Chemical Science

EDGE ARTICLE

View Article Online
View Journal | View Issue

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†

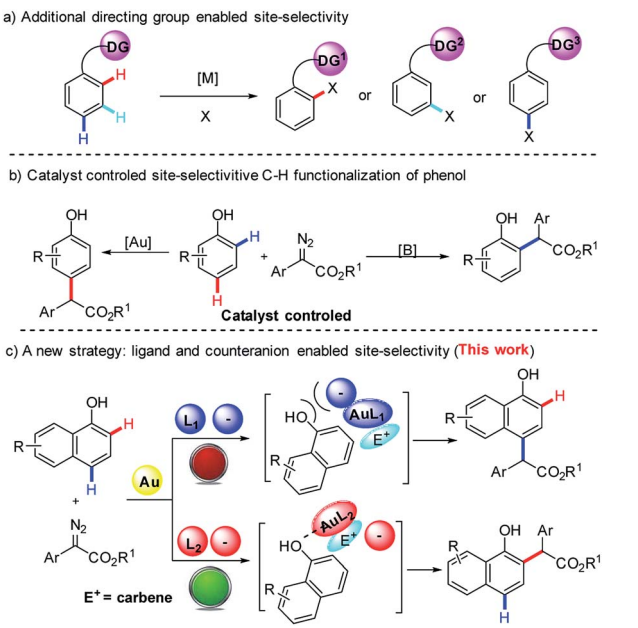
Zhunzhun Yu, Yongfeng Li, Peichao Zhang, Lu Liu * and Junliang Zhang *

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(sp^2)–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(sp^2)–H bond functionalization,[3] in some cases for *meta* selectivity,[4] and in few cases for *para* selectivity[5] (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(sp^2)–H bond functionalization of naphthols is highly attractive to the synthetic community. Recently, Shi[8] and our group[9a] independently developed gold-catalyzed highly site-selective *para* C(sp^2)–H bond functionalization of phenols with α-aryl-α-diazoesters. Later on, our group also realized the more challenging highly selective *ortho* C(sp^2)–H bond functionalization of phenols on catalysis by $(C_6F_5)_3B$ (Scheme 1b).[9b] As an ongoing interest in C(sp^2)–H bond functionalization,[9] we wanted to



Scheme 1 Different strategies to site-selective C(sp^2)–H bond functionalization.

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, 3663 N. Zhongshan Road, Shanghai 200062, China. E-mail: lliu@chem.ecnu.edu.cn; jlzhang@chem.ecnu.edu.cn

† 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

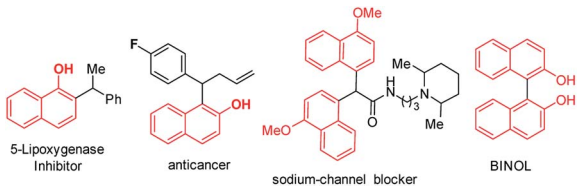


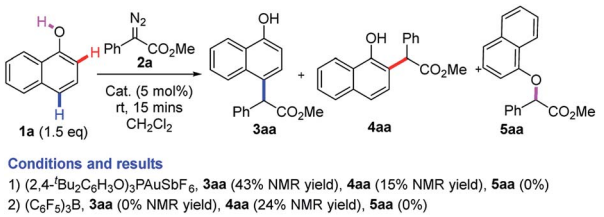
Fig. 1 Naphthol derivatives in bioactive molecules and ligands.

achieve direct and site-divergent C(sp^2)–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 $(C_6F_5)_3B$, respectively (Scheme 2). These results indicated that exploring an alternative strategy was highly necessary.

Recently, Yamaguchi[15] and Yi[16] reported *ortho* C–H bond alkenylation 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).

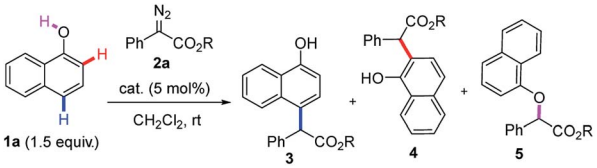
We envisioned that a bulky ligand might stop the coordination between gold complexes[17,18] and hydroxyl groups and thus favor *para*-selective C–H bond functionalization. But unfortunately, the use of bulky X-phos and ^{t}BuXPhos derived gold complexes still delivered a similar selectivity to the tris(2,4-di-*tert*-butylphenyl)phosphite/gold 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 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



