Palladium-Catalyzed Decarbonylative Borylation of Aryl Anhydrides

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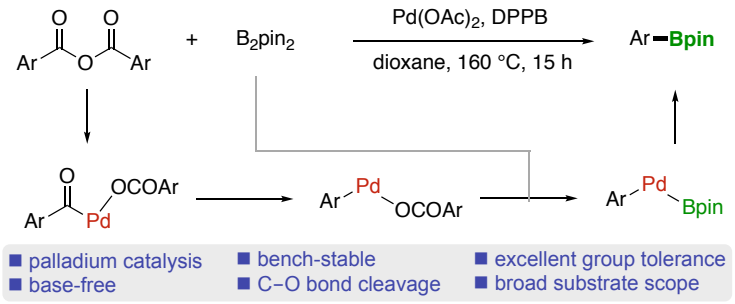


A palladium-catalyzed base-free decarbonylative borylation of aryl anhydrides has been developed. Catalyst system consisting of $Pd(OAc)_2$/dppb enables readily available aryl anhydrides to be employed as electrophiles for the synthesis of versatile arylboronate esters via O–C(O) bond activation and decarbonylation. This method is characterized by an excellent functional group tolerance and broad substrate scope, using bench stable aryl anhydrides as aryl electrophiles in C–B bond formation. Mechanistic studies and functionalization of late-stage pharmaceutical molecules are disclosed.

Suzuki-Miyaura cross-coupling is the most powerful method for the construction of C–C bonds, exploiting the reactivity of various electrophiles and organoboron reagents as cross-coupling partners.[1,2] In addition to the Suzuki-Miyaura cross-coupling, organoboron reagents represent versatile linchpins in organic synthesis, enabling the formation of a plethora of C–C, C–N, C–O and C–X bonds by transition-metal-catalyzed and transition-metal-free approaches.[3] Thus, as the key ingredients for Suzuki-Miyaura reaction and versatile intermediates in organic synthesis, efficient methods for the synthesis of organoboron reagents are highly desirable.

The traditional way for the synthesis of organoboron compounds is the reaction of borates and organometallic reagents, such as organomagnesium or organolithium.[3,4] With the developments in the cross-coupling arena, new catalytic methods have been established.[5,6] Among these methods, transition-metal-catalyzed Miyaura borylation of aryl halides or pseudohalides with B_2pin_2 as the diboron reagent represents arguably the most direct and effective approach for the preparation of organoboron reagents.[7] At present, Miyaura borylation has been achieved using various catalytic systems and hal-ide/pseudohalide equivalents (Figure 1A).[1–4]

In this context, recently major advances have been made using carboxylic acid derivatives as aryl electrophiles after selective oxidative addition of the C(acyl)–X bond to a transition metal and decarbonylation.[8–10] These reactions proceed under redox-neutral conditions in the absence of external oxidants and without the typical limitations of decarboxylative approaches in terms of restricted substrate scope and high barrier for decarboxylation.[10] Most crucially, the use of ubiquitous carboxylic acid derivatives permits to expand the toolbox of cross-coupling reactions to orthogonal carboxylic acid sub-strates ($R–CO_2H$ vs. R–X) that are inherently present in inter-mediates, pharmaceuticals and functional materials.

Within the decarbonylative cross-coupling framework, decarbonylative Miyaura borylation of carboxylic acid derivatives has emerged as a new strategy.[8–21] Thus, decarbonylative borylation of amides has been achieved via nickel,[11] palladium[12] or rhodium[13] catalysis (Figure 1B), demonstrating various approaches to overcoming the high resonance barrier of the N–C bond by amide bond twisting.[14]

Recent advances have been made in transition-metal-catalyzed cross-coupling of esters via the activation of inert C–O bond,[15] which prevents the presence of toxic halide salts. Nickel-catalyzed decarbonylative borylation of esters using NHC ligands has been developed,[16] which gives the desired organoboron compounds in excellent yields (Figure 1C). Afterwards, another nickel-catalyzed decarbonylative borylation of esters using phosphine ligands has been reported.[17] The decarbonylative cross-coupling of carboxylic acids has also been achieved using carboxylic acids as electrophiles via redox-neutral decarbonylative pathway (Figure 1D).[18] Furthermore, decarbonylative borylation of thioesters using rhodium-phosphine systems has been reported,[19] while more recent advances include decarbonylative borylation of acyl fluorides via nickel catalysis (not shown).[20,21] It is worthwhile to note that borylation of aryl halides and decarbonylative borylation of carboxylic acid derivatives requires inorganic bases and other additives as activators, which restricts the application of these approaches.[8–21]

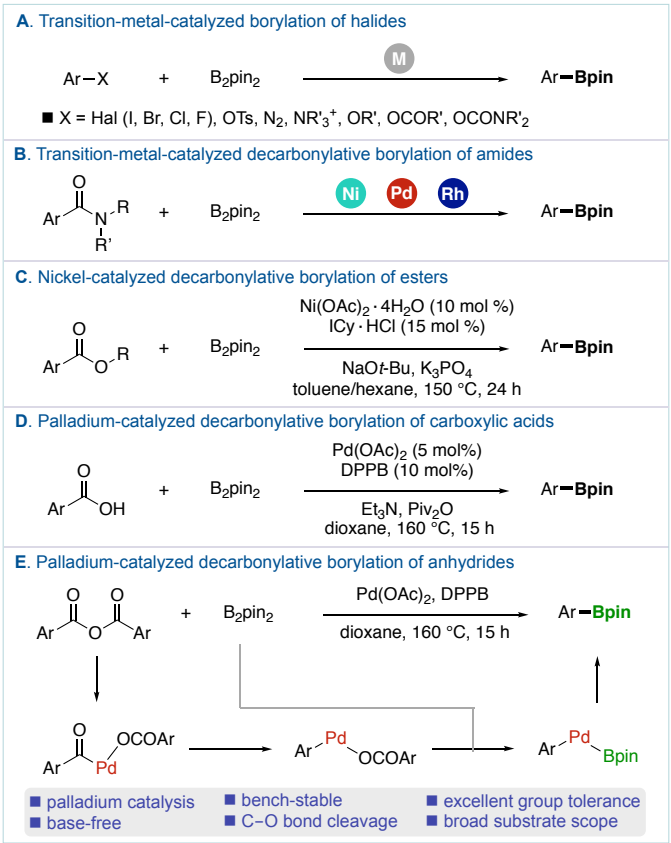
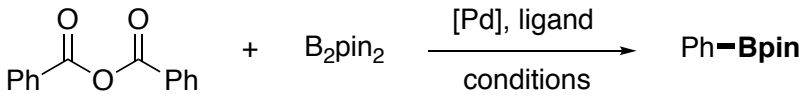


