Directed Catalytic C–H Functionalization of Organoboronic Acids Utilizing Removable Directing Groups on the Boron Atom

Hideki Ihara

2014

Preface

Studies presented in this thesis were conducted at Kyoto University under the direction of Professor Michinori Suginome between 2007 and 2009. These studies dealt with the directed catalytic C–H functionalization of organoboronic acids utilizing removable directing groups on the boron atom.

First, the author would like to express his sincere appreciation to Professor Michinori Suginome for his patience, graciousness, generosity as well as his unique and stimulating perception and wonderful insights.

The author would like to acknowledge Associate Professor Toshimichi Ohmura for his constructive suggestions and warm encouragement, Assistant Professor Yuuya Nagata for his generous support and performing the X-ray crystallographic analysis of pyrazolylaniline derivatives, and Assistant Professor Takeshi Yamamoto for his helpful support throughout this thesis.

The author is grateful to Professor Hideki Amii from Gunma University for introducing Professor Suginome to him.

The author was fortunate to have an opportunity to study with Mr. Masashi Koyanagi, and acknowledges his devoted cooperation and great contribution to this work, in particular. The author also wishes to express his gratitude to Mr. Akinori Ueda for earnest collaboration and Dr. Tomotsugu Awano for advice and willing support in the completion of this thesis.

The author wishes to express his gratitude to Dr. Yusuke Tanaka, Dr. Noriyuki Iwadate, Dr. Masaki Daini, Dr. Masamichi Shirakura, Dr. Hiroki Taniguchi, Dr. Tetsuya Yamada, Mr. Satoru Ohashi, Mr. Yuji Komatsu, Mr. Kentaro Sakano, Dr. Kohei Masuda, Dr. Takeharu Toyoshima, Dr. Kazuyuki Oshima, Mr. Takayuki Shioda, Mr. Yuta Takasaki, Mr. Akihito Kijima, Mr. Katsuya Shomizu, Ms. Kanayo Nakada, Mr. Kousuke Hidaka, Mr. Masato Fujita, Mr. Kenta Kuchida, Mr. Ichiro Takase, Mr. Hikaru Takahashi, Mr. Ryosuke Yasui, Mr. Hiroyuki Yanagi, Mr. Yuto Akai, Mr. Yusuke Komori, Mr. Hiroaki Nasu, Dr. Pierrick Nun, Mr. Nils Eichenauer and Ms. Yuki Sakai for their support, kindness, and memorable experiences.

The author would like to thank Ms. Junko Sasaki and Ms. Ayako Oyabu for their overall support, Dr. Keiko Kuwata for mass spectroscopy measurements, Mr. Haruo Fujita for nuclear magnetic resonance (NMR) spectroscopy measurements, and the staff at the Microanalysis Center of Kyoto University for elemental analysis.

The author is grateful to Sumitomo Chemical Co. Ltd for making this challenging opportunity worthwhile.

The author would like to express his gratitude to his parents, Mr. Tadayoshi Ihara and Mrs. Kazuko Ihara, for their encouragement.

Last but not least, the author thanks his wife, Mrs. Tomomi Ihara, for her considerable support and countless words of encouragement and his daughter, Ms. Ako Ihara, for being there for him.

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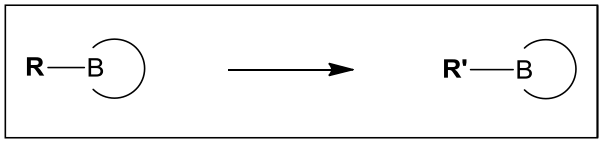
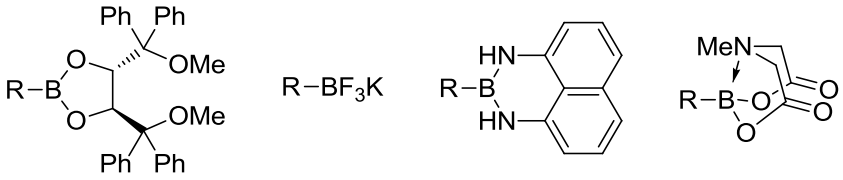
Contents

General Introduction

Organoboronic acids[1] play a central role in organic synthesis, and have been utilized in a variety of reactions, including Suzuki–Miyaura cross-coupling,[2] Matteson reaction,[3] Petasis reaction,[4] and Miyaura conjugate addition[5]. They have also been widely used as functional material components and biologically active compounds such as anticancer agents.[1]

Recently, the development of new strategies for the efficient functionalization of organoboronic acids has attracted increasing attention. Many studies have been conducted for an effective C–B bond formation. Although the boronyl group [$B(OH)_2$] tolerates various transformations, masking or protecting these functional groups has also been found advantageous during transformations involving organoboronic acids. For example, bulky boronic acid ester[6] and trifluoroborate[7] groups have been utilized to protect boronyl groups during cyclopropanations and oxidations. More recently, boronic acids have been masked efficiently using 1,8-diaminonaphthalene[8] and *N*-methyliminodiacetic acid,[9] enabling iterative cross-coupling systems for the selective synthesis of oligoarenes.



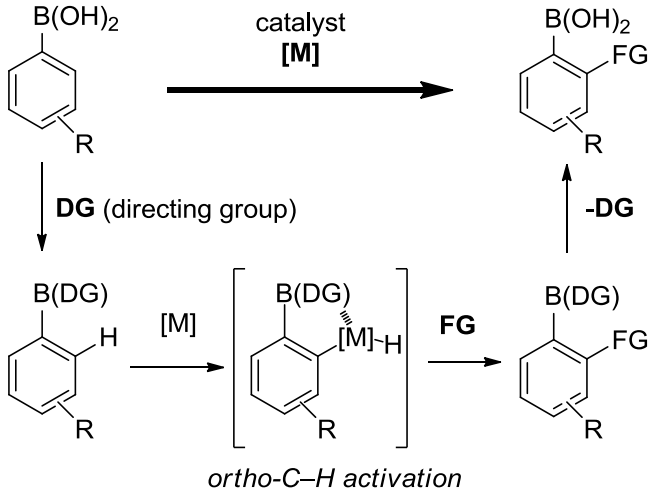


Since the 1990s, much attention has been paid to C–H bond activation by transition metal complexes using a directing group. This approach enables the site-selective functionalization of more readily available starting materials.[10] In conventional directed C–H activation systems, the directing groups are attached to a substrate in advance, significantly limiting substrate choice. To solve this problem, removable directing groups such as 2-pyridyl[11] and hydrosilyl groups[12] have been developed.[13]

To expand the scope of directed C–H activation strategy, the author was interested in designing new directing groups that are attachable and detachable to the boron atom of organoboronic acids. These removable directing groups facilitate the functionalization of simple and readily available organoboronic acids. Moreover, this strategy enables multiple

post-C–H-activation functionalizations of aromatic compounds through the conversion of boronyl groups into a variety of functional groups by the virtue of their rich reactivity.

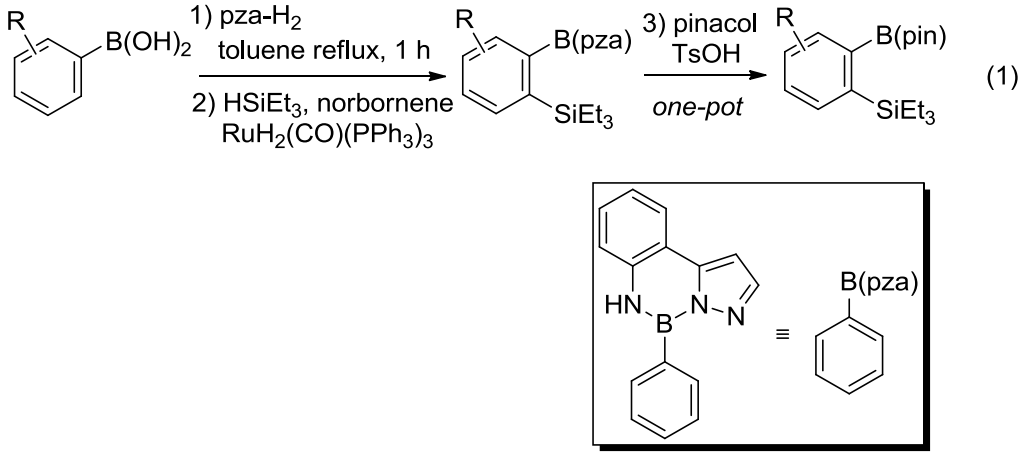
This thesis describes boron-based organic syntheses that effectively utilized newly designed directing groups. In this unprecedented strategy, the directing groups were easily removable, traceless, and recyclable. The thesis outline is given below.



Scheme 1. *ortho*-C–H Functionalization of Arylboronic Acids via Temporary Introduction of a Removable Directing Group

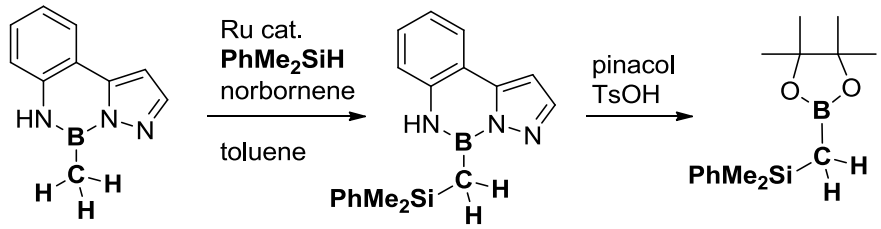
Chapter 1 presents the *ortho*-C–H silylation of arylboronic acids using 2-pyrazol-5-ylaniline as an *ortho*-directing agent. This directing agent was easily attachable, removable in a traceless manner, and recyclable.

The products of the condensation–dehydration between arylboronic acids and 2-pyrazol-5-ylaniline were allowed to react with hydrosilanes in the presence of $RuH_2(CO)(PPh_3)_3$ at 135 °C. Regioselective silylation proceeded in good yields at the *ortho*-position of the modified arylboronic acids. The silylated products were utilized in Suzuki–Miyaura coupling, followed by iodination with ICl (eq 1).



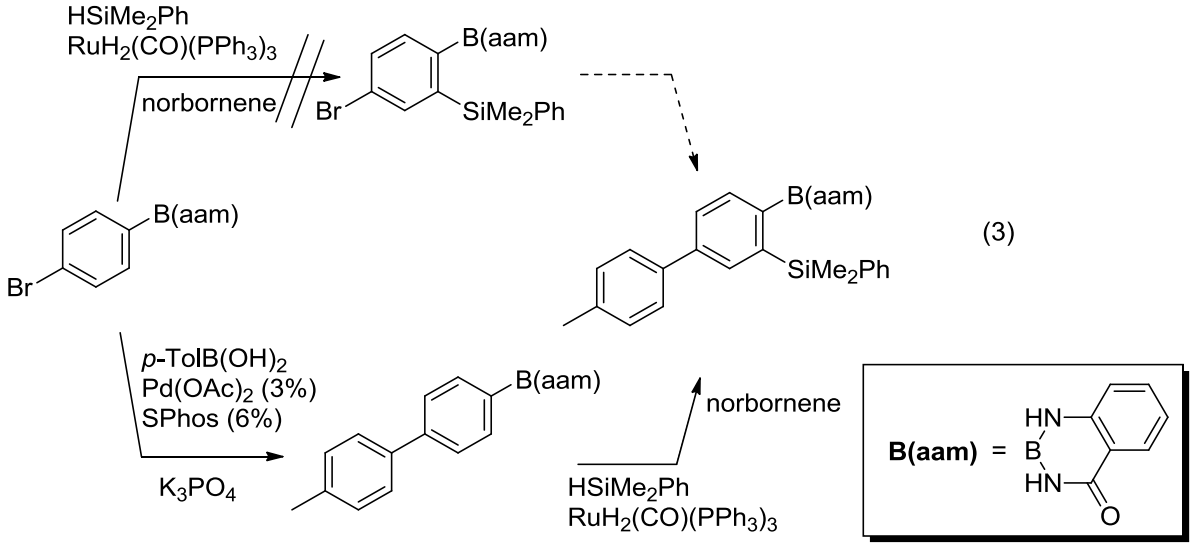
(1)

Chapter 2 deals with the ruthenium-catalyzed α-C–H bond silylation of methyl boronic acid (eq 2). This is the first example of the functionalization of α-C(sp^3)–H bond to boron atom under neutral conditions, which is usually considered to be difficult.



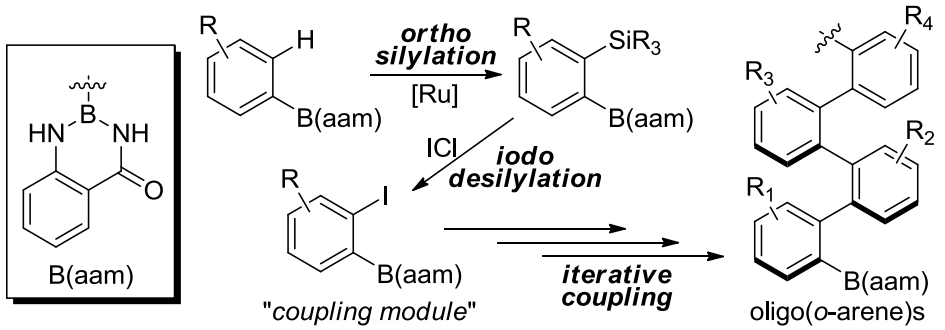
(2)

Chapter 3 reports the use of an anthranilamide as a bifunctional directing group. The anthranilamide also served as a protective group in the Suzuki–Miyaura coupling, and stabilized the boronic acids to a greater extent than pyrazolylaniline, making the products more tolerant to silica gel column chromatography (eq 3).



(3)

Chapter 4 describes the transformation of silylboronic acids into *ortho*-iodoboronic acids. The anthranilamide group acted as a protective group in the iodination step. The resulting *ortho*-iodophenylboronic acid derivatives served as the coupling module in the synthesis of oligoarenes. Iterative Suzuki–Miyaura coupling sequences produced oligo (*o*-phenylene)s and oligo (naphthalene-2,3-diyl)s (eq 4).



(4)

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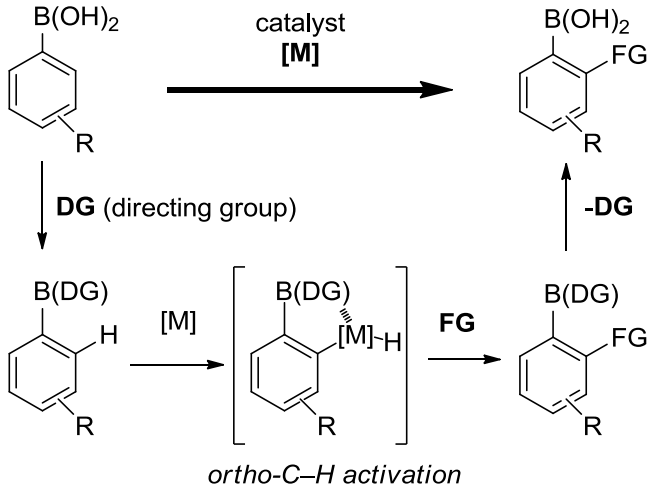
Chapter 1

Easily Attachable and Detachable *ortho*-Directing Agent for Arylboronic Acids in Ruthenium-Catalyzed Aromatic C-H Silylation

Abstract: *Ortho*-C–H silylation of arylboronic acids has been achieved using 2-pyrazol-5-ylaniline as an *ortho*-directing agent, which was temporarily attached to the boronyl group via Ru-catalyzed silylation with hydrosilanes. Condensation products of arylboronic acids with 2-pyrazol-5-ylaniline were prepared in situ and subjected to reaction with triorganosilanes in the presence of $RuH_2(CO)(PPh_3)_3$ at 135 °C. Regioselective silylation at their *ortho*-positions proceeded in good yields for phenylboronic acids bearing *p*-substituents such as chloro, fluoro, methyl, methoxy, and trifluoromethyl groups. *p*-Methoxycarbonyl-substituted phenylboronic acid provided the corresponding silylated product in moderate yield. *m*-Tolyl- and 2-naphthylboronic acids underwent silylation selectively at the less sterically hindered *ortho*-positions. The silylated products were utilized in Suzuki–Miyaura coupling, followed either by iodination with ICl or by Tamao oxidation to furnish iodine or hydroxy-substituted biaryls.

Introduction

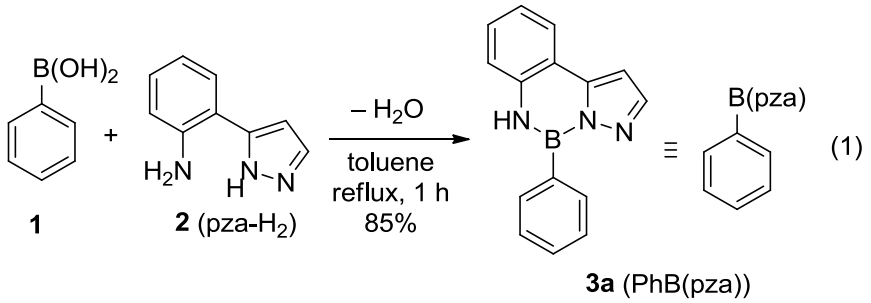
Directed metallation is recognized as an efficient strategy in organic synthesis, because of the enhanced reactivity, regioselectivity, and stereoselectivity through coordination of the directing group to a metal.[1] In particular, *ortho*-directed metallation of aromatic compounds has attracted much attention in the synthesis of functionalized arene derivatives.[2] In addition to stoichiometric metallations such as *ortho*-lithiation,[3] recent interest has also focused on *ortho*-C–H activation with transition-metal catalysts.[1c,4] Triggered by the work by Murai and co-workers,[5] *ortho*-directed C–H functionalization of aromatic compounds has become one of the most actively studied areas in organic synthesis. Although one major drawback of the strategy may be limited substrate scope because of the requirement of the *ortho*-directing group itself, a removable directing group has been reported to overcome this limitation.[6] It seems highly attractive to produce new directing groups that are easily attachable to the starting materials and detachable from the products.[7]



Results and Discussion

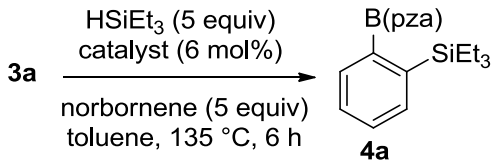
We tested our working hypothesis in ruthenium-catalyzed *ortho*-C–H silylation.[6b,9] In the original reaction system, various oxygen and nitrogen functionalities served as a directing group in the presence of a $Ru_3(CO)_{12}$ catalyst with 3,3-dimethyl-1-butene or norbornene as a hydrogen scavenger. We chose a pyrazole group as an *ortho*-directing element, which could

be introduced onto the boron atom via condensation of phenylboronic acid with 2-pyrazol-5-ylaniline (eq 1).[10] The reaction afforded the condensation product **3a** in high yield, which showed reasonable stability toward air and moisture,[11] although it was found to be less stable toward chromatography on silica gel than B(dan) derivatives (dan = naphthalene-1,8-diaminato), which we developed as a protective group for a boronyl group.[12]



The pza derivative **3a** was subjected to catalytic *o*-silylation with triethylsilane (eq 2). We found that $RuH_2(CO)(PPh_3)_3$ catalyst afforded the corresponding *o*-silylation product in high yield, while $Ru_3(CO)_{12}$ and $[RhCl(cod)]_2$ also afforded the same product in much lower yields. It should be remarked that we did not observe silylation at the other positions. All the control experiments using $PhB(OH)_2$, PhB(pin), and PhB(dan) resulted in no reaction under the same reaction conditions.

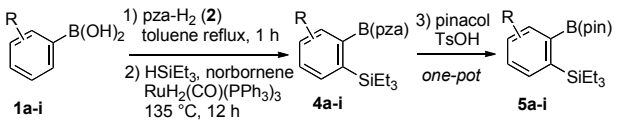
In the presence of the ruthenium catalyst, the reaction of **3a** with a series of hydrosilanes was examined (eq 3). Phenyl-substituted hydrosilanes afforded the corresponding products **4a′** and **4a′′** in high yields. We also obtained $BnMe_2Si$-substituted arene **4a′′′**, which can be utilized for further transformation by virtue of the ready cleavage of the Bn–Si bond.[13] Although TBDMS derivative **4a′′′′** could be obtained in low yield, the use of bulkier TIPS-H resulted in no reaction. Triethoxysilane gave no desired product under the current reaction conditions.



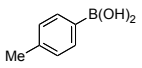
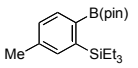
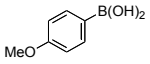
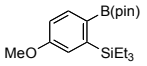
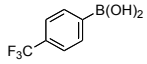
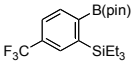
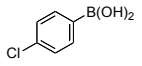
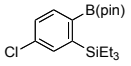
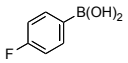
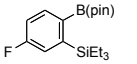
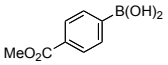
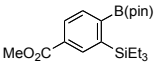
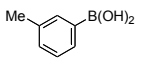
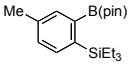
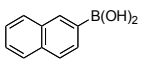
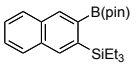
catalyst	NMR yield/%
$RuH_2(CO)(PPh_3)_3$	93
$Ru_3(CO)_{12}$	53
$[RhCl(cod)]_2$	16

(2)

Table 1. One-Pot *ortho*-Silylation of Arylboronic Acids by Using Pyrazolylaniline as a *ortho*-Directing Agent [a]

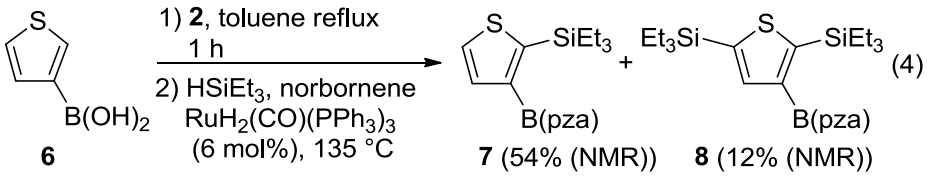


1a-i **4a-i** **5a-i**

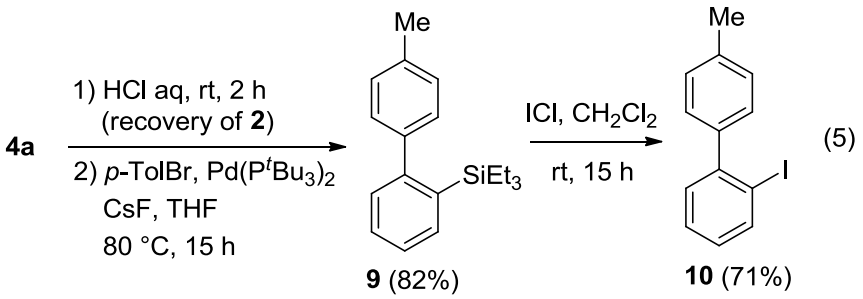
entry	**1**	% yield[b] **4**	% yield[c] **5**	isolated product
1	$PhB(OH)_2$ **(1a)**	97 (89)[d,e]	–	**4a**
2	 (**1b**)	94	80	 (**5b**)
3	 (**1c**)	83	77	 (**5c**)
4	 (**1d**)	86	71	 (**5d**)
5	 (**1e**)	85	78	 (**5e**)
6	 (**1f**)	91	84	 (**5f**)
7	 (**1g**)	47	40	 (**5g**)
8	 (**1h**)	88	74	 (**5h**)
9	 (**1i**)	70	62	 (**5i**)

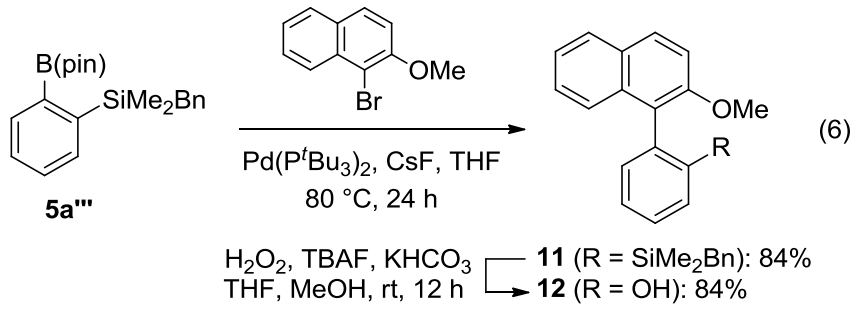
[a] **1a** (0.25 mmol) and **2** (0.25 mmol) were used for the 1st step. In the 2nd step, $RuH_2(CO)(PPh_3)_3$ (15 μmol), norbornene (1.25 mmol), hydrosilane (1.25 mmol), and toluene (0.13 mL) was used. [b] NMR yield. [c] Isolated yield. [d] Isolated yield for **4a** in the parenthesis. [e] $RuH_2(CO)(PPh_3)_3$ (7.5 μmol).

We then carried out the *o*-directed silylation of substituted phenylboronic acid derivatives (Table 1). To facilitate the isolation process, the products were converted into the corresponding pinacolate derivatives by treatment of the reaction mixture with pinacol and TsOH.[14] In the series of reactions shown in Table 1, preparation of the (pza)B derivatives (1 equiv **2**) and the subsequent silylation were carried out in one pot without isolating the pza-attached derivatives **3**. This protocol was found to work efficiently, as demonstrated in the reaction of **1a** (entry 1). Arylboronic acids **1b**–**e** bearing *p*-substituents such as methyl, methoxy, trifluoromethyl, chloro, fluoro, and methoxycarbonyl afforded the corresponding *o*-silylated products in moderate to high yields (entries 2–7). Although the product yields showed no remarkable dependence upon the electronic nature of the *para*-substituents, we observed faster reaction for the more electron-rich arene derivatives. Highly regioselective silylation at the less sterically hindered *ortho*-position was observed in the reaction of *m*-tolylboronic acid (**1h**) (entry 8). It should be noted that almost no formation of double silylation products was detected in these reactions. The sluggishness of the second silylation is likely due to steric factors, since no *o*-silylation was observed at all with *o*-tolylboronic acid.[15] 2-Naphthylboronic acid (**1i**) underwent silylation at the 3-position (entry 9). 3-Thiopheneboronic acid **6** also underwent the directed silylation selectively at its 2-position, although applying a longer reaction time resulted in further silylation at the 5-position, which was not assisted by the directing group (eq 4).[16]



The silylated areneboronic acids served as convenient building blocks for the synthesis of functionalized biaryl derivatives through Suzuki–Miyaura coupling.[17] Silylated product **4a** was transformed into the corresponding boronic acid by an acid treatment and subjected to Suzuki–Miyaura coupling with *p*-tolyl bromide (eq 5). In this reaction, pza-H_2 (**2**) was recovered in 85% yield on acid treatment. The silyl group of **9** was substituted with iodine by treatment with ICl to give biaryl iodide **10**. In another transformation, the silyl group of cross-coupling product **11** was converted into a hydroxy group by Tamao–Fleming oxidation,[12,18] leading to the formation of naphthyl-substituted phenol **12** (eq 6).





Conclusion

In summary, we have reported a new protocol for *ortho*-C-H functionalization of arylboronic acids by using 2-pyrazol-5-ylaniline as an *ortho*-directing group. The key feature of the new directing group is the ease of its installation and removal. Generalization of this protocol to other *o*-C–H functionalizations is now being undertaken in this laboratory.

Experimental Section

General

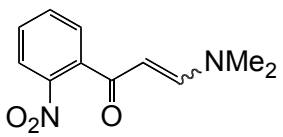
All reactions were carried out under an atmosphere of nitrogen with magnetic stirring. ^{1}H, ^{11}B and ^{13}C NMR spectra were recorded on a Varian Mercury vx400 or a JEOL JNM-A500 spectrometer at ambient temperature. ^{1}H NMR data are reported as follows: chemical shift in ppm downfield from tetramethylsilane (δ scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sex = sextet, m = multiplet, and br = broad), coupling constant (Hz), and integration. ^{13}C NMR chemical shifts are reported in ppm

downfield from tetramethylsilane (δ scale). ^{11}B NMR chemical shifts are reported in ppm downfield from BF_3•OEt_2. All ^{13}C NMR spectra were obtained with broadband proton decoupling. High-resolution mass spectra were recorded on a JEOL JMS-SX102A (EI) and JEOL JMS-HX110A (FAB) spectrometer. IR spectra were recorded on a FTIR SHIMADZU DR-8000 spectrometer. Preparative TLC was performed with silica gel $60PF_{254}$ (Merck). Preparative HPLC was performed with SHIMADZU LC system (LC-10AT, RID-6A, C-R6A) and LiChrosorb®CN (7 μm, 250-25) column. Column chromatography was performed with Ultra Pure Silica Gel (40-63 μm) (Silicycle).

Materials

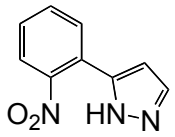
Toluene and THF were dried and deoxygenized using an alumina/catalyst column system (GlassContour Co.). triethylsilane (TCI), dimethylphenylsilane (Aldrich), diphenylmethylsilane (Aldrich), benzyldimethylsilane (Aldrich), *tert*-butyldimethylsilane (Aldrich), triisopropylsilane (TCI), norbornene (TCI), pinacol (TCI), *p*-toluenesulfonic acid monohydrate (Nacalai), phenylboronic acid (Wako), 4-methoxylphenylboronic acid (Aldrich), 4-trifluoromethylphenylboronic acid (Wako), 4-chlorophenylboronic acid (Wako), 4-fluorophenylboronic acid (Wako), 4-(methoxylcarbonyl)phenylboronic acid (TCI), 3-methylphenylboronic acid (TCI), 2-naphthaleneboronic acid (TCI), 3-thiopheneboronic acid (TCI), Florisil® (100-200 mesh, Wako), tetrabutylammonium fluoride (1 M in THF, Aldrich), methanol (Nacalai), *p*-bromotoluene (Wako), CH_2Cl_2 (Nacalai), H_2O_2 (Wako), and $KHCO_3$ (Nacalai) were used as received from the commercial sources. 1-Bromo-2-methoxylnaphtalene,[19] $RuH_2(CO)(PPh_3)_3$,[20] $[RhCl(cod)]_2$,[21] $[Rh(OH)(cod)]_2$,[22] and $Pd(P^tBu_3)_2$ [23] were prepared by the literature procedures. Cesium fluoride (Wako) was dried in an oven at 300 °C for 5 h *in vacuo* (1 mmHg).

Preparation of 2-Pyrazol-5-ylaniline (2): The compound was prepared by a literature procedure [24] with some modifications.



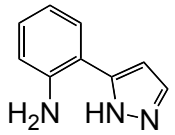
3-(Dimethylamino)-1-(2-nitrophenyl)prop-2-en-1-one:

A solution of *o*–nitroacetophenone (14.85 g, 90 mmol) and *N,N*-dimethylformamide dimethyl acetal (9.67g, 81.3 mmol) in DMF (40 mL) was heated at 100 °C for 2 h. The reaction mixture was concentrated, and the resultant solid was washed with Et_2O and collected by filtration (16.13 g, yellow solid, 90%).



5-(2-Nitrophenyl)-1*H*-pyrazole:

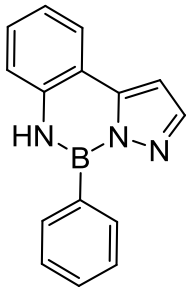
A solution of 3-(Dimethylamino)-1-(2-nitrophenyl)prop-2-en-1-one (16.13 g, 73.3 mmol) and hydrazine monohydrate (4.04 g, 80.6 mmol) in ethanol (73 mL) was refluxed for 9.5 h. The mixture was concentrated, and the resultant residue was subjected to column chlomatography on silica gel to give the title compound as dark oil. (hexane-EtOAc (10:1), 12.9 g, 93%)



2-(1*H*-Pyrazol-5-yl)aniline (2)

A mixture of 5-(2-nitrophenyl)-1*H*-pyrazole (12.9 g, 68.3 mmol) and 5% Pd/C (2.6 g) in ethanol (50 mL) was stirred under a hydrogen atmosphere (balloon pressure) at 50 °C for 24 h. The mixture was filtered, and the filtrate was concentrated. Resultant solid residue was subjected to bulb-to-bulb distillation (200-205 °C/6 mmHg). The crude product was washed with hexane-CH_2Cl_2 and dried to give **2** as white solid. (10.6 g, 98%)

Synthesis of 3a by Condensation of Phenylboronic Acid with 2 (Eq 1):



A mixture of phenylboronic acid (0.767 g, 6.29 mmol) and 2-Pyrazol-5-ylaniline(1.00 g, 6.29 mmol) in toluene (13mL) was heated under reflux in a Dean-Stark apparatus for 1 h. Distillation of the reaction mixture (170-180 °C/0.3 mmHg) gave **3a** (1.31 g, white solid, mp 156°C, 85%).

Procedures for Directed *ortho*-Silylation:

Synthesis of 4a by Directed *ortho*-Silylation of 3a with Triethylsilane (Eq 2): A mixture of **3a** (61.3 mg, 0.25 mmol), metal catalyst (6 mol%), norbornene (118 mg, 1.25 mmol), triethylsilane (199 μL, 1.25 mmol), and anisole (13.6 μL, internal standard) in toluene (0.13 mL) was heated in a glass tube sealed with a J-Young Teflon stopper at 135°C for 6 h. A portion of the sample was taken in an NMR tube and diluted with $CDCl_3$ to determine the NMR yields.

