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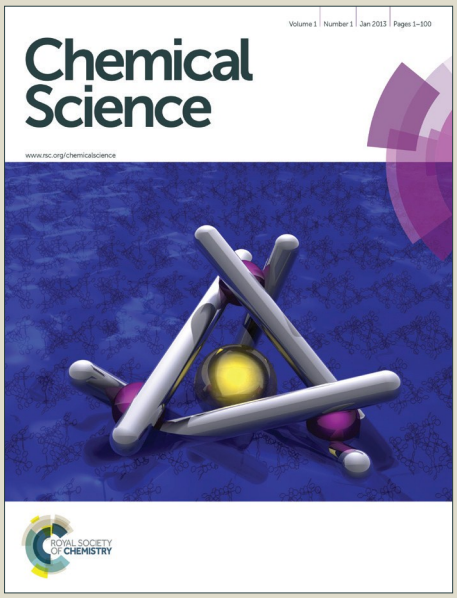

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ARTICLE

Nickel-Catalyzed Cyclization of Alkyne-Nitriles with Organoboronic Acids Involving *anti*-Carbometalation of Alkynes

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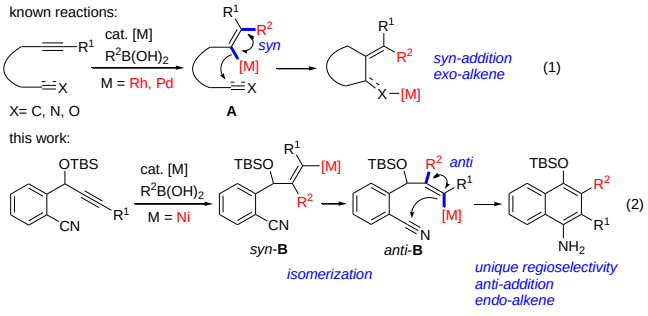
A nickel-catalyzed regioselective addition/cyclization of *o*-(cyano)phenyl propargyl ethers with arylboronic acids has been developed, which provides an efficient protocol for the synthesis of highly functionalized 1-naphthylamines with a wide range of structural diversity. The reaction is characterized by a regioselective and *anti*-addition of the arylboronic acids to the alkyne and subsequent facile nucleophilic addition of the resulting alkenylmetal to the tethered cyano group. Mechanistic studies reveal that Ni(I) species might be involved in the catalytic process.

Introduction

Transition-metal-catalyzed cascade reactions consisting of multiple carbometalation steps have attracted considerable attention in organic synthesis since these processes enable the rapid assembly of complex structures in an efficient, atom-economical and green manner.[1] Among these reactions, organoboron compounds are one of the most widely used reagents not only due to their chemical stability and easy availability, but also due to that they can undergo a series of addition reactions to unsaturated compounds such as alkynes, dienes, enones, aldehydes/ketones, nitriles and isocyanates etc. in the presence of a transition metal catalyst, especially a Rh, Pd or Ni complex.[2] The development of cascade reactions by combining of the different types of these elemental reactions is undoubtedly important and attractive. In this regard, the cascade reactions involving the addition of organoboron compounds to alkynes as the initial step have been realized mainly through Rh-[1b-c,3] or Pd-catalysis[4] reported by Murakami, Hayashi, Lu and other groups. These catalytic reactions generally proceed by *syn*-1,2-addition of organometal species generated through transmetalation between organoboron and metal complex across the carbon-carbon triple bond, followed by nucleophilic attack of the resulting alkenylmetal on the remained electrophiles (Scheme 1, eq 1). So far most of the reported reactions proceed via formation of regioisomer **A** in which R^2 group of $R^2B(OH)_2$ locates on a carbon adjacent to alkyne terminus R^1, leading to an *exo*-alkene upon cyclization[3,4] (Scheme 1, eq 1). Cyclizations involving the regioselective formation of alkenylmetal with a metal α-to the R^1 substituent such as *syn*-**B** are quite rare[5] (Scheme 1, eq 2), possibly due to that the subsequent cyclization process will evoke a highly strained transition state. Thus the development of new cyclization systems with controlled regiochemistry towards **B** is highly challenging. During our studies on nickel-catalyzed reactions, we found such transformation could be achieved by addition of organoborons to benzene-tethered alkyne-nitriles utilization of nickel as the catalyst, possibly through the isomerization of *syn*-**B** to *anti*-**B**. Herein, we report the first example of nickel-catalyzed carboarylative cyclization of alkyne-nitriles with organoboronic acids involving regioselective and *anti*-carbonickelation of alkynes, which provides an efficient protocol for the synthesis of highly functionalized 1-naphthylamines. In addition, mechanistic studies revealed that Ni(I) species[6] rather than Ni(II) species was involved as key intermediates, which has not been reported in Ni-catalyzed boron addition reactions.



