Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Stereoselective synthesis of five and six-membered carbocycles via Matteson homologation / ring closing metathesis

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Supporting Information

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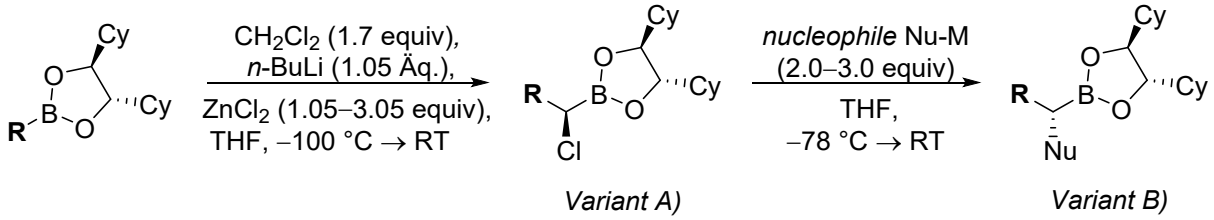
General information

All air and moisture sensitive reactions were carried out in dried glassware (> 100 °C) under nitrogen atmosphere. Anhydrous solvents were purchased from Acros Organics or dried before use (THF was distilled over sodium/benzophenone, diisopropylamine over CaH_2) and stored under nitrogen atmosphere. The products were purified by column chromatography on silica gel columns (Machery-Nagel 60, 0.063–0.2 mm). Mixtures of diethyl ether (Et_2O) and pentane (distilled prior to use) were generally used as eluents. For reverse-phase chromatography (indicated by C-18-SiO_2), a Büchi *Reveleris PREP Chromatography* system was used with *Telos Flash C18* columns and MeCN/H_2O solvents. Analytical TLC was performed on pre-coated silica gel plates (Machery-Nagel, Polygram Sil G/UV_{254}). Detection was accomplished with UV light (254 nm), $KMnO_4$ solution or cerium(IV)/ ammonium molybdate solution. Melting points were determined with a MEL-TEMP II (Laboratory devices) apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance II 400 MHz spectrometer [^{1}H 400 MHz and ^{13}C 100 MHz] or a Bruker Advance I 500 MHz spectrometer [^{1}H 500 MHz and ^{13}C 125 MHz]. Chemical shifts (δ) are reported in parts per million (ppm) relative to TMS or internal solvent signal. Peaks were assigned using (^{1}H,^{1}H)-cosy, (^{1}H,^{13}C)-hsqc and (^{1}H,^{13}C)-hmbc spectra. Mass spectra were recorded with a Finnigan MAT 95 spectrometer (quadrupole) using the CI technique. Optical rotations were measured with a Jasco P-2000 polarimeter in a thermostated (20 °C ± 1 °C) cuvette, using a sodium vapor lamp (λ = 589 nm) as radiation source. $[\alpha]_D^{20}$ values are given in 10^{-1} deg cm^2 g^{-1}. In all cases where no explicit diastereoselectivity is stated, the diastereoselectivity exceeds the ratio of at least 99:1 as observed in the crude ^{1}H NMR analysis.

General procedures

GP-1: Matteson Homologation



In a flame-dried Schlenk flask, anhydrous CH_2Cl_2 (1.7 equiv) was dissolved in anhydrous THF (2.0 mL/mmol) and cooled to a temperature between –110 °C to –100 °C using an ethanol/liquid nitrogen bath. To the cooled solution, *n*-BuLi (1.05 equiv, 2.5 M in hexanes) was dropwise added.[1] For larger quantities, the *n*-BuLi solution was diluted with 1–2 mL anhydrous THF, pre-cooled to –78 °C and added by cannulation. The mixture was stirred for 30 min at –100 °C before adding a solution of the boronate (1.0 equiv) in anhydrous THF (1.5 mL/mmol). After another 30 min of stirring, a solution of $ZnCl_2$ (1.05–3.05 equiv, flame-dried *in vacuo*) in anhydrous THF (0.8 mL/mmol $ZnCl_2$) was added. The mixture was

[1] The addition of *n*-BuLi should be carried out very carefully by adding the solution to the cooled inner wall of the flask. If the addition happens too fast, the mixture turns dark (gray to black) and should be discarded. If done correctly, the mixture remains colorless and/or the formed dichloromethyllithium precipitates as white solid. In this case, the reaction can be continued as described.

allowed to warm to room temperature and stirred for 6–24 h before continuing with either *variant A) or variant B)*.

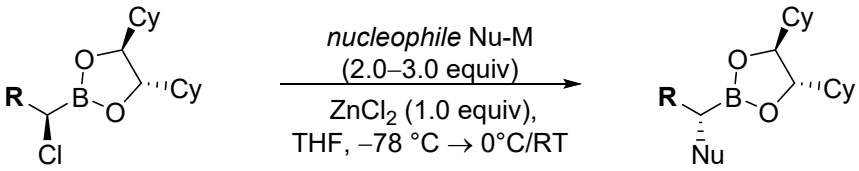
Variant A) Isolation of α-chloroboronic ester

To obtain the α-chloroboronic ester, the reaction mixture was added to a separating funnel with saturated NH_4Cl solution and pentane. The phases were separated, the aqueous phase was extracted with pentane and the combined organic phases were dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was dried *in vacuo*. The obtained α-chloroboronic ester was used in the next reactions without further purification.

Variant B) Conversion of the α-chloroboronic ester

To obtain the homologated, substituted boronic ester, the reaction mixture was again cooled to the specified temperature (–78 °C to 0 °C) and the nucleophile solution was slowly added. The reaction was allowed to warm to the specified temperature (0 °C or room temperature) and stirred for 16–48 h. Upon completion (checked by ^{1}H-NMR or TLC analysis), the reaction mixture was added to a separating funnel with saturated NH_4Cl solution and pentane. The phases were separated, the aqueous phase was extracted with pentane and the combined organic phases were dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography.

GP-2: Reaction of α-chloroboronic esters



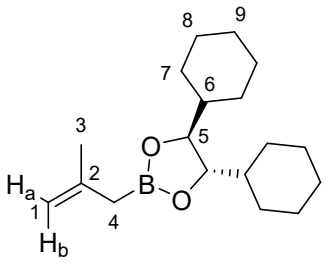
The α-chloroboronic ester (1.0 equiv) was dissolved in anhydrous THF (10 mL/mmol), $ZnCl_2$ (1.0 equiv, flame-dried *in vacuo*) was added at room temperature and the solution was stirred for 5 min before cooling to the specified temperature (–100 °C to 0 °C). Afterwards, the nucleophile solution (1.0–3.0 equiv) were slowly added and the solution was allowed to warm to room temperature and stirred for 1–3 days. Upon completion (checked by ^{1}H-NMR or TLC analysis), the reaction mixture was added to a separating funnel with saturated NH_4Cl solution and pentane. The phases were separated, the aqueous phase was extracted with pentane and the combined organic phases were dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography.

Synthesis of compounds

(4*S*,5*S*)-4,5-Dicyclohexyl-2-(2-methylallyl)-1,3,2-dioxaborolane (1)

For the preparation of the nucleophile solution, 18.2 g (750 mmol, 15 equiv) Mg turnings[2] were suspended in 70 mL anhydrous THF and a solution of 4.89 mL (4.53 g, 50.0 mmol, 1.0 equiv) 3-chloro-2-methylprop-1-ene in 70 mL anhydrous THF was added at 0 °C. The mixture was stirred for 4 h under warming to room temperature.

A solution of 4.62 g (15.7 mmol, 1.0 equiv) (4*S*,5*S*)-4,5-Dicyclohexyl-2-isopropoxy-1,3,2-dioxaborolane[3] in 63 mL anhydrous THF was cooled to –78 °C and 49.4 mL (17.3 mmol, 1.1 equiv, 0.35 M in THF) of the previously prepared nucleophile solution were added. The reaction mixture was stirred overnight under warming to room temperature and quenched by the addition of saturated NH_4Cl solution. After extraction with pentane (2x), the combined organic phases were dried over Na_2SO_4 and the solvent was evaporated. The residue was purified by column chromatography (SiO_2, pentane/Et_2O 95:5) and the product **1** (4.15 g, 14.3 mmol, 91%) was obtained as a colorless oil. R_f (**1**) = 0.51 (pentane/Et_2O 95:5). $[\alpha]_D^{20}$ = –34.3 [$CHCl_3$, c = 1.00].



1

^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.65-4.69 (m, 2 H, 1-H_a, 1-H_b), 3.84-3.87 (m, 2 H, 5-H), 1.56–1.81 (m, 15 H, 3-H, 4-H, 7-H‘, 8-H‘, 9-H), 1.30-1.38 (m, 2 H, 6-H), 0.91–1.26 (m, 10 H, 7-H, 8-H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.1 (s, C-2), 110.0 (t, C-1), 83.4 (d, C-5), 43.0 (d, C-6), 28.3 (t, C-7‘), 27.4 (t, C-8‘), 26.5 (t, C-9), 26.0 (t, C-7), 25.9 (t, C-8), 24.5 (q, C-3) ppm.

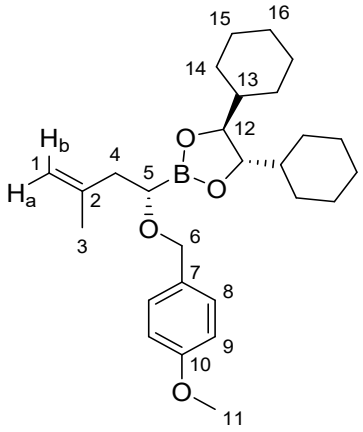
HRMS (CI) m/z calcd for $C_{18}H_{32}BO_2$ $[M+H]^+$: 291.2490, found: 291.2497.

(4*S*,5*S*)-4,5-Dicyclohexyl-2-((*S*)-1-((4-methoxybenzyl)oxy)-3-methylbut-3-en-1-yl)-1,3,2-dioxaborolane (3a)

According to **GP-1**, 1.65 g (5.68 mmol, 1.0 equiv) compound **1** were reacted with 0.62 mL (9.66 mmol, 1.7 equiv) anhydrous CH_2Cl_2, 2.39 mL (5.97 mmol, 1.05 equiv, 2.5 M in hexanes) *n*-BuLi and 1.59 g (11.7 mmol, 2.05 equiv) $ZnCl_2$ (formation of compound **2**, not isolated). To prepare the nucleophile solution, 341 mg (8.53 mmol, 1.50 equiv, 60% in mineral oil) NaH were suspended in 15 mL anhydrous DMSO and 5 mL anhydrous THF before adding 1.13 mL (1.26 g, 9.1 mmol, 1.6 equiv) (4-methoxyphenyl)-methanol at room temperature and stirring overnight. Following variant **B)**, the nucleophile solution was added at 0 °C. The reaction mixture was stirred for 24 h at room temperature and after corres-

[2] To activate the Mg, the turnings were dry-stirred for 24 h under an atmosphere of nitrogen prior to use.
[3] R. Stürmer, *Angew. Chem. Int. Ed.* **1990**, *29*, 59–60.

ponding workup, the crude product was purified by column chromatography (SiO_2, pentane/Et_2O 9:1–8:2). The product **3a** (2.06 g, 4.68 mmol, 82%) was obtained as a colorless oil. R_f (**3a**) = 0.53 (pentane/Et_2O 7:3). $[\alpha]_D^{20}$ = –19.6 [$CHCl_3$, c = 1.00].



3a

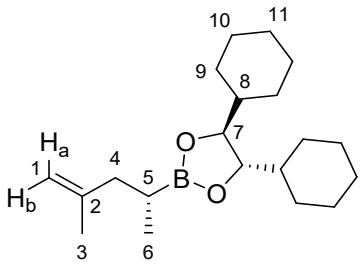
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.25–7.29 (m, 2 H, 8-H), 6.83–6.87 (m, 2 H, 9-H), 4.78 (s, 1 H, 1-H_a), 4.77 (s, 1 H, 1-H_b), 4.52 (d, *J* = 11.3 Hz, 1 H, 6-H‘), 4.44 (d, *J* = 11.3 Hz, 1 H, 6-H), 3.87–3.91 (m, 2 H, 12-H), 3.80 (s, 3 H, 11-H), 3.50 (dd, *J* = 8.2, 6.0 Hz, 1 H, 5-H), 2.44 (dd, *J* = 14.5, 8.2 Hz, 1 H, 4-H‘), 2.36 (dd, *J* = 14.5, 6.0 Hz, 1 H, 4-H), 1.56–1.81 (m, 13 H, 3-H, 14-H‘, 15-H‘, 16-H), 0.92–1.37 (m, 12 H, 13-H, 14-H, 15-H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.0 (s, C-19), 143.6 (s, C-2), 131.2 (s, C-7), 129.4 (d, C-8), 113.6 (d, C-9), 111.8 (t, C-1), 83.8 (d, C-12), 71.8 (t, C-6), 65.8 (d, C-5), 55.2 (q, C-11), 42.9 (d, C-13), 39.6 (t, C-4), 28.3 (t, C-14‘), 27.5 (t, C-15‘), 26.4 (t, C-16), 26.0 (t, C-14), 25.9 (t, C-15), 22.8 (q, C-3) ppm.

HRMS (CI) m/z calcd for $C_{27}H_{42}BO_4$ $[M+H]^+$: 441.3171, found: 441.3165.

(4*S*,5*S*)-4,5-Dicyclohexyl-2-((*R*)-4-methylpent-4-en-2-yl)-1,3,2-dioxaborolane (3b)

According to **GP-1**, 1.80g (6.20 mmol, 1.0 equiv) compound **1** were reacted with 0.68 mL (10.5 mmol, 1.7 equiv) anhydrous CH_2Cl_2, 2.60 mL (6.51 mmol, 1.05 equiv, 2.5 M in hexanes) *n*-BuLi and 888 mg (6.51 mmol, 1.05 equiv) $ZnCl_2$ (formation of compound **2**, not isolated). Following variant **B)**, the nucleophile solution consisting of 4.86 mL (12.4 mmol, 2.0 equiv, 2.55 M in THF) methylmagnesium bromide was added at –78 °C. The reaction mixture was stirred for 24 h at room temperature and after corresponding workup, the crude product was purified by column chromatography (SiO_2, pentane/Et_2O 95:5). The product **3b** (1.76 g, 5.53 mmol, 89%) was obtained as a colorless oil. R_f (**3b**) = 0.59 (pentane/Et_2O 95:5). $[\alpha]_D^{20}$ = –36.7 [$CHCl_3$, c = 1.00].



3b

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 4.65–4.73 (m, 2 H, 1-H_a, 1-H_b), 3.81–3.84 (m, 2 H, 7-H), 2.23 (dd, *J* = 14.2, 7.3 Hz, 1 H, 4-H‘), 1.96 (dd, *J* = 14.2, 8.5 Hz, 1 H, 4-H), 1.58–1.80 (m, 13 H, 3-H, 9-H‘, 10-H‘, 11-H), 0.98–1.34 (m, 13 H, 5-H, 8-H, 9-H, 10-H), 0.96 (d, *J* = 7.6 Hz, 3 H, 6-H) ppm.

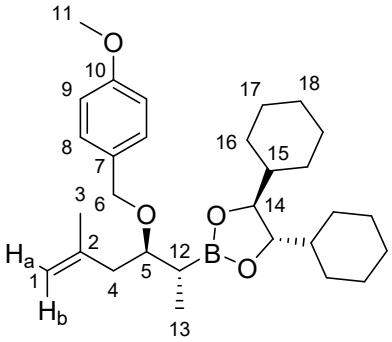
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 145.5 (s, C-2), 110.4 (t, C-1), 83.2 (d, C-7), 43.0 (d, C-8), 41.1 (t, C-4), 28.3 (t, C-9‘), 27.4 (t, C-10‘), 26.5 (t, C-11), 26.0 (t, C-9), 25.9 (t, C-10), 22.2 (q, C-3), 15.3 (q, C-6) ppm.

HRMS (CI) m/z calcd for $C_{20}H_{36}BO_2$ $[M+H]^+$: 319.2803, found: 319.2808.

(4*S*,5*S*)-4,5-Dicyclohexyl-2-((2*R*,3*R*)-3-((4-methoxybenzyl)oxy)-5-methylhex-5-en-2-yl)-1,3,2-dioxaborolane (4a)

According to **GP-1**, 950 mg (2.16 mmol, 1.0 equiv) compound **3a** were reacted with 0.24 mL (3.67 mmol, 1.7 equiv) anhydrous CH_2Cl_2, 0.91 mL (2.27 mmol, 1.05 equiv, 2.5 M in hexanes) *n*-BuLi and 588 mg (4.31 mmol, 2.0 equiv) $ZnCl_2$. Following variant **A)**, the α-chloroboronic ester **3a-Cl** (1.04 g, 2.12 mmol, 98%) was obtained as colorless oil and directly used in the next step.

Therefore, a part of the α-chloroboronic ester **3a-Cl** (919 mg, 1.88 mmol, 1.0 equiv) was reacted according to **GP-2** with 256 mg (1.88 mmol, 1.0 equiv) $ZnCl_2$ and 1.88 mL (5.64 mmol, 3.0 equiv, 3.0 M in Et_2O) methylmagnesium chloride. The nucleophile solution was added at –78 °C and the mixture was stirred at room temperature for 24 h. After corresponding workup, the crude product was purified by column chromatography (SiO_2, pentane/Et_2O 9:1) and the product **4a** (758 mg, 1.62 mmol, 86%) was obtained as a colorless oil. R_f (**4a**) = 0.37 (pentane/Et_2O 9:1). $[\alpha]_D^{20}$ = –34.7 [$CHCl_3$, c = 1.00].



4a

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23-7.27 (m, 2 H, 8-H), 6.83–6.86 (m, 2 H, 9-H), 4.76–4.79 (m, 2 H, 1-H_a, 1-H_b), 4.42–4.48 (m, 2 H, 6-H), 3.80–3.83 (m, 2 H, 14-H), 3.69 (dt, *J* = 7.3, 4.7 Hz, 1 H, 5-H), 2.34 (dd, *J* = 14.2, 7.6 Hz, 1 H, 4-H‘), 2.25 (dd, *J* = 13.9, 4.7 Hz, 1 H, 4-H), 1.55–1.79 (m, 14 H, 3-H, 12-H, 16-H‘, 17-H‘, 18-H), 0.91–1.34 (m, 15 H, 13-H, 15-H, 16-H, 17-H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.8 (s, C-10), 143.8 (s, C-2), 131.4 (s, C-7), 128.9 (d, C-8), 113.5 (d, C-9), 112.2 (t, C-1), 83.3 (d, C-14), 79.9 (d, C-5), 70.4 (t, C-6), 55.3 (q, C-11), 43.0 (d, C-15), 41.1 (t, C-4), 28.3 (t, C-16‘), 27.5 (t, C-17‘), 26.5 (t, C-18), 26.0 (t, C-16), 25.9 (t, C-17), 22.9 (q, C-3), 10.8 (q, C-13) ppm.

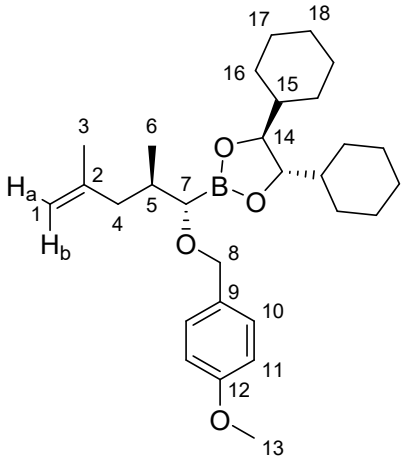
HRMS (CI) m/z calcd for $C_{29}H_{46}BO_4$ $[M+H]^+$: 469.3484, found: 469.3493.

(4*S*,5*S*)-4,5-Dicyclohexyl-2-((1*S*,2*R*)-1-((4-methoxybenzyl)oxy)-2,4-dimethylpent-4-en-1-yl)-1,3,2-dioxaborolane (4b)

According to **GP-1**, 1.70 g (6.34 mmol, 1.0 equiv) compound **3b** were reacted with 0.58 mL (9.08 mmol, 1.7 equiv) anhydrous CH_2Cl_2, 2.24 mL (5.61 mmol, 1.05 equiv, 2.5 M in hexanes) *n*-BuLi and 764 mg (4.31 mmol, 1.05 equiv) $ZnCl_2$. Following variant **A)**, the α-chloroboronic ester **3b-Cl** (1.95 g, 5.31 mmol, 99%) was obtained as colorless oil and directly used in the next step.

To prepare the nucleophile solution, 164 mg (4.09 mmol, 1.50 equiv, 60% in mineral oil) NaH were suspended in 6 mL anhydrous DMSO and 2 mL anhydrous THF before adding 0.54 mL (603 mg, 4.36 mmol, 1.6 equiv) (4-methoxyphenyl)methanol at room temperature and stirring overnight.

A part of the α-chloroboronic ester **3b-Cl** (1.00 g, 2.73 mmol, 1.0 equiv) was reacted according to **GP-2** with 390 mg (2.86 mmol, 1.0 equiv) $ZnCl_2$ and the previously preparred nucleophile solution. The nucleophile solution was added at 0 °C and the mixture was stirred at room temperature for 24 h. After corresponding workup, the crude product was purified by column chromatography (SiO_2, pentane/Et_2O 95:5) and the product **4b** (1.19 g, 2.54 mmol, 93%) was obtained as a colorless oil. R_f (**4b**) = 0.42 (pentane/Et_2O 85:15). $[\alpha]_D^{20}$ = –15.4 [$CHCl_3$, c = 1.00].



4b

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.26–7.29 (m, 2 H, 10-H), 6.83–6.87 (m, 2 H, 11-H), 4.73 (bs, 1 H, 1-H_a), 4.67 (bs, 1 H, 1-H_b), 4.52 (d, *J* = 11.3 Hz, 1 H, 8-H‘), 4.40 (d, *J* = 11.3 Hz, 1 H, 8-H), 3.87-3.91 (m, 2 H, 14-H), 3.80 (s, 3 H, 13-H), 3.12 (d, *J* = 6.3 Hz, 1 H, 7-H), 2.33 (dd, *J* = 13.6, 4.7 Hz, 1 H, 4-H‘), 2.02–2.09 (m, 1 H, 5-H), 1.58–1.83 (m, 14 H, 3-H, 4-H, 16-H‘, 17-H‘, 18-H), 0.93–1.36 (m, 12 H, 15-H, 16-H, 17-H), 0.90 (d, *J* = 6.9 Hz, 3 H, 6-H) ppm.

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 158.9 (s, C-12), 144.7 (s, C-2), 131.4 (s, C-9), 129.3 (d, C-10), 113.5 (d, C-11), 111.5 (t, C-1), 83.7 (d, C-14), 72.3 (t, C-8), 55.2 (q, C-13), 43.0 (d, C-15), 42.2 (t, C-4), 33.0 (d, C-

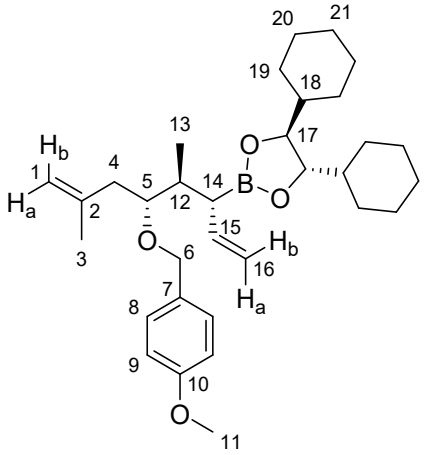
5), 28.4 (t, C-16‘), 27.5 (t, C-17‘), 26.4 (t, C-18), 26.0 (t, C-16), 25.9 (t, C-17), 22.2 (q, C-3), 16.4 (q, C-6) ppm.

HRMS (CI) m/z calcd for $C_{29}H_{46}BO_4$ $[M+H]^+$: 469.3484, found: 469.3479.

(4*S*,5*S*)-4,5-Dicyclohexyl-2-((3*R*,4*S*,5*R*)-5-((4-methoxybenzyl)oxy)-4,7-dimethylocta-1,7-dien-3-yl)-1,3,2-dioxaborolane (5a)

According to **GP-1**, 720 mg (1.54 mmol, 1.0 equiv) compound **4a** were reacted with 0.17 mL (2.61 mmol, 1.7 equiv) anhydrous CH_2Cl_2, 0.65 mL (1.64 mmol, 1.05 equiv, 2.5 M in hexanes) *n*-BuLi and 628 mg (4.61 mmol, 3.0 equiv) $ZnCl_2$. Following variant **A)**, the α-chloroboronic ester **4a-Cl** (794 mg, 1.54 mmol, 100%) was obtained as colorless oil and directly used in the next step.

Therefore, a part of the α-chloroboronic ester **4a-Cl** (780 mg, 1.51 mmol, 1.0 equiv) was reacted according to **GP-2** with 206 mg (1.51 mmol, 1.0 equiv) $ZnCl_2$ and 4.25 mL (3.02 mmol, 2.0 equiv, 0.71 M in THF) vinylmagnesium bromide. The nucleophile solution was added at –78 °C and the mixture was stirred at 0 °C for 24 h. After corresponding workup, the crude product was purified by column chromatography (SiO_2, pentane/Et_2O 9:1) and the product **5a** (708 mg, 1.39 mmol, 92%) was obtained as a colorless oil. R_f (**5a**) = 0.38 (pentane/Et_2O 9:1). $[\alpha]_D^{20}$ = –16.0 [$CHCl_3$, c = 1.00].



5a

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.24–7.28 (m, 2 H, 8-H), 6.83–6.87 (m, 2 H, 9-H), 5.76 (dt, *J* = 17.2, 9.9 Hz, 1 H, 15-H), 5.01 (dd, *J* = 17.2, 1.4 Hz, 1 H, 16-H_b), 4.95 (dd, *J* = 10.2, 2.0 Hz, 1 H, 16-H_a), 4.76 (s, 2 H, 1-H_a, 1-H_b), 4.50 (d, *J* = 11.3 Hz, 1 H, 6-H‘), 4.37 (d, *J* = 11.3 Hz, 1 H, 6-H), 3.81–3.84 (m, 2 H, 17-H), 3.79 (s, 3 H, 11-H), 3.58 (dt, *J* = 8.3, 3.9 Hz, 1 H, 5-H), 2.06–2.19 (m, 3 H, 4-H, 12-H), 1.93 (t, *J* = 9.8 Hz, 1 H, 14-H), 1.56–1.82 (m, 13 H, 3-H, 19-H‘, 20-H‘, 21-H), 0.95–1.34 (m, 12 H, 18-H, 19-H, 20-H), 0.93 (d, *J* = 6.9 Hz, 3 H, 13-H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.9 (s, C-10), 143.9 (s, C-2), 138.5 (d, C-15), 131.3 (s, C-7), 129.2 (d, C-8), 114.8 (t, C-16), 113.6 (d, C-9), 112.1 (t, C-1), 83.5 (d, C-17), 79.0 (d, C-5), 70.7 (t, C-6), 55.3 (q, C-11), 43.0 (d, C-18), 37.1 (t, C-4), 36.1 (d, C-12), 34.1 (d, C-14), 28.5 (t, C-19‘), 27.6 (t, C-20‘), 26.4 (t, C-21), 26.0 (t, C-19), 25.9 (t, C-20), 22.8 (q, C-3), 13.8 (q, C-13) ppm.

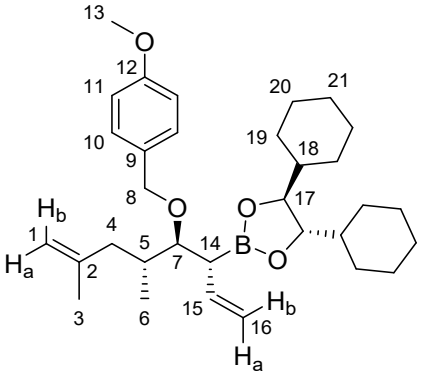
HRMS (CI) m/z calcd for $C_{32}H_{50}BO_4$ $[M+H]^+$: 509.3797, found: 509.3789.

(4*S*,5*S*)-4,5-Dicyclohexyl-2-((3*R*,4*S*,5*R*)-4-((4-methoxybenzyl)oxy)-5,7-dimethylocta-1,7-dien-3-yl)-1,3,2-dioxaborolane (5b)

According to **GP-1**, 1.10 g (2.35 mmol, 1.0 equiv) compound **4b** were reacted with 0.26 mL (3.99 mmol, 1.7 equiv) anhydrous CH_2Cl_2, 0.99 mL (2.47 mmol, 1.05 equiv, 2.5 M in hexanes) *n*-BuLi and 657 mg

(4.81 mmol, 2.05 equiv) $ZnCl_2$. Following variant **A)**, the α-chloroboronic ester **4b-Cl** (1.21 g, 2.34 mmol, 100%) was obtained as colorless oil and directly used in the next step.