Control experiments

Instead of **3a**, $PhB(OH)_2$ (0.25 mmol, 30.5 mg), PhB(pin) (0.25 mmol, 51.0 mg), or PhB(dan) (0.25 mmol, 61.0 mg) was reacted under the same reaction conditions as 2.3.1. All reactions resulted in complete recovery of the starting materials.

Effect of exogenous additives

A reaction of **3a** (61.3 mg, 0.25 mmol) with triethylsilane (199 μL, 1.25 mmol) was carried out in the presence of pyridine (0.25mmol, 20 μL) or acetophenone (0.25mmol, 29.1μL) under the same reaction conditions. The reaction was more sluggish than the corresponding reaction in the absence of the additives, resulting in 35 and 9% yields of 4a, respectively, after 12 h at 135 °C.

Synthesis of 4a′–4a′′′′ by Directed *ortho*-Silylation of 3a with Triorganosilanes (Eq 3): A mixture of **2** (61.3 mg, 0.25 mmol), $RuH_2(CO)(PPh_3)_3$ (13.8 mg, 0.0015 mmol), norbornene (118 mg, 1.25 mmol), hydrosilane (1.25 mmol), and anisole (13.6 μL, internal standard) in toluene (0.13 mL) was heated in a glass tube sealed with a J-Young Teflon stopper at 135 °C for 6–12 h. The NMR yields of the silylated compounds were determined by ^{1}H NMR spectroscopy as described in 2.3.1.

The products were identified after converting into the corresponding pinacol esters **5a′–5a′′′′**.

The following procedure was applied: To the reaction mixture were added pinacol (59 mg, 0.50mmol), *p*-toluenesulfonic acid monohydrate (95 mg, 0.50 mmol), and THF (1 mL) at room temperature. After stirring for 3 h, the reaction mixture was passed through a short pad of Florisil® (Hexane-AcOEt, 10:1). The filtrate was concentrated, and the residue was purified by preparative HPLC (hexane, 10 mL/min) to give the pinacol esters of **5a'**–**5a''''**. The NMR yields for the pza derivatives **4a'**–**4a''''** are given in eq 3. The isolated yields for the pinacol esters 5**a'**–**5a''''** were 87% (oil), 84% (oil), 75% (white solid, mp 105 °C), and 35% (oil), respectively.

Procedures for the One-Pot *ortho*-Silylation of Arylboronic Acids and Thiopheneboronic Acid by Using Pyrazolylaniline as a *ortho*-Directing Agent (Table 1 and Eq 4)

A mixture of arylboronic acid (0.25 mmol) and 2-pyrazol-5-ylaniline (**2**) (39.8 mg, 0.25 mmol) in toluene (1 mL) was heated under reflux with a Dean-Stark condenser for 1 h. After being cooled to room temperature, the solvent was evaporated *in vacuo*. To the residue, $RuH_2(CO)(PPh_3)_3$ (13.8 mg, 0.0015 mmol) was added. After filling dry nitrogen in the glass tube, norbornene (118 mg, 1.25 mmol), triethylsilane (199 μL, 1.25 mmol), anisole (13.6 μL, internal standard) and toluene (0.13 mL) were added under a nitrogen atmosphere. The mixture was heated at 135 °C for 12 h.

The products were converted into the corresponding pinacol esters. The following procedure was applied: To the reaction mixture were added pinacol (59 mg, 0.50 mmol), *p*-toluenesulfonic acid monohydrate (95 mg, 0.50 mmol), and THF (1 mL) at room temperature. After stirring for 3 h, the reaction mixture was passed through a short pad of Florisil® (Hexane-AcOEt, 10:1). The filtrate was concentrated, and the residue was purified by preparative HPLC (hexane, 10 mL/min).

***ortho*-Silylation of Phenylboronic Acid (Entry 1, Table 1):**

The silylation product **4a** was prepared according the general procedure with modification to the amount of the catalyst used (5 mol% Ru catalyst). **4a** (97% NMR yield) was isolated by bulb-to-bulb distillation (280-290 °C/4.7 mmHg, white solid, mp 138 °C, 89%) without converting it into the corresponding pinacol ester.

***ortho*-Silylation of *p*-Tolylboronic Acid (Entry 2, Table 1):** The product **4b** was prepared

according to the general procedure (2.3.3) (94% NMR yield). The corresponding pinacol ester **5b** (67.2 mg, oil, 80%) was prepared and isolated according to the general procedure.

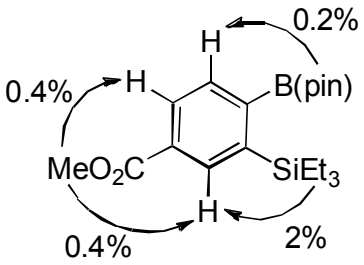
***ortho*-Silylation of *p*-Methoxyphenylboronic Acid (Entry 3, Table 1):** The product **4c** (83% NMR yield) was prepared according to the general procedure (2.3.3). The corresponding pinacol ester **5c** (67.0 mg, oil, 77%) was prepared and isolated according to the general procedure.

***ortho*-Silylation of *p*-Trifluoromethylphenylboronic Acid (Entry 4, Table 1):** The product **4d** (86% NMR yield) was prepared according to the general procedure (2.3.3). The corresponding pinacol ester **5d** (69.2 mg, oil, 71%) was prepared and isolated according to the general procedure.

***ortho*-Silylation of *p*-Chlorophenylboronic Acid (Entry 5, Table 1):** The product **4e** (85% NMR yield) was prepared according to the general procedure (2.3.3). The corresponding pinacol ester **5e** (68.8 mg, oil, 78%) was prepared and isolated according to the general procedure.

***ortho*-Silylation of *p*-Fluorophenylboronic Acid (Entry 6, Table 1):** The product **4f** (91% NMR yield) was prepared according to the general procedure (2.3.3). The corresponding pinacol ester **5f** (71.3 mg, oil, 84%) was prepared and isolated according to the general procedure.

***ortho*-Silylation of *p*-(Methoxycarbonyl)phenylboronic Acid (Entry 7, Table 1):** The product **4g** (47% NMR yield) was prepared according to the general procedure (2.3.3). The corresponding pinacol ester **5g** (37.6 mg, oil, 40%) was prepared and isolated according to the general procedure. The regioselectivity of the reaction was checked with an nOe experiment as shown below.



***ortho*-Silylation of *m*-Tolylphenylboronic Acid (Entry 8, Table 1):** The product **4h** (88% NMR yield) was prepared according to the general procedure (2.3.3). The corresponding pinacol ester **5h** (61.5 mg, oil, 74%) was prepared and isolated according to the general procedure.

***ortho*-Silylation of 2-Naphthaleneboronic Acid (Entry 9, Table 1):** The product **4i** (70% NMR yield after 24 h) was prepared according to the general procedure (2.3.3). The corresponding pinacol ester **5i** (57.6 mg, oil, 62%) was prepared and isolated according to the general procedure.

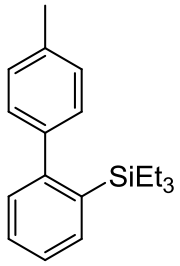
***ortho*-Silylation of *o*-Tolylboronic Acid (result not shown in Table 1 but shown in the main text):** Reaction of *o*-tolylboronic acid was carried out according to the general procedure, resulting in no reaction. In the presence of more catalysts (20 mol%), no *ortho*-silylation product was formed, but benzylic silylation product **S-13** (spectral data shown below) was isolated in 7% yield (oil, 3 days) after converting into the corresponding pinacol ester.

***ortho*-Silylation of 3-Thiopheneboronic Acid (Eq 4):** The product **7** (54 % NMR yield after 72 h) was prepared according to the general procedure (2.3.3). Double silylation product **8** (12% NMR yield) was also formed in the reaction. These primary products were identified after converting into the corresponding pinacol esters **S-14** and **S-15**.

The regiochemistry of double silylated product **8** was unambiguously assigned by converting **8** into known 2,5-bis(triethylsilyl)thiophene by Rh-catalyzed protodeborylation. The following procedure was applied for the protodeborylation. A mixture of **8** (2.0 mg, 0.0046mmol), $[Rh(OH)(cod)]_2$ (0.2 mg, 0.0004 mmol) in THF (0.1ml)-H_2O(0.01 ml) was

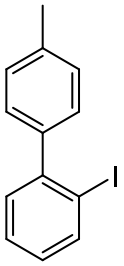
heated at 80 °C for 40 h. The reaction afforded protodeborylation product exclusively, which was identified as 2,5-bis(triethylsilyl)thiophene by ^{1}H NMR and GC-MS.[25]

Synthesis of 10 by Suzuki–Miyaura Cross-Coupling Followed by Iododesilylation (Eq 5):



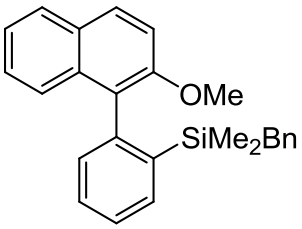
A solution of 5-(2-(triethylsilyl)phenyl)-5,6-dihydrobenzo[e]pyrazole[1,5-c][1,3,2]-diazaborinine **4a** (50 mg, 0.139 mmol) and 5N HCl (0.1 mL) in THF (1 mL) was stirred at room temperature for 2 h. The reaction mixture was extracted with Et_2O, dried over Na_2SO_4, concentrated to give a boronic acid as white solid. The acidic aqueous layer was basified with saturated aqueous $NaHCO_3$, and the solution was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and evaporated. The crude recovered pyrazolylaniline **2** was isolated in pure form (18.9 mg, 85%) by recrystallization from ethyl acetate.

A mixture of the boronic acid, Pd(*t*-$Bu_3P)_2$ (3.55 mg, 0.00695 mmol), CsF (42.3 mg, 0.278 mmol), and THF (0.28 mL) was heated at 80°C for 15 h. Preparative TLC (Hexane-AcOEt, 10:1) of the reaction mixture afforded the coupling product **9** (32.0 mg, oil, 82%).



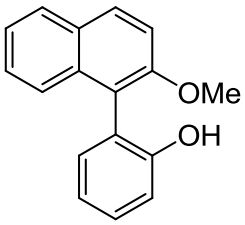
A solution of ICl (25 mg, 0.085 mmol) in CH_2Cl_2 (0.17 mL) was added to **9** (12.0 mg, 0.0426 mmol) at room temperature. The mixture was stirred for 15 h at room temperature. Preparative TLC (Hexane) of reaction mixture afforded the coupling product **10** (9.0 mg, oil, 71%).

Synthesis of 13 by Suzuki–Miyaura Cross-Coupling Followed by Tamao-Fleming Oxidation (Eq 6):



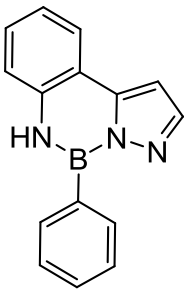
A solution of benzyldimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane **5a'''** (48.9 mg, 0.139 mmol), 1-bromo-2-methoxylnaphtalene (36.2 mg, 0.153 mmol), Pd(*t*-$Bu_3P)_2$ (3.55 mg, 0.00695 mmol), and CsF (42.3 mg, 0.278 mmol) in THF (0.28 mL) was heated at 80 °C for 24 h. Preparative TLC (Hexane-AcOEt, 10:1) of reaction mixture afforded coupling product **11** (45.0 mg, oil, 84%).

2-(2-Methoxynaphthalen-1-yl)phenol



Tetrabutylammonium fluoride (1.0M solution in THF, 0.47 mL) was added to **11** (45.0 mg, 0.117 mmol) at room temperature under air. After being stirred for 15 min, methanol (1.2 mL), $KHCO_3$ (23.4 mg, 0.234 mmol), and H_2O_2 (30%, 133 mg) were added, and the mixture was stirred for 12 h at room temperature. After quenching the reaction by adding $Na_2S_2O_3$ aq into the reaction mixture, organic materials were extracted with ether. Purification of the resulting mixture by preparative TLC (Hexane-AcOEt, 3:1) gave **12** (24.6 mg, waxy solid, 84%).

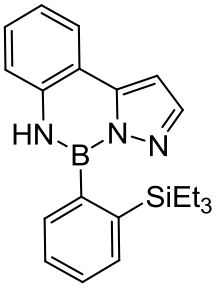
Spectral Data for New Compounds



5-Phenyl-5,6-dihydrobenzo[e]pyrazolo[1,5-c][1,3,2]diazaborinine (3a):

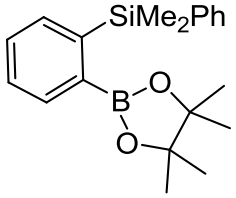
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29-8.26 (2H, m), 8.13 (1H, d, J = 2.0 Hz), 7.97-7.95 (1H, m), 7.56-7.52 (3H, m), 7.44-7.40 (1H, m), 7.26-7.22 (2H, m), 7.17 (1H, brs), 6.97 (1H, d, J = 2.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.7, 145.1,136.4, 134.3, 130.6, 128.8, 128.0, 124.8, 122.2, 117.6, 116.9, 100.0; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.4; IR (KBr) 3416, 3319, 1513, 1355, 911, 756, 698; HREIMS Calcd. for $C_{15}H_{12}BN_3$ (M^+): 245.1124, Found: 245.1125.

5-(2-(Triethylsilyl)phenyl)-5,6-dihydrobenzo[e]pyrazolo[1,5-c][1,3,2]diazaborinine (4a):



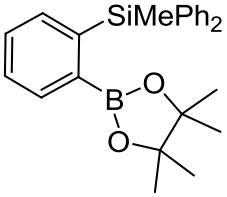
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (1H, d, J = 1.6 Hz), 7.99-7.97 (1H, m), 7.69-7.65 (2H, m), 7.45-7.40 (3H, m), 7.29-7.25 (1H, m), 7.17-7.15 (1H, m), 6.95 (1H, d, J = 1.6 Hz), 6.87 (1H, brs), 0.83 (9H, t, J = 7.8 Hz), 0.59 (6H, q, J = 7.8 Hz) ; ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.8, 144.4, 140.6, 136.0, 135.4, 132.7, 128.9, 128.2, 127.9, 125.0, 122.5, 117.6, 117.2, 10 0.2, 7.4, 4.0; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.5; IR (KBr) 3280, 2955, 1521, 1362, 912, 748; HREIMS Calcd. for $C_{15}H_{12}BN_3$ (M^+): 359.1989, Found: 359.1991.

1-Dimethylphenylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene(5a'):



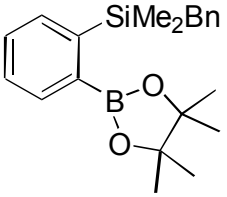
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.89 (1H, m), 7.58-7.56 (1H, m), 7.47-7.44 (2H, m), 7.42-7.36 (2H, m), 7.31-7.30 (3H, m), 1.10 (12H, s), 0.60 (6H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.7, 141.3, 136.4, 134.5, 130.1, 128.8, 128.6, 127.9, 84.1, 25.0, 0.0; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.2; IR (KBr) 2978, 1349, 1249, 1108, 734; HRFABMS Calcd. For $C_{20}H_{27}{}^{10}BO_2Si$ (M^+): 337.1910, Found: 337, 337.1915.

1-Methyldiphenylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (5a'):



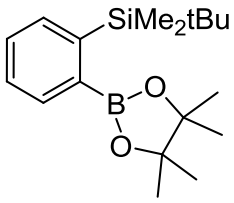
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.92 (1H, m), 7.47-7.45 (4H, m), 7.41-7.37 (1H, m), 7.34-7.28 (8H, m), 0.97 (15H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 138.6, 137.6, 135.9, 135.1, 129.7, 128.6, 128.4, 127.6, 83.6, 24.4, -2.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.4; IR (neat) 2978, 1350, 1248, 1108, 727; HREIMS Calcd. for $C_{25}H_{29}BO_2Si$(M^+): 400.2030, Found: 400.2025.

1-Benzyldimethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (5a'''):



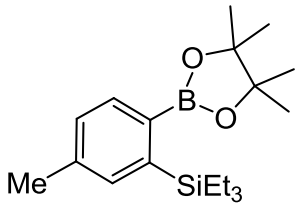
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.99 (1H, m), 7.57-7.55 (1H, m), 7.41-7.39 (2H, m), 7.19 (2H, t, J = 8.0 Hz), 7.08-7.01 (3H, m), 2.57 (2H, s), 1.43 (12H, s), 0.30 (6H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.1, 140.9, 136.4, 134.8, 129.8, 128.4, 128.4, 128.0, 127.9, 123.7, 83.9, 26.3, 25.0, -1.91; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.9; IR (KBr) 2976, 1348, 1142, 830; HRFABMS Calcd. For $C_{21}H_{30}BO_2Si$ (M^+): 353.2108, Found: 353.2113.

1-*tert*-Butyldimethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (5a””):



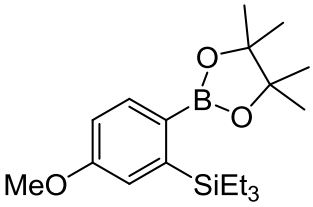
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.78 (1H, m), 7.61-7.58 (1H, m), 7.38-7.30 (2H, m), 1.35 (12H, s), 0.90 (9H, s), 0.34 (6H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 136.0, 135.2, 128.6, 127.6, 83.7, 27.3, 25.0, 17.5, -3.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.5; IR (neat) 2926, 1347, 1249, 1146, 825; HREIMS Calcd. for $C_{21}H_{29}BO_2Si$ (M^+): 319.2264, Found: 319.2267.

5-Methyl-1-triethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (5b):



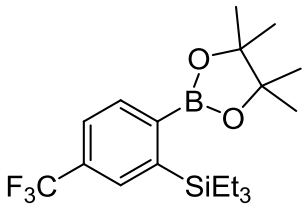
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (1H, d, J = 7.6 Hz), 7.36 (1H, m), 7.16-7.14 (1H, m), 2.35 (3H, s), 1.33 (12H, s), 0.93-0.90 (15H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 139.1, 136.3, 128.4, 83.5, 24.9, 21.8, 7.8, 4.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.7; IR (neat) 2953, 1593, 1343, 1145, 733; HRFABMS Calcd. For $C_{21}H_{29}BO_2Si$ (M^+): 332.2343, Found: 332.2345.

5-Methoxy-1-triethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (5c):



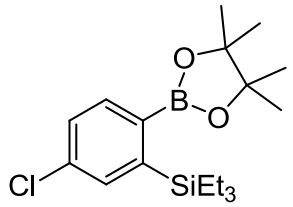
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (1H, d, J = 8.4 Hz), 7.12 (1H, d, J = 2.8 Hz), 6.84 (1H, dd, J = 8.4 Hz, 2.8 Hz), 3.82 (3H, s), 1.33 (12H, s), 0.92 (15H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4, 146.2, 138.3, 122.3, 111.6, 83.5, 54.8, 24.8, 7.8, 4.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.9; IR (neat) 2953, 1584, 1345, 1145, 731; HREIMS Calcd. For $C_{19}H_{33}BO_3Si$ (M^+): 348.2292, Found: 348.2303.

5-Trifluoromethyl-1-triethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (5d):



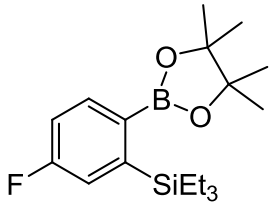
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (1H, d, J = 7.6 Hz), 7.77 (1H, m), 7.58-7.55 (1H, m), 1.37 (12H, s), 0.95-0.93 (15H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.1, 136.0, 131.3 (m), 130.9 (q, J = 31.2), 124.4 (q, J = 272.7), 124.1 (m), 84.2, 24.9, 7.7, 4.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.6; IR (neat) 2956, 1324, 1129, 733; HRFABMS Calcd. for $C_{19}H_{29}BF_3O_2Si$ (M^+): 385.1982, Found: 385.1991.

5-Chloro-1-triethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (5e):



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (1H, d, J = 8.0 Hz), 7.49 (1H, d, J = 2.2 Hz), 7.30 (1H, dd, J = 8.0 Hz, 2.2 Hz), 1.35 (12H, s), 0.92 (15H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.7, 137.6, 136.5, 135.1, 127.6, 83.9, 24.9, 8.0, 4.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.4; IR (neat) 2954, 1569, 1339, 1111, 731; HRFABMS Calcd. for $C_{18}H_{29}BClO_2Si$ (M^+) : 351.1718, Found: 351.1721.

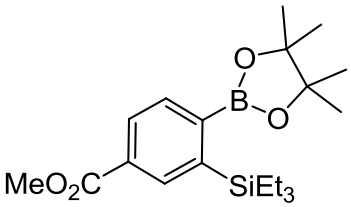
5-Fluoro-1-triethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (5f):



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (1H, dd, J = 8.0 Hz, 6.4 Hz), 7.23 (1H, dd, J = 10.4 Hz, 2.8 Hz), 7.01-6.97 (1H, m), 1.34 (12H, s), 0.91 (15H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.9 (d, J = 252.5), 147.9 (d, J = 4.9), 138.6 (d, J = 6.8), 122.2 (d, J = 17.6), 114.3 (d, J =19.5), 83.8, 24.9, 7.7, 4.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.1; IR (neat) 2953, 1570, 1343,

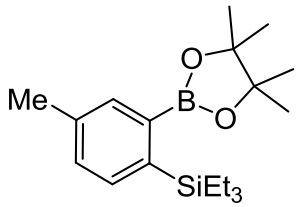
1145, 731; HREIMS Calcd. For $C_{18}H_{30}BFO_2Si$ (M^+): 336.2092, Found: 336.2081.

5-(Methoxycarbonyl)-1-triethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (5g):



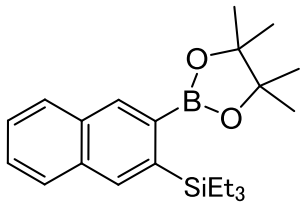
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (1H, m), 7.97-7.90 (2H, m), 3.92 (3H, s), 1.36 (12H, s), 0.95-0.91 (15H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 144.1, 135.9, 135.8, 130.3, 128.4, 84.1, 52.1, 24.9, 7.7, 4.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.7; IR (neat) 2952, 1727, 1284, 1120, 730; HREIMS Calcd. for $C_{20}H_{33}BO_4Si$ (M^+): 376.2241, Found: 376.2245.

4-Methyl-1-triethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (5h):



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (1H, s), 7.48 (1H, d, J = 7.6 Hz), 7.22 (1H, d, J = 7.6 Hz), 2.35 (3H, s), 1.36 (12H, s), 0.93-0.91 (15H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.9, 137.2, 136.9, 135.6, 130.3, 83.7, 24.9, 21.2, 7.8, 4.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.3; IR (neat) 2951, 1340, 1145, 856, 731; HRFABMS Calcd. for $C_{19}H_{33}BO_2Si$ (M^+): 332.2343, Found: 332.2352.

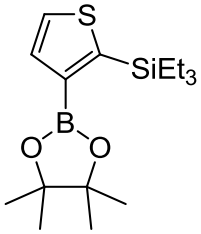
2-Triethylsilyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphtalene (5i):



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (1H, s), 8.01 (1H, s), 7.86-7.80 (2H, m), 7.52-7.45 (2H, m), 1.39 (12H, s), 1.03-0.92 (15H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 137.1, 136.0, 133.6, 132.4, 128.2, 127.8, 126.9, 126.2, 83.8, 24.9, 7.9, 4.3; ^{11}B NMR (128 MHz, $CDCl_3$)

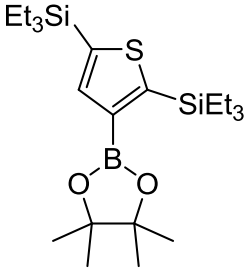
δ32.0; IR (neat) 2953, 1456, 1349, 1145, 1009, 734; HREIMS Calcd. for $C_{22}H_{33}BO_2Si$ (M^+): 368.2343, Found: 368.2340.

2-Triethylsilyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (S-14):



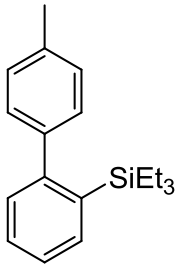
^{1}H NMR (400 MHz, $CDCl_3$) δ8.05 (1H, d, J = 2.4 Hz), 7.44 (1H, d, J = 2.4 Hz), 1.33 (12H, s), 0.95-0.84 (15H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ142.6, 138.6, 133.9, 83.5, 24.8, 7.7, 3.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ29.7; IR (neat) 2952, 1475, 1259, 1145, 1007, 732; HRFABMS Calcd. for $C_{16}H_{28}BO_2SSi$ (M^+): 323.1672, Found: 323.1659.

2,5-Bis(triethylsilyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (S-15):



^{1}H NMR (400 MHz, $CDCl_3$) δ7.70 (1H, s), 1.33 (12H, s), 1.01-0.97 (9H, m), 0.95 (15H, s), 0.84-0.78 (6H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ154.9, 143.5, 140.6, 83.4, 24.9, 7.7, 7.5, 4.60, 4.55; ^{11}B NMR (128 MHz, $CDCl_3$) δ29.8; IR (neat) 2954, 1495, 1232, 1136, 1019, 736; HREIMS Calcd. for $C_{22}H_{43}BO_2SSi_2$ (M^+): 438.2615, Found: 438.2617.

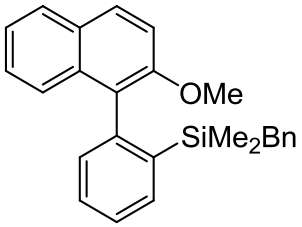
Triethyl(4'-methylbiphenyl-2-yl)silane (9):



^{1}H NMR (400 MHz, $CDCl_3$) δ7.56-7.54 (1H, m), 7.38-7.29 (2H, m), 7.21-7.18 (1H, m), 7.16

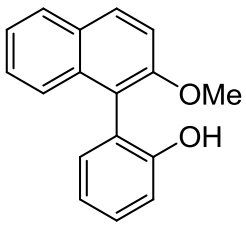
(4H, s), 2.41 (3H, s), 0.81 (9H, t, J = 8.0 Hz), 0.47 (6H, q, J = 8.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.7, 141.7, 136.6, 135.7, 135.1, 129.8, 129.0, 128.24, 128.20, 125.9, 21.2, 7.5, 4.2; IR (neat) 2952, 1464, 1237, 1003, 721; HREIMS Calcd. for $C_{19}H_{26}Si$ (M^+): 282.1804, Found: 282.1814.

Benzyl(2-(2-methoxynaphthalen-1-yl)phenyl)dimethylsilane (11):



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (1H, d, J = 9.2 Hz), 7.83-7.81 (1H, m), 7.65-7.63 (1H, m), 7.52-7.48 (1H, m), 7.43-7.39 (1H, m), 7.35 (1H, d, J = 8.8 Hz), 7.33-7.26 (2H, m), 7.22-7.20 (1H, m), 7.18-7.16 (1H, m), 7.09-7.06 (2H, m), 7.00-6.96 (1H, m), 6.71-6.69 (2H, m), 3.83 (3H, s), 1.88 (1H, d, J = 13.6 Hz), 1.83 (1H, d, J = 13.6 Hz), -0.31 (3H, s), -0.44 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.8, 142.9, 140.2, 138.8, 135.2, 134.6, 130.9, 129.2, 129.1, 128.5, 128.3, 127.8, 127.7, 126.4, 126.3, 126.2, 125.7, 123.7, 123.4, 112.7, 55.9, 25.9, -2.7, -2.9; IR (neat) 3055, 2895, 1593, 1508, 1260, 908, 734; HREIMS Calcd. for $C_{26}H_{26}OSi$ (M^+): 382.1753, Found: 382.1754

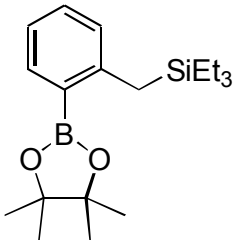
2-(2-Methoxynaphthalen-1-yl)phenol (12):



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (1H, d, J = 9.2 Hz), 7.87-7.83 (1H, m), 7.52-7.47 (1H, m), 7.42-7.36 (4H, m), 7.21 (1H, dd, J = 7.6 Hz, 1.6 Hz), 7.10 (1H, dd, J = 8.0 Hz, 1.2 Hz), 7.09-7.05 (1H, m), 4.93 (1H, s), 3.90 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 153.7, 133.7, 132.1, 130.5, 129.4, 128.0, 127.0, 124.9, 124.0 , 122.3, 120.5, 118.4, 116.0 , 113.4, 56.7; IR (neat) 3506, 3058, 2936, 1593, 1508, 1260, 1067, 811, 753; HREIMS Calcd. for

$C_{17}H_{14}O_2$ (M^+) : 250.0994, Found: 250.0991.

Triethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)silane (S-13):



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 7.4, 1.6 Hz, 1H), 7.27-7.23 (m, 1H), 7.05-6.99 (m, 2H) 2.57 (s,2H), 1.34 (s, 12H), 0.87 (t, J = 8.0, 9H), 0.51 (q, J = 8.0, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.3, 136.4, 130.6, 128.7, 122.9, 83.3, 24.9, 21.4, 7.3, 3.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.5; IR (neat) 2952, 1597, 1347, 1146, 773; HREIMS Calcd. for $C_{19}H_{33}BO_2Si$ (M^+): 332.2343. Found: 332.2340.

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10) 2-Pyrazol-5-ylaniline was prepared via three steps from *o*-nitroacetophenone in 83% overall yield.

11) PhB(pza) showed no decomposition over at least 10 months on storage in a vial in air.

12) (a) Noguchi, H.; Hojo, K.; Suginome, M. *J. Am. Chem. Soc*. **2007**, *129*, 758. (b) Noguchi, H.; Shioda, T.; Chou, C.-M.; Suginome, M. *Org. Lett.* **2008**, *10*, 377. (c) Iwadate, N.; Suginome, M. *J. Organomet. Chem*. **2009**, *694*, 1713.

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14) Some of the produced B(pin) derivatives were still unstable toward silica gel column chromatography.

15) Silylation of the benzylic C–H bond proceeded slowly in low yield.

16) Non-directed, Ir-catalyzed silylation of thiophenes has been reported. Lu, B.; Falck, J. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 7508.

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24) (a) Chene, A; Peignier, R; Vors, J-P. A.; Mortier, J.; Cantegril, R.; Croisat, D. United States Patent 5,663,119. See example 1, 2, 3. (b) Player, M. R.; Baindur, N.; Brandt, B., Chadha, N.; Patch, R. J.; Asgari, D.; Georgiadis, T. United States Patent US 2005/0113566 A1. See example 5.

25) Lu, B.; Falck, J. R. *Angew. Chem. Int. Ed.* **2008**, *47*, 7508.

Chapter 2

Ruthenium-Catalyzed C–H Silylation of Methylboronic Acid Using a Removable *α*-Directing Modifier on the Boron Atom

Abstract: Ruthenium-catalyzed C–H silylation of methylboronic acid was achieved by use of 2-(1*H*-pyrazol-3-yl)aniline as a removable *α*-directing modifier on the boron atom. Cross-coupling of the product, i.e., (phenyldimethylsilyl)methylpinacolborane, with aryl halides proceeded in the presence of a $PdCl_2$(dppf) catalyst and CsOH as a base.

Introduction

Directed catalytic functionalization of the sp^3-C–H bond is an attractive strategy for the synthesis of functionalized alkanes in organic synthesis.[1] Functional groups such as pyridyl, quinolinyl, oxazolinyl, carboxyl, aminocarbonyl, and imino groups are attached to alkanes as directing groups for C–H functionalization through arylation,[2] amination,[3] silylation,[4] acetoxylation,[5] halogenation,[6] etc. Despite the remarkable acceleration of the catalytic reaction by the directing groups, the need for their installation in the substrates significantly limits the scope of the reaction. It is likely that the development of "traceless" or "convertible" directing groups will make directed C–H activation really useful and applicable to organic synthesis.[7]

We have developed removable *o*-directing groups, which are attached to the boron atoms of arylboronic acids, for Ru-catalyzed *o*-C–H silylation at their sp^2-carbon atoms. 2-(1*H*-Pyrazol-3-yl)aniline and anthranilamide form six-membered diazaborine structures (**1** and **2**) containing N–B–N linkages upon condensation with arylboronic acids.[8,9] The nitrogen atoms in the attached directing group coordinate to the transition metal catalysts and enable the C–H functionalization reaction at the ortho positions. It would be highly attractive if the strategy could be extended to activation of alkylboronic acids. In particular, such a synthetic strategy is most attractive for the synthesis of α-functionalized methylboronic acids (Figure 1), because they are not accessible by hydroboration unlike the higher alkylboronic acids. It has been shown that even strong bases are not able to abstract α-hydrogen atoms of methylboronic acid esters.[10] It should be noted that, in spite of its potential usefulness, no catalytic C–H-functionalization at the α-hydrogen of alkylboronic acids has been reported. Herein, we describe α-C–H silylation of methylboronic acid using an α-directing modifier that is attached to the boron atom.