Scheme 1. Metal-catalyzed cascade addition/cyclization reactions

Results and discussion

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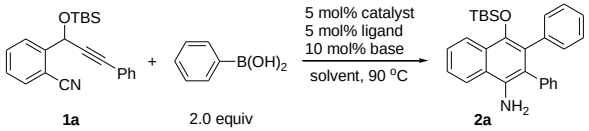
We chose the nickel-catalyzed reaction of *o*-(cyano)phenyl propargyl ether[7] **1a** and phenylboronic acid as a model reaction for the optimization of the reaction conditions. Initially, we examined the reactions in the presence of $Ni(cod)_2$ and various phosphine ligands such as PPh_3 in 1,4-dioxane at 90 °C. However, only trace of the desired cyclization product was observed, along with some byproducts (Table 1, entry 1). Replacing of $Ni(cod)_2$ with Ni(II) complex $Ni(acac)_2{\cdot}2H_2O$ (acac = acetylacetonate) could afford a cyclized product of 4-OTBS-substituted 1-naphthylamine **2a**, albeit in only 17-18% yields (entries 2-3). To our delight, the addition of 10 mol% of ^{t}BuOK as a base improved the yield of **2a** dramatically to 66% within a short reaction time (entry 4). The results suggest that a base is necessary for this reaction possibly for promoting the transmetalation step by formation of a borate[8] with organoboronic acid. The structure of **2a** also revealed that arylation in the initial step occurred regioselectively on the alkyne carbon closer to the OTBS group. Subsequently, the effects of bases, phosphine ligands and solvents were evaluated. Among various bases, Cs_2CO_3 gave the best result (73%, entry 5). Increasing the catalytic loading of Cs_2CO_3 to 20 mol% had little effect on the yield of **2a** (entry 8). However, when stoichiometric amount of Cs_2CO_3 was used, the yield was reduced rapidly (entry 9). It was remarkable that unlike the use of more than one equivalent of bases in most of the transition metal-catalyzed reactions involving organoborons, here only catalytic amounts of base were enough. Increasing the catalyst loading did not improve the yield of the product (entry 10). Triarylphosphine ligands and *N*-heterocyclic carbene ligand IPr (IPr =1,3-bis(2,6- diisopropylphenyl)imidazole-2-ylidene) were also effective, while the ligands such as PPh_2Me and PCy_3 were less efficient (entries 11-17). Changing the solvent to THF or toluene afforded **2a** in satisfied yields of 64-68% (entries 18-19). Addition of one equivalent of H_2O as a promoter or proton source did not afford a better result (entry 20). $Ni(acac)_2$ also catalyze the reaction efficiently (entry 21). When $Ni(cod)_2$ was used as the catalyst, only trace amounts of **2a** were obtained (entry 22). Without the phosphine ligand, the reaction also proceeded to afford **2a** in 65% yield, however, with a longer reaction time (entry 23). Without nickel catalyst, no reaction occurred (entry 24). On the basis of the above optimization studies, the reaction conditions shown in Table 1, entry 5 were chosen as the best conditions.

Table 1. Optimization studies for the formation of 1-naphthylamine **2a**.



