Suzuki–Miyaura Coupling

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Synthesis of Biaryls through Nickel-Catalyzed Suzuki–Miyaura Coupling of Amides by Carbon–Nitrogen Bond Cleavage

*Shicheng Shi, Guangrong Meng, and Michal Szostak**

Abstract: *The first Ni-catalyzed Suzuki–Miyaura coupling of amides for the synthesis of widely occurring biaryl compounds through N–C amide bond activation is reported. The reaction tolerates a wide range of electron-withdrawing, electron-neutral, and electron-donating substituents on both coupling partners. The reaction constitutes the first example of the Ni-catalyzed generation of aryl electrophiles from bench-stable amides with potential applications for a broad range of organometallic reactions.*

The Suzuki–Miyaura biaryl coupling reaction has emerged as one of the most powerful carbon–carbon bond-forming reactions for arene functionalization.[1,2] Although cross-coupling of aryl halides, triflates, and tosylates has been successfully achieved with Pd catalysts,[3] in recent years tremendous advances have been made in the use of new C–O and C–N electrophiles (leaving group (LG) = O, N) as attractive coupling partners using sustainable and more economically viable Ni catalysts.[4] In this context, notable progress has been reported in the cross-coupling of aryl ethers,[5a–c] acetates,[5d] pivalates,[5d,e] carbamates,[5f–h] sulfamates,[5f,g] and ammonium salts.[5i] Elegant examples of using aroyl electrophiles in the Suzuki–Miyaura reaction under redox neutral conditions, including anhydrides[6] and esters,[7] with Rh and Ni catalysts have been developed. Furthermore, oxidative cross-coupling of carboxylic acids with boronic acids using Pd has been reported;[8a,b] however, this process suffers from limited substrate scope and expensive oxidants. Furthermore, carboxylic acids have been employed for direct decarboxylative cross-coupling with aryl halides and olefins by the groups of Gooßen[8c] and Myers.[8d] Despite these notable advances, the Suzuki–Miyaura biaryl coupling of significantly more challenging amides (barrier to N-C resonance of 15–20 kcal mol^{-1}; Figure 1),[9a] after direct oxidative addition into an N–C bond, has yet to be reported, a notable deficiency given the pivotal role of amides as key building blocks in peptides and versatile bench-stable intermediates in organic synthesis.[9b]

Biaryls are key structural motifs in numerous bioactive medicinal agents, natural products, and polymers.[10] The development of biaryl syntheses through cross-coupling of readily accessible, bench-stable amide precursors would

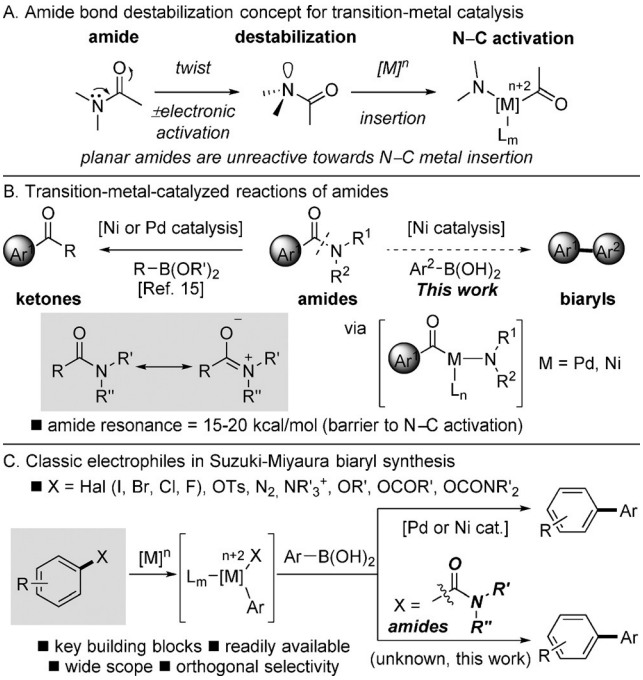

Figure 1. A) Amide bond activation concept for transition-metal catalysis. B) Metal-catalyzed activation of amides. C) Classic electrophiles in Suzuki–Miyaura reactions.

