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Co(III)-Catalyzed *Z*-Selective Oxidative C–H/C–H Cross-Coupling of Alkenes with Triisopropylsilylacetylene

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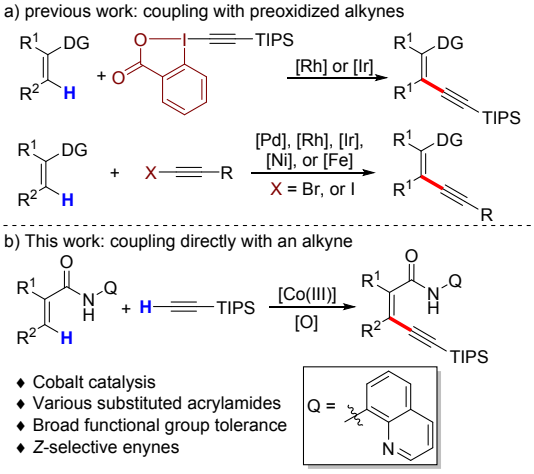
A Co(III)-catalyzed direct oxidative C–H/C–H cross-coupling reaction of acrylamides with triisopropylsilylacetylene is presented. It is applicable to unsubstituted, internal and terminal acrylamides with a broad functionality tolerance. The feasibility of this protocol is successfully demonstrated by the late-stage alkynylation of a derivative of steroid drug Epristeride.

Conjugated enynes are not only widely found in natural products,[1] pharmaceuticals,[2] bioactive molecules,[3] and organic functional materials,[4] but also important synthetic intermediates toward furan derivatives, polycyclic lactones, multisubstituted aromatics, metal complexes, polyynes, and allenes.[5] Therefore, concise and efficient protocols to synthesize enynes are very attractive and desired. During the past decades, significant advances have been made in the field of transition-metal catalyzed cross-coupling reactions for the C–C bond formation.[6] The direct oxidative C–H/C–H cross-coupling of alkenes with alkynes is an ideal strategy to build enynes due to the excellent atom- and step economy. However, this methodology is much less developed with only sporadic reports[7] in comparison with the cross-coupling of arenes with alkynes.[8]

The first example of the cross-coupling of alkenes with terminal alkynes was presented by Jung et al in 2009 using $Pd(TFA)_2$ as the catalyst, wherein (*E*)-enynes were obtained via a heck-type mechanism with inevitable homocoupling of alkynes.[7a] In 2012, Zhong's group reported the synthesis of (*Z*)-enynes via a $Pd(OAc)_2$-catalyzed cross-coupling of allylic ethers with terminal arylalkynes in the presence of a phosphine ligand.[7b] It is noted that only mono-substituted ethylenes were reported in these two methods, and a large excess of alkenes were necessary.

The main challenges encountered are the easy homocoupling of alkynes and side reactions of alkenes under oxidative conditions. To address these issues, the so called "inverse Sonogashira strategy" was applied by employing preoxidized alkyne sources such as ethynylbenziodoxolones (EBX)[9] and haloalkynes,[10] which apparently sacrifices the atom- and step economy (Scheme 1a). The protocols using EBX are generally mild enough to accommodate most alkenes, but only precious rhodium and iridium catalysts are now workable. Although non-precious nickel[10e] and iron catalysts[10g] are applicable when 1-bromoalkyne is employed, a very narrow scope of alkenes (only five examples) is reported. It should be noted that introduction of a proper directing group (DG) could exclusively provide (*Z*)-enynes.[11]



Scheme 1. Cross-coupling reactions of alkenes with alkynes.

Due to our continuous interest in C–H functionalization of alkene derivatives,[12] we herein would like to report our success in the direct alkynation of acrylamides with triisopropylsilylacetylene by using a cobalt catalyst and the 8-aminoquinoline directing group[13] (Scheme 1b). This reaction is the first example of a general and inexpensive oxidative C–H/C–H cross-coupling protocol between a broad scope of alkene derivatives and a terminal alkyne. Very recently, limited

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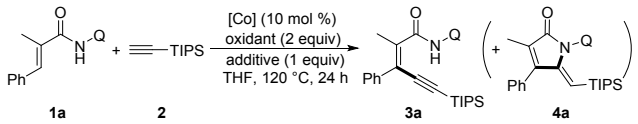
examples of an Ir-catalyzed cross-coupling of cinnamamides with triisopropylsilylacetylene was reported.[8g]

Table 1. Optimization of the reaction conditions[a,b]



