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# Cp\*Co(III)-Catalyzed C–H Alkenylation of Aromatic Ketones with Alkenes

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Abstract. Cost-effective and air-stable high-valent cobalt(III)-catalyzed weakly coordinating, ketone-directed regioselective mono-alkenylation of arenes and heteroarenes with alkenes is demonstrated. Various electron-rich and electron-deficient arenes are tolerated under the reaction conditions, providing E-alkenylated products exclusively. The tert-butyl-acrylates serve as an acrylic acid surrogate to provide cinnamic acid derivatives via direct C-H alkenylation. A two-step synthesis of a y-PPAR antagonist, the synthesis of indanone, and the modification of divinylsulfone are reported as applications. mechanistic details suggest a base-assisted The intermolecular electrophilic substitution reaction pathway.

**Keywords:** cobalt(III)-catalyzed; ketone-directed; C–H alkenylation; cinnamic acids; indanone and indenone

Alkenyl-arenes are a very important structural motif present in several biologically active compounds,<sup>[1]</sup> natural products,<sup>[2]</sup> organic materials,<sup>[3]</sup> and most significantly, they are utilized as synthetic intermediates to achieve different target molecules.<sup>[4]</sup> Hence, different methods have been developed to introduce the alkene functional unit into arenes or heteroarenes. In this regard, due to the step- and atom-economy<sup>[5]</sup> and regioselectivity, chelating group-assisted, oxidative Heck-type<sup>[6,7]</sup> coupling has become an attractive strategy to synthesize alkenylated arenes using transition metals such as Pd,<sup>[8]</sup> Rh,<sup>[9]</sup> Ru<sup>[10]</sup> and others.<sup>[11–12]</sup>

Due to the advantage of easy installation and facile functional group interconversion, simple and ubiquitous ketones have been used as directing groups (DGs) in the recent years. Since the pathbreaking work by Murai et al. on Ru-catalyzed ketone-directed C-H alkylation, ketones have been employed as DGs for several C–H functionalizations.[13,14] However, the weakcoordinating nature of ketones (weak Lewis basicity) makes the cyclometallated species vulnerable in the transition state, and the enolizable  $\alpha$ -C–H bonds make ketones, more specifically acetophenones, challenging DGs.<sup>[15]</sup>

Although the expensive noble metals, mainly Pd<sup>[8b]</sup> Rh,<sup>[9a,j]</sup> Ru<sup>[10c]</sup> and Ir,<sup>[11e]</sup> have been used for the ketone-directed oxidative C-H alkenylations, the use of the earth-abundant, cheap, first-row transition metals (3d-metals) is scarce.<sup>[16]</sup> Among the 3d-metals, recently cobalt have been a subject of investigation as an alternative to the noble metals. Particularly, after the pioneering work by Kanai and Matsunaga, air stable Cp\*Co(III)-catalysis has gained much attention for various C–H functionalizations.<sup>[17]</sup> However, the low reactivity of base-metals (such as cobalt), challenges with ketones (acetophenones), and the requirement of harsh reaction conditions for the oxidative alkenylation, are main obstacles for ketone directed C-H alkenylation with alkenes under cobalt catalysis.<sup>[18]</sup> To overcome such challenges, w developed a method of ketone-directed C-H alkenylation of aromatic ketones with alkenes under Co(III)-catalysis (Scheme 1). The method offers stereo- and regio-selective mono-alkenylation of arenes and heteroarenes with moderate to good yields.





When the 1,3-dioxole group is introduced at the 3 and 4 position of acetophenones or other DGs, the substrates show the activation of the more hindered C-H bond due to a very weak coordinating nature of the 1,3-dioxole oxygen. Influenced by this regioselectivity, we initiated our optimization taking benzo[d][1,3]dioxol-5-yl)ethan-1-one **1a** as a model substrate (Table 1). When *n*-butyl acrylate **2a** is used as an electrophile, **1a** provided the desired product **3a** in 27% yield (entry 1). The introduction of the fluorinated 2,2,2-trifluoro ethanol solvent was

effective to improve the yield (entry 2). Other solvents did not respond well (entries 3-4). This observation and our earlier report<sup>[18]</sup> corroborate the recent report on the assistance of fluorinated solvents cobalt-catalyzed C-H bond on functionalizations.<sup>[17m,p,q]</sup> Varying the oxidant to anhydrous copper acetate provided 3a in 43% yield (entry 5). No significant improvement was observed in the yield when other oxidants (entries 6-7) or silver salts (entries 8-10) were incorporated. Gratifyingly, we obtained the best yield by using 20 mol% of Cp\*Co(CO)I<sub>2</sub>, 50 mol% of AgSbF<sub>6</sub> and 90 mol% of Cu(OAc)<sub>2</sub> (about 100% conversion of 1a, entry 11). Yields decrease rapidly on reducing the amount of Cu(OAc)<sub>2</sub> oxidant (entries 12–14).

