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Cobalt(III)-Catalyzed Intermolecular Carboamination of Propiolates and Bicyclic Alkenes via Non-Annulative Redox-Neutral Coupling

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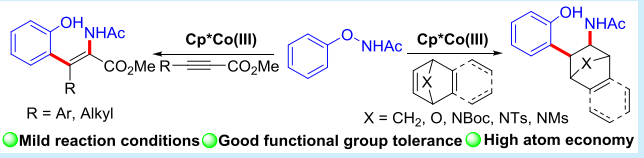
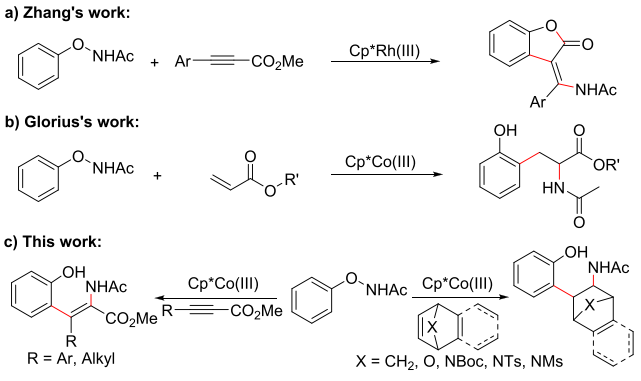
Supporting Information

ABSTRACT: A cobalt(III)-catalyzed, redox-neutral, intermolecular carboamination of propiolates and bicyclic alkenes was developed. This non-annulative coupling strategy features atom economy, high regioselectivity, good yields, and functional groups tolerance. Such a carboamination reaction was applied to modified phenols from the corresponding phenols under mild conditions.



An internal oxidant-directed, transition metal-catalyzed C−H bond activation was discovered as an atom-economic strategy for constructing the C−C bonds in the past decade.[1] Notably, the *N*-phenoxyacetamide (PhO-NHAc) group could utilize its unique redox-neutral reactivity for C−H bond functionalization cascade reactions, yielding phenols after the N−O bond cleavage.[2] In 2013, Lu et al. pioneered the redox-neutral olefination reactions in the synthesis of phenols by Cp*Rh(III) catalysis using O-NHAc as a powerful directing group.[3] Subsequently, C−H bond activation/cyclization was studied intensively.[4] In 2018, Zhang et al. reported the first Cp*Rh(III)-catalyzed isomerization and lactonization via C−H bond activation for the synthesis of benzofuran-2(3*H*)-ones, achieving great regio- and stereoselectivity (Scheme 1a).[5] Recently, Yi et al. discovered the selective β-F elimination directed by O-NHAc to generate monofluoroalkenyl dihydrobenzo[*d*]isoxazoles via a Rh(III)-catalyzed [4+1] annulation.[6]

Scheme 1. Carboamination of Alkynes and Alkenes



Despite significant progress, the metal catalysts, however, are still primarily based on noble metals, especially the 4d and 5d metals. Owing to the rising cost of noble metals and the benefits of green chemistry, directed C−H bond activation via the more available and more redox flexible 3d transition metal catalysts has been receiving an increasing amount of attention in recent years.[7] Cobalt has been shown to exhibit good activity and great functional group tolerance, rendering cobalt-based catalytic systems competitive alternatives in exploring new transformations.[8] In 2013, the first direct C−H bond functionalization activated by Cp*Co(III) was developed by Kanai et al.[9] The potent catalytic efficiency of Co(III) was particularly impressive for C−H bond activation that was comparable to that of the Cp*Rh(III) catalyst. Thereafter, more cases of cobalt-catalyzed C−H bond functionalization were reported. These cobalt catalysts displayed reactivity analogous to that of their rhodium counterparts.[10] However, there were few reports of the complementary catalytic activity of Co(III) to their Rh(III) congeners.[11] In 2016, a significant breakthrough by Glorius and co-workers showed that the direct difunctionalization of alkenes could be constructed by Cp*Co(III)-catalyzed carboamination (Scheme 1b). This report demonstrated a complementary property of Cp*Co(III) to its Rh(III) counterpart in O-NHAc-directed C−H bond activation.[12] Inspired by these reports, our group has been working on sustainable C−H bond activation methods to generate a variety of functional phenols.[13] Herein, we report an intermolecular carboamination of propiolates and bicyclic alkenes catalyzed by Cp*Co(III) via non-annulative redox-neutral couplings (Scheme 1c).

