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# Merging Iridium-Catalyzed C−H Borylations with Palladium-Catalyzed Cross-Couplings Using Triorganoindium Reagents

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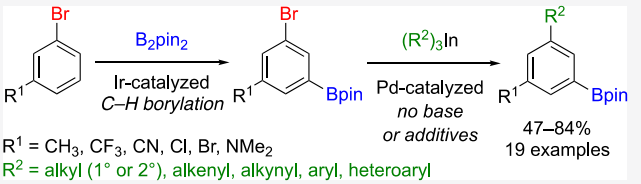
**ABSTRACT:** A versatile and efficient method to prepare borylated arenes furnished with alkyl, alkenyl, alkynyl, aryl, and heteroaryl functional groups is developed by merging Ir-catalyzed C−H borylations (CHB) with a chemoselective palladium-catalyzed cross-coupling of triorganoindium reagents (Sarandeses−Sestelo coupling) with aryl halides bearing a boronic ester substituent. Using triorganoindium cross-coupling reactions to introduce unsaturated moieties enables the synthesis of borylated arenes that would be difficult to access through the direct application of the CHB methodology. The sequential double catalyzed procedure can be also performed in one vessel.






Ir-catalyzed C−H borylation (CHB) is a commonly practiced reaction for the generation of borylated arenes and heteroarenes. CHBs tolerate many functional groups including halogens.[1] Halosubstituted aryl boronates so formed offer the potential for orthogonal reactivity in cross-coupling reactions. Despite the potential for competing self-polymerization,[2] halogen bearing arylboronates have been made to undergo chemoselective bond forming reactions with a C−X group where the boronic ester remains intact for subsequent chemistry.[3,4] Reactions of haloarenes bearing *N*-methyliminodiacetic acid[5−10] and 1,8-diaminonaphthalene[11,12] boronic esters (BMIDA and BDAN, respectively) avoid unwanted polyphenylene formation, as they are unreactive under certain Suzuki conditions (Scheme 1a). Such borylated biaryls have been employed in iterative Pd-catalyzed Suzuki−Miyaura cross-couplings popularized by Burke and others.[13] Molander and co-workers developed a complementary strategy whereby aryltrifluoroborate salts selectively couple with Bpin bearing haloarenes by way of photocatalysis (Scheme 1b).[14] Some successes have also been realized for the Negishi,[15−18] Stille,[19] Kumada,[20] and Hiyama[21] couplings of Bpin substituted haloarenes (Scheme 1c). In contrast, no examples of Bpin substituted haloarenes undergoing selective metal-catalyzed cross-coupling with triorganoindium reagents (Sarandeses−Sestelo coupling)[22,23] have been reported. Triorganoindium compounds ($R_3In$), easily available from organolithium or Grignard reagents, are efficient reagents in palladium-catalyzed cross-coupling reactions, highly versatile in the transference of aryl-, alkynyl-, or alkyl organic groups and are able to transfer all three groups attached to indium. In addition, they present lower toxicity compared to tin derivatives, and the palladium-catalyzed cross-coupling does not require the addition of base or additives.[24,25] Given these features, especially the ability to operate base-free and thereby minimize polyphenylene formation and that 1,3,5-trisubstituted (or triaryl) benzenes are a class of important compounds that are widely used ligands, in material science, etc.,[26−29] we looked to merge Sarandeses−Sestelo cross-coupling reaction with CHB and establish a method for the cross-coupling of $R_3In$ with CHB derived aryl halides bearing a Bpin substituent (Scheme 1d).

To begin, a variety of haloarenes were reacted with catalytic $[Ir(cod)OMe]_2$ and 4,4′-di-*tert*-butyl-2,2′-dipyridyl ligand (dtbpy) in a 1:2 molar ratio, and either bis(pinacolato)diboron ($B_2pin_2$) or pinacol borane (HBpin) at room temperature to isolate borylated haloarenes **1a−g** (Scheme 2).

With our CHB produced borylated haloarenes in hand, the plan was to react them with in situ generated triorganoindium compounds by combining dry $InCl_3$ with a organolithium or Grignard reagents. We began the cross-coupling studies with $Ph_3In$ prepared from commercial phenyllithium. Next, the capacity of borylated haloarenes to undergo Pd-catalyzed cross-coupling reactions with $R_3In$ was tested. After cannula transfer of a THF solution containing 0.40 mol equiv of $Ph_3In$ to a solution of $Pd(PPh_3)_2Cl_2$ (5 mol %) and **1a** in THF, the reaction was allowed to proceed at 65 °C (Scheme 3a). This reaction stalled after 16 h affording a 70:30 mixture of the desired cross-coupling product **2a**, unreacted **1a**, along with a substantial amount of biphenyl (∼35% yield).[30,31] Despite additional experimentation and the potential of $R_3In$ to transfer all three organic groups, elimination of biphenyl as a byproduct

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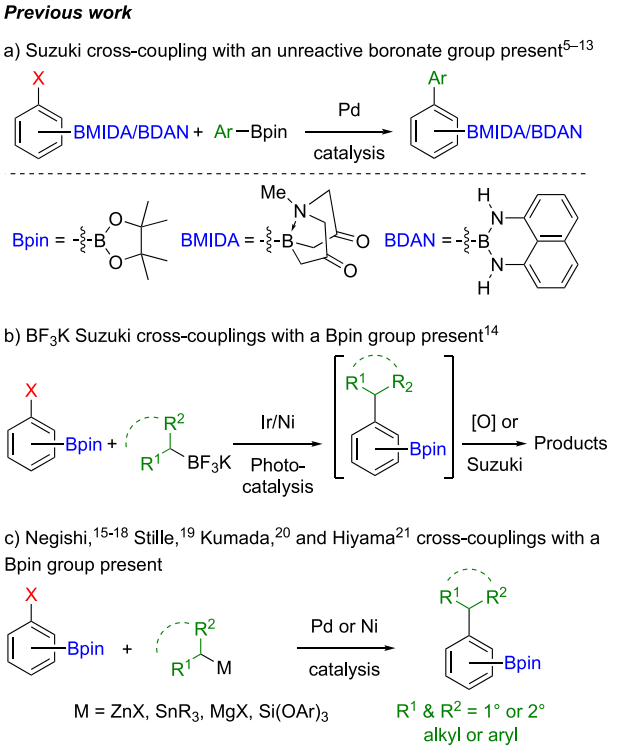
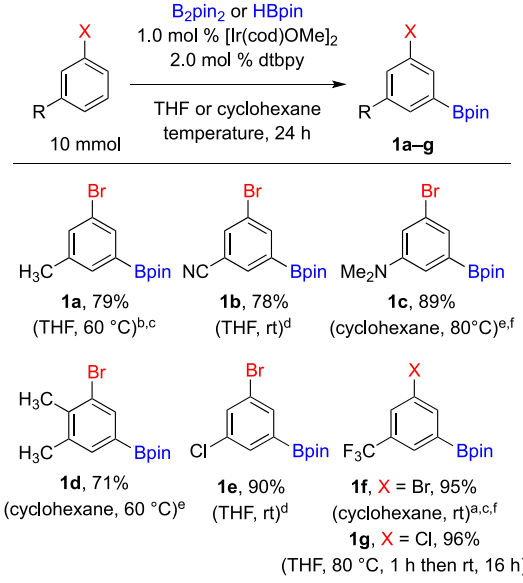
**Scheme 1**

