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# Rh(III)-Catalyzed N-nitroso Directed C-H Arylation for Facile Construction of Diverse N-hetero Biaryl Compounds

Pei-Long Wang,[+,a][b][c] Yan Wang,[+,a] Yan Li*,[a] and Xi-Sheng Wang*,[a]

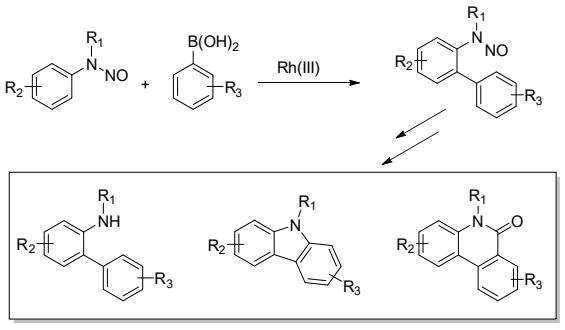
Dedication ((optional))

**Abstract:** A Rh(III)-catalyzed C-H arylation reaction of N-nitrosoanilines has been developed in which arylboronic acids were used as arylation reagents. It provides an efficient strategy for the synthesis of N-nitroso-[1,1'-biphenyl]-2-amine, which is an important starting material for the synthesis of N-hetero biaryl compounds, such as 2-amine-1,1'-biphenyl, carbazole, phenanthridone. This protocol can be applied to various N-alkyl substituted N-nitrosoanilines and N-nitrosoanilines with substituents on the phenyl ring. Arylboronic acids with both electron-donating and electron-withdrawing groups are tolerated.

In the past several decades, transition-metal-catalyzed C-H activation reaction has emerged as a powerful tool for the synthesis of useful organic molecules in an atom and step-economical way.[1] Considering there are always large number and various kinds of C-H bonds in one organic molecule, to selectively activate the C-H bond in a special position is a rather important issue. Accordingly, the introduction of directing groups into the target molecules has been widely used as the most effective strategy for solving this problem.[2] Indeed, the generally used directing groups are heteroatom-containing functional groups, which selectively activate the C-H bond that is most close to the metal center through coordination with the metal. Not only the site selectivity control, but also the low reactivity of the transition-metal catalysts could be well resolved by this directing group strategy. As results, many functional groups have been developed as directing groups, and applied successfully in C-H activation reactions. However, the extra steps for installation and removal of the directing groups would definitely reduce the step- and atom-economy of these C-H functionalization reactions. To address this issue, the development of easily removable or transformable directing groups to realize diverse metal-catalyzed C-H activations has attracted increasing attentions in the past years.

N-nitrosoanilines served widely as an important kind of biologically active compounds in biological and pharmaceutical chemistry, and have been studied intensively in different research areas.[3] Considering N-nitrosoanilines could be easily prepared in one step from anilines,[4] they are widely existing as a class of useful synthetic intermediates, which would afford various synthetically useful compounds through different kinds of transformations. Actually, N-nitrosoanilines could be converted to amines, hydrazines, acridones, oxadiazoliums,[5] pyridoindolobenzazepines, and etc.[6] Since the first example of C-H functionalization of N-nitrosoanilines by Zhu in 2013,[7] a few examples catalyzed by rhodium,[8] palladium[9] and cobalt[10] have been developed accordingly. As one part of our continuous efforts to develop novel C-H functionalization methods for facile construction of heterocycles,[11] we hence report a rhodium-catalyzed C-H arylation of N-nitrosoanilines. This method has demonstrated broad substrate scope, good functional group tolerance and mild conditions. The synthetic potential of this transformation has been well elaborated through various further transformations to diverse N-hetero biaryl compounds and N-heterocycles,[12,13] which are ubiquitous structural motifs found in many bioactive compounds and materials.[14]

We initiated our study by using N-ethyl-N-nitrosoaniline (**1a**) as the model substrate and phenylboronic acid (**2a**) as the coupling partner in the presence of a catalytic amount of $[Cp^*RhCl_2]_2$ (2.5 mol%) as a catalyst in 1,4-dioxane at 120 °C for 20 h. While the reaction was performed with $Ag_2CO_3$ used as the oxidant, to our delight, the desired arylation product **3a** was afforded successfully, albeit in a pretty low yield (9%, entry 1, table 1). Considering the exchanged anion from the additives has great influence on the catalytic activity of rhodium catalyst, a careful investigation to the extra silver additives was next carried out. Indeed, the addition of 20 mol% of $AgSbF_6$, which was commonly used for activating the catalyst $[Cp^*RhCl_2]_2$ as an additive, gave none of improvement for the yield of xx, and so did $AgBF_4$ and AgOAc (entries 2-4). To our excitement, further screening revealed that AgOTf was effective to increase the yield remarkably to 55% (entry 5). To our satisfactory, lowering the reaction temperature to 100 °C could give a higher yield (68%, entry 6). To further improve the yield, the screening of oxidant was next performed, which showed that only silver salts could promote this reaction effectively, and $Ag_2CO_3$ was still the best choice (entries 7-12). Meanwhile, the following screening of solvents indicated that the ethers, including 1,4-dioxane, THF and THP, gave the better results, and THF afforded the best




