Supporting Information

Directed cis-hydrosilylation of borylalkynes to borylsilylalkenes

Kinga Stefanowska\textsuperscript{a}, Tomasz Sokolnicki\textsuperscript{a,b}, Jędrzej Walkowiak\textsuperscript{a} Agnieszka Czapik\textsuperscript{b} and Adrian Franczyk*\textsuperscript{a}

\textsuperscript{a}Center for Advanced Technology, Adam Mickiewicz University in Poznań, Uniwersytetu Poznańskiego 10, Poznań 61-614, Poland

E-mail: adrian.franczyk@amu.edu.pl

\textsuperscript{b}Faculty of Chemistry, Adam Mickiewicz University in Poznań, Uniwersytetu Poznańskiego 8, Poznań 61-614, Poland

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1. Optimization of the reaction conditions

Table S1. Hydrosilylation of 2-ethynyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a) with silanes 1a-f.

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The results in gray are listed in Table 1 in the manuscript. Reaction conditions: mwa = 0.0414g, mwa = 0.0934g, mwa = 0.024g, mwa = 0.055g, mwa = 0.024g, mwa = 0.0934g, mwa = 0.024g, mwa = 0.055g; 2 ml of solvent; mwa/V0 = 0.116g/ml; *without solvent; **addition of 5mol% of NaI, mwa/V0 = 0.088g/ml; NaI and silane was mixed for 2h at room temperature. Then the mixture was cooled to 0°C and alkyne was added; 0°C for 2h. *product precipitated as a white solid during the process. **complex mixture of products observed on 1H NMR. Dvs= 1,3-divinyl-1,1,3,3-tetramethyldisiloxane; XPhos= 2-dicyclohexylphosphino- Z'-triisopropylbiphenyl. Conversions of reagents were determined by 1H NMR spectroscopy and GC-MS. The selectivity was determined by 1H NMR spectroscopy.
Table S2. Hydrosilylation of 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyne (2b) with silanes 1a-f.

![Chemical structure](image)

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<th>[H][2][M]</th>
<th>Temp. [°C]</th>
<th>Conversion of 1 [%]</th>
<th>Selectivity of 3a-4/5 [%]</th>
<th>NMR (GC-MS)</th>
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The results in gray are listed in Table 1 in the manuscript. Reaction conditions: m.w. = 0.0414 g, m.w. = 0.09554 g, m.w. = 0.08577 g, m.w. = 0.02945 g, m.w. = 0.055 g, 2 ml of toluene. d.c.w. = 1,3-diviny-1,1,3,3-tetramethylsiloxane; Conversions of reagents were determined by 1H NMR spectroscopy and GC-MS. The selectivity was determined by 1H NMR spectroscopy and ^{29}Si NMR spectroscopy.
Table S3. Hydrosilylation of 2-((tert-butyldimethylsilany)ethynyl)-4,4,5,5-tetramethyl-(1,3,2)dioxaborolane (2c) with silanes 1a-f.

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<th>Conversion of 1 [%]</th>
<th>Selectivity of 3/4/5 [%]</th>
<th>NMR (GC-MS)</th>
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<td>2c</td>
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The results in gray are listed in Table 1 in the manuscript. Reaction conditions: ma = 0.0414g, mb = 0.0954g, mc = 0.0802g, md = 0.034g, me = 0.05g, mf = 0.055g, 2ml of solvent. Dvs = 1,3-divinyl-1,1,3,3-tetramethyldisiloxane; Conversions of reagents were determined by ¹H NMR spectroscopy and GC-MS. The selectivity was determined by ¹H, ¹³C and ²⁹Si NMR spectroscopy.
Table S4. Hydrosilylation of 2-phenyl-1-ethynylboronic acid pinacol ester (2d) with silanes 1a-g.

The results in gray are listed in Table 1 in the manuscript. Reaction conditions: ms = 0.0414g, ms = 0.0802g, ms = 0.04g, ms = 0.05g/mL, ms = 0.055g, ms = 0.064g, 2mL of solvent; dive = 1,3-divinyl-1,1,3,3-tetramethyldisiloxane; Conversions of reagents were determined by 1H NMR spectroscopy and GC-MS. The selectivity was determined by 1H, 13C, and 29Si NMR spectroscopy.
Table S5. Hydrosilylation of 3-methoxy-1-propyn-1-ylboronic acid pinacol ester (2e) with silanes 1b-g.

![Diagram](image-url)

\[ \text{SiR}_2 \text{SiH} + \text{Alkyne} \rightarrow \text{SiR}_2 \text{SiH} + \text{H} \rightarrow \text{SiR}_2 \text{SiH} + \text{other products} \]

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</tbody>
</table>

The results in gray are listed in Table 1 in the manuscript. Reaction conditions: \( m_1b = 0.0934 \text{g}, m_1c = 0.0802 \text{g}, m_1f = 0.055 \text{g}, m_1g = 0.064 \text{g}, 2 \text{ml of solvent}; m_1f/V_{DCM} = 0.029 \text{g/ml}; m_1f/V_{DCM} = 0.022 \text{g/ml}; \) side-products were observed on \( ^{29} \text{Si NMR}. \) Dvs - 1,3-divinyl-1,1,3,3-tetramethyldisiloxane; Conversions of reagents were complete in each experiment and determined by \( ^{1} \text{H} \text{NMR spectroscopy} \) and for processes with 1b-f confirmed by GC-MS. The selectivity was determined by \( ^{1} \text{H}, ^{13} \text{C} \) and \( ^{29} \text{Si} \text{NMR spectroscopy}. \)
2. Literature screening

Table S6. Synthesis methods of borylsilylalkenes 3aa, 3ba, 4ba and 5ba, described in the literature.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>Synthesis method</th>
<th>Catalyst</th>
<th>Reaction yield of product (Isolated yield) [%]</th>
<th>Reaction conditions</th>
<th>Characterization method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image" alt="3aa" /></td>
<td>Hydroboration of (triethylsilyl)acetylene with pinacolborane(^1)</td>
<td>Ru(CO)Cl(H)(PPh(_3))(_3) (1mol%)</td>
<td>94 (78)</td>
<td>60°C, 24h, solvent: PEG 10, Argon atmosphere, 20% excess of pinacolborane.</td>
<td>(^1)H and (^13)C NMR, MS</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="3aa" /></td>
<td>Hydroboration (triethylsilyl)acetylene with pinacolborane(^2)</td>
<td>Ru(CO)Cl(H)(PPh(_3))(_3) (1mol%)</td>
<td>69-91 (82) for IL ([EMPyrr][OTf]) 70-91 (-) for IL ([EMPyrr] [NTf(_2)]) 10 catalytic cycles</td>
<td>100°C, 15 min., solvent: IL/scCO(_2), Argon atmosphere, 20% excess of pinacolborane.</td>
<td>(^1)H NMR, MS</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="3aa" /></td>
<td>Hydroboration (triethylsilyl)acetylene with pinacolborane (^3)</td>
<td>Ru(CO)Cl(H)(PPh(_3))(_3) (1mol%)</td>
<td>97 (99)</td>
<td>100°C, 3h, solvent: scCO(_2), Argon atmosphere, 20% excess of pinacolborane.</td>
<td>(^1)H, (^13)C, (^29)Si and (^11)B NMR, MS, Elemental. Anal.</td>
</tr>
<tr>
<td>4</td>
<td><img src="image" alt="3aa" /></td>
<td>Hydroboration (triethylsilyl)acetylene with pinacolborane (^3)</td>
<td>Ru(CO)Cl(H)(PPh(_3))(_3) (1mol%)</td>
<td>95 (-)</td>
<td>100°C, 3h, without solvent, Argon atmosphere, 20% excess of pinacolborane</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td><img src="image" alt="3aa" /></td>
<td>Hydroboration (triethylsilyl)acetylene with pinacolborane (^3)</td>
<td>Ru(CO)Cl(H)(PPh(_3))(_3) (1mol%)</td>
<td>60 (-)</td>
<td>100°C, 3h, solvent: toluene, Argon atmosphere, 20% excess of pinacolborane</td>
<td></td>
</tr>
<tr>
<td>Entry</td>
<td>Structure</td>
<td>Reaction</td>
<td>Catalyst</td>
<td>Temperature</td>
<td>Time</td>
<td>Solvent</td>
</tr>
<tr>
<td>-------</td>
<td>-----------</td>
<td>----------</td>
<td>----------</td>
<td>-------------</td>
<td>------</td>
<td>---------</td>
</tr>
<tr>
<td>6</td>
<td><img src="image" alt="Structure 4aa" /></td>
<td>Hydroboration of (triethylsilyl)acetylene with pinacolborane&lt;sup&gt;3&lt;/sup&gt;</td>
<td>Ru(CO)Cl(H)(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt; (1mol%)</td>
<td>100°C</td>
<td>3h</td>
<td>toluene. <strong>Obtained as a side product.</strong></td>
</tr>
<tr>
<td>7</td>
<td><img src="image" alt="Structure 4ba" /></td>
<td>Hydroboration of (triethylsilyl)acetylene with pinacolborane&lt;sup&gt;1&lt;/sup&gt;</td>
<td>Ru(CO)Cl(H)(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt; (1mol%)</td>
<td>60°C</td>
<td>24h</td>
<td>PEG 10. <strong>Obtained as a side product.</strong></td>
</tr>
<tr>
<td>8</td>
<td><img src="image" alt="Structure 3ba" /></td>
<td>Hydroboration of (triethylsilyl)acetylene with pinacolborane&lt;sup&gt;2&lt;/sup&gt;</td>
<td>Ru(CO)Cl(H)(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt; (1mol%)</td>
<td>100°C</td>
<td>15min – 1.5h</td>
<td>solvent: [EMPyr][OTf] or [EMPyr][NTf&lt;sub&gt;2&lt;/sub&gt;]. <strong>Obtained as a side product.</strong></td>
</tr>
<tr>
<td>9</td>
<td><img src="image" alt="Structure 3ba" /></td>
<td>Hydroboration of (triphenylsilyl)acetylene with pinacolborane&lt;sup&gt;3&lt;/sup&gt;</td>
<td>Ru(CO)Cl(H)(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt; (1mol%)</td>
<td>100°C</td>
<td>3h</td>
<td>toluene. <strong>Obtained as a side product.</strong></td>
</tr>
<tr>
<td>10</td>
<td><img src="image" alt="Structure 4ba" /></td>
<td>Hydroboration of (triphenylsilyl)acetylene with pinacolborane&lt;sup&gt;3&lt;/sup&gt;</td>
<td>Ru(CO)Cl(H)(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt; (1mol%)</td>
<td>100°C</td>
<td>3h</td>
<td>scCO&lt;sub&gt;2&lt;/sub&gt;; 20% excess of pinacolborane</td>
</tr>
<tr>
<td>11</td>
<td><img src="image" alt="Structure 4ba" /></td>
<td>Hydroboration of (triphenylsilyl)acetylene with pinacolborane&lt;sup&gt;3&lt;/sup&gt;</td>
<td>Ru(CO)Cl(H)(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt; (1mol%)</td>
<td>100°C</td>
<td>3h, without solvent</td>
<td>20% excess of pinacolborane</td>
</tr>
<tr>
<td>12</td>
<td><img src="image" alt="Structure 4ba" /></td>
<td>Hydroboration of (triphenylsilyl)acetylene with pinacolborane&lt;sup&gt;3&lt;/sup&gt;</td>
<td>Ru(CO)Cl(H)(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt; (1mol%)</td>
<td>100°C</td>
<td>3h, solvent: toluene; 20% excess of pinacolborane</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td><img src="image" alt="Structure 4ba" /></td>
<td>Gem-silylborylation of 1-bromo-1-lithioethene with (triphenylsilyl)(pinacolato)borane&lt;sup&gt;4&lt;/sup&gt;</td>
<td>-</td>
<td>-110°C</td>
<td>10 min.</td>
<td>solvent: THF, Et&lt;sub&gt;2&lt;/sub&gt;O.</td>
</tr>
<tr>
<td>14</td>
<td><img src="image" alt="Structure 4ba" /></td>
<td>Hydroboration of (triphenylsilyl)acetylene with pinacolborane&lt;sup&gt;3&lt;/sup&gt;</td>
<td>Ru(CO)Cl(H)(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt; (1mol%)</td>
<td>100°C</td>
<td>3h</td>
<td>toluene. <strong>Obtained as a side product.</strong></td>
</tr>
</tbody>
</table>
Advantages of this work:
➢ One-step catalytic process,
➢ 100% atom economy,
➢ Simple, straightforward, repeatable, scalable preparation approach,
➢ Reagents and catalysts commercially available,
➢ One method but wide spectrum of synthons with various number and type of SiR3 and boryl groups at different positions (different stereoisomers),
➢ Multifunctional building blocks for the synthesis of hybrid compounds,
➢ High yields and selectivities,
➢ Detailed characterization of obtained products.
Scheme S1. Methods for the synthesis of borylsilylalkenes described in our work.