significantly extend the pool of electrophiles available for the cross-coupling, given that: a) amides are traditionally derived from different precursors than halides, phenols, and anilines;[11] b) amides are easy to prepare;[12] and c) amides are typically inert to a variety of reaction conditions allowing for ring prefunctionalization.[12] However, the challenge in using amides as arylation precursors is the low reactivity of the N–C bond for direct oxidative addition and control of the deca13]

Herein, we report the first Suzuki–Miyaura biaryl coupling reaction of amides by N–C cleavage. This new Suzuki–Miyaura cross-coupling variant can be accomplished in high yields with a broad range of amide and boronic acid substrates. The reaction employs air-stable, inexpensive Ni catalysts, which are economically advantageous over Pd. The reaction proceeds with full selectivity for Ni insertion into the N–C amide bond, representing a general method for the synthesis of aryl electrophiles from amides under Ni catalysis. In light of the importance of amides and the advantages offered by nickel catalysis, we expect that this concept will provide a modular strategy for the application of ubiquitous amides as unconventional electrophiles in aryl cross-coupling manifolds.

[*] S. Shi, G. Meng, Prof. Dr. M. Szostak
Department of Chemistry, Rutgers University
73 Warren Street, Newark, NJ 07102 (USA)
E-mail: michal.szostak@rutgers.edu

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In 2015, our laboratory introduced a new mode of activation of amide bonds in transition-metal catalysis by geometric distortion[14] (Figure 1 A). We have established that twisted amides serve as robust and versatile precursors in elusive transformations of amide bonds for C–C bond construction by N–C activation under Pd catalysis.[15a,b] Independently, Garg et al.[15c] and Zou and Li[15d] reported the use of twisted imides[14] for the synthesis of ketones under Ni[15c,d] and Pd[15d] catalysis. Central to this strategy is ligand coordination to nitrogen to disrupt $n_N \rightarrow \pi^*_{CO}$ conjugation and facilitate oxidative addition.[16] Ground-state distortion and electronic activation contribute to the observed reactivity. In all cases, amides are readily available from carboxylic acid precursors by standard methods.[12] From a synthetic standpoint, the ability to promote previously elusive transformations of amides through generic metal-catalyzed activation modes with high functional group compatibility represents a significant advance for implementing neutral, bench-stable, readily accessible amides as precursors in cross-coupling reactions.[17]

Under appropriate conditions, the acylmetal intermediate resulting from metal insertion into the inert amide N–C bond might undergo transmetallation/decarbonylation, generating an organometal electrophile. Ni catalysts have been successfully utilized in Suzuki–Miyaura reactions of unconventional electrophiles (LG = O, N).[4,5] Seminal studies by Yamamoto on C(O)–Ni–O decarbonylation[18a] and more recent progress in related cross-couplings provide precedent that decarbonylation of acylnickel complexes could proceed with high selectivity.[18b,c] However, at the outset it was unclear whether such a pathway using significantly more challenging amides would be feasible given the inert nature of amide N–C bonds,[12] the reversibility of insertion/decarbonylation,[18] and the lack of precedent for aryl–aryl bond formation through amide bond cleavage.[13]

