Supporting Information

Selective synthesis of boron-substituted enynes *via* one-pot diboration/protodeboration sequence

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Outline

1. General information:

1.1. NMR analyzes

^{1}H, ^{11}B ^{13}C and ^{29}Si NMR spectra were recorded at 25 °C on Bruker UltraShield 300, 400 or 600 MHz with a number of scans (NS) for ^{1}H NMR = 16, ^{13}C NMR = 512 or 1024 (unless otherwise stated). Chemical shifts were reported in ppm with the reference to the residue portion solvent peak (^{1}H, ^{13}C NMR) or BF_3-Et_2O and TMS for ^{11}B and ^{29}Si, respectively. Chloroform-d_1 or toluene-d_8 were used as solvents and for internal deuterium lock. The multiplicities were reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), triplet (t), pentet (p), doublet of doublets of triplets (ddt).

1.2. GC-MS analysis

The mass spectra of the products were obtained by GC-MS analysis on a Bruker Scion 436-GC with a 30m Varian DB-5 0.25mm capillary column and a Scion SQ-MS mass spectrometry detector. Two temperature programs were used a) 60 °C (3 min), 10°C/min, 250 °C (30 min), b) 100 °C (3 min), 10°C/min, 280 °C (44.5 min).

1.3. FT-IR analysis

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

1.4. Elemental analysis

Elemental analyses were performed using the Vario EL III instrument.

1.5. Products purification

1.5.1. 1,3-Diynes (1a–s)

The UV-absorbing products (1,3-diynes) were purified on silica by flash chromatography (Biotage IsoleraOne chromatograph) with UV detector (λ1 = 255 nm, λ2= 280 nm). Purification details: cartridge 10 g, flow rate: 12 mL/min, length: 10 CV (CV = column volume), phase: *n*-hexane/dichloromethane (step 1: *n*-hexane 100% by 4 CV, step 2: gradient 10%/CV by 4 CV, step 3: *n*-hexane 50% by 2 CV). The non-aromatic products (1,3-diynes) were purified on silica using standard column chromatography using *n*-hexane/dichloromethane (95/5–7/3) as eluents. Products were characterized by GC-MS, ^{1}H, ^{13}C, ^{29}Si NMR, FT-IR analyses.

1.5.2. Boryl-functionalized enynes (4a–s)

The reaction mixture was evaporated to remove all volatiles. Subsequently, the crude product was dissolved in *n*-pentane and filtered through the syringe filter (0.2 μm). After evaporation of *n*-pentane, the product was heated (approx. 70–130 °C) and condensed at cold-finger trap under vacuum (<10^{-3} mbar). The products were obtained as oils.

2. Materials

Phenylacetylene (98%, Sigma-Aldrich), 1-ethynyl-4-fluorobenzene (99%, Sigma-Aldrich), 1-ethynyl-4-(trifluoromethyl)benzene (98%, Sigma-Aldrich), 1-octyne (97%, Sigma-Aldrich), ethynyltrimethylsilane (98%, abcr), ethynyltriethylsilane (97%, Sigma-Aldrich) (tri*iso*propylsilyl)acetylene (97%, Sigma-Aldrich), (*tert*-butyldimethylsilyl)acetylene (99%, Sigma-Aldrich), 3-cyclohexyl-1-propyne (97%, Sigma-Aldrich), 3-ethynylthiophene (96%, Sigma-Aldrich), 4-*tert*-butylphenylacetylene (96%, Sigma-Aldrich), 3-phenoxy-1-propyne (90%, Sigma-Aldrich), ethynylcyclopropane (98%, Apollo Scientific), iodobenzene (98%, Sigma-Aldrich), 1,4-bis(trimethylsilyl)buta-1,3-diyne (98%, Sigma-Aldrich), bis(pinacolato)diboron (98%, AmBeed), N-bromosuccinimide (98%, Sigma-Aldrich), hydroxylamine hydrochloride (98%, abcr), tributylamine (99%, Sigma-Aldrich), piperidine (99%, TCI), ammonium chloride (99%, Avantor Performance Materials Poland), silver nitrate (99%, Sigma-Aldrich), sodium sulfate (anhydrous, 99%, Sigma-Aldrich), cesium carbonate (99%, Sigma-Aldrich), iron(III) chloride anhydrous (>97,5%, Chempur), imidazole (99%, fluorochem), 1,8-diaminonaftalen, copper(I) iodide

(98%, Sigma-Aldrich), 1-iodo-4-nitrobenzene (98%, Sigma-Aldrich), tetrakis(triphenylphosphine) palladium(0) (99%, Sigma-Aldrich), tetrakis(triphenylphosphine)platinum(0) (98%, Acros Organics), silica gel (MN-Kieselgel 60, 0.04-0.063 mm (230-400 mesh ASTM; Sigma-Aldrich)) were used as received. Toluene, *n*-hexane, hexanes, ethyl acetate, acetone, acetonitrile were purchased from Avantor Performance Materials Poland. Toluene used in the reactions was dried, deoxygenated (SP5-800 MBraun) and stored over molecular sieves 4 Å under argon atmosphere. Argon (99,999%) was purchased from Messer.

3. General procedures

3.1. Synthesis of CuCl

A set was prepared to consist of two two-neck flasks equipped with septa and connected to each other by a Teflon tubing for SO_2 transport. In the first flask equipped with a reflux condenser, a magnetic stirrer and a cap with a hose for removing excess gas, a solution of 10.5 g of $CuSO_4 \cdot 5H_2O$ and 5.04 g of NaCl in 150 mL of water was placed. In the second flask (SO_2 generation system) equipped with a dropping funnel with concentrated hydrochloric acid (57 mL) and a magnetic stirrer, a concentrated aqueous solution of 41.46 g of Na_2SO_3 was prepared. Then, the content of the first flask was heated to a temperature of about 60 °C, and in the second flask, hydrochloric acid was started to be added dropwise to the concentrated Na_2SO_3 solution. The evolved gas (SO_2) was transported by means of a Teflon hose to the first flask and passed in a gentle stream through the heated solution until the product - copper(I) chloride precipitated out. After completion of the reaction, the mixture was cooled to room temperature and filtered off on a Büchner funnel. Then the obtained precipitate (CuCl) was purified by washing it with two small portions of concentrated acetic acid and three portions of diethyl ether.

3.2. Synthesis of alkynyl bromides

To a solution of N-bromosuccinimide (1.3 equiv.) and alkyne (1 equiv.) in acetone (1 mL of acetone/1 mmol of alkyne), silver nitrate (0,025 equiv.) was added under argon atmosphere. The reaction mixture was stirred at room temperature over 18 h and subsequently evaporated to remove all volatiles. The crude mixture was dissolved in hexane and filtered through a silica gel and concentrated to give a colourless or slightly yellow liquids.

Caution: All synthesized alkynyl bromides are strong lachrymators. The isolation should be performed under the hood.

*3.3. Synthesis of symmetrical diynes (**2a–d**)*

The CuCl (0.1 mmol) was placed in a round bottom flask equipped with a condenser and magnetic stirring bar. Subsequently, toluene (10 mL), piperidine (0.15 mmol), and alkyne (5 mmol) were placed in the reaction vessel. The reaction was performed at 80 °C for 18 hours in an air atmosphere. Afterwards, the reaction mixture was cooled and all volatiles were removed under vacuum. The crude residue was dissolved in hexanes (with a small amount of dichloromethane if necessary) and purified.

*3.4. Synthesis of unsymmetrical diynes (**2e–s**)*

The unsymmetrical 1,3-diynes were prepared according to the literature with some modifications:

CuCl was dissolved in a 2:3 mixture by volume of n-$BuNH_2$:H_2O (5 mL/mmol alkyne) and the solution was cooled to 0 °C in an ice bath. Hydroxylamine hydrochloride was slowly added until trace amounts of copper(II) were reduced and the colour of the solution changed from blue to colourless. The alkyne bromide and alkyne were dissolved in dichloromethane (5 mL/mmol alkyne), and this solution was added to the reaction flask at once. The biphasic mixture was vigorously stirred overnight under an argon atmosphere. Subsequently, the organic layer was removed and washed with portions of saturated aq. NH_4Cl until these portions no longer took on a blue colour. The organic layer was dried (Na_2SO_4) and concentrated by rotary evaporation. The crude residue was dissolved in hexanes and purified.

3.5. *Synthesis of monoborylenynes (**4a–s**)*

3.5.1. One step procedure

[$Pt(PPh_3)_4$] (0.0025 mmol), bis(pinacolato)diboron (0.3 mmol), diyne (0.25 mmol), toluene and aqueous solution of Cs_2CO_3 (3M, 2mL) were added into a Rotaflo®-type Schlenk vessel under an argon atmosphere and stirred for 18 h at 100 °C. Afterwards, the crude reaction mixture was analyzed by GC-MS and ^1H NMR analyses and purified by sublimation.

3.5.2. Two steps procedure

[$Pt(PPh_3)_4$] (0.0025 mmol), bis(pinacolato)diboron (0.25 mmol), diyne (0.25 mmol), and toluene were added into a Rotaflo®-type Schlenk vessel under an argon atmosphere and stirred for 18 h at 100 °C. Afterwards, aqueous solution of Cs_2CO_3 (3M, 2mL) was added and reaction mixture was stirred for another 1 h at 100 °C. The crude reaction mixture was analyzed by GC-MS and ^1H NMR analyses and purified by sublimation.

*3.6. Suzuki coupling (for product **7**)*

[$Pd(PPh_3)_4$] (0.01 mmol), **4a** (0.145 mmol), 4-iodotoluene (0.348 mmol) were placed in the Schlenk vessel and evacuated. Then the toluene (1.45 mL) and aqueous solution of Cs_2CO_3 (3M, 1.45 mL) were added under argon atmosphere and stirred for 48 h at 60 °C. Upon completion of reaction, crude mixture was purified by flash chromatography.

*3.7. Transformation of alkoxy to amionoborane (for product **8**)*

$FeCl_3$ (10.4 μmol), 1,8-diaminonaphthalene (0.13 mmol), imidazole (0.26 mmol) were dissolved in water (0.25 mL) and acetonitrile (0.25 mL) in a 4-mL screw-capped vial equipped with a magnetic stirring bar. Subsequently, **4a** (0.1 mmol) was transferred and rinsed with acetonitrile (0.75 mL) into the vial and stirred for 48 h at room temperature. After the completion of the reaction, the crude mixture was washed with brine and extracted with ethyl acetate. The organic layer was then dried over sodium sulfate, filtered and evaporated under vacuum to remove all volatiles. Afterwards, the crude product was purified by flash chromatography.

*3.8. Bromodesilylation (for product **9**)*

The **4a** (0.1 mmol) and N-bromosuccinimide (0.15mmol) and acetonitrile (1 mL) were placed in the round bottom flask. The reaction mixture was stirred at room temperature over 17 h. Afterwards, crude reaction mixture was analyzed by GC-MS and then purified by filtration through a silica gel and sublimation.

*3.9. Sila-Sonogashira (for product **10**)*

[$Pd(PPh_3)_4$] (0.0225 mmol), CuI (0.225 mmol), **4a** (0.3 mmol) and *p*-iodonitrobenzene (0.36 mmol) were placed in the Schlenk vessel and evacuated. Then the dry DMF (3 mL) was added under argon atmosphere and stirred for 18 h at 80 °C. Afterwards, crude reaction mixture was analyzed by GC-MS and purified by flash chromatography.

3.10. Mechanistic studies

The mechanism of the diboration of 1,3-diynes was proposed by our group earlier.[6]

The deuterium labelling experiments were conducted as follows:

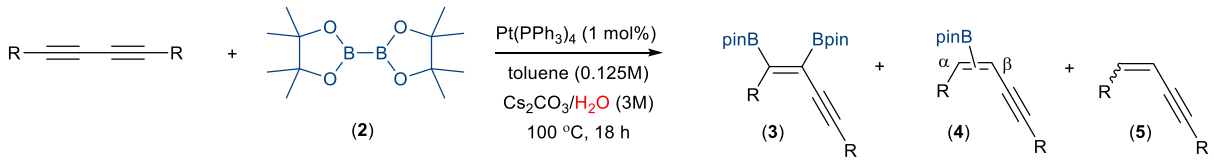
3.10.1. One step procedure

[$Pt(PPh_3)_4$] (0.0025 mmol), bis(pinacolato)diboron (0.3 mmol), diyne (0.25 mmol), toluene and aqueous solution (D_2O) of Cs_2CO_3 (3M, 2mL) were added into a Rotaflo®-type Schlenk vessel under an argon atmosphere and stirred for 18 h at 100 °C. Afterwards, the crude reaction mixture was analyzed by GC-MS and ^1H NMR analyses. Aqueous phase was analyzed by ^{11}B NMR.

3.10.2. Two steps procedure

[Pt(PPh$_3$)$_4$] (0.0025 mmol), bis(pinacolato)diboron (0.25 mmol), diyne (0.25 mmol), and toluene were added into a Rotaflo®-type Schlenk vessel under an argon atmosphere and stirred for 18 h at 100 °C. Afterwards, aqueous solution (D$_2$O) of Cs$_2$CO$_3$ (3M, 2mL) was added and reaction mixture was stirred for another 1 h at 100 °C. The crude reaction mixture was analyzed by GC-MS and ^{1}H NMR analyses. Aqueous phase was analyzed by ^{11}B NMR.

4. Results for diboration/protodeboration of symmetrical silyl and aryl substituted 1,3-diynes

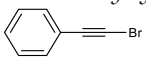


Entry	Diyne (1)	Conv. of 1 [%][a]	Selectivity [3/4/5][b]
1	R = Si(*i*-Pr)$_3$	19	0/100/0 (100/0)[c]
2	R = Ph	100	0/70/30 (83/17)[c]
3[d]		100	20/40/40 (81/19)[c]
4[e]		99	0/4/96

[a)] Based on GC-MS analysis. [b)] Based on GC-MS and ^{1}H NMR analyses. [c)] Ratio of (**4**) α-isomer and (**4**) β-isomers. [d)] K$_2$CO$_3$ as a base (3M). [e)] MeONa/MeOH as a base (3M).

5. Products characterization

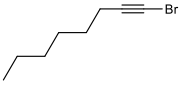
(Bromoethynyl)benzene



Chemical Formula: C_8H_5Br
Molecular Weight: 181,03

^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 7.54 – 7.43 (m, 2H, Ph), 7.40 – 7.28 (m, 3H, Ph). **^{13}C NMR** (75 MHz, CDCl$_3$, δ, ppm): 132.11, 128.81, 128.46, 122.79, 80.16 (C≡C-Br), 49.90 (C≡C-Br). **MS** (EI, m/z): 182 (M$^+$+2, 100), 180(M$^+$, 97), 101(93), 75(48), 62(5), 51(8). Pale yellow liquid. Isolated yield: 91% (8.5 g). Analytical data are in agreement with the literature.[1]

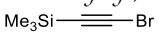
1-Bromooct-1-yne



Chemical Formula: $C_8H_{13}Br$
Molecular Weight: 189,10

^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 2.20 (t, $J_{H\text{-}H}$ = 7.0 Hz, 2H, CH$_2$C≡C), 1.51 (p, $J_{H\text{-}H}$ = 6.8 Hz, 2H), 1.38 – 1.24 (m, 6H), 0.89 (t, $J_{H\text{-}H}$ = 6.8 Hz, 3H, CH$_2$CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm): 80.63 (C≡C), 37.55, 31.43, 28.62, 28.42, 22.67, 19.83, 14.18. **MS** (EI, m/z): 161(M$^+$-28, 4), 159(M$^+$-30, 4), 147(4), 145(4), 132(7), 119(8), 117(9), 109(15), 79(41), 67(100). Colorless liquid. Isolated yield: 93% (12.8 g). Analytical data are in agreement with the literature.[1]

(Bromoethynyl)trimethylsilane



Chemical Formula: C_5H_9BrSi
Molecular Weight: 177,12

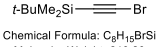
^{1}H NMR (300 MHz, CDCl3, δ, ppm): 0.19 (s, 9H, Si(CH$_3$)$_3$). **^{13}C NMR** (75 MHz, CDCl3, δ, ppm): 87.13 (C≡C), 61.56 (C≡C), -0.11. **^{29}Si NMR** (80 MHz, CDCl$_3$, δ, ppm): -15.64. **MS** (EI, m/z): 177(3), 175(3), 161(100), 133(12), 109(12), 97(27), 67(17), 53(14). Pale yellow liquid. Isolated yield: 69% (12,5g). Analytical data are in agreement with the literature.[2]

(Bromoethynyl)triisopropylsilane

Chemical Formula: $C_{11}H_{21}BrSi$
Molecular Weight: 261,28

^{1}H NMR (300 MHz, CDCl3, δ, ppm): 1.08 (s, 21H, (Si(C<u>H</u>(C<u>H</u>$_3$)$_2$)$_3$). **^{13}C NMR** (75 MHz, CDCl3, δ, ppm): 83.60 (C≡C-Br), 61.87 (C≡C-Br), 18.63 (Si(CH(CH$_3$)$_2$)$_3$), 11.44 (Si(CH(CH$_3$)$_2$)$_3$). **^{29}Si NMR** (80 MHz, CDCl$_3$, δ, ppm): -0.26. **MS** (EI, m/z): 262 (M^++2, 5) 260 (M^+, 5), 219(83), 217(83), 191(43), 189(42), 163(74), 161(68), 149(100), 147(93), 137(22), 109(31), 95(23), 69(17), 53(22). Colorless liquid. Isolated yield: 91% (5.4 g). Analytical data are in agreement with the literature.[3]

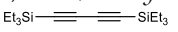
(Bromoethynyl)tert-butyldimethylsilane



Chemical Formula: $C_8H_{15}BrSi$
Molecular Weight: 219,20

^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 0.82 (s, 9H, C(C<u>H</u>$_3$)$_3$) 0.00. (s, 6H, Si(C<u>H</u>$_3$)$_2$). **^{13}C NMR** (75 MHz, CDCl$_3$,δ, ppm): δ 85.48, (C≡C), 61.62 (C≡C), 26.13 (C(CH$_3$)$_3$), 16.83 (C(CH$_3$)$_3$), -4.57 (Si(CH$_3$)$_2$). **^{29}Si NMR** (80 MHz, CDCl$_3$ δ, ppm): -6.05. **MS** (EI, m/z): 219(M^+, 0.2), 73(100), 81(12), 101(16), 107(19), 115(16), 121(16), 145(10). Colorless liquid. Isolated yield: 58% (6,1 g). Analytical data are in agreement with the literature.[4]

*1,4-Bis(triethylsilyl)buta-1,3-diyne (**2b**)*



Chemical Formula: $C_{16}H_{30}Si_2$
Molecular Weight: 278,59

^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 1.00 (t, $J_{H\text{-}H}$ = 7.9 Hz, 18H, Si(CH$_2$C<u>H</u>$_3$)$_3$), 0.64 (t, $J_{H\text{-}H}$ = 7.9 Hz, 12H, Si(C<u>H</u>$_2$CH$_3$)$_3$). **^{13}C NMR** (101 MHz, CDCl$_3$, δ, ppm): 89.38 (C≡C), 83.31 (C≡C), 7.48, 4.29. **^{29}Si NMR** (79 MHz, CDCl$_3$ δ, ppm): -5.84. **MS** (EI, m/z): 278(M^+, 7), 249(100), 221(94), 193(38), 165(27), 137(20), 109(11), 82(17), 68(8). **FT-IR** (cm^{-1}): 2955, 2936, 2912, 2875, 2064, 1457, 1004, 723, 695, 620. Colorless liquid. Isolated yield: 90% (1.24 g). Analytical data are in agreement with the literature.[5,6]

*1,4-Bis(tert-butyldimethylsilyl)buta-1,3-diyne (**2c**)*

Chemical Formula: $C_{16}H_{30}Si_2$
Molecular Weight: 278,59

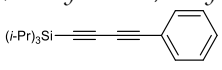
^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 0.95 (s, 18H, Si(CH$_3$)$_2$(C(C<u>H</u>$_3$)$_3$), 0.13 (s, 12H, Si(C<u>H</u>$_3$)$_2$(C(CH$_3$)$_3$). **^{13}C NMR** (75 MHz, CDCl$_3$, δ, ppm): 88.98 (<u>C</u>≡<u>C</u>), 84.17 (C≡<u>C</u>), 26.19, 16.89, -4.72. **^{29}Si NMR** (79 MHz, CDCl$_3$ δ, ppm): -6.37. **MS** (EI, m/z): 278(M^+, 6), 221(100), 179(17), 165(8), 123(11), 73(19). White solid. Isolated yield: 81% (1.13 g). Analytical data are in agreement with the literature.[7]

*1,6-Dicyclohexylhexa-2,4-diyne (**2d**)*

Chemical Formula: $C_{18}H_{26}$
Molecular Weight: 242,41

^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 2.15 (s, 2H, C≡CC<u>H</u>$_2$), 2.13 (s, 2H, C≡CC<u>H</u>$_2$), 1.82 – 1.60 (m, 10H), 1.53 – 1.42 (m, 2H), 1.30 – 1.07 (m, 6H), 1.04 – 0.92 (m, 4H). **^{13}C NMR** (75 MHz, CDCl$_3$, δ, ppm): 76.52, 66.25, 37.41, 32.83, 27.15, 26.29, 26.21 **MS** (EI, m/z): 242(M^+, 4), 199(6), 159(7), 145(13), 131(25), 117(39), 105(19), 91(34), 83(40), 67(20), 55(100). Orange oil. Isolated yield: 93% (1.12 g). Analytical data are in agreement with the literature.[8]

*(Phenylbuta-1,3-diyn-1-yl)trisopropylsilane (**2e**)*

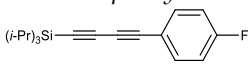


Chemical Formula: $C_{19}H_{26}Si$
Molecular Weight: 282,50

^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 7.55 – 7.27 (m, 5H, Ph), 1.12 (s, 21H, Si(C<u>H</u>(C<u>H</u>$_3$)$_2$)$_3$). **^{13}C NMR** (75 MHz, CDCl$_3$, δ, ppm): 132.84, 129.36, 128.54, 121.68, 89.63 (C≡C), 88.03 (C≡C), 75.69

(C≡C), 74.80 (C≡C), 18.72, 11.45. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -0.65. **MS** (EI, m/z): 282(M^+, 8), 239(98), 211(44), 197(40), 183(54), 169(100), 159(21), 153(27), 91(20) 59(10). **FT-IR** (cm^{-1}): 2942, 2890, 2865, 2204, 2101, 1488, 1461, 1070, 1018, 995, 881, 752, 729, 675, 602. Colorless oil. Isolated yield: 75% (1.05 g). Analytical data are in agreement with the literature.[6, 9]

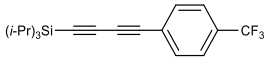
*((4-Fluorophenyl)buta-1,3-diyn-1-yl)triisopropylsilane (**2f**)*



Chemical Formula: $C_{19}H_{25}FSi$
Molecular Weight: 300,49

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.53 – 7.45 (m, 2H, Ph), 7.05 – 6.97 (m, 2H, Ph), 1.12 (s, 21H, Si(C<u>H</u>(C<u>H</u>$_3$)$_2$)$_3$) **^{13}C NMR** (101 MHz, $CDCl_3$, δ, ppm): 163.18 (d,$^1J_{C\text{-}F}$ = 251.5 Hz), 134.86 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 117.80 (d, $^4J_{C\text{-}F}$ = 3.6 Hz), 116.00 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 89.48 (<u>C</u>≡C), 88.11 (C≡<u>C</u>), 74.61 (<u>C</u>≡C), 74.58 (C≡<u>C</u>), 18.71, 11.45. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -0.57. **MS** (EI, m/z): 300(M+, 6), 257(66), 229(35), 201(54), 187(100), 171(29), 147(22). Pale yellow oil. Isolated yield: 81% (1.21 g). Analytical data are in agreement with the literature.[6, 9]

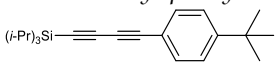
*Trisopropyl((4-(trifluoromethyl)phenyl)buta-1,3-diyn-1-yl)silane (**2g**)*



Chemical Formula: $C_{20}H_{25}F_3Si$
Molecular Weight: 350,50

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.68 – 7.50 (m, 4H, Ph), 1.12 (s, 21H, Si(C<u>H</u>(C<u>H</u>$_3$)$_2$)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, δ, ppm): 133.05, 131.09, 130.77, 125.50 (q, $J^3_{C\text{-}F}$ = 3.8 Hz), 122.54, 89.94 (<u>C</u>≡C), 89.07 (C≡<u>C</u>) , 73.98 (<u>C</u>≡C), 18.71, 11.43. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -0.28. **MS** (EI, m/z): 350(M^+, 5), 307(100), 279(38), 265(26), 251(55), 237(82), 197(12), 175(17), 151(7), 137(8), 125(6). Colorless oil. Isolated yield: 81% (1.42 g). Analytical data are in agreement with the literature.[6, 10]

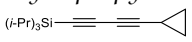
*((4-(Tert-butyl)phenyl)buta-1,3-diyn-1-yl)triisopropylsilane (**2h**)*



Chemical Formula: $C_{23}H_{34}Si$
Molecular Weight: 338,61

^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 7.44 (d, $J_{H\text{-}H}$ = 8.4 Hz, 2H, Ph), 7.34 (d, $J_{H\text{-}H}$ = 8.5 Hz, 1H, Ph), 1.31 (s, 9H, C(C<u>H</u>$_3$)$_3$), 1.12 (s, 21H, Si(C<u>H</u>(C<u>H</u>$_3$)$_2$)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, δ, ppm): 152.81, 132.63, 125.59, 118.56, 89.88 (<u>C</u>≡C), 87.44 (C≡<u>C</u>), 76.01 (<u>C</u>≡C), 74.21 (C≡<u>C</u>), 35.05, 31.24, 18.74, 11.48. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -0.77. **MS** (EI, m/z): 338(M^+, 18), 295(100), 267(43), 253(42), 239(33), 225(71), 112(23), 57(17). **Elemental Anal**. for $C_{23}H_{34}Si$ (%): calcd.: C, 81.58; H, 10.12 ; found: C, 81.79; H, 10.31. White solid. Isolated yield: 79% (1.33 g).

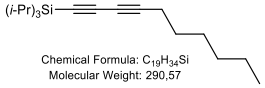
*(Cyclopropylbuta-1,3-diyn-1-yl)triisopropylsilane (**2i**)*



Chemical Formula: $C_{16}H_{26}Si$
Molecular Weight: 246,47

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.37 – 1.28 (m, 1H, C<u>H</u>), 1.07 (s, 21H, Si(C<u>H</u>(C<u>H</u>$_3$)$_2$)$_3$), 0.85 – 0.78 (m, 4H, CH_2CH_2).**^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 90.43 (C≡C), 81.92 (C≡C), 79.73 (C≡C), 61.47 (C≡C), 18.69, 11.45, 8.94, 0.17. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -1.15. **MS** (EI, m/z): 246(M^+, 4), 203(93), 175(42), 161(50), 147(48), 133(100), 118(17), 93(27), 59(23). Yellow oil. Isolated yield: 83% (1.02 g). Analytical data are in agreement with the literature.[6]

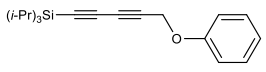
*Deca-1,3-diyn-1-yltrisopropylsilane (**2j**)*



Chemical Formula: $C_{19}H_{34}Si$
Molecular Weight: 290,57

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.28 (d, $J_{H\text{-}H}$ = 7.0 Hz, 2H, ≡CC<u>H</u>$_2$), 1.59 – 1.18 (m, 8H), 1.08 (s, 21H, Si(C<u>H</u>(C<u>H</u>$_3$)$_2$)$_3$), 0.89 (t, $J_{H\text{-}H}$ = 6.8 Hz, 3H, $CH_2C\underline{H}_3$). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 90.25 (<u>C</u>≡C), 80.09 (C≡<u>C</u>), 79.12 (<u>C</u>≡C), 65.94 (C≡<u>C</u>), 31.43, 28.75, 28.28, 22.64, 19.44, 18.70, 14.18, 11.44. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -1.14. **MS** (EI, m/z): 290(M^+, 3), 247(100), 219(38), 205(33), 191(28), 177(52), 163(5), 149(9), 137(11), 109(13), 95(10), 83(15), 59(20). **FT-IR** (cm^{-1}): 2941, 2865, 2223, 2104, 1462, 1181, 995, 881, 675. Pale yellow oil. Isolated yield: 82% (1.19g). Analytical data are in agreement with the literature.[6, 11]

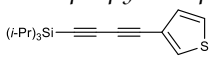
*(5-Phenoxypenta-1,3-diyn-1-yl)trisopropylsilane (**2k**)*



Chemical Formula: $C_{20}H_{28}OSi$
Molecular Weight: 312,53

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.42 – 7.31 (m, 2H, Ph), 7.08 – 6.96 (m, 3H, Ph) 4.80 (s, 2H, ≡CC<u>H</u>$_2$OPh), 1.11 (s, 21H, Si(C<u>H</u>(C<u>H</u>$_3$)$_2$)$_3$). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 157.69, 129.70, 125.27, 121.82, 114.97, 88.84 (C≡C), 85.52 (C≡C), 72.49 (C≡C), 71.48 (C≡C), 56.42, 18.64, 11.35. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -0.45. **MS** (EI, m/z): 312(M^+, 26), 269(100), 241(50), 225(29), 213(24), 199(38), 185(20), 173(30), 151(81), 137(32), 121(22), 106(34), 92(19), 59(25). **FT-IR** (cm^{-1}): 2943, 2891, 2865, 2225, 2106, 1598, 1588, 1494, 1461, 1211, 1172, 1032, 1015, 994, 881, 801, 750, 676. Yellow oil. Isolated yield: 69% (1.07 g). Analytical data are in agreement with the literature.[6]

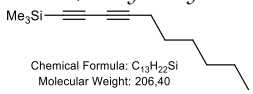
*Triisopropyl(thiophen-3-ylbuta-1,3-diyn-1-yl)silane (**2l**)*



Chemical Formula: $C_{17}H_{24}SSi$
Molecular Weight: 288,52

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.61 – 7.53 (m, 1H, Ar), 7.25 – 7.22 (m, 1H, Ar), 7.17 – 7.12 (m, 1H, Ar), 1.10 (s, 21H, Si(C<u>H</u>(C<u>H</u>$_3$)$_2$)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, δ, ppm): 131.74, 130.39, 125.68, 120.78, 89.60 (<u>C</u>≡C), 87.90 (C≡<u>C</u>), 74.47(<u>C</u>≡C), 70.92(C≡<u>C</u>), 18.72, 11.45. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -0.64. **MS** (EI, m/z): 288(M^+, 19), 245(100), 217(42), 203(39), 189(44), 175(87), 165(16), 159(17), 135(16), 95(15). Dark-brown oil. Isolated yield: 69% (0.99g). Analytical data are in agreement with the literature.[12]

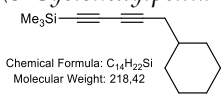
*Deca-1,3-diyn-1-yltrimethylsilane (**2m**)*



Chemical Formula: $C_{13}H_{22}Si$
Molecular Weight: 206,40

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.26 (t, $J_{H\text{-}H}$ = 7.0 Hz, 2H, C≡CC<u>H</u>$_2$), 1.56 – 1.49 (m, 2H), 1.40 – 1.26 (m, 6H) 0.88 (t, $J_{H\text{-}H}$ = 6.9 Hz, 3H, $CH_2C\underline{H}_3$), 0.18 (s, 9H, Si(CH_3)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, δ, ppm): 88.62 (<u>C</u>≡C), 83.09 (C≡<u>C</u>), 80.39 (<u>C</u>≡C), 65.55 (C≡<u>C</u>), 31.42, 28.67, 28.23, 22.65, 19.37, 14.18, -0.18. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -16.74. **MS** (EI, m/z): 206(M^+, 2), 191(100), 177(9), 149(4), 133(10), 121(10), 105(13), 97(20), 83(17), 73(31), 59(16). **Elemental Anal**. for $C_{13}H_{22}Si$ (%): calcd.: C, 75.65; H, 10.74; found: C, 76.01; H, 10.82. Pale yellow oil. Isolated yield: 79% (0.81g). Analytical data are in agreement with the literature.[13]

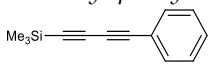
*(5-Cyclohexylpenta-1,3-diyn-1-yl)trimethylsilane (**2n**)*



Chemical Formula: $C_{14}H_{22}Si$
Molecular Weight: 218,42

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.17 (d, $J_{H\text{-}H}$ = 6.6 Hz, 2H), 1.84 – 1.44 (m, 5H), 1.30 – 0.92 (m, 6H), 0.18 (s, 9H, Si(CH_3)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, δ, ppm): 88.66 (C≡C), 83.04 (C≡C), 79.39, 66.37, 53.56, 37.30, 32.82, 27.15, 26.18, -0.16. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -16.76. **MS** (EI, m/z): 218(M^+, 5), 203(100), 176(5), 145(4), 120(12), 107(14), 83(22), 73(52), 55(34). Pale yellow oil. Isolated yield: 86% (0.94g). Title compound is known, but characterized for the first time.[14]

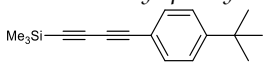
*Trimethyl(phenylbuta-1,3-diyn-1-yl)silane (**2o**)*



Chemical Formula: $C_{13}H_{14}Si$
Molecular Weight: 198,34

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.62 – 7.43 (m, 2H, Ph), 7.43 – 7.18 (m, 3H, Ph), 0.24 (s, 9H, Si(C<u>H</u>$_3$)$_3$). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 132.82, 129.47, 128.56, 121.53, 90.78 (C≡C), 87.96 (C≡C), 76.88 (C≡C), 74.28 (C≡C), -0.24 (Si(<u>C</u>H$_3$)$_3$). **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -16.1. **MS** (EI, m/z): 198(M$^+$, 26), 183(100), 167(3), 153(5), 129(8). **FT-IR** (cm^{-1}): 2959, 2205, 2104, 1489, 1442, 1250, 837, 751, 686, 632. Pale yellow oil. Isolated yield: 66% (0.65 g). Analytical data are in agreement with the literature.[6, 15]

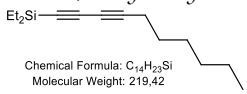
*((4-(Tert-butyl)phenyl)buta-1,3-diyn-1-yl)trimethylsilane (**2p**)*



Chemical Formula: $C_{17}H_{22}Si$
Molecular Weight: 254,45

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.45 – 7.40 (m, 2H, Ph), 7.36 – 7.31 (m, 2H, Ph), 1.30 (s, 9H, C(C<u>H</u>$_3$)$_3$), 0.23 (s, 9H, Si(C<u>H</u>$_3$)$_3$). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 152.97, 132.62, 125.62, 118.41, 90.27 (C≡C), 88.18 (C≡C), 73.66 (C≡C), 35.07, 31.23, -0.21 (Si(<u>C</u>H$_3$)$_3$). **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -16.29. **MS** (EI, m/z): 254(M$^+$, 30), 73(7), 84(4), 98(13), 209(7), 223(8), 234(100). Pale yellow oil. Isolated yield: 59% (0.75 g). Analytical data are in agreement with the literature.[16]

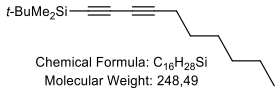
*Deca-1,3-diyn-1-yltriethylsilane (**2q**)*



Chemical Formula: $C_{14}H_{23}Si$
Molecular Weight: 219,42

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.27 (t, $J_{H\text{-}H}$ = 7.0 Hz, 2H, C≡CC<u>H</u>$_2$), 1.60 – 1.50 (m, 2H), 1.42 – 1.25 (m, 6H), 0.99 (t, $J_{H\text{-}H}$ = 7.8 Hz, 9H, Si(CH$_2$C<u>H</u>$_3$)$_3$), 0.94 – 0.83 (m, 3H), 0.66 – 0.56 (m, 6H, Si(C<u>H</u>$_2$CH$_3$)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, δ, ppm): 89.59 (C≡C), 81.09 (C≡C), 79.65 (C≡C), 65.77 (C≡C), 31.43, 28.71, 28.26, 22.64, 19.41, 14.18, 7.51, 4.41.**^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -6.34. **MS** (EI, m/z): 248(M$^+$, 1), 219(100), 191(70), 163(27), 133(12), 121(10), 107(14), 95(18), 79(15), 67(18), 55(23). **Elemental Anal**. for $C_{16}H_{28}Si$ (%): calcd.: C, 77.34; H, 11.36; found: C, 78.08; H, 11.53. Pale yellow oil. Isolated yield: 70% (0.87 g).

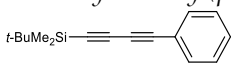
*Tert-butyl(deca-1,3-diyn-1-yl)dimethylsilane (**2r**)*



Chemical Formula: $C_{16}H_{28}Si$
Molecular Weight: 248,49

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.27 (t, $J_{H\text{-}H}$ = 7.1 Hz, 2H, C≡CC<u>H</u>$_2$), 1.56 – 1.49 (m, 2H), 1.39 – 1.25 (m, 6H), 0.94 (s, 9H, Si(CH$_3$)$_2$C(C<u>H</u>$_3$)$_3$) 0.89 (t, $J_{H\text{-}H}$ = 6.9 Hz, 3H, CH$_2$C<u>H</u>$_3$) 0.12 (s, 6H, Si(C<u>H</u>$_3$)$_2$C(CH$_3$)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, δ, ppm): 89.23 (<u>C</u>≡C), 81.68 (C≡<u>C</u>), 79.85 (<u>C</u>≡C) , 65.72, 31.43, 28.70, 28.25, 26.19, 22.65, 19.40, 16.85, 14.18, -4.62. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -6.99. **MS** (EI, m/z): 248(M$^+$, 3), 191(100), 133(3), 120(4), 83(7), 73(4), 59(7). Pale yellow oil. Isolated yield: 85% (1.06 g). Analytical data are in agreement with the literature.[17]

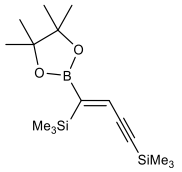
*Tert-butyldimethyl(phenylbuta-1,3-diyn-1-yl)silane (**2s**)*



Chemical Formula: $C_{16}H_{20}Si$
Molecular Weight: 240,42

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.52 – 7.47 (m, 2H, Ph), 7.38 – 7.28 (m, 3H, Ph), 0.99 (s, 9H, Si(CH$_3$)$_2$C(C<u>H</u>$_3$)$_3$), 0.18 (s, 6H, Si(C<u>H</u>$_3$)$_2$C(CH$_3$)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, δ, ppm): 132.83, 129.44, 128.56, 121.57, 89.48 (C≡C), 88.59 (C≡C), 76.38 (C≡C), 74.50 (C≡C), 26.22, 16.93, -4.67. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -6.43. **MS** (EI, m/z): 240(M$^+$, 19), 105(2), 129(6), 153(6), 169(5), 183(100). Pale yellow oil. Isolated yield: 88% (1.05 g). Analytical data are in agreement with the literature.[18]

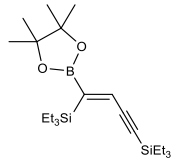
*(Z)-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-3-yne-1,4-diyl)bis(trimethylsilane) (**4a**)*



Chemical Formula: $C_{16}H_{31}BO_2Si_2$
Molecular Weight: 322,40

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 6.85 (s, 1H, C<u>H</u>=C), 1.23 (s, 12H, C(C<u>H</u>$_3$)$_2$), 0.22 (s, 9H, Si(C<u>H</u>$_3$)$_3$), 0.18 (s, 9H, Si(C<u>H</u>$_3$)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, δ, ppm): 134.88 (<u>C</u>H=C), 106.01 (<u>C</u>≡C), 102.37 (C≡<u>C</u>), 84.44 (<u>C</u>(CH$_3$)$_2$), 24.87 (C(<u>C</u>H$_3$)$_2$), -0.26 (Si(<u>C</u>H$_3$)$_3$). C*α* to boron atom was not observed. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -5.77 (SiC=C), -18.03 (SiC≡C). **MS** (EI, m/z): 322(M^+, 1), 307(7), 265(25), 225(22), 197(8), 181(19), 155(14), 83(100), 73(89), 55(38). **Elemental Anal**. for $C_{16}H_{31}BO_2Si_2$ (%): calcd.: C, 59.61; H, 9.69; found: C, 60.08; H, 9.77. Yellowish oil. Isolated yield: 88% (71 mg).

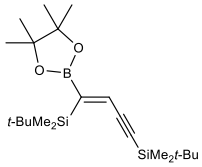
*(Z)-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-3-yne-1,4-diyl)bis(triethylsilane) (**4b**)*



Chemical Formula: $C_{22}H_{43}BO_2Si_2$
Molecular Weight: 406,56

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 6.98 (s, 1H, C<u>H</u>=C), 1.23 (s, 12H, C(C<u>H</u>$_3$)$_2$), 1.05 – 0.88 (m, 18H), 0.85 – 0.75 (m, 6H, Si(C<u>H</u>$_2$CH$_3$)$_3$), 0.62 (q, $J_{H\text{-}H}$ = 7.9 Hz, 6H, Si(C<u>H</u>$_2$CH$_3$)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, δ, ppm): 136.27 (<u>C</u>H=C), 107.09 (<u>C</u>≡C), 99.78 (C≡<u>C</u>), 83.34 (<u>C</u>(CH$_3$)$_2$), 24.86 (C(<u>C</u>H$_3$)$_2$), 7.77, 7.49, 4.38, 3.91. C*α* to boron atom was not observed. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -2.34 (SiC=C), -7.83 (SiC≡C). **^{11}B NMR** (128 MHz, $CDCl_3$, δ, ppm): 31.34. **MS** (EI, m/z): 406(M^+, 1), 391(1), 377(16), 350(13), 293(27), 267(43), 237(25), 209(13), 137(10), 107(8), 83(100), 69(89), 55(45). **Elemental Anal**. for $C_{22}H_{43}BO_2Si_2$ (%): calcd.: 64.99; H, 10.66; found: C, 65.27; H, 10.81. Yellowish oil. Isolated yield: 81% (82 mg).

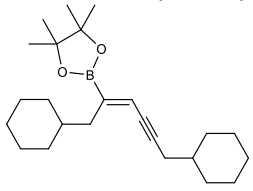
*(Z)-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-3-yne-1,4-diyl)bis(tert-butyldimethylsilane) (**4c**)*



Chemical Formula: $C_{22}H_{43}BO_2Si_2$
Molecular Weight: 406,56

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.04 (s, 1H C<u>H</u>=C), 1.22 (s, 12H, C(C<u>H</u>$_3$)$_2$), 0.92 (s, 9H, C(C<u>H</u>$_3$)$_3$), 0.90 (s, 9H, C(C<u>H</u>$_3$)$_3$), 0.23 (s, 6H, SiC<u>H</u>$_3$), 0.11 (s, 6H, SiC<u>H</u>$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, δ, ppm): 136.69 (<u>C</u>H=C), 107.31 (<u>C</u>≡C), 101.04 (C≡<u>C</u>), 83.37 (<u>C</u>(CH$_3$)$_2$), 27.20, 26.27, 24.87, 18.83, 16.82, -3.71, -4.70. C*α* to boron atom was not observed. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): 2.57 (SiC=C), -8.37 (SiC≡C). **MS** (EI, m/z): 406(M^+, 1), 349(16), 293(10), 265(16), 223(14), 211(82), 181(7), 167(8), 83(100), 73(44), 55(36), 57(8). **Elemental Anal**. for $C_{22}H_{43}BO_2Si_2$ (%): calcd.: C, 64.99; H, 10.66; found: C, 65.78; H, 10.90. Yellowish solid. Isolated yield: 72% (73 mg).

*(Z)-2-(1,6-Dicyclohexylhex-2-en-4-yn-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4d**)*

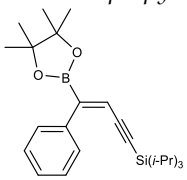


Chemical Formula: $C_{24}H_{39}BO_2$
Molecular Weight: 370,38

^{1}H NMR (600 MHz, C_6D_6, δ, ppm): 6.24 (C<u>H</u>=C), 2.27 (m, 2H, C<u>H</u>$_2$C$_6$H$_{11}$), 2.25 (m, 2H, C<u>H</u>$_2$C$_6$H$_{11}$), 1.83 – 1.79 (m, 2H), 1.74 – 1.63 (m, 9H), 1.54 – 1.45 (m, 2H), 1.26 (m, 3H), 1.24 (s, 12H, C(C<u>H</u>$_3$)$_2$), 1.18 – 0.91 (m,

5H). **^{13}C NMR** (151 MHz, $CDCl_3$, δ, ppm): 123.55 (C̲H=C), 97.70 (C̲≡C), 83.52 (C̲(CH_3)$_2$), 79.95 (C≡C̲), 39.25, 38.56, 37.75, 33.51, 32.83, 27.76, 26.83, 26.57, 26.42, 26.31, 24.80. Cα to boron atom was not observed. **MS** (EI, m/z): 370(M^+, 2), 355(2), 327(2), 288(10), 274(10), 231(6), 205(6), 187(16), 159(24), 146(28), 131(21), 101(52), 83(69), 67(22), 55(100). **Elemental Anal**. for $C_{24}H_{39}BO_2$ (%): calcd.: C, 77.83; H, 10.61; found: C, 78.12; H, 10.79. Pale yellow oil. Isolated yield 63% (58 mg).

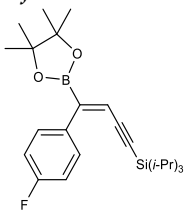
*(Z)-Triisopropyl(4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yn-1-yl)silane (**4e**)*



Chemical Formula: $C_{25}H_{39}BO_2Si$
Molecular Weight: 410,48

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.66 – 7.63 (m, 2H, Ph), 7.32 – 7.27 (m, 2H, Ph), 7.25 – 7.21 (m, 1H, Ph), 6.56 (s, 1H, CH̲=C), 1.29 (s, 12H, C(CH̲$_3$)$_2$), 1.01 (s, 21H, Si(CH̲(CH̲$_3$)$_2$)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, δ, ppm): 139.05, 129.16, 127.75, 127.38, 122.52 105.48 (C̲≡C), 100.32 (C≡C̲), 84.17 (C̲(CH_3)$_2$), 24.91 (C(C̲H$_3$)$_2$), 18.69, 11.41. Cα to boron atom was not observed. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -2.17. **^{11}B NMR** (128 MHz, $CDCl_3$, δ, ppm): 30.70. **MS** (EI, m/z): 410(M^+, 17), 367(100), 311(18), 297(29), 267(25), 239(22) 211(29), 197(47), 183(25), 169(37), 155(22), 129(16), 101(76), 83(77), 69(22), 59(58). **Elemental Anal**. for $C_{25}H_{39}BO_2Si$ (%): calcd.: C, 73.15; H, 9.58; found: C, 73.91; H, 9.93. Pale yellow oil. Isolated yield: 78% (80 mg).

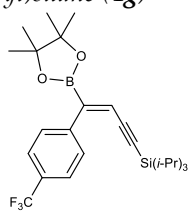
*(Z)-(4-(4-Fluorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yn-1-yl)triisopropylsilane (**4f**)*



Chemical Formula: $C_{25}H_{38}BFO_2Si$
Molecular Weight: 428,47

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 7.68 – 7.61 (m, 2H, Ph), 7.03 – 6.94 (m, 2H, Ph), 6.55 (s, 1H, CH̲=C), 1.29 (s, 12H, C(CH̲$_3$)$_2$)), 1.02 (s, 21H, Si(CH̲(CH̲$_3$)$_2$)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, δ, ppm): 162.19 (d, $^1J_{C\text{-}F}$ = 246.2 Hz), 135.04 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 132.26 (d, $^3J_{C\text{-}F}$ = 9.9 Hz), 130.92, 130.92, 128.71, 128.59, 122.56, 114.60 (d, $^2J_{C\text{-}F}$ = 21.2 Hz), 105.28 (C̲≡C) , 100.71 (C≡C̲), 84.27 (C̲(CH_3)$_2$), 24.90 (C(C̲H$_3$)$_2$), 18.68, 11.39. Cα to boron atom was not observed. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -2.03 **MS** (EI, m/z): 428(M^+, 42), 385(100), 357(13), 329(17), 301(8), 285(11), 257(10), 243(12), 215(48), 201(18), 173(18), 101(44), 83(74), 55(43). **Elemental Anal**. for $C_{25}H_{38}BFO_2Si$ (%): calcd.: C, 70.08; H, 8.94; found: C, 70.76; H, 9.03. Pale yellow oil. Isolated yield: 59% (63 mg).

*(Z)-Triisopropyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(4-(trifluoromethyl)phenyl)but-3-en-1-yn-1-yl)silane (**4g**)*

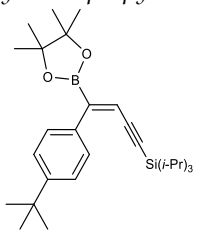


Chemical Formula: $C_{26}H_{38}BF_3O_2Si$
Molecular Weight: 478,48

^{1}H NMR (600 MHz, C_6D_6, δ, ppm): 7.70 (d, $J_{H\text{-}H}$ = 8.2 Hz, 2H), 7.50 – 7.42 (m, 2H, Ph), 6.93 (s, 1H, CH̲=C), 1.02 (s, 12H, C(CH̲$_3$)$_2$), 1.01 (s, 21H, Si(CH̲(CH̲$_3$)$_2$)$_3$). **^{13}C NMR** (151 MHz, C_6D_6, δ, ppm): 143.61, 132.50, 132.44, 131.66, 130.33, 130.13, 129.83, 129.33 (q, $J^3_{C\text{-}F}$ = 32.0 Hz), 126.07, 125.00 (q, $J^3_{C\text{-}F}$ = 3.7 Hz)., 124.27,

105.37 (C≡C), 101.71 (C≡C), 84.26 (C(CH$_3$)$_2$), 24.72 (C(CH$_3$)$_2$), 18.71, 11.56. Cα to boron atom was not observed. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -1.78. **MS** (EI, m/z): 478(M^+, 8), 435(100), 393(5), 265(6), 151(12), 133(10), 101(6), 83(15), 69(7), 59(15). **Elemental Anal**. for $C_{26}H_{38}BF_3O_2Si$ (%): calcd.: C, 65.27; H, 8.01; found: C, 65.90; H, 8.22. Pale yellow oil. Isolated yield: 63% (75 mg).

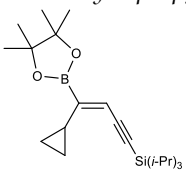
*(Z)-(4-(4-(Tert-butyl)phenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yn-1-yl)triisopropylsilane (**4h**)*



Chemical Formula: $C_{29}H_{47}BO_2Si$
Molecular Weight: 466,59

^{1}H NMR (600 MHz, C_6D_6, δ, ppm): 7.60 (d, $J_{H\text{-}H}$ = 8.4 Hz, 2H, Ph), 7.31 (d, $J_{H\text{-}H}$ = 8.4 Hz, 2H, Ph), 6.53 (s, 1H, CH=C), 1.31 (s, 9H, C(CH$_3$)$_3$), 1.30 (s, 12H, C(CH$_3$)$_2$), 1.02 (s, 21H, Si(CH(CH$_3$)$_2$)$_3$). **^{13}C NMR** (151 MHz, C_6D_6, δ, ppm): 150.08, 136.16, 128.84, 124.71, 122.06, 105.81 (C≡C), 99.85 (C≡C), 84.10 (C(CH$_3$)$_2$), 34.64, 31.44, 24.91 (C(CH$_3$)$_2$), 18.71, 11.44. Cα to boron atom was not observed. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -2.30. **MS** (EI, m/z): 466(M^+, 22), 423(25), 395(8), 365(8), 323(14), 265(8) 170(12), 133(10),101(31), 83(24), 57(100). **Elemental Anal**. for $C_{29}H_{47}BO_2Si$ (%): calcd.: C, 74.65; H, 10.15; found: C, 75.08; H, 10.29. Pale yellow oil. Isolated yield: 51% (59 mg).

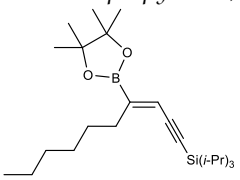
*(Z)-(4-Cyclopropyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yn-1-yl)triisopropylsilane (**4i**)*



Chemical Formula: $C_{22}H_{39}BO_2Si$
Molecular Weight: 374,45

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 6.23 (CH=C), 2.22 – 2.07 (m, 1H, CHCH$_2$CH$_2$), 1.21 (s, 12H, C(CH$_3$)$_2$), 1.07 (s, 21H, Si(CH(CH$_3$)$_2$)$_3$), 0.97 – 0.92 (m, 2H), 0.79 – 0.74 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$, δ, ppm): 12.55 (CH=C), 105.14 (C≡C), 98.55 (C≡C), 83.43 (C(CH$_3$)$_2$), 24.78 (C(CH$_3$)$_2$), 18.79 Si(CH(CH$_3$)$_2$)$_3$), 11.46 Si(CH(CH$_3$)$_2$)$_3$), 7.68. Cα to boron atom was not observed. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -2.17. **^{11}B NMR** (128 MHz, $CDCl_3$, δ, ppm): 30.37. **MS** (EI, m/z): 374(M^+, 11), 331(26), 289(14), 247(8), 205(12), 189(26) 161(42), 147(19), 133(31), 119(17), 83(100), 55(52). **Elemental Anal**. for $C_{22}H_{39}BO_2Si$ (%): calcd.: C, 70.57; H, 10.50; found: C, 71.02; H, 10.66. Pale Pale yellow oil. Isolated yield: 85% (80 mg).

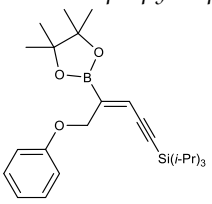
*(Z)-Triisopropyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dec-3-en-1-yn-1-yl)silane (**4j**)*



Chemical Formula: $C_{25}H_{47}BO_2Si$
Molecular Weight: 418,54

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 6.26 (s, 1H, CH=C), 2.41 (t, $J_{H\text{-}H}$ = 7.4 Hz, 2H, C=CCH$_2$), 1.43 – 1.27 (m, 8H), 1.25 (s, 12H, C(CH$_3$)$_2$), 1.08 (s, 21H, Si(CH(CH$_3$)$_2$)$_3$), 0.92-0.81 (m, 3H, CH$_2$CH$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, δ, ppm): 122.36 (CH=C), 106.68 (C≡C), 98.99 (C≡C), 83.67 (C(CH$_3$)$_2$), 32.28, 32.05, 29.66, 29.49, 24.85 (C(CH$_3$)$_2$, 22.80, 18.78, 14.24, 11.44. Cα to boron atom was not observed. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -2.09. **MS** (EI, m/z): 418(M^+, 7), 375(100), 347(8), 275(6), 233(8), 147(10), 135(14), 101(15), 83(36), 59(52). **Elemental Anal**. for $C_{25}H_{47}BO_2Si$ (%): calcd.: C, 71.74; H, 11.32;; found: C, 72.18; H, 11.81. Pale yellow oil. Isolated yield: 68% (71 mg).

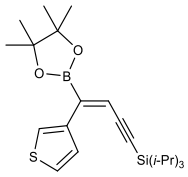
*(Z)-Triisopropyl(5-phenoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-en-1-yn-1-yl)silane (**4k**)*



Chemical Formula: $C_{26}H_{41}BO_3Si$
Molecular Weight: 440,51

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.34 – 7.27 (m, 2H, Ph), 7.03 – 6.93 (m, 3H, Ph), 6.52 (s, 1H, C<u>H</u>=C) 4.98 (s, 2H, C<u>H</u>$_2$OPh), 1.27 (s, 12H, C(C<u>H</u>$_3$)$_2$), 1.13 (s, 21H, Si(C<u>H</u>(C<u>H</u>$_3$)$_2$)$_3$). **^{13}C NMR** (175 MHz, $CDCl_3$, δ, ppm): 158.87, 129.33, 125.64 120.54, 115.18, 103.14 (<u>C</u>≡C), 102.75 (C≡<u>C</u>), 84.02 (<u>C</u>(CH$_3$)$_2$), 67.15, 24.77 (C(<u>C</u>H$_3$)$_2$), 18.73, 11.34. Cα to boron atom was not observed. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -1.47. **MS** (EI, m/z): 440(M^+, 4), 398(6), 347(15), 241(13), 227(16), 179(11) 151(21), 133(11), 121(25), 83(100), 55(42). **Elemental Anal**. for $C_{26}H_{41}BO_3Si$ (%): calcd.: C, 70.89; H, 9.38; found: C, 71.21; H, 9.84. Pale yellow oil. Isolated yield: 80% (88 mg).

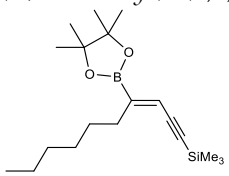
*(Z)-Triisopropyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(thiophen-3-yl)but-3-en-1-yn-1-yl)silane (**4l**)*



Chemical Formula: $C_{23}H_{37}BO_2SSi$
Molecular Weight: 416,50

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.00 (dd, $J_{H\text{-}H}$ = 3.0, 1.2 Hz, 1H, thienyl), 7.93 (dd, $J_{H\text{-}H}$ = 5.1, 1.3 Hz, 1H, thienyl), 7.21 (dd, $J_{H\text{-}H}$ = 5.1, 3.0 Hz, 1H, thienyl), 6.48 (s, 1H, C<u>H</u>=C)), 1.31 (s, 12H, C(C<u>H</u>$_3$)$_2$), 1.09 (s, 21H, Si(C<u>H</u>(C<u>H</u>$_3$)$_2$)$_3$). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 128.88, 125.86, 123.74, 120.01, 84.19, 24.95, 18.78, 11.53. Cα to boron atom and Csp atoms were not observed (512 scans). **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -2.16. **MS** (EI, m/z): 416(M^+, 45), 373(100), 317(19), 273(50), 245(32), 231(41), 217(36), 203(54), 189(29), 175(30), 129(22), 115(18), 101(47), 83(81), 73(19), 55(60). **Elemental Anal**. for $C_{23}H_{37}BO_2SSi$ (%): calcd.: C, 66.33; H, 8.95; found: C, 66.91; H, 9.17. Yellow oil. Isolated yield: 74% (77 mg).

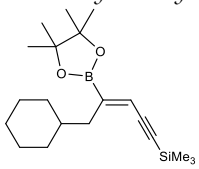
*(Z)-Trimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dec-3-en-1-yn-1-yl)silane (**4m**)*



Chemical Formula: $C_{19}H_{35}BO_2Si$
Molecular Weight: 334,38

^{1}H NMR (600 MHz, C_6D_6, δ, ppm): 6.09 (s, 1H, C<u>H</u>=C), 2.28 (t, $J_{H\text{-}H}$ = 7.4 Hz, 2H, C=CC<u>H</u>$_2$), 1.26 – 1.17 (m, 8H), 1.14 (s, 12H, C(C<u>H</u>$_3$)$_2$), 0.80-0.75 (m, 3H, CH$_2$C<u>H</u>$_3$) 0.09 (s, 9H, Si(C<u>H</u>$_3$)$_3$). **^{13}C NMR** (151 MHz, C_6D_6, δ, ppm): 122.44 (<u>C</u>H=C) 103.44 (<u>C</u>≡C), 102.53 (C≡<u>C</u>), 83.29 (<u>C</u>(CH$_3$)$_2$), 32.27, 31.82, 29.53, 29.41, 24.39 (C(<u>C</u>H$_3$)$_2$), 22.72, 13.98, -0.33. Cα to boron atom was not observed. **^{29}Si NMR** (119 MHz, $CDCl_3$ δ, ppm): -18.37. **^{11}B NMR** (128 MHz, $CDCl_3$, δ, ppm): 31.26, 28.47. **MS** (EI, m/z): 334(M^+, 2), 319(4), 235(20), 203(19), 192(53), 177(26), 147(46), 135(44), 121(17), 101(27), 73(100), 59(42). **Elemental Anal**. for $C_{19}H_{35}BO_2Si$ (%): calcd.: C, 68.25; H, 10.55; found: C, 68.71; H, 10.83. Pale yellow oil. Isolated yield: 77% (64 mg).

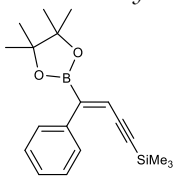
*(Z)-(5-Cyclohexyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-en-1-yn-1-yl)trimethylsilane (**4n**)*



Chemical Formula: $C_{20}H_{35}BO_2Si$
Molecular Weight: 346,39

^{1}H NMR (600 MHz, C_6D_6, δ, ppm): 6.81 (s, 1H), C<u>H</u>=C, 2.75 (d, $J_{H\text{-}H}$ = 6.7 Hz, 2H, C<u>H</u>$_2$C$_6$H$_{11}$), 1.94 – 1.88 (m, 2H), 1.75 – 1.71 (m, 2H), 1.64 – 1.58 (m, 2H), 1.28 – 1.11 (m, 5H), 1.02 (s, 12H, C(C<u>H</u>$_3$)$_2$), 0.19 (s, 9H Si(C<u>H</u>$_3$)$_3$). **^{13}C NMR** (151 MHz, C_6D_6, δ, ppm): 123.15 (<u>C</u>H=C), 103.89 (<u>C</u>≡C), 102.70 (C≡<u>C</u>), 83.29 (<u>C</u>(CH$_3$)$_2$), 39.66, 38.59, 33.60, 26.70, 26.43, 24.36, -0.35 (Si(<u>C</u>H$_3$)$_3$). C*α* to boron atom was not observed. **^{29}Si NMR** (119 MHz, $CDCl_3$ δ, ppm): -18.37. **MS** (EI, m/z): 346(M$^+$, 22) 331(12), 249(28), 235(19), 207(32), 165(18), 149(28), 134(15), 109(22), 101(44), 83(76), 73(100), 55(94). **Elemental Anal**. for $C_{20}H_{35}BO_2Si$ (%): calcd.: C, 69.35; H, 10.18; found: C, 70.02; H, 10.44. Pale yellow oil. Isolated yield: 82% (71 mg).

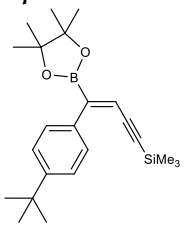
*(Z)-Trimethyl(4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yn-1-yl)silane (**4o**)*



Chemical Formula: $C_{19}H_{27}BO_2Si$
Molecular Weight: 326,32

^{1}H NMR (600 MHz, C_6D_6, δ, ppm): 8.01 – 7.98 (m, 2H, Ph), 7.29 – 7.25 (m, 2H, Ph), 7.14 – 7.10 (m, 1H, Ph), 7.01 (s, 1H, C<u>H</u>=C), 0.98 (s, 12H, C(C<u>H</u>$_3$)$_2$), 0.08 (s, 9H, Si(C<u>H</u>$_3$)$_3$). **^{13}C NMR** (151 MHz, C_6D_6, δ, ppm): 139.67, 129.72, 122.83, 104.75 (<u>C</u>≡C), 103.60 (C≡<u>C</u>), 84.04 (<u>C</u>(CH$_3$)$_2$), 24.71 (C(<u>C</u>H$_3$)$_2$), -0.34 (Si(<u>C</u>H$_3$)$_3$). C*α* to boron atom was not observed. **^{29}Si NMR** (119 MHz, $CDCl_3$ δ, ppm): -18.07. **MS** (EI, m/z): 326(M$^+$, 15), 311(24), 211(46), 169(15), 129(100), 112(24), 83(33), 55(51). Pale yellow oil. Isolated yield: 78% (64 mg). Analytical data are in agreement with the literature.[19]

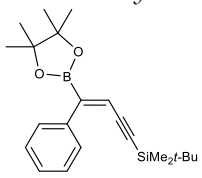
*(Z)-(4-(4-Ttert-butyl)phenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yn-1-yl)trimethylsilane (**4p**)*



Chemical Formula: $C_{23}H_{35}BO_2Si$
Molecular Weight: 382,43

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.64 (d, $J_{H\text{-}H}$ = 8.5 Hz, 1H), 7.34 (d, $J_{H\text{-}H}$ = 8.6 Hz, 2H, Ph), 6.44 (s, 1H, C<u>H</u>=C), 1.32 (s, 9H, C(C<u>H</u>$_3$)$_3$), 1.29 (s, 12H, C(C<u>H</u>$_3$)$_2$), 0.14 (s, 9H, Si(C<u>H</u>$_3$)$_3$). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 150.42, 135.93, 128.91, 124.60, 121.18, 104.40, 103.34, 84.14, 77.58, 76.74, 34.71, 31.46, 24.89, -0.20. C*α* to boron atom was not observed. **^{29}Si NMR** (119 MHz, $CDCl_3$ δ, ppm): -17.82 **MS** (EI, m/z): 382(M$^+$, 46), 367(100), 311(12), 267(15), 225(24), 211(12), 200(14), 183(15), 169(16), 101(22), 83(38), 73(60), 57(66). **Elemental Anal**. for $C_{23}H_{35}BO_2Si$ (%): calcd.: C, 72.24; H, 9.23; found: C, 72.78; H, 9.41. Yellowish solid. Isolated yield: 81% (78 mg).

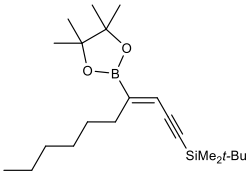
*(Z)-Tert-butyldimethyl(4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yn-1-yl)silane (**4q**)*



Chemical Formula: $C_{22}H_{33}BO_2Si$
Molecular Weight: 368,40

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.70 – 7.63 (m, 2H, Ph), 7.39 – 7.27 (m, 3H, Ph), 6.54 (s, 1H, C<u>H</u>=C), 1.32 (s, 12H, C(C<u>H</u>$_3$)$_2$), 0.90 (s, 9H, C(C<u>H</u>$_3$)$_3$), 0.09 (s, 6H, Si(C<u>H</u>$_3$)$_2$). **^{13}C NMR** (101 MHz, $CDCl_3$, δ, ppm): 138.97, 129.15, 127.71, 127.46, 122.15, 104.44 (<u>C</u>≡C), 101.91 (C≡<u>C</u>), 84.17 (<u>C</u>(CH$_3$)$_2$), 26.18, 24.89, 16.85, -4.71. Cα to boron atom was not observed. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -8.01. **^{11}B NMR** (128 MHz, $CDCl_3$, δ, ppm): 30.66. **MS** (EI, m/z): 368(M$^+$, 21), 311(100), 211(54), 169(19), 101(15), 83(15), 73(13), 67(9), 55(11). **Elemental Anal**. for $C_{22}H_{33}BO_2Si$ (%): calcd.: C, 71.73; H, 9.03; found: C, 71.98; H, 9.20. Yellow solid. Isolated yield: 72% (66 mg).

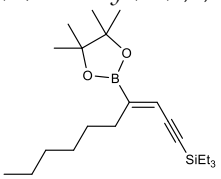
*(Z)-Tert-butyldimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dec-3-en-1-yn-1-yl)silane (**4r**)*



Chemical Formula: $C_{22}H_{41}BO_2Si$
Molecular Weight: 376,46

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 6.21 (s, 1H, C<u>H</u>=C), 2.39 (t, $J_{H\text{-}H}$ = 7.2 Hz, 2H, =C(B)C<u>H</u>$_2$), 1.49 – 1.27 (m, 8H), 1.24 (s, 12H, C(C<u>H</u>$_3$)$_2$), 0.95 (s, 9H, C(C<u>H</u>$_3$)$_3$)), 0.90 – 0.83 (m, 3H), 0.12 (s, 6H, Si(C<u>H</u>$_3$)$_2$). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 121.99 (C=<u>C</u>H), 103.57 (<u>C</u>≡C), 100.82 (C≡<u>C</u>), 83.69 (<u>C</u>(CH$_3$)$_2$), 32.20, 31.97, 29.51, 29.39, 26.25, 24.83, 22.80, 16.80, 14.25, -4.47. Cα to boron atom was not observed. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -8.21. **MS** (EI, m/z): 376(M$^+$, 2), 319(100), 219(10), 191(10), 177(9), 101(8), 83(32), 73(20), 59(16). **Elemental Anal**. for $C_{22}H_{41}BO_2Si$ (%): calcd.: C, 70.19; H, 10.98; found: C, 70.71; H, 11.11. Yellow oil. Isolated yield: 70% (66 mg).

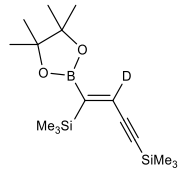
*(Z)-Triethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dec-3-en-1-yn-1-yl)silane (**4s**)*



Chemical Formula: $C_{22}H_{41}BO_2Si$
Molecular Weight: 376,46

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 6.23 (s, 1H, C<u>H</u>=C), 2.40 (t, $J_{H\text{-}H}$ = 7.4 Hz, 2H, =C(B)C<u>H</u>$_2$), 1.42 – 1.27 (m, 8H), 1.24 (s, 12H, C(C<u>H</u>$_3$)$_2$), 1.00 (t, $J_{H\text{-}H}$ = 7.8 Hz, 9H, Si(CH$_2$C<u>H</u>$_3$)$_3$), 0.91 – 0.84 (m, 3H, CH$_2$CH$_2$C<u>H</u>$_3$), 0.62 (q, $J_{H\text{-}H}$ = 7.9 Hz, 6H, Si(C<u>H</u>$_2$CH$_3$)$_3$). **^{13}C NMR** (151 MHz, $CDCl_3$, δ, ppm): 122.09 (C=<u>C</u>H), 104.10 (<u>C</u>≡C), 100.00 (C≡<u>C</u>), 83.68, 32.18, 31.96, 29.47, 29.39, 24.83, 22.80, 14.24, 7.62, 4.60. . Cα to boron atom was not observed. **^{29}Si NMR** (79 MHz, $CDCl_3$ δ, ppm): -7.36. **MS** (EI, m/z): 376(M$^+$, 4) 347(37), 247(14), 207(10), 191(16), 177(11), 163(21), 147(11), 131(16), 121(19), 101(28), 91(11), 83(70), 69(34), 59(100). **Elemental Anal**. for $C_{22}H_{41}BO_2Si$ (%): calcd.: C, 70.19; H, 10.98; found: C, 70.83; H, 11.17. Yellow oil. Isolated yield: 68% (59 mg).

