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# *Para*-selective borylation of monosubstituted benzenes using a transient mediator

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Herein, we conceptualized a transient mediator approach that has the capability of *para*-selective C–H functionalization of monosubstituted aromatics. This approach is enabled by *in situ* generation of a versatile sulfonium salt via highly electrophilic phenoxathiine or thianthrene dication intermediate which can be readily generated from its sulfoxide with trifluoromethanesulfonic anhydride. Preliminary mechanistic study implied that the remarkable *para* selectivity might be related to the incredible electrophilicity of thianthrene dication intermediate. The versatility of this approach was demonstrated via *para*-borylation of various monosubstituted simple aromatics combining the sulfonium salt formation with further photocatalyzed transformation.

**para-borylation, monosubstituted arene, transient mediator, thianthrenation, sulfide dication**

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Tremendous efforts have been made to the field of precise control the site selectivity in C–H functionalization of aromatics during the past two decades [1,2]. However, achieving *para*-selectivity in direct C–H functionalization reactions remains a significant challenge, especially when the targeted arene owns multiple reactive sites with subtle steric and electronic discrepancy. Typically, *para*-selectivity control was often dominated by steric and electronic factors of substrates, and high selectivity was observed mainly for electron-rich arenes, which have been represented in electrophilic aromatic substitution reaction of aromatics [3]. Recently, major progress to face this challenging *para*-C–H functionalization has been achieved through electronic recognition [4], steric control [5], template assistance [6], and radical involved processes [7] (Scheme 1(a)). Despite undisputable advances, those methods are still lack of generality and sufficient regioselectivity, either requiring large excess of arenes or working with the assistance of directing group (template), and normally resulting in a mixture of *para*-substituted product with other isomers. The development of general and efficient approaches to achieve *para*-C–H functionalization without directing group assistance remains a significant task. Herein, we conceptualized a *transient mediator approach* that enables *para*-selective functionalization of monosubstituted benzene derivatives (Scheme 1(b)). We envisioned that a mediator could be selectively introduced to the *para* position of the substituents via a highly electrophilic cation or dication with electron or steric recognition. This obtained species could be readily converted to other functionalities with high efficiency pro-

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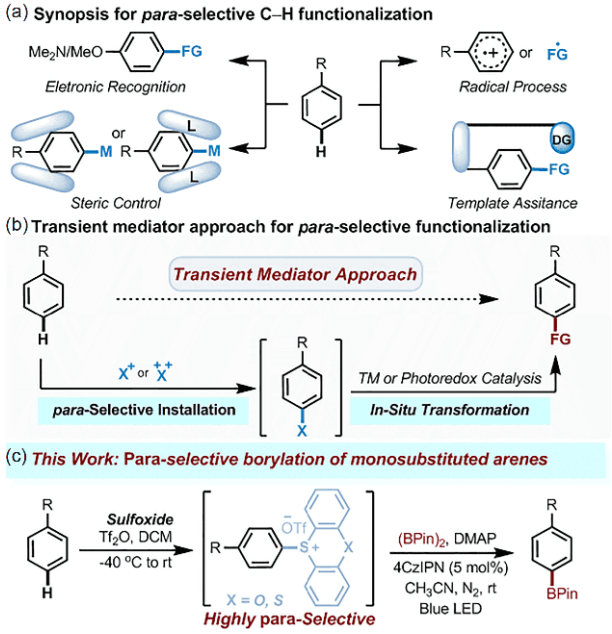
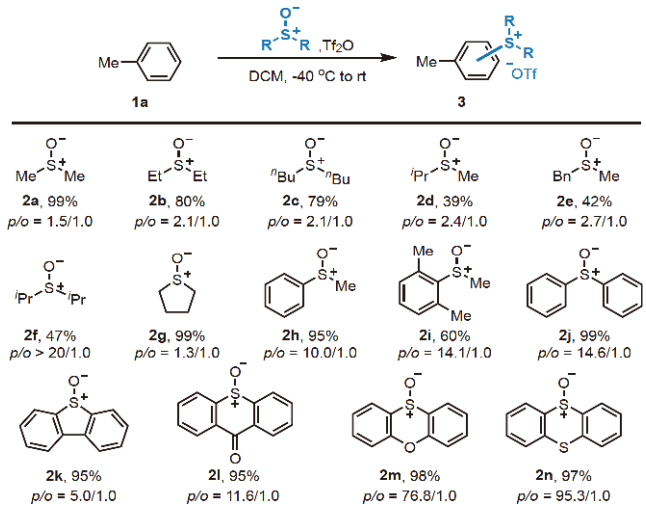