Therefore, a part of the α-chloroboronic ester **4b-Cl** (770 mg, 1.49 mmol, 1.0 equiv) was reacted according to **GP-2** with 203 mg (1.49 mmol, 1.0 equiv) $ZnCl_2$ and 4.26 mL (2.98 mmol, 2.0 equiv, 0.71 M in THF) vinylmagnesium bromide. The nucleophile solution was added at –78 °C and the mixture was stirred at 0 °C for 24 h. After corresponding workup, the crude product was purified by column chromatography (SiO_2, pentane/Et_2O 9:1) and the product **5b** (675 mg, 1.33 mmol, 89%) was obtained as a colorless oil. R_f (**5b**) = 0.41 (pentane/Et_2O 9:1). $[\alpha]_D^{20}$ = –10.2 [$CHCl_3$, c = 1.00].



5b

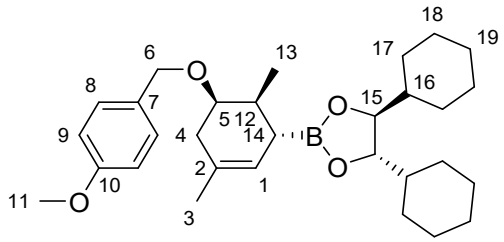
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.24–7.28 (m, 2 H, 10-H), 6.83–6.87 (m, 2 H, 11-H), 5.88 (dt, *J* = 17.0, 9.9 Hz, 1 H, 15-H), 5.08 (dd, *J* = 17.0, 1.6 Hz, 1 H, 16-H_b), 4.99 (dd, *J* = 10.2, 2.0 Hz, 1 H, 16-H_a), 4.72 (bs, 1 H, 1-H_a), 4.65 (bs, 1 H, 1-H_b), 4.58 (d, *J* = 11.7 Hz, 1 H, 8-H‘), 4.50 (d, *J* = 11.4 Hz, 1 H, 8-H), 3.78–3.82 (m, 5 H, 13-H, 17-H), 3.50 (dd, *J* = 6.8, 4.9 Hz, 1 H, 7-H), 2.44 (dd, *J* = 9.6, 7.1 Hz, 1 H, 14-H), 2.35 (dd, *J* = 13.6, 3.5 Hz, 1 H, 4-H‘), 1.91–2.00 (m, 1 H, 5-H), 1.53–1.81 (m, 14 H, 3-H, 4-H, 19-H‘, 20-H‘, 21-H), 0.87–1.33 (m, 15 H, 3-H, 18-H, 19-H, 20-H) ppm.

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 158.8 (s, C-12), 144.9 (s, C-2), 136.9 (d, C-15), 131.5 (s, C-9), 115.4 (t, C-16), 113.5 (t, C-11), 111.5 (t, C-1), 84.9 (d, C-7), 83.6 (d, C-17), 72.0 (t, C-8), 55.3 (q, C-13), 43.0 (d, C-18), 40.6 (t, C-4), 34.1 (d, C-5), 28.4 (t, C-19‘), 27.8 (t, C-20‘), 26.4 (t, C-21), 26.0 (t, C-19), 25.8 (t, C-20), 22.1 (q, C-3), 15.9 (q, C-6) ppm.

HRMS (CI) m/z calcd for $C_{32}H_{50}BO_4$ $[M+H]^+$: 509.3797, found: 509.3789.

(4*S*,5*S*)-4,5-Dicyclohexyl-2-((1*R*,5*R*,6*S*)-5-((4-methoxybenzyl)oxy)-3,6-dimethylcyclohex-2-en-1-yl)-1,3,2-dioxaborolane (6a)

415 mg (816 µmol, 1.0 equiv) compound **5a** were dissolved in 8.2 mL anhydrous CH_2Cl_2 and degassed with argon. Afterwards, 20.8 mg (24 µmol, 3 mol-%) Grubbs II catalyst (benzylidene [1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinyliden]dichloro(tricyclohexylphosphine)ruthenium) were added and the mixture was stirred over night at 40 °C. The solvent was evaporated *in vacuo* and the residue was purified by column chromatography (SiO_2, 100% CH_2Cl_2). The product **6a** (376 mg, 783 µmol, 96%) was obtained as a colorless oil. R_f (**6a**) = 0.43 (CH_2Cl_2 100%). $[\alpha]_D^{20}$ = –3.7 [$CHCl_3$, c = 1.00].



6a

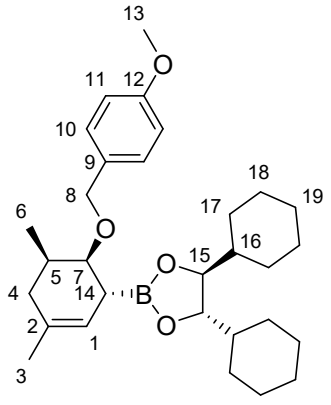
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.26–7.29 (m, 2 H, 8-H), 6.84–6.88 (m, 2 H, 9-H), 5.29 (dq, *J* = 4.4, 1.6 Hz, 1 H, 1-H), 4.45–4.52 (m, 2 H, 6-H), 3.81–3.85 (m, 2 H, 16-H), 3.80 (s, 3 H, 11-H), 3.69 (ddd, *J* = 7.2, 5.4, 3.2 Hz, 1 H, 5-H), 2.14–2.20 (m, 1 H, 12-H), 2.00–2.11 (m, 2 H, 4-H), 1.54–1.80 (m, 14 H, 3-H, 14-H, 17-H‘, 18-H‘, 19-H), 0.97–1.35 (m, 12 H, 16-H, 17-H, 18-H), 0.95 (d, *J* = 6.9 Hz, 3 H, 13-H) ppm.

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 158.9 (s, C-10), 131.6 (s, C-7), 129.3 (s, C-2), 129.1 (d, C-8), 119.9 (d, C-1), 113.6 (d, C-9), 83.3 (d, C-15), 75.8 (d, C-5), 69.7 (t, C-6), 55.2 (q, C-11), 43.0 (d, C-16), 33.1 (t, C-4), 31.1 (d, C-12), 28.2 (t, C-17‘), 27.4 (t, C-18‘), 26.5 (t, C-19), 26.0 (t, C-17), 25.9 (t, C-18), 23.6 (q, C-3), 15.0 (q, C-13) ppm.

HRMS (CI) m/z calcd for $C_{30}H_{45}BO_4$ $[M]^+$: 480.3405, found: 480.3403.

(4*S*,5*S*)-4,5-Dicyclohexyl-2-((1*R*,5*R*,6*S*)-6-((4-methoxybenzyl)oxy)-3,5-dimethylcyclohex-2-en-1-yl)-1,3,2-dioxaborolane (6b)

122 mg (240 µmol, 1.0 equiv) compound **5b** were dissolved in 4.8 mL anhydrous CH_2Cl_2 and degassed with argon. Afterwards, 6.1 mg (7.2 µmol, 3 mol-%) Grubbs II catalyst (benzylidene [1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinyliden]dichloro(tricyclohexylphosphine)ruthenium) were added and the mixture was stirred over night at 40 °C. The solvent was evaporated *in vacuo* and the residue was purified by column chromatography (SiO_2, pentane/Et_2O 9:1). The product **6b** (107 mg, 223 µmol, 93%) was obtained as a colorless oil. R_f (**6b**) = 0.29 (pentane/Et_2O 9:1). $[\alpha]_D^{20}$ = +24.0 [$CHCl_3$, c = 1.00].



6b

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.24–7.28 (m, 2 H, 10-H), 6.82–6.87 (m, 2 H, 11-H), 5.23 (dq, *J* = 3.3, 1.4 Hz, 1 H, 1-H), 4.43–4.52 (m, 2 H, 8-H), 3.82–3.86 (m, 2 H, 15-H), 3.80 (s, 3 H, 13-H), 3.66 (dd, *J* = 5.4, 2.5 Hz, 7-H), 2.11 (bs, 1 H, 5-H), 1.95–2.06 (m, 2 H, 4-H‘, 14-H), 1.85 (dd, *J* = 16.7, 6.9 Hz, 1 H, 4-H), 1.54–1.78 (m, 13 H, 3-H, 17-H‘, 18-H‘, 19-H), 0.96–1.35 (m, 17-H‘, 18-H‘, 19-H), 0.93 (d, *J* = 6.6 Hz, 3 H, 6-H) ppm.

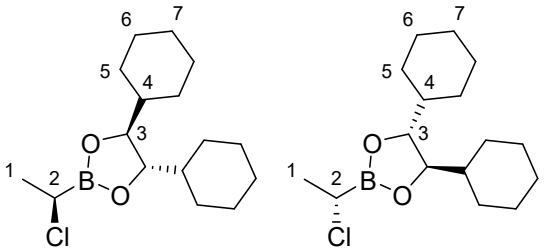
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 158.8 (s, C-12), 131.6 (s, C-2), 131.5 (s, C-9), 129.1 (d, C-10), 118.1 (d, C-1), 113.5 (d, C-11), 83.3 (d, C-15), 77.8 (d, C-7), 70.4 (t, C-8), 55.2 (q, C-13), 42.9 (d, C-16), 35.3 (d, C-5), 30.1 (t, C-4), 28.2 (t, C-17‘), 27.3 (t, C-18‘), 26.4 (t, C-19), 26.0 (t, C-17), 25.9 (t, C-18), 23.8 (q, C-3), 15.5 (q, C-6) ppm.

HRMS (CI) m/z calcd for $C_{30}H_{45}BO_4$ $[M]^+$: 480.3405, found: 480.3413.

(4*S*,5*S*)-2-((*R*)-1-Chloroethyl)-4,5-dicyclohexyl-1,3,2-dioxaborolane ((*R*)-**7)**[4]

According to **GP-1**, 9.98 g (39.9 mmol, 1.0 equiv) (4*S*,5*S*)-4,5-dicyclohexyl-2-methyl-1,3,2-dioxaborolane[5] were reacted with 4.36 mL (67.8 mmol, 1.7 equiv) anhydrous CH_2Cl_2, 16.8 mL (41.9 mmol, 1.05 equiv, 2.5 M in hexanes) *n*-BuLi and 5.71 g (41.9 mmol, 1.05 equiv) $ZnCl_2$. Following variant **A)**, the α-chloroboronic ester (*R*)-**7** (11.7 g, 39.2 mmol, 98%) was obtained as colorless oil, stored at 4 °C and used in the next step without further purification. $[\alpha]_D^{20}$ = –59.7 [$CHCl_3$, c = 1.00].

The enantiomer (4*R*,5*R*)-2-((*S*)-1-chloroethyl)-4,5-dicyclohexyl-1,3,2-dioxaborolane ((*S*)-**7**) was prepared accordingly using (4*R*,5*R*)-4,5-dicyclohexyl-2-methyl-1,3,2-dioxaborolane.[5]



(*R*)-**7** (*S*)-**7**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.94–3.98 (m, 2 H, 3-H), 3.57 (q, *J* = 7.6 Hz, 1 H, 2-H), 1.58–1.80 (m, 10 H, 5-H‘, 6-H‘, 7-H), 1.57 (d, *J* = 7.6 Hz, 3 H, 1-H), 1.34–1.42 (m, 2 H, 4-H), 0.94–1.28 (m, 10 H, 5-H, 6-H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 84.1 (d, C-3), 42.9 (d, C-4), 28.2 (t, C-5‘), 27.2 (t, C-6‘), 26.4 (t, C-7), 26.0 (t, C-5), 25.9 (t, C-6), 20.7 (q, C-1) ppm.

(4*S*,5*S*)-4,5-Dicyclohexyl-2-((*S*,*Z*)-pent-3-en-2-yl)-1,3,2-dioxaborolane ((*S*)-**8)**

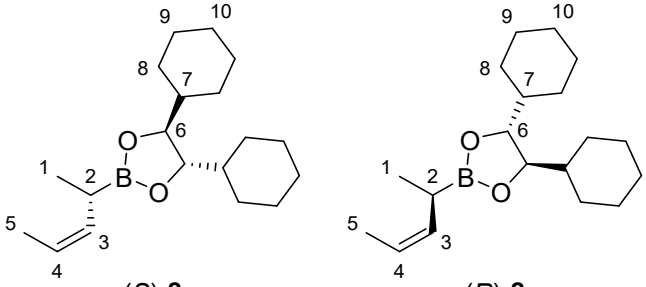
For the preparation of the nucleophile solution, 400 mg (16.5 mmol, 1.6 equiv) Mg turnings were suspended in 29 mL anhydrous THF, 1.66 mL (2.36 g, 19.5 mmol, 1.9 equiv) (*Z*)-1-bromoprop-1-ene was added and the mixture was stirred for 60 min at 40 °C (complete dissolving of Mg turnings).

According to **GP-2**, 3.07 g (10.3 mmol, 1.0 equiv) (*R*)-**7** were reacted with 1.54 g (11.3 mmol, 1.1 equiv) $ZnCl_2$ and the previously preparred nucleophile solution. The nucleophile solution was added at

[4] O. Andler, U. Kazmaier, *Org. Lett.* 2021, **23**, 8439–8444.
[5] T. Kinsinger, U. Kazmaier, *Org. Lett.* **2022**, *24*, 3599–3603.

–78 °C and the mixture was stirred at 0 °C for 24 h. After corresponding workup, the crude product was purified by column chromatography (SiO_2, pentane/Et_2O 95:5) and the product (*S*)-**8** (2.68 g, 8.20 mmol, 80%, purity 93% with impurity (4*S*,5*S*)-4,5-dicyclohexyl-2-((*Z*)-prop-1-en-1-yl)-1,3,2-dioxaborolane) was obtained as a colorless oil. R_f ((*S*)-**8**) = 0.52 (pentane/Et_2O 95:5). $[\alpha]_D^{20}$ = +23.0 [$CHCl_3$, c = 1.00].

The enantiomer (4*R*,5*R*)-4,5-dicyclohexyl-2-((*R*,*Z*)-pent-3-en-2-yl)-1,3,2-dioxaborolane ((*R*)-**8**) was prepared accordingly using (*S*)-**7**.



(*S*)-**8** (*R*)-**8**

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.34–5.42 (m, 2 H, 3-H, 4-H), 3.82–3.85 (m, 2 H, 6-H), 2.15–2.23 (m, 1 H, 2-H), 1.72–1.79 (m, 6 H, 8-H‘‘‘, 9-H‘‘, 10-H‘), 1.64–1.70 (m, 2 H, 10-H), 1.62 (d, *J* = 5.0 Hz, 3 H, 5-H), 1.55–1.61 (m, 2 H, 8-H‘‘), 1.28–1.36 (m, 2 H, 7-H), 0.90–1.26 (m, 13 H, 1-H, 8-H‘, 8-H, 9-H‘, 9-H) ppm.

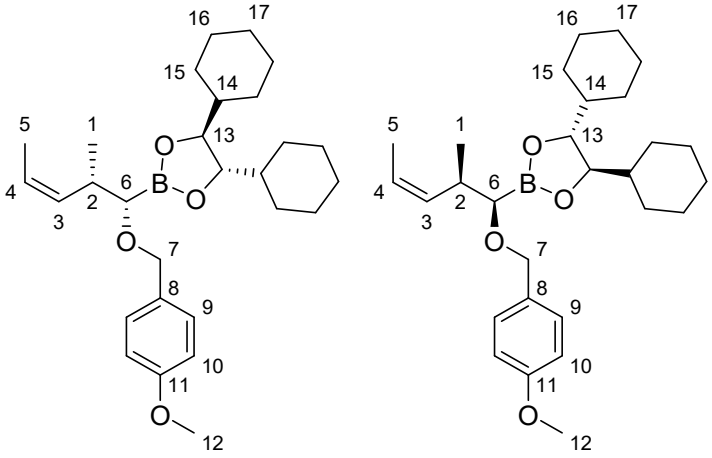
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 133.4 (d, C-3), 122.2 (d, C-4), 83.2 (d, C-6), 43.0 (d, C-7), 28.2 (t, C-8‘), 27.3 (t, C-9‘), 26.5 (t, C-10), 26.0 (t, C-8), 25.9 (t, C-9), 16.2 (q, C-1), 13.0 (q, C-5) ppm.

HRMS (CI) m/z calcd for $C_{19}H_{34}BO_2$ $[M+H]^+$: 305.2646, found: 305.2645.

(4*S*,5*S*)-4,5-Dicyclohexyl-2-((1*S*,2*S*,*Z*)-1-((4-methoxybenzyl)oxy)-2-methylpent-3-en-1-yl)-1,3,2-dioxaborolane (9)

According to **GP-1**, 952 mg (2.91 mmol, 1.0 equiv) compound (*S*)-**8** were reacted with 0.32 mL (4.95 mmol, 1.7 equiv) anhydrous CH_2Cl_2, 1.22 mL (3.06 mmol, 1.05 equiv, 2.5 M in hexanes) *n*-BuLi and 813 mg (5.96 mmol, 2.05 equiv) $ZnCl_2$. To prepare the nucleophile solution, 175 mg (4.36 mmol, 1.50 equiv, 60% in mineral oil) NaH were suspended in 9 mL anhydrous DMSO and 3 mL anhydrous THF before adding 0.58 mL (643 mg, 4.66 mmol, 1.6 equiv) (4-methoxyphenyl)methanol at room temperature and stirring overnight. Following variant **B)**, the nucleophile solution was added at 0 °C. The reaction mixture was stirred for 24 h at room temperature and after corresponding workup, the crude product was purified by column chromatography (SiO_2, pentane/Et_2O 85:5). The product **9** (4.15 g, 2.54 mmol, 87%, *Z*/*E* 78:22) was obtained as a colorless oil. R_f (**9**) = 0.40 (pentane/Et_2O 85:15). $[\alpha]_D^{20}$ = –7.1 [$CHCl_3$, c = 1.00].

The enantiomer (4*R*,5*R*)-4,5-Dicyclohexyl-2-((1*R*,2*R*,*Z*)-1-((4-methoxybenzyl)oxy)-2-methylpent-3-en-1-yl)-1,3,2-dioxaborolane (*ent*-**9**) was prepared accordingly using compound (*R*)-**8**.



9 *ent*-**9**

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.25-7.28 (m, 2 H, 9-H), 6.83–6.87 (m, 2 H, 10-H), 5.27–5.34 (m, 1 H, 3-H), 5.39–5.48 (m, 1 H, 4-H), 4.50–4.55 (d, *J* = 11.4 Hz, 1 H, 7-H‘), 4.41 (d, *J* = 11.6 Hz, 1 H, 7-H), 3.85–3.88 (m, 2 H, 13-H), 3.80 (s, 3 H, 12-H), 3.09 (d, *J* = 7.6 Hz, 1 H, 6-H), 2.86–2.95 (m, 2 H, 0.78/1.00 H, 2-H [*Z*-**9**]), 2.48–2.57 (m, 0.22/1.00 H, 2-H [*E*-**9**]), 1.56–1.83 (m, 13 H, 5-H, 15-H‘, 16-H‘, 17-H), 0.92–1.33 (m, 15 H, 1-H, 14-H, 15-H, 16-H) ppm.

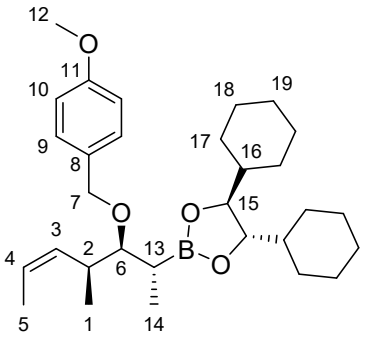
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 158.9 (s, C-11), 133.3 (s, C-8), 131.3 (d, C-3), 129.3 (d, C-9), 123.8 (d, C-4), 113.5 (d, C-10), 83.7 (d, C-13), 72.5 (t, C-7), 55.2 (q, C-12), 43.0 (d, C-14), 33.8 (d, C-2), 28.4 (t, C-15‘), 27.6 (t, C-16‘), 26.4 (t, C-17), 26.0 (t, C-15), 25.9 (t, C-16), 18.2 (q, C-1), 13.0 (q, C-5) ppm.

HRMS (CI) m/z calcd for $C_{28}H_{44}BO_4$ $[M+H]^+$: 455.3327, found: 455.3335.

(4*S*,5*S*)-4,5-Dicyclohexyl-2-((2*R*,3*S*,4*S*,*Z*)-3-((4-methoxybenzyl)oxy)-4-methylhept-5-en-2-yl)-1,3,2-dioxaborolane (10)

According to **GP-1**, 1.12 mg (2.46 mmol, 1.0 equiv) compound **9** were reacted with 0.27 mL (4.19 mmol, 1.7 equiv) anhydrous CH_2Cl_2, 1.04 mL (2.59 mmol, 1.05 equiv, 2.5 M in hexanes) *n*-BuLi and 689 mg (5.05 mmol, 2.05 equiv) $ZnCl_2$. Following variant **A)**, the α-chloroboronic ester **9-Cl** (1.26 g, 2.46 mmol, 100%) was obtained as colorless oil and directly used in the next step.

Therefore, a part of the α-chloroboronic ester **9-Cl** (1.18 g, 2.34 mmol, 1.0 equiv) was reacted according to **GP-2** with 319 mg (2.34 mmol, 1.0 equiv) $ZnCl_2$ and 2.34 mL (7.03 mmol, 3.0 equiv, 3.0 M in Et_2O) methylmagnesium chloride. The nucleophile solution was added at –78 °C and the mixture was stirred at room temperature for 24 h. After corresponding workup, the crude product was purified by column chromatography (SiO_2, pentane/Et_2O 9:1) and the product **10** (1.03 g, 2.12 mmol, 91%, *Z*/*E* 78:22) was obtained as a colorless oil. R_f (**10**) = 0.40 (pentane/Et_2O 9:1). $[\alpha]_D^{20}$ = –4.0 [$CHCl_3$, c = 1.00].



10

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.25–7.29 (m, 2 H, 9-H), 6.83–6.87 (m, 2 H, 10-H), 5.31–5.41 (m, 1 H, 4-H), 5.21 (tq, *J* = 10.6, 1.6 Hz, 1 H, 3-H), 4.42–4.59 (m, 2 H, 7-H), 3.75–3.81 (m, 5 H, 12-H, 15-H), 3.34 (dd, *J* = 8.8, 3.5 Hz, 0.78/1.00 H, 6-H [*Z*-**10**]), 3.29 (dd, *J* = 7.4, 4.6 Hz, 0.22/1.00 H, 6-H [*E*-**10**]), 2.77–2.87 (m, 0.78/1.00 H, 2-H [*Z*-**10**]), 2.42–2.52 (m, 0.22/1.00 H, 2-H [*E*-**10**]), 1.51–1.84 (m, 14 H, 5-H, 13-H, 17-H', 18-H', 19-H), 0.92–1.33 (m, 18 H, 1-H, 14-H, 16-H, 17-H, 18-H) ppm.

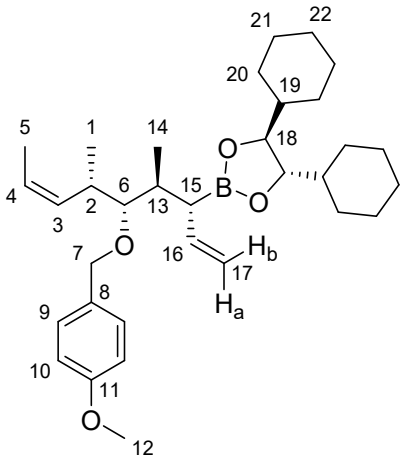
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 158.8 (s, C-11), 133.9 (d, C-3), 131.6 (s, C-8), 129.0 (d, C-9), 123.9 (d, C-4), 113.6 (d, C-10), 86.7 (d, C-6), 83.4 (d, C-3), 72.4 (t, C-7), 55.3 (q, C-12), 43.0 (d, C-16), 35.2 (d, C-2), 28.5 (t, C-17'), 27.8 (t, C-18'), 26.5 (t, C-19), 26.0 (t, C-17), 25.9 (t, C-18), 17.8 (q, C-1), 13.1 (q, C-5), 11.2 (q, C-14) ppm.

HRMS (CI) m/z calcd for $C_{30}H_{47}BO_4$ $[M]^+$: 482.3562, found: 482.3554.

(4*S*,5*S*)-4,5-Dicyclohexyl-2-((3*R*,4*S*,5*S*,6*S*,*Z*)-5-((4-methoxybenzyl)oxy)-4,6-dimethylnona-1,7-dien-3-yl)-1,3,2-dioxaborolane (11)

According to **GP-1**, 994 mg (2.06 mmol, 1.0 equiv) compound **10** were reacted with 0.23 mL (3.50 mmol, 1.7 equiv) anhydrous CH_2Cl_2, 0.87 mL (2.16 mmol, 1.05 equiv, 2.5 M in hexanes) *n*-BuLi and 576 mg (4.22 mmol, 2.05 equiv) $ZnCl_2$. Following variant **A)**, the α-chloroboronic ester **10-Cl** (1.05 g, 1.97 mmol, 96%) was obtained as colorless oil and directly used in the next step.

Therefore, a part of the α-chloroboronic ester **10-Cl** (491 mg, 786 µmol, 1.0 equiv) was reacted according to **GP-2** with 107 mg (786 µmol, 1.0 equiv) $ZnCl_2$ and 2.25 mL (1.57 mmol, 2.0 equiv, 0.7 M in THF) vinylmagnesium bromide. The nucleophile solution was added at –78 °C and the mixture was stirred at 0 °C for 24 h. After corresponding workup, the crude product was purified by column chromatography (SiO_2, pentane/Et_2O 9:1) and the product **11** (335 mg, 642 µmol, 82%, *Z*/*E* 78:22) was obtained as a colorless oil. R_f (**11**) = 0.46 (pentane/Et_2O 9:1). $[\alpha]_D^{20}$ = –10.8 [$CHCl_3$, c = 1.00].



11

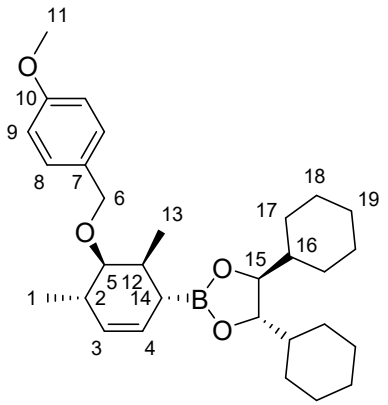
[1]H-NMR (500 MHz, $CDCl_3$): δ = 7.26–7.31 (m, 2 H, 9-H), 6.84–6.88 (m, 2 H, 10-H), 5.82–5.91 (m, 1 H, 16-H), 5.32–5.46 (m, 2 H, 3-H, 4-H), 4.94–5.05 (m, 2 H, 17-H_a, 17-H_b), 4.56–4.64 (m, 1 H, 7-H‘), 4.43–4.48 (m, 1 H, 7-H), 3.80 (s, 3 H, 12-H), 3.74–3.79 (m, 2 H, 18-H), 3.23 (t, *J* = 5.7 Hz, 1 H, 6-H), 2.77–2.86 (m, 0.73/1.00 H, 2-H [*Z*-**126**]), 2.42–2.49 (m, 0.27/1.00 H, 2-H [*E*-**126**]), 2.28 (dd, *J* = 8.8, 6.6 Hz, 1 H, 15-H), 1.93–2.06 (m, 1 H, 13-H), 1.51–1.83 (m, 13 H, 5-H, 20-H‘, 21-H‘, 22-H), 0.92–1.33 (m, 18 H, 1-H, 14-H, 19-H, 20-H, 21-H) ppm.

[13]C-NMR (125 MHz, $CDCl_3$): δ = 158.8 (s, C-11), 139.6 (d, C-16), 135.0 (d, C-3), 131.6 (s, C-8), 128.7 (d, C-9), 122.2 (d, C-4), 114.5 (t, C-17), 113.6 (d, C-10), 86.2 (d, C-6), 83.4 (d, C-18), 73.5 (t, C-7), 55.3 (q, C-12), 43.0 (d, C-19), 38.4 (d, C-13), 33.8 (d, C-2), 28.5 (t, C-20‘), 27.8 (t, C-21‘), 26.5 (t, C-22), 25.9 (t, C-20), 25.9 (t, C-21), 16.3 (q, C-1), 15.3 (q, C-14), 12.9 (q, C-5) ppm.

HRMS (CI) m/z calcd for $C_{33}H_{50}BO_4$ $[M-H]^-$: 521.3797, found: 521.3809.

