Sulfoxidation

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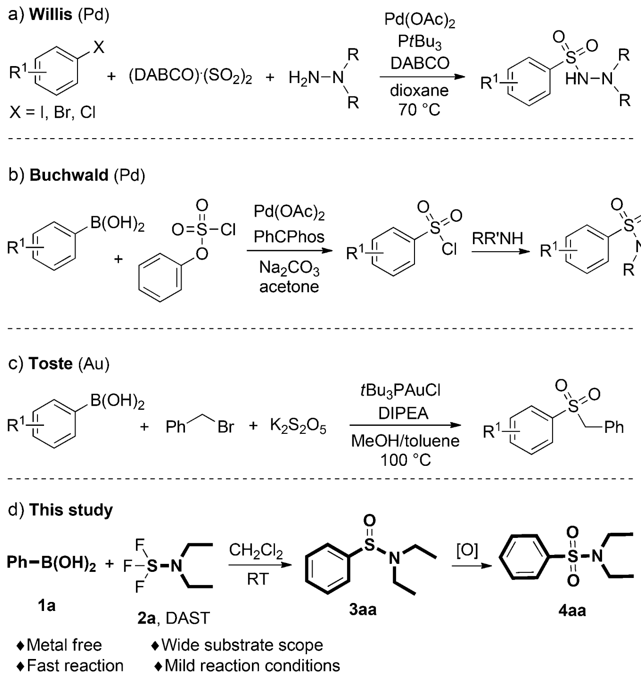
Metal-Free Cross-Coupling of Arylboronic Acids and Derivatives with DAST-Type Reagents for Direct Access to Diverse Aromatic Sulfinamides and Sulfonamides

Qiang Wang, Xiang-Ying Tang, and Min Shi**

Abstract: *We have developed a simple and convenient method for the cross-coupling of arylboronic acids and their derivatives with DAST-type reagents under mild and metal-free conditions to directly afford sulfinamides in moderate to good yields. Moreover, sulfonamides were obtained after a simple oxidation reaction. The reaction mechanism was investigated by ^{18}O-labeling experiments, and the synthetic utility was demonstrated by the sulfoxidation of natural products.*

Sulfonyl-derived compounds, including sulfones, sulfonic acids/sulfinic acids and their derivatives, are of great importance in medicinal chemistry, agricultural chemistry, and materials science.[1] Among those sulfonyl-containing molecules, sulfonamides are of the most importance owing to their medical significance. Many anticonvulsants, HIV protease inhibitors, and anticancer, antibacterial, anti-inflammatory, antitumor, and antiviral agents contain a sulfonamide subunit.[2] In general, there are two classes of traditional methods for the construction of sulfonamides: sulfide oxidation[3] and the amide coupling of sulfonyl chlorides with amines.[4] However, both methods have severe drawbacks. The oxidation approach usually requires the use of odorous thiols for the preparation of sulfide precursors. Although the amide-coupling method itself is simple, difficulties stem from the synthesis of the sulfonyl chloride: the range of possible substrates is limited by the harsh acidic conditions used for electrophilic aromatic sulfonation. Furthermore, only certain substitution patterns can be accessed by electrophilic aromatic substitution reactions because of the inherent electronic properties of the parent arene. Therefore, direct and simple methods to construct C−S=O bonds are in high demand.

In principle, a transition-metal-catalyzed cross-coupling reaction can be used for the direct introduction of an $-SO_2-$ moiety into suitably functionalized substrates, such as aryl halides or arylboronic acids. However, research in this area was extremely limited until 2010, when Willis first reported a breakthrough study on a direct aminosulfonylation of aryl halides in the presence of palladium catalyst (Scheme 1a).[5] In 2013, Buchwald and co-workers made another important contribution in the synthesis of aryl sulfonamides through palladium-catalyzed chlorosulfonylation of arylboronic acids (Scheme 1b).[6] Toste and co-workers also developed an elegant redox-neutral sulfinate synthesis with $K_2S_2O_5$ under gold catalysis (Scheme 1c).[7] Other exciting progress has also been made by Willis and co-workers since 2010, for example, the palladium-catalyzed cross-coupling of DABSO with (hetero)aryl iodides as well as arylboronic acids.[8] Similarly, Shavnya et al. reported a palladium-catalyzed cross-coupling of aryl halides with $K_2S_2O_5$ as the sulfur dioxide source and formate as the reductant.[9] Although great progress with different transition-metal catalysts has been made since these seminal studies,[10] no transition-metal-free cross-coupling reaction of arylboronic acids with a suitable reagent has yet been reported for the construction of sulfonamides. Herein, we report a metal-free method that provides ready access to sulfinamides through the cross-coupling of arylboronic acids



