Nickel-catalyzed cyclization of alkyne-nitriles with organoboronic acids involving anti-carbometalation of alkynes†

Xingjie Zhang, Xin Xie and Yuanhong Liu*

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 wide 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 alkynylmetal to the tethered cyano group. Mechanistic studies reveal that a Ni(0) 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-economic 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 ready availability, but also because 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 Rh, Pd or Ni complexes.2 The development of cascade reactions by combining different types of these elemental reactions is undoubtedly important and attractive. In this regard, cascade reactions involving the addition of organoboron compounds to alkynes as the initial step have been realized mainly through Rh3−6 or Pd-catalysis4 as reported by Murakami, Hayashi, Lu and other groups. These catalytic reactions generally proceed by syn-1,2-addition of the organometal species generated through transmetalation between the organoboron and the metal complex across the carbon–carbon triple bond, followed by nucleophilic attack of the resulting alkynylmetal on the remaining electrophile (Scheme 1, eqn (1)). So far most of the reported reactions proceed via formation of regioisomer A in which the R2 group of R2B(OH)2 locates on a carbon adjacent to the alkyne terminus R1, leading to an exo-alkene upon cyclization3−4 (Scheme 1, eqn (1)). Cyclizations involving the regioselective formation of the alkynylmetal with a metal α-to the R1 substituent such as syn-B are quite rare5 (Scheme 1, eqn (2)), possibly because the subsequent cyclization process will involve 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 that such a transformation could be achieved by the addition of organoboron compounds to benzene-tethered alkyne-nitriles utilizing nickel as the catalyst, possibly through the isomerization of syn-B to anti-B. Herein, we report the first example of a nickel-catalyzed carboarylationative 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† rather than Ni(0) species were involved as the key intermediates, which has not been reported in Ni-catalyzed boron addition reactions.

Scheme 1  Metal-catalyzed cascade addition/cyclization reactions.

† Electronic supplementary information (ESI) available. CCDC 1440646 and 1440647. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6sc01191h
Results and discussion

