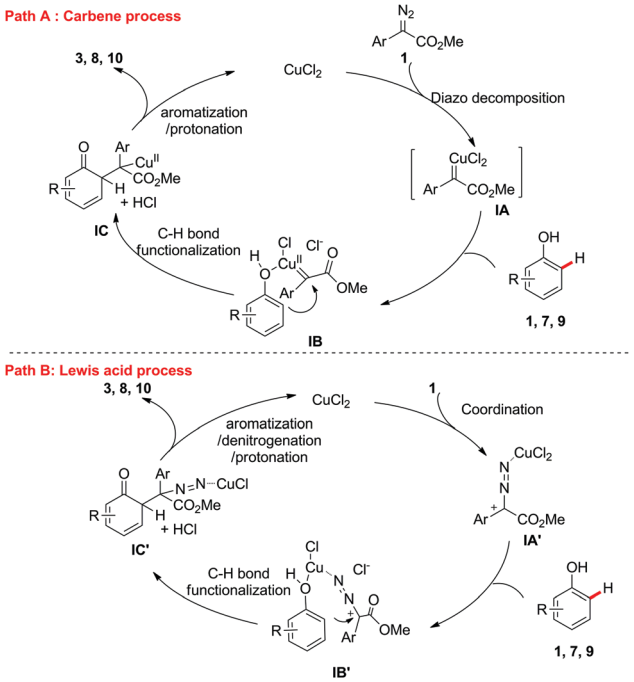
(1)

To further gain mechanistic insight into this copper-catalysed *ortho*-C–H alkylation of phenols, 1-methoxynaphthalene **13** was reacted with diazoester **2a** in the presence of $CuCl_2$, which only delivered a trace amount of *ortho*-selective C–H bond functionalization products (eqn (1)). This result indicated that the hydroxyl group was vital not only for site-selectivity but also for reactivity, and the interaction between the hydroxyl group and the copper catalyst could give rise to the *ortho*-selectivity.

Based on the aforementioned results, two possible catalytic cycles accounting for this transformation are depicted in Scheme 6. Path A is the Cu-carbene process. The Cu(II)-carbene intermediate **IA** was formed from α-aryl-α-diazoesters **2** with $CuCl_2$,[14] which results in the formation of intermediate **IB** *via* coordination. The electrophilic addition of copper-carbene at the *ortho*-position of the phenols generated **IC**, which then underwent aromatization and protonation to produce the target *ortho*-C–H bond functionalization products **3**, **8** or **10** and regenerate the copper catalyst. In path B, $CuCl_2$ serves as a Lewis acid to coordinate the nitrogen of α-aryl-α-diazoesters **2** to form the carbocation intermediate **IA′**, which would further



Scheme 5 Gram-scale reactions and transformations of products.



Scheme 6 Proposed catalytic cycle.

coordinate the oxygen of the phenols to generate **IB′**. The following electrophilic addition of the copper-carbocation at the *ortho*-position of the phenols generated **IC′**, which then underwent aromatization, denitrogenation and protonation to produce the target *ortho*-C–H bond functionalization products and regenerate the copper catalyst. Further mechanistic studies indicated that these two processes occurred in this reaction.[15]

To conclude, we have described the first example of a $CuCl_2$-catalyzed direct C–H functionalization of unprotected phenols and naphthols with α-aryl-α-diazoacetates under mild conditions, leading to diverse phenol derivatives with convertible functional groups. This work broadens the application scope of copper catalysts in carbene transfer reactions. The salient features of this reaction include an inexpensive catalyst, readily available starting materials, unprecedented C–H functionalization rather than O–H insertion, a good substrate scope, mild conditions, and diverse convenient transformations of the products. Further studies on the mechanism and the application of this protocol in organic synthesis are currently underway in our laboratory.

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Conflicts of interest

There are no conflicts to declare.

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15 According to the reviewer's suggestion, we did several control experiments to understand the mechanism. Because of the page limitation, all the details were in the ESI.† We thank the reviewer for his/her helpful suggestion.