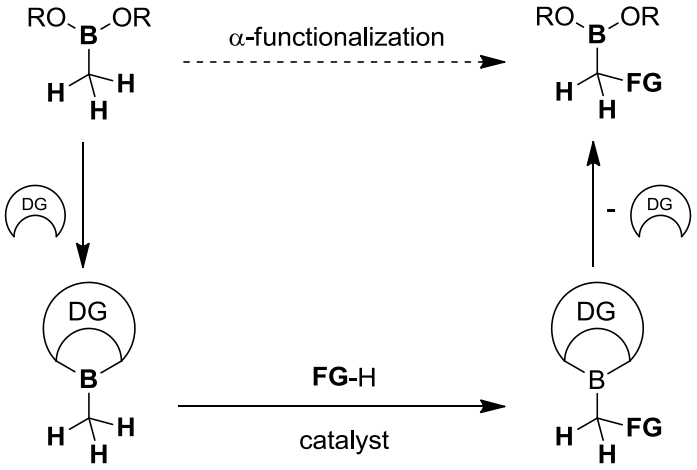
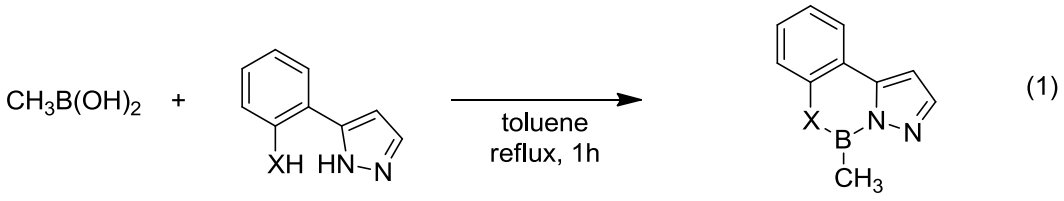


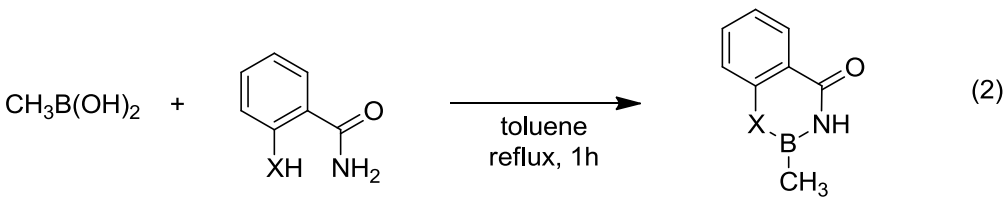
Figure 1. α-C–H Functionalization of methylboronic acid via introduction of a directing group (DG) to the boron atom.

Results and Discussion

Methylboronic acid was condensed with 2-(1*H*-pyrazol-3-yl)aniline and anthranilamide, giving MeB(pza) (**1**) and MeB(aam) (**2**), respectively, in high yields (eqs 1 and 2). A phenol analogue MeB(pzp) (**3**) of **1** was also prepared by the reaction with commercially available 2-(1*H*-pyrazol-3-yl)phenol in high yield (eq 1).



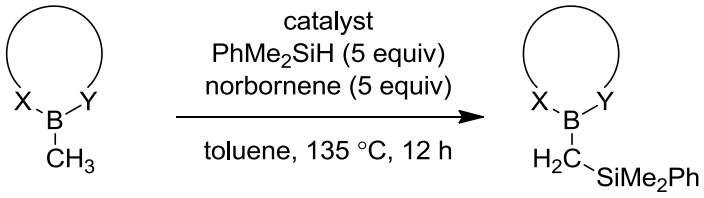
MeB(pza) (**1**) (X = NH: 89%)
MeB(pzp) (**3**) (X = O: 87%)



MeB(aam) (**2**) (80%)

The modified methylboronic acids **1**–**3** were subjected to Ru-catalyzed reaction with triorganosilanes in the presence of norbornene as a hydrogen scavenger (Table 1).[11] With the $[RhCl(cod)]_2$ catalyst, a trace amount of the expected α-silylation product was detected by ^{1}H NMR (entry 1). Ruthenium catalysts were found to be more effective for α-silylation. The $RuH_2(CO)(PPh_3)_3$ catalyst, which served as the best catalyst in the *o*-C–H silylation of PZA- and AAM-modified arylboronic acids, afforded the α-silylation product in high yield after 12 h under reflux in toluene (entry 3). Attempts at lowering the catalyst loading resulted in a decrease in the product yields (entries 4 and 5). It should be remarked that the AAM-modified methylboronic acid **2** completely failed to give the α-silylation product (entry 6). It is presumed that a four-membered metallacyclic intermediate or transition state, in which the AAM group assists the activation of the α-C–H bond, is not favorable, in contrast to the favorable formation of a five-membered metallacycle in the PZA-assisted reactions. It should also be noted that **3**, a phenol analogue of **1**, was found to be totally unreactive in the α-silylation reaction despite our expectation of forming a favorable five-memberd metallacycle, which is quite similar to that formed in the PZA-assisted reaction. The contrasted reactivity can be rationalized by the observed difference in the ^{11}B chemical shifts between **1** and **3**. The phenol analogue **3** showed its ^{11}B signal at 4.2 ppm in chloroform-*d*, which is unusually higher than typical three-coordinating organoboronic acid derivatives, including MeB(pza) (**1**, 32.7 ppm) and MeB(aam) (**2**, 32.3 ppm). The high-field shift of the ^{11}B signal can be ascribed to the formation of a four-coordinating species, in which the pyrazolyl nitrogen atoms coordinate to the boron atoms. Presumably, the lower donating ability of oxygen compared with nitrogen makes the boron atom of **3** more acidic than **1**, allowing the coordination of the pyrazolyl nitrogen to the boron atom.

Table 1. Reaction of methylboronic acid derivatives **1**–**3** with dimethylphenylsilane in the presence of transition metal catalysts[a]

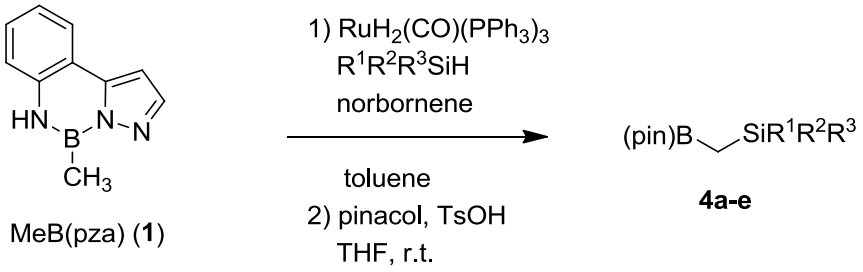


entry	substrate	catalyst (mol% metal)	NMR yield/%
1	**1**	$[RhCl(cod)]_2$ (6)	trace
2	**1**	$Ru_3(CO)_{12}$ (6)	37
3	**1**	$RuH_2(CO)(PPh_3)_3$ (6)	97
4	**1**	$RuH_2(CO)(PPh_3)_3$ (3)	58
5	**1**	$RuH_2(CO)(PPh_3)_3$ (1)	52
6	**2**	$RuH_2(CO)(PPh_3)_3$ (6)	0
7	**3**	$RuH_2(CO)(PPh_3)_3$ (6)	0

[a] **1**–**3** (0.25 mmol), a catalyst (15 μmol), norbornene (120 mg, 1.3 mmol), $PhMe_2SiH$ (1.3 mmol), and anisole (13.6 μL, internal standard) in toluene (0.13 mL) were heated at 135 °C for 12 h.

Under the optimized reaction conditions, α-C–H silylation with various hydrosilanes was carried out (Table 2). For these examinations, the primary silylation products were treated with pinacol in the presence of TsOH and isolated as pinacol esters. In the reactions with $PhMe_2SiH$, the one-pot procedure afforded the pinacol ester of (phenyldimethylsilyl)methylboronic acid in 85% isolated yield (entry 1). Likewise, Et_3SiH afforded the corresponding product in good yield (entry 2). Silyl hydride having a benzyl group, which is easily convertible to a fluorine group for further transformation,[12] also provided the corresponding product in high yield (entry 3). In the reaction of Ph_2MeSiH, a slight decrease in yield was encountered, presumably because of steric hindrance (entry 4). With a more bulky silyl hydride such as *t*-$BuMe_2SiH$, the silylated product was obtained only in low yield (entry 5). Neither $(EtO)_3SiH$ nor $(Me_3Si)Me_2SiH$ gave the silylated product at all under these reaction conditions.

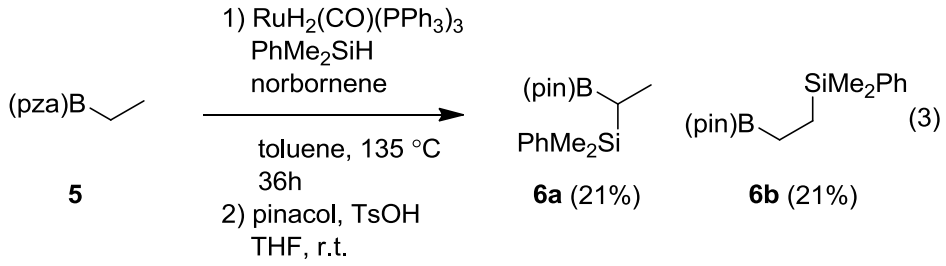
Table 2. Ru-catalyzed α-silylation of MeB(pza) (**1**) with silyl hydrides[a]

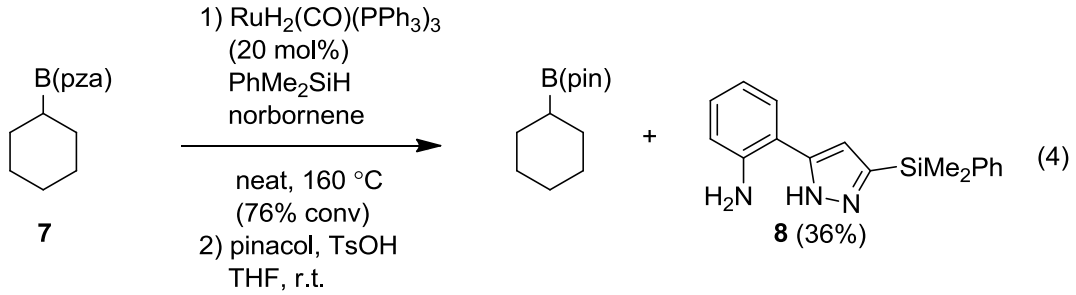


entry	silane	NMR yield /%	isolated yield/%
1	$PhMe_2SiH$	97	85 (**4a**)
2	Et_3SiH	95	81 (**4b**)
3	$BnMe_2SiH$	94	86 (**4c**)
4	Ph_2MeSiH	73	67 (**4d**)
5	*t*-$BuMe_2SiH$	29	28 (**4e**)

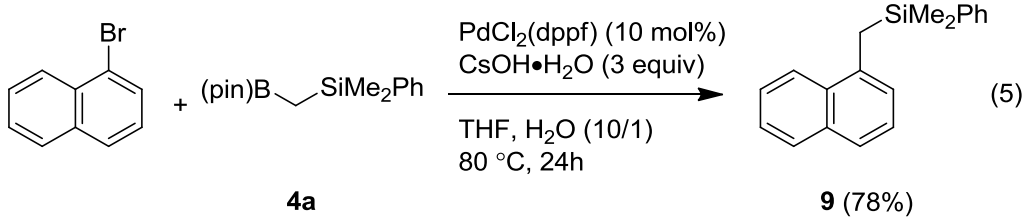
[a] **1** (46 mg, 0.25 mmol), $RuH_2(CO)(PPh_3)_3$ (14 mg, 15 μmol), norbornene (120 mg, 1.3 mmol), silane (1.3 mmol), and anisole (13.6 μL, internal standard) in toluene (0.13 mL) were heated at 135 °C for 12 h. The reaction mixture was treated with pinacol (59 mg, 0.5 mmol) and TsOH•H_2O (95 mg, 0.5 mmol) at r.t. for 1 h.

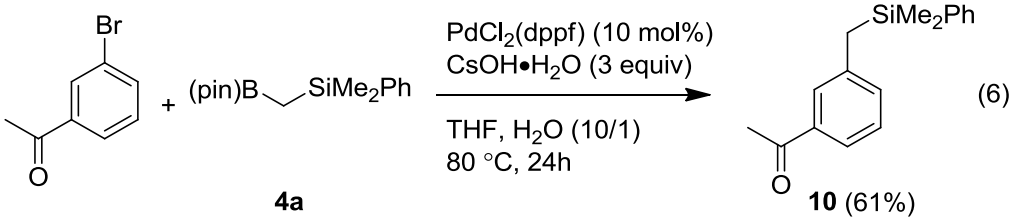
We attempted the reaction of PZA-derivatives of ethylboronic acid and cyclohexylboronic acid under the same reaction conditions. In the reaction of EtB(pza) (**5**), two silylated products via α- and β-silylation (**6a** and **6b**) were obtained, although the consumption of EtB(pza) was sluggish and incomplete (eq 3). Reaction of CyB(pza) was found to be extremely slow under the standard reaction conditions. Use of 20 mol% catalyst without solvent resulted in C–H silylation at the pyrazolyl group (eq 4). After treatment with pinacol, silylated pyrazolylaniline **8** was isolated in 36% yield. No product formed via silylation at the cyclohexane ring was found in the reaction mixture.





We then tried to optimize Suzuki–Miyaura coupling of the pinacol ester of α-silylmethylboronic acid with aryl halides.[13] We found that the coupling of **4a** with 1-naphthyl bromide proceeded in good yield in the presence of $PdCl_2$(dppf) as a catalyst and CsOH as a base (eq 5). Use of Cs_2CO_3 as a base or $PdCl_2(PPh_3)_2$ as a catalyst lowered the yields significantly. These reaction conditions could be applied to the coupling of 3-bromoacetophenone with **4a**, which afforded the products in 61% yield (eq 6). Although use of an excess amount of Ag(I) salt[14] or use of the corresponding trifluoroborates[15] has been recommended for cross-coupling of alkylboronic acid derivatives because of their low reactivity, we found that the coupling of silylmethylboronic ester **4a** proceeded without applying such modified reaction conditions.[16,17]





Conclusion

In summary, we have established that use of 2-(1*H*-pyrazol-3-yl)aniline as a modifier on the boron atom of methylboronic acid allows α-silylation with silyl hydrides in the presence of a ruthenium catalyst. The corresponding reaction of EtB(pza) afforded a mixture of α- and β-silylated products. In the silylation of PZA-modified cyclohexylboronic acid, silylation takes place at the PZA group rather than at the methyl group. Cross-coupling of the α-silylated products with aryl halides has been achieved with a $PdCl_2$(dppf) catalyst and CsOH as a base. Exploration of more efficient and selective C–H functionalization of alkylboronic acids is now being undertaken in this laboratory.

Experimental Section

General

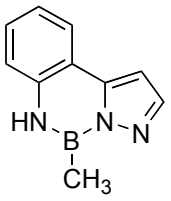
All reactions were carried out under an atmosphere of nitrogen with magnetic stirring. ^{1}H, ^{11}B and ^{13}C NMR spectra were recorded on a Varian Mercury vx400 or a JEOL JNM-A500 spectrometer at ambient temperature. ^{1}H NMR data are reported as follows: chemical shift in ppm downfield from tetramethylsilane (δ scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sex = sextet, m = multiplet, and br = broad), coupling constant (Hz), and integration. ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale). ^{11}B NMR chemical shifts are reported in ppm downfield from BF_3•OEt_2. All ^{13}C NMR spectra were obtained with broadband proton decoupling. High-resolution mass spectra were recorded on a JEOL JMS-SX102A (EI) and

JEOL JMS-HX110A (FAB) spectrometer. IR spectra were recorded on a FTIR SHIMADZU DR-8000 spectrometer. Preparative TLC was performed with silica gel $60PF_{254}$ (Merck). Recycling Preparative GPC was performed with JAI LC-908 equipped with JAIGEL-1H and -2H columns in a series ($CHCl_3$). Column chromatography was performed with Ultra Pure Silica Gel (40-63 μm) (Silicycle).

Materials

Toluene and THF were dried and deoxygenized using an alumina/catalyst column system (GlassContour Co.). Triethylsilane (TCI), dimethylphenylsilane (Aldrich), diphenylmethylsilane (Aldrich), benzyldimethylsilane (Aldrich), *tert*-butyldimethylsilane (Aldrich), triethoxysilane (TCI), pentamethyldisilane (Aldrich), norbornene (TCI), pinacol (TCI), *p*-toluenesulfonic acid monohydrate (Nacalai), methylboronic acid (TCI), ethylboronic acid (Wako), cyclohexylboronic acid (Aldrich), 1-bromonaphthalene (Wako), 3'-bromoacetophenone (TCI), Florisil® (100-200 mesh, Wako), $CsOH•H_2O$ (Nacalai), $Ru_3(CO)_{12}$ (Aldrich), and $PdCl_2$(dppf) (Wako) were used as received from the commercial sources. $RuH_2(CO)(PPh_3)_3$,[1] $[RhCl(cod)]_2$,[2] and 2-(1*H*-pyrazol-3-yl)aniline[3] were prepared by the literature procedures.

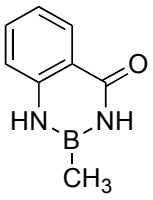
Procedures for the Synthesis of Modified Methylboronic Acids 1–3



1

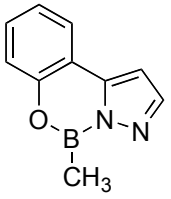
Synthesis of 5-Methyl-5,6-dihydrobenzo[*e*]pyrazolo[1,5-c][1,3,2]diazaborinine (**1**): A

mixture of methylboronic acid (0.24 g, 4.0 mmol) and 2-(1*H*-pyrazol-3-yl)aniline (0.64 g, 4.0 mmol) in toluene (8 mL) was heated for 1 h under reflux with azeotropic removal of water. After evaporation of volatile material under reduced pressure, the residual solid was subjected to bulb-to-bulb distillation (190-200 °C / 1.4 mmHg), giving the title compound **1** as white solid (0.65 g, 89%). **1**: ^{1}H NMR ($CDCl_3$) δ 8.45 (d, J = 1.7 Hz, 1H), 7.89 (dd, J = 1.3 Hz, 7.9 Hz, 1H), 7.41-7.34 (m, 1H), 7.23-7.16 (m, 1H), 7.15 (d, J = 8.3 Hz, 1H), 6.89 (d, J = 1.7 Hz, 1H), 6.89 (brs, 1H), 1.11 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 145.3, 144.0, 136.4, 128.8, 124.9, 121.9, 117.3, 116.7, 100.0. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR ($CDCl_3$) δ 32.7. IR (KBr) 3258, 1620, 1524, 1481, 750 cm^{-1}. HRMS (EI) *m/z* calcd for $C_{10}H_{10}BN_3$ (M^+): 183.0968, found: 183.0971.



2

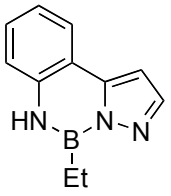
Synthesis of 2,3-dihydro-2-methylbenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (2): A mixture of methylboronic acid (90.0 mg, 1.5 mmol) and anthranilamide (204 mg, 1.5 mmol) in toluene (0.25 mmol/mL, 6 mL) was heated under reflux in a Dean-Stark apparatus for 1 h. After cooling a mixture to room temperature, the precipitates were collected by filtration to give **2** (191 mg, 80%). **2**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, J = 4.0 Hz, 1.6 Hz, 1H), 7.48 (ddd, J = 8.4 Hz, 7.2 Hz, 1.6 Hz, 1H), 7.21 (1H, brs), 7.10 (ddd, J = 8.0 Hz, 7.2 Hz, 1.2 Hz, 1H), 6.97 (dd, J = 4.0 Hz, 0.8 Hz, 1H), 6.44 (brs, 1H), 0.57 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 144.5, 133.8, 129.2, 121.5, 118.7, 117.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.3; IR (KBr) 3269, 1610, 1519, 1487, 748; HREIMS Calcd. for $C_8H_9BN_2O$ (M^+): 160.0808, Found: 160.0807.



3

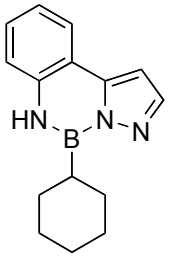
Synthesis of 5-Methyl-5H-benzo[*e*]pyrazolo[1,5-c][1,3,2]oxazaborinine (**3**): A mixture of methylboronic acid (0.12 g, 2.0 mmol) and 2-(1*H*-pyrazol-3-yl)phenol (0.32 g, 2.0 mmol) in

toluene (4 mL) was heated for 1 h under reflux with azeotropic removal of water. After evaporation of volatile material under reduced pressure, the residual solid was subjected to bulb-to-bulb distillation, giving the title compound **3** as white solid (0.32 g, 87%). **4**: ^{1}H NMR ($CDCl_3$) δ 7.95 (d, J = 2.6 Hz, 1H), 7.54 (dd, J = 1.6 Hz, 7.6 Hz, 1H), 7.35-7.28 (m, 1H), 7.07 (d, J = 8.0 Hz, 1H), 6.99-6.92 (m, 1H), 6.61 (d, J = 2.6 Hz, 1H), 0.26 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 154.1, 142.1, 133.4, 131.3, 125.2, 119.8, 119.5, 116.0, 100.9. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR ($CDCl_3$) δ 4.2. IR (KBr) 1616, 1500, 1305, 1057, 751 cm^{-1}. HRMS (EI) *m/z* calcd for $C_{10}H_9BN_2O$ (M^+): 184.0808, found: 184.0806.



5

Synthesis of 5-Ethyl-5,6-dihydrobenzo[*e*]pyrazolo[1,5-c][1,3,2]diazaborinine (**5**): According to a procedure similar to that for **1**, **5** (0.26 g, 87%) was prepared from ethylboronic acid (0.11 g, 1.5 mmol) and 2-(1*H*-pyrazol-3-yl)aniline (0.24 g, 1.5 mmol). The compound **5** was isolated by bulb-to-bulb distillation (180-190 °C / 2.2 mmHg) as white solid. **5**: ^{1}H NMR ($CDCl_3$) δ 8.03 (d, J = 1.6 Hz, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.37-7.34 (m, 1H), 7.19-7.15 (m, 2H), 6.92 (brs, 1H), 6.87 (d, J = 1.6 Hz, 1H), 1.70 (q, J = 8.0 Hz, 2H), 1.25 (t, J = 8.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 145.2, 144.0, 136.4, 128.7, 124.8, 122.0, 117.4, 116.8, 99.9, 8.1. The boron- bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR ($CDCl_3$) δ 33.5. IR(KBr) 3250, 1617, 1520, 1482, 752 cm^{-1}. Anal. Calcd for $C_{11}H_{12}BN_3$: C, 67.05; H, 6.14; N, 21.33. Found: C, 67.27; H, 6.13; N, 21.25.

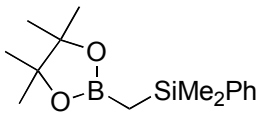


7

Synthesis of 5-Cyclohexyl-5,6-dihydrobenzo[*e*]pyrazolo[1,5-c][1,3,2]diazaborinine (**7**): According to a procedure similar to that for **1**, **7** (0.44 g, 87%) was prepared from

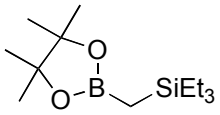
cyclohexylboronic acid (0.26 g, 2.0 mmol) and 2-(1*H*-pyrazol-3-yl)aniline (0.32 g, 2.0 mmol). The compound **7** was isolated by bulb-to-bulb distillation (240-260 °C / 1.6 mmHg) as white solid. **7**: ^{1}H NMR ($CDCl_3$) δ 8.04 (d, J = 1.5 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.42-7.32 (m, 1H), 7.24-7.12 (m, 2H), 6.87 (d, J = 1.5 Hz, 1H), 6.78 (brs, 1H), 2.16-2.01 (m, 3H), 1.87-1.77 (m, 3H), 1.58-1.24 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 145.1, 144.2, 136.3, 128.7, 124.8, 122.0, 117.5, 116.8, 99.9, 28.6, 27.4, 26.9. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR ($CDCl_3$) δ 32.6. IR (KBr) 3251, 2917, 1620, 1517, 1480, 751 cm^{-1}. HRMS (EI) *m/z* calcd for $C_{15}H_{18}BN_3$ (M^+): 251.1594, found: 251.1597.

Ruthenium-catalyzed o-Silylation



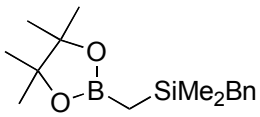
4a

Synthesis of 4,4,5,5-Tetramethyl-2-[(dimethylphenylsilyl)methyl]-1,3,2-dioxaborolane (**4a**) (Table 2): To a mixture of **1** (46 mg, 0.25 mmol) and $RuH_2(CO)(PPh_3)_3$ (14 mg, 15μmol) in a reaction tube sealed with a J-Young Teflon stopper was added norbornene (0.12 g, 1.3 mmol), dimethylphenylsilane (0.19 mL, 1.3 mmol), toluene (0.13 mL) and anisole (internal standard, 13.6 mL, 0.125mmol) under a nitrogen atmosphere. The mixture was stirred at 135 °C for 12 h. The crude mixture was transferred into screw-capped vial with THF (1 mL) after cooling to room temperature, then added pinacol (59 mg, 0.5 mmol) and p-TsOH·H_2O (95 mg, 0.5 mmol). After stirring the mixture at room temperature for 1 h, water was added to dissolve a precipitate followed by extraction with Et_2O. The organic phase was dried over $MgSO_4$ and then filtered. The concentrated residue was subjected to flash column chromatography on Florisil® (hexane : AcOEt = 20 : 1), then purified by HPLC (LiChrosorb® CN, hexane only), giving the compound **4a** as colorless liquid (59 mg, 85% in 2 steps). **4a**: ^{1}H NMR ($CDCl_3$) δ 7.58-7.51 (m, 2H), 7.36-7.31 (m, 3H), 1.18 (s, 12H), 0.36 (s, 2H), 0.33 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 140.2, 133.4, 128.8, 127.6, 82.8, 24.9, -0.9. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR ($CDCl_3$) δ 33.8. IR (neat) 2977, 1309, 1147, 1113, 847 cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{15}H_{24}BO_2Si$ ($[M-H]^+$): 275.1639, found: 275.1637.



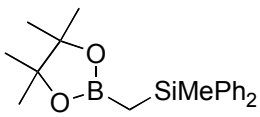
4b

Synthesis of 4,4,5,5-Tetramethyl-2-[(triethylsilyl)methyl]-1,3,2-dioxaborolane (**4b**): According to a procedure similar to that for **4a**, **4b** (53 mg, 81% in 2 steps) was obtained by using triethylsilane (0.20 mL, 1.3 mmol) instead of dimethylphenylsilane. The compound **4b** was isolated by HPLC (LiChrosorb® CN, hexane only) as colorless liquid. **4b**: ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 12H), 0.94 (t, J = 8.0 Hz, 9H), 0.54 (q, J = 8.0 Hz, 6H), 0.04 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 82.6, 24.9, 7.4, 5.0. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR ($CDCl_3$) δ 34.0. IR (neat) 2952, 13.8, 1148, 847, 754 cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{13}H_{30}BO_2Si$ ($[M+H]^+$): 257.2108, found: 257.2106. The detached directing group **3** (36 mg, 90%) was recovered from the aqueous phase by re-extraction with AcOEt after basifying with $NaHCO_3$ (s), followed by column chromatography on Florisil® (hexane : AcOEt = 1 : 1).



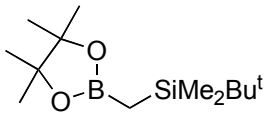
4c

Synthesis of 4,4,5,5-Tetramethyl-2-[(benzyldimethylsilyl)methyl]-1,3,2-dioxaborolane (**4c**): According to a procedure similar to that for **4a**, **4c** (63 mg, 86% in 2 steps) was obtained by using benzyldimethylsilane (0.20 mL, 1.3 mmol) instead of dimethylphenylsilane. The compound **4c** was isolated by HPLC (LiChrosorb® CN, hexane only) as colorless liquid. **4c**: ^{1}H NMR ($CDCl_3$) δ 7.23-7.17 (m, 2H), 7.06 (d, J = 7.4 Hz, 1H), 7.02 (d, J = 7.1 Hz, 2H), 2.12 (s, 2H), 1.24 (s, 12H), 0.09 (s, 2H), 0.02 (s, 6H). ^{13}C NMR ($CDCl_3$) d 140.2, 128.1, 128.1, 123.8, 82.8, 27.3, 24.9, -1.8. The boron- bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR ($CDCl_3$) δ 33.9. IR (neat) 2988, 1308, 1146, 846 cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{16}H_{28}BO_2Si$ ($[M+H]^+$): 291.1952, found: 291.1955.



4d

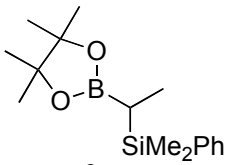
Synthesis of 4,4,5,5-Tetramethyl-2-[(methyldiphenylsilyl)methyl]-1,3,2-dioxaborolane (**4d**): According to a procedure similar to that for **4a**, **7d** (57 mg, 67% in 2 steps) was obtained by using methyldiphenylsilane (0.25 mL, 1.3 mmol) instead of dimethylphenylsilane. The compound **4d** was isolated by HPLC (LiChrosorb® CN, hexane only) as colorless liquid. **4d**: ^{1}H NMR ($CDCl_3$) δ 7.58-7.51 (m, 4H), 7.37-7.28 (m, 6H), 1.08 (s, 12H), 0.65 (s, 2H), 0.63 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 138.1, 134.4, 129.0, 127.6, 82.9, 24.8, -2.3. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR ($CDCl_3$) δ 33.9. IR (neat) 2976, 1308, 1146, 796, 699 cm^{-1}. Anal. Calcd for $C_{20}H_{27}BO_2Si$: C, 71.00; H, 8.04. Found: C, 71.07; H, 8.00.



4e

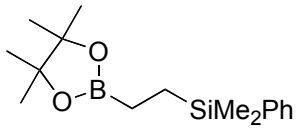
Synthesis of 4,4,5,5-Tetramethyl-2-[(tert-butyldimethylsilyl)methyl]-1,3,2-dioxaborolane (**4e**): According to a procedure similar to that for **4a**, **4e** (18 mg, 28% in 2 steps) was obtained by using *tert*-butyldimethylsilane (0.21 mL, 1.3 mmol) instead of dimethylphenylsilane. The compound **4e** was isolated by HPLC (LiChrosorb® CN, hexane only) as colorless liquid. **4e**: ^{1}H NMR ($CDCl_3$) δ 1.24 (s, 12H), 0.87 (s, 9H), 0.07 (s, 2H), 0.01 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 82.7, 26.2, 24.9, 16.8, -4.5. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR ($CDCl_3$) δ 34.0. IR (neat) 2928, 1308, 1148, 847 cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{13}H_{30}BO_2Si$ ($[M+H]^+$): 257.2108, found: 257.2113.

Reaction of 5 (eq 4): To a mixture of **5** (49 mg, 0.25 mmol) and $RuH_2(CO)(PPh_3)_3$ (14 mg, 15 mmol) in a sealed tube was added norbornene (0.12 g, 1.3 mmol), dimethylphenylsilane (0.19 mL, 1.3 mmol) and toluene (0.13 mL) under a nitrogen atmosphere. The mixture was stirred at 135 °C for 36 h. To the crude mixture was then added pinacol (59 mg, 0.5 mmol), THF (0.25 mL) and p-TsOH·H_2O (95 mg, 0.5 mmol) after cooling to room temperature. After stirring the mixture at room temperature for 1 h, water was added to dissolve a precipitate followed by extraction with Et_2O. The organic phase was dried over $MgSO_4$ and then filtered. The concentrated residue was subjected to flash column chromatography on Florisil® (hexane : AcOEt = 10 : 1), then purified by HPLC (LiChrosorb® CN, hexane only), giving the a-silylated product **6a** (16 mg, 21%) and b-silylated product **6b** (15 mg, 21%).



6a

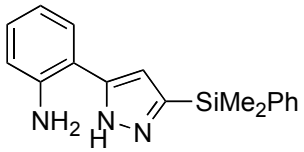
4,4,5,5-Tetramethyl-2-[1-(dimethylphenylsilyl)ethyl]-1,3,2-dioxaborolane (**6a**): ^{1}H NMR ($CDCl_3$) δ 7.56-7.50 (m, 2H), 7.36-7.30 (m, 3H), 1.19 (s, 6H), 1.17 (s, 6H), 1.01 (d, J = 7.2 Hz, 3H), 0.60 (q, J = 7.2 Hz, 1H), 0.32 (s, 3H), 0.31 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 138.9, 133.9, 128.7, 127.5, 82.7, 25.0, 24.8, 9.3, -2.6, -3.8. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR ($CDCl_3$) δ 34.5. IR (neat) 2958, 1342, 1146, 816, 699 cm^{-1}. HRMS (EI) *m/z* calcd for $C_{16}H_{27}BO_2Si$ (M^+): 290.1873, found: 290.1878.



6b

4,4,5,5-Tetramethyl-2-[2-(dimethylphenylsilyl)ethyl]-1,3,2-dioxaborolane (**6b**): ^{1}H NMR ($CDCl_3$) δ 7.53-7.46 (m, 2H), 7.35-7.30 (m, 3H), 1.22 (s, 12H), 0.83-0.71 (m, 4H), 0.25 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 139.4, 133.6, 128.7, 127.6, 82.9, 24.8, 8.5, -3.6. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR ($CDCl_3$) δ 34.3. IR (neat) 2977, 1361, 1320, 1147, 835, 699 cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{16}H_{26}BO_2Si$ ($[M-H]^+$): 289.1795, found: 289.1799.

