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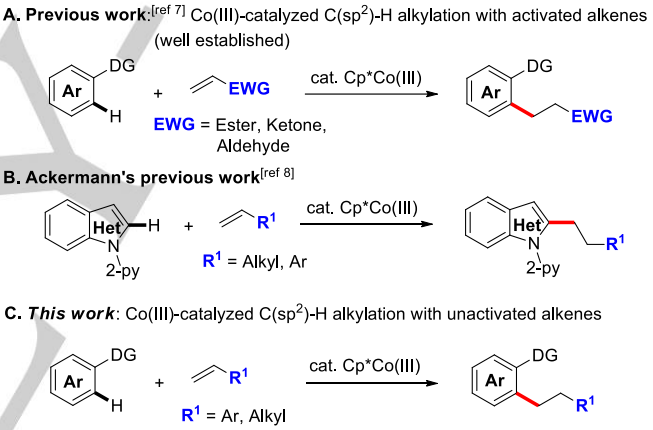
Cobalt-Catalyzed Direct C(sp^2)–H Alkylation with Unactivated Alkenes

Ye Lim Kim,[a] Sun-a Park[a] and Ju Hyun Kim [a]*

Abstract: A facile and efficient method for Cp*Co(III)-catalyzed C(sp^2)–H bond alkylation was developed using 2-aryl pyridines and unactivated alkenes. The reaction proceeded atom-economically with readily available styrene derivatives and an abundant cobalt catalyst. This reaction tolerates a broad range of functional groups, directing groups, styrenes and affords mono-diarylethane products with high linear selectivity. To demonstrate the synthetic utility and the potential application in organic synthesis, a gram-scale reaction and further C–H bond functionalizations of the mono-alkylated product were performed.

The C–C bond formation using a transition metal catalyst is an important reaction, which is at the forefront of modern organic synthesis.[1] With the advancement of catalytic C–H bond functionalization, C–H alkylation has become a powerful and atom-economical tool for constructing new carbon–carbon bonds and minimizing by-products. Among the strategies for C–H bond alkylation, coupling reactions with alkenes (i.e., hydroarylation) are the most reliable and attractive methods because alkenes are inexpensive, readily available, and free-from by-products. Various hydroarylation methods have been developed with various transition metals such as Ru, Rh, and Ir.[2] The reaction proceeds through the migratory insertion of alkenes into metallacycle, which leads to the metal–alkyl intermediate. This intermediate undergoes protodemetalation to offer the alkylation product.[3]

Despite the considerable progress in C–H bond functionalization achieved by precious transition metals, there is a continuous interest in developing direct functionalization using abundant 3d late-transition metals. Owing to the pioneering studies by Kanai,[4] Glorius,[5] and Ackermann,[6] cobalt has emerged as an excellent catalyst for various useful C–H bond functionalizations. Cp*Co(III)-catalyzed linear-selective C–H alkylation with alkenes has been also developed and demonstrates high regioselectivity and efficiency. The drawback of this otherwise powerful tool is that alkenes are still limited to activated alkenes such as acrylates (Scheme 1A).[7] Recently, an elegant method of cobalt-catalyzed regiodivergent C–H alkylation with unactivated alkenes providing linear- or branch-selective C–H alkylation has been reported by Ackermann. Therein, the examples of C(sp^2)–H bonds were limited to heteroarene such as indole (Scheme 1B).[8] Although low-valent cobalt-catalyzed hydroarylation of styrenes has also been developed, a stoichiometric amount of Grignard reagent is required.[9] Considering the significance of C–H alkylation method with alkenes using cobalt catalyst, developing a general method without excess organometallic reagent that allows a wide range of simple arenes and alkenes is desirable. In particular, it would be interesting to develop cobalt-catalyzed C(sp^2)–H alkylations with styrenes to provide phenylethylene groups, which are often found in biologically active compounds.[10] On the basis of our interest in Cp*Co(III)-catalyzed C–H bond activations,[11] we report herein a straightforward method for linear-selective C(sp^2)–H alkylation with styrene derivatives (Scheme 1C).



Scheme 1. Cobalt(III)-catalyzed C(sp^2)–H alkylation with alkenes.