Scheme 1. Transition-metal-catalyzed versus metal-free sulfonation. DABCO = 1,4-diazabicyclo[2.2.2]octane, DIPEA = *N*,*N*-diisopropylethylamine, PhCPhos = 2-diphenylphosphanyl-2′,6′-bis(dimethylamino)-1,1′-biphenyl.

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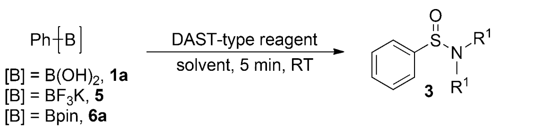
and their derivatives with diethylaminosulfur trifluoride (DAST)-type electrophilic fluorination reagents.

Arylboronic acids are important synthetic precursors in organic synthesis.[11] Both transition-metal-catalyzed and metal-free transformations of arylboronic acids have been studied extensively.[12,13] We therefore envisaged that a metal-free sulfonation of arylboronic acids might be possible with a suitable reagent. This kind of reagent should be able to activate the boronic acid, and it should contain a functional group that has an $-SO_2-$ moiety or a functionality that can be readily converted into a sulfonyl group. To our delight, this idea was realized when DAST was chosen as the reagent and sulfinamide **3aa** was obtained. Moreover, the corresponding sulfonamide **4aa** was readily afforded by a simple oxidation step (Scheme 1 d).

We used phenylboronic acid (**1a**) as a model substrate to optimize the reaction conditions (Table 1). It was found that **3aa** was obtained in 71 % yield when the reaction was carried out with 1.5 equivalents of DAST (**2a**) in CH_2Cl_2 at room temperature for 5 min (entry 1). An increase in the amount of DAST (**2a**) used to 2.0 equivalents led to the production of **3aa** in 86 % yield. When this reaction was carried out in a sealed tube under argon at room temperature, **3aa** was isolated in 81 % yield (entry 3). The effect of the solvent was also investigated, and it was identified that CH_2Cl_2 was better than other solvents, such as THF, toluene, and MeCN (Table 1, entries 4–6). However, a sharp decrease in the yield was observed when H_2O was present as an additive (entries 7 and 8). We reason that DAST, which is sensitive to moisture, may decompose in the presence of an excess amount of H_2O. Other phenylboronic acid derivatives were also examined. The reaction of potassium phenyltrifluoroborate (**5**) and phenylboronic acid pinacol ester (**6a**) with DAST (**2a**) gave the desired cross-coupling product **3aa** in 51 and 74 % yield, respectively (Table 1, entries 9 and 10). Moreover, bis(2-methoxyethyl)aminosulfur trifluoride (**2b**) and morpholinosulfur trifluoride (**2c**) were also examined in the reaction with phenylboronic acid **1a** and gave the corresponding products **3ab** and **3ac** in 74 and 64 % yield, respectively (entries 11 and 12).

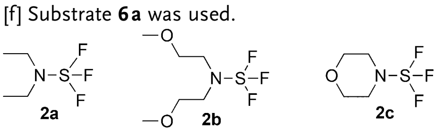
Having established the optimal reaction conditions, we next surveyed the scope of the reaction by varying the structure of arylboronic acids **1** (Scheme 2, method A). It was found that 3,5-dimethyl, 4-*tert*-butyl-, 2-methyl-, 4-methoxy-, and 4-benzyloxy-substituted arylboronic acids all afforded the desired cross-coupling products **3ba**–**ea** and **3ia** in 66–79 % yield. The use of 2-methoxyphenylboronic acid as a substrate only gave a trace amount of the corresponding product **3fa**. The reactions of 4-methyl-, 2,6-dimethyl-, 4-phenoxy-, and 4-