11. Hydrosilylation\textsuperscript{33,35}

\[
\text{HSiR}^1_3 + \text{R}^2 \xrightarrow{\text{cat.}} \text{BR}^3_2
\]

for \( \text{R}^2 = \text{nBu} \)

for \( \text{BR}^3_2 = \text{MIDA} \) \( \text{R}^2 = \text{CH}_3 \)

cat. \text{P(Cl)}_2/\text{XPhos} 

6 compounds
3. General information

3.1 Materials

2-Ethynyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (90%, Sigma-Aldrich), 1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyne (97%, Sigma-Aldrich), 2-((tert-Butyldimethylsilanyl)ethynyl)-4,4,5,5-tetramethyl-(1,3,2)dioxaborolane (97%, Sigma-Aldrich), 2-Phenyl-1-ethynylboronic acid pinacol ester (90%, Sigma-Aldrich), 3-methoxy-1-propyn-1-ylboronic acid pinacol ester (96%, Sigma-Aldrich), (3,3-Dimethyl-1-butylnyl)boronic acid diisopropyl ester (97%, Sigma-Aldrich), Triethylsilane (97%, Sigma-Aldrich), Triphenylsilane (97%, Sigma-Aldrich), 1,1,1,3,5,5,5-Heptamethyltrisiloxane (97%, Sigma-Aldrich), Dimethylmethoxyxilane (94%, Acros Organics), Dimethylphenylsilane (>98%, Sigma-Aldrich), Benzyltrimethylsilane (98%, Fluorochem), Tris(trimethylsiloxy)silane (≥98%, Sigma-Aldrich), Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Karstedt’s catalyst, solution in xylene, Pt 2%, Sigma-Aldrich), platinum (IV) oxide (surface area ≥ 75 m²/g, Sigma-Aldrich), XPhos (97%, Sigma-Aldrich), Tetrakis(triphenylphosphine)platinum(0) (97%, Sigma-Aldrich), TRIS(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate (98%, Acros Organics), Grubbs catalyst (97%, Sigma-Aldrich), The ruthenium catalyst [Ru(CO)Cl(H)(PCy₃)₂] was prepared according to literature procedures. Tris(triphenylphosphine)rhodium(I) chloride (99.9%, Sigma-Aldrich), chloroform-d (99.96 atom% D, Sigma-Aldrich), benzene-d₆ (99.6 atom% D, Sigma-Aldrich), dichloromethane (anhydrous, ≥99.8%, contains 40-150 ppm amylene as stabilizer, Sigma-Aldrich), 1,4-dioxane (anhydrous, 99.8%, Sigma-Aldrich), acetone (suitable for HPLC, ≥99.9%, Sigma-Aldrich), n-pentane (Lach-Ner). Toluene and tetrahydrofuran were dried using standard procedures, deoxygenated and stored over molecular sieves 4 Å under argon atmosphere (toluene). Argon (99.999%) was purchased from Linde. Silica gel (MN-Kieselgel 60, 0.04-0.063 mm (230-400 mesh ASTM; Sigma-Aldrich)) was used as received.

3.2 NMR analyses

¹H, ¹³C, ²⁹Si and ¹¹B NMR spectra were recorded at 25°C on a Bruker Ultra Shield 300 MHz and Bruker Ascend 400 MHz NANOBAY spectrometers. CDCl₃ or CD₂Cl₂ were used as solvents and for internal deuterium lock. Chemical shifts are reported in ppm with reference to the residual portion solvent peak for ¹H and ¹³C NMR, to TMS for ²⁹Si NMR and to BF₃-Et₂O for ¹¹B NMR. The multiplicities were reported as follow: singlet(s), doublet(d), triplet(t) and multiplet(m). To prove the regioselectivity of the process 2D Heteronuclear single quantum correlation (HSQC) and selective gradient NOE experiments for selected products were performed.

3.3 GC-MS analysis

GC-MS analyses were performed on a Bruker 450-GC with a 30 m Varian DB-5 0.25 mm capillary column and a Scion SQ-MS mass spectrometry detector. Two temperature programs were used a) 80°C (3 min), 10°C/min, 250°C (30 min), b) 150°C (3 min), 10°C/min, 280°C (44.5 min).

3.4 Elemental analyses

Elemental analyses were carried out on a Vario EL III analyzer. The content of hydrogen and carbon was obtained as data in percentage.

3.5 Melting points

Melting points were determined using Buchi Switzerland Melting Point M-565 instrument.

3.6 Electrospray ionization mass spectrometry (ESI MS)

High resolution mass spectra (HRMS) were obtained using Impact HD mass spectrometer (Q-TOF type instrument equipped with electrospray ion source; Bruker Daltonics, Germany). The sample solutions (DCM:MeOH) were infused into the ESI source by a syringe pump (direct inlet) at the flow rate of 3 µL/min. The instrument was operated under the following optimized settings: end plate voltage 500 V;
capillary voltage 4.2 kV; nebulizer pressure 0.3 bar; dry gas (nitrogen) temperature 200°C; dry gas flow rate 4 L/min. The spectrometer was previously calibrated with the standard tune mixture.

3.7 FT-IR analysis
FT-IR spectra were measured on a Nicolet iS50 FT-IR spectrometer (Thermo Scientific) equipped with a built-in ATR accessory with ATR diamond unit. In all experiments, 16 scans at a resolution of 2 cm\(^{-1}\) were used to record the spectra.

3.8 X-ray crystallography
A colourless single crystals of 3ba, 4ba, 3bb, 3fb, 6dc suitable for X-ray structural analysis were obtained by slow evaporation of dichloromethane (3ba), hexane (4ba), hexane (3bb), hexane (3fb), and chloroform (6dc). The diffraction data were collected at 130 K with an Oxford Diffraction SuperNova diffractometer using Cu K\(\alpha\) radiation (\(\lambda = 1.54184\) Å) equipped with mirror monochromator. The intensity data were collected and processed using CrysAlis PRO software. The structures were solved by direct methods with the program SHELXT 2018/2 and refined by full-matrix least-squares method on F\(^2\) with SHELXL 2018/3. The carbon-bound hydrogen atoms were refined as riding on their carriers and their displacement parameters were set equal to 1.5Ueq(C) for the methyl groups and 1.2Ueq(C) for the remaining H atoms. Absolute structures of the compounds were confirmed using Flack parameter. A summary of the crystallographic data is given in Table S7 and selected geometrical data are juxtaposed in Table S8.

3.9 Products purification
Purification of 3aa, 4aa, 3ba, 4ba, 3ca, 3fa, 4ac, 4bc, 4cc, 4dc, 4fc, 4ad, 4bd, 3cd, 4ed, 4fd, 3gd, 4be, 3ce, 4fe, 3fe, 3ge.

The UV-absorbing products were purified on silica by flash chromatography (Biotage IsoleraOne chromatograph) with UV detector (\(\lambda_1 = 255\) nm, \(\lambda_2 = 280\) nm). Purification details: cartridge 10 g, flow rate: 8 mL/min, length: 10 CV (CV = column volume), phase: hexane/ethyl acetate (step 1: hexane 100%
by 4 CV, step 2: gradient 10%/CV by 4 CV, step 3: hexane 50% by 2 CV). The non-aromatic products were purified on silica using standard column chromatography using n-hexane/ethyl acetate (97/3–8/2) as eluents. Products were characterized by GC-MS or ESI MS, $^1$H, $^{13}$C, $^{11}$B, $^{29}$Si NMR, FT-IR analyses. For new compounds in solid state, melting points were estimated as well.

**Purification of 3ab, 3bb, 3cb, 3fb, 4ea.**

The reaction mixture was evaporated to remove all volatiles. Subsequently, the crude product was dissolved in n-pentane and filtered through the syringe filter (0.2 µm). After evaporation of n-pentane, the product was heated (approx. 70-130 °C) and condensed at cold-finger trap under vacuum (<10⁻³ mbar). The products were dried for 6 hours under vacuum. Isolated products were characterized by $^1$H, $^{13}$C, $^{29}$Si NMR, GC-MS or ESI MS.

4. General procedures

4.1 Hydroborylation of alkyne 2a–e with silanes 1a–g in the presence of Karstedt’s catalyst and Pt(PPh₃)$_₄$.

To a solution of silane 1a–g (40 – 93.4 mg, 0.298 - 0.358 mmol) and an appropriate borylalkyne (2a–e) (0.298 - 0.358 mmol) in 2 ml of toluene, Karstedt’s catalyst or Pt(PPh₃)$_₄$ was added, depending on the experiment in the amount of 4x10⁻⁴–10⁻² mmol of Pt. Subsequently, the reaction mixture was heated to 60 - 120°C or kept at room temperature and stirred for 24 or 48h. Since the THF boiling point is 65-57°C, the reaction in this solvent at 120°C was performed in a Schlenk flask with a Rotafl® stopcock. Afterwards, crude reaction mixture was analyzed by GC-MS and $^1$H NMR analyzes and purified according to the procedure in 3.7 subsection.