We began our investigation using 2-phenyl pyridine (**1a**) and styrene (**2a**) as a coupling partner in the presence of Cp*Co(CO)I_2 (10 mol%) in 2,2,2-trifluoroethanol (TFE) at 100 ℃ (Table 1 and Table S1 in the Supporting Information). While the desired product was not detected without an acidic additive (entries 1–3), product **3aa** was obtained in a 16% yield with AcOH (2 equiv) (entry 4).[7,12] The C(sp^2)–H alkenylation product **4aa** (11% yield), which is synthesized through the β-hydride elimination after migratory insertion into alkenes,[13] was also isolated. In the presence of the $AgSbF_6$ additive, other acids were screened (entries 5–7), and pivOH (pivalic acid) was identified to be the most powerful for linear-selective C–H alkylation (entry 5). Other silver and sodium salts were also examined using 2 equiv of pivOH; however, the lower yield of the desired product **3aa** was obtained (entries 8–10). An increase in the amount of pivOH led to a slightly higher yield (entry 11). Further optimization conditions were determined by increasing reaction time and the amount of **2a**; **3aa** was synthesized in a 78% yield (entry 12). By reducing the catalyst loading to 5 mol%, the desired product was obtained with a similar yield of 76% (entry 13).

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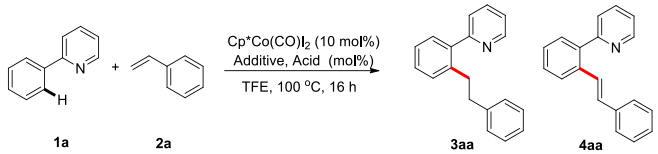
Table 1. Optimization of the reaction conditions.[a]

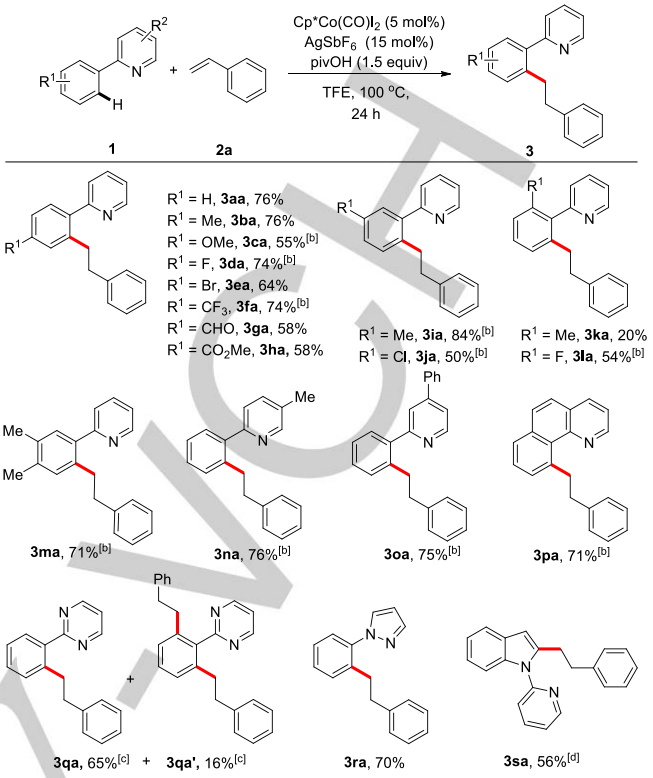


Entry	Additives (mol%)	Acid (equiv)	Yield (%)[b]	
			3aa	4aa
1	$AgSbF_6$ (20)	-	0	9
2	AgOAc (20)	-	0	5
3	$AgNTf_2$ (20)	-	0	7
4	$AgSbF_6$ (20)	AcOH (2)	16	11
5	$AgSbF_6$ (20)	1-AdCOOH (2)[c]	48	5
6	$AgSbF_6$ (20)	pivOH (2)	55	5
7	$AgSbF_6$ (20)	TFA (2)	0	0
8	AgOAc (20)	pivOH (2)	39	<5
9	$NaSbF_6$ (20)	pivOH (2)	24	<5
10	NaOAc (20)	pivOH (2)	35	<5
11	$AgSbF_6$ (20)	pivOH (3)	63	7
12[d,e]	$AgSbF_6$ (20)	pivOH (3)	78	10
13[d,e,f]	$AgSbF_6$ (15)	pivOH (1.5)	76	10

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), Cp*Co(CO)I_2 (10 mol%), and additives in TFE (1.0 mL) for 16 h under argon. [b] Isolated yield. [c] 1-AdCOOH = 1-Adamantanecarboxylic acid. [d] The reaction was performed for 24 h. [e] A total of 1.8 equiv of **2a** was used. [f] The reaction was carried out using 5 mol% of the Cp*Co(CO)I_2 catalyst.