Figure 1. (A-D) Decarbonylative cross-coupling of carboxylic acids. (E) Palladium-catalyzed decarbonylative borylation of aryl anhydrides (this work).

Considering that aryl anhydrides are readily available and broadly utilized class of substrates in organic synthesis, we set out to develop decarbonylative borylation of aryl anhydrides to produce arylboronate esters (Figure 1E). It is noteworthy that although various methods for decarbonylative cross-coupling of aryl anhydrides have been developed,[22–25] decarbonylative borylation is missing from this reactivity toolbox despite the tremendous importance of Miyaura borylation methods.[4–7] Herein, we report the palladium-catalyzed borylation of aryl anhydrides, which operates under base-free conditions. Compared with previous methods, in particular decarbonylative borylation of carboxylic acids, the following features of this method are noteworthy: (1) additives for activation of substrates are not required; (2) external bases are not needed; (3) comparatively higher efficiency of the cross-coupling; (4) broad scope, general and practical reaction conditions for the synthesis of organoboron compounds. It is worthwhile to note that aryl anhydrides are a class of fundamental and bench-stable carboxylic acid derivatives that can be prepared from acyl chlorides in a straightforward manner and the crude product purified by recrystallization or distillation.

Table 1. Summary of Optimization Studies[a]



1a **2a** **3a**

entry	catalyst	ligand	base	yield (%)
1	$Pd(OAc)_2$	dppb	Et_3N	93
2[b]	$Pd(OAc)_2$	dppb	Et_3N	88
3[c]	$Pd(OAc)_2$	dppb	Et_3N	79
4	$Pd(OAc)_2$	dppb	-	92
5	$Pd(OAc)_2$	XantPhos	-	20
6	$Pd(OAc)_2$	dppp	-	49
7	$Pd(OAc)_2$	dpppent	-	50
8	$Pd(OAc)_2$	dppf	-	54
9	$Pd(OAc)_2$	XPhos	-	<1

10	$Pd(OAc)_2$	SPhos	-	<1
11	$Pd(OAc)_2$	PCy_3	-	34
12	$Pd(OAc)_2$	$PCyPh_2$	-	23
13[d]	$Pd(OAc)_2$	dppb	-	69
14[e]	$Pd(OAc)_2$	dppb	-	63
15[f]	$Pd(OAc)_2$	dppb	-	46

[a]Conditions: **1a** (1.0 equiv), **2a** (1.1 equiv), [Pd] (3 mol%), ligand (6 mol%), base (1.1 equiv), dioxane, 160 °C, 15 h; [b]**2a** (1.5 equiv), base (1.5 equiv); [c]**2a** (2.0 equiv), base (2.0 equiv); [d]toluene; [e]140 °C; [f]120 °C.

The proposed palladium-catalyzed decarbonylative borylation of anhydrides was examined using benzoic anhydride and bis(pinacolato)diboron as model substrates (Table 1). We first screened the stoichiometric amount of the reagents under Lewis base conditions, and obtained the optimal stoichiometry (Table 1, entries 1-3). Notably, we next found that the conditions in the absence of Lewis bases delivered the desired product in excellent yield, showing that the presence of base is not needed for this protocol (Table 1, entry 4). Apparently, benzoate anion is effective in promoting transmetallation in this protocol,[10a] resulting in an attractive base-free approach to Miyaura borylation. After a range of experiments screening phosphine ligands, we identified dppb as the optimal ligand for this protocol (Table 1, entries 5-12). Furthermore, toluene had been identified as an alternative solvent for this transformation, albeit it gave slightly lower reactivity than dioxane (Table 1, entry 13). Finally, we tested lower reaction temperature, which afforded the cross-coupling product in 63% and 46% yields at 140 °C and 120 °C, respectively (Table 1, entries 14-15). The optimized conditions involve aryl anhydride (1.0 equiv), bis(pinacolato)diboron (1.1 equiv), $Pd(OAc)_2$ (3 mol%) and DPPB (6 mol%) in dioxane (0.20 M) at 160 °C (Table 1, entry 4). It is worth noting that the conditions with Pd:P ratio of 1:2 give the product in 40% yield (not shown).