**Scheme 1** Background and synopsis for *para*-C–H functionalization of monosubstituted arenes (color online).

viding the *para*-decorated aromatics. By carefully selecting the transient mediator and conditions, *para*-functionalization of monosubstituted benzene could be realized in a single synthetic operation. In this case, highly electrophilic phenoxathiine or thianthrene dication intermediate [8], *in situ* initiated by its sulfoxide with trifluoromethanesulfonic anhydride, was capable of generating the corresponding sulfonium salt with a high *para*-selectivity. *Para*-borylation of monosubsituted benzenes was realized by combining the sulfonium salt formation with further photocatalyzed borylation using phenoxathiine or thianthrene as the transient mediator.

We started our investigation by searching a suitable transient mediator, which has the capability of being installed at the *para*-position of the monosubstituted aromatics with high selectivity, and being readily converted to other functional groups. Being aware of the remarkable activity of sulfide ditriflate, a highly active intermediate formed *in situ* by treating sulfide oxide with $Tf_2O$ [9], we hypothesized that the electrophilic sulfate ditriflate reagents might be a potential handle for addressing this challenging problem by adjusting the steric effects. *In situ* generated dimethyl sulfide ditriflate (DMSD) reacted with toluene providing the corresponding sulfonium salts in 99% yield with an insufficient selectivity (*p*/*o*=1.5/1.0). The selectivity was slightly improved with the increase of steric hindrances (**2b**–**2e**). Diisopropyl sulfoxide (**2f**) gave a remarkable *para*/*ortho* ratio of >20/1.0, whereas the efficiency of sulfonium salt formation is unsatisfying and cannot be further improved probably due to bulky isopropyl substituent. It is noteworthy that methyl phenyl sulfoxide (**2h**) maintained the high efficiency and high selectivity simultaneously, giving 10.0/1.0 selectivity and 95% yield. Encouraged by this result, we decided to focus on evaluation of aryl sulfoxides (**2i**–**2n**) (Scheme 2). Although more steric hindrance sulfoxide **2i** led to lower reactivity, diphenyl sulfoxide **2j** provided its sulfonium salt in quantitative yield with similar selectivity. Compared to diphenyl sulfoxide, less steric hindrance dibenzothiophene sulfoxide (**2k**) and thioxanthone sulfoxide (**2l**) resulted in lower selectivities. Gratifyingly, phenoxathiine sulfoxide (**2m**) and thianthrene sulfoxide (**2n**) significantly improved the selectivity to >76/1 (*para*/*ortho*) with high efficiency.

To shed light on the causation for remarkable *para* selectivity using phenoxathiine and thianthrene derived sulfoxide, detailed mechanistic studies were carried out. Although the sulfoxide screening confirmed that the regioselectivity can be partially controlled by the steric effects, the electron paramagnetic resonance (EPR) experiment of the reaction system with various *in situ* generated sulfide ditriflates indicated that the striking *para*-selecitivity might also be related to the formation of phenoxathiine [10a] and thianthrene radical cation intermediates [10b–10f,11]. In comparison, thioxanthone sulfoxide (**2l**) with similar scaffold without EPR response resulted in a lower *para* selectivity (Figure 1(a)). However, the reaction did not proceed at low concentration of sulfoxide and $Tf_2O$, although the radical cation intermediate existed which confirmed by the EPR experiment. We hence doubted whether the radical cation intermediate is real reactive species for sulfonium salts formation, and were intrigued by the origin of the outstanding regioselectivity. To further understand this process, preliminary computational studies were performed at SMD-M062x/def2-TZVP level of theory, and three possible intermediates, radical cation, radical cation dimer and sulfide dication, were systematically investigated. The intermediates of C–S formation with toluene and thianthrene radical cation did not show apparently energy difference (<0.6 kcal/mol), indicating the poor selectivity of *para*/*ortho* position by the calculated energy scanning of forming C–S distance (Figure S8, Supporting Information online). Based on Dunsch's study [10g], a dimer intermediate could be formed via a reversible dimerization of thianthrene radical cation; however, the dimer can not lead to stable adducts for the reasonable *para*/*ortho* selectivity in the electrophilic substitution of toluene through calculations (Figure S9). We next turned our attention to the plausible thianthrene dication intermediate, and found the sulfide dication intermediate is facile from heterolysis of sulfide ditriflate **2n-OTf** with slightly endothermic rather than disproportionation from thianthrene radical cation. The large free energy difference (>4.0 kcal/mol) between *para*- and *ortho*- intermediates imply that the sulfide dication would be the possible active species responsible for the high regioselectivity. And the dispersedly positive NPA charge (Figure S11) on both




