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Weakly Coordinating, Ketone-Directed Cp*Co(III)-Catalyzed C−H Allylation on Arenes and Indoles

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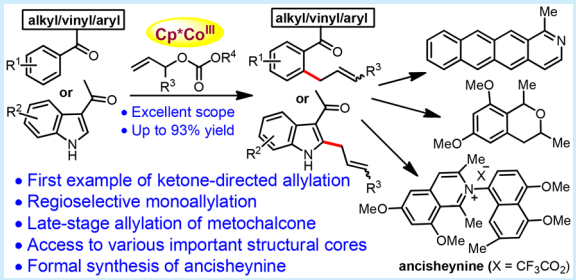
Supporting Information

ABSTRACT: Weakly coordinating, ketone-directed, regioselective monoallylation of arenes and indoles is reported using a stable and cost-effective high-valent cobalt(III)-catalyst to access several important molecular building blocks. The allylation proceeds smoothly with a variety of substrates in the presence of various electron-rich and -deficient substituents. The method was applied to the formal synthesis of an ancisheynine alkaloid, a highly conjugated azatetracene, and isochroman. The mechanistic study reveals that the allylation reaction follows a base-assisted intermolecular electrophilic substitution pathway.

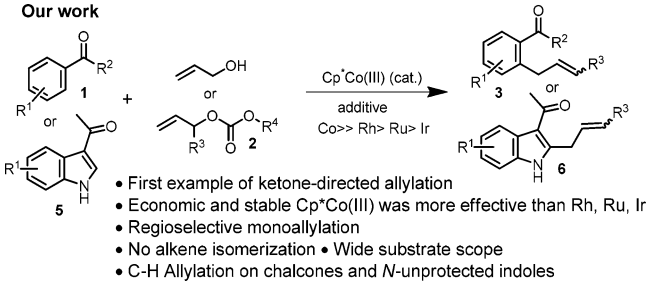


ortho-Allyl aromatic ketones are very useful synthons for many biologically active natural products,[1] and they are also used as important intermediates for different structural conversions.[2] They can also serve as key building blocks to access several π-extensions directly.[3] Method development to construct these core moieties is an important synthetic task. In this context, ketone-directed *ortho* C−H allylation of an sp^2 bond would be the most atom-[4] and step-economical pathway.[5] Previously, the stitching of allyl groups was mostly dependent on Lewis acid assisted Friedel−Crafts allylations[6] and metal-catalyzed cross-coupling reactions.[7] But low regioselectivities, overallylation, limited substrate scopes, and multistep reactions restrict their applications, hence rendering direct C−H allylation a superior method. To our knowledge, although weakly coordinating, ketone-directed C−H functionalizations with different electrophiles are reported,[8,9] ketone-directed allylation is still not encountered.

However, often preinstalled coordinating groups are obligatory for the reaction conditions, but detaching these directing groups is not operationally simple, which impedes the feasibility of synthetic applications. In this context, weakly coordinating, simple, and ubiquitous ketones can add value as a preferred alternative.[8,9] But, challenges with ketones include their weak Lewis basicity, which decreases the coordination power to a metal and, hence, diminishes the stability of the transition state.[8a] In addition, its enolizable α proton is another issue for directed *ortho* C−H activation.[9e,10] Hence, we looked to develop an elegant method of C−H allylation directed by ketones.

Over the past few years, several directed C−H allylations were reported on arene and indole systems using different transition metals such as Rh, Ru, Pd, Mn, Ni, Fe, etc.[11−13] In particular, Cp*Rh(III) catalysts had established their superiority due to their stability, high catalytic efficiency, and decent functional group compatibility. But their low abundance and high price demand a pragmatic substitute. In 2013, Kanai and Matsunaga,[14] in their pioneering work, reported Cp*Co(III) as an alternative to Cp*Rh(III)-catalytic systems. Later, from various reports,[15,16] the unique reactivity and selectivity of Cp*Co(III) was established over its Rh congener. Here, we have expanded this new reactivity and explored Cp*Co(III) as an effective catalyst for weakly coordinating, ketone-directed allylation reactions. To the best of our knowledge, we report the first example of weakly coordinating, ketone-directed stable, high valent cobalt catalyzed C−H allylation of acetophenones, diaryl ketones, chalcones, and indoles (Scheme 1). Our method offers complete regioselective monoallylated products exclusively without any alkene isomerization.

