# Pd-Catalyzed Suzuki−Miyaura and Hiyama−Denmark Couplings of Aryl Sulfamates

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S *Supporting Information*
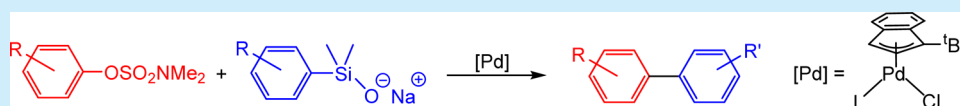
ABSTRACT: Using a recently discovered precatalyst, the first Pd-catalyzed Suzuki−Miyaura reactions using aryl sulfamates that occur at room temperature are reported. In complementary work, it is demonstrated that a related precatalyst can facilitate the coupling of aryl silanolates, which are less toxic and reactive nucleophiles than boronic acids with aryl chlorides. By combining our results using modern electrophiles and nucleophiles, the first Hiyama−Denmark reactions using aryl sulfamates are reported.

The discovery of Pd-catalyzed cross-coupling reactions has resulted in major advances in the synthesis of both pharmaceuticals and fine chemicals.[1] Typically, aryl halides are used as the electrophile in these reactions.[1] However, phenolic derivatives offer their own unique advantages.[2] They not only are robust and trivial to prepare from ubiquitous phenols[3] but can provide routes to prefunctionalize the electrophile through C−H activation and directed *ortho*-metalation.[4] Although simple phenol derivatives such as aryl sulfonates have been used for many years in cross-coupling reactions,[2b,5] these moieties are not useful directing groups for C−H activation. Therefore, there is interest in the use of aryl sulfamates as electrophiles in cross-coupling reactions.[2b−d] The first reports of Suzuki−Miyaura reactions involving aryl sulfamates utilized Ni catalysts but required elevated temperatures (>100 °C) and catalyst loadings (5−10 mol %).[6] Despite further studies on Ni-catalyzed Suzuki−Miyaura reactions with aryl sulfamates,[7] there is still only one system that can facilitate the coupling of a small number of naphthyl sulfamates with boronic acids at room temperature.[8] In related chemistry, Percec and co-workers reported Ni systems for the room temperature coupling of aryl sulfamates with neopentylglycol boronates using catalyst loadings of 5−10 mol %.[9] While these results are impressive, neopentylglycol boronates are not commercially available and are less atom efficient than boronic acids. In the last 3 years, there have been reports of Pd catalysts for Suzuki−Miyaura reactions with aryl sulfamates, but these systems also require elevated temperatures (80−100 °C) and catalyst loadings (4−10 mol %).[10] These conditions can limit the utility and functional group tolerance of Suzuki−Miyaura reactions between boronic acids and aryl sulfamates.

Organoboranes, utilized in Suzuki−Miyaura reactions, are the most common nucleophiles in cross-coupling.[11] This is in part due to the perceived low toxicity of boronic acids. However, recent reports suggest that some, but not all, boronic acids are mutagenic.[12] In contrast, silicon-based nucleophiles have not

shown similar toxicity problems, yet their application in cross-coupling is limited.[13] Early Hiyama couplings required fluoride-containing additives to promote transmetalation, which limited the utility of the reactions.[14] Subsequently, Denmark demonstrated that when aryl silanols and their derivatives are used as nucleophiles, only a Brønsted base is required for activation, eliminating the need for fluoride additives.[15] Currently, this chemistry remains most effective with aryl bromides and iodides,[16] and the scope of these reactions needs to be broadened to make the Hiyama−Denmark reaction a true alternative to Suzuki−Miyaura couplings.

