Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Catalytic Difunctionalization of Unactivated Alkenes with Unreactive Hexamethyldisilane through Regeneration of Silylium Ions

Qian Wu, Avijit Roy, Elisabeth Irran, Zheng-Wang Qu, Stefan Grimme, Hendrik F. T. Klare, and Martin Oestreich**

anie_201911282_sm_miscellaneous_information.pdf

Author Contributions

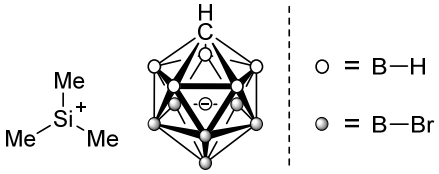
Dr. E. Irran: X-ray crystal-structure analysis.

Table of Contents

1 General Information

All reactions were performed in flame-dried glassware using an *MBraun* glovebox or conventional Schlenk techniques under a static pressure of argon (glovebox) or nitrogen (fume hood) unless otherwise stated. Solvents for chromatography and extraction were distilled prior to use. Toluene was dried over sodium/benzophenone, distilled, degassed by three freeze-pump-thaw cycles, and stored in a glovebox over thermally activated 4 Å molecular sieves. Dry benzene, *n*-hexane, and *n*-pentane were obtained from an *MBraun* solvent purification system (SPS-800), degassed by three freeze-pump-thaw cycles and stored in a glovebox over thermally activated 4 Å molecular sieves. All alkenes and disilanes were dried over CaH_2, distilled, degassed by three freeze-pump-thaw cycles, and stored in a glovebox over thermally activated 4 Å molecular sieves. Allylbenzenes **1d**, **1e**, **1g**, **1j**, **1l**,[S1] 1,2-di-*tert*-butyl-1,1,2,2-tetraphenyldisilane,[S2] 1,1,2,2,2-pentamethyldisilane,[S3] and $Ph_3C^+[CHB_{11}H_5Br_6]^-$[S4] were synthesized according to reported procedures. ^1H, ^{11}B, ^{13}C, ^{19}F and ^{29}Si NMR spectra were recorded in C_6D_6, C_6D_5Cl, $CDCl_3$, or CD_2Cl_2 on a *Bruker* AV500 and AV700 instrument, respectively. C_6D_6 and C_6D_5Cl were degassed by three freeze-pump-thaw cycles and stored in a glovebox over thermally activated 4 Å molecular sieves. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F254 glass plates. Flash column chromatography was performed on silica gel 60 (40–63 µm, 230–400 mesh, ASTM) by *Grace* using the indicated solvents. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard (C_6D_5H: δ 7.16 ppm for ^1H NMR and C_6D_6: δ 128.06 ppm for ^{13}C NMR; C_6D_4HCl: δ 6.96, 6.99, and 7.14 ppm for ^1H NMR and C_6D_5Cl: δ 125.96, 128.25, 129.26, and 134.19 ppm for ^{13}C NMR; $CHCl_3$: δ 7.26 ppm for ^1H NMR and $CDCl_3$: δ 77.16 ppm for ^{13}C; $CDHCl_2$: δ 5.32 ppm for ^1H NMR and $CDCl_3$: δ 53.84 ppm for ^{13}C). ^{11}B, ^9F, and ^{29}Si NMR spectra are referenced in compliance with the unified scale for NMR chemical shifts as recommended by the IUPAC stating the chemical shift relative to $BF_3{\cdot}Et_2O$, CCl_3F, and TMS, respectively.[S5] Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, m_c = centrosymmetric multiplet, br = broad signal), coupling constants (Hz), and integration. Infrared (IR) spectra were recorded on an *Agilent Technologies* Cary 630, and the signals are reported in wavenumbers (cm^{-1}). Melting points (m.p.) were determined with a *Stuart Scientific* SMP20 instrument and were not corrected. High resolution mass spectra (HRMS) were obtained from the *Laboratory of Mass Spectrometry* at the *Institut für Chemie*, *Technische Universität Berlin*.

2 Experimental Details for the Synthesis of $Me_3Si^+[CHB_{11}H_5Br_6]^-$

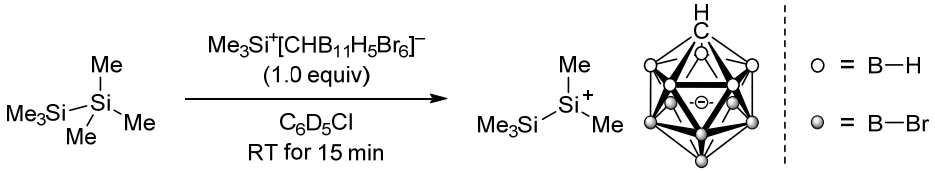


$C_4H_{15}B_{11}Br_6Si$
M = 689.58 g/mol

According to a reported procedure,[S6] $Ph_3C^+[CHB_{11}H_5Br_6]^-$ (50.0 mg, 0.058 mmol, 1.00 equiv) was suspended in toluene (~10 drops) and treated with dimethylphenylsilane (32.0 mg, 0.235 mmol, 4.0 equiv). After stirring the reaction mixture at room temperature for 1 day, *n*-pentane (0.5 mL) was added to the resulting white suspension. The precipitate was collected by filtration, washed with *n*-pentane (3 × ~10 drops), and briefly dried under vacuum to afford silylium carborate $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (36.2 mg, 91%) as a white solid. This can be stored for several weeks in the glove-box freezer at –30°C without loss in reactivity.

^{1}H NMR (500 MHz, C_6D_5Cl, 298 K): δ = 0.56 (s, 9H, SiCH_3), ~1.9–3.2 (br m, 6H, [CHB$_{11}H_5$Br$_6$]$^-$) ppm. **^{11}B NMR** (161 MHz, C_6D_5Cl, 298 K): δ = –19.8 (d, J = 146.7 Hz), –9.1 (s), –1.0 (s) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_5Cl, 298 K): δ = 3.4 (SiCH$_3$), 41.7 ([CHB$_{11}$H$_5$Br$_6$]$^-$) ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, C_6D_5Cl, 298 K, optimized for J = 7 Hz): δ = 0.56/92.1 ppm.

3 Experimental Details for the Generation of $Me_2(Me_3Si)Si^+[CHB_{11}H_5Br_6]^-$ by Dealkylative Silylation of Hexamethyldisilane with $Me_3Si^+[CHB_{11}H_5Br_6]^-$



$C_6H_{21}B_{11}Br_6Si_2$
M = 747.74 g/mol

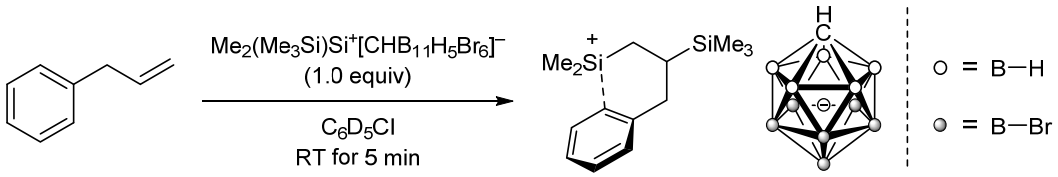
In a valved NMR tube, silylium carborate $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (6.9 mg, 0.010 mmol, 1.00 equiv) was suspended in C_6D_5Cl (0.6 mL) and treated with hexamethyldisilane (2.1 µL, 0.010 mmol, 1.0 equiv) at room temperature. The white suspension turned into a clear colorless solution upon vigorous shaking of the valved NMR tube. After 15 min, NMR spectroscopic analysis indicated the formation of both $Me_2(Me_3Si)Si^+[CHB_{11}H_5Br_6]^-$ and Me_4Si (88% conv.).

Selected NMR spectroscopic data for **$Me_2(Me_3Si)Si^+[CHB_{11}H_5Br_6]^-$**:
^{1}H NMR (500 MHz, C_6D_5Cl, 298 K): δ = 0.06 (s, 9H, SiCH_3), 0.86 (s, 6H, SiCH_2) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_5Cl, 298 K): δ = –3.16 (SiCH$_3$), 2.26 (SiCH$_2$) ppm. **^{1}H/^{29}Si HMQC NMR**

(500/99 MHz, C_6D_5Cl, 298 K, optimized for J = 7 Hz): δ = 0.06/–10.6, 0.06/99.3, 0.86/–10.6, 0.86/99.3 ppm.

NMR spectroscopic data for **Me_4Si**: **^{1}H NMR** (500 MHz, C_6D_5Cl, 298 K): δ = 0.03 (s, 12H, Si(CH_3)$_4$) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_5Cl, 298 K): δ = –0.01 (Si(CH_3)$_4$) ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, C_6D_5Cl, 298 K, optimized for J = 7 Hz): δ = 0.03/–0.09 ppm.

4 Experimental Details for the Reaction of $Me_2(Me_3Si)Si^+[CHB_{11}H_5Br_6]^–$ with Allylbenzene (1a): Generation of Intramolecular Arene-Stabilized Silylium Ion $3a^+[CHB_{11}H_5Br_6]^–$



1a

3a$^+$[$CHB_{11}H_5Br_6$]$^–$
$C_{15}H_{31}B_{11}Br_6Si_2$
M = 865.92 g/mol

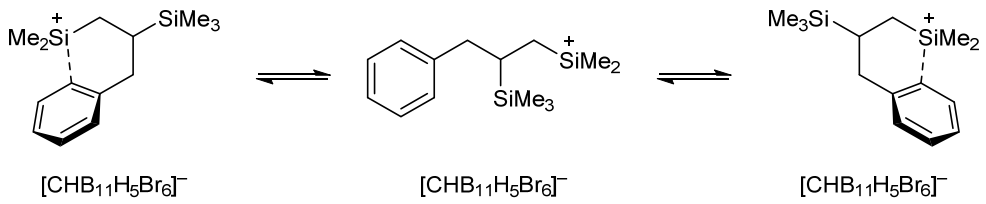
In a valved NMR tube, silyl-substituted silylium ion $Me_2(Me_3Si)Si^+[CHB_{11}H_5Br_6]^–$ (7.5 mg, 0.01 mmol, 1.0 equiv) was suspended in C_6D_5Cl (0.6 mL) and treated with allylbenzene (**1a**, 1.4 µL, 0.01 mmol, 1.0 equiv). The white suspension turned into a clear yellow solution upon vigorous shaking of the valved NMR tube. After 5 min, NMR spectroscopic analysis indicated the clean formation of intramolecular arene-stabilized silylium ion **3a**$^+$[$CHB_{11}H_5Br_6$]$^–$.

Selected NMR spectroscopic data for **3a**$^+$[$CHB_{11}H_5Br_6$]$^–$:

^{1}H NMR (500 MHz, C_6D_5Cl, 298 K): δ = 0.03 (s, 9H, Si(CH_3)$_3$), 0.62 (t, J = 15.2, 1.0 Hz, 1H, SiCHH), 0.69–0.74 (m, 2H, SiCHH, SiCH), 1.99 (t, J = 12.6 Hz, 1H, ArCHH), 2.37 (s, 1H, [CHB$_{11}$H$_5$Br$_6$]$^–$), 2.69 (dd, J = 12.6, 2.6 Hz, 1H, ArCHH), 6.81 (d, J = 6.0 Hz, 2H, *o*-H$_{Ar}$), 7.37 (t, J = 7.4 Hz, 1H, *p*-H$_{Ar}$), 7.81 (t, J = 7.2 Hz, 2H, *m*-H$_{Ar}$) ppm. **^{11}B NMR** (161 MHz, C_6D_5Cl, 298 K): δ = –19.6 (d, J = 110.0 Hz), –9.0 (s), –0.7 (s) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_5Cl, 298 K): δ = –3.4 (SiCH$_3$), 16.1 (SiCH$_2$), 30.6 (SiCH), 38.7 (ArCH$_2$), 41.5 ([CHB$_{11}$H$_5$Br$_6$]$^–$), 132.6 (*p*-C$_{Ar}$), 150.1 (*m*-C$_{Ar}$), 170.6 (*i*-C$_{Ar}$) ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, C_6D_5Cl, 298 K, optimized for J = 7 Hz): δ = 0.03/7.5, 0.69–0.74/7.5, 1.99/7.5, 0.62/100.7, 6.81/100.7 ppm. Due to chemical exchange of **3a**$^+$[$CHB_{11}H_5Br_6$]$^–$ in solution (Figure S1, top), the signals for the protons of the Si(CH$_3$)$_2$ moiety could not be observed in the ^{1}H NMR spectrum at room temperature. The same applies to the signals for the carbon atoms of the Si(CH$_3$)$_2$ moiety and the *ortho*-aryl carbon atom. However, these signals were detected using VT-NMR spectroscopy (Figure S1, bottom). **^{1}H NMR** (500 MHz, C_6D_5Cl, 233 K): δ = –1.11 (s, 3H, SiCH$_3$CH_3), 0.64 (s, 3H, SiCH$_3$CH_3) ppm. **^{1}H/^{13}C HSQC NMR** (500/126 MHz, C_6D_5Cl, 233 K): δ = –1.11/–8.1, 0.64/4.0 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, C_6D_5Cl, 233 K, optimized for J = 7 Hz):

δ = –1.11/100.4, 0.64/100.4 ppm. **^{1}H NMR** (500 MHz, C_6D_5Cl, 343 K): δ = 6.81 (d, *J* = 6.0 Hz, 2H, *o*-H_{Ar}) ppm. **^{1}H/^{13}C HSQC NMR** (500/126 MHz, C_6D_5Cl, 343 K): δ = 6.8/115.9 ppm.

Single crystals of **3a**$^{+}$$[CHB_{11}H_5Br_6]^{-}$ suitable for X-ray diffraction analysis were obtained from a solution in C_6D_5Cl by layer diffusion with *n*-hexane at room temperature (cf. Figure S92). CCDC 1951131 contains the supplementary crystallographic data. These data are provided free of charge by The Cambridge Crystallographic Data Centre.



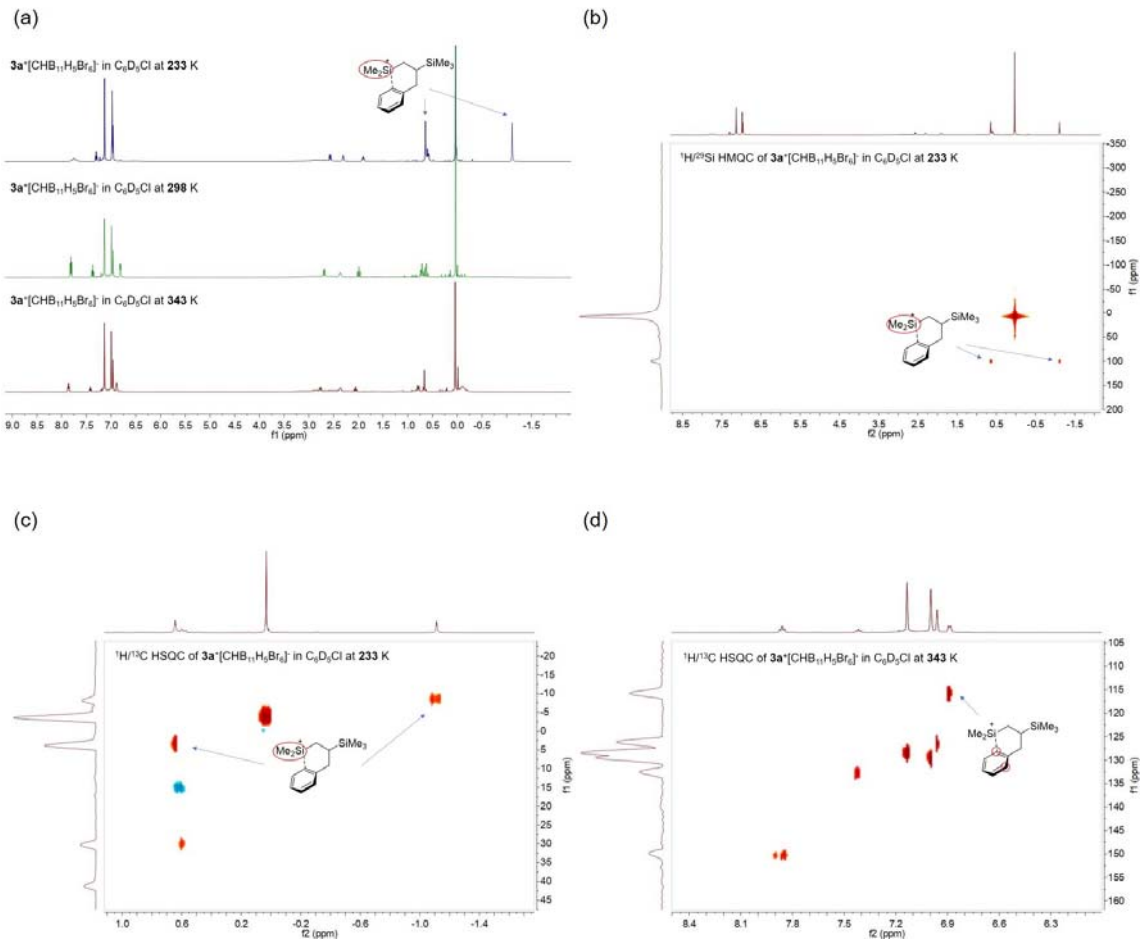
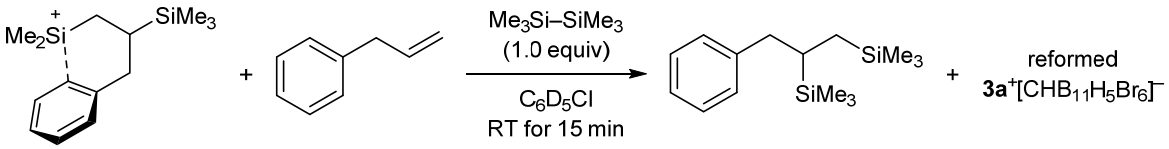


Figure S1. Chemical exchange of **3a**$^{+}$$[CHB_{11}H_5Br_6]^{-}$ in C_6D_5Cl solution (top) revealed by VT-NMR spectroscopic analysis (bottom): (a) ^{1}H NMR (500 MHz) at 233, 298, and 343 K; (b) ^{1}H/^{29}Si HMQC NMR (500/99 MHz) at 233 K; (c) ^{1}H/^{13}C HSQC NMR (500/126 MHz) at 233 K; (d) ^{1}H/^{13}C HSQC NMR (500/126 MHz) at 343 K.

5 Experimental Details for the Reactions of Silylium Ions $3a^+[CHB_{11}H_5Br_6]^-$ and $Me_2(Me_3Si)Si^+[CHB_{11}H_5Br_6]^-$ with Hexamethyldisilane and Allylbenzene (1a): Generation of 1,2-Bissilylated Adduct 4a

5.1 Stoichiometric Reaction with $3a^+[CHB_{11}H_5Br_6]^-$



$[CHB_{11}H_5Br_6]^-$

3a$^+[CHB_{11}H_5Br_6]^-$

1a
(1.0 equiv)

4a
$C_{15}H_{28}Si_2$
M = 264.55 g/mol

In a valved NMR tube, intramolecular arene-stabilized silylium ion **3a**$^+[CHB_{11}H_5Br_6]^-$ (8.6 mg, 0.01 mmol, 1.0 equiv) was suspended in C_6D_5Cl (0.6 mL) and treated with a solution of allylbenzene (**1a,** 1.4 µL, 0.01 mmol, 1.0 equiv) and hexamethyldisilane (1.4 µL, 0.01 mmol, 1.0 equiv) in C_6D_5Cl (0.6 mL). The valved NMR tube was shaken vigorously and directly subjected to NMR spectroscopic analysis. The generation of 1,2-bissilylated adduct **4a** along with reformed silylium ion **3a**$^+[CHB_{11}H_5Br_6]^-$ was observed (Figure S2).

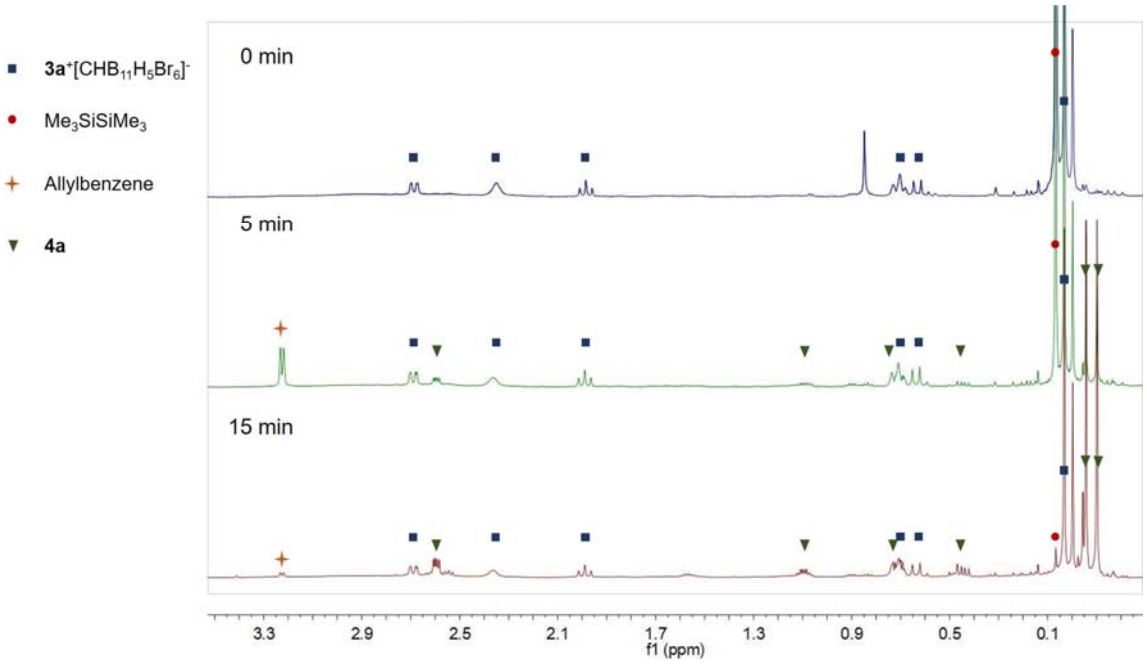
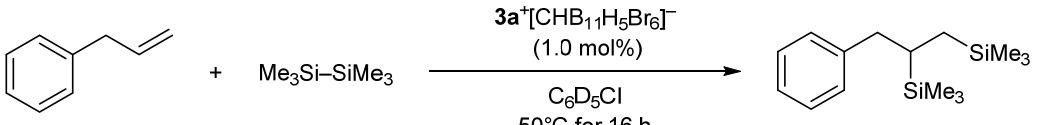


Figure S2. Reaction of silylium ion **3a**$^+[CHB_{11}H_5Br_6]^-$ with hexamethyldisilane and allylbenzene (**1a**) monitored by ^{1}H NMR spectroscopy (500 MHz, 298 K).

5.2 Catalytic Reaction with $3a^+[CHB_{11}H_5Br_6]^-$



1a **4a**

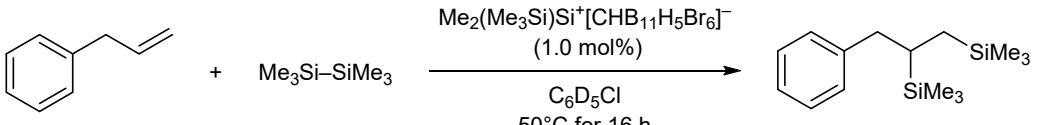
$C_{15}H_{28}Si_2$

M = 264.56 g/mol

In a glovebox, intramolecular arene-stabilized silylium ion **3a**$^+[CHB_{11}H_5Br_6]^-$ (1.8 mg, 0.002 mmol, 0.01 equiv) was suspended in C_6H_5Cl (~0.5 mL) and treated with hexamethyldisilane (43.9 mg, 0.30 mmol, 1.5 equiv). After stirring at 50°C for 5 min, a solution of allylbenzene (**1a**, 23.6 mg, 0.2 mmol, 1.0 equiv) in C_6H_5Cl (~0.3 mL) was added dropwise over a period of ~10 min, and the resulting mixture was stirred at 50°C for 16 h. The reaction mixture was allowed to cool to room temperature, and CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (96%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **4a** as a colorless oil (48.8 mg, 92% yield).

R_f = 0.81 (cyclohexane). **IR** (ATR): $\tilde{\nu}$ = 3063, 3025, 2951, 2894, 1937, 1798, 1602, 1494, 1453, 1410, 1245, 1112, 1069, 1030, 976, 828, 742, 696 cm^{-1}. **^{1}H NMR** (500 MHz, CD_2Cl_2, 298 K): δ = = –0.14 (s, 9H), –0.09 (s, 9H), 0.45 (dd, *J* = 15.2, 8.3 Hz, 1H), 0.70 (dd, *J* = 15.3, 3.8 Hz, 1H), 1.05 (qd, *J* = 8.0, 3.8 Hz, 1H), 2.64 (d, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 7.2, 1H), 7.18 (d, *J* = 7.0, 2H), 7.24 (t, *J* = 7.2, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 298 K): δ = –2.6, –0.9, 16.4, 22.8, 40.1, 126.0, 128.5, 129.5, 143.5 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, CD_2Cl_2, 298 K, optimized for *J* = 7 Hz): δ = –0.09/2.4, 0.45/2.4, 0.70/2.4, –0.14/5.1, 2.64/5.1 ppm. **HRMS** (APCI): calculated for $C_{14}H_{25}Si_2^{\bullet+}$ $[M–CH_3]^{\bullet+}$: 249.1489; found 249.1491.

5.3 Catalytic Reaction with $Me_2(Me_3Si)Si^+[CHB_{11}H_5Br_6]^-$



1a **4a**

$C_{15}H_{28}Si_2$

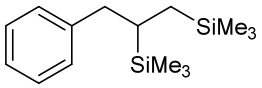
M = 264.56 g/mol

In a glovebox, silyl-substituted silylium ion $Me_2(Me_3Si)Si^+[CHB_{11}H_5Br_6]^-$ (1.5 mg, 0.002 mmol, 0.01 equiv) was suspended suspended in C_6H_5Cl (~0.5 mL) and treated with hexamethyldisilane (43.9 mg, 0.30 mmol, 1.5 equiv). After stirring at 50°C for 5 min, a solution of allylbenzene (**1a**, 23.6 mg, 0.2 mmol, 1.0 equiv) in C_6H_5Cl (~0.3 mL) was added dropwise over a period of ~10 min, and the resulting mixture was stirred at 50°C for 16 h. The reaction mixture was allowed to cool to room temperature, and CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (95%).

6 General Procedure for the Catalytic 1,2-Disilylation of Alkenes with Hexamethyldisilane Using $Me_3Si^+[CHB_{11}H_5Br_6]^-$ as Initiator

In a glovebox, silylium carborate $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) is suspended in C_6H_6 or C_6H_5Cl (~0.5–3 mL) and treated with hexamethyldisilane (1.5 equiv or 3.0 equiv). After stirring at the indicated temperature (50°C or 80°C) for 5 min, a solution of the alkene (0.2 mmol, 1.0 equiv) in C_6H_6 or C_6H_5Cl (~0.3–1 mL) is added dropwise over a period of 10 min, and the resulting mixture is stirred for additional 16 h at the indicated temperature. The reaction mixture is allowed to cool to room temperature, and CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) is added as internal standard to determine the yield by NMR spectroscopy. Purification by flash column chromatography on silica gel using *n*-pentane as eluent affords the 1,2-bissilylated alkanes in analytically pure form.

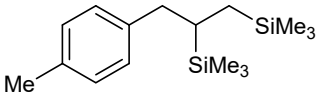
7 Experimental Details for the Catalytic 1,2-Disilylation of *α*-Olefins



4a
$C_{15}H_{28}Si_2$
M = 264.56 g/mol

(3-Phenylpropane-1,2-diyl)bis(trimethylsilane) (4a): Prepared from allylbenzene (**1a**, 23.6 mg, 0.2 mmol, 1.0 equiv) and hexamethyldisilane (43.9 mg, 0.3 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) in chlorobenzene (0.8 mL) at 50°C for 16 h according to the general procedure. CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (97%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **4a** as a colorless oil (50.2 mg, 95% yield).

$\mathbf{R_f}$ = 0.81 (cyclohexane). **^{1}H NMR** (500 MHz, CD_2Cl_2, 298 K): δ = = –0.15 (s, 9H), –0.09 (s, 9H), 0.44 (dd, *J* = 15.4, 8.6 Hz, 1H), 0.69 (dd, *J* = 15.3, 3.8 Hz, 1H), 1.08 (qd, *J* = 8.0, 3.8 Hz, 1H), 2.63 (d, *J* = 7.8 Hz, 2H), 7.12–7.20 (m, 3H), 7.24 (t, *J* = 7.0, 2H) ppm. The ^{1}H NMR spectroscopic data are in accordance with those in **5.2**.

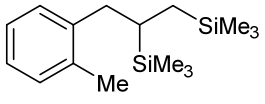


4b
$C_{16}H_{30}Si_2$
M = 278.59 g/mol

(3-(*para*-Tolyl)propane-1,2-diyl)bis(trimethylsilane) (4b): Prepared from 1-allyl-4-methylbenzene (**1b**, 26.4 mg, 0.2 mmol, 1.0 equiv) and hexamethyldisilane (43.9 mg, 0.3 mmol, 1.5

equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) in chlorobenzene (0.8 mL) at 80°C for 16 h according to the general procedure. CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (66%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **4b** as a colorless oil (29.5 mg, 53% yield).

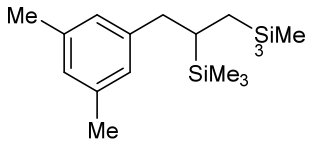
R_f = 0.78 (cyclohexane). **IR** (ATR): ṽ = 3046, 3018, 2951, 2919, 2894, 1893, 1789, 1512, 1445, 1412, 1245, 1109, 1021, 980, 917, 828, 748, 685 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = = –0.15 (s, 9H), –0.8 (s, 9H), 0.42 (dd, *J* = 15.2, 8.6 Hz, 1H), 0.66 (dd, *J* = 15.2, 3.8 Hz, 1H), 1.05 (qd, *J* = 8.4, 3.8 Hz, 1H), 2.31 (s, 3H), 2.57 (dd, *J* = 13.8, 8.3 Hz, 1H), 2.62 (dd, *J* = 13.5, 7.5 Hz, 1H), 7.05 (s, 4H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –2.5, –0.8, 16.3, 21.2, 22.6, 39.5, 128.9, 129.0, 135.2, 139.8 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = –0.08/2.4, 0.42/2.4, 0.66/2.4, –0.15/5.1, 2.62/5.1 ppm. **HRMS** (APCI): calculated for $C_{15}H_{27}Si_2^{\bullet+}$ $[M–CH_3]^{\bullet+}$: 263.1646; found 263.1646.



4c
$C_{16}H_{30}Si_2$
M = 278.59 g/mol

(3-(*ortho*-Tolyl)propane-1,2-diyl)bis(trimethylsilane) (4c): Prepared from 1-allyl-2-methyl-benzene (**1c**, 26.4 mg, 0.2 mmol, 1.0 equiv) and hexamethyldisilane (43.9 mg, 0.3 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) in chlorobenzene (0.8 mL) at 80°C for 16 h according to the general procedure. CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (99%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **4c** as a colorless oil (50.7 mg, 91% yield).

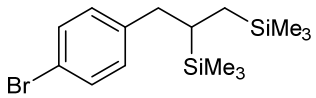
R_f = 0.77 (cyclohexane). **IR** (ATR): ṽ = 3062, 3016, 2950, 2893, 2863, 2000, 1931, 1907, 1602, 1491, 1456, 1412, 1245, 1150, 1121, 1049, 1024, 980, 937, 915, 827, 741, 685 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = = –0.19 (s, 9H), –0.8 (s, 9H), 0.46 (dd, *J* = 15.4, 7.2 Hz, 1H), 0.69 (dd, *J* = 15.2, 4.3 Hz, 1H), 1.06 (m_c, 1H), 2.32 (s, 3H), 2.49 (dd, *J* = 13.9, 9.2 Hz, 1H), 2.75 (dd, *J* = 13.9, 6.8 Hz, 1H), 7.06–7.13 (m, 4H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –2.7, –1.0, 15.9, 19.8, 20.1, 37.3, 125.7, 126.0, 130.1, 130.5, 136.2, 140.9 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = –0.19/2.3, 0.46/2.3, 0.69/2.3, –0.08/5.3, 2.49/5.3, 2.75/5.3 ppm. **HRMS** (APCI): calculated for $C_{15}H_{27}Si_2^{\bullet+}$ $[M–CH_3]^{\bullet+}$: 264.1646; found 263.1647.



4d
$C_{17}H_{32}Si_2$
M = 292.61 g/mol

(3-(3,5-Dimethylphenyl)propane-1,2-diyl)bis(trimethylsilane) (4d): Prepared from 1-allyl-3,5-dimethylbenzene (**1d**, 29.2 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (43.9 mg, 0.30 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) in chlorobenzene (0.8 mL) at 80°C for 16 h according to the general procedure. CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (94%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **4d** as a colorless oil (41.0 mg, 70% yield).

$\mathbf{R_f}$ = 0.83 (cyclohexane). **IR** (ATR): ṽ = 3013, 2950, 2895, 2098, 1925, 1605, 1447, 1412, 1245, 1111, 1036, 827, 748, 686 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = –0.13 (s, 9H), –0.09 (s, 9H), 0.42 (dd, *J* = 15.2, 8.4 Hz, 1H), 0.66 (dd, *J* = 15.2, 3.8 Hz, 1H), 1.05 (qd, *J* = 8.0, 3.8 Hz, 1H), 2.28 (s, 6H), 2.55 (d, *J* = 7.9 Hz, 2H), 6.78–6.80 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –2.6, –0.8, 16.2, 21.4, 22.4, 39.7, 127.1, 127.4, 137.5, 142.8 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = –0.09/2.2, 0.42/2.2, 0.66/2.2, –0.14/5.0, 2.55/4.9 ppm. **HRMS** (APCI): calculated for $C_{16}H_{29}Si_2^{\bullet+}$ [M–CH_3]$^{\bullet+}$: 277.1808; found 277.1800.

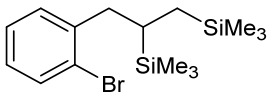


4e
$C_{15}H_{27}BrSi_2$
M = 343.46 g/mol

(3-(4-Bromophenyl)propane-1,2-diyl)bis(trimethylsilane) (4e): Prepared from 1-allyl-4-bromobenzene (**1e**, 39.2 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (43.9 mg, 0.30 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) in chlorobenzene (0.8 mL) at 80°C for 16 h according to the general procedure. CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (95%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **4e** as a colorless oil (55.0 mg, 80% yield).

$\mathbf{R_f}$ = 0.85 (cyclohexane). **IR** (ATR): ṽ = 2950, 2894, 2103, 1486, 1403, 1245, 1116, 1072, 1010, 826, 747, 686 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = –0.14 (s, 9H), –0.10 (s, 9H), 0.39

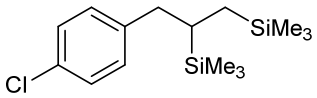
(dd, *J* = 15.3, 8.4 Hz, 1H), 0.67 (dd, *J* = 15.2, 3.8 Hz, 1H), 1.01 (qd, *J* = 8.0, 3.8 Hz, 1H), 2.57 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –2.5, –0.8, 16.2, 22.5, 39.3, 119.5, 130.9, 131.3, 142.0 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = –0.10/2.1, 0.39/2.1, 0.67/2.1, –0.14/5.0, 2.57/5.0 ppm. **HRMS** (APCI): calculated for $C_{14}H_{24}BrSi_2^{\bullet+}$ $[M–CH_3]^{\bullet+}$: 327.0600; found 327.0597.



4f
$C_{15}H_{27}BrSi_2$
M = 343.46 g/mol

(3-(2-Bromophenyl)propane-1,2-diyl)bis(trimethylsilane) (4f): Prepared from 1-allyl-2-bromobenzene (**1f**, 39.2 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (43.9 mg, 0.30 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) in chlorobenzene (0.8 mL) at 80°C for 16 h according to the general procedure. CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (97%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **4f** as a colorless oil (61.8 mg, 90% yield).

R_f = 0.84 (cyclohexane). **IR** (ATR): ṽ = 3058, 2950, 2892, 2093, 1912, 1565, 1439, 1245, 1105, 1022, 828, 745, 686 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = –0.22 (s, 9H), –0.05 (s, 9H), 0.44 (dd, *J* = 15.4, 6.8 Hz, 1H), 0.67 (dd, *J* = 15.4, 4.5 Hz, 1H), 1.28 (dtd, *J* = 9.6, 6.5, 4.5 Hz, 1H), 2.52 (dd, *J* = 13.6, 9.6 Hz, 1H), 2.92 (dd, *J* = 13.6, 6.3 Hz, 1H), 7.00–7.06 (m, 1H), 7.19–7.20 (m, 2H), 7.51 (d, *J* = 8.3 Hz, 1H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –2.7, –1.1, 15.4, 19.7, 40.0, 125.1, 127.1, 127.7, 131.7, 133.1, 142.1 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = –0.22/2.0, 0.44/2.0, 0.67/2.0, –0.05/5.4, 0.67/5.4 ppm. **HRMS** (APCI): calculated for $C_{14}H_{24}BrSi_2^{\bullet+}$ $[M–CH_3]^{\bullet+}$: 327.0600; found 327.0599.

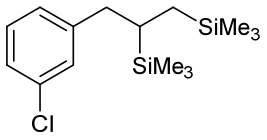


4g
$C_{15}H_{27}ClSi_2$
M = 299.00 g/mol

(3-(4-Chlorophenyl)propane-1,2-diyl)bis(trimethylsilane) (4g): Prepared from 1-allyl-4-chlorobenzene (**1g**, 30.5 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (43.9 mg, 0.30 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) in benzene (0.8

mL) at 80°C for 16 h according to the general procedure. CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (99%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **4g** as a colorless oil (53.2 mg, 89% yield).

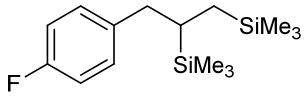
R_f = 0.85 (cyclohexane). **IR** (ATR): $\tilde{\nu}$ = 2951, 2894, 2308, 2090, 1490, 1406, 1245, 1092, 1014, 827, 747, 686 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = –0.14 (s, 9H), –0.09 (s, 9H), 0.39 (dd, *J* = 15.3, 8.4 Hz, 1H), 0.67 (dd, *J* = 15.2, 3.8 Hz, 1H), 1.01 (qd, *J* = 7.9, 3.8 Hz, 1H), 2.59 (d, *J* = 7.9 Hz, 2H), 7.08–7.11 (m, 2H), 7.21–7.23 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –2.5, –0.8, 16.2, 22.6, 39.3, 128.4, 130.5, 131.5, 141.5 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = –0.09/2.1, 0.39/2.1, 0.67/2.1, –0.14/5.0, 2.59/5.0 ppm. **HRMS** (APCI): calculated for $C_{14}H_{24}ClSi_2^{\bullet+}$ $[M–CH_3]^{\bullet+}$: 283.1105; found 283.1102.



4h
$C_{15}H_{27}ClSi_2$
M = 299.00 g/mol

(3-(3-Chlorophenyl)propane-1,2-diyl)bis(trimethylsilane) (4h): Prepared from 1-allyl-3-chlorobenzene (**1h**, 30.5 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (43.9 mg, 0.30 mmol, 1.0 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) in chlorobenzene (0.8 mL) at 80°C for 16 h according to the general procedure. CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (96%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **4h** as a colorless oil (49.0 mg, 82% yield).

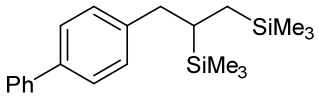
R_f = 0.80 (cyclohexane). **IR** (ATR): $\tilde{\nu}$ = 2951, 2894, 2323, 2094, 1929, 1595, 1474, 1411, 1246, 827, 775, 748, 684 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = –0.12 (s, 9H), –0.10 (s, 9H), 0.40 (dd, *J* = 15.3, 8.2 Hz, 1H), 0.68 (dd, *J* = 15.3, 3.9 Hz, 1H), 1.03 (qd, *J* = 8.0, 3.9 Hz, 1H), 2.55–2.64 (m, 2H), 7.05 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.13–7.20 (m, 3H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –2.6, –0.8, 16.2, 22.5, 39.6, 126.1, 127.4, 129.3, 129.5, 134.1, 145.2 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = –0.10/2.2, 0.40/2.2, 0.68/2.2, –0.12/5.1 ppm. **HRMS** (APCI): calculated for $C_{14}H_{24}ClSi_2^{\bullet+}$ $[M–CH_3]^{\bullet+}$: 283.1105; found 283.1100.



4i
$C_{15}H_{27}FSi_2$
M = 282.55 g/mol

(3-(4-Fluorophenyl)propane-1,2-diyl)bis(trimethylsilane) (4i): Prepared from 1-allyl-4-fluorobenzene (**1i**, 27.2 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (43.9 mg, 0.30 mmol, 1.0 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) in chlorobenzene (0.8 mL) at 80°C for 16 h according to the general procedure. CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (68%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **4i** as a colorless oil (35.1 mg, 62% yield).