4.2 Hydroborylation of alkene 2a with silanes 1a–f in the presence of PtO₂/XPhos system.

All reactions were carried out under an argon atmosphere. To a Schlenk flask with a Rotafl® stopcock equipped with a magnetic stirrer PtO₂ (1mol%) and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (2 mol%) (XPhos) were added. The catalyst and XPhos were dried under vacuum for 1 hour. Then the flask was flushed quickly with argon and 1ml of anhydrous and degassed THF was added. The mixture was stirred at 60°C for 30 minutes until the homogeneous system was obtained. After this time 2-ethyl-4,5,5-tetramethyl-1,3,2-dioxaborolane 2a (0.356 - 0.358 mmol), an appropriate silane (41.4 – 93.4 mg, 0.356 - 0.358 mmol) and 1mL of THF were added. Reactions were carried out at 60°C or 100°C and stirred for 24 or 48h, depending on the experiment. Afterwards, crude reaction mixture was analyzed by GC-MS and $^1$H NMR analyzes and purified according to the procedure in 3.7 subsection.

4.3 Hydroborylation of alkenes 2a, 2b, 2c, 2d and 2e with silane 1a–g in the presence of [CpRu(CH₃CN)₃][PF₆].

All reactions were carried out under an argon atmosphere. To a Schlenk flask with a Rotafl® stopcock equipped with a magnetic stirrer [CpRu(CH₃CN)₃][PF₆] and 2mL of toluene/THF/DCM/1,4-dioxane, CH₃CN or acetone were added. Than a silane 1a–g (40 – 93.4 mg, 0.298 - 0.358 mmol) and an appropriate borylalkyne (2a–e) (0.298 - 0.358 mmol) were added. Subsequently, the reaction mixture was heated to 60 - 120°C or kept at room temperature and stirred for 24 or 48h. Since the THF boiling point is 65-57°C, the reaction in this solvent at 120°C was performed in a Schlenk flask with a Rotafl® stopcock. Afterwards, crude reaction mixture was analyzed by GC-MS and $^1$H NMR analyzes and purified according to the procedure in 3.7 subsection.
5. Products characterization

\((E)\)-Triethyl(2-(4,4,5,5-tetramethyl-1,2-dioxaborolan-2-yl)vinyl)silane (3aa)

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

\(^1\)H NMR (CDCl\(_3\), 300 MHz, \(\delta\), ppm): 0.58 (q, 6H, \(J_{CH} = 7.45\) Hz), 0.93 (t, 9H, \(J_{CH} = 7.88\) Hz), 1.28 (s, 12H), 6.26 (d, 1H, \(J_{CH} = 22.04\) Hz), 7.06 (d, 1H, \(J_{CH} = 21.98\) Hz). \(^13\)C NMR (CDCl\(_3\), 75 MHz, \(\delta\), ppm): 3.13, 7.45, 24.96, 83.47, 154.83. Signal from carbon atom BC= is not observed. \(^29\)Si NMR (CDCl\(_3\), 79 MHz, \(\delta\), ppm): -0.62. GC-MS (EI, 70 eV) m/z (rel. int., %): 253.1 (M\(^+\) - 15.18, 0.7), 239.0 (10.6), 156.9 (22.9), 154.9 (7.6), 85.0 (9.1), 84.1 (9.1), 83.0 (100.0), 58.9 (9.1), 55.0 (24.2). FT-IR (cm\(^{-1}\)): 2954, 2911, 2875, 1599, 1493, 1451, 1371, 1354, 1295, 1245, 1206, 1142, 1071, 1057, 856, 831, 792, 760, 698.

Elem. Anal. calcd for C\(_{14}\)H\(_{29}\)BO\(_2\)Si: C, 62.68; H, 10.90; found C, 62.78; H, 10.95. Isolated yield = 93%, colorless oil.

Triethyl(1-(4,4,5,5-tetramethyl-1,2-dioxaborolan-2-yl)vinyl)silane (4aa)

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

\(^1\)H NMR (CDCl\(_3\), 300 MHz, \(\delta\), ppm): 0.63 (q, 6H, \(J_{CH} = 7.88\) Hz), 0.91 (t, 9H, \(J_{CH} = 7.82\) Hz), 1.24 (s, 12H), 6.22 (d, 1H, \(J_{CH} = 5.34\) Hz), 6.67 (d, 1H, \(J_{CH} = 5.63\) Hz). \(^13\)C NMR (CDCl\(_3\), 75 MHz, \(\delta\), ppm): 3.26, 7.55, 24.89, 83.04, 144.91. Signal from carbon atom BC= is not observed. \(^29\)Si NMR (CDCl\(_3\), 79 MHz, \(\delta\), ppm): 2.74. \(^11\)B NMR (CDCl\(_3\), 96 MHz, \(\delta\), ppm): 30.92. GC-MS (EI, 70 eV) m/z (rel. int., %): 253.1 (M\(^+\) - 15.18, 0.7), 239.0 (10.6), 156.9 (22.9), 154.9 (7.6), 85.0 (9.1), 84.1 (9.1), 83.0 (100.0), 58.9 (9.1), 55.0 (24.2). Elem. Anal. calcd for C\(_{14}\)H\(_{29}\)BO\(_2\)Si: C, 62.68; H, 10.90; found C, 62.83; H, 10.97. Isolated yield = 57%, colorless oil.

\((E)\)-Triphenyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (3ba)

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

\(^1\)H NMR (CDCl\(_3\), 300 MHz, \(\delta\), ppm): 1.29 (s, 12H), 6.39 (d, 1H, \(J_{CH} = 21.64\) Hz), 7.59 (d, 1H, \(J_{CH} = 21.62\) Hz), 7.33-7.54 (m, 16H). \(^13\)C NMR (CDCl\(_3\), 75 MHz, \(\delta\), ppm): 24.98, 83.67, 127.99, 129.70, 133.87, 136.21, 150.68. Signal from carbon atom BC= is not observed. \(^29\)Si NMR (CDCl\(_3\), 79 MHz, \(\delta\), ppm): -17.53. \(^11\)B NMR (CDCl\(_3\), 96 MHz, \(\delta\), ppm): 29.46. GC-MS (EI, 70 eV) m/z (rel. int., %): 397.1 (M\(^+\) - 15.3, 0.9), 355.0 (19.5), 259.0 (13.4), 225.0 (10.3), 206.9 (10.9), 180.9 (17.3), 104.8 (11.7), 83.9 (100.0), 68.9 (30.6). FT-IR (cm\(^{-1}\)): 3067, 1588, 1484, 1427, 1368, 1324, 1266, 1141, 1111, 1018, 997, 968, 892, 847, 763, 689, 615, 511, 480, 454.
Elem. Anal. calcd for C_{26}H_{29}BO_{2}Si: C, 75.72; H, 7.09; found C, 76.04; H, 7.23. mp = 138.5 °C. Isolated yield = 81%, white solid.

X-ray determined for the first time, data presented on page 86.

**Triphenyl(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (4ba)**

![Chemical Structure](image)

$^1$H NMR (CDCl₃, 300 MHz, δ, ppm): 1.14 (s, 12H), 6.29 (d, 1H, $J_{	ext{H,H}}$= 5.38 Hz), 6.96 (d, 1H, $J_{	ext{H,H}}$= 5.39 Hz), 7.33-7.60 (m, 15H). $^{13}$C NMR (CDCl₃, 75 MHz, δ, ppm): 24.72, 83.48, 127.66, 129.30, 134.89, 149.99. Signal from carbon atom BC= is not observed. $^{29}$Si NMR (CDCl₃, 96 MHz, δ, ppm): 31.62. FT-IR (cm⁻¹): 3067, 3047, 2979, 1588, 1571, 1482, 1380, 1371, 1360, 1323, 1301, 1217, 1149, 1129, 1108, 992, 970, 850, 735, 698, 625, 547, 516, 490, 468, 433. Element Anal. calcd for C_{26}H_{29}BO_{2}Si: C, 75.72; H, 7.09; found C, 75.98; H, 7.16. mp = 145.0 °C. Isolated yield = 72%, white solid.

X-ray determined for the first time, data presented on page 86.

**(E)-1,1,1,3,5,5,5-Heptamethyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)trisiloxane (3ca/4ca = 94/6)**

![Chemical Structure](image)

$^1$H NMR (CDCl₃, 300 MHz, δ, ppm): 0.08 (s, 21H), 1.27 (s, 12H), 6.28 (d, 1H, $J_{	ext{H,H}}$= 21.76 Hz), 6.36 (d, 1H, $J_{	ext{H,H}}$= 5.92 Hz, 4ca), 6.61 (d, 1H, $J_{	ext{H,H}}$= 6.13 Hz, 4ca), 6.89 (d, 1H, $J_{	ext{H,H}}$= 21.87 Hz). $^{13}$C NMR (CDCl₃, 75 MHz, δ, ppm): 1.99, 24.72, 24.92, 24.97, 83.51, 154.11. Signal from carbon atom BC= is not observed. $^{29}$Si NMR (CDCl₃, 79 MHz, δ, ppm): -36.02, 8.29. $^{11}$B NMR (CDCl₃, 96 MHz, δ, ppm): 29.54. Traces of product 4ca are visible on spectras. ESI MS (m/z) ([M+Na]⁺): 397.2. FT-IR (cm⁻¹): 2979, 2958, 1598, 1371, 1328, 1282, 1252, 1146, 1040, 970, 836, 800, 780, 753, 615. Element Anal. calcd for C_{15}H_{35}BO_{3}Si: C, 48.11; H, 9.42; found C, 48.15; H, 9.43. Isolated yield = 91%, colorless oil.

**(E)-Benzyldimethyl(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (3fa/4fa = 95/5)**

![Chemical Structure](image)
\(^1\)H NMR (CDCl\(_3\), 300 MHz, \(\delta, \text{ppm}\)): 0.05 (s, 6H), 1.29 (s, 12H), 2.16 (s, 2H), 6.28 (d, 1H, \(J_{HH} = 21.87\) Hz), 6.99-7.22 (m, 6H, multiplet and doublet overlapped). \(^13\)C NMR (CDCl\(_3\), 75 MHz, \(\delta, \text{ppm}\)): -3.82, 24.92, 25.43, 83.53, 124.15, 128.26, 128.36, 139.83, 155.88. Signal from carbon atoms BC= is not observed. \(^29\)Si NMR (CDCl\(_3\), 79 MHz, \(\delta, \text{ppm}\)): -6.28. Traces of product 4fa are visible on spectras. GC-MS (EI, 70 eV) m/z (rel. int., %): 302.3 (M\(^+\) - 15.4, 4.1), 210.9 (68.6), 209.9 (17.7), 126.8 (18.3), 110.8 (17.4), 84.9 (29.4), 82.9 (100.0), 58.9 (18.6), 55.0 (15.6). \textbf{Elem. Anal.} calcd for C\(_{17}\)H\(_{27}\)BO\(_2\)Si: C, 67.55; H, 9.00; found C, 67.72; H, 9.02. Isolated yield = 86%, colorless oil.

