DOI: 10.1002/ejoc.200800526

Improved Preparation of 4,6,6-Trimethyl-1,3,2-dioxaborinane and Its Use in a Simple [$PdCl_2(TPP)_2$]-Catalyzed Borylation of Aryl Bromides and Iodides

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Keywords: Borylation / Cross-coupling / Palladium / Pinacolborane / Biaryls

We describe a convenient preparation of 4,6,6-trimethyl-1,3,2-dioxaborinane (MethylPentaneDiolBorane, MPBH) and demonstrate that it is an excellent reagent for the [$PdCl_2(PPh_3)_2$]-catalyzed borylation of aryl bromides and iodides. The corresponding boronic esters undergo rapid Suzuki coupling reactions in the presence of cesium fluoride. Thus, MPBH is an excellent alternative to pinacolborane for Pd-catalyzed borylation and cross-coupling reactions.
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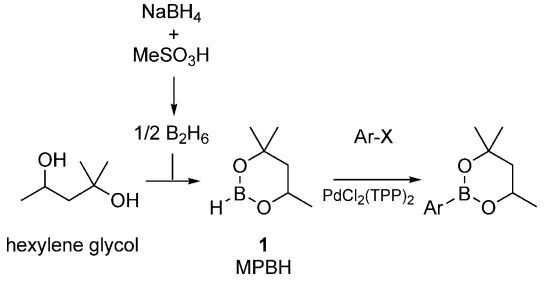
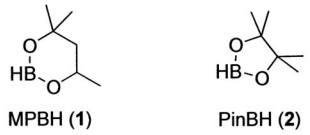
Introduction

The use of the Suzuki–Miyaura coupling reaction[1] is nowadays pervasive. Therefore, considerable effort has recently been devoted to improve the access to the most important component of the process, the boronic reagent itself. The reaction of organomagnesium[2] or lithium[3] reagents with trialkoxyboranes, leading after hydrolysis to boronic acids, is the oldest and most used pathway. Nevertheless, it can be limited by the access to the organometallic itself and also by difficulties in the purification of the arylboronic acids. The latter point has been addressed by the use of potassium trifluoroborates.[4] A very powerful alternative is the palladium-catalyzed cross-coupling reaction between aryl halides and bis-pinacolatodiboron.[5] Stable and easily purified boronic esters can be obtained from a great variety of aryl and heteroaryl iodides, bromides, chlorides and triflates. A further improvement is the replacement of the expensive bis-pinacolatodiboron by pinacolborane (4,4,5,5-tetramethyldioxaborolane, PinBH, **2**).[6] With this reagent, aryl iodides and bromides can be converted into the corresponding boronic esters in good yields and selectivities in an atom-economic manner. Thus, this borylation is now an excellent pathway to the preparation[6f,7] of arylboronic precursors to be engaged in Suzuki–Miyaura couplings.[5c,8] At this point, it should be noted that such arylboronic esters are also available by Ir-catalyzed aromatic C–H borylation with both bis(pinacolatodiboron) and pinacolborane.[9]

We recently studied[10] the use of 4,6,6-trimethyl-1,3,2-dioxaborinane[11] (MethylPentaneDiolBorane, MPBH, **1**) in the hydroboration[12] of 1-alkynes, which led to air- and chromatography-stable vinylboronic esters in good yields in mild conditions. We particularly noticed that MPBH reacted faster than the well-known pinacolborane (**2**),[13] in this hydroboration reaction. Yields were comparable and we did not find any difference in the stabilities of the vinylboronic esters[14] to air, water and chromatography. Moreover, MPBH (**1**) and PinBH (**2**) are both conveniently prepared by reaction of BH_3 with the corresponding diol, but hexylene glycol (a solvent) is considerably less expensive than pinacol. Finally, solutions of MPBH (**1**) are stable for months at 4 °C. In addition, the need for accessing increased quantities of MPBH (**1**) prompted us to design an improved preparation of **1** (Scheme 1), also described in the present work.



Scheme 1. Generation of MPBH (**1**).



At this stage, we wondered if MPBH (**1**) could replace PinBH (**2**) in a cost-effective version of the Pd-catalyzed borylation. Murata et al.[15] published in 2007 the borylation of aryl iodides with MPBH (**1**), as well as the Suzuki–Miyaura coupling of the corresponding boronic

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esters and aryl halides. Nevertheless, this work was limited to aryl iodides and used *t*Bu-DPEphos.[16] This ligand is efficient for borylation in the challenging cases of electron-depleted aryl halides,[6e] but it is poorly available and air-sensitive. Our own work has been more focused on the use of inexpensive and easily available reagents and we show below that MPBH allows the borylation of aryl bromides in high yields using the very common $[PdCl_2(TPP)_2]$ precatalyst. Both sets of data clearly complement each other in demonstrating that MPBH (**1**) is as effective as PinBH (**2**) in the borylation of aryl halides and in Suzuki coupling reactions, and is superior in terms of economy and preparation of dialkoxyboranes.

