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Synthesis of Pinacol Arylboronates from Aromatic Amines: A Metal-Free Transformation

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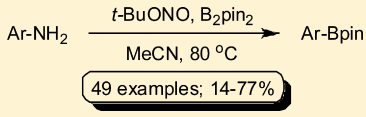
Supporting Information

ABSTRACT: A metal-free borylation process based on Sandmeyer-type transformation using arylamines derivatives as the substrates has been developed. Through optimization of the reaction conditions, this novel conversion can be successfully applied to a wide range of aromatic amines, affording borylation products in moderate to good yields. Various functionalized arylboronates, which are difficult to access by other methods, can be easily obtained with this metal-free transformation. Moreover, this transformation can be followed by Suzuki−Miyaura cross-coupling without purification of the borylation products, which enhances the practical usefulness of this method. A possible reaction mechanism involving radical species has been proposed.

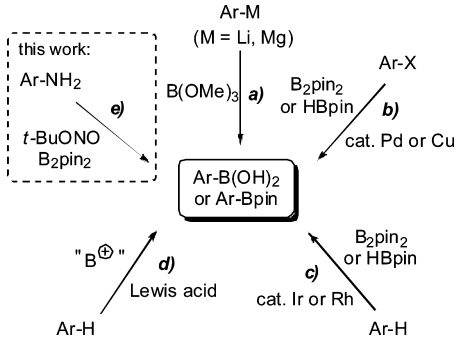


INTRODUCTION

Arylboronic acids and arylboronates have shown great importance due to their widespread applications in organic synthesis and other fields.[1,2] In particular, functionalized arylboronic acids and arylboronates are highly valuable because consecutive cross-coupling is possible from these compounds, which can rapidly construct the complex structure of target molecules.[3] Consequently, the syntheses of various functionalized arylboronic compounds have attracted significant attentions in recent years.

The reaction of aryl Grignard reagents or aryllithium species with trialkyl boronates remains the most general synthetic method to prepare aromatic boronic compounds (Scheme 1, path *a*).[4] In 1995, Miyaura et al. developed the palladium-catalyzed borylation of arylhalides using bis(pinacolato)diboron as the boron source.[5] Subsequently, Masuda et al. reported the palladium-catalyzed borylation from arylhalides using pinacolborane.[6] The groups of Ma and Marder then reported the copper-catalyzed borylation reaction (Scheme 1, path *b*).[7] In the past decade, direct borylation via aromatic C−H bond activation has been extensively explored in the groups of Smith III, Miyaura, Hartwig, Marder, and others (Scheme 1, path *c*).[8] Recently, Lewis acid catalyzed electrophilic borylation of electron-rich arenes has been explored (Scheme 1, path *d*).[9,10] These borylation methods have the advantage of being transition-metal-free processes and thus avoiding heavy metal contamination in the final products.

Scheme 1. Different Routes to Arylboronic Acids or Arylboronates



We have recently communicated an entirely different approach toward arylboronates synthesis by direct conversion of the amino group of aniline derivatives to the boronate group (Scheme 1, path *e*).[11] This transformation is under Sandmeyer-type reaction conditions by using *tert*-butyl nitrite (*t*-BuONO) as diazotization agent.[12,13] This borylation method has the following features: (1) the reaction is under metal-free conditions, (2) arylamines are cheap and abundant starting materials, (3) the borylation tolerates various functional groups, and (4) the reaction is under very mild conditions. As a result, this novel borylation will not only find wide application in organic synthesis but also shed light on the unique reactivity of aryldiazonium ion and diboron compounds.[14]

In this article, we report the further optimization of the reaction conditions and the expansion of the substrate scope to various aniline derivatives. Compared to the results reported in the preliminary communication, the newly optimized reaction conditions offered improved yields and have wider substrate scope. Moreover, this borylation has also been extended to heterocyclic amines, although with limited success.

RESULTS AND DISCUSSION

To further optimize the reaction that was reported in our preliminary communication,[11] we have chosen 2-aminobenzonitrile as the substrate, with which only a low yield of

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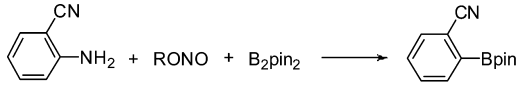
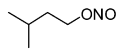
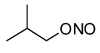
22% was obtained under the previous reaction conditions [*t*-BuONO, benzoyl peroxide (BPO, 2 mol %), MeCN, rt] (Table 1, entry 1). Thus, a number of experiments were conducted to

Table 1. Optimization of Reaction Conditions for 2-Aminobenzonitrile[a]



1aa **2a-c** **3** **4aa**

entry	RONO	solvent	additive (mol%)	temp (°C)	yield (%)[b]
1	*t*-BuONO (**2a**)	MeCN	BPO (2)	25	22[c]
2	*t*-BuONO (**2a**)	MeCN	--	40	55
3	*t*-BuONO (**2a**)	MeCN	--	60	68
4	*t*-BuONO (**2a**)	MeCN	--	80	77
5	*t*-BuONO (**2a**)	MeCN	BPO (2)	80	76
6	*t*-BuONO (**2a**)	MeCN	BPO (5)	80	79
7	*t*-BuONO (**2a**)	MeCN	BPO (10)	80	75
8	*t*-BuONO (**2a**)	$PhCH_3$	--	80	30
9	*t*-BuONO (**2a**)	DCE	--	80	54
10	*t*-BuONO (**2a**)	Dioxane	--	80	*trace*
11	 **2b**	MeCN	--	80	57
12	 **2c**	MeCN	--	80	64

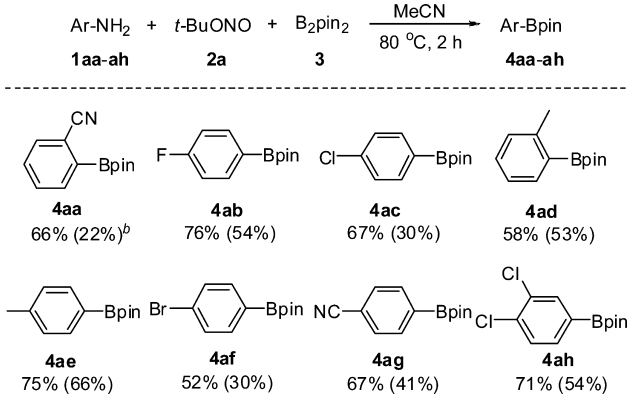
[a]Reaction conditions: arylamine (1 mmol), B_2pin_2 (1.1 mmol), RONO (1.5 mmol), 1 h. [b]GC yield measured with GC–MS, mesitylene was used as internal standard. [c]See ref 11. B_2pin_2: bis(pinacolato)diboron. Bpin: 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl.

improve the yield, and these experiments provide further insight into the factors that affect this transformation. First, it was observed that the reaction is significantly affected by temperature (entries 2–4). The yield of **4aa** could be improved when the reaction was carried at elevated temperature. At 80 °C, **4aa** could be obtained in 77% GC yield and 66% isolated yield. Addition of radical initiator BPO slightly affects the reaction at this temperature (entries 5–7). Use of other solvents, such as toluene, DCE, and dioxane, proved to be ineffective. Finally, alkyl nitrites **2b** and **2c** were found to be compatible with this reaction, albeit less efficient than **2a** (entries 11,12).

The optimization experiments demonstrate that by simply raising reaction temperature, the yield of the borylation product could be markedly improved. With this in hand, the aniline substrates that afforded the low yields of the corresponding borylation products under the previous conditions were examined, and the yields were compared (Scheme 2). The results show that in general the yields are improved when the reactions are carried out at high temperature, especially for those with halogen substituents (**4ab**, **4ac**, **4af**, **4ah**).

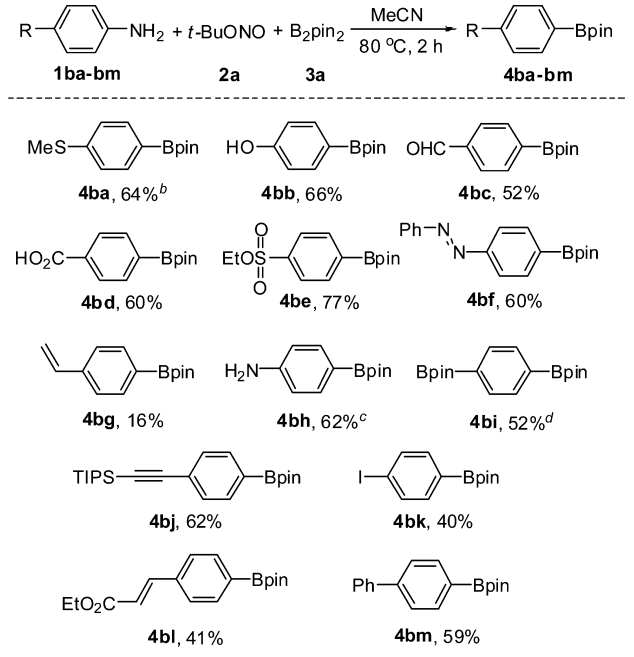
Encouraged by the results, we proceeded to apply this metal-free borylation to a series of new substrates. First, *para*-substituted aniline derivatives were investigated (Scheme 3). Moderate to good yields were obtained for most of the *para*-

Scheme 2. Comparison of Yields with Those Reported Previously[a]



[a]Current reaction conditions: arylamine (1 mmol), B_2pin_2 (1.1 mmol), *t*-BuONO (1.5 mmol), MeCN (3 mL), 80 °C, 2 h. [b]Isolated yield. The figure in brackets refers to the yields reported under the previous reaction conditions; see ref 11. The previous reaction conditions: arylamine (1 mmol), B_2pin_2 (1.1 mmol), *t*-BuONO (1.5 mmol), BPO (2 mol %), MeCN (3 mL), room temperature, 2 h.

