

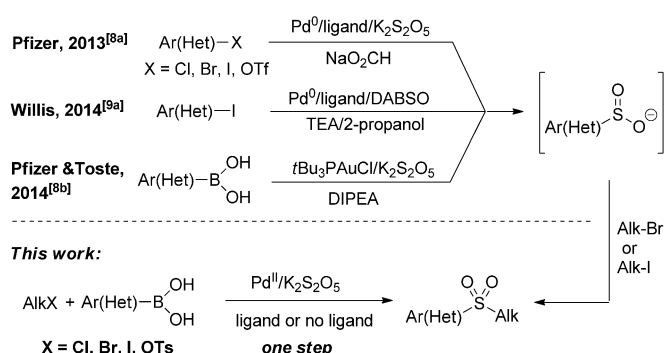
# Palladium-Catalyzed Synthesis of (Hetero)Aryl Alkyl Sulfones from (Hetero)Aryl Boronic Acids, Unactivated Alkyl Halides, and Potassium Metabisulfite

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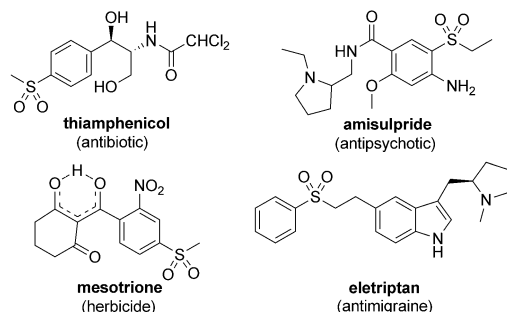
**Abstract:** A palladium-catalyzed one-step synthesis of (hetero)aryl alkyl sulfones from (hetero)arylboronic acids, potassium metabisulfite, and unactivated or activated alkylhalides is described. This transformation is of broad scope, occurs under mild conditions, and employs readily available reactants. A stoichiometric experiment has led to the isolation of a catalytically active dimeric palladium sulfinate complex, which was characterized by X-ray diffraction analysis.

The sulfone functional group is frequently encountered in many compounds of pharmaceutical,<sup>[1]</sup> agrochemical,<sup>[2]</sup> and materials science<sup>[3]</sup> importance (Figure 1). Despite its ubiquity in these areas, common methods for the preparation of sulfones typically require either sulfide oxidation<sup>[4]</sup> or the alkylation/arylation of sulfinate salts.<sup>[5]</sup> Given that oxidative methods are often incompatible with sensitive functional groups found in complex organic substrates, and that sulfinate salts have very limited commercial availability,<sup>[6]</sup> there has been an intense effort to identify mild and general alternatives for sulfone synthesis starting from readily available substrate feedstocks.<sup>[7]</sup>

can readily undergo transmetalation with arylboronic acids<sup>[10]</sup> and that sulfur dioxide can insert into the resulting carbon–palladium bond to form palladium sulfinate complexes.<sup>[11]</sup> In more recent investigations, these putative Pd species have been shown to liberate free sulfinate salts, which are then quenched with alkyl electrophiles in a net one-pot, two-step process (Scheme 1). Only a single example has been reported



**Scheme 1.** Aryl alkyl sulfone synthesis from readily available reactants.



**Figure 1.** Representative commercial products incorporating a sulfone motif.

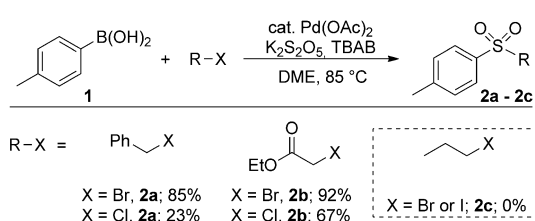
In order to overcome these limitations, our laboratories<sup>[8]</sup> and others<sup>[9]</sup> have recently developed transition-metal-catalyzed procedures for the preparation of aryl alkyl sulfones starting from readily available (hetero)aryl halide and boronic acid substrates. It is well-established that Pd<sup>II</sup> species

where the alkyl electrophile was present from the start of the reaction and, notably, this study relied on the use of an activated electrophile (benzyl bromide).<sup>[8b]</sup> Despite these advances, the development of a general and streamlined procedure that introduces a range of activated and unactivated alkyl electrophiles at the beginning of the reaction in a one-step procedure has thus far been elusive. Herein, we report a practical palladium-catalyzed three-component reaction of (hetero)arylboronic acids, (un)activated alkyl halides, and potassium metabisulfite to access a breadth of (hetero)-aryl alkyl sulfones in a single step (Scheme 1). Furthermore, we describe a stoichiometric experiment employing an isolated palladium sulfinate intermediate to probe the reaction mechanism.

