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Cobalt-Catalyzed C—H Allylation of Arenes with Allylic Amines

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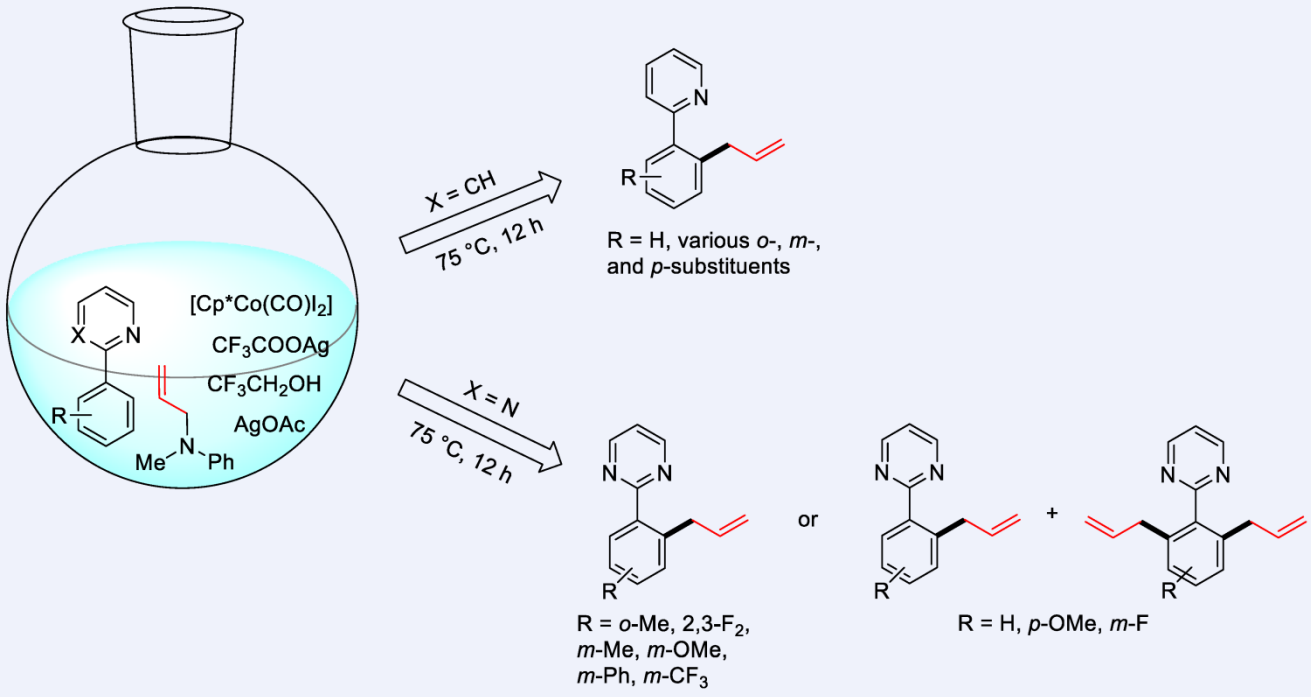
Keywords

C—H activation | C—N activation | Homogeneous catalysis | Cobalt catalysis | Allylation

Main observation and conclusion

[Cp*Co(CO)I_2] effectively catalyzes pyridyl-directed C—H allylation of arenes with allylic amines in the presence of AgOAc and CF_3COOAg. The reaction features *ortho*-position monoallylation of 2-pyridylarenes, giving the allylated arenes in moderate to high yields. A range of functional groups including OMe, Me, Ph, F, Cl, Br, CF_3, C(O)Me, COOEt, and COOH groups are tolerated. Pyrimidyl-directed C—H allylation of arenes were also performed under the same conditions. Reaction of 2-phenylpyrimidine, 2-(4-methoxyphenyl)pyrimidine, and 2-(3-fluorophenyl)pyrimidine leads to a mixture of *ortho*-position mono- and bisallylation products. Reaction of other 2-(substituted aryl)pyrimidines resulted in *ortho*-position monoallylation products.

