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Supporting Information

for

Diastereodivergent electrophilic trapping of α-boryl lithium derivatives

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Experimental section, characterization data and copies of spectra

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1. General information

Air- and moisture-sensitive reactions were conducted in flame-dried glassware under a positive pressure of argon. Solvents were dried via distillation according to standard procedures (CH_2Cl_2, Et_3N) or used from a solvent purification system (THF, Et_2O; Pure-Solv.® Purification System) and stored at least 72 hours over activated 4 Å molecular sieves before usage. Commercially available reagents were used as purchased unless otherwise stated. Commercially available organolithium reagents were titrated twice against *N*-benzylbenzamide before usage. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm) and visualized by exposure to UV light (254 nm) or stained with acidic *p*-anisaldehyde, cerium molybdate, or potassium permanganate solutions. Column chromatography was performed using Fluka silica gel 60 Å (40–63 mm, 230–400 mesh). PE (60–80 °C boiling range) was used for chromatographic separations. NMR spectra were recorded in $CDCl_3$ on a Bruker Avance instrument. ^{1}H NMR chemical shifts are provided using TMS as external standard (internal reference at δ = 7.26 ppm) and are reported as follows: chemical shift in ppm [multiplicity, coupling constant(s) *J* in Hz, integral]. The following abbreviations were used for peak multiplicities: br = broad, m = multiplet, s = singlet, d = doublet, t = triplet, q = quadruplet, quint = quintuplet, sext = sextuplet, sept = septuplet or combinations thereof. Carbon (^{13}C, APT) chemical shifts are referenced against the residual central solvent peak (δ = 77.16 ppm for $CDCl_3$) and are given in ppm. Boron (^{11}B), fluorine (^{19}F) and phosphorus (^{31}P) shifts are given in ppm using external calibration. High-resolution mass spectrometry (HRMS) was carried out on a FTICR instrument at the Mass Spectrometry Unit of the Schulich Faculty of Chemistry at the Technion – Israel Institute of Technology. Diastereomeric ratios (dr) were determined either by crude ^{1}H NMR (relaxation delay D1 = 6 s) or by GC/FID analysis using an Agilent Technologies 7820A GC with an Agilent Technologies 19091J-413 (30 m × 0.3 mm) column.

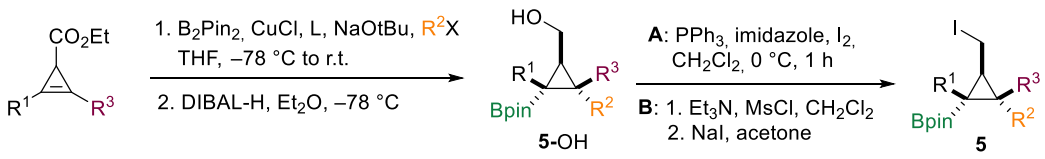
2. Synthesis of starting materials

Cyclopropyl iodides were prepared according to literature procedures.[1–3]

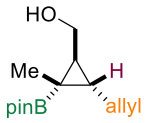
1.1 Compounds **5a**, **5e**, **5f** and **5h**

Compounds **5a**, **5e**, **5f**, and **5h** are known compounds; the experimental results were in agreement with the literature report.[1]

1.2 Compounds **5b** and **5c**



((1*S,2*R**,3*S**)-3-Allyl-2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)methanol (5b-OH)**



Chemical Formula: $C_{11}H_{20}BO_3$
Molecular Weight: 211,09

Prepared according to a literature procedure[1,2] from ethyl 2-methylcycloprop-2-ene-1-carboxylate (456 mg, 3.63 mmol).

Yield: 410 mg (1.63 mmol, 45% over two steps, dr >95:05 as determined by ^{1}H NMR spectroscopy) as a colorless oil.

R*f* = 0.50 (PE/Et_2O 1:1).

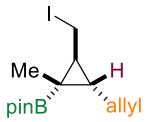
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (ddt, *J* = 16.4, 11.5, 5.9 Hz, 1H), 5.00 (dd, *J* = 17.2, 1.6 Hz, 1H), 4.92 (d, *J* = 10.3 Hz, 1H), 3.73 (dd, *J* = 11.4, 6.3 Hz, 1H), 3.53 (dd, *J* = 11.4, 8.6 Hz, 1H), 2.15 (hept, *J* = 8.3 Hz, 2H), 1.97 (s, 1H), 1.24 – 1.12 (m, 1H), 1.17 (s, 6H), 1.16 (s, 6H), 1.07 (s, 3H), 0.61 (q, *J* = 7.1 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 114.3, 83.2, 62.5, 34.1, 31.6, 31.0, 25.1, 24.6, 15.8 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ 33.1 ppm.

HRMS (TOF ESI+) m/z: calcd. for $C_{14}H_{25}BO_3Na^+$ [*M*+Na]$^+$: 275.1974, found: 275.1796.

2-((1*R,2*S**,3*S**)-2-Allyl-3-(iodomethyl)-1-methylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b)**



Chemical Formula: $C_{14}H_{24}BIO_2$
Molecular Weight: 362.06

Prepared according to a literature procedure **A**[2] from **5b**-OH (101 mg, 400 µmol).

Yield: 116 mg (320 µmol, 80%; dr >95:05 as determined by ^{1}H NMR spectroscopy using *p*-xylene as internal standard) as a colorless oil.

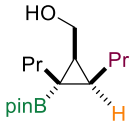
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (ddt, *J* = 16.4, 10.4, 6.0 Hz, 1H), 5.15 – 4.89 (m, 2H), 3.39 (dd, *J* = 9.7, 8.2 Hz, 1H), 3.28 – 3.19 (m, 1H), 2.37 – 2.24 (m, 1H), 2.21 – 2.10 (m, 1H), 1.53 (td, *J* = 8.2, 5.6 Hz, 1H), 1.22 (s, 6H), 1.20 (s, 6H), 1.11 (s, 3H), 0.66 (q, *J* = 6.6 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 114.4, 83.3, 37.5, 34.0, 32.9, 25.1, 24.7, 14.9, 9.0 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ 33.3 ppm.

HRMS (TOF ESI+) m/z: calcd. for $C_{14}H_{24}BIO_2^+$ [*M*+H]$^+$: 363.0993, found: 363.0997.

((1*S,2*R**,3*R**)-2,3-Dipropyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)methanol (5c-OH)**



Chemical Formula: $C_{16}H_{31}BO_3$
Molecular Weight: 282,23

Prepared according to a literature procedure[1,2] from ethyl 2,3-dipropylcycloprop-2-ene-1-carboxylate (968 mg, 4.93 mmol).

Yield: 710 mg (2.51 mmol, 51% over two steps, dr >95:05 as determined by ^{1}H NMR spectroscopy) as a colorless oil.

R*f* = 0.40 (PE/Et_2O 1:1).

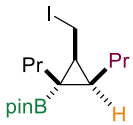
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 – 3.63 (m, 2H), 1.64 – 1.23 (m, 10H), 1.19 (s, 12H), 1.07 – 0.99 (m, 1H), 0.92 (t, *J* = 6.7 Hz, 3H), 0.89 (t, *J* = 6.7 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 83.0, 59.7, 27.2, 26.3, 25.9, 24.7, 24.7, 24.7, 23.6, 23.1, 15.0, 14.3 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ 33.2 ppm.

HRMS (APCI+) m/z: calcd. for $C_{16}H_{31}BIO_2^+$ [*M*–H_2O+H]$^+$: 265.2333, found: 265.2336.

2-((1*R,2*S**,3*R**)-2-(Iodomethyl)-1,3-dipropylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5c)**



Chemical Formula: $C_{16}H_{30}BIO_2$
Molecular Weight: 392.13

Prepared according to a literature procedure **B**[3] from **5c**-OH (141 mg, 500 µmol).

Yield: 196 mg (500 µmol, quantitative over two steps; dr >95:05 as determined by ^{1}H NMR spectroscopy using *p*-xylene as internal standard) as a colorless oil.

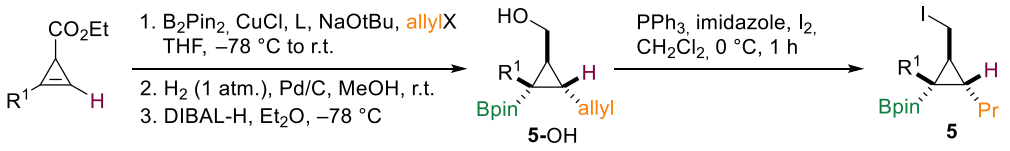
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.42 (dd, *J* = 9.8, 6.5 Hz, 1H), 3.20 (t, *J* = 10.0 Hz, 1H), 1.63 (ddd, *J* = 10.2, 8.5, 6.5 Hz, 1H), 1.56 – 1.22 (m, 8H), 1.19 (s, 6H), 1.19 (s, 6H), 1.09 (dt, *J* = 8.6, 6.5 Hz, 1H), 0.94 (t, *J* = 6.9 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 83.1, 28.1, 27.6, 26.6, 24.7, 24.6, 24.6, 23.5, 22.9, 14.9, 14.3, 5.7 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ 32.8 ppm.

HRMS (APCI+) m/z: calcd. for $C_{16}H_{31}BIO_2^+$ [*M*+H]$^+$: 393.1456, found: 393.1479.

1.3 Compounds **5d** and **5g**

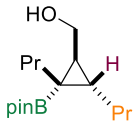


Step 1: Borylation was carried out according to a literature procedure and allyl phosphate as electrophile.[1]

Step 2: The above prepared pinacol borane was dissolved in MeOH (0.1 M) and Pd on charcoal (0.1 equiv w/w) was added. The mixture was stirred at room temperature under positive pressure of hydrogen (one balloon) for 4 h. The suspension was subsequently purged with argon, the solids were filtered and the mixture was concentrated under reduced pressure to give crude product.

Step 3: The crude ester was reduced according to a literature procedure.[1,2]

((1*S,2*R**,3*S**)-2,3-Dipropyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)methanol (5d-OH)**



Chemical Formula: $C_{16}H_{31}BO_3$
Molecular Weight: 282,23

Prepared from ethyl 2-propylcycloprop-2-ene-1-carboxylate (342 mg, 2.22 mmol).

Yield: 345 mg (1.22 mmol, 52% over three steps, dr >95:05 as determined by ^{1}H NMR spectroscopy) as a white solid.

R*f* = 0.35 (PE/Et_2O 1:1).

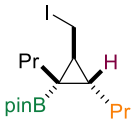
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 – 3.58 (m, 2H), 1.55 – 1.45 (m, 1H), 1.35 (td, *J* = 16.7, 8.6 Hz, 8H), 1.22 (s, 6H), 1.19 (s, 6H), 1.17 – 1.09 (m, 1H), 0.88 (t, *J* = 7.6 Hz, 3H), 0.86 (t, *J* = 7.6 Hz, 3H), 0.59 (q, *J* = 6.4 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 83.1, 63.0, 34.1, 32.7, 31.7, 31.2, 25.2, 24.6, 23.4, 23.2, 14.8, 14.0 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ 33.1 ppm.

HRMS (APCI+) m/z: calcd. for $C_{16}H_{30}BO_2^+$ [*M*–H_2O+H]$^+$: 265.2333, found: 265.2323.

2-((1*R,2*S**,3*S**)-2-(Iodomethyl)-1,3-dipropylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5d)**



Chemical Formula: $C_{16}H_{30}BIO_2$
Molecular Weight: 392.13

Prepared according to a literature procedure[2] from 5d-OH (115 mg, 410 µmol).

Yield: 123 mg (315 µmol, 77%; dr >95:05 as determined by ^{1}H NMR spectroscopy using *p*-xylene as internal standard) as a colorless oil.

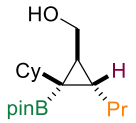
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.44 (dd, *J* = 9.5, 6.5 Hz, 1H), 3.21 (t, *J* = 9.8 Hz, 1H), 2.09 (t, *J* = 7.1 Hz, 1H), 1.50 – 1.41 (m, 2H), 1.41 – 1.29 (m, 6H), 1.20 (s, 6H), 1.18 (s, 6H), 0.88 (t, *J* = 7.6 Hz, 3H), 0.86 (t, *J* = 7.3 Hz, 3H), 0.58 (q, *J* = 6.5 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 83.1, 37.3, 33.8, 33.6, 32.6, 25.2, 24.5, 23.3, 23.2, 14.7, 14.1, 10.4 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ 32.8 ppm.

HRMS (APCI+) m/z: calcd. for $C_{16}H_{31}BIO_2^+$ [*M*+H]$^+$: 393.1456, found: 393.1489.

((1*S,2*R**,3*S**)-2-Cyclohexyl-3-propyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)methanol (5g-OH)**



Chemical Formula: $C_{19}H_{35}BO_3$
Molecular Weight: 322,30

Prepared from ethyl 2-cyclohexylcycloprop-2-ene-1-carboxylate (971 mg, 5.00 mmol).

Yield: 451 mg (1.4 mmol, 28% over three steps, dr >95:05 as determined by ^{1}H NMR spectroscopy) as a white solid.

R*f* = 0.40 (PE/Et_2O 1:2).

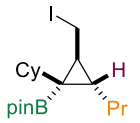
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (dd, *J* = 11.2, 7.7 Hz, 1H), 3.61 (dd, *J* = 11.3, 7.0 Hz, 1H), 1.89 (s, 1H), 1.71 (q, *J* = 7.5 Hz, 2H), 1.67 – 1.44 (m, 4H), 1.35 (ddd, *J* = 18.6, 13.4, 7.1 Hz, 4H), 1.30 – 1.02 (m, 5H), 1.19 (s, 6H), 1.16 (s, 6H), 0.86 (t, *J* = 6.9 Hz, 3H), 0.64 (ddd, *J* = 11.9, 8.3, 3.5 Hz, 1H), 0.52 (dt, *J* = 11.4, 5.5 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 82.8, 62.5, 41.9, 33.4, 32.6, 31.8, 31.6, 30.2, 27.4, 27.1, 26.6, 25.4, 24.4, 23.3, 14.0 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ 32.7 ppm.

HRMS (APCI+) m/z: calcd. for $C_{19}H_{34}BO_2^+$ [*M*–H_2O+H]$^+$: 305.2655, found: 305.2646.

2-((1*R,2*S**,3*S**)-1-Cyclohexyl-2-(iodomethyl)-3-propylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5g)**



Chemical Formula: $C_{19}H_{34}BIO_2$
Molecular Weight: 432.19

Prepared according to a literature procedure[2] from **5g**-OH (121 mg, 375 µmol).

Yield: 121 mg (281 µmol, 75%; dr >95:05 as determined by ^{1}H NMR spectroscopy using *p*-xylene as internal standard) as a colorless oil.

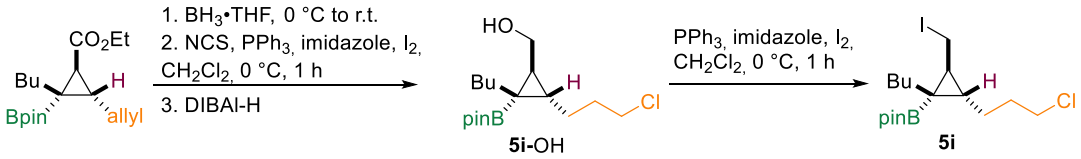
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.59 (dd, *J* = 9.5, 5.5 Hz, 1H), 3.26 – 3.16 (m, 1H), 1.84 – 1.60 (m, 5H), 1.55 (dq, *J* = 13.8, 7.0 Hz, 2H), 1.48 – 1.32 (m, 4H), 1.33 – 1.26 (m, 2H), 1.21 (s, 6H), 1.19 (s, 6H), 1.12 (t, *J* = 12.6 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.76 – 0.64 (m, 1H), 0.56 (q, *J* = 5.9 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 83.0, 42.3, 36.3, 33.7, 33.1, 33.1, 31.4, 27.4, 27.1, 26.5, 25.4, 24.5, 23.2, 14.2, 10.7 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

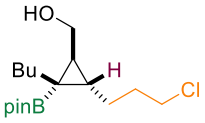
^{11}B NMR (128 MHz, $CDCl_3$): δ 32.5 ppm.

HRMS (APCI+) m/z: calcd. for $C_{19}H_{34}BO_2^+$ [*M*–HI+H]$^+$: 305.2646, found: 305.2641.

1.4 Compound **5i**



((1*S,2*R**,3*S**)-2-Butyl-3-(3-chloropropyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)methanol (5i-OH)**



Chemical Formula: $C_{17}H_{32}BClO_3$
Molecular Weight: 330,70

Step 1: A flame-dried Schlenk flask was charged with a solution of pinacolborane **S1**[1] (336 mg, 1.00 mmol) in dry THF (5.0 mL) under argon atmosphere. The solution was cooled to 0 °C and BH_3•THF (1.5 mL, 1.0 M solution in THF) was added dropwise. The mixture was stirred for 1 h when TLC analysis indicated full consumption of **S1**. The mixture was quenched by a dropwise addition of MeOH at 0 °C, until the evolution of hydrogen gas ceased. Sodium perborate (1.09 g, 4.00 mmol) was added, followed by a dropwise addition of water (1.0 mL) at 0 °C and the mixture was stirred for 1 h at this temperature. Na_2SO_3 satd. solution (10 mL) was added, the layers were separated and the aqueous one was extracted with EtOAc (3 × 10 mL). The organic layers were washed with brine, dried over Na_2SO_4, filtered, the filtrate was concentrated under reduced pressure and the crude residue was purified by silica gel column chromatography (PE/EtOAc 99:1 to 7:3) to give the desired alcohol.

Step 2: A solution of PPh_3 (249 mg, 948 µmol) and *N*-chlorosuccinimide (116 mg, 869 µmol) in dry DCM (5 mL) was stirred for 30 min, then cooled to 0 °C and imidazole (11 mg, 157 µmol) was added. A solution of the above prepared ester in dry DCM (2 mL) was added dropwise, the mixture was stirred for 2 h at 0 °C and then overnight at room temperature. It was diluted with PE (20 mL), filtered over a short plug of silica gen and washed with 5% Et_2O in PE. The volatiles were removed under reduced pressure and the crude residue was used in the next step without further purification.

Step 3: The ester was reduced according to a literature procedure.[1,2]

Yield: 100 mg (302 µmol, 30% over three steps, dr >95:05 as determined by ^{1}H NMR spectroscopy) as a colorless oil.

R*f* = 0.65 (PE/Et_2O 1:1).

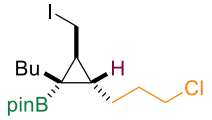
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 – 3.58 (m, 2H), 3.54 (t, *J* = 6.7 Hz, 2H), 1.81 (hept, *J* = 7.3 Hz, 2H), 1.65 – 1.52 (m, 2H), 1.52 – 1.40 (m, 1H), 1.37 – 1.11 (m, 6H), 1.21 (s, 6H), 1.17 (s, 6H), 0.86 (t, *J* = 6.9 Hz, 3H), 0.58 (q, *J* = 7.1 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 83.2, 62.7, 45.0, 33.2, 32.3, 31.6, 31.2, 30.3, 28.0, 25.2, 24.6, 23.2, 14.2 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ 32.9 ppm.

HRMS (TOF ESI+) m/z: calcd. for $C_{17}H_{33}BClNaO_3^+$ [*M*+Na]$^+$: 353.2031, found: 353.2025.

2-((1*R,2*S**,3*S**)-1-Butyl-2-(3-chloropropyl)-3-(iodomethyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5i)**



Chemical Formula: $C_{17}H_{31}BClIO_2$
Molecular Weight: 440.60

Prepared according to a literature procedure[2] from **5i**-OH (100 mg, 302 µmol).

Yield: 79 mg (180 µmol, 60%; *dr* > 95:05 as determined by ^{1}H NMR spectroscopy using *p*-xylene as internal standard) as a colorless oil.

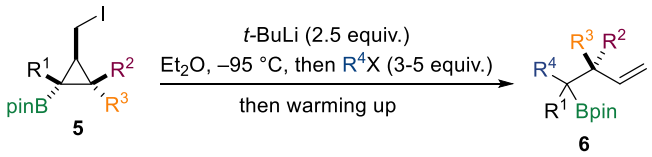
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62 – 3.52 (m, 2H), 3.49 (dd, *J* = 9.6, 6.1 Hz, 1H), 3.19 (t, *J* = 10.0 Hz, 1H), 1.99 – 1.76 (m, 2H), 1.70 – 1.54 (m, 2H), 1.55 – 1.44 (m, 2H), 1.39 – 1.23 (m, 5H), 1.23 (s, 6H), 1.21 (s, 6H), 0.88 (t, *J* = 6.9 Hz, 3H), 0.59 (td, *J* = 7.2, 5.5 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 83.3, 45.1, 36.1, 33.5, 32.9, 32.4, 31.1, 27.8, 25.2, 24.6, 23.2, 14.2, 9.9 ppm. *Note*: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ 32.9 ppm.

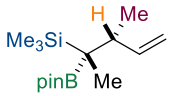
HRMS (APCI+) m/z: calcd. for $C_{17}H_{32}BClIO_2^+$ $[M+H]^+$: 441.1229, found: 441.1238.

3. Scope of ring opening/silylation



General procedure for Li–halogen exchange-mediated ring opening/silylation (GP1):[3] A flame-dried Schlenk flask was charged with dry Et_2O (0.2 M with respect to **5**, typically 1 mL) under argon and a solution of *t*-BuLi (2.5 equiv, typically 1.4 M in pentane, freshly titrated before use against *N*-benzyl benzamide)[4] was added at −78 °C. The mixture was cooled to −95 °C with good stirring and a solution of iodide **5** (typically 200 µmol) in dry Et_2O (0.2 M) was added via a cannula. A bright yellow precipitate formed. Electrophile (3–5 equiv) was added and the mixture was stirred with warming up to the required temperature while monitored by TLC against the proton-quench product (R*f* ≈ 0.45 vs. 0.70 for silylated compounds **6**). Completion was accompanied by decoloration and was typically reached after 30–40 min of stirring at −30 °C. The reaction mixture was subsequently quenched with MeOH (10 equiv), diluted with Et_2O and filtered over a short plug of silica gel. The crude residue was purified by flash column chromatography (silica gel, gradient PE/Et_2O 999:1 to 99:1; majority of compounds elute at 997:3) to obtain title compounds **6**.

Trimethyl((2*R,3*R**)-3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-2-yl)silane (6a)**



Chemical Formula: $C_{15}H_{31}BO_2Si$
Molecular Weight: 282.31

Prepared according to general procedure **GP1** from **5a** (67 mg, 200 µmol) and Me_3SiCl (63 µL, 500 µmol).

Yield: 40 mg (142 µmol, 71%, dr >95:05 as determined by ^{1}H NMR spectroscopy) as a colorless oil.

R*f* = 0.65 (PE/Et_2O 40:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (ddd, *J* = 17.1, 10.1, 9.1 Hz, 1H), 4.95 (dd, *J* = 17.1, 1.4 Hz, 1H), 4.89 (dd, *J* = 10.1, 2.0 Hz, 1H), 2.61 – 2.50 (m, 1H), 1.23 (s, 12H), 1.04 (d, *J* = 6.9 Hz, 3H), 0.97 (s, 3H), 0.03 (s, 9H) ppm.

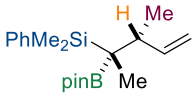
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 113.0, 82.9, 41.3, 25.4, 25.3, 19.7, 11.8, -1.6 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{29}Si NMR (80 MHz, $CDCl_3$) δ 4.6 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.5 ppm.

HRMS (APCI+) m/z: calcd. for $C_{15}H_{32}BO_2Si^+$ [*M*+H]$^+$: 283.2259, found: 283.2254.

Trimethyl((2*R,3*R**)-3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-2-yl)silane (6b)**



Chemical Formula: $C_{20}H_{33}BO_2Si$
Molecular Weight: 344,38

Prepared according to general procedure **GP1** from **5a** (61 mg, 180 µmol) and $Me_2PhSiCl$ (92 µL, 540 µmol).

Yield: 38 mg (110 µmol, 61%, dr >95:05 as determined by ^{1}H NMR spectroscopy) as a colorless oil.

R*f* = 0.45 (PE/Et_2O 40:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (m, 2H), 7.36 – 7.26 (m, 3H), 5.79 (ddd, *J* = 17.2, 10.0, 8.9 Hz, 1H), 5.00 – 4.74 (m, 2H), 2.56 (p, *J* = 7.0 Hz, 1H), 1.19 (s, 6H), 1.09 (s, 6H), 1.09 (s, 3H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.39 (s, 3H), 0.33 (s, 3H) ppm.

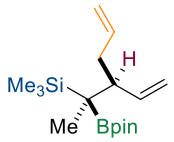
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 139.1, 135.1, 128.7, 127.3, 113.5, 83.0, 41.2, 25.4, 25.2, 19.5, 12.4, -2.6, -3.0 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{29}Si NMR (80 MHz, $CDCl_3$) δ -0.8 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.5 ppm.

HRMS (APCI+) m/z: calcd. for $C_{20}H_{34}BO_2Si^+$ [*M*+H]$^+$: 345.2416, found: 345.2415.

Trimethyl((2*S,3*S**)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-vinylhex-5-en-2-yl)silane (6c)**



Chemical Formula: $C_{17}H_{33}BO_2Si$
Molecular Weight: 308.34

Prepared according to general procedure **GP1** from **5b** (116 mg, 320 µmol) and Me_3SiCl (203 µL, 1.6 mmol).

Yield: 55 mg (178 µmol, 56%, dr >95:05 as determined by ^{1}H NMR spectroscopy) as a colorless oil.

R*f* = 0.60 (PE/Et_2O 40:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 – 5.69 (m, 1H), 5.65 (dt, *J* = 17.1, 9.9 Hz, 1H), 4.99 (dd, *J* = 10.2, 2.2 Hz, 1H), 4.96 – 4.86 (m, 3H), 2.40 (td, *J* = 10.7, 2.6 Hz, 1H), 2.21 (td, *J* = 12.4, 7.0 Hz, 1H), 2.01 (ddt, *J* = 13.6, 7.1, 1.3 Hz, 1H), 1.24 (s, 12H), 1.01 (s, 3H), 0.02 (s, 9H) ppm.

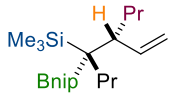
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 138.6, 115.4, 114.8, 83.0, 47.7, 38.6, 25.4, 11.7, -1.6 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{29}Si NMR (80 MHz, $CDCl_3$) δ 4.4 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.5 ppm.

HRMS (APCI+) m/z: calcd. for $C_{17}H_{33}BO_2Si^+$ $[M+H]^+$: 309.2422, found: 309.2421.

Trimethyl((4*R,5*R**)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinyloctan-4-yl)silane (6d)**



Chemical Formula: $C_{19}H_{39}BO_2Si$
Molecular Weight: 338.41

Prepared according to general procedure **GP1** from **5c** (141 mg, 360 µmol) and Me_3SiCl (137 µL, 1.1 mmol).

Yield: 62 mg (183 µmol, 51%) as a partially separable mixture of diastereomers (*dr* 80:20 as determined by ^{1}H NMR spectroscopy) as a colorless oil.

Prepared according to general procedure **GP1** from **5d** (118 mg, 300 µmol) and Me_3SiCl (190 µL, 1.5 mmol).

Yield: 45 mg (133 µmol, 44%) as a partially separable mixture of diastereomers (dr 80:20 as determined by ^{1}H NMR spectroscopy) as a colorless oil.

R*f* = 0.65 (PE/Et_2O 40:1).

Major diastereomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (dt, *J* = 17.1, 10.0 Hz, 1H), 4.97 (dd, *J* = 10.2, 2.3 Hz, 1H), 4.89 (dd, *J* = 17.1, 2.3 Hz, 1H), 2.41 – 2.24 (m, 1H), 1.63 – 1.34 (m, 6H), 1.23 – 1.21 (m, 1H), 1.22 (s, 6H), 1.21 (s, 6H), 1.16 – 1.02 (m, 1H), 0.88 – 0.83 (m, 6H), 0.06 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 114.8, 82.5, 46.3, 33.7, 32.4, 25.6, 25.2, 21.07, 20.5, 15.5, 14.3, 0.8 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{29}Si NMR (80 MHz, $CDCl_3$) δ 4.0 ppm.

Minor diastereomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (dt, *J* = 17.1, 10.1 Hz, 1H), 4.97 (dd, *J* = 10.2, 2.3 Hz, 1H), 4.93 – 4.82 (m, 1H), 2.41 – 2.24 (m, 1H), 1.63 – 1.34 (m, 6H), 1.23 – 1.21 (m, 1H), 1.21 (s, 6H), 1.20 (s, 6H), 1.16 – 1.02 (m, 1H), 0.88 – 0.83 (m, 6H), 0.07 (s, 9H) ppm.

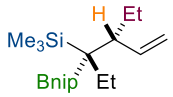
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 114.7, 82.5, 46.6, 36.4, 32.3, 25.4, 25.2, 21.6, 21.12, 15.6, 14.2, 0.4 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{29}Si NMR (80 MHz, $CDCl_3$) δ 4.2 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.4 ppm.

HRMS (APCI+) m/z: calcd. for $C_{19}H_{40}BO_2Si^+$ $[M+H]^+$: 339.2885, found: 339.2884.

((3*R,4*R**)-4-Ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-3-yl)trimethylsilane (6e)**



Chemical Formula: $C_{17}H_{35}BO_2Si$
Molecular Weight: 310,36

Prepared according to general procedure **GP1** from **5b** (100 mg, 275 µmol) and Me_3SiI (174 µL, 1.37 mmol).

Yield: 42 mg (137 µmol, 49%) as an inseparable mixture of diastereomers (dr 87:13 as determined by ^{1}H NMR spectroscopy) as a colorless oil.

R*f* = 0.65 (PE/Et_2O 40:1).

Major diastereomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.69 (dt, *J* = 17.1, 10.0 Hz, 1H), 5.00 (dd, *J* = 10.2, 2.3 Hz, 1H), 4.92 (dd, *J* = 17.1, 2.3 Hz, 1H), 2.22 – 2.12 (m, 1H), 1.72 (dq, *J* = 14.9, 7.5 Hz, 1H), 1.64 – 1.53 (m, 1H), 1.50 (ddd, *J* = 13.5, 6.9, 3.8 Hz, 1H), 1.38 (tdd, *J* = 14.7, 7.9, 2.9 Hz, 1H), 1.22 (s, 6H), 1.22 (s, 6H), 0.97 (t, *J* = 7.5 Hz, 3H), 0.81 (t, *J* = 7.3 Hz, 3H), 0.07 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 115.1, 82.6, 48.8, 26.8, 25.4, 25.2, 22.2, 13.2, 12.7, 0.3 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{29}Si NMR (80 MHz, $CDCl_3$) δ 3.9 ppm.

Minor diastereomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (dt, *J* = 17.1, 10.0 Hz, 1H), 5.03 – 4.88 (m, 2H), 2.19 – 2.09 (m, 1H), 1.72 (dq, *J* = 14.9, 7.5 Hz, 1H), 1.64 – 1.45 (m, 2H), 1.45 – 1.31 (m, 1H), 1.22 (s, 6H), 1.20 (s, 6H), 0.92 (t, *J* = 7.5 Hz, 3H), 0.79 (t, *J* = 1.9 Hz, 3H), 0.02 (s, 9H) ppm.

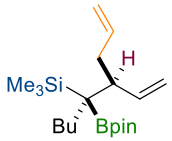
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 115.1, 82.5, 48.4, 26.8, 25.6, 25.3, 22.3, 12.8, 12.1, 0.7 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{29}Si NMR (80 MHz, $CDCl_3$) δ 4.2 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.4 ppm.

HRMS (APCI+) m/z: calcd. for $C_{17}H_{36}BO_2Si^+$ [*M*+H]$^+$: 311.2572, found: 311.2578.

Trimethyl((4*S,5*S**)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-vinylnon-1-en-5-yl)silane (6f)**



Chemical Formula: $C_{20}H_{39}BO_2Si$
Molecular Weight: 350.43

Prepared according to general procedure **GP1** from **5f** (101 mg, 250 µmol) and Me_3SiCl (159 µL, 1.25 mmol).

Yield: 60 mg (173 µmol, 69%) as a partially separable mixture of diastereomers (dr 75:25 as determined by ^{1}H NMR spectroscopy) as a colorless oil.

R*f* = 0.70 (PE/Et_2O 40:1).

Major diastereomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 – 5.65 (m, 2H), 5.04 – 4.84 (m, 4H), 2.49 – 2.25 (m, 2H), 2.21 – 2.09 (m, 1H), 1.66 – 1.55 (m, 1H), 1.54 – 1.44 (m, 2H), 1.40 – 1.29 (m, 3H), 1.22 (s, 12H), 0.88 (t, *J* = 7.1 Hz, 3H), 0.08 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 139.2, 115.2, 114.5, 82.6, 47.0, 38.6, 29.8, 29.6, 25.4, 25.2, 24.2, 14.4, 0.4 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{29}Si NMR (80 MHz, $CDCl_3$) δ 4.1 ppm.

Minor diastereomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 (dt, *J* = 17.1, 10.0 Hz, 1H), 5.84 – 5.65 (m, 1H), 5.04 – 4.84 (m, 4H), 2.49 – 2.25 (m, 2H), 2.02 (td, *J* = 12.7, 7.0 Hz, 1H), 1.66 – 1.55 (m, 2H), 1.54 – 1.44 (m, 1H), 1.40 – 1.29 (m, 3H), 1.22 (s, 6H), 1.21 (s, 6H), 0.89 (t, *J* = 7.1 Hz, 3H), 0.08 (s, 9H) ppm.

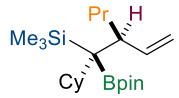
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 139.1, 115.3, 114.7, 82.6, 46.9, 36.3, 29.7, 29.3, 25.5, 25.2, 24.1, 14.4, 0.7 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{29}Si NMR (80 MHz, $CDCl_3$) δ 4.3 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.4 ppm.

HRMS (APCI+) m/z: calcd. for $C_{20}H_{40}BO_2Si^+$ [*M*+H]$^+$: 351.2885, found: 351.2903.

((1*S,2*S**)-1-Cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-vinylpentyl)trimethylsilane (6g)**



Chemical Formula: $C_{22}H_{43}BO_2Si$
Molecular Weight: 378.48

Prepared according to general procedure **GP1** from **5g** (121 mg, 281 µmol) and Me_3SiI (120 µL, 843 µmol).

