

Chemoselective Borono-Catellani Arylation for Unsymmetrical Biaryls Synthesis

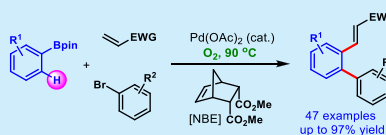
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Supporting Information

ABSTRACT: Reported is the borono-Catellani arylation process for unsymmetrical biaryls synthesis, utilizing the readily available pinacol ester of arylboronic acids, aryl bromides, and olefins as the reactants. The distinct reactivity of arylboronic ester and aryl bromides secures the excellent chemoselectivity in the pivotal arylation step. The reaction is enabled by the cooperative catalysis of Pd(OAc)₂ and the NBE derivative N⁷, with molecular oxygen as the terminal oxidant.



- Widely accessible starting materials
- Scalable, and chemo-selective
- Pd^{II} initiated mechanism
- Oxygen as the oxidant
- Novel mediator

47 examples up to 97% yield

Biaryl motifs are ubiquitous in bioactive natural products, pharmaceuticals, chiral ligands, and materials.¹ Consequently, extensive efforts have been devoted to the development of efficient methods for biaryls assembly. The Catellani reaction is known as a powerful strategy for the expeditious synthesis of highly substituted arenes. Catellani-type arylation involving two different aryl halides as the substrates for biaryls preparation seems an attractive method. However, this strategy has been impeded due to the innate poor chemoselectivity.^{2,3b} As illustrated in Figure 1A, four theoretically possible biaryls can be formed when two different aryl halides are utilized. Nevertheless, Catellani and co-workers have discovered an

elegant solution to this issue by selecting aryl iodides with an *ortho* electron-donating substituent and aryl bromide with an electron-withdrawing or *ortho*-coordinating group as the reaction partners (Figure 1B).³ The subtle reactivity differences of aryl iodides and bromides toward Pd⁰ catalyst to Pd^{II} complexes in the first oxidative addition and in the subsequent reaction with palladacycle species (ANP) to Pd^{IV} complexes, respectively, accounts for the satisfactory selectivity observed.⁴ However, the substrate scope is rather limited. Thus, more general and efficient Catellani-type strategies for biaryls preparation are highly desirable.

Recently, the group of Yu and others have developed the elegant *meta*-C–H arylation strategy for unsymmetrical biaryl synthesis via Pd^{II}/NBE cooperative catalysis.⁵ Later, the group of Zhang and us independently reported the Pd^{II}/NBE catalyzed borono-Catellani reaction to achieve the *ortho*-C–H alkylation of arylboronic acids and esters.^{6,7} Inspired by this chemistry, we envisaged that the aforementioned poor chemoselectivity issue in Pd⁰/NBE catalyzed unsymmetrical arylation might be solved through the distinct Pd^{II}/NBE catalyzed “borono-Catellani arylation reaction”, with readily available arylboronic acids or derivatives, aryl bromides, and olefins as the reactants. As shown in Figure 1C, it is surmised that the reaction would be triggered by a palladium(II) catalyst, which selectively reacts with aryl boronic acid derivative 1 to provide aryl palladium(II) intermediate I through transmetalation. The following insertion of NBE to I and subsequent *ortho*-C–H activation generates the aryl/NBE palladacycle complex II. The oxidative addition of aryl bromide 2 to II gives palladium(IV) complex III, which then undergoes reductive elimination and successive release of NBE to afford palladium(II) species IV. The capture of IV by olefin 3 provides the desired product 4 and the palladium(0) species, which is then recycled through oxidation. Mechanistically, owing to the distinct reactivity of aryl boronic acid derivatives and aryl