Results and Discussion

Preparation of MPBH

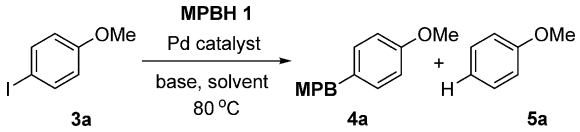
Very pure solutions of MPBH can be obtained by reaction of hexylene glycol with borane–dimethyl sulfide.[10,15] The reagent can be distilled[11a] and stored in neat form. In our previous study,[10] we used a procedure inspired by the work of Suseela and Periasamy:[17] gaseous diborane was generated by dropwise addition of a solution of I_2 to $NaBH_4$ in diglyme. The gas was absorbed in a separate flask in a solution of hexylene glycol in dichloromethane, toluene or dioxane. Although efficient on a small scale, this procedure was hampered by the limited solubility of I_2 in diglyme. It turned out that diborane is much more conveniently produced by the slow addition of $MeSO_3H$ to $NaBH_4$[18] in diglyme (Scheme 1). ^{11}B and ^1H NMR of such DMS-free MPBH solutions showed excellent purity. The yields were quantitative and thus the solutions were diluted to a known volume and the concentration calculated on this basis. We describe in the Exp. Sect. a convenient procedure for a 50 mmol batch; batches of 350 mmol of pure **1** have also been performed.[19] Dioxane and toluene solutions of **1** could be stored at 4 °C for several months without decomposition.

Borylation of Aryl Halides

With the reagent in hand, we turned our attention to the borylation of aryl halides.[5b,6,20] We first examined the influence of the catalyst, base and solvent on the borylation of the model substrate 4-iodoanisole (**3a**). The results of this screening are gathered in Table 1.

As expected, the nature of the base was the main factor influencing the outcome of the reaction. TEA promoted the borylation (Table 1, entry 1), whereas oxygenated bases like KOAc (Table 1, entry 2) strongly favoured the reduction pathway to give anisole (**5a**). A stronger base like K_3PO_4 (Table 1, entry 3) also promoted the Suzuki coupling of the arylboronate product **4a** with the remaining aryl iodide **3a**, which resulted in the competing formation of the homocoupled biaryl compound. Next, various palladium sources were screened. The reaction was efficiently catalyzed by Pd^{II} complexes with only two phosphane ligands (Table 1, entries 1 and 4). We were pleased to observe that $[PdCl_2(TPP)_2]$, a simple, robust and fully air-stable catalyst increased the overall efficiency. The use of this catalyst, along with TEA as the base, resulted in the complete conversion of **3a**. Complexes with additional phosphane ligands (Table 1, entry 5) tended to retard the reaction, whereas the absence of phosphane ligands (Table 1, entries 6 and 7) resulted in lower conversion and the predominance of the reduction product **5**. DMF (Table 1, entry 9) resulted in a low **4/5** ratio, whereas both toluene and dioxane (Table 1, entries 1 and 8) were of comparable efficiency.

Table 1. Borylation of 4-iodoanisole **3a** with MPBH under various conditions.[a]



3a **4a** **5a**

Entry	Catalyst	Base	Solvent	Yield (%)	
				4a	**5a**
1	$[PdCl_2(TPP)_2]$	TEA	toluene	89	07
2	$[PdCl_2(TPP)_2]$	KOAc	toluene	26	60
3	$[PdCl_2(TPP)_2]$	K_3PO_4	toluene	26[b]	30
4	$[PdCl_2(dppf)]$	TEA	toluene	78	20
5	$[Pd(TPP)_4]$	TEA	toluene	70	30
6	$[Pd_2(dba)_3]$	TEA	toluene	10[c]	13
7	$[Pd(OAc)_2]$	TEA	toluene	70	26
8	$[PdCl_2(TPP)_2]$	TEA	dioxane	89	07
9	$[PdCl_2(TPP)_2]$	TEA	DMF	40	40

[a] Reaction conditions: 4-iodoanisole (**3a**; 1.0 mmol) with MPBH (**1**; 1.5 mmol), the catalyst (3 mol-%) and the base (3.0 mmol) in solvent (4 mL) at 80 °C for 3 h. Reported yields were determined by GC (internal standard) based on **3a**. [b] The homocoupling product 4,4′-dimethoxybiphenyl (34%) was also formed. [c] Unreacted aryl halide was the major product.

Thus, we carried out the borylation of various aryl halides in the presence of $[PdCl_2(TPP)_2]$ and TEA, which gave the corresponding arylboronates. The results are summarized in Table 2.

Note that aryl bromides (Table 2, entries 2, 4, 6, 9, 11 and 18) could also be used.[6d] The reaction of triflates was sluggish and stopped before completion; chlorides did not react. The present procedure tolerates a wide variety of functional groups. A small amount of reduced byproduct **5** was formed in all cases. Separation of this byproduct was easily achieved by flash chromatography. The reaction could be run on a 10-mmol scale with a slightly reduced catalyst loading (2 mol%, Table 2, entry 1, 87% yield after Kugelrohr distillation). Steric hindrance at the *ortho* position had little influence (Table 2, entries 15 and 17). In the presence of electron-donating groups such as OMe (entries 1 and 2), NMe_2 (entries 3 and 4) or Me (entries 5 and 6), the reactions were high-yielding with significantly shorter reaction times and better borylation/reduction ratios. These results are comparable to those of Murata et al.[15] in terms of conditions, yields and functional-group compatibility.

