Supplementary Information

A convenient and clean synthetic method for borasiloxanes by Pd-catalysed reaction of silanols with diborons

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1. General comments

Unless otherwise noted, all manipulations were performed under a nitrogen atmosphere using Schlenk techniques or a glove box. All reagents were purchased from commercial suppliers and used without further purification except for PhMe₂SiOH. PhMe₂SiOH (Wako Pure Chemical Industries, Ltd., No. 328-90483, Lot ECH3187) was used after distillation to remove a contaminated disiloxane (PhMe₂SiOSiMe₂Ph). All solvents were dried and/or distilled by standard methods. The products were isolated by a preparative GPC instrument (Japan Analytical Industry Co., Ltd., LC-908) or a short-path distillation apparatus (Sibata Scientific Technology Ltd., Glass tube oven GTO-350RD). All the products 2a-i were obtained in reasonably pure forms (≥95%).

As for Pd acetate catalysts, the compound obtained from Strem Chemicals Inc. (No. 46-1780, Lot 142265-SA) as Pd(OAc)₂ was mainly Pd₃(OAc)₆, while the compound purchased from Tokyo Chemical Industry Co., Ltd. as Pd(OAc)₂ (No. A1424, Lot TBFTE-MA) was found to be almost pure Pd₃(OAc)₅(NO₂). Their ¹H NMR spectra shown in Fig. S1 (a) and (b) were in good agreement with their reported spectra.¹¹

¹H, ¹³C, ²⁹Si, and ¹¹B NMR spectra were recorded on a Bruker AVANCE III HD 600 spectrometer equipped with a CryoProbe (600 MHz for ¹H, 150 MHz for ¹³C, 119 MHz for ²⁹Si, and 193 MHz for ¹¹B; pulse programs: zg30 for ¹H, zgpg30 for ¹³C, zgig30 for ²⁹Si, and zg for ¹¹B) using CDCl₃, C₆D₆, or THF-d₈ solvent. The chemical shifts are referenced to tetramethylsilane (0 ppm) for ¹H, ¹³C, and ²⁹Si NMR, boron trifluoride diethyl ether complex (0 ppm) for ¹¹B NMR, or the solvent resonances for ¹H and ¹³C NMR as internal standards (for ¹H, CHCl₃: 7.26 ppm, C₆D₆: 7.15 ppm, THF-d₇ (H at 2-C): 3.58 ppm; for ¹³C, CDCl₃: 77.0 ppm, C₆D₆: 128.0 ppm, THF-d₈ (2-C): 67.2 ppm). The high-resolution ESI mass spectra were obtained on a Bruker microTOF II. Melting points were determined on Opti Melt MPA100 apparatus (TOKYO INSTRUMENT, INC.).
Fig. S1 $^1$H NMR spectra (in CDCl$_3$) of the Pd acetates, (a) Pd$_3$(OAc)$_6$ and (b) Pd$_3$(OAc)$_5$(NO$_2$), which were obtained from Strem Chemicals Inc. and Tokyo Chemical Industry Co., Ltd., respectively.
2. Experimental procedures

2-1. General procedure for the synthesis of 1a by transition metal-catalysed reaction of a Et₃SiOH with a B₂pin₂ in Table 1

In a 10 mL Schlenk flask were placed bis(pinacolato)diboron (0.50 mmol), catalysts (0.5-26 mol%), and Et₃SiOH (1.0 mmol) under nitrogen. The mixture was stirred under the reaction conditions specified in Table 1. After the reaction, the yield of the product 1a was determined by $^{29}$Si NMR spectroscopy using PhMe₃Si as an internal standard. In $^1$H NMR, the peak separation between the starting materials and the products has not been sufficient in some cases. On the other hand, all the peaks of the starting materials and the products can be observed clearly in $^{29}$Si NMR, and therefore, we have chosen $^{29}$Si NMR for estimation of the yields of the products. A typical example of the $^{29}$Si NMR spectrum of the reaction mixture containing PhMe₃Si (10 μL) in C₆D₆ is shown in Fig. S2.