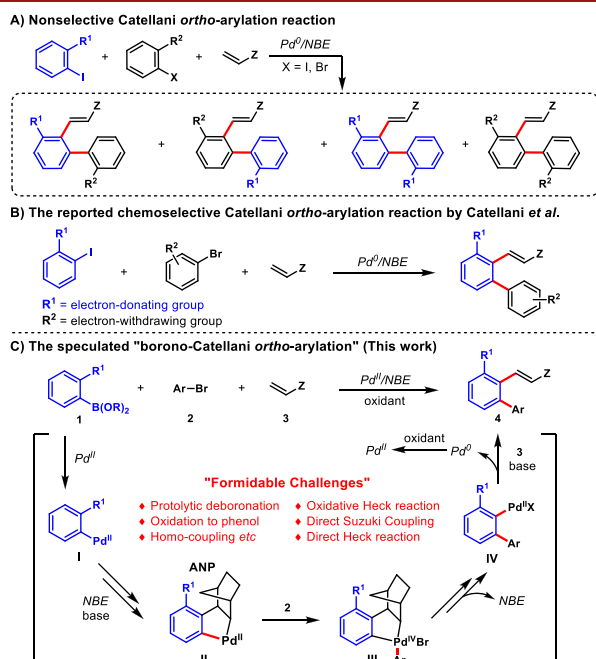


Figure 1. Unsymmetrical aryl coupling via the Catellani strategy.

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bromides toward transmetalation and oxidative addition of ANP **II** to **III**, respectively, this intriguing process will perfectly solve the selectivity issue. Nevertheless, the requirement of a stoichiometric oxidant to regenerate the palladium(II) catalyst will bring along multiple challenges. First, the oxidant may not be compatible with aryl boronic acid derivative **1**, which will cause multiple side reactions, for example, homocoupling,⁸ oxidation to phenols,⁹ and protolytic deboronation.⁹ Second, the oxidative Heck reaction between **1** and **3** will also become a highly competitive pathway,¹⁰ as well as potential Suzuki coupling between **1** and **2**, and Heck reaction between **2** and **3**.

To address the aforementioned challenges and realize this intriguing process, our efforts started with a model reaction involving pinacol ester of *o*-tolylboronic acid (**1a**, 3.0 equiv), methyl 2-bromobenzoate (**2a**, 1.2 equiv), and *tert*-butyl acrylate (**3a**, 1.0 equiv) as the reactants (Table 1). Initially, Pd(OAc)₂ was

Table 1. Optimization of Reaction Conditions^a

entry	[NBE]	x	y	yield [%] ^b
1	N ¹	1.2	1.0	34
2	N ²	1.2	1.0	19
3	N ³	1.2	1.0	22
4	N ⁴	1.2	1.0	56
5	N ⁵	1.2	1.0	49
6	N ⁶	1.2	1.0	46
7	N ⁷	1.2	1.0	58
8 ^c	N ⁷	1.0	1.2	75
9 ^d	N ⁷	1.0	1.2	90 (85) ^e

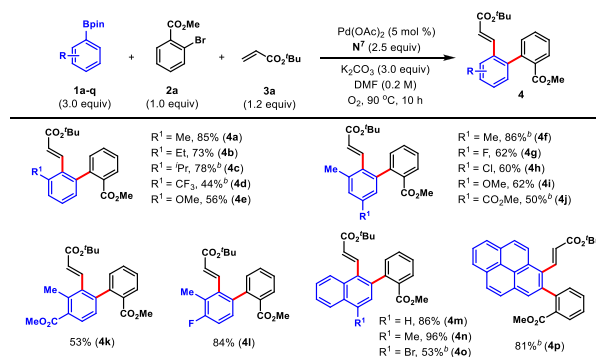
^aThe reaction was performed on a 0.1 mmol scale. ^bGC yield with biphenyl as an internal standard. ^c2.5 equiv of N⁷ was applied. ^d5 mol % Pd(OAc)₂, 3.0 equiv of K₂CO₃, 90 °C reaction temperature, and 0.2 M concentration were applied. ^eIsolated yield in parentheses. Tol: tolyl.