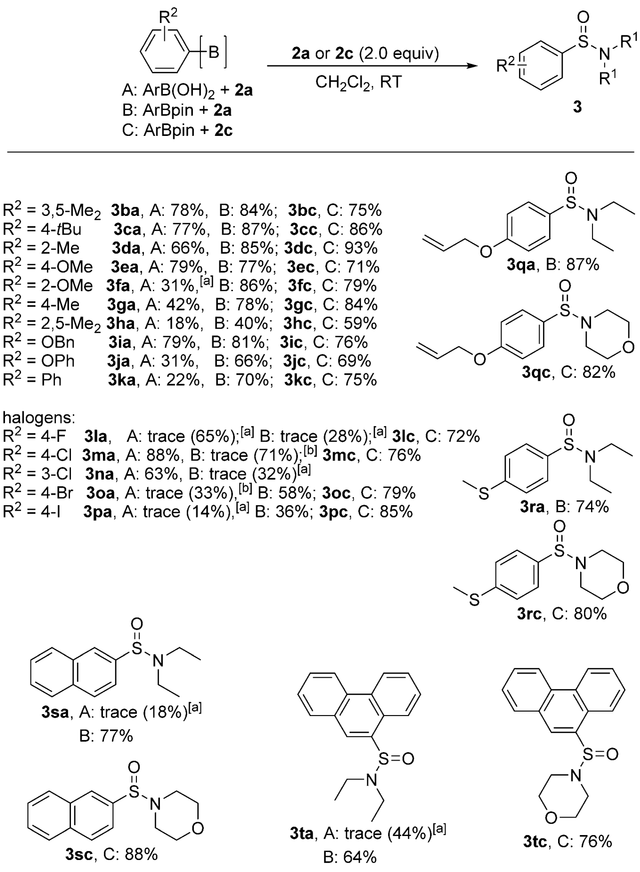
Table 1: Optimization of the reaction conditions for the metal-free cross-coupling of phenylboronic acid derivatives with DAST-type reagents.



Entry[a]	DAST-type reagent (*x* equiv)	Additive (*x* equiv)	Solvent	Product	Yield [%][b]
1	**2a** (1.5)	–	CH_2Cl_2	**3aa**	71
2	**2a** (2.0)	–	CH_2Cl_2	**3aa**	86
3	**2a** (2.0)	–	CH_2Cl_2	**3aa**	81[c]
4	**2a** (2.0)	–	THF	**3aa**	41[d]
5	**2a** (2.0)	–	toluene	**3aa**	57[d]
6	**2a** (2.0)	–	MeCN	**3aa**	78[d]
7	**2a** (2.0)	H_2O (1.0)	CH_2Cl_2	**3aa**	43
8	**2a** (2.0)	H_2O (3.0)	CH_2Cl_2	**3aa**	trace
9	**2a** (2.0)	–	CH_2Cl_2	**3aa**	51[e]
10	**2a** (2.0)	–	CH_2Cl_2	**3aa**	74[f]
11	**2b** (2.0)	–	CH_2Cl_2	**3ab**	74
12	**2c** (2.0)	–	CH_2Cl_2	**3ac**	64

[a] Reactions were carried out on a 0.2 mmol scale in 1.0 mL of the solvent at room temperature in air for 5 min. [b] Yield of the isolated product. [c] The reaction was carried out in a sealed tube under argon at room temperature. [d] The yield was determined by ^1H NMR spectroscopy. [e] Substrate **5** was used. The reaction time was prolonged to 3 h. [f] Substrate **6a** was used.





Scheme 2. Scope of the reaction in terms of the arylboronic acid or arylboronic acid pinacol ester. All reactions were carried out on a 0.2 mmol scale in CH_2Cl_2 (1.0 mL) at room temperature in air for 5 min. Yields are for the isolated products. [a] K_2CO_3 (0.4 mmol) was added, and the reaction mixture was stirred for 30 min. Without K_2CO_3, only a trace amount of the product was formed. [b] Na_2CO_3 (0.4 mmol) was added, and the reaction mixture was stirred for 30 min. Bn = benzyl.

phenyl-substituted arylboronic acids afforded the corresponding cross-coupling products **3ga**,**ha** and **3ja**–**ka** in yields ranging from 18 to 42%. Substrates **1l**–**p** bearing halogen substituents (F, Cl, Br, I) at the *meta* or *para* position were also examined, and we found that only the 3-chloro- and 4-chloro-substituted arylboronic acids **1m**,**n** afforded the corresponding cross-coupling products in satisfactory 63 and 88% yield, respectively. Boronic acids **1s**,**t** featuring fused aromatic rings gave the corresponding products in trace amounts.