Yield: 40 mg (106 µmol, 38%) as a partially separable mixture of diastereomers (dr 75:25 as determined by ^{1}H NMR spectroscopy) as a colorless oil.

R*f* = 0.45 (PE/Et_2O 40:1).

Major diastereomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (dt, *J* = 17.0, 10.1 Hz, 1H), 4.96 – 4.80 (m, 2H), 2.44 (t, *J* = 10.5 Hz, 1H), 1.85 – 1.64 (m, 4H), 1.63 – 1.46 (m, 6H), 1.39 – 1.07 (m, 5H), 1.22 (s, 6H), 1.21 (s, 6H), 0.86 (t, *J* = 7.2 Hz, 3H), 0.13 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 114.5, 82.5, 46.7, 42.5, 36.3, 32.8, 31.9, 28.2, 28.0, 26.7, 25.7, 25.3, 21.3, 14.3, 2.7 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{29}Si NMR (80 MHz, $CDCl_3$) δ 3.9 ppm.

Minor diastereomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 (dt, *J* = 17.3, 9.9 Hz, 1H), 4.96 – 4.80 (m, 2H), 2.28 (t, *J* = 10.1 Hz, 1H), 1.85 – 1.64 (m, 4H), 1.63 – 1.46 (m, 6H), 1.39 – 1.07 (m, 5H), 1.24 (s, 6H), 1.22 (s, 6H), 0.85 (t, *J* = 7.2 Hz, 3H), 0.12 (s, 9H) ppm.

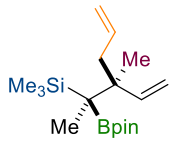
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 113.6, 82.5, 46.3, 42.7, 36.4, 33.4, 30.9, 28.3, 27.8, 26.7, 25.8, 25.6, 21.6, 14.2, 2.0 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{29}Si NMR (80 MHz, $CDCl_3$) δ 5.5 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 33.6 ppm.

HRMS (APCI+) m/z: calcd. for $C_{22}H_{44}BO_2Si^+$ [*M*+H]$^+$: 379.3198, found: 378.3199.

Trimethyl((2*S*,3*S*)-3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-vinylhex-5-en-2-yl)silane (6h)



Chemical Formula: $C_{18}H_{35}BO_2Si$
Molecular Weight: 322.37

Prepared according to general procedure **GP1** from **5h** (41mg, 110 µmol) and Me_3SiCl (70 µL, 550 µmol).

Yield: 12 mg (37 µmol, 34%) as an inseparable mixture of diastereomers (dr 90:10 as determined by ^{1}H NMR spectroscopy) as a colorless oil.

R*f* = 0.35 (PE/Et_2O 40:1).

Major diastereomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.74 – 5.58 (m, 1H), 5.06 – 4.88 (m, 3H), 4.80 (dd, *J* = 17.5, 1.5 Hz, 1H), 2.68 (dd, *J* = 13.6, 5.7 Hz, 1H), 2.12 (dd, *J* = 13.6, 8.5 Hz, 1H), 1.23 (s, 12H), 1.03 (s, 3H), 1.02 (s, 3H), 0.09 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 137.1, 116.0, 112.2, 82.9, 44.3, 29.9, 25.6, 25.2, 20.5, 14.2, 1.1 ppm. *Note*: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{29}Si NMR (80 MHz, $CDCl_3$) δ 3.7 ppm.

Minor diastereomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 (dd, *J* = 16.6, 10.6 Hz, 1H), 5.74 – 5.58 (m, 1H), 5.24 – 5.07 (m, 1H), 5.06 – 4.88 (m, 2H), 4.82 (dd, *J* = 17.6, 1.5 Hz, 1H), 2.37 (dd, *J* = 13.4, 8.7 Hz, 1H), 2.12 (dd, *J* = 13.6, 8.5 Hz, 1H), 1.25 (s, 12H), 1.02 (s, 3H), 1.01 (s, 3H), 0.08 (s, 9H) ppm.

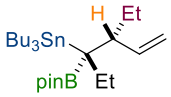
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 136.9, 116.0, 111.9, 82.9, 44.5, 29.9, 25.6, 25.2, 20.2, 14.3, 1.0 ppm. *Note*: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{29}Si NMR (80 MHz, $CDCl_3$) δ 3.3 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.3 ppm.

HRMS (APCI+) m/z: calcd. for $C_{18}H_{36}BO_2Si^+$ $[M+H]^+$: 323.2572, found: 323.2572.

Tributyl((3*R,4*R**)-4-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-3-yl)stannane (6i)**



Chemical Formula: $C_{26}H_{53}BO_2Sn$
Molecular Weight: 527.23

Prepared according to general procedure **GP1** from **5e** (73 mg, 200 µmol) and *n*-Bu_3SnCl (163 µL, 600 µmol).

Yield: 60 mg (114 µmol, 57%) as a partially separable mixture of diastereomers (dr 75:25 as determined by ^{1}H NMR spectroscopy) as a colorless oil.

R*f* = 0.65 (PE/Et_2O 40:1).

Major diastereomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.58 (dt, *J* = 17.1, 9.9 Hz, 1H), 5.04 – 4.82 (m, 2H), 2.25 – 2.14 (m, 1H), 1.90 – 1.71 (m, 2H), 1.67 – 1.58 (m, 1H), 1.56 – 1.38 (m, 6H), 1.31 (ddt, *J* = 10.4, 7.3, 3.3 Hz, 6H), 1.24 – 1.15 (m, 1H), 1.21 (s, 6H), 1.19 (s, 6H), 0.94 – 0.83 (m, 18H), 0.82 (t, *J* = 7.2 Hz, 3H) ppm.

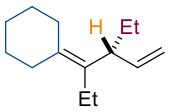
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 114.8, 82.3, 49.4, 29.48, 28.2, 27.8, 25.6, 25.0, 23.7, 13.8, 13.3, 13.0, 10.9 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

Minor diastereomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (dt, *J* = 17.1, 10.0 Hz, 1H), 5.02 – 4.92 (m, 2H), 2.25 – 2.14 (m, 1H), 1.90 – 1.71 (m, 2H), 1.67 – 1.58 (m, 1H), 1.56 – 1.38 (m, 6H), 1.31 (ddt, *J* = 10.4, 7.3, 3.3 Hz, 6H), 1.24 – 1.15 (m, 1H), 1.21 (s, 6H), 1.19 (s, 6H), 0.94 – 0.83 (m, 18H), 0.80 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 114.6, 82.3, 49.1, 29.51, 28.2, 27.9, 25.6, 25.0, 23.7, 14.0, 13.6, 13.0, 11.1 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ 33.6 ppm.

(4-Ethylhex-5-en-3-ylidene)cyclohexane (6j)



Chemical Formula: $C_{14}H_{24}$
Molecular Weight: 192.35

Prepared according to general procedure **GP1** from **5e** (55 mg, 150 µmol) and cyclohexanone (79 µL, 750 µmol). The reaction mixture was and stirred overnight at rt before being quenched by MeOH.

Yield: 16 mg (84 µmol, 56%) as a colorless oil.

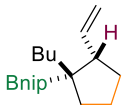
R*f* = 0.75 (PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (ddd, *J* = 17.2, 10.6, 6.8 Hz, 1H), 4.98 (dt, *J* = 8.3, 1.4 Hz, 1H), 4.94 (d, *J* = 1.3 Hz, 1H), 3.15 (q, *J* = 6.8 Hz, 1H), 2.16 (dddd, *J* = 24.7, 20.5, 13.0, 4.9 Hz, 4H), 1.96 (q, *J* = 7.5 Hz, 2H), 1.64 – 1.46 (m, 4H), 1.42 (dq, *J* = 20.9, 7.5 Hz, 4H), 0.93 (t, *J* = 7.5 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 135.0, 132.1, 113.4, 47.2, 31.3, 30.6, 28.8, 28.7, 27.3, 25.5, 21.4, 15.7, 12.5 ppm.

HRMS (APCI+) m/z: calcd. for $C_{14}H_{23}$ $[M–H]^+$: 191.1794, found: 191.1794.

2-((1*R,2*S**)-1-Butyl-2-vinylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6k)**



Chemical Formula: $C_{17}H_{31}BO_2$
Molecular Weight: 278.24

Prepared according to general procedure **GP1** from **5i** (66 mg, 150 µmol).

Yield: 35 mg (126 µmol, 84%, dr >95:05 as determined by ^{1}H NMR spectroscopy) as a colorless oil.

R*f* = 0.50 (PE/Et_2O 40:1).

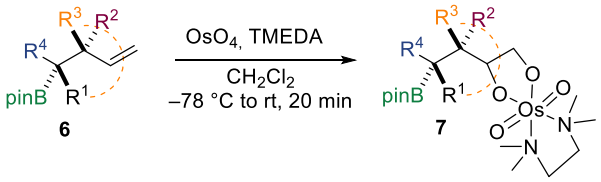
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (ddd, *J* = 17.1, 10.0, 8.8 Hz, 1H), 5.05 – 4.94 (m, 1H), 4.90 (dd, *J* = 10.1, 2.1 Hz, 1H), 2.07 (q, *J* = 8.8 Hz, 1H), 1.95 (ddd, *J* = 12.8, 8.5, 4.8 Hz, 1H), 1.79 (td, *J* = 8.4, 4.7 Hz, 2H), 1.62 (dddd, *J* = 19.4, 16.4, 9.4, 4.7 Hz, 2H), 1.52 – 1.43 (m, 1H), 1.31 – 1.25 (m, 6H), 1.22 (s, 6H), 1.21 (s, 6H), 0.87 (t, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 113.7, 83.0, 55.8, 38.2, 34.4, 32.0, 29.9, 25.2, 24.9, 23.8, 23.0, 14.3 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

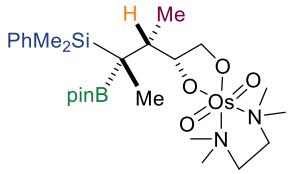
^{11}B NMR (128 MHz, $CDCl_3$): δ 34.6 ppm.

HRMS (APCI+) m/z: calcd. for $C_{17}H_{32}BO_2^+$ [*M*+H]$^+$: 279.2490, found: 279.2498.

4. Determination of the stereochemical outcome



Dioxo[*N*,*N*,*N*,*N*-tetramethylethane-1,2-diaminetetramethylehylendiamine][(2*R,3*R**,4*R**)-4-(dimethyl(phenyl)silyl)-3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentane-1,2-diol]osmium complex (7b)**



Chemical Formula: $C_{26}H_{49}BN_2O_6OsSi$
Molecular Weight: 714.81

Prepared by according to a literature procedure[5] from **6b** (36 mg, 105 µmol).

Yield: 75 mg (105 µmol, quantitative; dr >95:05 as determined by ^{1}H NMR spectroscopy) as a dark red solid.

R*f* = 0.30 (DCM/MeOH 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 6.4, 2.9 Hz, 2H), 7.27 (dd, *J* = 5.3, 2.7 Hz, 3H), 4.53 (ddd, *J* = 10.7, 6.2, 4.5 Hz, 1H), 4.14 (dd, *J* = 9.7, 4.4 Hz, 1H), 4.05 (t, *J* = 10.2 Hz, 1H), 3.02 (ddd, *J* = 24.1, 19.7, 12.1 Hz, 4H), 2.82 (s, 6H), 2.81 (s, 3H), 2.79 (s, 3H), 2.51 (p, *J* = 7.0 Hz, 1H), 1.23 (s, 3H), 1.12 (s, 6H), 1.08 (d, *J* = 7.1 Hz, 3H), 0.98 (s, 6H), 0.53 (s, 3H), 0.37 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 135.2, 128.4, 127.3, 91.6, 83.3, 82.8, 64.6, 64.1, 52.2, 51.9, 51.4, 51.1, 40.1, 25.5, 25.2, 16.4, 13.8, -1.7, -2.4 ppm.

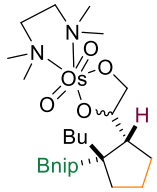
^{11}B NMR (128 MHz, $CDCl_3$): δ 36.2 ppm.

^{29}Si NMR (80 MHz, $CDCl_3$) δ -0.9 ppm.

HRMS (APCI+) m/z: calcd. for $C_{26}H_{50}BN_2O_6OsSi^+$ [*M*+H]$^+$: 717.3141, found: 717.3126.

Recrystallization by vapour diffusion (THF with pentane as antisolvent) yielded X-ray quality crystals.

Dioxo[*N*,*N*,*N*,*N*-tetramethylethane-1,2-diaminetetramethylehylendiamine][(1-((1*R,2*R**)-2-butyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)ethane-1,2-diol]osmium complex (7k)**



Chemical Formula: $C_{23}H_{47}BN_2O_6Os$
Molecular Weight: 648.68

Prepared by according to a literature procedure[5] from **6k** (28 mg, 90 µmol).

Yield: 58 mg (89 µmol, quantitative) as a partially separable mixture of diastereomers (dr 75:25 as determined by ^{1}H NMR spectroscopy) as a dark red solid.

R*f* = 0.35 (DCM/MeOH 9:1).

Major diastereomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.50 – 4.43 (m, 1H), 4.37 (dd, *J* = 9.8, 4.7 Hz, 1H), 4.13 – 4.05 (m, 1H), 3.14 – 2.97 (m, 4H), 2.87 – 2.81 (m, 12H), 2.17 (q, *J* = 7.2 Hz, 1H), 1.99 – 1.77 (m, 3H), 1.73 – 1.55 (m, 4H), 1.55 – 1.45 (m, 1H), 1.45 – 1.37 (m, 1H), 1.32 – 1.15 (m, 3H), 1.22 (s, 6H), 1.20 (s, 6H), 0.85 (t, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 91.7, 85.1, 82.9, 64.4, 64.2, 52.2, 52.0, 51.3, 51.3, 51.1, 38.7, 34.4, 29.5, 28.6, 25.2, 25.1, 23.9, 23.8, 14.3 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

Minor diastereomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.45 – 4.40 (m, 1H), 4.25 (dd, *J* = 9.7, 4.4 Hz, 1H), 3.97 (t, *J* = 9.1 Hz, 1H), 3.14 – 2.97 (m, 4H), 2.87 – 2.81 (m, 12H), 2.17 (q, *J* = 7.2 Hz, 1H), 1.99 – 1.77 (m, 3H), 1.73 – 1.55 (m, 4H), 1.55 – 1.45 (m, 1H), 1.45 – 1.37 (m, 1H), 1.32 – 1.15 (m, 3H), 1.18 (s, 12H), 0.84 (t, *J* = 7.5 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 93.3, 85.9, 82.4, 64.5, 64.2, 52.5, 52.4, 51.6, 51.0, 50.9, 39.4, 35.5, 31.4, 29.0, 25.3, 24.8, 24.7, 24.1, 14.4 ppm.
Note: Carbon atom attached to boron is not visible due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ 36.5 ppm.

HRMS (APCI+) m/z: calcd. for $C_{23}H_{48}BN_2O_6Os^+$ [*M*+H]$^+$: 651.3215, found: 651.3229.

Recrystallization by vapour diffusion (DCM/Et_2O 1:3 with pentane as antisolvent) yielded X-ray quality crystals.

Crystal structures of 7b and 7k
The single crystal of light brown plate (**7b**, Marek15R) from THF/pentane and the single crystal of light brown plate (**7k**, Marek44R) from Et_2O/DCM/pentane, in Paratone–N oil and mounted on a Rigaku Oxford Diffraction - XtaLAB Synergy-S at 100 K. Data collection was performed using monochromated Mo Kα radiation, λ = 0.71073 Å. Accurate cell parameters were obtained with the amount of indicated reflections. Using Olex2[6], the structure was solved with the olex2.solve[7] structure solution program using Charge Flipping and refined with the ShelXL[8] refinement package using Least Squares minimisation. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically in calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the

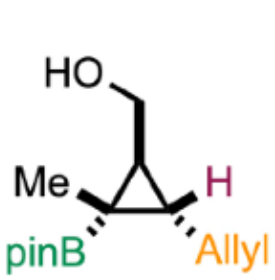
U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Software used for molecular graphics: Mercury 2022.3.0.[9]

Crystal structure determination of 7b and 7k

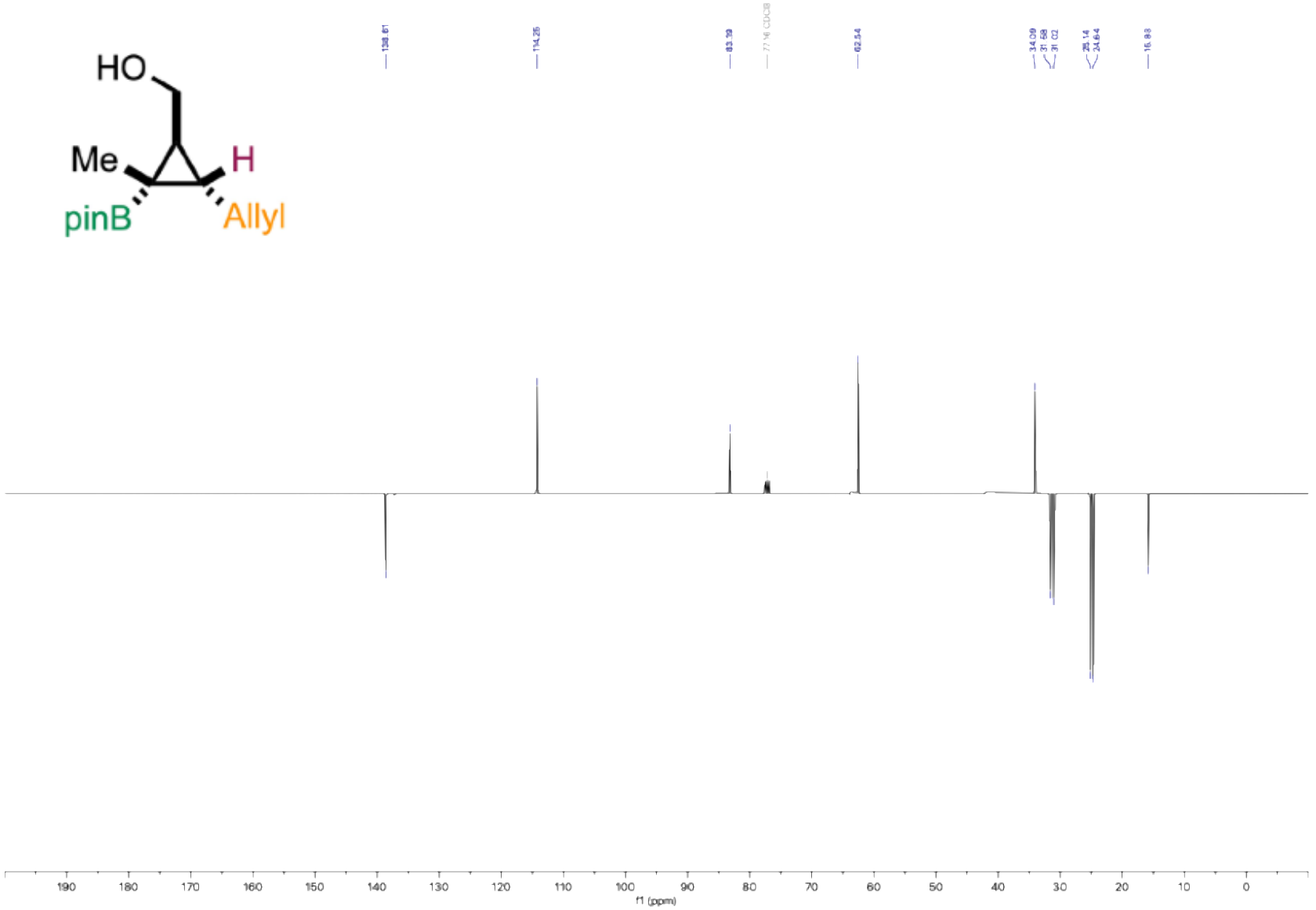
Crystal data	Marek15R (**7b**)	Marek44R (**7k**)
CCDC code	**2537818**	**2537817**
Empirical formula	$C_{26}H_{49}BClN_2O_6OsSi$	$C_{46}H_{94}B_2N_4O_{12}Os_2$
Formula weight	750.22	1297.34
Temperature (K)	100.15	100.15
Wavelength (Å)	0.71073	0.71073
Crystal system,	triclinic	triclinic
space group	P-1	P-1
a (Å)	9.35848(18)	9.9793(6)
b (Å)	12.2804(3)	12.4650(6)
c (Å)	29.0612(6)	21.9750(13)
alpha	84.4348(18)	87.307(4)
beta	85.4484(17)	84.945(5)
gamma	89.9944(17)	89.968(4)
Volume ($Å^3$)	3313.57(12)	2719.9(3)
Z	4	2
Calculated density (mg/m^3)	1.504	1.584
Absorption coefficient (mm^{-1})	4.003	4.726
F(000)	1516	1312
Crystal size (mm)	0.24 × 0.18 × 0.15	0.18 × 0.18 × 0.09
2Theta range	4.574 - 59.82	4.648 - 60.3
Reflection collected/unique	47960 / 15023	34192 / 12525
Rint	0.0605	0.0832
Completeness (%)	98.9	99.8
Absorption correction	semi-empirical	semi-empirical
Data/restraints/ parameters	15023 / 1164 / 814	12525 / 626 / 614
Goodness-of-fit on F^2	1.030	1.033
R1, wR2 [I>2sigma(I)]	0.0615, 0.1629	0.0668, 0.1658
R1, wR2 (all data)	0.0765, 0.1728	0.0928, 0.1804
Largest diff. peak and hole	3.73/-3.15	3.04/-2.40
Diffractometer	XtaLAB Synergy-S	XtaLAB Synergy-S

5. NMR spectra

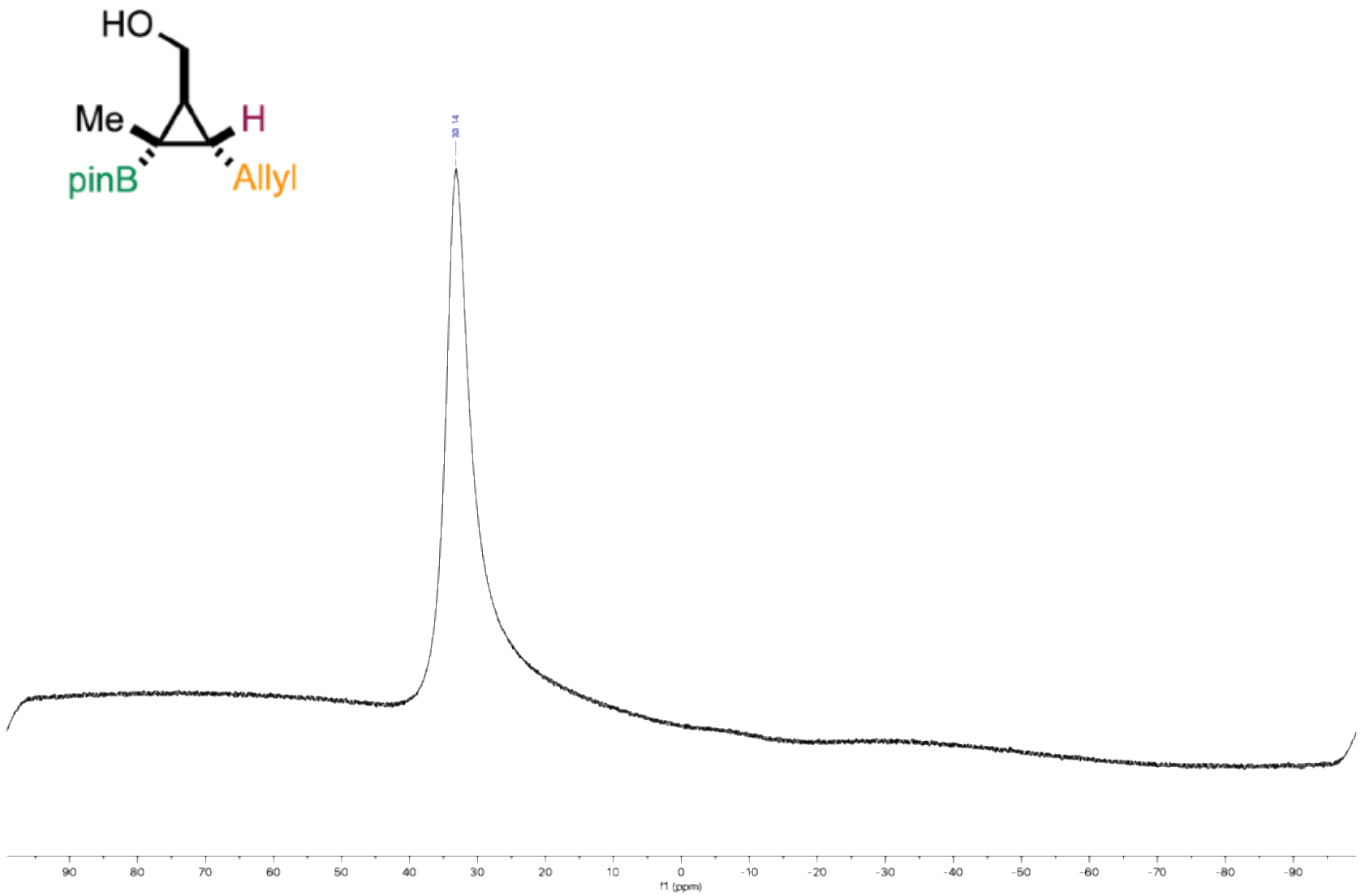
((1*S,2*R**,3*S**)-3-Allyl-2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)methanol (5b-OH)**



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

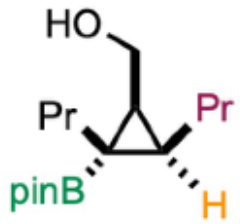


^{13}C NMR spectrum (101 MHz, $CDCl_3$)

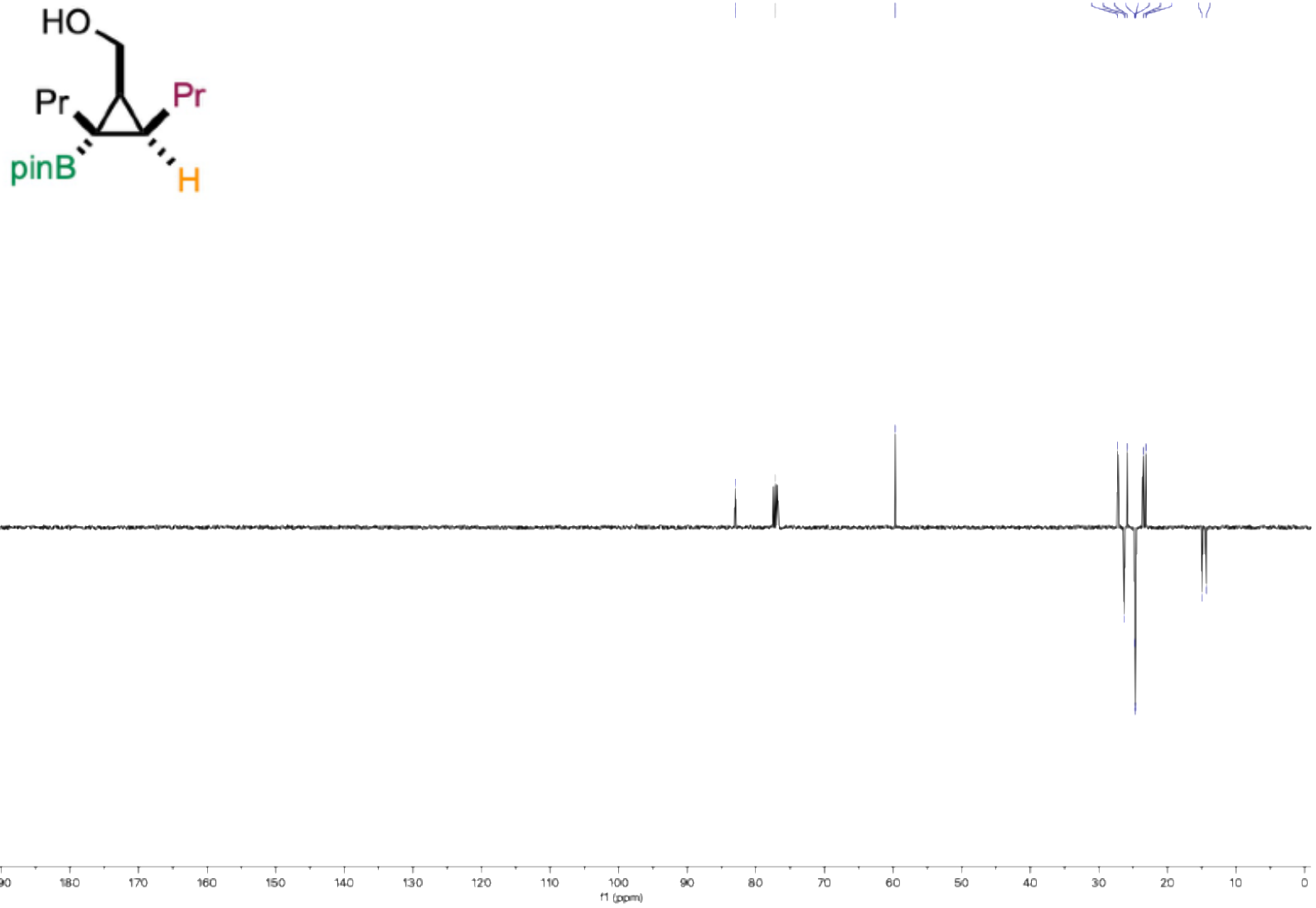


^{11}B NMR spectrum (128 MHz, $CDCl_3$)

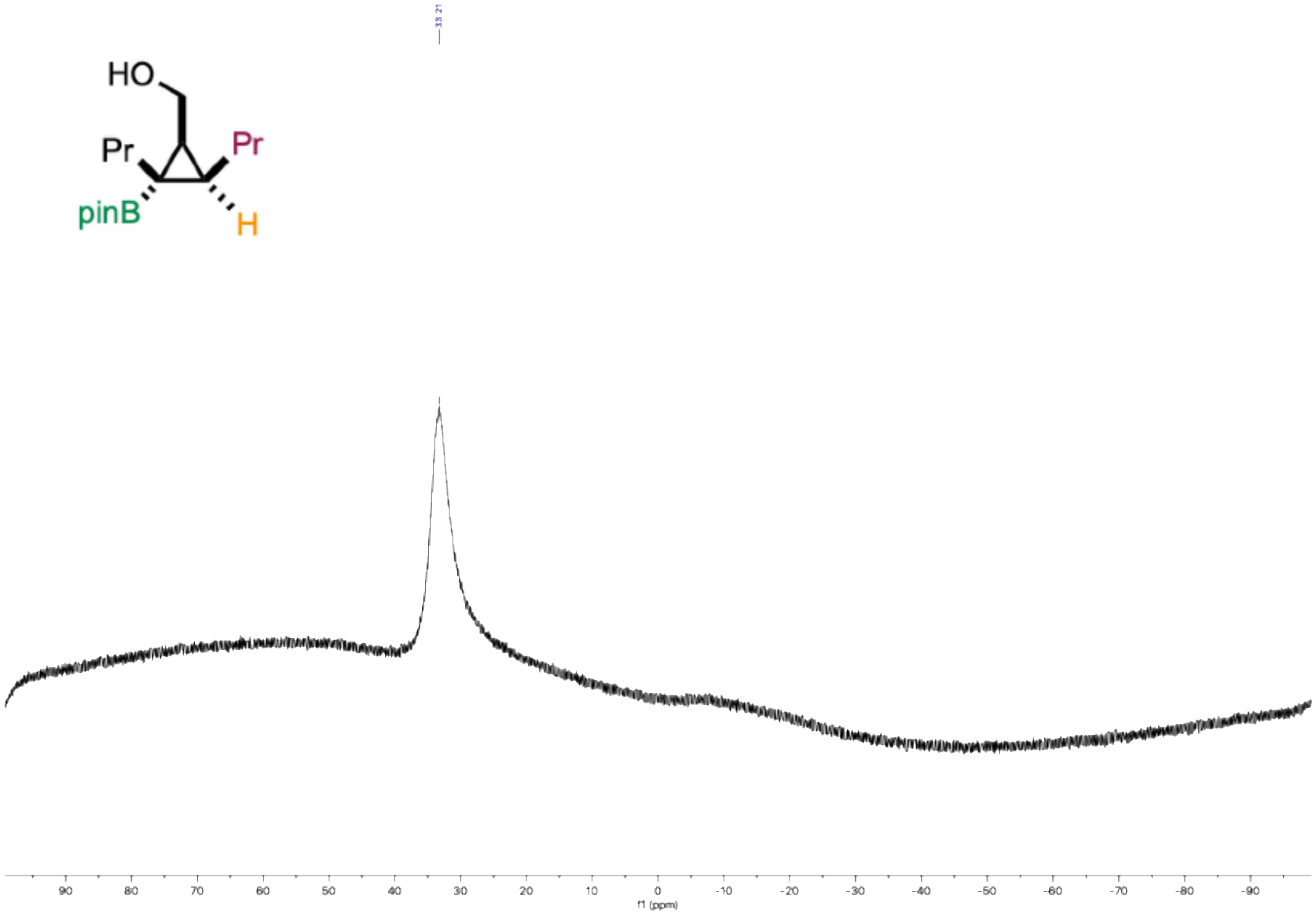
((1*S,2*R**,3*R**)-2,3-dipropyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)methanol**
5c-OH



