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Cp*Co^{III}-Catalyzed Dehydrative C−H Allylation of 6-Arylpurines and Aromatic Amides Using Allyl Alcohols in Fluorinated Alcohols

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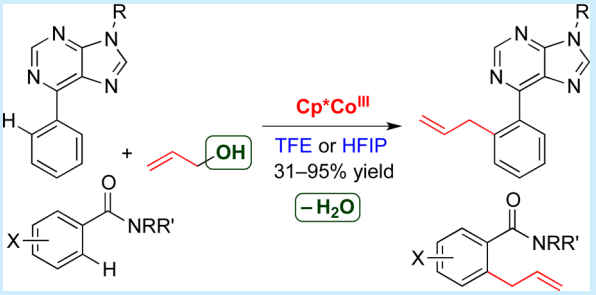
Supporting Information

ABSTRACT: Cp*Co^{III}-catalyzed C−H allylation of various aromatic C−H bonds using allyl alcohols as allylating reagents is described. Improved reaction conditions using fluorinated alcohol solvents afforded efficient directed C−H allylation of 6-arylpurines, benzamides, and a synthetically useful Weinreb amide with good functional group compatibility.



Allylation of aromatic compounds is very important in organic synthesis because the allyl moiety can be further converted into a wide variety of functional groups. In terms of atom economy,[1] step economy,[2] and functional group compatibility, direct allylation of inert C−H bonds under transition metal catalysis[3] is more attractive than classical allylation methods, such as cross-coupling reactions of functionalized arenes.[4,5] Therefore, aromatic and olefinic C−H allylation reactions using allyl acetates,[6] carbonates,[7] phosphates,[8] halides,[9] and ethers[10] as allylating reagents were developed over the past decade using various transition metals. Among them, Cp*Rh^{III}-catalyzed[11] C−H allylation reactions using preactivated allyl alcohols[6c,7b−d,8d,9d,10b] are especially noteworthy due to their mild reaction conditions and broad substrate scope.[12] Those reactions are thought to proceed via C−H metalation, olefin insertion, and subsequent β-elimination of oxygen-containing functional groups.

We[13] and other groups[14,15] have investigated Cp*Co^{III} catalysts for C−H bond functionalization as an inexpensive alternative[16] to Cp*Rh^{III} catalysts after our first report in 2013.[13a] Glorius[17] and Ackermann[18] independently reported Cp*Co^{III}-catalyzed C−H allylation of indoles, pyrroles, and 2-phenylpyridines using preactivated allyl alcohol derivatives under mild conditions. The scope of this reaction was further expanded to benzamide derivatives.[19] On the other hand, we recently reported that unactivated allyl alcohols can be used directly for aromatic C−H allylation under Cp*Co^{III} catalysis, while Cp*Rh^{III} exhibited inferior catalytic activity.[20] Key to this reaction is likely the more favored β-hydroxy elimination over the potentially competing β-hydride elimination after insertion of a C−C double bond.[21] The substrate scope of our previous protocol, however, was limited to indoles and 1-phenylpyrazole. Although it was reported that *N*-methylbenzamide can be allylated using an allyl alcohol, the yield was low, and its generality was not demonstrated.[19] During the preparation of our manuscript, Kapur reported Ru^{II}-catalyzed C−H allylation using allyl alcohols, but the scope was still limited to indoles, an indoline, and 2-phenylpyridine.[22] Here we report an improved protocol for Cp*Co^{III}-catalyzed dehydrative C−H allylation of aromatic compounds using allyl alcohols. The use of fluorinated alcohol solvent significantly enhanced the reactivity, enabling allylation of 6-arylpurines, benzamides, and an aromatic Weinreb amide in moderate to excellent yield.