**Scheme 1.** Rh(III)-Catalyzed C-H arylation of N-nitrosoanilines.

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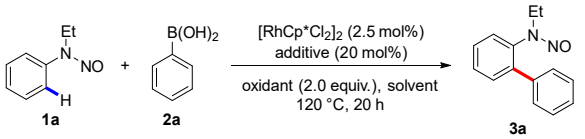
**Table 1.** Optimization of the reaction conditions.[a][b]



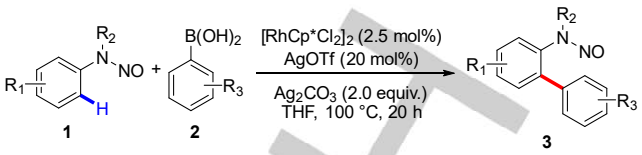

| entry | additive | oxidant | solvent | yield(%) |
|---|---|---|---|---|
| 1 | - | $Ag_2CO_3$ | 1,4-dioxane | 9 |
| 2 | $AgSbF_6$ | $Ag_2CO_3$ | 1,4-dioxane | 12 |
| 3 | $AgBF_4$ | $Ag_2CO_3$ | 1,4-dioxane | 28 |
| 4 | AgOAc | $Ag_2CO_3$ | 1,4-dioxane | trace |
| 5 | AgOTf | $Ag_2CO_3$ | 1,4-dioxane | 55 |
| 6[c] | AgOTf | $Ag_2CO_3$ | 1,4-dioxane | 68 |
| 7[c] | AgOTf | $Ag_2O$ | 1,4-dioxane | 60 |
| 8[c][d] | AgOTf | $Ag_2CO_3$, $Ag_2O$ | 1,4-dioxane | 64 |
| 9[c] | AgOTf | AgOAc | 1,4-dioxane | 10 |
| 10[c] | AgOTf | $Cu(OAc)_2$ | 1,4-dioxane | 5 |
| 11[c] | AgOTf | $Cu(TFA)_2$ | 1,4-dioxane | 0 |
| 12[c] | AgOTf | $K_2S_2O_8$ | 1,4-dioxane | 0 |
| 13[c] | AgOTf | $Ag_2CO_3$ | PhCl | 13 |
| 14[c] | AgOTf | $Ag_2CO_3$ | acetone | 40 |
| 15[c] | AgOTf | $Ag_2CO_3$ | MeCN | 0 |
| 16[c] | AgOTf | $Ag_2CO_3$ | THF | 70 |
| 17[c] | AgOTf | $Ag_2CO_3$ | THP | 55 |
| 18[c][e] | AgOTf | $Ag_2CO_3$ | THF | 75(73)[f] |
| 19[c][e][g] | AgOTf | $Ag_2CO_3$ | THF | 0 |

