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Directed *ortho*-Metalation–Cross-Coupling Strategies. One-Pot Suzuki Reaction to Biaryl and Heterobiaryl Sulfonamides

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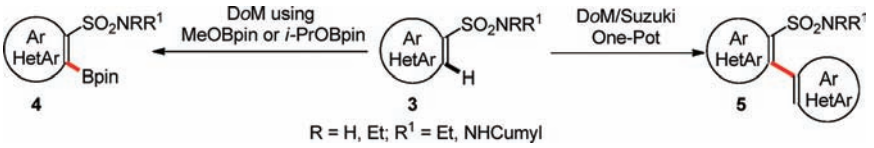
ABSTRACT



A general synthesis of stable *ortho*-boropinacolato aryl and heteroaryl sulfonamides by directed *ortho*-metalation (D*o*M) and either MeOBPin or *i*-PrOBpin electrophile quench, 3 → 4, is described. A one-pot metalation–Suzuki cross-coupling procedure for the synthesis of biaryls and heterobiaryls, 3 → 5, and a complementary D*o*M–Ir-catalyzed boronation sequence (Scheme 6) are delineated.

The original and significant directed *ortho*-metalation (D*o*M) work on aryl sulfonamides **1** reported by Hauser et al.[1] coupled with our interest to fortify and expand the metalation chemistry of these systems **2**[2] and the growing prevalence of the sulfonamide pharmacophore in medicinal agents (Figure 1)[3,4] has prompted further investigations of this powerful directed metalation group (DMG) in carbanionic aromatic and heteroaromatic reactions and its impact in further synthetically useful processes.[5,6]

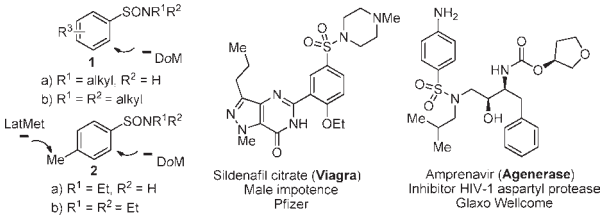


Figure 1. Sulfonamides as DMGs and pharmaceuticals.

Herein we report studies concerning the D*o*M-mediated synthesis of aryl and heteroaryl sulfonamide boropinacolates **3**→**4** and their general and efficient Suzuki–Miyaura cross-coupling reactions in one pot to a series of biaryl and heterobiaryl sulfonamides **5** (Scheme 1). This work

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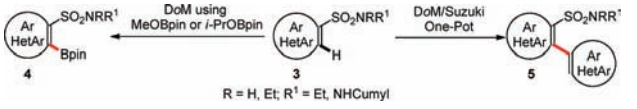
overcomes previous failings in the preparation of aryl sulfonamide boronic acids,[7] namely protodeboronation which was observed in the preparation of the corresponding pyridine boronates.[8] We also introduce Ir-catalyzed borylation reactions (Scheme 6) which allows complementarity and enhancement of the Suzuki coupling chemistry to that derived from the D*o*M-based coupling protocol. The presented general methodology should be of value for the construction of biaryl and heterobiaryl sulfonamides for application, especially in the design and development of medicinal chemistry programs centered on the sulfonamide functional group.[3a,9]

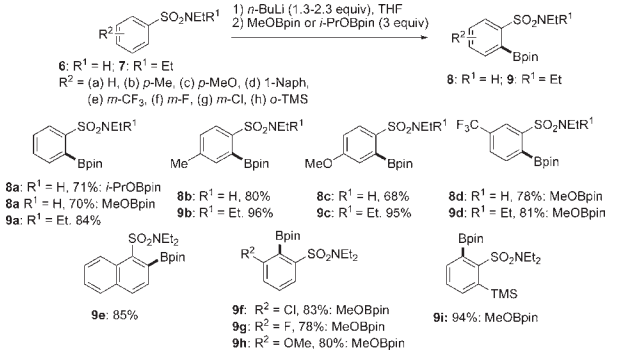
Scheme 1. Synthesis of *ortho*-Bpin (Het)Aryl Sulfonamides and One-Pot Process for Bi(Het)Aryl Sulfonamides