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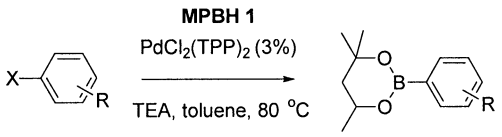
Table 2. Borylation of representative aryl halides with MPBH.[a]



3a-r 4a-m

Entry	Aryl halide **3a–h**	X	Time (h)	Product	Yield (%)[b]
1	4-MeO-phenyl	I	3	**4a**	89 (87[c])
2	4-MeO-phenyl	Br	6	**4a**	89
3	4-NMe_2-phenyl	I	3	**4b**	79
4	4-NMe_2-phenyl	Br	6	**4b**	83
5	4-Me-phenyl	I	6	**4c**	85
6	4-Me-phenyl	Br	16	**4c**	71
7	4-Br-phenyl	I	6	**4d**	65
8	phenyl	I	6	**4e**[d]	91[d]
9	phenyl	Br	16	**4e**[d]	82[d]
10	1-naphthyl	I	6	**4f**	60
11	1-naphthyl	Br	16	**4f**	51
12	4-MeO_2C-phenyl	I	16	**4g**	68
13	4-CN-phenyl	I	16	**4h**	73
14	3-NO_2-phenyl	I	16	**4i**	50
15	2,4-dimethylphenyl	I	16	**4j**	78
16	4-aminophenyl	I	3	**4k**	71
17	2-aminophenyl	I	6	**4l**	88
18	2-thienyl	Br	6	**4m**	60

[a] Reaction conditions: halide **3** (1.0 mmol), MPBH (**1**; 1.5 mmol), $[PdCl_2(TPP)_2]$ (3 mol-%) and TEA (3 mmol) in toluene (3 mL) at 80 °C for the indicated time. [b] Isolated yields of **4** based on **3**. [c] Isolated yield of a run using 10 mmol of **3a** with 2 mol-% of $[PdCl_2(TPP)_2]$. [d] GC yields.

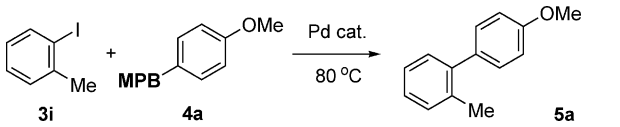
Aryl halides bearing electron-withdrawing groups usually led to a less favourable borylation/reduction ratio. In such cases, the superiority of Murata et al.'s catalytic system was apparent. 4-Iodobenzoic ester **3g**, borylated in 68% isolated yield in this work, was obtained in 78% yield in the work of Murata et al.[15] 4-Nitrophenyl iodide was totally hydrodehalogenated in the presence of $[PdCl_2(TPP)_2]$, whereas the *t*Bu-DPEphos-based catalyst produced the boronic ester in 77% yield.[15]

Thus, MPBH (**1**) is a very convenient reagent for the borylation of aryl iodides and also aryl bromides. In the borylation reaction, it behaves identically to PinBH (**2**) in terms of scope and yields. Moreover this borylation reaction can often be performed with a very common, air-stable Pd precatalyst.

Suzuki–Miyaura Coupling

With an easy access to functionalized boronate esters in hand, we sought to confirm that MPB esters were also efficient in the preparation of unsymmetrical biphenyls. Various conditions tested for the coupling of 2-iodotoluene (**3i**) and (4-methoxyphenyl)boronic ester **4a** are gathered in Table 3.

Table 3. Suzuki–Miyaura cross-coupling reactions of **4a** under various conditions.[a]



3i 4a 5a

Entry	Catalyst	Base	Solvent	Time (h)	Yield (%)
1	$[PdCl_2(TPP)_2]$	TEA	toluene	16	0
2	$[PdCl_2(TPP)_2]$	TEA	DMF	16	0
2	$[PdCl_2(TPP)_2]$	K_3PO_4	DMF	4	90
4	$[Pd_2(dba)_3]$	K_3PO_4	DMF	4	84
5	$[PdCl_2(TPP)_2]$	CsF	DMF	0.5	94
6	$[Pd(TPP)_4]$	CsF	DMF	2	90
7	$[Pd(OAc)_2]$	CsF	DMF	2	88
8	$[PdCl_2(TPP)_2]$	CsF	toluene	4	<10

[a] Reaction conditions: arylboronate (1.0 mmol), aryl iodide (1.0 mmol), base (3.0 mmol), Pd catalyst (3 mol%) in solvent (2 mL) at 80 °C for the given time. Reported yields are determined by GC (internal standard) based on **3a**.

Triethylamine as base did not produce the desired Suzuki coupling product (entries 1 and 2). As a consequence we never observed any homocoupling product in our borylation reactions. Changing the base from TEA to K_3PO_4 (entry 3) resulted in complete Suzuki coupling in 4 h. Finally, the choice of CsF[21] (entry 5) as base gratifyingly produced the desired biaryl product in excellent yield within 30 min. Other Pd sources (entries 6 and 7), although effective, were not as efficient as $[PdCl_2(TPP)_2]$. Murata et al. performed the cross-coupling of hexylene glycol boronic esters[15] and aryl halides by using K_3PO_4 as the base. For the sake of complementarity we provide examples with CsF.