Scheme 1. Ketone-Directed C−H Allylation



We started our optimization taking 4-methoxy acetophenone **1a** as a model substrate (Table 1). Though simple allyl alcohol provided **3a** in 44% yield,[17] more facile β-oxygen elimination with allyl carbonate **2** makes it a better allylating agent for our reaction. After studying other allylating agents, allyl isobutyl carbonate **2a** proved to be the best one.[17] After extensive screening of the additives, 30 mol % of $Cu(OAc)_2 \cdot H_2O$ and 30 mol % of $AgSbF_6$ were found to be optimal (entry 2).[17] Changing either solvents or

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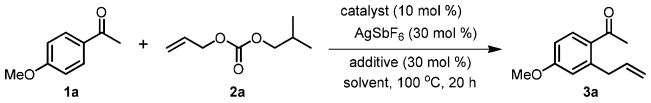
Table 1. Optimization of Reaction Conditions[a]



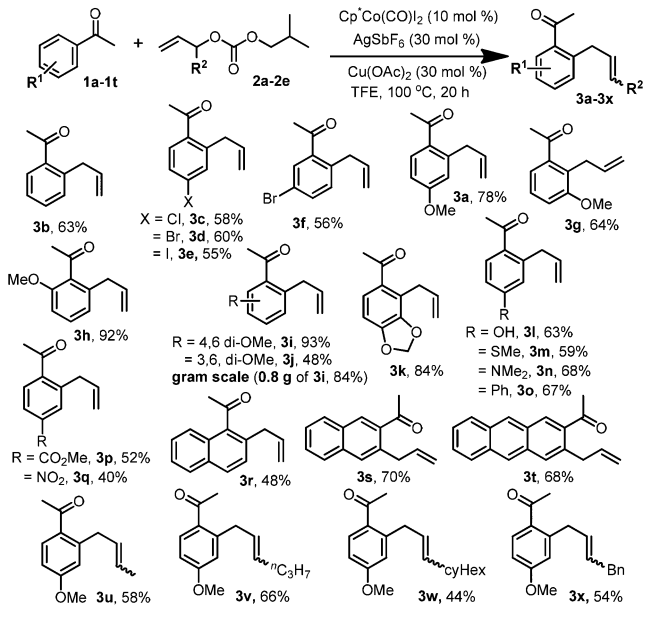
entry	solvent	catalyst	additive	yield [3a%][b]
1	DCE	$Cp^*Co(CO)I_2$	none	trace
2[c]	DCE	$Cp^*Co(CO)I_2$	$Cu(OAc)_2·H_2O$	42
3	^{t}AmOH	$Cp^*Co(CO)I_2$	$Cu(OAc)_2·H_2O$	0
4	TFE	$Cp^*Co(CO)I_2$	$Cu(OAc)_2·H_2O$	64
5	**TFE**	**$Cp^*Co(CO)I_2$**	**$Cu(OAc)_2$**	**78**
6[c]	TFE	$Cp^*Co(CO)I_2$	$Cu(OAc)_2$	75
7	TFE	$Cp^*Co(CO)I_2$	NaOAc	28
8	TFE	$Cp^*Co(CO)I_2$	$Mn(OAc)_2·4H_2O$	35
9	TFE	$[Cp^*CoCl_2]_2$	$Cu(OAc)_2$	42
10[d]	TFE	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2$	40
11[d]	TFE	$[Ru(p\text{-cymene})Cl_2]_2$	$Cu(OAc)_2$	18
12[d]	TFE	$[Cp^*IrCl_2]_2$	$Cu(OAc)_2$	0

