Supplementary Information (SI) for Organic Chemistry Frontiers.

Synthesis of Oxylipids via a Boronic Ester Cycloetherification Approach

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Supporting Information

Materials and methods

All air- or moisture-sensitive reactions were carried out in dried glassware (>100 °C) under an atmosphere of nitrogen. Anhydrous solvents were purchased from *Acros Organics* or dried before use (THF was distilled over Na/benzophenone and diisopropylamine DIPA over CaH_2). $ZnCl_2$ was fused in vacuo at 0.1 mbar prior to use. Ethyl acetate and pentane were additionally distilled before use. Reactions at low temperature (-100 °C) were stirred using elliptical high magnetic force stirring bars (rare earth) purchased from *Avantor*. Reactions that required heating above rt were heated using an oil bath. Warming to rt was accomplished by removal of the cooling bath, while slow warming was carried out in the cooling bath reaching rt.

Reactions were monitored by NMR or analytical TLC, which was performed on precoated silica gel on TLC PET-foils by *Macherey Nagel*. Visualization was accomplished with UV-light (254 nm), $KMnO_4$ solution or Ce(IV) / ammonium molybdate solution.

The products were purified by flash chromatography on silica gel columns (*Macherey-Nagel* 60, 0.063-0.2 mm or 0.04-0.063 mm) or by automated flash chromatography (*Büchi Pure C-815* Chromatography System and *Teledyne Isco RediSep Rf Silver* Normal-phase Silica Flash 30-70 µm columns). Reversed-phase flash chromatography was accomplished by automated flash chromatography (*Büchi Reveleris Prep* Chromatography System and *Büchi FlashPure Select* C18 30 µm spherical cartridges or *Telos* C18 cartridges). Preparative HPLC was performed on a *Büchi Reveleris* Prep Chromatography System using a *Phenomenex Luna* C18(2) 100 Å column (250 x 21.1 mm, 5 µm).

^{1}H- and ^{13}C-NMR spectra were recorded with a *Bruker AV II 400* [400 MHz (^{1}H), 100 MHz (^{13}C)], a *Bruker AV 500* [500 MHz, (^{1}H), 125 MHz (^{13}C)] or a *Bruker Avance Neo 500* [500 MHz, (^{1}H), 125 MHz (^{13}C)] spectrometer in $CDCl_3$ or DMSO-d_6. NMR spectra were evaluated using *NMR Processor* Version 12.01 from *ACD* or *TopSpin* Version 4.1.1 from *Bruker*. Chemical shifts are reported in ppm relative to $Si(CH_3)_4$ and the solvent residual peak was used as the internal standard. Selected signals for the minor diastereomers/enantiomers are extracted from the spectra of the isomeric mixture. Multiplicities are reported as bs (broad signal), s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Structural assignments were made with additional information from gCOSY, gNOESY, gHSQC and gHMBC experiments.

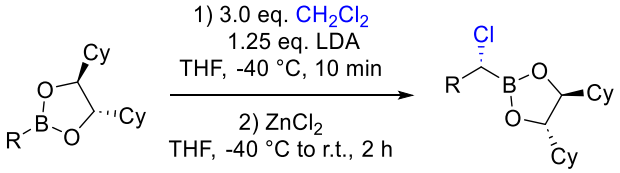
Melting points were determined with a melting point apparatus *MEL-TEMP II* by *Laboratory Devices* and are uncorrected.

High resolution mass spectra (HRMS) were recorded with a *Finnigan MAT 95* spectrometer using the CI technique (CI). Alternatively, HRMS were performed using a *maXis 4G hr-ToF* machine from *Bruker Daltonics* using ESI technique for ionization (ESI-ToF). Further HRMS were performed using an *Orbitrap Q exactive* mass spectrometer, equipped with a heated ESI source and a quadrupole-orbitrap coupled mass detector and an *Ultimate3000* HPLC from *Thermo Finnigan* (ESI-Orbitrap). The MS detection was carried out at a spray voltage of 3.8 kV in positive ionisation mode, a nitrogen sheath gas pressure of $4.0 * 10^5$ Pa, an auxiliary gas pressure of $1.0 * 10^5$ Pa and a capillary temperature of 300 °C. All samples were injected by autosampler with an injection volume of 15 µL. A RP *Macherey-Nagel Nucleoshell Phenyle-hexyle*® (50-2, 3.0 µm) column was used as stationary phase. The solvent system consisted of formic acid 0.1% (A) and acetonitrile with formic acid 0.1% (B). HPLC method: flow rate 700 µL/min. The percentage of B started at an initial of 50%, was increased to 100% in 5.0 min, then kept at 100% for 7 min and flushed back to the initial 50 %. *Xcalibur* software was used for data acquisition and plotting.

Optical rotations were measured in $CHCl_3$ with a *Perkin-Elmer* polarimeter *Model 341*, a *Jasco* polarimeter *P-2000* polarimeter or a *Krüss* polarimeter *P8000-T80* in thermostated (20 °C ± 1 °C) cuvettes and are given in 10^{-1} deg cm^2 g^{-1}. The radiation source used was a sodium vapor lamp ($\lambda = 589$ nm). The concentrations are given in g/100 mL.

General procedures

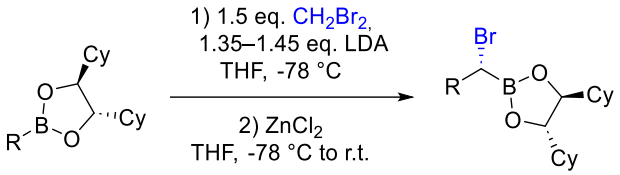
GP1: Matteson homologation with $CHCl_2Li$ to secondary α-Chloroboronic esters



Preparation of LDA: Diisopropylamine (1.35 equiv., 0.71 g/ml) was dissolved in anhydrous THF (0.2 ml/mmol boronic ester, 5 M) and cooled to -40 °C (acetone/dry ice). To this solution, *n*-BuLi (1.25 equiv., 1.6 M in hexane) was slowly added. The resulting suspension was stirred at this temperature for 10 min, warmed to rt and stirred for 20 min.

Homologation: The boronic ester (1.0 equiv.) and anhydrous DCM (3.0 equiv., 1.32 g/ml) were dissolved in anhydrous THF (1.25 ml/mmol boronic ester, 0.8 M) and cooled to -40 °C. The previously prepared LDA solution was added slowly at -40 °C and stirred for 10 min (yellowish after addition). A solution of zinc chloride (2.0-4.0 equiv.) dissolved in anhydrous THF (0.6 ml/mmol $ZnCl_2$, 1.67 M) was added rapidly and the mixture was warmed to room temperature and stirred for 2 h (brownish color).

GP2: Matteson homologation with $CHBr_2Li$ to secondary α-Bromoboronic esters



Preparation of LDA: Diisopropylamine (1.35 equiv., 0.71 g/ml) was dissolved in anhydrous THF (0.2 ml/mmol boronic ester, 5 M) and cooled to -40 °C (acetone/dry ice). To this solution, *n*-BuLi (1.25 equiv., 1.6 M in hexane) was slowly added. The resulting suspension was stirred at this temperature for 10 min, warmed to rt and stirred for 20 min.

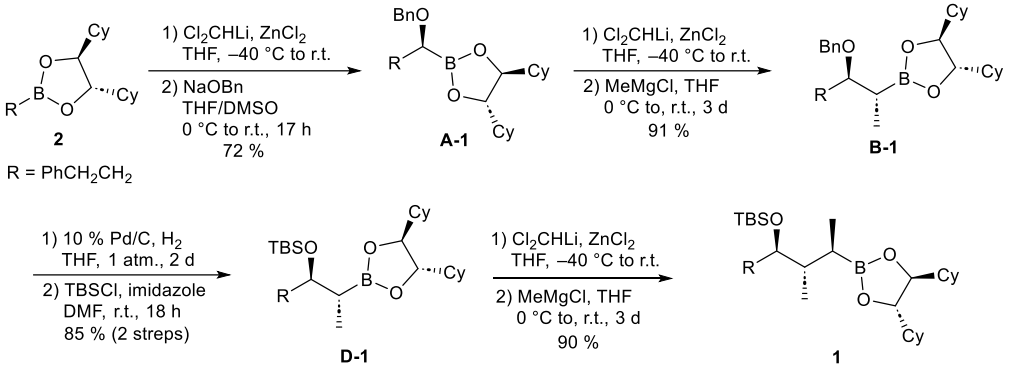
Homologation: In another Schlenk tube, the boronic ester (1.0 equiv.) and dibromomethane DBM (1.35 equiv., 2.06 g/ml) were dissolved in anhydrous THF (1.4 ml/mmol boronic ester, 0.71 M) and cooled to -78 °C (acetone/dry ice). The previously prepared LDA solution was added slowly to the carbenoid solution at -78 °C and stirred for 15-60 min. A solution of zinc chloride (2.0-4.0 equiv.) dissolved in anhydrous THF (0.6 ml/mmol $ZnCl_2$, 1.67 M) was added rapidly and the mixture was slowly warmed to room temperature (overnight, brownish color).

GP3: Workup of α-haloboronic esters and boronic esters

The reaction mixture was poured into *n*-pentane and saturated NH_4Cl-solution. The phases were separated, and the aqueous phase extracted twice with *n*-pentane. The combined organic extracts were dried over Na_2SO_4 and the solvent removed under reduced pressure.

Synthetic procedures

Synthesis of compound 1



(4*S*,5*S*)-2-[(*S*)-1-(Benzyloxy)-3-phenylpropyl]-4,5-dicyclohexyl-1,3,2-dioxaborolane (A-1). A NaOBn-solution was prepared by reacting 589 mg (14.7 mmol, 1.25 equiv.) sodium hydride (60 % in paraffine) with 1.65 ml (15.9 mmol, 1.35 equiv.) benzyl alcohol in 5.89 ml anhydrous THF (0.4 ml/mmol NaH) and 16.2 ml anhydrous DMSO (1.1 ml/mmol NaH) at r.t. and stirring for 5.5 h. According to **GP1** 4.01 g (11.8 mmol, 1.0 equiv.) boronic ester **2**[1] was reacted with 2.27 ml (35.3 mmol, 3.0 equiv.) anhydrous DCM, 2.27 ml (15.9 mmol, 1.35 equiv.) DIPA, 9.30 ml (14.9 mmol, 1.25 equiv.) *n*-BuLi (1.6 M in *n*-hexane) and 3.24 g (23.8 mmol, 2.0 equiv.) $ZnCl_2$ in 33.0 ml anhydrous THF and stirred for 2 h. The reaction mixture was cooled to 0 °C and the previously prepared alcoholate added and stirred for 18 h. It was worked up according to **GP3** and the obtained residue purified by flash chromatography (*n*-pentane/EtOAc 96:4). Yield: 3.29 g (8.52 mmol, 72 %); colourless cloudy resin; R_f 0.22 (*n*-pentane/EtOAc 96:4); α_D^{20} = –15.6 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.98 (m, 2 H), 1.09 (m, 2 H), 1.14–1.27 (m, 6 H), 1.35 (m, 2 H), 1.62 (m, 2 H), 1.69 (m, 2 H), 1.73–1.83 (m, 6 H), 2.00 (m, 2 H), 2.72 (ddd, *J*= 13.7, 10.1, 6.3 Hz, 1 H), 2.81 (ddd, *J* = 13.7, 10.4, 5.7 Hz, 1 H), 3.39 (dd, *J* = 8.2, 5.4 Hz, 1 H), 3.93 (m, 2 H), 4.50 (d, *J* = 11.7 Hz, 1 H), 4.64 (d, *J* = 12.0 Hz, 1 H), 7.16–7.21 (m, 3 H), 7.25–7.30 (m, 3 H), 7.35 (m, 2 H), 7.39 (m, 2 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.9, 26.0, 26.4, 27.3, 28.2, 32.8, 33.5, 42.9, 67.0, 72-3, 83.7, 125.6, 127.4, 128.0, 128.2, 128.2, 128.6, 139.1, 142.5 ppm; HRMS (CI) calcd. for $C_{30}H_{42}O_3B^+$ $[M+H]^+$: 461.3222, found: 461.3240.

(4*S*,5*S*)-2-[(2*R*,3*R*)-3-(Benzyloxy)-5-phenylpentan-2-yl]-4,5-dicyclohexyl-1,3,2-dioxaborolane (B-1). According to **GP1** 6.99 g (15.2 mmol, 1.0 equiv.) boronic ester **A-1** was reacted with 2.93 ml (45.6 mmol, 3.0 equiv.) anhydrous DCM, 2.92 ml (20.5 mmol, 1.35 equiv.) DIPA, 7.59 ml (19.0 mmol, 1.25 equiv.) *n*-BuLi (2.5 M in *n*-hexane) and 6.21 g (45.6 mmol, 3.0 equiv.) $ZnCl_2$ in 51.7 ml anhydrous THF and stirred for 2 h. The reaction mixture was cooled to 0 °C and 12.7 ml (38.0 mmol, 2.5 equiv.) MeMgCl (3.0 M in anhydrous THF) added dropwise. The reaction mixture was warmed to r.t. and stirred for 3 d. It was worked up according to **GP3** and the obtained residue purified by flash chromatography (*n*-pentane/EtOAc 98:2 – 97:3). Yield: 11.2 g (20.9 mmol, 91 %); colourless resin; R_f 0.34 (*n*-pentane/EtOAc 96:4); α_D^{20} = –14.4 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92–0.99 (m, 2 H), 1.00–1.11 (m, 5 H), 1.12–1.23 (m, 6 H), 1.25–1.35 (m, 2 H), 1.59 (m, 2 H), 1.67 (m, 2 H), 1.73–1.85 (m, 8 H), 1.95 (m, 1 H), 2.65 (ddd, ^2J = 13.7, 10.4, 6.1 Hz, 1 H), 2.82 (ddd, *J* = 13.7, 10.6, 5.1 Hz,

[1] G. A. Molander, S. R. Wisniewski, *J. Am. Chem. Soc.* **2012**, *134*, 16856–16868.

1 H), 3.63 (ddd, *J* = 8.2, 4.8, 3.8 Hz, 1 H), 3.84 (m, 2 H), 4.48 (d, *J* = 11.6 Hz, 1 H), 4.59 (d, *J* = 11.6 Hz, 1 H), 7.15–7.20 (m, 3 H), 7.24–7.30 (m, 3 H), 7.34 (m, 2 H), 7.38 (m, 2 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 10.1, 20.4, 25.9, 26.0, 26.4, 27.5, 28.4, 32.1, 34.1, 43.0, 70.7, 80.7, 83.3, 125.5, 127.2, 127.5, 128.2, 128.4, 139.3, 142.8 ppm; HRMS (CI) calcd. for $C_{32}H_{45}O_3B^+$ $[M]^+$: 488.3456, found: 488.3448.

(3*R*,4*R*)-4-[(4*S*,5*S*)-4,5-Dicyclohexyl-1,3,2-dioxaborolan-2-yl]-1-phenylpentan-3-ol (C-1). 5.55 g (13.4 mmol, 1.0 equiv.) boronic ester **B-1** was dissolved in 56.8 ml THF (0.2 M). 604 mg Pd/C (10 m-%) was added and the mixture set under an atmosphere of H_2 (1 atm.) and stirred for 2 d at r.t. The reaction mixture was filtered through a plug of Celite with DCM. After removal of the solvent, the residue was used in the next step without further purification. Yield: 4.50 g (11.3 mmol, 99 %); colourless solid; m.p. 41 °C (from DCM); R_f 0.28 (*n*-pentane/EtOAc 9:1); α_D^{20} = –30.4 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95–1.12 (m, 7 H), 1.14–1.27 (m, 6 H), 1.28–1.37 (m, 3 H), 1.60 (m, 2 H), 1.68 (m, 2 H), 1.72 (m, 7 H), 1.85 (dddd, *J* = 13.9, 10.2, 6.5, 3.5 Hz, 1 H), 2.43 (d, *J* = 6.5 Hz, 1 H), 2.66 (ddd, *J* = 13.7, 10.2, 6.4 Hz, 1 H), 2.87 (ddd, *J* = 13.7, 10.4, 5.1 Hz, 1 H), 3.58 (dddd, *J* = 9.3, 6.5, 6.1, 3.5 Hz, 1 H), 3.87 (m, 2 H), 7.15–7.23 (m, 3 H), 7.27 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.9, 24.6, 25.8, 26.0, 26.4, 27.4, 28.4, 32.3, 38.7, 74.4, 83.5, 125.6, 128.3, 128.4, 142.7 ppm; HRMS (CI) calcd. for $C_{25}H_{40}O_3B^+$ $[M+H]^+$: 399.3067, found: 399.3065.

***tert*-Butyl({(3*R*,4*R*)-4-[(4*S*,5*S*)-4,5-dicyclohexyl-1,3,2-dioxaborolan-2-yl]-1-phenylpentan-3-yl}oxy)dimethylsilane (D-1).** 4.49 g (11.3 mmol, 1.0 equiv.) boronic ester **C-1** was dissolved in 11.3 ml anhydrous DMF (1.0 M). 843 mg (12.4 mmol, 1.1 equiv.) imidazole and 1.78 g (11.8 mmol, 1.05 equiv.) TBSCl was added and stirred for 18 h at r.t. The reaction misture was diluted with diethyl ether and washed three times with H_2O and once with brine. The organic phase was dried over Na_2SO_4, the solvent removed under reduced pressure and the residue purified by flash chromatography (*n*-pentane/EtOAc 100:0 – 98:2). Yield: 4.96 g (9.67 mmol, 86 %); colourless resin; R_f 0.13 (*n*-pentane/EtOAc 99:1); α_D^{20} = –26.6 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.10 (s, 6 H), 0.96 (s, 9 H), 0.98–1.14 (m, 7 H), 1.16–1.29 (m, 6 H), 1.35 (m, 2 H), 1.48 (dq, *J* = 7.3, 3.5 Hz), 1.63 (m, 2 H), 1.71 (m, 2 H), 1.75–1.88 (m, 8 H), 2.57 (ddd, *J* = 13.6, 10.1, 6.6 Hz, 1 H), 2.70 (ddd, *J* = 13.6, 10.1, 6.3 Hz, 1 H), 3.86 (m, 2 H), 3.93 (ddd, *J* = 7.3, 5.4, 3.5 Hz, 1 H), 7.14–7.21 (m, 3 H), 7.27 (m, 2 H) ppm; ^{13}C NMR (125 MHz, CD_3OD): δ = -4.4, -4.4, 10.4, 18.2, 24.6, 25.9, 26.0, 26.1, 26.5, 27.5, 28.4, 33.1, 37.6, 43.1, 74.3, 83.2, 125.5, 128.2, 128.4, 143.0 ppm; HRMS (CI) calcd. for $C_{31}H_{54}O_3BSi^+$ $[M+H]^+$: 513.3930, found: 513.3925.

***tert*-Butyl({(3*R*,4*S*,5*R*)-5-[(4*S*,5*S*)-4,5-dicyclohexyl-1,3,2-dioxaborolan-2-yl]-4-methyl-1-phenylhexan-3-yl}oxy)dimethylsilane (1)**. According to **GP1** 2.27 g (4.43 mmol, 1.0 equiv.) boronic ester **E-1** was reacted with 855 µl (13.3 mmol, 3.0 equiv.) anhydrous DCM, 852 µl (5.98 mmol, 1.35 equiv.) DIPA, 3.47 ml (5.54 mmol, 1.25 equiv.) *n*-BuLi (1.6 M in *n*-hexane) and 1.81 g (13.3 mmol, 3.0 equiv.) $ZnCl_2$ in 15.1 ml anhydrous THF and stirred for 2 h. It was worked up according to **GP3** and the obtained α-chloroboronic ester used without further purification. 634 mg (4.65 mmol, 1.05 equiv.) $ZnCl_2$ was dissolved in 8.85 ml anhydrous THF (0.5 M), cooled to 0 °C and 3.10 ml (9.30 mmol, 2.1 equiv.) MeMgCl (3.0 M in anhydrous THF) was added. The mixture was warmed to r.t., stirred for 5 min and cooled to 0 °C again. The previously obtained α-chloroboronic ester was dissolved in 8.85 ml anhydrous THF (0.5 M), added dropweise to this mixture, warmed to r.t. and stirred for 3 d. It was worked up according to **GP3** and the obtained residue purified by flash chromatography (*n*-pentane/EtOAc 99:1 – 95:5). Yield: 2.15 g (3.97 mmol, 90 %); colourless resin; R_f 0.17 (*n*-pentane/EtOAc 98:2); α_D^{20} = –24.1 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.08 (s, 3 H), 0.10 (s,

3 H), 0.88 (d, *J* = 6.9 Hz, 3 H), 0.94 (s, 9 H), 0.96–1.10 (m, 7 H), 1.12–1.23 (m, 7 H), 1.28 (m, 2 H), 1.58 (m, 2 H), 1.63–1.71 (m, 5 H), 1.72–1.81 (m, 6 H), 2.55 (dt, *J* = 14.2, 8.2 Hz, 1 H), 2.79 (dt, *J* = 14.2, 8.2 Hz, 1 H), 3.79 (m, 2 H), 3.82 (m, 1 H), 7.15–7.21 (m, 3 H), 7.28 (m, 2 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = -4.4, -4.3, 13.1, 14.7, 18.2, 19.7, 25.9, 26.0, 26.0, 26.5, 27.6, 28.5, 32.1, 33.3, 42.0, 43.1, 73.8, 83.3, 125.5, 128.3, 128.4, 143.2 ppm; HRMS (CI) calcd. for $C_{33}H_{56}O_3BSi^+$ $[M+H]^+$: 539.4086, found: 539.4066.

(2-{(*S*)-1-[(4*S*,5*S*)-4,5-Dicyclohexyl-1,3,2-dioxaborolan-2-yl]-3-phenylpropoxy}ethyl)trimethylsilane (3). 4.94 ml (34.5 mmol, 1.1 equiv.) 2-(trimethylsilyl)ethan-1-ol was dissolved in 39.2 ml anhydrous THF (0.88 M) and cooled to 0 °C. 13.2 ml (32.9 mmol, 1.05 equiv.) *n*-BuLi (2.5 M in *n*-hexane) was added dropwise at this temperature, stirred for 15 min and then warmed to r.t. According to **GP1** 10.9 g (32.2 mmol, 1.0 equiv.) boronic ester **2** was reacted with 6.21 ml (97.0 mmol, 3.0 equiv.) anhydrous DCM, 6.19 ml (43.4 mmol, 1.35 equiv.) DIPA, 16.1 ml (40.2 mmol, 1.25 equiv.) *n*-BuLi (2.5 M in *n*-hexane) and 8.77 g (64.3 mmol, 2.0 equiv.) anhydrous $ZnCl_2$ in 90.0 ml anhydrous THF and stirred for 2 h. The reaction mixture was worked up according to **GP3** and the obtained α-chloroboronic ester used without any further purification. The obtained α-chloroboronic ester was dissolved in 39.2 ml anhydrous THF (0.8 M) and cooled to 0 °C. The previously prepared alcoholate solution was then added dropwise, the solution warmed to r.t. and stirred for 17 h. The reaction mixture was worked up according to **GP3**. The residue was purified by flash chromatography (*n*-pentane/EtOAc 98:2 – 95:5) and the desired compound **3** stored under an atmosphere of N_2 at –20 °C. Yield: 12.9 g (27.4 mmol, 85 %); colourless resin; R_f 0.35 (*n*-pentane/EtOAc 95:5); α_D^{20} = –19.4 (c = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.02 (s, 9 H), 0.95–1.12 (m, 6 H), 1.12–1.26 (m, 6 H), 1.34 (m, 2 H), 1.60 (m, 2 H), 1.68 (m, 2 H), 1.73–1.82 (m, 6 H), 1.92 (dddd, *J* = 13.7, 9.8, 6.6, 6.2 Hz, 1 H), 1.98 (dddd, *J* = 13.7, 9.4, 7.4, 5.7 Hz, 1 H), 2.69 (ddd, *J* = 13.7, 9.4, 6.6 Hz, 1 H), 2.76 (ddd, *J* = 13.7, 9.8, 5.7 Hz, 1 H), 3.27 (dd, *J* = 7.4, 6.2 Hz, 1 H), 3.52 (m, 2 H), 3.92 (m, 2 H), 7.15–7.22 (m, 3 H), 7.28 (m, 2 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = -1.4, 18.6, 25.9, 26.0, 26.4, 27.3, 28.2, 32.8, 33.4, 42.9, 67.0, 67.2, 83.6, 125.6, 128.2, 128.5, 142.6 ppm; HRMS (ESI-ToF) calcd. for $C_{23}H_{34}O_2B^+$ [M–TMSEO]$^+$: 353.2646, found: 353.2665.

(2-{(*S*)-1-[(4*S*,5*S*)-4,5-Dicyclohexyl-1,3,2-dioxaborolan-2-yl]-3-phenylpropoxy}ethyl)trimethylsilane (4). According to **GP1** 12.9 g (27.4 mmol, 1.0 equiv.) boronic ester **3** was reacted with 5.28 ml (82.0 mmol, 3.0 equiv.) anhydrous DCM, 5.27 ml (37.0 mmol, 1.35 equiv.) DIPA, 13.7 ml (34.2 mmol, 1.25 equiv.) *n*-BuLi (2.5 M in *n*-hexane) and 11.2 g (82.0 mmol, 3.0 equiv.) $ZnCl_2$ in 93.1 ml anhydrous THF and stirred for 2 h. It was worked up according to **GP3** and the obtained α-chloroboronic ester used without further purification. 3.92 g (28.7 mmol, 1.05 equiv.) $ZnCl_2$ was dissolved in 54.8 ml anhydrous THF (0.5 M), cooled to 0 °C and 19.2 ml (57.5 mmol, 2.1 equiv.) MeMgCl (3.0 M in anhydrous THF) was added. The mixture was warmed to r.t., stirred for 5 min and cooled to 0 °C again. The previously obtained α-chloroboronic ester was dissolved in 54.8 ml anhydrous THF (0.5 M), added dropwise to this mixture, warmed to r.t. and stirred for 3 d. It was worked up according to **GP3** and the obtained residue purified by flash chromatography (*n*-pentane/EtOAc 99.5:0.5 – 99:1). Yield: 11.7 g (23.5 mmol, 86 %); colourless resin; R_f 0.27 (*n*-pentane/EtOAc 95:5); α_D^{20} = –19.3 (c = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.03 (s, 9 H), 0.93–1.10 (m, *J* = 7.3 Hz, 9 H), 1.12–1.26 (m, 6 H), 1.31 (m, 2 H), 1.55–1.63 (m, 3 H), 1.67 (m, 2 H), 1.72–1.81 (m, 7 H), 1.85 (dddd, *J* = 13.7, 10.4, 7.7, 5.1 Hz, 1 H), 2.62 (ddd, *J* = 13.7, 10.4, 6.2 Hz, 1 H), 2.77 (ddd, *J* = 13.7, 10.6, 5.1 Hz, 1 H), 3.37–3.47 (m, 2 H), 3.56 (ddd, *J* = 9.6, 9.6, 7.2 Hz, 1 H), 3.83 (m, 2 H), 7.14–7.21 (m, 3 H), 7.27 (m, 2 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.3, 10.1, 18.7, 20.5, 25.9,

26.0, 26.5, 27.5, 28.3, 32.0, 34.0, 43.0, 65.7, 80.2, 83.3, 125.5, 128.2, 128.4, 143.0 ppm; HRMS (ESI-ToF) calcd. for $C_{25}H_{38}O_2B^+$ [M–TMSEO]$^+$: 381.2959, found: 381.2955.

[2-({(3*R*,4*S*,5*R*)-5-[(4*S*,5*S*)-4,5-Dicyclohexyl-1,3,2-dioxaborolan-2-yl]-4-methyl-1-phenyl-hexan-3-yl}oxy)ethyl]trimethylsilane (5). According to **GP1** 3.98 g (7.99 mmol, 1.0 equiv.) boronic ester **4** was reacted with 1.54 ml (24.0 mmol, 3.0 equiv.) anhydrous DCM, 1.54 ml (10.8 mmol, 1.35 equiv.) DIPA, 3.99 ml (9.98 mmol, 1.25 equiv.) *n*-BuLi (2.5 M in *n*-hexane) and 3.27 g (82.0 mmol, 3.0 equiv.) $ZnCl_2$ in 27.2 ml anhydrous THF and stirred for 2 h. It was worked up according to **GP3** and the obtained α-chloroboronic ester used without further purification. 1.14 g (8.39 mmol, 1.05 equiv.) $ZnCl_2$ was dissolved in 16.0 ml anhydrous THF (0.5 M), cooled to 0 °C and 5.59 ml (16.8 mmol, 2.1 equiv.) MeMgCl (3.0 M in anhydrous THF) was added. The mixture was warmed to r.t., stirred for 5 min and cooled to 0 °C again. The previously obtained α-chloroboronic ester was dissolved in 16.0 ml anhydrous THF (0.5 M), added dropwise to this mixture, warmed to r.t. and stirred for 4 d. It was worked up according to **GP3** and the obtained residue purified by flash chromatography (*n*-pentane/EtOAc 99:1 – 98:2). Yield: 3.16 g (6.00 mmol, 75 %); colourless resin; R_f 0.33 (*n*-pentane/EtOAc 97:3); α_D^{20} = –24.4 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.02 (s, 9 H), 0.87 (d, = 7.0 Hz, 3 H), 0.91–1.09 (m, 9 H), 1.10–1.25 (m, 6 H), 1.25–1.33 (m, 3 H), 1.59 (m, 2 H), 1.64–1.71 (m, 3 H), 1.71 (m, 7 H), 2.61 (ddd, *J* = 13.7, 10.3, 6.2 Hz, 1 H), 2.80 (ddd, *J* = 13.7, 10.2, 4.9 Hz, 1 H), 3.30 (ddd, *J* = 8.2, 6.5, 2.9 Hz, 1 H), 3.44 (m, 1 H), 3.57 (m, 1 H), 3.79 (m, 2 H), 7.15–7.22 (m, 3 H), 7.27 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.0, 15.1, 15.8, 20.2, 20.3, 27.2, 27.3, 27.8, 29.0, 29.8, 33.1, 33.2, 40.1, 44.4, 67.8, 82.0, 84.6, 126.9, 129.6, 129.8, 144.4 ppm; HRMS (CI) calcd. for $C_{32}H_{56}O_3BSi^+$ [M+H]$^+$: 527.4086, found: 527.4087.

[2-({(3*R*,4*S*,5*R*)-5-[(4*S*,5*S*)-4,5-Dicyclohexyl-1,3,2-dioxaborolan-2-yl]-4-methyl-1-phenyl-hexan-3-yl}oxy)ethyl]trimethylsilane (6). According to **GP1** 3.22 g (6.12 mmol, 1.0 equiv.) boronic ester **5** was reacted with 1.18 ml (18.4 mmol, 3.0 equiv.) anhydrous DCM, 1.18 ml (8.26 mmol, 1.35 equiv.) DIPA, 3.06 ml (7.64 mmol, 1.25 equiv.) *n*-BuLi (2.5 M in *n*-hexane) and 2.50 g (18.4 mmol, 3.0 equiv.) $ZnCl_2$ in 20.8 ml anhydrous THF and stirred for 2 h. It was worked up according to **GP3** and the obtained residue purified by flash chromatography (*n*-pentane/EtOAc 99:1 – 95:5). Yield: 1.80 g (4.11 mmol, 67 %); colourless resin; R_f 0.24 (*n*-pentane/EtOAc 95:5); α_D^{20} = –2.5 (c = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (d, *J* = 7.1 Hz, 3 H), 0.96 (d, *J* = 7.0 Hz, 3 H), 0.98–1.29 (m, 10 H), 1.37 (m, 2 H), 1.61 (m, 2 H), 1.67 (m, 2 H), 1.71–1.95 (m, 9 H), 2.30 (ddq, 1 H, *J* = 9.5, 8.3, 7.1 Hz, 1 H), 2.67 (ddd, *J* = 13.8, 10.3, 6.2 Hz, 1 H), 2.84 (ddd, *J* = 13.8, 10.4, 5.6 Hz, 1 H), 3.27 (d, *J* = 9.5 Hz, 1 H), 3.47 (ddd, *J* = 7.0, 5.7, 5.7 Hz, 1 H), 3.93 (m, 2 H), 7.16 (m, 1 H), 7.21 (m, 2 H), 7.27 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.9, 13.2, 25.9, 26.0, 26.4, 27.4, 28.2, 32.5, 36.9, 39.3 (d, 41.9, 42.9, 72.1, 83.6, 86.7, 125.5, 128.2, 128.4, 142.8 ppm; HRMS (ESI-ToF) calcd. for $C_{28}H_{44}O_3B^+$ [M+H]$^+$: 439.3378, found: 439.3359.

(4*S*,5*S*)-4,5-Dicyclohexyl-2-pentyl-1,3,2-dioxaborolane (7). 6.08 g (26.8 mmol, 1.0 equiv.) (1*S*,2*S*)-1,2-Dicyclohexylethane-1,2-diol was suspended in 53.7 ml (0.5 M) diethyl ether. 3.27 g (28.2 mmol, 1.05 equiv.) *n*-pentylboronic acid were added at r.t. and the mixture was stirred for 2 h. The reaction mixture was filtered trough a plug of Celite and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography (*n*-pentane/EtOAc 98:2). Yield: 7.92 g (25.9 mmol, 96 %); colourless resin; R_f 0.10 (*n*-pentane/EtOAc 99:1); α_D^{20} = –65.3 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.80 (t, *J* = 7.8 Hz, 2 H), 0.87 (t, *J* = 7.0 Hz, 3 H), 0.96 (m, 2 H), 1.05 (m, 2 H), 1.10–1.25 (m, 6 H), 1.26–1.35 (m, 6 H), 1.42 (tt, *J* = 7.8, 7.2 Hz, 2 H), 1.58 (m, 2 H), 1.67 (m, 2 H), 1.72–1.81 (m, 6 H), 3.83 (m, 2 H) ppm; ^{13}C NMR

(125 MHz, $CDCl_3$): δ = 13.7, 14.1, 22.5, 23.9, 25.9, 26.0, 26.5, 27.3, 28.3, 34.7, 43.0, 83.2 ppm; HRMS (CI) calcd. for $C_{19}H_{34}O_2B^+$ $[M–H]^+$: 305.2646, found: 305.2678.

(4*R*,5*R*)-4,5-Dicyclohexyl-2-pentyl-1,3,2-dioxaborolane (*ent*-7). 6.47 g (28.6 mmol, 1.0 equiv.) (1*R*,2*R*)-1,2-Dicyclohexylethane-1,2-diol was suspended in 57.1 ml (0.5 M) diethyl ether. 3.48 g (30.0 mmol, 1.05 equiv.) *n*-pentylboronic acid were added at r.t. and the mixture was stirred for 2 h. The reaction mixture was filtered trough a plug of Celite and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography (*n*-pentane/EtOAc 98:2). Yield: 8.47 g (27.7 mmol, 97 %); colourless resin; R_f 0.47 (*n*-pentane/EtOAc 97:3); α_D^{20} = +60.4 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.80 (t, *J* = 7.8 Hz, 2 H), 0.87 (t, *J* = 7.0 Hz, 3 H), 0.96 (m, 2 H), 1.05 (m, 2 H), 1.10–1.25 (m, 6 H), 1.26–1.35 (m, 6 H), 1.42 (tt, *J* = 7.8, 7.2 Hz, 2 H), 1.58 (m, 2 H), 1.67 (m, 2 H), 1.72–1.81 (m, 6 H), 3.83 (m, 2 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.7, 14.1, 22.5, 23.9, 25.9, 26.0, 26.5, 27.3, 28.3, 34.7, 43.0, 83.2 ppm; HRMS (CI) calcd. for $C_{19}H_{34}O_2B^+$ $[M+H]^+$: 307.2803, found: 307.2803.

[2-({(*S*)-1-[(4*S*,5*S*)-4,5-Dicyclohexyl-1,3,2-dioxaborolan-2-yl]hexyl}oxy)ethyl]trimethylsilane (8). 1.23 ml (8.56 mmol, 1.35 equiv.) 2-(trimethylsilyl)ethan-1-ol was dissolved in 7.93 ml anhydrous THF (1.08 M) and cooled to 0 °C. 5.15 ml (8.25 mmol, 1.30 equiv.) *n*-BuLi (1.6 M in *n*-hexane) was added dropwise at this temperature, stirred for 15 min and then warmed to r.t. According to **GP1** 1.94 g (6.34 mmol, 1.0 equiv.) boronic ester **7** was reacted with 1.22 ml (19.0 mmol, 3.0 equiv.) anhydrous DCM, 1.22 ml (8.56 mmol, 1.35 equiv.) DIPA, 4.96 ml (7.92 mmol, 1.25 equiv.) *n*-BuLi (1.6 M in *n*-hexane) and 1.73 g (12.7 mmol, 2.0 equiv.) anhydrous $ZnCl_2$ in 17.8 ml anhydrous THF and stirred for 2 h. The reaction mixture was worked up according to **GP3** and the obtained α-chloroboronic ester used without any further purification. The obtained α-chloroboronic ester was dissolved in 7.93 ml anhydrous THF (0.8 M) and cooled to 0 °C. The previously prepared alcoholate solution was then added dropwise, the solution warmed to r.t. and stirred for 40 h. The reaction mixture was worked up according to **GP3**. The residue was purified by flash chromatography (*n*-pentane/EtOAc 98:2 – 95:5) and the desired compound **8** stored under an atmosphere of N_2 at –20 °C. Yield: 2.50 g (5.73 mmol, 90 %); colourless resin; R_f 0.34 (*n*-pentane/EtOAc 95:5); α_D^{20} = –46.6 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.00 (s, 9 H), 0.88 (t, *J* = 6.9 Hz, 3 H), 0.92–0.97 (m, 2 H), 0.97–1.13 (m, 4 H), 1.13–1.25 (m, 6 H), 1.26–1.40 (m, 8 H), 1.56–1.70 (m, 6 H), 1.72–1.81 (m, 6 H), 3.23 (t, *J* = 6.9 Hz, 2 H), 3.44–3.54 (m, 2 H), 3.90 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = –1.4, 14.0, 18.6, 22.6, 25.9, 26.0, 26.4, 27.4, 28.3, 31.5, 32.0, 42.9, 67.1, 67.6, 83.6 ppm; HRMS (ESI-Orbitrap) calcd. for $C_{25}H_{49}O_3SiBNa^+$ $[M+Na]^+$: 459.3436, found: 459.3430.

[2-({(*R*)-1-[(4*R*,5*R*)-4,5-Dicyclohexyl-1,3,2-dioxaborolan-2-yl]hexyl}oxy)ethyl]trimethylsilane (*ent*-8). 1.92 ml (13.4 mmol, 1.35 equiv.) 2-(trimethylsilyl)ethan-1-ol was dissolved in 12.4 ml anhydrous THF (1.08 M) and cooled to 0 °C. 8.08 ml (12.9 mmol, 1.30 equiv.) *n*-BuLi (1.6 M in *n*-hexane) was added dropwise at this temperature, stirred for 15 min and then warmed to r.t. According to **GP1** 3.05 g (9.94 mmol, 1.0 equiv.) boronic ester ***ent*-7** was reacted with 1.92 ml (29.8 mmol, 3.0 equiv.) anhydrous DCM, 1.91 ml (13.4 mmol, 1.35 equiv.) DIPA, 7.77 ml (12.4 mmol, 1.25 equiv.) *n*-BuLi (1.6 M in *n*-hexane) and 2.71 g (19.9 mmol, 2.0 equiv.) anhydrous $ZnCl_2$ in 27.8 ml anhydrous THF and stirred for 2 h. The reaction mixture was worked up according to **GP3** and the obtained α-chloroboronic ester used without any further purification. The obtained α-chloroboronic ester was dissolved in 12.4 ml anhydrous THF (0.8 M) and cooled to 0 °C. The previously prepared alcoholate solution was then added

dropwise, the solution warmed to r.t. and stirred for 40 h. The reaction mixture was worked up according to **GP3**. The residue was purified by flash chromatography (*n*-pentane/EtOAc 98:2 – 95:5) and the desired compound ***ent*-8** stored under an atmosphere of N_2 at –20 °C. Yield: 3.76 g (8.61 mmol, 87 %); colourless resin; R_f 0.19 (*n*-pentane/EtOAc 97:3); α_D^{20} = +40.8 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.00 (s, 9 H), 0.88 (t, *J* = 6.9 Hz, 3 H), 0.92–0.97 (m, 2 H), 0.97–1.13 (m, 4 H), 1.13–1.25 (m, 6 H), 1.26–1.40 (m, 8 H), 1.56–1.70 (m, 6 H), 1.72–1.81 (m, 6 H), 3.23 (t, *J* = 6.9 Hz, 2 H), 3.44–3.54 (m, 2 H), 3.90 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = –1.4, 14.0, 18.6, 22.6, 25.9, 26.0, 26.4, 27.4, 28.3, 31.5, 32.0, 42.9, 67.1, 67.6, 83.6 ppm; HRMS (CI) calcd. for $C_{25}H_{50}O_3SiB^+$ $[M+Na]^+$: 437.3617, found: 437.3614.

[2-({(1*S*,2*R*)-1-[(4*S*,5*S*)-4,5-Dicyclohexyl-1,3,2-dioxaborolan-2-yl]-1-[(4-methoxybenzyl)oxy]heptan-2-yl}oxy)ethyl]trimethylsilane (9). A NaOPMB-solution was prepared by reacting 310 mg (7.74 mmol, 1.5 equiv.) sodium hydride (60 % in paraffine) with 1.03 ml (8.26 mmol, 1.6 equiv.) 4-methoxybenzyl alcohol in 3.10 ml anhydrous THF (0.4 ml/mmol NaH) and 8.51 ml anhydrous DMSO (1.1 ml/mmol NaH) at r.t. and stirring for 5.5 h. According to **GP2** 2.25 g (5.16 mmol, 1.0 equiv.) boronic ester **8** was reacted with 1.08 ml (15.5 mmol, 3.0 equiv.) DBM, 993 µl (6.97 mmol, 1.35 equiv.) DIPA, 4.03 ml (6.45 mmol, 1.25 equiv.) *n*-BuLi (1.6 M in *n*-hexane) and 2.11 g (15.5 mmol, 3.0 equiv.) $ZnCl_2$ in 17.5 ml anhydrous THF and stirred overnight. The reaction mixture was cooled to 0 °C and the previously prepared alcoholate added and stirred for 3 d. It was worked up according to **GP3** and the obtained residue purified by flash chromatography (*n*-pentane/EtOAc 98:2 – 96:4). Yield: 2.42 g (4.12 mmol, 80 %); colourless cloudy resin; R_f 0.28 (*n*-pentane/EtOAc 95:5); α_D^{20} = –20.1 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.00 (s, 9 H, 14-H), 0.86–0.94 (m, $^3J_{6,7}$ = 6.8 Hz, 5 H, 6-H, 13-H_a, 13-H_b), 0.95–1.10 (m, 4 H), 1.13–1.24 (m, 6 H), 1.26–1.40 (m, 8 H), 1.58–1.71 (m, 6 H), 1.73–1.85 (m, 6 H), 3.43 (ddd, *J* = 10.9, 9.5, 6.5 Hz, 1 H), 3.46 (d, *J* = 2.9 Hz, 1 H), 3.50 (ddd, *J* = 7.3, 4.6, 2.8 Hz, 1 H), 3.72 (ddd, *J* = 10.9, 9.3, 5.7 Hz, 1 H), 3.80 (s, 3 H), 3.90 (m, 2 H), 4.50 (d, *J* = 12.0 Hz, 1 H), 4.58 (d, *J* = 12.0 Hz, 1 H), 6.84 (d, *J* = 8.7 Hz, 2), 7.27 (d, *J* = 8.7 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = –1.4, 14.1, 18.7, 22.6, 25.8, 25.9, 26.0, 26.4, 27.6, 28.2, 31.9, 31.9, 42.9, 55.2, 66.8, 70.7, 72.2, 81.0, 83.7, 113.5, 129.2, 131.3, 158.9 ppm; HRMS (ESI-Orbitrap) calcd. for $C_{34}H_{60}O_5BSi^+$ $[M+H]^+$: 587.4298, found: 587.4286.

