Synthesis S. Pinet et al. Special Topic

# Radical Metal-Free Borylation of Aryl Iodides

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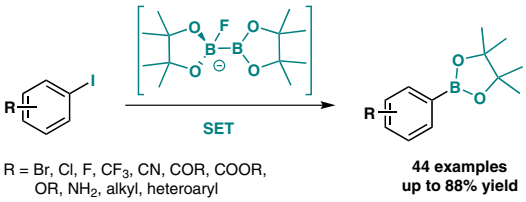


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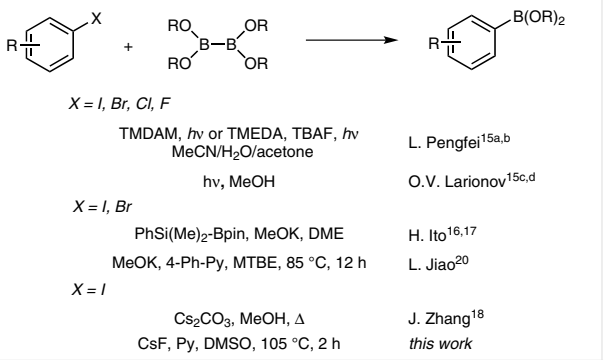
**Abstract** A simple metal-free borylation of aryl iodides mediated by a fluoride $sp^2$–$sp^3$ diboron adduct is described. The reaction conditions are compatible with various functional groups. Electronic effects of substituents do not affect the borylation while steric hindrance does. The reaction proceeds via a radical mechanism in which pyridine serves to stabilize the boryl radicals, generated in situ.

**Key words** metal-free borylation, radical process, cesium fluoride, pyridine

Arylboronic acids and their derivatives are known to be very important compounds in organic chemistry, as both chemical intermediates and building blocks.[1] Traditional methods of preparation include a metal–halogen exchange with lithium or magnesium on an aryl halide, followed by reaction with trialkoxyboranes.[1] Very recently, such reactions have been extended to encompass aminoboranes[2] and bench-stable amine borane complexes.[3] In parallel, metal-catalyzed Miyaura's borylation of aryl halides, sulfonates, and diazonium salts with either alkoxyboron and dialkoxydiboron,[4] or aminoboranes,[5] and amine-borane complexes[6] have been largely developed. Very recently, thermal[7] and photochemical[8] metal-free borylation of isolated diazonium salts or those generated in situ from anilines and triazenes, have been studied. One example of metal-free borylation of diaryliodonium salts has also been reported.[9] In contrast, metal-free borylation of aryl halides has been less investigated (Scheme 1). In 2016, metal-free borylation of aryl halides under irradiation was described by Mfuh et al.[10] and Chen et al.[10c,d] In 2012, Ito et al. reported an alkoxy-mediated borylation of aryl bromides with silylborane,[11] leading to the proposal of a carbanion-mediated mechanism.[12] In 2013, Zhang et al. showed that cesium carbonate was also able to mediate the borylation of aryl iodides with diboron in methanol.[13] In this case, the authors ruled out a radical mechanism, only mentioning a possible C–I bond cleavage by cesium.

In 2009, Marder's group published a copper-catalyzed borylation of aryl iodides in the presence of dialkoxydiboron and potassium *tert*-butoxide.[14] According to the authors, in such conditions, a borylcopper species is formed, promoting the borylation. If one considers examples of base-mediated aryl halide borylations, the necessity for the formation of a copper-boryl complex can be questioned. In other words, can borylation of aryl halides be promoted by *tert*-butoxide alone, or by other nucleophiles known to form with dialkoxydiboron $sp^2$–$sp^3$ diboron adducts? In this context, we present here a metal-free borylation of aryl iodides triggered by fluoride salts in the presence of pyridine operating via a radical mechanism. During the preparation of this paper, Zhang et al. reported a very similar borylation method with potassium methoxide, in the presence of 4-phenylpyridine.[15]




**Scheme 1** Metal-free borylation of aryl halides

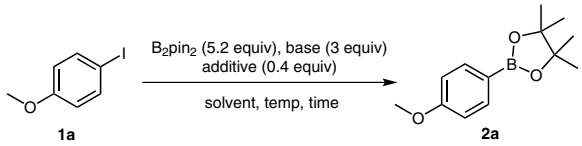
Using an excess of bispinacolatodiboron as the borylating agent and 3 equivalents of potassium *tert*-butoxide, known to form $sp^2$–$sp^3$ diboron adduct,[16] as starting conditions the reaction mixture was heated to 100 °C in DMF for 24 hours leading to the desired borylated product **2a** in 9% yield (Table 1, entry 1). Despite the low yield, this clearly indicates that copper is not compulsory, providing that the mixture is sufficiently heated. This in turn, prompted us to investigate the use of additives. Ethanol, likely to generate a more nucleophilic ethoxide in situ, slightly improved the yield (entry 2) whilst increasing the temperature to 140 °C had a negative impact on the reaction (entry 3). Use of phenanthroline led to better results. Indeed, at 80 °C **2a** was obtained in 49% yield, which was increased to a decent 78% at 105 °C (entries 4 and 5). Yields were similar in NMP or DMAC but improved in DMSO, **2a** reaching 87% (entries 6 to 8). Using sodium instead of potassium as the counter ion did not significantly affect the course of the reaction (entry 9). On the other hand, replacing the *tert*-butoxide by either phenoxide or methoxide affected the product's yield drastically (entries 9 and 11). Replacing potassium *tert*-butoxide by cesium fluoride improved the yield of **2a** to 94%. Keeping cesium fluoride as the nucleophile, this reaction was conducted at 105 °C in other solvents such as toluene, DMF, *N*-methylpyrrolidinone, pyridine, dichloroethane, nitromethane, ethylene glycol diacetate, and isoamyl acetate. This, however, mostly led to poor conversion (inferior to 20%) of the aryl iodide.

Results obtained in the presence of sodium methoxide were surprisingly not in agreement with the mechanism proposed by Marder to explain Zhang's aryl iodide borylation.[13] Following the proposed mechanism, methanol would be deprotonated by cesium carbonate. The resulting nucleophilic methoxide would then attack one boron atom of the diboron to form the $sp^2$–$sp^3$ diboron adduct $[B_2pin_2OMe]^-$, nucleophilic enough to facilitate the synthesis of the pinacolboranate ester.[16] As methylate is more nucleophilic than *tert*-butoxide, one would expect a better result with methoxide. Nevertheless, the opposite was observed. In the absence of phenanthroline, the reaction became sluggish (Table 1, entries 1 and 13). One can therefore wonder if an ionic mechanism is really implied in this arylborylation or a radical process occurs. *tert*-Butoxide is known to be a reducing agent by itself,[17] or as adduct with ligands[18] such as phenantholine,[19] phenylhydrazine,[20] dialkylamines,[21] and diols.[22] Furthermore, fluoride has also been used as a reductant in single-electron-transfer processes.[23]

During this preliminary study, the formation of anisole was noticed. This by-product may result from either a protodeborylation phenomenon or the direct protonation of an intermediate. Reaction optimization was continued using 1-iodonaphthalene, which had usually led to mitigate results and can therefore be used to increase the discrepancies between reaction conditions (Tables 2 and 3). Various experiments were conducted varying the bispinacolatodiboron:CsF ratio (Table 2, entries 1 to 14). In the absence of cesium fluoride, no reaction occurred, indicating that this reagent is mandatory to the reaction (entry 1). Moreover, it seems that three equivalents of cesium fluoride are required to reach a complete conversion of **1b** (entries 4, 5, 8, 12, and 13). A minimum of 2 equivalents of bispinacolatodiboron is essential to attain an acceptable yield of **3a** (entries 8, 9 12, and 13 vs entries 4 and 5). Using higher amounts of diboron does not improve **3a** formation (entries 10 to13) and increasing the cesium fluoride quantity favors the formation the by-product **4** (entry 4 vs 5, and entry 8 vs 9).

