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Note

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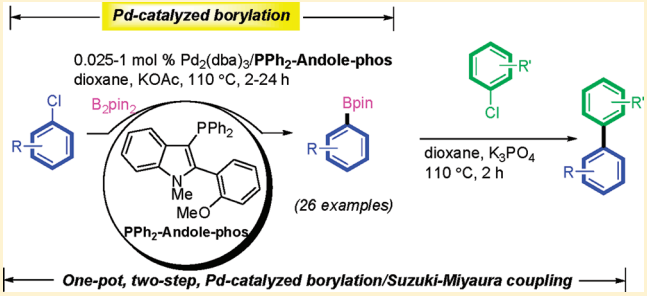
Carbon–Boron Bond Cross-Coupling Reaction Catalyzed by $-PPh_2$ Containing Palladium–Indolylphosphine Complexes

Wing Kin Chow, On Ying Yuen, Chau Ming So, Wing Tak Wong, and Fuk Yee Kwong*

State Key Laboratory of Chirosciences and Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Kowloon, Hong Kong

Supporting Information

ABSTRACT: This study describes the application of indolylphosphine ligands with a diphenylphosphino moiety to the palladium-catalyzed borylation of aryl chlorides. The combination of palladium metal precursor with PPh_2-Andole-phos, which comprises an inexpensive $-PPh_2$ group, provides highly effective catalysts for the borylation of aryl chlorides. A range of functional groups such as $-CN$, $-NO_2$, $-CHO$, $-COMe$, $-COOMe$, and $-CF_3$ was compatible, and the catalyst loading down to 0.025 mol % of Pd can be achieved. The Pd/PPh_2-Andole-phos system is able to catalyze both borylation reaction and Suzuki–Miyaura coupling reaction in a one-pot sequential manner for the direct synthesis of biaryl compounds in excellent yields.



Arylboronic acids, boronate esters, and potassium trifluoroborate salts are used as important chemical building blocks and intermediates in organic synthesis. They have versatile applications in metal-catalyzed cross-coupling reactions. Notably, Suzuki–Miyaura cross-coupling reaction is one of the most successful methodologies to utilize the organoboron for carbon–carbon bond formation.[1] Arylboronic acids/boronate esters are highly stable and nontoxic, which are desirable properties for coupling reactions. The conventional route for preparing arylboronic acids and esters goes through the metal–halogen exchange (e.g., Mg or Li) from aryl bromides/iodides and subsequent trapping with trialkylborates. However, this synthetic pathway is incompatible with base-sensitive functional groups (e.g., aldehyde, ketone, nitrile, etc.).[1] Therefore, additional protection and deprotection steps are required in these routes. Moreover, the aforementioned synthetic protocol is incompatible with relatively inexpensive and broadly available aryl chlorides. To expand the scope of organoboron reagents, transition-metal-catalyzed borylation of aryl halides with alkoxyboranes has emerged. Re, Ru, Rh, and especially Ir catalysts were found to be applicable for the direct C–H borylation of arenes.[2] Miyaura pioneered a Pd-catalyzed borylation of aryl halides in 1995.[3] Recently, a number of palladium-catalyzed processes have emerged for the conversion of aryl iodides/bromides to the corresponding boronate esters.[4,5] Nickel-catalyzed protocols have also been reported by Percec and co-workers.[6] In fact, there are limited palladium catalyst systems that are effective for the borylation of unactivated aryl chlorides, which are generally more desirable as they are relatively low cost and with broad availability.[4c,d,j,p,7] Recently, Buchwald and co-workers reported an active catalyst for the borylation of aryl chlorides.[8] Molander also reported the direct synthesis of arylboronic acids from aryl chlorides using the Pd/XPhos system.[4d] The application of dialkylphosphino-substituted ligands is believed to be the key to generate the highly active Pd catalyst in these borylations. However, the cost of the dialkylphosphino moiety is more readily available than the diphenylphosphino analogue from commercial sources.[9] Therefore, diphenyl-substituted phosphino ligands would be attractive if they can reach certain catalytic activity with respect to dialkylphosphino-derived ligands.[10] Herein, we report our findings of effective ligands bearing a $-PPh_2$ moiety only, for the Pd-catalyzed borylation of aryl chlorides at 0.05–2 mol % Pd loading.

We initially tested the feasibility of aryl chloride borylation using nonactivated 4-chlorotoluene and B_2pin_2 as the model substrates (Table 1). It is well-known that highly electron-rich phosphines (e.g., phosphine containing $-PCy_2$ or $-P$-t-Bu_2 groups) can handle a range of aryl chloride/tosylate couplings. On the contrary, we are interested in investigating the inexpensive $Ar-PPh_2$ scaffold that deals with an aromatic bond-forming reaction from aryl chlorides. Thus, replacing the $-PCy_2$ group with the $-PPh_2$ moiety in our previously reported indolyl ligands gave a series of $Ar-PPh_2$ phosphines **L1**–**L4**.[11] In our initial trials, ligand **L3** (PPh_2-Andole-phos) was found to be the best ligand of choice in this reaction (Table 1, entry 3).