\((E)-(1,2\text{-Bis}(4,4,5,5\text{-tetramethyl-1,3,2-dioxaborolan-2-yl})\text{vinyl})\text{triethylsilane (3ab)}\)

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

\(^1\)H NMR (CDCl\(_3\), 300 MHz, \(\delta, \text{ppm}\)): 0.62 (q, 6H, \(J_{HH} = 7.79\) Hz), 0.92 (t, 9H, \(J_{HH} = 7.88\) Hz), 1.26 (s, 12H), 1.32 (s, 12H), 6.57 (s, 1H). \(^13\)C NMR (CDCl\(_3\), 75 MHz, \(\delta, \text{ppm}\)): -3.32, 7.52, 24.67, 25.03, 25.36, 83.52, 83.63. Signals from carbon atoms BC= are not observed. \(^29\)Si NMR (CDCl\(_3\), 79 MHz, \(\delta, \text{ppm}\)): -14.97. \textbf{FT-IR} (cm\(^{-1}\)): 2977, 2953, 2911, 2975, 1578, 1445, 1369, 1292, 1269, 1232, 1139, 1110, 1006, 968, 856, 789, 734, 671, 578. GC-MS (EI, 70 eV) m/z (rel. int., %): 368.3 (M\(^+\) - 25.94, 0.3), 365.1 (32.8), 364.0 (14.0), 253.1 (19.3), 182.9 (10.2), 55.0 (22.7), 101.0 (12.0), 84.1 (20.6), 83.0 (100.0), 69.0 (14.4). \textbf{Elem. Anal.} calcd for C\(_{20}\)H\(_{40}\)B\(_2\)O\(_4\)Si: C, 60.93; H, 10.23; found C, 61.17; H, 10.27. Isolated yield = 90%, pale yellow oil. The traces of alkyne 2b are visible on spectras.

\((E)-(1,2\text{-Bis}(4,4,5,5\text{-tetramethyl-1,3,2-dioxaborolan-2-yl})\text{vinyl})\text{triphenylsilane (3bb)}\)

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

\(^1\)H NMR (CDCl\(_3\), 300 MHz, \(\delta, \text{ppm}\)): 0.96 (s, 12H), 1.19 (s, 12H), 6.65 (s, 1H), 7.21 - 7.53 (m, 15H). \(^13\)C NMR (CDCl\(_3\), 75 MHz, \(\delta, \text{ppm}\)): 25.01, 25.04, 83.69, 83.82, 127.67, 129.35, 134.43, 136.80. Signals from carbon atoms BC= are not observed. \(^29\)Si NMR (CDCl\(_3\), 79 MHz, \(\delta, \text{ppm}\)): -14.97. \(^11\)B NMR (CDCl\(_3\), 96 MHz, \(\delta, \text{ppm}\)): 22.34, 29.11. \textbf{FT-IR} (cm\(^{-1}\)): 3067, 3049, 2978, 2930, 1568, 1428, 1370, 1305, 1268, 1232, 1188, 1137, 1108, 1028, 969, 909, 846, 831, 786, 732, 698, 673, 646, 572, 498. \textbf{ESI MS} (m/z) ([M+Na]): 561.3. \textbf{Elem. Anal.} calcd for C\(_{32}\)H\(_{40}\)B\(_2\)O\(_4\)Si: C, 71.39; H, 7.49; found C, 71.50; H, 7.50. \textbf{mp} = 132.9 °C. Isolated yield = 98%, white solid.

X-ray determined for the first time, data presented on page 87.
(E)-3-(1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (3cb/4cb = 96/4)

\[
\begin{align*}
\text{Me}_3\text{Si} & \quad \text{O} & \quad \text{B} & \quad \text{O} \\
& / & & \\
& & & / \\
& & & \text{SiMe}_3
\end{align*}
\]

\( ^{1} \text{H NMR} \) (CDCl\textsubscript{3}, 300 MHz, \( \delta \), ppm): 0.09 (s, 21H), 1.26 (s, 12H), 1.30 (s, 12H), 6.67 (s, 1H). \( ^{13} \text{C NMR} \) (CDCl\textsubscript{3}, 75 MHz, \( \delta \), ppm): 0.14, 2.08, 25.01, 25.20, 83.44, 83.64. Signals from carbon atoms BC= are not observed. \( ^{29} \text{Si NMR} \) (CDCl\textsubscript{3}, 79 MHz, \( \delta \), ppm): -35.11, 7.83. \( ^{11} \text{B NMR} \) (CDCl\textsubscript{3}, 96 MHz, \( \delta \), ppm): 28.69.

Traces of product 4cb are visible on spectras. \textbf{FT-IR} (cm\textsuperscript{-1}): 2978, 2958, 1585, 1370, 1331, 1302, 1250, 1232, 1140, 1039, 836, 801, 785, 753, 688, 578, 542. \textbf{ESI MS} (m/z) ([M+Na]): 523.3. \textbf{Elem. Anal.} calcd for C\textsubscript{21}H\textsubscript{46}B\textsubscript{2}O\textsubscript{6}Si\textsubscript{3}: C, 50.40; H, 9.26; found C, 50.51; H, 9.27. Isolated yield = 90%, colorless oil. MALDI TOF MS analysis from this sample was unsuccessful.

\( (E)-\text{Benzyl}(1,2\text{-bis}(4,4,5,5\text{-tetramethyl-1,3,2-dioxaborolan-2-yl})\text{vinyl})\text{dimethylsilane (3fb)} \)

\[
\begin{align*}
\text{BnMe}_2\text{Si} & \quad \text{B} & \quad \text{O} & \quad \text{O} & \quad \text{O} \\
& / & & & \\
& & & & / \\
& & & & \text{H}
\end{align*}
\]

\( ^{1} \text{H NMR} \) (CDCl\textsubscript{3}, 300 MHz, \( \delta \), ppm): 0.03 (s, 6H), 1.28 (s, 12H), 1.35 (s, 12H), 2.20 (s, 2H), 6.62 (s, 1H), 6.99 – 7.21 (m, 5H). \( ^{13} \text{C NMR} \) (CDCl\textsubscript{3}, 75 MHz, \( \delta \), ppm): -3.65, 25.04, 25.37, 25.56, 83.78, 83.79, 124.02, 128.21, 128.48, 140.26. Signals from carbon atoms BC= are not observed. \( ^{29} \text{Si NMR} \) (CDCl\textsubscript{3}, 79 MHz, \( \delta \), ppm): -2.64. \( ^{11} \text{B NMR} \) (CDCl\textsubscript{3}, 96 MHz, \( \delta \), ppm): 28.31. \textbf{GC-MS} (EI, 70 eV) m/z (rel. int., %): 370.4 (M\textsuperscript{+} - 57.86, 1.2), 337.4 (8.9), 237.3 (8.1), 83.2 (100.0), 55.1 (23.9). \textbf{FT-IR} (cm\textsuperscript{-1}): 2978, 1597, 1492, 1449, 1368, 1334, 1270, 1233, 1202, 1136, 1054, 970, 848, 814, 763, 700, 671, 579, 482. \textbf{Elem. Anal.} calcd for C\textsubscript{23}H\textsubscript{38}B\textsubscript{2}O\textsubscript{4}Si: C, 64.51; H, 8.94; found C, 64.68; H, 8.97. \textbf{mp} = 95.1 \textdegreeC. Isolated yield = 91%, white solid.

X-ray determined for the first time, data presented on page 87.

\( (E)-\text{Tert-butyl} \text{dimethyl}(2\text{-}(4,4,5,5\text{-tetramethyl-1,3,2-dioxaborolan-2-yl})\text{2\text{-}(triethylsilyl)}\text{vinyl})\text{silane (4ac)} \)

\[
\begin{align*}
\text{Et}_3\text{Si} & \quad \text{B} & \quad \text{O} & \quad \text{Si} & \quad \text{H} \\
& / & & & \\
& & & & / \\
& & & & \text{H}
\end{align*}
\]

\( ^{1} \text{H NMR} \) (CDCl\textsubscript{3}, 300 MHz, \( \delta \), ppm): 0.10 (s, 6H), 0.62 (q, 6H, \( J_{HH} \text{=7.34 Hz} \)), 0.89 – 0.94 (m, 18H), 1.28 (s, 12H), 7.07 (s, 1H). \( ^{13} \text{C NMR} \) (CDCl\textsubscript{3}, 75 MHz, \( \delta \), ppm): -4.84, 3.53, 7.63, 16.94, 25.64, 26.69, 83.24, 160.01.
Signal from carbon atoms BC= is not observed. $^{31}$Si NMR (CDCl$_3$, 79 MHz, $\delta$, ppm): -2.40, 3.58. $^{11}$B NMR (CDCl$_3$, 96 MHz, $\delta$, ppm): 31.39. GC-MS (EI, 70 eV) m/z (rel. int., %): 369.3 (M$^+$ - 13.24, 0.2), 326.2 (27.0), 325.1 (100.0), 324.0 (22.7), 243.0 (41.2), 184.9 (45.2), 183.8 (11.0), 86.9 (11.1), 84.1 (10.1), 83.0 (70.9), 72.9 (29.2), 68.9 (10.5), 58.9 (17.2), 55.0 (18.7). FT-IR (cm$^{-1}$): 2978, 2951, 2875, 2856, 1540, 1462, 1415, 1371, 1295, 1245, 1142, 1110, 1005, 972, 855, 836, 823, 808, 792, 736, 717. Elem. Anal. calcd for C$_{20}$H$_{43}$BOSi$_2$: C, 62.80; H, 11.33; found C, 63.04; H, 11.37. Isolated yield = 89%, pale yellow oil.

$$^{1}$H NMR (CDCl$_3$, 300 MHz, $\delta$, ppm): 0.00 (s, 6H), 0.69 (s, 9H), 0.87 (s, 12H), 7.10-7.48 (m, 16H, overlapped singlet and multiplet). $^{13}$C NMR (CDCl$_3$, 75 MHz, $\delta$, ppm): -4.91, 16.94, 25.30, 26.59, 83.47, 127.59, 129.24, 135.30, 136.77, 167.08. Signal from carbon atoms BC= is not observed. $^{31}$Si NMR (CDCl$_3$, 79 MHz, $\delta$, ppm): -14.53, -1.41. GC-MS (EI, 70 eV) m/z (rel. int., %): 511.4 (M$^+$ - 15.27, 0.9), 471.4 (15.9), 470.4 (40.1), 469.3 (100.0), 309.2 (40.9), 291.2 (50.2), 259.2 (26.6), 197.2 (23.2), 135.1 (45.9), 105.1 (32.6), 83.2 (93.1), 84.2 (49.9), 73.2 (64.2), 69.3 (56.4), 68.3 (21.3). FT-IR (cm$^{-1}$): 3049, 2852, 1528, 1467, 1428, 1349, 1300, 1244, 1139, 1107, 972, 853, 823, 738, 504. Elem. Anal. calcd for C$_{32}$H$_{43}$BOSi$_2$: C, 72.98; H, 8.23; found C, 72.78; H, 8.21. mp = 87.2 °C. Isolated yield = 93%, white solid.

$(E)$-3-[(Tert-butyldimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yI)vinyl]-1,1,3,5,5,5-heptamethyltrisiloxane (4cc)

$^{1}$H NMR (CDCl$_3$, 300 MHz, $\delta$, ppm): 0.09, 0.10 (s, 27H), 0.91 (s, 9H), 1.27 (s, 12H), 7.33 (s, 1H). $^{13}$C NMR (CDCl$_3$, 75 Hz, $\delta$, ppm): -4.95, 0.27, 2.09, 16.92, 25.39, 26.65, 83.21, 161.67. Signal from carbon atoms BC= is not observed. $^{31}$Si NMR (CDCl$_3$, 79 MHz, $\delta$, ppm): -35.46, -2.10, 7.40. Elem. Anal. calcd for C$_{21}$H$_{49}$BOSi$_4$: C, 51.61; H, 10.11; found C, 51.72; H, 10.13. Isolated yield = 87%, colorless oil.