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

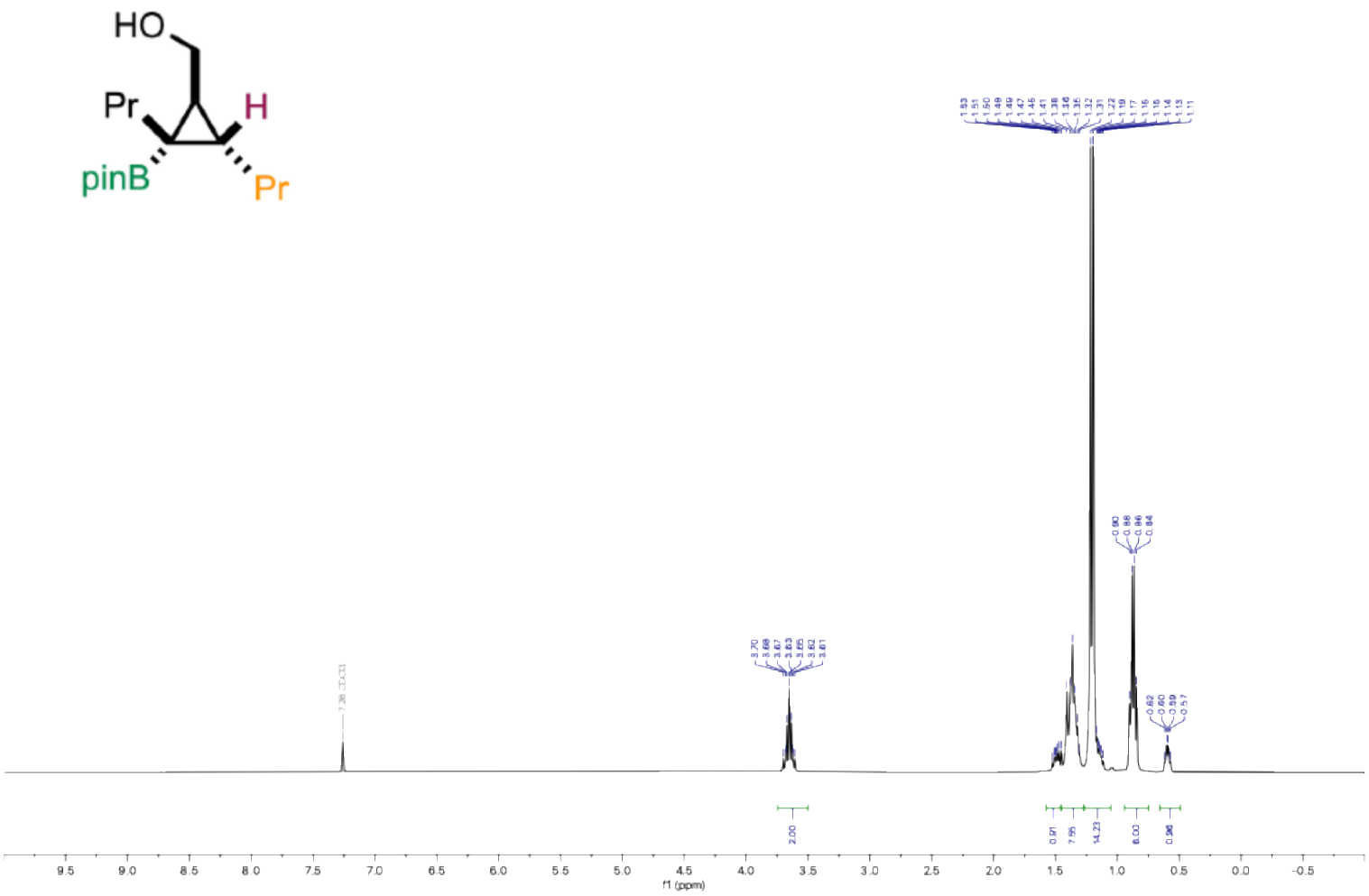


^{13}C NMR spectrum (101 MHz, $CDCl_3$)

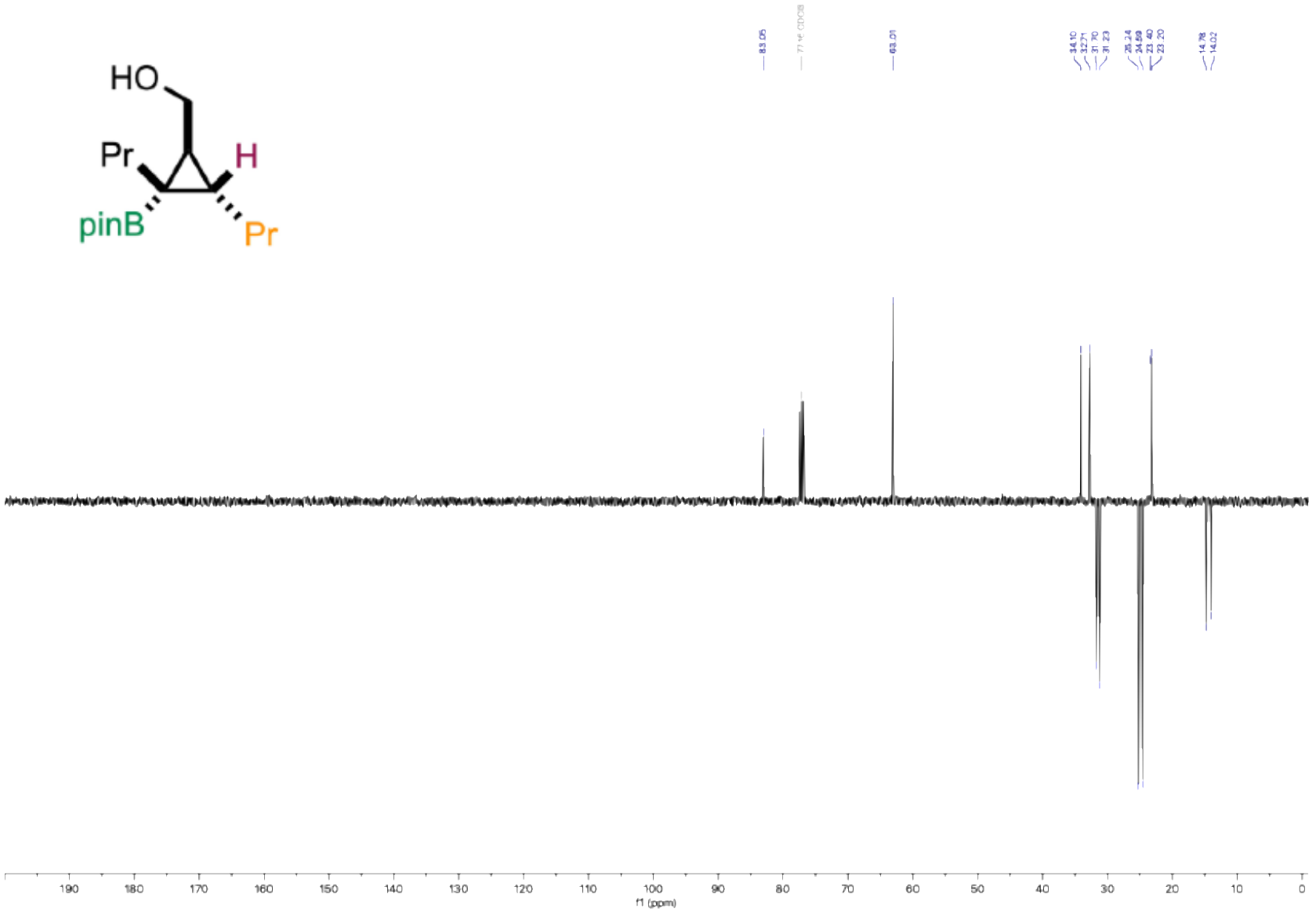


^{11}B NMR spectrum (128 MHz, $CDCl_3$)

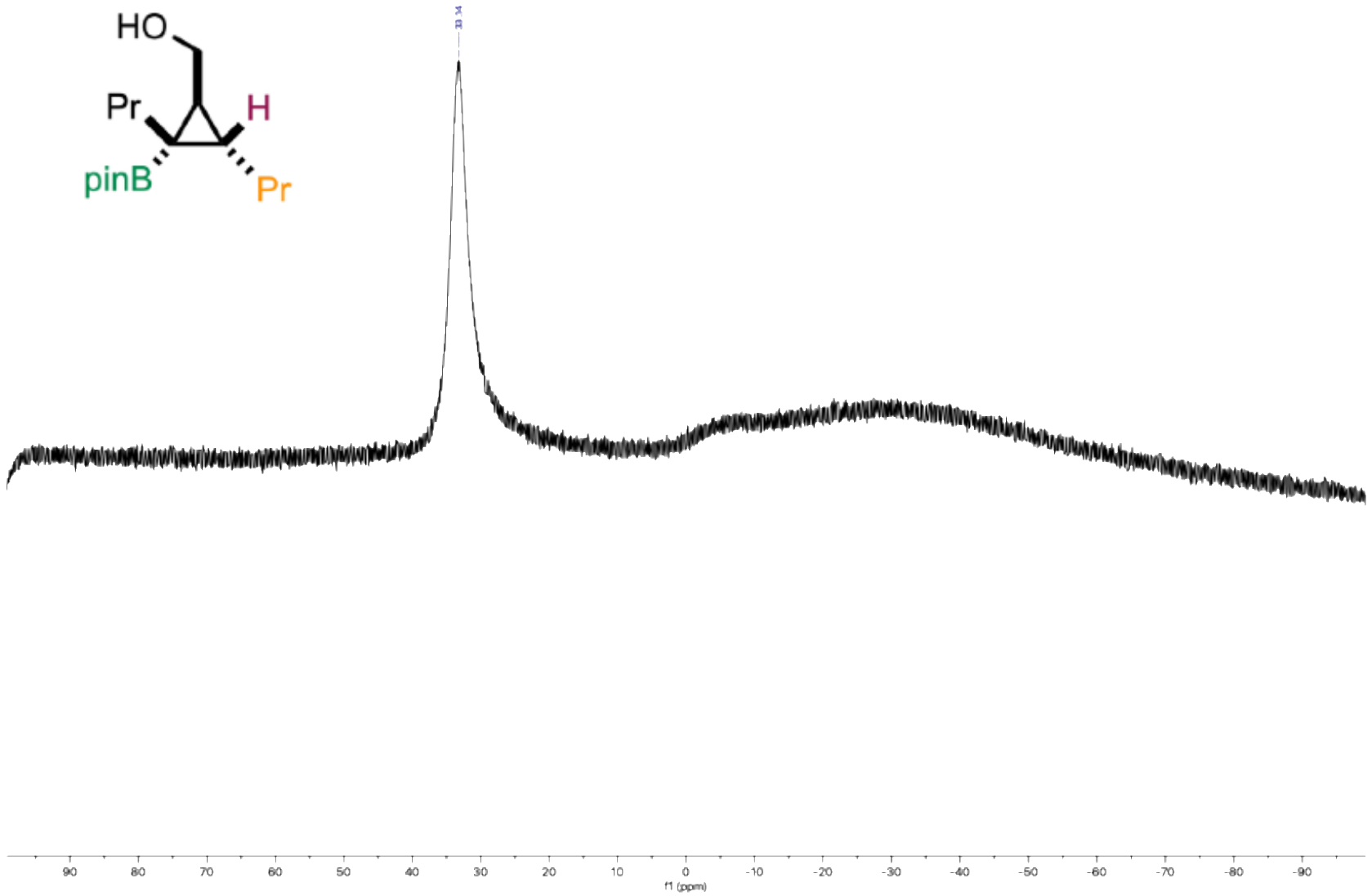
((1*S,2*R**,3*S**)-2,3-Dipropyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)methanol (5d-OH)**



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

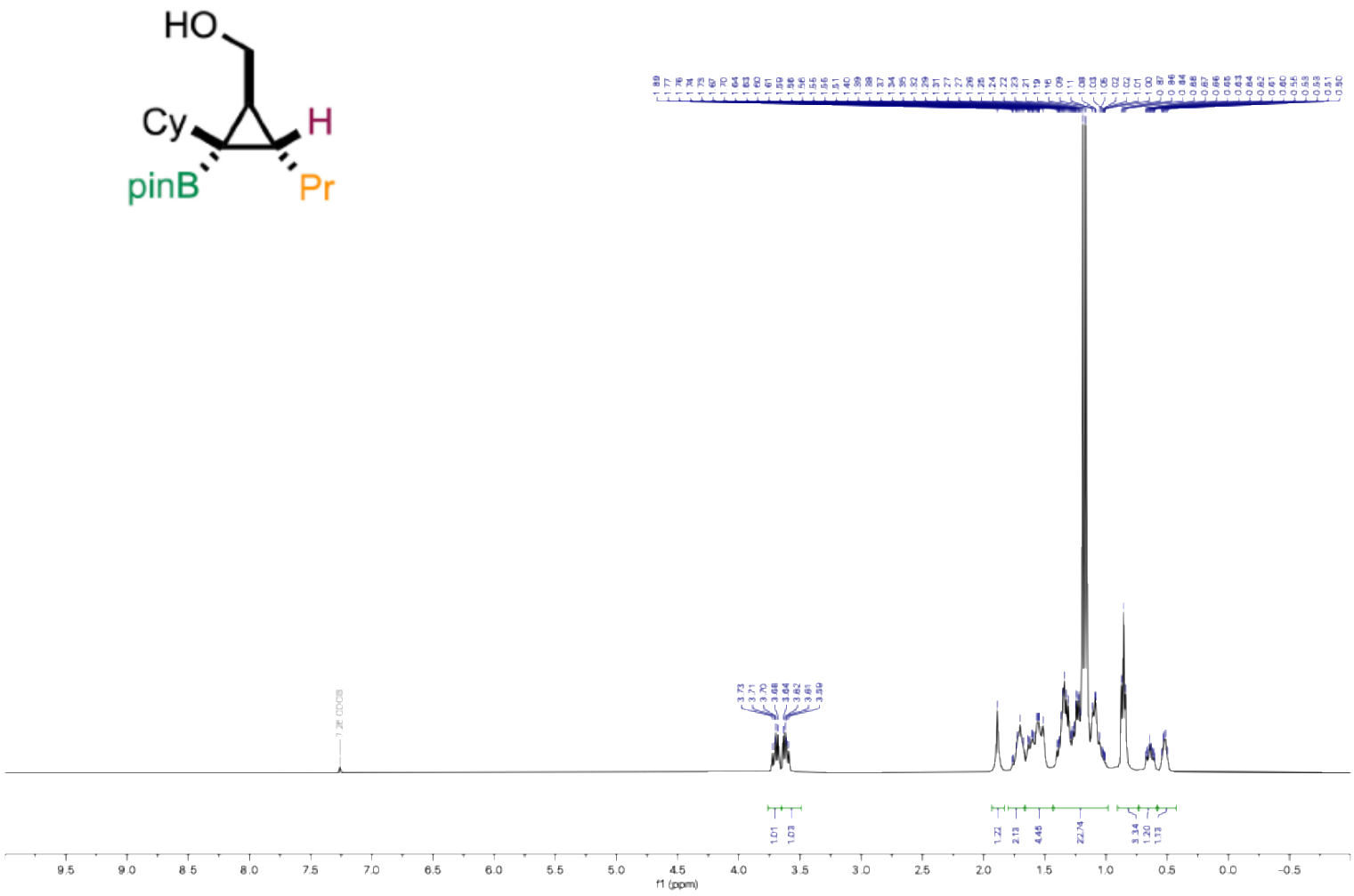


^{13}C NMR spectrum (101 MHz, $CDCl_3$)

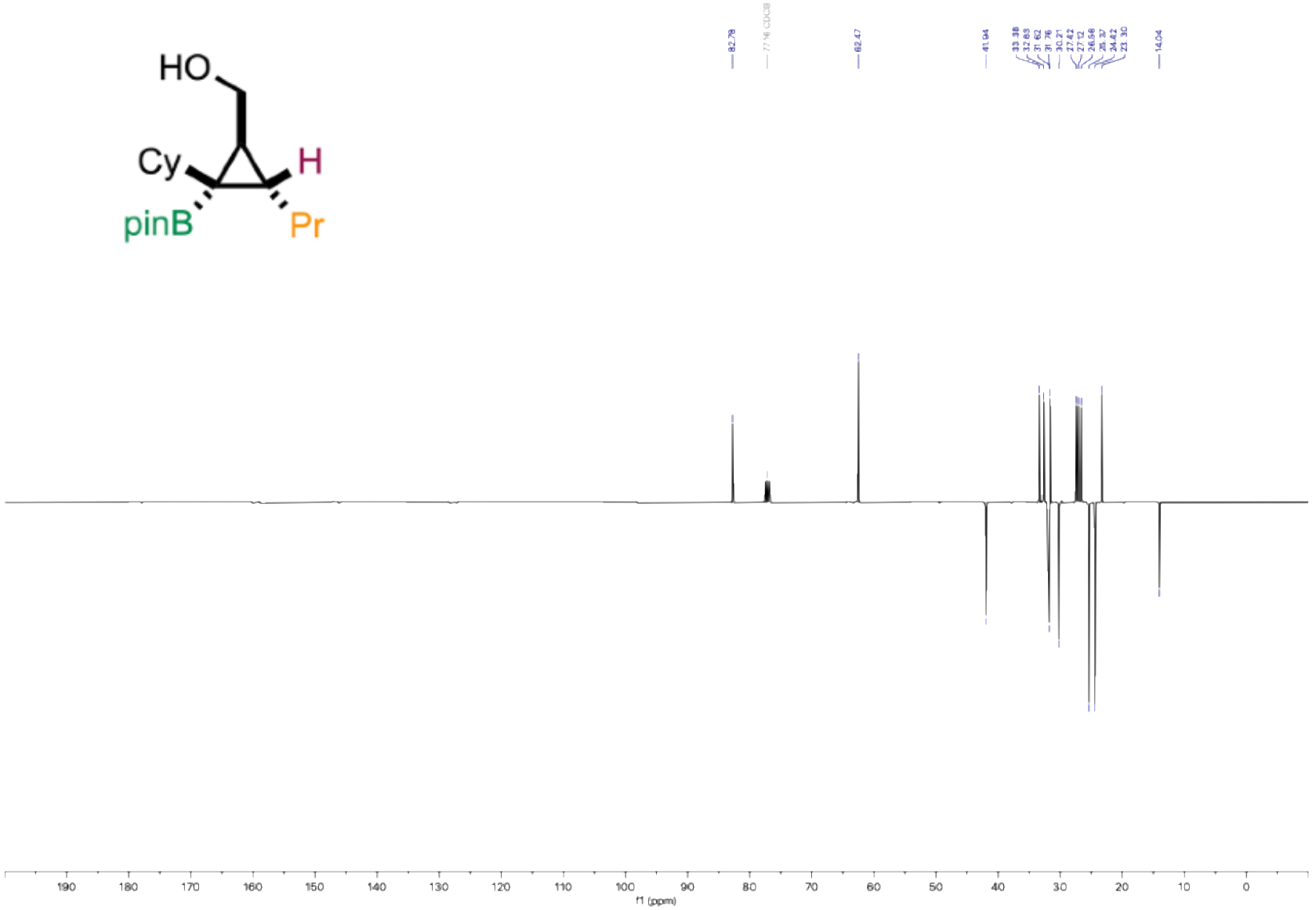


^{11}B NMR spectrum (128 MHz, $CDCl_3$)

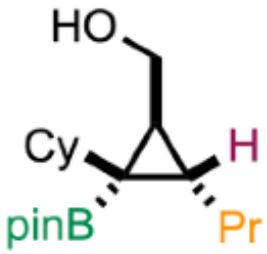
((1*S,2*R**,3*S**)-2-Cyclohexyl-3-propyl-2- (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)methanol (5g-OH)**

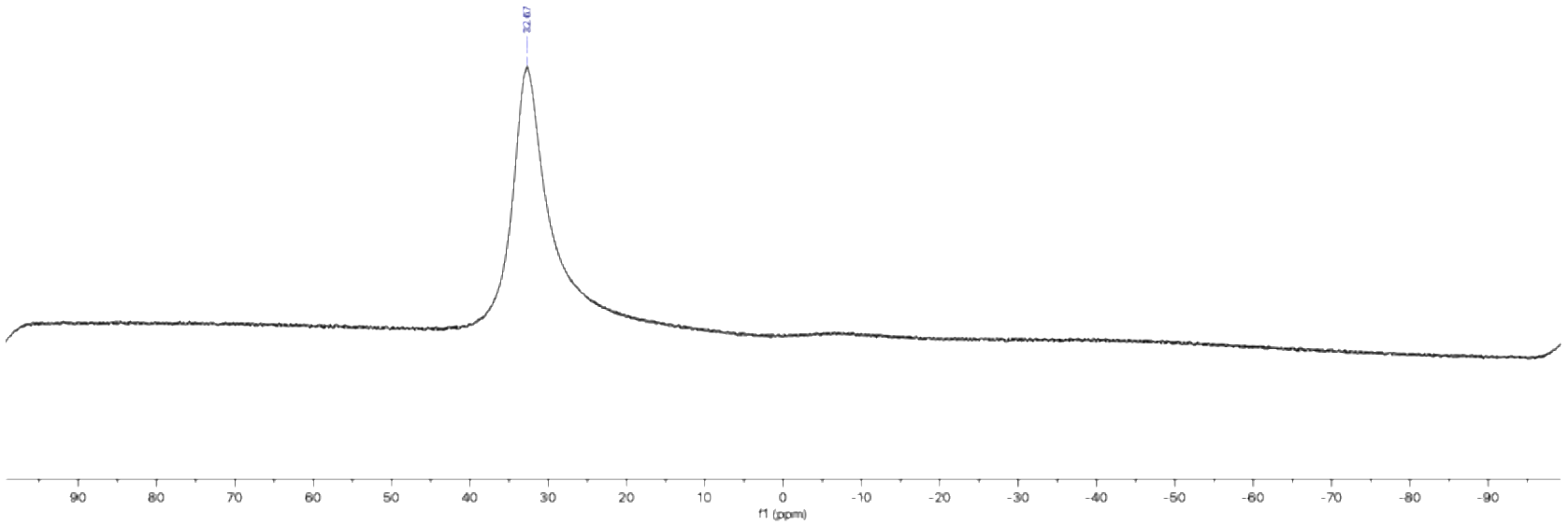


^{1}H NMR spectrum (400 MHz, $CDCl_3$)



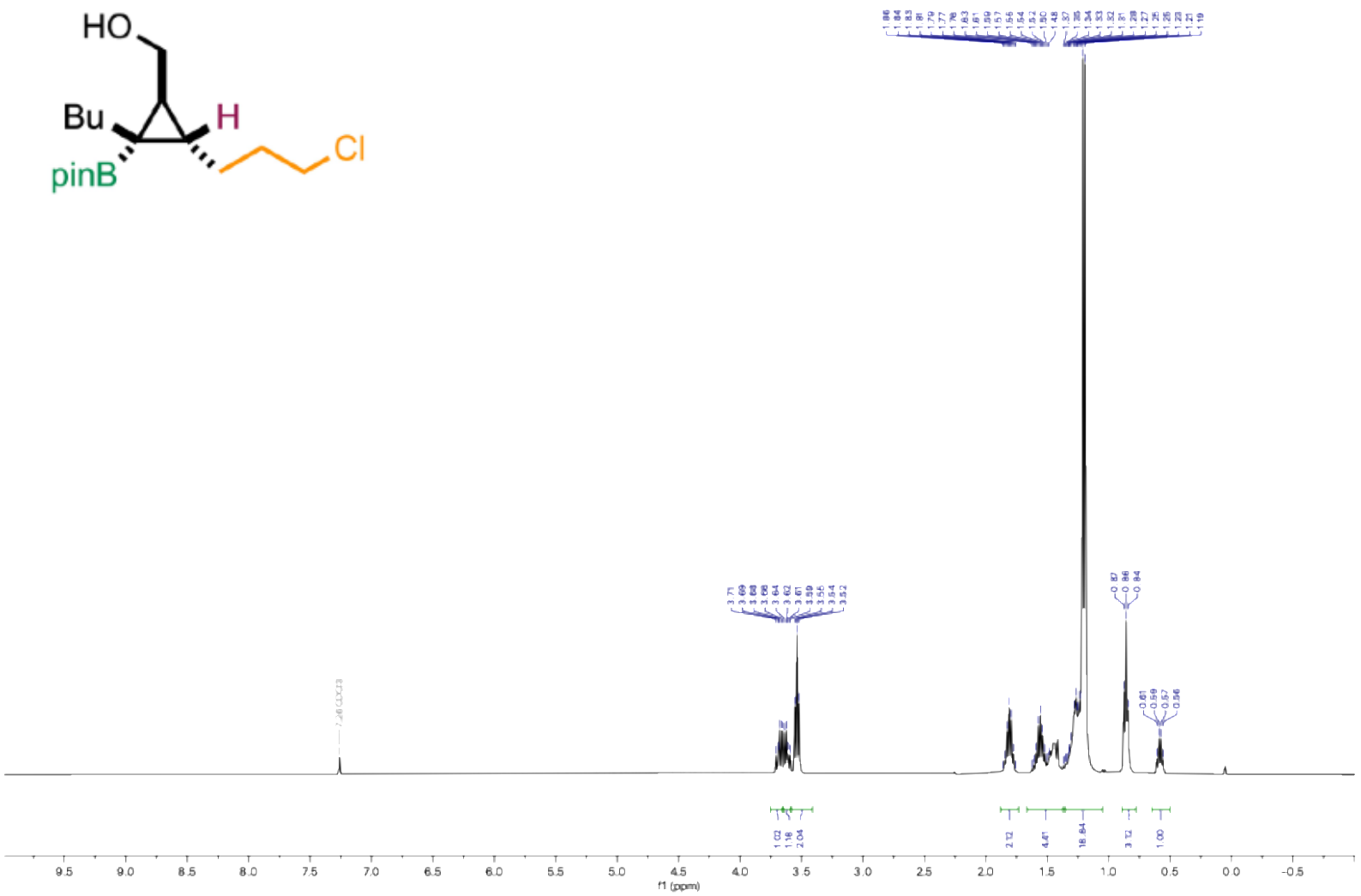
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



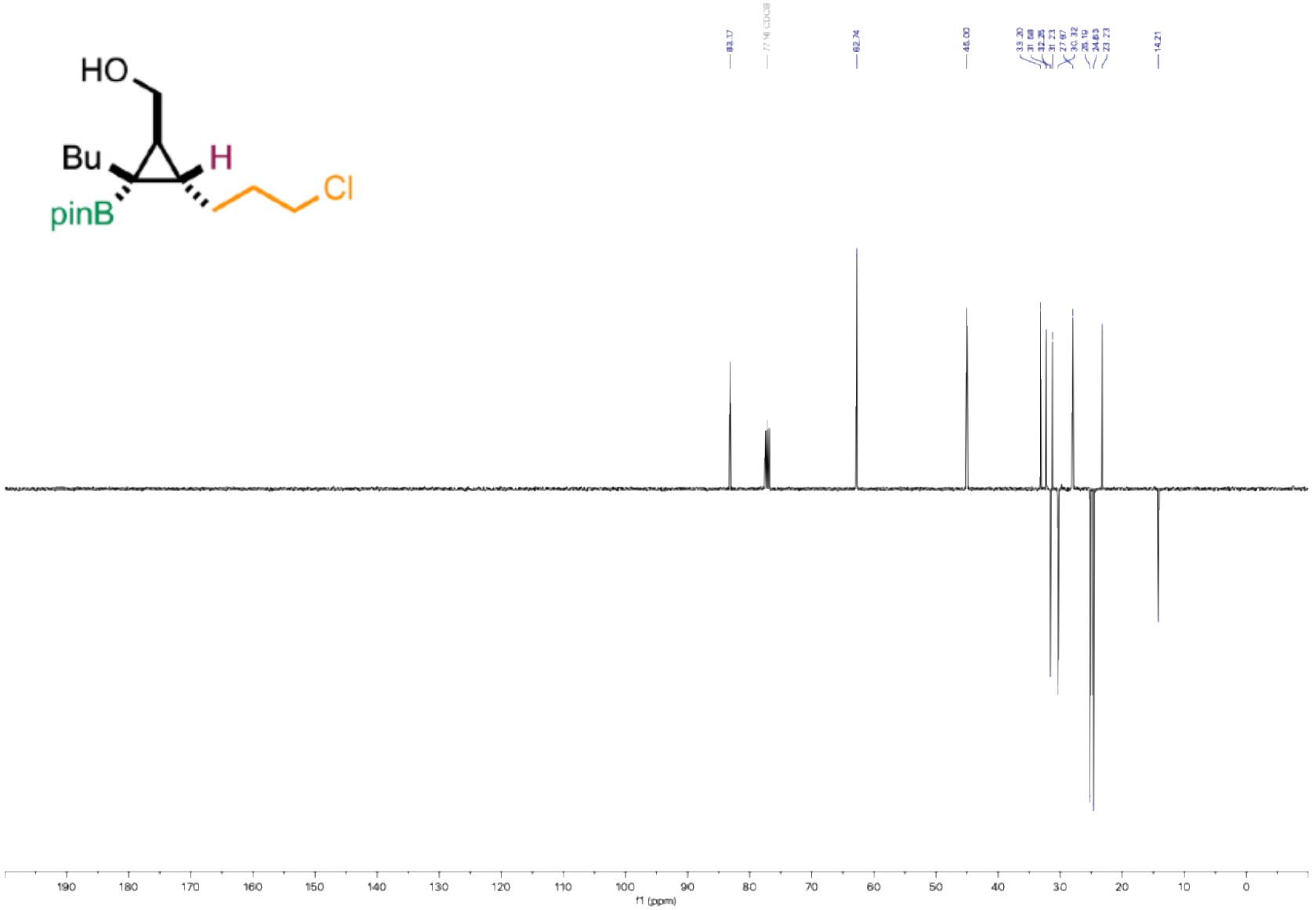


^{11}B NMR spectrum (128 MHz, $CDCl_3$)

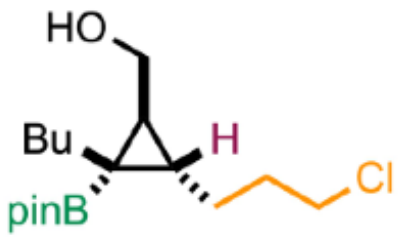
((1*S,2*R**,3*S**)-2-Butyl-3-(3-chloropropyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)methanol (5i-OH)**

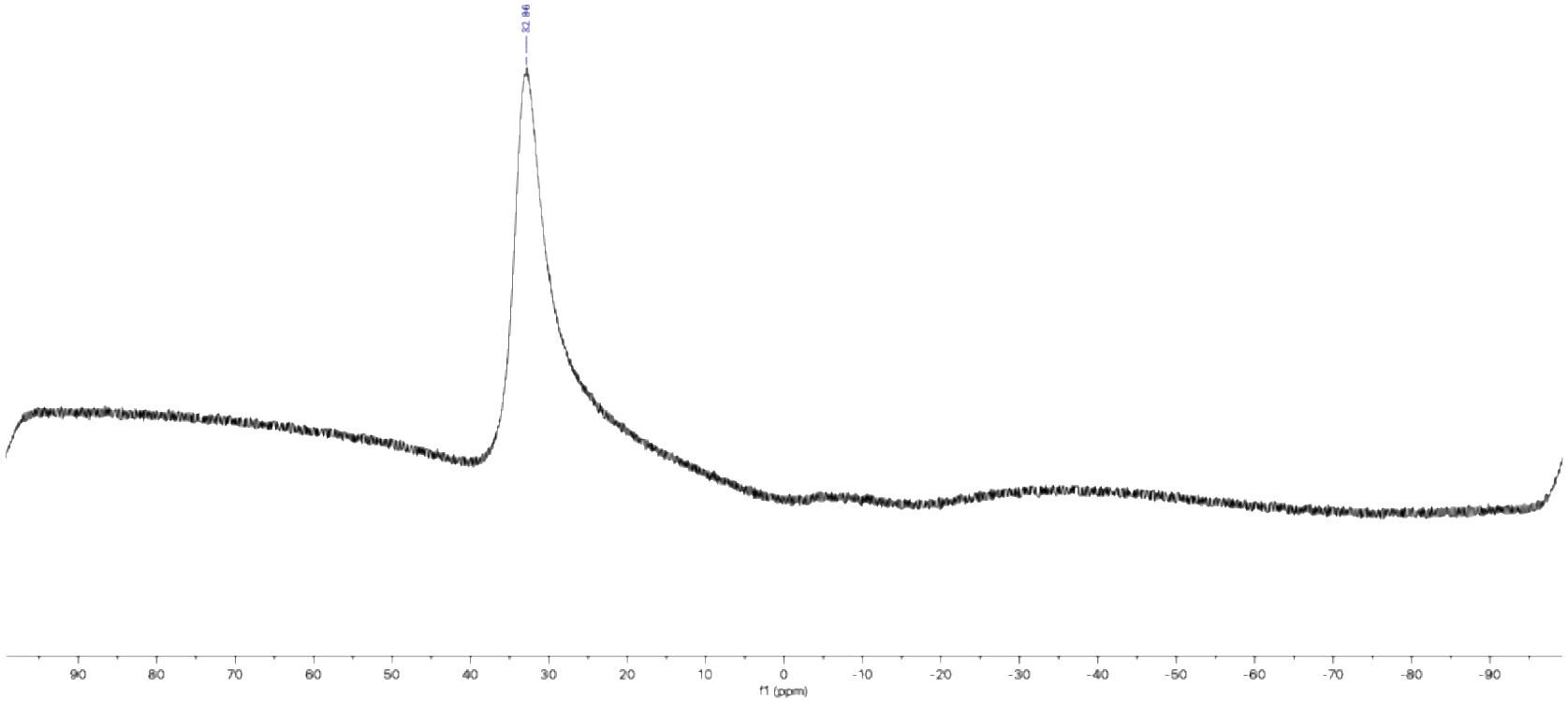


^{1}H NMR spectrum (400 MHz, $CDCl_3$)