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

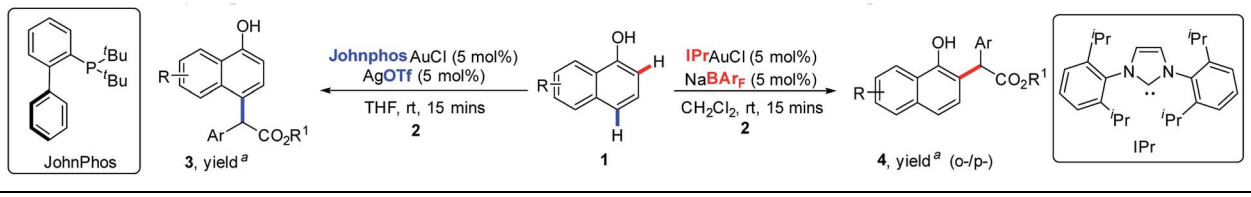
[a] NMR yield, the number in parentheses is the isolated yield. [b] THF as the solvent. XPhos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl; ^{t}BuXPhos = 2-di-*t*-butylphosphino-2′,4′,6′-tri-i-propyl-1,1′-bipheny; Johnphos = 2-(di-*tert*-butylphosphino)biphenyl; and IPr = 1,3-bis(2,6-di-ipropyl-phenyl)imidazol-2-ylidene. $NaBAr_F$ = sodium tetrakis[3,5-bis (trifluoro methyl)phenyl]borate.

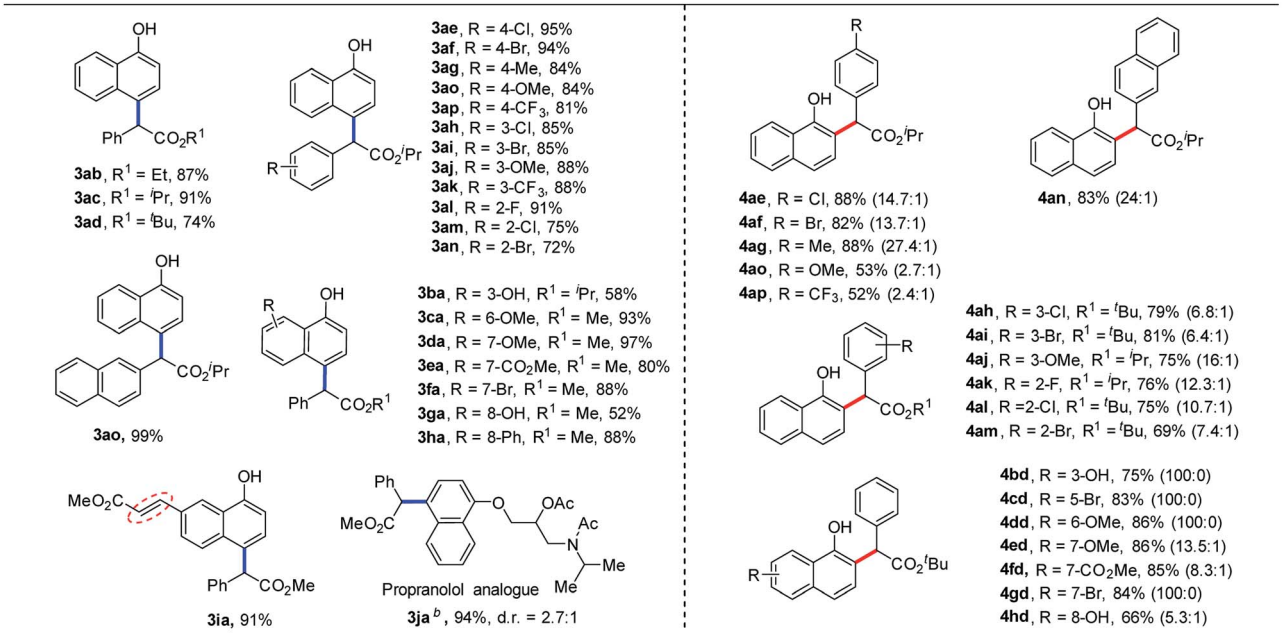
electron-donating or electron-withdrawing groups in the phenyl ring could deliver the site-specific products **3ab–3ao** in good to excellent yields (72% to 99%). Moreover, a range of substituted 1-naphthols were also applicable to *para*-selective C–H bond functionalization, delivering the corresponding products **3ba–3ia** in moderate to excellent yields (52% to 97%). However, C5-substituted 1-naphthol was incompatible with this transformation due to the bulky allylic 1,3-strain. It is well known that cyclopropanation[22] would take place when an alkene is treated with a diazo compound using metal catalysts. However, no cyclopropanation product was detected in our reaction because of the low reactivity of this double bond (Table 2, **3ia**). Finally, this *para*-selective C–H functionalization reaction could be used for the late-stage modification of β-blockers (propranolol), delivering the desired product in 94% yield (Table 2, **3ja**). It is noteworthy that the diastereoselectivity was perfect for this transformation and the dr ratio was from the inversion isomer of the nitrogen atom. The structure of the product was further confirmed by single-crystal X-ray diffraction analysis of **3ah**.[23]