(4*S*,5*S*)-4,5-Dicyclohexyl-2-((1*R*,4*S*,5*S*,6*S*)-5-((4-methoxybenzyl)oxy)-4,6-dimethylcyclohex-2-en-1-yl)-1,3,2-dioxaborolane (12)

300 mg (436 µmol, 1.0 equiv) compound **11** were dissolved in 7.2 mL anhydrous CH_2Cl_2 and degassed with argon. Afterwards, 11.1 mg (13 µmol, 3 mol-%) Grubbs II catalyst (benzylidene [1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinyliden]dichloro(tricyclohexylphosphine)ruthenium) were added and the mixture was stirred over night at 40 °C. The solvent was evaporated *in vacuo* and the residue was purified by column chromatography (SiO_2, pentane/Et_2O 99:1–95:5). The product **12** (204 mg, 425 µmol, 97%) was obtained as a colorless oil. R_f (**12**) = 0.46 (pentane/Et_2O 95:5). $[\alpha]_D^{20}$ = +1.6 [$CHCl_3$, c = 1.00].



12

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.27–7.31 (m, 2 H, 8-H), 6.84–6.88 (m, 2 H, 9-H), 5.56 (ddd, *J* = 9.9, 4.5, 2.4 Hz, 1 H, 4-H), 5.35 (dt, *J* = 10.0, 2.2 Hz, 1 H, 3-H), 4.55 (d, *J* = 11.3 Hz, 1 H, 6-H‘), 4.39 (d, *J* = 11.7 Hz, 1 H, 6-H), 3.83–3.86 (m, 2 H, 15-H), 3.80 (s, 3 H, 11-H), 3.20 (dd, *J* = 7.7, 3.3 Hz, 1 H, 5-H), 2.36 (qt, *J* = 6.8, 3.5 Hz, 1 H, 12-H), 2.22 (dtdd, *J* = 9.7, 7.2, 4.7, 2.5 Hz, 1 H, 2-H), 1.81 (bs, 1 H, 14-H), 1.56–1.78 (m, 10 H, 17-H‘, 18-H‘, 19-H), 0.92–1.34 (m, 18 H, 1-H, 13-H, 16-H, 17-H, 18-H) ppm.

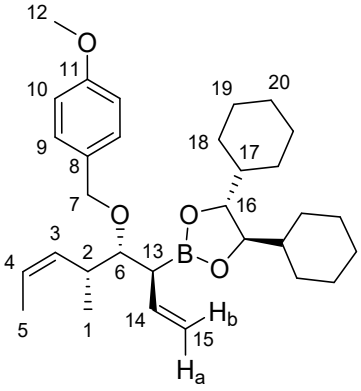
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 159.0 (s, C-10), 131.4 (s, C-7), 129.5 (d, C-8), 128.8 (d, C-3), 125.0 (d, C-4), 113.5 (d, C-9), 83.3 (d, C-15), 81.8 (d, C-5), 69.9 (t, C-6), 55.2 (q, C-11), 43.0 (d, C-16), 32.5 (d, C-2), 29.4 (d, C-12), 28.2 (t, C-17‘), 27.3 (t, C-18‘), 26.4 (t, C-19), 26.0 (t, C-17), 25.9 (t, C-18), 18.9 (q, C-1), 14.5 (q, C-13) ppm.

HRMS (CI) m/z calcd for $C_{30}H_{45}BO_4$ $[M]^+$: 480.3405, found: 480.3408.

(4*R*,5*R*)-4,5-Dicyclohexyl-2-((3*S*,4*R*,5*R*,*Z*)-4-((4-methoxybenzyl)oxy)-5-methylocta-1,6-dien-3-yl)-1,3,2-dioxaborolane (13)

According to **GP-1**, 2.13 g (4.69 mmol, 1.0 equiv) compound *ent*-**9** were reacted with 0.51 mL (7.97 mmol, 1.7 equiv) anhydrous CH_2Cl_2, 1.97 mL (4.92 mmol, 1.05 equiv, 2.5 M in hexanes) *n*-BuLi and 1.31 g (9.61 mmol, 2.05 equiv) $ZnCl_2$. Following variant **A)**, the α-chloroboronic ester *ent*-**9-Cl** (2.28 g, 4.53 mmol, 97%) was obtained as colorless oil and directly used in the next step.

Therefore, a part of the α-chloroboronic ester *ent*-**9-Cl** (485 mg, 964 µmol, 1.0 equiv) was reacted according to **GP-2** with 131 mg (964 µmol, 1.0 equiv) $ZnCl_2$ and 2.76 mL (1.93 mmol, 2.0 equiv, 0.7 M in THF) vinylmagnesium bromide. The nucleophile solution was added at –78 °C and the mixture was stirred at 0 °C for 24 h. After corresponding workup, the crude product was purified by column chromatography (SiO_2, pentane/Et_2O 9:1) and the product **13** (405 mg, 819 µmol, 95%) was obtained as a colorless oil. R_f (**13**) = 0.39 (pentane/Et_2O 9:1). $[\alpha]_D^{20}$ = –9.3 [$CHCl_3$, c = 1.00].



13

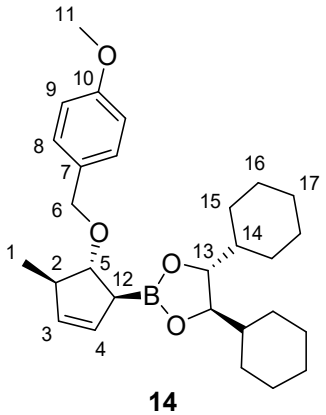
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.23–7.29 (m, 2 H, 9-H), 6.82–6.88 (m, 2 H, 10-H), 5.93 (dt, *J* = 17.1, 9.9 Hz, 1 H, 14-H), 5.25–5.46 (m, 2 H, 3-H, 4-H), 4.94–5.09 (m, 2 H, 15-H_a, 15-H_b), 4.47–4.62 (m, 2 H, 7-H), 3.75–3.83 (m, 5 H, 12-H, 16-H), 3.46 (dd, *J* = 7.0, 5.3 Hz, 1 H, 6-H), 2.83 (dquint, *J* = 9.8, 6.8 Hz, 1 H, 2-H), 2.36 (dd, *J* = 9.7, 5.0 Hz, 1 H, 13-H), 1.51–1.83 (m, 13 H, 5-H, 18-H‘, 19-H‘, 20-H), 0.86–1.43 (m, 15 H, 1-H, 17-H, 18-H, 19-H) ppm.

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 158.8 (s, C-11), 137.2 (d, C-14), 134.1 (d, C-4), 131.4 (s, C-8), 128.8 (d, C-9), 123.9 (d, C-3), 115.8 (t, C-15), 113.5 (d, C-10), 85.6 (d, C-6), 83.6 (d, C-16), 72.5 (t, C-7), 55.3 (q, C-12), 43.0 (d, C-17), 35.4 (d, C-2), 28.5 (t, C-18‘), 27.8 (t, C-19‘), 26.4 (t, C-20), 26.0 (t, C-18), 25.8 (t, C-19), 16.7 (q, C-1), 13.1 (q, C-5) ppm.

HRMS (CI) m/z calcd for $C_{31}H_{48}BO_4$ $[M+H]^+$: 495.3640, found: 495.3646.

(4*R*,5*R*)-4,5-Dicyclohexyl-2-((1*S*,4*R*,5*R*)-5-((4-methoxybenzyl)oxy)-4-methylcyclopent-2-en-1-yl)-1,3,2-dioxaborolane (14)

158 mg (321 µmol, 1.0 equiv) compound **13** were dissolved in 6.4 mL anhydrous CH_2Cl_2 and degassed with argon. Afterwards, 8.1 mg (9.6 µmol, 3 mol-%) Grubbs II catalyst (benzylidene [1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinyliden]dichloro(tricyclohexylphosphine)ruthenium) were added and the mixture was stirred over night at 40 °C. The solvent was evaporated *in vacuo* and the residue was purified by column chromatography (SiO_2, pentane/Et_2O 9:1). The product **14** (137 mg, 303 µmol, 94%) was obtained as a colorless oil. R_f (**14**) = 0.19 (pentane/Et_2O 9:1). $[\alpha]_D^{20}$ = –14.3 [$CHCl_3$, c = 1.00].



14

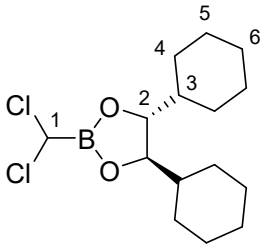
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.26–7.30 (m, 2 H, 8-H), 6.84–6.88 (m, 2 H, 9-H), 5.56 (dt, *J* = 5.8, 2.2 Hz, 1 H, 3-H), 5.54–5.58 (m, 1 H, 4-H), 4.51 (d, *J* = 11.3 Hz, 1 H, 6-H‘), 4.45 (d, *J* = 11.3 Hz, 1 H, 6-H), 3.90 (t, *J* = 3.0 Hz, 1 H, 5-H), 3.84–3.88 (m, 2 H, 13-H), 3.80 (s, 3 H, 11-H), 2.81 (q, *J* = 7.1 Hz, 1 H, 2-H), 2.35 (d, *J* = 1.9 Hz, 1 H, 12-H), 1.55–1.80 (m, 10 H, 15-H‘, 16-H‘, 17-H), 0.92–1.35 (m, 12 H, 14-H, 15-H, 16-H), 1.04 (d, *J* = 7.3 Hz, 3 H, 1-H) ppm.

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 158.9 (s, C-10), 133.0 (d, C-4), 131.0 (s, C-7), 129.2 (d, C-8), 128.4 (d, C-3), 113.6 (d, C-9), 88.3 (d, C-5), 83.5 (d, C-13), 70.4 (t, C-6), 55.2 (q, C-11), 43.0 (d, C-14), 28.3 (t, C-15‘), 27.3 (t, C-16‘), 26.4 (t, C-17), 26.0 (t, C-15), 25.8 (t, C-16), 19.2 (q, C-1) ppm.

HRMS (CI) m/z calcd for $C_{28}H_{41}BO_4$ $[M]^+$: 452.3092, found: 452.3114.

(4*R*,5*R*)-4,5-Dicyclohexyl-2-(dichloromethyl)-1,3,2-dioxaborolane (15)[6]

3.39 g (15.9 mmol, 1.0 equiv) diisopropyl (dichloromethyl)boronate[7] were dissolved in 64 mL *n*-hexane, 3.61 g (15.9 mmol, 1.0 equiv) (*R*,*R*)-DICHED[8] were added and the mixture was stirred at room temperature. Once the starting materials were completely dissolved (approx. 10 min), complete conversion was indicated by TLC analysis. The mixture was filtrated, the solvent was evaporated and the product was dried *in vacuo*. Compound **15** (5.07 g, 15.9 mmol, 100%) was obtained as a colorless oil, which solidified to a white, wax-like solid upon storing in the fridge. The compound was stored at 4 °C and used in the next step without further purification. $[\alpha]_D^{20}$ = +52.1 [$CHCl_3$, c = 1.00]



15

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.39 (s, 1 H, 1-H), 4.03–4.09 (m, 2 H, 2-H), 1.59–1.83 (m, 10 H, 4-H‘, 5-H‘, 6-H), 1.37–1.48 (m, 2 H, 3-H), 0.94–1.29 (m, 10 H, 4-H, 5-H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 84.9 (d, C-2), 42.7 (d, C-3), 28.0 (t, C-4‘), 27.1 (t, C-5‘), 26.3 (t, C-6), 25.9 (t, C-4), 25.8 (t, C-5) ppm.

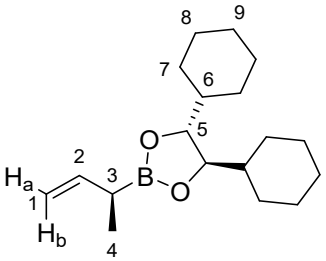
HRMS (CI) m/z calcd for $C_{15}H_{26}BCl_2O_2$ $[M+H]^+$: 319.1397, found: 319.1403.

(4*R*,5*R*)-2-((*S*)-But-3-en-2-yl)-4,5-dicyclohexyl-1,3,2-dioxaborolane (16)

1.50 g (4.70 mmol, 1.0 equiv) **15** and 801 mg (5.88 mmol, 1.25 equiv) $ZnCl_2$ (flame-dried *in vacuo*) were dissolved in 31.3 mL anhydrous THF and 7.72 mL (5.41 mmol, 1.15 equiv, 0.7 M in THF) vinylmagnesium

[6] K. Ditrich, T. Bube, R. Stürmer, R. W. Hoffmann, *Angew. Chem. Int. Ed.* **1986**, *25*, 1028–1030.
[7] M. W. Rathke, E. Chao, G. Wu, *J. Organomet. Chem.* **1976**, *122*, 145–149.
[8] W. C. Hiscox, D. S. Matteson, *J. Org. Chem.* **1996**, *61*, 8315–8316.

bromide were added at –78 °C. The reaction mixture stirred overnight under warming to 0 °C, cooled to –100 °C and 4.61 mL (11.8 mmol, 2.5 equiv, 2.55 M in THF) methylmagnesium bromide were added. Afterwards, the mixture was stirred at –100 °C for 30 min and then transferred to a separating funnel with saturated NH_4Cl solution and pentane without further warming. The phases were separated, the aqueous phase was extracted with pentane and the combined organic phases were dried over Na_2SO_4. The solvent was evaporated and the crude product was purified by column chromatography (SiO_2, pentane/Et_2O 98:2). The product **16** (1.08 g, 3.70 mmol, 79%) was obtained as a colorless oil. The amount of formed byproduct (4*R*,5*R*)-4,5-dicyclohexyl-2-methyl-1,3,2-dioxaborolane was determined by ^{1}H NMR analysis of the crude reaction mixture and was 9%. R_f (**16**) = 0.69 (pentane/Et_2O 9:1). $[\alpha]_D^{20}$ = +41.5 [$CHCl_3$, c = 1.00].



16

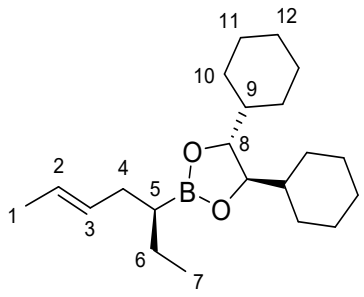
^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.98 (ddd, *J* = 17.2, 10.2, 7.3 Hz, 1 H, 2-H), 4.98 (dt, *J* = 17.2, 1.7 Hz, 1 H, 1-H_b), 4.93 (dt, *J* = 10.2, 1.7 Hz, 1 H, 1-H_b), 3.83–3.87 (m, 2 H, 5-H), 1.96 (quint, *J* = 7.3 Hz, 1 H, 3-H), 1.71–1.80 (m, 6 H, 7-H‘‘‘, 8-H‘‘, 9-H‘), 1.64–1.70 (m, 2 H, 9-H), 1.56–1.60 (m, 2 H, 7-H‘‘), 1.29–1.37 (m, 2 H, 6-H), 1.14–1.26 (m, 6 H, 7-H‘, 8-H‘), 1.13 (d, *J* = 7.3 Hz, 3 H, 4-H), 0.99–1.08 (m, 2 H, 7-H), 0.90–0.98 (m, 2 H, 8-H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.2 (d, C-2), 111.7 (t, C-1), 83.3 (d, C-5), 42.0 (d, C-6), 28.1 (t, C-7), 27.3 (t, C-8), 26.4 (t, C-9), 26.0 (t, C-7), 25.9 (t, C-8), 14.3 (q, C-4) ppm.

HRMS (CI) m/z calcd for $C_{18}H_{32}BO_2$ $[M+H]^+$: 291.2490, found: 291.2496.

(4*R*,5*R*)-4,5-Dicyclohexyl-2-((*S*,*E*)-hept-5-en-3-yl)-1,3,2-dioxaborolane (17)

According to **GP-1**, 554 mg (1.91 mmol, 1.0 equiv) compound **16** were reacted with 0.21 mL (3.24 mmol, 1.7 equiv) anhydrous CH_2Cl_2, 0.80 mL (2.00 mmol, 1.05 equiv, 2.5 M in hexanes) *n*-BuLi and 273 mg (2.00 mmol, 1.05 equiv) $ZnCl_2$. Following variant **B)**, the nucleophile solution consisting of 2.03 mL (4.77 mmol, 2.5 equiv, 2.35 M in Et_2O) ethylmagnesium bromide was added at –78 °C. The reaction mixture was stirred for 24 h at 0 °C and after corresponding workup, the crude product was purified by column chromatography (SiO_2, pentane/Et_2O 97:3). The product **17** (557 mg, 1.68 mmol, 88%) was obtained as a colorless oil. R_f (**17**) = 0.56 (pentane/Et_2O 95:5). $[\alpha]_D^{20}$ = –39.2 [$CHCl_3$, c = 1.00].



17

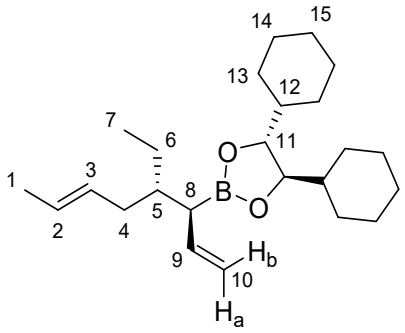
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.35–5.47 (m, 2 H, 2-H, 3-H), 3.81–3.84 (m, 2 H, 8-H), 2.09–2.21 (m, 2 H, 4-H), 1.56–1.82 (m, 13 H, 1-H, 10-H‘, 11-H‘, 12-H), 1.41–1.49 (m, 2 H, 6-H), 0.94–1.34 (m, 13 H, 5-H, 9-H, 10-H, 11-H), 0.92 (t, *J* = 7.4 Hz, 3 H, 7-H) ppm.

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 130.7 (d, C-3), 123.8 (d, C-2), 83.3 (d, C-8), 43.1 (d, C-9), 28.4 (t, C-10‘), 28.0 (t, C-4), 27.5 (t, C-11‘), 26.5 (t, C-12), 26.0 (t, C-10), 25.9 (t, C-11), 23.9 (t, C-6), 13.6 (q, C-7), 12.9 (q, C-1) ppm.

HRMS (CI) m/z calcd for $C_{21}H_{38}BO_2$ $[M+H]^+$: 333.2959, found: 333.2951.

(4*R*,5*R*)-4,5-Dicyclohexyl-2-((3*S*,4*S*,*E*)-4-ethylocta-1,6-dien-3-yl)-1,3,2-dioxaborolan (18)

According to **GP-1**, 502 mg (1.51 mmol, 1.0 equiv) compound **17** were reacted with 0.17 mL (2.57 mmol, 1.7 equiv) anhydrous CH_2Cl_2, 0.64 mL (1.59 mmol, 1.05 equiv, 2.5 M in hexanes) *n*-BuLi and 216 mg (1.59 mmol, 1.05 equiv) $ZnCl_2$. Following variant **B)**, the nucleophile solution consisting of 5.39 mL (3.78 mmol, 2.5 equiv, 0.7 M in THF) vinylmagnesium bromide was added at –78 °C. The reaction mixture was stirred for 24 h at 0 °C and after corresponding workup, the crude product was purified by column chromatography (SiO_2, pentane/Et_2O 97:3). The product **18** (527 mg, 1.36 mmol, 90%, purity 96% with impurity (4*R*,5*R*)-4,5-dicyclohexyl-2-vinyl-1,3,2-dioxaborolane) was obtained as a colorless oil. R_f (**18**) = 0.41 (pentane/Et_2O 97:3). $[\alpha]_D^{20}$ = +17.5 [$CHCl_3$, c = 1.00].



18

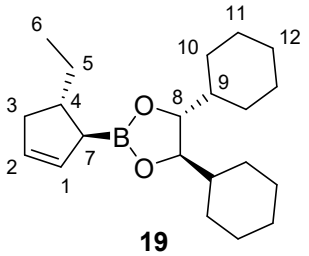
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.81 (dt, *J* = 16.9, 10.0 Hz, 1 H, 9-H), 5.43–5.41 (m, 1 H, 2-H), 5.34–5.42 (m, 1 H, 3-H), 4.95–5.02 (m, 2 H, 10-H_a, 10-H_b), 3.79–3.85 (m, 2 H, 11-H), 2.09–2.18 (m, 1 H, 4-H‘), 1.94–2.06 (m, 2 H, 4-H, 8-H), 1.55–1.82 (m, 14 H, 1-H, 5-H, 13-H‘, 14-H‘, 15-H), 0.93–1.36 (m, 14 H, 6-H, 12-H, 13-H, 14-H), 0.87 (t, *J* = 7.4 Hz, 3 H, 7-H) ppm.

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 138.5 (d, C-9), 129.2 (d, C-3), 124.6 (d, C-2), 114.9 (t, C-10), 83.4 (d, C-11), 43.0 (d, C-12), 41.1 (d, C-5), 29.1 (t, C-4), 28.4 (t, C-13‘), 27.6 (t, C-14‘), 26.5 (t, C-15), 26.0 (t, C-13), 25.9 (t, C-14), 25.4 (t, C-6), 13.0 (q, C-1), 11.6 (q, C-7) ppm.

HRMS (CI) m/z calcd for $C_{24}H_{42}BO_2$ $[M+H]^+$: 373.3272, found: 373.3280.

(4*R*,5*R*)-4,5-Dicyclohexyl-2-((1*R*,5*S*)-5-ethylcyclopent-2-en-1-yl)-1,3,2-dioxaborolane (19)

476 mg (1.28 mmol, 1.0 equiv) compound **18** were dissolved in 25.6 mL anhydrous CH_2Cl_2 and degassed with argon. Afterwards, 33.0 mg (38 µmol, 3 mol-%) Grubbs II catalyst (benzylidene [1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinyliden]dichloro(tricyclohexylphosphine)ruthenium) were added and the mixture was stirred over night at 40 °C. The solvent was evaporated *in vacuo* and the residue was purified by column chromatography (C-18-SiO_2, MeCN/H_2O). The product **19** (395 mg, 1.20 mmol, 94%) was obtained as a colorless oil. R_f (**19**) = 0.54 (pentane/Et_2O 95:5). $[\alpha]_D^{20}$ = +10.7 [$CHCl_3$, c = 1.00].



19

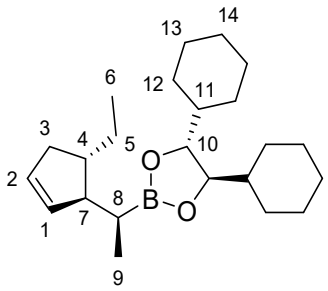
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.61–5.66 (m, 2 H, 1-H, 2-H), 3.83–3.87 (m, 2 H, 8-H), 2.49–2.59 (m, 1 H, 7-H), 2.24–2.32 (m, 1 H, 4-H), 1.97–2.03 (m, 1 H, 3-H‘), 1.86 (dd, *J* = 6.5, 3.0 Hz, 1 H, 3-H), 1.55–1.76 (m, 10 H, 10-H‘, 11-H‘, 12-H), 1.37–1.51 (m, 2 H, 5-H), 0.93–1.36 (m, 12 H, 9-H, 10-H, 11-H), 0.90 (t, *J* = 7.3 Hz, 3 H, 6 H) ppm.

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 130.8 (d, C-2), 128.8 (d, C-1), 83.3 (d, C-8), 43.0 (d, C-9), 42.6 (d, C-4), 39.1 (t, C-3), 29.7 (t, C-5), 28.2 (t, C-10‘), 27.3 (t, C-11‘), 26.5 (t, C-12), 26.0 (t, C-10), 25.9 (t, C-11), 12.7 (q, C-6) ppm.

HRMS (CI) m/z calcd for $C_{21}H_{34}BO_2$ $[M-H]^-$: 329.2657, found: 329.2657.

(4*R*,5*R*)-4,5-Dicyclohexyl-2-((*S*)-1-((1*R*,5*S*)-5-ethylcyclopent-2-en-1-yl)ethyl)-1,3,2-dioxaborolane (20)

According to **GP-1**, 280 mg (848 µmol, 1.0 equiv) compound **19** were reacted with 0.10 mL (1.44 mmol, 1.7 equiv) anhydrous CH_2Cl_2, 0.36 mL (890 µmol, 1.05 equiv, 2.5 M in hexanes) *n*-BuLi and 121 mg (890 µmol, 1.05 equiv) $ZnCl_2$. Following variant **B)**, the nucleophile solution consisting of 0.83 mL (2.12 mmol, 2.5 equiv, 2.55 M in THF) methylmagnesium bromide was added at –78 °C. The reaction mixture was stirred for 24 h at room temperature and after corresponding workup, the crude product was purified by column chromatography (C-18-SiO_2, MeCN/H_2O). The product **20** (187 mg, 747 µmol, 88%) was obtained as a colorless oil. R_f (**20**) = 0.43 (pentane/Et_2O 97:3). $[\alpha]_D^{20}$ = +67.6 [$CHCl_3$, c = 1.00].



20

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.59–5.63 (m, 2 H, 1-H, 2-H), 3.80–3.83 (m, 2 H, 10-H), 2.48 (ddd, *J* = 16.6, 8.6, 2.8 Hz, 1 H, 3-H‘), 2.37 (bs, 1 H, 4-H), 1.93 (dd, *J* = 15.4, 4.4 Hz, 1 H, 3-H), 1.80–1.86 (m, 1 H, 7-H), 1.56–1.79 (m, 10 H, 12-H‘, 13-H‘, 14-H), 1.44–1.53 (m, 1 H, 5-H‘), 1.00–1.34 (m, 14 H, 5-H, 8-H, 11-H, 12-H, 13-H), 0.98 (d, *J* = 7.3 Hz, 3 H, 9-H), 0.89 (t, *J* = 7.4 Hz, 3 H) ppm.

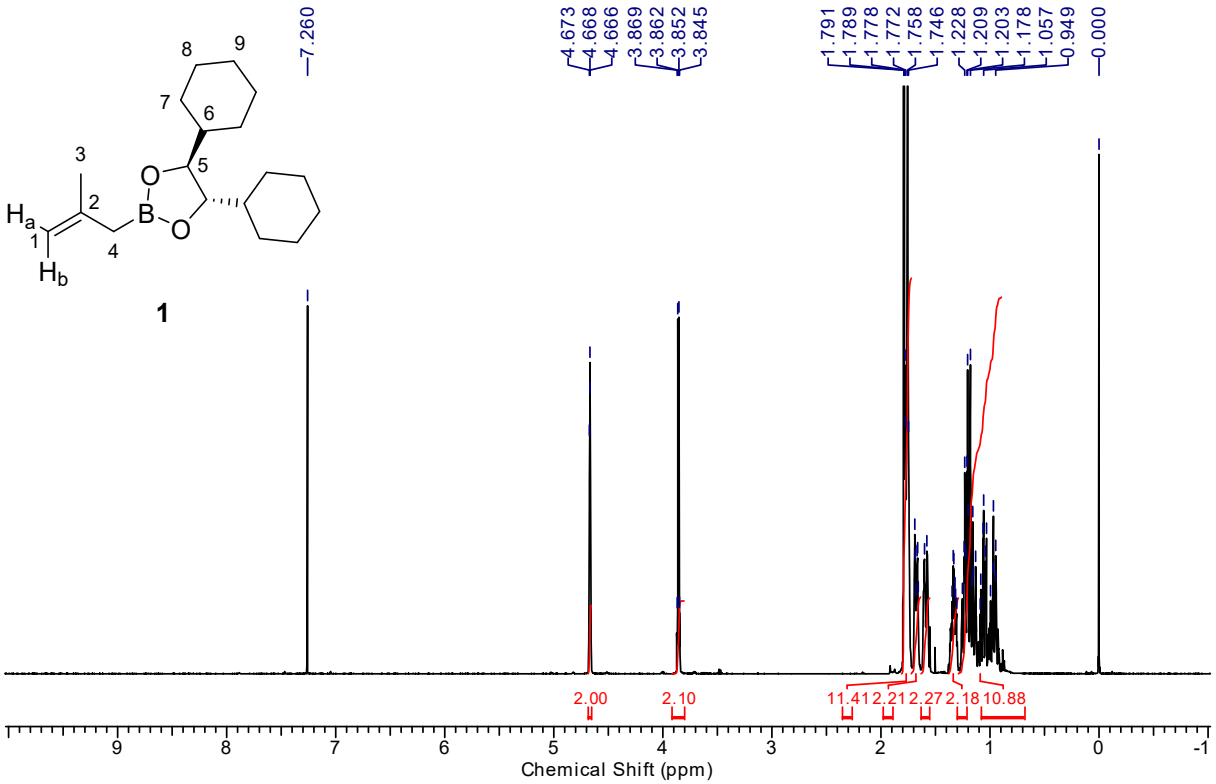
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 133.9 (d, C-1), 128.9 (d, C-2), 83.2 (d, C-10), 54.7 (d, C-4), 43.4 (d, C-7), 43.1 (d, C-11), 38.5 (t, C-3), 29.7 (t, C-5), 28.3 (t, C-12‘), 27.5 (t, C-13‘), 26.5 (t, C-14), 26.0 (t, C-12), 25.9 (t, C-13), 13.6 (q, C-9), 12.2 (q, C-6) ppm.