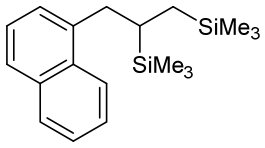
R_f = 0.78 (cyclohexane). **IR** (ATR): $\tilde{\nu}$ = 3038, 2951, 2895, 1930, 1883, 1600, 1507, 1444, 1413, 1292, 1246, 1221, 1156, 1113, 1088, 1015, 977, 917, 827, 748, 712, 685 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = –0.14 (s, 9H), –0.09 (s, 9H), 0.40 (dd, *J* = 15.3, 8.4 Hz, 1H), 0.67 (dd, *J* = 15.4, 3.8 Hz, 1H), 1.00 (qd, *J* = 8.0, 3.8 Hz, 1H), 2.60 (d, *J* = 7.8 Hz, 2H), 7.94 (t, *J* = 8.7 Hz, 2H), 7.11 (dd, *J* = 8.7, 5.6 Hz, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –2.6, –0.8, 16.2, 22.8, 39.1, 115.0 (d, *J* = 21.2 Hz), 130.4 (d, *J* = 7.6 Hz), 138.6 (d, *J* = 3.6 Hz), 161.4 (d, *J* = 243.4 Hz) ppm. **^{19}F{^{1}H} NMR** (471 MHz, $CDCl_3$, 298 K): δ = –117.9 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = –0.09/2.2, 0.40/2.2, 0.67/2.2, –0.14/5.0, 0.40/5.0, 0.67/5.0, 1.00/5.0, 2.60/5.0, ppm. **HRMS** (APCI): calculated for $C_{14}H_{24}FSi_2^{\bullet+}$ $[M–CH_3]^{\bullet+}$: 267.1395; found 267.1395.



4j
$C_{21}H_{32}Si_2$
M = 340.66 g/mol

(3-([1,1'-Biphenyl]-4-yl)propane-1,2-diyl)bis(trimethylsilane) (4j): Prepared from 4-allyl-1,1'-biphenyl (**1j**, 38.9 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (43.9 mg, 0.30 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) in chlorobenzene (0.8 mL) at 80°C for 16 h according to the general procedure. CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (84%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **4j** as a white solid (51.1 mg, 75% yield).

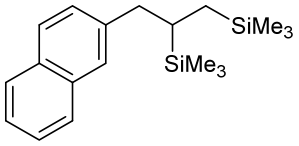
R_f = 0.66 (cyclohexane). **M.P.**: 59–60°C. **IR** (ATR): ṽ = 3026, 2949, 2888, 2341, 2114, 1908, 1599, 1482, 1408, 1243, 1118, 1006, 827, 751, 692 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = –0.12 (s, 9H), –0.08 (s, 9H), 0.46 (dd, *J* = 15.2, 8.4 Hz, 1H), 0.70 (dd, *J* = 15.2, 3.8 Hz, 1H), 1.10 (qd, *J* = 7.9, 3.8 Hz, 1H), 2.67 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.31–7.34 (m, 1H), 7.41–7.44 (m, 2H), 7.49–7.51 (m, 2H), 7.58–7.60 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –2.5, –0.8, 16.3, 22.6, 39.5, 127.0, 127.1, 128.8, 129.6, 138.8, 141.4, 142.2 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = –0.08/2.2, 0.70/2.2, –0.12/5.0, 2.67/5.0 ppm. **HRMS** (APCI): calculated for $C_{20}H_{29}Si_2^{\bullet+}$ [M–CH_3]$^{\bullet+}$: 325.1808; found 325.1806.



4k
$C_{19}H_{30}Si_2$
M = 314.62 g/mol

(3-(Naphthalen-1-yl)propane-1,2-diyl)bis(trimethylsilane) (4k): Prepared from 1-allylnaphthalene (**1k**, 33.6 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (43.9 mg, 0.30 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) in chlorobenzene (0.8 mL) at 80°C for 16 h according to the general procedure. CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (86%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **4k** as a white solid (51.0 mg, 81% yield).

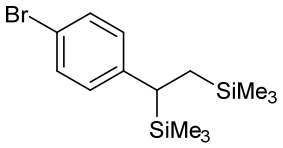
R_f = 0.75 (cyclohexane). **M.P.**: 68–69°C. **IR** (ATR): ṽ = 3063, 2947, 2889, 2646, 2115, 1926, 1594, 1412, 1244, 1119, 1014, 829, 789, 746, 685 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = –0.36 (s, 9H), –0.05 (s, 9H), 0.51 (dd, *J* = 15.3, 6.6 Hz, 1H), 0.72 (dd, *J* = 15.3, 4.6 Hz, 1H), 1.27 (dtd, *J* = 9.8, 6.4, 4.6 Hz, 1H), 2.81 (dd, *J* = 13.8, 9.7 Hz, 1H), 3.31 (dd, *J* = 13.9, 6.2 Hz, 1H), 7.30 (d, *J* = 6.9 Hz, 1H), 7.37 (dd, *J* = 8.1, 7.0 Hz, 1H), 7.48 (m_c, 2H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.84 (dd, *J* = 8.3, 1.1 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –2.7, –1.2, 16.1, 21.1, 37.3, 124.1, 125.3, 125.4, 125.6, 126.8, 127.2, 129.0, 132.4, 134.3, 138.8 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = –0.36/2.0, 0.51/2.0, 0.72/2.0, –0.05/5.1, 3.31/5.1 ppm. **HRMS** (APCI): calculated for $C_{18}H_{27}Si_2^{\bullet+}$ [M–CH_3]$^{\bullet+}$: 299.1651; found 299.1644.



4l
$C_{19}H_{30}Si_2$
M = 314.62 g/mol

(3-(Naphthalen-2-yl)propane-1,2-diyl)bis(trimethylsilane) (4l): Prepared from 2-allylnaphthalene (**1l**, 33.6 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (43.9 mg, 0.30 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) in chlorobenzene (0.8 mL) at 80°C for 16 h according to the general procedure. CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (96%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **4l** as a white solid (45.3 mg, 72% yield).

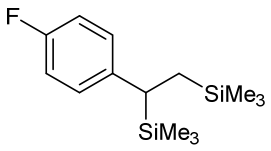
R_f = 0.70 (cyclohexane). **M.P.**: 37–38°C. **IR** (ATR): $\tilde{\nu}$ = 3054, 2950, 2900, 2648, 2284, 2096, 1626, 1598, 1505, 1409, 1243, 1110, 1017, 957, 830, 742, 687 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = –0.13 (s, 9H), –0.10 (s, 9H), 0.50 (dd, *J* = 15.2, 8.4 Hz, 1H), 0.72 (dd, *J* = 15.2, 3.8 Hz, 1H), 1.19 (qd, *J* = 8.0, 3.9 Hz, 1H), 2.80 (d, *J* = 7.8 Hz, 2H), 7.34 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.43 (dtd, *J* = 16.1, 6.9, 1.3 Hz, 2H), 7.60 (s, 1H), 7.74–7.80 (m, 3H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –2.5, –0.7, 16.4, 22.4, 40.1, 125.1, 125.9, 127.2, 127.5, 127.7, 127.8, 128.0, 132.2, 133.7, 140.5 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ –0.10/2.1, 0.50/2.1, 0.72/2.1, = –0.13/5.1, 2.80/5.1 ppm. **HRMS** (APCI): calculated for $C_{18}H_{27}Si_2^{\bullet+}$ $[M–CH_3]^{\bullet+}$: 299.1651; found 299.1649.



4m
$C_{14}H_{25}BrSi_2$
M = 329.43 g/mol

(1-(4-Bromophenyl)ethane-1,2-diyl)bis(trimethylsilane) (4m): Prepared from 1-bromo-4-vinylbenzene (**1m**, 36.6 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (87.8 mg, 0.60 mmol, 3.0 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) in chlorobenzene (4 mL) at 80°C for 16 h according to the general procedure. CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (80%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **4m** as a white solid (50.2 mg, 76% yield).

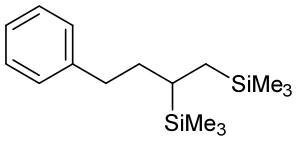
R_f = 0.79 (cyclohexane). **M.P.**: 78–79°C. **IR** (ATR): ṽ = 3036, 2949, 2899, 2863, 2789, 1985, 1932, 1897, 1774, 1701, 1652, 1581, 1559, 1543, 1482, 1447, 1402, 1291, 1242, 1219, 1181, 1143, 1096, 1069, 1003, 942, 829, 768, 748, 716, 689 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = –0.20 (s, 9H), –0.09 (s, 9H), 0.84 (dd, *J* = 15.0, 2.3 Hz, 1H), 1.00 (dd, *J* = 15.3, 13.0 Hz, 1H), 2.04 (dd, *J* =13.0, 2.3 Hz, 1H), 6.90 (dt, *J* = 8.4, 2.6 Hz, 2H), 7.31 (dt, *J* = 8.4, 2.7 Hz, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –3.3, –0.9, 16.0, 31.4, 117.7, 129.5, 131.0, 144.3 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = –0.20/3.0, 0.84/3.0, 1.00/3.4, –0.09/4.7 ppm. **HRMS** (APCI): calculated for $C_{13}H_{22}BrSi_2^{\bullet+}$ [M–CH_3]$^{\bullet+}$: 313.0438, 315.0417; found 313.0439, 315.0420.



4n
$C_{14}H_{25}FSi_2$
M = 268.52 g/mol

(1-(4-Fluorophenyl)ethane-1,2-diyl)bis(trimethylsilane) (4n): Prepared from 1-fluoro-4-vinylbenzene (**1n**, 36.6 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (87.8 mg, 0.60 mmol, 3.0 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) in chlorobenzene (4 mL) at 80°C for 16 h according to the general procedure. CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (55%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **4n** as a colorless oil (25.5 mg, 47% yield).

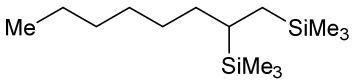
R_f = 0.81 (cyclohexane). **IR** (ATR): ṽ = 3036, 2952, 2896, 2484, 2254, 2096, 2075, 1931, 1879, 1757, 1644, 1601, 1504, 1452, 1409, 1319, 1289, 1246, 1221, 1182, 1157, 1100, 1013, 828, 747, 687 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = –0.18 (s, 9H), –0.06 (s, 9H), 0.87 (dd, *J* = 15.0, 2.4 Hz, 1H), 1.02 (dd, *J* = 15.0, 13.0 Hz, 1H), 2.08 (dd, *J* =13.0, 2.3 Hz, 1H), 6.92 (tt, *J* = 8.7, 2.2 Hz, 2H), 6.99 (ddt, *J* = 8.7, 5.4, 2.2 Hz, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –3.1, –1.1, 16.2, 30.8, 114.6 (d, *J* = 20.9 Hz), 128.7 (d, *J* = 7.6 Hz), 140.7 (d, *J* = 3.0 Hz), 160.3 (d, *J* = 241.6 Hz) ppm. **^{19}F{^{1}H} NMR** (471 MHz, $CDCl_3$, 298 K): δ = –119.9 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = –0.18/2.9, 0.87/2.9, 1.02/2.9, –0.06/4.3 ppm. **HRMS** (APCI): calculated for $C_{13}H_{22}FSi_2^{\bullet+}$ [M–CH_3]$^{\bullet+}$: 253.1239; found 253.1240.



4o
$C_{16}H_{30}Si_2$
M = 278.59 g/mol

(4-Phenylbutane-1,2-diyl)bis(trimethylsilane) (4o): Prepared from but-3-en-1-ylbenzene (**1o**, 26.4 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (43.9 mg, 0.30 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) in chlorobenzene (0.8 mL) at 50°C for 16 h according to the general procedure. CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (78%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **4o** as a colorless oil (42.0 mg, 75% yield).

R_f = 0.79 (cyclohexane). **IR** (ATR): ṽ = 3062, 3026, 2950, 2895, 2856, 2480, 2330, 2261, 2088, 1996, 1935, 1858, 1798, 1737, 1602, 1495, 1453, 1409, 1345, 1245, 1113, 1075, 1029, 971, 828, 743, 694 cm^{-1}. **^{1}H NMR** (500 MHz, CD_2Cl_2, 298 K): δ = 0.02 (s, 9H), 0.03 (s, 9H), 0.49 (dd, *J* = 15.3, 9.8 Hz, 1H), 0.66 (dd, *J* = 15.3, 3.4 Hz, 1H), 0.80 (m_c, 1H), 1.60 (m_c, 1H), 1.73 (m_c, 1H), 2.58 (dd, *J* =9.3, 8.0 Hz, 1H), 7.13–7.19 (m, 3H), 7.24–7.27 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –2.3, –0.7, 16.4, 20.9, 36.1, 36.2, 125.9, 128.6, 128.7, 143 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = 0.02/3.5, 0.03/3.5 ppm. **HRMS** (APCI): calculated for $C_{16}H_{30}Si_2^{\bullet+}$ $[M–CH_3]^{\bullet+}$: 263.1646; found 263.1645.

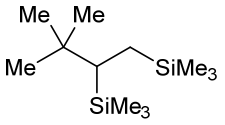


4p
$C_{14}H_{34}Si_2$
M =258.60 g/mol

Octane-1,2-diylbis(trimethylsilane) (4p): Prepared from oct-1-ene (**1p**, 22.5 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (43.9 mg, 0.30 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) in benzene (0.8 mL) at 50°C for 16 h according to the general procedure. CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (74%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **4p** as a colorless oil (34.1 mg, 66% yield).

R_f = 0.87 (cyclohexane). **IR** (ATR): ṽ = 2953, 2923, 2854, 2481, 2310, 2183, 2113, 2065, 1995, 1922, 1461, 1410, 1377, 1246, 1170, 1134, 1097, 1051, 829, 747, 685 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = –0.04 (s, 9H), –0.01 (s, 9H), 0.37 (dd, *J* = 15.0, 9.8 Hz, 1H), 0.56 (dd,

J = 15.3, 3.4 Hz, 1H), 0.67 (m_c, 1H), 0.88 (t, 3H), 1.26–1.42 (m, 10H) ppm. **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$, 298 K): δ = –2.3, –0.6, 14.3, 16.3, 20.4, 22.9, 29.3, 30.2, 32.0, 33.3 ppm. **$^1H/^{29}Si$ HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = –0.01/2.4, 0.37/2.4, –0.04/4.7 ppm. **HRMS** (LIFDI): calculated for $C_{14}H_{32}Si_2^{\bullet+}$ $[M]^{\bullet+}$: 258.2194; found 258.2194.

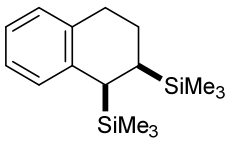


4q
$C_{12}H_{30}Si_2$
M = 230.54 g/mol

(3,3-Dimethylbutane-1,2-diyl)bis(trimethylsilane) (4q): Prepared from 3,3-dimethylbut-1-ene (**1q**, 16.9 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (43.9 mg, 0.30 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) in benzene (0.8 mL) at 50°C for 16 h according to the general procedure. CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (42%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **4q** as a colorless oil (16.7 mg, 36% yield).

$\mathbf{R_f}$ = 0.88 (cyclohexane). **IR** (ATR): ṽ = 2951, 2900, 2871, 2484, 2356, 2327, 2140, 2107, 2071, 1931, 1468, 1410, 1391, 1363, 1247, 1214, 1118, 1049, 1014, 983, 829, 750, 682 cm^{-1}. **^1H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.00 (s, 9H), 0.03 (s, 9H), 0.52 (dd, *J* = 16.0, 5.2 Hz, 1H), 0.58 (dd, *J* = 16.0, 5.2 Hz, 1H), 0.71 (s, 9H) ppm. **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$, 298 K): δ = 0.0, 1.01, 12.9, 30.7, 32.9, 34.5 ppm. **$^1H/^{29}Si$ HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = 0.01/2.7, 0.03/2.7, 0.58/2.7 ppm. **HRMS** (LIFDI): calculated for $C_{12}H_{30}Si_2^{\bullet+}$ $[M]^{\bullet+}$: 230.1881; found 230.1884.

8 Experimental Details for the Catalytic 1,2-Disilylation of Internal Alkenes

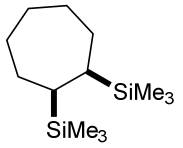


cis-**6a**
$C_{16}H_{28}Si_2$
M = 276.57 g/mol

***cis*-1,2,3,4-Tetrahydronaphthalene-1,2-diyl)bis(trimethylsilane) (*cis*-6a):** Prepared from 1,2-dihydronaphthalene (**5a**, 26.1 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (43.9 mg, 0.30 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) in chlorobenzene (4 mL) at 50°C for 16 h according to the general procedure. CH_2Br_2 (7.0 µL,

0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (91%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct *cis*-**6a** as a colorless oil (48.3 mg, 87% yield, d.r. > 98:2).

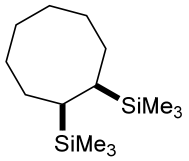
R_f = 0.74 (cyclohexane). **IR** (ATR): ṽ = 3057, 3012, 2949, 2917, 2894, 2855, 2791, 2483, 2208, 2146, 2099, 2060, 2012, 1935, 1906, 1866, 1798, 1681, 1598, 1575, 1487, 1447, 1344, 1300, 1246, 1152, 1134, 1113, 1089, 1036, 1015, 984, 901, 826, 743, 720, 683 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.02 (s, 9H), 0.11 (s, 9H), 1.31 (dt, *J* = 13.8, 3.4 Hz, 1H), 1.97–2.03 (m, 1H), 2.42 (t, *J* = 2.4 Hz, 1H), 2.88 (dd, *J* = 6.0, 8.4 Hz, 2H), 6.89–6.92 (m, 2H), 7.01–7.11 (m, 3H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –1.3, 0.9, 23.3, 27.7, 28.8, 34.5, 124.4, 124.5, 127.9, 129.6, 136.2, 144.6 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = 0.02/2.1, 0.11/2.1 ppm. **HRMS** (APCI): calculated for $C_{16}H_{29}Si_2^{\bullet+}$ $[M+H]^{\bullet+}$: 277.1802; found 277.1803.



cis-**6b**
$C_{13}H_{30}Si_2$
M = 242.55 g/mol

***cis*-1,2-Bis(trimethylsilyl)cycloheptane (*cis*-6b):** Prepared from cycloheptene (**5b**, 19.3 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (43.9 mg, 0.30 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) in benzene (0.8 mL) at 50°C for 16 h according to the general procedure. CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (62%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct *cis*-**6b** as a colorless oil (25.0 mg, 51% yield, d.r. > 98:2).

R_f = 0.88 (cyclohexane). **IR** (ATR): ṽ = 2918, 2849, 2670, 2483, 2320, 2100, 1927, 1705, 1680, 1447, 1404, 1356, 1246, 1160, 1110, 1054, 965, 938, 875, 825, 746, 681 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.04 (s, 18H), 1.13–1.16 (m, 1H), 1.43–1.66 (m, 10H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –0.1, 28.7, 29.0, 29.4, 31.0 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = 0.04/2.4, 1.13–1.16/2.4, 1.43–1.66/2.4 ppm. **HRMS** (LIFDI): calculated for $C_{13}H_{30}Si_2^{\bullet+}$ $[M]^{\bullet+}$: 242.1881; found 242.1882.



cis-**6c**
$C_{14}H_{32}Si_2$
M = 256.58 g/mol

***cis*-1,2-Bis(trimethylsilyl)cyclooctane (*cis*-6c):** Prepared from *cis*-cyclooctene (*cis*-**5c**, 22.1 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (43.9 mg, 0.30 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) in benzene (0.8 mL) at 50°C for 16 h according to the general procedure. CH_2Br_2 (7.0 µL, 0.1 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (83%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct *cis*-**6c** as a colorless oil (40.4 mg, 78% yield, d.r. > 98:2).

$\mathbf{R_f}$ = 0.87 (cyclohexane). **IR** (ATR): $\tilde{\nu}$ = 2948, 913, 2848, 2479, 2093, 2058, 1927, 1468, 1443, 1403, 1362, 1341, 1300, 1245, 1182, 1159, 1122, 1098, 1069, 1049, 1015, 985, 825, 740, 681 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.10 (s, 18H), 1.11–1.34 (m, 1H), 1.35–1.77 (m, 12H) ppm. **^{1}H NMR** (500 MHz, C_6D_6, 338 K): δ = 0.09 (s, 18H), 1.23–1.24 (m, 1H), 1.50–1.63 (m, 12H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 338 K): δ = –0.2, 25.1, 27.6, 29.0, 30.2 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, C_6D_6, 338 K, optimized for J = 7 Hz): δ = 0.09/2.6, 1.23–1.24/2.6 ppm. **HRMS** (LIFDI): calculated for $C_{14}H_{32}Si_2^{\bullet+}$ $[M]^{\bullet+}$: 256.2037; found 256.2038.

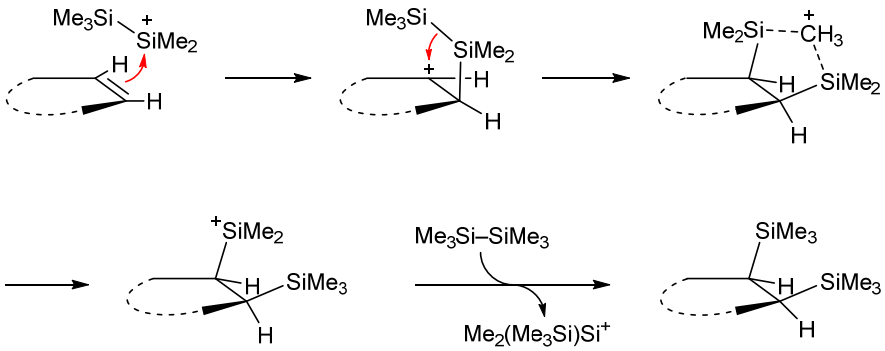
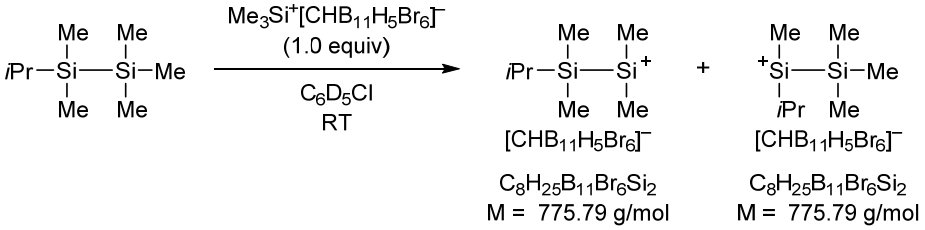


Figure S3. Proposed model for the observed *syn*-diastereoselectivity in the 1,2-disilylation of cyclic 1,2-disubstituted alkenes.

9 Experimental Details for the Catalytic 1,2-Disilylation of Allylbenzene (1a) with 1-Isopropyl-1,1,2,2,2-pentamethyldisilane

9.1 Stoichiometric Dealkylative Silylation of 1-Isopropyl-1,1,2,2,2-pentamethyldisilane with $Me_3Si^+[CHB_{11}H_5Br_6]^-$

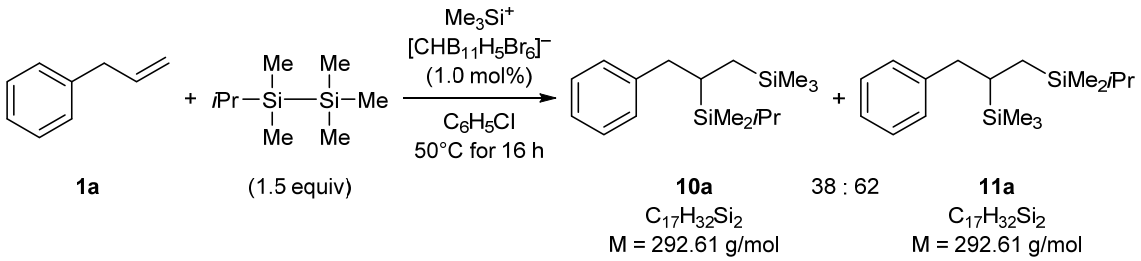


In a valved NMR tube, silylium carborate $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (6.9 mg, 0.010 mmol, 1.00 equiv) was suspended in C_6D_5Cl (0.6 mL) and treated with 1,1,2,2,2-pentamethyldisilane (1.8 mg, 0.020 mmol, 1.0 equiv) at room temperature for 15 min. Incomplete conversion (64%) of both $Me_3Si^+[CHB_{11}H_5Br_6]^-$ and disilane was observed. NMR spectroscopic analysis indicated the formation of $Me_2(iPrMe_2Si)Si^+$ and $iPrMe(Me_3Si)Si^+$ (ratio ~60:40) along with Me_4Si.

Selected NMR spectroscopic data for **$Me_2(iPrMe_2Si)Si^+[CHB_{11}H_5Br_6]^-$**:
^{1}H NMR (500 MHz, C_6D_5Cl, 298 K): δ = –0.01 (s, 6H, Si(CH_3)$_2$*i*Pr), 0.77–0.78 (m, 6H, CH(CH_3)$_2$), 0.90 (s, 6H, Si(CH_3)$_2$) ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, C_6D_5Cl, 298 K, optimized for *J* = 7 Hz): δ = –0.01/–3.6, 0.77–0.78/–3.6, –0.01/102.2, 0.90/102.2 ppm.

Selected NMR spectroscopic data for ***i*PrMe(Me$_3$Si)Si$^+$[CHB$_{11}$H$_5$Br$_6$]$^-$**:
^{1}H NMR (500 MHz, C_6D_5Cl, 298 K): δ = 0.08 (s, 9H, Si(CH_3)$_3$), 0.84 (s, 3H, SiCH_3*i*Pr), 0.93 (d, *J* = 7.6 Hz, 6H, CH(CH_3)$_2$), 1.57 (sept, *J* = 7.6 Hz, 1H, C*H*(CH$_3$)$_2$) ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, C_6D_5Cl, 298 K, optimized for *J* = 7 Hz): δ = 0.08/–10.9, 0.08/102.7 ppm.

9.2 Catalytic 1,2-Disilylation of Allylbenzene (1a) with 1-Isopropyl-1,1,2,2,2-pentamethyldisilane Using $Me_3Si^+[CHB_{11}H_5Br_6]^-$ as Initiator



In a glovebox, silylium carborate $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 0.002 mmol, 0.01 equiv) was suspended in C_6H_5Cl (~0.5 mL) and treated with 1-isopropyl-1,1,2,2,2-pentamethyldisilane (52.4 mg, 0.3 mml, 1.5 equiv). After stirring at 50°C for 5 min, a solution of allylbenzene (**1a**, 23.6 mg, 0.2 mmol, 1.0 equiv) in C_6H_5Cl (~0.3 mL) was added dropwise over a period of 10

min, and the resulting mixture was stirred for additional 16 h at 50°C. Purification by flash column chromatography on silica gel using *n*-pentane afforded a mixture of 1,2-bissilylated adducts **10a** and **11a** as a colorless oil (27.8 mg, 47% combined yield, ratio **10a**:**11a** = 38:62).

Selected NMR spectroscopic data for **10a**:
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = –0.14 (s, 3H), –0.09 (s, 3H), –0.05 (s, 9H), 1.25 (m_c, 1H) ppm. **^{13}C NMR** (126 MHz, C_6D_6, 298 K): δ = –6.7, –0.7, 12.4, 16.6, 17.87, 17.92, 20.8, 40.4 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, C_6D_6, 298 K, optimized for J = 7 Hz): δ = –0.14/9.0, –0.7/9.0, –0.5/1.9 ppm.

Selected NMR spectroscopic data for **11a**:
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = –0.13 (s, 3H), –0.08 (s, 9H), –0.05 (s, 3H), 1.13 (sept, J = 8.0, 3.9 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, C_6D_6, 298 K): δ = –4.6, –2.5, 13.1, 14.2, 18.0, 18.2, 40.3 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, C_6D_6, 298 K, optimized for J = 7 Hz): δ = –0.13/6.6, –0.05/6.6, –0.08/4.7 ppm.

10 NMR Spectra

Figure S4. ^{1}H NMR spectrum (500 MHz, C_6D_5Cl, 298 K) of $Me_3Si^+[CHB_{11}H_5Br_6]^-$ from the reaction of Me_2PhSiH with $Ph_3C^+[CHB_{11}H_5Br_6]^-$ (+ = water adduct).

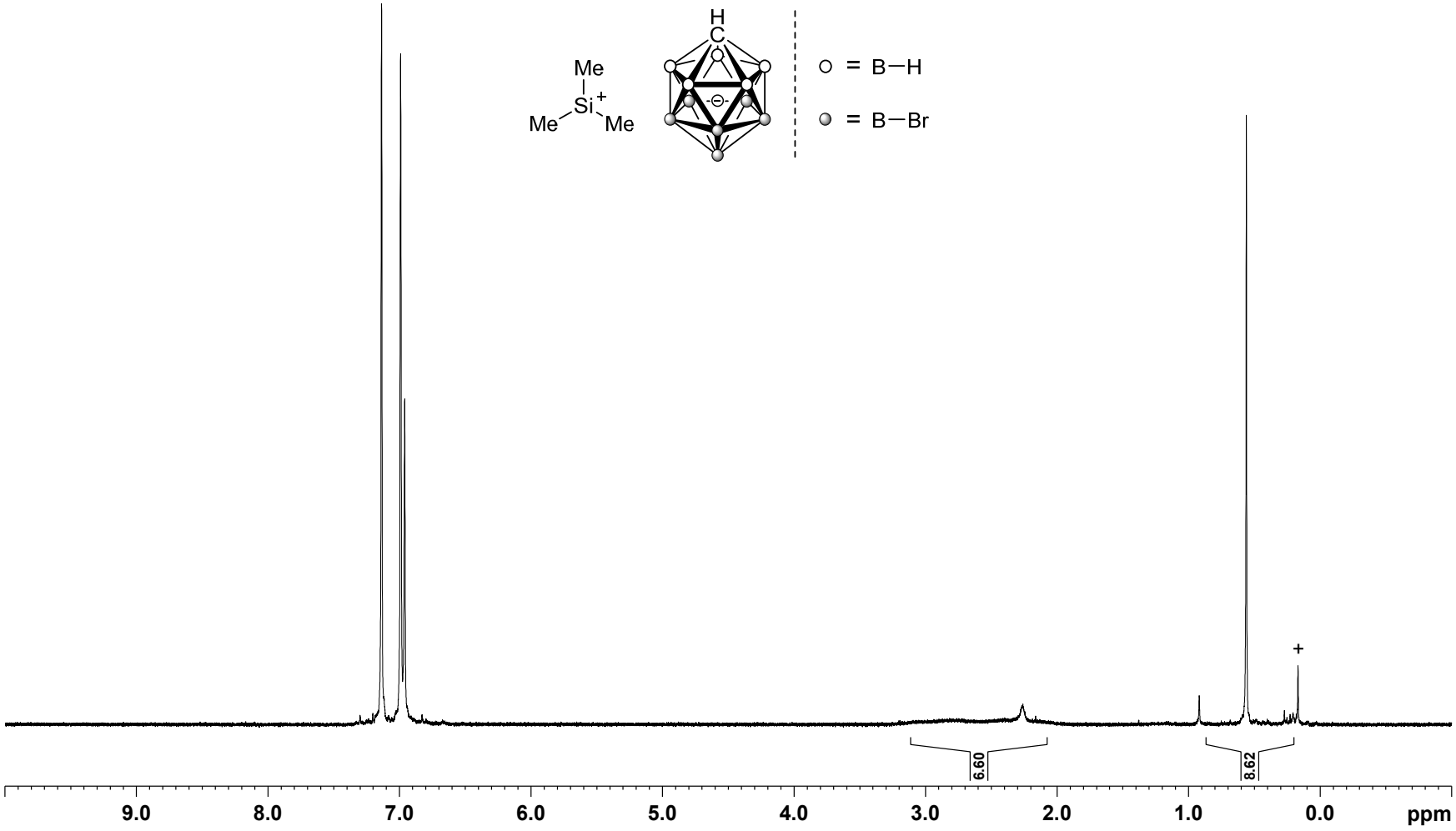


Figure S5. ^{11}B NMR spectrum (161 MHz, C_6D_5Cl, 298 K) of $Me_3Si^+[CHB_{11}H_5Br_6]^-$ from the reaction of Me_2PhSiH with $Ph_3C^+[CHB_{11}H_5Br_6]^-$.

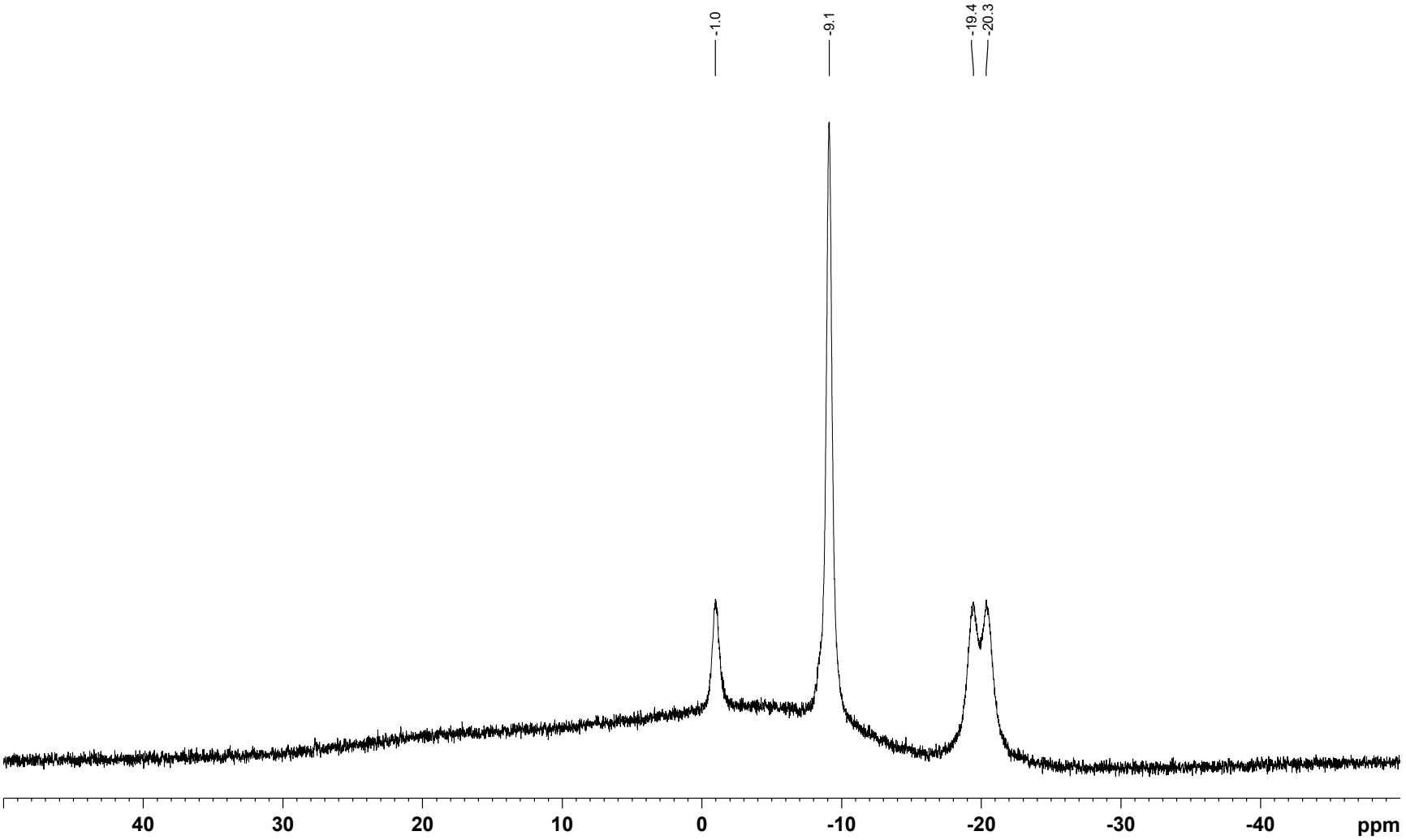


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_5Cl, 298 K) of $Me_3Si^+[CHB_{11}H_5Br_6]^-$ from the reaction of Me_2PhSiH with $Ph_3C^+[CHB_{11}H_5Br_6]^-$.

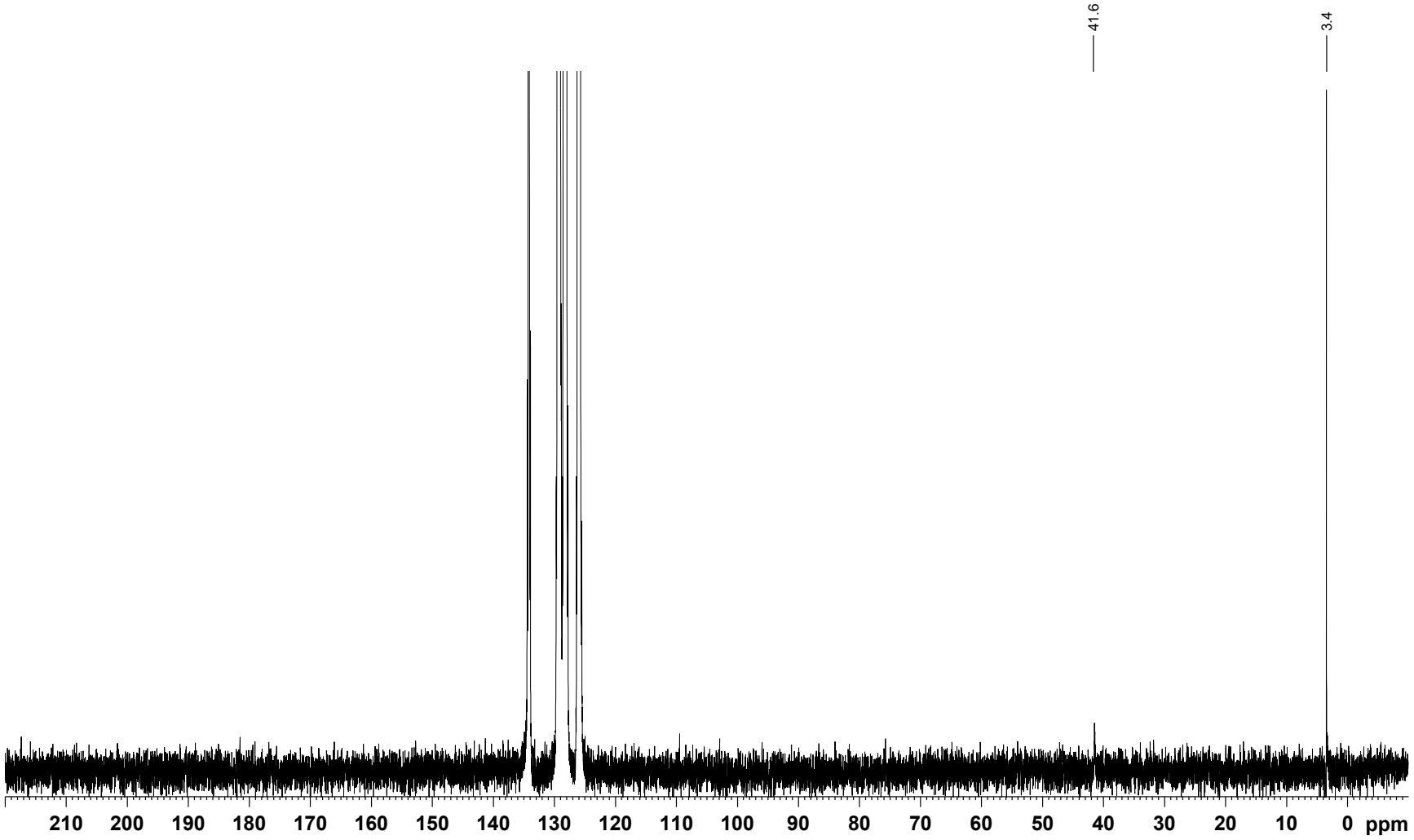


Figure S7. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, C_6D_5Cl, 298 K, optimized for J = 7 Hz) of $Me_3Si^+[CHB_{11}H_5Br_6]^-$ from the reaction of Me_2PhSiH with $Ph_3C^+[CHB_{11}H_5Br_6]^-$.

