Copper-catalyzed Highly Selective Approach to 2-Boroallylic Silanes
from Allenylsilanes

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Table of contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>General information</td>
<td>S2</td>
</tr>
<tr>
<td>Experimental details and analytical data of all the products</td>
<td>S3-30</td>
</tr>
<tr>
<td>References</td>
<td>S31</td>
</tr>
<tr>
<td>\textsuperscript{1}H and \textsuperscript{13}C NMR spectra of the products</td>
<td>S32-S106</td>
</tr>
</tbody>
</table>
**General Information.** All reactions were carried out in oven dried Schlenk tubes under argon atmosphere. THF was distilled over sodium wire using benzophenone as the indicator under argon atmosphere. LiAlH₄ (1 M in THF) was purchased from Energy Chemical. i-PrOH was distilled using magnesium turnings as drying agent under argon.¹ The starting materials 3a-3l,² 3p-3q,² 3m,³ 3x,³ 3z,³ 3o,⁴ and 3n⁵ were prepared according to the literature.
1. Synthesis of 3-(dimethyl(phenyl)silyl)penta-3,4-dien-1-ol 4 (3r) (sl-6-3)

To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially 3m \(^3\) (739.0 mg, 3 mmol) and THF (6 mL) under argon at rt. The resulting mixture was placed with a bath pre-set at -78 °C and stirred. LiAlH\(_4\) (3 mL, 3 mmol, 1 M in THF) was then slowly added dropwise over 10 minutes, followed by removing the cool bath, and the resulting mixture was stirred at rt for another 60 minutes as monitored by TLC. Upon completion, the resulting mixture was slowly quenched with a saturated aqueous solution of NH\(_4\)Cl (0.5 mL), filtered through a short column of silica gel eluted with Et\(_2\)O (10 mL × 3), and concentrated. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford 3r (546.1 mg, 87%) as a liquid: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.60-7.50 (m, 2 H, Ar-H), 7.41-7.33 (m, 3 H, Ar-H), 4.49 (t, \(J = 3.0\) Hz, 2 H, \(=\)CH\(_2\)), 3.69 (q, \(J = 6.3\) Hz, 2 H, OCH\(_2\)), 2.21-2.14 (m, 2 H, =CCH\(_2\)), 1.59 (t, \(J = 5.6\) Hz, 1 H, OH), 0.40 (s, 6 H, SiMe\(_2\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 208.9, 137.4, 133.8, 129.3, 127.9, 90.5, 69.9, 62.0, 32.0, -3.3; IR (neat, cm\(^{-1}\))): 1926, 1427, 1249, 1111, 1040; MS (70 ev, El) m/z (%) 218 (M\(^+\), 1.02), 135 (100); HRMS Calcd for C\(_{13}\)H\(_{18}\)OSi (M\(^+\)): 218.1127, Found: 218.1125.

2. Synthesis of 4-trimethylsilyl-4,5-dienenitrile 5 (3n)

(1) Synthesis of 3-trimethylsilyl-3,4-dien-1-ol (3y) (sl-6-22)

To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially 3x \(^3\) (1382.1 mg, 7.0 mmol) and THF (15 mL) under argon at rt. The resulting mixture was placed with a bath pre-set at -78 °C and stirred. LiAlH\(_4\) (7.5
mL, 7.5 mmol, 1 M in THF) was then slowly added dropwise over 10 minutes, followed by removing the cool bath, stirred at rt for another 60 minutes as monitored by TLC. Upon completion, the resulting mixture was slowly quenched with a saturated aqueous solution of NH₄Cl (0.5 mL), the mixture was dried over MgSO₄, filtered through a short column of silica gel eluting with Et₂O (10 mL × 3), and concentrated. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford 3y (989.1 mg, 90%) as a liquid: ¹H NMR (400 MHz, CDCl₃) δ 4.42 (t, J = 3.2 Hz, 2 H, =CH₂), 3.78 (t, J = 6.4 Hz, 2 H, OCH₂), 2.27-2.15 (m, 2 H, =CCH₂), 1.83 (brs, 1 H, OH), 0.12 (s, 9 H, SiMe₃); ¹³C NMR (100 MHz, CDCl₃) δ 207.8, 91.5, 69.3, 62.0, 31.7, -1.9; IR (neat, cm⁻¹): 2956, 1927, 1248, 1041; MS (70 ev, EI) m/z (%) 156 (M⁺, 1.63), 73 (100); HRMS Calcd for C₈H₁₆OSi (M⁺): 156.0970, Found: 156.0969.

(2) Synthesis of 4-trimethylsilyl-4,5-pentadienitrile (3n) (sl-6-23)

To an ice-cooled solution of 3y (625.7 mg, 4 mmol), DMAP (24.5 mg, 0.2 mmol), Et₃N (0.67 mL, d = 0.726 g/cm³, 486.4 mg, 4.8 mmol) in dry DCM (10 mL) was dropwised a solution of p-TsCl (799.9 mg, 4.2 mmol) in dry DCM (10 mL) over 70 minutes under argon atmosphere. Then the resulting mixture was warmed up to rt for another 3 h followed by the addition of 30 mL of DCM. The organic layer was separated and washed with water (10 mL × 3), dried over MgSO₄, filtered, and concentrated under vacuum. The crude product was then used in the next step without further purification.

To a solution of the tosylate prepared above and anhydrous DMSO (4 mL) was added NaCN (251.1 mg, 5 mmol) at rt. The resulting mixture was stirred for 7 h at rt, quenched with H₂O (5 mL), and extracted with AcOEt (10 mL × 3). The combined organic layer was dried over MgSO₄, filtered, and concentrated in vacuum. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl
acetate = 100/1) to afford \(3n\) (394.8 mg, 60%) as a liquid: H NMR (400 MHz, CDCl₃) \(\delta 4.54 (t, J = 3.6 \text{ Hz}, 2 \text{ H}, =\text{CH}_2), 2.50 (t, J = 7.4 \text{ Hz}, 2 \text{ H}, =\text{CCH}_2), 2.32-2.23 (m, 2 \text{ H}, =\text{CCH}_2), 0.12 (s, 9 \text{ H}, \text{SiMe}_3); ^{13} \text{C NMR (100 MHz, CDCl}_3) \delta 207.6, 119.7, 92.8, 71.9, 24.0, 16.2, -2.0; IR (neat, cm⁻¹): 2957, 1928, 1422, 1250, 1061; MS (70 ev, EI) m/z (%) 165 (M⁺, 11.72), 73 (100); HRMS Calcd for C₉H₁₅NSi (M⁺): 165.0974, Found: 165.0975.

3. Synthesis of 3-trimethylsilyl-1-phenyl-3,4-dien-1-one

(1) Synthesis of 3-trimethylsilyl-1-phenyl-3,4-pentadien-1-ol (3z) (sl-6-118)

To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially Fe(NO₃)₃·9H₂O (403.1 mg, 1 mmol), NaCl (58.6 mg, 1 mmol), TEMPO (156.5 mg, 1.0 mmol)/DCE (8 mL) under the atmosphere of oxygen. A solution of \(3y\) (1564.1 mg, 10 mmol) in DCE (2 mL) was added. The resulting mixture was stirred at rt for 6 h with oxygen from a balloon until the reaction was complete as monitored by TLC. Then THF (10 mL) was added. The resulting mixture was cooled with an ice bath, PhMgBr (20 mL, 20 mmol, 1 M in THF) was slowly added dropwise over 10 minutes. Then the resulting mixture was warmed up to rt for another 40 min as monitored by TLC. Upon completion, the resulting mixture was slowly quenched with a saturated aqueous of NH₄Cl (1 mL), filtered through a short column of silica gel eluted with DCM (20 mL × 3), and concentrated. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80/1) to afford \(3z\) (756.4 mg, 33%) as a liquid: \(^{1}\)H NMR (400 MHz, CDCl₃) \(\delta 7.42-7.32 (m, 4 \text{ H}, \text{Ar-H}), 7.31-7.24 (m, 1 \text{ H}, \text{Ar-H}), 4.91-4.84 (m, 1 \text{ H}, \text{OCH}), 4.52-4.41 (m, 2 \text{ H}, =\text{CH}_2), 2.45-2.41 (m, 1 \text{ H}, \text{OH}), 2.40-2.28 (m, 2 \text{ H}, =\text{CCH}_2), 0.11 (s, 9 \text{ H}, \text{SiMe}_3); ^{13} \text{C NMR (100 MHz, CDCl}_3) \delta 208.2, 143.9, 128.3, 127.4, 125.8, 92.0, 73.4, 69.7, 39.1, -1.8; IR (neat, cm⁻¹): 3380, 3064, 3031, 2897, 1925, 1494, 1453, 1405, 1248, 1023; MS (70 ev,
EI) m/z (%) 232 (M⁺, 1.26), 73 (100); HRMS Calcd for C₁₄H₂₀O₅Si (M⁺): 232.1283, Found: 232.1285.

(2) Synthesis of 3-trimethylsilyl-1-phenyl-3,4-pentadien-1-one (3o) (sl-6-119)

![Chemical structure of 3z and 3o](image)

To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially Fe(NO₃)₃·9H₂O (121.3 mg, 0.3 mmol), NaCl (17.9 mg, 0.3 mmol), TEMPO (46.6 mg, 0.3 mmol)/DCE (4 mL) under the atmosphere of oxygen. Then a solution of 3z (697.0 mg, 3 mmol) in DCE (1 mL) was added. The resulting mixture was stirred at rt for 6 h with oxygen from a balloon until the reaction was complete as monitored by TLC. After filtration through a short column of silica gel eluted with DCM (10 mL × 3) and evaporation, the residue was purified by chromatography on silica gel (eluent: petroleum ether) to afford 3o (334.8 mg, 36%) as a liquid: δ 7.98-7.92 (m, 2 H, Ar-H), 7.59-7.52 (m, 1 H, Ar-H), 7.49-7.41 (m, 2 H, Ar-H), 4.34 (t, J = 2.8 Hz, 2 H, =CH₂), 3.63 (m, J = 2.8 Hz, 2 H, =CCH₂), 0.14 (s, 9 H, SiMe₃); ¹³C NMR (100 MHz, CDCl₃) δ 210.1, 198.2, 136.6, 132.9, 128.55, 128.47, 89.6, 69.5, 39.9, -1.6; IR (neat, cm⁻¹): 2956, 1930, 1681, 1598, 1580, 1449, 1407, 1329, 1317, 1280, 1248, 1206, 1181, 1066, 1001; MS (70 ev, EI) m/z (%) 230 (M⁺, 9.76), 73 (100); HRMS Calcd for C₁₄H₁₈O₅Si (M⁺): 230.1127, Found: 230.1126.

