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Transition-Metal-Free *ipso*-Trifluoromethylthiolation of Lithium Aryl Boronates

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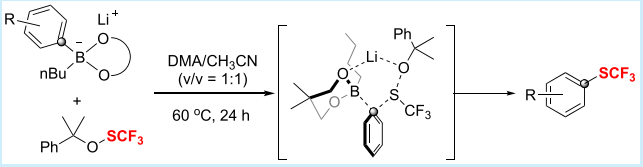
Supporting Information

ABSTRACT: A transition-metal-free direct trifluoromethylthiolation of the *ipso*-carbon of lithium aryl boronates with trifluoromethanesulfenate under mild conditions was described. In addition, late-stage site-selective C−H borylation/trifluoromethylation and C−Cl borylation/trifluoromethylthiolation of biologically active molecules was developed. Initial mechanistic study suggested that the Li^+ cation plays a vital role by coordinating to the oxygen atom of an aryl boronate complex and the oxygen of the reagent, thus allowing the aryl group to directly attack the trifluoromethylthio group of the trifluoromethylthiolating reagent.



Recently, the reaction of an electrophile with a lithium aryl boronate complex,[1] a type of so-called "ate complex" that could be readily generated in situ by mixing an aryl pinacol boronate with an alkyl lithium at room temperature,[2] has attracted great interests. The reaction often occurs under mild conditions in the absence of any transition metal catalyst, thus circumventing the drawbacks commonly associated with transition metal catalysts such as high cost, toxicity, and the need of an extra removal step from the pharmaceutical products.[3]

These studies have determined that the reaction pattern and the structure of the product were versatile and highly dependent on the substituents on the aryl group of the ate complex. For instance, pioneer work from Aggarwal's group showed that a lithium aryl boronate complex with a *meta*-electron-donating group could be activated by a suitable electrophile (NBS or DDQ) to induce the stereospecific formation of a $C(sp^2)$−$C(sp^3)$ bond (Figure 1A).[4] It was proposed that the reaction is triggered by an initial electrophilic attack (S_EAr) of the aryl group by an electrophile, followed by subsequent 1,2-migration of the alkyl group to the *ipso*-carbon of the dearomatized intermediate with the simultaneous elimination of halide and the boron moiety to give the final product. Alternatively, it was found that in the presence of an appropriate acylating reagent, lithium *ortho*- or *para*-hydrazinyl or *para*-phenoxide aryl boronate underwent N−N bond or O−Bi bond cleavage with concomitant 1,2-metalate rearrangement to give stereospecific $C(sp^2)$−$C(sp^3)$ bond formation (Figure 1B),[5] whereas, interestingly, with other substituents at the *ortho*- or *para*-position, the lithium aryl boronate complex often acts as a nucleophilic alkylating reagent to react with various of electrophiles such as NIS, NBS, TCAA, DIAD, or Selectfluor to give the functionalized alkane with inversion of the stereoconfiguration (Figure 1C).[6] Nevertheless, reaction of a lithium aryl boronate complex with an electrophile, wherein the boronate acts as an aryl nucleophile to give an *ipso*-carbon functionalized arene, has never been observed previously.

In 2013, our group initiated a project to develop a toolbox of electrophilic fluoroalkylthiolating reagents as it was reported that the fluoroalkylthiolating groups are highly lipophilic and may improve significantly the drug molecule's pharmacokinetics.[7] Since then, a series of trifluoromethylthiolating (CF_3S-),[8] difluoromethylthiolating (HCF_2S-),[9] and monofluoromethylthiolating (CH_2FS-)[10] reagents have been successfully invented. During the investigation of the reactions of these electrophilic reagents with lithium aryl boronate complexes, we unexpectedly discovered that reaction of lithium aryl boronate complexes with one of these reagents, trifluoromethanesulfenate **1a**, exclusively gave *ipso*-carbon trifluoromethylthiolated arenes in good yields (Figure 1D). The unprecedented reaction pattern for the reaction of a lithium aryl boronate with reagent **1a** differed dramatically from those with other electrophiles, thus prompting us to study the mechanism of the reaction. The mechanistic studies disclosed that Li^+ cation of the lithium aryl boronate complex played a vital role by coordinating to the oxygen atom of boronate and the oxygen of reagent **1a**, thus allowing the aryl group to directly attack the trifluoromethylthio group of the reagent. Herein, we would like to present these discoveries.

