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Highly Site-Selective Direct C−H Bond Functionalization of Phenols with α-Aryl-α-diazoacetates and Diazooxindoles via Gold Catalysis

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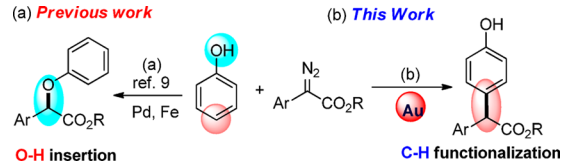
Supporting Information

ABSTRACT: An unprecedented direct C−H bond functionalization of unprotected phenols with α-aryl α-diazoacetates and diazooxindoles was developed. A tris(2,4-di-*tert*-butylphenyl) phosphite derived gold complex promoted the highly chemoselective and site-selective C−H bond functionalization of phenols and *N*-acylanilines with gold-carbene generated from the decomposition of diazo compounds, furnishing the corresponding products in moderate to excellent yields at rt. The salient features of this reaction include readily available starting materials, unprecedented C−H functionalization rather than X−H insertion, good substrate scope, mild conditions, high efficiency, and ease in further transformation. To the best of our knowledge, this is the first example of C−H functionalization of unprotected phenols with diazo compounds.

Phenols motifs are widely found in natural products and pharmaceutics as well as common versatile synthons in organic synthesis due to their wide availability and low price.[1] Thus, developing site-selective C−H functionalization of phenols is highly attractive to the synthetic community. In the past decade, many indirect methodologies have been developed via installing the directing group on the hydroxyl to realize *ortho*/*meta*/*para* functionalization of phenols.[2] Maximizing synthetic efficiency to utilize as much as possible the atoms of reactants is a very important but challenging task in organic chemistry.[3] Therefore, the development of a novel approach to site-selective direct C−H functionalization of unprotected phenols would be highly desirable. Ideally, such a strategy requires finishing in one conveniently operational step and being scalable. In addition, mild conditions and a low catalyst loading are also important. Recently, Bedford et al. realized direct *ortho* C−H arylation of phenols using a catalytic amount of phosphites as traceless directing groups.[4] Additional ground-breaking work by Larrosa et al. includes direct *meta* C−H arylation of unprotected phenols using CO_2 as a traceless relay directing group.[5]

Yet, one of the most effective methods for aromatic C−H functionalization is the carbene transfer reaction of diazo compounds in the presence of transition-metal complexes, with, e.g., rhodium, copper, silver, palladium, etc.[6] Yu,[7a] Rovis,[7b] Péres and co-workers[8] have made significant contributions to the transition-metal-catalyzed direct C−H functionalization of aromatic compounds involving diazo compounds. However, the direct C−H functionalization of phenols with diazo compounds is highly challenging because of the competitive chemoselective O−H bond insertion in the presence of various transition-metal catalysts including Rh, Cu, Ru, Fe, and Pd (Scheme 1a).[9] It should be noted that Fu[9n] and Zhou[9o,p] have

Scheme 1. Selective Transformations of Phenol with Diazo Compounds



reported the elegant catalytic asymmetric O−H bond insertion of phenol with methyl α-aryl α-diazoacetates by the application of chiral transition metal complexes. Despite the fact that gold complexes have received a marked increase in interest in organic synthesis because of the specific carbophilic π-acidic and catalytic activities,[10] the application of gold catalysts to the carbene transfer reaction has been less explored.[8,11] Herein, we wish to present the first example of a gold-catalyzed intermolecular[12] highly site-selective direct C−H bond functionalization of phenols and *N*-acylanilines with α-aryl α-diazoacetates under mild conditions (Scheme 1b). This strategy provides a facile access to diarylacetates, which are important motifs in natural products, bioactive and pharmaceutic molecules, and functional materials (Figure 1).[13]

The initial experiment was performed with methyl α-phenyl-α-diazoacetate **1a** and phenol **2a** in the presence of Ph_3PAuCl (5 mol %) and $AgSbF_6$ (5 mol %) in dichloromethane (DCM) at rt. We were pleased to find that the desired *para* C−H bond

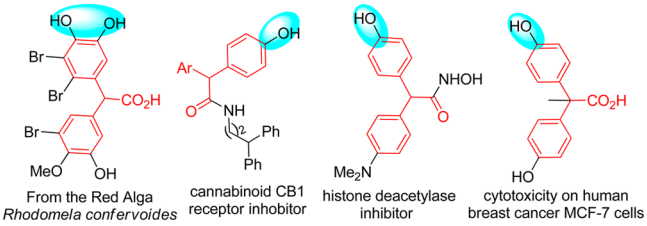


Figure 1. Diarylacetate subunit in natural products and bioactive molecules.