Scheme 3. Scope of *para*-Substitued Aniline Derivatives[a]



[a]Reaction conditions: arylamine (1 mmol), B_2pin_2 (1.1 mmol), *t*-BuONO (1.5 mmol), MeCN (3 mL), 2 h. [b]Isolated yield. [c]*t*-BuONO (1.1 mmol). [d]B_2pin_2 (2.2 mmol), *t*-BuONO (3 mmol).

substituted aniline substrates. The borylation showed good tolerance to various functional groups, including methylthio (**4ba**), hydroxyl (**4bb**), formyl (**4bc**), carboxyl (**4bd**), sulfonyl (**4be**), azo (**4bf**), amino (**4bh**), iodo (**4bk**), and alkynyl (**4bj**) groups. In the cases of **4bc**, **4bg**, and **4bl**, the low yields are due to their low stability on column chromatography or TLC. When 4-aminostryne was employed as the substrate, the corresponding boronate **4bg** was isolated in very low yield. In this case, a large quantity of precipitate was observed. We speculate that polymerization occurs in this reaction, which may be initiated by a radical intermediate (*vide infra*). Interestingly, with *p*-aminoaniline as the substrate, selective

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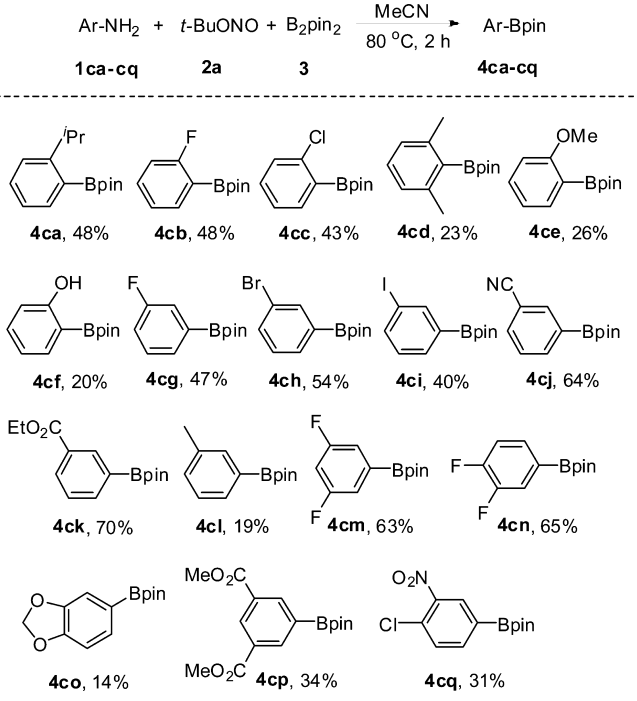
mono- or diborylation could be realized by simply controlling the amount of *t*-BuONO and B_2pin_2 used in the reaction (**4bh** and **4bi**).

Furthermore, we expanded the scope of substrates to *meta*-, *ortho*-, or *multi*-substituted arylamine substrates (Scheme 4).

Scheme 4. Reaction with *meta*, *ortho*, or *multi*-Substituted Arylamines[a]



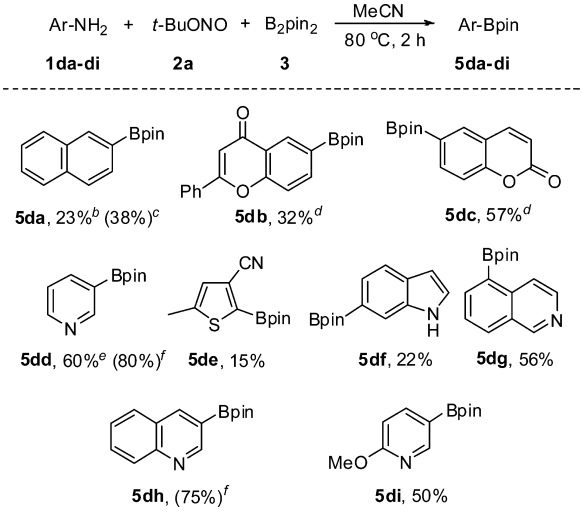
[a]Reaction conditions: arylamine (1 mmol), B_2pin_2 (1.1 mmol), *t*-BuONO (1.5 mmol), MeCN (3 mL), 2 h. [b]Isolated yield.

The borylation in general affords relatively low to moderate yields. Compared with electron-rich aniline derivatives, electron-deficient ones usually give higher yields when the corresponding borylation products are stable toward column chromatography (for example, **4cj**, **4ck**, and **4cn**). Moreover, the steric bulkiness of the *ortho* substitution seems to affect the borylation reaction. The substrates with *ortho* substitution generally afforded diminished yields. For example, reaction with 2,6-dimethylaniline gave only 23% yield (**4cd**).

Subsequently, we proceeded to extend the reaction to some complicated aromatic amines and heterocyclic amines. These results are shown in Scheme 5. The reaction with 2-aminonaphthalene afforded **5da** with low yield, and large amount of B_2pin_2 was recovered. This is likely due to the facile oxidation of 2-aminonaphthalene under the reaction conditions. In the case of **5db** and **5dc**, the low yields are attributed to the instability of these products.

Heterocyclic boronic acids or boronates have found wide applications in organic synthesis, especially for pharmaceuticals. However, these boron compounds are usually not easy to synthesize as a result of the limitations of other methodologies that have been discussed in the Introduction. Thus, we investigated the application of this new borylation method to access heterocyclic boronates. We found that electron-deficient heterocyclic amines demonstrate high reactivity with nearly complete conversion of B_2pin_2. However, electron-rich heterocyclic amines are prone to be oxidized in the presence

Scheme 5. Scope of Other Aromatic Derivatives[a]

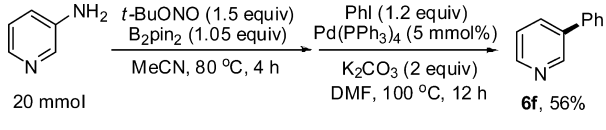


[a]Reaction conditions: arylamine (1 mmol), B_2pin_2 (1.1 mmol), *t*-BuONO (1.5 mmol), 2 h, MeCN (3 mL). [b]Isolated yield. [c]The isolated yield of **5da** in brackets refer to the reaction in water: a mixture of arylamine (1 mmol), $NaNO_2$ (1.1 mmol), HCl (0.41 mL, 12 mol/L), and H_2O (1 mL) was stirred at 0 °C for 15 min, then to the mixture was added B_2pin_2 (1.1 mmol) in MeCN (1 mL), and stirring was continued at 80 °C for 2 h. [d]Arylamine (0.5 mmol), B_2pin_2 (1.1 equiv), *t*-BuONO (1.5 equiv), MeCN (1.5 mL), 2 h. [e]Isolated by recrystallization. [f]Yields in brackets refer to GC yield measured with a GC–MS instrument (mesitylene as internal standard).

of *t*-BuONO, resulting in low yields of borylation products (**5de** and **5df**).

It is noteworthy that most of the heterocyclic boronates are not stable on silica gel column chromatography. To simplify the synthetic procedure and in particular to avoid the problem of product decomposition during the purification process, a sequential borylation and Pd-catalyzed cross-coupling reaction has been demonstrated in our preliminary communication.[11] Such a sequential process avoids the troublesome purification process and significantly strengthens the usefulness of this new borylation method. Herein we further expand the scope of this sequential process, especially for the heterocyclic substrates (Scheme 6). Thus, upon completion of the borylation, MeCN is removed under reduced pressure to give crude borylation product, which is then subjected next to Pd-catalyzed Suzuki–Miyaura cross-coupling reaction without further purification to afford coupling products in moderately high yields in general. However, in some cases the yields are less satisfactory (**6d**, **6h**, **6r**, and **6s**).

Finally, to demonstrate the practical usefulness of this borylation method, the reaction has been carried out in gram-scale for selected substrates. As shown in Scheme 7, the reaction provided the desired boronates in good yields. The sequential borylation and Pd-catalyzed cross-coupling has also been scaled up (eq 1).



(1)

Since it is well documented that Sandmeyer reaction proceeds through a radical mechanism,[13b,15] a possible reaction

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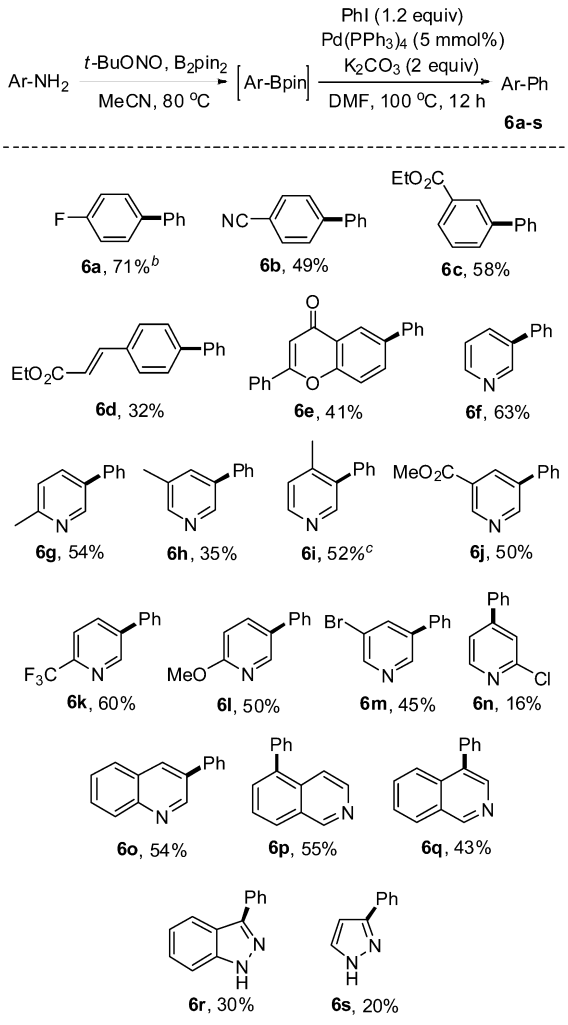
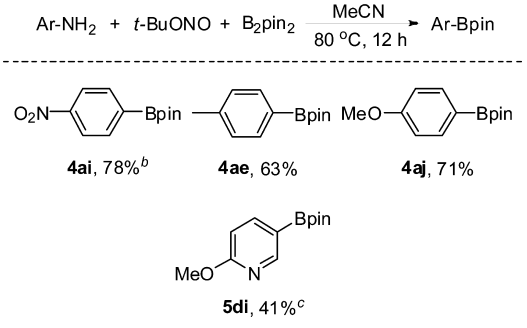
Scheme 6. Sequential Borylation and Pd-Catalyzed Cross-Coupling Reaction[a]



[a]Reaction condition for the first step: arylamine (1 mmol), B_2pin_2 (1.1 mmol), *t*-BuONO (1.5 mmol), 2 h; second step: DMF (1.5 mL). [b]Isolated yield. [c]Reaction conditions for the second step: $Pd(PPh_3)_4$ (5 mmol %), 10% aq Na_2CO_3 (2 mL), toluene (4 mL), EtOH (2 mL), 12 h.