Commonly used inorganic bases were also screened. CsOAc and KOAc were found to be superior to other bases (Table 2, entries 1–7). Stronger bases such as K_2CO_3, K_3PO_4, and CsF (Table 2, entries 3, 4, and 6) undesirably promoted further coupling reactions to generate symmetrical biaryl compounds. This implies an opportunity to undergo sequential Suzuki

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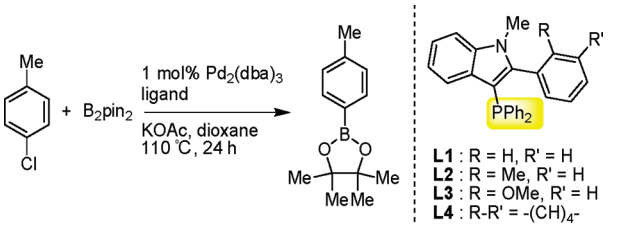
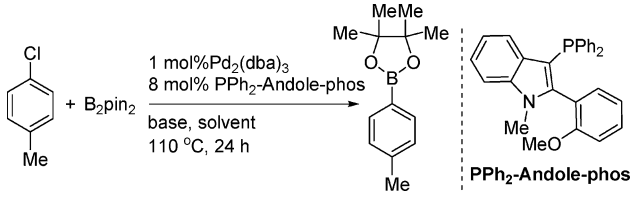
Table 1. Screening of Ligands[a]



entry	ligand	Pd/ligand	yield %[b]
1	**L1**	1:2	20
2	**L2**	1:2	26
3	**L3**	1:2	43
4	**L4**	1:2	33
5	**L3**	1:4	73
6	**L3**	1:8	64

[a]Reaction conditions: ArCl (0.5 mmol), B_2pin_2 (0.75 mmol), KOAc (1.5 mmol), and dioxane (1.5 mL) were stirred for 24 h at 110 °C under nitrogen. [b]Calibrated GC yields were reported using dodecane as internal standard.

Table 2. Initial Optimization of Reaction Parameters[a]



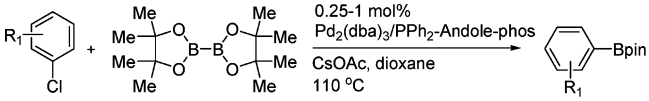
entry	base	solvent	yield %[b]
1	KOAc	dioxane	73
2	CsOAc	dioxane	88
3	K_3PO_4	dioxane	70
4	K_2CO_3	dioxane	81
5	KOPiv	dioxane	70
6	CsF	dioxane	52
7	KF	dioxane	31
8	KOAc	THF	64
9	KOAc	toluene	18
10	KOAc	*t*-BuOH	27
11[c]	KOAc	dioxane	43
12[d]	KOAc	dioxane	36
13[e]	CsOAc	dioxane	69
14[f]	CsOAc	dioxane	88

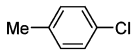
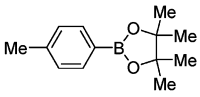
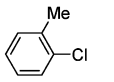
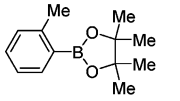
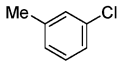
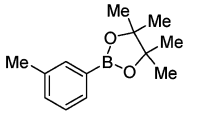
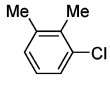
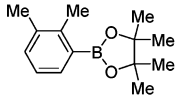
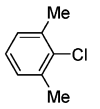
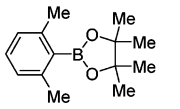
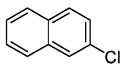
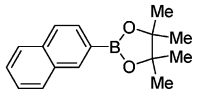
[a]Reaction conditions: ArCl (0.5 mmol), B_2pin_2 (0.75 mmol), base (1.5 mmol), Pd/ligand = 1:4, and solvent (1.5 mL) were stirred for 24 h at 110 °C under nitrogen. [b]Calibrated GC yields were reported using dodecane as internal standard. [c]The reaction was conducted at 90 °C. [d]The reaction was conducted at 130 °C. [e]B_2neop_2 acts as the boron source. [f]B_2pin_2 (0.55 mmol) was used.

reaction to synthesize unsymmetrical biaryl compounds after modifying the reaction conditions. Among organic solvents surveyed, dioxane provided the best product yield when compared with THF, *t*-butyl alcohol, and toluene (Table 2, entries 1 and 8−10). In general, the reaction proceeds faster if the reaction temperature is higher. In our reaction temperature study, either increasing or decreasing the reaction temperature would decrease the desired product yield. A temperature of 110 °C gave the best yield (Table 2, entries 1, 11, and 12) and was thus chosen as the reaction temperature for further study. The use of 1.1 equiv of B_2pin_2 provided the same yield as 1.5 equiv (Table 2, entry 14).