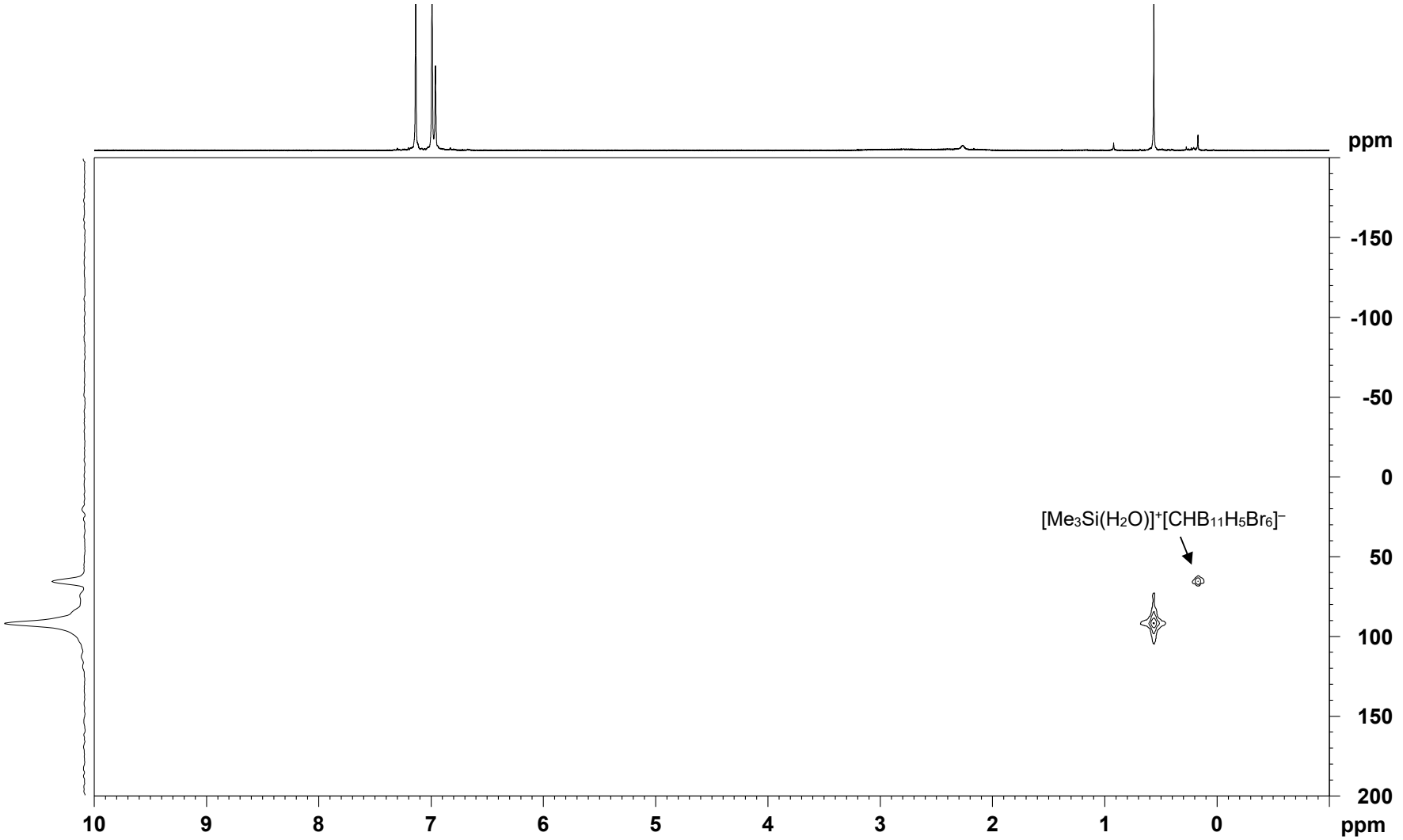


Figure S8. ^{1}H NMR spectrum (500 MHz, C_6D_5Cl, 298 K) of $Me_2(Me_3Si)Si^+[CHB_{11}H_5Br_6]^-$ from the dealkyative silylation of $Me_3SiSiMe_3$ with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (* = $Me_3Si^+[CHB_{11}H_5Br_6]^-$, # = $Me_3SiSiMe_3$, + = Me_4Si).

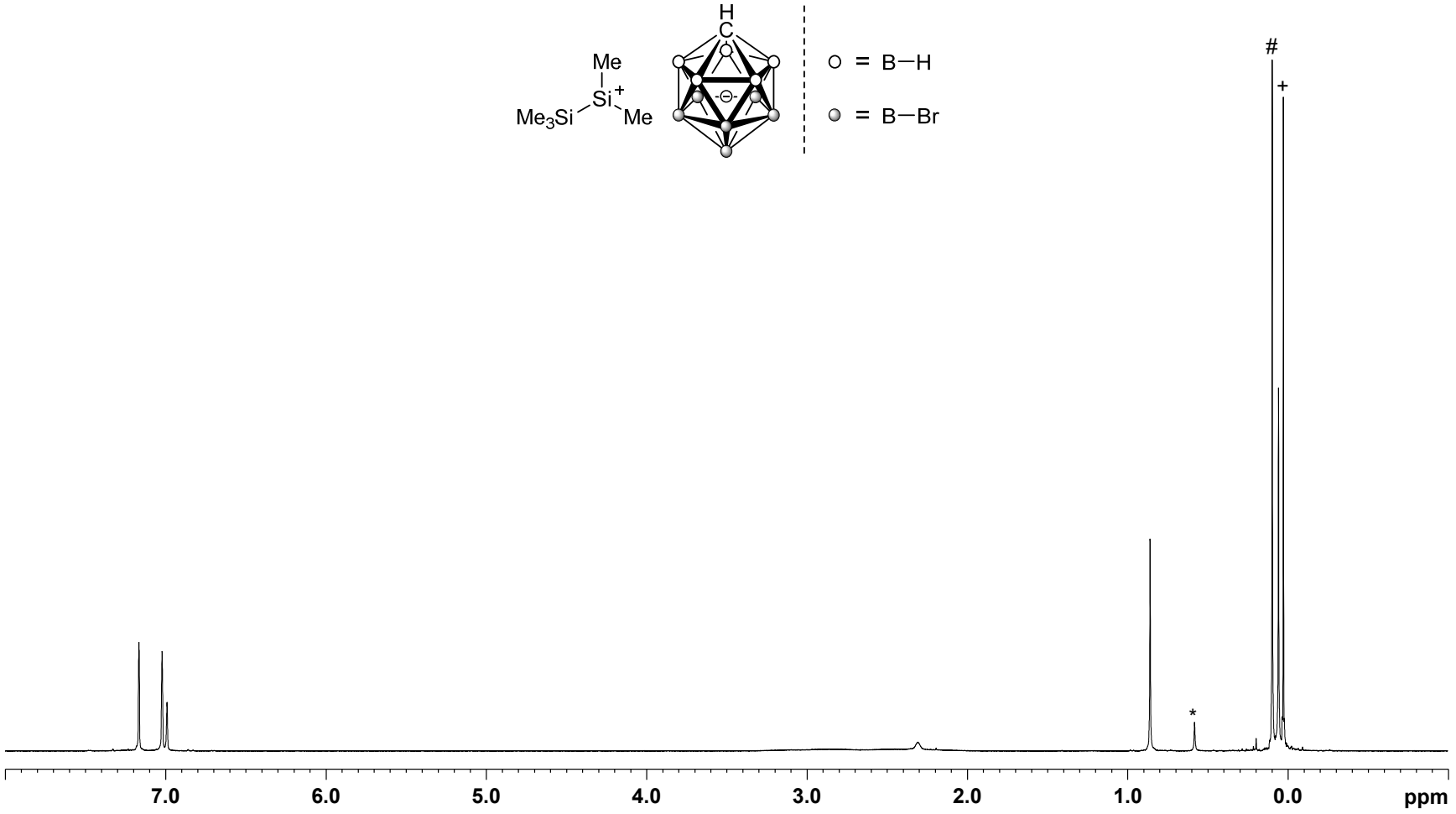


Figure S9. ^{11}B NMR spectrum (161 MHz, C_6D_5Cl, 298 K) of $Me_2(Me_3Si)Si^+[CHB_{11}H_5Br_6]^-$ from the dealkyative silylation of $Me_3SiSiMe_3$ with $Me_3Si^+[CHB_{11}H_5Br_6]^-$.

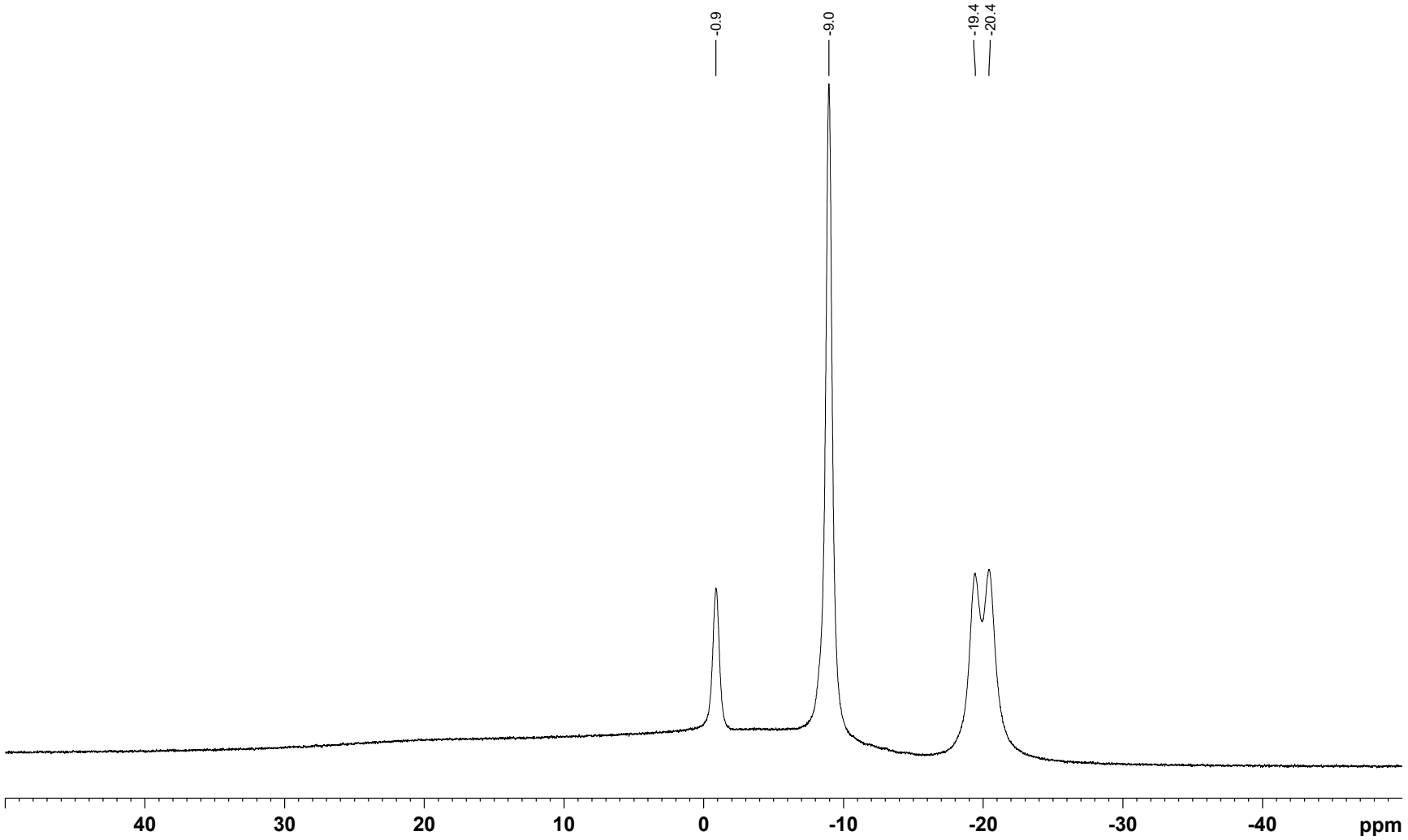


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_5Cl, 298 K) of $Me_2(Me_3Si)Si^+[CHB_{11}H_5Br_6]^-$ from the dealkyative silylation of $Me_3SiSiMe_3$ with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (+ = Me_4Si, # = $Me_3SiSiMe_3$).

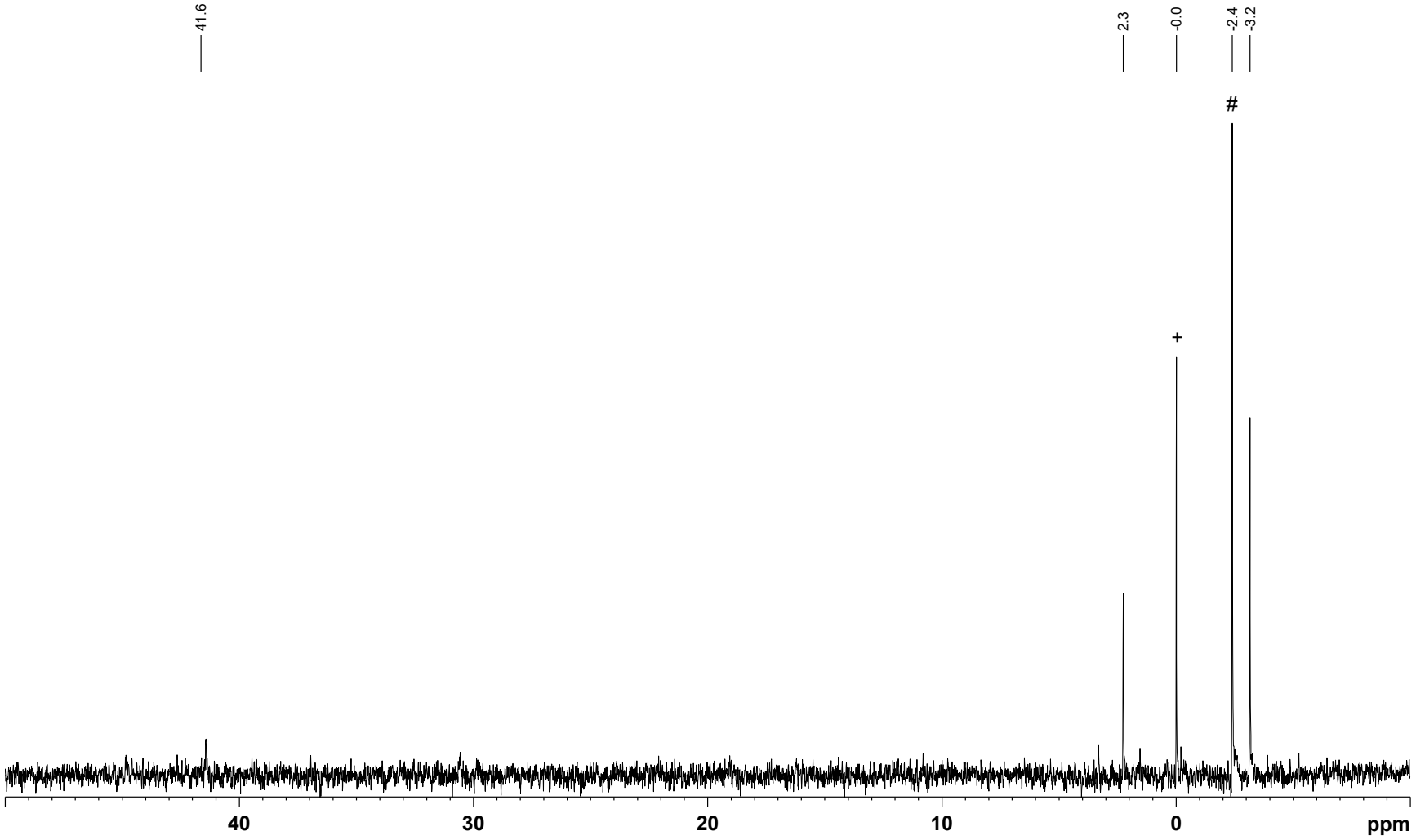


Figure S11. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, C_6D_5Cl, 298 K, optimized for J = 7 Hz) of $Me_2(Me_3Si)Si^+[CHB_{11}H_5Br_6]^-$ from the dealkyative silylation of $Me_3SiSiMe_3$ with $Me_3Si^+[CHB_{11}H_5Br_6]^-$.

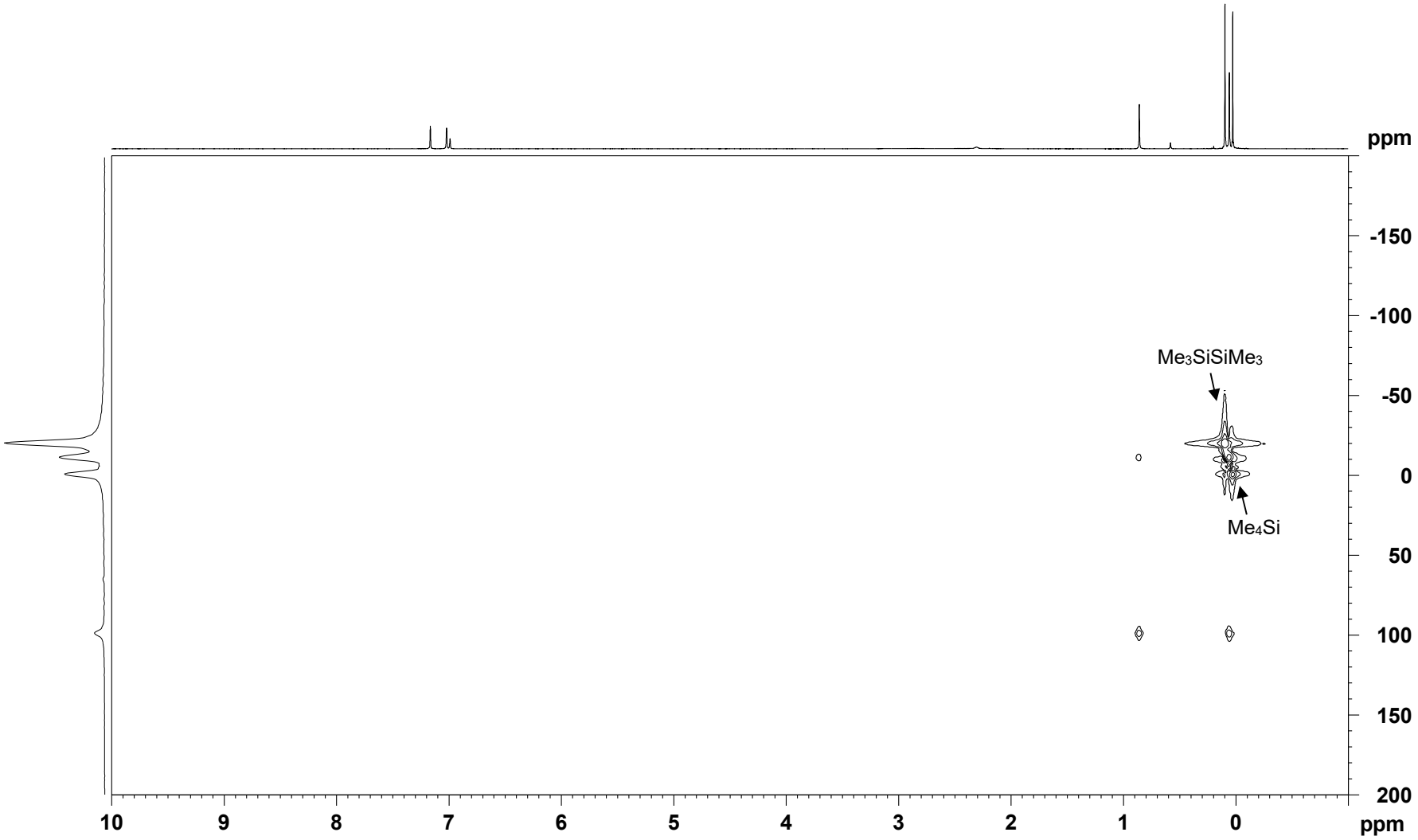


Figure S12. ^{1}H NMR spectrum (500 MHz, C_6D_5Cl, 298 K) of **3a**$^{+}$[$CHB_{11}H_5Br_6$]$^{-}$ from the reaction of $Me_2(Me_3Si)Si^{+}$[$CHB_{11}H_5Br_6$]$^{-}$ with allylbenzene (**1a**).

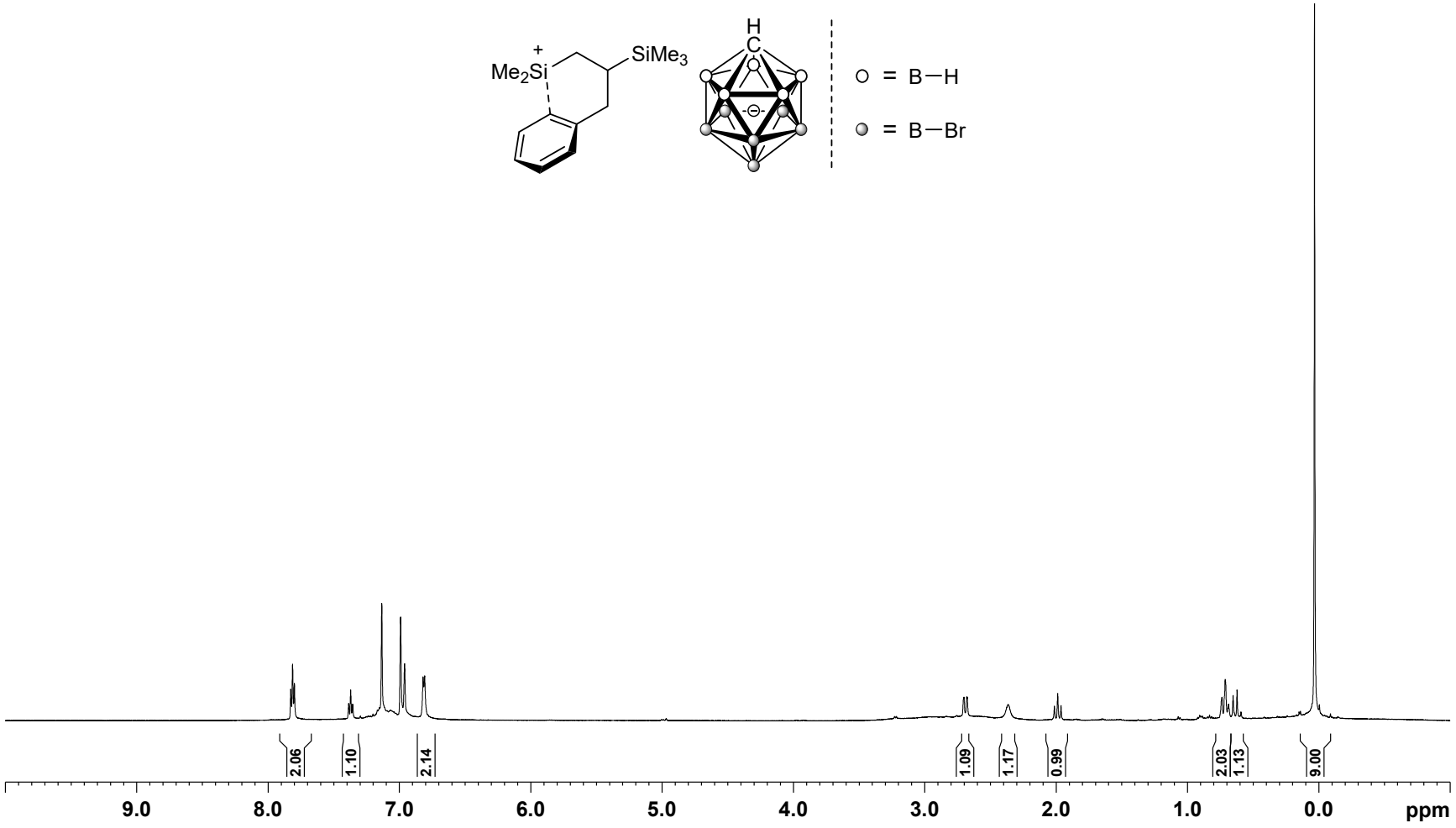


Figure S13. ^{11}B NMR spectrum (161 MHz, C_6D_5Cl, 298 K) of **3a**$^+$[$CHB_{11}H_5Br_6$]$^-$ from the reaction of $Me_2(Me_3Si)Si^+$[$CHB_{11}H_5Br_6$]$^-$ with allylbenzene (**1a**).

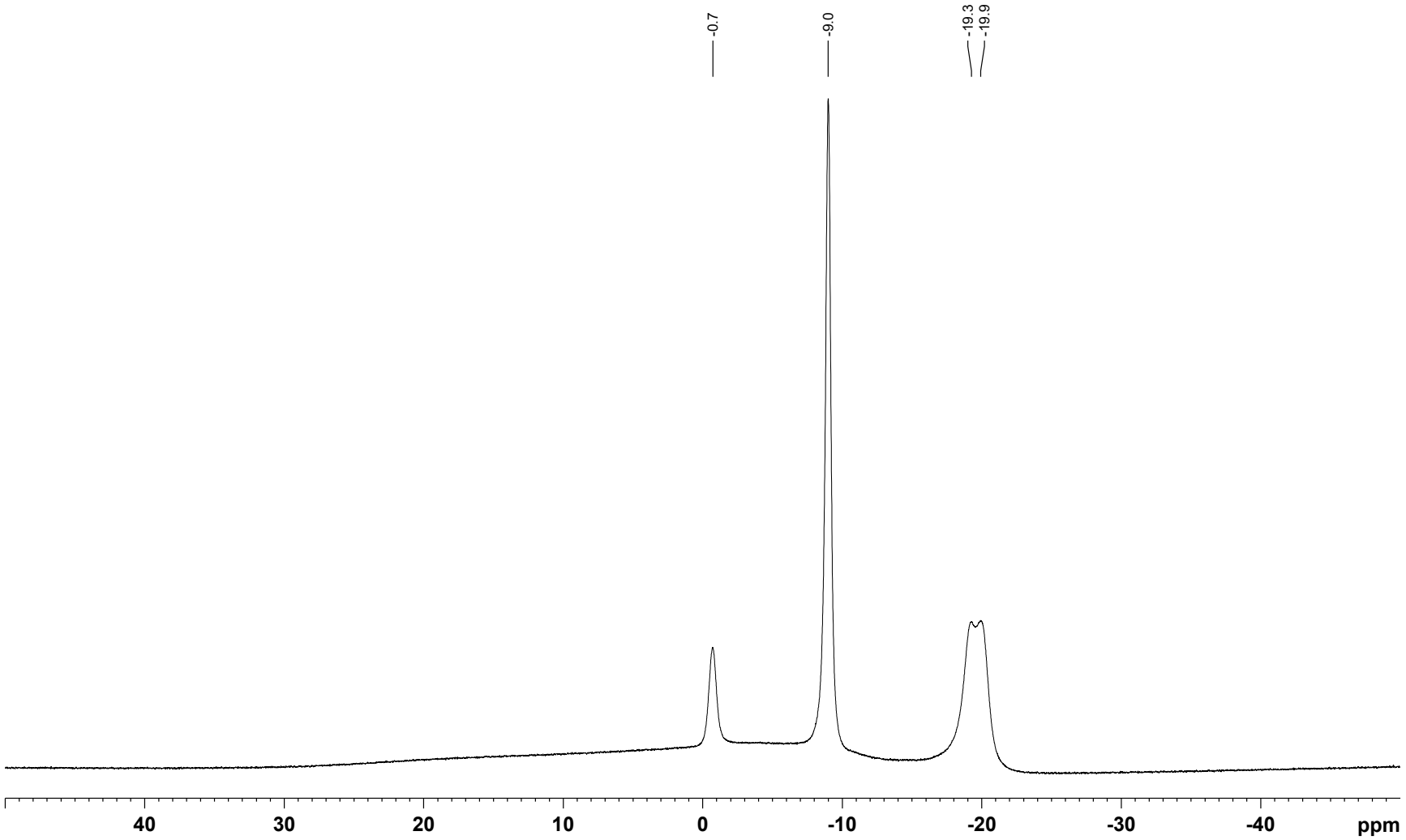


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_5Cl, 298 K) of **3a**$^{+}[CHB_{11}H_5Br_6]^{-}$ from the reaction of $Me_2(Me_3Si)Si^{+}[CHB_{11}H_5Br_6]^{-}$ with allylbenzene (**1a**).

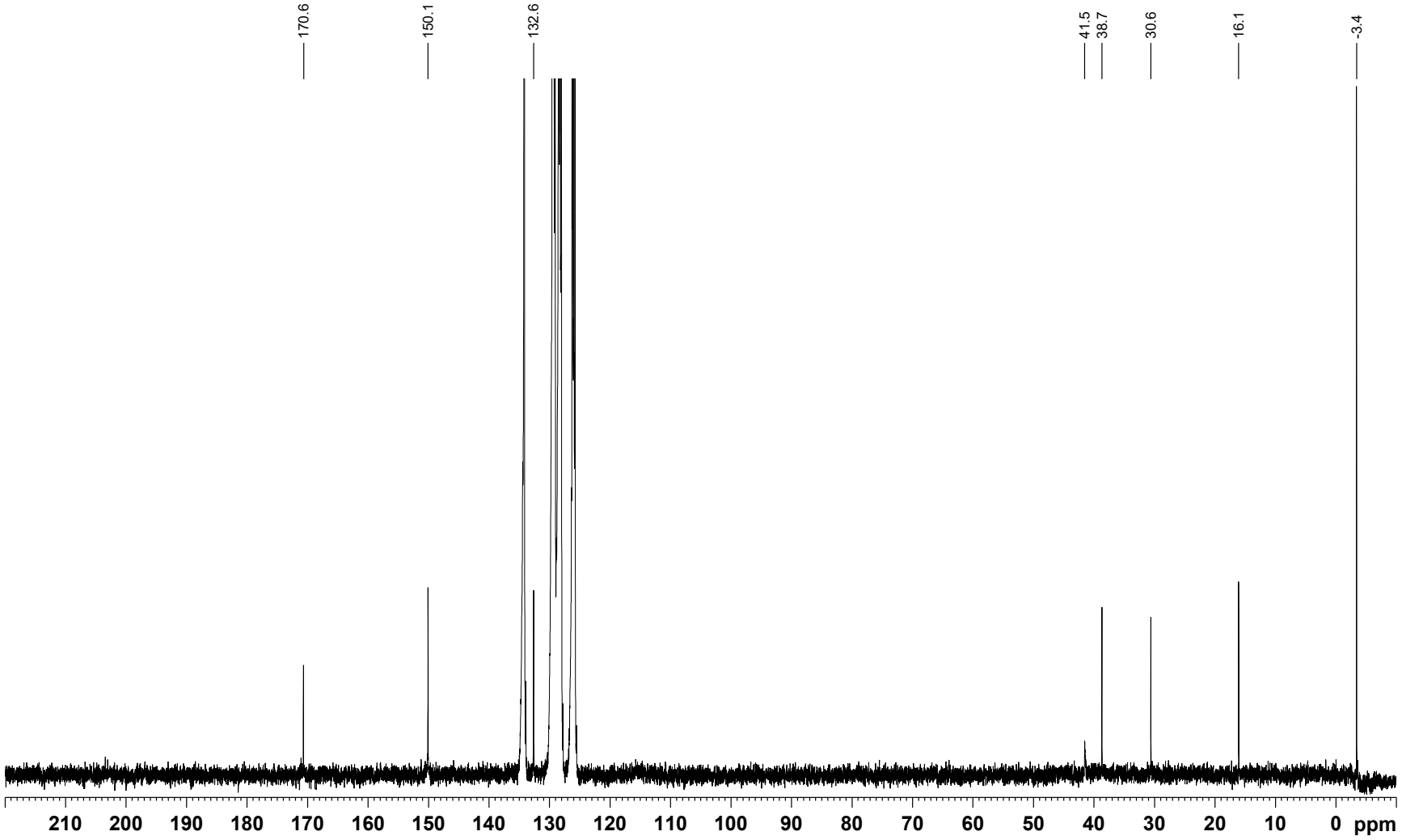


Figure S15. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, C_6D_5Cl, 298 K, optimized for J = 7 Hz) of **3a**$^{+}[CHB_{11}H_5Br_6]^{-}$ from the reaction of $Me_2(Me_3Si)Si^{+}[CHB_{11}H_5Br_6]^{-}$ with allylbenzene (**1a**).

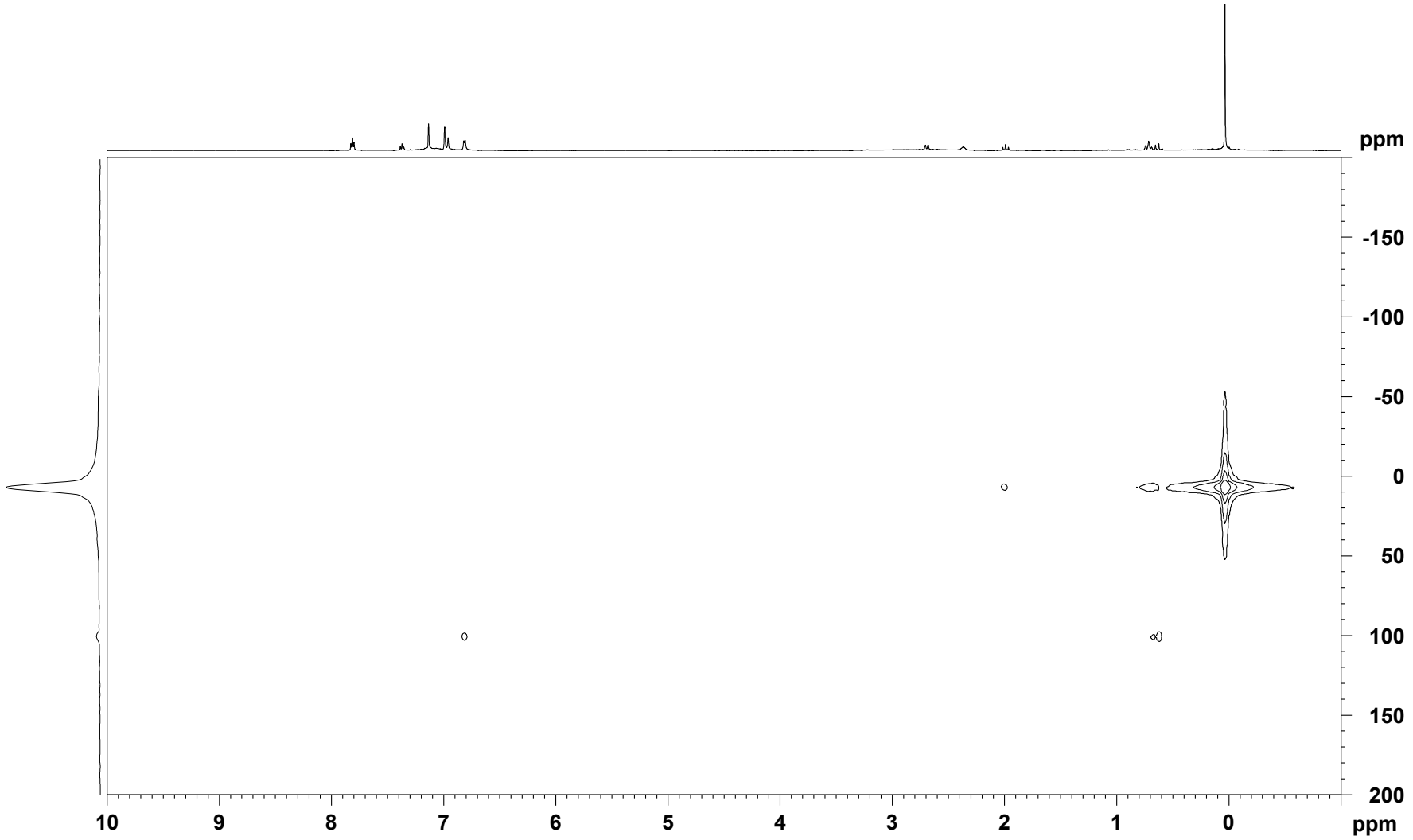


Figure S16. ^{1}H NMR spectrum (500 MHz, C_6D_5Cl, 233 K) of **3a**$^{+}$[$CHB_{11}H_5Br_6$]$^{-}$ from the reaction of $Me_2(Me_3Si)Si^{+}$[$CHB_{11}H_5Br_6$]$^{-}$ with allylbenzene (**1a**).

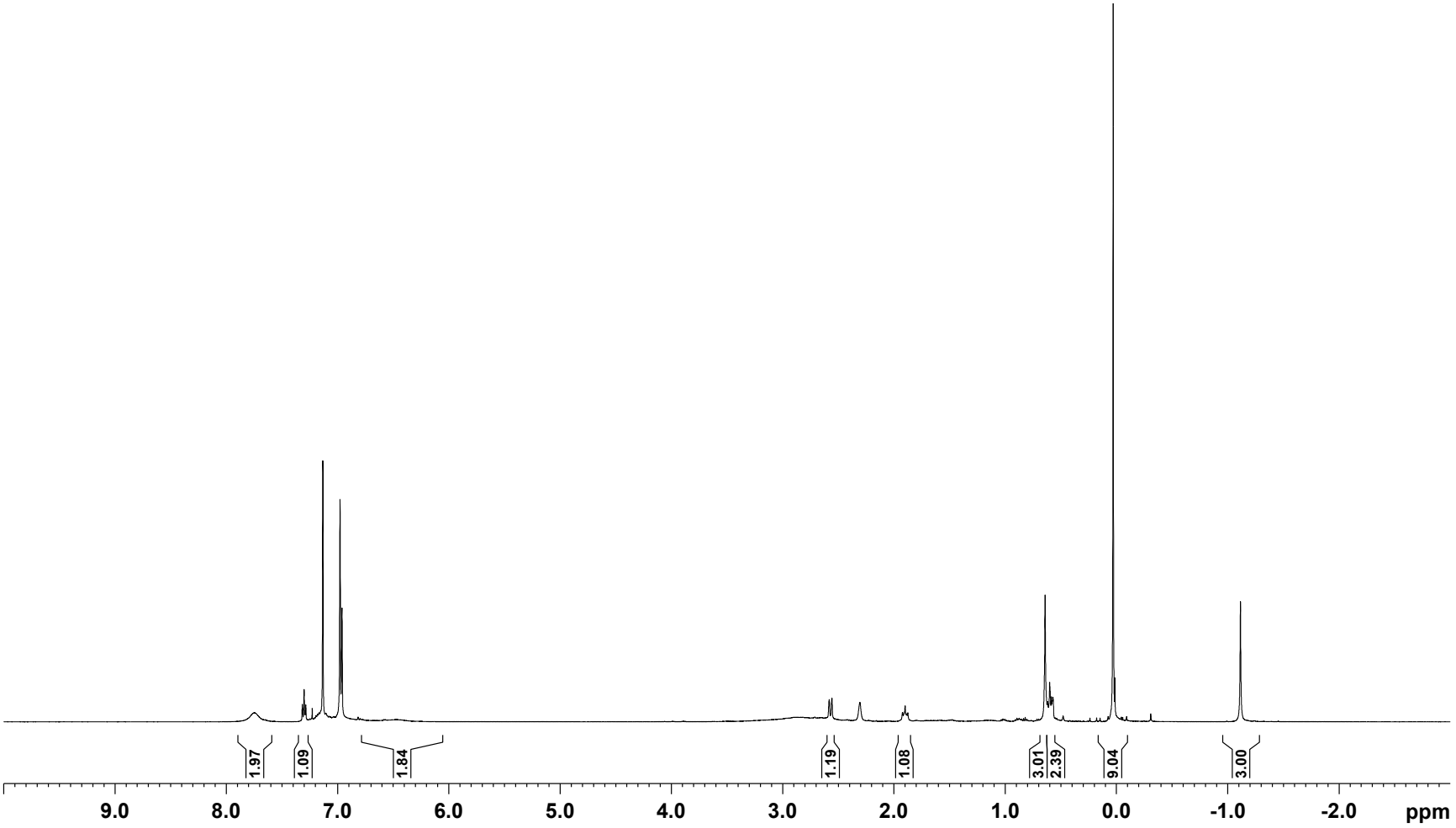


Figure S17. $^{1}H/^{3}C$ HSQC NMR spectrum (500/126 MHz, C_6D_5Cl, 233 K) of **3a**$^{+}[CHB_{11}H_5Br_6]^{-}$ from the reaction of $Me_2(Me_3Si)Si^{+}[CHB_{11}H_5Br_6]^{-}$ with allylbenzene (**1a**).

