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Expedient Cobalt-Catalyzed C−H Alkynylation of (Enantiopure) Benzylamines

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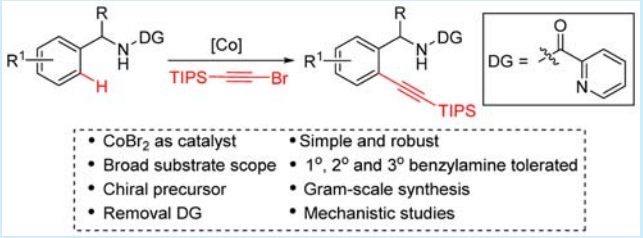
Supporting Information

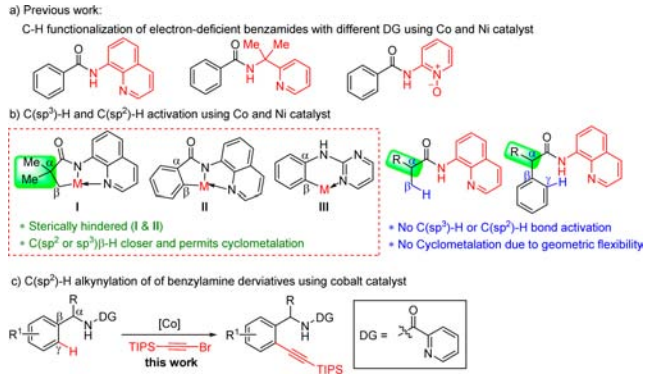
ABSTRACT: A unified strategy for cobalt-catalyzed *ortho*-C−H bond alkynylation of benzylamines is reported. Simple, commercially available $CoBr_2$ was used as a cobalt source. The developed alkynylation strategy is robust and efficient and has a broad substrate scope including 1°, 2°, and 3° benzylamines. The mechanistic study shows that C−H bond cleavage is reversible, and the kinetic study illustrates that the rate of reaction depends solely on the catalyst.



Transition-metal-catalyzed ubiquitous C−H bond activation circumvents the necessity of prefunctionalization of an organic molecule and has great demand in chemical synthesis, pharmaceuticals, and the development of functional materials.[1] In particular, C−H bond alkynylations have been identified as increasingly powerful alternatives to the classical palladium-catalyzed cross-coupling reaction.[2] Until recently, a majority of C−H bond alkynylation strategies have relied on precious and less abundant 4d and 5d transition metals.[3] However, the development of catalysts based on the naturally more abundant and economical first-row transition metals[4−6] for similar or better reactivity is still rare. On the other hand, after Daugulis's promising work[7] on bidentate directing-group assisted transition-metal-catalyzed activation of inert C−H bonds, several groups have been extensively exploiting this strategy. It is well recognized that the bidentate directing-group stabilizes transition metals in high oxidation states and is able to deliver the active catalytic site to a proximal C−H bond, typically via the formation of a five- or a six-membered metallacycle intermediate, and entails the C−H bond activation. In this context, the directing group assisted C−H bond activation of arenes catalyzed by inexpensive, benign first-row transition metals has gained considerable momentum with great potential applications to emulate the selectivity and reactivity of precious-metal catalysts.[8] In recent times, a notable progress in C−H bond functionalization has been accomplished using air-stable, inexpensive cobalt catalysts.[8k,9]

Despite notable efforts in bidentate group directed C−H bond alkynylation catalyzed by cobalt(II)- and nickel(II)-based systems, previous reports have been limited to electron-deficient benzamide derivatives.[4d−h,6c,d] Moreover, Cp*Co(III)-catalyzed C_2-selective C−H bond alkynylation of indole derivatives was also reported using hypervalent iodine−alkyne reagents[6a] and bromoalkynes.[6b] However, the activation of the *ortho*-C(sp^2)−H bond located further away from the coordinating functional group (or directing group; DG) remains a noteworthy challenge. To the best of our knowledge, there is no report on C−H bond activation of the *ortho*-C(sp^2)−H bond of benzylamines catalyzed by first-row transition metals except one pioneering example of cobalt-catalyzed alkenylation developed by Daugulis and co-workers.[8g] This is due to the geometric flexibility of the substrate, which does not permit cyclometalation (Scheme 1b).