Subsequently, we turned to investigate the scope of gold-catalyzed *ortho*-selective C–H bond functionalization of 1-naphthols. All the reactions proceeded smoothly, affording the desired *ortho*-selective C–H functionalization products in moderate to excellent yields (52% to 88%) with up to 100 : 0 site-selectivity. Besides, the installation of strong electron-donating or electron-withdrawing groups in the phenyl ring of diazo compounds would decrease the regioselectivity (**4ao** and **4ap**). In general, substituted 1-naphthols would increase the regioselectivity of the desired products. To our surprise, no C–H bond functionalization occurred at the *ortho* position to the methoxyl group (**4dd** and **4ed**) in this transformation. The structure of *ortho*-selective products was also determined by single-crystal X-ray crystallography of **4al**.[23]

Finally, we also studied the *ortho* C–H bond functionalization of 2-naphthols and the corresponding *ortho*-selective products were obtained in 77% to 99% yields in the presence of IPrAuCl and $NaBAr_F$ (Table 3). Furthermore, the late-stage modification of naproxen was achieved, which is an important nonsteroidal anti-inflammatory drug (Table 3, **7k**, 87%). We found that the steric hindrance played a key role in the late-stage modification of naproxen, but we could not obtain the desired product when more bulky isopropyl 2-diazo-2-phenyl-acetate was used. This result could also rationalize why C–H bond functionalization did not take place at the *ortho* position to the methoxyl group in the aforementioned cases (**4dd** and **4ed**). It should be mentioned that all reactions had shown high chemo- and site-selectivity, and no O–H insertion product and other regioisomers *via* C–H bond functionalization were detected.

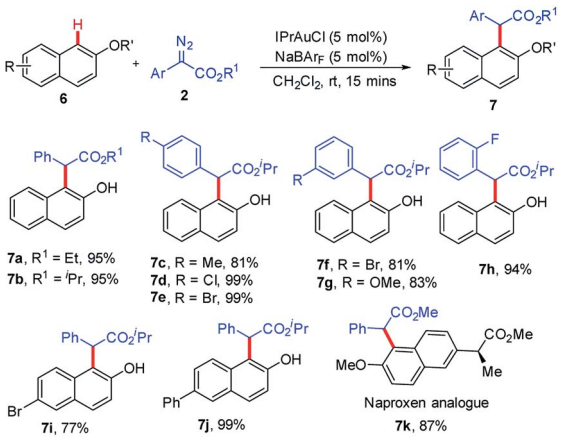
Table 2 Gold(I)-catalyzed *para*-selective and *ortho*-selective C–H bond functionalization of 1-naphthols





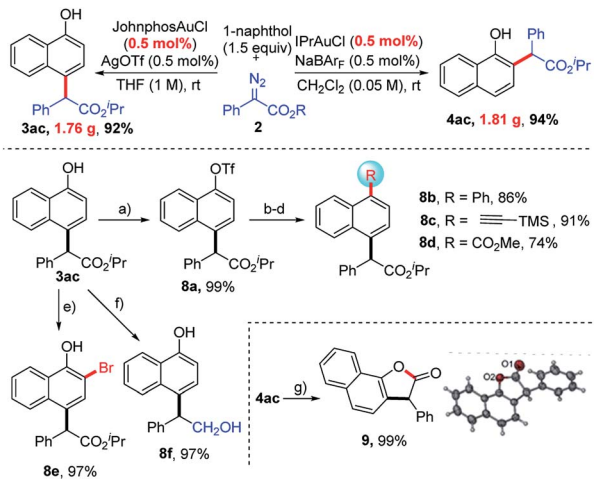
[a] Isolated yield of a single isomer. [b] 2.0 equiv. diazo compound was used.