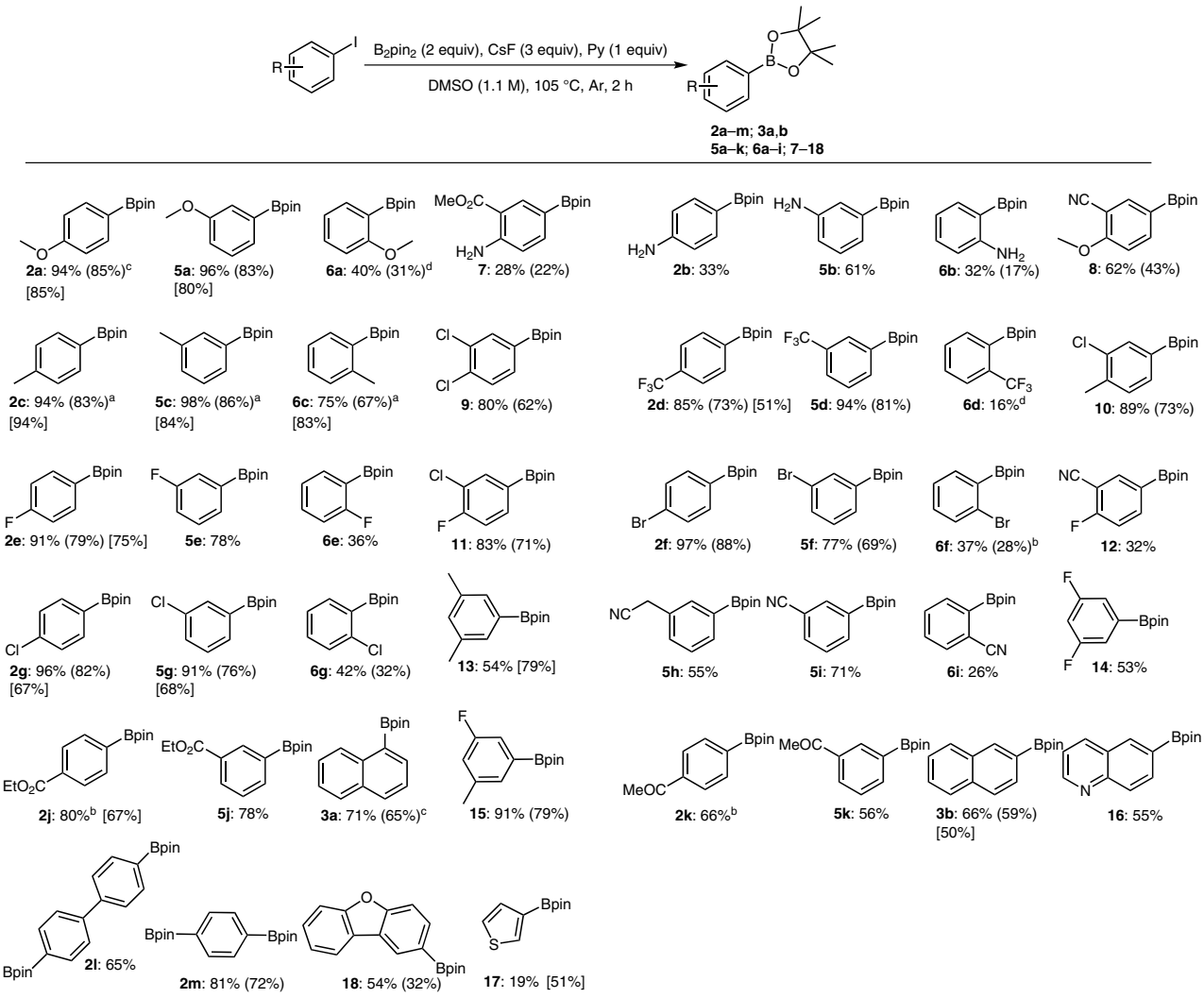
As a result, a 2:3 $B_2pin_2$/CsF ratio was kept. Varying the halide source, we clearly demonstrated that the softer the fluoride counter ion is, the better the results are (Table 2, entries 8, 14 to 16). Interestingly, tetramethylammonium fluoride (entry 16) led to complete conversion and **3a** is obtained in 30% yield and **4** in 29% yield. The high amount of **4** is most likely due to the water present in the hygroscopic ammonium salt. This attempt with tetrametylammonium fluoride proves that the cesium ion is not implicated in the cleavage of the C–I bound. This is confirmed by the experiment carried out with cesium chloride in which almost no conversion of **1b** was observed (entry 17).

**Table 1** Metal-Free Borylation of 4-Iodoanisole Using Bispinacolatodiboron as the Borylating Agent




| Entry | Base | Additive | Solvent[a] | Temp (°C) | Time (h) | Yield (%)[b] |
|---|---|---|---|---|---|---|
| 1 | *t*-BuOK | none | DMF | 100 | 24 | 9 |
| 2 | *t*-BuOK | EtOH | DMF | 100 | 24 | 25 |
| 3 | *t*-BuOK | EtOH | DMF | 140 | 24 | 8 |
| 4 | *t*-BuOK | Phen | DMF | 80 | 18 | 49 |
| 5 | *t*-BuOK | Phen | DMF | 105 | 18 | 78 |
| 6 | *t*-BuOK | Phen | NMP | 105 | 18 | 64 |
| 7 | *t*-BuOK | Phen | DMAC | 105 | 18 | 76 |
| 8 | *t*-BuOK | Phen | DMSO | 105 | 18 | 87 |
| 9 | *t*-BuONa | Phen | DMF | 105 | 18 | 74 |
| 10 | PhONa | Phen | DMF | 105 | 18 | 30 |
| 11 | MeONa | Phen | DMF | 105 | 18 | 23 |
| 12 | CsF | Phen | DMSO | 105 | 18 | 94 |
| 13 | CsF | none | DMSO | 105 | 18 | 14 |

[a] A 0.5 M solution 4-iodoanisole was used.
[b] Yields were determined by GC/MS using decalin as internal reference.

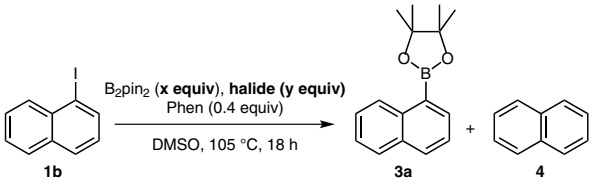



**Scheme 2** Aryl iodide borylation: scope and limitations. *Reagents and conditions*: ArI (0.5 mmol, 1 equiv), bispinacolatodiboron (2 equiv), CsF (3 equiv), pyridine (1 equiv) in distilled DMSO (0.4 mL), argon, 105 °C for 2 h. The reaction was conducted with (a) 0.8 equiv, (b) 0.5 equiv, and (c) 0.4 equiv of pyridine; (d) 2 to 3% of the regioisomer **5** was detected by GC/MS analysis. Yields were determined by GC/MS using decalin as internal reference. Yields of isolated products are given in parenthesis. For comparison, yield of isolated products from ref. 20 are shown in square brackets.

The influence of the additive was then studied (Table 3). In the absence of nitrogen heteroaromatics, **3a** was obtained in 15% yield besides a significant amount of naphthalene (**4**; 20%); in these conditions, the conversion of **1b** reached only 56% (Table 3, entry 1). With phenylhydrazine, 2,2′-bipyridine, pyrrole, 2-aminopyrimidine, 1,2,3,4-tetrahydroquinoline, imidazole or piperazine derivatives, and dimethylfuran, conversions of **1b** were deceiving (entries 3, 5, 6, 10, 18 to 20, and 22 to 24), the best yield in **3a** being obtained in the presence of *N*-methylimidazole (41%, entry 18). Thiophene derivatives and sulfides favor the formation of naphthalene (entries 7–9) although with 2,2′-bithiophene, the desired borylated product **3a** was obtained in a yield comparable to phenanthroline (entries 8 and 2).