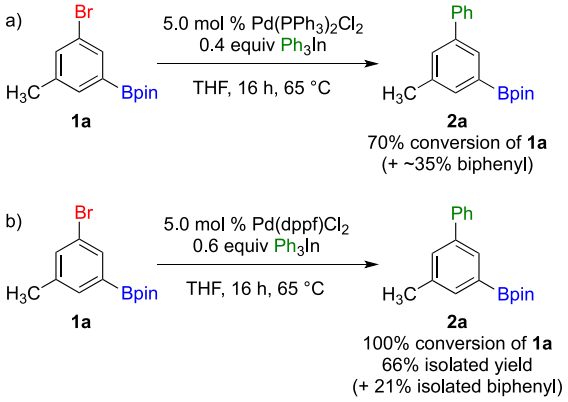



**Scheme 2. Ir-Catalyzed Borylation of Haloarenes**[a]




[a]Isolated yields. [b]0.55 equiv of $B_2pin_2$ were used. [c]Run with 0.5 mol % of $[Ir(cod)OMe]_2$ and 1.0 mol % of dtbpy. [d]2.1 equiv of HBpin were used. [e]1.5 equiv of HBpin were used. [f]Run for 48 h. [g]1.1 equiv of HBpin were used.

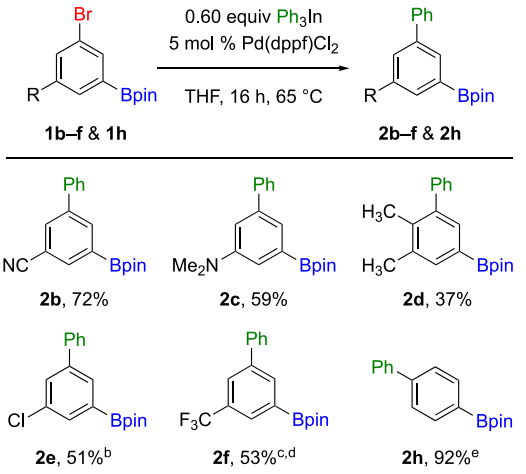
**Scheme 3. Pd-Catalyzed Cross-Couplings of $Ph_3In$ with Borylated Haloarene 1a**




was never possible, even when reactions were run under argon with degassed solvents. Nonetheless, increasing the stoichiometry of the $Ph_3In$ to 0.60 mol equiv and changing the catalyst to $Pd(dppf)Cl_2$ resulted in the complete consumption of **1a** after 16 h in refluxing THF (Scheme 3b). Aside from biphenyl formation, NMR and GC analyses of the crude reaction mixture indicated that no other unwanted cross-coupling products had occurred, nor was there loss of the Bpin group. On the other hand, the complete coupling reaction using just 0.6 equiv of $R_3In$ indicates that more than one organic group is efficiently transferred.

After these optimizations, we examined the reaction of $Ph_3In$ with various borylated haloarenes (Scheme 4). As with **1a**, borylated 3-bromobenzonitrile (**1b**) gave **2b**[32] in 72% isolated yield without any evidence of unreacted starting material, other cross-coupling products (aside from biphenyl), or deborylated materials in the crude product mixture. Likewise, aniline derivative **1c** and 4-(Bpin)bromobenzene (**1h**) coupled without incident, affording **2c** and **2h** in 59% and 92% isolated yields, respectively. $^1H$ NMR spectra of the crude product mixture also indicated a clean reaction for **1d**, but **2d** was

**Scheme 4. Pd-Catalyzed Cross-Couplings of $Ph_3In$ with Borylated Haloarenes**[a,b]




[a]Isolated yields. [b]0.63 equiv of $Ph_3In$ were used. [c]Minor amounts of byproducts were also observed. [d]No product was formed when the boronic ester form the aryl chloride (**1g**) was used as starting material. [e]Run at 80 °C.



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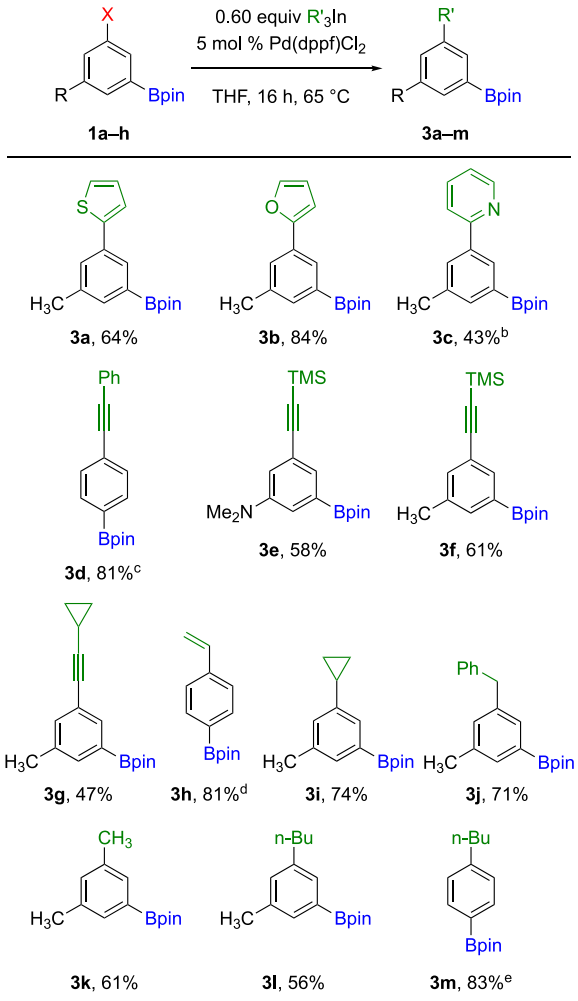
isolated in only 37% yield, presumably due to losses during chromatographic purification. In contrast, while the cross-coupling reaction of **1e** and **1f** gave desired products in 51% and 53% yield, respectively, these reactions showed side products derived from the starting borylated haloarenes. Specifically, compounds stemming from the deboronation (~10−20%) of the cross-coupling products were observed for these substrates. In addition, small amounts (1−4%) of over coupled products could also be seen in the crude reaction mixtures (see the Experimental Section for details). Lastly, under the previous developed reaction conditions, we were unable to affect the cross-coupling of chloroarene **1g**.

The scope of the reaction was then extended to triorganoindium species with various organic moieties (C-sp$^3$, C-sp$^2$, and C-sp) (Scheme 5). Under the previously optimized

**Scheme 5. Pd-Catalyzed Cross-Couplings of $R_3In$ with Borylated Haloarenes**[a]




[a]Isolated yields. [b]Run at 80 °C for 40 h; the isolated material contained minor impurities. [c]Run at 80 °C for 24 h. [d]Run at 75 °C for 36 h. [e]Run at 80 °C for 16 h.