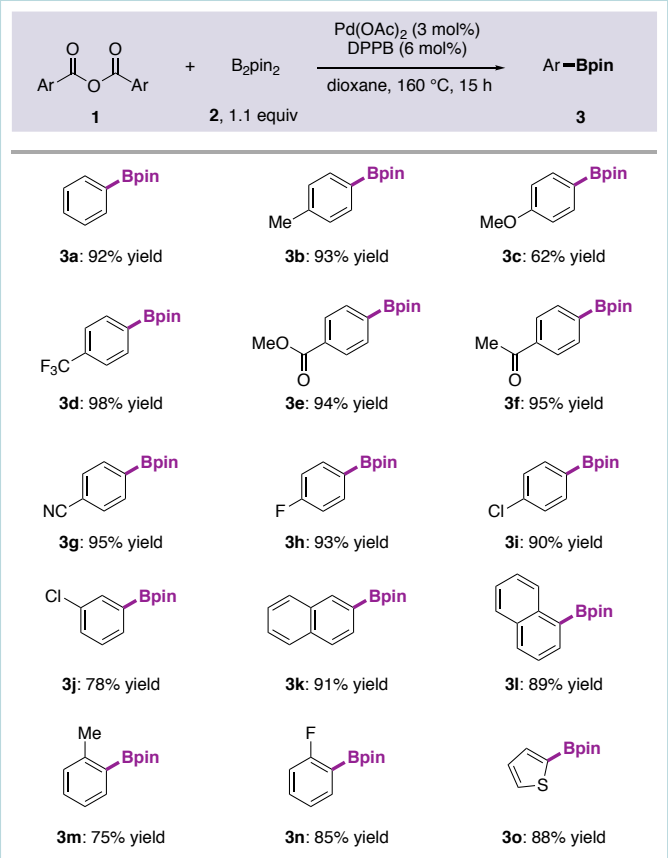


Figure 2. Pd-catalyzed base-free decarbonylative borylation of anhydrides. Conditions: anhydrides (1.0 equiv), B_2pin_2 (1.1 equiv), $Pd(OAc)_2$ (3 mol%), DPPB (6 mol%), dioxane, 160 °C, 15 h. Isolated yields.

With the optimized conditions in hand, we next investigated the substrate scope for this palladium-catalyzed base-free decarbonylative borylation of anhydrides (Figure 2). As shown, a wide range of aryl anhydrides bearing electron-neutral (**3a-b**), electron-donating (**3c**) and electron-withdrawing (**3d**) substituents are compatible with this method. Notably, electrophilic functional groups that would not be compatible in the classic organometallic addition, including esters (**3e**) and ketones (**3f**) are well compatible with this method. Moreover, cyano- (**3g**), fluoro- (**3h**) and chloro- (**3i-j**) groups can also be well tolerated. Furthermore, polycyclic aromatic anhydrides (**3k-l**) can be readily employed, delivering the desired arylboronate esters in excellent yield. Interestingly, sterically-hindered substrates (**3m**) and ortho-substituted substrates (**3n**) are also compatible in this approach. Furthermore, heterocyclic anhydrides can also be employed in this method, exemplified by 2-thienyl anhydride, which produced 2-thienylboronate ester (**3o**) in excellent yield. At this stage of reaction development, cyclic anhydrides are not tolerated under standard reaction conditions.

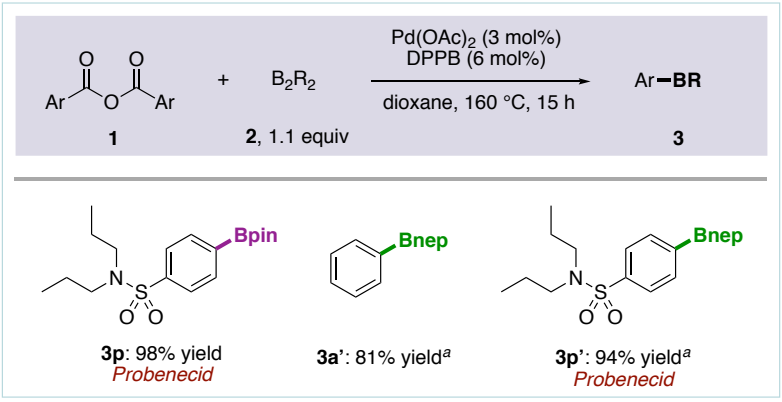


Figure 3. Pd-catalyzed base-free decarbonylative borylation of anhydrides. Conditions: anhydrides (1.0 equiv), B_2pin_2 (1.1 equiv), $Pd(OAc)_2$ (3 mol%), DPPB (6 mol%), dioxane, 160 °C, 15 h. Isolated yields. [a] B_2nep_2 (1.1 equiv).

Encouraged by the successful application of a range of aryl anhydrides as substrates in this decarbonylative Miyaura protocol, we next tested more challenging substrates using this method (Figure 3). To our delight, late-stage derivatization of pharmaceuticals can also be tolerated, as exemplified by Probenecid anhydride, which delivered the desired arylboronate ester in 98% yield (**3p**).

Moreover, alternative diboron reagents, such as B_2nep_2, can also be tolerated in this approach, which delivered the Ph–Bnep product (**3a'**) in 81% yield. It is noteworthy that this borylating reagent is also applicable to Probenecid anhydride (**3p'**), demonstrating high reactivity in more complex settings.

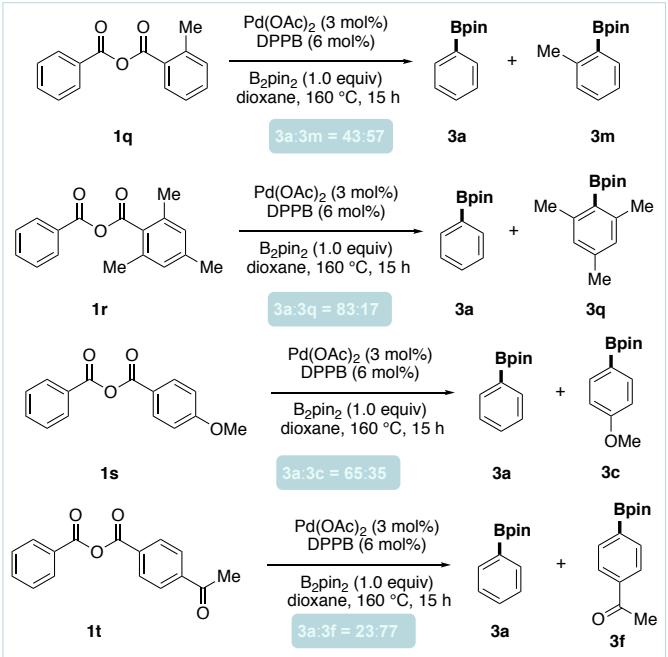


Figure 4. Selectivity studies in palladium-catalyzed base-free decarbonylative borylation of anhydrides. Conditions: anhydrides (1.0 equiv), B_2pin_2 (1.0 equiv), $Pd(OAc)_2$ (3 mol%), DPPB (6 mol%), dioxane, 160 °C, 15 h.

