



Cite this: *Chem. Sci.*, 2019, 10, 6553

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 4th April 2019
Accepted 25th May 2019

DOI: 10.1039/c9sc01657k

rsc.li/chemical-science

Ligand and counteranion enabled regiodivergent C–H bond functionalization of naphthols with α -aryl- α -diazoesters†

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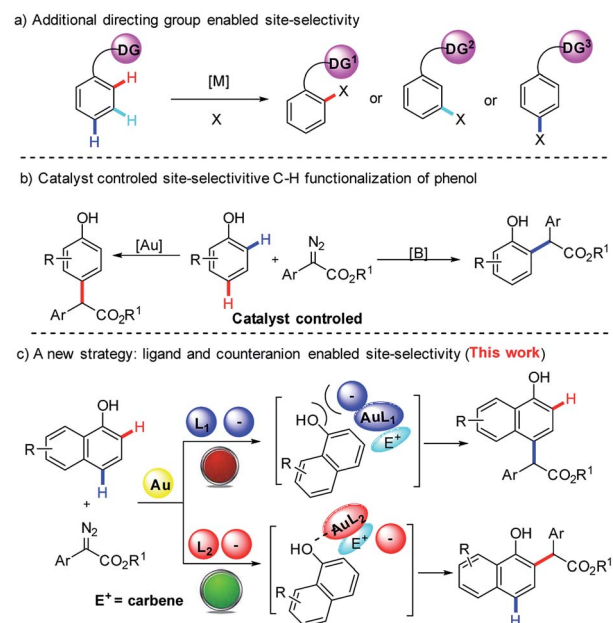
Here, an unprecedented ligand and counteranion-controlled and site-selectivity switchable direct C–H bond functionalization of unprotected naphthols with α -aryl- α -diazoesters was developed. In this transformation, site selectivities are realized by turning on/off the coordination between metal complexes and hydroxy groups. The preliminary mechanism revealed that the interaction between the hydroxy group and gold catalyst plays a key role in switching the site-selectivity of gold-carbene. This protocol potentially provides a novel design for C–H bond functionalization.

Compared to traditional convergent synthesis, divergent synthesis can generate molecule libraries with a high level of structural diversity in an efficient manner, which is of great importance in modern organic synthesis and drug discovery.¹ Although recent years have witnessed significant achievements in this field,² the development of a new strategy to achieve divergent synthesis with high chemo- and site-selectivity is still highly desirable.

Recently, site-selective C(sp²)-H bond functionalization of aromatic rings has emerged as one of the most effective and powerful methods to construct C–C bonds in organic synthesis. One useful and popular strategy to ensure high selectivity entails the use of a coordinating directing group (DG) on arenes (Scheme 1a).^{3–5} This chelation-assisted approach has been significantly exploited successfully for *ortho* C(sp²)-H bond functionalization,³ in some cases for *meta* selectivity,⁴ and in few cases for *para* selectivity⁵ (Scheme 1a). However, the site-selectivity of C–H bond functionalization is normally dependent on the length and structure of the DG, which limit the utilization of this approach in organic synthesis. The development of controllable site-divergent C–H bond functionalization without the installation of an additional DG is urgent and challenging.⁶

Naphthols and their derivatives are widely found in natural products, dyes, pharmaceuticals, bioactive compounds, materials, privileged ligands and so on (Fig. 1).⁷ Besides, they also

represent one class of ideal and versatile starting materials and building blocks in organic synthesis. Thus, the development of straightforward access to naphthol derivatives *via* site-selective C(sp²)-H bond functionalization of naphthols is highly attractive to the synthetic community. Recently, Shi⁸ and our group^{9a} independently developed gold-catalyzed highly site-selective *para* C(sp²)-H bond functionalization of phenols with α -aryl- α -diazoesters. Later on, our group also realized the more challenging highly selective *ortho* C(sp²)-H bond functionalization of phenols on catalysis by (C₆F₅)₃B (Scheme 1b).^{9b} As an ongoing interest in C(sp²)-H bond functionalization,⁹ we wanted to



Scheme 1 Different strategies to site-selective C(sp²)-H bond functionalization.

