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Sequential dehydrogenation–arylation of di*iso*propylamine–borane complex catalyzed by palladium nanoparticles

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ABSTRACT

Palladium nanoparticles have been prepared using different techniques, CO_2-assisted microfluidics coflow or thermolysis using ionic liquids. Both techniques displayed interesting activities in dehydrogenation of di*iso*propylamine–borane complex, and allowed performing a dehydrogenation–arylation sequence with the creation of a carbon–boron bond.

1. Introduction

In recent years, dehydrogenation of borane–ammonia has received a great deal of attention as a valuable reservoir of hydrogen, which can be released using various catalysts.[1–3] In general most studies are performed on ammonia borane and fewer studies focus on the dehydrogenation of substituted amine–borane complexes.[4–16] Among those, homogeneous catalysts based on transition metal complexes (Zr,[17,18] Ti,[17,18] Hf) are usually more active than the heterogeneous ones. Nonetheless, some alternative (rhodium nanoparticle NP,[19] ruthenium[9,20,21] or iron[22,23] complexes) displayed promising results.[24] Palladium complexes,[25] or NPs[26–30] however have been more scarcely used although exhibiting interesting features with ammonia borane. In view of our recent work showing that palladium NPs were compatible with boron chemistry,[31,32] we wondered how those catalysts could contribute to the dehydrogenation of aminoboranes endeavor.

2. Results and discussion

Palladium nanoparticles (Pd NPs) are prepared following the previously reported microfluidic coflow method assisted by supercritical CO_2.[31,32] This approach provides a flexible and reliable method for producing NC with definite size and surface functionalization. It also detaches the nucleation-growth steps from the surface stabilization, allowing independent control of the NP size and surface properties. We therefore decided to prepare a series of six Pd NPs dispersion in toluene and to evaluate their activity for the dehydrogenation of di*iso*propylamine–borane complex **1**. Most catalysts, which convert ammonia borane in a few minutes often take hours if not days to fully convert the dialkylamine–borane, especially bearing two bulky groups such as isopropyl. First, bidentate ligands like dppf (Table 1, entry 1) and dppe (Table 1, entry 4) led to inactive NPs. Little conversion was obtained when Buchwald's diarylmonophosphines were used (Table 1, entries 2 and 3). However, when trialkylphosphines were used, the NPs dispersion efficiently promoted the dehydrogenation of di*iso*propylamine–borane complex and 95% of *N*,*N*-di*iso*propylaminoborane was obtained after 1 h at room temperature (Table 1, entry 6). In most cases, higher temperature led to degradation of the resulting aminoborane, which is prone to degradation by hydrolysis over extended period of time.

With these results in hand, we envisioned to use the same Pd NPs for the sequential dehydrogenation–arylation of the starting di*iso*propylamine–borane complex. Indeed, Pd@PCy_3 is known to catalyze the borylation of arylbromide[31,32] (Scheme 1) and seemed to be equally efficient in the dehydrogenation process. We

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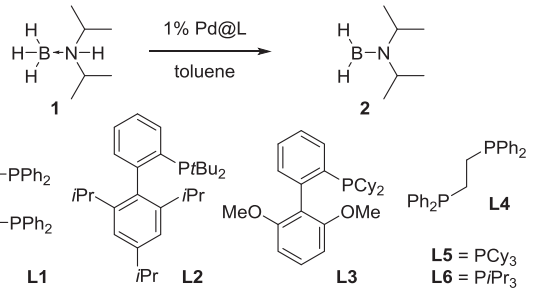
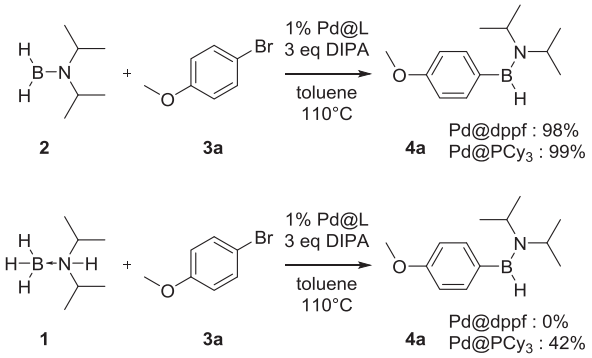
Table 1
Palladium NPs catalyzed dehydrogenation of di*iso*propylamine–borane complex



Entry	Catalyst	25 °C, 1 h	25 °C, 12 h	100 °C, 45 min
1	Pd@**L1**	0%[a]	0%[a]	0%[a]
2	Pd@**L2**	0%[a]	0%[a]	<3%[a]
3	Pd@**L3**	0%[a]	22%[a]	12%[a]
4	Pd@**L4**	0%[a]	0%[a]	0%[a]
5	Pd@**L5**	41%[a]	>95%[a]	43%[a]
6	Pd@**L6**	>95%[a]	n.d.	n.d.