The use of aryl anhydrides allows to conduct intramolecular competition experiments to gain insight into the selectivity of decarbonylative Miyaura borylation (Figure 4). The competition studies indicate that ortho-substituted O–C(O)Ar bonds show comparable reactivity to sterically-unbiased electrophiles (**3a:3m** = 43:57). However, increase in steric hindrance, such as 2,6-di-ortho-substitution of O–C(O)Ar, exerts a substantial effect on the coupling (**3a:3q** = 83:17). Moreover, electron-deficient O–C(O)Ar bonds are more reactive than electron-rich counterparts (**3a:3c** = 65:35; **3a:3f** = 23:77), which is consistent with facility of oxidative addition/decarbonylation.

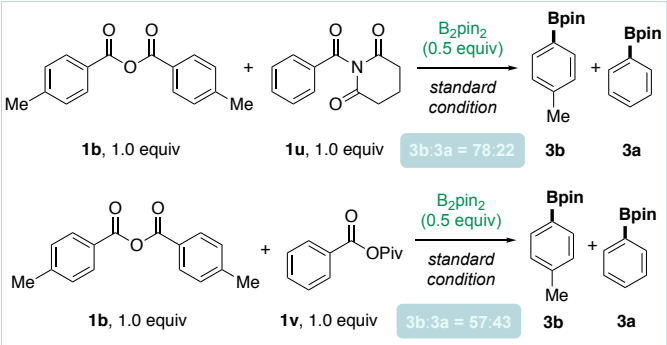


Figure 5. Selectivity studies in palladium-catalyzed base-free decarbonylative borylation of anhydrides. Conditions: anhydrides (1.0 equiv), B_2pin_2 (1.0 equiv), $Pd(OAc)_2$ (3 mol%), DPPB (6 mol%), dioxane, 160 °C, 15 h.

To investigate the selectivity in decarbonylative borylation of aryl anhydrides over other carboxylic acid derivatives, competition studies between different carboxylic acid derivatives were conducted (Figure 5). As such, aryl anhydrides show significantly higher reactivity than amides (**3b:3a** = 78:22), while the reactivity vs. aryl alkyl anhydrides is also higher (**3b:3a** = 57:43). Furthermore, competition experiments between aryl anhydrides and carboxylic acids give the selectivity of 51:49, which indicates that when carboxylic acids and anhydrides are in the same catalytic system, carboxylic acids can form mixed anhydrides (not shown). Further, competition between anhydrides and acyl fluorides give the selectivity of >95:5, which indicates that anhydrides show much higher reactivity than acyl fluorides

under standard conditions (not shown). These experiments indicate that the O–C(O) bond in aryl anhydrides undergoes more facile oxidative addition/decarbonylative than other inert acyl bonds.

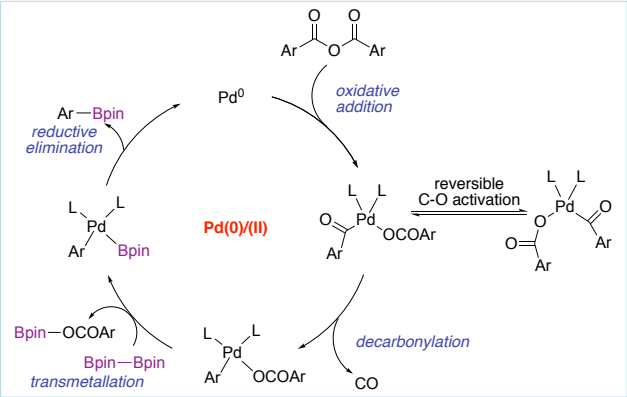


Figure 6. Proposed mechanism.

The proposed mechanism for this Pd-catalyzed base-free decarbonylative borylation of anhydrides is shown in Figure 6. First, the O–C(O) bond oxidatively adds to palladium, a process which likely involves reversible C–O activation. This is followed by decarbonylation. Next, transmetallation between Ar–Pd–OC(O)Ar and B_2pin_2 gives Ar–Pd–Bpin. Finally, reductive elimination affords the desired arylboronate product and regenerates the Pd catalyst. We tentatively propose that Bpin–OCOAr is formed as a by-product, however its presence has not been detected due to decomposition. Control experiments in the absence of activator result in unproductive reactions, indicating that decarboxylative process is unlikely.

Conclusions

In summary, we have reported palladium-catalyzed base-free decarbonylative Miyaura borylation of aryl anhydrides. The method is notable for general and practical borylation conditions under base-free conditions using readily available aryl anhydrides. This versatile decarbonylation method allows for a broad substrate scope and excellent functional group tolerance, permitting rapid access to valuable arylboronate esters. The utility of this approach has been demonstrated in the decarbonylative borylation of pharmaceuticals as well as utilization of challenging substrates for borylation and double decarbonylative borylation of cyclic anhydrides. We expect that this decarbonylative borylation method

will provide an important alternative method for the synthesis of organoboron compounds.[25] Further studies on decarbonylative cross-coupling are underway and will be reported in due course.

Experimental Section

General Methods. All starting materials reported in the manuscript have been prepared according to the method reported previously.[24] All compounds reported in this manuscript have been previously reported or are commercially available. Spectroscopic data matched literature values. General methods have been published.[24] All reactions were performed in oven-dried sealed microwave tube vials.