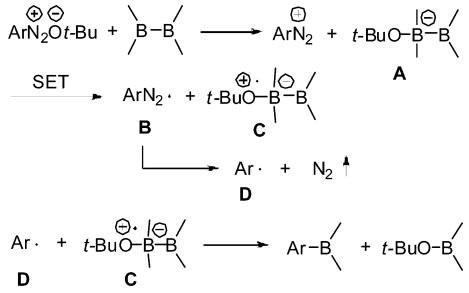
Scheme 7. Gram-Scale Experiments[a]



[a]Reaction conditions: arylamine (20 mmol), B_2pin_2 (1.05 equiv), *t*-BuONO (1.5 equiv), 12 h, MeCN (60 mL). [b]Isolated yield. [c]Arylamine (10 mmol).

pathway involving radical species is proposed for this borylation reaction as shown in Scheme 8. First, the *tert*-butoxide anion interacts with B_2pin_2 to form a tetra-coordinated boron

Scheme 8. Possible Reaction Mechanism



complex **A**. Single electron transfer (SET) between ate complex **A** and aryldiazonium ion is then followed to afford aryl radical **D** through N_2 extrusion from radical **B**. Finally, reaction of aryl radical **D** with intermediate **C** gives the borylation product.

This reaction mechanism is substantiated by the following experimental observations: (1) When the borylation was carried out in the presence of 1.5 equiv of the radical scavenger TEMPO, the reaction became sluggish and phenylboronate was formed in only 8% yield after 4 h, while a control experiment has demonstrated that TEMPO does not react directly with B_2pin_2 under these conditions (eq 2). (2) Heating a 1:1 mixture

$$\underset{1.1\ \text{equiv}}{\text{Ph-NH}_2} + \underset{1.5\ \text{equiv}}{\text{B}_2\text{pin}_2} + \underset{1.5\ \text{equiv}}{\textit{t}\text{-BuONO}} + \text{TEMPO} \xrightarrow[\text{rt, 4 h}]{\text{MeCN}} \underset{8\%}{\text{Ph-Bpin}} \qquad (2)$$

of BPO and B_2pin_2 in MeCN at 100 °C for 4 h affords the phenylboronate in 37% yield (eq 3). It is known that BPO

$$\underset{}{(\text{PhCOO})_2} + \underset{1\ \text{equiv}}{\text{B}_2\text{pin}_2} \xrightarrow[\text{100 °C, 4 h}]{\text{MeCN}} \underset{37\%}{\text{Ph-Bpin}} \qquad (3)$$

cleaves under thermolytic conditions to benzoic acid radical upon heating, which generates phenyl radical by further decomposition. Thus, the desired product is likely formed by the reaction of benzoic acid radical and/or phenyl radical with B_2pin_2. (3) EPR experiments provide supportive evidence for a radical process.[16]

However, when B_2pin_2 was set to react with phenyl radical, which was generated by an alternative process (PhI, *n*-Bu_3SnH, and AIBN),[17] the product Ph-Bpin was formed only in 7% yield (eq 4). Consequently, even though most of the experimental

$$\underset{\substack{1\ \text{equiv}\\ \\ }}{\text{PhI}} + \underset{1\ \text{equiv}}{\text{B}_2\text{pin}_2} + \underset{\substack{1\ \text{equiv}\\ 0.2\ \text{equiv}}}{\textit{n}\text{-Bu}_3\text{SnH}} + \underset{\substack{1\ \text{equiv}\\ 0.2\ \text{equiv}}}{\text{AIBN}} \xrightarrow[\text{reflux, 4 h}]{\text{PhH}} \underset{\substack{7\%\\ 5\%}}{\text{Ph-Bpin}} \qquad (4)$$

observations are consistent with the mechanism shown in Scheme 8, alternative mechanisms involving an ionic process, such as nucleophilic aromatic substitution of the aryldiazonium salt by the boron ate complex, cannot be completely ruled out. Further rigorous investigation is required to unambiguously establish the reaction mechanism.

■ CONCLUSION

In this report we have further optimized the metal-free deaminoborylation reaction. The yields are improved, and the substrate scope has been significantly expanded, especially to heterocyclic amine derivatives, for which the corresponding boronate products are highly important both in academic

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research and in the pharmaceutical industry. A radical mechanism involving SET between aryldiazonium ion and tetra-coordinated boron complex has been proposed. Since arylamines are inexpensive and ubiquitous starting materials, this borylation method is expected to find wide applications in organic synthesis.

EXPERIMENTAL SECTION

The solvents were all distilled prior to use. MeCN and DMF were distilled from calcium hydride. Silica gel, 200−300 mesh, was used for the chromatography. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in ppm using tetramethylsilane (TMS) as the internal standard; IR spectra are reported in wave numbers, cm^{-1}. For HRMS measurements, the mass analyzer is FT-ICR. Melting points are reported as uncorrected.

Typical Procedure of Borylation Reaction. B_2pin_2 (279 mg, 1.1 mmol) and 2-aminobenzonitrile (**1aa**, 118 mg, 1.0 mmol) were weighed in a 25 mL round-bottom flask. MeCN (3 mL) and *t*-BuONO (**2a**, 155 mg, 1.5 mmol) were then added in succession. The resulting reaction solution was stirred for 2 h at 80 °C (N_2 evolution completed within 5 to 15 min). The solution was then concentrated under reduced pressure, and the crude residue was purified by flash chromatography (silica gel, petroleum ether/EtOAc = 200:1). 2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (**4aa**)[11] was obtained (152 mg, 66%) as pale yellow solid; mp 80−82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, J = 1.2, 7.3 Hz, 1H), 7.70 (dd, J = 1.2, 7.5 Hz, 1H), 7.55 (m, 2H), 1.39 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 133.4, 131.5, 131.0, 118.9, 117.3, 84.8, 24.8; IR (film) 2981 (w), 2228 (w), 1488 (w), 1441 (m), 1382 (s), 1356 (s), 1143 (m), 1119 (m), 857 (m), 731 (m), 654 (m) cm^{-1}; EI-MS (m/z, relative intensity) 229 (M$^+$, 24), 214 (46), 188 (50), 186 (61), 171 (45), 130 (100), 129 (29), 103 (24), 85 (17).

*2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4ab**).*[11] Flash chromatography (silica gel, petroleum ether/EtOAc = 500:1) afforded **4ab** (169 mg, 76%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (t, J = 7.2 Hz, 2H), 7.04 (t, J = 8.8 Hz, 2H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1 (d, J = 250.3 Hz), 137.0 (d, J = 8.2 Hz), 114.8 (d, J = 20.3 Hz), 83.8, 24.8; IR (film) 2980 (w), 1603 (m), 1399 (m), 1361 (s), 1143 (m), 1088 (m), 860 (w), 668 (w) cm^{-1}; EI-MS (m/z, relative intensity) 222 (M$^+$, 21), 207 (87), 136 (41), 123 (100), 122 (31), 85 (14).

*2-(4-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4ac**).*[11] Flash chromatography (silica gel, petroleum ether, then petroleum ether/EtOAc = 200:1) afforded **4ac** (160 mg, 67%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.8 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 136.1, 127.9, 83.9, 24.8; IR (film) 2979 (w), 1597 (m), 1393 (m), 1360 (s), 1144 (m), 1094 (s), 1017 (m), 858 (m) cm^{-1}; EI-MS (m/z, relative intensity) 240 (13), 238 (M$^+$, 38), 225 (34), 223 (100), 152 (63), 141 (33), 139 (95).

*4,4,5,5-Tetramethyl-2-o-tolyl-1,3,2-dioxaborolane (**4ad**).*[11] Flash chromatography (silica gel, then petroleum ether/EtOAc = 500:1) afforded **4ad** (126 mg, 58%); white solid; mp 32−34 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78−7.74 (m, 1H), 7.30 (m, 1H), 7.16 (m, 2H), 2.53 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 135.8, 130.7, 129.7, 124.7, 83.4, 24.9, 22.2; IR (film) 2978 (w), 2926 (w), 1380 (m), 1346 (s), 1146 (m), 1073 (m), 862 (m), 730 (m), 659 (m) cm^{-1}; EI-MS (m/z, relative intensity) 218 (M$^+$, 25), 203 (35), 161 (85), 119 (100), 118 (84), 91 (20).

*4,4,5,5-Tetramethyl-2-p-tolyl-1,3,2-dioxaborolane (**4ae**).*[11] Flash chromatography (silica gel, petroleum ether, then petroleum ether/EtOAc = 250:1) afforded **4ae** (163 mg, 75%); white solid; mp 53−54 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.7 Hz, 2H), 7.17 (d, J = 7.7 Hz, 2H), 2.35 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 134.8, 128.4, 83.5, 24.8, 21.6; IR (film) 2978 (w), 1613 (w), 1517 (w), 1398 (m), 1360 (s), 1318 (m), 1304 (w), 1144 (m), 860 (m) cm^{-1}; EI-MS (m/z, relative intensity) 218 (M$^+$, 44), 203 (61), 132 (67), 119 (100), 118 (50), 91 (17).