Comprehensive Graphic Content



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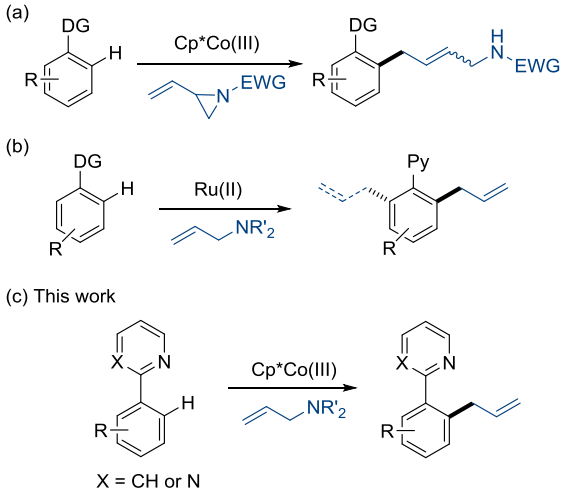
View HTML Article | Supporting Information

Background and Originality Content

Allyl compounds are important in organic synthesis because the allyl moiety can be further converted into various functional groups. The compounds containing an allyl moiety are also found in a number of biologically active molecules.[1] Therefore, synthesis of allyl compounds have attracted much attention over the years.[1,2] In the known synthetic methods, transition-metal-catalyzed allylation of inert C—H bonds is attractive in terms of atom- and step-economy. Ruthenium, rhodium, iridium, palladium, cobalt, iron, and manganese have been used as catalysts for allylation of aryl or alkenyl C—H bonds employing various allylating reagents such as allylic halides,[3] allylic alcohols[4] or their derivatives,[5] allylic amines,[6] allenes,[7] and 1,3-dienes.[8] Among the allylating reagents, allylic amines have been rarely used because of stability of the C—N bonds and poor leaving ability of the amino groups. Clavier *et al.* reported cobalt(III)-catalyzed C—H allylation of arenes with strained vinylaziridines (Scheme 1a).[6a] We and Gooßen's group respectively performed ruthenium-catalyzed C—H allylation of arenes with allylic amines (Scheme 1b).[6b,c] These ruthenium-catalyzed reactions lead to *ortho*-position bisallylation products of arenes in the absence of *ortho*- or hindered *meta*-substituents. In the further study, we found that cobalt can catalyze similar reaction, which features *ortho*-monoallylation of arenes (Scheme 1c). Herein, we report the results.

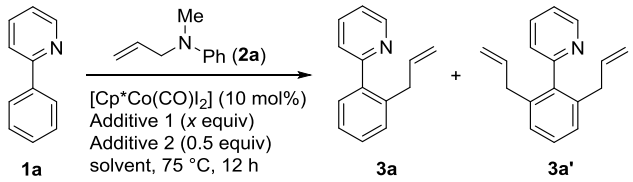
Scheme 1 C—H allylation of arenes with allylic amines



Results and Discussion

Cp*Co(III) has been reported to catalyze C—H allylation of arenes using various allylating reagents.[3a,4b,4c,6a] We chose [Cp*Co(CO)I_2] as catalyst and employed 2-phenylpyridine (**1a**) and *N*-allyl-*N*-methylaniline (**2a**) as the model substrates to screen reaction conditions. In an earlier study, we performed Ru-catalyzed allylation of arenes with allylic amines.[8b] In present study, we first used the same conditions to test the cobalt-catalyzed reaction. Encouragingly, monoallylation product was obtained in 50% yield (Table 1, entry 1). It was reported that cobalt-catalyzed allylation reaction often required other silver salt additive to improve reaction results. 0.5 equiv of $AgSbF_6$ additive did lead to increase of product yield (Table 1, entry 2). Reducing loading of AgOAc to 0.2 equiv gave rise to further increase of product yield (Table 1, entry 3). However, reducing loading of AgOAc to 0.1 equiv caused markedly decrease of yield (Table S1 in Supporting Information). The combination of other silver salts and $AgSbF_6$ was also tested and they were less effective than AgOAc (Table 1, entries 5—7). KOAc and the combination of KOAc and