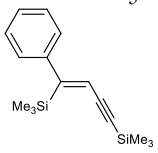
*(Z)-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-3-yne-1,4-diyl-2-d)bis(trimethylsilane) (**6a**)*



Chemical Formula: $C_{16}H_{30}DBO_2Si_2$
Molecular Weight: 323,41

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.23 (s, 12H, C(C<u>H</u>$_3$)$_2$), 0.22 (s, 9H, Si(C<u>H</u>$_3$)$_3$), 0.18 (s, 9H, Si(C<u>H</u>$_3$)$_3$). **MS** (EI, m/z): 323(M^+, 1), 308(4), 266(8), 226(36), 198(10), 166(11), 84(100), 73(64), 69(25), 55(28). Yellow oil. Isolated yield: 87% (84 mg).

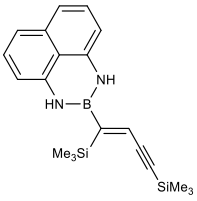
*(Z)-(1-Phenylbut-1-en-3-yne-1,4-diyl)bis(trimethylsilane) (**7**)*



Chemical Formula: $C_{16}H_{24}Si_2$
Molecular Weight: 272,54

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.37 – 7.27 (m, 3H, Ph), 7.12 – 7.07 (m, 2H, Ph), 6.19 (s, 1H, C<u>H</u>=C), 0.31 (s, 9H, Si(C<u>H</u>$_3$)$_3$), 0.28 (s, 9H, Si(C<u>H</u>$_3$)$_3$). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 159.98, 145.26, 128.11, 126.85, 126.56, 122.17, 105.11, 100.66, -0.16, -0.28. **MS** (EI, m/z): 272 (M^+, 40), 257(66), 73(100), 241(12), 199(34), 183(24), 169(8), 159(42), 155(49), 135(15), 97(22). Colorless oil. Isolated yield: 78% (31 mg). Analytical data are in agreement with the literature.[20]

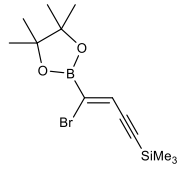
*(Z)-2-(1,4-Bis(trimethylsilyl)but-1-en-3-yn-1-yl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (**8**)*



Chemical Formula: $C_{20}H_{27}BN_2Si_2$
Molecular Weight: 362,43

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.13 – 7.06 (m, 2H, Ar), 7.04 – 6.99 (m, 2H, Ar), 6.58 (s, 1H, C<u>H</u>=C), 6.30 (dd, $J_{H\text{-}H}$ = 7.2, 1.1 Hz, 2H, Ar), 5.48 (s, 2H, N<u>H</u>), 0.29 (s, 9H, Si(C<u>H</u>$_3$)$_3$), 0.21 (s, 9H, Si(C<u>H</u>$_3$)$_3$). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 139.05, 134.39, 127.33, 125.68, 117.69, 115.84, 103.95, 103.73, 99.02, -2.10, -2.27. Cα to boron atom was not observed. **^{29}Si NMR** (80 MHz, $CDCl_3$ δ, ppm): -6.59, -17.94. **MS** (EI, m/z): 362(M^+,100), 346(18), 289(9), 273(11), 192(14), 155(13), 129(8), 84(8), 73(34). Dark brown-green solid. Isolated yield: 55% (26 mg). Analytical data are in agreement with the literature.[21]

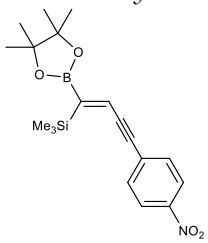
*(Z)-(4-Bromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yn-1-yl)trimethylsilane (**9**)*



Chemical Formula: $C_{13}H_{22}BBrO_2Si$
Molecular Weight: 329,12

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 6.92 (1H, s, C<u>H</u>=C), 1.29 (12H, s, C(C<u>H</u>$_3$)$_2$) , 0.23 (s, 9H, SiC<u>H</u>$_3$)$_3$). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 126.86 (BC=<u>C</u>H), 107.60 (<u>C</u>≡C), 101.80 (C≡<u>C</u>), 85.35 (<u>C</u>(CH$_3$)$_2$), 24.82 (C(<u>C</u>H$_3$)$_2$), -0.15 (Si(<u>C</u>H$_3$)$_3$). Cα to boron atom was not observed. **^{29}Si NMR** (80 MHz, $CDCl_3$ δ, ppm): -16.54. **MS** (EI, m/z): 330(M+2)$^+$, 14), 328(M^+, 13), 315(22), 313(21), 191(11), 163(34), 149(21), 139(16), 133(17), 121(12), 105(46), 91(18), 84(100), 73(28), 67(12), 55(59). Yellow oil. Isolated yield: 36% (12 mg).

*(Z)-Trimethyl(4-(4-nitrophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-3-yn-1-yl)silane (**10**)*



Chemical Formula: $C_{19}H_{26}BNO_4Si$
Molecular Weight: 371,32

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.19 (d, $J_{H\text{-}H}$ = 9.0 Hz, 2H, Ph), 7.56 (d, $J_{H\text{-}H}$ = 9.0 Hz, 2H, Ph), 7.07 (s, 1H, C<u>H</u>=C), 1.27 (s, 12H, C($C\underline{H}_3$)$_2$), 0.28 (s, 9H, Si$C\underline{H}_3$)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, δ, ppm): 147.23, 133.45, 132.19, 130.36, 123.81, 95.48 (<u>C</u>≡C), 93.86 (C≡<u>C</u>), 83.70 (<u>C</u>(CH_3)$_2$), 24.91 (C(<u>C</u>H_3)$_2$), -0.03 (Si(<u>C</u>H_3)$_3$). **^{29}Si NMR** (80 MHz, $CDCl_3$ δ, ppm): -4.70. **MS** (EI, m/z): 371(M^+, 1), 314(4), 204(11), 158(9), 127(4), 83(100), 69(32), 55(46). Yellowish solid. Isolated yield: 56% (62 mg).

5. NMR spectra

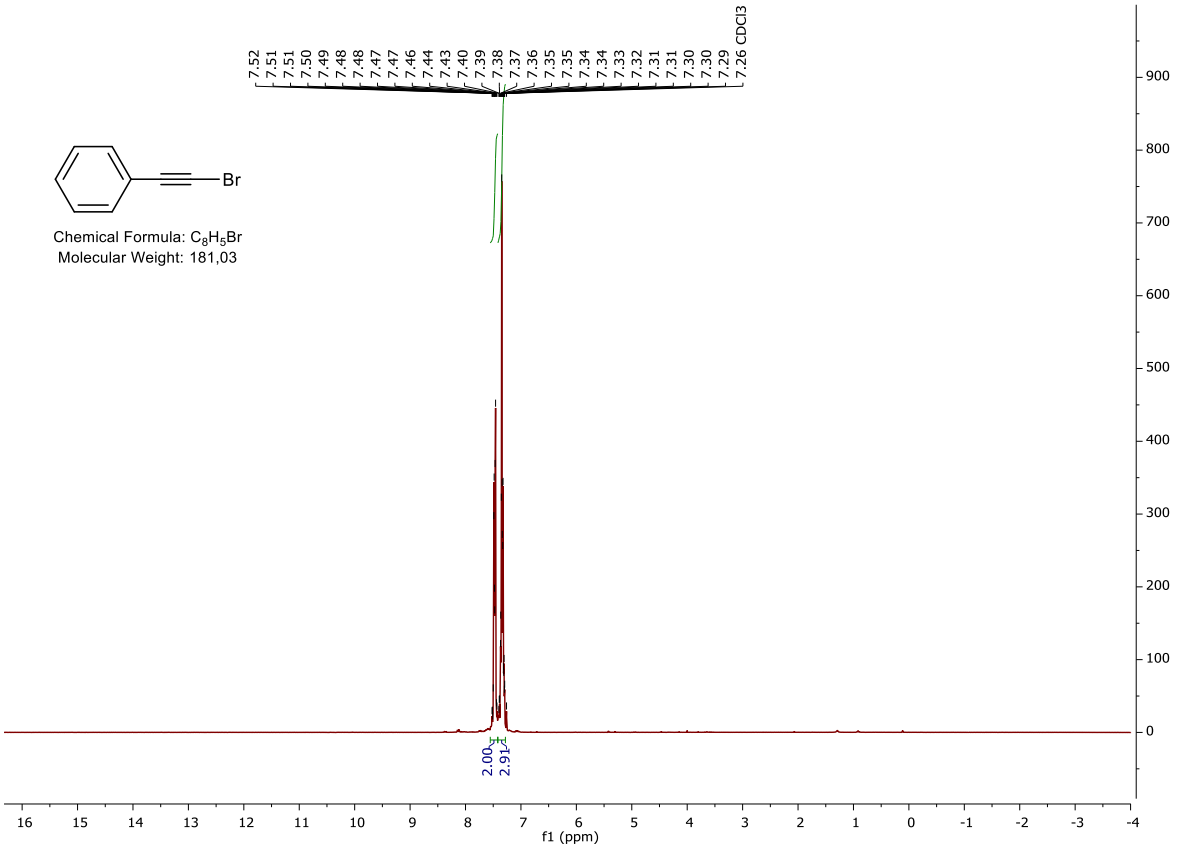


Figure S1. ^{1}H NMR spectrum of (bromoethynyl)benzene.

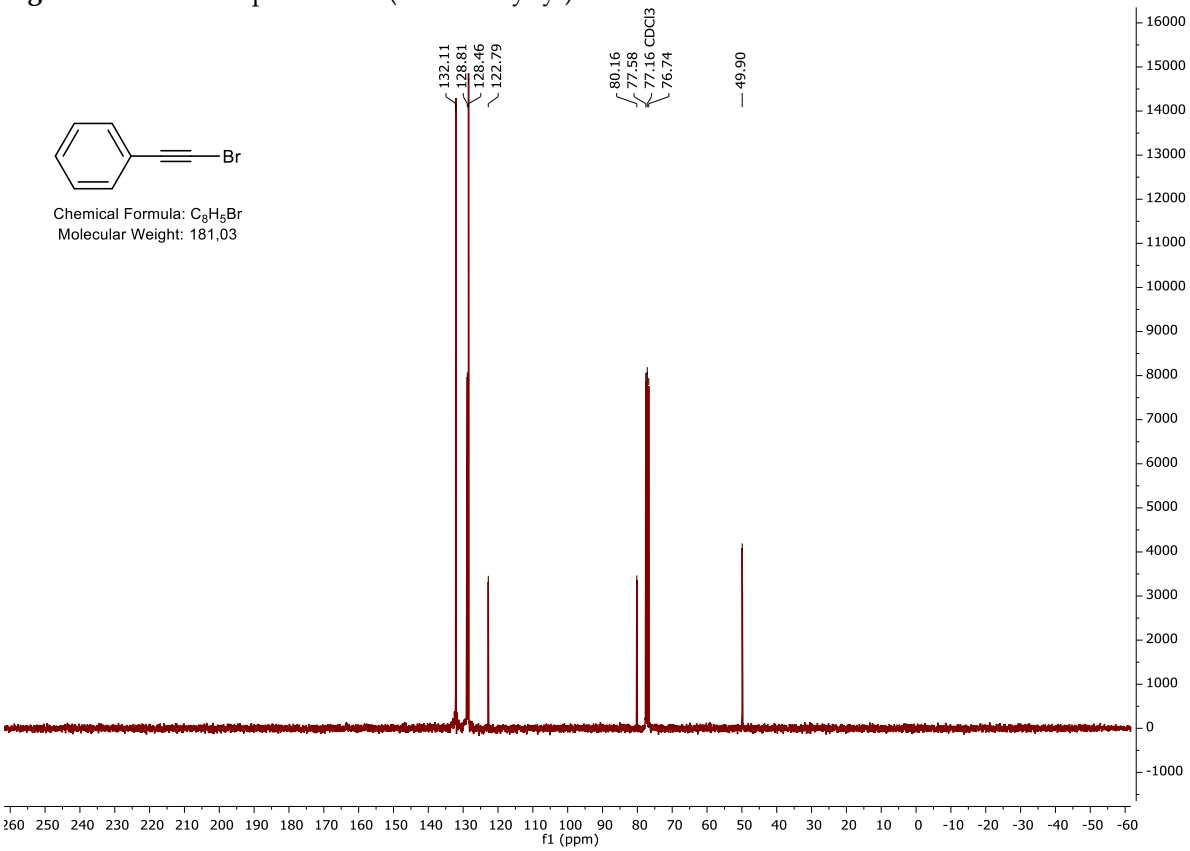


Figure S2. ^{13}C NMR spectrum of (bromoethynyl)benzene.

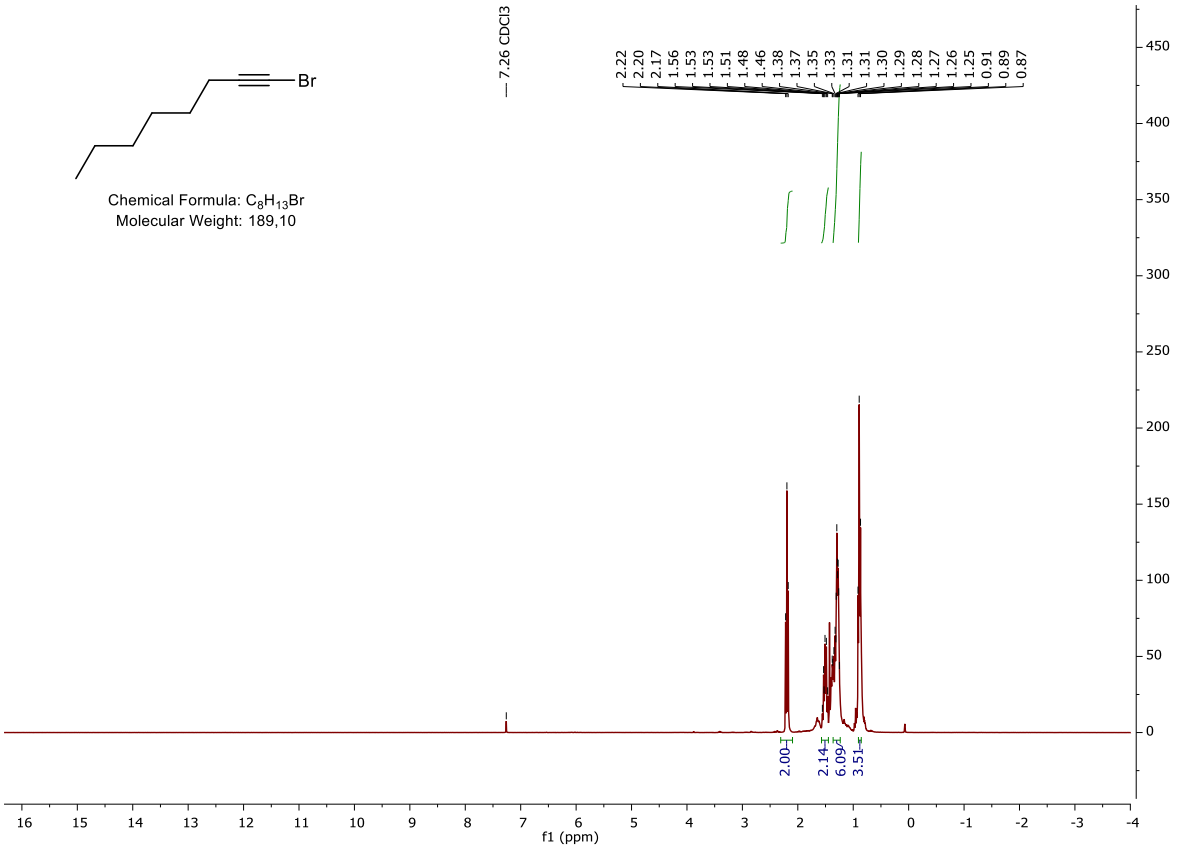


Figure S3. [1]H NMR spectrum of *1-bromooct-1-yne*.

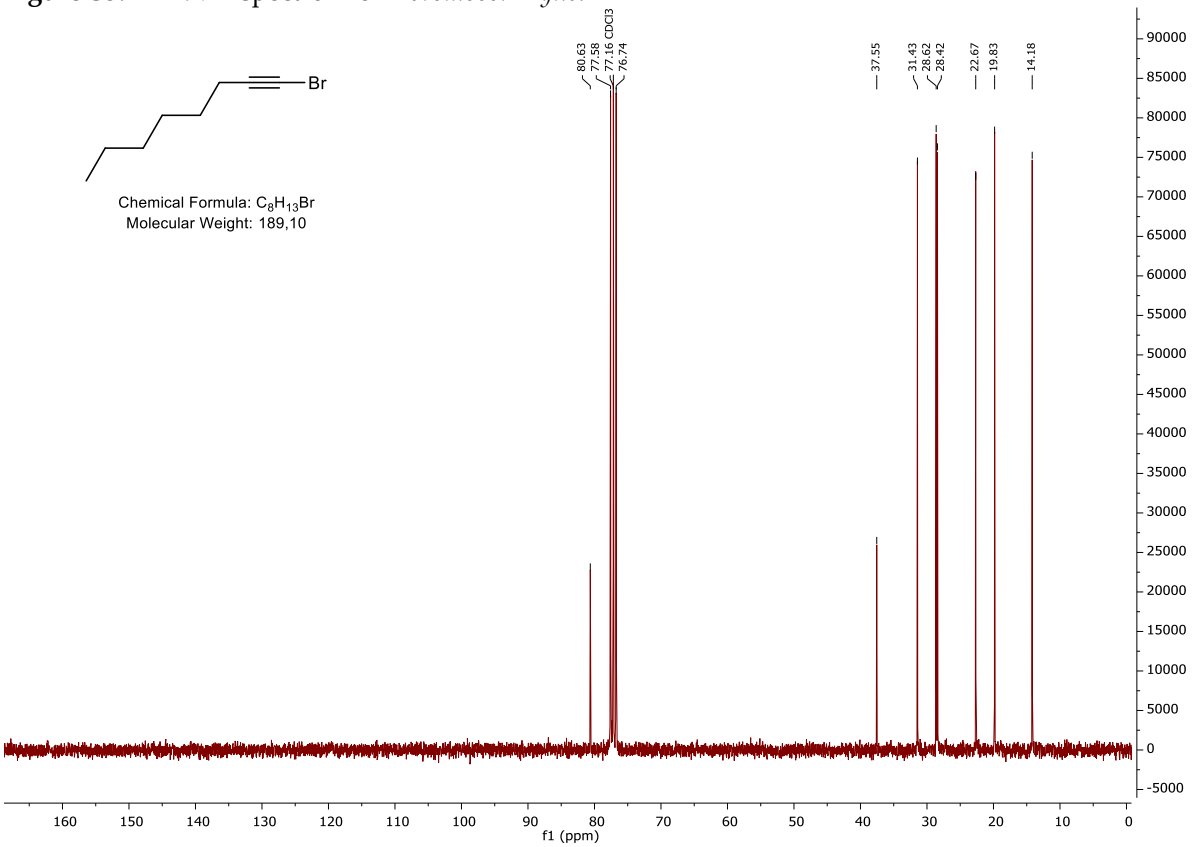


Figure S4. [13]C NMR spectrum of *1-bromooct-1-yne.*

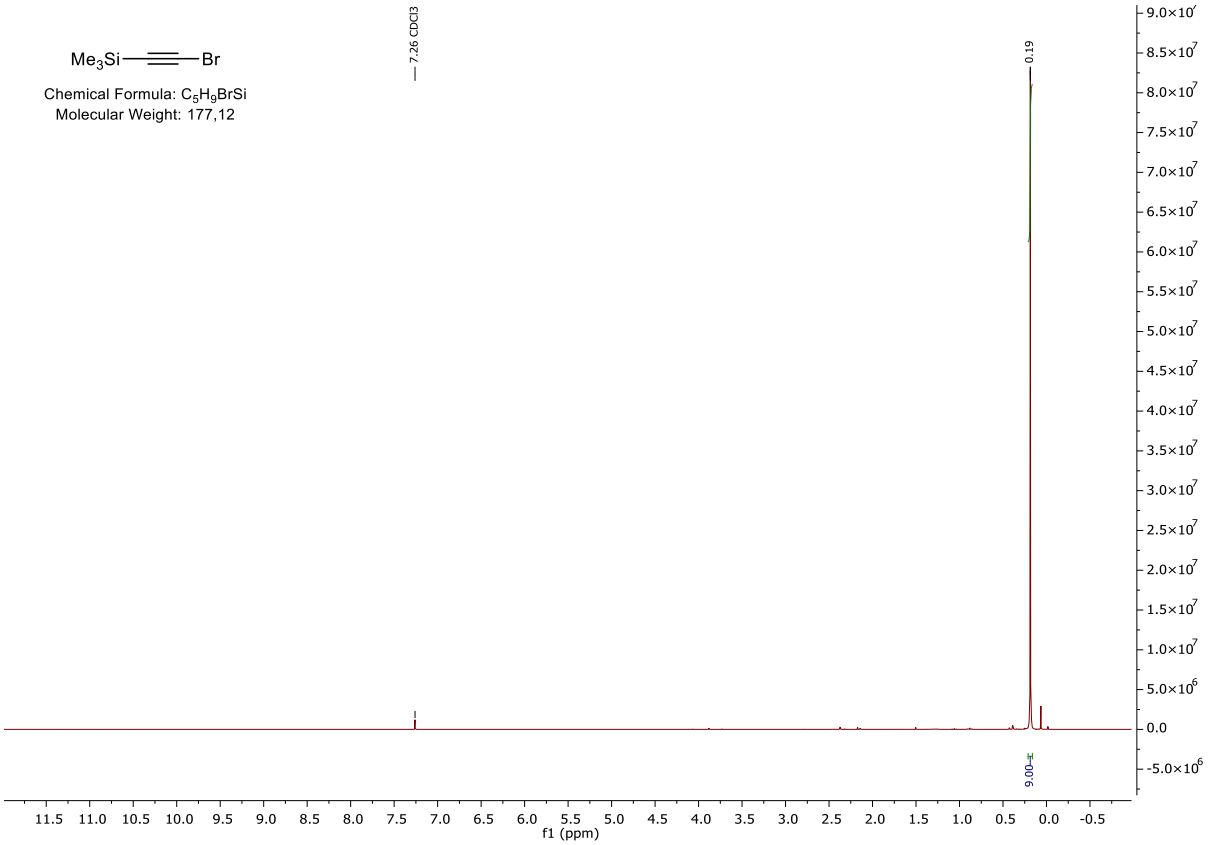


Figure S5. ^{1}H NMR spectrum of *(bromoethynyl)trimethylsilane.*

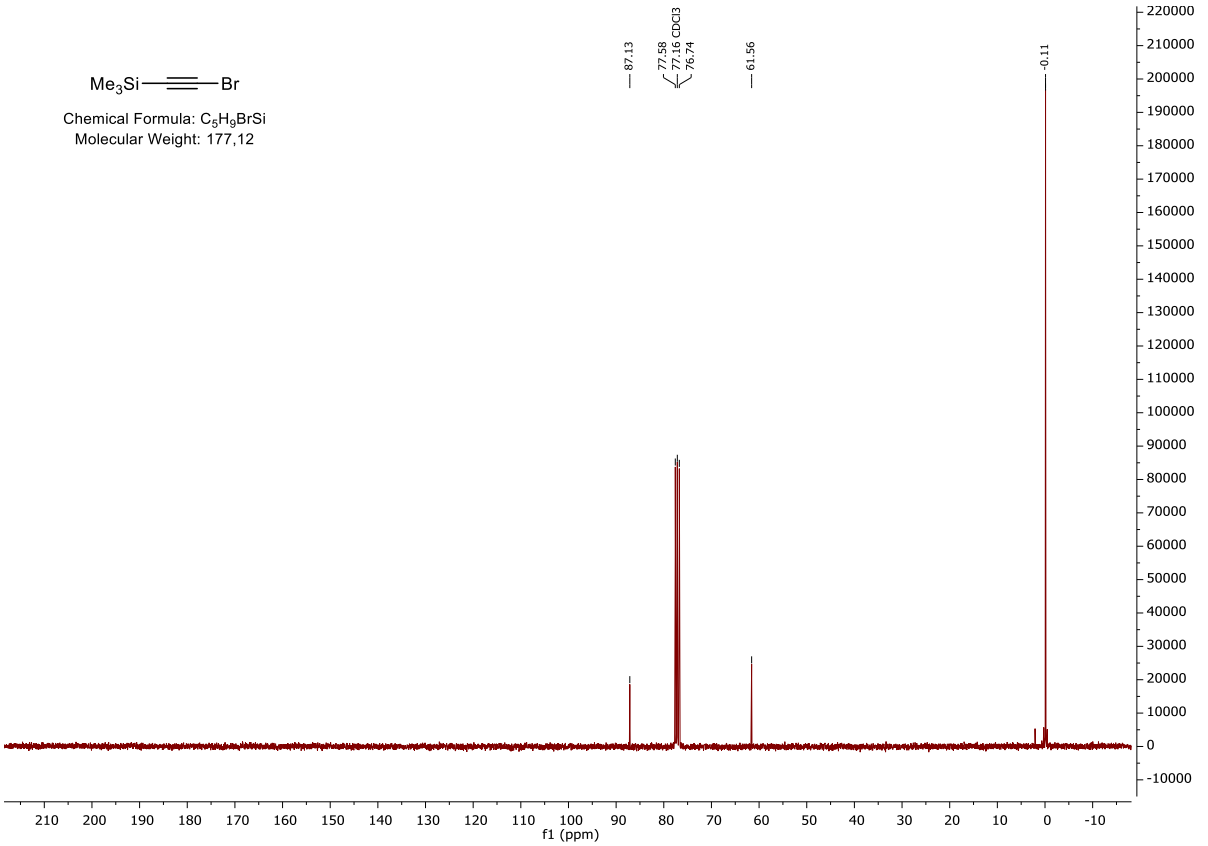


Figure S6. ^{13}C NMR spectrum of *(bromoethynyl)trimethylsilane.*

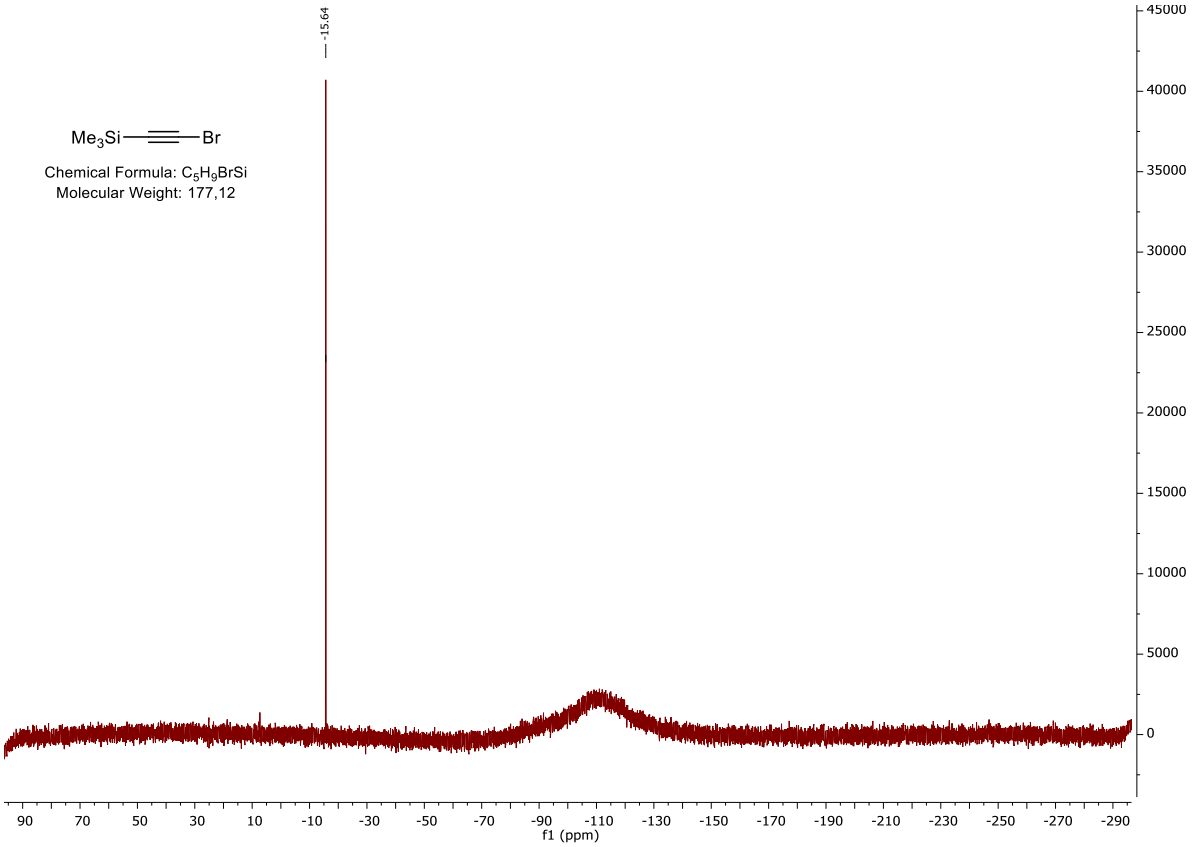


Figure S7. ^{29}Si NMR spectrum of *(bromoethynyl)trimethylsilane.*

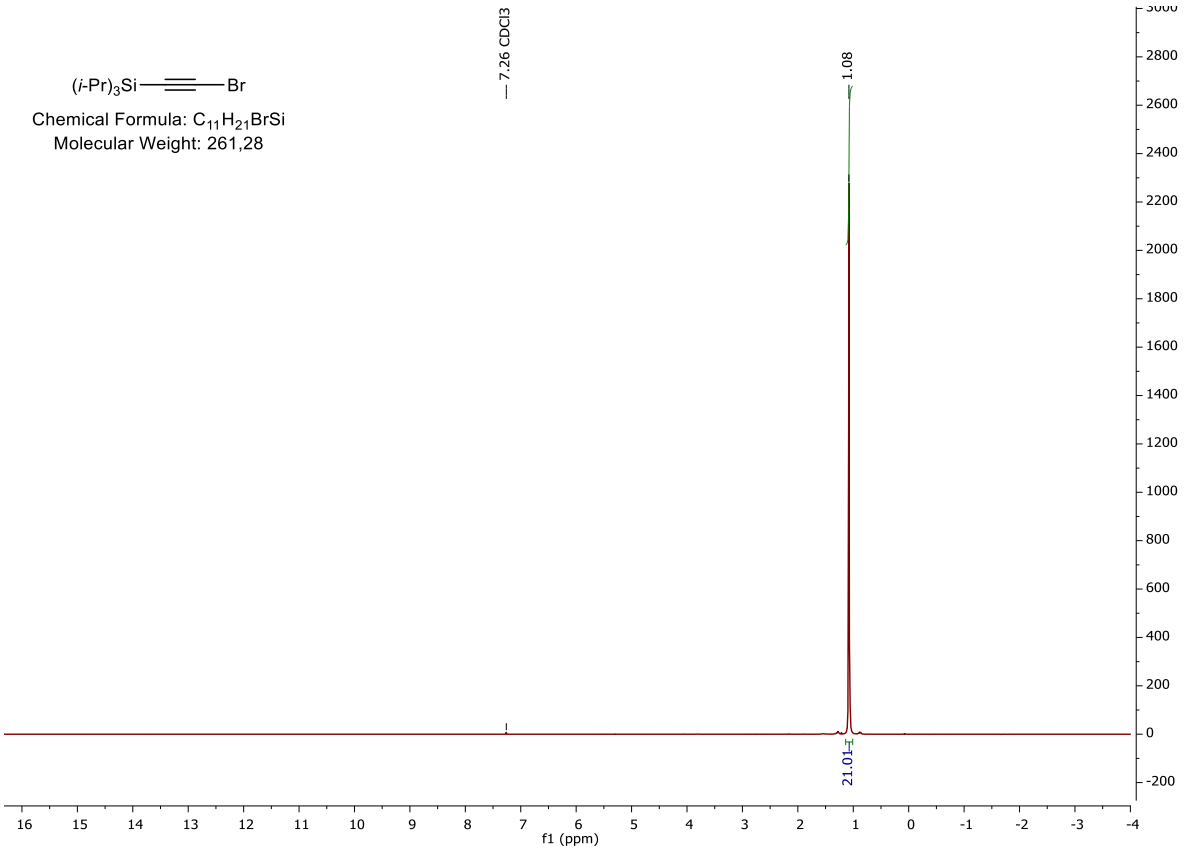


Figure S8. ^{1}H NMR spectrum of *(bromoethynyl)triisopropylsilane.*

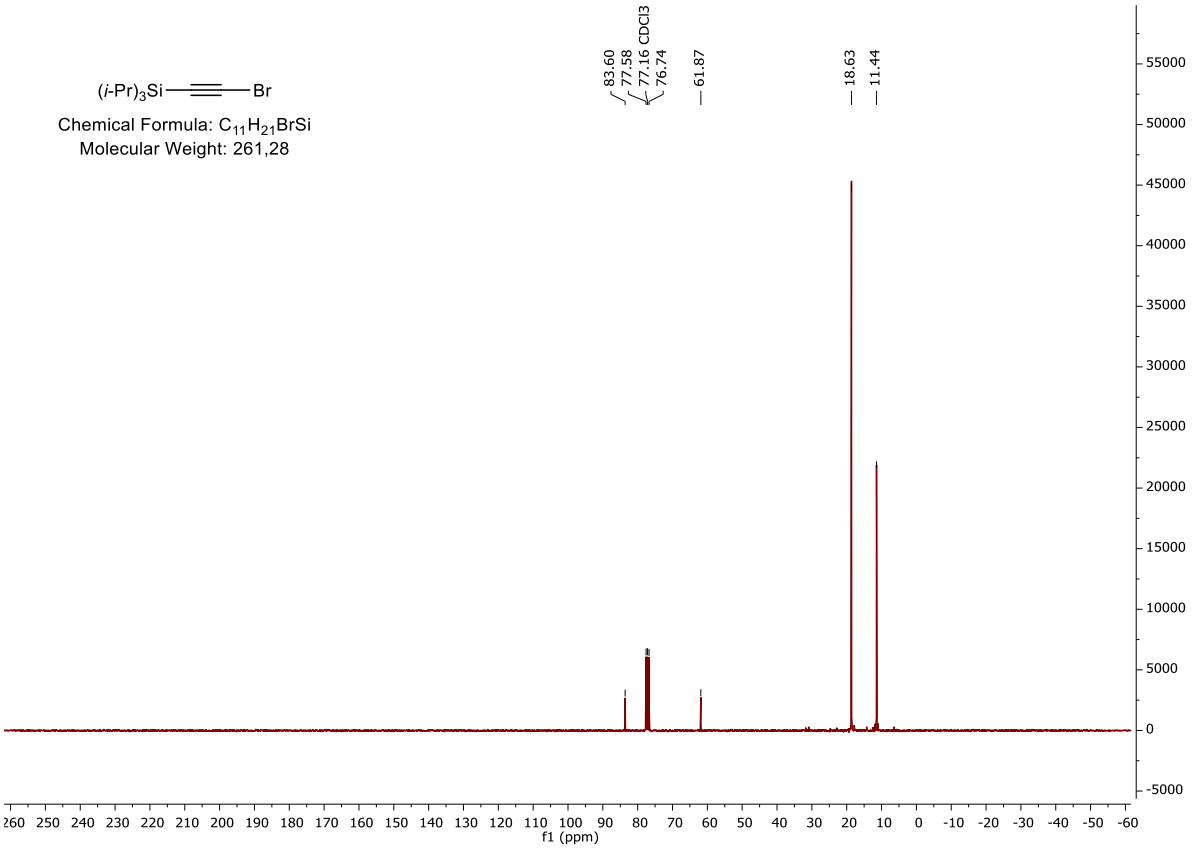


Figure S9. ^{13}C NMR spectrum of *(bromoethynyl)triisopropylsilane.*

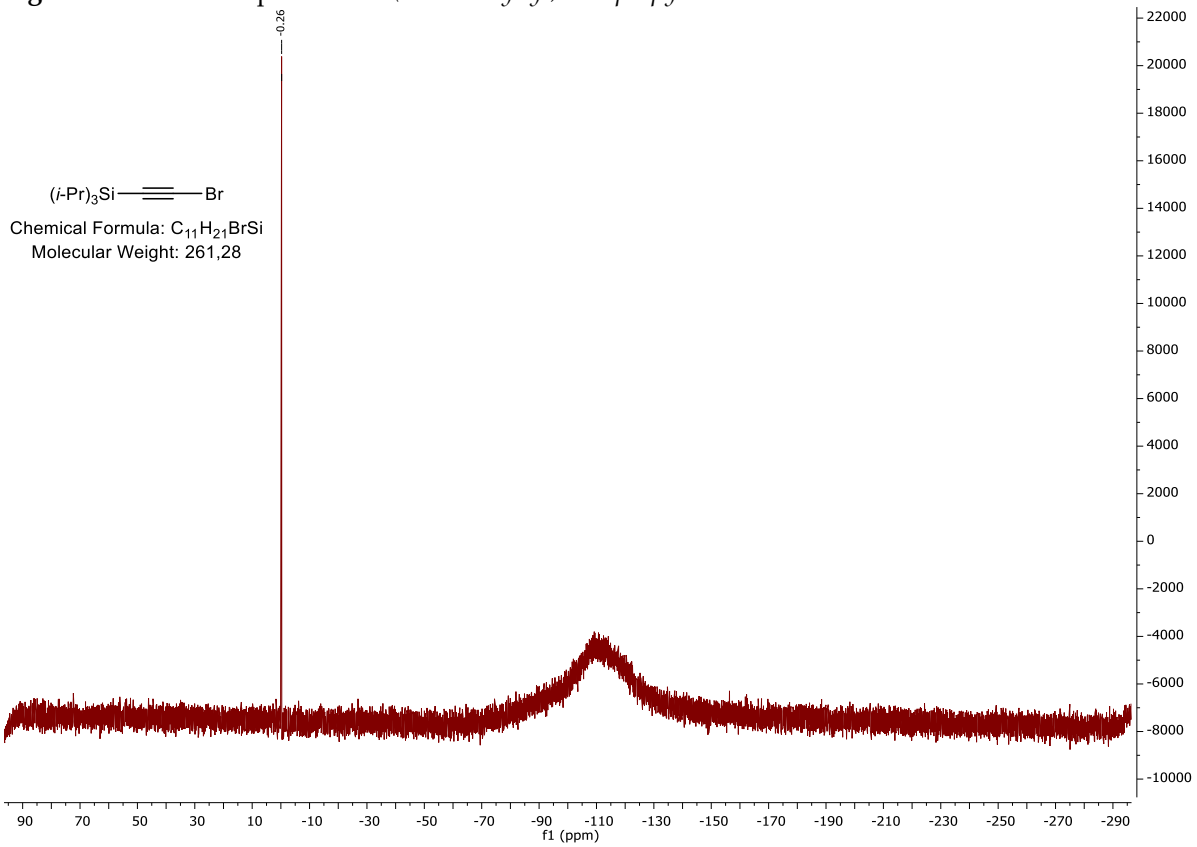


Figure S10. ^{29}Si NMR spectrum of *(bromoethynyl)triisopropylsilane.*

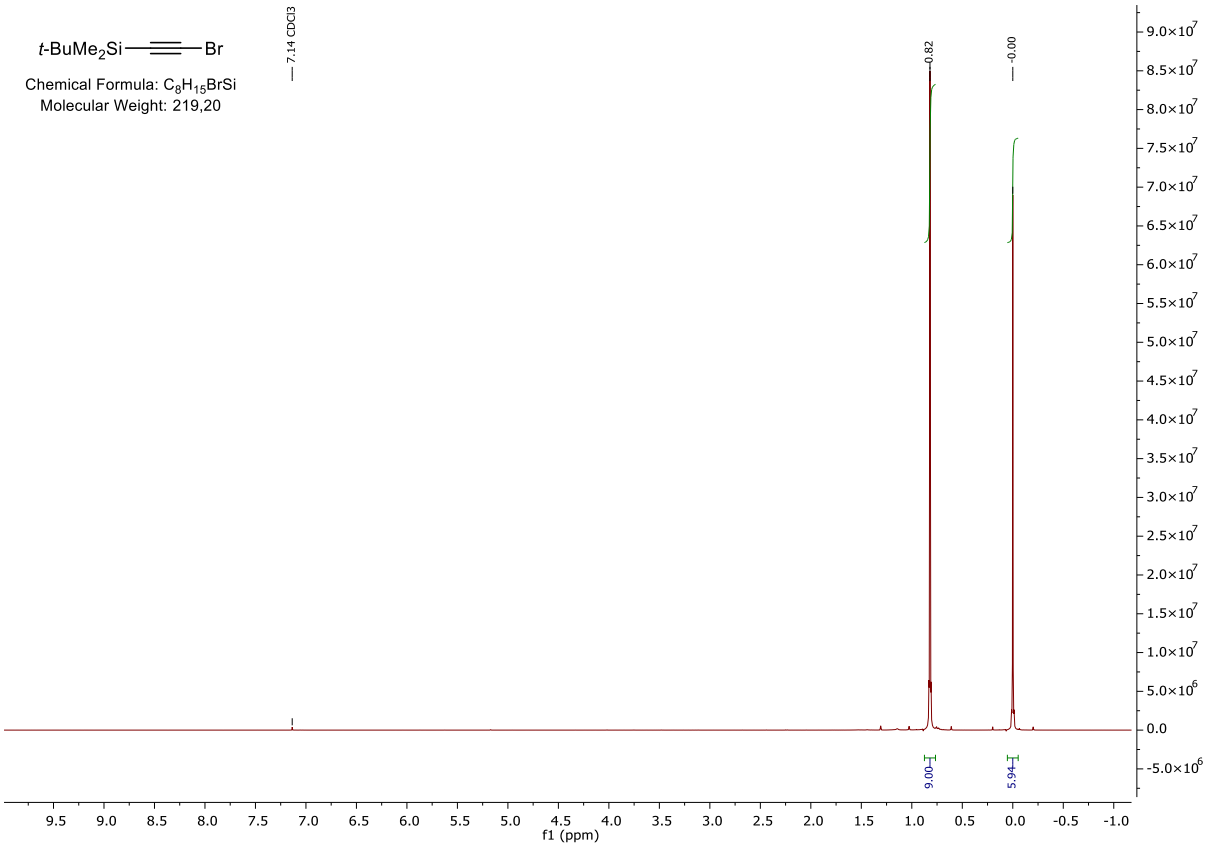


Figure S11. [1]H NMR spectrum of *(bromoethynyl)tert-butyldimethylsilane.*

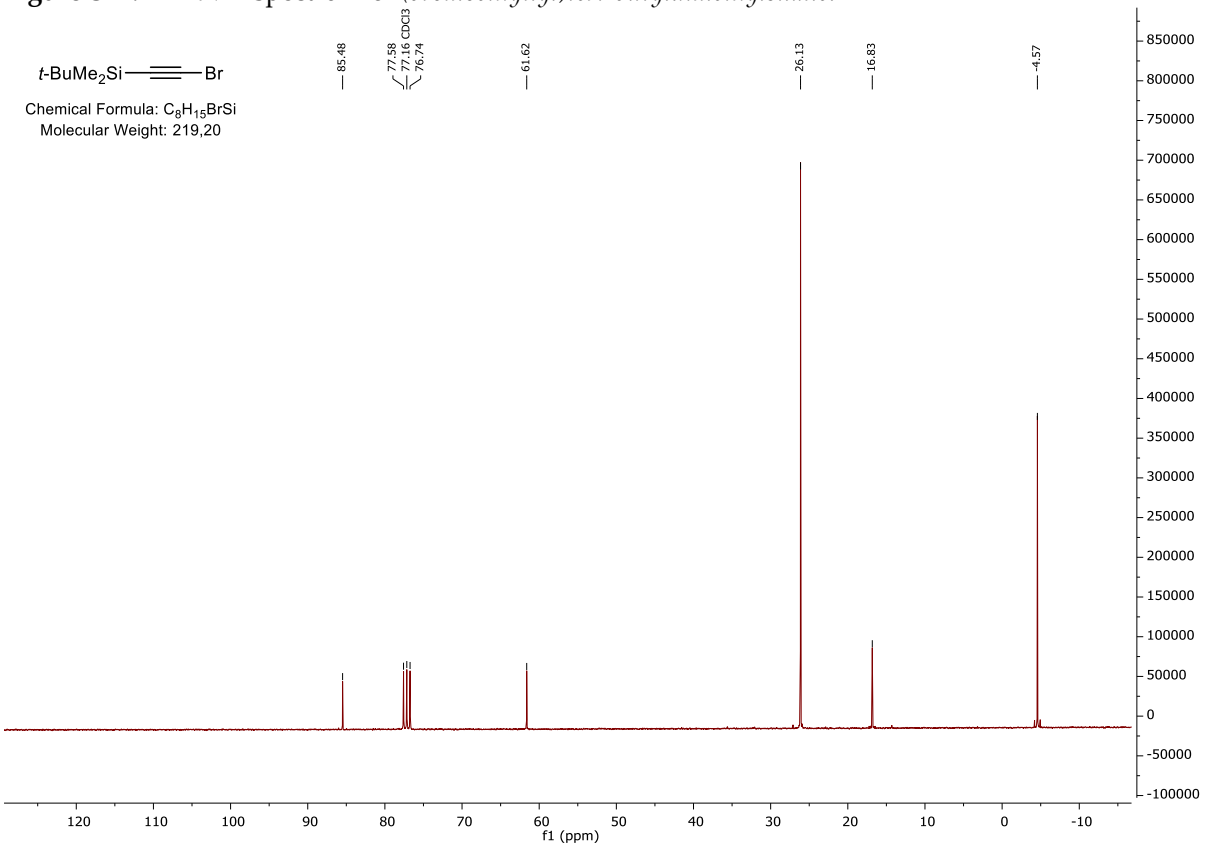


Figure S12. [13]C NMR spectrum of *(bromoethynyl)tert-butyldimethylsilane.*

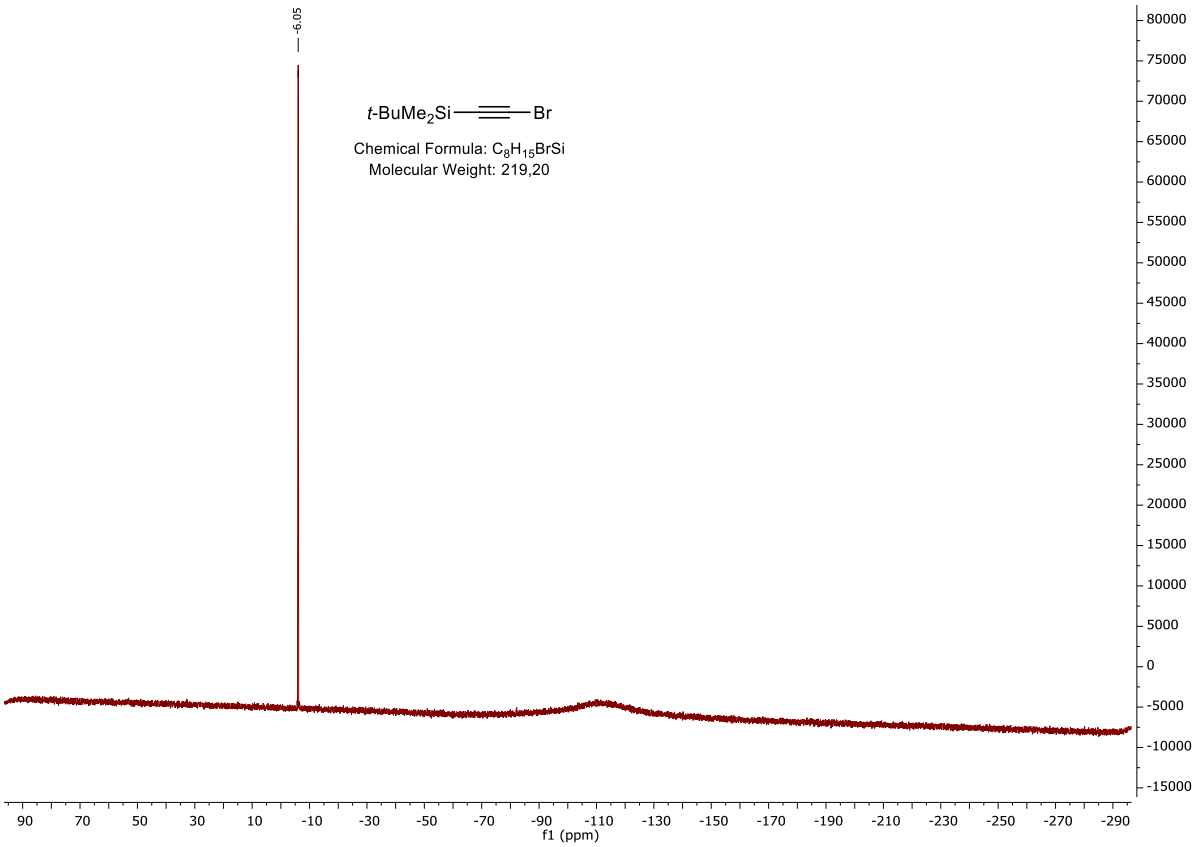


Figure S13. ^{29}Si NMR spectrum of *(bromoethynyl)tert-butyldimethylsilane.*

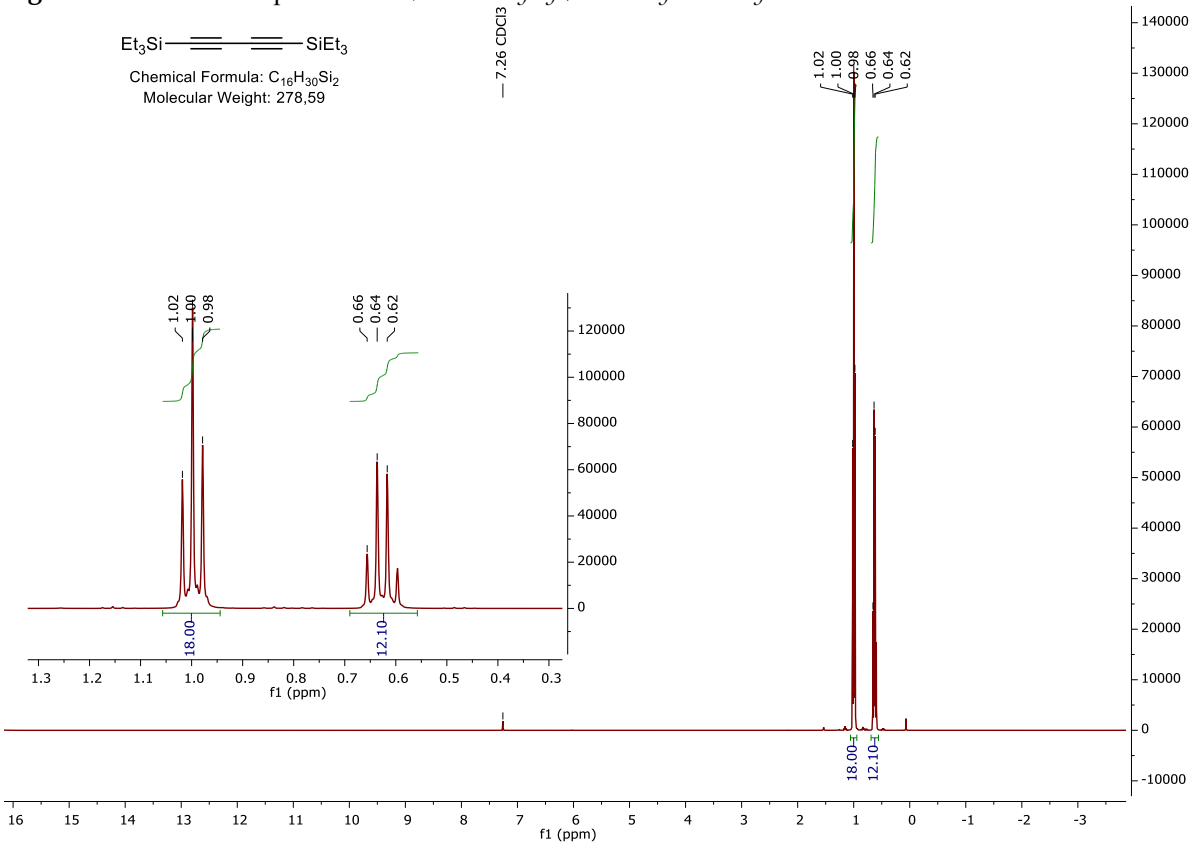


Figure S14. ^{1}H NMR spectrum of **2b**.

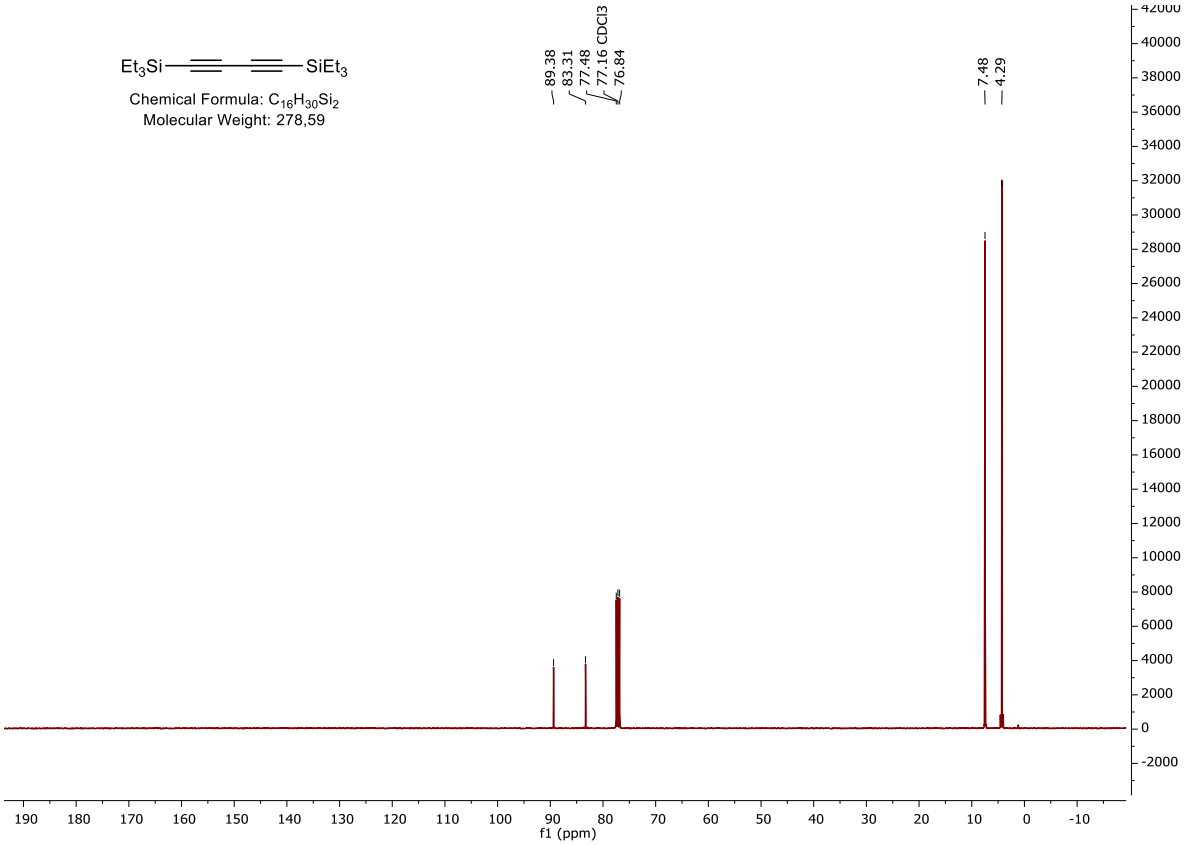


Figure S15. ^{13}C NMR spectrum of **2b**.

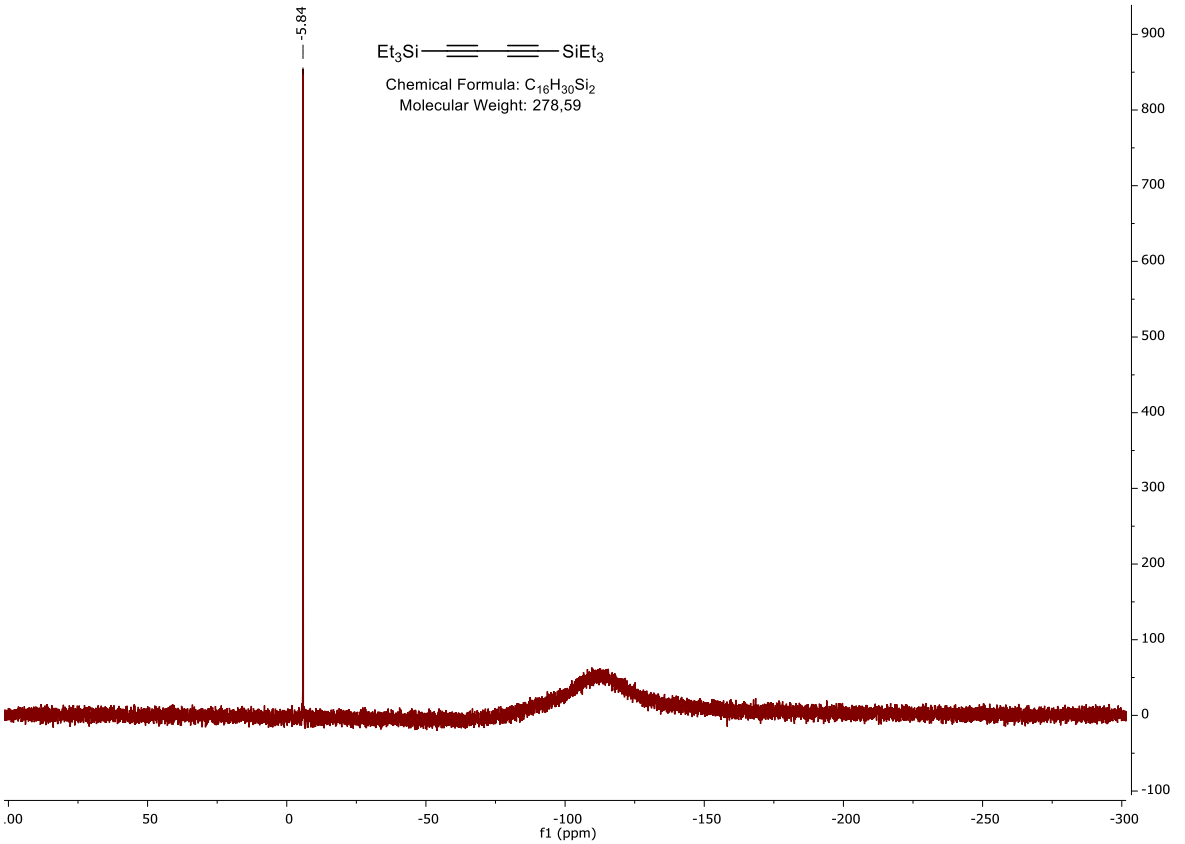


Figure S16. ^{29}Si NMR spectrum of **2b**.

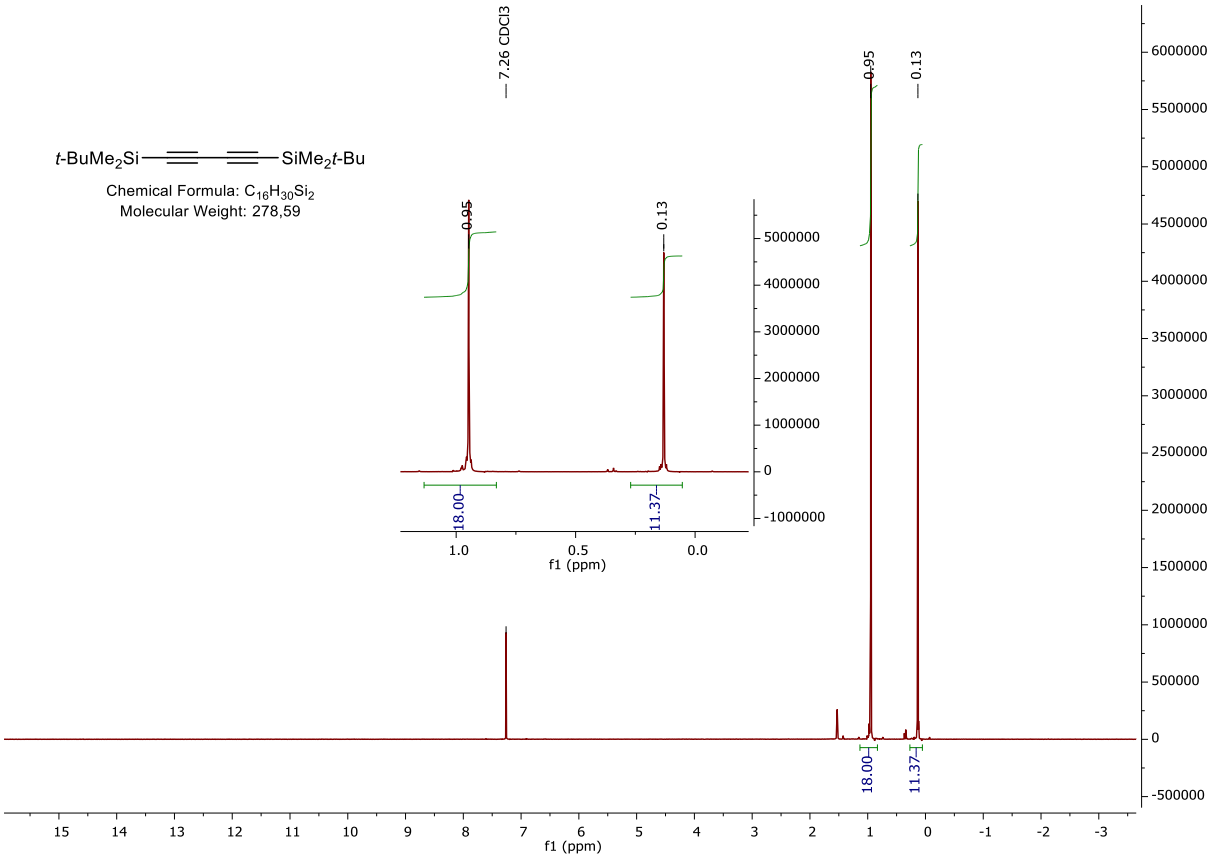


Figure S17. ^{1}H NMR spectrum of **2c**.

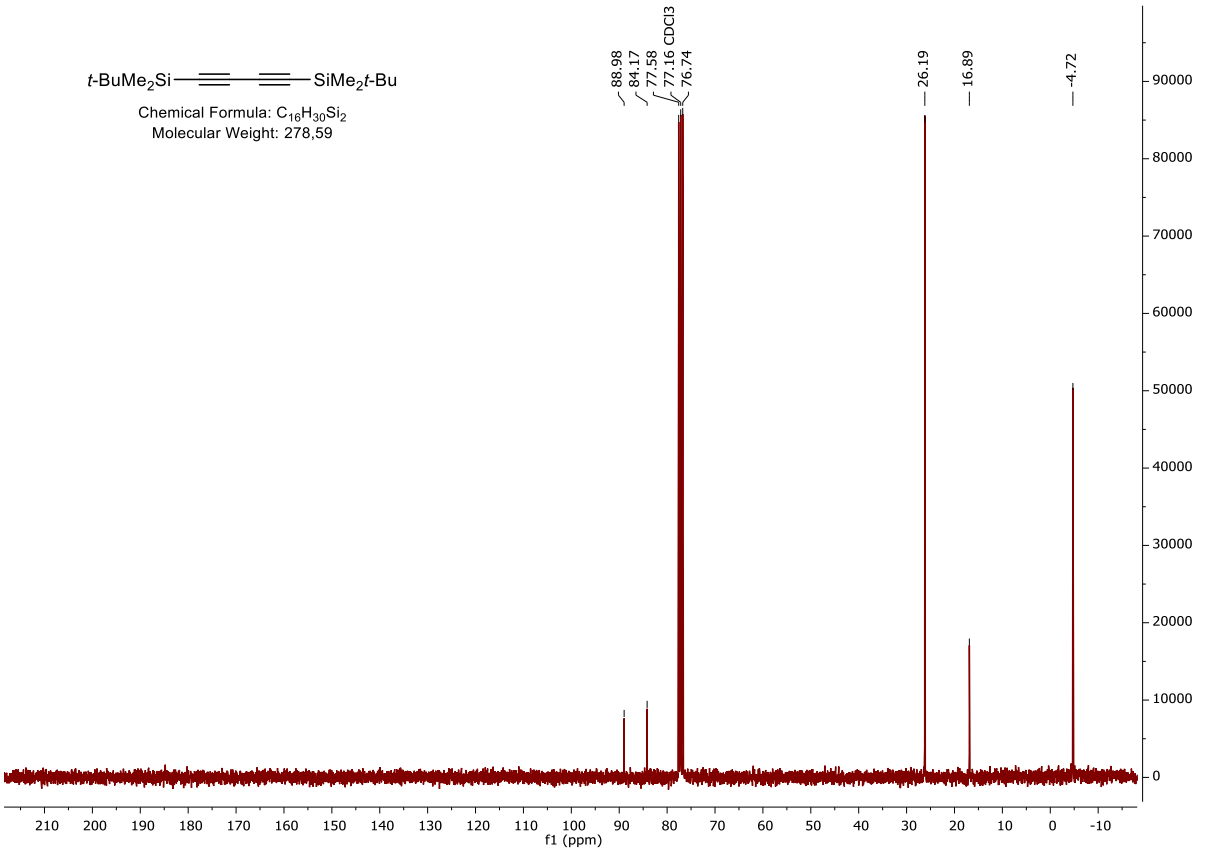


Figure S18. ^{13}C NMR spectrum of **2c**.

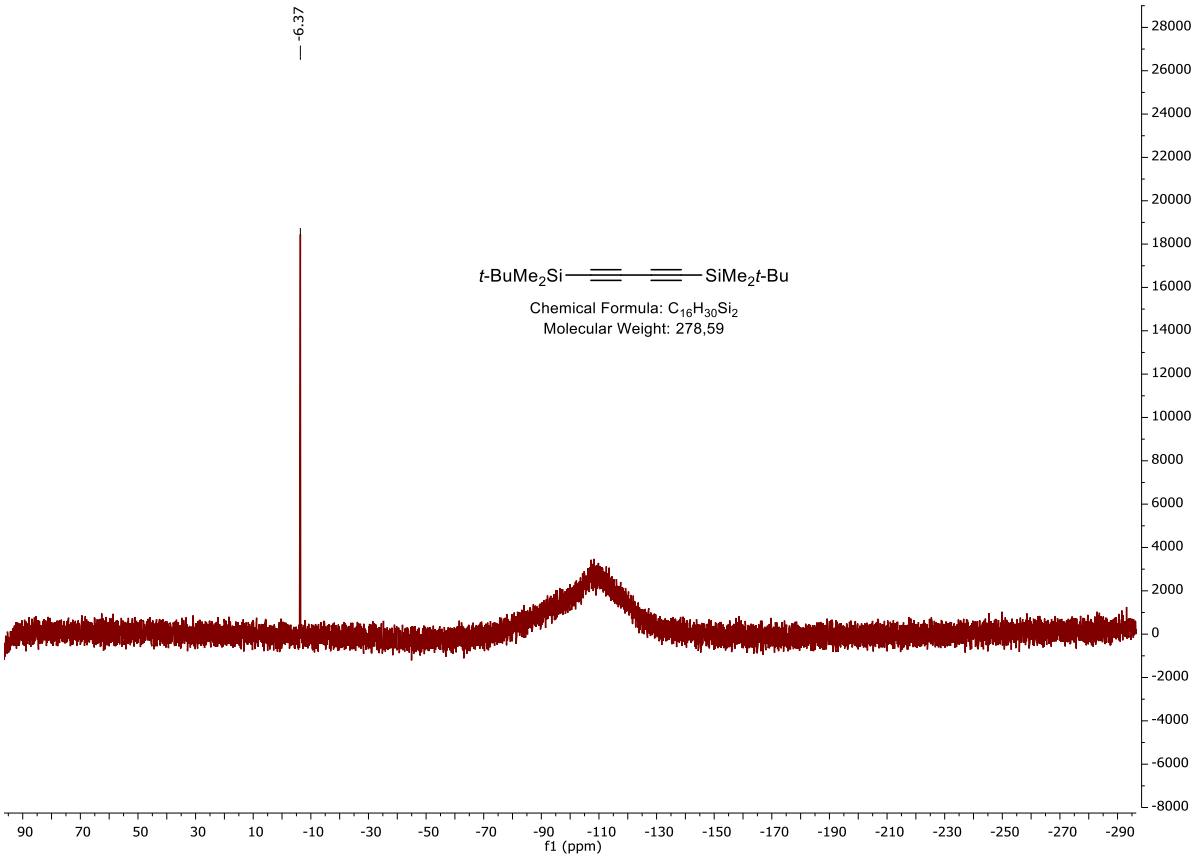


Figure S19. ^{29}Si NMR spectrum of **2c**.