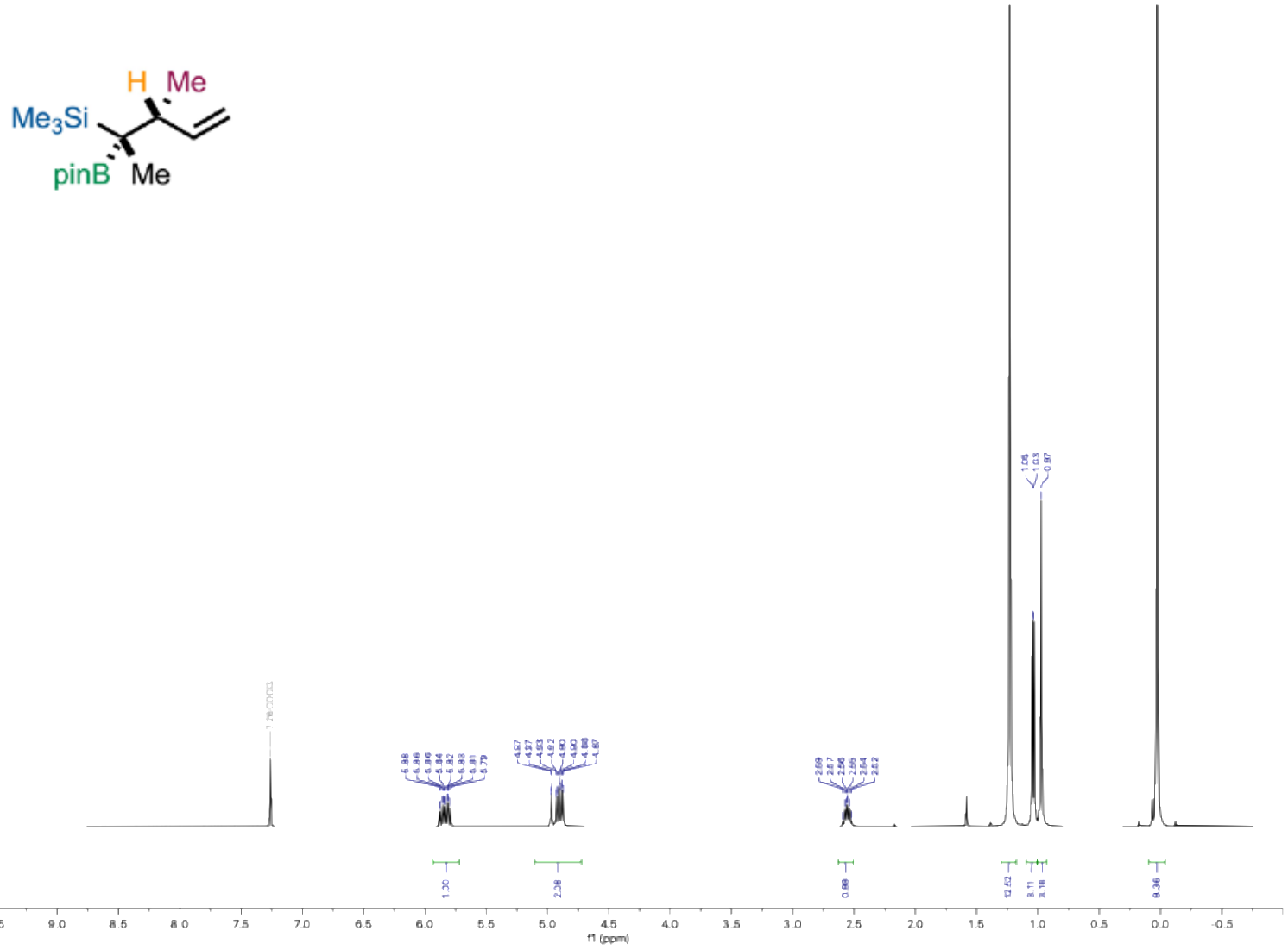
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



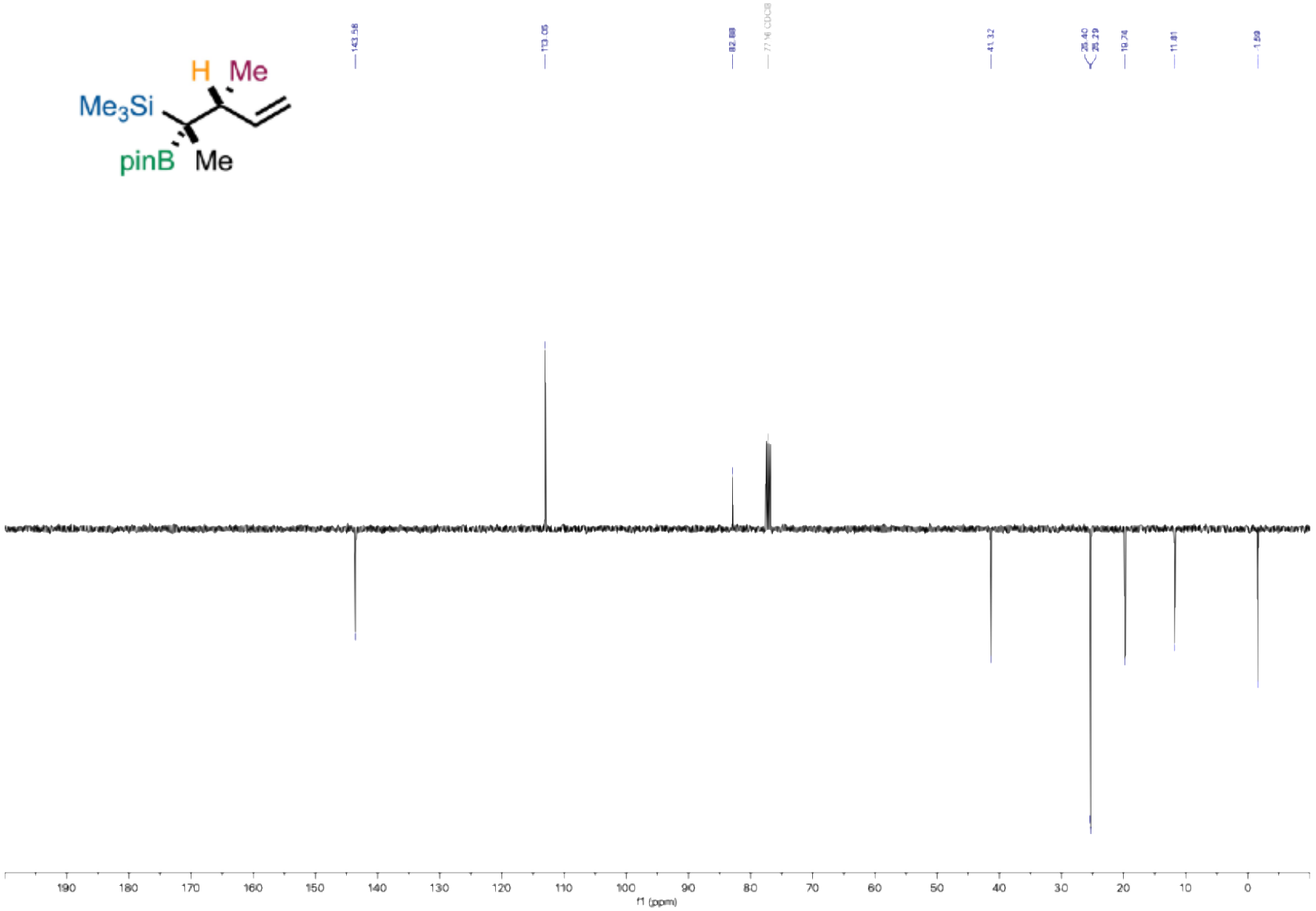


^{11}B NMR spectrum (128 MHz, $CDCl_3$)

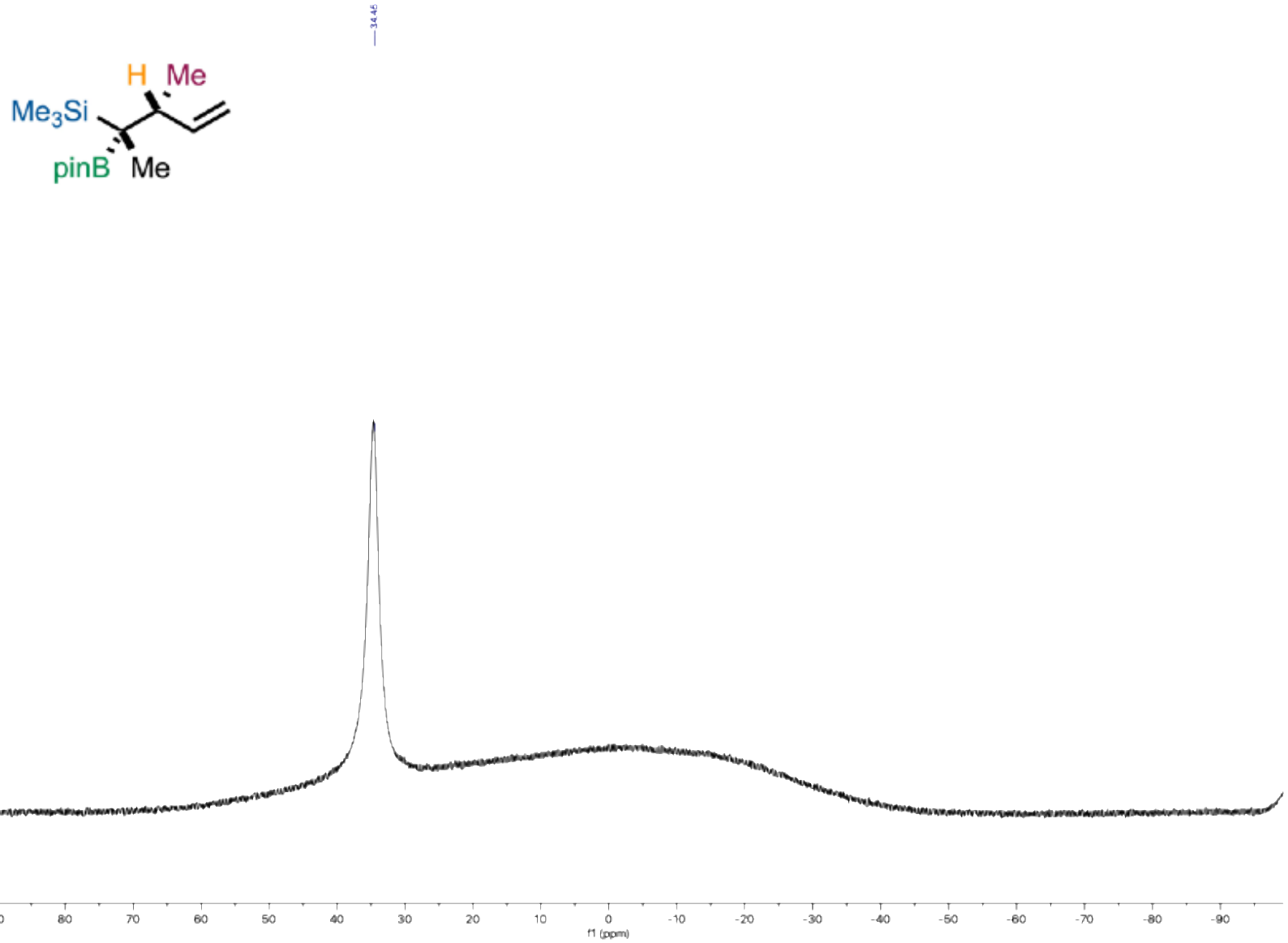
Trimethyl((2*R,3*R**)-3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-2-yl)silane (6a)**



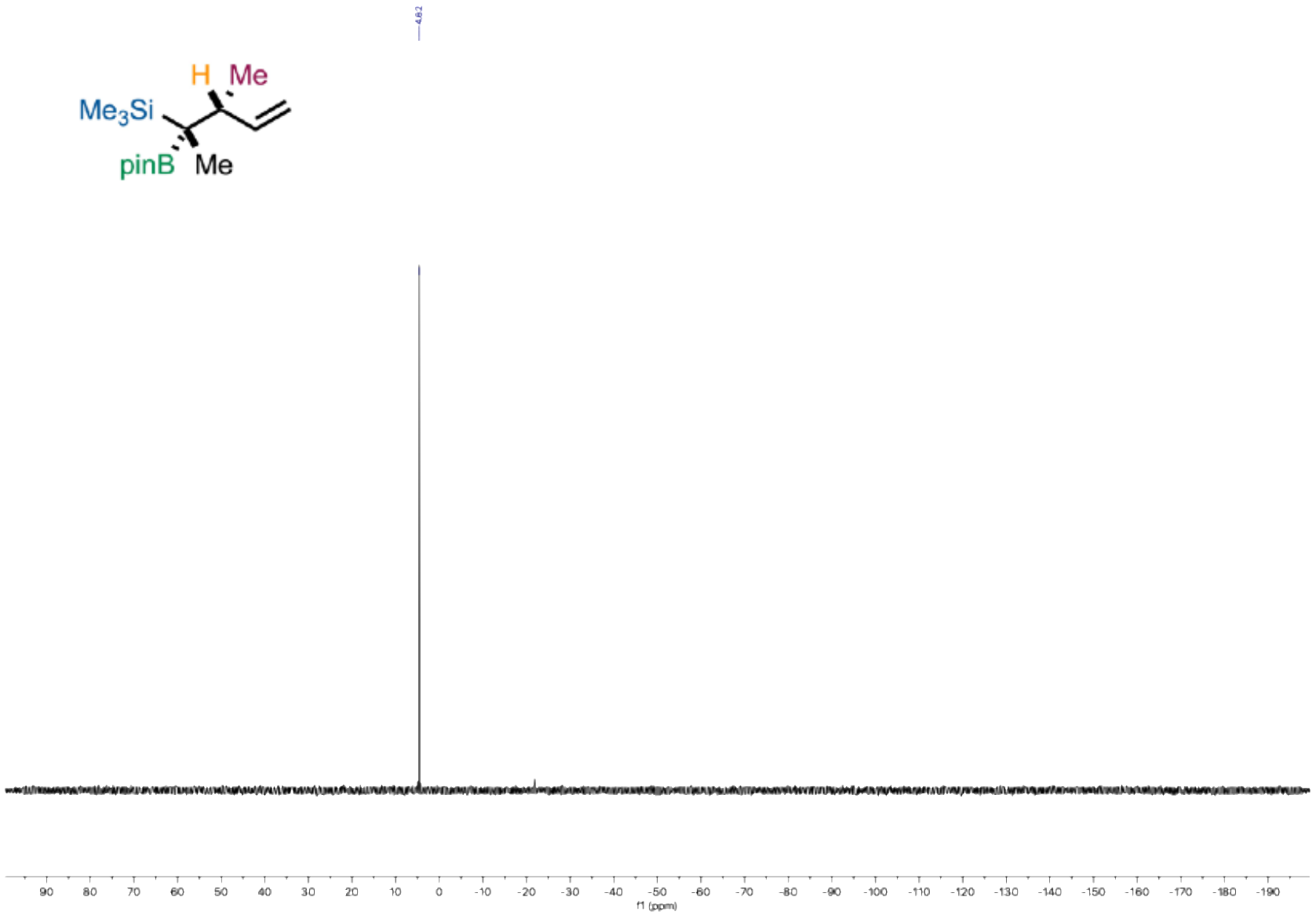
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



^{13}C NMR spectrum (101 MHz, $CDCl_3$)

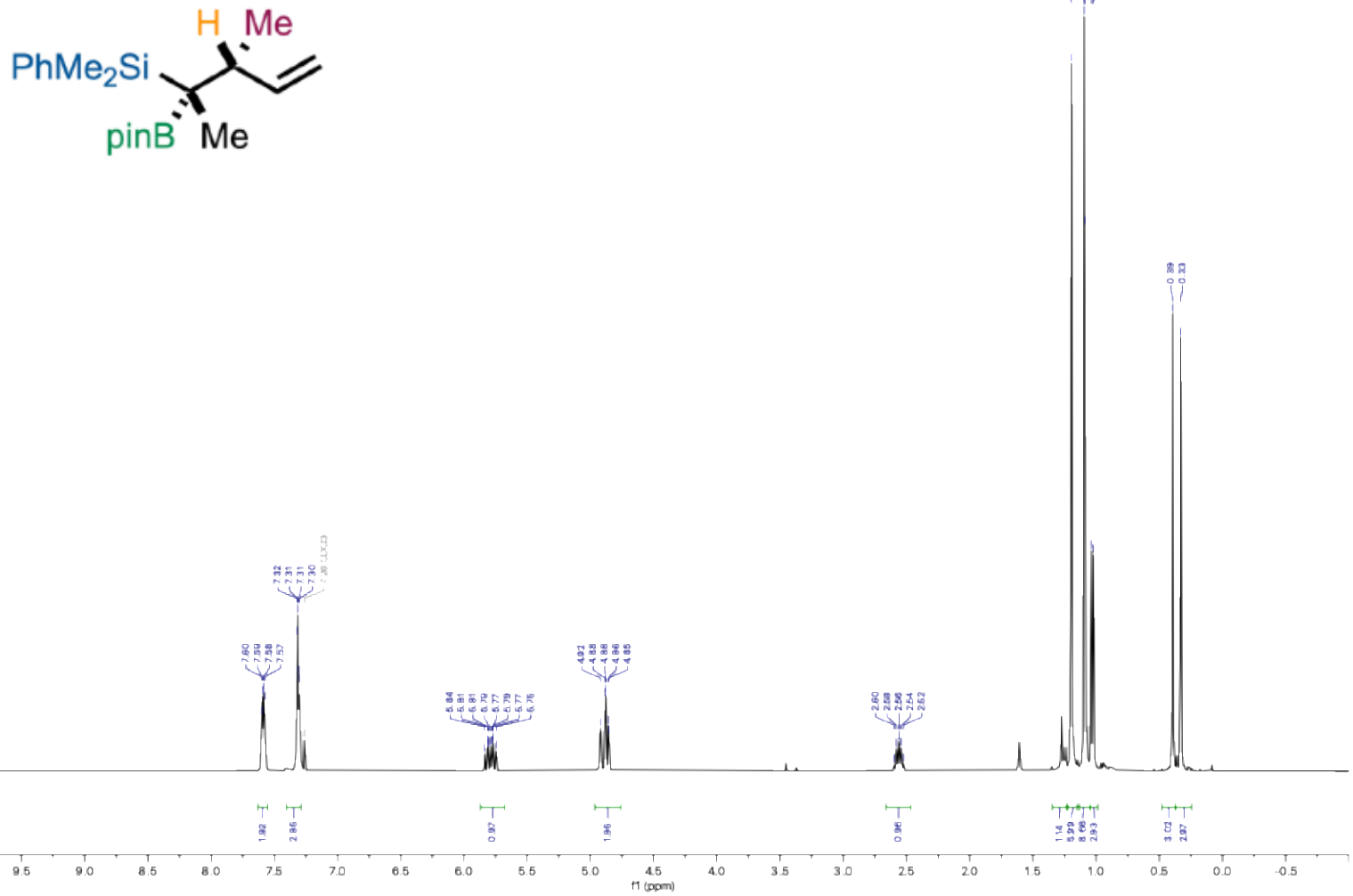


^{11}B NMR spectrum (128 MHz, $CDCl_3$)

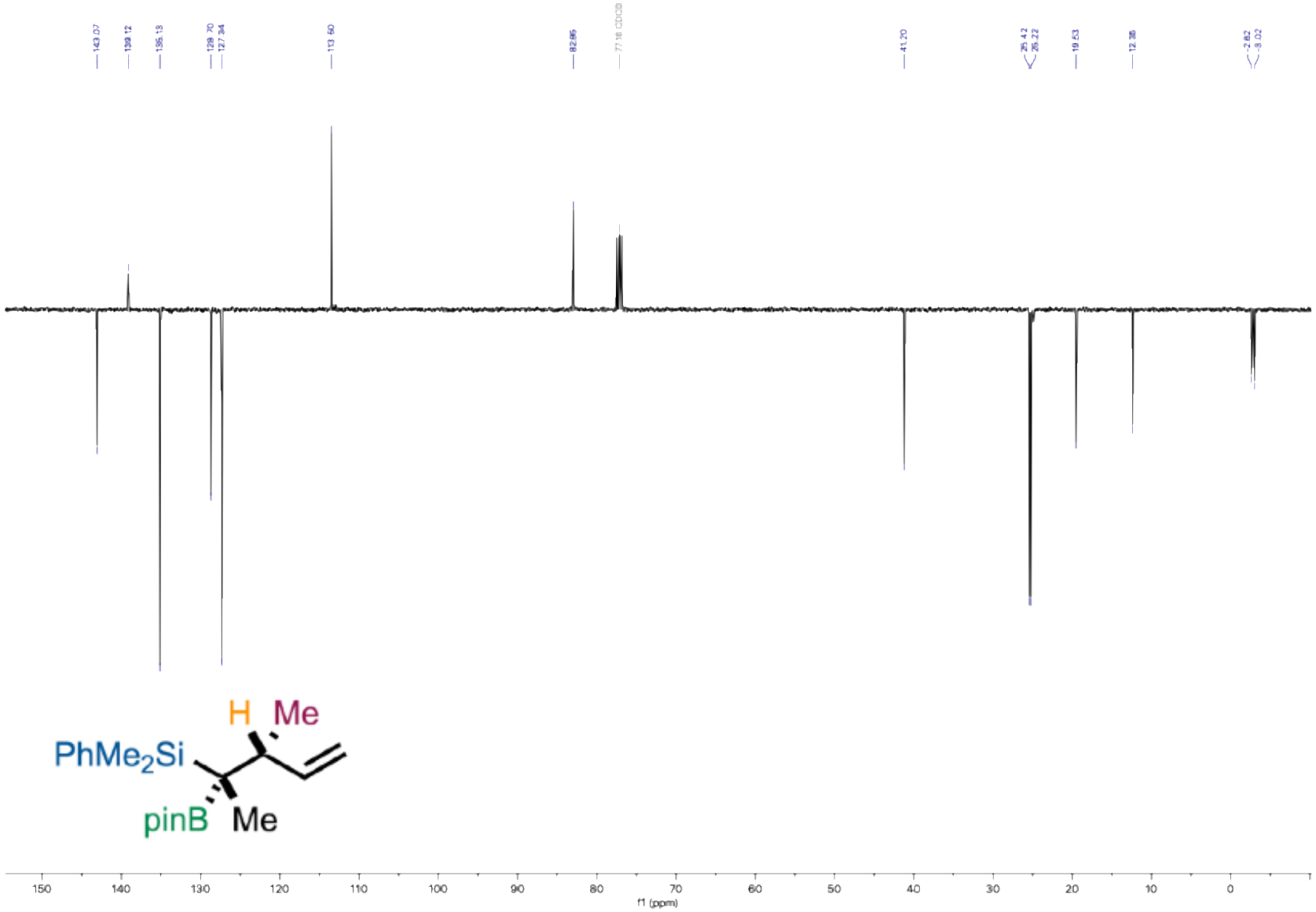


^{29}Si NMR spectrum (80 MHz, $CDCl_3$)

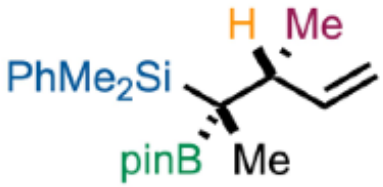
Trimethyl((2*R,3*R**)-3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-2-yl)silane (6b)**

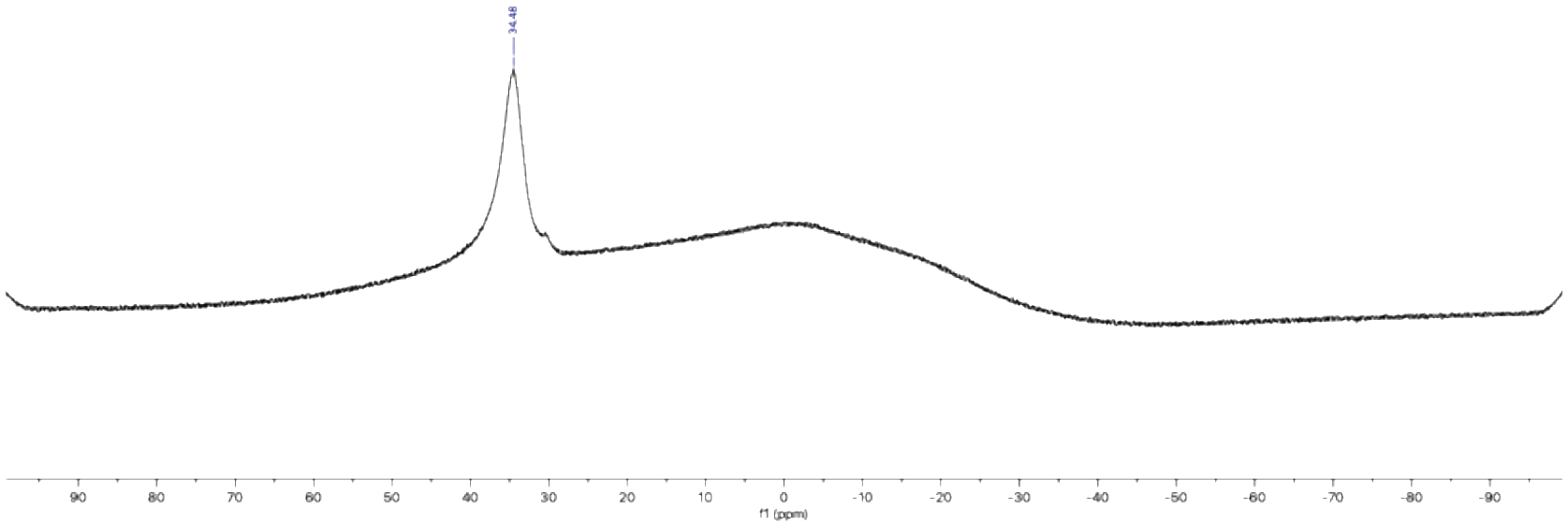


^{1}H NMR spectrum (400 MHz, $CDCl_3$)

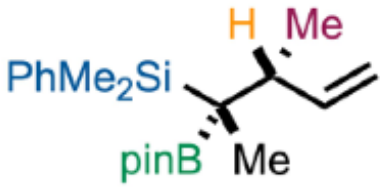


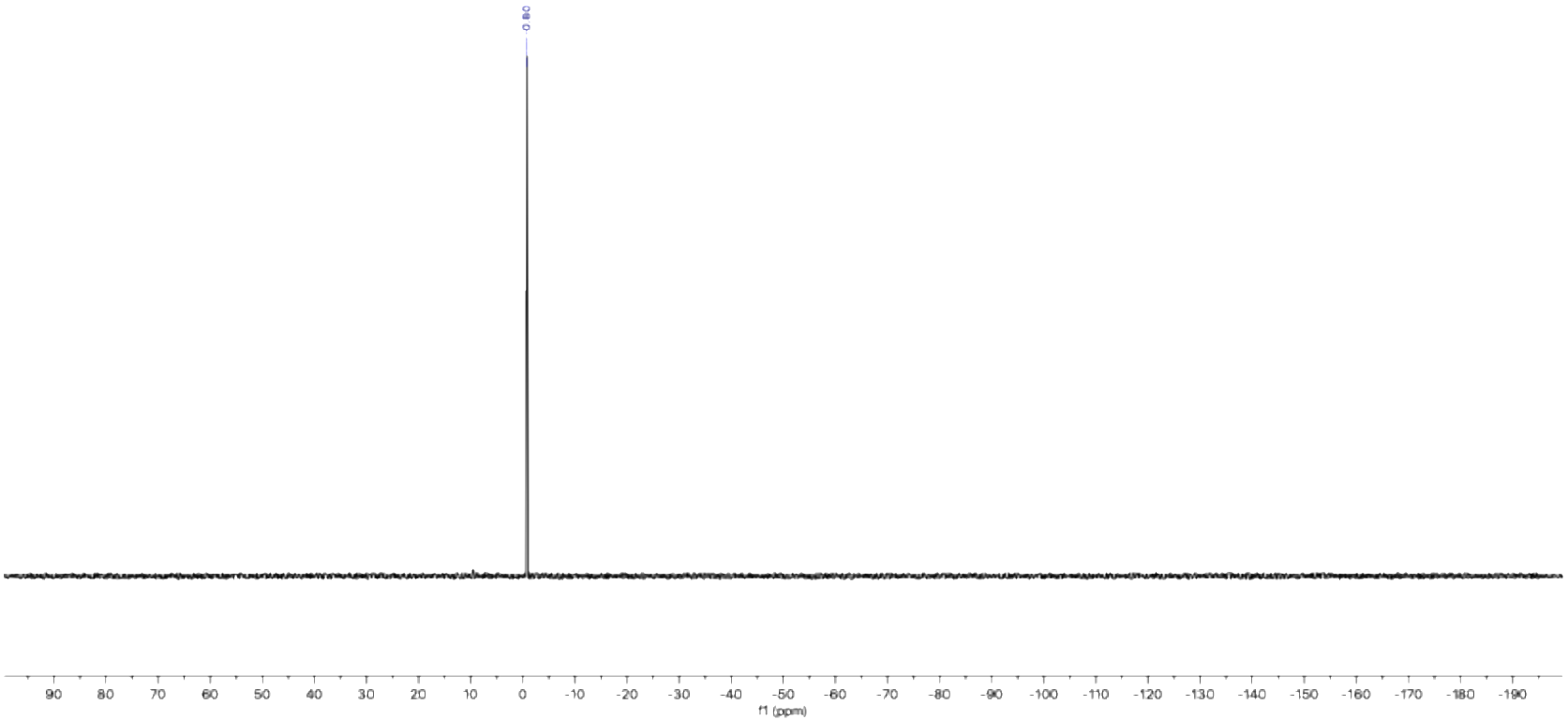
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





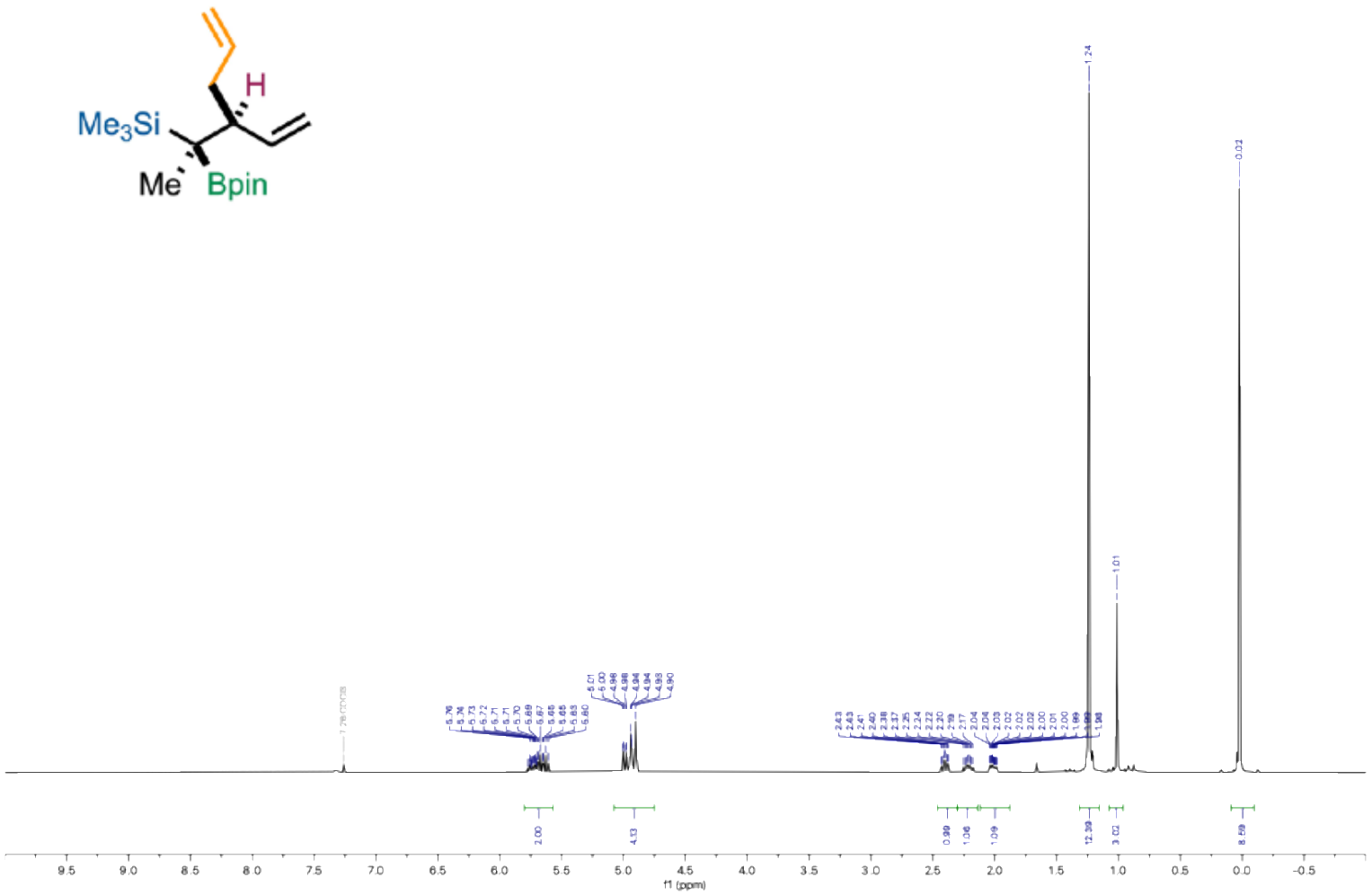
^{11}B NMR spectrum (128 MHz, $CDCl_3$)