General Procedure for Anhydride Synthesis. An oven-dried vial (20 mL) equipped with a stir bar was charged with pyridine (10.0 mmol, 1.0 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Acyl chloride (typically, 0.5 equiv) was added dropwise to the reaction mixture with vigorous stirring at 0 °C, and the reaction mixture was stirred 1 h at room temperature. After the indicated time, the reaction mixture was diluted with ice-cold water (50 mL). Then the solid that precipitated was filtrated, washed with ice-cold water and dried. Unless stated otherwise, the crude product was purified by recrystallization (toluene) to give analytically pure product.

General Procedure for Borylation Reaction of Aryl Anhydrides. An oven-dried vial equipped with a stir bar was charged with anhydride (neat, 1.0 equiv), diboronate ester (neat, 1.1 equiv), $Pd(OAc)_2$ (typically, 3 mol%), and ligand (typically, 6 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Dioxane (0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 160 °C, and stirred for the indicated time at 160 °C. After the indicated time, the reaction mixture was cooled down to room temperature. Then the sample was analyzed by 1H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples. All substrates' yields reported in the manuscript refer to isolated yields after purification by chromatography on silica gel (ethyl acetate/hexane = 1/15 to 1/10).

Representative Procedure for Borylation Reaction of Aryl Anhydrides. An oven-dried vial equipped with a stir bar was charged with benzoic anhydride (neat, 45.3 mg, 0.2 mmol), bis(pinacolato)diboron (neat, 55.9 mg, 1.1 equiv), $Pd(OAc)_2$ (1.4 mg, 3 mol%), and 1,4-bis(diphenylphosphino)butane (5.2 mg, 6 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Dioxane (1.0 mL) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 160 °C, and stirred for 15 h at 160 °C. After the indicated time, the reaction mixture was cooled down to room temperature. Then the sample was analyzed by 1H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (ethyl acetate/hexane = 1/15 to 1/10) afforded the title product. Yield 92% (37.6 mg, 0.184 mmol). White solid. Characterization data are included in the section below.

Benzoic anhydride (1a). This compound was commercially available.

4-Methylbenzoic anhydride (1b).[24] White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.07-8.05 (d, *J* = 8.2 Hz, 4 H), 7.34-7.33 (d, *J* = 8.0 Hz, 4 H), 2.48 (s, 6 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 162.6, 145.6, 130.7, 129.6, 126.3, 21.9.

4-Methoxybenzoic anhydride (1c).[24] White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.13-8.11 (d, *J* = 8.8 Hz, 4 H), 7.01-6.99 (d, *J* = 8.8 Hz, 4 H), 3.92 (s, 6 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 164.6, 162.3, 132.9, 121.3, 114.2, 55.6.

4-(Trifluoromethyl)benzoic anhydride (1d).[24] White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.31-8.29 (d, *J* = 8.2 Hz, 4 H), 7.85-7.84 (d, *J* = 8.3 Hz, 4 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 160.8, 136.1 (q, $^2J_{C\text{-}F}$ = 32.9 Hz), 131.7, 131.0, 126.1 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 123.3 (q, $^1J_{C\text{-}F}$ = 271.5 Hz).

4-(Methoxycarbonyl)benzoic anhydride (1e).[24] White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.23-8.17 (m, 8 H), 3.97 (s, 6 H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 166.0, 161.4, 135.6, 132.3, 130.7, 130.2, 52.8.

4-Acetylbenzoic anhydride (1f).[24] White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.28-8.26 (d, J = 8.4 Hz, 4 H), 8.13-8.11 (d, J = 8.4 Hz, 4 H), 2.70 (s, 6 H). **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)** δ 197.2, 161.2, 141.5, 132.2, 130.9, 128.7, 27.0.

4-Cyanobenzoic anhydride (1g).[24] White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.26-8.24 (d, J = 8.6 Hz, 4 H), 7.87-7.85 (d, J = 8.6 Hz, 4 H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 160.2, 132.8, 132.0, 131.0, 118.2, 117.4.

4-Fluorobenzoic anhydride (1h).[24] White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.19-8.14 (m, 4 H), 7.23-7.17 (m, 4 H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 166.7 (d, $^{1}J^{C\text{-}F}$ = 255.8 Hz), 161.2, 133.3 (d, $^{3}J^{C\text{-}F}$ = 9.7 Hz), 125.0 (d, $^{4}J^{C\text{-}F}$ = 2.9 Hz), 116.3 (d, $^{2}J^{C\text{-}F}$ = 22.1 Hz). **^{19}F (377 MHz, $CDCl_3$)** δ -102.03.

4-Chlorobenzoic anhydride (1i).[24] White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.11-8.09 (d, J = 8.7 Hz, 4 H), 7.55-7.53 (d, J = 8.7 Hz, 4 H). **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)** δ 161.3, 141.4, 131.9, 129.4, 127.1.

3-Chlorobenzoic anhydride (1j).[24] White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.10-8.10 (d, J = 1.3 Hz, 2 H), 8.04-8.02 (d, J = 9.8 Hz, 2 H), 7.67-7.65 (m, 2 H), 7.51-7.47 (m, 2 H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 160.9, 135.2, 134.8, 130.5, 130.3, 130.2, 128.7.

2-Naphthoic anhydride (1k).[24] White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.81 (s, 2 H), 8.23-8.21 (d, J = 8.3 Hz, 2 H), 8.06-8.04 (d, J = 8.1 Hz, 2 H), 8.02-8.00 (d, J = 8.7 Hz, 2 H), 7.98-7.96 (d, J = 8.2 Hz, 2 H), 7.71-7.68 (t, J = 7.4 Hz, 2 H), 7.65-7.62 (t, J = 7.6 Hz, 2 H). **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)** δ 162.8, 136.3, 132.8, 132.5, 129.7, 129.3, 128.9, 128.0, 127.2, 126.1, 125.4.

