Organic & Biomolecular Chemistry

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DOI: 10.1039/C7OB00540G

Journal Name

COMMUNICATION

Cp*Co(III)-Catalyzed *ortho*-Amidation of Azobenzenes with Dioxazolones

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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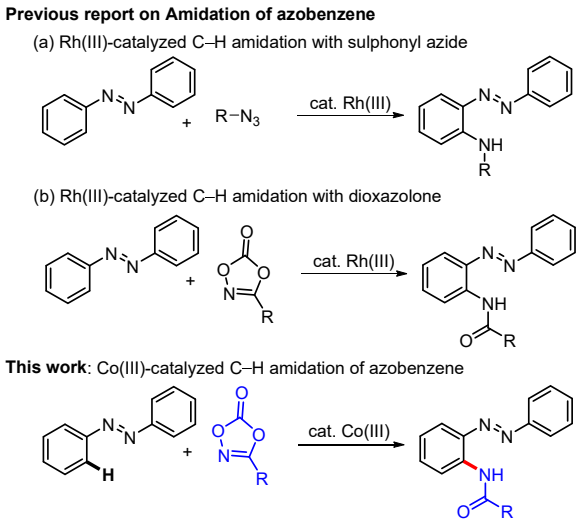
Cp*Co(III)-catalyzed C–H amidation of azobenzene with dioxazolones has ben developed. The amidation reaction does not require external oxidants and gives carbon dioxide as the only by-product. Both symmetrical and unsymmetrical azobenzenes were found to undergo amidation smoothly with broad functional group tolerance.

Over the past decades, azobenzene derivatives have attracted a great deal of attention due to their extensive application in various fields such as photochemical switches,[1] molecular machines,[2] protein probes,[3] organic dyes,[4] nonlinear optical devices,[5] chemosensors,[6] and polymers.[7] As a consequence much effort have been put for the efficient synthesis and functionalization of azobenzene.[8] Recently, transition metal catalyzed *ortho*-functionalization of azobenzenes using azo group as a directing group have found considerable attention for the synthesis of unsymmetrical azobenzenes.[9-19] In this context, Fahey et al. reported the Palladium catalyzed first *ortho*-halogenations of azobenzenes.[10] Following this, numerous *ortho*-functionalization of azobenzenes including alkoxylation,[11] acylation,[12] halogenation,[13] nitration,[14] phosphorylation,[15] addition,[16] alkenylation/cyclization,[17] alkylation/cyclization[18] and amidation/cyclization[19] have been widely investigated. Despite of these progresses, the *ortho*-amidation of azobenzenes has not been well explored. Recently group of Lee, Xu and Jia independently demonstrated the C−H amidation of azobenzenes with sulphonyl azides employing Rh(III)-catalytic system (Scheme 1a).[20] Additionally, Lee and Kim groups independently reported the Rh-catalyzed C−H amidation of azobenzenes using dioxazolones as coupling partner (Scheme 1b).[21] However all the above *ortho*-functionalization of azobenzenes had been carried out using precious transition metals such as Pd, or Rh, where as reports on first row transition metal catalyzed C–H functionalization of azobenzenes are very rare.[16b, 22] In recent years, majority of research has been focused on the employment Cp*Co(III)-catalyzed C–H activation because of its high natural abundance, and inexpensive nature.[23] Following the pioneering work from Kanai/Matsunaga,[24] on Co(III)-catalyzed C–H activation, many other groups including Ackermann,[25] Glorius,[26] Chang,[27] Ellman[28] and others[29] have also contributed significantly to further advancing this field on C–C and C–N bond formation.



Scheme 1 Transition metal catalyzed *ortho*-amidation of azobenzene.

Despite of these considerable advancement on Co(III)-catalyzed C–H activations, to the best of our knowledge Co(III)-catalyzed C–H amidation of azobenzene has not been realized so far. In continuation to our transition metal catalyzed C–H functionalizations,[30] herein we report Cp*Co(III)-catalyzed C–H amidation of azobenzene with dioxazolones (Scheme 1c).[31]

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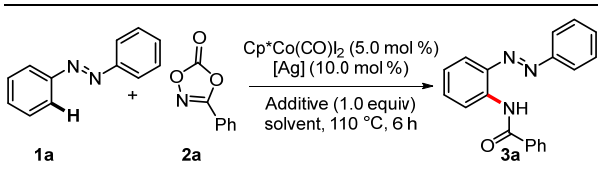
Electronic Supplementary Information (ESI) available: [*Full experimental details* and NMR spectra of the synthesized products]. See DOI: 10.1039/x0xx00000x