We chose the nickel-catalyzed reaction of \( o \)-(cyanophenyl)propargyl ether\(^\text{a}\) \(1\) 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 a trace of the desired cyclization product was observed, along with some byproducts (Table 1, entry 1). Replacing Ni(COD)\(_2\) with a Ni(II) complex, Ni(acac)\(_2\) affording the cyclized product 4-OTBS-substituted 1-naphthylamine \(2a\), albeit in only 17–18% yields (entries 2–3). To our delight, the addition of 10 mol% of \( \text{BuOK} \) 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\(^\text{a}\) with the organoboronic acid. The structure of \(2a\) also revealed that arylation in the initial step occurred regioselectively on the alkyne carbon that is closer to the OTBS group. Subsequently, the effects of bases, phosphine ligands and solvents were evaluated. Of the various bases, Cs\(_2\)CO\(_3\) gave the best result (73%, entry 5). Increasing the catalytic loading of Cs\(_2\)CO\(_3\) to 20 mol% had little effect on the yield of \(2a\) (entry 6). However, when a stoichiometric amount of Cs\(_2\)CO\(_3\) was used, the yield was reduced rapidly (entry 9). It was remarkable that, unlike the use of more than one equivalent of base in most of the transition metal-catalyzed reactions involving organoborons, here only catalytic amounts of base were needed. Increasing the catalyst loading did not improve the yield of the product (entry 10). Triarylphosphine ligands and the N-heterocyclic carbene ligand IPr (IPr = 1,3-bis(2,6-disopropylphenyl)imidazol-2-ylidene) were also effective, while ligands such as PPh\(_2\)Me and PCy\(_3\) were less effective (entries 11–17). Changing the solvent to THF or toluene afforded \(2a\) in satisfactory yields of 64–68% (entries 18–19). Addition of one equivalent of H\(_2\)O as a promoter or proton source did not afford a better result (entry 20). Ni(acac)\(_2\) also catalyzed the reaction efficiently (entry 21). When Ni(COD)\(_2\) was chosen as the best conditions, only trace amounts of \(2a\) were obtained (entry 22). Without the phosphine ligand, the reaction also proceeded to afford \(2a\) in 65% yield, albeit with a longer reaction time (entry 23). Without a 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 \(2a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Ligand</th>
<th>Base</th>
<th>Solvent</th>
<th>Time [h]</th>
<th>Yield(^\text{d}) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni(COD)(_2)</td>
<td>PPh(_3)(^b)</td>
<td>—</td>
<td>1,4-Dioxane</td>
<td>3</td>
<td>Trace</td>
</tr>
<tr>
<td>2</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>PPh(_3)</td>
<td>—</td>
<td>1,4-Dioxane</td>
<td>24</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>P(p-CF(_3)C(_6)H(_4))(_3)</td>
<td>—</td>
<td>1,4-Dioxane</td>
<td>24</td>
<td>17</td>
</tr>
<tr>
<td>4</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>P(p-CF(_3)C(_6)H(_4))(_3)</td>
<td>(\text{BuOK})</td>
<td>1,4-Dioxane</td>
<td>4</td>
<td>66</td>
</tr>
<tr>
<td>5</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>P(p-CF(_3)C(_6)H(_4))(_3)</td>
<td>Cs(_2)CO(_3)</td>
<td>1,4-Dioxane</td>
<td>3</td>
<td>73</td>
</tr>
<tr>
<td>6</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>P(p-CF(_3)C(_6)H(_4))(_3)</td>
<td>CsF</td>
<td>1,4-Dioxane</td>
<td>6</td>
<td>67</td>
</tr>
<tr>
<td>7</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>P(p-CF(_3)C(_6)H(_4))(_3)</td>
<td>K(_2)CO(_3)</td>
<td>1,4-Dioxane</td>
<td>10</td>
<td>31</td>
</tr>
<tr>
<td>8</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>P(p-CF(_3)C(_6)H(_4))(_3)</td>
<td>Cs(_2)CO(_3)(^c)</td>
<td>1,4-Dioxane</td>
<td>3</td>
<td>68</td>
</tr>
<tr>
<td>9</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>P(p-CF(_3)C(_6)H(_4))(_3)</td>
<td>Cs(_2)CO(_3)(^c)</td>
<td>1,4-Dioxane</td>
<td>10</td>
<td>8 (59)</td>
</tr>
<tr>
<td>10(^\text{f})</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>P(p-CF(_3)C(_6)H(_4))(_3)</td>
<td>Cs(_2)CO(_3)(^c)</td>
<td>1,4-Dioxane</td>
<td>3</td>
<td>74</td>
</tr>
<tr>
<td>11</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>PPh(_3)</td>
<td>—</td>
<td>1,4-Dioxane</td>
<td>5</td>
<td>69</td>
</tr>
<tr>
<td>12</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>P(p-MeC(_6)H(_5))(_3)</td>
<td>Cs(_2)CO(_3)</td>
<td>1,4-Dioxane</td>
<td>4</td>
<td>68</td>
</tr>
<tr>
<td>13</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>P(p-CF(_3)C(_6)H(_4))(_3)</td>
<td>Cs(_2)CO(_3)</td>
<td>1,4-Dioxane</td>
<td>5</td>
<td>63</td>
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<tr>
<td>14</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>PPh(_3)Me</td>
<td>—</td>
<td>1,4-Dioxane</td>
<td>7</td>
<td>45</td>
</tr>
<tr>
<td>15</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>PCy(_3)</td>
<td>Cs(_2)CO(_3)</td>
<td>1,4-Dioxane</td>
<td>17</td>
<td>55</td>
</tr>
<tr>
<td>16</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>IPr</td>
<td>Cs(_2)CO(_3)</td>
<td>1,4-Dioxane</td>
<td>6</td>
<td>64</td>
</tr>
<tr>
<td>17</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>IPr</td>
<td>(\text{BuOK})</td>
<td>1,4-Dioxane</td>
<td>7</td>
<td>62</td>
</tr>
<tr>
<td>18</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>P(p-CF(_3)C(_6)H(_4))(_3)</td>
<td>Cs(_2)CO(_3)</td>
<td>THF</td>
<td>8</td>
<td>64</td>
</tr>
<tr>
<td>19</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>P(p-CF(_3)C(_6)H(_4))(_3)</td>
<td>Cs(_2)CO(_3)</td>
<td>Toluene</td>
<td>3</td>
<td>68</td>
</tr>
<tr>
<td>20(^\text{f})</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>P(p-CF(_3)C(_6)H(_4))(_3)</td>
<td>Cs(_2)CO(_3)</td>
<td>1,4-Dioxane</td>
<td>6</td>
<td>57</td>
</tr>
<tr>
<td>21</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>P(p-CF(_3)C(_6)H(_4))(_3)</td>
<td>Cs(_2)CO(_3)</td>
<td>1,4-Dioxane</td>
<td>3</td>
<td>72</td>
</tr>
<tr>
<td>22</td>
<td>Ni(COD)(_2)</td>
<td>P(p-CF(_3)C(_6)H(_4))(_3)</td>
<td>Cs(_2)CO(_3)</td>
<td>1,4-Dioxane</td>
<td>9</td>
<td>Trace</td>
</tr>
<tr>
<td>23</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>—</td>
<td>Cs(_2)CO(_3)</td>
<td>1,4-Dioxane</td>
<td>5</td>
<td>65</td>
</tr>
<tr>
<td>24</td>
<td>Ni(acac)(_2)·2H(_2)O</td>
<td>P(p-CF(_3)C(_6)H(_4))(_3)</td>
<td>Cs(_2)CO(_3)</td>
<td>1,4-Dioxane</td>
<td>10</td>
<td>(99)</td>
</tr>
</tbody>
</table>