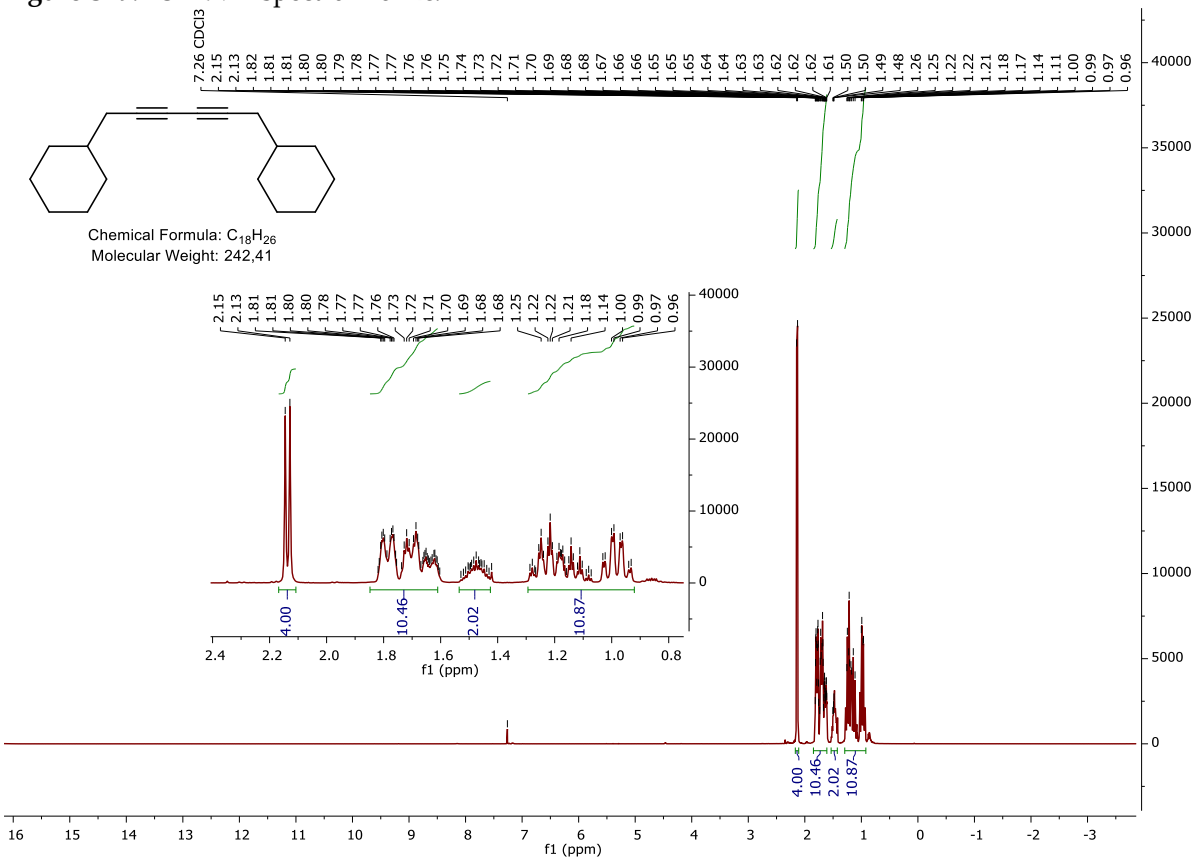


Figure S20. ^{1}H NMR spectrum of **2d**.

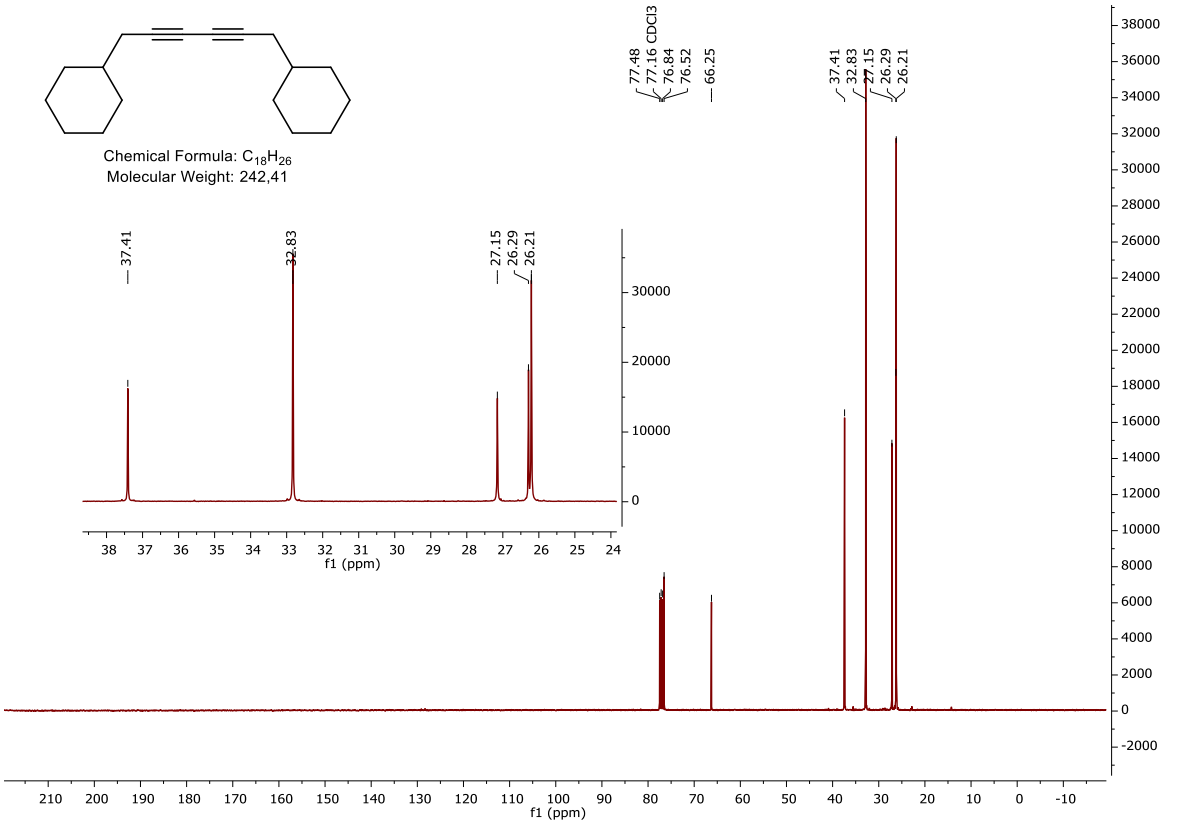


Figure S21. ^{13}C NMR spectrum of **2d**.

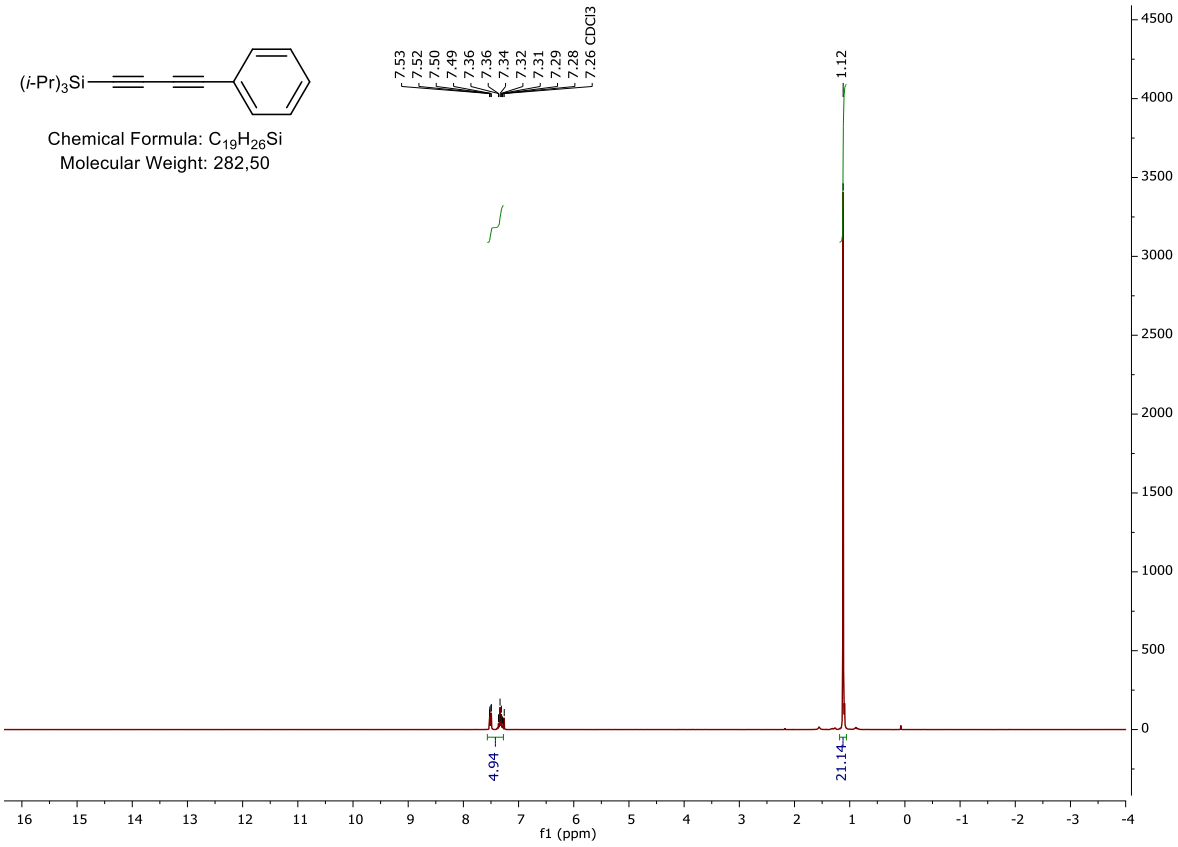


Figure S22. ^{1}H NMR spectrum of **2e**.

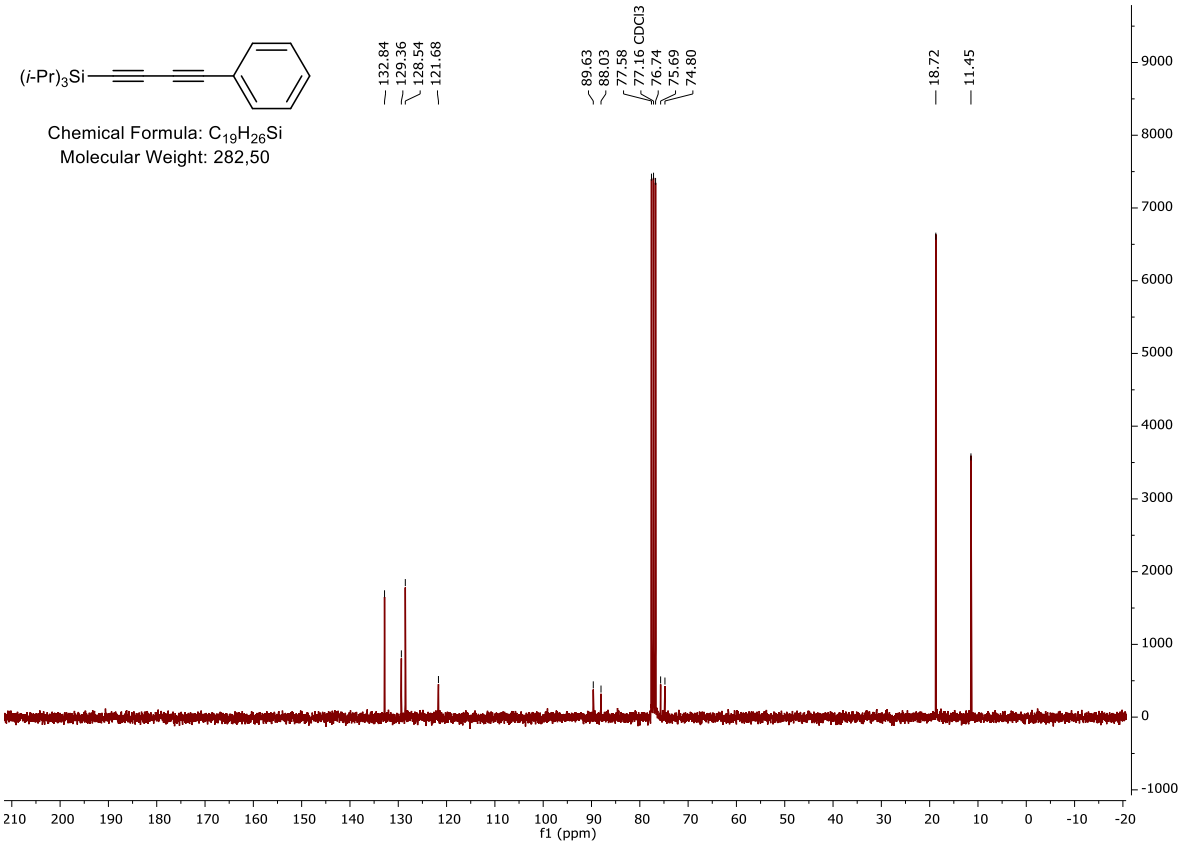


Figure S23. ^{13}C NMR spectrum of **2e**.

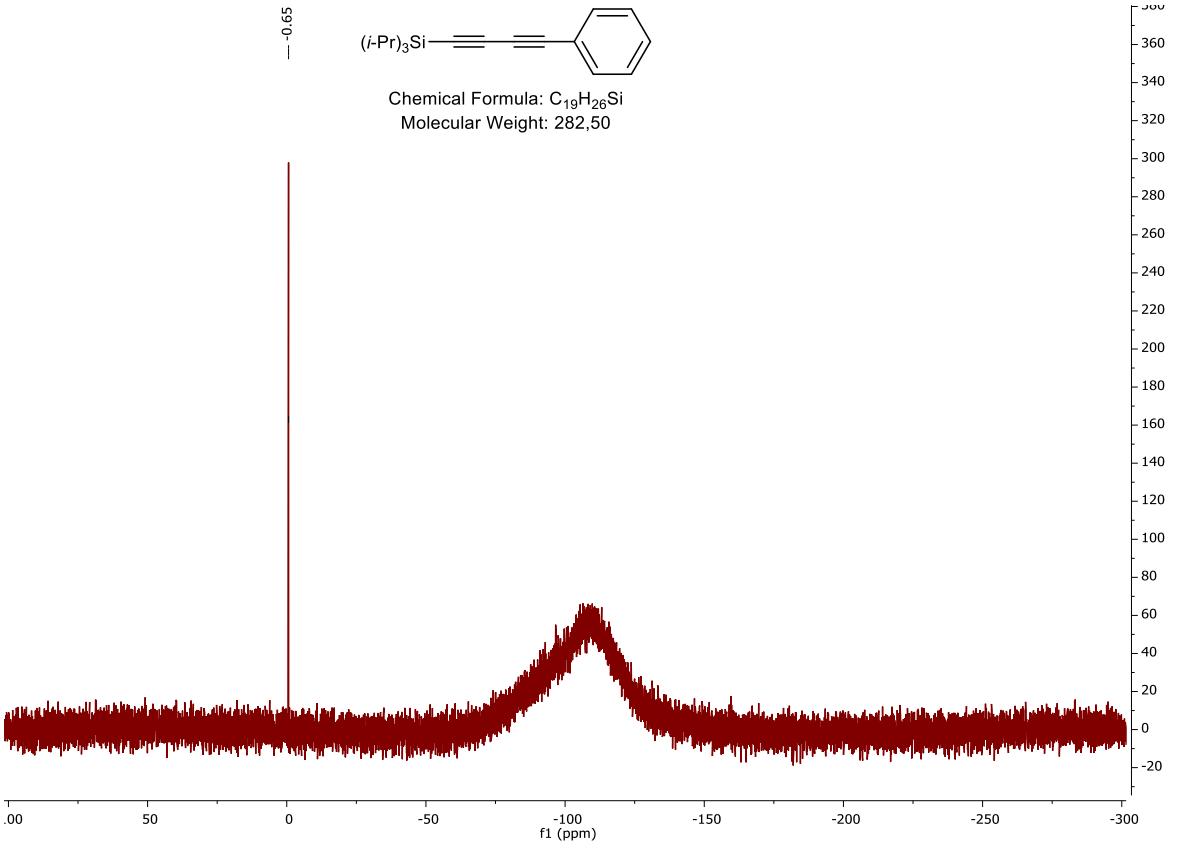


Figure 24. ^{29}Si NMR spectrum of **2e**.

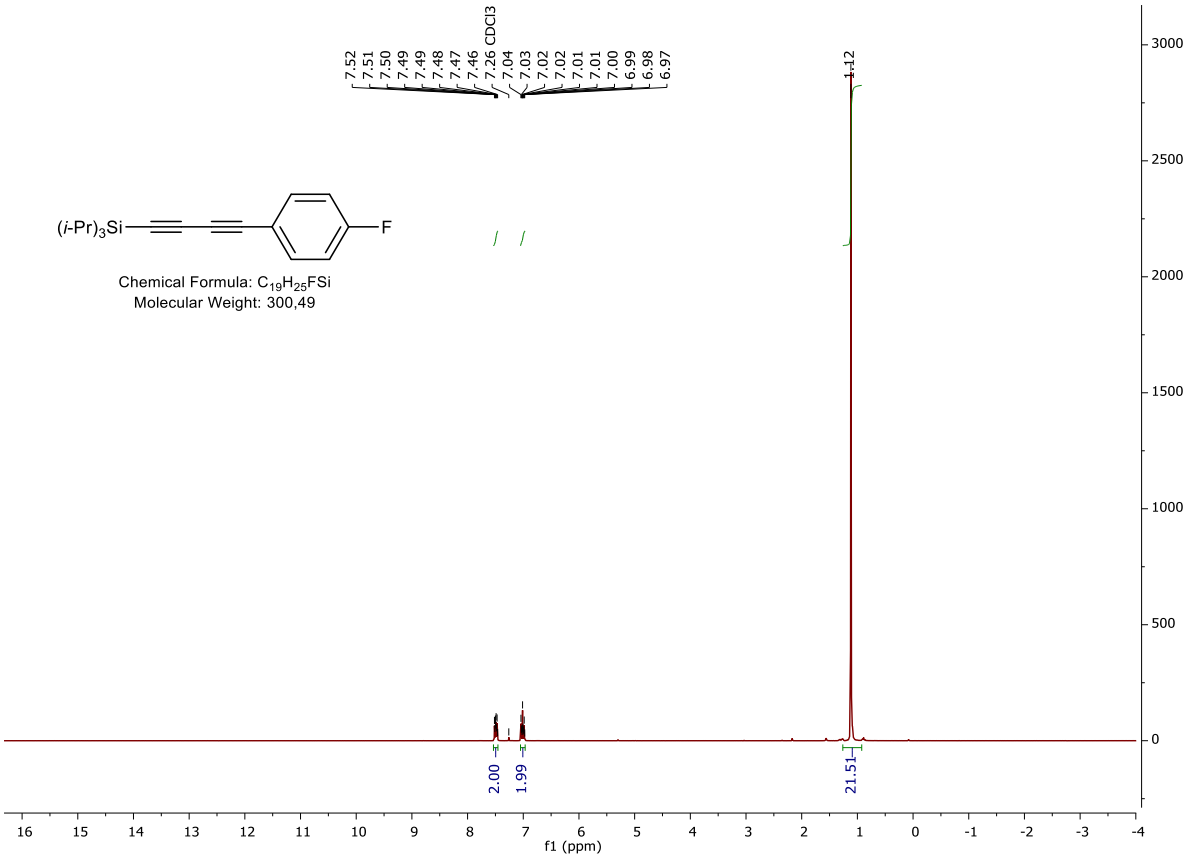


Figure 25. ^{1}H NMR spectrum of **2f**.

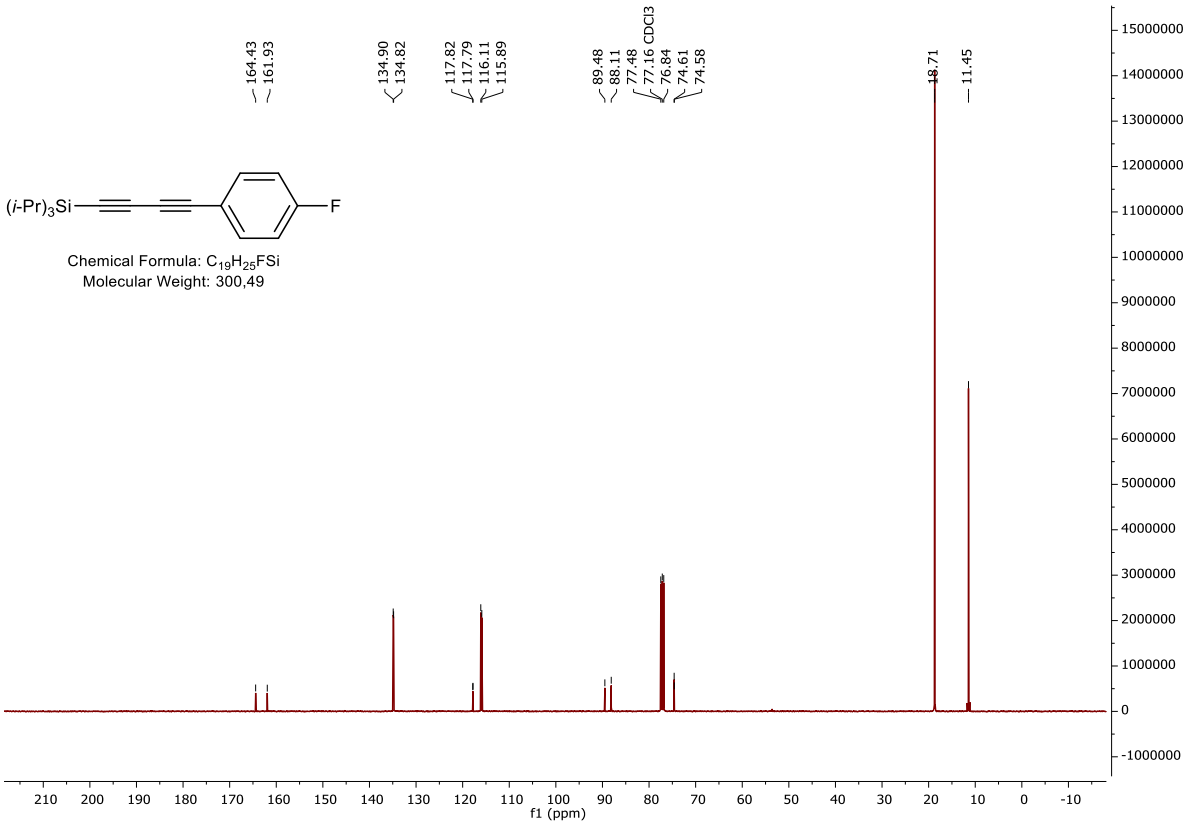


Figure S26. ^{13}C NMR spectrum of **2f**.

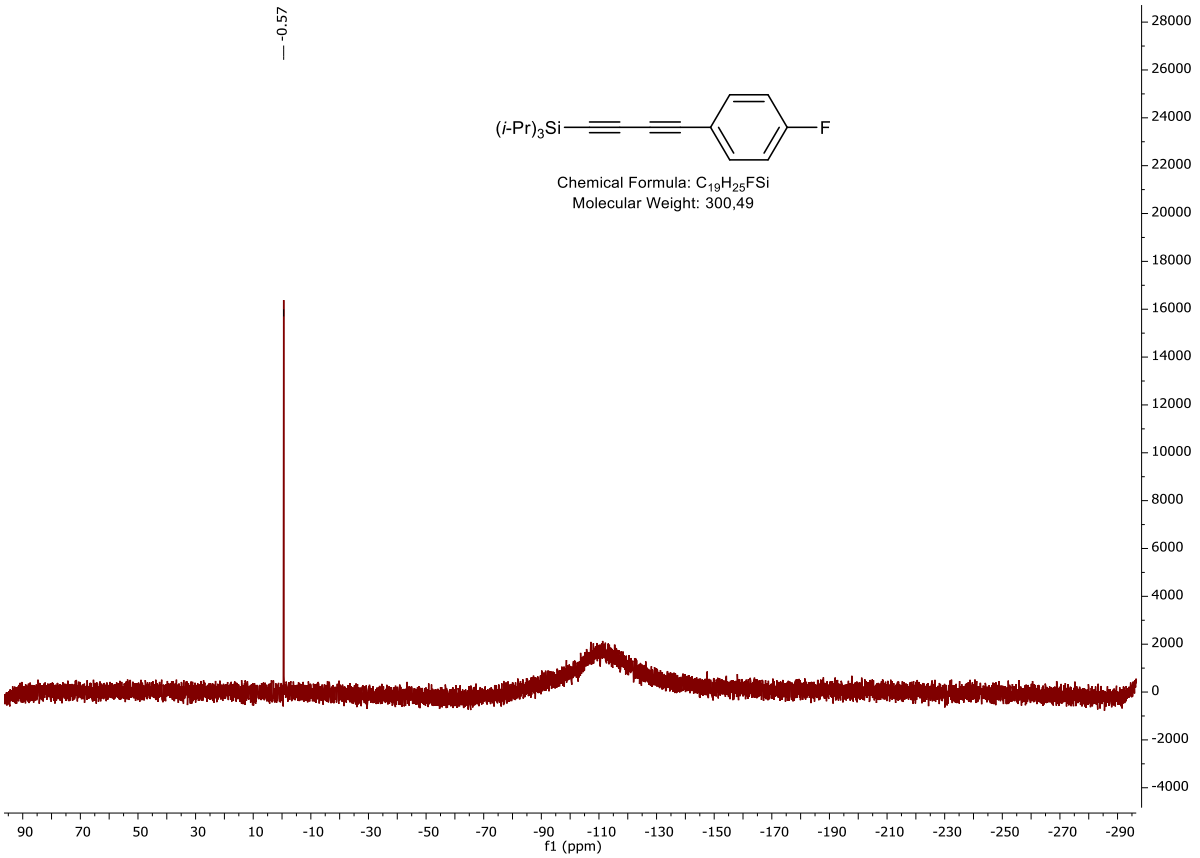


Figure S27. ^{29}Si NMR spectrum of **2f**.

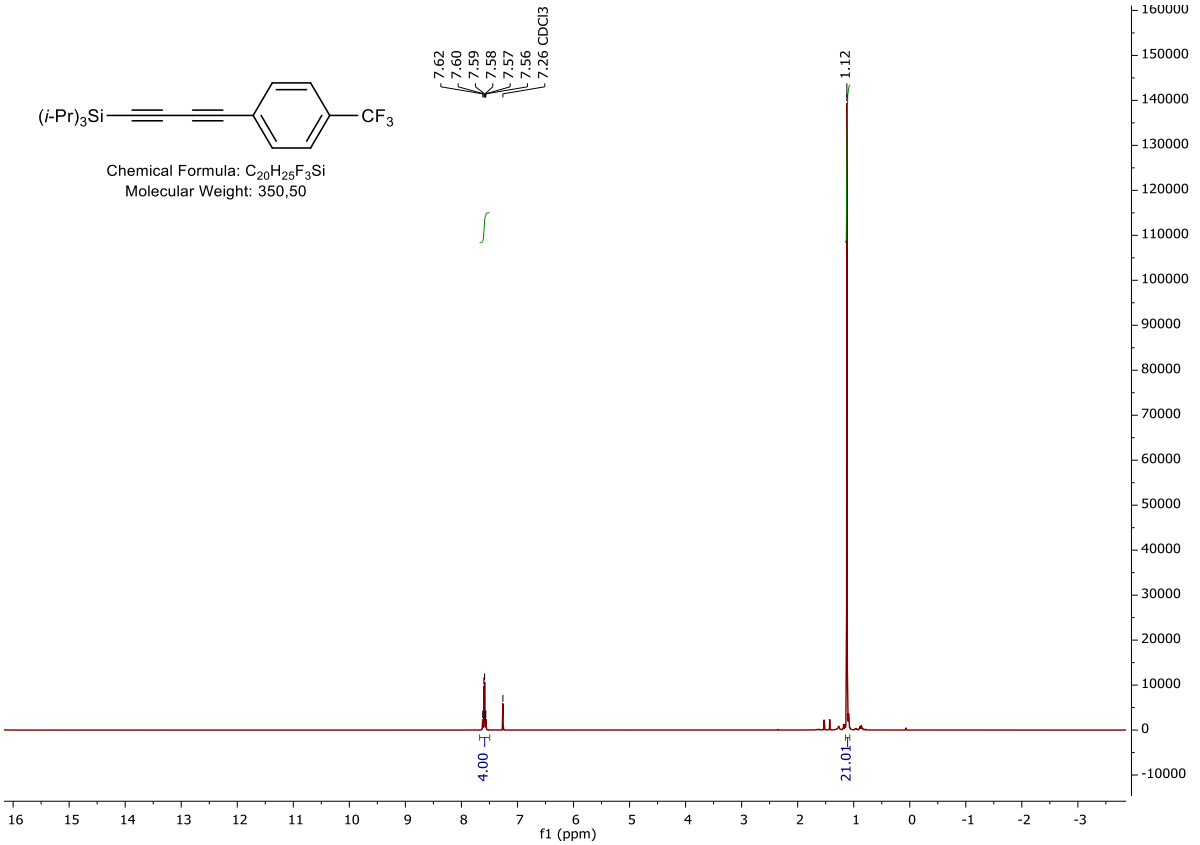


Figure S28. ^{1}H NMR spectrum of **2g**.

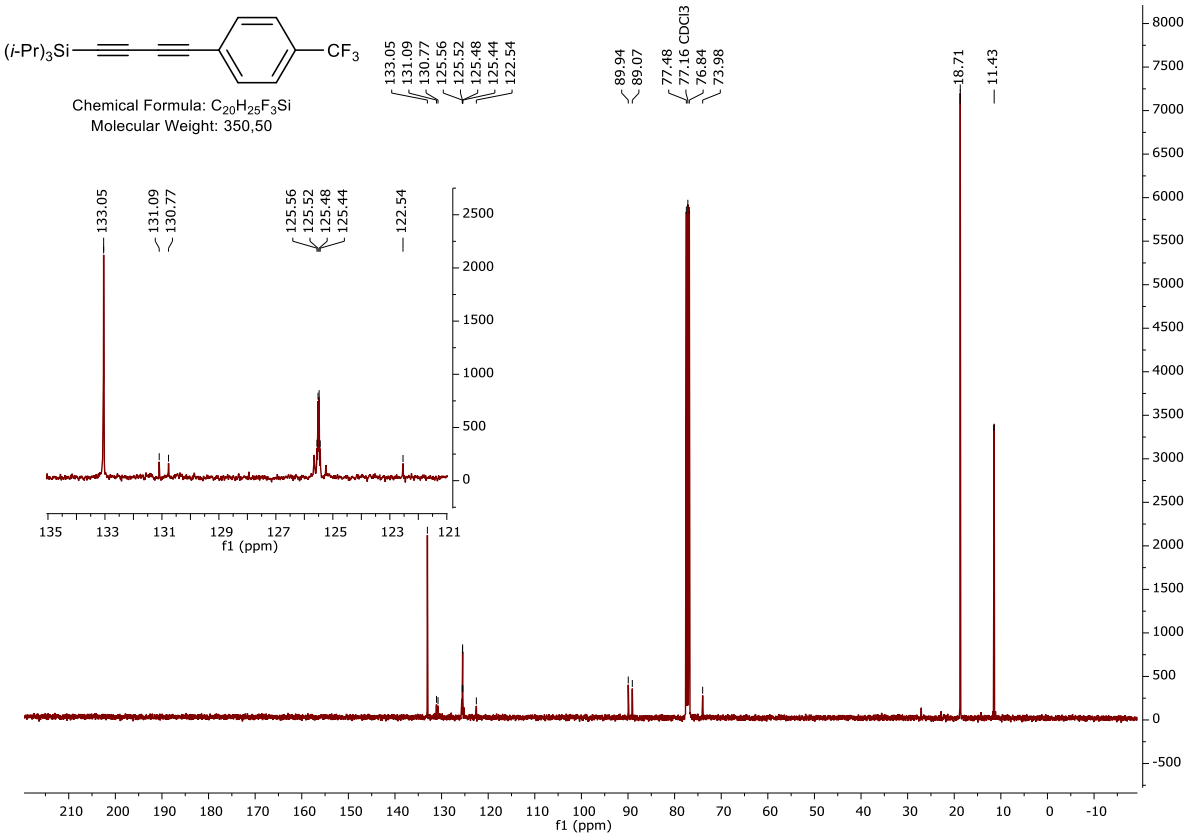


Figure S29. ^{13}C NMR spectrum of **2g**.

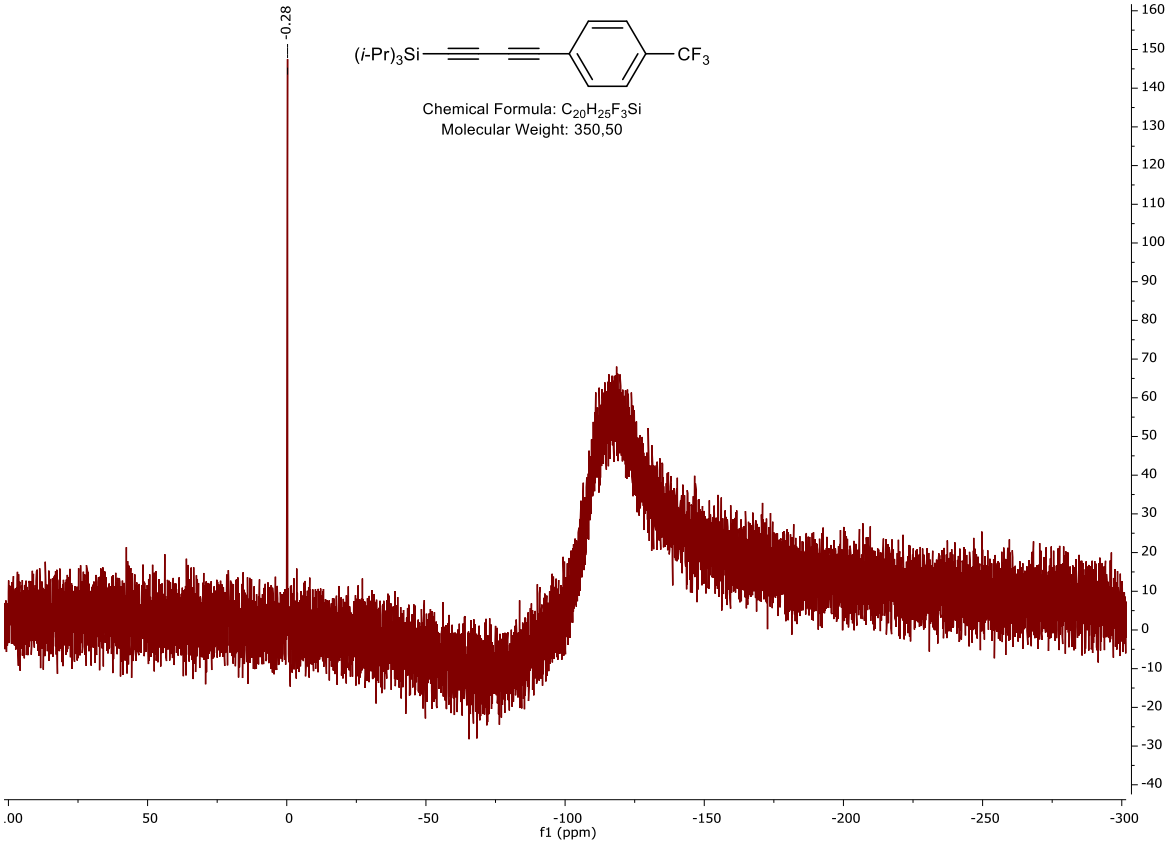


Figure S30. ^{29}Si NMR spectrum of **2g**.

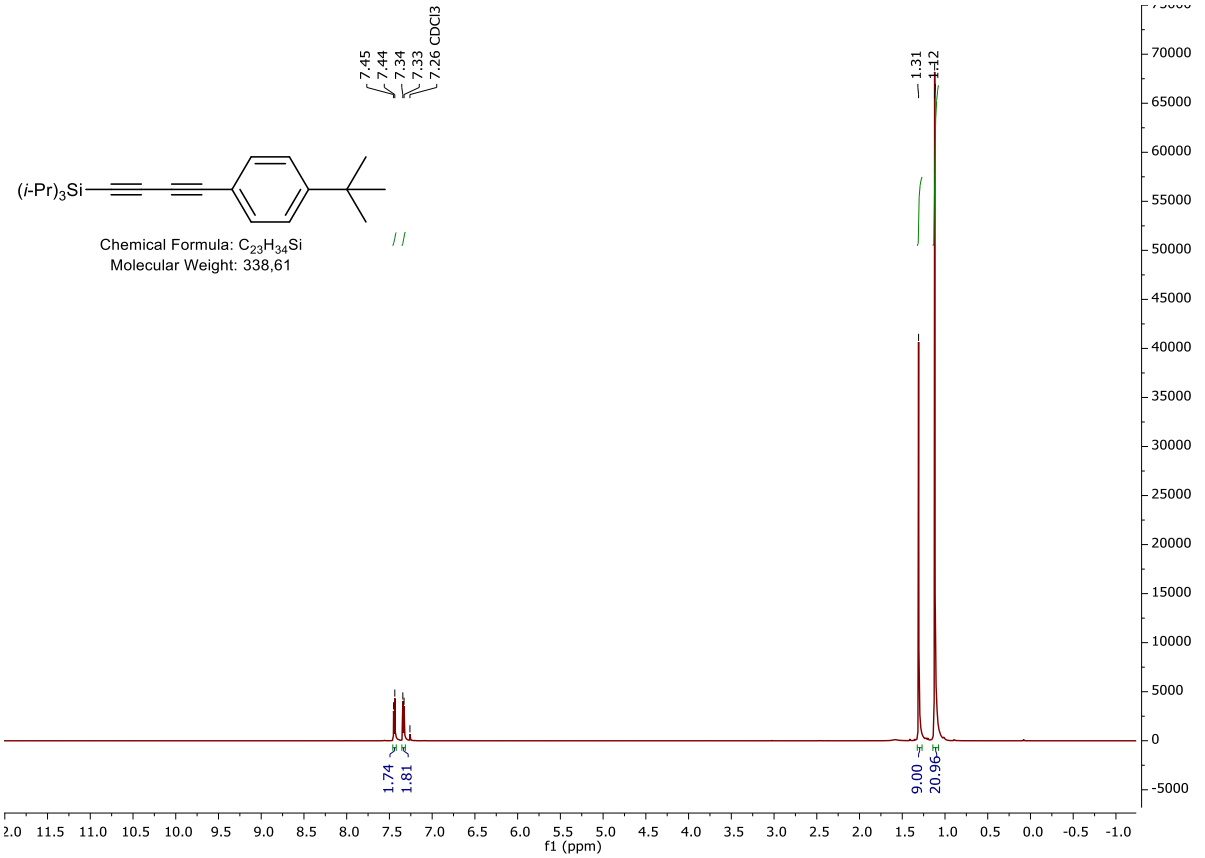


Figure S31. ^{1}H NMR spectrum of **2h**.

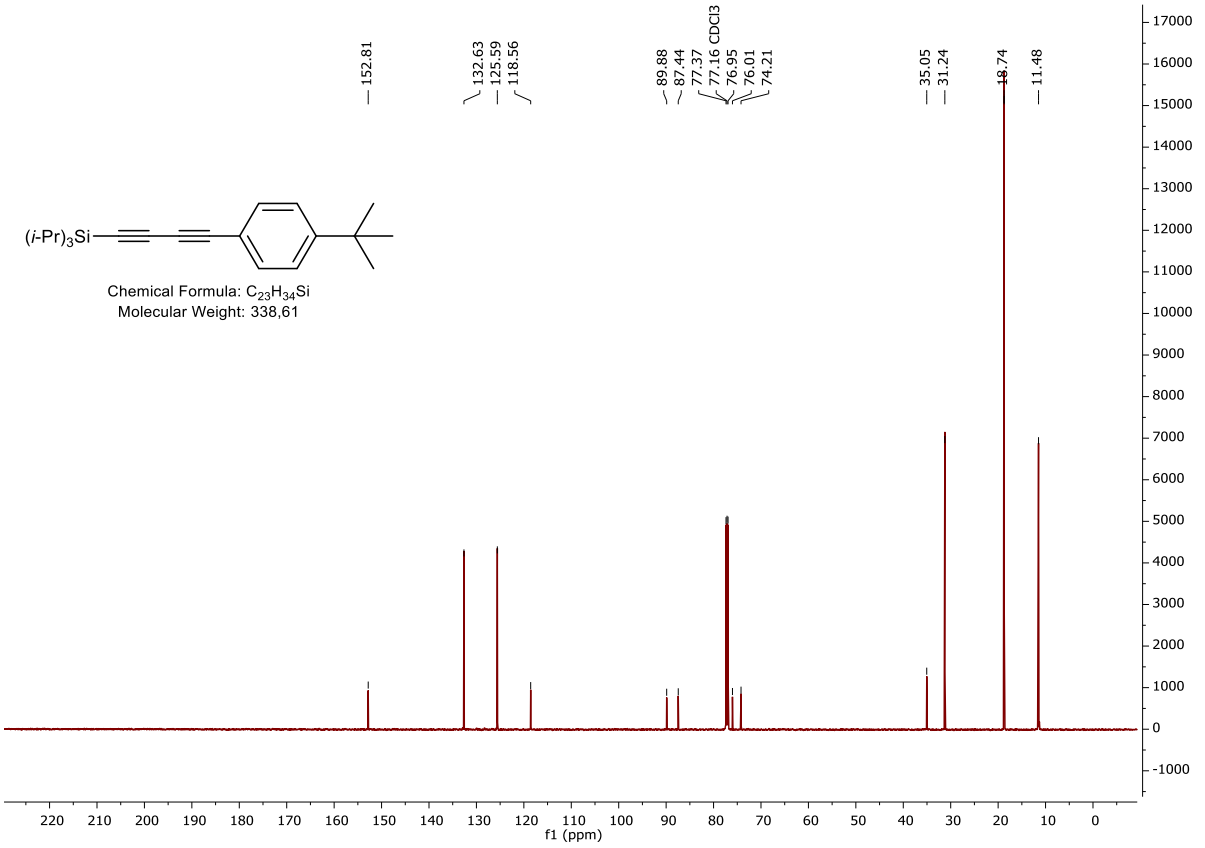


Figure S32. ^{13}C NMR spectrum of **2h**.

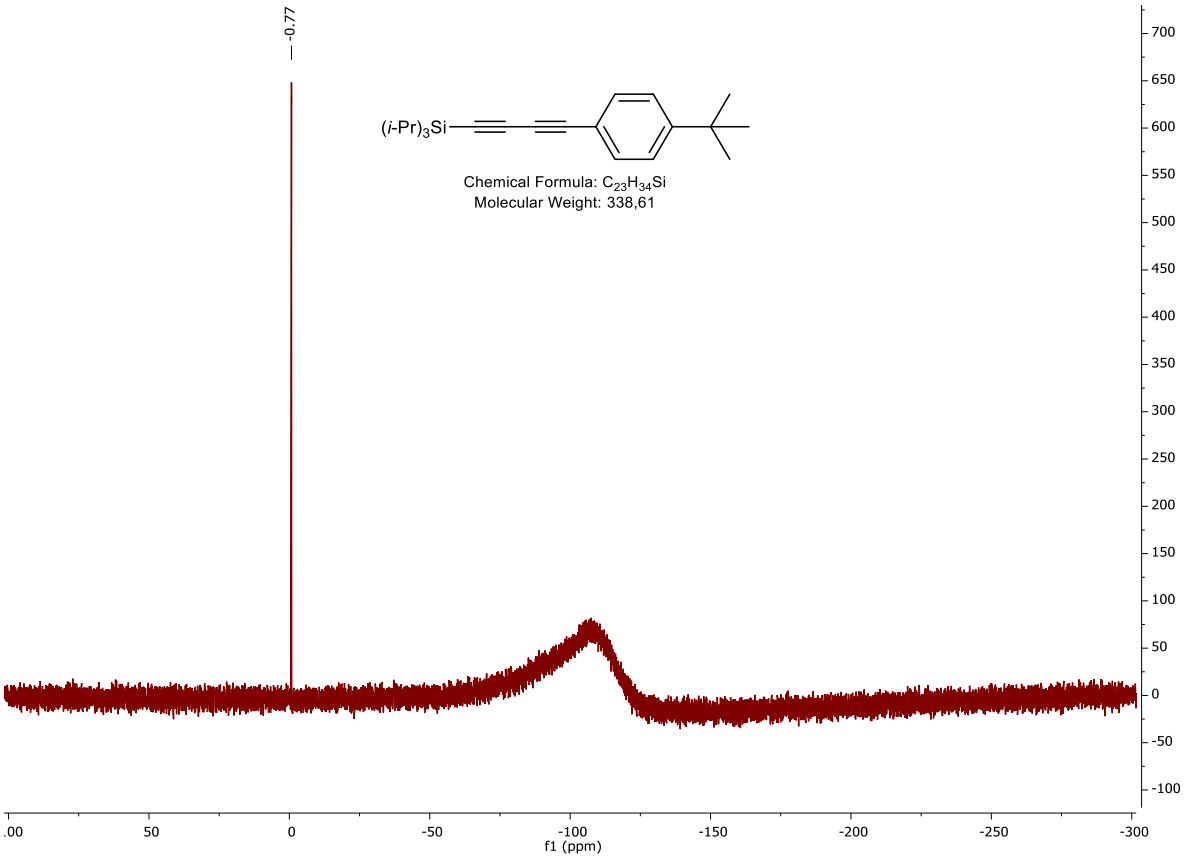


Figure S33. ^{29}Si NMR spectrum of **2h**.

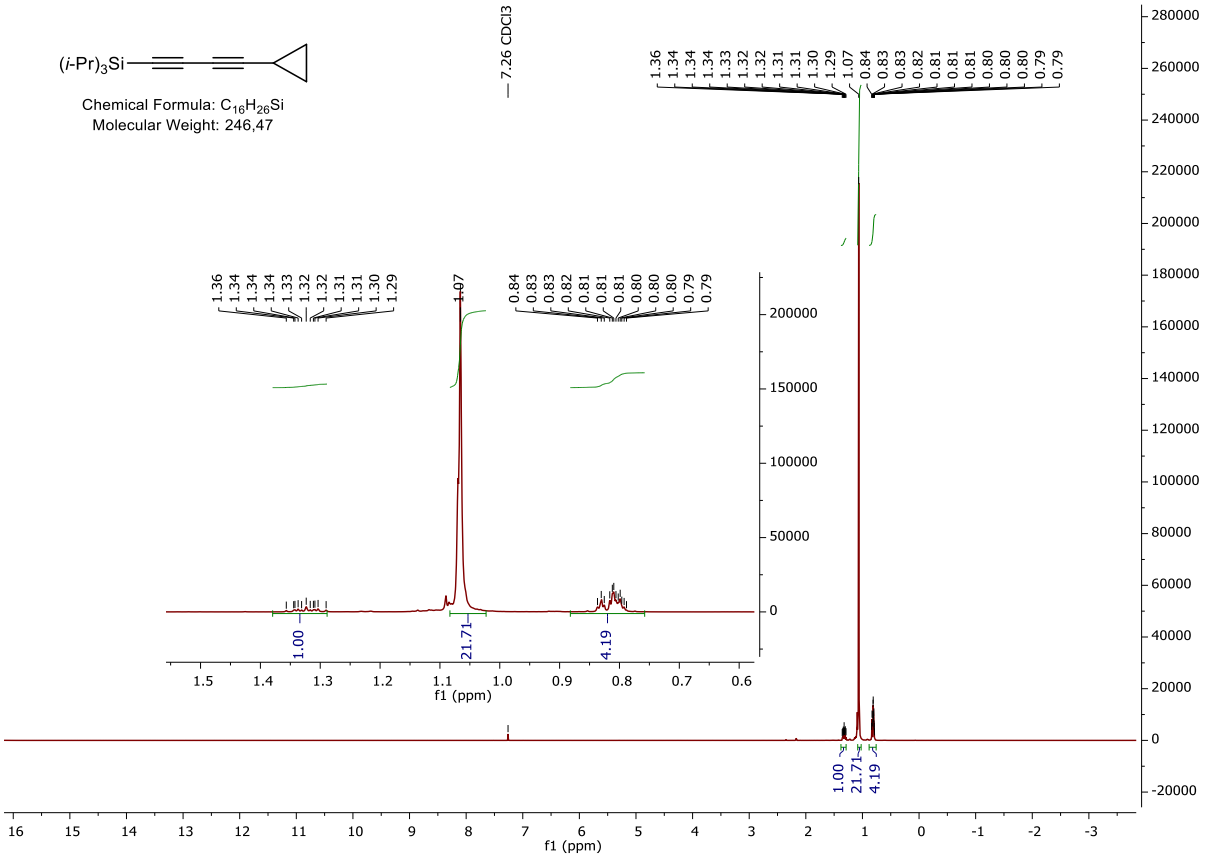


Figure S34. ^{1}H NMR spectrum of **2i**.

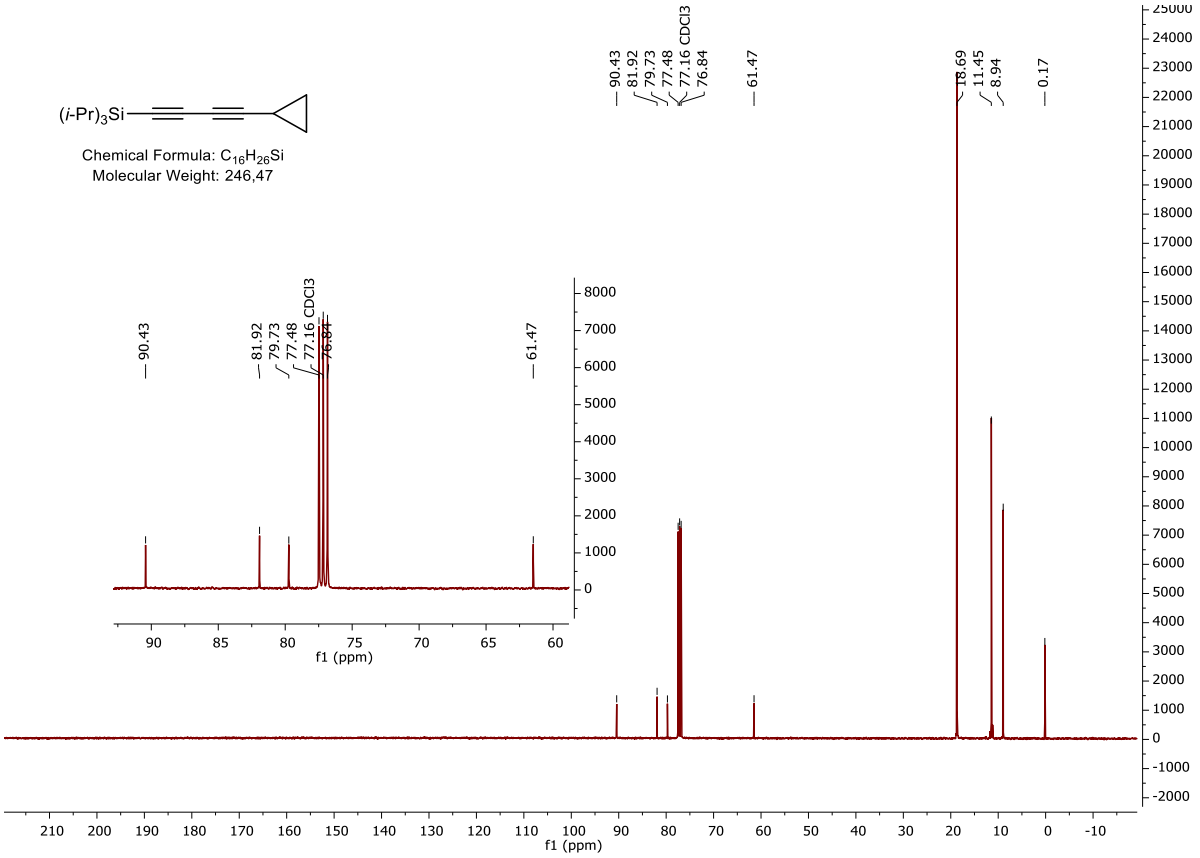


Figure S35. ^{11}C NMR spectrum of **2i**.

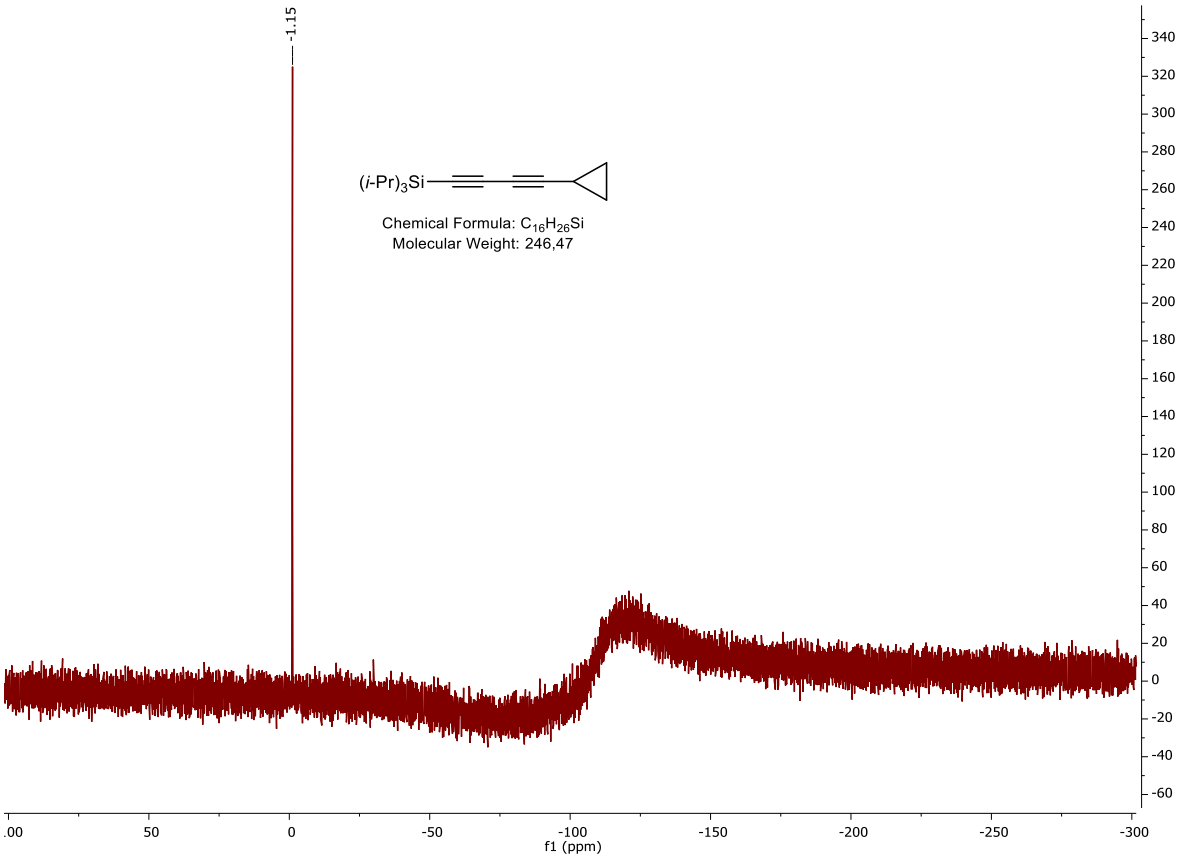


Figure S36. ^{29}Si NMR spectrum of **2i**.

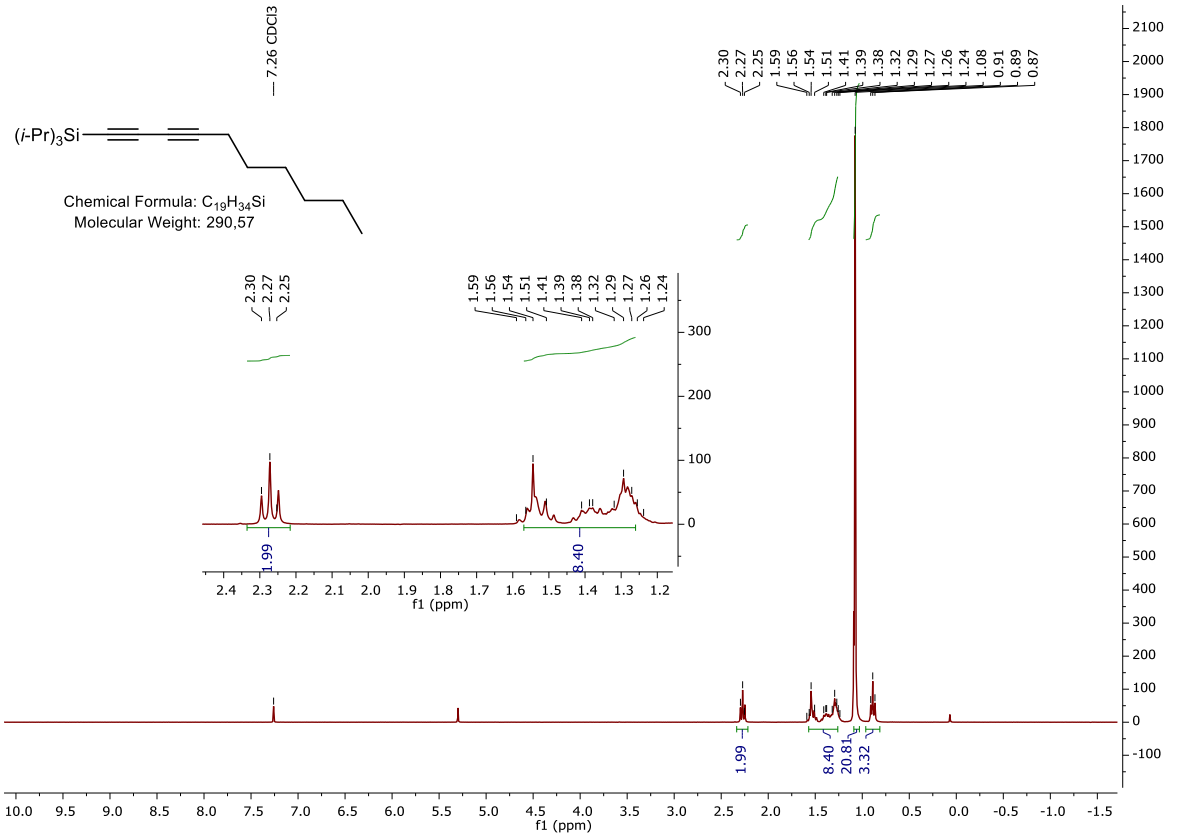


Figure S37. ^{1}H NMR spectrum of **2j**.

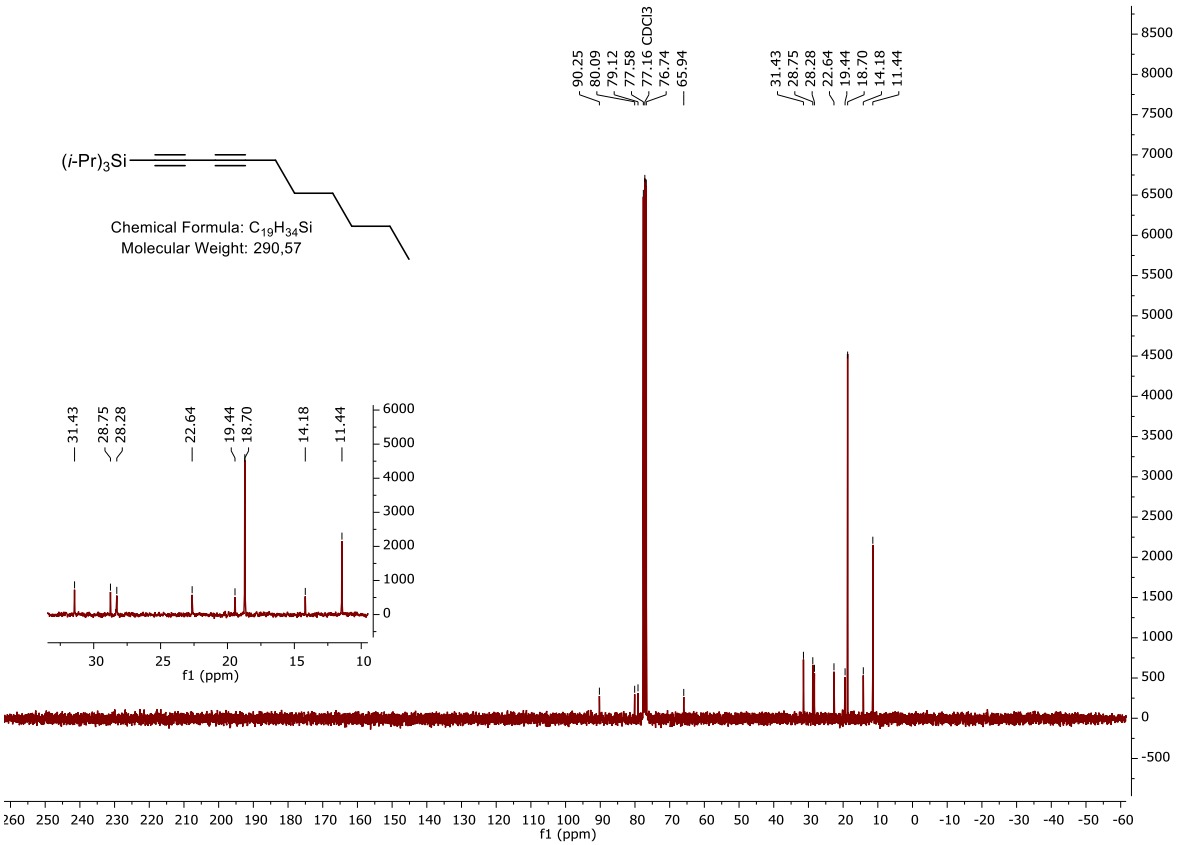


Figure S38. ^{13}C NMR spectrum of **2j**.

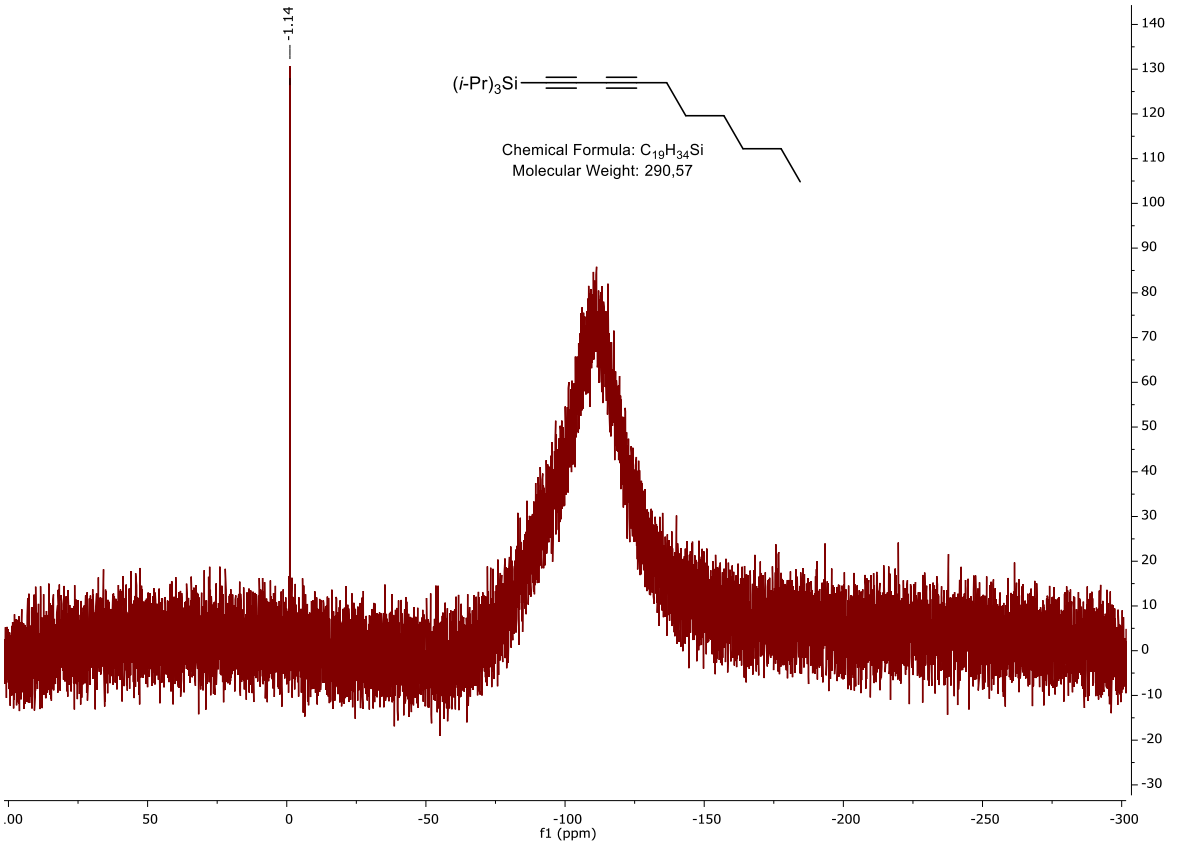


Figure S39. ^{29}Si NMR spectrum of **2j**.

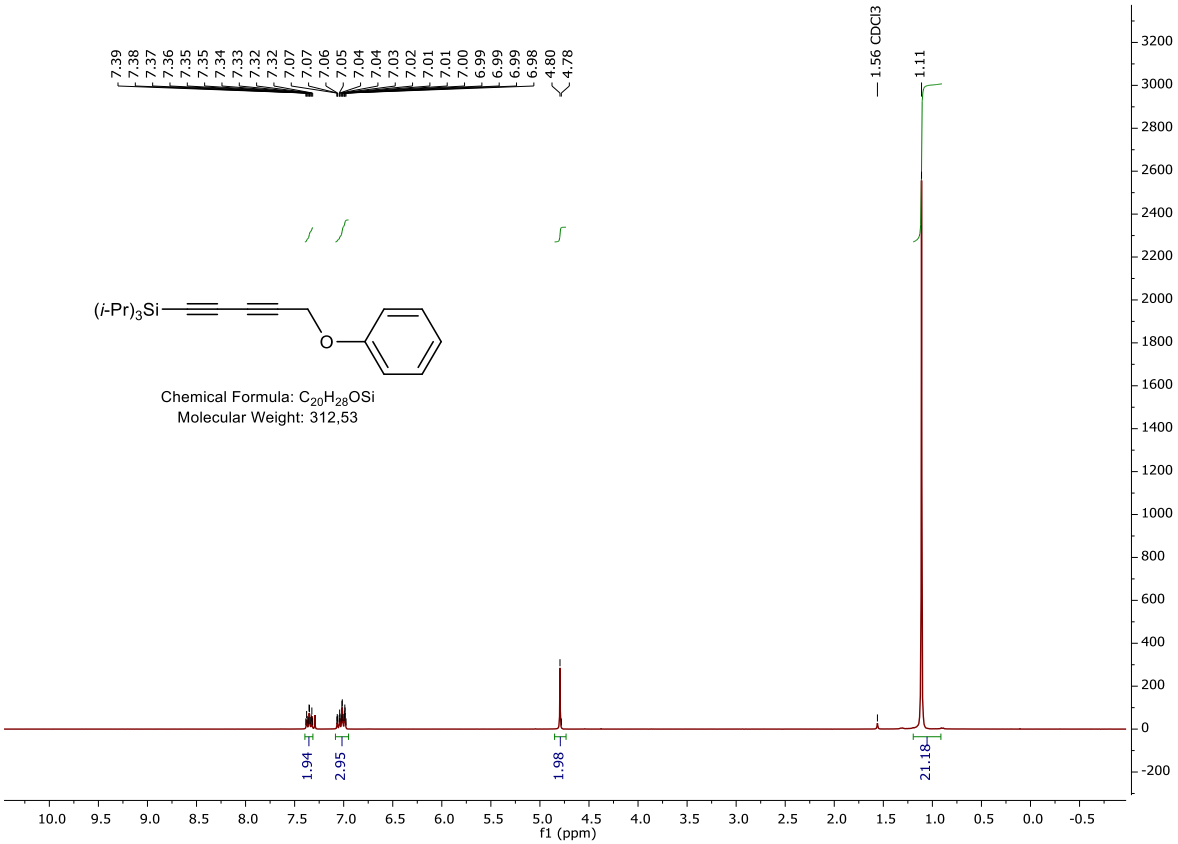


Figure S40. ^{1}H NMR spectrum of **2k**.