[2-({(2*S*,3*R*)-1-[(4*S*,5*S*)-4,5-Dicyclohexyl-1,3,2-dioxaborolan-2-yl]-2-[(4-methoxybenzyl)-oxy]octan-3-yl}oxy)ethyl]trimethylsilane (10). According to **GP2** 2.32 g (3.95 mmol, 1.0 equiv.) boronic ester **9** was reacted with 828 µl (11.9 mmol, 3.0 equiv.) DBM, 761 µl (5.34 mmol, 1.35 equiv.) DIPA, 3.09 ml (4.94 mmol, 1.25 equiv.) *n*-BuLi (1.6 M in *n*-hexane) and 2.16 g (15.8 mmol, 4.0 equiv.) $ZnCl_2$ in 15.8 ml anhydrous THF and stirred overnight. The reaction mixture was worked up according to **GP3**. The residue was dissolved in 39.5 ml MeOH/THF (0.1 M, 3:1) and reacted with 172 mg (4.55 mmol, 1.15 equiv.) $NaBH_4$ at r.t. and stirred for 6 h. The reaction mixture was worked up according to **GP3** and the obtained residue purified by flash chromatography (*n*-pentane/EtOAc 99:1 – 97:3). Yield: 1.66 g (2.75 mmol, 70 %); colourless cloudy resin; R_f 0.21 (*n*-pentane/EtOAc 97:3); α_D^{20} = –26.3 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.01 (s, 9 H), 0.86–0.95 (m, *J* = 7.1 Hz, 7 H), 0.97–1.10 (m, 4 H), 1.10–1.21 (m, 6 H), 1.23–1.34 (m, 8 H), 1.48 (m, 2 H), 1-58 (m, 2 H), 1.66 (m, 2 H), 1.70–1.81 (m, 6 H), 3.28 (ddd, *J* = 5.6, 5.6, 3.5 Hz, 1 H), 3.44 (m, 1 H), 3.69 (ddd, *J* = 15.8, 9.7, 6.6 Hz, 1 H), 3.74 (ddd, *J* = 6.8, 6., 3.5 Hz, 1 H), 3.79 (s, 3), 3.82 (m, 2 H), 4.53 (d, *J* = 11.6 Hz, 1 H), 4.57 (d, *J* = 11.5 Hz, 1 H), 6.84 (d, *J* = 8.7 Hz, 2 H), 7.26 (d, *J* = 8.6 Hz, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = –1.4, 13.4, 14.1, 18.8, 22.7, 25.8, 25.8, 26.0, 26.4, 27.5, 28.5, 30.5, 32.0,

43.0, 55.3, 67.3, 71.2, 78.0, 81.9, 83.4, 113.5, 129.0, 131.5, 158.8 ppm; HRMS (ESI-Orbitrap) calcd. for $C_{35}H_{62}O_5BSi^+$ $[M+H]^+$: 601.4454, found: 601.4461.

(4*S*,5*S*)-4,5-Dicyclohexyl-2-{(2*S*,4*S*,5*R*)-4-[(4-methoxybenzyl)oxy]-5-pentyltetrahydrofuran-2-yl}-1,3,2-dioxaborolane (11). According to **GP1** 615 mg (1.02 mmol, 1.0 equiv.) boronic ester **10** was reacted with 198 µl (3.07 mmol, 3.0 equiv.) anhydrous DCM, 197 µl (1.38 mmol, 1.35 equiv.) DIPA, 800 µl (1.28 mmol, 1.25 equiv.) *n*-BuLi (1.6 M in *n*-hexane) and 558 mg (4.09 mmol, 4.0 equiv.) $ZnCl_2$ in 4.08 ml anhydrous THF and stirred for 5 h. It was worked up according to **GP3** and the obtained residue purified by flash chromatography (*n*-pentane/EtOAc 94:6 – 9:1). Yield: 341 mg (666 µmol, 65 %); colourless resin; R_f 0.26 (*n*-pentane/EtOAc 9:1); α_D^{20} = –9.4 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.0 Hz, 3 H), 0.94–1.10 (m, 4 H), 1.13–1.23 (m, 6 H), 1.25–1.38 (m, 8 H), 1.46 (m, 2 H), 1.57 (m, 2 H), 1.67 (m, 2 H), 1.72–1.79 (m, 6 H), 1.84 (ddd, *J* = 13.2, 11.6, 6.2 Hz, 1 H), 2.12 (ddd, *J* = 13.2, 6.0, 1.1 Hz, 1 H), 3.74–3.85 (m, 6 H), 3.91 (m, 2 H, 5-H), 4.38 (d, *J* = 11.4 Hz, 1 H), 4.48 (d, *J* = 11.4 Hz, 1 H), 6.87 (d, *J* = 8.6 Hz, 2 H), 7.25 (d, *J* = 8.6 Hz, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.6, 25.5, 25.9, 26.0, 26.4, 27.3, 28.2, 31.9, 34., 35.0, 42.8, 55.3, 64.9, 70.7, 83.7, 83.9, 85.7, 113.8, 129.2, 130.4, 159.1 ppm; HRMS (CI) calcd. for $C_{31}H_{49}O_5B^+$ $[M]^+$: 512.3669, found: 512.3632.

(4*S*,5*S*)-4,5-Dicyclohexyl-2-((*R*)-1-{(2*R*,4*S*,5*R*)-4-[(4-methoxybenzyl)oxy]-5-pentyltetrahydrofuran-2-yl}dec-9-en-1-yl)-1,3,2-dioxaborolane (12). A 9-bromononenylmagnesium bromide solution was prepared by reacting 948 mg (39.0 mmol) magnesium and 10.0 mg (39.0 µmol) iodine with a solution 4.00 g (19.5 mmol) 9-bromonon-1-ene in 19.5 ml anhydrous THF (1.0 M) and refluxing for 1 h. The mixture was decanted and stored in a Schlenk-flask. Titration against iodine in THF resulted in a 0.86 M concentration of the Grignard-reagent.
94.0 µl (1.46 mmol, 1.5 equiv.) DCM was dissolved in 1.09 ml anhydrous THF (0.75 ml/mmol DCM) and cooled to –100 °C. 400 µl (640 µmol, 1.1 equiv.) *n*-BuLi was added dropwise alongside the glass wall and the resulting suspension stirred for 30 min at this temperature.
Boronic ester **11** was dissolved in 0.73 ml anhydrous THF (0.8 M) and added dropwise to the previously pepared carbenoid solution. It was stirred for 10 min in which a clarification of the suspension was observed. A solution of 242 mg (1.78 mmol, 3.05 equiv.) anhydrous $ZnCl_2$ dissolved in 1.07 ml anhydrous THF (0.6 ml/mmol $ZnCl_2$) was added rapidly and the reaction mixture slowly warmed to r.t. overnight. The reaction mixture was worked up according to **GP3** and the obtained α-chloroboronic ester used without further purification. 83.0 mg (611 µmol, 1.05 equiv.) anhydrous $ZnCl_2$ were reacted with the previously pepared 1.42 ml (1.22 mmol, 2.1 equiv.) 9-bromononenylmagnesium bromide at r.t. and cooled to 0 °C. The previously obtained α-chloroboronic ester was dissolved in 2.89 ml anhydrous THF (0.2 M), added dropwise to this mixture, warmed to r.t. and stirred for 18 h. It was worked up according to **GP3** and the obtained residue purified by flash chromatography (*n*-pentane/EtOAc 98:2 – 95:5). Yield: 165 mg (254 µmol, 44 %); colourless resin; R_f 0.32 (*n*-pentane/EtOAc 95:5); α_D^{20} = –6.0 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.6 Hz, 3 H), 0.94–1.08 (m, 4 H), 1.12–1.48 (m, 24 H), 1.53–1.70 (m, 5 H), 1.71–1.82 (m, 6 H), 1.98–2.07 (m, 3 H), 3.64–3.72 (m, 2 H), 3.78–3.85 (m, 5 H), 4.07 (ddd, *J* = 10.0, 6.1, 6.1 Hz, 1 H, 20-H), 4.37 (d, *J* = 11.4 Hz, 1 H), 4.46 (d, *J* = 11.4 Hz, 1 H), 4.92 (ddt, *J* = 10.2, 2.1, 1.1 Hz, 1 H), 4.98 (ddt, *J* = 17.1, 2.1, 1.5 Hz, 1), 5.81 (ddt, ^{3}*J* = 17.0, 10.2, 6.7 Hz, 1 H), 6.87 (d, *J* = 8.6 Hz, 2 H), 7.25 (d, *J* = 8.6 Hz, 2 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 22.0, 22.6, 25.9, 26.0, 26.0, 26.5, 27.5, 27.8, 28.4, 29.0, 29.1, 29.5, 29.6, 29.8, 32.0, 33.8, 34.5, 37.5, 43.0, 55.3, 70.9, 80.0, 83.3, 83.6, 83.9, 113.8, 114.1, 129.2, 130.5, 139.3, 159.1 ppm; HRMS (ESI Q-exactive) calcd. for $C_{41}H_{68}O_5B^+$ $[M+H]^+$: 651.5154, found: 651.5156.

(*R*)-1-{(2*R*,4*S*,5*R*)-4-[(4-Methoxybenzyl)oxy]-5-pentyltetrahydrofuran-2-yl}dec-9-en-1-ol (13). 150 mg (231 µmol, 1.0 equiv.) boronic ester **12** was dissolved in 462 µl THF (0.5 M) and cooled to 0 °C. 107 µl (1.16 mmol, 5.0 equiv.) hydrogen peroxide (33 % in H_2O) and 46.0 mg (1.16 mmol, 5.0 equiv.) sodium hydroxide dissolved in 462 µl H_2O (0.5 M) were added. The reaction mixture was warmed to r.t. and stirred for 45 min. Brine was added and the aqueous phase extracted three times with diethyl ether. The combined organic extracts were dried over Na_2SO_4 and the solvent removed under reduced pressure. The obtained residue purified by flash chromatography (*n*-pentane/EtOAc 9:1 – 7:3) and additionally by reversed-phase chromatography (H_2O/MeCN 9:1 – MeCN). Yield: 68.7 mg (159 µmol, 69 %); colourless resin; R_f 0.57 (*n*-pentane/EtOAc 8:2); α_D^{20} = +17.1 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.0 Hz, 3 H), 1.25–1.32 (m, 10 H), 1.33–1.54 (m, 10 H), 1.80 (ddd, *J* = 13.1, 9.8, 6.4 Hz, 1 H), 1.94 (ddd, *J* = 13.0, 5.9, 1.8 Hz, 1 H), 2.04 (tddd, *J* = 7.4, 6.6, 1.5, 1.1 Hz, 1 H), 2-13 (bs, 1 H), 3.38 (ddd, *J* = 8.2, 5.5, 3.7 Hz, 1 H), 3.76 (ddd, *J* = 6.4, 3.2, 1.8 Hz, 1 H), 3.80 (s, 3 H), 3.90 (ddd, *J* = 7.0, 5.9, 3.1 Hz, 1 H), 3.97 (ddd, *J* = 9.8, 5.9, 5.5 Hz, 1 H), 4.41 (d, *J* = 11.4 Hz, 1 H), 4.45 (d, *J* = 11.4 Hz, 1 H), 4.93 (ddt, *J* = 10.2, 2.2, 1.1 Hz, 1 H), 4.99 (ddt, *J* = 17.1, 2.2, 1.5 Hz, 1 H), 5.81 (ddt, *J* = 17.0, 10.3, 6.6 Hz, 1 H), 6.88 (d, *J* = 8.7 Hz, 2 H), 7.25 (d, *J* = 8.7 Hz, 2 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0, 22.6, 25.6, 25.6, 28.9, 29.1, 29.4, 29.6 , 31.8, 33.8, 34.1, 34.2, 34.6, 55.3, 70.8, 73.9, 81.2, 83.2, 84.2, 113.8, 114.1, 129.2, 130.2, 139.2, 159.2 ppm; HRMS (ESI Q-exactive) calcd. for $C_{27}H_{45}O_4^+$ $[M+H]^+$: 433.3312, found: 433.3323.

(*R*)-1-{(2*R*,4*S*,5*R*)-4-[(4-Methoxybenzyl)oxy]-5-pentyltetrahydrofuran-2-yl}dec-9-en-1-ol (14). 41.9 mg (97.0 µmol, 1.0 equiv.) **13** was dissolved in 968 µl DCM/H_2O (0.1 M, 5:1) and 26.0 mg (116 µmol, 1.2 equiv.) DDQ was added at r.t. The reaction mixture was stirred for 1 h and saturated $NaHCO_3$-solution was added. The phases were separated and the organic phase washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue purified by flash chromatography (*n*-pentane/EtOAc 8:2 – 6:4). Yield: 28.7 mg (92.0 µmol, 95 %); colourless solid; m.p. 53 °C (*n*-pentane/EtOAc); R_f 0.34 (*n*-pentane/EtOAc 8:2); α_D^{20} = +9.4 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 3 H), 1.24–1.53 (m, 20 H), 1.82 (ddd, *J* = 13.1, 5.8, 1.8 Hz, 1 H), 1.90 (ddd, *J* = 13.1, 9.4, 6.4 Hz, 1 H), 1.95–2.11 (m, *J* = 7.0, 6.7 Hz, 3 H), 3.38 (ddd, *J* = 8.6, 5.3, 3.4 Hz, 1 H), 3.75 (ddd, *J* = 6.0, 6.0, 2.6 Hz, 1 H), 3.99 (ddd, *J* = 9.4, 6.0, 5.8 Hz, 1 H), 4.07 (ddd, *J* = 6.4, 3.4, 1.8 Hz, 1 H), 4.92 (d, *J* = 10.1 Hz, 1 H), 4.98 (d, *J* = 17.1 Hz, 1 H), 5.80 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0, 22.5, 25.6, 25.6, 28.9, 29.0, 29.4, 29.6, 31.8, 33.8, 33.9, 34.3, 37.2, 74.1, 76.5, 81.0, 86.8, 114.1, 139.2 ppm; HRMS (ESI Q-exactive) calcd. for $C_{27}H_{45}O_4^+$ $[M+H]^+$: 313.2737, found: 313.2735.

Trimethyl[2-({(*R*)-1-[(3a*R*,4*R*,6*R*,7a*S*)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[*d*]-[1,3,2]dioxaborol-2-yl]hexyl}oxy)ethyl]silane (15). Based on a procedure by Hirschhäuser *et al*.[2] 3.61 g (8.27 mmol, 1.0 equiv.) ***ent*-8** was dissolved in 33.1 ml *n*-pentane (0.25 M). 1.76 g (10.3 mmol, 1.25 equiv.) (–)-pinanediol was added at r.t. and the mixture stirred for 2 h. The resulting colorless solid was filtered off and washed with cold *n*-pentane to recover 1.63 g (7.19 mmol, 87 %) (1*R*,2*R*)-1,2-Dicyclohexylethane-1,2-diol. The filtrate was concentrated and the residue purified by flash chromatography (*n*-pentane/EtOAc 98:2 – 6:4). 308 mg (1.81 mmol, 87 %) (–)-pinanediol was recovered. Yield: 2.98 g (7.84 mmol, 95 %); colourless resin; R_f 0.39 (*n*-pentane/EtOAc 95:5); α_D^{20} = –20.3 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.00 (s, 9 H), 0.84 (s, 3 H), 0.87 (t, *J* = 6.8 Hz, 3 H), 0.97 (dd, *J* = 8.4, 8.4 Hz, 2 H), 1.15 (d, *J* = 10.9 Hz, 1 H), 1.24–1.35 (m, 7 H), 1.35–1.44 (m, 5 H), 1.65 (m, 2 H), 1.87 (m, 1 H),

[2] S. Kirupakaran, G. Arago, C. Hirschhäuser, *Chem. Sci.* **2023**, *14*, 9838–9842.

1.91 (m, 1 H), 2.08 (dd, *J* = 6.0, 5.2 Hz, 1 H), 2.22 (dddd, *J* = 10.9, 6.0, 6.0, 2.2 Hz, 1 H), 2.35 (dddd, *J* = 14.4, 8.9, 2.6, 2.2 Hz, 1 H), 3.25 (t, *J* = 6.6 Hz, 1 H), 3.48 (dt, *J* = 9.0, 8.4 Hz, 1 H), 3.52 (dt, *J* = 9.0, 8.4 Hz, 1 H), 4.32 (dd, *J* = 8.8, 2.0 Hz, 1 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = –1.4, 14.0, 18.5, 22.6, 24.0, 26.2, 26.6, 27.1, 28.6, 31.5, 32.0, 35.5, 38.1, 39.4, 51.1, 67.2, 67.7, 78.0, 86.1 ppm; HRMS (CI) calcd. for $C_{21}H_{40}O_3BSi^+$ $[M+H]^+$: 379.2834, found: 379.2844.

[2-({(1*S*,2*S*)-1-[(4-Methoxybenzyl)oxy]-1-[(3a*R*,4*R*,6*R*,7a*S*)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[*d*][1,3,2]dioxaborol-2-yl]heptan-2-yl}oxy)ethyl]trimethylsilane (16). A NaOPMB-solution was prepared by reacting 401 mg (10.0 mmol, 1.5 equiv.) sodium hydride (60 % in paraffine) with 1.33 ml (10.7 mmol, 1.6 equiv.) 4-methoxybenzyl alcohol in 4.01 ml anhydrous THF (0.4 ml/mmol NaH) and 11.0 ml anhydrous DMSO (1.1 ml/mmol NaH) at r.t. and stirring for 5.5 h. According to **GP2** 2.54 g (6.68 mmol, 1.0 equiv.) boronic ester **15** was reacted with 1.40 ml (20.0 mmol, 3.0 equiv.) DBM, 1.29 ml (9.02 mmol, 1.35 equiv.) DIPA, 5.22 ml (8.35 mmol, 1.25 equiv.) *n*-BuLi (1.6 M in *n*-hexane) and 2.73 g (20.0 mmol, 3.0 equiv.) $ZnCl_2$ in 22.7 ml anhydrous THF and stirred overnight. The reaction mixture was cooled to 0 °C and the previously prepared alcoholate added and stirred for 18 h. It was worked up according to **GP3** and the obtained residue purified by flash chromatography (*n*-pentane/EtOAc 98:2 – 96:4). Yield: 2.91 g (5.49 mmol, 82 %); colourless cloudy resin; R_f 0.16 (*n*-pentane/EtOAc 95:5); α_D^{20} = –2.0 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.02 (s, 9 H), 0.84 (s, 3 H), 0.85–0.97 (m, 5 H), 1.19–1.32 (m, 11 H), 1.39 (s, 3 H), 1.46 (m, 1 H), 1.61 (m, 1 H), 1.84–1.94 (m, 2 H), 2.09 (dd, *J* = 5.4, 5.4 Hz, 1 H), 2.22 (m, 1 H), 2.33 (m, 1 H), 3.36 (d, *J* = 5.9 Hz, 1 H), 3.46 (ddd, *J* = 7.3, 5.9, 5.4 Hz, 1 H), 3.53 (ddd, *J* = 11.1, 9.4, 6.1 Hz, 1 H), 3.63 (ddd, *J* = 11.1, 9.4, 6.1 Hz, 1 H), 3.79 (s, 3 H), 4.31 (dd, *J* = 8.8, 1.6 Hz, 1 H), 4.46 (d, *J* = 11.7 Hz, 1 H), 4.60 (d, *J* = 11.7 Hz, 1 H), 6.84 (d, *J* = 8.7 Hz, 2 H), 7.26 (d, *J* = 8.6 Hz, 1 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = –1.4, 14.1, 18.9, 22.6, 24.0, 25.6, 26.5, 27.1, 28.7, 31.1, 32.0 35.4, 38.1, 39.5, 51.1, 55.2, 67.5, 70.3, 72.8, 78.1, 80.4, 86.1, 113.5, 129.5, 131.3, 159.0 ppm; HRMS (ESI-Orbitrap) calcd. for $C_{30}H_{51}O_5BSiNa^+$ $[M+Na]^+$: 553.3491, found: 553.3492.

[2-({(2*S*,3*S*)-2-[(4-Methoxybenzyl)oxy]-1-[(3a*R*,4*R*,6*R*,7a*S*)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[*d*][1,3,2]dioxaborol-2-yl]octan-3-yl}oxy)ethyl]trimethylsilane (17). According to **GP2** 2.95 g (5.56 mmol, 1.0 equiv.) boronic ester **16** was reacted with 1.16 ml (16.7 mmol, 3.0 equiv.) DBM, 1.07 ml (7.50 mmol, 1.35 equiv.) DIPA, 4.34 ml (6.95 mmol, 1.25 equiv.) *n*-BuLi (1.6 M in *n*-hexane) and 3.03 g (22.2 mmol, 4.0 equiv.) $ZnCl_2$ in 22.2 ml anhydrous THF and stirred overnight. The reaction mixture was worked up according to **GP3**. The residue was dissolved in 11.1 ml anhydrous THF (0.5 M), cooled to 0 °C and reacted with 6.39 ml (6.39 mmol, 1.15 equiv.). After warming to r.t., the mixture was stirred for 6 h. The reaction mixture was worked up according to **GP3** and the obtained residue purified by flash chromatography (*n*-pentane/EtOAc 99:1 – 97:3). Yield: 2.05 g (3.76 mmol, 68 %); colourless resin; R_f 0.31 (*n*-pentane/EtOAc 95:5); α_D^{20} = –18.0 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.01 (s, 9 H), 0.83 (s, 3 H), 0.87 (t, *J* = 6.9 Hz, 3 H), 0.89–0.95 (m, 2 H), 1.10–1.19 (m, 2 H), 1.20–1.31 (m, 8 H), 1.37 (s, 3 H), 1.37–1.45 (m, 2 H), 1.50 (m, 1 H), 1.79–1.81 (m, 2 H), 2.03 (dd, *J* = 5.5, 5.5 Hz, 1 H), 2.15 (dddd, *J* = 11.1, 6.3, 5.5, 2.3 Hz, 1 H), 2.32 (m, 1 H), 3.25 (ddd, *J* = 8.3, 4.8, 4.0 Hz, 1 H), 3.43 (ddd, *J* = 10.9, 9.3, 6.3 Hz, 1 H), 3.62 (ddd, *J* = 10.9, 9.5, 6.1 Hz, 1 H), 3.76 (td, *J* = 7.0, 4.8 Hz, 1 H), 3.79 (s, 3 H), 4.24 (dd, *J* = 8.7, 1.6 Hz, 1 H), 4.50 (d, *J* = 11.2 Hz, 1 H), 4.58 (d, *J* = 11.3 Hz, 1 H), 6.84 (d, *J* = 8.7 Hz, 2 H), 7.26 (d, *J* = 8.6 Hz, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = –1.7, 12.7, 14.1, 18.9, 22.6, 24.0, 25.8, 26.4, 27.1, 28.6, 29.7, 32.0, 35.5, 38.1, 39.5, 51.3, 55.2, 67.8, 71.5, 77.5, 77.6, 81.4, 85.4, 113.5,

129.2, 131.4, 158.9 ppm; HRMS (CI) calcd. for $C_{31}H_{52}O_5BSi^+$ $[M–H]^+$: 543.3672, found: 543.3647.

(4*S*,5*S*)-4,5-Dicyclohexyl-2-{(2*S*,4*S*,5*R*)-4-[(4-methoxybenzyl)oxy]-5-pentyltetrahydrofuran-2-yl}-1,3,2-dioxaborolane (18). According to **GP2** 999 mg (1.83 mmol, 1.0 equiv.) boronic ester **17** was reacted with 384 µl (5.50 mmol, 3.0 equiv.) DBM, 353 µl (2.48 mmol, 1.35 equiv.) DIPA, 1.43 ml (2.29 mmol, 1.25 equiv.) *n*-BuLi (1.6 M in *n*-hexane) and 1.00 g (7.33 mmol, 4.0 equiv.) $ZnCl_2$ in 7.34 ml anhydrous THF and stirred for 18 h. In contrast to **GP2**, the reaction mixture was heated to 65 °C for 3 h. It was worked up according to **GP3** and the obtained residue purified by flash chromatography (*n*-pentane/EtOAc 9:1 – 7:3). Yield: 553 mg (1.21 mmol, 66 %); colourless resin; R_f 0.16 (*n*-pentane/EtOAc 9:1); α_D^{20} = +32.1 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84 (s, 3 H), 0.86 (t, *J* = 7.0 Hz, 3 H), 1.11 (d, *J* = 11.0 Hz, 1 H), 1.16–1.36 (m, 9 H), 1.40 (s, 3 H), 1.60–1.67 (m, 2 H), 1.84–1.92 (m, 3 H), 2.07 (dd, *J* = 5.8, 5.5 Hz, 1 H), 2.22 (dddd, *J* = 11.0, 7.9, 5.8, 1.8 Hz, 1 H), 2.26 (ddd, *J* = 12.7, 6.6, 1.5 Hz, 1 H), 2.33 (m, 1 H), 3.80 (s, 3 H), 3.90 (ddd, *J* = 7.0, 7.0, 4.1 Hz, 1 H), 3.95 (dd, *J* = 11.7, 6.5 Hz, 1 H), 4.00 (ddd, *J* = 4.3, 4.1, 1.5 Hz, 1 H), 4.33 (dd, *J* = 8.6, 1.6 Hz, 1 H), 4.34 (d, *J* = 11.6 Hz, 2 H), 4.56 (d, *J* = 11.6 Hz, 1 H), 6.86 (d, *J* = 8.7 Hz, 2 H), 7.25 (d, *J* = 8.7 Hz, 2 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 22.6, 22.9, 26.0, 26.4, 27.0, 28.5, 28.8, 32.1, 34.4, 35.2, 38.1, 39.4, 51.2, 55.3, 63.3, 70.8, 78.1, 78.9, 82.8, 86.4, 113.7, 129.1, 130.6, 159.1 ppm; HRMS (CI) calcd. for $C_{27}H_{40}O_5B^+$ $[M–H]^+$: 455.2963, found: 455.2960.

(3a*R*,4*R*,6*R*,7a*S*)-2-((*R*)-1-{(2*R*,4*S*,5*S*)-4-[(4-Methoxybenzyl)oxy]-5-pentyltetrahydrofuran-2-yl}dec-9-en-1-yl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol (19). According to **GP2** 530 mg (1.16 mmol, 1.0 equiv.) boronic ester **18** was reacted with 243 µl (3.48 mmol, 3.0 equiv.) DBM, 224 µl (1.57 mmol, 1.35 equiv.) DIPA, 908 µl (1.45 mmol, 1.25 equiv.) *n*-BuLi (1.6 M in *n*-hexane) and 633 mg (4.65 mmol, 4.0 equiv.) $ZnCl_2$ in 4.65 ml anhydrous THF and stirred for 16 h. The reaction mixture was worked up according to **GP3** and the obtained α-bromoboronic ester used without further purification. 166 mg (1.22 mmol, 1.05 equiv.) anhydrous $ZnCl_2$ were reacted with 3.21 ml (1.22 mmol, 2.1 equiv.) 9-bromononenylmagnesium bromide (0.76 M in THF) at r.t. and cooled to 0 °C. The previously obtained α-bromoboronic ester was dissolved in 4.64 ml anhydrous THF (0.2 M), added dropwise to this mixture, warmed to r.t. and stirred for 3 d. It was worked up according to **GP3** and the obtained residue purified by flash chromatography (*n*-pentane – *n*-pentane/EtOAc 95:5). Yield: 315 mg (542 µmol, *d.r.* 88:12, 47 %); colourless resin; R_f 0.45 (*n*-pentane/EtOAc 8:2); α_D^{20} = +11.5 (c = 1.0, $CHCl_3$); major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83 (s, 3 H), 0.87 (t, *J* = 6.7 Hz, 3 H), 1.19 (m, 1 H), 1.21–1.39 (m, 25 H), 1.50–1.65 (m, 2 H), 1.68 (ddd, *J* = 13.2, 8.2, 5.3 Hz, 1 H), 1.83 (m, 1 H), 1.90 (m, 1 H), 1.98–2.07 (m, 3 H), 2.09–2.23 (m, 2 H), 2.33 (m, 1 H), 3.80 (s, 3 H), 3.86 (ddd, *J* = 7.3, 6.4, 3.8, 1 H), 3.93 (m, 1 H), 4.18 (m, 1 H), 4.25 (ddd, *J* = 8.6, 7.7, 2.0 Hz, 1 H), 4.34 (d, *J* = 11.7 Hz, 1 H), 4.53 (d, *J* = 11.7 Hz, 1 H), 4.92 (ddt, *J* = 10.1, 2.0, 1.1 Hz, 1 H), 4.98 (ddt, *J* = 17.1, 2.0, 1.5 Hz, 1 H), 5.80 (ddt, *J* = 17.1, 10.2, 6.7 Hz, 1 H), 6.86 (d, *J* = 8.7 Hz, 2 H), 7.25 (d, *J* = 8.7 Hz, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 24.1, 26.0, 26.4, 27.1, 28.0, 28.8, 28.9, 28.9, 29.1, 29.4, 29.7, 29.8, 31.5, 32.1, 33.8, 35.6, 37.6, 38.1, 39.5, 51.2, 55.3, 70.7, 77.5, 78.7, 79.3, 81.2, 85.4, 113.6, 114.1, 129.1, 130.7, 139.3, 159.0 ppm; minor diastereomer (selected signals): ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.6, 26.5, 36.9, 51.1, 70.7, 79.2, 81.0, 129.0, 130.8 ppm; HRMS (ESI Orbitrap) calcd. for $C_{37}H_{59}O_5BNa^+$ $[M+Na]^+$: 617.4348, found: 617.4347.

(*R*)-1-{(2*R*,4*S*,5*S*)-4-[(4-Methoxybenzyl)oxy]-5-pentyltetrahydrofuran-2-yl}dec-9-en-1-ol (20). 263 mg (442 µmol, 1.0 equiv.) boronic ester **19** was dissolved in 885 µl THF (0.5 M) and

cooled to 0 °C. 205 µl (2.21 mmol, 5.0 equiv.) hydrogen peroxide (33 % in H_2O) and 88.0 mg (2.21 mmol, 5.0 equiv.) sodium hydroxide dissolved in 885 µl H_2O (0.5 M) were added. The reaction mixture was warmed to 50 °C and stirred for 1 h. Brine was added and the aqueous phase extracted three times with diethyl ether. The combined organic extracts were dried over Na_2SO_4 and the solvent removed under reduced pressure. The obtained residue purified by reversed-phase flash chromatography (H_2O/MeCN 9:1 – MeCN). Yield: 166 mg (383 µmol, *d.r.*, 87 %); colourless resin; R_f 0.46 (*n*-pentane/EtOAc 8:2); α_D^{20} = +41.5 (c = 1.0, $CHCl_3$); major diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.2, 3 H), 1.20–1.32 (m, 10 H), 1.32–1.43 (m, 8 H), 1.65 (m, 2 H), 1.73 (ddd, *J* = 13.3, 8.8, 4.7 Hz, 1 H), 2.04 (m, 2 H), 2.13 (ddd, *J* = 13.2, 6.5, 1.1 Hz, 1 H), 2.29 (bs, 1 H), 3.37 (m, 1 H), 3.78 (m, 4 H), 3.95 (m, 1 H), 3.98 (ddd, *J* = 12.7, 8.9, 6.3 Hz, 1 H), 4.36 (d, *J* = 11.7 Hz, 1 H), 4.56 (d, *J* = 11.7 Hz, 1 H), 4.93 (m, 1 H), 4.99 (ddt, *J* = 17.1, 1.7, 1.7 Hz, 1 H), 5.81 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1 H), 6.87 (m, *J* = 8.7 Hz, 2 H), 7.25 (m, 2 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0, 22.6, 25.6, 25.9, 28.9, 28.9, 29.1, 29.4, 29.6, 32.0, 33.5, 22.8, 34.0, 55.3, 70.7, 74.1, 79.2, 80.1, 82.3, 113.7, 114.1, 129.1, 130.4, 139.2, 159.2 ppm; minor diastereomer (selected signals): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.97 (m, 1 H), 3.84 (m, 1 H), 3.88 (ddd, *J* = 6.9, 6.9, 3.7 Hz, 1 H), 4.10 (ddd, *J* = 9.5, 6.4, 3.4 Hz, 1 H), 4.37 (d, *J* = 11.6 Hz, 1 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.6, 25.9, 28.9, 29.1, 29.2, 29.3, 29.6, 30.2, 32.1, 32.3, 70.8, 71.9, 79.2, 80.0, 83.1, 129.1, 130.5, 139.2, 159.1 ppm; HRMS (ESI Q-exactive) calcd. for $C_{27}H_{43}O_4^+$ $[M–H]^+$: 431.3156, found: 431.3167.

(2*S*,3*S*,5*R*)-5-[(*R*)-1-Hydroxydec-9-en-1-yl]-2-pentyltetrahydrofuran-3-ol (21) and **(2*S*,3*S*,5*R*)-5-((*S*)-1-hydroxydec-9-en-1-yl)-2-pentyltetrahydrofuran-3-ol (22)**. 154 mg (356 µmol, 1.0 equiv.) **20** was dissolved in 3.56 ml DCM/H_2O (0.1 M, 5:1) and 97.0 mg (427 µmol, 1.2 equiv.) DDQ was added at r.t. The reaction mixture was stirred for 1 h and saturated $NaHCO_3$-solution was added. The phases were separated and the organic phase washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue purified by flash chromatography (*n*-pentane/EtOAc 85:15 – 6:4).

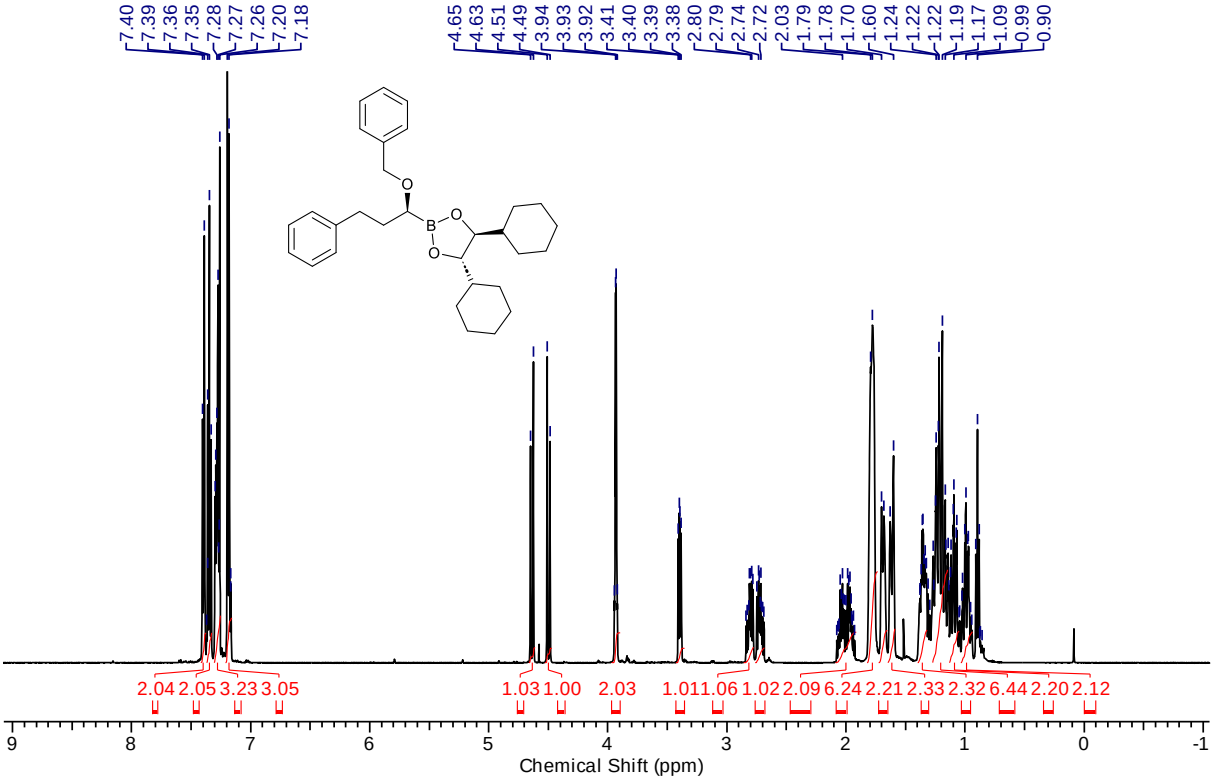
21: Yield: 94.3 mg (302 µmol, 85 %); colourless solid; m.p. 55 °C (*n*-pentane/EtOAc); R_f 0.26 (*n*-pentane/EtOAc 7:3); α_D^{20} = +18.0 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.9 Hz, 3 H), 1.22–1.35 (m, 11 H), 1.35–1.45 (m, 6 H), 1.50 (m, 1 H), 1.55–1.80 (m, 3 H), 1.86 (ddd, *J* = 13.5, 9.0, 4.6 Hz, 1 H), 1.97–2.06 (m, 3 H), 2.32 (bs, 1 H), 3.37 (m, 1 H), 3.74 (ddd, *J* = 6.9, 2.6 Hz, 1 H), 4.01 (ddd, *J* = 9.0, 6.0, 6.0 Hz, 1 H), 4.24 (m, 1 H), 4.92 (ddt, *J* = 10.3, 2.0, 1.1 Hz, 1 H), 4.98 (ddt, *J* = 17.1, 2.0, 1.4 Hz, 1 H), 5.80 (ddt, J_1 = 17.1, 10.3, 6.7 Hz, 1 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0, 22.6, 25.6, 26.0, 28.8, 28.9, 29.1, 29.4, 29.6, 32.0, 33.1, 33.8, 37.9, 73.4, 74.1, 80.2, 82.5, 114.1, 139.2 ppm; HRMS (CI) calcd. for $C_{19}H_{37}O_3^+$ $[M+H]^+$: 313.2737, found: 313.2744.

22: Yield: 12.4 mg (40.0 µmol, 11 %); colourless solid; m.p. 86 °C (*n*-pentane/EtOAc); R_f 0.17 (*n*-pentane/EtOAc 7:3); α_D^{20} = +7.1 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.9 Hz, 3 H), 1.25–1.43 (m, 16 H), 1.50 (m, 2 H, 4-H), 1.54–1.66 (m, 3 H), 1.85 (dd, = 13.3, 6.1 Hz, 1 H), 1.98 (bs, 1 H), 2.04 (m, 2 H), 2.12 (ddd, *J* = 13.1,10.2, 4.3 Hz, 1 H), 3.81–3.88 (m, 2 H), 4.16 (ddd, *J* = 10.0, 6.2, 3.5 Hz, 1 H), 4.28 (m, 1 H), 4.92 (ddt, *J* = 10.2, 2.0, 1.1 Hz, 1 H), 4.99 (ddt, *J* = 17.2, 2.0, 1.7 Hz, 1 H), 5.80 (ddt, *J* = 17.1, 10.3, 6.7 Hz, 1 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0, 22.6, 25.9, 26.0, 28.9, 29.0, 29.2, 29.4, 29.6, 32.0, 32.2, 33.8, 34.2, 72.0, 73.2, 80.0, 83.6, 114.1, 139.2 ppm; HRMS (CI) calcd. for $C_{19}H_{37}O_3^+$ $[M+H]^+$: 313.2737, found: 313.2744.