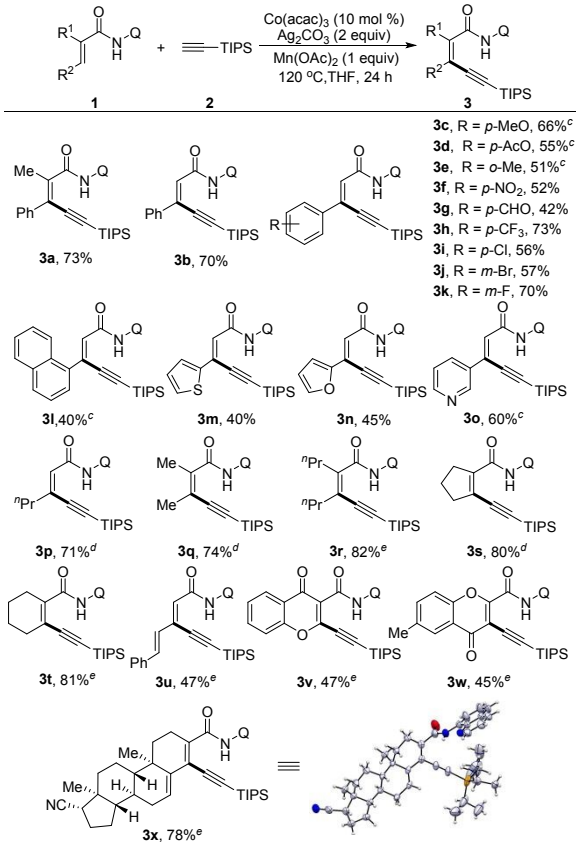
Entry	Oxidant	Additive	Yield of **3a** (%)
1	Ag_2CO_3	KOAc	39%
2	Ag_2CO_3	HOAc	trace
3	Ag_2CO_3	$Mn(OAc)_3$	56%
4	**Ag_2CO_3**	**$Mn(OAc)_2$**	**73%**
5	Ag_2CO_3	$Zn(OAc)_2$	29%
6	Ag_2CO_3		27%
7	Ag_2O	$Mn(OAc)_2$	29%
8	Ag_2SO_4	$Mn(OAc)_2$	trace
9	AgOAc	$Mn(OAc)_2$	trace
10	$Cu(OAc)_2$	$Mn(OAc)_2$	11%
11[c]	Ag_2CO_3	$Mn(OAc)_2$	n.d
12		$Mn(OAc)_2$	n.d

[a]Reaction conditions: $Co(acac)_3$ (0.01 mmol, 10 mol %), oxidant (0.2 mmol, 2.0 equiv), acrylamide **1a** (0.1 mmol, 1.0 equiv), alkyne **2** (0.15 mmol, 1.5 equiv), additive (0.1 mmol, 1.0 equiv), and THF (1 mL) at 120 °C for 24 h under a N_2 atmosphere. n.d. = not detected. [b]Isolated yield. [c]Without $Co(acac)_3$. Q = 8-quinolinyl.

We initiated our study with the reaction of (*E*)-2-methyl-3-phenyl-*N*-(quinolin-8-yl)acrylamide **1a** with triisopropylsilylacetylene **2** catalyzed by various nonprecious metal salts. It was found that $Co(acac)_2$ and $Co(acac)_3$ provided **3a** in around 40% yields. Interestingly, a mixture of the cross-coupled product **3a** (35%) and the annulated product **4a** (5%) was obtained under the catalysis of $Co(acac)_2$, while $Co(acac)_3$ gave **3a** in 39% yield as the single product (Table 1, entry 1. For the detailed catalyst screening, see Table S1). Addition of HOAc instead of KOAc ceased the reaction (Table 1, entry 2). The use of $Mn(OAc)_3$ increased the yield of **3a** to 56%, and its yield was further improved to 73% yield by using $Mn(OAc)_2$, while $Zn(OAc)_2$ showed no beneficial effect and gave a similar result to the reaction with no additive (Table 1, entries 3-6). The exact role of $Mn(OAc)_2$ is unclear at current stage.[14] Varying different oxidants revealed that Ag_2CO_3 was the most effective (Table 1, entries 7-10). No reaction took place in the absence of either $Co(acac)_3$ or Ag_2CO_3 (Table 1, entries 11-12), indicating this is a Co(III)-catalyzed oxidative cross-coupling reaction. Finally, the optimal reaction was set to be $Co(acac)_3$ (10 mol %), Ag_2CO_3 (2.0 equiv), $Mn(OAc)_2$ (1.0 equiv) in THF (1.0 mL) at 120 °C for 24 h under N_2 (Table 1, entry 4).