We instigated our investigation of Co(III)-catalyzed *ortho*-amidation of azobenzenes using (*E*)-1,2-diphenyldiazene **1a** as a model substrate and 3-phenyl-1,4,2-dioxazol-5-one **2a** as amide source (Table 1). Reaction of azobenzene **1a** with **2a** in presence of Cp*Co(CO)I_2 (5 mol %) and $AgSbF_6$ (10 mol %) in 2,2,2-trifluoroethanol (TFE) at 110 °C did not afford the desired amidated product **3a** (entry 1, Table 1). Gratifyingly, addition of acetic acid as additive (1.0 equiv), lead to the formation of mono amidated product **3a** in excellent yield (entry 2). However, formation diamidated product **4** (5%) was also observed in very little amount (see the Electronic Supporting Information for details). Amongst different acid additives screened, acetic acid was found to be most effective (entries 3 − 4). Reaction efficiency decreased on reducing the amount of additive (entry 5). Screening of various silver salts revealed $AgSbF_6$ as the best choice (entry 6 − 8). As expected, both Cp*Co(CO)I_2 and $AgSbF_6$ were found to be essential for the reaction (entries 9 − 10). Decreasing the reaction temperature also resulted in a reduced yield of the product **3a** (entry 11). Role of solvent was found to be crucial for the reaction, as use of other solvents result in decreased product yields (entries 12 − 14). Replacing the cobalt catalyst with pre-generated cationic Cp*Co(III) complex resulted in slight decrease in the product yield (entry 15).

Table 1 Optimization studies[a]

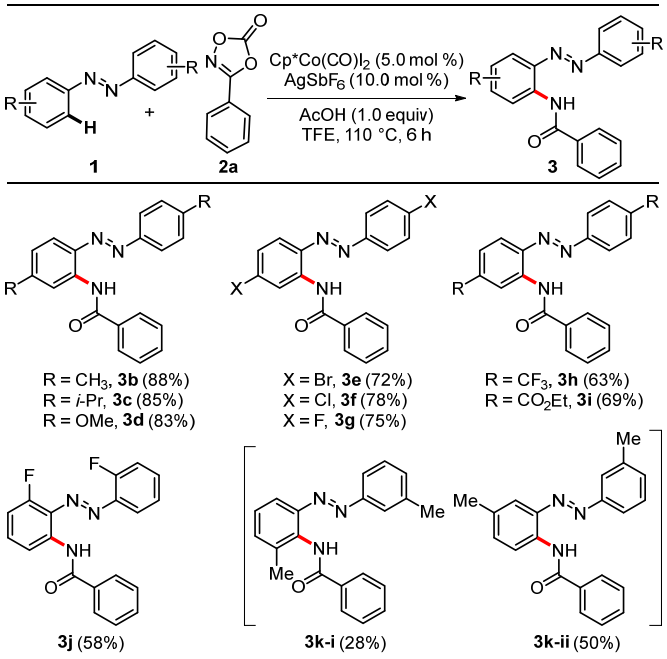


entry	[Ag] salt	additive	solvent	yield (%)[b]
1	$AgSbF_6$	--	TFE	<5
2	$AgSbF_6$	AcOH	TFE	85 (82)[c]
3	$AgSbF_6$	PivOH	TFE	80
4	$AgSbF_6$	$PhCO_2H$	TFE	65
5[d]	$AgSbF_6$	AcOH	TFE	60
6	AgOAc	AcOH	TFE	<10
7	$AgBF_4$	AcOH	TFE	65
8	AgOTf	AcOH	TFE	20
9	--	AcOH	TFE	<5
10[e]	$AgSbF_6$	AcOH	TFE	<5
11[f]	$AgSbF_6$	AcOH	TFE	25
12	$AgSbF_6$	AcOH	Toluene	<5
13	$AgSbF_6$	AcOH	EtOH	<5
14	$AgSbF_6$	AcOH	DCE	15
15[g]	--	AcOH	TFE	70

[a]Reaction conditions: **1a** (0.10 mmol, 1.0 equiv), **2a** (0.11 mmol, 1.1 equiv), Cp*Co(CO)I_2 (5.0 mol %), Ag-salt (10.0 mol %) and additive (1.0 equiv) in solvent (1 mL) at 110 °C for 6 h. [b]^{1}H NMR yield (CH_2Br_2 as internal standard). [c]Isolated yield in parentheses. [d]0.5 Equiv of AcOH was used. [e]Reaction without Co-catalyst. [f]Reaction at 80 °C. [g][Cp*Co(CH_3CN)$_3$](SbF_6)$_2$ was used as catalyst.