**Scheme 2** Evaluation of sulfoxides. Conditions: toluene (0.5 mmol), sulfoxide (0.6 mmol), $Tf_2O$ (0.6 mmol), DCM (0.5 mL), $N_2$; −40 °C for 30 min, then rt for 1 h. The yield was determined by $^1H$ NMR using $CH_2Br_2$ as the internal standard. The selectivity was determined by the $^1H$ NMR (color online).

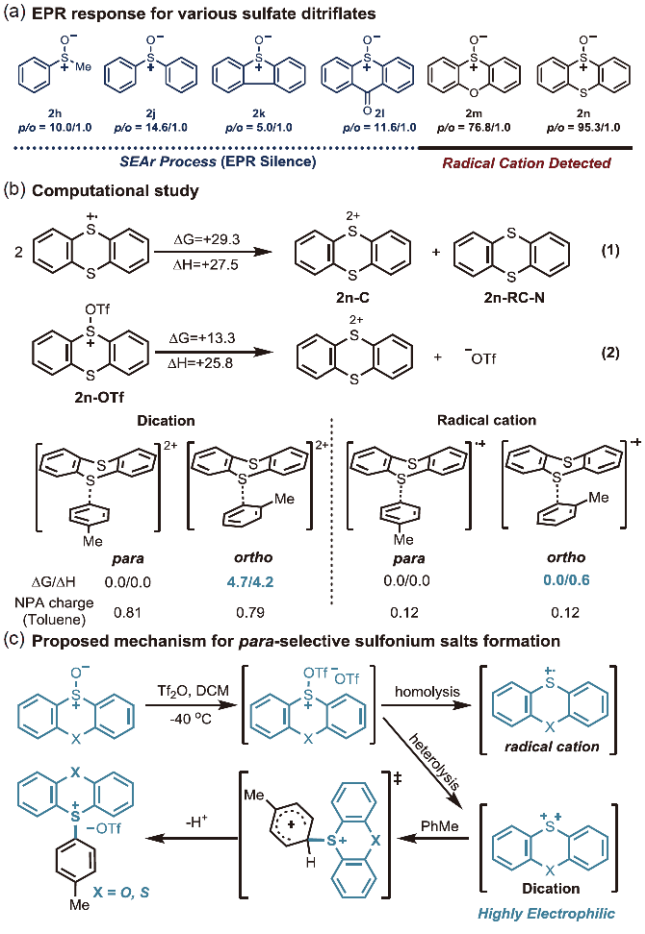
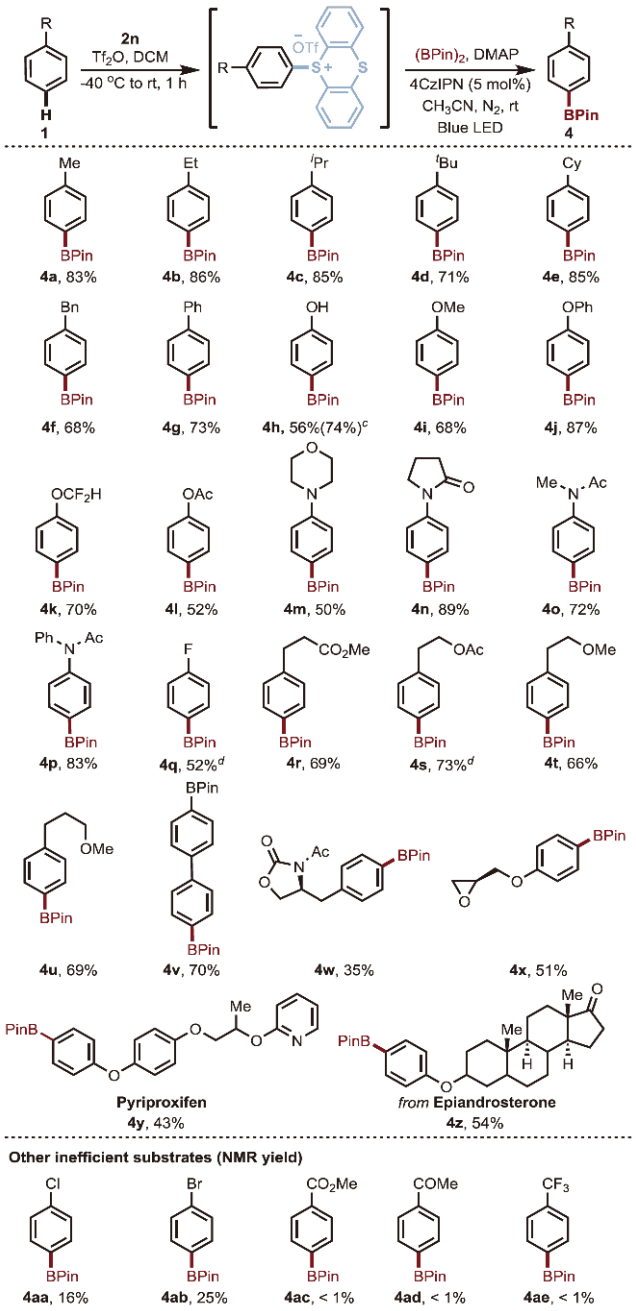