1a 2.0 equiv **2a**

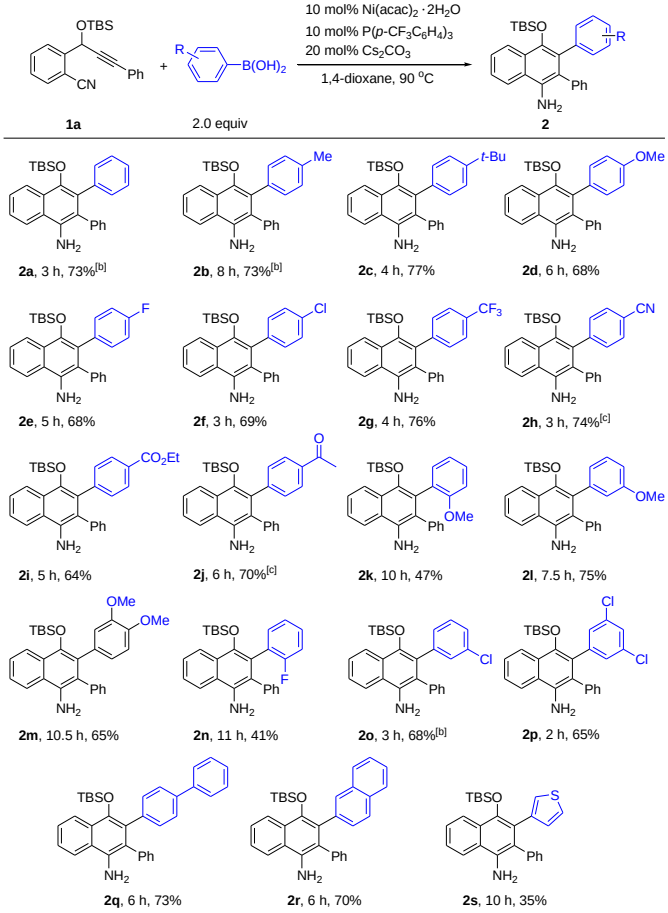
Entry	Catalyst	Ligand	Base	Solvent	Time [h]	Yield [%][a]
1	$Ni(cod)_2$	PPh_3[b]	-	1,4-dioxane	3	trace
2	$Ni(acac)_2 \cdot 2H_2O$	PPh_3	-	1,4-dioxane	24	18
3	$Ni(acac)_2 \cdot 2H_2O$	$P(p\text{-}CF_3C_6H_4)_3$	-	1,4-dioxane	24	17
4	$Ni(acac)_2 \cdot 2H_2O$	$P(p\text{-}CF_3C_6H_4)_3$	^{t}BuOK	1,4-dioxane	4	66
5	$Ni(acac)_2 \cdot 2H_2O$	$P(p\text{-}CF_3C_6H_4)_3$	Cs_2CO_3	1,4-dioxane	3	73
6	$Ni(acac)_2 \cdot 2H_2O$	$P(p\text{-}CF_3C_6H_4)_3$	CsF	1,4-dioxane	6	67
7	$Ni(acac)_2 \cdot 2H_2O$	$P(p\text{-}CF_3C_6H_4)_3$	K_2CO_3	1,4-dioxane	10	31
8	$Ni(acac)_2 \cdot 2H_2O$	$P(p\text{-}CF_3C_6H_4)_3$	Cs_2CO_3[c]	1,4-dioxane	3	68
9	$Ni(acac)_2 \cdot 2H_2O$	$P(p\text{-}CF_3C_6H_4)_3$	Cs_2CO_3[d]	1,4-dioxane	10	8 (59)
10[e]	$Ni(acac)_2 \cdot 2H_2O$	$P(p\text{-}CF_3C_6H_4)_3$	Cs_2CO_3	1,4-dioxane	3	74
11	$Ni(acac)_2 \cdot 2H_2O$	PPh_3	Cs_2CO_3	1,4-dioxane	5	69
12	$Ni(acac)_2 \cdot 2H_2O$	$P(p\text{-}MeC_6H_4)_3$	Cs_2CO_3	1,4-dioxane	4	68
13	$Ni(acac)_2 \cdot 2H_2O$	$P(C_6F_5)_3$	Cs_2CO_3	1,4-dioxane	5	63
14	$Ni(acac)_2 \cdot 2H_2O$	PPh_2Me	Cs_2CO_3	1,4-dioxane	7	45
15	$Ni(acac)_2 \cdot 2H_2O$	PCy_3	Cs_2CO_3	1,4-dioxane	17	55
16	$Ni(acac)_2 \cdot 2H_2O$	IPr	Cs_2CO_3	1,4-dioxane	6	64
17	$Ni(acac)_2 \cdot 2H_2O$	IPr	^{t}BuOK	1,4-dioxane	7	62
18	$Ni(acac)_2 \cdot 2H_2O$	$P(p\text{-}CF_3C_6H_4)_3$	Cs_2CO_3	THF	8	64
19	$Ni(acac)_2 \cdot 2H_2O$	$P(p\text{-}CF_3C_6H_4)_3$	Cs_2CO_3	toluene	3	68
20[f]	$Ni(acac)_2 \cdot 2H_2O$	$P(p\text{-}CF_3C_6H_4)_3$	Cs_2CO_3	1,4-dioxane	6	57
21	$Ni(acac)_2$	$P(p\text{-}CF_3C_6H_4)_3$	Cs_2CO_3	1,4-dioxane	3	72
22	$Ni(cod)_2$	$P(p\text{-}CF_3C_6H_4)_3$[b]	Cs_2CO_3	1,4-dioxane	9	trace
23	$Ni(acac)_2 \cdot 2H_2O$	-	Cs_2CO_3	1,4-dioxane	5	65
24	-	$P(p\text{-}CF_3C_6H_4)_3$	Cs_2CO_3	1,4-dioxane	10	(99)