Reaction of lithium biphenyl neopentylglycolato boronate complex **2a** with electrophilic trifluoromethylthiolating reagent **1a** was initially chosen to probe the reaction pattern and reactivity. It was found that treatment of boronate **2a** with 1.5

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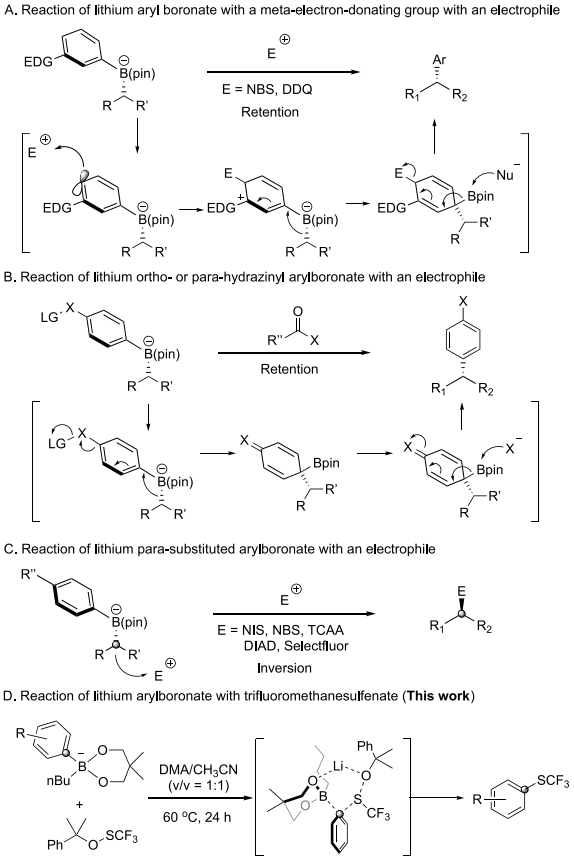
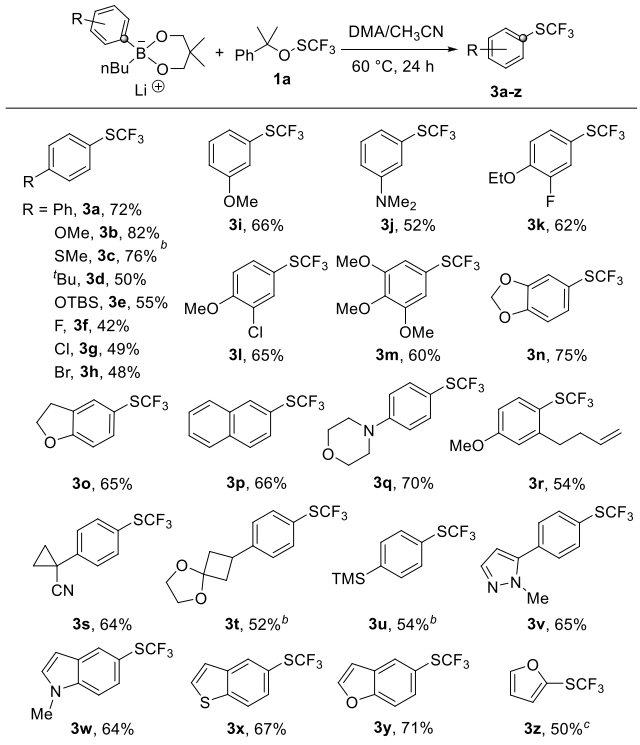


