Supporting Information

Potassium *tert*-butoxide-mediated regioselective silaboration of aromatic alkenes

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General.

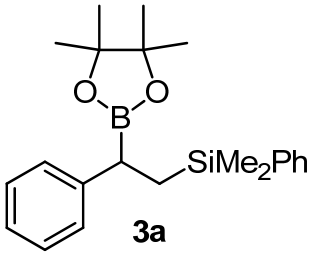
Materials were obtained from commercial suppliers and purified by the standard procedure unless otherwise noted. Dry solvents for the catalytic reaction were purchased from commercial suppliers and used as recieved. NMR spectra were recorded on JEOL JNM-ECX400P spectrometer (^{1}H: 396 MHz and ^{13}C: 99.5 MHz) Tetramethylsilane (^{1}H) and $CDCl_3$ (^{31}C) were employed as external standards, respectively. ^{11}B{^{1}H} NMR was recorder on JEOL JNM-600ECA spectrometer (^{1}H: 600 MHz and ^{11}B: 192.6 MHz). K(O-*t*-Bu) / THF (1.0 M, 328650-50ML) were purchased from Sigma-Aldrich Co. and used as received. Mesitylene and 1,1,2,2-tetrachloroethane were used as the internal standard for determining NMR yield. Recycle preparative gel permeation chromatography (GPC) was conducted with JAI LC-9101 using $CHCl_3$ as an eluent. Low- and High-resolution mass spectra were recorded at the Center for Instrumental Analysis, Hokkaido University.

A Representative Procedure for the Silylboration Reaction of 1a (Table 1):

A vial sealed with a screw cap containing a silicon-coated rubber septum was evacuated and backfilled with nitrogen through a needle connected with a vacuum grass manifold. THF (0.57 mL), (dimethylphenylsilyl)boronic acid pinacol ester **2** (0.36 mmol), and K(O-*t*-Bu)/THF (1.0 M, 0.03 mL, 0.03 mmol) were added in the vial through the rubber septum at room temperature. After 30 min. stirring, an aromatic alkene **3** (0.30 mmol) was added dropwise with a syringe. After the reaction was complete, the reaction mixture was passed through a short silica column eluting with hexane and then 5% ethyl acetate/hexane. The product was purified by flash column chromatography with 0–5% ethyl acetate/hexane eluent. When the product purity was not satisfactory, the yield of the reaction was determined by ^{1}H NMR analysis of the crude material using internal standard and the product was subjected to a recycle gel permeation chromatography.

Supporting Information

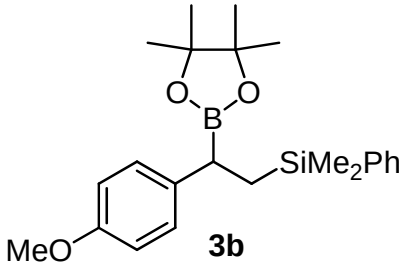
Dimethyl(phenyl)[2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]silane (3a).



3a

^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.14 (s, 3H), 0.19 (s, 3H), 1.06–1.19 (m, 1H), 1.107 (s, 6H), 1.112 (s, 6H), 1.47 (dd, *J* = 8.9, 14.7 Hz, 1H), 2.41 (t, *J* = 7.6 Hz, 1H), 7.07–7.51 (m, 10H). ^{13}C NMR (99.5 MHz, $CDCl_3$, δ): –2.8 (*C*H_3), –2.6 (*C*H_3), 18.4 (*C*H_2), 24.4 (*C*H_3), 24.6 (*C*H_3), 26.7 (broad, *C*B), 83.2 (*C*), 125.0 (*C*H), 127.6 (*C*H), 128.0 (*C*H), 128.1 (*C*H), 128.7 (*C*H), 133.6 (*C*H), 139.3 (*C*), 145.4 (*C*). HRMS–EI (m/z): [M]+ calcd for $C_{22}H_{31}BO_2Si$, 366.2186; found, 366.2185.

[2-(4-Methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]dimethyl(phenyl)silane (3b).