[a] Product formation monitored by ^{11}B NMR.

performed a series of experiments with the various Pd@L described in Table 1, and most of them turned out to be completely inactive, including Pd@dppf, which was reported as one of the best catalysts for borylation (Scheme 1). Only Pd@PCy_3 led to the formation of 42% of amino arylborane. Despite our tries, including the splitting of the two steps either in batch or using continuous microfluidic processes, we never succeeded to improve yields or selectivity.

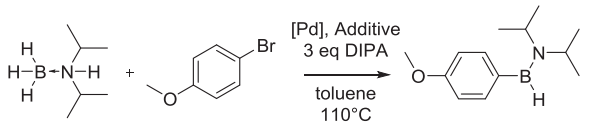


Scheme 1. Arylation of aminoborane and amine–borane.

Because of that, we decided to fully optimize the catalytic system, starting with simple homogeneous catalysts. We used directly di*iso*propylamine (DIPA) as base. Indeed, inorganic bases usually react with the aminoborane or the starting amine–borane complex. Other organic bases could also be used. Employing 3 equiv of amine would lead to a redistribution of the amine–borane complex. Namely, with tertiary amine, dehydrogenation did not occur; with smaller secondary amines or primary amine, dehydrogenation would yield the aminoborane as dimer, trimer, or oligomer, all being poorly reactive in borylation process. The palladium source has very little impact on conversion, $PdCl_2$, $Pd(hfa)_2$, $Pd(NO_3)_2$, and $Pd(OAc)_2$ led to similar conversion. Indeed, in the first step palladium(II) is reduced by the borane into Pd(0), leading to nanoparticles when some additives are present to prevent aggregation, or to inactive 'palladium black' when none are used.

In presence of 5% $Pd(OAc)_2$ in toluene, 4-bromoanisole **3a** reacted with di*iso*propylamine–borane complex **1** leading to the arylaminoborane **4a** in 41% yield, isolated as the pinacol boronic ester obtained after methanolysis and transesterification (Table 2,

Table 2
Palladium NP catalyzed sequential dehydrogenation–arylation



Entry	[Pd]	Additive	Conversion (%)	Yield (%)
1	$Pd(OAc)_2$ 5 mol %	—	100	41[a]
2	$Pd(OAc)_2$ 5 mol %	CTA-NTf_2 35 mol %	100	41[b]
3	$Pd(OAc)_2$ 0.05 mol %	—	74	32[a]
4	$Pd(OAc)_2$ 0.05 mol %	CTA-NTf_2 35 mol %	75	36[b]
5	$Pd(OAc)_2$ 5 mol %	PCy_3 10 mol %	100	15[b]
6	$Pd(OAc)_2$ 5 mol %	dppf 5 mol %	100	10[a]

[a] Isolated product as pinacol ester.
[b] Product formation monitored by ^{11}B NMR.

entry 1). Clearly during the reaction most palladium was lost as bulk black palladium. In the presence of cetyltrimethylammonium triflimide (CTA-NTf_2), the palladium was stabilized under colloidal form, but the yields remained unchanged (Table 2, entry 2). Consistent with the formation of Pd NPs, 0.05% palladium was found to catalyze the reaction, in the presence of CTA-NTf_2 or not; in those cases (Table 2, entries 3 and 4), conversion reached a maximum of 75% after 16 h and 8–9% of dehalogenation reduced product was observed. As PCy_3 and dppf were reported previously to be highly suited for the borylation step, we investigated the stabilization by those ligands. Unfortunately, neither PCy_3 (Table 2, entry 5) nor dppf (Table 2, entry 6) led to good results, and most of the reagent was transformed into anisole. Overall, regardless of the stabilizing agent, we found that with low catalyst loadings, the reaction was not reproducible enough, probably because of the poor control of NPs formation under the reaction conditions. Hence we tackled the preparation of NPs with CTA-NTf_2, under controlled conditions.