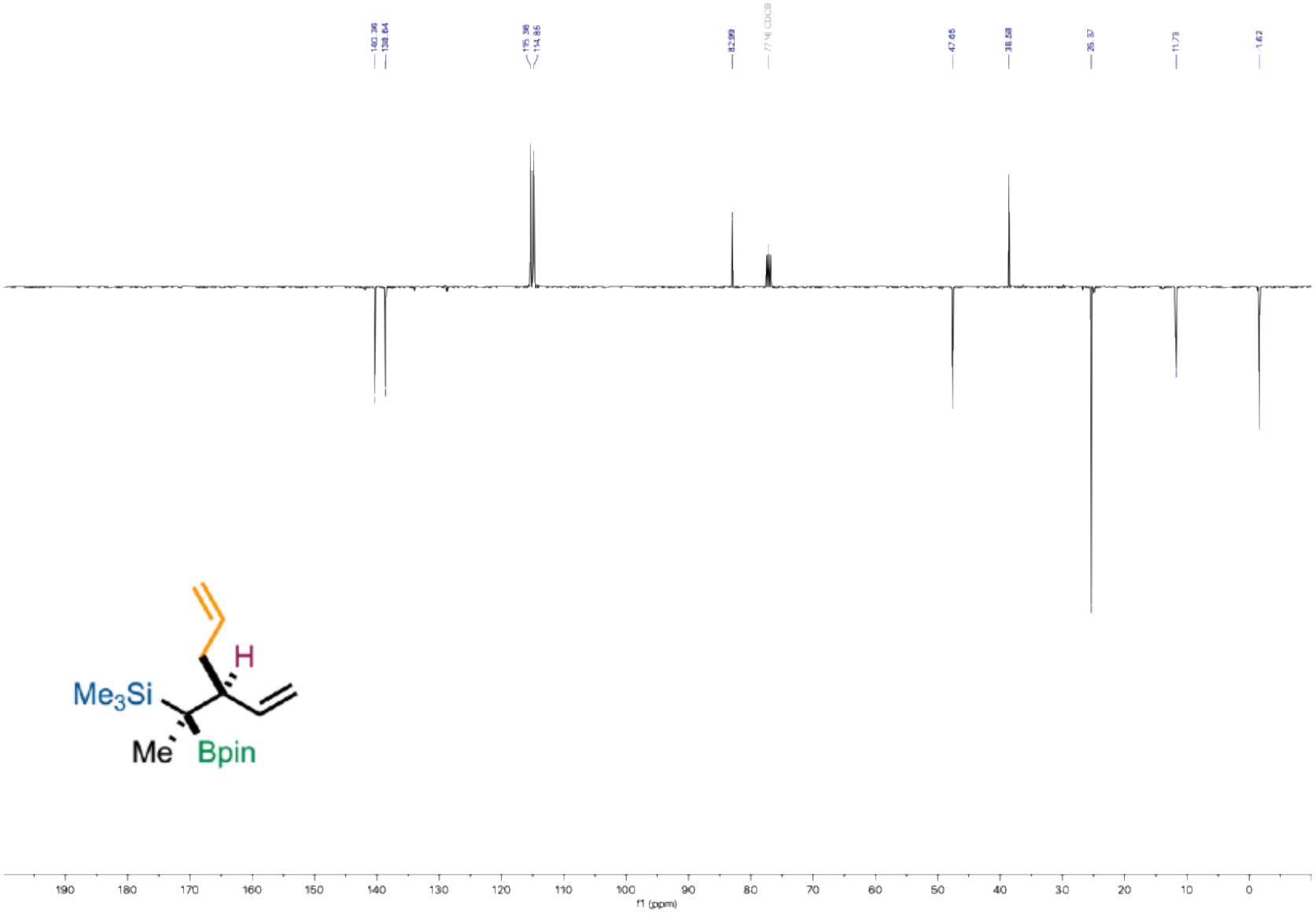


^{29}Si NMR spectrum (80 MHz, $CDCl_3$)

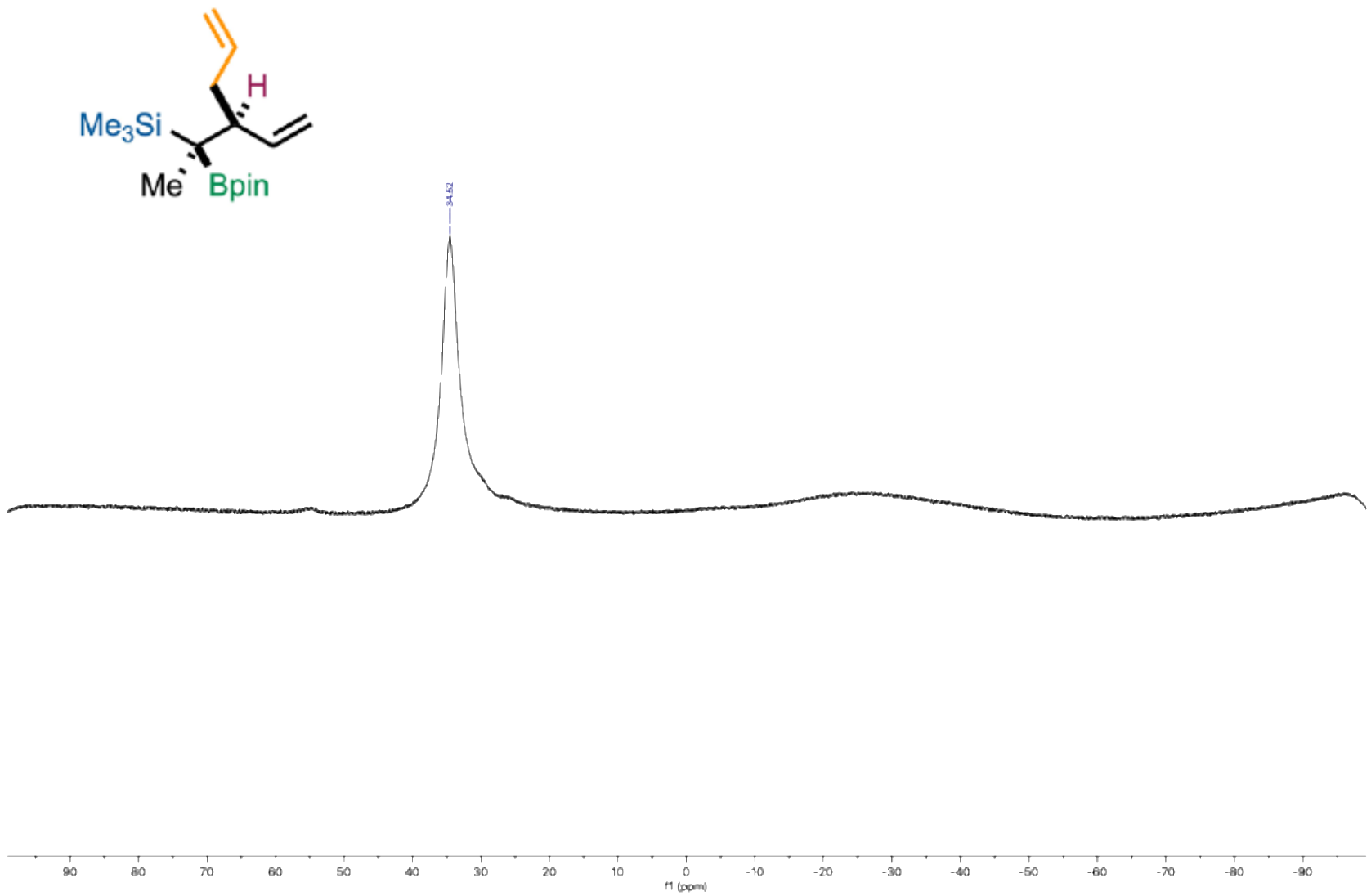
Trimethyl((2*S,3*S**)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-vinylhex-5-en-2-yl)silane** (**6c**)



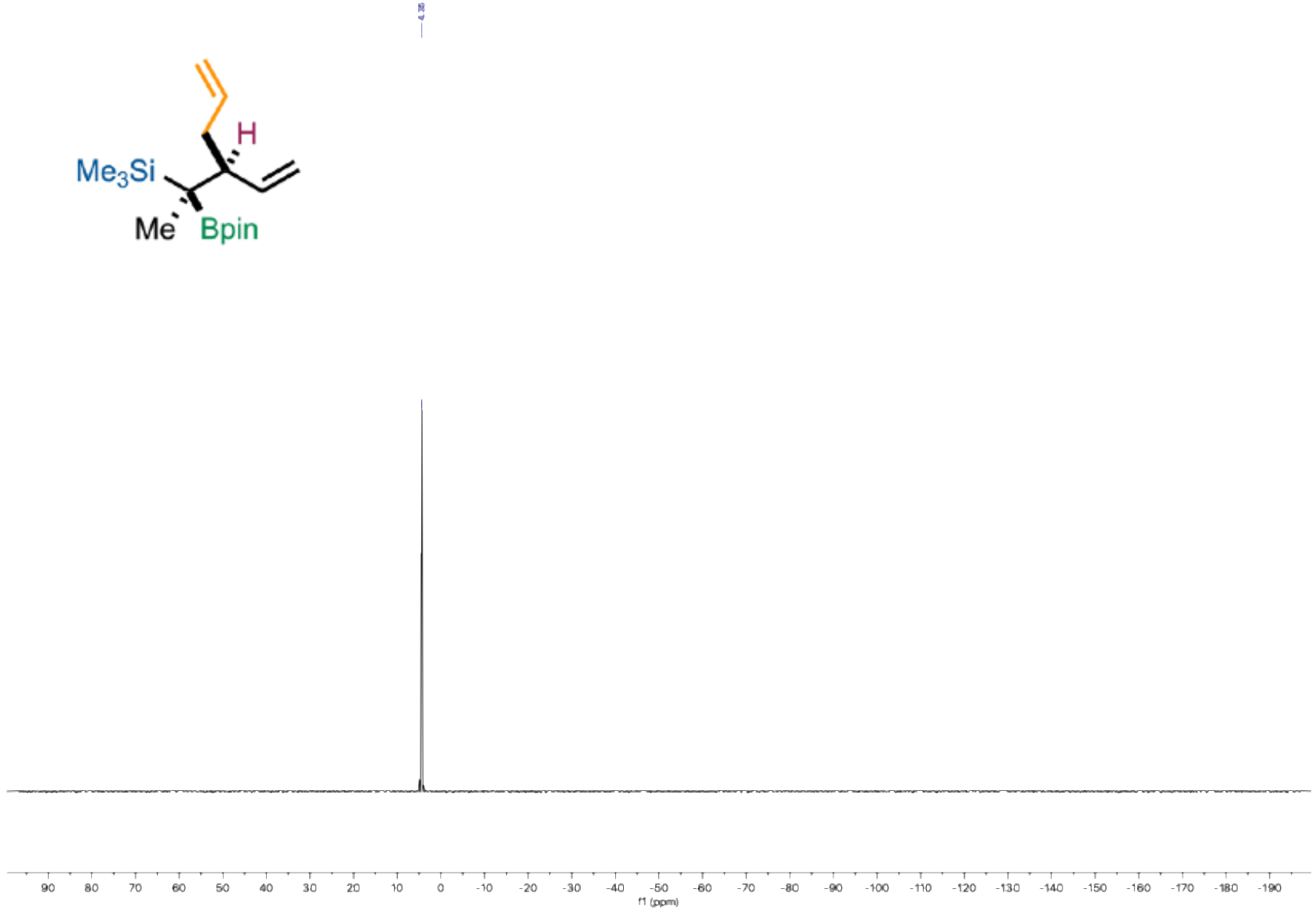
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



^{13}C NMR spectrum (101 MHz, $CDCl_3$)

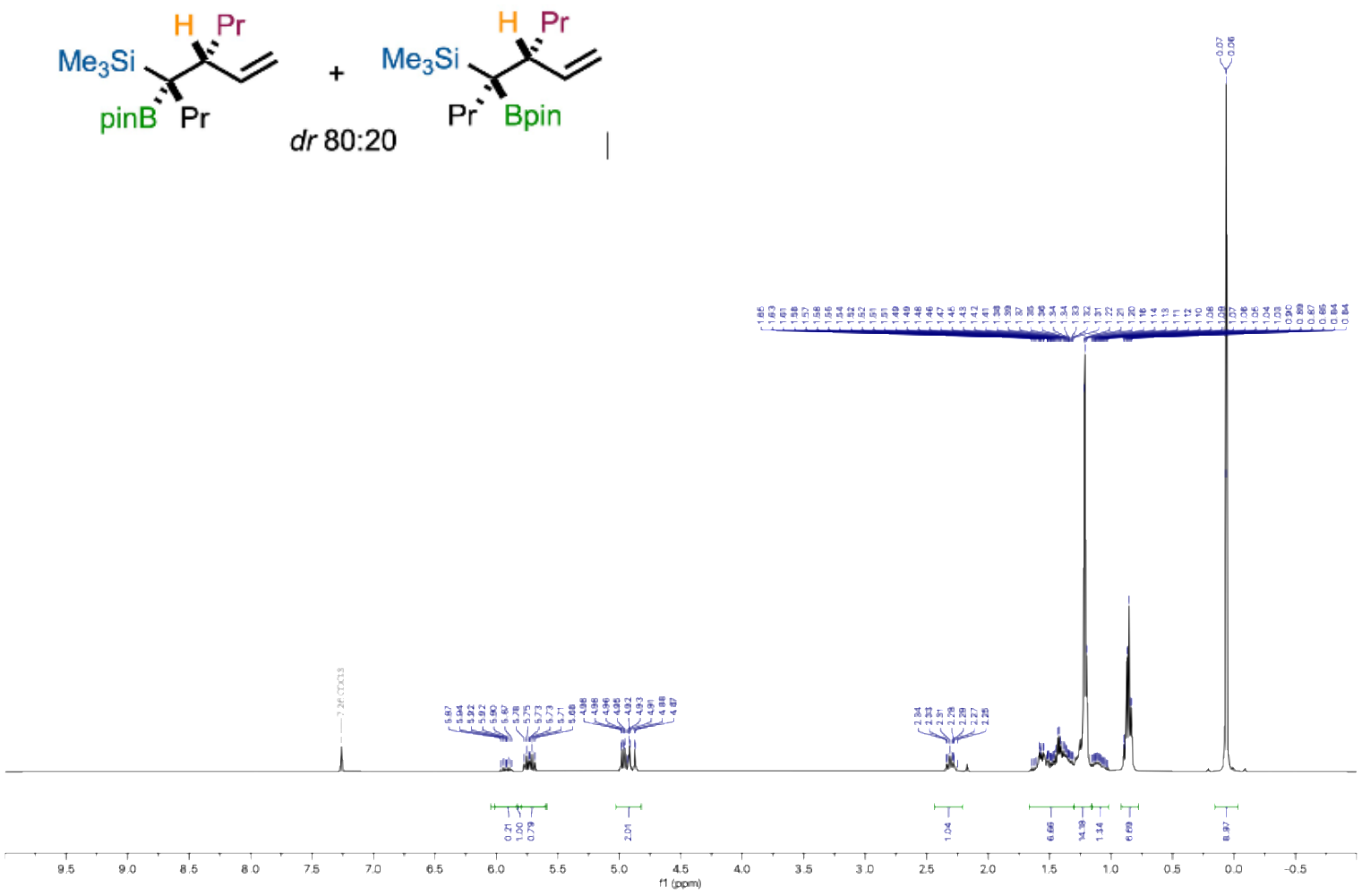


^{11}B NMR spectrum (128 MHz, $CDCl_3$)

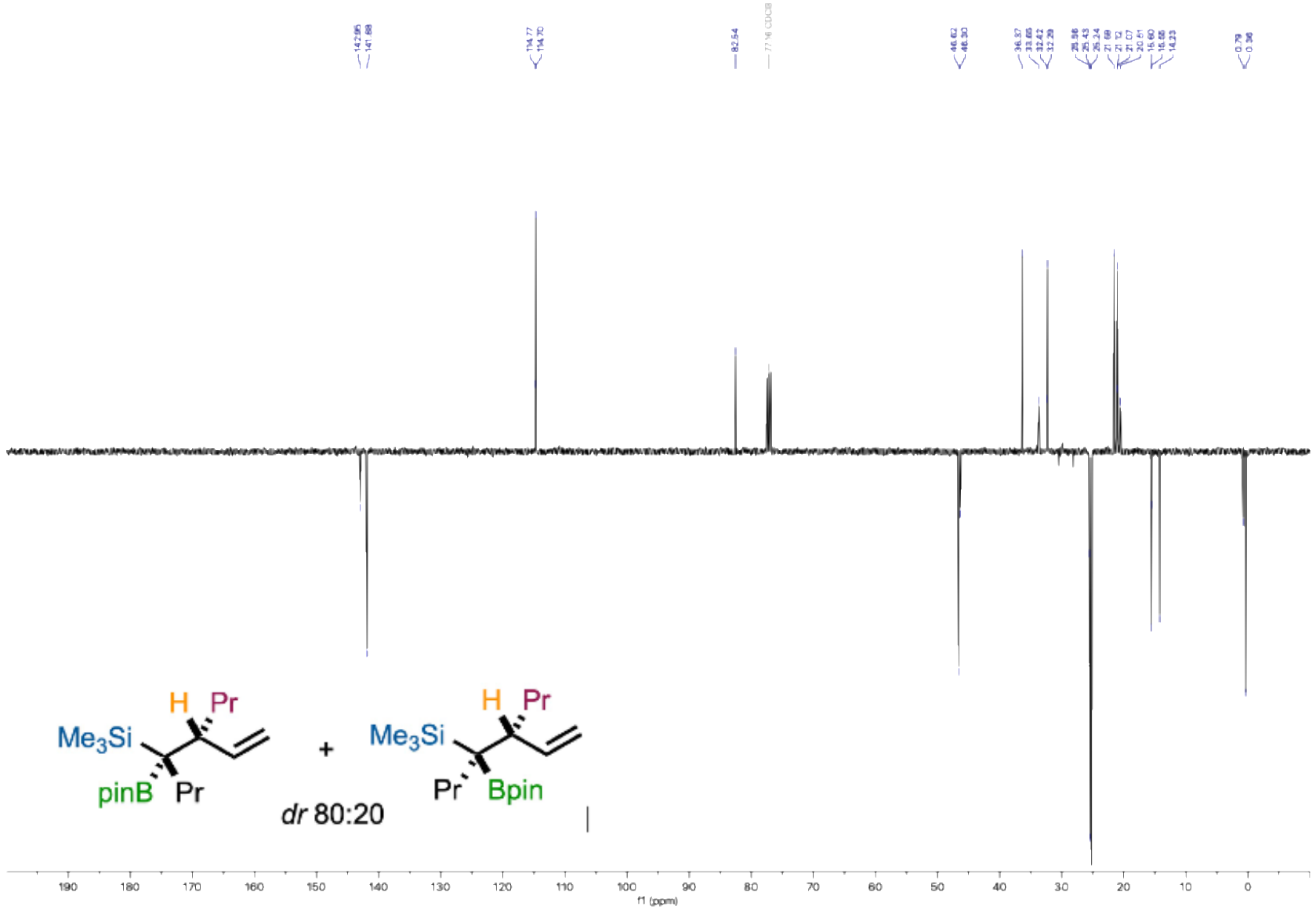


^{29}Si NMR spectrum (80 MHz, $CDCl_3$)

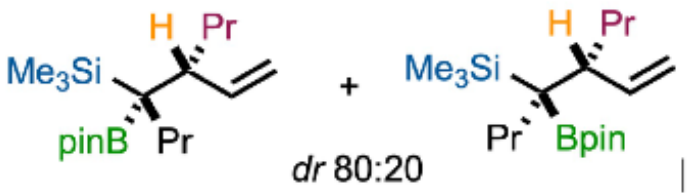
Trimethyl((4*R,5*R**)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-vinyloctan-4-yl)silane (6d)**

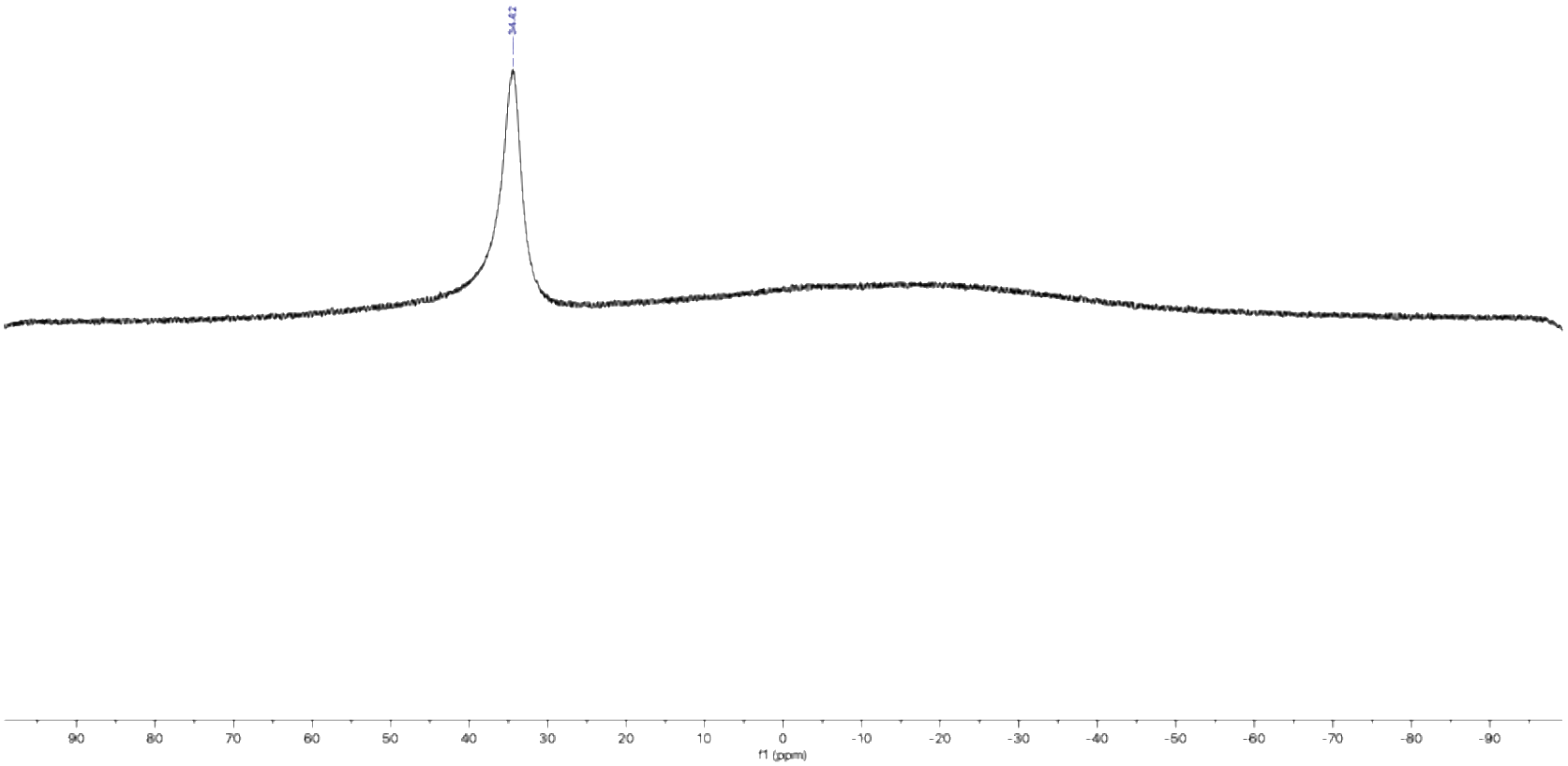


^{1}H NMR spectrum (400 MHz, $CDCl_3$)

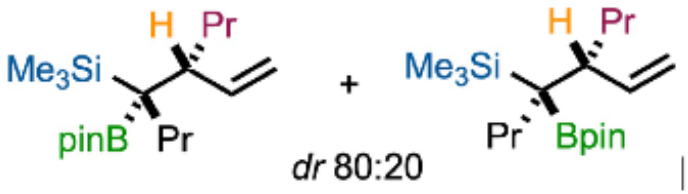


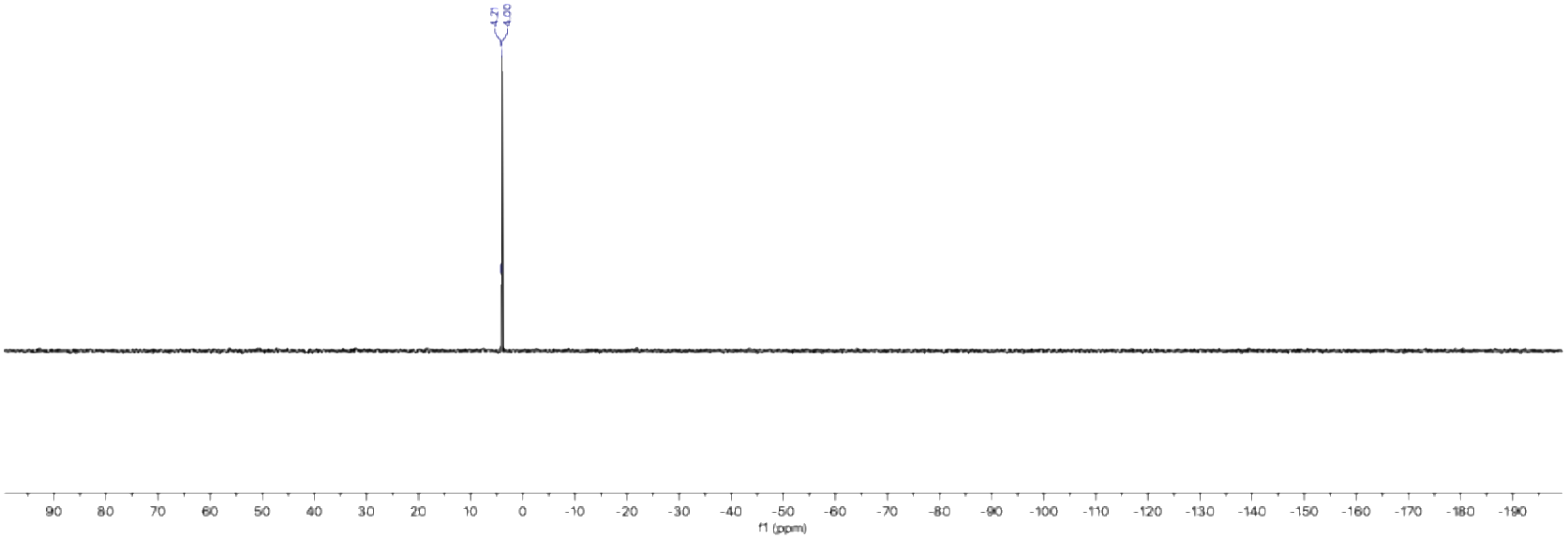
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





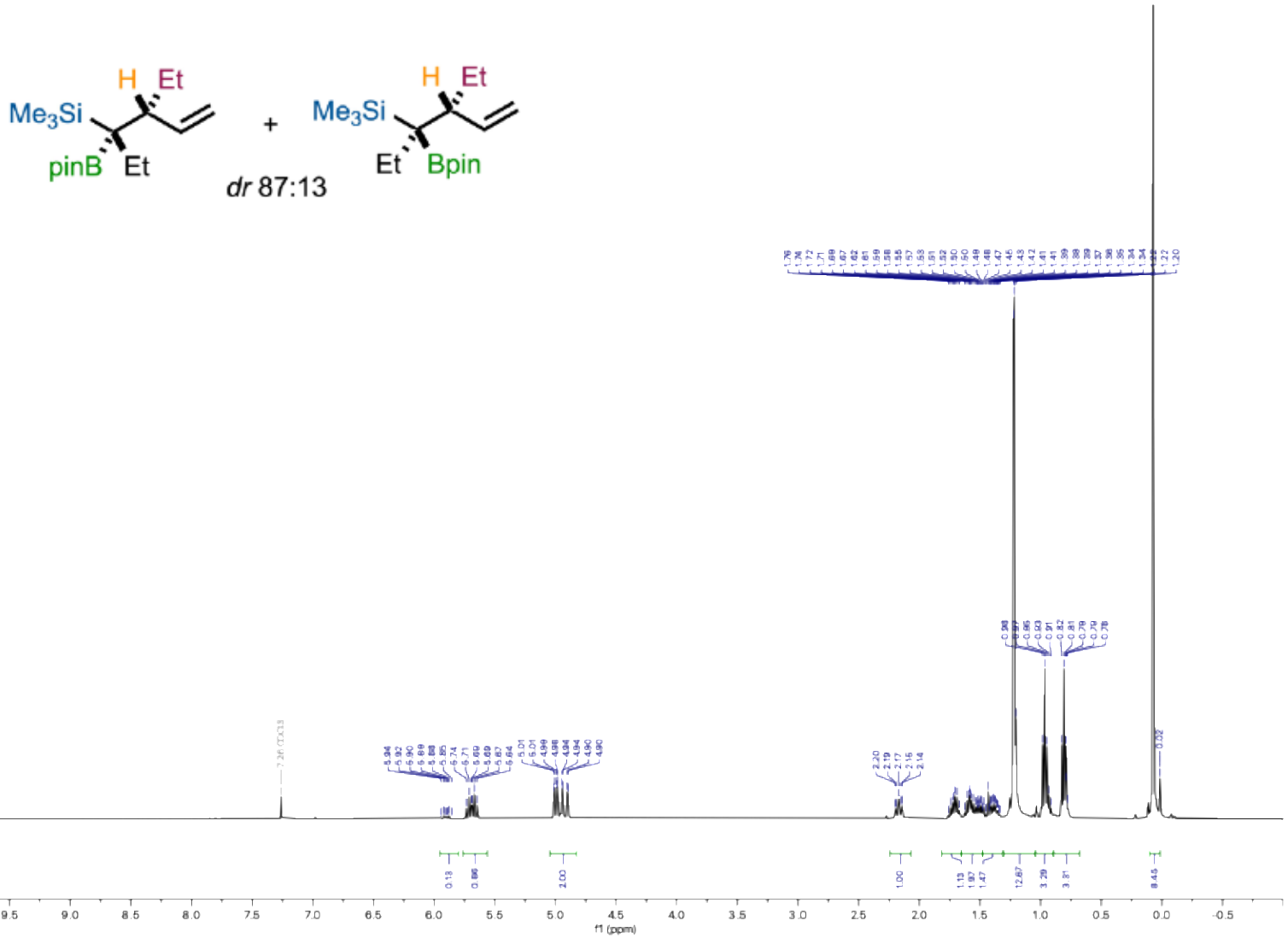
^{11}B NMR spectrum (128 MHz, $CDCl_3$)



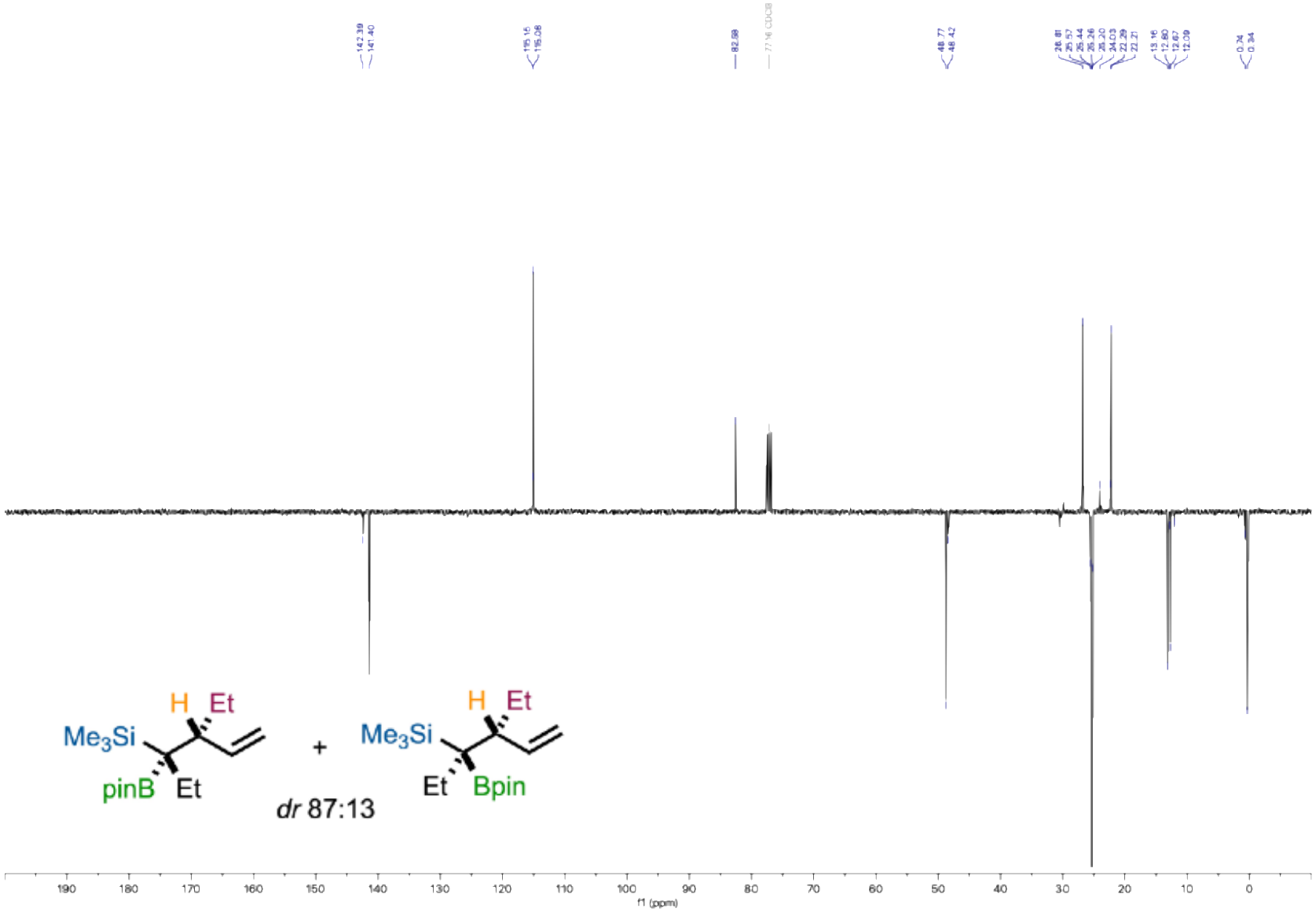


^{29}Si NMR spectrum (80 MHz, $CDCl_3$)

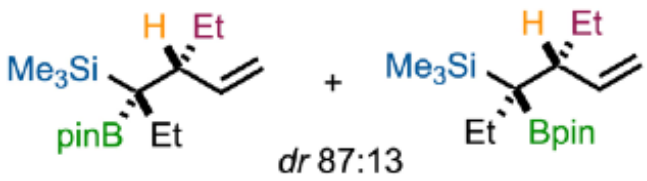
((3*R,4*R**)-4-Ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-3-yl)trimethylsilane (6e)**