![Fig. S2 $^{29}$Si NMR of the reaction mixture obtained in the reaction of Et₃SiOH with B₂pin₂ catalysed by Pd₃(OAc)₅(NO₂) (Table 1, entry 1).](image)
2-2. Preparation of 1a-1i in Table 2

In each reaction, Pd acetate (Pd$_3$(OAc)$_5$(NO$_2$) or Pd$_3$(OAc)$_6$) was used. Their catalytic activities were similar to each other.

Preparation of 1a

In a 10 mL Schlenk flask were placed Pd acetate (Pd$_3$(OAc)$_6$, 0.5 mol% Pd), bis(pinacolato)diboron (0.55 mmol), and Et$_3$SiOH (1.0 mmol) under nitrogen. The mixture was stirred at 25 °C for 3 h. After the reaction, the product 1a was obtained in 94% NMR yield. The product was isolated in 81% yield by preparative GPC using toluene (super dehydrated) as an eluent.

Preparation of 1b

In a 10 mL Schlenk flask were placed Pd acetate (Pd$_3$(OAc)$_5$(NO$_2$), 1 mol% Pd), bis(pinacolato)diboron (0.55 mmol), and PhMe$_2$SiOH (1.0 mmol) under nitrogen. The mixture was stirred at 25 °C for 3 h. After the reaction, the product 1b was obtained in 99% NMR yield. The product was isolated in 92% yield by short-path distillation under a reduced pressure (bp 150–160 °C/200 mmHg).

Preparation of 1c

In a 10 mL Schlenk flask were placed Pd acetate (Pd$_3$(OAc)$_5$(NO$_2$), 1 mol% Pd), bis(pinacolato)diboron (0.55 mmol), Ph$_3$SiOH (1.0 mmol), and distilled THF (0.25 mL) under nitrogen. The mixture was stirred at 80 °C for 4 h. After the reaction, the product 1c was obtained in 95% NMR yield. The product was isolated in 84% yield by short-path distillation under a reduced pressure (bp 190–200 °C/0.9 mmHg).

Preparation of 1d

In a 10 mL Schlenk flask were placed Pd acetate (Pd$_3$(OAc)$_5$(NO$_2$), 1 mol% Pd), bis(pinacolato)diboron (1.0 mmol), (tBuO)$_3$SiOH (1.0 mmol), and distilled THF (0.25 mL) under nitrogen. The mixture was stirred at 80 °C for 4 h. After the reaction, the product 1d was obtained in 99% NMR yield. The product was isolated in 83% yield by short-path distillation under a reduced pressure (bp 145–155 °C/22 mmHg).

Preparation of 1e

In a 10 mL Schlenk flask were placed Pd acetate (Pd$_3$(OAc)$_5$(NO$_2$), 1 mol% Pd), bis(pinacolato)diboron (1.0 mmol), and Me$_3$SiOH (1.0 mmol) under nitrogen. The mixture was stirred at 25 °C for 4 h. After the reaction, the product 1e was obtained in 98% NMR yield. The product was isolated in 64% yield by short-path distillation under a reduced pressure (bp 90–100 °C/245 mmHg).

Preparation of 1f
In a 10 mL Schlenk flask were placed a Pd acetate (Pd$_3$(OAc)$_5$(NO$_2$), 1 mol% Pd), bis(pinacolato)diboron (2.0 mmol), Ph$_2$Si(OH)$_2$ (1.0 mmol), and distilled THF (0.25 mL) under nitrogen. The mixture was stirred at 80 °C for 4 h. After the reaction, the product 1f was obtained in 97% NMR yield. The product was isolated in 86% yield by short-path distillation under a reduced pressure (bp 190–200 °C/0.9 mmHg).

Preparation of 1g

In a 10 mL Schlenk flask were placed Pd acetate (Pd$_3$(OAc)$_5$(NO$_2$), 1 mol% Pd), bis(neopentyl glycolato)diboron (1.0 mmol), and Et$_3$SiOH (1.0 mmol) under nitrogen. The mixture was stirred at 80 °C for 4 h. After the reaction, the product 1g was obtained in 94% NMR yield. The product was isolated in 77% yield by short-path distillation under a reduced pressure (bp 110–120 °C/25 mmHg).