Scheme 1. Directed-Group-Assisted Cobalt-Catalyzed C−H Bond Activation



Benzylamines constitute important synthetic precursors and are ubiquitous in agrochemical, peptide, pharmaceutical, and functional materials.[10] Various effective, practical methods have been developed to access benzylamines. Indeed, the stereochemistry at the benzylic position of α-substituted benzylamines can also be readily introduced using well-explored asymmetric synthesis technologies. Herein, we disclose a versatile and

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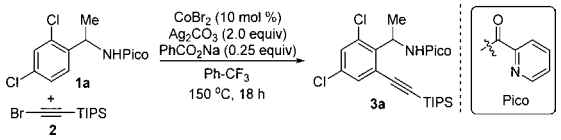
efficient cobalt-catalyzed *ortho*-C(sp^2)−H alkynylation of the benzylamine precursor with directing assistance. The present cobalt-catalyzed alkynylation has a broad substrate scope and can be scaled up under mild conditions. Significantly, 1°, 2°, 3°, and enantiopure benzylamines were well tolerated.

We began our cobalt-catalyzed C−H alkynylation of the benzylamine precursor with an evaluation of a range of cobalt salt, oxidant, base, solvent, and temperature in the presence of *N*-(1-(2,4-dichlorophenyl)ethyl)picolinamide (**1a**) and (triisopropylsilyl)ethynyl bromide **2** as representative coupling partners (Table 1). Initially, the reaction of **1a** and **2** in the

Table 1. Optimization of the Reaction Conditions



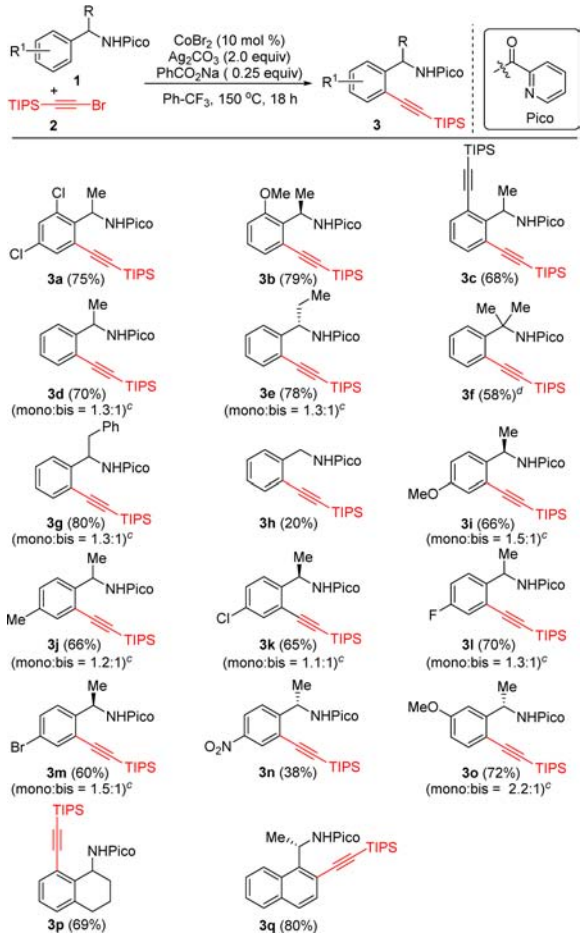
entry	reaction conditions[a]	yield[b] (%)
1	$Co(acac)_3$ used as [Co] source	41
2	$Cp^*Co(CO)I_2$	nr
3	$[Cp^*Co(C_6H_6)][PF_6]_2$	nr
4	standard conditions	75 (69)[c]
5	Cobalt(II)oxalate	40
6	$Co(OAc)_2$ used as [Co] source	55
7	$CoCl_2$ used as [Co] source	65
8	$Co(acac)_2$ used as [Co] source	60
9	at 100 °C	32
10	without [Co] cat	nr
11	without Ag_2CO_3	6
12	without $PhCO_2Na$	56
13	$AgSbPF_6$ instead of Ag_2CO_3	nr
14	NaOPiv instead of $PhCO_2Na$	51
15	CF_3CH_2OH used as solvent	trace