We first selected 6-phenylpurine **1a** as a model substrate (Table 1). Transition-metal-catalyzed C−H bond functionalization of 6-arylpurines has recently attracted much attention[23] due to their biological activities.[24] Previously reported conditions for allylation of indoles[20] using [Cp*Co(CO)I$_2$] (5 mol %), AgOTf (10 mol %), and AgOAc (10 mol %) in DCE at 60 °C selectively afforded monoallylated product **3a**, but in only 13% yield (entry 1). Screening of the solvent led to a significantly improved yield of **3a** (entries 2−6). Although most of the solvents were ineffective, 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) exhibited high reactivity,[25] and **3a** was obtained in good yields (entries 5, 6). Changing AgOTf to other Ag salts did not affect the reactivity (entries 7−10), whereas the yield was decreased when no cationic Ag salts were used (entry 11). Other acetate bases were less effective than AgOAc (entries 12−14). Almost no product was detected in the absence of acetate bases (entry 15), indicating that a carboxylate-assisted concerted

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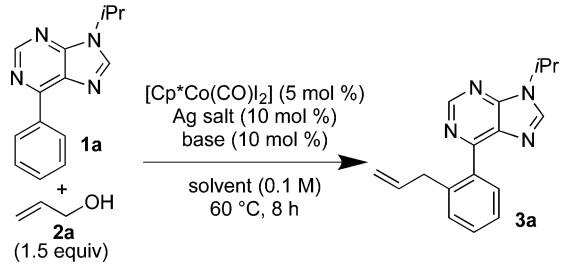
Table 1. Optimization of Reaction Conditions[a]



entry	solvent	Ag salt	base	yield[b] (%)
1	DCE	AgOTf	AgOAc	13
2	THF	AgOTf	AgOAc	trace
3	toluene	AgOTf	AgOAc	6
4	MeOH	AgOTf	AgOAc	3
5	TFE	AgOTf	AgOAc	81 (78[c])
6	HFIP	AgOTf	AgOAc	72
7	TFE	$AgSbF_6$	AgOAc	78
8	TFE	$AgNTf_2$	AgOAc	79
9	TFE	$AgBF_4$	AgOAc	80
10	TFE	$AgPF_6$	AgOAc	73
11	TFE	none	AgOAc	42
12	TFE	AgOTf	NaOAc	8
13	TFE	AgOTf	KOAc	29
14	TFE	AgOTf	CsOAc	12
15	TFE	AgOTf	none	trace

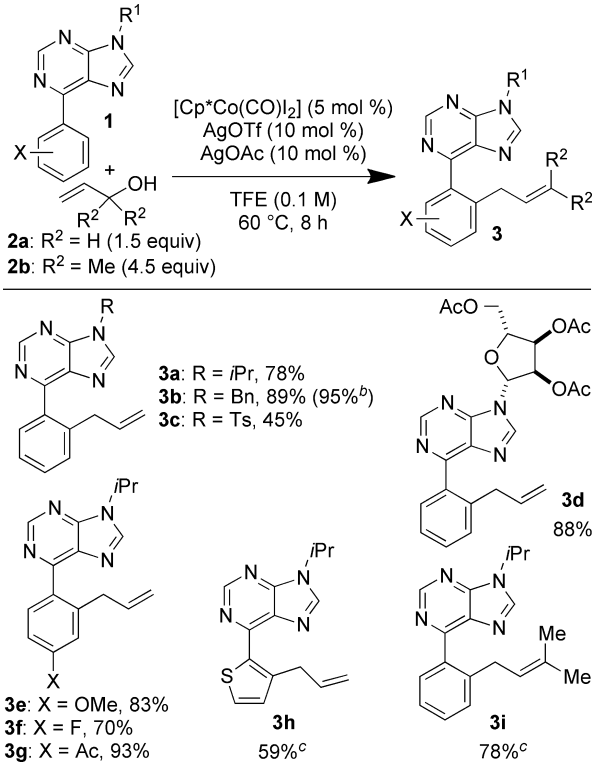
[a]The reactions were run using **1a** (0.10 mmol) and **2a** (0.15 mmol) in indicated solvent (0.1 M) at 60 °C. [b]Determined by ^1H NMR analysis of the crude mixture using dibenzyl ether as an internal standard. [c]Isolated yield after silica gel column chromatography at 0.30 mmol scale.

metalation−deprotonation mechanism works in this reaction.[26] Under the best reaction conditions in entry 5, the allylated product **3a** was isolated in 78% yield after chromatographic purification.