4. Synthesis of 2-Borylallylic silanes 5

(1) Synthesis of (3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-yl)dimethyl(phenyl)silane (5a) (ywm-11-99)

![Chemical structure of 3a and 5a](image)
**Typical Procedure:** To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.3 mg, 0.05 mmol), NaOtt-Bu (19.4 mg, 0.2 mmol), bis(pinacolato)diboron (306.3 mg, 1.2 mmol)/THF (2 mL), 3a (189.4 mg, 1.0 mmol)/THF (1 mL), and i-PrOH (153 μL, d = 0.784 g/cm³, 120.2 mg, 2.0 mmol) under argon. The resulting mixture was stirred at rt for 3 h as monitored by TLC. Upon completion, the resulting mixture was filtered through a short column of silica gel eluted with Et₂O (20 mL × 3) and concentrated. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl ether = 70/1) to afford 5a (286.8 mg, 90%) as a liquid. 

\[ \delta_{1H} NMR (300 MHz, CDCl₃) \delta 7.56-7.47 (m, 2 H, Ar-H), 7.37-7.29 (m, 3 H, Ar-H), 5.78 (d, J = 2.7 Hz, 1 H, one proton of =CH₂), 5.35 (brs, 1 H, one proton of =CH₂), 2.19 (q, J = 7.3 Hz, 1 H, =CCH), 1.20 (s, 6 H, B(pin)), 1.18 (s, 6 H, B(pin)), 1.08 (d, J = 7.5 Hz, 3 H, CH₃), 0.25 (s, 6 H, SiMe₂); \]

\[ \delta_{13C} NMR (75.4 MHz, CDCl₃) \delta 138.2, 134.2, 128.7, 127.4, 125.5, 83.2, 26.2, 24.8, 24.7, 14.4, -4.1, -5.6; IR (neat, cm⁻¹): 2978, 1600, 1426, 1388, 1372, 1358, 1305, 1247, 1136, 1111; MS (ESI) m/z 340 [M⁺(¹¹B)+Na⁺H], 339 [M⁺(¹¹B)+Na] or [M⁺(¹⁰B)+Na⁺H], 338 [M⁺(¹⁰B)+Na]; HRMS Calcd for C₁₈H₂₉O₂Si¹¹B (M⁺): 316.2030, Found: 316.2027.

**Synthesis of 5a on one gram scale (ywm-13-188)**

The reaction of CuCl (26.8 mg, 0.27 mmol), BIPHEP (141.3 mg, 0.27 mmol), NaOtt-Bu (101.7 mg, 1.06 mmol), bis(pinacolato)diboron (1.6179 g, 6.37 mmol)/THF (8 mL), 3a (1.0003 g, 5.31 mmol)/THF (2 mL), and i-PrOH (0.8 mL, d = 0.784 g/cm³, 638.3 mg, 10.62 mmol) afforded 5a (1.5065 g, 90%) (eluent: petroleum ether/ethyl ether = 70/1) as a liquid: 

\[ \delta_{1H} NMR (300 MHz, CDCl₃) \delta 7.55-7.47 (m, 2 H, Ar-H), 7.36-7.29 (m, 3 H, Ar-H), 5.78 (d, J = 3.3 Hz, 1 H, one proton of =CH₂), 5.36 (d, J =

S7
2.1 Hz, 1 H, one proton of \(=\text{CH}_2\), 2.19 (q, \(J = 7.5\) Hz, 1 H, \(=\text{CCH}\)), 1.20 (s, 6 H, B(pin)), 1.19 (s, 6 H, B(pin)), 1.09 (d, \(J = 7.5\) Hz, 3 H, CH\(_3\)), 0.25 (s, 6 H, SiMe\(_2\)); \(^{13}\)C NMR (75.4 MHz, CDCl\(_3\)) \(\delta\) 138.2, 134.2, 128.7, 127.4, 125.5, 83.2, 26.2, 24.8, 24.7, 14.5, -4.1, -5.6.

The following compounds were prepared according to this Typical Procedure.

(2) Synthesis of (3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-yl)methyldiphenylsilane (5b) (ywm-13-178)

\[
\begin{align*}
\text{SiMePh}_2 & \quad \text{Me} \\
3b & \quad \text{CuCl (5 mol%), BIPHEP (5 mol%)}
\end{align*}
\]

The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.2 mg, 0.05 mmol), NaO\text{t-Bu} (19.2 mg, 0.2 mmol), bis(pinacolato) diboron (304.6 mg, 1.2 mmol)/THF (2 mL), 3b (250.5 mg, 1.0 mmol)/THF (1 mL), and i-PrOH (153 \(\mu\)L, \(d = 0.784\) g/cm\(^3\), 120.2 mg, 2.0 mmol) afforded 5b (333.1 mg, 88%) (eluent: petroleum ether/ethyl ether = 70/1) as a liquid: \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.61-7.48 (m, 4 H, Ar-H), 7.41-7.22 (m, 6 H, Ar-H), 5.82 (d, \(J = 3.0\) Hz, 1 H, one proton of \(=\text{CH}_2\)), 5.37 (d, \(J = 2.1\) Hz, 1 H, one proton of \(=\text{CH}_2\)), 2.65 (q, \(J = 7.4\) Hz, 1 H, \(=\text{CCH}\)), 1.17 (d, \(J = 7.2\) Hz, 3 H, CH\(_3\)), 1.11 (s, 6 H, B(pin)), 1.07 (s, 6 H, B(pin)), 0.51 (s, 3 H, SiMe); \(^{13}\)C NMR (75.4 MHz, CDCl\(_3\)) \(\delta\) 136.7, 135.7, 135.2, 129.0, 128.9, 127.4, 126.5, 83.2, 24.7, 24.3, 15.3, -6.0; IR (neat, cm\(^{-1}\)): 2977, 1600, 1427, 1358, 1307, 1136, 1108; MS (ESI) m/z 402 [M\(^+\)(11B)+Na+H], 401 [M\(^+\)(11B)+Na] or [M\(^+\)(10B)+Na+H], 400 [M\(^+\)(10B)+Na]; HRMS Calcd for C\(_{23}\)H\(_{31}\)O\(_2\)Si\(_{10}\)B (M\(^+\)): 377.2223, Found: 377.2220.

(3) Synthesis of (3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-yl)triphenylsilane (5c) (ywm-13-179)
The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.0 mg, 0.05 mmol), NaO-t-Bu (19.3 mg, 0.2 mmol), bis(pinacolato) diboron (304.8 mg, 1.2 mmol)/THF (2 mL), 3c (312.4 mg, 1.0 mmol)/THF (1 mL), and i-PrOH (153 μL, d = 0.784 g/cm³, 120.2 mg, 2.0 mmol) afforded 5c (396.3 mg, 90%) (eluent: petroleum ether/ethyl ether = 70/1) as a white solid: m.p. 99-100 °C (ethyl ether); ¹H NMR (300 MHz, CDCl₃) δ 7.64-7.55 (m, 6 H, Ar-H), 7.42-7.27 (m, 9 H, Ar-H), 5.82 (d, J = 2.4 Hz, 1 H, one proton of =CH₂), 5.22 (d, J = 2.4 Hz, 1 H, one proton of =CH₂), 2.96 (q, J = 7.5 Hz, 1 H, CH), 1.29 (d, J = 7.5 Hz, 3 H, CH₃), 1.11 (s, 6 H, B(pin)), 1.05 (s, 6 H, B(pin)); ¹³C NMR (75.4 MHz, CDCl₃) δ 136.5, 134.5, 129.1, 128.6, 127.5, 83.2, 24.7, 23.3, 17.2; IR (neat, cm⁻¹): 2978, 1598, 1485, 1427, 1371, 1307, 1130, 1107; MS (ESI) m/z 464 [M⁺(¹ⁱB)+Na⁺H], 463 [M⁺(¹¹B)+Na⁺] or [M⁺(¹⁰B)+Na⁺H], 462 [M⁺(¹⁰B)+Na⁺]; Anal. Calcd. for C₂₈H₃₃BO₂Si (%): C 76.35, H 7.55; Found: C 76.28, H 7.55.