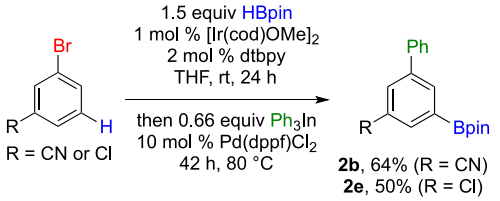
reaction conditions, triheteroarylindium reagents prepared from 2-lithio forms of thiophene, furan, and pyridine afforded products **3a**, **3b**, and **3c** in good yields under mild reaction conditions. Using triorganoindium cross-couplings to introduce these heterocycles is notable as **3a**, **3b**, and **3c** would be difficult to access through the direct application of the CHB methodology. This is because CHB of heteroarenes tend to be very facile.[1] Hence, CHB on 2-tolyl derivatives of thiophene, furan, or pyridines would borylate the heterocycle instead of generating **3a**−**c**.[33−35]

Alkenes and alkynes are often problematic substituents in CHB owing to their ability to be hydroborated and/or otherwise compromise the effectiveness of the catalyst. This incompatibility creates the need for methods that can incorporate unsaturated groups post-CHB. With this purpose in mind, we were gratified to find that different trialkynylindium reagents successfully coupled with three different borylated haloarenes, affording compounds **3d**−**g** in good (81%) to modest (47%) isolated yields. Of similar utility, the cross-coupling reaction of trivinylindium with **1h** gave **3h** in 81% isolated yield, an example that could be extended to other alkenyl groups.

The substrate scope was also extended to alkyl (sp$^3$) organoindium reagents. The secondary alkyl cyclopropyl unit was efficiently transfer to bromoaryl boronic ester **1a** in 74% yield (**3i**). Analogously, $Bn_3In$ and $Me_3In$ coupled giving products **3j**, and **3k** in synthetically useful yields (71% and 62%, respectively). Notably, even the *n*-butyl groups of *n*-$Bu_3In$ were transferable, with **1a** and **1h** leading to products **3l** and **3m** in 56% and 83% isolated yields, respectively.

Finally, we investigated performing the CHB and Sarandeses−Sestelo cross-coupling in a single vessel (Scheme 6). Following their respective generation, to crude solutions of

**Scheme 6. One-Pot CHB/Sarandeses−Sestelo Cross-Coupling**




**1b** and **1d** a THF solution of $Ph_3In$ was added. For both substrates, the final products (**2b** and **2d**) corresponding to the Ir-catalyzed borylation and Pd-catalyzed coupling were formed in yields comparable to the two-pot protocol. However, to achieve full conversion, longer reaction times and higher palladium catalyst loadings were required. We have observed the same phenomena in past efforts to telescope CHB and subsequent Pd-catalyzed transformations.[4] We attribute this trend to residuals from the CHB step causing a loss of catalytic activity.

In summary, we have established a new route to borylated aryl compounds that marries Ir-catalyzed C−H borylations with Pd-catalyzed cross-coupling with triorganoindium reagents. Good substrate scope for both the borylated bromoarenes and $R_3In$ is demonstrated. This process appears to avoid the potential for polyphenylene formation that is inherent in palladium(0) reactions with borylated haloaromatics. Using triorganoindium cross-couplings to introduce unsaturated moieties also enables the synthesis of borylated arenes that would be difficult to access through the direct application of the CHB methodology. Finally, telescoping the borylation and Pd-cross-coupling into a single reaction flask is viable.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## EXPERIMENTAL SECTION

**Materials and Methods.** Unless indicated otherwise, all reactions were carried out in oven-dried glassware under an atmosphere of argon, with magnetic stirring, and monitored by GC-MS or $^{1}$H NMR/$^{19}$F NMR. Tetrahydrofuran was freshly distilled from sodium/benzophenone under nitrogen. $InCl_3$ was dried under a high vacuum at 80 °C prior use. Column chromatography was performed with silica gel (230−400 mesh). Spectra taken in $CDCl_3$ were referenced to 7.26 ppm in $^{1}$H NMR and 77.2 ppm in $^{13}$C NMR. Resonances for the boron-bearing carbon atom were not observed due to quadrupolar relaxation. Heating for all reactions run above room temperature was accomplished by use of an oil bath.

For compounds **1a−g**, **2a−b**, **2e−h**, **3c−d**, **3h**, and **3m**, $^{1}$H, $^{13}$C{$^{1}$H}, $^{11}$B, and $^{19}$F NMR spectra were recorded on a 500 MHz NMR spectrometer operating at 499.7 MHz for $^{1}$H NMR, 125.7 MHz for $^{13}$C NMR, 470.1 MHz for $^{19}$F NMR, and 160.3 MHz for $^{11}$B NMR. Elemental composition was determined by high resolution/accurate mass spectrometry. Samples were introduced to the mass spectrometer by direct infusion electrospray ionization in positive ionization mode, and data were acquired at a resolution of 100 000 defined at $m/z$ 400. Melting points are uncorrected.

For compounds **2c−d**, **3a−b**, **3e−g**, and **3i−l**, $^{1}$H and $^{13}$C{$^{1}$H} NMR spectra were recorded on a 300 MHz NMR spectrometer equipped with a QNP probe operating at 300 and 75 MHz respectively. $^{11}$B NMR spectra were recorded on a 400 MHz NMR spectrometer equipped with a multinuclear BBFO probe operating at 128 MHz. Liquid chromatography−mass spectrometry was performed using an HPLC coupled with QSTAR Elite time-of-flight mass spectrometer operating in positive ionization mode.

**General Procedure A: C−H Borylation with $B_2pin_2$.** In a nitrogen atmosphere glovebox, bis(pinacolato)boron ($B_2pin_2$) (1.40 g, 5.5 mmol, 0.55 equiv) was weighed into a 20 mL vial containing a magnetic stir bar. [Ir(cod)OMe]$_2$ (33 mg, 0.05 mmol, 0.5 mol %) and 4,4′-di-*tert*-butyl-2,2′-dipyridyl ligand (27 mg, 0.10 mmol, 1.0 mol %) were weighed into two test tubes separately, each being diluted with THF or cyclohexane. The [Ir(cod)OMe]$_2$ solution was transferred into the 20 mL vial containing $B_2pin_2$. This mixture was stirred until a golden yellow clear solution was obtained (∼ 1 min). Next the solution containing ligand was transferred into the vial, and upon stirring the resulting solution turned a dark brown color. Finally, the substrate (10.0 mmol, 1.0 equiv) was added to the vial, which was then sealed and taken out of the glovebox. The reaction mixture was stirred at the indicated temperature. Then, the reaction mixture was passed through a plug of silica (BD 60 mL Syringe/Luer-Lok Tip-silica up to 50 mL mark) eluting with a hexane/ethyl acetate solution as eluent. The volatiles were removed by rotary evaporation.

**General Procedure B: C−H Borylation with HBpin.** In a nitrogen atmosphere glovebox, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin) (1.5−2.0 equiv) was weighed into a 5 mL vial containing a magnetic stir bar. [Ir(cod)OMe]$_2$ (6.6 mg, 0.01 mmol, 1.0 mol %) and 4,4′-di-*tert*-butyl-2,2′-dipyridyl ligand (5.4 mg, 0.02 mmol, 2.0 mol %) were weighed into two test tubes separately, each being diluted with 1 mL of THF or cyclohexane. The [Ir(cod)OMe]$_2$ solution was transferred into the 5 mL vial containing HBpin. This mixture was stirred until a golden yellow clear solution was obtained (∼ 1 min). Next the solution containing ligand was transferred into the vial, and upon stirring the resulting solution turned a dark brown. Finally, the substrate (1 mmol, 1.0 equiv) was added to the vial, which was then sealed and was taken out of the glovebox. The reaction mixture was stirred at the indicated temperature. Then, the reaction mixture was passed through a plug of silica (BD 60 mL Syringe/Luer-Lok Tip-silica up to 50 mL mark) eluting with a hexane/dichloromethane or hexane/ethyl acetate solution as eluent. The volatiles were removed by rotary evaporation.