With the optimized reaction conditions in hand (Table 1, entry 4), the scope of internal acrylamides **1** was investigated (Table 2). Acrylamides bearing methoxy, acetoxy, methyl, nitro, formyl, trifluoromethyl, chloro, bromo, and fluoro groups on the β-phenyl ring were all affordable to provide the targeted products (**3a**-**3k**) in moderate to good yields. Nevertheless, active functionalities such as hydroxy, amine and carboxylic acid were incompatible. It is noted that the acrylamides with electron-donating groups reacted sluggish and prolonged time was necessary. The same situation happened for sterically hindered substrates (**1e** and **1l**), and the corresponding enynes were obtained in 51% and 40% yields, respectively. The reactions of 2-thienyl and 2-furyl substituted acrylamides gave complicated mixtures due to their decomposition under the catalytic conditions, and the desired coupled products were isolated in moderate yields. For the 3-pyridinyl substituted acrylamide, however, the reaction ran clearly but slowly, affording **3o** in 60% yield after 36 h.

Table 2. Scope of internal acrylamides[a,b]

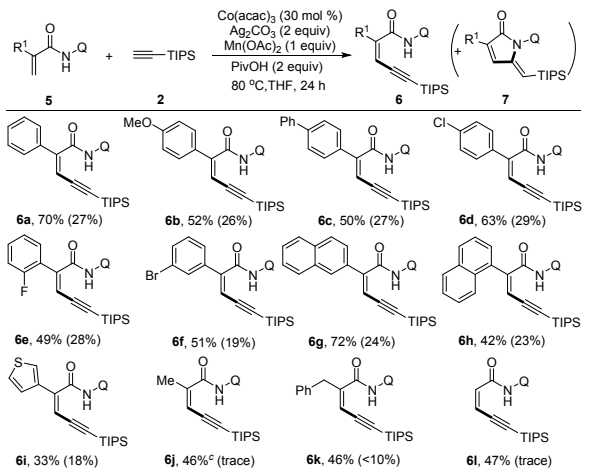


[a]Reaction conditions: $Co(acac)_3$ (0.01 mmol, 10 mol %), Ag_2CO_3 (0.2 mmol, 2.0 equiv), $Mn(OAc)_2$ (0.1 mmol, 1.0 equiv), internal acrylamide **1** (0.1 mmol, 1.0 equiv), alkyne **2** (0.15 mmol, 1.5 equiv), and THF (1 mL) at 120 °C for 24 h under a N_2 atmosphere. [b]Isolated yield. [c]36 h. [d]$Co(acac)_3$ (0.02mmol, 20 mol %), Ag_2CO_3 (0.2 mmol, 2.0 equiv), $Mn(OAc)_2$ (0.2 mmol, 2.0 equiv), 26 h. [e]The same conditions as in *d* except reacting for 48 h.

β-Alkyl acrylamides are inert substrates toward the cross coupling reaction with **2**. The reaction could not finish under the standard conditions even after extended time. Fortunately, addition of 20 mol% $Co(acac)_3$ and 2 equiv of $Mn(OAc)_2$ was found effective. The reactions nicely afforded **3p** and **3q** in 71% and 74% yields, respectively.

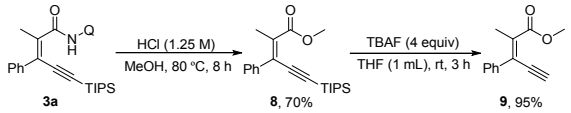
However, the acrylamide **1r** with longer *n*-propyl chains on both the α and β positions is even more inert, the reaction took 48 h to give **3r** in a yield of 82%. Interestingly, although the enyne products were both obtained in similar yields around 80%, the cyclohexenyl substrate exhibited much lower reactivity than the cyclopentenyl counterpart as much longer reaction time was needed. It is also noted that the sp^3 carbon alkynylated products were not observed.[15] The reaction of the (2*E*,4*E*)-5-phenylpenta-2,4-dienamide substrate installed the alkynyl group on the 3-position to give **3u** in 47% yield, suggesting that the directing group plays an important role in this reaction. The present protocol provides an efficient and concise method for the late-stage modification of natural products and pharmaceuticals. For examples, a pair of isomeric derivatives of chromone were directly alkynylated in moderate yields (**3v** and **3w**). Epristeride is a steroid drug used in the treatment of enlarged prostate. A smooth alkynylation of its derivative **1x** with **2** provided the desired product **3x** in 78% yield. The structure of **3x** was confirmed to perserve the configuration by the single crystal X-ray diffraction analysis.[16]

Table 3. Scope of terminal acrylamides[a,b]