Recently, we described new precatalysts for cross-coupling, (η^3-1-^{t}Bu-indenyl)Pd(L)(Cl), which are compatible with both phosphine and NHC ligands and are commercially available.[17] The precatalysts can be generated in situ through the reaction of the unligated dimeric precursor (η^3-1-^{t}Bu-indenyl)$_2$Pd$_2$(μ-Cl)$_2$ (**1**) with 2 equiv of free ligand, which is convenient for ligand screening. We demonstrated that our precatalysts are highly active for a range of standard cross-coupling reactions using aryl halides as electrophiles, including Buchwald−Hartwig and α-arylation reactions and Suzuki−Miyaura couplings using both aryl and alkyl organoboranes.[17] Here, we demonstrate the ability of our precatalysts to broaden the scope of cross-coupling (Figure 1). Through application of ligand screening, we describe the first examples of Pd-catalyzed Suzuki−Miyaura reactions using aryl sulfamates at room temperature. Additionally, our precatalysts are compatible with less reactive nucleophiles and are capable of coupling aryl silanolates with a variety of aryl chlorides. The culmination of this work is the coupling of aryl silanolates with aryl sulfamates, which represent the first Hiyama−Denmark reactions using aryl sulfamates.

Based on pioneering work by Garg and co-workers, Ni precatalysts have been preferred for Suzuki−Miyaura reactions
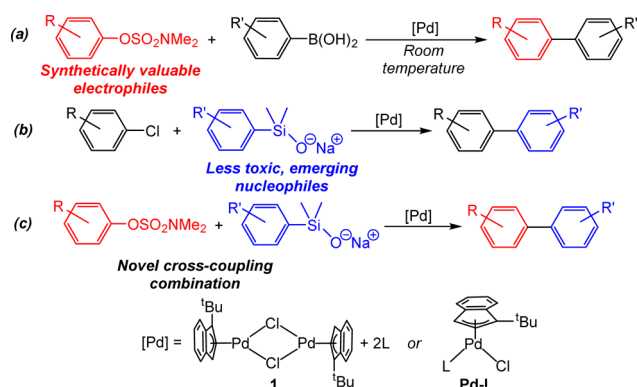
Figure 1. Summary of this work: (a) first examples of room-temperature Pd-catalyzed Suzuki−Miyaura couplings using aryl sulfamates; (b) Hiyama−Denmark couplings using aryl chlorides; and (c) Hiyama−Denmark couplings with aryl sulfamates.

using aryl sulfamates.[6] This is because it is proposed that oxidative addition of the aryl sulfamate is more facile for Ni compared to Pd.[6b] However, there have only been limited computational studies of oxidative addition of aryl sulfamates to Pd,[6b] and the effects of state-of-the-art ligands for cross-coupling, which can promote oxidative addition, are unclear.[18] We performed a ligand screen for the coupling of 1-naphthyl sulfamate with (4-methoxyphenyl)boronic acid using our unligated dimeric precursor **1** and 2 equiv of a range of free ligands (Table 1 and SI). Using K_3PO_4 as the base and toluene as

**Table 1. Yields for Ligand Screening for Pd-Catalyzed Suzuki−Miyaura Reactions of Aryl Sulfamates[a]**

entry	ligand	solvent	base	yield[b] (%)
1	P^{t}Bu$_3$	toluene	K$_3$PO$_4$	<5
2	SPhos	toluene	K$_3$PO$_4$	42
3	RuPhos	toluene	K$_3$PO$_4$	48
4	XPhos	toluene	K$_3$PO$_4$	61
5[c]	XPhos	toluene	K$_3$PO$_4$	97
6[d]	XPhos	toluene/MeOH	K$_3$PO$_4$	84
7[d]	XPhos	toluene/MeOH	K$_2$CO$_3$	98

[a]Conditions: 1-naphthyl sulfamate (0.1 mmol), (4-methoxyphenyl)-boronic acid (0.15 mmol), base (0.2 mmol), **1** (0.00125 mmol), ligand (0.0025 mmol), toluene (1 mL), 25 °C, 4 h. [b]Yields are the average of two runs and were determined by GC. [c]Performed at 50 °C. [d]Solvent: toluene (0.66 mL), methanol (0.33 mL).

the solvent, no product was observed using simple phosphines such as PCy$_3$, P^{t}Bu$_3$, or PPh$_3$ or the N-heterocycle carbene ligand IPr (see SI), consistent with computational predictions from Garg and co-workers.[6b] When Buchwald-type phosphines that are designed to increase the rate of oxidative addition[18] were used as the ancillary ligand, moderate conversions were achieved at room temperature (entries 2−4). Consistent with our previous results,[17] our precatalyst gives superior results compared to other related systems, such as Nolan's (η^3-allyl)Pd(L)(Cl) precatalysts (see SI).[1a] Using XPhos, complete conversion was achieved at 50 °C (entry 5). When methanol was used as a co-solvent, excellent conversion was obtained using XPhos at room temperature (entry 6). We suggest that there are two main reasons why the

addition of methanol improves the efficiency of this reaction: (i) both the boronic acid and the base are more soluble, and (ii) methanol can potentially play a key role in the activation of the precatalyst from Pd(II) to Pd(0).[19] Finally, switching the base from K_3PO_4 to K_2CO_3 provided full conversion to product at room temperature (entry 7).