We used a simple method allowing the preparation of metal NPs in the absence of molecular solvent,[33] which can interfere largely with the surface properties. By simply mixing the CTA-NTf_2 and Pd precursor at temperature above the Onium Salt melting point (mp 62 °C), a Pd(II) solution is obtained, which thermally decomposed into Pd(0) nanoparticle colloidal dispersion. Upon cooling, a gray powder of ammonium salt containing 7±2 nm NPs (monodispersed or aggregated) embedded in the solid matrix are obtained (Fig. 1). This method is quite general and was also applied to TBAB (mp 102 °C) and other Onium Salts.

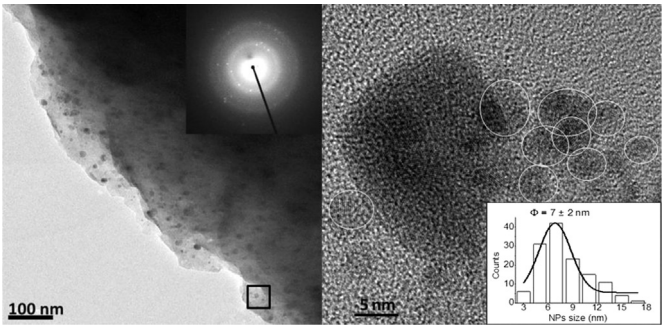
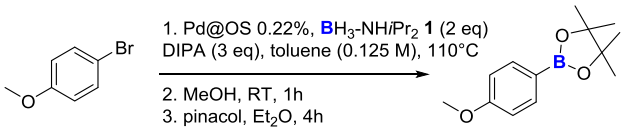


Fig. 1. Left image: TEM picture of Pd NPs embedded in the solid CTA-NTf_2 with its electron diffraction as inset. Right image corresponds to a higher magnification, where monodispersed NPs (white circle) are clearly visible with their Gaussian size distribution.

The most active catalyst was prepared by heating a solution of $Pd(OAc)_2$ (440 μmol, 5 mg) in 1 g of CTA-NTf_2 at 100 °C for 1 h, this

catalyst will be referred to Pd@CTA-NTf_2 and used in the standard reaction test of sequential dehydrogenation followed by arylation with 4-bromoanisole **3a** (Table 3). With 3 equiv of DIPA in toluene at 110 °C, the product was isolated in 50% yield after methanolysis and treatment with pinacol. Noteworthy, when isolated arylaminoborane is submitted to the same methanolysis/pinacol treatment, boronate is isolated in 97% yield.[34–36] The precursor used for NPs formation has very little influence on the outcome of the reaction, Pd@CTA-NTf_2 prepared from $PdCl_2$ instead of $Pd(OAc)_2$ led to similar conversion and isolated yield (Table 3, entry 2). However, the Onium Salt nature has a great influence on the reaction, when Pd NP is prepared in TBAB, the yield dropped to 32%, most likely due to interference with bromide anions (Table 3, entry 3). Indeed, when 5% CTAB was added to the reaction mixture, the yield decreased to similar level (38%, Table 3, entry 4). An increased catalyst loading was detrimental (46% yield, Table 3, entry 5) and a higher concentration affected slightly the reaction yield (54% Table 3, entry 6). The temperature of NPs formation is not a critical parameter for the reaction as the yield was maintained at 48–49% when the NPs have been pre formed at 80 °C (Table 3, entry 7), 120 °C (Table 3, entry 8) or 140 °C (Table 3, entry 9) instead of 100 °C. In order to rule out the influence of residual acetic acid originating from the metal precursor in the reaction mixture, the NPs have also been prepared under vacuum instead of inert argon atmosphere. Their catalytic activity remained unchanged (Table 3, entry 10). When an Onium Salt is used alone (without palladium), unsurprisingly no reaction occurred (Table 3, entry 11). Aiming at separating the dehydrogenation from the arylation step, addition of arylbromide after 30 min of putative dehydrogenation reaction was performed. Yield remained unchanged (47%).