The scope of the borylation reaction was then investigated under the optimized conditions. A range of nonactivated aryl chlorides were examined, and the results are listed in Table 3.

Table 3. Palladium-Catalyzed Borylation of Nonactivated Aryl Chlorides[a]



entry	ArCl	product	Pd (mol%)	yield (%)[b]
1			2	88
2			2	85
3			2	73
4			2	93
5			2	66
6			0.5	90

[a]Reaction conditions: ArCl (0.5 mmol), B_2pin_2 (0.55 mmol), CsOAc (1.5 mmol), Pd/ligand = 1:4, and solvent (1.5 mL) were stirred for 24 h at 110 °C under nitrogen; mol % of Pd (from Pd_2dba_3) with respect to ArCl. [b]Isolated yields.

The nonactivated aryl chlorides containing *ortho*-methyl-substituted groups were found to be compatible coupling partners (Table 3, entries 2 and 4). The highly sterically hindered aryl chlorides could also be coupled to furnish product in moderate yield (Table 3, entry 5).[12]

Apart from nonactivated aryl chlorides, activated aryl chlorides were also applicable substrates in the Pd/PPh_2-Andole-phos catalytic system (Table 4). KOAc was found to be a better base than CsOAc for the borylation of activated aryl chlorides. Common functional groups such as −CN, $-NO_2$, −CHO, −COMe, −COOMe, and $-CF_3$ were compatible under these mild reaction conditions (Table 4, entries 1−9). Excellent yields were generally obtained using 0.05 to 1 mol % of Pd. 4-Chlorobenzaldehyde showed a better yield when a higher catalyst loading and shorter reaction time were used (Table 4, entry 9). It is noteworthy that the scope of borylation of chloride can also be extended to vinyl chloride (Table 4, entry 11). Excellent product yield from 1-chlorocyclopent-1-ene was obtained. Heteroaryl chloride was also examined. 2-Chlorothiophene provided moderate product yield (Table 4, entry 12).

In light of further application of borylation for subsequent biaryl synthesis, we are attracted to examine a one-pot procedure for generating unsymmetrical biaryls starting from both electrophilic partners. The one-pot two-step unsymmetrical biaryl synthesis could be successfully achieved by adding the second

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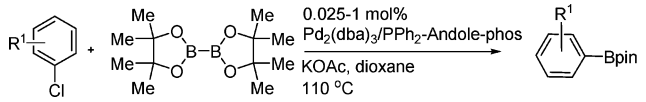
Table 4. Palladium-Catalyzed Borylation of Activated Aryl, Heteroaryl, and Vinyl Chlorides[a]



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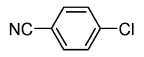
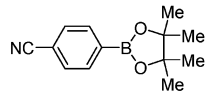
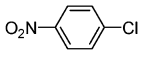
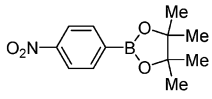
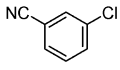
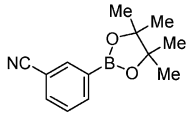
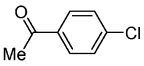
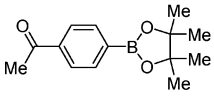
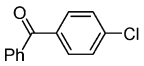
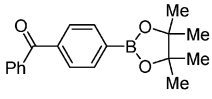
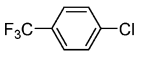
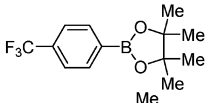
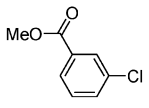
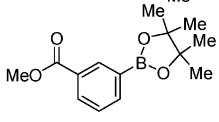
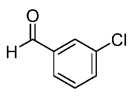
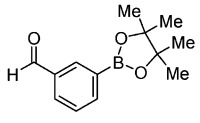
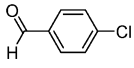
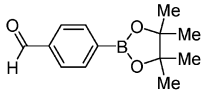
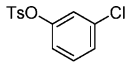
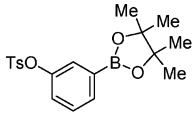
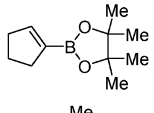
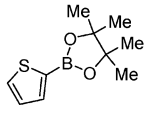
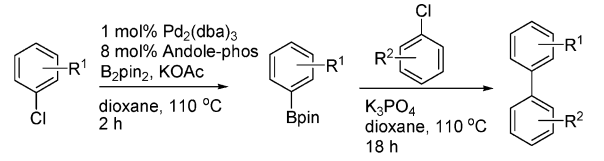
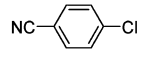
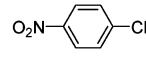
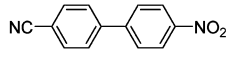
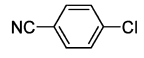
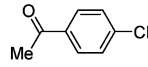
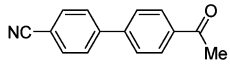
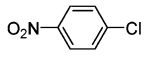
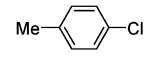
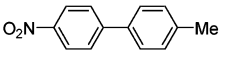
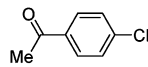
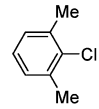
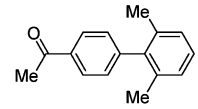
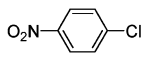
1			0.05	90
2			0.05	88
3			0.1	80
4			0.1	97
5			0.1	90
6			0.2	90
7			0.6	91
8			0.6	91
9[c]			1.0	88
10			0.5	80
11			2.0	86
12			2.0	40