Using our optimized ligand and conditions, we expanded the substrate scope to other boronic acids and aryl sulfamates (Figure 2). In these reactions, we used the ligated XPhos
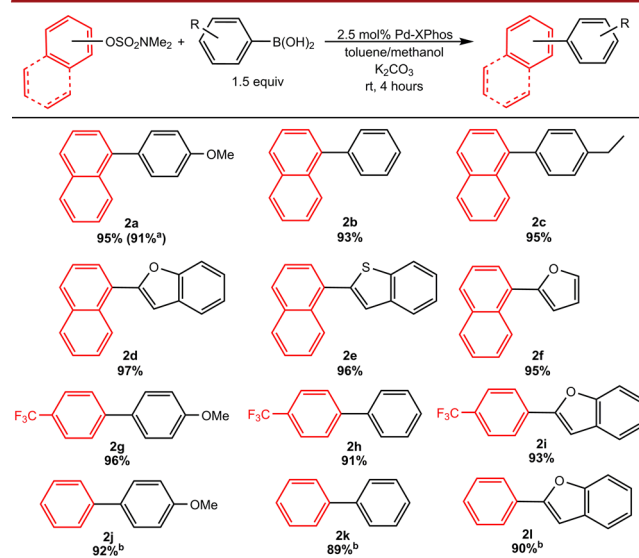
Figure 2. Isolated yields of products in Suzuki−Miyaura reactions using naphthyl and phenyl sulfamates. Conditions: sulfamate (0.1 mmol), boronic acid (0.15 mmol), K$_2$CO$_3$ (0.2 mmol), Pd-XPhos precatalyst (0.0025 mmol), toluene (0.66 mL), methanol (0.33 mL). [a]Performed on 1 mmol scale in relation to aryl sulfamate. [b]Performed at 80 °C for 24 hours. Yields are the average of two runs.

precatalyst (**Pd-XPhos**) instead of the in situ generated system for operational simplicity and to ensure the ideal 1:1 Pd/ligand ratio. Couplings using naphthyl (Figure 2) and substituted naphthyl sulfamates (see SI) were successful with a variety of boronic acids at room temperature. Even 2-heteroaryl boronic acids, which readily undergo protodeborylation,[20] yielded product in greater than 95% yield (**2d−f**). In general, oxidative addition of naphthyl sulfamates is easier than phenyl sulfamates,[2g,21] but our optimized system facilitated the coupling of 4-(trifluoromethyl)phenyl sulfamate with both an unactivated boronic acid as well as a 2-heteroaryl boronic acid at room temperature (Figure 2). Unsubstituted phenyl sulfamate proved to be more difficult and excellent yields were only obtained when the reactions were performed at 80 °C.

These results represent the first examples of Pd-catalyzed Suzuki−Miyaura reactions involving aryl sulfamates at room temperature. Furthermore, the conditions employed require a significantly lower number of equivalents of boronic acid (1.5 equiv vs 2.5 equiv) as well as external base (2.5 equiv vs 4.5 equiv) compared to state-of-art Ni catalysts.[6] Our results suggest that it may be possible to develop systems for the coupling of even less activated phenol derived electrophiles such as aryl carbamates and esters, which have been proposed to be incompatible with Pd catalysts.[2g]

The reactions with aryl sulfamates show that our precatalysts are compatible with valuable electrophiles. We were also interested in exploring their activity with modern nucleophiles

such as organosilanes. Denmark and co-workers have advanced the field of fluoride-free Hiyama coupling through their discovery of silanolates as viable nucleophiles.[15] For example, using Pd(P^{t}Bu$_3$)$_2$, they were able to effectively couple heteroaryl iodides and bromides with various aryl and alkenyl silanolates.[16a] However, examples of the coupling of less reactive aryl chlorides with aryl silanolates are rare and generally require catalyst loadings of 5 mol % or more and temperatures ranging from 70 to 100 °C.[16] Given the ubiquitous nature of aryl chlorides, developing systems that can perform Hiyama−Denmark reactions using these electrophiles at milder conditions would be beneficial.[22]