We initially examined conditions for the one-pot synthesis of sulfones using activated alkyl electrophiles and boronic acids (Scheme 2). Our initial experiments consisted of heating a mixture of 4-tolylboronic acid, an excess of the alkyl electrophile, and potassium metabisulfite<sup>[12]</sup> in DME in the presence of tetrabutylammonium bromide (TBAB) and a catalytic amount of palladium acetate. For benzyl bromide and  $\alpha$ -bromoacetate substrates, this afforded the desired alkyl-aryl sulfones in 85 % (**2a**) and 92 % (**2b**) yields, respectively. However, our attempts to extend these conditions to the corresponding less reactive activated chloride

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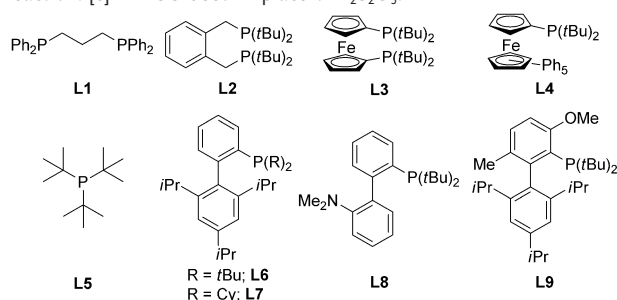


**Scheme 2.** Initial results of aryl alkyl sulfone synthesis from boronic acids.

**Table 1:** Reaction optimization with unactivated electrophiles.<sup>[a]</sup>

entry	[Pd]	Ligand	Yield <sup>[b]</sup>
1	Pd(OAc) <sub>2</sub>	—	0
2	Pd(OAc) <sub>2</sub>	L1	8
3	Pd(OAc) <sub>2</sub>	L2	22
4	Pd(OAc) <sub>2</sub>	L3	25
5	Pd(OAc) <sub>2</sub>	L4	22
6	Pd(OAc) <sub>2</sub>	L5	0
7	Pd(OAc) <sub>2</sub>	L6	37
8	Pd(OAc) <sub>2</sub>	L7	6
9	Pd(OAc) <sub>2</sub>	L8	15
10	Pd(OAc) <sub>2</sub>	L9	22
11 <sup>[c]</sup>	Pd(OAc) <sub>2</sub>	L6	56
12 <sup>[c]</sup>	[Pd <sub>2</sub> dba <sub>3</sub> ]	L6	0
13 <sup>[d]</sup>	[Pd(MeCN) <sub>2</sub> Cl <sub>2</sub> ]	L6	74
14 <sup>[c,d]</sup>	[Pd(MeCN) <sub>2</sub> Cl <sub>2</sub> ]	L6	52
15 <sup>[c]</sup>	[Pd(MeCN) <sub>2</sub> Cl <sub>2</sub> ]	—	61
16 <sup>[c,e]</sup>	[Pd(MeCN) <sub>2</sub> Cl <sub>2</sub> ]	L6	16

[a] Reaction conditions: 4-TolB(OH)<sub>2</sub> (0.52 mmol), Ph(CH<sub>2</sub>)<sub>2</sub>Br (2 equiv), K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (2.2 equiv), TBAB (1.1 equiv), [Pd] (10 mol %), ligand (10 mol %), DME (0.3 M), 85 °C, 22 h. [b] Yield of isolated sulfone **2d** product (%). [c] DMF used in place of DME. [d] TBAB omitted from reaction. [e] DABSO used in place of K<sub>2</sub>S<sub>2</sub>O<sub>5</sub>.

