

# Cobalt-Catalyzed Mild Ring-Opening Addition of Arenes C–H Bond to 7-Oxabicyclic Alkenes

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Abstract: A mild approach for a Cp\*Co(III)-catalyzed C–H naphthylation of arenes by 7-oxabicyclic alkenes has been developed. In some cases, intermediate products with a 1,2-dihydronaphthalen-1ol group have been isolated at room temperature in good yield. The catalytic reaction proceeds via C–H activation, insertion,  $\beta$ -oxygen elimination, protonation, and dehydration, respectively. These simple protocols, featuring mild conditions and tolerance of functional groups, exhibit great potential for a variety of synthetic applications.

**Keywords:** cobalt; oxabicyclic alkenes; ring opening addition; C–H activation; naphthylation

Various approaches to chelation-assisted *ortho*-C–H functionalization of arenes, catalyzed by transition metals, have been established over the past decades. This has led to the development of several effective methods for the synthesis of polyaromatic compounds with pharmaceutical relevance.<sup>[1]</sup> In particular, strategies involving atom- and step-economical C–H functionalization and biaryl formations constitute an important tool in modern organic synthetic protocols.<sup>[1,2]</sup> Such approaches are comparatively well established in the presence of noble metals,<sup>[3]</sup> but have been scarcely developed using the more abundant first-row metals.<sup>[4]</sup>

In this context, the transition-metal-catalyzed addition of a C–H bond to strained heterobicyclic alkenes, resulting in ring opening of the bicyclic species, is an interesting approach to access naphthylated compounds. However, until recently, this approach has rarely been explored. Li et al.<sup>[5a]</sup> and Miura et al.<sup>[5b]</sup> independently reported Rh(III)-catalyzed C–H activation and ring-opening addition to strained 7-oxabenzonorbornadienes to afford *ortho*-naphthylated products (Scheme 1a). Moreover, we have recently developed directing group-assisted Co-catalyzed arene C–H functionalization<sup>[6a]</sup> and oxidative annulation reactions to furnish heterocyclic derivatives.<sup>[6b-e]</sup> We also reported a bidentate directing group-assisted Cocatalyzed [3+2] annulation reaction of aromatic/ vinylic amides with bicyclic alkenes to produce highly diastereoselective dihydroepoxybenzofluorenones (Scheme 1b).<sup>[6e]</sup> These observations have prompted us to further examine the reactivity of bicyclic alkenes in Co-catalyzed C–H activation reactions.

In this paper, we report two different Cp\*Co(III)catalyzed directing group-assisted C–H additions to 7oxabenzonorbornadienes to afford polyaromatic compounds: C–H addition of pyrimidinylindoles and C–H addition of 2-arylpyridines to 7-oxabenzonorbornadienes. Different reaction conditions are required for



Scheme 1. Metal catalyzed C-H addition to bicyclic alkenes.

these two reactions. During the preparation of this manuscript, Li et al. reported a similar cobalt(III)-catalyzed C–H functionalization of *N*-pyrimidinylindoles with 7-oxabenzonorbornadienes, resulting in 2-naphthylation of the former compound.<sup>[7]</sup> However, different reaction conditions were used in this case.;

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#### Table 1. Screening the reaction conditions.<sup>[a,b]</sup>



Entry	Additive	Solvent	Yield (3aa%)
1	_	TFE	60
2	NaOAc	TFE	78
3	KOAc	TFE	82
4	CsOAc	TFE	<i>99 (95)</i>
5	AgOAc	TFE	74
6	$Cu(OAc)_2$	TFE	26
7	$Mn(OAc)_2$	TFE	65
8	$Mn(OAc)_{3} \cdot 2H_{2}O$	TFE	38
9	Ad-COOH	TFE	88
10	Mes-COOH	TFE	71
11 <sup>c</sup>	AcOH	TFE	58
12	CsOAc	PhCl	42
13	CsOAc	DCE	46
14	CsOAc	toluene	52
15	CsOAc	o-xylene	37
16	CsOAc	acetone	25
17	CsOAc	EtOH	N.R
18	CsOAc	CH <sub>3</sub> CN	N.R
19	CsOAc	1,4-dioxane	N.R
20 <sup>d</sup>	CsOAc	TFE	75
21 <sup>e</sup>	CsOAc	TFE	80

<sup>[a]</sup> Unless otherwise mentioned, all reactions were carried out using **1a** (0.20 mmol), **2a** (0.30 mmol), [CoCp\*(CO)I<sub>2</sub>] (5 mol%), AgSbF<sub>6</sub> (20 mol%), additive (30 mol%), solvent (2 mL) at 90 °C for 18 h under N<sub>2</sub>.