$(E)$-Tert-butyl(2-ethoxydimethylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]dimethylsilane (4dc)
1H NMR (CDCl₃, 300 MHz, δ, ppm): 0.10 (s, 6H), 0.20 (s, 6H), 0.89 (s, 9H), 1.17 (t, 3H, J₁₁₀ = 6.98 Hz), 1.29 (s, 12H), 3.64 (q, 2H, J₁₂₀ = 6.99 Hz), 7.23 (s, 1H). ¹³C NMR (CDCl₃, 75 Hz, δ, ppm): -4.97, -1.42, 16.87, 18.58, 25.48, 26.67, 58.60, 83.43, 160.59. Signal from carbon atoms BC= is not observed. ²⁸Si NMR (CDCl₃, 79 MHz, δ, ppm): -1.62, 6.67. GC-MS (EI, 70 eV) m/z (rel. int., %): 313.1 (M⁺, 17.5), 214.1 (19.8), 212.0 (24.5), 185.0 (46.3), 183.9 (12.0), 142.9 (16.5), 84.0 (30.0), 74.9 (29.7), 73.0 (48.6), 69.0 (20.4), 59.0 (16.3), 55.0 (21.0). FT-IR (cm⁻¹): 2978, 2953, 2933, 2922, 2849, 1536, 1470, 1381, 1369, 1352, 11330, 1296, 1244, 1145, 1086, 978, 933, 872, 858, 824, 800, 780, 760, 723, 659. **Elem. Anal.** calcd for C₆₇H₈₅BO₅Si: C, 58.36; H, 10.61; found C, 58.34; H, 10.61. Isolated yield = 91%, colorless oil.

1,3-Bis((E)-2-(tert-butylimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-1,1,3,3-tetramethyldisiloxane (6dc)

1H NMR (CDCl₃, 300 MHz, δ, ppm): 0.99 (s, 12H), 0.16 (s, 12H), 0.90 (s, 18H), 1.27 (s, 24H), 7.25 (s, 2H). ¹³C NMR (CDCl₃, 75 Hz, δ, ppm): -4.86, 1.34, 16.92, 25.47, 26.72, 83.24, 159.63. Signals from carbon atoms BC= are not observed. ²⁸Si NMR (CDCl₃, 79 MHz, δ, ppm): -3.24, -2.14. ¹¹B NMR (CDCl₃, 96 MHz, δ, ppm): 31.86. FT-IR (cm⁻¹): 2983, 2953, 2933, 2922, 2849, 1536, 1381, 1369, 1352, 11330, 1296, 1242, 1145, 1086, 978, 933, 872, 858, 824, 800, 780, 760, 723, 659. **Elem. Anal.** calcd for C₆₇H₈₅BO₅Si: C, 57.64; H, 10.28; found C, 57.62; H, 10.28. Isolated yield = 85%, colorless oil.

X-ray determined for the first time, data presented on page 88.

(E)-**Tert-butyl((2-dimethyl(phenyl)silyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)dimethylsilane (4ec)**

1H NMR (CDCl₃, 300 MHz, δ, ppm): 0.03 (s, 6H), 0.32 (s, 6H), 0.80 (s, 9H), 1.09 (s, 12H), 7.06 (s, 1H), 7.24-7.47 (m, 5H). ¹³C NMR (CDCl₃, 75 Hz, δ, ppm): -4.95, -2.10, 16.94, 25.44, 26.66, 83.36, 127.59, 128.81, 134.52, 139.11, 160.99. Signal from carbon atoms BC= is not observed. ²⁸Si NMR (CDCl₃, 79 MHz, δ, ppm): -7.10, -1.93. ¹¹B NMR (CDCl₃, 96 MHz, δ, ppm): 31.38. GC-MS (EI, 70 eV) m/z (rel. int., %): 345.0 (M⁺, 57.3, 48.7), 185.0 (100.0), 186.0 (17.6), 183.9 (25.9), 142.9 (20.3), 134.9 (47.5), 104.9 (16.3), 82.9 (52.3), 72.9 (35.3), 55.0 (17.5). FT-IR (cm⁻¹): 2978, 2952, 2926, 2882, 2855, 1541, 1470, 1346, 1297, 1242, 1141, 1112, 974, 812, 772, 730, 698. **Elem. Anal.** calcd for C₇₂H₇₃BO₅Si: C, 65.64; H, 9.77; found C, 65.97; H, 9.91. Isolated yield = 89%, colorless oil.
(E)-Benzyl(2-(tert-butyldimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)dimethylsilane (4fc)

\[
\begin{align*}
\text{H NMR} & \quad (\text{CDCl}_3, 300 \text{ MHz}, \delta, \text{ppm}): 0.05 \text{ (s, 6H)}, 0.10 \text{ (s, 6H)}, 0.86 \text{ (s, 9H)}, 1.32 \text{ (s, 12H)}, 2.20 \text{ (s, 2H)}, 6.97-7.17 \text{ (m, 6H, overlapped singlet and multiplet)}. \\
\text{13}C \text{ NMR} & \quad (\text{CDCl}_3, 75 \text{ Hz}, \delta, \text{ppm}): -4.89, -3.25, 16.94, 25.62, 26.18, 26.64, 83.45, 123.83, 128.07, 128.91, 140.59, 160.90. \text{Signal from carbon atoms BC= is not observed.}
\end{align*}
\]

\[
\begin{align*}
\text{29Si NMR} & \quad (\text{CDCl}_3, 79 \text{ MHz}, \delta, \text{ppm}): -2.30, -2.29. \\
\text{11B NMR} & \quad (\text{CDCl}_3, 96 \text{ MHz}, \delta, \text{ppm}): 31.55. \text{GC-MS (EI, 70 eV) m/z (rel. int., %): 359.5} \text{ (M}^+\text{-56.8, 31.9)}, 260.4 (23.7), 259.3 (100.0), 258.3 (23.6), 243.3 (25.4), 149.2 (17.9), 83.2 (82.0), 73.2 (81.0), 69.3 (20.6), 55.2 (31.5). \text{FT-IR (cm}^{-1}): 2951, 2856, 1597, 1469, 1335, 1298, 1239, 1155, 1057, 972, 698, 645, 477. \text{Elem. Anal.} \text{ calcd for C}_{23}H_{41}BO_2Si_2: C, 66.32; H, 9.92; found C, 66.45; H, 9.95. \text{mp} = 62.1 \text{ °C. Isolated yield = 91%, white solid.}
\end{align*}
\]

(E)-Triethyl(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (4ad)

\[
\begin{align*}
\text{H NMR} & \quad (\text{CDCl}_3, 300 \text{ MHz}, \delta, \text{ppm}): 0.77 \text{ (q, 6H, J\text{H,H} = 7.91 Hz)}, 1.04 \text{ (t, 9H, J\text{H,H} = 7.87 Hz)}, 1.32 \text{ (s, 12H)}, 7.25 - 7.47 \text{ (m, 6H, overlapped singlet and multiplet)}. \\
\text{13C NMR} & \quad (\text{CDCl}_3, 75 \text{ MHz}, \delta, \text{ppm}): 3.76, 7.56, 25.26, 83.69, 127.77, 127.95, 128.10, 140.75, 151.30. \text{Signal from carbon atoms BC= is not observed.}
\end{align*}
\]

\[
\begin{align*}
\text{29Si NMR} & \quad (\text{CDCl}_3, 79 \text{ MHz}, \delta, \text{ppm}): -14.24. \\
\text{11B NMR} & \quad (\text{CDCl}_3, 96 \text{ MHz}, \delta, \text{ppm}): 32.53. \text{FT-IR (cm}^{-1}): 2978, 2952, 2910, 2874, 1591, 1568, 1493, 1459, 1371, 1292, 1252, 1210, 1140, 1109, 1005, 976, 940, 856, 797, 747, 695. \text{Elem. Anal.} \text{ calcd for C}_{20}H_{33}BOSi: C, 69.75; H, 9.66; found C, 69.86; H, 9.68. \text{Isolated yield = 76%, colorless oil.}
\end{align*}
\]

(E)-Triphenyl(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (4bd)

\[
\begin{align*}
\text{H NMR} & \quad (\text{CDCl}_3, 300 \text{ MHz}, \delta, \text{ppm}): 0.96 \text{ (s, 12H)}, 7.26-7.70 \text{ (m, 21H, overlapped singlet and multiplet)}. \\
\text{13C NMR} & \quad (\text{CDCl}_3, 75 \text{ MHz}, \delta, \text{ppm}): 24.89, 83.69, 127.76, 128.17, 128.27, 128.35, 129.47, 134.85, 136.82, 140.25, 156.79. \text{Signal from carbon atom SiBC=} \text{is not observed.}
\end{align*}
\]

\[
\begin{align*}
\text{29Si NMR} & \quad (\text{CDCl}_3, 79 \text{ MHz}, \delta, \text{ppm}): -14.24. \text{FT-IR (cm}^{-1}): 3068, 2984, 2926, 1591, 1568, 1481, 1427, 1387, 1371, 1343, 1304, 1251, 1206, 1137, 1107, 978, 947, 854, 800, 740, 697, 592, 574, 493. \text{Elem. Anal.} \text{ calcd for C}_{32}H_{33}BOSi: C, 78.68; H, 6.81; found C, 78.92; H, 6.83. \text{Isolated yield = 85%, white solid.}
\end{align*}
\]
(E)-1,1,3,5,5,5-Heptamethyl-3-(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)trisiloxane (4cd)

\[ \text{\textbf{H NMR}} (\text{CDCl}_3, 300 \text{ MHz,} \delta, \text{ppm}): 0.01 (s, 18H), 0.14 (s, 3H), 1.09 (s, 12H), 6.20 (s, 1H), 7.12-7.23 (m, 5H). \text{\textbf{C NMR}} (\text{CDCl}_3, 75 \text{ MHz,} \delta, \text{ppm}): -0.43, 1.86, 24.73, 83.35, 126.17, 127.52, 127.87, 143.92, 164.19. Signal from carbon atom SiBC= is not observed. \text{\textbf{Si NMR}} (\text{CDCl}_3, 79 \text{ MHz,} \delta, \text{ppm}): -38.13, 8.16. \text{\textbf{GC-MS}} (EI, 70 eV) m/z (rel. int., %): 450.6 (M+, 3.5), 335.0 (12.2), 293.0 (7.7), 223.0 (7.4), 222.1 (12.6), 221.0 (57.2), 206.9 (19.8), 84.0 (100.0), 82.9 (7.9), 73.0 (53.4), 69.0 (10.9). \text{\textbf{FT-IR}} (cm\(^{-1}\)): 2958, 1725, 1588, 1499, 1371, 1346, 1252, 1144, 1046, 838, 783, 754, 698, 540. \text{Elem. Anal.} calcd for C\(_x\)H\(_y\)BOSi: C, 55.98; H, 8.72; found C, 55.78; H, 8.69. Isolated yield = 79\%, colorless oil.