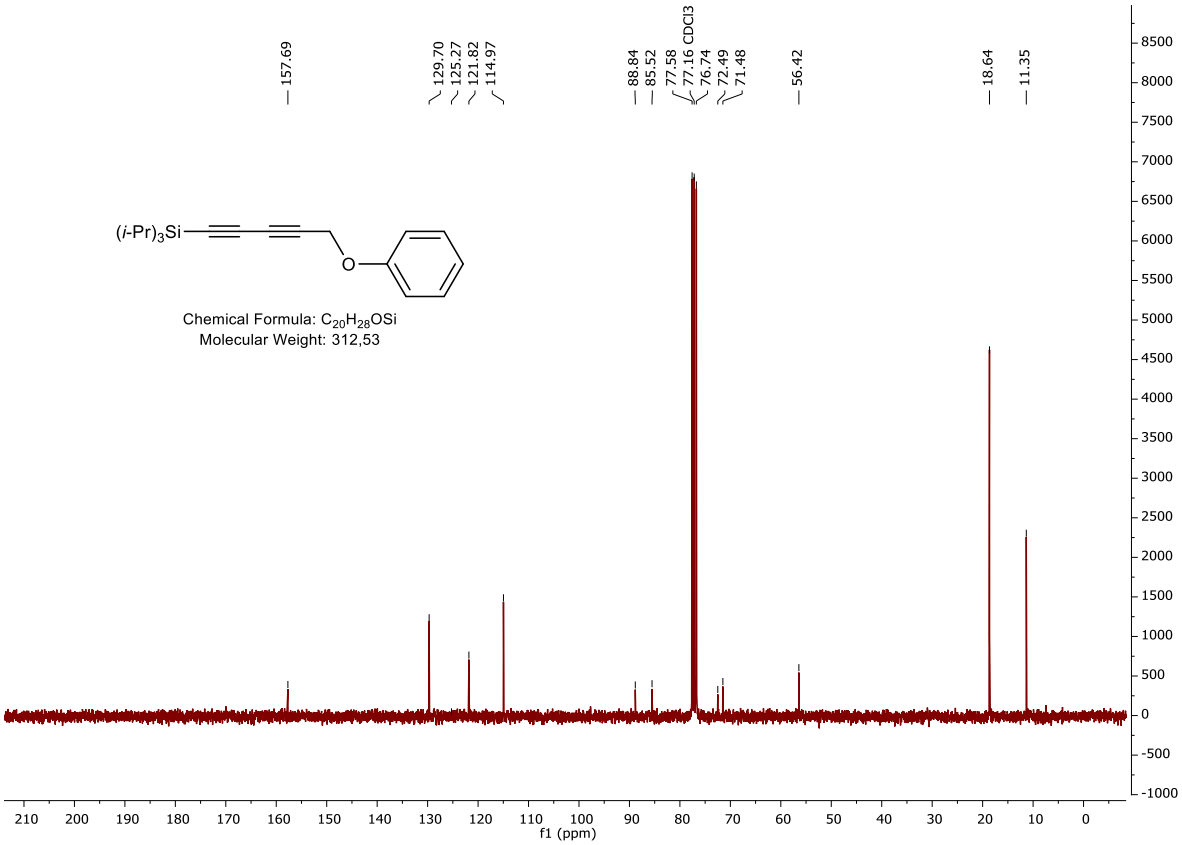


Figure S41. ^{13}C NMR spectrum of **2k**.

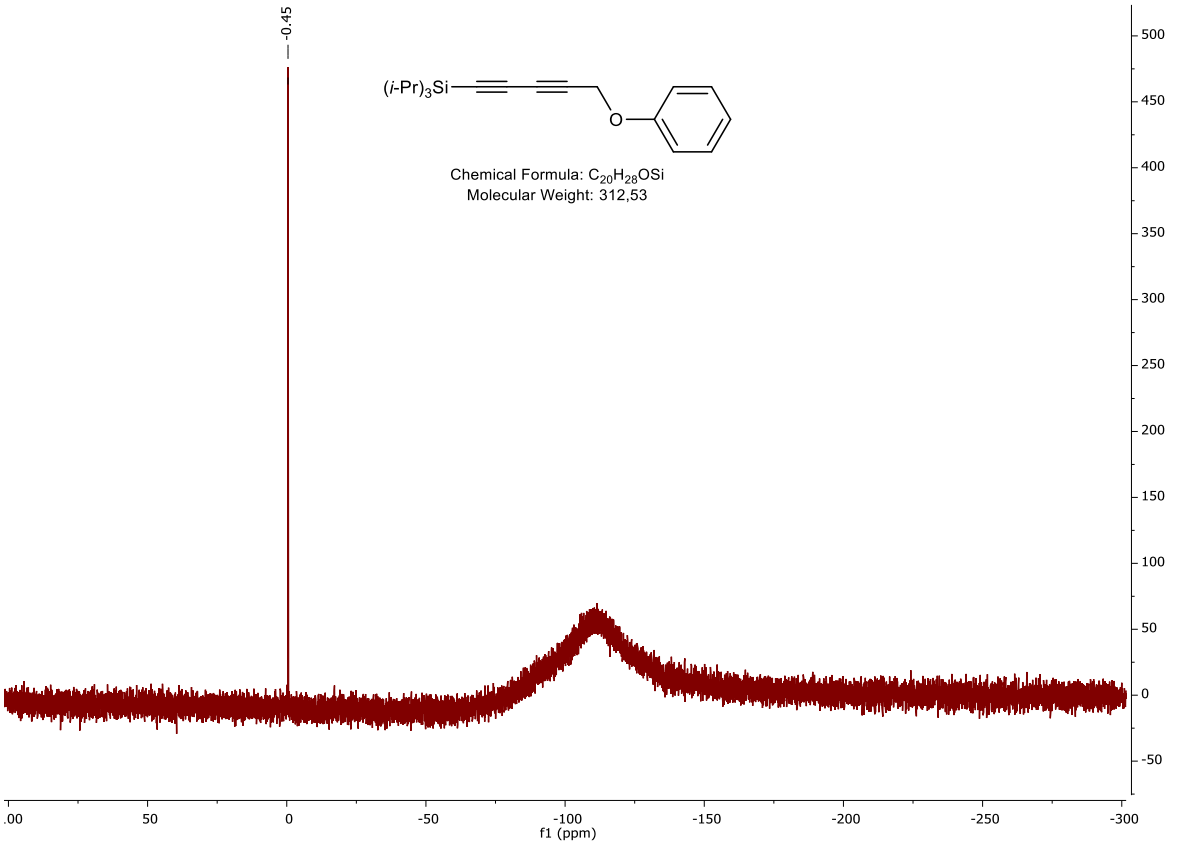


Figure S42. ^{29}Si NMR spectrum of **2k**.

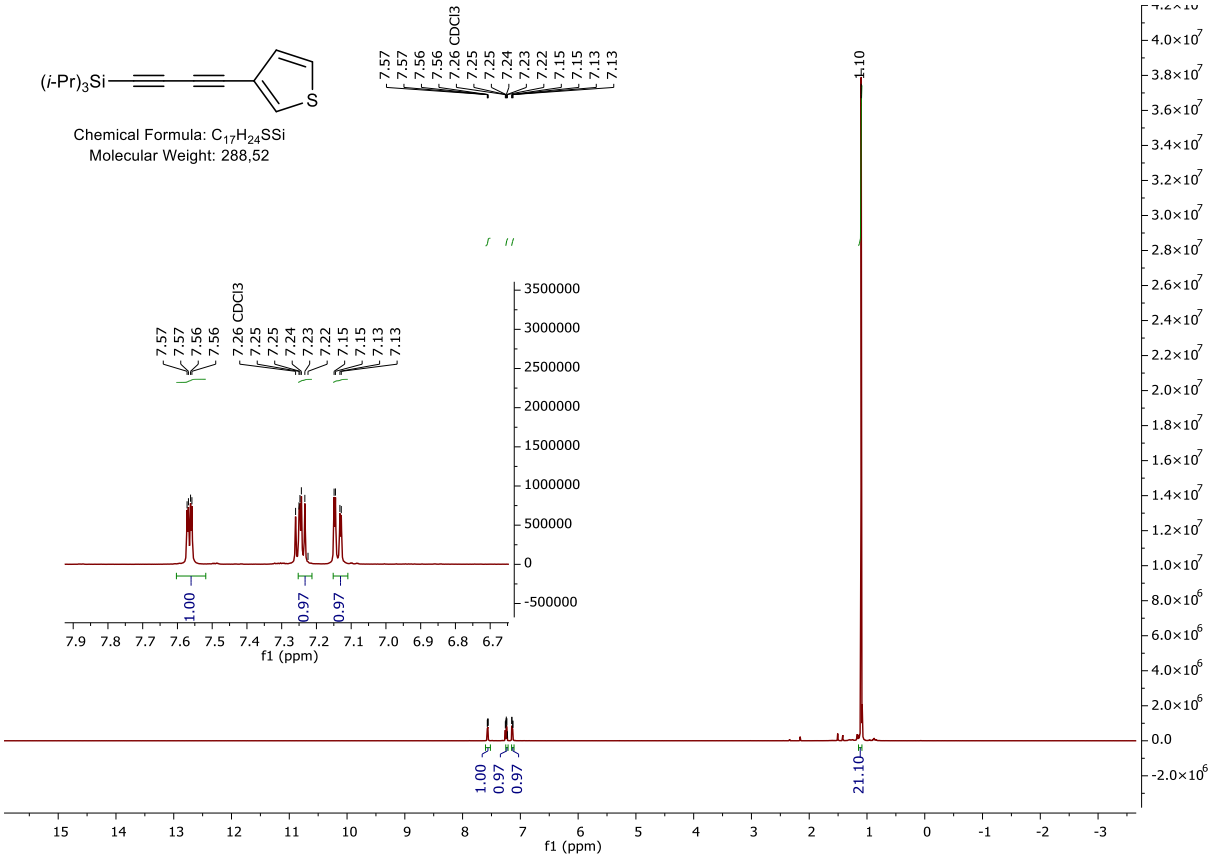


Figure S43. [1]H NMR spectrum of **2l**.

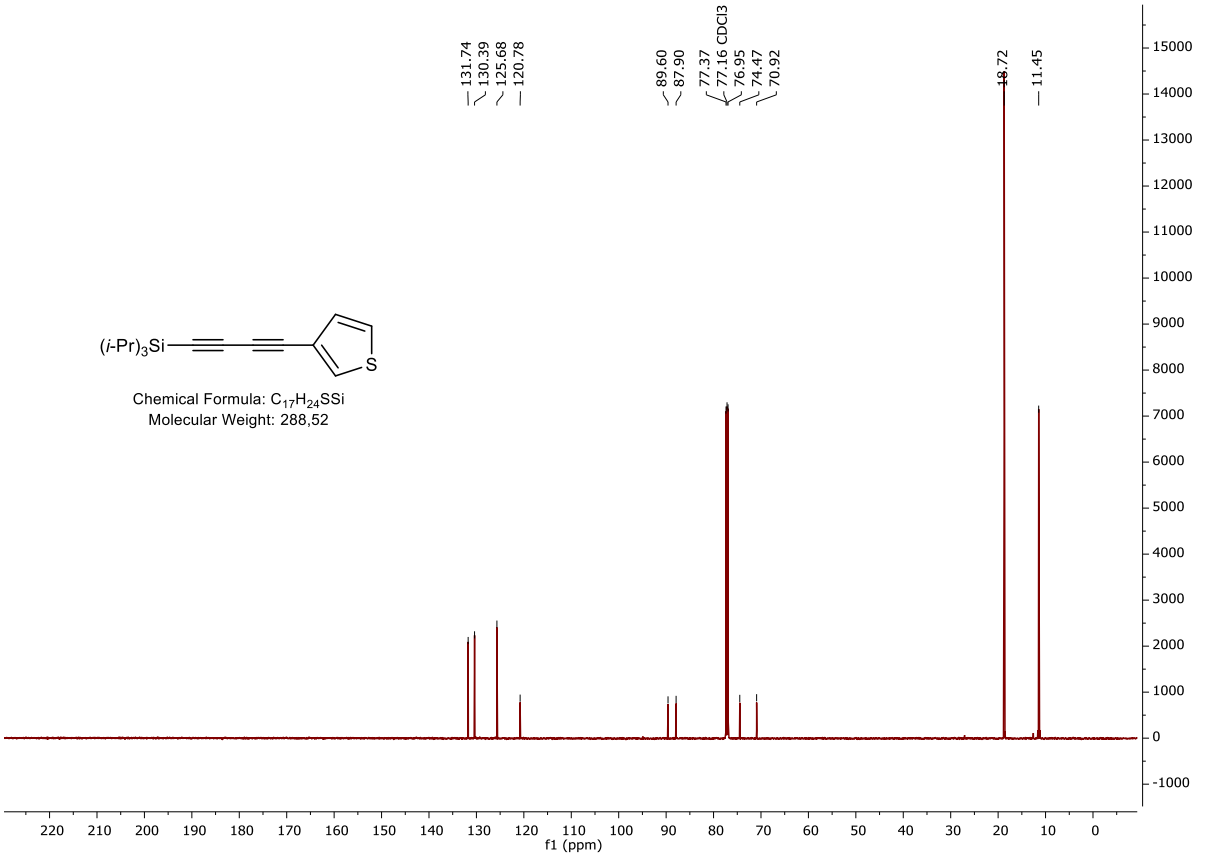


Figure S44. [13]C NMR spectrum of **2l**.

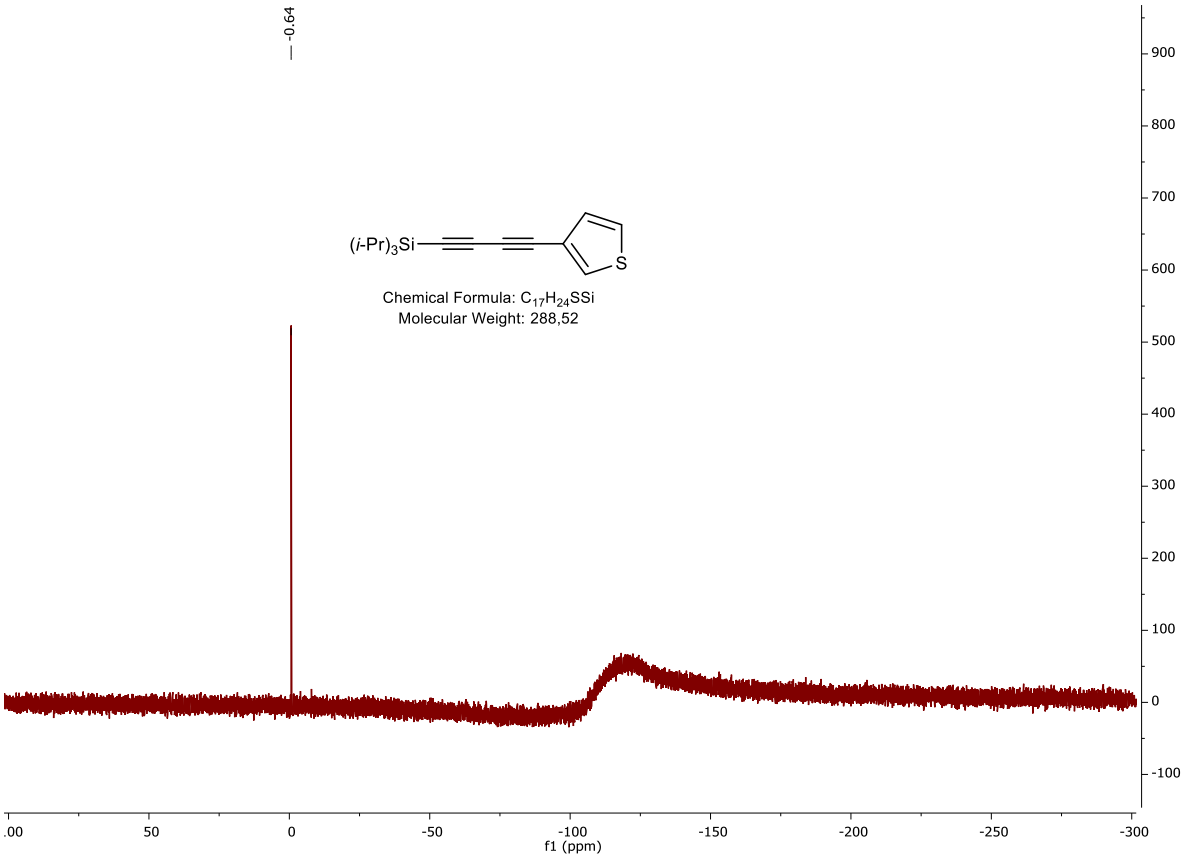


Figure S45. ^{29}Si NMR spectrum of **2l**.

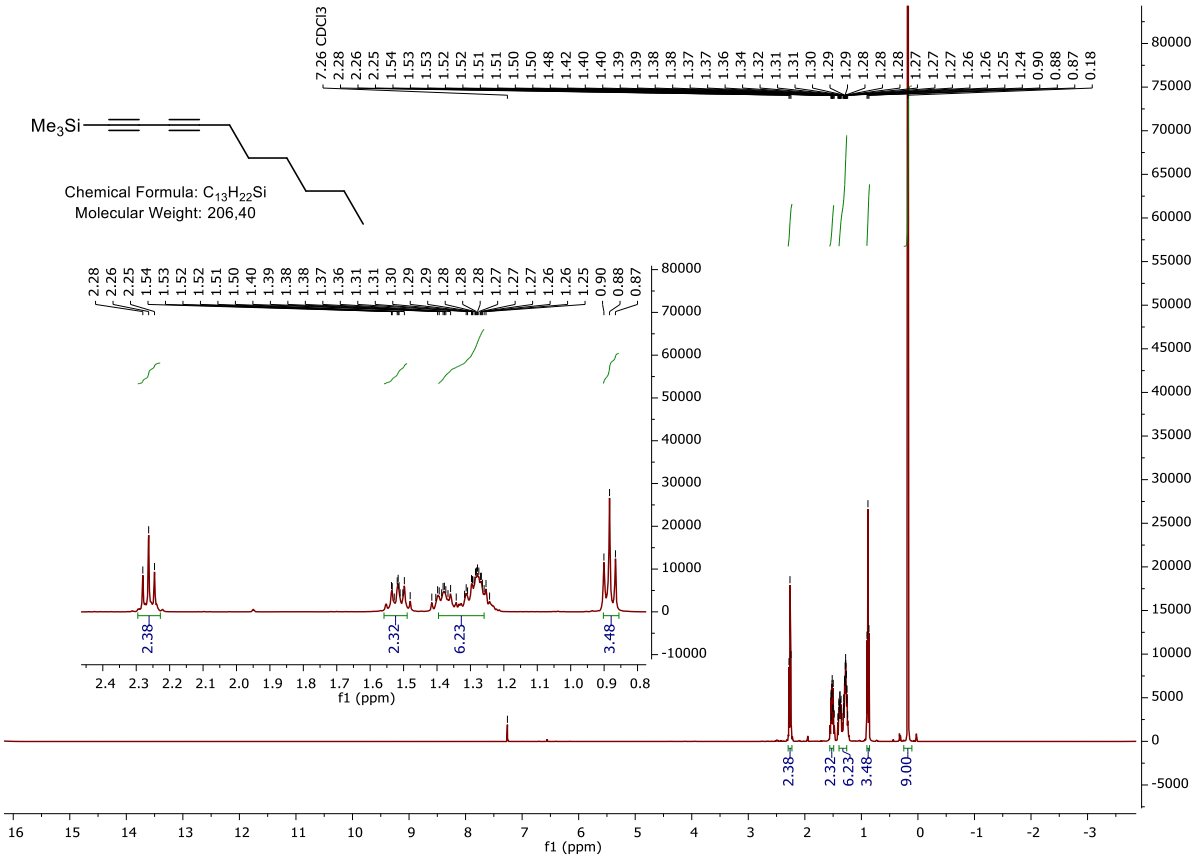


Figure S46. ^{1}H NMR spectrum of **2m**.

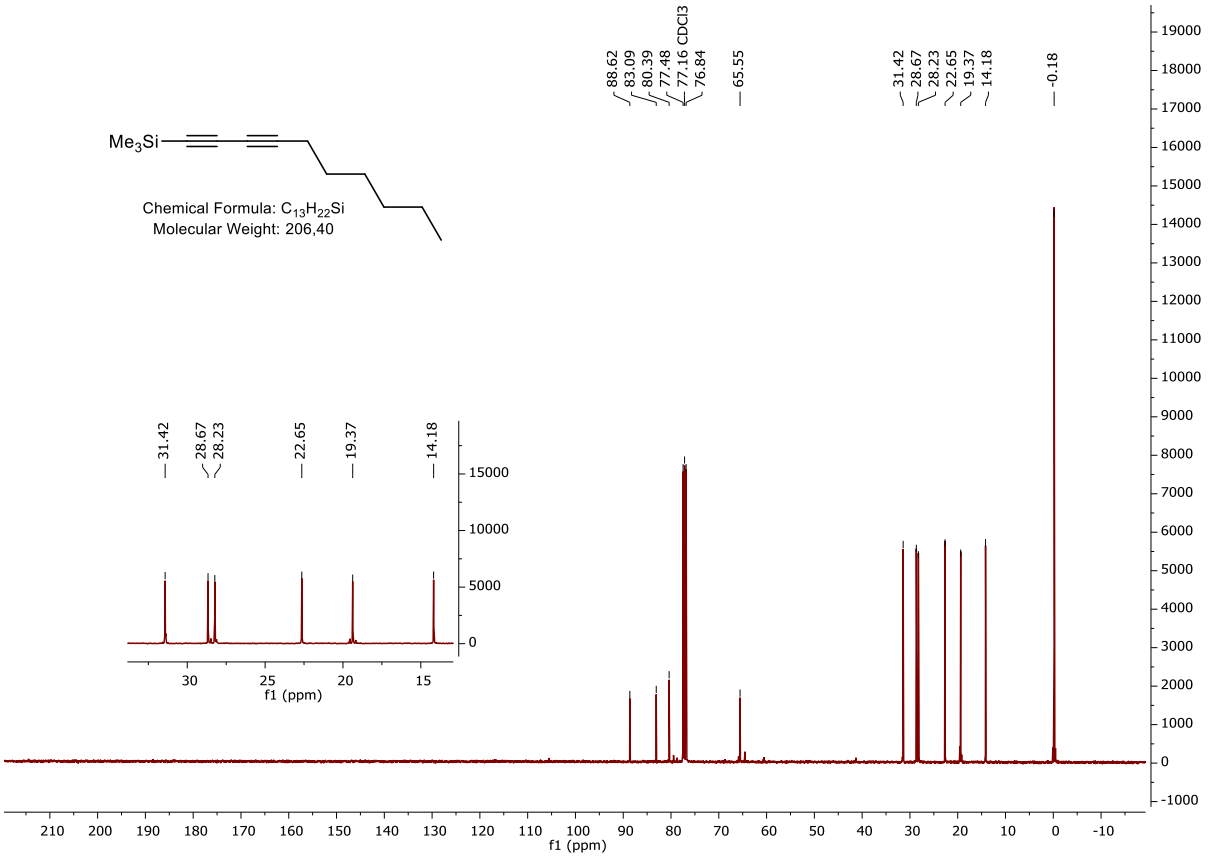


Figure S47. ^{13}C NMR spectrum of **2m**.

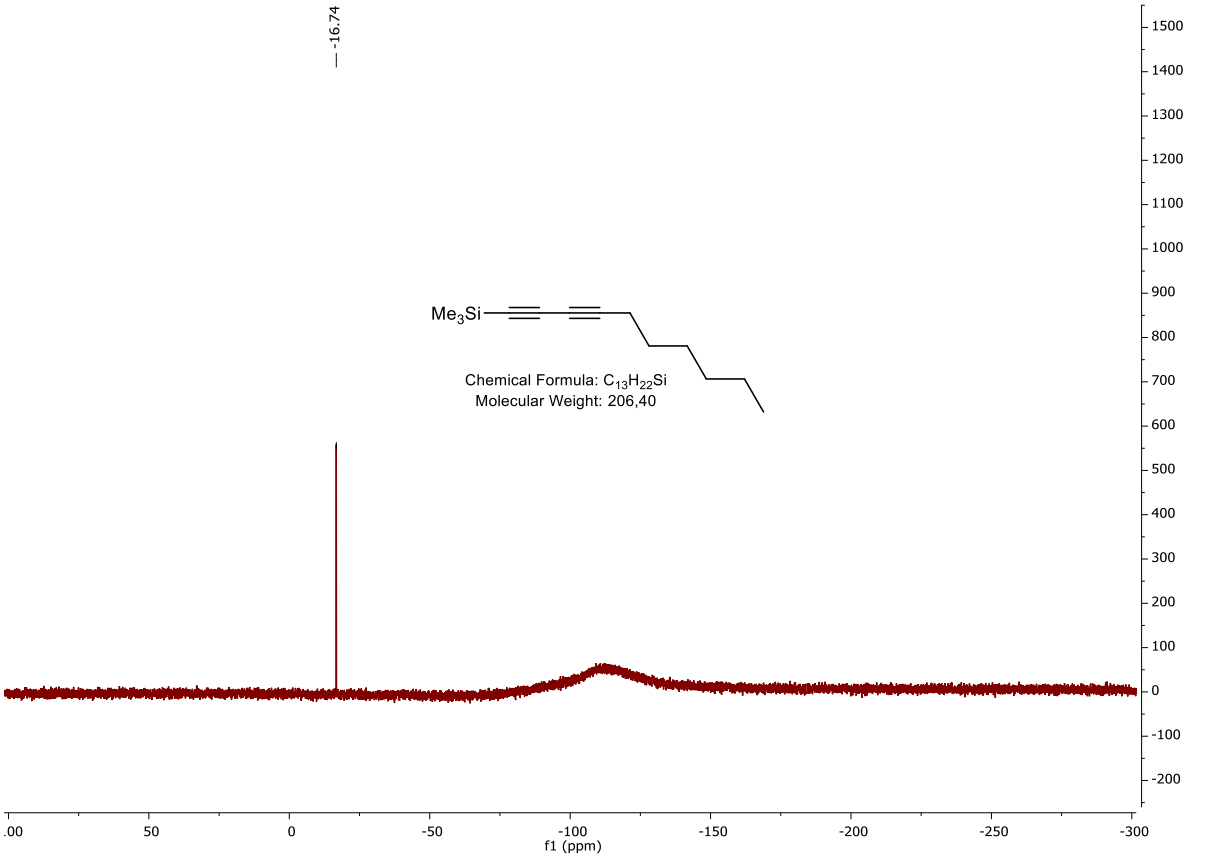


Figure S48. ^{29}Si NMR spectrum of **2m**.

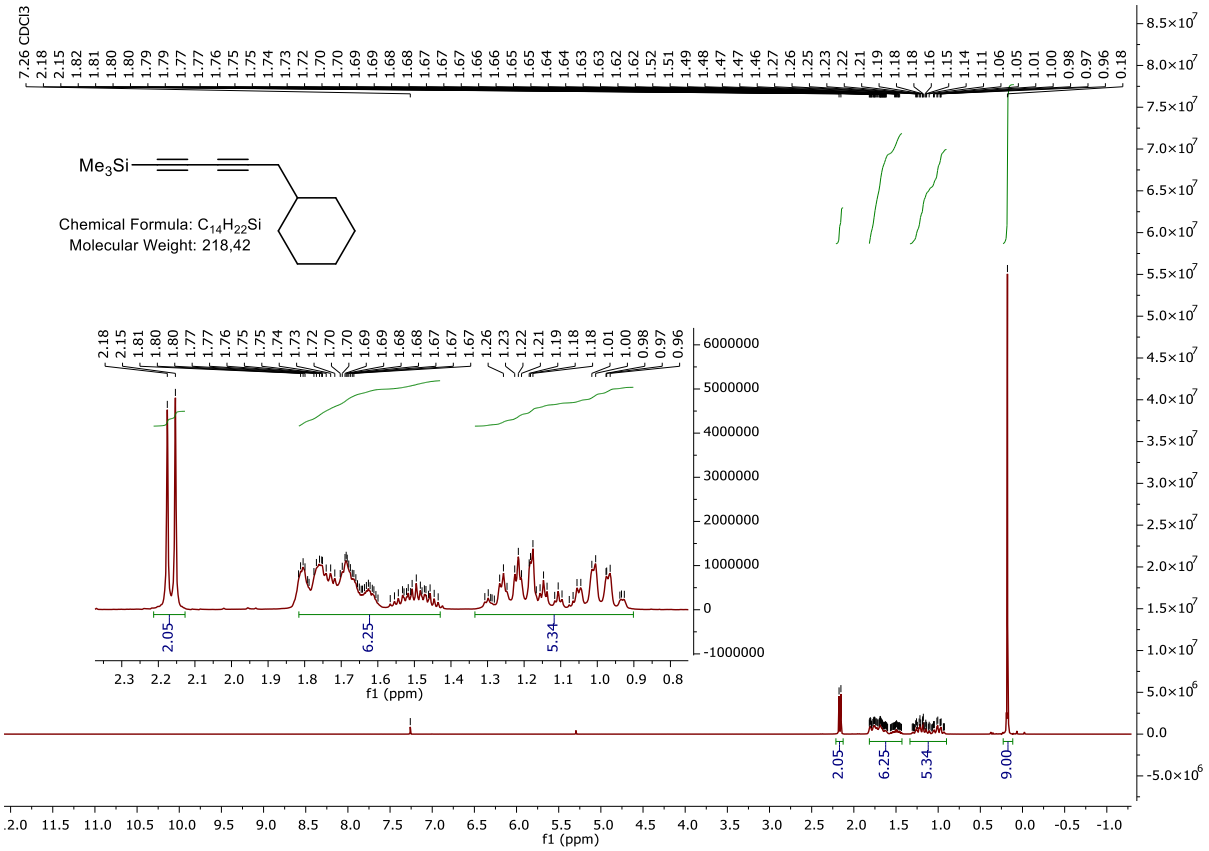


Figure S49. ^{1}H NMR spectrum of **2n**.

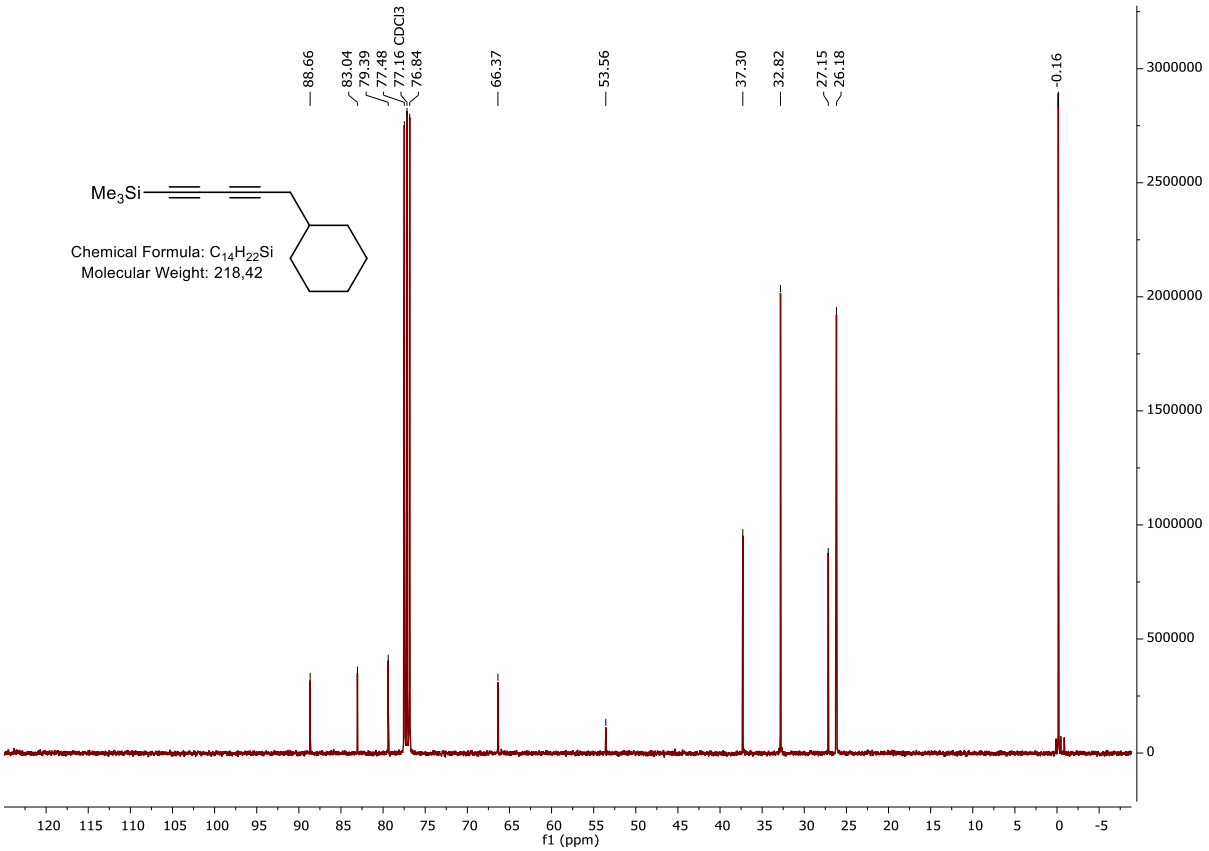


Figure S50. ^{13}C NMR spectrum of **2n**.

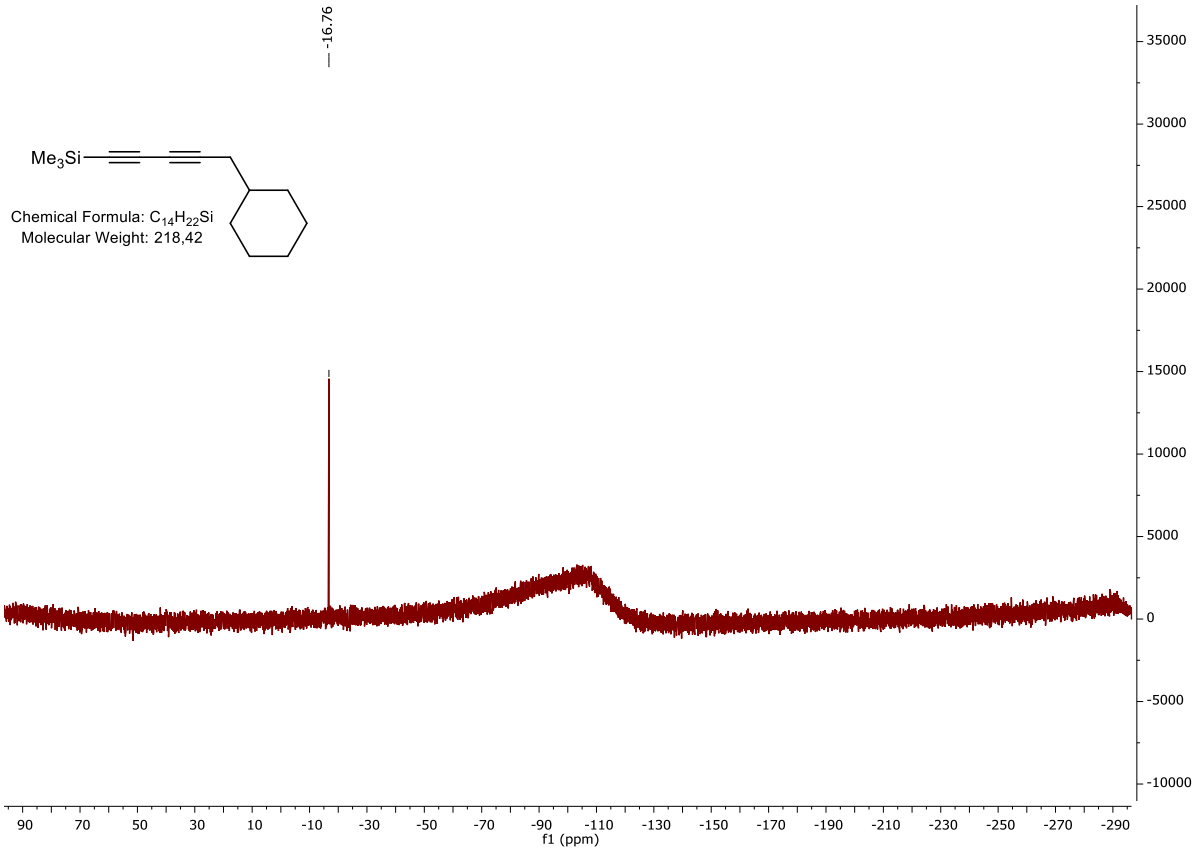


Figure S51. ^{29}Si NMR spectrum of **2n**.

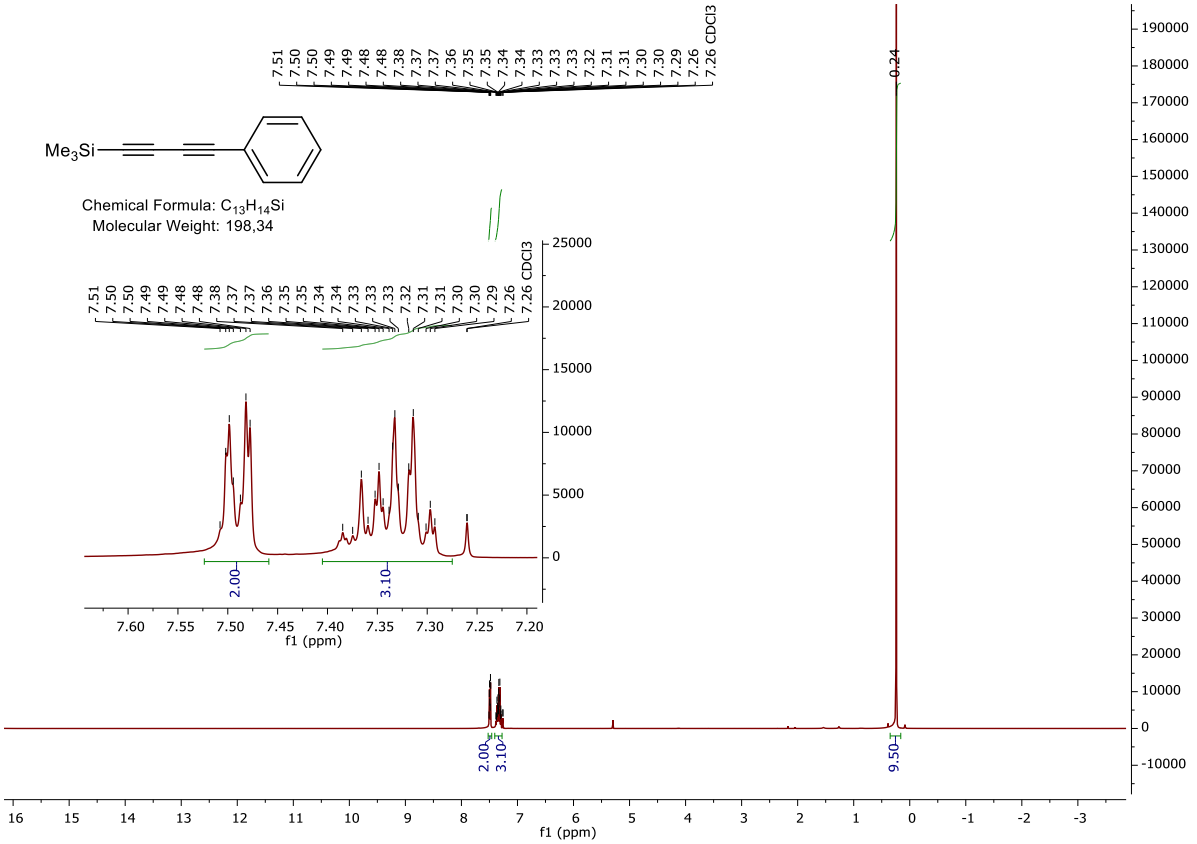


Figure S52. ^{1}H NMR spectrum of **2o**.

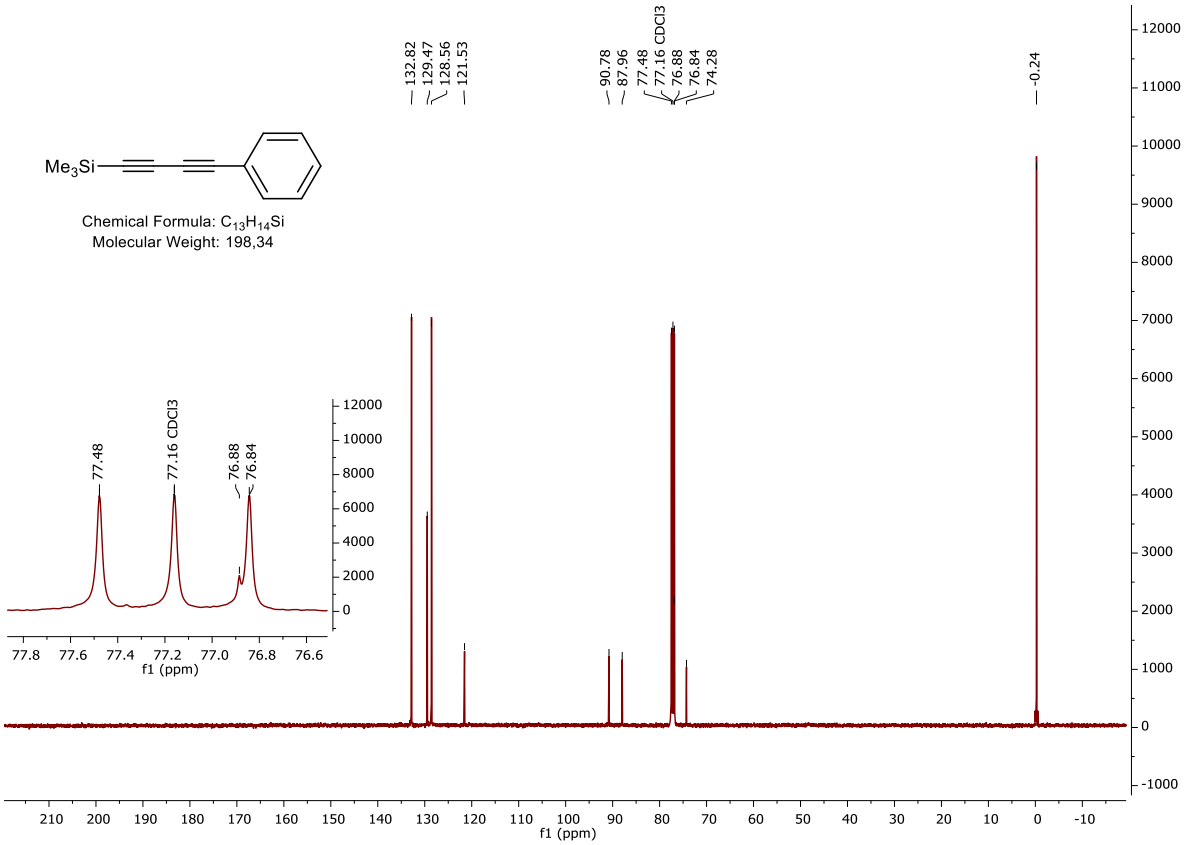


Figure S53. ^{13}C NMR spectrum of **2o**.

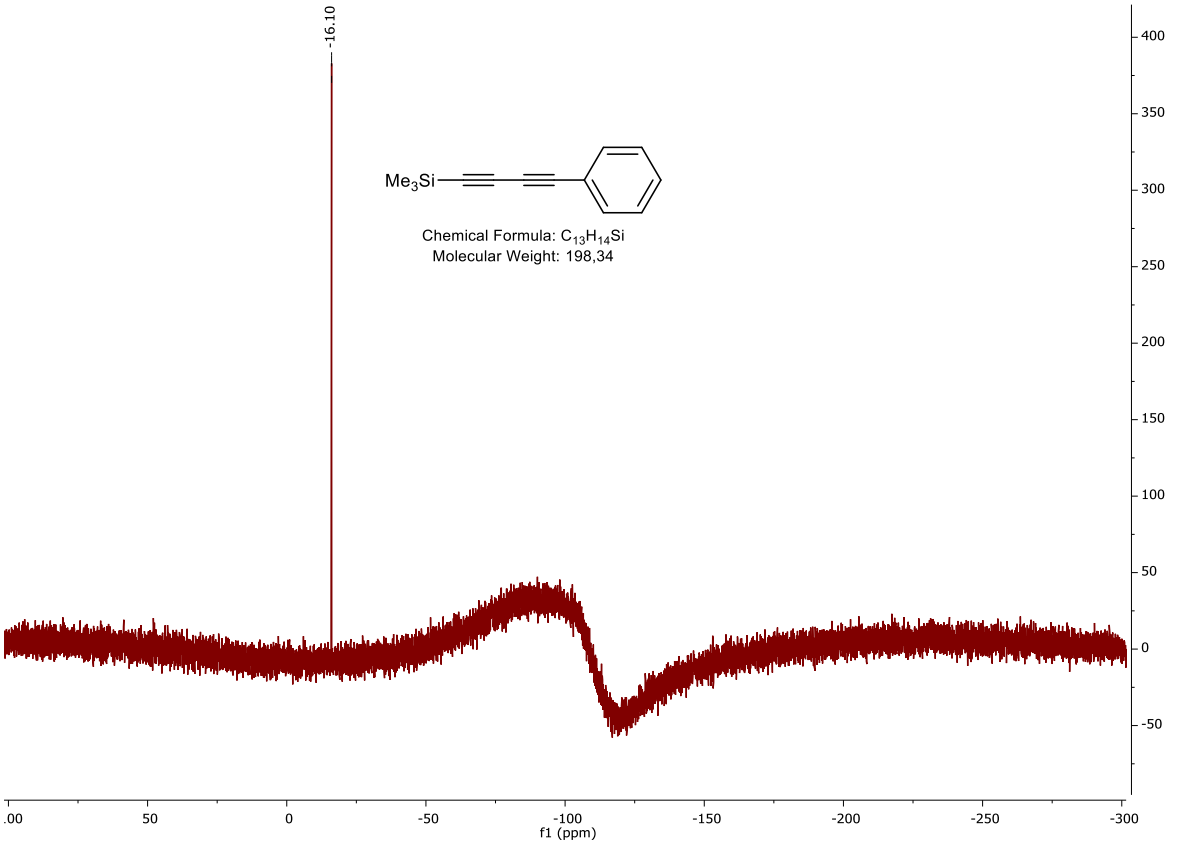


Figure S54. ^{29}Si NMR spectrum of **2o**.

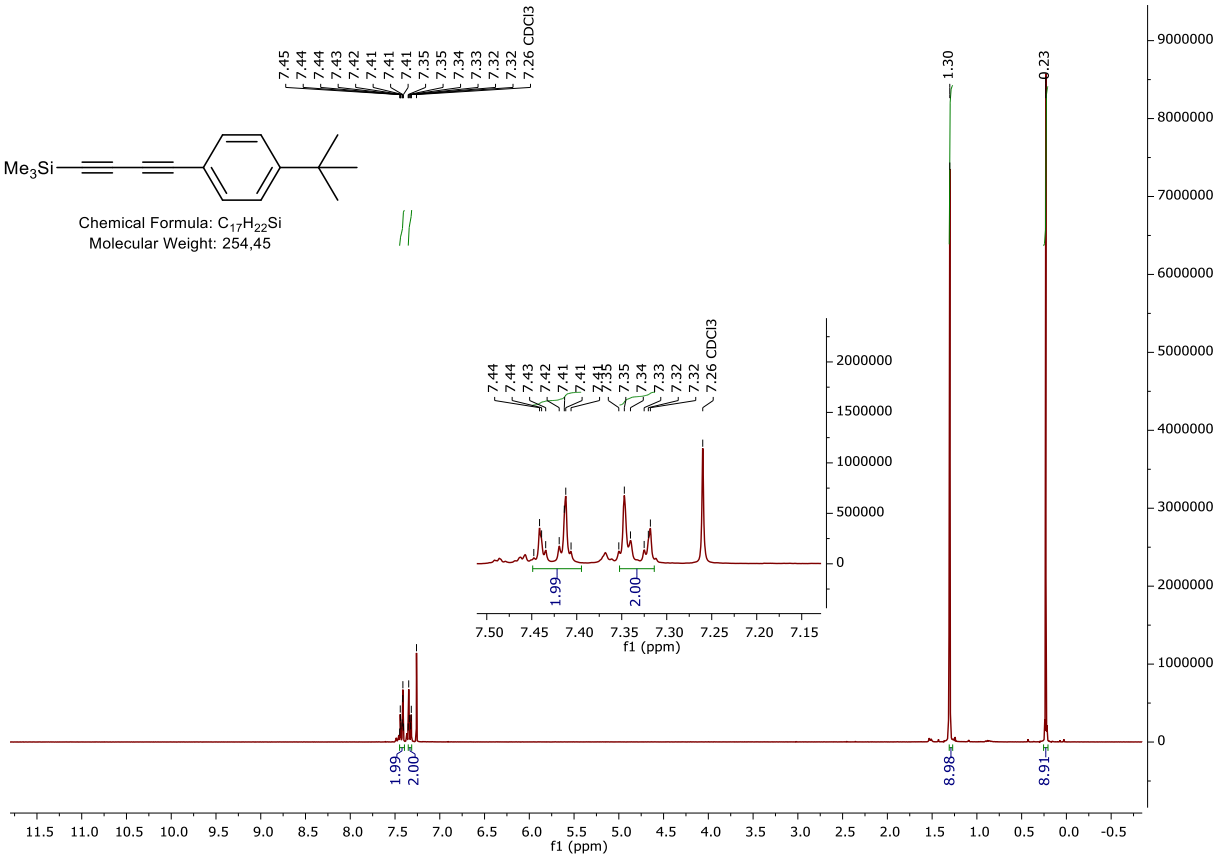


Figure S55. ^{1}H NMR spectrum of **2p**.

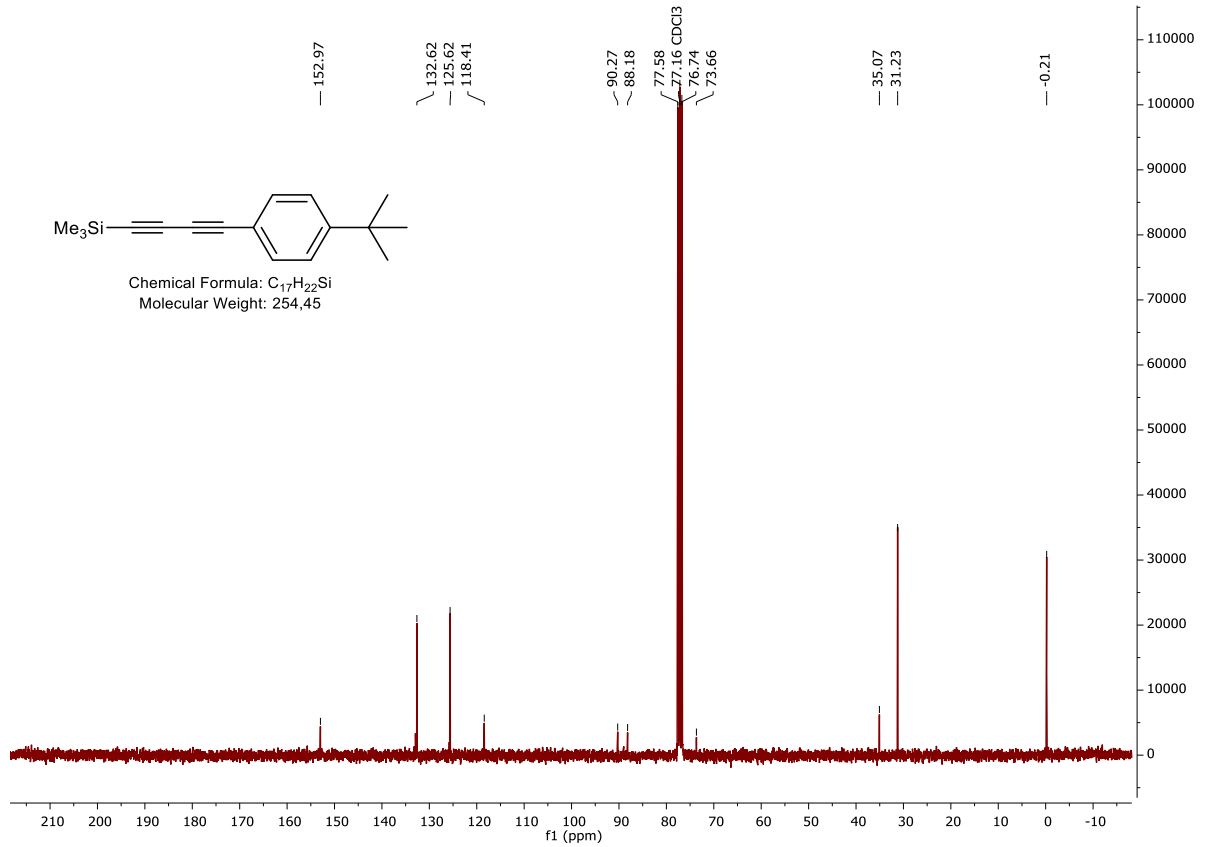


Figure S56. ^{13}C NMR spectrum of **2p**.

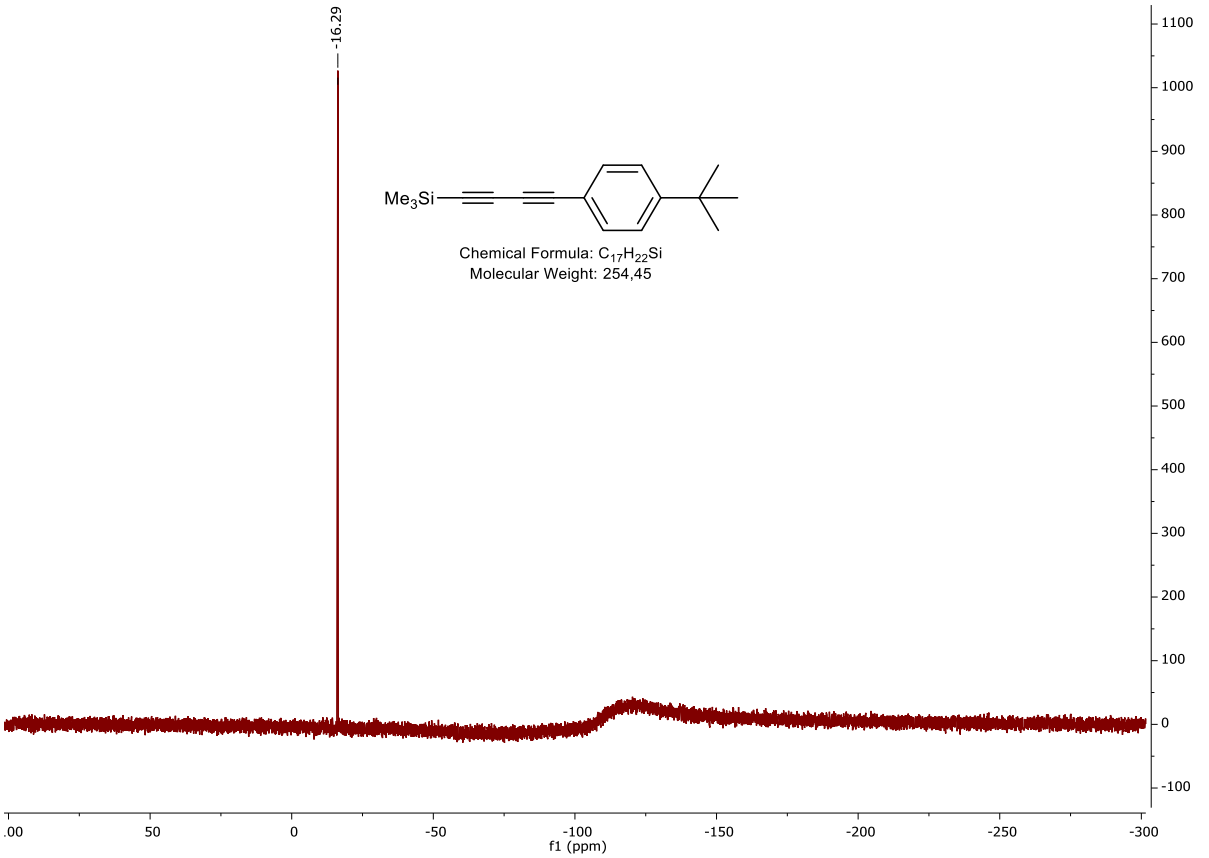


Figure S57. ^{29}Si NMR spectrum of **2p**.

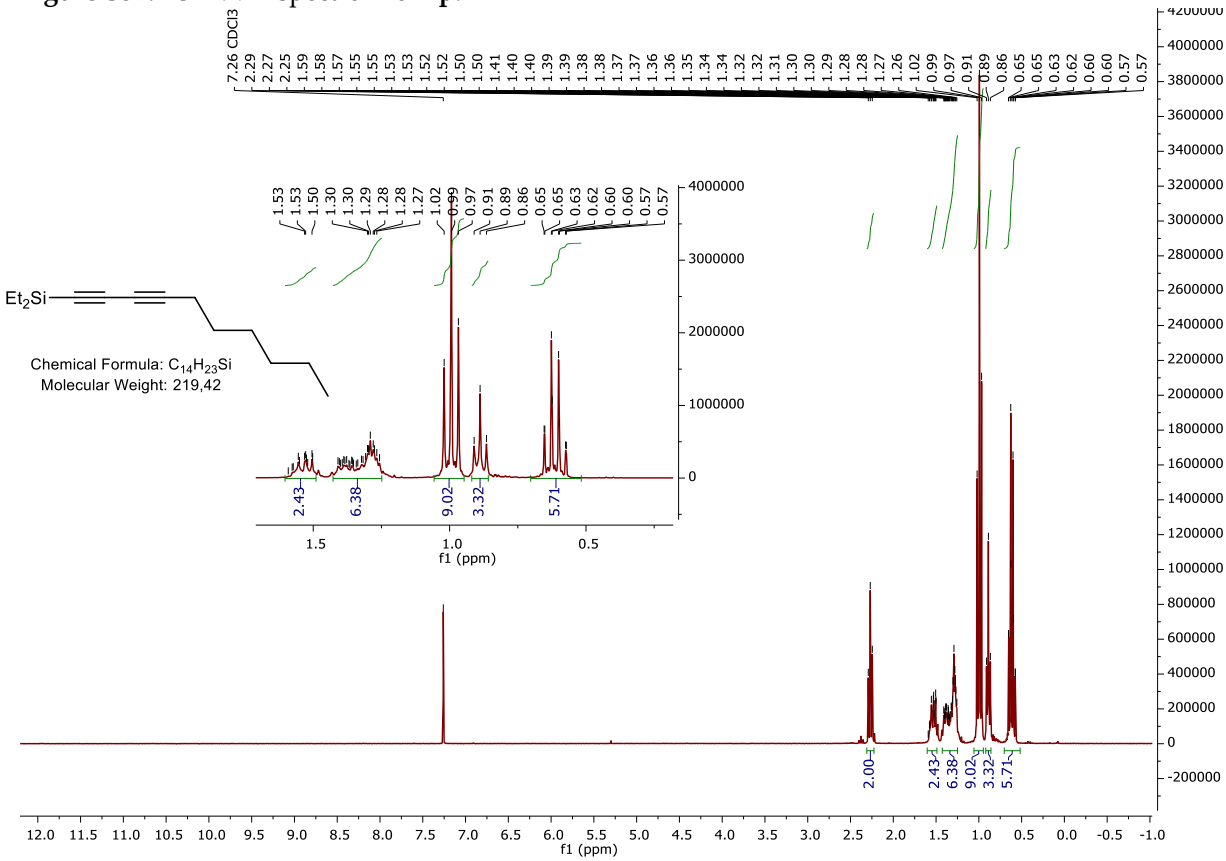


Figure S58. ^{1}H NMR spectrum of **2q**.

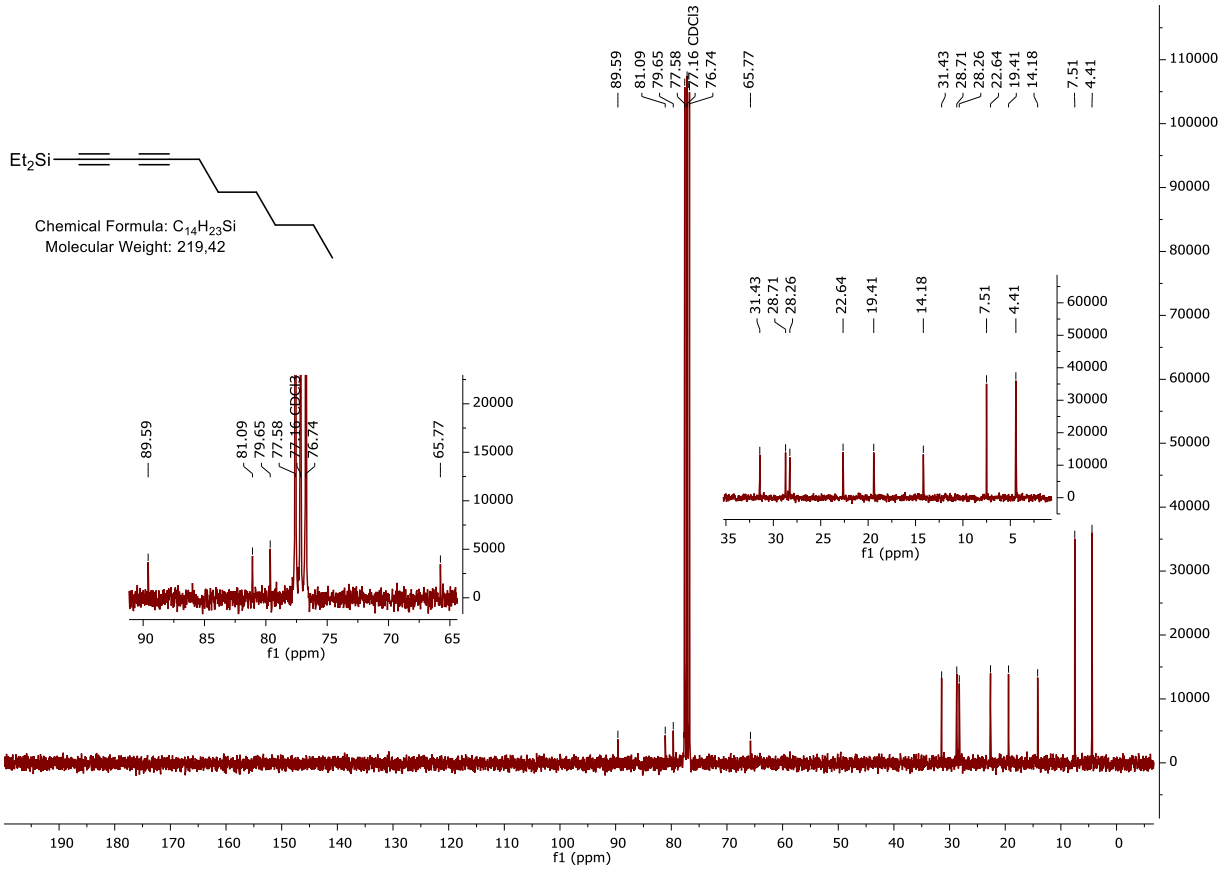


Figure S59. ^{13}C NMR spectrum of **2q**.

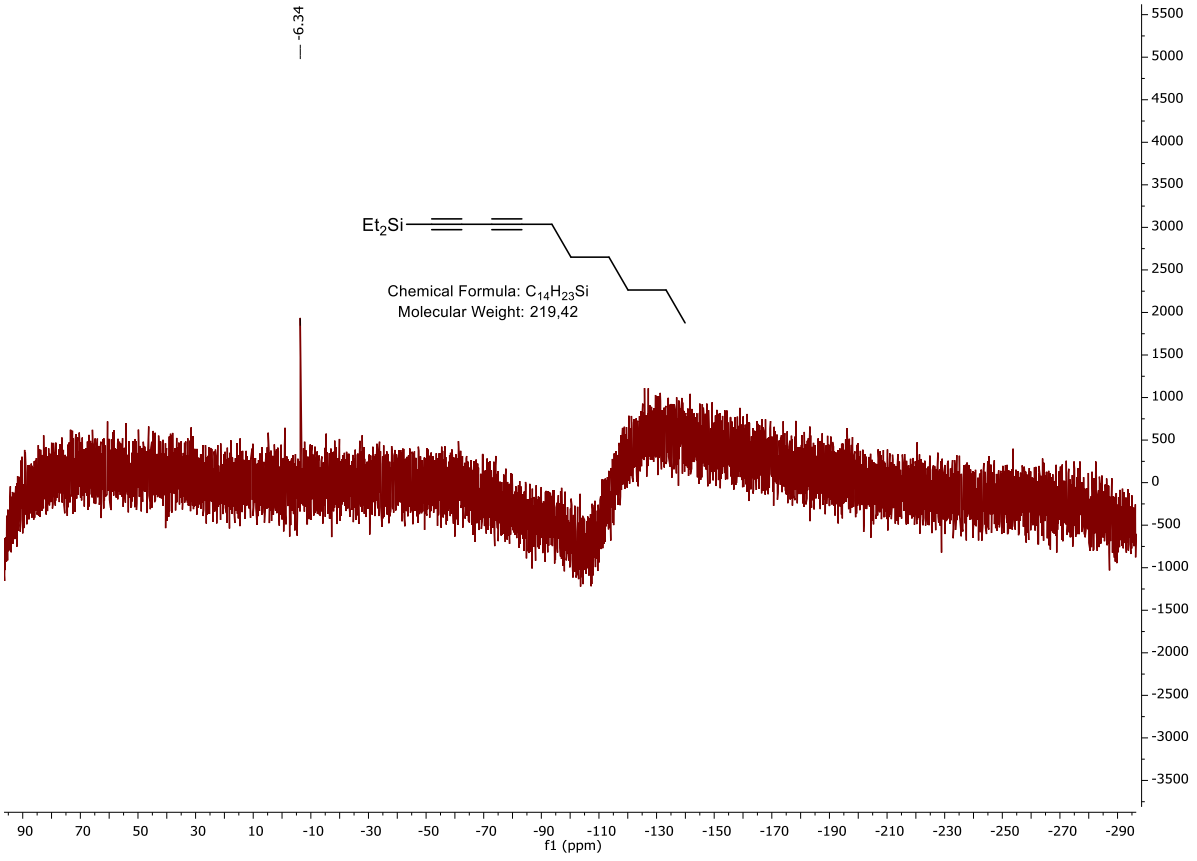


Figure S60. ^{29}Si NMR spectrum of **2q**.

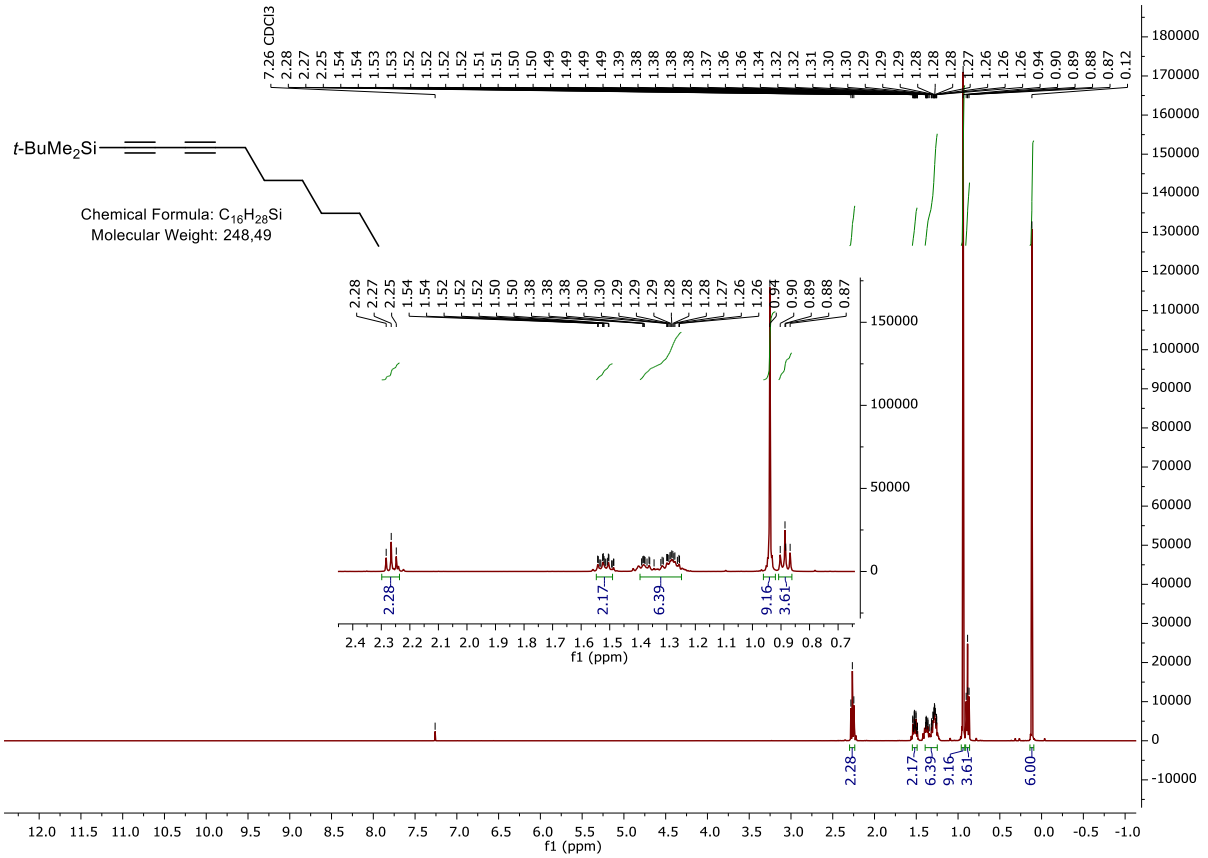


Figure S61. ^{1}H NMR spectrum of **2r**.