We began our investigations by evaluating the coupling of amides (**1**) with 2-naphthyl boronic acid (**2**) as a standard nucleophile (Figure 2). We focused on the challenging neutral, aryl amide electrophiles with the aim of developing a generally applicable method with a wide substrate scope. Ni-catalyzed coupling of unconventional electrophiles is facilitated using conjugated aromatics, limiting the preparative scope of the chemistry.[5b,c] Although biaryl products were not detected using Pd catalysts, we were delighted to find, after very extensive optimization, that the proposed Suzuki–Miyaura coupling of amides was indeed feasible using the sterically distorted amide (**1d**) and a Ni^0/PCy_3 catalyst system. Using the less distorted anilides such as (**1a–1c**),[14] only a trace quantity of the cross-coupled product was formed, consistent with metal insertion into the neutral amide N–C bond.[13] The use of a significantly less distorted amide (**1e**)[14] resulted in a promising yield of the biaryl product, demonstrating the high activity of the catalyst system. In all cases examined, negligible formation of ketone products was detected in crude reaction mixtures, consistent with the high capability of the Ni catalyst to facilitate decarbonylation.[18] The insertion occurred selectively at the N–C bond, with cleavage of the alternative σ N–C bond not observed.[17]

Key optimization results are shown in Table 1. A $Ni(cod)_2$ precatalyst with the addition of bulky, electron-rich phosphane ligands gave low yields of the biaryl product.[5–7] Bidentate phosphanes resulted in markedly poor coupling.[18c] $Ni(PPh_3)_2Cl_2$ as the precatalyst gave lower yields than $Ni(PCy_3)_2Cl_2$, consistent with the ease of oxidative addition. Additional ligands resulted in inferior results, which may

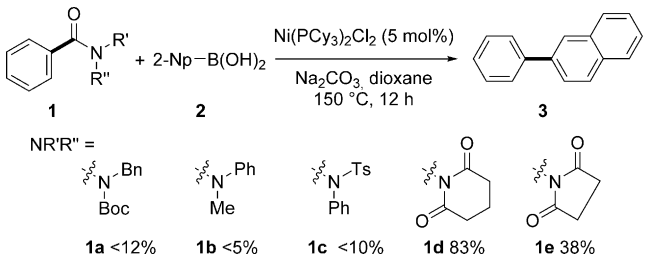
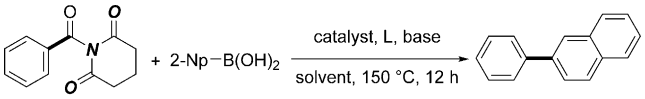


Figure 2. Nickel-catalyzed Suzuki biaryl synthesis of amides: the effect of different N substituents. Conditions: **1** (1.0 equiv), 2-Np-$B(OH)_2$ (1.5 equiv), $Ni(PCy_3)_2Cl_2$ (5 mol%), Na_2CO_3 (4.5 equiv), dioxane (0.25 M), 150 °C. See the Supporting Information for details. Np = naphthyl.

Table 1: Optimization of Ni-catalyzed Suzuki biaryl synthesis through coupling of amides with boronic acids.[a]



Entry	Catalyst	L	Base	Yield[b] [%]
1	$Ni(cod)_2$	PCy_3	Na_2CO_3	11
2	$Ni(cod)_2$	*n*-Bu_3P	Na_2CO_3	22
3	$Ni(cod)_2$	P*t*-Bu_3	Na_2CO_3	28
4	$Ni(cod)_2$	dppf	Na_2CO_3	18
5	$Ni(cod)_2$	dppe	Na_2CO_3	< 2
6	$Ni(cod)_2$	dppp	Na_2CO_3	24
7	$Ni(cod)_2$	dppb	Na_2CO_3	16
8	$Ni(cod)_2$	IMes	Na_2CO_3	< 2
9	$Ni(cod)_2$	SPhos	Na_2CO_3	14
10	$Ni(cod)_2$	PPh_3	Na_2CO_3	20
11	$Ni(OAc)_2$	*n*-Bu_3P	Na_2CO_3	20
12	$Ni(PCy_3)_2Cl_2$	*n*-Bu_3P	Na_2CO_3	29
13	$Ni(PCy_3)_2Cl_2$	PCy_3	Na_2CO_3	40
14	$Ni(PCy_3)_2Cl_2$	-	Na_2CO_3	42
15[d]	$Ni(PCy_3)_2Cl_2$	-	Na_2CO_3	68
16[d]	$Ni(PPh_3)_2Cl_2$	-	Na_2CO_3	59
17[d]	$Ni(dppf)_2Cl_2$	-	Na_2CO_3	21
18[d,e]	$Ni(PCy_3)_2Cl_2$	-	Na_2CO_3	76
19[d–f]	$Ni(PCy_3)_2Cl_2$	-	Na_2CO_3	83[c]
20[d–f]	$Ni(PCy_3)_2Cl_2$	-	K_3PO_4	< 5
21[d–g]	$Ni(PCy_3)_2Cl_2$	-	Na_2CO_3	77