These conditions were very general and highly efficient for the reaction of a variety of aryl iodides, bromides and triflates with various arylboronates, as shown in Table 4. The reactions were rapid (<2 h) with both electron-poor and -rich aryl halides (entries 2 and 3). Hindered arylboronates are not inhibited from coupling to sterically demanding aryl halides as seen in entry 10. Heteroaromatic halides can also be used (entry 11).

Because the borylation reaction is high-yielding and clean, it is possible to run the borylation and Suzuki coupling reactions in the same pot.[6d] The product was not contaminated by either of the two possible homocoupling products. Two examples are summarized in Scheme 2.

The same catalyst loading was used for both steps. Note that the coupling itself was slower than in the two-step protocol. In both experiments, the homocoupling product was not detected (<5%). Thus, the conversion of the starting iodide **3a** or **3j** in the borylation step was total.

In our former work on Zr-catalyzed hydroboration,[10] we used competition experiments to demonstrate that MPBH reacted much faster than PinBH. We attempted to apply the same kind of protocol to compare the hexylene glycol and pinacol derivatives in the borylation and Suzuki–Miyaura coupling reactions. Equal amounts of **1** and **2** were treated with 4-iodoanisole, TEA and $[PdCl_2(TPP)_2]$ in tolu-

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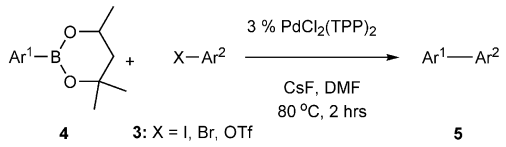
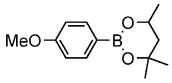
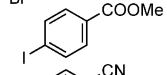
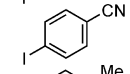
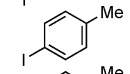
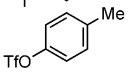
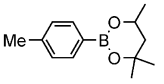
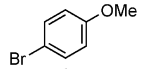
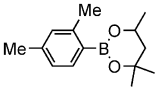
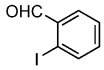
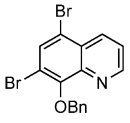
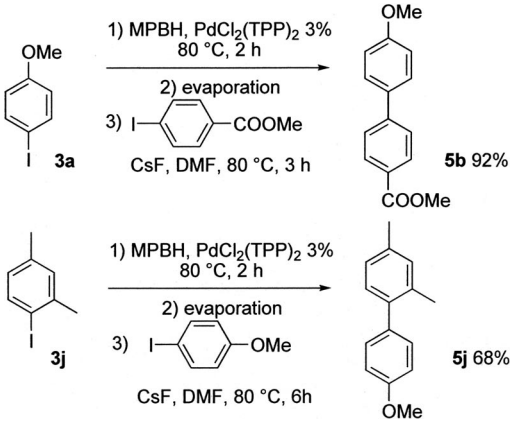
Table 4. Examples of palladium-catalyzed biaryl coupling of aryl MPB derivatives.[a]



4 3: X = I, Br, OTf 5

Entry	Boronic ester **4**	Aryl halide **3**	Yield (%)[b]
1			**5a**: 84
2	"		**5a**: 92
3	"		**5b:** 96
4	"		**5c:** 80
5	"		**5d:** 78
6	"		**5d:** 85
7			**5d:** 72
8	"		**5e:** 87
9	"		**5f:** 87
10			**5g:** 92
11	"		**5h:** 97[c]

[a] Reaction conditions: arylboronate (1.0 mmol), aryl halide (or triflate) (1.0 mmol), CsF (3.0 mmol) and $[PdCl_2(TPP)_2]$ (0.03 mmol) in DMF (4.0 mL) at 80 °C for 2 h. [b] Isolated yields. [c] Yield of 8-benzyloxy-5,7-di(*p*-tolylyl)quinoline from 2 equiv. of **4**. The reaction of a single equivalent of boronic ester was not regioselective.



Scheme 2. One-pot borylation/Suzuki coupling.

ene, and the reaction was monitored by gas chromatography. We found that MPB-anisyl **4a** and PinB-anisyl were evolved at equal rates within experimental error. In a second experiment, we submitted equimolar mixtures of hexylene glycol-protected tolylboronic ester **4c** and the corresponding pinacol-protected tolylboronic ester to Suzuki coupling with excess 4-iodoanisole. Again, both esters reacted identically.[15,22] These results suggest that the boronic esters are involved only in the fast, non-rate-determining steps of the catalytic cycle.

Conclusions

In conclusion, we have shown that MPBH (**1**) is the reagent of choice for an easy preparation of arylboronic esters from not only aryl iodides, but also bromides. A very common, air-stable commercial palladium catalyst can be used. Our work, together with that of Murata et al.,[15] clearly demonstrates that the reactivity and scope of MPBH (**1**) equals that of PinBH (**2**) in this borylation reaction, leading to comparable yields of boronic esters. The stability and ease of handling of both series of arylboronic esters are also identical. Finally, the hexylene glycol boronic esters can also undergo Suzuki–Miyaura reactions with aryl iodides, bromides or triflates in excellent yields. Thus, we could not find any drawback in using MPBH (**1**) instead of PinBH (**2**) in the borylation of aryl halides. MPBH is much less expensive than PinBH, very easily prepared and stable. It appears that the use of MPBH (**1**) in the borylation of halides is an atom-economic and very easy pathway to a large array of stable and useful arylboronic esters.