1-Naphthoic anhydride (1l).[24] White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.13-9.12 (d, *J* = 8.7 Hz, 2 H), 8.46-8.44 (d, *J* = 7.2 Hz, 2 H), 8.14-8.12 (d, *J* = 8.2 Hz, 2 H), 7.96-7.94 (d, *J* = 8.2 Hz, 2 H), 7.71-7.68 (t, *J* = 7.1 Hz, 2 H), 7.61-7.57 (m, 4 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 173.0, 135.6, 134.7, 134.0, 131.9, 131.7, 128.7, 128.2, 126.4, 125.9, 124.6.

2-Methylbenzoic anhydride (1m).[24] White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.09-8.07 (d, *J* = 7.9 Hz, 2 H), 7.55-7.52 (t, *J* = 7.5 Hz, 2 H), 7.37-7.33 (m, 4 H), 2.73 (s, 6 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 163.0, 142.6, 133.6, 132.3, 131.5, 127.8, 126.1, 22.0.

2-Fluorobenzoic anhydride (1n).[24] White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.10-8.05 (m, 2 H), 7.67-7.61 (m, 2 H), 7.31-7.27 (m, 2 H), 7.24-7.16 (m, 2 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 162.6 (d, $^{1}J^{C\text{-}F}$ = 261.3 Hz), 159.4 (d, $^{5}J^{C\text{-}F}$ = 2.7 Hz), 136.4 (d, $^{3}J^{C\text{-}F}$ = 9.8 Hz), 132.9, 124.5 (t, $^{6}J^{C\text{-}F}$ = 2.1 Hz), 117.4 (d, $^{2}J^{C\text{-}F}$ = 22.3 Hz), 117.1 (d, $^{4}J^{C\text{-}F}$ = 8.5 Hz). **^{19}F (377 MHz, $CDCl_3$)** δ -107.67.

Thiophene-2-carboxylic anhydride (1o).[24] White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.93-7.92 (m, 2 H), 7.68-7.67 (m, 2 H), 7.18-7.16 (m, 2 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 167.7, 135.0, 134.0, 132.9, 128.1.

4-(*N*,*N*-Dipropylsulfamoyl)benzoic anhydride (1p).[24] White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.28-8.26 (d, *J* = 10.8 Hz, 4 H), 7.98-7.96 (d, *J* = 10.8 Hz, 4 H), 3.14-3.11 (m, 8 H), 1.60-1.51 (m, 8 H), 0.89-0.85 (t, *J* = 9.3 Hz, 12 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 160.6, 146.1, 131.5, 131.2, 127.5, 49.9, 21.9, 11.2.

Benzoic 2-methylbenzoic anhydride (1q).[24] White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.18-8.17 (d, *J* = 7.3 Hz, 2 H), 8.09-8.07 (d, *J* = 7.9 Hz, 1 H), 7.71-7.68 (t, *J* = 7.5 Hz, 1 H), 7.57-7.52 (m, 3 H), 7.37-7.34 (t, *J* = 7.4 Hz, 2 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 162.8, 162.5, 142.7, 134.4, 133.7, 132.3, 131.5, 130.5, 129.1, 128.9, 127.7, 126.1, 22.0.

Benzoic 2,4,6-trimethylbenzoic anhydride (1r).[24] White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.20-8.18 (d, *J* = 7.2 Hz, 1 H), 8.14-8.13 (d, *J* = 7.2 Hz, 1 H), 7.66-7.63 (t, *J* = 7.4 Hz, 1 H), 7.57-7.54 (t, *J* = 8.0 Hz, 1 H), 7.52-7.49 (t, *J* = 7.7 Hz, 1 H), 6.91 (s, 2 H), 2.42 (s, 6 H), 2.32 (s, 3 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 175.0, 171.8, 140.1, 136.1, 133.8, 130.6, 130.2, 128.9, 128.8, 128.5, 21.2, 20.3.

Benzoic 4-methoxybenzoic anhydride (1s).[24] White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.18-8.17 (d, *J* = 7.2 Hz, 2 H), 8.14-8.12 (d, *J* = 9.0 Hz, 2 H), 7.70-7.67 (t, *J* = 7.4 Hz, 1 H), 7.56-7.53 (t, *J* = 8.1 Hz, 2 H), 7.02-7.00 (d, *J* = 9.0 Hz, 2 H), 3.92 (s, 3 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 164.7, 162.6, 162.1, 134.4, 132.9, 130.5, 129.1, 128.8, 121.1, 114.2, 55.6.

4-Acetylbenzoic benzoic anhydride (1t).[24] White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.28-8.27 (d, *J* = 7.9 Hz, 2 H), 8.19-8.18 (d, *J* = 7.9 Hz, 2 H), 8.13-8.10 (m, 2 H), 7.74-7.69 (m, 1 H), 7.59-7.54 (m, 2 H), 2.70 (s, 3 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 197.2, 162.4, 161.6, 141.4, 134.5, 132.5, 130.8, 130.6, 129.0, 128.9, 128.6, 27.0.