[a] Isolated yields. The yields of the recovered **1a** were shown in parentheses. [b] 10 mol% of the ligand was used. [c] 20 mol% of Cs_2CO_3 was used. [d] 1.0 equiv of Cs_2CO_3 was used. [e] 10 mol% $Ni(acac)_2{\cdot}2H_2O$, 10 mol% $P(p\text{-}CF_3C_6H_4)_3$ and 20 mol% Cs_2CO_3 were used. [f] One equiv of H_2O was added.

Next, we proceeded to investigate the scope of this new cascade addition/cyclization reaction catalyzed by $Ni(acac)_2{\cdot}2H_2O$. The reactivity of various organoboronic acids was first examined using **1a** as a reaction partner (Table 2). During this process, we found that the 5 mol% catalyst loading was not effective in some cases, thus 10 mol% $Ni(acac)_2{\cdot}2H_2O$, 10 mol% $P(p\text{-}CF_3C_6H_4)_3$ and 20 mol% Cs_2CO_3 were used in most of the cases to achieve the better product yields. As shown in Table 2, a wide range of diversely substituted aryl- or heteroaryl-boronic acids were suitable for this reaction, leading to the desired 1-naphthylamines **2a**-**2s** in generally good to high yields. Arylboronic acids bearing the electron-donation groups such as *p*-Me, *p*-^{t}Bu and *p*-MeO or electron-withdrawing groups such as *p*-F, *p*-Cl, *p*-CF_3, *p*-CN, *p*-CO_2Et and *p*-Ac on the aryl rings underwent the cyclization smoothly to provide the corresponding 1-naphthylamines **2b**-**2j** in 64-77% yields, and these functional groups were well tolerated during the reaction. Of note is that a CN and Ac group remained intact under the reaction conditions, and no nickel-catalyzed boron additions to these groups were observed. The results indicated that electron-poor or -rich aryl substituents on arylboronic acids had little influence on the yields of products **2**. Sterically demanding *o*-MeO substituted arylboronic acid afforded **2k** with a longer reaction time in lower yield of 47%, indicating that the reaction is markedly influenced by steric effect. Arylboronic acids with -MeO or -Cl substituents at 3-, 3,4- or 3,5-positions of the phenyl ring, or with a biphenyl or 2-naphthyl ring transformed into products **2l**-**2m** and **2o-2r** efficiently in good yields. The use of 2-fluorophenylboronic acid gave **2n** in 41% yield. 2-Thienylboronic acid also participated in this cascade reaction, albeit with a lower yield of **2s**. However, when alkylboronic acid such as n-butylboronic acid was employed, no desired product was obtained.