selected as the catalyst (10 mol %), NBE as the mediator (2.0 equiv), K₂CO₃ as the base (4.0 equiv), DMF as the solvent (0.1 M), and oxygen gas as the oxidant. Gratifyingly, when the reaction was run at 100 °C for 10 h, the desired product **4a** was generated in 34% yield (entry 1). Subsequent studies focused on finding the optimal mediator. An array of readily available NBE derivatives were screened (entries 2–7), including the Yu mediator (N²),¹² the Dong mediator (N³),¹³ the methyl ester of 5-norbornene-2-carboxylic acid (N⁴),^{14a,b} and inexpensive 5-norbornene-2-carboxitrile (N⁵).^{6b} The yield of **4a** dropped significantly, while N² or N³ was employed as the mediator (entries 2–3). In contrast, N⁴, N⁵, and (N⁶)^{14c} provided remarkably increased yields (entries 4–6). Nevertheless, (N⁷)^{12,14d} was among the best, delivering **4a** in the highest yield (58%) (entry 7). Considering the major isolated side product was originated from the oxidative Heck reaction between **1a** and **3a**, we thus changed the loading of **2a** to 1.0 equiv and **3a** to 1.2 equiv, respectively. Accordingly, the subsequent reaction yields were calculated based on **2a**. Further increasing the loading of N⁷ to 250 mol % led to a substantially improved yield (75%, entry 8). Additional optimization regarding base, oxidant, solvent, and the palladium catalyst did

not provide obvious improvement in the efficiency (see the Supporting Information for details). Nevertheless, a lower loading of catalyst and base and a higher concentration were determined to be beneficial. Thus, the optimal conditions utilized 5 mol % of Pd(OAc)₂, 3.0 equiv of K₂CO₃, and 0.2 M concentration, which delivered **4a** in 85% isolated yield (entry 9).

Scheme 1 outlines the application of the optimized conditions to probe the scope of arylboronic esters, with **2a** and **3a** as the

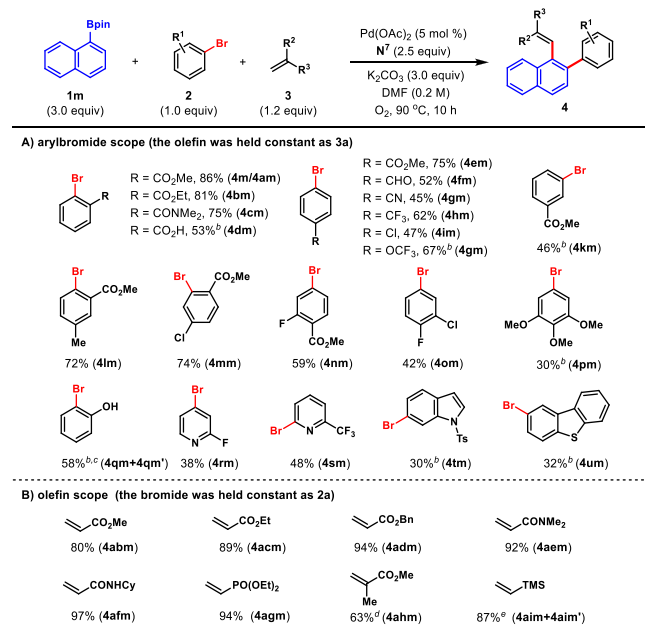
Scheme 1. Substrate Scope of Arylboronic Esters^a



^aUnless otherwise stated, all reactions were performed on a 0.1 mmol scale. Isolated yields are reported. ^bThe reaction was performed with 4.0 equiv of **1** and heated at 100 °C.

reaction partners. To our delight, arylboronic esters containing electron-donating (**1a–1c**, **1e–1i**, and **1l**) and electron-withdrawing groups (**1d**, **1j–1k**) all proved to be suitable substrates, providing the desired products (**4a–4l**) in moderate to excellent yields (44–86%). The process also exhibited good chemoselectivity: various functional groups were tolerated, including fluoro (**1g** and **1l**), chloro (**1h**), bromo (**1o**), methoxy (**1e** and **1i**), and ester (**1j** and **1k**) groups. Especially, the tolerance of bromo function in **1o** is very intriguing, indicating the reactivity difference between the two aryl bromides **2a** and **1o** is significant. When bicyclic arylboronic esters **1m–1o** and polycyclic arylboronic ester **1p** were used, the unsymmetrical aryl coupling products **4m–4p** were obtained in good to excellent yields (53–96%).