2,4,6-Tris(2-pyridyl)-*s*-triazine and 4-methylquinoline (lepidine) seem to be as efficient as phenanthroline (Table 3, entries 21 and 25). Pyridine appeared to be the best additive with 100% conversion and 71% yield (entry 4). Use of various substituted pyridines did not allow for an increase in the yield (entries 11 to 16). $^1$H NMR experiments carried out in order to determine the optimal temperature show that the aryl iodide is consumed only at temperatures higher than 80 °C (Figure 1S, Supporting Information). With these optimized conditions in hand, the scope and limitations of this reaction were investigated (Scheme 2). The concentration of aryl iodide was fixed at 1 M. In such conditions, 1-iodonaphthalene was consumed completely in 1.5 hours. Reactions were carried out at 105 °C for 2 hours before GC/MS analysis. Overall, yields positively correlated to

**Table 2** Influence of the Diboron/Fluoride Ratio and the Halide Source



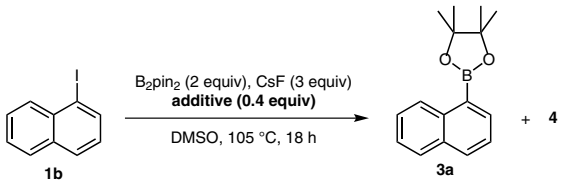

| Entry[a] | $B_2pin_2$ (equiv) | Halide | Conv. (%)[b] | Yield (%)[b] | |
|---|---|---|---|---|---|
| | | | | **3a** | **4** |
| 1 | 2 | none | 0 | 0 | 0 |
| 2 | 1 | CsF (1 equiv) | 43 | 20 | 12 |
| 3 | 1 | CsF (2 equiv) | 73 | 27 | 18 |
| 4 | 1 | CsF (3 equiv) | 100 | 28 | 18 |
| 5 | 1 | CsF (4 equiv) | 100 | 24 | 24 |
| 6 | 2 | CsF (1 equiv) | 49 | 25 | 5 |
| 7 | 2 | CsF (2 equiv) | 84 | 45 | 6 |
| 8 | 2 | CsF (3 equiv) | 100 | 58 | 11 |
| 9 | 2 | CsF (4 equiv) | 100 | 55 | 21 |
| 10 | 3 | CsF (1 equiv) | 55 | 28 | 6 |
| 11 | 3 | CsF (2 equiv) | 85 | 51 | 8 |
| 12 | 3 | CsF (3 equiv) | 100 | 60 | 12 |
| 13 | 3 | CsF (4 equiv) | 100 | 57 | 10 |
| 14 | 2 | KF (3 equiv) | 86 | 46 | 16 |
| 15 | 2 | NaF (3 equiv) | 11 | 1 | 1 |
| 16 | 2 | $NMe_4F$ (3 equiv) | 100 | 30 | 29 |
| 17 | 2 | CsCl (3 equiv) | 4 | 1 | 2 |
| 18 | 2 | KI (3 equiv) | 6 | 1 | 0 |

[a] A 0.5 M solution 1-iodonaphthalene was used.
[b] Conversions and yields were determined by $^1$H NMR analysis after workup and filtration though silica gel.

the amount of pyridine added, maximizing at 0.8 equivalent. The amount of pyridine was therefore stated to 1 equivalent. In some cases, it was possible to diminish the pyridine quantity without hampering yields. For instance, with 4-iodoanisole **2a** is obtained in an excellent yield of 94%, using only 0.5 equivalent of additive. Likewise, 4-methylphenyl and 3-methylphenyl boronates (**2c** and **5c**) were obtained with 0.8 equivalent of pyridine in 94% and 98% yield, respectively.

As shown in Scheme 2, the reaction works well on substrates with substituents in *para* or *meta* positions to the iodine atom (compounds **2** and **5**). This is efficient for both electron-donating and -withdrawing groups in yields varying from 55 to 98%. Substrates with two substituents in the either *meta* and *para* positions (compounds **7** to **12**) or in *meta* and *meta′* positions (compounds **13** to **15**) were obtained in comparable or slightly lower yields. Diiodoarenes can be bisborylated in good yields as shown in the case of compounds **2l** and **2m**, obtained in 65% and 81% yield, respectively. The reaction conditions are compatible with fluorides and chlorides but also bromides, esters, ketones nitriles, or methoxy groups. Although less efficient, the borylation is also possible in the presence of free amines. For instance, anilines **2b** and **5b** were synthesized in 33% and 61% yield, respectively. 1-Iodo- and 2-iodonaphthalene led to comparable results. Finally, heteroaromatic iodides such as quinoline and dibenzofuran also react, leading to **16** and **18** in 55% and 54% yield, respectively. In contrast, thiophene does not react well (compound **17** obtained in 19% yield on-

**Table 3** Lewis Base Additive Effect

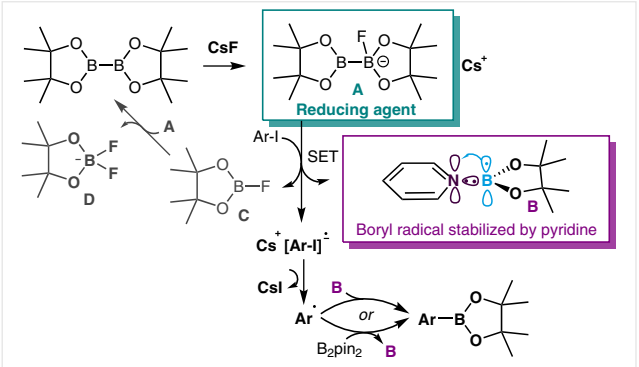



| Entry[a] | Additive | Conv. (%)[b] | Yields (%)[b] | |
|---|---|---|---|---|
| | | | **3a** | **4** |
| 1 | none | 56 | 15 | 20 |
| 2 | 1,10-phenanthroline | 100 | 58 | 11 |
| 3 | phenylhydrazine | 78 | 37 | 21 |
| 4 | pyridine | 100 | 71 | 6 |
| 5 | 2,2′-bipyridine | 62 | 29 | 2 |
| 6 | pyrrole | 84 | 23 | 8 |
| 7 | thiophene | 67 | 17 | 20 |
| 8 | 2,2′-bithiophene | 100 | 55 | 42 |
| 9 | diphenyl sulfide | 81 | 35 | 41 |
| 10 | 2,5-dimethylfuran | 79 | 21 | 19 |
| 11 | *N*,*N*-dimethylaminopyridine | 100 | 42 | 28 |
| 12 | 4-aminopyridine | 87 | 41 | 6 |
| 13 | 3-aminopyridine | 58 | 27 | 3 |
| 14 | 2-amino-4-methylpyridine | 70 | 27 | 13 |
| 15 | 2-phenylpyridine | 100 | 46 | 31 |
| 16 | 2-methylpyridine | 93 | 47 | 21 |
| 17 | 3,5-dimethylpyrazole | 100 | 44 | 20 |
| 18 | *N*-methylimidazole | 91 | 41 | 9 |
| 19 | imidazole | 73 | 30 | 11 |
| 20 | 2-aminopyrimidine | 87 | 35 | 13 |
| 21 | 2,4,6-tris(2-pyridyl)-*s*-triazine | 100 | 56 | 17 |
| 22 | 1-methylpiperazine | 85 | 19 | 48 |
| 23 | 1,2,3,4-tetrahydroquinoline | 60 | 17 | 4 |
| 24 | piperazine | 61 | 16 | 7 |
| 25 | 4-methylquinoline | 100 | 56 | 20 |

[a] A 0.5 M solution 1-iodonaphthalene was used.
[b] Conversions and yields were determined by $^1$H NMR analysis after workup and filtration though silica gel.