HRMS (CI) m/z calcd for $C_{23}H_{40}BO_2$ $[M+H]^+$: 359.3116, found: 359.3120.

Copies of NMR spectra

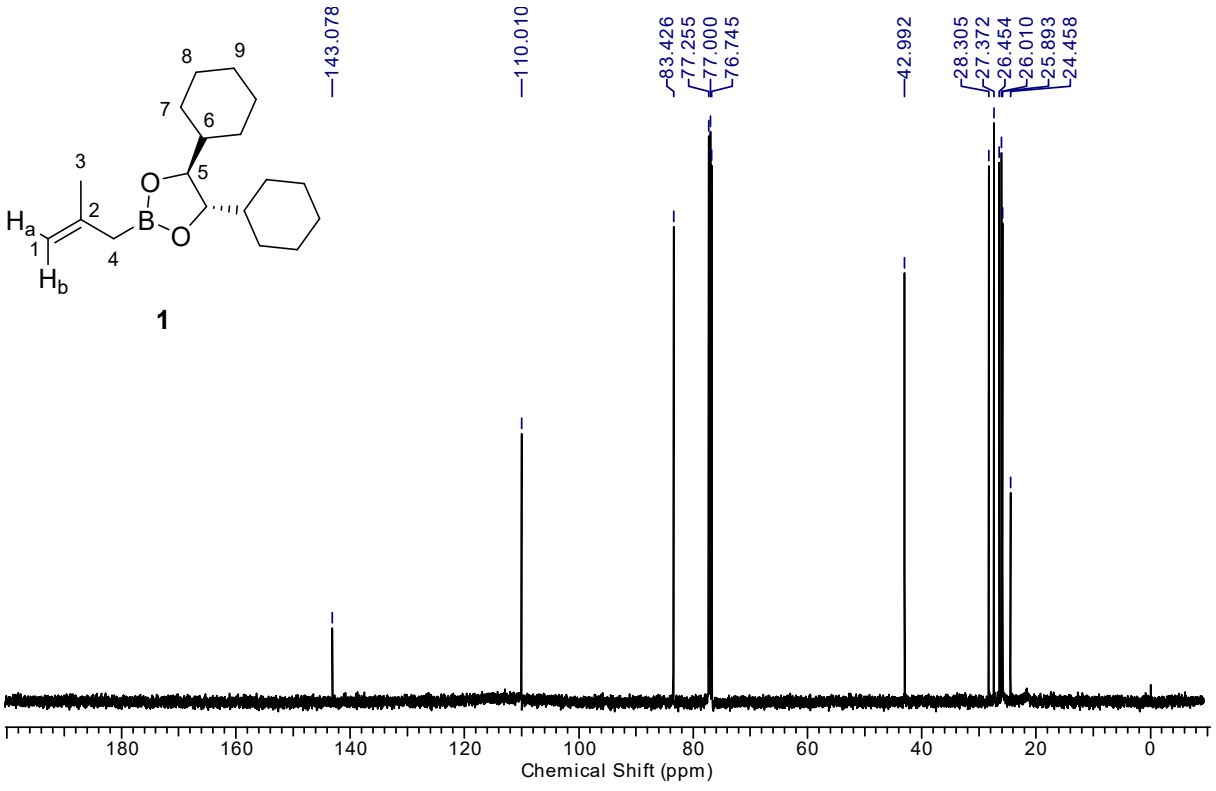
(4*S*,5*S*)-4,5-Dicyclohexyl-2-(2-methylallyl)-1,3,2-dioxaborolane (1)

^{1}H NMR (500 MHz, $CDCl_3$):



1

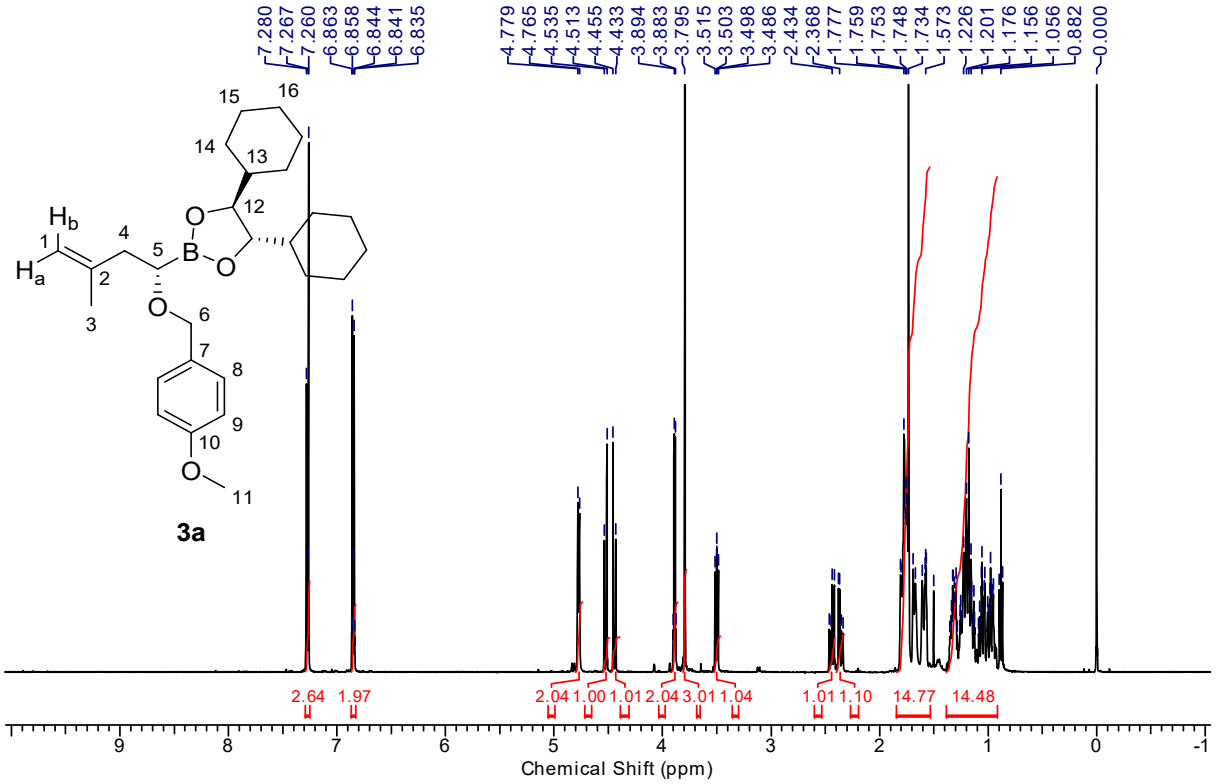
^{13}C NMR (125 MHz, $CDCl_3$):



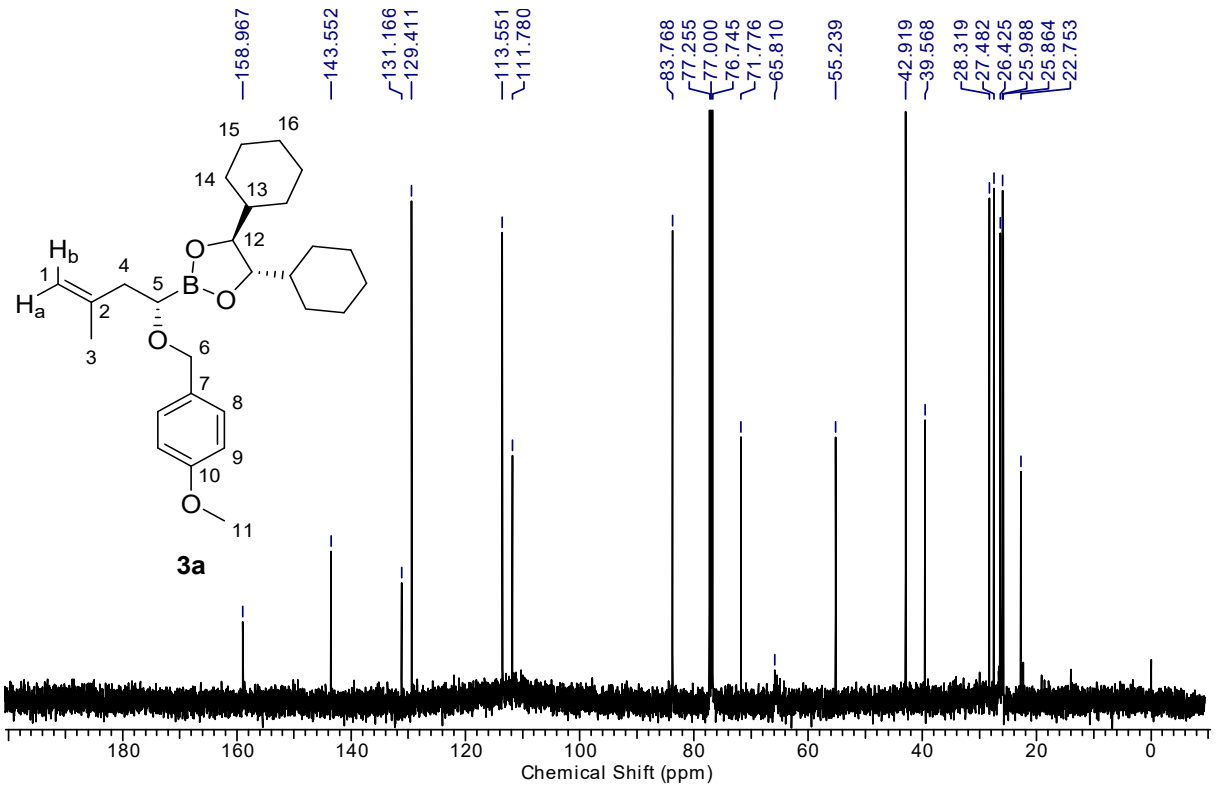
1

(4*S*,5*S*)-4,5-Dicyclohexyl-2-((*S*)-1-((4-methoxybenzyl)oxy)-3-methylbut-3-en-1-yl)-1,3,2-dioxaborolane (3a)

^{1}H NMR (500 MHz, $CDCl_3$):

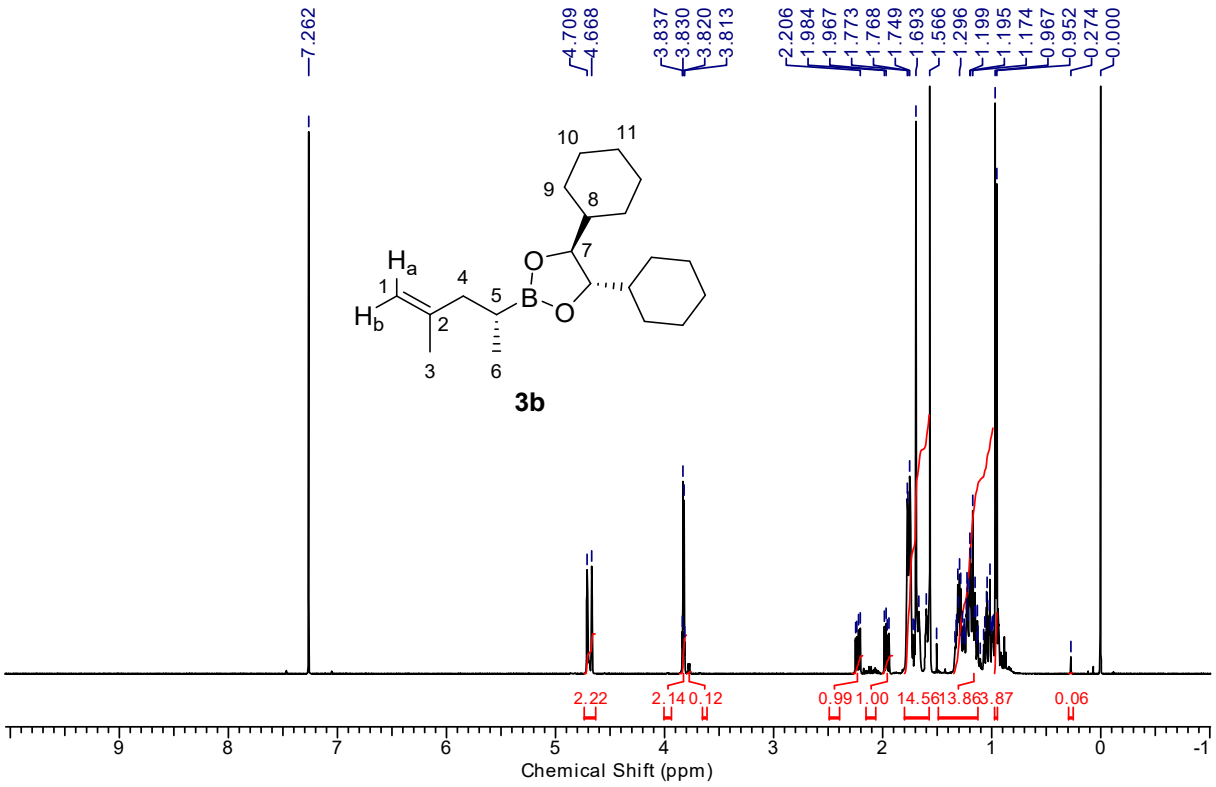


^{13}C NMR (125 MHz, $CDCl_3$):

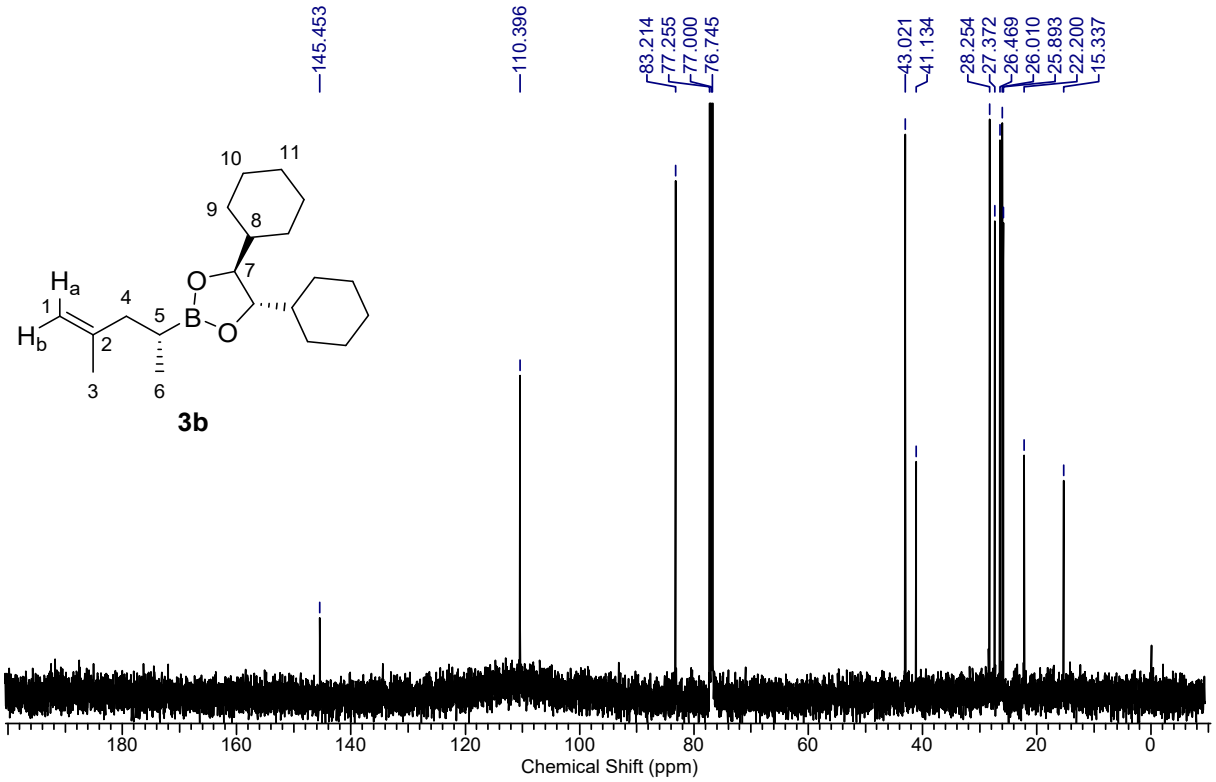


(4*S*,5*S*)-4,5-Dicyclohexyl-2-((*R*)-4-methylpent-4-en-2-yl)-1,3,2-dioxaborolane (3b)

^{1}H NMR (500 MHz, $CDCl_3$):

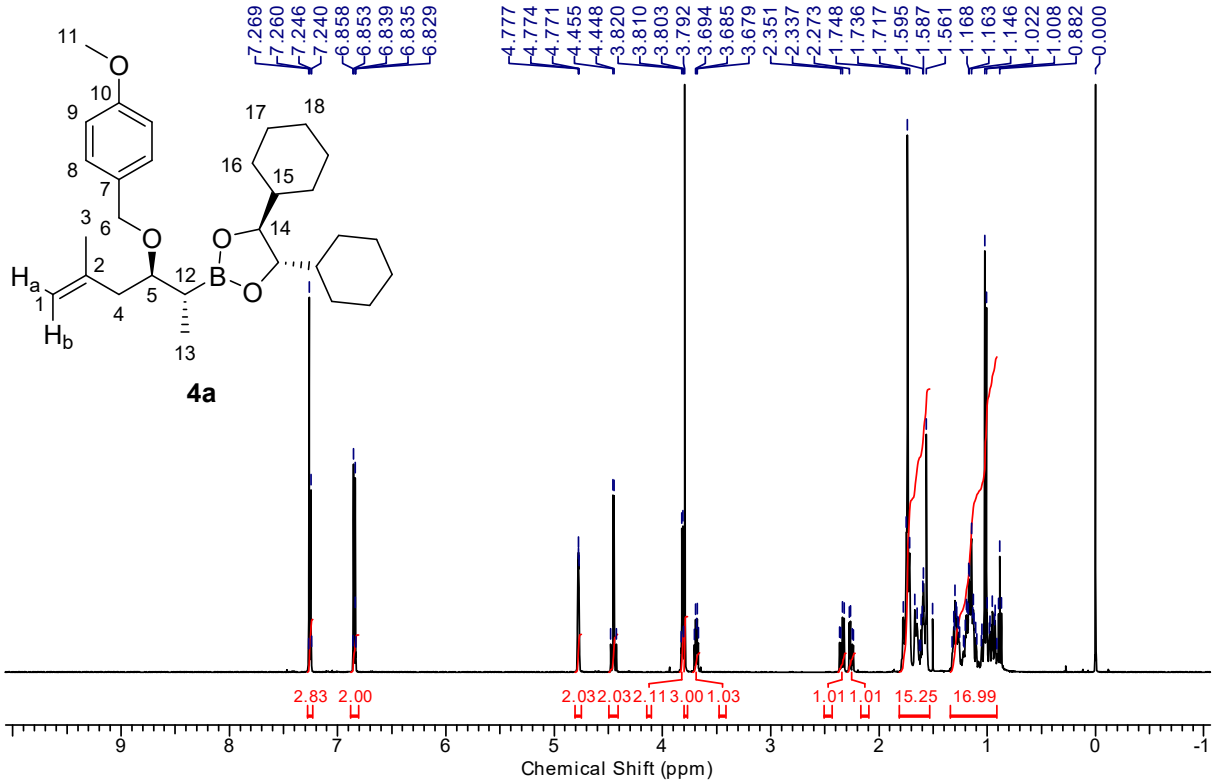


^{13}C NMR (125 MHz, $CDCl_3$):

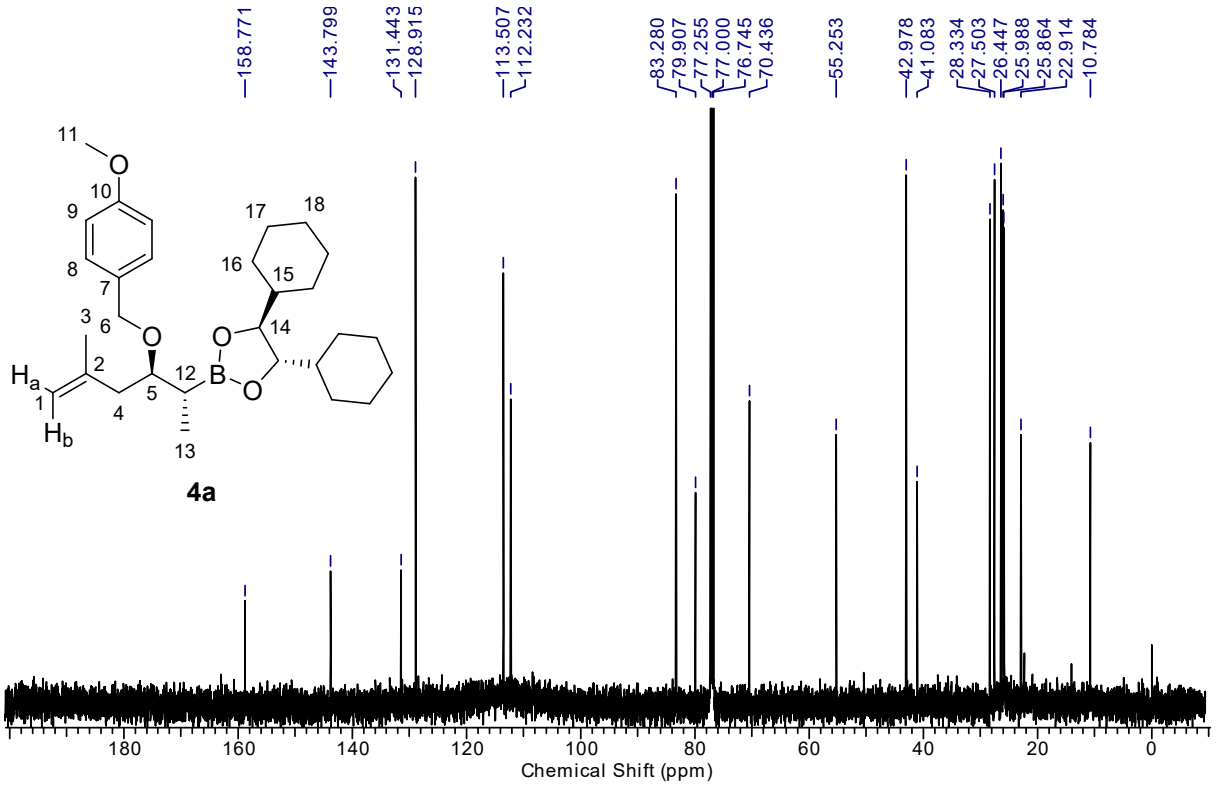


(4*S*,5*S*)-4,5-Dicyclohexyl-2-((2*R*,3*R*)-3-((4-methoxybenzyl)oxy)-5-methylhex-5-en-2-yl)-1,3,2-dioxaborolane (4a)

^{1}H NMR (500 MHz, $CDCl_3$):

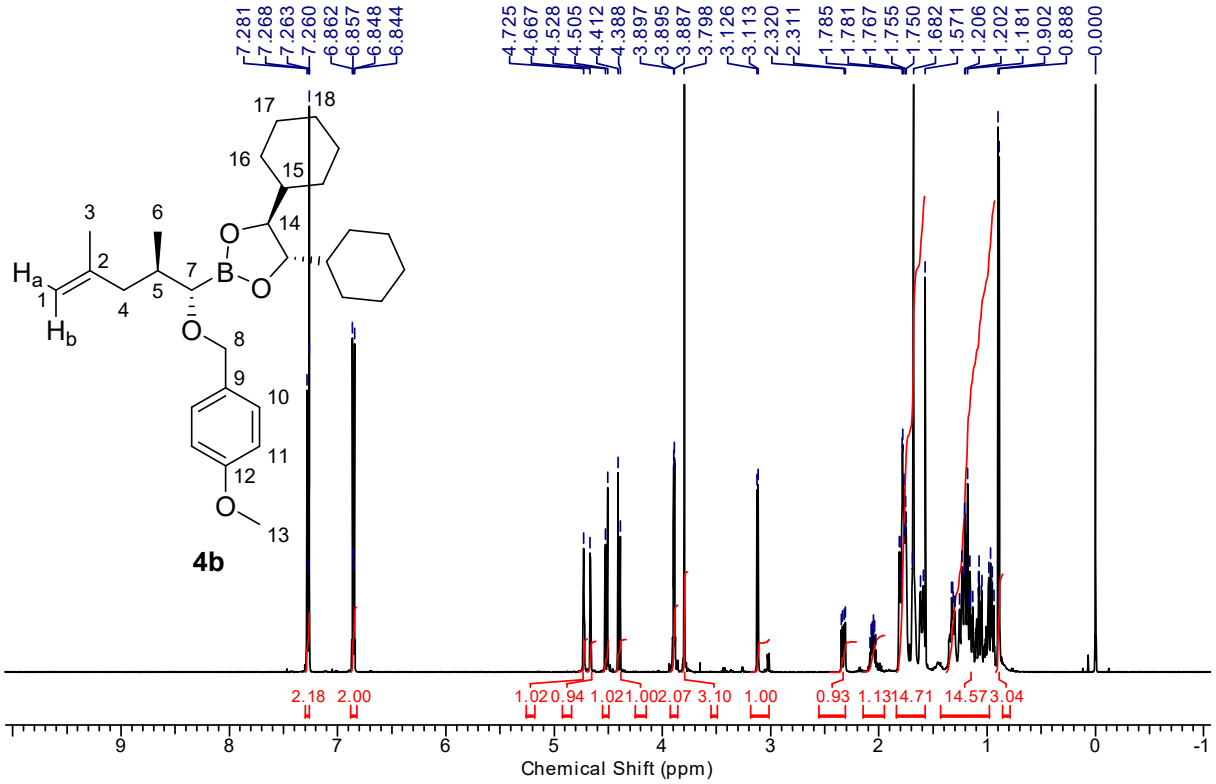


^{13}C NMR (125 MHz, $CDCl_3$):

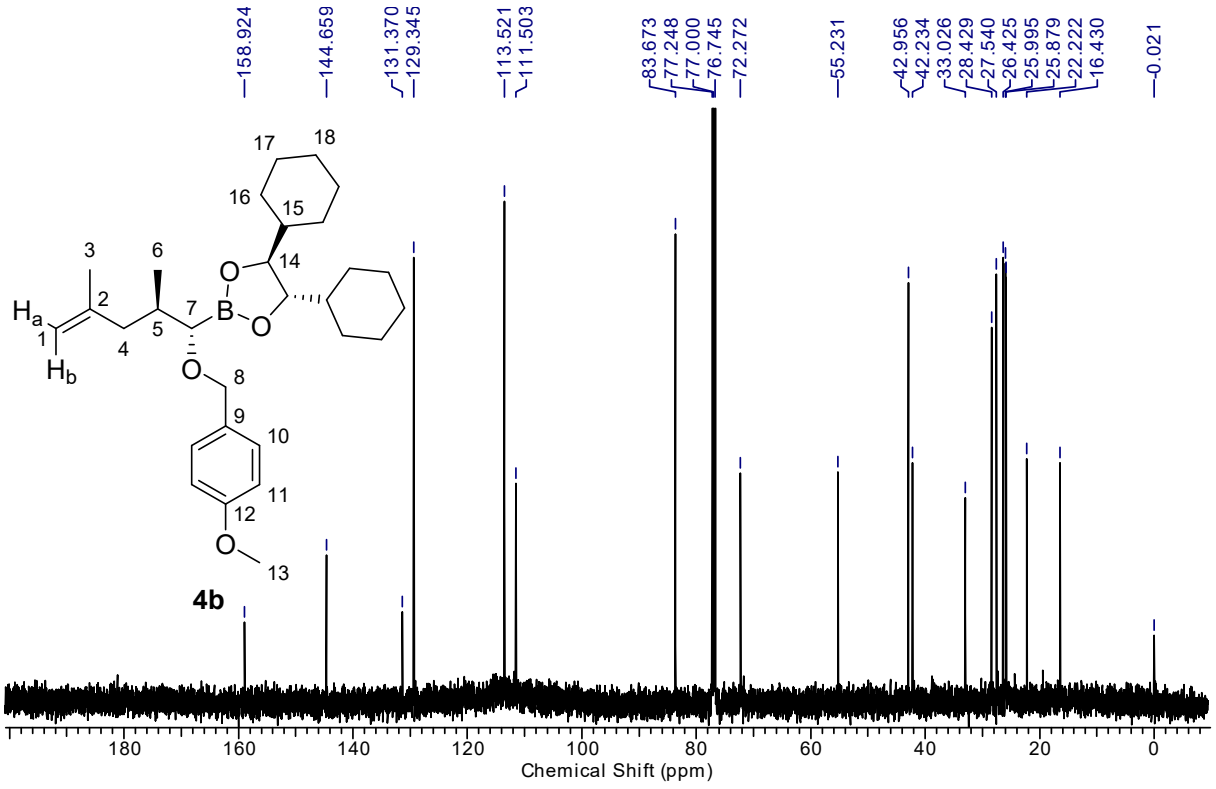


(4*S*,5*S*)-4,5-Dicyclohexyl-2-((1*S*,2*R*)-1-((4-methoxybenzyl)oxy)-2,4-dimethylpent-4-en-1-yl)-1,3,2-dioxaborolane (4b)