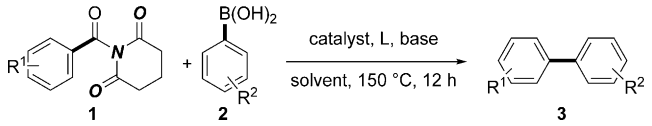
See the Supporting Information for full experimental details. [a] Amide (0.1 mmol), R-$B(OH)_2$ (1.5 equiv), catalyst (10 mol%), base (2.0 equiv), ligand (40 mol%), toluene (0.25 M), 150 °C, 12 h. [b] GC/^{1}H NMR yields. [c] Yield of isolated product. [d] Dioxane. [e] $Ni(PCy_3)_2Cl_2$ (5 mol%). [f] Na_2CO_3 (4.5 equiv). [g] H_2O (5 equiv). cod = 1,5-cyclooctadiene; dppf = 1,1′-bis(diphenylphosphanyl)ferrocene; dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane; dppb = 1,4-bis(diphenylphosphino)butane; IMes = 1,3-di(2,4,6-trimethylphenyl)imidazolin-2-ylidene; SPhos = 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl.

indicate saturation of the coordination sphere of the Ni catalyst. Previous studies suggested that a single phosphane ligand might be required to facilitate metal insertion into a C–X bond (X = N, O).[7b,15a] π-Deficient ligands had a negative impact on the reaction (see the Supporting Information).[19] Nucleophilic additives had a deleterious effect on the reaction, rendering a nucleophilic catalysis mechanism unlikely (see the Supporting Information). Importantly, efficient coupling is observed with only 5 mol% of Ni catalyst, which compares favorably with the related C–X biaryl couplings (X = O, N).[5a–i] The reaction is highly practical and tolerates water, in contrast to C–O couplings, in which boronic acid/ester equilibria complicate the reaction.[5d–h] Finally, we note that the reaction can proceed at temperatures as low as 80 °C.