3b

^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.14 (s, 3H), 0.18 (s, 3H), 1.06–1.15 (m, 1H), 1.11 (s, 6H), 1.12 (s, 6H), 1.42 (dd, *J* = 8.4, 14.7 Hz, 1H), 2.35 (t, *J* = 7.7 Hz, 1H), 3.77 (s, 3H), 6.73–6.79 (m, 2H), 7.06–7.13 (m, 2H), 7.29–7.35 (m, 3H), 7.43–7.50 (m, 2H). ^{13}C NMR (99.5 MHz, $CDCl_3$, δ): –2.8 (*C*H_3), –2.5 (*C*H_3), 18.6 (*C*H_2), 24.4 (*C*H_3), 24.6 (*C*H_3), 25.5 (broad), 55.0 (*C*H_3), 83.1 (*C*), 113.6 (*C*H), 127.6 (*C*H), 128.6 (*C*H), 128.8 (*C*H), 133.6 (*C*H), 137.3 (*C*), 139.4 (*C*), 157.2 (*C*). HRMS–EI (m/z): [M]+ calcd for $C_{23}H_{33}BO_3Si$, 396.22911; found, 396.22920.

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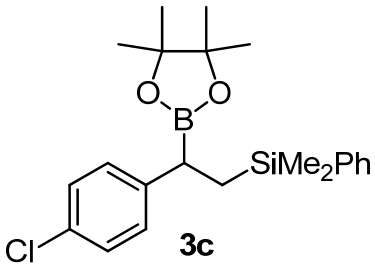
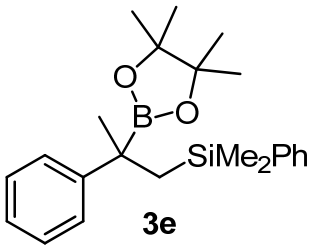
[2-(4-Chlorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]dimethyl(phenyl)silane (3c).



3c

^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.15 (s, 3H), 0.18 (s, 3H), 1.05–1.17 (m, 1H), 1.11 (s, 12H), 1.43 (dd, *J* = 8.4, 14.7 Hz, 1H), 2.38 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 7.28–7.36 (m, 3H), 7.42–7.47 (m, 2H). ^{13}C NMR (99.5 MHz, $CDCl_3$, δ): –2.7 (*C*H_3), –2.6 (*C*H_3), 18.4 (*C*H_2), 24.4 (*C*H_3), 24.6 (*C*H_3), 26.2 (broad), 83.4 (*C*), 127.7 (*C*H), 128.2 (*C*H), 128.8 (*C*H), 129.3 (*C*H), 130.6 (*C*), 133.6 (*C*H), 139.1 (*C*), 143.9 (*C*). HRMS–EI (m/z):[M]+ calcd for $C_{22}H_{30}BClO_2Si$, 400.1797, 399.1833; found, 400.1819, 399.1826.

Dimethyl(phenyl)[2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl]silane (3e).



3e

^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.08 (s, 3H), 0.11 (s, 3H), 1.13 (s, 6H), 1.14 (s, 6H), 1.37 (s, 3H), 1.43 (d, *J* = 15.5 Hz, 1H), 1.48 (d, *J* = 15.3 Hz, 1H), 7.06–7.49 (m. 10H). ^{13}C NMR (99.5 MHz, $CDCl_3$, δ): –1.11 (*C*H_3), –1.05 (*C*H_3), 23.8 (*C*H_3), 24.4 (*C*H_3), 24.7 (*C*H_3), 27.4 (*C*H_2), 83.3 (*C*), 124.9 (*C*H), 126.7 (*C*H), 127.5 (*C*H), 127.9 (*C*H), 128.8 (*C*H), 133.5 (*C*H), 141.0 (*C*), 148.4 (*C*). HRMS–EI (m/z): [M]+ calcd for $C_{23}H_{33}BO_2Si$, 380.2343; found, 380.2354.