Experimental Section

General: All reactions were performed by using the usual Schlenk techniques in oven-dried glassware with magnetic stirring under nitrogen. 2-Methyl-2,4-pentanediol was distilled from CaH_2, triethylamine from KOH, dioxane from sodium/benzophenone and toluene from sodium. CsF was dried by heating at 150 °C under vacuum overnight. Note that in the ^{13}C NMR spectra, carbon atoms that are directly bonded to boron are broad and remained undetected.

Caution: *Diborane is a toxic and pyrophoric gas. All preparations should be carried out in a well-ventilated fume hood.*

Preparation of MPBH (1) from $NaBH_4$ and Methanesulfonic Acid: In a 100-mL two-necked round-bottom flask fitted with a pressure-equalizing dropping funnel, an efficient magnetic stirrer and a N_2 inlet, $NaBH_4$ (3.7 g, 100 mmol) was suspended in bis(2-methoxyethyl) ether (diglyme; 40 mL). The flask was connected through a double-ended needle to a second 100-mL cylindrical flask containing a magnetically stirred solution of 2-methyl-2,4-pentanediol (5.9 g, 50 mmol) in dry dioxane (45 mL) cooled to 8–10 °C. The double-ended needle was positioned so that gas evolving from the first flask would bubble through the solution of the second. The second flask was vented through a double-ended needle bubbling into ethanol (to trap the excess diborane). The dropping funnel was loaded with a solution of methanesulfonic acid (9.6 g, 100 mmol) in diglyme (20 mL). This solution was added dropwise over 30–

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45 min to the $NaBH_4$ suspension, during which time the temperature increased to 40 °C. The evolved gases were bubbled through the solution of diol in the second flask. Throughout the process, a small stream of nitrogen (2–5 bubbles per second) was applied to the whole apparatus to ensure complete transfer of the diborane. At the end of the addition of methanesulfonic acid, the temperature of the second flask was increased to 20 °C and the flow of N_2 was continued for 1 h. This step allowed the elimination of excess diborane from the solution of MPBH. The solution was transferred to a volumetric flask and diluted to 50 mL. ^{11}B and ^1H NMR indicated that the conversion of diol was quantitative. Thus, the solution was considered 1 M in MPBH. The solution could be kept at 4 °C for several months without any change. Storage at room temperature was deleterious.

4,4,6-Trimethyl-1,3,2-dioxaborinane (1: MPBH):[11] ^1H NMR (300 MHz, $CDCl_3$): δ = 4.16 (dqd, J = 11.8, 6.2, 3.0 Hz, 1 H), 1.76 (ddd, J = 13.9, 3.0, 1.7 Hz, 1 H), 1.50 (dd, J = 13.9, 11.8 Hz, 1 H), 1.27 (s, 3 H), 1.26 (s, 3 H), 1.23 (d, J = 6.21 Hz, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 70.8, 64.6, 46.1, 31.0, 28.1, 22.9 ppm. ^{11}B NMR (96 MHz, $CDCl_3$): δ = 25.2 (d, J = 170 Hz) ppm. IR (neat): $\tilde{\nu}$ = 2551, 2498 cm^{-1}.

General Procedure for the Borylation of Aryl Halides: In a 20-mL Schlenk tube, $[PdCl_2(TPP)_2]$ (21 mg, 0.03 mmol) was dissolved in toluene (4.0 mL). TEA (0.420 mL, 3.0 mmol), the aryl halide (1.0 mmol) and a 1 M solution of MPBH in toluene (1.5 mL, 1.5 mmol) were then added and the reaction mixture stirred for the indicated time at 80 °C. After completion of the reaction, the mixture was diluted with diethyl ether and washed once with brine. The organic layer was dried with $MgSO_4$ and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (SiO_2 deactivated with 3% Et_3N, eluent: pentane/ether) to give the expected arylboronate (Table 2).

The same procedure was repeated on a 10-mmol scale (Table 2, entry 1): In a 50-mL Schlenk tube, $[PdCl_2(TPP)_2]$ (140 mg, 0.2 mmol) was dissolved in toluene (40 mL). TEA (4.20 mL, 3.0 mmol), 4-iodoanisole (**3a**; 2.30 g, 10 mmol) and a 1 M solution of MPBH in toluene (15 mL; 15 mmol) were then added and the reaction mixture stirred for 3 h at 80 °C. The mixture was diluted with diethyl ether (100 mL) and washed once with brine (10 mL). The organic layer was dried with $MgSO_4$ and concentrated. The material was purified by kugelrohr distillation.

