ACS Catalysis

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Cobalt(III)-Catalyzed C−H Amidation of Arenes using Acetoxycarbamates as Convenient Amino Sources under Mild Conditions

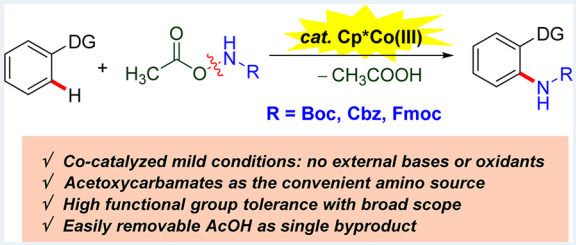
Pitambar Patel[†,‡] and Sukbok Chang*[,†,‡]

[†]Center for Catalytic Hydrocarbon Functionalizations, Institute for Basic Science (IBS), Daejeon 305-701, Korea

[‡]Department of Chemistry, Korea Advanced Institute of Science & Technology (KAIST), Daejeon 305-701, Korea

Supporting Information

ABSTRACT: The Co(III)-catalyzed direct C−H amidation of arenes has been developed using *O*-acylcarbamates as a convenient amino source. This reaction proceeded in high efficiency under external oxidant-free conditions with a broad range of arene substrates, including 6-arylpurines bearing sensitive functional groups, thus furnishing synthetically versatile arene *N*-carbamate products.

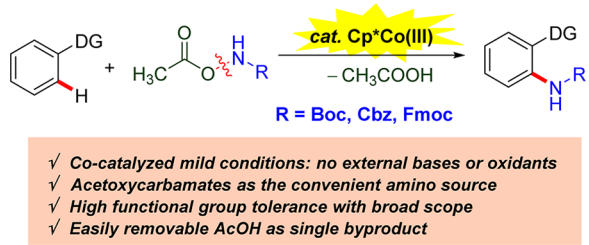


KEYWORDS: *cobalt catalysis, C−H amidation, acetoxycarbamates, 6-arylpurines, arylamines*

INTRODUCTION

In recent years, transition-metal-catalyzed direct C−H amination has been extensively investigated as a selective and straightforward method for the synthesis of (hetero)aryl amines.[1,2] This approach displays certain advantages over the traditional methods in that arenes are directly employed as substrates without prefunctionalization. As a result, a list of metal-catalyzed procedures, including Pd,[3] Rh,[4] Ru,[5] and Ir[6] catalyses, have been scrutinized. In this regard, we also have developed Cp*-based catalytic systems of Rh(III)[7a−d] and Ir(III)[7e−i] for the C−H amination of arenes, alkenes, and alkanes using organic azides as the amino source. The fact that the currently available procedures are mediated mainly by precious late transition metals, albeit being efficient and mild, has led us to search for an alternative catalytic system employing earth-abundant first-row transition metals.[8] In the past few years, while copper and iron species have been scrutinized as catalysts for C−H amination,[9] cobalt has emerged as one of the promising metal species for C−H bond functionalization, being especially effective in C−C bond formation.[10] In this line, we envisaged that our previous catalytic systems of Rh or Ir could be extended to their group 9 cousin, cobalt.[11] Indeed, we already reported a comparative study of the Cp*-based group 9 metal-catalyzed C−H amination using *organic azides* to reveal that [Cp*Co^{III}] showed much poorer catalytic activity in comparison to the corresponding Rh or Ir systems.[12] However, a recent report from the Kanai group demonstrated that C-2 amidation of indoles could be highly efficient with CoCp*(CO)I_2 catalyst using sulfonyl azides.[13,14] Herein, we report the development of Co(III)-catalyzed direct C−H amidation using *acetoxycarbamates* as the new and convenient amidating source[15,16] to afford synthetically versatile N-substituted aniline products (Scheme 1). This protocol was also successfully extended to the selective amidation of 6-arylpurines.