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† Electronic supplementary information (ESI) available: Data for new compounds, experimental procedures and theoretical studies on mechanisms. CCDC 1822536–1822538, 1884847. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9sc01657k



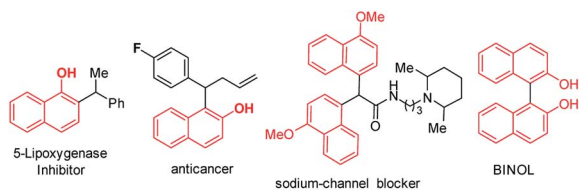
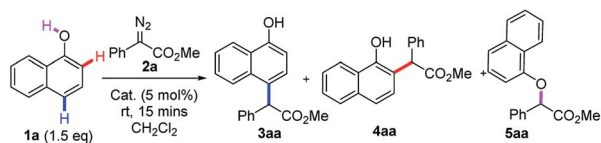


Fig. 1 Naphthol derivatives in bioactive molecules and ligands.

achieve direct and site-divergent C(sp²)-H bond functionalization of 1-naphthol *via* diazo compounds.^{10,11} However, our target is a very challenging issue. First, the free naphthol hydroxyl group is very reactive towards diazo compounds, typically resulting in O-H functionalization rather than C-H functionalization. To date, only the O-H insertion reactions of naphthols with diazo compounds have been reported.¹² Second, the functionalization of *ortho* C-H bonds is more difficult than that of the *para* position due to similar nucleophilicity but more steric hindrance at the *ortho* position.¹³ Third, 1-naphthol is more reactive toward electrophiles than phenol,¹⁴ thus the control of the site-selectivity easily becomes more challenging. Indeed, we found that the reaction of 1-naphthol **1a** and phenyl diazoester **2a** gave a mixture of products with low site-selectivity on catalysis by a gold/phosphite catalyst and a low yield of *ortho*-substituted products in the presence of (C₆F₅)₃B, respectively (Scheme 2). These results indicated that exploring an alternative strategy was highly necessary.

Recently, Yamaguchi¹⁵ and Yi¹⁶ reported *ortho* C-H bond alkylation and alkylation *via* the coordination between the hydroxyl group and metal. Inspired by their nice findings, we envisioned that *ortho*-selectivity might be observed when the catalyst can turn on the coordination between the directing group and metal. In contrast, the *para*-substituted product becomes dominant if the catalyst can turn off the coordination between the directing group and metal, and meanwhile prevent the intermolecular electrophilic attack of carbene (Scheme 1c).

We envisioned that a bulky ligand might stop the coordination between gold complexes^{17,18} and hydroxyl groups and thus favor *para*-selective C-H bond functionalization. But unfortunately, the use of bulky X-phos and ^tBuXPhos derived gold complexes still delivered a similar selectivity to the tris(2,4-di-*tert*-butylphenyl)phosphite/gold complex (Table 1, entries 1 and 2). These results indicate that increasing only the steric hindrance at the phosphorus center of the phosphine ligand is not enough to suppress the coordination between gold and 1-naphthol because of the linear coordination geometry of the



Conditions and results

- 1) (2,4-^tBu₂C₆H₃O)₃PAuSbF₆, **3aa** (43% NMR yield), **4aa** (15% NMR yield), **5aa** (0%)
- 2) (C₆F₅)₃B, **3aa** (0% NMR yield), **4aa** (24% NMR yield), **5aa** (0%)

Scheme 2 Initial studies under our previous conditions.