**Figure 1** Mechanistic study (color online).

thianthrene and toluene lead to the *exo*-conformation in the favorable *para*-intermediate to minimize the electrostatic repulsions, which can rationalize the experimental observation of high *p*/*o* ration. Based on the DFT study, we therefore postulated that the *para*-selective sulfonium formation proceeded via electronic substitution with the highly electrophilic sulfide dication intermediate, followed by deprotonation to form sulfonium salts (Figure 1(c)). Besides, the low efficiency with electron-deficient substrates, like $PhCF_3$, $PhCO_2Me$, also supported this reaction proceeded via cation intermediates [11a].

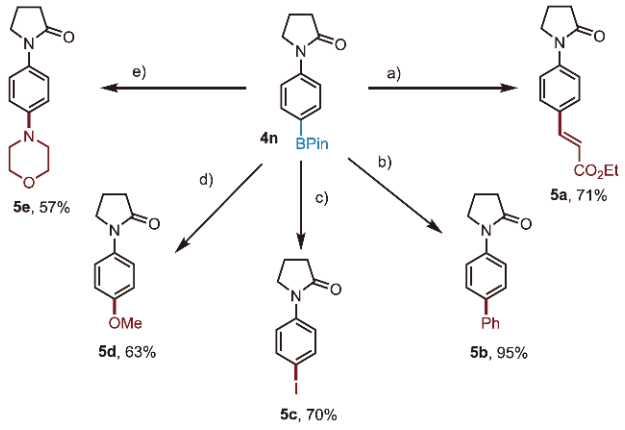
Given the versatility of aryl boronic acid in organic synthesis [12] , we are curious if we can achieve the *para*-borylation of monosubstituted benzenes by *in situ* converting the resulted sulfonium salt [13] in a single synthetic operation. Several elegant examples towards the challenging *para*-C–H borylation of arenes have been witnessed in the last decade. For example, Itami and coworkers [5b] have reported an Ir-catalyzed *para*-C–H borylation by altering the steric hindrance on ligands, and moderate to poor *para* selectivity was obtained using less congested monosubstituted arenes, such as cumene (*para*:others=58:42) and ethylbenzene(*para*:others=32:68). Recently, Nakao's group [5d–5f] and Chattopadhyay's group [6c] have achieved the Ir-catalyzed *para*-selective borylation of aromatic esters and amides in high selectivity by adopting the rational designed bimetallic or noncovalent interaction strategy. However, those strategies can not be extended to undirected aromatics without polar functional group assistance. After scrupulously evaluated the reaction parameters for *para*-borylation, we found the *para*-borylated toluene can be obtained in 83% yield using DMAP as base and activator, 4CzIPN as photocatalyst in $CH_3CN$ (For detailed screening, see Supporting Information online). With the optimized conditions in hand, the generality of this protocol was examined. As summarized in Scheme 3, alkylated benzene derivatives provided desired borylated products in high yields (**4a**–**4e**), while diphenylmethane gave moderate yield (**4f**, 68% yield). Biphenyl also produced the corresponding boronic acid pinacol ester in 73% yield (**4g**). Electron rich phenol (**1h**–**1l**) and aniline (**1m**–**1p**) derivatives are also suitable substrates for this protocol, in which the tolerance with difloromethoxybenzene, *N*-phenylmorpholine, 1-phenyl-2-pyrrolidinone is noteworthy. TIPS-protected phenol (**1h**) provided the unmasked *para* borylated phenol in 74% yield, whereas phenol also can be used in the reaction with slightly lower yield. Electron-deficient fluorobenzene (**1q**) was compatible with this procedure along with high *para* selectivity. Derivatives of hydrocinnamic acid (**1r**), 2-phenylethanol (**1s**, **1t**), phenylpropanol (**1u**), borylated biphenyl (**1v**), *L*-phenylalaninol (**1w**), and (*S*)-2-oxiranylanisole (**1x**) underwent this protocol yielding the desired products in moderate to high yields. Some complex scaffolds (**1y, 1z**) were also compatible, demonstrating this protocol is versatile for late-stage functionalization of drug molecules. Moreover, the electron deficient substrates provided low activities (**1aa**–**1ae**) probably due to the electro-




