Advanced Synthesis & Catalysis

Accepted Article

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To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201701406

Link to VoR: http://dx.doi.org/10.1002/adsc.201701406

10.1002/adsc.201701406

COMMUNICATION

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Cobalt(III)–Catalyzed C–H Activation: A Secondary Amide Directed Decarboxylative Functionalization of Alkynyl Carboxylic Acids Wherein Amide NH–group Remains Unreactive

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Received: ((will be filled in by the editorial staff))

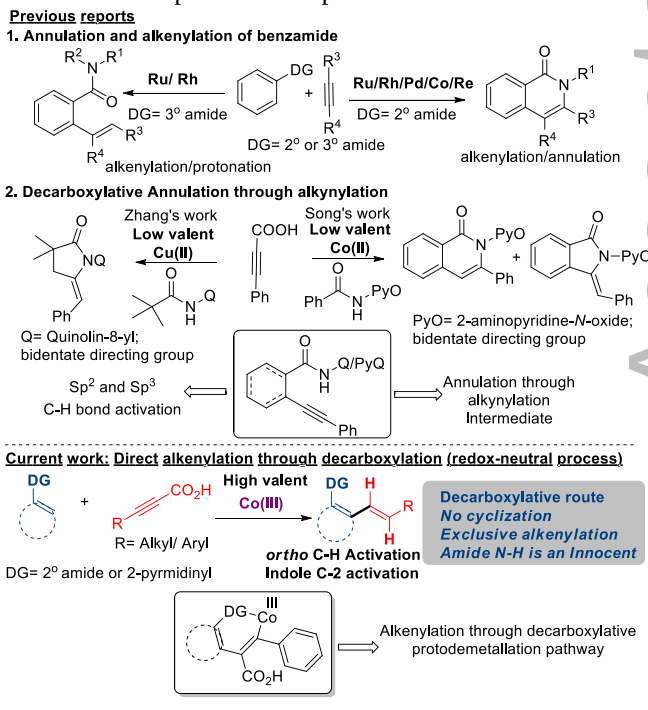
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######

Abstract. A Co(III)-catalyzed C-H activation reaction for *ortho*-alkenylation of benzamides (aryl/heteroaryl) and C2-alkenylation of indole derivatives have been developed using alkynyl carboxylic acid as an alkene source. A high regioselectivity has been achieved in the formation of disubstituted alkenes, and the possible cyclic products were not observed. This efficient alkenylation shows a broad range of substrate scope with a good functional group tolerance. The application of the methodology has been showcased by transforming an alkenylated amide to a 3-hydroxy isoindolinone derivative.

Keywords: Cobalt; amides; alkynyl carboxylic acid; alkenylation; C-H activation

Co-Catalyzed C-H activation strategies are emerging as powerful methods for C-H functionalization, which are on par with other precious transition metal catalyzed reactions using Ru-, Rh-, Ir-catalysts.[1] The *ortho*-alkenylation of benzamides using directing group strategy has been achieved using either alkenes (oxidative process) or alkynes (redox neutral process) as coupling partners.[2-5] In the oxidative process, the insertion of alkenes followed by β-hydride elimination leads to the alkenylation of benzamides. The reaction of benzamides with alkynes involves either alkenylation/protonation or alkenylation/annulation, which depends on the nature of the amide (secondary or tertiary) employed in the reaction. Alkenylation of tertiary benzamides with alkynes has been accomplished using either Ru- or Rh-catalysts.[6,7] Due to the unavailability of a free NH-group, these reactions proceed through an alkyne insertion followed by the protodemetallation furnishing the corresponding alkenylated product. A similar reaction with an amide that has a free NH-group, most of the time, leads to an annulated product in the presence of Pd,[8] Ru,[9] Rh,[10] Re,[11a] Ni,[11b] or Co[12] catalysts (Scheme 1). In the reaction of secondary benzamide with alkynes, the NH-group of benzamide is a reactive directing group, which participates in the reaction leading to the formation of a cyclic product. Therefore, obtaining an olefin derivative, exclusively, in the reaction of a secondary benzamide with alkyne derivatives without forming the cyclic product is a challenging task, which offers the advantage of modifying the olefins into a variety of functional groups. Nevertheless, coupling the terminal alkynes is one of the strategies for synthesizing disubstituted olefin derivatives using directing group strategy. For example, high-valent Co-catalysts were used for the alkenylation of indoles, pyrroles, 6-aryl purine derivatives, etc.[13] Whereas low-valent Co-catalysts are known to furnish the corresponding annulated products.[13] Compared to