Table 1. Optimization of the reaction conditions.<sup>[a]</sup>

	↓ + ≠	Cf2 <sup>//</sup> Bu — 2a	*Co(CO)I <sub>2</sub> (10 mol%) Ag-salt (30 mol%) oxidant, solvent 90 °C, 24 h, air	CO2 <sup>n</sup> Bu
Entry	Solvent	Ag-salt	Oxidant (mol%)	Yield
				[ <b>3a</b> %] <sup>[9]</sup>
1	DCE	AgSbF <sub>6</sub>	$Cu(OAc)_2 \cdot H_2O(100)$	27
2	TFE	AgSbF <sub>6</sub>	$Cu(OAc)_2 \cdot H_2O(100)$	34
3	C <sub>6</sub> H <sub>5</sub> Cl	AgSbF <sub>6</sub>	$Cu(OAc)_2 \cdot H_2O(100)$	16
4	C <sub>6</sub> H <sub>5</sub> CF <sub>3</sub>	AgSbF <sub>6</sub>	$Cu(OAc)_2 \cdot H_2O(100)$	19
5	TFE	AgSbF <sub>6</sub>	$Cu(OAc)_2(100)$	43
6	TFE	AgSbF <sub>6</sub>	Co(OAc) <sub>2</sub> ·4H <sub>2</sub> O (100)	17
7	TFE	AgSbF <sub>6</sub>	Mn(OAc) <sub>3</sub> ·2H <sub>2</sub> O (100)	0
8	TFE	AgBF <sub>4</sub>	Cu(OAc) <sub>2</sub> (100)	29
9	TFE	AgOTf	Cu(OAc) <sub>2</sub> (100)	36
10	TFE	AgOAc	Cu(OAc) <sub>2</sub> (100)	22
11 <sup>[c]</sup>	TFE	AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub> (90)	72
12 <sup>[c]</sup>	TFE	AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub> (60)	59
13 <sup>[c]</sup>	TFE	AgSbF <sub>6</sub>	$Cu(OAc)_2$ (30)	27
14 <sup>[c]</sup>	TFE	AgSbF <sub>6</sub>	$Cu(OAc)_2(0)$	0

<sup>[a]</sup>**1a** (0.3 mmol), **2a** (0.45 mmol) and 2.0 mL of TFE were used. <sup>[b]</sup>Isolated yield. <sup>[c]</sup>20 mol% of Cp\*Co(CO)I<sub>2</sub> and 50 mol% of the Ag-salt were used.

With the optimized conditions in hand (Table 1, entry 11), we first studied the scope of the reaction by varying different aromatic ketones (Scheme 2). The reactions were effective for both electron-rich and deficient substrates. Halogen groups, for examples, fluoro, bromo, and iodo at the *para* position of acetophenone provided **3b–3d** in 47–51% yields. Simple acetophenone furnished **3e** in 59% yield. The methyl, phenyl or methoxy groups at the *para* position of the acetophenone also provided products **3f–3h** in good yields (53–64%). The free hydroxyl group of piceol **1i** does not require any protection for this alkenylation reaction (**3i**, 58%).



Scheme 2. Scope of aromatic ketones. 1a-1s (0.3 mmol), 2a or 2b (0.45 mmol) and 2 mL TFE were used. All yields are isolated yields.

The readily oxidizable sulfur-containing SMe group was also survived under this oxidative reaction conditions (**3j**, 47%). Unlike **1a**, the acetophenone with 3,4-dimethoxy substitution yielded **3k** in 46% yield where the alkenylation occurs at the sterically less hindered position indicates that here steric-effec. overcomes electronic-effect. Ketone bearing electron-withdrawing CO<sub>2</sub>Me also responded well to give **3l** in 41% yield. To avoid *peri*-interaction **1m** produced **3m**. The alkyl aryl ketone **1n**, diaryl ketone **1o–1p**, chalcone **1q**, heteroaryl ketone **1r**, and biologically relevant chromone **1s** also provided mono-alkenylated products **3n–3s** in 44–61% yields.