Table 1 Optimization of reaction conditions[a]



1a **3a** **3a'**

Entry	Additive 1 (equiv)	Additive 2	Equiv of **2a**	Solvent	Yield[b]/% **3a** (**3a'**)
1	AgOAc (0.5)	–	2	CF_3CH_2OH	50 (0)
2	AgOAc (0.5)	$AgSbF_6$	2	CF_3CH_2OH	66 (0)
3	AgOAc (0.2)	$AgSbF_6$	2	CF_3CH_2OH	81 (0)
4	AgOTf (0.2)	$AgSbF_6$	2	CF_3CH_2OH	34 (0)
5	$AgPF_6$ (0.2)	$AgSbF_6$	2	CF_3CH_2OH	64 (0)
6	CF_3COOAg (0.2)	$AgSbF_6$	2	CF_3CH_2OH	52 (0)
7	Ag_2CO_3 (0.2)	$AgSbF_6$	2	CF_3CH_2OH	57 (0)
8	KOAc (0.2)		2	CF_3CH_2OH	22 (0)
9	KOAc (0.2)	$AgSbF_6$	2	CF_3CH_2OH	60 (8)
10	AgOAc (0.2)	CF_3COOAg	2	CF_3CH_2OH	88 (0)
11	AgOAc (0.2)	CF_3COOAg	1.5	CF_3CH_2OH	80 (0)
12	AgOAc (0.2)	CF_3COOAg	3	CF_3CH_2OH	80 (11)
13[c]	AgOAc (0.2)	CF_3COOAg	2	CF_3CH_2OH	60 (0)
14[d]	AgOAc (0.2)	CF_3COOAg	2	CF_3CH_2OH	86/85[e] (0)
15[d]	AgOAc (0.2)	CF_3COOAg	2	EtOH	Trace
16[d]	AgOAc (0.2)	CF_3COOAg	2	Toluene	–
17[d]	AgOAc (0.2)	CF_3COOAg	2	DMF	–
18[d]	AgOAc (0.2)	CF_3COOAg	2	THF	–
19[d]	AgOAc (0.2)	CF_3COOAg	2	DCE	Trace
20[f]	AgOAc (0.2)	CF_3COOAg	2	CF_3CH_2OH	–

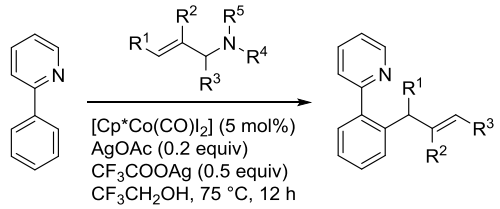
[a] Unless otherwise stated, reactions were run in 1.5 mL of solvent under nitrogen atmosphere; 0.2 mmol of 2-phenylpyridine was employed. [b] Determined by ^{1}H NMR analysis of the crude mixture using 1,1,2,2-tetrachloroethane as an internal standard. [c] 0.2 equiv CF_3COOAg was employed. [d] 5 mol% of [Cp*Co(CO)I_2] was employed. [e] Isolated yield. [f] No [Cp*Co(CO)I_2] was employed.

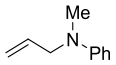
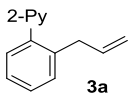
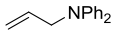
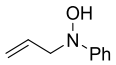
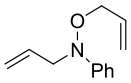
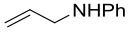
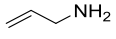
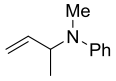
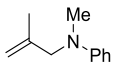
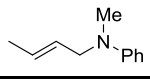
$AgSbF_6$ were also less effective than AgOAc-$AgSbF_6$ combination (Table 1, entries 8 and 9). Further tests showed that the additive AgOAc-CF_3COOAg combination was more effective, which led to 88% products yields (Table 1, entry 10). Role of the silver salts may be to react with the cobalt complex to produce an active catalyst.[4c] The study on temperature effect showed that reaction at 60 °C gave lower product yield compared with that at 75 °C; and reaction at 100 °C gave close yield to that at 75 °C, but along with small amount of bisallylation product (Table S1 in Supporting Information). Examination of loading amount of **2a** showed that employing 2 equiv of **2a** was suitable. Higher loading (3 equiv) led to formation of small amount of bisallylation species besides monoallylation product (Table 1, entries 10—12). Reducing loading of CF_3COOAg caused decrease of product yield (Table 1, entry 13). Reducing amount of catalyst to 5 mol% resulted in almost same product yield as that employing 10 mol% of catalyst (Table 1, entry 14). Next, reaction time was examined and 12 h was demonstrated to be suitable (Table S1 in Supporting Information). Screening of reaction solvents showed that EtOH, toluene, DMF,