Figure 1. Reaction of the lithium aryl boronate complex with an electrophile.

equiv of reagent **1a** in DMF or DMA gave, unexpectedly, the direct *ipso*-C(sp^2)-trifluoromethylthiolated product **3a** in 10% and 14% yield, respectively, after 24 h at room temperature, whereas reactions in other common solvents such as CH_3CN, THF, CH_2Cl_2, or toluene did not occur at all. The yield of compound **3a** increased to 48% when the reaction was conducted in DMA at 60 °C. Interestingly, using mixed DMA/CH_3CN (v/v = 50/50) as the solvent improved the yield to 67%. In addition, the yield was further increased to 75% when the amount of reagent **1a** was increased to 2.0 equiv. Under these conditions, we then further examined the effect of other boronates and electrophilic trifluoromethylthiolating reagents. It was found that reaction using of pinacol boronate gave comparable yield, and using boronate derived from 1,3-diol gave slightly lower yield, whereas reaction using boronate derived from MeLi was ineffective and using boronate derived from ^{t}BuLi occurred in 36% yield. On the other hand, reactions of lithium aryl boronate **2a** with several other electrophilic trifluoromethylthiolating reagents **1b**−**1d**[8] did not take place at all, indicating the unique and crucial role of reagent **1a** in this reaction (see Table S1 in the Supporting Information for details). Notably, under these conditions, products for the reaction of a lithium aryl boronate with other electrophiles such as the C(sp^2)−C(sp^3) bond-forming compounds or functionalized alkanes were not observed.

The unique reaction pattern for the reaction of lithium aryl boronate with electrophilic trifluoromethylthiolating reagent **1a** prompted us to investigate the generality of the reaction, and the results are summarized in Scheme 1. In general, lithium aryl boronates with both electron-rich (**3a**−**3e**, **3i**−**3j**, **3m**−**3u**) and

Scheme 1. Scope for the Reaction of Lithium Aryl Boronates with Reagent 1a[a]



[a]Reaction conditions: lithium biphenylboronate (0.2 mmol), reagent **1a** (0.4 mmol) in DMA/CH_3CN (v/v = 1/1, 2.0 mL) at 60 °C for 24 h under an argon atmosphere. Isolated yields. [b]Reagent **1a** (0.6 mmol) was used. [c]Yields were determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

electron-deficient aryl groups (**3f**−**3h**, **3k**−**3l**) reacted smoothly after 24 h at 60 °C to give the corresponding trifluoromethylthiolation products in good yields (42−82%). Unlike previous reported transition-metal-free coupling reactions of lithium aryl boronates with electrophiles, in which the reaction pattern was greatly affected by the position of the substituents on the aryl group,[1] the current reaction was not affected by the substituents at all. Reactions of lithium aryl boronates with substituents at the *ortho*-position (**3r**), *meta*-position (**3i**−**3o**), or *para*-position (**3a**−**3h**, **3k**−**3o**, **3q**−**3u**) of the aryl group reacted smoothly to give the corresponding products in good yields. It is worth mentioning that reactions of lithium aryl boronate containing a *meta*-electron-donating methoxy or dimethylamino group also afforded the desired *ipso*-carbon-trifluoromethylthiolated product in high yields (**3i**−**3j**). In these cases, the formation of sp^2−sp^3 cross-coupling products was not observed. Gratifyingly, this methodology was successfully applied to trifluoromethylthiolation of lithium heteroaryl boronates to give the corresponding trifluoromethylthiolated heteroarenes including indole (**3w**), benzothiophene (**3x**), benzofuran (**3y**), furan (**3z**), and pyrazole (**3v**) in high yields. Furthermore, many common functional groups including fluorine, chlorine, bromine, and phenol protected by *tert*-butyldimethylsilyl, dimethylamino, acetal, ketal, morpholine, olefin, cyano, and trimethylsilyl were well-tolerated.