Scheme 1. Comparision with previous work



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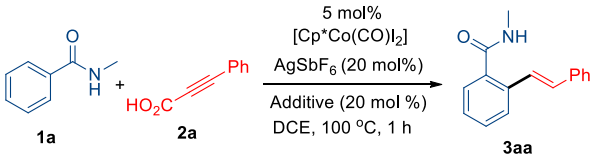
the terminal alkynes, it is advantageous to use alkynyl carboxylic acids as coupling partners as alkynyl carboxylic acids are bench stable and easy to synthesize.[14a,b] Besides, most of the aryl acetylene derivatives are obtained either from the deprotection of aryl silyl acetylenes or the decarboxylation of the corresponding aryl alkynyl carboxylic acids.[14c] Zhang[15a] and Song[15b] have reported the sequential decarboxylative alkynylation followed by annulation of sp^3 and sp^2 C-H bonds catalyzed by low-valent metal catalysts such as Cu(II)- and Co(II)-catalysts using bidentate directing group (Scheme 1). Recently, Ellman's group has used tertiary amide as a directing group for Co(III)-catalyzed three-component transformation to obtain alkenyl halides.[16] This method relies on thiophene/furan derived amides. In continuation of our efforts,[17] we have employed alkynyl carboxylic acid as a source of an alkene, for the first time, in the presence of high-valent metal catalytic system. Thus, herein we report a Co(III)-catalyzed, amide-directed, alkenylation of secondary benzamides using alkynyl carboxylic acid as an alkene source, in which the NH-group of the amide does not facilitate the cyclization.

The optimization studies were started by examining the reaction of *N*-methyl benzamide **1a** (0.3 mmol) with phenylpropiolic acid **2a** (0.45 mmol). The reaction of **1a** with **2a** in the presence of Cp*Co(CO)I_2 (5 mol%) as a catalyst, $AgSbF_6$ (20 mol%) as an activator and NaOAc (20 mol%) as an additive in DCE (2 mL) at 100 °C for 1 h furnished the corresponding alkenylated product **3aa** in 24% yield (Table 1, entry 1). Changing the additive to AcOH or PivOH has no significant bearing on the outcome of the reaction (entries 2 and 3). AdCOOH as an additive was recently employed in related hydroarylation reactions.[18] Thereby, using AdCOOH as an additive has resulted in improving the yield of the product **3aa** to 45% (entry 4). Further screening with 1 equiv of both **1a** and **2a** furnished the desired product **3aa** in 54% (entry 5). Finally, increasing the amount of **2a** to 1.5 and 2 equiv increased the yield of **3aa** to 67 and 78%, respectively (entries 6 and 7). Switching the acid additive to KOAc, CsOAc, and NaOPiv did not help in improving the yield of **3aa** (entries 8, 9, and 10). There was no considerable improvement in the yield when the reaction was performed at 120°C or 80°C (entries 11 and 12). Using cationic cobalt complex, $[Cp^*Co(CH_3CN)_3][SbF_6]_2$ (10 mol%), furnished the product **3aa** in 49% yield (entry 13). Reactions in the absence of [Cp*Co(CO)I_2] or $AgSbF_6$ or AdCOOH did not provide the product **3aa** (entries 14-16). Performing the reaction with phenyl acetylene instead of phenylpropiolic acid (**2a**) afforded the product **3aa** in 68% yield (entry 17). As aryl acetylene derivatives are obtained either from the deprotection of aryl silyl acetylenes or from the decarboxylation of aryl alkynyl carboxylic acids,[14] and the reaction of phenylpropiolic acid yielded a better result than phenyl acetylene, the scope of the reaction has been explored using arylalkynyl carboxylic acids. Further screening of solvents, additives, silver salts, catalyst loading and temperature did not show any remarkable improvement in the yield of **3aa** (see the SI for detailed optimization studies).