THF, and DCE were less effective than CF_3CH_2OH (Table 1, entries 15—19). In addition, in the absence of AgOAc, the reaction gave markedly lower product yield. In the absence of cobalt catalyst, the reaction cannot occur at all (Table S1 in Supporting Information and Table 1, entry 20).

Next, we examined scope of allylic amines *via* reaction with 2-phenylpyridine under the above optimized conditions (Table 2). Besides *N*-allyl-*N*-methylaniline, allylic amines including *N*-allyl-*N*-phenylaniline, *N*-allyl-*N*-phenylhydroxylamine, *N*,*O*-diallyl-*N*-phenylhydroxylamine, *N*,*N*-diallylaniline and *N*-allylaniline can react with 2-phenylpyridine to afford monoallylation product 2-(2-allylphenyl)pyridine in 32%—84% yields (entries 2—6). *N*-Allylaniline exhibited similar reactivity to *N*-allyl-*N*-methylaniline. Other allylic amines showed lower reactivity than *N*-allylaniline and *N*-allyl-*N*-methylaniline. Among them, *N*,*O*-diallyl-*N*-phenylhydroxylamine exhibited the lowest reactivity. Its reaction with 2-phenylpyridine gave the desired product in 32% yield (entry 4). Prop-2-en-1-amine cannot react with 2-phenylpyridine under the standard conditions (entry 7). Several *N*-(methylallyl)-*N*-methylanilines including *N*-(but-3-en-2-yl)-*N*-methylaniline, *N*-methyl-*N*-(2-methylallyl)aniline, and *N*-methyl-*N*-(2-methylallyl)aniline were also tested. The reaction of each of them with 2-phenylpyridine cannot form the desired product (entries 8—10).

Table 2 Scope of allylic amines[a]



Entry	Allylic amine	Product	Yield[b]/%
1		 **3a**	85
2		**3a**	55
3		**3a**	57
4		**3a**	32
5	$PhN(CH_2CH{=}CH_2)_2$	**3a**	75
6		**3a**	84
7		**3a**	–
8		none	–
9		none	–
10		none	–

[a] Unless otherwise specified, the reactions were carried out on a 0.2 mmol scale according to the conditions indicated by the above equation, 2 equiv of allylic amines were employed. [b] Isolated yield.