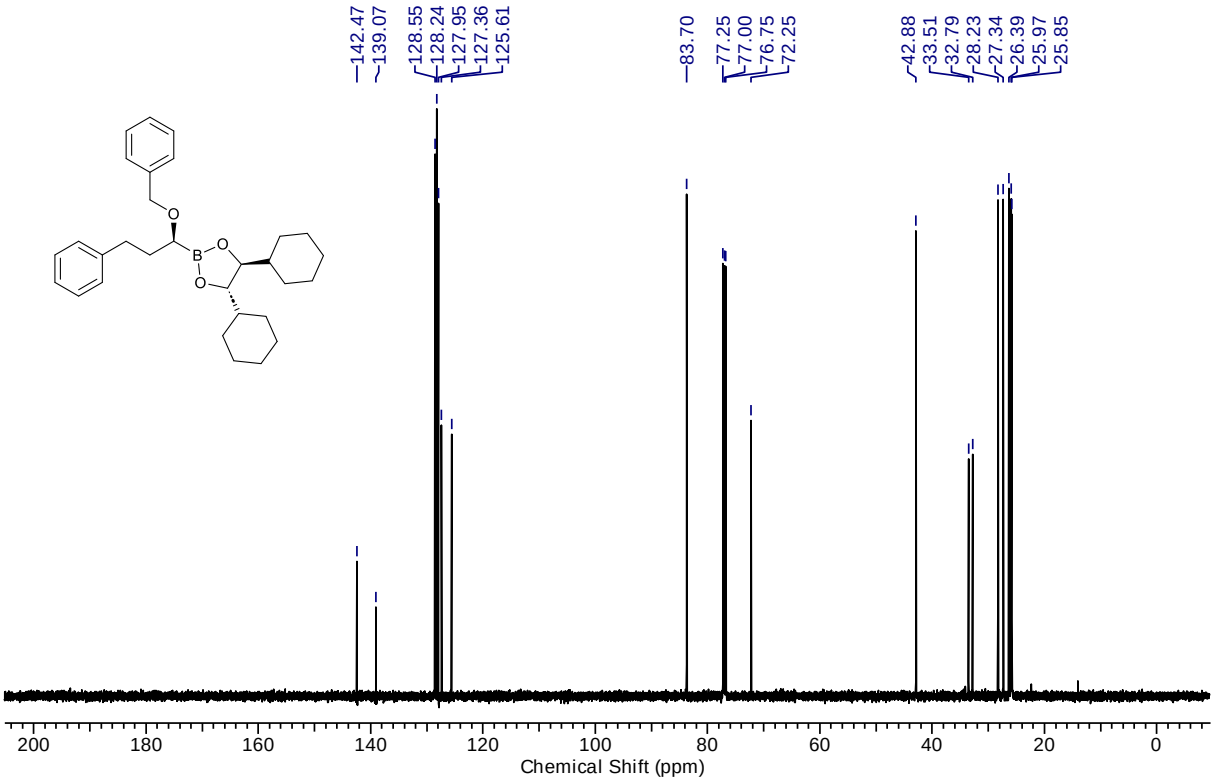
Copies of the NMR spectra

(4*S*,5*S*)-2-[(*S*)-1-(Benzyloxy)-3-phenylpropyl]-4,5-dicyclohexyl-1,3,2-dioxaborolane (A-1)

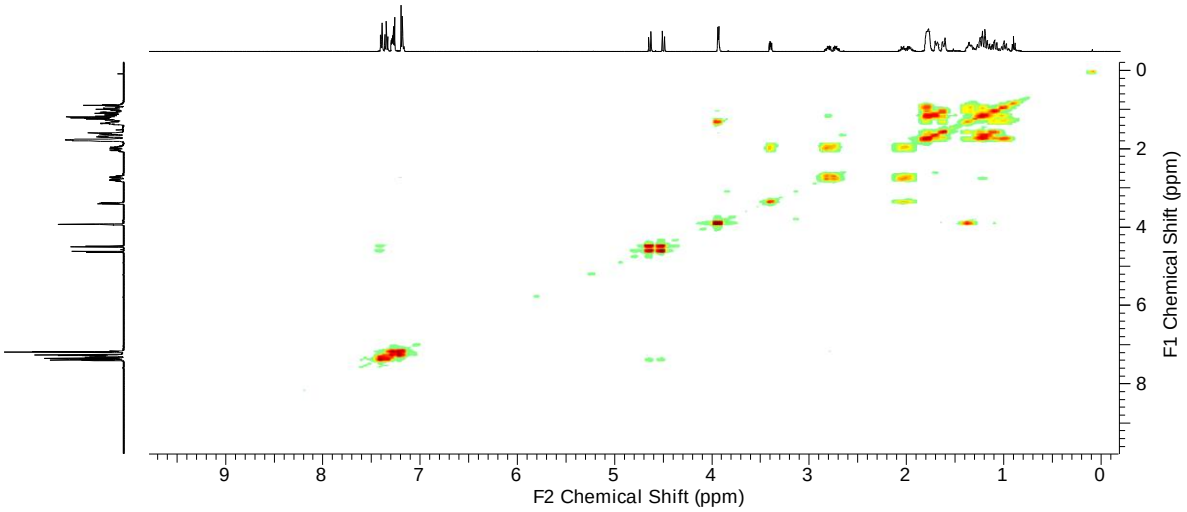
^{1}H NMR (500 MHz, $CDCl_3$):



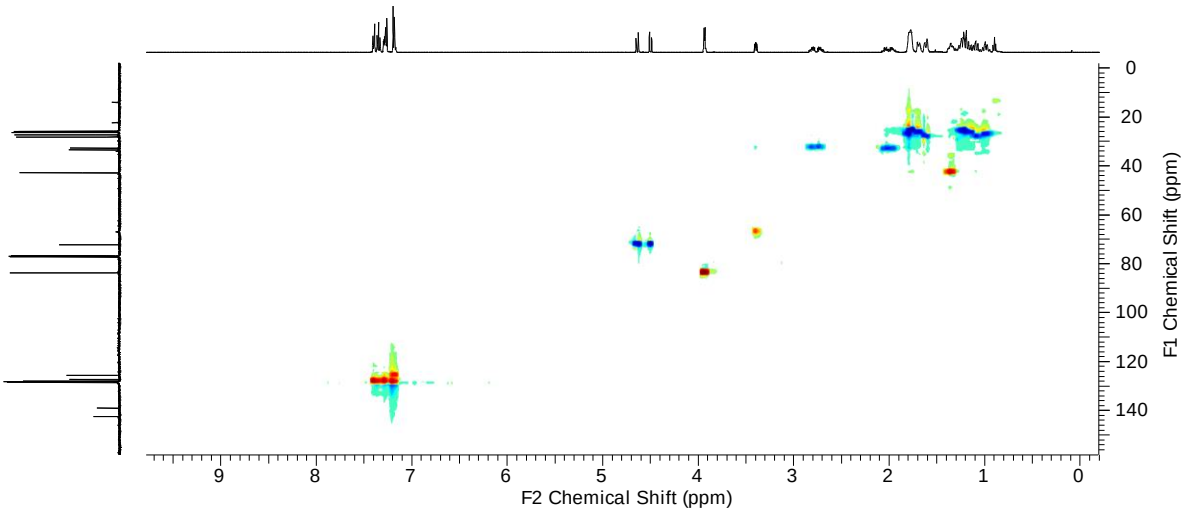
^{13}C NMR (125 MHz, $CDCl_3$):



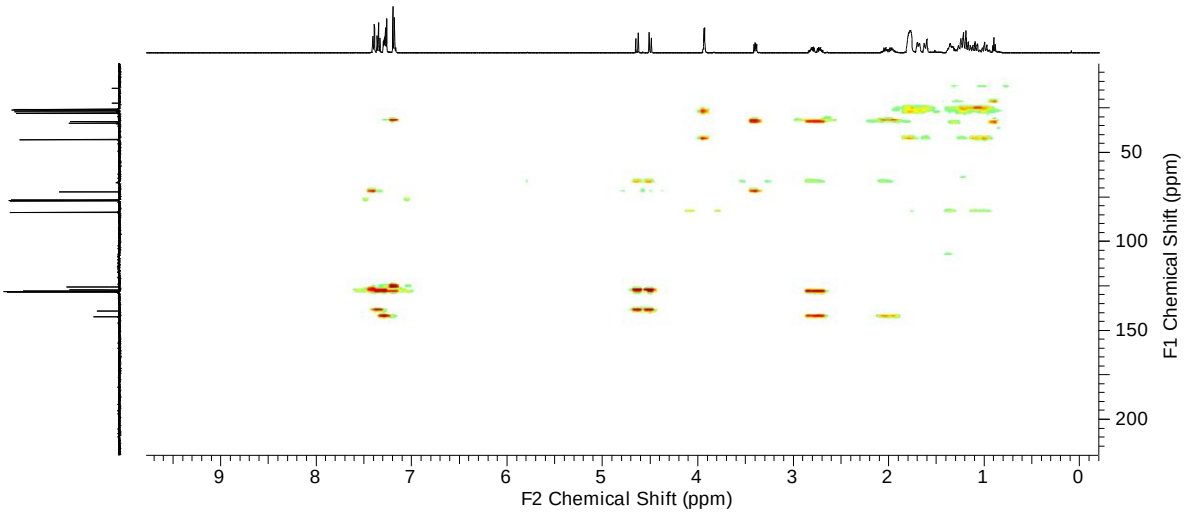
HH-COSY NMR (500 MHz, $CDCl_3$)



HSQC NMR (500 MHz, $CDCl_3$)

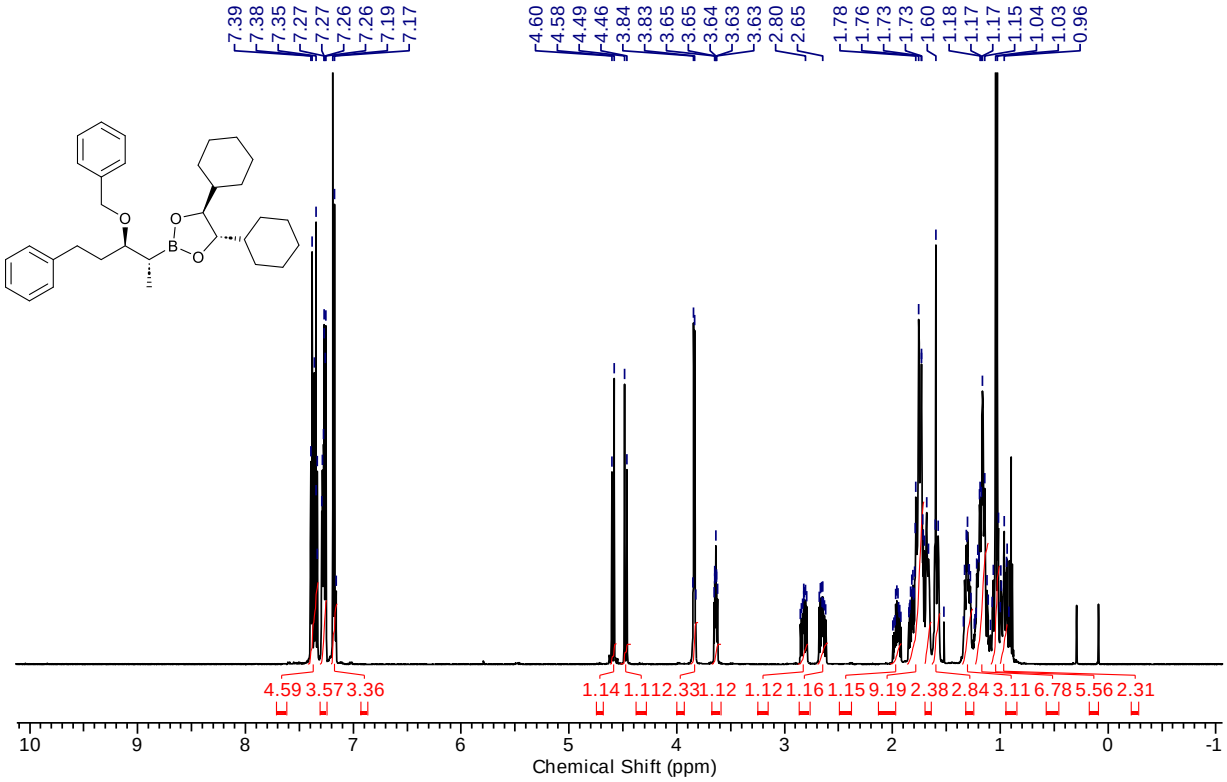


HMBC NMR (500 MHz, $CDCl_3$)

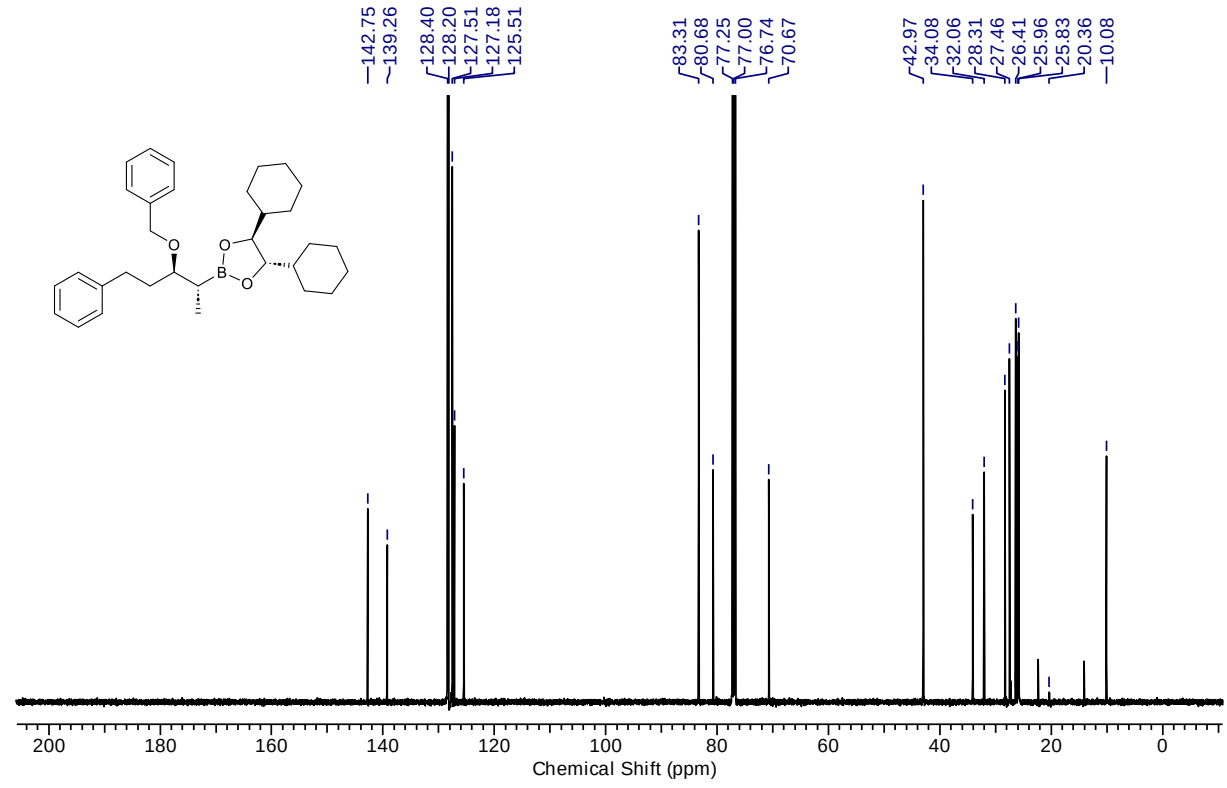


(4*S*,5*S*)-2-[(2*R*,3*R*)-3-(Benzyloxy)-5-phenylpentan-2-yl]-4,5-dicyclohexyl-1,3,2-dioxaborolane (B-1)

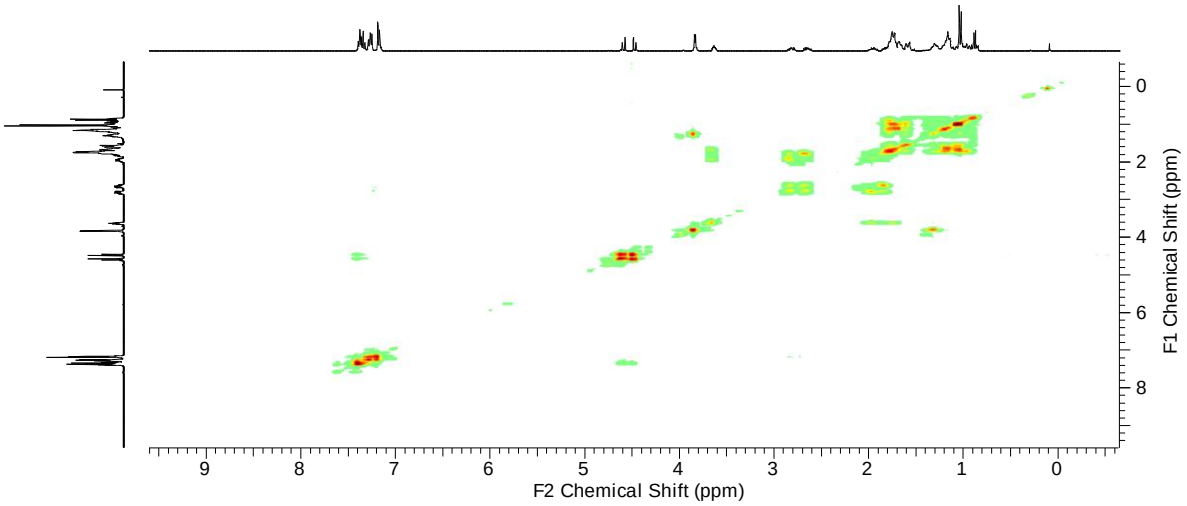
^{1}H NMR (500 MHz, $CDCl_3$):



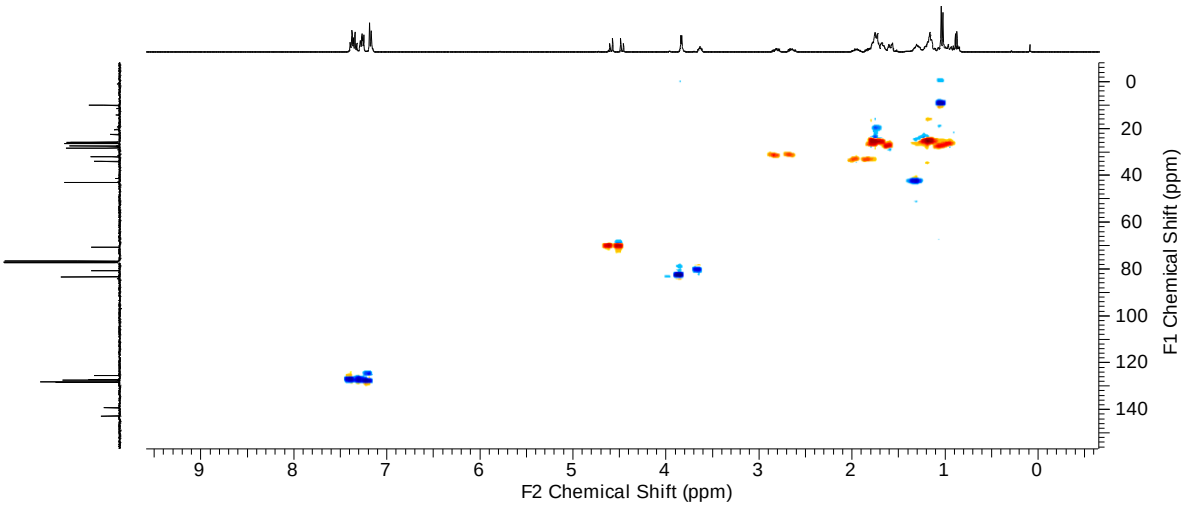
^{13}C NMR (125 MHz, $CDCl_3$):



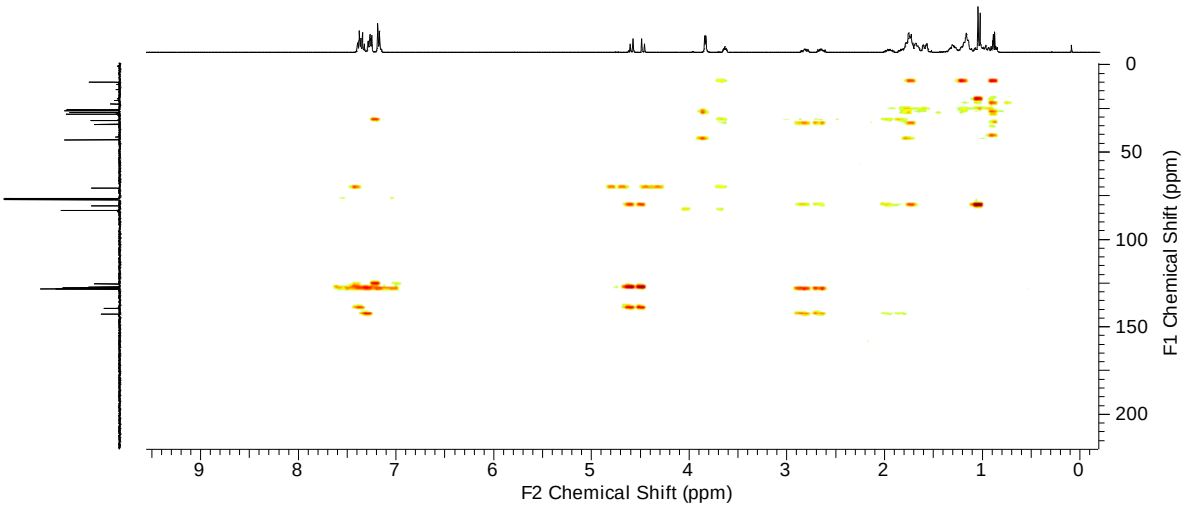
HH-COSY NMR (400 MHz, $CDCl_3$)



HSQC NMR (400 MHz, $CDCl_3$)

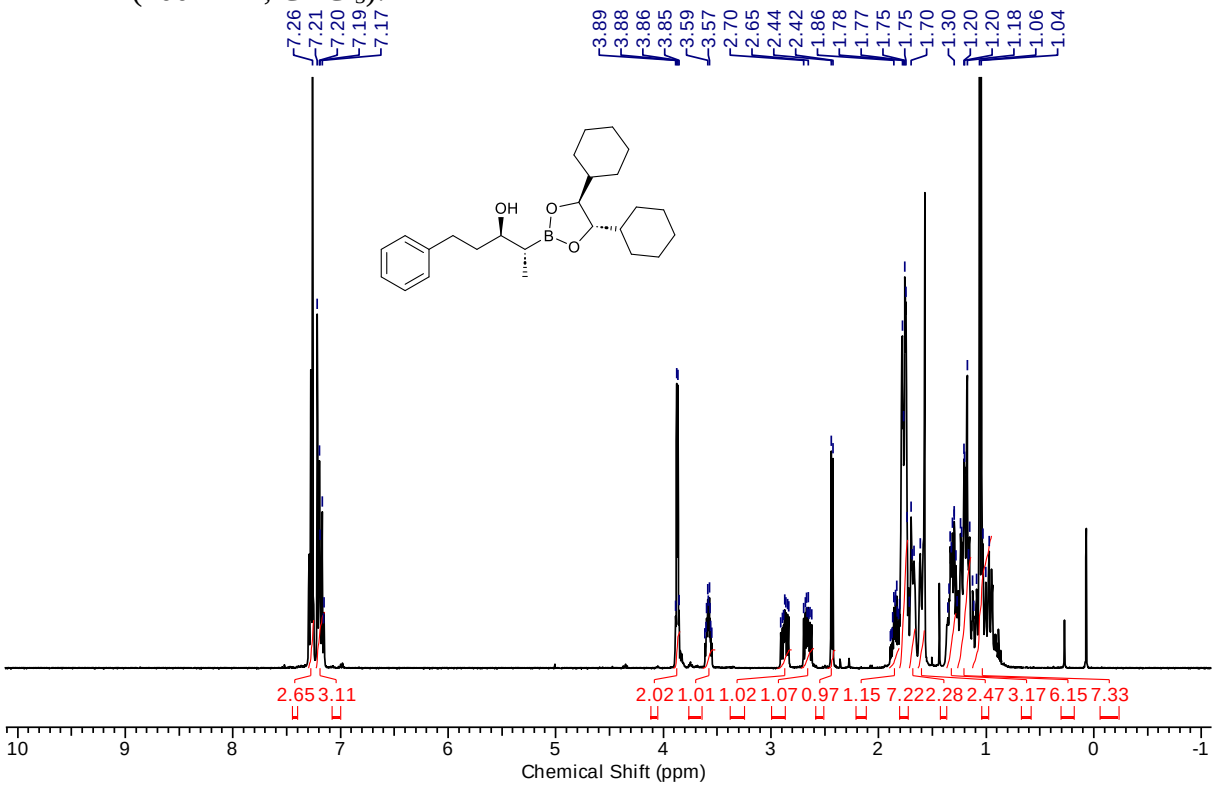


HMBC NMR (400 MHz, $CDCl_3$)

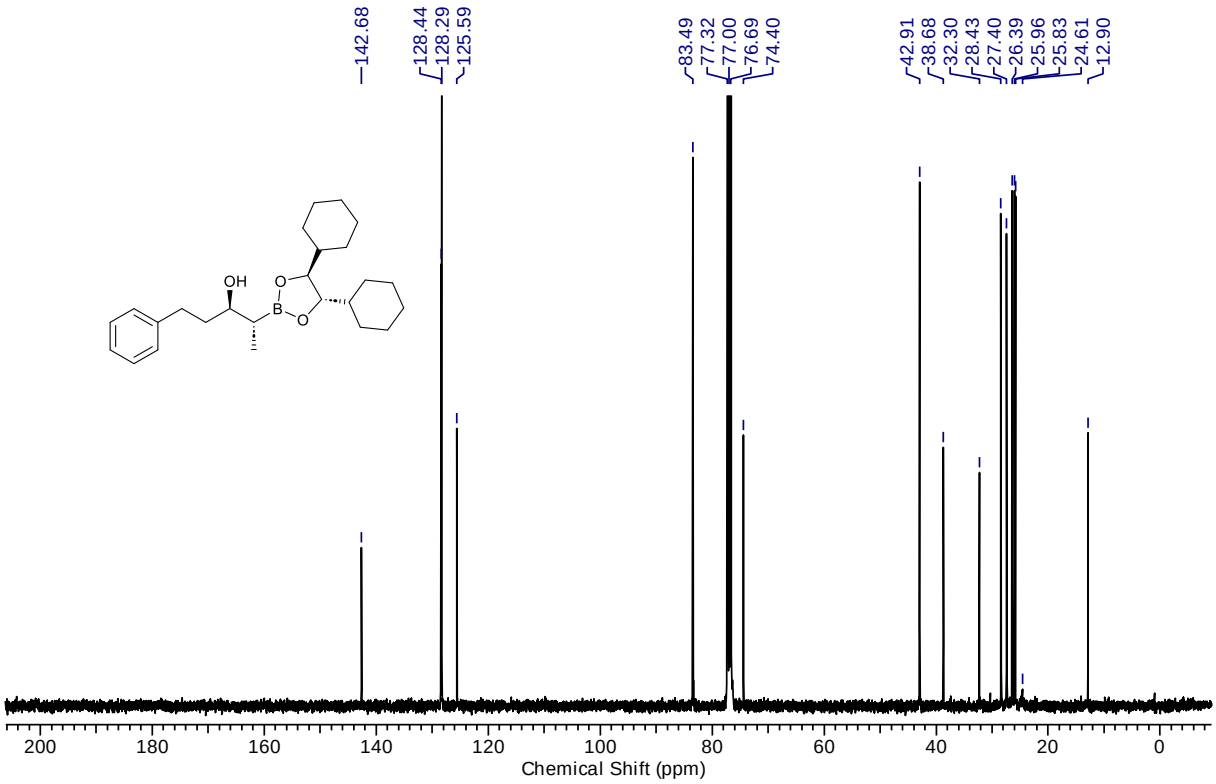


(3*R*,4*R*)-4-[(4*S*,5*S*)-4,5-Dicyclohexyl-1,3,2-dioxaborolan-2-yl]-1-phenylpentan-3-ol (C-1)

^{1}H NMR (400 MHz, $CDCl_3$):

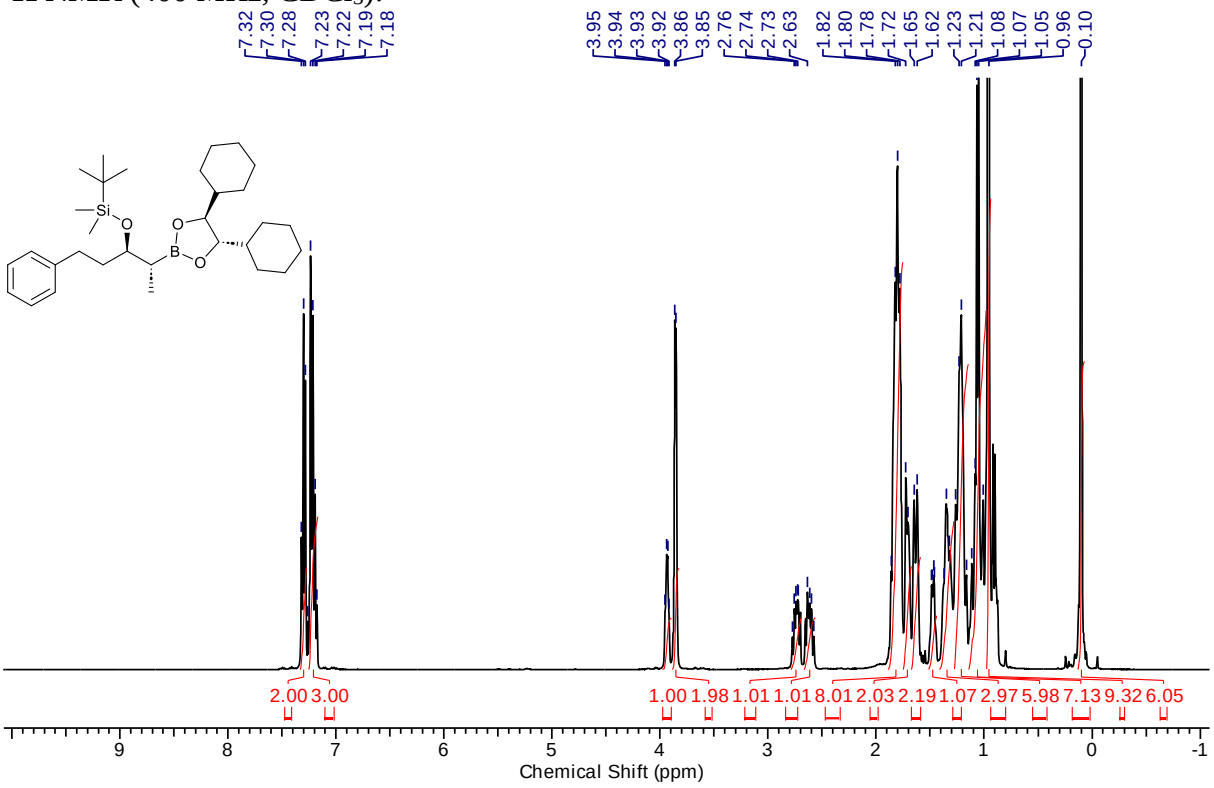


^{13}C NMR (100 MHz, $CDCl_3$):

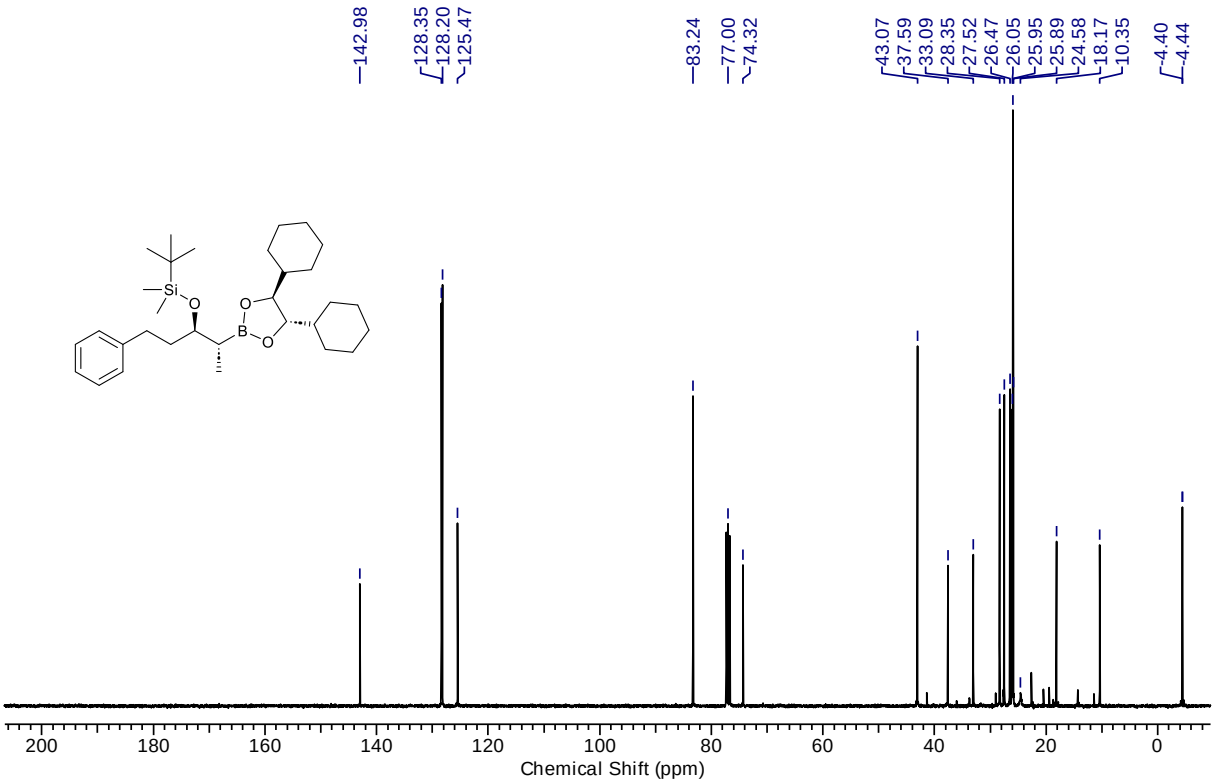


***tert*-Butyl({(3*R*,4*R*)-4-[(4*S*,5*S*)-4,5-dicyclohexyl-1,3,2-dioxaborolan-2-yl]-1-phenylpentan-3-yl}oxy)dimethylsilane (D-1)**

^{1}H NMR (400 MHz, $CDCl_3$):

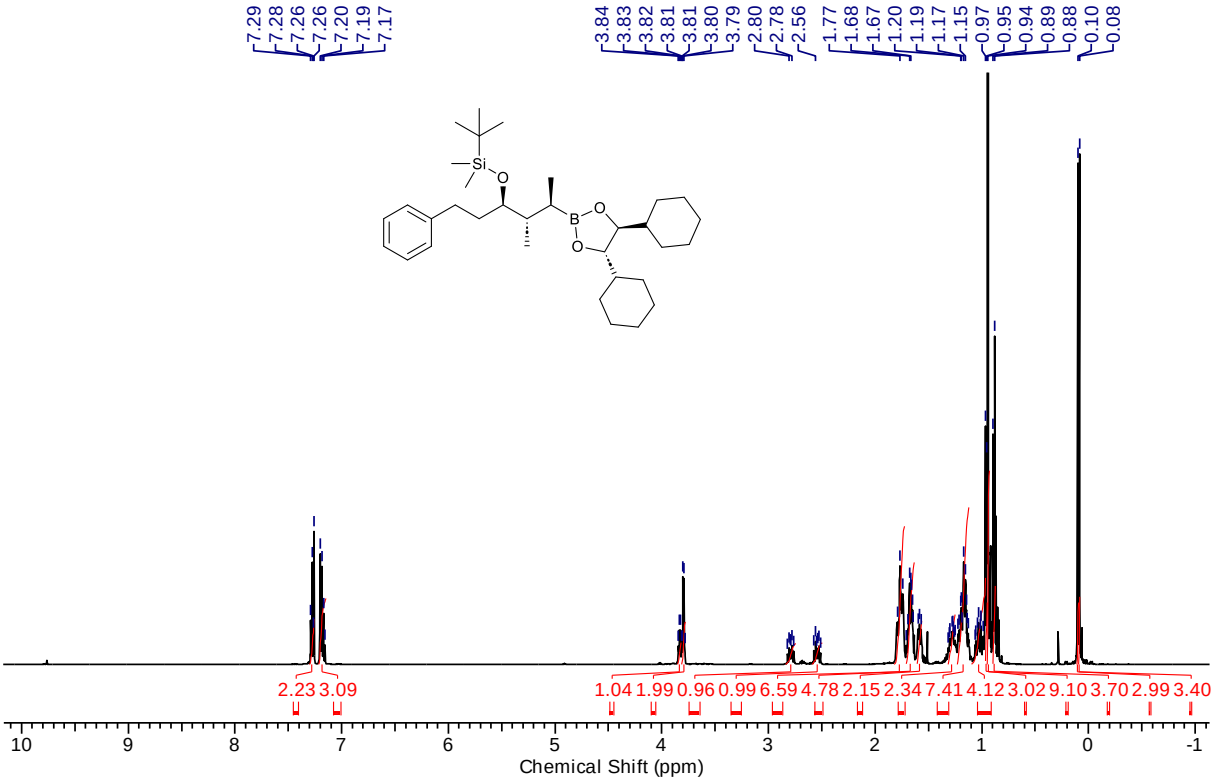


^{13}C NMR (100 MHz, $CDCl_3$):

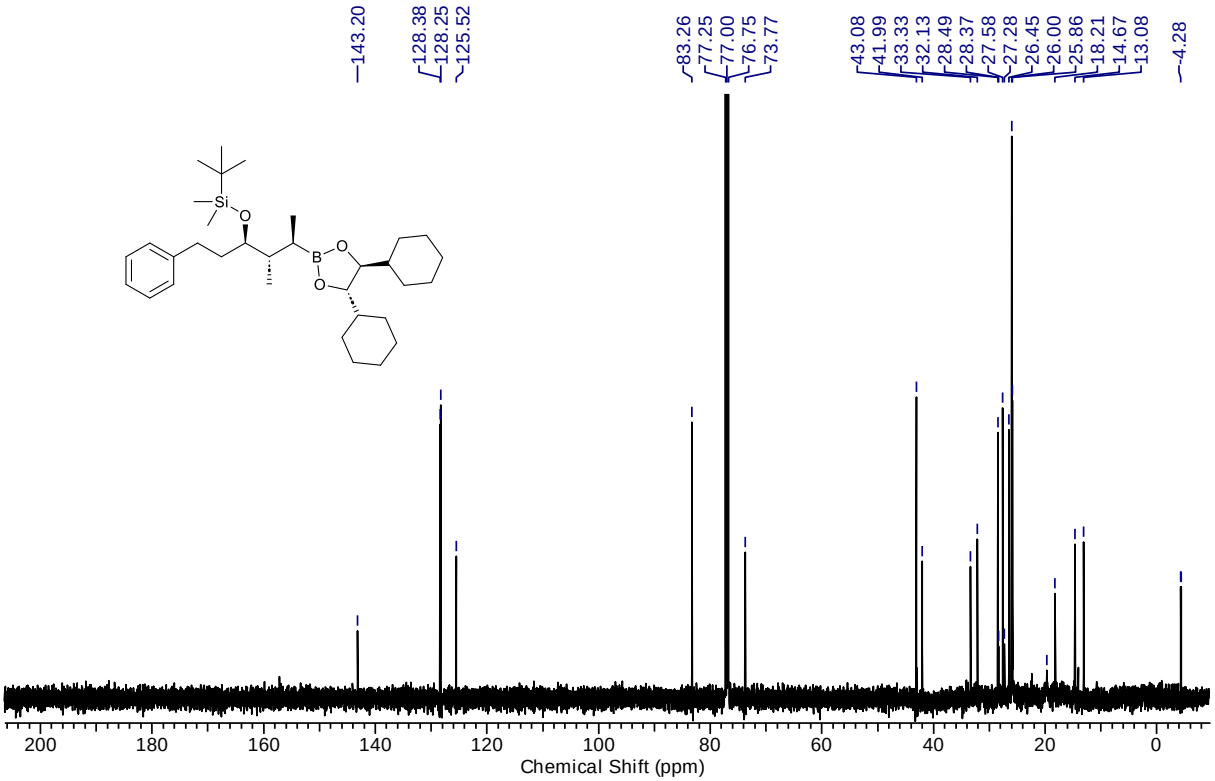


***tert*-Butyl({(3*R*,4*S*,5*R*)-5-[(4*S*,5*S*)-4,5-dicyclohexyl-1,3,2-dioxaborolan-2-yl]-4-methyl-1-phenylhexan-3-yl}oxy)dimethylsilane (1)**

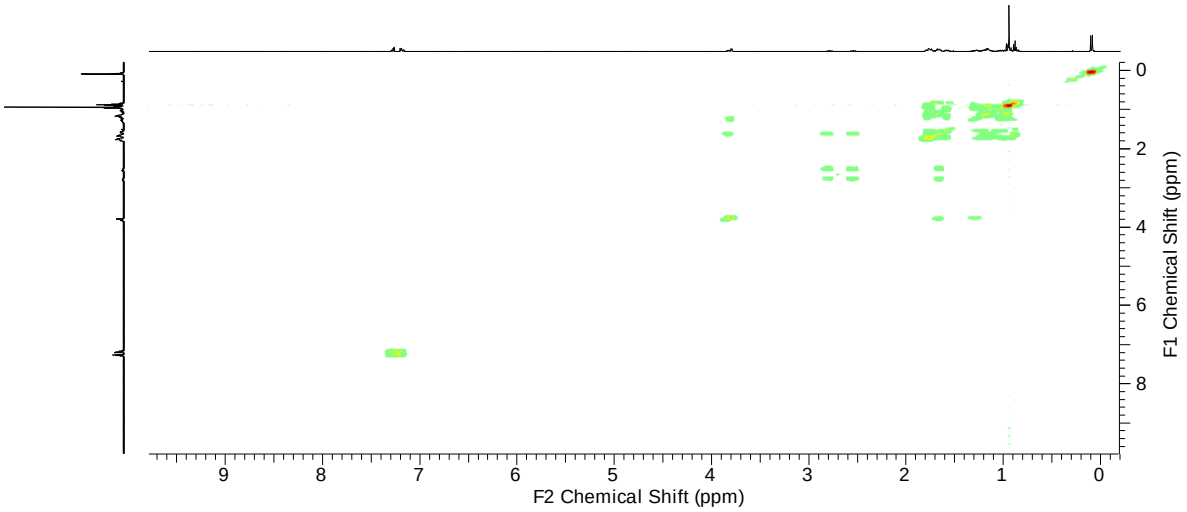
^{1}H NMR (500 MHz, $CDCl_3$):



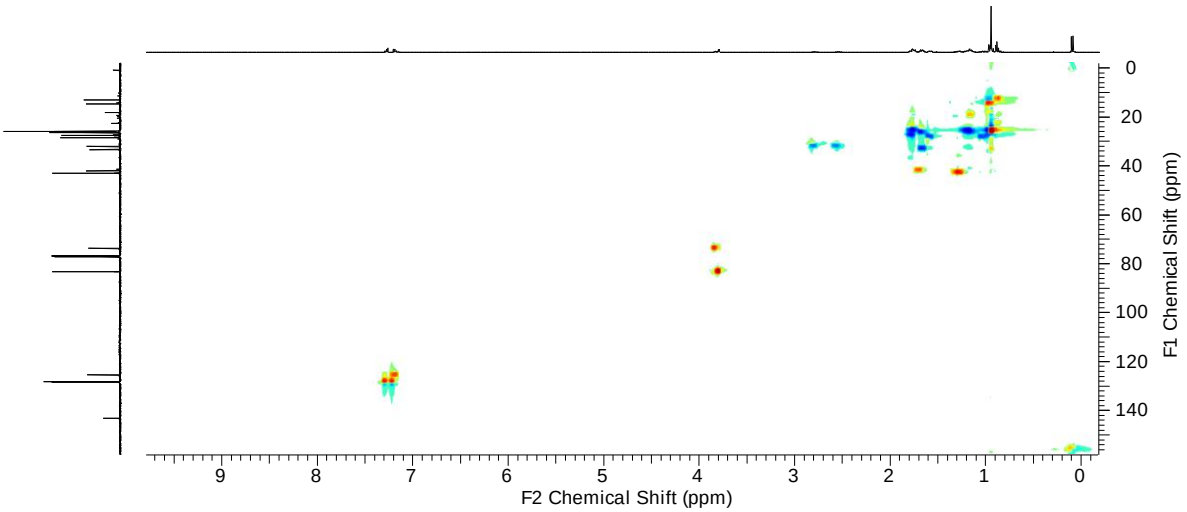
^{13}C NMR (125 MHz, $CDCl_3$):



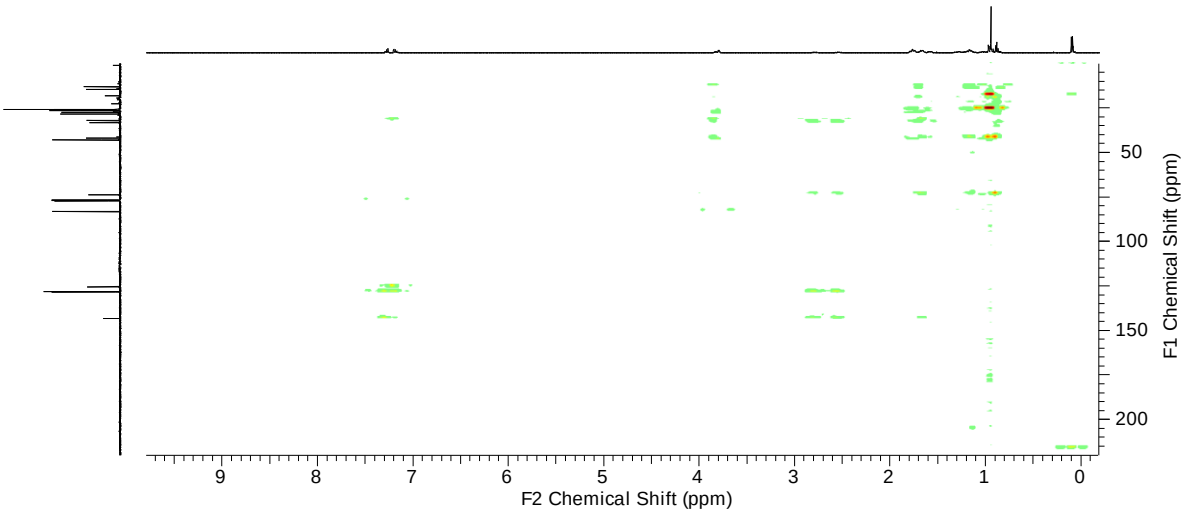
HH-COSY NMR (500 MHz, $CDCl_3$)



HSQC NMR (500 MHz, $CDCl_3$)

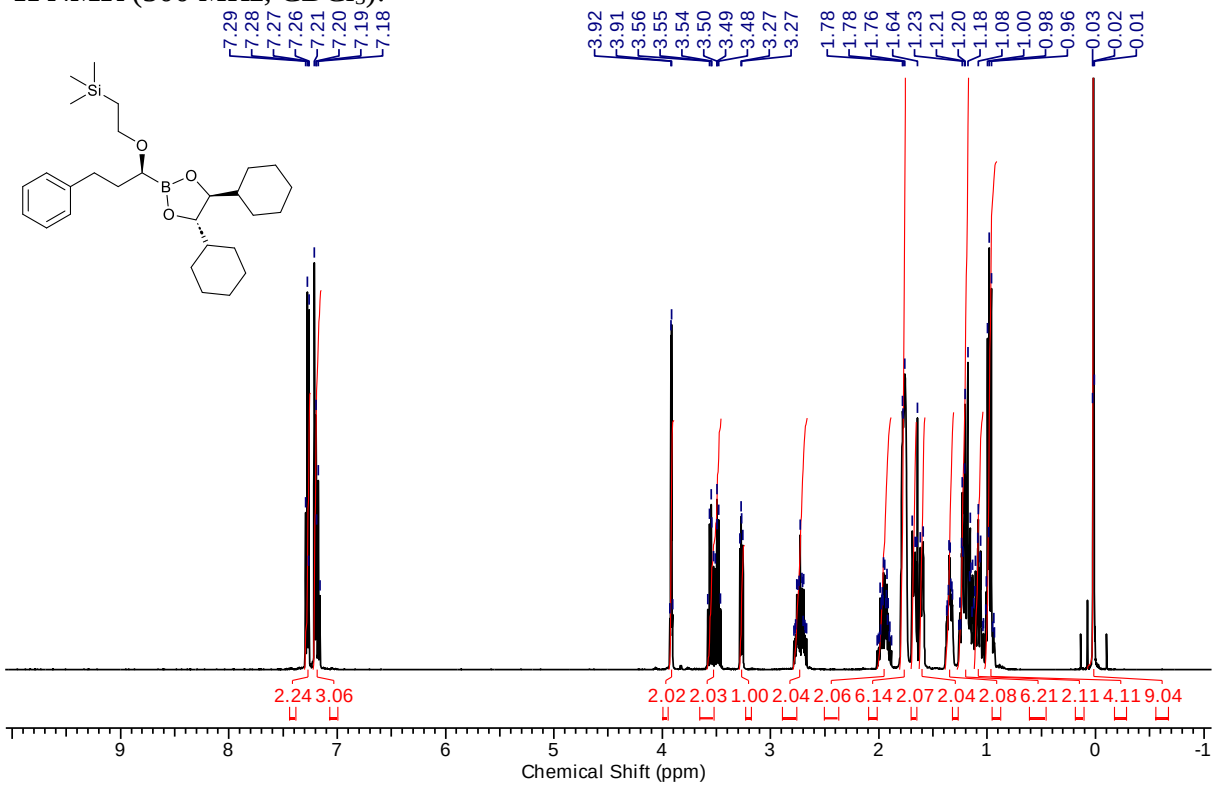


HMBC NMR (500 MHz, $CDCl_3$)