\(^{a}\) Isolated yields. The yields of the recovered \(1\) were shown in parentheses. \(^{b}\) 10 mol% of the ligand was used. \(^{c}\) 20 mol% of Cs\(_2\)CO\(_3\) was used. \(^{d}\) 1.0 equiv. of Cs\(_2\)CO\(_3\) was used. \(^{e}\) 10 mol% Ni(acac)\(_2\)·2H\(_2\)O, 10 mol% P(p-CF\(_3\)C\(_6\)H\(_4\))\(_3\), and 20 mol% Cs\(_2\)CO\(_3\) were used. \(^{f}\) One equiv. of H\(_2\)O was added.
Next, we proceeded to investigate the scope of this new cascade addition/cyclization reaction catalyzed by Ni(acac)_2·2H_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 and thus 10 mol% Ni(acac)_2·2H_2O, 10 mol% P(p-CF_3C_6H_4)_3 and 20 mol% Cs_2CO_3 were used in most of the cases to achieve 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 products in generally good to high yields. Arylboronic acids bearing electron-donating groups such as p-Me, p- tBu 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 ring underwent the cyclization smoothly to provide the corresponding 1-naphthylamines 2a–2s in 64–77% yields, and these functional groups were well tolerated during the reaction. Of note is that the CN and Ac groups 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 the arylboronic acid had little influence on the yields of products 2. The stericly demanding o-MeO substituted arylboronic acid afforded 2k with a longer reaction time and a lower yield of 47%, indicating that the reaction is markedly influenced by steric effects. Arylboronic acids with –MeO or –Cl substituents at the 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 alkylboric acids such as n-butylboronic acid were 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-thienylboronic acid, the presence of a 2-thienyl or 3-benzothienyl ring as the alkyne terminal did not have much influence on the reaction, and the corresponding products 2z and 2za were obtained in high yields of 80% and 74%, respectively. A 9H-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 alkyne, such as cyclohexenyl, cyclopropyl and propyl-substituted ones, however, afforded the desired products 2zc–2ze in low yields of 23–35%. The structure of the 1-naphthylamine product was unambiguously confirmed by X-ray crystallographic analysis of 2o.