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

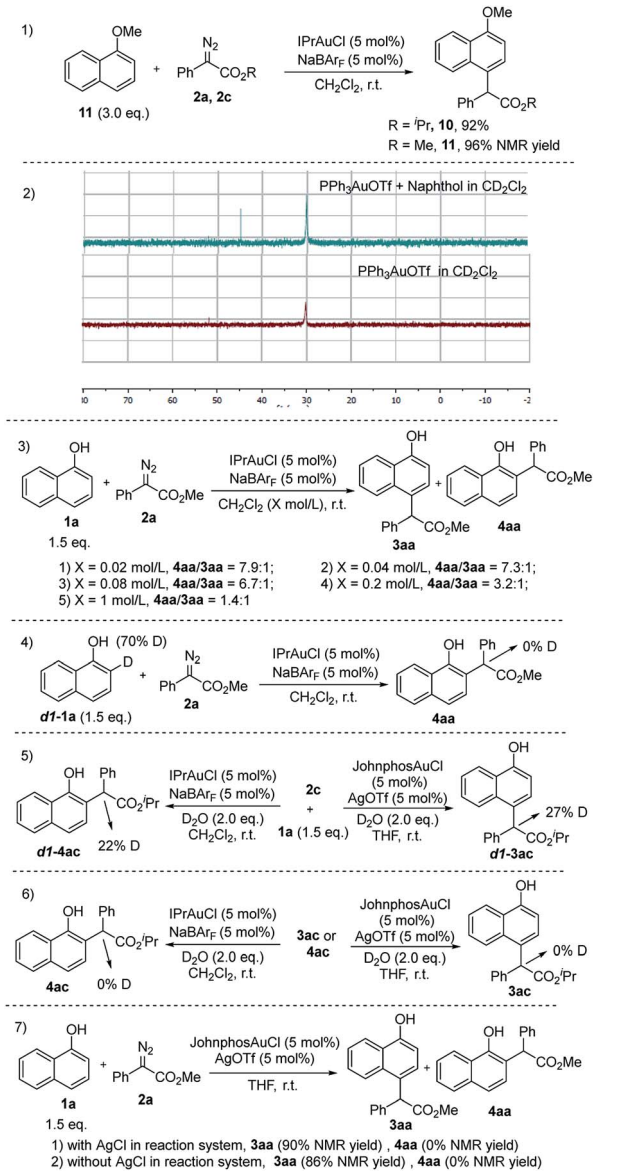


To our delight, this regiodivergent transformation was easy to scale-up to a gram-scale with even 0.5 mol% catalyst loading, affording the desired products **3ac** (1.76 g, 92%) and **4ac** (1.81 g, 94%), respectively. Moreover, C–H bond functionalization products could serve as versatile synthons. For 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 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 3 Gram-scale reactions and synthetic applications.



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 proceeded *via* a [1,2]-H shift[25] but a possible water assisted [1,3]-H shift[9g] (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.

Notes and references

1 (*a*) B. M. Trost, *Science*, 1983, **219**, 245–250; (*b*) S. L. Schreiber, *Science*, 2000, **287**, 1964–1969; (*c*) J. Mahatthananchai, A. M. Dumas and J. W. Bode, *Angew. Chem., Int. Ed.*, 2012, **51**, 10954–10990; (*d*) W. R. J. D. Galloway, A. Isidro-Llobet and D. R. Spring, *Nat. Commun.*, 2010, **1**, 80.

2 For recent examples, see: (*a*) C. Guo, M. Fleige, D. Janssen-Müller, C. G. Daniliuc and F. Glorius, *Nat. Chem.*, 2015, **7**, 842–847; (*b*) R. Mose, G. Preegel, J. Larsen, S. Jakobsen, E. H. Iversen and K. A. Jørgensen, *Nat. Chem.*, 2016, **9**, 487–492; (*c*) Z. Zhou, Z.-X. Wang, Y.-C. Zhou, W. Xiao, Q. Ouyang, W. Du and Y.-C. Chen, *Nat. Chem.*, 2017, **9**, 590–594; (*d*) Q.-Q. Cheng, J. Yedoyan, H. Arman and M. P. Doyle, *J. Am. Chem. Soc.*, 2016, **138**, 44–47; (*e*) Q.-Q. Cheng, M. Lankelma, D. Wherritt, H. Arman and M. P. Doyle, *J. Am. Chem. Soc.*, 2017, **139**, 9839–9842; (*f*) Y. Deng, L. A. Massey, Y. A. Rodriguez Núñez, H. Arman and M. P. Doyle, *Angew. Chem., Int. Ed.*, 2017, **56**, 12292; (*g*) J.-Y. Liao, P.-L. Shao and Y. Zhao, *J. Am. Chem. Soc.*, 2015, **137**, 628–631; (*h*) P. A. Donets and N. Cramer, *Angew. Chem., Int. Ed.*, 2015, **54**, 633; (*i*) T. Hashimoto, H. Nakatsu and K. Maruoka, *Angew. Chem., Int. Ed.*, 2015, **54**, 4617–4621; (*j*) D. Ding, T. Mou, M. Feng and X. Jiang, *J. Am. Chem. Soc.*, 2016, **138**, 5218–5221; (*k*) S. Okumura, T. Komine, E. Shigeki, K. Semba and Y. Nakao, *Angew. Chem., Int. Ed.*, 2018, **57**, 929–932; (*l*) S. Xu, Z.-M. Zhang, B. Xu, B. Liu, Y. Liu and J. Zhang, *J. Am. Chem. Soc.*, 2018, **140**, 2278–2283; (*m*) L. Dell'Amic, G. Rassu, V. Zambrano, A. Sartori, C. Curti, L. Battistini, G. Pelosi, G. Casiraghi and F. Zanardi, *J. Am. Chem. Soc.*, 2014, **136**, 11107–11114; (*n*) L. Liu and J. Zhang, *Angew. Chem., Int. Ed.*, 2009, **48**, 6093–6096; (*o*) C. Guo, B. Sahoo, C. G. Daniliuc and F. Glorius, *J. Am. Chem. Soc.*, 2014, **136**, 17402–17405.