(4) Synthesis of (3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-yl) tert-butyldimethylsilane (5d) (ywm-13-174)

The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.0 mg, 0.05 mmol), NaO-t-Bu (19.2 mg, 0.2 mmol), bis(pinacolato) diboron (304.6 mg, 1.2 mmol)/THF (2 mL), 3d (168.5 mg, 1.0 mmol)/THF (1 mL), i-PrOH (153 μL, d = 0.784 g/cm³, 120.2 mg, 2.0 mmol) afforded 5d (224.3 mg, 76%) (eluent: petroleum ether/ethyl ether = 70/1) as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 5.74 (d, J = 3.3 Hz, 1 H, one proton of =CH₂), 5.43 (d, J = 2.4 Hz, 1 H, one proton of =CH₂), 2.09 (q, J = 7.4 Hz, 1 H,
\begin{align*}
&=\text{CCH}, 1.26 \ (\text{s}, 6 \ \text{H}, \text{B(pin)}), 1.25 \ (\text{s}, 6 \ \text{H}, \text{B(pin)}), 1.16 \ (\text{d}, J = 7.2 \ \text{Hz}, 3 \ \text{H}, \text{CH}_3), \\
&0.91 \ (\text{s}, 9 \ \text{H}, 3 \times \text{CH}_3), -0.09 \ (\text{s}, 3 \ \text{H}, \text{SiMe}), -0.11 \ (\text{s}, 3 \ \text{H}, \text{SiMe}); \\
\text{\textsuperscript{13}C NMR} \ (75.4 \\
\text{MHz, CDCl}_3) \ \delta \ 125.1, 83.2, 27.2, 24.9, 24.7, 24.0, 17.6, 16.1, -6.1, -8.4; \\
\text{IR} \ (\text{neat,} \\
\text{cm}^{-1}): 2978, 2955, 2857, 1600, 1470, 1358, 1305, 1248, 1138; \\
\text{MS (ESI)} \ m/z \ 315 \\
[M^{+}(\text{11B})+\text{NH}_4] , 297 [M^{+}(\text{11B})+\text{H}]; \ \\
\text{HRMS Caled for C}_{16}\text{H}_{33}\text{BO}_2\text{Si} (M^+) : 296.2343, \\
\text{Found: 296.2344.}
\end{align*}

(5) Synthesis of (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)dimethyl-
(phenyl)dimethylsilane (5e) (sl-4-68)

\begin{center}
\begin{tikzpicture}
\draw[thick, ->] (0,0) -- (2,0) node[midway, above] {$\text{CuCl} \ (5 \ \text{mol}%), \ \text{BIPHEP} \ (5 \ \text{mol\%})$};
\draw[thick, ->] (2,0) -- (4,0) node[midway, above] {$\text{NaO}t\text{-Bu} \ (20 \ \text{mol\%}), \ \text{B}_2(\text{pin})_2 \ (1.2 \ \text{equiv})$};
\draw[thick, ->] (4,0) -- (6,0) node[midway, above] {$\text{i-PrOH} \ (2.0 \ \text{equiv}), \ \text{THF}, \ \text{rt,} \ 3 \ \text{h}, 76\%$};
\end{tikzpicture}
\end{center}

The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.3 mg, 0.05 mmol), \\
NaO\text{-Bu} (19.3 mg, 0.2 mmol), bis(pinacolato)diboron (304.9 mg, 1.2 mmol)/THF (2 \\
mL), 3e (174.6 mg, 1.0 mmol)/THF (1 mL), i-PrOH (153 \ \mu L, d = 0.784 \ \text{g/cm}^3, 120.2 \\
mg, 2.0 mmol) afforded 5e\textsuperscript{8} (230.0 mg, 76\%) (eluent: petroleum ether/ethyl ether = \\
100/1) as an oil: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \ \delta \ 7.56-7.49 (m, 2 \ H, Ar-H), 7.36-7.29 \\
(m, 3 \ H, Ar-H), 5.67 \ (d, J = 2.8 \ Hz, 1 \ H, \text{one proton of} =\text{CH}_2), 5.38 \ (d, J = 2.8 \ Hz, 1 \\
H, \text{one proton of} =\text{CH}_2), 1.91 \ (s, 2 \ H, =\text{CCH}_2), 1.20 \ (s, 12 \ H, \text{B(pin)}), 0.26 \ (s, 6 \ H, \\
\text{SiMe}_2); \ \text{\textsuperscript{13}C NMR} \ (100 \ MHz, CDCl\textsubscript{3}) \ \delta \ 139.1, 133.8, 128.8, 127.6, 83.4, 24.7, 24.2, \\
-3.3; \ \text{IR} \ (\text{neat,} \ \text{cm}^{-1}): 2978, 1605, 1425, 1358, 1308, 1247, 1192, 1142, 1113, 1092; \\
\text{MS (ESI)} \ m/z \ 326 [M^{+}(\text{11B})+\text{Na}+\text{H}], 325 [M^{+}(\text{11B})+\text{Na}], \text{or} [M^{+}(\text{10B})+\text{Na}+\text{H}], 324 \\
[M^{+}(\text{10B})+\text{Na}].

(6) Synthesis of (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-3-yl) \\
dimethyl(phenyl)dimethylsilane (5f) (ywm-12-9)
The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.4 mg, 0.05 mmol), NaOr-Bu (19.6 mg, 0.2 mmol), bis(pinacolato)diboron (305.8 mg, 1.2 mmol)/THF (2 mL), 3f (201.3 mg, 1.0 mmol)/THF (1 mL), i-PrOH (153 μL, d = 0.784 g/cm³, 120.2 mg, 2.0 mmol) afforded 5f (293.6 mg, 89%) (eluent: petroleum ether/ethyl ether = 70/1) as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.55-7.47 (m, 2 H, Ar-H), 7.36-7.28 (m, 3 H, Ar-H), 5.82 (d, J = 3.0 Hz, 1 H, one proton of =CH₂), 5.36 (d, J = 3.0 Hz, 1 H, one proton of =CH₂), 1.97 (dd, J₁ = 10.8 Hz, J₂ = 4.5 Hz, 1 H, CH), 1.70-1.47 (m, 2 H, CH₂), 1.199 (s, 6 H, B(pin)), 1.195 (s, 6 H, B(pin)), 0.81 (t, J = 7.4 Hz, 3 H, CH₃), 0.26 (s, 3 H, SiMe), 0.23 (s, 3 H, SiMe); ¹³C NMR (75.4 MHz, CDCl₃) δ 138.7, 134.2, 128.6, 127.4, 126.7, 83.1, 35.8, 24.8, 24.7, 21.8, 13.9, -3.7, -5.2; IR (neat, cm⁻¹): 2977, 2959, 1601, 1463, 1427, 1389, 1370, 1360, 1335, 1305, 1247, 1241, 1166, 1140, 1111, 1060, 1026; MS (ESI) m/z 369 [M⁺(¹¹B)+K], 353 [M⁺(¹¹B)+Na], 352 [M⁺(¹⁰B)+Na]; HRMS Calcd for C₁₉H₃₁O₂Si¹¹B (M⁺): 330.2186, Found: 330.2188.

(7) Synthesis of (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-3-yl)dimethyl(phenyl)silane (5g) (yw12-8)

The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.7 mg, 0.05 mmol), NaOr-Bu (19.4 mg, 0.2 mmol), bis(pinacolato)diboron (306.2 mg, 1.2 mmol)/THF (2 mL), 3g (215.8 mg, 1.0 mmol)/THF (1 mL), i-PrOH (153 μL, d = 0.784 g/cm³, 120.2 mg, 2.0 mmol) afforded 5g (300.1 mg, 87%) (eluent: petroleum ether/ethyl ether =
70/1) as a liquid: $^1$H NMR (300 MHz, CDCl$_3$) δ 7.54-7.47 (m, 2 H, Ar-H), 7.36-7.28 (m, 3 H, Ar-H), 5.81 (d, $J = 3.3$ Hz, 1 H, one proton of $=CH_2$), 5.35 (d, $J = 3.0$ Hz, 1 H, one proton of $=CH_2$), 2.10 (dd, $J_1 = 11.9$ Hz, $J_2 = 3.2$ Hz, 1 H, CH), 1.72-1.54 (m, 1 H, one proton of CH$_2$), 1.48-1.27 (m, 2 H, CH$_2$), 1.21-1.02 (m, 13 H, one proton of CH$_2$ and B(pin)), 0.78 (t, $J = 7.1$ Hz, 3 H, CH$_3$), 0.26 (s, 3 H, SiMe), 0.23 (s, 3 H, SiMe); $^{13}$C NMR (75.4 MHz, CDCl$_3$) δ 138.6, 134.2, 128.6, 127.4, 126.7, 83.1, 33.1, 30.8, 24.70, 24.67, 21.9, 13.8, -3.8, -5.1; IR (neat, cm$^{-1}$): 2977, 2956, 1601, 1465, 1426, 1418, 1388, 1361, 1344, 1305, 1273, 1246, 1226, 1165, 1141, 1111, 1067; MS (ESI) m/z 368 [M$^{+}$($^{11}$B)+Na+H], 367 [M$^{+}$($^{11}$B)+Na] or [M$^{+}$($^{10}$B)+Na+H], 366 [M$^{+}$($^{10}$B)+Na]; HRMS Calcd for C$_{20}$H$_{33}$O$_2$Si$_{11}$B (M$^+$): 344.2343, Found: 344.2340.

(8) Synthesis of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-1-en-3-yl trimethylsilane (5h) (yw-m-13-161)

\[
\begin{align*}
\text{3h} & \quad \text{TMS} & \quad \text{CuCl (5 mol%), BIPHEP (5 mol%)} & \quad \text{NaO}_2\text{-Bu (20 mol%), } \text{B}_2\text{(pin)}_2 \text{ (1.2 equiv)} & \quad \text{i-PrOH (2.0 equiv), THF, rt, 3 h, 79%} & \quad \text{5h} & \quad \text{TMS} \\
\end{align*}
\]

The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.2 mg, 0.05 mmol), NaO$_2$-Bu (19.1 mg, 0.2 mmol), bis(pinacolato) diboron (304.6 mg, 1.2 mmol)/THF (2 mL), 3h (224.6 mg, 1.0 mmol)/THF (1 mL), i-PrOH (153 µL, d = 0.784 g/cm$^3$, 120.2 mg, 2.0 mmol) afforded 5h (279.4 mg, 79%) (eluent: petroleum ether/ethyl ether = 70/1) as a liquid: $^1$H NMR (300 MHz, CDCl$_3$) δ 5.79 (d, $J = 3.3$ Hz, 1 H, one proton of $=CH_2$), 5.40 (d, $J = 3.0$ Hz, 1 H, one proton of $=CH_2$), 1.80 (dd, $J_1 = 11.6$ Hz, $J_2 = 3.2$ Hz, 1 H, =CCH), 1.72-1.04 (m, 26 H, 7 × CH$_2$ and B(pin)), 0.87 (t, $J = 6.8$ Hz, 3 H, CH$_3$), -0.06 (s, 9 H, SiMe$_3$); $^{13}$C NMR (75.4 MHz, CDCl$_3$) δ 126.0, 83.1, 34.2, 31.9, 29.60, 29.56, 29.4, 28.4, 28.3, 24.8, 24.7, 22.7, 14.1, -2.8; IR (neat, cm$^{-1}$): 2924, 2854, 1600, 1466, 1418, 1360, 1304, 1246, 1142; MS (70 ev, EI) m/z 352 [M$^{+}$($^{11}$B), 1.09], 73 (100); HRMS Calcd for C$_{20}$H$_{41}$O$_2$Si$_{10}$B (M$^+$): 351.3005, Found: 351.2999.
(9) Synthesis of (5-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-3-yl)trimethylsilane (5i) (ywm-13-158)