Table 2 Scope of the reaction with respect to arylboronic acids

<table>
<thead>
<tr>
<th>Arylboronic Acid</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Me</td>
<td>73</td>
</tr>
<tr>
<td>p- tBu</td>
<td>68</td>
</tr>
<tr>
<td>p-MeO</td>
<td>66</td>
</tr>
<tr>
<td>p-F</td>
<td>68</td>
</tr>
<tr>
<td>p-Cl</td>
<td>69</td>
</tr>
<tr>
<td>p-CF_3</td>
<td>76</td>
</tr>
<tr>
<td>p-CN</td>
<td>74</td>
</tr>
<tr>
<td>p-CO_2Et</td>
<td>76</td>
</tr>
<tr>
<td>p-Ac</td>
<td>88</td>
</tr>
</tbody>
</table>

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

Table 3 Scope of the o-(cyano)phenyl propargyl ethers

<table>
<thead>
<tr>
<th>Arylboronic Acid</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Me</td>
<td>76</td>
</tr>
<tr>
<td>p-OMe</td>
<td>76</td>
</tr>
<tr>
<td>p-F</td>
<td>76</td>
</tr>
<tr>
<td>p-Cl</td>
<td>69</td>
</tr>
<tr>
<td>p-CF_3</td>
<td>76</td>
</tr>
<tr>
<td>p-CN</td>
<td>74</td>
</tr>
<tr>
<td>p-CO_2Et</td>
<td>66</td>
</tr>
<tr>
<td>p-Ac</td>
<td>88</td>
</tr>
</tbody>
</table>

a The yields given are for the isolated products.
synthetic chemistry and the dyestuffs industry. However, efficient methods for their synthesis are quite limited.\textsuperscript{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)\textsubscript{2} (1 equiv.), IPr (1 equiv.), PhB(OH)\textsubscript{2} (2 equiv.) and 'BuOK (2 equiv.) was carried out (Scheme 2, eqn (1)). It was found that in addition to a biphenyl product, a red crystalline compound IPrNi(acac)\textsubscript{3} was isolated in 62\% yield. Complex 3 is paramagnetic as indicated by the appearance of broad signals in the \textsuperscript{1}H NMR spectrum. The X-ray crystal analysis of 3 (ref. 9) clearly shows a rare, three-coordinate distorted T-shaped Ni(I) structure.\textsuperscript{6e, f} When Cs\textsubscript{2}CO\textsubscript{3} was used instead of 'BuOK, the same Ni(I) complex was also observed, albeit in a low yield of 14\%. In this case, a large amount of precipitate could be observed. The precipitate was assumed to be the PhB(OH)\textsubscript{2}–Cs\textsubscript{2}CO\textsubscript{3} adduct. Thus, the formation of this low-soluble adduct might prevent further reaction with the nickel complex. In fact, stirring a 1 : 1 mixture of PhB(OH)\textsubscript{2} and Cs\textsubscript{2}CO\textsubscript{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\textsubscript{2}CO\textsubscript{3} provided the cyclized product 2a in a low yield (Table 1, entry 9). Complex 3 might be formed by the comproportionation of Ni(0) and Ni(II) species.\textsuperscript{6c, d} To confirm this point, the stoichiometric reaction of Ni(COD)\textsubscript{2} with Ni(acac)\textsubscript{2} in the presence of IPr was carried out. To our delight, the same Ni(I) complex 3 was formed in moderate yield (Scheme 2, eqn (2)). This Ni(i) complex 3 was found to catalyze the cyclization of 1a with PhB(OH)\textsubscript{2} to afford 2a (Scheme 2, eqn (3)), implying that the Ni(i) species was likely involved in the catalytic process. Recently, a Ni(i) species was proposed to be relevant in Ni-catalyzed cross-coupling reactions.\textsuperscript{6} Our results demonstrate that Ni(i) may also be involved in the Ni-catalyzed addition reactions of organoboron reagents to alkynes. In addition, the reaction of allene 4 with PhB(OH)\textsubscript{2} under Ni-catalyzed conditions afforded indeno[1,2-b]quinoline 5 via base-promoted cyano-Schmittel cyclization,\textsuperscript{7} while the desired 2a was not observed (Scheme 2, eqn (4)), indicating that the reaction does not involve the allene intermediate.