[a]**1a** (0.25 mmol), **2a** (0.50 mmol), and 1.5 mL TFE were used. [b]Isolated yield. [c]1.0 equiv of additive. [d]5.0 mol % catalyst loading.

silver additives did not produce any better result.[17] Introduction of the fluoro solvent TFE (2,2,2-trifluoro ethanol) significantly improved the yield (entry 4). Gratifyingly, on changing the additive to anhydrous copper acetate, we obtained our best yield (78%, entry 5). Further optimization with other additives did not provide any further improvement (entries 7−8). Incorporation of other catalysts (entries 9−12) under our optimized conditions (entry 5) did not produce encouraging results.

After having the optimized conditions, we first studied the scope of this allylation and found a wide range of acetophenones took part in the reaction (Scheme 2). Under our reaction conditions, simple acetophenone provided **3b** in 63% yield. Halogens such as chloro, bromo, and iodo at the *para* position of acetophenone also furnished **3c**−**3e** in 55−60% yields. Likewise, *meta* bromo-substituted acetophenone also delivered product **3f**

Scheme 2. Scope of Allylation on Arenes[a,b]

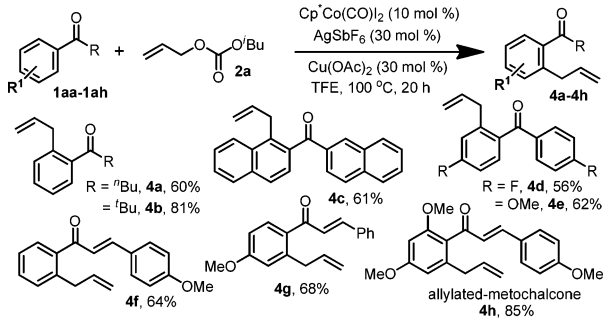


[a]**1** (0.25 mmol), **2** (0.50 mmol), and 1.5 mL TFE were used. [b]Isolated yield.

in similar yield. Next, we introduced electron-donating functional groups at the different positions of acetophenones. Methoxy-substitition at the *meta* position offered allylated product **3g** in 64% yield. Interestingly, here allylation at the more hindered position indicates that an electronic effect is predominant over the steric effect. *ortho*-Methoxy acetophenone provided **3h** in excellent yield (92%). Other electron-rich acetophenones also reacted well to provide **3i**−**3k** in 48−93% yields. Considering the applicability of this method, a gram scale synthesis of **3i** was also executed. An acetophenone derivative bearing a strongly coordinating hydroxy functional group was also a suitable substrate (**3l**, 63%). Other electron-donating functional groups such as SMe, NMe_2, and phenyl were also tolerated in our reaction conditions (**3m**−**3o**, 59−68% yields). Gratifyingly, substrates having electron-withdrawing CO_2Me and NO_2 functional groups at the *para* position also responded well (**3p**−**3q**, 40−52%). Allylations on naphthalenes and anthracene were also achieved to produce products **3r**, **3s**, and **3t**. A 3-butene-2-ol derived isobutyl carbonate also reacted well, and **3u** was isolated in 58% yield as a 1.6:1 isomeric mixture. Similar results were recorded with other substituted allylating agents (**3v**−**3x**, 44−66% yields).

The scope of this reaction was further explored by varying the directing group (Scheme 3). *n*-Butyl and *tert*-butyl ketones

Scheme 3. Scope of Diaryl Ketones and Chalcones[a,b]



[a]**1aa**−**1ah** (0.25 mmol), **2a** (0.50 mmol), and 1.5 mL TFE were used. [b]Isolated yield.

provided decent yields (**4a**−**4b**, 60−81% yields). Dinaphthyl ketone and benzophenone having electron-withdrawing fluoro and electron-donating methoxy groups reacted well (**4c**−**4e**, 56−62% yields). Out of four possible C−H allylations, only monoallylated products **4c**−**4e** were obtained exclusively. Chalcone is a common structural motif present in many natural products and bioactive molecules.[18a] This attracted us to employ the method to execute late-stage diversification of relatively unexplored chalcones. Starting from respective chalcones, products **4f** and **4g** were obtained in 64−68% yields. We were also successful in achieving a late-stage allylation of a choleretic drug, metochalcone,[18b] in excellent yield (**4h**, 85%).

