Advanced Synthesis & Catalysis

Accepted Article

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To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201801598

Link to VoR: http://dx.doi.org/10.1002/adsc.201801598

10.1002/adsc.201801598

COMMUNICATION

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Free-Amine-Directed Iridium-Catalyzed C–H Bond Activation and Cyclization of Naphthalen-1-amines with Diazo Compounds Leading to Naphtho[1,8-*bc*]pyridines

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Received: ((will be filled in by the editorial staff))

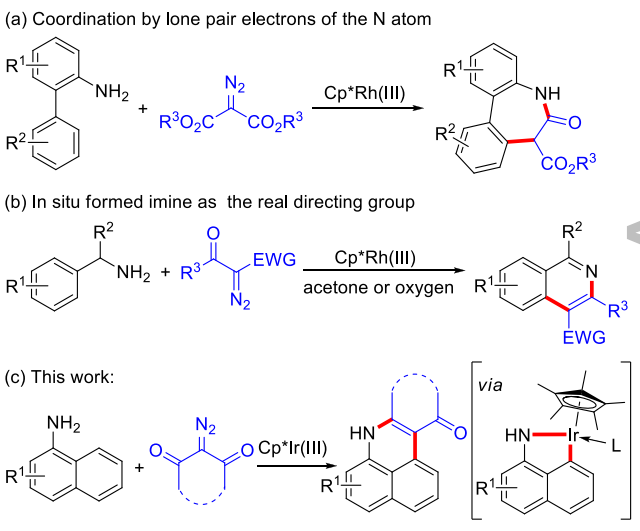
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

Abstract: Iridium-catalyzed C–H activation and cyclization of naphthalen-1-amines with diazo compounds leading to naphtho[1,8-*bc*]pyridines have been developed. Different from the previous free-amine-directed C−H functionalization with diazo compounds that relied on the coordination of lone pair electrons or in situ formation of imine, this transformation passes through a five-membered iridacycle intermediate containing an N-Ir σ-bond. It offers an alternative approach for the synthesis of useful diverse naphtho[1,8-*bc*]pyridine derivatives in mild conditions.

Keywords: C–H activation; diazo compounds; iridium; naphtho[1,8-*bc*]pyridines

Seeking novel, practical, and efficient methods for the construction of nitrogen-containing fused aromatics have attracted much attention for their broad applications in biological, photo- and electrochemical materials.[1] Naphtho[1,8-*bc*]pyridines are an important class of nitrogen-containing heterocyclic compounds. They possess potential applications as organic semiconductors and luminescence materials for their important electrochemical and photochemical properties.[2] Therefore, the development of novel and efficient methods for the synthesis of naphtho[1,8-*bc*]pyridines is of great importance. However, investigations on the synthetic methods for the formation of naphtho[1,8-*bc*]pyridine motifs are rather limited. Very recently, our group reported an elegant rhodium-catalyzed C–H activation and annulations of *β*–enaminonitriles with alkynes leading to substituted naphtho[1,8-*bc*]pyridines.[3] Despite some great advantages of this conversion, the reaction yields based on aliphatic alkynes decreased seriously and the regioselectivity for unsymmetrical alkynes is also difficult to control. Therefore, there is still an urgent need to establish new methods to synthesize naphtho[1,8-*bc*]pyridine derivatives with various substituents.

In the past decades, transition-metal-catalyzed direct C–H bond functionalization has flourished as a powerful and atom-economical method to construct C–C and C–X bonds without prior functionalization.[4] Free amino groups which widely occur in natural products and synthetic compounds are one of the best directing and assisting groups for C−H functionalization reactions catalyzed by Pd(II),[5] Rh(III),[6] Ir(III),[7] Ru(II),[8] and other metals.[9] At the same time, diazo compounds have been widely employed as powerful cross-coupling partners for the construction of various organic frameworks by transition-metal-catalyzed conversions.[10] However, investigations on the transformations of free-amine-directed C−H functionalization with diazo