[a]Reaction conditions: **1a** (0.1 mmol), **2** (0.12 mmol), $CoBr_2$ (0.01 mmol), Ag_2CO_3 (0.20 mmol), sodium benzoate (0.025 mmol), and trifluorotoluene (1 mL) heated at 150 °C (bath temperature) for 18 h under argon atm. [b]Isolated yields. [c]Gram-scale synthesis. nr = no reaction.

presence of $Co(acac)_3$ (10 mol %), $PhCO_2Na$ (0.25 equiv), and Ag_2CO_3 as oxidant in trifluorotoluene was heated at 150 °C (bath temperature) for 18 h to yield the expected product **3a** in 41% isolated yield (Table 1, entry 1). Among a variety of cobalt salts, $CoBr_2$ proved to give optimal results (Table 1, entries 1−8). The necessity of each of the key reaction components was demonstrated through a series of control experiments (Table 1, entries 9−12). By lowering the temperature from 150 to 100 °C, we obtained the product **3a** in lower yield (32%; Table 1, entry 9), and no reaction was observed in the absence of the cobalt catalyst (Table 1, entry 10). Notably, trace amounts of **3a** were observed in the absence of an oxidant Table 1, entry 11). The efficiency of the cobalt-catalyzed C−H bond alkynylation reaction was significantly affected in the absence of $PhCO_2Na$ (Table 1, entries 12 and 14) and evidence that the coordination of the bidentate piconamide (DG) to the cobalt complex followed by a ligand exchange was accelerated by the (carboxylate) base. The effect of solvent was also investigated (Table 1, entry 15), and we found that the reaction proceeds efficiently in trifluorotoluene. Other solvents such as DMA, DCE, and CF_3CH_2OH were found to be ineffective, and no (or trace) alkynylated product **3a** was observed under optimal conditions. The synthetic application of this new cobalt-catalyzed C(sp^2)−H alkynylation strategy was further demonstrated through a gram-scale preparation of *ortho*-alkynylated benzylamine. As illustrated in Table 1 (entry 4), under the standard conditions, **1a** and **2** were smoothly converted to **3a** (1.1 g) in 69% isolated yield.[11] This representative transformation helps manifest the practical value that this method may offer for rapid and reliable access of *ortho*-alkynylated benzylamines under very mild reaction conditions.

With an optimized catalytic system in hand (Table 1), we set out to probe its versatility in the *ortho*-C(sp^2) alkynylation of various substituted benzylamines. The developed synthetic methodology is general and has a broad substrate scope as well as functional group tolerance. As shown in Scheme 2, the present cobalt-catalyzed C−H activation strategy is compatible with various benzylamines containing an electron-rich and electron-deficient substituent, affording the expected alkynylated products in moderate to good yields. Various *ortho*-substituted benzylamines such as 2,4-dichloro, -OMe, and **1c** were processed smoothly under our optimized conditions and gave the desired

Scheme 2. Cobalt-Catalyzed *ortho*-C−H Alkynylation of Benzylamines[a,b]



[a]Reaction conditions: **1** (0.1 mmol), **2** (0.12 mmol (**1a−c** and **1p−q**) or 0.25 mmol (**1d−o**)), $CoBr_2$ (0.01 mmol), Ag_2CO_3 (0.20 mmol), $PhCO_2Na$ (0.025 mmol), and trifluorotoluene (1 mL) heated at 150 °C (bath temperature) for 18 h under argon atmosphere. [b]Isolated yields. [c]The ratios of mono- (**3**)/bis-alkynylation (**4**) products are based upon the individual isolated yields. [d]0.05 mmol of **2** was used, and the yield was based on **2**.