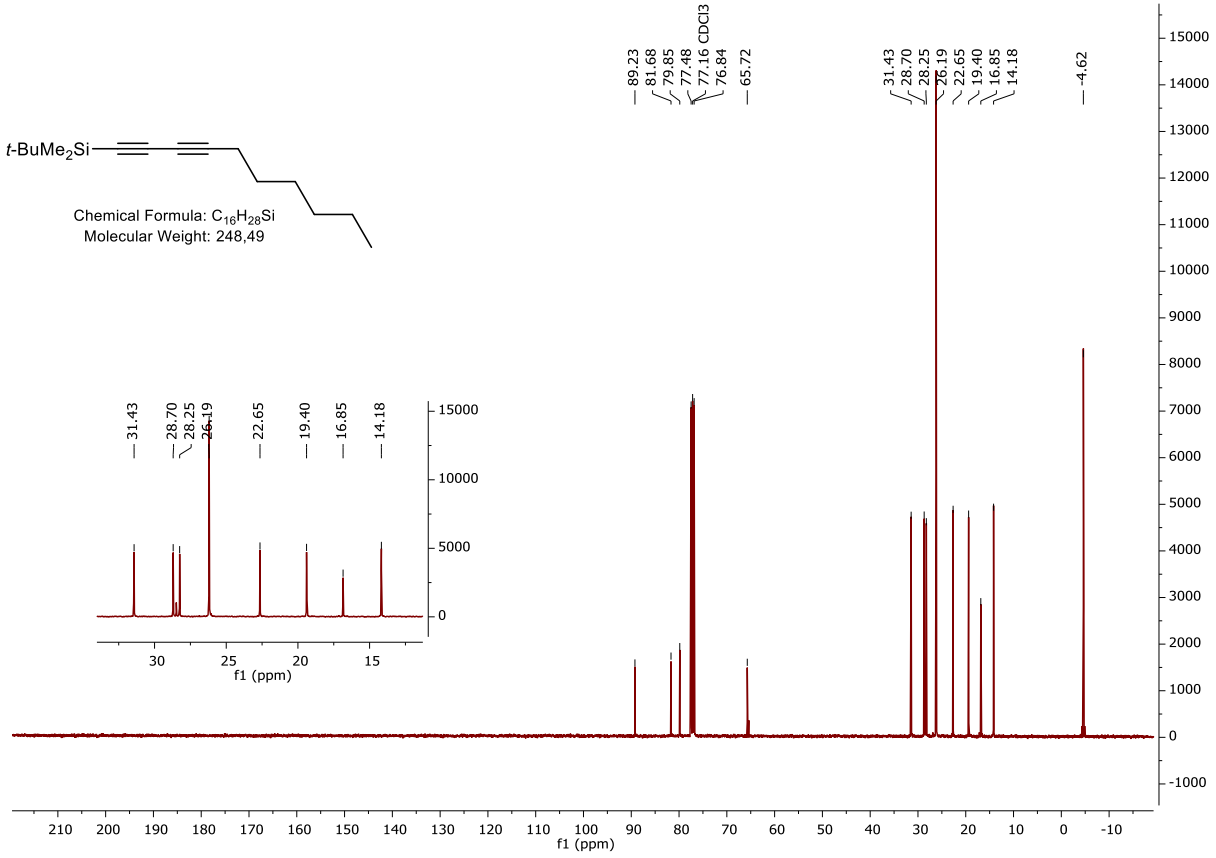


Figure S62. ^{13}C NMR spectrum of **2r**.

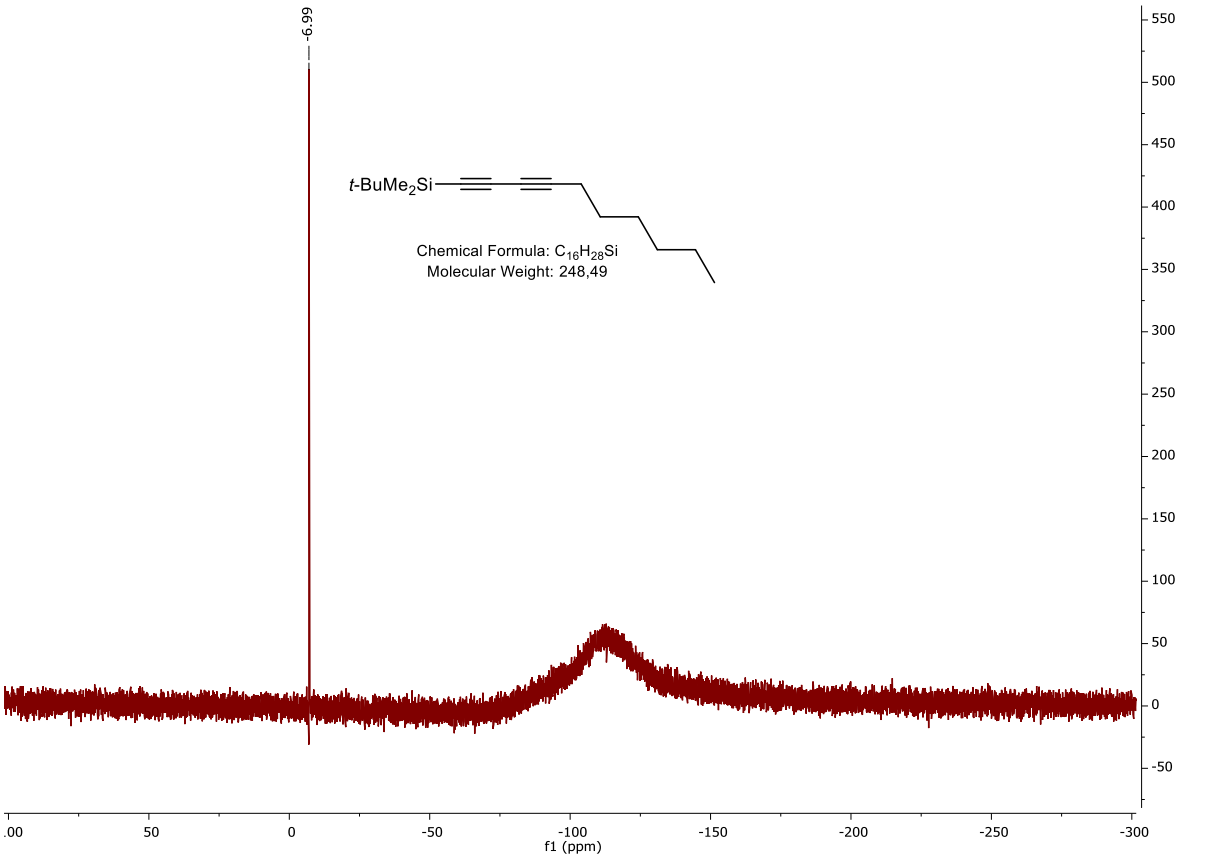


Figure S63. ^{29}Si NMR spectrum of **2r**.

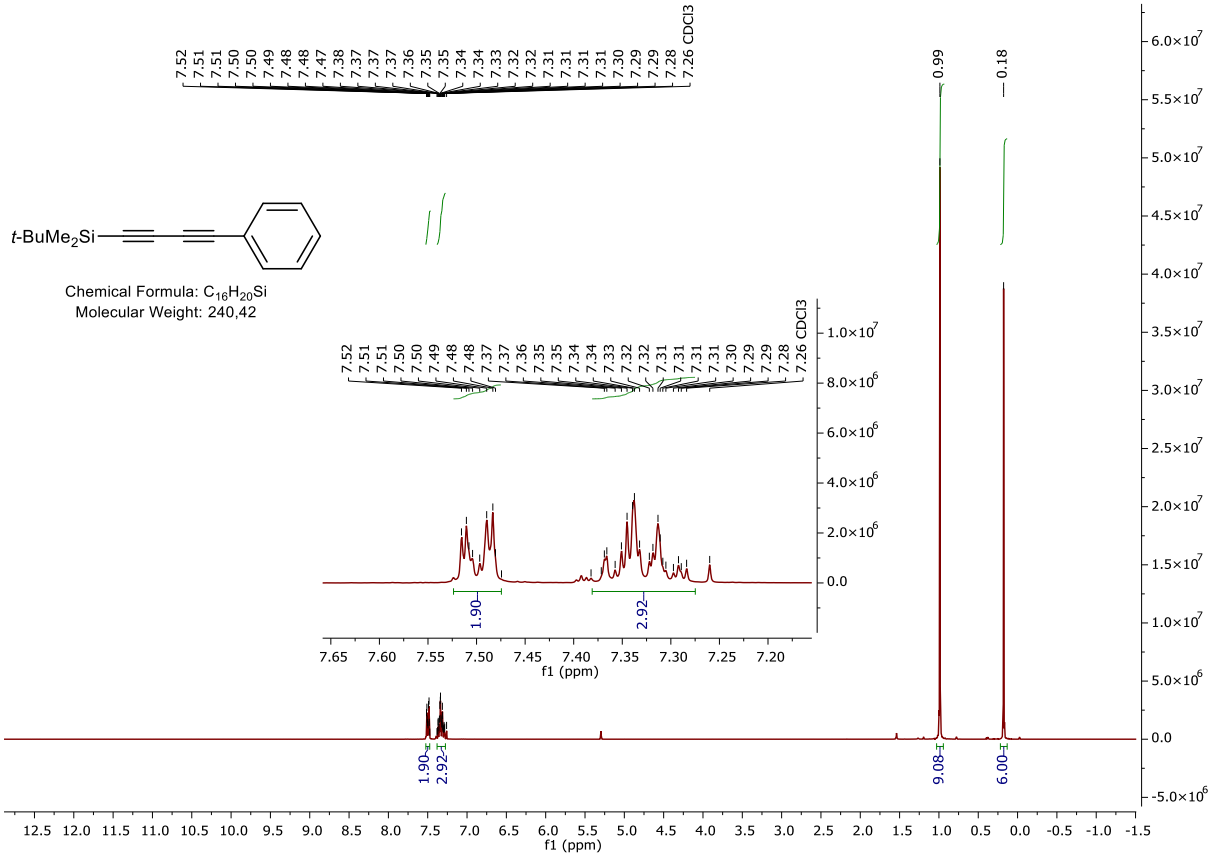


Figure S64. ^{1}H NMR spectrum of **2s**.

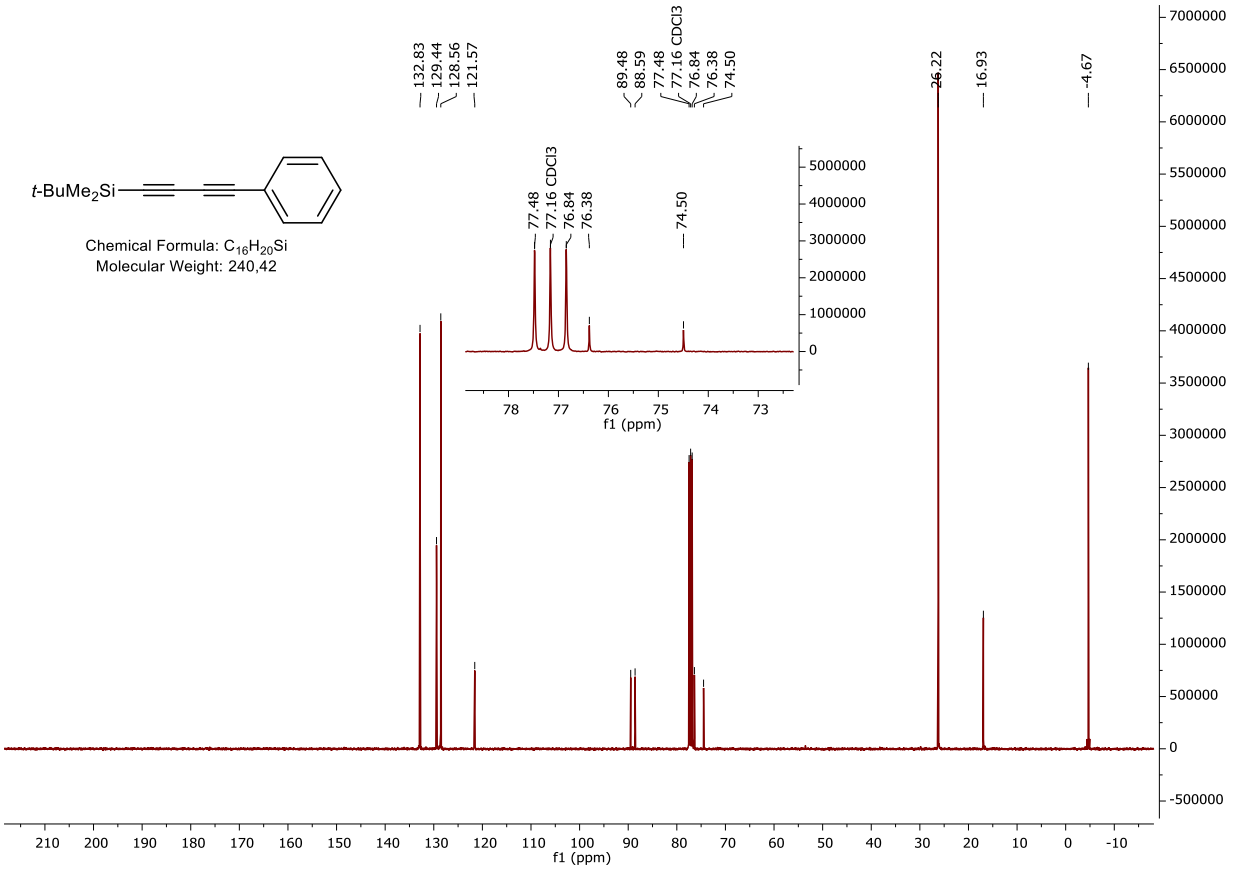


Figure S65. ^{13}C NMR spectrum of **2s**.

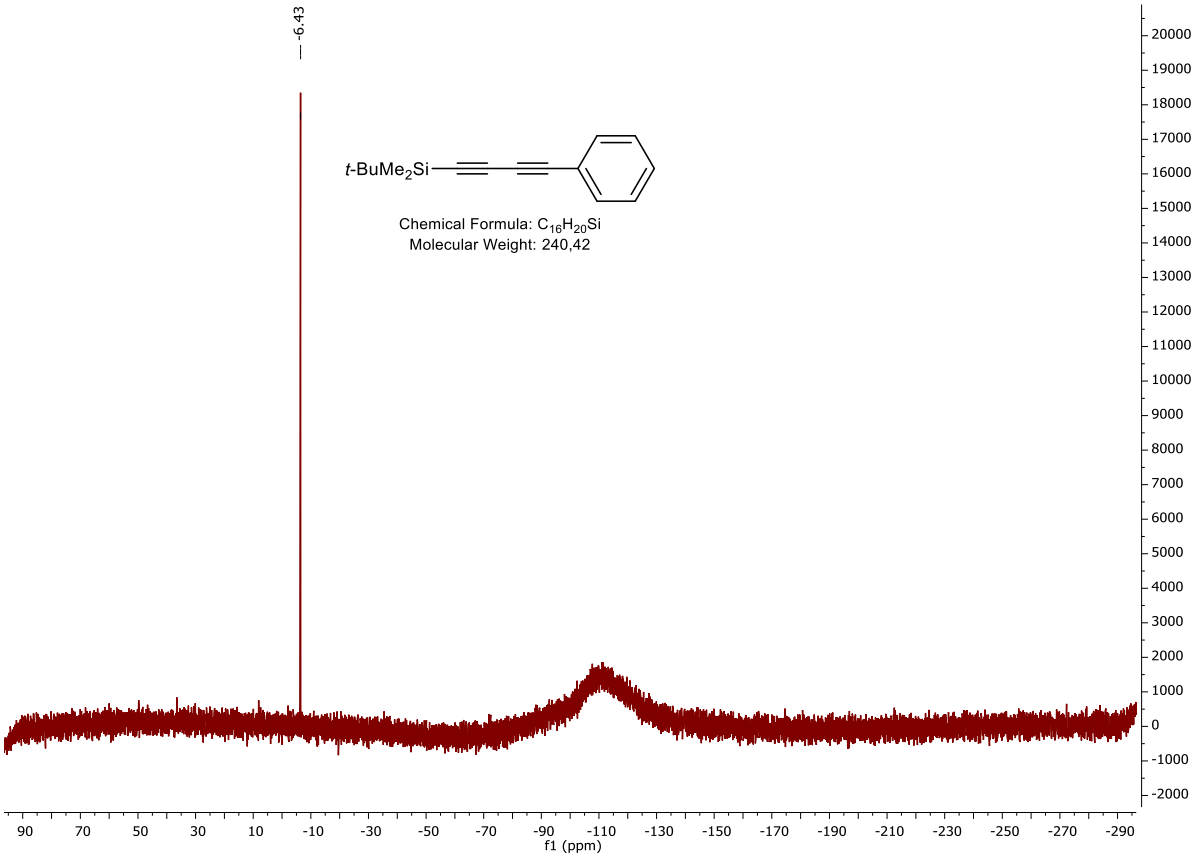


Figure S66. ^{29}Si NMR spectrum of **2s**.

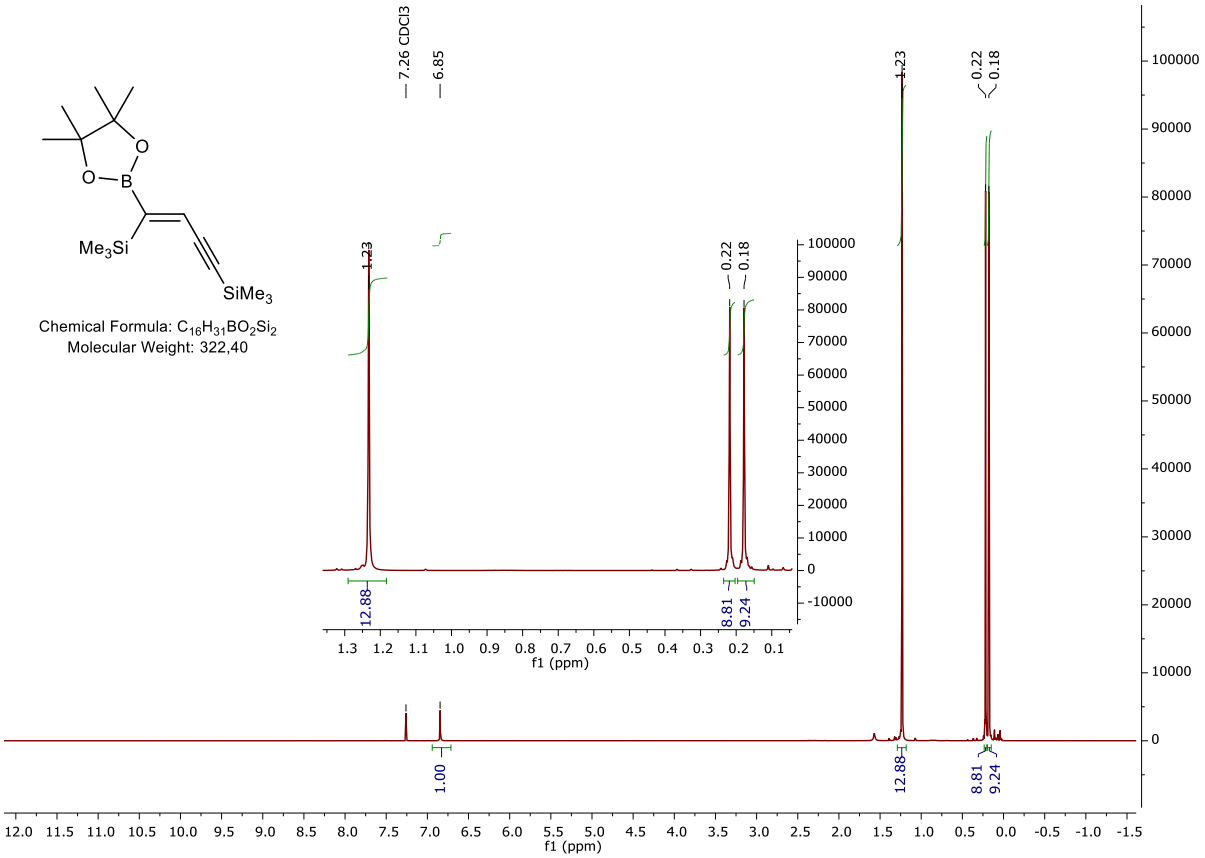


Figure S67. ^{1}H NMR spectrum of **4a**.

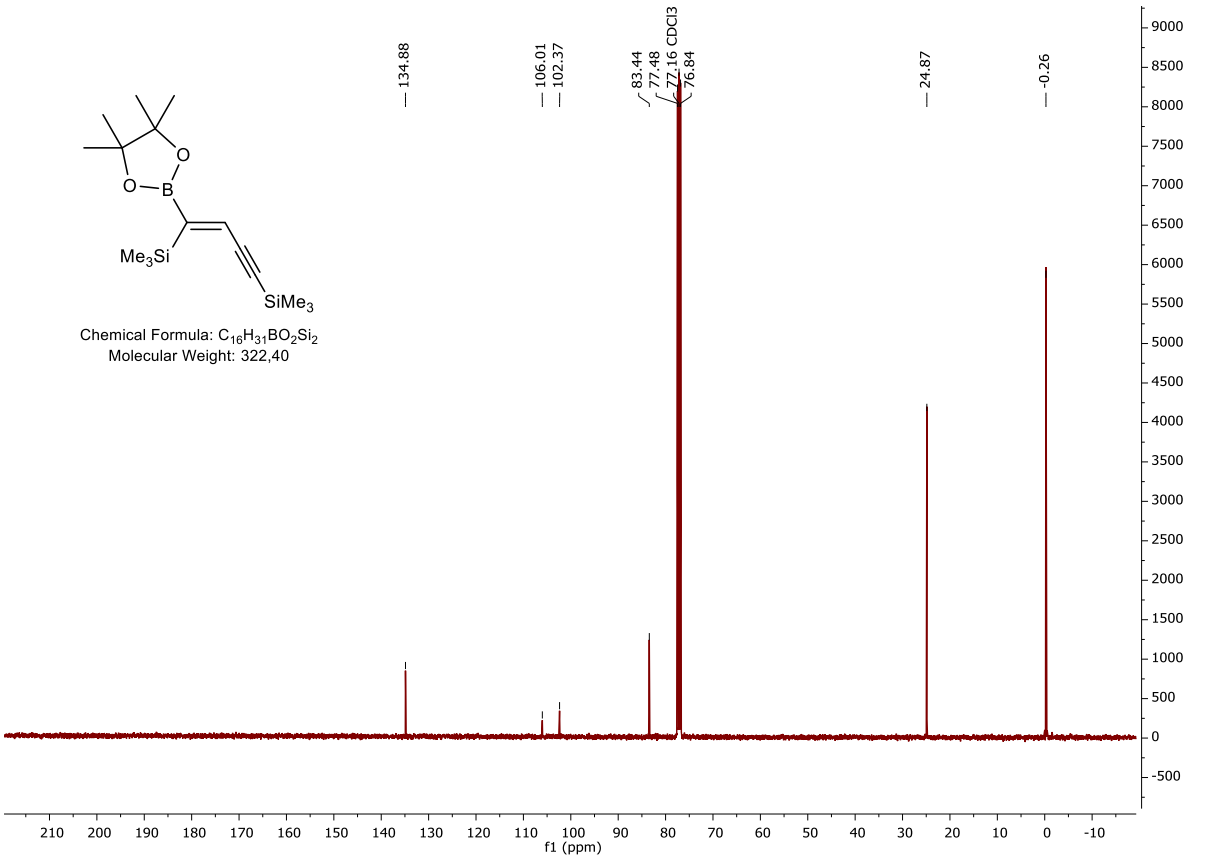


Figure S68. ^{13}C NMR spectrum of **4a**.

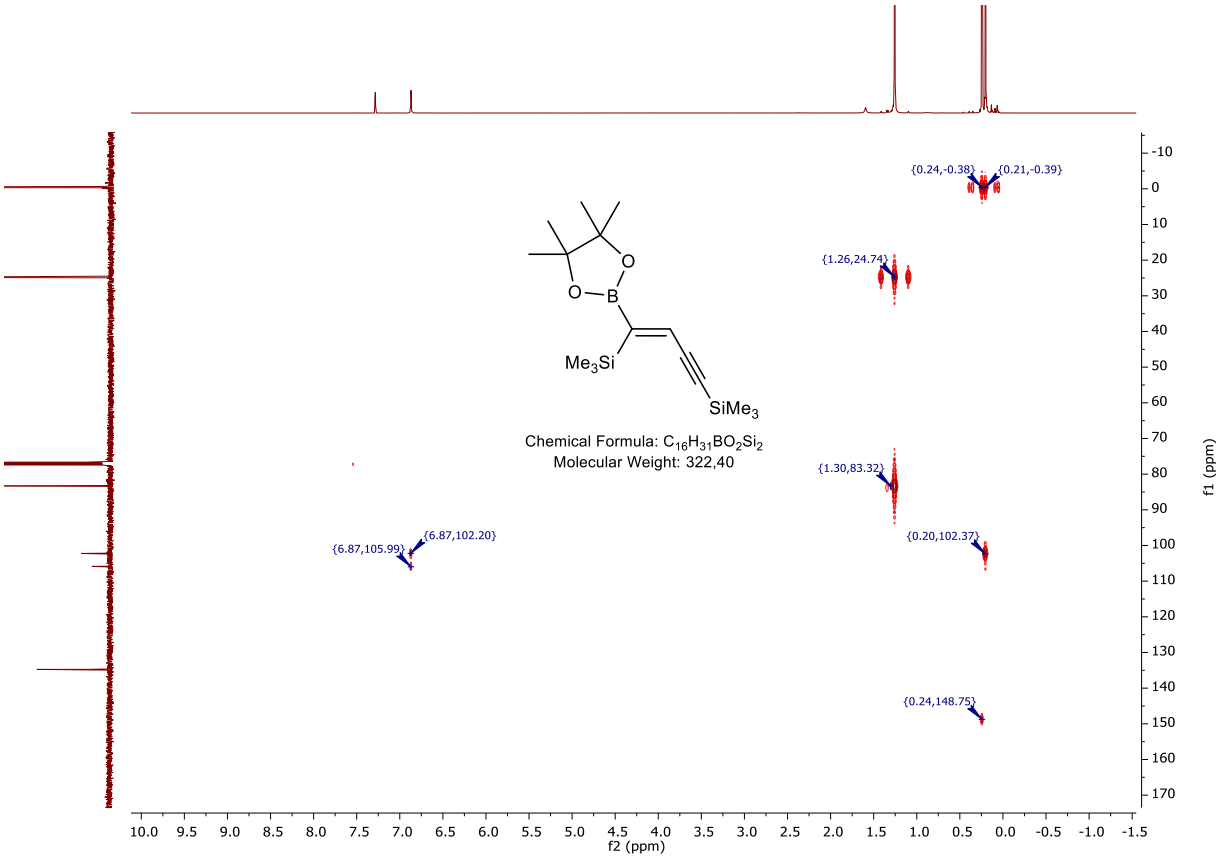


Figure S69. ^{1}H-^{13}C HMBC NMR spectrum of **4a**.

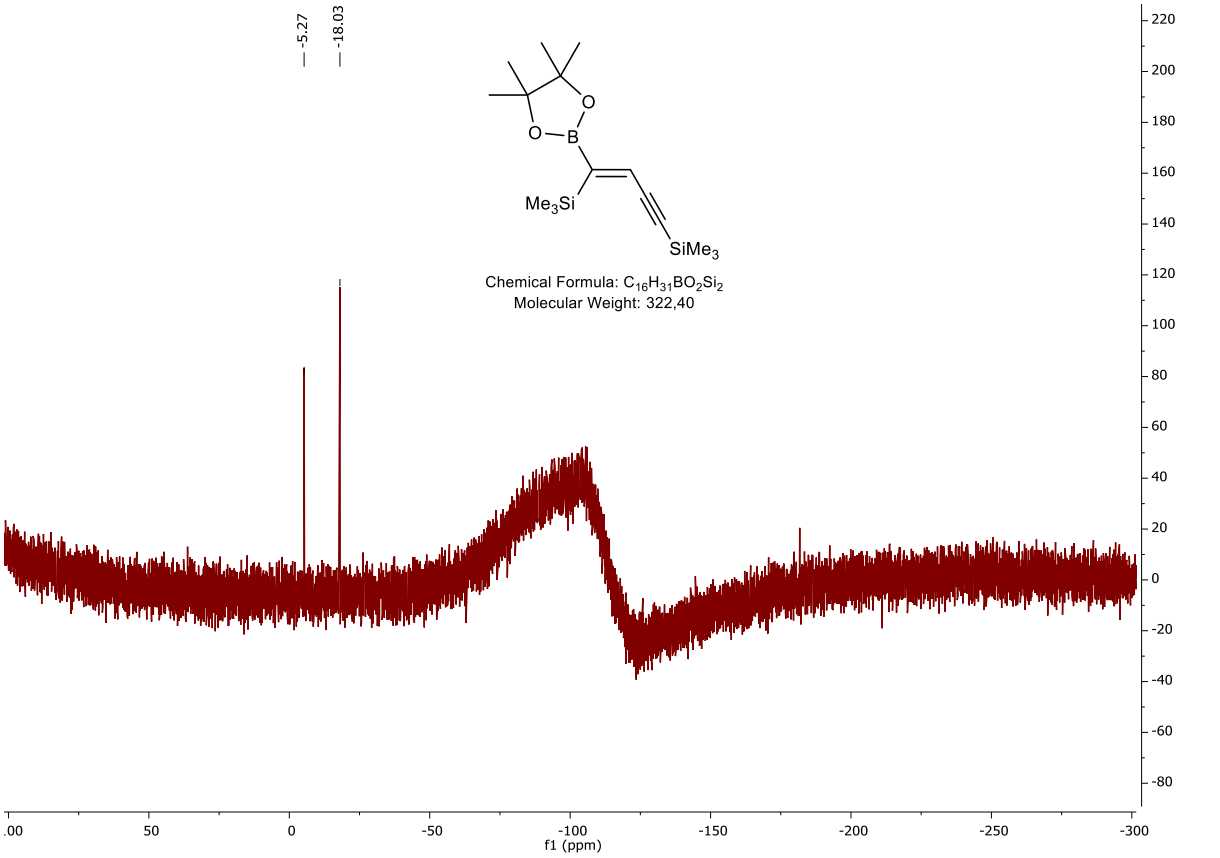


Figure S70. ^{29}Si NMR spectrum of **4a**.

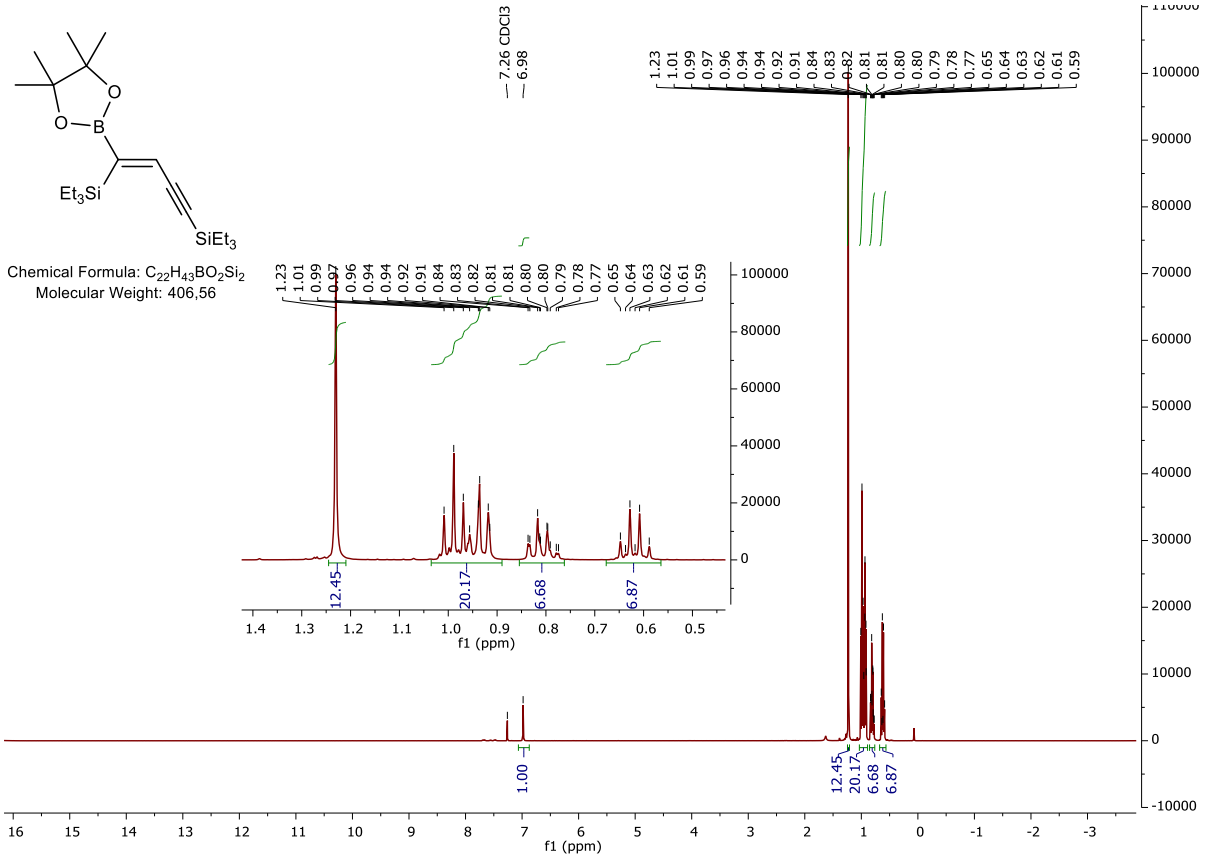


Figure S71. ^{1}H NMR spectrum of **4b**.

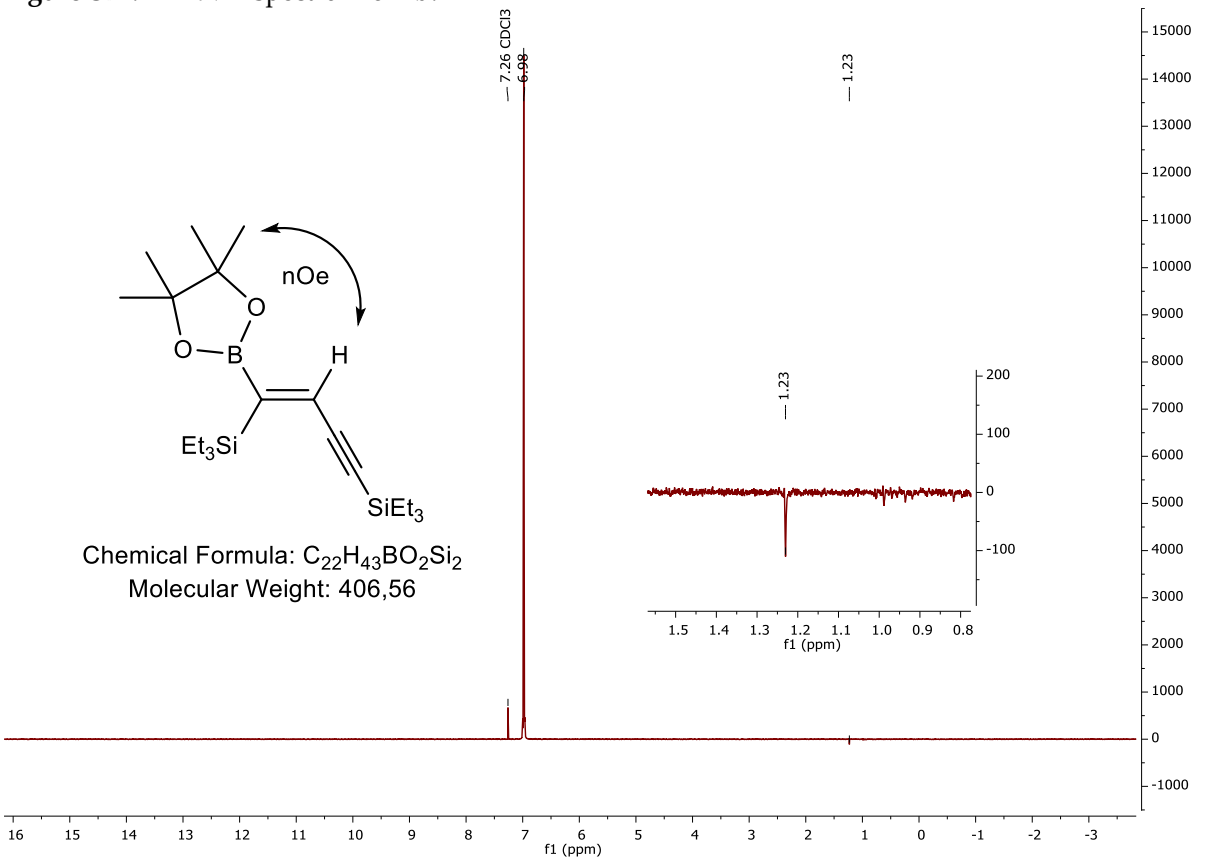


Figure S72. Selective 1D NOESY spectrum of **4b**; freq. 6.98 ppm.

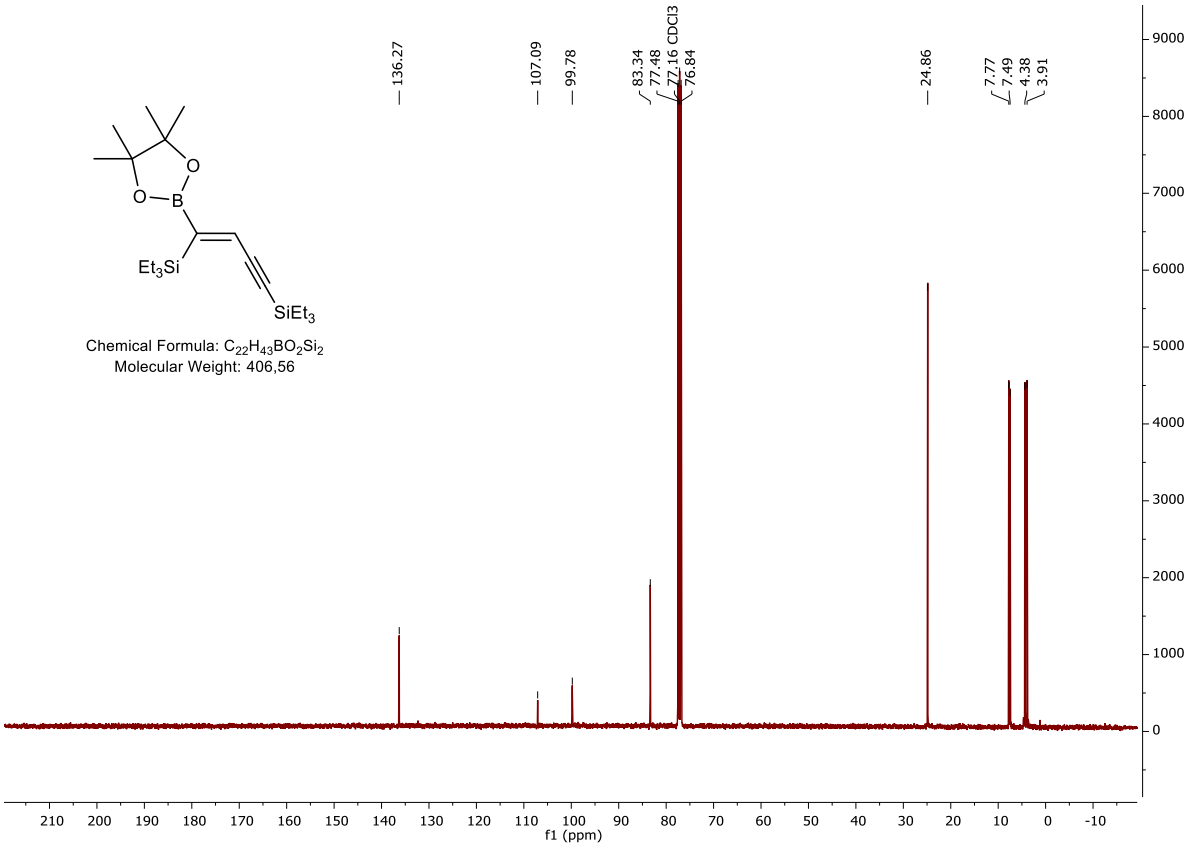


Figure S73. ^{13}C NMR spectrum of **4b**.

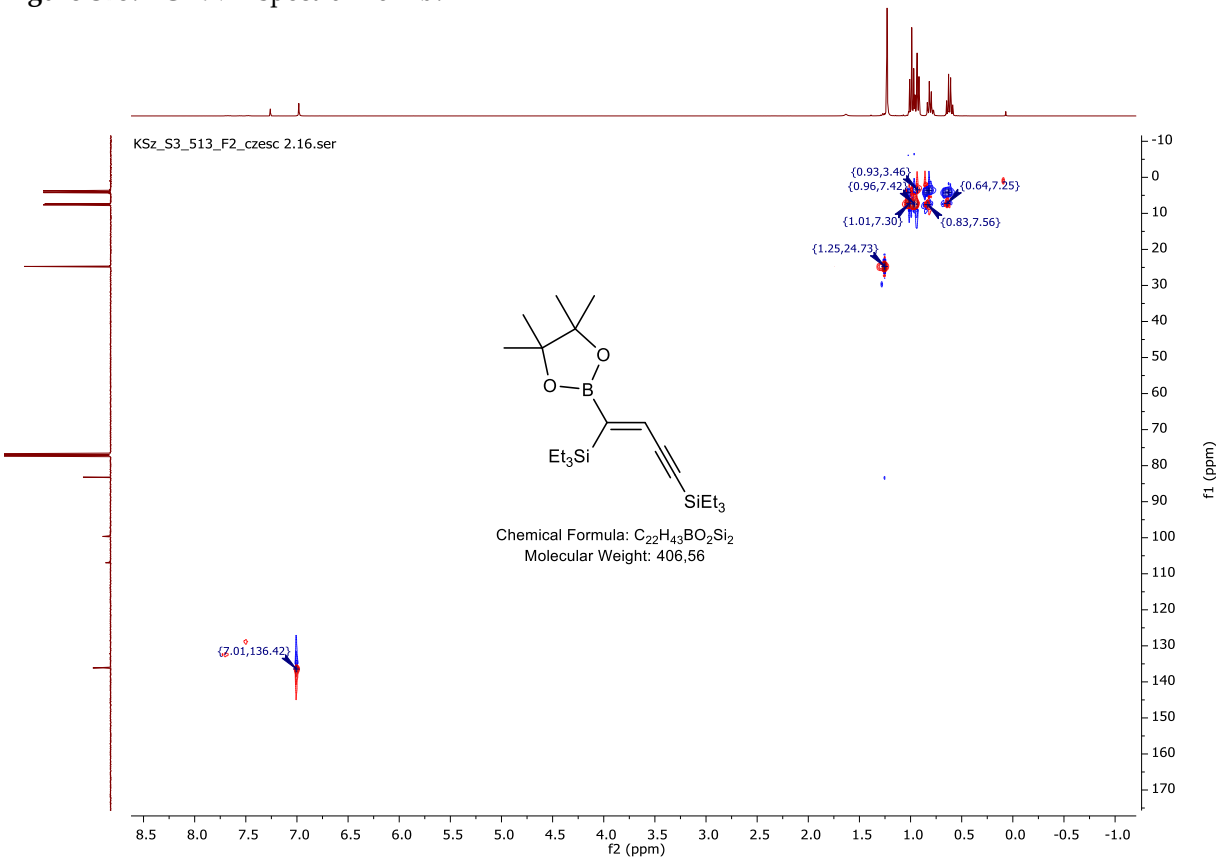


Figure S74. ^{1}H-^{13}C HSQC NMR spectrum of **4b**.

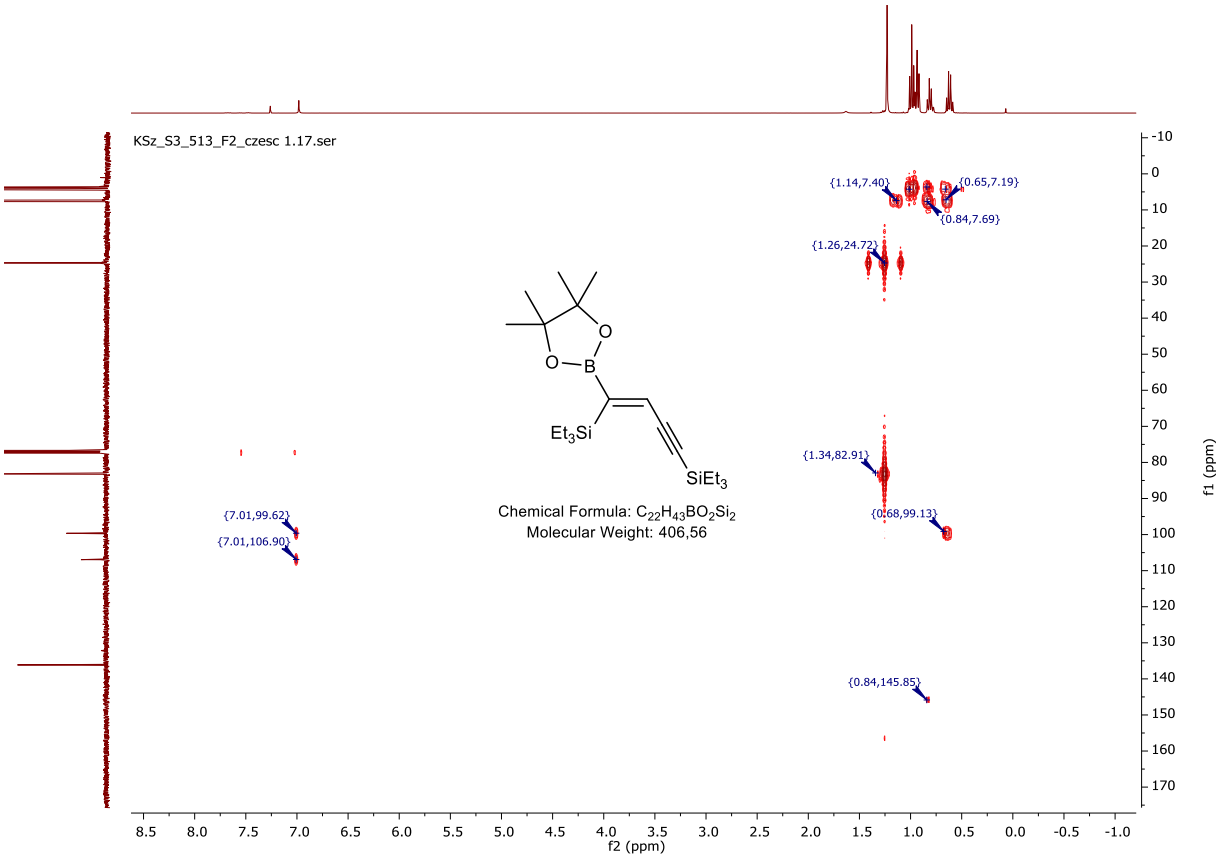


Figure S75. ^{1}H-^{13}C HMBC NMR spectrum of **4b**.

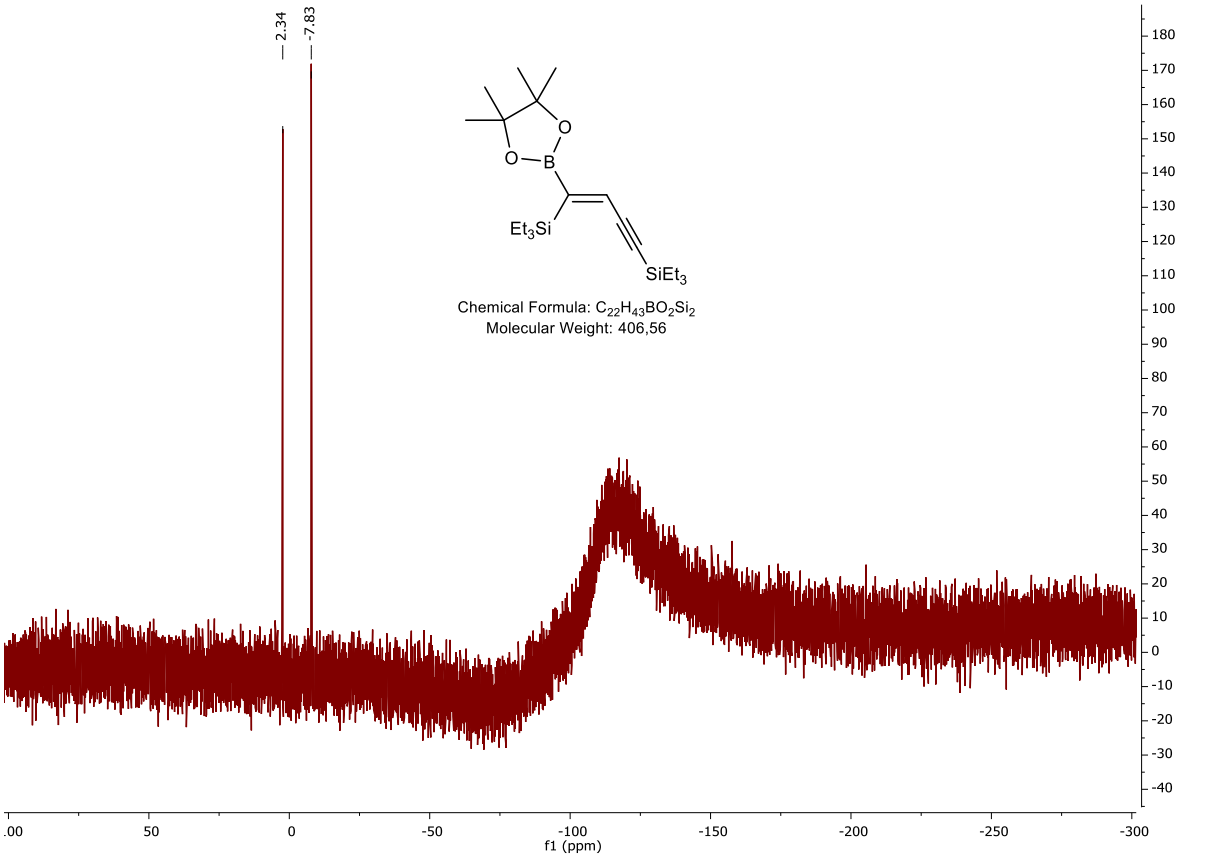


Figure S76. ^{29}Si NMR spectrum of **4b**.

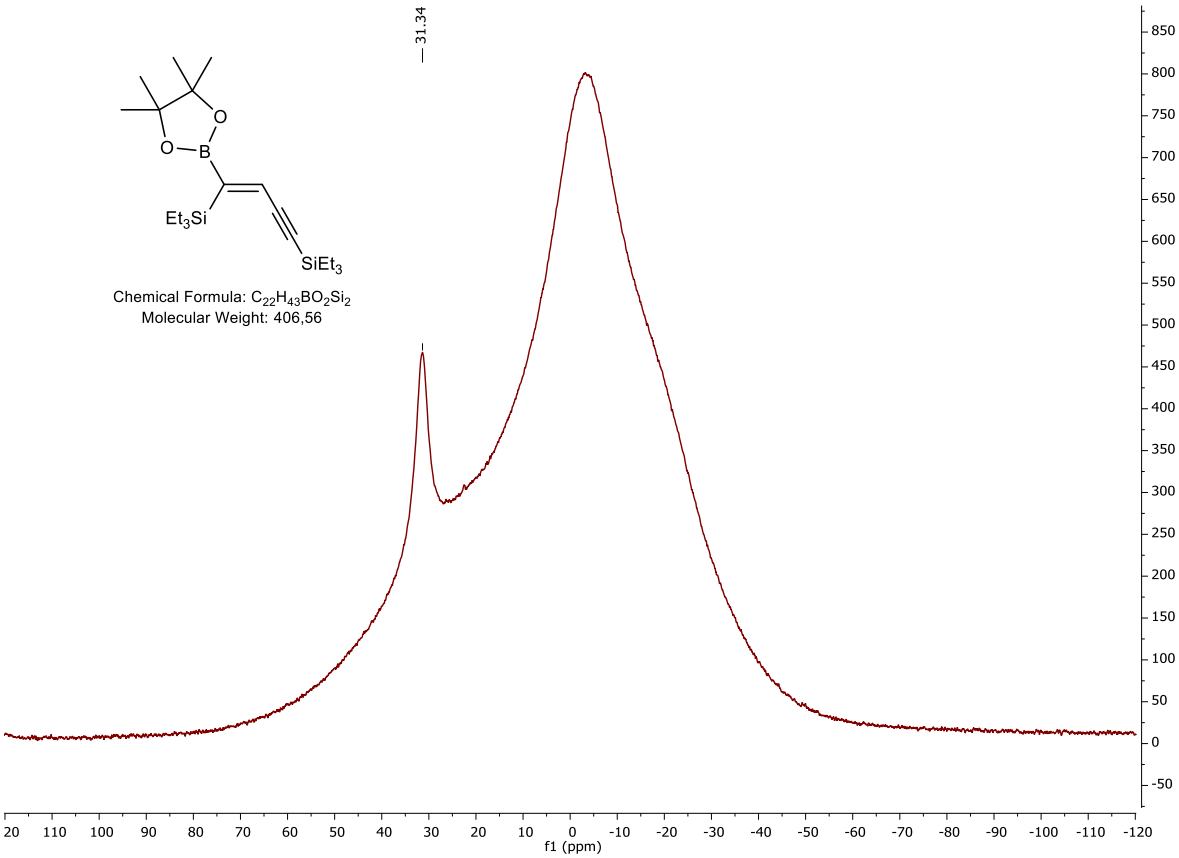


Figure S77. [21]B NMR spectrum of **4b**.

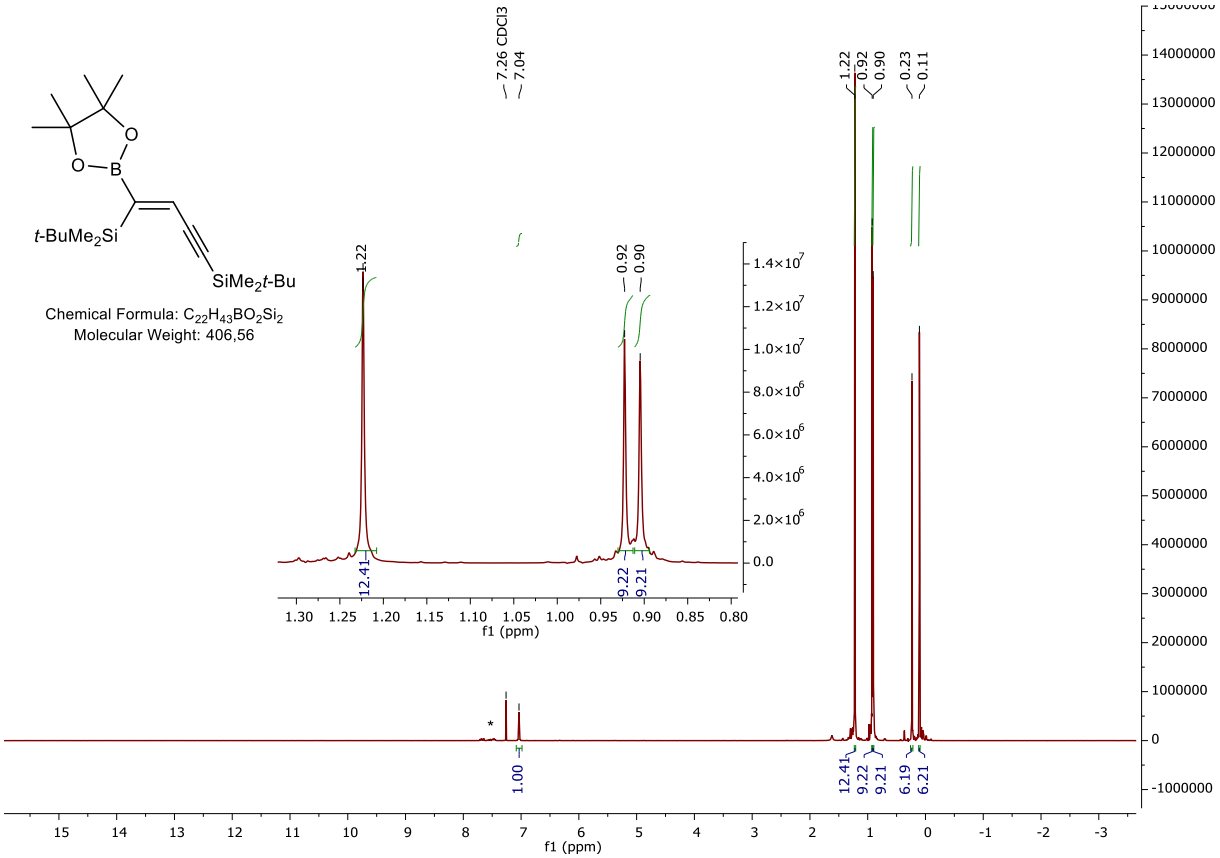


Figure S78. [1]H NMR spectrum of **4c**; * - traces of PPh_3.

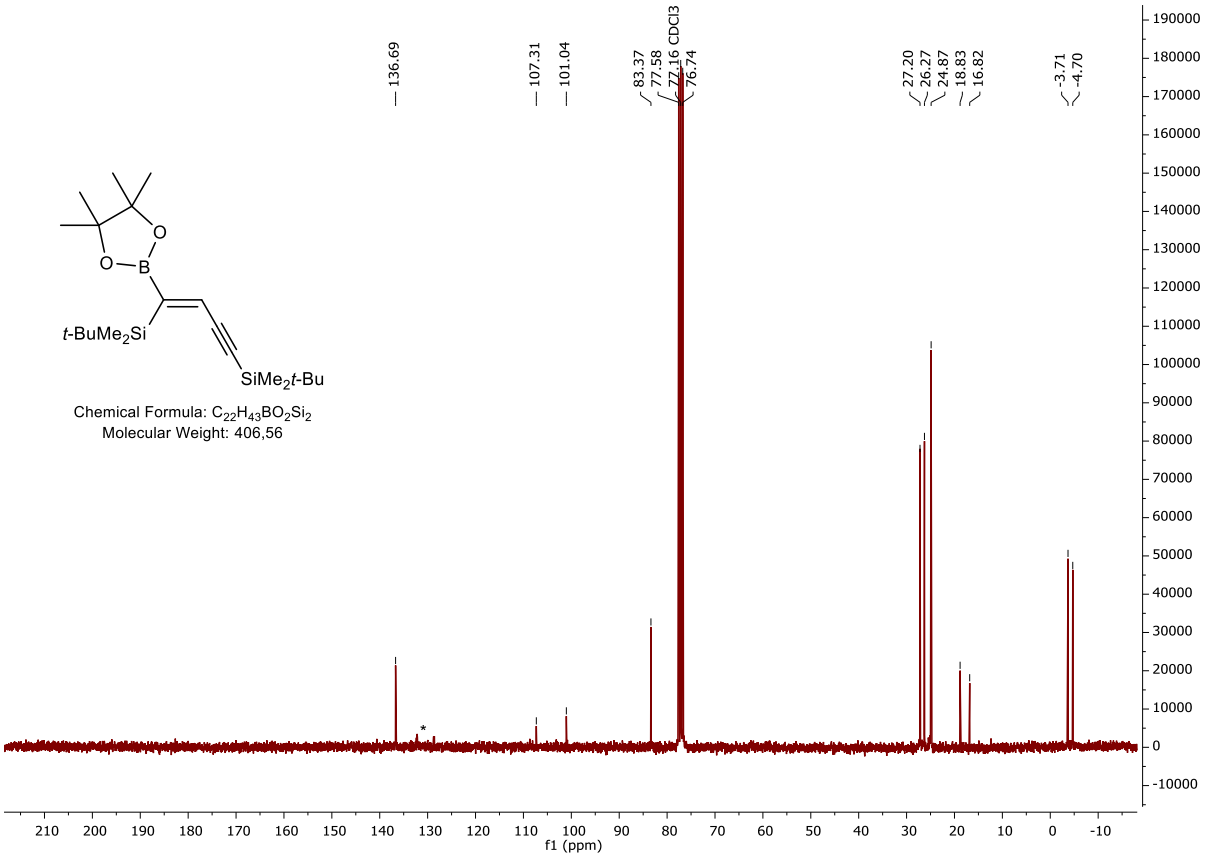


Figure S79. ^{13}C NMR spectrum of **4c**; * - traces of PPh_3.

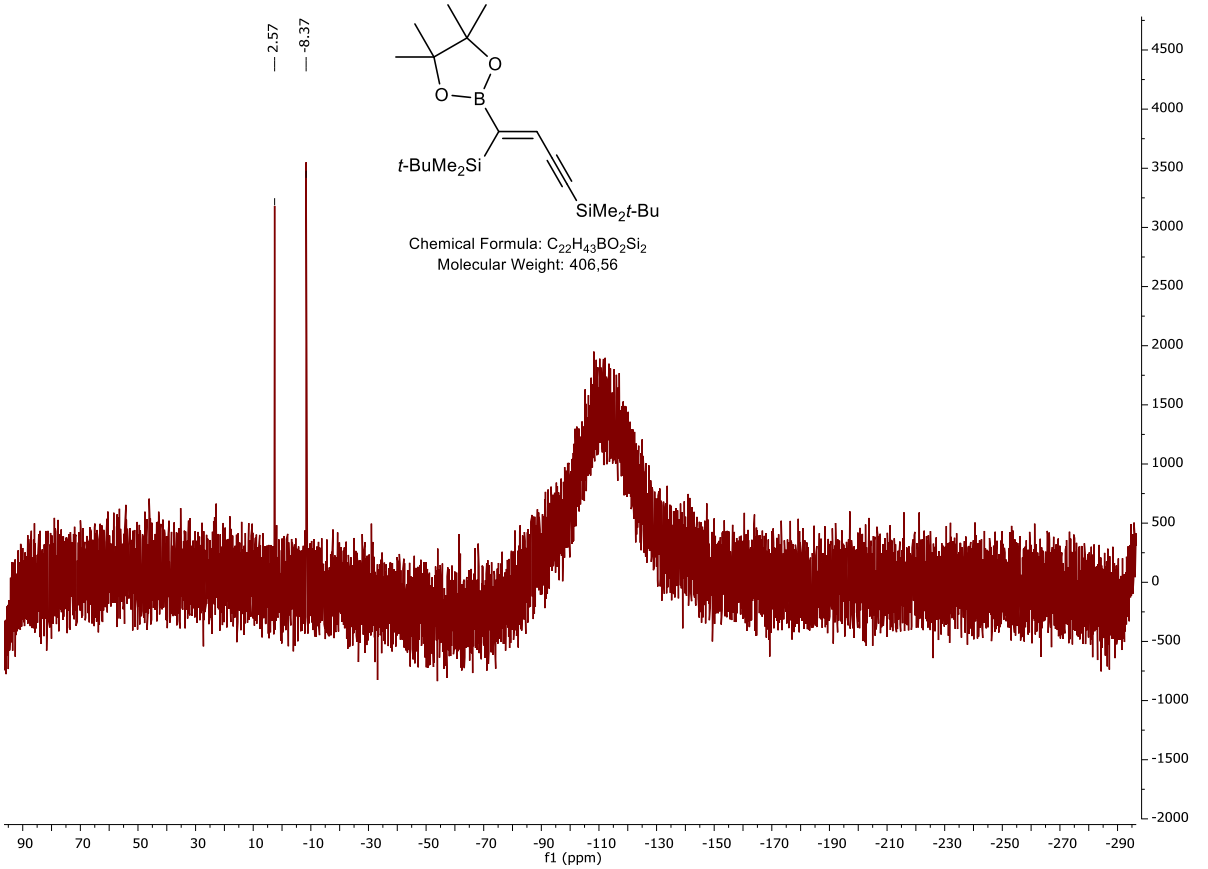


Figure S80. ^{29}Si NMR spectrum of **4c**.

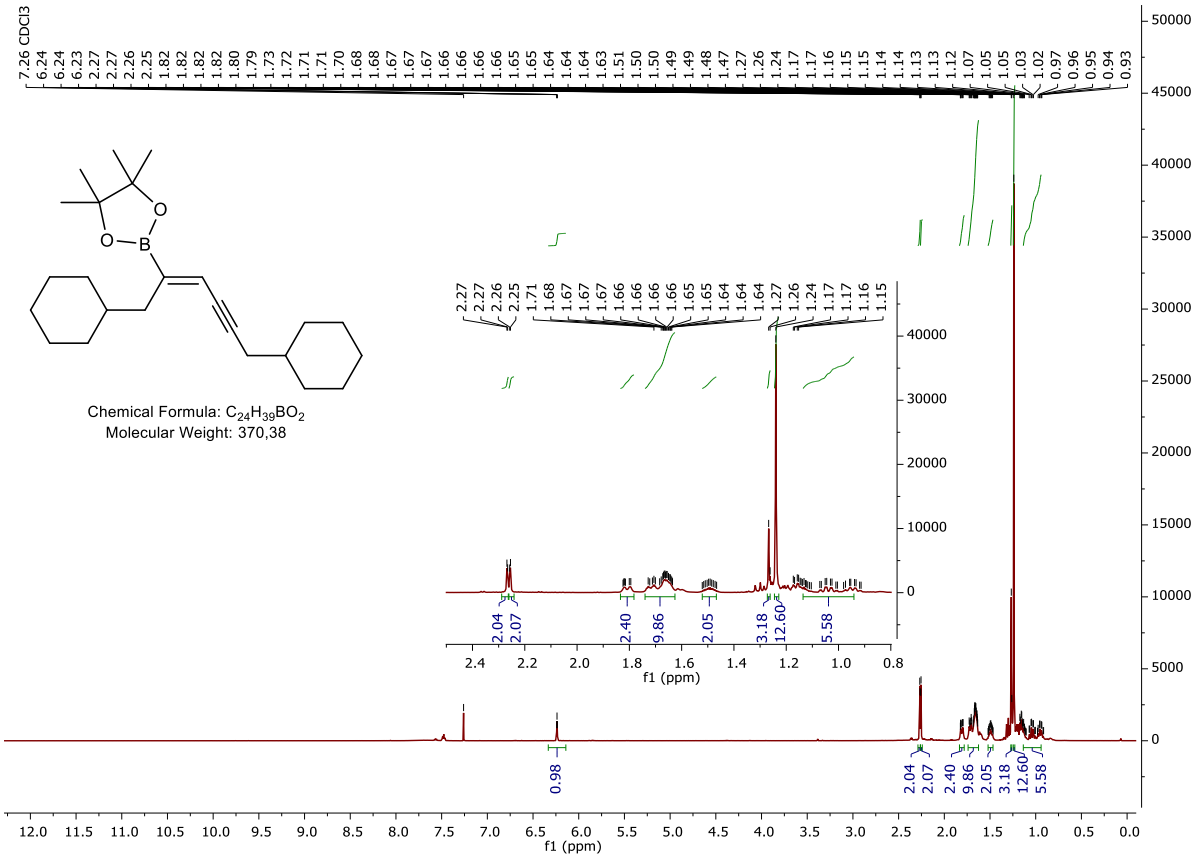


Figure S81. ^{1}H NMR spectrum of **4d**.

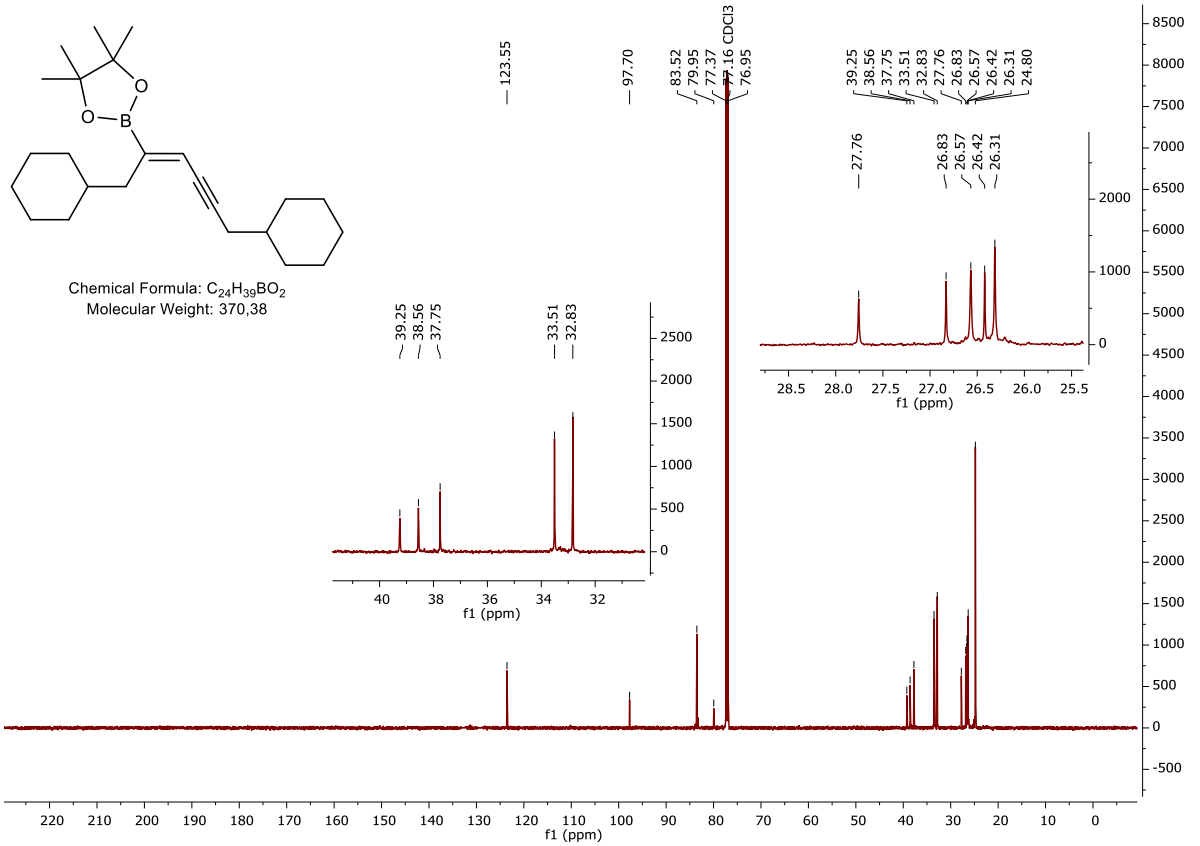


Figure S82. ^{13}C NMR spectrum of **4d**.