Preparation of 1h

In a 10 mL Schlenk flask were placed Pd acetate (Pd$_3$(OAc)$_5$(NO$_2$), 1 mol% Pd), bis(hexylene glycolato)diboron (1.0 mmol), and Et$_3$SiOH (1.0 mmol) under nitrogen. The mixture was stirred at 80 °C for 4 h. After the reaction, the product 1h was obtained in 98% NMR yield. The product was isolated in 85% yield by short-path distillation under a reduced pressure (bp 120–130 °C/19 mmHg).

Preparation of 1i

In a 10 mL Schlenk flask were placed Pd acetate (Pd$_3$(OAc)$_5$(NO$_2$), 1 mol% Pd), bis(catecolato)diboron (1.0 mmol), and Et$_3$SiOH (1.0 mmol) under nitrogen. The mixture was stirred at 25 °C for 3 h. After the reaction, the product 1i was obtained in 99% NMR yield. The product was isolated in 94% yield by short-path distillation under a reduced pressure (bp 160–170 °C/50 mmHg).

2-3. Procedures for the stoichiometric reactions (eqns 1 and 2)

(1) Treatment of Pd acetate with bis(pinacolato)diboron and then with Et$_3$SiOH (eqn 1)

A Young NMR tube was charged with Pd$_3$(OAc)$_5$(NO$_2$) (10.8 mg, 0.05 mmol Pd), bis(pinacolato)diboron (12.3 mg, 0.05 mmol), and THF-$d_8$ (30 μL) under nitrogen. The mixture was kept at 25 °C for 3 h, and then, Et$_3$SiOH (0.1 mmol) was added, and the resulting mixture was kept at 25 °C for additional 3 h. The $^1$H and $^{29}$Si NMR spectra of the reaction mixture (Fig. S3 (a) and (b), respectively) showed the formation of 1a in 68% yield along with unreacted Et$_3$SiOH.

(2) Treatment of Pd acetate with Et$_3$SiOH and then with bis(pinacolato)diboron (eqn 2)

A Young NMR tube was charged with Pd$_3$(OAc)$_5$(NO$_2$) (11.5 mg, 0.05 mmol Pd), Et$_3$SiOH (8 μL, 0.05 mmol), and THF-$d_8$ (30 μL) under nitrogen. The mixture was kept at 25 °C for 3 h, and then, bis(pinacolato)diboron (0.05 mmol) was added, and the resulting mixture was kept at 25 °C for additional 3 h. The $^1$H and $^{29}$Si NMR spectra of the reaction mixture (Fig. S4 (a) and (b), respectively) showed the formation of 1a and Et$_3$SiOSiEt$_3$ in 73% and 26% yields, respectively.
Fig. S3 (a) $^1$H NMR and (b) $^{29}$Si NMR of the reaction mixture obtained by treatment of Pd$_3$(OAc)$_3$(NO$_2$) with bis(pinacolato)diboron and then with Et$_3$SiOH (eqn 1).
Fig. S4 (a) $^1$H NMR and (b) $^{29}$Si NMR of the reaction mixture obtained by treatment of Pd$_3$(OAc)$_5$(NO$_2$) with Et$_3$SiOH and then bis(pinacolato)diboron (eqn 2).
2-4. Spectral data of the products 1a-i

1a

\[
\begin{array}{c}
\text{Et}_3\text{Si-O-B-O-}
\end{array}
\]

Colorless oil; \(^1\)H NMR (\(\text{C}_6\text{D}_6\), 600 MHz) \(\delta\) 0.62 (q, \(J = 8.1\) Hz, 6H, SiCH\(_2\)), 0.97 (t, \(J = 8.1\) Hz, 9H, SiCCH\(_3\)), 1.04 (s, 12H, OCCH\(_3\)) \(13\)C NMR (\(\text{C}_6\text{D}_6\), 150 MHz) \(\delta\) 5.9, 6.8, 24.6, 81.8; \(^{29}\)Si NMR (\(\text{C}_6\text{D}_6\), 119 MHz) \(\delta\) 17.0; \(^{11}\)B NMR (\(\text{C}_6\text{D}_6\), 193 MHz) \(\delta\) 20.4.