Table 1. Optimization studies[a]



entry	**1a** (equiv)	**2a** (equiv)	Additive (20 mol%)	NMR yield (%)[b]
1	1	1.5	NaOAc	24
2	1	1.5	AcOH	33
3	1	1.5	PivOH	24
4	1	1.5	AdCOOH	45
5	1	1	AdCOOH	54
6	1.5	1	AdCOOH	67
7	**2**	**1**	**AdCOOH**	**78 (72)[c]**
8	2	1	KOAc	20
9	2	1	CsOAc	43
10	2	1	NaOPiv	54
11	2	1	AdCOOH	78[d]
12	2	1	AdCOOH	60[e]
13	2	1	AdCOOH	49[f]
14	2	1	AdCOOH	nd[g]
15	2	1	AdCOOH	nd[h]
16	2	1	none	nd
17	2	1	AdCOOH	68[i]

[a] Reaction conditions: **1a** (XX mmol), **2a** (YY mmol), [Cp*Co(CO)I_2] (5 mol%), [$AgSbF_6$] (20 mol%), additive (20 mol%), DCE (2 mL), at 100 °C for 1 h. [b] ^{1}H NMR yield (using terephthaldehyde as an internal standard). [c] Isolated yield. [d] Reaction was performed at 120 °C. [e] Reaction was performed at 80 °C. [f] 10 mol% of $[Cp^*Co(CH_3CN)_3][SbFb_6]_2$ was used instead of [Cp*Co(CO)I_2]. [g] Absence of Co-catalyst. [h] Absence of $AgSbF_6$. nd= not detected. AdCOOH= Adamantane-1-carboxylic acid. [i] Phenylacetylene instead of **2a**.

With the optimal conditions (entry 7, Table 1), the scope of the alkenylation reaction was evaluated (Scheme 2). The reaction of *N*-methylbenzamide, *N*, 4-dimethylbenzamide, and 4-methoxy-*N*-methylbenzamide with phenylpropiolic acid **2a** under the optimal reaction conditions furnished the corresponding alkenylated products **3aa**, **3ba**, and **3ca** in good yields (72, 67 and 69%, respectively). Halogen substituted benzamides such as 4-F, 4-Br, and 4-I substituted *N*-methyl benzamide derivatives afforded the corresponding products **3da**, **3ea**, and **3fa** in good yields (66, 72, and 77%, respectively). Electron-withdrawing groups such as 4-CF_3 and 4-NO_2-substituted benzamide derivatives also underwent smooth reaction leading to the corresponding alkenylated products **3ga** and **3ha** in

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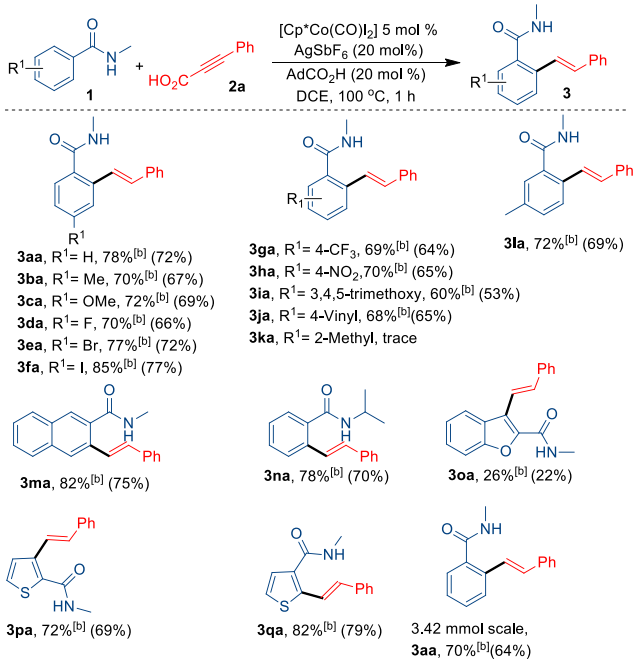
64 and 65% yields, respectively. 3,4,5-Trimethoxy- and 4-vinyl-substituted *N*-methyl benzamides furnished the products **3ia** and **3ja** in moderate to