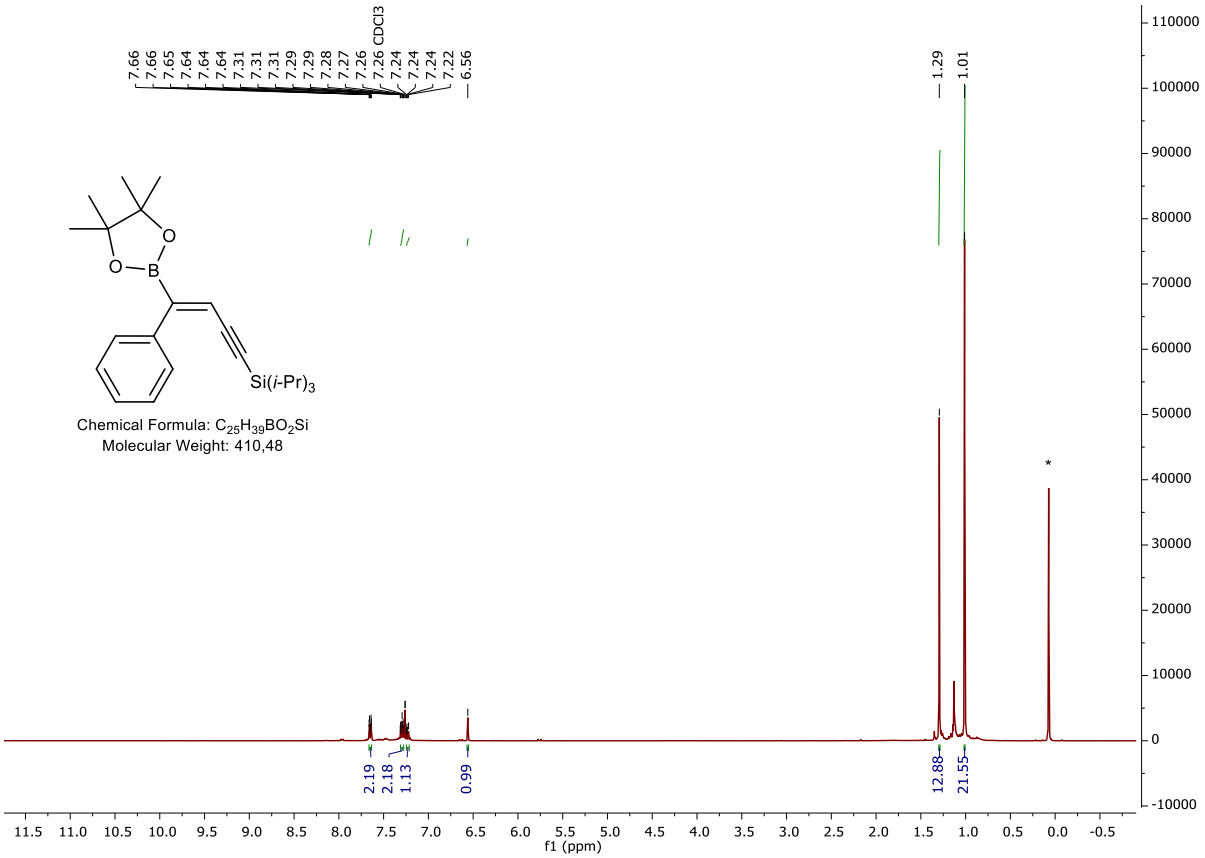


Figure S83. [1]H NMR spectrum of **4e**.

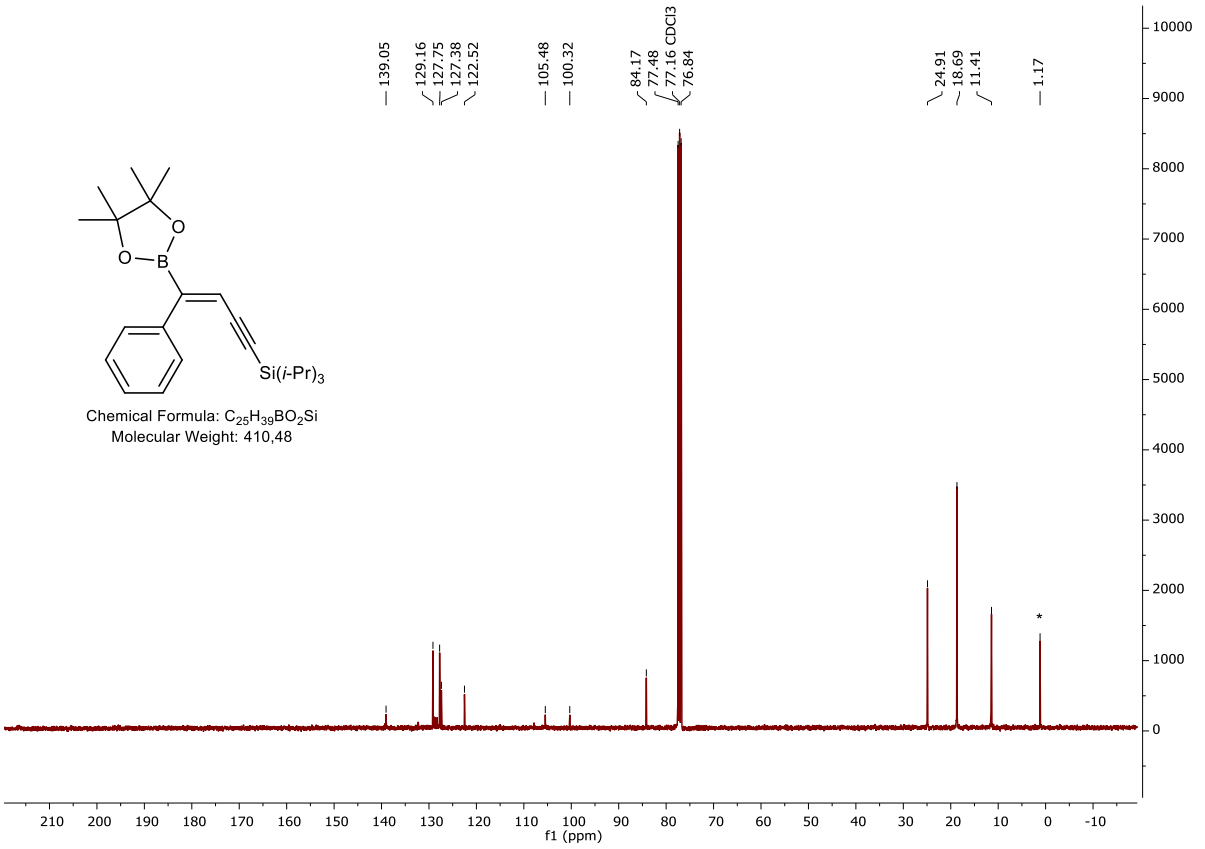


Figure S84. [13]C NMR spectrum of **4e**.

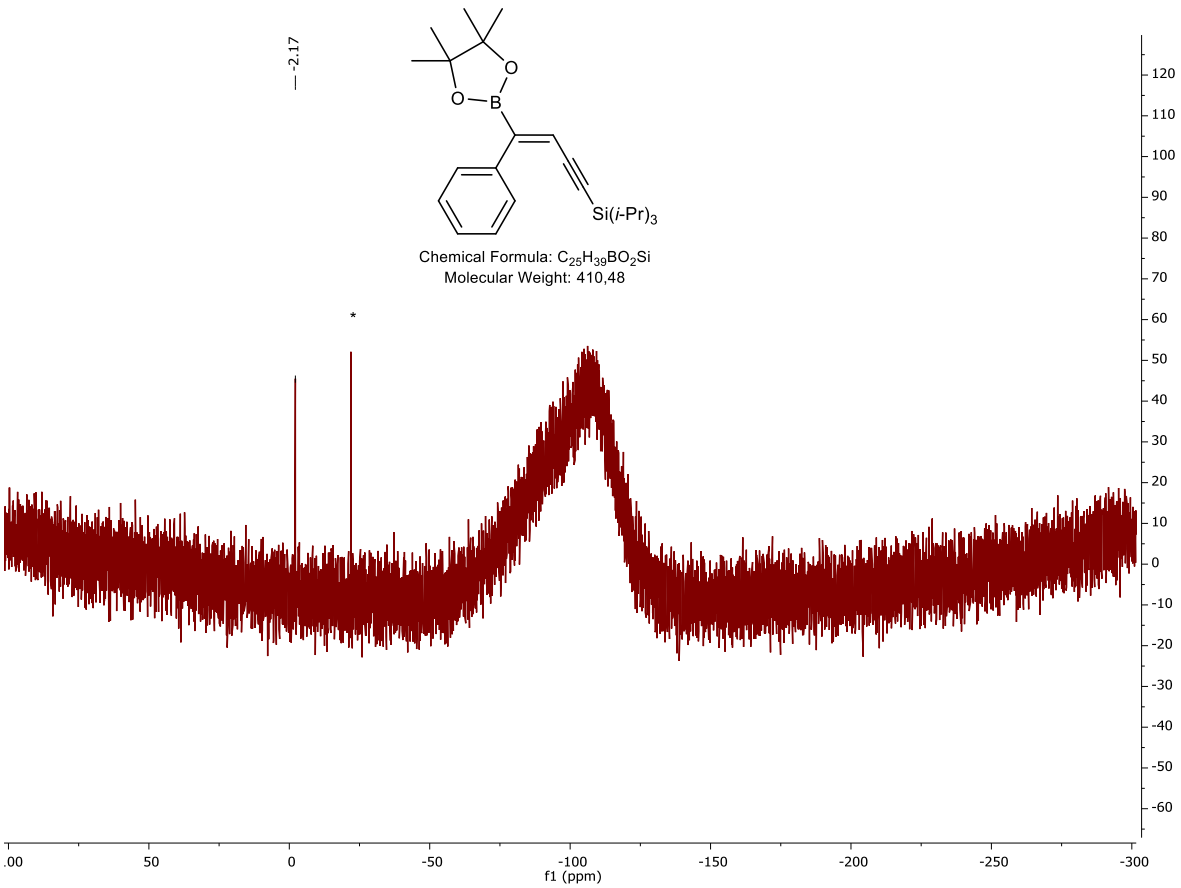


Figure S85. ^{29}Si NMR spectrum of **4e**; * - grease.

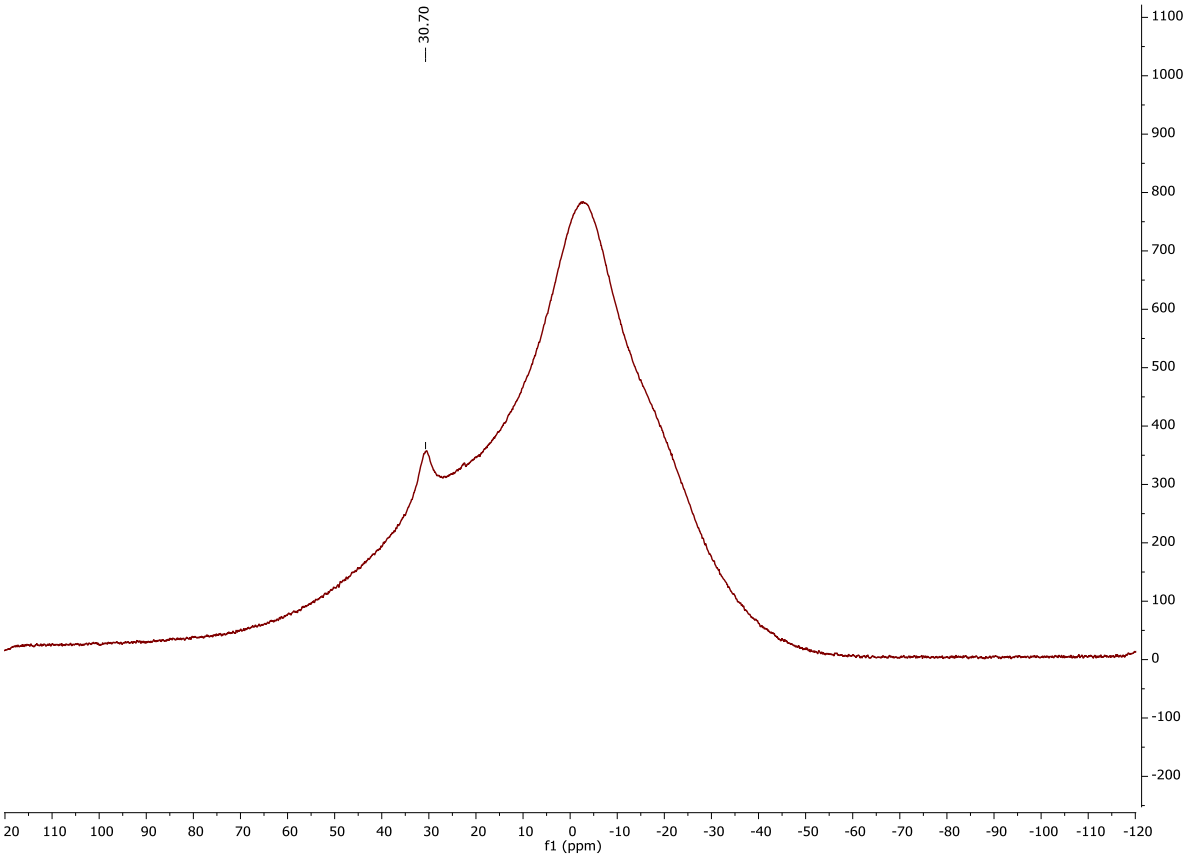


Figure S86. ^{11}B NMR spectrum of **4e**.

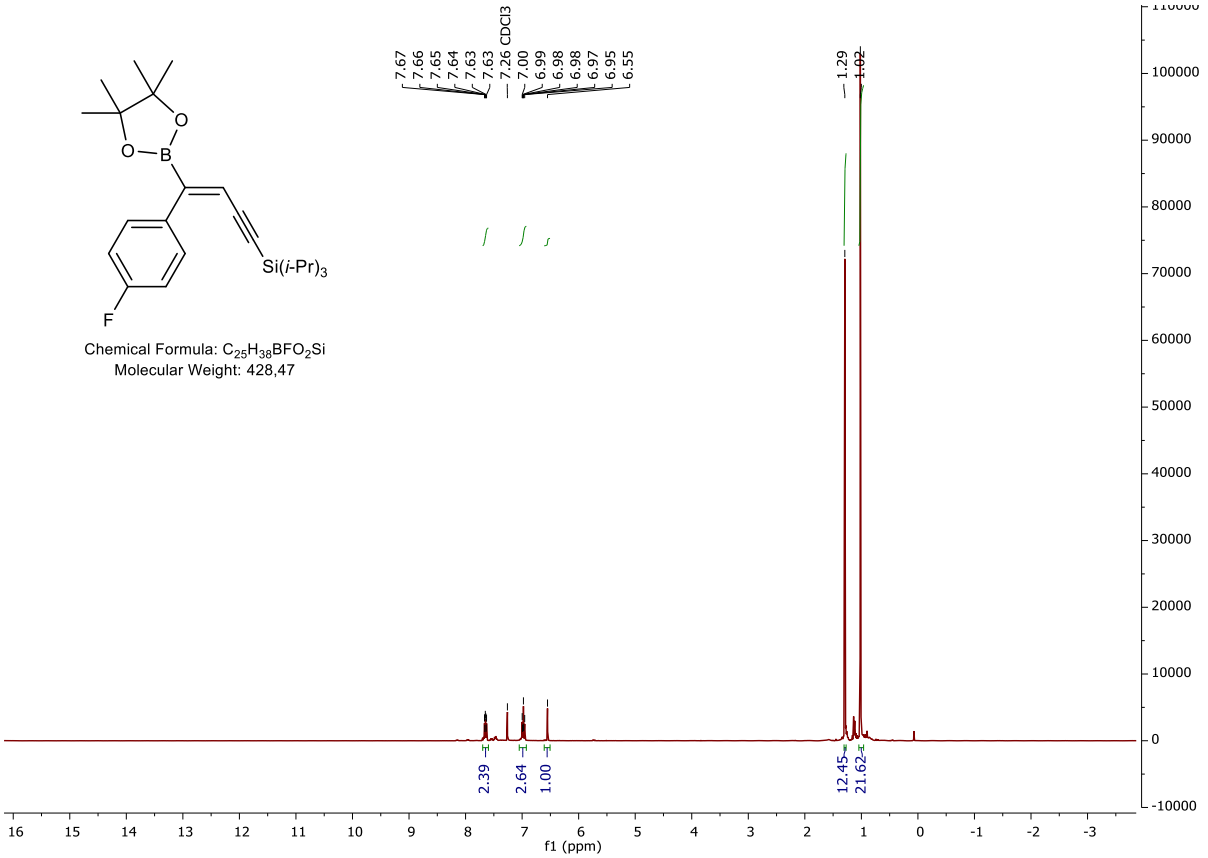


Figure S87. [1]H NMR spectrum of **4f**.

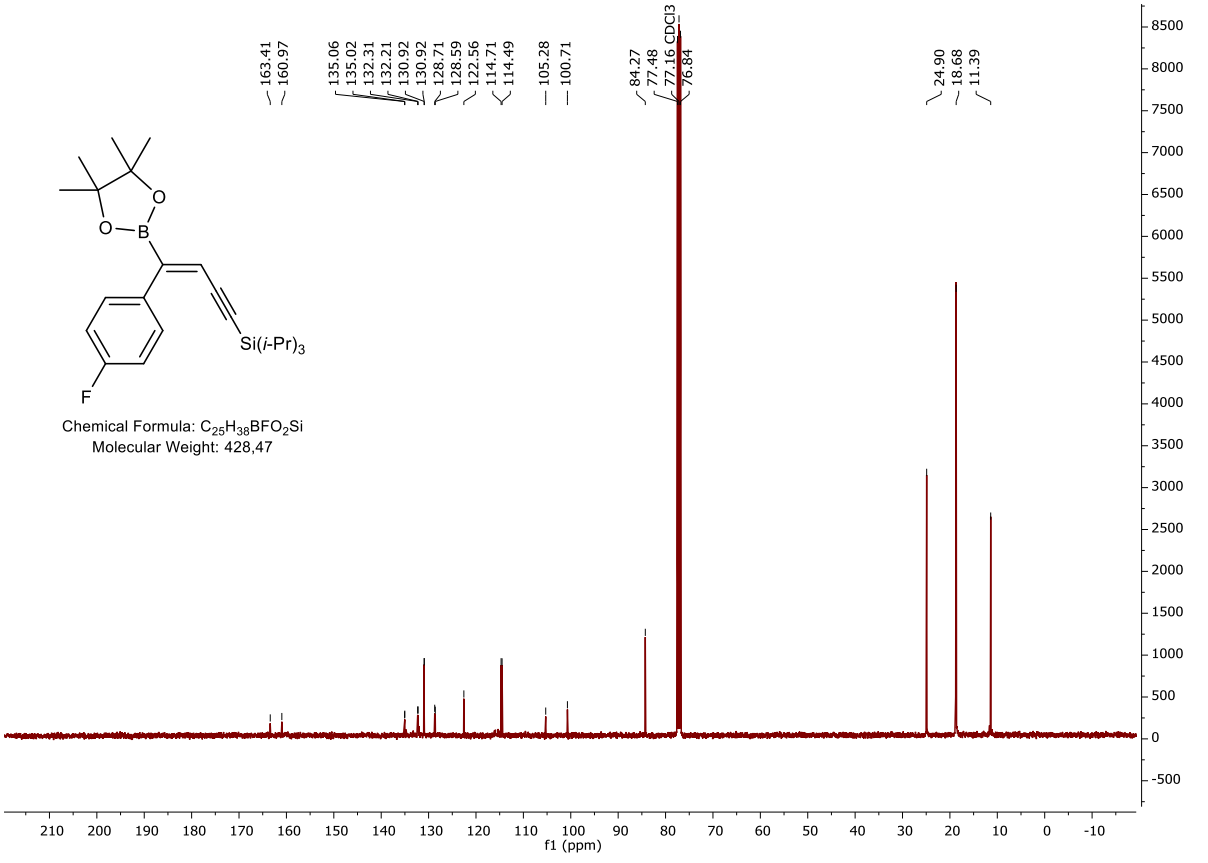


Figure S88. [13]C NMR spectrum of **4f**.

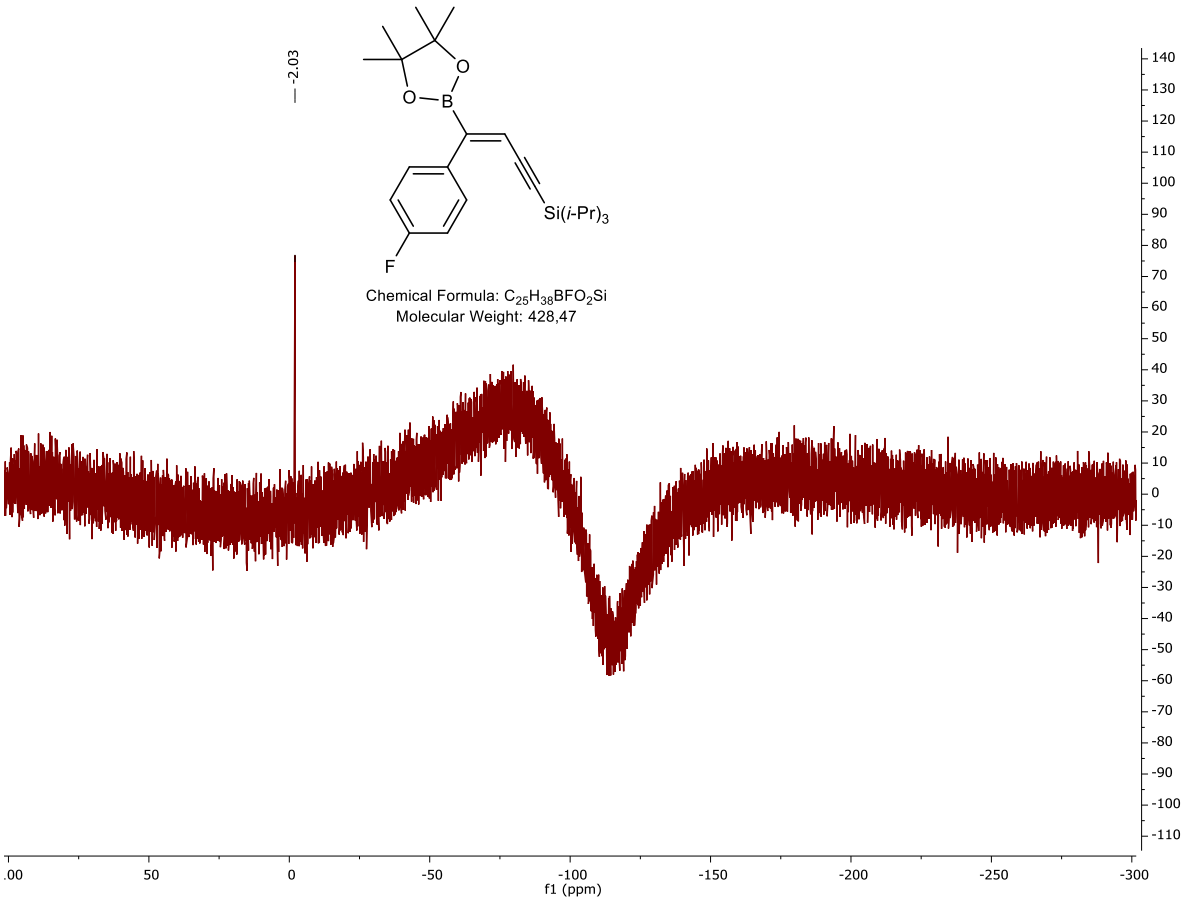


Figure S89. ^{29}Si NMR spectrum of **4f**.

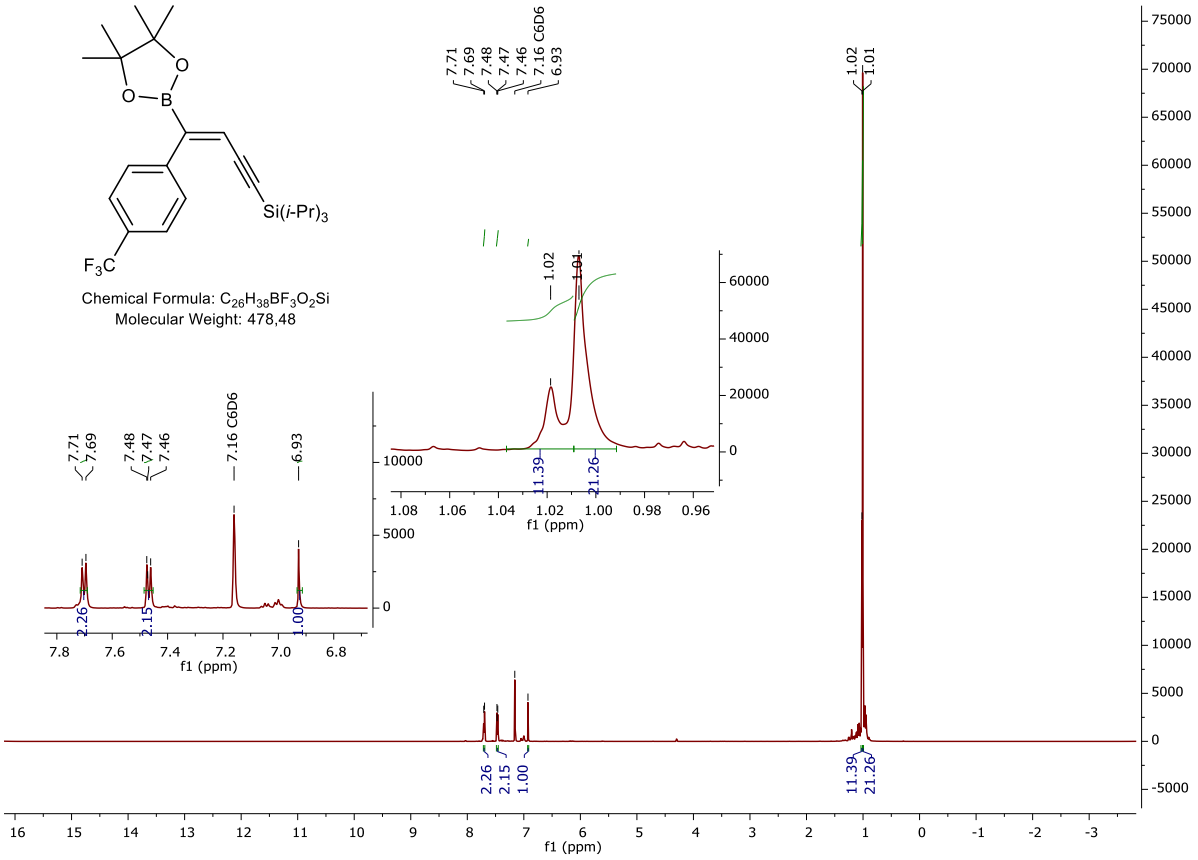


Figure S90. ^{1}H NMR spectrum of **4g**.

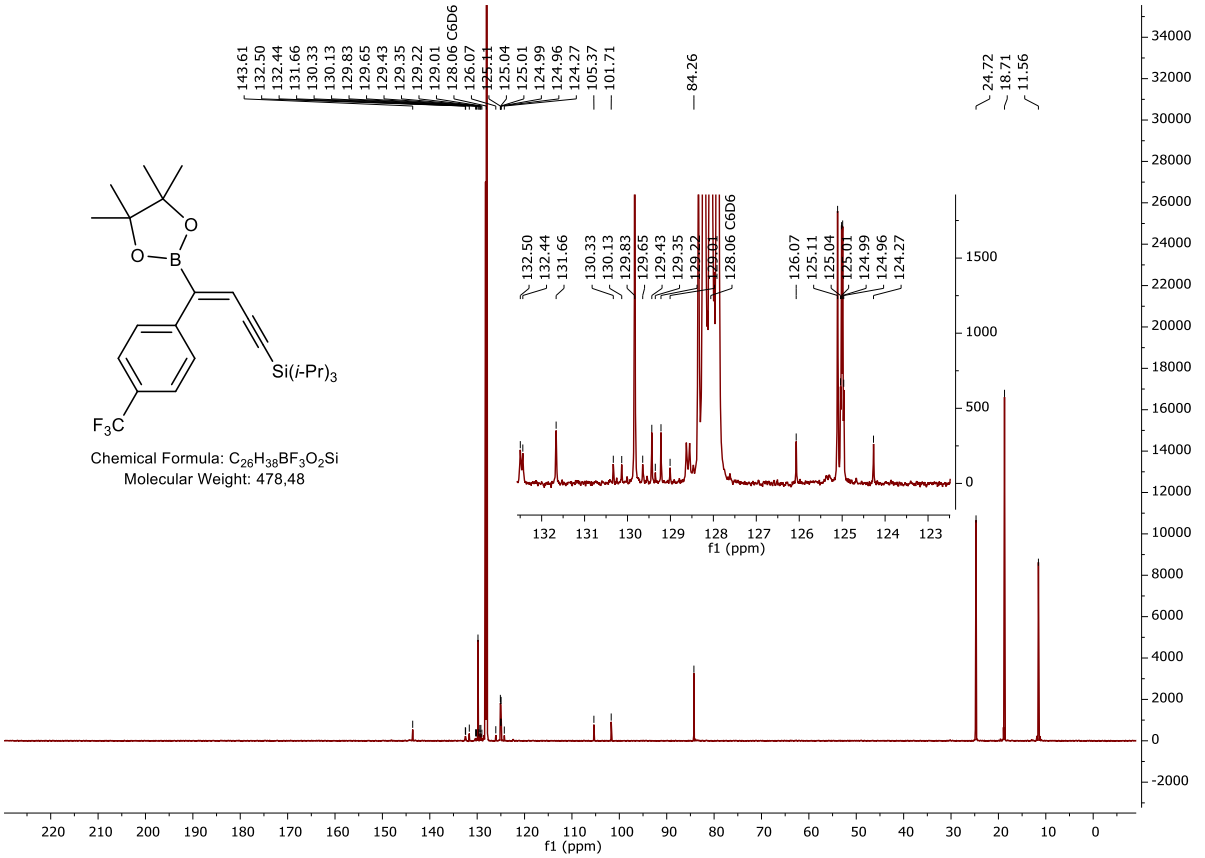


Figure S91. ^{13}C NMR spectrum of **4g**.

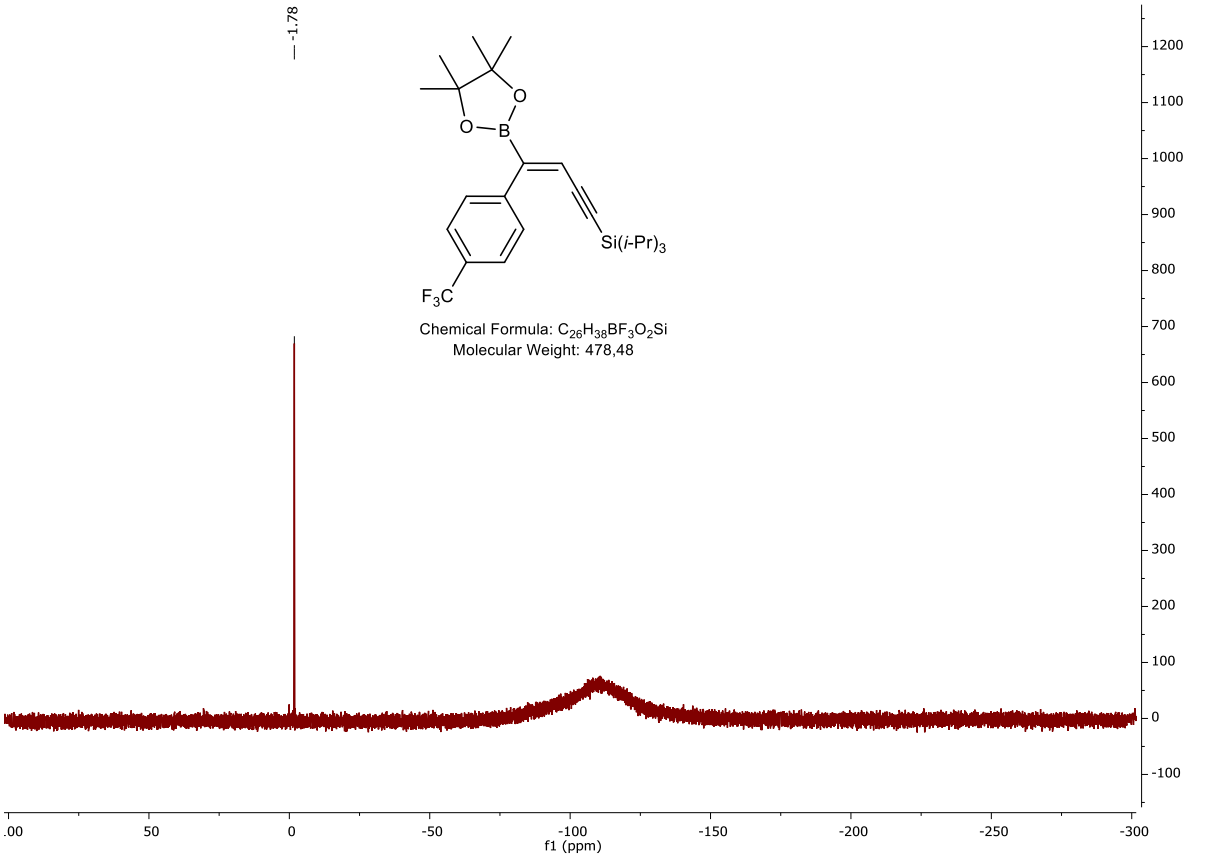


Figure S92. ^{29}Si NMR spectrum of **4g**.

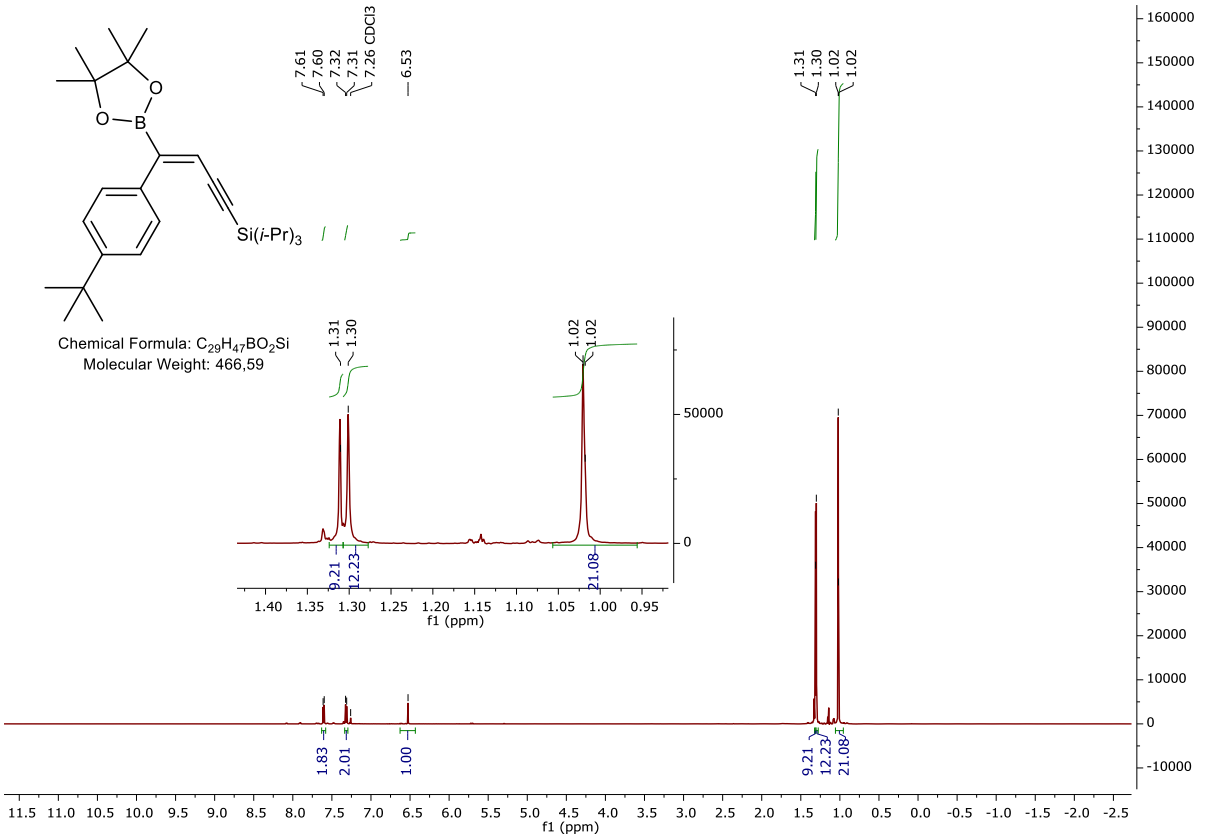


Figure S93. ^{1}H NMR spectrum of **4h**.

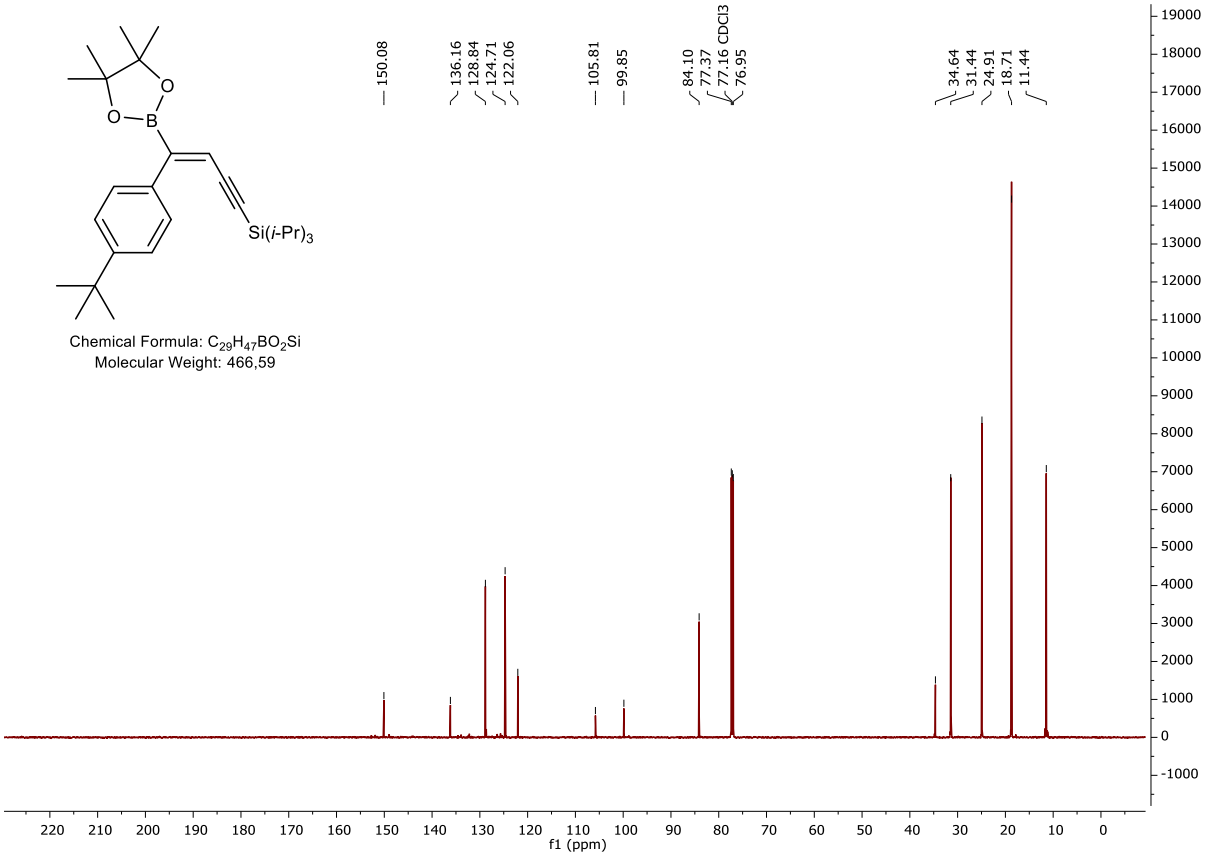


Figure S94. ^{11}C NMR spectrum of **4h**.

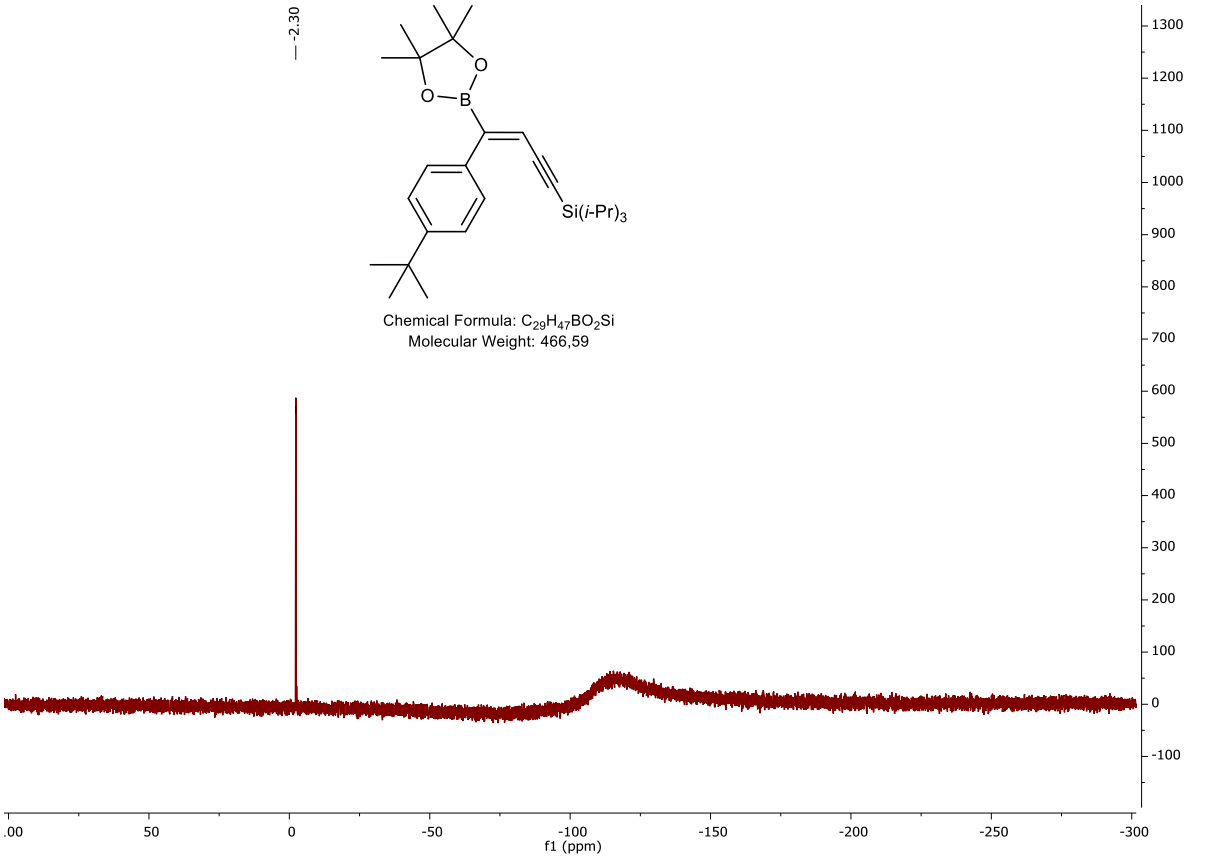


Figure S95. ^{29}Si NMR spectrum of **4h**.

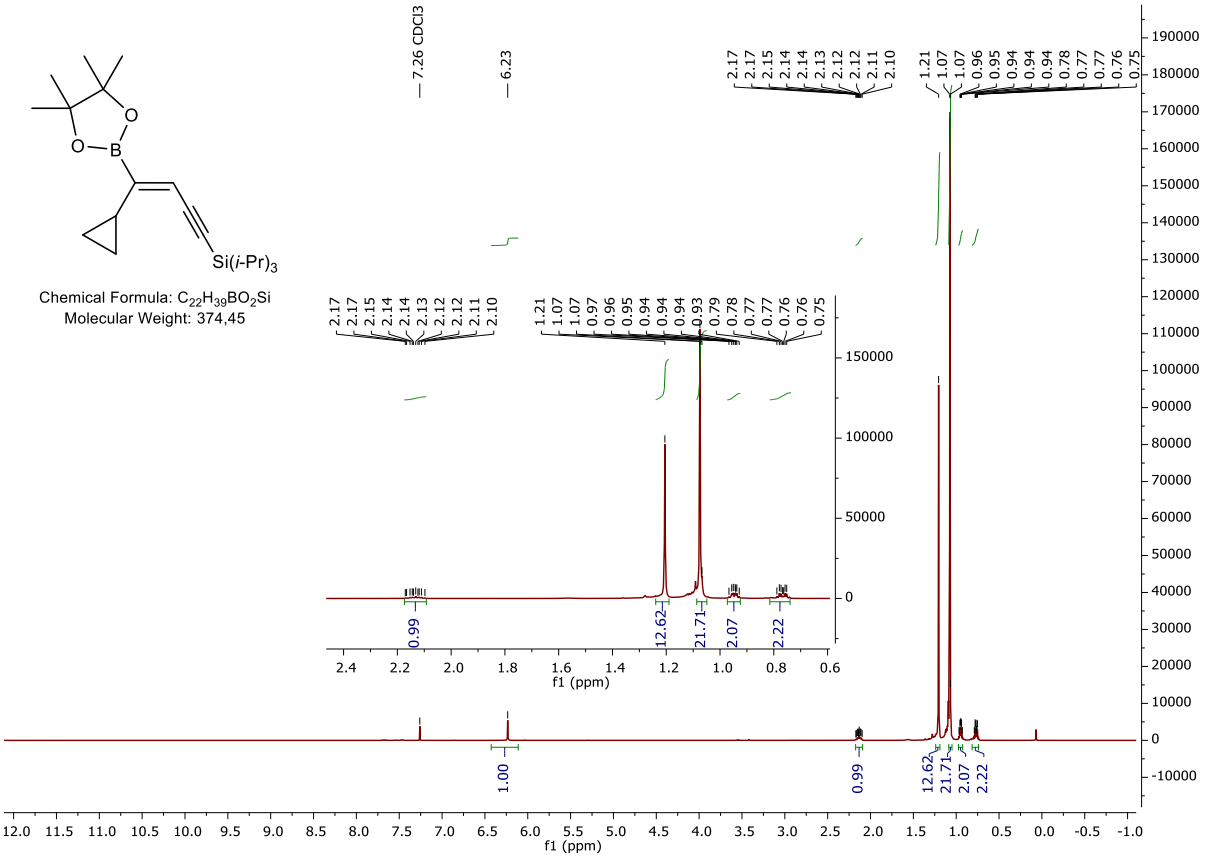


Figure S96. ^{1}H NMR spectrum of **4i**

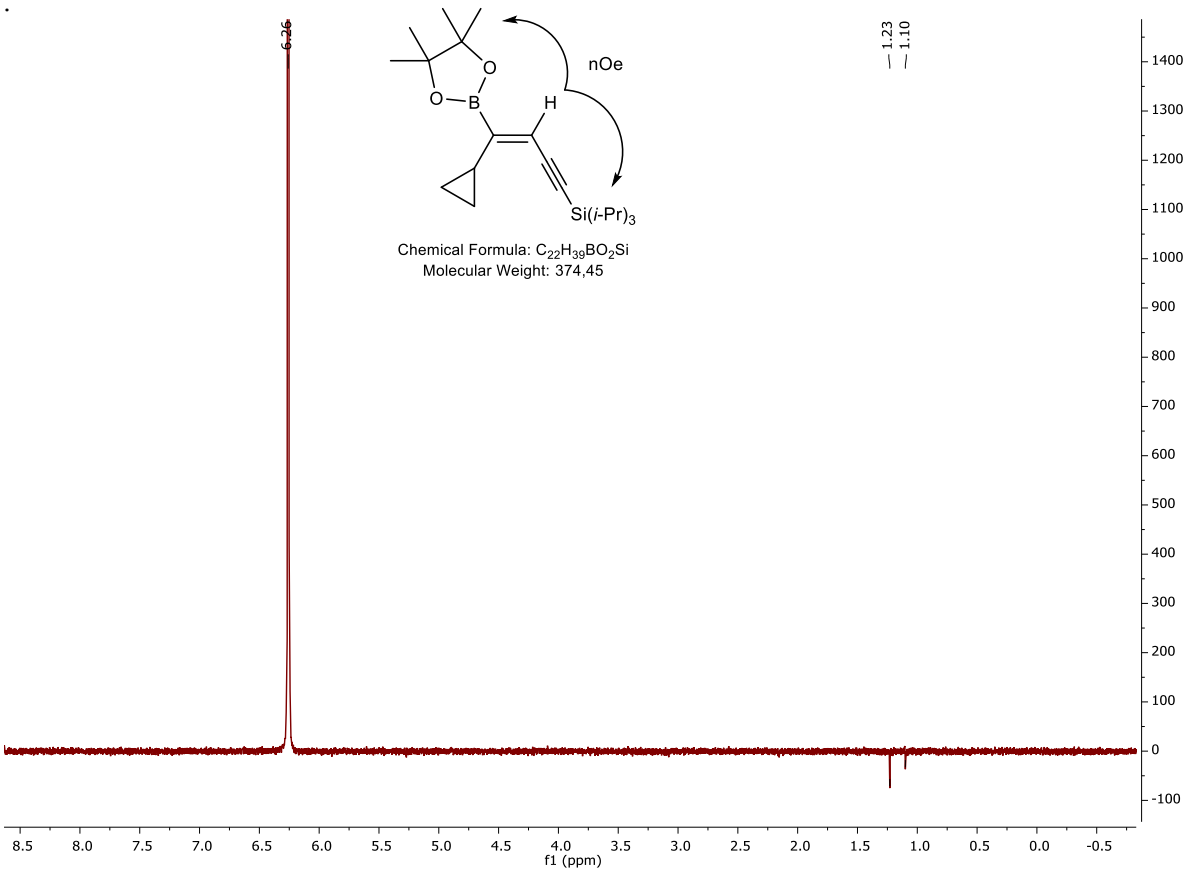


Figure S97. Selective 1D NOESY spectrum of spectrum of **4i**.; freq.: 6.26 ppm.

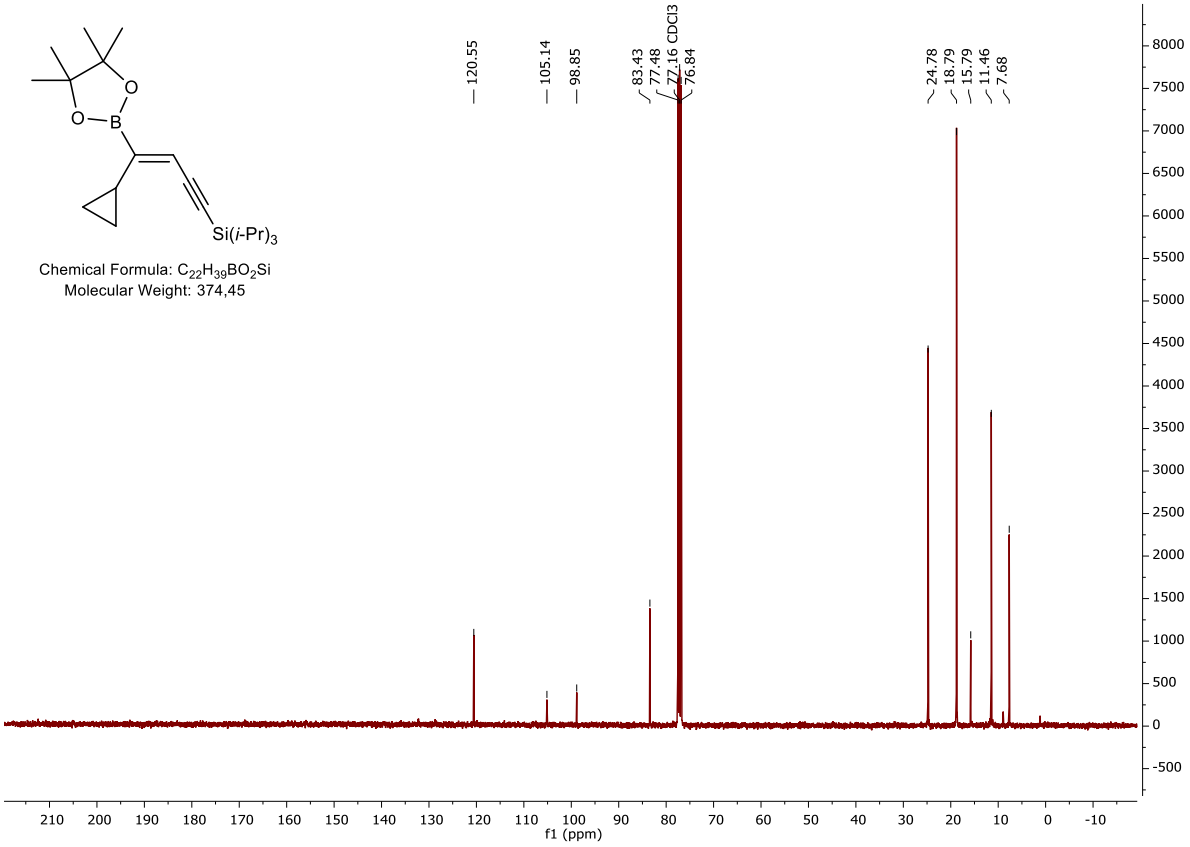


Figure S98. [11]C NMR spectrum of **4i**.

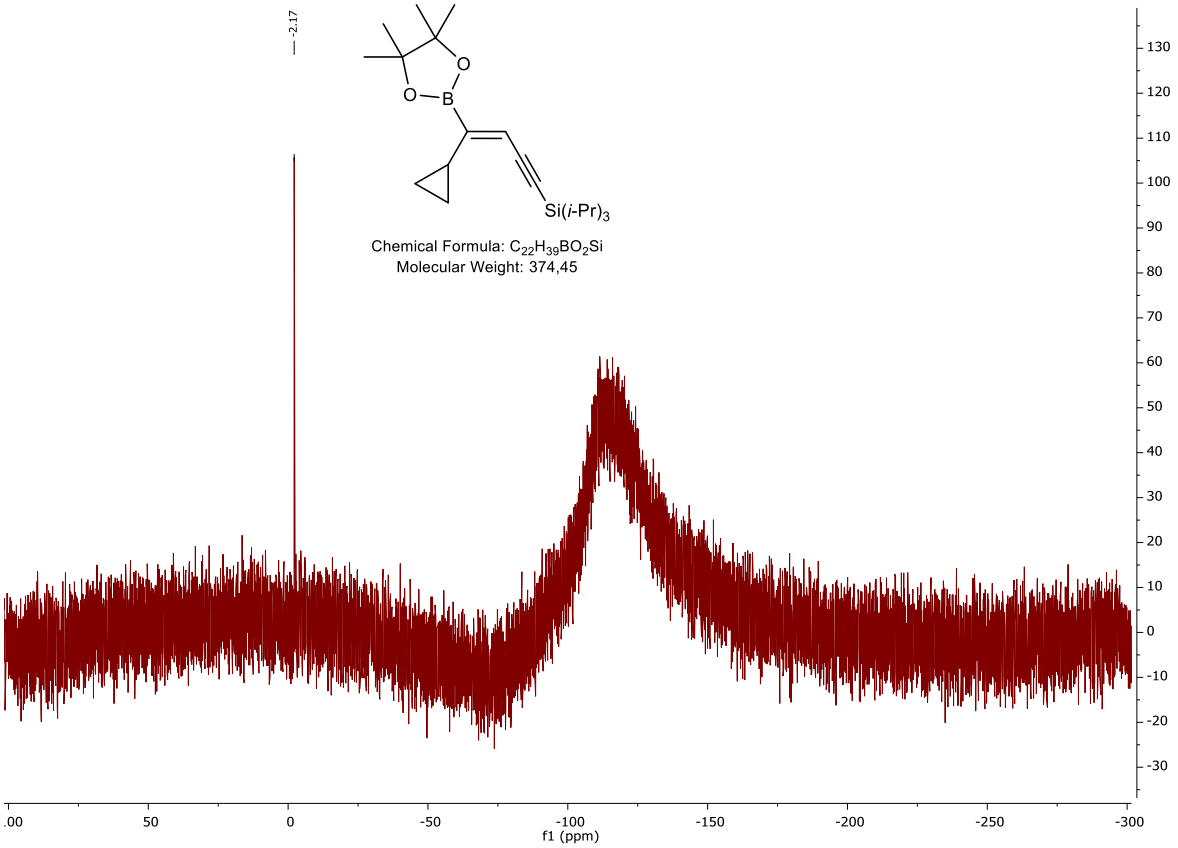


Figure S99. ^{29}Si NMR spectrum of **4i**.

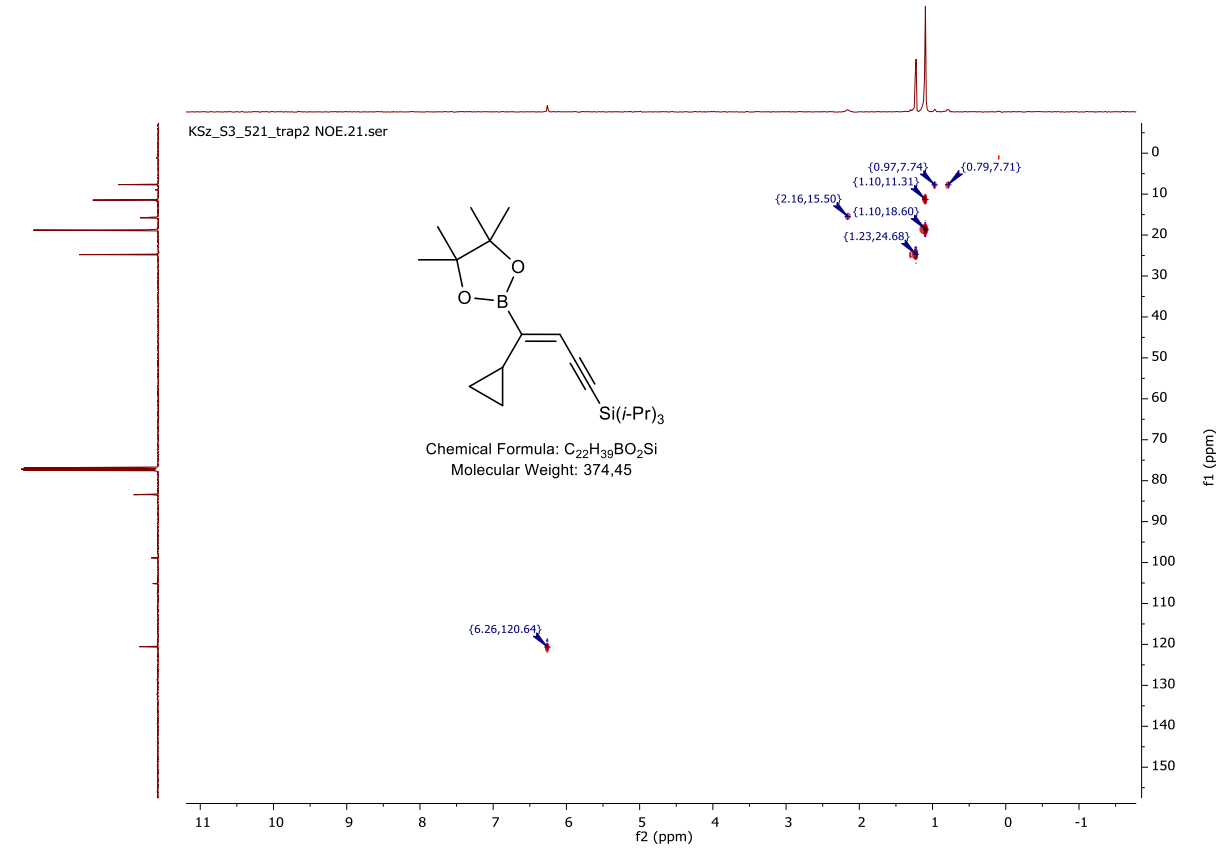


Figure S100. ^{1}H-^{13}C HSQC NMR spectrum of **4i**.

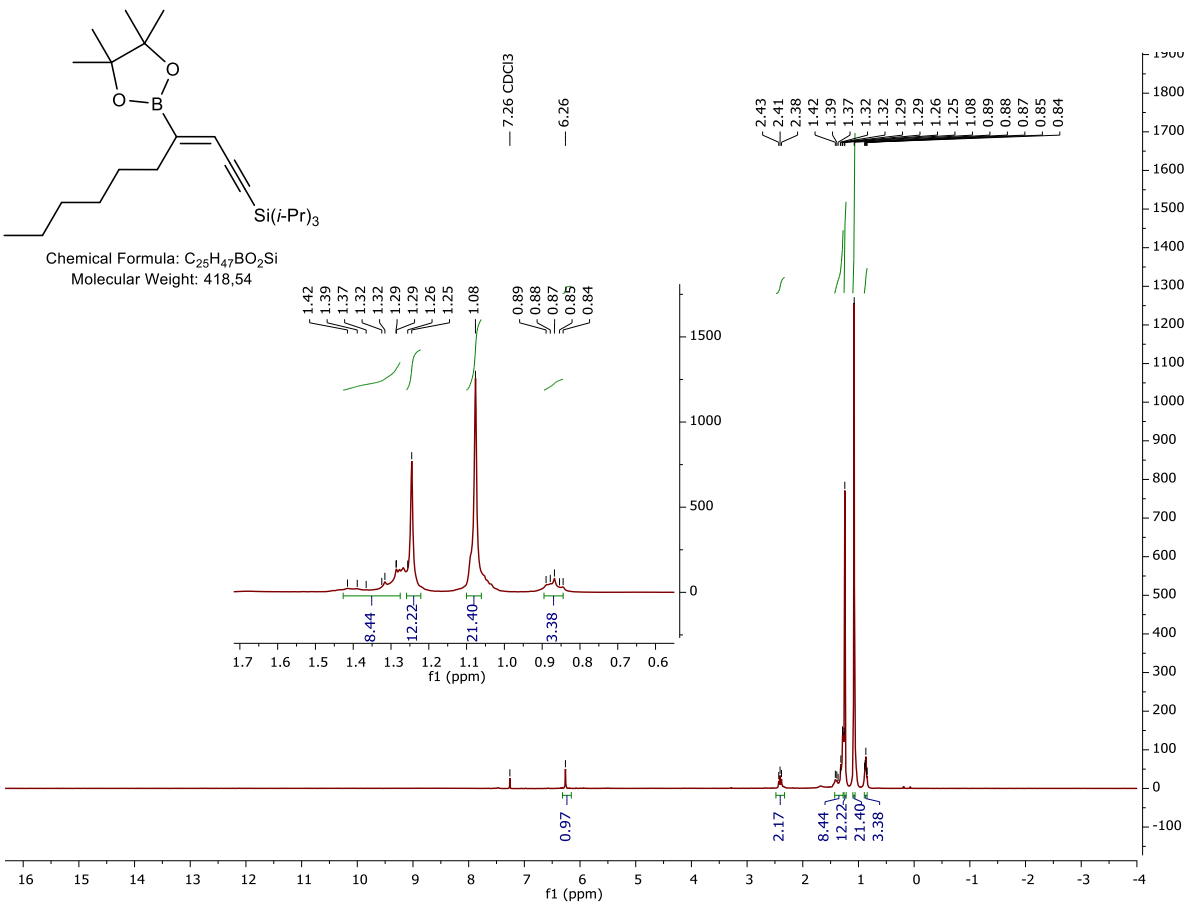


Figure S101. ^{1}H NMR spectrum of **4j**.

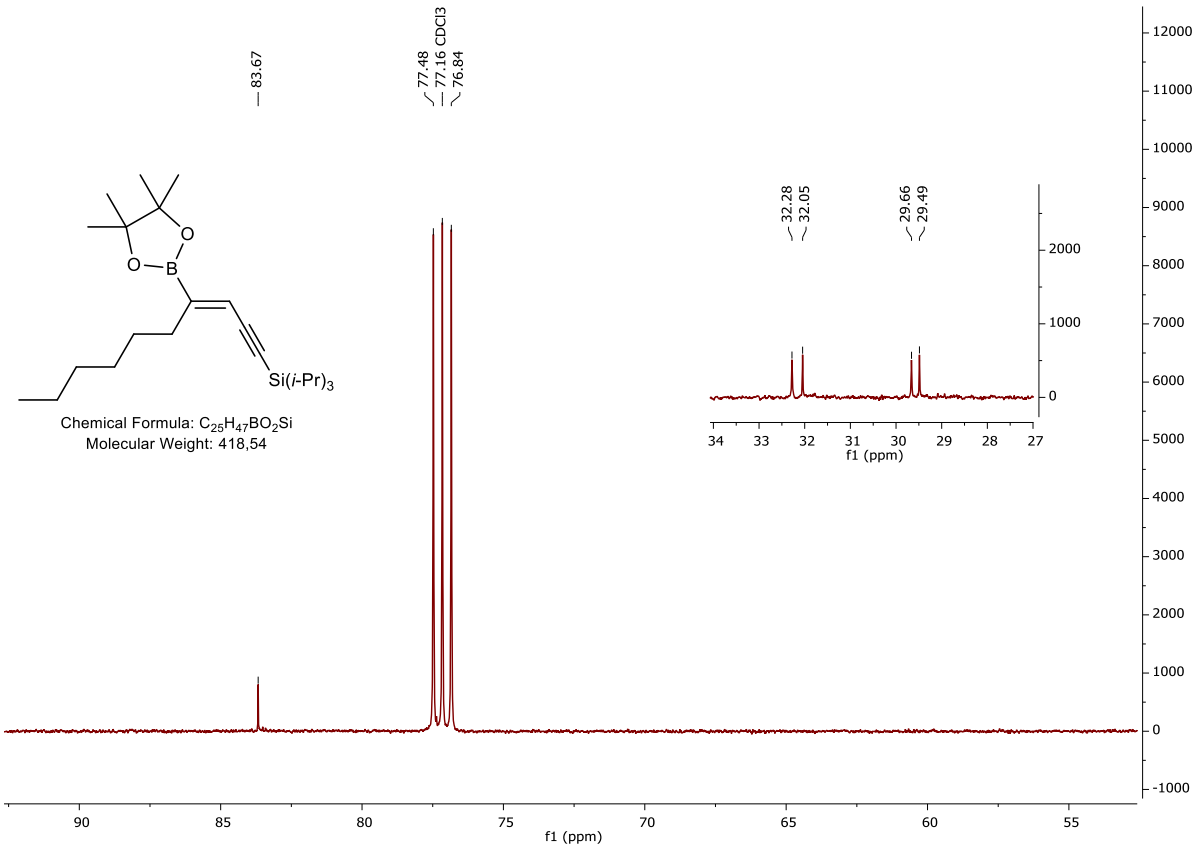


Figure S102. ^{13}C NMR spectrum of **4j**.

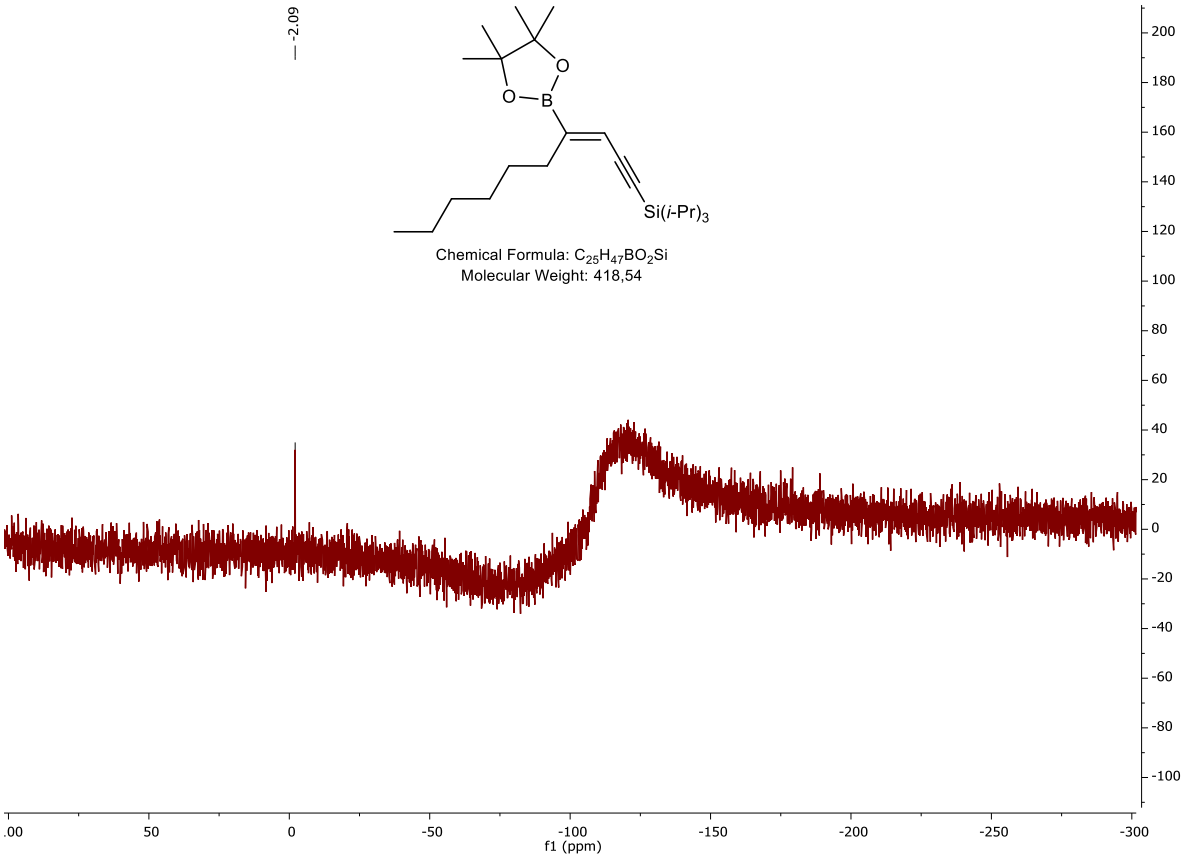


Figure S103. ^{29}Si NMR spectrum of **4j**.