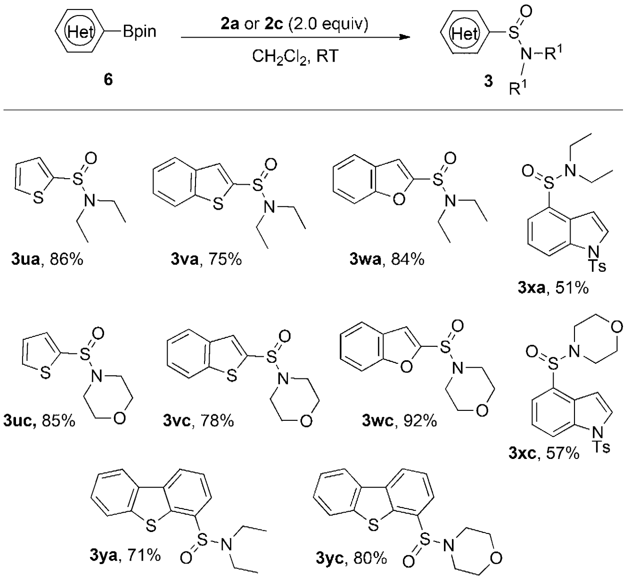
When phenylboronic acid pinacol esters **6** were employed as substrates with **2a** (Scheme 2, method B), substrates **6b**–**k** and **6q**–**t** were all smoothly converted into the corresponding sulfoxidized products **3ba**–**ka** and **3qa**–**ta** in moderate to excellent yields. Substrates **6l**–**p** bearing halogen substituents (F, Cl, Br, I) at the *meta* or *para* position were also examined. 4-Bromo- and 4-iodo-substituted arylboronic acid pinacol esters **6o** and **6p** afforded the desired products **3oa** and **3pa** in 58 and 36% yield, whereas when 4-fluoro-, 4-chloro-, and 3-chloro-substituted arylboronic acid pinacol esters **6l**–**n** were tested, only trace amounts of the products were observed. In these cases, the addition of K_2CO_3 or Na_2CO_3 to the reaction mixture improved the yield of the desired products. We assume that such arylboronic acids or the relevant intermediates are not stable under acidic conditions.[14]

We also examined the cross-coupling of different arylboronic acid pinacol esters **6** with morpholinosulfur trifluoride (**2c**; Scheme 2, method C). We were pleased to find that substrates **6b**–**k**, **6q**, and **6r** could all be efficiently converted into the corresponding sulfinamides **3bc**–**kc**, **3qc**, and **3rc** in moderate to excellent yields. Halogen substituents (F, Cl, Br, and I) at the *para* position were all well-tolerated in this transformation, and the products **3lc**, **3mc**, **3oc**, and **3pc** were obtained in good yields. The halogen atom in these products can be used for further transformations (see the Supporting Information). The polycyclic aromatic substrates **6s**,**t** also gave the corresponding products **3sc** and **3tc** in 88 and 76% yield.

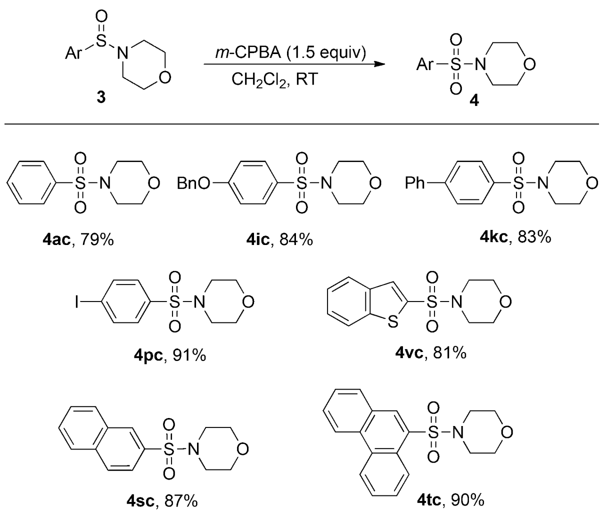
Some heteroaromatic boronic acid pinacol ester derivatives were also examined with **2a** and **2c** (Scheme 3). The sulfur-containing substrates 2-thiophenylboronic acid pinacol ester (**6u**), 2-benzothienylboronic acid pinacol ester (**6v**), and dibenzothiophenylboronic acid pinacol ester (**6y**) were smoothly transformed into the corresponding products **3ua**, **3va**, **3uc**, **3vc**, **3ya**, and **3yc** in yields ranging from 71 to 86%. Moreover, the oxygen-containing heteroaromatic boronic acid derivative 2-benzofuranylboronic acid pinacol ester (**6w**) was smoothly sulfoxidized to the desired products **3wa** and **3wc** in 84 and 92% yield, respectively. More importantly, the indole-containing substrate **6x** underwent the reaction smoothly to give the corresponding products **3xa** and **3xc** in 51 and 57% yield.