<sup>[b]</sup> Yields were determined by the <sup>1</sup>HNMR integration method; the value in the parenthesis indicates isolated yield.

<sup>[c]</sup> 1 equiv. AcOH was used.

<sup>[d]</sup> NaSbF<sub>6</sub> was used instead of AgSbF<sub>6</sub>.

<sup>[e]</sup> AgBF<sub>4</sub> was used instead of AgSbF<sub>6</sub>. PhCl=chlorobenzene, DCE=1,2-dichloroethane, Ad=adamantane, and Mes= mesitylene.

we used 30 mol% of CsOAc, 20 mol% of AgSbF<sub>6</sub> as additives and TFE as a solvent, while Li employed 2 equiv. of AcOH, 30 mol% of AgSbF<sub>6</sub> as additives and DCE as a solvent.

Initially, we observed that the reaction of Npyrimidinylindole 1a (0.20 mmol) with 7-oxabenzonorbornadiene 2a (0.30 mmol) in the presence of 5 mol% of [CoCp\*(CO)I<sub>2</sub>] and 20 mol% of AgSbF<sub>6</sub> in TFE (2,2,2-trifluoroethanol) at 90 °C under N<sub>2</sub> for 18 h gave **3aa** in 60% yield (Table 1, entry 1). The results summarized in Table 1 indicate that the nature of the additives and solvents greatly influences the reaction yield. The presence of 30 mol% of CsOAc afforded 3aa in 99% (95% isolated) yield (entry 4). On the other hand, the other additives such as NaOAc, AgOAc,  $Mn(OAc)_2$ , KOAc.  $Cu(OAc)_2$ , Mn (OAc)<sub>3</sub>·2H<sub>2</sub>O, Ad-COOH, Mes-COOH and AcOH were examined and afforded 3aa in moderate yields (entries 2, 3 and 5-11). The role of the solvent was also found to be crucial in obtaining high yields. Among the solvents inspected, TFE provided the highest yield, whereas PhCl, DCE, toluene, *o*-xylene and acetone afforded the product in lower yields (entries 12–16). Other solvents including EtOH, CH<sub>3</sub> CN, and 1,4-dioxane, were totally ineffective (entries 17–19). Further, AgSbF<sub>6</sub> (20 mol%) was found to be more effective than either NaSbF<sub>6</sub> or AgBF<sub>4</sub>, (entries 4, 20 and 21). Other cobalt salts such as CoBr<sub>2</sub>, Co(acac)<sub>2</sub>, and Co(acac)<sub>3</sub> were also tested and found to be ineffective under standard reaction conditions. Thus, the reaction conditions in entry 4 were used as the standard conditions for substrate scope studies.

The yields from the reactions between *N*-pyrimidinylindoles **1** and 7-oxabicyclic alkenes **2** are displayed in Table 2. The reactions of 5-methoxy-, 5-iodo-, 5-(pyrimidin-2-yloxy)- and 4-bromo-*N*-pyrimidinylindoles (**1b**-e) with **2a** provided the corresponding products **3ba-ea** in excellent yield. The reaction of 7-

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**Table 2.** Reaction of *N*-pyrimidinylindoles (1) with 7-oxabicyclic alkenes (2).<sup>[a,b]</sup>

<sup>[a]</sup> Unless otherwise mentioned, all reactions were carried out using **1** (0.20 mmol), **2** (0.30 mmol), [CoCp\*(CO)I<sub>2</sub>] (5 mol%), AgSbF<sub>6</sub> (20 mol%), CsOAc (30 mol%), TFE (2 mL) at 90°C for 18 h under N<sub>2</sub>.