[2-(4-Methoxyphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (**4a**; RN 934558-31-3, 208 mg, 89%], 2-phenyl-4,4,6-trimethyl-1,3,2-dioxaborinane (**4e**; RN 15961-35-0, 123 mg, 81% isolated yield) and 4-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)]phenylamine, (**4k**; RN 934558-32-4, 135 mg, 71%) have been described elsewhere.[15]

Dimethyl[4-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)phenyl]amine (4b): Yield 205 mg, 83%. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, J = 8.7 Hz, 2 H), 6.67 (d, J = 8.7 Hz, 2 H), 4.29 (dqd, J = 11.7, 6.2, 3.0 Hz, 1 H), 2.95 (s, 6 H), 1.81 (dd, J = 13.8, 3.0 Hz, 1 H), 1.54 (dd, J = 13.8, 11.7 Hz, 1 H), 1.34 (s, 3 H), 1.32 (s, 3 H), 1.31 (d, J = 6.2 Hz, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 152.1 (C), 135.0 (CH), 111.4 (CH), 70.5 (C), 64.6 (CH), 46.1 (CH_2), 40.3 (2 × CH_3), 31.4 (CH_3), 28.2 (CH_3), 23.3 (CH_3) ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 26.9 ppm. IR (neat): $\tilde{\nu}$ = 2970, 2930, 2906, 1605, 1300, 945, 816 cm^{-1}. MS (DCI): m/z = 248 $[M + H]^+$. HRMS (ES): calcd. for $C_{14}H_{23}O_2N^{10}B$ 247.18527; found 247.18500.

2-(4-Methylphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (4c): Yield 171 mg, 85%. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.70 (d, J = 7.7 Hz, 2 H), 7.14 (d, J = 7.7 Hz, 2 H), 4.32 (dqd, J = 11.8, 6.7, 3.0 Hz, 1 H), 2.34 (s, 3 H), 1.84 (dd, J = 13.7, 3.0 Hz, 1 H), 1.57 (dd, J = 13.7, 11.8 Hz, 1 H), 1.36 (s, 3 H), 1.35 (s, 3 H), 1.33 (d, J = 6.7 Hz, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 140.1 (C), 133.8 (CH), 128.2 (CH), 70.7 (C), 64.8 (CH), 46.0 (CH_2), 31.3 (CH_3), 28.1 (CH_3), 23.2 (CH_3), 21.6 (CH_3) ppm. ^{11}B NMR (96.3 MHz, $CDCl_3$): δ = 27.1 ppm. IR (neat): $\tilde{\nu}$ = 2971, 2932, 2908, 1612, 1406, 815, 766, 724 cm^{-1}. MS (DCI): m/z (%) = 236 (100) $[M + NH_4]^+$, 144 (50). HRMS (ES): calcd. for $C_{13}H_{19}O_2{}^{11}B$ 218.1473; found 218.1479.

2-(4-Bromophenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (4d): Yield 185 mg, 65%. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, J = 8.2 Hz, 2 H), 7.45 (d, J = 8.2 Hz, 2 H), 4.32 (dqd, J = 11.7, 6.2, 3.0 Hz, 1 H), 1.86 (dd, J = 13.9, 3.0 Hz, 1 H), 1.57 (dd, J = 13.9, 11.7 Hz, 1 H), 1.36 (s, 3 H), 1.35 (s, 3 H), 1.33 (d, J = 6.2 Hz, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 135.4 (2 × CH), 133.7 (C), 130.6 (2 × CH), 125.1 (C), 71.2 (C), 65.1 (CH), 46.0 (CH_2), 31.2 (CH_3), 28.1 (CH_3), 23.1 (CH_3) ppm. ^{11}B NMR (96.3 MHz, $CDCl_3$): δ = 26.7 ppm. IR (neat): $\tilde{\nu}$ = 2968, 2928, 2906, 1583, 1403, 1304, 823, 767, 723 cm^{-1}. MS (DCI): m/z (%) = 284 (100) $[M]^+$, 283 (27), 282 (98), 281 (29). HRMS (ES): calcd. for $C_{12}H_{16}BrO_2{}^{11}B$ 282.0463; found 282.0459.

4,4,6-Trimethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborinane (4f): Yield 136 mg, 60%. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.79 (d, J = 8.4 Hz, 1 H), 8.02 (d, J = 6.8 Hz, 1 H), 7.85 (d, J = 8.3 Hz, 1 H), 7.79 (d, J = 8.1 Hz, 1 H), 7.50–7.38 (m, 3 H), 4.42 (dqd, J = 12.0, 6.2, 3.0 Hz, 1 H), 1.88 (dd, J = 13.6, 3.0 Hz, 1 H), 1.67 (dd, J = 13.6, 12.0 Hz, 1 H), 1.44 (s, 3 H), 1.43 (s, 3 H), 1.40 (d, J = 6.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.8 (C), 134.2 (CH), 133.4 (C), 130.6 (CH), 128.4 (CH), 128.4 (CH), 125.8 (CH), 125.1 (CH), 125.0 (CH), 71.5 (C), 65.3 (CH), 46.0 (CH_2), 31.4 (CH_3), 28.3 (CH_3), 23.3 (CH_3) ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 27.8 ppm. IR (neat): $\tilde{\nu}$ = 3038, 2973, 2926, 1509, 1459, 1303, 804, 779 cm^{-1}. MS (DCI): m/z (%) = 272 (100) $[M + NH_4]^+$, 271 (62), 144 (29). HRMS (APPI-APCI): calcd. for $C_{16}H_{19}O_2{}^{11}B$ 254.1473; found 254.1463.