C−H bond functionalization at the C2-position of indoles primarily relies on the *N*-protected indoles.[19] These protections always restrict their use by imposing additional steps of protection and deprotection. In a few cases, deprotection requires very rigorous reaction conditions. Interestingly, on applying our method, C2-allylation was achieved for *N*-unprotected 3-acetylindoles. The scope of the reaction was also excellent, as several bromo, chloro, methoxy, and methyl substituted 3-acylindoles **5a**−**5e** underwent smooth reaction to provide **6a**−**6f** in moderate to high yields (Scheme 4).

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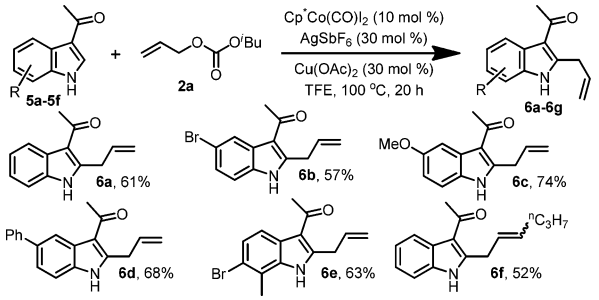
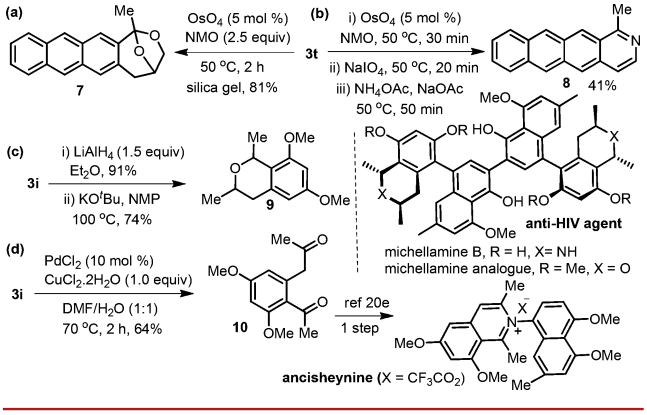
Scheme 4. Scope of Allylation on Indoles[a,b]



[a]**5** (0.25 mmol), **2** (0.50 mmol), and 1.5 mL of TFE were used. [b]Isolated yield.

The allylated products can easily be functionalized to various important structural motifs. Dioxabicyclo core structure **7**, present in many biologically active molecules, has been synthesized as an application (Scheme 5a).[20a,b] Because

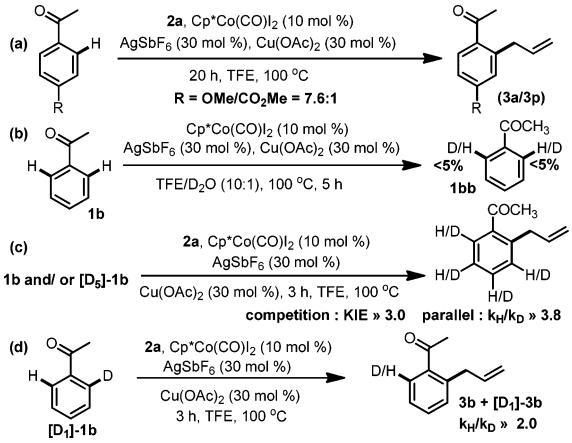
Scheme 5. Applications of Allylated Products



azaacenes are important materials for application in field effect transistors (OFET), organic light-emitting diodes (OLED), solar cells, and memory devices,[20c] azatetracene **8** was synthesized from **3t** in a one-pot procedure (Scheme 5b). From the allylated product **3i**, biologically active isochroman **9**, a precursor for anti-HIV analogue, has been synthesized in 2 steps (Scheme 5c), whereas Konnig et al. made this structural motif over 10 steps.[20d] Furthermore, a formal synthesis of an ancisheynine alkaloid was achieved by Wacker oxidation of **3i** to furnish the advanced intermediate **10** (Scheme 5d).[20e]