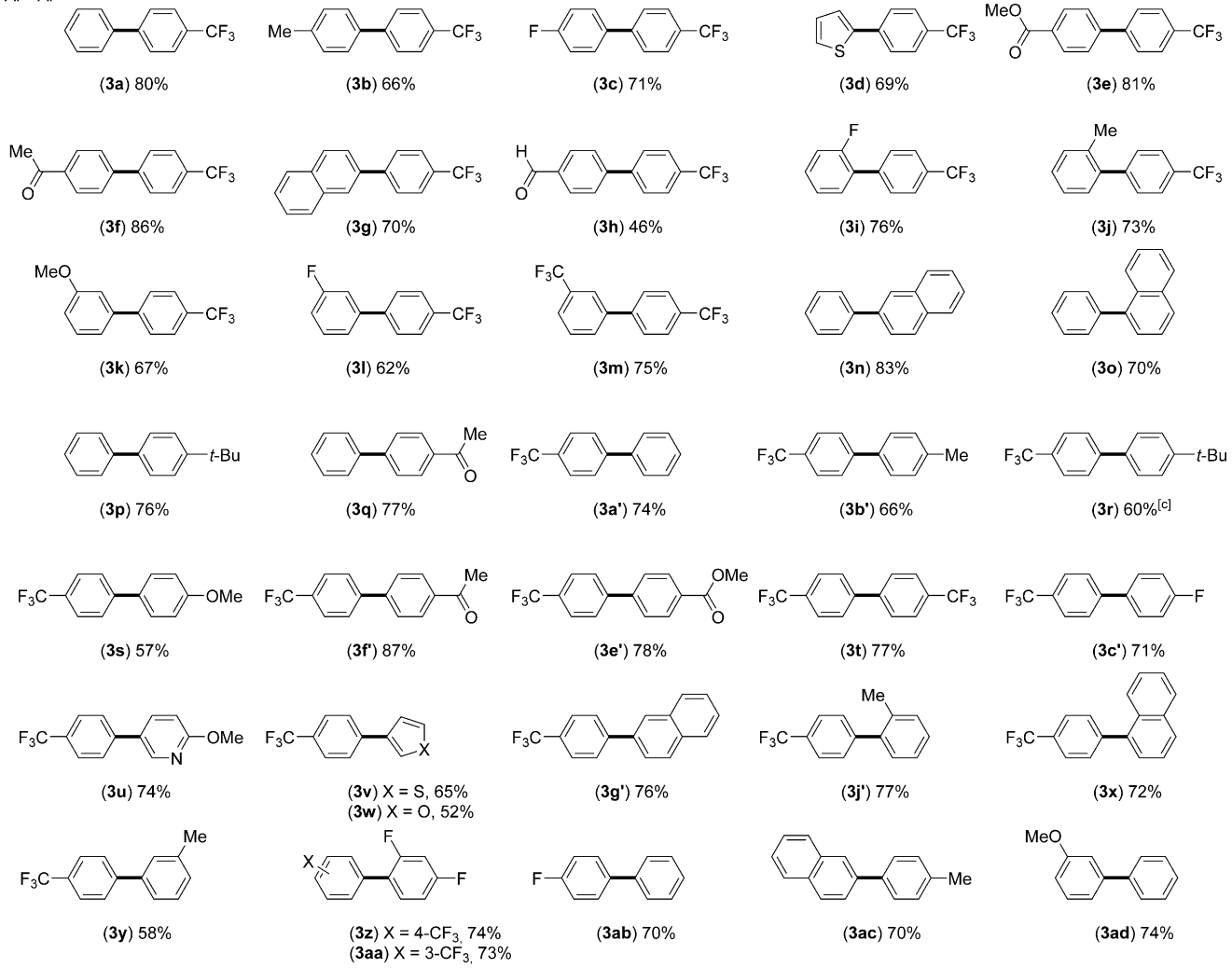
Overall, the optimized process is highly efficient and operationally simple; the reaction employs an air-stable $Ni(PCy_3)_2Cl_2$ complex, does not require the presence of additional ligands or hygroscopic additives, and utilizes commercially available boronic acids. This transformation represents the first Suzuki–Miyaura biaryl coupling of amides.

With the optimized conditions in hand, we explored the preparative scope of the biaryl coupling of amides (Table 2). As shown, the scope of the reaction is very broad and tolerates the coupling of electron-neutral, electron-withdrawing, and electron-rich substrates. The generality of the amide component was investigated using 4-trifluoromethylphenyl boronic acid to facilitate product isolation (yielding products **3a**–**3m**).[5h] The generality was further demonstrated in additional examples employing electronically varied sub-

Table 2: Nickel-catalyzed Suzuki biaryl synthesis through cross-coupling of amides with boronic acids.[a,b]