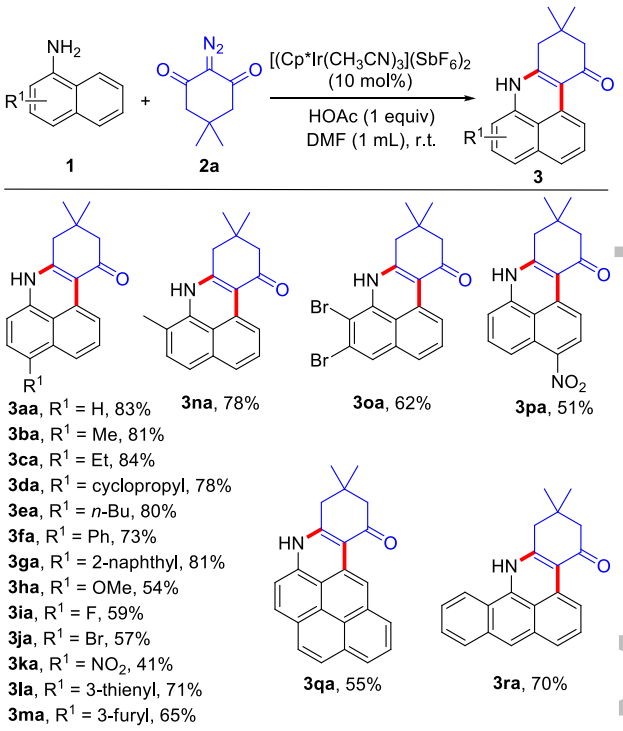
Scheme 1. Free-amine-directed C−H functionalization with diazo compounds

compounds are rather limited. In 2016, Huang and coworkers developed a Rh(III)-catalyzed free-amine-directed C−H functionalization/amidation reaction for synthesis of azepinone derivatives (Scheme 1a).[6k] This reaction relies on the coordination of the lone pair electrons of the N atom on the free amino groups. Subsequently, Cheng,[6l] Li,[6m] and Cui[6n] reported similar Rh(III)-catalyzed annulations of benzylamines with diazo compounds toward isoquinolines (Scheme 1b). In these three reactions, benzylamines needed to react with acetone or be oxidized to imines, and the in situ formed imines have been proposed to be the real directing group. In addition, all of this kind of conversions employ a Rh(III) catalyst. In contrast Ir(III)-catalyzed C–H activation reactions[11] employing diazo compounds as coupling partners were reported not as much as Rh(III)-catalyzed reactions. Following our growing interest in building heterocyclic compounds using diazo compounds[11h,12] and iridium-catalyzed C–H bond functionalizations,[13] we herein report a free-amine-directed iridium-catalyzed C–H bond activation and cyclization of naphthalen-1-amines with diazo compounds leading to naphtho[1,8-*bc*]pyridines in mild conditions (Scheme 1c). Different from the previous free-amine-directed C−H functionalization with diazo compounds that relied on the coordination of lone pair electrons or in situ formation of imine, this reaction passes through a five-membered iridacycle intermediate containing an N-Ir σ-bond.

By treating naphthalen-1-amine (**1a**) (42.9 mg, 0.3 mmol, 1.5 equiv.) with 2-diazo-5,5-dimethylcyclohexane-1,3-dione (**2a**) (33.2 mg, 0.2 mmol, 1.0 equiv.) in the presence of $[Cp^*Ir(CH_3CN)_3](SbF_6)_2$ (10 mol%) and HOAc (1.0 equiv.) in *N*,*N*-dimethylformamide (DMF) (1.0 mL) at room temperature for 12 h under Ar, product 9-dimethyl-9,10-dihydro-7*H*-benzo[*kl*]acridin-11(8*H*)-one (**3aa**) was obtained in 83% yield (for detailed optimization studies, see Table S1 in the ESI). The structure of **3aa** was confirmed by its ^1H, ^{13}C NMR spectra and high-resolution mass spectrometry.

With the establishment of the optimized conditions, we explored the applicability of the scope of diversely substituted naphthalen-1-amines (**1a**–**1r**), and the results are summarized in Table 1. To our delight, most reactions proceeded smoothly to afford corresponding products (**3aa**–**3ra**) in moderate to good yields. Substituted naphthalen-1-amines bearing alkyl, phenyl, and 2-naphthyl groups at the C4-position afforded corresponding products (**3ba**–**3ga**) in good yields (73–84%). While, 4-methoxyl and electron-withdrawing groups substituted naphthalen-1-amines afforded corresponding products (**3ha**–**3ka**) in moderate yields (41–59%). Delightfully, the substrate bearing a thiophene/furan ring also gave the desired products (**3la**, **3ma**) in 65–71% yields. Subsequently, the *ortho*-substituted naphthalen-1-amine (**1n**) was also explored and the expected product (**3na**) was obtained in 78% yield. When 2,3-dibromonaphthalen-1-amine (**1o**) was employed as the substrate, the corresponding product **3oa** was obtained in 62% yield. Meanwhile, the study of substrate with a substituent at the C5-position was also examined and the corresponding product **3pa** was obtained in 51% yield. In addition, the reactions of pyren-1-amine (**1q**) and anthracen-9-amine (**1r**) with **2a** provided the desired products **3qa** and **3ra** in 55% and 70% yields, respectively.