Table 1 Variation of reaction parameters

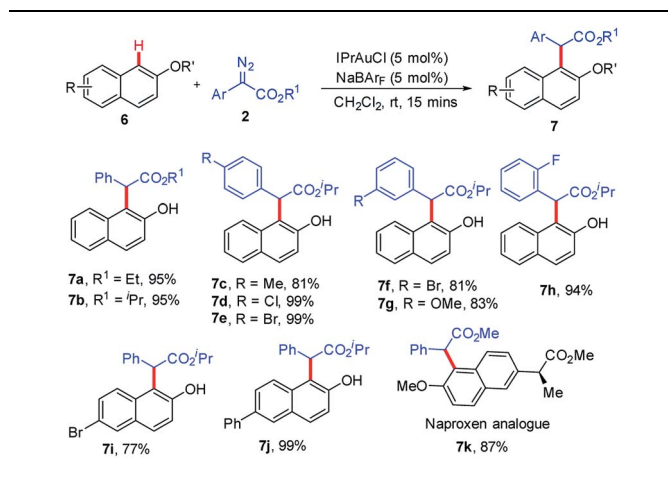
Entry	R (2)	Cat. (5 mol%)	Yield ^a (%)	
			3/4/5	
1	Me (2a)	X-PhosAuCl/AgSbF ₆	50/31/0	
2	Me (2a)	^t BuXPhosAuCl/AgSbF ₆	49/27/0	
3	Me (2a)	JohnphosAuCl/AgOTf	70/0/0	
4 ^b	Me (2a)	JohnphosAuCl/AgOTf	90(87)/0	
5	Me (2a)	JohnphosAuCl/NaBAR _F	26/54	
6	Me (2a)	IPrAuCl/NaBAR _F	13/90(82)/0	
7	Et (2b)	IPrAuCl/NaBAR _F	8/(87)/0	
8	ⁱ Pr (2c)	IPrAuCl/NaBAR _F	4/(91)/0	
9	^t Bu (2d)	IPrAuCl/NaBAR _F	3/(90)/0	

^a NMR yield, the number in parentheses is the isolated yield. ^b THF as the solvent. XPhos = 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl; ^tBuXPhos = 2-di-*t*-butylphosphino-2',4',6'-triisopropyl-1,1'-biphenyl; Johnphos = 2-(di-*tert*-butylphosphino)biphenyl; and IPr = 1,3-bis(2,6-di-isopropyl-phenyl)imidazol-2-ylidene. NaBAR_F = sodium tetrakis[3,5-bis(trifluoro methyl)phenyl]borate.

gold complex.¹⁹ In 2013, an elegant study of the Echavarren group disclosed that congested chloride-bridged digold complexes were formed when JohnphosAuCl was treated with AgOTf.²⁰ Inspired by this result, we conceived that this complex was an ideal catalyst for *para*-selectivity. Indeed, we did obtain exclusively *para*-substituted products in 70% NMR yield (Table 1, entry 3). The NMR yield increased to 90% *via* switching the solvent to THF (Table 1, entry 4). In contrast, we envisioned that enhancing the coordination between the catalyst and hydroxyl group might elevate *ortho*-selectivity by using a weakly coordinated tetrakis[3,5-bis(trifluoro methyl)phenyl]borate (NaBAR_F) anion instead of the chloride one (Table 1, entry 5). Inspired by the work of Echavarren,²¹ we speculated that 1-naphthol could also coordinate with the NHC-gold complex using BarF⁻ as a counteranion. Subsequently, we tested the combination of the NHC ligand (IPr) and NaBAR_F, affording the *ortho*-selective product **4aa** in 82% isolated yield with 88 : 12 ratio of *ortho*- vs. *para*-selectivity (Table 1, entry 5). In addition, the yield and selectivity of the *ortho*-substituted product would be easily elevated *via* switching the R substituent on the ester group of diazo compounds **2** (Table 1, entries 6–8). It should be noted that other metals, such as Rh, Cu, Pd,¹⁰ which were widely used in diazo chemistry, could not give comparable results (for more details, please see the ESI, Table S1†).