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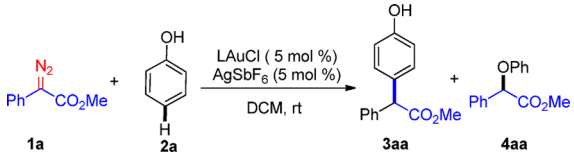
functionalization product **3aa** could be isolated with a promising 33% yield as a single regioisomer, albeit the O−H insertion product **4aa** was still isolated as the major product in 46% yield (Table 1, entry 1). Then various types of ligands were screened.

Table 1. Screening Ligands[a]



1a 2a 3aa 4aa

entry	ligand (L)	yield[b] (%) **3aa**	yield[b] (%) **4aa**
1	Ph_3P	(32)	(46)
2	(2-biphenyl)Cy_2P	39	49
3	$(EtO)_3P$	47	27
4	$(PhO)_3P$	82	0
5	$(2,4\text{-}^tBu_2C_6H_3O)_3P$	100 (99)	0

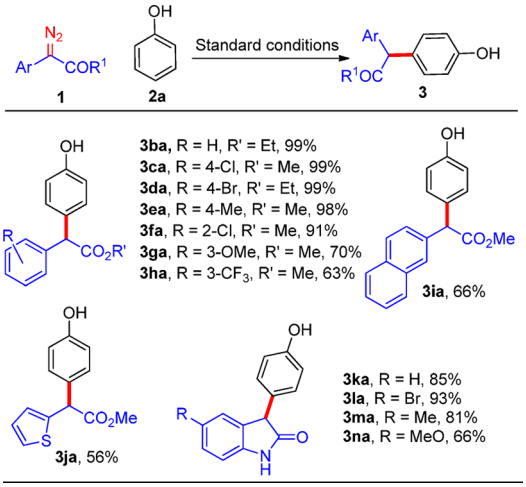
[a]The reaction was carried out with **1a** (0.4 mmol), **2a** (0.6 mmol), catalyst (5 mol %) in solvent (4 mL) at room temperature. The solution of **1a** in 1 mL of CH_2Cl_2 was introduced into the reaction mixture by a syringe in 5 min and then being stirred for another 1 min. [b]NMR yield. The numbers in parentheses are isolated yields.

A slightly better result was obtained by adding more electron-rich phosphine ligand [1,1′-biphenyl]-2-yldicyclohexylphosphine ((2-biphenyl)Cy_2P) (Table 1, entry 2). The yield of product **3aa** was improved to 47% with 27% **4aa** by the use of triethyl phosphite as the ligand (Table 1, entry 3). Gratifyingly, a triphenyl phosphite derived gold complex could give the *para* C−H functionalization product **3aa** in 82% yield (Table 1, entry 4). Tris(2,4-di-*tert*-butylphenyl) phosphite was then identified to be optimal in terms of reactivity and selectivity, furnishing **3aa** in 99% isolated yield, and no any **4aa** and *ortho* and *meta* C−H functionalization product was detectable (Table 1, entry 5, standard conditions). Other gold catalysts, silver salts, and solvents gave poorer results, and control experiments showed that silver salt acts as the halide scavenger rather than a cocatalyst (for more details, see Table S1, Supporting Information).