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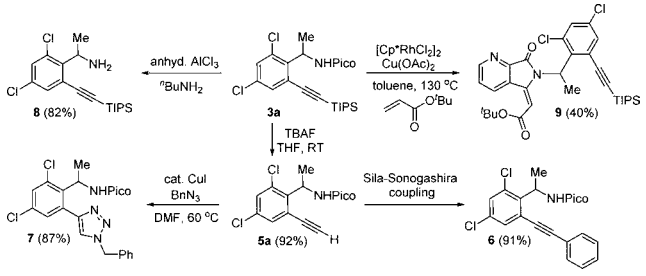
product in good yields (products **3a** in 75%, **3b** in 79%, and **3c** in 68% isolated yields). To our delight, diverse α-substituted benzylamines were also successfully alkynylated at the *ortho* position. Thus, alkynylation of secondary and tertiary amines gave higher yields (**3d**–**g**) compared to those of the the corresponding primary benzylamine (e.g., in the case of **1h**, a relatively lower yield of **3h** was observed). This is due to the geometric flexibility of the primary benzylamine, which leads to the difficulty of a picolinamide-directed cyclometalation. It was found that a range of benzylamines bearing various electron-donating, -withdrawing, and halogen substituents at the *para* position of the arene ring were effectively coupled with **2** and yielded the *ortho*-alkynylated benzylamines (**3i**–**m**) in 60–70% isolated yields. However, synthesis of halo-substituted *o*-alkynylbenzylamines using the traditional approach, Pd-catalyzed "Sonogashira coupling", is very difficult and rather scare. The strong electron-withdrawing nitro group gave only monoalkynylated product **3n** in low yield (38%). It is noteworthy that the cyclic amine (**1p**) and α-methyl naphthyl amine (**1q**) also proceeded efficiently and yielded the corresponding alkynylated products in good yields (products **3p** in 69% and **3q** in 80% isolated yields) under our catalytic conditions. Both mono- and bis-alkynylated products were isolated easily because of their different R_f values. Notably, the developed cobalt-catalyzed C–H alkynylation strategy is applicable for practical synthesis of enantiomerically pure *ortho*-alkynylated benzylamines, and no racemization was observed under our optimal conditions (products **3b**, **3e**, **3i**, **3k**, **3m**–**o**, and **3q** in Scheme 2 and Scheme 4f).

The diversification of alkynylated benzylamine derivatives is shown in Scheme 3. The chemoselective removal of the TIPS

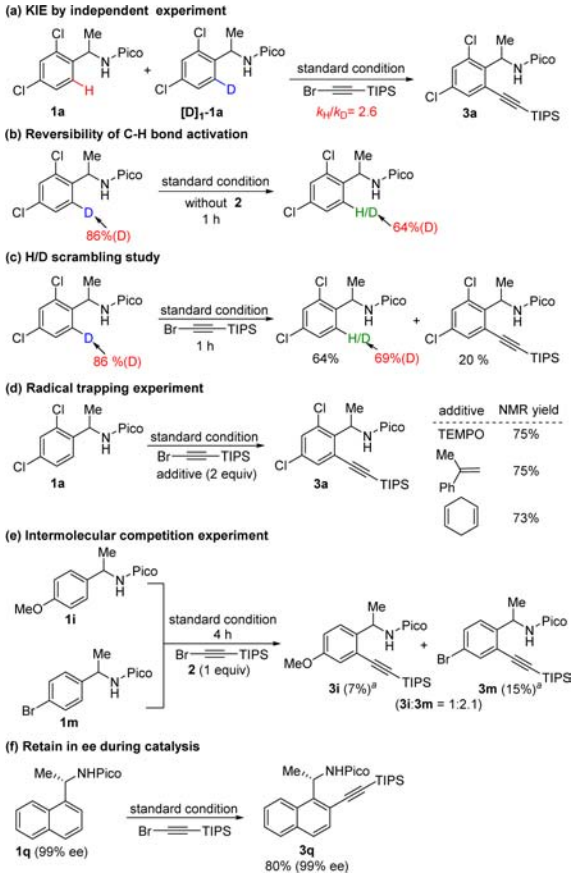
Scheme 3. Diversification of *Ortho*-Alkynylated Benzylamines