*2-(3-Bromo-5-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**).*[36,37] General Procedure A was carried out on 1-bromo-3-methylbenzene (10 mmol, 1.71 g) in THF at 60 °C for 24 h. After workup 2.36 g of compound **1a** was obtained as a white solid (mp 74−76 °C, lit 74−76 °C)36 in 79% yield. $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.73 (s, 1H), 7.53 (s, 1H), 7.42 (s, 1H), 2.33 (s, 3H), 1.34 (s, 12H); $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) $\delta$ 139.5, 134.8, 134.5, 133.9, 122.4, 84.1, 24.8, 20.9; $^{11}$B NMR (160 MHz, $CDCl_3$) $\delta$ 30.5 (brs). The spectral data were in accordance with those reported in the literature.[37] HRMS (ESI) $m/z$ calcd for $C_{13}H_{19}BBrO_2$ $[M + H]^+$ 297.0661, found 297.0640.

*3-Bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzonitrile (**1b**).*[38,39] General Procedure B was carried out on 3-bromobenzonitrile (182 mg, 1.0 mmol, 1.0 equiv) with HBpin (300 $\mu$L, 2.1 mmol, 2.1 equiv) as the boron source in THF at room temperature for 24 h. After workup 0.238 g of compound **1b** was obtained as a white solid (mp 87−88 °C, lit 83−86 °C)39 in 78% yield. $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.13 (dd, $J$ = 2.0, 1.0 Hz, 1H), 8.00 (dd, $J$ = 1.6, 1.0 Hz, 1H), 7.85 (dd, $J$ = 2.0, 1.6 Hz, 1H), 1.35 (s, 12H); $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) $\delta$ 141.9, 136.9, 136.9, 122.8, 117.5, 114.0, 85.0, 25.0; $^{11}$B NMR (160 MHz, $CDCl_3$) $\delta$ 29.5 (brs). The spectral data were in accordance with those reported in the literature.[38] HRMS (ESI) $m/z$ calcd for $C_{13}H_{16}BBrNO_2$ $[M + H]^+$ 308.0457, found 308.0435.

*3-Bromo-N,N-dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (**1c**).* The General Procedure B was carried out on 3-bromo-*N*,*N*-dimethylaniline (200 mg, 1.0 mmol, 1.0 equiv) with HBpin (1.5 mmol, 1.5 equiv) as the boron source in cyclohexane at 80 °C for 48 h. After workup 0.29 g of compound **1c** was obtained as a white solid (mp 121−123 °C) in 89% yield. $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.28 (m, 1H) (overlap with the solvent peak), 7.07 (brs, 1H), 6.94 (brs, 1H), 2.96 (s, 6H), 1.33 (s, 12H); $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) $\delta$ 151.2, 125.1, 123.3, 117.8, 117.0, 84.0, 40.5, 24.9; $^{11}$B NMR (160 MHz, $CDCl_3$) $\delta$ 29.9 (brs). HRMS (ESI) $m/z$ calcd for $C_{14}H_{22}BBrNO_2$ $[M + H]^+$ 326.0927, found 326.0911.

*2-(3-Bromo-4,5-dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1d**).* The General Procedure B was carried out on 1-bromo-2,3-dimethylbenzene (185 mg, 1.0 mmol, 1.0 equiv) with HBpin (1.5 mmol, 1.5 equiv) as the boron source in cyclohexane at 60 °C for 24 h. After workup 0.22 g of compound **1d** was obtained as a white solid (mp 103−105 °C) in 71% yield. $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.82 (s, 1H), 7.49 (s, 1H), 2.37 (s, 3H), 2.32 (s, 3H), 1.33 (s,12H); $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) $\delta$ 139.5, 138.0, 136.4, 134.9, 125.7, 83.9, 24.8, 21.0, 19.7; $^{11}$B NMR (160 MHz, $CDCl_3$) $\delta$ 30.3 (brs). HRMS (ESI) $m/z$ calcd for $C_{14}H_{21}BBrO_2$ $[M + H]^+$ 311.0818, found 311.0848.

*2-(3-Bromo-5-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1e**).*[40] The General Procedure B was carried out on 1-bromo-3-chlorobenzene (191 mg, 1.0 mmol, 1.0 equiv) with HBpin (300 $\mu$L, 2.1 mmol, 2.1 equiv) as the boron source in THF at room temperature for 24 h. After workup 0.29 g of compound **1e** was obtained as a white solid (mp 51−53 °C) in 90% yield. $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.80 (dd, $J$ = 1.8, 0.9 Hz, 1H), 7.69 (dd, $J$ = 2.1, 0.9 Hz, 1H), 7.59 (dd, $J$ = 2.1, 1.8 Hz, 1H), 1.34 (s, 12H); $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) $\delta$ 135.7, 135.0, 134.0, 133.3, 122.8, 84.7, 25.0; $^{11}$B NMR (160 MHz, $CDCl_3$) $\delta$ 29.9 (brs). The spectral data were in accordance with those reported in the literature.[40] HRMS (EI) $m/z$ calcd for $C_{12}H_{15}BBrClO_2$ $[M]^+$ 316.0032, found 316.0050.

*2-(3-Bromo-5-(trifluoromethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1f**).*[38] The General Procedure A was carried out on 1-bromo-3-(trifluoromethyl)benzene (2.25 g, 10 mmol) in cyclohexane at room temperature for 48 h. After workup 3.31 g of compound **1f** was obtained as a white solid (mp 51−52 °C) in 95% yield. $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.10 (d, $J$ = 2.0 Hz, 1H), 7.97 (dt, $J$ = 1.7, 0.9 Hz, 1H), 7.83 (td, $J$ = 1.9, 0.8 Hz, 1H), 1.35 (s, 12H); $^{19}$F NMR (470 MHz, $CDCl_3$) $\delta$ −62.7; $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) $\delta$ 141.0 (q, $J$ = 1.2 Hz), 132.0 (q, $J$ = 32.7 Hz), 131.0 (q, $J$ = 3.8 Hz), 130.0 (q, $J$ = 3.5 Hz), 123.4 (q, $J$ = 272.8 Hz), 122.6, 84.8, 25.0; $^{11}$B NMR (160 MHz, $CDCl_3$) $\delta$ 29.8 (brs). The NMR spectral data were in accordance with those reported in the literature.[38] HRMS (EI) $m/z$ calcd for $C_{13}H_{15}BBrF_3O_2$ $[M]^+$ 350.0295, found 350.0289.