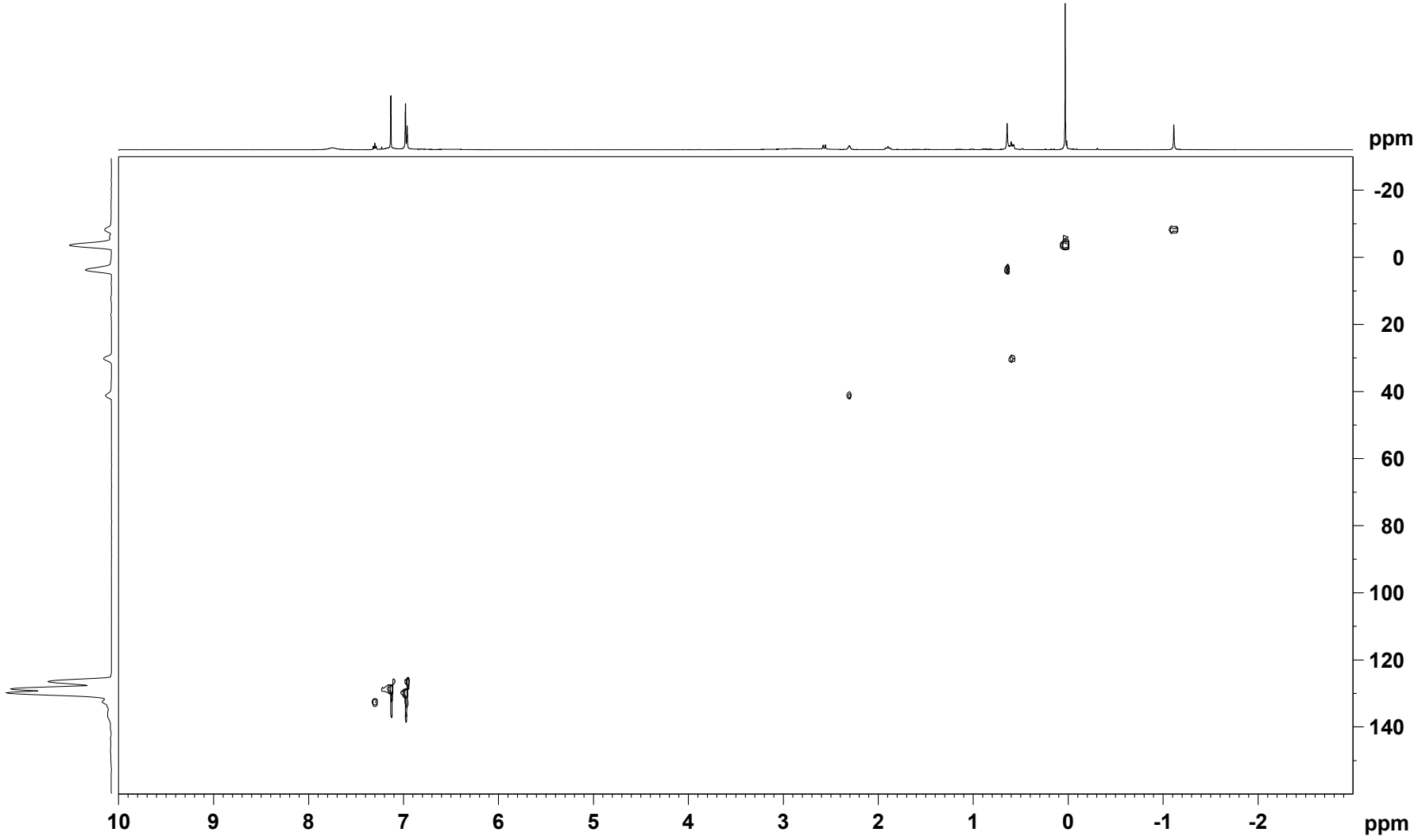


Figure S18. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, C_6D_5Cl, 233 K, optimized for J = 7 Hz) of **3a**$^{+}[CHB_{11}H_5Br_6]^{-}$ from the reaction of $Me_2(Me_3Si)Si^{+}[CHB_{11}H_5Br_6]^{-}$ with allylbenzene (**1a**).

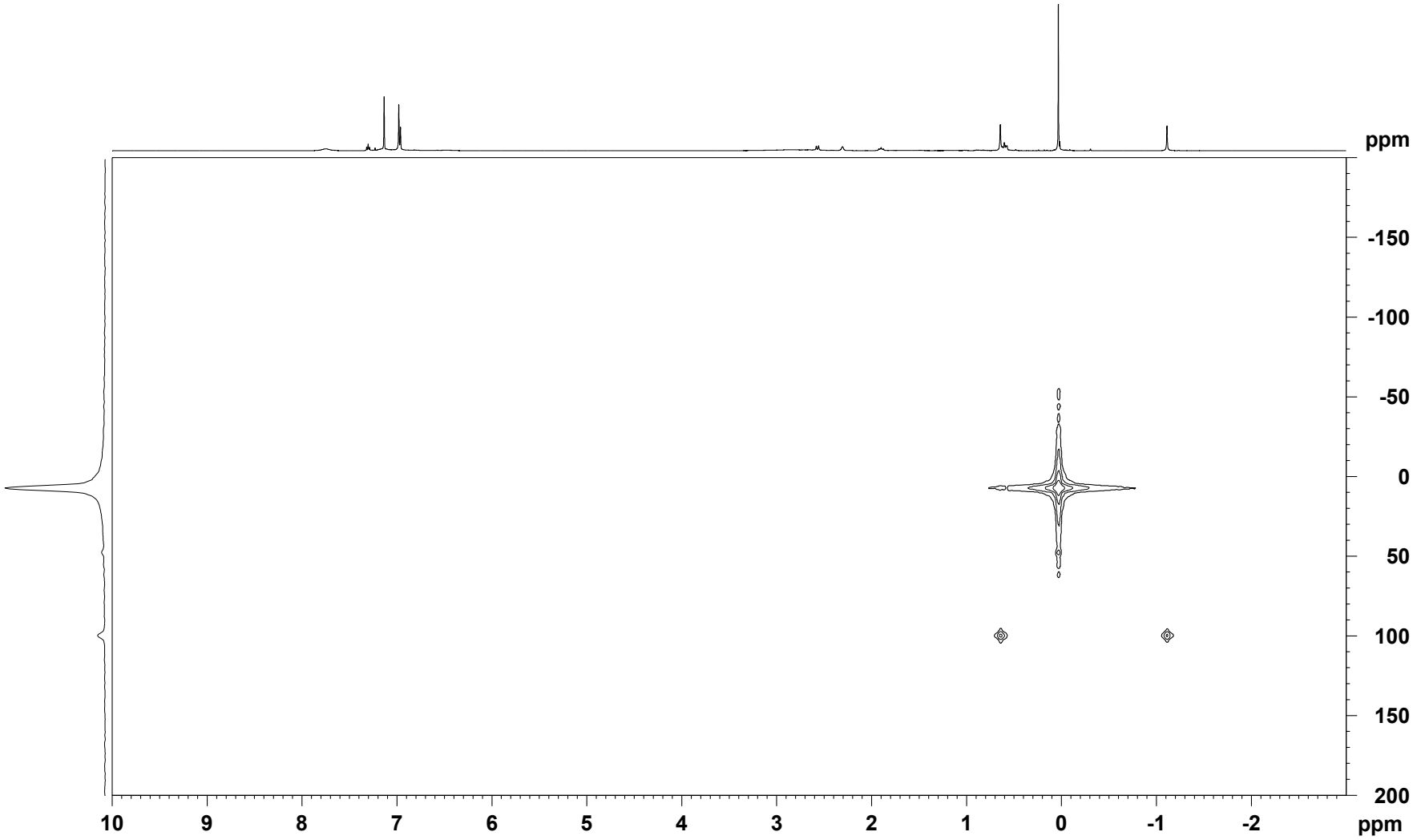


Figure S19. ^{1}H NMR spectrum (500 MHz, C_6D_5Cl, 343 K) of **3a**$^{+}[CHB_{11}H_5Br_6]^{-}$ from the reaction of $Me_2(Me_3Si)Si^{+}[CHB_{11}H_5Br_6]^{-}$ with allylbenzene (**1a**) (+ = impurity).

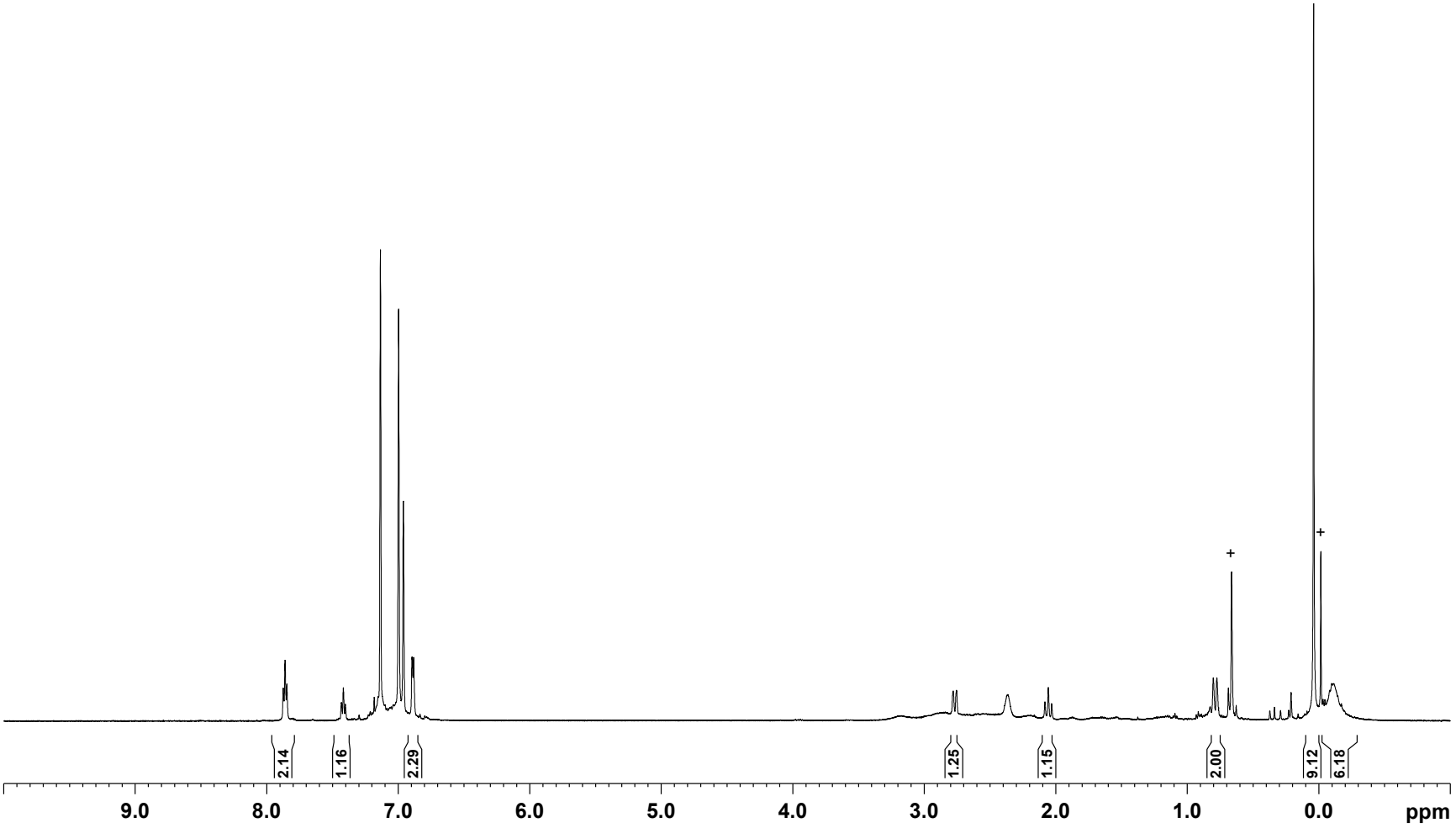


Figure S20. $^{1}H/^{3}C$ HSQC NMR spectrum (500/126 MHz, C_6D_5Cl, 343 K) of **3a**$^{+}[CHB_{11}H_5Br_6]^{-}$ from the reaction of $Me_2(Me_3Si)Si^{+}[CHB_{11}H_5Br_6]^{-}$ with allylbenzene (**1a**).

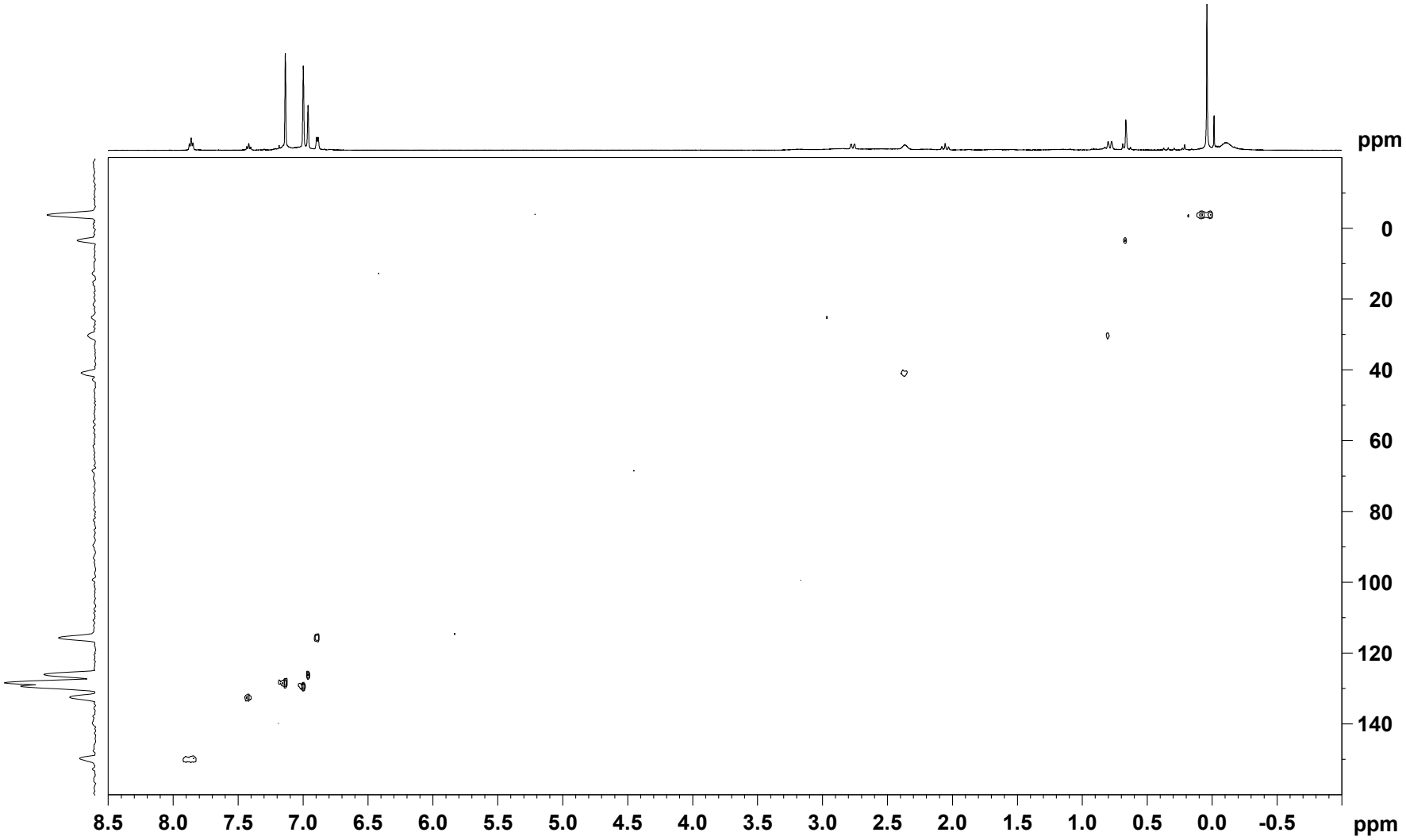


Figure S21. ^{1}H NMR spectrum (500 MHz, C_6D_5Cl, 298 K) of the stoichiometric reaction of **3a**$^{+}[CHB_{11}H_5Br_6]^{-}$ with allylbenzene (**1a**) and $Me_3SiSiMe_3$ after 15 min (* = **1a**, # = **3a**$^{+}[CHB_{11}H_5Br_6]^{-}$, + = **4a**).

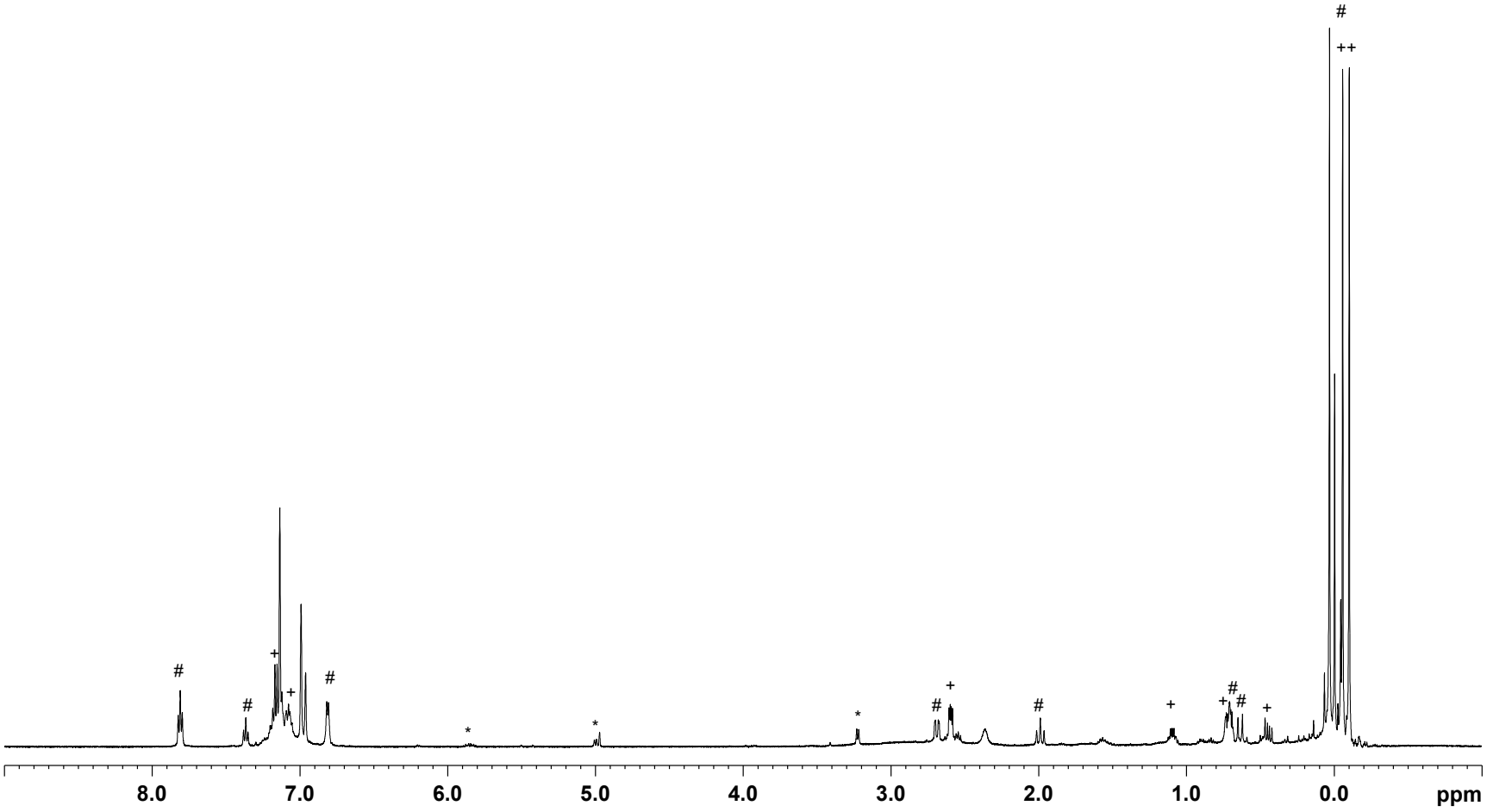


Figure S22. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 298 K) of **4a** from the catalytic 1,2-disilylation of allylbenzene (**1a**) with $Me_3SiSiMe_3$ using **3a**$^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

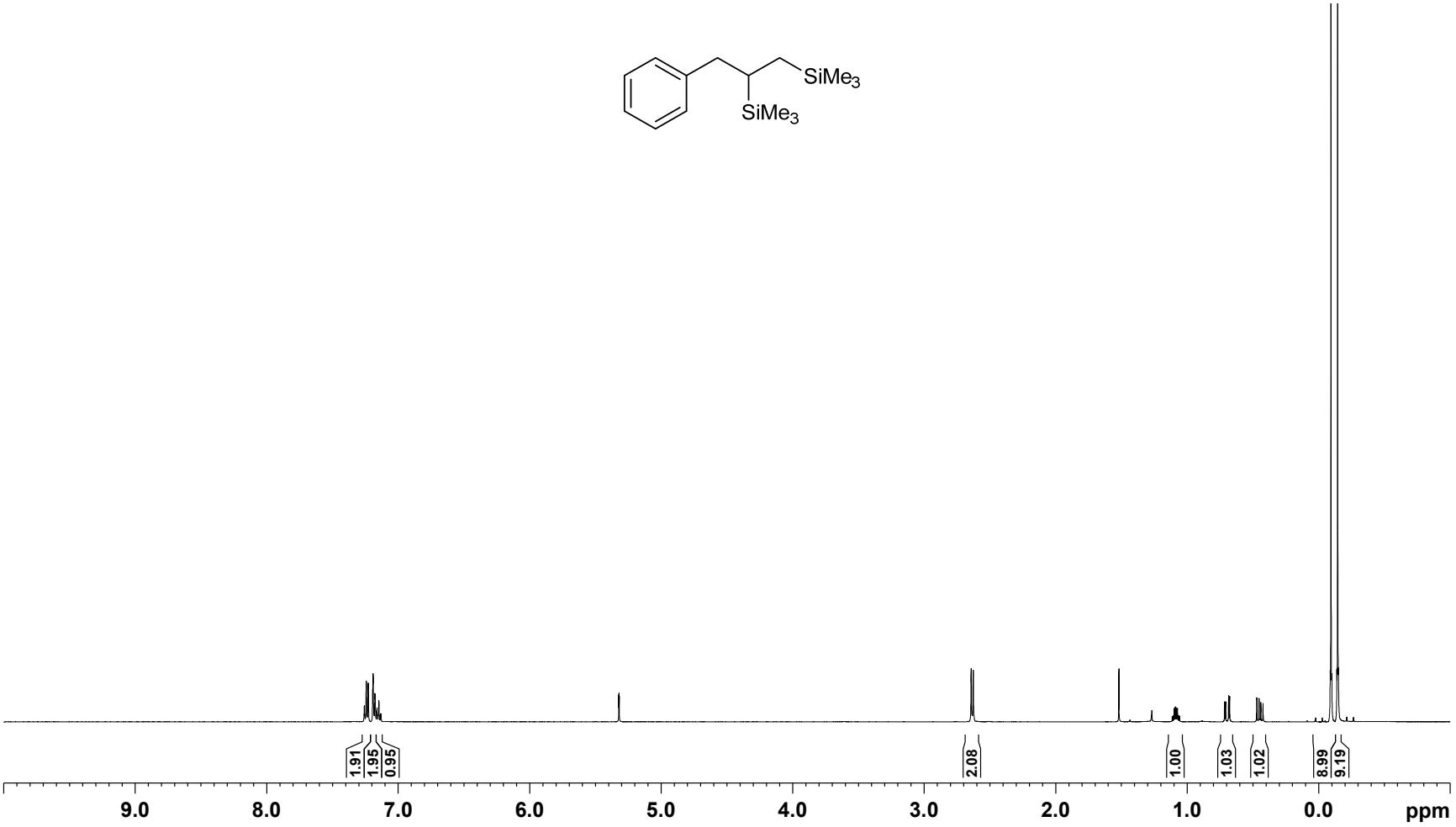


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, CD_2Cl_2, 298 K) of **4a** from the catalytic 1,2-disilylation of allylbenzene (**1a**) with $Me_3SiSiMe_3$ using **3a**$^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

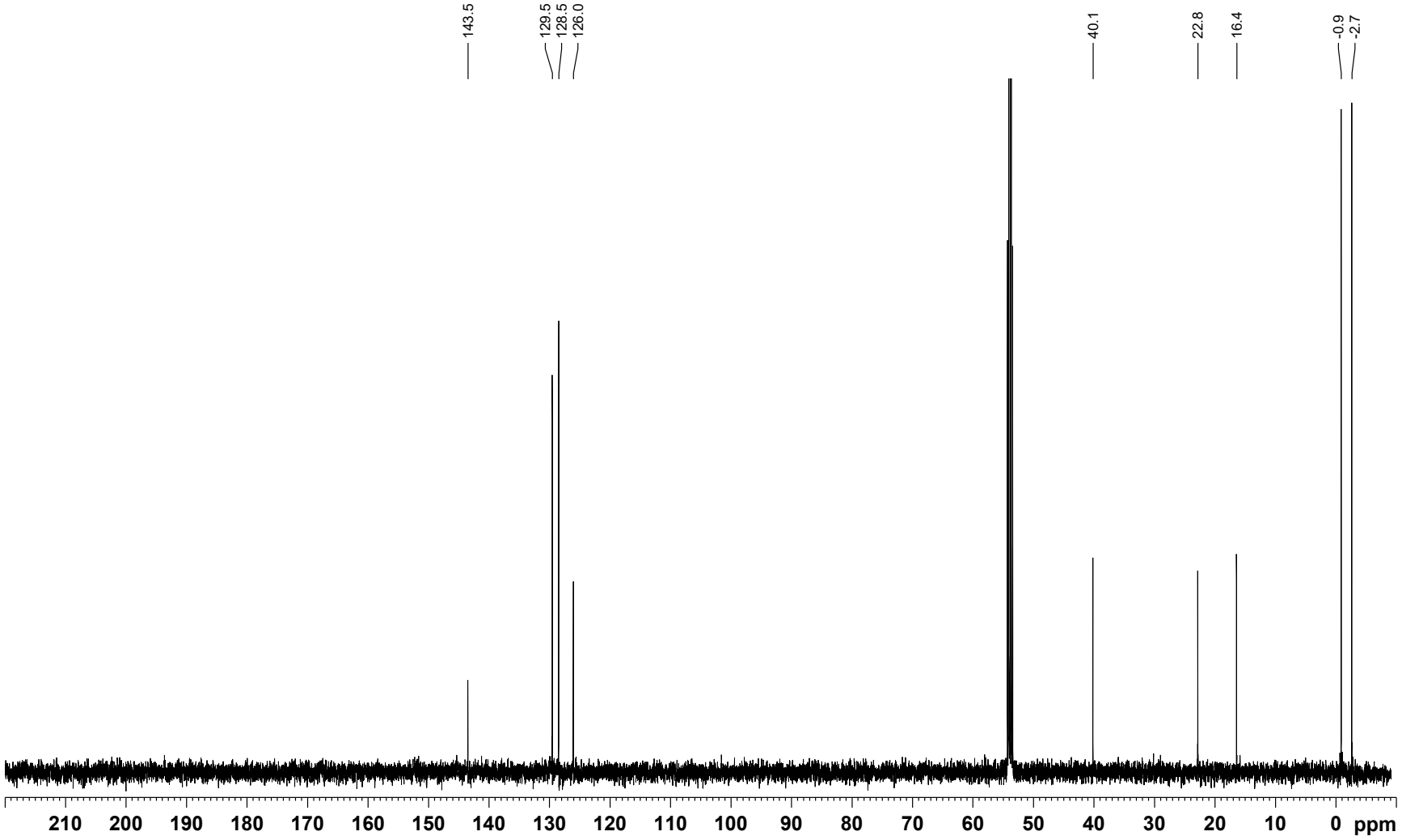


Figure S24. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, CD_2Cl_2, 298 K, optimized for J = 7 Hz) of **4a** from the catalytic 1,2-disilylation of allylbenzene (**1a**) with $Me_3SiSiMe_3$ using **3a**$^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

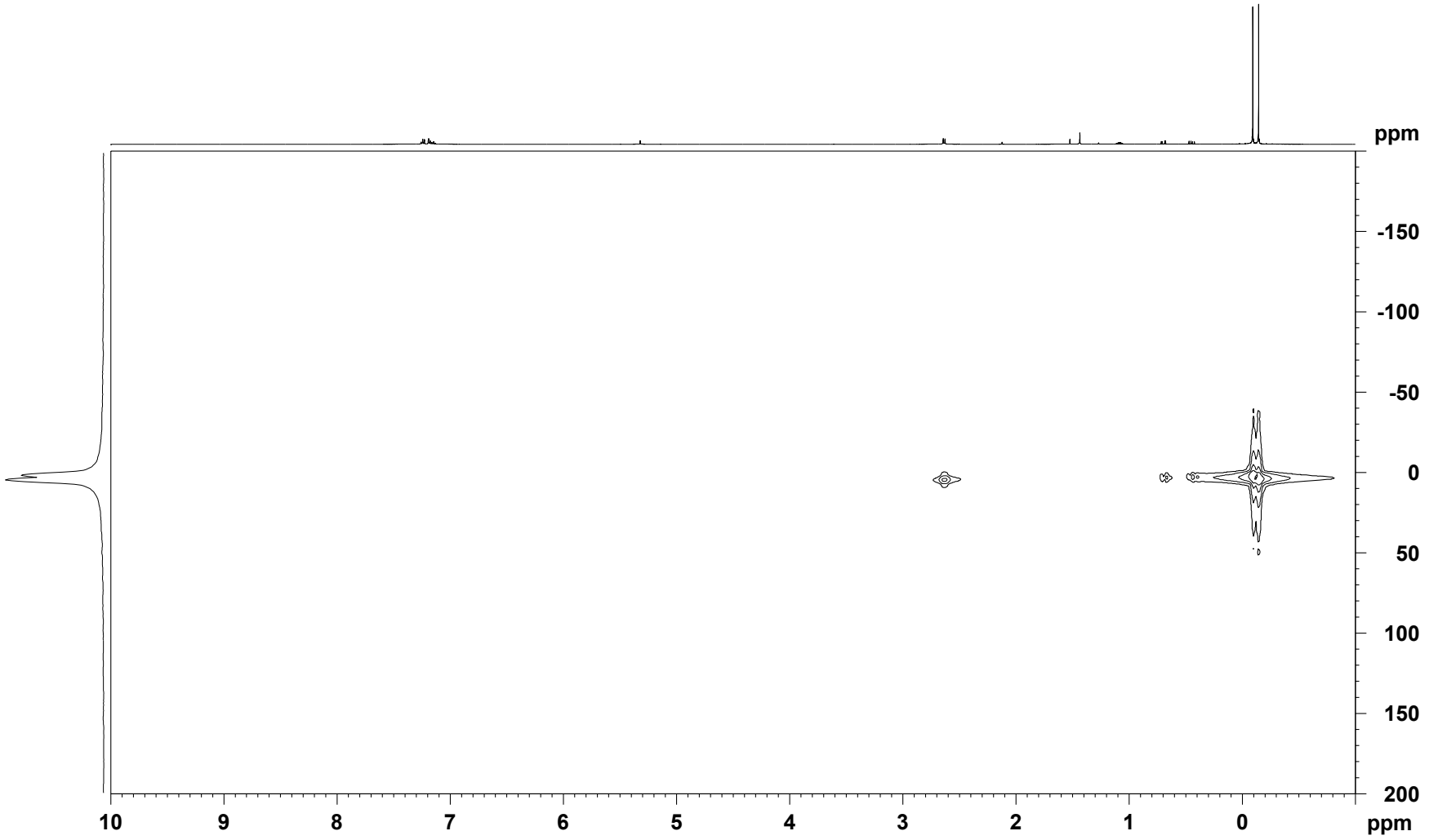


Figure S25. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4a** from the catalytic 1,2-disilylation of allylbenzene (**1a**) with $Me_3SiSiMe_3$ using $Me_2(Me_3Si)Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

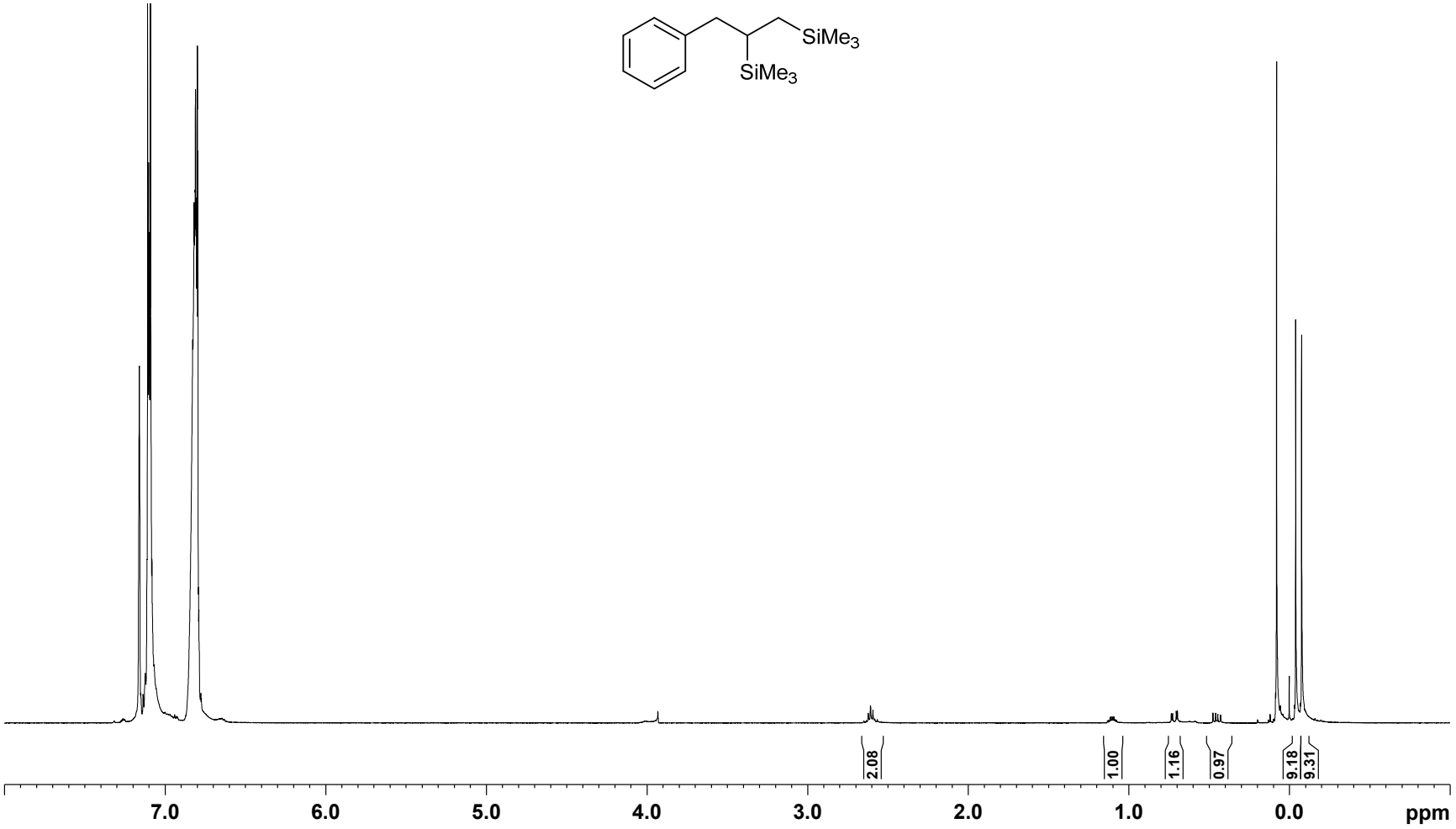


Figure S26. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 298 K) of **4a** from the catalytic 1,2-disilylation of allylbenzene (**1a**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

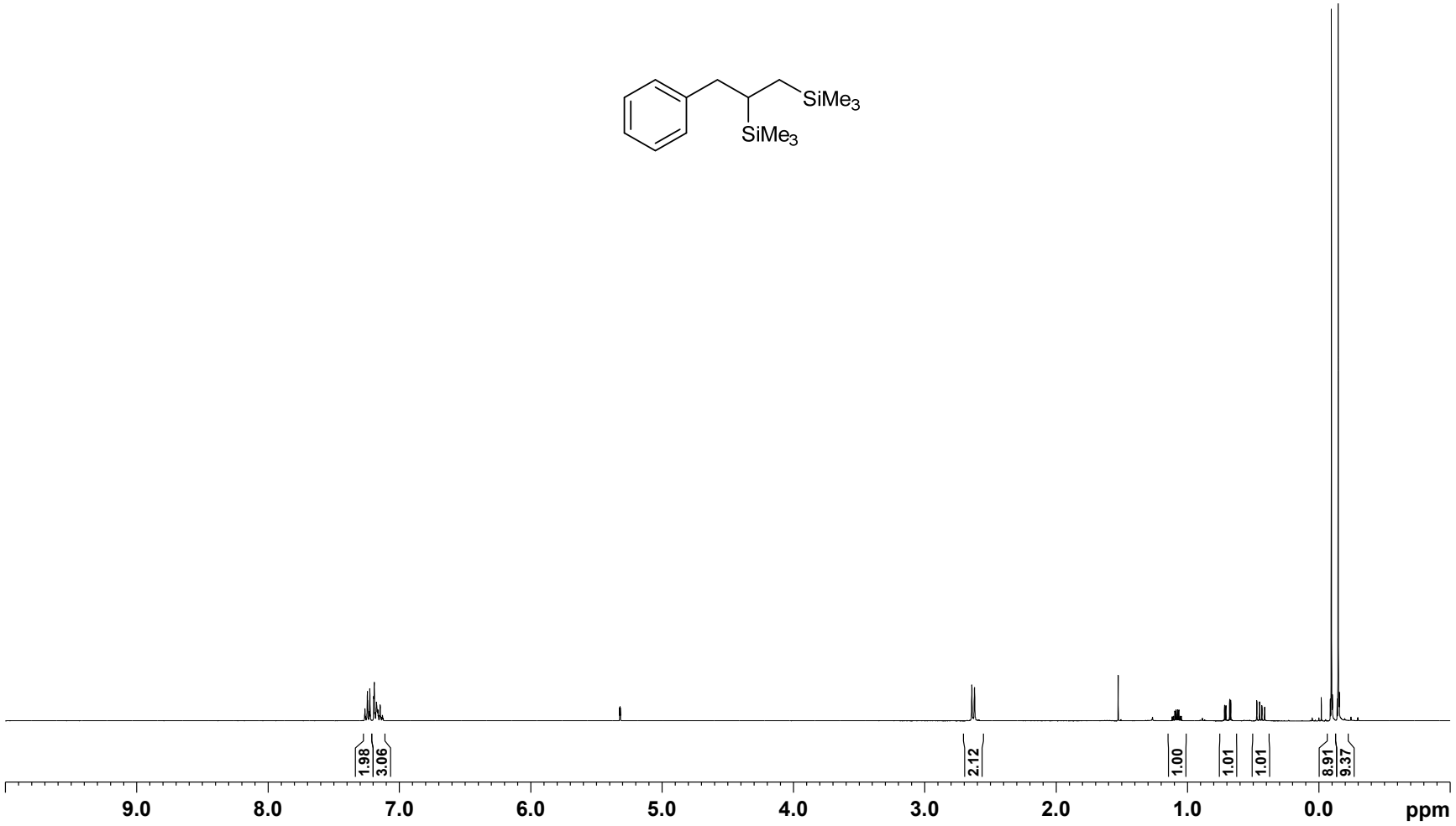


Figure S27. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4b** from the catalytic 1,2-disilylation of 1-allyl-4-methylbenzene (**1b**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

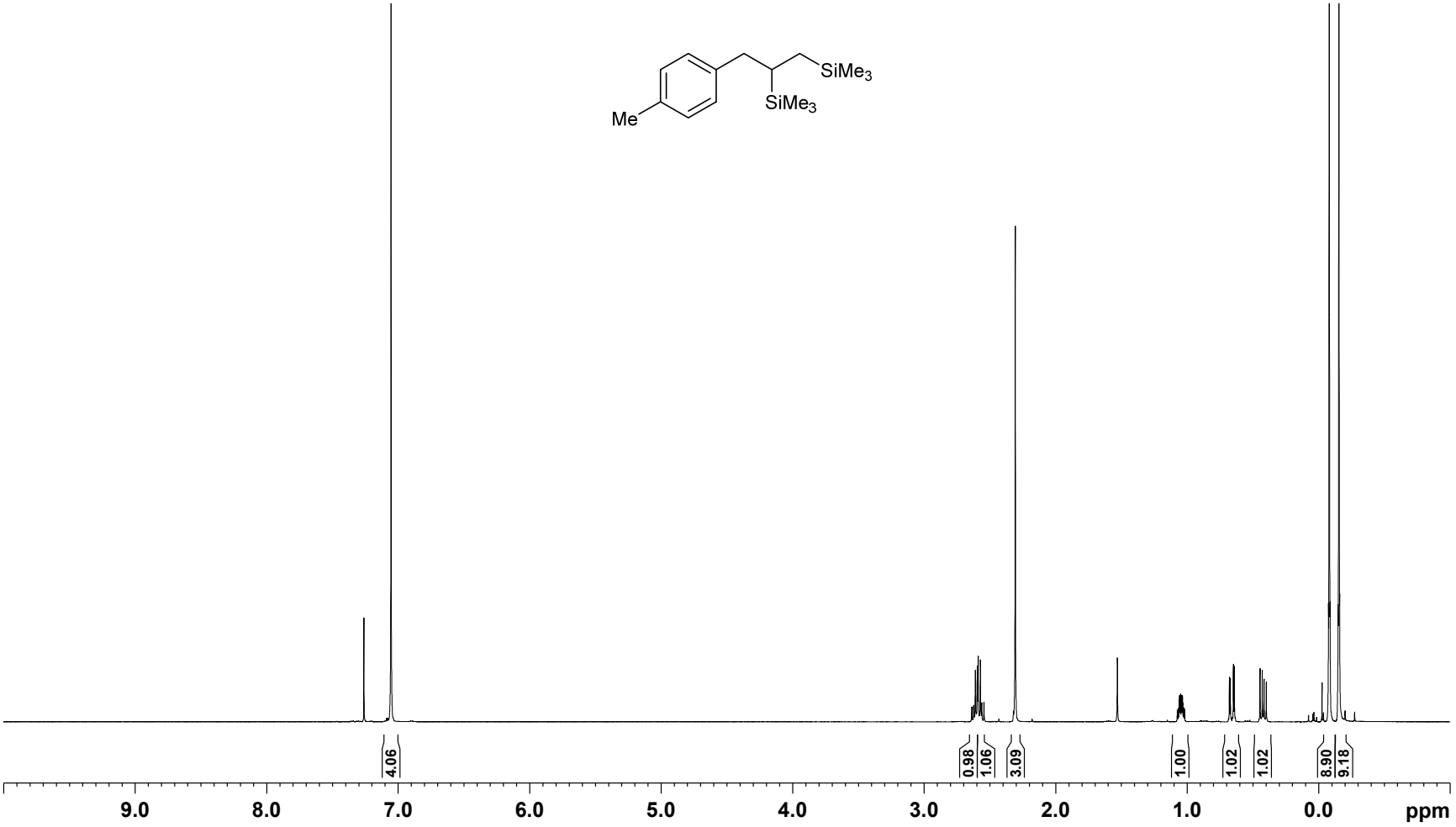


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298 K) of **4b** from the catalytic 1,2-disilylation of 1-allyl-4-methylbenzene (**1b**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