^{1}H NMR (500 MHz, $CDCl_3$):

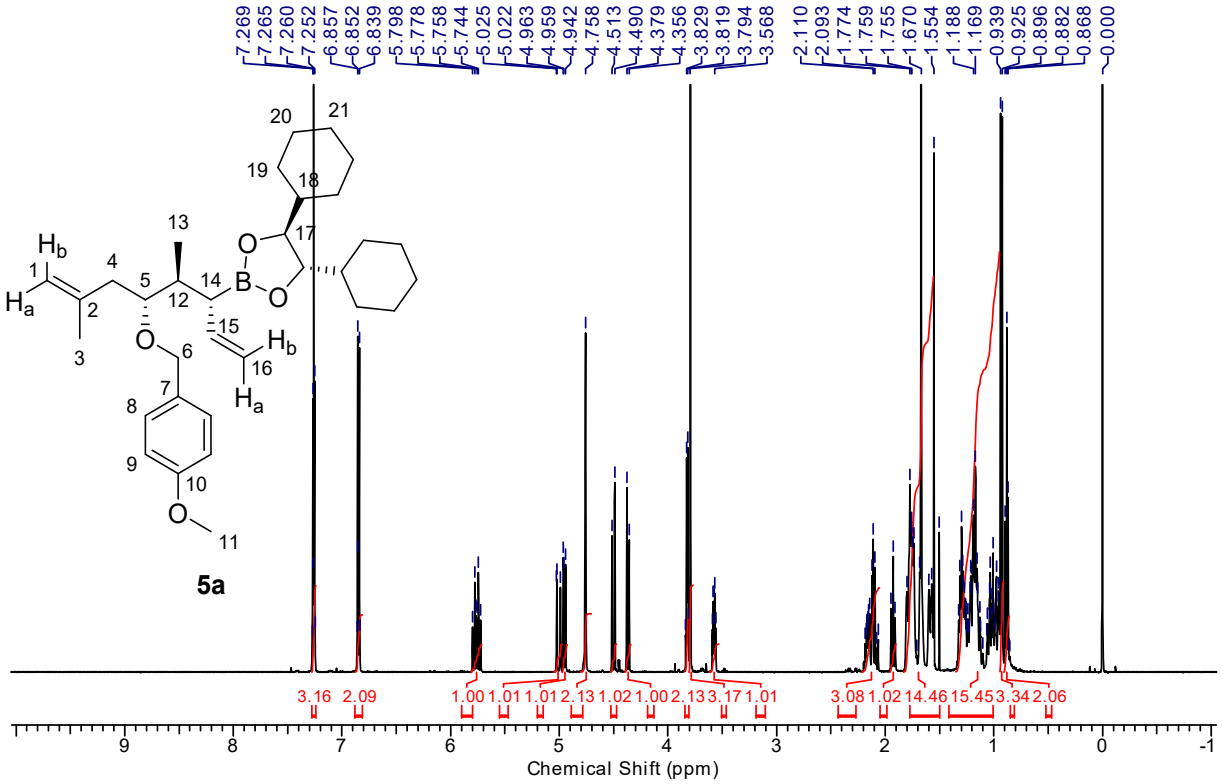


^{13}C NMR (125 MHz, $CDCl_3$):

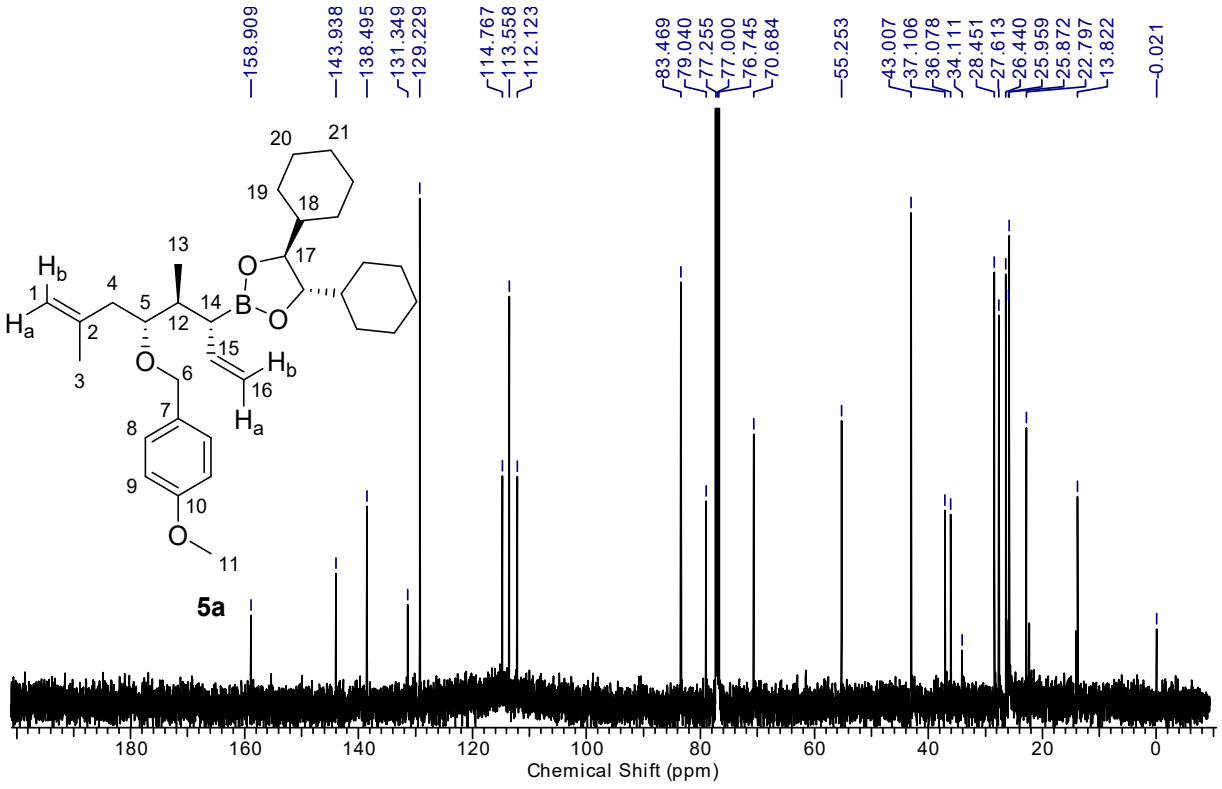


(4*S*,5*S*)-4,5-Dicyclohexyl-2-((3*R*,4*S*,5*R*)-5-((4-methoxybenzyl)oxy)-4,7-dimethylocta-1,7-dien-3-yl)-1,3,2-dioxaborolane (5a)

^{1}H NMR (500 MHz, $CDCl_3$):

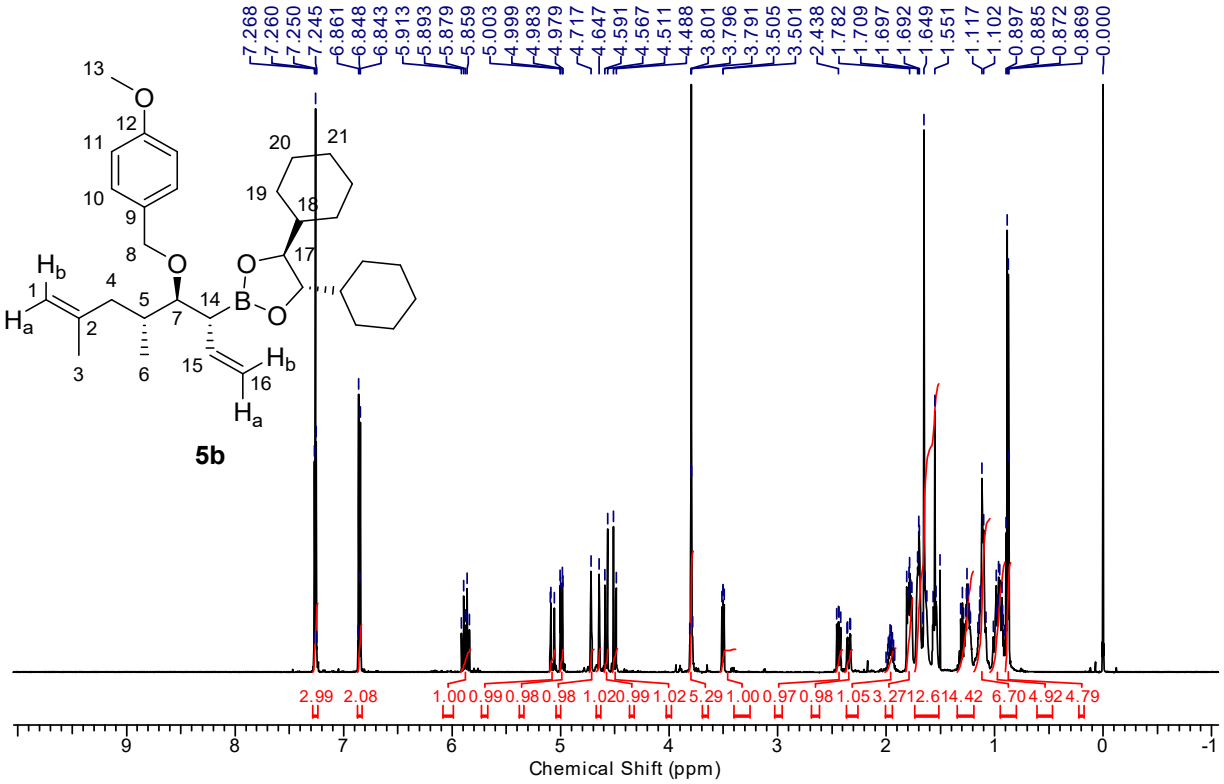


^{13}C NMR (125 MHz, $CDCl_3$):

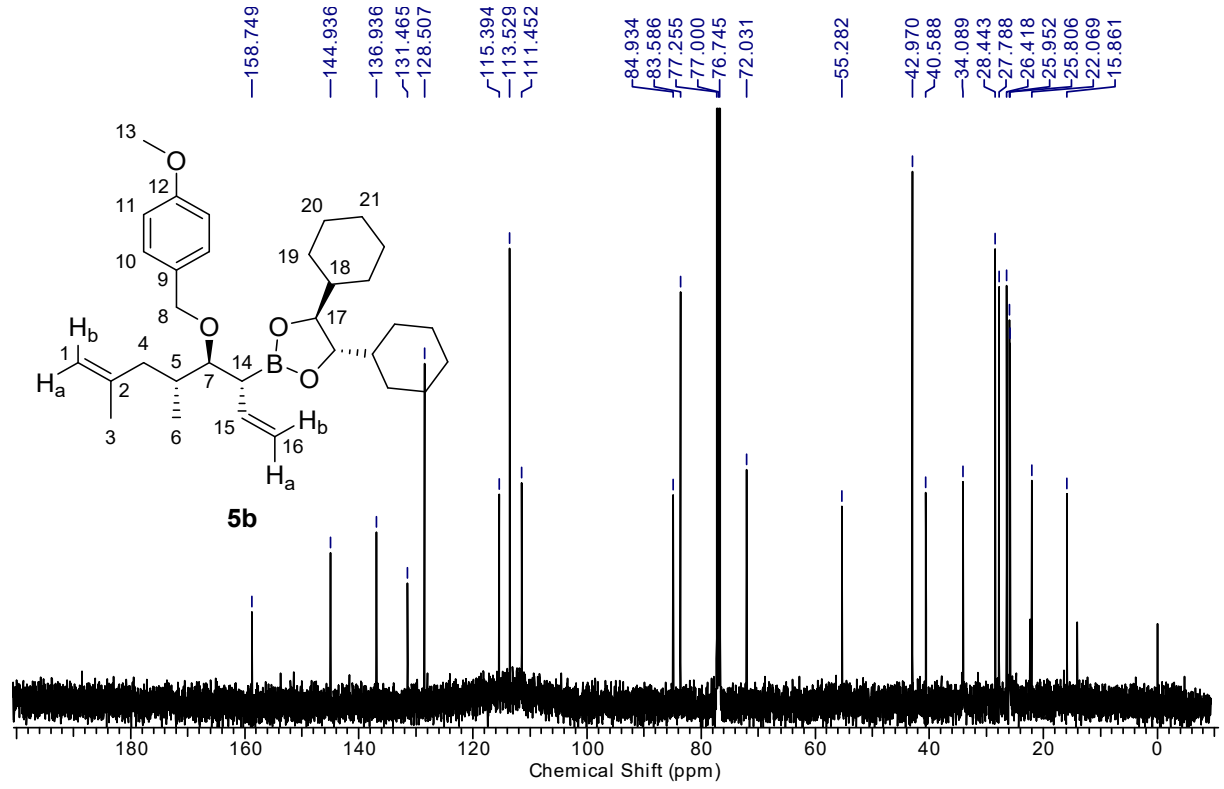


(4*S*,5*S*)-4,5-Dicyclohexyl-2-((3*R*,4*S*,5*R*)-4-((4-methoxybenzyl)oxy)-5,7-dimethylocta-1,7-dien-3-yl)-1,3,2-dioxaborolane (5b)

^{1}H NMR (500 MHz, $CDCl_3$):

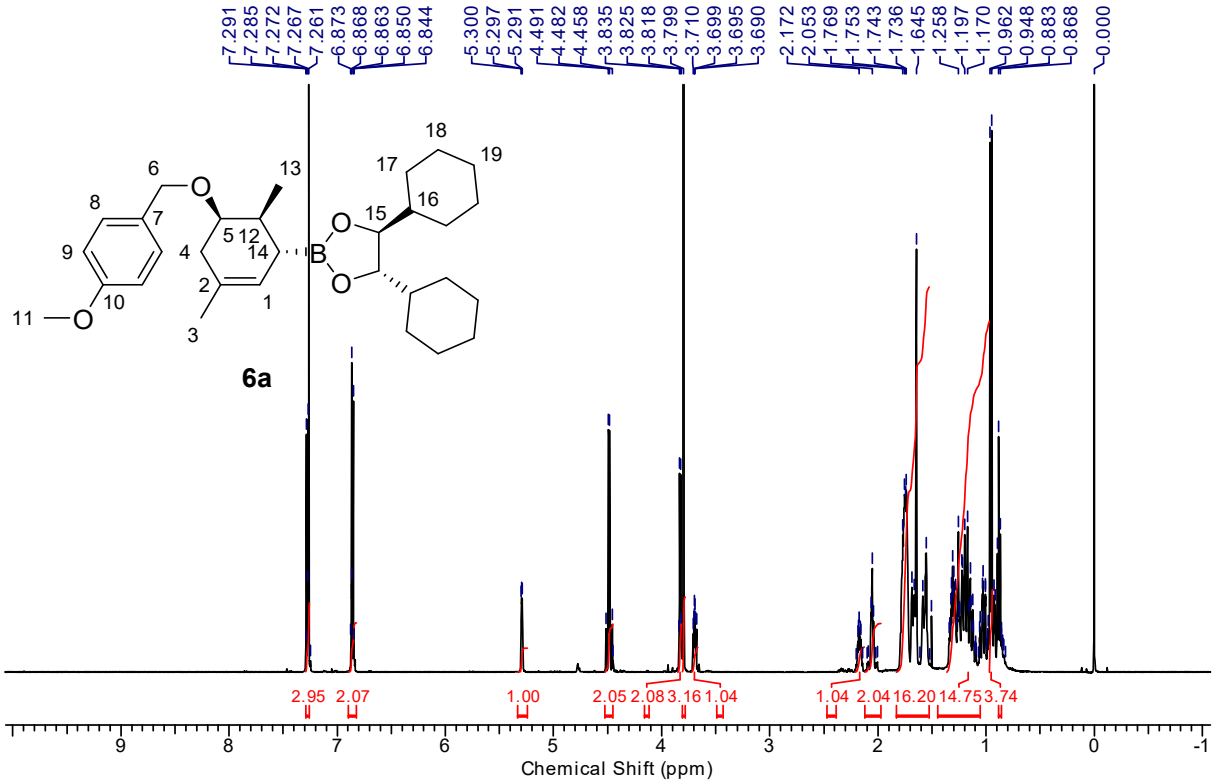


^{13}C NMR (125 MHz, $CDCl_3$):

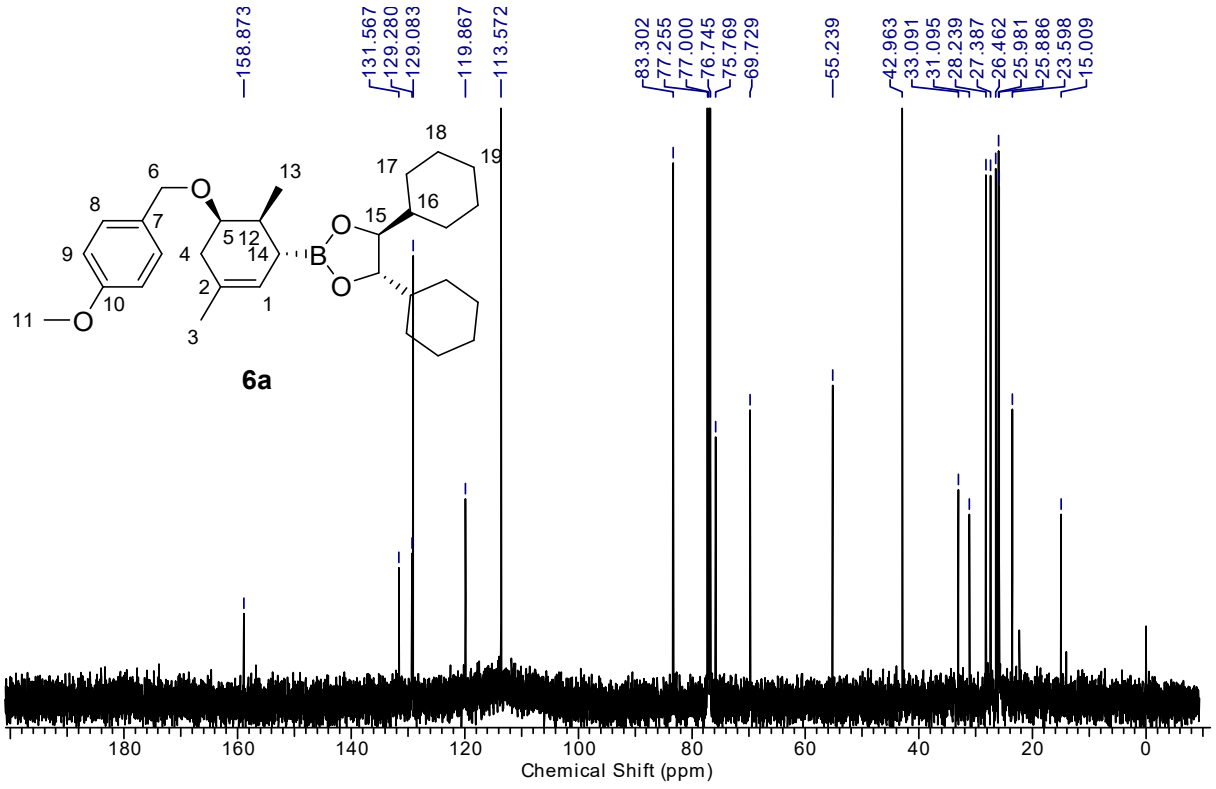


(4*S*,5*S*)-4,5-Dicyclohexyl-2-((1*R*,5*R*,6*S*)-5-((4-methoxybenzyl)oxy)-3,6-dimethylcyclohex-2-en-1-yl)-1,3,2-dioxaborolane (6a)

^{1}H NMR (500 MHz, $CDCl_3$):

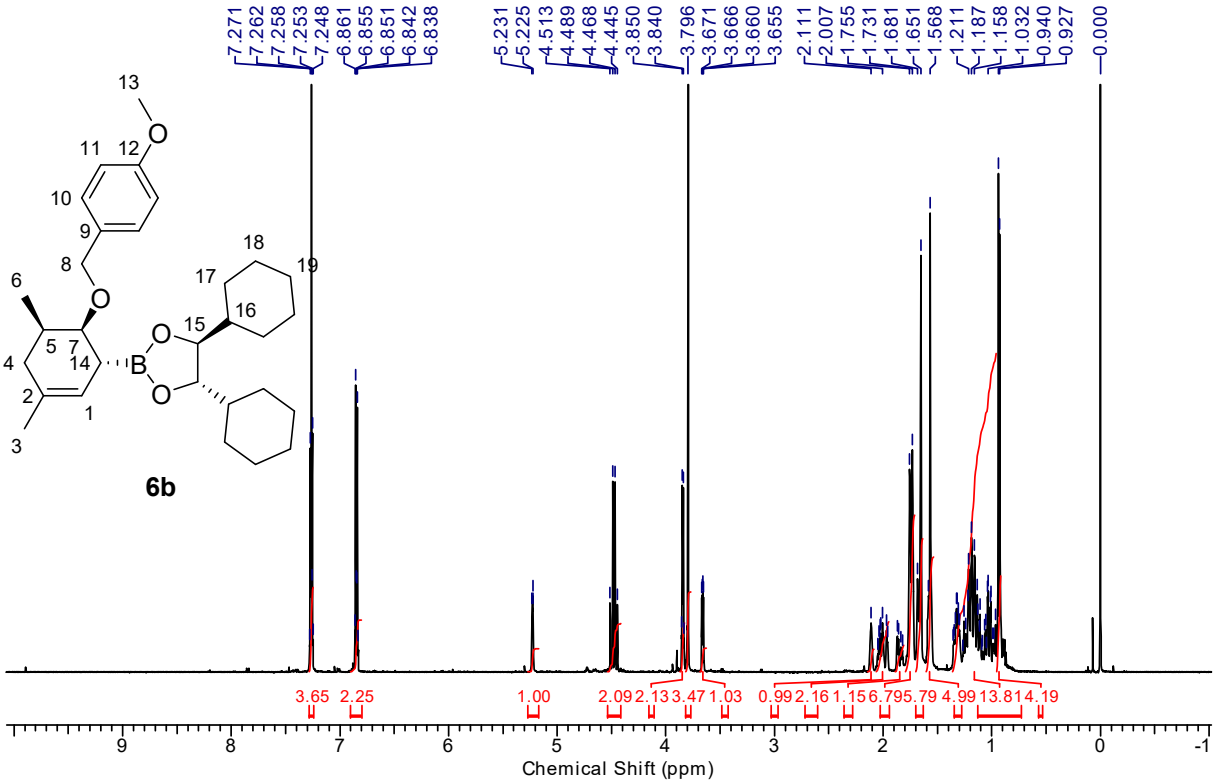


^{13}C NMR (125 MHz, $CDCl_3$):

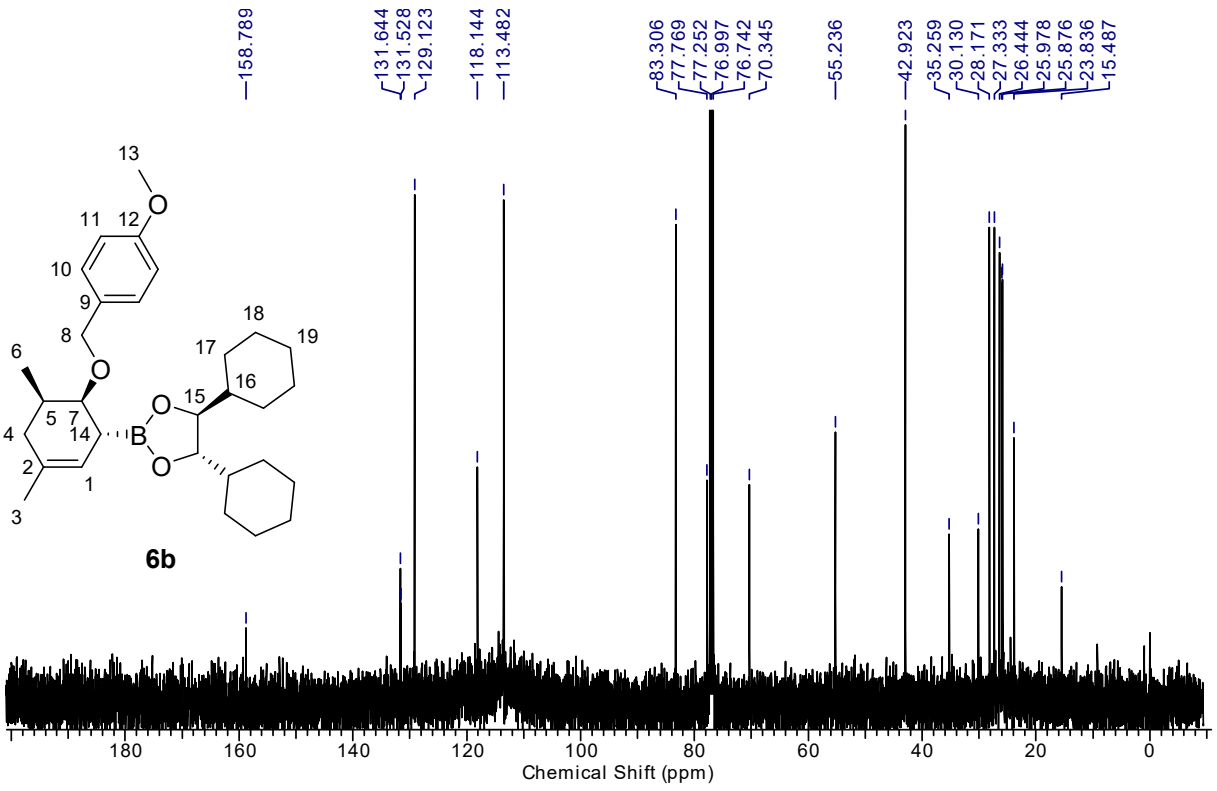


(4*S*,5*S*)-4,5-Dicyclohexyl-2-((1*R*,5*R*,6*S*)-6-((4-methoxybenzyl)oxy)-3,5-dimethylcyclohex-2-en-1-yl)-1,3,2-dioxaborolane (6b)

^{1}H NMR (500 MHz, $CDCl_3$):