*2-(4-Bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4af**).*[11] Flash chromatography (silica gel, petroleum ether, then petroleum ether/EtOAc = 500:1) afforded **4af** (147 mg, 52%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.1 Hz, 2H), 7.50 (d, J = 8.1 Hz, 2H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 130.9, 126.2, 84.0, 24.8; IR (film) 2978 (w), 1589 (m), 1389 (m), 1359 (s), 1166 (m), 1144 (m), 1089 (s), 1012 (m), 821 (m) cm^{-1}; EI-MS (m/z, relative intensity) 284 (51), 282 (M$^+$, 50), 269 (100), 267 (100), 198 (71), 196 (72), 185 (89), 183 (96), 103 (36).

*4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (**4ag**).*[11] Flash chromatography (silica gel, petroleum ether/EtOAc = 30:1 then 0:1) afforded **4ag** (153 mg, 67%); pale yellow solid; mp 93−95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.8 Hz, 2H), 7.64 (d, J = 7.8 Hz, 2H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 131.1, 118.8, 114.5, 84.4, 24.8; IR (film) 2980 (w), 2229 (w), 1398 (m), 1360 (s), 1168 (m), 1143 (s), 1125 (m), 1088 (s), 668 (m) cm^{-1}; EI-MS (m/z, relative intensity) 229 (M$^+$, 14), 214 (100), 213 (20), 186 (12), 143 (81), 130 (50), 58 (16).

*2-(3,4-Dichlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4ah**).*[11] Flash chromatography (silica gel, petroleum ether) afforded **4ah** (194 mg, 71%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.43 (d, J = 7.9 Hz, 1H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 135.5, 133.7, 132.2, 130.0, 84.3, 24.8; IR (film) 2978 (w), 1590 (w), 1381 (m), 1354 (s), 1143 (m), 1094 (m), 1032 (w), 867 (m) cm^{-1}; EI-MS (m/z, relative intensity) 274 (31), 272 (M$^+$, 46), 259 (69), 257 (100), 188 (65), 186 (95), 175 (48), 173 (84), 85 (23).

*4,4,5,5-Tetramethyl-2-(4-(methylthio)phenyl)-1,3,2-dioxaborolane (**4ba**).*[18] Flash chromatography (silica gel, petroleum ether/EtOAc = 500:1) afforded **4ba** (160 mg, 64%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.8 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 2.47 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 135.0, 125.0, 83.6, 24.8, 15.0; IR (film) 2978 (w), 1597 (m), 1395 (m), 1359 (s), 1327 (m), 1103 (s), 859 (m), 668 (m) cm^{-1}; EI-MS (m/z, relative intensity) 250 (M$^+$, 100), 249 (28), 235 (29), 164 (30), 151 (63), 150 (95).

*4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (**4bb**).*[19] Flash chromatography (silica gel, petroleum ether/EtOAc = 10:1) afforded **4bb** (145 mg, 66%); pale yellow solid; mp 113−114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.0 Hz, 2H), 6.81 (d, J = 8.0 Hz, 2H), 6.68 (s, 1H), 1.34 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 136.7, 115.0, 83.9, 24.7; IR (film) 3364 (w), 2979 (w), 1607 (s), 1397 (m), 1358 (s), 1170 (m), 1141 (s), 1084 (m), 670 (m) cm^{-1}; EI-MS (m/z, relative intensity) 220 (M$^+$, 48), 205 (58), 134 (40), 121 (100), 120 (97).

*4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (**4bc**).*[20] Flash chromatography (silica gel, petroleum ether/EtOAc = 50:1 then 20:1) afforded **4bc** (121 mg, 52%); pale yellow solid; mp 55−58 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 7.97 (d, J = 7.9 Hz, 2H), 7.86 (d, J = 7.9 Hz, 2H), 1.36 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 138.0, 135.2, 128.6, 84.2, 24.8; IR (film) 2979 (w), 1707 (s), 1508 (m), 1358 (s), 1169 (m), 1086 (s), 857 (m), 825 (m), 800 (m) cm^{-1}; EI-MS (m/z, relative intensity) 232 (M$^+$, 21), 217 (78), 146 (90), 133 (100), 85 (25).

*4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic Acid (**4bd**).*[21] Flash chromatography (silica gel, petroleum ether/EtOAc = 50:1) afforded **4bd** (150 mg, 60%); yellow solid; mp 228−231 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.0 Hz, 2H), 7.91 (d, J = 8.0 Hz, 2H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 134.7, 133.8, 129.2, 84.3, 24.8; IR (film) 2981 (w), 1686 (m), 1360 (s), 1167 (w), 1143 (m), 1126 (m), 856 (m), 739 (w) cm^{-1}; EI-MS (m/z, relative intensity) 248 (M$^+$, 23), 233 (90), 162 (84), 149 (100), 148 (20), 85 (16).

*Ethyl 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-benzenesulfonate (**4be**).* Flash column chromatography (silica gel, petroleum ether/EtOAc = 30:1 then 10:1) afforded **4be** (240 mg, 77%); yellow solid; mp 82−84 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.3 Hz, 2H), 7.89 (d, J = 8.3 Hz, 2H), 4.12 (q, J = 7.1 Hz, 2H), 1.36 (s, 12H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 135.3, 126.7, 84.5, 67.1, 24.8, 14.7; IR (film) 2981

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(w), 1393 (m), 1358 (s), 1188 (m), 1143 (m), 1099 (w), 962 (w), 668 (m) cm^{-1}; EI-MS (*m*/*z*, relative intensity) 312 (M^+, 7), 297 (52), 226 (100), 213 (27), 185 (18), 104 (18); HRMS (ESI) calcd for $C_{14}H_{22}BO_3S$ $[M + H]^+$ 313.1278, found 313.1272.

*(E)-1-Phenyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl)diazene (**4bf**).*[22] Flash chromatography (silica gel, petroleum ether/EtOAc = 200:1) afforded **4bf** (184 mg, 60%); red solid; mp 87−89 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.98−7.89 (m, 6H), 7.50−7.43 (m, 3H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 152.6, 135.6, 131.1, 129.0, 122.9, 121.9, 84.0, 24.8; IR (film) 2978 (w), 1603 (w), 1397 (m), 1358 (s), 1142 (s), 1087 (s), 858 (m), 688 (m), 667 (w) cm^{-1}; EI-MS (*m*/*z*, relative intensity) 308 (M^+, 55), 203 (100), 202 (24), 105 (32), 77 (84).

*4,4,5,5-Tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (**4bg**).*[23] Flash chromatography (silica gel, petroleum ether/EtOAc = 500:1 then 100:1) afforded **4bg** (37 mg, 16%); pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 2H), 6.72 (dd, *J* = 10.9, 17.6 Hz, 1H), 5.81 (d, *J* = 17.6 Hz, 1H), 5.29 (d, *J* = 10.9 Hz, 1H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 136.9, 135.0, 125.5, 114.8, 83.8, 24.8; IR (film) 2979 (w), 1610 (w), 1398 (m), 1360 (s), 1144 (m), 1108 (w), 963 (w), 859 (m), 668 (m) cm^{-1}; EI-MS (*m*/*z*, relative intensity) 230 (M^+, 52), 215 (40), 144 (82), 131 (90), 130 (100).

*4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (**4bh**).*[20] Flash chromatography (silica gel, petroleum ether/EtOAc = 25:1) afforded **4bh** (135 mg, 62%); yellow solid; mp 148−150 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 2H), 6.65 (d, *J* = 7.8 Hz, 2H), 1.32 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 136.4, 114.0, 83.2, 24.8; IR (film) 3450 (w), 3358 (w), 2927 (w), 1628 (w), 1359 (s), 1182 (w), 1143 (s), 860 (m), 738 (s) cm^{-1}; EI-MS (*m*/*z*, relative intensity) 219 (M^+, 65), 204 (16), 161 (13), 133 (22), 120 (77), 119 (100).

*1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (**4bi**).*[5a] Flash chromatography (silica gel, petroleum ether/EtOAc = 500:1 then 100:1) afforded **4bi** (172 mg, 52%); pale yellow solid; mp 232−233 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 4H), 1.34 (s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.8, 83.8, 24.8; IR (film) 2977 (w), 1439 (w), 1394 (m), 1371 (m), 1354 (s), 1142 (s), 1101 (s), 858 (s), 701 (w) cm^{-1}; EI-MS (*m*/*z*, relative intensity) 330 (M^+, 35), 315 (52), 273 (27), 244 (88), 231 (100), 230 (50), 131 (30).

*Triisopropyl((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl)ethynyl)silane (**4bj**).*[24] Flash chromatography (silica gel, petroleum ether/EtOAc = 500:1) afforded **4bj** (238 mg, 62%); orange solid; mp 80−82 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 1.33 (s, 12H), 1.13 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 131.1, 126.2, 107.2, 92.0, 83.9, 24.8, 18.6, 11.3; IR (film) 2943 (w), 2866 (w), 1606 (m), 1398 (m), 1358 (s), 1143 (m), 1019 (m), 860 (m), 675 (s) cm^{-1}; EI-MS (*m*/*z*, relative intensity) 384 (M^+, 4), 342 (21), 341 (100), 313 (18), 299 (30), 285 (35), 271 (54), 185 (16), 171 (22).