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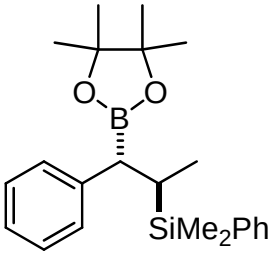
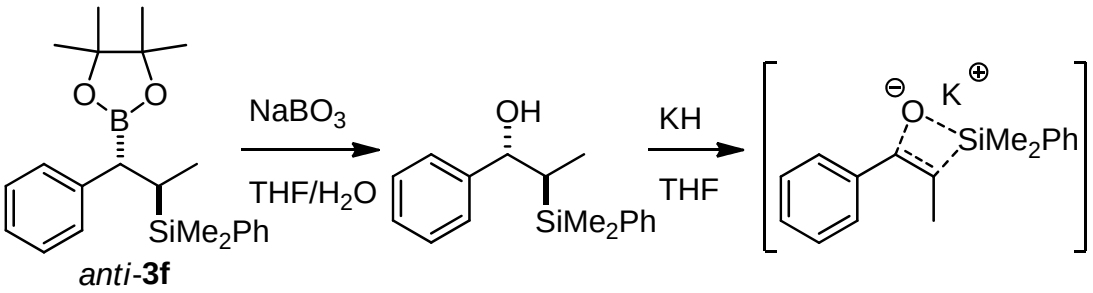
Dimethyl(phenyl)[1-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl]silane (*anti*-3f).



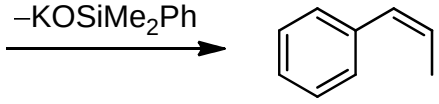
anti-**3f**

^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.123 (s, 3H), 0.127 (s, 3H), 1.16 (d, J = 7.2 Hz, 3H), 1.23 (s, 6H), 1.27 (s, 6H), 1.67–1.76 (m, 1H), 2.42 (d, *J* = 11.3 Hz, 1H), 7.18–7.53 (m, 10H). ^{13}C NMR (99.5 MHz, $CDCl_3$, δ): –5.0 (*C*H_3), –3.0 (*C*H_3), 16.2 (*C*H_3), 22.9 (*C*H), 24.5 (*C*H_3), 24.6 (*C*H_3), 36.0 (broad), 83.2 (*C*), 125.3 (*C*H), 127.4 (*C*H), 128.0 (*C*H), 128.4 (*C*H), 129.2 (*C*H), 133.9 (*C*H), 139.0 (*C*), 142.6 (*C*). HRMS–EI (m/z): [M]+ calcd for $C_{23}H_{33}BO_2Si$, 380.23451; found, 380.23429.

The stereochemistry of this compoud was determined by the following procedure. Oxidation of C–B bond in *anti*-**3f** and subsequent base-mediated Peterson reaction gave *cis*-β-methyl styrene, indicating *anti* stereochemisty of **3f**.



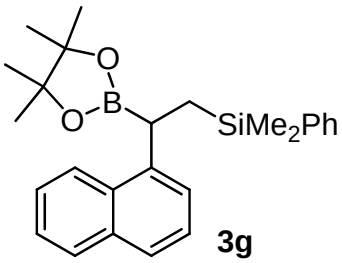
anti-**3f**



cis-β-methylstyrene

Supporting Information

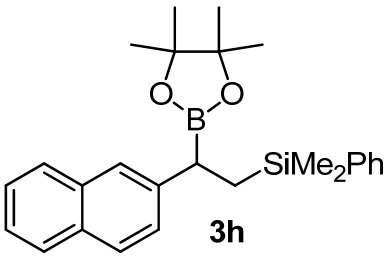
Dimethyl[2-(naphthalen-1-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl](phenyl)silane (3g).



3g

^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.17 (s, 3H), 0.19 (s, 3H), 1.08 (s, 6H), 1.13 (s, 6H), 1.26 (dd, *J* = 5.9, 14.5 Hz, 1H), 1.65 (dd, *J* = 8.6, 15.0 Hz, 1H), 3.08 (t, *J* = 7.0 Hz, 1H), 7.28–7.50 (m, 9H), 7.60–7.64 (m, 1H), 7.77–7.82 (m, 1H), 8.01–8.06 (m, 1H). ^{13}C NMR (99.5 MHz, $CDCl_3$, δ): –2.7 (*C*H_3), –2.6 (*C*H_3), 18.6 (*C*H_2), 24.6 (*C*H_3), 24.7 (*C*H_3), 83.4 (*C*), 124.5 (*C*H), 125.1 (*C*H), 125.2 (*C*H), 125.4 (*C*H), 125.6 (*C*H), 125.8 (*C*H), 127.6 (*C*H), 128.6 (*C*H), 128.7 (*C*H), 131.7 (*C*), 133.7 (*C*H), 134.0 (*C*), 139.4 (*C*), 142.2 (*C*). HRMS–EI (m/z):[M]+ calcd for $C_{26}H_{33}BO_2Si$, 416.2343; found, 416.2352.