Table 3
Pd@OS catalyzed sequential dehydrogenation–arylation of di*iso*propylborane

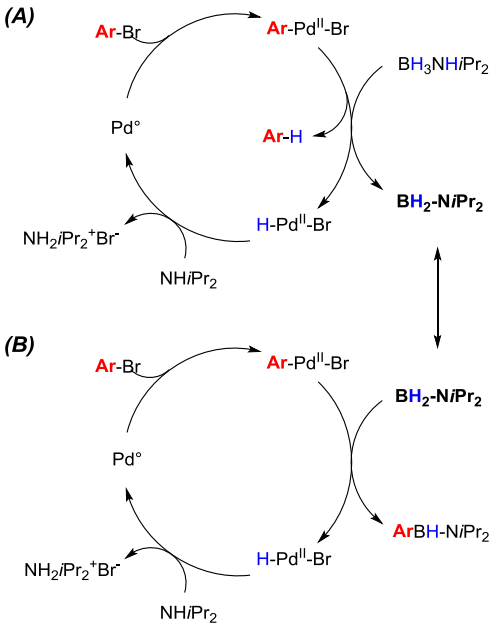


3a **5a**

Entry	PdNP@OS	Conversion (%)	Yield[a] (%)
1	Pd@CTA-NTf_2	100	50
2	Pd@CTA-NTf_2[b]	100	50
3	Pd@TBAB	100	32
4	Pd@CTA-NTf_2+5% CTAB	100	38
5	Pd@CTA-NTf_2 (0.44%)	100	46
6	Pd@CTA-NTf_2[c]	100	54
7	Pd@CTA-NTf_2[d]	100	49
8	Pd@CTA-NTf_2[e]	100	49
9	Pd@CTA-NTf_2[f]	100	48
10	Pd@CTA-NTf_2[g]	100	44
11	CTA-NTf_2	0	—
12	Pd@CTA-NTf_2[h]	100	48

[a] Isolated product as pinacol ester.
[b] Prepared with $PdCl_2$.
[c] Reaction was performed at 0.25 M.
[d] Pd NP formed at 80 °C.
[e] Pd NP formed at 120 °C.
[f] Pd NP formed at 140 °C.
[g] Pd NP formed under vacuum.
[h] BH_3–$NHCy_2$ was used instead of BH_3-NH^iPr_2.

The main issue in this reaction remains the competition between the borylation and the direct reduction of the Ar–Pd–Br. This side reaction occurs in all borylation reactions, but in our case BH_3–NHR_2 is a much stronger reducing agent than the commonly used pinacol borane or dialkylaminoborane. Most surprisingly, the dehydrogenation of BH_3-NH^iPr_2 does not occur in the presence of Pd@CTA-NTf_2 meaning that the reaction pathway probably proceeds through a mechanism, which is not closely related to the classical one.[29,37] Indeed, reaction of Pd(0) with Ar–Br leads to the formation of Ar–Pd(II)–Br, which is reduced by the amine–borane complex yielding back to the $Pd(0)L_2$ complex, the arene ArH, and the aminoborane (Scheme 2). The resulting aminoborane would then react in a classical borylation reaction.[38,39] Hence, two arylbromides are required to yield a single $ArBHN^iPr_2$, one being sacrificed to transform the amine–borane complex into the aminoborane. Unfortunately, the reaction between 2 equiv of arylbromides and one amine–borane complex is not a better solution[39] as the aminoborane intermediate decomposed rapidly at 110 °C limiting the yields. Overall, when using this system, it seems that yields are theoretically limited to 50% when the arylbromide is the limiting reagent and when dehydrogenation alone is inefficient.



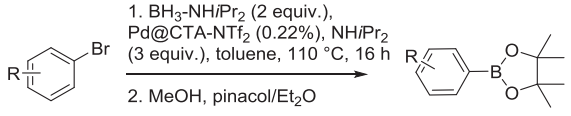
Scheme 2. Competing schematic catalytic cycles: (A) formation of the aminoborane, (B) borylation.