(E)-Dimethyl(phenyl)(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (4ed)

\[ \text{\textbf{H NMR}} (\text{CDCl}_3, 300 \text{ MHz,} \delta, \text{ppm}): 0.38 (s, 6H), 1.05 (s, 12H), 7.12-7.52 (m, 11H, overlapped singlet and multiplet). \text{\textbf{C NMR}} (\text{CDCl}_3, 75 \text{ MHz,} \delta, \text{ppm}): -1.91, 25.06, 83.59, 127.76, 128.05, 128.08, 128.12, 129.08, 134.58, 138.53, 140.34, 152.25. Signal from carbon atom SiBC= is not observed. \text{\textbf{Si NMR}} (\text{CDCl}_3, 79 MHz, \delta, ppm): -6.29. \text{\textbf{FT-IR}} (cm\(^{-1}\)): 3068, 2978, 1624, 1592, 1569, 1494, 1449, 1427, 1378, 1371, 1351, 1246, 1210, 1140, 1111, 998, 974, 944, 856, 820, 790, 771, 748, 695, 643, 577, 469. \text{Elem. Anal.} calcd for C\(_x\)H\(_y\)BOSi: C, 72.52; H, 8.02; found C, 72.65; H, 8.04. Isolated yield = 88\%, colorless oil.

(E)-Benzyl(dimethyl(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (4fd)

\[ \text{\textbf{H NMR}} (\text{CDCl}_3, 300 \text{ MHz,} \delta, \text{ppm}): 0.21 (s, 6H), 1.36 (s, 12H), 2.36 (s, 2H), 7.11-7.47 (m, 11H, overlapped singlet and multiplet). \text{\textbf{C NMR}} (\text{CDCl}_3, 75 MHz, \delta, ppm): -3.07, 25.22, 26.22, 83.63, 124.01, 127.95, 127.97, 128.10, 128.15, 128.54, 140.15, 140.45, 151.51. Signal from carbon atom SiBC= is not observed. \text{\textbf{Si NMR}} (\text{CDCl}_3, 79 MHz, \delta, ppm): -1.74. \text{\textbf{B NMR}} (\text{CDCl}_3, 96 MHz, \delta, ppm): 32.45. \text{\textbf{GC-MS}} (EI, 70 eV) m/z (rel. int., %): 363.1 (M+, 15.3, 1.5), 288.2 (17.3), 287.0 (81.6), 285.9 (18.7), 205.0 (77.7), 203.8 (19.1), 188.9 (45.8), 186.9 (39.1), 158.9 (26.5), 144.9 (36.9), 134.9 (42.8), 120.9 (35.4), 84.1 (18.3), 83.0 (100.0), 68.9 (15.3), 55.0 (51.7). \text{\textbf{FT-IR}} (cm\(^{-1}\)): 2960, 2865, 1592, 1570, 1493, 1451, 1371, 1294, 1251, 1206, 1140, 1086, 945, 908, 827,
Isolated yield = 86%, colorless oil.

**Elemental Analysis**

- **Elemental Analysis**
  - **Calculated for C\textsubscript{23}H\textsubscript{45}BO\textsubscript{5}Si\textsubscript{4}:**
    - C, 52.64%;
    - H, 8.63%
  - **Found:**
    - C, 52.60%;
    - H, 8.63%
  - Isolated yield = 91%, colorless oil.

**FT-IR** (cm\(^{-1}\)):
- 2959, 1590, 1443, 1371, 1348, 1251, 1051, 968, 837, 754, 734, 698, 602, 545.

**GC-MS** (EI, 70 eV) m/z (rel. int., %):
- 524.1 (M\(^+\), 9.6), 410.2 (11.4), 409.0 (29.0), 367.0 (10.5), 282.1 (13.9), 281.0 (49.9), 209.0 (12.5), 208.1 (20.2), 206.9 (100.0), 84.0 (42.5), 83.0 (23.4), 72.9 (95.3), 69.0 (16.7).

**Elemental Analysis**

- **Calculated for C\textsubscript{23}H\textsubscript{45}BO\textsubscript{5}Si\textsubscript{4}:**
  - C, 52.64%;
  - H, 8.63%
- **Found:**
  - C, 52.60%;
  - H, 8.63%
- Isolated yield = 91%, colorless oil.
\( ^1\text{H NMR} \) (CDCl\(_3\), 300 MHz, \( \delta \), ppm): 0.93 (s, 12H), 3.26 (s, 3H), 4.07 (d, 2H, \( J_{\text{HH}} = 4.37 \text{ Hz} \)), 6.42 (t, 1H, \( J_{\text{HH}} = 4.35 \text{ Hz} \)), 7.21-7.54 (m, 15H). \( ^{13}\text{C NMR} \) (CDCl\(_3\), 75 MHz, \( \delta \), ppm): 24.87, 58.41, 74.60, 83.37, 127.65, 129.32, 134.88, 136.67, 156.91. Signal from carbon atom SiBC= is not observed. \( ^2\text{Si NMR} \) (CDCl\(_3\), 79 MHz, \( \delta \), ppm): -14.34. \( \text{FT-IR} \) (cm\(^{-1}\)): 3068, 3048, 2979, 2927, 2821, 1597, 1483, 1428, 1371, 1299, 1256, 1190, 1141, 1107, 1030, 972, 910, 853, 737, 698, 491. \( \text{GC-MS} \) (EI, 70 eV) m/z (rel. int., %): 441.2 (M- 15.3, 1.2), 380.2 (22.0), 379.0 (74.3), 377.9 (16.3), 260.1 (23.1), 259.0 (100.0), 219.0 (19.8), 212.9 (35.4), 183.0 (25.8), 180.9 (57.7), 179.0 (21.1), 174.9 (22.5), 104.9 (37.3), 82.9 (76.3), 58.9 (19.8), 55.0 (30.4). \( \text{Elem. Anal.} \) calcld for C\(_{29}\)H\(_{33}\)BOSi: C, 73.68; H, 7.29; found C, 73.83; H, 7.30. Isolated yield = 71\%, colorless oil.

\( \text{(E)-3-(3-Methoxy-1(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)-1,1,3,5,5,5-}
\text{heptamethyltrisiloxane (3ce)} \)

\( \text{H NMR} \) (C\(_{6}\)D\(_6\), 300 MHz, \( \delta \), ppm): 0.20 (s, 18H), 0.37 (s, 3H), 1.05 (s, 12H), 3.24 (s, 3H), 4.66 (s, 2H), 6.57 (s, 1H). \( ^{13}\text{C NMR} \) (C\(_{6}\)D\(_6\), 75 MHz, \( \delta \), ppm): 1.19, 2.05, 24.94, 57.94, 75.32, 83.12, 164.28. Signal from carbon atom SiBC= is not observed. \( ^2\text{Si NMR} \) (C\(_{6}\)D\(_6\), 79 MHz, \( \delta \), ppm): -36.55, 7.39. \( \text{FT-IR} \) (cm\(^{-1}\)): 2978, 2958, 2819, 1601, 1449, 1371, 1251, 1146, 1046, 837, 785, 753. \( \text{GC-MS} \) (EI, 70 eV) m/z (rel. int., %): 403.1 (M- 15.5, 4.4), 303.0 (14.0), 238.2 (15.8), 237.0 (73.8), 223.1 (11.2), 222.2 (16.4), 221.0 (76.3), 207.0 (40.0), 190.9 (10.4), 84.1 (12.3), 83.0 (11.6), 72.9 (100.0). \( \text{Elem. Anal.} \) calcld for C\(_{27}\)H\(_{35}\)BOSi: C, 48.78; H, 9.39; found C, 48.83; H, 9.40. Isolated yield = 89\%, colorless oil.

\( \text{(E)-Benzyl(3-methoxy-1(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)dimethylsilane}
\text{(3fe)} \)

\( ^1\text{H NMR} \) (CDCl\(_3\), 300 MHz, \( \delta \), ppm): 0.05 (s, 6H), 1.29 (s, 12H), 2.22 (s, 2H), 3.33 (s, 3H), 4.31 (d, 2H, \( J_{\text{HH}} = 1.60 \text{ Hz} \)), 5.95 (t, 1H, \( J_{\text{HH}} = 1.57 \text{ Hz} \)), 5.96-7.22 (m, 5H). \( ^{13}\text{C NMR} \) (CDCl\(_3\), 75 MHz, \( \delta \), ppm): -3.43, 25.02, 25.56, 58.07, 75.24, 83.36, 124.05, 128.19, 128.43, 140.25, 163.49. Signal from carbon atom SiBC= is not observed. \( ^2\text{Si NMR} \) (CDCl\(_3\), 79 MHz, \( \delta \), ppm): -3.46. \( \text{FT-IR} \) (cm\(^{-1}\)): 3024, 2977, 2927, 2817, 1598, 1493, 1451, 1370, 1325, 1245, 1206, 1142, 1106, 1066, 989, 966, 824, 792, 761, 698, 476. \( \text{GC-MS} \) (EI, 70 eV) m/z (rel. int., %): 255.0 (M- 91.4, 30.3), 156.1 (11.9), 154.9 (94.2), 153.8 (22.1), 148.9 (11.0), 132.8 (28.6), 123.0 (16.9), 120.9 (25.2), 112.9 (60.7), 90.9 (15.0), 88.9 (100.0), 83.0 (52.7), 81.0 (16.1), 59.0 (28.6), 55.0 (15.6). \( \text{Elem. Anal.} \) calcld for C\(_{27}\)H\(_{35}\)BOSi: C, 65.89; H, 9.02; found C, 65.80; H, 9.00. Isolated yield = 70\%, colorless oil.
(E)-Benzyl(3-methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)dimethylsilane (4fe)

![Structural formula of (E)-Benzyl(3-methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)dimethylsilane (4fe)]

$^1$H NMR (CDCl$_3$, 300 MHz, $\delta$, ppm): 0.05 (s, 6H), 1.31 (s, 12H), 2.21 (s, 2H), 3.33 (s, 3H), 4.11 (d, 2H, $J_{\text{H,H}}$= 4.67 Hz), 6.43 (t, 1H, $J_{\text{H,H}}$= 4.64 Hz), 6.66-7.21 (m, 5H). $^1$C NMR (CDCl$_3$, 75 MHz, $\delta$, ppm): -3.25, 25.20, 26.06, 58.28, 74.38, 83.31, 123.92, 128.12, 128.43, 128.46, 140.45, 152.73. Signal from carbon atom SiBC= is not observed. $^2$Si NMR (CDCl$_3$, 79 MHz, $\delta$, ppm): -2.32. FT-IR (cm$^{-1}$): 2977, 2928, 2818, 1599, 1493, 1451, 1371, 1354, 1295, 1245, 1206, 1142, 1108, 1071, 1056, 856, 831, 761, 698. GC-MS (EI, 70 eV) m/z (rel. int., %): 332.2 (M$^+$- 14.1, 0.2), 255.0 (17.8), 172.9 (15.2), 154.9 (34.2), 120.9 (10.3), 114.1 (10.2), 112.9 (100.0), 90.9 (16.3), 88.9 (15.3), 83.0 (23.8), 58.9 (13.1), 55.0 (20.2). Elem. Anal. calcd for C$_{33}$H$_{32}$BO$_2$Si: C, 65.89; H, 9.02; found C, 65.90; H, 9.02. Isolated yield = 73%, colorless oil.