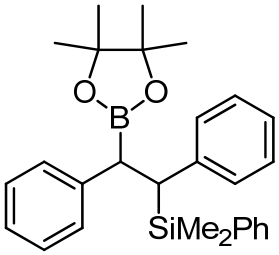
Dimethyl[2-(naphthalen-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl](phenyl)silane (3h).



3h

^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.16 (s, 3H), 0.20 (s, 3H), 1.10 (s, 6H), 1.11 (s, 6H), 1.24 (dd, *J* = 6.6, 14.2 Hz, 1H), 1.56 (dd, *J* = 8.6, 15.0 Hz, 1H), 2.59 (t, *J* = 7.7 Hz, 1H), 7.28–7.79 (m, 12H). ^{13}C NMR (99.5 MHz, $CDCl_3$, δ): –2.7 (*C*H_3), –2.5 (*C*H_3), 18.3 (*C*H_2), 24.4 (*C*H_3), 24.7 (*C*H_3), 27.0 (broad), 83.3 (*C*), 124.7 (*C*H), 125.6 (*C*H), 125.8 (*C*H), 127.2 (*C*H), 127.4 (*C*H), 127.5 (*C*H), 127.6 (*C*H), 128.7 (*C*H), 131.7 (*C*), 133.67 (*C*H), 133.72 (*C*), 139.3 (*C*), 143.0 (*C*). HRMS–EI (m/z): [M]+ calcd for $C_{26}H_{33}BO_2Si$, 416.2343; found, 416.2349.

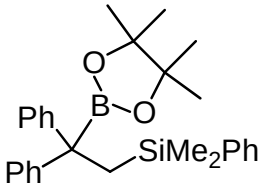
[1,2-Diphenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]dimethyl(phenyl)silane (3i).



3i
syn and *anti*

^{1}H NMR (396 MHz, $CDCl_3$, δ) *syn* and *anti* mixture: –0.13 (d, *J* = 9.5 Hz), 0.25 (s), 0.30 (s), 0.73 (s), 0.81 (s), 1.01 (s), 1.03 (s), 2.94 (d, *J* = 5.0 Hz), 3.03 (d, *J* = 12.7 Hz), 3.22 (d, *J* = 13.1 Hz), 6.63–7.57 (m). ^{13}C NMR (99.5 MHz, $CDCl_3$, δ): –3.6 (*C*H_3), –3.5 (*C*H_3), –3.4 (*C*H_3), –3.1 (*C*H_3), 23.9 (*C*H_3), 24.1 (*C*H_3), 24.2 (*C*H_3), 24.8 (*C*H_3), 32.9 (broad *C*B), 34.6 (broad *C*B), 35.7 (*C*H), 38.9 (*C*H), 82.9 (*C*), 83.3 (*C*), 123.7 (*C*H), 124.56 (*C*H), 124.63 (*C*H), 125.6 (*C*H), 126.4 (*C*H), 127.0 (*C*H), 127.3 (*C*H), 127.4 (*C*H), 127.6 (*C*H), 128.1 (*C*H), 128.5 (*C*H), 128.6 (*C*H), 128.9 (*C*H), 129.0 (*C*H), 129.2 (*C*H), 134.2 (*C*H), 134.6 (*C*H), 137.2 (*C*), 137.4 (*C*), 141.2 (*C*), 141.4 (*C*), 141.9 (*C*), 144.0 (*C*). HRMS–ESI(m/z): [M]+ calcd for $C_{28}H_{35}BO_2Si$, 442.2499; found, 442.2508.