To initiate the study, we noted the lack of literature on the preparation of aryl sulfonamide *ortho*-boronic acid derivatives by D*o*M−borylation protocols.[10] To test the standard procedures, sulfonamides **7b** (R^2 = H and R^1 = Et) and **7h** (R^1 = Et, R^2 = 3-OMe), when subjected to metalation under *n*-BuLi/−78 °C/THF conditions followed by borylation using $B(OMe)_3$ and $B(O\text{-}iPr)_3$ at several temperatures, resulted in recovery of starting material or, at best, formation of a low yield of product **9a** by ^{1}H NMR analysis (see Supporting Information (SI) for details, Table S1). On the assumption that protodeboronation occurred on aqueous workup and with the knowledge of C−B compound stability,[11] we decided to prepare directly the Bpin derivatives using MeOBpin and *i*-PrOBpin.[12]

In the event, metalation of **6a** (R^2 = R^1 = H)and **7a** (R^2 = H and R^1 = Et) under standard *n*-BuLi/−78 °C/THF

Scheme 2. Synthesis of *ortho*-Bpin Aryl Sulfonamides



conditions followed by *i*-PrOBpin and MeOBpin quench smoothly gave the corresponding *ortho*-Bpin derivatives **8a** and **9a** respectively in good yields, irrespective of the borylating reagent. However, once established, *i*-PrOBpin was used owing to its lower cost. The reaction was explored in scope with variation of EWG and EDG substitution and the results are summarized in Scheme 2. While good to excellent yields were observed for sulfonamides without *ortho* and *meta* substitution (**8a**−**c**, **9a**−**c**, Scheme 2), steric hindrance for the latter derivatives played a role in both regioselectivity and yield (**8d** and **9d**−**i**), which could be ameliorated by switching from *i*-PrOBpin to the MeOBpin borylating reagent. For example, using *i*-PrOBpin the reaction of 3-chloro-*N*,*N*-diethylbenzenesulfonamide **7f** afforded 32% of product **9f** while the corresponding MeOBpin afforded **9f** in 83% yield. Similar observations were made for 3-fluoro-*N*,*N*-diethylbenzenesulfonamide **7g** (*i*-PrOBpin: 34% yield by GC/MS; MeOBpin: 78% yield). In contrast to the expected synergistic effect of two DMGs in a *meta* relationship favoring in between metalation[2] (**9f**−**h**, Cl, F, and MeO DMGs), the CF_3 group, a known weak DMG, led to alternate ring regioselective borylation to afford products **8d** and **9d**.[13]

The metalation−borylation of the secondary cumyl aryl sulfonamide, already recognized as a well-behaved DMG,[6a] was explored to provide, after facile post-D*o*M TFA-mediated decumylation, primary sulfonamides for further manipulation which has value in drug design.[14] Thus, when compound **10a**, prepared conveniently by reaction of phenyl sulfonyl chlorides with cumylamine

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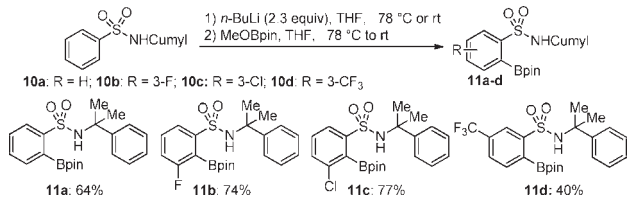
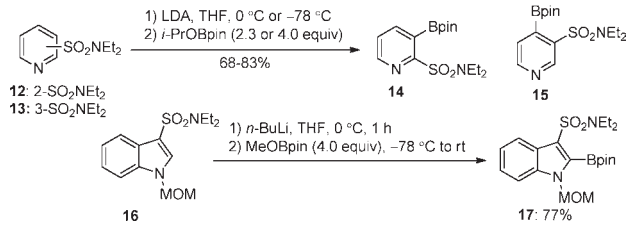
Scheme 3. Synthesis of *ortho*-Bpin Cumyl Aryl Sulfonamides



(see SI, Table S2 for details), was subjected to *s*-BuLi/TMEDA/−78 °C metalation conditions, product **11a** was obtained in 45% yield (see SI). Yet, when Hauser's[1] original conditions were adapted, **11a** was obtained in 64% yield after quenching with MeOBpin (Scheme 3). Adaption of the optimized conditions to the 3-F (**10b**), 3-Cl (**10c**), and 3-CF_3 (**10d**) substituted sulfonamides led to the respective products **11b**−**d** in modest but preparatively useful yields. An increase of electrophile equivalents was advantageous while use of Barbier conditions (**10d**) was unsuccessful (see SI).