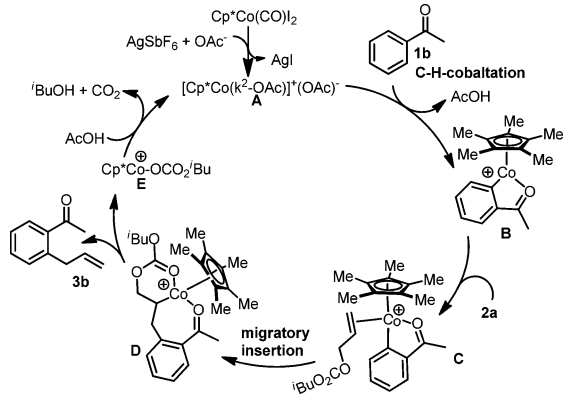
To understand the catalyst's mode of action, we first performed an intermolecular competition experiment and deuterium labeling study. A competition experiment between electron-rich and -deficient benzophenones revealed that electron-rich acetophenone reacted more efficiently, with an almost 7.6:1 ratio (Scheme 6a). This result indicates that a base-assisted intermolecular electrophilic substitution (BIES) mechanism is operative.[21a−c] H/D Exchange with D_2O and CD_3OD did not provide a significant amount of deuterium scrambling at the *ortho* position of **1b** (Scheme 6b), suggesting an irreversible C−H activation step. A kinetic value of 3.0 from an intermolecular competition experiment and k_H/k_D value of 3.8 from a parallel experiment (Scheme 6c) provide information about the rate-determining C−H activation step. This conclusion was further corroborated by the k_H/k_D value (~2.0) from an intramolecular competition experiment (Scheme 6d).[21d,e]

Scheme 6. Competition Experiment, Deuterium Labelling Study, and Kinetic Isotopic Effect (KIE) Study



Based on kinetic studies and previous reports, we propose that the allylation reaction proceeds via a facile BIES-type C−H cobaltation step (Scheme 7). In the presence of $AgSbF_6$, the active

Scheme 7. Proposed Mechanism



catalyst **A** is formed. Then *in situ* generated **A** reacts with **1b** to assemble the cyclometalated species **B** by acetate assisted C−H bond activation, and then in the presence of allylating agent, **C** is generated from **B**. 1,2-Migratory insertion on the allyl double bond of **2a** and coordination with carbonate oxygen delivers species **D**. Unlike the free alcohol, an additional coordination to the cobalt center for the carbonates probably facilitates the geometrically more favored β-oxygen elimination from **D** over β-hydride elimination. Finally, **D** produces the desired allylated product **3b** along with the release of alcohol and CO_2 as byproducts.

In conclusion, weakly coordinating, simple, and ubiquitous ketone-directed regioselective monoallylation of arenes, chalcones, and *N*-unprotected indoles has been achieved. The unique reactivity of a cost-effective, high-valent cobalt catalyst overpowered the other expensive transition metal catalysts in our reaction conditions. The synthesized allylated products hold the key in preparing various synthetic intermediates. We have successfully prepared highly conjugated azatetracene as a unique application. Finally, a mechanistic investigation suggests a BIES mechanism is operative here. We believe this method will be highly useful for the rapid generation of several functionalized ketones.

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■ ASSOCIATED CONTENT

Supporting Information

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Experimental details, analytical data for all new compounds, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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