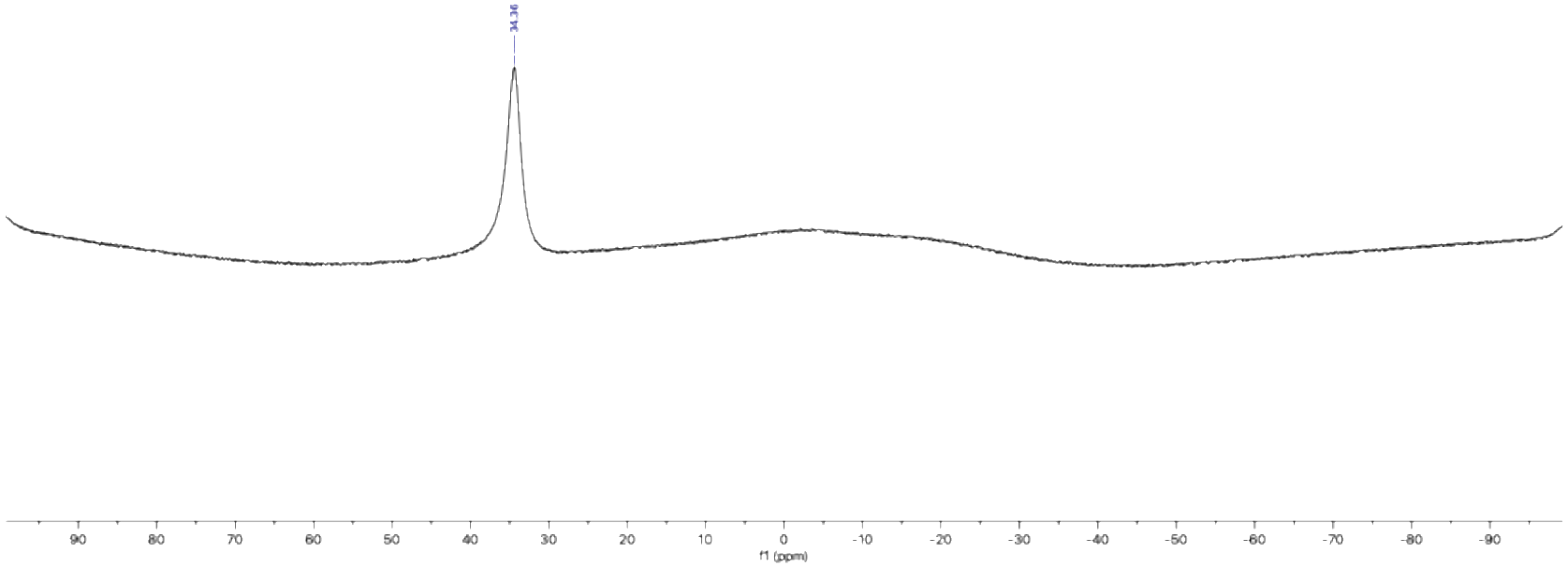


^{1}H NMR spectrum (400 MHz, $CDCl_3$)

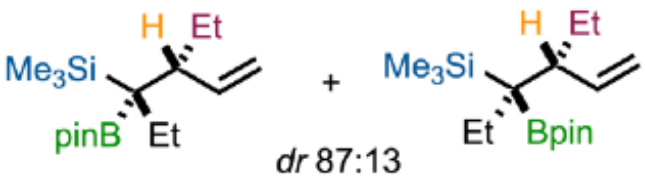


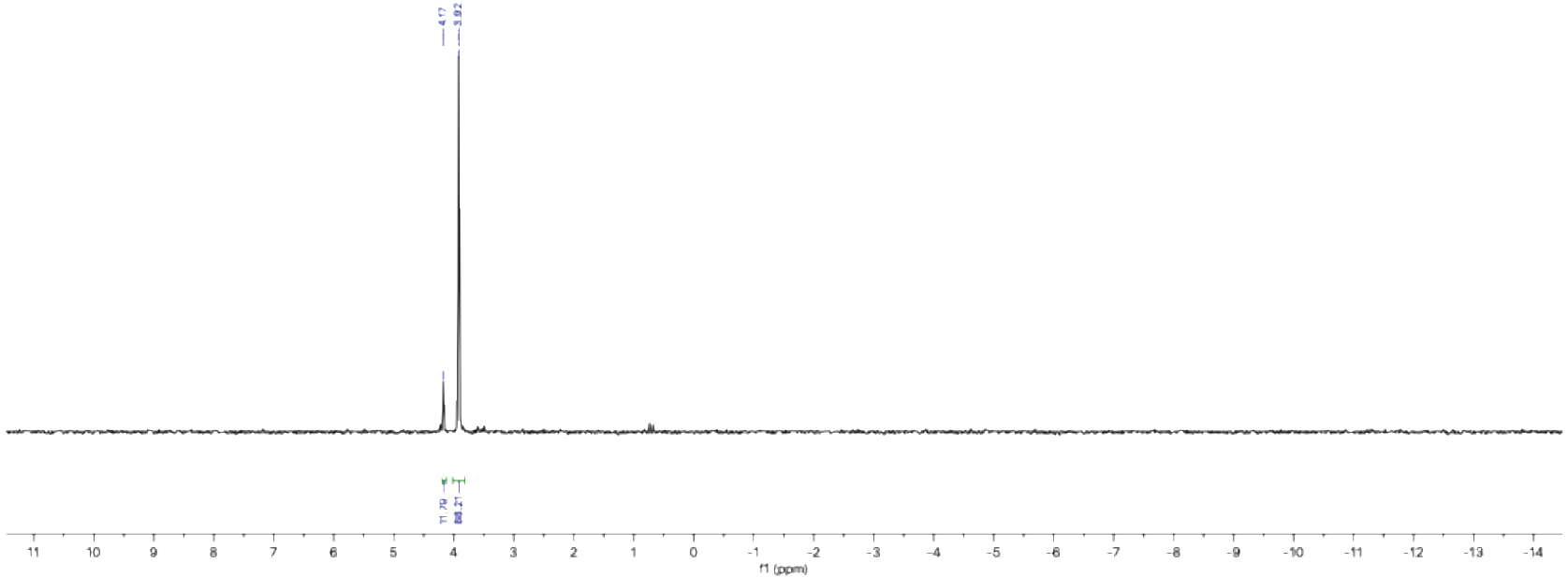
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





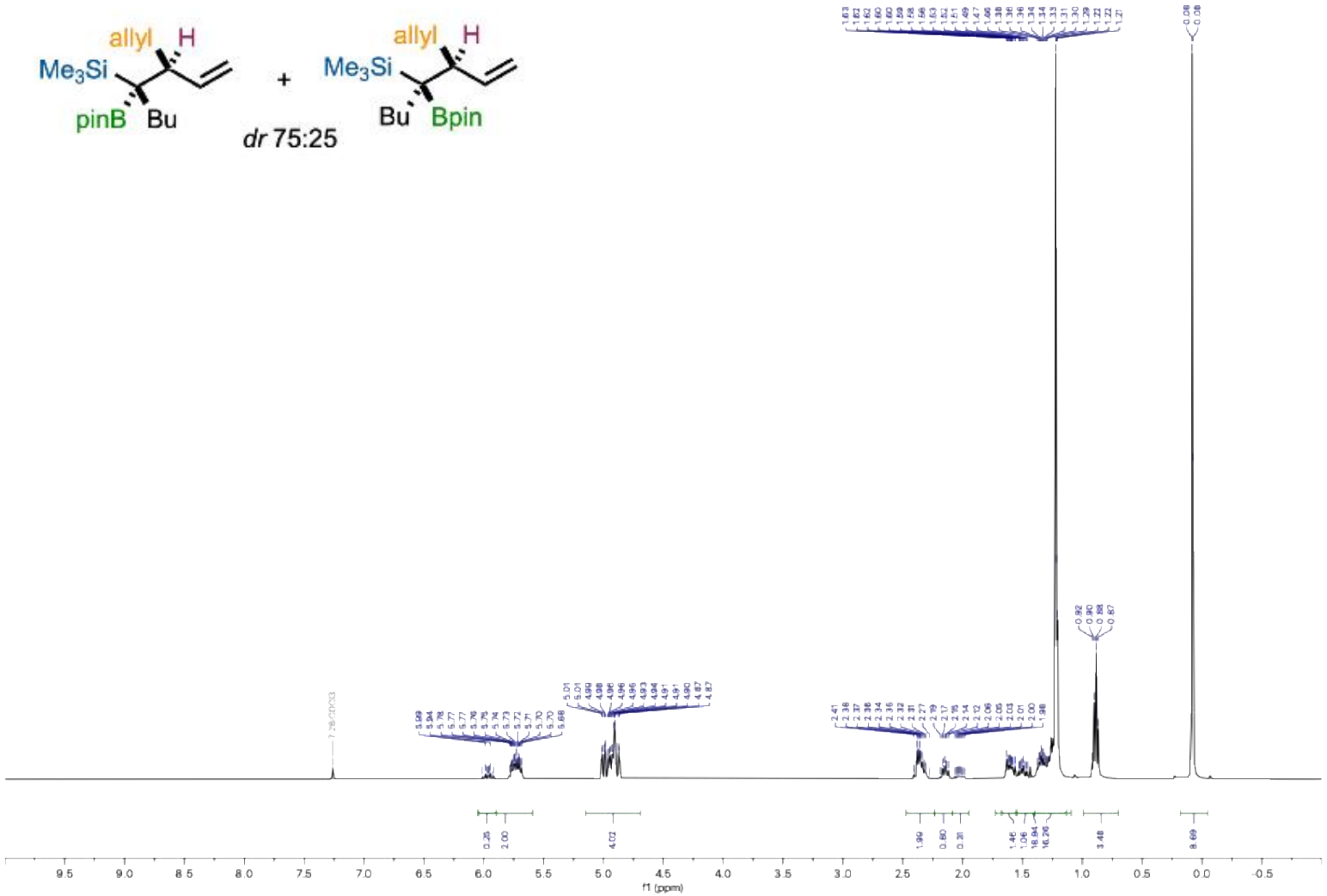
^{11}B NMR spectrum (128 MHz, $CDCl_3$)



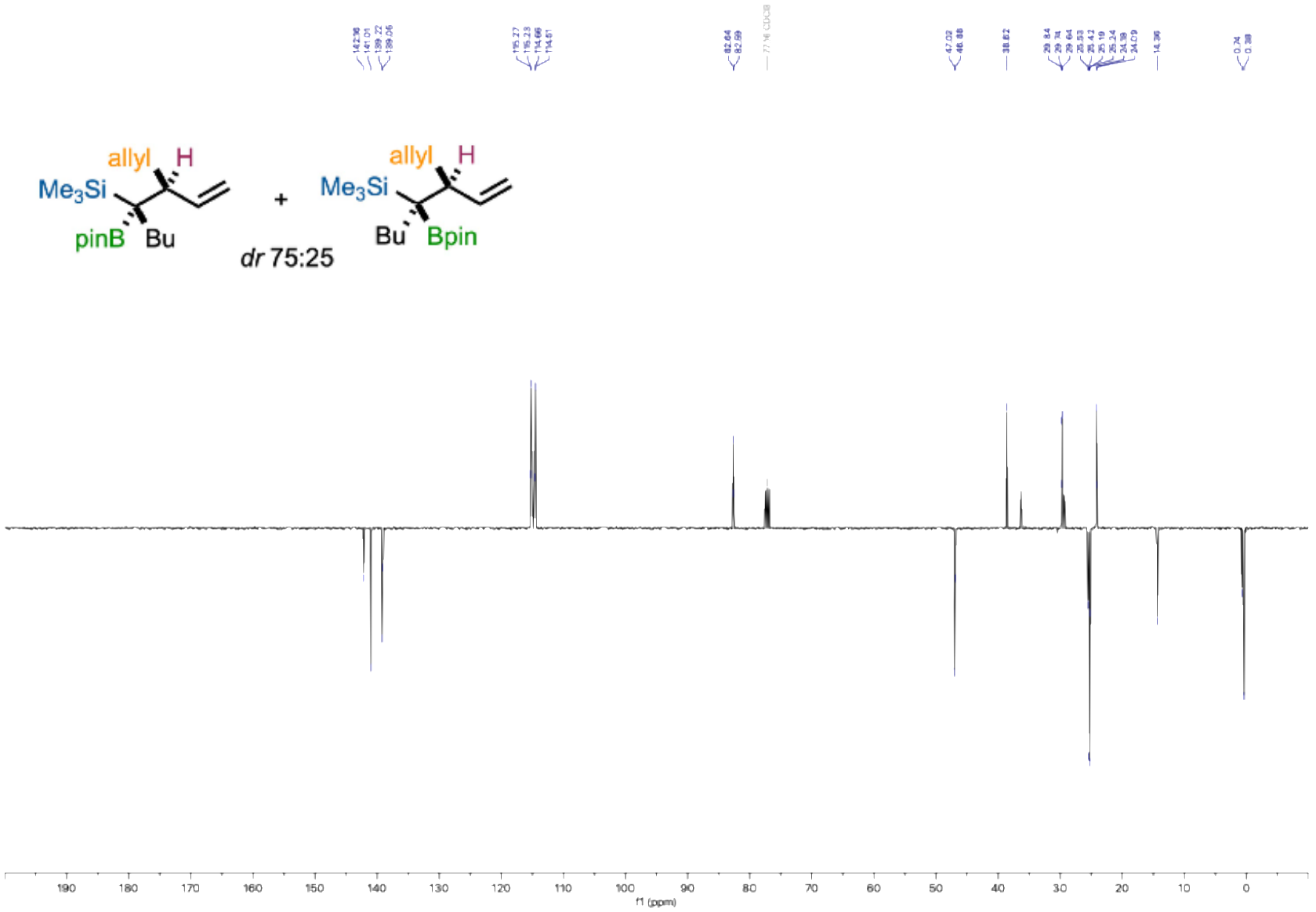


^{29}Si NMR spectrum (80 MHz, $CDCl_3$)

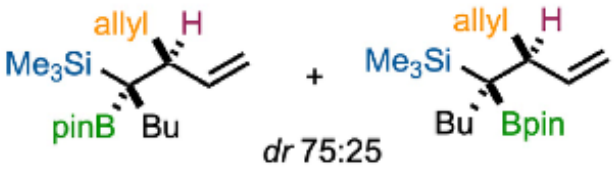
Trimethyl((4*S,5*S**)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-vinylnon-1-en-5-yl)silane (6f)**

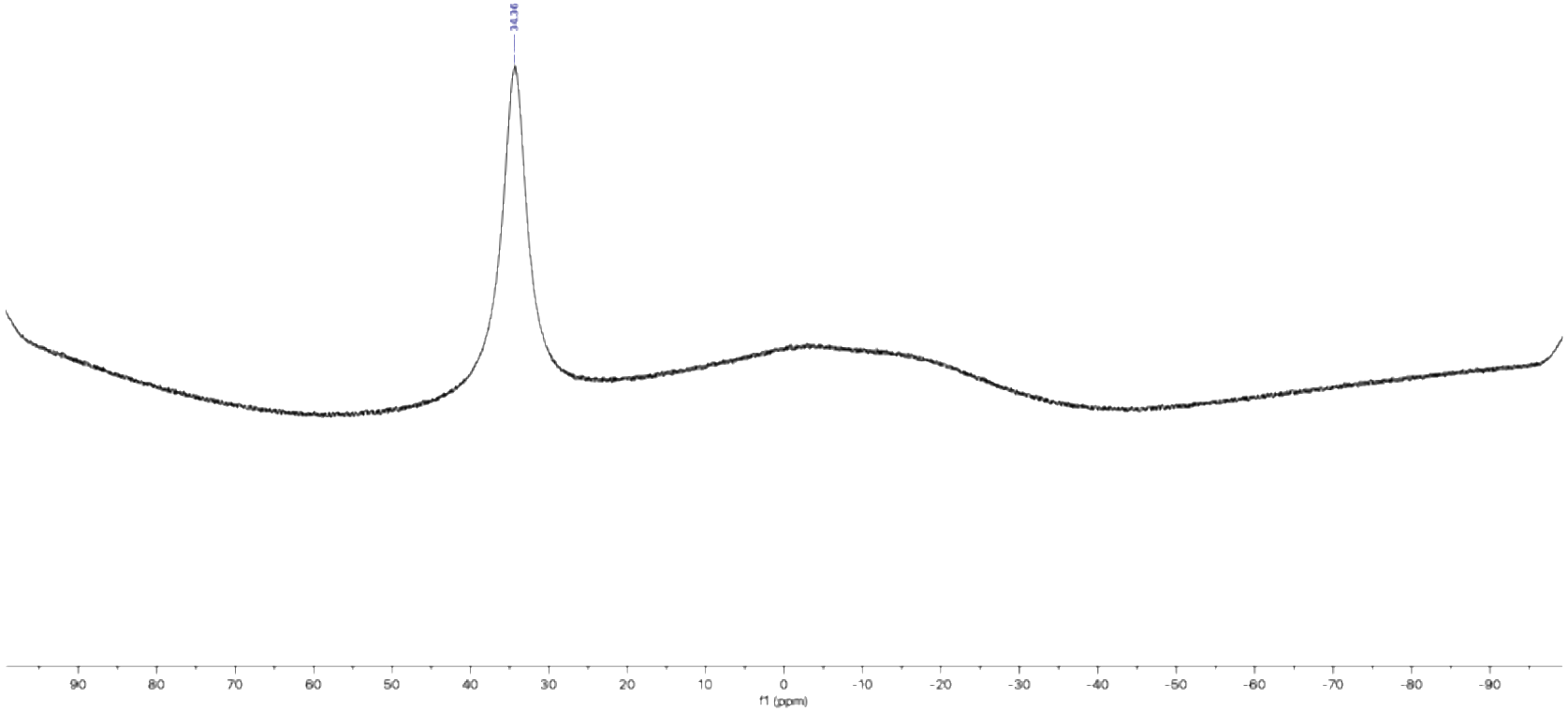


^{1}H NMR spectrum (400 MHz, $CDCl_3$)

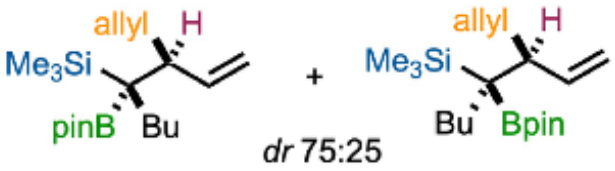


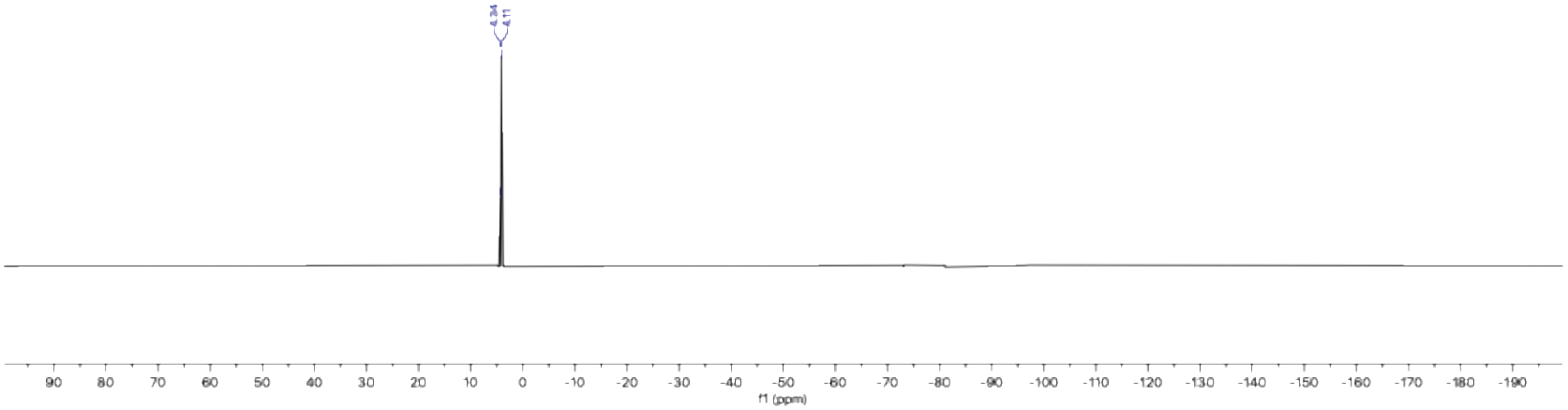
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





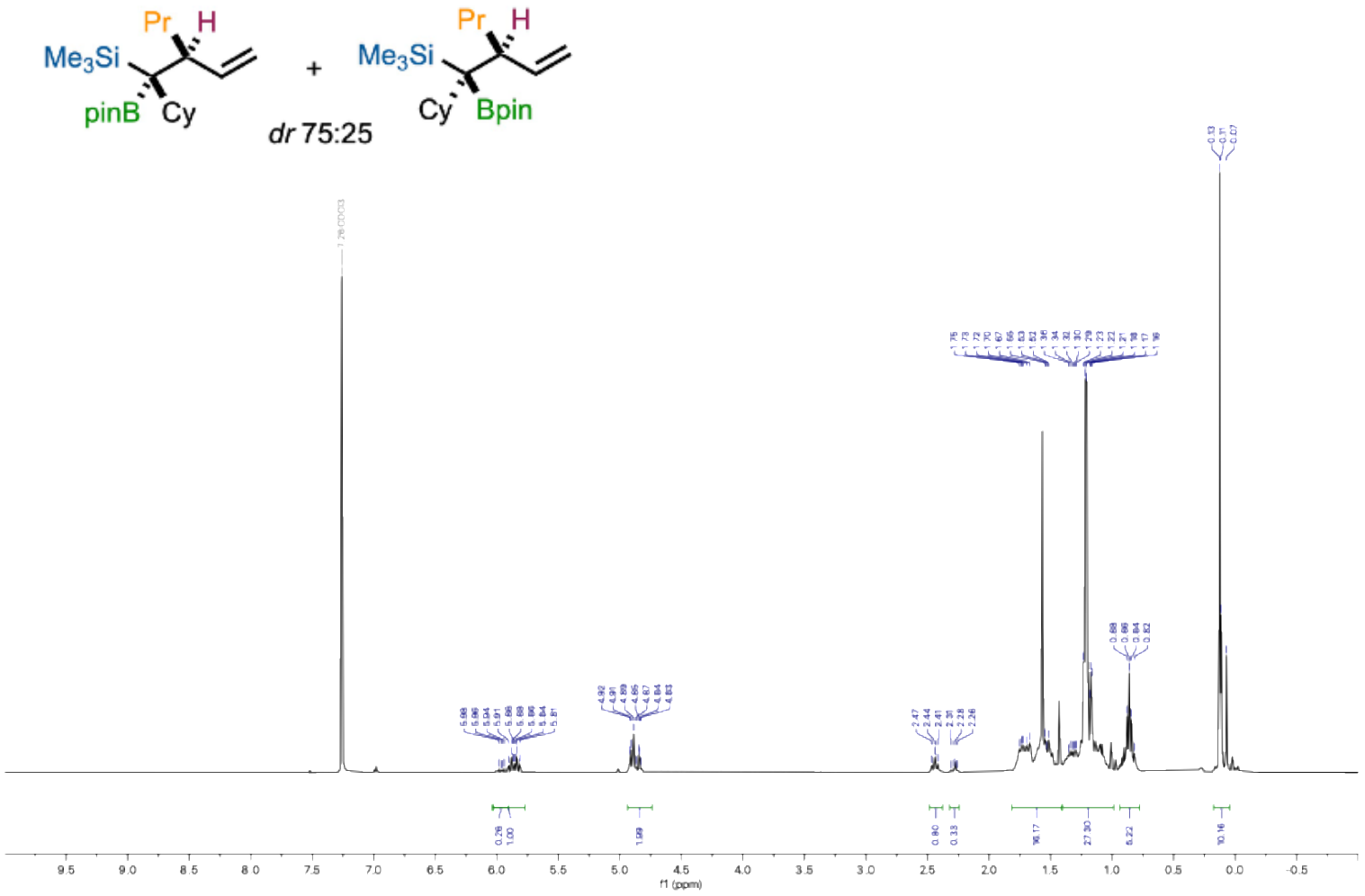
^{11}B NMR spectrum (128 MHz, $CDCl_3$)



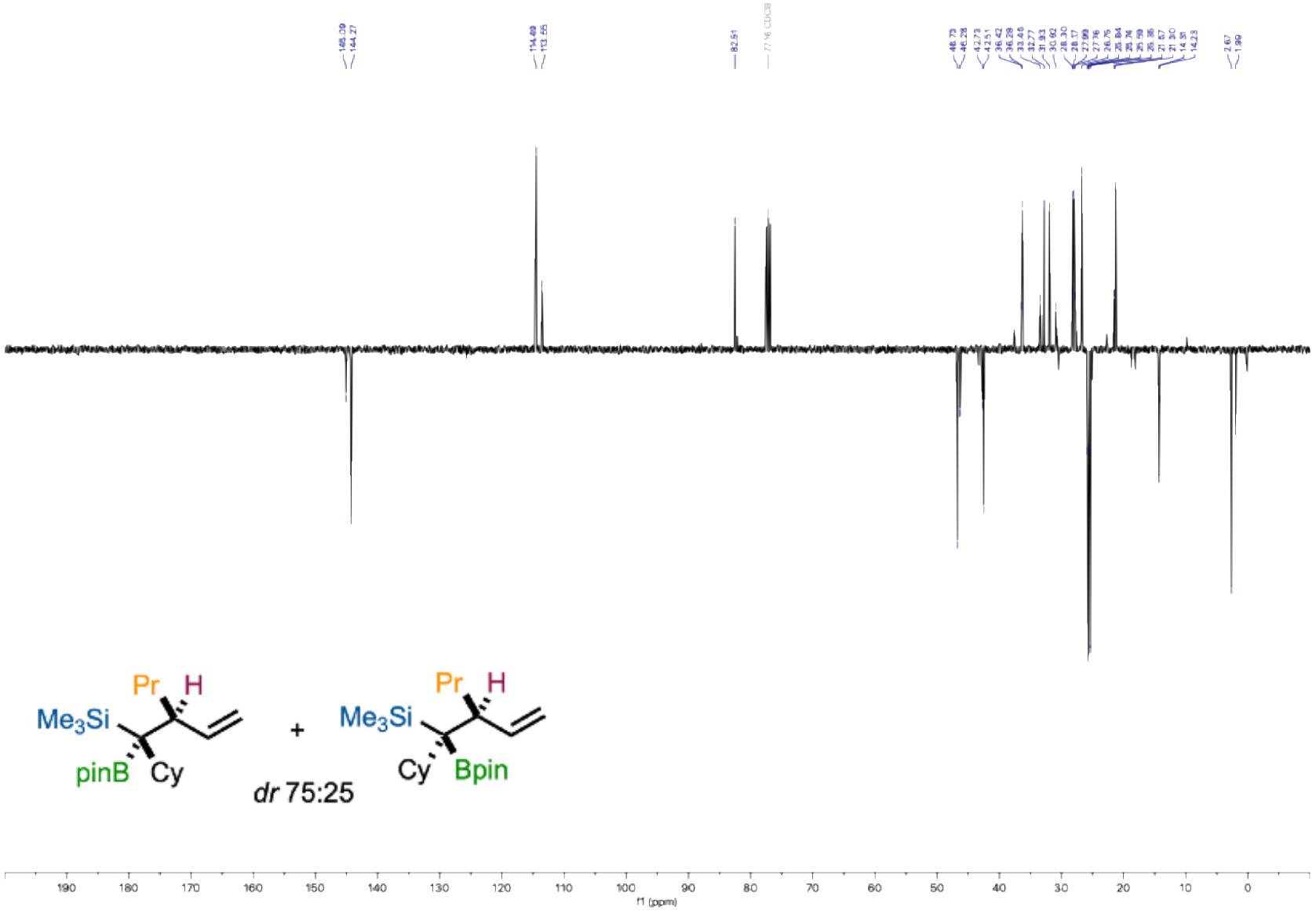


^{29}Si NMR spectrum (80 MHz, $CDCl_3$)

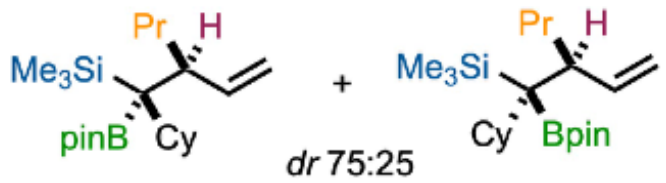
((1*S,2*S**)-1-Cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-vinylpentyl)trimethylsilane 6g**

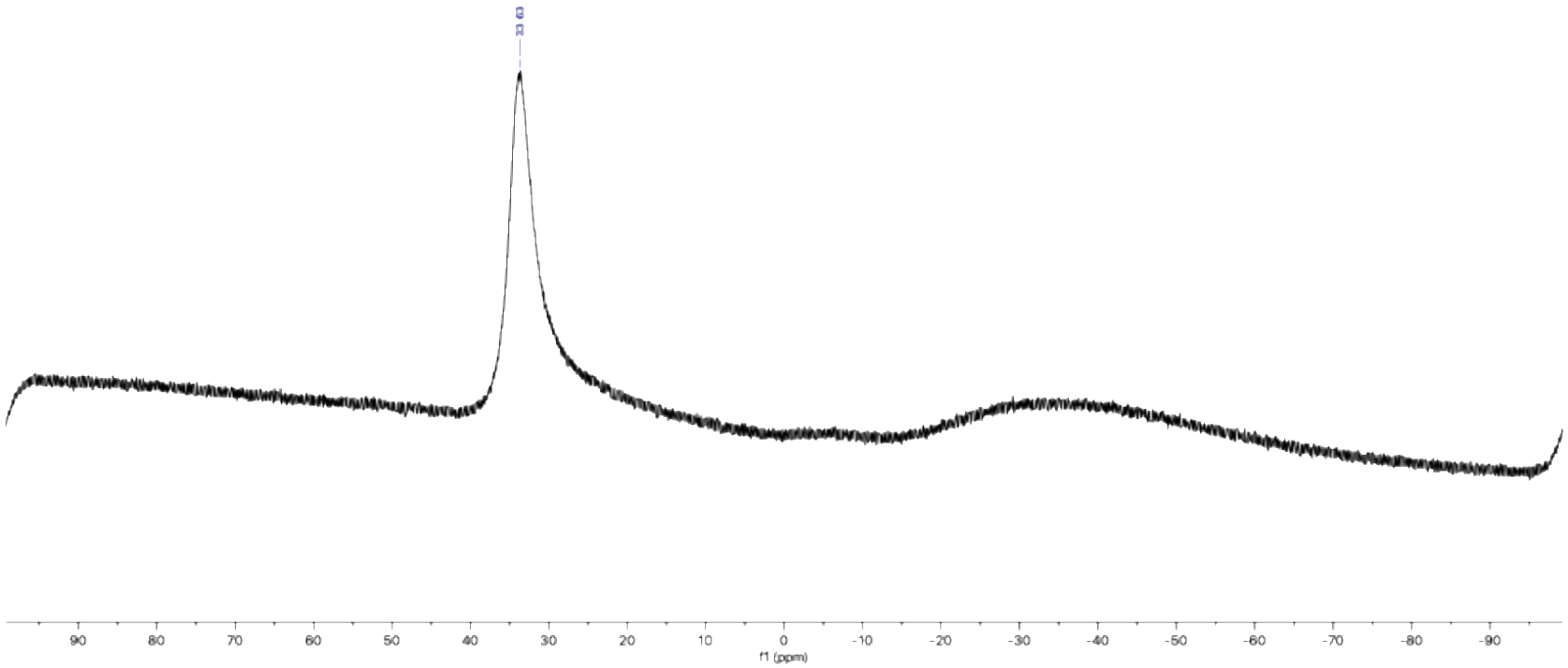


^{1}H NMR spectrum (400 MHz, $CDCl_3$)

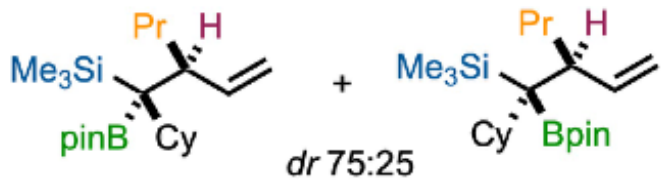


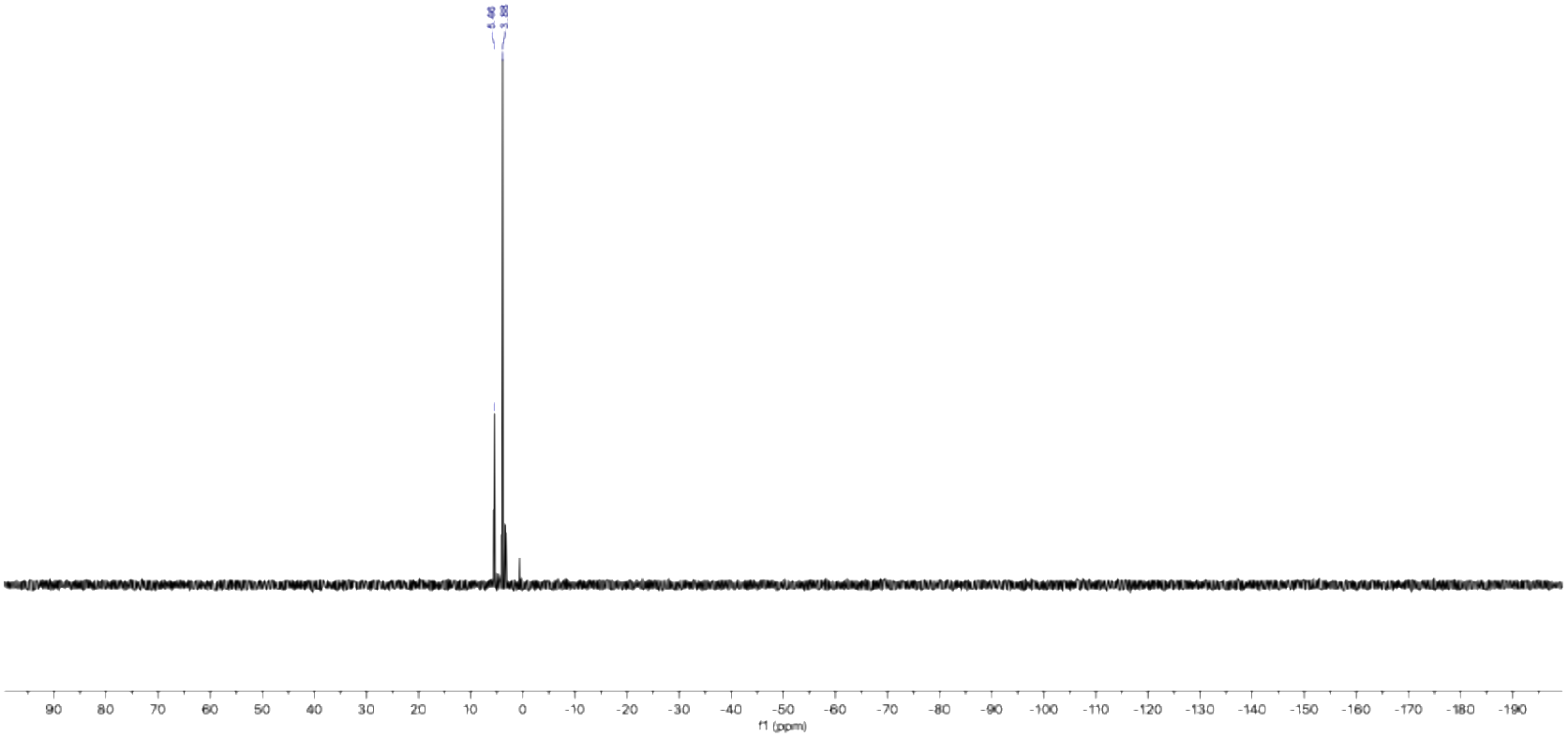
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