Scheme 4. Synthesis of Bpin Pyridyl and Indolyl Sulfonamides



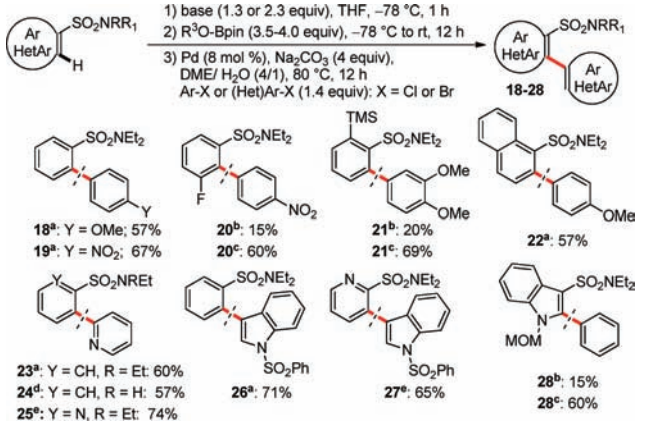
In view of the presence of heteroaromatic sulfonamides in bioactive molecules and natural products,[15,16] we examined the metalation−borylation sequence on selected pyridine **12**−**13** and indole **16** derivatives (Scheme 4).[17]

Despite the increasing availability of heteroaromatic boron derivatives[18] in the pyridine boronic acid and ester series,[19] protodeboronation problems are common in the synthesis of these compounds. In the case of **15**, that issue was overcome by adaptation of the Caron and Hawkins procedure[20] to prepare the product in a reasonable yield. Yet, sulfonamide **14**, prepared from **12** according to the metalation procedure of Quéguiner,[18] quenched with *i*-PrOBpin gave product **14** in an improved 83% yield. Indole Bpin derivative **17** was obtained in good yields from **16** under the standard conditions.

To take advantage of the reaction which has revolutionized our concept and practice for sp^2−sp^2 bond formation[21] and extend the tactical advantage of the D*o*M−cross-coupling strategy for the construction of polysubstituted (hetero)-aromatic compounds,[22] we investigated the Suzuki−Miyaura reaction on the now readily available Bpin derivatives. Previous results from our laboratories showed that Suzuki−Miyaura coupling of *ortho*-iodo arylsulfonamides with arylboronic acids proceeds sluggishly.[23] Furthermore, to the best of our knowledge, the one-pot D*o*M−Suzuki reaction with inverted coupling partners had not been reported. These deficiencies are overcome by use of coupling of the *ortho*-boropinacolato aryl sulfonamides with aryl and heteroaryl iodides as evidenced for selective Bpin sulfonamide coupling reactions (Scheme 5).

Initial studies on the selected substrates *p*-methoxyphenyl bromide and 2-chloropyridine in coupling with *ortho*-Bpin aryl sulfonamides **8a** and **9a** to give products **18** and **23**, **24** (82−90% yields) (see SI) established optimized conditions of catalyst $Pd(dppf)Cl_2{\bullet}CH_2Cl_2$ (8 mol %) and stoichiometry (1.4 equiv of aryl halide). These were then applied and generalized for the one-pot metalation−boronation−cross-coupling procedure for the reaction of tertiary and secondary sulfonamides with a variety of aryl and heteroaryl halides into the corresponding biaryls and heterobiaryls **18**−**28** (Scheme 5).