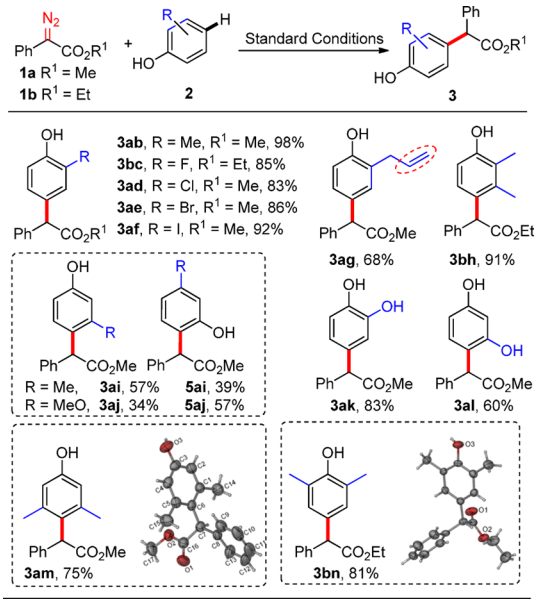
With the optimal reaction conditions in hands, we next investigated the scope of this gold-catalyzed highly site-selective C−H bond functionalization of phenol **2a** by variation of the component diazo compounds **1**. The results are summarized in Scheme 2. The substituent on the ester group of **1** has no effect on the yield and selectivity of the reaction. Those α-aryl α-diazoacetates with both electron-donating and -withdrawing substituents on the phenyl ring (**1c**−**1f**) reacted smoothly with phenol to give the desired products **3ca**−**3fa** in moderate to excellent yields (63−99%, Scheme 2). The α-naphth-2-yl α-diazoacetate **1i** and α-thien-2-yl α-diazoacetate **1j** also worked, leading to the corresponding products **3ia** and **3ja** in 66% and 56% yields, respectively. Besides α-aryl α-diazoacetates, diazooxindoles **1l**−**o** are applicable to the present transformation, highly selectively furnishing the *para* C−H bond functionalization products **3la**−**3oa** in good to excellent yields (66−93%; Scheme 2). This transformation provided an alternative strategy to synthesize 3-aryl oxoindoles with a free hydroxyl group.[14] It is noteworthy that all these reactions are site-specific and chemospecific, leading to the *para* C−H bond functionalization products as the sole product.

The reactions of various substituted phenols **2b**−**2n** with α-diazoacetates **1a**−**b** were then examined. As shown in Scheme 3, the reactions proceeded smoothly, affording moderate to

Scheme 2. Scope of Diazo Compounds



Scheme 3. Scope of Substituted Phenols



excellent yields of the corresponding C−H functionalization products **3ab**−**3bn** in a chemo- and regioselective manner. It should be noted that the reaction of the phenol equipped with an *ortho*-allyl substituent gave the *para* C−H bond functionalization product **3ag** without formation of any product via cyclopropanation[11a−g,15] or O−H insertion, indicating that this gold catalyst prefers to promote the C−H bond functionalization rather than the cyclopropanation of an alkene and the O−H insertion. When *meta*-methylphenols **2i** and *meta*-methoxyphenol **2j** were employed, *ortho* C−H functionalization products **5ai** and **5aj** could be also isolated along with the *para* C−H functionalization products **3ai** and **3aj**, indicating that the methyl and methyoxy groups could also act as the directing groups. It is noteworthy that the reaction 3,5-dimethylphenol **2m** bearing a sterically hindered *para* C−H bond still gave the corresponding *para* C−H functionalization product **3am** rather than the less hindered O−H insertion product, showing that the *para* C−H functionalization is favored under the reaction conditions. The structures of **3am** and **3bn** were confirmed by single-crystal X-ray crystallography.[16]

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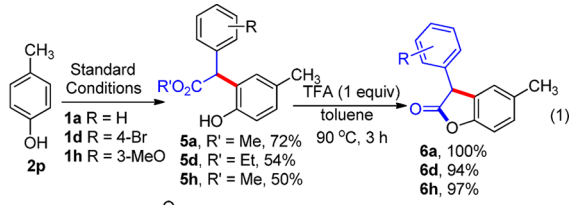
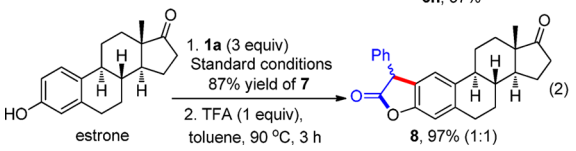
Furthermore, we became interested in the outcome (O−H insertion or *ortho* C−H functionalization) when the *para*-substituted phenols were employed. To our delight, the reaction of **1a** and *para*-mehyl phenol **2p** produced the *ortho* C−H bond functionalization products **5a** in 72% yield. Aryl benzofuranone **6a**, a prominent structural motif in natural products (eq 1),[17]