*2-(3-Chloro-5-(trifluoromethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1g**).*[41] In a nitrogen atmosphere glovebox, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin) (1.6 mL, 11 mmol,


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1.1 equiv) was weighed into a 20 mL vial containing a magnetic stir bar. $[Ir(cod)OMe]_2$ (33 mg, 0.05 mmol, 0.5 mol %), 4,4′-di-*tert*-butyl-2,2′-dipyridyl ligand (27 mg, 0.1 mmol, 1.0 mol %), and 1-chloro-3-(trifluoromethyl)benzene (1.80 g, 10 mmol, 1.0 equiv) were added to the vial with THF as solvent. The vial was sealed and taken out of the glovebox. The reaction mixture was stirred at 80 °C for 1 h and then at room temperature for 16 h. Then, the reaction mixture was passed through a plug of silica (BD 60 mL Syringe/Luer-Lok Tip-silica up to 50 mL mark). The volatiles were removed by rotary evaporation to yield 2.700 g of compound **1g** as a colorless oil in 96% yield. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.95 (dd, $J$ = 2.2, 0.7 Hz, 1H), 7.93 (dd, $J$ = 1.7, 0.8 Hz, 1H), 7.67 (dd, $J$ = 2.4, 0.7 Hz, 1H), 1.36 (s, 12H); $^{19}$F NMR (470 MHz, $CDCl_3$) $\delta$ −62.8; $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 138.1 (q, $J$ = 1.4 Hz), 134.7, 131.9 (q, $J$ = 32.8 Hz), 129.5 (q, $J$ = 3.6 Hz), 128.1 (q, $J$ = 3.8 Hz), 123.6 (q, $J$ = 272.8 Hz), 84.8, 25.0; $^{11}$B NMR (160 MHz, $CDCl_3$) $\delta$ 30.1 (brs). The spectral data were in accordance with those reported in the literature.[41]

**General Procedure C: Palladium-Catalyzed Cross-Coupling Reactions Using Triorganoindium Reagents.** A 25 mL round-bottomed flask with a stir bar was charged with dry $InCl_3$ (133 mg, 0.6 mmol, 0.6 equiv). A positive argon pressure was established and dry THF (3.0 mL) was added. The resulting solution was cooled to −78 °C, and a solution of RLi or RMgBr (vinyl) (1.8−2.0 mmol, 1.8−2.0 equiv) was slowly added (30−60 min). After 60 min stirring, the reaction mixture was warmed to room temperature for 1−2 h. The freshly prepared solution of $R_3In$ (0.6 mmol in dry THF) was added to mixture of the aryl boronic ester (1 mmol, 1 equiv) and $Pd(dppf)Cl_2$ (36.6 mg, 0.05 mmol, 5.0 mol %) or $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (40.8 mg, 0.05 mmol, 5.0 mol %) in dry THF (6 mL). The resulting mixture was placed under argon and heated at reflux using an oil bath until the starting material was consumed (NMR or GC). The reaction was then quenched by the addition of few drops of MeOH, concentrated under reduced pressure, and redissolved in dichloromethane. The crude mixture was passed through a plug of silica (BD 60 mL Syringe/Luer-Lok Tip-silica up to 50 mL mark) with hexane as eluent to yield a mixture that was purified further by silica chromatography with a hexane/ethyl acetate solution as eluent to afford the cross-coupled product.

*4,4,5,5-Tetramethyl-2-(5-methyl-[1,1′-biphenyl]-3-yl)-1,3,2-dioxaborolane (**2a**).*[42] Following the General Procedure C the reaction of **1a** (297 mg, 1.0 mmol, 1.0 equiv) with a solution of $Ph_3In$ (0.60 mmol, 0.60 equiv) in THF (4 mL) at 65 °C for 16 h afforded, after column chromatography (hexane/ethyl acetate 98:2), 193 mg of compound **2a** as a white solid (66% yield, mp 93−95 °C, lit 106−107 °C).[42] $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.85 (m, 1H), 7.62 (m, 3H), 7.51 (m, 1H), 7.41 (m, 2H), 7.33 (tt, $J$ = 7.3, 1.2 Hz, 1H), 2.43 (q, $J$ = 0.7 Hz, 3H), 1.37 (s, 12H). $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$) $\delta$ 141.4, 140.8, 137.8, 134.4, 131.0, 130.8, 128.7, 127.4, 127.2, 84.0, 25.0, 21.5. $^{11}$B NMR (160 MHz, $CDCl_3$) $\delta$ 30.8 (brs). The spectral data were in accordance with those reported in the literature.[42] HRMS (ESI) $m/z$ calcd for $C_{19}H_{24}BO_2$ $[M + H]^+$ 295.1869, found 295.1867.

*5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1′-biphenyl]-3-carbonitrile (**2b**).* Following the General Procedure C the reaction of **1b** (308 mg, 1.0 mmol, 1.0 equiv) with a solution of $Ph_3In$ (0.60 mmol, 0.60 equiv) in THF (4 mL) at 65 °C for 16 h afforded, after column chromatography (hexane/ethyl acetate 98:2 as eluent), 221 mg of compound **2b** as a white solid (72% yield, mp 98−99 °C). $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.22 (dd, $J$ = 2.0, 1.0 Hz, 1H), 8.06 (dd, $J$ = 1.6, 1.0 Hz, 1H), 7.93 (dd, $J$ = 2.0, 1.6 Hz, 1H), 7.60 (m, 2H), 7.47 (m, 2H), 7.41 (m, 1H), 1.37 (s, 12H). $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 141.8, 139.0, 137.7, 137.1, 133.0, 129.2, 128.4, 127.3, 119.0, 112.7, 84.7, 25.0. $^{11}$B NMR (160 MHz, $CDCl_3$) $\delta$ 30.0 (brs). The spectral data were in accordance with those reported in the literature. HRMS (ESI) $m/z$ calcd for $C_{19}H_{21}BNO_2$ $[M + H]^+$ 306.1665, found 306.1693.

*N,N-Dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1′-biphenyl]-3-amine (**2c**).* Following the General Procedure C the reaction of **1c** (110 mg, 0.34 mmol, 1.0 equiv) with a solution of $Ph_3In$ (0.204 mmol, 0.60 equiv) in THF (5 mL) at 65 °C for 16 h afforded, after column chromatography (hexane/ethyl acetate 98:2 as eluent), 65 mg of compound **2c** as a white solid (59% yield, mp 125−129 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.68−7.60 (m, 2H), 7.46−7.37 (m, 3H), 7.36−7.29 (m, 1H), 7.22−7.21 (m, 1H), 7.07−7.05 (m,1H), 3.03 (s, 6H), 1.37 (s, 12H). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) $\delta$ 150.7, 142.2, 141.8, 128.6, 127.6, 127.1, 122.5, 117.9, 114.8, 83.8, 41.0, 25.0. $^{11}$B NMR (128 MHz, $CDCl_3$) $\delta$ 31.3 (brs). HRMS (ESI) $m/z$ calcd for $C_{20}H_{27}BNO_2$ $[M + H]^+$ 324.2135, found 324.2137.

*2-(5,6-Dimethyl-[1,1′-biphenyl]-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2d**).* Following the General Procedure C the reaction of **1d** (106 mg, 0.34 mmol, 1.0 equiv) with a solution of $Ph_3In$ (0.204 mmol, 0.60 equiv) in THF (5 mL) at 65 °C for 16 h afforded, after column chromatography, 39 mg of compound **2d** as a white solid (37% yield, mp 102−106 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.59 (s, 1H), 7.52 (s, 1H), 7.43−7.28 (m, 5H), 2.33 (s, 3H), 2.16 (s, 3H), 1.31 (s, 12H). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) $\delta$ 142.6, 142.0, 137.7, 136.8, 135.2, 134.3, 129.6, 128.0, 126.7, 83.7, 25.0, 20.5, 17.6. $^{11}$B NMR (128 MHz, $CDCl_3$) $\delta$ 30.7 (brs). HRMS (ESI) $m/z$ calcd for $C_{20}H_{26}BO_2$ $[M + H]^+$ 309.2026, found 309.2020.