(E)-3-(3-Methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)-1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxane (3ge)

![Structural formula of (E)-3-(3-Methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)-1,1,5,5,5-hexamethyl-3-((trimethylsilyl)oxy)trisiloxane (3ge)]

$^1$H NMR (CDCl$_3$, 300 MHz, $\delta$, ppm): 0.10 (s, 27H), 1.27 (s, 12H), 3.29 (s, 3H), 4.18 (d, 2H, $J_{\text{H,H}}$= 1.73 Hz), 6.04 (s, 1H). $^1$C NMR (CDCl$_3$, 75 MHz, $\delta$, ppm): 1.92, 25.02, 58.01, 74.20, 83.19, 156.78. Signal from carbon atom SiBC= is not observed. $^2$Si NMR (CDCl$_3$, 79 MHz, $\delta$, ppm): -81.59, 8.05. FT-IR (cm$^{-1}$): 2958, 1603, 1448, 1371, 1338, 1250, 1050, 836, 754, 686, 595. GC-MS (EI, 70 eV) m/z (rel. int., %): 477.1 (M$^+$- 15.6, 7.8), 311.0 (35.5), 281.0 (13.0), 276.0 (11.3), 261.0 (13.3), 223.0 (13.9), 209.0 (12.6), 208.0 (19.9), 206.9 (100.0), 192.9 (10.9), 88.9 (13.9), 83.0 (11.7), 73.0 (99.5). Elem. Anal. calcd for C$_{33}$H$_{32}$BO$_2$Si: C, 46.32; H, 9.21; found C, 46.40; H, 9.22. Isolated yield = 92%, colorless oil.

Diisopropyl (E)-(3,3-dimethyl-1-(triethylsilyl)but-1-en-1-yl)boronate (4af)

![Structural formula of Diisopropyl (E)-(3,3-dimethyl-1-(triethylsilyl)but-1-en-1-yl)boronate (4af)]

$^1$H NMR (CD$_2$Cl$_2$, 300 MHz, $\delta$, ppm): 0.74-0.81 (q, 6H, $J_{\text{H,H}}$= 7.63 Hz), 1.07-1.20 (m, 30H, overlapped singlet, doublet and triplet), 4.45-4.53 (m, 2H), 6.24 (s, 1H). $^1$C NMR (CD$_2$Cl$_2$, 75 MHz, $\delta$, ppm): 4.72, 7.87, 24.71, 29.45, 37.75, 65.72, 160.43. Signal from carbon atoms BC= is not observed. $^2$Si NMR (CD$_2$Cl$_2$, 79 MHz, $\delta$, ppm): 0.97. $^1$B NMR (CD$_2$Cl$_2$, 96 MHz, $\delta$, ppm): 29.92. GC-MS (EI, 70 eV) m/z (rel. int., %): 297.4 (M$^+$- 29, 100.0), 220.4 (37.7), 191.4 (12.6), 187.4 (15.8), 183.4 (10.3), 154.4 (13.9), 150.4 (10.2), 136.4 (100.0), 128.4 (10.9), 112.4 (10.2), 109.4 (12.3), 98.4 (10.3), 94.4 (100.0), 88.4 (15.8), 82.4 (11.7), 74.4 (99.5). Elem. Anal. calcd for C$_{30}$H$_{30}$BO$_2$Si: C, 65.89; H, 9.02; found C, 65.90; H, 9.02. Isolated yield = 73%, colorless oil.
30.9), 214.4 (16.9), 213.3 (100), 212.3 (24.9), 87.2 (22.5), 75.2 (8.6), 59.1 (26.3), 57.1 (10.1). **FT-IR (cm⁻¹):** 3182, 2261, 1410, 1192, 712, 631, 544. **Elem. Anal.** calcd for C₁₈H₃₉BOSi: C, 66.24; H, 12.04; found C, 66.38; H, 12.06. Isolated yield = 75%, colorless oil.
6. NMR spectra

Figure S1. $^1$H NMR of compound 3aa.

Figure S2. $^{13}$C NMR of compound 3aa.
Figure S3. $^{29}\text{Si}$ NMR of compound 3aa.

Figure S4. $^1\text{H}$ NMR of compound 4aa.
Figure S5. $^{13}$C NMR of compound 4aa.

Figure S6. $^{29}$Si NMR of compound 4aa.
Figure S7. $^{11}$B NMR of compound 4aa.

Figure S8. $^1$H NMR of compound 3ba.
Figure S9. $^{13}$C NMR of compound 3ba.

Figure S10. $^{29}$Si NMR of compound 3ba.
Figure S11. $^1$B NMR of compound 3ba.

Figure S12. $^1$H NMR of compound 4ba.
Figure S13. $^{13}$C NMR of compound 4ba.

Figure S14. $^{29}$Si NMR of compound 4ba.
Figure S15. $^1$H NMR of compound 4ba.

Figure S16. $^3$H NMR of 3ca/4ca mixture 94/6.
Figure S17. $^{13}$C NMR of 3ca/4ca mixture 94/6.

Figure S18. $^{29}$Si NMR of 3ca/4ca mixture 94/6.
Figure S19. $^1$B NMR of 3ca/4ca mixture 94/6.

Figure S20. $^1$H NMR of 3fa/4fa mixture 95/5.
Figure S21. $^{13}$C NMR of 3fa/4fa mixture 95/5.

Figure S22. $^{29}$Si NMR of 3fa/4fa mixture 95/5.
Figure S23. $^1$H NMR of compound 3ab.

Figure S24. $^{13}$C NMR of compound 3ab.
Figure S25. $^{29}$Si NMR of compound 3ab.

Figure S26. $^1$H NMR of compound 3bb.
Figure S27. $^{13}$C NMR of compound 3bb.

Figure S28. $^{29}$Si NMR of compound 3bb.
Figure S29. $^1$B NMR of compound 3bb.

Figure S30. $^1$H NMR of 3cb/4cb mixture 96/4.
Figure S31. $^{13}$C NMR of 3cb/4cb mixture 96/4.

Figure S32. $^{29}$Si NMR of 3cb/4cb mixture 96/4.
Figure S33. $^1$B NMR of 3cb/4cb mixture 96/4.

Figure S34. $^1$H NMR of compound 3fb.
Figure S35. $^{13}$C NMR of compound 3fb.

Figure S36. $^{29}$Si NMR of compound 3fb.
Figure S37. $^{11}$B NMR of compound 3fb.

Figure S38. $^1$H NMR of compound 4ac.
Figure S39. $^1$H NMR of compound 4ac.

Figure S40. $^{29}$Si NMR of compound 4ac.
Figure S4.1. $^{11}$B NMR of compound 4ac.

Figure S4.2. $^1$H - $^{13}$C HSQC of compound 4ac.
Figure S43. $^1$H NMR of compound 4bc.

Figure S44. $^{13}$C NMR of compound 4bc.
Figure S45. $^{29}$Si NMR of compound 4bc.

Figure S46. $^1$H NMR of 3cc/4cc mixture 5/95.
Figure S47. $^{13}$C NMR of 3cc/4cc mixture 5/95.

Figure S48. $^{29}$Si NMR of 3cc/4cc mixture 5/95.
Figure S49. $^1$H NMR of compound 4dc.

Figure S50. $^{13}$C NMR of compound 4dc.
Figure S51. $^{29}$Si NMR of compound 4dc.

Figure S52. $^1$H NMR of compound 6dc.
Figure S53. $^{13}$C NMR of compound 6dc.

Figure S54. $^{29}$Si NMR of compound 6dc.
Figure S55. $^1$H NMR of compound 6dc.

Figure S56. $^1$H NMR of compound 4ec.
Figure S57. $^{13}$C NMR of compound 4ec.

Figure S58. $^{29}$Si NMR of compound 4ec.
Figure S59. $^{11}$B NMR of compound 4ec.

Figure S60. $^1$H NMR of compound 4fc.
Figure S61. $^{13}$C NMR of compound 4fc.

Figure S62. $^{29}$Si NMR of compound 4fc.
Figure S63. $^1$B NMR of compound 4fc.

Figure S64. $^1$H NMR of compound 4ad.
Figure S65. $^{13}$C NMR of compound 4ad.

Figure S66. $^{29}$Si NMR of compound 4ad.
Figure S67. $^{11}$B NMR of compound 4ad.

Figure S68. $^1$H – $^{13}$C HSQC of compound 4ad.
Figure S69. $^1$H NMR of compound 4bd.

Figure S70. $^{13}$C NMR of compound 4bd.
Figure S71.$^3$Si NMR of compound 4bd.

Figure S72.$^1$H NMR of compound 4cd.
Figure S73. $^{13}$C NMR of compound 4cd.

Figure S74. $^{29}$Si NMR of compound 4cd.
Figure S75. $^1$H NMR of compound 4ed.

Figure S76. $^{13}$C NMR of compound 4ed.
Figure S7. $^{29}$Si NMR of compound 4ed.

Figure S78. $^1$H NMR of compound 4fd.
Figure S79. $^{13}$C NMR of compound 4fd.

Figure S80. $^{29}$Si NMR of compound 4fd.
Figure S81. $^1$B NMR of compound 4fd.

Figure S82. $^1$H NMR of 3fd/5fd mixture 89/11.
Figure S8. $^{13}$C NMR of 3fd/5fd mixture 89/11.

Figure S84. $^{29}$Si NMR of 3fd/5fd mixture 89/11.
Figure S8. $^1$H NMR of compound 3gd.
Figure S8. $^1$C NMR of compound 3gd.

Figure S8. $^{29}$Si NMR of compound 3gd.
Figure S88. $^1$H NMR of compound 4be.

Figure S89. $^{13}$C NMR of compound 4be.
Figure S90. $^2$Si NMR of compound 4be.

Figure S91. $^1$H NMR of compound 3ce.
Figure S92. $^{13}$C NMR of compound 3ce.

Figure S93. $^{29}$Si NMR of compound 3ce.
Figure S94. $^1$H - $^{13}$C HSQC of compound 3ce.

Figure S95. $^1$H NMR of compound 3fe.
Figure S96. $^{13}$C NMR of compound 3fe.

Figure S97. $^{29}$Si NMR of compound 3fe.
**Figure S98.** $^1$H – $^{13}$C HSQC of compound 3fe.

**Figure S99.** 1D NOE NMR of compound 3fe.
Figure S100. $^1$H NMR of compound 4fe.

Figure S101. $^{13}$C NMR of compound 4fe.
Figure S102. $^{29}\text{Si}$ NMR of compound 4fe.

Figure S103. $^1\text{H} - ^{13}\text{C}$ HSQC of compound 4fe.
Figure S104. 1D NOE of compound 4fe.

Figure S105. $^1$H NMR of compound 3ge.
Figure S106. $^{13}$C NMR of compound 3ge.