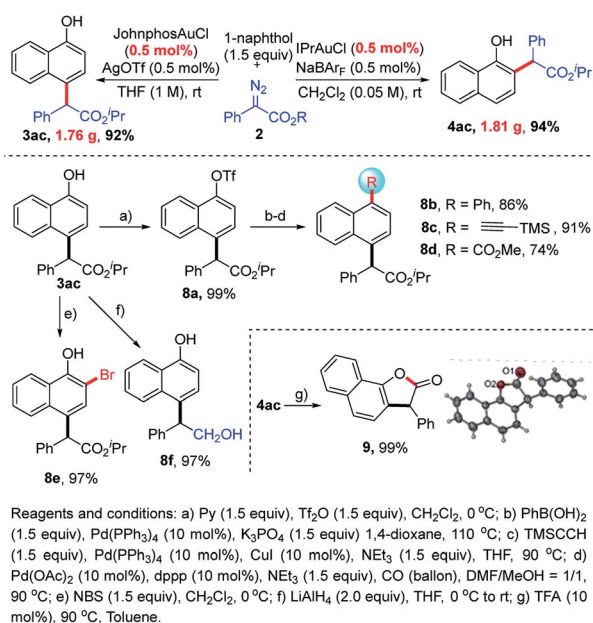
Under the optimal reaction conditions in hand, we next investigated the scope of this gold-catalyzed *para*-selective C-H functionalization of 1-naphthol. Gratifyingly, our protocol was applicable to a series of α -aryl- α -diazoacetates for the *para*-selective C-H functionalization of 1-naphthols. The reactions between 1-naphthol and α -aryl- α -diazoacetates bearing



Table 3 *Ortho*-C–H functionalization of 2-naphthols

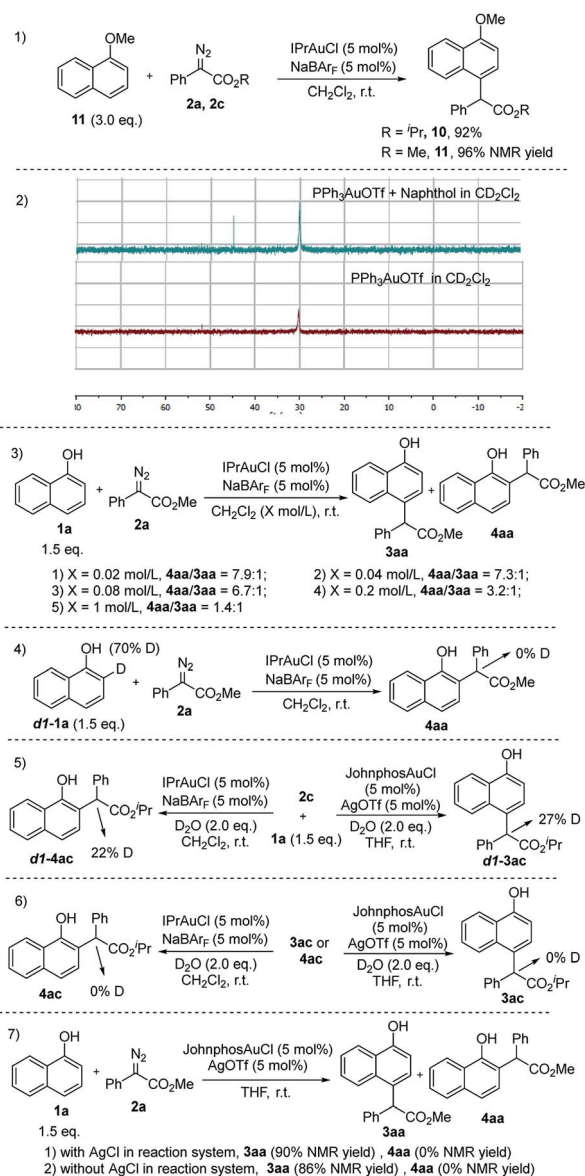
To our delight, this regiodivergent transformation was easy to scale-up to a gram-scale with even 0.5 mol% catalyst loading, affording the desired products **3ac** (1.76 g, 92%) and **4ac** (1.81 g, 94%), respectively. Moreover, C–H bond functionalization products could serve as versatile synthons. For example, a series of different groups could be incorporated into the phenyl ring *via* coupling reactions, such as phenyl groups (**8b**, 86%), alkynyl groups (**8c**, 91%) and ester groups (**8d**, 74%). The bromination of **3ac** afforded **8e** in 97% yield. The reduction of **3ac** with LiAlH_4 led to an alcohol (**8f**, 97%). TFA-catalyzed lactonization of **4ac** could deliver synthetically valuable lactone **9** in 99% yield, whose structure was also confirmed by single-crystal X-ray diffraction analysis (Scheme 3).²³