Then, the reaction scope with respect to the aryl bromide **2** was examined. As illustrated in Scheme 2A, aryl bromides bearing *ortho*-, *meta*-, or *para*-substitutions were demonstrated as suitable substrates (**2a–2q**), providing the desired products in moderate to excellent yields (30–86%). Notably, aryl bromides with an electron-withdrawing substitution (**2a–2h**, **2k–2n**) gave relatively higher yields than those with an electron-donating substitution (**2i**, **2j**, **2o–2q**). Polysubstituted aryl bromides (**2l–2p**) were also viable substrates under current reaction conditions. Among the aryl bromides tolerated were those featuring halogens (**2i**, **2m–2o**) and reactive groups (carboxylic acid in **2d**, aldehyde in **2f**, cyano in **2g**, and hydroxy in **2q**) that can serve as useful synthetic handles for subsequent chemical manipulations. Similar to previous discoveries, 2-bromophenol **2q** was also a proper substrate for this chemistry,^{4a,h,15} and two major products were obtained.¹⁶ One was a dibenzopyran derivative **4qm**, generated by a following intramolecular oxa-Michael addition (30% yield),^{4h,15} and the other was **4qm'**, afforded through *ortho* arylation/*ipso* protonation (28% yield).¹⁶ Importantly, the challenging heteroaryl bromides also proved viable in this protocol (**2r–2u**). Pyridine, indole, and dibenzothiophene

Scheme 2. Substrate Scope of Aryl Bromides and Olefins^a

^aUnless otherwise stated, all reactions were performed on a 0.1 mmol scale. Reported yield are for the isolated product. ^bThe reaction was performed with 4 equiv of **1l** and heated at 100 °C. ^cTwo products were obtained including oxa-Michael addition product (30% yield) and *ortho* arylation/*ipso* protonation product (28% yield). ^dFor the Heck termination, the β -H elimination took place specifically at the methyl group. ^eIncluding 20% yield of desilylation product. TMS: trimethylsilyl.

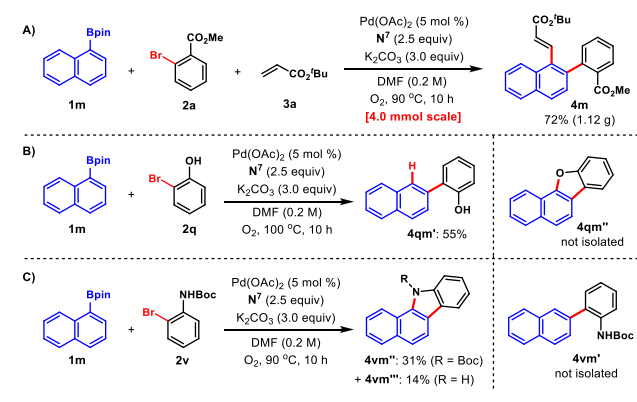
derived bromides were suitable substrates, providing the corresponding arylated products in moderate yields.

Next, the reaction scope with respect to the olefins was investigated. As shown in Scheme 2B, various *mono*-substituted olefins with an electron-withdrawing group are competent substrates (3a–g), including acrylates (3a–d), amide of acrylic acid (3e–f), and diethyl vinylphosphonate (3g), providing the desired products in good to excellent yields (80–97%). As expected, the 1,1-disubstituted olefin methyl methacrylate (3h) exhibited lower reactivity during this process, delivering the product in 63% yield, whereby the olefin was formed through final β -H elimination at the methyl group dominantly. Interestingly, the reaction of electron-rich olefin TMS-substituted ethylene (3i) also proceeded smoothly to afford the corresponding product in good yield, and desilylation of product was observed concurrently.

The practicality of this cascade process are evident from the scale-up experiment (4.0 mmol of **2a**) depicted in Scheme 3A, wherein application of the standard reaction conditions afforded the product **4m** in a good yield (1.12 g, 72%).