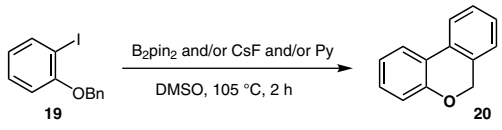
ly). The borylation is also very sensitive to steric hindrance as shown in the case of *ortho*-substituted compounds **6**, for which the yields drop drastically; they are between 25% and 40% except in the case of **6c** (R = Me: 75%). These results differ slightly from those described by Jiao[15] (yields given between square brackets for comparison). Comparable yields are obtained for methoxy and methyl substituents in *para*- and *meta*-positions (compounds **2a**, **5a**, **2c**, and **5c**), higher yields in the case of the *ortho*-substituted compound **6c**. Under Jiao's conditions, the thiophene **17** was borylated in 51% yield. On the other hand, with electron-withdrawing groups such as trifluoromethyl, chloride, and fluoride (compounds **2d**, **2e**, and **2g**), our system leads to better results. Moreover, in the present case, the borylation is possible in the presence of bromides, which react using the previously described system. These results clearly show that both methods are complementary. By GC/MS analysis, we noticed that 2 to 3% of regioisomers **5a** and **5d** were formed during the syntheses of **6a** and **6d**, respectively. The presence of such by-products indicates that a 1,2-migration of hydrogen atom occurs during the reaction, probably to compensate for the steric hindrance. Such migration, added to the fact that conversion in the borylated product could not be correlated to the solvent's ionic constant, favors the radical mechanism. To check this hypothesis, complementary experiments were conducted on compound **19** known to give the cyclic product **20** via radical intermediate (Table 4). In the absence of either cesium fluoride or bispinacolatodiboron, with or without pyridine (Table 4, entries 1 to 3), only starting material **19** was recovered.

The introduction of CsF to diboron leads to the formation of cyclic compound **20**, indicating that a radical intermediate is generated (Table 4, entry 4). Moreover, this radical cannot be generated from only a fluoride ion, although it is known to be a possible reducing agent. Comparison of experiments carried out in the presence or absence of pyridine shows that pyridine has an impact on the starting material/cyclic product ratio (entries 4 and 5). In the absence of pyridine, cyclization remained limited, with 84% of remaining **19**. In the presence of pyridine, the **19**:**20** ratio was reversed in favor of the cyclic compound **20** that now represents 83% of the mixture. Thus, the pyridine would stabilize radical intermediates. Such stabilization of boryl radicals has been already proposed in literature.[24] From these results, we propose the possible mechanism described in Scheme 3. The fluoride ion reacts with bispinacolatodiboron to form adduct **A**. This negatively charged intermediate **A** would be reductive enough to reduce the aryl iodide via a single-electron-transfer process and generate the radical anion, precursor to the aryl radical. Simultaneously, boryl radical pyridine adduct **B** and fluoropinacolborane **C** would be formed. Intermediate **C** can react with **A** to drive out **D** and regenerate the starting diboron. The formation of **A**, **C**, and **D** has been confirmed by $^{19}F$ and $^{11}B$ NMR spectroscopy (Figures S2 and S3, Supporting Information). The final product is then obtained by reaction of the aryl radical with either **B** or $B_2pin_2$. In this last case, the boryl radical intermediate **B** would be formed again. The mechanism proposed by Zhang et al. is slightly different. In their case the 'ate' complex resulting from the addition of methylate to the diboron reacts with pyridine to form a $Bsp^3$–$Bsp^3$ adduct.




**Scheme 3** Proposed reaction mechanism

**Table 4** Complementary Experiments




| Entry | Experimental conditions | | | Obtained products (ratio) |
|---|---|---|---|---|
| | CsF (equiv) | $B_2pin_2$ (equiv) | Pyridine (equiv) | |
| 1 | 0 | 2 | 0.4 | **19** |
| 2 | 3 | 0 | 0 | **19** |
| 3 | 3 | 0 | 0.4 | **19** |
| 4 | 3 | 2 | 0 | **19**/**20** (84:16) |
| 5 | 3 | 2 | 0.4 | **19**/**20** (13:87) |

Homolytic cleavage of the intermediate generates a pyridine stabilized boryl radical and an alkoxyboronate radical anion responsible for the SET process. In our case, as the reaction is possible in the absence of pyridine, we think that the species undergoing the SET process is the 'ate' complex **A**. Pyridine is, however, useful for stabilization of boryl radical **B** reacting subsequently with aryl radicals in the downstream process.

To conclude, a metal-free borylation method has been developed showing that fluoride can promote single-electron transfer to the aryl iodide by forming a $sp^2$–$sp^3$ diboron adduct. The absence of strong base such as *t*-BuOK rules out an entirely ionic mechanism and may widen the scope of this reaction.

DMSO and pyridine were purchased from Sigma Aldrich, dried over $CaH_2$, and freshly distilled before use. All commercially available reagents were used directly as received, unless otherwise specified. CsF was purchased from Aldrich, dried, and maintained anhydrous at 35 °C under vacuum. Aryl iodides were purchased from various commercial sources (TCI, Aldrich, Fluorochem). Bispinacolatodiboron and borylated products used as references for GC calibration curves were purchased from Fluorochem. Analytical TLC was carried out using 0.25 mm silica gel plates purchased from Merck. Eluted plates were visualized using KMnO4 solution. Purification of products was accomplished by flash column chromatography on silica gel (Sigma Aldrich silica gel, 230–400 mesh particle size). Melting points were measured using a Kofler Heizbank melting point bench (model 7841). NMR spectra were recorded on a Bruker Avance 300 or Avance 400 spectrometers relative to TMS (external standard). All coupling constants are reported in Hz. Standard abbreviations were used for the NMR spectral splitting patterns. GC/MS analyses were performed on an Agilent 7890A instrument equipped with a J & W Scientific DB-1701 capillary column and an Agilent 5975C VL MSD with triple axis detector (EI). The following methods were used. Method 1: 70 °C for 1 min, then 20 °C/min until 230 °C. Method 2: 20 °C/min from 100 to 280 °C. Response coefficients of both aryl iodides and borylated products were determined using decalin as internal reference and commercially available pure chemicals or purified borylated products. Benzyl 2-iodophenyl ether (**19**) was synthesized according to published procedure.[25]

### Metal-Free Borylation of Aryl Iodides

#### For Solid Aryl Iodides; General Procedure A

An oven-dried Schlenk tube, containing a Teflon-coated magnetic stir bar was charged with CsF (228 mg, 1.5 mmol, 3 equiv), bispinacolatodiboron (254 mg, 1 mmol, 2 equiv), and the appropriate aryl iodide (0.5 mmol). Under an argon atmosphere, freshly distilled DMSO (0.4 mL) and pyridine (0.4 to 1 equiv) were added successively using a syringe. The reaction mixture was heated to 105 °C and stirred and stirred for 2 h under argon.

#### For Liquid Aryl Iodides; General Procedure B

An oven-dried Schlenk tube, containing a Teflon-coated magnetic stir bar was charged with CsF (228 mg, 1.5 mmol, 3 equiv) and bispinacolatodiboron (254 mg, 1 mmol, 2 equiv). Under an argon atmosphere, freshly distilled DMSO (0.4 mL), the appropriate aryl iodide (0.5 mmol), and pyridine (0.4 to 1 equiv) were added successively. The reaction mixture was heated to 105 °C and stirred for 2 h under argon.

#### Analysis (A or B)

For analysis purpose by GS/MS only, DMF (2 to 4 mL) was added to the mixture in order to dissolve the solid residue and a precisely weighed amount of decalin (internal standard) was added (40 µL).