3 For selected reviews, see: (*a*) C. Cheng and J. F. Hartwig, *Chem. Rev.*, 2015, **115**, 8946–8975; (*b*) G. Song and X. Li, *Acc. Chem. Res.*, 2015, **48**, 1007–1020; (*c*) B. Ye and N. Cramer, *Acc. Chem. Res.*, 2015, **48**, 1308–1318; (*d*) K. Shin, H. Kim and S. Chang, *Acc. Chem. Res.*, 2015, **48**, 1040–1052; (*e*) O. Daugulis, J. Roane and L. D. Tran, *Acc. Chem. Res.*, 2015, **48**, 1053–1064; (*f*) Y. Segawa, T. Maekawa and K. Itami, *Angew. Chem., Int. Ed.*, 2015, **54**, 66–81; (*g*) T. W. Lyons and M. S. Sanford, *Chem. Rev.*, 2010, **110**, 1147–1169; (*h*) D. A. Colby, R. G. Bergman and J. A. Ellman, *Chem. Rev.*, 2010, **110**, 624–655; (*i*) P. B. Arockiam, C. Bruneau and P. H. Dixneuf, *Chem. Rev.*, 2012, **112**, 5879–5918; (*j*) B.-J. Li and Z.-J. Shi, *Chem. Soc. Rev.*, 2012, **41**, 5588–5598; (*k*) K. M. Engle, T.-S. Mei, M. Wasa and J.-Q. Yu, *Acc. Chem. Res.*, 2011, **45**, 788–802.

4 For selected *meta*-selective C–H functionalization, see: (*a*) D. Leow, G. Li, T.-S. Mei and J.-Q. Yu, *Nature*, 2012, **486**, 518–522; (*b*) L. Wan, N. Dastbaravardeh, G. Li and J.-Q. Yu, *J. Am. Chem. Soc.*, 2013, **135**, 18056–18059; (*c*) N. Hofmann and L. Ackermann, *J. Am. Chem. Soc.*, 2013, **135**, 5877–5884; (*d*) Y. Kuninobu, H. Ida, M. Nishi and M. Kanai, *Nat. Chem.*, 2015, **7**, 712–717; (*e*) X.-C. Wang, W. Gong, L.-Z. Fang, R.-Y. Zhu, S. Li, K. M. Engle and J.-Q. Yu, *Nature*, 2015, **519**, 334–338; (*f*) Z. Dong, J. Wang and G. Dong, *J. Am. Chem. Soc.*, 2015, **137**, 5887–5890; (*g*) Z. Fan, J. Ni and A. Zhang, *J. Am. Chem. Soc.*, 2016, **138**, 8470–8475.

5 For *para*-selective C–H functionalization, see: (*a*) S. Bag, T. Patra, A. Modak, A. Deb, S. Maity, U. Dutta, A. Dey, R. Kancherla, A. Maji, A. Hazra, M. Bera and D. Maiti, *J. Am. Chem. Soc.*, 2015, **137**, 11888–11891; (*b*) T. Patra, S. Bag, R. Kancherla, A. Mondal, A. Dey, S. Pimparkar, S. Agasti, A. Modak and D. Maiti, *Angew. Chem., Int. Ed.*, 2016, **55**, 7751–7755; (*c*) C. Yuan, L. Zhu, R. Zeng, Y. Lan and Y. Zhao, *Angew. Chem., Int. Ed.*, 2018, **57**, 1277–1281.