*2-(4-Iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4bk**).*[7a] Flash chromatography (silica gel, petroleum ether/EtOAc = 500:1) afforded **4bk** (132 mg, 40%); pale yellow solid; mp 89−91 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 136.2, 98.8, 84.0, 24.8; IR (film) 2976 (w), 1587 (m), 1387 (m), 1359 (s), 1325 (m), 1088 (s), 1007 (m), 857 (m) cm^{-1}; EI-MS (*m*/*z*, relative intensity) 330 (M^+, 100), 315 (52), 244 (82), 230 (71), 229 (76), 104 (35), 103 (30).

*(E)-Ethyl 3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl)acrylate (**4bl**).*[25] Flash chromatography (silica gel, petroleum ether/EtOAc = 50:1 then 10:1) afforded **4bl** (124 mg, 41%); Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 16.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 6.49 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.36−1.34 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 144.4, 136.9, 135.2, 127.2, 119.1, 84.0, 60.5, 24.8, 14.3; IR (film) 2979 (w), 1714 (m), 1398 (m), 1359 (s), 1143 (s), 1089 (s), 858 (m), 706 (m) cm^{-1}; EI-MS (*m*/*z*, relative intensity) 302 (M^+, 100), 287 (72), 257 (22), 216 (60), 203 (92), 157 (64), 129 (58), 77 (38).

*2-(Biphenyl-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4bm**).*[26] Flash chromatography (silica gel, petroleum ether/EtOAc = 500:1 then 100:1) afforded **4bm** (165 mg, 59%); yellow solid; mp 104−106 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.3 Hz, 2H), 7.61 (d, *J* = 7.1 Hz, 4H), 7.43 (t, *J* = 7.3 Hz, 2H), 7.35 (t, *J* = 7.1 Hz, 1H), 1.36 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 141.0, 135.2, 128.7, 127.5, 127.2, 126.4, 83.8, 24.8; IR (film) 2978 (w), 1609 (w), 1398 (m), 1360 (s), 1144 (m), 1092 (m), 766 (m), 697 (m) cm^{-1}; EI-MS (*m*/*z*, relative intensity) 280 (M^+, 67), 265 (21), 194 (60), 181 (74), 180 (100), 152 (18).

*2-(2-Isopropylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4ca**).*[27] Flash chromatography (silica gel, petroleum ether/EtOAc = 500:1) afforded **4ca** (118 mg, 48%); pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.3 Hz, 1H), 7.39−7.35 (m, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.15 (m, 1H), 3.68 (m, 1H), 1.33 (s, 12H), 1.23 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 135.7, 130.9, 124.8, 124.4, 83.3, 31.5, 24.8, 24.4; IR (film) 2976 (w), 1599 (w), 1380 (m), 1346 (s), 1310 (m), 1144 (s), 1060 (m), 861 (m), 766 (m) cm^{-1}; EI-MS (*m*/*z*, relative intensity) 246 (M^+, 20), 231 (15), 189 (50), 146 (56), 145 (60), 131 (74), 101 (62), 84 (100).

*2-(2-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4cb**).*[7a] Flash chromatography (silica gel, petroleum ether/EtOAc = 500:1) afforded **4cb** (108 mg, 48%); pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.76−7.72 (m, 1H), 7.42 (m, 1H), 7.13 (m, 1H), 7.02 (m, 1H), 1.36 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2 (d, *J* = 250.8 Hz), 136.8 (d, *J* = 8.0 Hz), 133.2 (d, *J* = 8.8 Hz), 123.5 (d, *J* = 3.2 Hz), 115.2 (d, *J* = 23.8 Hz), 83.8, 24.8; IR (film) 2980 (w), 1615 (m), 1389 (m), 1356 (s), 1324 (m), 1144 (m), 1074 (m), 790 (w) cm^{-1}; EI-MS (*m*/*z*, relative intensity) 222 (M^+, 23), 207 (38), 160 (19), 123 (100), 122 (33), 85 (18).

*2-(2-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4cc**).*[28] Flash chromatography (silica gel, petroleum ether/EtOAc = 500:1) afforded **4cc** (102 mg, 43%); yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.2 Hz, 1H), 7.35−7.32 (m, 2H), 7.24−7.20 (m, 1H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 136.4, 131.8, 129.3, 125.8, 84.1, 24.7; IR (film) 2979 (w), 1593 (w), 1380 (m), 1352 (s), 1144 (s), 1039 (m), 758 (m), 670 (m) cm^{-1}; EI-MS (*m*/*z*, relative intensity) 240 (6), 238 (M^+, 18), 223 (21), 203 (100), 161 (44), 139 (90), 103 (20).

*2-(2,6-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4cd**).*[19] Flash chromatography (silica gel, petroleum ether/EtOAc = 500:1) afforded **4 cd** (53 mg, 23%); pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.11 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 2H), 2.39 (s, 6H), 1.38 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 129.1, 126.4, 83.6, 24.9, 22.2; IR (film) 2978 (w), 1597 (w), 1371 (m), 1332 (s), 1302 (s), 1144 (s), 1060 (s), 859 (m), 770 (m) cm^{-1}; EI-MS (*m*/*z*, relative intensity) 232 (M^+, 32), 175 (100), 174 (35), 133 (53), 132 (66).

*2-(2-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4ce**).*[29] Flash chromatography (silica gel, petroleum ether/EtOAc = 100:1 then 50:1) afforded **4ce** (61 mg, 26%); colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.69−7.65 (m, 1H), 7.39 (m, 1H), 6.94 (m, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 3.83 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 136.7, 132.4, 120.2, 110.5, 83.4, 55.8, 24.8; IR (film) 2979 (w), 1600 (m), 1461 (m), 1386 (m), 1353 (s), 1273 (m), 1145 (m), 1073 (m), 760 (m) cm^{-1}; EI-MS (*m*/*z*, relative intensity) 234 (M^+, 67), 219 (28), 203 (11), 161 (33), 134 (100), 133 (60), 105 (47), 91 (69).

*2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (**4cf**).*[30] Flash chromatography (silica gel, petroleum ether/EtOAc = 100:1) afforded **4cf** (44 mg, 20%); pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.61 (dd, *J* = 1.6, 7.5 Hz, 1H), 7.37 (m, 1H), 6.90−6.86 (m, 2H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 135.7, 133.8, 119.5, 115.4, 84.4, 24.8; IR (film) 3448 (w), 2980 (w), 1620 (s), 1486 (m), 1390 (s), 1167 (m), 1140 (s), 860 (m), 671 (m) cm^{-1}; EI-MS (*m*/*z*, relative intensity) 220 (M^+, 18), 163 (100), 162 (25), 121 (20), 120 (47).

*2-(3-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4cg**).*[31] Flash chromatography (silica gel, petroleum ether/EtOAc = 500:1) afforded **4cg** (104 mg, 47%); pale yellow liquid. ^1H NMR (400

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MHz, $CDCl_3$) δ 7.57 (d, J = 7.2 Hz, 1H), 7.48 (m, 1H), 7.33 (m, 1H), 7.13 (m, 1H), 1.34 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, J = 246.4 Hz), 130.3 (d, J = 2.9 Hz), 129.4 (d, J = 7.0 Hz), 120.9 (d, J = 19.3 Hz), 118.1 (d, J = 21.0 Hz), 84.1, 24.8; IR (film) 2980 (w), 1431 (m), 1381 (m), 1355 (s), 1144 (m), 1091 (w), 901 (m), 716 (m) cm^{-1}; EI-MS (m/z, relative intensity) 222 (M^+, 39), 207 (85), 136 (98), 123 (100), 122 (37), 85 (18), 58 (18).

*2-(3-Bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4ch**).*[32] Flash chromatography (silica gel, petroleum ether/EtOAc = 500:1) afforded **4ch** (153 mg, 54%); pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.71−7.56 (m, 2H), 7.22 (t, J = 7.7 Hz, 1H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 134.1, 133.0, 129.4, 122.4, 84.1, 24.8; IR (film) 2979 (w), 1407 (m), 1372 (m), 1351 (s), 1321 (m), 1143 (s), 1101 (w), 700 (s) cm^{-1}; EI-MS (m/z, relative intensity) 284 (43), 282 (M^+, 51), 269 (78), 267 (81), 198 (98), 196 (100), 185 (71), 183 (76), 103 (36), 85 (33).

*2-(3-Iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4ci**).*[33] Flash chromatography (silica gel, petroleum ether/EtOAc = 500:1) afforded **4ci** (132 mg, 40%); yellow solid; mp 64−66 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.77−7.73 (m, 2H), 7.10 (t, J = 7.6 Hz, 1H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 140.0, 133.6, 129.6, 94.5, 84.1, 24.8; IR (film) 2978 (w), 1402 (m), 1372 (m), 1349 (s), 1320 (m), 1143 (s), 1097 (w), 701 (m) cm^{-1}; EI-MS (m/z, relative intensity) 330 (M^+, 98), 315 (67), 244 (100), 231 (67), 230 (64), 104 (30), 103 (28).

*3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (**4cj**).*[29] Flash chromatography (silica gel, petroleum ether/EtOAc = 30:1) afforded **4cj** (147 mg, 64%); colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.01 (d, J = 7.5 Hz, 1H), 7.72−7.47 (m, 2H), 1.36 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 138.2, 134.2, 128.3, 118.7, 111.9, 84.4, 24.7; IR (film) 2980 (w), 2230 (w), 1603 (w), 1358 (s), 1167 (w), 1143 (s), 880 (m), 700 (s), 672 (m) cm^{-1}; EI-MS (m/z, relative intensity) 229 (M^+, 23), 214 (96), 186 (17), 143 (100), 130 (65), 58 (31).

*Ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**4ck**).*[18] Flash chromatography (silica gel, petroleum ether/EtOAc = 50:1 then 30;1) afforded **4ck** (192 mg, 70%); pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.14 (d, J = 7.8 Hz, 1H), 7.99−7.44 (m, 2H), 4.39 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 139.0, 135.6, 132.2, 129.8, 127.6, 83.9, 60.8, 24.7, 14.3; IR (film) 2980 (w), 1720 (s), 1390 (m), 1358 (s), 1280 (m), 1252 (s), 1167 (m), 1144 (s), 734 (w), 659 (m) cm^{-1}; EI-MS (m/z, relative intensity) 276 (M^+, 25), 261 (40), 233 (100), 205 (64), 177 (86), 149 (28), 131 (33), 103 (35).