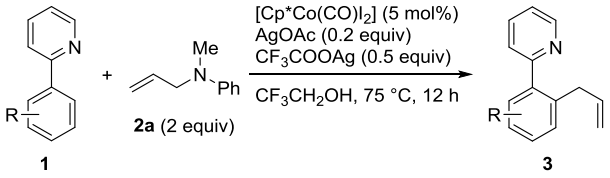
Next we examined scope of 2-arylpyridines *via* reaction with **2a** (Table 3). A series of 2-(*para*-substituted phenyl)pyridines were demonstrated to react smoothly with **2a** to afford *ortho*-monoallylation products in 70%—82% yields (entries 1—10). From the reaction results, it seems that reactivity of the substrates is not regularly related to electron effect of the substituents. A range of functional groups including OMe, Ph, F, Cl, Br, CF_3, C(O)Me, COOEt, and COOH were tolerated. Reaction of 4-(pyridin-2-yl)benzoic acid is a little surprising. The presence of acidic COOH group did not affect the reaction result. We speculated that excess **2a** neutralized the acid and the carboxylate salt participated in the following coupling reaction. Reaction of 2-(*p*-tolyl)pyridine required higher temperature (100 °C) and higher loading of catalyst (10 mol%) to achieve good yield for unclear reasons (entry 1). Reaction of 2-([1,1'-biphenyl]-4-yl)pyridine and 2-(4-chlorophenyl)pyridine required lower loading of **2a** (1.5 equiv) to make sure of formation of monoallylation products (entries 3 and 5). 2-(*meta*-Substituted phenyl)pyridines also reacted smoothly with **2a** to afford *ortho*-monoallylation products in 69%—78% yields (entries 11—15). In each case, the substitution took place on the side of less steric hindrance. Reaction of 2-(*m*-tolyl)pyridine also required higher temperature and higher loading of catalyst (entry 11). 1.5 equiv of **2a** was employed in the reaction of 2-(3-fluorophenyl)pyridine to guarantee monoallylation (entry 14). Reaction of 2-(3,4-dimethyl phenyl)pyridine and 2-(naphthalen-2-yl)pyridine also gave monoallylation products. Reaction of the former proceeded at 100 °C in the presence of 10 mol% of catalyst (entry 16). Several 2-(*ortho*-substituted phenyl)pyridines including 2-(*o*-tolyl)pyridine, 2-(2-methoxyphenyl)pyridine, and 2-(2-halophenyl)pyridine (halo = F, Cl, and Br) were tested and each of them reacted with **2a** to give the desired *ortho*-monoallylation product (entries 18—22). Reaction of 2-(*o*-tolyl)pyridine and 2-(2-bromophenyl)pyridine with **2a** can achieve higher yields when the reactions were performed at 100 °C in the presence of 10 mol% of $[Cp^*Co(CO)I_2]$. The reaction of 2-(2,4-difluorophenyl)pyridine with **2a** under the standard conditions gave 2-(2-allyl-4,6-difluorophenyl)pyridine in 71% yield (entry 23).

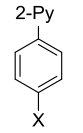
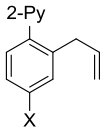
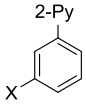
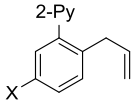
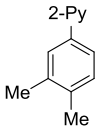
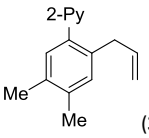
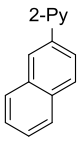
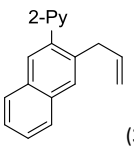
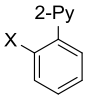
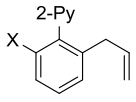
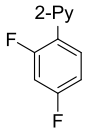
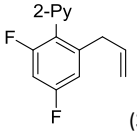
The effect of substituent on the directing group was also tested (Scheme 2). Reaction of 5-methyl-2-phenylpyridine with **2a** was first examined under the standard conditions. The desired product was obtained in 88% yield. This result is very close to that of reaction of 2-phenylpyridine with **2a**. Surprisingly, reaction of 2-methyl-6-phenylpyridine with **2a** did not give any desired product. This is ascribed to steric effect of the methyl group. Thus, the methyl group adjoining the pyridyl nitrogen atom blocks coordination of the nitrogen atom to the cobalt center.

Pyrimidyl group also directed allylation of arenes with **2a**. However, respective reaction of 2-phenylpyrimidine and 2-(4-methoxyphenyl)pyrimidine with **2a** under the standard conditions formed a mixture of mono- and bisallylation products (Scheme 3). Reducing loading amount of **2a** and shortening reaction time cannot lead to formation of single product. For example, reaction of 2-phenylpyrimidine with 1.5 equiv of **2a** for 4 h afforded a about 7.4 : 1 mixture of **4a** and **4a'** in 67% overall yield.