#### Workup and Purification (A or B)

$Et_2O$ (100 mL) and aq 0.1 N HCl (10 mL) were added to the crude mixture. The aqueous phase was extracted with $Et_2O$ (2 × 10 mL). The combined organic layers were dried (anhyd $Na_2SO_4$), concentrated under reduced pressure, and the residue was purified by silica gel flash column chromatography to yield the pure aryl pinacolboronate.

#### 2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a)

[CAS Reg. No. 171364-79-7]

Compound **2a** was synthesized according to General Procedure A from 4-iodoanisole (117 mg) and pyridine (16 µL, 0.4 equiv). Purification by column chromatography (elution gradient: 100:0 to 95:5 pentane/EtOAc) gave **2a** (110 mg, 0.47 mmol, 85%) as a colorless oil; $R_f$ = 0.32 (pentane/EtOAc 95:5).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.66 (d, $J$ = 8.7 Hz, 2 H, ArH), 6.79 (d, $J$ = 8.7 Hz, 2 H, ArH), 3.70 (s, 3 H, $OCH_3$), 1.23 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 161.1, 135.4, 112.2, 82.5, 54.0, 23.8.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 30.9 (s, Bpin).

GC/MS (EI, Method 1): $t_R$ = 8.88 min; $m/z$ (%) = 234.1 ($M^{+\cdot}$, 64), 219.1 (42), 148.1 (47), 134.0 (100).

#### 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)toluene (2c)

[CAS Reg. No. 195062-57-8]

Compound **2c** was synthesized according to General Procedure from 4-iodotoluene (109 mg) and pyridine (32 µL, 0.8 equiv). Purification by column chromatography (eluent: pentane/EtOAc 98:5) gave **2c** (91 mg, 0.42 mmol, 83%) as a pale yellow oil; $R_f$ = 0.20 (pentane/EtOAc 98:2).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.62 (d, $J$ = 7.9 Hz, 2 H, ArH), 7.09 (d, $J$ = 7.9 Hz, 2 H, ArH), 2.28 (s, 3 H, $CH_3$), 1.25 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 141.3, 134.8, 128.5, 83.6, 24.8, 21.7.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 30.9 (s, Bpin).

GC/MS (EI, Method 1): $t_R$ = 7.78 min; $m/z$ (%) = 219.1 ($M^{+\cdot}$, 38), 203.1 (53), 130.1 (66), 119.0 (100).

#### 4,4,5,5-Tetramethyl-2-(4-trifluoromethylphenyl)-1,3,2-dioxaborolane (2d)

[CAS Reg. No. 214360-65-3]

Compound **2d** was synthesized according to General Procedure B from 4-iodobenzotrifluoride (136 mg) and pyridine (40 µL, 1 equiv). Purification by column chromatography (eluent: pentane/EtOAc 98:2) gave **2d** (99 mg, 0.36 mmol, 73%) as a white solid; mp 71 °C (Lit.[4g] mp 68–69 °C); $R_f$ = 0.15 (pentane/EtOAc 98:2).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.83 (d, $J$ = 7.7 Hz, 2 H, ArH), 7.52 (d, $J$ = 7.7 Hz, 2 H, ArH), 1.27 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 135.0, 132.8 (q, $J_{C,F}$ = 32.1 Hz), 124.3 (q, $J_{C,F}$ = 3.8 Hz), 124.0 (q, $J_{C,F}$ = 272.3 Hz), 84.2, 24.8.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 30.5 (s, Bpin).

GC/MS (EI, Method 1): $t_R$ = 6.85 min; $m/z$ (%) = 272.1 ($M^{+\cdot}$, 9), 257.1 (100), 229 (9), 186 (73), 173.0 (76).

#### 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)fluorobenzene (2e)

[CAS Reg. No. 214360-58-4]

Compound **2e** was synthesized according to General Procedure B from 1-fluoro-4-iodobenzene (58 µL, 111 mg) and pyridine (40 µL, 1 equiv). Purification by column chromatography (elution gradient: 100:0 to 7:3 PE/EtOAc) gave **2e** (88 mg, 0.44 mmol, 79%) as a colorless oil; $R_f$ = 0.15 (PE/EtOAc 98:2).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.71 (dd, $J$ = 8.7 Hz, $J_{H,F}$ = 6.2 Hz, 2 H, ArH), 6.96 (dd, $J_{H,F}$ = 8.8 Hz and $J$ = 8.7 Hz, 2 H, ArH), 1.26 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 165.1 (d, $J_{C,F}$ = 250.3 Hz), 137.0 (d, $J_{C,F}$ = 8.2 Hz), 114.8 (d, $J_{C,F}$ = 20.2 Hz), 83.9, 24.8.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 30.6 (s, Bpin).

$^{19}$F NMR ($CDCl_3$, 282 MHz): δ = –108.4 (tt, $J_{H,F}$ = 8.8, 6.2 Hz, Ar–F).

GC/MS (EI, Method 1): $t_R$ = 6.85 min; *m*/*z* (%) = 222.1 ($M^{+\cdot}$, 17), 207.1 (79), 136.0 (38), 123.0 (100), 85.0 (14).

**2-(4-Bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f)**

[CAS Reg. No. 68716-49-4]

Compound **2f** was synthesized according to General Procedure A from 1-bromo-4-iodobenzene (142 mg) and pyridine (40 µL, 1 equiv). Purification by column chromatography (elution gradient: 100:0 to 7:3 PE/EtOAc) gave **2f** (124 mg, 0.44 mmol, 88%) as a white solid; mp 68–70 °C ; $R_f$ = 0.21 (PE/EtOAc, 98:2).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.58 (d, *J* = 8.4 Hz, 2 H, ArH), 7.42 (d, *J* = 8.4 Hz, 2 H, ArH), 1.26 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 135.3, 129.9, 125.2, 83.0, 23.8.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 30.7 (s, Bpin).

GC/MS (EI, Method 1): $t_R$ = 8.77 min; *m*/*z* (%) = 282.0 ($M^{+\cdot}$, 41), 267.0 (100), 196.9 (71), 182.3 (100), 103.0 (32), 85.0 (22), 77 (19), 59 (13).

**2-(4-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2g)**

[CAS Reg. No. 195062-61-4]

Compound **2g** was synthesized according to General Procedure A from 1-chloro-4-iodobenzene (119 mg) and pyridine (40 µL, 1 equiv). Purification by column chromatography (eluent: cyclohexane/$CH_2Cl_2$ 95:5) gave **2g** (98 mg, 0.41 mmol, 82%) as a white solid; mp 48–50 °C; $R_f$ = 0.54 (cyclohexane/$CH_2Cl_2$ 95:5$^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.65 (d, *J* = 8.4 Hz, 2 H, ArH), 7.25 (d, *J* = 8.4 Hz, 2 H, ArH), 1.26 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 137.3, 135.9, 127.8, 83.8, 24.7.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 30.7 (s, Bpin).

GC/MS (EI, Method 1): $t_R$ = 8.16 min; *m*/*z* (%) = 238.0 ($M^{+\cdot}$, 35), 223.0 (100), 154 (20), 139 (89), 103.0 (9), 85.0 (13), 77 (10), 59 (8).

**1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (2m)**

[CAS Reg. No. 99770-93-1]

Compound **2m** was synthesized according to General Procedure A from 1,4-diiodobenzene (165 mg) and pyridine (40 µL, 1 equiv). Purification by column chromatography (elution gradient: 98:2 to 9:1 PE/EtOAc) gave **2m** (119 mg, 0.36 mmol, 72%) as a white solid; mp 230–232 °C; $R_f$ = 0.23 (PE/EtOAc, 95:5).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.73 (s, 4 H, ArH), 1.28 (s, 24 H, 8 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 133.9, 83.8, 24.9.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 30.9 (s, Bpin).