*2-(5-Chloro-[1,1′-biphenyl]-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2e**).* The General Procedure C was carried out with **1e** (301 mg, 0.95 mmol, 1.0 equiv) and a solution of $Ph_3In$ (0.60 mmol, 0.63 equiv) in THF (4 mL) at 65 °C. After 16 h, an aliquot was taken and analyzed by NMR and GC-MS to find that a mixture of **2e**, 3-chloro-1,1′-biphenyl and 5′-chloro-1,1′:3′,1″-terphenyl in ratio of 85:11:4 was obtained. The reaction was then quenched by the addition of few drops of MeOH, concentrated under reduce pressure and redissolved in dichloromethane. The residue was passed through a plug of silica gel (hexane as eluent). The fractions containing product were collected and concentrated to yield a mixture of the product with biphenyl. The mixture was passed through a silica column chromatography (hexane/ethyl acetate 100:0 → hexane/ethyl acetate 99:1 as eluent). The fractions containing product were collected and concentrated to yield 160 mg of compound **2e** as a white solid (mp 87−89 °C, 51% yield). $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.90 (dd, $J$ = 1.8, 0.9 Hz, 1H), 7.75 (dd, $J$ = 2.1, 0.9 Hz, 1H), 7.66 (t, $J$ = 2.0 Hz, 1H), 7.60 (m, 2H), 7.44 (m, 2H), 7.36 (tt, $J$ = 7.4, 1.3 Hz, 1H), 1.36 (s, 12H). $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 142.6, 139.9, 134.6, 133.3, 131.7, 130.0, 128.9, 127.9, 127.4, 84.4, 25.0. $^{11}$B NMR (160 MHz, $CDCl_3$) $\delta$ 30.1 (brs). HRMS (ESI) $m/z$ calcd for $C_{18}H_{21}BClO_2$ $[M + H]^+$ 315.1323, found 315.1302.

*4,4,5,5-Tetramethyl-2-(5-(trifluoromethyl)-[1,1′-biphenyl]-3-yl)-1,3,2-dioxaborolane (**2f**).*[7] The General Procedure C was carried out with **1f** (351 mg, 1.0 mmol, 1.0 equiv) and a solution of $Ph_3In$ (0.60 mmol, 0.60 equiv) in THF (4 mL) at 65 °C. After 16 h, an aliquot was taken and analyzed by NMR and GC-MS to find that a mixture of **2f**, 3-(trifluoromethyl)-1,1′-biphenyl and 3,5′-bis(trifluoromethyl)-1,1′:3′,1″-terphenyl in ratio of 72:20:8 was obtained. The reaction was then quenched by the addition of few drops of MeOH, concentrated under reduce pressure and redissolve in dichloromethane. The residue was passed through a plug of silica gel (hexane as eluent). The fractions containing product were collected and concentrated. The mixture was passed through a silica column chromatography (hexane/ethyl acetate 97:3). The fractions containing product were collected and concentrated to yield 219 mg of a white sticky solid mixture of compound **2f** (53%) and with a minor (10%) byproduct corresponding to 3,5′-bis(trifluoromethyl)-1,1′:3′,1″-terphenyl. Separating **2f** from this byproduct proved difficult. $^1$H NMR (500 MHz, $CDCl_3$) 8.21 (m, 1H), 8.05 (m, 1H), 7.91 (m, 1H), 7.64 (m, 2H), 7.47 (m, 2H), 7.39 (tt, J= 7.3, 1.3 Hz, 1H), 1.38 (s, 12H). $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 141.4, 139.9, 136.8 (q, $J$ = 1.5 Hz), 130.8 (q, $J$ = 32.2 Hz), 130.2 (q, $J$ = 3.7 Hz), 129.0, 128.4 (q, $J$ = 217.9 Hz), 128.1, 127.4, 126.6 (q, $J$ = 3.6 Hz), 84.5, 25.0. We note that $^1$H and $^{13}$C NMR spectra of compound **2f** were previously reported with similar impurity peaks present.[7] $^{19}$F NMR (470 MHz, $CDCl_3$) $\delta$ −62.5. $^{11}$B NMR (160 MHz, $CDCl_3$) $\delta$ 30.1 (brs). The spectral data were in accordance with those reported in the literature.[7] HRMS (ESI) $m/z$ calcd for $C_{19}H_{21}BF_3O_2$ $[M + H]^+$ 349.1587, found 349.1561.



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*2-([1,1′-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2h**).*[43,44] Following the General Procedure C the reaction of 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2- dioxaborolane (**1h**) (282 mg, 1.0 mmol, 1.0 equiv) with a solution of $Ph_3In$ (0.60 mmol, 0.60 equiv) in THF (4 mL) at 80 °C for 16 h afforded, after column chromatography (hexane as eluent), 257 mg of **2h** as a white solid (92% yield, mp 100−101 °C, lit 111−112 °C).[44] $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.89 (d, $J$ = 8.3 Hz, 2H), 7.63−7.61 (m, 4H), 7.45 (t, $J$ = 7.4 Hz, 2H), 7.36 (tt, $J$ = 7.4, 1.3 Hz, 1H), 1.37 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) $\delta$ 144.0, 141.2, 135.4, 128.9, 127.7, 127.4, 126.6, 84.0, 25.0. $^{11}$B NMR (160 MHz, $CDCl_3$) $\delta$ 30.7 (brs). The spectral data were in accordance with those reported in the literature.[43] HRMS (ESI) $m/z$ calcd for $C_{18}H_{22}BO_2$ $[M + H]^+$ 281.1713, found 281.1708.

*4,4,5,5-Tetramethyl-2-(3-methyl-5-(thien-2-yl)phenyl)-1,3,2-dioxaborolane (**3a**).* Following the General Procedure C the reaction of **1a** (101 mg, 0.34 mmol, 1.0 equiv) with a solution of tri(thiophen-2-yl)indium (0.204 mmol, 0.60 equiv) in THF (5 mL) at 65 °C for 16 h afforded, after column chromatography, 65 mg of compound **3a** as a white solid (64% yield, mp 95−98 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.88 (s, 1H), 7.57 (s, 1H), 7.53 (s, 1H), 7.36 (dd, $J$ = 3.6, 1.2 Hz, 1H), 7.26 (dd, $J$ = 5.1, 1.2 Hz, 1H), 7.07 (dd, $J$ = 5.1, 3.6 Hz, 1H), 2.40 (s, 3H), 1.37 (s, 12H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) $\delta$ 144.6, 137.9, 134.7, 134.0, 129.7, 129.5, 128.0, 124.7, 123.3, 84.0, 25.0, 21.4. $^{11}$B NMR (128 MHz, $CDCl_3$) $\delta$ 31.0 (brs). HRMS (ESI) $m/z$ calcd for $C_{17}H_{22}BO_2S$ $[M + H]^+$ 301.1428, found 301.1434.