Scheme 1. Co(III)-Catalyzed C−H Amidation



RESULTS AND DISCUSSION

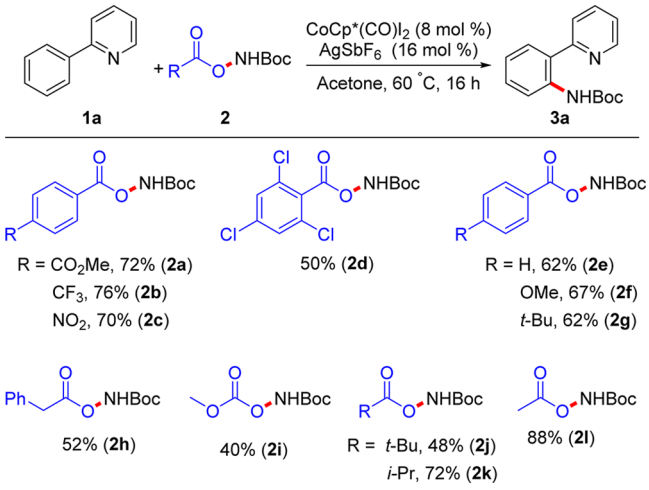
At the outset of our studies, 2-phenylpyridine (**1a**) was chosen as a model substrate to react with 1.1 equiv of *N*-Boc-substituted benzoylhydroxylamine (**2a**) for the initial screening of Co-catalyzed optimal amidation conditions. After a series of preliminary reactions, we were pleased to observe that the desired monoamidated product (**3a**) could be obtained in 72% yield using an ester-substituted aroyloxy carbamate (**2a**) as an amidating reagent when CoCp*(CO)I_2 (8 mol %) was employed as a catalyst in the presence of $AgSbF_6$ (16 mol %) in acetone at 60 °C (see the Supporting Information for details). With this promising initial result, we decided to search

Received: November 24, 2014
Revised: December 19, 2014
Published: December 22, 2014

DOI: 10.1021/cs501860b
ACS Catal. 2015, 5, 853−858

for additional carbamates to see the effects of leaving groups on the reaction efficiency (Scheme 2).

Scheme 2. Screen of Amidating Reagents[a]



[a]Reaction conditions: **1a** (0.1 mmol), **2** (1.1 equiv), $CoCp^*(CO)I_2$ (8 mol %), and $AgSbF_6$ (16 mol %) in acetone (0.7 mL) at 60 °C for 16 h. Yields are based on ^1H NMR of the crude reaction mixture ($Cl_2CHCHCl_2$ as an internal standard).

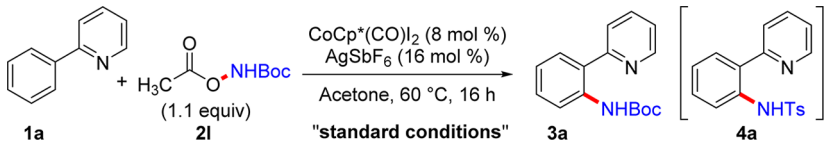
It was found that aroyloxy carbamates bearing electron-withdrawing (**2a**–**c**) groups, except for **2d**, were slightly more effective than either that with a unsubstituted benzoyl group (**2e**) or those having electron-donating groups (**2f**,**g**). In addition, acyloxy analogues such as phenylacetyl (**2h**), methoxycarbonyl (**2i**), pivaloyl (**2j**), and isobutyryl (**2k**) also participated in the amidation with slightly lower efficiency in comparison to that of aroyloxy carbamates. Most significantly, on the other hand, acetoxycarbamate (**2l**) was found to be a highly efficient amidating reagent to afford the desired product (**3a**) in good yield. It should be emphasized that an easily removable byproduct (acetic acid) is generated from this reaction using **2l**, thus making this procedure highly convenient to perform.

With the finding of a readily available amidating reagent in hand, we subsequently optimized reaction parameters using *tert*-butyl acetoxycarbamate (**2l**) in the amidation of 2-phenylpyridine (**1a**; Table 1).

While the amidation at higher temperature (80 °C; entry 2) proceeded with similar efficiency, the reaction efficiency decreased at a lower temperature (entry 3). No reaction was observed in the absence of cobalt catalyst or silver salt additive (entries 4 and 5). Among the various silver additives screened, $AgSbF_6$ turned out to be most effective (entries 6–8), and $NaSbF_6$ was found to be totally inhibitory (entry 9). The reaction efficiency decreased to some extent when the catalyst loading was reduced to 5 mol % (entry 10). Interestingly, a similar result was obtained with the use of a dimeric cobalt species $[CoCp^*I_2]_2$ (4 mol %; entry 11).[17] On the other hand, the observation that sulfonyl azide was totally ineffective (entry 12) under the present Co catalytic conditions is in distinct contrast to our previous results that organic azides were highly efficient amidating reagents under the Rh, Ir, or Ru catalyst systems.[5c,7] In addition, C–H amidation using *tert*-butyl acetoxycarbamate (**2l**) did not occur when other cobalt species such as $CoCl_2$, $Co(acac)_3$, and $Co(OAc)_2$ were used as catalysts (see the Supporting Information for details).