Table 1. Substrate scope of naphthalen-1-amines.[a]



[a] Reaction conditions: **1a** (0.3 mmol), **2** (0.2 mmol) $[Cp^*Ir(CH_3CN)_3](SbF_6)_2$ (10 mol%), HOAc (0.2 mmol), DMF (1.0 mL), r.t., 12 h, under Ar, isolated yield.

Then, we investigated the scope of diazo compounds with naphthalen-1-amine (**1a**) as the reaction partner (Table 2). By treating **1a** with different six-membered cyclic diazo compounds, products **3ab**–**3ad** were obtained in good yields (63–85%). The reaction of **1a** with a *meta*-substituted six-membered cyclic diazo compound **2e** afforded a mixture of two isomers in a ratio of 1:0.8. Unfortunately, we failed to separate this pair of isomers. Product **3af** was obtained in 51% yield when five-membered cyclic 2-diazo-1,3-dione (**2f**) was employed in this reaction. Furthermore, different kinds of open chain diazo substrates were also investigated, and the desired products **3ag**–**3ao** containing diverse substituents such as alkyl, ether, ketone, phenyl, and ester were given in 41–92% yields. These regioselective products with various alkyl groups are difficult to prepare for the reactions employing alkynes as coupling partners.[3]

To gain more insight into the mechanism, a series of preliminary mechanistic experiments have been conducted. A hydrogen–deuterium exchange experiment of **1a** using 0.2 mL of AcOD or D_2O was

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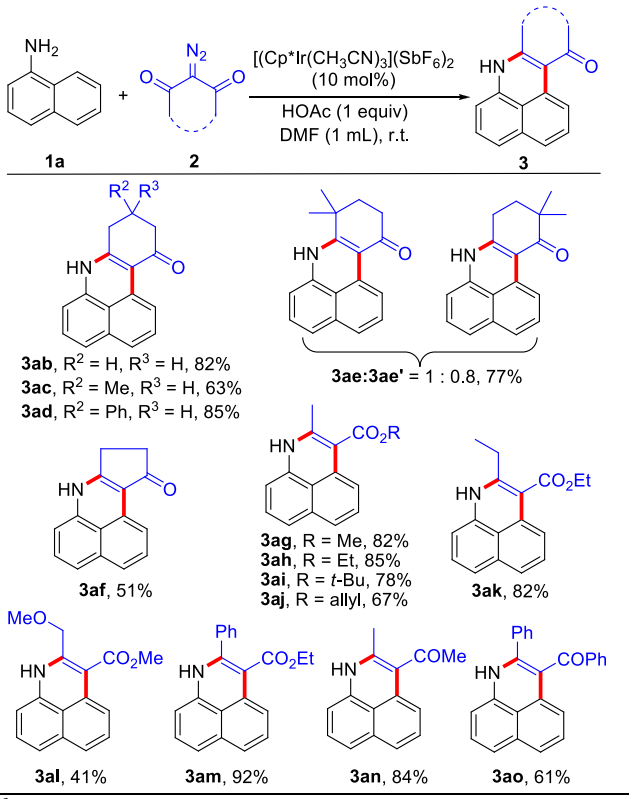
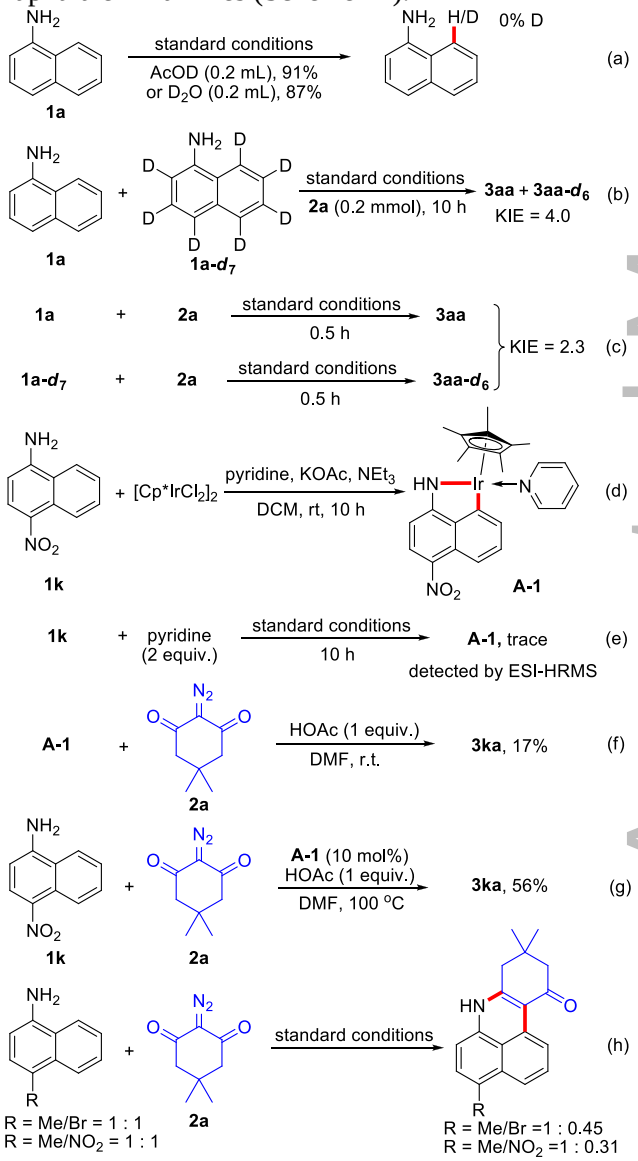
Table 2. Substrate scope of diazo compounds.[a]



