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One-pot borylation/Suzuki-Miyaura sp^2–sp^3 cross-coupling

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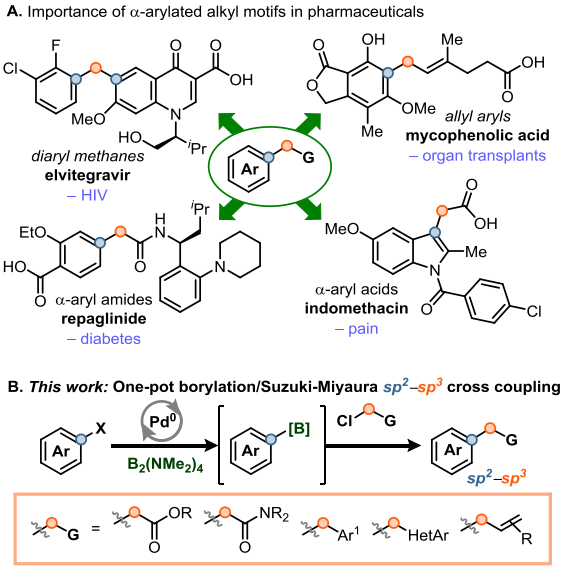
We describe the first one-pot borylation/Suzuki-Miyaura sp^2–sp^3 cross-coupling between readily available aryl (pseudo)halides and activated alkyl chlorides. This method streamlines the synthesis of diaryl methanes, α-aryl carbonyls and allyl aryl compounds, substructures that are commonly found in life changing drug molecules.

The Suzuki-Miyaura (SM) cross-coupling[1] is a powerful method for the construction of organic molecules[2] and as a result has become a staple carbon-carbon bond forming reaction in chemical synthesis, particularly in pharmaceutical discovery.[3] The classic SM reaction is the palladium catalysed union of an aryl boron and an aryl halide (or pseudo-halide) to form biaryl compounds,[2] and still receives significant attention from the scientific community.[4] However, there remains a number of drawbacks associated with the preparation of the required boron based coupling partner. Isolation and storage of the more reactive organoborane building blocks is often non trivial and the addition of an extra discrete synthetic step reduces overall process efficiency.[5, 6]

The Miyaura borylation,[7-11] where aryl boronic esters are formed from aryl (pseudo)halides and diboranes under palladium catalysis,[12,13] has opened the door for the development of efficient processes where isolation of the aryl boron coupling partner is avoided. Miyaura,[14] Giroux[15] and others[16] subsequently reported the efficient one-pot borylation/SM sp^2–sp^2 cross-coupling for the stepwise, one-pot synthesis of biaryls from aryl (pseudo)halides, which encompasses impressive scope in both sp^2 coupling partners.

SM coupling processes are not limited to the formation of sp^2–sp^2 carbon bonds.[17] However, the more efficient one-pot borylation/SM cross-coupling strategy has not been previously applied to the union of sp^2 and sp^3 carbon atoms despite the prevalence of such linkages in natural products and bioactive molecules. For example, diaryl methanes, allyl aryls and α-arylated carbonyls are commonly found in major pharmaceutical compounds, such as elvitegravir, mycophenolic acid, repaglinide and indomethacin (Scheme 1A and ESI for additional examples).[18]

Herein we report the first one-pot borylation/SM sp^2–sp^3 cross-coupling for the efficient construction of diaryl methanes, allyl aryls and α-arylated carbonyls (Scheme 1B). We utilise aryl (pseudo)halides and the most economical diborane reagent, tetrakis(dimethylamino)diboron [$B_2(NMe_2)_4$], and propylene glycol in a palladium catalysed borylation event and subsequently couple the in situ generated aryl borons with activated alkyl chlorides, such as benzyl chlorides, α-chloro carbonyls, and allyl chlorides, in a one-pot procedure. This efficient method is operationally simple and is broadly applicable to a range of substrates.



Scheme 1. The prevalence of sp^2–sp^3 linkages in pharmaceuticals (A) and this work describing efficient one-pot borylation/Suzuki-Miyaura sp^2–sp^3 cross-coupling (B).