Using conditions similar to those reported by Denmark for coupling aryl iodides and bromides,[16a] a ligand screen was performed using **1**, free ligand, 4-(trifluoromethyl)phenyl chloride, and 4-(methoxy)phenyl silanolate, which was prepared using a literature method.[16a] In an analogous fashion to Denmark's results,[16a] the best activity was observed using P^{t}Bu$_3$ as the ancillary ligand. Many other standard cross-coupling ligands (PPh$_3$, PCy$_3$, IPr) were unsuccessful at coupling the silanolate with the aryl chloride (see SI). Notably, several Buchwald-type phosphines were moderately effective in this transformation (SPhos and XPhos).

With optimal conditions and ligand found, our focus shifted to expanding the scope to other aryl chlorides (Figure 3). Using the
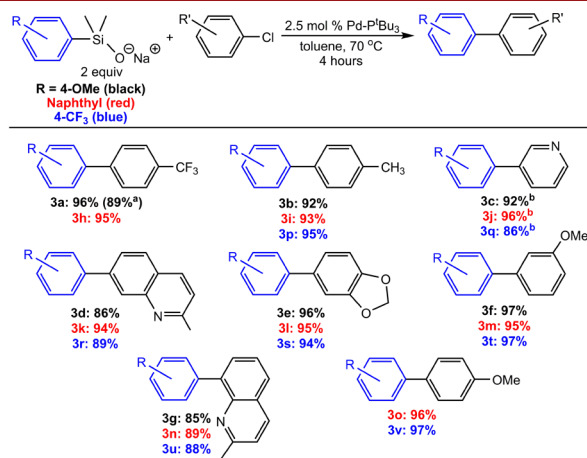
Figure 3. Isolated yields of products for silanolate couplings with aryl chlorides. Conditions: silanolate (0.2 mmol), aryl chloride (0.1 mmol), Pd-P^{t}Bu$_3$ precatalyst (0.0025 mmol), toluene (1 mL), 70 °C, 4 hours. [a]Performed on 1 mmol scale in relation to aryl chloride. [b]Performed at 90 °C. Yields are the average of two runs.

electron-rich 4-(methoxy)phenyl silanolate,[16a] seven aryl chlorides were coupled using the **Pd−P^{t}Bu$_3$** precatalyst. In each case, isolated yields were greater than 85%, including deactivated substrates (**3b** and **3f**) as well as heterocyclic aryl chlorides (**3c−e,g**). The scope of these reactions with 1-naphthyl (**3h−o**) and 4-(trifluoromethyl)phenyl (**3p−v**) silanolates[16a] is shown in Figure 3. Again, yields greater than 85% were achieved using the same conditions. No significant differences exist between the silanolate substrates, despite the differences in their electronic properties. In total, we have performed over 20 different Hiyama−Denmark reactions using aryl chlorides. Our results continue the expansion of this exciting cross-coupling reaction and highlight the improved activity observed with our precatalyst.

To further show the versatility of our precatalyst system, we aimed to couple silanolates with sulfamates, a combination of substrates that has never been used together. Initial efforts to combine 1-naphthyl sulfamate with aryl silanolates proved to be unsuccessful using the conditions described in Figure 3. This is presumably related to the fact that our precatalyst ligated with P^{t}Bu$_3$ was inactive for Suzuki−Miyaura reactions with aryl sulfamates. However, using XPhos as the ligand, some activity was observed for the coupling of 2-naphthyl sulfamate with 4-methoxyphenyl silanolate (Table 2, entry 1). Changing the

Table 2. Yields for Ligand Screening for Pd-Catalyzed Coupling of Aryl Silanolates with Aryl Sulfamates[a]

| entry	ligand	Pd loading (mol %)	additive	temp (°C)	yield[b] (%)
1	XPhos	2.5	none	110	18
2	RuPhos	2.5	none	110	37
3	RuPhos	5.0	none	110	62
4	RuPhos	5.0	NaOMe	110	<5
5	RuPhos	5.0	NaO^{t}Bu	110	<5
6	RuPhos	5.0	RuPhos[c]	110	95
7[d]	RuPhos	5.0	RuPhos[c]	80	98