With the optimized cobalt catalyst system with *tert*-butyl acetoxycarbamate (**2l**), the scope of substrates was investigated next (Scheme 3). The amidation proceeded efficiently over a broad range of substrates, irrespective of their electronic and/or steric variation. In fact, 2-phenylpyridine derivatives bearing alkyl groups underwent amidation smoothly (**3b**–**e**), and this efficiency was not altered by the position of the substituents. The reaction of an amino-containing substrate was smooth (**3f**), and substrates bearing an ether functionality such as methoxy (**3g**) or benzyloxy (**3h**) were also facile for the amidation. Synthetically important functional groups such as acetyl (**3i**), ester (**3j**), chloro (**3l**,**n**), and bromo (**3m**) were well tolerated under the present conditions. Regioselective amidation took place at the sterically less demanding C–H bond of substrates bearing meta substituents (**3c**,**d**,**n**). In addition, it needs to be mentioned that amidation occurred at the ortho position relative to the 2-pyridyl moiety in the

Table 1. Variation of Reaction Parameters

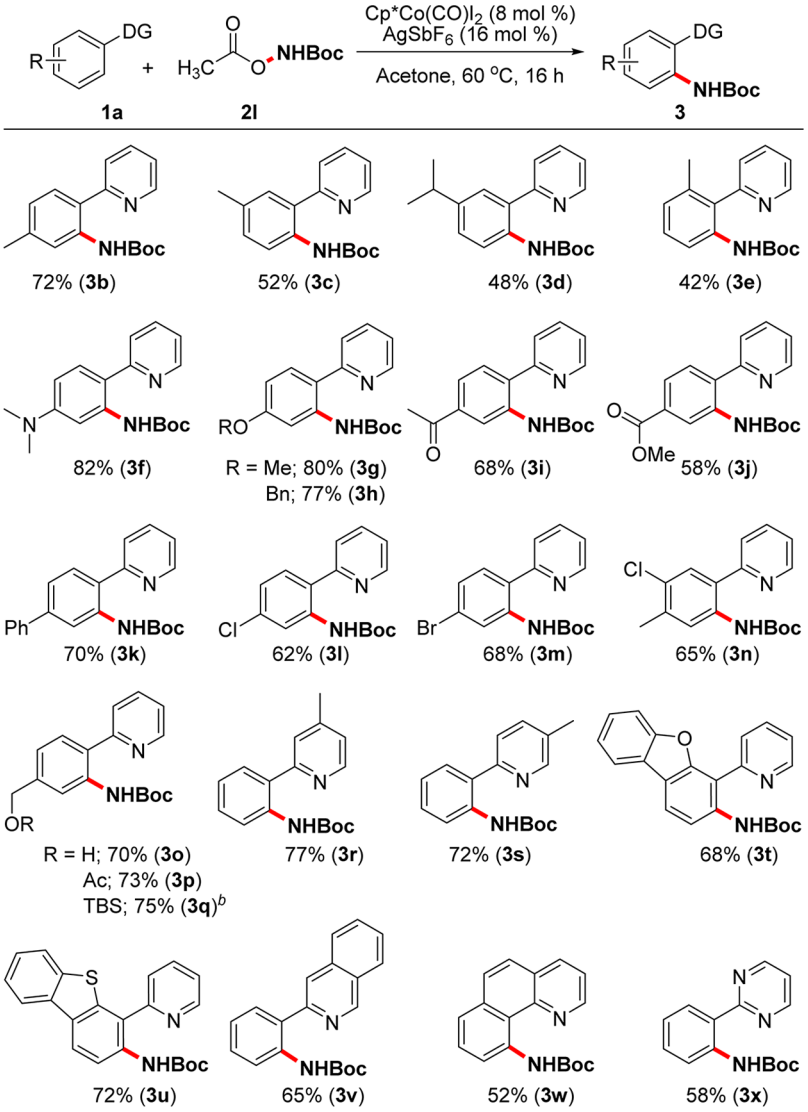


entry	change from the "standard conditions"	yield of **3a** (%)[a]
1	none	88 (84)
2	80 °C instead of 60 °C	82
3	50 °C instead of 60 °C	66
4	no $CoCp^*(CO)I_2$	0
5	no $AgSbF_6$	0
6	$AgNTf_2$ instead of $AgSbF_6$	68
7	AgOAc instead of $AgSbF_6$	12
8	Ag_2CO_3 instead of $AgSbF_6$	10
9	$NaSbF_6$ instead of $AgSbF_6$	0
10	5 mol % of $CoCp^*(CO)I_2$ instead of 8 mol %	60
11	4 mol % of $[CoCp^*I_2]_2$ instead of $CoCp^*(CO)I_2$	74
12	TsN_3 instead of **2l** to give **4a**	0

[a]^1H NMR yield ($Cl_2CHCHCl_2$ as an internal standard); isolated yield in parentheses.