[a]Reaction conditions: ArCl (1.0 mmol), B_2pin_2 (1.1 mmol), CsOAc (3.0 mmol), Pd/ligand = 1:4, and solvent (3.0 mL) were stirred for 24 h at 110 °C under nitrogen; mol % of Pd (from Pd_2dba_3) with respect to ArCl. [b]Isolated yields. [c]The reaction was stirred for 2 h.

aryl chlorides and K_3PO_4 base after the borylation reaction without isolation of the borylated intermediates (Table 5). In particular, no additional catalyst was added before conducting the second Suzuki step in the reaction sequence. A wide range of substrate scope can be tolerated by using this catalytic system (Table 5), including heteroaryl and sterically hindered aryl chlorides (Table 5, entries 4–8).

Table 5. Palladium-Catalyzed One-Pot Two-Step Preparation of Unsymmetrical Biaryl Compounds[a]



entry	1st ArCl	2nd ArCl	product	yield (%)[b]
1[c]				88
2[c]				95
3				87
4				88
5				78
6				89
7				76
8				68

[a]Reaction conditions: 1st aryl chlorides (0.5 mmol), 2nd aryl or heteroaryl chlorides (0.5 mmol), B_2pin_2 (0.505 mmol), KOAc(1.5 mmol), K_3PO_4 (1.5 mmol), dioxane (2.0 mL), Pd/ligand =1:4. [b]Isolated yields. [c]Second step was stirred for 2 h.

In summary, we have achieved the first general borylation of aryl chlorides using a ligand with only a $-PPh_2$ moiety. The indolyl phosphine ligands with a significantly cheaper diphenylphosphino moiety are able to handle the borylation of aryl chlorides which could only deal with dialkylphosphino-substituted phosphine ligands in the previous reports. With the Pd/PPh_2-Andole-phos catalyst system, a range of aryl chlorides bearing base-sensitive functional groups ($-CN$, $-NO_2$, $-CHO$, $-COMe$, $-COOMe$) can be converted to their borylated products. The catalyst loading ranges from 0.05 to 2 mol % of Pd in general. A direct synthesis of unsymmetrical biaryls from aryl chlorides using one-pot two-step procedures can also be successfully accomplished using this catalyst system.

EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All borylation reactions were performed in resealable screw cap Schlenk flasks (approximately 20 mL volume) in the presence of a Teflon-coated magnetic stir bar (4 mm × 10 mm). Dioxane, toluene,

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and tetrahydrofuran (THF) were distilled from sodium and sodium benzophenone ketyl under nitrogen. All indolyl ligands were prepared according to the reported procedures.[11] Commercially available aryl chlorides (liquid form only) were purified by passing through a short plug (0.5 cm width × 4 cm height) of neutral alumina or distillation. Thin layer chromatography was performed on precoated silica gel 60 F_{254} plates. Silica gel (70−230 and 230−400 mesh) was used for column chromatography. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm) or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak). Coupling constants (J) were reported in hertz (Hz). High-resolution mass spectra (HRMS) were obtained on a FT-ICR mass spectrometer (ESIMS).

General Procedure for Screening: $Pd_2(dba)_2$ (0.0046 g, 0.005 mmol) and ligand (Pd/L = 1:4) were loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar. The tube was evacuated and flushed with nitrogen for three cycles. Precomplexation was applied by adding freshly distilled solvent (0.5 mL) into the tube. The palladium complex stock solution was stirred for 10 min. 4-Chlorotoluene (0.5 mmol), boron source (0.75 mmol), and base (1.5 mmol) were loaded into the tube. The solvent (1 mL) was added with continuous stirring at room temperature. The tube was then placed into a preheated oil bath with the temperature indicated in the table and stirred for 24 h. After the completion of the reaction, the reaction tube was allowed to cool at room temperature. Ethyl acetate (~10 mL), dodecane (113 μL, internal standard), and water were added. The organic layer was subjected to GC analysis. The GC yield obtained was previously calibrated by authentic sample/dodecane calibration curve.