Figure S107. $^{29}$Si NMR of compound 3ge.
Figure S108. $^1$H – $^{13}$C HSQC of compound 3ge.

Figure S109. $^1$H NMR of compound 4af.
Figure S110. $^{13}$C NMR of compound 4af.

Figure S111. $^{29}$Si NMR of compound 4af.
Figure S112. $^1$H NMR of compound 4af.

7. ESI spectra

Figure S113. ESI MS spectra of 3ca/4ca mixture 94/6.
**Figure S114.** ESI MS spectra of 3ca/4ca mixture 94/6.

Chemical Formula: $C_{13}H_{13}BO_{3}Si_{3}$
Molecular Weight: 374.51

**Figure S115.** ESI MS spectra of compound 3bb.

Chemical Formula: $C_{32}H_{40}B_{2}O_{4}Si$
Molecular Weight: 538.37
Figure S116. ESI MS spectra of compound 3bb.

Figure S117. ESI MS spectra of 3cb/5cb mixture 96/4.
Figure S118. ESI MS spectra of 3cb/5cb mixture 96/4.

Figure S119. ESI MS spectra of compound 4cc.
8. X-Ray crystallography

**Figure S120.** Molecular structure of compound 3ba and atoms numbering scheme (one of the six symmetrically independent molecules). Hydrogen atoms omitted for clarity. Displacement ellipsoids shown at the 50% probability level. The box shows an exemplary model of the disorder of four symmetrically independent molecules.

**Figure S121.** Molecular structure of compound 4ba and atoms numbering scheme. Hydrogen atoms omitted for clarity. Displacement ellipsoids shown at the 50% probability level.
Figure S12. Molecular structure of compound 3bb and atoms numbering scheme. Hydrogen atoms omitted for clarity. Displacement ellipsoids shown at the 50% probability level. The disorder model is highlighted in the box.

Figure S123. Molecular structure of compound 3fb and atoms numbering scheme (one of the two symmetrically independent molecules). Hydrogen atoms omitted for clarity. Displacement ellipsoids shown at the 50% probability level. The disorder model is highlighted in the box.
Figure S124. Molecular structure of compound 6dc and atoms numbering scheme (shown only for asymmetric part of molecule). Hydrogen atoms omitted for clarity. Displacement ellipsoids shown at the 50% probability level.

Figure S125. Molecular packing in crystal of 3bb (view along c-axis). Symmetrically independent molecules are shown in different colour. Atoms of Si, B and O are showed as balls.
Figure S126. a) Molecular packing in crystal of 4ba viewed along b axis (atoms of Si, B and O are showed as balls) and b) centrosymmetric sixfold phenyl embrace (6PE) supramolecular synthons (shown as space-fill models).

Figure S127. Molecular packing in crystal of 3bb (view along a-axis). Atoms of Si, B and O are showed as balls.
Figure S128. Molecular packing in crystal of 3fb view along a-axis). Atoms of Si, B and O are showed as balls. Symmetrically independent molecules are shown with different colors.

Figure S129. Molecular packing in crystal of 6dc a) viewed along a-axis and b) viewed along b-axis. Atoms of Si, B and O are showed as balls. Symmetrically independent molecules are shown with different colors.
Table S7. Selected crystal data and structure refinement details.

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<td>C_{26}H_{29}BO_{2Si}</td>
<td>C_{26}H_{29}BO_{2Si}</td>
<td>C_{32}H_{40}B_{2}O_{4}Si</td>
<td>C_{32}H_{68}B_{2}O_{5}Si</td>
<td>C_{32}H_{68}B_{2}O_{5}Si</td>
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<tr>
<td>Mr</td>
<td>412.41</td>
<td>412.4</td>
<td>538.35</td>
<td>428.2</td>
<td>666.84</td>
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<td>Crystal system, space group</td>
<td>Triclinic, P̅</td>
<td>Triclinic, P̅</td>
<td>Monoclinic, Cc</td>
<td>Monoclinic, P21/c</td>
<td>Monoclinic, P21/a</td>
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<td>Temperature (K)</td>
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<tr>
<td>α,β,γ(°)</td>
<td>96.7187 (14), 112.3612 (19), 114.9700 (17)</td>
<td>71.204 (2), 84.767 (2), 87.048 (2)</td>
<td>90</td>
<td>90</td>
<td>90</td>
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<tr>
<td>V (Å³)</td>
<td>6977.9 (3)</td>
<td>1158.91 (5)</td>
<td>3055.13 (5)</td>
<td>5135.71 (10)</td>
<td>4181.33 (7)</td>
</tr>
<tr>
<td>Z</td>
<td>12</td>
<td>2</td>
<td>4</td>
<td>8</td>
<td>4</td>
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<tr>
<td>D_e (Mg m⁻³)</td>
<td>1.178</td>
<td>1.182</td>
<td>1.170</td>
<td>1.108</td>
<td>1.059</td>
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<tr>
<td>Radiation type</td>
<td>Cu Kα</td>
<td>Cu Kα</td>
<td>Cu Kα</td>
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<td>Cu Kα</td>
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<tr>
<td>μ(mm⁻¹)</td>
<td>1.03</td>
<td>1.03</td>
<td>0.94</td>
<td>0.99</td>
<td>1.57</td>
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<tr>
<td>Crystal size (mm)</td>
<td>0.2 × 0.15 × 0.05</td>
<td>0.25 × 0.08 × 0.08</td>
<td>0.4 × 0.3 × 0.28</td>
<td>0.4 × 0.3 × 0.08</td>
<td>0.30 × 0.20 × 0.07</td>
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<tr>
<td>No. of measured, independent</td>
<td>106159, 28031, 21060</td>
<td>29645, 4823, 4398</td>
<td>17756, 5832, 5799</td>
<td>78859, 10722, 10363</td>
<td>41793, 4300</td>
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<tr>
<td>and observed [I &gt; 2σ(I)] reflections</td>
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<tr>
<td>R_int</td>
<td>0.027</td>
<td>0.028</td>
<td>0.018</td>
<td>0.035</td>
<td>0.027</td>
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<tr>
<td>Range of h, k, l</td>
<td>h = -24→24, k = -25→22, l = -27→27</td>
<td>h = -11→11, k = -12→12, l = -16→16</td>
<td>h = -12→12, k = -20→20, l = -22→22</td>
<td>h = -43→43, k = -10→9, l = -22→22</td>
<td>h = -19→19, k = -13→13, l = -30→27</td>
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<tr>
<td>R[I² &gt; 2σ(F²)]</td>
<td>0.044, 0.143</td>
<td>0.033, 0.087</td>
<td>0.027, 0.076</td>
<td>0.058, 0.159</td>
<td>0.038, 0.111</td>
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<tr>
<td>wR(F²), S</td>
<td>1.07</td>
<td>1.05</td>
<td>1.08</td>
<td>1.03</td>
<td>1.05</td>
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<td>No. of parameters</td>
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<td>275</td>
<td>437</td>
<td>868</td>
<td>206</td>
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<tr>
<td>∆ρ_{max}, ∆ρ_{min} (e Å⁻³)</td>
<td>0.34,-0.37</td>
<td>0.33,-0.27</td>
<td>0.24,-0.16</td>
<td>0.57,-0.26</td>
<td>0.55,-0.31</td>
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<tr>
<td>Absolute structure parameter</td>
<td>-</td>
<td>-</td>
<td>-0.016 (13)</td>
<td>-</td>
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Table S8. Selected geometric parameters [°] for 3ba, 3bb and 6dc.

<p>| | | | |</p>
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<thead>
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<td>3ba</td>
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<tr>
<td>C1A—C2A—B1A—O2A</td>
<td>6.8 (2)</td>
<td>C1D—C2D—B1D—O2D</td>
<td>-13.9 (2)</td>
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<tr>
<td>C1B—C2B—B1B—O2B</td>
<td>13.3 (3)</td>
<td>C1E—C2E—B1E—O2E</td>
<td>-7.5 (3)</td>
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<td>C1B’—C2B’—B1B’—O2B’</td>
<td>16 (2)</td>
<td>C1E’—C2E’—B1E’—O2E’</td>
<td>-10 (3)</td>
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<td>C1C—C2C—B1C—O2C</td>
<td>13.4 (3)</td>
<td>C1F—C2F—B1F—O2F</td>
<td>-6.9 (3)</td>
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<td>C1C’—C2C’—B1C’—O2C’</td>
<td>14 (2)</td>
<td>C1F’—C2F’—B1F’—O2F’</td>
<td>-15 (2)</td>
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<tr>
<td>O2A—B1A—O1A</td>
<td>113.57 (12)</td>
<td>O1D—B1D—O2D</td>
<td>113.47 (12)</td>
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<td>O2B—B1B—O1B</td>
<td>113.01 (16)</td>
<td>O2E—B1E—O1E</td>
<td>113.81 (13)</td>
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<td>O1B’—B1B’—O2B’</td>
<td>118.9 (13)</td>
<td>O1E’—B1E’—O2E’</td>
<td>113.1 (15)</td>
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<td>O2C—B1C—O1C</td>
<td>113.46 (16)</td>
<td>O2F—B1F—O1F</td>
<td>113.60 (13)</td>
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<tr>
<td>O1C’—B1C’—O2C’</td>
<td>116.7 (12)</td>
<td>O1F’—B1F’—O2F’</td>
<td>114.4 (13)</td>
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<td>C2—C1—B1—O2</td>
<td>21.54 (18)</td>
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<td>O1—B1—O2</td>
<td>112.90 (10)</td>
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<td>B1—C1—C2—B2</td>
<td>2.0 (3)</td>
<td>C2—C1—B1—O1</td>
<td>107.8 (3)</td>
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<td>C1—C2—B2—O3</td>
<td>-12.8 (3)</td>
<td>C2—C1—B1—O1A</td>
<td>88.2 (9)</td>
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<td>O1A—B1—O2A</td>
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<td>O1—B1—O2</td>
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<td>O3—B2—O4</td>
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<td>B1A—C1A—C2A—B2A</td>
<td>-4.3 (4)</td>
<td>B1C—C1C—C2C—B2C</td>
<td>3.9 (4)</td>
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<td>C2A—C1A—B1A—O1A</td>
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<td>C2C—C1C—B1C—O1C</td>
<td>16.6 (4)</td>
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<td>C2A—C1A—B1A—O2B</td>
<td>-43.7 (5)</td>
<td>C2C—C1C—B1C—O1D</td>
<td>-84.0 (4)</td>
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<td>O2A—B1A—O1A</td>
<td>117.8 (2)</td>
<td>O1C—B1C—O2C</td>
<td>109.0 (3)</td>
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<td>O4A—B2A—O3A</td>
<td>114.2 (3)</td>
<td>O3C—B2C—O4C</td>
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<td>O1B—B1A—O2B</td>
<td>107.2 (3)</td>
<td>O2D—B1C—O1D</td>
<td>117.8 (3)</td>
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<td>O3B—B2A—O4B</td>
<td>112.8 (2)</td>
<td>O3D—B2C—O4D</td>
<td>111.9 (3)</td>
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<td>C1—C2—B1—O1</td>
<td>14.1 (2)</td>
<td>Si1—C1—C2—Si2</td>
<td>177.55 (8)</td>
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9. References