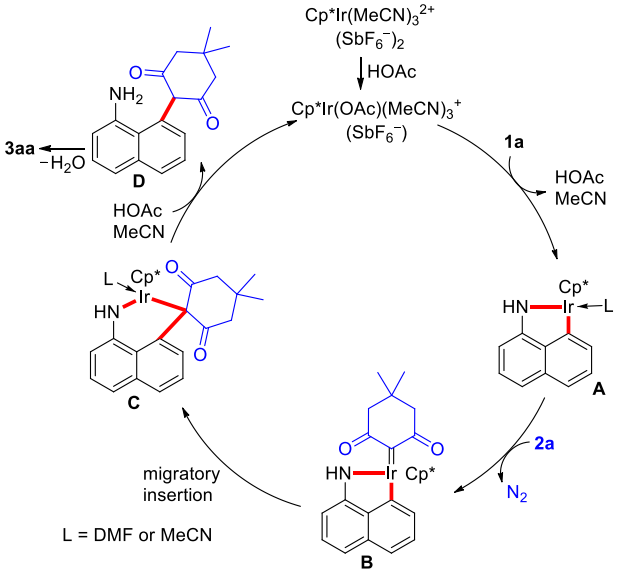
[a] Reaction conditions: **1a** (0.3 mmol), **2** (0.2 mmol) $[Cp^*Ir(CH_3CN)_3](SbF_6)_2$ (10 mol%), HOAc (0.2 mmol), DMF (1.0 mL), r.t., 12 h, under Ar, isolated yield.