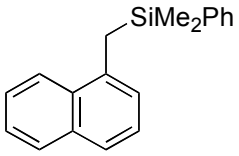
Reaction of 7 (eq 5): To **7** (63 mg, 0.25 mmol) in a sealed tube was added $RuH_2(CO)(PPh_3)_3$ (14 mg, 15 μmol), norbornene (0.12 g, 1.3 mmol), dimethylphenylsilane (0.19 mL, 1.3 mmol) and anisole (13.6 mL, 0.125 mmol) under a nitrogen atmosphere. The mixture was stirred at 160 °C for 24 h. The crude mixture was transferred into screw-capped vial with THF (1 mL) after cooling to room temperature, then added pinacol (59 mg, 0.5 mmol) and p-TsOH·H_2O (95 mg, 0.5 mmol). After stirring the mixture at room temperature for 1 h, satd. $NaHCO_3$ aq. was added followed by extraction with AcOEt. The organic phase was dried over Na_2SO_4 and then filtered. From the concentrated residue was detected both cyclohexylboronic acid and **8** by GC-MS analysis. The compound **8** was isolated by column chromatography on silica gel (27 mg, 36% in 2 steps) as viscous dark green liquid.



8

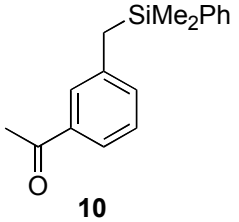
2-(3-Dimethylphenylsilyl-1*H*-pyrazol-5-yl)aniline (**8**): ^{1}H NMR ($CDCl_3$) δ 7.60-7.54 (m, 3H), 7.47-7.37 (m, 3H), 7.13-7.07 (m, 1H), 6.82 (s, 1H), 6.81-6.73 (m, 2H), 0.62 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 152.7, 144.7, 140.8, 135.6, 134.0, 130.0, 128.4, 128.3, 128.2, 117.3, 116.5, 116.4, 111.5, -2.4. IR (neat) 3330, 1615, 813, 703 cm^{-1}. HRMS (EI) *m/z* calcd for $C_{17}H_{19}N_3Si$ (M^+): 293.1348, found: 293.1345.

Suzuki-Miyaura Cross-Coupling of 4a



9

1-(Dimethylphenylsilylmethyl)naphthalene (**9**) (**eq 6**): To $PdCl_2$(dppf)·CH_2Cl_2 (16 mg, 20 μmol) in a sealed tube was added **4a** (55 mg, 0.20 mmol) with dissolving in THF (1 mL), then $CsOH·H_2O$ (0.10 g, 0.6 mmol), 1-bromonaphthalene (42 mL, 0.3 mmol) and H_2O (0.1 mL) under a nitrogen atmosphere. After stirring the mixture at 80 °C for 24 h, the organic phase which was extracted with Et_2O was dried over $MgSO_4$ and then filtered. Evaporation of the volatile material under vacuum followed by purification by preparative TLC (hexane : ether = 30 : 1) afforded **9** (44 mg, 78%) as colorless liquid. **9**: ^{1}H NMR ($CDCl_3$) δ 7.86 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.51-7.47 (m, 2H), 7.45-7.29 (m, 6H), 7.09 (d, J = 6.8 Hz, 1H), 2.79 (s, 2H), 0.21 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 138.7, 136.4, 133.9, 133.6, 131.7, 129.1, 128.5, 127.8, 125.7, 125.4, 125.3, 125.0, 124.9, 124.7, 22.7, -2.9. IR (neat) 2959, 1249, 1114, 835, 775 cm^{-1}. HRMS (EI) *m/z* calcd for $C_{19}H_{20}Si$ (M^+): 276.1334, found: 276.1332.



10

3-(Dimethylphenylsilylmethyl)acetophenone (**10**) (**eq 7**): To $PdCl_2$(dppf) (15 mg, 20 μmol) in a sealed tube was added **4a** (55 mg, 0.20 mmol) with dissolving in THF (1 mL), then $CsOH \cdot H_2O$ (0.10 g, 0.6 mmol), 3'-bromoacetophenone (53 mL, 0.4 mmol) and H_2O (0.1 mL) under a nitrogen atmosphere. After stirring the mixture at 80 °C for 24 h, the organic phase which was extracted with CH_2Cl_2 was dried over $MgSO_4$ and then filtered. Evaporation of the volatile material under vacuum followed by purification by preparative TLC (hexane : AcOEt = 5 : 1) afforded **10** (33 mg, 61%) as colorless liquid. **10**: ^{1}H NMR ($CDCl_3$) δ 7.66 (d, J = 7.6 Hz, 1H), 7.46-7.31 (m, 6H), 7.29-7.23 (m, 1H), 7.11 (d, J = 7.6 Hz, 1H), 2.47 (s, 3H), 2.36 (s, 2H), 0.27 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 140.2, 137.8, 136.9, 133.7, 132.9, 129.2, 128.3, 128.1, 127.8, 124.2, 26.6, 26.3, -3.7. IR (neat) 2956, 1683, 1274, 837, 696 cm^{-1}. HRMS (EI) *m/z* calcd for $C_{17}H_{20}OSi$ (M^+): 268.1283, found: 268.1279.

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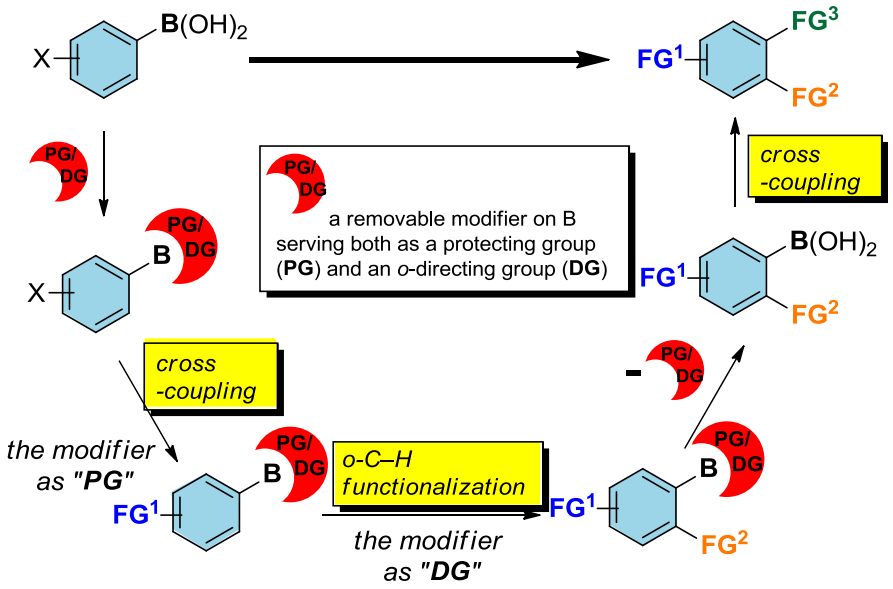
Chapter 3

Anthranilamide: A Simple, Removable Ortho-Directing Modifier for Arylboronic Acids Serving also as a Protecting Group in Cross-Coupling Reactions

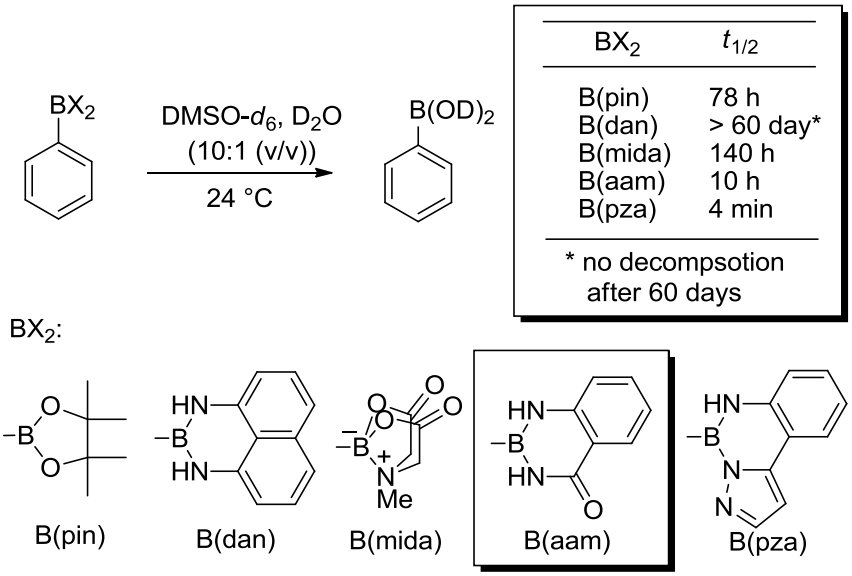
Abstract: Anthranilamide (AAM) serves as a bifunctional modifier on the boron atom in catalytic transformations of arylboronic acids. It makes boronyl groups unreactive in Suzuki-Miyaura coupling and promotes Ru-catalyzed ortho-silylation. Suzuki-Miyaura coupling of AAM-modified bromophenylboronic acids with tolylboronic acid gave 1,1'-biaryl-4-boronic acid bearing AAM on the boron atom, which subsequently underwent Ru-catalyzed *o*-silylation at the 3-position by virtue of the *o*-directing effect of the AAM group.

Introduction



Scheme 1. Use of a removable modifier on the boron atom that serves both as protecting and *o*-directing groups for the synthesis of highly functionalized arene derivatives.

Much interest has focused on the synthesis and use of arylboronic acids in organic synthesis.[1] In addition to the conventional synthesis using transmetalation with more nucleophilic organometallic reagents such as Grignard and organolithium reagents, catalytic C–B bond formation reactions have gained increasing attention. Transition-metal-catalyzed C–H and C–X borylations are recognized as the most promising, efficient access to arylboronic acids.[2,3] Efforts are now devoted to the synthesis of organoboronic acids with retention of the boron functionality throughout the synthesis.[4] For this purpose, robust protecting groups for organoboronic acids especially in the Suzuki–Miyaura cross-coupling reaction have been developed.[5,6] They have made possible the synthesis of rather complex organoboronic acids through iterative Suzuki–Miyaura coupling.[4,7,8] As a new boron-retaining strategy, we recently reported use of 2-(pyrazol-5-yl)aniline (PZA) as an agent for Ru-catalyzed *o*-silylation,[9,10] in which coordination of the sp^2-nitrogen atom of PZA to the catalyst is crucial.[11,12,13]



Scheme 2. Stabilities of modified phenylboronic acids.

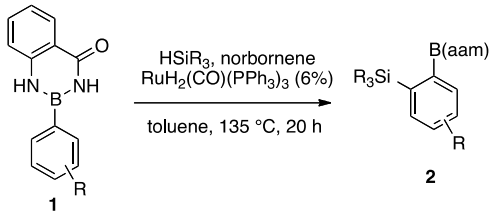
These boron-retaining syntheses of arylboronic acids are particularly useful in the synthesis of elaborated arylboronic acids that are otherwise difficult to synthesize. Our interest has focused on finding a simple modifier on the boron atom serving both as an *o*-directing group in the *o*-C–H functionalization reactions and as a protecting group in the cross-coupling reactions (Scheme 1). Such a bifunctional modifier would allow us to develop new synthetic access to highly elaborated arylboronic acids, which is in turn beneficial for the synthesis of highly functionalized arene derivatives. Herein, we describe the use of anthranilamide as such a bifunctional agent for arylboronic acid synthesis. It shows a higher ability for *o*-direction and much higher robustness toward SMC and isolation procedures than PZA.

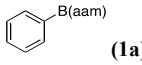
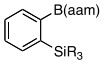
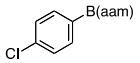
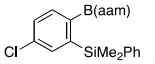
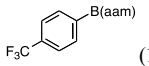
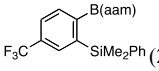
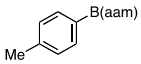
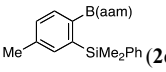
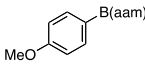
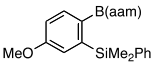
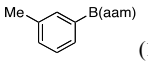
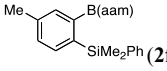
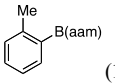
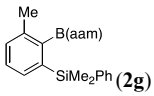
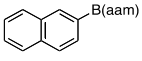
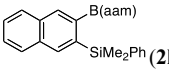
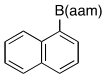
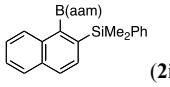
Results and Discussion

After brief screening of some 1,3,2-diazaboracyclohexane structures, we found that PhB(aam) **1a** (see Scheme 2 and Table 1 for the structure), which was prepared by condensation of $PhB(OH)_2$ with commercially available anthranilamide in toluene under reflux in high yield, shows high stability toward moisture, oxygen, and even chromatography

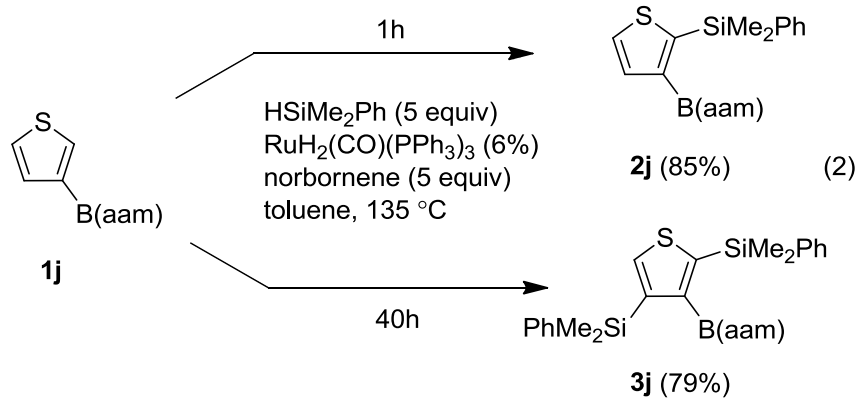
on silica gel.[14] The stabilities of the cyclic diaminoborane derivatives were compared in DMSO/D_2O (10/1) at room temperature (Scheme 2). To our surprise, even PhB(pin) decomposed gradually under these reaction conditions. The half-life was determined to be 78 h by ^1H NMR measurement. In contrast, PhB(dan) showed no hint of decomposition under the same reaction conditions. PhB(mida) (mida: *N*-methyliminodiacetato) was also robust, although it too underwent slow hydrolysis ($t_{1/2}$ = 140 h). Although being less stable than the DAN and MIDA protecting groups, AAM exhibited much higher stability than the previous directing group PZA.

Table 1. *ortho*-Silylation of Arylboronic Acids Using Anthranilamide as an *ortho*-Directing Agent.[a]

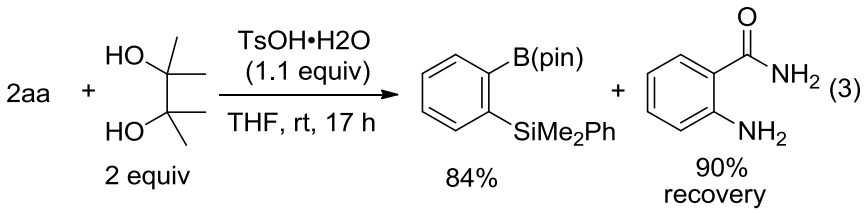


entry	**1**	$HSiR_3$	% yield [b]	isolated product
1 [c]		$HSiMe_2Ph$	(88)	
2		$HSiEt_3$	(64)	
3	 **(1a)**	$HSiMePh_2$	90 (80)	 (**2aa-2ad**)
4		$HSiMe_2Bu$-*t*	0	
5	 (**1b**)	$HSiMe_2Ph$	97 (91)	 (**2b**)
6	 (**1c**)	$HSiMe_2Ph$	94 (77)	 (**2c**)
7	 (**1d**)	$HSiMe_2Ph$	96 (88)	 (**2d**)
8	 (**1e**)	$HSiMe_2Ph$	95 (85)	 (**2e**)
9 [d]	 (**1f**)	$HSiMe_2Ph$	91 (81)	 (**2f**)
10 [e]	 (**1g**)	$HSiMe_2Ph$	32 (19)	 (**2g**)
11	 (**1h**)	$HSiMe_2Ph$	97 (90)	 (**2h**)
12 [e]	 (**1i**)	$HSiMe_2Ph$	54 (30)	 (**2i**)

[a] **1** (0.25 mmol), $RuH_2(CO)(PPh_3)_3$ (15 μmol), norbornene (1.25 mmol), hydrosilane (1.25 mmol), and toluene (0.13 mL) at 135 °C (bath temperature) for 20 h unless otherwise noted. [b] NMR yield. Isolated yields in parenthesis. [c] 3 h. [d] 37 h. [e] 51 h.



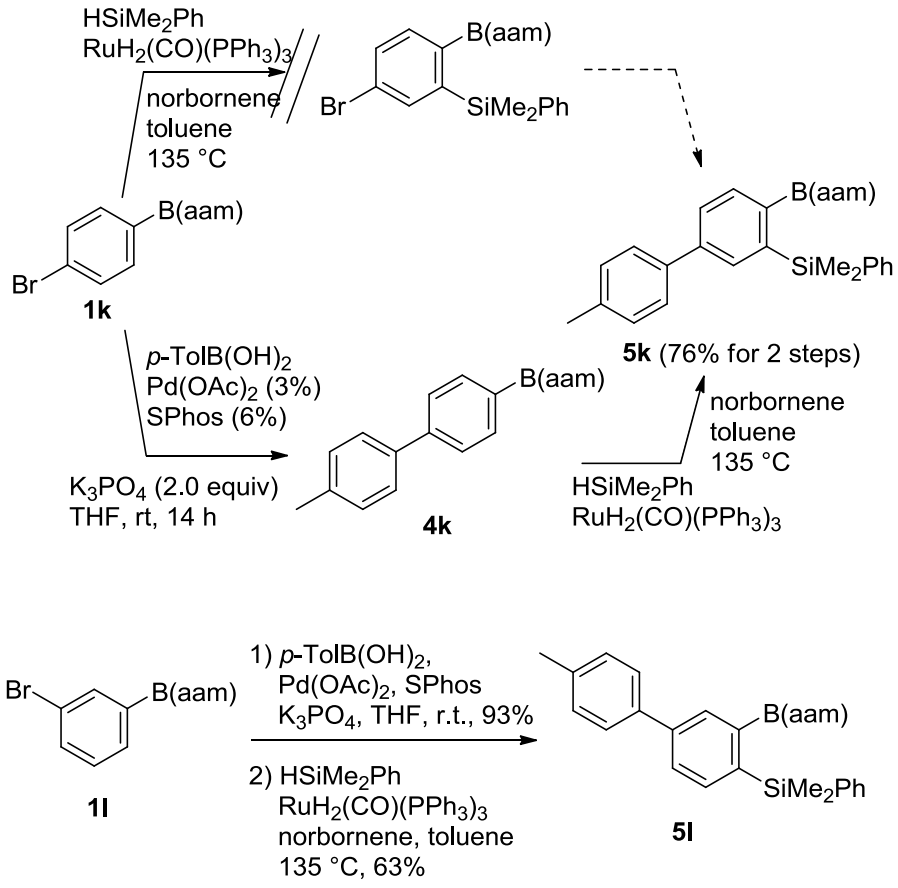
Scheme 3. AAM-directed silylation of 3-thiopheneboronic acid derivative **1j**.



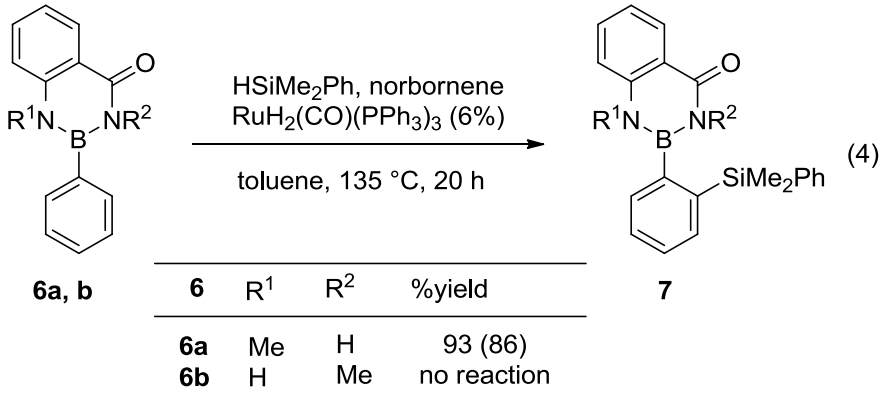
Scheme 4. Acid-mediated conversion of ArB(aam) to ArB(pin).

Ru-catalyzed *o*-silylation of PhB(aam) (**1a**) with dimethylphenylsilane proceeded in high yield in the presence of $RuH_2(CO)(PPh_3)_3$ with norbornene as a hydrogen scavenger at 135 °C (Table 1).[5b-d] The *o*-silylated product **2aa** was isolated by silica gel flash column chromatography. Among the hydrosilanes examined for the reaction, dimethylphenylsilane showed the highest reactivity. Triethylsilane, which was the most reactive in the PZA-directed reaction, resulted in a slightly lower yield. It should be remarked here that no silylation at the phenyl ring of phthalimide took place at all. Using dimethylphenylsilane, isolated AAM-modified substituted arylboronic acids were subjected to the silylation reaction. Arylboronic acids having electron-donating and electron-withdrawing groups at their para-positions afforded the corresponding *o*-silylated products in high yields (entries 5–8). *Meta*-tolylboronic acid derivative **1f** underwent silylation at the less sterically demanding *o*-position selectively in high yield (entry 9). Although the yield was low, *o*-Me substituted **1g** afforded *o*-silylated 1,2,3-trisubstituted benzene derivative **2g** (entry 10). Note that PZA-modified *o*-tolylboronic acid does not give the desired *o*-silylation product at all. The

2-naphthyl derivative was silylated at the 3-position selectively in good yield (entry 11) as observed in the PZA system. 1-Naphthylboronic acid gave the 2-silylated product **2i** selectively, albeit in low yield, whereas the corresponding PZA derivative was not reactive at all (entry 12). A remarkable difference between the present AAM and the previous PZA system has been demonstrated by the reaction of 3-thienyl derivative **1j** (Scheme 3). In both systems, the first silylation takes place at the 2-positions. The second silylation in the AAM system took place at the 4-position of the thiophene ring, in contrast to exclusive silylation at the 5-position in the PZA system via non-directed silylation.[15] This clearly suggests that the AAM group has a stronger directing ability than does PZA. In these syntheses of *o*-silylated organoboronic acids, the AAM group on the boron atoms was readily converted into the PIN group by acid-catalyzed ligand exchange (Scheme 4). Hydrolysis of **2aa** was accomplished cleanly in the presence of aqueous acid at room temperature, giving the corresponding arylboroxine in high yield.



Scheme 5. Cross-coupling/silylation sequence with bromo-substituted arylboronic acids.



6a, b

6	R^1	R^2	%yield
6a	Me	H	93 (86)
6b	H	Me	no reaction

7

Scheme 6. Reactions of phenylboronic acid drrivatives **6a** and **6b** modified by *N*-methylated anthranilamides.

Attempted *o*-silylation of *p*-bromophenylboronic acid derivative **1k** resulted in the substitution of the bromine group by a silyl group (Scheme 5). Instead, we carried out Suzuki–Miyaura coupling of **1k** with *p*-tolylboronic acid. In the presence of SPhos (2-dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl) as a ligand, the coupling proceeded at room temperature with complete retention of the AAM group on the boron atom. The isolated AAM derivative of biphenylboronic acid **4k** underwent Ru-catalyzed silylation selectively at the *ortho* position, giving silylborylbiphenyl **5k**. The sequential cross-coupling/*o*-silylation protocol could also be applied to *m*-bromoboronic acid derivative **1l**, affording **5l** (room temperature, 14 h). The B(aam) group was completely retained even in the attempted cross-coupling of **1l** with *p*-tolylboronic acid at 80 °C, giving the same coupling product in 94% yield (1.5 h). In the corresponding transformation of *o*-bromophenylboronic acid, the first step, i.e., coupling with $TolB(OH)_2$, proceeded in high yield, although *o*-silylation afforded the silylated biphenyl only in low yield. In these examples, the AAM group serves not only as a directing group but also as a protecting group for the boronyl group in the Suzuki–Miyaura coupling reaction.

To gain insight into the origin of the directing effect of the AAM group, we compared two *N*-methylated derivatives **6a** and **6b** of anthranilamides in the *o*-silylation reactions (Scheme 6). Anthranilamide **6a** bearing a methyl group on the aniline nitrogen atom underwent the *o*-silylation smoothly under the same reaction conditions as those for the parent anthranilamide. In contrast, its isomer **6b** bearing a methyl group on the amide nitrogen was not reactive at all. These results suggest that the amide nitrogen rather than the aniline

nitrogen serves as the coordinating element in the Ru-catalyzed *o*-silylation. It may be presumed that a tautomerized form, which carries an sp^2 lone pair on the nitrogen atom, may play a key role in coordination to the catalyst.

Conclusion

In summary, anthranilamide has been established as a new directing agent for transition-metal-catalyzed *o*-C–H silylation. The B(aam) group exhibited higher ability in *o*-direction in comparison with the previously reported B(pza) group. The stronger directing effect resulted in *o*-silylation of sterically demanding arylboronic acids such as *o*-tolylboronic acid and 1-naphthylboronic acid, albeit in low yields, which could not be achieved with the B(pza) group. Furthermore, a sharp switch of regioselectivity was observed in the silylation of 2-silylated 3-thiopheneboronic acid. The AAM group also serves as a protecting group in the Suzuki–Miyaura coupling reaction, enabling the synthesis of silylated biphenylboronic acids through a cross-coupling/*o*-silylation sequence. Application of these directing groups in other catalytic C–H functionalizations is being undertaken in this laboratory.

Experimental Section

General

All reactions were carried out under an atmosphere of nitrogen with magnetic stirring. ^{1}H, ^{11}B and ^{13}C NMR spectra were recorded on a Varian Mercury vx400 or a JEOL JNM-A500 spectrometer at ambient temperature. ^{1}H NMR data are reported as follows: integration , chemical shift in ppm downfield from tetramethylsilane (δ scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sex = sextet, m = multiplet, and br = broad), and coupling constant (Hz). ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale). ^{11}B NMR chemical shifts are reported in ppm downfield from BF_3•OEt_2. All ^{13}C NMR spectra were obtained with broadband proton decoupling. High-resolution mass spectra were recorded on a JEOL JMS-SX102A (EI) and JEOL

JMS-HX110A (FAB) spectrometer. IR spectra were recorded on a FTIR SHIMADZU DR-8000 spectrometer. Preparative TLC was performed with silica gel $60PF_{254}$ (Merck). Recycling Preparative GPC was performed with JAI LC-908 equipped with JAIGEL-1H and -2H columns in a series($CHCl_3$).

Column chromatography was performed with Ultra Pure Silica Gel (40-63 μm) (Silicycle).

Materials

Toluene and THF were dried and deoxygenized using an alumina/catalyst column system (GlassContour Co.). Anthranilamide (TCI), triethylsilane (TCI), dimethylphenylsilane (Aldrich), diphenylmethylsilane (Aldrich), *tert*-butyldimethylsilane (Aldrich), norbornene (TCI), pinacol (TCI), *p*-toluenesulfonic acid monohydrate (Nacalai), phenylboronic acid (Wako), 4-methoxyphenylboronic acid (Aldrich), 4-trifluoromethylphenylboronic acid (Wako), 4-chlorophenylboronic acid (Wako), 4-methylphenylboronic acid (Wako), 4-bromophenylboronic acid (Aldrich), 3-bromophenylboronic acid (Aldrich), 3-methylphenylboronic acid (TCI), 2-methylphenylboronic acid (Wako), 2-naphthaleneboronic acid (TCI), 1-naphthaleneboronic acid (Aldrich), 3-thiopheneboronic acid (TCI), Florisil® (75-150 μm, Kanto), $Pd(OAc)_2$ (Tanaka Rare-metal) and SPhos (Strem) were used as received from the commercial sources. $RuH_2(CO)(PPh_3)_3$,[16] were prepared by the literature procedures. Potassium phosphate (Nacalai) was dried in an oven at 300 °C for 5 h *in vacuo* (1 mmHg).

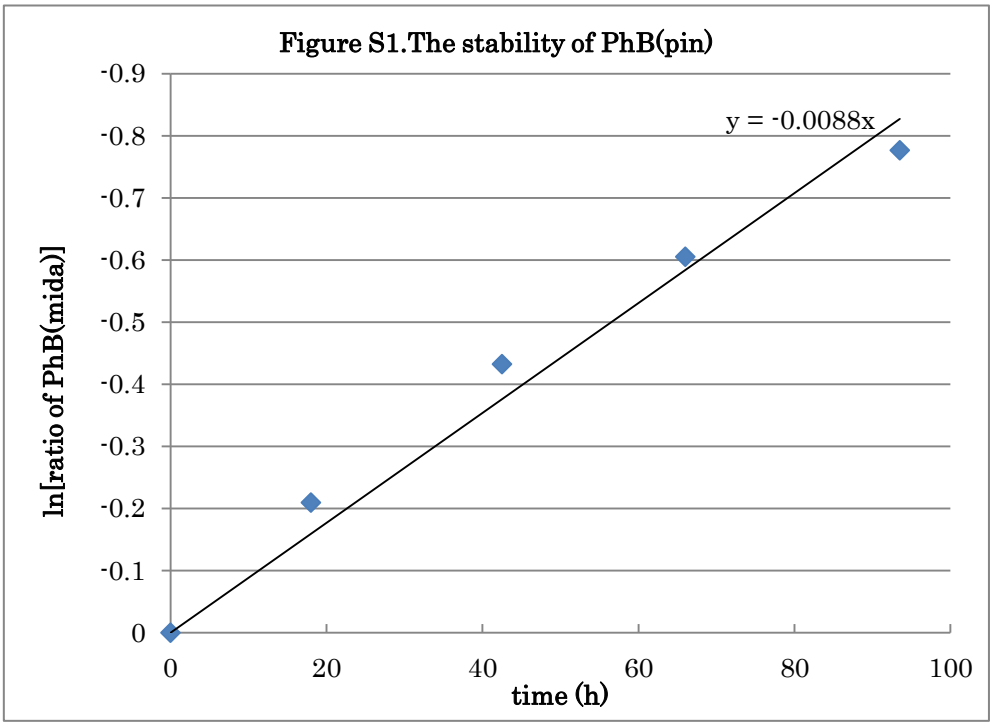
Experimental Procedures

Determination of the stabilities of the phenylboronic acid derivatives by ^{1}H NMR in DMSO/D_2O (10/1) (eq 1):

To a solution of $PhBX_2$ (0.020 mmol) and dibenzylether (3.81 μL, internal standard) in DMSO-d_6 (0.70 mL) was added D_2O (0.07 mL) at 24 °C. Conversion of $PhBX_2$ was monitored by ^{1}H NMR spectroscopy.

Stability of PhB(pin)

The half-life of PhB(pin) (4.08 mg) was determined to be 78 h.

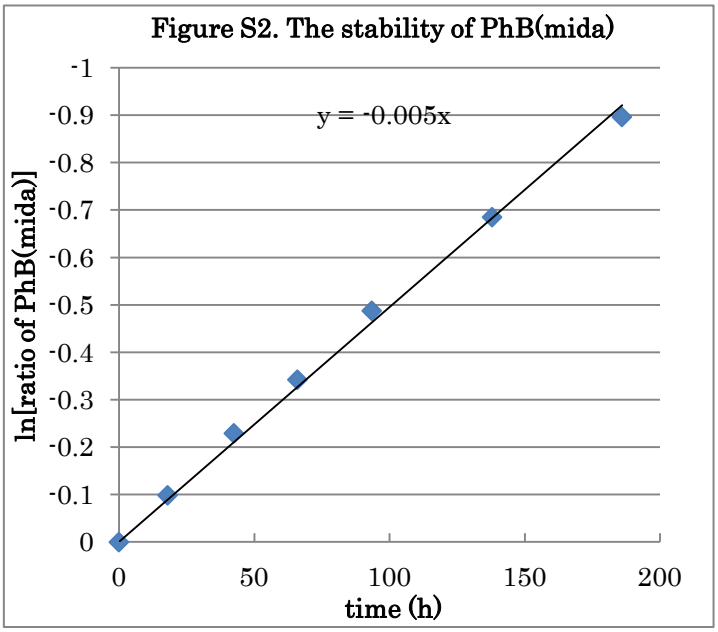


Stability of PhB(dan)

No hydrolylsis or decomposition of PhB(dan) (4.88 mg) was observed after 60 days.

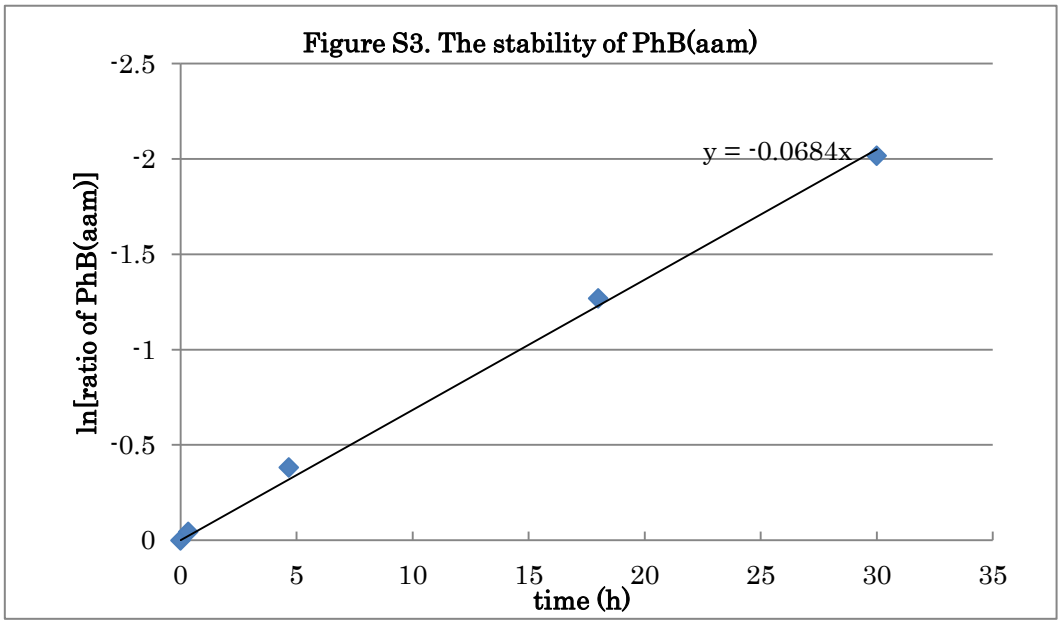
Stability of PhB(mida)

The half-life of PhB(mida) (4.66 mg) was determined to be 140 h.