The scope of *o*-(cyano)phenyl propargyl ethers was then examined (Table 3). A variety of electron-donating and -withdrawing groups on the aryl rings at the alkyne terminus were found to be compatible, such as *p*-Me, *p*-OMe, *p*-F, *p*-Cl, *p*-CF_3 and *p*-CO_2Me substituents, and the corresponding products **2t**-**2y** were formed in 61-76% yields. Interestingly, in contrast to the results of the reaction of **1a** with 2-

Table 2. Scope of the reaction with respect to arylboronic acids.[a]



[a] The yields given are for the isolated products. [b] 5 mol% $Ni(acac)_2{\cdot}2H_2O$, 5 mol% $P(p\text{-}CF_3C_6H_4)_3$ and 10 mol% Cs_2CO_3 were used. [c] THF was used as the solvent.

thienylboronic acid, the presence of 2-thienyl or 3-benzothienyl ring as the alkyne terminals did not give much influence to the reaction, and the corresponding products **2z** and **2za** were obtained in high yields of 80% and 74%, respectively. A 9*H*-fluorene substituent, which is a very useful unit in organofunctional materials, was also successfully incorporated into the product **2zb** in 70% yield. Alkenyl or alkyl-substituted alkynes, such as cyclohexenyl, cyclopropyl and propyl-substituted one, however, afforded the desired products **2zc**-**2ze** in low yields of 23-35%. The structure of 1-naphthylamine products was unambiguously confirmed by X-ray crystallographic analysis of **2o**.[9] 1-Naphthylamines are important structural motifs found in a variety of biologically active substances. They are also acted as useful building blocks in synthetic chemistry and dyestuffs industry. However, efficient methods for their synthesis are quite limited.[10] Our reaction provides a convenient route to 1-naphthylamines.

To understand the reaction mechanism, we tried to isolate the possible reaction intermediates. First, a stoichiometric reaction of $Ni(acac)_2$ (1 equiv), IPr (1 equiv), $PhB(OH)_2$ (2 equiv) and ^{t}BuOK (2 equiv) was carried out (Scheme 2, eq 1). It was found that in addition to a biphenyl product, a red crystalline

Table 3. Scope of the *o*-(cyano)phenyl propargyl ethers.[a]

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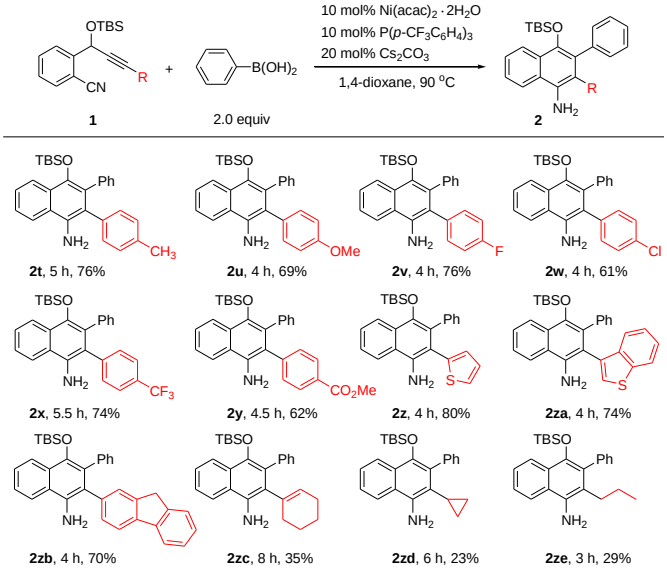
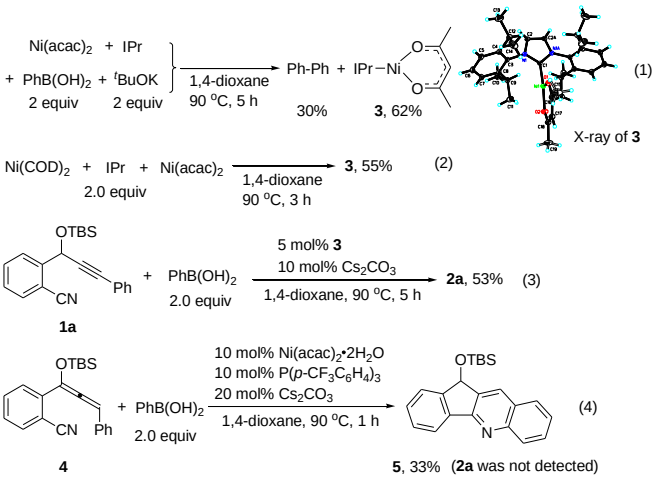
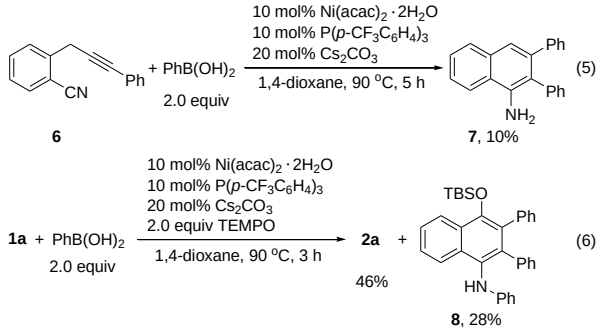