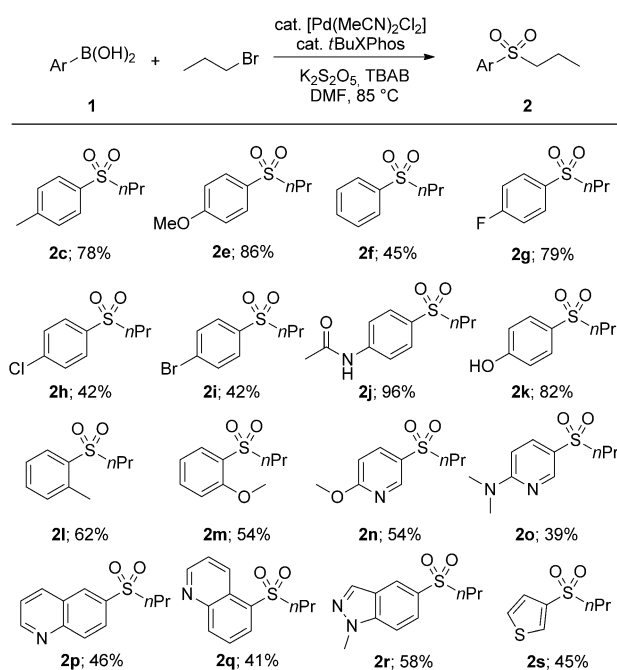


substrates resulted in significantly diminished yields of isolated sulfone. More importantly, employing these conditions for unactivated *n*-propyl halides resulted in no conversion to the desired aryl alkyl sulfone **2c** and led to unproductive protodeboronation. To develop a more effective and general method, we focused our efforts on the identification of conditions amenable to the use of unactivated alkyl electrophiles (Table 1).

We initiated our optimization studies by evaluating a series of structurally diverse ligands to support the

palladium-catalyzed synthesis of sulfone **2d** from 4-tolylboronic acid and phenethyl bromide (2 equiv) in the presence of 10 mol % Pd(OAc)<sub>2</sub>, 10 mol % ligand, tetrabutylammonium bromide (1.1 equiv), and K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (2.2 equiv) in DME at 85 °C for 22 h (Table 1, entries 2–10).<sup>[13]</sup> A constant observation over the course of these studies was that electron-rich, sterically encumbered ligands featuring P(*t*Bu)<sub>2</sub> substitution consistently supported efficient catalysis for this transformation (Table 1, entries 7,8). Having identified *t*BuXPhos (**L6**) as the optimal ligand, we screened the other reaction parameters (palladium source, solvent, additives) in search of improved reaction yields. Notably, the source of palladium and solvent had a dramatic impact on the reaction outcome, whereby the use of [Pd(MeCN)<sub>2</sub>Cl<sub>2</sub>] and DMF was shown to provide superior yields of **2d** (Table 1, entry 13). Whereas most other Pd<sup>II</sup> sources provided modest yields of **2d**, the use of Pd<sup>0</sup> sources, such as [Pd<sub>2</sub>dba<sub>3</sub>], resulted in no observable sulfone product. The effect of TBAB on the reaction was tested by preparing sulfone **2d** in the absence of this additive (Table 1, entry 14). The observed decrease in yield from 74 % to 52 % prompted us to further use TBAB in reaction scope exploration. The heterogeneous nature of the reaction mixture has thus far precluded further investigation into the beneficial effect of TBAB; however, it is reasonable to postulate that its presence contributes to increasing the solubility of the inorganic salt employed. Whereas partial catalytic activity was also observed in the absence of **L6** (Table 1, entry 15), the notable increase in yield of **2d** with the ligand present warranted its use in further defining the substrate scope of this reaction. Interestingly, replacement of K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> with DABSO<sup>[51,14]</sup> (an alternative surrogate of SO<sub>2</sub>) produced sulfone **2d** in only 16 % yield (Table 1, entry 16). Sulfur dioxide and K<sub>2</sub>SO<sub>3</sub> also proved to be ineffective.

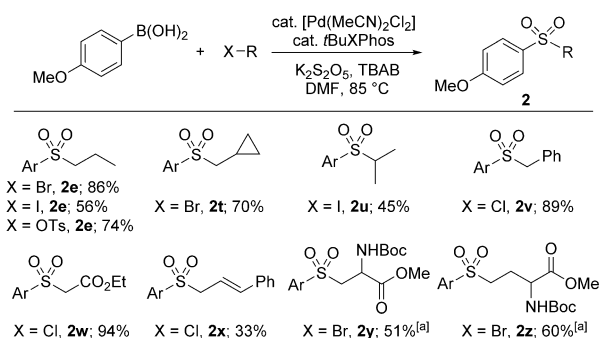
Having defined an effective catalyst system and reaction conditions for the synthesis of aryl alkyl sulfone **2d** from readily available precursors, we sought to explore the scope of suitable (hetero)aromatic boronic acid substrates (Scheme 3). When reacted with *n*-propyl bromide, both electron-rich and -neutral aromatic boronic acids gave the corresponding *n*-propylsulfones in good yields (**2c**, **2e,f**; 45–86 %). Halo-substituted substrates were equally competent under standard conditions (**2g–2i**), which may provide further opportunities for subsequent derivatization by metal-mediated couplings. Hydroxy and acetamide functional groups were well tolerated under the reaction conditions and no side-products arising from alkylation of these groups were isolated (**2j**, **2k**). *Ortho*-substituted boronic acids were also compatible substrates for this reaction, providing the products **2l** and **2m** in 62 % and 54 % yields, respectively. The compatibility of this reaction with boronic acids featuring protic functional groups and *ortho*-substitution, in addition to capitalizing on another set of widely available monomers, makes it complementary to our previously reported method using heteroaryl halides.<sup>[8a,15]</sup> Given the value of substituted heterocycles in the pharmaceutical industry, where control of the lipophilicity of drug candidates is of prime importance, we were pleased to observe that the method was compatible with substituted pyridines (**2n**, **2o**), quinolines (**2p**, **2q**), indazole (**2r**), and thiophene (**2s**). Of note, alternative boron coupling partners