group of **3a** was easily achieved by treatment with TBAF under standard reaction conditions to afford **5a**.[11] The desilylated compound **5a** (derived from **3a**) provided the sila-Sonogashira coupling product **6** in 91% isolated yield, and the "click" reaction of **5a** with benzyl azide yielded **7** in 87% yield. The deprotection of bidentate DG (picolinamide) can be easily achieved by using Lewis catalyst to obtain terminal *o*-alkynylbenzylamine **8** in 82% yield. A Rh(III)-catalyzed cascade oxidative olefination and cyclization of **3a** with *tert*-butyl acrylate to enable **9** in 40% yield was also achieved.

Given the observed reactivity of the present $CoBr_2$ catalyzed alkynylation of benzylamine precursor, we embarked on the mechanistic studies to delineate a plausible catalytic pathway. In this regard, several control experiments were performed under standard conditions (Scheme 4). The intermolecular isotopic study of two parallel competition reactions between **1a** and [$\mathbf{D}_1$]-**1a**, a kinetic isotope effect (KIE) of k_H/k_D = 2.6 was observed. The H/D exchange experiment indicates that the present cobalt-catalyzed *ortho* C–H bond activation of benzylamines is

Scheme 4. Mechanistic Studies



[a]Combined yields of mono- and bis-alkynylated products.

reversible. H/D scrambling was observed when the reaction was performed with an isotopically labeled substrate ([$\mathbf{D}_1$]-**1a**), signifying that insertion of cobalt–metal into the C–H bond is also reversible. This study may indicate that the proto-decobaltation is faster than the alkyne insertion step. Furthermore, radical trapping experiment carried out using (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO), cyclohexa-1,4-diene, and prop-1-en-2-ylbenzene under standard reaction condition, and it was observed that the reaction was not inhibited, which confirms that the single-electron transfer (SET) mechanism could be ruled out. A competition experiment with a different electronic substituent on benzylamine revealed that the reaction favors the electron-withdrawing group.

The order of reaction in each component of the current cobalt-catalyzed alkynylation of benzylamine **1a** with **2** was determined by individually by using the initial rate approximation (Figure 1). The rate of alkynylation reaction is nearly the same for various

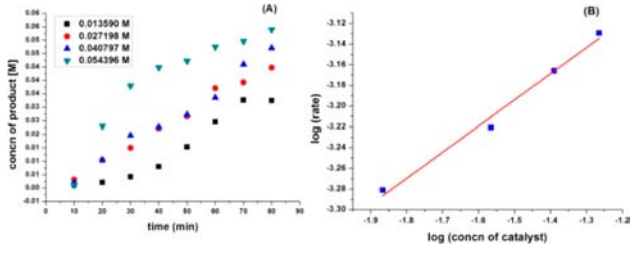


Figure 1. Kinetic studies.

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concentration of **1a**. It shows that the reaction is zeroth order with respect to the various concentrations of **1a**. Similarly, the dependence of reaction with **2**, oxidant, and additive was carried out, and the results indicate that the reaction time was not affected in various concentrations of **2**, oxidant, and additive. However, by changing different loadings of cobalt catalyst, the rate of reaction increased and a slope of 0.25 was obtained from the plot of log(rate) vs log(concn of catalyst), indicating a fractional order alkynylation reaction. Thus, the rate of reaction depends on the catalyst.

In conclusion, we have developed expedient, robust cobalt-catalyzed C−H alkynylation of benzylamines using easily removable piconamide as a bidentate auxiliary. This unified strategy has broad substrate scope including 1°, 2°, 3°, and enantiopure benzylamines and various functional group tolerances. The mechanistic study shows that C−H bond cleavage is reversible, and the kinetic study illustrates that the rate of reaction depends solely on the catalyst.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02549.

Details on experimental procedures, mechanistic studies, characterization data of all compounds, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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