6 J. F. Hartwig and M. A. Larsen, *ACS Cent. Sci.*, 2016, **2**, 281–292.

7 (*a*) F. H. Fiege, H.-W. Voges, T. Hamamoto, S. Umemura; T. Iwata, H. Miki, Y. Fujita, H.-J. Buysch, D. Garbe and W. Paulus, Phenol derivatives, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley VCH, Weinheim, 2000; (*b*) J. M. Brunel, *Chem. Rev.*, 2005, **105**, 857–897; (*c*) B. Das, C. R. Reddy, J. Kashanna, S. K. Mamidyala and C. G. Kumar, *Med. Chem. Res.*, 2012, **21**, 3321–3325; (*d*) I. Roufos, S. J. Hays, J. D. J. Dooley, R. D. Schwarz, G. W. Campbell and A. W. Probert Jr, *J. Med. Chem.*, 1994, **37**, 268–274; (*e*) D. G. Batt, G. D. Maynard, J. J. Petraitis, J. E. Shaw, W. Galbraith and R. R. Harris, *J. Med. Chem.*, 1990, **33**, 360–370; (*f*) R. J. Altenbach, L. A. Black, M. I. Strakhova, A. M. Manelli, T. L. Carr, K. C. Marsh, J. M. Wetter, E. J. Wensink, G. C. Hsieh, P. Honore, T. R. Garrison, J. D. Brioni and M. D. Cowart, *J. Med. Chem.*, 2010, **53**, 7869–7873; (*g*) E. S. Tan, M. Miyakawa, J. R. Bunzow, D. K. Grandy and T. S. Scanlan, *J. Med. Chem.*, 2007, **50**, 2787–2798.

8 Y. Xi, Y. Su, Z. Yu, B. Dong, E. J. McClain, Y. Lan and X. Shi, *Angew. Chem., Int. Ed.*, 2014, **53**, 9817–9821.

9 (*a*) Z. Yu, B. Ma, M. Chen, H.-H. Wu, L. Liu and J. Zhang, *J. Am. Chem. Soc.*, 2014, **136**, 6904–6907; (*b*) Z. Yu, Y. Li, J. Shi, B. Ma, L. Liu and J. Zhang, *Angew. Chem., Int. Ed.*, 2016, **55**, 14807–14811; (*c*) Z. Yu, H. Qiu, L. Liu and J. Zhang, *Chem. Commun.*, 2016, **52**, 2257–2260; (*d*) B. Ma, Z. Wu, B. Huang, L. Liu and J. Zhang, *Chem. Commun.*, 2016, **52**, 9351–9354; (*e*) B. Ma, Z. Chu, B. Huang, Z. Liu, L. Liu and J. Zhang, *Angew. Chem., Int. Ed.*, 2017, **56**, 2749–2753; (*f*) B. Ma, J. Wu, L. Liu and J. Zhang, *Chem. Commun.*, 2017, **53**, 10164–10167; (*g*) Y. Liu, Z. Yu, J. Z. Zhang, L. Liu, F. Xia and J. Zhang, *Chem. Sci.*, 2016, **7**, 1988–1995.

10 For selected reviews, see: (*a*) M. P. Doyle and M. A. McKervey, in *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*, Wiley, New York, 1998; (*b*) M. P. Doyle, R. Duffy, M. Ratnikov and L. Zhou, *Chem. Rev.*, 2010, **110**, 704–724; (*c*) H. M. L. Davies and Y.-J. Lian, *Acc. Chem. Res.*, 2012, **45**, 923–935; (*d*) H. M. L. Davies and D. Morton, *Chem. Soc. Rev.*, 2011, **40**, 1857–1869; (*e*) M. M. Díaz-Requejo and P. J. Pérez, *Chem. Rev.*, 2008, **108**, 3379–3394; (*f*) T. Ye and M. A. McKervey, *Chem. Rev.*, 1994, **94**, 1091–1160; (*g*) A. Ford, H. Miel, A. Ring, C. N. Slattery, A. R. Maguire and M. A. McKervey, *Chem. Rev.*, 2015, **115**, 9981; (*h*) Y. Xia, D. Qiu and J. Wang, *Chem. Rev.*, 2017, **117**, 13810–13889.

11 For selected examples for aromatic C(sp^2)–H bond functionalization with diazo compounds, see: (*a*) W.-W. Chan, S.-F. Lo, Z. Zhou and W.-Y. Yu, *J. Am. Chem. Soc.*, 2012, **134**, 13565–13568; (*b*) T. K. Hyster, K. E. Ruhl and T. Rovis, *J. Am. Chem. Soc.*, 2013, **135**, 5364–5367; (*c*) H. Qiu, M. Li, L.-Q. Jiang, F.-P. Lv, L. Zan, C.-W. Zhai, M. P. Doyle and W.-H. Hu, *Nat. Chem.*, 2012, **4**, 733–738; (*d*) B. Xu, M.-L. Li, X.-D. Zuo, S.-F. Zhu and Q.-L. Zhou, *J. Am. Chem. Soc.*, 2015, **137**, 8700–8703; (*e*) D. Best, D. J. Burns and H. W. Lam, *Angew. Chem., Int. Ed.*, 2015, **54**, 7410–7413; (*f*) A. Conde, G. Sabenya, M. Rodríguez, V. Postils, J. M. Luis, M. M. Díaz-Requejo, M. Costas and P. J. Pérez, *Angew. Chem., Int. Ed.*, 2016, **55**, 6530–6534.