[2,2-Diphenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]dimethyl (phenyl)silane (3j).

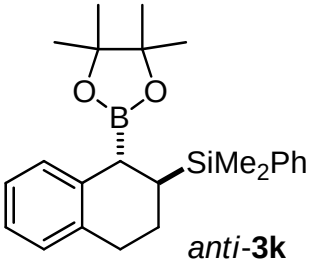


3j

^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.13 (s, 6H), 1.17 (s, 12H), 1.99 (s, 2H), 7.21–7.60 (m, 15H). ^{13}C NMR (99.5 MHz, $CDCl_3$, δ): –2.2 (*C*H_3), 24.3 (*C*H_3), 26.5 (*C*H_2), 83.5 (*C*), 125.4 (*C*H), 127.4 (*C*H), 127.7 (*C*H), 128.4 (*C*H), 129.5 (*C*H), 133.8 (*C*H), 140.8 (*C*), 148.2 (*C*). HRMS–EI (m/z): [M]+ calcd for $C_{28}H_{35}BO_2Si$, 442.2499; found, 442.2497.

Supporting Information

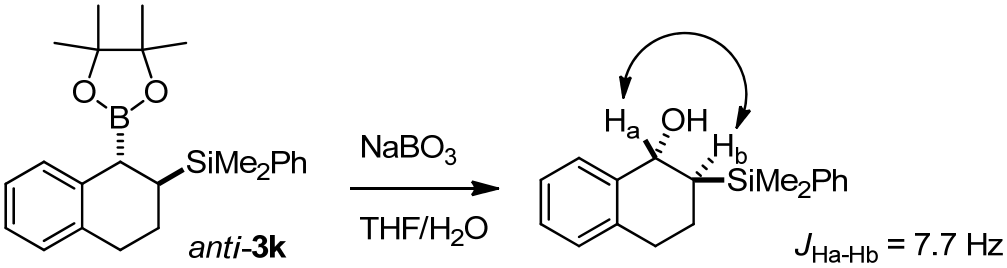
Dimethyl(phenyl)[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydronaphthalen-2-yl]silane (*anti*-3k).



anti-**3k**

^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.27 (s, 3H), 0.28 (s, 3H), 1.09 (s, 6H), 1.14 (s, 6H), 1.23–1.40 (m, 1H), 1.47–1.59 (m, 1H), 1.90 (dq, J = 4.1 and 13.2 Hz, 1H), 2.59–2.72 (m, 3H), 6.95–7.58 (m, 9H). ^{13}C NMR (99.5 MHz, $CDCl_3$, δ): –4.9 (*C*H_3), –4.0 (*C*H_3), 22.1 (*C*H), 23.7 (*C*H_2), 24.6 (*C*H_3), 24.7 (*C*H_3), 25.2 (broad), 31.1 (*C*H_2), 83.2 (*C*), 124.3 (*C*H), 125.4 (*C*H), 127.6 (*C*H), 128.7 (*C*H), 128.8 (*C*H), 129.1 (*C*H), 134.1 (*C*H), 137.1 (*C*), 137.7 (*C*), 138.2 (*C*). HRMS–EI (m/z): [M]+ calcd for $C_{24}H_{33}BO_2Si$, 392.2343; found, 392.2347.

The stereochemisry of ***anti*-3k** is determined by the coupling constant between two α protons (J = 7.7 Hz, H_a and H_b) observed in the ^{1}H NMR spectrum after oxidation of the C–B bond.