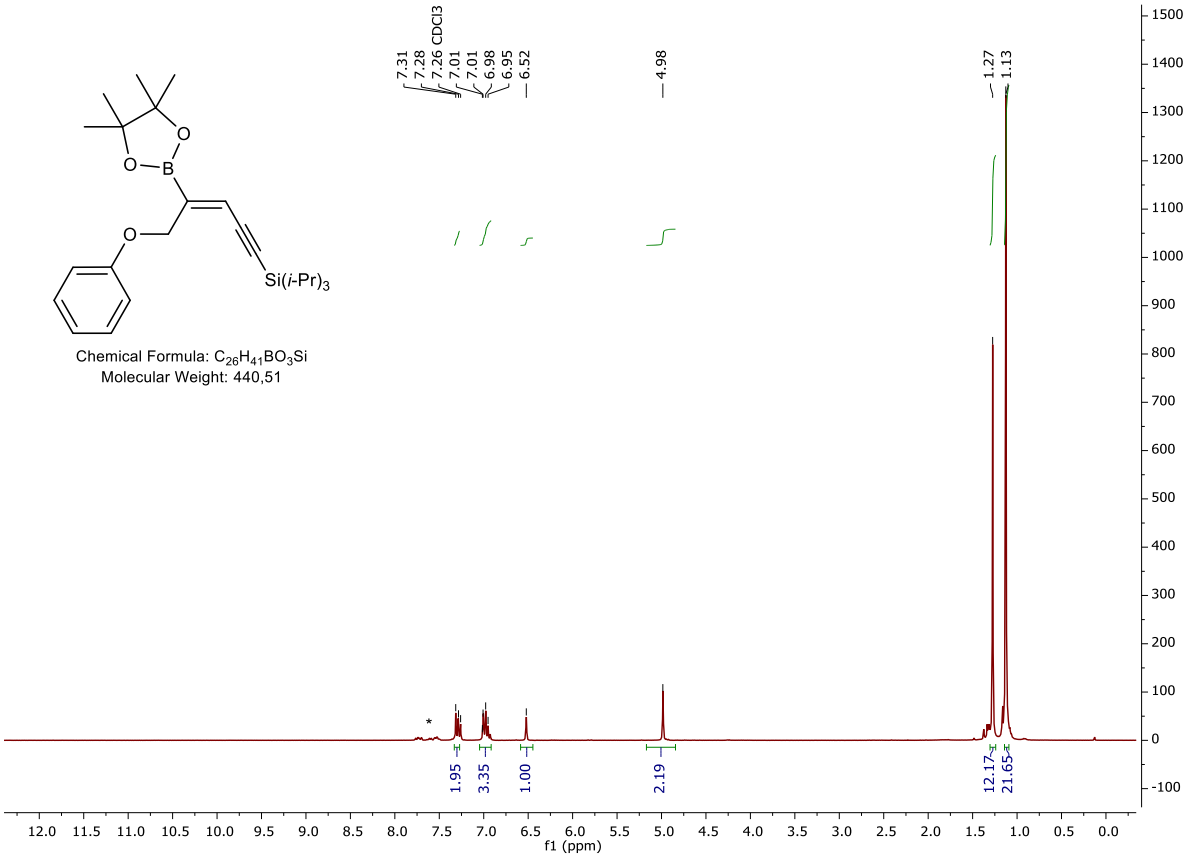


Figure S104. ^{1}H NMR spectrum **4k**; * - traces of PPh_3.

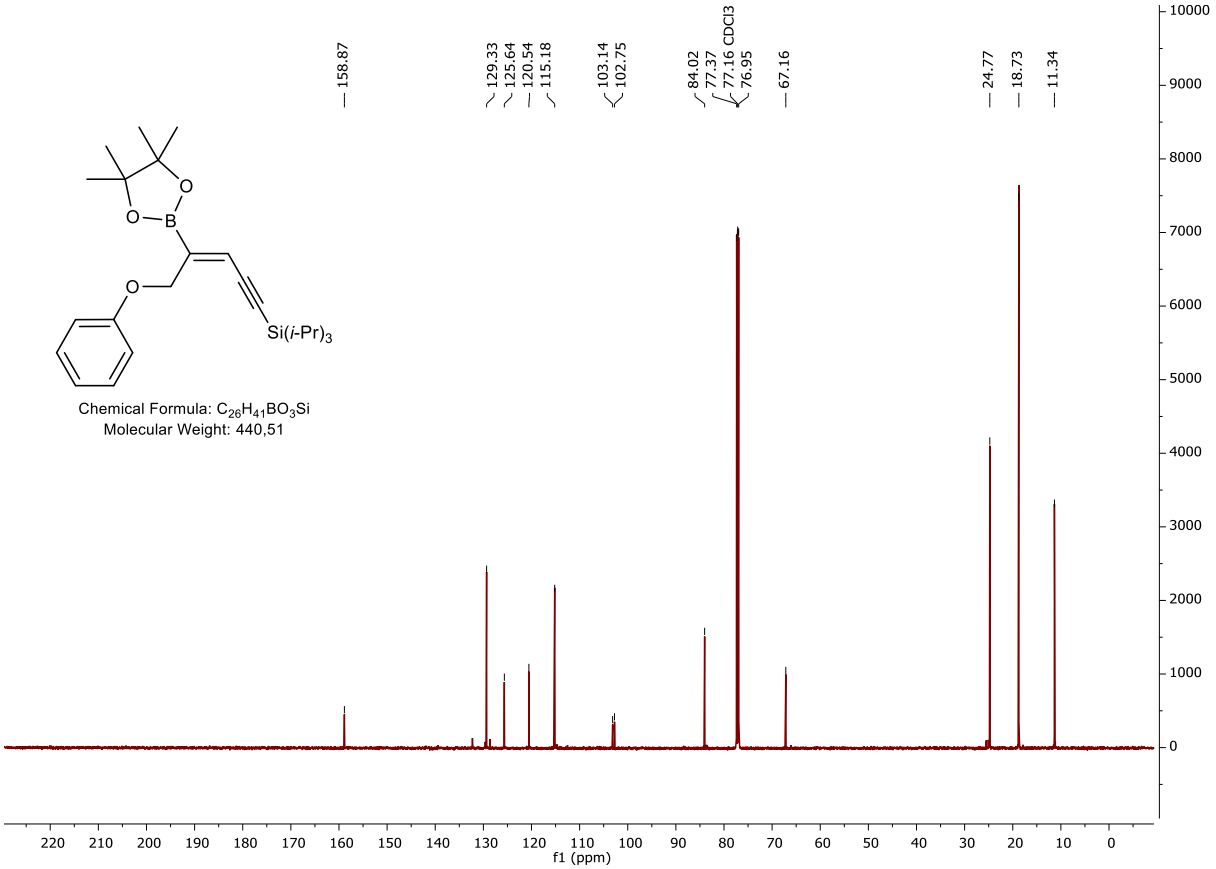


Figure S105. ^{13}C NMR spectrum of **4k**.

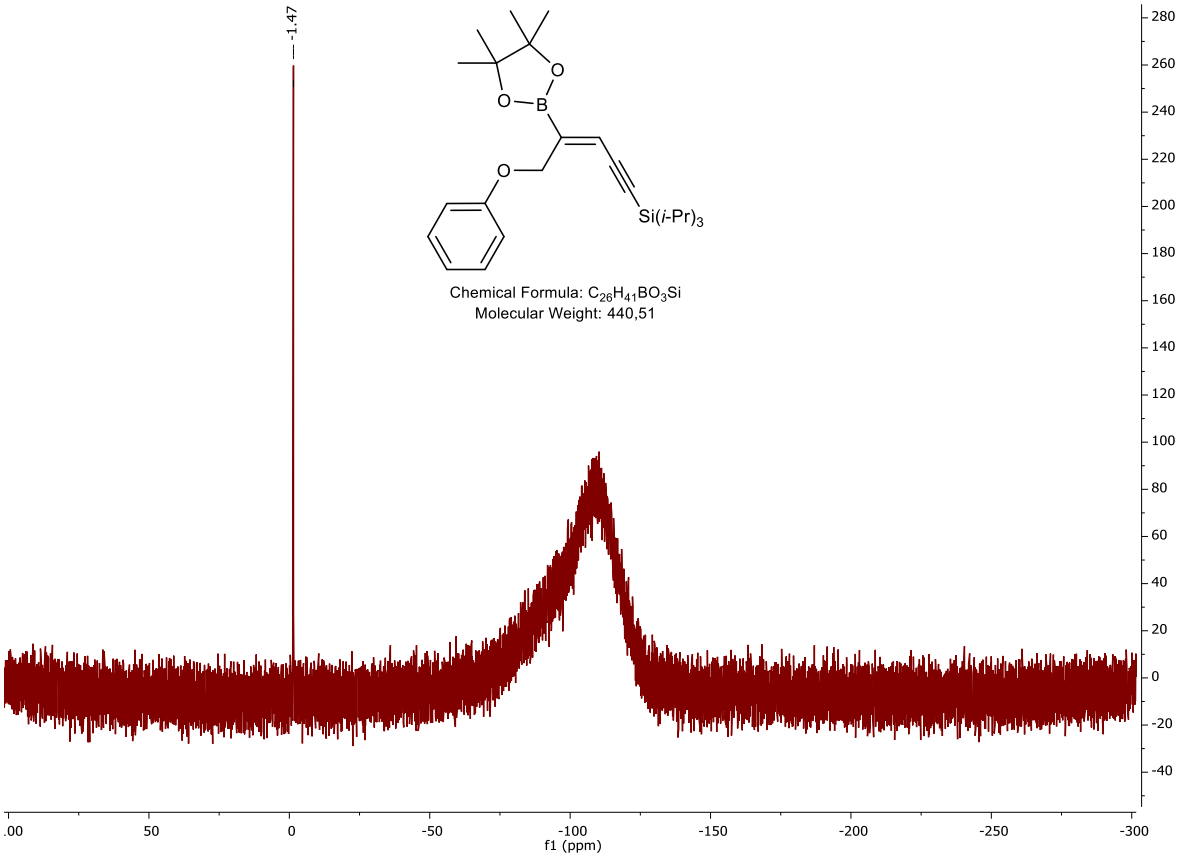


Figure S106. ^{29}Si NMR spectrum of **4k**.

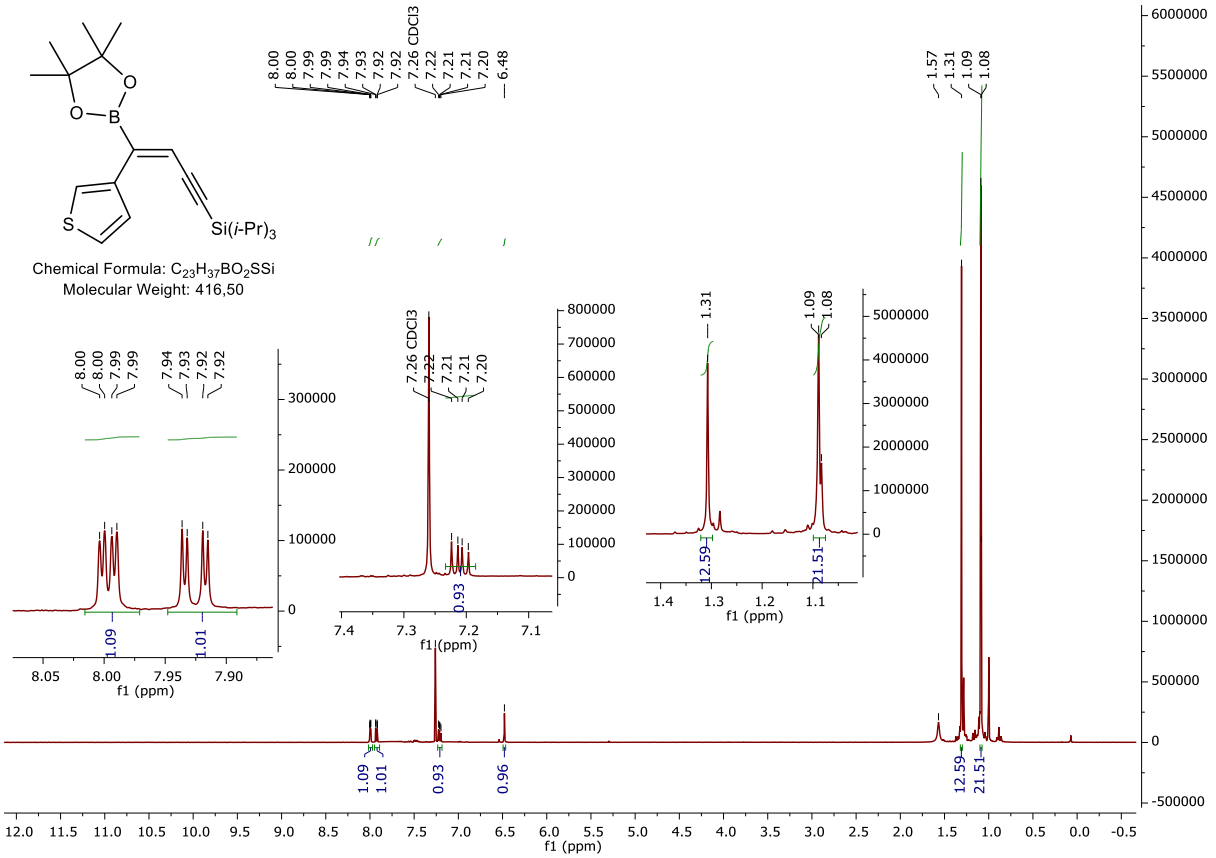


Figure S107. ^{1}H NMR spectrum of **4l**.

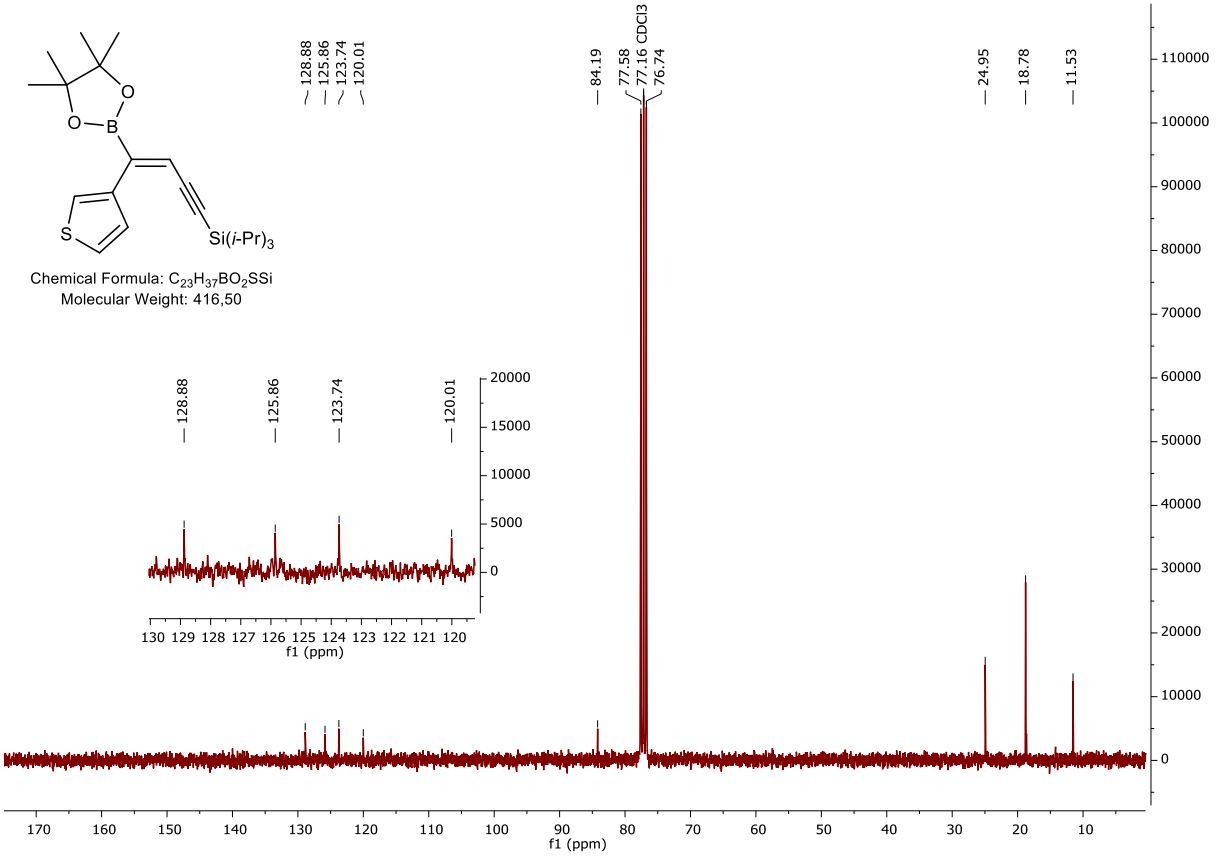


Figure S108. ^{13}C NMR spectrum of **4l**.

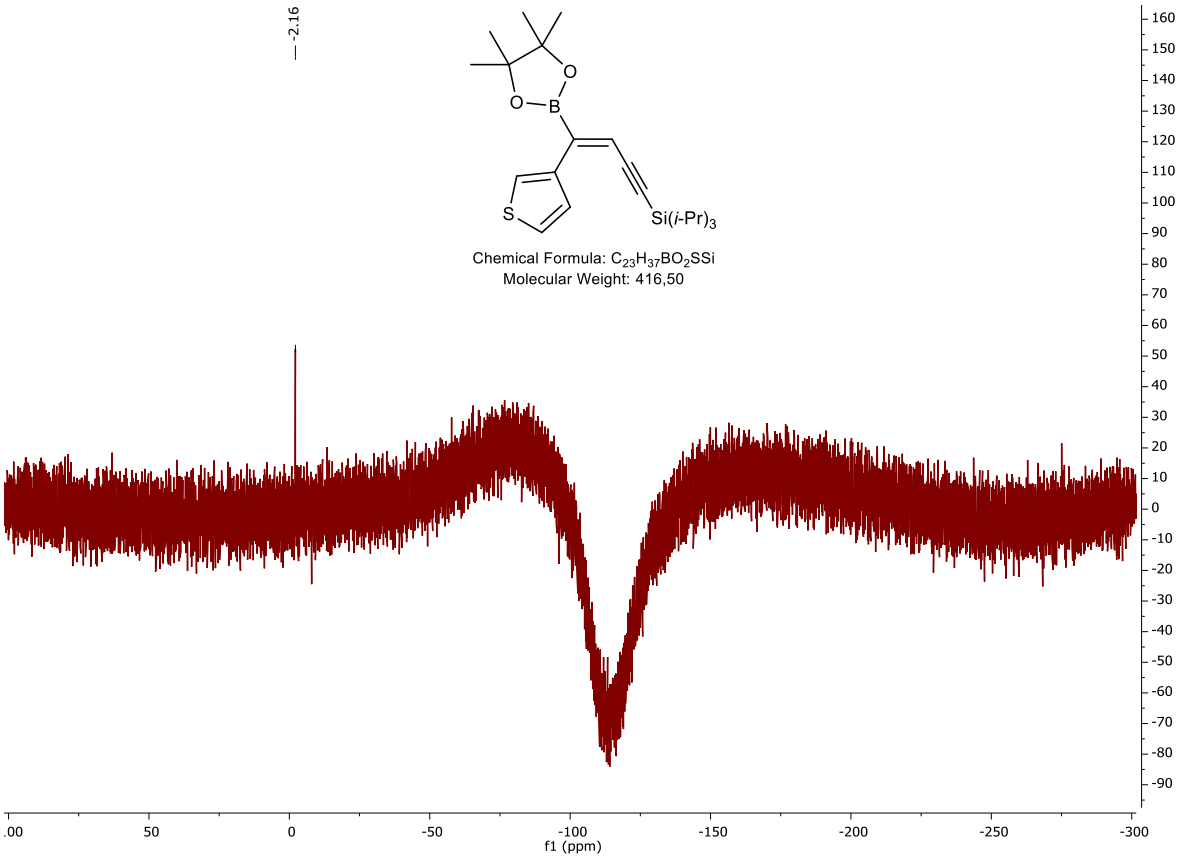


Figure S109. ^{29}Si NMR spectrum of **4l**.

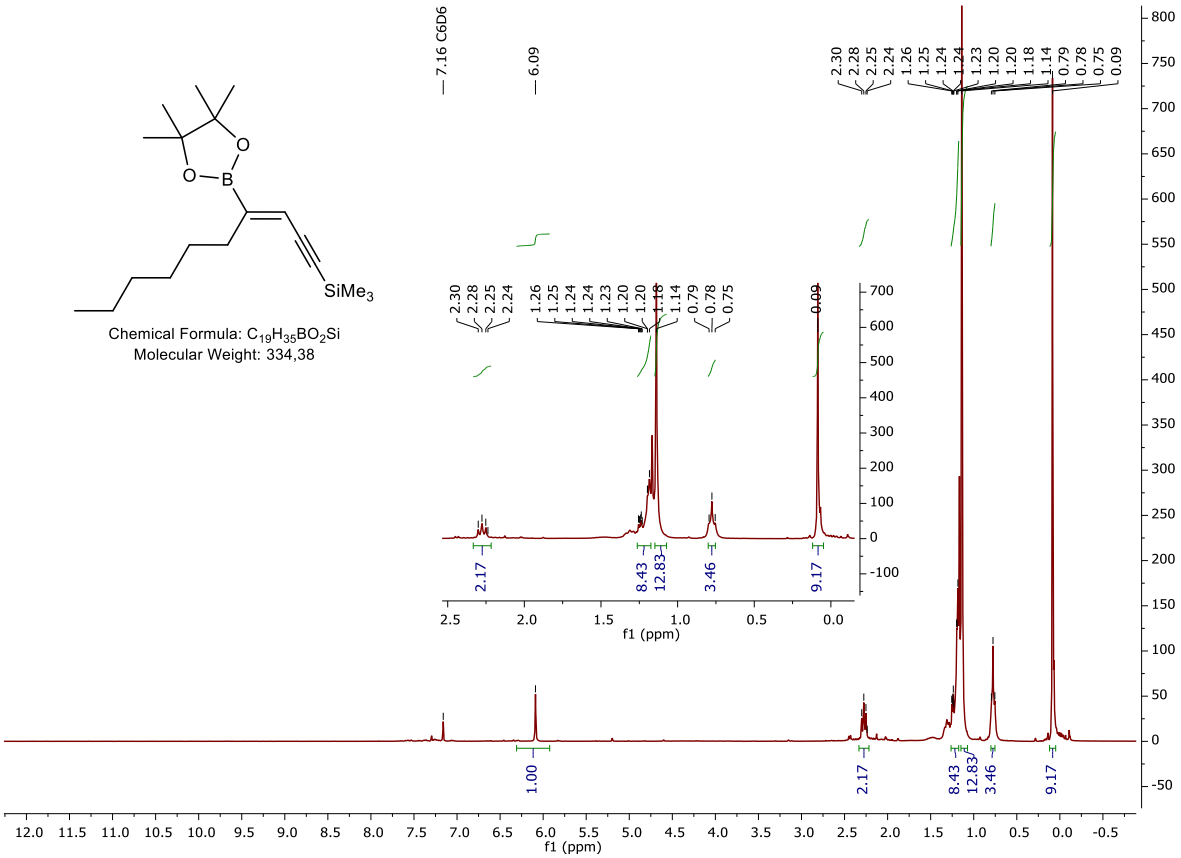


Figure S110. ^{1}H NMR spectrum of **4m**.

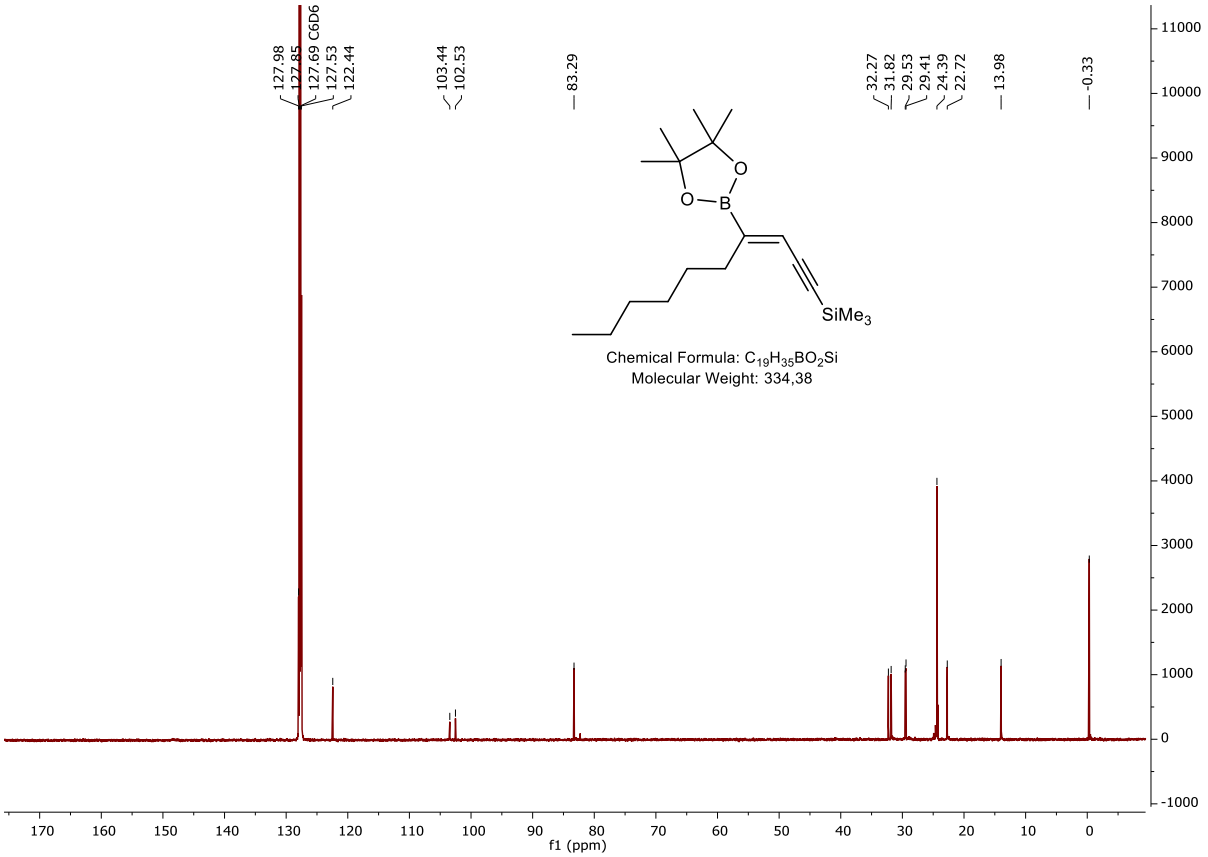


Figure S111. ^{13}C NMR spectrum of **4m**.

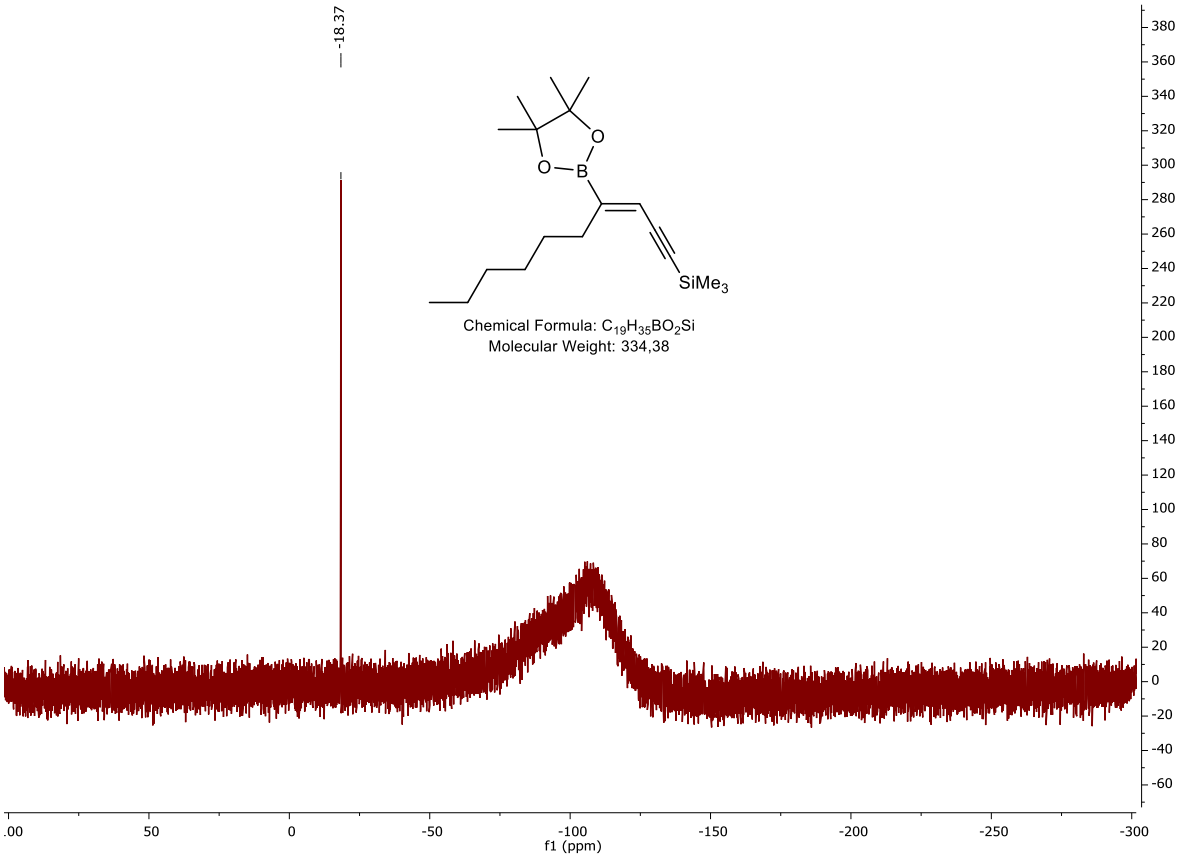


Figure S112. ^{29}Si NMR spectrum of **4m**.

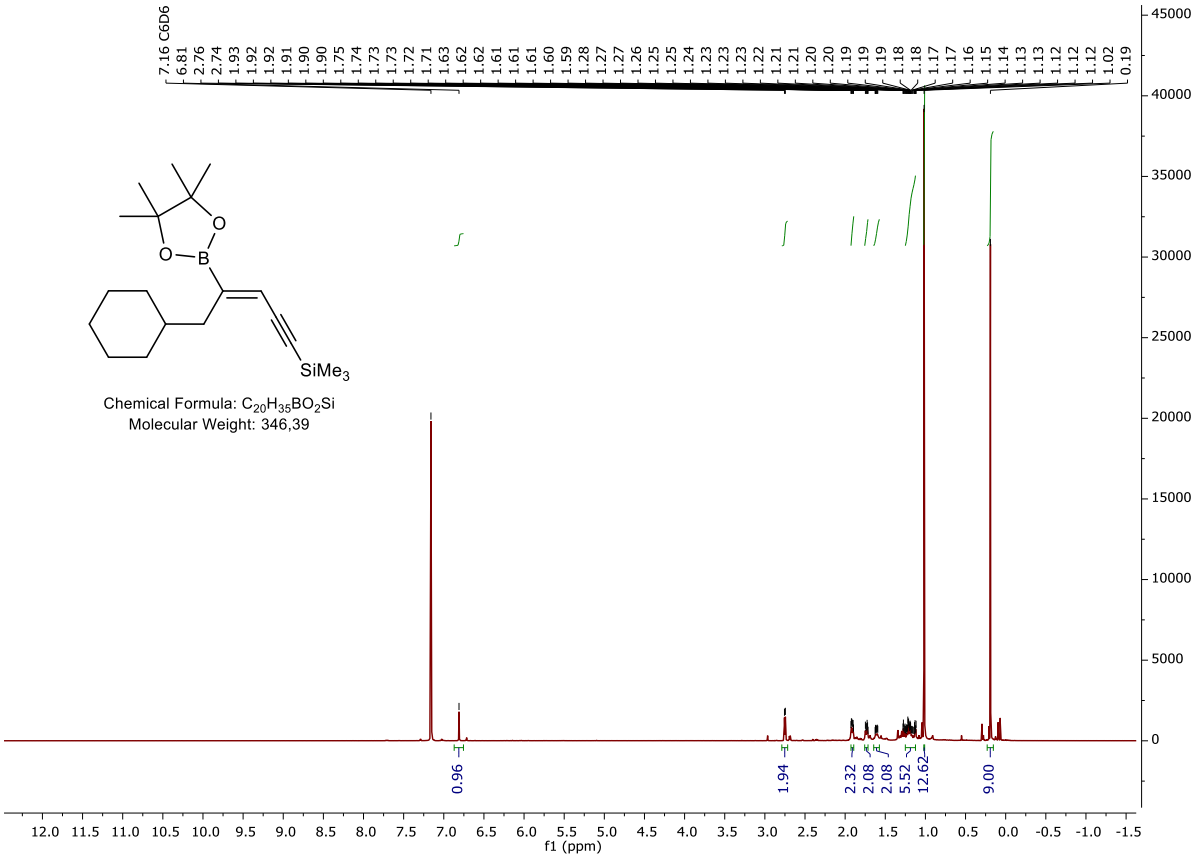


Figure S113. ^{1}H NMR spectrum of **4n**.

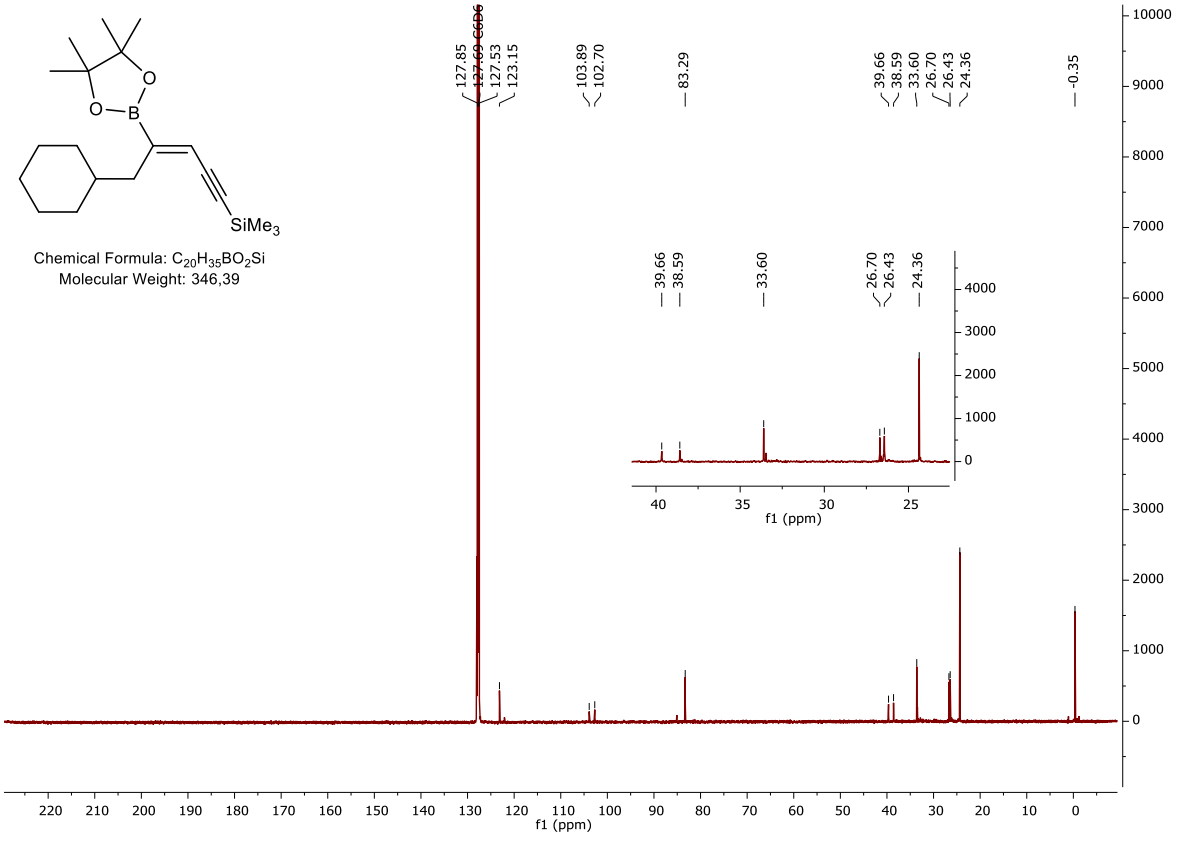


Figure S114. ^{13}C NMR spectrum of **4n**.

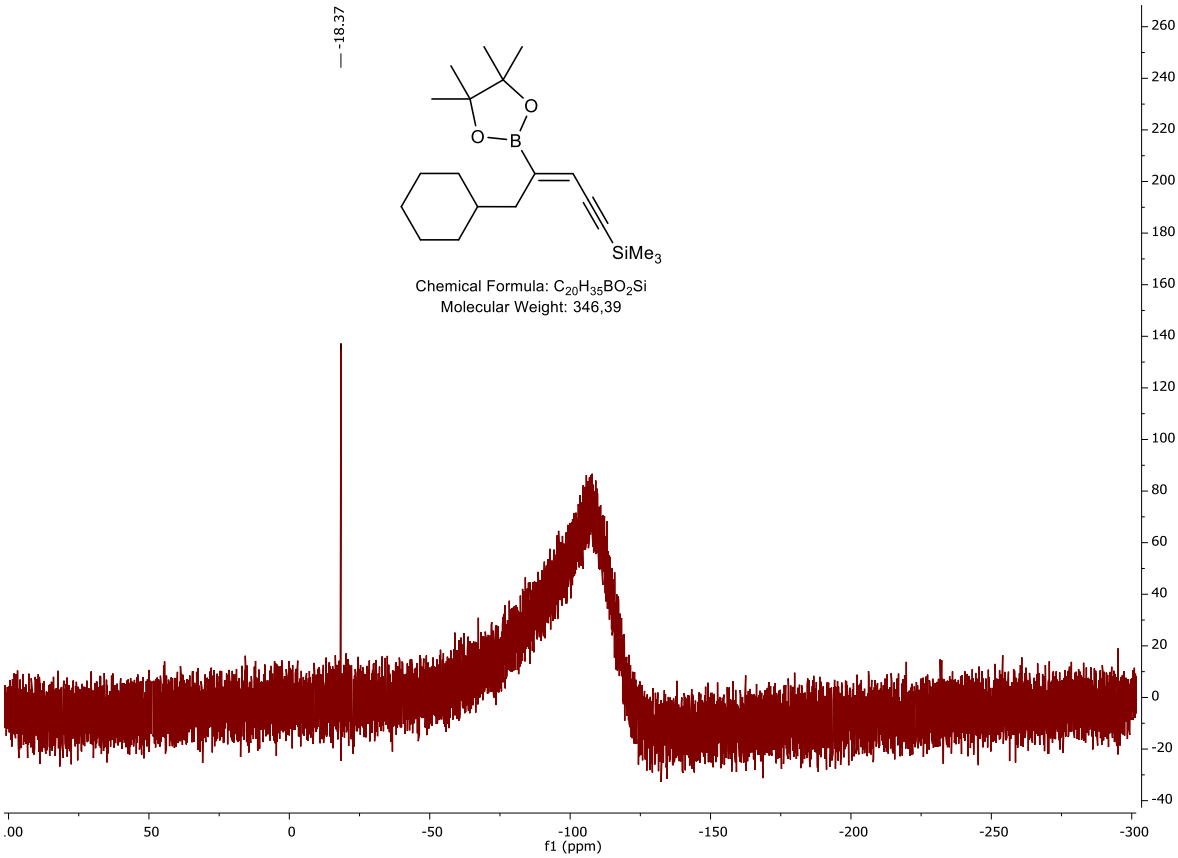


Figure S115. ^{29}Si NMR spectrum of **4n**.

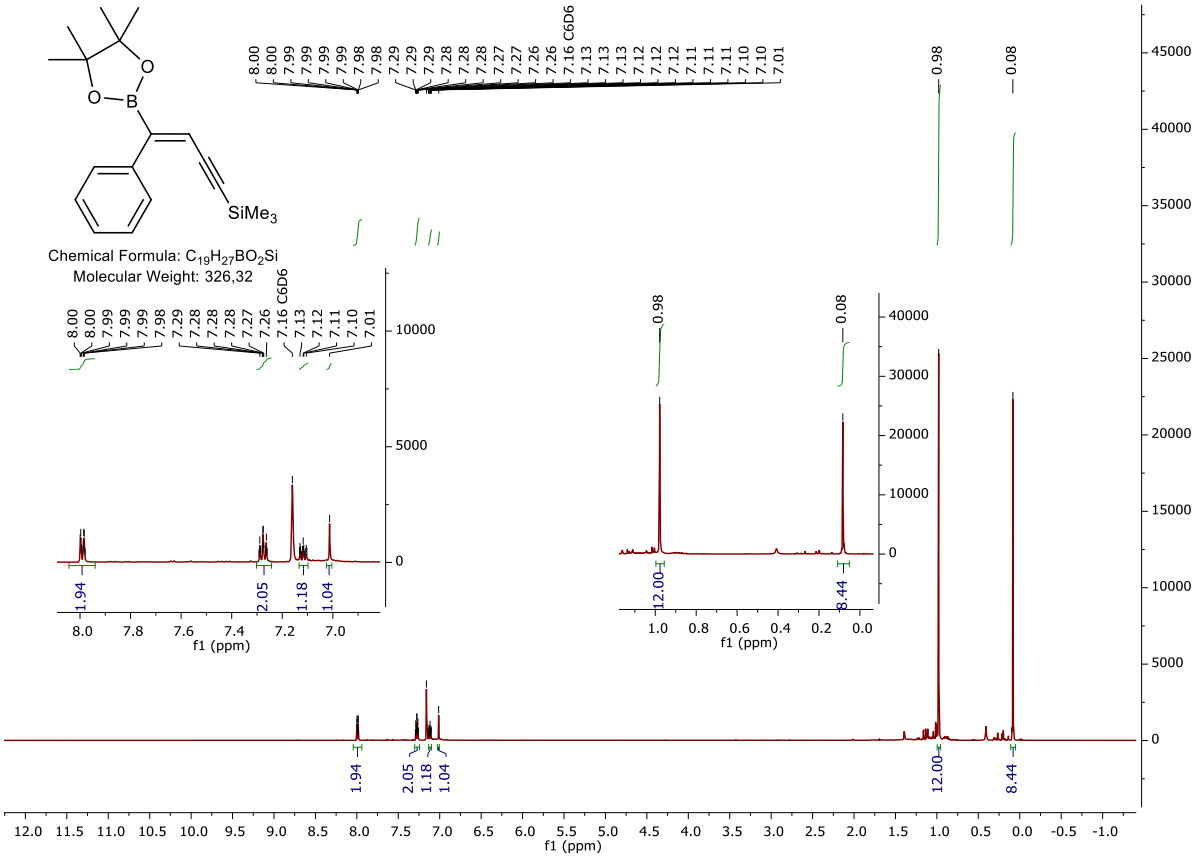


Figure S116. ^{1}H NMR spectrum of **4o**.

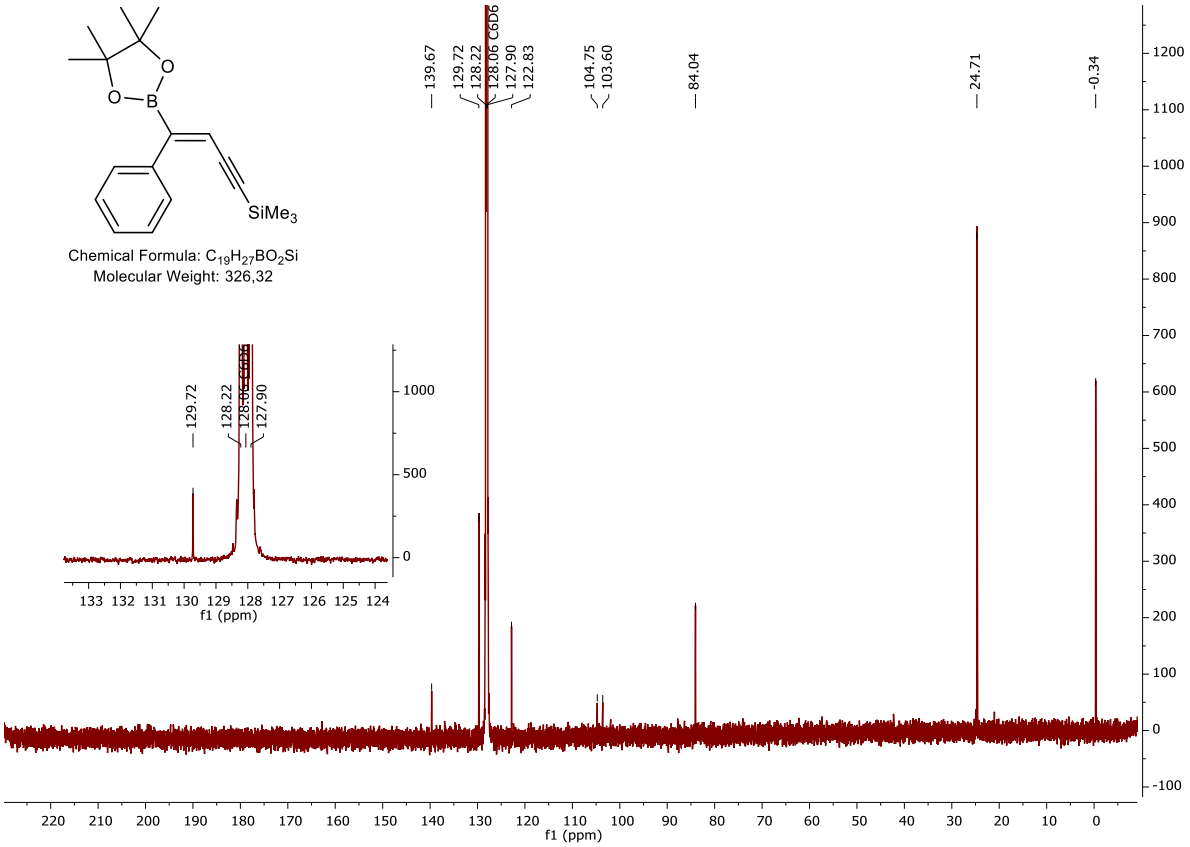


Figure S117. ^{13}C NMR spectrum of **4o**.

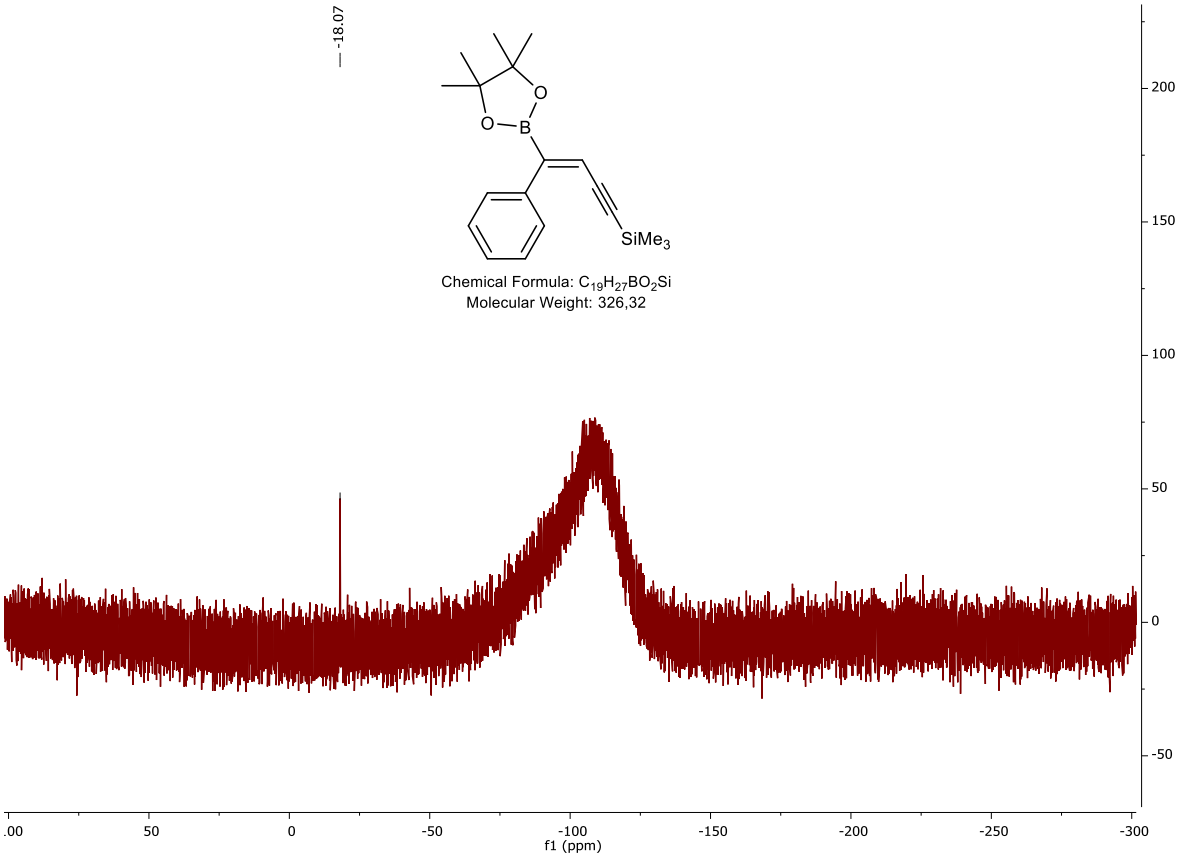


Figure S118. ^{29}Si NMR spectrum of **4o**.

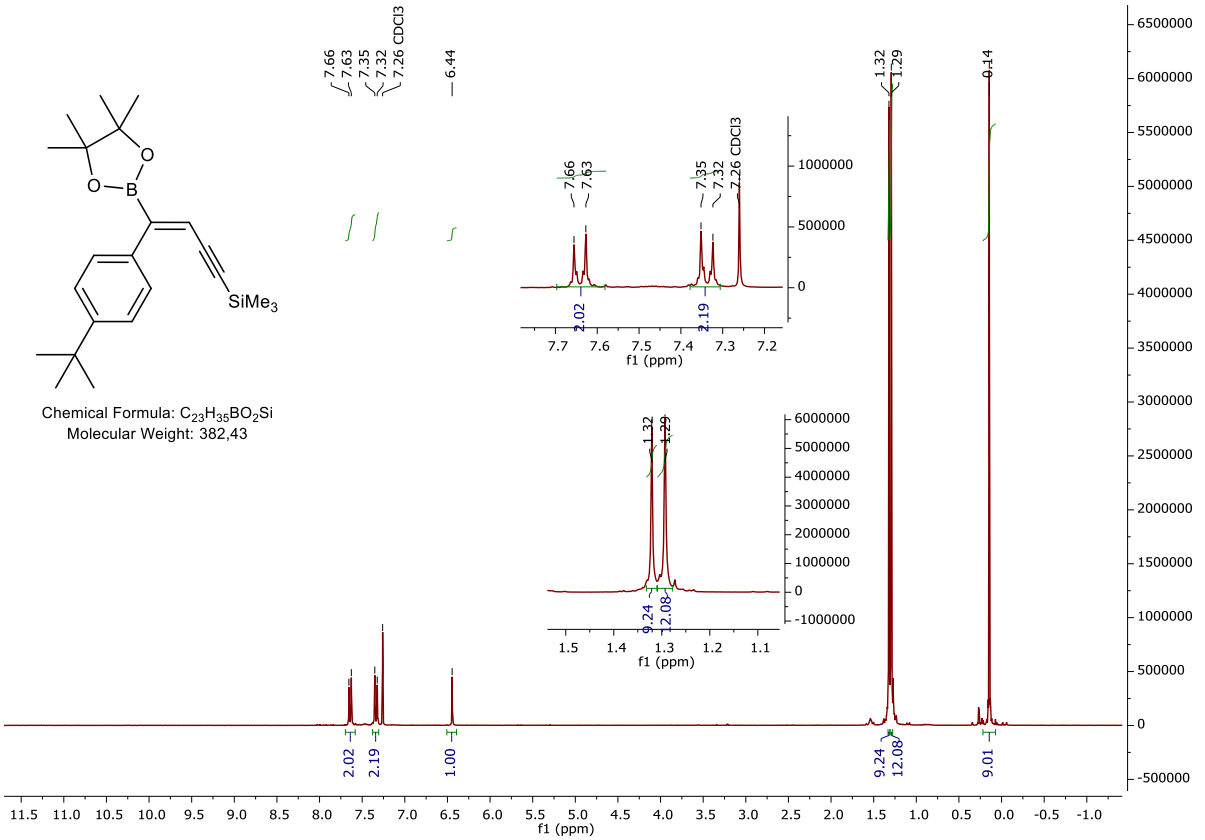


Figure S119. ^{1}H NMR spectrum of **4p**.

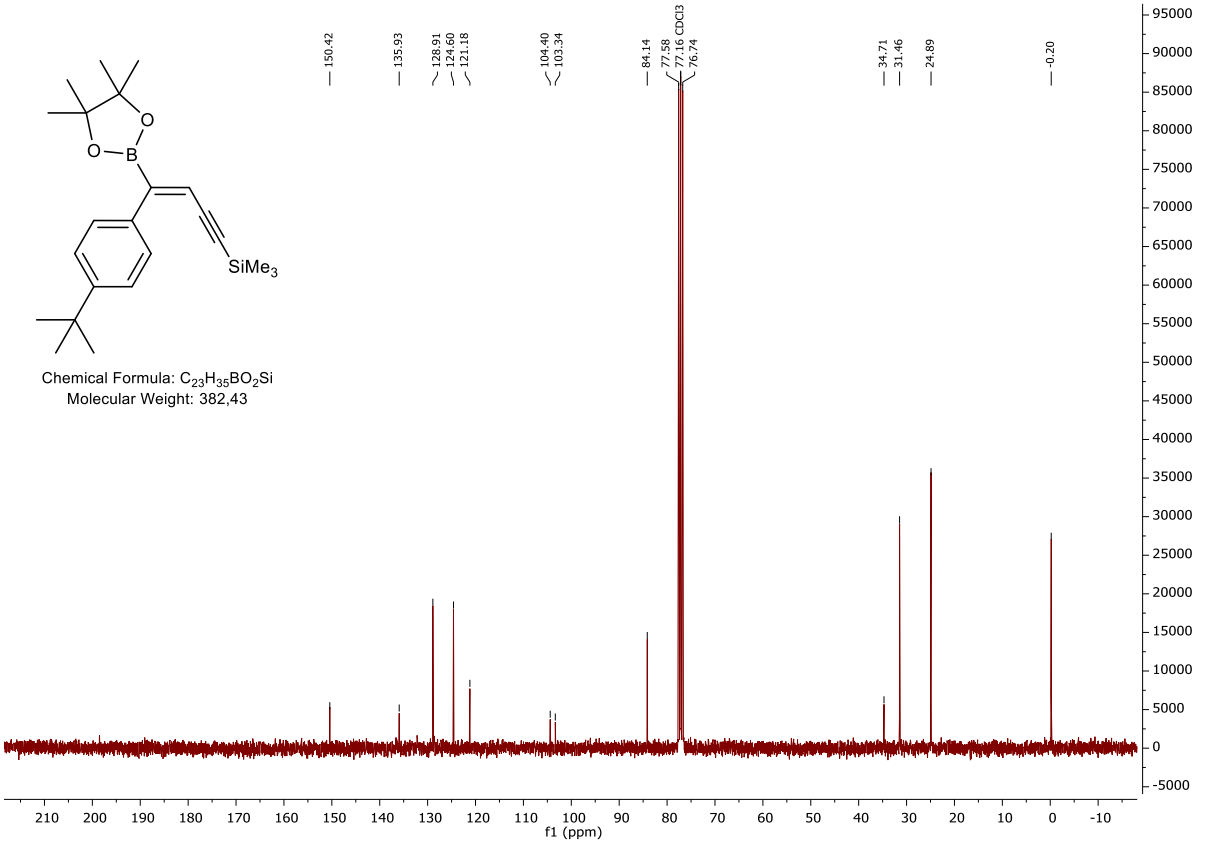


Figure S120. ^{13}C NMR spectrum of **4p**.

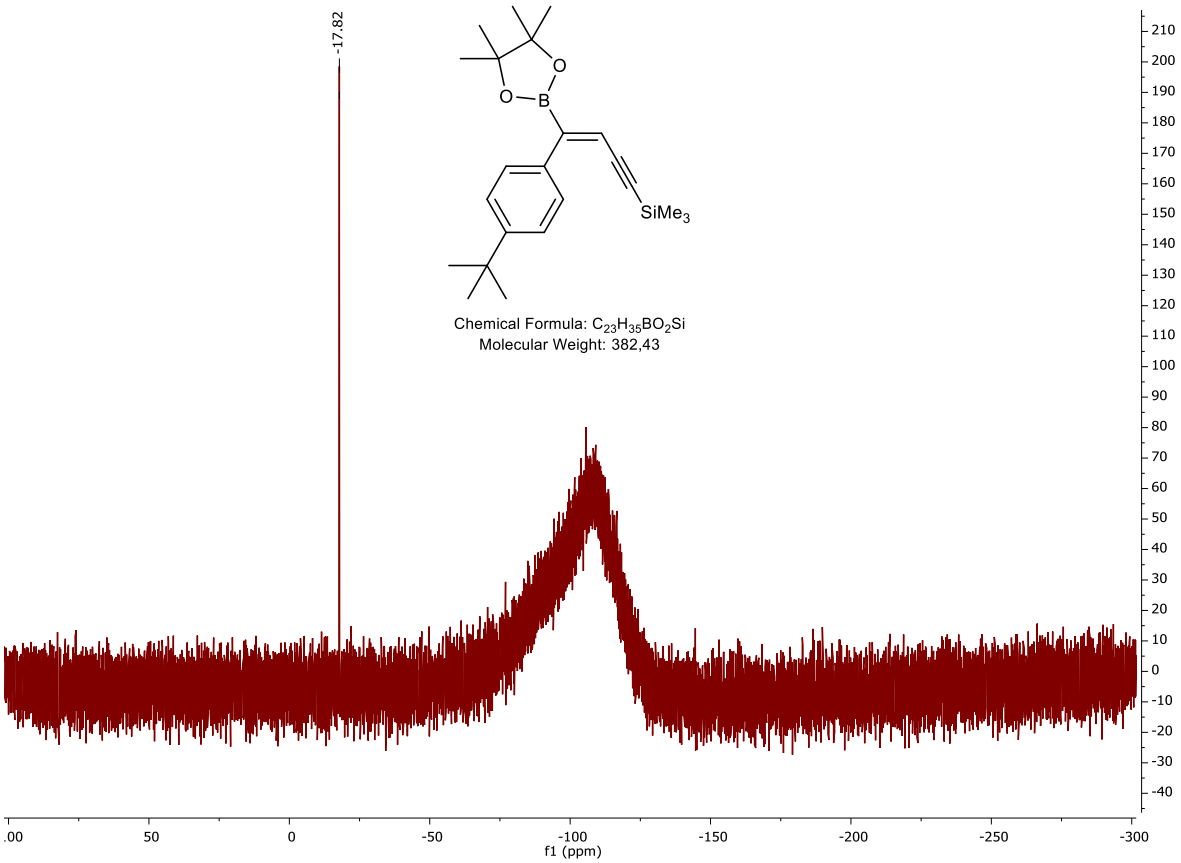


Figure S121. ^{29}Si NMR spectrum of **4p**.

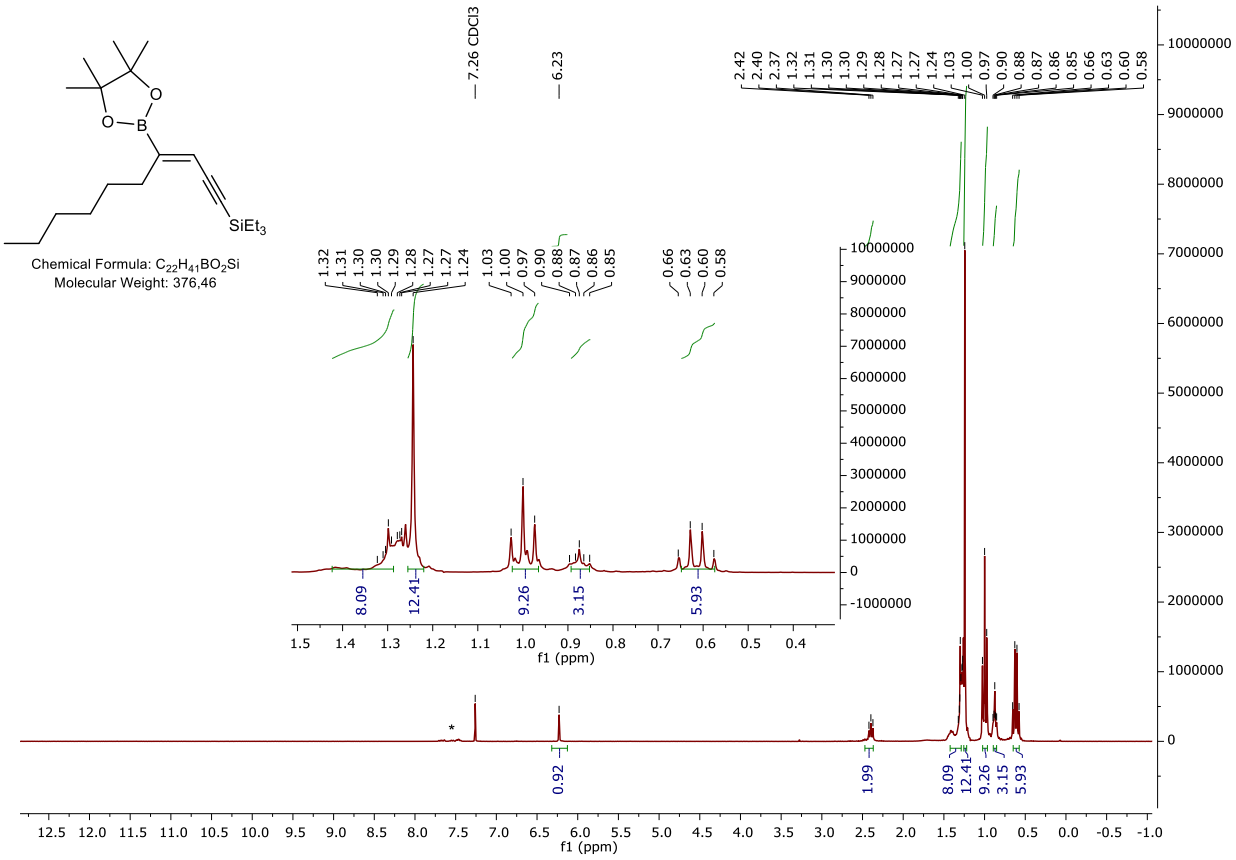


Figure S122. ^{1}H NMR spectrum of **4q**.

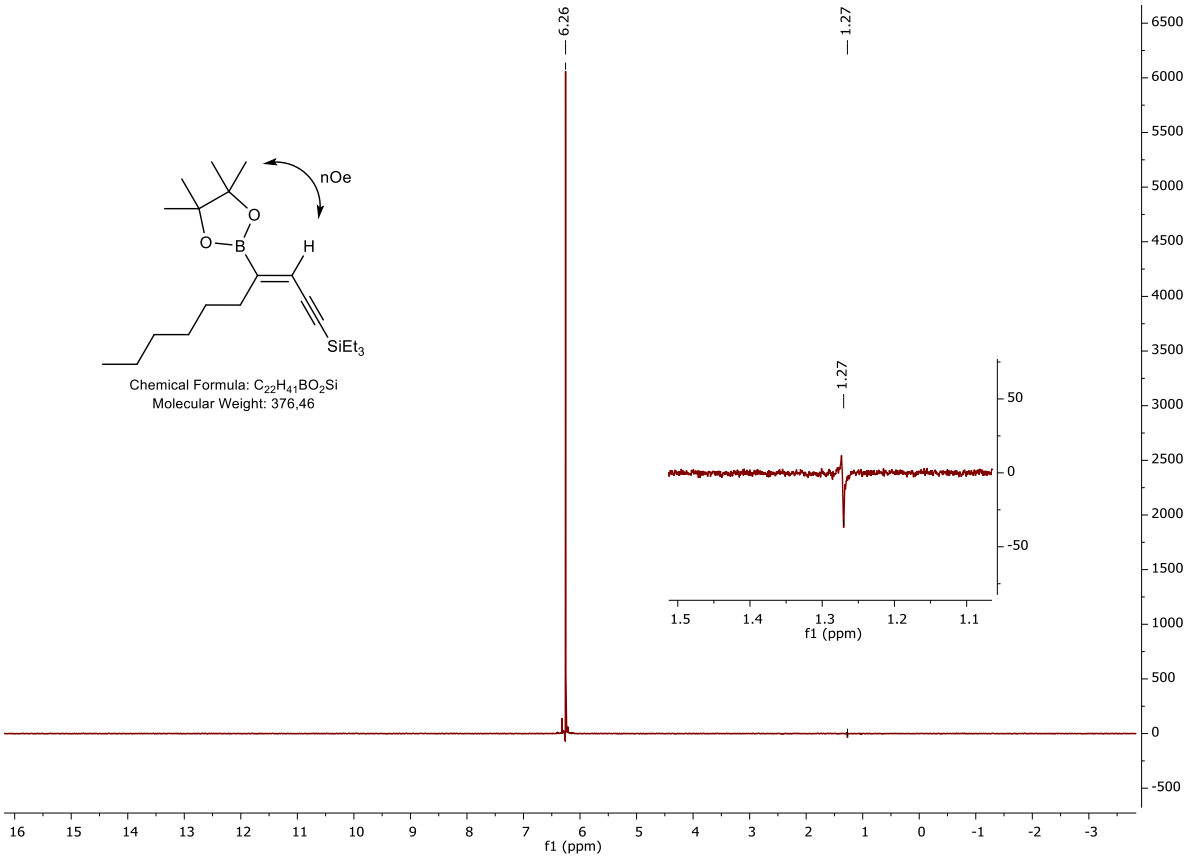


Figure S123. Selective 1D NOESY spectrum of **4q**; freq.: 6.26 ppm.

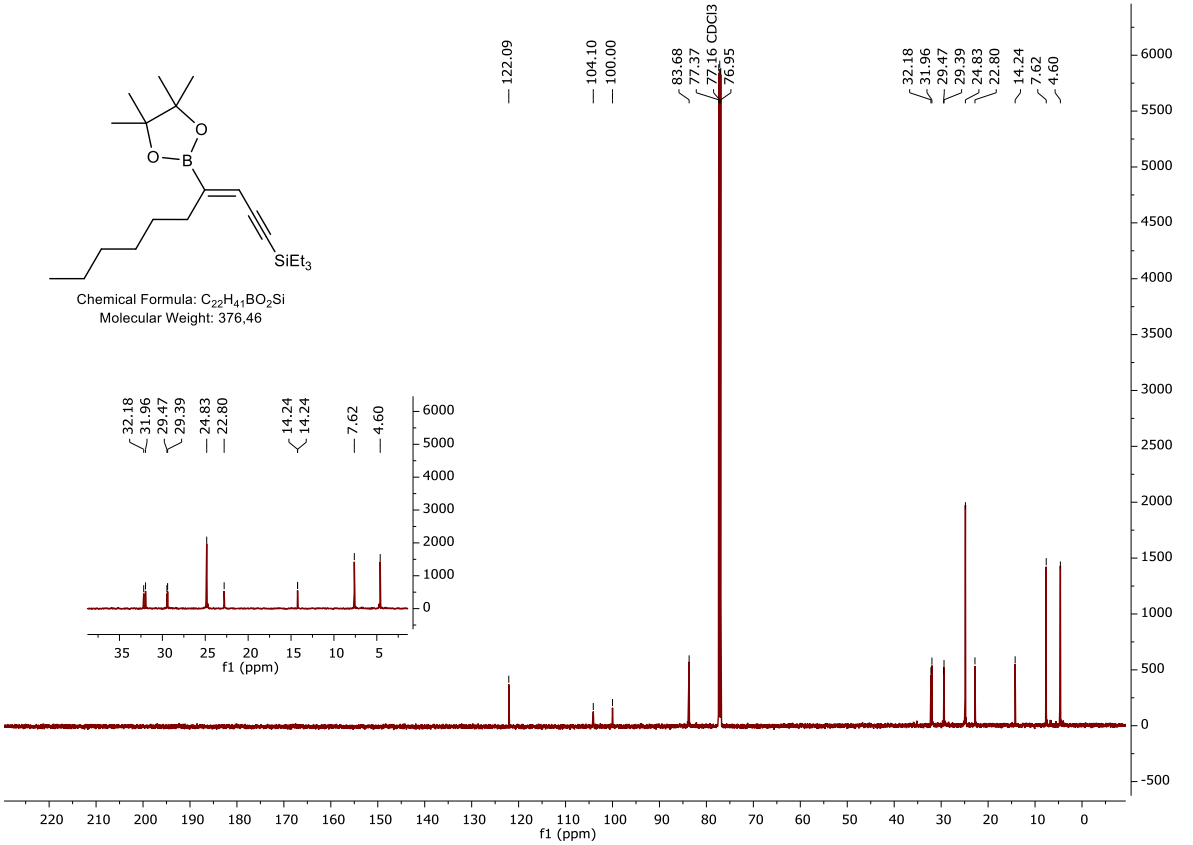


Figure S124. ^{13}C NMR spectrum of **4q**.