To further expand the scope of the current site-specific trifluoromethylthiolating protocol, we developed a C−H activation borylation/trifluoromethylthiolation sequence. As shown in Scheme 2, under the conditions developed by Hartwig

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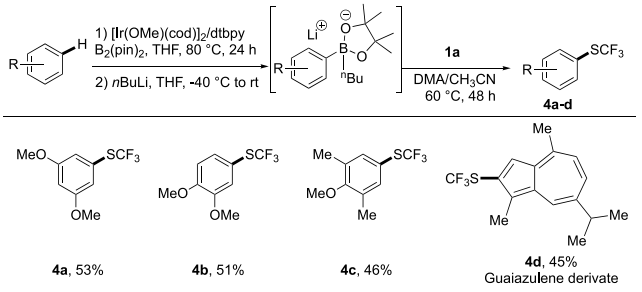
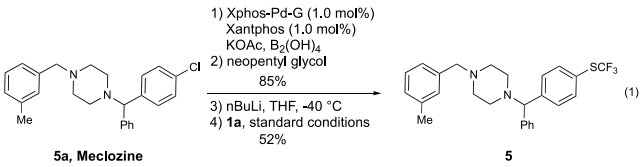
Scheme 2. C−H Borylation/Trifluoromethylthiolation of Arenes

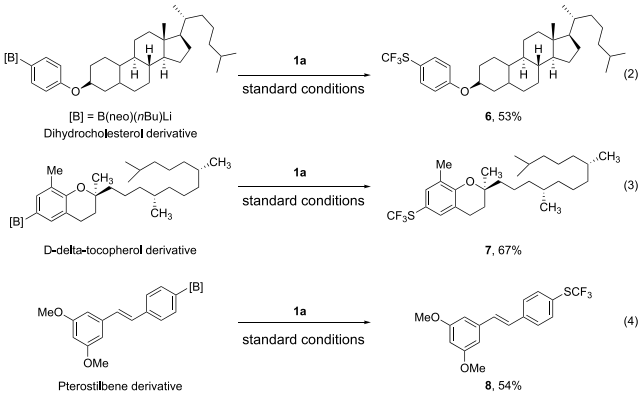


and co-workers for Ir-catalyzed highly selective C−H borylation of arenes,[11] a few 1,2- or 1,3-disubstituted arenes were selectively borylated. Without isolation, the aryl boronates were treated with ^{n}BuLi and reagent **1a** to give the corresponding trifluoromethylthiolated arenes **4a−d** in good yields.

Many drug molecules and agrochemicals contain a C−Cl bond, and the trifluoromethylthio group is generally considered as a pseudohalogen.[12] We, therefore, envisaged whether the C−Cl bond in these compounds can be converted to their analogous trifluoromethylthiolated derivatives. For example, Meclozine (**5a**), an antihistamine used to treat motion sickness,[13] contains a C−Cl bond that could be easily converted into aryl boronic ester (**5b**) through palladium-catalyzed coupling with diboronic acid, followed by *in situ* esterification with neopentyl glycol. Treatment of the boronic neopentyl glycol esters (**5b**) with ^{n}BuLi generated *in situ* lithium aryl boronate, which was further converted to the trifluoromethylthioated arene (**5**) in 52% yield under standard reaction conditions (eq 1).



To illustrate the applicability of this protocol, we applied it to transition-metal-free late-stage trifluoromethylthiolation of natural products or drug molecules including dihydrocholesterol, D-δ-tocopherol, and pterostilbene. As shown in eqs 2−4, these reactions occurred smoothly to give the corresponding products **6−8** in good yields.