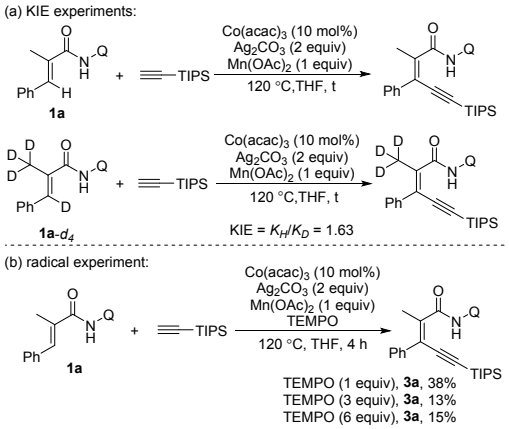
[a]Reaction conditions: $Co(acac)_3$ (0.03 mmol, 30 mol %), Ag_2CO_3 (0.2 mmol, 2.0 equiv), $Mn(OAc)_2$ (0.1 mmol, 1.0 equiv), PivOH (0.2 mmol, 2.0 equiv), terminal acrylamide **5** (0.1 mmol, 1.0 equiv), alkyne **2** (0.15 mmol, 1.5 equiv), and THF (1 mL) at 80 °C for 24 h under a N_2 atmosphere. [b]Isolated yield. [c]48 h. Yields of **7** are in the parentheses.

A different situation was encountered when terminal acrylamides **5** were tested (Table 3). The desired coupled products **6** were generated in low yield accompanying with a comparable amount of annulated products **7** under the standard conditions.[17] For example, the cross-coupling of **5a** with **2** furnished **6a** in only 20% yield and the annulated product **7a** in 13% yield. No **5a** was left and a lot of impurities also emerged. Modification of the standard conditions was then conducted (see Table S2 in ESI) and the key findings are: 1) Lowering the temperature to 80 °C resulted in a cleaner reaction giving both **6a** and **7a** in low yields with **5a** recovered; 2) The yields of **6a** and **7a** were simultaneously raised with increased amounts of $Co(acac)_3$, and reached about 40% when 30 mol% of $Co(acac)_3$ was employed; 3) **7a** was inevitably generated, but addition of 2 equiv of pivalic acid could suppress the annulation to the maximum extent. Under the modified conditions, a range of α-aryl acrylamides (**5a**-**h**) were successfully converted into the (*Z*)-enyne products (**6a**-**h**) in 42-72% yields and the corresponding annulated products (**7a**-**h**) in 19-29% yields. The same trend as for β-aryl acrylamides was found: Products with an electron-donating group on the phenyl ring (**6b** vs **6d**) and more steric hindrance (**6h** vs **6g**) were obtained in lower yields. The instability of α-(3-thienyl) acrylamide resulted in a low yield of 33% for **6i**. For α-alkyl and unsubstituted acrylamides, the targeted enynes **6j**-**l** were attained in moderate yields and almost no annulated by-products were observed. It should be pointed out that with this loading of $Co(acac)_3$ (30 mol %) and Ag_2CO_3 (2.0 equiv), the cost of our protocol is still much lower than those methods utilizing Rh and Ir catalysts, even not considering the preparation of preoxidized alkyne reagents.[18] Moreover, Ag_2CO_3 could also be easily recycled by using a reported procedure (see Section V in ESI).[19]



Scheme 2. Removal of the directing and protecting groups

The 8-aminoquinolinyl group could be easily removed under acidic conditions.[20] For example, enyne **3a** was converted to its methyl ester form **8** in 70% yield by refluxing in methanol in the presence of hydrochloric acid for 8 h. Then the silyl group was removed by treating with TBAF in THF at room temperature to afford the corresponding terminal 1,3-enyne **9** in almost quantitative yield (Scheme 2), providing opportunity for further derivation. To show the practicability of this method, a gram-scale experiment was conducted. The reaction of **1a** on 4 mmol scale under the standard conditions for 48 h provided **3a** in 68% yield (see Section VII in ESI).



Scheme 3. Mechanistic study.

To shed light on the reaction mechanism, the kinetic isotopic effect (KIE) was calculated to be 1.63 based on two independent reactions of **2** with **1a** and **1a**-d_4 (Scheme 3a), suggesting that the C–H bond cleavage in **1a** might not be involved in the rate-determining step. Although the attempts to isolate the coordinated acrylamide-Co intermediates were unsuccessful, the key intermediates were

detected by the MALDI-TOF analysis (see Section VIII in ESI). Moreover, when a radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was added, the cross-coupling of **1a** with **2** was largely but incompletely suppressed, suggesting both a radical and nonradical pathways could be involved (Scheme 3). Based on the preliminary results and previous reports,[20,21] a plausible mechanism is proposed in Scheme S1.

In summary, we have developed a direct oxidative C–H/C–H cross-coupling of acrylamides with triisopropylsilylacetylene by employing a cobalt catalyst with the assistance of the bidentate 8-aminoquinoline directing group. This reaction features mild reaction conditions, inexpensive reagents, a broad acrylamide scope, good functional group tolerance and *Z*-selectivity of enyne products, which makes it a very useful protocol for late-stage modifications of pharmaceuticals and natural products.

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Conflicts of interest

There are no conflicts to declare.

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