With the optimized conditions in hand, we next explored the scope of azobenzenes in reaction with 3-phenyl-1,4,2-dioxazol-5-one **2a** (Table 2). We were delighted to observe that the amidation took place efficiently irrespective of the position and electronic nature of substituents on azobenzene and furnished the corresponding amidated products in good to high yields. In fact, symmetrical azobenzenes bearing alkyl (**3b** and **3c**), alkoxy (**3d**), bromo (**3e**), chloro (**3f**) fluoro (**3g**), trifluoromethyl (**3h**) and ester (**3i**) groups at the *para*-position were found to be facile for the present amidation reactions. Similarly, *ortho*-substituted azobenzene underwent amidation to furnish the desired amidated product (**3j**) in moderate yield. However, amidation of azobenzene bearing a methyl group at *meta*-position gave a mixture of regioisomers **3k-i** and **3k-ii** in 78% overall yield. Nevertheless, formation of diamidated product was observed in trace amount in most of the cases.

Table 2 Scope of symmetrical azobenzene[a]



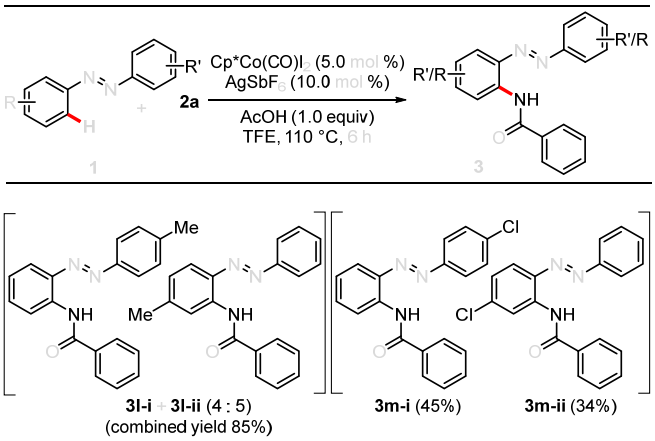
[a]Reaction conditions: **1** (0.1 mmol), **2a** (1.1 equiv.), Cp*Co(CO)I_2 (5.0 mol%), $AgSbF_6$ (10.0 mol%), and AcOH (1.0 equiv) in TFE (1 mL) at 110 °C for 6 h. Isolated yields are given.

Subsequently, amidation of symmetrical azobenzene was next investigated under optimized cobalt catalytic conditions (Table 3). Amidation of unsymmetrical azobenzenes bearing both electron-donating (**3l**) as well as electron-withdrawing groups (**3m**) were smoothly amidated to give a mixture of isomeric product. It was observed that the amidation reaction was comparatively more favorable on the electron-rich aromatic ring.

After successful exploration of substrate scope for azobenzenes, we next examine the scope of various dioxazolones with azobenzene **1a** under standard reaction conditions (Table 4). Dioxazolones bearing both electron-donating as well as electron-withdrawing aryl substituents

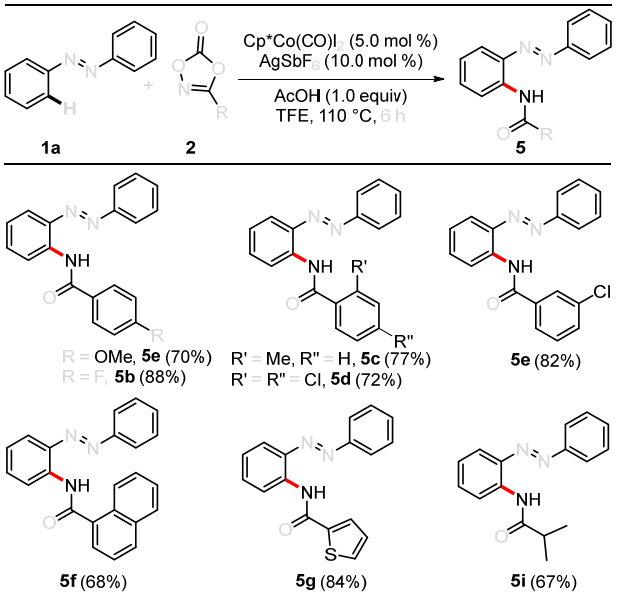
were found to couple efficiently with **1a** to give the corresponding amidated product **5a–5e** in high yields. Similarly, polycyclic dioxazolone 3-(naphthalen-1-yl)-1,4,2-dioxazol-5-one was found to smoothly react with **1a** to furnish the amidated product **5f** in good yield. The dioxazolone derived from heterocycles was also well compatible to give the desired amidated product **5g** in 80 % yield. Furthermore, amidation with aliphatic dioxazolones was also found to be facile to give the corresponding amidated product **5i** in 67 % yield. However, amidation with 3-benzyl-1,4,2-dioxazol-5-one was found to be sluggish.