Scheme 3. Scope of alkenylating agents. 1a or 1h (0.3 mmol), 2b-2h (0.45 mmol) and 2 mL of TFE were used. All yields are isolated yields.

Next, the scope of the alkenylation was explored with various alkenes (Scheme 3). The methyl and

ethyl acrylates were equally effective to furnish the corresponding alkenylated products (4a-4b, 71-76% yields). When the menthyl ester of the acrylic acid was used, the yield of the alkenylated product was reduced significantly (4c, 42%). In case of the phenyl acrylate, along with the desired product 4d (44%), a by-product 4e was also isolated due to in situ transesterification with the solvent alcohol. Vinyl phosphonate was also a suitable alkenvlating partner to provide 4f in 40% yield. The desired alkenylation with vinyl sulfones underwent smoothly to provide the corresponding products **4g–4h** in 53–75% yields. Interestingly, by employing 2.0 equivalent of 1a with respect to divinylsulfone, two-fold C-H alkenylation was also achieved to obtain 4i in 56% yield. We observed, except for 3a, the unreacted ketones 1 were detected in the reaction mixture and not consumed even after prolonged reaction time.



Scheme 4. One-pot synthesis of cinnamic acids. 1 (0.3 mmol), 2i (0.45 mmol) and 2 mL of TFE were used. All yields are isolated yields. <sup>[a]</sup>50 mol% of AgSbF<sub>6</sub> used.

The direct C–H alkenylation by employing acrylic acid electrophile is scarce in the literature.<sup>[10a]</sup> Our attempts to employ acrylic acid as alkene partner provided only a trace amount of **5a**. However, during our optimization study by using **2i** we observed that *tert*-butyl group of the product ester undergoes *in situ* hydrolysis to provide cinnamic acid derivative **5a**, opening a route to the direct synthesis of several cinnamic acids derivatives **5a–5e** in 41–58% yields (Scheme 4). Our method eliminated the use of strong bases for the hydrolysis of cinnamates in the presence of base-sensitive functional groups like enolizable ketones.



**Scheme 5.** Applications of the alkenylated ketones. Standard conditions: 20 mol% of  $Cp*Co(CO)I_2$ , 50 mol% of AgSbF<sub>6</sub> and 90 mol% of Cu(OAc)<sub>2</sub> were used in TFE solvent.

The importance of 2-alkenylated aromatic ketones was realized through the synthesis of various important structural motifs.<sup>[19]</sup> A base mediated intramolecular 1,4-addition of acetophenone to acrylates produced indanone **6** (Scheme 5a), a very demanding motif of biological importance.<sup>[19a]</sup> Divinyl sulfone can be modified by incorporating two different arenes using our alkenylation protocol. The best yield was obtained when electron-rich aromatic ketone was incorporated in the second step (Scheme 5b). Most importantly, a two-step, gram-scale synthesis of a  $\gamma$ -PPAR antagonist **11** was accomplished starting from the ketone **9**, whereas the reported synthesis required six-steps from the simple starting materials.<sup>[19b]</sup>



Scheme 6. Intermolecular competition experiment, deuterium labelling study, Kinetic Isotopic Effect study, and detection of cyclocobalted intermediates 13-14 by LC-MS analysis.

To understand the nature and mechanism of the present alkenylation reaction, we first performed a competition experiment between electron-rich **1h** and -deficient **1l** acetophenones (Scheme 6a). The more efficiency of the electron-rich acetophenone (**3h/3l** = 11.4:1 ratio) suggest a base (acetate)-assisted intermolecular electrophilic substitution (BIES)-type mechanism.<sup>[20a]</sup> H/D scrambling was observed at the *ortho* position of [**D**<sub>5</sub>]-**1e** and **1e** in the absence of alkene, supporting a reversible C–H activation step (Scheme 6b-6c). Furthermore, the low value of

kinetic isotope effect (KIE) from both the intermolecular competition experiment ( $k_{\rm H}/k_{\rm D} = 1.9$ ) and parallel experiment ( $k_{\rm H}/k_{\rm D} = 1.3$ ) indicate that the C–H bond cleavage is probably not involved in the rate-limiting step (Scheme 6d).<sup>[20b–c]</sup> To eliminate the possibility of alkylation followed by subsequent oxidation to the corresponding alkene,<sup>[171]</sup> first we prepared the alkylated product **12** from **3h** by hydrogenation, and then subjected to the standard reaction conditions. The absence of any alkenylated product **3h** in the reaction mixture further support the  $\beta$ -hydride elimination pathway (Scheme 6e).