Ar1–Ar2

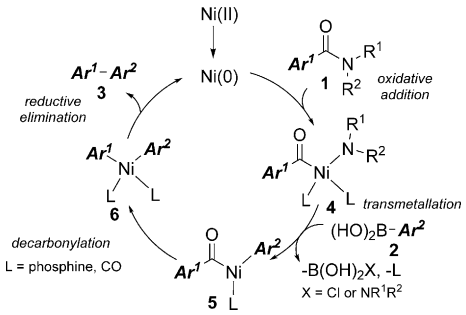


[a] Amide (1.0 equiv), R-$B(OH)_2$ (1.5 equiv), base (4.5 equiv), $Ni(PCy_3)_2Cl_2$ (5 mol%), dioxane (0.25 M), 150 °C. [b] Yield of isolated product. [c] Gram scale. See the Supporting Information for details.

strates (yielding **3n**–**3q**). Electron-deficient nucleophiles are generally less reactive in transmetallation.[1–5] Fluorine-containing biaryls are of great value in medicinal and materials chemistry.[21] Importantly, the coupling proceeds in high yields in the presence of carbonyl derivatives, such as esters and ketones (products **3e**, **3f**). Remarkably, the reaction tolerates even an unprotected aldehyde (product **3h**), albeit in lower yield. Aldehydes are not tolerated in related C–O couplings,[5] clearly showing the advantage of amide electrophiles in coupling manifolds. Ketone-containing substrates are yet to be reported in C–O ester couplings.[7] Sterically hindered substrates showed good reactivity (yielding products **3i** and **3j**). The scope of the boronic acid component was investigated using 4-trifluoromethylphenyl amide as a standard substrate (to form products **3o**–**3z**). The generality was additionally demonstrated through the coupling of electronically varied substrates with neutral boronic acids (yielding products **3ab**–**3ad**). The coupling with 4-trifluoromethyl boronic acid affords the symmetrical biaryl compound **3t**. In the absence of amide, less than 9% of the biaryl is formed. The reaction with 4-*tert*-butylboronic acid (forming compound **3r**) demonstrates a gram-scale coupling. Medicinally relevant heterocycles, including sensitive pyridine, thiophene, and furan rings, are well-tolerated (**3u**–**3w**). Notably, the reaction tolerates strongly electron-withdrawing substrates (forming products **3z** and **3aa**),[20] complementing C–O coupling manifolds.[5] Overall, the Suzuki–Miyaura biaryl coupling of amides demonstrates a broad reaction scope. Selected examples highlight complementarity to C–O coupling reactions.[5] At present, the major limitation is the presence of C–Cl bonds and the coupling of electron-donating amides with electron-donating boronic acids; however, the former are also not tolerated in C–O coupling reactions,[5] while the latter is the only combination that results in low efficiency.

Studies were conducted to shed light on the mechanism (see the Supporting Information). a) Intermolecular competition experiments revealed that the electronic nature of the boronic acid does not affect the reactivity, while electron-poor arenes are more reactive, consistent with facility of metal insertion.[21] b) Sterically hindered amides and boronic acids react preferentially. It is well-established that decarbonylation is favored as a result of the steric demand of acylmetal complexes.[18] c) Stoichiometric ESI-MS measurements with amide **1d** indicated the presence of Ni–aryl intermediates, as well as $ArCONiCO_3^{2-}$ cluster complexes,[7a] consistent with amide activation by Ni^0 and the key role of the carbonate base. A possible mechanism is shown in Scheme 1. Alternatively, a mechanism involving the formation of an Ar-Ni-$CONR_2$ intermediate by direct oxidative addition to the aryl–acyl bond might be operative. Further studies to elucidate the mechanism are ongoing.

In conclusion, we have developed the first biaryl Suzuki–Miyaura coupling of amides by N–C bond activation. The reaction is characterized by a broad substrate scope with regard to both the amide and boronic acid components, employs a cost-effective, air-stable $Ni(PCy_3)_2Cl_2$ precatalyst, and shows high tolerance towards water. This process complements the traditional cross-coupling methods, highlighting the power of transition-metal-catalyzed activation of bonds traditionally considered to be inert.



Scheme 1. Proposed mechanism.

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Keywords: amide bonds · biaryls · cross-coupling · N–C activation · nickel

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