1b

\[
\begin{array}{c}
\text{PhMe}_2\text{Si-O-B-O-}
\end{array}
\]

Colorless oil; \(^1\)H NMR (\(\text{C}_6\text{D}_6\), 600 MHz) \(\delta\) 0.45 (s, 6H, SiCH\(_3\)), 1.02 (s, 12H, OCCH\(_3\)), 7.18–7.23 (m, 3H, phenyl proton), 7.64–7.69 (m, 2H, phenyl proton); \(^{13}\)C NMR (\(\text{C}_6\text{D}_6\), 150 MHz) \(\delta\) -0.0, 24.6, 82.1, 128.1, 129.8, 133.5, 138.6; \(^{29}\)Si NMR (\(\text{C}_6\text{D}_6\), 119 MHz) \(\delta\) 5.1; \(^{11}\)B NMR (\(\text{C}_6\text{D}_6\), 193 MHz) \(\delta\) 20.7.

1c

\[
\begin{array}{c}
\text{Ph}_3\text{Si-O-B-O-}
\end{array}
\]

White solid; mp 96–97 °C; \(^1\)H NMR (\(\text{C}_6\text{D}_6\), 600 MHz) \(\delta\) 0.99 (s, 12H, OCCH\(_3\)), 7.15–7.19 (m, 9H, phenyl proton), 7.82–7.85 (m, 6H, phenyl proton); \(^{13}\)C NMR (\(\text{C}_6\text{D}_6\), 150 MHz) \(\delta\) 24.6, 82.5, 128.1, 130.3, 135.2, 135.7; \(^{29}\)Si NMR (\(\text{C}_6\text{D}_6\), 119 MHz) \(\delta\) -15.6; \(^{11}\)B NMR (\(\text{C}_6\text{D}_6\), 193 MHz) \(\delta\) 21.1.

1d

\[
\begin{array}{c}
\text{(BuO)}_3\text{Si-O-B-O-}
\end{array}
\]

Colorless oil; \(^1\)H NMR (\(\text{C}_6\text{D}_6\), 600 MHz) \(\delta\) 1.06 (s, 12H, OCCH\(_3\)), 1.45 (s, 27H, C(CH\(_3\))\(_3\)); \(^{13}\)C NMR (\(\text{C}_6\text{D}_6\), 150 MHz) \(\delta\) 24.7, 31.5, 73.2, 81.9; \(^{29}\)Si NMR (\(\text{C}_6\text{D}_6\), 119 MHz) \(\delta\) -100.8; \(^{11}\)B NMR (\(\text{C}_6\text{D}_6\), 193 MHz) \(\delta\) 19.9; HRMS (ESI): m/z calcd for [C\(_{18}\)H\(_{39}\)BO\(_6\)SiNa]\(^+\) (M+Na): 413.2501; found: 413.2492.

1e

\[
\begin{array}{c}
\text{Me}_3\text{Si-O-B-O-}
\end{array}
\]
Colorless oil; $^1$H NMR (C$_6$D$_6$, 600 MHz) $\delta$ 0.21 (s, 9H, SiCH$_3$), 1.04 (s, 12H, OCCH$_3$); $^{13}$C NMR (C$_6$D$_6$, 150 MHz) $\delta$ 1.0, 24.7, 81.9; $^{29}$Si NMR (C$_6$D$_6$, 119 MHz) $\delta$ 15.5; $^{11}$B NMR (C$_6$D$_6$, 193 MHz) $\delta$ 20.4.

$^1$f$^{55}$

![Chemical structure](image)

Colorless oil; $^1$H NMR (C$_6$D$_6$, 600 MHz) $\delta$ 1.01 (s, 24H, OCCH$_3$), 7.14–7.16 (m, 6H, phenyl proton), 7.95–7.99 (m, 4H, phenyl proton); $^{13}$C NMR (C$_6$D$_6$, 150 MHz) $\delta$ 24.6, 82.5, 128.0, 130.6, 134.0, 135.0; $^{29}$Si NMR (C$_6$D$_6$, 119 MHz) $\delta$ -39.8; $^{11}$B NMR (C$_6$D$_6$, 193 MHz) $\delta$ 20.7.