DOI: 10.1021/cs501860b
ACS Catal. 2015, 5, 853–858

Scheme 3. Substrate Scope of Amidation Reaction[a]



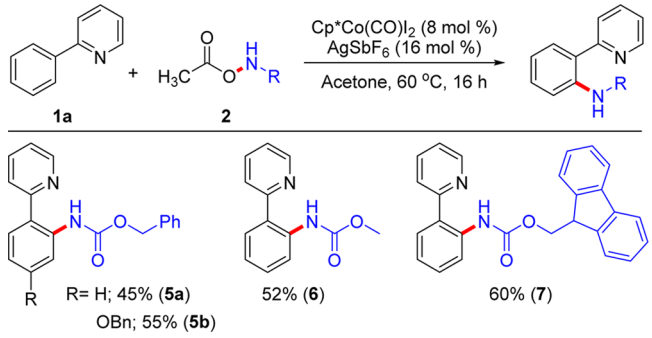
[a]Reaction conditions: **1a** (0.1 mmol), **2l** (1.1 equiv), $CoCp^*(CO)I_2$ (8 mol %), and $AgSbF_6$ (16 mol %) in acetone (0.7 mL) at 60 °C for 16 h. [b]TBS = *tert*-butyldimethylsilyl.

presence of potential directing groups such as ketone and ester (**3i,j**).[7g] On the other hand, amidation of 2-(3,5-disubstituted phenyl)pyridines was not successful, presumably due to steric congestion.

Functional group tolerance was again verified in the successful amidation of compounds bearing free hydroxyl (**3o**), acetyl (**3p**), and silyl (**3q**) groups. The reaction of fused heterocyclic arenes such as dibenzofuryl (**3t**) and dibenzothiophenyl (**3u**) was smooth. In addition, the amidation of 3-phenylisoquinoline (**3v**), benzo[*h*]quinoline (**3w**), and 2-phenylpyrimidine (**3x**) was observed to be facile under the cobalt-catalyzed conditions. However, the amidation of arenes containing amide, ester, and oxime directing groups was sluggish to give low product yields under the present conditions.

As the next step, we were interested in the introduction of different amido groups in addition to the *N*-Boc moiety by examining various carbamates (Scheme 4). We were pleased to see that a range of amidating reagents was successfully employed under the presently developed Co catalytic system,

Scheme 4. Scope of Various N-Protecting Groups[a]

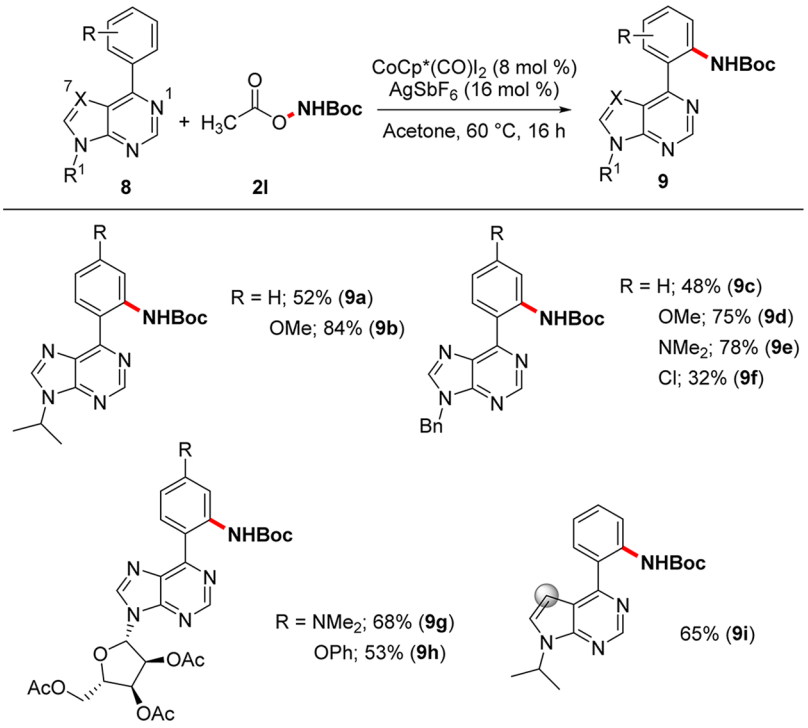


[a]Reaction conditions: **1a** (0.1 mmol), **2** (1.1 equiv), $CoCp^*(CO)I_2$ (8 mol %), and $AgSbF_6$ (16 mol %) in acetone (0.7 mL) at 60 °C for 16 h.