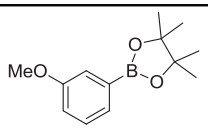
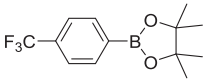
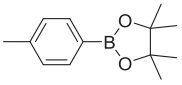
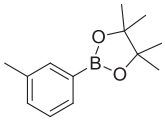
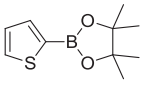
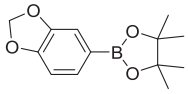
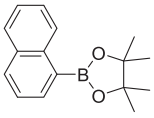
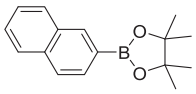
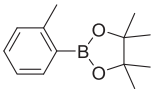
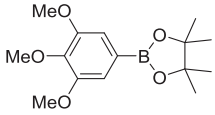
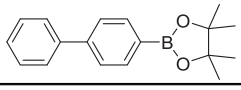
We then decided to apply our methodology to the synthesis of few boronates. Overall, the reaction was not as efficient as we could expect from the efficiency of the borylation catalytic cycle alone. Direct reduction of Ar–Pd^{II}–Br by borane appeared much faster than the borylation process and the C–B bond formation. As observed in most borylation processes,[40–44] the boron transfer is rate-determining[45] and favored by electron-donating groups. Best results were obtained with 4-methoxy (Table 3, entry 1), 3-methoxy (Table 4, entry 1), 4-methyl (Table 4, entry 3), 3-methyl (Table 4, entry 4) or dioxolane substituted (Table 4, entry 6) arylbromides. Nonetheless, naphthylbromide (Table 4, entries 7 and 8) and 2-methylbromobenzene (Table 4, entry 9) can also be borylated using this method. As an example of the fast competing reduction process, along with biphenylboronate, biphenyl can be isolated in 58% yield when 4-bromobiphenyl is used as substrate (Table 4, entry 11).

3. Conclusion

Overall, the developed methodology is not yet fully applicable to the synthesis of boron derivatives. Nevertheless, we showed that simple borane can be used as boron source for borylation. Owing to the NPs reactivity and flexibility, this methodology allowed performing unprecedented transformations, namely a sequential dehydrogenation–arylation of amine–borane complex. We are

Table 4
Synthesis of boronates using BH_3-NH^iPr_2 as borylating agent



Entry	Ar–B(pin) **5a–l**	Product	Yield[a] (%)
1		**5b**	40
2		**5c**	26
3		**5d**	45
4		**5e**	37
5		**5f**	35
6		**5g**	45
7		**5h**	27
8		**5i**	28
9		**5j**	30
10		**5k**	26
11		**5l**	33

[a] Isolated yield after column chromatography.

currently investigating alternative dual catalysts, which would separate the dehydrogenation process from the borylation, either by using two metals or by using a mixture of NPs.

4. Experimental section

4.1. Preparation of *N,N,N*-trimethylhexadecan-1-aminium bis((trifluoromethyl)sulfinyl)amide (CTA-NTf_2)

A solution of lithium bis(trifluoromethanesulfonyl) imide (11.05 g, 38.5 mmol) in water (5.5 mL) was added to a solution of *N,N,N*-trimethylhexadecan-1-aminium bromide (12.9 g, 35 mmol) in water (170 mL) and the mixture was stirred at room temperature for 1 h. The reaction mixture was extracted with CH_2Cl_2 (3×70 mL), dried ($NaSO_4$), and then the solvent was evaporated in vacuo to afford CTA-NTf_2 (17.3 g, 93%) as a white solid; mp 61–63 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.03–3.96 (m, 2H), 3.80 (s, 3H), 2.41–2.37 (m, 2H), 1.85–1.73 (m, 28H), 1.33 (t, 3H, J=7.0 Hz); ^{13}C NMR (400 MHz, DMSO-d_6) δ 215.8, 132.3, 129.1, 77.8, 63.4, 42.3, 36.6, 33.2, 33.0, 24.0.

4.2. Preparation of Pd@CTA-NTf_2

In a flask $Pd(OAc)_2$ (5 mg, 0.22 mmol) was introduced with CTA-NTf_2 (1 g, 1.88 mmol), then heated under argon at 110 °C for 1 h. The reaction mixture was cooled down and solidification occurred to afford Pd@CTA-NTf_2.

4.3. Preparation of amine–borane complex

To a stirred solution of di*iso*propylamine (70.6 mL, 0.5 mol) and $NaBH_4$ (30 g, 0.79 mol) in THF (500 mL) was added sulfuric acid (21.5 ml, 0.6 mol) at 0 °C over a period of 45 min. The mixture was allowed to warm to room temperature and stirred for 3 h. The crude was concentrated under vacuum and the residue was taken with CH_2Cl_2, and then filtered to eliminate all solid residues. The filtrate was washed with water (4×100 mL). The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure to give the amine–borane complex as colorless oil, which solidified upon cooling (51.8 g, 90%).