$^1$g

![Chemical structure](image)

Colorless oil; $^1$H NMR (C$_6$D$_6$, 600 MHz) $\delta$ 0.57 (s, 6H, C(CH$_3$)$_2$), 0.75 (q, $J$ = 7.9 Hz, 6H, SiCH$_2$), 1.09 (t, $J$ = 7.9 Hz, 9H, SiCCH$_3$), 3.31 (s, 4H, OCH$_2$); $^{13}$C NMR (C$_6$D$_6$, 150 MHz) $\delta$ 6.1, 7.0, 21.3, 31.4, 72.9; $^{29}$Si NMR (C$_6$D$_6$, 119 MHz) $\delta$ 14.5; $^{11}$B NMR (C$_6$D$_6$, 193 MHz) $\delta$ 16.2; HRMS (ESI): m/z calcd for [C$_{11}$H$_{25}$BO$_3$SiNa]$^+$ (M+Na): 267.1558; found: 267.1555.

$^1$h

![Chemical structure](image)

Colorless oil; $^1$H NMR (C$_6$D$_6$, 600 MHz) $\delta$ 0.73 (q, $J$ = 8.0 Hz, 6H, SiCH$_2$), 1.00 (s, 3H, C(CH$_3$)$_2$)(CH$_3$)$_2$), 1.03 (d, $J$ = 6.1 Hz, 3H, OCHCH$_3$), 1.08 (d, $J$ = 5.7 Hz, 2H, OCHCH$_2$), 1.09 (t, $J$ = 8.0 Hz, 9H, SiCCH$_3$), 1.09 (s, 3H, C(CH$_3$)$_2$)(CH$_3$)$_2$), 3.88–3.93 (m, 1H, OCH); $^{13}$C NMR (C$_6$D$_6$, 150 MHz) $\delta$ 5.6, 6.5, 112.1, 122.4, 148.7; $^{29}$Si NMR (C$_6$D$_6$, 119 MHz) $\delta$ 14.3; $^{11}$B NMR (C$_6$D$_6$, 193 MHz) $\delta$ 16.4; HRMS (ESI): m/z calcd for [C$_{12}$H$_{27}$BO$_3$SiNa]$^+$ (M+Na): 281.1715; found: 281.1693.

$^1$i$^{56}$

![Chemical structure](image)

Colorless oil; $^1$H NMR (C$_6$D$_6$, 600 MHz) $\delta$ 0.63 (q, $J$ = 8.1 Hz, 6H, SiCH$_2$), 0.95 (t, $J$ = 8.1 Hz, 9H, SiCCH$_3$), 6.73 (dd, $J$ = 5.9, 3.3 Hz, 2H, phenylene proton), 6.93 (dd, $J$ = 5.9, 3.3 Hz, 2H, phenylene proton); $^{13}$C NMR (C$_6$D$_6$, 150 MHz) $\delta$ 5.6, 6.5, 112.1, 122.4, 148.7; $^{29}$Si NMR (C$_6$D$_6$, 119 MHz) $\delta$ 20.6; $^{11}$B NMR (C$_6$D$_6$, 193 MHz) $\delta$ 21.0.
3. References and notes


S6 In spite of repeated trials, satisfactory HRMS data of 1i could not be obtained because of its highly hydrolysable property. However, the $^1$H, $^{13}$C, $^{29}$Si and $^{11}$B NMR spectral data were fully consistent with the proposed structure.
4. NMR Spectra of 1a-i (copies of the NMR charts)

1a

$^1$H NMR

$^{13}$C NMR
$^2$H NMR

$^1$B NMR
$^{1}H$ NMR

$^{13}C$ NMR
**$^{29}$Si NMR**

**$^{11}$B NMR**
$1c$

$^1$H NMR

$^{13}$C NMR
$^{29}$Si NMR

$^{11}$B NMR
1d

$^1$H NMR

$^{13}$C NMR
$^{29}$Si NMR

$^{11}$B NMR
**1H NMR**

**13C NMR**
$^{29}$Si NMR

$^{11}$B NMR
If

$^1$H NMR

$^{13}$C NMR
$^{29}$Si NMR

$^{11}$B NMR
$^{1}$H NMR

$^{13}$C NMR
$^{29}$Si NMR

$^{11}$B NMR
$^{1}H$ NMR

$^{13}C$ NMR
$^{29}$Si NMR

$^{11}$B NMR
**1H NMR**

![1H NMR spectrum](image1)

**13C NMR**

![13C NMR spectrum](image2)
$^{29}\text{Si NMR}$

$^{11}\text{B NMR}$