To evaluate the scope of C(sp^2)–H hydroarylation, various aryl groups and directing groups were examined with styrene (**2a**) under the optimal reaction conditions (Table 2). 2-Aryl pyridines bearing electron-rich, halogen, and electron-deficient groups at the para-position of the phenyl ring readily reacted with **2a**, which afforded **3ba**–**3ha** in moderate to good yields (55%–76%). Specifically, versatile functional groups (e.g., –Br, aldehyde, and ester substituents) on arenes were well tolerated for this C–H alkylation and produced **3ea**, **3ga**, and **3ha**. Although reactivity was lower, the 2-aryl pyridine analogs of **1** that had –Me and –Cl substituents on meta- and ortho-positions of phenyl rings were also compatible with this linear-selective alkylation. In addition, this reaction was applicable to aryl pyridine analogs of **1** bearing either –Me at the 5-position or –Ph at the 4-position of the pyridine ring and produced **3na** and **3oa** in 76% and 75% yields, respectively. Different directing groups were also investigated. The reactions of benzoquinoline and 1-phenyl-1H-pyrazole with **2a** proceeded selectively to give mono-alkylated products **3pa** and **3ra** in good yields. However, 2-phenyl pyrimidine produced the mixture of mono-alkylated product **3qa** as the major product and di-alkylated product **3qa'** as the minor product with a total of 81% yield. The linear-selective alkylation of indole derivative was also viable and afforded **3sa**, albeit with a slightly decreased yield.

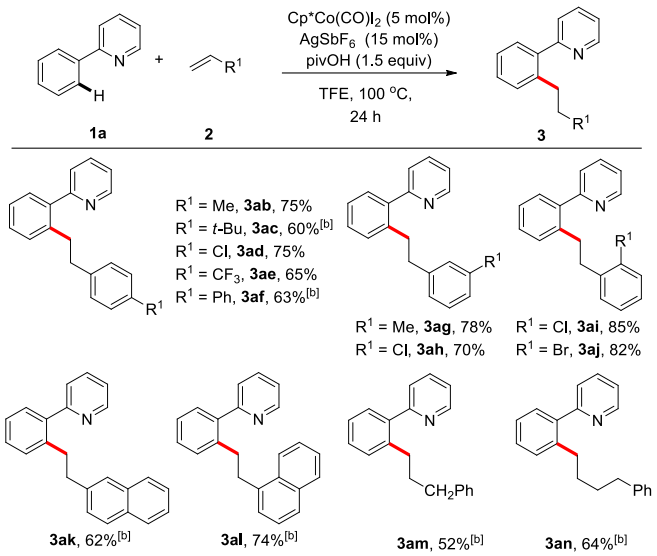
Table 2. Scope of 2-aryl pyridines.[a]



[a] Reaction conditions: **1** (0.20 mmol), **2a** (0.36 mmol), Cp*Co(CO)I_2 (5 mol%), $AgSbF_6$ (15 mol%), and pivOH (1.5 equiv) in TFE (2.0 mL) at 100 °C under argon, 24 h, isolated yields. [b] Cp*Co(CO)I_2 (10 mol%), $AgSbF_6$ (20 mol%), and pivOH (3.0 equiv) in TFE (2.0 mL). [c] The yield data was determined by ^{1}H NMR ratio. [d] A total of 1.3 equiv of styrene was used.

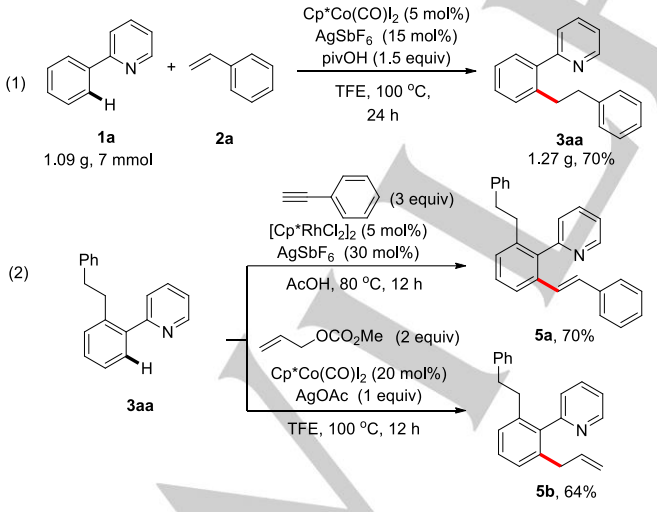
Subsequently, the scope of alkenes was investigated (Table 3). The electronic variation of substituents at the *para*-position on aryl alkene did not affect the reaction efficiency, and the desired products **3ab**–**3af** were isolated in good yields. When the donating group (–Me) and electron-withdrawing groups (–Br, –Cl) were located at the *meta*- and *ortho*-positions, the linear alkylation proceeded smoothly to give **3ag**–**3aj** in good yields ranging from 70% to 85%. Vinyl naphthalenes were also tolerated and afforded the corresponding **3ak** and **3al** in good yields. Notably, the reaction was not restricted to aryl alkenes. Allyl benzene (**2m**) and 4-phenyl-1-butene (**2n**) were also feasible for this transformation to afford **3am** and **3an** in moderate to good yields.