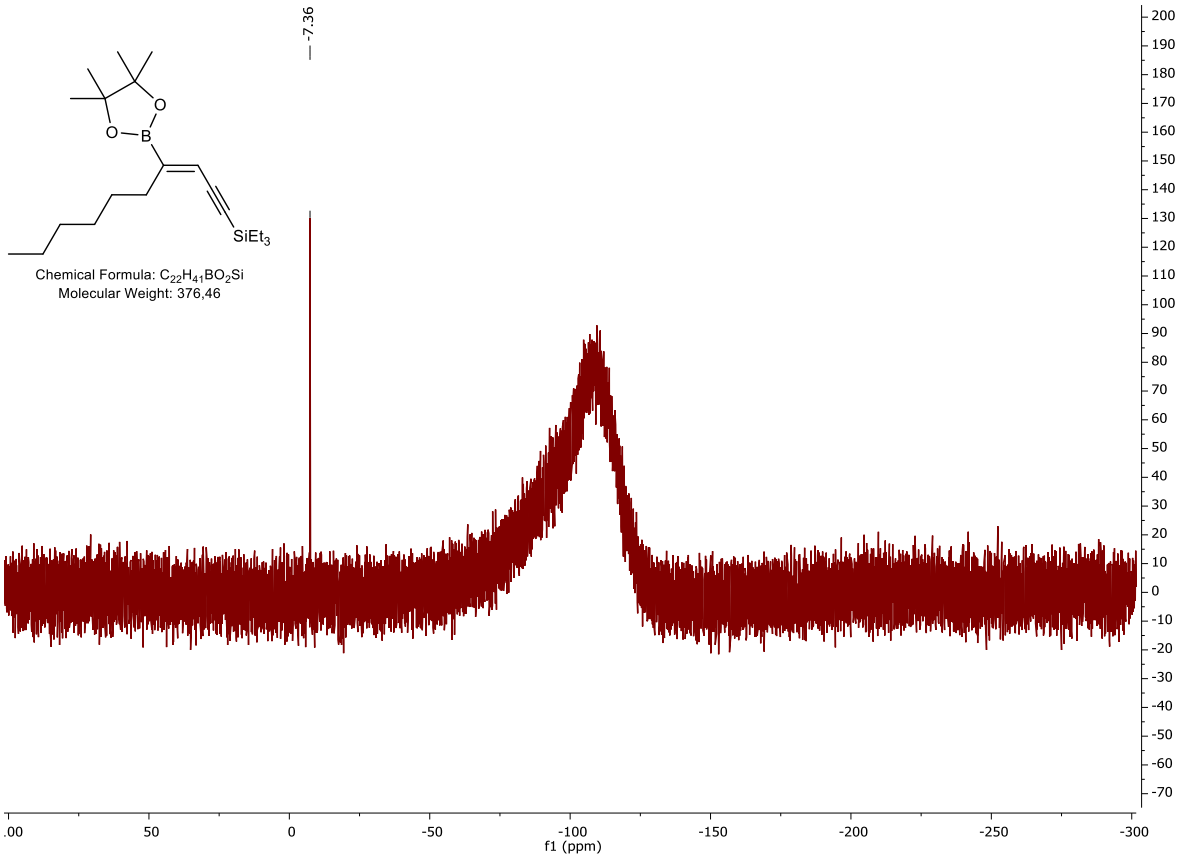


Figure S125. ^{29}Si NMR spectrum of **4q**.

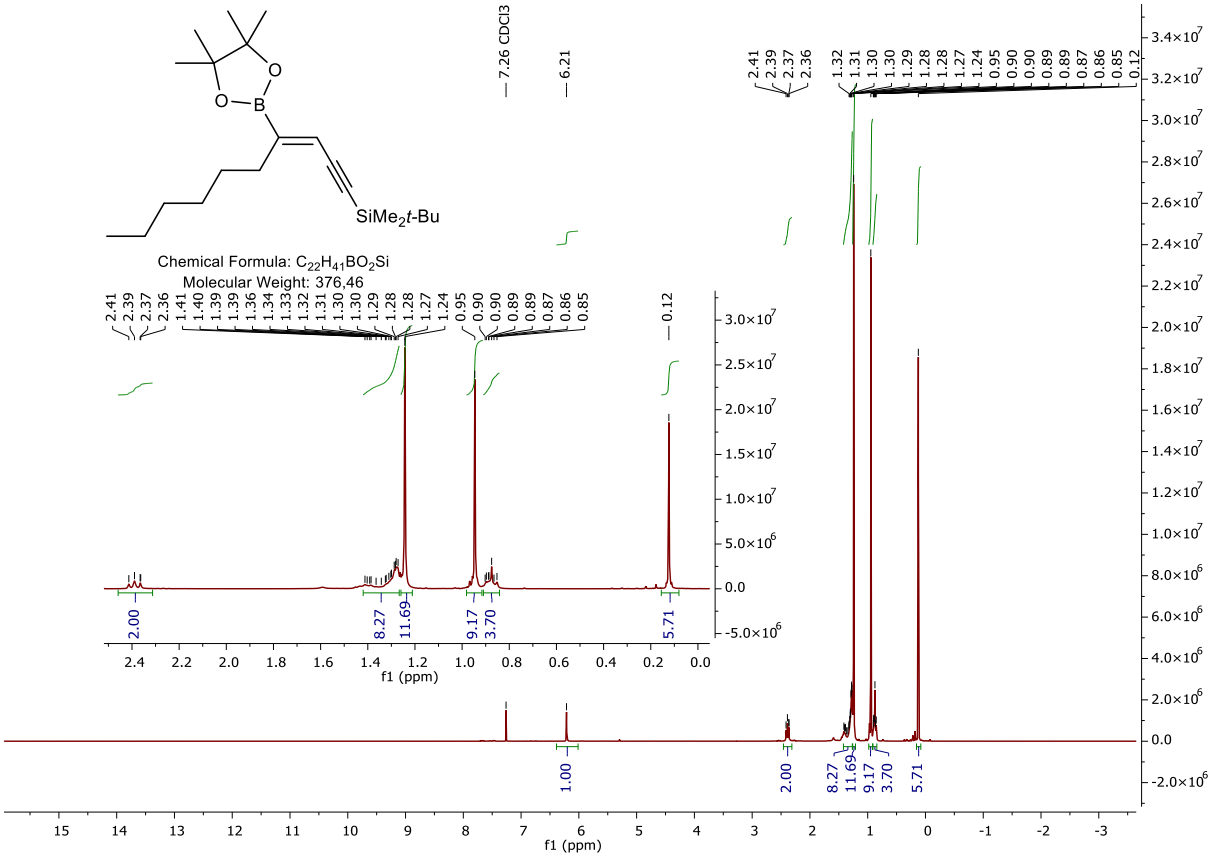


Figure S126. ^{1}H NMR spectrum of **4r**.

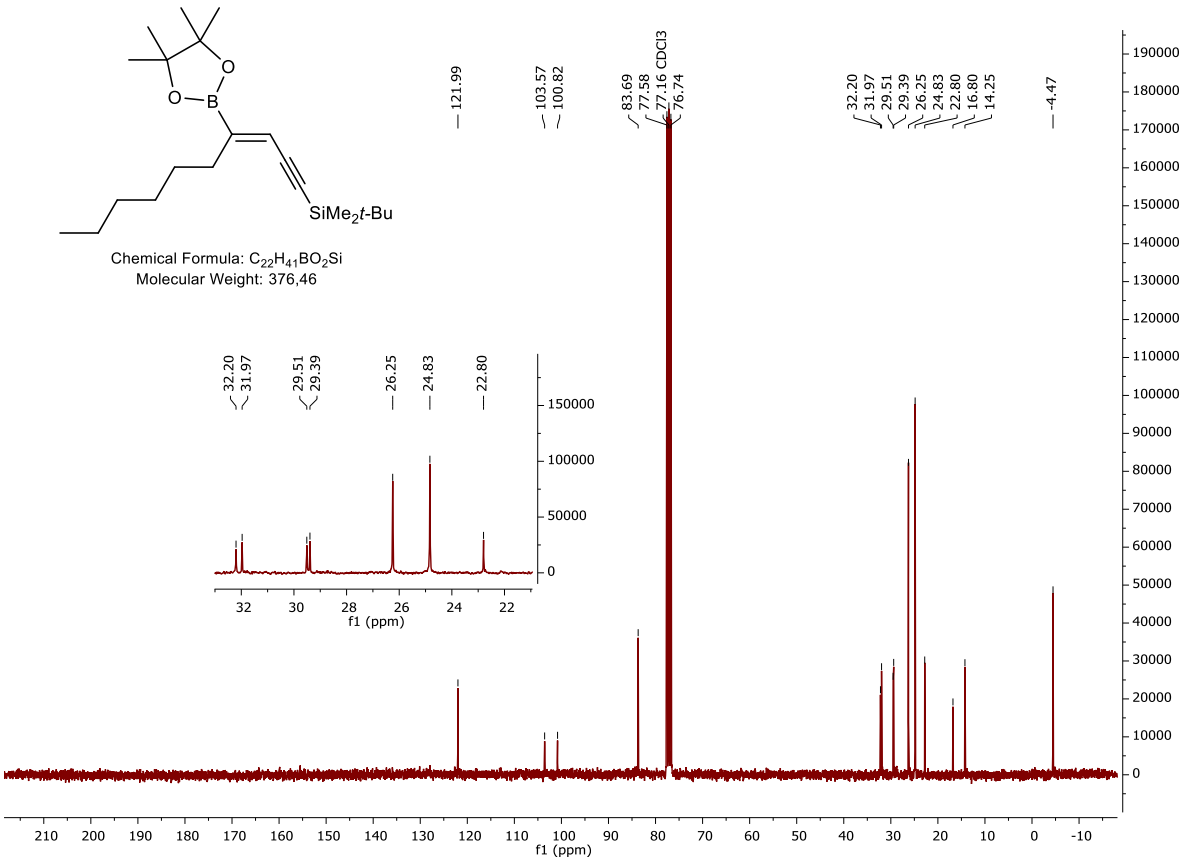


Figure S127. ^{13}C NMR spectrum of **4r**.

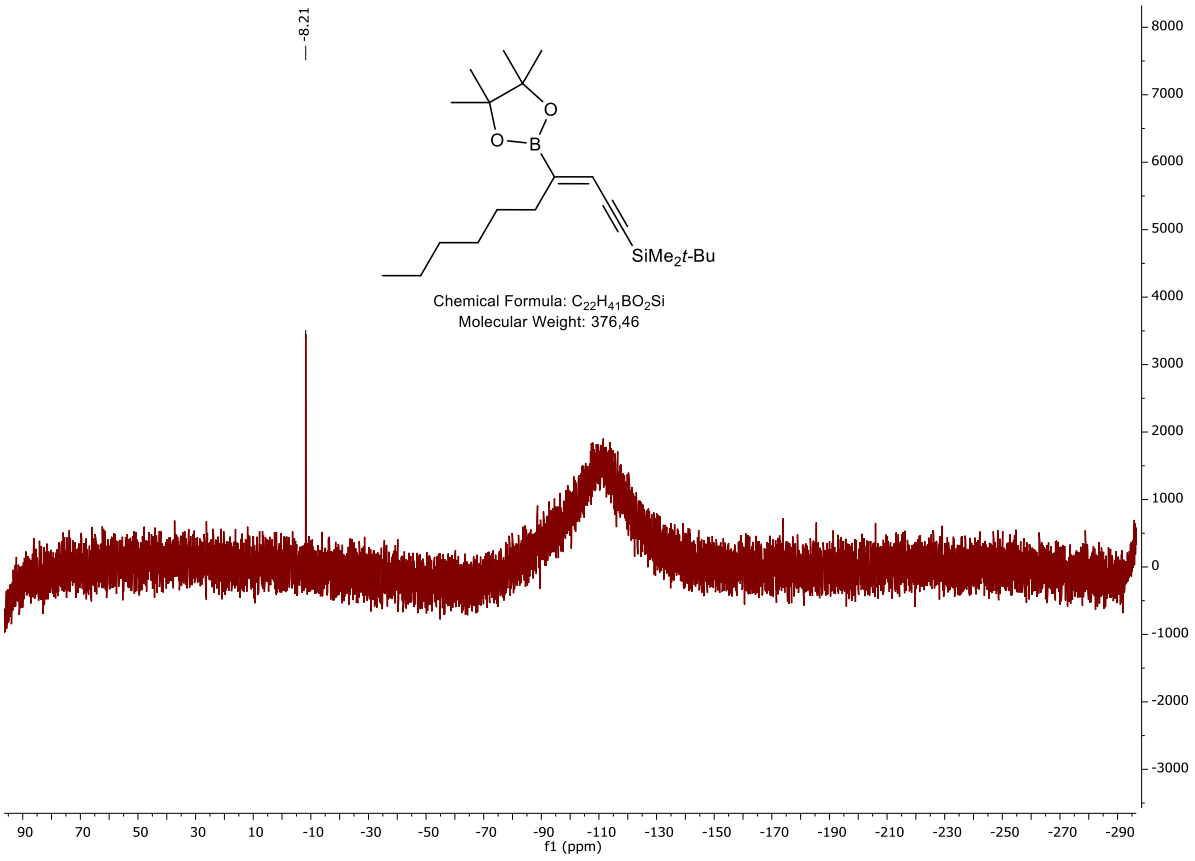


Figure S128. ^{29}Si NMR spectrum of **4r**.

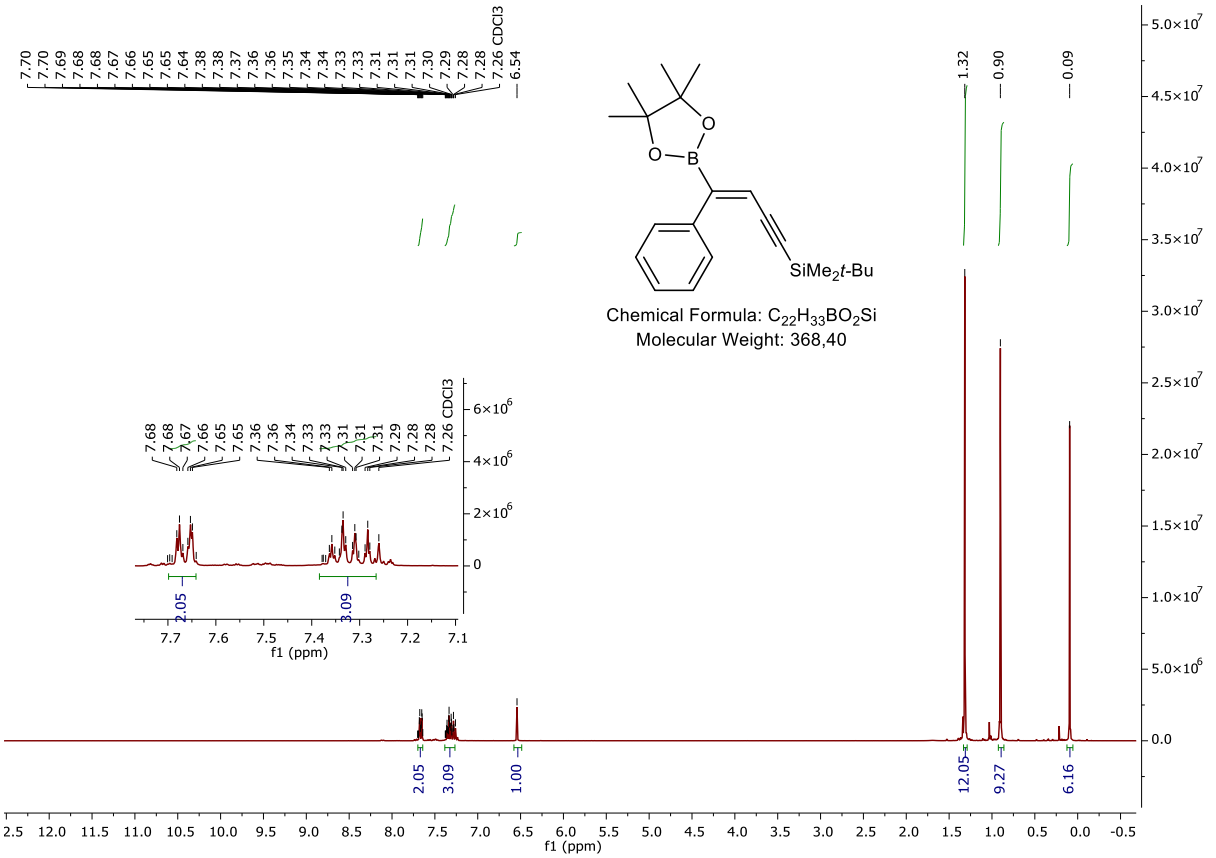


Figure S129. ^{1}H NMR spectrum of **4s**.

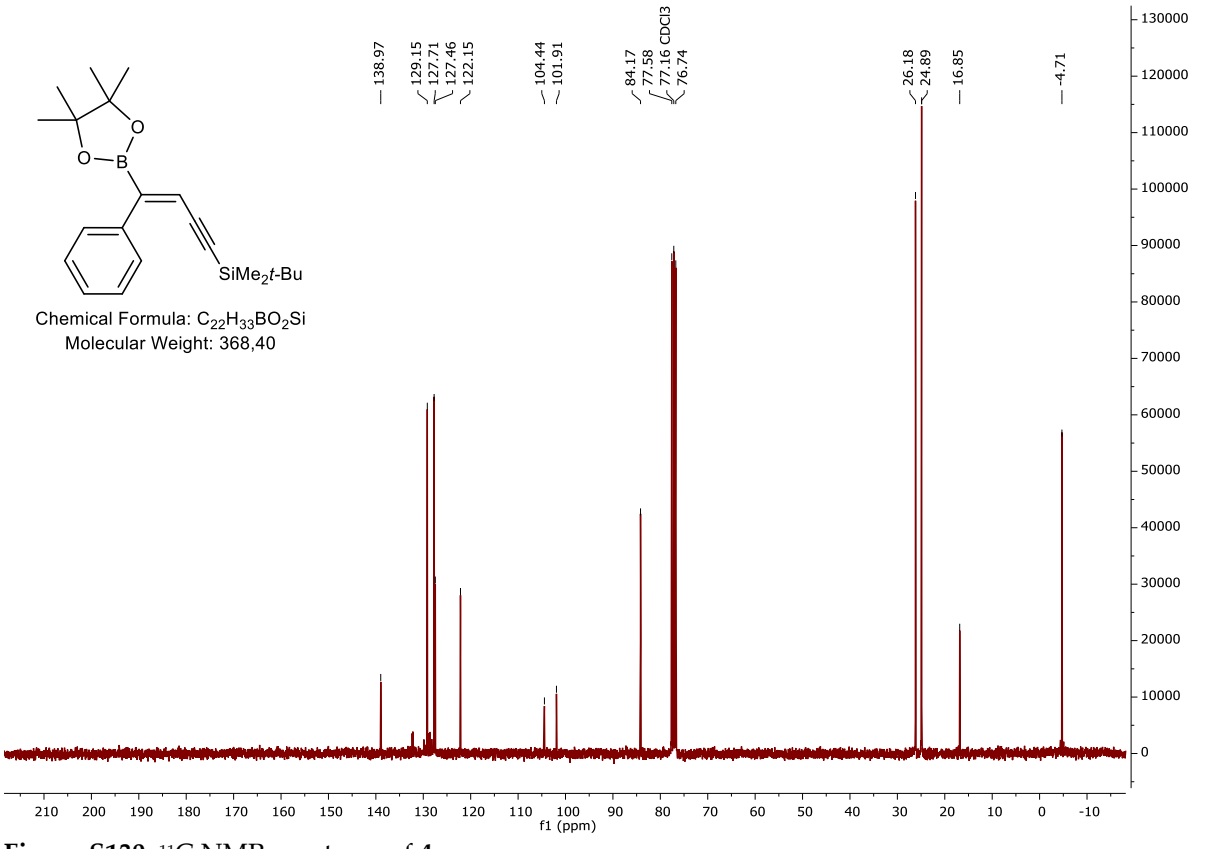


Figure S130. ^{11}C NMR spectrum of **4s**.

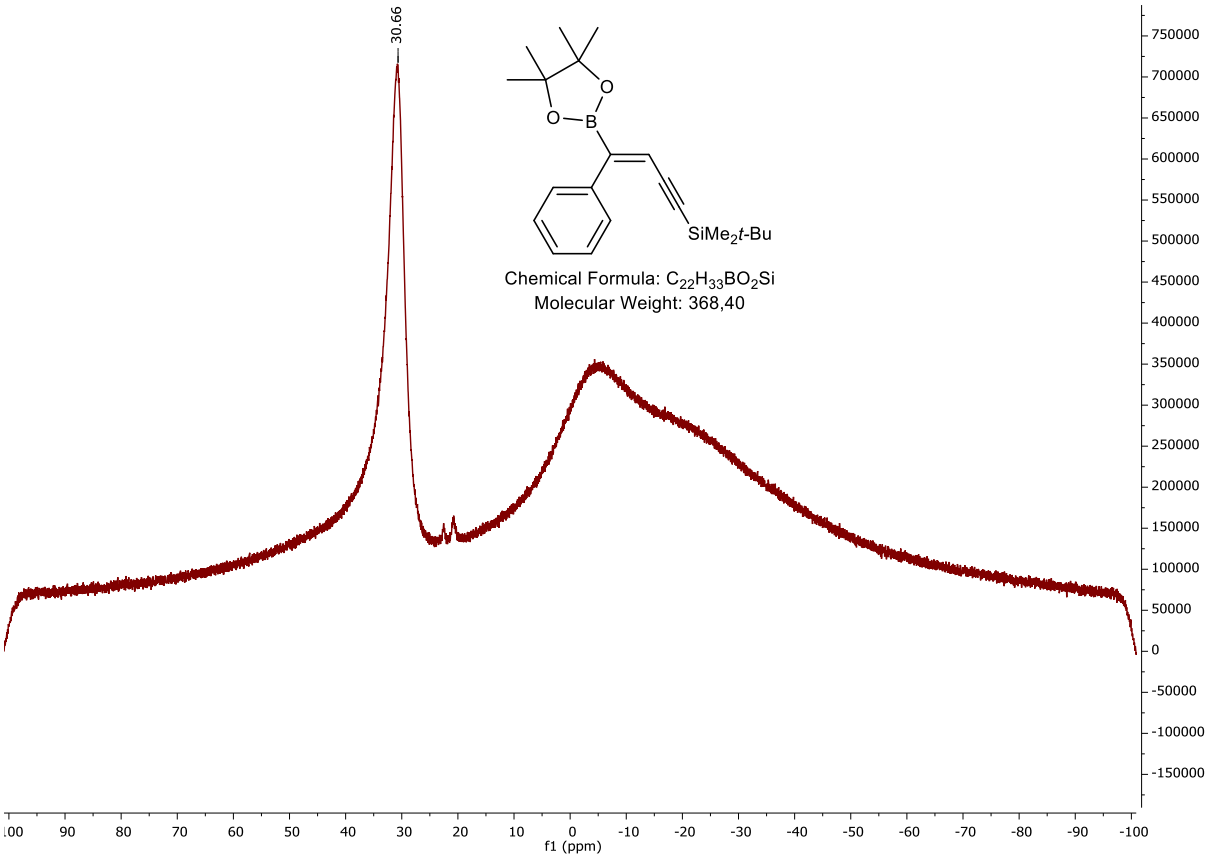


Figure S131. ^{11}B NMR spectrum of **4s**.

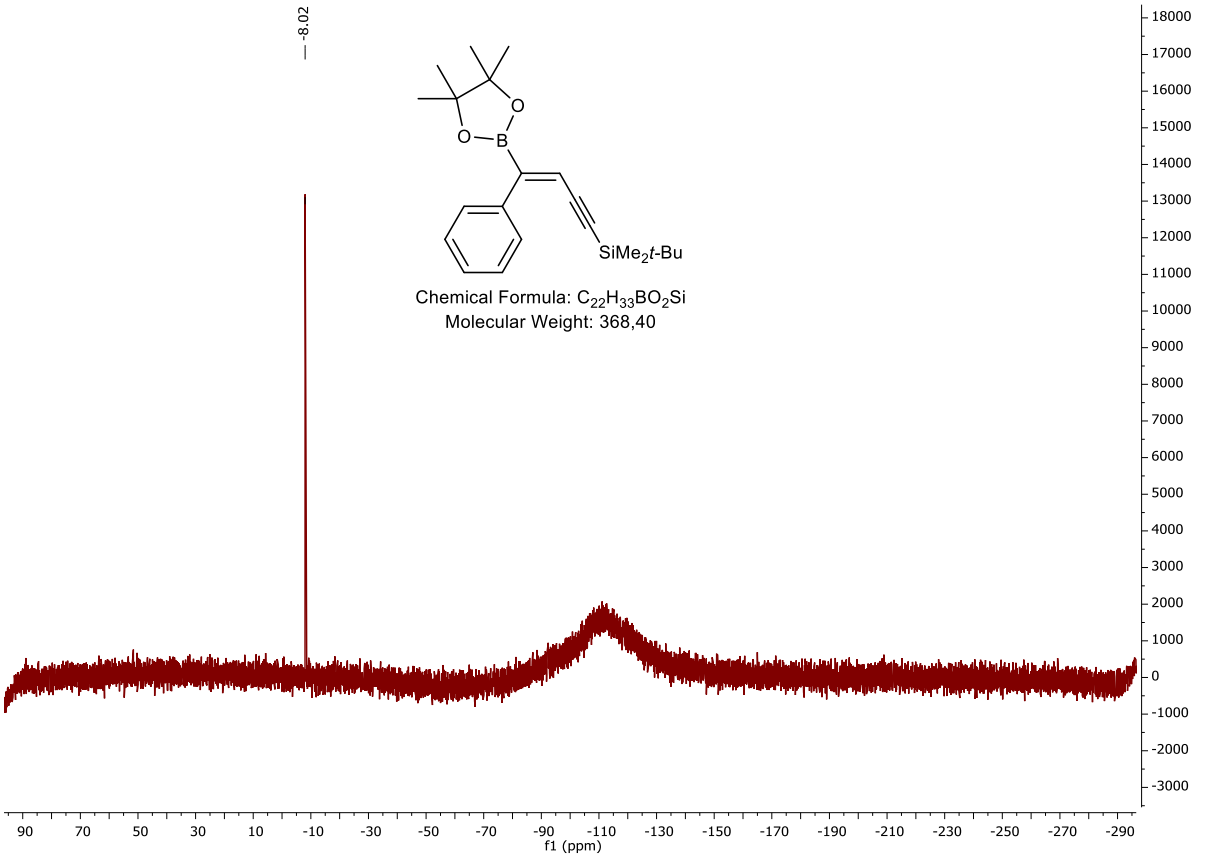


Figure S132. ^{29}Si NMR spectrum of **4s**.

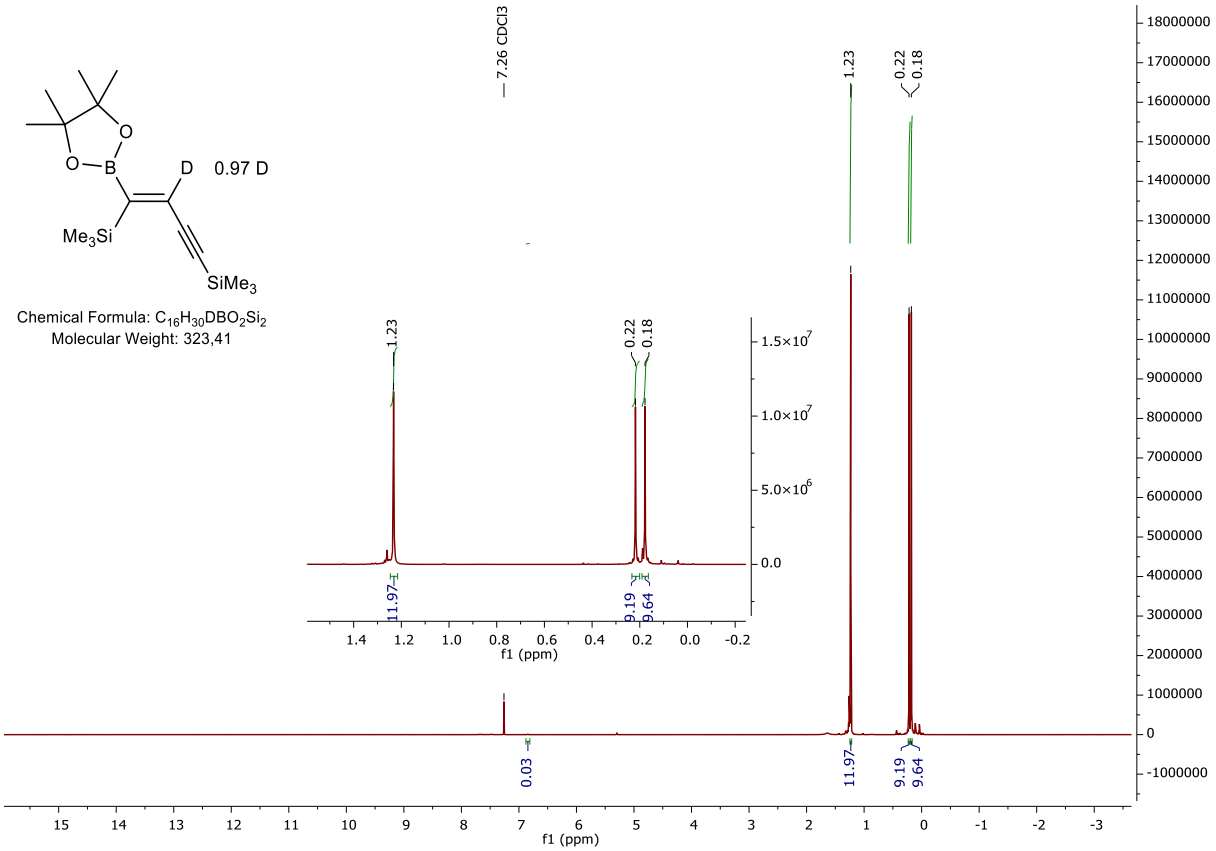


Figure S133. ^{1}H NMR spectrum of **6a**.

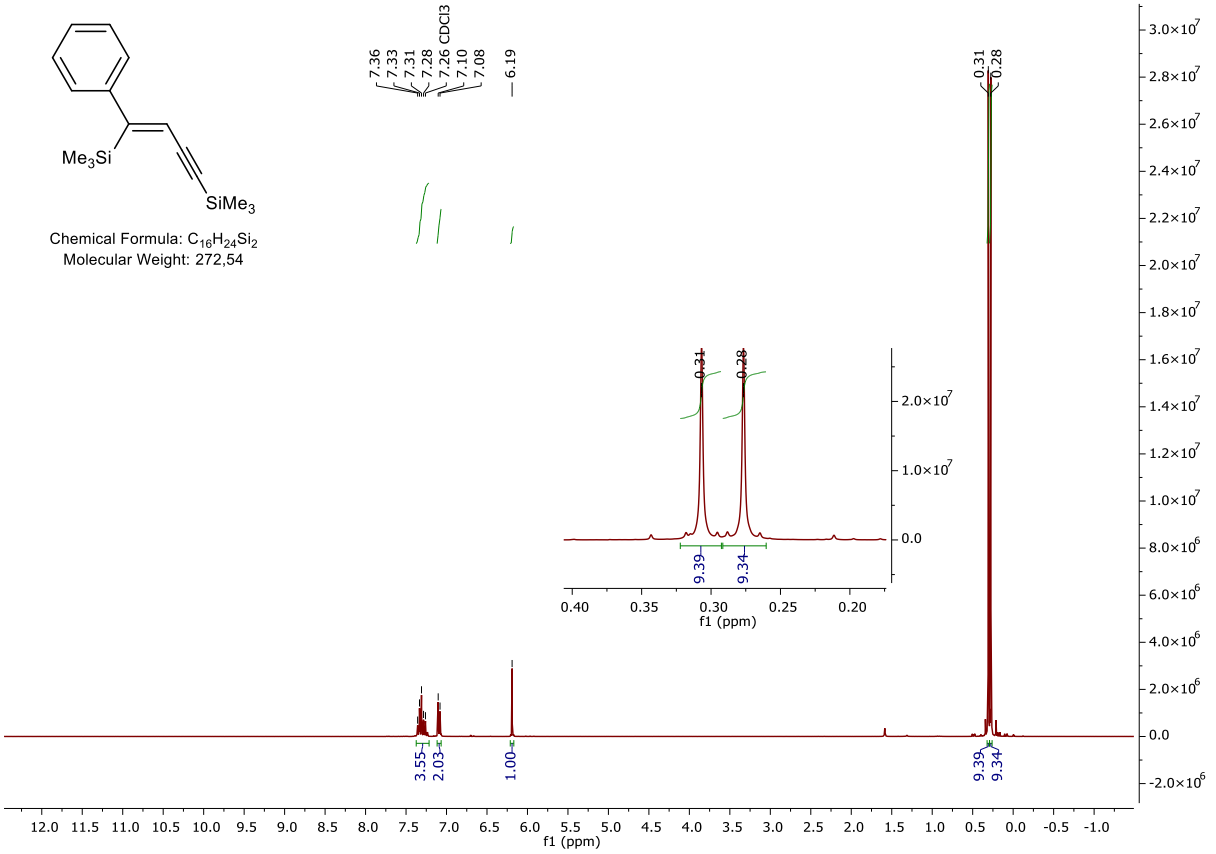


Figure S134. ^{1}H NMR spectrum of **7**.

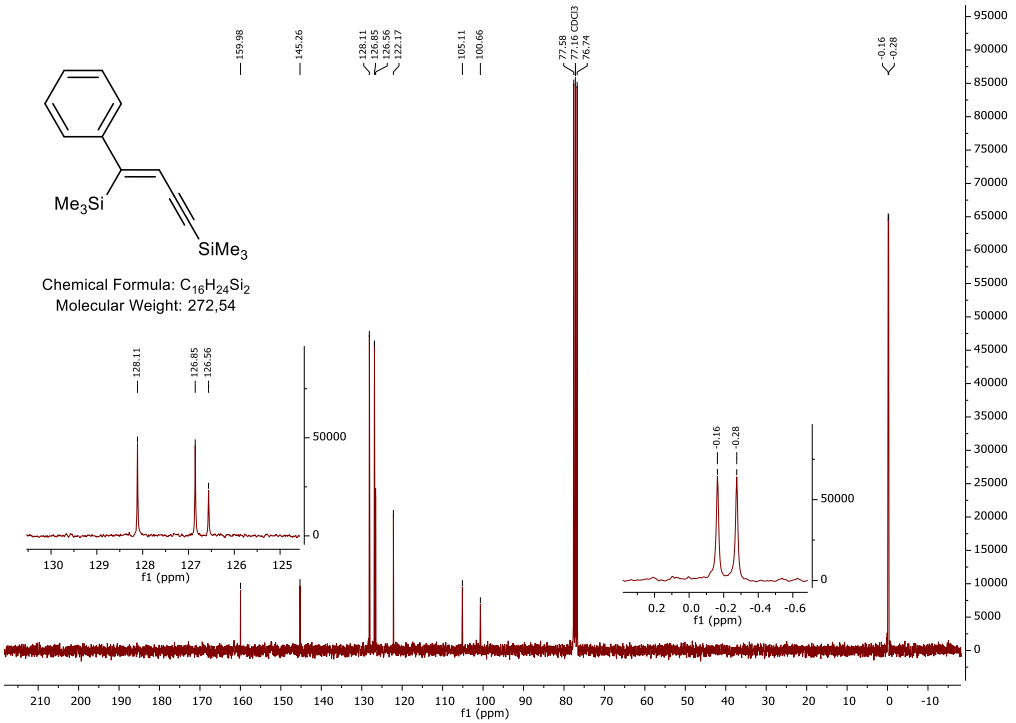


Figure S135. ^{13}C NMR spectrum of **7**.

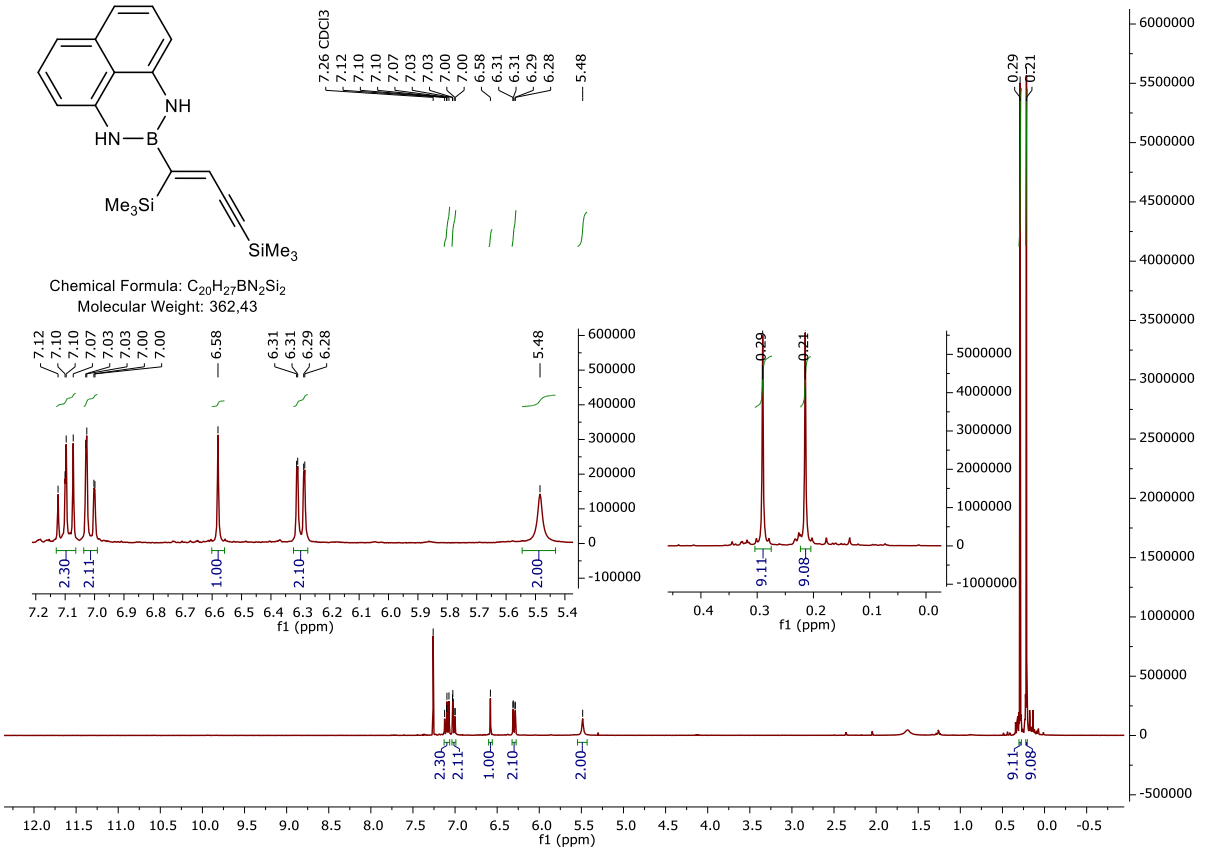


Figure S136. ^{1}H NMR spectrum of **8**.

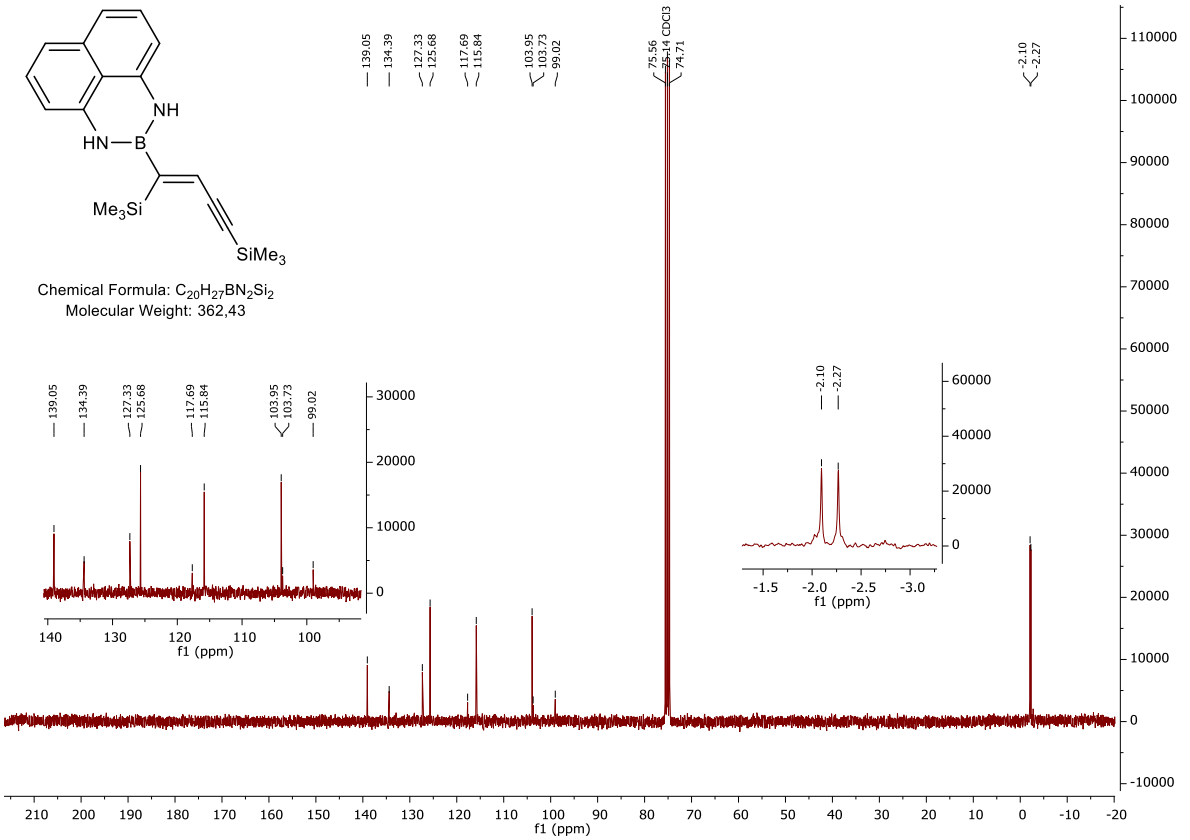


Figure S137. ^{13}C NMR spectrum of **8**.

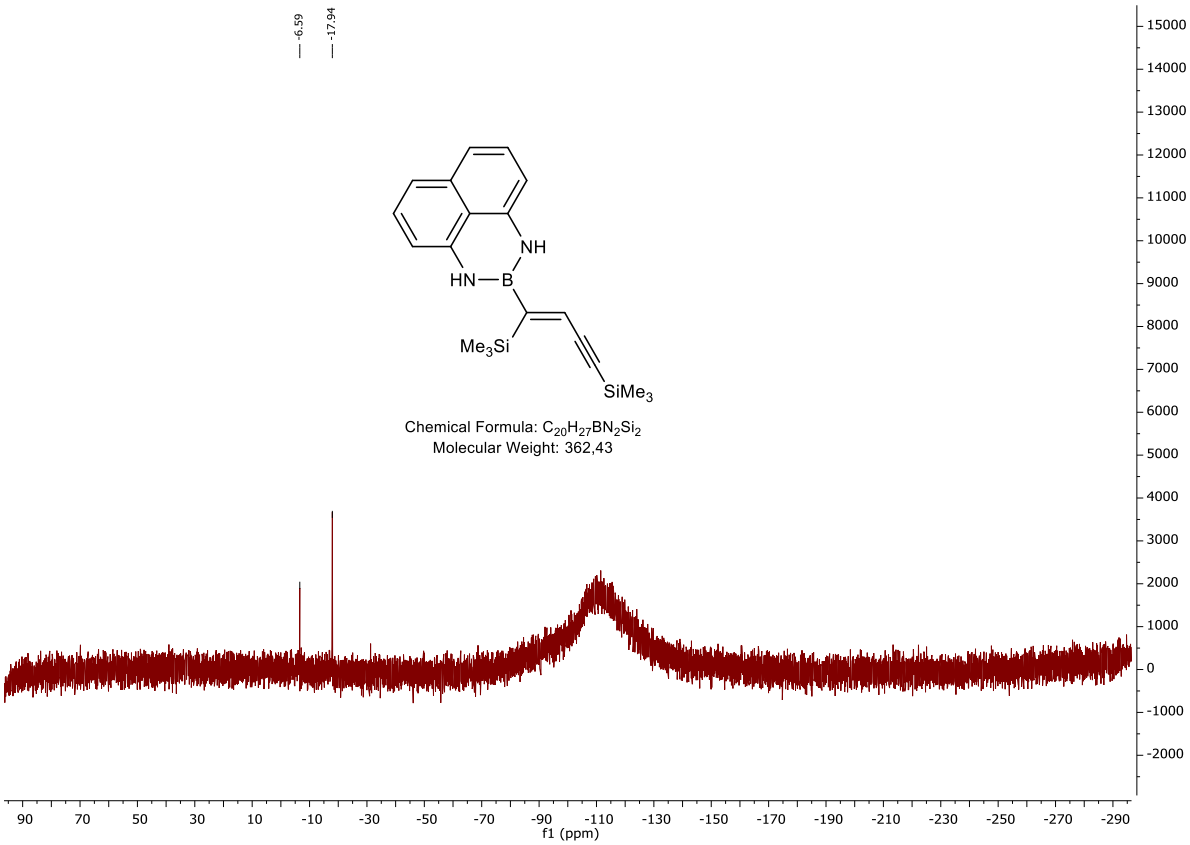


Figure S138. ^{29}Si NMR spectrum of **8**.

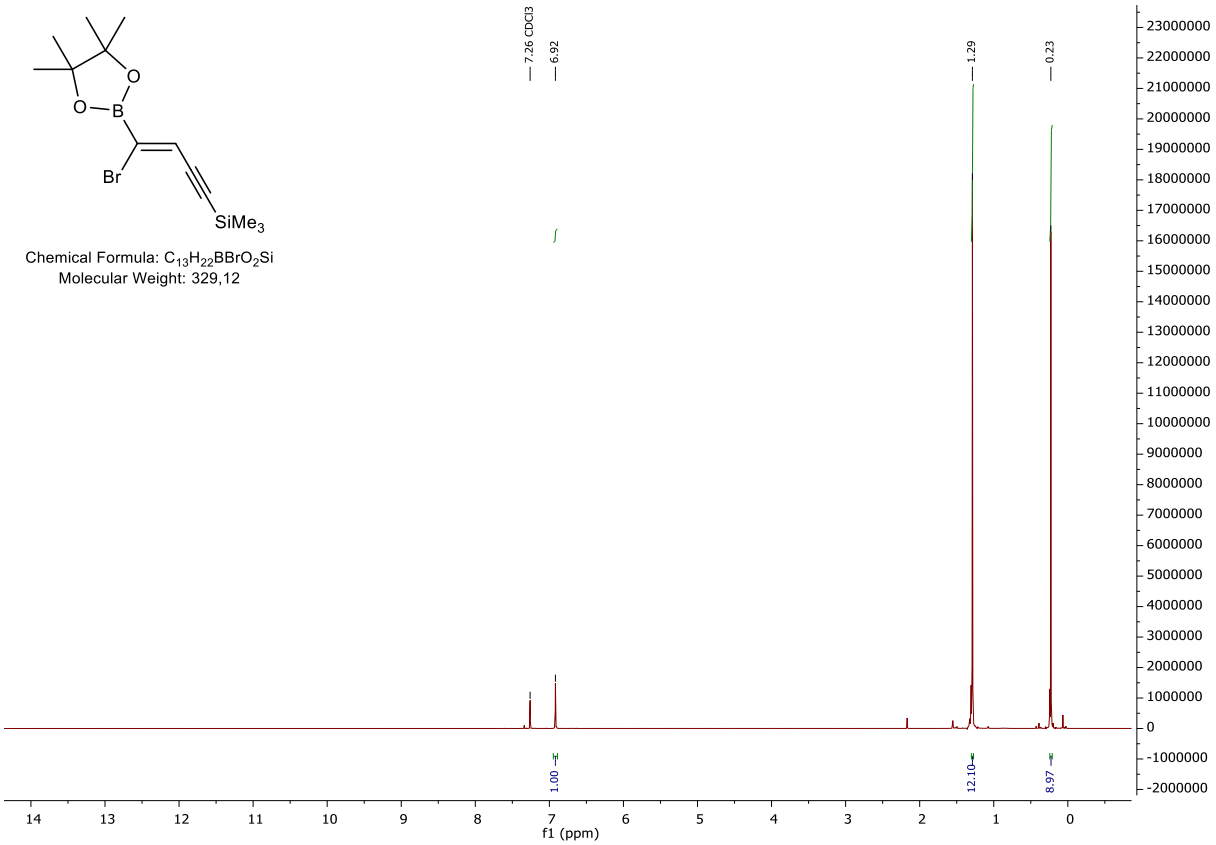


Figure S139. ^{1}H NMR spectrum of **9**.

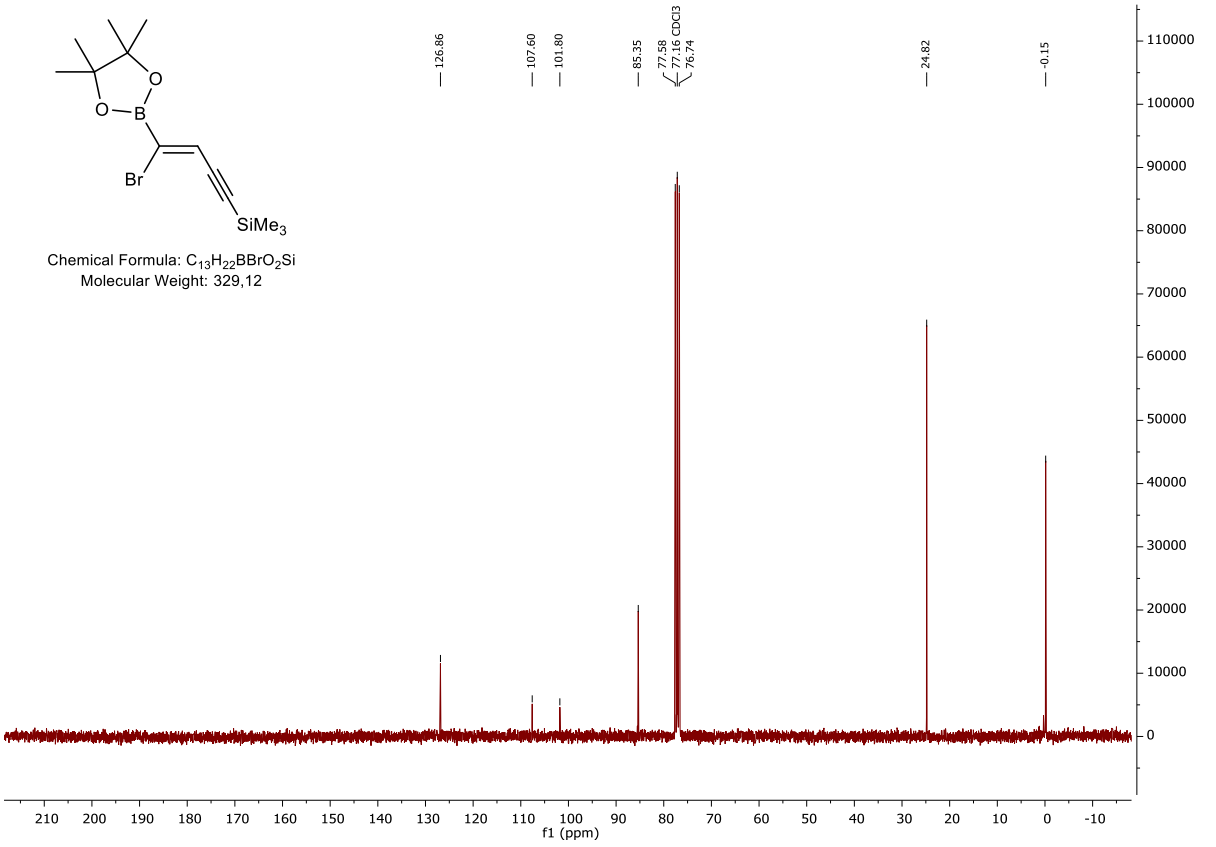


Figure S140. ^{13}C NMR spectrum of **9**.

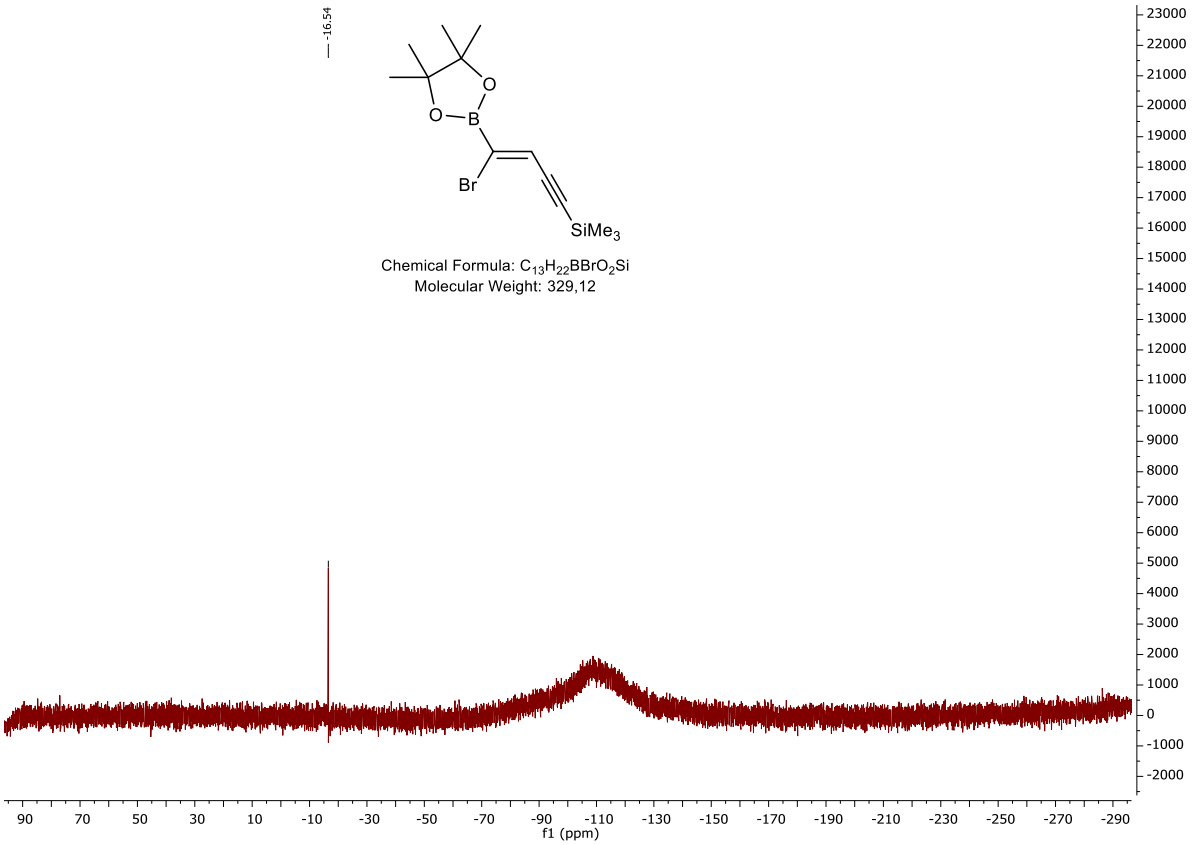


Figure S141. ^{29}Si NMR spectrum of **9**.

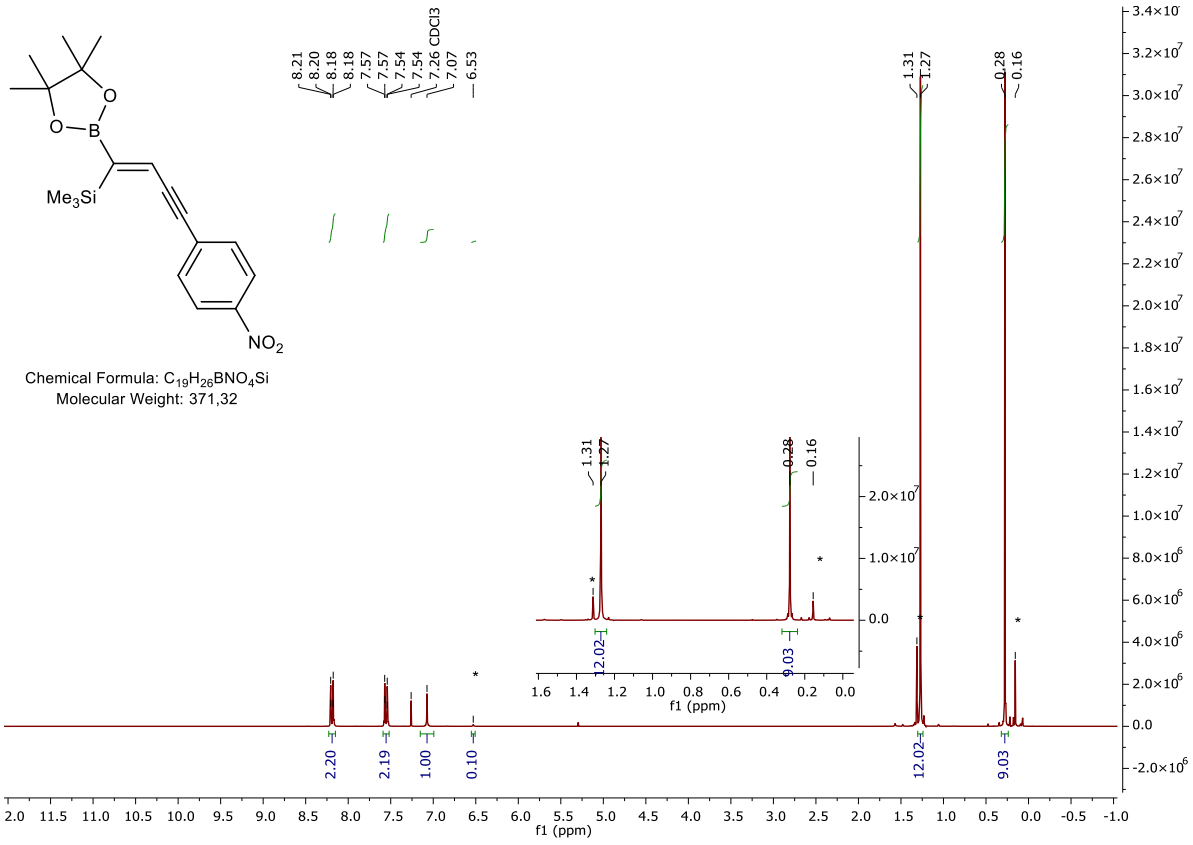


Figure S142. ^{1}H NMR spectrum of **10**. * ≈ 10% of (*E*)-isomer.

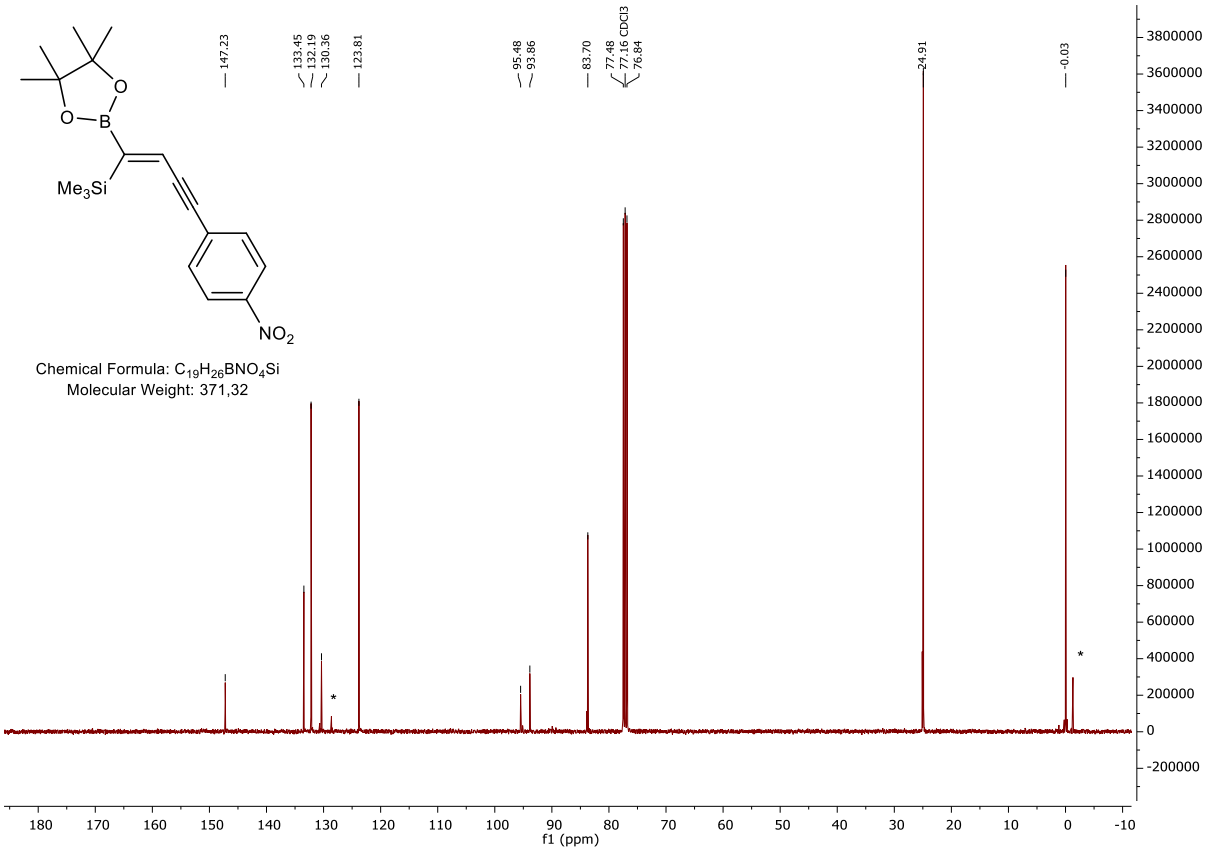


Figure S143. ^{13}C NMR spectrum of **10**. * ≈ 10% of (*E*)-isomer.

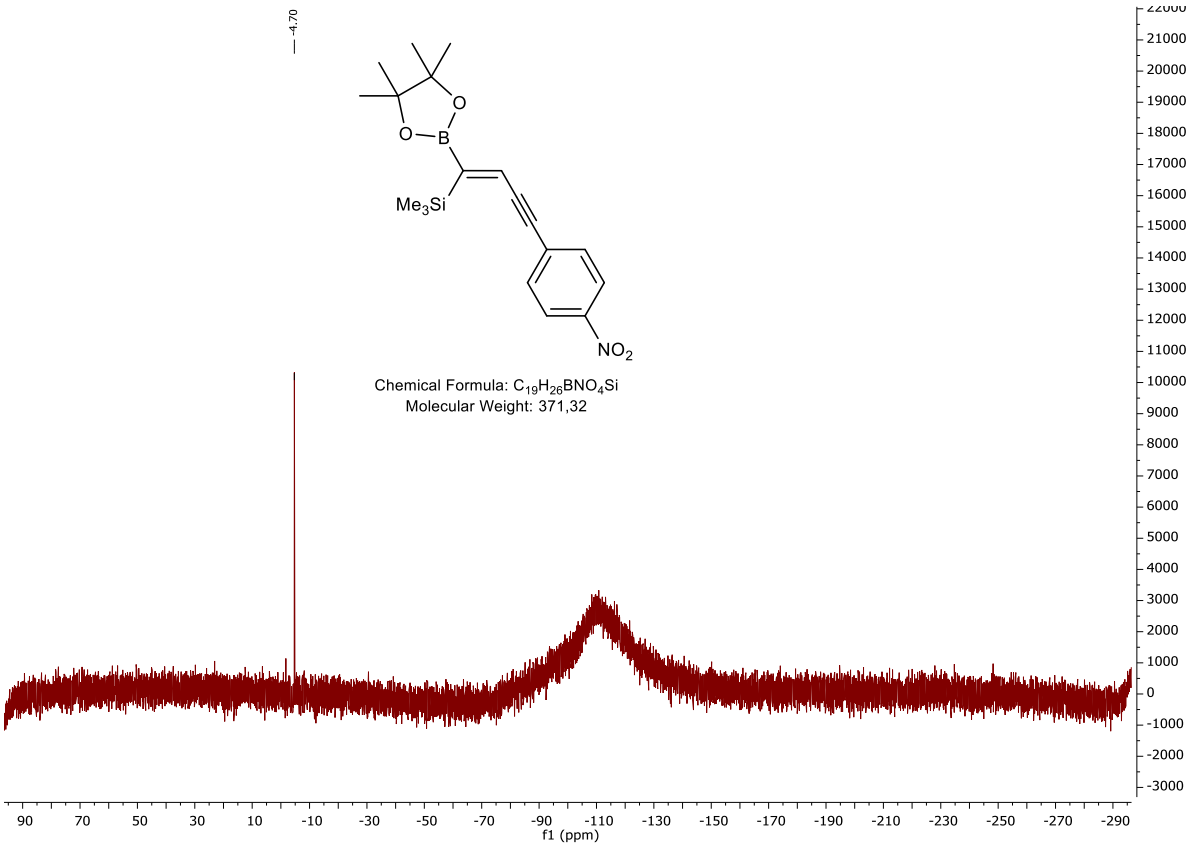


Figure S144. ^{29}Si NMR spectrum of **10**.

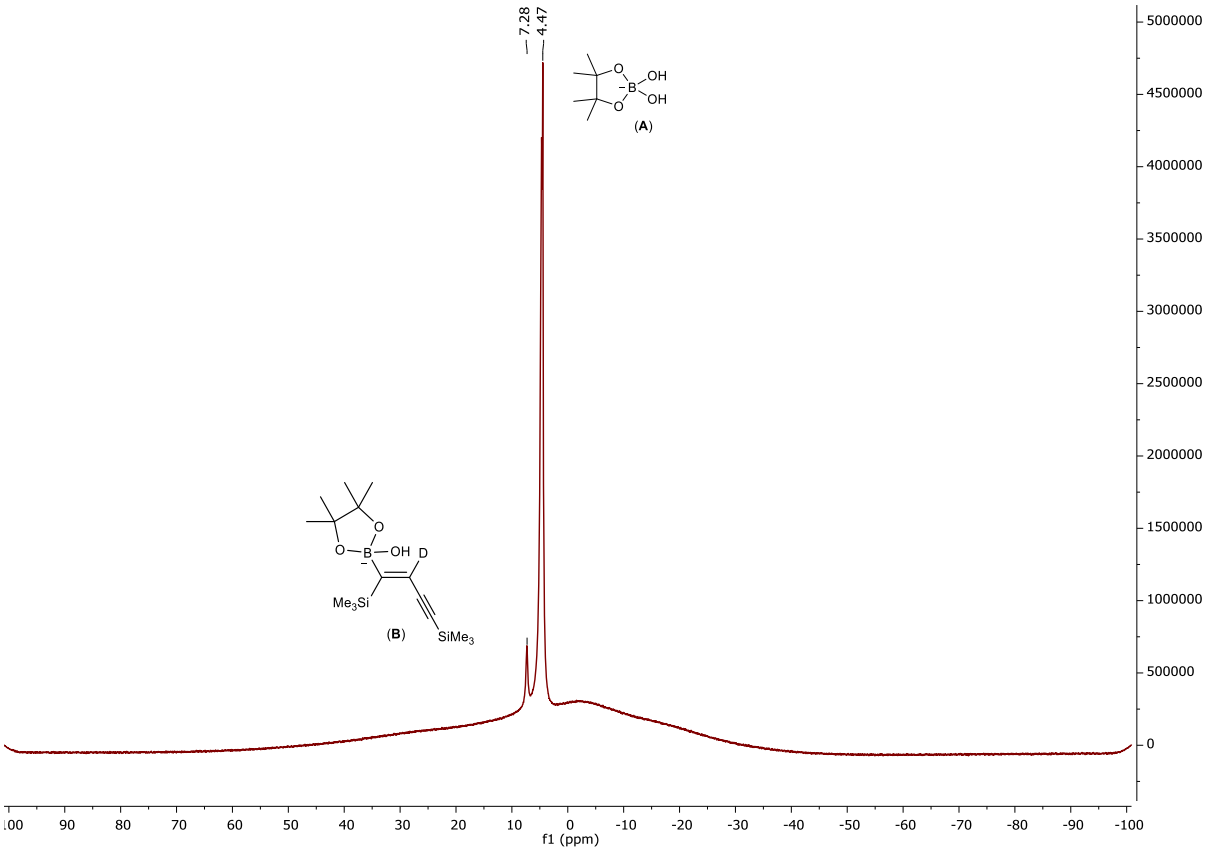


Figure S145. ^{11}B NMR spectrum of aqueous phase (D_2O) from deuterium labelling studies. (A) – $pinB(OH)_2^-$ anion at 4.47 ppm. (B) – hydroxylated reaction product at 7.28 ppm.

7. References

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