*2-(3-(Furan-2-yl)-5-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3b**).* Following the General Procedure C the reaction of **1a** (101 mg, 0.34 mmol, 1.0 equiv) with a solution of tri(furan-2-yl) indium (0.204 mmol, 0.60 equiv) in THF (5 mL) at 65 °C for 16 h afforded, after column chromatography, 81 mg of compound **3b** as an orange oil (84% yield). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.91 (s, 1H), 7.6−7.59 (m, 1H), 7.53 (s, 1H), 7.45 (dd, $J$ = 1.8, 0.8 Hz, 1H), 6.66 (dd, $J$ = 3.4, 0.8 Hz, 1H), 6.44 (dd, $J$ = 3.4, 1.8 Hz, 1H), 2.39 (s, 3H), 1.36 (s, 12H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) $\delta$ 154.1, 141.9, 137.6, 134.4, 130.4, 127.4, 127.3, 111.6, 105.0, 83.9, 24.9, 21.3. $^{11}$B NMR (128 MHz, $CDCl_3$) $\delta$ 30.1 (brs). HRMS (ESI) $m/z$ calcd for $C_{17}H_{22}BO_3$ $[M + H]^+$ 285.1656, found 285.1662.

*2-(3-Methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl)pyridine (**3c**).* Following the General Procedure C the reaction of **1a** (297 mg, 1.0 mmol, 1.0 equiv) with a solution of tri(pyridin-2-yl)indium (0.60 mmol, 0.60 equiv) in THF (3.8 mL) at 80 °C for 40 h afforded, after column chromatography (hexane/ethyl acetate 100:0 → 50:50 as eluent), 162 mg of a white solid (mp 123−125 °C) containing **3c** and an impurity (∼12%) that is detected in the 1H and 13C NMR spectra, but that could not be detected by GC. Hence, we propose this impurity to be a high molecular weight oligomer. After accounting for the amount of presumed impurity present in the 1H NMR spectrum, the yield of **3c** is ∼43% $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.69 (ddd, $J$ = 4.8, 1.8, 1.0 Hz, 1H), 8.15 (p, $J$ = 0.8 Hz,1H), 7.98 (td, $J$ = 1.9, 0.8 Hz, 1H), 7.79 (dt, $J$ = 8.0, 1.1 Hz, 1H), 7.73 (ddd, $J$ = 8.0, 7.4, 1.8 Hz, 1H), 7.69 (dd, $J$ = 1.7, 0.9 Hz, 1H), 7.22 (ddd, $J$ = 7.4, 4.8, 1.2 Hz, 1H), 2.44 (q, J= 0.8 Hz, 3H),1.36 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) $\delta$ 157.8, 149.7, 138.9, 138.0, 136.8, 136.2, 130.8, 130.5, 122.1, 121.0, 84.0, 25.0, 21.4. $^{11}$B NMR (160 MHz, $CDCl_3$) $\delta$ 30.4 (brs). HRMS (ESI) $m/z$ calcd for $C_{18}H_{23}BNO_2$ $[M + H]^+$ 296.1822, found 296.1839.

*2-([1,1″-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3d**).*[45] Following the General Procedure C the reaction of **1h** (283 mg, 1.0 mmol, 1.0 equiv) with a solution of tris(phenylethynyl) indium (0.6 mmol, 0.6 equiv) in THF (4.8 mL) at 80 °C for 24 h afforded, after column chromatography, 247 mg of compound **3d** as a brown solid (81% yield, mp 88−89 °C, lit 93−95 °C).[45] $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.79 (d, $J$ = 8.0 Hz, 2H), 7.55−7.53 (m, 4H), 7.37−7.34 (m, 3H), 1.36 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) $\delta$ 136.4, 134.7, 131.8, 130.9, 128.5, 126.1, 123.3, 90.8, 89.7, 84.1, 25.0. $^{11}$B NMR (160 MHz, $CDCl_3$) $\delta$ 30.6 (brs). HRMS (ESI) $m/z$ calcd for $C_{20}H_{22}BO_2$ $[M + H]^+$ 305.1713, found 305.1710. Spectral data were consistent with literature reported values except the $^{13}$C peak reported at 137.13 was not observed.[45] Presumably this peak is that of the carbon bearing boron. Such carbons are often difficult to observe.

*N,N-Dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-((trimethylsilyl)ethynyl) Aniline (**3e**).* Following the General Procedure C the reaction of **1c** (111 mg, 0.34 mmol, 1.0 equiv) with a solution of tris((trimethylsilyl)ethynyl)indium (0.204 mmol, 0.60 equiv) in THF (5 mL) at 65 °C for 16 h afforded, after column chromatography, 68 mg of compound **3e** as a yellow oil (58% yield). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.31 (dd, $J$ = 1.4, 0.9 Hz, 1H), 7.13 (dd, $J$ = 2.8, 0.9 Hz, 1H), 6.91 (dd, $J$ = 2.8, 1.4 Hz, 1H), 2.95 (s, 6H), 1.33 (s, 12H), 0.23 (s, 9H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) $\delta$ 149.9, 127.1, 123.2, 119.1, 118.4, 106.3, 92.8, 83.9, 40.8, 25.0, 0.2. $^{11}$B NMR (128 MHz, $CDCl_3$) $\delta$ 31.0 (brs). HRMS (ESI) $m/z$ calcd for $C_{19}H_{31}BNO_2Si$ $[M + H]^+$ 344.2217, found 344.2226.

*Trimethyl((3-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethynyl)silane (**3f**).* Following the General Procedure C the reaction of **1a** (111 mg, 0.34 mmol, 1.0 equiv) with a solution of tris((trimethylsilyl)ethynyl)indium (0.204 mmol, 0.60 equiv) in THF (5 mL) at 65 °C for 16 h afforded, after column chromatography, 65 mg of compound **3f** as a white solid (61% yield, mp 77−79 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.74 (s, 1H), 7.56 (s, 1H), 7.38 (s, 1H), 2.31 (s, 3H), 1.34 (s, 12H),0.23 (s, 9H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) $\delta$ 137.3, 135.7, 135.5, 135.2, 122.7, 105.4, 93.8, 84.1, 25.0, 21.1, 0.2. $^{11}$B NMR (128 MHz, $CDCl_3$) $\delta$ 30.6 (brs). HRMS (ESI) $m/z$ calcd for $C_{18}H_{28}BO_2Si$ $[M + H]^+$ 315.1952, found 315.1935.

*2-(3-(Cyclopropylethynyl)-5-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3g**).* Following the General Procedure C the reaction of **1a** (111 mg, 0.34 mmol, 1.0 equiv) with a solution of tris(cyclopropylethynyl)indium (0.204 mmol, 0.60 equiv) in THF (5 mL) at 65 °C for 16 h afforded, after column chromatography, 45 mg of compound **3g** as a yellow solid (47% yield, mp 68−70 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.65 (s, 1H), 7.50 (s, 1H), 7.29 (s, 1H), 2.30 (s, 3H), 1.48−1.37 (m, 1H), 1.33 (s, 12H), 0.87−0.73 (m, 4H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) $\delta$ 137.2, 135.4, 134.9, 134.5, 123.5, 93.2, 84.0, 75.9, 25.0, 21.1, 8.7, 0.3. $^{11}$B NMR (128 MHz, $CDCl_3$) $\delta$ 31.1 (brs). HRMS (ESI) $m/z$ calcd for $C_{18}H_{23}BO_2Na$ $[M + Na]^+$ 305.1689, found 305.1672.