[a]Conditions: 4−(methoxy)phenyl silanolate (0.2 mmol), 2-naphthyl sulfamate (0.1 mmol), toluene (1 mL), 8 h. [b]Yields are the average of two runs and were determined by GC. [c]5.0 mol % of RuPhos. [d]24 h.

ligand to RuPhos resulted in increased yields, consistent with the trend seen for Hiyama−Denmark coupling with aryl chlorides (see SI). To further improve the yield, we screened potentially useful additives. Addition of external bases did not lead to coupling, as they caused degradation of the aryl sulfamate (entries 4 and 5). When 5.0 mol % of free RuPhos was added, the yield of product increased (entry 6), as has been observed in some Buchwald−Hartwig reactions.[17] It is unclear why the addition of excess RuPhos assists in the reaction, but it could reduce catalyst decomposition through the formation of unligated Pd(0) species. For our best conditions, the temperature could be lowered to 80 °C while still achieving high yields, albeit with longer reaction times (entry 7).

This method is compatible with a variety of 2-naphthyl sulfamate derivatives (Figure 4). Using both 4-(methoxy)phenyl and naphthyl silanolates, heterocyclic sulfamates as well as sulfamates with ester and ether functionalities could be coupled with good to excellent isolated yields (**4b−d**). When moving to phenyl sulfamates, it was necessary to increase the equivalents of silanolate. For phenyl sulfamates with electron-withdrawing groups, good to excellent yields were obtained (**4i−k**), whereas for unsubstituted and 4-fluorophenyl sulfamate there was a decrease in yield (**4h,l**). No product was observed with 1-naphthyl sulfamate derivatives, presumably due to the increased steric bulk of these substrates. Our results represent the first use of phenol-derived electrophiles, which can be used as directing groups, in Hiyama−Denmark reactions.

In conclusion, we have demonstrated the utility of our (1-^{t}Bu-indenyl)Pd(L)(Cl) precatalysts by describing the room-temperature Pd-catalyzed Suzuki−Miyaura couplings of aryl sulfamates, Hiyama−Denmark reactions with aryl chlorides, and the first examples of Hiyama−Denmark couplings using aryl sulfamates.
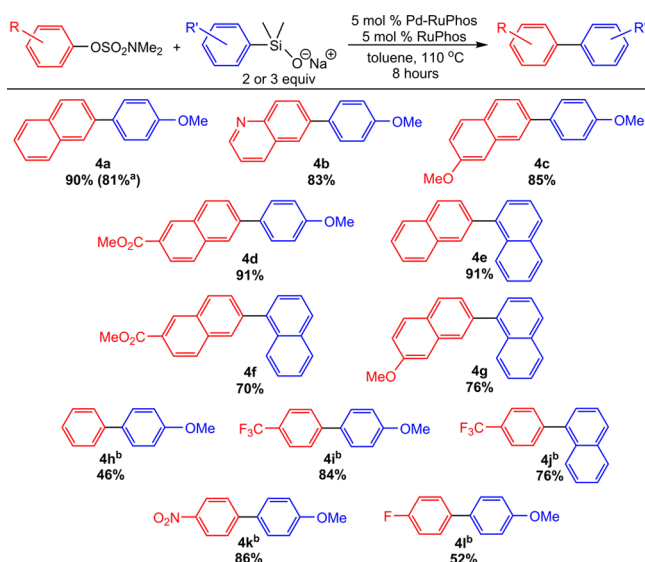
Figure 4. Isolated yields of products for couplings of aryl sulfamates with aryl silanolates. Conditions: silanolate (0.2 mmol), aryl sulfamate (0.1 mmol), Pd-RuPhos precatalyst (0.005 mmol), RuPhos (0.005 mmol), toluene (1 mL), 110 °C, 8 hours. [a]Performed on 1 mmol scale in relation to aryl sulfamate. [b]Silanolate (0.3 mmol). Yields are the average of two runs.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02330.

Experimental procedures and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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