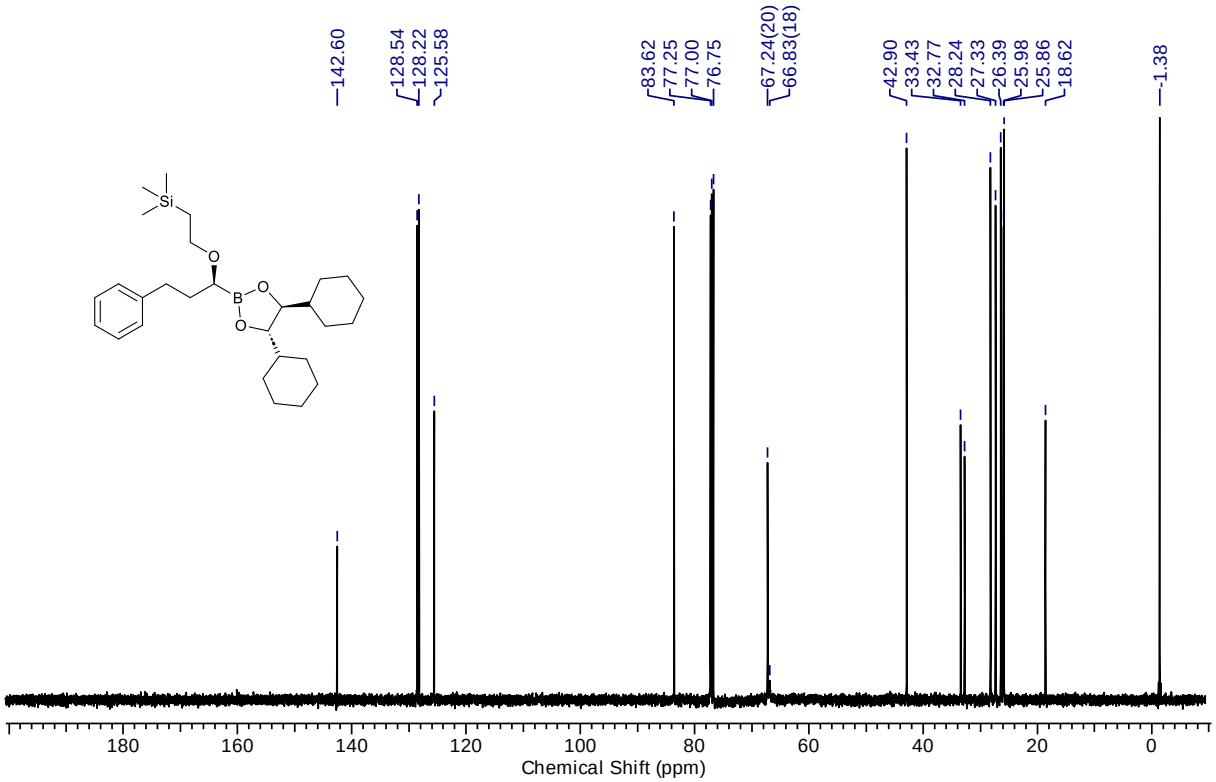


(2-{(*S*)-1-[(4*S*,5*S*)-4,5-Dicyclohexyl-1,3,2-dioxaborolan-2-yl]-3-phenylpropoxy}ethyl)trimethylsilane (3)

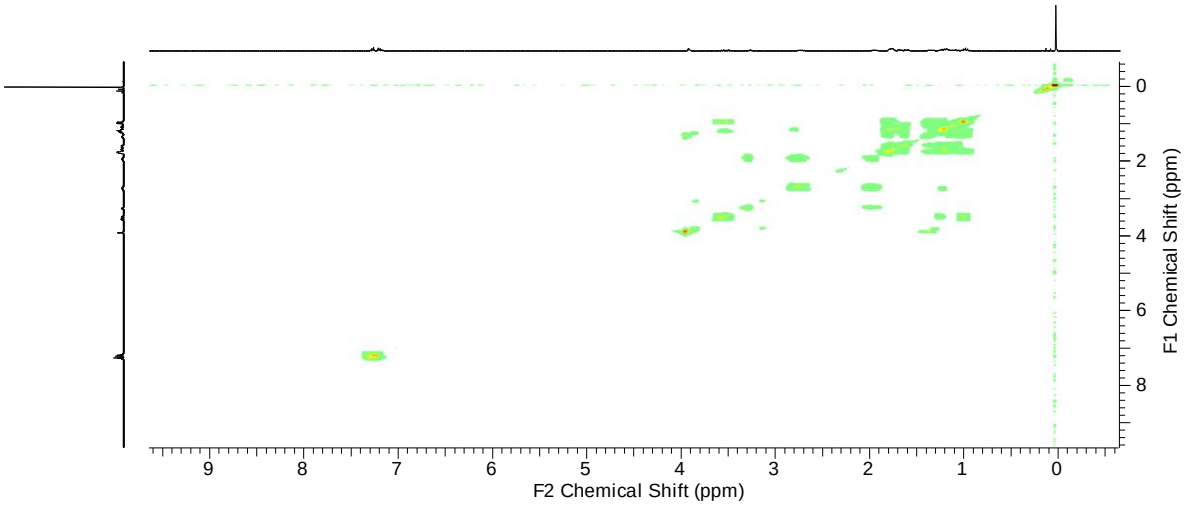
^{1}H NMR (500 MHz, $CDCl_3$):



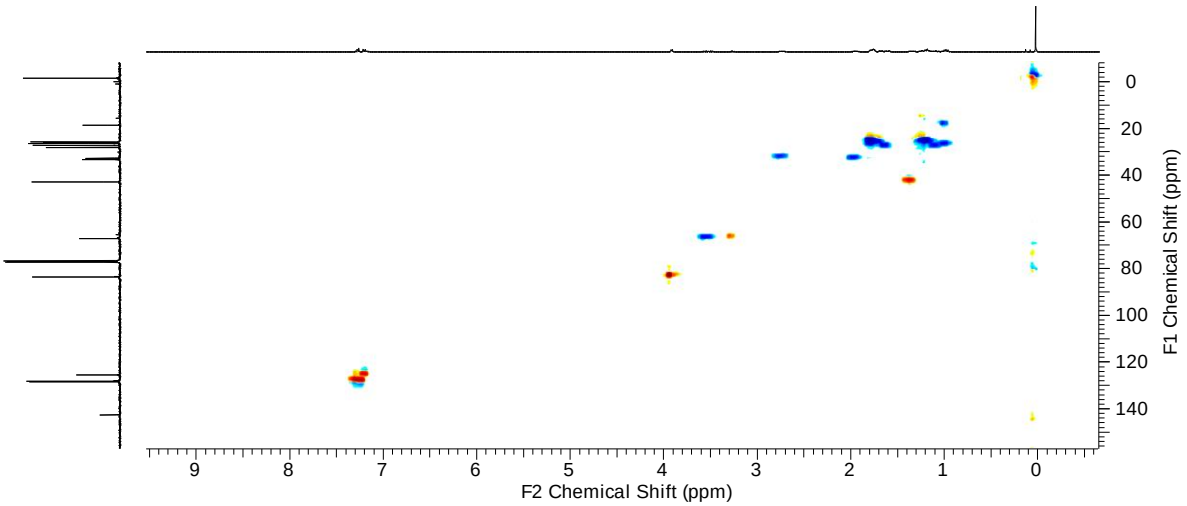
^{13}C NMR (125 MHz, $CDCl_3$):



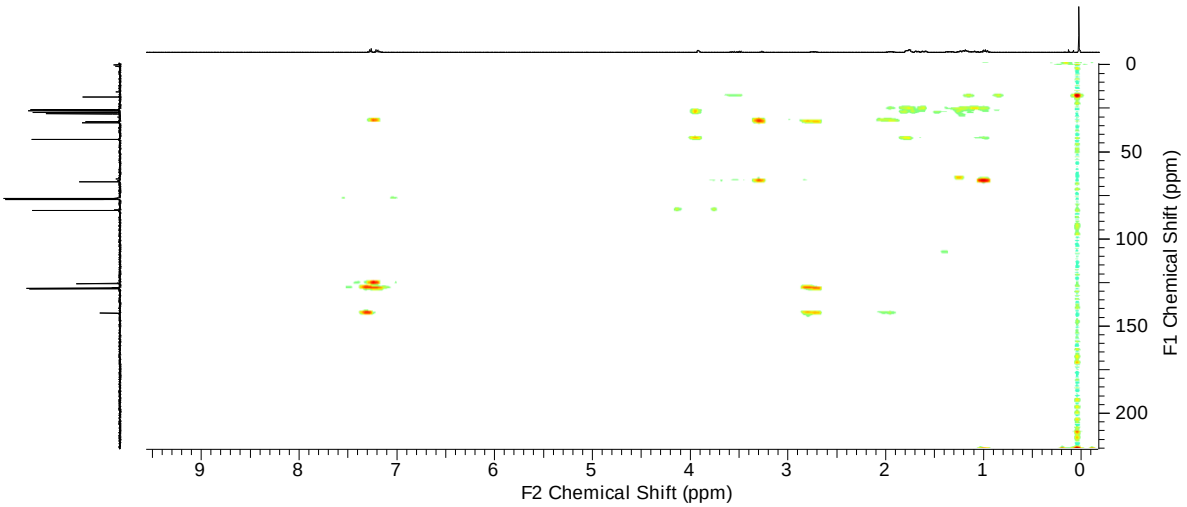
HH-COSY NMR (400 MHz, $CDCl_3$)



HSQC NMR (400 MHz, $CDCl_3$)

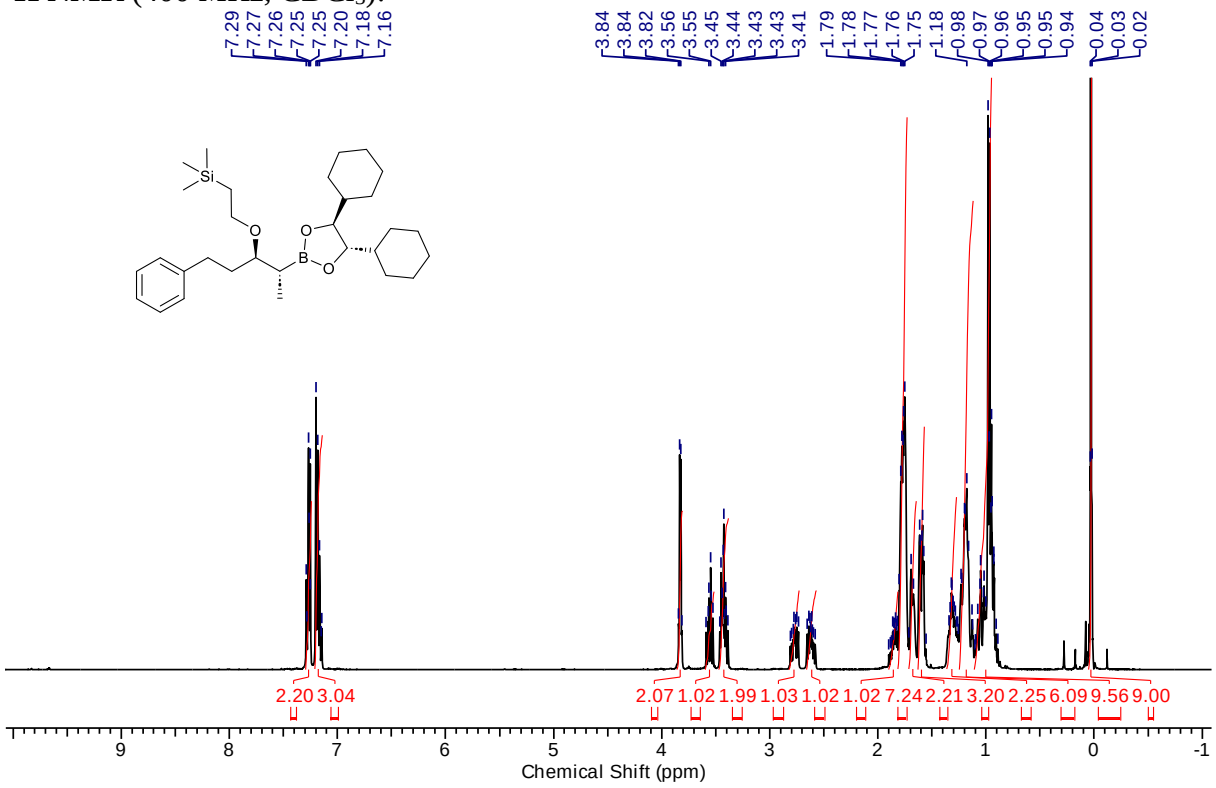


HMBC NMR (400 MHz, $CDCl_3$)

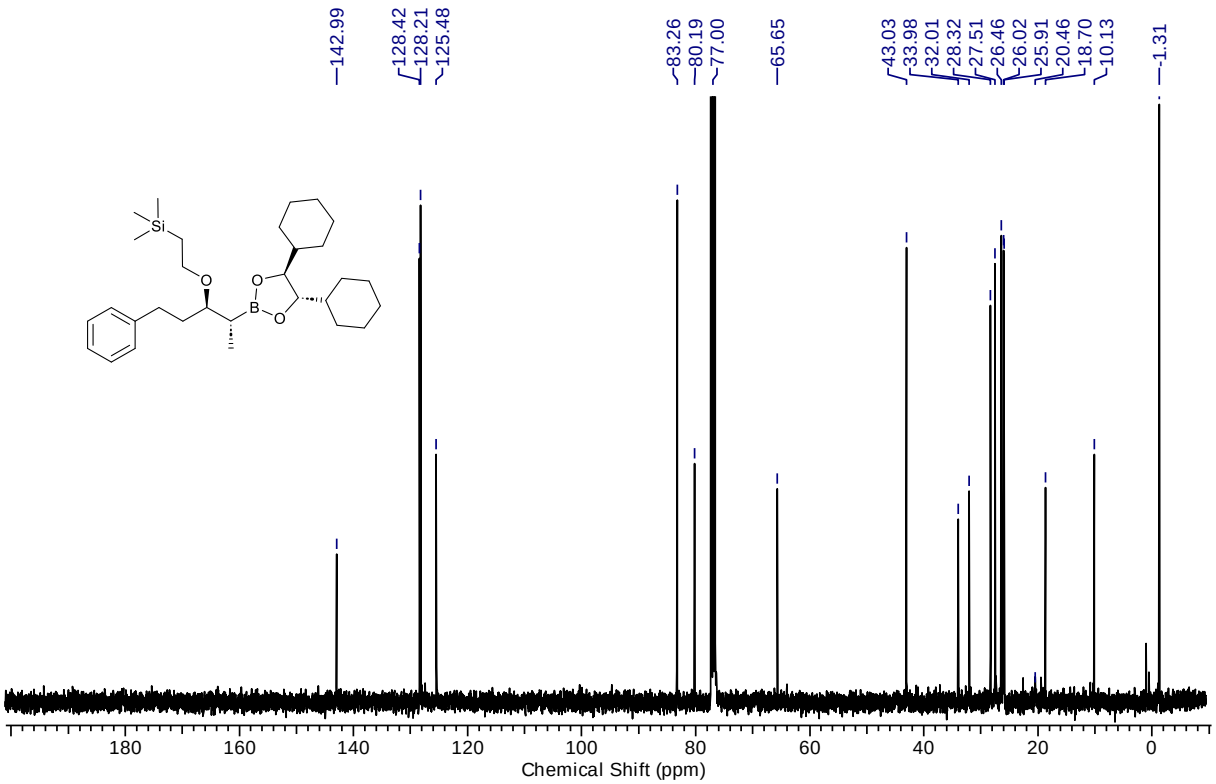


(2-{(*S*)-1-[(4*S*,5*S*)-4,5-Dicyclohexyl-1,3,2-dioxaborolan-2-yl]-3-phenylpropoxy}ethyl)trimethylsilane (4)

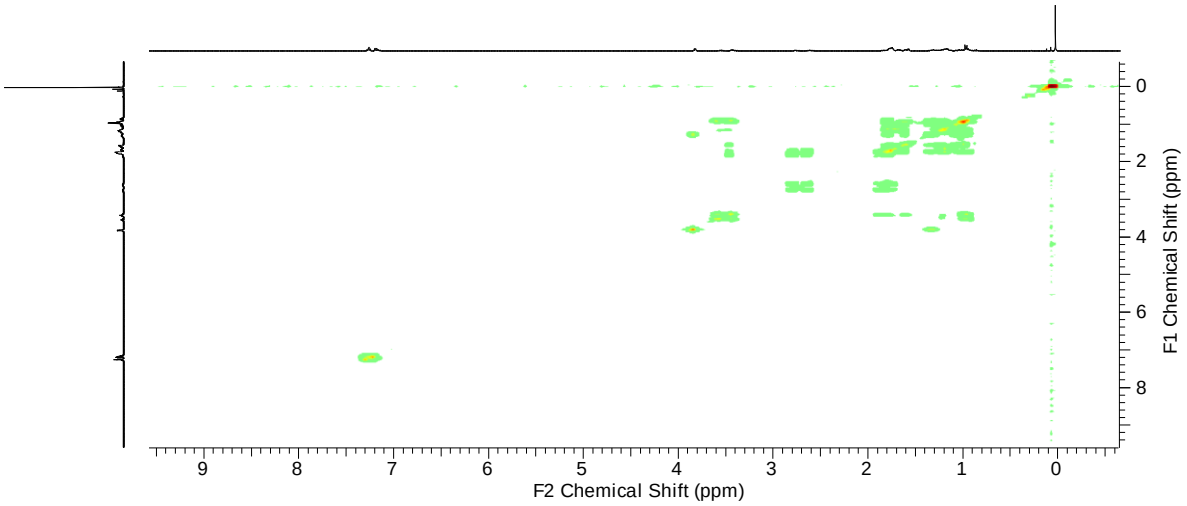
^{1}H NMR (400 MHz, $CDCl_3$):



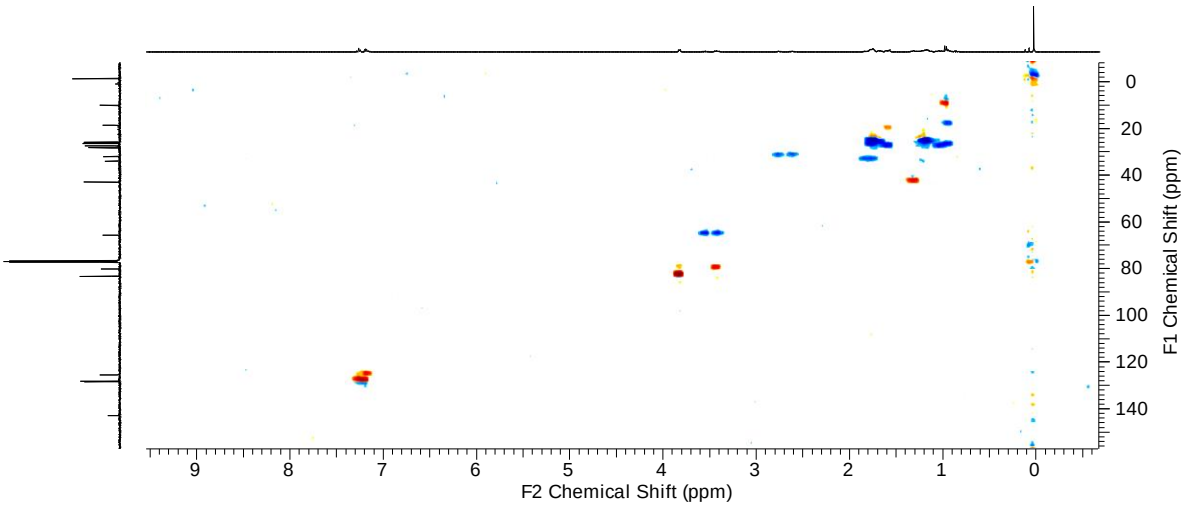
^{13}C NMR (100 MHz, $CDCl_3$):



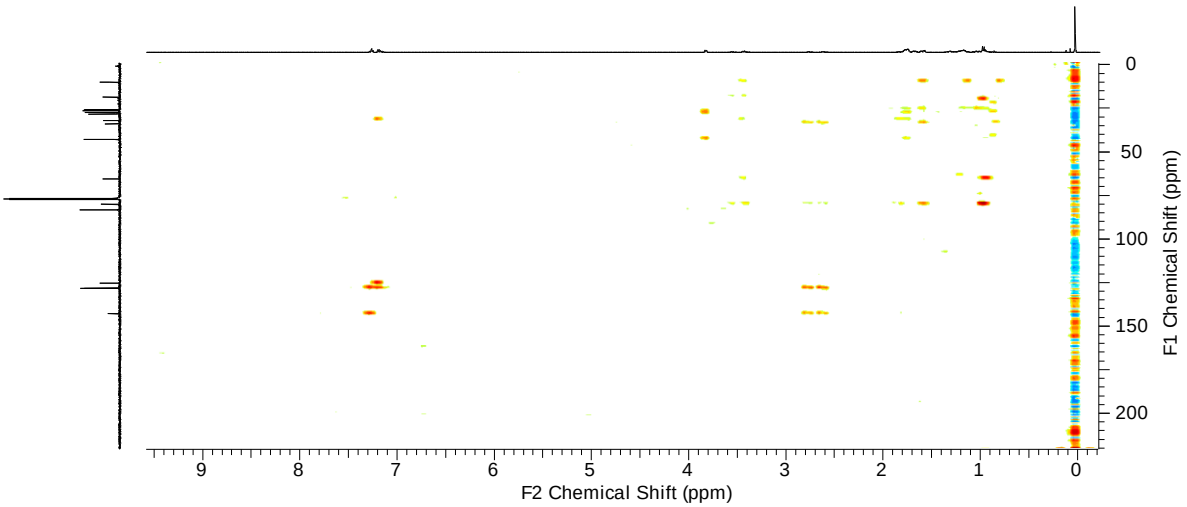
HH-COSY NMR (400 MHz, $CDCl_3$)



HSQC NMR (400 MHz, $CDCl_3$)

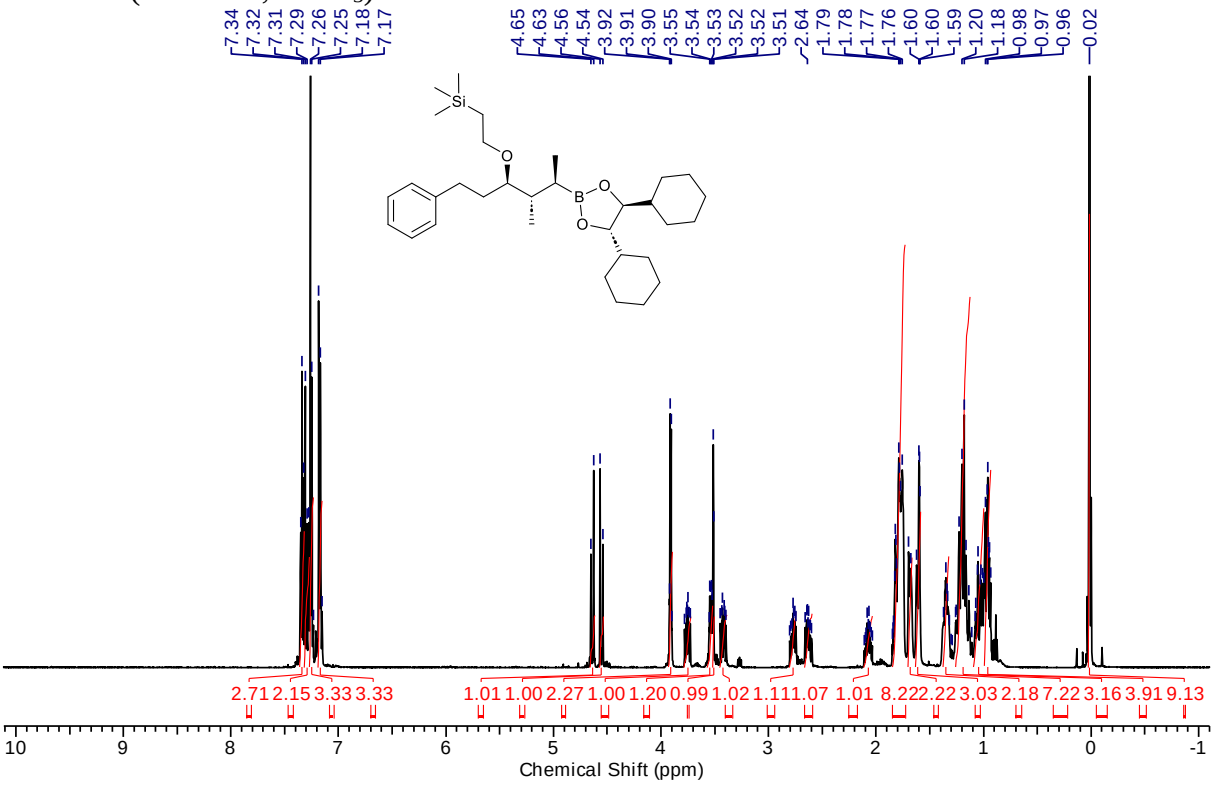


HMBC NMR (400 MHz, $CDCl_3$)

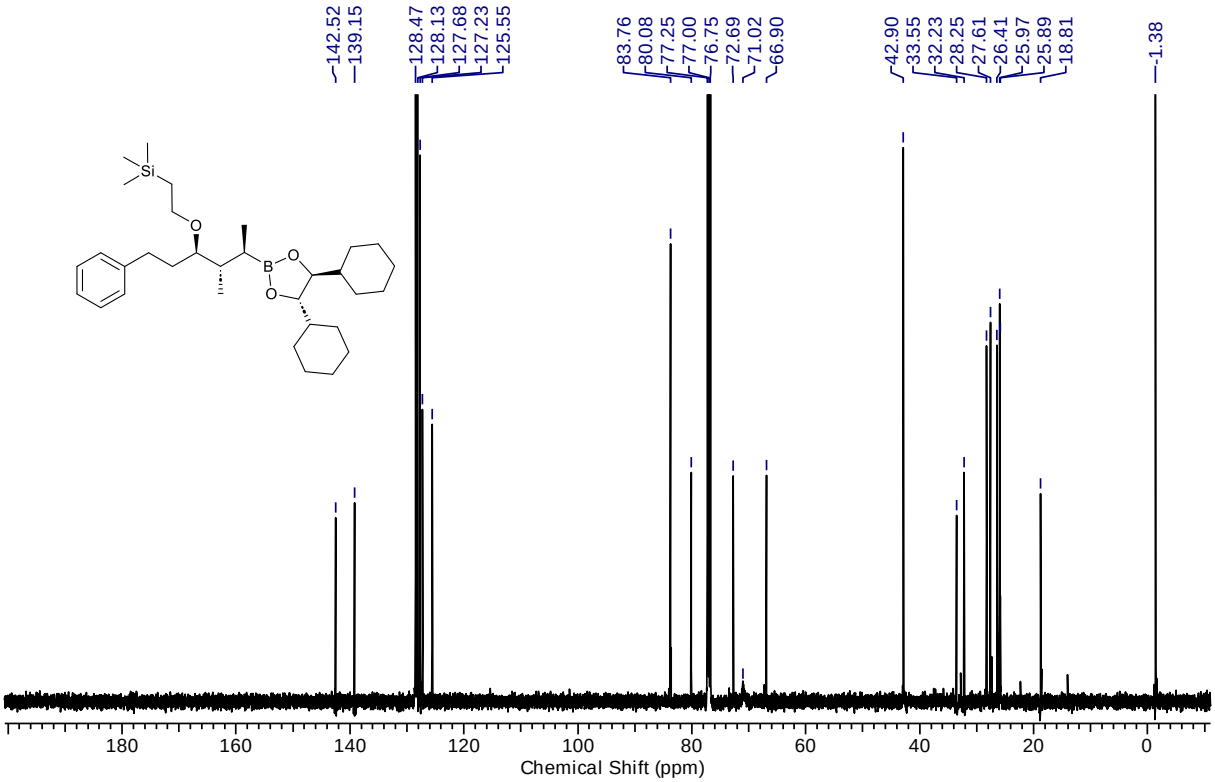


[2-({(3*R*,4*S*,5*R*)-5-[(4*S*,5*S*)-4,5-Dicyclohexyl-1,3,2-dioxaborolan-2-yl]-4-methyl-1-phenyl-hexan-3-yl}oxy)ethyl]trimethylsilane (5)

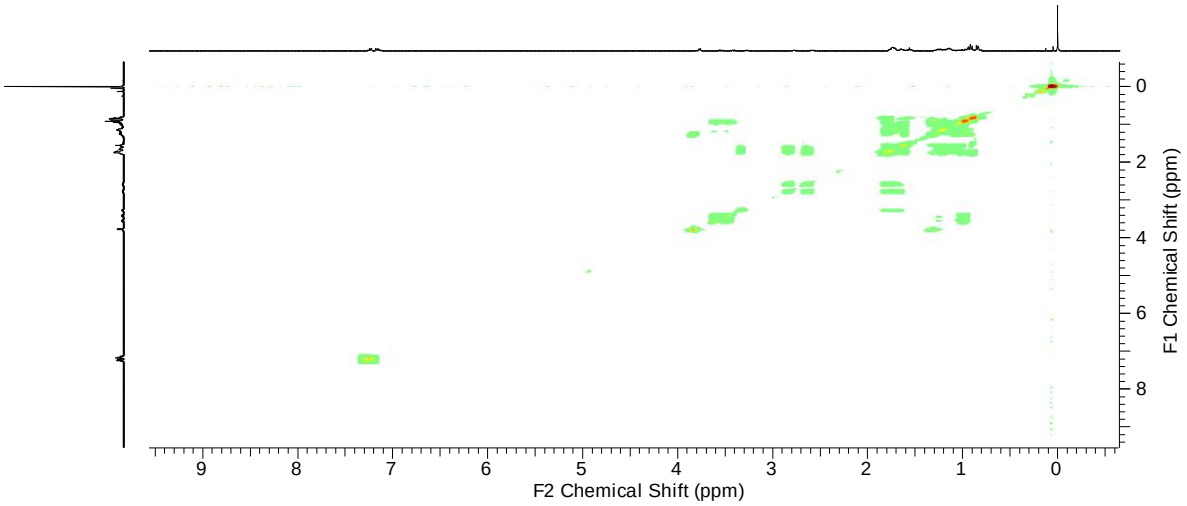
^{1}H NMR (500 MHz, $CDCl_3$):



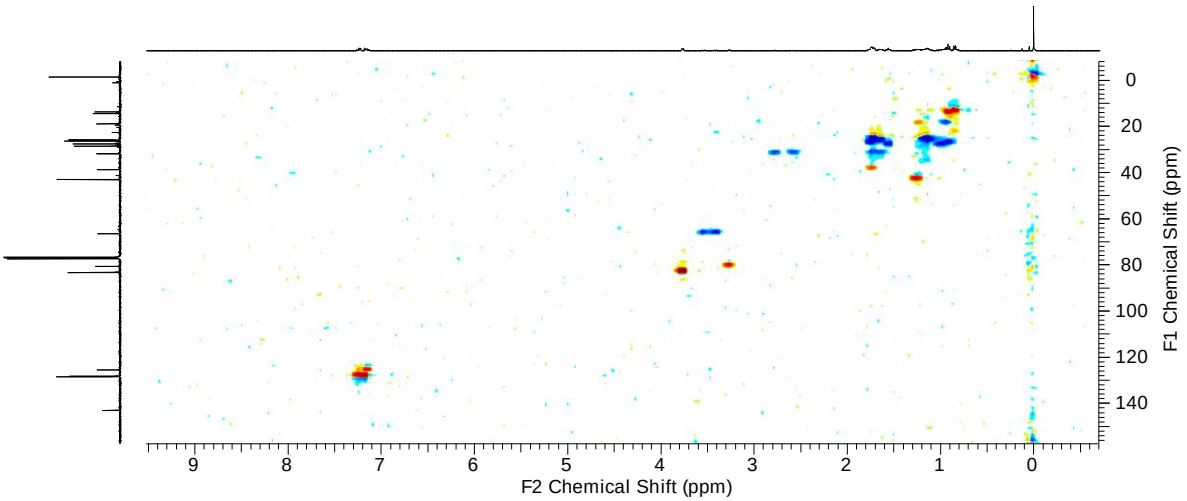
^{13}C NMR (125 MHz, $CDCl_3$):



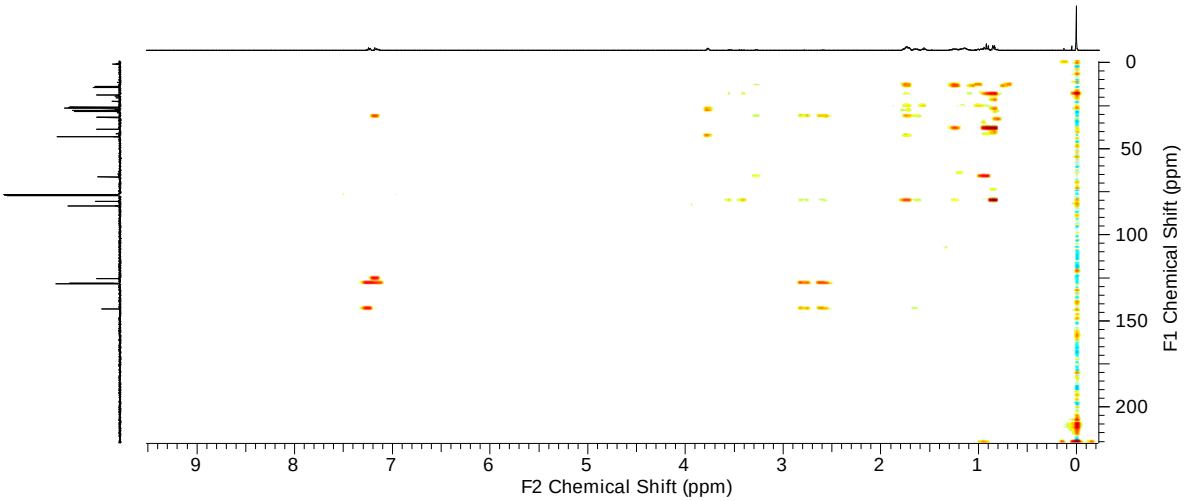
HH-COSY NMR (400 MHz, $CDCl_3$)



HSQC NMR (400 MHz, $CDCl_3$)

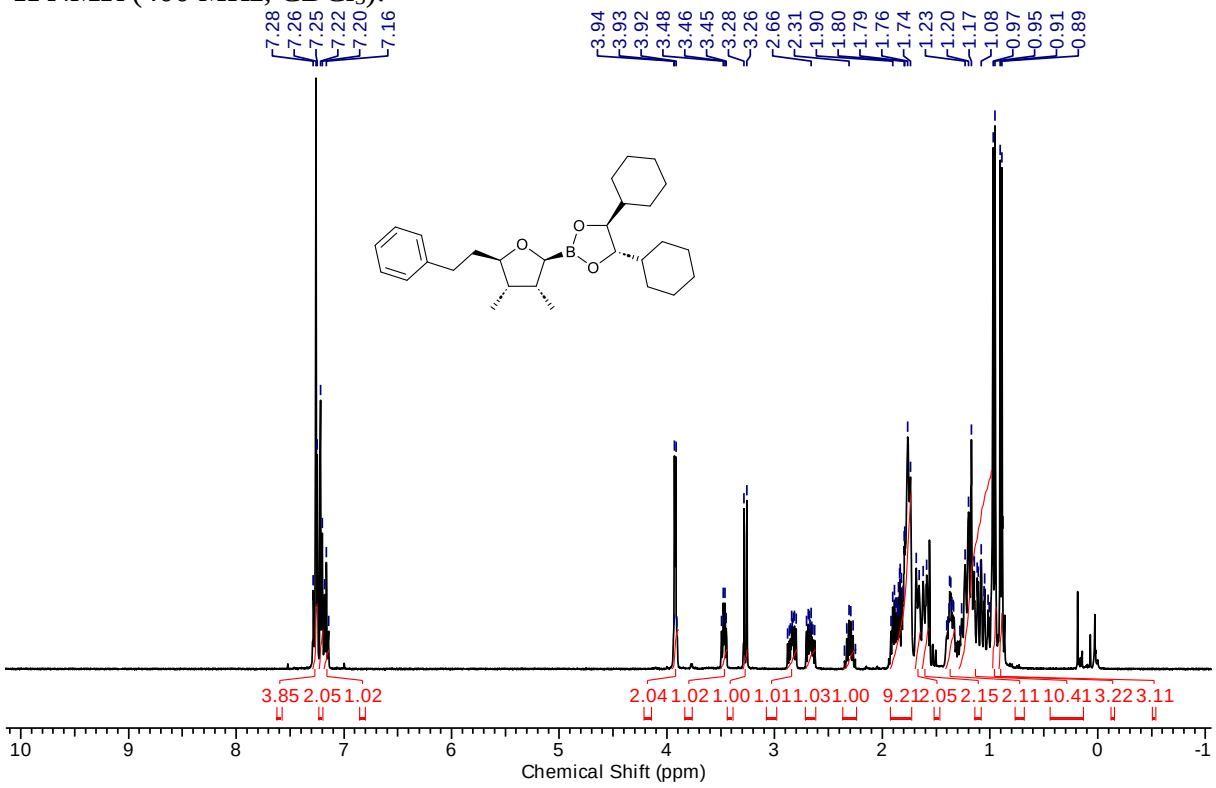


HMBC NMR (400 MHz, $CDCl_3$)

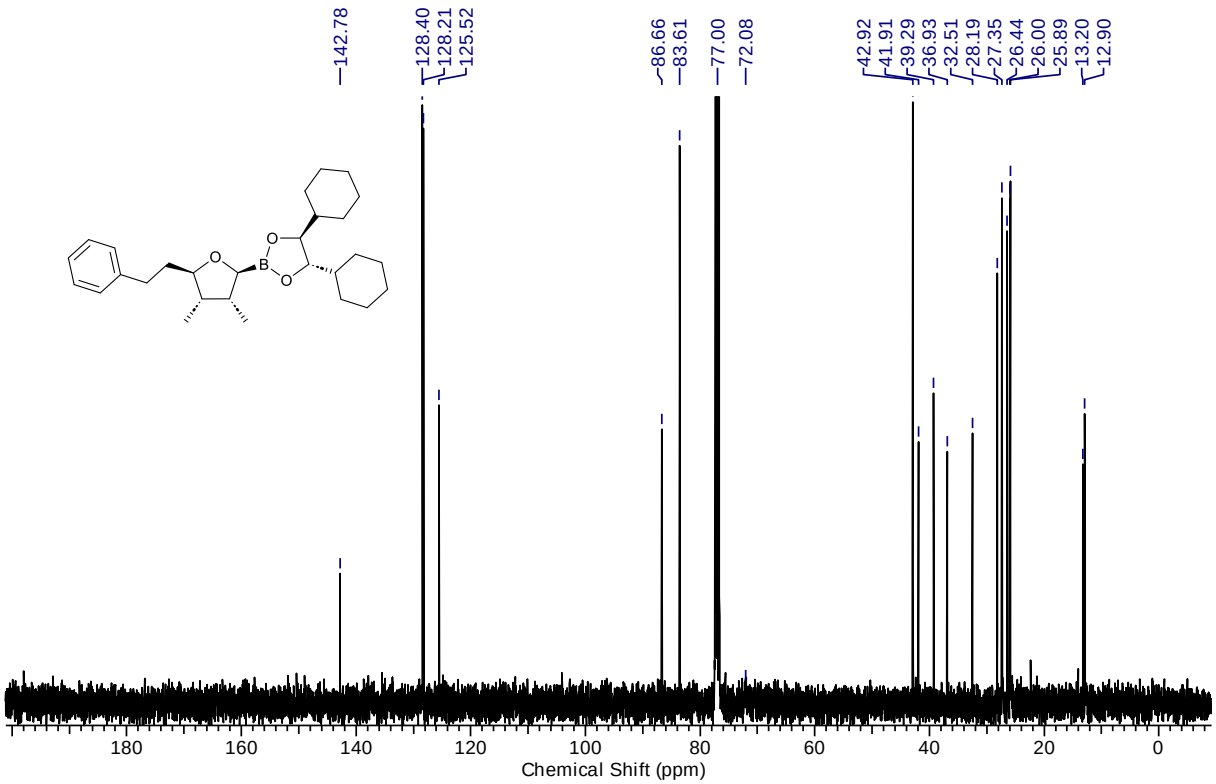


[2-({(3*R*,4*S*,5*R*)-5-[(4*S*,5*S*)-4,5-Dicyclohexyl-1,3,2-dioxaborolan-2-yl]-4-methyl-1-phenyl-hexan-3-yl}oxy)ethyl]trimethylsilane (6)

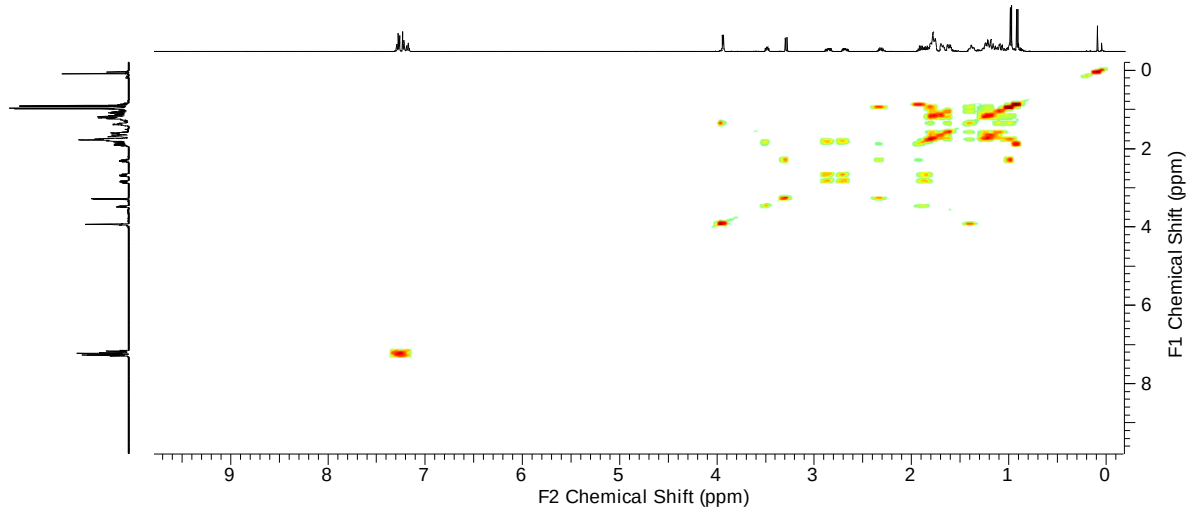
^{1}H NMR (400 MHz, $CDCl_3$):



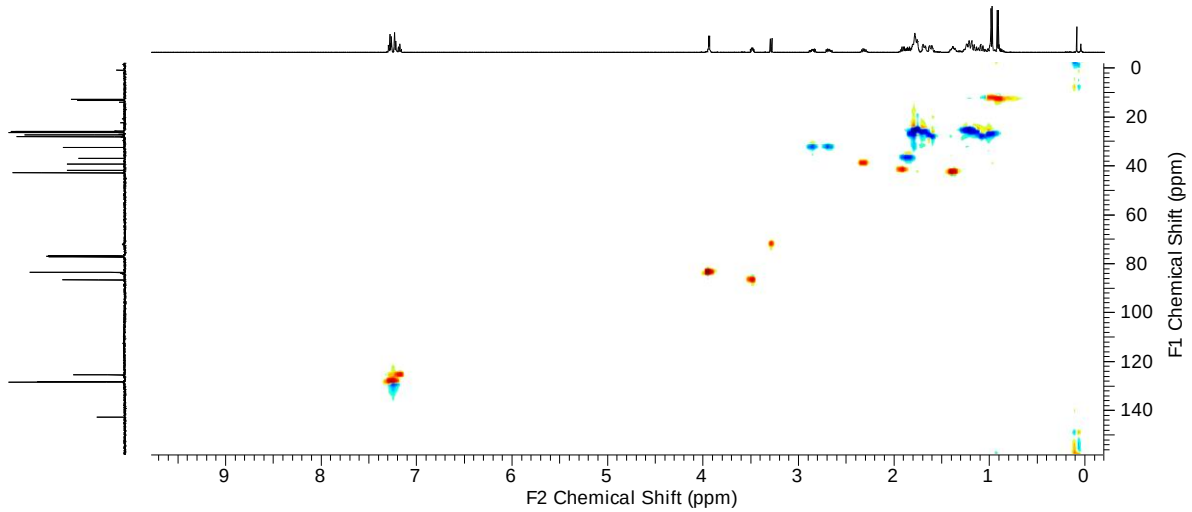
^{13}C NMR (100 MHz, $CDCl_3$):



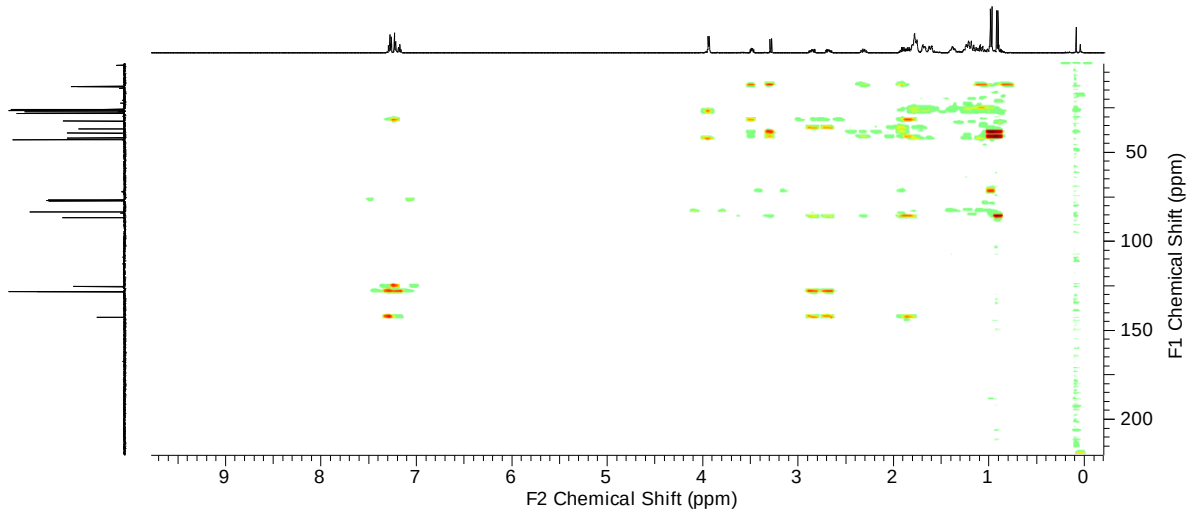
HH-COSY NMR (500 MHz, $CDCl_3$)