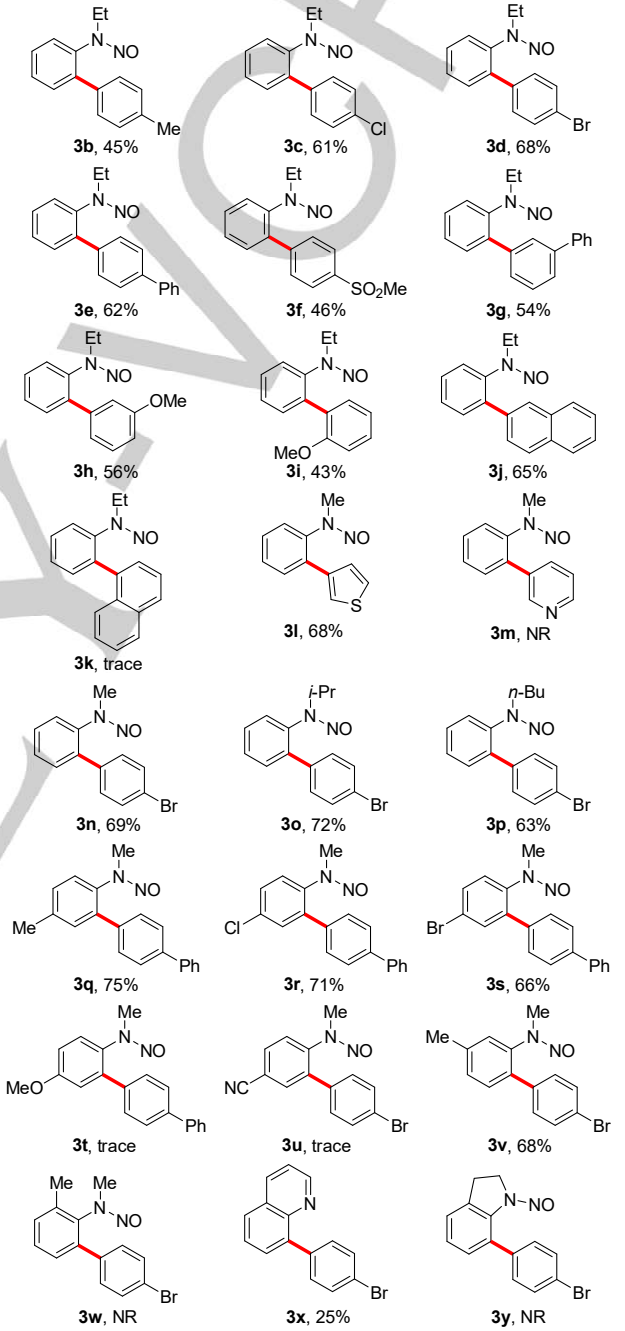
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol, 3 equiv), $[Cp^*RhCl_2]_2$ (2.5 mol%), AgOTf (20 mol%), oxidant (2.0 equiv), solvent (1.5 mL) at 120 ˚C for 20 h. [b] yield was determined by $^1H$ NMR using $CH_2Br_2$ as internal standard. [c] 100 ˚C. [d] 1 equivalent of $Ag_2CO_3$ and 1 equivalent of $Ag_2O$ were used. [e] 20 mol% of AgOTf was used. [f] isolated yield. [g] without $[Cp^*RhCl_2]_2$.

yield to 70% (entry 16). It is worth noting that increasing the loading of AgOTf from 10 mol% to 20 mol% had a positive effect on the reaction, giving the arylation product **3a** in 73% isolated yield (entry 18). Lastly, a control experiment in the absence of rhodium catalyst afforded none of the desired product **3a** (entry 19).

With the optimized reaction conditions in hand, we next tried to expand the scope of the aryl boronic acids and N-nitrosoanilines (Table 2). As shown in Table 2, a variety of arylboronic acids bearing both electron-donating and electron-withdrawing groups were well tolerated, affording the corresponding products **3** in moderate yields generally (**3b**-**3i**). Compared with the N-nitrososnilines, the substituted position on the phenyl ring of arylboronic acids has only relatively slight effect on the yield (**3h** and **3i**). Not surprisingly, halogen substituents, including chloro and bromo, were also well compatible with this catalytic system to give the arylated biaryls

**Table 2.** Arylation of N-nitrosoanilines with arylboronic acids.[a][b]




[a] Reaction conditions: **1** (0.2 mmol), **2** (0.6 mmol, 3 equiv), $[Cp^*RhCl_2]_2$ (2.5 mol%), AgOTf (20 mol%), $Ag_2CO_3$ (2.0 equiv), THF (1.5 mL) at 100 ˚C for 20 h. [b] isolated yield.

(**3c**, **3d**), which could be used for further transformations to other useful compounds through known transition-metal catalyzed coupling reactions. 2-Naphthaleneboronic acid was coupled to N-ethyl-N-nitrosoaniline smoothly (**3j**), but 1-naphthaleneboronic