Table 3. Scope of alkenes.[a]



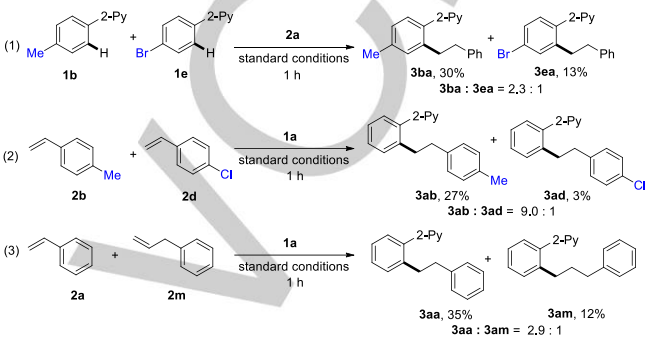
[a] Reaction conditions: **1** (0.20 mmol), **2a** (0.36 mmol), Cp*Co(CO)I_2 (5 mol%), $AgSbF_6$ (15 mol%), and pivOH (1.5 equiv) in TFE (2.0 mL) at 100 °C under argon, 24 h, isolated yields. [b] Cp*Co(CO)I_2 (10 mol%), $AgSbF_6$ (20 mol%), and pivOH (3.0 equiv) in TFE (2.0 mL).

To demonstrate the synthetic utility of this protocol, the scalability of this reaction was examined (Scheme 2-1). The linear-selective C–H alkylation produced the desired product **3aa** with a similar yield of 70% on a 7 mmol scale of **1a**. By taking advantage of the mono-alkylation product, we further functionalized the second *ortho*-C(sp^2)–H bond starting from **3aa**. Under the reaction with Cp*Co(III) or Cp*Rh(III) catalysts, selective *ortho*-olefination and allylation were achieved,[11,14] and the corresponding products **5a** and **5b** were obtained in good yields (Scheme 2-2).



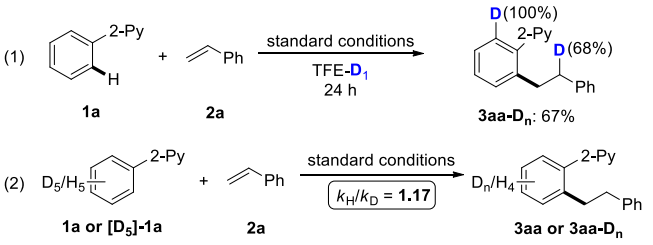
Scheme 2. Gram-scale reaction for the synthesis of **3aa** and additional *ortho*-C(sp^2)–H functionalizations using **3aa**.

To gain a better understanding of the reaction mechanism, a series of experiments was conducted (Scheme 3). An intermolecular competition experiment between electronically different 2-aryl pyridines **1b** and **1e** showed that an electron-rich arene is preferred over an electron-deficient substrate in a 2.3:1 ratio, which suggests an electrophilic C–H bond activation process (Scheme 3-1).[7a] The more electron-rich aryl alkene **2b** also produced the higher yield of the alkylation product than that of electron-deficient aryl alkene **2d** in a 9.0:1 ratio (Scheme 3-2). This result may suggest that this C–H alkylation favored a substrate with electron-rich aryl alkene for the coordination of alkenes to metallacycles.[6c] As expected, a styrene (**2a**) is favored than alkyl alkenes **2m** in a 2.9:1 ratio for C–H alkylation of 2-phenyl pyridine (Scheme 3-3).



Scheme 3. Intermolecular competition reactions.