Methyl 4-(4,4,6-Trimethyl-1,3,2-dioxaborinan-2-yl)benzoate (4g): Yield 179 mg, 68%. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.00 (d, J = 8.1 Hz, 2 H), 7.88 (d, J = 8.1 Hz, 2 H), 4.38 (dqd, J = 11.5, 6.2, 3.0 Hz, 1 H), 3.93 (s, 3 H), 1.91 (dd, J = 13.9, 3.0 Hz, 1 H), 1.62 (dd, J = 13.9, 11.5 Hz, 1 H), 1.41 (s, 3 H), 1.40 (s, 3 H), 1.38 (d, J = 6.2 Hz, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 167.3 (C), 133.6 (C), 131.4 (CH), 128.3 (CH), 71.2 (C), 65.1 (CH), 51.9 (CH_3), 45.9 (CH_2), 31.1 (CH_3), 28.1 (CH_3), 23.0 (CH_3) ppm. ^{11}B NMR (96.3 MHz, $CDCl_3$): δ = 27.1 ppm. IR (neat): $\tilde{\nu}$ = 2971, 2949, 2908, 1725, 1561, 1432, 1166, 766, 711 cm^{-1}. MS (ESI): m/z = 263 $[M + H]^+$, 279 $[M + Na]^+$. HRMS (APPI-APCI): calcd. for $C_{14}H_{20}O_4{}^{11}B$ 263.14492; found 263.14503.

4-(4,4,6-Trimethyl-1,3,2-dioxaborinan-2-yl)benzonitrile (4h): Yield 166 mg, 73%. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, J = 7.9 Hz, 2 H), 7.59 (d, J = 7.9 Hz, 2 H), 4.35 (dqd, J = 11.6, 6.2, 3.0 Hz, 1 H), 1.89 (dd, J = 14.0, 3.0 Hz, 1 H), 1.59 (dd, J = 14.0, 11.6 Hz, 1 H), 1.38 (s, 3 H), 1.37 (s, 3 H), 1.35 (d, J = 6.2 Hz, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 134.1 (CH), 130.8 (CH), 119.2 (C), 113.5 (C), 71.6 (C), 65.3 (CH), 45.9 (CH_2), 31.1 (CH_3), 28.1 (CH_3), 23.0 (CH_3) ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 26.3 ppm. IR (neat): $\tilde{\nu}$ = 2972, 2928, 2226, 1408, 1304, 1164, 834, 768, 738 cm^{-1}. MS (DCI): m/z (%) = 247 (100) $[M + NH_4]^+$. HRMS (ES): calcd. for $C_{13}H_{16}NO_2{}^{11}B$ 229.1269; found 229.1277.

4,4,6-Trimethyl-2-(3-nitrophenyl)-1,3,2-dioxaborinane (4i): Yield 125 mg, 50%. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.62 (d, J = 2.5 Hz, 1 H), 8.23 (ddd, J = 7.7, 2.5, 1.1 Hz, 1 H), 8.10 (td, J = 7.7, 1.1 Hz, 1 H), 7.49 (t, J = 7.7 Hz, 1 H), 4.38 (dqd, J = 11.8, 6.2, 3.0 Hz, 1 H), 1.91 (dd, J = 13.9, 3.0 Hz, 1 H), 1.62 (dd, J =

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13.9, 11.8 Hz, 1 H), 1.40 (s, 3 H), 1.38 (s, 3 H), 1.37 (d, J = 6.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8 (C), 139.8 (CH), 128.4 (CH), 128.3 (CH), 125.0 (CH), 71.7 (C), 65.4 (CH), 45.9 (CH_2), 31.1 (CH_3), 28.1 (CH_3), 23.0 (CH_3) ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 26.3 ppm. IR (neat): $\tilde{\nu}$ = 2972, 2924, 1609, 1528, 1304, 837, 771, 697 cm^{-1}. MS (DCI): m/z (%) = 250 (90) [M + H]$^+$, 220 (100). HRMS (ES): calcd. for $C_{12}H_{16}NO_4{}^{11}B$ 249.1167; found 249.1170.

2-(2,4-Dimethylphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (4j): Yield 181 mg, 78%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63 (d, J = 8.1 Hz, 1 H), 6.97–6.92 (m, 2 H), 4.32 (dqd, J = 11.7, 6.2, 3.0 Hz, 1 H), 2.48 (s, 3 H), 2.28 (s, 3 H), 1.83 (dd, J = 13.8, 3.0 Hz, 1 H), 1.56 (dd, J = 13.7, 11.7 Hz, 1 H), 1.35 (s, 6 H), 1.32 (d, J = 6.2 Hz, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 143.9 (C), 139.5 (C), 135.0 (CH), 130.8 (CH), 125.4 (CH), 70.9 (CH), 64.9 (CH), 46.0 (CH_2), 31.4 (CH_3), 28.2 (CH_3), 23.3 (CH_3), 22.3 (CH_3), 21.3 (CH_3) ppm. ^{11}B NMR (96.3 MHz, $CDCl_3$): δ = 27.8 ppm. IR (KBr): $\tilde{\nu}$ = 2972, 2920, 1610, 1379, 1301 cm^{-1}. MS (DCI): m/z (%) = 250 (100) [M + NH_4]$^+$, 233 (42) [M + H]$^+$, 144 (75). HRMS (ES): calcd. for $C_{14}H_{21}O_2{}^{11}B$ 232.1629; found 232.1626.