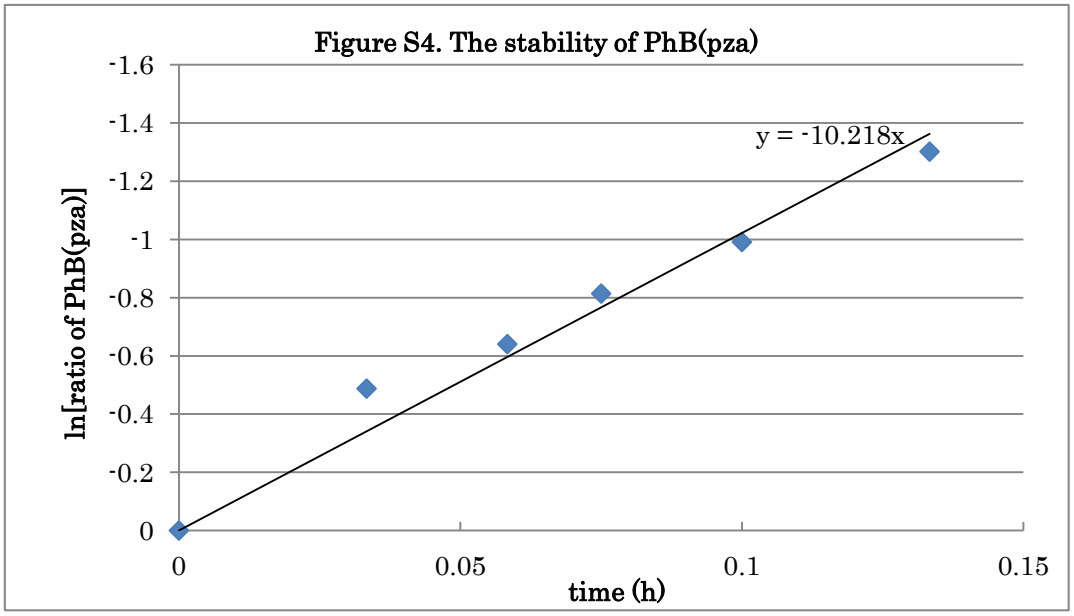
Stability of PhB(aam)

The half-life of PhB(aam) (4.88 mg) was determined to be 10 h.



Stability of PhB(pza)

The half-life of PhB(pza) (4.90 mg) was determined to be 4 min.



General Procedure for the Synthesis of 1 by Condensation of Arylboronic Acid with

Anthranilamide:

A mixture of arylboronic acid (30 mmol) and anthranilamide (4.08 g, 30 mmol) in toluene (0.25 mL/mmol, 7.5 mL) was heated under reflux in a Dean-Stark apparatus for 1 h. After cooling a mixture to room temperature, the precipitates were collected by filtration to give **1**.

Synthesis of 1a

According to the general procedure, **1a** (6.11 g, 91%) was prepared from phenylboronic acid (3.66 g, 30.0 mmol) and anthranilamide (4.08 g, 30.0 mmol).

Synthesis of 1b

According to the general procedure, **1b** (361 mg, 94%) was prepared from 4-chlorophenylboronic acid (234 mg, 1.5 mmol) and anthranilamide (204 mg, 1.5 mmol).

Synthesis of 1c

According to the general procedure, **1c** (415 mg, 95%) was prepared from 4-trifluoromethylphenylboronic acid (285 mg, 1.5 mmol) and anthranilamide (204 mg, 1.5 mmol).

Synthesis of 1d

According to the general procedure, **1d** (337 mg, 95%) was prepared from 4-methylphenylboronic acid (204 mg, 1.5 mmol) and anthranilamide (204 mg, 1.5 mmol).

Synthesis of 1e

According to the general procedure, **1e** (335 mg, 88%) was prepared from 4-methoxyphenylboronic acid (228 mg, 1.5 mmol) and anthranilamide (204 mg, 1.5 mmol).

Synthesis of 1f

According to the general procedure, **1f** (335 mg, 94%) was prepared from 3-methylphenylboronic acid (204 mg, 1.5 mmol) and anthranilamide (204 mg, 1.5 mmol).

Synthesis of 1g

According to the general procedure, **1g** (264 mg, 74%) was prepared from 2-methylphenylboronic acid (204 mg, 1.5 mmol) and anthranilamide (204 mg, 1.5 mmol).

Synthesis of 1h

According to the general procedure, **1h** (384 mg, 94%) was prepared from 2-naphthaleneboronic acid (258 mg, 1.5 mmol) and anthranilamide (204 mg, 1.5 mmol).

Synthesis of 1i

According to the general procedure, **1i** (364 mg, 89%) was prepared from 1-naphthaleneboronic acid (258 mg, 1.5 mmol) and anthranilamide (204 mg, 1.5 mmol).

Synthesis of 1j

According to the general procedure, **1j** (310 mg, 90%) was prepared from 3-thiopheneboronic acid (192 mg, 1.5 mmol) and anthranilamide (204 mg, 1.5 mmol).

Synthesis of 1k

According to the general procedure, **1k** (439 mg, 97%) was prepared from 4-bromophenylboronic acid (300 mg, 1.5 mmol) and anthranilamide (204 mg, 1.5 mmol).

Synthesis of 1l

According to the general procedure, **1l** (814 mg, 90%) was prepared from 3-bromophenylboronic acid (600 mg, 3.0 mmol) and anthranilamide (408 mg, 3.0 mmol).

Synthesis of 6a

According to the general procedure, **6a** (532 mg, 75%) was prepared from phenylboronic acid (366 mg, 3.0 mmol) and 2-(methylamino)benzamide (450 mg, 3.0 mmol).

Synthesis of 6b

According to the general procedure, **6b** (436 mg, 62%) was prepared from phenylboronic acid (336 mg, 3.0 mmol) and 2-amino-N-methylbenzamide (450 mg, 3.0 mmol).

General procedure for C–H silylation of ArB(aam) (Table 1):

A mixture of **1** (0.25 mmol), $RuH_2(CO)(PPh_3)_3$ (13.8 mg, 0.015 mmol), norbornene (118 mg, 1.25 mmol), and hydrosilane (1.25 mmol) in toluene (0.13 mL) was heated in a glass tube

sealed with a J-Young Teflon stopper at 135 °C. The reaction was run for 20 h unless otherwise noted. After cooling to temperature, the mixture was subjected to column chromatography on Florisil® (hexane/EtOAc), giving *o*-silylated product **2**.

Synthesis of 2aa (entry 1, Table 1)

According to the general procedure, a mixture of **1a** (333mg, 1.5 mmol), $RuH_2(CO)(PPh_3)_3$ (82.6 mg, 0.090 mmol), norbornene (707 mg, 7.5 mmol), and dimethylphenylsilane (140 mL) in toluene (0.78 ml) was heated for 3 h. **2aa** (470 mg, 88%) was isolated by column chromatography on silica gel (hexane-AcOEt, 10:1 – 2:1).

Synthesis of 2ab (entry 2, Table 1)

According to the general procedure, a mixture of **1a** (55.5 mg), $RuH_2(CO)(PPh_3)_3$, norbornene, and triethylsilane (199 μL) in toluene (0.13 mL) was heated. **2aa** (54.3 mg, 64%) was isolated by column chromatography on Florisil® (hexane-AcOEt, 10:1 – 2:1).

Synthesis of 2ac (entry 3, Table 1)

According to the general procedure, a mixture of **1a** (55.5 mg), $RuH_2(CO)(PPh_3)_3$, norbornene, and methyldiphenylsilane (249 μL) in toluene (0.13 mL) was heated. **2ac** (83.6 mg, 80%) was isolated by column chromatography on Florisil® (hexane-AcOEt, 10:1 – 2:1).

Synthesis of 2b (entry 5, Table 1)

According to the general procedure, a mixture of **1b** (64.0 mg), $RuH_2(CO)(PPh_3)_3$, norbornene, and dimethylphenylsilane (191 μL) in toluene (0.13 mL) was heated. **2b** (88.7 mg, 91%) was isolated by column chromatography on Florisil® (hexane-AcOEt, 10:1 – 2:1).

Synthesis of 2c (entry 6, Table 1)

According to the general procedure, a mixture of **1c** (72.5 mg), $RuH_2(CO)(PPh_3)_3$, norbornene, and dimethylphenylsilane (191 μL) in toluene (0.13 mL) was heated. **2c** (82.0 mg, 77%) was isolated by column chromatography on Florisil® (hexane-AcOEt, 10:1 – 3:1).

Synthesis of 2d (entry 7, Table 1)

According to the general procedure, a mixture of **1d** (59.0 mg), $RuH_2(CO)(PPh_3)_3$,

norbornene, and dimethylphenylsilane (191 μL) in toluene (0.13 mL) was heated. **2d** (81.5 mg, 88%) was isolated by column chromatography on Florisil® (hexane-AcOEt, 10:1 – 2:1).

Synthesis of 2e (entry 8, Table 1)

According to the general procedure, a mixture of **1e** (63.0 mg), $RuH_2(CO)(PPh_3)_3$, norbornene, and dimethylphenylsilane (191 μL) in toluene (0.13 mL) was heated. **2e** (82.2 mg, 85%) was isolated by column chromatography on Florisil® (hexane-AcOEt, 10:1 – 2:1).

Synthesis of 2f (entry 9, Table 1)

According to the general procedure, a mixture of **1f** (59.0 mg), $RuH_2(CO)(PPh_3)_3$, norbornene, and dimethylphenylsilane (191 μL) in toluene (0.13 mL) was heated for 37 h. **2f** (75.2 mg, 81%) was isolated by column chromatography on Florisil® (hexane-AcOEt, 10:1 – 5:1).

Synthesis of 2g (entry 10, Table 1)

According to the general procedure, a mixture of **1g** (59.0 mg), $RuH_2(CO)(PPh_3)_3$, norbornene, and dimethylphenylsilane (191 μL) in toluene (0.13 mL) was heated for 51 h. The reaction mixture was passed through a short pad of Florisil® (hexane-AcOEt, 5:1) and then **2g** (18.1mg, 19%) was isolated by preparative GPC.

Synthesis of 2h (entry 11, Table 1)

According to the general procedure, a mixture of **1h** (68.0 mg), $RuH_2(CO)(PPh_3)_3$, norbornene, and dimethylphenylsilane (191 μL) in toluene (0.13 mL) was heated. **2h** (92.1 mg, 90%) was isolated by column chromatography on Florisil® (hexane-AcOEt, 10:1 – 4:1).

Synthesis of 2i (entry 12, Table 1)

According to the general procedure, a mixture of **1i** (68.0 mg), $RuH_2(CO)(PPh_3)_3$, norbornene, and dimethylphenylsilane (191 μL) in toluene (0.13 mL) was heated for 51 h. The reaction mixture was passed through a short pad of Florisil® (hexane-AcOEt, 10:1 – 5:1) and then **2i** (31.0mg, 30%) was isolated by preparative GPC.

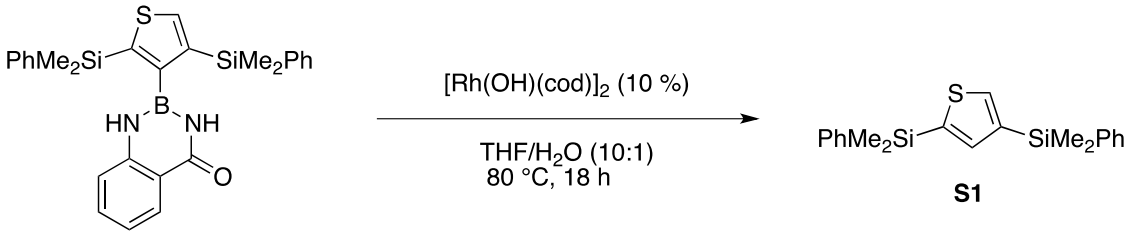
Synthesis of 2j (eq 2)

According to the general procedure, a mixture of **1j** (57.0 mg), $RuH_2(CO)(PPh_3)_3$, norbornene, and dimethylphenylsilane (191 μL) in toluene (0.13 mL) was heated for 1 h. **2j** (77.5 mg, 85%) was isolated by column chromatography on Florisil® (hexane-AcOEt, 10:1 – 5:1).

Synthesis of 3j (eq 2)

According to the general procedure, a mixture of **1j** (57.0 mg), $RuH_2(CO)(PPh_3)_3$, norbornene, and dimethylphenylsilane (191 μL) in toluene (0.13 mL) was heated for 40 h. **3j** (98.4 mg, 79%) was isolated by column chromatography on Florisil® (hexane-AcOEt, 10:1 – 5:1).

Identification of the structure of 3j



3j was converted into the corresponding 2,4-bis(dimethylphenylsilyl)thiophene **S1**. The following procedure was applied: A mixture of **3j** (98.0 mg, 0.20 mmol), $[Rh(OH)(cod)]_2$ (9.0 mg, 0.02 mmol) in THF/H_2O (THF 0.6 mL, H_2O 0.06 mL) was heated at 80 °C for 18 h. After extraction with diethyl ether, the organic phase was dried over $MgSO_4$. **S1** (52.0 mg, 74%) was isolated by column chromatography of Florisil® (hexane-AcOEt, 10:1). The ^1H NMR of the obtained material revealed the formation of unsymmetrical bis(dimethylphenylsilyl)thiophene **S1.**

Synthesis of 7a (eq 4)

According to the general procedure, a mixture of **6a** (59.0 mg), $RuH_2(CO)(PPh_3)_3$, norbornene, and dimethylphenylsilane (191 μL) in toluene (0.13 mL) was heated. **7a** (79.8 mg, 86%) was isolated by column chromatography on Florisil® (hexane-AcOEt, 10:1).

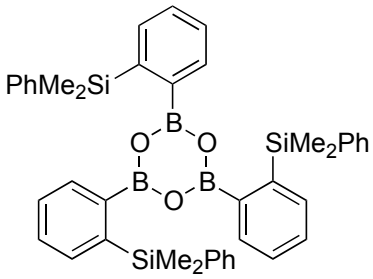
Conversion of the AAM group on the boron atom

Conversion into PIN group (eq 3):

A mixture of **2aa** (107 mg, 0.30 mmol), pinacol (70.8 mg, 0.60 mmol), *p*-toluenesulfonic acid monohydrate (62.7 mg, 0.33 mmol) in THF (0.6 mL) was stirred at room temperature for 17 h. After extraction with diethyl ether, the organic phase was dried over Na_2SO_4. Filtration, evaporation, and purification by column chromatography on Florisil® (hexane-AcOEt, 10:1 – 1:2) gave the pinacolate derivative (85.8 mg, 84%) with a small amount of anthlanilamide. $NaHCO_3$ was added to the water phase and organic maetrials were extracted with ethyl acetate. The organic phase was dried over Na_2SO_4, filtered, and evaporated, giving additional anthlanilamide (total recovery of anthranilamide, 37 mg, 90%).

Acidic Hydrolysis:

To a solution of **2aa** (71.2 mg, 0.2 mmol) in THF (1.0 mL) was added HCl aq. (5 N, 160 μL, 0.8 mmol) at room temperature. The reaction mixture was stirred at room temperature for 48 h. Water (1 mL) and ether (2 mL) were added to the reaction mixture, and the organic phase was separated. The aqueous phase was extracted with ether (2 mL) three times. The organic phase was combined and dried over Na_2SO_4. After filtration and evaporation, the residual oil was kept under vacuum for 5 h at room temperature, giving 2,4,6-tris[2-(dimethylphenylsilyl)phenyl]boroxine (46.1 mg, 96%).



2,4,6-tris[2-(dimethylphenylsilyl)phenyl]boroxine: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (3H, dd, J = 7.2 Hz, 0.8 Hz), 7.53 (3H, dd, J = 7.2 Hz, 0.8 Hz), 7.44 (3H, ddd, J = 7.4 Hz, 7.4 Hz, 1.2 Hz), 7.36 (3H, ddd, J = 7.4 Hz, 7.4 Hz, 1.2 Hz), 7.30-7.25 (6H, m), 7.21-7.12 (9H, m), 0.43 (18H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 139.5, 135.6, 135.4, 134.5, 129.8, 129.0, 128.1, 127.8, -0.35; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.0; IR (neat) 3047, 1334, 1120, 813, 731, 700; HRFABMS Calcd. for $C_{42}H_{45}B_3NaO_3Si_3$ (M+Na): 737.2853, Found: 737.2838.

Procedure for one-pot cross-coupling/*o*-silylation of *p*-BrC_6H_4B(aam):

A mixture of **1k** (90 mg, 0.30 mmol), *p*-tolylboronic acid (61.2 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 0.009mmol), SPhos (7.4 mg, 0.018mmol), and K_3PO_4 (127mg, 0.60 mmol) in THF

(0.6 ml) was stirred for 14 h at room temperature. After being cooled to room temperature, the solvent was evaporated *in vacuo*. The residue was washed with Et_2O and then dried by azeotropic removal of water (toluene, twice). After filling dry nitrogen in the glass tube, norbornene (141 mg, 1.50 mmol), dimethylphenylsilane (229 μL, 1.50 mmol) and toluene (0.15 mL) were added under a nitrogen atmosphere. The mixture was heated at 135 °C for 12 h. After being cooled to room temperature, the solution was directly subjected to column chromatography on Florisil® (Hexane:AcOEt = 10:1 then hexane:AcOEt = 2:1), giving (102 mg, 76 %).

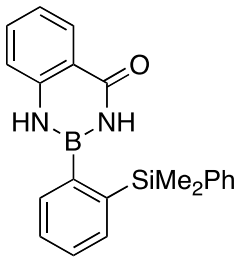
Procedure for one-pot cross-coupling/*o*-silylation of *m*-BrC_6H_4B(aam):

A mixture of **1l** (90 mg, 0.30 mmol), *p*-tolylboronic acid (61.2 mg, 0.45 mmol), $Pd(OAc)_2$ (2.0 mg, 0.009mmol), SPhos (7.4 mg, 0.018mmol), and K_3PO_4 (127mg, 0.60 mmol) in THF (0.6 ml) was stirred for 14 h at room temperature. After being cooled to room temperature, the solvent was evaporated *in vacuo*. The coupling product (87.6 mg, 93 %) was isolated by column chromatography on silica gel (chloroform). The same cross-coupling reaction was also carried out at 80 °C. The reaction was complete within 1.5 h and gave product in 94% yield after isolation by silica gel column chromatography.

According to the general procedure (2.3), a mixture of **1a** (78.0 mg), $RuH_2(CO)(PPh_3)_3$, norbornene, and dimethylphenylsilane (191 μL) in toluene was reacted. **5l** (70.6 mg, 63%) was isolated by column chromatography on Florisil® (hexane-AcOEt, 10:1 – 5:1).

Spectral Data for New Compounds

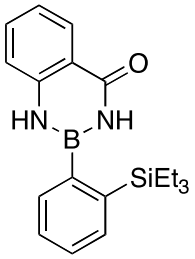
2-[2-(dimethylphenylsilyl)phenyl]-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (2aa):



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (1H, dd, J = 8.0 Hz, 1.6 Hz), 7.84-7.79 (1H, m), 7.56-7.34 (9H, m), 7.20 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 1.2 Hz), 7.07 (1H, brs), 6.23 (1H, dd, J

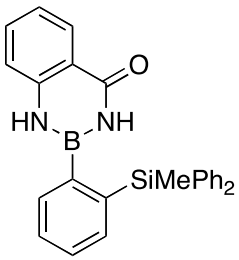
= 8.0 Hz, 0.6 Hz), 5.96 (1H, brs), 0.49 (6H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ166.2, 143.4, 141.4, 140.0, 135.3, 134.0, 133.6, 132.8, 129.4, 128.9, 128.8, 128.4, 121.7, 118.7, 117.6, -1.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ31.5; IR (KBr) 3272, 2953, 1660, 1515, 1259, 759; HREIMS Calcd. for $C_{21}H_{21}BN_2OSi$ (M^+): 356.1516, Found: 356.1515.

2,3-dihydro-2-[2-(triethylsilyl)phenyl]benzo[d][1,3,2]diazaborinin-4(1H)-one (2ab):



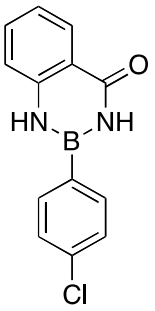
^{1}H NMR (400 MHz, $CDCl_3$) δ8.28 (1H, d, J = 8.0 Hz), 7.62-7.59 (1H, m), 7.58-7.54 (1H, m), 7.49-7.45 (1H, m), 7.44-7.37 (1H, m), 7.22-7.18 (1H, m), 7.15 (1H, brs), 7.02 (1H, d, J = 8.0 Hz), 6.48 (1H, brs), 0.93-0.89 (6H, m), 0.78-0.72 (9H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ166.1, 143.9, 140.1, 135.4, 133.9, 132.2, 129.3, 128.3, 128.0, 122.0, 118.9, 1117.5, 7.5, 4.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ32.3; IR (KBr) 3315, 2953, 1638, 1524, 1486, 722; HREIMS Calcd. for $C_{19}H_{25}BN_2OSi$ (M^+): 336.1829, Found: 336.1832.

2,3-dihydro-2-[2-(methyldiphenylsilyl)phenyl]benzo[d][1,3,2]diazaborinin-4(1H)-one (2ac):



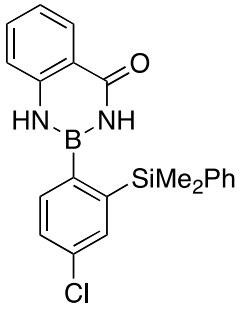
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15-8.11 (1H, m), 7.58-7.54 (1H, m), 7.53-7.34 (14H, m), 7.08 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 0.8 Hz), 6.99 (1H, brs), 6.05 (1H, d, J = 8.0 Hz), 5.96 (1H, brs), 0.69 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ166.2, 143.4, 140.1, 137.0, 136.8, 135.2, 133.6, 133.0, 129.7, 129.1, 128.9, 128.7, 128.3, 121.7, 118.7, 117.5, -2.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ31.6; IR (KBr) 3396, 1046, 1665, 1515, 1488, 759; HREIMS Calcd. for $C_{26}H_{23}BN_2OSi$ (M^+): 418.1673, Found: 418.1674.

2-(4-chlorophenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1b):



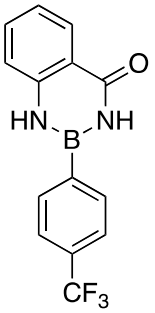
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.77 (1H, s), 9.38 (1H, m), 8.09-8.05 (2H, m), 8.01 (1H, dd, J = 8.0 Hz, 1.6 Hz), 7.61-7.55 (1H, m), 7.55-7.51 (2H, m), 7.44-7.39 (1H, m), 7.15-7.09 (1H, m); ^{13}C NMR (126 MHz, DMSO-d_6) δ 167.2, 146.3, 136.6, 136.2, 134.4, 128.9, 122.0, 119.7, 119.1; ^{11}B NMR (128 MHz, DMSO-d_6) δ 34.4; IR (KBr) 3330, 3245, 1636, 1489, 1270, 757; HREIMS Calcd. for $C_{13}H_{10}BClN_2O$ (M^+): 256.0575, Found: 256.0576.

2-[4-chloro-2-(dimethylphenylsilyl)phenyl]-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (2b):



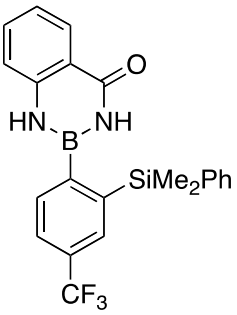
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.14 (1H, m), 7.76-7.73 (1H, m), 7.46-7.36 (8H, m), 7.12 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 1.2 Hz), 7.00 (1H, brs), 6.24-6.19 (1H, m), 5.88 (1H, brs), 0.49 (6H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 144.4, 143.3, 139.2, 135.7, 135.0, 134.3, 133.9, 133.7, 129.7, 129.0, 128.9, 128.5, 121.9, 118.7, 117.6, -1.6; ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.1; IR (KBr) 3418, 3198, 1654, 1513, 1402, 772; HREIMS Calcd. for $C_{21}H_{20}BClN_2OSi$ (M^+): 390.1126, Found: 390.1129.

2,3-dihydro-2-(4-trifluoromethylphenyl)benzo[d][1,3,2]diazaborinin-4(1H)-one (1c):



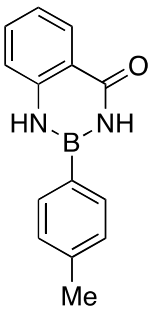
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.88 (1H, s), 9.51 (1H, s), 8.27-8.22 (2H, m), 8.03 (1H, dd, J = 8.0 Hz, 1.2 Hz), 7.80 (2H, d, J = 8.0 Hz), 7.59 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 1.6 Hz), 7.43 (1H, dd, J = 7.6 Hz, 0.8 Hz), 7.13 (1H, ddd, J = 7.6 Hz, 7.2 Hz, 1.2 Hz); ^{13}C NMR (126 MHz, DMSO-d_6) δ 167.2, 146.2, 138.2, 135.0, 134.4, 131.4 (q, J = 31.2 Hz), 128.9, 125.2, 125.2 (q, J = 277.2 Hz), 122.1, 119.9, 119.2; ^{11}B NMR (128 MHz, DMSO-d_6) δ 37.2; IR (KBr) 3334, 1634, 1323, 1116, 1132, 764; HREIMS Calcd. for $C_{14}H_{10}BF_3N_2O$ (M^+): 290.0838, Found: 290.0844.

2-[2-(dimethylphenylsilyl)-4-trifluoromethylphenyl]-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (2c):



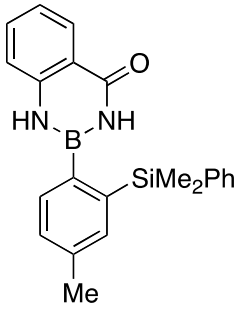
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20-8.15 (1H, m), 8.03-8.00 (1H, m), 7.74-7.69 (1H, m), 7.63 (1H, d, J = 7.6 Hz), 7.45-7.33 (6H, m), 7.14 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 1.2 Hz), 7.00 (1H, brs), 6.27-6.23 (1H, m), 5.89 (1H, brs), 0.53 (6H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 143.4, 143.3, 139.0, 134.1, 133.9, 133.2, 131.2, 130.8 (q, J = 37.8 Hz), 129.9, 129.1, 128.6, 125.5, 124.4 (q, J = 340.2 Hz), 122.2, 118.9, 117.8, -1.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.8; IR (KBr) 3415, 3209, 1655, 1515, 1326, 772; HREIMS Calcd. for $C_{22}H_{20}BF_3N_2OSi$ (M^+): 424.1390, Found: 424.1393.

2,3-dihydro-2-(4-methylphenyl)benzo[d][1,3,2]diazaborinin-4(1H)-one (1d):



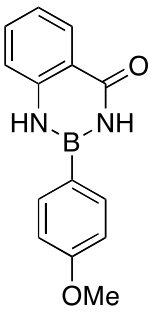
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27-8.22 (1H, m), 7.60 (2H, d, J = 7.6 Hz), 7.55 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 1.6 Hz), 7.49 (1H, brs), 7.33-7.28 (2H, m), 7.20-7.13 (1H, m), 7.12-7.07 (1H, m), 6.75 (1H, brs), 2.42 (3H, s); ^{13}C NMR (126 MHz, DMSO-d_6) δ 167.3, 146.5, 141.1, 134.3, 134.3, 129.4, 128.9, 121.6, 119.6, 119.0, 22.1; ^{11}B NMR (128 MHz, DMSO-d_6) δ 33.1; IR (KBr) 3332, 1638, 1490, 1273, 755; HREIMS Calcd. for $C_{14}H_{13}BN_2O$ (M^+): 236.1121, Found: 236.1120.

2-[2-(dimethylphenylsilyl)-4-methylphenyl]-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (2d):



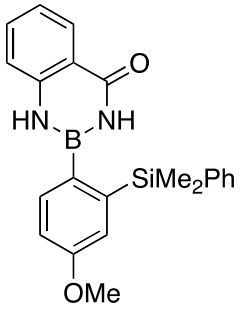
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.13 (1H, m), 7.64-7.61 (1H, m), 7.48-7.34 (7H, m), 7.32-7.28 (1H, m), 7.09 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 0.8 Hz), 7.04 (1H, brs), 6.19-6.15 (1H, m), 5.91 (1H, brs), 2.46 (3H, s), 0.48 (6H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 143.5, 141.3, 140.2, 138.4, 136.2, 134.0, 133.5, 133.0, 129.6, 129.4, 128.9, 128.4, 121.6, 118.6, 117.5, 21.6, -1.4 ; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.8; IR (KBr) 3277, 1653, 1517, 1487, 761; HREIMS Calcd. for $C_{22}H_{23}BN_2OSi$ (M^+): 370.1673, Found: 370.1669.

2,3-dihydro-2-(4-methoxyphenyl)benzo[d][1,3,2]diazaborinin-4(1H)-one (1e):



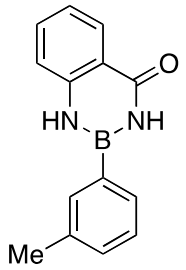
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26-8.22 (1H, m), 7.66-7.62 (2H, m), 7.57-7.51 (1H, m), 7.44 (1H, brs), 7.16 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 0.8 Hz), 7.11-7.07 (1H, m), 7.04-6.99 (2H, m), 6.69 (1H, brs), 3.87 (3H, s); ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.4, 161.3, 145.6, 135.1, 133.3, 127.9, 120.6, 118.6, 118.0, 113.5, 55.0; ^{11}B NMR (128 MHz, DMSO-d_6) δ 30.7; IR (KBr) 3306, 1645, 1509, 1490, 758; HREIMS Calcd. for $C_{14}H_{13}BN_2O_2$ (M^+) : 252.1070, Found: 252.1072.

2-[2-(dimethylphenylsilyl)-4-methoxyphenyl]-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (2e):



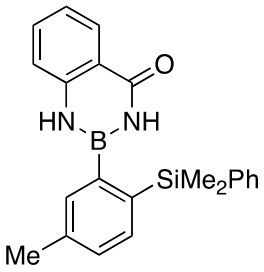
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.12 (1H, m), 7.50 (1H, d, J = 8.0 Hz), 7.48-7.35 (7H, m), 7.11-7.07 (1H, m), 7.05 (1H, brs), 7.01 (1H, dd, J = 8.0 Hz, 2.8 Hz), 6.14 (1H, d, J = 8.4 Hz), 5.91 (1H, brs), 3.90 (3H, s), 0.48 (6H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 159.8, 143.5, 143.4, 139.8, 134.7, 133.9, 133.5, 129.5, 128.8, 128.4, 122.4, 121.5, 118.6, 117.5, 113.0, 55.0, -1.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.6; IR (KBr) 3413, 1653, 1514, 1222, 800; HREIMS Calcd. for $C_{22}H_{23}BN_2O_2Si$ (M^+): 386.1622, Found: 386.1623.

2,3-dihydro-2-(3-methylphenyl)benzo[d][1,3,2]diazaborinin-4(1H)-one (1f):



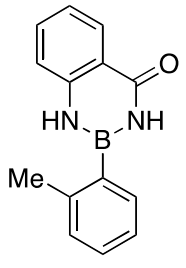
^{1}H NMR (400 MHz, $CDCl_3$) δ8.28-8.24 (1H, m), 7.59-7.47 (4H, m), 7.41-7.31 (2H, m), 7.17 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 0.8 Hz), 7.13-7.09 (1H, m), 6.78 (1H, brs), 2.43 (3H, s); ^{13}C NMR (126 MHz, DMSO-d_6) δ166.4, 145.6, 136.7, 134.0, 133.4, 131.1, 130.4, 128.0, 127.7, 120.8, 118.8, 118.2, 21.1; ^{11}B NMR (128 MHz, DMSO-d_6) δ33.1; IR (KBr) 3332, 1638, 1490, 755; HREIMS Calcd. for $C_{14}H_{13}BN_2O$ (C): 236.1121, Found: 236.1115.