N-Phenoxyacetamide **1a** was first reacted with 3-phenyl-propiolate **2a** in 2,2,2-trifluoroethanol (TFE) to obtain an

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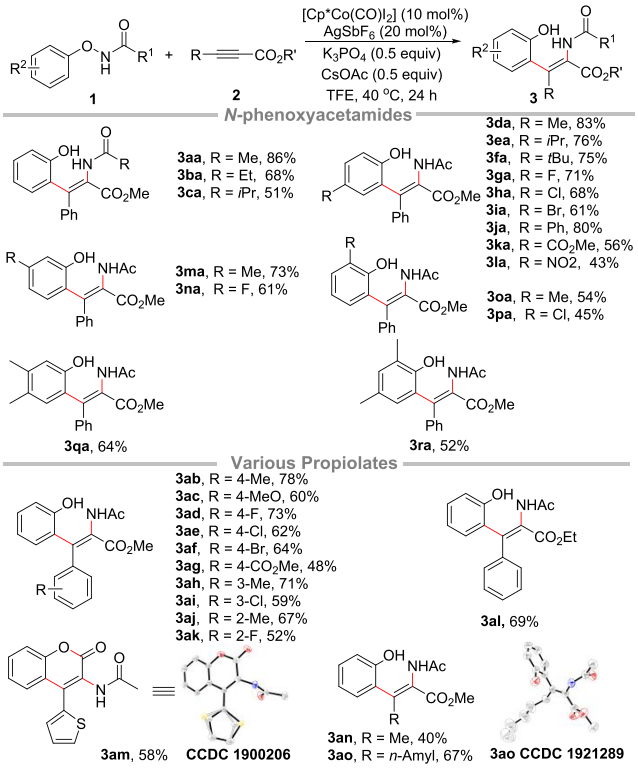
intermolecular carboamination product **3aa** with a yield of 19% when [Cp*Co(CO)I_2], $AgSbF_6$, and NaOAc were used (see Table S1). After an extensive screening of various acids and bases, **3aa** was obtained in 86% yield when [Cp*Co(CO)I_2], $AgSbF_6$, K_3PO_4, and CsOAc were used. However, no reaction occurred when $CoBr_2$, $CoCl_2$, and $Co(acac)_2$ were used, indicating an essential role of Cp*Co(III) in obtaining the desired product.

Next, we explored the range of substrates under the carboamination reaction (Scheme 2). *N*-Phenoxyamides with different acyl substituents were found to provide the carboamination products (**3aa**–**3ca**) in 51–86% yields. *para*-Substituted *N*-phenoxyacetamides bearing electron-rich and -poor moieties provided the corresponding products with 43–83% yields (**3da**–**3la**). When the *N*-phenoxyacetamides were *meta*-occupied, carboaminations occurred regioselectively at the less steric position (**3ma** and **3na**). Additionally, *ortho* substituents were used to produce **3oa** and **3pa** as desired products with 54% and 45% yields, respectively. For the disubstituted *N*-phenoxyacetamides, the reaction provided excellent selectivity for the C–H bond with less steric hindrance, giving **3qa** and **3ra** with yields of 64% and 52%, respectively. A range of propiolates were explored by tolerating the electron-rich and -poor moieties on aromatic rings, giving the carboamination products in 48–78% yields (**3ab**–**3ak**). In addition, 3-phenylpropiolates with a carbethoxy group afforded **3al** in a 69% yield. Interestingly, lactonated product **3am** was formed in 58% yield when using 3-thiophen-2-yl propiolate as the substrate, presumably due to the tautomerization of the enamine and the imine and the rotation of the C–C single bond.[5] Moreover, 3-alkyl propiolates gave **3an** and **3ao** with 40% and 67% yields, respectively.

We then examined the carboamination of alkenes and found that the coupling reaction of **1a** with 1,4-dihydro-1,4-methanonaphthalene (**4a**) proceeded smoothly by fine-tuning of the reaction conditions (for details, see Table S2). The range of *N*-phenoxyacetamide was investigated under optimized reaction conditions (Scheme 3). First, we focused on the acyl-substituted group of *N*-phenoxyamides and obtained the desired products (**5aa**–**5ac**) in 68–86% yields; *N*-phenoxyacetamides with electron-rich and -poor substituents gave 39–82% yields (**5da**–**5qa**). With disubstituted *N*-phenoxyacetamides, the C–H bond that possessed less steric hindrance exhibited excellent selectivity, and the reaction delivered **5ra** and **5sa** with 74% and 32% yields, respectively. 2-*N*-(Naphthalen-2-yloxy)acetamide delivered carboamination product **5ta** with a 56% yield. Various bicyclic olefins also gave the corresponding carboamination products. 7-Azabenzonorbornadienes with various protecting groups, such as tosyl (Ts), mesyl (Ms), and *tert*-butyloxycarbonyl (Boc), were also performed well, giving the corresponding products in 46–71% yields. Derivatives of 1,4-dihydro-1,4-epoxynaphthalene and 7-oxabicyclo 2,5-diene delivered the desired products in 55–81% yields (**5ae**, **5af**, and **5ag**). Moreover, using a norbornadiene derivative as the substrate, the carboamination product (**5ah**) was obtained in 77% yield.