Table 3 Amidation of unsymmetrical azobenzene[a]



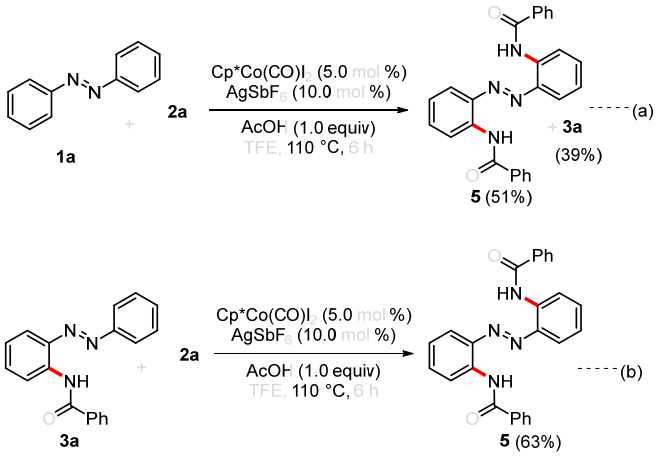
[a]Reaction conditions: **1** (0.1 mmol), **2a** (1.1 equiv), Cp*Co(CO)I_2 (5.0 mol%), $AgSbF_6$ (10.0 mol%), and AcOH (1.0 equiv) in TFE (1 mL) at 110 °C for 6 h. Isolated yields are given.

Table 4 Scope of dioxazolone[a]



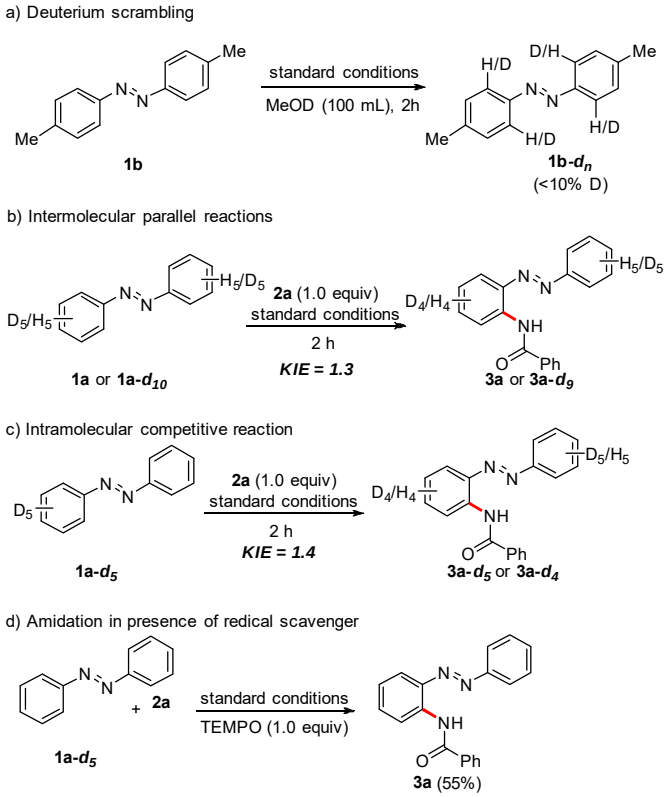
[a]Reaction conditions: 1a (0.1 mmol), 2 (1.1 equiv.), Cp*Co(CO)I_2 (5.0 mol%), $AgSbF_6$ (10.0 mol%), and AcOH (1.0 equiv) in TFE (1 mL) at 110 °C for 6 h. Isolated yields are given.