*4,4,5,5-Tetramethyl-2-m-tolyl-1,3,2-dioxaborolane (**4cl**).*[34] Flash chromatography (silica gel, petroleum ether/EtOAc = 500:1) afforded **4cl** (42 mg, 19%); colorless solid; mp 33−34 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64−7.61 (m, 2H), 7.27 (s, 2H), 2.35 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 135.3, 132.0, 131.8, 127.6, 83.6, 24.8, 21.2; IR (film) 2978 (w), 1379 (m), 1356 (s), 1145 (s), 1103 (w), 852 (m), 708 (s), 665 (m) cm^{-1}; EI-MS (m/z, relative intensity) 218 (M^+, 38), 203 (43), 132 (77), 119 (100), 118 (57), 91 (20).

*2-(3,5-Difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4cm**).*[35] Flash chromatography (silica gel, petroleum ether/EtOAc = 500:1) afforded **4 cm** (151 mg, 63%); colorless solid; yellow solid; mp 36−38 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, J = 1.9, 7.8 Hz, 2H), 6.87 (tt, J = 2.4, 9.1 Hz, 1H), 1.34 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (dd, J = 11.0, 249.7 Hz), 116.8 (dd, J = 5.7, 17.1 Hz), 106.5 (t, J = 25.1 Hz), 84.4, 24.8; IR (film); 2981 (w), 1587 (m), 1427 (s), 1368 (s), 1144 (m), 980 (m), 872 (m), 717 (w) cm^{-1}; EI-MS (m/z, relative intensity) 240 (M^+, 27), 225 (81), 197 (10), 154 (100), 141 (61), 85 (15), 58 (31).

*2-(3,4-Difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4cn**).*[36] Flash chromatography (silica gel, petroleum ether/EtOAc = 500:1 then 100:1) afforded **4cn** (156 mg, 65%); yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.60−7.51 (m, 2H), 7.17−7.10 (m, 1H), 1.34 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6 (dd, J = 12.7, 252.2 Hz), 150.2 (dd, J = 12.0, 248.6 Hz), 131.4 (dd, J = 3.8, 6.7 Hz), 123.3 (d, J = 15.1 Hz), 116.9 (d, J = 16.3 Hz), 84.2, 24.8; IR (film) 2981 (w), 1614 (m), 1519 (m), 1390 (s), 1360 (s), 1272 (s), 1167 (m), 1144 (s), 890 (w), 689 (m) cm^{-1}; EI-MS (m/z, relative intensity) 240 (M^+, 21), 225 (84), 154 (80), 141 (100), 131 (18), 79 (38), 58 (56).

*2-(Benzo[d][1,3]dioxol-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4co**).*[37] Flash chromatography (silica gel, petroleum ether/EtOAc = 500:1) afforded **4co** (35 mg, 14%); yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 7.7 Hz, 1H), 7.24 (s, 1H), 6.83 (d, J = 7.7 Hz, 1H), 5.95 (s, 2H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 147.2, 129.7, 113.9, 108.3, 100.7, 83.7, 24.8; EI-MS (m/z, relative intensity) 248 (M^+, 76), 233 (20), 162 (43), 149 (67), 148 (100), 147 (50).

*Dimethyl 5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-isophthalate (**4cp**).*[38] Flash chromatography (silica gel, petroleum ether/EtOAc = 50:1) afforded **4 cP** (109 mg, 34%); yellow solid; mp 125−127 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.64 (d, J = 1.4 Hz, 2H), 3.95 (s, 6H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 139.8, 133.2, 130.0, 84.3, 52.2, 24.8; IR (film) 1726 (s), 1381 (m), 1334 (m), 1287 (m), 1262 (s), 1244 (s), 1008 (m), 736 (s) cm^{-1}; EI-MS (m/z, relative intensity) 320 (M^+, 11), 305 (28), 289 (25), 277 (100), 221 (55), 189 (24), 161 (22).

*2-(4-Chloro-3-nitrophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4cq**).*[39] Flash column chromatography (silica gel, petroleum ether/EtOAc = 200:1) afforded **4cq** (88 mg, 31%); yellow solid; mp 39−41 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 138.9, 131.3, 131.2, 129.5, 84.8, 24.8; IR (film) 2981 (w), 1604 (m), 1537 (m), 1390 (m), 1348 (s), 1143 (s), 1097 (m), 851 (m) cm^{-1}; EI-MS (m/z, relative intensity) 285 (2), 283 (M^+, 7), 270 (30), 268 (90), 223 (26), 197 (40), 181 (80), 155 (100), 85 (42), 58 (51); HRMS (ESI) calcd for $C_{12}H_{15}B^{35}ClNNaO_4$ $[M + Na]^+$ 306.0677, found 306.0668.

*4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (**5da**).*[40] Flash chromatography (silica gel, petroleum ether/EtOAc = 500:1) afforded **5da** (58 mg, 23%); white solid; mp 64−66 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.89−7.82 (m, 4H), 7.49−7.47 (m, 2H), 1.39 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 135.0, 132.8, 130.4, 128.6, 127.7, 126.9, 125.8, 83.9, 24.9; IR (film) 2978 (w), 1476 (m), 1383 (s), 1351 (s), 1144 (s), 1080 (m), 877 (m), 747 (s), 687 (m) cm^{-1}; EI-MS (m/z, relative intensity) 254 (M^+, 45), 239 (10), 168 (64), 154 (100), 128 (10).

*2-Phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4H-chromen-4-one (**5db**).*[41] Flash chromatography (silica gel, petroleum ether/EtOAc = 15:1 then 10:1) afforded **5db** (56 mg, 32%); yellow solid; mp 88−90 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 1.2 Hz, 1H), 8.10 (dd, J = 1.4, 8.4 Hz, 1H), 7.94−7.92 (m, 2H), 7.56−7.52 (m, 4H), 6.85 (s, 1H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 163.3, 158.2, 139.6, 133.3, 131.7, 131.6, 129.0, 126.3, 123.2, 117.3, 107.9, 84.2, 24.9; IR (film) 2978 (w), 2924 (w), 1644 (s), 1608 (m), 1351 (s), 1306 (m), 1143 (m), 712 (m) cm^{-1}; EI-MS (m/z, relative intensity) 348 (M^+, 73), 333 (44), 305 (39), 262 (20), 249 (100), 248 (71), 220 (19), 102 (54).

*6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2H-chromen-2-one (**5dc**).* Flash column chromatography (silica gel, petroleum ether/EtOAc = 20:1 then 10:1) afforded **5dc** (78 mg, 57%); white solid; mp 105−107 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.96−7.94 (m, 2H), 7.72 (d, J = 9.5 Hz, 1H), 7.32 (d, J = 8.6 Hz, 1H), 6.42 (d, J = 9.5 Hz, 1H), 1.36 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 156.1, 143.6, 138.1, 135.0, 118.3, 116.5, 116.2, 84.2, 24.8; IR (film) 2984 (w), 1753 (m), 1730 (s), 1393 (m), 1382 (s), 1371 (s), 1180 (m), 1131 (m) cm^{-1}; EI-MS (m/z, relative intensity) 272 (M^+, 71), 257 (69), 186 (100), 173 (96), 144 (58), 116 (20), 85 (15); HRMS (ESI) calcd for $C_{15}H_{18}BO_4$ $[M + H]^+$ 273.1295, found 273.1291.

*3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (**5dd**).*[19] Recrystallization from cyclohexane afforded **5dd** (123 mg, 60%); white solid; mp 99−101 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.69−8.65 (m, 1H), 8.06 (d, J = 7.5 Hz, 1H), 7.30−7.27 (m, 1H), 1.36 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 151.8, 142.2, 123.0, 84.2, 24.8; IR (film) 2976 (w), 1474 (m), 1413 (m), 1363 (m), 1156 (s), 1048 (s), 1024 (m), 876 (m), 734 (m) cm^{-1}; EI-

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MS (m/z, relative intensity) 205 (M^+, 36), 190 (100), 148 (44), 120 (15), 106 (87), 105 (33).

*5-Methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-thiophene-3-carbonitrile (**5de**).* Flash column chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded **5de** (37 mg, 15%); yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 1H), 2.52 (s, 3H), 1.36 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 129.4, 117.9, 84.9, 24.7, 15.2; IR (film) 2926 (w), 2228 (w), 1726 (w), 1463 (s), 1364 (s), 1167 (m), 1140 (s), 1048 (s), 851 (s) cm^{-1}; EI-MS (m/z, relative intensity) 249 (M^+, 62), 234 (31), 219 (15), 207 (54), 191 (54), 163 (28), 150 (100), 59 (30); HRMS (ESI) calcd for $C_{12}H_{17}BNO_2S$ $[M + H]^+$ 250.1070, found 250.1066.

*6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (**5df**).*[42] Flash chromatography (silica gel, petroleum ether/EtOAc = 20:1 then 10:1) afforded **5df** (53 pmg, 22%); orange solid; mp 181−183 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.90 (s, 1H), 7.65 (d, J = 7.9 Hz, 1H), 7.56 (d, J = 7.9 Hz, 1H), 7.24 (d, J = 1.5 Hz, 1H), 6.55 (s, 1H), 1.36 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 130.4, 125.6, 125.5, 120.0, 118.0, 102.7, 83.5, 24.9; IR (film) 3320 (w), 2925 (w), 1514 (m), 1392 (m), 1358 (s), 1166 (w), 1142 (s), 894 (w) cm^{-1}; EI-MS (m/z, relative intensity) 243 (M^+, 79), 228 (25), 170 (17), 157 (26), 144 (54), 143 (100), 116 (17).