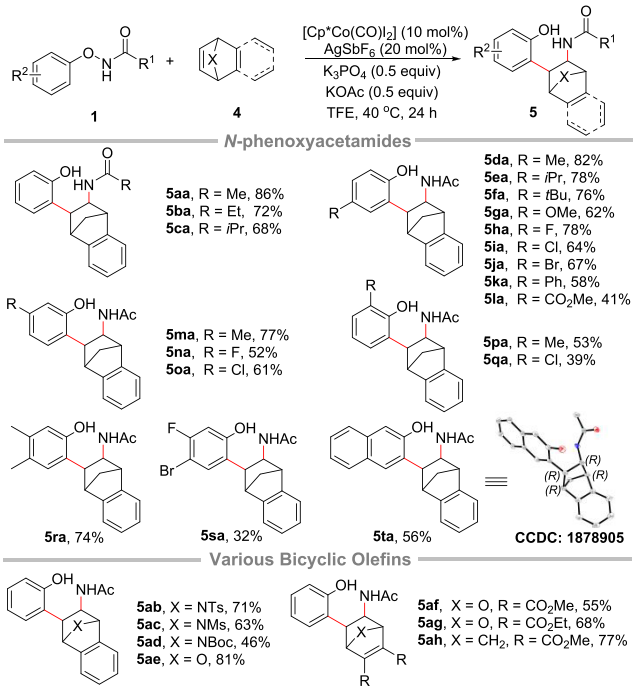
Phenols are the pivotal scaffolds in pharmaceuticals and many natural products.[14] Advantages of the mild reaction conditions encouraged us to apply this strategy to the natural

Scheme 2. Variations of *N*-Phenoxyacetamides and Propiolates[a,b]



[a]Reaction conditions: **1** (0.2 mmol), **2** (0.22 mmol), [Cp*Co(CO)I_2] (10 mol %), $AgSbF_6$ (20 mol %), K_3PO_4 (0.5 equiv), CsOAc (0.5 equiv), TFE (1.0 mL), 40 °C, 24 h. [b]Isolated yields.

Scheme 3. Variations of *N*-Phenoxyacetamides and Alkenes[a,b]



[a]Reaction conditions: **1** (0.2 mmol), **4** (0.22 mmol), [Cp*Co(CO)I_2] (10 mol %), $AgSbF_6$ (20 mol %), K_3PO_4 (0.5 equiv), KOAc (0.5 equiv), TFE (1.0 mL), 40 °C, 24 h. [b]Isolated yields.

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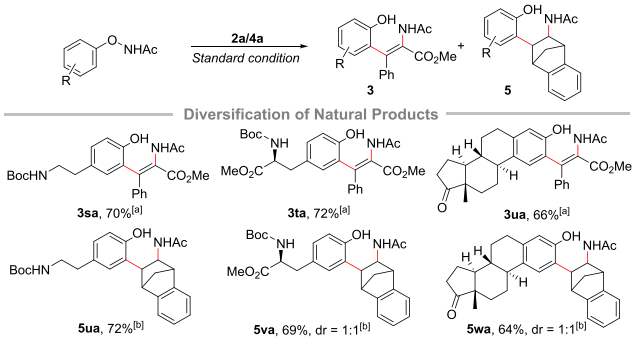
bioactive scaffolds (Scheme 4). Under the optimized conditions, substrates derived from nature products, such as