Reaction of 2-(*meta*-substituted phenyl)pyrimidine with **2a** under the standard conditions exhibited good selectivity. Reaction of each of 2-(*m*-tolyl)pyrimidine, 2-(3-methoxyphenyl)pyrimidine, 2-([1,1'-biphenyl]-3-yl)pyrimidine, and 2-(3-(trifluoromethyl)phenyl)pyrimidine with **2a** gave the corresponding *ortho*-monoallylation product in good yield (Table 4, entries 1—4). Exceptionally, reaction of 2-(3-fluorophenyl)pyrimidine under the same conditions gave a mixture of mono- and bisallylation products (Table 4, entry 5). This is attributable to small steric hindrance of the fluorine atom. For comparison, we examined reaction of 2-(3,5-difluorophenyl)pyrimidine and 2-(3,5-dimethylphenyl)pyrimidine, respectively. Reaction of the former gave *ortho*-monoallylation product in 47% yield. No bisallylation product was observed. Reaction of the latter cannot occur (Table 4, entries 6 and 7). Reaction of

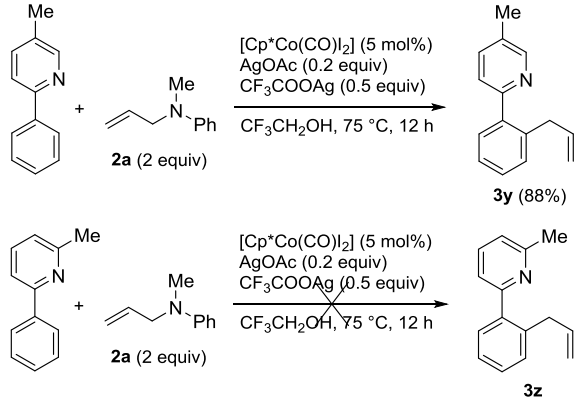
Table 3 Scope of 2-arylpyridines[a]



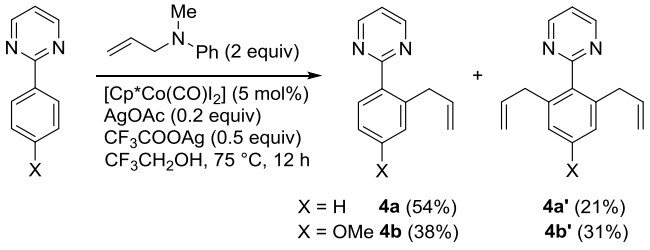
Entry	2-Arylpyridine	Product	Yield[b]/%
			
1		X = Me (**3b**)	70[c,d]
2		X = OMe (**3c**)	82
3		X = Ph (**3d**)	80[e]
4		X = F (**3e**)	75
5		X = Cl (**3f**)	80[e]
6		X = Br (**3g**)	73
7		X = CF_3 (**3h**)	72
8		X = C(O)Me (**3i**)	72
9		X = COOEt (**3j**)	82
10		X = COOH (**3k**)	71
			
11		X = Me (**3l**)	69[c,d]
12		X = OMe (**3m**)	71
13		X = Ph (**3n**)	78
14		X = F (**3o**)	73[e]
15		X = Cl (**3p**)	77
16		 (**3q**)	62[c,d]
17		 (**3r**)	60
			
18		X = Me (**3s**)	50 (65[c,d])
19		X = OMe (**3t**)	81
20		X = F (**3u**)	82
21		X = Cl (**3v**)	69
22		X = Br (**3w**)	56 (67[c,d])
23		 (**3x**)	71

[a] Unless otherwise specified, the reactions were carried out on a 0.2 mmol scale according to the conditions indicated by the above equation, 2 equiv of **2a** was employed. [b] Isolated yield. [c] Reaction was run at 100 °C. [d] 10 mol% of [Cp*Co(CO)I_2] was employed. [e] 1.5 equiv of **2a** was employed.

Scheme 2 Reaction of 2-methyl-6-phenylpyridine and 5-methyl-2-phenylpyridine with **2a**



Scheme 3 Cobalt-catalyzed reaction of 2-phenylpyrimidine and 2-(4-methoxyphenyl)pyrimidine with **2a**



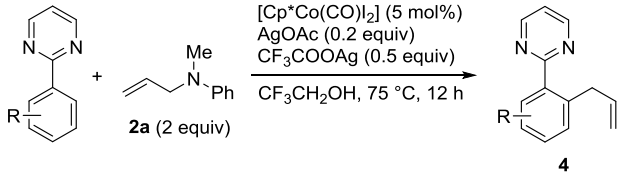
2-(*o*-tolyl)pyrimidine and 2-(2,3-difluorophenyl)pyrimidine under the standard conditions afforded the desired products in relatively low yields. The reaction can be improved by employing 10 mol% of catalyst (Table 4, entries 8 and 9). Finally, reaction of 1-(pyrimidin-2-yl)-1*H*-indole with **2a** was tested, which gave 2-allyl-1-(pyrimidin-2-yl)-1*H*-indole in 76% yield (Table 4, entry 10).