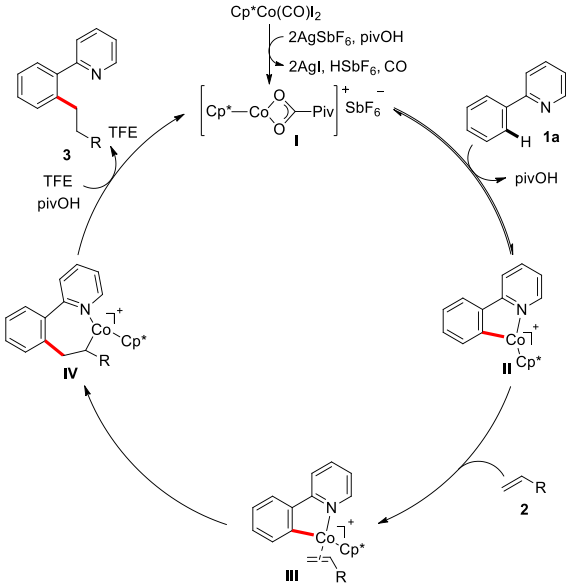
Deuterium labeling experiments were also carried out (Scheme 4). When substrates **1a** and **2a** reacted in the deuterated TFE-D_1 solvent under optimized conditions, 68% of deuterium was incorporated into one benzylic CH_2 group (Scheme 4-1). This result suggests that the protic solvent may transfer deuterium during the protodemetalation process.[10] In addition, 100% of deuterium incorporation in another *ortho*-position of phenyl was observed, which suggests that C–H activation step is reversible under the reaction conditions.[7d] The kinetic isotope effect (KIE) value of 1.17 indicated that the C–H bond cleavage was not involved in the rate-determining step (Scheme 4-2).[15]



Scheme 4. Deuterium-labeling experiments.

On the basis of these control experiments and previous reports,[2g,7a,7d,12,16] the plausible catalytic cycle is shown in Scheme 5. The active cationic species **I** is generated in the presence of Cp*Co(CO)I_2, $AgSbF_6$, and pivOH, which then undergoes electrophilic metalation with **1a** in a reversible manner to form cobaltacycle **II** upon the release of pivOH. The coordination of alkene to metallacycle **II** leads to intermediate **III**, which subsequently undergoes alkene insertion to give cobalt complex **IV**. The decobaltation of **IV** occurs by TFE (Scheme 4-1, deuterium labelling experiments in the Supporting Information),

and produces product **3** along with the regeneration of reactive cobalt species **I**.



Scheme 5. Plausible reaction mechanism.

In conclusion, we have achieved direct C–H alkylation with styrenes using cobalt(III) catalyst, which produced regioselective linear and mono-diarylethane products. This method extended the scope of Cp*Co(III)-catalyzed C–H alkylation, and provided a simple, practical, and atom-economical way to construct phenethyl groups on sp^2 carbon. A wide range of arenes, styrenes, and alkyl arenes were well tolerated under the reaction conditions and showed high functional group compatibility. This reaction was scaled up to gram scale, and the mono-alkylation products were subjected to further C–H bond functionalizations to demonstrate the synthetic utility in organic reactions.

Experimental Section

General procedure for C–H alkylation

An oven-dried Schlenk tube was evacuated and flushed with argon three times. Then, it was evacuated and transferred to the glovebox. $AgSbF_6$ (10.3 mg, 0.03 mmol) was added, and the Schlenk tube was transferred to the fume hood and connected to the argon atmosphere. $Cp^*Co(CO)I_2$ (4.8 mg, 0.01 mmol), 2-aryl pyridine **1** (0.2 mmol, 1.0 equiv), alkene **2** (0.36 mmol, 1.8 equiv), pivOH (30.6 mg, 0.3 mmol), and 2,2,2-trifluoroethanol (TFE) (2.0 mL) were added. The resulting mixture was sealed with a Teflon-lined cap and stirred at 100 ℃ for 24 h. The solvent was evaporated under vacuum and the desired product **3** was obtained by column chromatography using an appropriate eluent.

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Keywords: C–H alkylation • Co(III)-catalyst • phenylethyl group • unactivated alkenes

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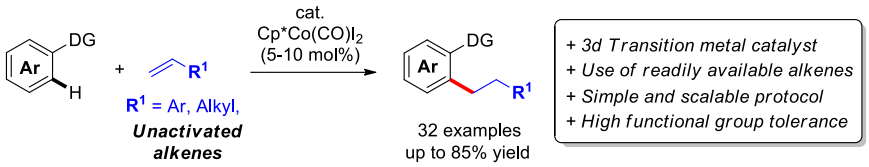

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Page No. – Page No.

Cobalt-Catalyzed Direct C(sp^2)–H Alkylation with Unactivated Alkenes

An efficient Cp*Co(III)-catalyzed direct C(sp^2)–H bond alkylation with unactivated alkenes was developed, affording mono-diarylethane products with high linear selectivity. This reaction provided a simple, practical, and atom-economical way to construct phenethyl groups on sp^2 carbon. A wide range of arenes, styrenes, and alkyl arenes were well tolerated under mild reaction conditions and showed high functional group compatibility.

Key topic : C–H alkylation