**Scheme 3.** Substrate scope in boronic acids. Reaction conditions:  $\text{ArB(OH)}_2$  (0.52 mmol),  $n\text{PrBr}$  (2 equiv),  $\text{K}_2\text{S}_2\text{O}_5$  (2.2 equiv), TBAB (1.1 equiv),  $[\text{Pd}(\text{MeCN})_2\text{Cl}_2]$  (10 mol %),  $t\text{BuXPhos}$  (10 mol %), DMF (1.5 mL), 85 °C, 22 h. All examples are shown with yields of isolated sulfone **2** product.

such as potassium 4-tolyltrifluoroborate, pinacol 4-tolueneboronate, and neopentylglycol 4-tolueneboronate were found to be incompatible substrates under these optimized conditions, producing **2c** in less than 10 % yields.

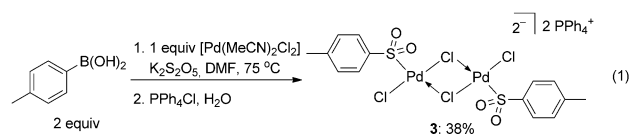
The scope of alkylating agents is illustrated in Scheme 4. Unactivated primary alkyl bromides, iodides, and tosylates are all competent reagents for the synthesis of sulfone **2e** (56–86 % yields). Furthermore, the use of more hindered electrophiles, such as cyclopropylmethyl bromide and isopropyl iodide, provided the desired sulfone products in synthetically useful yields (**2t** and **2u**, 70 % and 45 %, respectively). Using the optimized conditions, useful to excellent yields were also



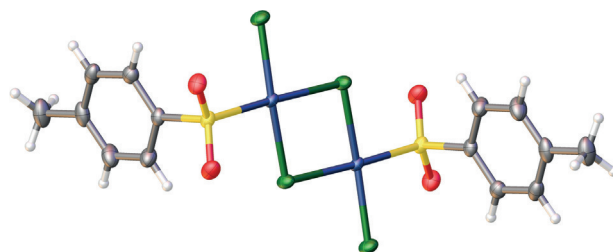
**Scheme 4.** Substrate scope in alkyl electrophiles. Reaction conditions:  $\text{ArB(OH)}_2$  (0.52 mmol), electrophile (2 equiv),  $\text{K}_2\text{S}_2\text{O}_5$  (2.2 equiv), TBAB (1.1 equiv),  $[\text{Pd}(\text{MeCN})_2\text{Cl}_2]$  (10 mol %),  $t\text{BuXPhos}$  (10 mol %), DMF (1.5 mL), 85 °C, 22 h. All examples are shown with yields of isolated sulfone **2** product. [a]  $\text{ArB(OH)}_2$ :electrophile = 1.2:1.

obtained for benzyl chloride (**2v**; 89 %),  $\alpha$ -chloroacetate (**2w**; 94 %), and substituted allyl chloride (**2x**; 33 %) substrates. The utility of this transformation is further demonstrated by the one-step synthesis of unnatural amino acid derivatives **2y** and **2z**, which feature pendant aryl sulfone groups.<sup>[16]</sup>

Drawing inspiration from previous studies concerning the synthesis of discrete palladium sulfinate complexes,<sup>[11f,17]</sup> we became interested in investigating the mechanism of this reaction through the use of stoichiometric experimentation. To isolate putative palladium sulfinate intermediates under catalytically relevant conditions, the reaction of 4-tolylboronic acid,  $\text{K}_2\text{S}_2\text{O}_5$ , and stoichiometric  $[\text{Pd}(\text{MeCN})_2\text{Cl}_2]$  was executed in the absence of an alkyl electrophile, TBAB, and  $t\text{BuXPhos}$ . Treatment of the crude product with an aqueous solution of  $\text{PPh}_4\text{Cl}$  led to the isolation of anionic Pd complex **3** as an orange solid [Eq. (1)].<sup>[18]</sup> The assignment of **3** as a  $\text{C}_2$ -