The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.3 mg, 0.05 mmol), NaOt-Bu (19.3 mg, 0.2 mmol), bis(pinacolato)boron (304.9 mg, 1.2 mmol)/THF (2 mL), 3i (168.4 mg, 1.0 mmol)/THF (1 mL), i-PrOH (153 μL, d = 0.784 g/cm³, 120.2 mg, 2.0 mmol) afforded 5i (257.3 mg, 87%) (eluent: petroleum ether/ethyl ether = 70/1) as a liquid: 1H NMR (300 MHz, CDCl₃) δ 5.79 (d, J = 3.3 Hz, 1 H, one proton of =CH₂), 5.39 (d, J = 3.3 Hz, 1 H, one proton of =CH₂), 1.93 (dd, J₁ = 12.8 Hz, J₂ = 3.2 Hz, 1 H, =CCH), 1.81-1.67 (m, 1 H, one proton of CH₂), 1.65-1.49 (m, 1 H, CH), 1.24 (s, 12 H, B(pin)), 1.13-1.02 (m, 1 H, one proton of CH₂), 0.84 (d, J = 6.6 Hz, 3 H, CH₃), 0.77 (d, J = 6.6 Hz, 3 H, CH₃), -0.06 (s, 9 H, SiMe₃); 13C NMR (75.4 MHz, CDCl₃) δ 126.3, 83.1, 37.4, 32.0, 26.0, 24.7, 23.9, 20.8, -2.9; IR (neat, cm⁻¹): 2953, 2901, 1602, 1468, 1418, 1361, 1304, 1246, 1142; MS (70 ev, EI) m/z (%) 296 [M⁺(¹¹B), 1.78], 295 [M⁺(¹⁰B), 0.47], 73 (100); HRMS Calcd for C₁₅H₃₃O₂Si¹₀B (M⁺): 295.2379, Found: 295.2378.

(10) Synthesis of (1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-yl)trimethylsilane (5j) (ywm-13-138)

The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.2 mg, 0.05 mmol), NaOt-Bu (19.1 mg, 0.2 mmol), bis(pinacolato)boron (304.3 mg, 1.2 mmol)/THF (2 mL), 3j (202.5 mg, 1.0 mmol)/THF (1 mL), i-PrOH (153 μL, d = 0.784 g/cm³, 120.2
mg, 2.0 mmol) afforded 5j (275.5 mg, 83%) (eluent: petroleum ether/ethyl ether = 70/1) as a liquid: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.25-7.07 (m, 5 H, Ar-H), 5.75 (d, $J$ = 3.3 Hz, 1 H, one proton of =CH$_2$), 5.42 (d, $J$ = 2.4 Hz, 1 H, one proton of =CH$_2$), 2.99 (dd, $J_1$ = 14.6 Hz, $J_2$ = 11.0 Hz, 1 H, one proton of Ar-CH$_2$), 2.88 (dd, $J_1$ = 14.4 Hz, $J_2$ = 5.1 Hz, 1 H, =CH), 1.24 (s, 6 H, B(pin)), 1.22 (s, 6 H, B(pin)), 0.004 (s, 9 H, SiMe$_3$); $^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ 142.6, 128.6, 127.8, 127.3, 125.2, 83.1, 35.3, 34.6, 24.8, 24.6, -2.7; IR (neat, cm$^{-1}$): 2978, 2956, 1602, 1495, 1417, 1361, 1247, 1212, 1139; MS (70 ev, EI) m/z (%) 330 [M$^+$($^{11}$B), 2.45], 329 [M$^+$($^{10}$B), 0.53], 73 (100); HRMS Calcd for C$_{19}$H$_{31}$O$^1$BO$_2$Si (M$^+$): 329.2223, Found: 329.2226.

(11) Synthesis of (5-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-3-yl)trimethylsilane (5k) (yw-13-160)

The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.2 mg, 0.05 mmol), NaO$_t$-Bu (19.3 mg, 0.2 mmol), bis(pinacolato)diboron (304.5 mg, 1.2 mmol)/THF (2 mL), 3k (216.5 mg, 1.0 mmol)/THF (1 mL), $i$-PrOH (153 $\mu$L, d = 0.784 g/cm$^3$, 120.2 mg, 2.0 mmol) afforded 5k (292.5 mg, 85%) (eluent: petroleum ether/ethyl ether = 70/1) as a liquid: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.31-7.22 (m, 2 H, Ar-H), 7.20-7.11 (m, 3 H, Ar-H), 5.89 (d, $J$ = 3.3 Hz, 1 H, one proton of =CH$_2$), 5.50 (d, $J$ = 2.7 Hz, 1 H, one proton of =CH$_2$), 2.80-2.67 (m, 1 H, =CH), 2.47-2.34 (m, 1 H, one proton of CH$_2$), 2.08-1.67 (m, 3 H, one proton of CH$_2$ and Ar-CH$_2$), 1.27 (s, 12 H, B(pin)), -0.06 (s, 9 H, SiMe$_3$); $^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ 143.2, 128.4, 128.1, 126.5, 125.4, 83.1, 35.3, 34.3, 30.7, 24.8, -2.9; IR (neat, cm$^{-1}$): 2978, 2955, 1601, 1496, 1418, 1359, 1305, 1246, 1134; MS (70 ev, EI) m/z (%) 344 [M$^+$($^{11}$B), 1.82], 73 (100); HRMS Calcd for C$_{20}$H$_{33}$O$_2$Si$^{10}$B (M$^+$): 343.2379, Found: 343.2382.
(12) Synthesis of (1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)-dimethyl(phenyl)silane (5l) (sl-2-175)

The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.3 mg, 0.05 mmol), NaO\textsubscript{t}-Bu (38.4 mg, 0.4 mmol), bis(pinacolato)diboron (355.9 mg, 1.4 mmol)/THF (2 mL), 3l (250.7 mg, 1.0 mmol)/THF (1 mL), i-PrOH (153 μL, d = 0.784 g/cm\textsuperscript{3}, 120.2 mg, 2.0 mmol) afforded 5l\textsuperscript{8} (273.0 mg, 72%) (eluent: petroleum ether/ethyl ether = 70/1) as a liquid\textsuperscript{5}: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.53-7.47 (m, 2 H, Ar-H), 7.43-7.33 (m, 3 H, Ar-H), 7.30-7.22 (m, 2 H, Ar-H), 7.21-7.14 (m, 3 H, Ar-H), 5.99 (d, \(J = 2.8\) Hz, 1 H, one proton of =CH\textsubscript{2}), 5.76 (d, \(J = 2.0\) Hz, 1 H, one proton of =CH\textsubscript{2}), 3.65 (s, 1 H, =CCH), 1.25 (s, 6 H, B(pin)), 1.23 (s, 6 H, B(pin)), 0.41 (s, 3 H, SiMe), 0.37 (s, 3 H, SiMe); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 142.5, 138.1, 134.4, 129.0, 128.8, 127.8, 127.3, 124.7, 83.4, 42.2, 24.7, 24.6, -3.0, -3.5; IR (neat, cm\textsuperscript{-1}): 2978, 1597, 1492, 1426, 1357, 1310, 1251, 1141, 1074; MS (ESI) m/z 402 [M\textsuperscript{+}(\textsuperscript{11}B)+Na+H], 401 [M\textsuperscript{+}(\textsuperscript{11}B)+Na] or [(\textsuperscript{10}B)+Na+H], 400 [M\textsuperscript{+}(\textsuperscript{10}B)+Na].

(13) Synthesis of methyl 3-(dimethyl(phenyl)silyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (5m) (sl-4-93)

The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.3 mg, 0.05 mmol), NaO\textsubscript{t}-Bu (19.3 mg, 0.2 mmol), bis(pinacolato)diboron (304.9 mg, 1.2 mmol)/THF (2
mL), 3m (246.7 mg, 1.0 mmol)/THF (1 mL), i-PrOH (153 μL, d = 0.784 g/cm³, 120.2 mg, 2.0 mmol) afforded 5m (320.1 mg, 85%) (eluents: petroleum ether/ethyl ether = 50/1) as a liquid; 1H NMR (400 MHz, CDCl₃) δ 7.52-7.43 (m, 2 H, Ar-H), 7.36-7.30 (m, 3 H, Ar-H), 5.79 (d, J = 2.8 Hz, 1 H, one proton of =CH₂), 5.36 (d, J = 2.4 Hz, 1 H, one proton of =CH₂), 3.52 (s, 3 H, OCH₃), 2.72-2.56 (m, 2 H, CH₂), 2.41 (dd, J₁ = 14.6 Hz, J₂ = 3.4 Hz, 1 H, =CCH), 1.22 (s, 6 H, B(pin)), 1.21 (s, 6 H, B(pin)), 0.29 (s, 3 H, SiMe), 0.27 (s, 3 H, SiMe); 13C NMR (100 MHz, CDCl₃) δ 173.8, 137.2, 134.2, 129.0, 127.6, 127.2, 83.3, 51.3, 34.3, 29.8, 24.71, 24.68, -3.9, -5.4; IR (neat, cm⁻¹): 2977, 1737, 1428, 1363, 1308, 1249, 1137, 1112; MS (ESI) m/z (%) 398 [M⁺(¹¹B)+Na⁺H], 397 [M⁺(¹¹B)+Na] or [M⁺(¹⁰B)+Na⁺H], 396 [M⁺(¹⁰B)+Na⁺]; HRMS Calcd for C₂₀H₃₁O₄Si₁₁B (M⁺): 374.2085, Found: 374.2083.