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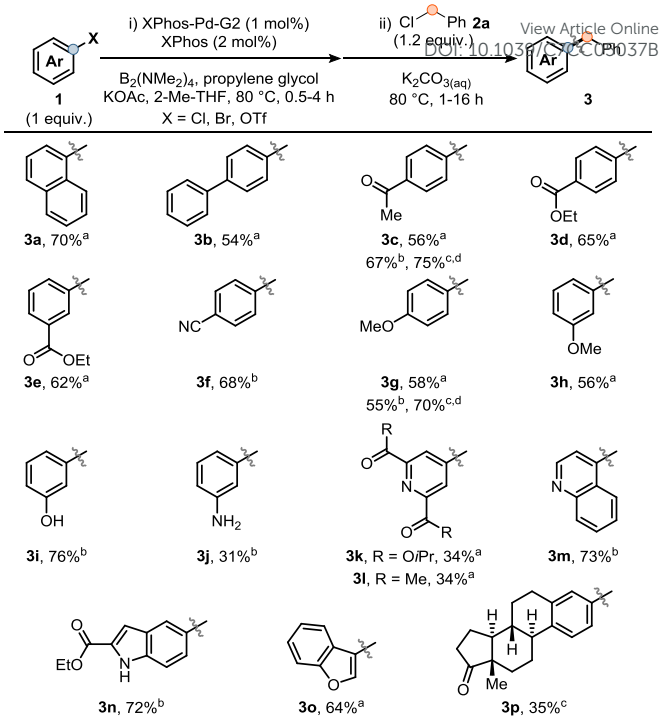
We began our investigation by using the previously reported one-pot borylation/SM sp^2–sp^2 cross-coupling conditions, that use atom efficient borylating agents, to the desired sp^2–sp^3 couplings.[9] We discovered that these conditions were not transferrable to sp^3 coupling partners since poor yields were obtained and significant homocoupling was observed: using 1-bromonaphthylene **1a**, $B_2(OH)_4$, benzyl chloride **2a**, XPhos-Pd-G2 precatalyst,[19] and ethanol as the solvent, diaryl methane **3a** was obtained in only 29% yield along with homocoupled product 1,1'-binaphthalene in 60% yield.[20] We were also keen to avoid limiting the scope of the reaction by eliminating ethanol, since we anticipated alkylation of the solvent by the activated alkyl chloride coupling partners and palladium catalysed hydride reduction of functional groups such as nitro and keto which was previously observed under these borylation conditions.[9b] Based on work by Molander[10] and Schmidt-Leithoff,[11] we decided on the use of the most atom economical diboron reagent, $B_2(NMe_2)_4$. Indeed, commercially available $B_2(NMe_2)_4$ is the synthetic precursor to other more common diboranes such as $B_2(pin)_2$ and $B_2(OH)_4$,[21] but has not been previously utilised in any one-pot borylation/SM cross-coupling processes. After extensive optimisation, we arrived at the use of Buchwald's XPhos-Pd-G2 precatalyst,[19] the environmentally friendly solvent 2-methyltetrahydrofuran[22] and propylene gylcol for the in situ esterification of $B_2(NMe_2)_4$. Under these conditions, we were able to efficiently borylate 1-bromonaphthylene **1a** and subsequently, in the same pot, couple the in situ generated boronic ester with benzyl chloride **2a**[23] to afford the sp^2–sp^3 SM cross-coupling product, diaryl methane **3a**, in 70% isolated yield (84% average yield for each stage of the reaction, Scheme 2). Crucially, no trace of homocoupled products were observed in this or subsequent examples.

The method is operationally simple[24] as all reagents are used as received and addition of more pre-catalyst is not required after the initial reaction set up.