[a] The yields given are for the isolated products.

compound IPrNi(acac) **3** was also isolated in 62% yield. Complex **3** is paramagnetic as indicated by the appearance of broad signals in ^{1}H NMR. The X-ray crystal analysis of **3**[9] clearly shows a rare, three-coordinate distorted T-shape Ni(I) structure.[6e,f] When Cs_2CO_3 was used instead of ^{t}BuOK, the same Ni(I) complex was also observed, however, in a low yield of 14%. In this case, a large amount of precipitate could be observed. The precipitate was assumed to be $PhB(OH)_2$-Cs_2CO_3 adduct. It might be due to the formation of this low soluble adduct, thus preventing their further reaction with the nickel complex. In fact, stirring a 1:1 mixture of $PhB(OH)_2$ and Cs_2CO_3 in 1,4-dioxane at 90 °C resulted in the formation of a large amount of white precipitate. This might also explain why the use of 1 equivalent of Cs_2CO_3 provided the cyclized product **2a** in low yield (Table 1, entry 9). Complex **3** might be formed by the comproportionation of Ni(0) and Ni (II) species.[6c,d] To confirm this point, the stoichiometric reaction of $Ni(COD)_2$ with





Scheme 2. Mechanistic studies

$Ni(acac)_2$ in the presence of IPr was carried out. To our delight, the same complex **3** was formed in moderate yield (Scheme 2, eq 2). This Ni(I) complex **3** was found to catalyze the cyclization of **1a** with $PhB(OH)_2$ to **2a** (Scheme 2, eq 3), implying that Ni(I) species was likely involved in the catalytic process. Recently, Ni(I) species was proposed to be relevant in Ni-catalyzed cross-coupling reactions.[6] Our results demonstrate that Ni(I) may also be involved in Ni-catalyzed addition reactions of organoboron reagents to the alkynes. In addition, reaction of allene **4** with $PhB(OH)_2$ under Ni-catalyzed conditions afforded indeno[1,2-*b*]quinoline **5** via base-promoted cyano-Schmittel cyclization,[7] while the desired **2a** was not observed (Scheme 2, eq 4), indicating that the reaction does not involve the allene intermediate.

The origin of the regioselectivity in this reaction is not clear yet, possibly it is controlled by electronic factors in π-complex **12** (see Scheme 3).[11] To understand the role of OTBS group, the alkyne-nitrile **6** without the OTBS group was synthesized. The Ni-catalyzed reaction of **6** with $PhB(OH)_2$ afforded only 10% of the desired naphthylamine **7**, along with a small amounts of an unidentified byproduct (Scheme 2, eq 5). The results indicate that the presence of OTBS group is crucial for this reaction.

In addition, it was found that in the presence of a radical scavenger such as TEMPO, the desired **2a** and an *N*-arylated product **8** were formed in 74% combined yield (Scheme 2, eq 6). **8** was possibly formed by Ni-catalyzed oxidative amination of arylboronic acid with amine **2a**.[12,13] The results indicated that the reaction was not inhibited by TEMPO, and this suggests that radical species is not involved in this system.