(14) Synthesis of 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trimethylsilyl)hex-5-enenitrile (5n) (sl-6-54)

\[
\begin{align*}
\text{3n} & \xrightarrow{\text{CuCl (5 mol%), BIPHEP (5 mol%)}} \text{5n} \\
\text{CuCl (5 mol%), BIPHEP (5 mol%)} & \text{NaO}t\text{-Bu (35 mol%), } \text{B}_2(\text{pin})_2 \text{(1.4 equiv)} \\
i\text{-PrOH (2.0 equiv), THF, rt, 10 h, 80\%} & \text{TMS} \\
\end{align*}
\]

The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.2 mg, 0.05 mmol), NaO-t-Bu (33.6 mg, 0.35 mmol), bis(pinacolato)diboron (355.6 mg, 1.4 mmol)/THF (8 mL), 3n (165.6 mg, 1.0 mmol)/THF (2 mL), i-PrOH (153 μL, d = 0.784 g/cm³, 120.2 mg, 2.0 mmol) afforded 5n (232.7 mg, 80%) (eluents: petroleum ether/ethyl ether = 40/1) as an oil; 1H NMR (400 MHz, CDCl₃) δ 5.86 (d, J = 2.4 Hz, 1 H, one proton of =CH₂), 5.45 (d, J = 2.8 Hz, 1 H, one proton of =CH₂), 2.45-2.35 (m, 1 H, =CCH), 2.24-2.12 (m, 1 H, one proton of CH₂), 2.12-2.00 (m, 1 H, one proton of CH₂), 1.94-1.79 (m, 2 H, CH₂), 1.24 (s, 12 H, B(Pin)), -0.02 (s, 9 H, SiMe₃); 13C NMR (100 MHz, CDCl₃) δ 128.0, 120.2, 83.5, 34.5, 24.8, 24.7, 24.6, 16.6, -3.0; IR (neat, cm⁻¹): 2978, 2959, 2245, 1600, 1420, 1380, 1371, 1659, 1309, 1248, 1213, 1202, 1165, 1138;
MS (70 ev, EI) m/z (%): 293 [M+\(^{(11}B\), 9.57], 292 [M+\(^{(10}B\), 2.48], 113 (100). HRMS Calcd for C\(_{15}\)H\(_{28}\)NO\(_2\)Si\(^{11}B\) (M\(^+\)): 293.1982, Found: 293.1981.

**Synthesis of 1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)pent-4-en-1-one (5o) (sl-6-117)**

The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.2 mg, 0.05 mmol), NaO\(_t\)-Bu (19.3 mg, 0.2 mmol), bis(pinacolato) diboron (305.1 mg, 1.2 mmol)/THF (2 mL), 3o (230.5 mg, 1.0 mmol)/THF (1 mL), \(i\)-PrOH (153 μL, d = 0.784 g/cm\(^3\), 120.2 mg, 2.0 mmol) afforded 5o (222.8 mg, 62%) (eluent: petroleum ether/ethyl ether = 40/1) as a liquid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.95-7.90 (m, 2 H, Ar-H), 7.58-7.49 (m, 1 H, Ar-H), 7.47-7.40 (m, 2 H, Ar-H), 5.76 (d, \(J = 2.8\) Hz, 1 H, one proton of \(-CH_2\)), 5.44 (d, \(J = 2.4\) Hz, 1 H, one proton of \(-CH_2\)), 3.50 (dd, \(J_1 = 16.8\) Hz, \(J_2 = 10.4\) Hz, 1 H, one proton of COCH\(_3\)), 3.01 (dd, \(J_1 = 16.8\) Hz, \(J_2 = 4.8\) Hz, 1 H, one proton of COCH\(_3\)), 2.57 (dd, \(J_1 = 10.8\) Hz, \(J_2 = 4.8\) Hz 1 H, \(-CH\)), 1.21 (s, 6 H, B(Pin)), 1.20 (s, 6 H, B(Pin)), 0.03 (s, 9 H, SiMe\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 200.3, 137.6, 132.5, 128.3, 128.0, 126.8, 83.3, 38.3, 29.9, 24.72, 24.70 , -2.8; IR (neat, cm\(^{-1}\)): 2978, 1687, 1598, 1580, 1447, 1421, 1359, 1306, 1165, 1139; MS (70 ev, El) m/z (%) : 358 [M+\(^{(11}B\), 4.70], 357 [M+\(^{(10}B\), 2.39], 73 (100). HRMS Calcd for C\(_{20}\)H\(_{32}\)O\(_3\)Si\(^{11}B\) [M+\(^{(11}B)+H\): 359.2214, Found: 359.2219.

**Synthesis of ((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)pent-4-en-1-yl)oxy)\textit{tert}-butyldimethylsilane (5p) (ywm-12-26)**
The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.7 mg, 0.05 mmol), NaO-t-Bu (19.1 mg, 0.2 mmol), bis(pinacolato)diboron (305.0 mg, 1.2 mmol)/THF (2 mL), 3p (271.3 mg, 1.0 mmol)/THF (1 mL), i-PrOH (153 μL, d = 0.784 g/cm³, 120.2 mg, 2.0 mmol) afforded 5p (287.7 mg, 72%) (eluent: petroleum ether/ethyl ether = 70/1) as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 5.78 (d, J = 3.3 Hz, 1 H, one proton of =CH₂), 5.43 (d, J = 2.7 Hz, 1 H, one proton of =CH₂), 3.67-3.56 (m, 1 H, =CCH), 3.49-3.38 (m, 1 H, one proton of CH₂), 1.93-1.82 (m, 2 H, CH₂), 1.76-1.64 (m, 1 H, one proton of CH₂), 1.24 (s, 12 H, B(pin)), 0.88 (s, 9 H, (CH₃)₃), 0.02 (s, 6 H, (CH₃)₂), -0.04 (s, 9 H, SiMe₃); ¹³C NMR (75.4 MHz, CDCl₃) δ 126.1, 83.2, 62.8, 31.5, 30.3, 26.0, 24.9, 24.7, 18.4, -2.9, -5.2; IR (neat, cm⁻¹): 2955, 2930, 2858, 1600, 1469, 1418, 1361, 1306, 1249, 1142, 1098; MS (ESI) m/z 422 [M⁺(¹¹B)+Na⁺H], 421 [M⁺(¹¹B)+Na] or [M⁺(¹⁰B)+Na⁺H], 420 [M⁺(¹⁰B)+Na]; HRMS Calcd for C₂₀H₄₄O₃Si₂¹¹B (M⁺): 398.2844, Found: 398.2849.

(17) Synthesis of ((5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trimethylsilyl)hex-5-en-1-yl)oxy)tert-butyldimethylsilane (5q) (ywm-13-175)

The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.3 mg, 0.05 mmol), NaO-t-Bu (19.1 mg, 0.2 mmol), bis(pinacolato)diboron (304.8 mg, 1.2 mmol)/THF (2 mL), 3q (284.4 mg, 1.0 mmol)/THF (1 mL), i-PrOH (153 μL, d = 0.784 g/cm³, 120.2 mg, 2.0 mmol) afforded 5q (291.4 mg, 71%) (eluent: petroleum ether/ethyl ether =
70/1) as a liquid: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.80 (d, $J = 3.3$ Hz, 1 H, one proton of =CH$_2$), 5.40 (d, $J = 2.7$ Hz, 1 H, one proton of =CH$_2$), 3.56 (t, $J = 6.2$ Hz, 2 H, CH$_2$OTBS), 1.84-1.77 (m, 1 H, =CCH), 1.71-1.49 (m, 3 H, one proton of CH$_2$ and CH$_2$), 1.47-1.33 (m, 1 H, one proton of CH$_2$), 1.24 (s, 12 H, B(pin)), 0.89 (s, 9 H, (CH$_3$)$_3$), 0.04 (s, 6 H, (CH$_3$)$_2$), -0.05 (s, 9 H, SiMe$_3$); $^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ 126.1, 83.1, 63.1, 33.7, 32.0, 26.0, 24.8, 24.7, 24.3, 18.3, -2.9, -5.3; IR (neat, cm$^{-1}$): 2954, 2858, 1601, 1471, 1361, 1305, 1247, 1142, 1100; MS (ESI) m/z 451 [M$^+$(11B)+K], 436 [M$^+$(11B)+Na+H], 435 [M$^+$(11B)+Na] or [M$^+$(10B)+Na], 434 [M$^+$(10B)+Na]; HRMS Calcd for C$_{21}$H$_{45}$O$_3$Si$_2$B$_{11}$ (M$^+$): 412.3000, Found: 412.3003.