Scheme 2. Scope for benzamide derivatives[a,b]

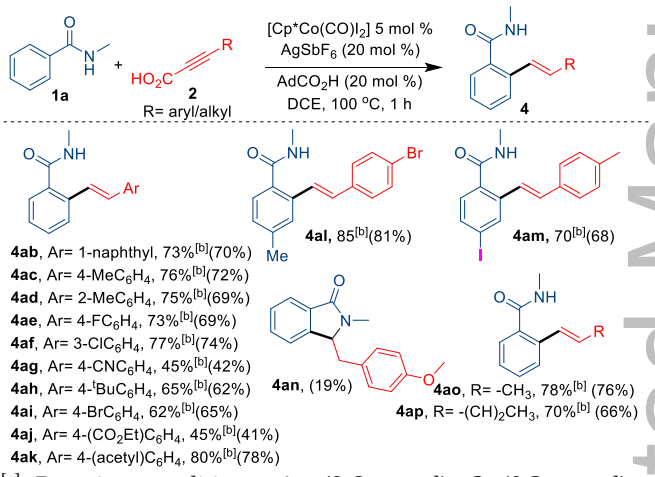


[a] Reaction conditions: **1** (0.6 mmol), **2a** (0.3 mmol), [Cp*Co(CO)I_2] (5 mol%), [$AgSbF_6$] (20 mol%), $AdCO_2H$ (20 mol%), DCE (2 mL), at 100 °C for 1 h. [b] Measured by ^{1}H NMR with terephthalaldehyde as the internal standard. Isolated yields are in parentheses.

good yields (53 and 65%, respectively). *N*,2-Dimethylbenzamide afforded the corresponding product **3ka** in a trace amount, which may be attributed to the steric factors. The reaction of *N*,3-dimethylbenzamide, which has a sterically free *ortho*-position, afforded the corresponding alkenylated product **3la** in 69% yield. *N*-Methyl-2-napthamide and *N*-isopropyl benzamides furnished the desired products **3ma** and **3na** in good yields (75 and 70%, respectively). The reaction of benzofuran-derived amide furnished the corresponding alkenylated product (**3oa**) in low yield, whereas thiophene-derived amides furnished their corresponding alkenylated products **3pa** and **3qa** in 69 and 79% yields, respectively. A scale up experiment of phenylpropiolic acid **2a** (3.42 mmol, 500 mg) with **1a** under optimal reaction conditions afforded the corresponding product **3aa** in 64% yield.

After examining the scope of the reaction with a variety of benzamide derivatives with phenylpropiolic acid, an investigation was undertaken to explore the scope of the alkenylation reaction with a few alkynyl carboxylic acid derivatives (Scheme 3). Thus, 1-naphthyl, 4-methyl, 2-methyl, 4-fluoro and 3-chloro substituted phenylpropiolic acid derivatives underwent a facile reaction with *N*-methyl benzamide (**1a**) furnishing the corresponding alkenylated products **4ab**, **4ac**, **4ad**, **4ae**, and **4af** in good yields (70, 72, 69, 69, and 74%, respectively). Further, performing the reaction of several derivatives of propiolic acids such as 3-(4-cyanophenyl)propiolic acid, 3-(4-(tert-butyl)phenyl)propiolic acid, 3-(4-bromophenyl)propiolic acid, 3-(4-(ethoxycarbonyl)phenyl)propiolic acid, and 3-(4-acetylphenyl)propiolic acid with **1a** afforded the corresponding alkenylated products **4ag**–**4ak** in moderate to good yields. Additionally, substituted benzamides such as *N*,4-dimethylbenzamide, and 4-iodo-*N*-methylbenzamide reacted well with 3-(4-bromophenyl)propiolic acid and 3-(p-tolyl)propiolic acid, respectively, furnishing the products **4al** and **4am** in 81% and 68%, respectively. However, 4-methoxyphenylpropiolic acid under the optimal reaction conditions failed to afford the corresponding alkenylated product but the corresponding cyclic product **4ag** was obtained in 19% yield. Alkyl substituted alkynyl carboxylic acids were also found to be effective substrates. Thus, the reaction of but-2-ynoic acid and hex-2-ynoic acid with **1a** furnished their corresponding alkenylated products **4ah** and **4ai** in good yields (76 and 66%, respectively).