12 For reviews, see: (*a*) D. Gillingham and N. Fei, *Chem. Soc. Rev.*, 2013, **42**, 4918–4931; (*b*) X. Guo and W. Hu, *Acc. Chem. Res.*, 2013, **46**, 2427–2440; (*c*) S.-F. Zhu and Q.-L. Zhou, *Acc. Chem. Res.*, 2012, **45**, 1365–1377; (*d*) D. J. Miller and C. J. Moody, *Tetrahedron*, 1995, **51**, 10811–10843For O–H insertion of 1-naphthol, see: (*e*) C. Chen, S.-F. Zhu, B. Liu, L.-X. Wang and Q.-L. Zhou, *J. Am. Chem. Soc.*, 2007, **129**, 12616–12617; (*f*) T. Osako, D. Panichakul and Y. Uozumi, *Org. Lett.*, 2012, **14**, 194–197For O–H insertion of 2-naphthol, see: (*g*) X.-L. Xie, S.-F. Zhu, J.-X. Guo, Y. Cai and Q.-L. Zhou, *Angew. Chem., Int. Ed.*, 2014, **53**, 2978–2981; (*h*) X. Gao, B. Wu, W.-X. Huang, M.-W. Chen and Y.-G. Zhou, *Angew. Chem., Int. Ed.*, 2015, **54**, 11956–11960; (*i*) Y. Zhang, Y. Yao, L. He, Y. Liu and L. Shi, *Adv. Synth. Catal.*, 2017, **359**, 2754–2761.

13 In general, *para*-substituted product is the major one when 1-naphthol is treated with electrophile without intermolecular weak interaction. The references please see:(*a*) M. C. Carreño, J. L. G. Ruano, G. Sanz, M. A. Toledo and A. Urbano, *Synlett*, 1997, **11**, 1241–1242; (*b*) P. Bovonsombat, J. Leykajarakul, C. Khan, K. Pla-on, M. M. Krause, P. Khanthapura, R. Ali and N. Doowa, *Tetrahedron Lett.*, 2009, **50**, 2664–2667; (*c*) H. Kajita and A. Togni, *ChemistrySelect*, 2017, **2**, 1117–1121.

14 O. S. Tee and N. R. Yengar, *Can. J. Chem.*, 1987, **65**, 1714–1718.

15 (*a*) M. Yamaguchi, A. Hayashi and M. Hirama, *J. Am. Chem. Soc.*, 1995, **117**, 1151–1152; (*b*) K. Kobayashi, M. Arisawa and M. Yamaguchi, *J. Am. Chem. Soc.*, 2002, **124**, 8528–8529.

16 D.-H. Lee, K.-H. Kwon and C. S. Yi, *J. Am. Chem. Soc.*, 2012, **134**, 7325–7328.

17 For selected recent general reviews, see:(*a*) A. S. K. Hashmi and F. D. Toste, *Modern Gold Catalyzed Synthesis*, Wiley-VCH, Weinheim, 2012; (*b*) D. J. Gorin and F. D. Toste, *Nature*, 2007, **446**, 395–403; (*c*) A. S. K. Hashmi, *Chem. Rev.*, 2007, **107**, 3180–3211; (*d*) Z. Li, C. Brouwer and C. He, *Chem. Rev.*, 2008, **108**, 3239–3265; (*e*) A. Arcadi, *Chem. Rev.*, 2008, **108**, 3266–3325; (*f*) E. Jiménez-Núñez and A. M. Echavarren, *Chem. Rev.*, 2008, **108**, 3326–3350; (*g*) D. Garayalde and C. Nevado, *ACS Catal.*, 2012, **2**, 1462–1479; (*h*) N. Krause and C. Winter, *Chem. Rev.*, 2011, **111**, 1994–2009; (*i*) M. Bandini, *Chem. Soc. Rev.*, 2011, **40**, 1358–1367; (*j*) L. Zhang, *Acc. Chem. Res.*, 2014, **47**, 877–888; (*k*) A. Fürstner, *Acc. Chem. Res.*, 2014, **47**, 925–938; (*l*) L. Fensterbank and M. Malacria, *Acc. Chem. Res.*, 2014, **47**, 953–965; (*m*) R. Dorel and A. M. Echavarren, *Chem. Rev.*, 2015, **115**, 9028–9072.