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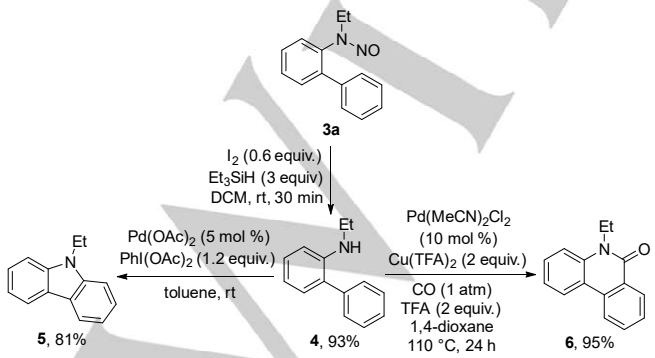
acid failed (**3k**) caused possibly by the steric hindrance. Additionally, the heteroarylboronic acids were also investigated. Comparing with thiophene-3-boronic acid gave the corresponding product in 68% yield (**3l**), the reaction with pyridine-3-boronic acid cannot proceed (**3m**) for its strong coordination ability to palladium catalyst. Subsequently, we then expanded the scope of N-nitrosoanilines, which disclosed that a variety of N-nitrosoanilines were arylated smoothly to furnish the corresponding N-nitroso biarylamines in good to moderate yields. To our satisfactory, a series of N-alkyl protecting-groups, including methyl, ethyl, *n*-butyl and *i*-propyl, on the N-nitrosoanilines could be well tolerated in the reaction conditions, and the steric hindrance of the alkyl group has no obvious influence on this transformation (**3n**-**3p**). The investigation of the electronic effect on the phenyl ring revealed that moderate electron-donating (**3q**) and -withdrawing groups (**3r**, **3s**) were suited in this arylation. However, the substrates bearing strong electron-donating (**3t**) and -withdrawing groups (**3u**) gave only trace amount of the corresponding products. The examination of substituent's effect on the phenyl ring of N-nitrosoanilines showed that both *meta*- and *para*-substituted substrates were compatible with this catalytic reaction, but the *ortho*-substituent (**3w**) was incompatible. Only less-hindered *ortho*-C-H bond on the phenyl ring could be arylated successfully for the *meta*-substituted substrates (**3v**). Both results demonstrated the obvious steric influence on this transformation brought by the substituents on the phenyl ring. At last, it was noteworthy to mention that N-nitrsotetrahydroquinoline was transformed to 8-arylquinoline directly in this reaction system, in which the desired C-H arylation followed by denitrosation and dehydro-aromatization proceeded in a sequence (**3x**). In contrast, no reaction took place when the similar 1-nitrosoindoline was used as substrate (**3y**), that might be due to inappropriate angle of the directing group caused by the rigid five-membered ring.

To demonstrate the synthetic potential of this N-nitroso directed arylation reaction, the resulted N-nitroso biarylamines were next tried to be transformed to diverse N-hetero biaryl compounds and N-heterocycles. As shown in Scheme 2, the nitroso group could be deprotected smoothly in the presence of iodine (0.5 equiv) and triethylsilane (3.0 equiv) in dichloromethane solution at room temperature, affording the corresponding 2-ethylamino-1,1'-biphenyl **4** in 93% yield.[14] As an important synthetic intermediate for further derivations, biphenyl **4** could be used for further cyclization to produce N-heterocycles




**Scheme 2.** Transformations of **3a**.

through reported methods. As shown in Scheme 2, an oxidative palladium-catalyzed amination of C-H bond afforded the desired carbazole at ambient temperature in 81% yield.[12a] Meanwhile, a palladium(II)-catalyzed C-H carbonylation of biaryl-2-amine **4** proceeded smoothly to furnish the corresponding phenanthridone **6** in high yield. [13a]

In summary, we have developed a Rh(III)-catalyzed, N-nitroso directed C-H arylation reaction employing arylboronic acids as arylation reagents. A wide range of functional groups such as bromo, chloro, methoxy, phenyl, sulphonate groups were compatible with this reaction condition. While the nitroso group could act as a good transformable directing group, the synthetic potential of this method has been well demonstrated by facile construction of diverse N-hetero biaryl compounds, including [1,1'-biphenyl]-2-amine, carbazole, and phenanthridone, using the arylation products as useful precursors for varous further transformations.

## Experimental Section

General procedure for the Rh(III)-catalyzed arylation of N-nitrosoanilines:

In a 35 mL oven-dried sealed tube, N-nitrosoaniline **1** (0.2 mmol), arylboronic acid **2** (0.6 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol%), AgOTf (10.3 mg, 20 mol%), $Ag_2CO_3$ (110.3 mg, 2 equiv), THF (1.5 mL) were added in sequence. The tube was then sealed with a Teflon lined cap and placed into a preheated oil bath at 100 °C with vigorous stirring. 20 hours later, the reaction mixture was cooled to room temperature. 10 mL ethyl acetate was added and the resulting mixture was filtered through a plug of silica (eluted with EtOAc). The solvent was evaporated to dryness under reduced pressure and the residue was purified by flash column chromatography to give product **3**.

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**Keywords:** N-nitrosoaniline • arylboronic acid • rhodium • C-H activation • arylation

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**Rh(III)-Catalyzed N-nitroso Directed C-H Arylation for Facile Construction of Diverse N-hetero Biaryl Compounds**

A Rh(III)-catalyzed C-H arylation reaction of N-nitrosoanilines was developed in which arylboronic acids were used as arylation reagents. N-nitroso was used as a transformable directing group. The product N-nitroso-[1,1'-biphenyl]-2-amine can be used for the synthesis of diverse N-hetero biaryl compounds, such as [1,1'-biphenyl]-2-amine, carbazole, phenanthridone.