2-[2-(dimethylphenylsilyl)-5-methylpheny]-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (2f):



^{1}H NMR (400 MHz, $CDCl_3$) δ8.19-8.14 (1H, m), 7.71 (1H, d, J = 7.6 Hz), 7.47-7.32 (8H, m), 7.12-7.07 (1H, m), 7.05 (1H, brs), 6.20-6.16 (1H, m), 5.92 (1H, brs), 2.40 (3H, s), 0.46 (6H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ166.3, 143.5, 140.3, 138.7, 137.7, 135.5, 133.9, 133.9, 133.5 129.5, 129.4, 128.9, 128.4, 121.7, 118.7, 117.6, 21.4, -1.38; ^{11}B NMR (128 MHz, $CDCl_3$) δ32.0; IR (KBr) 3392, 1665, 1519, 1486, 759; HREIMS Calcd. for $C_{22}H_{23}BN_2OSi$ (M^+): 370.1673, Found: 370.1677.

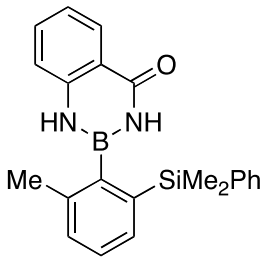
2,3-dihydro-2-(2-methylphenyl)benzo[d][1,3,2]diazaborinin-4(1H)-one (1g):



^{1}H NMR (400 MHz, $CDCl_3$) δ8.25-8.29 (1H, m), 7.56 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 1.6 Hz),

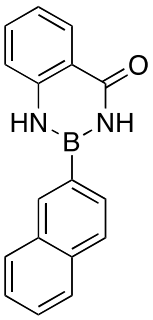
7.48-7.45 (1H, m), 7.39-7.34 (1H, m), 7.28-7.23 (3H, m), 7.19 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 0.8 Hz), 7.08-7.04 (1H, m), 6.60 (1H, brs), 2.49 (3H, s); ^{13}C NMR (126 MHz, DMSO-d_6) δ166.9, 146.4, 141.5, 134.2, 134.0, 130.1, 130.0, 128.9, 125.7, 121.8, 119.7, 119.0, 23.1; ^{11}B NMR (128 MHz, DMSO-d_6) δ38.7; IR (KBr) 3206, 1641, 1522, 1261, 746; HREIMS Calcd. for $C_{14}H_{13}BN_2O$ (M^+): 236.1121, Found: 236.1127.

2-[2-(dimethylphenylsilyl)-6-methylphenyl]-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (2g):



^{1}H NMR (400 MHz, $CDCl_3$) δ7.59 (1H, d, J = 7.2 Hz), 7.46-7.41 (1H, m), 7.38 (1H, dd, J = 7.6 Hz, 7.6 Hz), 7.32-7.20 (7H, m), 7.14 (1H, ddd, J = 8.0 Hz, 7.6 Hz, 1.2 Hz), 6.88 (1H, brs), 6.44-6.40 (1H, m), 5.84 (1H, brs), 2.30 (3H, s), 0.45 (6H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ166.0, 143.7, 141.8, 140.3, 139.8, 134.0, 133.7, 132.4, 130.6, 129.1, 128.6, 128.1, 122.0, 118.9, 117.8, 22.7, -1.7 δ; ^{11}B NMR (128 MHz, $CDCl_3$) δ30.3; IR (KBr) 3274, 1654, 1487, 765 ; HRFABMS Calcd. for $C_{22}H_{23}BO_2Si$ (M^+): 370.1673, Found: 370.1674.

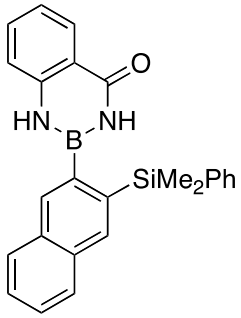
2,3-dihydro-2-(naphthalen-2-yl)benzo[d][1,3,2]diazaborinin-4(1H)-one (1h):



^{1}H NMR (400 MHz, $CDCl_3$) δ8.30-8.27 (1H, m), 8.23 (1H, s), 7.97-7.87 (3H, m), 7.76-7.72 (1H, m), 7.69 (1H, brs), 7.61-7.53 (3H, m), 7.23-7.18 (1H, m), 7.15-7.14 (1H, m), 6.92 (1H, brs); ^{13}C NMR (126 MHz, DMSO-d_6) δ166.4, 145.6, 134.4, 134.1, 133.4, 132.5, 129.9, 129.6, 128.4, 128.0, 127.6, 127.0, 126.9, 126.1, 120.9, 118.9, 118.2; ^{11}B NMR (128 MHz, DMSO-d_6) δ28.9; IR (KBr) 3338, 1641, 1526, 739; HRESIMS Calcd. for $C_{17}H_{13}BN_2NaO$ (M+Na):

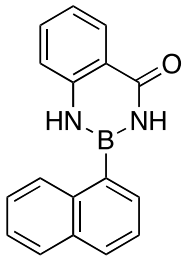
295.1019, Found: 295.1012.

2-[3-(dimethylphenylsilyl)naphthalen-2-yl]-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (2h):



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (1H, s), 8.21-8.17 (1H, m), 8.04 (1H, s), 7.96-7.91 (1H, m), 7.88-7.84 (1H, m), 7.62-7.55 (2H, m), 7.50-7.35 (6H, m), 7.17 (1H, brs), 7.11 (1H, ddd, *J* = 8.0 Hz, 7.2 Hz, 0.8 Hz), 6.18-6.14 (1H, m), 5.96 (1H, brs), 0.57 (6H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 143.6, 140.2, 137.5, 136.4, 134.2, 133.7, 133.6, 133.1, 133.0, 129.7, 129.1, 128.7, 128.2, 128.0, 127.4, 127.3, 121.9, 118.9, 117.8, -1.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.1; IR (KBr) 3398, 1669, 1514, 799; HRESIMS Calcd. for $C_{25}H_{23}BN_2NaOSi$ (M+Na): 429.1570, Found: 429.1554.

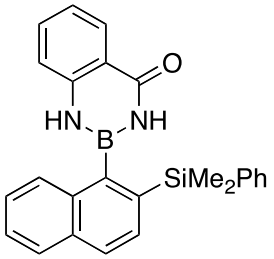
2,3-dihydro-2-(naphthalen-1-yl)benzo[d][1,3,2]diazaborinin-4(1H)-one (1i):



^{1}H NMR (400 MHz, DMSO-d_6) δ 9.66 (1H, s), 9.43 (1H, s), 8.07 (1H, dd, *J* = 8.0 Hz, 1.2 Hz), 8.04-7.94 (3H, m), 7.74-7.69 (1H, m), 7.61-7.51 (4H, m), 7.35 (1H, d, *J* = 8.0 Hz), 7.18-7.12 (1H, m); ^{13}C NMR (126 MHz, DMSO-d_6) δ 167.0, 146.4, 136.0, 135.3, 134.3, 133.7, 132.6, 130.0, 129.3, 128.9, 127.0, 126.6, 126.2, 121.9, 119.9, 119.1; ^{11}B NMR (128 MHz, DMSO-d_6) δ 33.3; IR (KBr) 3373, 1611, 1515, 767; HRESIMS Calcd. for $C_{17}H_{13}BN_2O$ (M^+): 272.1121, Found: 272.1118.

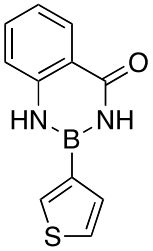
2-[2-(dimethylphenylsilyl)naphthalen-1-yl]-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H

)-one (2i):



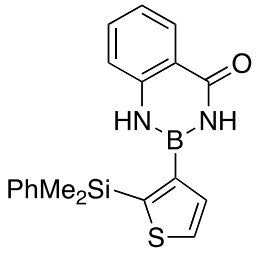
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26-8.22 (1H, m), 7.95 (1H, dd, J = 8.0 Hz, 0.8 Hz), 7.90-7.86 (1H, m), 7.90-7.86 (1H, m), 7.84 (1H, d, J = 8.4 Hz), 7.81-7.77 (1H, m), 7.53-7.39 (3H, m), 7.37-7.33 (2H, m), 7.31-7.15 (4H, m), 7.07 (1H, brs), 6.51-6.47 (1H, m), 6.08 (1H, brs), 0.58 (3H, s), 0.5 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 143.6, 140.5, 139.4, 135.4, 133.9, 133.6, 133.0, 130.8, 129.2, 129.1, 128.4, 128.1, 128.0, 126.5, 126.2, 122.0, 118.9, 117.7, 0.6, -1.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.1; IR (KBr) 3269, 1651, 1512, 1486, 733; HREIMS Calcd. for $C_{25}H_{23}BN_2OSi$ (M^+) : 406.1673, Found: 406.1679.

2,3-dihydro-2-(thiophen-3-yl)benzo[d][1,3,2]diazaborinin-4(1H)-one (1j):



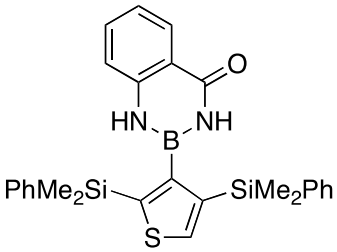
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27-8.22 (1H, m), 7.84 (1H, dd, J = 2.8 Hz, 1.2 Hz), 7.61 (1H, brs), 7.55 (1H, ddd, J = 8.4 Hz, 7.2 Hz, 1.6 Hz), 7.50 (1H, dd, J = 4.8 Hz, 2.4 Hz), 7.41 (1H, dd, J = 4.8 Hz, 1.2 Hz), 7.17 (1H, ddd, J = 8.0 Hz, 7.6 Hz, 1.2 Hz), 7.10 (1H, ddd, J = 8.0 Hz, 0.8 Hz, 0.4 Hz), 6.72 (1H, brs); ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.3, 145.5, 134.9, 133.4, 131.7, 128.0, 126.1, 120.7, 118.8, 118.0; ^{11}B NMR (128 MHz, DMSO-d_6) δ 27.2; IR (KBr) 3349, 1639, 1533, 755; HRESIMS Calcd. for $C_{11}H_9BN_2NaOS$ (M+Na): 251.0426, Found: 251.0419.

2-[2-(dimethylphenylsilyl)thiophen-3-yl]-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (2j):



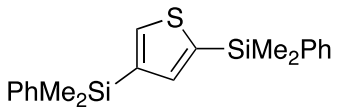
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (1H, dd, J = 8.0 Hz, 1.6 Hz), 7.76 (1H, d, J = 4.8 Hz), 7.60-7.55 (2H, m), 7.51-7.43 (4H, m), 7.39 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 1.6, Hz), 7.17 (1H, brs), 7.09 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 1.2 Hz), 6.21 (1H, d, J = 8.4 Hz), 6.06 (1H, brs), 0.60 (6H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 144.8, 143.9, 138.9, 134.2, 134.1, 133.7, 131.2, 130.2, 129.0, 128.8, 121.8, 118.8, 117.5, -0.81; ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.3; IR (KBr) 3382, 1654, 1518, 754; HRESIMS Calcd. for $C_{19}H_{19}BN_2NaOSSi$ (M+Na): 385.0978, Found: 385.0969.

2-[2,4-bis(dimethylphenylsilyl)thiophen-3-yl]-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (3j):



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (1H, d, J = 8.0 Hz), 7.95 (1H, s), 7.49-7.23 (11H, m), 7.09 (1H, dd, J = 7.6 Hz, 7.6 Hz), 6.18 (1H, d, J = 8.0 Hz), 5.62 (1H, brs), 0.54 (6H, s), 0.47 (6H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 145.8, 145.5, 143.5, 139.6, 138.9, 138.4, 134.0, 133.9, 133.5, 129.7, 129.5, 129.0, 128.2, 128.2, 121.8, 118.7, 117.6, -0.65, -1.38; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.0; IR (KBr) 3294, 1648, 1486, 775; HRESIMS Calcd. for $C_{27}H_{29}BN_2NaOSSi_2$ (M+Na): 519.1530, Found: 519.1521.

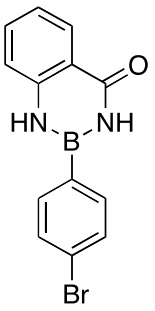
thiophene-2,4-diylbis(dimethylphenylsilane) (S1):



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (1H, d, J = 0.8 Hz), 7.58-7.49 (4H, m), 7.40-7.32 (6H, m), 7.34 (1H, d, J = 1.2 Hz), 0.59 (6H, s), 0.53 (6H, s) s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.4,

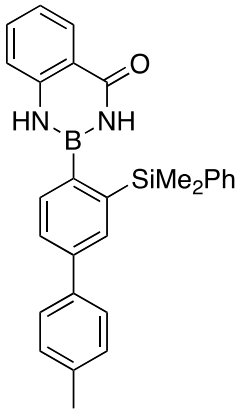
140.3, 139.1, 138.6, 138.6, 138.2, 134.1, 134.0, 129.4, 129.2, 128.0, 127.9, 0.94, -1.45; HRESIMS Calcd. for $C_{20}H_{24}SSi_2$ (M^+): 352.1137, Found: 352.1137.

2-(4-bromophenyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (1k):



^{1}H NMR (400 MHz, DMSO-d_6) δ 9.77 (1H, s), 9.38 (1H, s), 8.03-7.97 (3H, m), 7.68-7.64 (2H, m), 7.57 (1H, ddd, J = 8.4 Hz, 7.2 Hz, 1.6 Hz), 7.43-7.39 (1H, m), 7.11 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 1.2 Hz); ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.2, 145.3, 135.4, 133.4, 130.8, 127.9, 124.7, 121.0, 118.8, 118.2; ^{11}B NMR (128 MHz, DMSO-d_6) δ 31.4; IR (KBr) 3333, 1635, 1490, 755; HREIMS Calcd. for $C_{13}H_{10}BBrN_2O$ (M^+): 300.0070, Found: 300.0073.

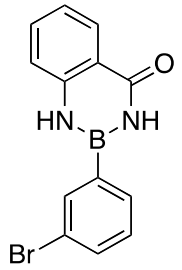
2-{3-(dimethylphenylsilyl)-4'-methyl-[1,1'-biphenyl]-4-yl}-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (5k):



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20-8.16 (1H, m), 8.01 (1H, dd, J = 1.6 Hz, 0.8 Hz), 7.69 (1H, dd, J = 7.6 Hz, 2.0 Hz), 7.60 (1H, dd, J = 7.6 Hz, 0.4 Hz), 7.59-7.55 (2H, m), 7.50-7.46 (2H, m), 7.44-7.35 (4H, m), 7.34-7.29 (2H, m), 7.14-7.07 (2H, m), 6.20 (1H, dd, J = 8.0 Hz, 0.8 Hz), 5.96 (1H, brs), 2.43 (3H, s), 0.53 (6H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 143.6, 142.2, 141.4, 140.1, 138.1, 137.7, 134.1, 134.0, 133.7, 133.6, 129.8, 129.6, 129.1, 128.6, 127.5, 127.2, 121.9, 118.8, 117.7, 21.3, -1.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3; IR (KBr)

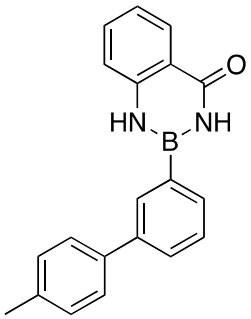
3412, 3207, 1663, 1514, 816, 768; HREIMS Calcd. for $C_{28}H_{27}BN_2OSi$ (M^+): 446.1986, Found: 446.1985.

2-(3-bromophenyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (1l):



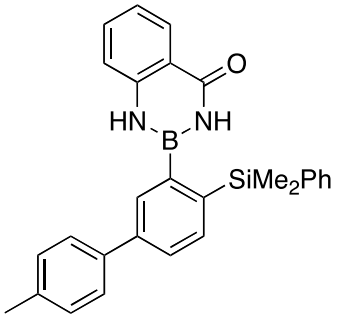
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (1H, d, J = 7.6 Hz), 7.83 (1H, s), 7.68-7.49 (4H, m), 7.37 (1H, dd, J = 7.6 Hz, 7.6 Hz), 7.20 (1H, dd, J = 7.6 Hz, 7.6 Hz), 7.12 (1H, d, J = 7.6 Hz), 6.77 (1H, brs); ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.3, 145.3, 135.8, 135.4, 133.4, 133.2, 132.2, 130.1, 128.0, 122.2, 121.0, 118.9, 118.2; ^{11}B NMR (128 MHz, DMSO-d_6) δ 28.5; IR (KBr) 3327, 1635, 1528, 758; HRESIMS Calcd. for $C_{13}H_{10}BBrN_2NaO$ (M+Na): 322.9967, Found: 322.9967.

2,3-dihydro-2-[4'-methyl-(1,1'-biphenyl)-3-yl]benzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (4l):



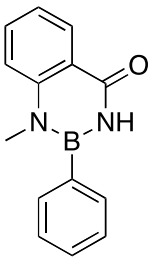
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (1H, dd, J = 8.0 Hz, 1.6 Hz), 7.90, (1H, s), 7.73 (1H, ddd, J = 7.6 Hz, 1.6 Hz, 1.2 Hz), 7.66 (1H, ddd, J = 7.2 Hz, 1.2 Hz, 1.2 Hz), 7.60-7.51 (4H, m), 7.29 (2H, d, J = 7.6 Hz), 7.18 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 0.8 Hz) 7.13 (1H, d, J = 8.0 Hz), 6.86 (1H, brs), 2.42 (3H, s); ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.4, 145.5, 139.5, 137.2, 136.7, 133.4, 132.0, 131.4, 129.4, 128.4, 128.3, 127.9, 126.7, 120.8, 118.8, 118.1, 20.7; ^{11}B NMR (128 MHz, DMSO-d_6) δ 26.7; IR (KBr) 3334, 1635, 1525, 1486, 755; HRESIMS Calcd. for $C_{10}H_{17}BN_2NaO$ (M+Na): 335.1332, Found: 335.1338.

2-{4-(dimethylphenylsilyl)-4'-methyl-[1,1'-biphenyl]-3-yl}-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (5l):



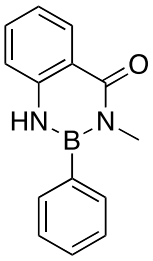
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (1H, dd, J = 7.6 Hz, 0.4 Hz), 7.76 (1H, d, J = 1.6 Hz), 7.72 (1H, dd, J = 7.6 Hz, 2.0 Hz), 7.56-7.52 (2H, m), 7.51-7.46 (2H, m), 7.46-7.35 (5H, m), 7.28 (2H, d, J = 8.0 Hz), 7.19 (1H, brs), 7.11 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 0.8 Hz), 6.23 (1H, dd, J= 8.0 Hz, 0.8 Hz), 6.01 (1H, brs), 2.41 (3H, s), 0.52 (6H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 143.6, 141.5, 140.2, 139.8, 137.7, 137.7, 136.1, 134.2, 133.7, 131.6, 129.8, 129.6, 129.1, 128.6, 127.2, 127.1, 121.9, 118.9, 117.7, 21.3, -1.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.8; IR (KBr) 3404, 1654, 1513, 815; HRAPCIMS Calcd. for $C_{28}H_{28}BN_2OSi$ (M+H): 447.2064, Found: 447.2049.

2,3-dihydro-1-methyl-2-phenylbenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (6a):



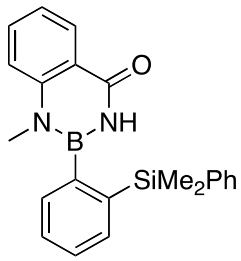
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (1H, ddd, J = 7.6 Hz, 1.6 Hz, 0.4 Hz), 7.69 (1H, ddd, J = 8.4 Hz, 7.2 Hz, 1.6 Hz), 7.61-7.56 (2H, m), 7.50-7.44 (3H, m), 7.32 (1H, d, J = 8.0 Hz), 7.28-7.21 (2H, m), 3.40 (3H, s); ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.2, 146.4, 133.7, 133.1, 129.0, 128.4, 127.7, 121.2, 120.0, 115.2, 34.3; ^{11}B NMR (128 MHz, DMSO-d_6) δ 31.5; IR (KBr) 3202, 1663, 1481, 757; HRESIMS Calcd. for $C_{14}H_{13}BN_2NaO$ (M+Na): 259.1019, Found: 259.1011.

2,3-dihydro-3-methyl-2-phenylbenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (6b):



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33-8.28 (1H, m), 7.63-7.56 (2H, m), 7.54-7.48 (1H, m), 7.48-7.42 (3H, m), 7.20-7.14 (1H, m), 7.02 (1H, d, J = 8.0 Hz), 6.61 (1H, brs), 3.29 (3H, s); ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.2, 144.3, 135.3, 133.0, 132.8, 129.1, 128.0, 127.7, 121.0, 118.2, 117.8, 31.5; ^{11}B NMR (128 MHz, DMSO-d_6) δ 31.5; IR (KBr) 3281, 3040, 1620, 1520, 751; HRESIMS Calcd. for $C_{14}H_{13}BN_2NaO$ (M+Na): 259.1019, Found: 259.1009.

2-[2-(dimethylphenylsilyl)phenyl]-2,3-dihydro-1-methylbenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (7a):



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30-8.26 (1H, m), 7.56-7.20 (1H, m), 7.59 (1H, dddd, J = 8.4 Hz, 7.2 Hz, 1.6 Hz, 0.4 Hz), 7.48-7.38 (2H, m), 7.37-7.32 (3H, m), 7.23-7.18 (1H, m), 7.12-7.06 (3H, m), 7.02 (1H, d, J = 8.4 Hz), 6.82 (1H, brs), 2.80 (3H, s), 0.54-0.47 (6H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4, 146.3, 141.6, 137.8, 135.2, 134.1, 133.8, 131.7, 129.5, 129.2, 128.6, 128.1, 127.7, 121.6, 120.1, 114.6, 34.5, -1.16, -1.49; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.3; IR (KBr) 3197, 2955, 1664, 1482, 816; HRESIMS Calcd. for $C_{22}H_{23}BN_2NaOSi$ (M+Na): 393.1570, Found: 393.1557.

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Chapter 4

Anthranilamide-Masked *o*-Iodoarylboronic Acids as Coupling Modules for Iterative Synthesis of *ortho*-Linked Oligoarenes

Abstract: Anthranilamide (AAM)-masked *o*-iodoarylboronic acids were prepared from AAM-masked arylboronic acids via Ru-catalyzed *o*-C-H silylation followed by iododesilylation with ICl. Suzuki-Miyaura coupling of AAM-masked *o*-haloarylboronic acids with arylboronic acids proceeded under ligand-free conditions. Oligo(*o*-phenylene)s and oligo(naphthalene-2,3-diyl)s were synthesized via iterative Suzuki-Miyaura coupling sequences.

Introduction

Increasing interest has been focused on the synthesis and structure of *ortho*-linked oligoarenes and hetarenes.[1–4] They cannot adopt planar structure, but form helical structures due to the steric repulsion of the substituents on the aromatic rings. In addition to their static helical structures, dynamic change of the helical structures has gained increasing attention from the viewpoint of application to functional materials.[5] For instance, we have recently established solvent-dependent, reversible switch of helical conformation of poly(quinoxaline-2,3-diyl)s with high molecular weight.[6] This system was successfully applied to a new chiral catalyst system in which either enantiomer can be produced with high enantioselectivity from a single enantiomer of the chiral catalyst.[7] Although being attractive, *ortho*-linked oligoarenes and hetarenes have not been explored in-depth yet, mainly because of paucity of robust synthetic approaches. Therefore, it is highly desirable to establish general, efficient synthetic methods which would also allow synthesis of functionalized oligoarenes in a sequence selective manner.

We have been interested in the development of cross-coupling-based organic synthesis including iterative synthesis of oligoarene derivatives on the basis of boron-masking strategy using 1,8-diaminonaphthalene (DAN) as a highly effective masking group.[8] We subsequently established a removable *ortho*-directing group (*o*-DG), which is attached to the boron atom of the boronyl group and allows Ru-catalyzed *o*-silylation.[9] Although pyrazolylaniline (PZA) was reported also as the first-generation *o*-DG, we later on showed that anthranilamide (AAM) exhibited higher ability of *o*-direction as well as higher stability, which allowed us to utilize AAM as a protective group in Suzuki-Miyaura coupling.[10] We envisioned that AAM-protected *o*-haloarylboronic acids **3** may serve as highly convenient building modules in the synthesis of helical oligo(*o*-arene)s via iterative Suzuki-Miyaura cross-coupling. The modules **3** may be obtained directly by halodesilylation of AAM-protected *o*-silylarylboronic acids **2**, which in turn are conveniently prepared by *o*-silylation of AAM-protected arylboronic acids **1**. It should be noted that a report on direct *ortho*-iodination of unprotected arylboronic acids has appeared recently.[11,12] The direct iodination, however, still requires use of silver salt to promote the reaction and encounters difficulty in iodination of electron-poor and electron-neutral arenes. In this paper, we demonstrate convenient synthesis of AAM-protected *o*-iodoarylboronic acids and their use in

iterative Suzuki-Miyaura coupling for the synthesis of oligo(*o*-phenylene)s and oligo(naphthalene-2,3-diyl)s.

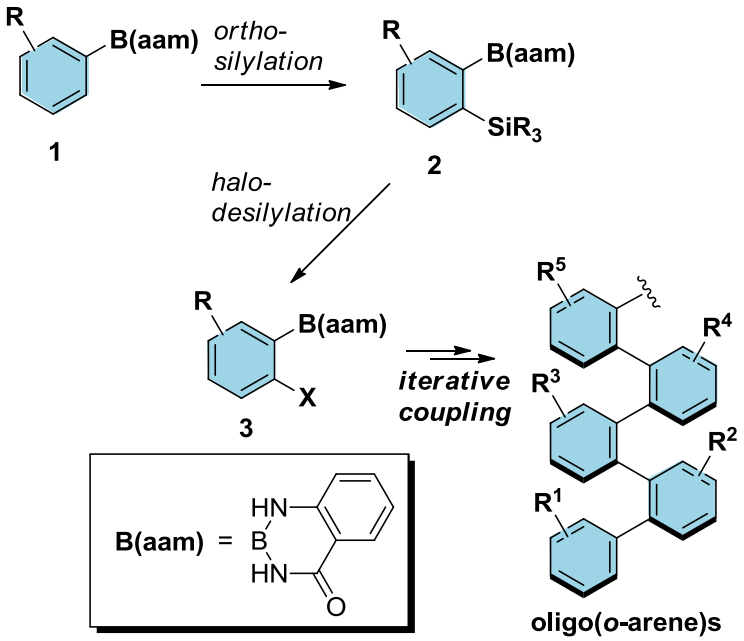


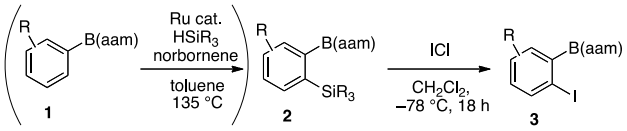
Figure 1. Synthetic strategies of oligo(*o*-arene)s.

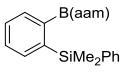
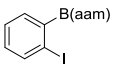
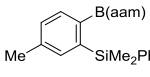
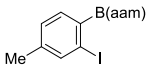
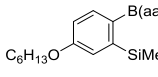
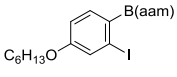
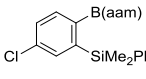
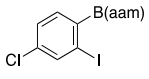
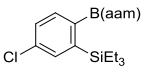
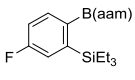
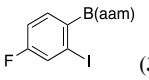
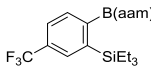
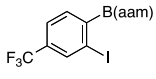
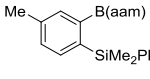
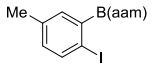
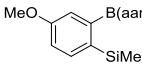
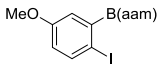
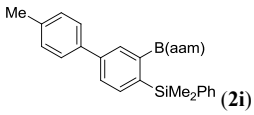
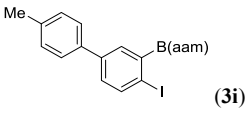
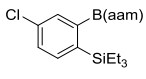
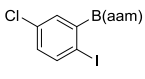
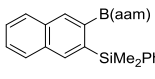
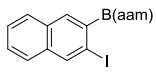
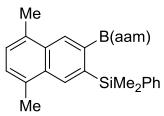
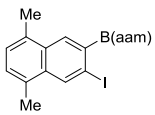
Results and Discussion

AAM-protected *o*-silylarylboronic acids **2** were prepared according to the reported procedure for Ru-catalyzed *o*-silylation of arylboronic acids.[10] In addition to the *o*-silylboronic acids **2a**, **2b**, **2d**, **2g**, and **2k** reported in the previous paper, we also synthesized new derivatives in good yields from the corresponding AAM-protected arylboronic acids (Table 1). Iododesilylation was accomplished efficiently by use of ICl at low temperature.[12] Attempted use of I_2 or Br_2 failed to give the corresponding *o*-halogenated products in reasonable yields. In the iododesilylation, use of the electron-deficient AAM group rather than the electron-rich PZA group was essential to avoid undesirable iodination on the masking group. The present synthesis of *o*-iodoarylboronic acids through iododesilylation was found to be complementary to Hall's silver-mediated direct iodination, which requires electron-donating substituents such as alkoxy and amino groups on the aromatic rings. Our method could successfully be applied to alkyl- (entries 2 and 8), aryl- (entry 10), chloro-

(entries 5 and 11), and even fluoro-substituted arylboronic acids (entry 6), in addition to alkoxy-substituted arylboronic acids (entries 3 and 9). Note that attempted iododesilylation of the phenyldimethylsilyl group on the electron-deficient aromatic ring failed (entry 4), leading to iodination at the phenyl group of the $PhMe_2Si$ group. This problem was overcome by use of Et_3Si derivative (entries 5, 6, 7 and 11). It should also be noted that AAM-masked 5,8-dimethylnaphthyl-2-boronic acid, which was used for the synthesis of **2l** (entry 13) was conveniently prepared from 1,4-dimethylnaphthalene via Ir-catalyzed aromatic C–H borylation. This example demonstrates that the synthetic utility of the *ortho*-C-H silylation is significantly enhanced by combining it with the C-H borylation chemistry.

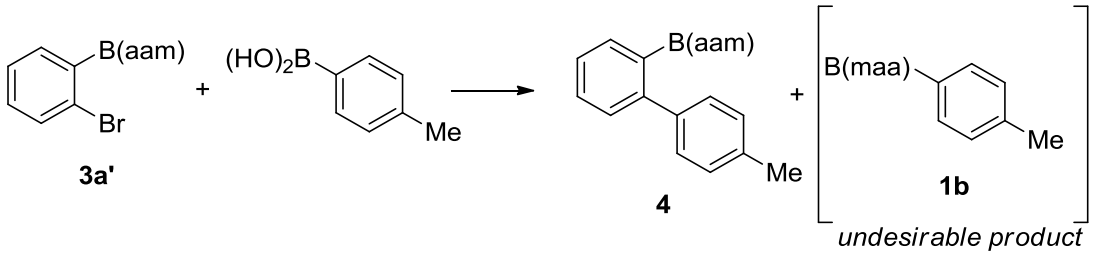
Table 1. Iododesilylation of AAM-protected *o*-silylarylboronic acids produced by Ru-catalyzed *o*-directed silylation of AAM-protected arylboronic acids.[a]



entry	product **2**	yield[d]	product **3**	yield[f] (%)
1	 (**2a**)	80[e]	 (**3a**)	87
2	 (**2b**)	88[e]	 (**3b**)	96
3	 (**2c**)	90	 (**3c**)	90
4	 (**2d**)	91[e]	 (**3d**)	0
5[b]	 (**2d'**)	82	**3d**	95
6[b]	 (**2e'**)	65	 (**3e**)	94
7[c]	 (**2f'**)	53	 (**3f**)	71
8	 (**2g**)	81[e]	 (**3g**)	94
9	 (**2h**)	87	 (**3h**)	94
10	 (**2i**)	63	 (**3i**)	92
11[b]	 (**2j'**)	83	 (**3j**)	97
12	 (**2k**)	90	 (**3k**)	84
13	 (**2l**)	72	 (**3l**)	86

[a]**2** (0.1 mmol), ICl (0.2 mmol), CH_2Cl_2 (0.5 mL), –78 °C, 18 h. [b] –78 to –9 °C. [c]–78 °C to room temperature. [d]Isolated yield of **2** in Ru-catalyzed ortho-silylation of the corresponding ArB(aam). [e]Reported in reference 10. [f]Isolated yield.

Table 2. Optimization of cross-coupling of *o*-halophenylboronic acid **3a'** with *p*-tolylboronic acid.



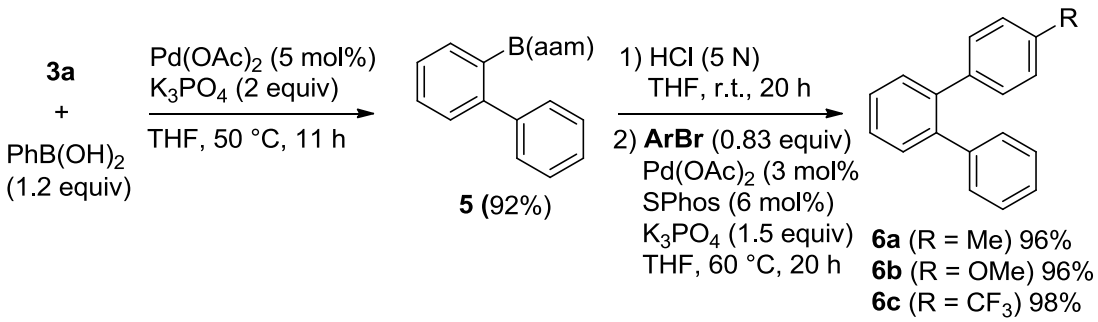
entry	reaction conditions	% yield **4** (**1b**)[a]
1	$Pd(OAc)_2$ (3 mol%), SPhos (6 mol%), K_3PO_4 (2 equiv), THF, rt, 89 h	0 (98)
2	$Pd(OAc)_2$ (3 mol%), SPhos (6 mol%), K_3PO_4 (2 equiv), THF, 50 °C, 62 h	0 (65)
3	$Pd(P^tBu_3)_2$ (5 mol%), CsF (2 equiv), THF, rt, 19 h	0 (0)
4	$Pd(OAc)_2$ (3 mol%), K_3PO_4 (2 equiv), THF, rt, 19 h	96 (0)

[a]Isolated yield of **4**. NMR yield of **1b** is in the parenthesis.