Furthermore, an array of related control experiments were then performed to gain insight into the reaction mechanism. First, we wanted to know whether a weak coordination



Scheme 3 Gram-scale reactions and synthetic applications.

interaction between the hydroxy group and gold catalyst played a key role in *ortho*-selectivity or not.²⁴ Treatment of 1-methoxynaphthalene with the diazo compound only delivered *para*-selective C–H bond functionalization products (Scheme 4, eqn (1)), indicating that the *ortho*-selectivity indeed arose from the weak interaction between the hydroxy group and gold catalyst. Meanwhile, the ^{31}P -NMR titration experiments (Scheme 4, eqn (2)) had shown that a new species was generated when PPh_3 - AuOTf was mixed with 1-naphthol, disclosing that the gold catalyst could ligate to the hydroxy group. Besides, NMR titration experiments disclosed that no hydrogen bonding interactions existed between 1-naphthol and the gold catalyst (see the ESI†). On the other hand, further ^{19}F -NMR and ^{11}B -NMR experiments showed that there was no weak interactions between the hydroxyl group and boron atom (see the ESI†). Based on the above results, it is reasonable that the



Scheme 4 Preliminary mechanistic study.



coordination between the hydroxy group and gold catalyst played a key role in *ortho*-selectivity. Further studies showed that a low concentration would facilitate *ortho* C–H bond functionalization, which was consistent with our conclusion that *ortho* C–H bond functionalization was a weak interaction enabled intramolecular process (Scheme 4, eqn (3)).²⁴ Later on, deuterium labeling experiments disclosed that the C–H bond functionalization of 1-naphthol did not proceed via a [1,2]-H shift²⁵ but a possible water assisted [1,3]-H shift^{9c} (Scheme 4, eqn (4) and (5)). Control experiments also demonstrated that no enolization of the product took place (Scheme 4, eqn (6)). Further experiments indicated that the C–H bond functionalization of 2-naphthols also proceeded via a similar process (see the ESI†). Besides, we also studied the silver effect^{20,26} and the results indicated that there is no silver effect in *para* C–H bond functionalization (Scheme 4, eqn (7)).

In conclusion, we have described the first unprecedented and efficient example of gold-catalyzed regiodivergent and chemoselective direct C–H bond functionalization of naphthols with α -aryl- α -diazoesters, which has potential applications in the synthesis of bioactive compounds, natural products and late-stage modification of medicines containing a naphthol skeleton. Our research demonstrated that the control of the interactions between the hydroxy group and gold catalyst can enable the site-selectivities of this reaction. This work, we believe, would not only deepen the understanding of carbene chemistry, but also open a new window to directed C–H bond functionalization.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (No. 21572065, 21772042, 21425205), the Science and Technology Commission of Shanghai Municipality (18JC1412300) and the Program for Changjiang Scholars and Innovative Research Team in University (IRT_16R25) for financial support.

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