(18) Synthesis of 4-(dimethyl(phenyl)silyl)-3-methylene-2-hydroxy-1,2-oxaborinane (5r) (sl-6-5)

![Diagram]

The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.1 mg, 0.05 mmol), NaOt-Bu (19.4 mg, 0.2 mmol), bis(pinacolato) diboron (304.9 mg, 1.2 mmol)/THF (2 mL), 3r (218.7 mg, 1.0 mmol)/THF (1 mL), i-PrOH (120.2 mg, d = 0.784 g/cm$^3$, 2.0 mmol) afforded 5r (140.2 mg, 57%, the desired hydroboration product was instable on silica gel.) (eluent: petroleum ether/ethyl acetate = 20/1) as an oil: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53-7.47 (m, 2 H, Ar-H), 7.40-7.30 (m, 3 H, Ar-H), 5.75 (dd, $J_1 = 2.4$ Hz, $J_2 = 1.6$ Hz, 1 H, one proton of =CH$_2$), 5.34 (s, 1 H, one proton of =CH$_2$), 4.29 (brs, 1 H, OH), 4.05-3.85 (m, 2 H, OCH$_2$), 2.23 (t, $J = 5.2$ Hz, =CCH), 2.02-1.85 (m, 1 H, one proton of CH$_2$), 1.82-1.72 (m, 1 H, one proton of CH$_2$), 0.33 (s, 3 H, SiMe), 0.32 (s, 3 H, SiMe); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.7, 134.0, 129.1, 127.8, 125.0, 65.0, 31.6, 28.9, -3.96, -4.04; IR (neat, cm$^{-1}$): 3384, 2901, 1483, 1425, 1411, 1365, 1339, 1296, 1248, 1187, 1146, 1111, 1034; MS (70 ev, EI) m/z (%): 246 (M$^+$(11B), 1.89], 245 [M$^+$(10B), 0.67], 135 (100). HRMS Calcd for C$_{13}$H$_{19}$O$_2$Si$_{11}$B (M$^+$): 246.1247, Found: 246.1249.
(19) Synthesis of bis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)methyl (phenyl) silane (5s) (sl-4-83)

The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.4 mg, 0.05 mmol), K₂CO₃ (27.7 mg, 0.2 mmol), bis(pinacolato)diboron (635.2 mg, 2.5 mmol), THF (2 mL), 3s (198.2 mg, 1.0 mmol), THF (1 mL), i-PrOH (306 μL, d = 0.784 g/mL, 240.4 mg, 4.0 mmol) afforded 5s (311.7 mg, 69%) (eluent: petroleum ether/ethyl ether = 50/1) as a white solid: m.p. 42.1-43.1 °C (Hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.54-7.47 (m, 2 H, Ar-H), 7.32-7.24 (m, 3 H, Ar-H), 5.64 (d, J = 4.0 Hz, 2 H, =CH₂), 5.39 (d, J = 3.2 Hz, 2 H, =CH₂), 1.96 (s, 4 H, 2 × =CCH₂), 1.15 (s, 24 H, 2 × B(pin)), 0.26 (s, 3 H, SiMe); ¹³C NMR (100 MHz, CDCl₃) δ 137.4, 134.5, 128.6, 127.8, 127.3, 83.3, 24.7, 24.6, 22.3, -5.8; IR (neat, cm⁻¹): 2984, 1603, 1469, 1423, 1372, 1356, 1316, 1248, 1193, 1111, 1083; MS (ESI) m/z 478 [M⁺(¹¹B)+Na+H], 477 [M⁺(¹¹B)+Na] or [M⁺(¹⁰B)+Na+H], 476 [M⁺(¹⁰B)+Na]; Anal. Calcd. for C₂₅H₄₀B₂O₄Si (%): C 66.10, H 8.87; Found: C 66.04, H 8.93.

(20) Synthesis of bis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)diphenyl silane (5t) (sl-4-82)
The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.2 mg, 0.05 mmol), K$_2$CO$_3$ (27.8 mg, 0.2 mmol), bis(pinacolato)diboron (635.3 mg, 2.5 mmol), THF (2 mL), 3t (260.8 mg, 1.0 mmol), THF (1 mL), i-PrOH (306 uL, d = 0.784 g/ml, 240.2 mg, 4.0 mmol) afforded 5t (351.9 mg, 70%) (eluent: petroleum ether/ethyl ether = 50/1) as a white solid: m.p. 78.1-78.8 °C (Hexane); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.55-7.49 (m, 4 H, Ar-H), 7.36-7.24 (m, 6 H, Ar-H), 5.65 (d, $J = 4.0$ Hz, 2 H, =CH$_2$), 5.41 (d, $J = 3.2$ Hz, 2 H, =CH$_2$), 2.27 (s, 4 H, 2 × =CCH$_2$), 1.06 (s, 24 H, 2 × B(pin)); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 135.9, 135.3, 128.9, 128.7, 127.3, 83.2, 24.6, 20.1; IR (neat, cm$^{-1}$): 2979, 2931, 2894, 1606, 1428, 1380, 1370, 1356, 1215, 1192, 1138, 1110, 1082; MS (ESI) m/z 555 [M$^+$(11B)+K], 540 [M$^+$(11B)+Na+H], 539 [M$^+$(11B)+Na] or [M$^+$(10B)+Na+H], 538 [M$^+$(10B)+Na]; Anal. Calcd. for C$_{30}$H$_{42}$O$_4$SiB$_2$ (%): C 69.78, H 8.20; Found: C 69.96, H 8.19.

(21) Synthesis of (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-1,6-dien-3-yl)trimethylsilane (5u) (ywm-13-159)

The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.2 mg, 0.05 mmol), NaO$_r$-Bu (19.1 mg, 0.2 mmol), bis(pinacolato)diboron (304.5 mg, 1.2 mmol)/THF (2
mL), 3u (166.4 mg, 1.0 mmol)/THF (1 mL), i-PrOH (153 μL, d = 0.784 g/cm³, 120.2 mg, 2.0 mmol) afforded 5u (243.2 mg, 83%) (eluuent: petroleum ether/ethyl ether = 70/1) as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 5.86-5.70 (m, 2 H, one proton of =CH₂ and =CH), 5.42 (d, J = 2.7 Hz, 1 H, one proton of =CH₂), 5.00-4.88 (m, 2 H, =CH₂), 2.21-2.06 (m, 1 H, =CCH), 1.99-1.68 (m, 3 H, one proton of CH₂ and CH₂), 1.59-1.44 (m, 1 H, one proton of CH₂), 1.25 (s, 12 H, B(pin)), -0.05 (s, 9 H, SiMe₃); ¹³C NMR (75.4 MHz, CDCl₃) δ 139.2, 126.3, 114.2, 83.1, 33.7, 33.1, 27.8, 24.8, 24.7, -2.9; IR (neat, cm⁻¹): 2979, 1640, 1601, 1418, 1360, 1246, 1142; MS (70 ev, EI) m/z (%) 294 (M⁺, 1.21), 73 (100); HRMS Calcd for C₁₆H₃₁¹¹BO₂Si (M⁺): 294.2186, Found: 294.2191.

(22) Synthesis of (6-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-1,6-dien-3-yl)trimethylsilane (5v) (ywm-13-180)

The reaction of CuCl (5.0 mg, 0.05 mmol), BIPHEP (26.3 mg, 0.05 mmol), NaO₂t-Bu (19.1 mg, 0.2 mmol), bis(pinacolato)diboron (304.5 mg, 1.2 mmol)/THF (2 mL), 3v (180.5 mg, 1.0 mmol)/THF (1 mL), i-PrOH (153 μL, d = 0.784 g/cm³, 120.2 mg, 2.0 mmol) afforded 5v (240.7 mg, 78%) (eluuent: petroleum ether/ethyl ether = 50/1) as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 5.82 (d, J = 3.0 Hz, 1 H, one proton of =CH₂), 5.42 (d, J = 3.0 Hz, 1 H, one proton of =CH₂), 4.67 (s, 1 H, one proton of =CH₂), 4.63 (s, 1 H, one proton of =CH₂), 2.13-2.01 (m, 1 H, =CCH), 1.94-1.72 (m, 3 H, one proton of CH₂ and CH₂), 1.69 (s, 3 H, CH₃), 1.67-1.53 (m, 1 H, one proton of CH₂), 1.25 (s, 12 H, B(pin)), -0.04 (s, 9 H, SiMe₃); ¹³C NMR (75.4 MHz, CDCl₃) δ 146.3, 126.2, 109.8, 83.1, 37.2, 34.0, 26.6, 24.7, 22.3, -2.9; IR (neat, cm⁻¹): 2979, 1648, 1600, 1418, 1360, 1304, 1246, 1138; MS (ESI) m/z 347 [M⁺(¹¹B)+K], 332 [M⁺(¹¹B)+Na+H], 331 [M⁺(¹¹B)+Na] or [M⁺(¹⁰B)+Na+H], 330 [M⁺(¹⁰B)+Na]; HRMS
Calcd for C_{17}H_{33}O_{2}Si_{10}B (M\(^{+}\)): 307.2379, Found: 307.2383.

(23) Synthesis of (prop-1-yn-3-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) allyldiphenylsilane (5w) (sl-4-106)

\[
\text{Ph}_2\text{Si} = \begin{array}{c}
\text{CuCl (5 mol%), BIPHEP (5 mol%)} \\
\text{K}_2\text{CO}_3 (20 mol%), \text{B}_2(\text{pin})_2 (2.5 equiv) \\
\text{i-PrOH (4.0 equiv), THF, rt, 3 h, 61%}
\end{array}
\]

The reaction of CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.3 mg, 0.05 mmol), K₂CO₃ (27.8 mg, 0.2 mmol), bis(pinacolato) diboron (635.1 mg, 2.5 mmol), THF (2 mL), 3w (260.7 mg, 1.0 mmol), THF (1 mL), i-PrOH (306 μL, d = 0.784 g/cm³, 240.4 mg, 4.0 mmol) afforded 5w (236.1 mg, 61%) (eluent: petroleum ether/ethyl ether = 150/1) as a white solid: m.p. 71.1-71.7 °C (Hexane); \(^1\)H NMR (400 MHz, CDCl₃) δ 7.62-7.55 (m, 4 H, Ar-H), 7.43-7.30 (m, 6 H, Ar-H), 5.73 (d, \(J\) = 3.2 Hz, 1 H, one proton of =CH₂), 5.52 (d, \(J\) = 2.8 Hz, 1 H, one proton of =CH₂), 2.37 (s, 2 H, =CCH₂), 2.09 (d, \(J\) = 2.8 Hz, 2 H, =CCH₂), 1.85 (t, \(J\) = 2.8 Hz, 1 H, =CH), 1.08 (s, 12 H, B(pin)); \(^{13}\)C NMR (100 MHz, CDCl₃) δ 135.2, 134.0, 129.6, 129.2, 127.7, 83.4, 81.7, 68.6, 24.6, 19.9, 2.9; IR (neat, cm\(^{-1}\)): 1608, 1428, 1391, 1380, 1373, 1359, 1310, 1273, 1198, 1160, 1140, 1111, 1092; MS (70 ev, El) m/z (%): 388 (M\(^{+}\)(\(^{11}\)B), 1.29), 221 (100); Anal. Calcd. for C₂₄H₂₉BO₂Si (%): C 74.22, H 7.53; Found: C 74.07, H 7.54.