<sup>[b]</sup> Isolated yield.

methoxy substituted N-pyrimidinylindole 1f with 2a at 120°C furnished 3fa in 91% yield. Moreover, the reaction of 3-methyl substituted N-pyrimidinylindole 1g with 2a afforded naphthylation product 3ga in 78% yield. Under the same catalytic conditions, treatment of bicyclic alkenes 2b-f with 1a delivered the corresponding C-H naphthylation products, 3ab-af effectively with up to 93% yield. In contrast, using 1a with the electron-withdrawing heterobicyclic alkene 2g led to dehydration product 3ag in 55% yield and the ring-opening product **3AG** in 29% yield. Notably, **3AG** is an intermediate, which can be converted to **3ag** on further heating or by treatment with acid. N-Pyrimidinylbenzoimidazole 1h, with a structure similar to that of indoles 1, also reacted with 2a and 2g. However, in this case, it underwent C-H addition to the carbon-carbon double bond to form products 3ha and 3hg in good yield. The bridged oxa moiety found in 2a and 2g was retained in these products. Other bicyclic alkenes such as 7-azabicyclic alkene and

norbornene did not react with **1** to afford the expected product.

According to our previous studies,<sup>[8a]</sup> ring-opening products of bicyclic alkenes can be easily produced from earth-abundant metals.<sup>[8b-e]</sup> However, this reaction pattern is heavily underdeveloped in C-H activation. The results of C-H naphthylation in Table 2 prompted us to find appropriate catalytic reaction conditions for the isolation of the ring-opening addition products, which are the intermediates for the C-H naphthylation. After several tests, we found the 1a reacted with 2a at 25 °C for 5 h in the absence of AgSbF<sub>6</sub>, affording the ring-opening addition product 3AA in 92% isolated yield. Notably, 3AA can be converted to the corresponding naphthylation product in the presence of an acid.<sup>[6e]</sup> We did not observe any dehydration products under these reaction conditions. Similarly, various substituted N-pyrimidinylindoles, including 5-methoxy, 5-iodo and 4-bromo moieties (1b, 1c and 1e) reacted with 2 to give the ringopening addition products 3BA, 3CA and 3EA, respectively, in good to excellent yield. Moreover, when the electron-rich heterobicyclic alkene 2d was tested, it afforded the desired product 3AD in 78% yield. This is the first time that the addition and isolation of a ring-opening product from cobaltcatalyzed C-H activation has been recorded in literature (Scheme 2).



Scheme 2. The scope of the cobalt-catalyzed ring opening reaction. <sup>[a]</sup> at  $35 \degree C$ .<sup>[b]</sup> < 5% 3ad was observed.

To further apply this Co(III)-catalyzed C–H addition reaction, we examined the reaction of 2-arylpyridines with bicyclic alkenes (Table 3). From the afforded results, the optimized reaction conditions were determined as 10 mol% of  $[CoCp^*(CO)I_2]$ , 30 mol% of Ad–COOH and 20 mol% of AgSbF<sub>6</sub> at 120 °C for 30 h. These were suitable for both the C–H addition and the dehydration reactions. To the best of our knowledge, this is the first example of Co(III)catalyzed C–H *ortho* naphthylation of 2-arylpyridines.

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**Table 3.** Reaction of 2-arylpyridines **4** with 7-oxabicyclic alkenes  $2.^{[a,b]}$ 

<sup>[a]</sup> Unless otherwise mentioned, all reactions were carried out using **4** (0.20 mmol), **2** (0.30 mmol),  $[CoCp^*(CO)I_2]$  (10 mol%), AgSbF<sub>6</sub> (20 mol%), Ad-COOH (30 mol%), TFE (2 mL) at 120 °C for 30 h under N<sub>2</sub>.

<sup>[b]</sup> Isolated yield.