Next, we examined the transformation of the sulfinamides into the corresponding sulfones upon treatment with *m*-chloroperbenzoic acid (*m*-CPBA) in CH_2Cl_2 at room temperature (Scheme 4). Sulfinamide **3ac** was converted into the corresponding sulfone **4ac** in 79% yield, and the 4-benzyloxy- and 4-phenylbenzenesulfinamides **3ic** and **3kc** were smoothly oxidized to the desired sulfones **4ic** and **4kc** in 84 and 83% yield, respectively. The 4-iodobenzenesulfinamide **3pc** could also be transformed into **4pc** in 91% yield. Notably, the 2-thiophenyl-substituted substrate **3vc** was oxidized to the corresponding sulfone **4vc** in 81% yield. The oxidation of sulfinamides **3sc** and **3tc**, containing naphthalene and phenanthrene rings, gave the corresponding products **4sc** and **4tc** in 87 and 90% yield.

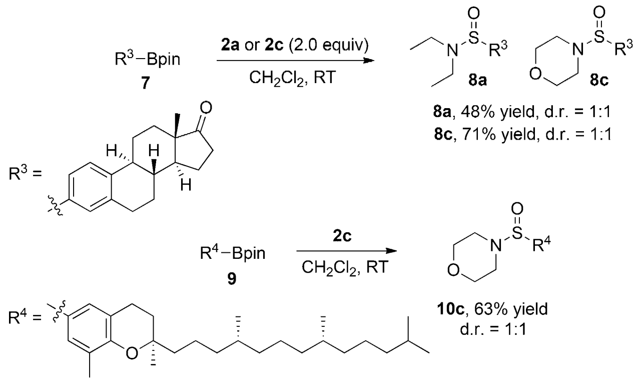
To further illustrate the synthetic utility of this method, we treated the estrone- and (+)-δ-tocopherol-derived arylboronic acid pinacol esters **7** and **9** with DAST-type reagents. The sulfoxidation reactions afforded **8a**, **8c**, and **10c** in 48, 71, and 63% yield, respectively, each as a 1:1 mixture of diastereomeric isomers (Scheme 5).



Scheme 3. Metal-free cross-coupling of heteroaromatic boronic acid pinacol esters with DAST-type reagents. All reactions were carried out on a 0.2 mmol scale in CH_2Cl_2 (1.0 mL) at room temperature in air for 5 min. Yields are for the isolated products. Ts = *p*-toluenesulfonyl.

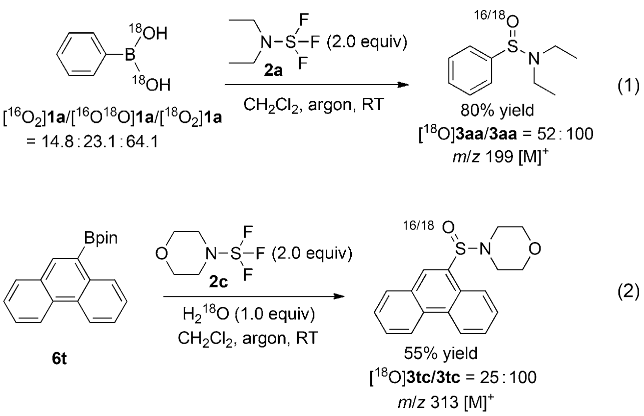


Scheme 4. Oxidation of sulfinamides by *m*-CPBA. All reactions were carried out on a 0.1 mmol scale in CH_2Cl_2 (1.0 mL) at room temperature in air for 5 h. Yields are for the isolated products.