We then examined cross-coupling of AAM-protected *o*-halophenylboronic acids with arylboronic acids. An initial trial under the reaction conditions utilized for the coupling of AAM-protected *p*- and *m*-bromophenylboronic acids completely failed giving no desired coupling products. Indeed, the attempted coupling of AAM-protected *o*-bromophenylboronic acid **3a'** in the presence of SPhos[13] (P/Pd = 2) as a ligand at room temperature resulted in transfer of the AAM group from **3a'** to *p*-tolylboronic acid, giving AAM-protected *p*-tolylboronic acid **1b** with no formation of the coupling product (entry 1, Table 2). Applying higher reaction temperature did not improve the reaction outcome at all (entry 2). Use of the *t*-Bu_3P/CsF system[14] gave no desirable product, although no AAM-transfer product was formed either (entry 3). We finally found that a ligand-free palladium catalyst worked efficiently in the cross-coupling of **3a'**, giving the AAM-protected biarylboronic acid **4** in high isolated yield (entry 4). The reaction conditions were successfully applied to the cross-coupling of *o*-iodo derivative **3a**, giving the corresponding biaryl product **5** in high yield (Scheme 1). Thus obtained AAM-protected biarylboronic acid

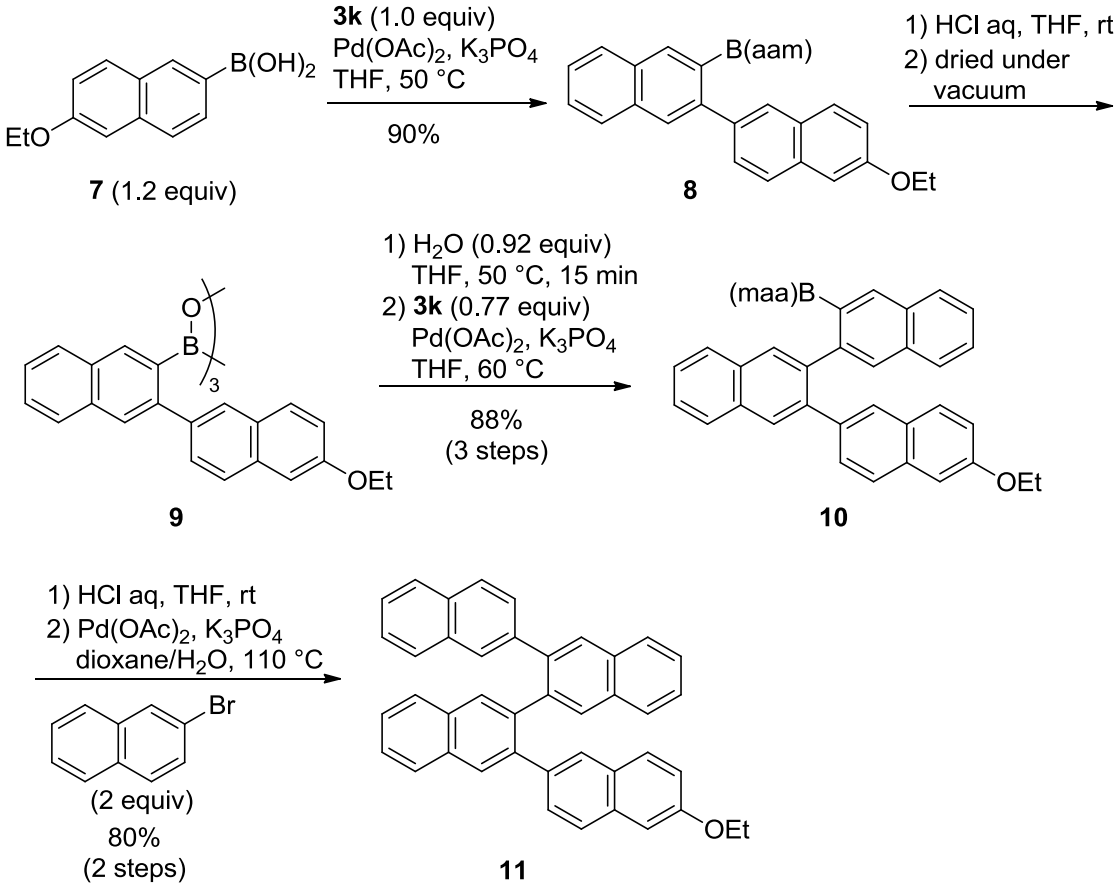
5 was cross-coupled with various aryl bromides after deprotection of the AAM group by acidic hydrolysis, giving teraryls **6a-c** in high yields.

Having established the basis for the preparation and reactivities of AAM-masked *o*-iodoarylboronic acids, we pursued the iterative synthesis of oligo(naphthalene-2,3-diyl)s using our AAM system. Cross-coupling conditions for the synthesis of oligonaphthalene were further optimized on the basis of the examination for the oligophenylene synthesis. We again observed better outcome with ligand-free palladium catalyst in the coupling of AAM-masked 3-iodo-2-naphthylboronic acid **3k** with 6-ethoxy-2-naphthylboronic acid **7**. After the coupling, the AAM group remaining untouched was removed by acidic treatment. Use of the unmasked binaphthylboronic acid in cross-coupling with **3k**, however, resulted in ill-reproducible results.



Scheme 1. Synthesis of ter(*o*-phenylene)s via iterative Suzuki-Miyaura coupling

It turned out that the presence of even a small amount of water led to AAM transfer from **3k** to the binaphthylboronic acid, whereas complete dehydration then led to the formation of boroxine **9**, which was totally unreactive toward cross-coupling. Indeed, the degree of dehydration after the unmasking step affected the result of subsequent cross-coupling step significantly. We could finally adapt the procedure in which boroxine **9**, obtained by complete dehydration, was hydrolyzed to binaphthylboronic acid by adding a stoichiometric amount of water prior to the coupling step. According to this procedure, AAM-masked ternaphthylboronic acid **10** was isolated in high yield. The iterative coupling sequence was terminated by coupling with 2-naphthyl bromide, giving quaternaphthalene **11** bearing a terminal ethoxy group.



Scheme 2. Synthesis of quarter(naphthalene-2,3-diyl) via iterative Suzuki-Miyaura coupling

Conclusion

In summary, we have established a new synthetic route to *o*-iodoarylboronic acid derivatives via Ru-catalyzed *o*-directed silylation of AAM-masked arylboronic acids followed by iododesilylation with ICl. The present synthesis of *o*-iodoarylboronic acids is complementary to the *ortho*-directed, Ag-mediated iodination of arylboronic acids[11] and show wider applicability to electronically unactivated arylboronic acids. Application to iterative synthesis of oligo(*o*-phenylene)s and oligo(naphthalene-2,3-diyl)s has also been demonstrated. Synthesis of more densely functionalized oligo(*o*-phenylene)s and oligo(naphthalene-2,3-diyl)s including those adapting non-racemic helical structures are now being undertaken in this laboratory.

Experimental Section

General

All reactions were carried out under an atmosphere of nitrogen with magnetic stirring. ^{1}H, ^{11}B and ^{13}C NMR spectra were recorded on a Varian Mercury vx400 or a JEOL JNM-A500 spectrometer at ambient temperature. ^{1}H NMR data are reported as follows: chemical shift in ppm downfield from tetramethylsilane (δ scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sex = sextet, m = multiplet, and br = broad), coupling constant (Hz), and integration. ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale). ^{11}B NMR chemical shifts are reported in ppm downfield from $BF_3 \cdot OEt_2$. All ^{13}C NMR spectra were obtained with broadband proton decoupling. High-resolution mass spectra were recorded on a JEOL JMS-SX102A (EI) and Thermo Fisher Scientific EXACTIVE (ESI and APCI) spectrometer. IR spectra were recorded on a FTIR SHIMADZU DR-8000 spectrometer. Preparative TLC was performed with silica gel $60PF_{254}$ (Merck). Recycling Preparative GPC was performed with JAI LC-908 equipped with JAIGEL-1H and -2H columns in a series($CHCl_3$). Column chromatography was performed with Ultra Pure Silica Gel (40-63 μm) (Silicycle).

Materials

Toluene and THF were dried and deoxygenized using an alumina/catalyst column system (GlassContour Co.). Anthranilamide (TCI), hydrochloric acid (Nacalai), iodine monochloride (Wako), 4-bromotoluene (Wako), 4-bromoanisole (TCI), 4-bromobenzotrifluoride (TCI), 2-Bromonaphthalene (TCI), triethylsilane (TCI), dimethylphenylsilane (Aldrich), Bis(pinacolato)diboron (ChemICHIBA), norbornene (TCI), phenylboronic acid (Wako), 4-methoxyphenylboronic acid (Aldrich), 4-trifluoromethylphenylboronic acid (Wako), 4-chlorophenylboronic acid (Wako), 4-fluorophenylboronic acid (Wako), 3-chlorophenylboronic acid (TCI) 4-methylphenylboronic acid (Wako), 3-methylphenylboronic acid (TCI), 2-naphthaleneboronic acid (TCI), 6-ethoxy-2-naphthaleneboronic acid (TCI), 1,4-dimethylnaphthalene (TCI), Florisil® (75-150 μm, Kanto), $Pd(OAc)_2$ (Tanaka Rare-metal), and SPhos (Strem) were used as received from the commercial sources. $RuH_2(CO)(PPh_3)_3$,[15] $[IrCl(COD)(OMe)]_2$,[16] were prepared by the

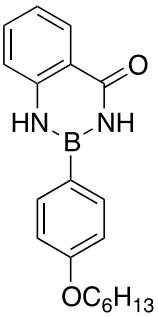
literature procedures. Potassium phosphate (Nacalai) was dried in an oven at 300 °C for 5 h *in vacuo* (1 mmHg).

Synthesis of New ArB(aam) by Condensation of Arylboronic Acid with Anthranilamide

General Procedure

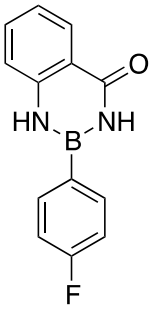
A mixture of arylboronic acid (8.8 mmol) and anthranilamide (1.09 g, 8 mmol) in toluene (0.25 mmol/mL, 32 mL) was heated under reflux in a Dean-Stark apparatus for 1 h. After cooling the mixture to room temperature, the precipitates were collected by filtration to give **1**.

Synthesis of 1c



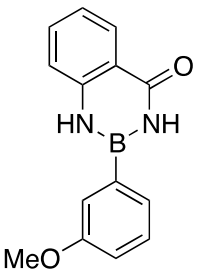
According to the general procedure, **1c** (2.27 g, 88%) was prepared from 4-hexyloxyphenylboronic acid (1.95 g) and anthranilamide (1.09 g). mp 204.1-207.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ9.60 (1H, s), 9.19 (1H, s), 8.01 (3H, d, J = 8.4 Hz), 7.54 (1H, ddd, J = 8.4 Hz, 7.2 Hz, 1.6 Hz), 7.41 (1H, d, J = 7.6 Hz), 7.07 (1H, ddd, J = 8.0 Hz, 7.6 Hz, 1.2 Hz), 6.98 (2H, d, J = 8.8 Hz), 3.99 (2H, t, J = 6.8 Hz), 1.73-1.66 (2H, m), 1.43-1.36 (2H, m), 1.30-1.26 (4H, m), 0.86 (3H, t); ^{13}C NMR (100 MHz, DMSO-d_6) δ166.3, 160.8, 145.6, 135.1, 133.3, 127.9, 123.4, 120.5, 118.6, 118.0, 113.9, 67.3, 31.0, 28.6, 25.2, 22.1, 13.9; ^{11}B NMR (128 MHz, DMSO-d_6) δ25.0; IR (ATR) 3300, 1645, 1487, 758; HRESIMS Calcd. for $C_{19}H_{24}BN_2O_2$ ($[M+H]^+$): 323.1925, Found: 323.1920.

Synthesis of 1e



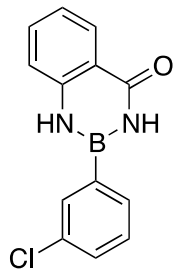
According to the general procedure, **1e** (608 mg, 84%) was prepared from 4-fluorophenylboronic acid (462 mg, 3.3 mmol) and anthranilamide (408 g, 3.0 mmol). mp 228.0-233.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ9.75 (1H, s), 9.32 (1H, s), 8.14-8.10 (2H, m), 8.03 (1H, dd, J = 8.0 Hz, 1.2 Hz), 7.52 (1H, ddd, J = 8.4 Hz, 7.6 Hz, 1.6 Hz), 7.41 (1H, d, J = 7.6 Hz), 7.25-7.21 (2H, m), 7.08-7.04 (1H, m); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.5, 164.1 (d, J = 247 Hz), 145.5, 135.9 (d, J = 7.9 Hz), 133.4, 128.6, 128.0, 120.9, 118.8, 118.2, 114.8 (d, J = 19.7 Hz); ^{11}B NMR (128 MHz, DMSO-d_6) δ29.4; IR (ATR) 3333, 1616, 1458, 758; HRESIMS Calcd. for $C_{13}H_{11}BFN_2O$ ([M+H]$^+$): 241.0943, Found: 241.0939.

Synthesis of 1h



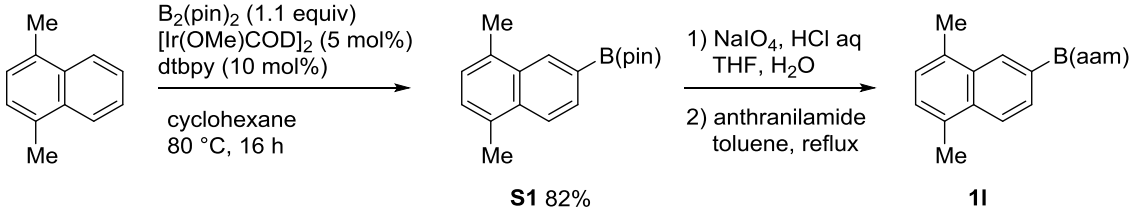
According to the general procedure, **1h** (1.12 g, 88%) was prepared from 3-methoxylphenylboronic acid (832 mg, 5.5 mmol) and anthranilamide (680 mg, 5.0 mmol). mp 189.9-193.2 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ9.78 (1H, s), 9.33 (1H, s), 8.05 (1H, dd, J = 8.0 Hz, 0.8 Hz), 7.68-7.64 (2H, m), 7.57 (1H, ddd, J = 8.4 Hz, 6.8 Hz, 1.6 Hz), 7.46 (1H, dd, J = 8.0 Hz, 0.4 Hz), 7.36 (1H, dd, J = 7.6 Hz, 7.6 Hz), 7.11 (1H, ddd, J = 8.0 Hz, 6.8 Hz, 1.2 Hz), 7.03 (1H, ddd, J = 8.4 Hz, 2.8 Hz, 0.8 Hz), 3.83 (3H, s); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.4, 159.0, 145.5, 133.7, 133.4, 129.0, 128.0, 125.6, 120.9, 118.8, 118.3, 118.2, 116.5, 55.1; ^{11}B NMR (128 MHz, DMSO-d_6) δ28.4; IR (ATR) 3190, 1616, 1483, 761; HRESIMS Calcd. for $C_{14}H_{14}BN_2O_2$ ([M+H]$^+$): 253.1143, Found: 253.1137.

Synthesis of 1j



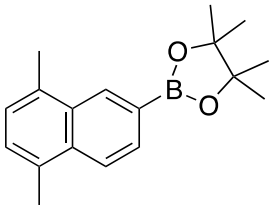
According to the general procedure, **1j** (502 mg, 98%) was prepared from 3-chlorophenylboronic acid (343 mg, 3.3 mmol) and anthranilamide (272 mg, 3.0 mmol). mp 219.9-222.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ9.82 (1H, s), 9.53 (1H, s), 8.16 (1H, s), 8.05 (2H, d, J = 7.6 Hz), 7.57 (1H, ddd, J = 8.8 Hz, 7.2 Hz, 1.6 Hz), 7.52-7.43 (3H, m), 7.11 (1H, ddd, J = 8.0 Hz, 6.8 Hz, 1.2 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ166.3, 145.4, 135.0, 133.4, 133.3, 132.9, 131.9, 130.3, 129.8, 127.9, 121.0, 118.9, 118.3; ^{11}B NMR (128 MHz, DMSO-d_6) δ26.7; IR (ATR) 3325, 1616, 1479, 756; HRESIMS Calcd. for $C_{13}H_{11}BClN_2O$ ([M+H]$^+$): 257.0647, Found: 257.0641.

Synthesis of ArB(aam) (1l) via Ir-catalyzed Aromatic C–H Borylation[17]



Scheme S1. Synthesis of **1l**

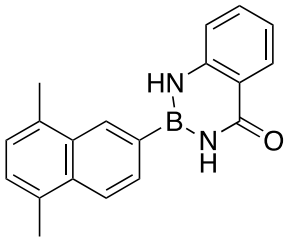
***o*-C-H Borylation of 1,4-Dimethylnaphthalene**



A mixtuer of [Ir(COD)(OMe)]$_2$ (33.1 mg, 0.05 mmol), 4,4'-di-tert-butyl-2,2'-bipyridine (26.8 mg, 0.1 mmol), bispinacolatodiboron (279 mg, 1.1 mmol) and 1,4-dimethylnaphthalene (154 μL, 1.0 mmol) in cyclohexane (3.8 mL) was heated for 20 h at 60 °C. After being cooled to

room temperature, the solvent was evaporated *in vacuo*. The borylated product **S1** (231 mg, 82%) was isolated by column chromatography on Florisil® (hexane-AcOEt, 9:1). mp 70.8-72.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (1H, s), 8.40 (1H, dd, J = 8.4 Hz, 0.4 Hz), 7.97 (1H, dd, J = 8.4 Hz, 1.2 Hz), 7.28-7.23 (2H, m), 2.78 (s, 3H), 2.70 (s, 3H), 1.45 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.5, 133.4, 132.9, 132.2, 132.1, 130.2, 127.5, 126.3, 123.8, 84.0, 25.0, 19.7, 19.5; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.6; IR (ATR) 2979, 1342, 1139, 692; HREIMS Calcd. for $C_{18}H_{23}BO_2$ (M^+): 282.1791, Found: 282.1794.

Conversion of ArB(pin) to ArB(aam)



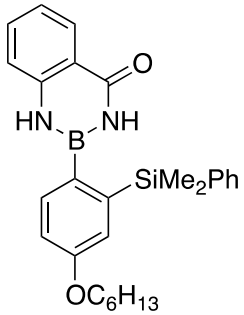
S1 (231 mg, 0.82 mmol) and sodium perodate (525 mg, 2.46 mmol) were stirred in 5.3 mL of a mixture of THF and water for 30 min, at which time aqueous hydrochloric acid (1 N, 573 μL, 0.57 mmol) was added to the suspension. The reaction mixture was stirred at room temperature for 17 h. The reaction mixture was diluted with water (3 mL) and extracted with ethyl acetate (3 x 6 mL). The combined extracts were washed with water (2 x 3 mL) and brine (3 mL), dried over sodium sulfate, filtered, and concentrated to dryness by evaporation. The material was used for condensation of arylboronic acid with anthranilamide without further purification. A mixture of arylboronic acid and anthranilamide (106 mg, 0.78 mmol) in toluene (5 mL) was heated under reflux in a Dean-Stark apparatus for 1 h. After cooling a mixture to room temperature, the precipitates were collected by filtration to give **1l** (229 mg, 93%). mp 208.2-210.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (1H, s), 8.29 (1H, dd, J = 8.0 Hz, 1.2 Hz), 8.08, (1H, d, J = 8.4 Hz), 7.88 (1H, brs), 7.77 (1H, dd, J = 8.4 Hz, 1.2 Hz), 7.59-7.55 (1H, m), 7.31-7.25 (2H, m), 7.21-7.17 (2H,m), 7.02 (1H, brs), 2.75 (3H, s), 2.68 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 144.6, 134.1, 134.0, 133.0, 132.5, 132.3, 129.8, 129.4, 127.8, 127.4, 127.1, 125.0, 122.0, 119.2, 117.8, 19.6, 19.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.5; IR (ATR) 3334, 1620, 1529, 750; HREIMS Calcd. for $C_{19}H_{17}BN_2O$ (M^+): 300.1434, Found: 300.1432.

C–H silylation of AAM-Protected Arylboronic Acids (Table 1)

General Procedure

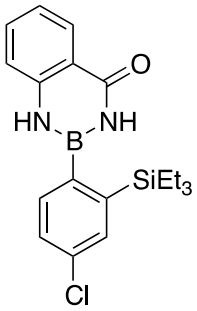
A mixture of **1** (0.25 mmol), $RuH_2(CO)(PPh_3)_3$ (13.8 mg, 0.015 mmol), norbornene (118 mg, 1.25 mmol), and hydrosilane (1.25 mmol) in toluene (0.13 mL) was heated in a glass tube sealed with a J-Young Teflon stopper at 135 °C. The reaction was run for 20 h unless otherwise noted. After cooling to temperature, the mixture was subjected to column chromatography on Florisil® (hexane/EtOAc), giving *o*-silylated product **2**.

Synthesis of 2c



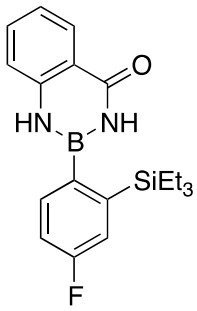
According to the general procedure, a mixture of **1c** (1.29 g, 4.0 mmol), $RuH_2(CO)(PPh_3)_3$ (220 mg, 0.24 mmol), norbornene (1.88g, 20 mmol), and dimethylphenylsilane (3.1 mL) in toluene (2.0 mL) was heated. **2c** (1.48 g, 81%) was isolated by column chromatography on Florisil® (hexane-AcOEt, 10:1). mp 137.2-139.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (1H, dd, J = 8.0 Hz, 1.2 Hz), 7.48-7.44 (3H, m), 7.43-7.34 (5H, m), 7.08-7.02 (2H, m), 6.97 (1H, dd, J = 8.0 Hz, 2.8 Hz), 6.12 (1H, dd, J = 8.0 Hz, 0.8 Hz), 5.90 (1H, brs), 4.03 (2H, t, J = 6.4 Hz), 1.83 (2H, quint, J = 7.2 Hz), 1.53-1.46 (2H, m), 1.39-1.33 (4H, m), 0.93-0.89 (3H, m), 0.48 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 159.6, 143.7, 143.5, 140.1, 134.9, 134.1, 133.6, 129.6, 129.0, 128.6, 123.1, 121.7, 118.8, 117.7, 113.8, 67.9, 31.7, 29.4, 25.9, 22.8, 14.2, -1.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3; IR (KBr) 3201, 1652, 1512, 767; HRESIMS Calcd. for $C_{27}H_{34}BN_2O_2Si$ ($[M+H]^+$): 457.2477, Found: 457.2469.

Synthesis of 2d'



According to the general procedure, a mixture of **1d** (192 mg), $RuH_2(CO)(PPh_3)_3$, norbornene and triethylsilane (597 μL) in toluene was heated. **2d'** (229 mg, 82%) was isolated by column chromatography on Florisil® (hexane-AcOEt, 10:1 – 4:1 – 3:1). mp 189.0-192.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29-8.27 (1H, m), 7.57 (1H, ddd, J = 8.8 Hz, 7.2 Hz, 0.8 Hz), 7.54 (1H, dd, J = 2.0 Hz, 0.8 Hz), 7.42-7.35 (2H, m), 7.22 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 0.8 Hz), 7.11 (1H, brs), 7.02 (1H, dd, J = 8.0 Hz, 0.8 Hz) 6.45 (1H, m), 0.93-0.89 (9H, m), 0.78-0.71 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 143.9, 143.4, 135.5, 135.3, 134.2, 133.8, 129.5, 128.3, 122.4, 119.0, 117.7, 7.6, 4.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.5; IR (ATR) 3371, 1651, 1517, 725; HRESIMS Calcd. for $C_{19}H_{25}BClN_2OSi$ ($[M+H]^+$): 371.1512, Found: 371.1502.

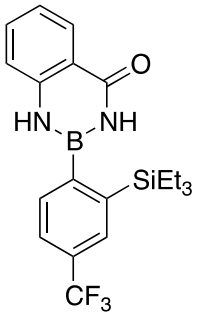
Synthesis of 2e'



According to the general procedure, a mixture of **1e** (180 mg), $RuH_2(CO)(PPh_3)_3$, norbornene and triethylsilane (597 μL) in toluene was heated. **2e'** (230 mg, 86%) was isolated by column chromatography on Florisil® (hexane-AcOEt, 8:1 – 5:1 – 4:1). mp 169.5-173.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29-8.27 (1H, m), 7.57 (1H, ddd, J = 8.8 Hz, 7.2 Hz, 1.6 Hz), 7.47 (1H, dd, J = 8.0 Hz, 5.6 Hz), 7.29 (1H, dd, J = 9.6 Hz, 2.4 Hz), 7.21 (1H, ddd, J = 8.0 Hz, 7.6 Hz, 1.2 Hz), 7.12 (1H, brs), 7.08 (1H, ddd, J = 8.8 Hz, 8.8 Hz, 2.4 Hz), 7.02 (1H, dd, J = 8.0 Hz, 0.8Hz) 6.45 (1H, brs), 0.93-0.89 (9H, m), 0.78-0.72 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 163.0 (d, J = 250 Hz), 144.1 (d, J = 3.5 Hz), 143.8, 134.3 (d, J = 6.5 Hz), 134.0,

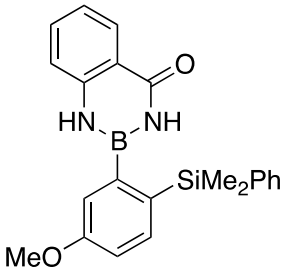
129.3, 122.1, 122.0 (d, J = 17.4 Hz), 118.9, 117.5, 115.0 (d, J = 20.4 Hz), 7.4, 4.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.8; IR (ATR) 3288, 1635, 1521, 719; HRESIMS Calcd. for $C_{19}H_{25}BFN_2OSi$ ($[M+H]^+$): 355.1808, Found: 355.1800.

Synthesis of 2f'



According to the general procedure, a mixture of **1f** (218 mg), $RuH_2(CO)(PPh_3)_3$, norbornene and triethylsilane (597 μL) in toluene was heated. **2f'** (231 mg, 83%) was isolated by column chromatography on Florisil® (hexane-AcOEt, 10:1 – 4:1 – 3:1). mp 199.6-203.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (1H, dd, J = 8.4 Hz, 1.2 Hz), 7.79 (1H, dd, J = 0.8 Hz, 0.8 Hz), 7.63-7.54 (3H, m), 7.21 (1H, ddd, J = 8.4 Hz, 7.2 Hz, 0.8 Hz), 7.15 (1H, brs), 7.03 (1H, dd, J = 8.4 Hz, 2.4 Hz), 6.50 (1H, brs), 0.92-0.87 (9H, m), 0.79-0.72 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 143.8, 142.0, 134.3, 132.5, 131.5 (q, J = 3.5 Hz), 130.5 (q, J = 31.7 Hz), 129.5, 124.7 (q, J = 271 Hz), 124.4 (q, J = 3.6 Hz), 122.5, 119.1, 117.7, 7.57, 4.25; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3; IR (ATR) 3294, 1649, 1521, 734; HRESIMS Calcd. for $C_{20}H_{25}BF_3N_2OSi$ ($[M+H]^+$): 405.1776, Found: 405.1771.

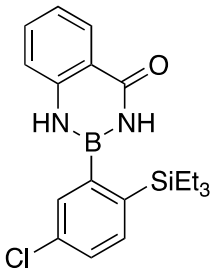
Synthesis of 2h



According to the general procedure, a mixture of **1h** (189 mg), $RuH_2(CO)(PPh_3)_3$, norbornene and dimethylphenylsilane (573 μL) in toluene was heated. **2h** (250 mg, 87%) was isolated by column chromatography on Florisil® (hexane-AcOEt, 10:1 – 4:1 – 3:1). mp 170.2-173.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (1H, dd, J = 8.0 Hz, 0.8 Hz), 7.72 (1H, d, J = 8.0 Hz),

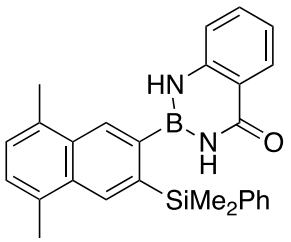
7.44-7.32 (6H, m), 7.11-7.01 (4H, m) 6.17 (1H, d, J = 8.4 Hz), 5.93 (1H, brs), 3.84 (3H, s), 0.44 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ166.4, 160.2, 143.5, 140.7, 137.3, 134.1, 133.7, 132.2, 129.5, 129.0, 128.5, 121.9, 118.9, 118.8, 117.8, 114.2, 55.2, -1.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ30.1; IR (ATR) 3394, 1652, 1517, 761; HRESIMS Calcd. for $C_{22}H_{24}BN_2O_2Si$ ($[M+H]^+$): 387.1695, Found: 387.1686.

Synthesis of 2j'



According to the general procedure, a mixture of **1j** (192 mg), $RuH_2(CO)(PPh_3)_3$, norbornene and triethylsilane (597 μL) in toluene was heated. **2j'** (231 mg, 83%) was isolated by column chromatography on Florisil® (hexane-AcOEt, 10:1 – 8:1). mp 193.8-197.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ8.27-8.25 (1H, m), 7.59-7.55 (1H, m), 7.52 (1H, d, J = 8.0 Hz), 7.46 (1H, d, J = 2.4 Hz), 7.38 (1H, dd, J = 8.4 Hz, 2.4 Hz), 7.22-7.17 (2H, m), 7.05 (1H, d, J = 8.0 Hz) 6.59 (1H, brs), 0.91-0.85 (9H, m), 0.76-0.69 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ166.0, 143.8, 138.5, 137.1, 134.9, 134.2, 132.2, 129.5, 128.6, 122.4, 119.1, 117.7, 7.6, 4.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ29.9; IR (ATR) 3292, 1637, 1519, 759; HRESIMS Calcd. for $C_{19}H_{25}BClN_2OSi$ ($[M+H]^+$): 371.1512, Found: 371.1503.

Synthesis of 2l



According to the general procedure, a mixture of **1l** (150 mg, 0.5 mmol), $RuH_2(CO)(PPh_3)_3$ (27.5 mg, 0.03mmol), norbornene (236 mg, 2.5 mmol), and dimethylphenylsilane (260 μL) in toluene was reacted. Silylated product **2l** (158 mg, 72%) was isolated by column chromatography on Florisil® (hexane-AcOEt, 10:1 – 3:1). mp 235.1-240.3 °C; ^{1}H NMR (400

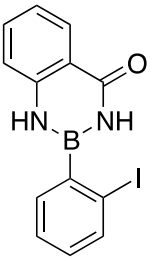
MHz, $CDCl_3$) δ 8.47 (1H, s), 8.21-8.19 (2H, m), 7.50-7.37 (6H, m), 7.33-7.29 (2H, m), 7.26 (1H, brs), 7.12 (1H, dd, J = 7.6 Hz, 7.6 Hz), 6.16 (1H, d, J = 8.0 Hz), 6.01 (1H, brs), 2.76 (3H, s), 2.68 (3H, s), 0.59 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 143.6, 140.4, 136.8, 134.2, 133.8, 132.9, 132.7, 132.6, 132.2, 132.1, 130.3, 129.7, 129.1, 128.7, 127.8, 121.9, 118.8, 117.8, 19.3, 19.2, –1.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3; IR (ATR) 3396, 1666, 1512, 729; HRESIMS Calcd. for $C_{27}H_{28}BN_2OSi$ ($[M+H]^+$): 435.2058, Found: 435.2056.

Iododesilylation of AAM-Protected *o*-Silylarylboronic Acids (Table 1)

General Procedure

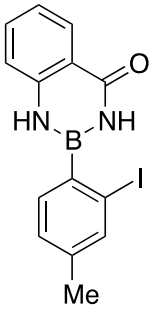
ICl (10 μL, 0.2 mmol) was added to a solution of ArB(aam) (0.1 mmol) in CH_2Cl_2 at –78 °C. After being stirred for 18 h, 2-metyl-2-butene (32 μL, 0.3 mmol) was added, and the mixture was stirred for 5 min at room temperature. The mixture was subjected to column chromatography on Florisil® (hexane/EtOAc, 10:1 - chloroform), giving *o*-iodonated product **3**.