Scheme 3. Scope for alkynylcarboxylic acids[a,b]



[a] Reaction conditions: **1a** (0.6 mmol), **2** (0.3 mmol), [Cp*Co(CO)I_2] (5 mol%), [$AgSbF_6$] (20 mol%), $AdCO_2H$ (20 mol%), DCE (2 mL), at 100 °C for 1 h. [b] Measured by ^{1}H NMR with terephthalaldehyde as the internal standard. Isolated yields are in parentheses.

After successfully demonstrating the scope of the alkenylation reaction of benzamide derivatives with alkynyl carboxylic acid derivatives, we turned our attention to the scope of the reaction with indole systems (Scheme 4). In the initial experiments, the reaction of *N*,*N*-dimethyl-1H-indole-1-carboxamide with phenylpropiolic acid (**2a**) under the optimal reaction conditions found to be less effective (17%, see the SI). As it is well-known that 2-pyrimidinyl group is compatible with Co-catalyzed reactions,[1],[19] we employed *N*-pyrimidyl indole as a substrate. The reaction of *N*-pyrimidyl indole with phenylpropiolic acid **2a** under slightly modified conditions (NaOAc was used instead of AdCOOH see SI) afforded the corresponding 2-alkenylated indole derivative in good yields. Thus, the reaction of *N*-pyrimidyl indole

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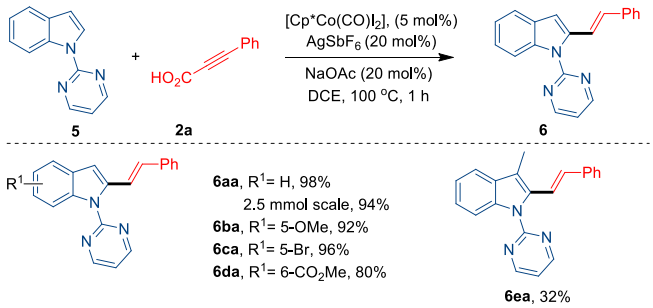
and its derivatives such as 5-methoxy indole, 5-bromo indole, and methyl indole-6-carboxylate with phenylpropiolic acid (**2a**) furnished their corresponding alkenylated products **6aa**, **6ba**, **6ca**, and **6da** in excellent yields (98, 92, 96, and 80%, respectively, Scheme 4).

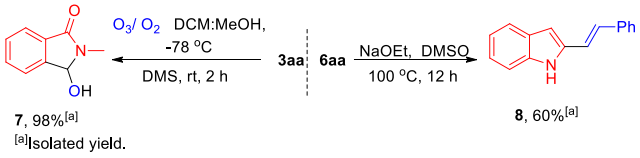
Scheme 4. Substrate scope for indole derivatives[a,b]



[a] Reaction conditions: **5** (0.2 mmol), **2a** (0.3 mmol), [Cp*Co(CO)I$_2$] (5 mol%), [AgSbF$_6$] (20 mol%), NaOAc (20 mol%), DCE (2 mL), at 100 °C for 1 h. [b] Isolated yields.