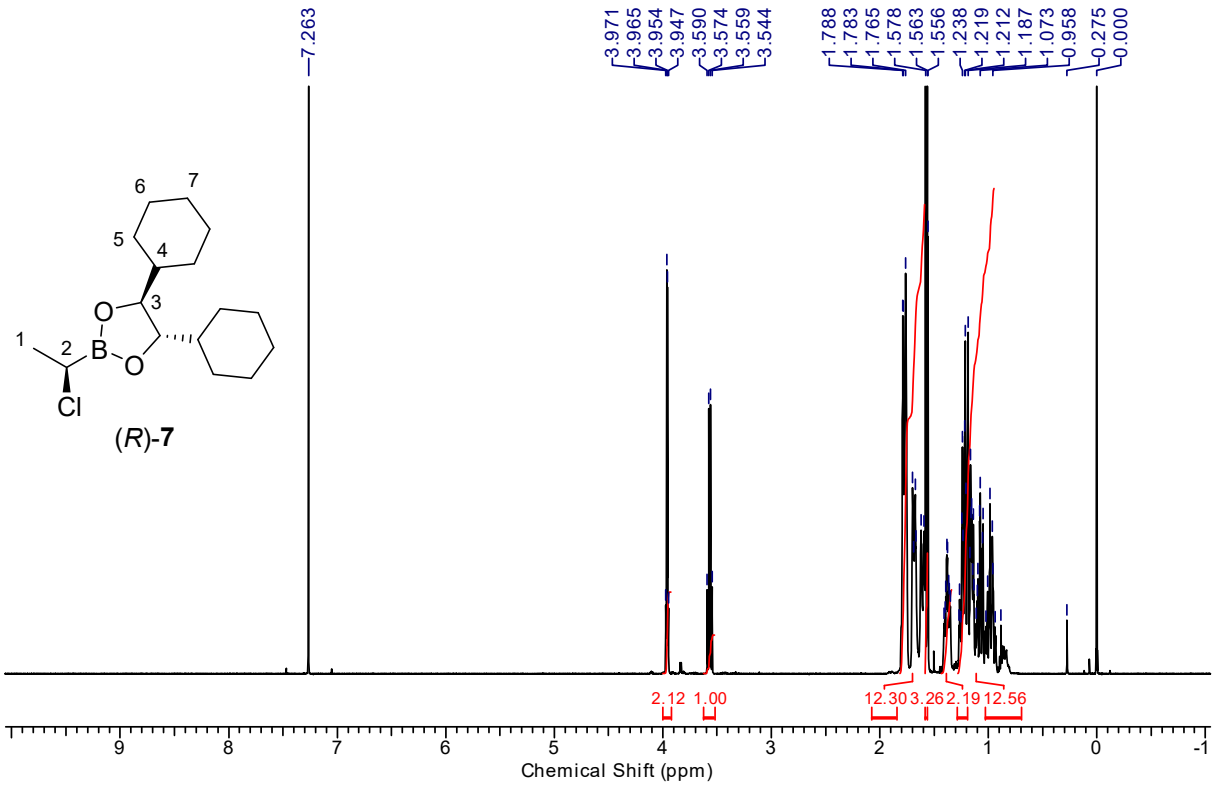


^{13}C NMR (125 MHz, $CDCl_3$):



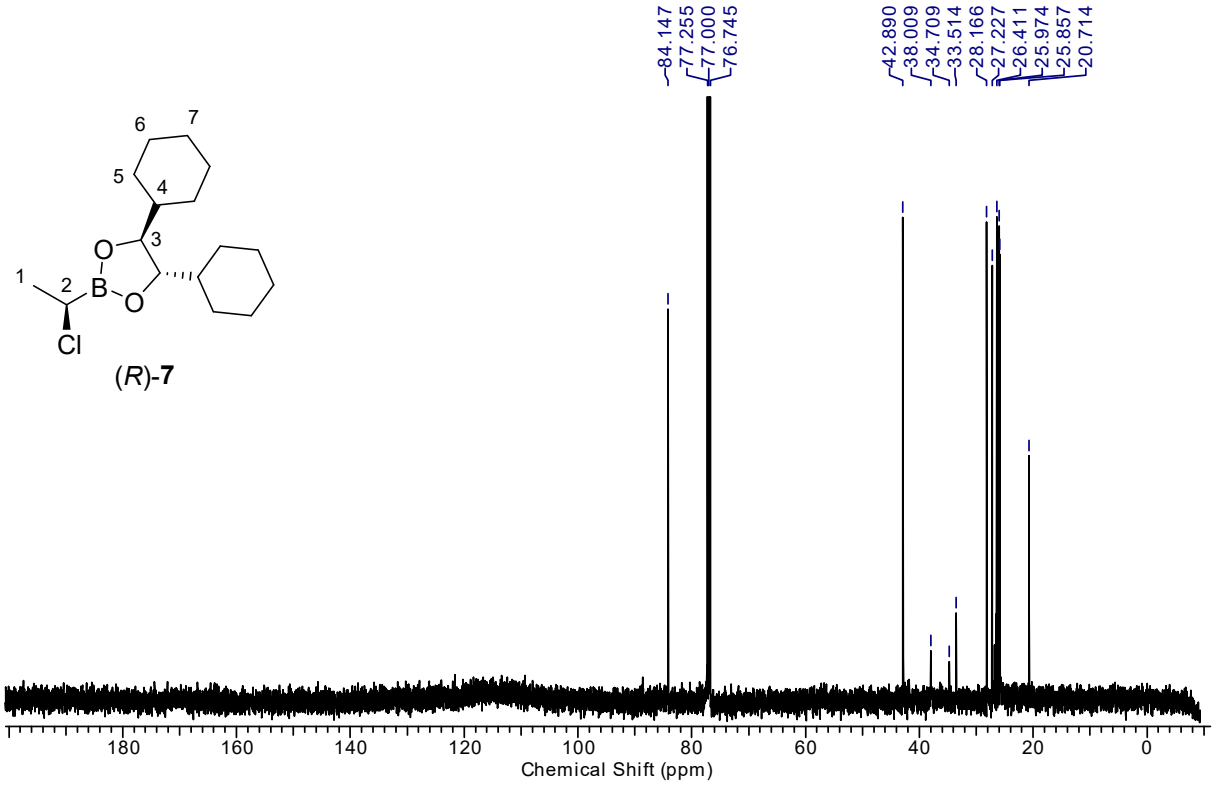
(4*S*,5*S*)-2-((*R*)-1-Chloroethyl)-4,5-dicyclohexyl-1,3,2-dioxaborolane ((*R*)-7)

^{1}H NMR (500 MHz, $CDCl_3$):



(*R*)-**7**

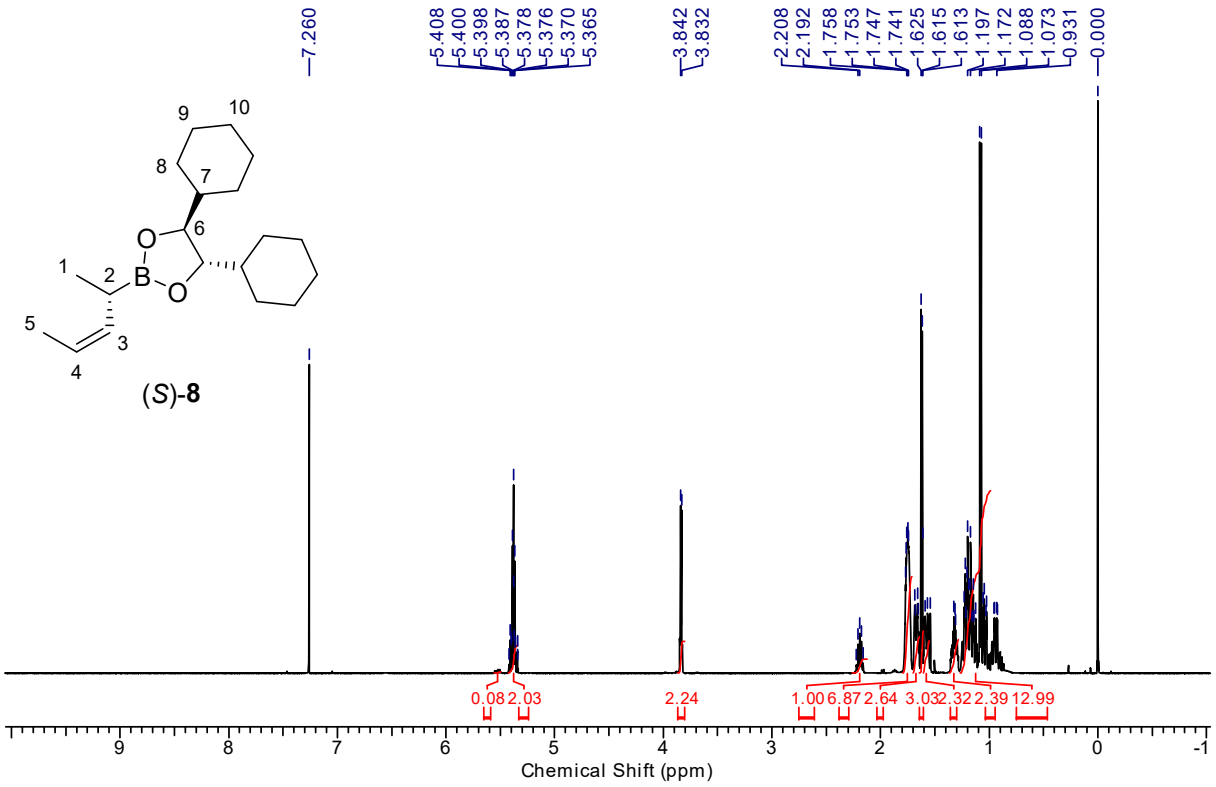
^{13}C NMR (125 MHz, $CDCl_3$):



(*R*)-**7**

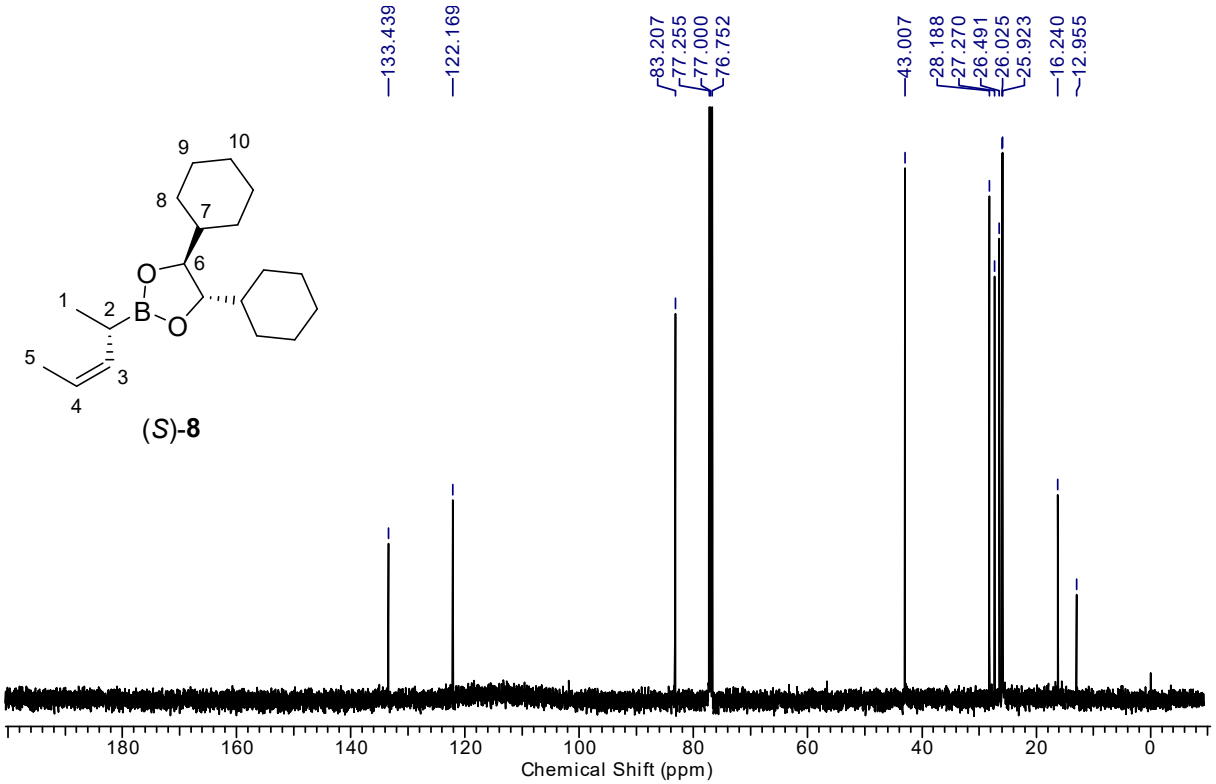
(4*S*,5*S*)-4,5-Dicyclohexyl-2-((*S*,*Z*)-pent-3-en-2-yl)-1,3,2-dioxaborolane ((*S*)-8)

^{1}H NMR (500 MHz, $CDCl_3$):



(*S*)-**8**

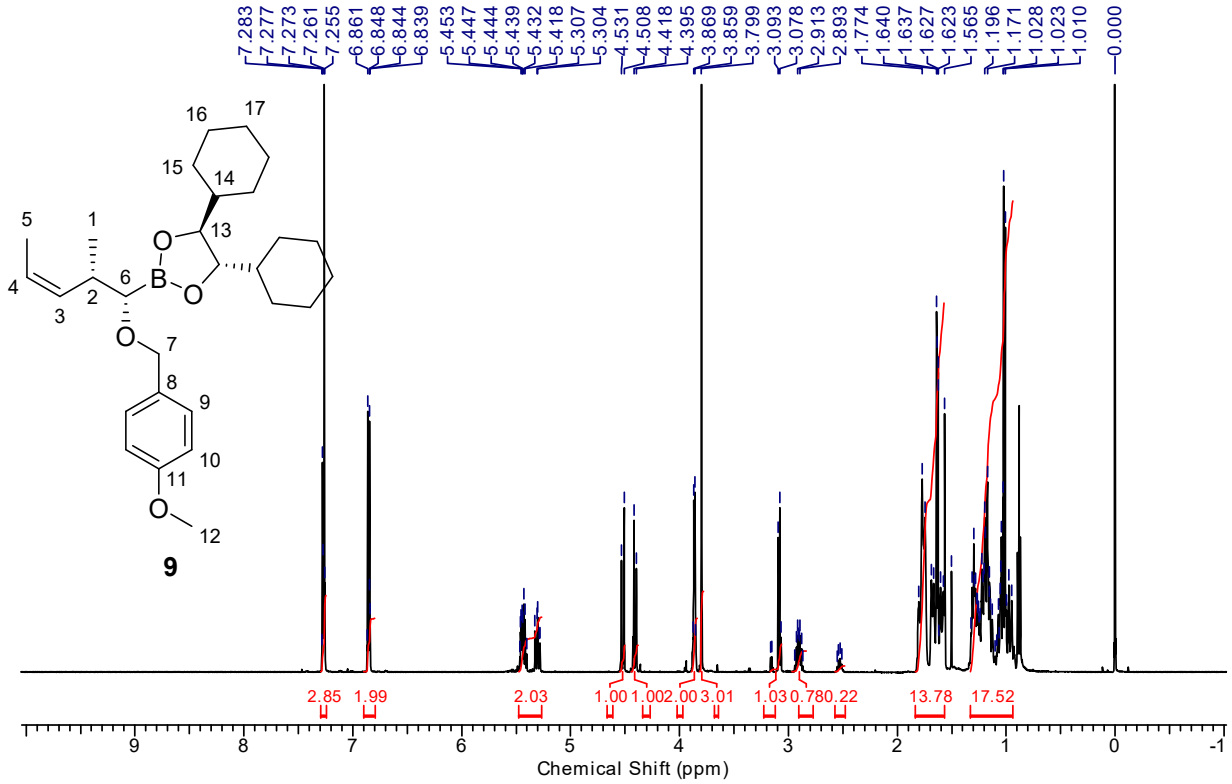
^{13}C NMR (125 MHz, $CDCl_3$):



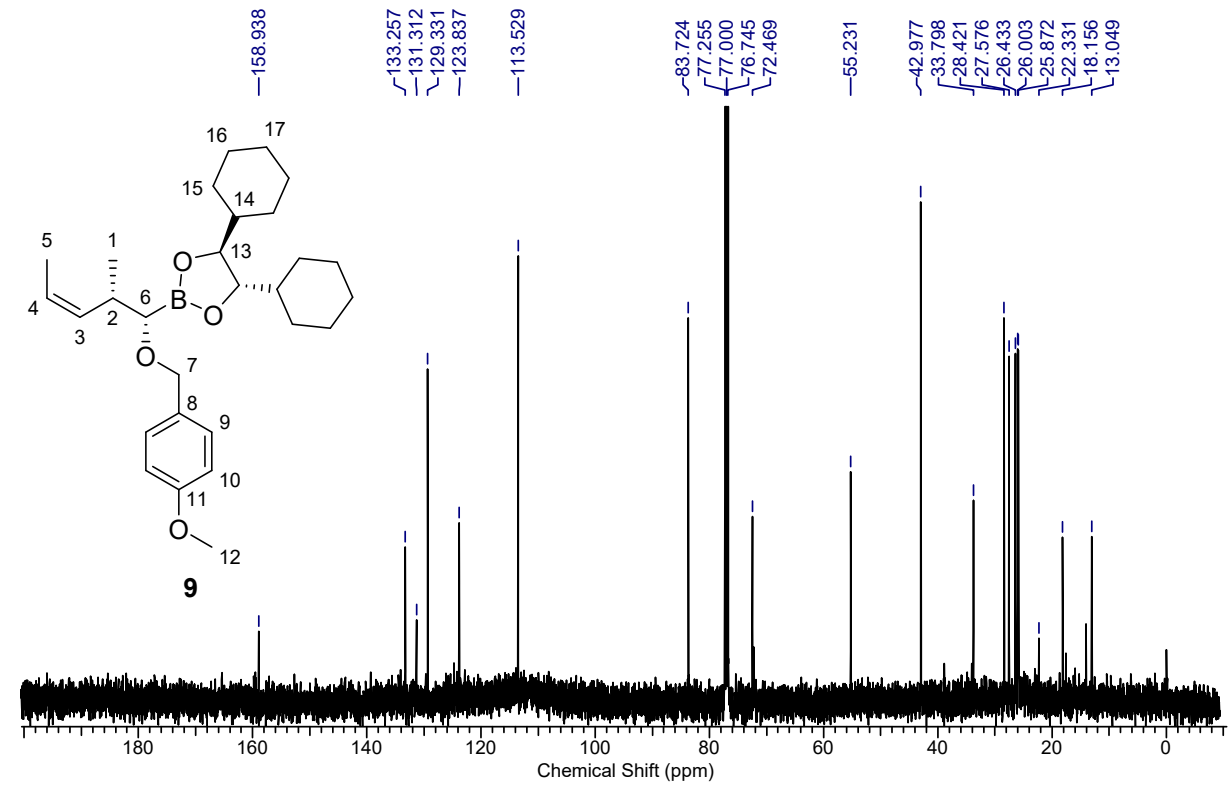
(*S*)-**8**

(4*S*,5*S*)-4,5-Dicyclohexyl-2-((1*S*,2*S*,*Z*)-1-((4-methoxybenzyl)oxy)-2-methylpent-3-en-1-yl)-1,3,2-dioxaborolane (9)

^{1}H NMR (500 MHz, $CDCl_3$):

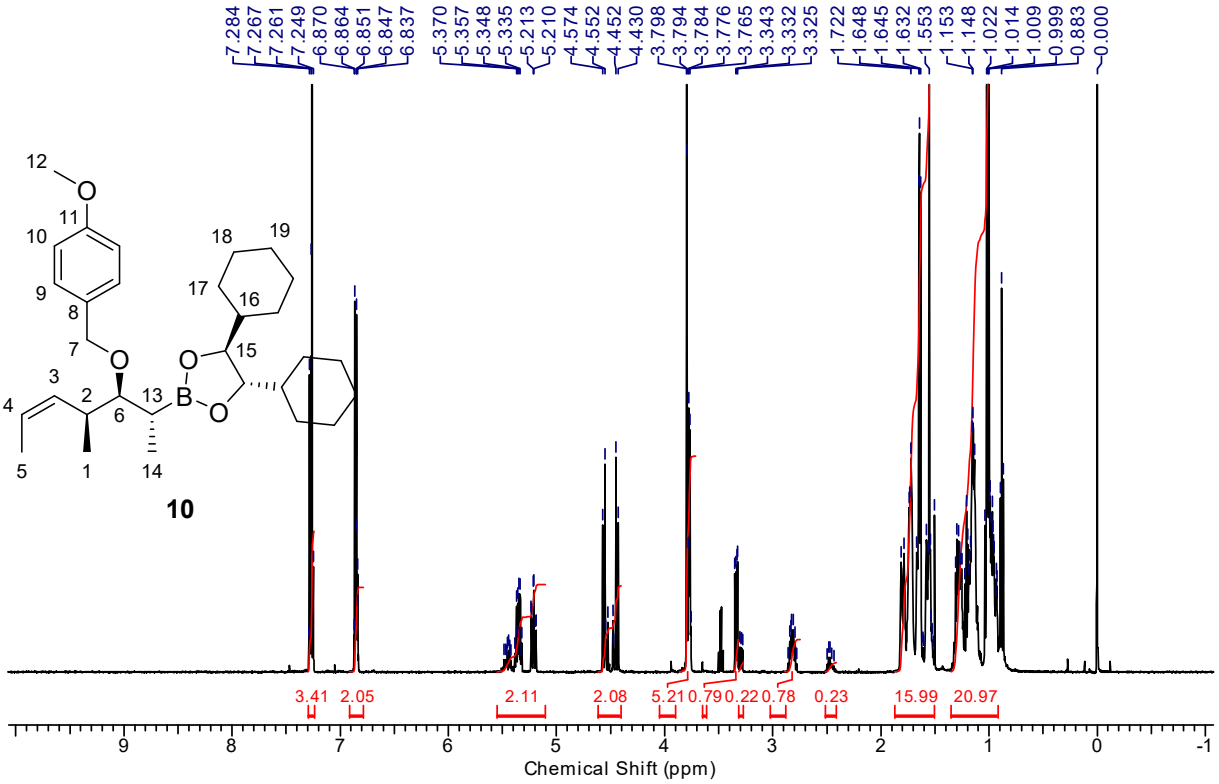


^{13}C NMR (125 MHz, $CDCl_3$):

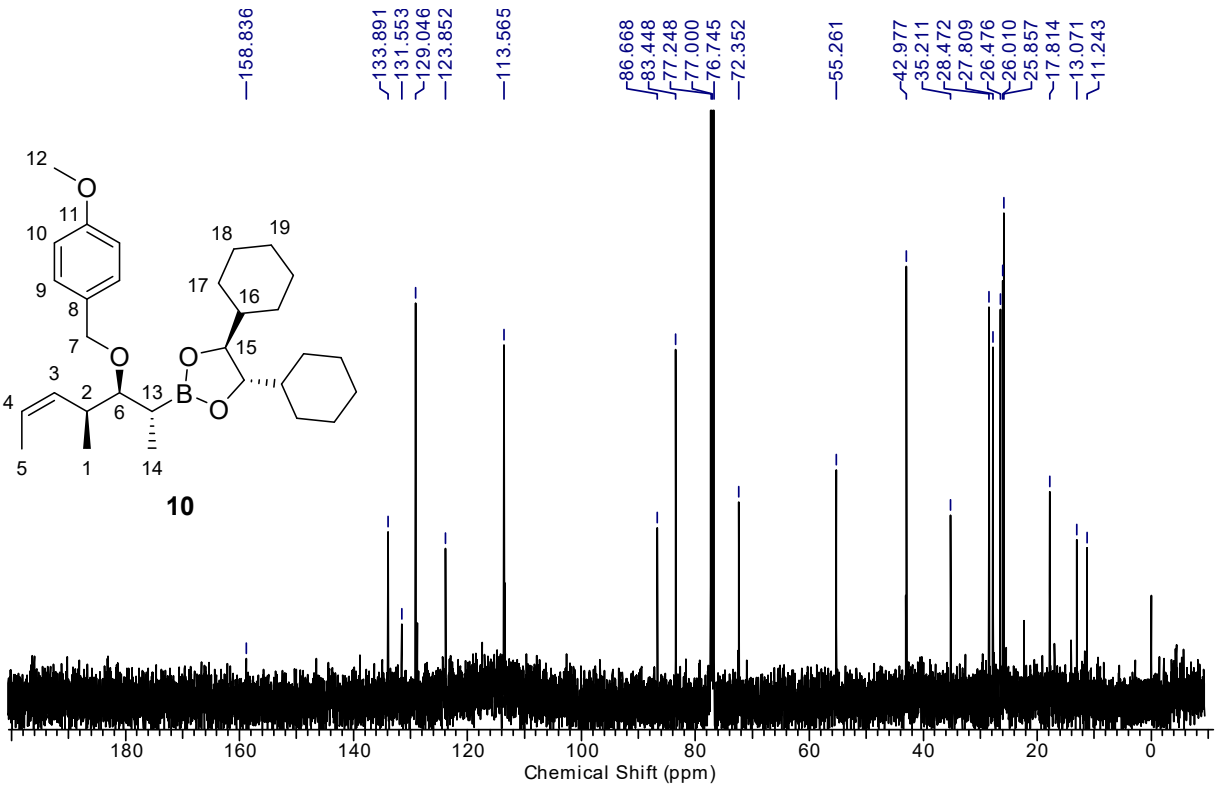


(4*S*,5*S*)-4,5-Dicyclohexyl-2-((2*R*,3*S*,4*S*,*Z*)-3-((4-methoxybenzyl)oxy)-4-methylhept-5-en-2-yl)-1,3,2-dioxaborolane (10)

^{1}H NMR (500 MHz, $CDCl_3$):

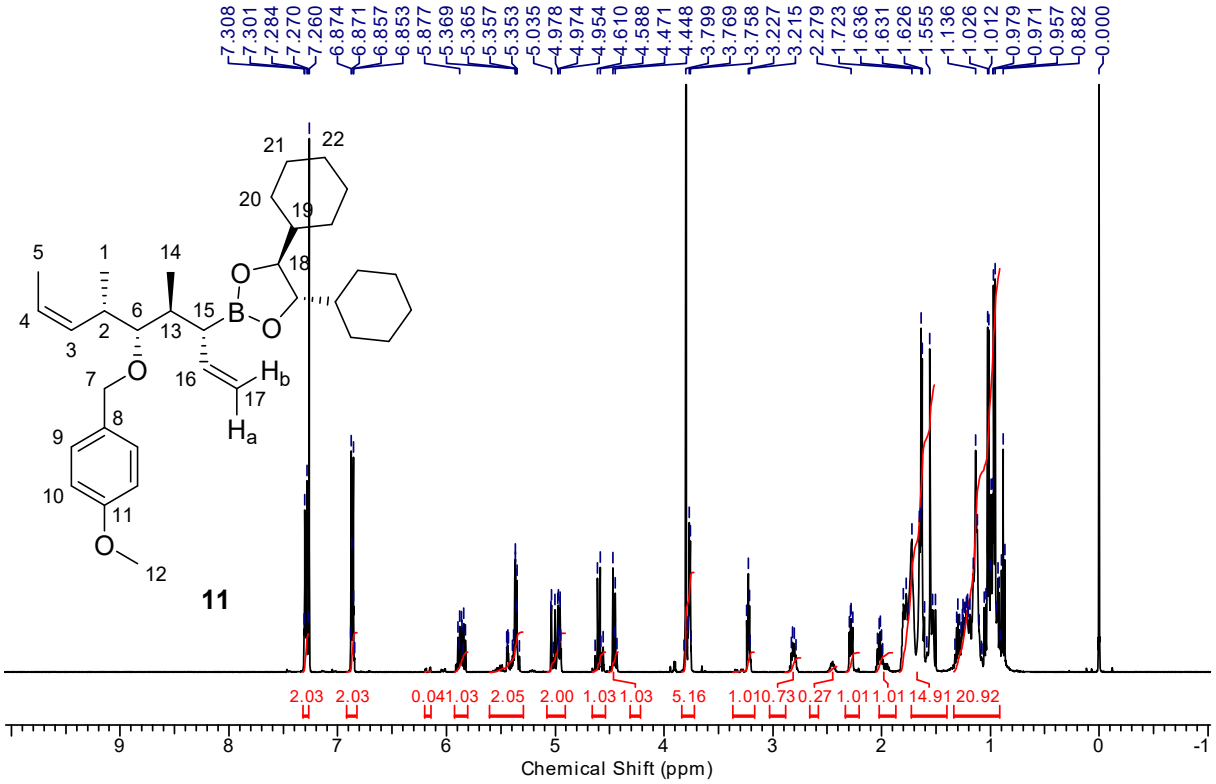


^{13}C NMR (125 MHz, $CDCl_3$):