Based on previous reports<sup>[9a,10c,12]</sup> and kinetic studies, we propose a plausible mechanism for the alkenylation in Scheme 7. The catalyst  $Cp*Co(CO)I_2$ with  $AgSbF_6$  generates an active catalyst A that forms a five-membered cyclometallated species B reversibly with 1e. The analogous to the intermediate **B**, a cyclometallated species **13** formed from **1a**, was observed by LC-MS analysis of the crude reaction mixture (Scheme 6f).<sup>[21]</sup> Then, the coordination of **2a** to the cobalt center of **B** followed by a migratory insertion of alkene delivers the intermediate **D**. The acetate decordinated cationic species 14 was also detected by LC-MS analysis of the crude reaction mixture showing the incorporation of acrylate 2a to the cobaltacycle 13 (Scheme 6g).<sup>[21]</sup> Finally, product **3e** is formed by  $\beta$ -hydride elimination from intermediate **E** and a reduced cobalt species  $Cp*Co(I)L_n F$  is also generated which in the presence of  $Cu(OAc)_2$  oxidizes to the active cobalt-catalyst A for the next catalytic cycle.



Scheme 7. Proposed mechanism.

In conclusion, we successfully achieved weaklycoordinating, ubiquitous ketone-directed stereo- and regio-selective C–H mono-alkenylation of aromatic ketones using an earth-abundant, cheap high-valent cobalt-catalyst. The importance of the products has been demonstrated by the synthesis of cinnamic acid analogues, indanone, modification of the divinyl sulfone, and more importantly by a two-step synthesis of a  $\gamma$ -PPAR antagonist. We hope our method will lead to the access of diverse functionalized aromatic and hetero-aromatic ketones, and this work could be an important finding to develop such oxidative reactions with basemetals.

#### **Experimental Section**

General procedure for the alkenylation: The aryl/heteroaryl ketone 1 (0.3 mmol, 1.0 equiv) was taken in a 15.0 mL screw capped sealed tube and 2.0 mL of 2,2,2-trifluro ethanol was added. Then catalyst Cp\*Co(CO)I<sub>2</sub> (28.5 mg, 0.06 mmol, 20.0 mol%), AgSbF<sub>6</sub> (51.5 mg, 0.150 mmol, 50.0 mol%) and Cu(OAc)<sub>2</sub> (49 mg, 0.27 mmol, 90.0 mol%) were added successively to the reaction mixture and was stirred for 5 min at the room temperature. After that, the alkenylating agent 2 (0.45 mmol, 1.5 equiv) was added to the reaction mixture and the resultant reaction mixture was allowed to stir at 90 °C for 24 h. After completion of the reaction as indicated by TLC, the crude product was directly purified by silica gel column chromatography using petroleum ether/ ethylacetate eluent.

General procedure for the one-pot cinnamic acid derivative synthesis: The aryl/heteroaryl ketone 1 (0.3 mmol, 1.0 equiv) was taken in a 15.0 mL screw capped sealed tube and 2.0 mL of 2,2,2-trifluro ethanol was added. Then catalyst Cp\*Co(CO)I<sub>2</sub> (28.5 mg, 0.06 mmol, 20.0 mol%), AgSbF<sub>6</sub> (41.2 mg, 0.150 mmol, 40.0 mol%) and Cu(OAc)<sub>2</sub> (49 mg, 0.27 mmol, 90.0 mol%) were added successively to the reaction mixture and was stirred for 5 min at the room temperature. After that, the alkenylating agent 2i (0.45 mmol, 1.5 equiv) was added to the reaction mixture was allowed to stir at 90 °C for 24 h. After completion of the reaction as indicated by TLC, the crude product was directly purified by silica gel column chromatography by using petroleum ether/ ethylacetate eluent.

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- [21] See Supporting Information for LC-MS spectra.

### UPDATE

Cp\*Co(III)-Catalyzed C–H Alkenylation of Aromatic Ketones with Alkenes

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