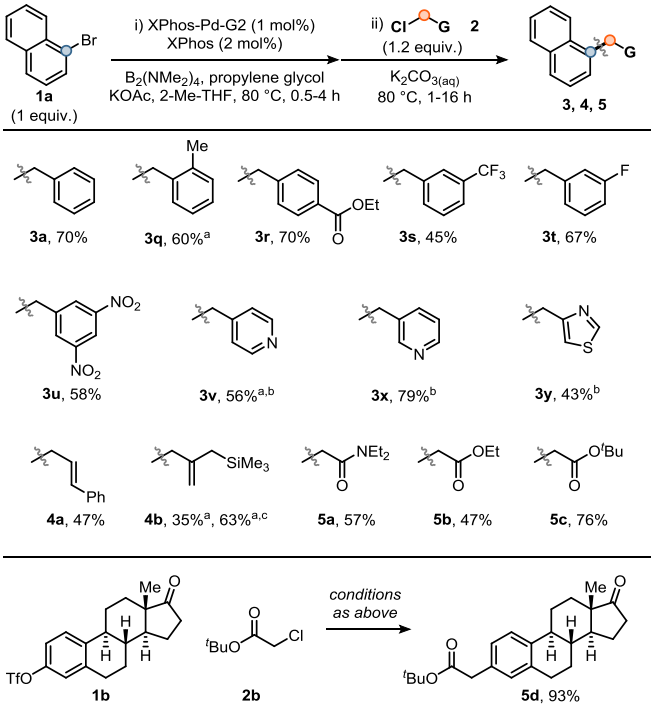
In exploring the scope of the sp^2 unit in the one-pot borylation/SM sp^2–sp^3 cross-coupling, we found that the reaction was broadly amenable to a range of aryl (pseudo)halides with different steric and electronic parameters as well as bearing a variety of functional groups (Scheme 2). Electron deficient (**3c**-**f**) and electron rich aryl halides (**3g**-**j**) were successfully coupled with benzyl chloride, as were heteroaromatic halides including pyridine (**3k**,**l**), quinoline (**3m**), indole (**3n**) and benzofuran (**3o**). The reaction displayed excellent functional group tolerance and substrates bearing functional groups such as phenyl (**3b**), ester (**3d**,**e**,**k**,**n**), ketone (**3c**,**l**,**p**), nitrile (**3f**), methyl ether (**3g**,**h**), and unprotected hydroxy (**3i**) and amino (**3j**) were effective sp^2 units in the coupling reaction. In addition, aryl bromides, chlorides and triflates reacted with similar efficiency (*cf*. entries for **3c** and **3g**), with the latter allowing for the functionalisation of estrone (**3p**).



Scheme 2. Scope of the aryl halide in the one-pot borylation/SM sp^2–sp^3 cross-coupling. [a] X = Br; [b] X = Cl; [c] X = OTf; [d] Internal standard NMR yield. Conditions: $B_2(NMe_2)_4$ (3 equiv.), potassium acetate (3 equiv.), XPhos-Pd-G2 (1 mol%), XPhos (2 mol%), propylene glycol (6 equiv.), 2-Me-THF, **1** (1 equiv.), 80 °C; then $K_2CO_{3(aq)}$, **2** (1.2 equiv.), 80 °C.

We then examined the sp^3 coupling partner in the one-pot borylation/SM sp^2–sp^3 cross-coupling reaction. We decided upon the use of activated alkyl chlorides since they are readily accessible, often commercially available, and more stable than other activated alkyl halides. Whilst secondary alkyl chlorides, such as 2-chloropropanoate did not yield the desired cross-coupled product, pleasingly we found that a variety of primary alkyl chlorides could be employed and allowed the efficient generation of diaryl methanes, α-aryl esters, α-aryl amides and allyl aryl compounds (Scheme 3). Thus, benzylic chlorides with ortho substitution (**3q**), electron withdrawing groups such as ester (**3r**), trifluoromethyl (**3s**), fluoro (**3t**), and dinitro (**3u**), as well as heterocycles such as pyridines (**3v**,**x**) and thiazole (**3y**) were successfully coupled to 1-bromonapthalene **1a** to deliver a variety of diaryl methanes. The use of *para*-methoxy benzyl chloride failed to yield the desired cross-coupled product.