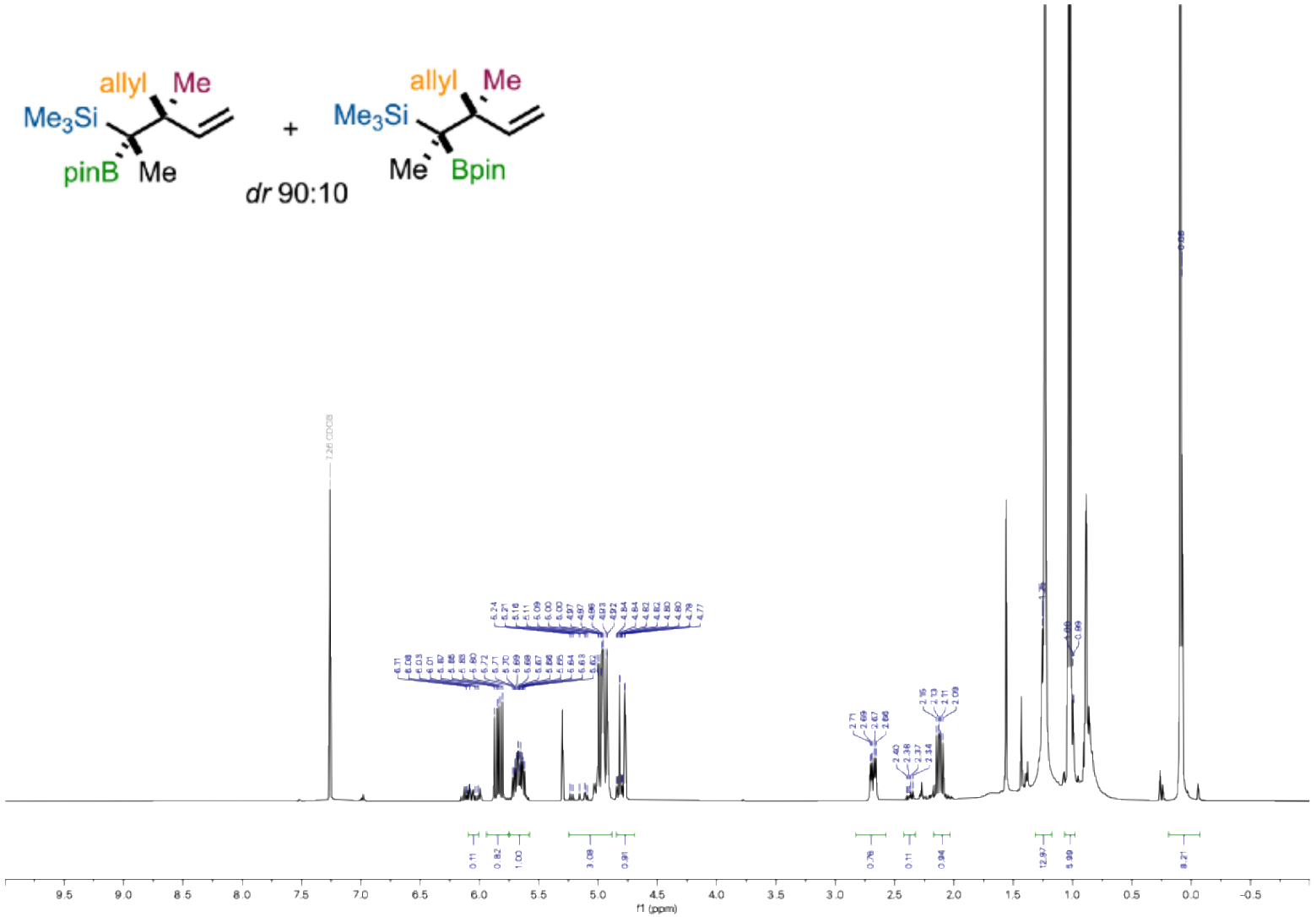
^{11}B NMR spectrum (128 MHz, $CDCl_3$)



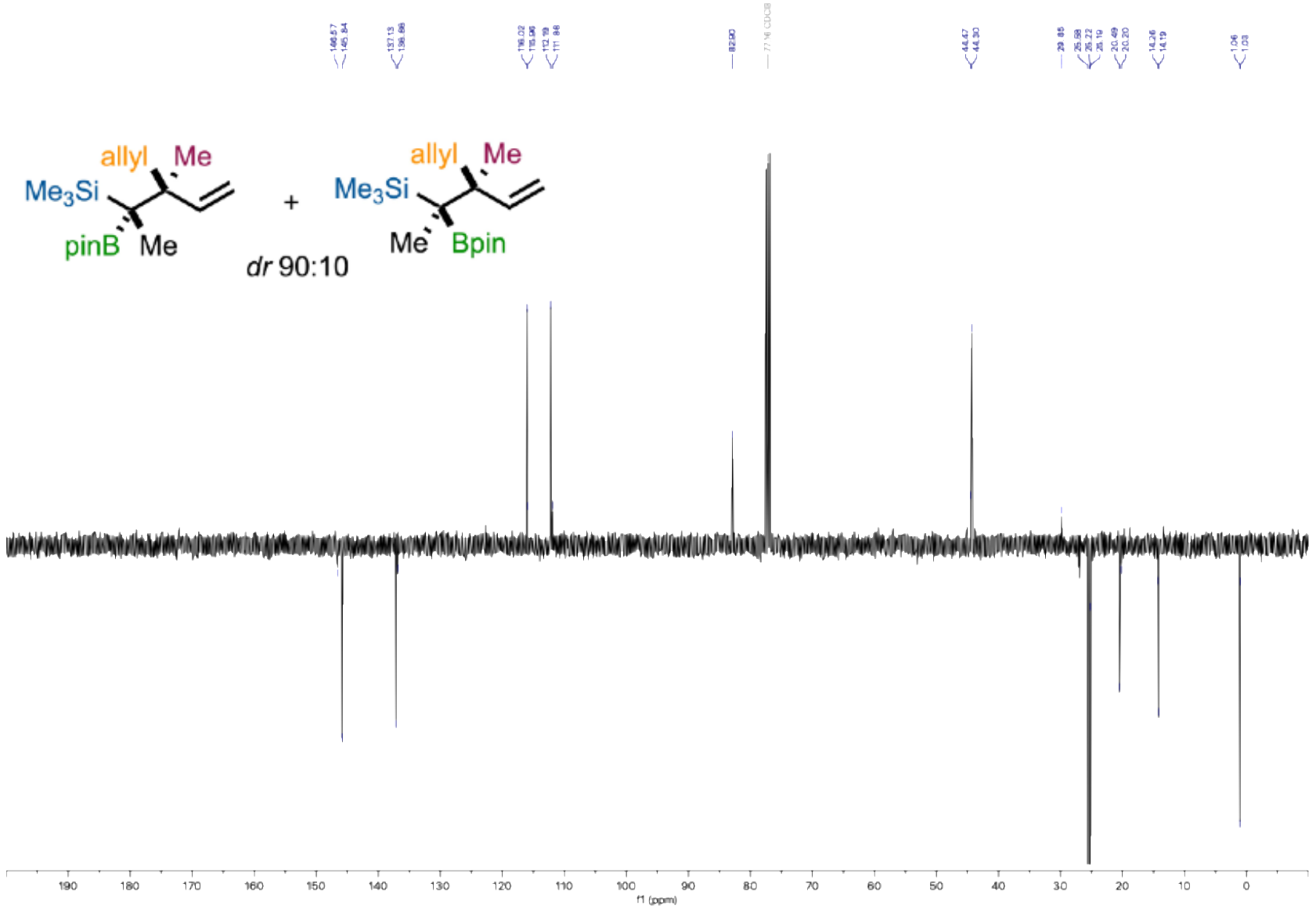


^{29}Si NMR spectrum (80 MHz, $CDCl_3$)

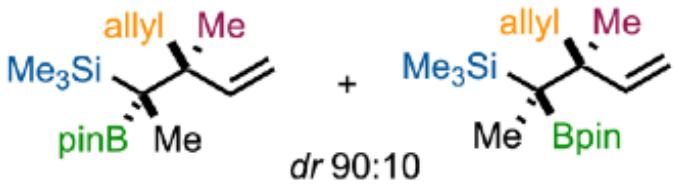
Trimethyl((2*S*,3*S*)-3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-vinylhex-5-en-2-yl)silane (6h)

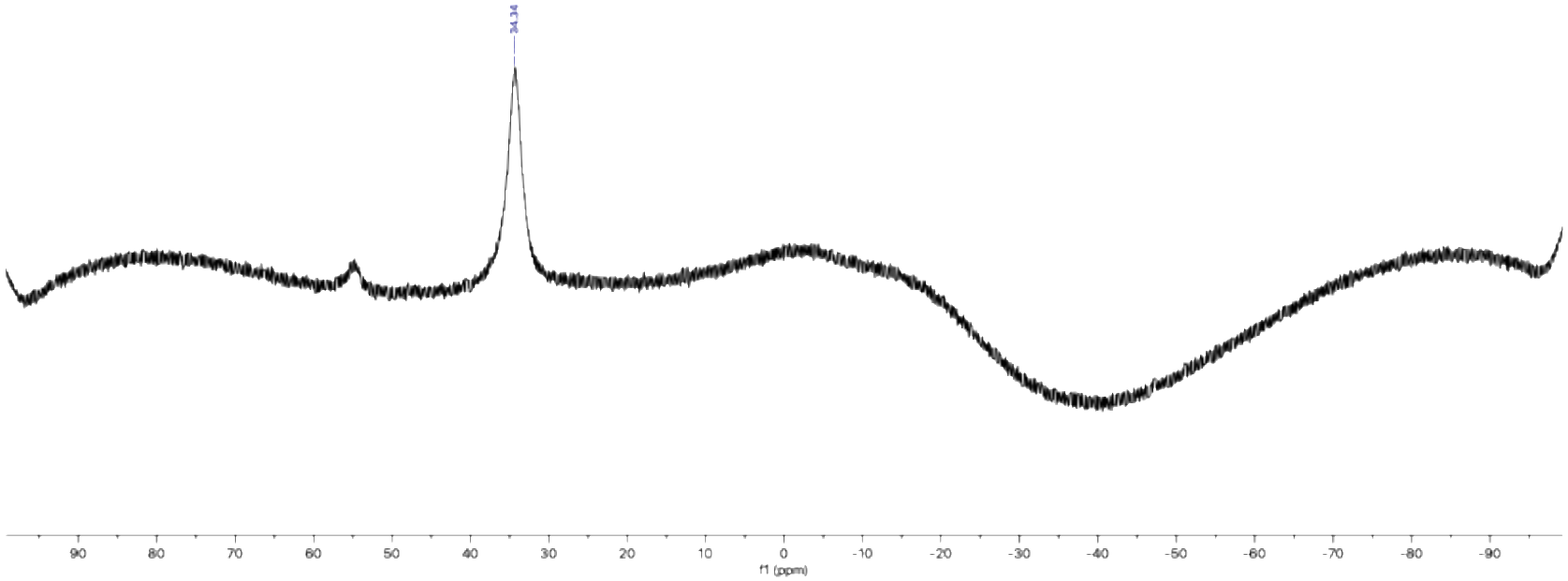


^{1}H NMR spectrum (400 MHz, $CDCl_3$)

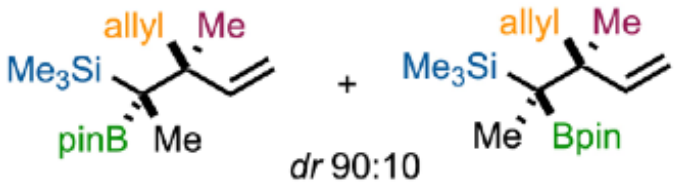


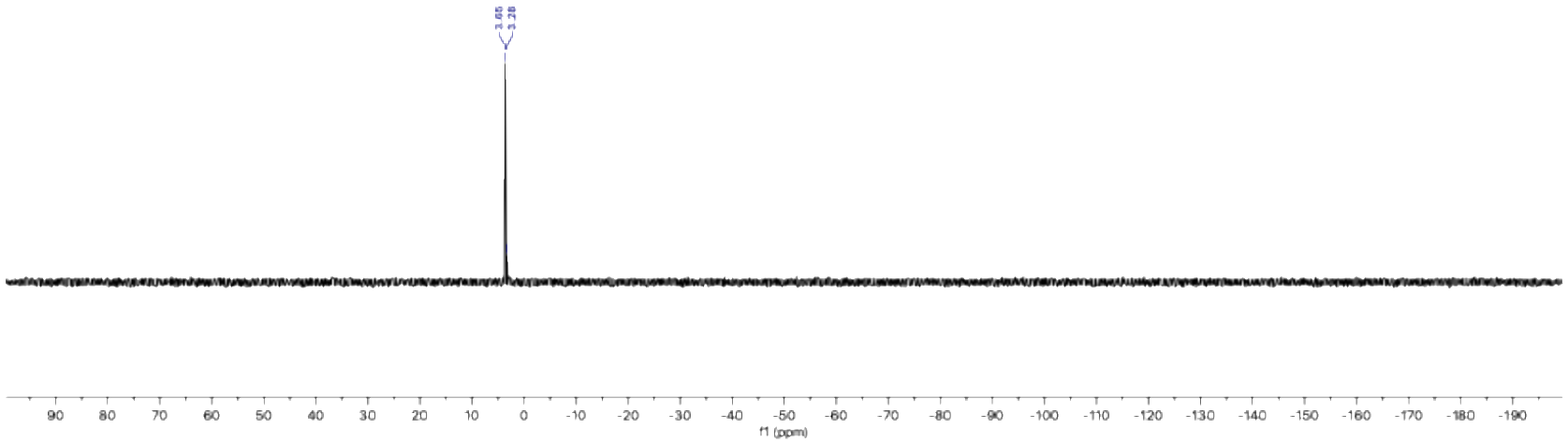
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





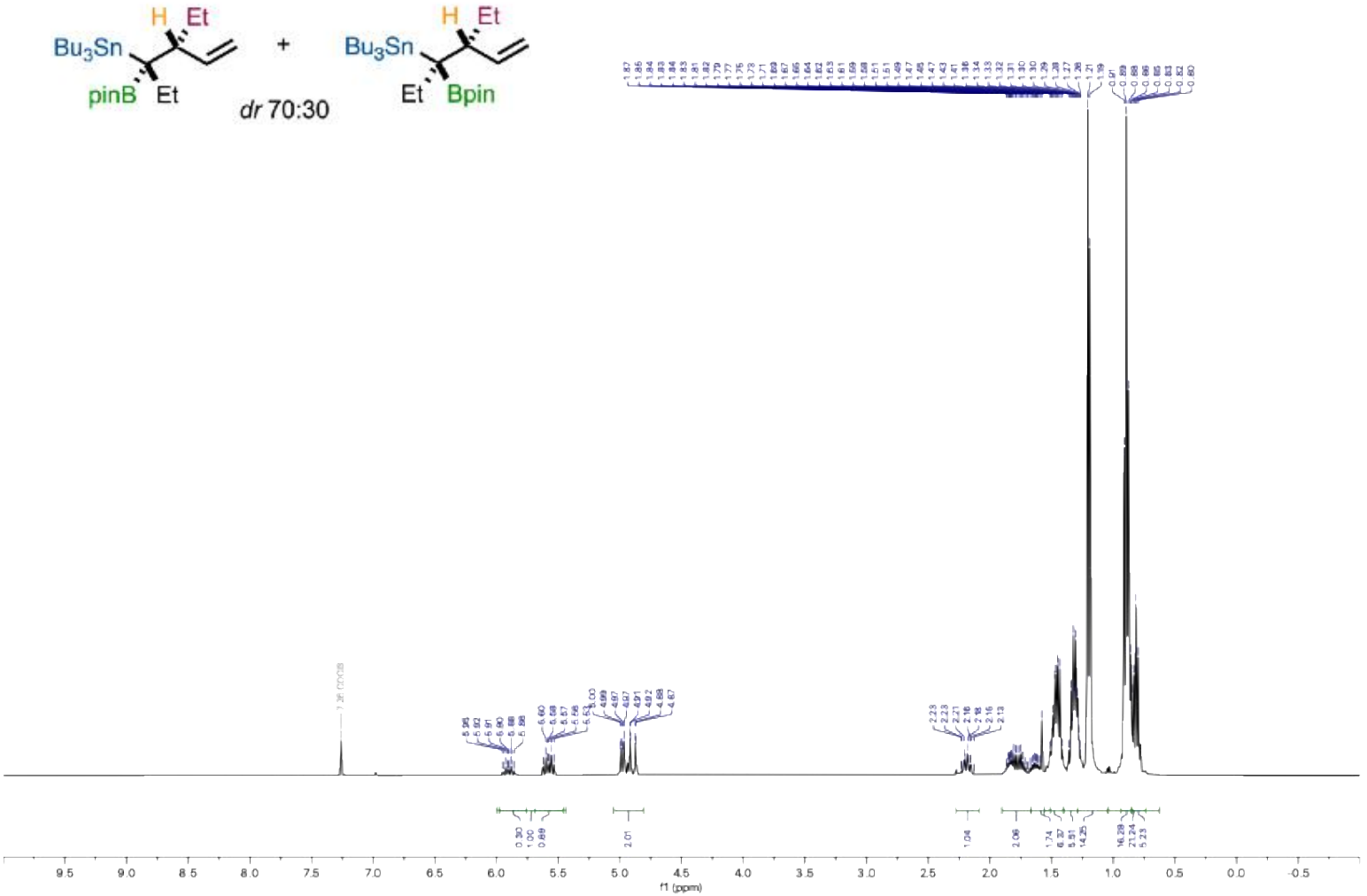
^{11}B NMR spectrum (128 MHz, $CDCl_3$)



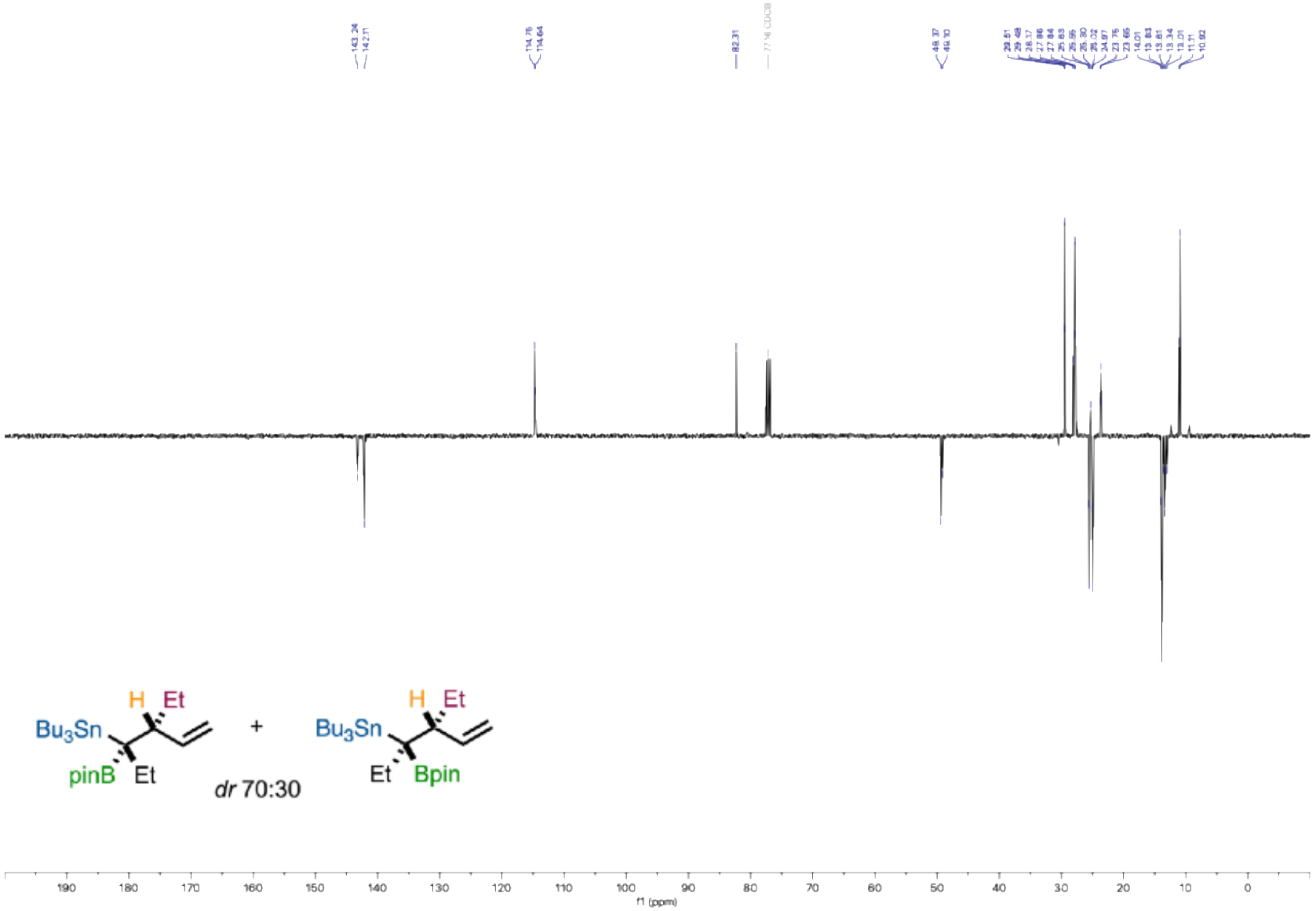


^{29}Si NMR spectrum (80 MHz, $CDCl_3$)

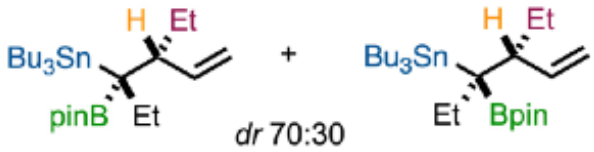
Tributyl((3*R,4*R**)-4-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-3-yl)stannane (6i)**

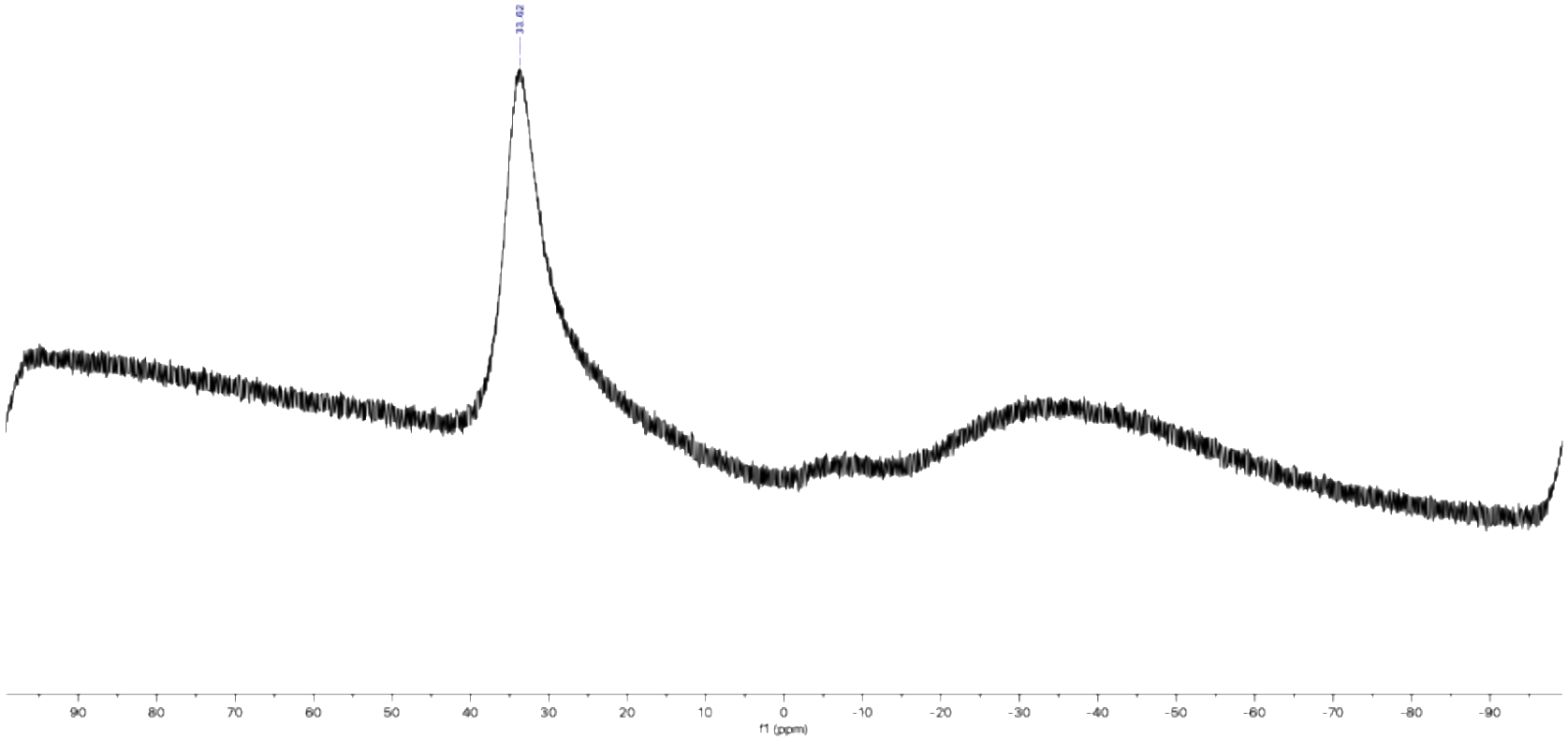


^{1}H NMR spectrum (400 MHz, $CDCl_3$)



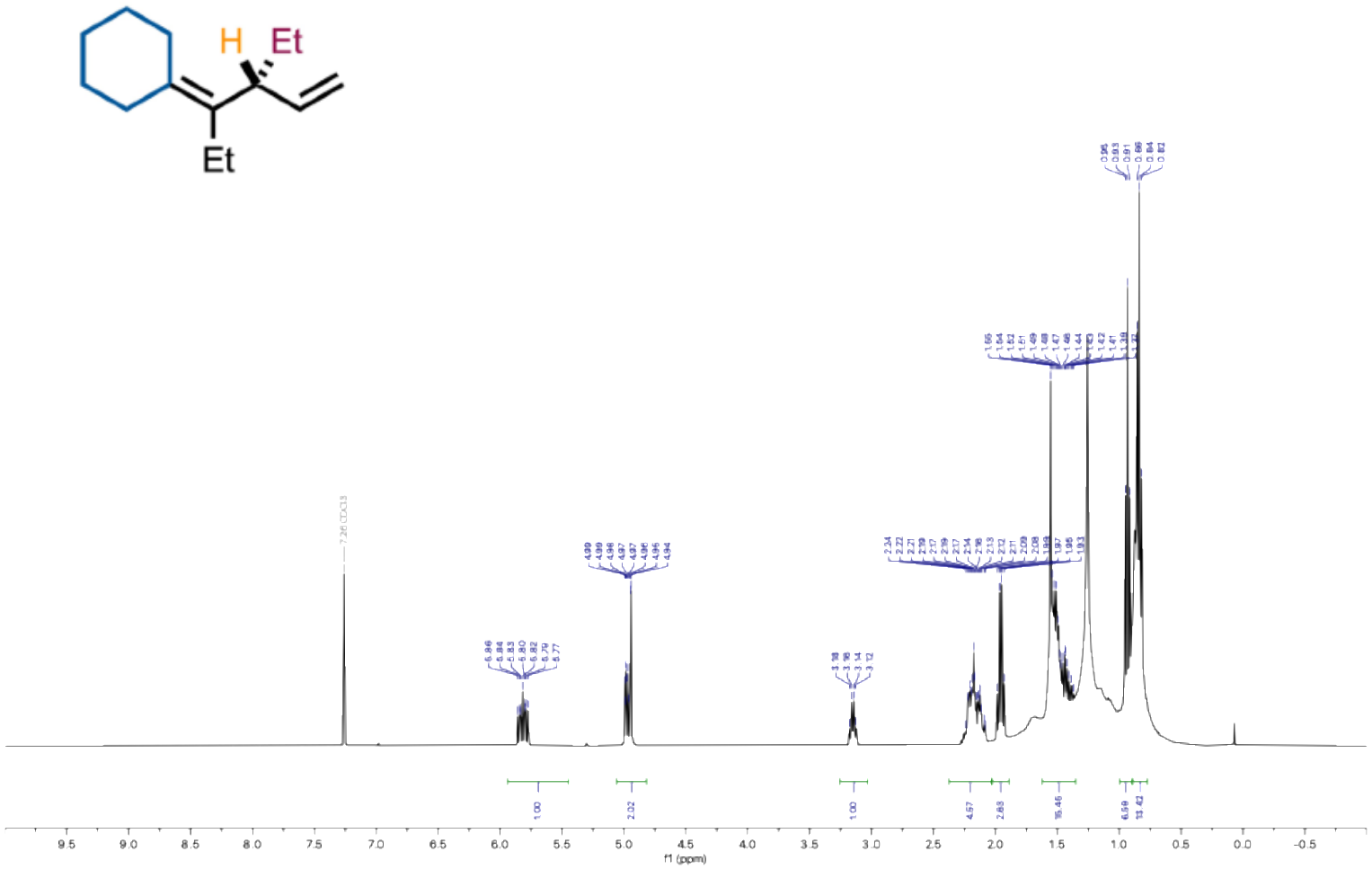
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



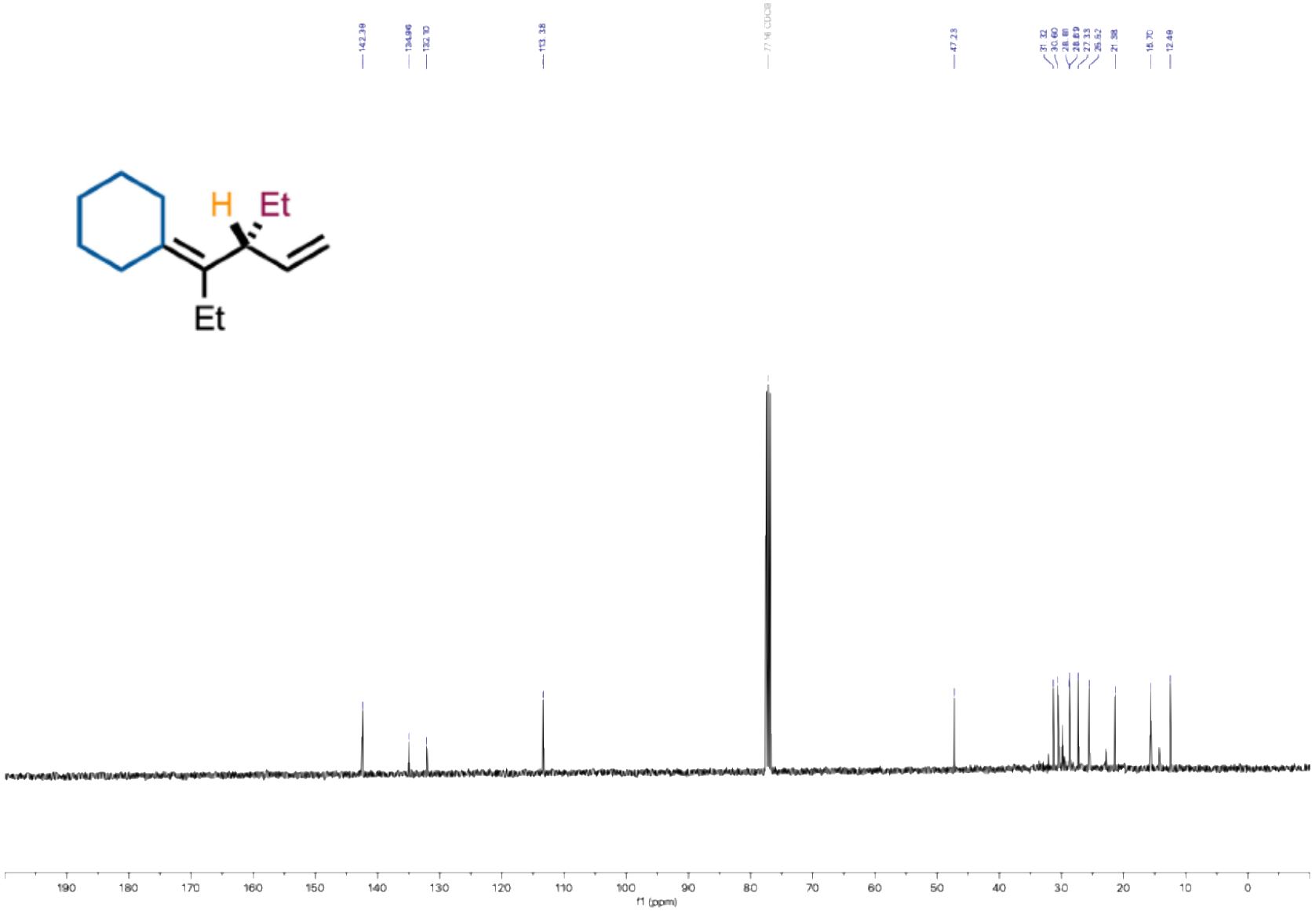


^{11}B NMR spectrum (128 MHz, $CDCl_3$)