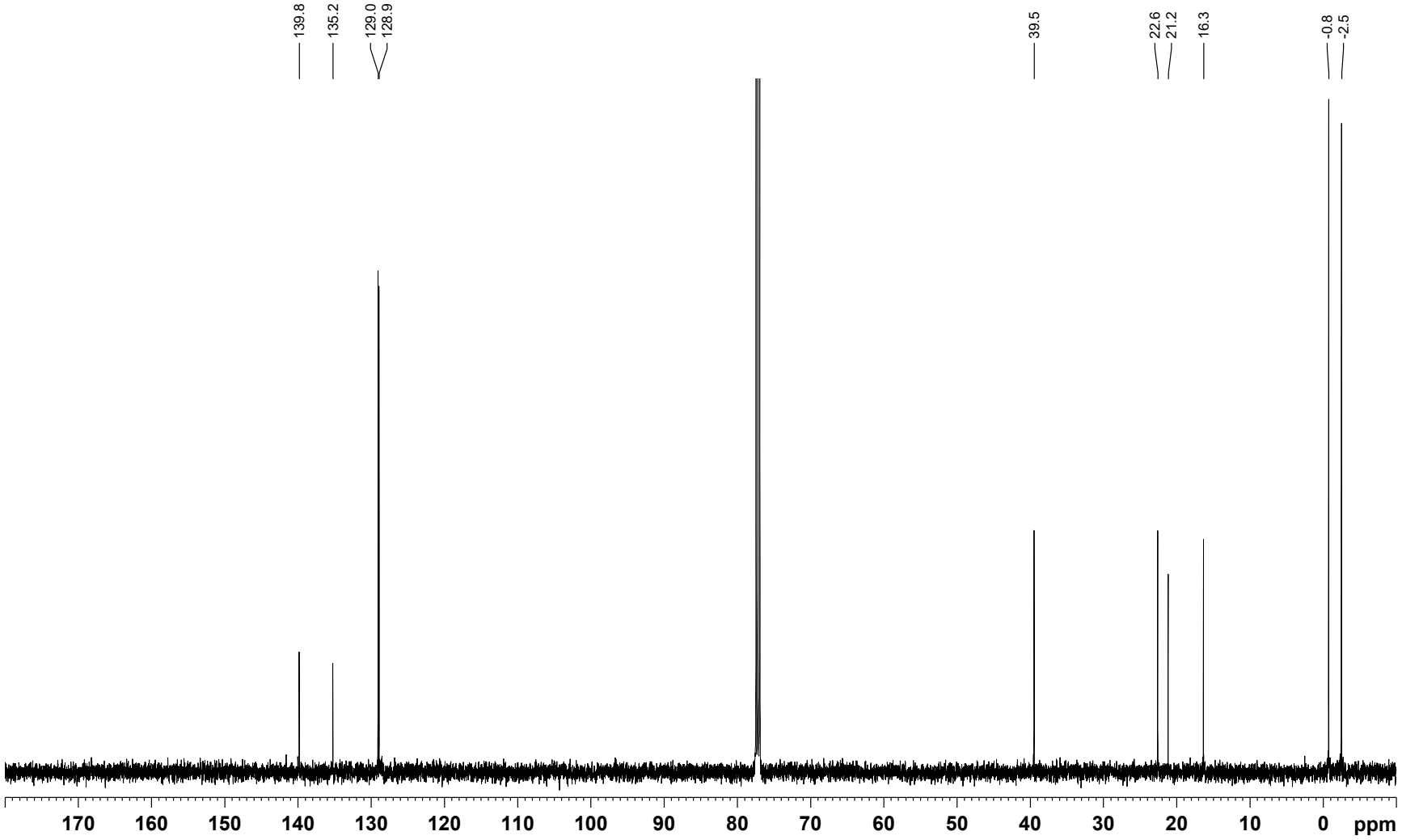


Figure S29. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **4b** from the catalytic 1,2-disilylation of 1-allyl-4-methyl-benzene (**1b**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

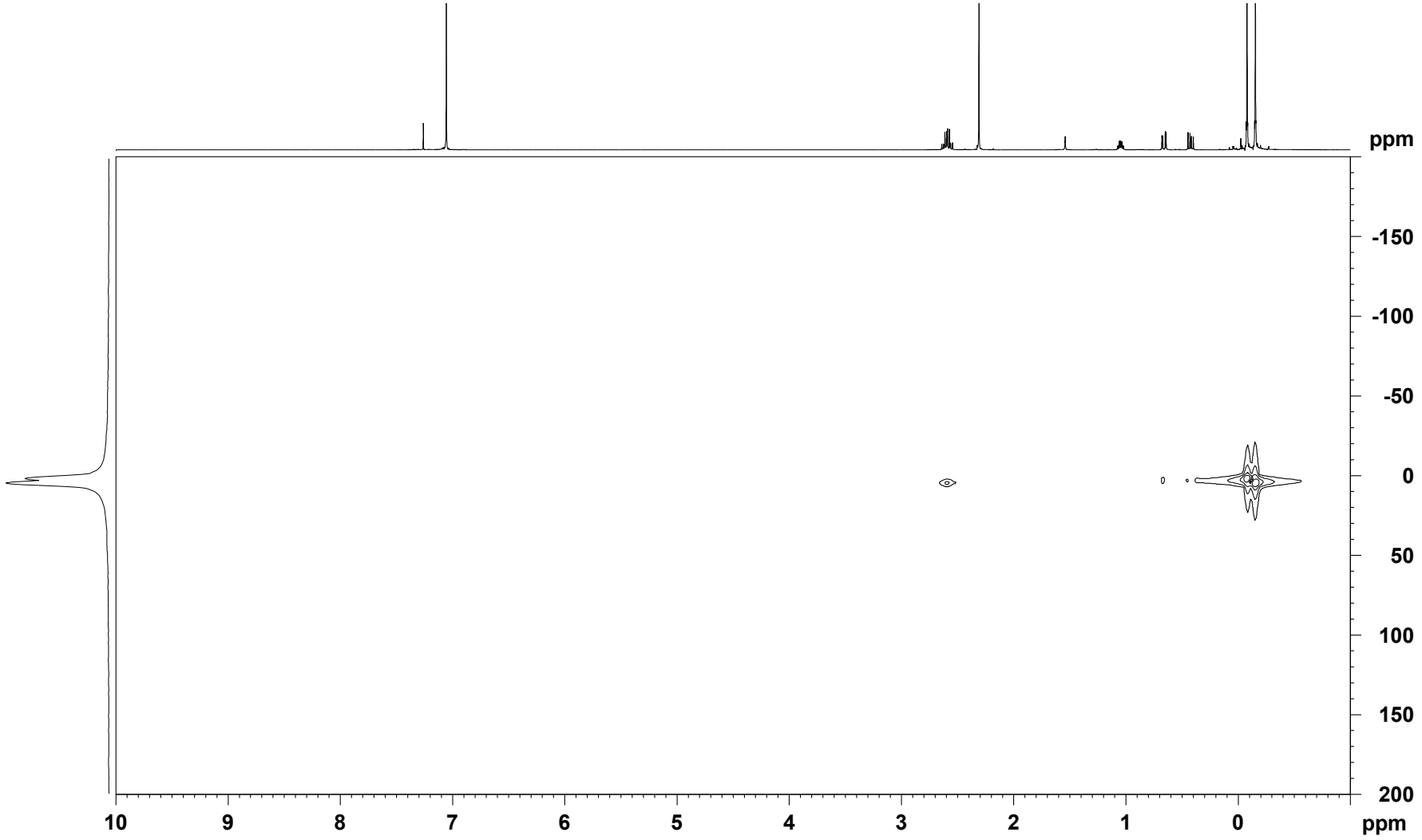


Figure S30. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4c** from the catalytic 1,2-disilylation of 1-allyl-2-methylbenzene (**1c**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

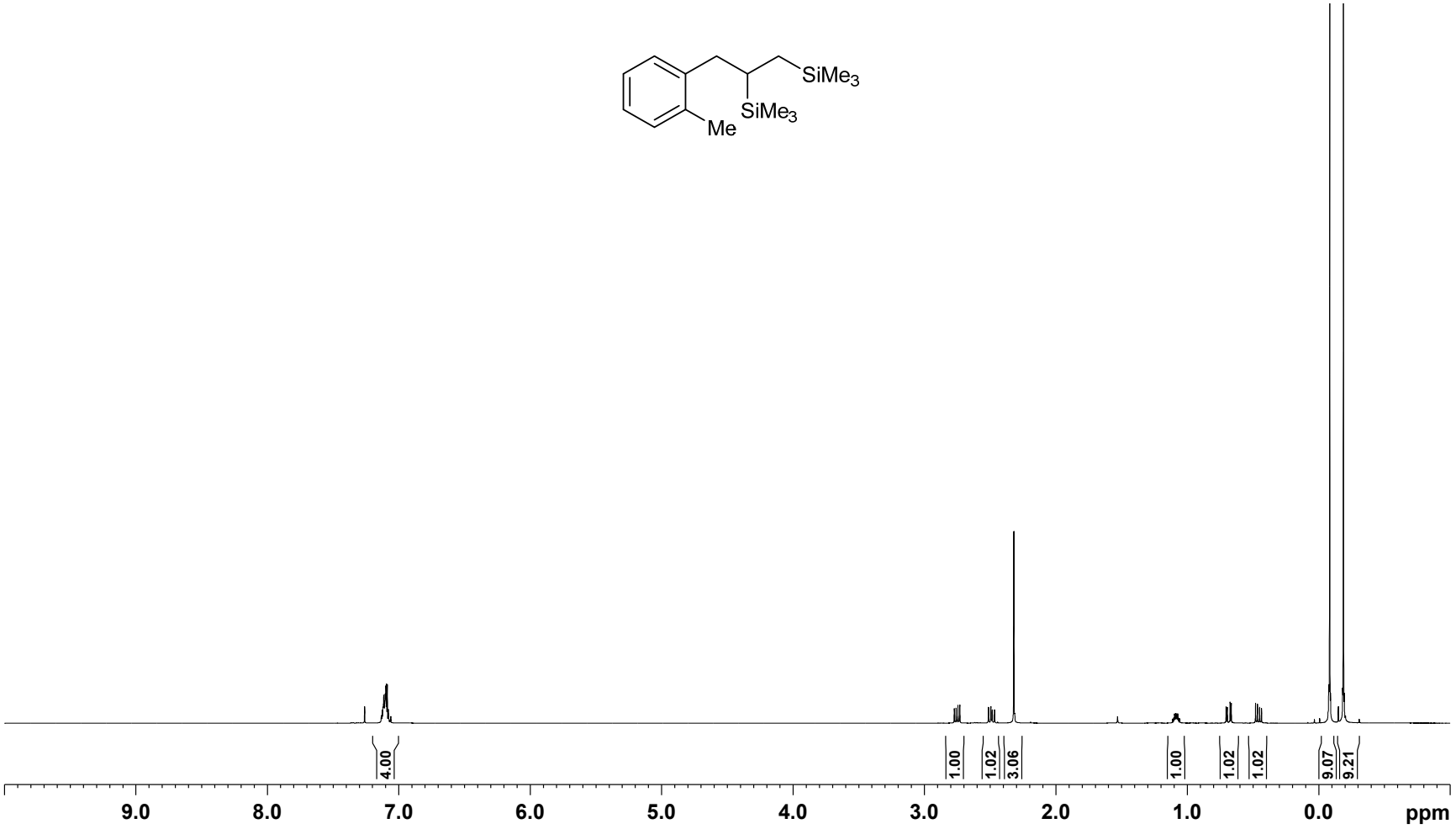


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298 K) of **4c** from the catalytic 1,2-disilylation of 1-allyl-2-methylbenzene (**1c**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

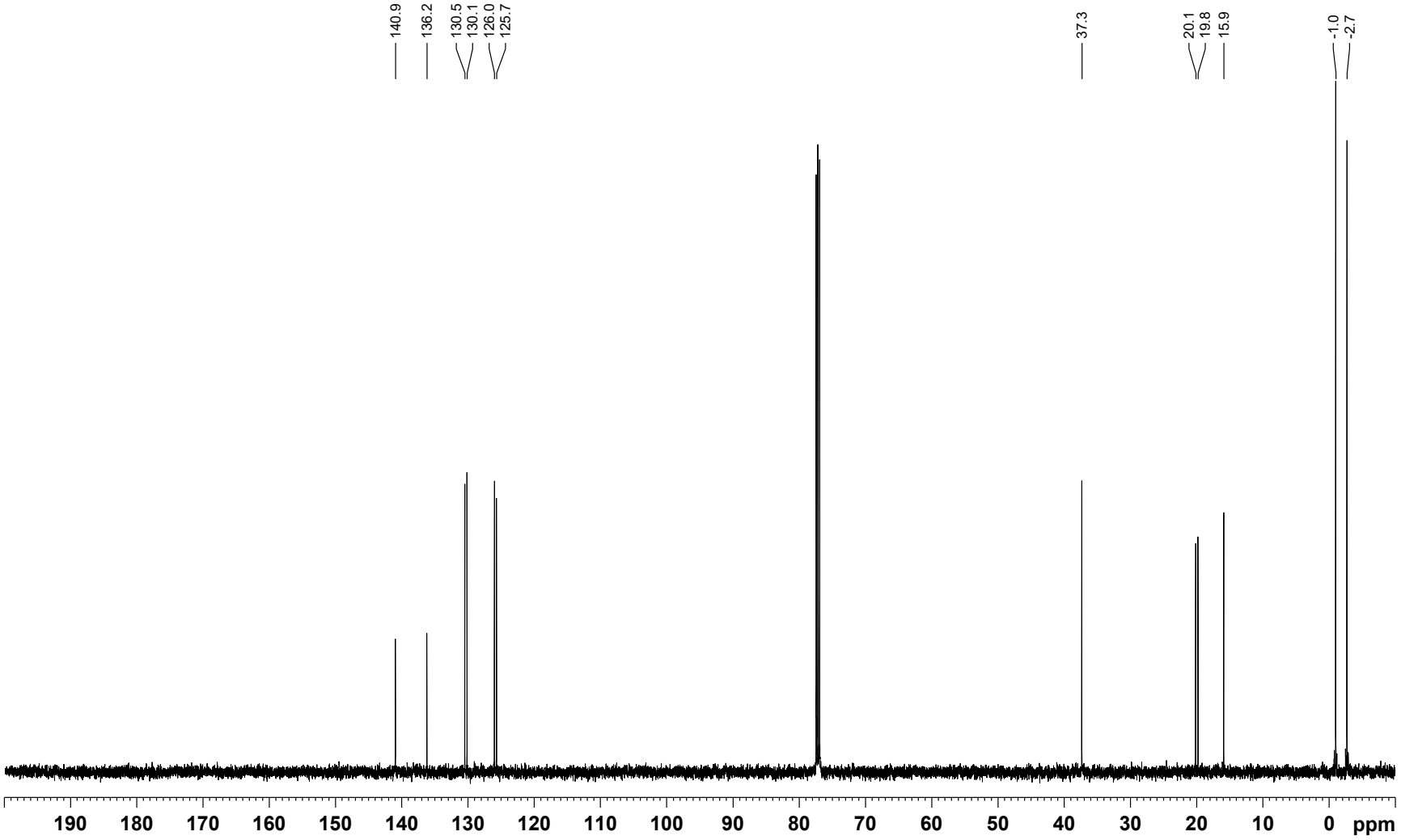


Figure S32. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **4c** from the catalytic 1,2-disilylation of 1-allyl-2-methyl-benzene (**1c**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

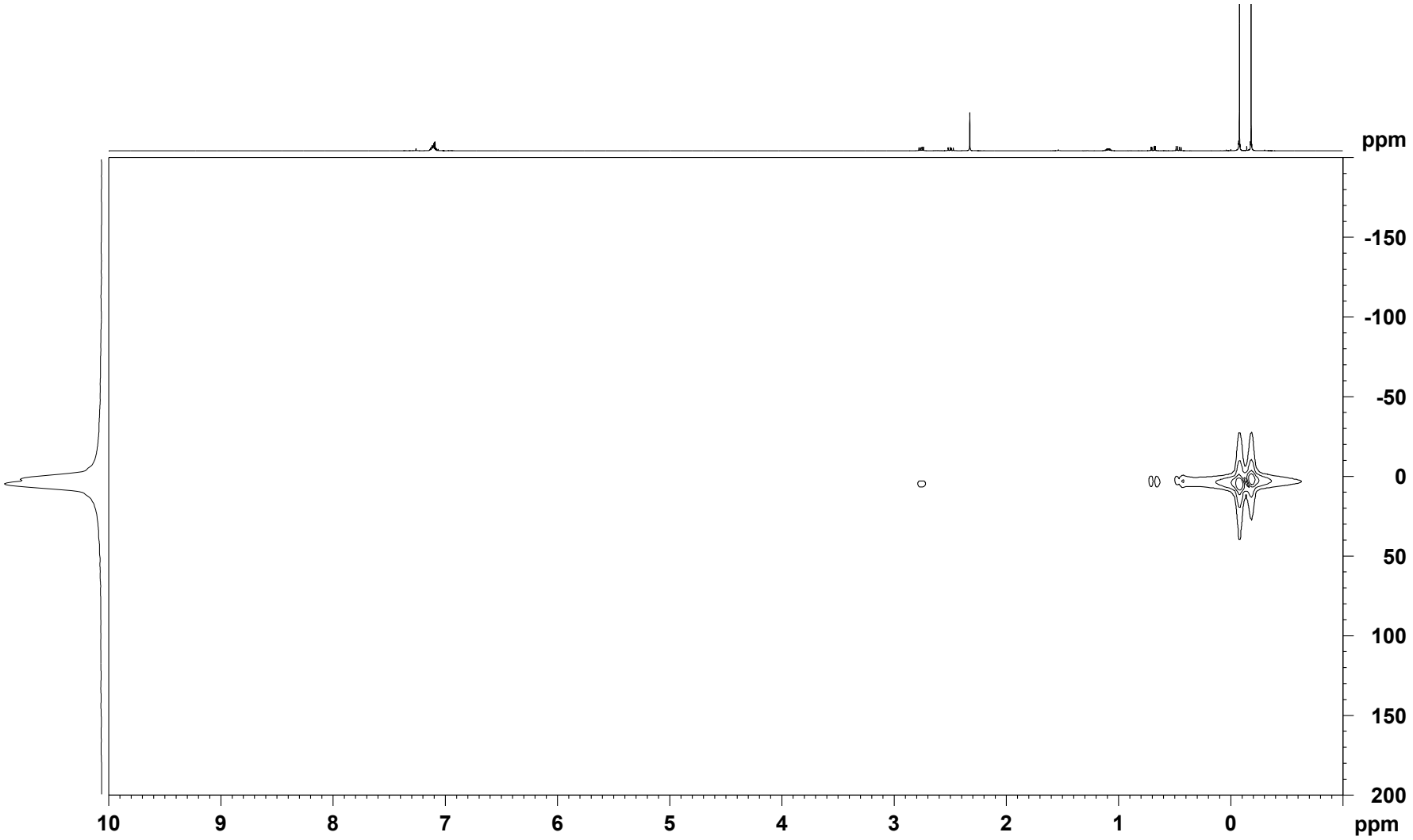


Figure S33. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4d** from the catalytic 1,2-disilylation of 1-allyl-3,5-dimethylbenzene (**1d**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

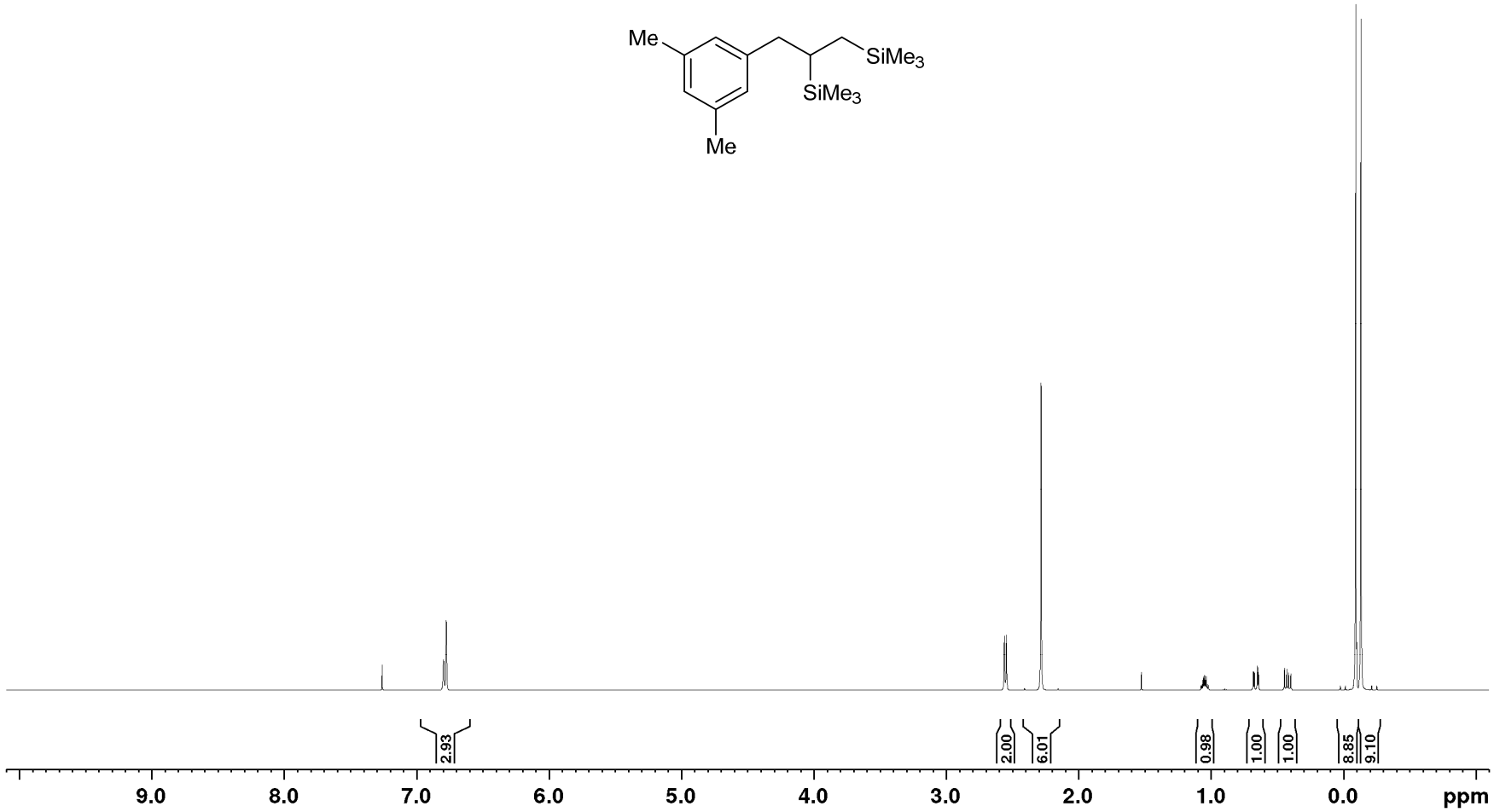


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298 K) of **4d** from the catalytic 1,2-disilylation of 1-allyl-3,5-dimethylbenzene (**1d**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

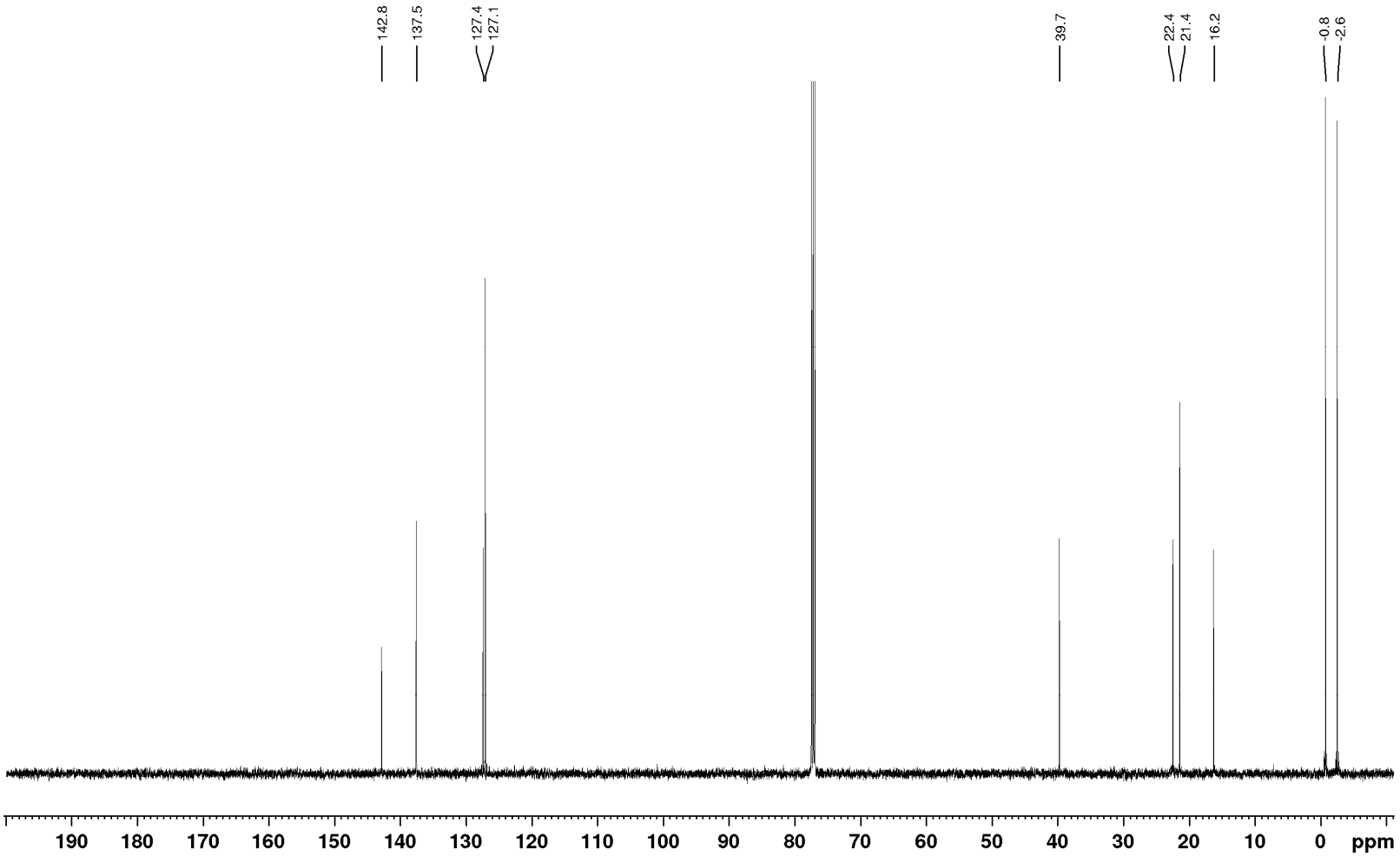


Figure S35. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **4d** from the catalytic 1,2-disilylation of 1-allyl-3,5-dimethyl-benzene (**1d**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

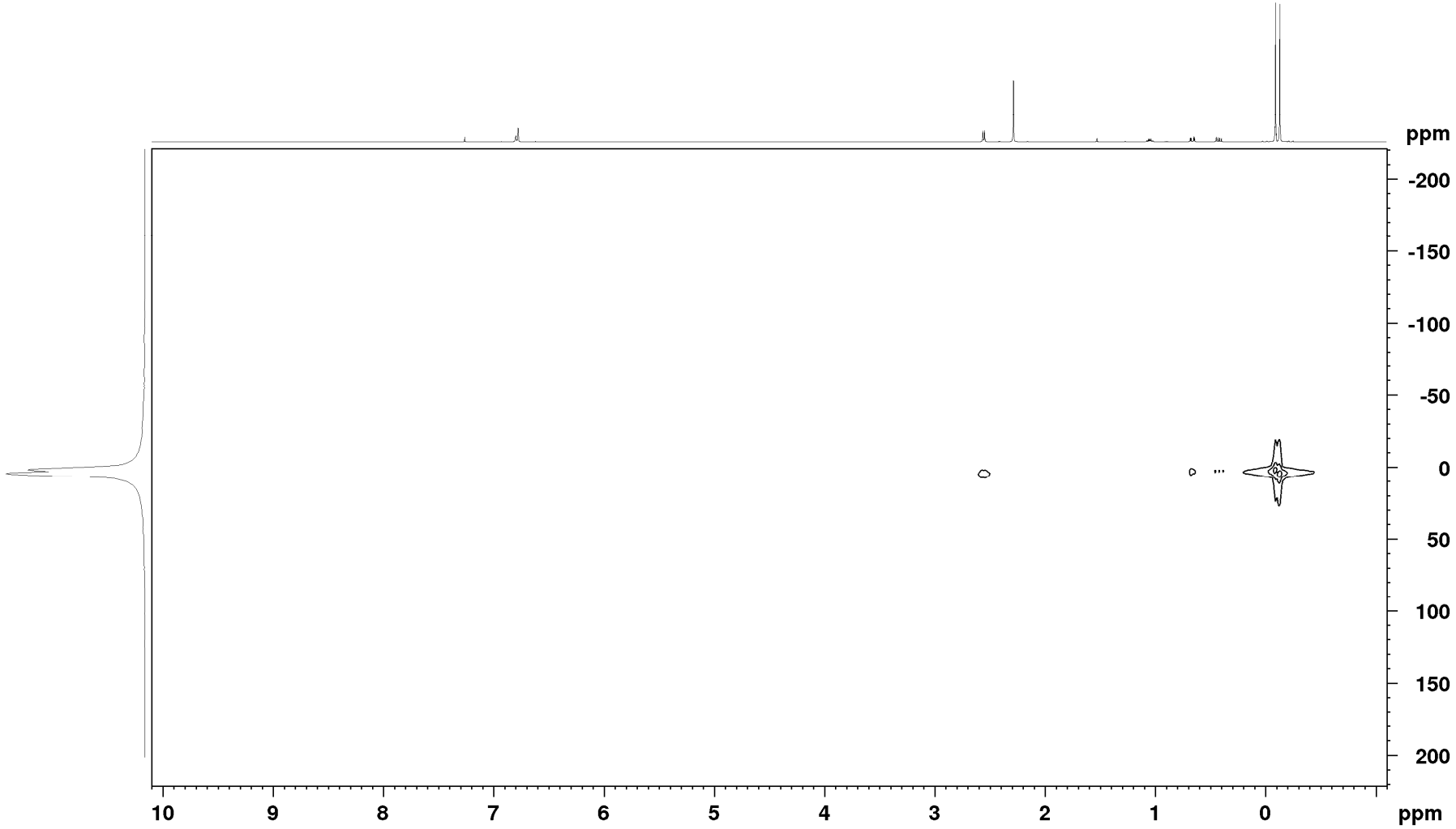


Figure S36. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4e** from the catalytic 1,2-disilylation of 1-allyl-4-bromobenzene (**1e**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

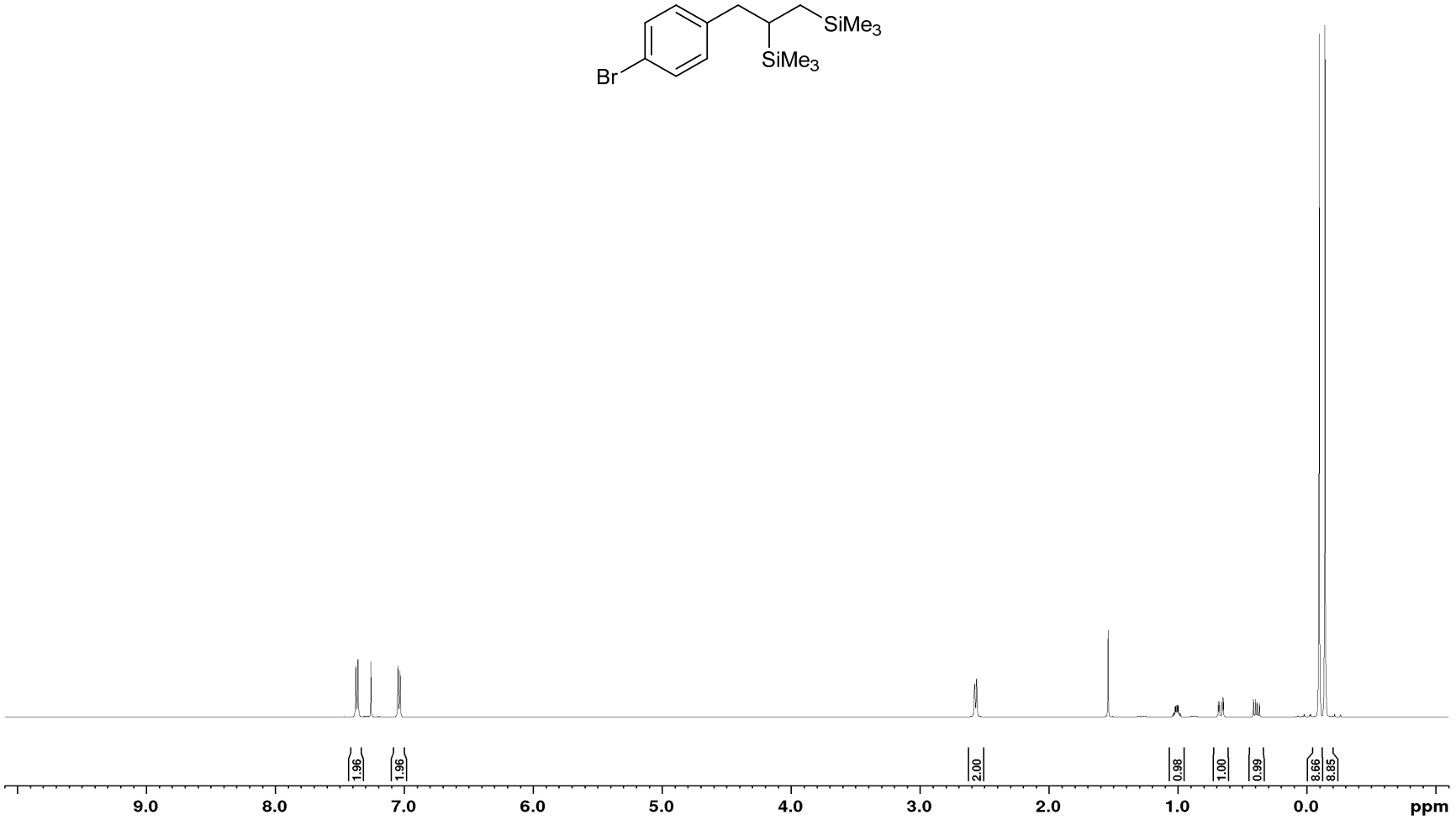


Figure S37. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298 K) of **4e** from the catalytic 1,2-disilylation of 1-allyl-4-bromobenzene (**1e**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

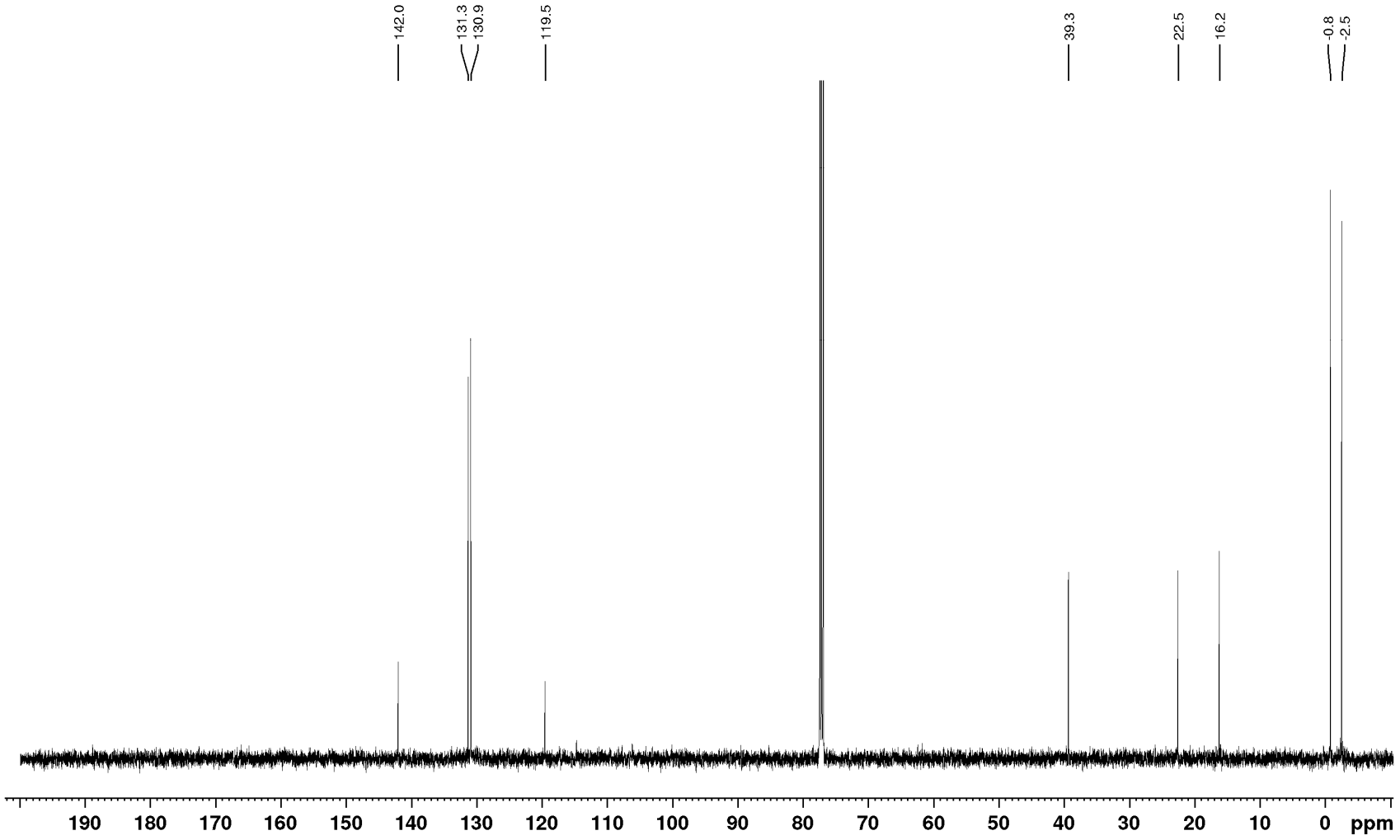


Figure S38. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **4e** from the catalytic 1,2-disilylation of 1-allyl-4-bromo-benzene (**1e**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