5. Synthetic applications

(1) Synthesis of 2,3-dihydro-3-methylene-1\(H\)-inden-1-ol (7) (sl-5-38)

\[
\begin{array}{c}
\text{1) Pd}_2(\text{dba})_3 \text{CHCl}_3 (2.5 mol%), \text{PPh}_3 (11 mol%)} \\
\text{1.5 (equiv)} \\
\text{NaOt-Bu (4.0 equiv), toluene/H}_2\text{O} = 4/3, 95 °C, 37 h} \\
\text{2) Bu}_3\text{NF (1.25 equiv), THF, rt, 0.5 h} \\
\text{67% (two steps)}
\end{array}
\]
To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially Pd$_2$(dba)$_3$·CHCl$_3$ (10.4 mg, 0.01 mmol), Ph$_3$P (11.9 mg, 0.044 mmol), NaOr-Bu (153.7 mg, 1.6 mmol), 2-iodobenzoaldehyde (139.0 mg, 0.6 mmol), 5e (120.7 mg, 0.4 mmol)/toluene (2 mL), and H$_2$O (1.5 mL) under argon. The mixture was stirred at rt for 10 min and then at 95 °C with a preheated oil bath for 37 h. Upon completion, the resulting mixture was cooled to rt, filtered through a short column of silica gel eluted with Et$_2$O (10 mL × 3), and concentrated. The residue was dissolved in 3 mL of THF followed by the addition of n-Bu$_4$NF (0.5 mL, 1 M in THF, 0.5 mmol). The resulting mixture was stirred at rt for 0.5 h. Upon completion, the resulting mixture was filtered through a short column of silica gel eluting with Et$_2$O (10 mL × 3) and concentrated. The residue was purified by chromatography on silica gel to afford 7 (39.3 mg, 67%) (eluent: petroleum ether/ethyl acetate = 10/1) as a white solid: m.p. 69.5-70.6 °C (Hexane); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.57-7.49 (m, 1 H, Ar-H), 7.48-7.42 (m, 1 H, Ar-H), 7.36-7.27 (m, 2 H, Ar-H), 5.52 (t, $J$ = 2.4 Hz, 1 H, one proton of =CH$_2$), 5.25 (brs, 1 H, OCH), 5.09 (t, $J$ = 1.8 Hz, 1 H, one proton of =CH$_2$), 3.19 (ddt, $J_1$ = 16.8 Hz, $J_2$ = 2.0 Hz, $J_3$ = 1.9 Hz, 1 H, one proton of CH$_2$), 2.69-2.60 (m, 1 H, one proton of CH$_2$), 2.00 (s, 1 H, OH); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 146.9, 146.3, 140.1, 128.9, 128.7, 125.0, 120.6, 104.3, 73.3, 42.5; IR (neat, cm$^{-1}$): 3303, 3217, 1641, 1470, 1422, 1333, 1094, 1040, 1002; MS (70 ev, EI) m/z (%): 146 (M$^+$, 97.0), 131 (100).

(2) Synthesis of 4-ethoxyhexen-2-yl 4,4,5,5-tetramethyl-1,3,2-dioxaborolan 8a (sl-4-74)

$$\begin{align*}
\text{5e} & \quad + \quad \text{EtOEt} \\
\text{TiCl}_4 (1.2 \text{ equiv}) & \quad \text{CH}_2\text{Cl}_2, -78 \degree \text{C, 5 h} \quad \text{86\%} \\
\text{8a} & \quad \text{8a}
\end{align*}$$

To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially 5e (151.2 mg, 0.5 mmol), CH$_2$Cl$_2$ (1.25 mL), 1,1-diethoxypropane (95μL, d = 0.83 g/cm$^3$, 79.3 mg, 0.6 mmol), and CH$_2$Cl$_2$ (1.25 mL) under argon at rt. The
mixture was cooled to -78 °C and TiCl₄ (0.6 mL, 1 M in CH₂Cl₂, 0.6 mmol) was added dropwise over 10 minutes. Upon completion as monitored by TLC, the resulting mixture was quenched with a saturated aqueous solution of NaHCO₃ (10 mL) at -78 °C. After warming up to room temperature, the organic phase was separated and the aqueous layer was extracted with CH₂Cl₂ (10 mL × 3). The combined organic layer was washed with brine, dried over Na₂SO₄, filtered, and concentrated. The residue was purified by chromatography on silica gel to afford 8a¹⁰ (108.7 mg, 86%) (eluent: petroleum ether/ethyl ether = 50/1) as a liquid: ¹H NMR (400 MHz, CDCl₃) δ 5.83 (d, J = 3.6 Hz, 1 H, one proton of =CH₂), 5.65 (d, J = 3.6 Hz, 1 H, one proton of =CH₂), 3.60-3.40 (m, 2 H, OCH₂), 3.35-3.26 (m, 1 H, OCH), 2.41 (dd, J₁ = 13.4 Hz, J₂ = 6.2 Hz, 1 H, one proton of =CCH₂), 2.24 (dd, J₁ = 13.2 Hz, J₂ = 6.8 Hz, 1 H, one proton of =CCH₂), 1.57-1.44 (m, 1 H, one proton of CH₂), 1.43-1.34 (m, 1 H, one proton of CH₂), 1.27 (s, 12 H, B(pin)), 1.17 (t, J = 7.0 Hz, 3 H, CH₃), 0.91 (t, J = 7.4 Hz, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 131.2, 83.3, 80.1, 64.3, 40.2, 26.7, 24.8, 24.7, 15.5, 9.8; IR (neat, cm⁻¹): 2975, 2930, 2874, 1615, 1430, 1367, 1344, 1307, 1214, 1166, 1142, 1108, 1081; MS (ESI) m/z 278 [M⁺(¹¹B)+Na+H], 277 [M⁺(¹¹B)+Na] or [M⁺(¹⁰B)+Na+H], 276 [M⁺(¹⁰B)+Na], 255 [M⁺(¹¹B)+H], 254 [M⁺(¹¹B)].

(3) Synthesis of 4-benzyloxyhexen-2-yl 4,4,5,5-tetramethyl-1,3,2-dioxaborolane. (8b) (sl-5-119)

To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially 5e (151.4 mg, 0.5 mmol), CH₂Cl₂ (1.5 mL), propionaldehyde dibenzyl acetal (152.3 mg, 0.6 mmol), and CH₂Cl₂ (1.5 mL) under argon. The mixture was cooled to -78 °C and TiCl₄ (0.6 mL, 1 M in CH₂Cl₂, 0.6 mmol) was added dropwise over 10 minutes. Upon completion, the resulting mixture was quenched with a saturated aqueous solution of NaHCO₃ (10 mL) at -78 °C. After warming up to room
temperature, the organic phase was separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (10 mL × 3). The combined organic layer was dried over Na$_2$SO$_4$, filtered, and concentrated. The residue was purified by chromatography on silica gel to afford 8b (137.6 mg, 87%) (elucent: petroleum ether/ethyl ether = 80/1) as a liquid:

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39-7.29 (m, 4 H, Ar-H), 7.28-7.21 (m, 1 H, Ar-H), 5.86 (d, $J$ = 3.6 Hz, 1 H, one proton of =CH$_2$), 5.68 (d, $J$ = 3.2 Hz, 1 H, one proton of =CH$_2$), 4.59 (d, 1 H, $J$ = 11.6 Hz, one proton of Ar-CH$_2$), 4.49 (d, 1 H, $J$ = 12.0 Hz, one proton of Ar-CH$_2$), 3.51-3.43 (m, 1 H, OCH), 2.53 (dd, $J_1$ = 13.2 Hz, $J_2$ = 6.0 Hz, 1 H, one proton of =CCH$_2$), 2.31 (dd, $J_1$ = 13.2 Hz, $J_2$ = 6.8 Hz, 1 H, one proton of =CCH$_2$), 1.61-1.34 (m, 2 H, CH$_2$), 1.24 (s, 6 H, B(pin)), 1.23 (s, 6 H, B(pin)), 0.91 (t, $J$ = 7.4 Hz, 3 H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 139.2, 131.5, 128.1, 127.7, 127.2, 83.3, 79.8, 70.8, 39.9, 26.4, 24.7, 24.6, 9.7; IR (neat, cm$^{-1}$): 2874, 1614, 1496, 1454, 1428, 1368, 1368, 1307, 1213, 1166, 1141, 1109, 1096, 1066, 1028; MS (70 ev, EI) m/z (%) 316 [M$^+$($^{11}$B), 1.07], 315 [M$^+$($^{10}$B), 0.27], 91 (100); HRMS Calcd for C$_{19}$H$_{29}$O$_3$($^{11}$B) (M$^+$): 316.2210, Found: 316.2208.

(4). Synthesis of 2-phenyl-2-propenyl dimethylphenylsilane  (9) (sl-4-73)

![Diagram](image)

To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially Pd(PPh$_3$)$_4$ (17.3 mg, 0.015 mmol), Ba(OH)$_2$·8H$_2$O (236.8 mg, 0.75 mmol), PhI (153.2 mg, 0.75 mmol)/DME (1.5 mL), 5e (151.4 mg, 0.5 mmol)/DME (1.0 mL), and H$_2$O (0.4 mL) under argon. The mixture was stirred under reflux with an oil bath preheated at 100 °C for 3 h as monitored by TLC. Upon completion, the resulting mixture was cooled to rt, filtered through a short column of silica gel eluted with Et$_2$O (10 mL × 3), and concentrated. The residue was purified by chromatography on silica gel to afford 9$^{10}$ (101.8 mg, 85%) (elucent: petroleum ether) as a liquid: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50-7.42 (m, 2 H, Ar-H), 7.39-7.29 (m, 5
H, Ar-H), 7.29-7.18 (m, 3 H, Ar-H), 5.13 (d, J = 1.6 Hz, 1 H, one proton of =CH₂), 4.84 (d, J = 1.2 Hz, 1 H, one proton of =CH₂), 2.25 (d, J = 1.2 Hz, 2 H, CH₂), 0.14 (s, 6 H, SiMe₂); ^13C NMR (100 MHz, CDCl₃) δ 145.9, 142.6, 138.9, 133.5, 128.9, 128.0, 127.6, 127.2, 126.3, 110.9, 25.2, -3.0; IR (neat, cm⁻¹): 1615, 1493, 1426, 1299, 1248, 1160, 1112, 1028; MS (70 ev, EI) m/z (%): 252 (M⁺, 10.42), 135 (100).