2-(4,4,6-Trimethyl-1,3,2-dioxaborinan-2-yl)phenylamine (4l): Yield 193 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (dd, J = 7.9, 1.6 Hz, 1 H) 7.18 (ddd, J = 8.2, 7.9, 1.6 Hz, 1 H), 6.71 (td, J = 8.1, 1.0 Hz, 1 H), 6.65 (d, J = 8.0 Hz, 1 H), 5.3 (br., NH), 4.37 (dqd, J = 11.9, 6.2, 3.0 Hz, 1 H), 1.87 (dd, J = 13.8, 3.0 Hz, 1 H), 1.62 (dd, J = 13.8, 11.9 Hz, 1 H), 1.39 (s, 3 H), 1.38 (s, 3 H), 1.35 (d, J = 6.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.1 (C), 136.0 (CH), 131.7 (CH), 116.9 (CH), 115.1 (CH), 71.2 (C), 65.0 (CH), 45.7 (CH_2), 31.3 (CH_3), 28.1 (CH_3), 23.2 (CH_3) ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 27.4 ppm. IR (neat): $\tilde{\nu}$ = 3480, 3385, 3019, 2971, 2930, 2909, 1601, 1565, 1451, 755 cm^{-1}. MS (DCI): m/z (%) = 219 (85) [M]$^+$, 220 (100) [M + H]$^+$. HRMS (ES): calcd. for $C_{12}H_{19}O_2N^{10}B$ 219.15397; found 219.15371.

4,4,6-Trimethyl-2-(thiophen-2-yl)-1,3,2-dioxaborinane (4m): Yield 126 mg, 60%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (dd, J = 3.4, 0.9 Hz, 1 H), 7.52 (dd, J = 4.7, 0.9 Hz, 1 H), 7.13 (dd, J = 4.7, 3.4 Hz, 1 H), 4.33 (dqd, J = 11.7, 6.2, 3.0 Hz, 1 H), 1.84 (dd, J = 13.8, 3.0 Hz, 1 H), 1.60 (dd, J = 13.8, 11.7 Hz, 1 H), 1.36 (s, 6 H), 1.33 (d, J = 6.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.2 (CH), 130.8 (CH), 127.8 (CH), 71.3 (C), 65.2 (CH), 46.0 (CH_2), 31.1 (CH_3), 28.0 (CH_3), 23.1 (CH_3) ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 25.4 ppm. IR (neat): $\tilde{\nu}$ = 2974, 2933, 2913, 1520, 1421, 1283 cm^{-1}. MS (DCI): m/z (%) = 111 (100), 210 (83) [M]$^+$, 211 (64) [M + H]$^+$. HRMS (APPI-APCI): calcd. for $C_{10}H_{15}O_2{}^{11}BS$ 210.08804; found 210.08812.

General Procedure for the Suzuki–Miyaura Biaryl Coupling Reaction: A mixture of 2-aryl-4,4,6-trimethyl-1,3,2-dioxaborinane **4** (1.0 mmol) and aryl substrate **3** (1.0 mmol) in DMF (1 mL), followed by [$PdCl_2(TPP)_2$] (0.03 mmol) were added to a suspension of CsF (456 mg, 3.0 mmol) in DMF (3.0 mL). The reaction mixture was stirred at 80 °C for 2 h or until GC analysis showed completion. The mixture was then diluted with diethyl ether (20 mL) and washed with water. The organic layer was dried with $MgSO_4$, the solvent removed under vacuum and the residue purified by flash chromatography (eluent: cyclohexane/ethyl acetate) (Table 4).

One-Pot Procedure: [$PdCl_2(TPP)_2$] (21 mg, 0.03 mmol) in dioxane (4.0 mL) was placed in a 20-mL Schlenk tube. TEA (0.420 mL, 3.0 mmol) was then added and the reaction mixture stirred for 30 min. The aryl iodide (1.0 mmol) and MPBH solution (1 M, 1.5 mmol) in toluene were then successively added and the reaction mixture stirred at 80 °C for 3 (**3a**) or 6 h (**3j**). The reaction was monitored by GC analysis of reaction aliquots. After completion, the solvent was evaporated to dryness and a solution of CsF (5.0 mmol) and the second aryl halide (1.0 mmol) in DMF (4.0 mL) was added. The reaction was stirred at 80 °C for 6 h. After completion, it was diluted with diethyl ether and washed with water. The organic layer was dried with $MgSO_4$, the solvent removed under vacuum and the residue purified by flash chromatography (eluent: cyclohexane/ethyl acetate).

Supporting Information (see also the footnote on the first page of this article): Detailed experimental procedures, characterization and copies of NMR spectra of MPBH (**1**), boronic esters **4a**–**g** and Suzuki coupling products **5a**–**h**.

Acknowledgments

We gratefully thank the Université J. Fourier (DCM-SERCO, ICMG FR-2607) and the Centre National de la Recherche Scientifique (CNRS) (UMR-5250) for financial support.

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Received: May 29, 2008
Published Online: August 12, 2008

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