General Procedure for Borylation of Aryl Chlorides: $Pd_2(dba)_3$ (0.0046 g, 0.005 mmol) and ligand (Pd/L = 1:4) were loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar. The tube was evacuated and flushed with nitrogen three times. Precomplexation was applied by adding freshly distilled dioxane (0.5 mL) into the tube. The solution was stirred for 10 min. Aryl chloride (0.5 mmol), B_2pin_2 (0.55 mmol), and KOAc (1.5 mmol) were loaded into the tube. Dioxane (1.0 mL) was then added with continuous stirring at room temperature. The tube was placed into a preheated oil bath (110 °C) for the time period as indicated in the table. After the completion of the reaction, the reaction tube was allowed to cool at room temperature. Ethyl acetate (~10 mL) and water were added. The organic layer was subjected to GC analysis. The aqueous layer was washed with ethyl acetate. The filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (230−400 mesh) to afford the desired product.

General Procedure for One-Pot Two-Step Coupling of Aryl Chloride: $Pd_2(dba)_3$ (0.0046 g, 0.005 mmol) and ligand (Pd/L = 1:4) were loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar. The tube was evacuated and flushed with nitrogen three times. Precomplexation was applied by adding freshly distilled dioxane (0.5 mL) into the tube. The solution was stirred for 10 min. The first aryl chloride (0.5 mmol), B_2pin_2 (0.505 mmol), and KOAc (1.5 mmol) were loaded into the tube. Dioxane (1 mL) was then added with continuous stirring at room temperature. The tube was then placed into a preheated oil bath (110 °C) for the time period as indicated in the table. After the completion of the reaction, the reaction tube was allowed to cool at room temperature. K_3PO_4 and the second aryl or heteroaryl chlorides were loaded into the tube under nitrogen. Dioxane (0.5 mL) was added with continuous stirring at room temperature. The tube was then placed into a preheated oil bath (110 °C) for the time period as indicated in the table. After the completion of the reaction, the reaction tube was allowed to cool at room temperature. Ethyl acetate (~10 mL) and water were added. The organic layer was subjected to GC analysis. After analyzing GC spectra, the crude product in the organic layer was extracted. The aqueous layer was washed with EtOAc. The filtrate was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230−400 mesh) to afford the desired product.

4,4,5,5-Tetramethyl-2-*p*-tolyl-1,3,2-dioxaborolane (Table 3, entry 1).[4e] Eluents (EtOAc/hexane = 1:40, R_f = 0.38) was used for flash column chromatography: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 12H), 2.42 (s, 3H), 7.25 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 24.8, 83.5, 128.5, 134.8, 141.3; MS (EI) m/z (relative intensity) 218.1 (M^+, 31), 203.1 (43), 132.1 (60), 119.1 (100), 91.1 (14).

4,4,5,5-Tetramethyl-2-*o*-tolyl-1,3,2-dioxaborolane (Table 3, entry 2).[4e] Eluents (EtOAc/hexane = 1:40, R_f = 0.35) was used for flash column chromatography: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (s, 12H), 2.61 (s, 3H), 7.21−7.24 (m, 2H), 7.38 (t, J = 7.6 Hz, 1H), 7.84 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 24.9, 83.3, 124.7, 129.7, 130.8, 135.8, 144.8; MS (EI) m/z (relative intensity) 218.1 (M^+, 23), 203.1 (36), 161.1 (83), 119.1 (100), 91.1 (21).

4,4,5,5-Tetramethyl-2-*m*-tolyl-1,3,2-dioxaborolane (Table 3, entry 3).[13] Eluents (EtOAc/hexane = 1:40, R_f = 0.35) was used for flash column chromatography: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 12H), 2.41 (s, 3H), 7.33 (d, J = 4.8 Hz, 2H), 7.67−7.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 24.8, 83.6, 127.6, 131.7, 132.0, 135.3 137.0; MS (EI) m/z (relative intensity) 218.1 (M^+, 36), 203.1 (43), 132.1 (77), 119.1 (100), 91.1 (17).

4,4,5,5-Tetramethyl-2-(2,3-dimethylphenyl)-1,3,2-dioxaborolane (Table 3, entry 4).[14] Eluents (EtOAc/hexane = 1:40, R_f = 0.38) was used for flash column chromatography: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (s, 12H), 2.34 (s, 3H), 2.55 (s, 3H), 7.15 (t, J = 7.4 Hz, 1H), 7.28 (d, J = 6.8 Hz, 1H), 7.69 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4, 20.4, 24.8, 83.4, 124.8, 132.3, 133.5, 136.4, 143.0; MS (EI) m/z (relative intensity) 232.1 (M^+, 36), 217.1 (20), 175.1 (100), 132.1 (77).