Thus, treatment of 2-phenylpyridine 4a with 2a under the mentioned reaction conditions afforded 5aa in 85% isolated yield. Table 3 describes the scope of the C–H naphthylation reaction; the 2-arylpyridines were converted to the products in good yield with excellent functional group (Me, OMe, t-Bu, SiMe<sub>3</sub>, F, CHO, COMe, and CN) tolerance. The presence of both electron-donating (4b-d) and withdrawing (4f-j)groups at the para position of the phenyl group did not affect the product yield greatly (74-84%). However, 4e with a p-SiMe<sub>3</sub> group afforded only 61% of the expected product 5ea. In particular, to study the selective C-H naphthylation reaction, a set of unsymmetrically substituted 2-arylpyridines were also subjected to the optimized reaction conditions. The reaction of 2-naphthyl 4k and 3-methyl 4l with 2a afforded highly regioselective C-H naphthylation products **5ka** and **5la** in 71 and 86% yield, respectively. We also investigated the reactions of substrates **4** (contain substituents on the pyridine ring **4m-p**) with **2a**. The reaction effectively underwent C–H addition with bicyclic alkene **2a** to give *ortho* naphthylation products in good yield. Moreover, the reaction of **4a** and **4g** with sterically hindered heterobicyclic alkenes including **2f** and **2e** could also afforded the products with good efficiency.

To understand the catalytic reaction of 1a with 2a, we performed deuterated experiments using  $[D_1]$ -1a, 1a, and 2a as the substrates (Scheme 3). First, heating  $[D_1]$ -1a in the absence of 2a under the standard reaction conditions resulted in 99% D/H exchange of the C2 deuterium. This result suggests that the fivemembered cobaltacycle intermediate is highly reversible. In contrast, the time-related investigations of  $[D_1]$ -1a with 2a revealed the presence of substrate  $[D_1]$ -1a (30% with 89% D/H exchange), product 3aa (22%) and intermediate product 3AA (43%). These results suggest that the D/H exchange rate is comparable to the rate of insertion in bicyclic alkene 2a.



Scheme 3. Mechanistic related experiments.

Based on the cobalt-catalyzed C-H activation and our previous heterocyclic ring-opening reactions,<sup>[6,8,9]</sup> herein, we propose a plausible mechanism (Scheme 4) using 1a and 2a as the substrates. The intermediate  $[CoCp^*(OAc)]^+$  is generated from  $[CoCp^*(CO)I_2]$  by reaction with CsOAc and AgSbF<sub>6</sub>, possibly initiating the reaction by coordination with the nitrogen atom in 1a. This is followed by C-H bond cleavage in 1a at the C2 position to afford the five-membered cobaltacycle C. Next, the alkene  $\pi$ -bond in 2a coordinates with cobaltacycle C and is subsequently inserted into the Co–C bond of the resulting intermediate **D**. This in turn affords the seven-membered cobaltacycle E. The latter then undergoes  $\beta$ -oxygen elimination to afford ring-opening product F. Finally, protonation of F by AcOH releases 3AA and Co(III) species A. Later, 3AA undergoes dehydration to afford the aromatized product 3aa.

In conclusion, we have developed a mild protocol for C–H bond activation and naphthylation of arenes with 7-oxabicyclic alkenes using the earth-abundant cobalt metal as the catalyst. A number of naphthalene

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Scheme 4. A plausible reaction mechanism.

substituted heteroarenes can be produced in good to excellent yield. We also successfully developed a cobalt-catalyzed arene C–H addition to 7-oxabicyclic alkenes at room temperature. This produced arenes containing a 1,2-dihydronaphthalen-1-ol group with high efficiency. These simple C–H naphthylation, hydroarylation, and ring-opening addition reactions feature mild conditions and functional group tolerance. Thus they show great potential for various synthetic applications.

### **Experimental Section**

A glass tube containing *N*-pyrimidinylindoles **1** (0.20 mmol), **7**-oxabicyclic alkenes **2** (0.30 mmol),  $[CoCp^*(CO)I_2]$ (5 mol%), AgSbF<sub>6</sub> (20 mol%) and CsOAc (30 mol%) was evacuated and purged with nitrogen gas three times. Then, TFE (2.0 mL) was added to the system via syringe under a nitrogen atmosphere and the reaction mixture was allowed to stir at 90 °C for 18 h. When the reaction was complete, the mixture was cooled and diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The mixture was filtered through a Celite pad and the Celite pad was washed with CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The filtrate was concentrated and the residue was purified by column chromatography using a mixture of *n*-hexane and EtOAc as eluent to give the corresponding pure naphthylation product **3**.

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## UPDATES

Cobalt-Catalyzed Mild Ring-Opening Addition of Arenes C–H Bond to 7-Oxabicyclic Alkenes

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Cat. [CoCp\*(CO)l<sub>2</sub>] FG + 2-pv