Further, to demonstrate the usefulness of the alkenylated product, an ozonolysis experiment was performed on **3aa**, which furnished the 3-hydroxy isoindolinone derivative **7** in 98% yield (Scheme 4). Next, the pyrimidinyl group was successfully deprotected by treating **6aa** with NaOEt/DMSO to obtain **8** in 60% yield (Scheme 5).[20]

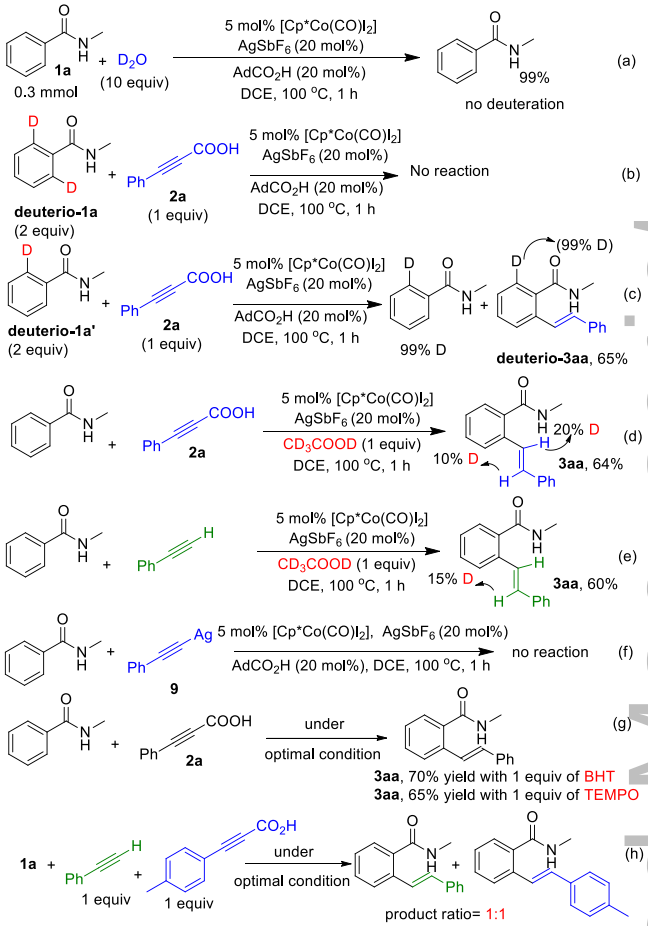
Scheme 5. Synthetic utility and removal of directing group



[a]Isolated yield.

To probe the reaction mechanism, a few control experiments were performed (Scheme 6). In the reaction of **1a** with D$_2$O, under optimal reaction conditions, the *ortho*-hydrogens of benzamide were not deuterated (Scheme 5a). The reaction of deuterio-**1a** with **2a** under the optimal reaction conditions did not furnish the alkenylated product (Scheme 6b). Further, experiments with **deuterio-1a** (2 equiv) with **2a** (1 equiv) under the optimal reaction conditions, the product **deuterio-3aa** was isolated in 65% yield (Scheme 6c). No deuterium/proton exchange was observed either in the product **deuterio-3aa** or in the recovered starting material. The lack of scrambling is not common in Cp*Co(III) catalytic system, which has been also observed by Ellman.[16] Further, the reaction of **1a** with **2a** in the presence of CD$_3$COOD, under the optimal reaction conditions, deuterium incorporation was observed on the olefinic carbon of **3aa** (10 and 20% D, Scheme 6d). Additionally, performing the same experiment with phenylacetylene instead of **2a**, 15% of deuterium incorporation was observed in the one of the olefinic carbon (Scheme 6e). These reactions suggest the involvement of the acid additive in the protodemetallation step.