although the reaction efficiency was slightly lower in comparison to that of the corresponding *N*-Boc. It is noteworthy that those installed N substituents can readily be

DOI: 10.1021/cs501860b
ACS Catal. 2015, 5, 853−858

Scheme 5. Direct C−H Amidation of 6-Arylpurine Derivatives[a]



[a]Reaction conditions: **8** (0.1 mmol), **2l** (1.1 equiv), $CoCp^*(CO)I_2$ (8 mol %), and $AgSbF_6$ (16 mol %) in acetone (0.7 mL) at 60 °C for 16 h.

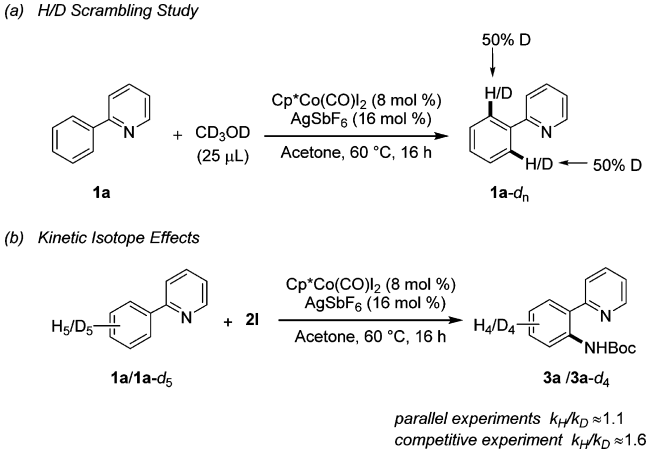
removed under varied conditions: acidic (*N*-Boc), reductive (*N*-Cbz; **5a**,**b**), or basic (*N*-Fmoc; **7**).[18]

6-Arylpurine compounds are biologically interesting in that they often exhibit high potency in antimycobacterial, cytostatic, and anti-HCV activities.[19] Whereas purine is an important building unit in the synthesis of nucleosides, it also serves as an effective directing group in the direct C−H functionalization of 6-arylpurines in Ru,[20a] Pd,[20b,c] or Rh catalytic systems.[20d] In particular, we recently demonstrated that the purinyl N1 atom plays a key role in the Rh-catalyzed amidation in generating a rhodacycle intermediate, while N7 promotes an intramolecular H bonding of amidated products.[20d] In this aspect, we were curious whether similar directing effects can also be displayed by the purine moiety even in the present cobalt catalyst system.

We were pleased to observe that the amidation indeed occurs over a wide range of 6-arylpurines in the Co-catalyzed system by using *tert*-butyl acetoxycarbamate (**2l**) as the amino source (Scheme 5). While its efficiency was found to be little influenced by the type of N9 substituent, a series of 6-phenylpurines bearing an *N*9-isopropyl or readily removable *N*9-benzyl group was amidated selectively at the desired position (**9a**,**b** and **9c**−**f**, respectively). In addition, substrates bearing a pendant *N*9-(*O*-acetyl-*β*-ribofuranosyl) group were also amidated in synthetically acceptable yields (**9g**,**h**), thus demonstrating an excellent level of functional group tolerance. It was also noteworthy that an analogous substrate lacking an N7 nitrogen was amidated in good yield (**9i**), suggesting that the N1 rather than the N7 atom serves as a chelating group to lead to the present amidation, as in the case of the corresponding Rh catalyst system using organic azides.[20d]

To obtain mechanistic insights into the present Co-catalyzed direct C−H amidation, preliminary experiments were carried out. A significant level of deuterium incorporation (50%) was observed at the ortho position of 2-phenylpyridine when it was subjected to the Co-catalytic system in CD_3OD in the absence of amidating reagents (Scheme 6a) to suggest that the cobalt-

Scheme 6. Preliminary Mechanistic Studies: (a) Deuterium Scrambling and (b) KIE Study