HSQC NMR (500 MHz, $CDCl_3$)

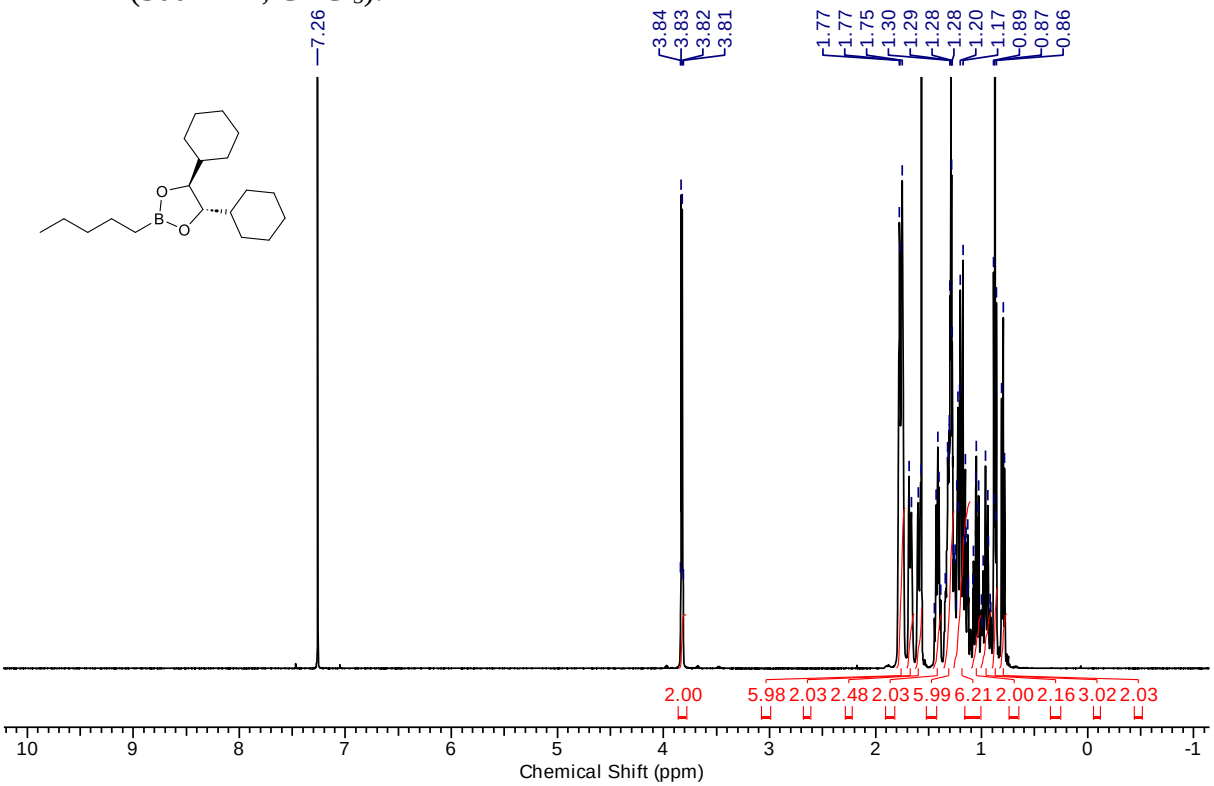


HMBC NMR (500 MHz, $CDCl_3$)

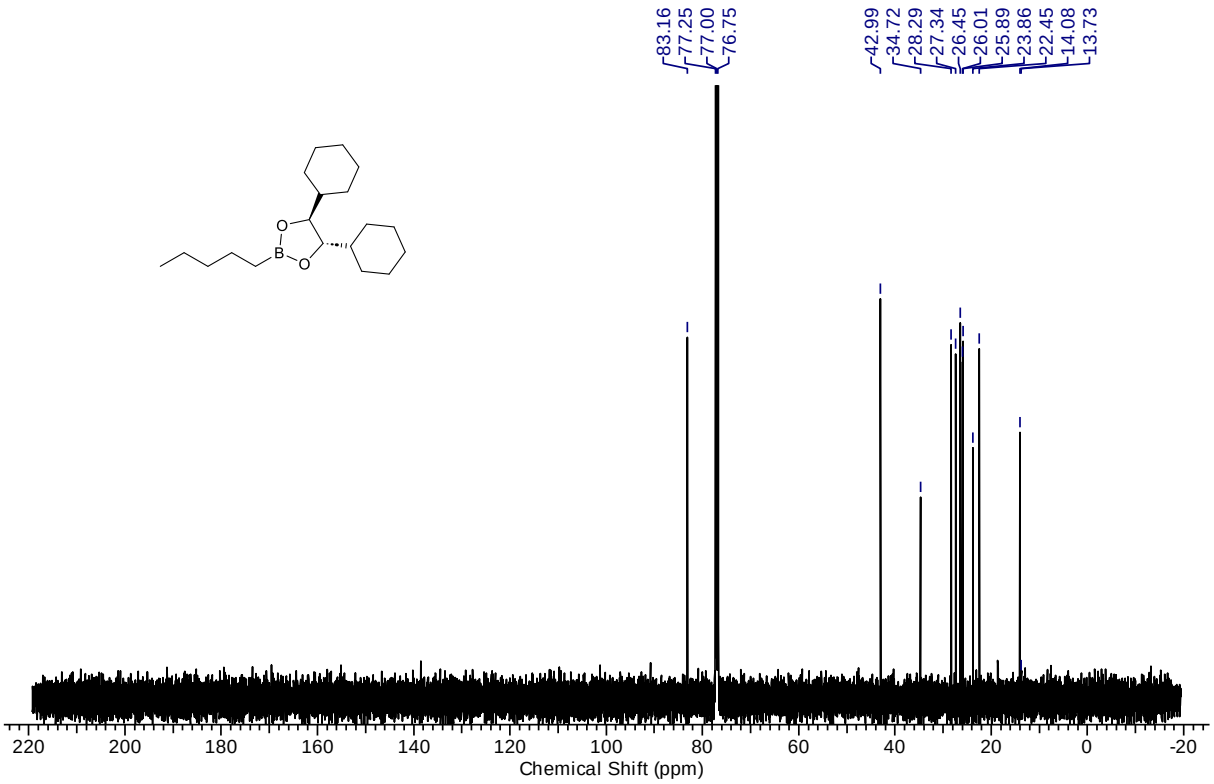


(4*S*,5*S*)-4,5-Dicyclohexyl-2-pentyl-1,3,2-dioxaborolane (7)

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

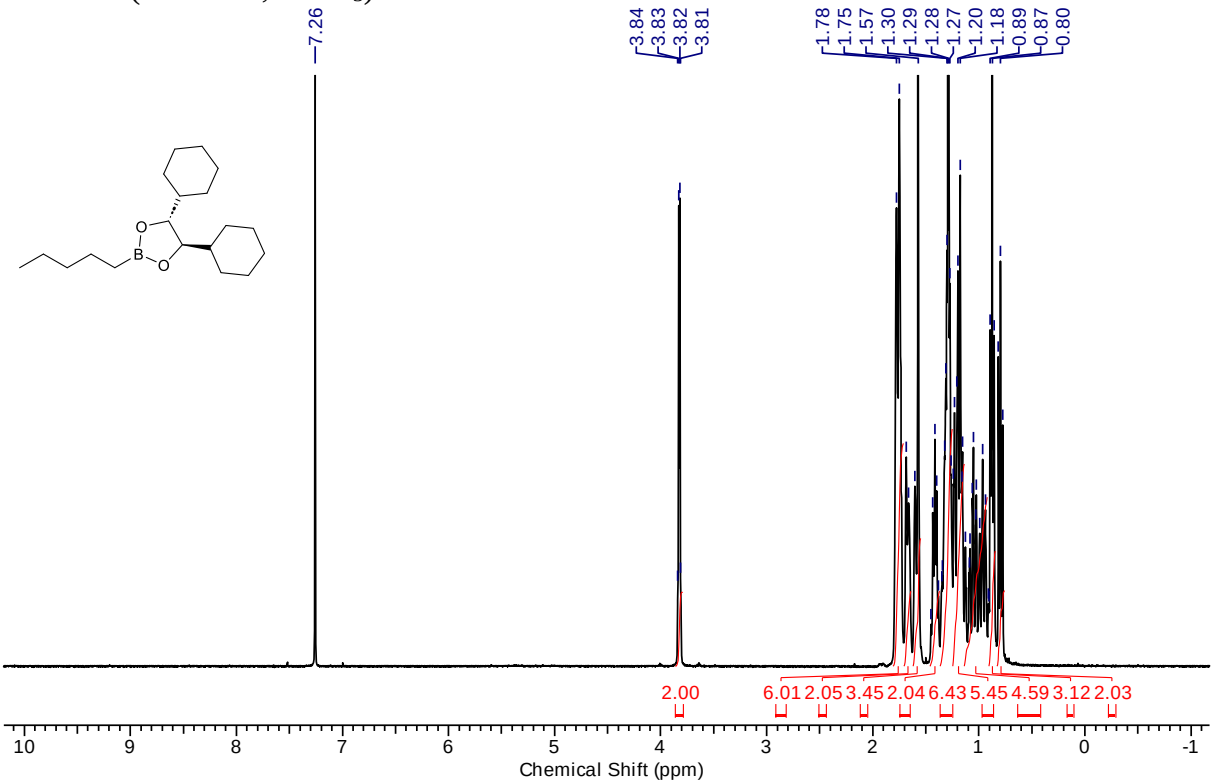


^{13}C NMR (125 MHz, $CDCl_3$):

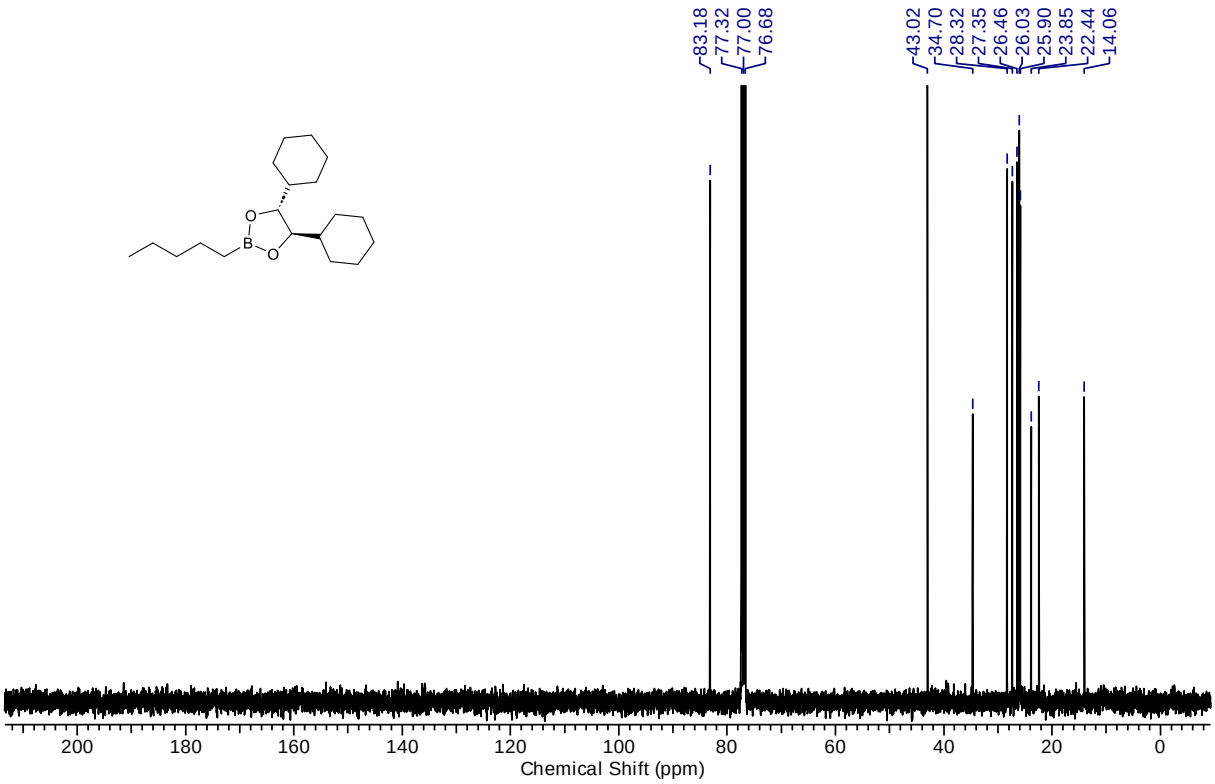


(4*R*,5*R*)-4,5-Dicyclohexyl-2-pentyl-1,3,2-dioxaborolane (*ent*-7)

^{1}H NMR (400 MHz, $CDCl_3$):

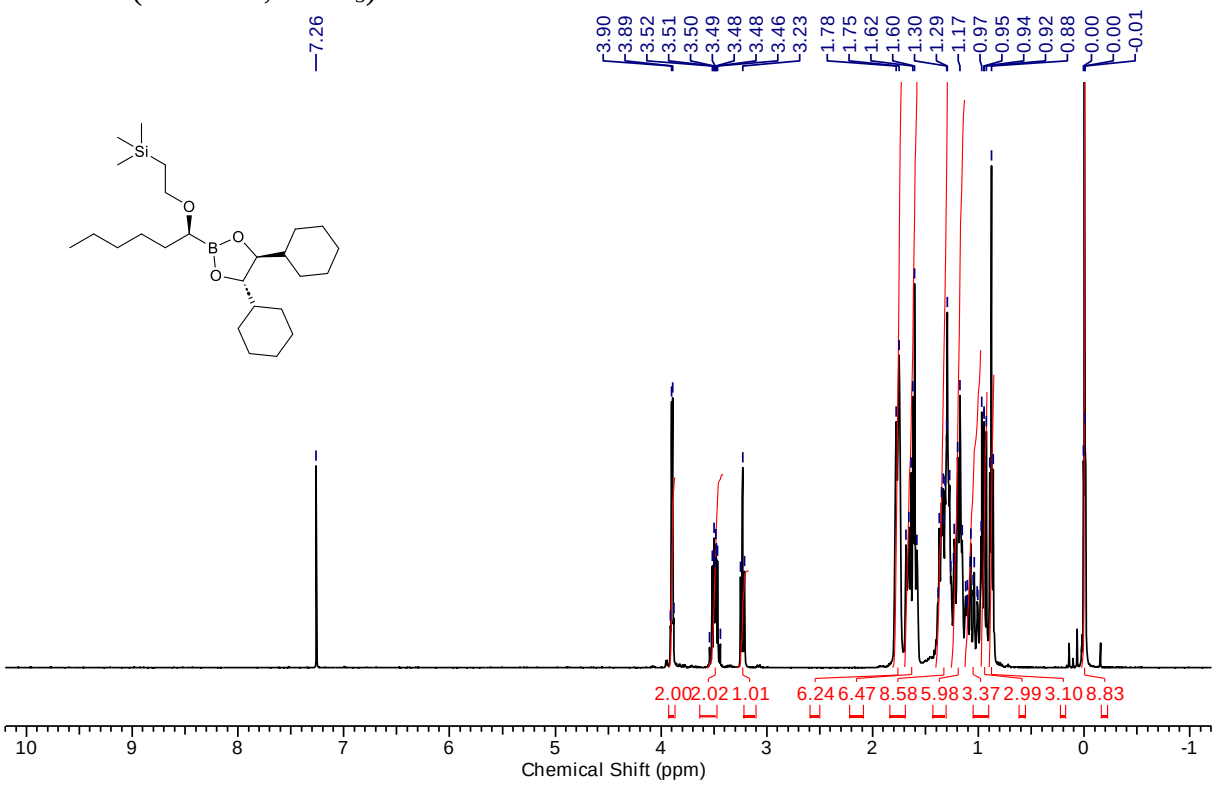


^{13}C NMR (100 MHz, $CDCl_3$):

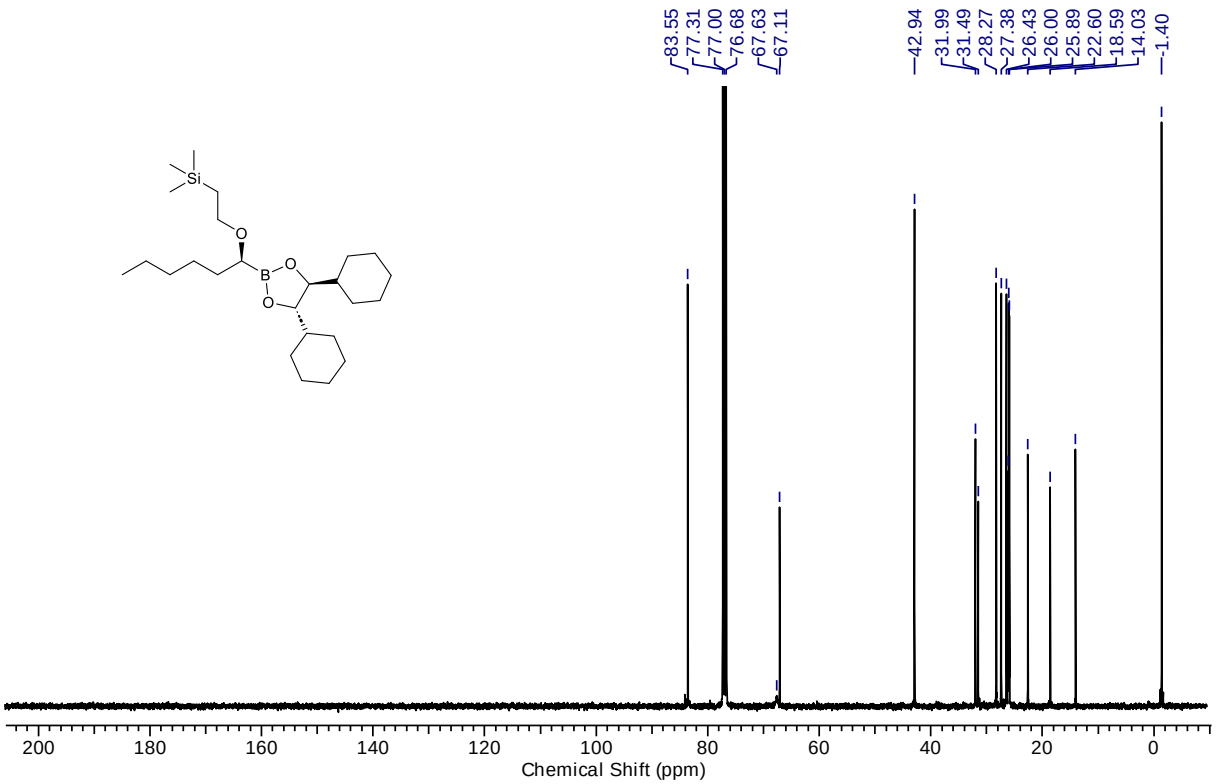


[2-({(*S*)-1-[(4*S*,5*S*)-4,5-Dicyclohexyl-1,3,2-dioxaborolan-2-yl]hexyl}oxy)ethyl]trimethyl-silane (8)

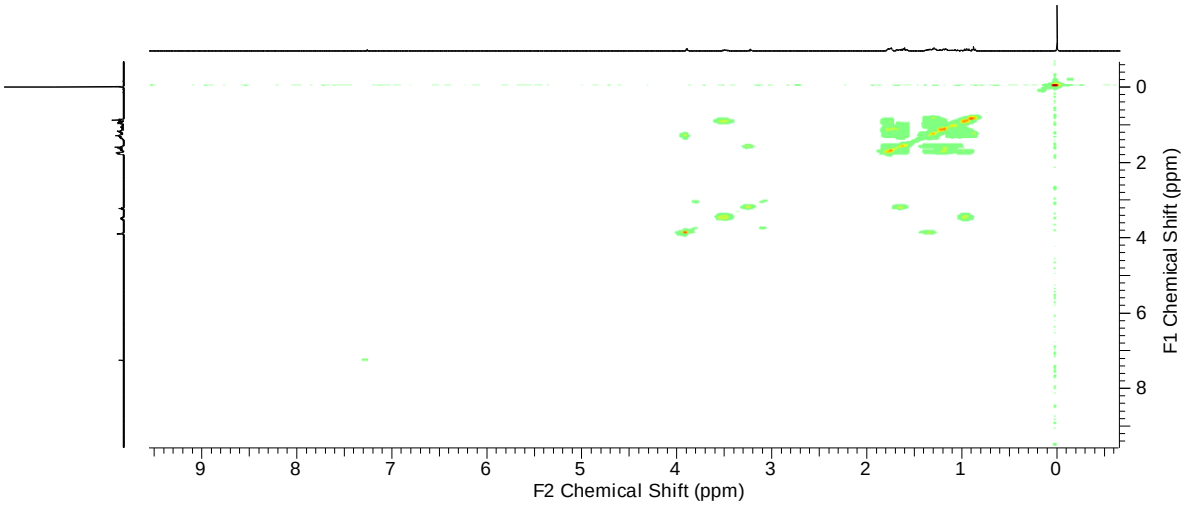
^{1}H NMR (400 MHz, $CDCl_3$):



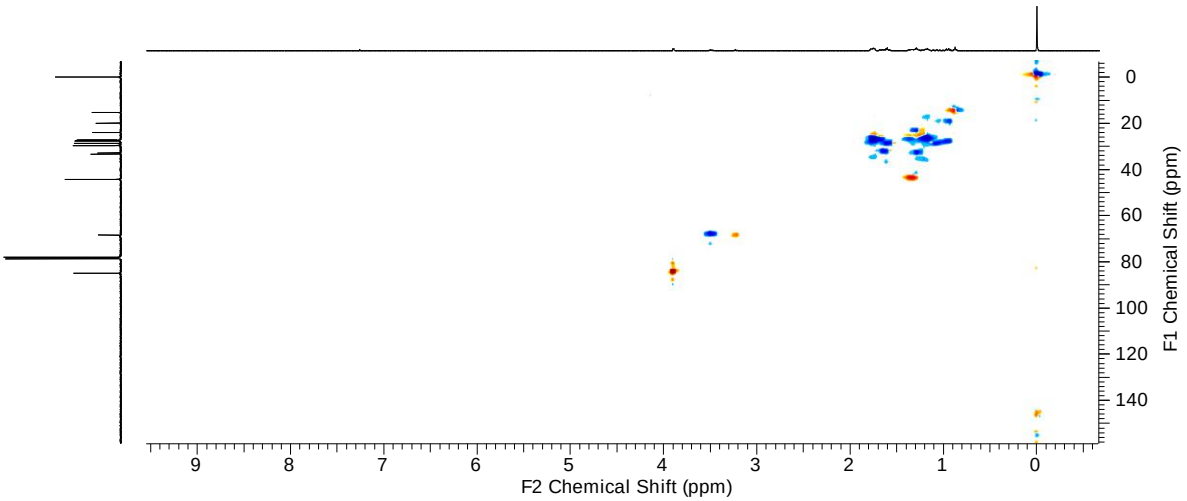
^{13}C NMR (100 MHz, $CDCl_3$):



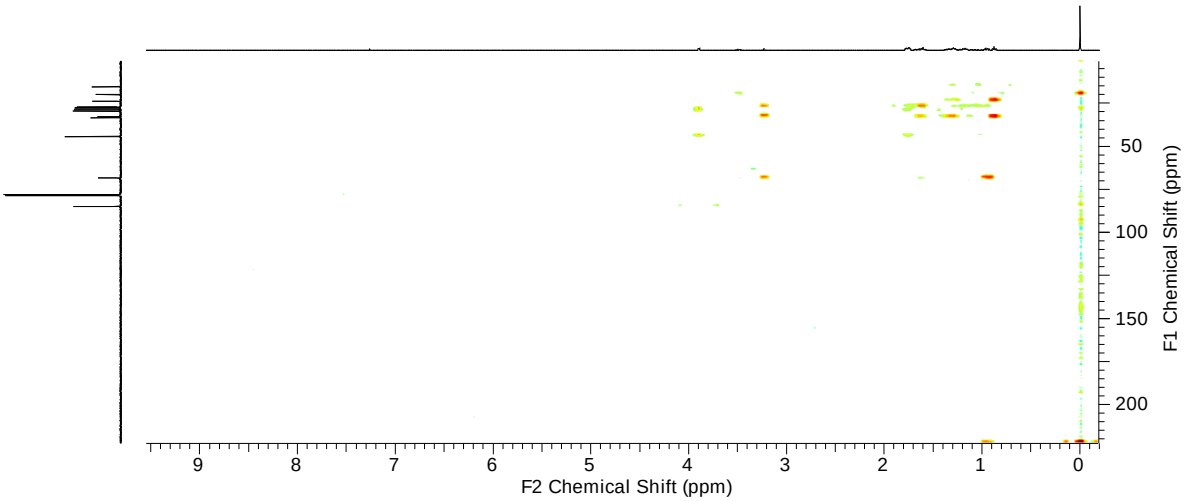
HH-COSY NMR (400 MHz, $CDCl_3$)



HSQC NMR (400 MHz, $CDCl_3$)

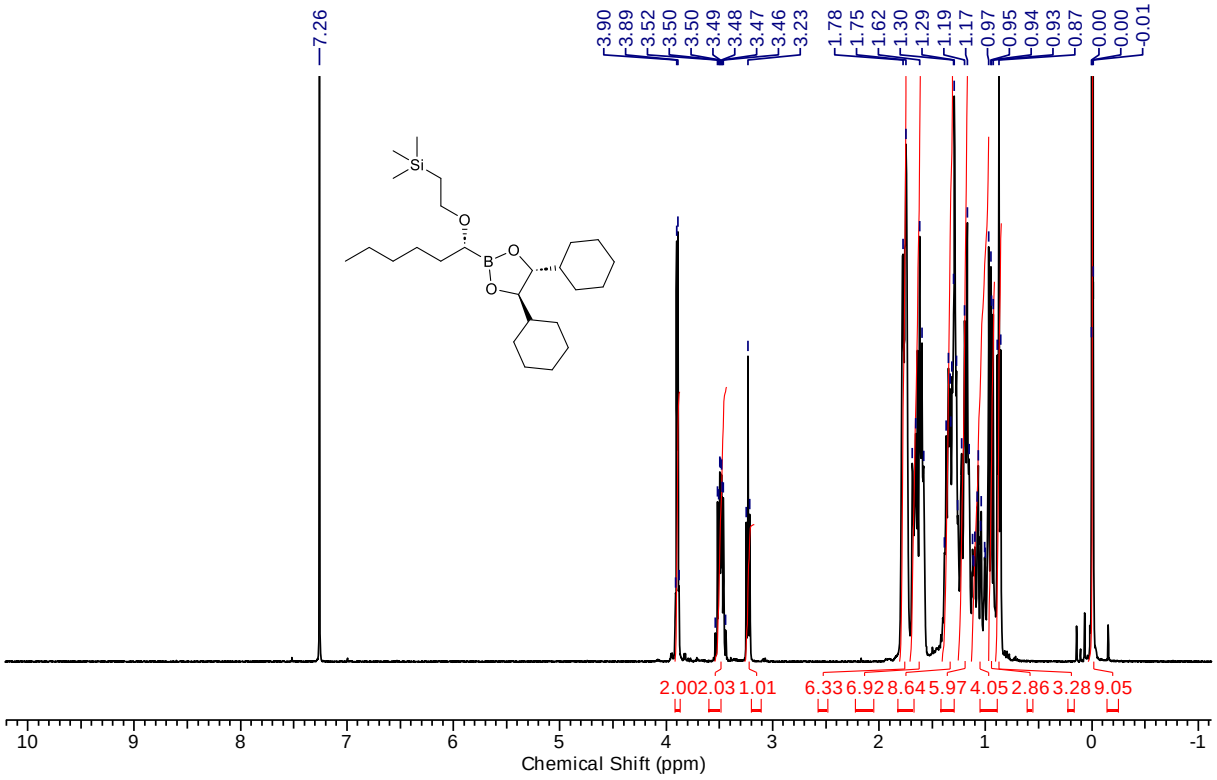


HMBC NMR (400 MHz, $CDCl_3$)

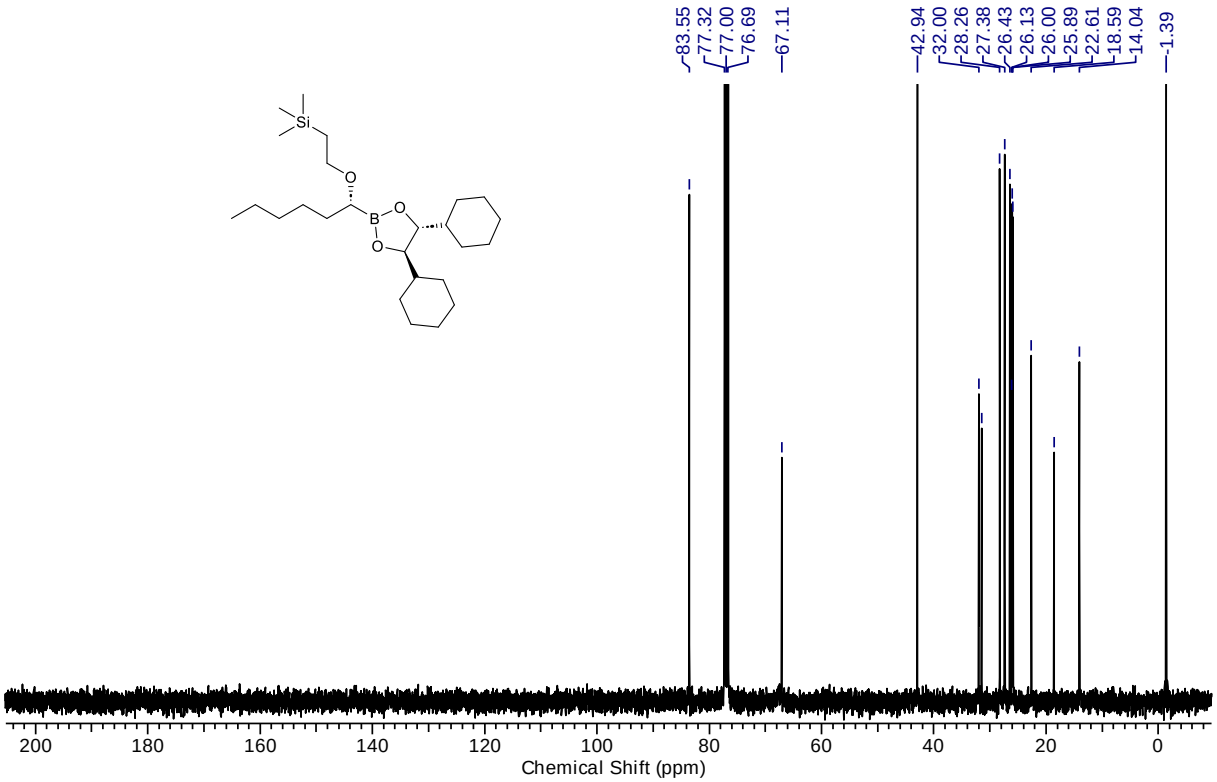


[2-({(*R*)-1-[(4*R*,5*R*)-4,5-Dicyclohexyl-1,3,2-dioxaborolan-2-yl]hexyl}oxy)ethyl]trimethylsilane (*ent*-8)

^{1}H NMR (400 MHz, $CDCl_3$):

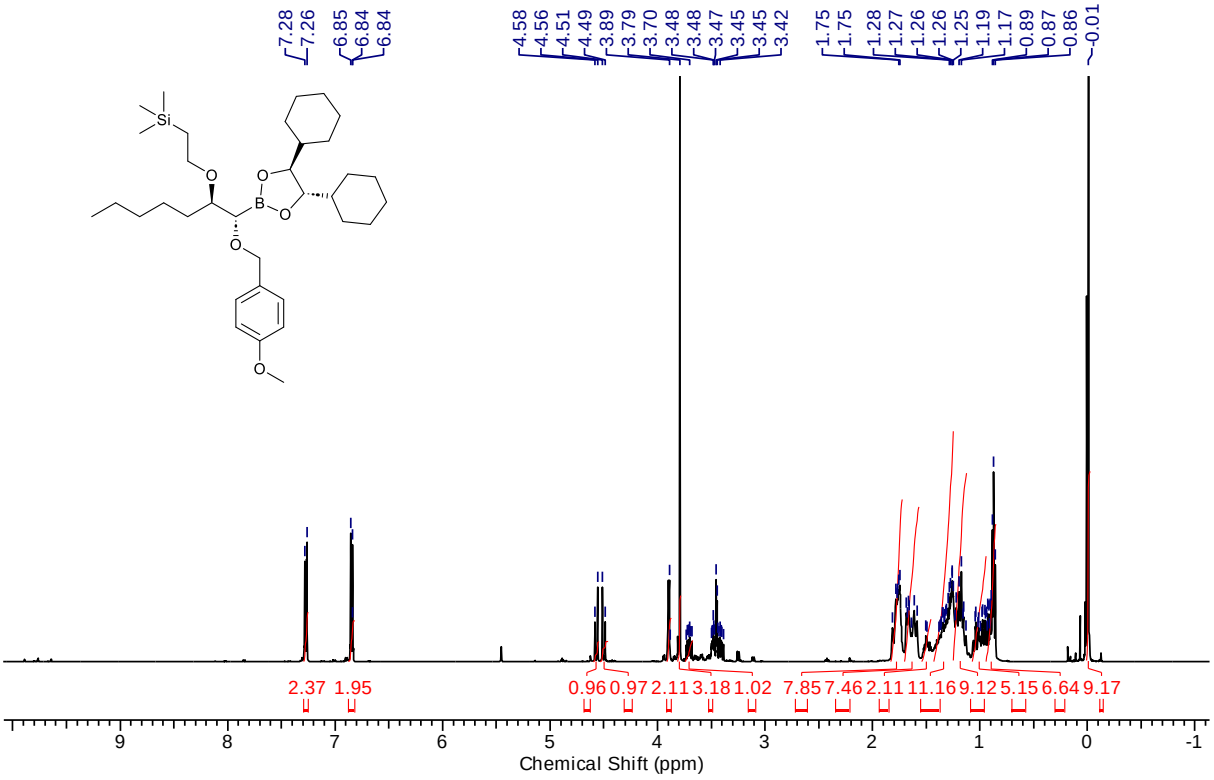


^{13}C NMR (100 MHz, $CDCl_3$):

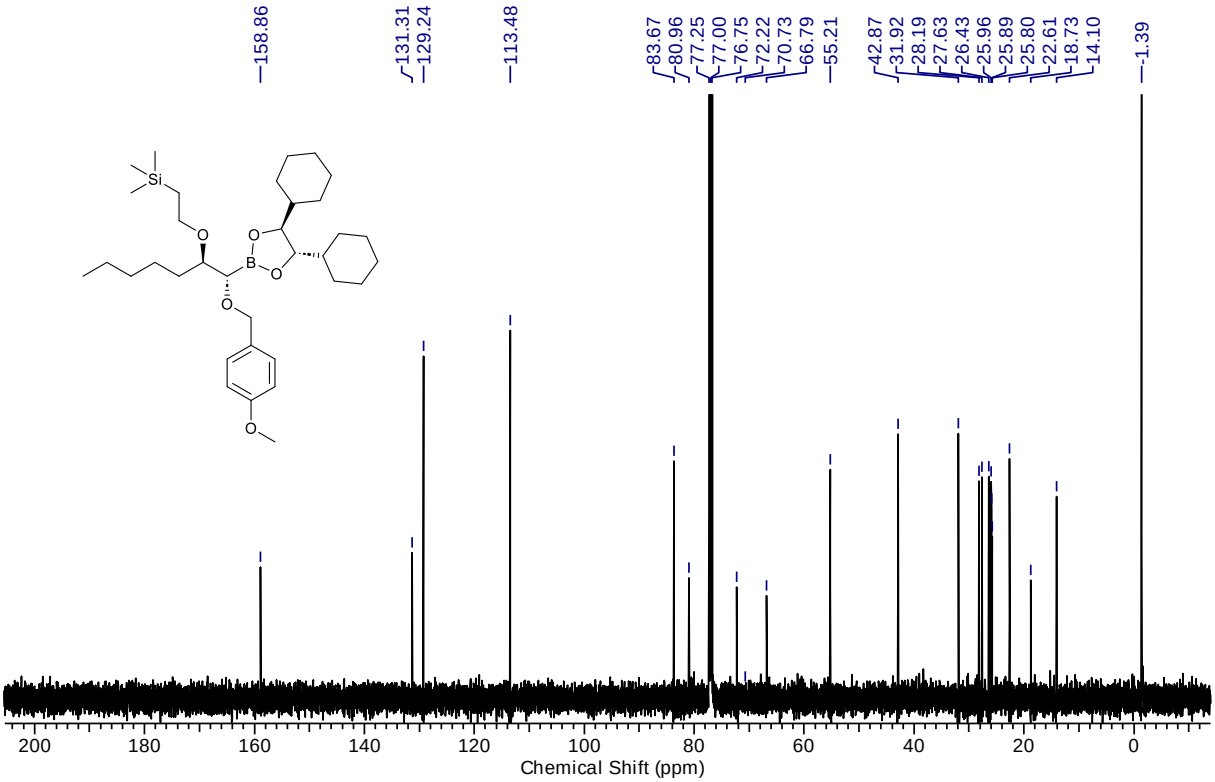


[2-({(1*S*,2*R*)-1-[(4*S*,5*S*)-4,5-Dicyclohexyl-1,3,2-dioxaborolan-2-yl]-1-[(4-methoxybenzyl)-oxy]heptan-2-yl}oxy)ethyl]trimethylsilane (9)

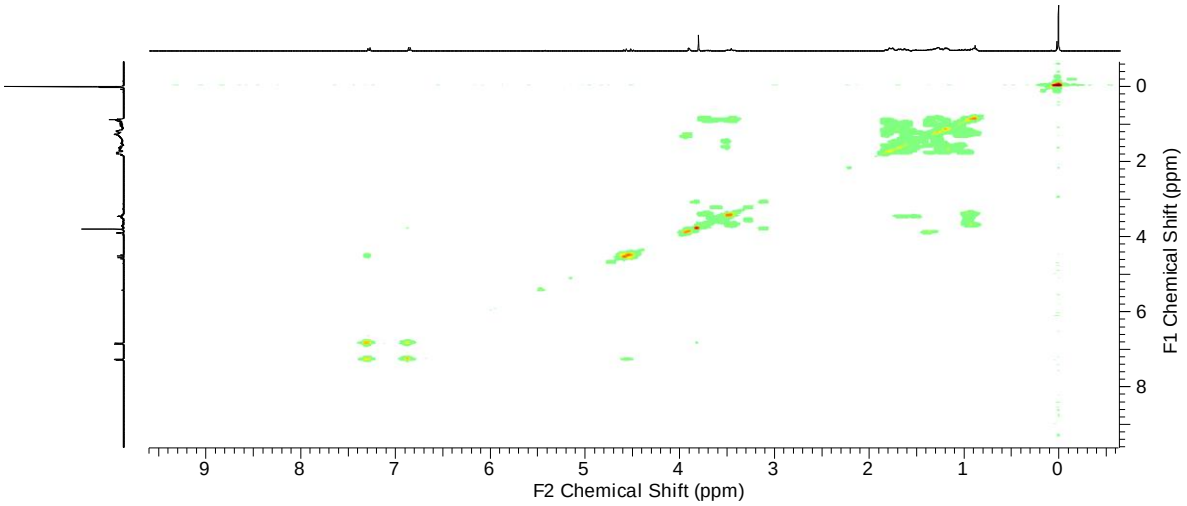
^{1}H NMR (500 MHz, $CDCl_3$):



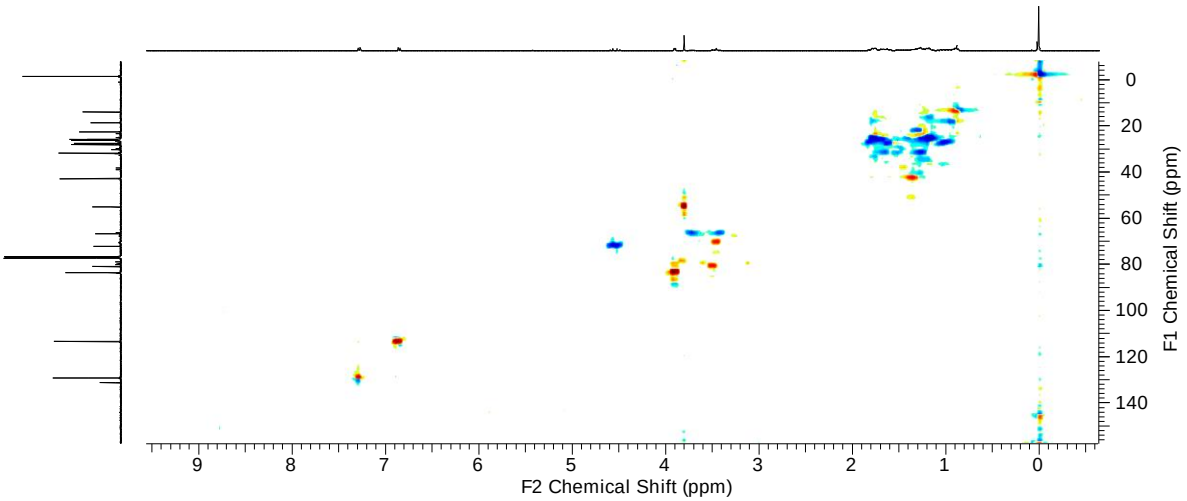
^{13}C NMR (125 MHz, $CDCl_3$):



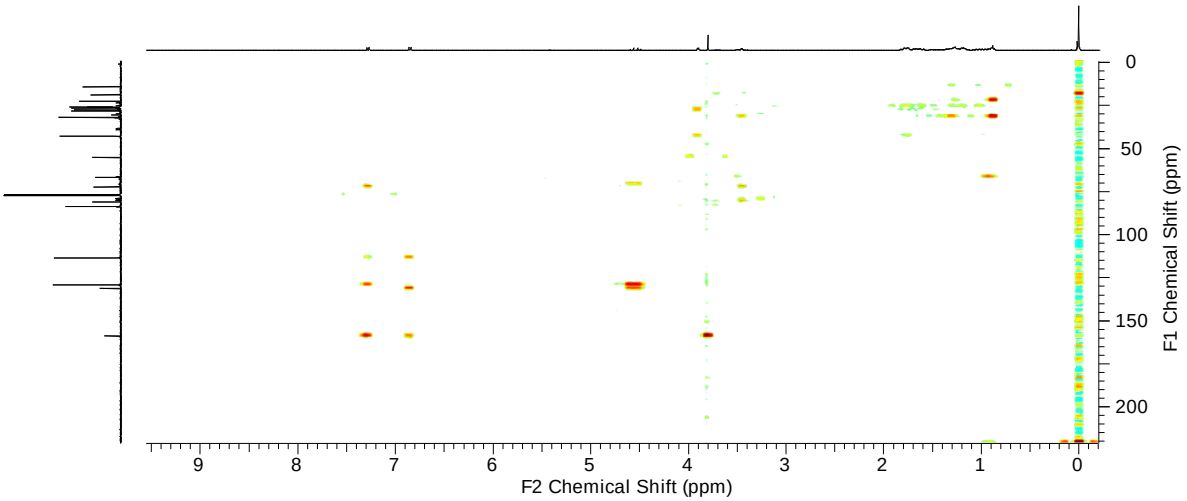
HH-COSY NMR (400 MHz, $CDCl_3$)



HSQC NMR (400 MHz, $CDCl_3$)