Scheme 5. One-Pot D*o*M−Suzuki−Miyaura Reaction



[a] *n*-BuLi (1.3 equiv), *i*-PrOBpin, $Pd(dppf)Cl_2{\bullet}CH_2Cl_2$. [b] *n*-BuLi (1.3 equiv), MeOBpin, $Pd(dppf)Cl_2{\bullet}CH_2Cl_2$. [c] *n*-BuLi (1.3 equiv), MeOBpin, $Pd(DtBPF)Cl_2$. [d] *n*-BuLi (2.3 equiv), *i*-PrOBpin, $Pd(dppf)Cl_2{\bullet}CH_2Cl_2$. [e] LDA (2.3 equiv), *i*-PrOBPin, $Pd(dppf)Cl_2{\bullet}CH_2Cl_2$.

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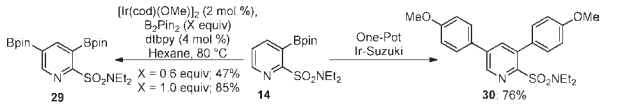
Both electron-rich and -poor aryl and heteroaryl bromides and, significantly, chlorides undergo coupling reactions uneventfully whereas the one-pot D*o*M−cross-coupling process with *meta* or *ortho* substituted sulfonamides require Pd(dtbpf)Cl_2 instead of Pd(dppf)Cl_2•CH_2Cl_2 as a catalyst to obtain acceptable yields of products (Scheme 5). With the assumption that the rate-limiting step in the Suzuki−Miyaura is reductive elimination, a more sterically hindered catalyst is required to obtain synthetically useful results.[24] To further include biheteroaryl sulfonamides in the repertoire of results, 2-pyridyl (**12**) and indole (**16**) sulfonamides were subjected to the one-pot cross-coupling process to afford biheteroarylsulfonamides **25**, **27**, and **28** respectively in good yields. As observed for sterically hindered sulfonamides (**20** and **21**), the yield of product is significantly affected by using catalyst Pd(dtbpf)Cl_2.

Having defined generality for the D*o*M−Bpin Suzuki−Miyaura methodology for the synthesis of biaryl and heterobiaryl sulfonamides, we sought to explore the further elaboration of these compounds in orthogonal coupling processes. In particular, the use of Ir-catalyzed C−H borylation, currently of interest in our laboratories,[25] was examined to provide potential bis-borylated substrates for differential coupling chemistries.

Hence, the pyridyl 3-Bpin-2-sulfonamide **14**, upon treatment under the Hartwig conditions[26] using 1 equiv of B_2pin_2, afforded bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) pyridine sulfonamide (**29**) in high yield (Scheme 6).[27] Furthermore, the potential for orthogonality of Ir- and Pd-catalyzed processes was demonstrated by the one-pot conversion of **14** into the azateraryl **30** in good yield.

In conclusion, a general robust D*o*M-based method for the preparation of *ortho*-Bpin aryl and heteroaryl sulfonamides (Schemes 2−4) has been developed using

Scheme 6. Ir-Catalyzed C−H Borylation



MeOBpin or *i*-PrOBPin as boron electrophile sources. Of bench-manipulation advantage, the majority of the produced arylsulfonamide *ortho*-boropinacolates are air stable and may be purified by flash chromatography. As an additional link in the D*o*M−cross-coupling synthetic strategy,[22] the Suzuki−Miyaura cross-coupling reaction of the Bpin sulfonamides with aryl and heteroaryl halides has been demonstrated (Scheme 5). The resulting products, already of interest due to the presence of the sulfonamide pharmacophore,[3,4] have evident synthetic potential for further D*o*M and cross coupling chemistry.[9b,c] The application of the attractive Ir-catalyzed borylation reaction which leads to bis-Bpin derivative **29** and its azateraryl coupling product **30** offers potential development of *in situ* boron group protection[25] and orthogonal coupling strategies for the construction of polyaryl frameworks. Some of these notions are under investigation.

Acknowledgment. We are grateful for support under the NSERC Discovery Grant (DG) program. E.B. is grateful to Prof. Paul Knochel (LMU, München) for support of work in the V.S. laboratories.

Supporting Information Available. Detailed experimental procedures and spectral data of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

(18) For commercial availability, see: http://www.combiphos.com/ and http://www.frontiersci.com/.

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