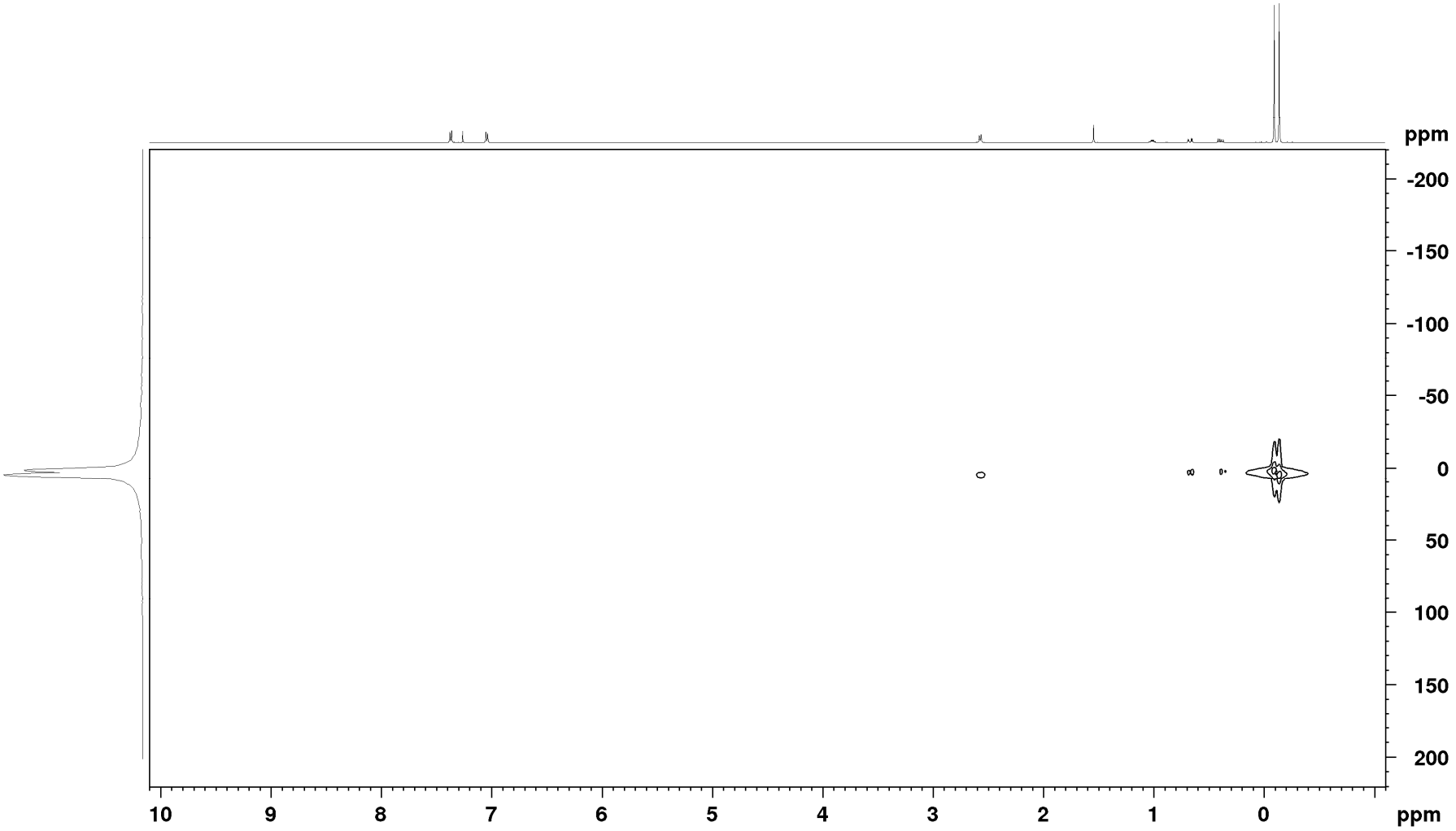


Figure S39. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4f** from the catalytic 1,2-disilylation of 1-allyl-2-bromobenzene (**1f**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

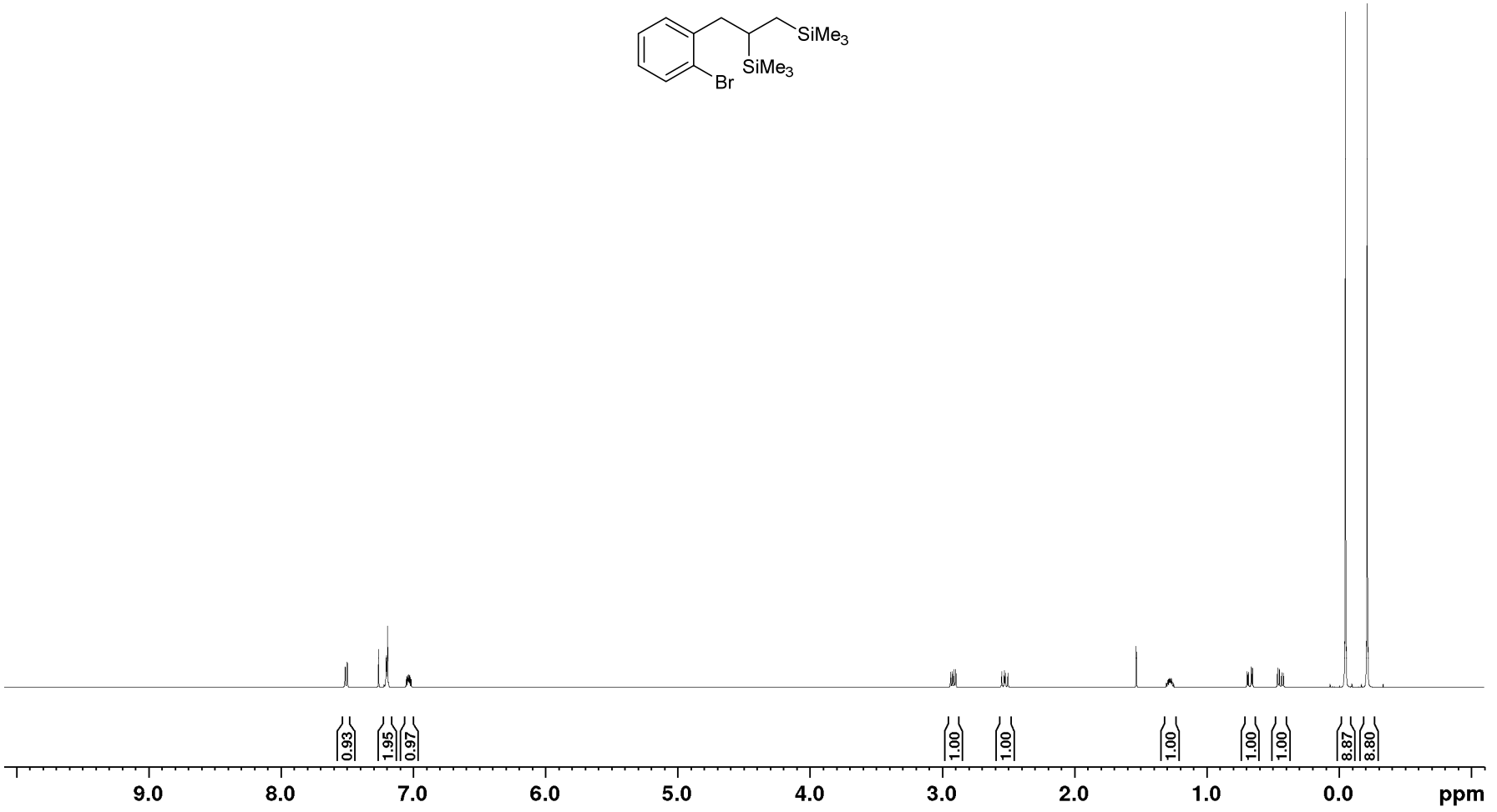


Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298 K) of **4f** from the catalytic 1,2-disilylation of 1-allyl-2-bromobenzene (**1f**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

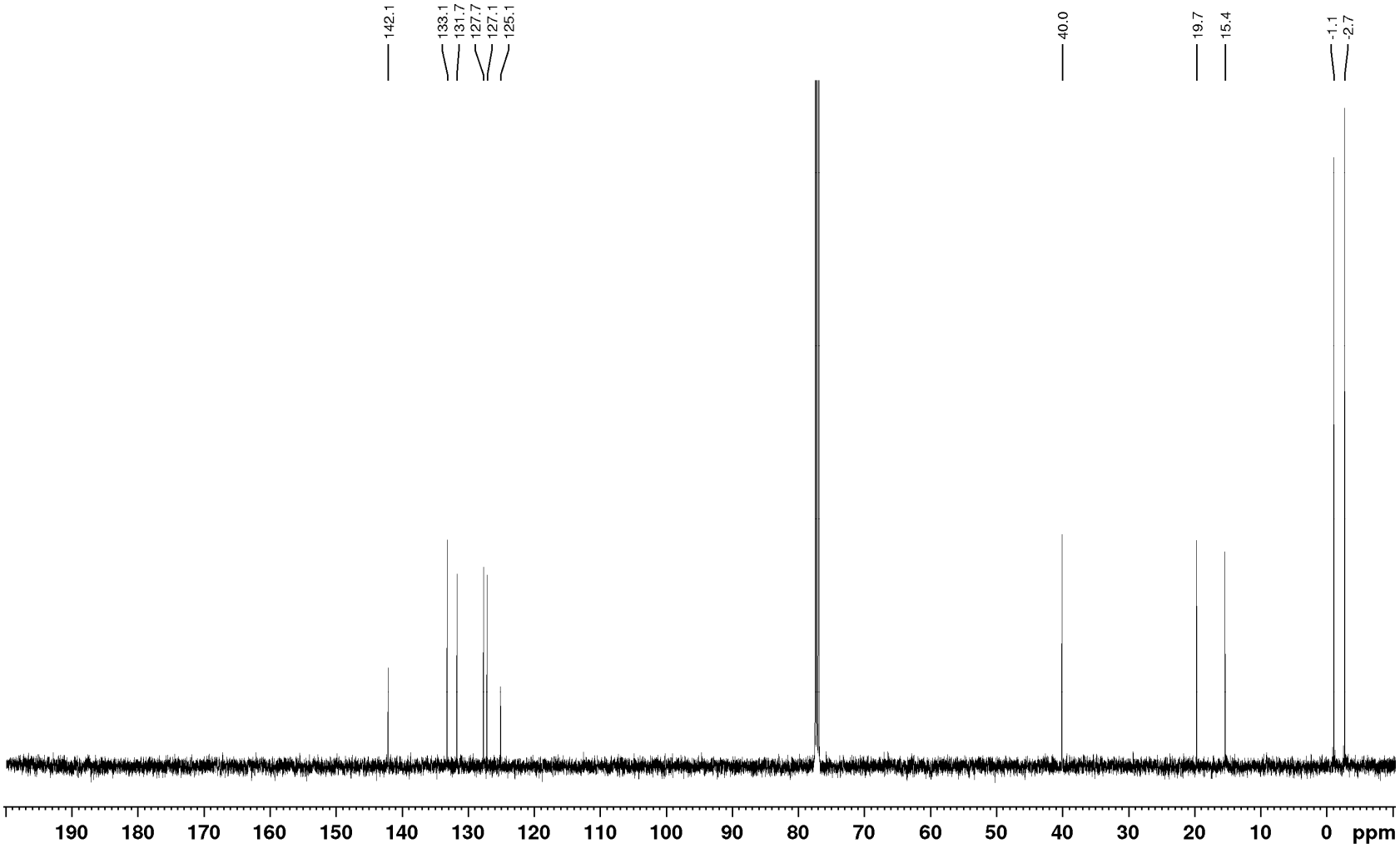


Figure S41. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **4f** from the catalytic 1,2-disilylation of 1-allyl-2-bromo-benzene (**1f**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

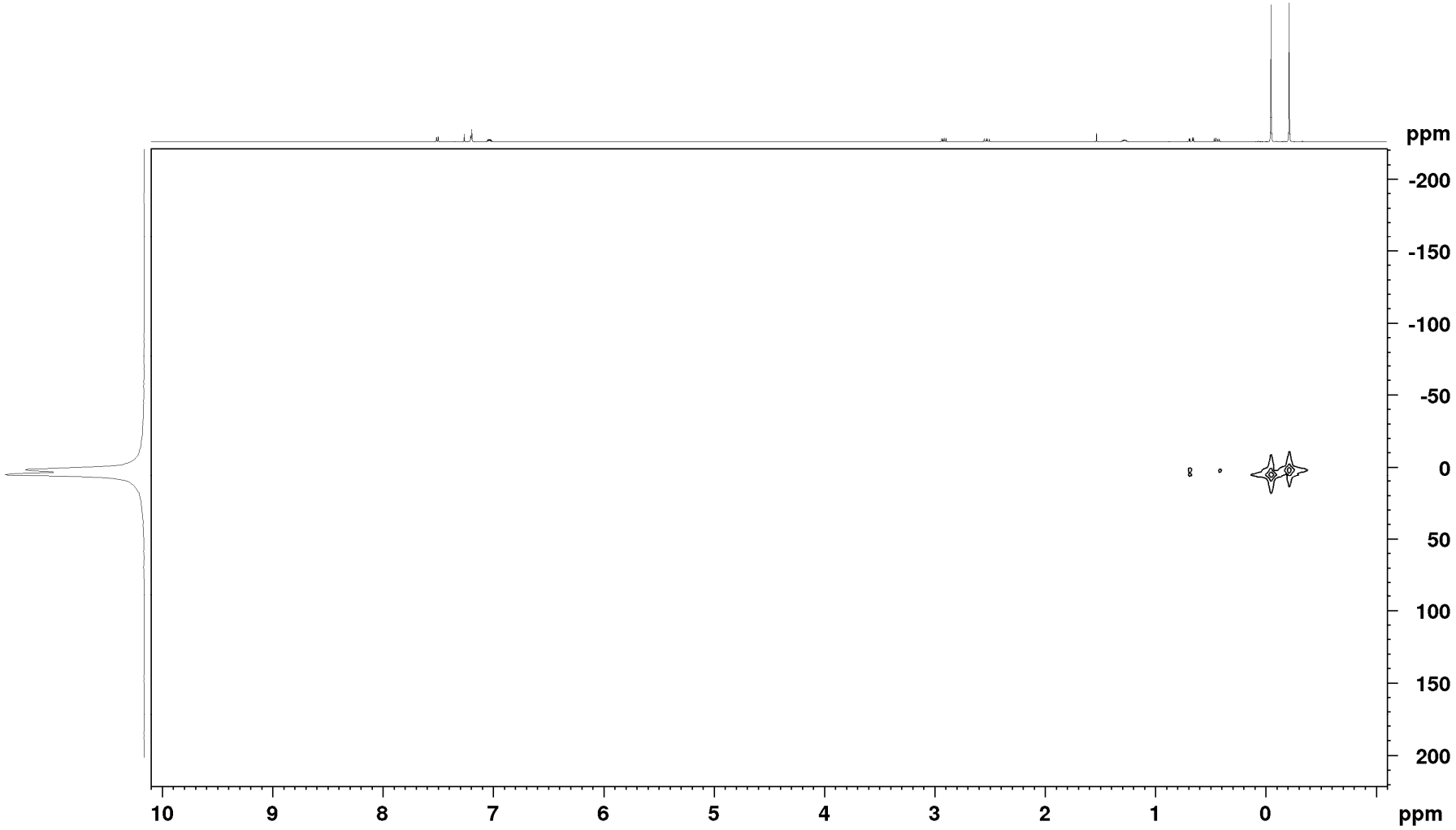


Figure S42. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4g** from the catalytic 1,2-disilylation of 1-allyl-4-chlorobenzene (**1g**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

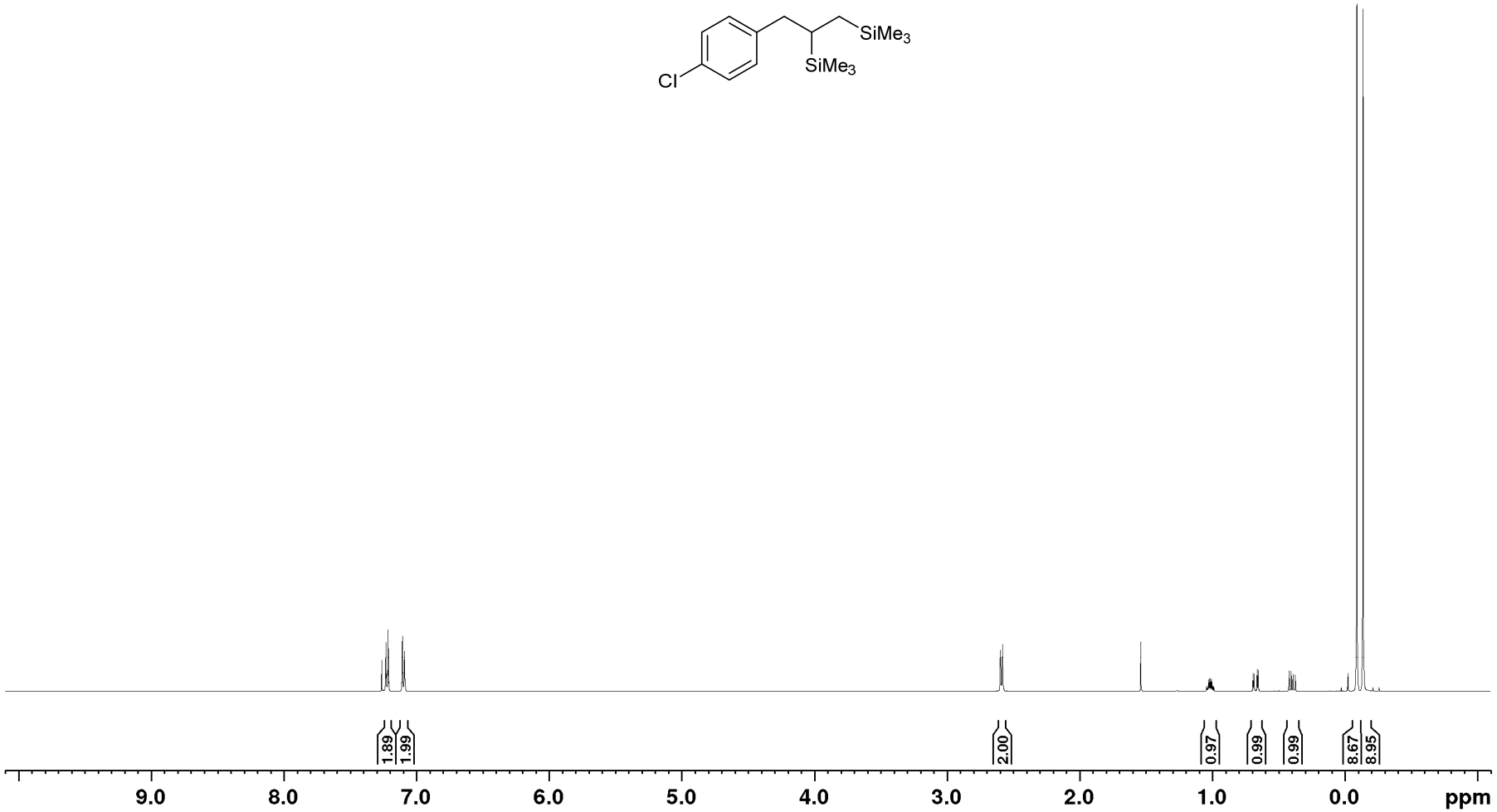


Figure S43. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298 K) of **4g** from the catalytic 1,2-disilylation of 1-allyl-4-chlorobenzene (**1g**) and $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

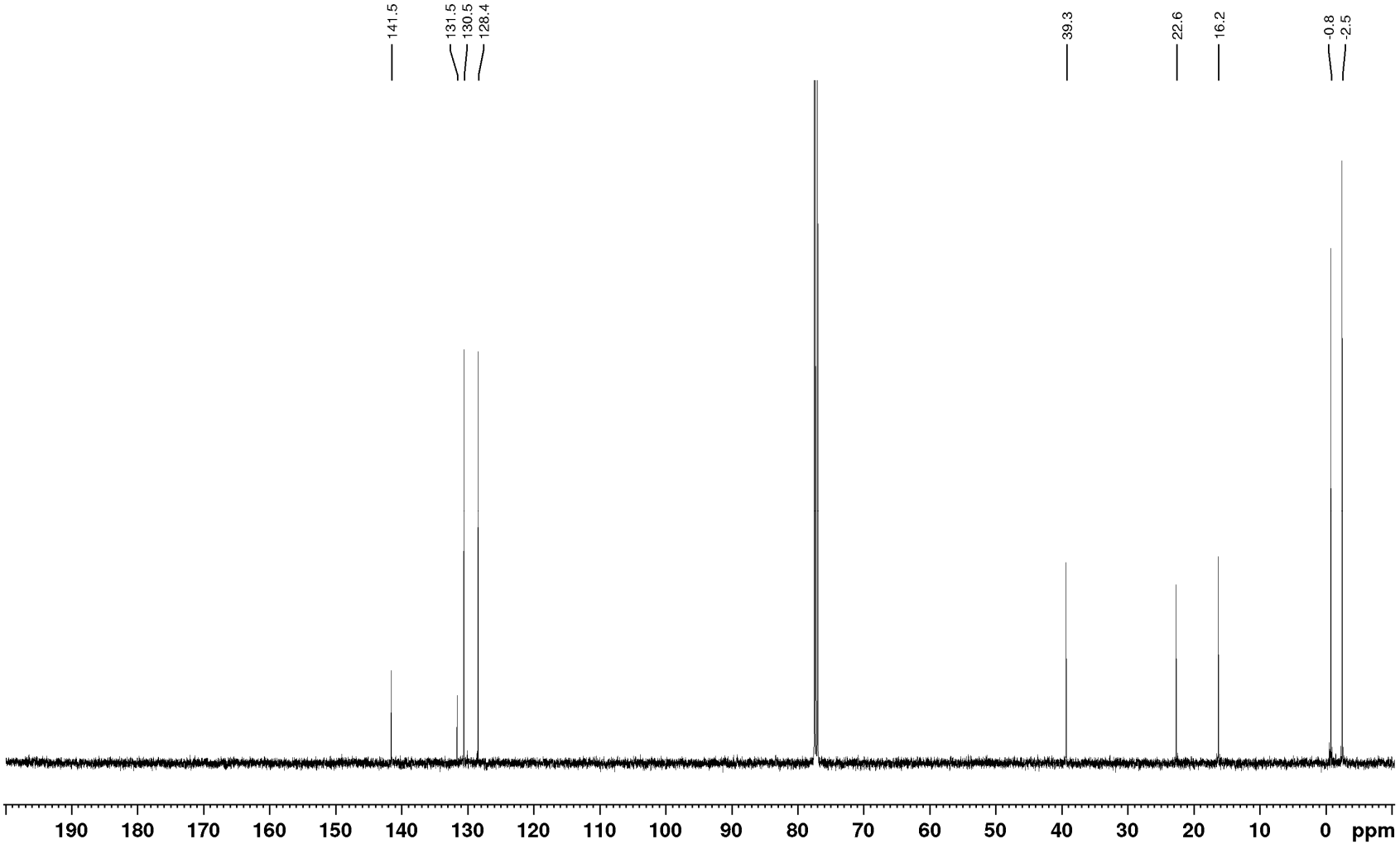


Figure S44. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **4g** from the catalytic 1,2-disilylation of 1-allyl-4-chloro-benzene (**1g**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

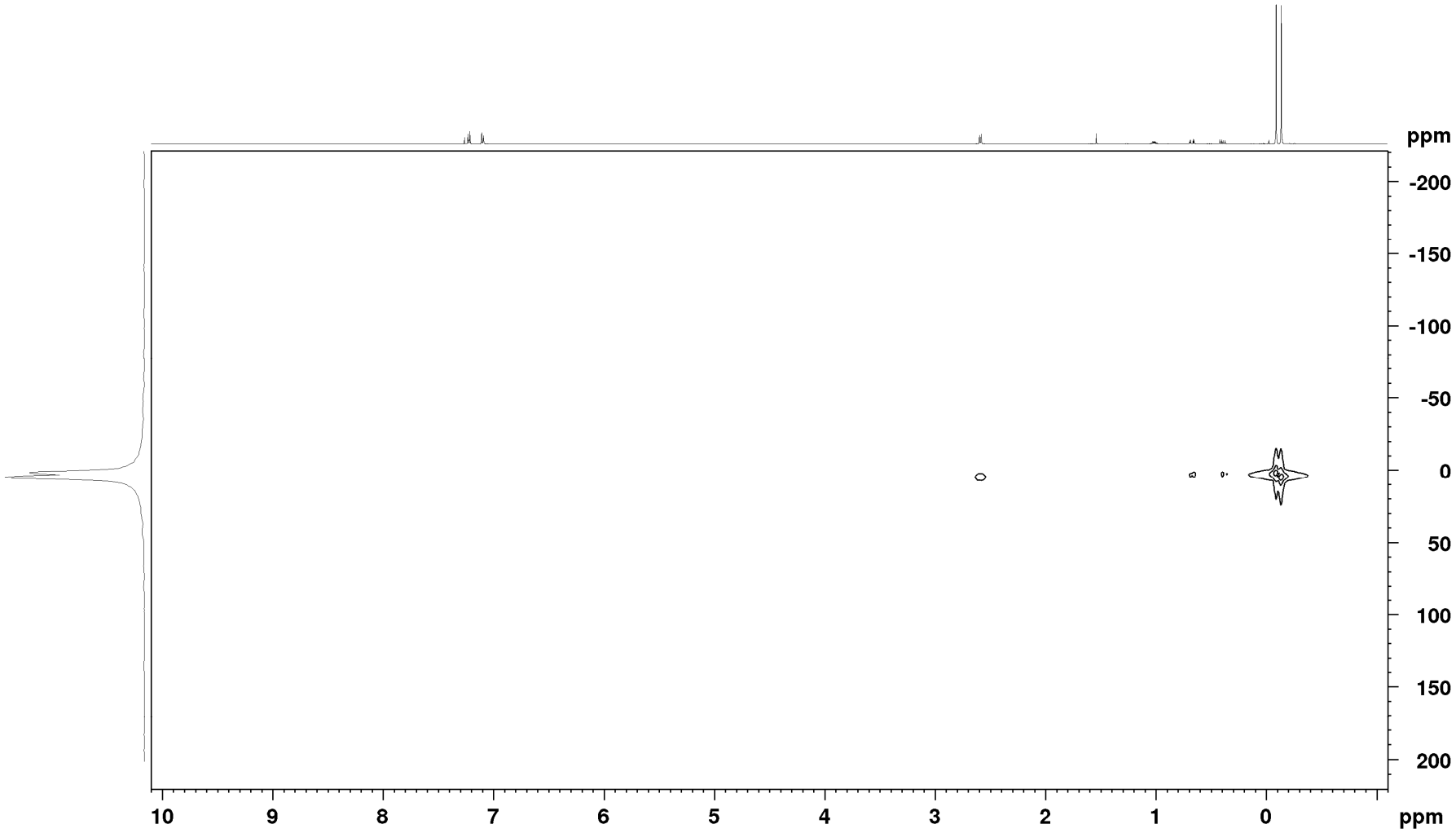


Figure S45. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4h** from the catalytic 1,2-disilylation of 1-allyl-3-chlorobenzene (**1h**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

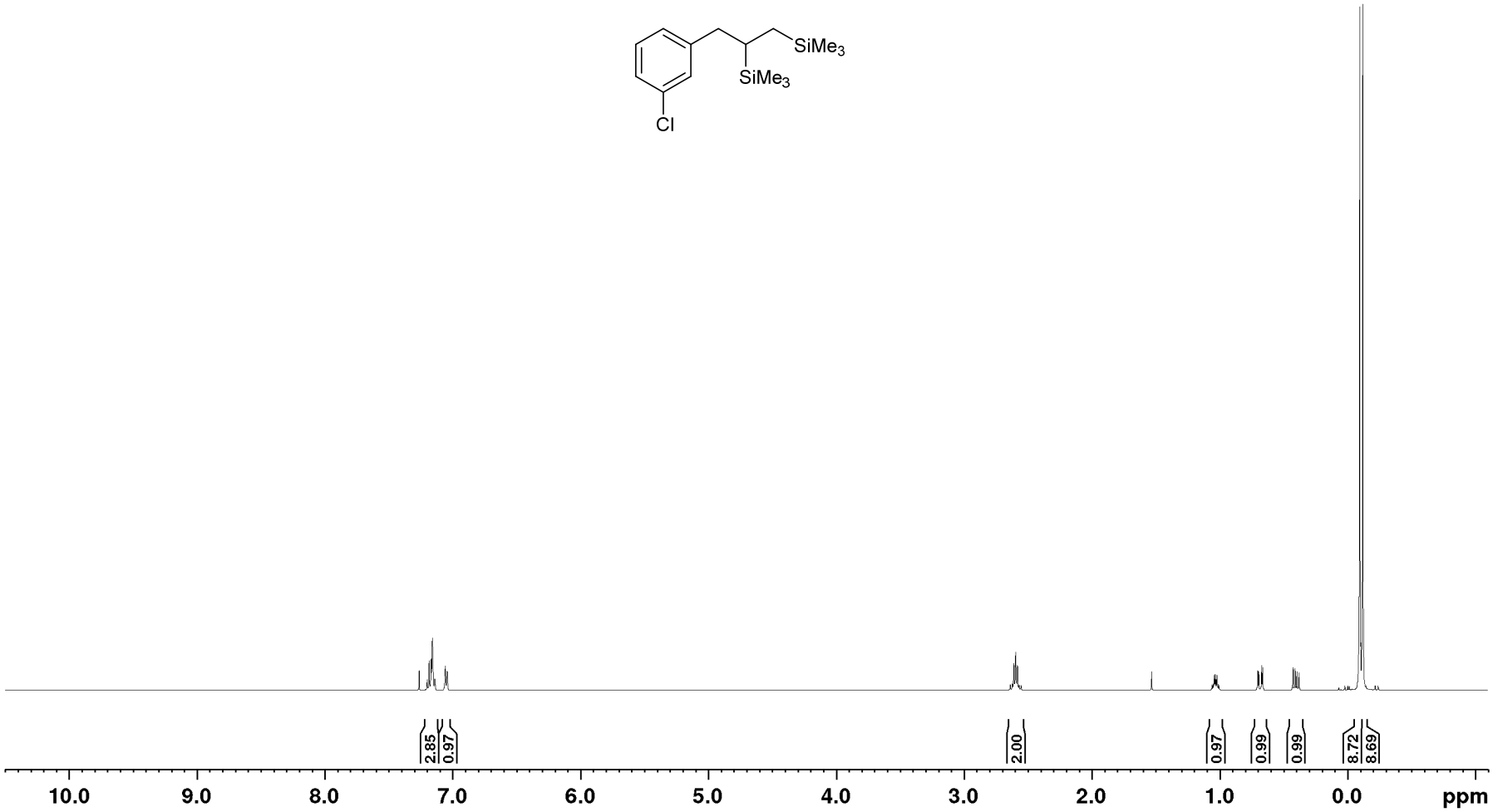


Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298 K) of **4h** from the catalytic 1,2-disilylation of 1-allyl-3-chlorobenzene (**1h**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

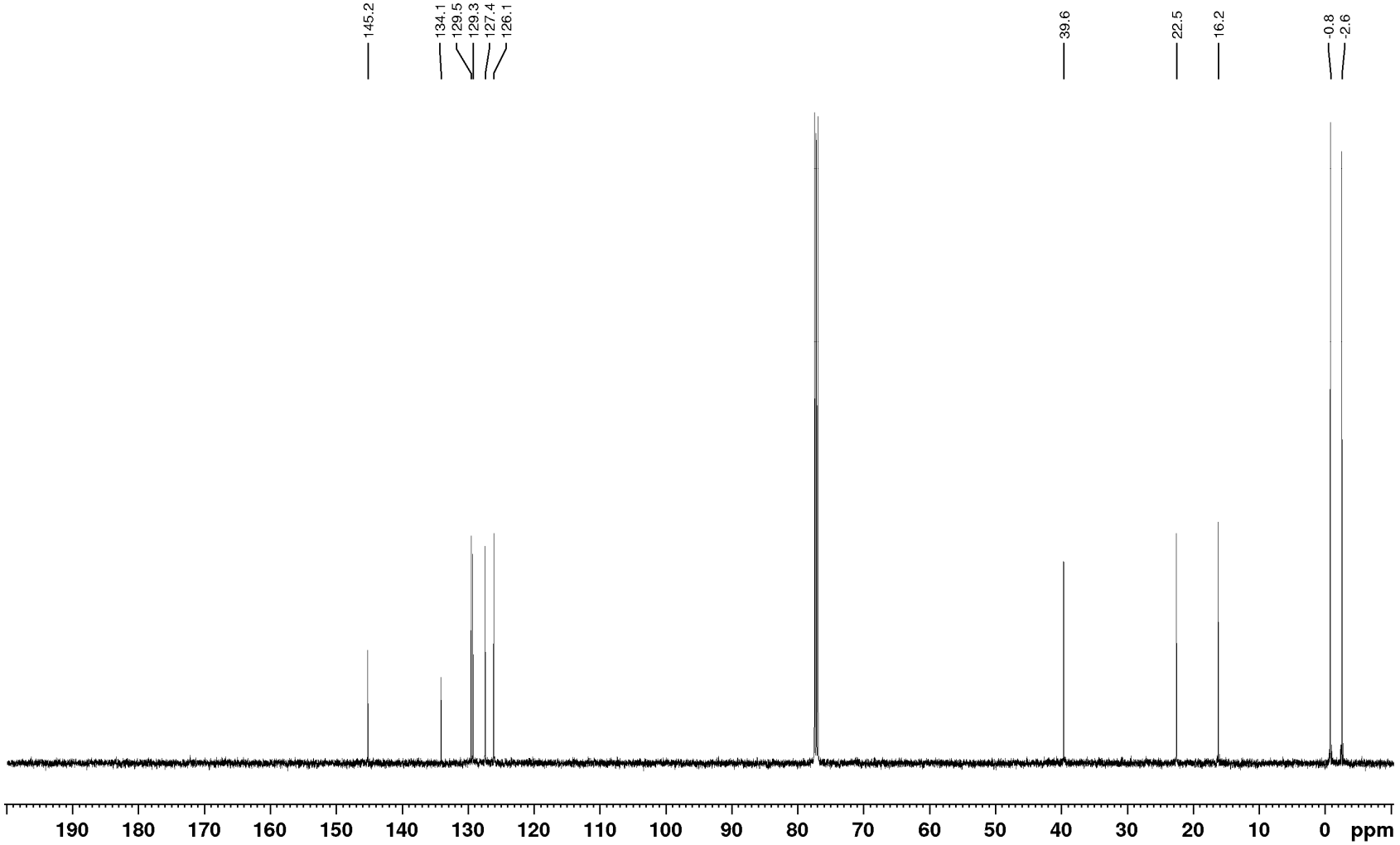


Figure S47. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **4h** from the catalytic 1,2-disilylation of 1-allyl-3-chloro-benzene (**1h**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

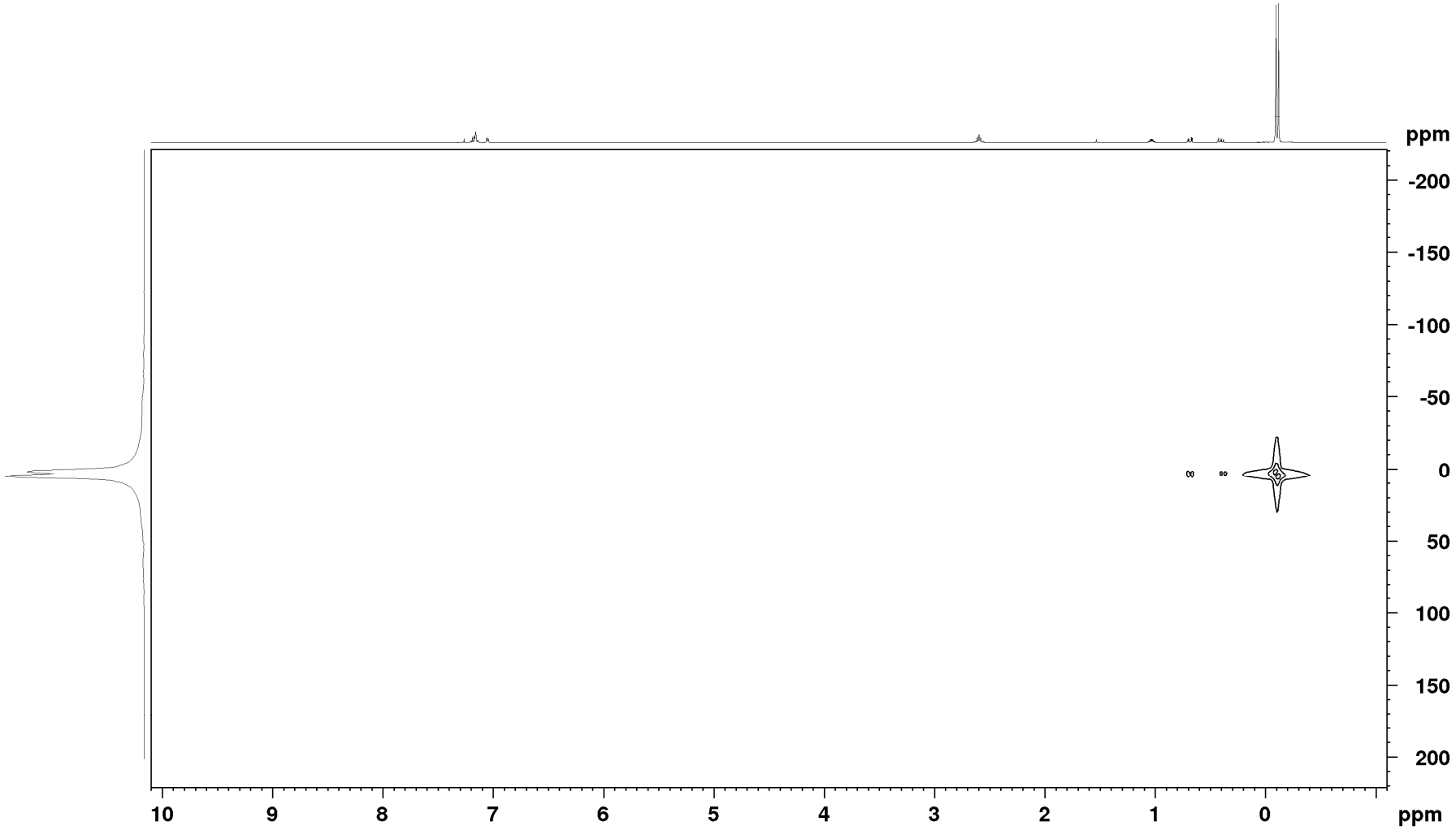


Figure S48. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4i** from the catalytic 1,2-disilylation of 1-allyl-4-fluorobenzene (**1i**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

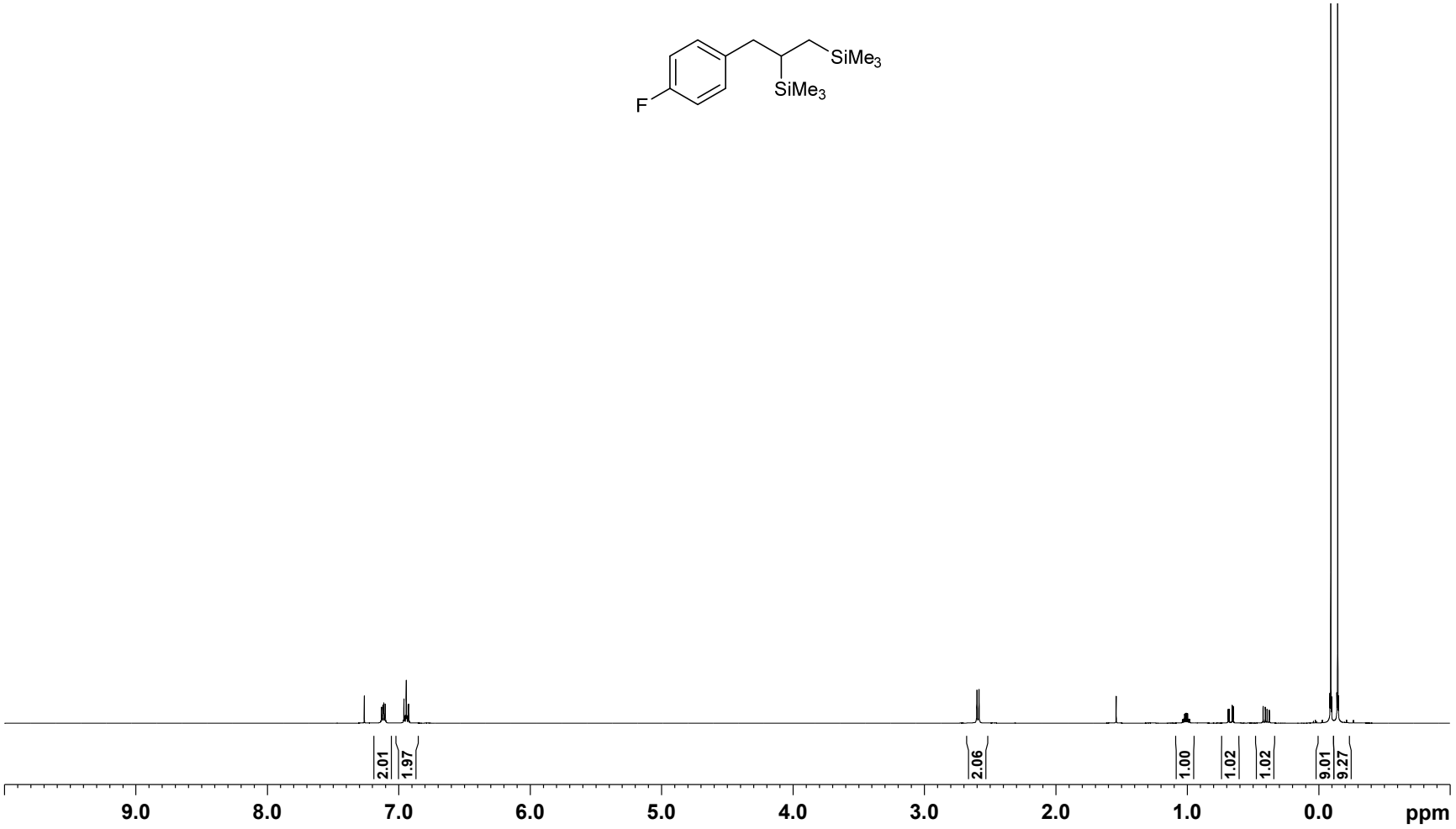


Figure S49. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298 K) of **4i** from the catalytic 1,2-disilylation of 1-allyl-4-fluorobenzene (**1i**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