*5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)isoquinoline (**5dg**).*[43] Flash chromatography (silica gel, petroleum ether/EtOAc = 10:1) afforded **5dg** (143 mg, 56%); yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.57 (s, 2H), 8.27 (d, J = 6.8 Hz, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.57 (m, 1H), 1.41 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 143.5, 139.7, 139.4, 130.9, 128.3, 126.2, 121.0, 83.9, 24.8; IR (film) 2978 (w), 1612 (w), 1488 (w), 1371 (m), 1344 (s), 1136 (s), 1111 (w), 868 (m) cm^{-1}; EI-MS (m/z, relative intensity) 255 (M^+, 63), 240 (20), 182 (18), 169 (40), 156 (55), 155 (100), 128 (19).

*2-Methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-pyridine (**5di**).*[44] Flash chromatography (silica gel, petroleum ether/EtOAc = 20:1) afforded **5di** (117 mg, 50%); yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.92 (d, J = 8.3 Hz, 1H), 6.71 (d, J = 8.3 Hz, 1H), 3.95 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 154.1, 144.3, 110.1, 83.6, 53.2, 24.7; IR (film) 2979 (w), 1600 (s), 1500 (w), 1372 (m), 1354 (s), 1145 (m), 859 (m), 687 (w) cm^{-1}; EI-MS (m/z, relative intensity) 235 (M^+, 80), 234 (100), 220 (19), 206 (15), 136 (88), 135 (63), 105 (28).

Borylation of 2-Naphthylamine (1da) in Water. 2-Naphthylamine (**1da**, 1 mmol, 143 mg), aqueous HCl (0.41 mL, 12 mol/L), and H_2O (0.5 mL) were stirred with ice bath. Then, $NaNO_2$ (1.1 mmol, 76 mg) in H_2O (0.5 mL) was added by dropping funnel. The reaction system was stirred for 15 min. B_2pin_2 (1.1 mmol, 279 mg) and MeCN (1 mL) solution were then added in succession. The resulting solution was stirred at 80 °C for 2 h. The reaction mixture was then concentrated under reduced pressure, and the crude residue was purified by silica gel flash chromatography (petroleum ether). 4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (**5da**) was obtained (95 mg, 38%).

Typical Procedure of Consecutive Suzuki−Miyaura Cross-Coupling Reactions. B_2pin_2 (279 mg, 1.1 mmol) and 3-aminopyridine (94 mg, 1.0 mmol) were weighed in a 25 mL round-bottom flask. MeCN (3 mL) and *t*-BuONO (**2a**, 155 mg, 1.5 mmol) were then added in succession. The resulting reaction solution was stirred for 2 h at 80 °C (N_2 evolution completed within 5−15 min). After the MeCN was removed by evaporation under reduced pressure, the system was degassed 3 times and was set under nitrogen atmosphere. Then $Pd(PPh_3)_4$ (58 mg, 5 mmol %), K_2CO_3 (276 mg, 2 mmol), DMF (1.5 mL), and PhI (245 mg, 1.2 mmol) were added, and the solution was stirred at 100 °C for 12 h. The solution was then concentrated by rotovap under reduced pressure to leave a crude residue, which was purified by silica gel column chromatography (petroleum ether/EtOAc = 50:1, then 5:1) to give 3-phenylpyridine **6f**[45] in 63% isolated yield as pale yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.59 (d, J = 4.1 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.57 (d, J = 7.5 Hz, 2H), 7.47 (t, J = 7.5 Hz, 2H), 7.42−7.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 148.3, 137.7, 136.5, 134.2, 129.0, 128.0, 127.0, 123.4; IR (film) 3031 (w), 1582 (w), 1473 (m), 1407 (m), 1024 (w), 1006 (w), 754 (s), 697 (s) cm^{-1}; EI-MS (m/z, relative intensity) 155 (M^+, 100), 154 (50), 127 (14), 102 (10), 63 (8), 51 (13).

*4-Fluorobiphenyl (**6a**).*[46] Flash chromatography (silica gel, petroleum ether) afforded **6a** (122 mg, 71%); white solid; mp 75−77 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.51 (m, 4H), 7.41 (t, J = 7.2 Hz, 2H), 7.32 (t, J = 7.2 Hz, 1H), 7.12−7.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, J = 246.1 Hz), 140.2, 137.3 (d, J = 3.1 Hz), 128.8, 128.6 (d, J = 8.0 Hz), 127.2, 127.0, 115.6 (d, J = 21.4 Hz); IR (film) 1517 (m), 1485 (m), 1235 (m), 1196 (w), 907 (s), 837 (m), 760 (m), 732 (s) cm^{-1}; EI-MS (m/z, relative intensity) 172 (M^+, 100), 171 (41), 170 (27), 142 (18), 100 (9), 85 (9).

*Biphenyl-4-carbonitrile (**6b**).*[47] Flash chromatography (silica gel, petroleum ether/EtOAc = 100:1) afforded **6b** (88 mg, 49%); white solid; mp 83−85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (m, 4H), 7.59−7.42 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 139.1, 132.5, 129.1, 128.6, 127.7, 127.2, 118.9, 110.8; IR (film) 2227 (m), 1606 (m), 1485 (m), 1265 (w), 1008 (w), 844 (m), 766 (s), 698 cm^{-1}; EI-MS (m/z, relative intensity) 179 (M^+, 100), 178 (25), 151 (14), 76 (10), 63 (5).

*Ethyl Biphenyl-3-carboxylate (**6c**).*[48] Flash chromatography (silica gel, petroleum ether, then petroleum ether/EtOAc = 100:1) afforded **6c** (131 mg, 58%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.02 (d, J = 7.9 Hz, 1H), 7.75−7.61 (m, 3H), 7.50−7.42 (m, 3H), 7.35 (t, J = 7.3 Hz, 1H), 4.40 (q, J = 7.2 Hz, 2H), 1.40 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 141.3, 140.1, 131.3, 131.0, 128.8, 128.7, 128.2, 128.1, 127.6, 127.1, 61.0, 14.3; IR (film) 1717 (s), 1305 (m), 1272 (w), 1239 (s), 1108 (m), 1084 (w), 742 (s), 697 (m) cm^{-1}; EI-MS (m/z, relative intensity) 226 (M^+, 73), 198 (30), 181 (100), 153 (55), 152 (75), 76 (21).

*(E)-Ethyl 3-(Biphenyl-4-yl)acrylate (**6d**).*[49] Flash chromatography (silica gel, petroleum ether/EtOAc = 200:1 then 100:1) afforded **6d** (81 mg, 32%); white solid; mp 77−79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 16.0 Hz, 1H), 7.63−7.58 (m, 6H), 7.45−7.37 (m, 3H), 6.47 (d, J = 16.0 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 144.1, 143.0, 140.2, 133.4, 128.9, 128.5, 127.8, 127.5, 127.0, 118.1, 60.5, 14.3; EI-MS (m/z, relative intensity) 252 (M^+, 100), 224 (19), 207 (100), 180 (46), 178 (78), 165 (32), 76 (20).

*2,6-Diphenyl-4H-chromen-4-one (**6e**).*[50] Flash column chromatography (silica gel, petroleum ether/EtOAc = 100:1, then 20:1) afforded **6e** (122 mg, 41%); white solid; mp 152−155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 2.3 Hz, 1H), 7.96−7.93 (m, 3H), 7.69−7.63 (m, 3H), 7.55−7.53 (m, 3H), 7.47 (t, J = 7.4 Hz, 2H), 7.39 (t, J = 7.4 Hz, 1H), 6.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 163.4, 155.6, 139.2, 138.4, 132.6, 131.7, 131.6, 129.0, 128.9, 127.8, 127.1, 126.3, 124.0, 123.5, 118.6, 107.5; IR (film) 1634 (s), 1616 (s), 1496 (w), 1473 (m), 1359 (s), 1049 (w), 772 (m), 687 (m) cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{15}O_2$ $[M + H]^+$ 299.1067, found 299.1063.

*2-Methyl-5-phenylpyridine (**6g**).*[51] Flash chromatography (silica gel, petroleum ether/EtOAc = 20:1 then 5:1) afforded **6g** (91 mg, 54%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.55 (d, J = 7.6 Hz, 2H), 7.45−7.20 (m, 4H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 147.4, 137.8, 134.6, 133.6, 128.9, 127.7, 126.8, 123.0, 24.0; IR (film) 1604 (w), 1479 (m), 1445 (w), 1374 (w), 1030 (w), 759 (s), 731 (w), 697 (s) cm^{-1}; EI-MS (m/z, relative intensity) 169 (M^+, 100), 168 (24), 141 (23), 115 (18), 102 (10), 51 (8).

*3-Methyl-5-phenylpyridine (**6h**).*[52] Flash chromatography (silica gel, petroleum ether/EtOAc = 50:1 then 5:1) afforded **6h** (59 mg, 35%); pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.42 (s, 1H), 7.66 (s, 1H), 7.56−7.38 (m, 5H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 145.4, 137.8, 136.0, 134.8, 132.9, 128.9, 127.8, 127.0, 18.3; IR (film) 3033 (w), 1453 (w), 1414 (m), 1150 (w), 1028 (w), 875 (m), 760 (s), 697 (s) cm^{-1}; EI-MS (m/z, relative intensity) 169 (M^+, 100), 168 (35), 141 (15), 115 (16), 102 (6).

*4-Methyl-3-phenylpyridine (**6i**).*[52] Flash chromatography (silica gel, petroleum ether/EtOAc = 50:1 then 5:1) afforded **6i** (88 mg, 52%); yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 2H), 7.45−7.31 (m, 5H), 7.18 (d, J = 2.6 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz,

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$CDCl_3$) δ 149.9, 148.2, 144.4, 137.8, 137.6, 129.2, 128.3, 127.5, 125.1, 19.7; IR (film) 1590 (m), 1444 (m), 1401 (m), 1007 (m), 995 (w), 766 (s), 732 (w), 702 (s) cm^{-1}; EI-MS (m/z, relative intensity) 169 (M^+, 95), 168 (100), 167 (49), 154 (20), 115 (18), 91 (18).