4.4. General procedure for the synthesis of pinacol arylboronates

In a reaction flask charged with CTA-NTf_2 (100 mg) under argon atmosphere were added, in this following order: anhydrous toluene (4 mL), distilled $^iPr_2NH$ (0.42 mL, 3 mmol), arylbromide (1 mmol), and amine–borane complex (0.3 mL, 2 mmol). The reaction mixture was then heated at 110 °C for 16 h. After total consumption of either starting material, the reaction mixture was cooled at −5 °C, quenched with anhydrous MeOH (2 mL), and stirred for 1 h at room temperature. All volatiles were removed under vacuum before adding pinacol (153 mg, 1.3 mmol) and Et_2O (2 mL), and the mixture was stirred for 4 h at room temperature. Then the reaction mixture was diluted with Et_2O (10 mL), and the organic phase was washed first with a solution of HCl (0.1 N, 2×10 mL), followed by an aqueous solution of $CuCl_2$ (50 g/L, 3×10 mL), dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude oil was passed through a pad of silica gel, eluting with Et_2O. The resulting filtrate was concentrated under vacuum and eventually purified by flash chromatography if some impurities were present in the residue.

4.5. Characterization data

*4.5.1. 2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [171364-79-7] (**5a**).* Following the general procedure, compound **5a** was obtained in 50% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, 2H, J=8.7 Hz), 6.94 (d, 2H, J=8.7 Hz), 3.87 (s, 3H), 1.36 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.15, 136.51, 113.30, 83.54, 55.08, 24.86; ^{11}B NMR (96 MHz, $CDCl_3$) δ +30.11; GC–MS (EI) t_R=9.032 min; m/z: 234 (M^+, 100%).

*4.5.2. 2-(3-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [325142-84-5] (**5b**).* Following the general procedure, compound **5b** was obtained in 40% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42–7.39 (m, 1H), 7.34–7.27 (m, 2H), 7.01 (ddd, 1H, J=8.2, 2.8, 1.1 Hz), 3.84 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.19, 129.08,

127.33, 118.84, 118.05, 83.97, 55.39, 25.01; ^{11}B NMR (96 MHz, $CDCl_3$) δ +31.66; GC–MS (EI) t_R=8.872 min; *m*/*z*: 234 (M^+, 100%).

*4.5.3. 4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane [214360-65-3] (**5c**).* Following the general procedure, compound **5c** was obtained in 26% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, 2H, *J*=8.0 Hz), 7.62 (d, 2H, *J*=8.0 Hz), 1.36 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.16, 133.19, 132.77, 129.71, 126.10, 124.53, 124.48, 124.43, 124.38, 122.50, 84.42, 25.00; ^{11}B NMR (96 MHz, $CDCl_3$) δ +31.19; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ 64.07; GC–MS (EI) t_R=6.984 min; *m*/*z*: 272 (M^+, 100%).

*4.5.4. 4,4,5,5-Tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane [195062-57-8] (**5d**).* Following the general procedure, compound **5d** was obtained in 45% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, 2H, *J*=8.0 Hz), 7.23 (d, 2H, *J*=8.0 Hz), 2.41 (s, 3H), 1.38 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.53, 134.95, 128.65, 83.75, 25.0, 21.87; ^{11}B NMR (96 MHz, $CDCl_3$) δ +30.99; GC–MS (EI) t_R=7.918 min; *m*/*z*: 218 (M^+, 100%).

*4.5.5. 4,4,5,5-Tetramethyl-2-(m-tolyl)-1,3,2-dioxaborolane [253342-48-2] (**5e**).* Following the general procedure, compound **5e** was obtained in 37% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64–7.60 (m, 2H), 7.28–7.26 (m, 2H), 2.36 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.53, 134.95, 128.65, 83.75, 25.00, 21.87; ^{11}B NMR (96 MHz, $CDCl_3$) δ +31.15; GC–MS (EI) t_R=7.837 min; *m*/*z*: 218 (M^+, 100%).

*4.5.6. 4,4,5,5-Tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane [193978-23-3] (**5f**).* Following the general procedure, compound **5f** was obtained in 35% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71–7.67 (m, 2H), 7.24 (d, 1H, *J*=4.7, 3.5 Hz), 1.39 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.30, 132.50, 128.36, 84.22, 24.91; ^{11}B NMR (96 MHz, $CDCl_3$) δ +29.05; GC–MS (EI) t_R=7.346 min; *m*/*z*: 210 (M^+, 100%).