18 For reviews and selected examples of gold-catalyzed transformations of diazoacetates, see: (*a*) L. Liu and J. Zhang, *Chem. Soc. Rev.*, 2016, **45**, 506–516; (*b*) F. Wei, C. Song, Y. Ma, L. Zhou, C.-H. Tung and Z. Xu, *Sci. Bull.*, 2015, **60**, 1479–1492; (*c*) M. R. Fructos, M. M. Díaz-Requejo and P. J. Pérez, *Chem. Commun.*, 2016, **52**, 7326–7335; (*d*) M. R. Fructos, T. R. Belderrain, P. de Frémont, N. M. Scott, S. P. Nolan, M. M. Díaz-Requejo and P. J. Pérez, *Angew. Chem., Int. Ed.*, 2005, **44**, 5284–5288; (*e*) J. F. Briones and H. M. L. Davies, *J. Am. Chem. Soc.*, 2012, **134**, 11916–11919;

(*f*) J. F. Briones and H. M. L. Davies, *J. Am. Chem. Soc.*, 2013, **135**, 13314–13317; (*g*) D. Zhang, G. Xu, D. Ding, C. Zhu, J. Li and J. Sun, *Angew. Chem., Int. Ed.*, 2014, **53**, 11070–11074; (*h*) G. Lonzi and L. A. López, *Adv. Synth. Catal.*, 2013, **355**, 1948–1954; (*i*) J. Wang, X. Yao, T. Wang, J. Han, J. Zhang, X. Zhang, P. Wang and Z. Zhang, *Org. Lett.*, 2015, **17**, 5124–5127; (*j*) Z. Cao, X. Wang, C. Tan, X. Zhao, J. Zhou and K. Ding, *J. Am. Chem. Soc.*, 2013, **135**, 8197–8200; (*k*) V. V. Pagar and R.-S. Liu, *Angew. Chem., Int. Ed.*, 2015, **54**, 4923–4926; (*l*) F. Zhao, N. Li, T. Zhang, Z.-Y. Han, S.-W. Luo and L.-Z. Gong, *Angew. Chem., Int. Ed.*, 2017, **56**, 3247–3251; (*m*) F.-M. Liao, Z.-Y. Cao, J.-S. Yu and J. Zhou, *Angew. Chem., Int. Ed.*, 2017, **56**, 2459–2463.

19 For a review, see: R. E. M. Brooner and R. A. Widenhoefer, *Angew. Chem., Int. Ed.*, 2013, **52**, 11714–11724.

20 A. Homs, I. Escofet and A. M. Echavarren, *Org. Lett.*, 2013, **15**, 5782–5785.

21 N. Huguet, D. Leboeuf and A. M. Echavarren, *Chem.–Eur. J.*, 2013, **19**, 6581–6585.

22 (*a*) D. Bykowski, K.-H. Wu and M. P. Doyle, *J. Am. Chem. Soc.*, 2006, **128**, 16038–16039; (*b*) S. Chuprakov, S. W. Kwok, L. Zhang, L. Lercher and V. V. Fokin, *J. Am. Chem. Soc.*, 2009, **131**, 18034–18035; (*c*) V. N. G. Lindsay, D. Fiset, P. J. Gristch, S. Azzi and A. B. Charette, *J. Am. Chem. Soc.*, 2013, **135**, 1463–1470; (*d*) X. Xu, H.-J. Lu, J. V. Ruppel, X. Cui, S. L. Mesa, L. Wojtas and X. P. Zhang, *J. Am. Chem. Soc.*, 2011, **133**, 15292–15295; (*e*) Y. Wang, X. Wen, X. Cui, L. Wojtas and X. P. Zhang, *J. Am. Chem. Soc.*, 2017, **139**, 1049–1052.

23 CCDC 1822536 (**3ah**), 1884847 (**4al**), 1822537 (**7i**), 1822538 (**9**).†

24 The references on tri-coordinated Au(I) complexes: (*a*) M. C. Gimeno and A. Laguna, *Chem. Rev.*, 1997, **97**, 511–522; (*b*) C. Khin, A. S. K. Hashmi and F. Rominger, *Eur. J. Inorg. Chem.*, 2010, 1063–1069; (*c*) Y. Luo, K. Ji, Y. Li and L. Zhang, *J. Am. Chem. Soc.*, 2012, **134**, 17412–17415; (*d*) P. Gualco, S. Mallet-Ladeira, H. Kameo, H. Nakazawa, M. Mercy, L. Maron, A. Amgoune and D. Bourissou, *Organometallics*, 2015, **34**, 1449–1453; (*e*) H. Yang and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2015, **137**, 13425–13432.

25 A. Padwa, D. J. Austin, A. T. Price, M. A. Semones, M. P. Doyle, M. N. Protopopova, W. R. Winchester and A. Tran, *J. Am. Chem. Soc.*, 1993, **115**, 8669–8680.

26 D. Wang, R. Cai, S. Sharma, J. Jirak, S. K. Thummanapelli, N. G. Akhmedov, H. Zhang, X. Liu, J. L. Petersen and X. Shi, *J. Am. Chem. Soc.*, 2012, **134**, 9012–9019.