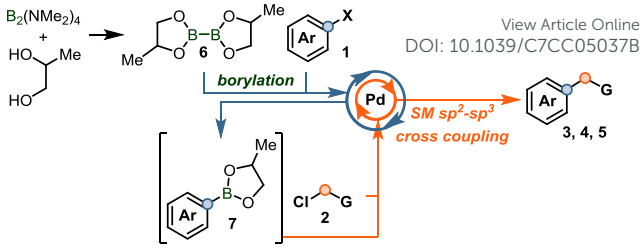
As other functional groups are often attached to the sp^3 carbon of the sp^2–sp^3 linkage of biologically important compounds (*cf*. Scheme 1A) we examined other readily available classes of activated alkyl chloride coupling partners. We found that allyl chlorides, such as cinnamyl chloride and 2-(trimethylsilylmethyl)allyl chloride, gave the desired cross-coupled product 1,3-diaryl propene **4a** and versatile allyl silane **4b**, without isomerisation or migration of the double bond.



Scheme 3. Scope of the alkyl chloride in the one-pot borylation/SM sp^2–sp^3 cross-coupling. [a] Internal standard NMR yield; [b] the corresponding hydrochoride salt of **2** was used directly in reaction. [c] Using 3 equiv. of 2-(chloromethyl)allyl-trimethylsilane. Conditions: as in Scheme 2.

In addition, α-chloro amides and α-chloro esters, which have only previously been employed in the SM coupling with aryl trifluoroborate salts,[25] were successfully utilised in the efficient one-pot borylation/SM sp^2–sp^3 cross-coupling and delivered α-aryl amide **5a**, and α-aryl esters **5b** and **5c**. The triflate derived from estrone (**1b**) was also coupled to *tert*-butyl chloroacetate **2b** to give **5d** in high yield. Pleasingly, homocoupling of the in situ generated boronic ester was not observed despite being a common and significant side-reaction in SM couplings with α-halo carbonyl coupling partners.[26,20] It is worth noting that these sp^2-sp^3 cross couplings operate under the same reaction conditions, regardless of the nature of the coupling partners involved.

The mechanism of the one-pot borylation/SM sp^2–sp^3 cross-coupling is proposed to begin with the in situ esterification of $B_2(NMe_2)_4$ with propylene gylcol to form diborane **6** (Scheme 4).[11a] Subsequently, Miyaura borylation of aryl (pseudo)halide **1** with diborane **6**, catalysed by Pd(0) generated in situ from Buchwald's XPhos-Pd-G2 precatalyst,[19] yields aryl boronic ester **7**. Borylation was not observed in the absence of the diol. Upon addition of aqueous K_2CO_3, any remaining diborane is destroyed, preventing deleterious side reactions of the diborane and alkyl chloride.[10] Addition of alkyl chloride **2** then allows the SM sp^2–sp^3 cross-coupling with the in situ generated aryl boronic ester **7**, catalysed by the same Pd(0) that mediated the borylation stage, yielding diaryl methanes **3**, allyl aryls **4**, and α-aryl carbonyl compounds **5**.



Scheme 4. Proposed mechanism of the one-pot borylation/SM sp^2–sp^3 cross-coupling.

In summary, we found that the conditions used in the previously reported one-pot borylation/SM sp^2-sp^2 cross couplings afforded low yields and significant homocoupling in the sp^2-sp^3 reaction.[20] However, under our conditions, yields are higher and homocoupling is completely avoided. This has led to the development of the first one-pot borylation/SM sp^2–sp^3 cross-coupling for the operationally simple, efficient construction of diaryl methanes, α-aryl carbonyls and allyl aryl compounds. We employ readily available aryl (pseudo)halides and the most economical diborane, $B_2(NMe_2)_4$, with a commercially available palladium pre-catalyst, to generate boronic esters in situ, saving the need for isolation after a discrete synthetic step. The in situ generated boronic esters undergo SM sp^2–sp^3 cross-coupling, catalysed by the same Pd(0) that mediates the borylation stage, with readily accessible activated alkyl chlorides, such as benzyl chlorides, α-chloro esters, α-chloro amides and allyl chlorides, to deliver diaryl methanes, α-aryl esters, α-aryl amides and allyl aryl compounds. In addition, we use the same general and simple procedure across all of the investigated classes of sp^2 and sp^3 coupling partners, making the procedure particularly relevant to the straightforward generation of diverse molecular libraries. We are currently investigating the use of this efficient synthetic strategy for the coupling of sp^3 partners bearing β-hydrogens. The present study has significantly streamlined the synthesis of important substructures found in validated pharmaceuticals and we anticipate the methodology will be of particular interest to medicinal chemists.

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