4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (3a, Figure 2).[13] According to the general procedure, the reaction of benzoic anhydride (0.2 mmol), bis(pinacolato)diboron (0.22 mmol), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (silica gel, hexane/DCM = 20/1) the title compound in 92% yield (37.6 mg). White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.84-7.83 (d, *J* = 6.9 Hz, 2 H), 7.50-7.47 (t, *J* = 7.4 Hz, 1 H), 7.41-7.38 (t, *J* = 7.6 Hz, 2 H), 1.37 (s, 12 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 134.8, 131.3, 127.7, 83.8, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

4,4,5,5-Tetramethyl-2-(*p*-tolyl)-1,3,2-dioxaborolane (3b, Figure 2).[13] According to the general procedure, the reaction of 4-methylbenzoic anhydride (0.2 mmol), bis(pinacolato)diboron (0.22 mmol), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (silica gel, hexane/DCM = 20/1) the title

compound in 93% yield (40.6 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72-7.70 (d, *J* = 7.9 Hz, 2 H), 7.20-7.18 (d, *J* = 7.6 Hz, 2 H), 2.37 (s, 3 H), 1.34 (s, 12 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 141.4, 134.8, 128.5, 83.6, 24.9, 21.7. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c, Figure 2).[13] According to the general procedure, the reaction of 4-methoxybenzoic anhydride (0.2 mmol), bis(pinacolato)diboron (0.22 mmol), Pd(OAc)2 (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (silica gel, hexane/DCM = 20/1) the title compound in 62% yield (29.1 mg). White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.79-7.77 (d, *J* = 8.6 Hz, 2 H), 6.93-6.91 (d, *J* = 8.7 Hz, 2 H), 3.85 (s, 3 H), 1.36 (s, 12 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 162.2, 136.5, 113.3, 83.6, 55.1, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (3d, Figure 2).[13] According to the general procedure, the reaction of 4-(trifluoromethyl)benzoic anhydride (0.2 mmol), bis(pinacolato)diboron (0.22 mmol), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (silica gel, hexane/DCM = 20/1) the title compound in 98% yield (53.4 mg). White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.94-7.93 (d, *J* = 7.7 Hz, 2 H), 7.64-7.63 (d, *J* = 7.9 Hz, 2 H), 1.38 (s, 12 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 135.0, 132.8 (q, $^{2}J^{C\text{-}F}$ = 31.9 Hz), 124.3 (q, $^{3}J^{C\text{-}F}$ = 3.7 Hz), 124.1 (q, $^{1}J^{C\text{-}F}$ = 270.7 Hz), 84.3, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -62.97.

Methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (3e, Figure 2).[13] According to the general procedure, the reaction of 4-(methoxycarbonyl)benzoic anhydride (0.2 mmol), bis(pinacolato)diboron (0.22 mmol), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%)

in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (silica gel, hexane/DCM = 20/1) the title compound in 94% yield (49.3 mg). White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.05-8.03 (d, *J* = 8.2 Hz, 2 H), 7.90-7.88 (d, *J* = 8.2 Hz, 2 H), 3.95 (s, 3 H), 1.38 (s, 12 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 167.2, 134.7, 132.3, 128.6, 84.2, 52.2, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethanone (3f, Figure 2).[13] According to the general procedure, the reaction of 4-acetylbenzoic anhydride (0.2 mmol), bis(pinacolato)diboron (0.22 mmol), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (silica gel, hexane/DCM = 20/1) the title compound in 95% yield (46.8 mg). White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.96-7.91 (m, 4 H), 2.64 (s, 3 H), 1.38 (s, 12 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 198.5, 139.0, 134.9, 127.3, 84.2, 26.8, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (3g, Figure 2).[13] According to the general procedure, the reaction of 4-cyanobenzoic anhydride (0.2 mmol), bis(pinacolato)diboron (0.22 mmol), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (silica gel, hexane/DCM = 20/1) the title compound in 95% yield (43.6 mg). White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.91-7.90 (d, *J* = 8.0 Hz, 2 H), 7.67-7.66 (d, *J* = 8.0 Hz, 2 H), 1.38 (s, 12 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 135.1, 131.2, 118.9, 114.6, 84.5, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h, Figure 2).[13] A According to the general procedure, the reaction of 4-fluorobenzoic anhydride (0.2 mmol), bis(pinacolato)diboron (0.22 mmol), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (silica gel, hexane/DCM = 20/1) the title

compound in 93% yield (41.3 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81-7.78 (m, 2 H), 7.07-7.02 (t, J = 9.0 Hz, 2 H), 1.34 (s, 12 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.1 (d, $^{1}J^{C\text{-}F}$ = 248.8 Hz), 137.0 (d, $^{3}J^{C\text{-}F}$ = 8.2 Hz), 114.8 (d, $^{2}J^{C\text{-}F}$ = 20.1 Hz), 83.9, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. **^{19}F NMR (377 MHz, $CDCl_3$)** δ-108.47.

2-(4-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i, Figure 2).[13] A According to the general procedure, the reaction of 4-chlorobenzoic anhydride (0.2 mmol), bis(pinacolato)diboron (0.22 mmol), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (silica gel, hexane/DCM = 20/1) the title compound in 90% yield (43.0 mg). White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.76-7.74 (d, J = 8.3 Hz, 2 H), 7.37-7.36 (d, J = 8.3 Hz, 2 H), 1.36 (s, 12 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 137.5, 136.1, 128.0, 84.0, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

2-(3-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j, Figure 2).[13] A According to the general procedure, the reaction of 3-chlorobenzoic anhydride (0.2 mmol), bis(pinacolato)diboron (0.22 mmol), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (silica gel, hexane/DCM = 20/1) the title compound in 78% yield (37.2 mg). White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.80 (s, 1 H), 7.69-7.68 (d, J = 7.3 Hz, 1 H), 7.46-7.43 (m, 1 H), 7.34-7.31 (t, J = 7.7 Hz, 1 H), 1.37 (s, 12 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 134.6, 134.1, 132.7, 131.3, 129.2, 84.2, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (3k, Figure 2).[13] According to the general procedure, the reaction of 2-naphthoic anhydride (0.2 mmol), bis(pinacolato)diboron (0.22 mmol), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%) in 1,4-dioxane (0.20 M) for

15 h at 160 °C, afforded after work-up and chromatography (silica gel, hexane/DCM = 20/1) the title compound in 91% yield (46.3 mg). White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.40 (s, 1 H), 7.92-7.90 (d, *J* = 7.9 Hz, 1 H), 7.88-7.84 (m, 3 H), 7.55-7.48 (m, 2 H), 1.42 (s, 12 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 136.3, 135.0, 132.8, 130.4, 128.7, 127.7, 127.0, 127.0, 125.8, 83.9, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