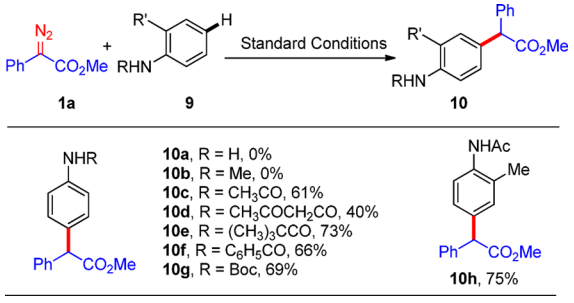


could be efficiently prepared from **5a** by TFA-mediated lactonization. Similarly, **5d**, **5h**, and benzofuranones **6d** and **6h** could be efficiently synthesized following the same procedure; the relatively lower yield of **5d** and **5h** resulted from the competitive dimerization of the diazo compounds under the standard conditions. The present procedure might be applicable to *late-stage modification* of natural products or pharmaceutical compounds because of its operational convenience and mild reaction conditions.[18] To demonstrate this potential application, estrone was subjected to the optimized conditions. To our delight, the catalytic *ortho* C−H functionalization took place smoothly to afford **7** in 87% yield, which could undergo a similar lactonization to give **8** in 97% yield (eq 2).

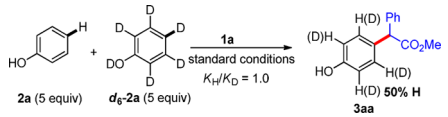
We then wondered whether aniline derivatives are applicable to the present highly site-selective C−H functionalization, which is also a challenging issue due to the competitive N−H bond insertion under the metal catalysis.[19] When aniline **9a** and *N*-methyl aniline **9b** were subjected to the reaction under standard conditions, no reaction occurred. We envisaged that the basic aniline may inhibit the reactivity of the gold complex via coordination. Indeed, the reactions proceeded smoothly, when the basic amine group of aniline was protected by acyl groups such as acetyl, benzoyl, Boc, etc., furnishing the corresponding *para* C−H functionalization products **10c**−**10g** in moderate to good yields (Scheme 4). The *ortho*-methyl on *N*-acetanilide could slightly improve the yield (**10h**).

Although a precise reaction mechanism of the gold-catalyzed C−H functionalization reaction is unclear, a preliminary mechanistic study showed that the reaction does not exhibit a kinetic isotope effect (Scheme 5), thus, indicating that the

Scheme 4. *para* C−H Bond Functionalization of Anilines

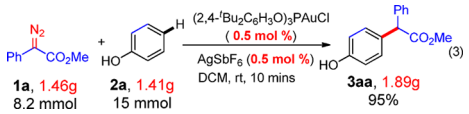


Scheme 5. Kinetic Isotope Effect



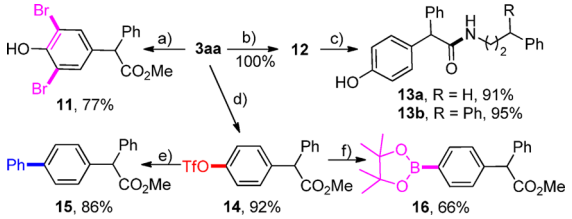
breaking of the C−H bond on phenol was not involved in the rate-determining step. This result may support that the reaction proceeds via electrophilic addition of the gold-carbene followed by rapid 1,2-hydride migration.[8,20]

It should be noted that this gold-catalyzed site-selective C−H functionalization of phenols is easy to scale-up. A gram-scale reaction of 1.46 g of **1a** and 1.41 g of **2a** was carried out with a much lower catalyst loading (0.5 mol %), furnishing 1.89 g of the desired product **3aa** in 95% isolated yield (eq 3).



Most importantly, these products could be viewed as versatile precursors to synthetic useful building blocks and bioactive compounds (Scheme 6). For example, the bromination of **3aa** led

Scheme 6. Synthetic Applications of 3aa



to product **11** in 77% yield.[13c] Cannabinoid CB1 receptors **13a** and **13b** could be efficient prepared from **3aa** via successive hydrolysis and amidation.[13b] In addition, the hydroxyl is another versatile group for further transformation. For example, triflate **14** could be easily prepared in 92% yield, which upon metal-catalyzed coupling reactions furnished compound **15** and useful arylboron **16** in 86% and 66% yields, respectively.

In summary, we have described the first example of gold-catalyzed direct C−H functionalization of unprotected phenols and *N*-acyl anilines with α-aryl α-diazoacetates and diazooxindoles under mild conditions, leading to synthetic useful diarylacetates with convertible functional groups. This work would broaden the application of gold catalysts in carbene transfer reactions. The salient features of this reaction include readily available starting materials, unprecedented C−H functionalization rather than X−H insertion and cyclopropanation, good substrate scope, mild conditions, and diverse convenient transformations of the products.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

[†]Z.Y. and B.M. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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