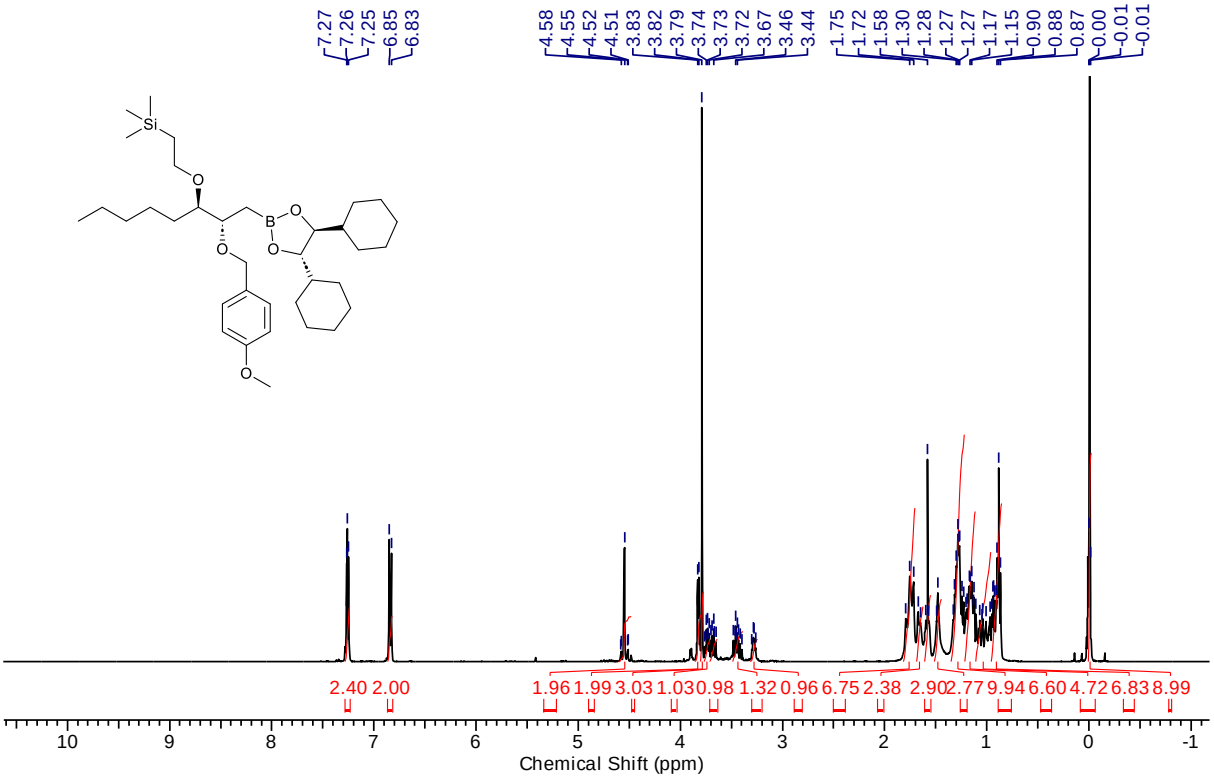


HMBC NMR (400 MHz, $CDCl_3$)

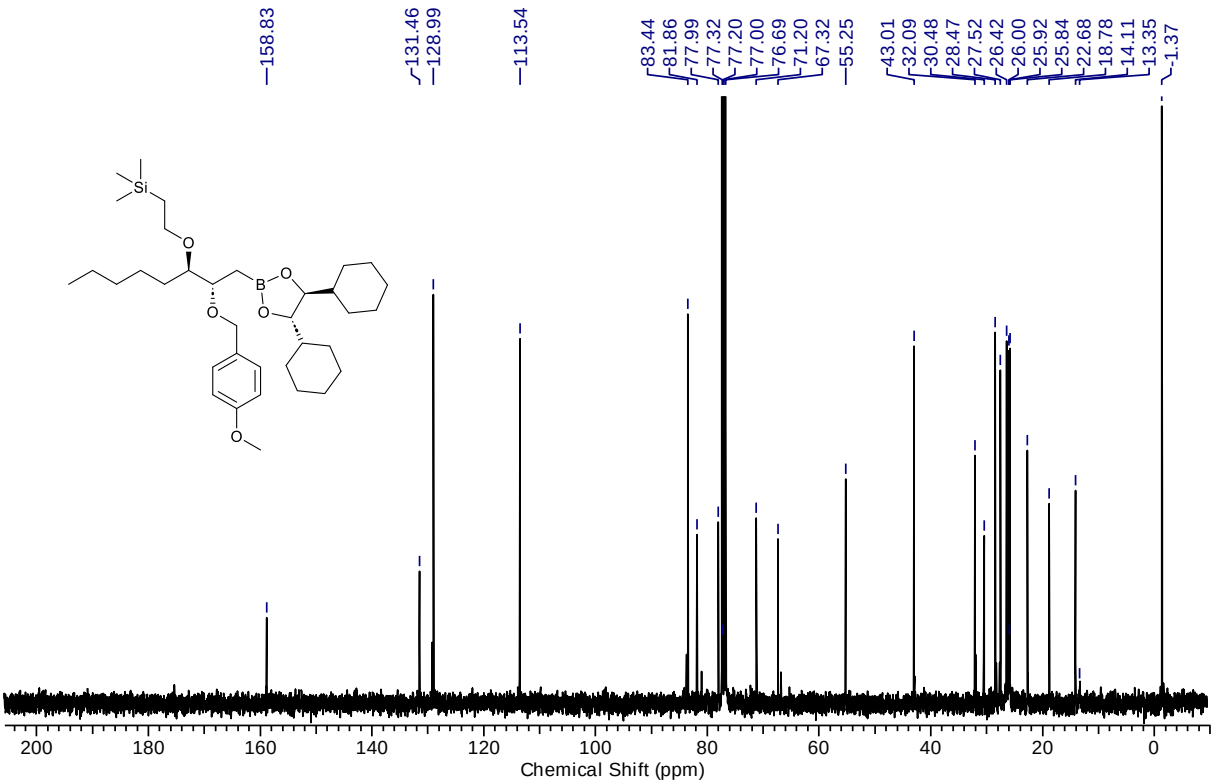


[2-({(2*S*,3*R*)-1-[(4*S*,5*S*)-4,5-Dicyclohexyl-1,3,2-dioxaborolan-2-yl]-2-[(4-methoxybenzyl)-oxy]octan-3-yl}oxy)ethyl]trimethylsilane (10)

^{1}H NMR (400 MHz, $CDCl_3$):

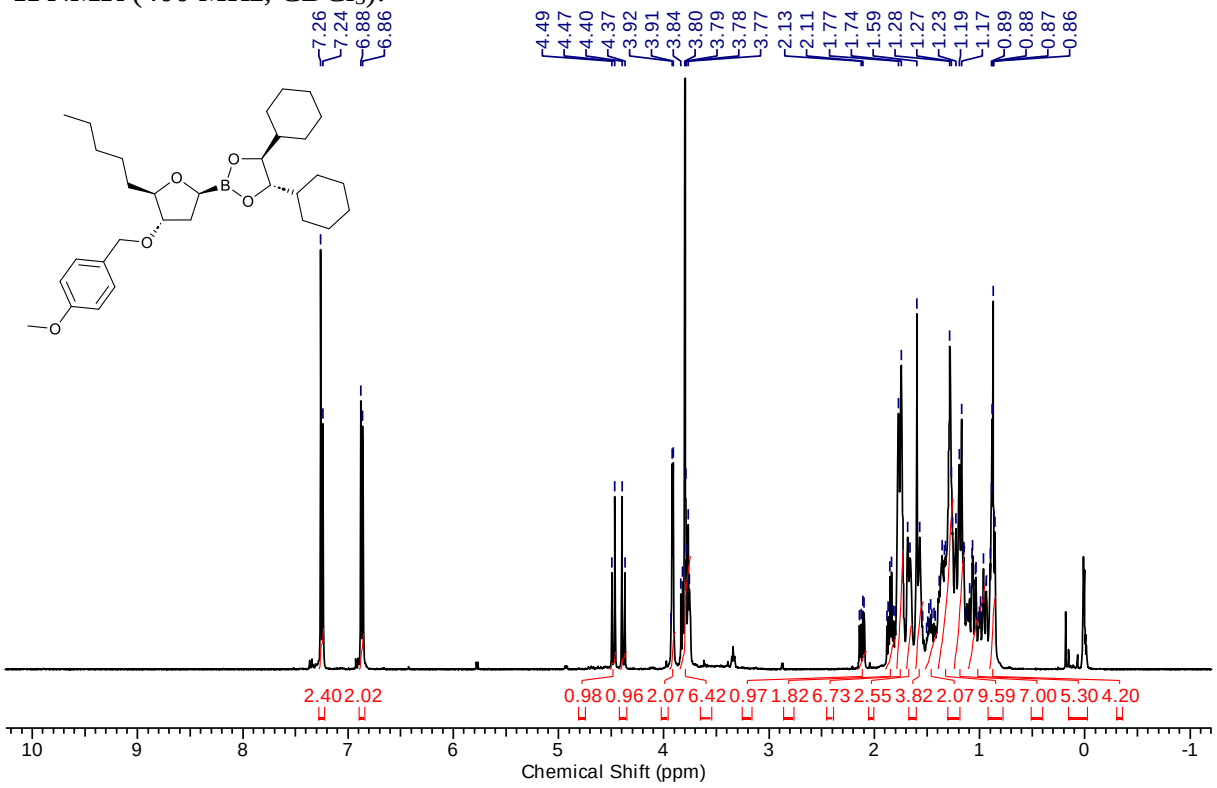


^{13}C NMR (100 MHz, $CDCl_3$):

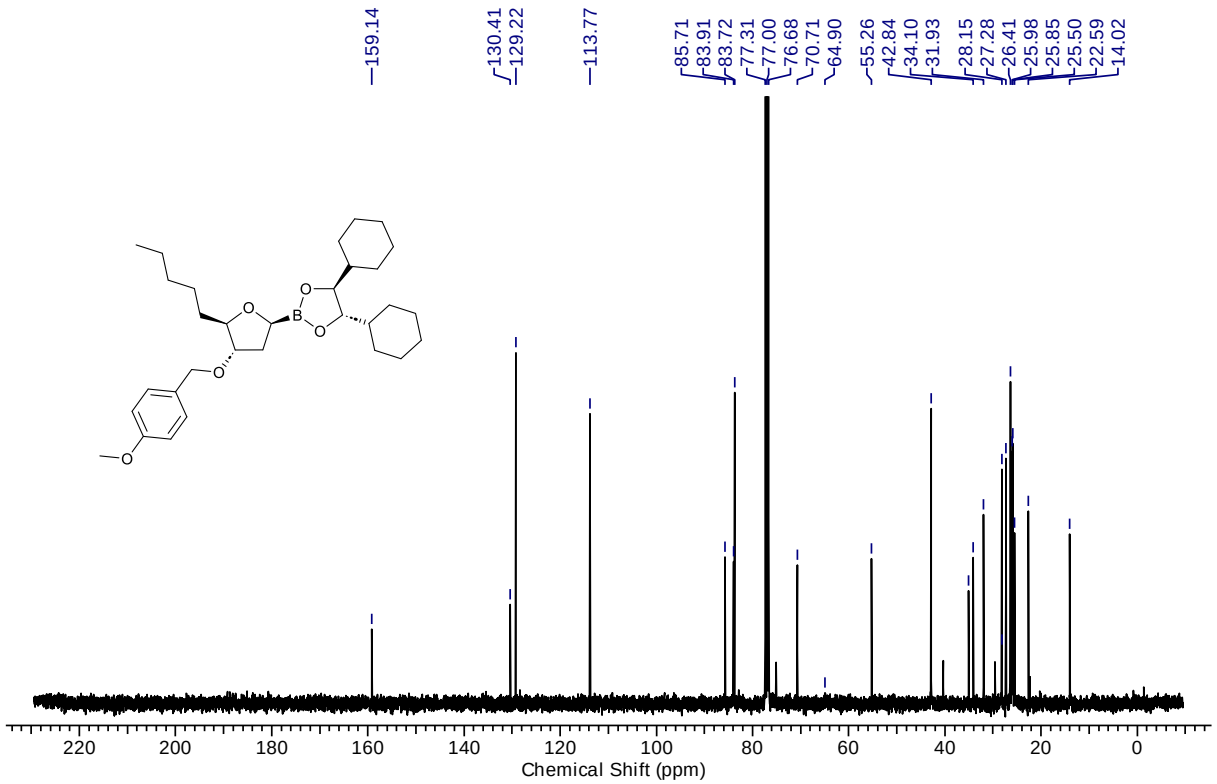


(4*S*,5*S*)-4,5-Dicyclohexyl-2-{(2*S*,4*S*,5*R*)-4-[(4-methoxybenzyl)oxy]-5-pentyltetrahydrofuran-2-yl}-1,3,2-dioxaborolane (11)

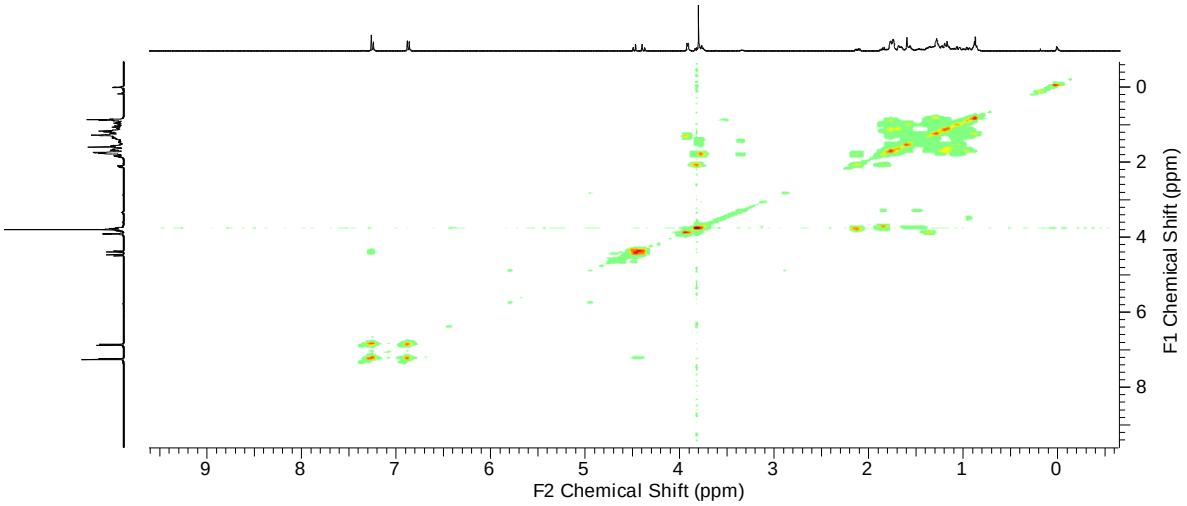
^{1}H NMR (400 MHz, $CDCl_3$):



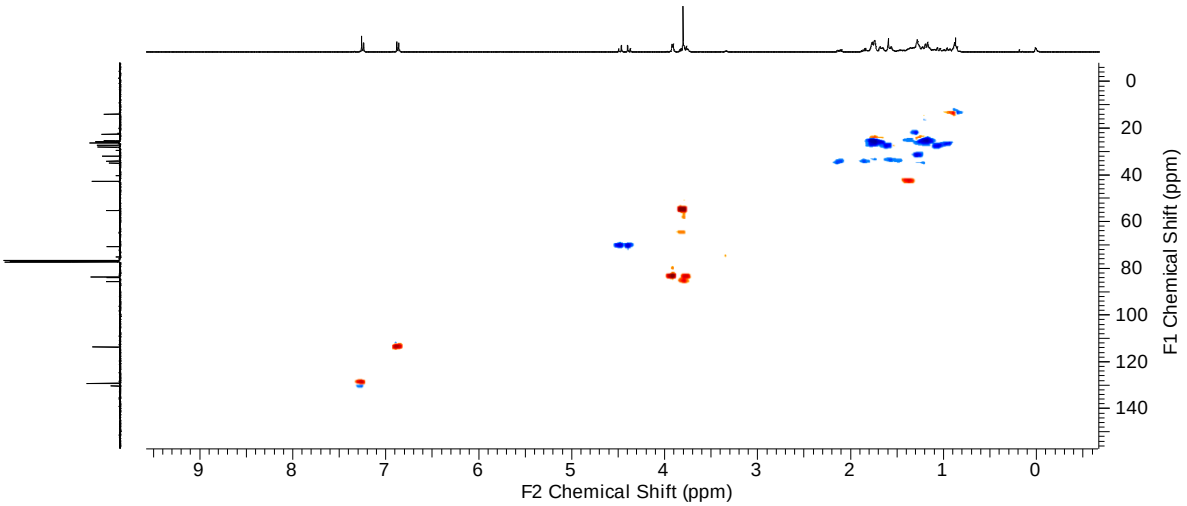
^{13}C NMR (100 MHz, $CDCl_3$):



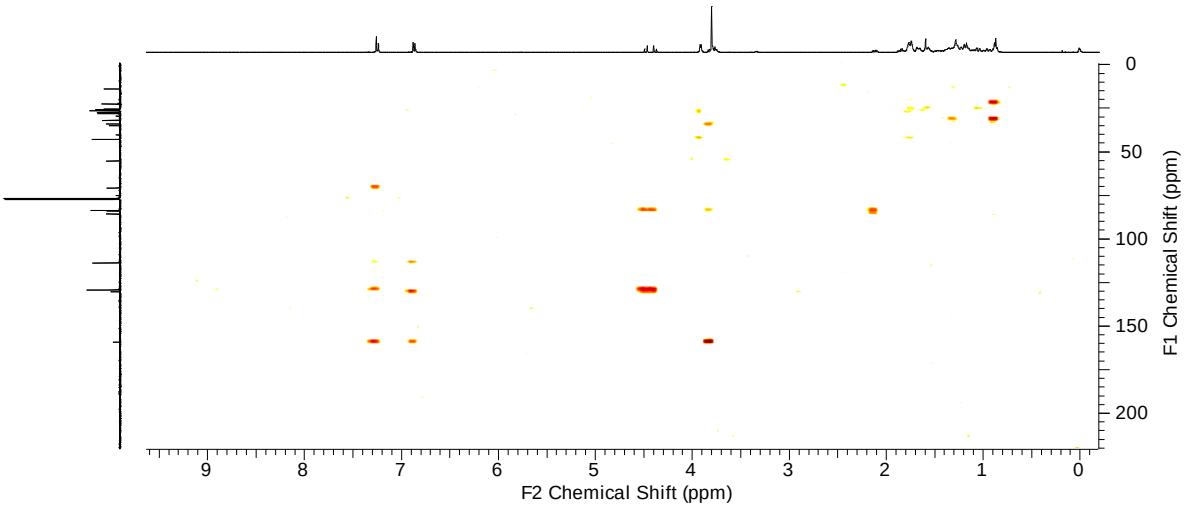
HH-COSY NMR (400 MHz, $CDCl_3$)



HSQC NMR (400 MHz, $CDCl_3$)

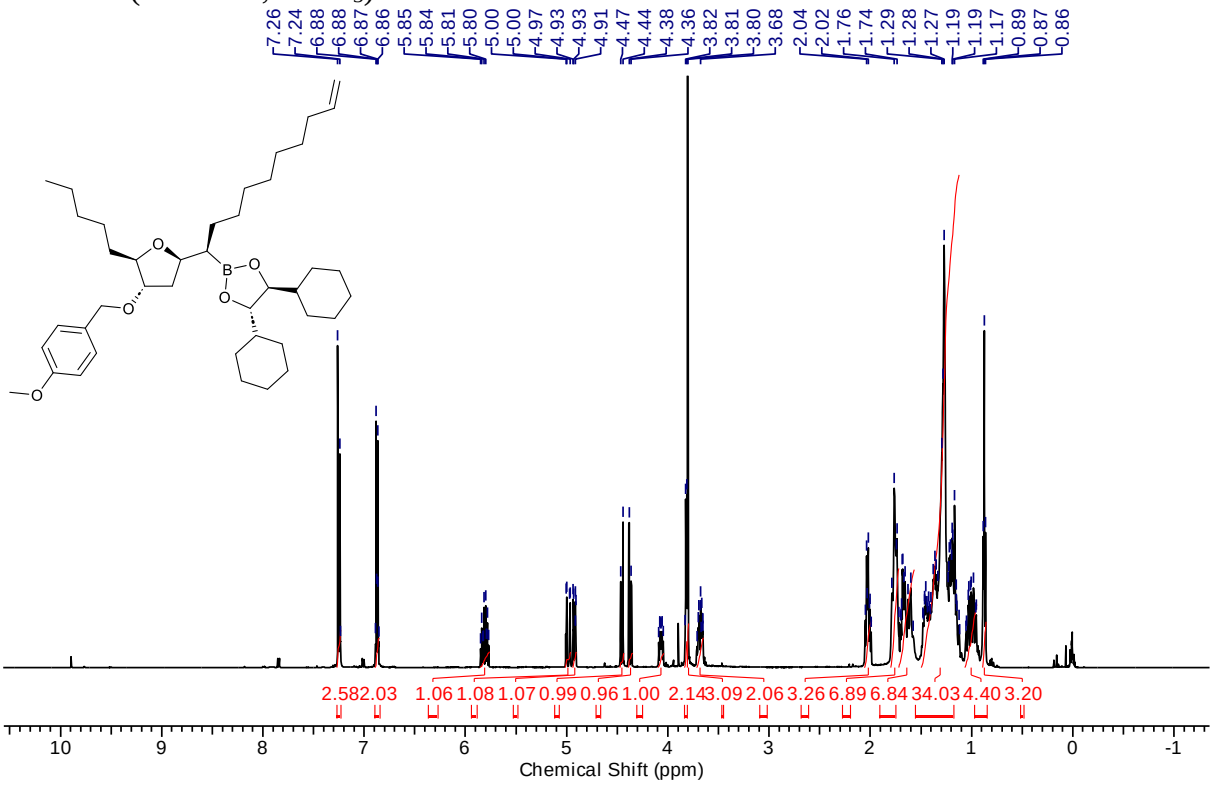


HMBC NMR (400 MHz, $CDCl_3$)

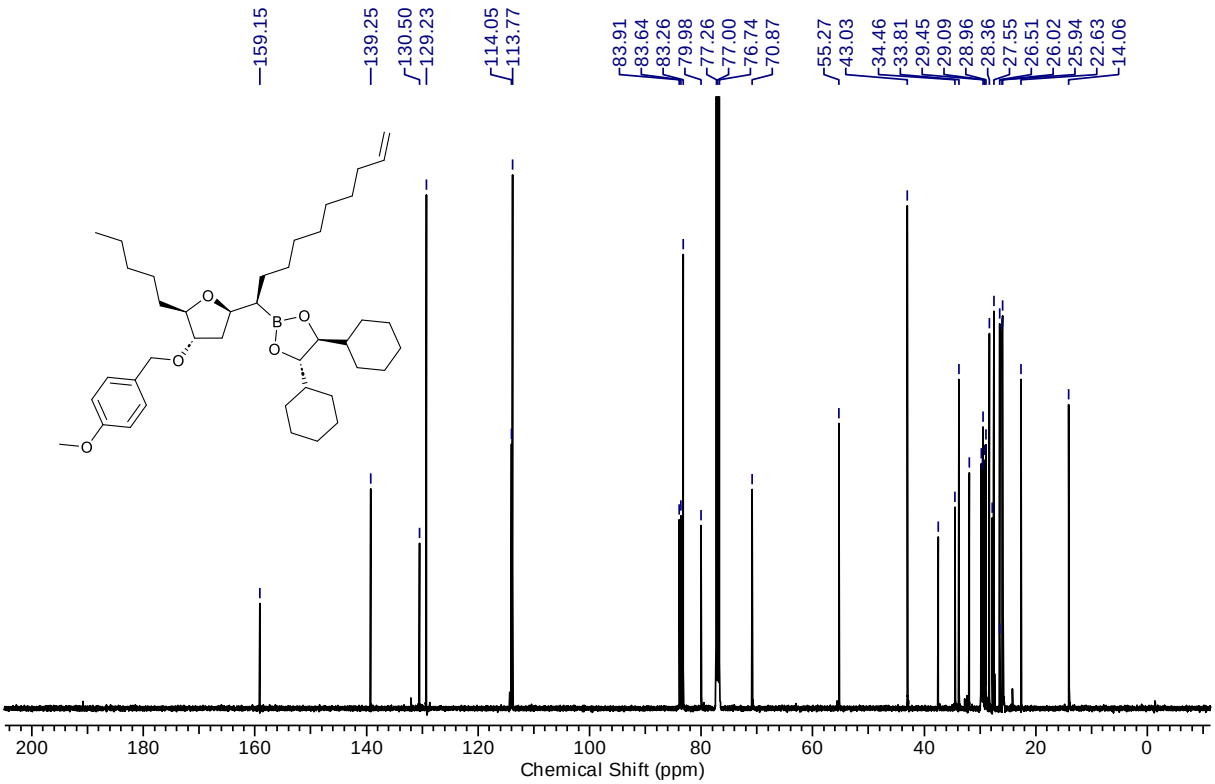


(4*S*,5*S*)-4,5-Dicyclohexyl-2-((*R*)-1-{(2*R*,4*S*,5*R*)-4-[(4-methoxybenzyl)oxy]-5-pentyltetrahydrofuran-2-yl}dec-9-en-1-yl)-1,3,2-dioxaborolane (12)

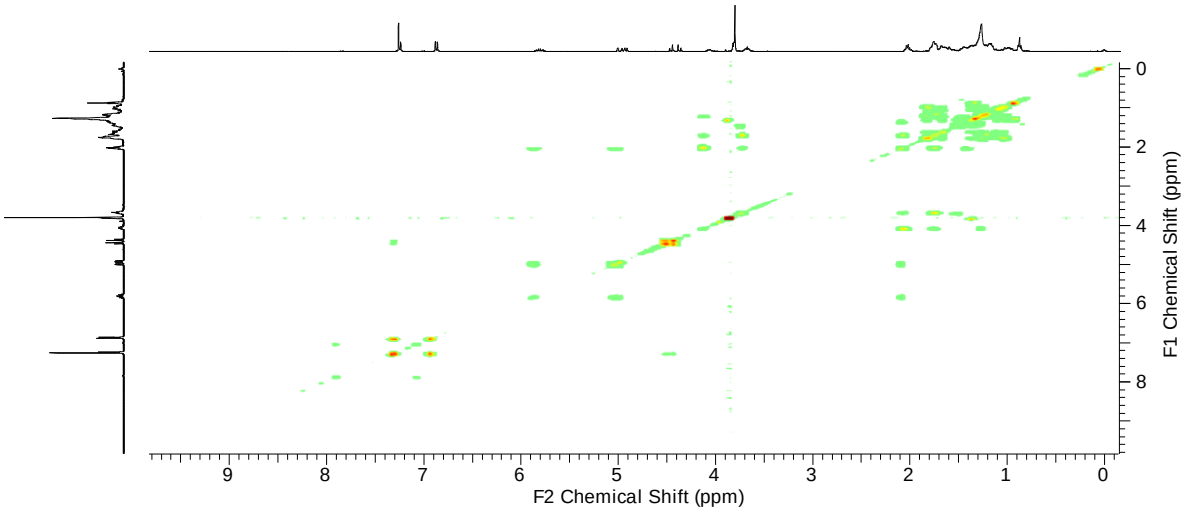
^{1}H NMR (500 MHz, $CDCl_3$):



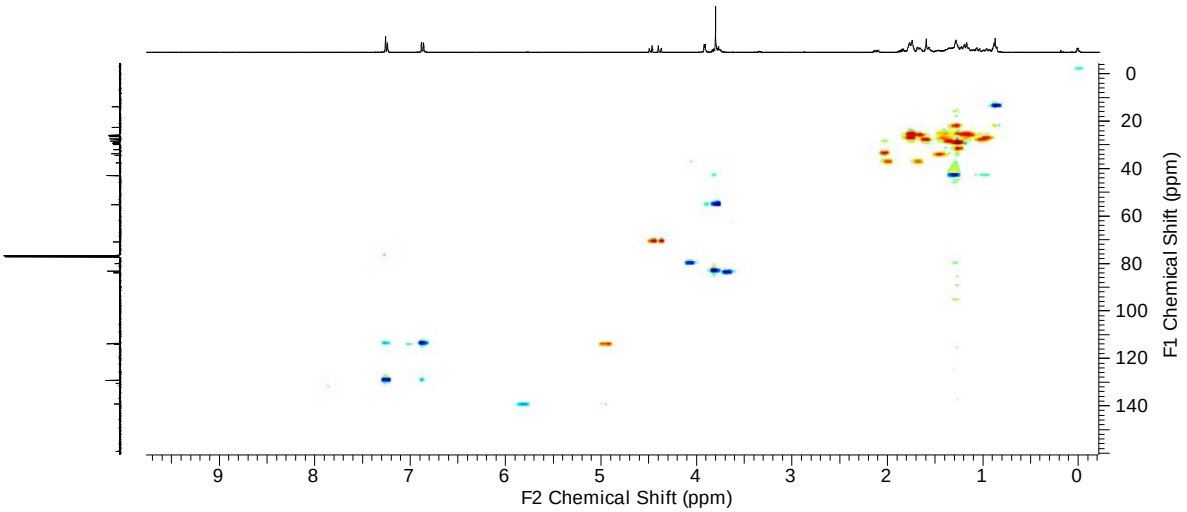
^{13}C NMR (125 MHz, $CDCl_3$):



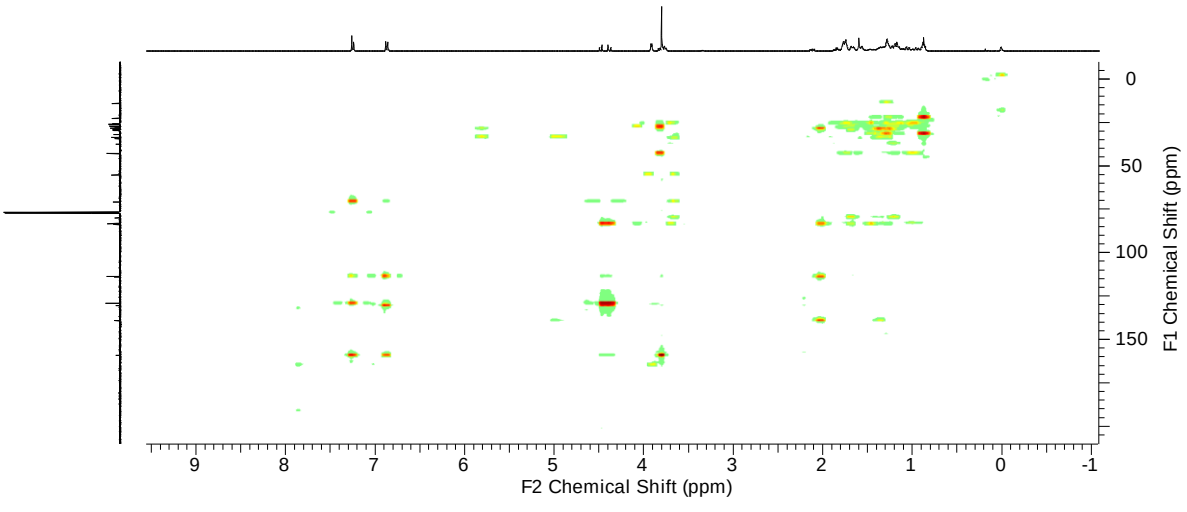
HH-COSY NMR (400 MHz, $CDCl_3$)



HSQC NMR (500 MHz, $CDCl_3$)

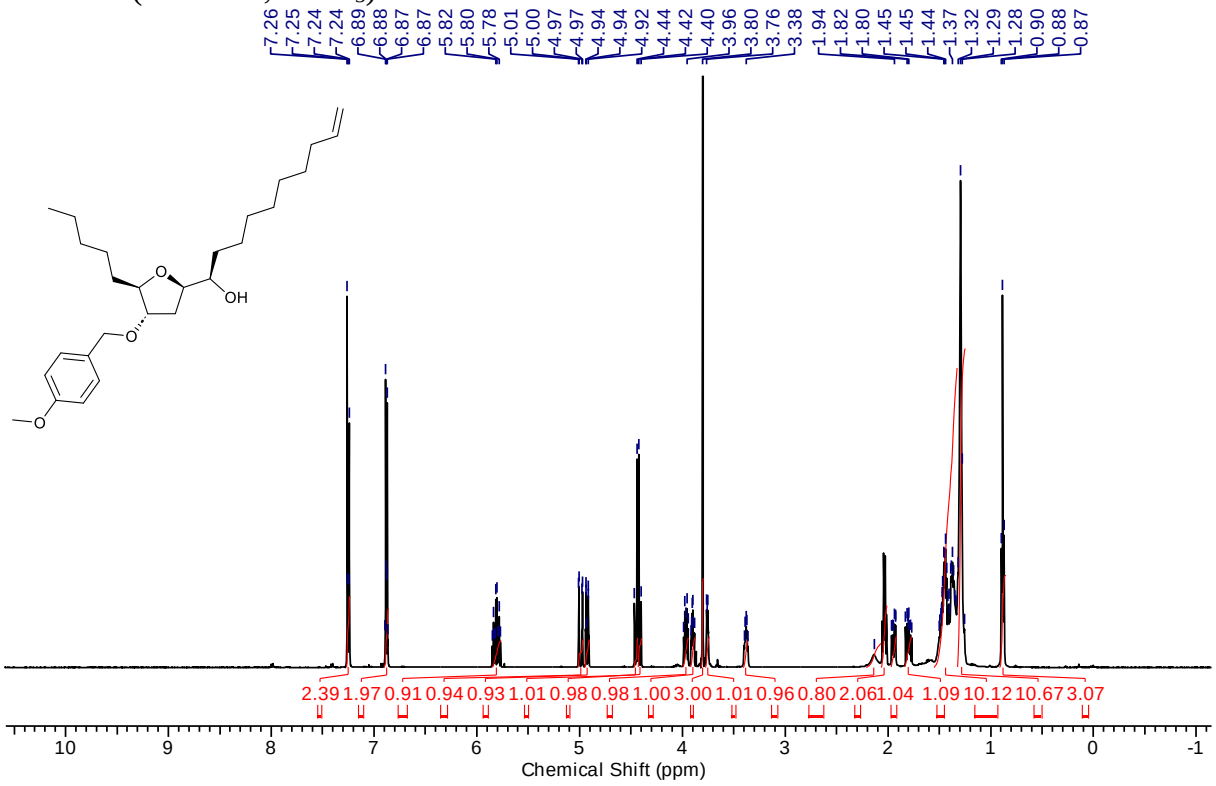


HMBC NMR (500 MHz, $CDCl_3$)

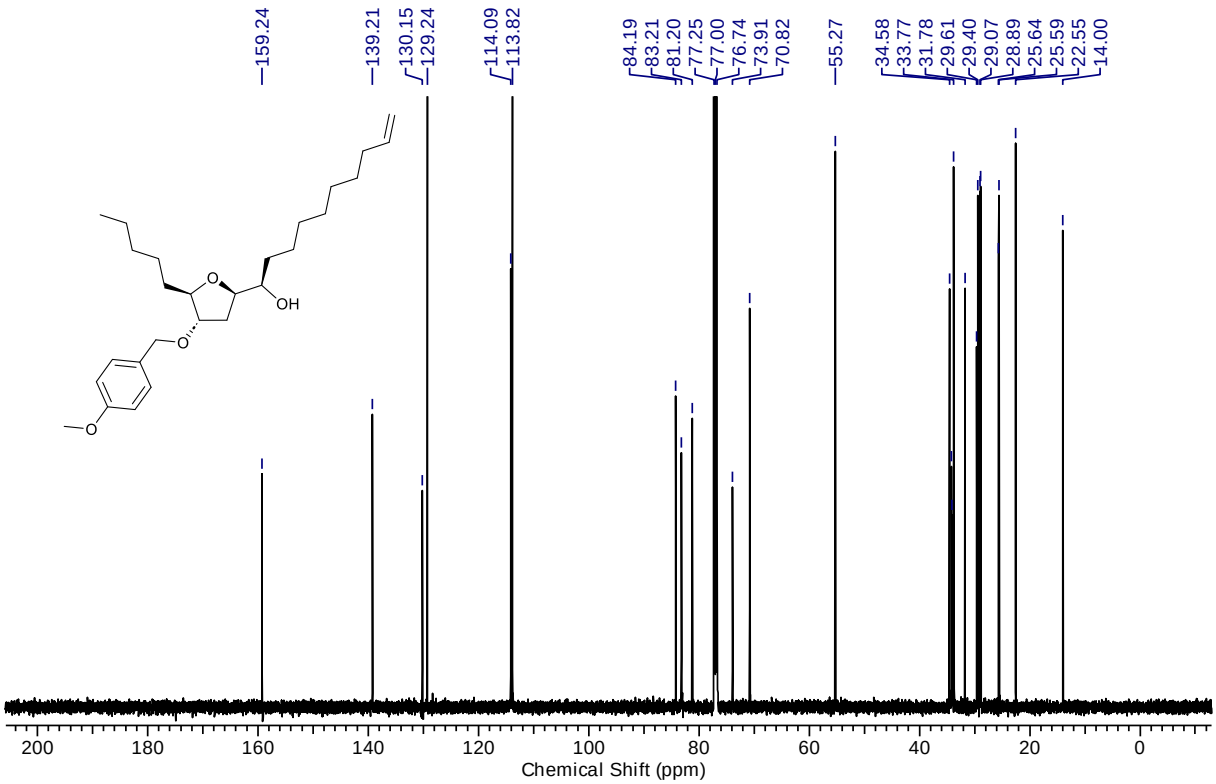


(*R*)-1-{(2*R*,4*S*,5*R*)-4-[(4-Methoxybenzyl)oxy]-5-pentyltetrahydrofuran-2-yl}dec-9-en-1-ol (13)

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

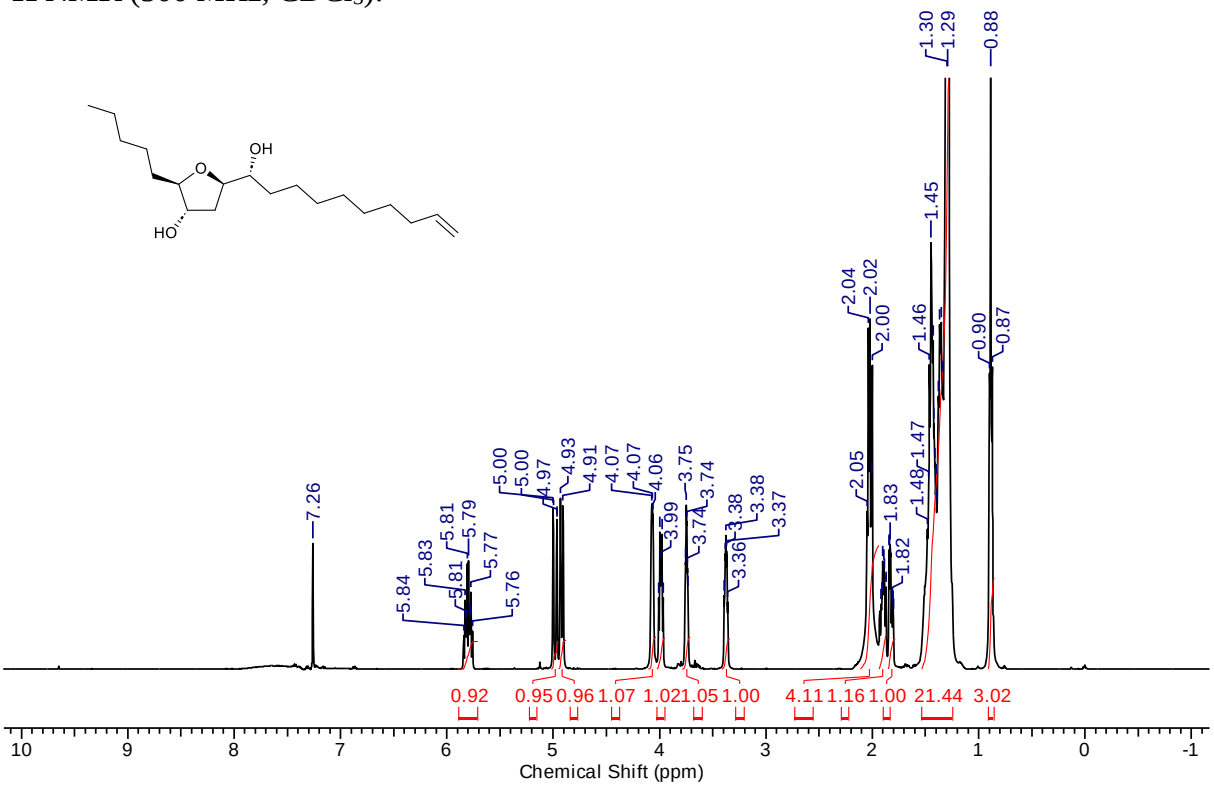


^{13}C NMR (125 MHz, $CDCl_3$):

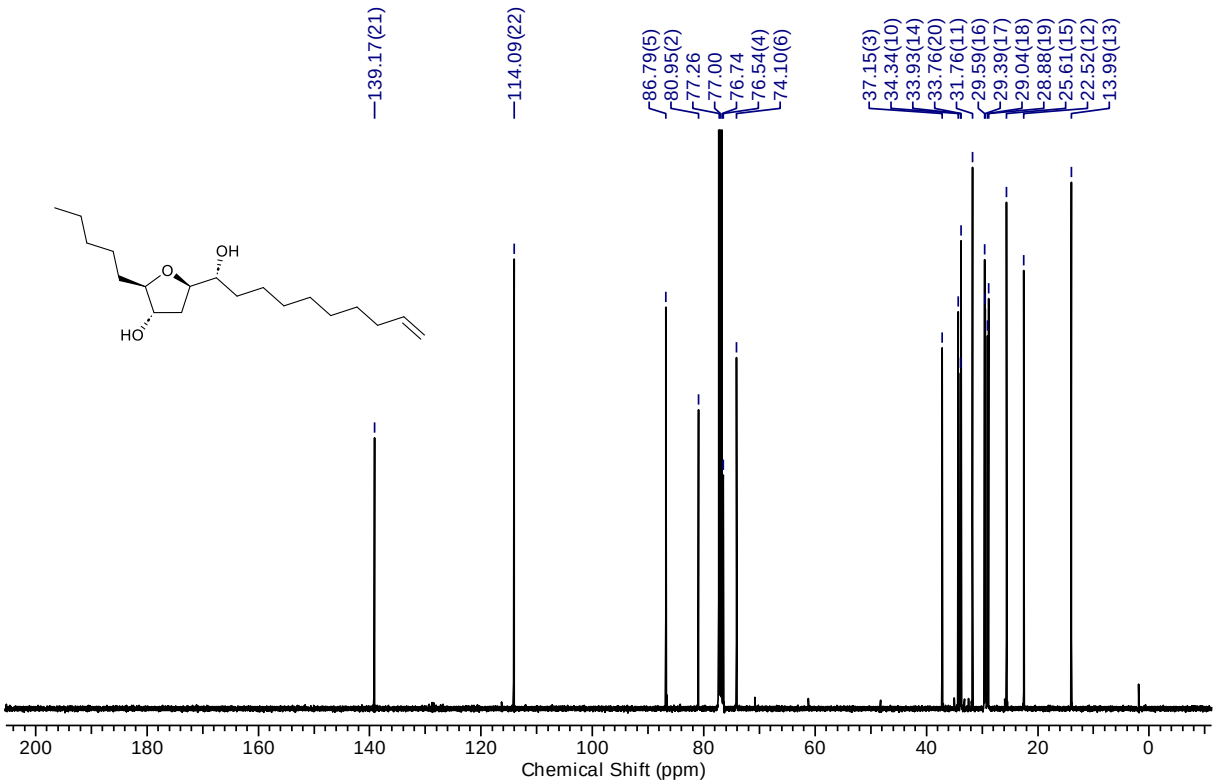


(*R*)-1-{(2*R*,4*S*,5*R*)-4-[(4-Methoxybenzyl)oxy]-5-pentyltetrahydrofuran-2-yl}dec-9-en-1-ol (14)

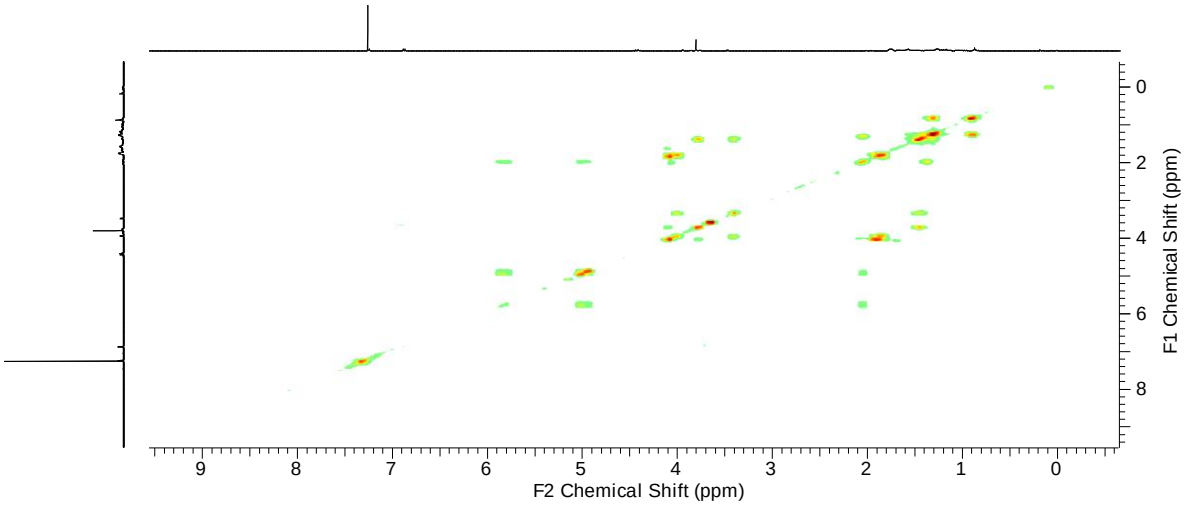
^{1}H NMR (500 MHz, $CDCl_3$):