performed under standard conditions, and no H/D exchange was detected (Scheme 2a). This result indicated that the cleavage of the C–H bond at the C8-position of naphthalen-1-amine was an irreversible process. Then, a deuterium competition experiment between substrates **1a** and **1a-*d*$_7$** illustrated a kinetic isotope effect (KIE) of 4.0 (Scheme 2b). Meanwhile, two parallel independent reactions of **1a** and **1a-*d*$_7$** were performed, and a KIE of 2.3 was observed (Scheme 2c). Both results indicated that the C–H bond cleavage might be involved in the rate-determining step. An iridacycle intermediate **A-1** was isolated in 99% yield by the reaction of 4-nitronaphthalen-1-amine (**1k**) with $[Cp^*IrCl_2]_2$ and pyridine in the presence of triethylamine at room temperature (Scheme 2d). Its structure was fully characterized by ^{1}H and ^{13}C NMR spectra and high-resolution mass spectrometry. However, when the reaction of **1k** with $[Cp^*IrCl_2]_2$ was conducted under the standard catalytic conditions, no iridacycle intermediate was detected. The formation of **A-1** could be observed only in trace amount in the presence of pyridine (Scheme 2e) and detected by ESI–HRMS from the reaction mixture (see 5e in the SI). This may be because the catalytic conditions are not conducive to the formation of a stable **A-1** but to the formation of an unstable iridacycle intermediate that facilitates conversion to a product. By treating intermediate **A-1** with **2a** in standard conditions, the final product **3ka** was obtained in 17% yield (Scheme 2f). When intermediate **A-1** was used as the catalyst instead of $[Cp^*Ir(CH_3CN)_3](SbF_6)_2$ in standard conditions, the desired product **3ka** was obtained in 56% yield (Scheme 2g). These results supported the idea that the reaction may engage a cyclometalation step and a five-membered iridacycle intermediate containing an N-Ir σ-bond probably was an active species in this reaction. In addition, the intermolecular competition experiment between electronically differentiated 4-methylnaphthalen-1-amine (**1b**) and 4-bromonaphthalen-1-amine (**1j**) with **2a** was performed to determine the electronic preference of the reaction. The ^{1}H NMR spectrum of the obtained products showed that the corresponding products **3ba** and **3ja** were produced in a ratio of 1:0.45. A competition experiment starting from 4-methylnaphthalen-1-amine (**1b**) and 4-nitronaphthalen-1-amine (**1k**) with **2a** was also performed, and the corresponding products **3ba** and **3ka** were produced in a ratio of 1:0.31. Both results indicated that the reaction favored the electron-rich naphthalen-1-amines (Scheme 2h).



Scheme 2. The mechanism study experiments.

On the basis of known transition-metal-catalyzed C–H bond activation reactions[4] and our group's related research,[11h,12] a possible mechanism is proposed for this present catalytic reaction (Scheme 3). The first step is likely to be a ligand exchange between $[Cp^*Ir(CH_3CN)_3](SbF_6)_2$ and HOAc to form the catalytic species $[Cp^*Ir(OAc)(MeCN)](SbF_6)$, which then coordinates with **1a** and subsequently occurs C(sp^2)–H bond activation to form a five-membered iridacycle intermediate **A** by releasing HOAc. Then **A** reacts with the diazo compound **2a** to afford the iridium-carbene intermediate **B** with extrusion of nitrogen. Migratory insertion of the carbene into the Ir–C bond generates the intermediate **C**. Protonolysis of **C** leads to the intermediate **D** and release catalytic species for next catalytic cycle. Finally, condensation of intermediate **D** generates the final product **3aa** and water.



Scheme 3. Proposed mechanistic pathway.

In conclusion, we have successfully developed a novel and efficient iridium-catalyzed C–H activation and cyclization of naphthalen-1-amines with diazo compounds to build substituted naphtho[1,8-*bc*]pyridines. Various regioselective products were prepared in moderate to good yields under mild conditions. Several related mechanistic studies have been performed. Further investigations and applications on electrochemical and photochemical properties of the obtained compounds in this work are in progress in our laboratory.

Experimental Section

A mixture of substituted naphthalen-1-amines (**1**) (0.3 mmol, 1.5 equiv.), diazo compounds (**2**) (0.2 mmol, 1.0 equiv.), $[(Cp^*Ir(CH_3CN)_3](SbF_6)_2$ (18.4 mg, 0.02 mmol, 10.0 mol%), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv.) were weighted in a Schlenk sealed tube equipped with a stir bar. Dry DMF (1.0 mL) was added and the mixture was stirred at room temperature for 12 h under Ar atmosphere. Afterwards, it was diluted with CH_2Cl_2 (5 mL) and filtered through a short pad of Celite. The sealed tube and Celite pad were washed with an additional 30 mL of CH_2Cl_2. The filtrate was concentrated in vacuo, and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether.

Acknowledgements

We thank the National Natural Science Foundation of China (No. 21672108) and the Natural Science Foundation of Tianjin (No. 16JCZDJC31700) for financial support.

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10.1002/adsc.201801598

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