4,4,5,5-Tetramethyl-2-(2,6-dimethylphenyl)-1,3,2-dioxaborolane (Table 3, entry 5).[4c] Eluents (EtOAc/hexane = 1:40, R_f = 0.35) was used for flash column chromatography: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (s, 12H), 2.47 (s, 6H), 7.00 (d, J = 7.6 Hz, 2H), 7.18 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 24.9, 83.6, 126.4, 129.1, 141.7; MS (EI) m/z (relative intensity) 232.1 (M^+, 31), 217.1 (7), 175.1 (100), 132.1 (64), 105.1 (13).

4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (Table 3, entry 6).[15] Eluents (EtOAc/hexane = 1:40, R_f = 0.33) was used for flash column chromatography: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (s, 12H), 7.55−7.59 (m, 2H), 7.90−7.94 (m, 2H), 7.99 (d, J = 8.4 Hz, 2H), 8.53 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.8, 83.8, 125.7, 126.9, 127.6, 128.5, 130.4, 132.8, 135.0, 136.2; MS (EI) m/z (relative intensity) 254.1 (M^+, 46), 239.1 (11), 168.1 (64), 154.1 (100).

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (Table 4, entry 1).[16] Eluents (EtOAc/hexane = 1:30, R_f = 0.24) was used for flash column chromatography: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (s, 12H), 7.61 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7, 84.3, 114.4, 118.6, 130.9, 134.9; MS (EI) m/z (relative intensity) 229.1 (M^+, 10), 214.1 (100), 143.1 (71), 130.1 (46), 103.0 (6).

4,4,5,5-Tetramethyl-2-(4-nitrophenyl)-1,3,2-dioxaborolane (Table 4, entry 2).[17] Eluents (EtOAc/hexane = 1:30, R_f = 0.24) was used for flash column chromatography: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (s, 12H), 7.95 (d, J = 8.4 Hz, 2H), 8.17 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.8, 84.5, 122.3, 135.6, 149.7; MS (EI) m/z (relative intensity) 249.1 (M^+, 4), 234.1 (100), 163.1 (61), 150.0 (29).

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (Table 4, entry 3).[18] Eluents (EtOAc/hexane = 1:30, R_f = 0.21) was used for flash column chromatography: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (s, 12H), 7.46 (t, J = 9.5 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 8.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7, 84.3, 111.9, 118.6, 128.3, 134.2, 138.2, 138.6; MS (EI) m/z (relative intensity) 229.1 (M^+, 19), 214.1 (94), 143.1 (100), 130.1 (61).

1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-ethanone (Table 4, entry 4).[19] Eluents (EtOAc/hexane = 1:30, R_f = 0.12) was used for flash column chromatography: ^{1}H NMR

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(400 MHz, $CDCl_3$) δ 1.34 (s, 12H), 2.59 (s, 3H), 7.90 (d, J = 12.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7, 26.6, 84.1, 127.1, 134.8, 138.9, 198.2; MS (EI) m/z (relative intensity) 246.1 (M^+, 14), 231.1 (100), 203.1 (7), 160.1 (36), 147.0 (99), 131.0 (26).

(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-(phenyl)methanone (Table 4, entry 5).[18] Eluents (EtOAc/hexane = 1:30, R_f = 0.30) was used for flash column chromatography: ^1H NMR (400 MHz, $CDCl_3$) δ 1.38 (s, 12H), 7.48 (t, J = 7.6 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.80 (t, J = 8.6 Hz, 4H), 7.95 (d, J = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.8, 84.1, 128.2, 128.9, 130.0, 132.4, 134.5, 137.4, 139.7, 196.7; MS (EI) m/z (relative intensity) 308.1 (M^+, 68), 293.1 (70), 231.1 (25), 209.1 (100), 105.1 (77), 77.1 (38).

2-(4-(Trifluoromethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 4, entry 6).[4e] Eluents (EtOAc/hexane = 1:30, R_f = 0.35) was used for flash column chromatography: ^1H NMR (400 MHz, $CDCl_3$) δ 1.38 (s, 12H), 7.65 (d, J = 7.6 Hz, 2H), 7.96 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.8, 84.2, 122.8, 124.2, 125.5, 128.2, 132.8; ^{19}F NMR (400 MHz, $CDCl_3$) δ −63.0; MS (EI) m/z (relative intensity) 272.1 (M^+, 9), 257.1 (100), 186.1 (79), 173.1 (80), 153.0 (7).

Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzoate (Table 4, entry 7).[18] Eluents (EtOAc/hexane = 1:30, R_f = 0.24) was used for flash column chromatography: ^1H NMR (400 MHz, $CDCl_3$) δ 1.35 (s, 12H), 3.91 (s, 3H), 7.45 (t, J = 7.6 Hz, 1H), 7.99 (d, J = 7.2 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 8.48 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.8, 51.9, 84.0, 127.7, 129.4, 132.2, 135.7, 139.1, 167.0; MS (EI) m/z (relative intensity) 262.1 (M^+, 10), 247.1 (27), 231.1 (14), 219.1 (100), 163.1 (79), 131.0 (29), 103.1 (29).

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-benzaldehyde (Table 4, entry 8).[20] Eluents (EtOAc/hexane = 1:30, R_f = 0.21) was used for flash column chromatography: ^1H NMR (400 MHz, $CDCl_3$) δ 1.33 (s, 12H), 7.49 (t, J = 7.4 Hz, 1H), 7.94 (d, J = 7.6 Hz, 1H), 8.03 (d, J = 7.2 Hz, 1H), 8.28 (s, 1H), 10.1 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7, 84.0, 128.2, 131.1, 135.6, 136.9, 140.4, 192.2; MS (EI) m/z (relative intensity) 232.1 (M^+, 29), 217.1 (46), 189.1 (50), 172.1 (14), 146.1 (27), 133.1 (100).

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-benzaldehyde (Table 4, entry 9).[18] Eluents (EtOAc/hexane = 1:30, R_f = 0.24) was used for flash column chromatography: ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (s, 12H), 7.84 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 8.0 Hz, 2H), 10.02 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7, 84.2, 128.5, 135.1, 138.0, 192.3; MS (EI) m/z (relative intensity) 232.1 (M^+, 19), 217.1 (96), 203.1 (1), 146,1 (89), 133.1 (100).

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl 4-methylbenzenesulfonate (Table 4, entry 10). Eluents (EtOAc/hexane = 1:20, R_f = 0.25) was used for flash column chromatography: colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 12H), 2.44 (s, 3H), 7.02−7.05 (m, 1H), 7.26−7.32 (m, 3H), 7.44 (s, 1H), 7.68 (d, J = 7.2 Hz, 1H), 7.71 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 24.7, 84.0, 124.9, 128.3, 128.4, 129.0, 129.6, 132.3, 133.2, 145.2, 149.2; MS (EI) m/z (relative intensity) 374.1 (M^+, 39), 359.1 (16), 177.1 (24), 155.0 (77), 91.1 (100); HRMS (ESI) calcd for $C_{19}H_{23}O_5SB$ [M + Na^+] 397.1257, found 397.1266.

2-Cyclopentenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 4, entry 11).[8a] Eluents (EtOAc/hexane = 1:40, R_f = 0.16) was used for flash column chromatography: ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (s, 12H), 1.80−1.89 (m, 2H), 2.39−2.47 (m, 4H), 6.56 (t, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.9, 24.7, 34.4, 34.7, 83.0, 147.5; MS (EI) m/z (relative intensity) 194.1 (M^+, 23), 179.1 (31), 165.1 (29), 108.1 (100), 67.1 (46).

4,4,5,5-Tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (Table 4, entry 12).[21] Eluents (EtOAc/hexane = 1:40, R_f = 0.23) was used for flash column chromatography: ^1H NMR (400 MHz, $CDCl_3$) δ 1.38 (s, 12H), 7.22−7.24(m, 1H), 7.66−7.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7, 84.0, 128.2, 132.3, 137.1; MS (EI) m/z (relative intensity) 210 (M^+, 43), 195.0 (41), 124 (72), 111.0 (100), 85 (24).

4-(4-Nitrophenyl)benzonitrile (Table 5, entry 1).[22] Eluents (EtOAc/hexane = 1:4, R_f = 0.34) was used for flash column chromatography: ^1H NMR (400 MHz, $CDCl_3$) δ 7.75−7.83 (m, 6H), 8.37 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.7, 118.3, 124.3, 128.0, 128.1, 132.9, 143.1, 145.4, 147.9; MS (EI) m/z (relative intensity) 224.0 (M^+, 100), 194.0 (36), 177.0 (50), 151.0 (57), 140.0 (14).

4-(4-Acetophenyl)benzonitrile (Table 5, entry 2).[23] Eluents (EtOAc/hexane = 1:9, R_f = 0.15) was used for flash column chromatography: ^1H NMR (400 MHz, $CDCl_3$) δ 2.61 (s, 3H), 7.65−7.71 (m, 6H), 8.04 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.5, 111.5, 118.4, 127.2, 127.7, 128.9, 132.5, 136.6, 143.2, 143.9, 197.2; MS (EI) m/z (relative intensity) 221.1 (M^+, 33), 206.1 (100), 178.0 (23), 151.0 (24), 103.1 (3).