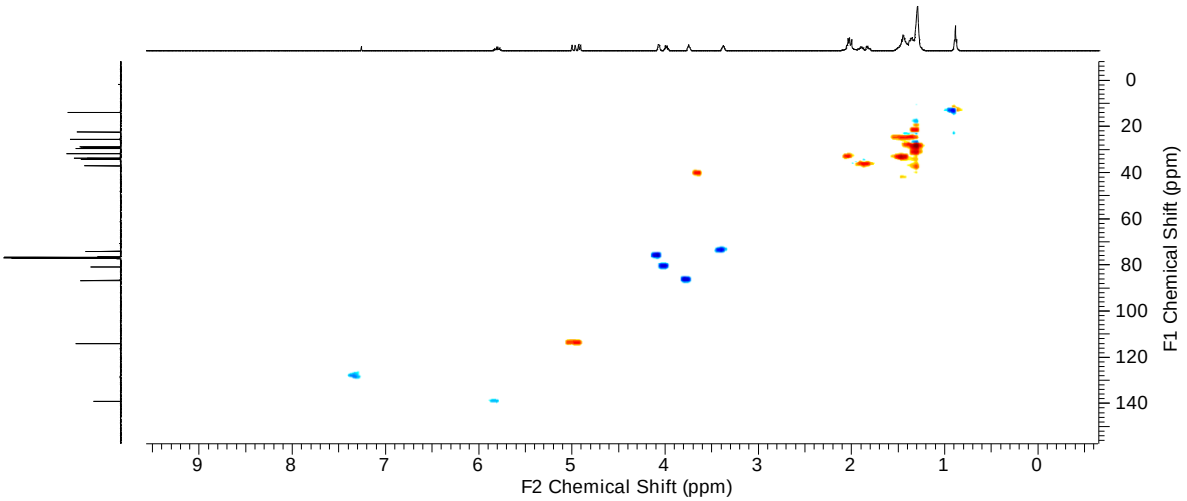
^{13}C NMR (125 MHz, $CDCl_3$):



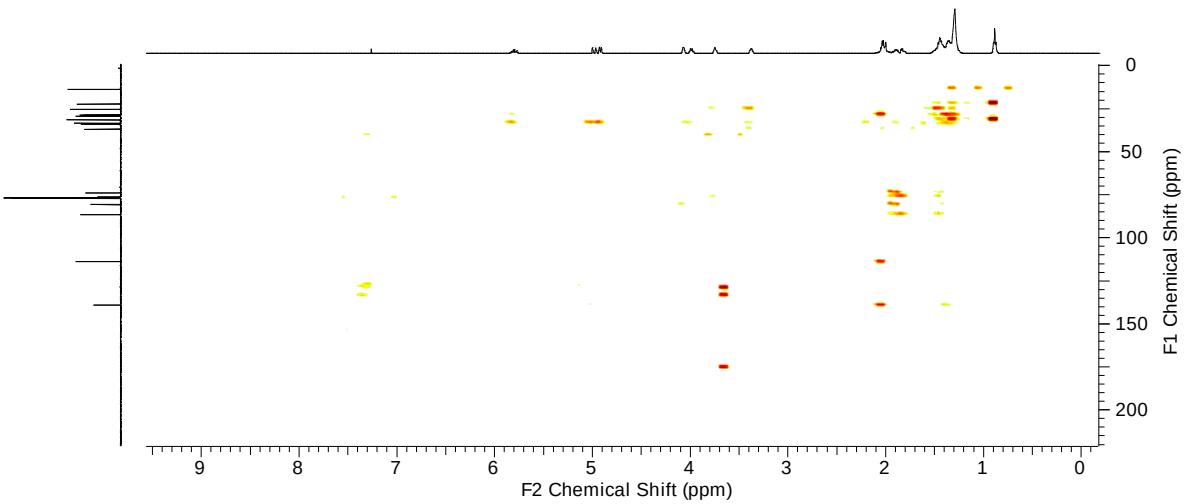
HH-COSY NMR (400 MHz, $CDCl_3$)



HSQC NMR (400 MHz, $CDCl_3$)

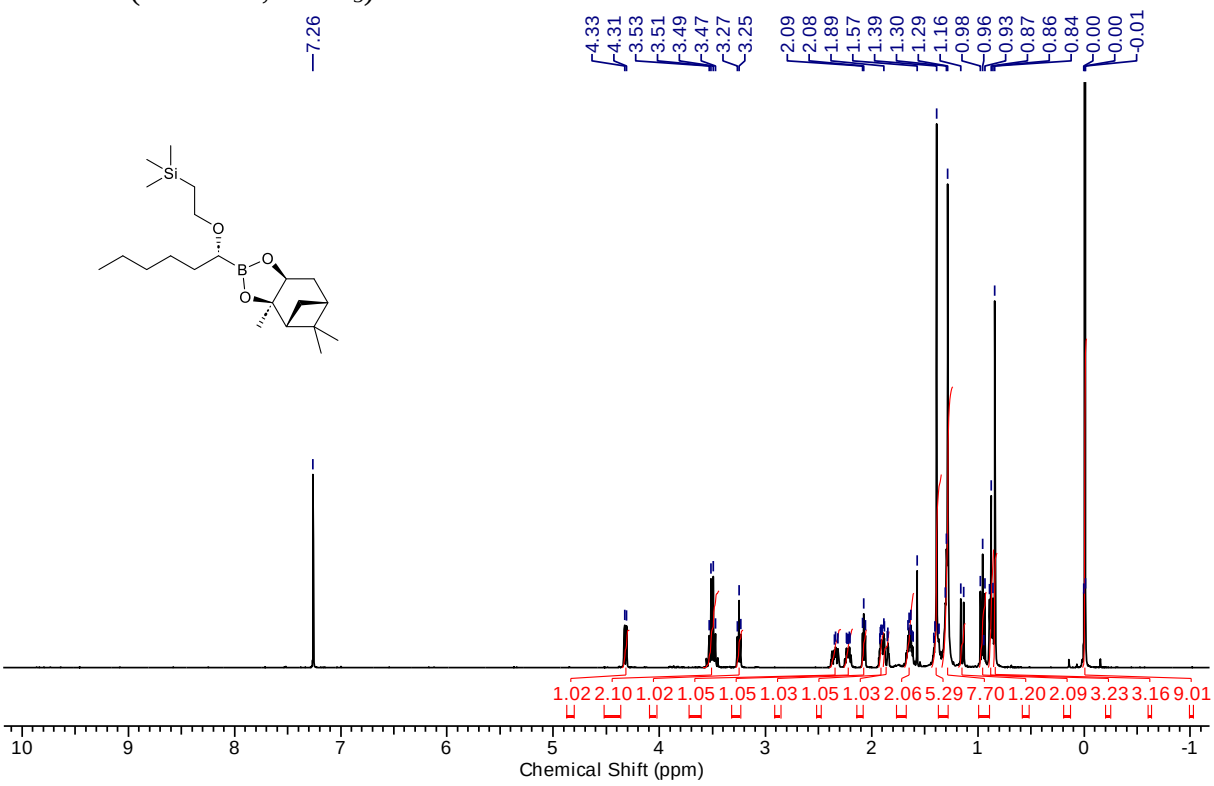


HMBC NMR (400 MHz, $CDCl_3$)

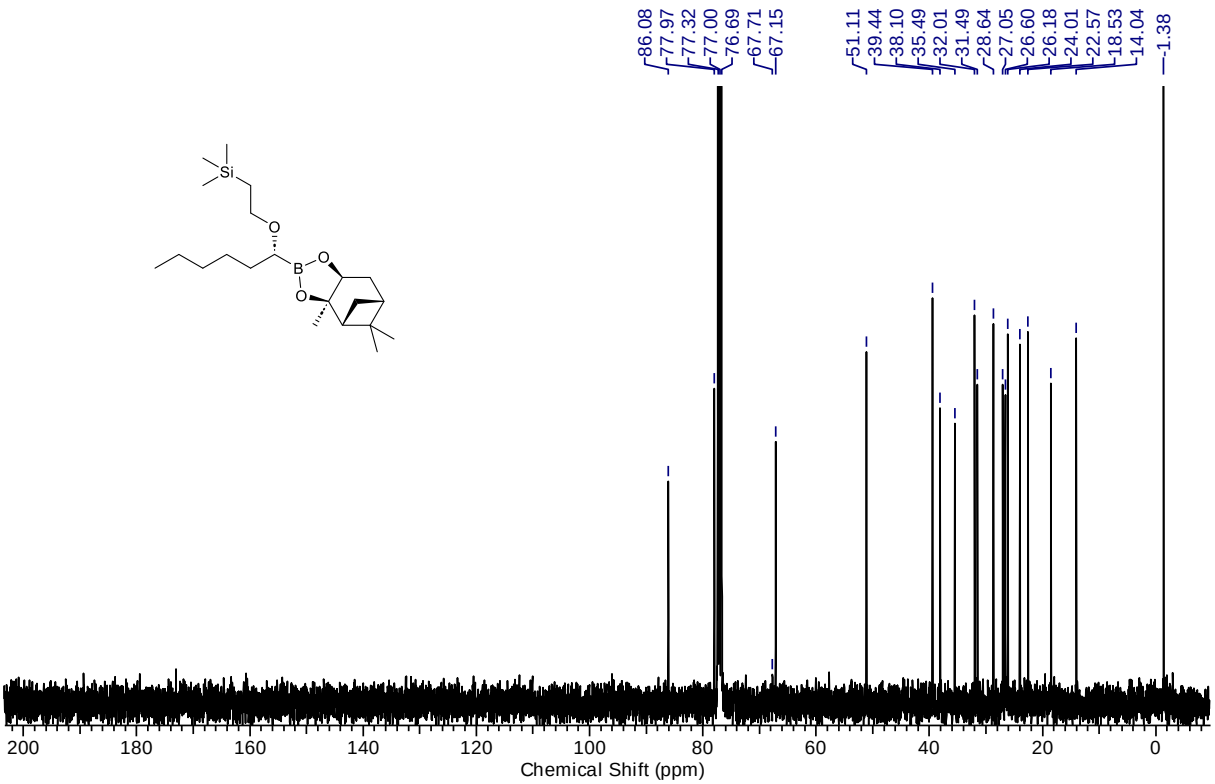


Trimethyl[2-({(*R*)-1-[(3a*R*,4*R*,6*R*,7a*S*)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[*d*]-[1,3,2]dioxaborol-2-yl]hexyl}oxy)ethyl]silane (15)

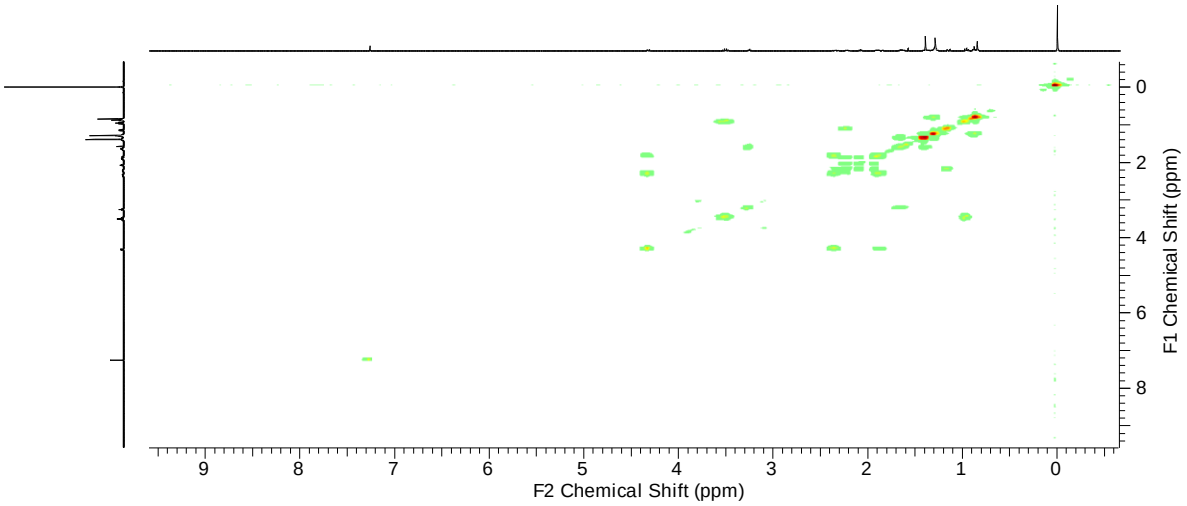
^{1}H NMR (400 MHz, $CDCl_3$):



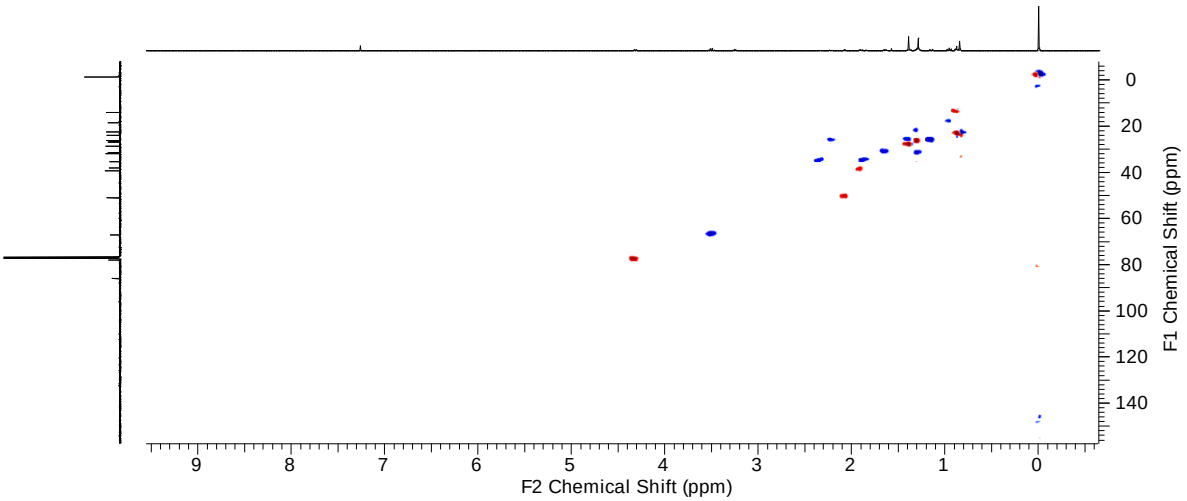
^{13}C NMR (100 MHz, $CDCl_3$):



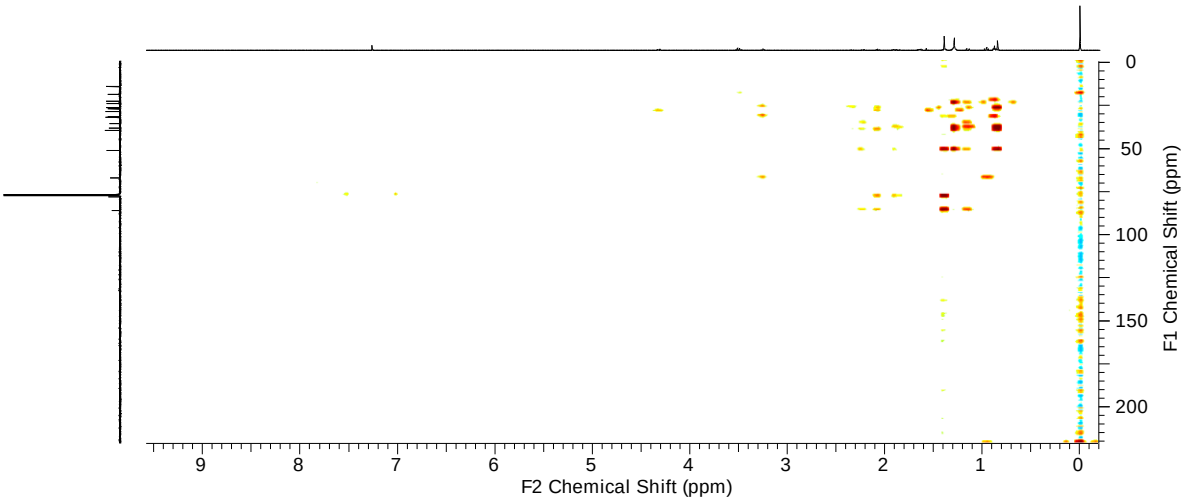
HH-COSY NMR (400 MHz, $CDCl_3$)



HSQC NMR (400 MHz, $CDCl_3$)

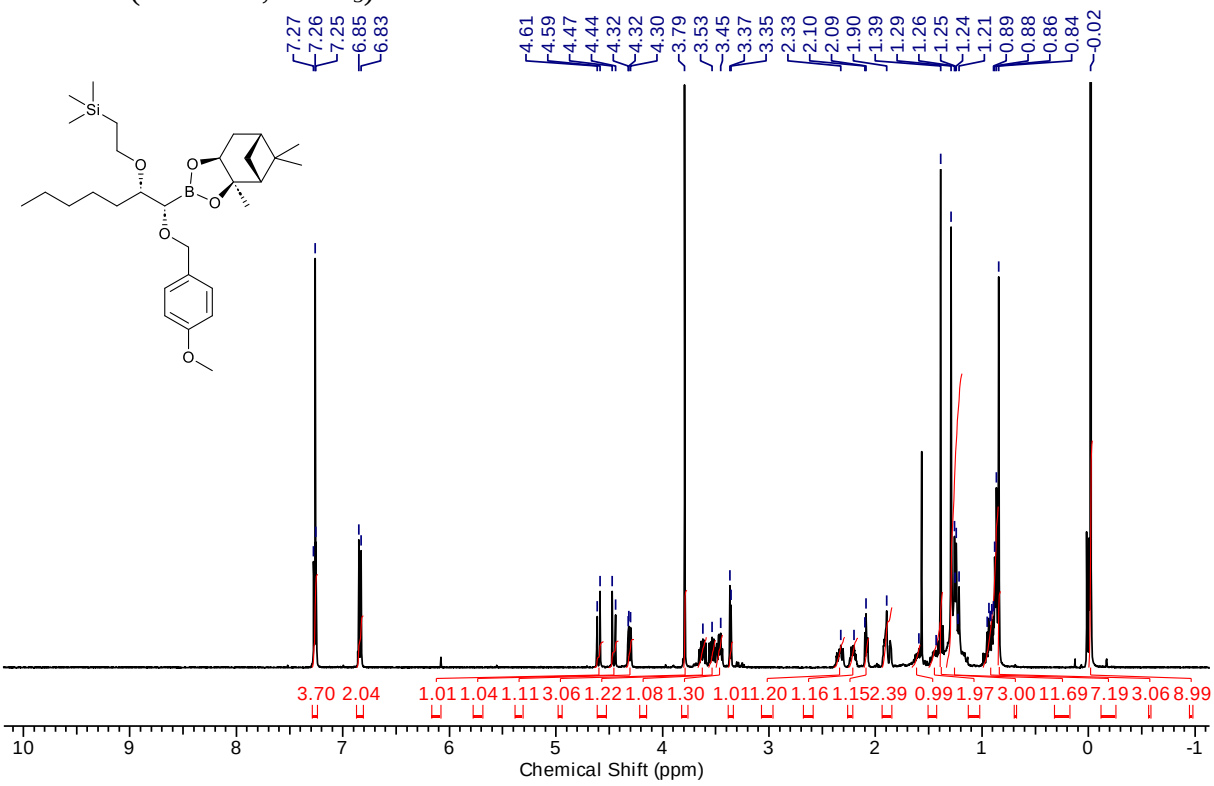


HMBC NMR (400 MHz, $CDCl_3$)

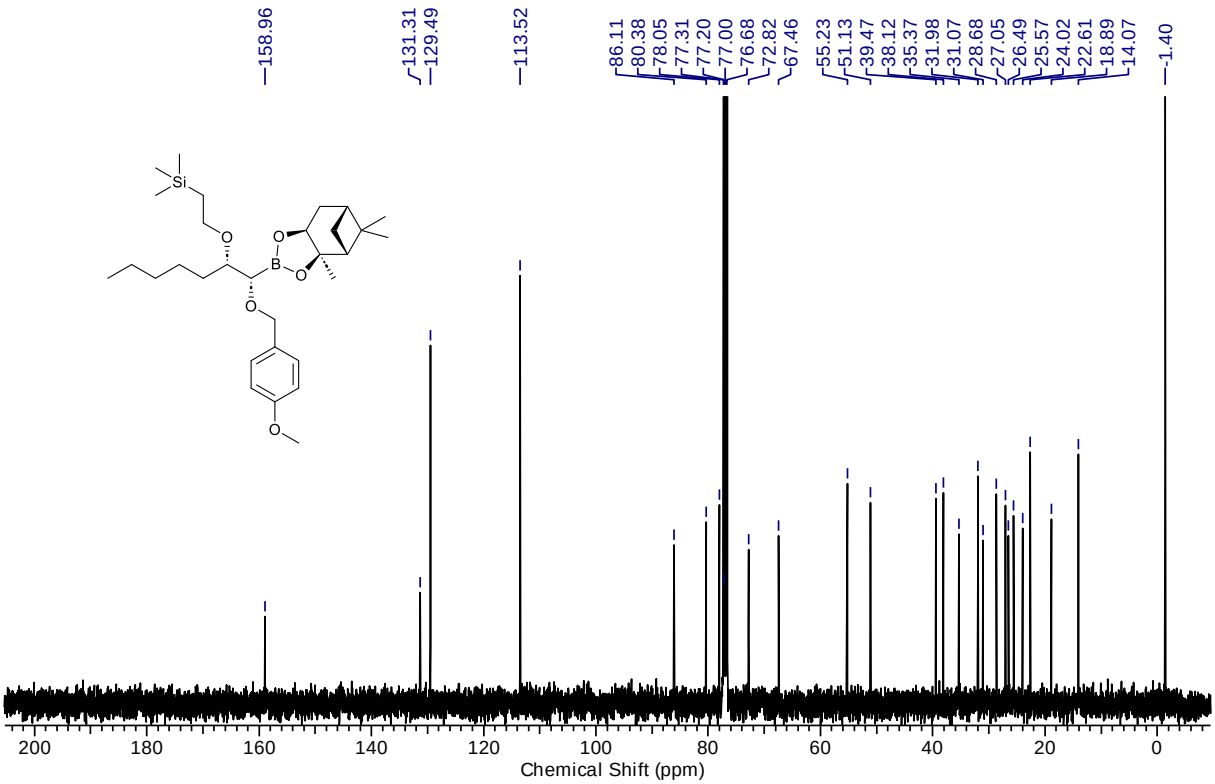


[2-({(1*S*,2*S*)-1-[(4-Methoxybenzyl)oxy]-1-[(3a*R*,4*R*,6*R*,7a*S*)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[*d*][1,3,2]dioxaborol-2-yl]heptan-2-yl}oxy)ethyl]trimethylsilane (16)

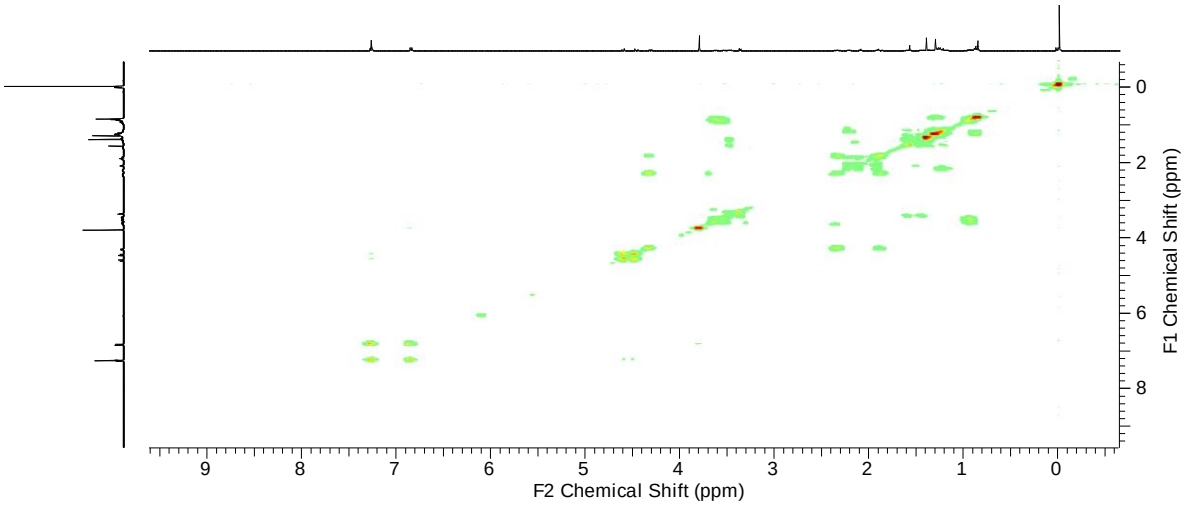
^{1}H NMR (400 MHz, $CDCl_3$):



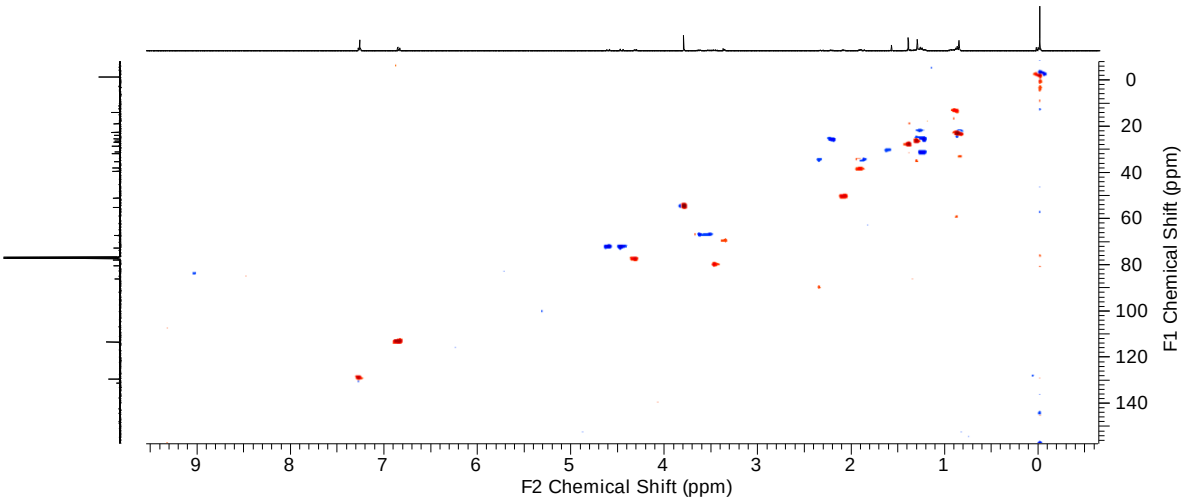
^{13}C NMR (100 MHz, $CDCl_3$):



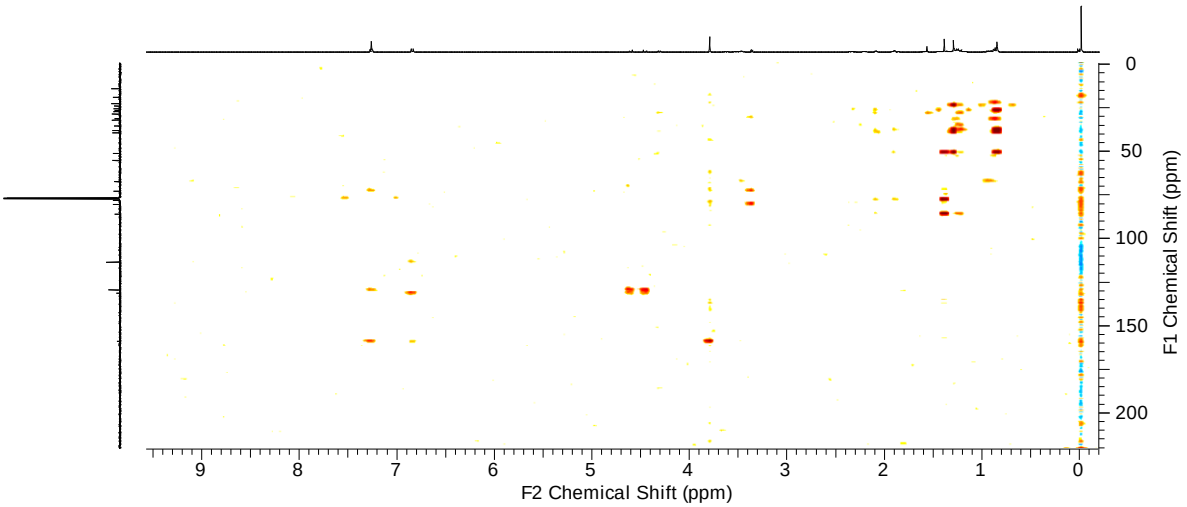
HH-COSY NMR (400 MHz, $CDCl_3$)



HSQC NMR (400 MHz, $CDCl_3$)

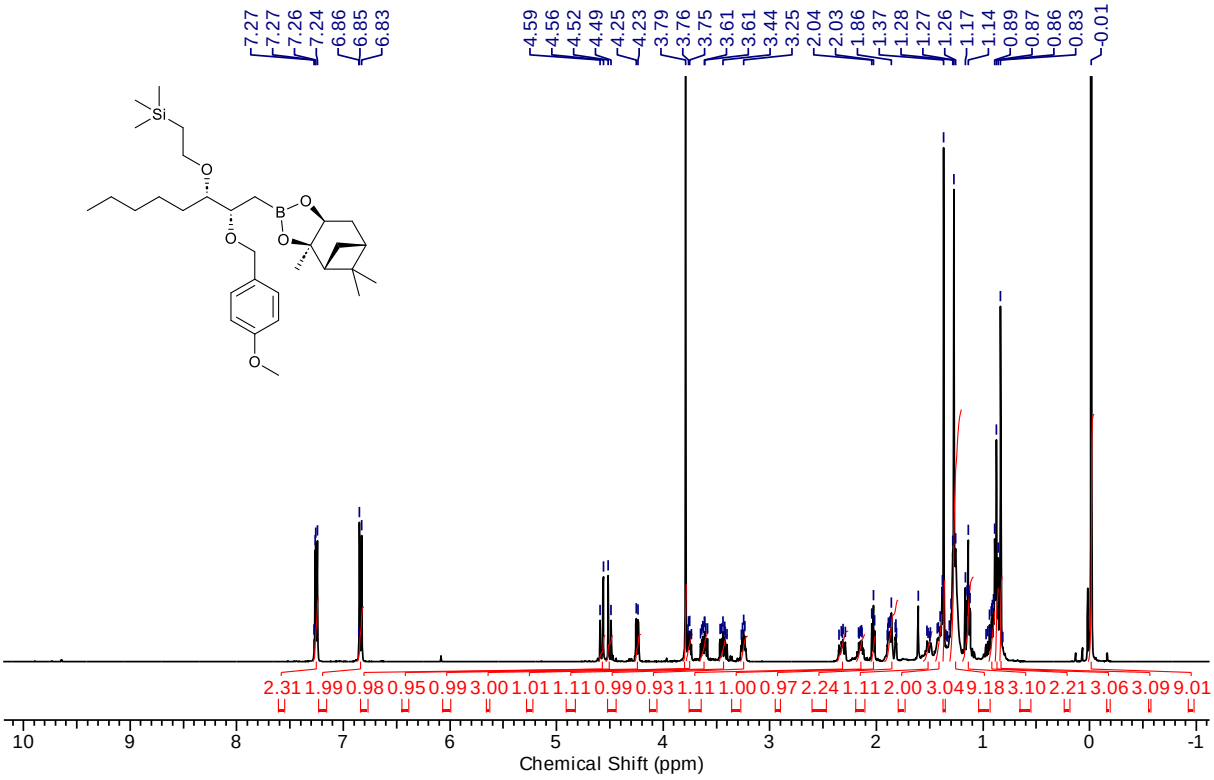


HMBC NMR (400 MHz, $CDCl_3$)

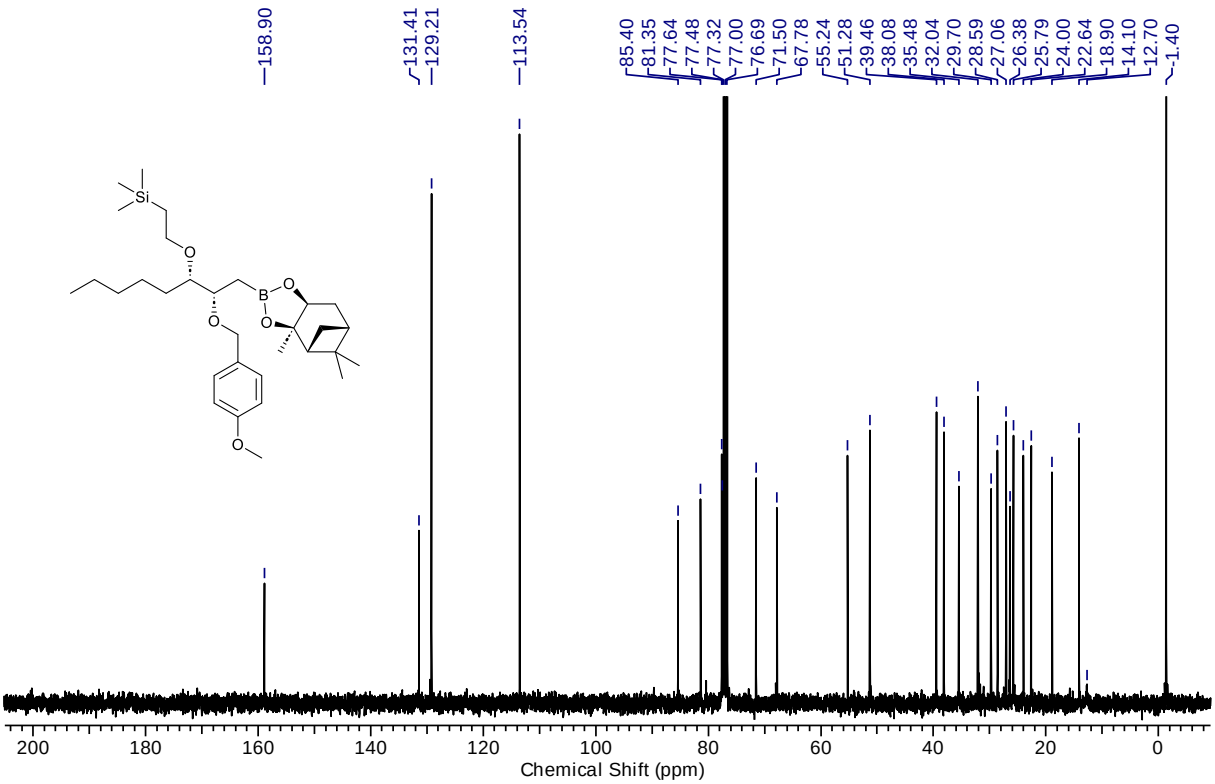


[2-({(2*S*,3*S*)-2-[(4-methoxybenzyl)oxy]-1-[(3a*R*,4*R*,6*R*,7a*S*)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[*d*][1,3,2]dioxaborol-2-yl]octan-3-yl}oxy)ethyl]trimethylsilane (17)

^{1}H NMR (400 MHz, $CDCl_3$):

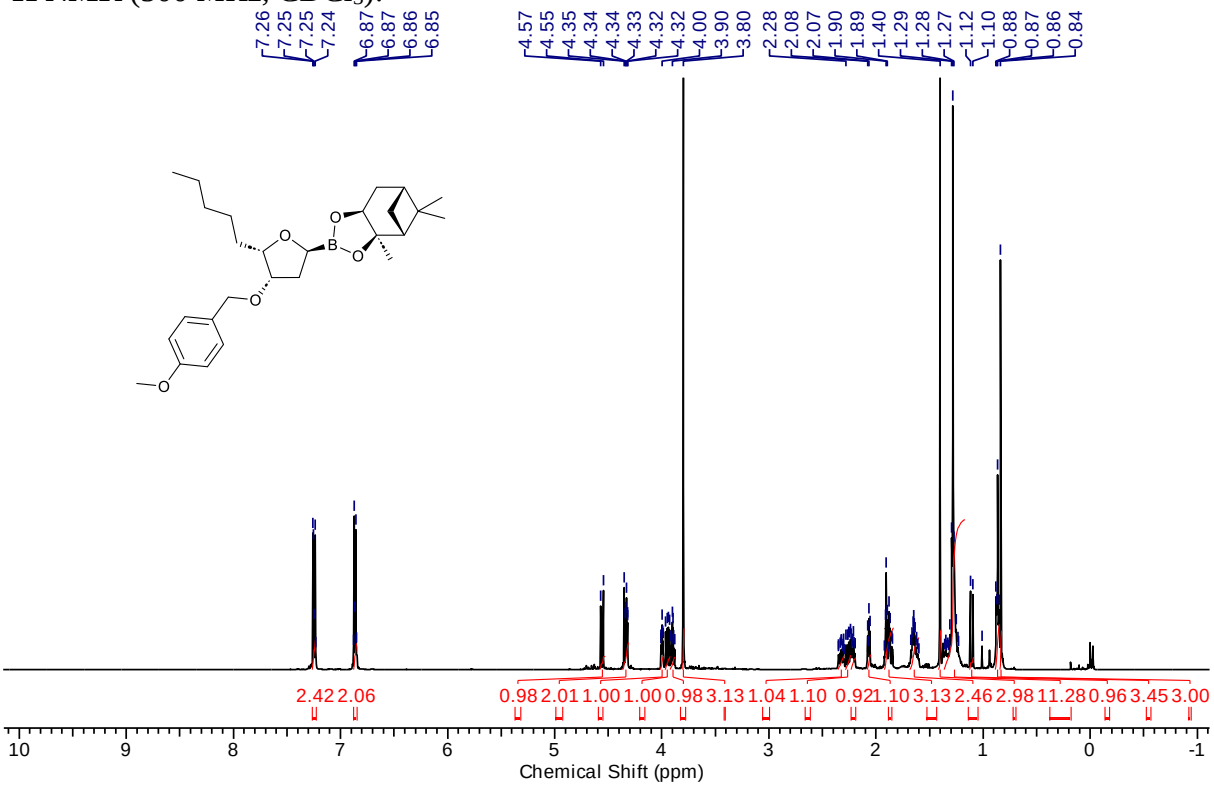


^{13}C NMR (100 MHz, $CDCl_3$):

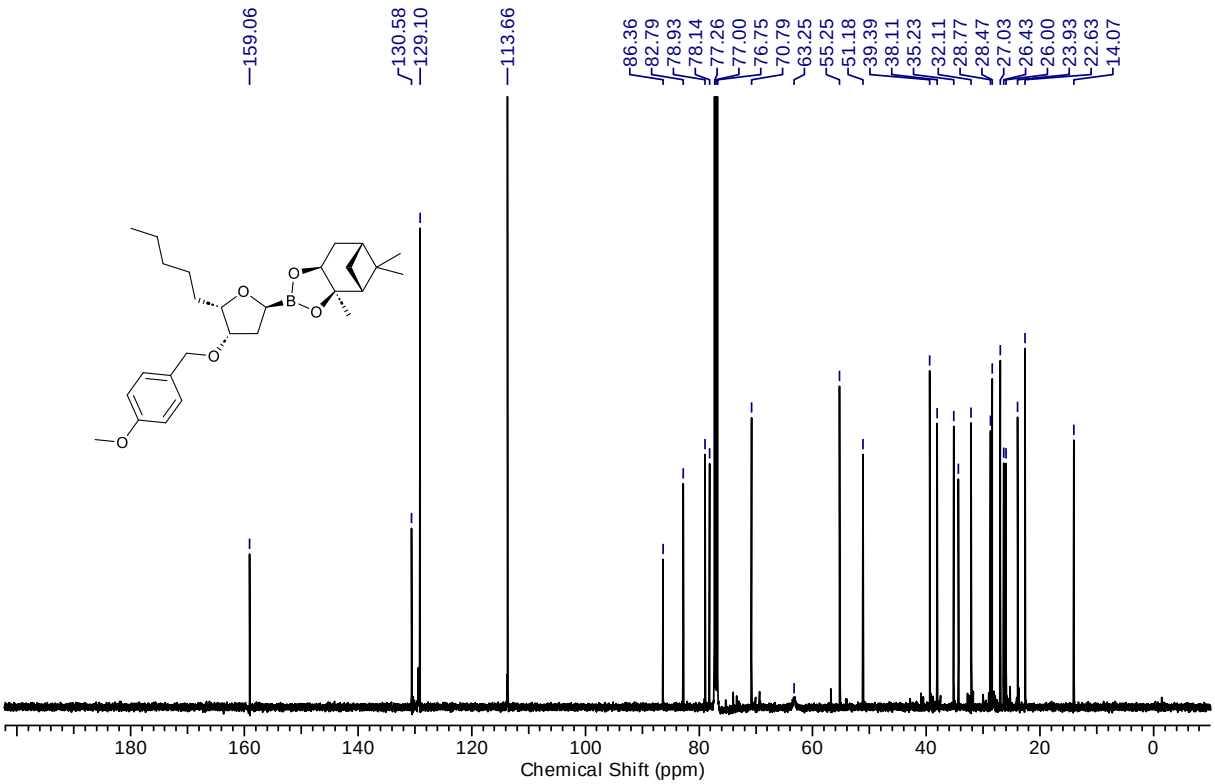


(4*S*,5*S*)-4,5-Dicyclohexyl-2-{(2*S*,4*S*,5*R*)-4-[(4-methoxybenzyl)oxy]-5-pentyltetrahydrofuran-2-yl}-1,3,2-dioxaborolane (18)

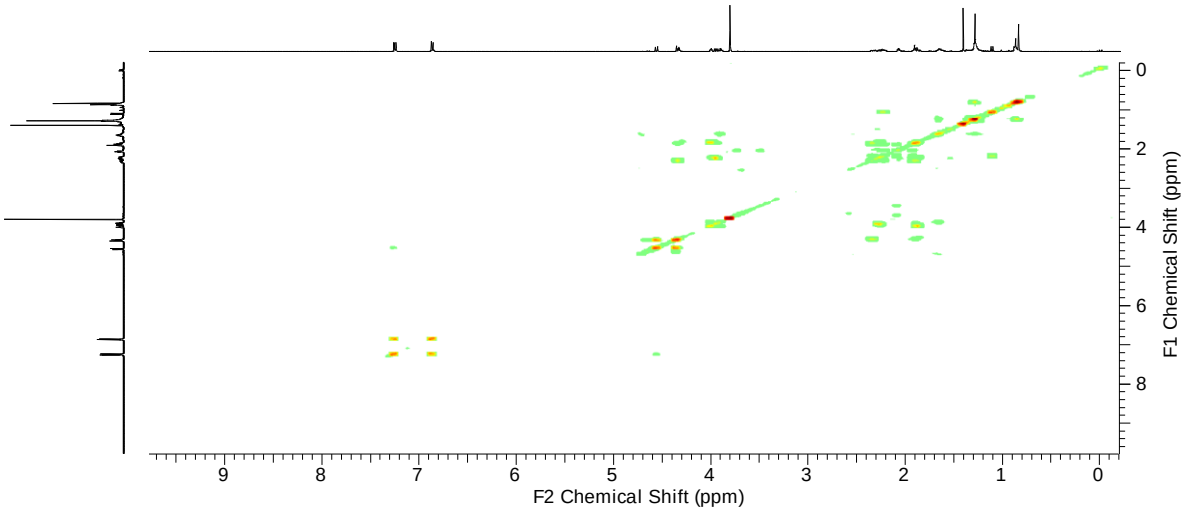
^{1}H NMR (500 MHz, $CDCl_3$):