The origin of the regioselectivity in this reaction is not clear yet; it is possibly controlled by electronic factors in π–complex 12 (see Scheme 3).\textsuperscript{11} To understand the role of the OTBS group, alkylene-nitrile 6 without the OTBS group was synthesized. The Ni-catalyzed reaction of 6 with PhB(OH)\textsubscript{2} afforded only 10\% of the desired naphthylamine 7, along with small amounts of an unidentified byproduct (Scheme 2, eqn (5)). The results indicate that the presence of the 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, eqn (6)). 8 was possibly formed by the Ni-catalyzed oxidative amination of the arylboronic acid with amine 2a.\textsuperscript{12, 13} The results indicate that the reaction was not inhibited by TEMPO, and this suggests that a radical species is not involved in this system.

Based on the above results, we propose the following reaction mechanism (Scheme 3). Initially, transmetalation of the arylboronic acid with the Ni(II) complex, promoted by a base, provides diarylnickel(ii) species 9, together with HOBO, HCsCO\textsubscript{3} and Cs(acac).\textsuperscript{14} 9 undergoes reductive elimination to form a Ni(0) species. The observation of biphenyl\textsuperscript{15} in the catalytic reaction of 1a with PhB(OH)\textsubscript{2} also indicates that Ni(ii) was
reduced in the reaction process. This Ni(0) species compro-
portions with Ni(ii) to afford Ni(i) complex 10, which
undergoes transmetalation with the arylboronic acid to give
arylnickel(i) species 11. Regioselective 1,2-addition of arylnick-
el(i) species 11 to the alkyne moiety in a syn-fashion takes place
to give an alkynelnickel(i) intermediate syn-13. cis-to-trans
isomerization of 13, possibly through a carbene-like zwitter-
tonic resonance species yields alkynelnickel(i) intermediate
anti-13 with a metal trans-to the Ar substituent. It was noted that
most of the metal-catalyzed reactions of organoborons to
alkynes gave the syn-addition product while few reactions
produced the anti-addition product. The regio- and stereo-
chemistry for the addition process here are consistent with
those observed for the cobalt(n)-catalyzed hydroylation of
propargyl-alcohols or -carbamates with arylboronic acids. The
cyano group may play a role in facilitating the cis-trans iso-
erization by stabilizing the metal species and directing the
subsequent addition reaction. Nucleophilic attack of the alke-
nymetal in anti-13 to the cyano group forms a cyclized inter-
mediate 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 regio-
selective 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
wide 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 alkylnickel to the tethered cyano group. Mechanistic
studies reveal that a 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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13 The reaction of amine 2a with phenylboronic acid under the reaction conditions shown in Scheme 2, eqn (6) gave 8 in 43% yield.


15 Without ligand, only biphenyl was observed. With 10 mol% of P(p-CF₂C₆H₄)₃ as the ligand, in addition to biphenyl, 4,4′-bis(trifluoromethyl)biphenyl and 4-(trifluoromethyl)biphenyl were also observed, possibly due to aryl transfer from the phosphine ligand. See: I. Colon and D. R. Kelsey, *J. Org. Chem.*, 1986, 51, 2627–2637.