GC/MS (Method 1): $t_R$ = 12.54 min; *m*/*z* (%) = 330.2 ($M^{+\cdot}$, 23), 315.2 (43), 273.1 (21), 244.2 (76), 231.1 (100), 215.0 (20), 188.1 (10), 158.1 (15), 131.0 (38), 85.0 (21), 59.0 (18).

**2-(1-Naphthyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a)**

[CAS Reg. No. 68716-52-9]

Compound **3a** was synthesized according to General Procedure B from 1-iodonaphthalene (73 µL, 127 mg) and pyridine (16 µL, 0.4 equiv). Purification by column chromatography (elution gradient: 100:0 to 95:5 pentane/EtOAc) gave **3a** (83 mg, 0.33 mmol, 65%) as a pale yellow solid; mp 57–58 °C (Lit.[4g] mp 54–55 °C); $R_f$ = 0.36 (pentane/EtOAc 95:5).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 8.68 (d, *J* = 8.6 Hz, 1 H, ArH), 8.00 (dd, *J* = 6.8, 1.2 Hz, 1 H, ArH), 7.85 (d, *J* = 8.2 Hz, 1 H, ArH), 7.75 (dd, *J* = 7.7, 1.4 Hz, 1 H, ArH), 7.45 (td, *J* = 7.1, 1.4 Hz, 1 H, ArH), 7.44–7.34 (m, 2 H, Ar), 1.34 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 136.9, 135.6, 133.1, 131.6, 128.4, 128.3, 126.3, 125.4, 124.9, 83.7, 24.9.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 30.5 (s, Bpin).

GC/MS (EI, Method 1): $t_R$ = 10.91 min; *m*/*z* (%) = 254.1 ($M^{+\cdot}$, 61), 239.1 (11), 210.1 (11), 181.1 (16), 168.1 (23), 154.1 (100), 128.0 (8), 77.0 (5), 59.0 (3).

**4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (3b)**

[CAS Reg. No. 256652-04-7]

Compound **3b** was synthesized according to General Procedure A from 2-iodonaphthalene (127 mg) and pyridine (40 µL, 1 equiv). Purification by column chromatography (elution gradient: 98:2 to 95:5 pentane/EtOAc) gave **3b** (38 mg, 0.30 mmol, 59%) as a white solid; mp 62–63 °C (Lit.[26] mp 62–65 °C); $R_f$ = 0.40 (PE/EtOAc, 95:5).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 8.38 (s, 1 H, ArH), 7.93–7.79 (m, 4 H, ArH), 7.56–7.43 (m, 2 H, ArH), 1.40 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 136.2, 135.0, 132.8, 130.4, 128.6, 127.7, 126.9, 125.8, 83.9, 24.9.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 31.1 (s, Bpin).

GC/MS (EI, Method 1): $t_R$ = 10.93 min; *m*/*z* (%) = 254.1 ($M^{+\cdot}$, 47), 239.1 (11), 168.1 (66), 154.0 (100), 128.0 (9), 77.0 (5), 59.0 (3).

**2-(3-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5a)**

[CAS Reg. No. 325142-84-5]

Compound **5a** was synthesized according to General Procedure B from 3-iodoanisole (66 µL, 117 mg) and pyridine (40 µL, 1 equiv). Purification by column chromatography (elution gradient: 98:2 to 95:5 PE/EtOAc) gave **5a** (97 mg, 0.41 mmol, 83%) as a pale yellow oil; $R_f$ = 0.35 (PE/EtOAc 95:5).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.40–7.15 (m, 3 H, ArH), 6.93 (ddd, *J* = 8.7, 2.8, 1.8 Hz, 1 H, ArH), 3.75 (s, 3 H, $OCH_3$), 1.26 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 159.0, 128.9, 127.9, 118.7, 117.9, 83.8, 55.2, 24.8.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 31.0 (s, Bpin).

GC/MS (EI, Method 1): $t_R$ = 8.67 min; *m*/*z* (%) = 234.1 ($M^{+\cdot}$, 81), 219.1 (36), 177.0 (8), 161.0 (6), 148.0 (92), 134.0 (100), 104.0 (13), 91.0 (12), 77.0 (10), 59.0 (5).

**3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)toluene (5c)**

[CAS Reg. No. 253342-48-2]

Compound **5c** was synthesized according to General Procedure B from 3-iodotoluene (64 µL, 109 mg) and pyridine (32 µL, 0.8 equiv). Purification by column chromatography (elution gradient: 98:2 to 95:5 PE/EtOAc) gave **5c** (94 mg, 0.43 mmol, 86%) as a pale yellow oil; $R_f$ = 0.61 (PE/EtOAc 95:5).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.70–7.55 (m, 2 H, ArH), 7.35–7.20 (m, 2 H, Ar), 2.36 (s, 3 H, $CH_3$), 1.35 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 137.1, 135.3, 132.0, 131.7, 127.7, 83.7, 24.8, 21.2.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 31.0 (s, Bpin).

GC/MS (EI, Method 1): $t_R$ = 7.68 min; *m*/*z* (%) = 218.0 ($M^{+\cdot}$, 25), 203.0 (37), 160.9 (9), 132.0 (76), 119.0 (100), 90.0 (16), 85.0 (13), 77 (5), 59.0 (9).

### 4,4,5,5-Tetramethyl-2-(3-trifluoromethylphenyl)-1,3,2-dioxaborolane (5d)

[CAS Reg. No. 325142-82-3]

Compound **5d** was synthesized according to General Procedure B from 3-iodobenzotrifluoride (72 µL, 136 mg) and pyridine (40 µL, 1 equiv). Purification by column chromatography (elution gradient: 98:2 to 95:5 toluene/EtOAc) gave **5d** (110 mg, 0.40 mmol, 81%) as a white solid; mp 40–42 °C; $R_f$ = 0.81 (toluene/EtOAc 95:5).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.99 (d, *J* = 0.6 Hz, 1 H, ArH), 7.90 (d, *J* = 7.4 Hz, 1 H, Ar), 7.62 (dd, *J* = 7.8, 0.6 Hz, 1 H, ArH), 7.40 (dd, *J* = 7.8, 7.4 Hz, 1 H, ArH), 1.28 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 138.0 (q, *J* = 1.2 Hz), 131.3 (q, *J* = 3.7 Hz), 130.0 (q, $J_{C,F}$ = 32.1 Hz), 128.0, 127.8 (q, $J_{C,F}$ = 3.8 Hz), 124.2 (q, $J_{C,F}$ = 272.2 Hz), 84.3, 24.0.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 30.3 (s, Bpin).

$^{19}$F NMR ($CDCl_3$, 282 MHz): δ = –62.6 (s, Bpin).

GC/MS (EI, Method 1): $t_R$ = 6.83 min; *m*/*z* (%) = 272.0 ($M^{+\cdot}$, 7) 257.0 (100), 229 (6), 215 (5), 185.9 (46), 172.9 (70), 152.9 (6), 85.0 (7), 58.0 (7).

### 2-(3-Bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5f)

[CAS Reg. No. 594823-67-3]

Compound **5f** was synthesized according to General Procedure B from 1-bromo-3-iodobenzene (64 µL, 141 mg) and pyridine (40 µL, 1 equiv). Purification by column chromatography (elution gradient: 98:2 to 95:5 PE/EtOAc) gave **5f** (98 mg, 0.35 mmol, 69%) as a pale yellow oil; $R_f$ = 0.53 (PE/EtOAc 95:5).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.86 (d, *J* = 1.2 Hz, 1 H, ArH), 7.64 (ddd, *J* = 7.3, 2.1, 1.2 Hz, 1 H, ArH), 7.50 (ddd, *J* = 8.0, 2.1, 1.2 Hz, 1 H, ArH), 7.16 (dd, *J* = 7.6, 8.0 Hz, 1 H, ArH), 1.27 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 137.9, 134.6, 133.5, 129.9, 122.8, 84.5, 25.3.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 30.4 (s, Bpin).