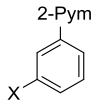
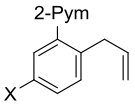
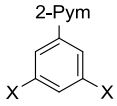
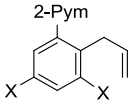
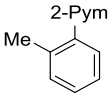
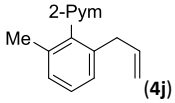
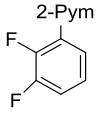
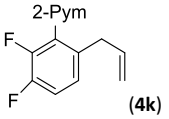
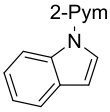
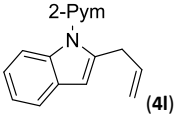
Preliminary mechanistic studies were performed. Firstly, in the absence of an allylic amine, reaction of **1a** with D_2O was run under the standard conditions for 2 h and the resulting product **1aa** contained 45% of *ortho*-D content (Scheme 4a). Next, in the absence of an allylic amine, treatment of 2-(phenyl-d_5)pyridine **1ab** for 2 h resulted in **1ac**, which contained 18% of *ortho*-D content (Scheme 4b). These facts showed that a reversible H/D exchange can occur under the experimental conditions. Finally, we measured the kinetic isotopic effect *via* the reaction of **1a** and **1ab** with **2a** under the standard conditions. A k_H/k_D value of 1.1 was obtained by analyzing the ^{1}H NMR spectrum of the product (Scheme 4c). This result suggests that the C—H bond cleavage may not be the rate-limiting step. Based on the experimental facts and literature reports,[4c,9] we proposed a plausible catalytic cycle as shown in Scheme 5. [Cp*Co(CO)I_2] reacts with AgOAc in the presence of CF_3COOAg to form active catalyst [Cp*Co^{III}(OAc)]$^+$ (**A**). Next, C—H bond metalation takes place to produce cobaltacycle **B**. C—C double bond insertion of the allylic amine leads to intermediate **C**. β-Amino elimination generates the allylated product and amino cobalt complex **D**, which further converts to active catalyst **A** *via* reaction with AcOH. In the step of β-amino elimination, the protic solvent might promote the C—N bond cleavage of allylic amines *via* a hydrogen-bond activation.[10]

Conclusions

In summary, we developed a cobalt-catalyzed method for the allylation of arenes *via* pyridyl- or pyrimidyl-directed aryl C—H bond activation and cleavage of the C—N bond of allylic amines. The reaction proceeded under mild conditions and afforded the

Table 4 Cobalt-catalyzed reaction of 2-arylpyrimidines with **2a**[a]