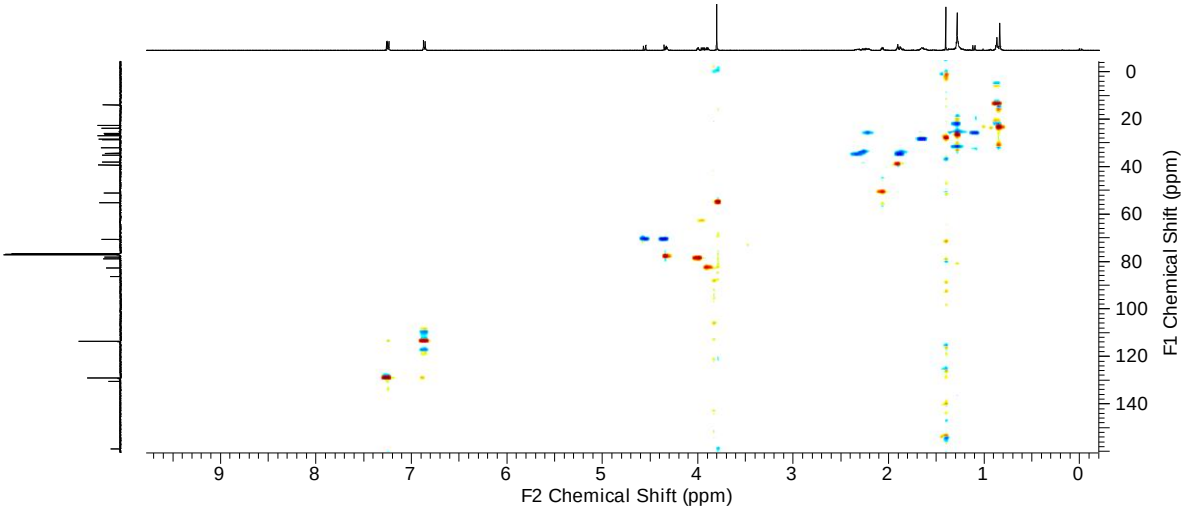
^{13}C NMR (125 MHz, $CDCl_3$):



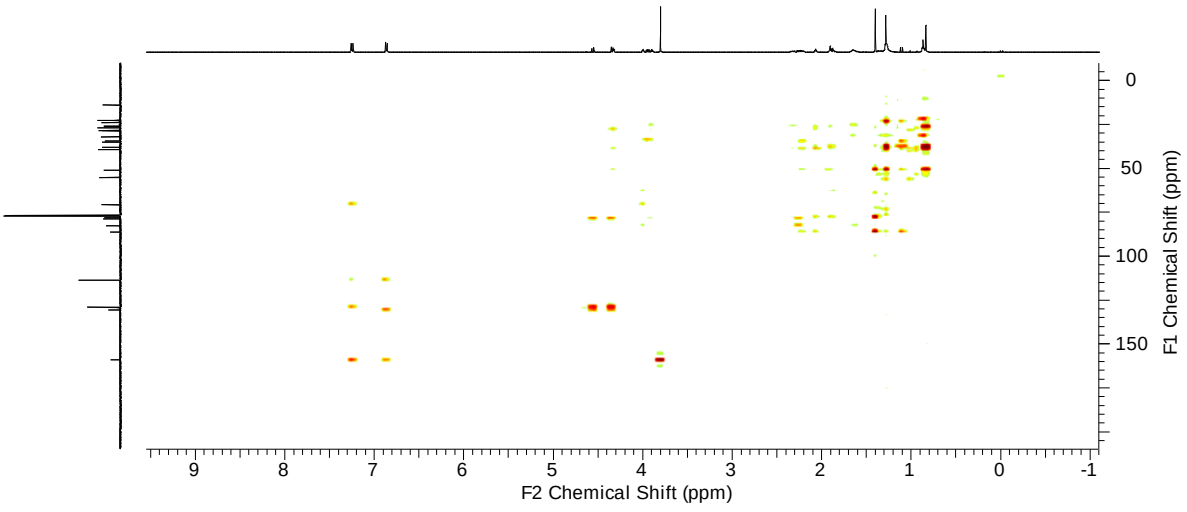
HH-COSY NMR (500 MHz, $CDCl_3$)



HSQC NMR (500 MHz, $CDCl_3$)

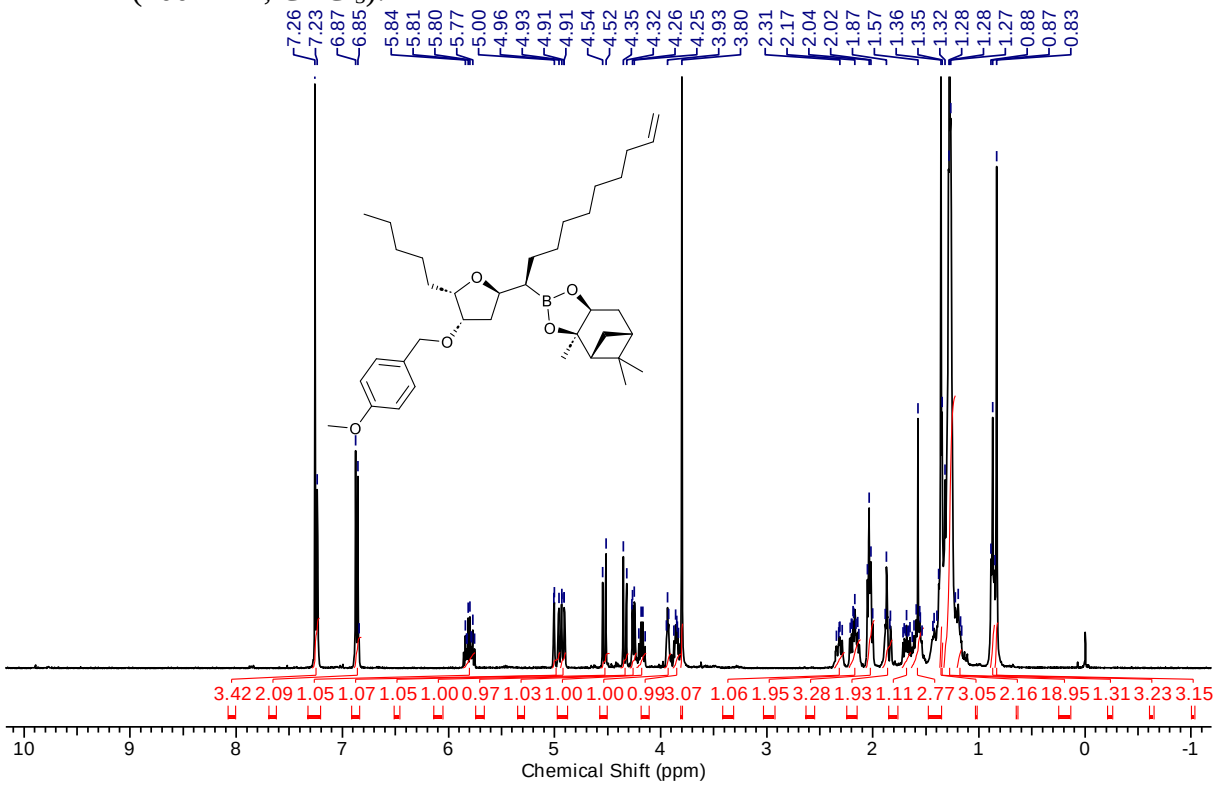


HMBC NMR (500 MHz, $CDCl_3$)

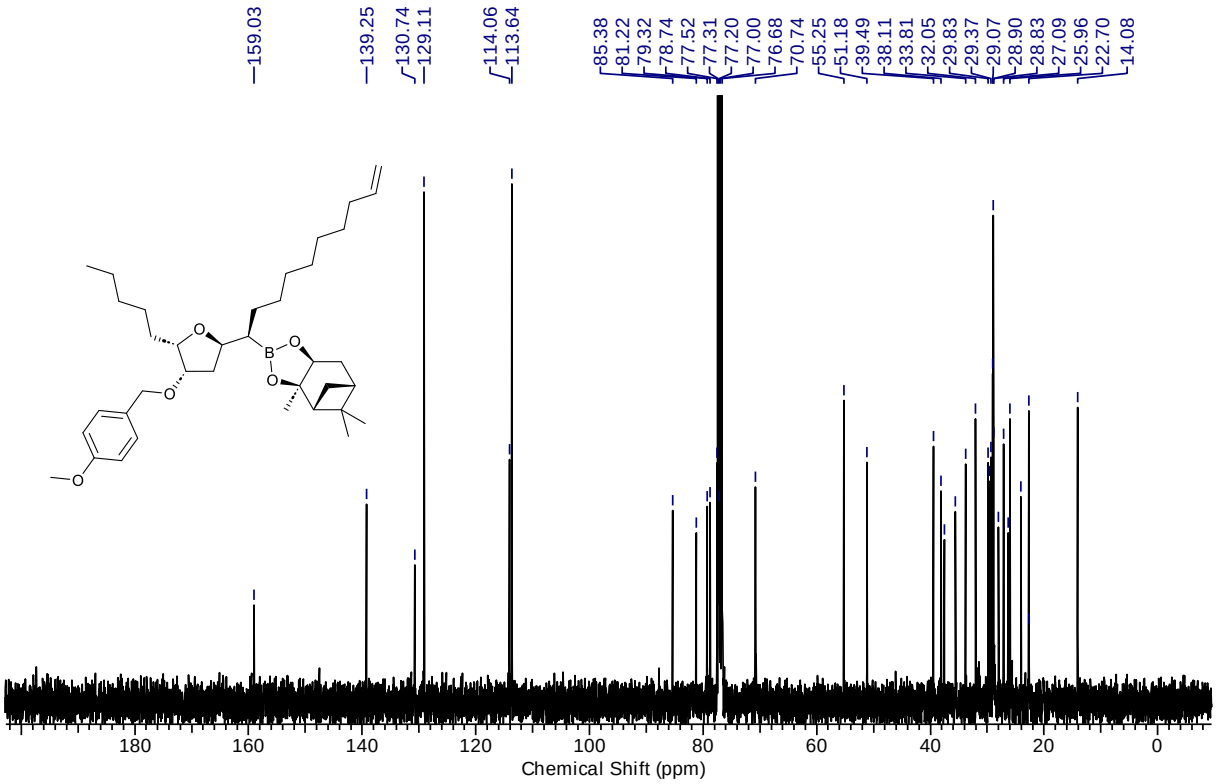


(3a*R*,4*R*,6*R*,7a*S*)-2-((*R*)-1-{(2*R*,4*S*,5*S*)-4-[(4-Methoxybenzyl)oxy]-5-pentyltetrahydrofuran-2-yl}dec-9-en-1-yl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol (19)

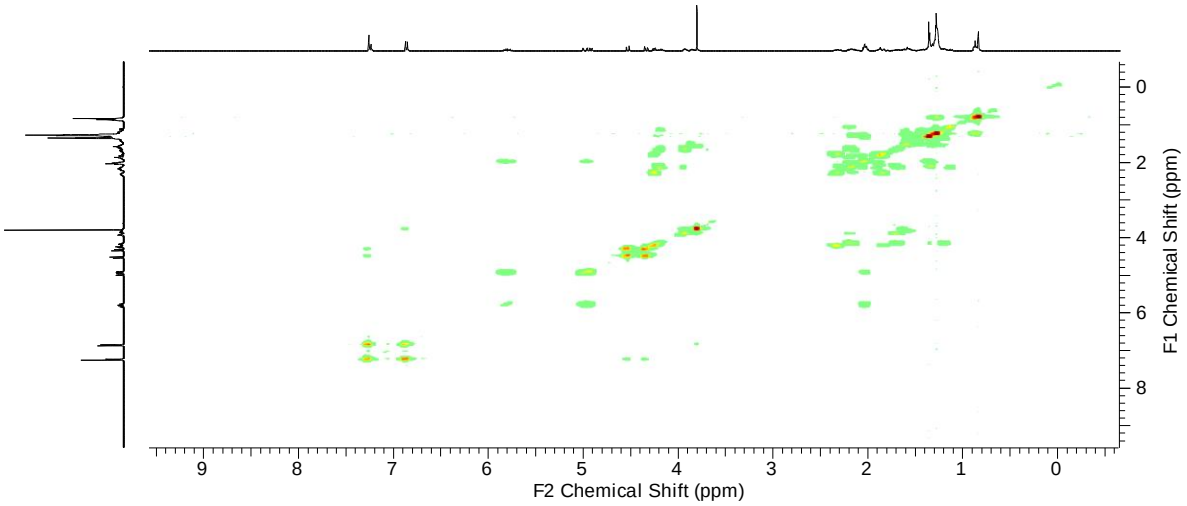
^{1}H NMR (400 MHz, $CDCl_3$):



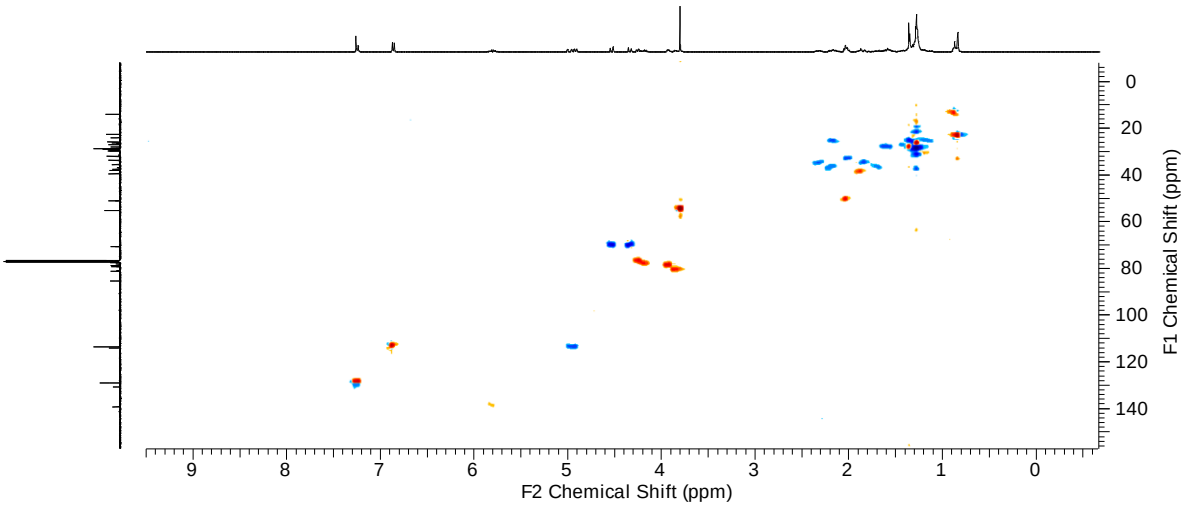
^{13}C NMR (100 MHz, $CDCl_3$):



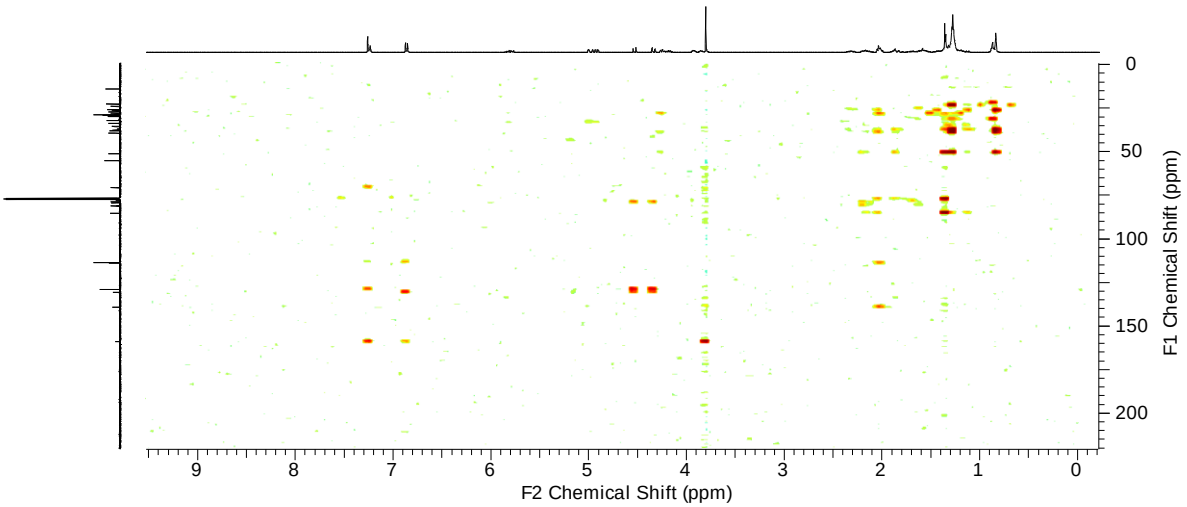
HH-COSY NMR (400 MHz, $CDCl_3$)



HSQC NMR (400 MHz, $CDCl_3$)

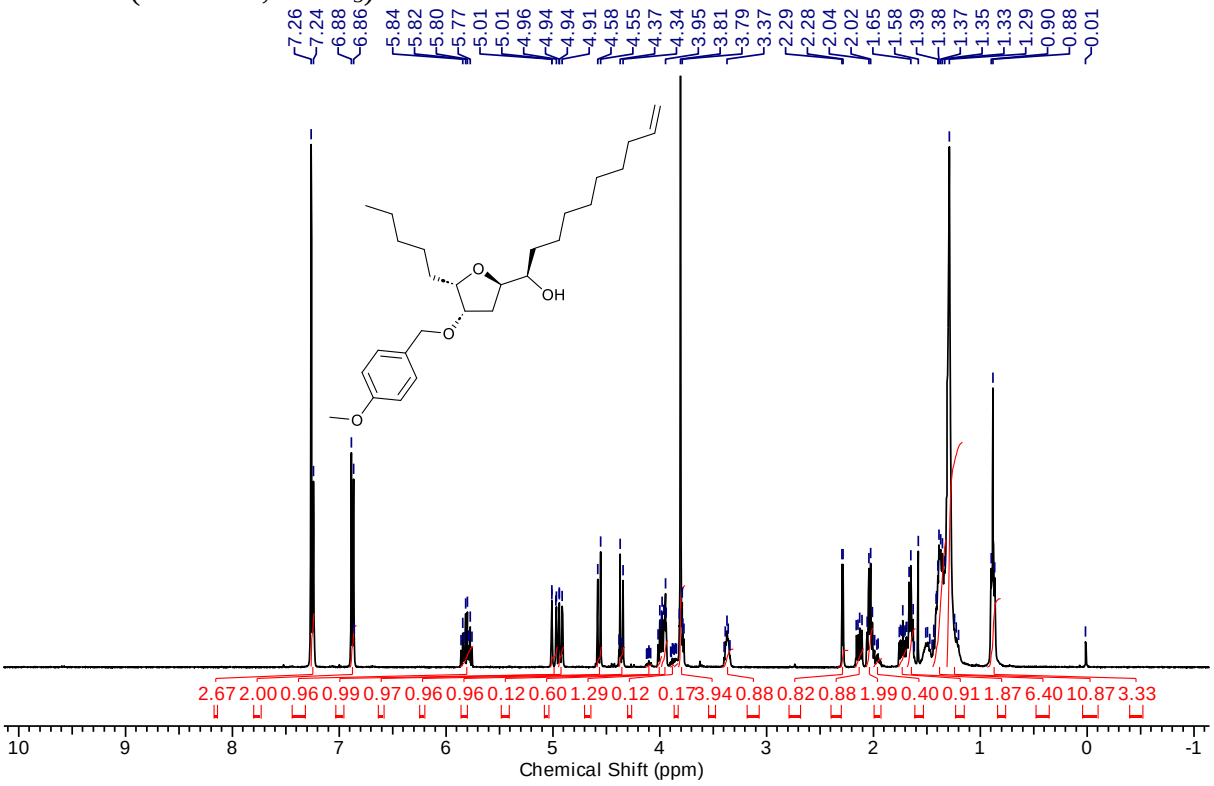


HMBC NMR (400 MHz, $CDCl_3$)

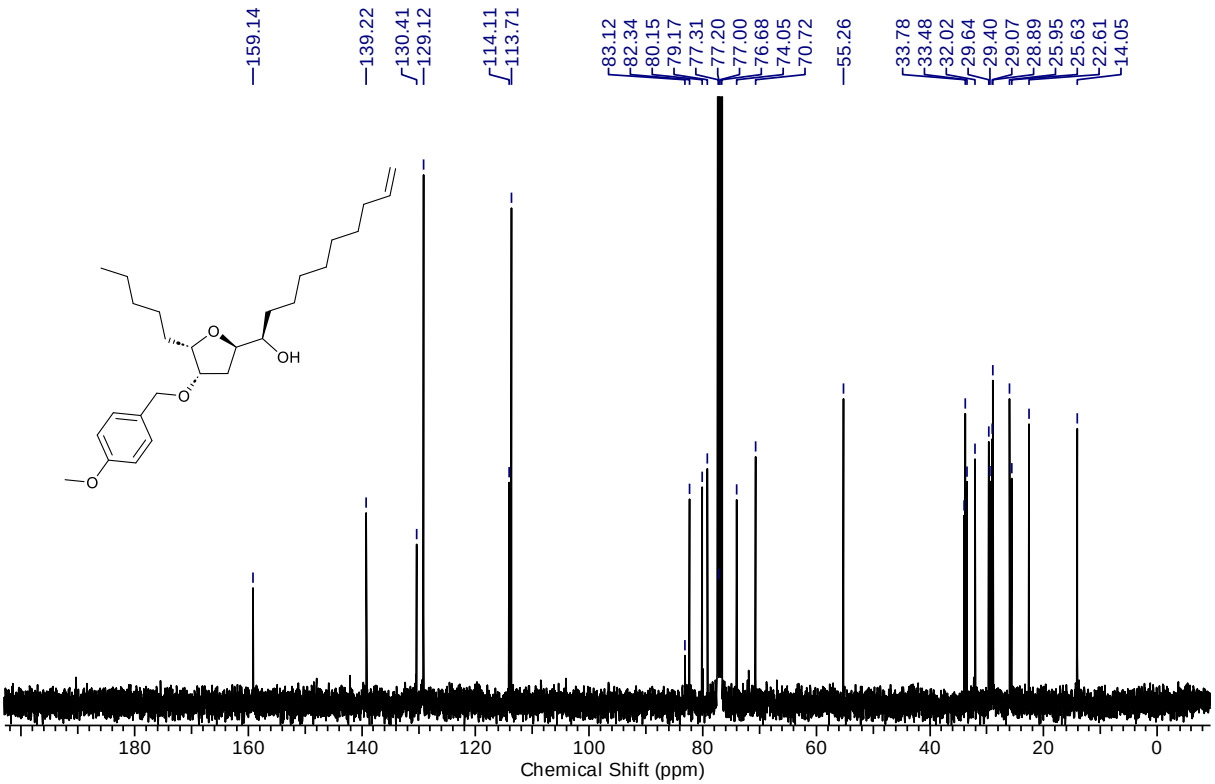


(*R*)-1-{(2*R*,4*S*,5*S*)-4-[(4-Methoxybenzyl)oxy]-5-pentyltetrahydrofuran-2-yl}dec-9-en-1-ol (20)

^{1}H NMR (400 MHz, $CDCl_3$):

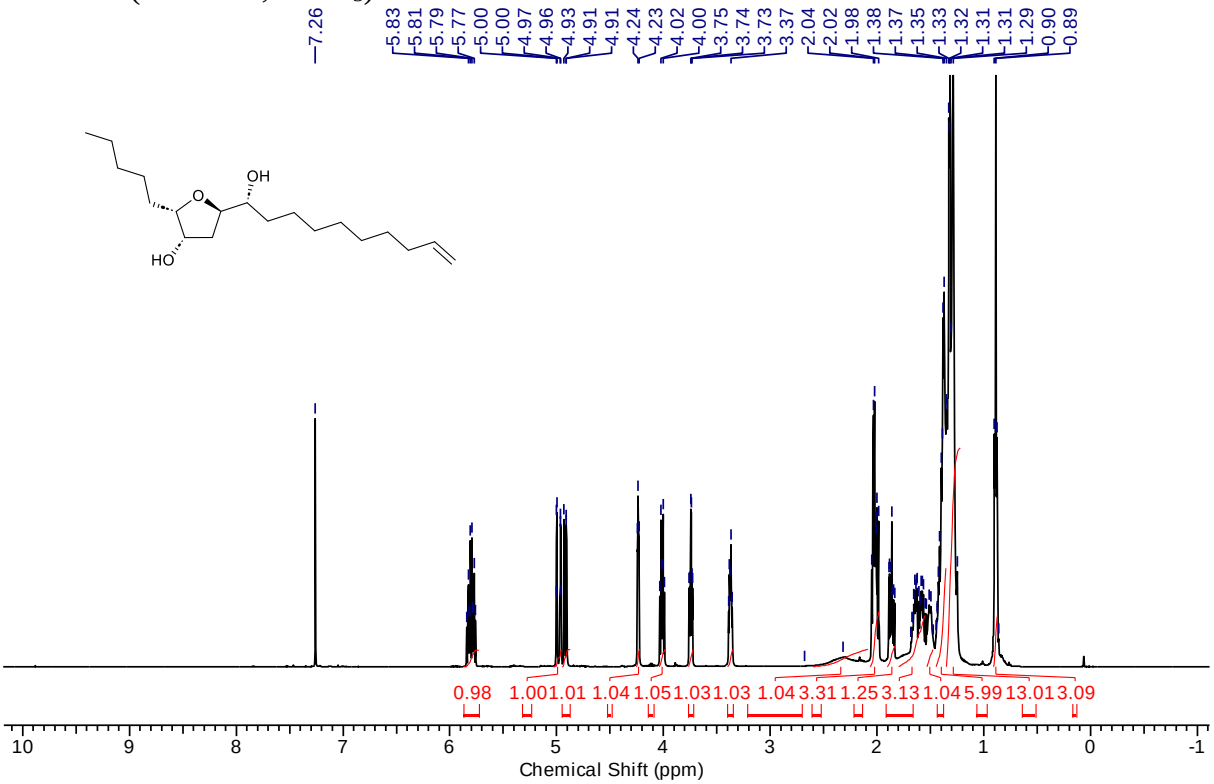


^{13}C NMR (100 MHz, $CDCl_3$):

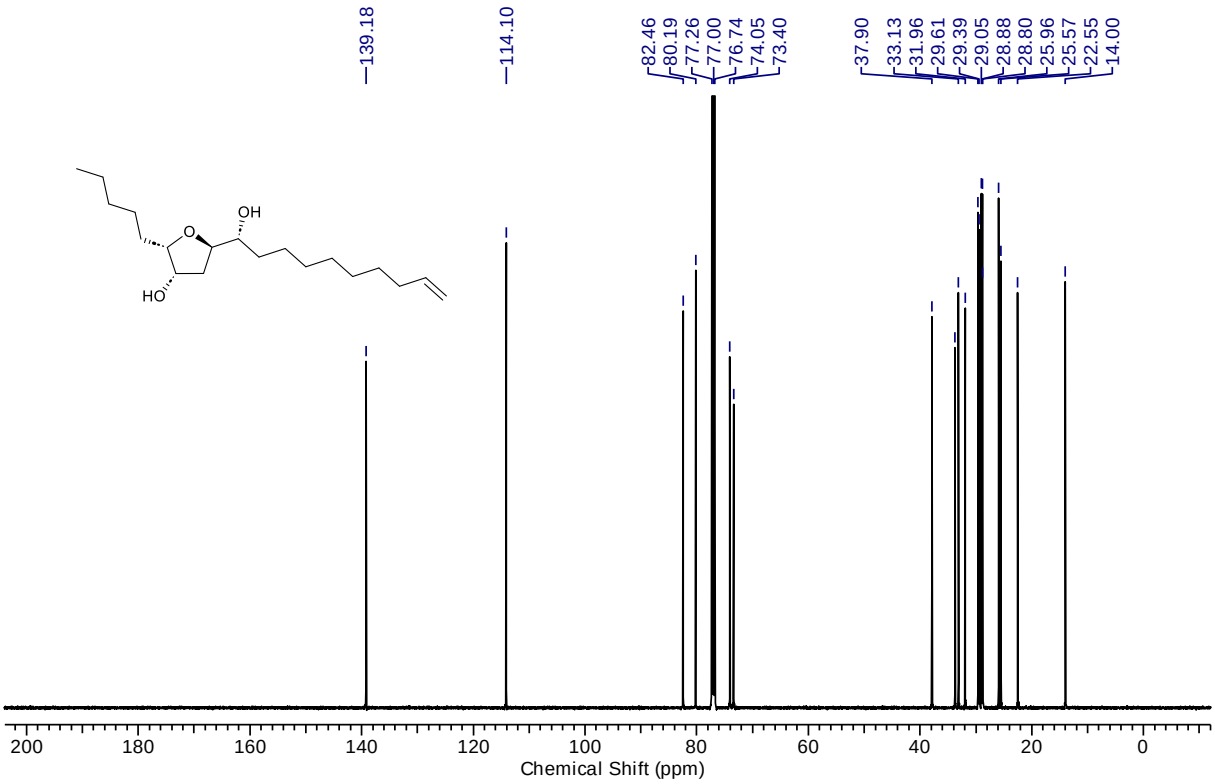


(2*S*,3*S*,5*R*)-5-[(*R*)-1-Hydroxydec-9-en-1-yl]-2-pentyltetrahydrofuran-3-ol (21)

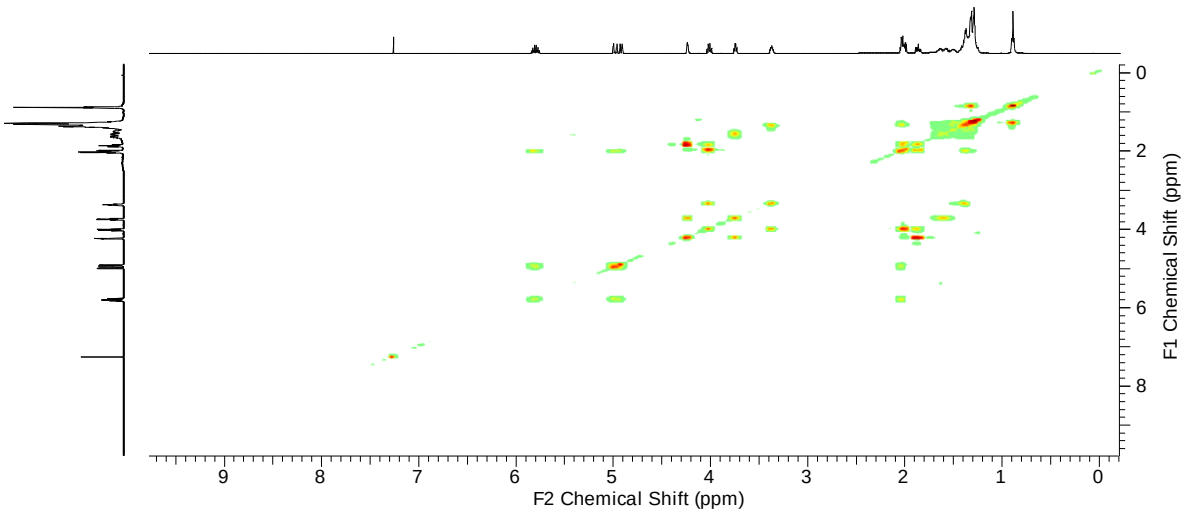
^{1}H NMR (500 MHz, $CDCl_3$):



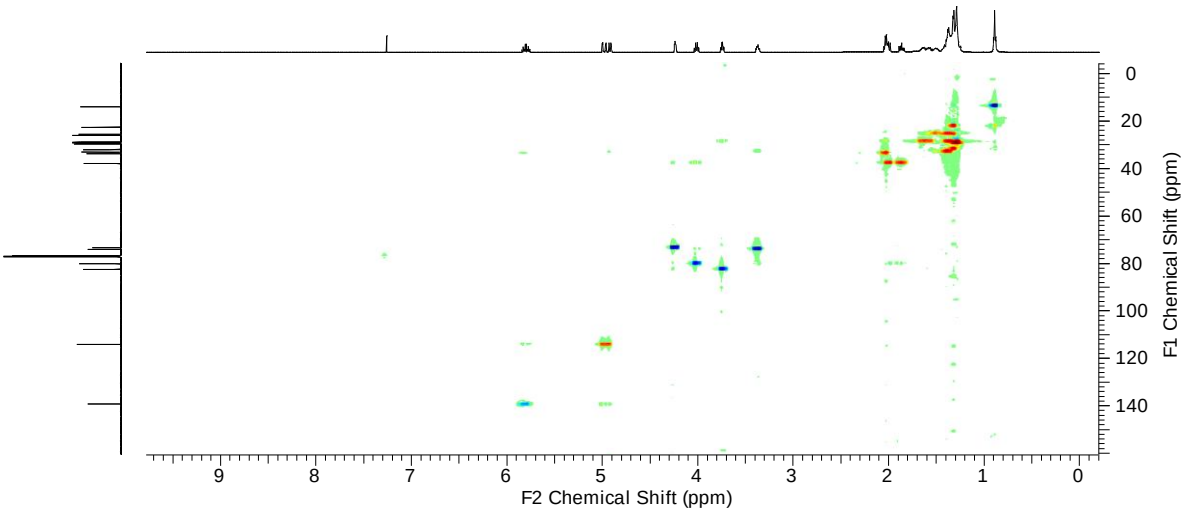
^{13}C NMR (125 MHz, $CDCl_3$):



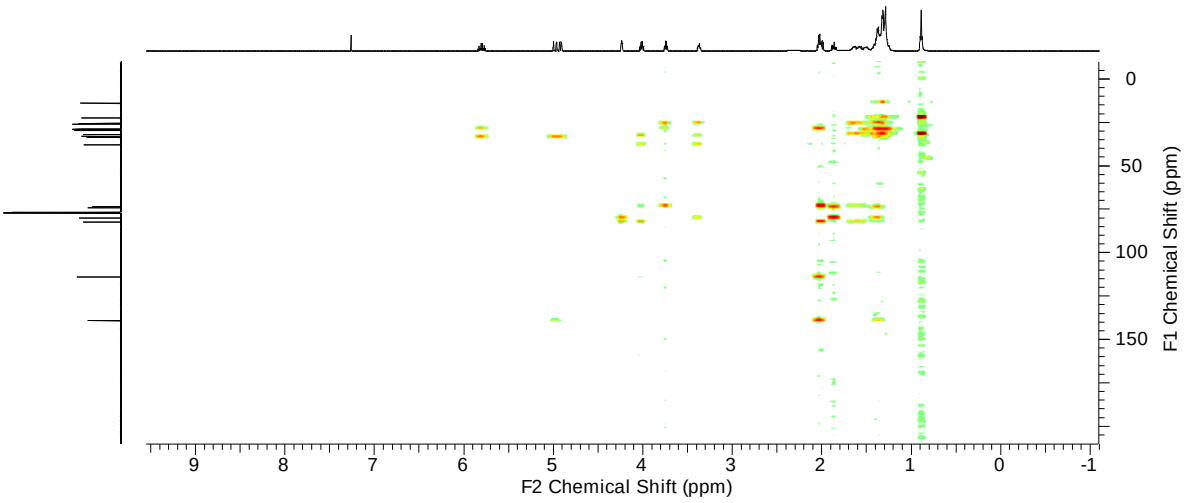
HH-COSY NMR (500 MHz, $CDCl_3$)



HSQC NMR (500 MHz, $CDCl_3$)

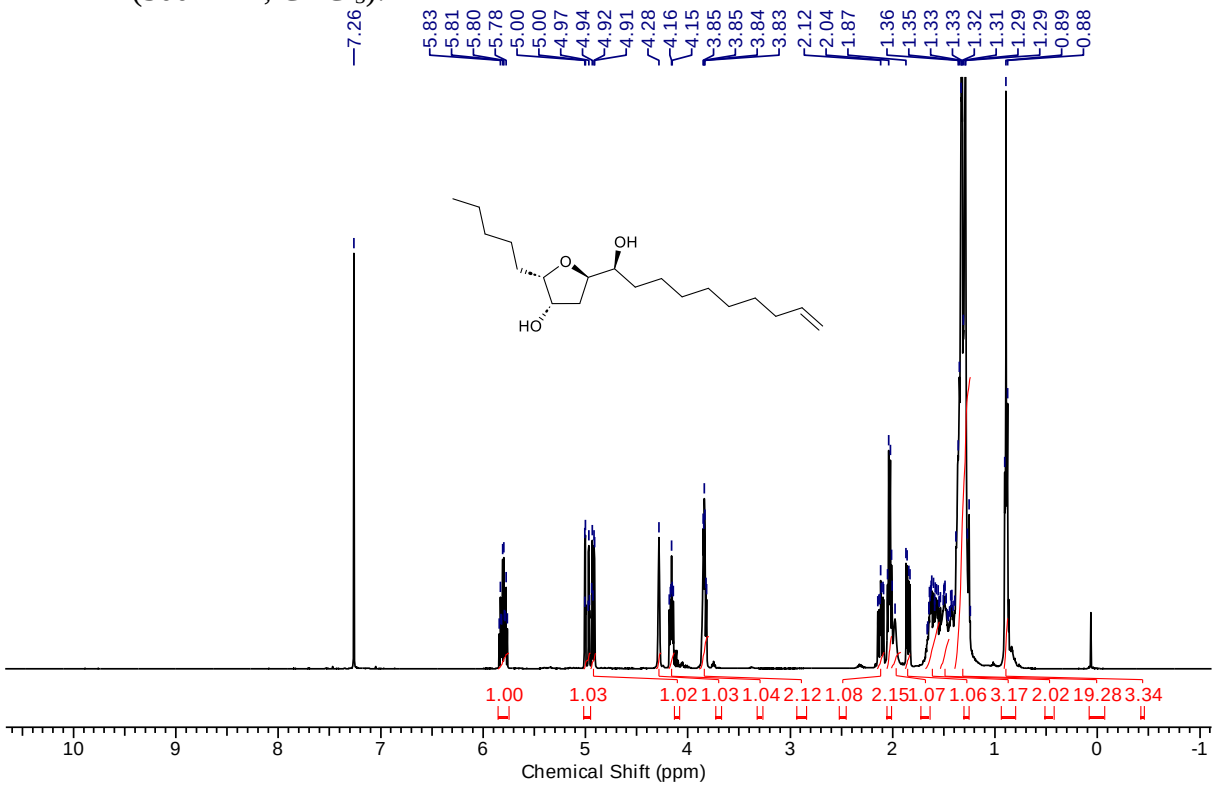


HMBC NMR (500 MHz, $CDCl_3$)

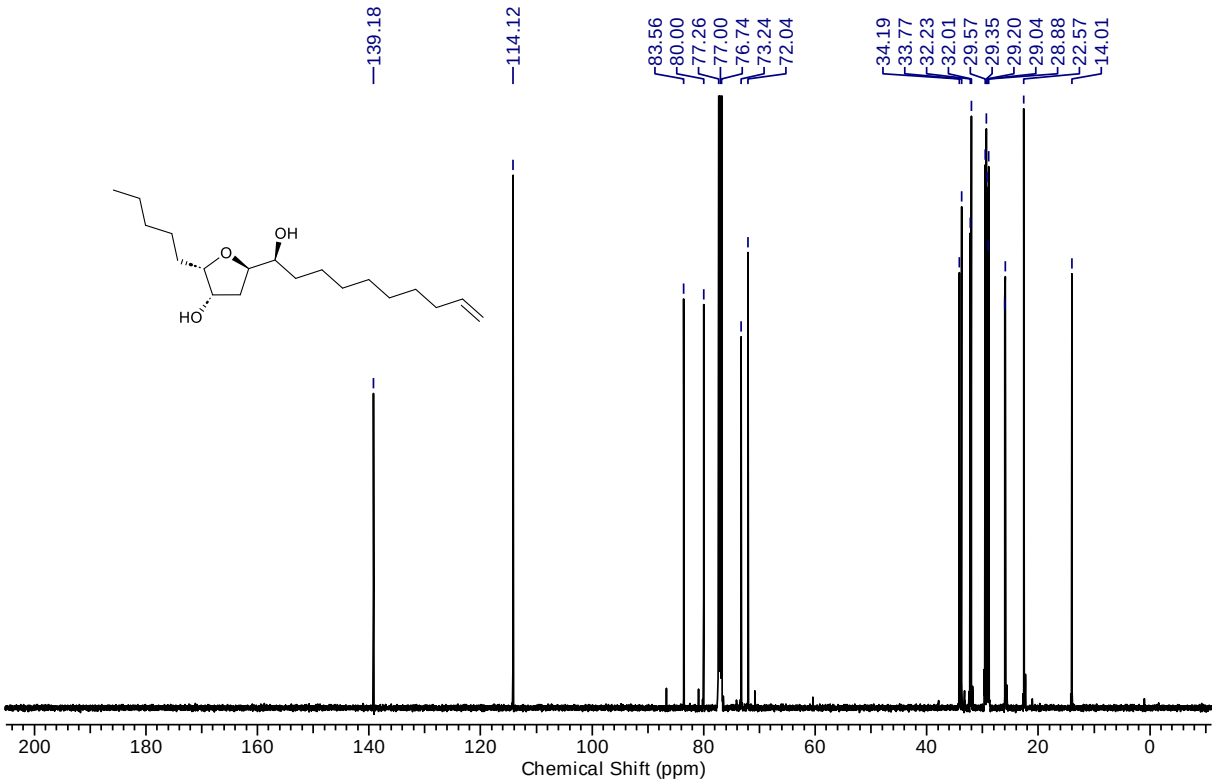


(2*S*,3*S*,5*R*)-5-((*S*)-1-hydroxydec-9-en-1-yl)-2-pentyltetrahydrofuran-3-ol (22)

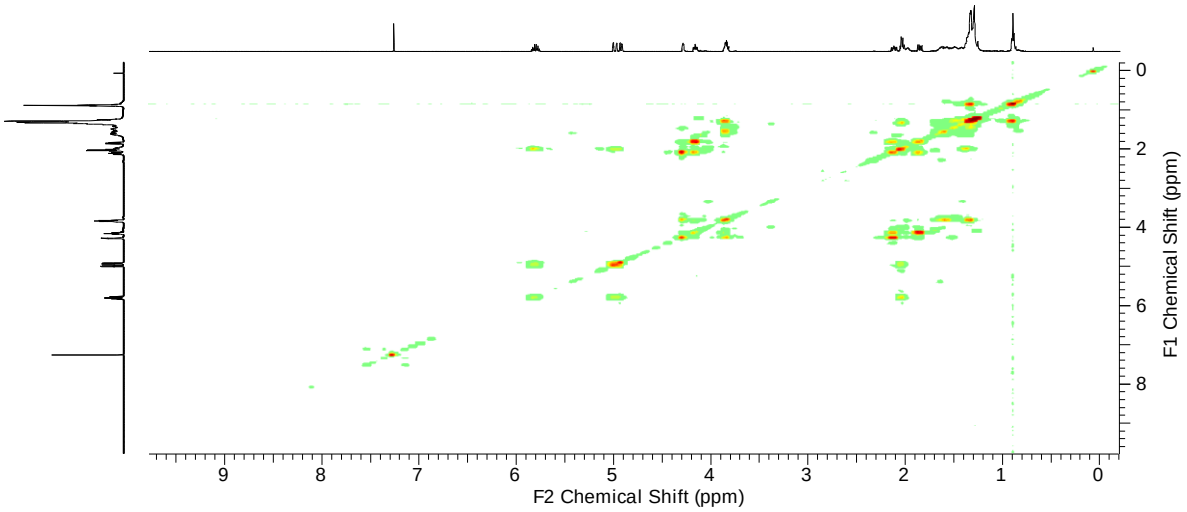
^{1}H NMR (500 MHz, $CDCl_3$):



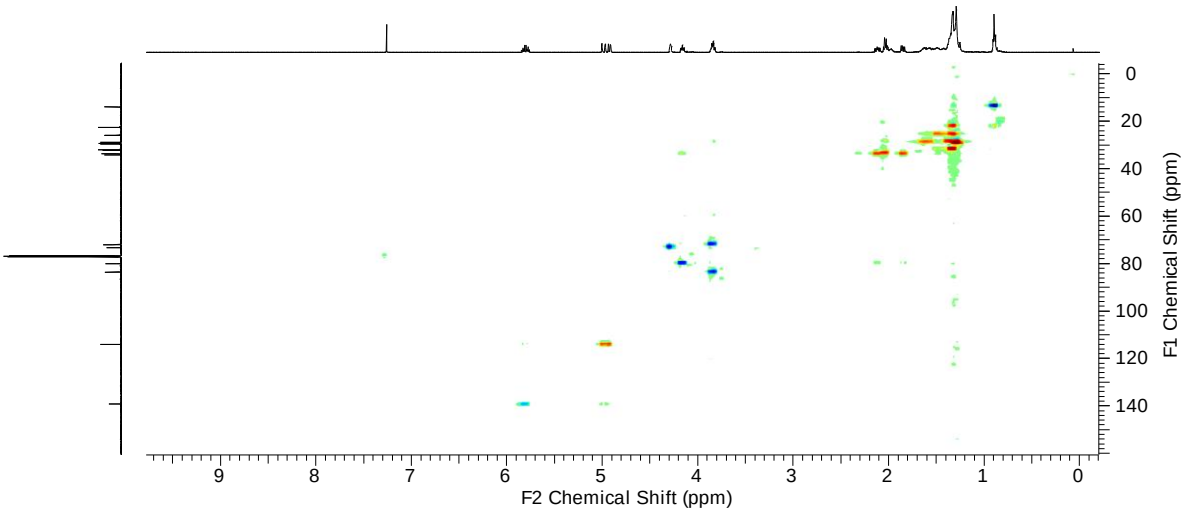
^{13}C NMR (125 MHz, $CDCl_3$):



HH-COSY NMR (500 MHz, $CDCl_3$)



HSQC NMR (500 MHz, $CDCl_3$)



HMBC NMR (500 MHz, $CDCl_3$)