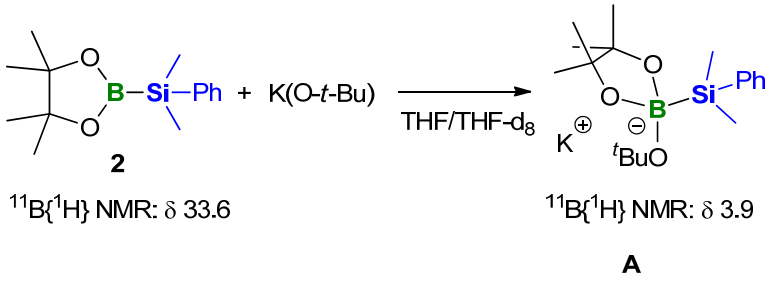


anti-**3k**

Supporting Information

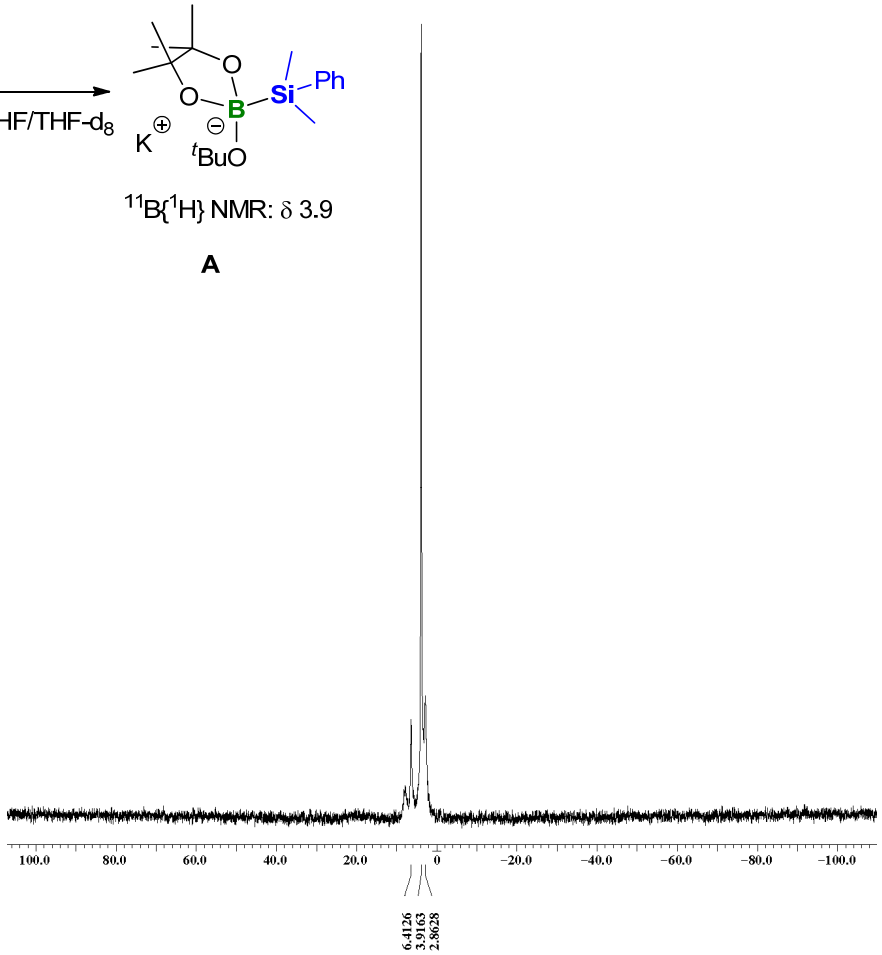
Experimental Procedure for In situ $^{11}B\{^1H\}$ NMR Observation of K(O-*t*-Bu) adduct of 2 (Scheme 1):

In a glove box filled with nitrogen, 0.1 mL of dry THF-d^8 was added into a reaction vial with a screw cap. After the vial was sealed with a a silicon-coated rubber septum, the vial was removed from the glove box and connected with a nitrogen grass manifold through a needle. After dry THF (0.9 mL) and $PhMe_2SiH$ (26. 2 mg, 0.10 mmol) was added, a solution of K(O-t-Bu) (1.0 M, 0,10 mL, 0.10 mmol) was added at room temperature with stirring. The mixture was then transferred into a, boron free, quartz NMR sample tube under nitrogen. The $^{11}B\{^1H\}$ NMR signal (δ 3.92) that can be attributed to the adduct **A** was recorded at 27°C as shown in the following chart.



2 $^{11}B\{^1H\}$ NMR: δ 33.6

A $^{11}B\{^1H\}$ NMR: δ 3.9



$^{11}B\{^1H\}$ NMR (192.6 MHz, THF/THF-d^8, 10:1)