*Methyl 5-Phenylnicotinate (**6j**).*[53] Flash chromatography (silica gel, petroleum ether/EtOAc = 50:1 then 5:1) afforded **6j** (106 mg, 50%); yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 9.00 (s, 1H), 8.48 (s, 1H), 7.61−7.43 (m, 5H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 151.7, 149.2, 136.5, 136.3, 135.1, 129.1, 128.5, 127.1, 125.9, 52.4; IR (film) 1726 (s), 1440 (m), 1310 (s), 1251 (s), 1111 (m), 1026 (w), 754 (s), 700 (m) cm^{-1}; EI-MS (m/z, relative intensity) 213 (M^+, 100), 182 (67), 154 (68), 127 (48), 77 (30), 63 (9).

*5-Phenyl-2-(trifluoromethyl)pyridine (**6k**).*[54] Flash chromatography (silica gel, petroleum ether/EtOAc = 100:1) afforded **6k** (134 mg, 60%); white solid; mp 90−92 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.61 (d, J = 8.1 Hz, 1H), 7.46 (d, J = 7.4 Hz, 2H), 7.40−7.33 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 146.6 (q, J = 34.7 Hz), 139.4, 136.2, 135.4, 129.2, 128.9, 127.2, 121.8 (q, J = 272 Hz), 120.3; IR (film) 1376 (w), 1339 (s), 1245 (m), 1174 (m), 1121 (s), 1093 (s), 1042 (w), 754 (m) cm^{-1}; EI-MS (m/z, relative intensity) 223 (M^+, 100), 222 (21), 154 (25), 127 (20), 102 (10), 77 (10).

*2-Methoxy-5-phenylpyridine (**6l**).*[55] Flash chromatography (silica gel, petroleum ether/EtOAc = 50:1) afforded **6l** (92 mg, 50%); yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.77 (d, J = 8.5 Hz, 1H), 7.51 (d, J = 7.6 Hz, 2H), 7.43−7.34 (m, 3H), 6.81 (d, J = 8.5 Hz, 1H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 144.9, 137.9, 137.4, 130.0, 128.9, 127.2, 126.6, 110.8, 53.5; IR (film) 1606 (m), 1508 (m), 1480 (s), 1286 (s), 1046 (w), 1019 (m), 830 (m), 769 (s) cm^{-1}; EI-MS (m/z, relative intensity) 185 (M^+, 98), 184 (100), 156 (42), 154 (46), 128 (12), 115 (31).

*3-Bromo-5-phenylpyridine (**6m**).*[56] Flash chromatography (silica gel, petroleum ether/EtOAc = 50:1 then 5:1) afforded **6m** (105 mg, 45%); white solid. mp 43−45 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.64 (s, 1H), 8.00 (s, 1H), 7.54−7.42 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 146.3, 138.2, 136.8, 136.2, 129.1, 128.6, 127.1, 120.8; IR (film) 1580 (w), 1428 (m), 1405 (m), 1045 (w), 1011 (m), 798 (m), 760 (s), 698 (s) cm^{-1}; EI-MS (m/z, relative intensity) 235 (98), 233 (M^+, 100), 154 (32), 127 (71), 77 (28), 63 (22), 51 (18).

*2-Chloro-4-phenylpyridine (**6n**).*[57] Flash chromatography (silica gel, petroleum ether/EtOAc = 50:1 then 10:1) afforded **6n** (30 mg, 16%); pale yellow solid; mp 64−66 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 3.8 Hz, 1H), 7.52 (d, J = 6.1 Hz, 2H), 7.45 (s, 1H), 7.43−7.37 (m, 3H), 7.34 (d, J = 2.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 151.5, 149.9, 136.8, 129.6, 129.2, 127.0, 122.0, 120.4; IR (film) 1604 (w), 1588 (s), 1535 (s), 1375 (m), 1130 (m), 878 (w), 760 (s), 730 (w) cm^{-1}; EI-MS (m/z, relative intensity) 191 (35), 189 (M^+, 100), 154 (57), 127 (36), 77 (14), 51 (10).

*3-Phenylquinoline (**6o**).*[58] Flash chromatography (silica gel, petroleum ether/EtOAc = 50:1 then 10:1) afforded **6o** (111 mg, 54%); pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.20 (s, 1H), 8.13 (d, J = 8.5 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.68−7.64 (m, 3H), 7.52−7.45 (m, 3H), 7.38 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 147.1, 137.6, 133.6, 132.9, 129.2, 129.0, 129.0, 127.9, 127.8, 127.2, 126.8; IR (film) 3058 (w), 1597 (w), 1493 (m), 1362 (w), 1141 (w), 1025 (w), 786 (s), 761 (s), 696 (s) cm^{-1}; EI-MS (m/z, relative intensity) 205 (M^+, 100), 204 (58), 176 (14), 102 (9), 88 (8), 76 (11).

*5-Phenylisoquinoline (**6p**).*[59] Flash chromatography (silica gel, petroleum ether/EtOAc = 50:1 then 5:1) afforded **6p** (113 mg, 55%); yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.48 (d, J = 5.7 Hz, 1H), 7.96 (s, 1H), 7.71 (d, J = 5.7 Hz, 1H), 7.63 (d, J = 4.1 Hz, 2H), 7.52−7.43 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 143.3, 139.1, 138.9, 134.0, 130.8, 129.8, 128.9, 128.4, 127.7, 127.0, 126.7, 118.4; IR (film) 3055 (w), 1618 (m), 1485 (m), 1058 (w), 829 (s), 799 (w), 758 (s), 701 (s) cm^{-1}; EI-MS (m/z, relative intensity) 205 (M^+, 100), 204 (76), 178 (19), 176 (30), 151 (13), 102 (18), 88(18).

*4-Phenylisoquinoline (**6q**).*[60] Flash chromatography (silica gel, petroleum ether/EtOAc = 50:1 then 5:1) afforded **6q** (88 mg, 43%); yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 9.25 (s, 1H), 8.49 (s, 1H), 8.01 (d, J = 7.7 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.64−7.59 (m, 2H), 7.50−7.46 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 142.7, 136.9, 134.1, 133.2, 130.4, 130.0, 128.5, 128.3, 127.8, 127.8, 127.0, 124.7; IR (film) 3030 (w), 1620 (w), 1504 (w), 1390 (m), 1219 (w), 1073 (w), 828 (w), 760 (s), 703 (s) cm^{-1}; EI-MS (m/z, relative intensity) 205 (M^+, 100), 204 (73), 178 (15), 176 (22), 151 (8), 102 (15), 88 (12), 76 (11).

*3-Phenyl-1H-indazole (**6r**).*[61] Flash chromatography (silica gel, petroleum ether/EtOAc = 50:1 then 10:1) afforded **6r** (58 mg, 30%); yellow solid; mp 92−94 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 10.4 (br, 1H), 7.98 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 7.4 Hz, 2H), 7.46 (t, J = 7.4 Hz, 2H), 7.38−7.34 (m, 3H), 7.18 (d, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 141.7, 133.5, 128.8, 128.1, 127.6, 126.8, 121.4, 121.2, 121.0, 110.0; EI-MS (m/z, relative intensity) 194 (M^+, 100), 193 (22), 167 (14), 165 (12), 77 (16), 51 (12).

*3-Phenyl-1H-pyrazole (**6s**).*[61] Flash chromatography (silica gel, petroleum ether/EtOAc = 50:1 then 10:1) afforded **6s** (29 mg, 20%); colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 1.3 Hz, 1H), 7.74 (s, 1H), 7.61 (d, J = 2.0 Hz, 1H), 7.41 (t, J = 7.4 Hz, 2H), 7.33 (t, J = 7.4 Hz, 1H), 6.61 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 133.2, 131.9, 128.8, 128.1, 125.8, 102.7; IR (film) 3213 (m), 2978 (w), 1370 (m), 1353 (w), 1155 (m), 1113 (m), 757 (s), 693 (s) cm^{-1}; EI-MS (m/z, relative intensity) 144 (M^+, 100), 143 (14), 117 (14), 115 (31), 89 (15), 77 (15), 51 (13).

Typical Procedure of Gram-Scale Borylation. 4-Nitroaniline (**1ai**, 20 mmol, 2.76 g) and B_2pin_2 (5.334 g, 21 mmol) were weighed in a 250 mL round-bottom flask. MeCN (60 mL), and *t*-BuONO (3.09 g, 30 mmol) were then added in succession. The resulting reaction solution was allowed to stir for 12 h at 80 °C (nitrogen gas evolution completed within 1 h). The solution was then concentrated under reduced pressure and the crude residue was purified by silica gel flash chromatography (petroleum ether/EtOAc = 500:1) to give 4,4,5,5-tetramethyl-2-(4-nitrophenyl)-1,3,2-dioxaborolane (**4ai**)[11] (3.88 g, 78%).

*2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4aj**).*[11] Flash chromatography (silica gel, petroleum ether/EtOAc = 500:1 then 100:1) afforded **4aj** (3.302 g, 71%). Colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 3.82 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 136.4, 113.2, 83.5, 55.0, 24.8; IR (film) 2978 (w), 1605 (s), 1396 (m), 1360 (s), 1318 (m), 1277 (m), 1247 (s), 1175 (w), 1143 (s), 1091 (m), 1031 (m), 962 (w), 860 (m), 831 (m), 736 (w) cm^{-1}; EI-MS (m/z, relative intensity) 234 (M^+, 62), 219 (27), 148 (39), 135 (86), 134 (100), 133 (22), 43 (30), 41 (33).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

EPR experiments, copies of ^1H and ^{13}C spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to the memory of Prof. Howard E. Zimmerman.

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