*4.5.7. 5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-benzodioxole [94838-82-1] (**5g**).* Following the general procedure, compound **5g** was obtained in 45% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (dd, 1H, *J*=7.7, 1.1 Hz), 7.24 (d, 1H, *J*=0.8 Hz), 6.83 (d, 1H, *J*=7.7 Hz), 5.95 (s, 2H), 1.32 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.48, 161.84, 130.42, 129.59, 121.04, 118.38, 84.24, 25.0; ^{11}B NMR (96 MHz, $CDCl_3$) δ +30.63; GC–MS (EI) t_R=9.594 min; *m*/*z*: 248 (M^+, 100%).

*4.5.8. 4,4,5,5-Tetramethyl-2-(1-naphthalenyl)-1,3,2-dioxaborolane [68716-52-9] (**5h**).* Following the general procedure, compound **5h** was obtained in 27% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.82 (d, 1H, *J*=8.3 Hz), 8.13 (d, 1H, *J*=6.8 Hz), 7.98 (d, 1H, *J*=8.2 Hz), 7.85 (d, 1H, *J*=8.1 Hz), 7.55–7.50 (m, 3H), 1.48 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.96, 135.59, 133.24, 131.64, 128.45, 128.31, 126.26, 125.46, 124.93, 83.69, 25.05; ^{11}B NMR (96 MHz, $CDCl_3$) δ +31.96; GC–MS (EI) t_R=11.21 min; *m*/*z*: 254 (M^+, 100%).

*4.5.9. 4,4,5,5-Tetramethyl-2-(2-naphthalenyl)-1,3,2-dioxaborolane [256652-04-7] (**5i**).* Following the general procedure, compound **5i** was obtained in 28% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.94–7.86 (m, 4H), 7.58–7.48 (m, 2H), 1.44 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.24, 130.40, 128.44, 127.66, 126.97, 125.73, 83.93, 24.93; ^{11}B NMR (96 MHz, $CDCl_3$) δ +29.97; GC–MS (EI) t_R=11.23 min; *m*/*z*: 254 (M^+, 100%).

*4.5.10. 4,4,5,5-Tetramethyl-2-(o-tolyl)-1,3,2-dioxaborolane [195062-59-0] (**5j**).* Following the general procedure, compound **5j** was obtained in 30% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (dd, 1H, *J*=7.6, 1.2 Hz), 7.37 (td, 1H, *J*=7.5, 1.5 Hz), 7.23–7.19 (m, 2H), 2.59 (s, 3H), 1.40 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.97, 136.00, 130.92, 129.91, 124.84, 83.54, 25.09, 22.36; ^{11}B NMR (96 MHz, $CDCl_3$) δ +31.47; GC–MS (EI) t_R=7.813 min; *m*/*z*: 218 (M^+, 100%).

*4.5.11. 4,4,5,5-Tetramethyl-2-(3,4,5-trimethoxyphenyl)-1,3,2-dioxaborolane [214360-67-5] (**5k**).* Following the general procedure, compound **5k** was obtained in 26% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (s, 2H), 3.94 (s, 6H), 3.91 (s, 3H), 1.38 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.90, 141.08, 111.14, 83.71, 60.70, 55.87, 24.57; ^{11}B NMR (96 MHz, $CDCl_3$) δ +29.27; GC–MS (EI) t_R=11.65 min; *m*/*z*: 296 (M^+, 100%).

*4.5.12. 2-[1,1′-Biphenyl]-4-yl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [144432-80-4] (**5l**).* Following the general procedure, compound **5l** was obtained in 33% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, 2H, *J*=8.2 Hz), 7.67 (d, 4H, *J*=6.6 Hz), 7.50 (t, 2H, *J*=7.4 Hz), 7.40 (t, 1H, *J*=6.6 Hz), 1.39 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 141.2, 135.1, 128.5, 127.5, 127.1, 126.3, 83.9, 24.3; ^{11}B NMR (96 MHz, $CDCl_3$) δ+29.76; GC–MS (EI) t_R=13.648 min; *m*/*z*: 280 (M^+, 100%).

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