(4-Ethylhex-5-en-3-ylidene)cyclohexane (6j)

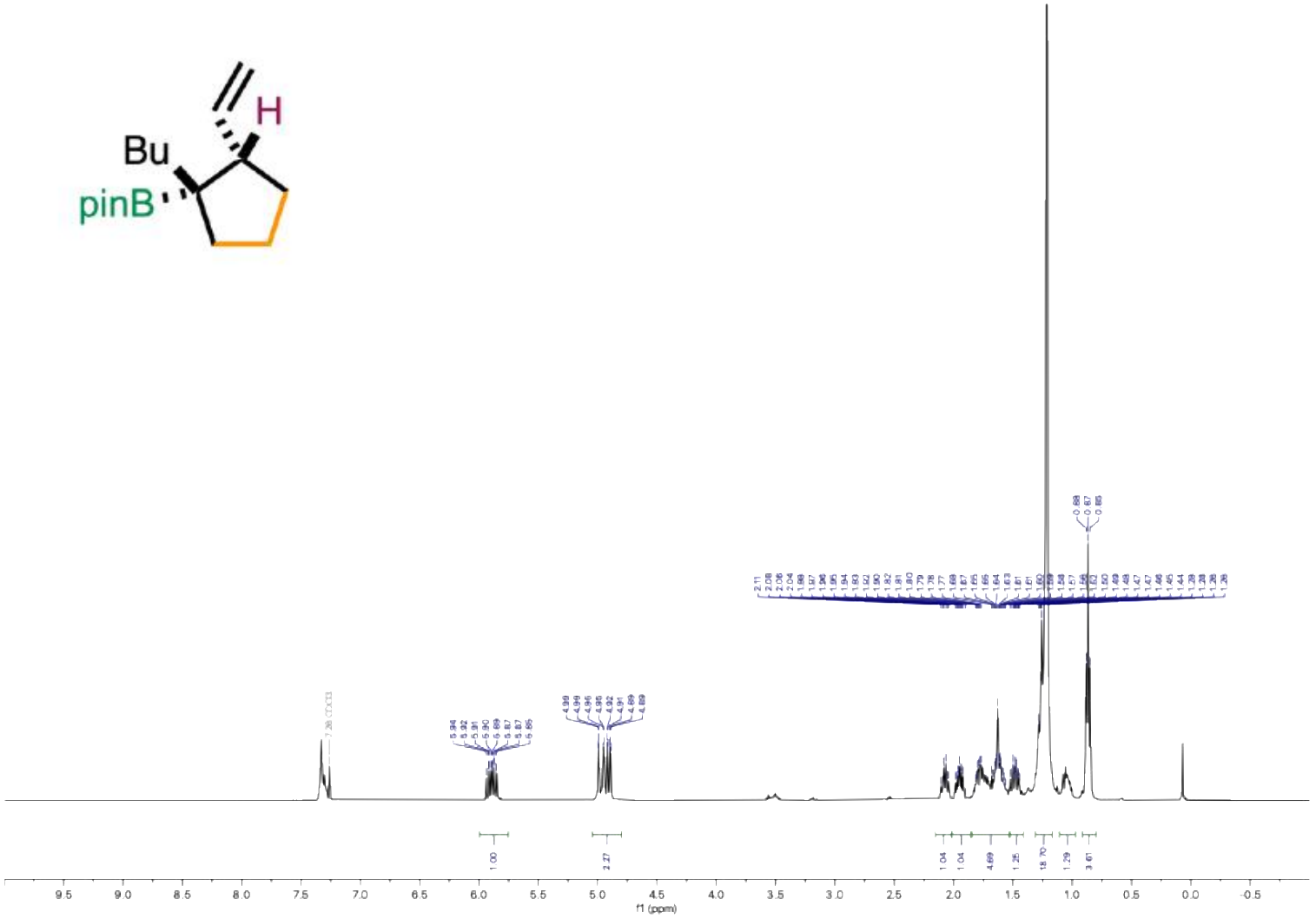


^{1}H NMR spectrum (400 MHz, $CDCl_3$)

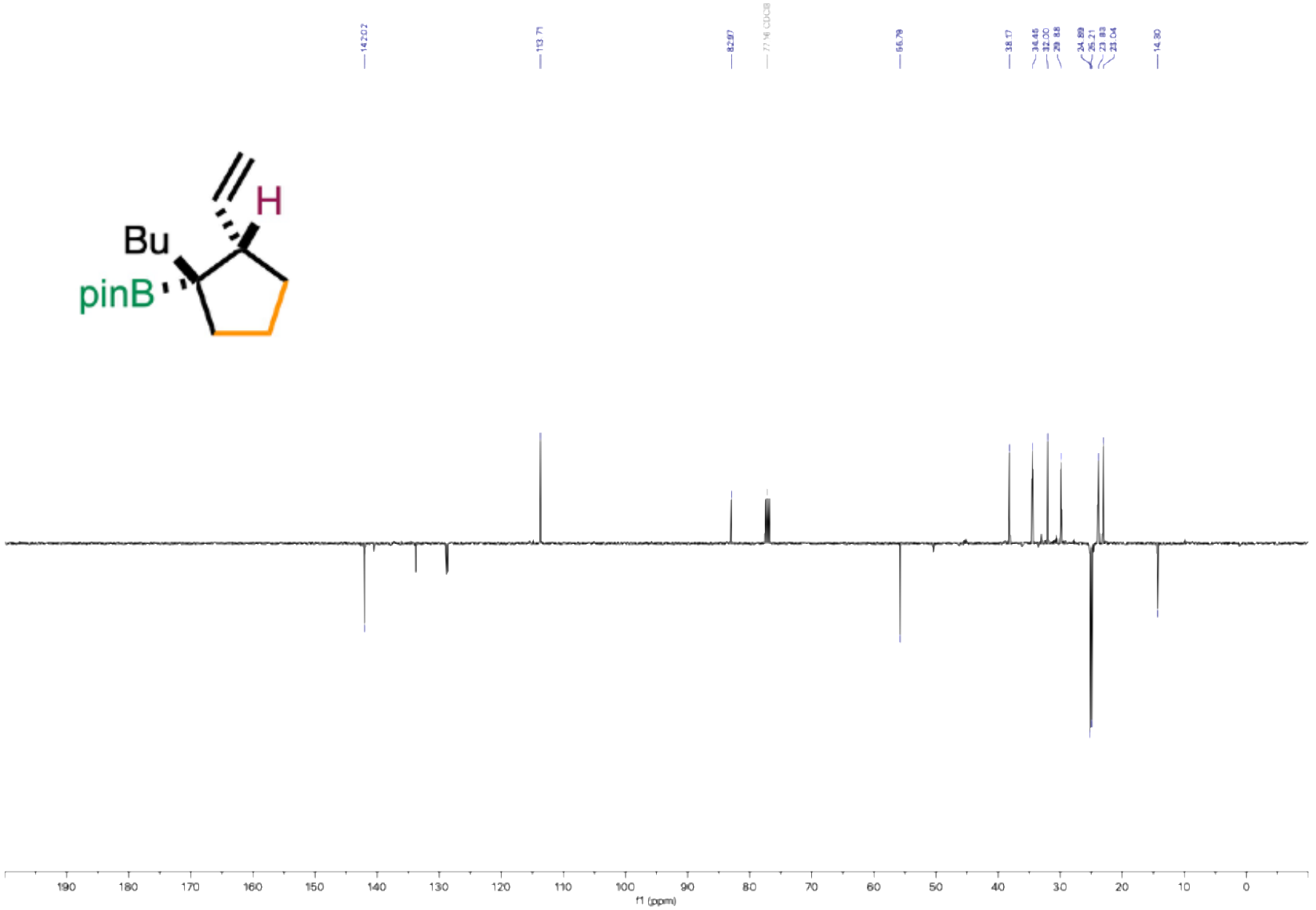


^{13}C NMR spectrum (101 MHz, $CDCl_3$)

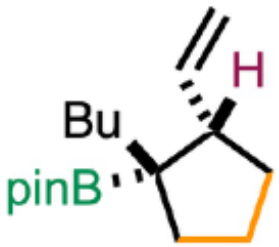
2-((1*R,2*S**)-1-Butyl-2-vinylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6k)**

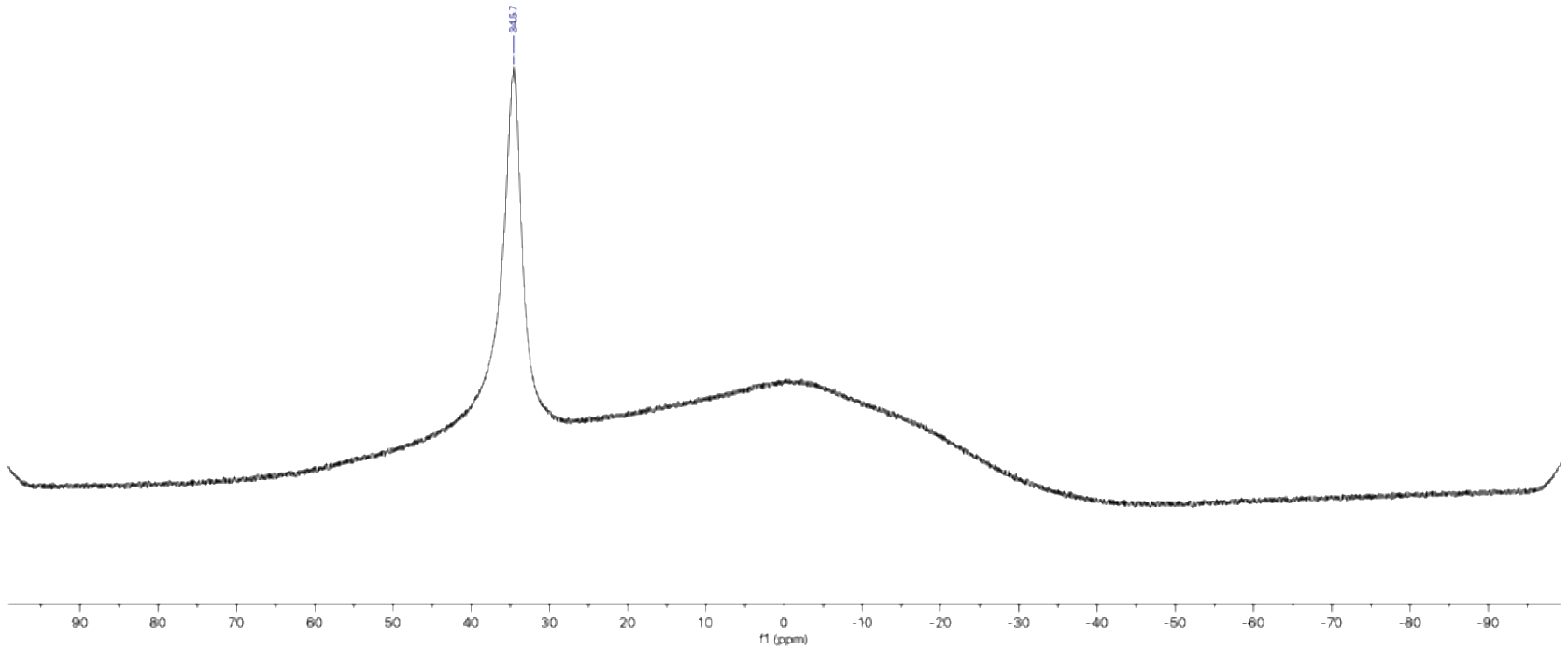


^{1}H NMR spectrum (400 MHz, $CDCl_3$)



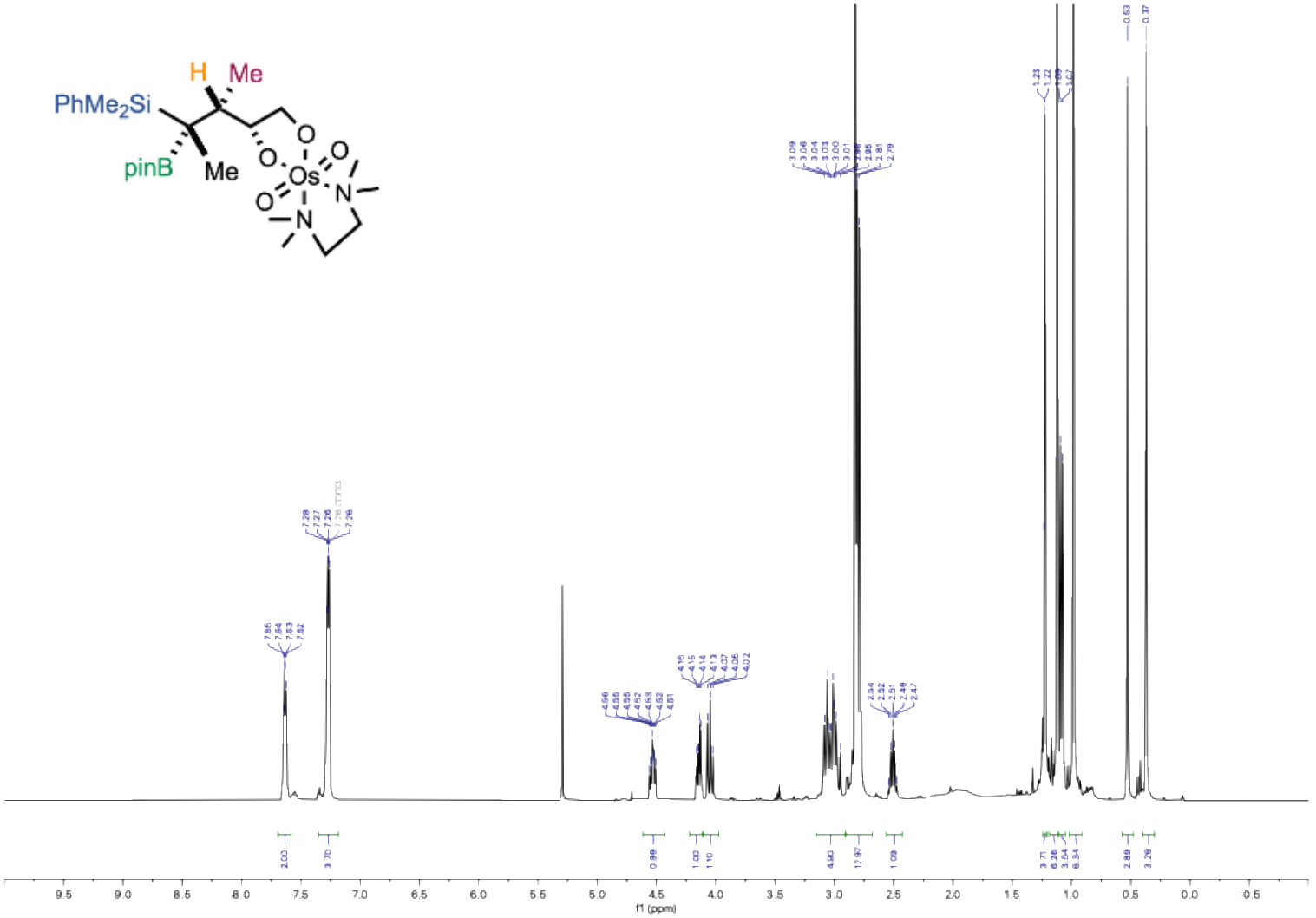
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



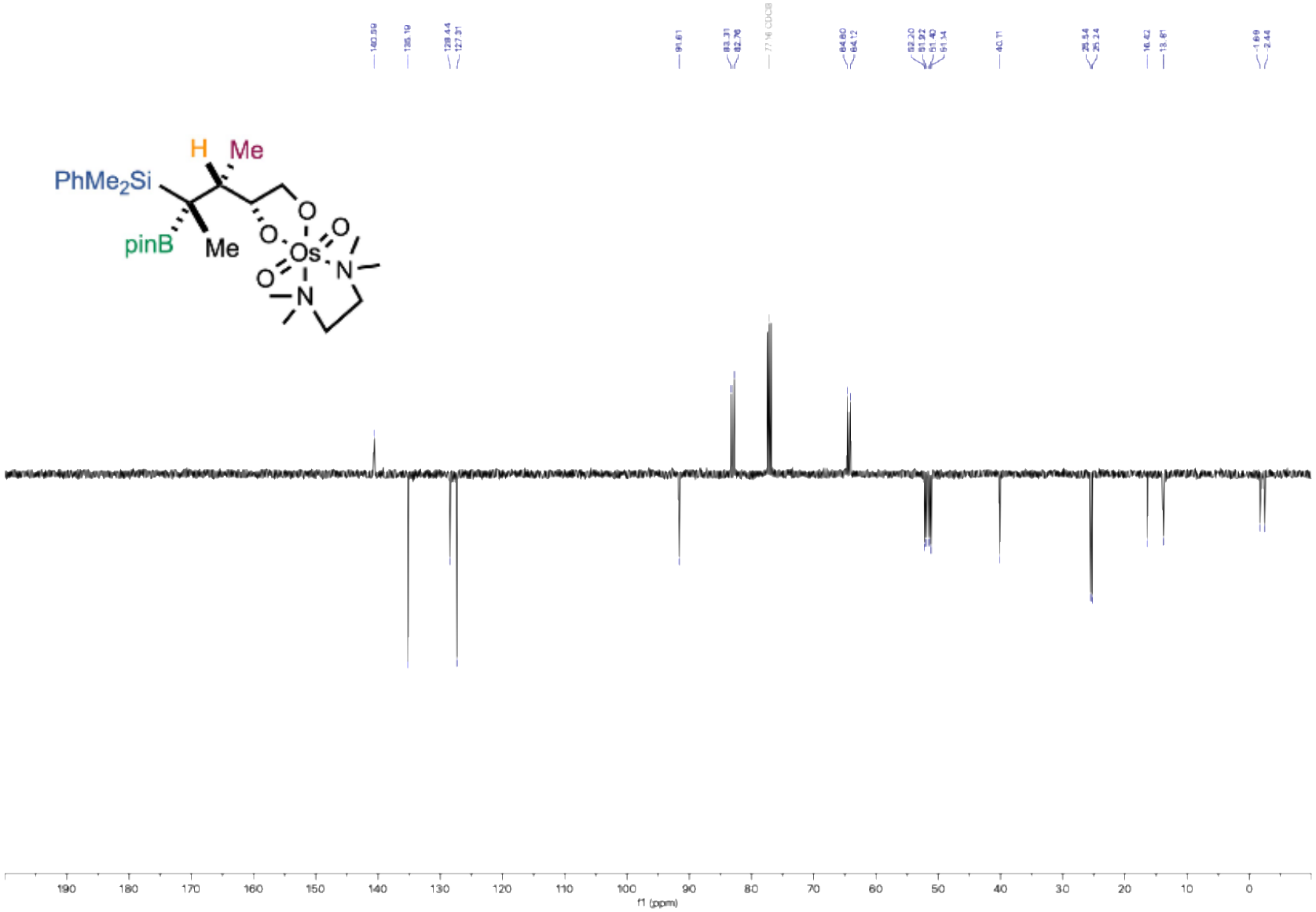


^{11}B NMR spectrum (128 MHz, $CDCl_3$)

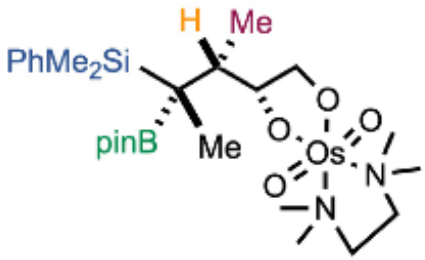
Dioxo[*N*,*N*,*N*,*N*-tetramethylethane-1,2-diaminetetramethylehylendiamine][(2*R,3*R**,4*R**)-4-(dimethyl(phenyl)silyl)-3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentane-1,2-diol]osmium complex 7b**

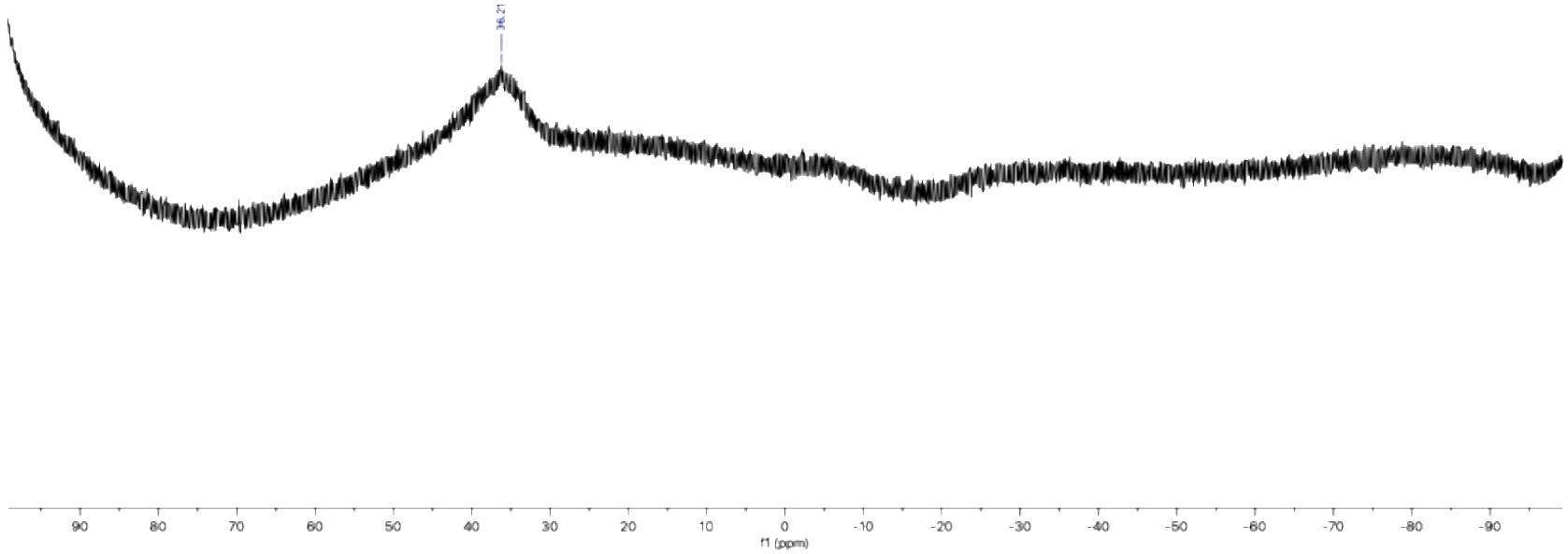


^{1}H NMR spectrum (400 MHz, $CDCl_3$)

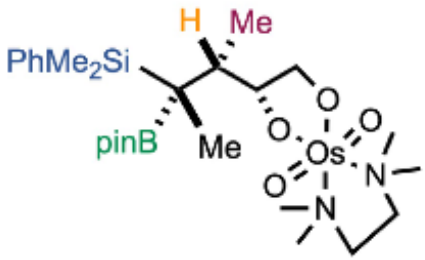


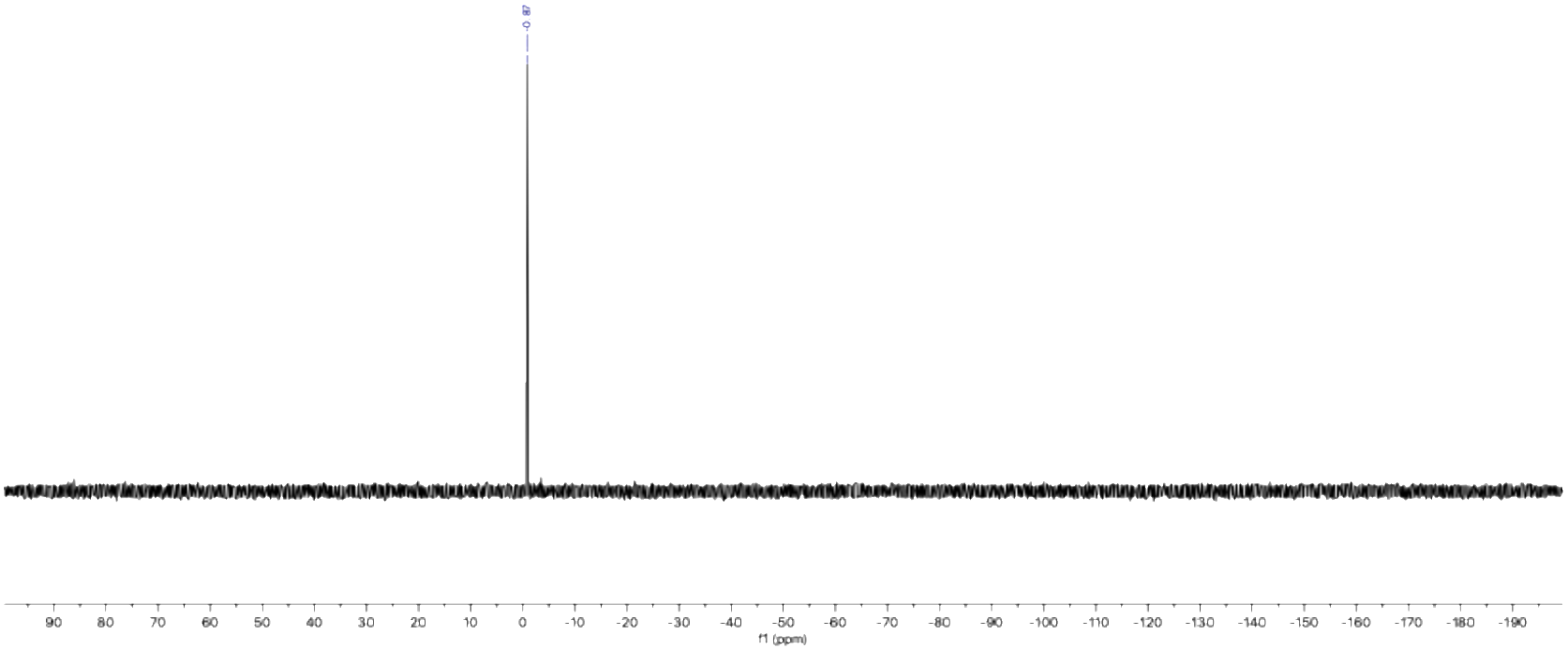
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





^{11}B NMR spectrum (128 MHz, $CDCl_3$)



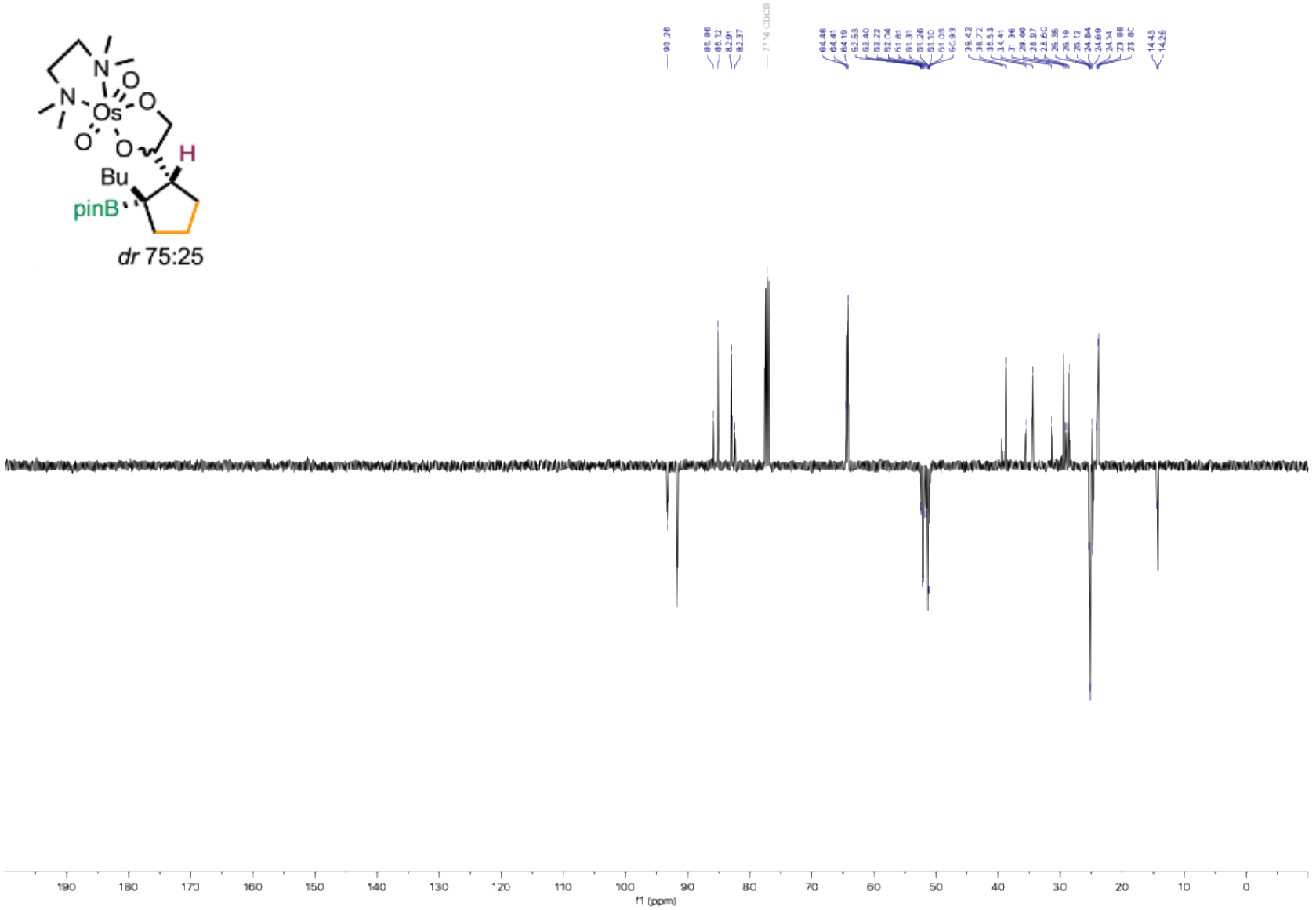


^{29}Si NMR spectrum (80 MHz, $CDCl_3$)

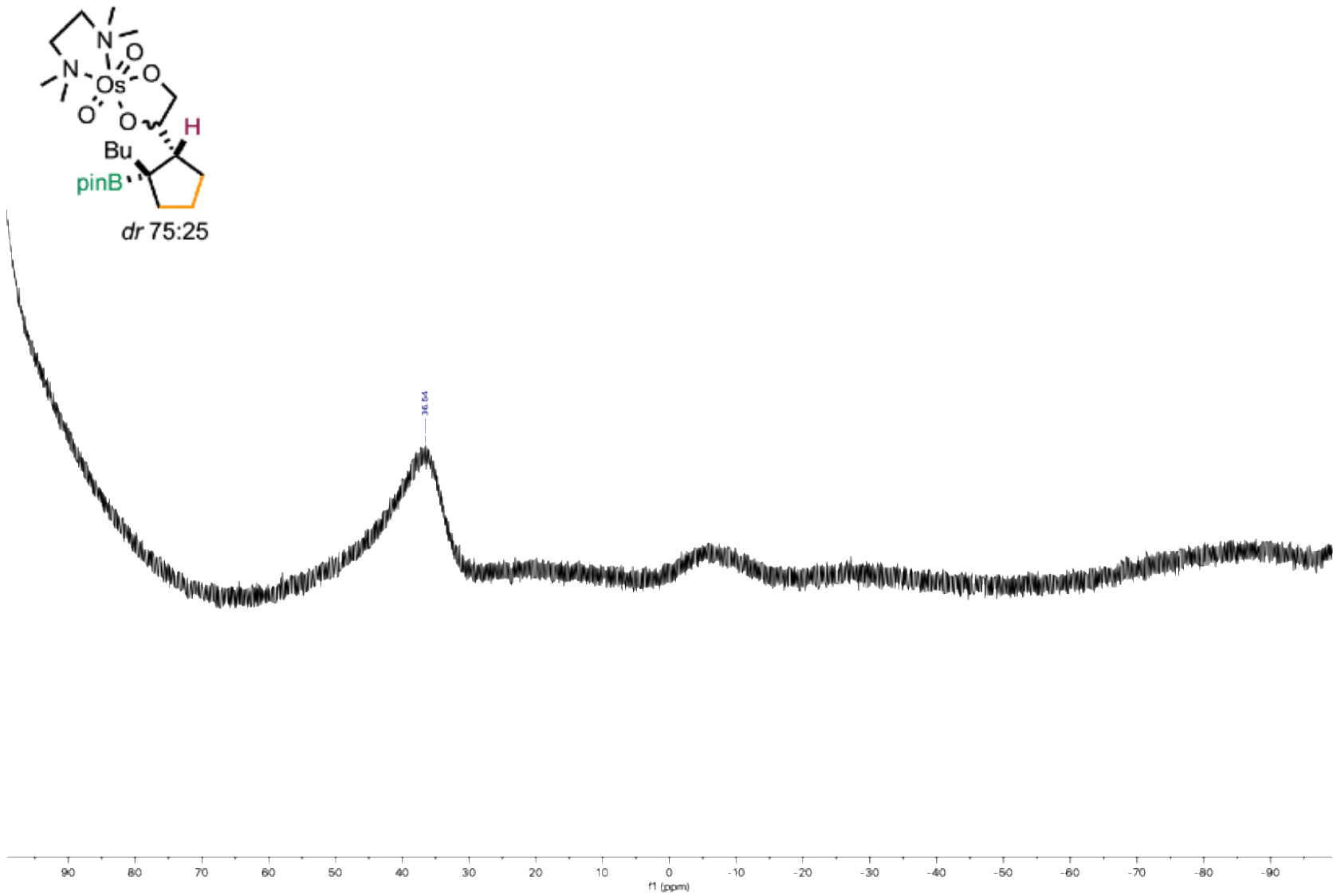
Dioxo[*N*,*N*,*N*,*N*-tetramethylethane-1,2-diaminetetramethylehylendiamine][(1-((1*R,2*R**)-2-butyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)ethane-1,2-diol]osmium complex 7k**

dr 75:25

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



^{13}C NMR spectrum (101 MHz, $CDCl_3$)



^{11}B NMR spectrum (128 MHz, $CDCl_3$)

6. References

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