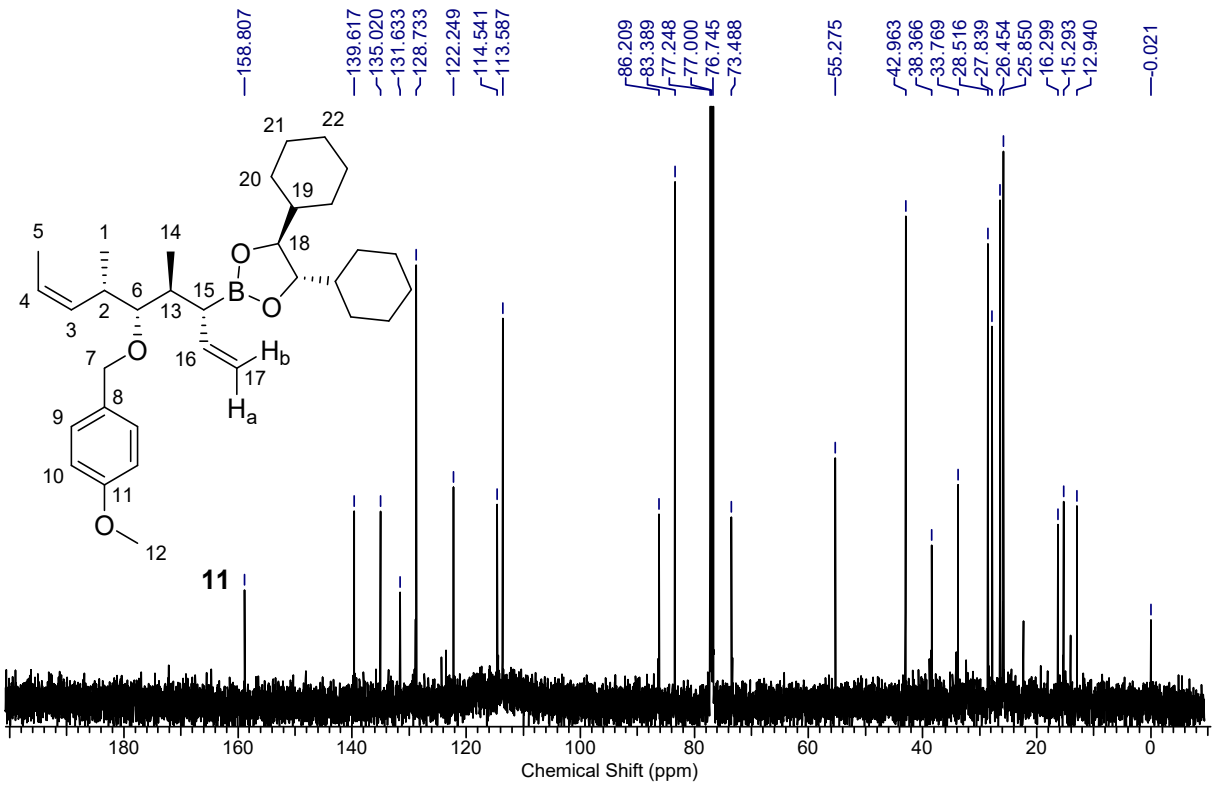


(4*S*,5*S*)-4,5-Dicyclohexyl-2-((3*R*,4*S*,5*S*,6*S*,*Z*)-5-((4-methoxybenzyl)oxy)-4,6-dimethylnona-1,7-dien-3-yl)-1,3,2-dioxaborolane (11)

^{1}H NMR (500 MHz, $CDCl_3$):

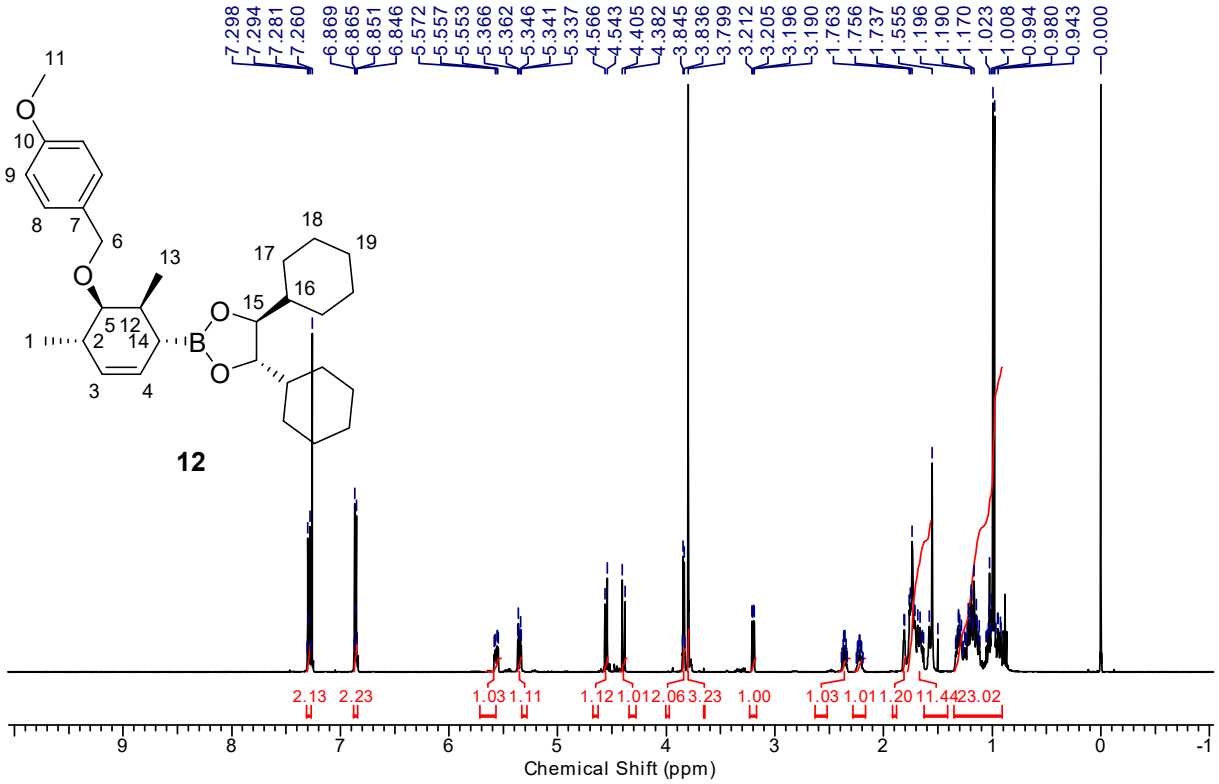


^{13}C NMR (125 MHz, $CDCl_3$):

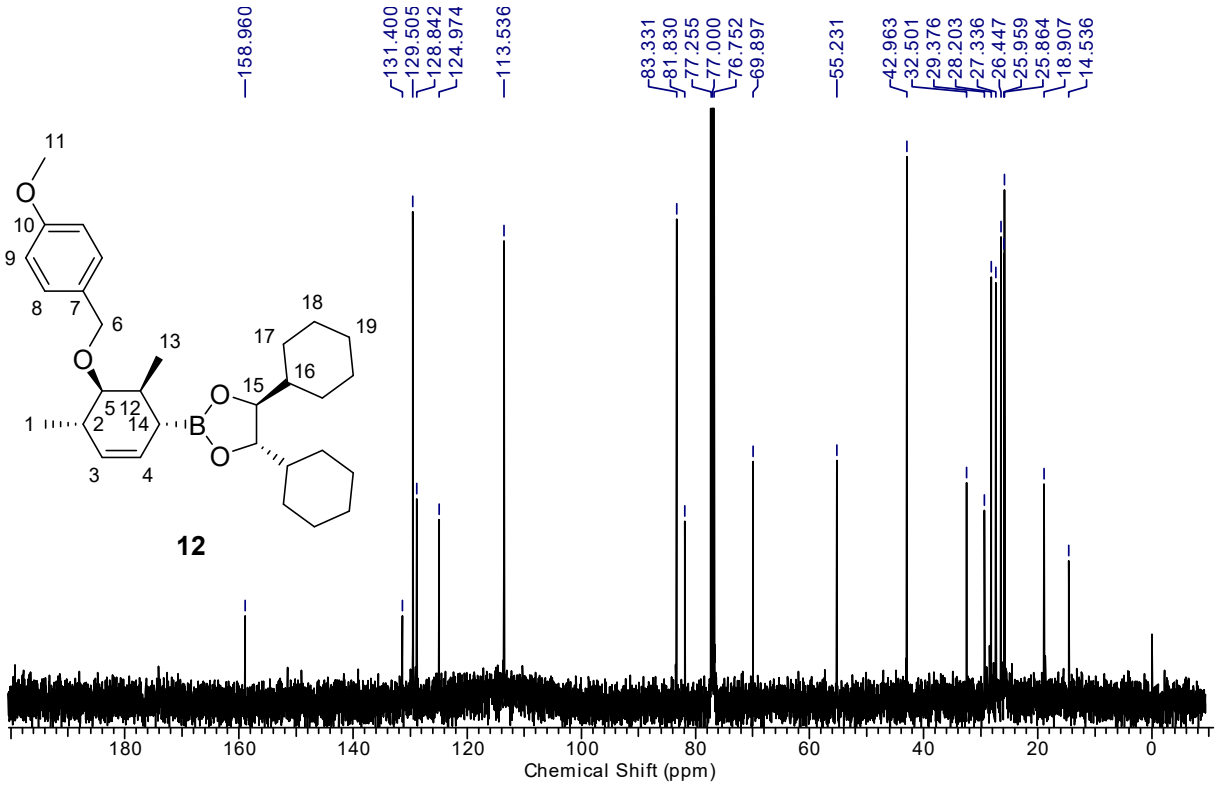


(4*S*,5*S*)-4,5-Dicyclohexyl-2-((1*R*,4*S*,5*S*,6*S*)-5-((4-methoxybenzyl)oxy)-4,6-dimethylcyclohex-2-en-1-yl)-1,3,2-dioxaborolane (12)

^{1}H NMR (500 MHz, $CDCl_3$):

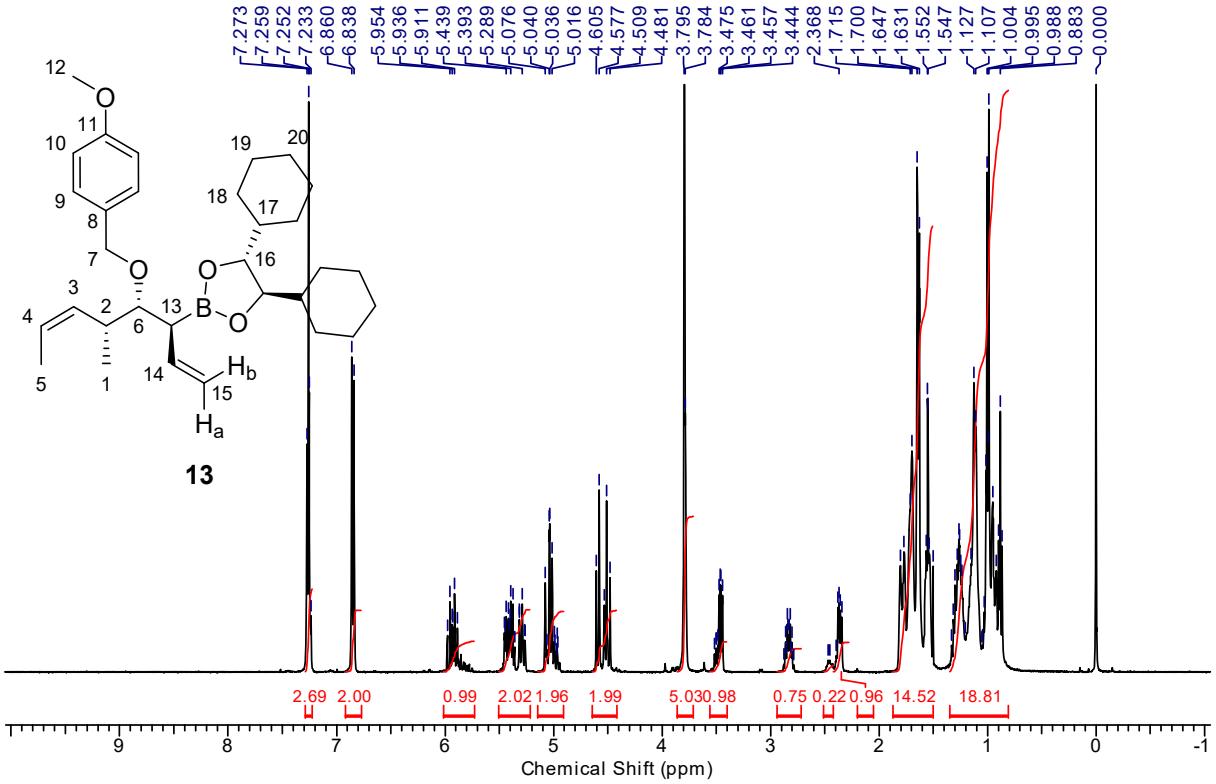


^{13}C NMR (125 MHz, $CDCl_3$):

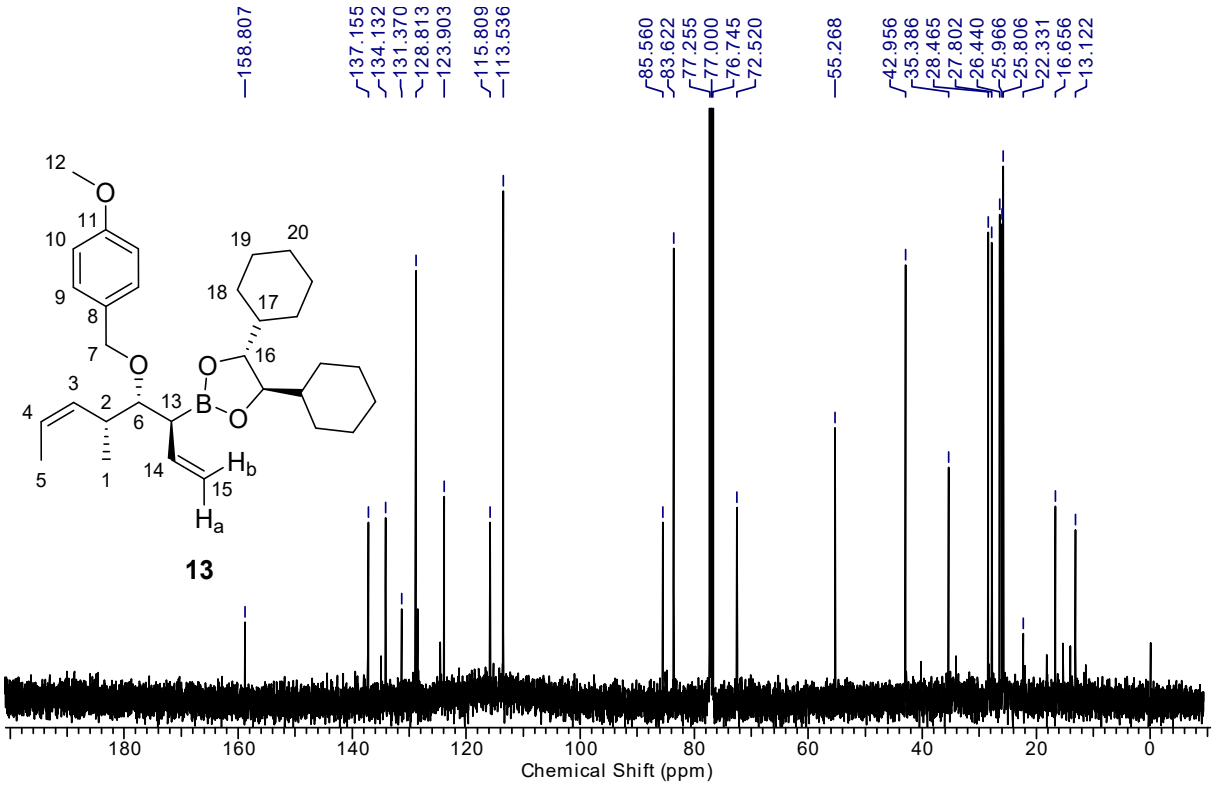


(4*R*,5*R*)-4,5-Dicyclohexyl-2-((3*S*,4*R*,5*R*,*Z*)-4-((4-methoxybenzyl)oxy)-5-methylocta-1,6-dien-3-yl)-1,3,2-dioxaborolane (13)

^{1}H NMR (500 MHz, $CDCl_3$):

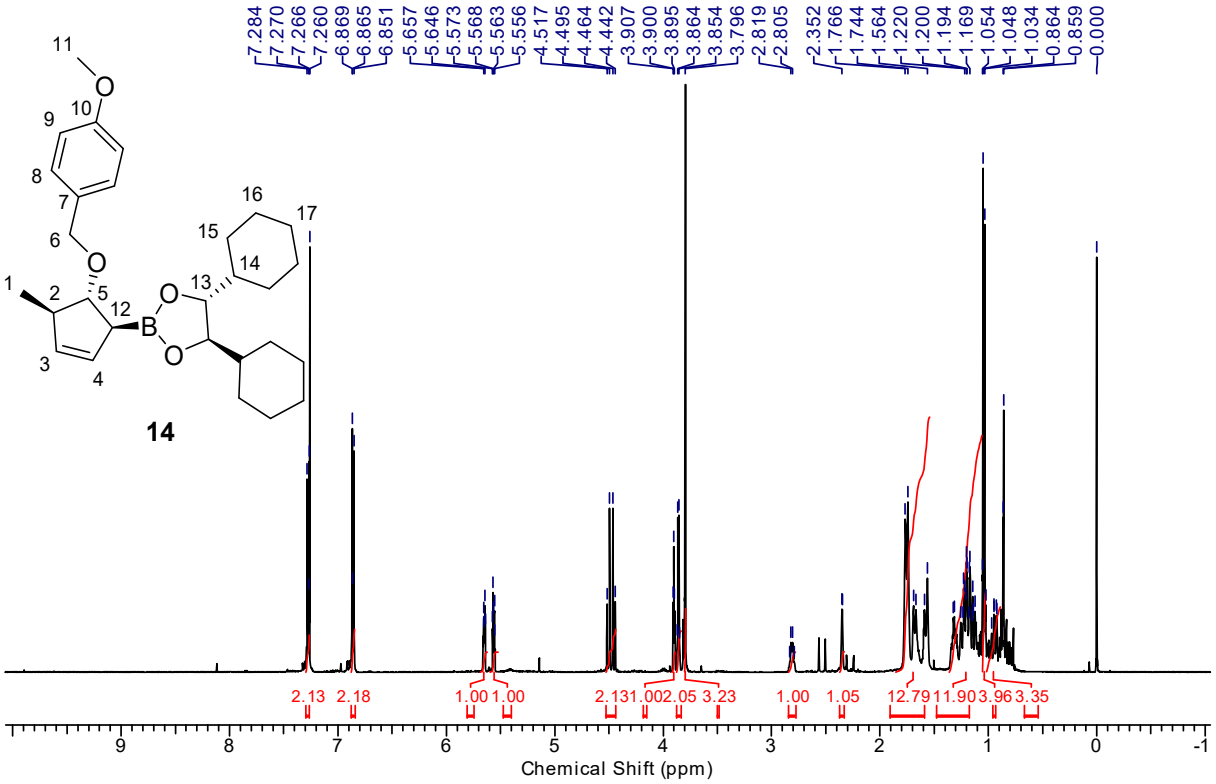


^{13}C NMR (125 MHz, $CDCl_3$):

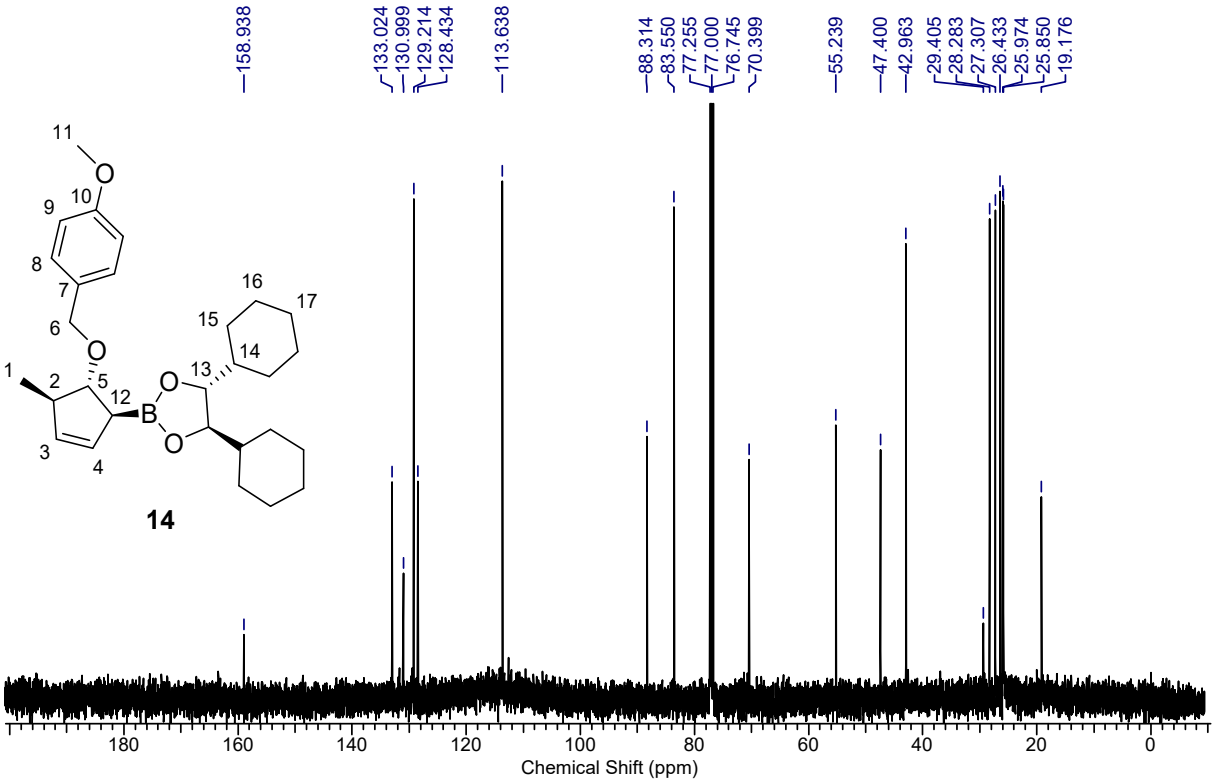


(4*R*,5*R*)-4,5-Dicyclohexyl-2-((1*S*,4*R*,5*R*)-5-((4-methoxybenzyl)oxy)-4-methylcyclopent-2-en-1-yl)-1,3,2-dioxaborolane (14)

^{1}H NMR (500 MHz, $CDCl_3$):

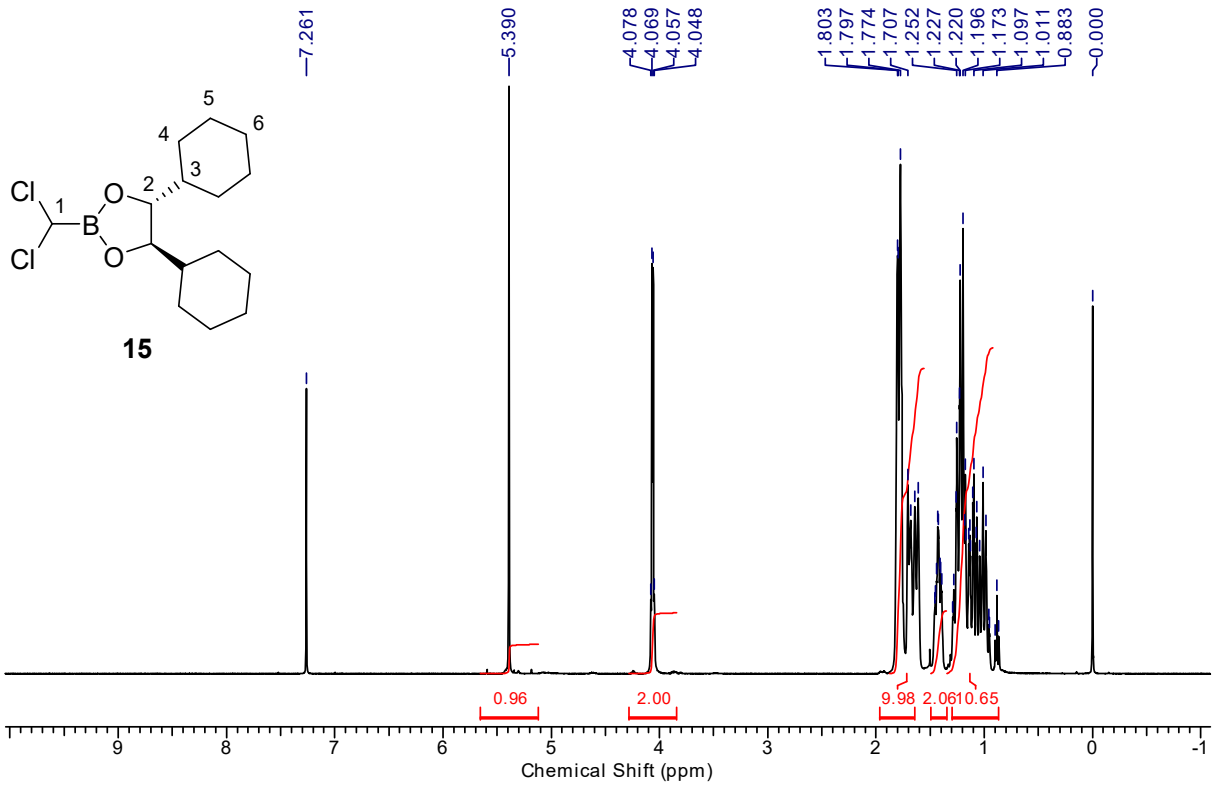


^{13}C NMR (125 MHz, $CDCl_3$):



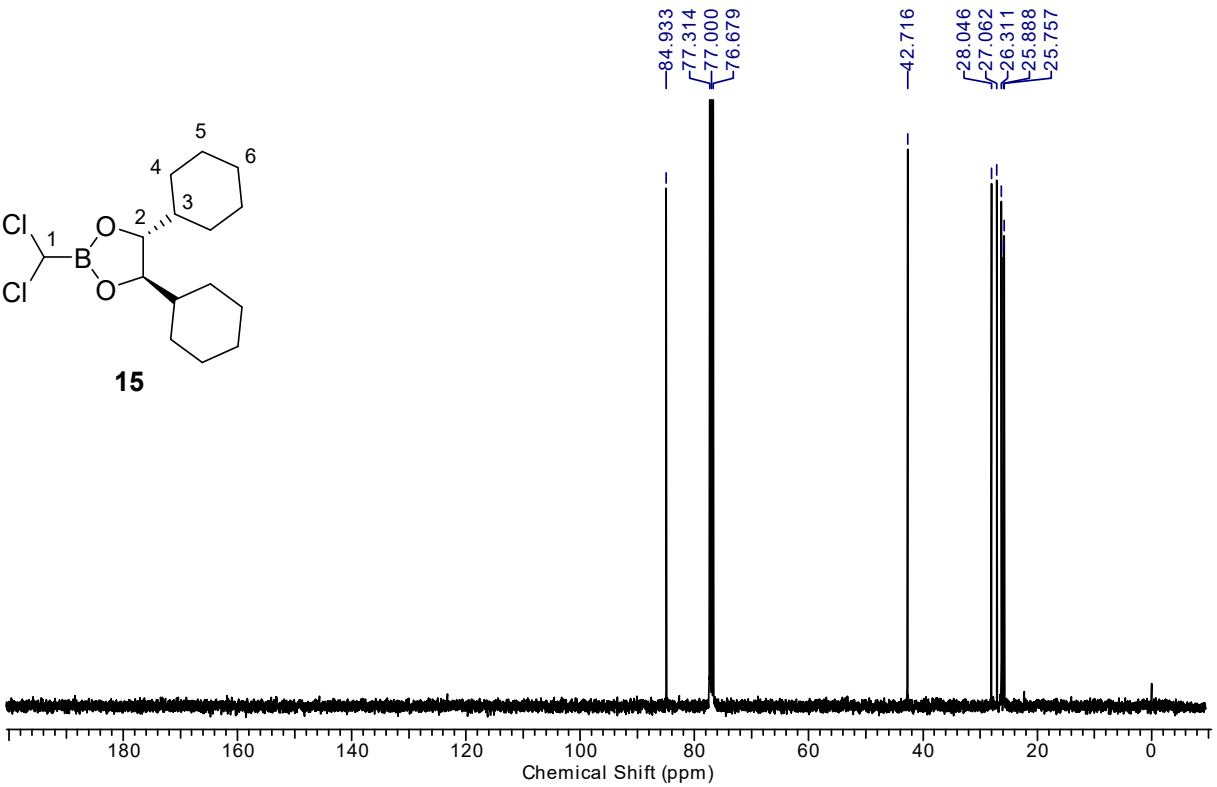
(4*R*,5*R*)-4,5-Dicyclohexyl-2-(dichloromethyl)-1,3,2-dioxaborolane (15)

^{1}H NMR (500 MHz, $CDCl_3$):