Scheme 4. Diversification of Natural Products

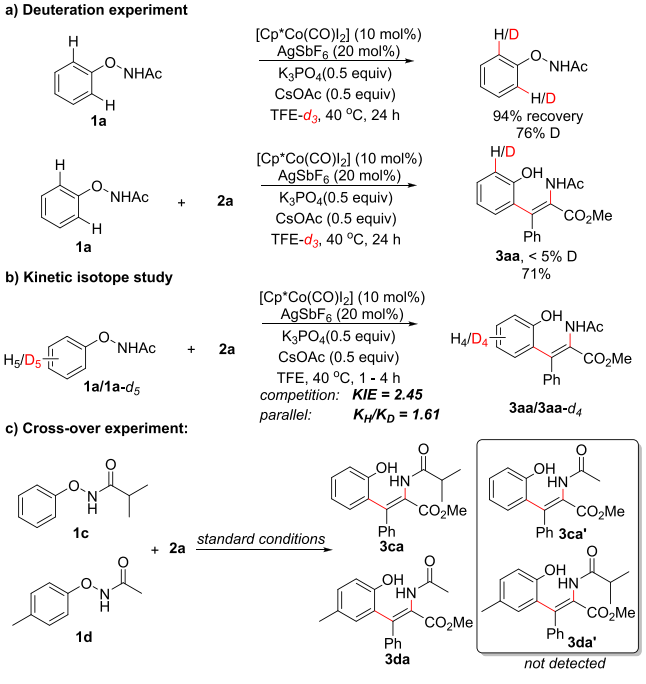


[a]Reaction conditions: **1** (0.2 mmol), **2a** (0.22 mmol), [Cp*Co(CO)I_2] (10 mol %), $AgSbF_6$ (20 mol %), K_3PO_4 (0.5 equiv), CsOAc (0.5 equiv), TFE (1.0 mL), 40 °C, 24 h. [b]Reaction conditions: **1** (0.2 mmol), **4a** (0.22 mmol), [Cp*Co(CO)I_2] (10 mol %), $AgSbF_6$ (20 mol %), K_3PO_4 (0.5 equiv), KOAc (0.5 equiv), TFE (1.0 mL), 40 °C, 24 h.

tyrosine, tyramine, and estrone, were also tested in this reaction. The catalytic carboamination proceeded smoothly, yielding the corresponding products with 64−72% yields.

Several control experiments were conducted to explore the reaction mechanisms (Scheme 5). First, to investigate the

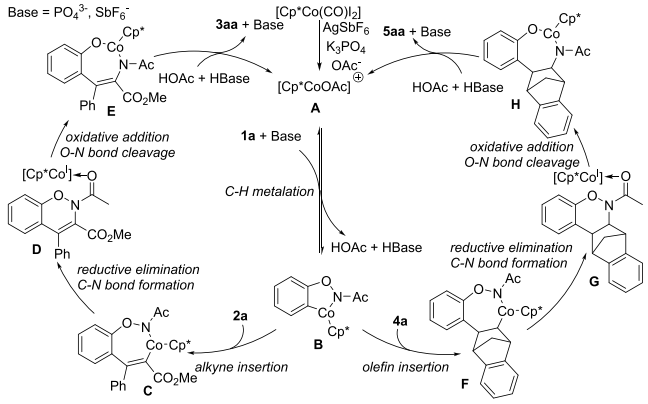
Scheme 5. Mechanistic Experiments



reversibility of C−H bond activation, the reaction in deuterated TFE was performed without addition of the propionate substrate (**2a**). The ^{1}H NMR spectrum showed that ∼76% protons on the *ortho* positions of **1a** were deuterated after 24 h, indicating a reversibility of the C−H activation process (Scheme 5a). However, <5% deuteration of **3aa** was achieved when **2a** was added, and this might suggest that the migratory insertion reaction rate of **2a** with **1a** was faster than the deuteration of **1a**. The parallel experiments of **1a** and **1a**-d_5 with **2a** were also carried out for the measurement of the kinetic isotope effect (KIE), giving a KIE value of 2.45, and a K_H/K_D ratio of 1.61, which indicated that the rate-determining step could be influenced by the C−H bond cleavage (Scheme 5b).[15] Under the standard reaction conditions, when compounds **1a** and **1d** were used as reactants, high-resolution mass spectrometry (HRMS) detected only the product of intramolecular amide migration, but mixed amide migration products **3ca′** and **3da′** were not detected. This result suggested that the formation of the C−N bond might occur intramolecularly (Scheme 5c).

On the basis of the experiments described above and related reports,[5,11,16] a possible cycle of reaction mechanism was proposed (Scheme 6). First, the active species (**A**) was formed

Scheme 6. Plausible Mechanism



by reacting [Cp*Co(CO)I_2] with $AgSbF_6$ and a base. **A** coordinated with **1a**, activating the *o*-C−H bond by elimination of HOAc to form a five-membered cobaltacyclic species (**B**). The seven-membered intermediate (**C**) was generated after the insertion of alkyne into intermediate **B**. Next, the formation of the Co(I) intermediate (**D**) delivered the desired C−N bond by reductive elimination of C(sp^2)−metal species (**C**). Subsequently, an oxidative addition by the O−N bond to intermediate **D** led to the seven-membered cobaltacyclic species (**E**). Lastly, **E** regenerates active catalytic species **A**, which was available for the next catalytic cycle. Thus, the carboamination of alkenes was achieved through C−H bond metalation, olefin insertion, reductive elimination, and oxidative addition processes.

To conclude, we described an efficient, highly regioselective, and atom-economic process of *o*-C−H bond functionalization of phenols by Cp*Co(III)-catalyzed intramolecular carboamination of the propiolates and bicyclic alkenes via non-annulative redox-neutral couplings. This strategy possesses the advantages of the appropriate tolerance of the functional groups and mild reaction conditions. This cobalt-catalyzed reactivity is complementary to the rhodium(III)-catalyzed route to intermolecular carboamination.

■ ASSOCIATED CONTENT

Supporting Information

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Experimental procedures, characterization, and spectral data (PDF)

Accession Codes

CCDC 1878905, 1900206, and 1921289 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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