Next, we were inquisitive to see the selectivity of diamidation reaction of azobenzenes on the two aryl rings after the first amidation. When **1a** was subjected for amidation with 3 equivalent of **2a** under the standard reaction conditions, gave the diamidated product **4** (51%) along with mono amidated product **3a** (Scheme 2a). It is important to note that the second amidation occur exclusively on the other phenyl ring, which is in contrast to the Rh-catalytic system where both amidation occurred on the same phenyl ring.[21] Similarly, when **3a** was treated with **2a** under optimum conditions, the amidation reaction proceed smoothly, providing the corresponding diamidated azobenzenes **4** in 63% yield (Scheme 2).

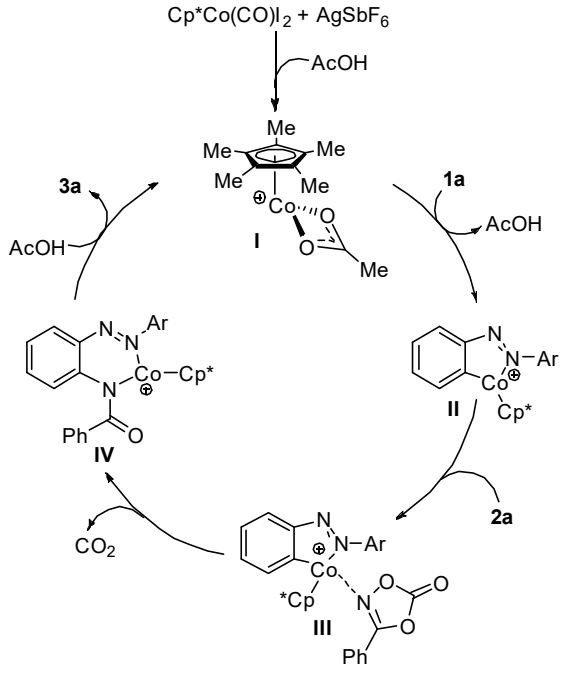


Scheme 2 Diamidation of azobenzene

In order to shed light on the plausible mechanism of amidation reaction, several controlled experiments were carried out (Scheme 3). Deuterium exchange experiments of **1b** using CD_3OD as co-solvent under the standard cobalt catalytic system in absence of **2a** did not show a significant amount of H/D scrambling at the *ortho*-positions, suggesting an irreversible C−H activation process (Scheme 3a). A relatively low KIE value was observed both in parallel reaction (k_H/k_D = 1.3, Scheme 3b) as well as in intramolecular competitive reaction (k_H/k_D = 1.4, Scheme 3c), indicating that the C–H bond cleavage is not involved in the rate determining step. Finally, the C–H amidation of **1a** performed in presence of radical scavenger gave the desired amidated product **3a** with only a minor loss in reaction yield (Scheme 3d). This result ruled out the possible involvement of a radical-based mechanism.



Scheme 3 Preliminary mechanistic investigation



Scheme 4 Plausible catalytic cycle

Based on above experimental results and precedent literature, a plausible catalytic cycle for the present amidation reaction is depicted in Scheme 4.[24-29] First, exposure of Cp*Co(CO)I_2 to $AgSbF_6$ and AcOH provides the active cationic Co(III) species **I**, which coordinates to azobenzene **1a** and further undergoes C–H activation to afford a five-membered cobalt metallacycle **II**. Subsequent coordination of dioxazolones **2a** with **II** generates intermediate **III**, which upon decarboxylation followed by migratory insertion delivers the six-membered amido species **IV**. Finally, proto-decobaltation of **IV** furnish the desired product **3a** along with regeneration of the active Co(III) species.

Conclusions

In summary, we have successfully disclosed an efficient Co(III)-catalyzed C–H amidation of azobenzenes with 1,4,2-dioxazol-5-ones. The reaction does not require any external oxidant, and generates gaseous carbondioxide as the only side product. More significantly, this reaction represents the first example of cobalt-catalyzed C–H amidation of azobenzenes.

Acknowledgements

We thank DST-INSPIRE Faculty program for fellowship and funding (GAP-0738). We also thank Dr. D. Ramaiah, Director, CSIR-NEIST, Jorhat, for his support and providing all the facility. We also thank Dr. Arup Roy, scientist, CSTD, CSIR-NEIST, for his helpful discussion.

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