15

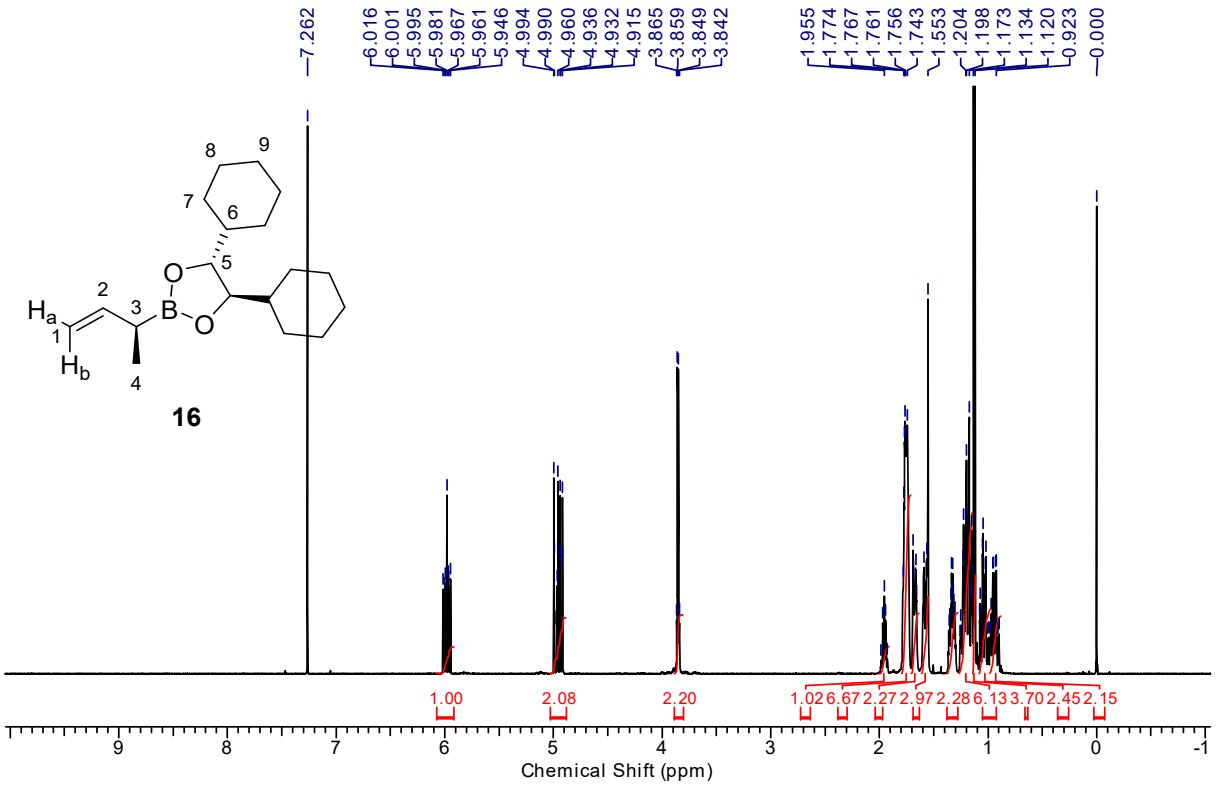
^{13}C NMR (125 MHz, $CDCl_3$):



15

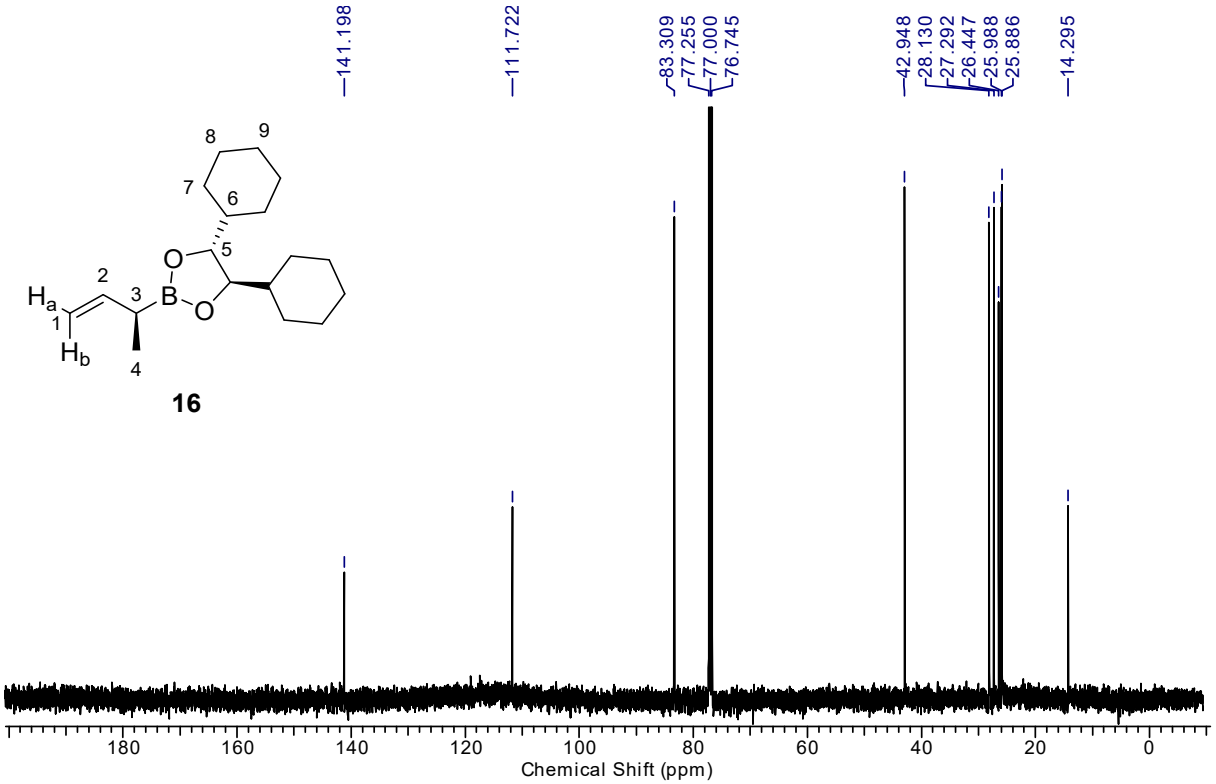
(4*R*,5*R*)-2-((*S*)-But-3-en-2-yl)-4,5-dicyclohexyl-1,3,2-dioxaborolane 16)

^{1}H NMR (500 MHz, $CDCl_3$):



16

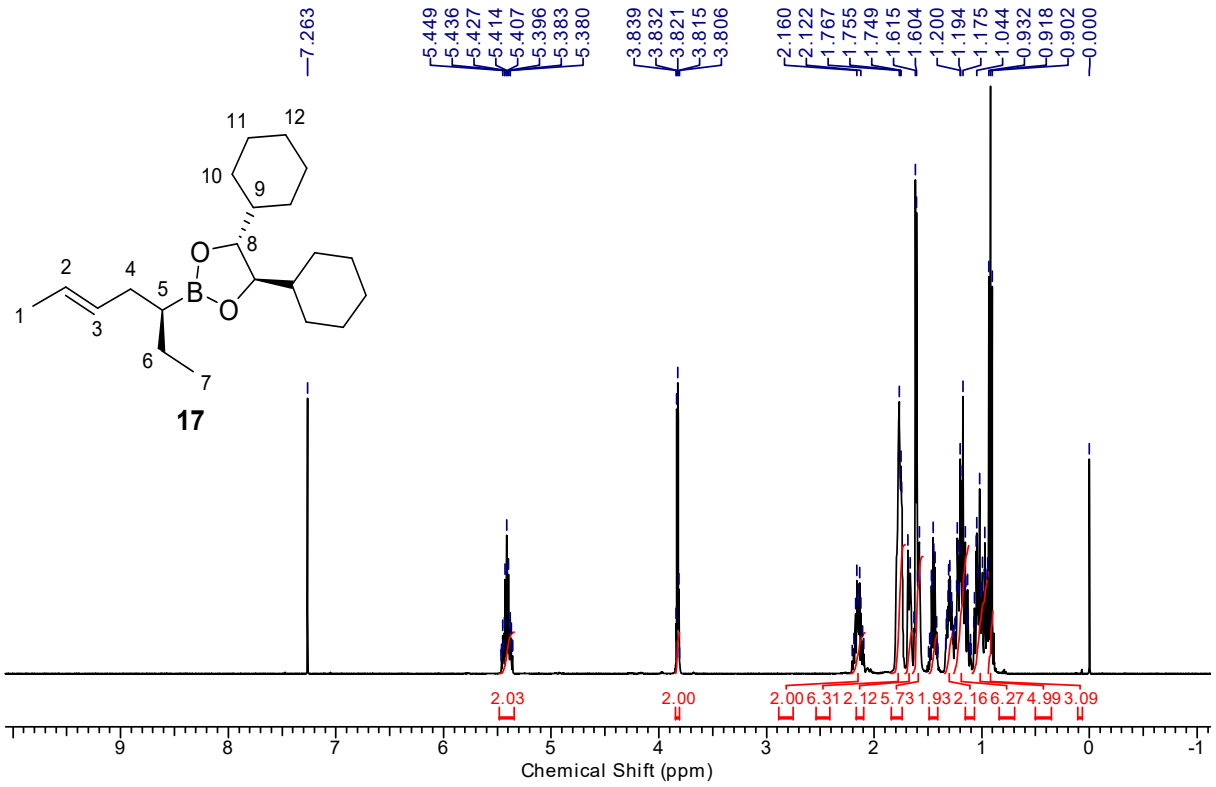
^{13}C NMR (125 MHz, $CDCl_3$):



16

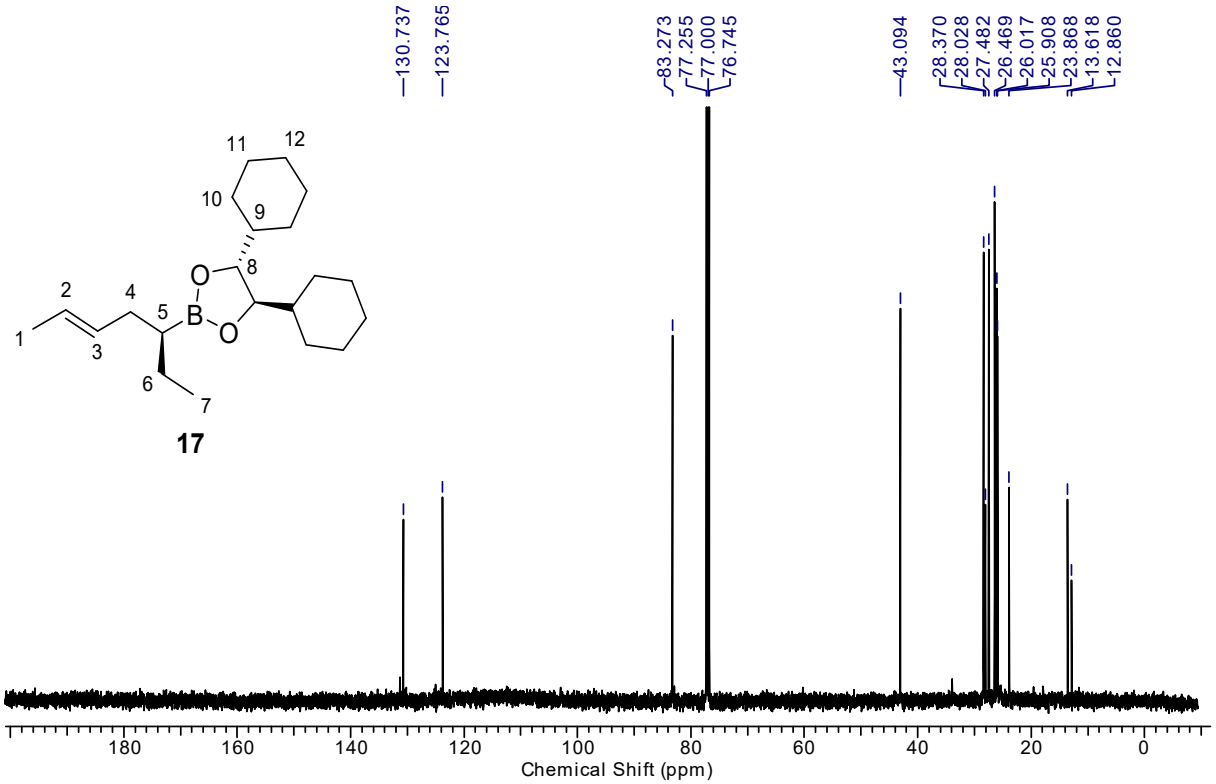
(4*R*,5*R*)-4,5-Dicyclohexyl-2-((*S*,*E*)-hept-5-en-3-yl)-1,3,2-dioxaborolane (17)

^{1}H NMR (500 MHz, $CDCl_3$):



17

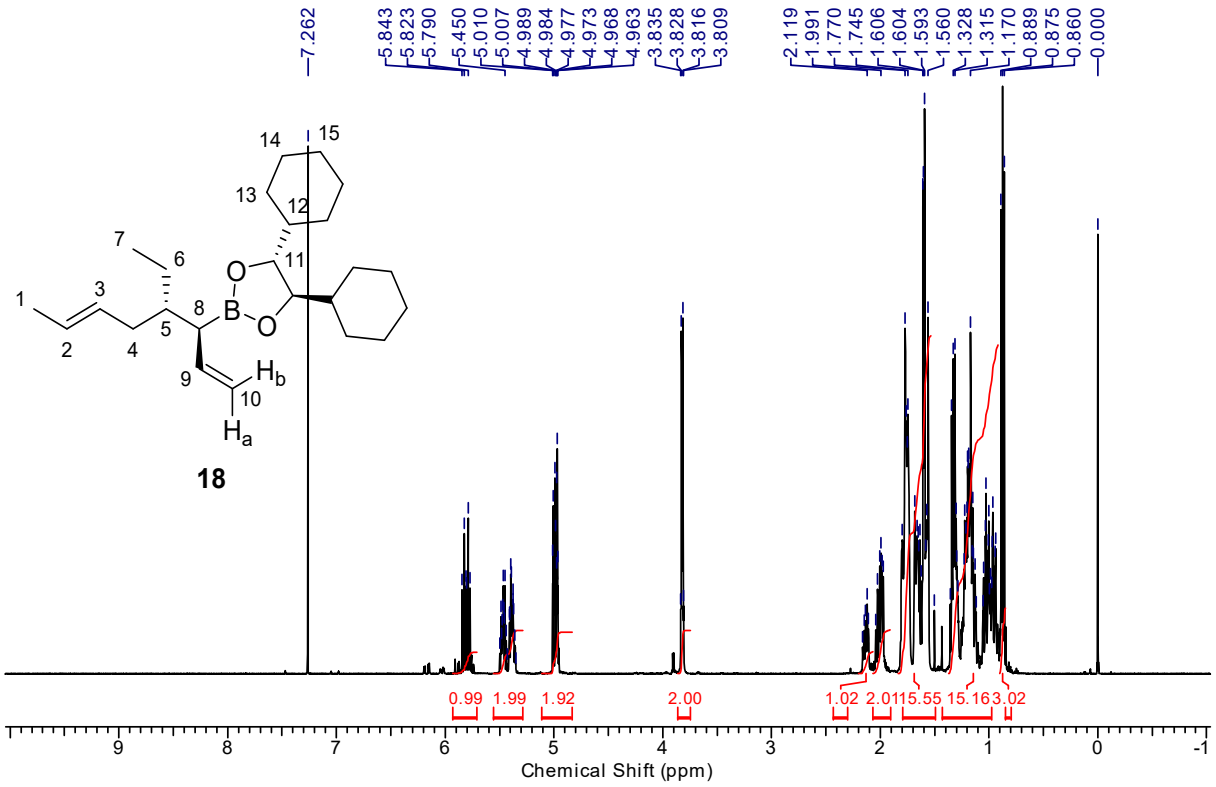
^{13}C NMR (125 MHz, $CDCl_3$):



17

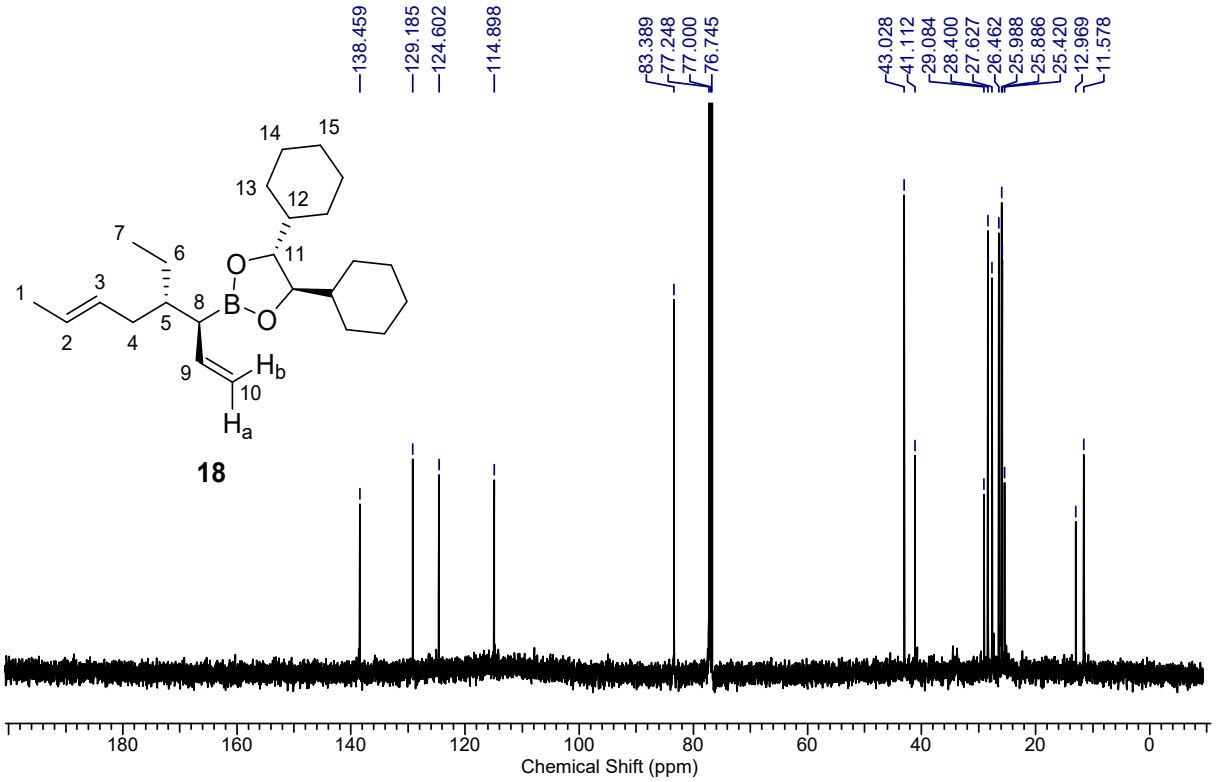
(4*R*,5*R*)-4,5-Dicyclohexyl-2-((3*S*,4*S*,*E*)-4-ethylocta-1,6-dien-3-yl)-1,3,2-dioxaborolan (18)

^{1}H NMR (500 MHz, $CDCl_3$):



18

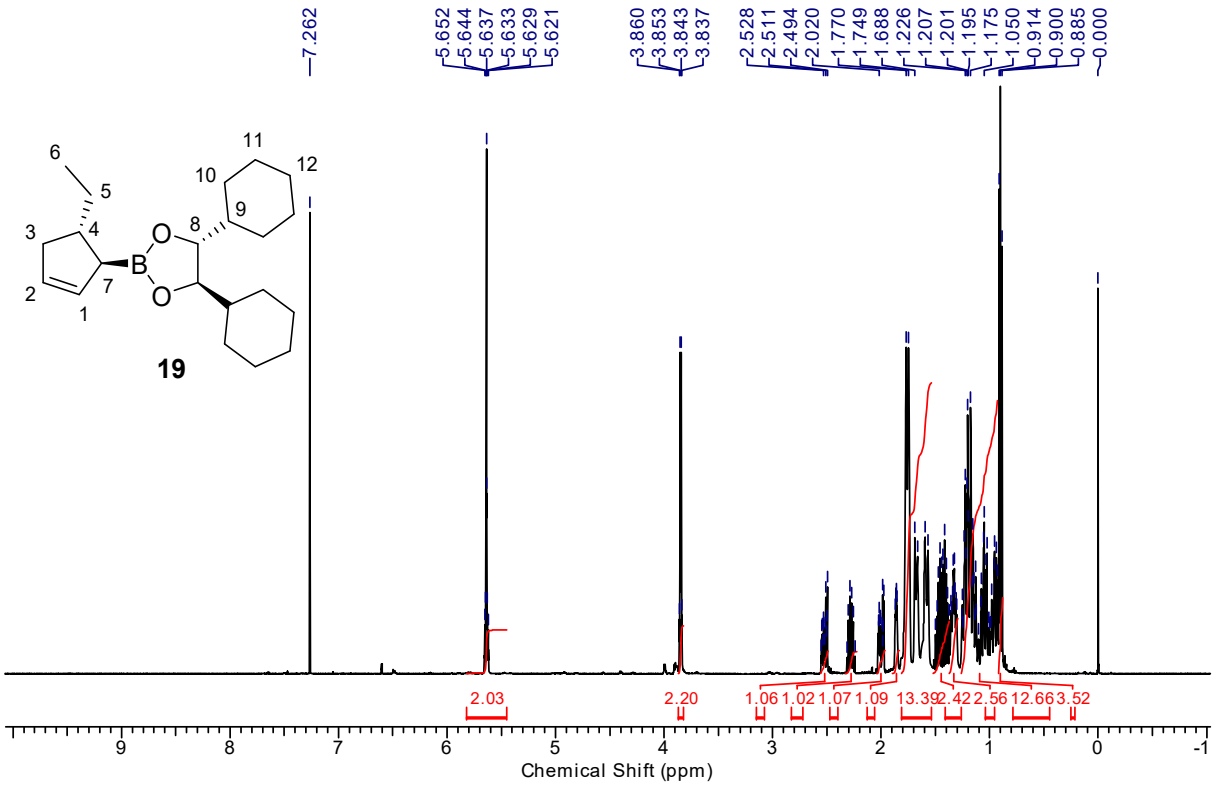
^{13}C NMR (125 MHz, $CDCl_3$):



18

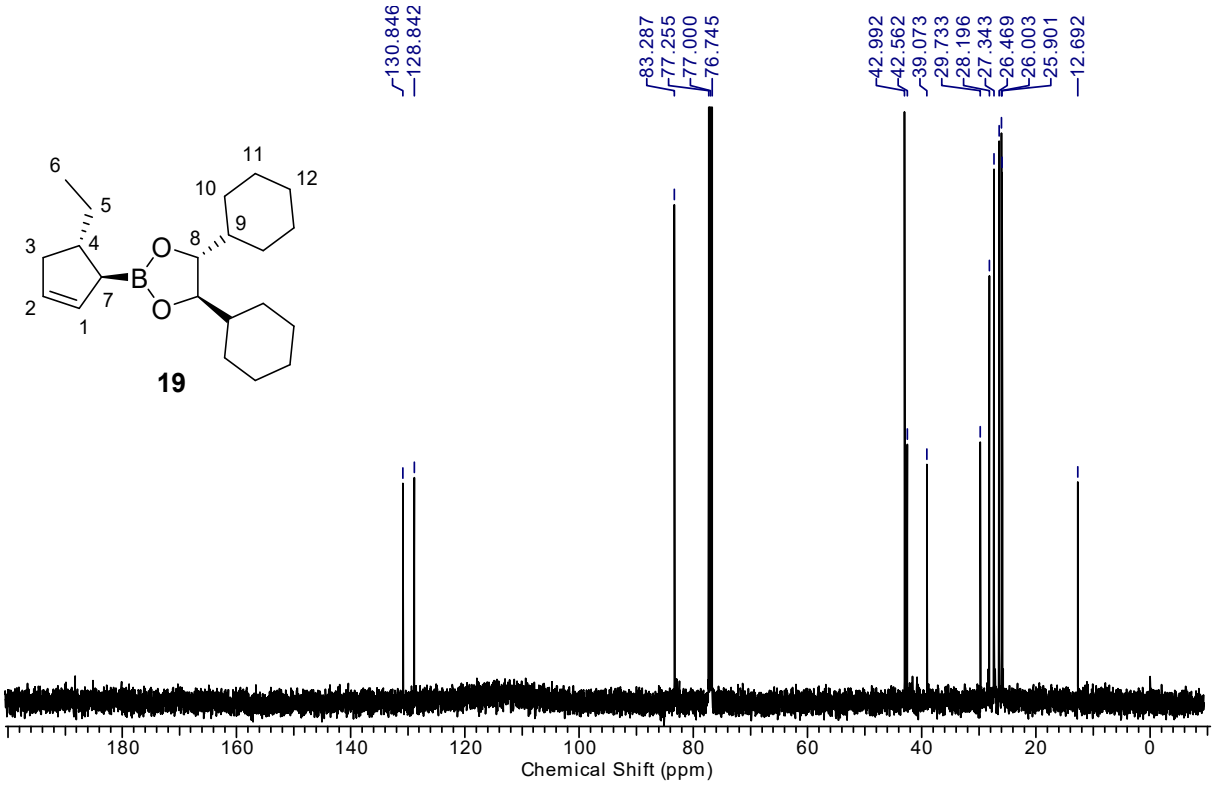
(4*R*,5*R*)-4,5-Dicyclohexyl-2-((1*R*,5*S*)-5-ethylcyclopent-2-en-1-yl)-1,3,2-dioxaborolane (19)

^{1}H NMR (500 MHz, $CDCl_3$):



19

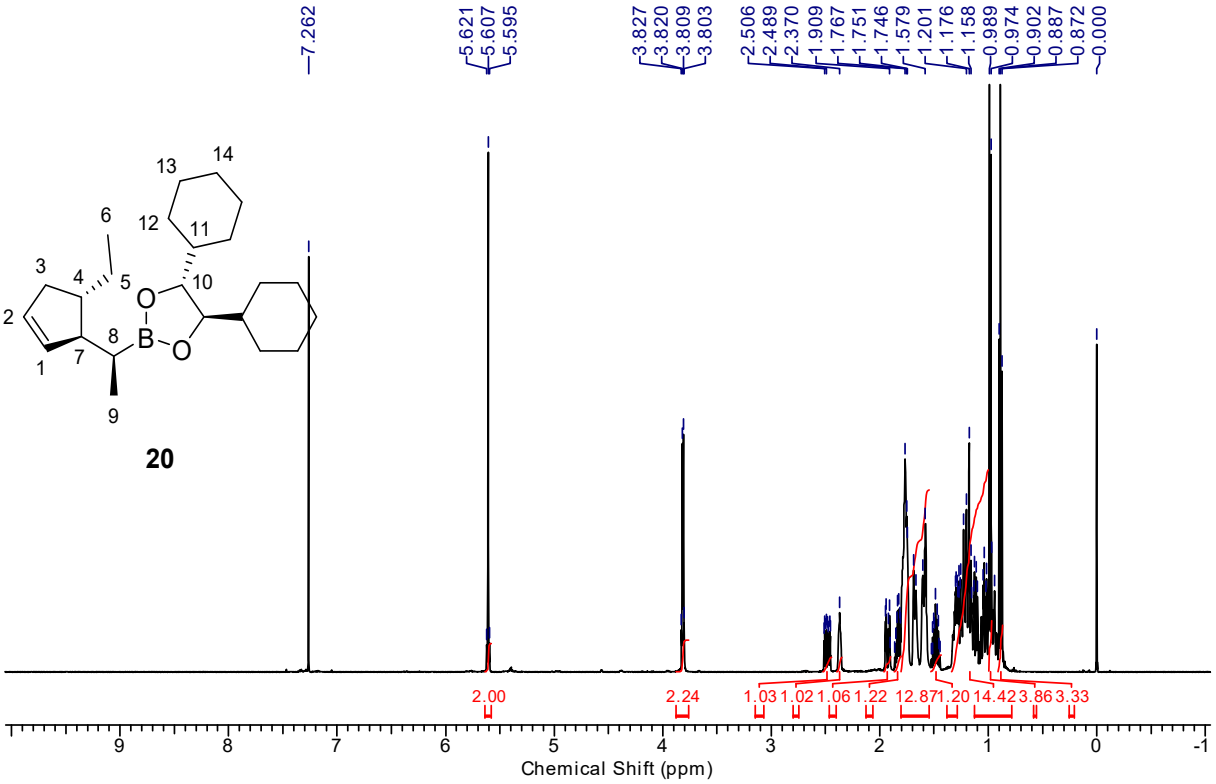
^{13}C NMR (125 MHz, $CDCl_3$):



19

(4*R*,5*R*)-4,5-Dicyclohexyl-2-((*S*)-1-((1*R*,5*S*)-5-ethylcyclopent-2-en-1-yl)ethyl)-1,3,2-dioxaborolane (20)

^{1}H NMR (500 MHz, $CDCl_3$):



^{13}C NMR (125 MHz, $CDCl_3$):