Synthesis of 3a



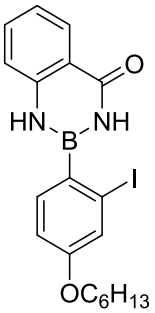
According to the general procedure, **3a** (30.3 mg, 87%) was prepared from **2a** (35.6 mg). mp 164.0-167.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30-8.26 (1H, m), 7.89 (1H, d, J = 8.0 Hz), 7.57 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 1.2 Hz), 7.45-7.34 (2H, m), 7.32 (1H, brs), 7.21 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 0.8 Hz), 7.15 (1H, ddd, J = 8.0 Hz, 6.8 Hz, 2.4 Hz),, 7.09 (1H, dd, J = 8.0 Hz, 0.4 Hz) 6.73 (1H, brs); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 144.0, 139.3, 134.2, 134.1, 131.6, 129.3, 127.7, 122.3, 119.1, 117.9, 99.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.2; IR (ATR) 3310, 1654, 1521, 754; HRMS (APCI) Calcd. for $C_{13}H_{11}BIN_2O$ ($[M+H]^+$): 349.0004, Found: 349.0006.

Synthesis of 3b



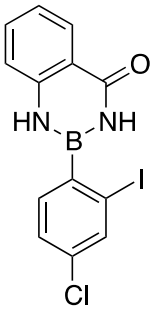
According to the general procedure, **3b** (34.8 mg, 96%) was prepared from **2b** (37.0 mg). mp 186.3-189.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (1H, dd, J = 8.0 Hz, 1.2 Hz), 7.72 (1H, s), 7.55 (1H, ddd, J = 8.8 Hz, 7.2 Hz, 1.6 Hz), 7.36 (1H, brs), 7.28 (1H, d, J = 7.6 Hz), 7.22-7.16 (2H, m), 7.10 (1H, d, J = 8.0 Hz), 6.85 (1H, brs), 2.33 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 144.1, 142.2, 140.0, 134.1, 134.0, 129.3, 128.7, 122.2, 119.0, 117.8, 100.0, 21.0; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.0; IR (ATR) 3413, 1656, 1508, 750; HRESIMS Calcd. for $C_{14}H_{13}BIN_2O$ ($[M+H]^+$): 363.0160, Found: 363.0156.

Synthesis of 3c



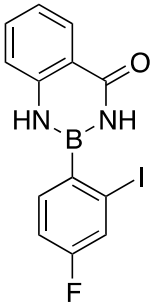
According to the general procedure, **3c** (40.7 mg, 96%) was prepared from **2c** (45.6 mg). mp 125.0-127.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (1H, dd, J = 8.0 Hz, 1.2 Hz), 7.54 (1H, ddd, J = 8.4 Hz, 7.2 Hz, 1.6 Hz), 7.41 (1H, d, J = 2.4 Hz), 7.38 (1H, brs), 7.29 (1H, d, J = 8.4 Hz), 7.17 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 0.8 Hz), 7.09 (1H, d, J = 8.0 Hz), 6.93 (1H, dd, J = 8.4 Hz, 2.4 Hz), 6.86 (1H, brs), 3.95 (2H, t, J = 6.4 Hz), 1.78 (2H, quint, J = 6.8 Hz), 1.49-1.42 (2H, m), 1.37-1.32 (4H, m), 0.93-0,90 (3H,m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 160.7, 144.0, 135.0, 133.8, 129.1, 125.6, 122.0, 118.9, 117.7, 114.2, 100.1, 68.2, 31.5, 29.0, 25.6, 22.6, 14.0; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.6; IR (ATR) 3386, 1651, 1589, 758; HRESIMS Calcd. for $C_{19}H_{23}BIN_2O_2$ ($[M+H]^+$): 449.0892, Found: 451.0891.

Synthesis of 3d



ICl (10 μL, 0.2 mmol) was added to a solution of **2d'** (37.0 mg, 0.1 mmol) in CH_2Cl_2 at –78 °C. After the reaction was warmed to –9 °C, and further stirred for 1h. 2-Metyl-2-butene (32 μL, 0.3 mmol) was added, and the mixture was stirred for 5 min at room temperature. The mixture was subjected to column chromatography on Florisil® (hexane/EtOAc, 10:1 - chloroform), giving **3d** (36.6 mg, 95%). mp 230.5-234.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (1H, dd, J = 8.0 Hz, 1.2 Hz), 7.90 (1H, d, J = 2.0 Hz), 7.57 (1H, ddd, J = 8.8 Hz, 7.2 Hz, 1.6 Hz), 7.41 (1H, dd, J = 8.0 Hz, 2.0 Hz), 7.31 (1H, d, J = 8.0 Hz), 7.29-7.19 (2H, m), 7.09 (1H, dd, J = 8.0 Hz, 0.4 Hz), 6.68 (1H, brs); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.7, 145.0, 136.5, 135.2, 134.2, 133.3, 127.9, 127.1, 121.1, 119.0, 118.1, 101.2; ^{11}B NMR (128 MHz, DMSO-d_6) δ 27.4; IR (ATR) 3386, 1678, 1515, 756; HRESIMS Calcd. for $C_{13}H_{10}BClIN_2O$ ($[M+H]^+$): 382.9614, Found: 382.9613.

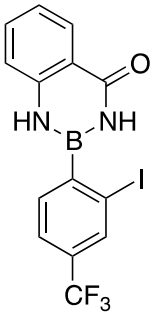
Synthesis of 3e



ICl (10 μL, 0.2 mmol) was added to a solution of **2e'** (35.4 mg, 0.1 mmol) in CH_2Cl_2 at –78 °C. After the reaction was warmed to –9 °C, and further stirred for 1h. 2-Metyl-2-butene (32 μL, 0.3 mmol) was added, and the mixture was stirred for 5 min at room temperature. The mixture was subjected to column chromatography on Florisil® (hexane/EtOAc, 10:1 – chloroform), giving **3e** (34.4 mg, 94%). mp 198.9-201.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (1H, dd, J = 8.0 Hz, 1.6 Hz), 7.63 (1H, dd, J = 8.4 Hz, 1.6 Hz), 7.57 (1H, ddd, J = 8.8 Hz, 7.6 Hz, 1.6 Hz), 7.37 (1H, dd, J = 8.4 Hz, 6.4 Hz), 7.29-7.19 (2H, m), 7.15 (1H, ddd, J =

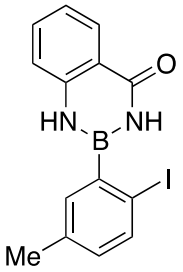
10.8 Hz, 8.4 Hz, 2.4 Hz), 7.10-7.07 (1H, m), 6.68 (1H, brs); ^{13}C NMR (100 MHz, DMSO-d_6) δ165.7, 162.0 (d, J = 249 Hz), 145.1, 139.7, 135.5 (d, J = 7.8 Hz), 133.3, 127.9, 124.5 (d, J = 22.1 Hz), 121.0, 118.9, 118.1, 114.3 (d, J = 19.6 Hz), 100.5 (d, J = 7.3 Hz); ^{11}B NMR (128 MHz, DMSO-d_6) δ29.7; IR (ATR) 3390, 1651, 1519, 752; HREIMS Calcd. for $C_{13}H_{10}BFIN_2O$ ([M+H]$^+$): 366.9909, Found: 366.9909.

Synthesis of 3f



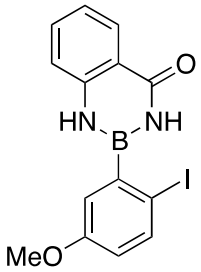
ICl (40 μL, 0.8 mmol) was added to a solution of **2f** (80.8 mg, 0.2 mmol) in CH_2Cl_2 at –78 °C. After the reaction was warmed to rt, and further stirred for 1h. 2-Metyl-2-butene (126 μL, 1.2 mmol) was added, and the mixture was stirred for 5 min at room temperature. The mixture was subjected to column chromatography on Florisil® (hexane/EtOAc, 10:1 – chloroform) and then **3f** (59.1 mg, 71%) was isolated by preparative GPC. mp 209.3-213.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ8.30-8.28 (1H, m), 8.12 (1H, s), 7.68 (1H, ddd, J = 8.4 Hz, 0.8 Hz, 0.4 Hz), 7.60 (1H, ddd, J = 8.8 Hz, 7.2 Hz, 1.6 Hz) 7.50 (1H, d, J = 8.0 Hz), 7.30-7.22 (2H, m), 7.11-7.09 (1H, m), 6.67 (1H, brs); ^{13}C NMR (100 MHz, $CDCl_3$) δ165.7, 148.6, 145.0, 134.5, 133.5, 133.4, 130.7 (q, J = 32.0 Hz), 128.0, 123.5 (q, J = 3.5 Hz), 123.1 (q, J = 271 Hz), 121.2, 119.1, 118.1, 100.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ25.5; IR (ATR) 3173, 1684, 1506, 1105, 756; HRESIMS Calcd. for $C_{14}H_{10}BF_3IN_2O$ ([M+H]$^+$): 416.9877, Found: 416.9865.

Synthesis of 3g



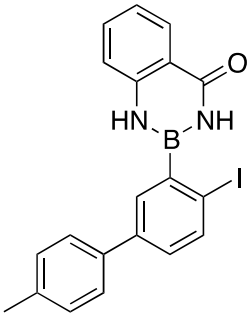
According to the general procedure, **3g** (34.1 mg, 94%) was prepared from **2g** (37.0 mg). mp 173.8-177.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (1H, dd, J = 8.0 Hz, 1.6 Hz), 7.70 (1H, d, J = 8.0 Hz), 7.55 (1H, ddd, J = 8.8 Hz, 7.6 Hz, 1.6 Hz), 7.37 (1H, brs), 7.22 (1H, d, J = 2.0 Hz), 7.17 (1H, ddd, J = 8.0 Hz, 6.8 Hz, 1.2 Hz), 7.11 (1H, d, J = 8.4 Hz), 6.91-6.70 (2H, m), 2.30 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 144.1, 139.1, 137.6, 135.3, 134.0, 132.6, 129.2, 122.2, 119.1, 117.9, 95.8, 21.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.4; IR (ATR) 3151, 1654, 1508, 754; HREIMS Calcd. for $C_{14}H_{13}BIN_2O$ ($[M+H]^+$): 363.0160, Found: 363.0156.

Synthesis of 3h



According to the general procedure, **3h** (35.8 mg, 94%) was prepared from **2h** (38.6 mg). mp 229.1–231.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28–8.26 (1H, m), 7.73 (1H, d, J = 8.8 Hz), 7.57 (1H, ddd, J = 8.8 Hz, 7.2 Hz, 1.6 Hz), 7.30 (1H, brs), 7.21 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 1.2 Hz), 7.10-7.08 (1H, m), 6.94 (1H, d, J = 3.2 Hz), 6.74-6.71 (2H, m), 3.81 (3H, s); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.7, 158.5, 145.1, 138.6, 133.3, 127.9, 121.0, 119.8, 118.9, 118.1, 117.1, 89.0, 55.2; ^{11}B NMR (128 MHz, DMSO-d_6) δ 27.2; IR (ATR) 3361, 1647, 1515, 754; HRESIMS Calcd. for $C_{14}H_{13}BIN_2O_2$ ($[M+H]^+$): 379.0109, Found: 379.0109.

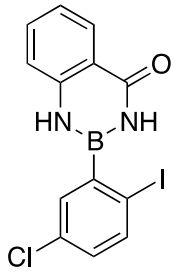
Synthesis of 3i



According to the general procedure, **3i** (40.3 mg, 92%) was prepared from **2i** (44.6 mg). mp 227.8-233.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (1H, dd, J = 8.0 Hz, 1.6 Hz), 7.91 (1H, d,

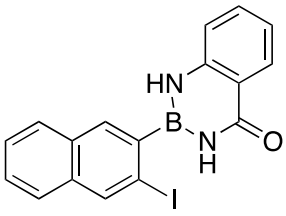
J = 8.4 Hz), 7.60-7.54 (2H, m), 7.48-7.39 (3H, m), 7.34 (1H, dd, *J* = 8.4 Hz, 2.4 Hz), 7.27-7.25 (2H, m), 7.20 (1H, ddd, *J* = 8.0 Hz, 7.2 Hz, 1.2 Hz), 7.10 (1H, d, *J* = 8.0 Hz), 6.82 (1H, brs), 2.40 (3H, s); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.8, 145.1, 138.7, 138.3, 137.2, 136.3, 133.3, 132.1, 129.6, 128.8, 127.9, 126.3, 121.0, 119.0, 118.1, 99.3, 20.7; ^{11}B NMR (128 MHz, DMSO-d_6) δ 26.0; IR (ATR) 3303, 1649, 1485, 760; HRESIMS Calcd. for $C_{20}H_{17}BIN_2O$ ($[M+H]^+$): 439.0473, Found: 439.0473.

Synthesis of 3j



ICl (10 μL, 0.2 mmol) was added to a solution of **2j'** (37.0 mg, 0.1 mmol) in CH_2Cl_2 at –78 °C. After the reaction was warmed to –9 °C, and further stirred for 1h. 2-metyl-2-butene (32 μL, 0.3 mmol) was added, and the mixture was stirred for 5 min at room temperature. The mixture was subjected to column chromatography on Florisil® (hexane/EtOAc, 10:1 - chloroform), giving **3j** (37.1 mg, 97%). mp 214.3-217.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (1H, dd, *J* = 8.0 Hz, 1.6 Hz), 7.79 (1H, d, *J* = 8.4 Hz), 7.58 (1H, ddd, *J* = 8.8 Hz, 7.2 Hz, 0.8 Hz), 7.37 (1H, d, 2.8 Hz), 7.30-7.20 (2H, m), 7.12 (1H, dd, *J* = 8.4 Hz, 2.8 Hz), 7.09 (1H, dd, *J* = 8.0 Hz, 0.8 Hz), 6.68 (1H, brs); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.7, 145.0, 139.5, 133.5, 133.4, 132.7, 130.6, 127.9, 121.1, 119.0, 118.1, 98.5; ^{11}B NMR (128 MHz, DMSO-d_6) δ 28.4; IR (ATR) 3386, 1678, 1515, 756; HRESIMS Calcd. for $C_{13}H_{10}BClIN_2O$ ($[M+H]^+$): 382.9614, Found: 382.9614.

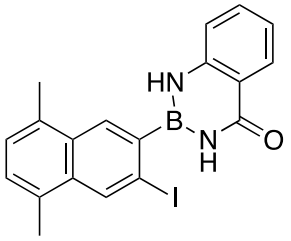
Synthesis of 3k



According to the general procedure, **3k** (37.2 mg, 93%) was prepared from **2k** (37.2 mg). mp 217.6-220.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (1H, s), 8.30 (1H, dd, *J* = 8.0 Hz, 1.6 Hz),

7.91 (1H, s) 7.84-7.81 (1H, m), 7.77-7.74 (1H, m), 7.61-7.52 (3H,m), 7.40 (1H, brs), 7.22 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 1.2 Hz), 7.12 (1H, dd, J = 8.0 Hz, 0.8 Hz) 6.81 (1H, brs); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.8, 145.2, 136.3, 134.7, 133.7, 133.4, 131.3, 128.0, 127.9, 127.1, 126.7, 126.5, 121.1, 119.0, 118.1, 97.6; ^{11}B NMR (128 MHz, DMSO-d_6) δ 26.2; IR (ATR) 3411, 1672, 1512, 748; HRESIMS Calcd. for $C_{17}H_{13}BIN_2O$ (M+H): 399.0160, Found: 399.0160.

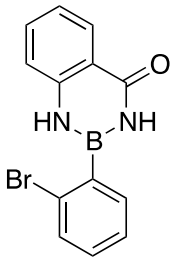
Synthesis of 3l



According to the general procedure (**3**), ICl (14 μL, 0.28 mmol) was added to a solution of **9** (60.8 mg, 0.14 mmol) in CH_2Cl_2 at –78 °C. After being stirred for 18 h, 2-metyl-2-butene (44 μL, 0.42 mmol) was added, and the mixture was stirred for 5 min at room temperature. The mixture was subjected to column chromatography on Florisil® (hexane/EtOAc, 10:1 – chloroform), giving *o*-iodonated product **3l** (51.1 mg, 86%). mp 255.0-256.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.56 (1H, s), 9.35 (1H, s), 8.47-8.46 (1H, m), 8.07-8.04 (2H, m), 7.58 (1H, dd, J = 8.0 Hz, 8.0 Hz), 7.35-7.33 (1H, m), 7.29 (2H, s), 7.14 (1H, dd, J = 7.6 Hz, 7.6 Hz), 2.62 (3H, s), 2.60 (3H, s); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.8, 145.2, 134.1, 133.4, 132.3,130.8, 130.7, 130.5, 128.0, 127.5, 127.0, 121.0, 119.0, 118.2, 97.9, 18.8; ^{11}B NMR (128 MHz, DMSO-d_6) δ 26.5; IR (ATR) 3264, 1643, 1517, 736; HRESIMS Calcd. for $C_{19}H_{17}BIN_2O$ ($[M+H]^+$): 427.0473, Found: 427.0466.

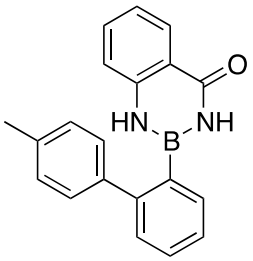
Procedure for Cross-Coupling of *o*-BrC_6H_4B(aam) (Table 2)

Synthesis of 3a'



According to the general procedure (**3.1**), **3a'** (1.63 g, 90%) was prepared from 2-bromophenylboronic acid (1.20 g, 6.0 mmol) and anthranilamide (816 mg, 6.0 mmol). mp 178.0-180.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.48 (1H, s), 9.30 (1H, s), 8.00 (1H, dd, *J* = 7.2 Hz, 1.2 Hz), 7.60 (1H, dd, *J* = 8.0 Hz, 0.8 Hz), 7.52 (1H, ddd, *J* = 8.4 Hz, 7.2 Hz, 1.6 Hz), 7.48 (1H, dd, *J* = 7.2 Hz, 1.6Hz), 7.39 (1H, ddd, *J* = 8.8 Hz, 7.6 Hz, 1.6 Hz), 7.33 (1H, ddd, *J* = 9.6 Hz, 7.6 Hz, 2.0 Hz), 7.28 (1H, d, *J* = 8.0 Hz), 7.09 (1H, ddd, *J* = 8.0 Hz, 6.8 Hz, 1.2 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.8, 145.2, 137.9, 134.7, 133.3, 131.0, 127.9, 126.7, 126.2, 121.1, 118.9, 118.1; ^{11}B NMR (128 MHz, DMSO-d_6) δ 29.2; IR (ATR) 3417, 1651, 1515, 744; HRESIMS Calcd. for $C_{13}H_{11}BBrN_2O$ ($[M+H]^+$): 301.0142, Found: 301.0135.

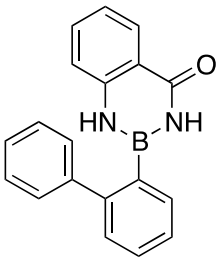
Synthesis of 4



A mixture of **3a'** (60.0 mg, 0.20 mmol), *p*-tolylboronic acid (40.8 mg, 0.30 mmol), $Pd(OAc)_2$ (1.34 mg, 6 μmol), and K_3PO_4 (84.8mg, 0.40 mmol) in THF (0.4 ml) was stirred for 19 h at room temperature. After being cooled to room temperature, the solvent was evaporated *in vacuo*. The coupling product (60.3 mg, 96 %) was isolated by column chromatography on silica gel (hexane-AcOEt, 10:1 – 2:1). mp 195.3-199.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (1H, dd, *J* = 8.0 Hz, 1.2 Hz), 7.66, (1H, d, *J* = 7.2 Hz), 7.54-7.40 (4H, m), 7.27 (2H, d, *J* = 6.8 Hz), 7.19 (2H, d, *J* = 6.8 Hz), 7.14-7.10 (1H, m), 7.08 (1H, brs) 6.80 (1H, d, *J* = 8.0 Hz), 6.30 (1H, brs), 2.38 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 146.8, 144.3, 139.4, 137.6, 133.8, 133.4, 130.4, 129.7, 129.4, 129.1, 129.0, 127.0, 121.8, 118.7, 117.6, 21.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.2; IR (ATR) 3311, 1643, 1519, 1485, 740; HRESIMS Calcd. for $C_{20}H_{18}BN_2O$ ($[M+H]^+$): 313.1507, Found: 313.1499.

Synthesis of Ter(*o*-phenylene)s via Iterative Suzuki-Miyaura Coupling (Scheme 1)

Synthesis of 5



A mixture of **3a** (69.6 mg, 0.20 mmol), phenylboronic acid (29.3 mg, 0.24 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01mmol), and K_3PO_4 (84.8mg, 0.40 mmol) in THF (0.4 ml) was stirred for 11 h at 50 °C. After being cooled to room temperature, the solvent was evaporated *in vacuo*. The coupling product **5** (55.1 mg, 92 %) was isolated by column chromatography on silica gel (hexane-AcOEt, 10:1 – chloroform). mp 187.0-189.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.99 (1H, s), 8.94 (1H, s), 7.94, (1H, dd, J = 8.0 Hz, 1.6 Hz), 7.61 (1H, dd, J = 7.2 Hz, 0.8 Hz), 7.54-7.40 (6H, m), 7.37-7.33 (2H, m), 7.29-7.25 (1H, m), 7.17 (1H, dd, J = 8.0 Hz, 0.8 Hz), 7.06 (1H, ddd, J = 8.4 Hz, 7.2 Hz, 1.2 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.5, 145.3, 145.2, 142.5, 133.4, 133.1, 129.2, 128.7, 128.6, 128.2, 127.8, 127.0, 126.3, 120.7, 118.5, 117.9; ^{11}B NMR (128 MHz, DMSO-d_6) δ 28.8; IR (ATR) 3311, 1647, 1517, 734; HRESIMS Calcd. for $C_{19}H_{16}BN_2O$ ($[M+H]^+$): 299.1350, Found: 299.1343.

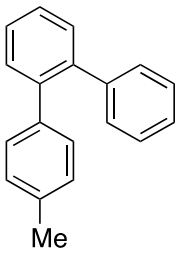
Hydrolysis of 5

To a solution of **5** (298 mg, 1.0 mmol) in THF (10 mL) was added HCl aq. (5N, 1.0 mL 5.0 mmol) at room temperature. The reaction mixture was stirred at room temperature for 20 h. After extraction with diethyl ether, the organic phase was dried over $MgSO_4$. Filtration and evaporation gave the 2-biphenylboronic acid. A portion of the material was used for cross coupling reaction without further purification.

General Prodcedure for Synthesis of 6[18]

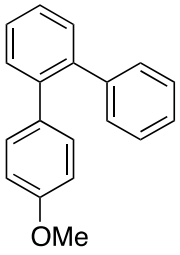
A mixture of aryl bromide (0.20 mmol), 2-biphenylboronic acid (47.5 mg, 0.24 mmol), $Pd(OAc)_2$ (2.24 mg, 6 μmol), SPhos (4.93 mg, 0.012mmol) and K_3PO_4 (84.8mg, 0.40 mmol) in THF (0.4 ml) was stirred for 20 h at 60 °C. After being cooled to room temperature, the solvent was evaporated *in vacuo*. The coupling product was isolated by column chromatography on silica gel (hexane-Et_2O).

Synthesis of 6a



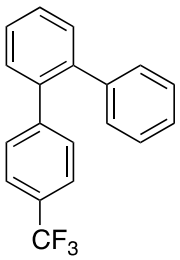
According to the general procedure, a mixture of *p*-bromotoluene (34.0 mg), 2-biphenylboronic acid, $Pd(OAc)_2$, SPhos and K_3PO_4 in THF was heated. **6a** (47.1 mg, 96%) was isolated by column chromatography on silica gel (hexane- Et_2O, 40:1).

Synthesis of 6b



According to the general procedure, a mixture of *p*-bromoanisole (37.0 mg), 2-biphenylboronic acid, $Pd(OAc)_2$, SPhos and K_3PO_4 in THF was heated. **6b** (50.2 mg, 96%) was isolated by column chromatography on silica gel (hexane- Et_2O, 20:1).

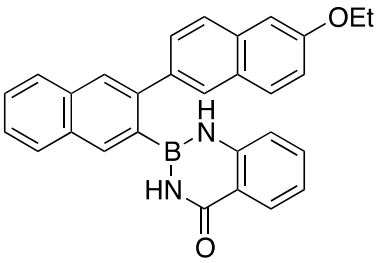
Synthesis of 6c



According to the general procedure, a mixture of *p*-bromobenzotrifluoride (44.8 mg), 2-biphenylboronic acid, $Pd(OAc)_2$, SPhos and K_3PO_4 in THF was heated. **6c** (58.5 mg, 98%) was isolated by column chromatography on silica gel (hexane- Et_2O, 20:1).

Synthesis of Quarter(naphthalene-2,3-diyl) via Iterative Suzuki-Miyaura Coupling (Scheme 2)

Synthesis of 8

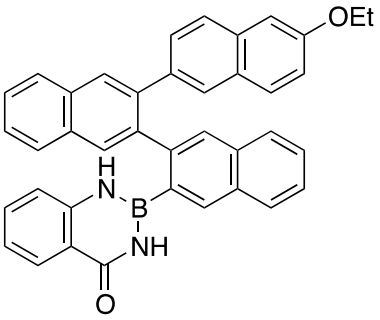


According to the general procedure (**7.3**), a mixture of **3k** (39.8 mg, 0.1 mmol), 6-ethoxynaphthaleneboronic acid (25.9 mg, 0.12 mmol), $Pd(OAc)_2$ (1.12 mg, 0.005mmol), and K_3PO_4 (42.4 mg, 0.2 mmol) in THF (0.2 ml) was stirred for 11 h at 50 °C. After being cooled to room temperature, the solvent was evaporated *in vacuo*. The coupling product **8** (39.9 mg, 92 %) was isolated by column chromatography on Florisil® (hexane-AcOEt, 10:1 – chloroform). mp 228.8-231.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (1H, s), 8.18-8.16 (1H, m), 7.99 (1H, s), 7.94-7.91 (3H, m), 7.77 (1H, d, J = 9.2 Hz), 7.73 (1H, d, J = 8.8 Hz), 7.62-7.54 (2H, m), 7.52-7.49 (1H, m), 7.43-7.38 (1H, m), 7.21-7.14 (3H, m), 7.09 (1H, ddd, J = 8.0 Hz, 7.2 Hz, 0.8 Hz), 6.64 (1H, dd, J = 0.8 Hz) 6.21 (1H, brs), 4.18 (2H, q, J = 7.2 Hz), 1.50 (3H, q, J = 7.2 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.5, 156.6, 145.3, 142.2, 137.4, 134.0, 133.4, 133.2, 131.3, 129.5, 128.3, 127.9, 127.8, 127.7, 127.4, 127.1, 126.8, 126.4, 126.1, 120.7, 119.2, 118.5, 118.0, 106.4, 63.1, 14.6; ^{11}B NMR (128 MHz, DMSO-d_6) δ 25.2; IR (ATR) 3230, 1668, 1512, 759; HRESIMS Calcd. for $C_{29}H_{24}BN_2O_2$ ($[M+H]^+$): 443.1925, Found: 443.1916.

Hydrolysis of 8

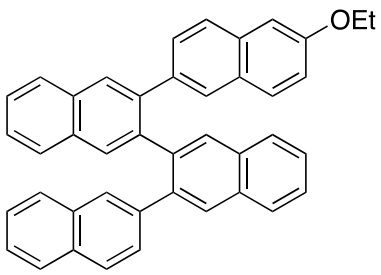
To a solution of **8** (950 mg, 2.15 mmol) in THF (22 mL) was added HCl aq. (5N, 2.2 mL 11.0 mmol) at room temperature. The reaction mixture was stirred at room temperature for 12 h. After extraction with chloroform, the organic phase was dried over $MgSO_4$. Filtration and evaporation gave the corresponding boroxine **9**. A portion of the material was used for cross coupling reaction without further purification.

Synthesis of 10



A solution of **9** (44.5 mg, 0.13 mmol) and water (1.1 μL, 0.06 mmol) in THF (0.2 mL) was heated at 50 °C. After 30 min, to the solution was added **3k** (39.8 mg, 0.1 mmol), $Pd(OAc)_2$ (1.12 mg, 0.005mmol), and K_3PO_4 (42.4 mg, 0.2 mmol). The mixture was stirred for 15 h at 60 °C. After being cooled to room temperature, the solvent was evaporated *in vacuo*. The coupling product **10** (50.2 mg, 88 %) was isolated by column chromatography on Florisil® (hexane-AcOEt, 10:1 – chloroform). mp 169.8-172.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.11 (3H, m), 8.01-7.99 (2H, m), 7.93-7.90 (2H, m), 7.82 (1H, d, J = 8.0 Hz), 7.76 (1H, s), 7.65-7.52 (4H, m), 7.33-7.25 (2H, m), 7.20 (1H, d, J = 8.4 Hz), 7.10-7.06 (1H, m), 7.02-7.00 (1H, m), 6.94 (1H, d, J = 2.0 Hz), 6.89 (1H, dd, J = 8.8 Hz, 2.4 Hz), 6.84 (1H, dd, J = 8.4 Hz, 2.0 Hz), 6.37 (1H, brs), 6.18 (1H, d, J = 8.4 Hz), 5.41 (1H, brs), 4.11 (2H, q, J = 7.2 Hz), 1.47 (3H, q, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 157.3, 144.3, 142.6, 139.5, 139.3, 135.5, 134.5, 133.6, 135.5, 133.2, 133.1, 132.9, 132.0, 130.2, 129.8, 129.5, 129.0, 128.8, 128.7, 128.2, 128.1, 128.0, 127.9, 127.4, 126.9, 126.5, 125.9, 121.5, 119.2, 118.5, 117.8, 106.1, 63.6, 15.0; ^{11}B NMR (128 MHz, $CDCl_3$) δ 25.8; IR (ATR) 3402, 1660, 1485, 744; HRESIMS Calcd. for $C_{39}H_{30}BN_2O_2$ ($[M+H]^+$): 569.2395, Found: 569.2385.

Synthesis of 11



To a solution of **10** (103 mg, 0.18 mmol) in THF (1.8 mL) was added HCl aq. (5N, 0.18 mL 0.9 mmol) at room temperature. After the reaction was warmed to room temperature, the

reaction mixture was stirred at room temperature for 12 h. After extraction with chloroform, the organic phase was dried over $MgSO_4$. Filtration and evaporation gave the corresponding arylboronic acid. A portion of arylboronic acid was used for cross coupling reaction without further purification. A mixture of arylboronic acid (23.4 mg, 0.05 mmol), 2-bromonaphthalene (20.6 mg, 0.1 mmol), $Pd(dba)_2$ (0.56 mg, 2.5 μmol), SPhos (2.06 mg, 5.0 μmol) and K_3PO_4 (42.4 mg, 0.2 mmol) in 1,4-dioxane/H_2O (v/v = 10/1, 0.22 ml) was stirred for 24 h at 110 °C. After being cooled to room temperature, the solvent was evaporated *in vacuo*. The coupling product **11** (22.1 mg, 80 %) was isolated by column chromatography on silica gel (hexane-CH_2Cl_2, 10:1 – 5:1 – 4:1 – 2:1). mp 141.0-143.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (2H, s), 8.01 (2H, d, J = 8.0 Hz), 7.85-7.82 (2H, m), 7.67 (1H, d, J = 8.0 Hz), 7.62 (2H, d, J = 12.0 Hz), 7.60-7.50 (4H, m), 7.40 (1H, ddd, J = 8.0 Hz, 6.8 Hz, 1.2 Hz), 7.27 (1H, ddd, J = 8.0 Hz, 6.8 Hz, 1.2 Hz), 7.23 (1H, d, J = 8.4 Hz), 7.12-7.09 (2H, m), 6.97 (1H, s), 6.94 (1H, s), 6.93 (1H, s), 6.76 (1H, d, J = 1.2 Hz), 6.66 (1H, dd, J = 8.4 Hz, 1.2 Hz), 6.63-6.60 (2H, m), 4.18-4.12 (2H, m), 1.51 (3H, t, 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 139.8, 139.7, 139.5, 139.4, 138.5, 136.3, 133.3, 133.2, 133.2, 133.0, 132.9, 132.8, 131.8, 130.9, 129.7, 129.1, 129.0, 128.8, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.8, 127.5, 127.3, 126.5, 126.3, 126.2, 125.6, 125.5, 125.4, 118.6, 106.0, 63.5, 15.0; IR (ATR) 3055, 1603, 850, 744; HREIMS Calcd. for $C_{42}H_{30}O$ (M^+): 550.2297, Found: 550.2297.

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List of Publications

Chapter 1

Easily Attachable and Detachable *ortho*-Directing Agent for Arylboronic Acids in Ruthenium-Catalyzed Aromatic C–H Silylation

Hideki Ihara, Michinori Suginome

J. Am. Chem. Soc. **2009**, *131*, 7502-7503.

Chapter 2

Ruthenium-Catalyzed C–H Silylation of Methylboronic Acid Using a Removable *a*-Directing Modifier on the Boron Atom

Hideki Ihara, Akinori Ueda, Michinori Suginome

Chem. Lett. **2011**, *40*, 916-918.

Chapter 3

Anthranilamide: A Simple, Removable Ortho-Directing Modifier for Arylboronic Acids Serving also as a Protecting Group in Cross-Coupling Reactions

Hideki Ihara, Masashi Koyanagi, Michinori Suginome

Org. Lett. **2011**, *13*, 2662-2665.

Chapter 4

Anthranilamide-Masked *o*-Iodoarylboronic Acids as Coupling Modules for Iterative Synthesis of *ortho*-Linked Oligoarenes

Masashi Koyanagi, Nils Eichenauer, Hideki Ihara, Takeshi Yamamoto, Michinori Suginome

Chem. Lett. **2013**, *42*, 541-543.