Based on the above results, we propose the following reaction mechanism (Scheme 3). Initially, transmetalation of arylboronic acid with Ni(II) complex promoted by a base provides diarylnickel(II) species **9**, together with HOBO, $HCsCO_3$ and Cs(acac).[14] **9** undergoes reductive elimination to form a Ni(0) species. The observation of biphenyl[15] in the catalytic reaction of **1a** with $PhB(OH)_2$ also supported that Ni(II) was reduced in the reaction process. This Ni(0) species comproportionates with Ni(II) to afford Ni(I) complex **10**, which undergoes transmetalation with arylboronic acid to give arylnickel(I) species **11**. Regioselective 1,2-addition of arylnickel(I) species **11** to the alkyne moiety in a *syn*-fashion takes place to give an alkenylnickel(I) intermediate *syn*-**13**. *Cis*-to-*trans* isomerization of **13**,[16] possibly through a carbene-like zwitterionic resonance species[17] yields alkenylnickel(I) intermediate *anti*-**13** with a metal *trans*-to Ar substituent. It was noted that most of the metal-catalyzed reactions of

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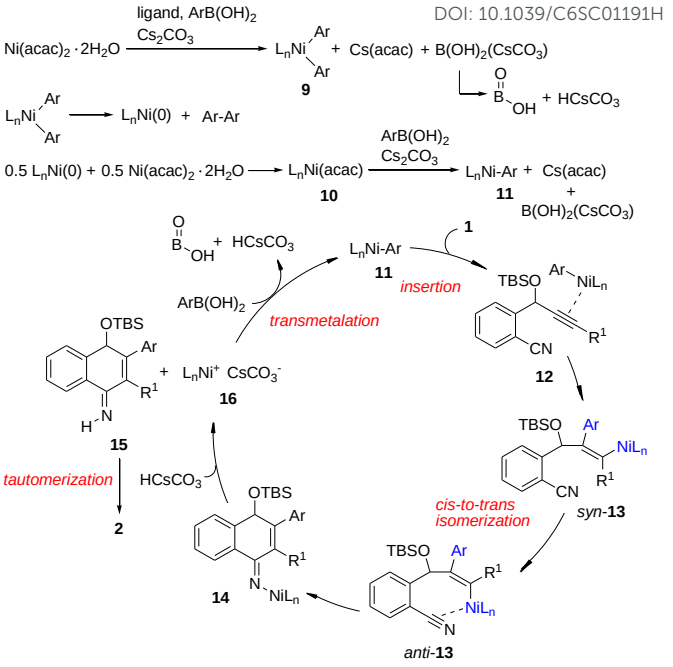

Scheme 3. Possible reaction mechanism

organoborons to alkynes gave the *syn*-addition product while few reactions produce the *anti*-addition product.[2r, 17] The regio- and stereochemistry for addition process here are consistent with those observed by cobalt(II)-catalyzed hydroarylation of propargyl -alcohols or -carbamates with arylboronic acids.[18] Cyano group may play a role in facilitating the *cis-trans*-isomerization by stabilizing the metal species and directing the subsequent addition reaction. Nucleophilic attack of alkenylmetal in *anti*-**13** to the cyano group forms a cyclized intermediate **14**. Subsequent protonation of **14** produces the *N*-H imine **15** and a nickel(I) species **16**. Tautomerization of **15** affords the observed product **2**. **16** undergoes transmetalation with $ArB(OH)_2$ to regenerate the arylnickel(I) catalyst **11**.

Conclusions

In summary, we have developed a nickel-catalyzed regioselective addition/cyclization of *o*-(cyano)phenyl propargyl ethers with arylboronic acids, which provides an efficient protocol for the synthesis of highly functionalized 1-naphthylamines with a wide range of structural diversity. The reaction is characterized by a regioselective and *anti*-addition of the arylboronic acids to the alkyne and subsequent facile nucleophilic addition of the resulting alkenylmetal to the tethered cyano group. Mechanistic studies reveal that Ni(I) species might be involved in the catalytic process. Further mechanistic studies and the extension to alkynes tethered with a wide variety of electrophiles are currently ongoing in our laboratory.

Acknowledgements

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