To further evaluate the utility of this protocol, we tried to synthesize Tiflorex, a marketed drug for the treatment of anorexia nervosa, under the standard conditions.[14] Aryl boronic ester **10a** could be obtained in 90% yield through lithium−halogen exchange of **9**, followed by addition of tri*iso*propyl borate and neopentyl glycol. Treatment of boronic ester **10**a with 1.0 equiv of ^{n}BuLi generated *in situ* the corresponding lithium aryl boronate **10**. Without isolation, lithium aryl boronate was allowed to react with reagent **1a** under the standard conditions to give compound **11** in 53% yield. Hydrolysis of the acetal protecting group in compound **12**, followed by reductive amination, afforded Tiflorex in 89% yield (Figure 2).

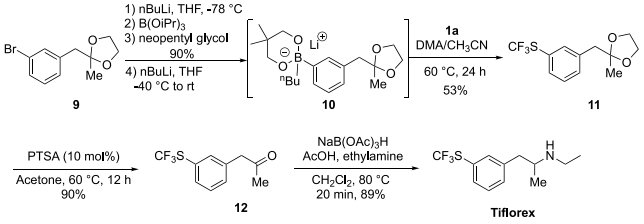


Figure 2. Transition-metal-free preparation of Tiflorex.

We have now established a unique, general reaction between lithium aryl boronates and electrophilic trifluoromethylthiolating reagent **1a**, which differed greatly from reactions of lithium aryl boronates with other electrophiles. Mechanistically, the current reaction should proceed through a different pathway other than those illustrated in Figure 1A−C. We next shifted our investigation to explore the mechanism of the reaction.

First, to probe whether the reaction goes through a free radial or single-electron transfer (SET) process, we studied the reaction in the presence of 1.0 equiv of free radical inhibitor, such as the radical trap (TEMPO) and 2,6-di-*tert*-butyl-4-methylphenol or SET inhibitor 1,4-dinitrobenzene. It was found that the yields of the reaction in the presence of these agents decreased slightly. Yet, the reactions were not completely inhibited (Figure 3a). In addition, reaction of lithium aryl boronate, which contained an alkene moiety and can serve as a radical cyclization probe under the standard conditions, afforded

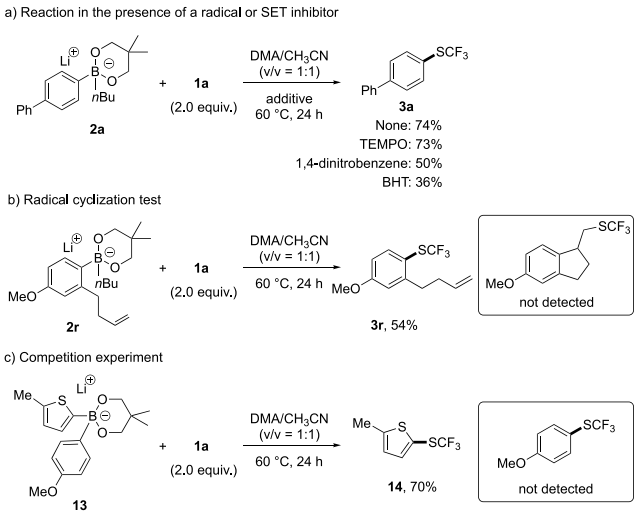


Figure 3. Mechanistic investigation.

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the *ipso*-C(sp^2)-trifluoromethylthiolated product **3r** in 54% yield. In this case, the radical cyclization product was not observed (Figure 3b). These results are against a free radical or SET pathway.

Next, an intramolecular competition experiment of lithium diaryl boronate **13** with two different aryl groups showed that trifluoromethylthiolated thiophene **14** was obtained exclusively in 70% yield, along with 4-methoxyphenylbronic neopentyl glycol ester, which was detected by GC-MS (Figure 3c). If the reaction proceeds via a homolytic cleavage of the aromatic carbon−boron bond to form an aryl radical, which then attacks reagent **1a** to afford the product, we would observe two trifluoromethylthiolated products because the bond strength of both carbon−boron bonds in lithium diaryl boronate **13** is similar. The fact that the reaction was highly selectively to afford compound **14** supports that the reaction did not proceed via a free radical pathway.