**Scheme 3** Scope of monosubstituted arenes. a) Reaction conditions: 1) **1** (0.2 mmol), **2n** (1.2 equiv.), $Tf_2O$ (1.2 equiv.), DCM (1.0 mL), −40 °C to rt, 1 h; 2) 4-dimethylaminopyridine (DMAP) (2.0+2.0 equiv.), 4-CzIPN (5 mol%), $(BPin)_2$ (4.0 equiv.), blue LED, 8 h. b) Isolated yield; for all substrates, high *para* selectivities were obtained (*para*/*others*>50/1). c) TIPS-protected phenol was used. d) Reaction conditions: **2n** (2.4 equiv.), $Tf_2O$ (2 equiv.) and DMAP (3+2 equiv.) were used (color online).

philic nature of dication intermediate in the sulfonium salts formation step.

The *para*-borylated products can be readily transformed to various *para*-decorated arenes efficiently as summarized in Scheme 4. Using **4n** as model scaffold, the boronic acid pinacol ester can be smoothly converted to alkenyl, aryl, iodide, methoxyl, and aminyl in high efficiency. This protocol opens a new avenue for synthesis of 1,4-disubstituted arenes, a scaffold frequently found in biologically active compounds.




**Scheme 4** Transformation of aryl boronate. Conditions: a) $CH{=}CHCO_2Et$, $Pd(OAc)_2$ (10 mol%), $Na_2CO_3$ (2.0 equiv.), DMF, 50 °C, $O_2$, 3 h; b) PhBr (1.0 equiv.), $Pd(dppf)Cl_2$ (5 mol %), $K_3PO_4$ (3.0 equiv.), $H_2O$ (5.0 equiv.), THF, 70 °C, 3 h; c) KI (1.5 equiv.), CuI (10 mol%), 1,10-phenanthroline (20 mol%), $MeOH/H_2O$, 80 °C, 20 h; d) MeOH, $Cu(OAc)_2$ (1.0 equiv.), DMAP (2.0 equiv.), 4 Å MS, rt, air, 24 h; e) morpholine (2.0 equiv.), $Cu(OAc)_2$ (1.0 equiv.), $Et_3N$ (2.0 equiv.), 4 Å MS, $CH_3CN$, 80 °C, air, 24 h (color online).

In summary, *para*-borylation of monosubstituted benzenes has been demonstrated using phenoxathiine or thianthrene as the transient mediator. Preliminary mechanistic study indicated that the key to the remarkable *para*-selectivity might be the use of highly electrophilic phenoxathiine or thianthrene dication species. Detailed mechanistic study and the application of this transient mediator approach for site-selective functionalization are ongoing projects in our laboratory.

**Supporting information** Experimental procedures, complete characterization data, copies of $^1H$ and $^{13}C$ NMR spectra. The supporting information is available online at http://chem.scichina.com and http://link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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**Conflict of interest** The authors declare that they have no conflict of interest.

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