*4,4,5,5-Tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (**3h**).*[46] The General Procedure C was carried out with **1h** (283 mg, 1.0 mmol, 1.0 equiv) and a solution of trivinylindium (0.80 mmol, 0.80 equiv) in THF (5.4 mL) at 75 °C for 36 h. The reaction was then quenched by the addition of few drops of MeOH, concentrated under reduce pressure and redissolve in dichloromethane. The residue was passed through a plug of silica gel (hexane/ethyl acetate 100:0 → hexane/ethyl acetate 90:10 as eluent). The fractions containing product were collected and concentrated. The mixture was passed through a column chromatography (hexane as eluent and a mixture of silica/Celite 1:4 as stationary phase). The fractions containing product were collected and concentrated to yield 187 mg of compound **3h** as a colorless oil (81% yield). $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.77 (d, $J$ = 8.0 Hz, 2H), 7.41 (d, $J$ = 8.0 Hz, 2H), 6.73 (dd, $J$ = 17.6, 10.9 Hz, 1H), 5.82 (dd, $J$ = 17.6, 0.9 Hz, 1H), 5.29 (dd, $J$ = 10.9, 0.9 Hz, 1H), 1.35 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) $\delta$ 140.3, 137.0, 135.2, 125.7, 115.0, 83.9, 25.0. $^{11}$B NMR (160 MHz, $CDCl_3$) $\delta$ 30.6 (brs). The spectral data were in accordance with literature.[46] HRMS (ESI) $m/z$ calcd for $C_{14}H_{20}BO_2$ $[M + H]^+$ 231.1556, found 231.1546.

*2-(3-Cyclopropyl-5-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3i**).* Following the General Procedure C the reaction of **1a** (111 mg, 0.34 mmol, 1.0 equiv) with a solution of tricyclopropylindium (0.204 mmol, 0.60 equiv) in THF (5 mL) at 65 °C for 16 h afforded, after column chromatography, 65 mg of compound **3i** as a yellow solid (74% yield, mp 76−78 °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.44 (s, 1H), 7.36 (s, 1H), 6.99 (s, 1H), 2.33 (s, 3H), 1.97−1.84 (m, 1H), 1.35 (s, 12H), 0.98−0.88 (m, 2H), 0.77−0.68 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) $\delta$ 143.3, 137.2, 132.7, 129.6, 129.4, 83.8, 25.0, 21.3, 15.3, 9.0. $^{11}$B NMR (128 MHz, $CDCl_3$) $\delta$ 30.7 (brs). HRMS (ESI) $m/z$ calcd for $C_{16}H_{23}BO_2Na$ $[M + Na]^+$ 281.1689, found 281.1678.



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*2-(3-Benzyl-5-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3j**).* Following the General Procedure C the reaction of **1a** (111 mg, 0.34 mmol, 1.0 equiv) with a solution of tribenzylindium (0.204 mmol, 0.60 equiv) in THF (5 mL) at 65 °C for 16 h afforded, after column chromatography, 74 mg of compound **3j** as a white solid (71% yield, mp 116−119 °C). $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.53−7.46 (m, 2H), 7.31−7.25 (m, 2H), 7.22−7.15 (m, 3H), 7.09 (s, 1H), 3.96 (s, 2H), 2.32 (s, 3H), 1.35 (s, 12H). $^{13}$C{$^{1}$H} NMR (75 MHz, CDCl3) $\delta$ 141.5, 140.5, 137.6, 133.5, 133.0, 132.6, 129.1, 128.6, 126.2, 83.9, 42.0, 25.1, 21.3. $^{11}$B NMR (128 MHz, $CDCl_3$) $\delta$ 30.7 (brs). HRMS (ESI) $m/z$ calcd for $C_{20}H_{26}BO_2$ $[M + H]^+$ 309.2026, found 309.2035.

*2-(3,5-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3k**).*[47] Following the General Procedure C the reaction of **1a** (111 mg, 0.34 mmol, 1.0 equiv) with a solution of trimethylindium (0.204 mmol, 0.60 equiv) in THF (5 mL) at 65 °C for 16 h afforded, after column chromatography, 48 mg of compound **3k** as a white solid (61% yield, mp 91−93 °C, lit 90−91 °C).[47] $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.46 (s, 2H), 7.12 (s, 1H), 2.34 (s, 6H), 1.36 (s, 12H). $^{13}$C{$^{1}$H} NMR (75 MHz, $CDCl_3$) $\delta$ 137.3, 133.1, 132.5, 83.8, 25.0, 21.3. $^{11}$B NMR (128 MHz, $CDCl_3$) $\delta$ 31.1 (brs). The spectral data were in accordance with those reported in the literature.[47] HRMS (ESI) $m/z$ calcd for $C_{14}H_{22}BO_2$ $[M + H]^+$ 233.1713, found 233.1715.

*2-(3-Butyl-5-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3l**).* Following the General Procedure C the reaction of **1a** (111 mg, 0.34 mmol, 1.0 equiv) with a solution of tributylindium (0.204 mmol, 0.60 equiv) in THF (5 mL) at 65 °C for 16 h afforded, after column chromatography, 52 mg of compound **3l** as a yellow oil (56% yield). $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.46 (s,1H), 7.44 (s, 1H), 7.10 (s, 1H), 2.62−2.54 (m, 2H), 2.33 (s, 3H), 1.66−1.53 (m, 2H), 1.43−1.36 (m, 2H), 1.35 (s, 12H), 0.92 (t, $J$ = 7.3 Hz, 3H). $^{13}$C{$^{1}$H} NMR (75 MHz, $CDCl_3$) $\delta$ 142.4, 137.2, 132.9, 132.5, 132.0, 83.8, 35.7, 34.0, 25.0, 22.7, 21.3, 14.1. $^{11}$B NMR (128 MHz, $CDCl_3$) $\delta$ 31.0 (brs). HRMS (ESI) $m/z$ calcd for $C_{17}H_{28}BO_2$ $[M + H]^+$ 275.2182, found 275.2168.

*2-(4-Butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3m**).*[48] Following the General Procedure C the reaction of **1h** (282 mg, 1.0 mmol, 1.0 equiv) with a solution of tributylindium (0.60 mmol, 0.60 equiv) in THF (3.72 mL) at 80 °C for 16 h afforded, after column chromatography (hexane as eluent) 215 mg of compound **3m** as a colorless oil (83% yield). $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.73 (d, $J$ = 8.0 Hz, 2H), 7.20 (d, $J$ = 8.0 Hz, 2H), 2.62 (t, $J$ = 8.0 Hz, 2H), 1.63−1.57 (m, 2H), 1.36−1.33 (m, 2H), 1.34 (s, 12H), 0.92 (t, $J$ = 7.4 Hz, 3H). $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) $\delta$ 146.5, 134.9, 128.1, 83.7, 36.0, 33.6, 25.0, 22.5, 14.1. $^{11}$B NMR (160 MHz, $CDCl_3$) $\delta$ 30.8 (brs). The NMR spectral data were in accordance with those reported in the literature;[43] however, the acquired HRMS (ESI) data were beyond the usual deviation from the calculated value, i.e., (ESI) $m/z$ calcd for $C_{16}H_{26}BO_2$ $[M + H]^+$ 261.2026, found 261.1986; LRSM afforded an $m/z$ of $[M]^+$ 260.20.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c01978.

Copies of $^{1}$H and $^{13}$C{$^{1}$H} NMR spectra (PDF)

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