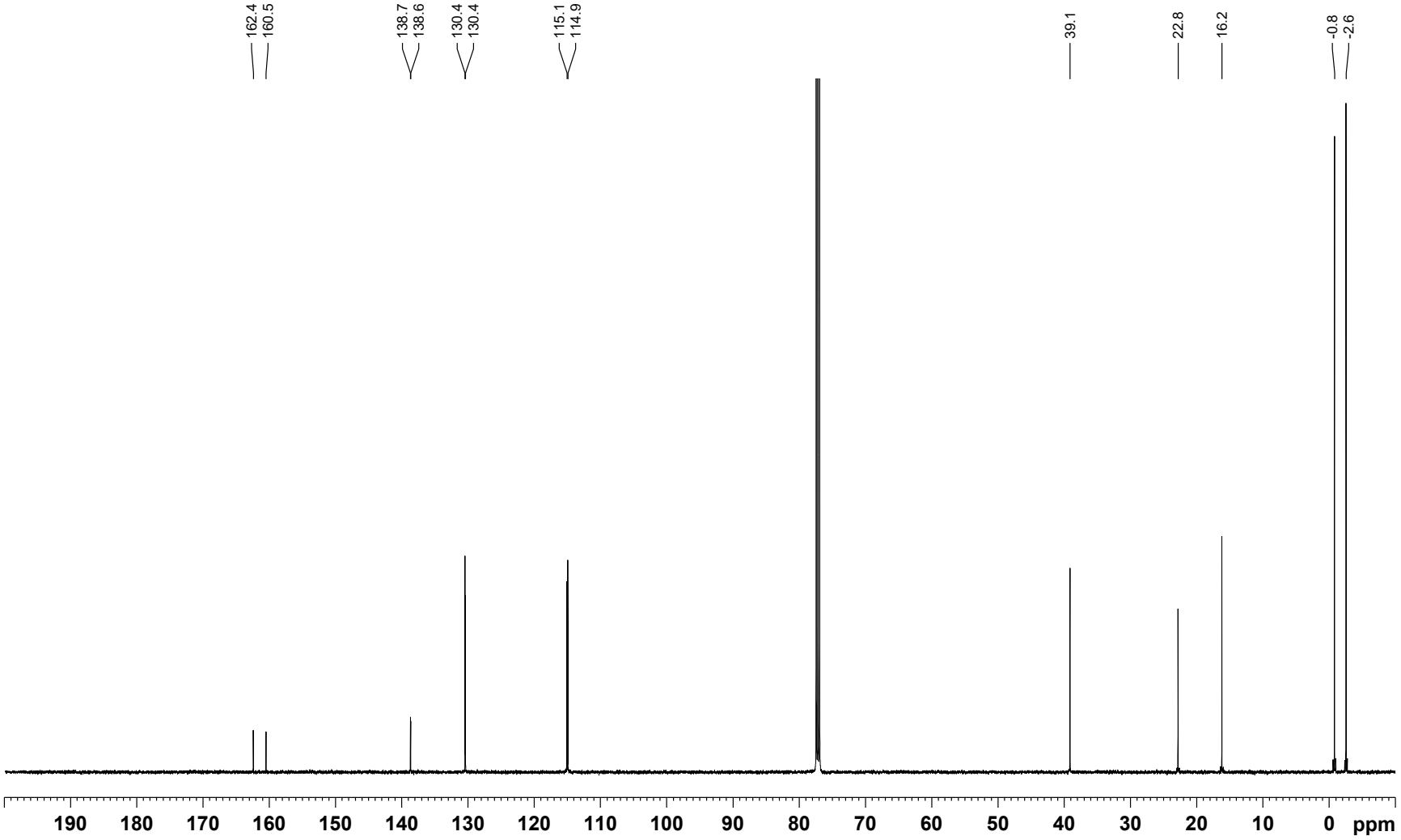


Figure S50. $^{19}F\{^{1}H\}$ NMR spectrum (471 MHz, $CDCl_3$, 298 K) of **4i** from the catalytic 1,2-disilylation of 1-allyl-4-fluorobenzene (**1i**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

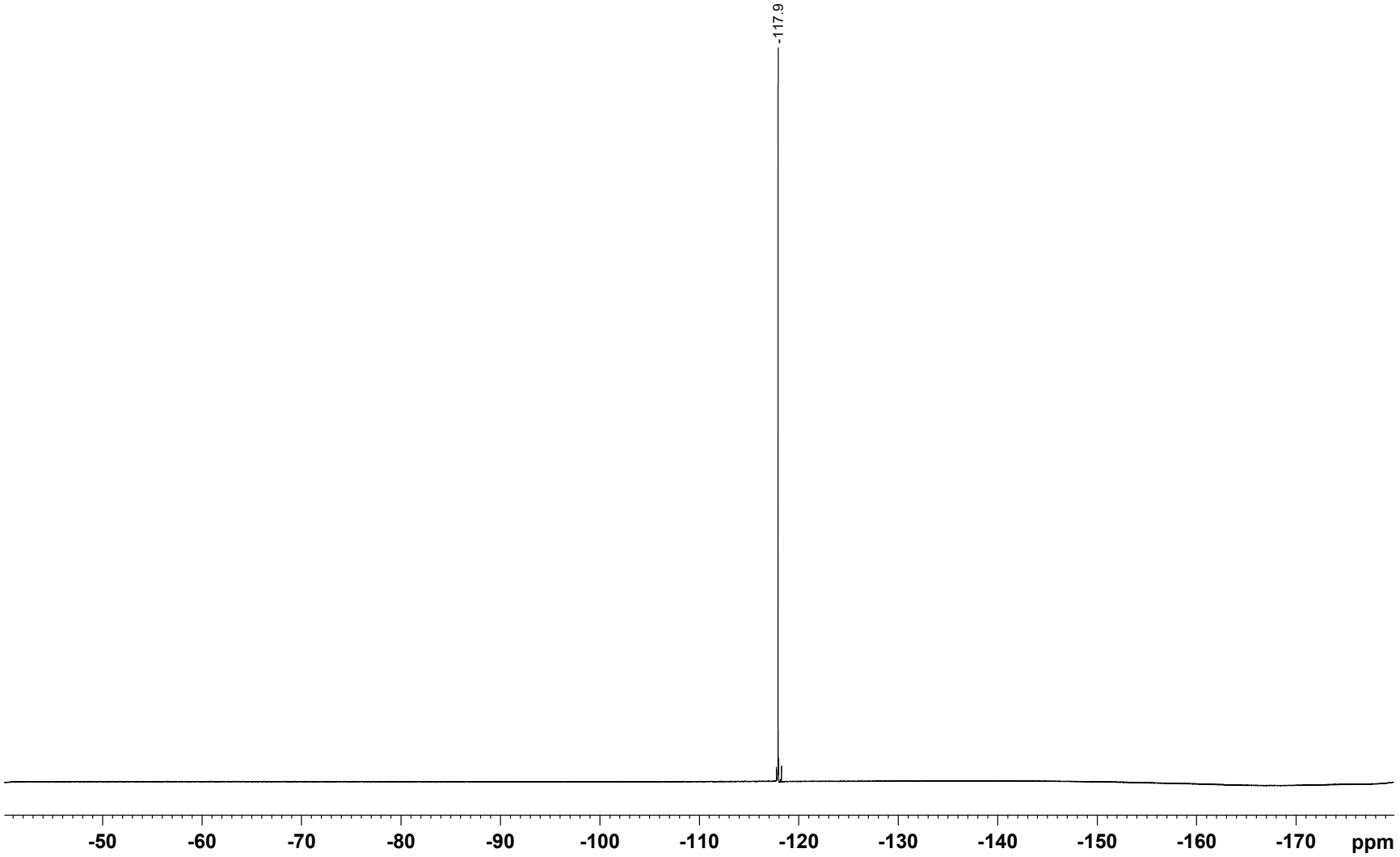


Figure S51. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **4i** from the catalytic 1,2-disilylation of 1-allyl-4-fluorobenzene (**1i**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

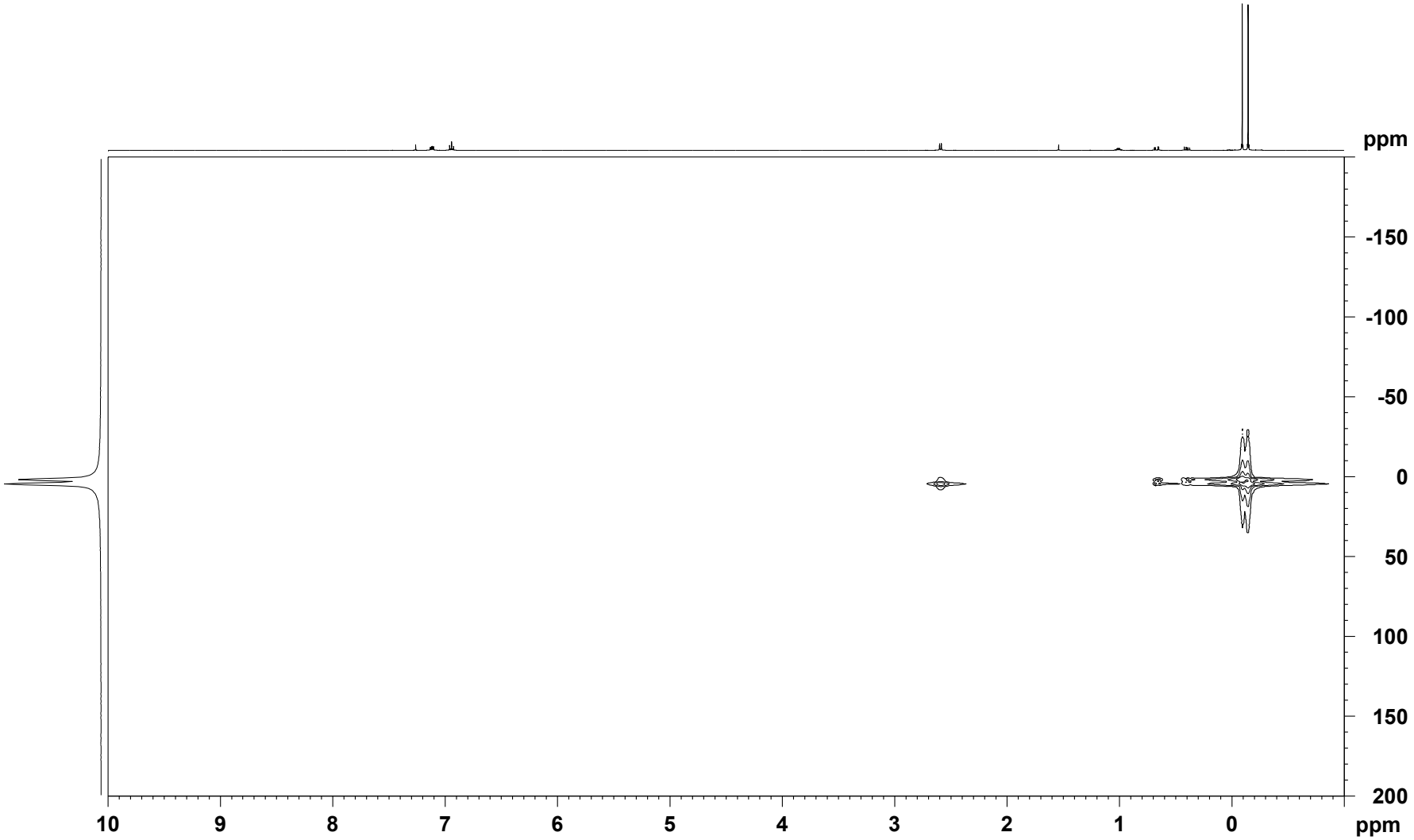


Figure S52. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4j** from the catalytic 1,2-disilylation of 4-allyl-1,1'-biphenyl (**1j**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

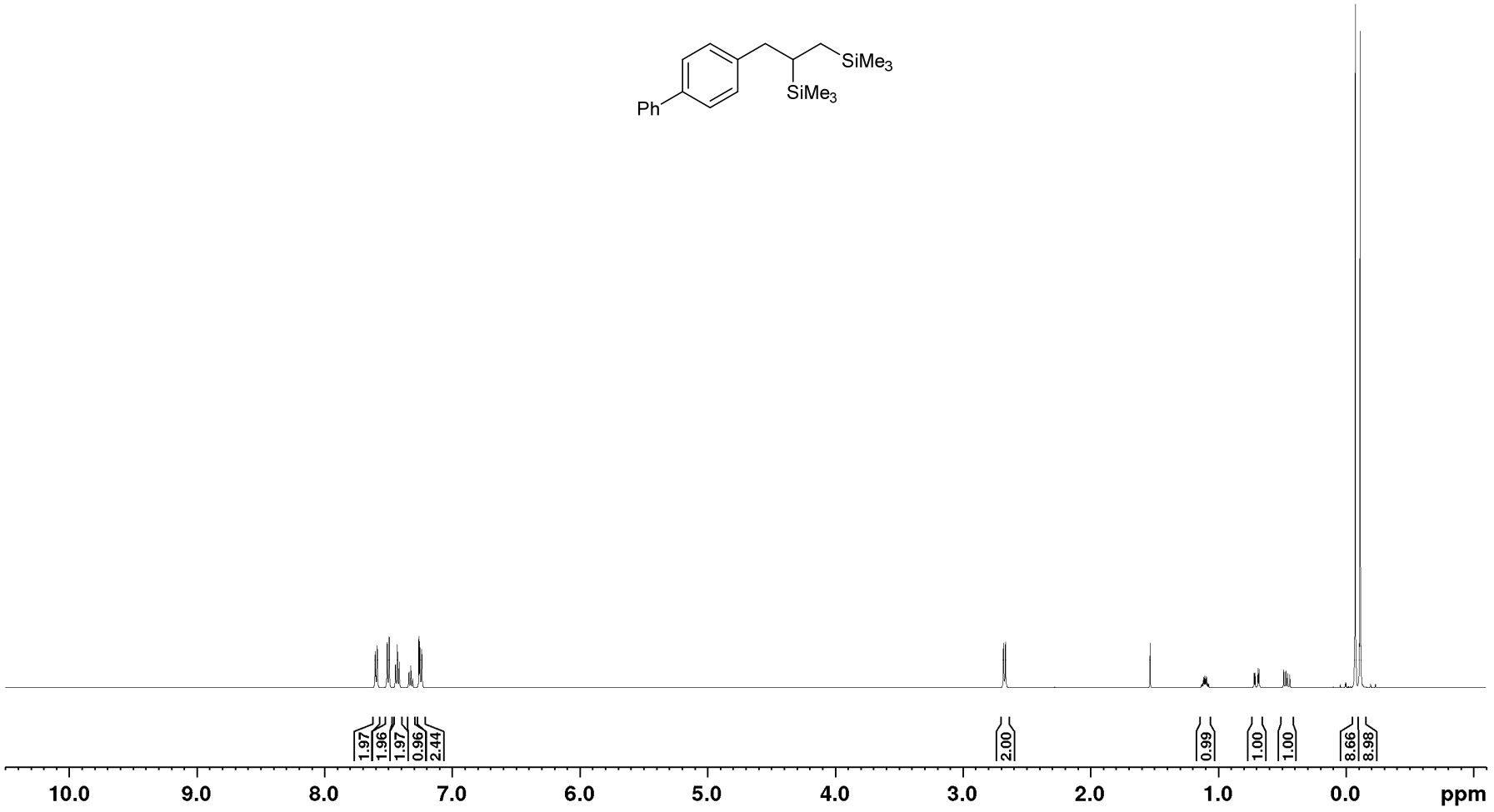


Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298 K) of **4j** from the catalytic 1,2-disilylation of 4-allyl-1,1'-biphenyl (**1j**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

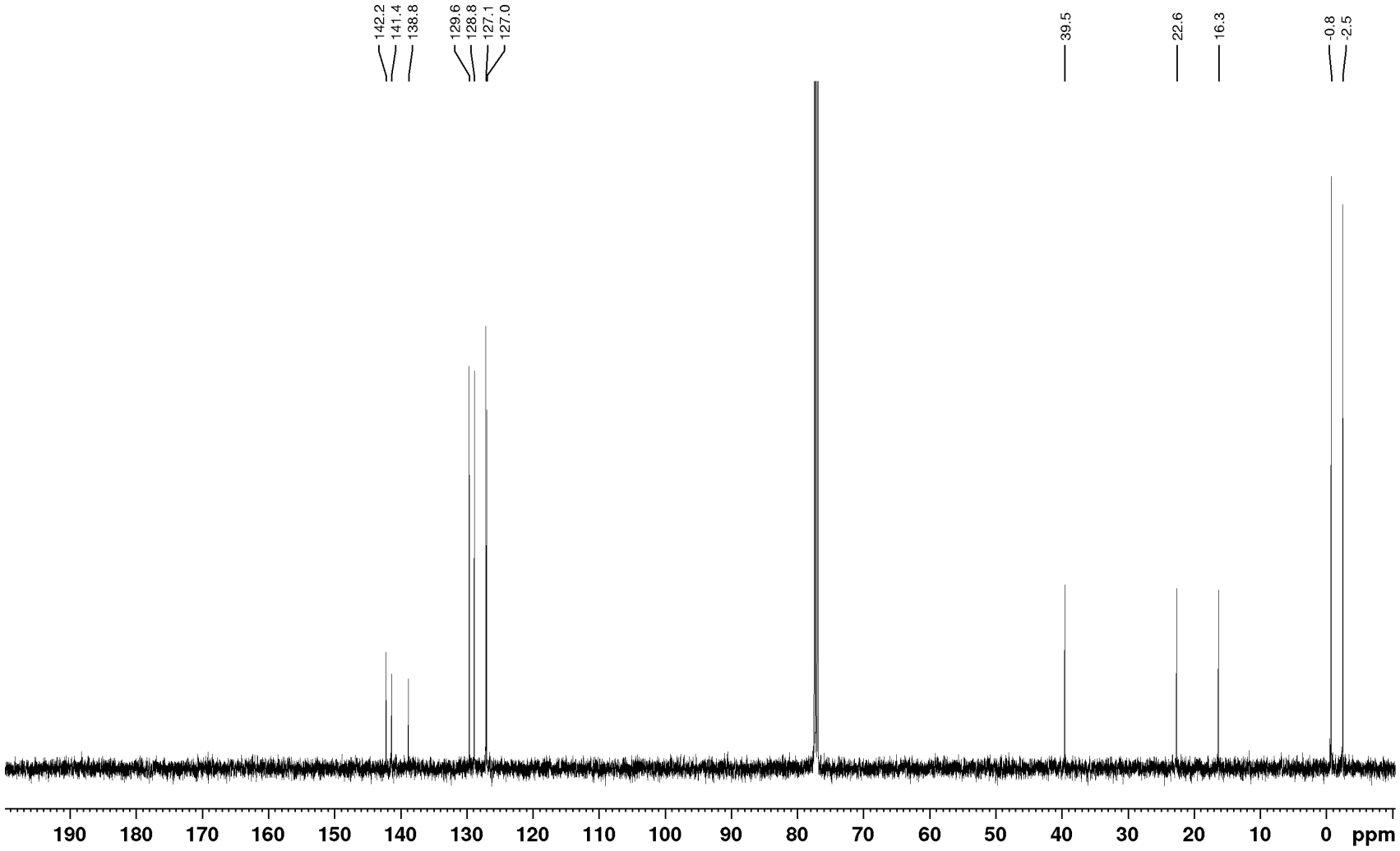


Figure S54. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **4j** from the catalytic 1,2-disilylation of 4-allyl-1,1'-biphenyl (**1j**) with $Me_3SiSiMe_3$ using $Me_3Si^+[CHB_{11}H_5Br_6]^-$ as initiator.

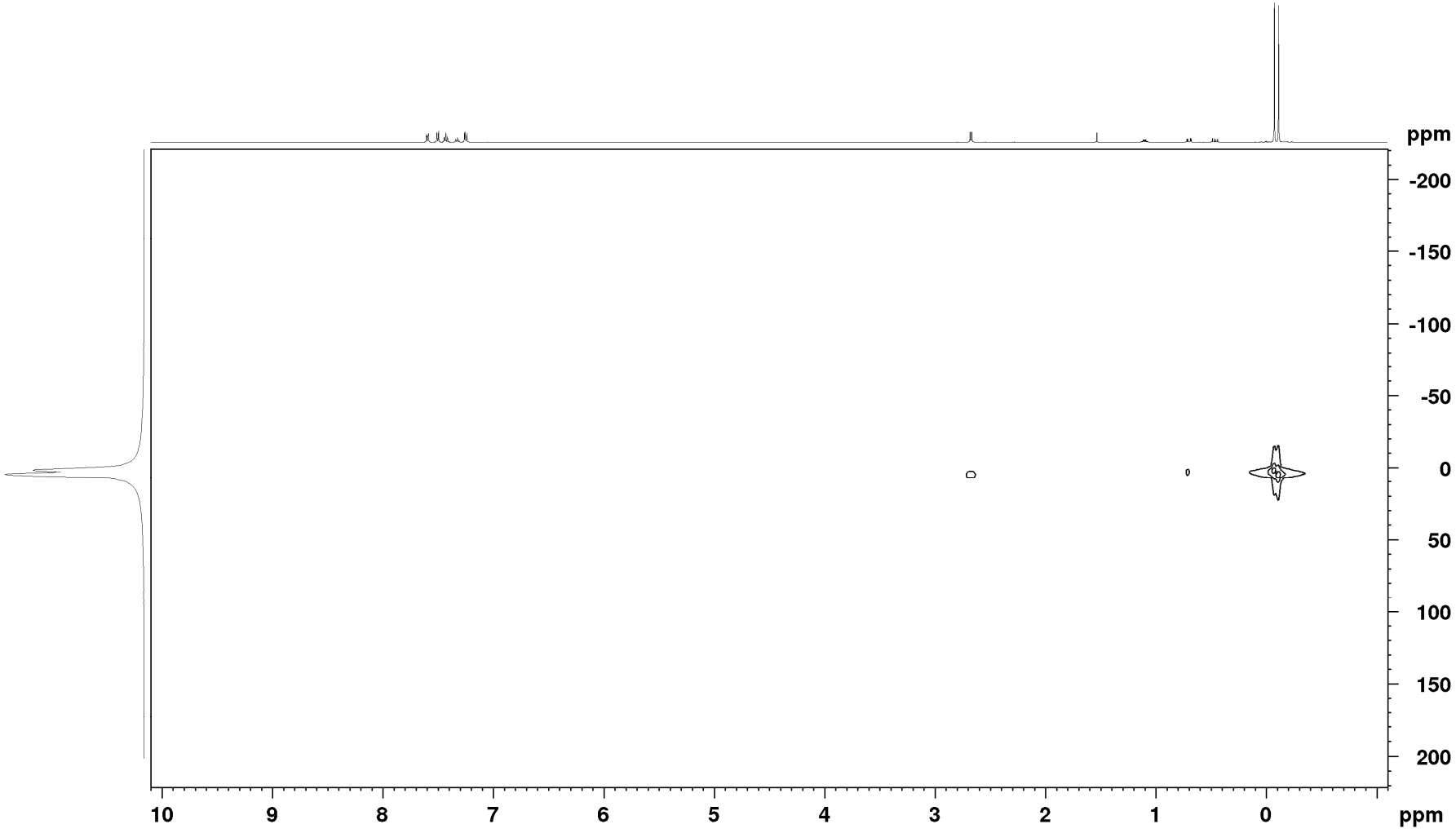


Figure S55. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4k** from the catalytic 1,2-disilylation of 1-allylnaphthalene (**1k**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

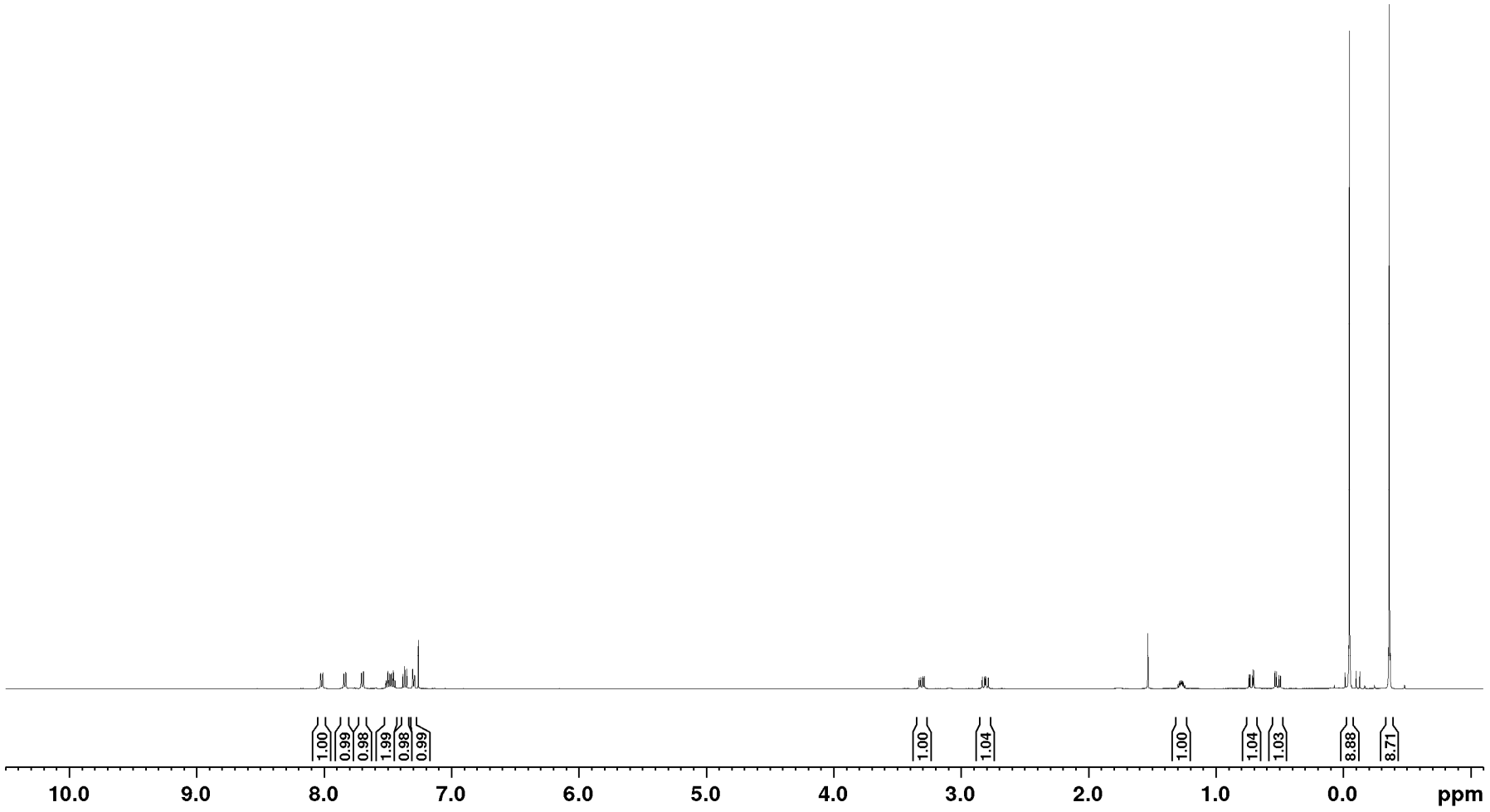


Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298 K) of **4k** from the catalytic 1,2-disilylation of 1-allylnaphthalene (**1k**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

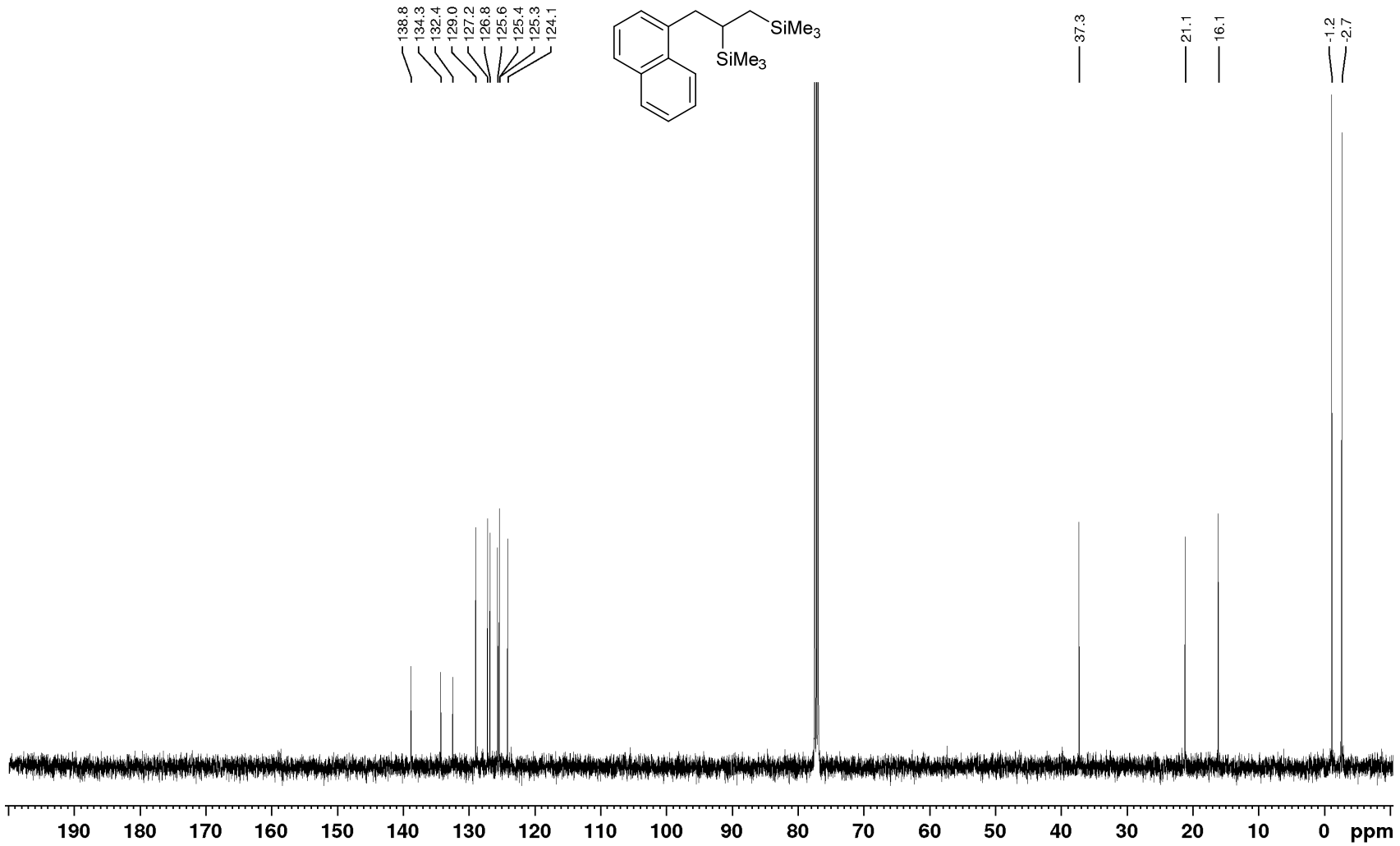


Figure S57. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **4k** from the catalytic 1,2-disilylation of 1-allylnaphthalene (**1k**) with $Me_3SiSiMe_3$ using $Me_3Si^+[CHB_{11}H_5Br_6]^-$ as initiator.

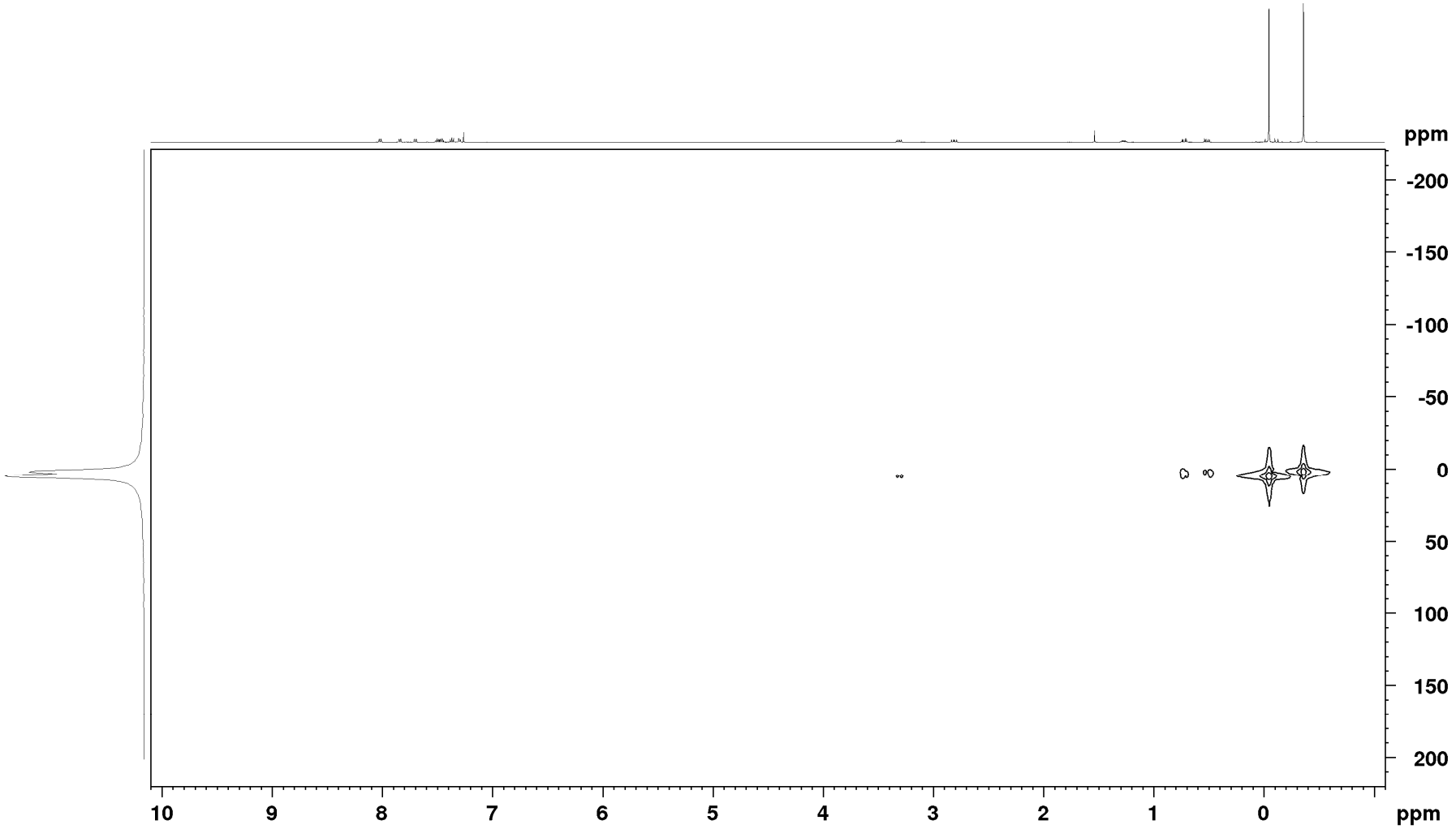


Figure S58. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4l** from the catalytic 1,2-disilylation of 2-allylnaphthalene (**1l**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

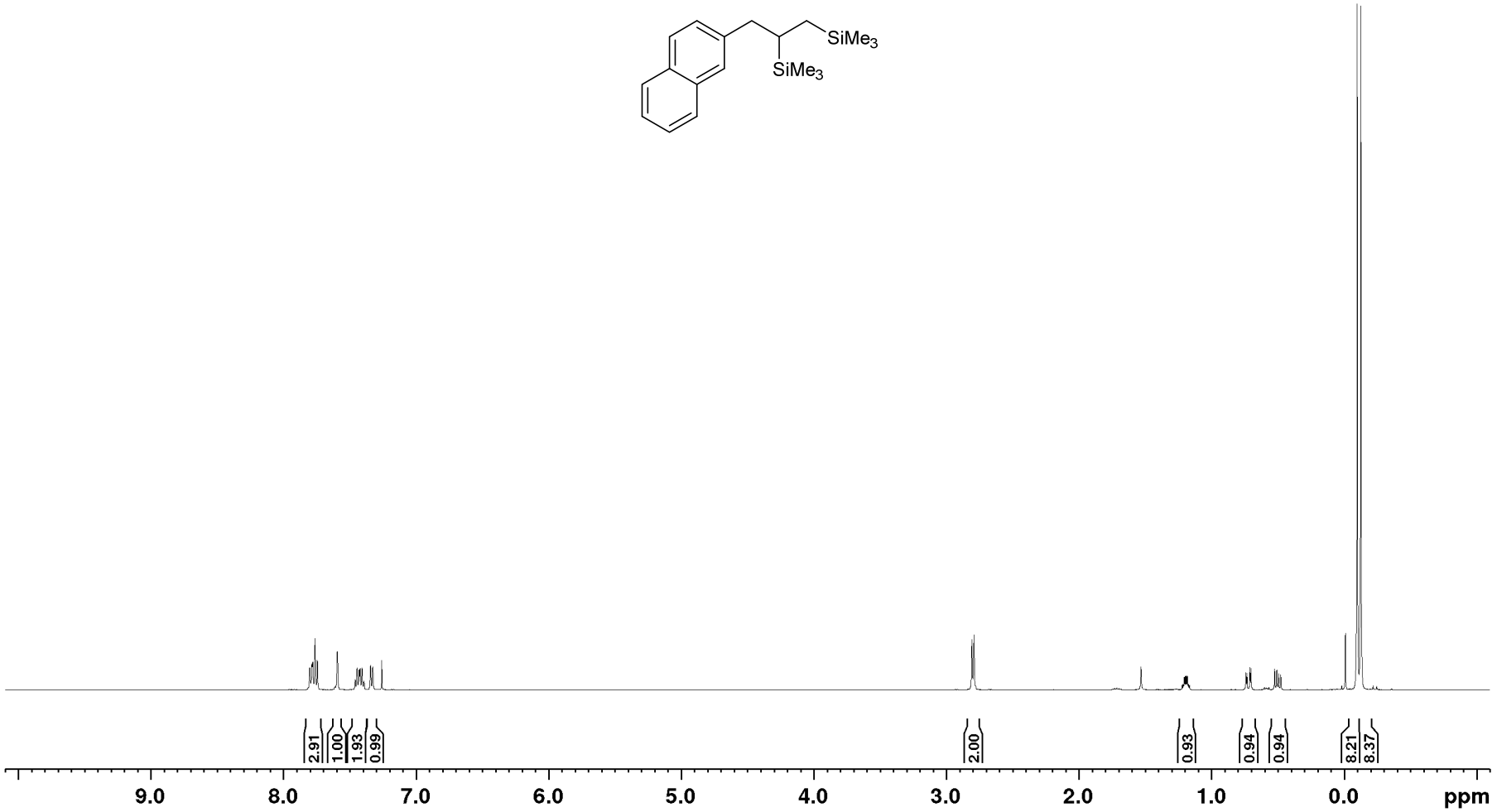


Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298 K) of **4l** from the catalytic 1,2-disilylation of 2-allylnaphthalene (**1l**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