GC/MS (EI, Method 1): $t_R$ = 8.86 min; *m*/*z* (%) = 281.9 ($M^{+\cdot}$, 83), 266.9 (79), 238.9 (6), 224.9 (7), 195.9 (100), 182.8 (83), 160.9 (7), 117.0 (20), 102.9 (34), 85.0 (24), 76.9 (21), 59.0 (17).

### 2-(3-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5g)

[CAS Reg. No. 635305-47-4]

Compound **5g** was synthesized according to General Procedure B from 1-chloro-3-iodobenzene (62 µL, 119 mg) and pyridine (40 µL, 1 equiv). Purification by column chromatography (elution gradient: 98:2 to 95:5 PE/EtOAc) gave **5g** (91 mg, 0.38 mmol, 76%) as a pale yellow oil; $R_f$ = 0.42 (PE/EtOAc, 95:5).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.70 (d, *J* = 2.1 Hz, 1 H, ArH), 7.59 (dt, *J* = 7.4, 1.1 Hz, 1 H, ArH), 7.34 (ddd, *J* = 8.0, 2.1, 1.2 Hz, 1 H, ArH), 7.22 (dd, *J* = 8.0, 7.4 Hz, 1 H, ArH), 1.27 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 134.5, 134.0, 132.6, 131.2, 129.2, 84.1, 24.8.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 30.6 (s, Bpin).

GC/MS (EI, Method 1): $t_R$ = 8.27 min; *m*/*z* (%) = 238.0 ($M^{+\cdot}$, 38), 223.0 (80), 151.9 (100), 138.9 (92), 117.0 (11), 102.9 (11), 85.0 (18), 76.9 (14), 59.0 (12).

### 2-(2-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6a)

[CAS Reg. No. 190788-60-4]

Compound **6a** was synthesized according to General Procedure B from 2-iodoanisole (65 µL, 117 mg) and pyridine (40 µL, 1 equiv). Purification by column chromatography (eluent: toluene/EtOAc 95:5) gave **6a** (36 mg, 0.15 mmol, 31%) as a pale yellow oil; $R_f$ = 0.33 (toluene/EtOAc 95:5).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.60 (dd, *J* = 7.3, 1.8 Hz, 1 H, ArH), 7.32 (ddd, *J* = 7.4, 7.3, 1.8 Hz, 1 H, ArH), 6.86 (td, *J* = 7.3, 0.7 Hz, 1 H, ArH), 7.78 (dd, *J* = 7.4, 0.7 Hz, 1 H, ArH), 3.75 (s, 3 H, $OCH_3$), 1.28 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 163.0, 135.5, 131.3, 119.0, 109.3, 82.3, 54.6.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 31.0 (s, Bpin).

GC/MS (EI, Method 1): $t_R$ = 8.55 min; *m*/*z* (%) = 234.1 ($M^{+\cdot}$, 68), 219.1 (28), 203.0 (12), 176.0 (10), 161.0 (32), 148.0 (6) 134.0 (100), 118.0 (17), 105.0 (44), 91.0 (58), 77.0 (12), 59.0 (6).

### 2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (6b)

[CAS Reg. No. 191171-55-8]

Compound **6b** was synthesized according to General Procedure A from 2-iodoaniline (110 mg) and pyridine (40 µL, 1 equiv). Purification by column chromatography (elution gradient: 100:0 to 8:2 PE/EtOAc) gave **6b** (19 mg, 0.09 mmol, 17%) as a yellow solid; mp 68–69 °C (Lit.[27] mp 67–68 °C); $R_f$ = 0.46 (PE/EtOAc 8:2).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.54 (dd, *J* = 7.4, 1.6 Hz, 1 H, ArH), 7.14 (ddd, *J* = 7.4 , 7.3, 1.6 Hz, 1 H, ArH), 6.60 (td, *J* = 7.3, 1.1 Hz, 1 H, ArH), 6.52 (dd, *J* = 7.4, 1.1 Hz, 1 H, ArH), 4.52 (br s, 2 H, $NH_2$), 1.26 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 153.6, 136.8, 132.7, 116.9, 114.7, 83.5, 24.9.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 31.0 (s, Bpin).

GC/MS (EI, Method 1): $t_R$ = 9.18 min; *m*/*z* (%) = 219.1 ($M^{+\cdot}$, 69), 162.1 (83), 141.0 (53), 119.0 (100), 91.0 (14), 77.0 (15).

### 2-(2-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6g)

[CAS Reg. No. 870195-94-1]

Compound **6g** was synthesized according to General Procedure B from 1-chloro-2-iodobenzene (61 µL, 119 mg) and pyridine (40 µL, 1 equiv). Purification by column chromatography (elution gradient: 100:0 to 9:1 PE/EtOAc) gave **6g** (38 mg, 0.16 mmol, 32%) as a pale yellow oil; $R_f$ = 0.22 (PE/EtOAc 98:2).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.61 (dd, *J* = 6.9, 1.0 Hz, 1 H, ArH), 7.30–7.24 (m, 2 H, ArH), 7.21–7.11 (m, 1 H, ArH), 1.30 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 138.8, 135.7, 131.1, 128.7, 125.1, 83.4, 24.1.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 30.7 (s, Bpin).

GC/MS (EI, Method 1): $t_R$ = 8.33 min; *m*/*z* (%) = 238.1 ($M^{+\cdot}$, 9), 223.0 (20), 203 (100), 161 (45), 139.0 (100), 117.0 (7), 103.0 (23), 85.0 (23), 77 (13), 59.0 (12).

**Methyl 2-Amino-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (7)**

[CAS Reg. No. 363185-87-9]

Compound **7** was synthesized according to General Procedure A from methyl 2-amino-5-iodobenzoate (139 mg) and pyridine (40 µL, 1 equiv). Purification by column chromatography (elution gradient: 1:1 cyclohexane/$CH_2Cl_2$ to pure $CH_2Cl_2$) gave **7** (31 mg, 0.11 mmol, 22%) as a pale beige solid; mp 108–110 °C; $R_f$ = 0.31 ($CH_2Cl_2$).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 8.27 (d, *J* = 1.5 Hz, 1 H, ArH), 7.61 (dd, *J* = 8.2, 1.5 Hz, 2 H, ArH), 6.57 (d, *J* = 8.2 Hz, 1 H, ArH), 5.90 (br s, 2 H, $NH_2$), 3.80 (s, 3 H, $OCH_3$), 1.27 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 168.6, 152.5, 140.0, 138.8, 115.8, 110.1, 83.4, 51.3, 24.1.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 30.9 (s, Bpin).

GC/MS (EI, Method 1): $t_R$ = 13.13 min; *m*/*z* (%) = 277.1 ($M^{+\cdot}$, 100), 262.1 (15), 245.1 (25), 234.0 (9), 220.1 (15), 204.0 (10), 191.0 (9), 177.0 (68), 145.0 (39), 118.0 (21), 91 (10).

**2-Methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (8)**

[CAS Reg. No. 1220219-22-6]

Compound **8** was synthesized according to General Procedure A from 5-iodo-2-methoxybenzonitrile (130 mg) and pyridine (40 µL, 1 equiv). Purification by column chromatography (elution gradient: 1:1 cyclohexane/$CH_2Cl_2$ to pure $CH_2Cl_2$) gave **8** (56 mg, 0.22 mmol, 43%) as a colorless oil; $R_f$ = 0.45 ($CH_2Cl_2$).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.94 (d, *J* = 1.6 Hz, 1 H, ArH), 7.88 (dd, *J* = 8.5, 1.6 Hz, 2 H, ArH), 6.89 (d, *J* = 8.5 Hz, 1 H, ArH), 3.88 (s, 3 H, $OCH_3$), 1.27 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 163.2, 140.9, 140.6, 116.4, 110.5, 101.7, 84.2, 56.0, 24.8.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 30.2 (s, Bpin).