After optimizing the conditions, the scope of 6-arylpurines was investigated (Scheme 1). In addition to *N*9-alkylated purine derivatives **1a**, **1b**, and *N*9-tosylated purine **1c**, fully acetylated 6-phenylpurine riboside **1d** was allylated without any difficulty to give **3d** in 88% yield. Both electron-donating and -withdrawing groups were compatible on the phenyl moiety, and products **3e−g** were obtained in 70%−93% yield. Heteroarylpurine **1h** also successfully afforded allylated product **3h** in 59% yield. The reaction using tertiary allyl alcohol **2b** proceeded γ-selectively to afford prenylated product **3i**. The scalability of the new protocol was also confirmed by a gram-scale experiment in which **3b** was obtained in 95% yield.

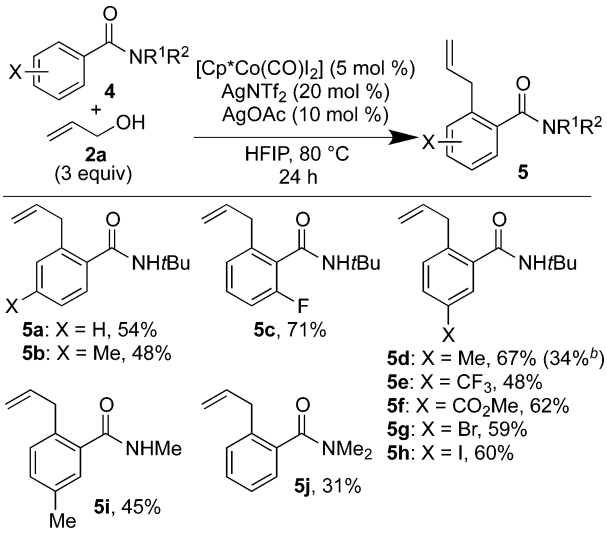
Next we turned our attention to the allylation of other aromatic compounds. After minor modification of the reaction conditions,[27] benzamide derivatives **4** were also allylated using 20 mol % of $AgNTf_2$ and HFIP solvent, as shown in Scheme 2. Unsubstituted benzamide **4a** and *p*-Me-benzamide **4b** afforded the corresponding allylated products in moderate yields along with the bis-allylated byproducts.[28] Allylation of *o*-F-benzamide **4c** proceeded in 71% yield. Various *m*-substituted benzamide derivatives, including I-substituted substrate **4h**, afforded the monoallylated products in acceptable yields with >10/1 regioselectivity (**5d−5h**). *N*-Methylbenzamide **4i** and *N*,*N*-dimethylbenzamide **4j** also afforded the allylated products **5i** and **5j** albeit in diminished yields. To confirm the importance of the fluorinated alcohol, a negative control experiment using previously

Scheme 1. Scope of Dehydrative Allylation of 6-Arylpurines[a]



[a]The reactions were run using **1** (0.30 mmol), **2**, [Cp*Co(CO)I_2] (5 mol %), AgOTf (10 mol %), AgOAc (10 mol %) in TFE (0.1 M) at 60 °C for 8 h unless otherwise noted. The indicated yields are isolated yields after silica gel column chromatography. [b]1.0 g (3.5 mmol) of **1b** was used, and 1.08 g of **3b** was isolated. [c]The reaction time was 24 h. [d]The reaction was run at 70 °C.

Scheme 2. Dehydrative Allylation of Benzamides[a]



[a]The reactions were run using **4** (0.30 mmol), **2** (0.90 mmol), [Cp*Co(CO)I_2] (5 mol %), $AgNTf_2$ (20 mol %), AgOAc (10 mol %) in HFIP (1.0 M) at 80 °C for 24 h unless otherwise noted. The indicated yields are isolated yields after silica gel column chromatography. [b]Using DCE instead of HFIP as solvent.

used DCE as a solvent was performed for **4d**. As expected, a lower yield was obtained compared with that in HFIP (34% in DCE vs 67% in HFIP).