Entry	2-Arylpyrimidine	Product	Yield[b]/%
			
1		X = Me (**4c**)	84
2		X = OMe (**4d**)	76
3		X = Ph (**4e**)	82
4		X = CF_3 (**4f**)	86
5		X = F (**4g**)	40 (51[c])
			
6		X = F (**4h**)	47
7		X = Me (**4i**)	0
8		 (**4j**)	53 (70[d])
9		 (**4k**)	34 (57[d])
10		 (**4l**)	76

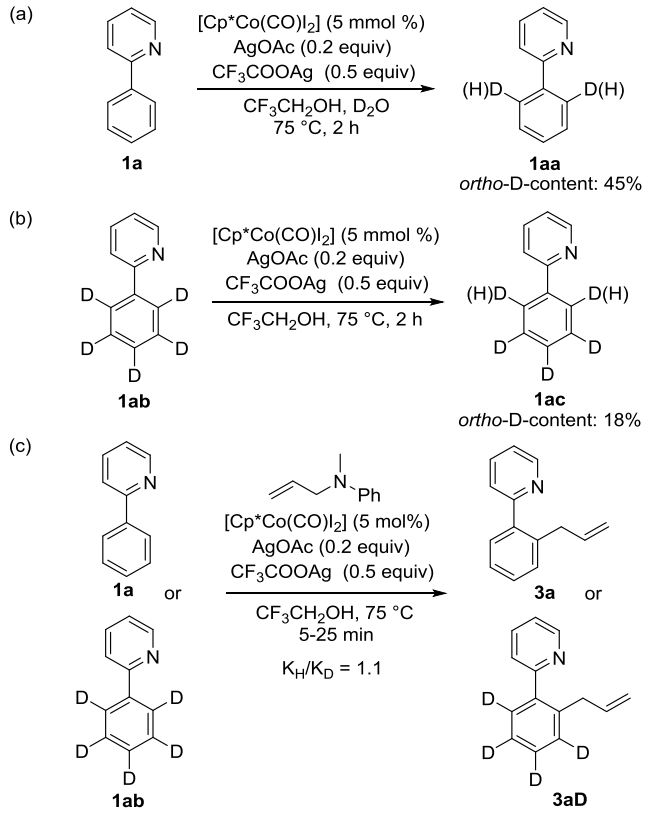
[a] Unless otherwise specified, the reactions were carried out on a 0.2 mmol scale according to the conditions indicated by the above equation. [b] Isolated yield. [c] Yield of 2-(2,6-diallyl-3-fluorophenyl)pyrimidine. [d] Yield of monoallylation product when 10 mol% of $[Cp^*Co(CO)I_2]$ was employed.

allylation products in moderate to high yields. Pyridyl-directed reactions exhibited higher selectivity. *ortho*-Position monoallylation products of the phenyl groups were obtained whether it is *ortho*-, *meta*- or *para*-substituted phenyl substrates to be used. A range of functional groups including electron-donating and electron-withdrawing groups such as OMe, Me, Ph, F, Cl, Br, CF_3, C(O)Me, COOEt, and COOH on the phenyl rings can be tolerated. This protocol is complementary with Ru-catalyzed allylation of 2-arylpyridines with allylation amines, which led to bisallylation products of 2-(*para*-substituted phenyl)pyridines and less sterically hindered 2-(*meta*-substituted phenyl)pyridines.

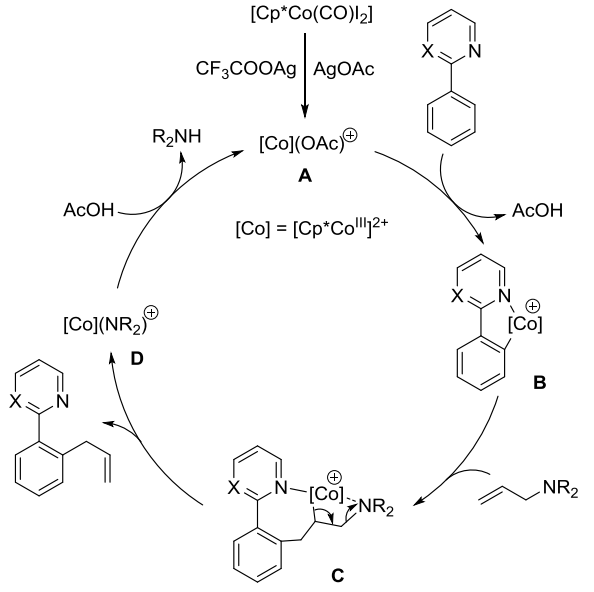
Experimental

2-Arylpyridines (0.2 mmol), allylic amines (0.4 mmol), AgOAc (0.04 mmol), CF_3COOAg (0.1 mmol), $[Cp^*Co(CO)I_2]$ (0.01 mmol), and CF_3CH_2OH (1.5 mL) were successively added into a Schlenk tube. The mixture was stirred at 75 °C for 12 h. Upon cooling to room temperature, the resulting mixture was diluted with EtOAc and filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography to afford the desired product.

Scheme 4 Mechanistic studies



Scheme 5 Plausible mechanism



Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.202000680.

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