GC/MS (EI, Method 1): $t_R$ = 12.36 min; *m*/*z* (%) = 259.1 ($M^{+\cdot}$, 57), 244.1 (100), 216.0 (11), 202.0 (9), 173.0 (83), 160.0 (80), 130.0 (17), 85 (8).

**2-(3,4-Dichlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9)**

[CAS Reg. No. 401797-02-2]

Compound **9** was synthesized according to General Procedure A from 1,2-dichloro-4-iodobenzene (136 mg) and pyridine (40 µL, 1 equiv). Purification by column chromatography (elution gradient: 100:0 to 7:3 PE/EtOAc) gave **9** (85 mg, 0.31 mmol, 62%) as a colorless oil; $R_f$ = 0.37 (PE/EtOAc 9:1).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.79 (d, *J* = 1.4 Hz, 1 H, ArH), 7.52 (dd, *J* = 7.9, 1.4 Hz, 2 H, ArH), 7.36 (d, *J* = 7.9 Hz, 1 H, ArH), 1.27 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 136.5, 135.5, 133.7, 132.2, 130.0, 84.3, 24.8, 20.3.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 30.1 (s, Bpin).

GC/MS (EI, Method 1): $t_R$ = 9.34 min; *m*/*z* (%) = 272.0 ($M^{+\cdot}$, 43), 257.0 (100), 229.0 (7), 186.0 (95), 174.0 (79), 136.9 (6), 109.9 (6), 85.0 (18), 77.0 (10), 58 (13).

**2-(3-Chloro-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10)**

[CAS Reg. No. 445303-10-6]

Compound **10** was synthesized according to General Procedure B from 2-chloro-4-iodotoluene (71 µL, 126 mg) and pyridine (40 µL, 1 equiv). Purification by column chromatography (elution gradient: 100:0 to 7:3 PE/EtOAc) gave **10** (93 mg, 0.37 mmol, 73%) as a white solid; mp 46–48 °C; $R_f$ = 0.24 (PE/EtOAc 9 :1).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.59 (d, *J* = 0.9 Hz, 1 H, ArH), 7.49 (dd, *J* = 7.5, 0.9 Hz, 2 H, ArH), 7.16 (d, *J* = 7.5 Hz, 1 H, ArH), 2.32 (s, 3 H, $CH_3$), 1.26 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 139.2, 135.1, 134.2, 132.8, 130.5, 84.0, 24.8, 20.3.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 30.5 (s, Bpin).

GC/MS (EI, Method 1): $t_R$ = 8.89 min; *m*/*z* (%) = 252.1 ($M^{+\cdot}$, 52), 237.1 (78), 217.1 (8), 195.1 (8), 166.0 (93), 153.0 (100), 131.1 (9), 117.0 (38), 85.0 (13), 59.0 (7).

**2-(3-Chloro-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11)**

[CAS Reg. No. 445303-10-6]

Compound **11** was synthesized according to General Procedure B from 3-chloro-4-fluoroiodobenzene (64 µL, 128 mg) and pyridine (40 µL, 1 equiv). Purification by column chromatography (elution gradient: 100:0 to 7:3 PE/EtOAc) gave **11** (91 mg, 0.35 mmol, 71%) as an oil; $R_f$ = 0.40 (PE/EtOAc 9:1).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 8.37 (br s, 1 H, ArH), 7.89 (dm, 1 H, ArH), 7.86 (dd, *J* = 8.3, 1.3 Hz, 1 H, ArH), 7.52–7.45 (2 superimposed dm, 2 H, ArH), 7.37 (ddd, *J* = 7.3, 6.9, 1.4 Hz, 1 H, ArH), 7.27 (ddd, *J* = 7.5, 7.3, 1.0 Hz, 1 H, ArH), 1.32 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 158.4, 156.2, 133.8, 127.8, 127.1, 124.1, 123.9, 122.9, 121.8, 83.9, 24.9.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 31.0 (s, Bpin).

GC/MS (EI, Method 1): $t_R$ = 8.15 min; *m*/*z* (%) = 256.0 ($M^{+\cdot}$, 31), 241.0 (100), 213.0 (7), 199.0 (6), 170.0 (66), 157.0 (78), 85.0 (13), 75.0 (9), 59.0 (12).

**2-(3-Fluoro-5-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15)**

[CAS Reg. No. 1583286-47-8]

Compound **15** was synthesized according to General Procedure A from 3-fluoro-5-iodotoluene (118 mg) and pyridine (40 µL, 1 equiv). Purification by column chromatography (elution gradient: 100:0 to 7:3 PE/EtOAc) gave **15** (93 mg, 0.39 mmol, 79%) as a colorless oil; $R_f$ = 0.53 (PE/EtOAc 9:1).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 7.32 (br d, *J* = 0.6 Hz, 1 H, ArH), 7.20 (dd, $J_{H,F}$ = 8.9, 2.5 Hz, 1 H, ArH), 6.88 (dm, $J_{H,F}$ = 9.8 Hz, 1 H, ArH), 2.27 (q, *J* = 0.6 Hz, 3 H, $CH_3$), 1.27 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 161.5 (d, $J_{C,F}$ = 245.9 Hz), 138.8 (d, $J_{C,F}$ = 7.3 Hz), 129.9 (d, $J_{C,F}$ = 2.6 Hz), 117.8 (d, $J_{C,F}$ = 21.0 Hz), 116.8 (d, $J_{C,F}$ = 19.5 Hz), 83.0, 23.8, 20.0 (d, $J_{C,F}$ = 1.7 Hz).

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 30.6 (s, Bpin).

$^{19}$F NMR ($CDCl_3$, 282 MHz): δ = –115.4 (dd, $J_{F,H}$ = 9.8, 8.9 Hz, Ar–F).

GC/MS (EI, Method 1): $t_R$ = 7.67 min; *m*/*z* (%) = 236.2 ($M^{+\cdot}$, 42), 221.1 (62), 193.0 (6), 179.0 (10), 150.0 (100), 137.0 (98), 109.0 (9), 85.0 (11), 59.0 (8).

**2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-dibenzofuran (18)**

[CAS Reg. No. 947770-80-1]

Compound **18** was synthesized according to General Procedure B from 2-iododibenzofuran (147 mg) and pyridine (40 µL, 1 equiv). Purification by column chromatography (elution gradient: 98:2 to 7:3 PE/EtOAc) gave **18** (47 mg, 0.16 mmol, 32%) as a white solid; mp 74–76 °C; $R_f$ = 0.37 (PE/EtOAc 95:5).

$^1$H NMR ($CDCl_3$, 300 MHz): δ = 8.48 (br s, 1 H, ArH), 8.0 (ddd, *J* = 7.6, 1.4, 0.7 Hz, 1 H, ArH), 7.96 (dd, *J* = 7.3, 1.4 Hz, 1 H, ArH), 7.62–6.56 (2 dm, 2 H, ArH), 6.48 (ddd, *J* = 7.6, 7.3, 1.4 Hz, 1 H, ArH), 6.38 (td, *J* = 7.6, 1.1 Hz, 1 H, ArH), 1.43 (s, 12 H, 4 × $CH_3$).

$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 158.4, 156.1, 133.8, 127.8, 127.1, 124.1, 123.9, 122.9, 120.8, 111.6, 111.1, 83.9, 24.9.

$^{11}$B NMR ($CDCl_3$, 96 MHz): δ = 31.0 (s, Bpin).

GC/MS (EI, Method 2): $t_R$ = 9.68 min; *m*/*z* (%) = 294.1 ($M^{+\cdot}$, 53), 279.1 (13), 217.1 (8), 204.0 (51), 165.0 (20), 139.0 (11), 85.0 (5), 59.0 (4).

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## Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1588431.

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