4-(4-Nitrophenyl)toluene (Table 5, entry 3).[24] Eluents (EtOAc/hexane = 1:20, R_f = 0.53) was used for flash column chromatography: ^1H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3H), 7.33 (d, J = 7.6 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 7.0 Hz, 2H), 8.29 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 124.0, 127.1, 127.4, 129.8, 135.7, 139.0, 146.8, 147.5; MS (EI) m/z (relative intensity) 213.0 (M^+, 100), 183.0 (26), 165.0 (49), 152.0 (69), 139.0 (10).

2-Acetophenyl-1,3-dimethylbenzene (Table 5, entry 4).[25] Eluents (EtOAc/hexane = 1:50, R_f = 0.31) was used for flash column chromatography: ^1H NMR (400 MHz, $CDCl_3$) δ 2.07 (s, 6H), 2.70 (s,3H), 7.17 (d, J = 6.0 Hz, 2H), 7.23 (t, J = 6.0 Hz, 1H), 7.31 (d, J = 6.8 Hz, 2H), 8.09 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 26.4, 127.3, 127.4, 128.5, 129.3, 135.4, 135.6, 140.6, 146.3, 197.6; MS (EI) m/z (relative intensity) 224.1 (M^+, 44), 209.1 (100), 178.1 (6), 165.1 (39), 115.1 (3), 106.0 (1).

3-Methyl-2-(4-nitrophenyl)thiophene (Table 5, entry 5). Eluents (EtOAc/hexane = 1:15, R_f = 0.35) was used for flash column chromatography: yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 7.02 (d, J = 8.4 Hz, 1H), 7.36 (d, J = 5.2 Hz, 1H), 7.64 (d, J = 7.0 Hz, 2H), 8.28 (d, J = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 123.8, 125.5, 129.1, 131.8, 135.3, 135.4, 141.5, 146.4; MS (EI) m/z (relative intensity) 219.0 (M^+, 100), 203.0 (1), 189.0 (28), 171.0 (36), 128.1 (27); HRMS (ESI) calcd for $C_{11}H_9NO_2S$ [M + H^+] 220.0432, found 220.0441.

2-(4-Nitrophenyl)quinoline (Table 5, entry 6). Eluents (EtOAc/hexane = 1:4, R_f = 0.41) was used for flash column chromatography: yellow solid; mp 123.5−127.9 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (t, J = 7.2 Hz, 1H), 7.78 (t, J = 7.2 Hz, 1H), 7.87 (t, J = 9.6 Hz, 2H), 8.19 (d, J = 8.4 Hz, 1H), 8.27 (d, J = 8.4 Hz, 1H), 8.33 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.6, 123.9, 127.2, 127.5, 128.1, 129.8, 130.1, 137.2, 145.3, 148.2, 154.3; MS (EI) m/z (relative intensity) 250 (M^+, 100), 220 (7), 204 (99), 128 (10); HRMS (ESI) calcd for $C_{15}H_{10}N_2O_2$ [M + H^+] 251.0821, found 251.0811.

3-(5-Acetylthiophen-2-yl)benzonitrile (Table 5, entry 7). [CAS Registry Number; 893741-59-8] Eluents (EtOAc/hexane = 1:4, R_f = 0.16) was used for flash column chromatography: ^1H NMR (400 MHz, $CDCl_3$) δ 2.58 (s, 3H), 7.37 (d, J = 4.0 Hz, 1H), 7.53 (t, J = 8.0 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.69 (d, J = 4.0 Hz, 1H), 7.83−7.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.5, 113.3, 118.0, 125.1, 129.3, 130.2, 131.9, 133.3, 134.4, 144.4, 149.1, 190.3; MS (EI) m/z (relative intensity) 227.0 (M^+, 40), 212.0 (100), 140.0 (44), 113.0 (6).

3-(Acridin-9-yl)benzonitrile (Table 5, entry 8). Eluents (EtOAc/hexane = 1:1, R_f = 0.55) was used for flash column chromatography: yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48−7.52 (m, 2H), 7.57−7.59 (m, 2H), 7.72−7.85 (m, 5H), 7.91−7.94 (m, 1H), 8.33 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.1, 118.3, 124.7, 125.8, 126.4, 129.5, 129.9, 130.2, 132.1, 133.8, 134.9, 137.5, 143.8, 148.7; MS (EI) m/z (relative intensity) 280.1 (M^+, 100), 251.0 (10), 207.0 (6), 177.0 (1), 126.0 (14); HRMS (ESI) calcd for $C_{20}H_{12}N_2$ [M + H^+] 281.1079, found 281.1070.

■ ASSOCIATED CONTENT

Supporting Information

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

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AUTHOR INFORMATION

Corresponding Author

*E-mail: bcfyk@inet.polyu.edu.hk.

Notes

The authors declare no competing financial interest.

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