Scheme 6. Mechanistic investigation

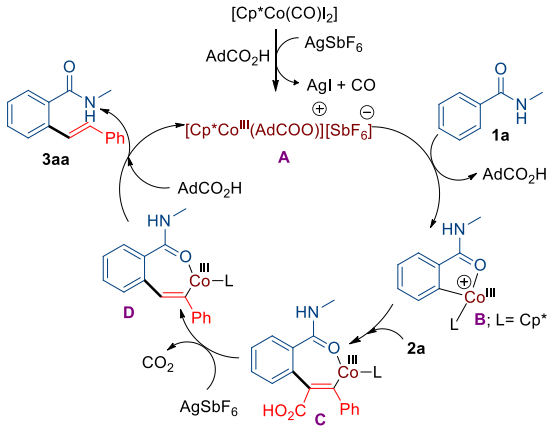


we presumed that phenylpropiolic acid (**2a**) could form silver phenylacetylide **9**, in the presence of AgSbF$_6$ and can lead to the corresponding alkenylated product. Therefore, we performed the reaction of **1a** with **9**, which failed to give the product **3aa**, indicating that the silver phenylacetylide **9** may not be an intermediate in this reaction (Scheme 6f). Further to check whether the reaction is proceeding through a radical pathway, we have performed a reaction of benzamide (**1a**) with phenyl propionic acid (**2a**) in the presence of BHT and TEMPO under the optimal reaction conditions. These reactions furnished the product **3aa** in 70 and 65% yields, respectively, which rules out the radical pathway (Scheme 6g). A competitive experiment using phenylacetylene and 4-methylphenyl propiolic acid with benzamide (**1a**) provided the corresponding alkenylated products in a ratio of 1:1 (Scheme 6h).

Based on the control experiments, and the literature precedence,[6,7,13,14] a plausible mechanism has been proposed in Scheme 7. The reaction of Cp*Co(CO)I$_2$ with AdCOOH and AgSbF$_6$ forms the

catalytically active species **A**, which reacts with **1a** forming a cobaltocycle **B** and AdCOOH. An alkyne insertion to the species **B** leads to the formation of 7-membered intermediate **C**, which undergoes decarboxylation forming the species **D**. Subsequently, AdCOOH promotes the protodemetallation thereby furnishing the product **3aa** along with active catalyst **A**. Alternatively, phenyl acetylene, which is generated from **2a**, can react with the species **B** furnishing the product **3aa**. Further work is underway to understand the mechanism of this reaction.

Scheme 7. Proposed mechanism



In conclusion, we have developed a Co(III)-catalyzed *ortho*-alkenylation of *N*-methyl benzamide derivatives and the alkenylation of indole at the C2-position using alkynyl carboxylic acid as a coupling partner through decarboxylation route. Unlike other reactions, this reaction leads to an exclusive alkenylation and the possible cyclic product was not observed under the reaction conditions. The NH-group of secondary benzamide remains unreactive without participating in the reaction.

Experimental Section

(a) Procedure for *ortho* alkenylation of benzamide derivatives

In a 8-mL screw-cap reaction vial, *N*-Methyl benzamide derivative (0.6 mmol), alkynyl carboxylic acid (0.3 mmol), cobalt catalyst (Cp^*CoCOI_2, 7.1 mg, 5 mol%), AdCOOH (10.8 mg, 20 mol%), $AgSbF_6$ (20.6 mg, 20 mol%) in DCE (2 mL) were taken. The vial was sealed with a screw cap and placed in a pre-heated metal block at 100 °C and the reaction mixture was stirred at the same temperature for 1h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and concentrated under vacuum. The crude products were purified on a silica gel column using EtOAc/ petroleum ether mixture.

(b) Procedure for C-2 alkenylation of *N*-Pyrimidinyl indole derivatives

In a 8-mL screw cap reaction vial, *N*-Pyrimidinyl indole derivatives (0.2 mmol), alkynyl carboxylic acid (0.24 mmol), cobalt catalyst (4.76 mg, 5 mol%), NaOAc (3.28 mg, 20 mol%), $AgSbF_6$ (13.7 mg, 20 mol%) in DCE (2 mL) were taken. The vial was sealed with a screw cap and placed in a pre-heated metal block at 100 °C and the reaction mixture was stirred at the same temperature for 1h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and concentrated under vacuum. The crude products were purified on a silica gel column using EtOAc/ petroleum ether mixture.

Acknowledgements

This work was supported by, SERB (NO.SB/S1/OC-56/2013), New-Delhi, CSIR (No. 02(0226)15/EMR-II), Indian Institute of Science, and R L Fine Chem, Bangalore. N. M.. thanks, UGC, New-Delhi for a fellowship.

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10.1002/adsc.201701406

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