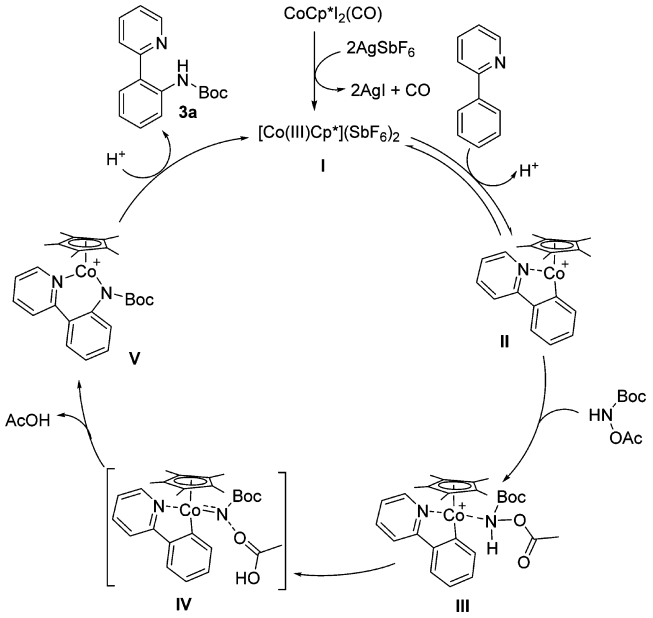


mediated C−H bond cleavage is reversible. Whereas a low level of primary kinetic isotope effects (KIE = 1.1) was measured in parallel experiments (Scheme 6b), more significant effects (KIE = 1.6) were observed in intermolecular competition reactions in the same vessel. Although it is not conclusive at the present stage, these rather low KIE values may imply that the C−H bond cleavage may not be involved in the rate-limiting stage.[21]

On the basis of the above mechanistic studies and relevant reports on Rh- or Ir-catalyzed amidation reactions,[15,16b,22] a plausible catalytic cycle of the present Co(III)-catalyzed direct C−H amidation is depicted in Scheme 7 using 2-phenylpyridine as a representative substrate. First, the treatment of the

DOI: 10.1021/cs501860b
ACS Catal. 2015, 5, 853−858

Scheme 7. Plausible Catalytic Cycle



$CoCp^*(CO)I_2$ precursor with $AgSbF_6$ additive will generate a cationic Co(III) species (**I**) with the dissociation of CO, which can facilitate the key C−H bond cleavage to afford the five-membered metallacyclic intermediate **II**.[22] The observation described above that the dimeric cobalt complex $[CoCp^*I_2]_2$ showed only slightly lower catalytic reactivity in comparison to $CoCp^*(CO)I_2$ (Table 1, entry 11) suggests that the carbonyl (CO) ligand is not essential for high activity in the present cobalt catalyst system. Coordination of an amidating reagent to **II** is assumed to follow leading to **III**,[6a] and then insertion of a carbamido moiety will take place to afford Co(III) amido species **V** presumably via **IV** with the release of acetic acid.[15] However, a pathway involving the intermediacy of a Co(V) nitrenoid species can also be plausible leading to **V**.[23] Finally, protonolysis of **V** will deliver the desired product (**3a**) with the concomitant regeneration of **I**. On the other hand, an alternative order of C−H bond cleavage cannot be completely ruled out, in which a cationic cobalt species (**I**) coordinates to an amidating reagent first to form a cobalt amide complex that then reacts with a substrate, leading to a metallacyclic intermediate.

CONCLUSION

In summary, we have developed the direct C−H amidation of arenes using acetoxycarbamates as a new and convenient amino source with a cobalt catalyst system. This amidation does not require external oxidants or bases and releases acetic acid as a readily removable byproduct. A range of arenes, including 6-arylpurines, was selectively amidated with high efficiency and excellent functional group compatibility. Various types of synthetically versatile *N*-carbamates could be also accessed by the present cobalt-catalyzed protocol.

ASSOCIATED CONTENT

Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/cs501860b (PDF).

General experimental procedures, characterization details, and ^1H and ^{13}C NMR spectra of new compounds

AUTHOR INFORMATION

Corresponding Author

*E-mail for S.C.: sbchang@kaist.ac.kr.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Dedicated to Professor Youngkyu Do (KAIST) for his honorable retirement. This work was supported by the Institute for Basic Science (IBS-R10-D1) in Korea. We thank Dr. Jeung Gon Kim and Dr. Amit B. Pawar for valuable discussions.

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DOI: 10.1021/cs501860b
ACS Catal. 2015, 5, 853−858