4,4,5,5-Tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (3l, Figure 2).[13] According to the general procedure, the reaction of 1-naphthoic anhydride (0.2 mmol), bis(pinacolato)diboron (0.22 mmol), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (silica gel, hexane/DCM = 20/1) the title compound in 89% yield (45.3 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.79-8.77 (d, *J* = 8.4 Hz, 1 H), 8.10-8.09 (d, *J* = 6.1 Hz, 1 H), 7.96-7.93 (d, *J* = 8.2 Hz, 1 H), 7.85-7.83 (d, *J* = 8.0 Hz, 1 H), 7.57-7.53 (m, 1 H), 7.50-7.46 (t, *J* = 7.7 Hz, 2 H), 1.44 (s, 12 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 135.9, 134.6, 132.2, 130.6, 127.4, 127.3, 125.3, 124.4, 123.9, 82.7, 23.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

4,4,5,5-Tetramethyl-2-(o-tolyl)-1,3,2-dioxaborolane (3m, Figure 2).[13] According to the general procedure, the reaction of 2-methylbenzoic anhydride (0.2 mmol), bis(pinacolato)diboron (0.22 mmol), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (silica gel, hexane/DCM = 20/1) the title compound in 75% yield (32.8 mg). White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.79-7.77 (d, *J* = 6.8 Hz, 1 H), 7.35-7.32 (t, *J* = 7.5 Hz, 1 H), 7.19-7.17 (t, *J* = 7.0 Hz, 2 H), 2.56 (s, 3 H), 1.37 (s, 12 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 144.8, 135.9, 130.8, 129.8, 124.7, 83.4, 24.9, 22.2. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

2-(2-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3n, Figure 2).[13] According to the general procedure, the reaction of 2-fluorobenzoic anhydride (0.2 mmol), bis(pinacolato)diboron (0.22

mmol), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (silica gel, hexane/DCM = 20/1) the title compound in 85% yield (37.8 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76-7.72 (m, 1 H), 7.46-7.40 (m, 1 H), 7.15-7.12 (t, *J* = 7.4 Hz, 1 H), 7.05-7.00 (t, *J* = 8.7 Hz, 1 H), 1.36 (s, 12 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 167.2 (d, $^1J^{C\text{-}F}$ = 249.2 Hz), 136.8 (d, $^4J^{C\text{-}F}$ = 8.0 Hz), 133.3 (d, $^3J^{C\text{-}F}$ = 8.7 Hz), 123.6 (d, $^5J^{C\text{-}F}$ = 3.3 Hz), 115.3 (d, $^2J^{C\text{-}F}$ = 23.8 Hz), 83.9, 24.8. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -102.68.

4,4,5,5-Tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (3o, Figure 2).[13] According to the general procedure, the reaction of thiophene-2-carboxylic anhydride (0.2 mmol), bis(pinacolato)diboron (0.22 mmol), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (silica gel, hexane/DCM = 20/1) the title compound in 88% yield (37.0 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66-7.63 (m, 2 H), 7.21-7.18 (m, 1 H), 1.35 (s, 12 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 137.2, 132.4, 128.2, 84.1, 24.8. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

***N*,*N*-Dipropyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzenesulfonamide (3p, Figure 3).**[13] According to the general procedure, the reaction of 4-(*N*,*N*-dipropylsulfamoyl)benzoic anhydride (0.2 mmol), bis(pinacolato)diboron (0.22 mmol), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (silica gel, hexane/DCM = 20/1) the title compound in 98% yield (72.0 mg). White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.94-7.93 (d, *J* = 8.2 Hz, 2 H), 7.81-7.80 (d, *J* = 8.3 Hz, 2 H), 3.10-3.07 (t, *J* = 7.7 Hz, 4 H), 1.59-1.52 (m, 4 H), 1.38 (s, 12 H), 0.90-0.87 (t, *J* = 7.4 Hz, 6 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 142.4, 135.2, 126.0, 84.4, 50.0, 24.9, 22.0, 11.2. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

5,5-Dimethyl-2-phenyl-1,3,2-dioxaborinane (3a', Figure 3).[13] According to the general procedure, the reaction of benzoic anhydride (0.2 mmol), bis(neopentyl glycolato)diboron (0.22 mmol), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (silica gel, hexane/DCM = 20/1) the title compound in 81% yield (30.8 mg). White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.83-7.82 (d, *J* = 7.2 Hz, 2 H), 7.46-7.43 (t, *J* = 7.0 Hz, 1 H), 7.39-7.36 (t, *J* = 7.4 Hz, 2 H), 3.80 (s, 4 H), 1.05 (s, 6 H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 133.8, 130.7, 127.6, 72.3, 31.9, 21.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

4-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)-*N*,*N*-dipropylbenzenesulfonamide (3p', Figure 3).[13] According to the general procedure, the reaction of 4-(*N*,*N*-dipropylsulfamoyl)benzoic anhydride (0.2 mmol), and bis(neopentyl glycolato)diboron (0.22 mmol), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%) in 1,4-dioxane (0.20 M) for 15 h at 160 ° C, afforded after work-up and chromatography (silica gel, hexane/DCM = 20/1) the title compound in 94% yield (66.5 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91-7.89 (d, *J* = 8.2 Hz, 2 H), 7.77-7.75 (d, *J* = 8.2 Hz, 2 H), 3.78 (s, 4 H), 3.08-3.04 (t, *J* = 7.6 Hz, 4 H), 1.57-1.48 (m, 4 H), 1.03 (s, 6 H), 0.87-0.83 (t, *J* = 7.4 Hz, 6 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 140.7, 133.3, 124.9, 71.4, 48.9, 30.9, 20.9, 20.8, 10.2. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Supporting Information Available. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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