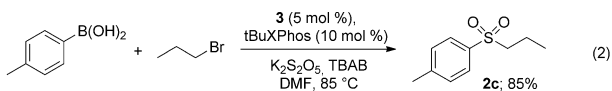


symmetric dimer has been confirmed by single crystal X-ray diffraction analysis (Figure 2).<sup>[19]</sup> NMR and IR spectroscopic data, as well as elemental analysis are also in support of structure **3**. The stoichiometric preparation of complex **3** from  $p$ -tolyl boronic acid likely proceeds via initial transmetalation with the  $\text{Pd}^{\text{II}}$  species.<sup>[10]</sup> Subsequent insertion of  $\text{SO}_2$  (liberated from in situ disproportionation of  $\text{K}_2\text{S}_2\text{O}_5$ ) into the resulting carbon–palladium bond then affords the palladium sulfinate linkage in complex **3**.<sup>[11]</sup>

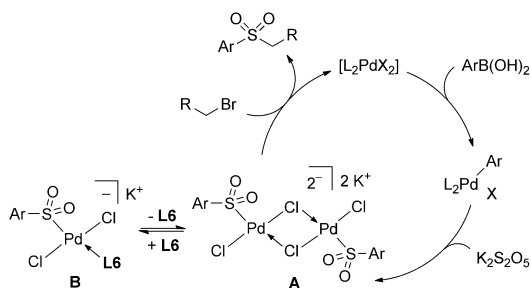


**Figure 2.** X-ray crystal structure of **3**; two  $\text{PPh}_4^+$  counterions are omitted for clarity. Ellipsoids set at 50% probability.

The catalytic activity of this dimeric palladium species was then evaluated by conducting the alkylsulfonylation reaction of 4-tolyl boronic acid with  $\text{K}_2\text{S}_2\text{O}_5$  and  $n$ -propyl bromide in the presence of **3** (5 mol %), TBAB, and  $t\text{BuXPhos}$  (10 mol %).<sup>[20]</sup> When compared with the optimized conditions presented in Table 1, complex **3** was found to be an equally active catalyst for the synthesis of sulfone **2c** [Eq. (2)]. Collectively, these results provide support for the possible role of **3** as an intermediate in the catalytic cycle of this transformation. Furthermore, the reaction of complex **3** with piperidine in the presence of NCS led to formation of 1-tosylpiperidine in 96 % yield, which presents an opportunity for the future development of Pd-catalyzed sulfonamide synthesis.<sup>[13]</sup>



A preliminary catalytic cycle that accounts for the intermediacy of dimeric Pd complex **3**, under phosphine-free conditions, is illustrated in Scheme 5. The initial Pd<sup>II</sup> species would transmetalate with the boronic acid and following SO<sub>2</sub> insertion into the Pd–C bond would afford complex **A** (cf. complex **3**).<sup>[10,11]</sup> Subsequent alkylation with either activated or unactivated alkyl halides would then produce the aryl alkyl sulfone product, as well as regenerate the Pd<sup>II</sup> catalyst. Notably, when the catalysis is conducted in the presence of a strongly coordinating ligand, such as **L6**, the dimeric complex **A** is more likely to dissociate into its monomeric form, complex **B**.



**Scheme 5.** Preliminary catalytic cycle that accounts for the intermediacy of **3**.

In conclusion, we have developed a practical one-step palladium-catalyzed synthesis of (hetero)aryl alkyl sulfones from readily available (hetero)arylboronic acids, alkyl halides, and potassium metabisulfite. This represents the first general approach to (hetero)aryl alkyl sulfone synthesis that introduces the electrophile at the beginning of the reaction and does not rely on two-step sulfinate salt synthesis-alkylation methods. Furthermore, we have conducted stoichiometric experiments that have provided preliminary insight into the structure of catalytically active palladium-sulfinate complexes. Given its mild experimental conditions and broad scope, this method is well-suited for any applications where the rapid synthesis and evaluation of alkyl sulfones is required.

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**Keywords:** alkylation · boronic acids · homogeneous catalysis · palladium · sulfones

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- [20] Attempts to prepare a discrete palladium sulfinate-*t*BuXPhos complexes were thwarted by multiple side-products and decomposition.

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