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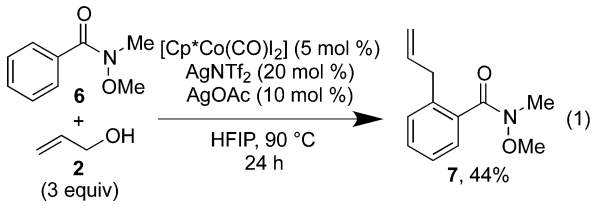
Synthetically useful Weinreb amide[29] **6** was also allylated in moderate yield (eq 1). It is noteworthy that the Weinreb



amide-directed C−H bond functionalization reaction is rather limited possibly due to its weak coordinating ability,[30] and this is the first example of Weinreb amide-directed C−H bond functionalization under high-valent cobalt catalysis.

Figure 1 shows a plausible catalytic cycle for the allylation of 6-arylpurine **1** based on previous Cp*Rh^{III}-[7b] and

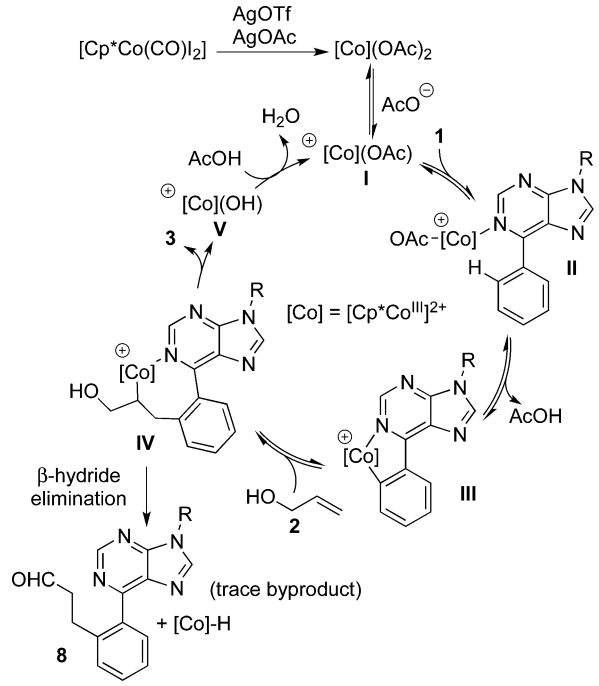


Figure 1. Plausible catalytic cycle for allylation of **1**.

Cp*Co^{III}-catalyzed[17−20] allylation reactions, and C−H functionalization reactions of **1**.[23] The active catalyst would be coordinatively unsaturated cationic complex **I** generated from [Cp*Co(CO)I$_2$], AgOTf, and AgOAc. Coordination of **1** (**II**) followed by acetate-assisted C−H metalation would afford metallacycle intermediate **III**. After insertion of allyl alcohol **2** (**IV**), *β*-hydroxy elimination would release product **3** and hydroxide complex **V**,[31] which would undergo protonation by AcOH to regenerate **I**. We observed trace amounts of aldehyde **8** as a byproduct in the reaction of **1b**. This byproduct supports the intermediate **IV**, from which *β*-hydride elimination to afford **8** is unfavorable but possible.[21] The reason for the observed notable solvent effect is unclear, but the high polarity, moderate acidity, and weak coordinating ability of TFE and HFIP may facilitate the dissociation of acetate or other ligands and promote the generation of coordinatively unsaturated active species such as **I** and **III**. Coordination of acetate or another substrate **1** to these species could interfere with the desired reaction pathway.

In summary, efficient and general reaction conditions for Cp*Co^{III}-catalyzed aromatic C−H allylation of 6-arylpurines, and benzamide derivatives using allyl alcohols as allylating reagents were developed. Use of fluorinated alcohol solvents was crucial for improving the scope of the dehydrative C−H allylation. We also describe our preliminary result of allylation of an aromatic Weinreb amide to further demonstrate the possibility of Cp*Co^{III}-catalyzed C−H functionalization reactions for the production of synthetically useful compounds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00846.

Experimental procedures, characterization data, and copy of NMR spectrum (PDF)

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Notes

The authors declare no competing financial interest.

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