Following the success of this three-component cascade reaction, we did some preliminary study on the two-component reactions between arylboronic ester **1** and aryl bromide **2**, as inspired by the interesting results obtained from 2-bromophenol **2q** in Scheme 2. We found that under the same conditions, **1m** reacted with **2q** smoothly to afford **4qm'** in a good yield (55%, Scheme 3B), while no cyclized product (**4qm''**) was detected, indicating the termination through intramolecular aryl ether formation is a thermodynamically unfavored process.¹⁷ In contrast, the coupling of **1m** with bromide **2v** affords mainly the cyclized product in 44% overall yield, including **4vm''** and

Scheme 3. Scale-up Experiment and Follow-up Chemistry



some Boc-deprotected product **4vm'''**, while the product generated from *ipso*-protonation (**4vm'**) was not isolated (Scheme 3C).^{4c,18} These results demonstrated the intricate effects of the *ortho*-substitution of aryl bromides on the products formation and distribution, including the acidity, nucleophilicity, and steric hindrance. Efforts toward more generalized and efficient catalytic systems for the two-component reaction between arylboronic ester **1** and aryl bromide **2** are underway.

In summary, we have developed the first intriguing borono-Catellani arylation strategy for unsymmetrical biaryls synthesis, utilizing the readily available pinacol ester of arylboronic acids, aryl bromides and olefins as the reactants. The distinct reactivity of arylboronic ester and aryl bromides enabled the excellent selectivity in the pivotal arylation step. The reaction was promoted by the cooperative catalysis of Pd(OAc)₂ and the readily available NBE derivative **N7**, with molecular oxygen as the terminal oxidant. This mild, scalable, and chemoselective protocol is compatible with a wide variety of functionalized arylboronic esters and aryl bromides, as well as terminating olefins. Moreover, the chemistry can be extended to the two-component reaction between arylboronic esters and aryl bromides. Preliminary studies revealed the termination could be tuned by the *ortho*-coordinating group of aryl bromides. We believe this work will shed light on the future development of Catellani reaction.

■ ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b01072.

Experimental procedures, characterization data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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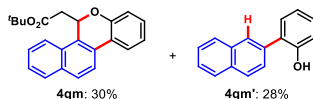
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(16) The two products obtained were **4qm** and **4qm'**. Recently, the Dong group also reported the borono-Catellani reactions terminated by *ipso* protonation, see ref 7.



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(18) For selected examples regarding termination through *N*-aryl coupling, see: (a) Ferraccioli, R.; Carezzi, D.; Rombolà, O.; Catellani, M. Synthesis of 6-Phenanthridinones and Their Heterocyclic Analogues through Palladium-Catalyzed Sequential Aryl–Aryl and *N*-Aryl Coupling. *Org. Lett.* **2004**, *6*, 4759–4762. (b) Della Ca', N.; Sassi, G.; Catellani, M. A Direct Palladium-Catalyzed Route to Selectively Substituted Carbazoles through Sequential C–C and C–N Bond Formation: Synthesis of Carbazomycin A. *Adv. Synth. Catal.* **2008**, *350*, 2179–2182. (c) Candito, D. A.; Lautens, M. Palladium-Catalyzed Domino Direct Arylation/*N*-Arylation: Convenient Synthesis of Phenanthridines. *Angew. Chem., Int. Ed.* **2009**, *48*, 6713–6716. (d) Maestri, G.; Larraufie, M.-H.; Derat, É.; Ollivier, C.; Fensterbank, L.; Lacôte, E.; Malacria, M. Expeditious Synthesis of Phenanthridines from Benzylamines via Dual Palladium Catalysis. *Org. Lett.* **2010**, *12*, 5692–5695. (e) Yamamoto, Y.; Murayama, T.; Jiang, J.; Yasui, T.; Shibuya, M. The Vinylogous Catellani Reaction: A Combined Computational and Experimental Study. *Chem. Sci.* **2018**, *9*, 1191–1199.