Scheme 5. Application to substrates derived from natural products.

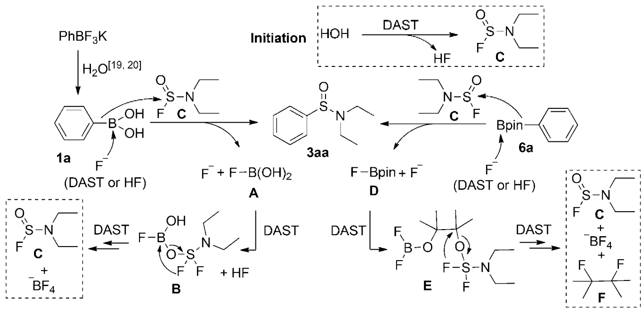
To gain some insight into the reaction mechanism, we performed an ^{18}O-labeling experiment with PhB(^{18}OH)$_2$ under the standard reaction conditions and obtained [^{18}O]**3aa** in 80% yield with 52% ^{18}O incorporation [Scheme 6, Eq. (1)]. Furthermore, when substrate **6t** was



Scheme 6. Mechanistic investigation.

treated with **2c** under the standard conditions in the presence of $H_2{}^{18}O$ (1.0 equiv), the corresponding product **3tc** was obtained in 55% yield with 25% ^{18}O incorporation [Scheme 6, Eq. (2)]. These results indicated that the sulfoxide oxygen atom originated from both phenylboronic acid and residual H_2O in the reagents or solvent.

On the basis of the control experiments and previous reports, a plausible mechanism is outlined in Scheme 7. Initially, intermediate **C** can be generated by the reaction of DAST with trace H_2O in the solvent or reagents.[15] Substrate **1a** or **6a**, which is activated by a fluoride anion generated from DAST or HF, then undergoes nucleophilic sulfuration[16] with intermediate **C** to provide the corresponding sulfinamide with the release of intermediate **A** or **D**,[17] which is then captured by DAST to deliver intermediate **B** or **E**.[15] Migration of a fluorine atom forms intermediate **C** and BF_4^-, which was observed by ^{19}F NMR spectroscopy (see the Supporting Information). 2,3-Difluoro-2,3-dimethylbutane (**F**) was also detected by ^{19}F NMR spectroscopy (see the Supporting Information)[18]



Scheme 7. Proposed mechanism.

when phenylboronic acid pinacol ester (**6a**) was used as the substrate. Phenyltrifluoroborate is hydrolyzed by H_2O to give the corresponding arylboronic acid,[19] which is transformed through the above mentioned pathway to give **3aa**.[20]

In conclusion, we have developed a simple and convenient method for the cross-coupling (sulfoxidation) of arylboronic acids and their derivatives with DAST-type reagents under mild and metal-free conditions. This reaction directly affords various sulfinamides in moderate to good yields within 5 min. The corresponding sulfonamides can then be readily obtained by a simple oxidation reaction. A plausible mechanism has been proposed on the basis of ^{18}O-labeling experiments, and the synthetic utility of the obtained products has been also demonstrated. Further applications of this method are under investigation in our laboratory.

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Keywords: arylboronic acids · cross-coupling · sulfinamides · sulfonamides · synthetic methods

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[21] See the Supporting Information for the crystal data of **3tc**. CCDC 1400684 (**3tc**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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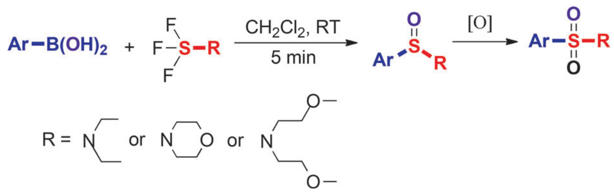

Mighty mild: A wide range of arylboronic acids and their derivatives underwent efficient cross-coupling under mild and metal-free conditions with reagents based on the electrophilic fluorination reagent diethylaminosulfur trifluoride (DAST). This simple and convenient method directly afforded sulfinamides, which could be further converted into sulfonamides through a straightforward oxidation step (see scheme).