To get more insight into the reaction mechanism, we studied the kinetics of the reaction. It was found that the reaction was first-order in reagent **1a** and aryl boronate complex **2i** (see Supporting Information for details), which indicated that both the lithium aryl boronate and the reagent were involved in the rate-determining step of the reaction.

Finally, to probe the effect of the lithium cation on the reaction, we studied the reaction in the presence of different amounts of 12-C-4. It was found that the yields decreased significantly with the increase of the amount of 12-C-4 (Figure 4). These results suggest that the lithium cation played a vital role in the formation of the desired product.

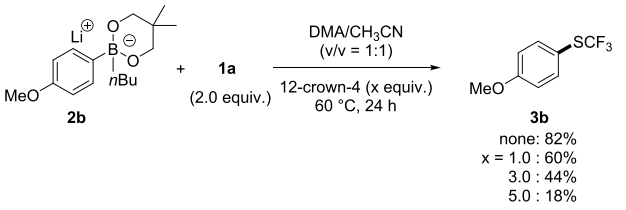

Figure 4. Reaction of lithium aryl boronates with reagent **1a** in the presence of 12-C-4.

We proposed that the reaction likely proceeds via a transition state in which the lithium cation coordinates to both the oxygen atom of the aryl boronate complex and the oxygen atom of reagent **1a** at the same time, as shown in Figure 1d. The aryl group then attacks the trifluoromethylthio group to give the product. To gain more support for this mechanistic assumption, DFT calculations were conducted.[15] As shown in Figure 5, it was found that the transition state in which the lithium cation coordinates to the two oxygen atoms of both reagents was 8.2 kcal/mol lower than the transition state in which the lithium cation coordinates to the oxygen atom of the aryl boronate and the fluorine atom of reagent **1a**. Consequently, the attack of the aryl group of the boronate to the trifluoromethylthio group of reagent **1a** is much easier than the attack of the butyl group of the boronate.

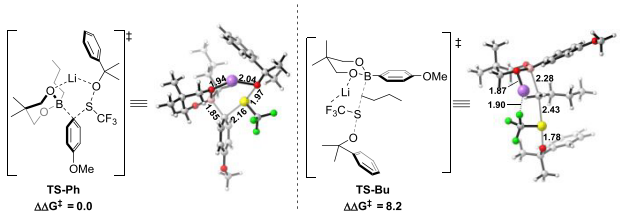

Figure 5. Computed transition state structures for aryl and alkyl trifluoromethylthiolation and their relative free energies in kcal/mol using the (SMD)-B3LYP-D3(BJ)/6-311+G(2d,p)//(SMD)-M06-2X/6-31G(d,p) method.

In summary, an unprecedented transition-metal-free direct *ipso*-C(sp^2)-trifluoromethylthiolation of lithium aryl boronate complexes was developed. This reaction represents a new reaction pattern for the reaction of a lithium aryl boronate with an electrophile. Moreover, the current protocol is a complementary method for the preparation of trifluoromethylthiolated arenes.[16] With this protocol, late-stage site-specific C−H and C−Cl trifluoromethylthiolation of biologically active molecules was realized. Furthermore, the protocol was successfully applied to the synthesis of Tiflorex, a marketed drug for the treatment of anorexia nervosa. Mechanistic study indicates that the lithium cation plays a vital role by coordinating to both oxygen atoms of boronate and the trifluoromethylthiolating reagent at the same time, thus promoting the attack of the aryl group toward to the trifluoromethylthio group. Studies of lithium aryl boronate complexes with other electrophilic fluoroalkylating reagents developed in our laboratory are currently underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02236.

Synthesis, analytical data, computational details, and NMR data of **2a**, **2b**, **3a**−**3z**, **4a**−**4d**, and **5**−**14** (PDF)

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Notes

The authors declare no competing financial interest.

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