(5) Synthesis of 1,3-diphenylbut-3-en-1-ol (10) (sl-5-196)

![Chemical structure](image)

To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially CsF (33.6 mg, 0.22 mmol), 4 Å MS (50.1 mg), PhCHO (30 µL, d = 1.048 g/cm³, 41.8 mg, 0.3 mmol, fresh distilled)/DMF (0.5 mL), and 9 (50.5 mg, 0.2 mmol)/DMF (0.5 mL) under argon. The mixture was stirred at rt for 3 h as monitored by TLC. Upon completion, the resulting mixture was quenched with HCl (1 M, 5 mL), extracted with DCM (20 mL × 3), dried over Na₂SO₄, filtered, and concentrated. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford 10¹¹ (31.3 mg, 70%) as a solid: m.p. 50.2-51.2 °C (Hexane); ^1H NMR (400 MHz, CDCl₃) δ 7.47-7.42 (m, 2 H, Ar-H), 7.40-7.22 (m, 8 H, Ar-H), 5.41 (d, J = 0.4 Hz, 1 H, one proton of =CH₂), 5.16 (s, 1 H, one proton of =CH₂), 4.75-4.68 (m, 1 H, OCH), 3.00 (dd, J₁ = 14.2 Hz, J₂ = 3.4 Hz, 1 H, one proton of =CH₂), 2.85 (dd, J₁ = 14.2 Hz, J₂ = 9.0 Hz, 1 H, one proton of =CCH₂), 2.07 (q, J = 2.1 Hz, 1 H, OH); ^13C NMR (100 MHz, CDCl₃) δ 145.0, 143.9, 140.2, 128.5, 128.4, 127.8, 127.5, 126.3, 125.8, 115.8, 72.0, 45.9; IR (neat, cm⁻¹): 3280, 1629, 1494, 1447, 1354, 1322, 1199, 1050, 1029, 1009; MS (ESI) 207 (M⁺-OH).

(6) Synthesis of 2-hexyl-2,3,6,7-tetrahydro 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) oxepine (11) (yw-12-176)
To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially 5p (76.7 mg, 0.2 mmol), CH₂Cl₂ (2 mL), n-C₆H₁₃CHO (25.9 mg, 0.22 mmol), and CH₂Cl₂ (2 mL) under argon. The resulting mixture was cooled to -78 °C and TMSOTf (43 µL, d = 1.15 g/cm³, 48.9 mg, 0.22 mmol) was added dropwise for 5 min. The resulting mixture was stirred for an additional 55 min at -78 °C and quenched with a saturated aqueous solution of NaHCO₃ (3 mL). The organic phase was separated and the aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed with brine, dried over Na₂SO₄, filtered, and concentrated. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1 to 30/1) to afford 11 (50.4 mg, 85%) as a liquid: ¹H NMR (400 MHz, CDCl₃) δ 6.79-6.73 (m, 1 H, =CH), 4.10-3.90 (dt, J₁ = 12.4 Hz, J₂ = 3.8 Hz, 1 H, OCH), 3.44-3.35 (m, 1 H, one proton of CH₂), 3.33-3.24 (m, 1 H, one proton of CH₂), 2.58-2.44 (m, 2 H, OCH₂), 2.36-2.25 (m, 2 H, CH₂), 1.57-1.39 (m, 3 H, one proton of CH₂ and =CCH₂), 1.36-1.19 (m, 19 H, one proton of CH₂ and 3 × CH₂ and B(pin)), 0.88 (t, J = 6.8 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 146.3, 83.4, 80.2, 68.5, 38.1, 36.9, 34.1, 31.8, 29.3, 25.9, 24.8, 22.6, 14.1; IR (neat, cm⁻¹): 2930, 2856, 1632, 1467, 1326, 1304, 1147, 1052; MS (70 ev, EI) m/z (%): 308 (M⁺(¹¹B), 12.83), 307 [M⁺(¹⁰B), 3.45], 194 (100).

(7) Synthesis of 2-hexyl-4-phenyl-2,3,6,7-tetrahydrooxepine (12) (ywm-12-194)
To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially Pd(PPh₃)₄ (11.9 mg, 0.01 mmol), Na₂CO₃ (64.5 mg, 0.6 mmol), I (61.5 mg, 0.2 mmol), 1,4-dioxane (1 mL), PhI (48.6 mg, 0.24 mmol), and H₂O (1 mL). The resulting mixture was stirred at 80 °C for 5 h as monitored by TLC. Upon completion, Et₂O (5 mL) was added. The organic phase was separated and the aqueous layer was extracted with Et₂O (5 mL × 3). The combined organic layer was washed with brine, dried over Na₂SO₄, filtered, and concentrated. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) to afford 12 (43.3 mg, 84%) as a liquid: ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.19 (m, 5 H, Ar-H), 6.14-6.06 (m, 1 H, =CH), 4.09-4.00 (m, 1 H, OCH), 3.59-3.43 (m, 2 H, OCH₂), 2.89-2.78 (m, 1 H, one proton of CH₂), 2.69-2.54 (m, 2 H, CH₂), 2.39-2.25 (m, 1 H, one proton of CH₂), 1.66-1.54 (m, 1 H, one proton of CH₂), 1.52-1.20 (m, 9 H, one proton of CH₂ and 4 × CH₂), 0.88 (t, J = 6.4 Hz, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 144.7, 142.8, 128.9, 128.2, 126.6, 125.7, 79.0, 69.1, 41.5, 37.1, 31.9, 31.8, 29.3, 25.9, 22.6, 14.1; IR (neat, cm⁻¹): 2928, 2855, 1598, 1492, 1456, 1377, 1110; MS (70 ev, EI) m/z (%): 258 (M⁺, 7.44), 129 (100); HRMS Calcd for C₁₈H₂₆O (M⁺): 258.1984, Found: 258.1981.

5. Synthesis of (2-Deutero-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-but-3-en-2-yl) dimethyl(phenyl)silane ([D]-5a) (sl-6-144)
To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially CuCl (4.9 mg, 0.05 mmol), BIPHEP (26.1 mg, 0.05 mmol), NaO-t-Bu (19.3 mg, 0.2 mmol), bis(pinacolato)diboron (304.9 mg, 1.2 mmol)/THF (2 mL), 3a (188.4 mg, 1.0 mmol)/THF (1 mL), and i-PrOH-d8 (136.3 mg, 2.0 mmol) under argon. The resulting mixture was stirred at rt for 4 h as monitored by TLC. Upon completion, the resulting mixture was filtered through a short column of silica gel eluted with Et2O (10 mL x 3) and concentrated. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethylic ether = 70/1) to afford [D]-5a (275.5 mg, 87%) as a liquid: ¹H NMR (400 MHz, CDCl₃) δ 7.53-7.46 (m, 2 H, Ar-H), 7.36-7.28 (m, 3 H, Ar-H), 5.78 (d, J = 2.4 Hz, 1 H, one proton of =CH₂), 5.36 (d, J = 2.8 Hz, 1 H, one proton of =CH₂), 1.20 (s, 6 H, B(pin)), 1.18 (s, 6 H, B(pin)), 1.08 (s, 3 H, CH₃), 0.24 (s, 6 H, SiMe₂), the following signal is discernible for 5a: 2.19 (q, J = 7.5 Hz, 0.08 H, =CCH); ¹³C NMR (100 MHz, CDCl₃) δ 138.3, 134.2, 128.7, 127.4, 125.5, 83.3, 26.2, 24.9, 24.7, 14.5, 14.4, -4.1, -5.6, the following signal is discernible for 5a: 2.19 (q, J = 7.5 Hz, 0.08 H, =CCH); IR (neat, cm⁻¹): 1596, 1426, 1388, 1372, 1356, 1306, 1247, 1213, 1187, 1165, 1143, 1110; MS (ESI) m/z 341 [M⁺(¹¹B)+Na+H], 340 [M⁺(¹¹B)+Na] or [M⁺(¹⁰B)+Na+H], 319 [M⁺(¹¹B)+H], 318 [M⁺(¹¹B)] or 318 [M⁺(¹⁰B)+H], 317 [M⁺(¹⁰B)]; HRMS Calcd for C₁₈H₃₂D¹¹BNO₂Si (M⁺+NH₄): 335.2436, Found: 335.2432.
References:


Aug 30 2016
si-6-3C
NA = 256
Solvent = cdcl3
P/Std = 32768
F1 = 100.527597 MHz
F2 = 399.749146 MHz

PhMe2Si
3r
Sep 9 2016
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PTSNd = 32768
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F2 = 399.743146 MHz
Oct 22 2016
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F2 = 100.528004 MHz
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Fin Dec 27 19:03:38 2013
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NA = 6
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F2 = 100.526031 MHz
Sep 21 2016
si-6-54H
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Solvent = cdcl3
PTSLd = 16384
F1 = 396.749542 MHz
F2 = 100.526031 MHz

O

B=O

TMS

CN

5n
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F2 = 100.526031 MHz
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spectral, CDCl3
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12.35

TMS

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Jun 2 2016
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Sep 9 2016
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Solvent = cdd3
PTSid = 32768
F1 = 100.527557 MHz
F2 = 399.749145 MHz
Nov 17 2016
sl-G-144H
NA = 4
Solvent = ccd3
PTSTD = 16364
F1 = 399.749542 MHz
F2 = 100.526031 MHz

92% D incorporation

[D]-5a