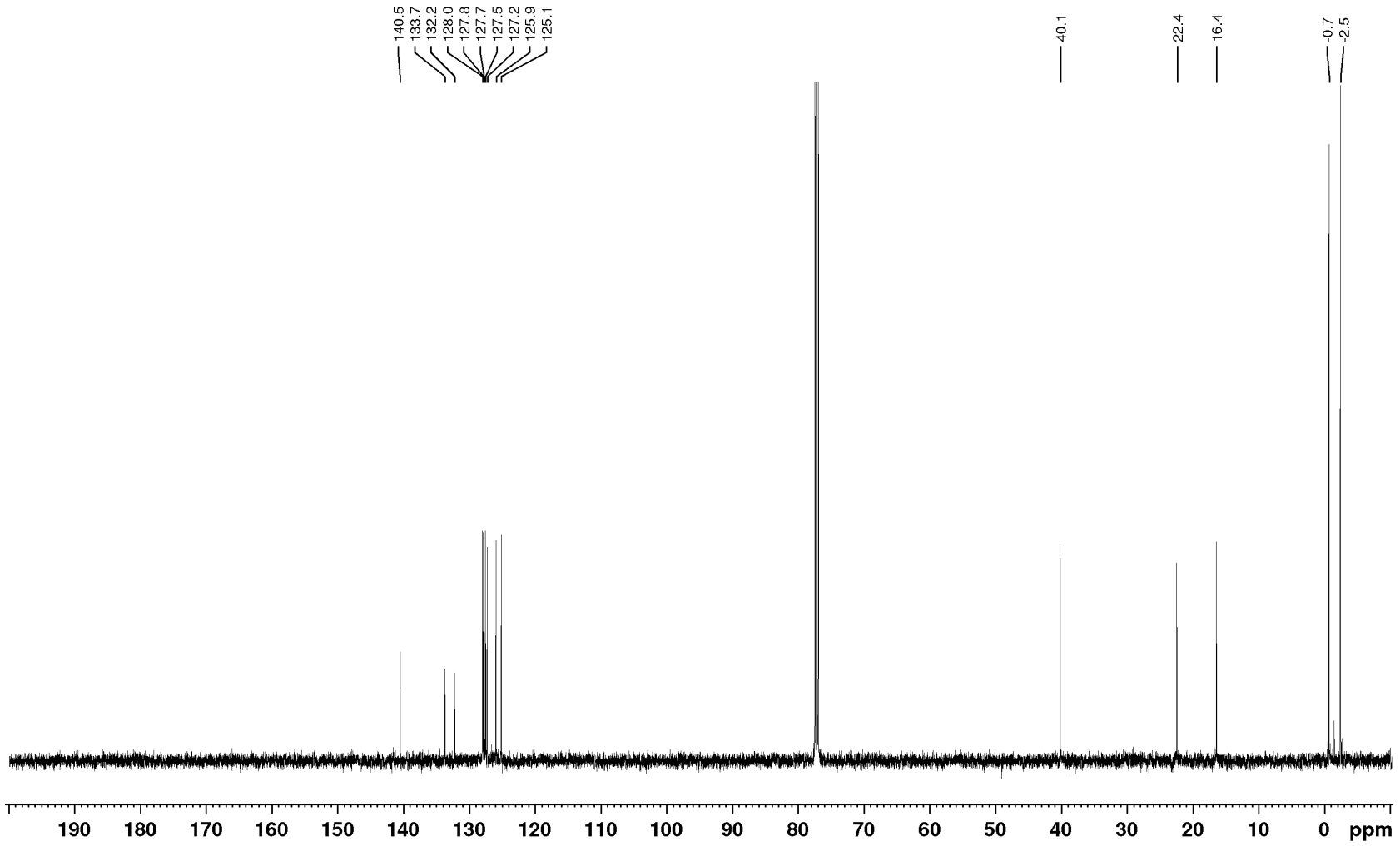


Figure S60. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **4l** from the catalytic 1,2-disilylation of 2-allylnaphthalene (**1l**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

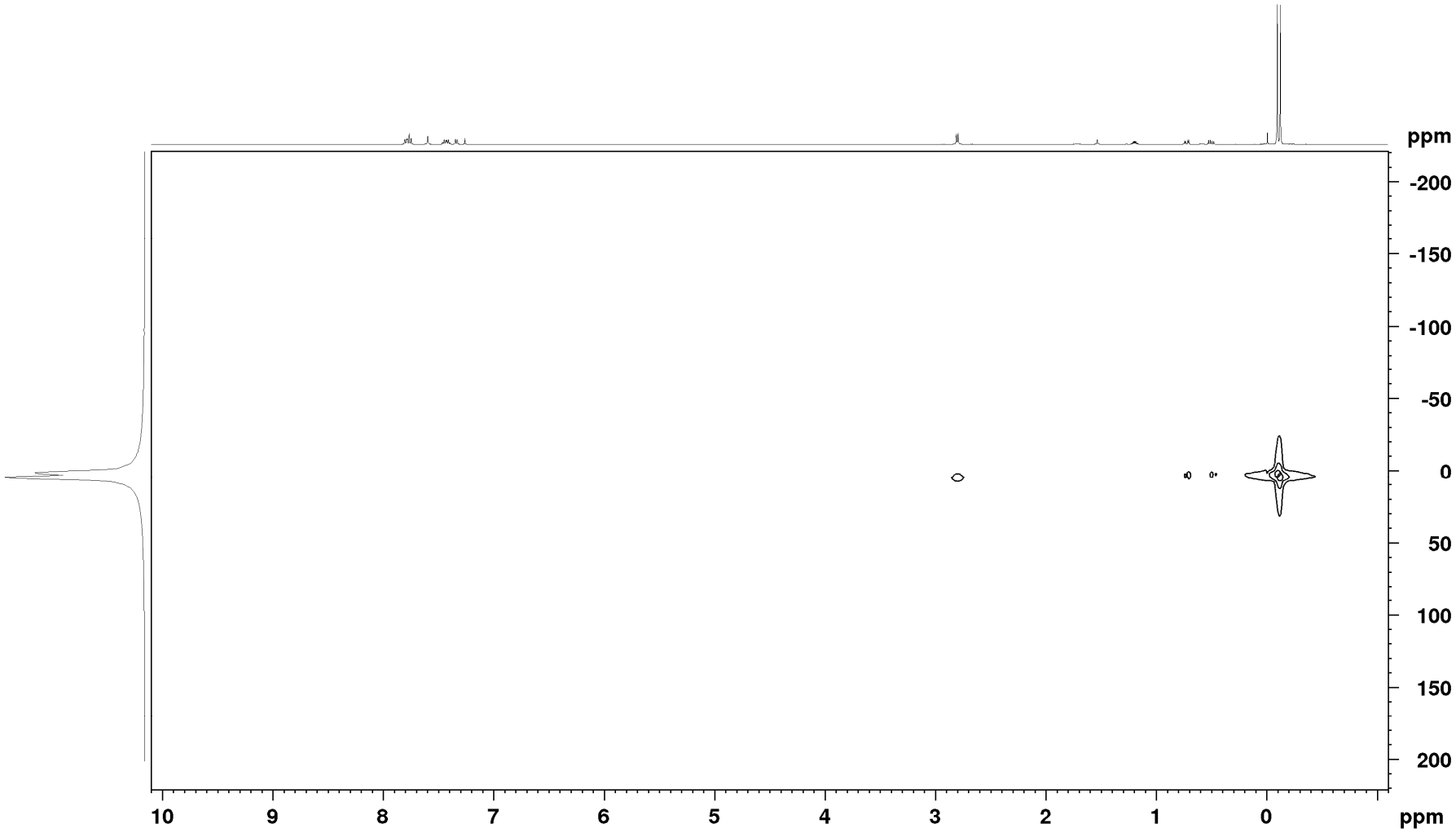


Figure S61. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4m** from the catalytic 1,2-disilylation of 1-bromo-4-vinylbenzene (**1m**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

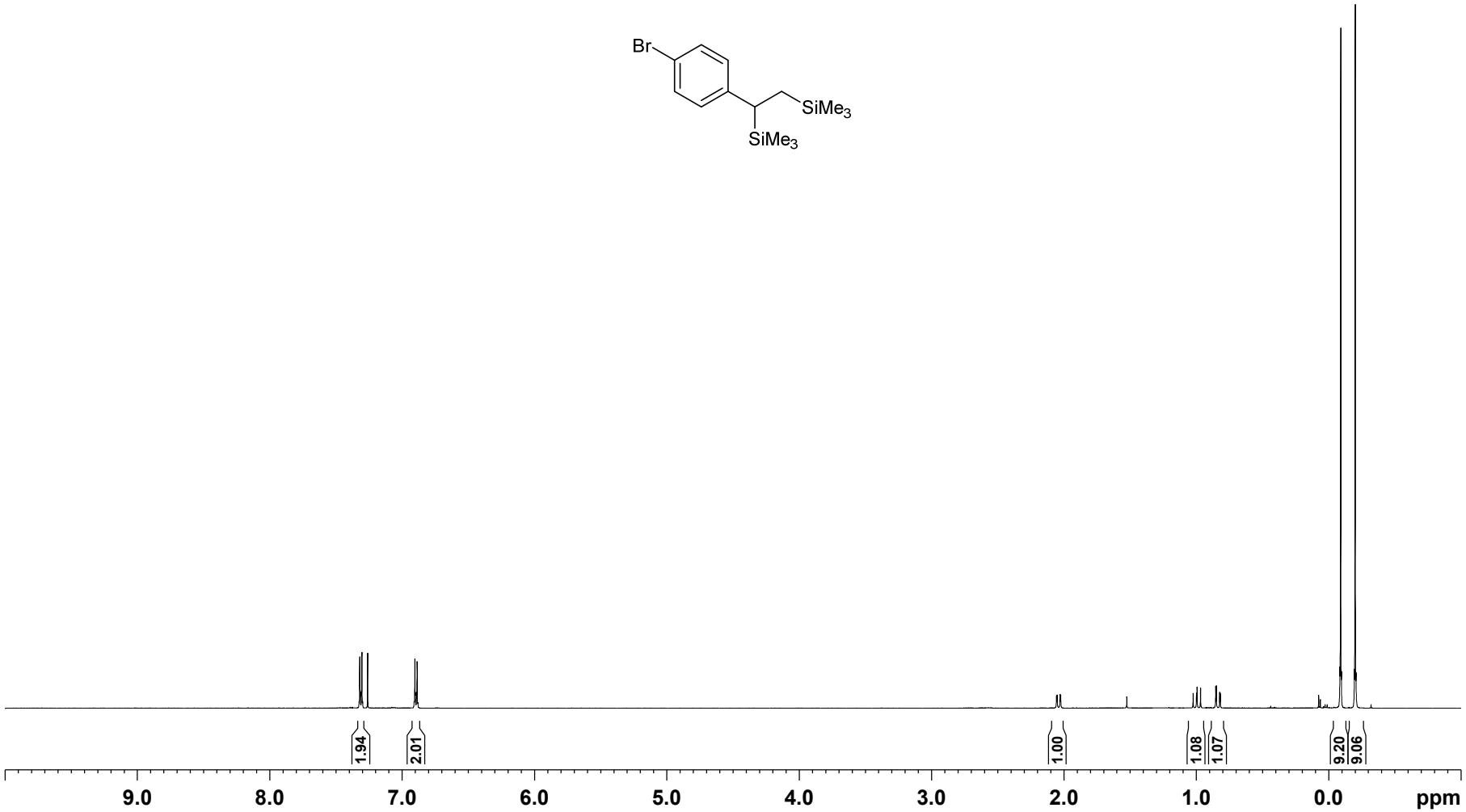


Figure S62. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298 K) of **4m** from the catalytic 1,2-disilylation of 1-bromo-4-vinylbenzene (**1m**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

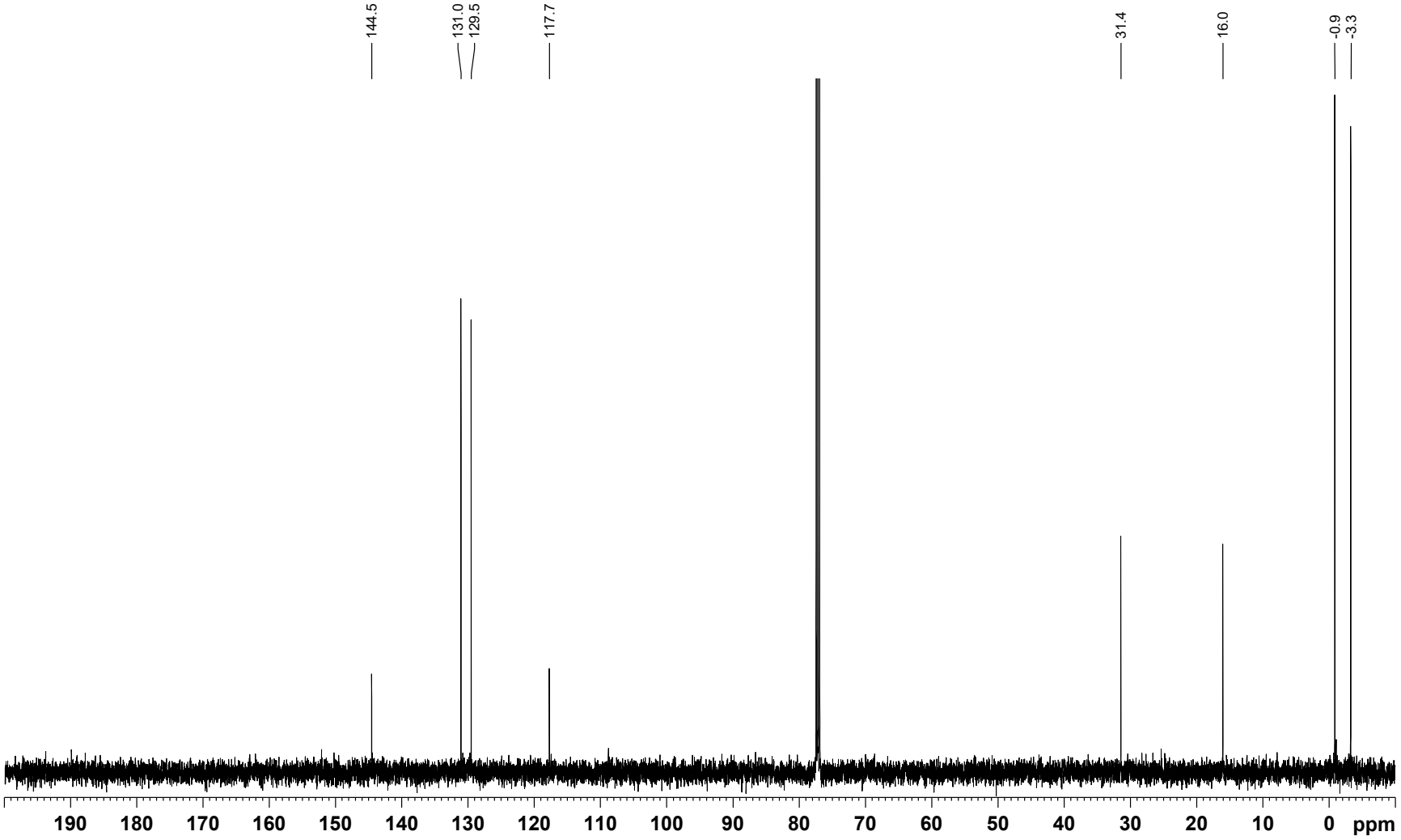


Figure S63. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **4m** from the catalytic 1,2-disilylation of 1-bromo-4-vinylbenzene (**1m**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

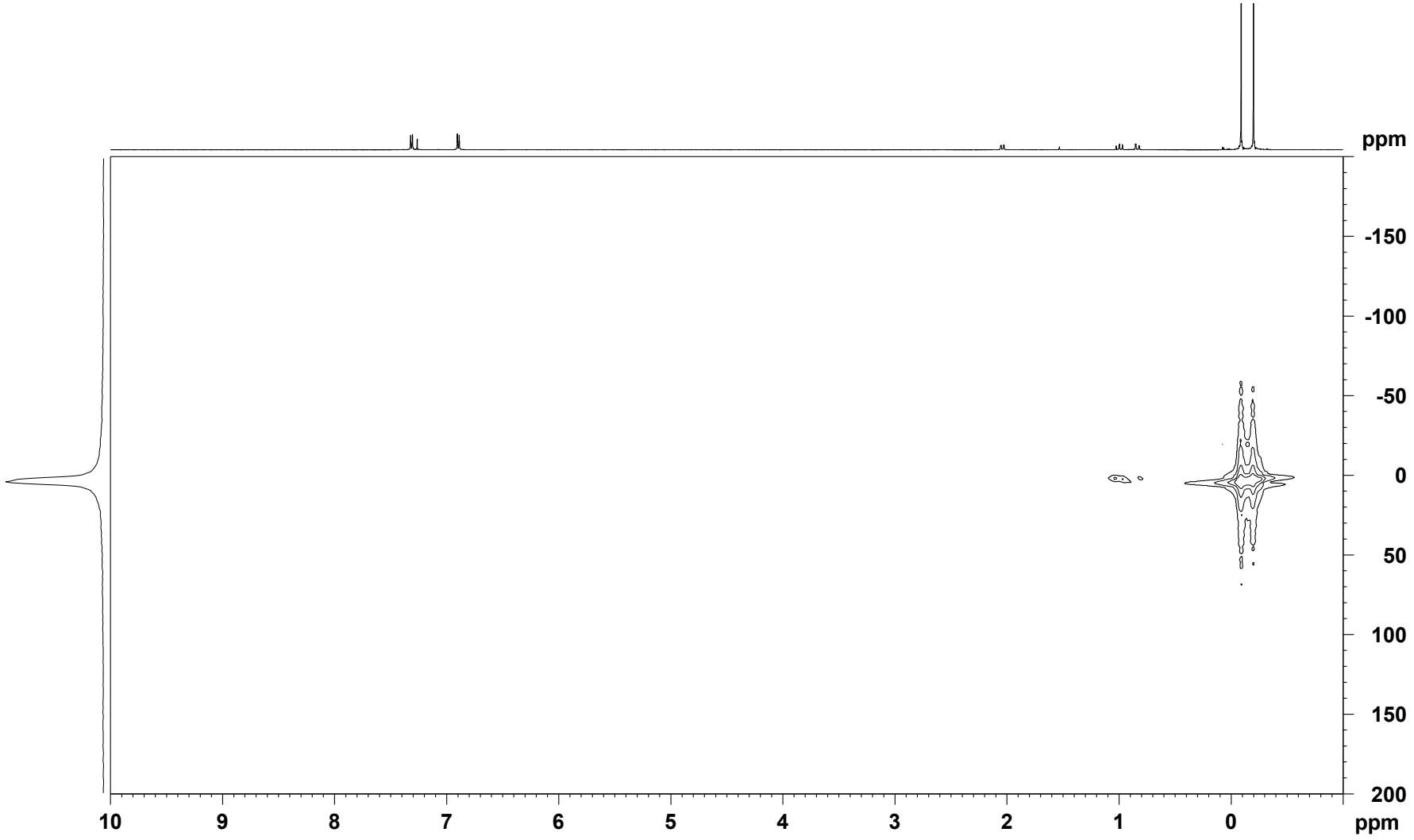


Figure S64. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4n** from the catalytic 1,2-disilylation of 1-fluoro-4-vinylbenzene (**1n**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

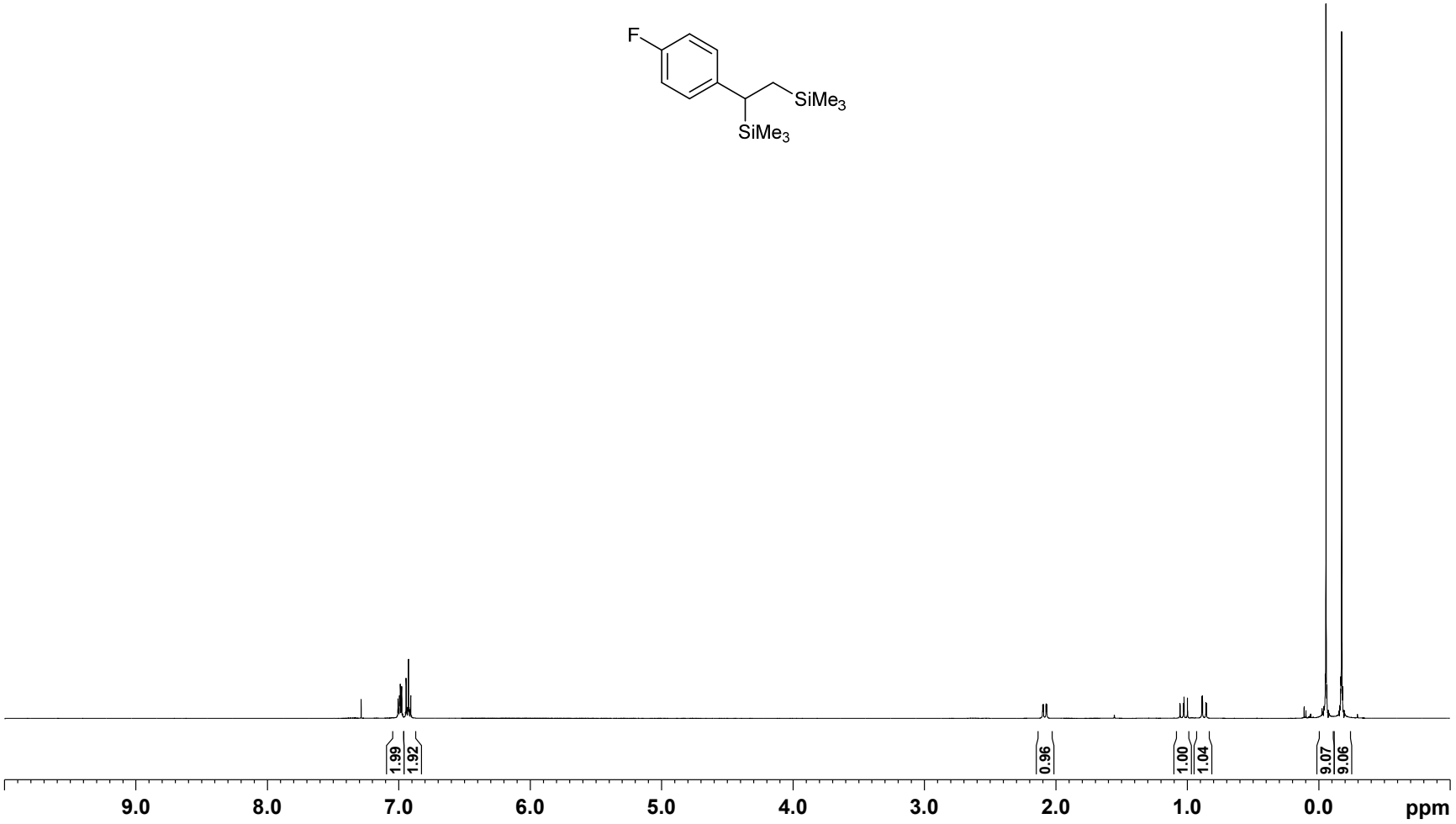


Figure S65. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298 K) of **4n** from the catalytic 1,2-disilylation of 1-fluoro-4-vinylbenzene (**1n**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

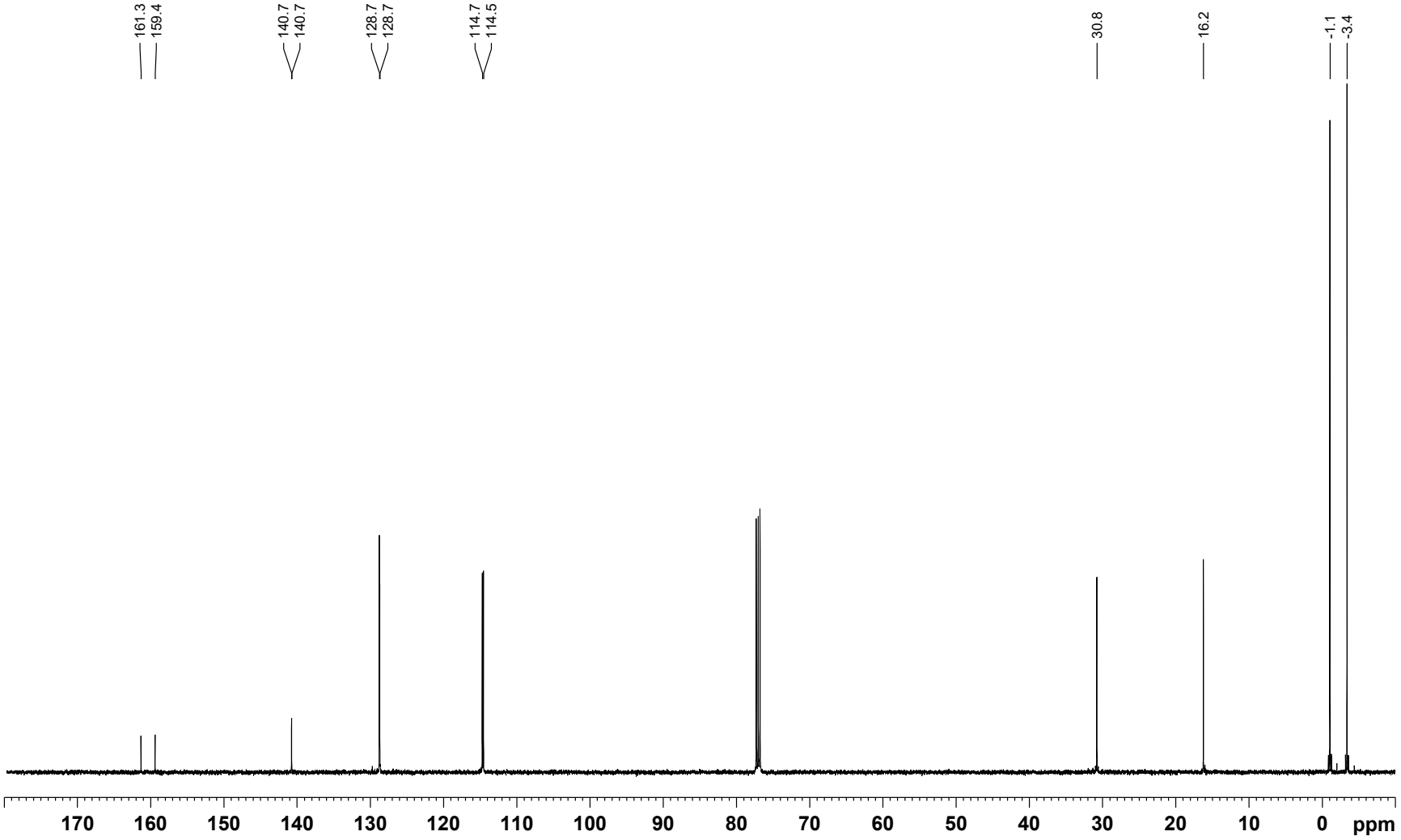


Figure S66. $^{19}F\{^{1}H\}$ NMR spectrum (471 MHz, $CDCl_3$, 298 K) of **4n** from the catalytic 1,2-disilylation of 1-fluoro-4-vinylbenzene (**1n**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

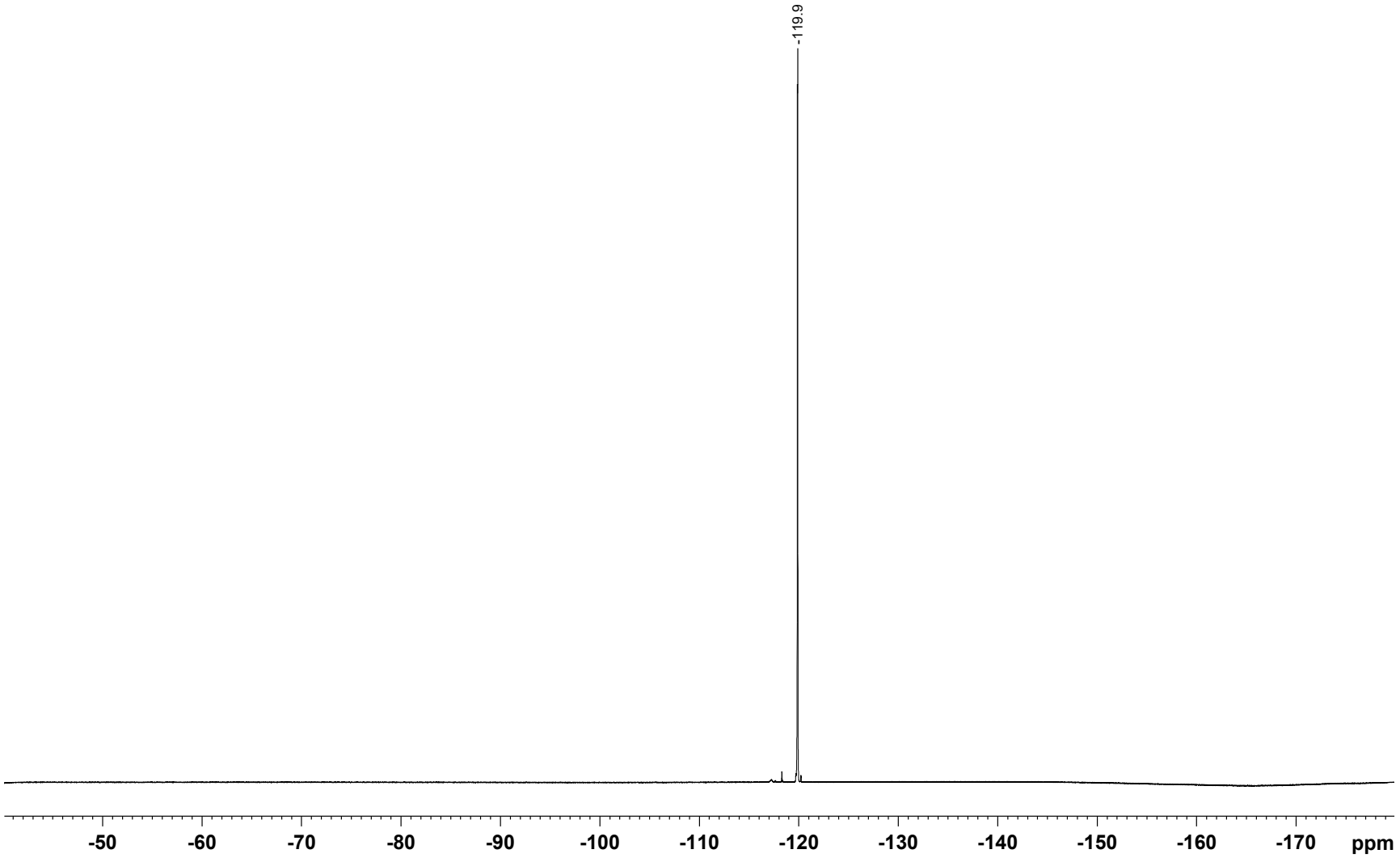


Figure S67. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **4n** from the catalytic 1,2-disilylation of 1-fluoro-4-vinylbenzene (**1n**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

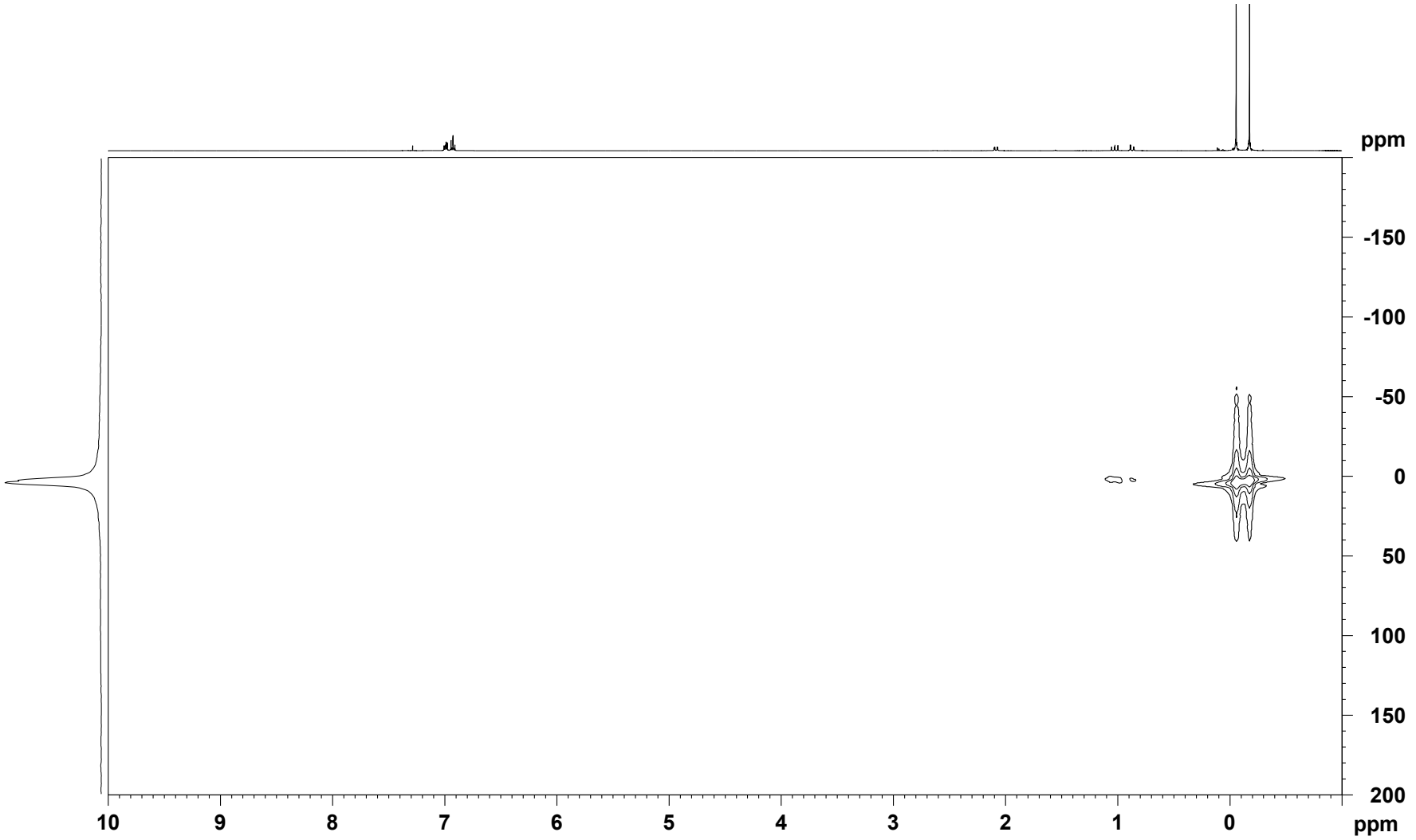


Figure S68. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4o** from the catalytic 1,2-disilylation of but-3-en-1-ylbenzene (**1o**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

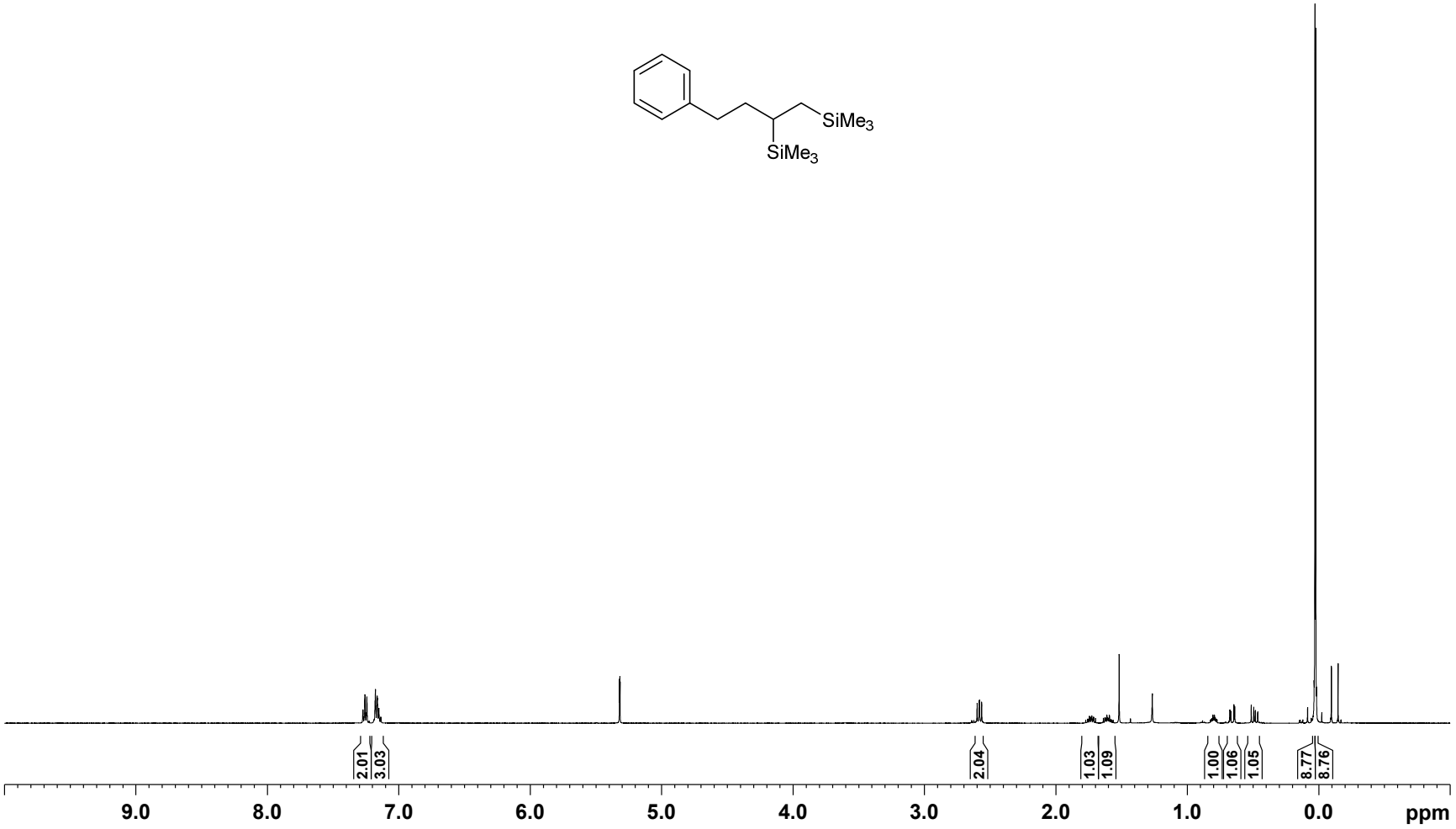


Figure S69. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298 K) of **4o** from the catalytic 1,2-disilylation of but-3-en-1-ylbenzene (**1o**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

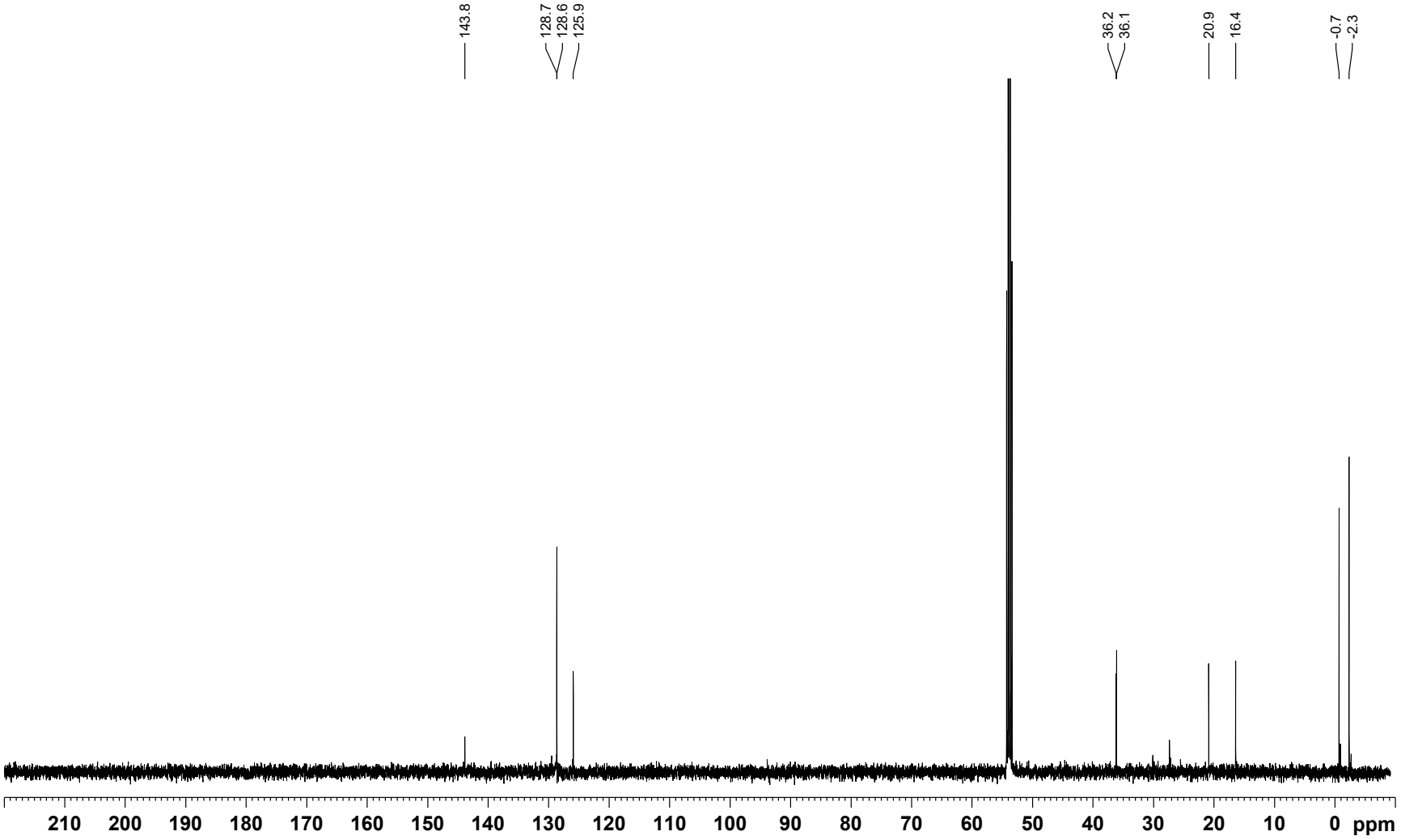


Figure S70. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **4o** from the catalytic 1,2-disilylation of but-3-en-1-ylbenzene (**1o**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

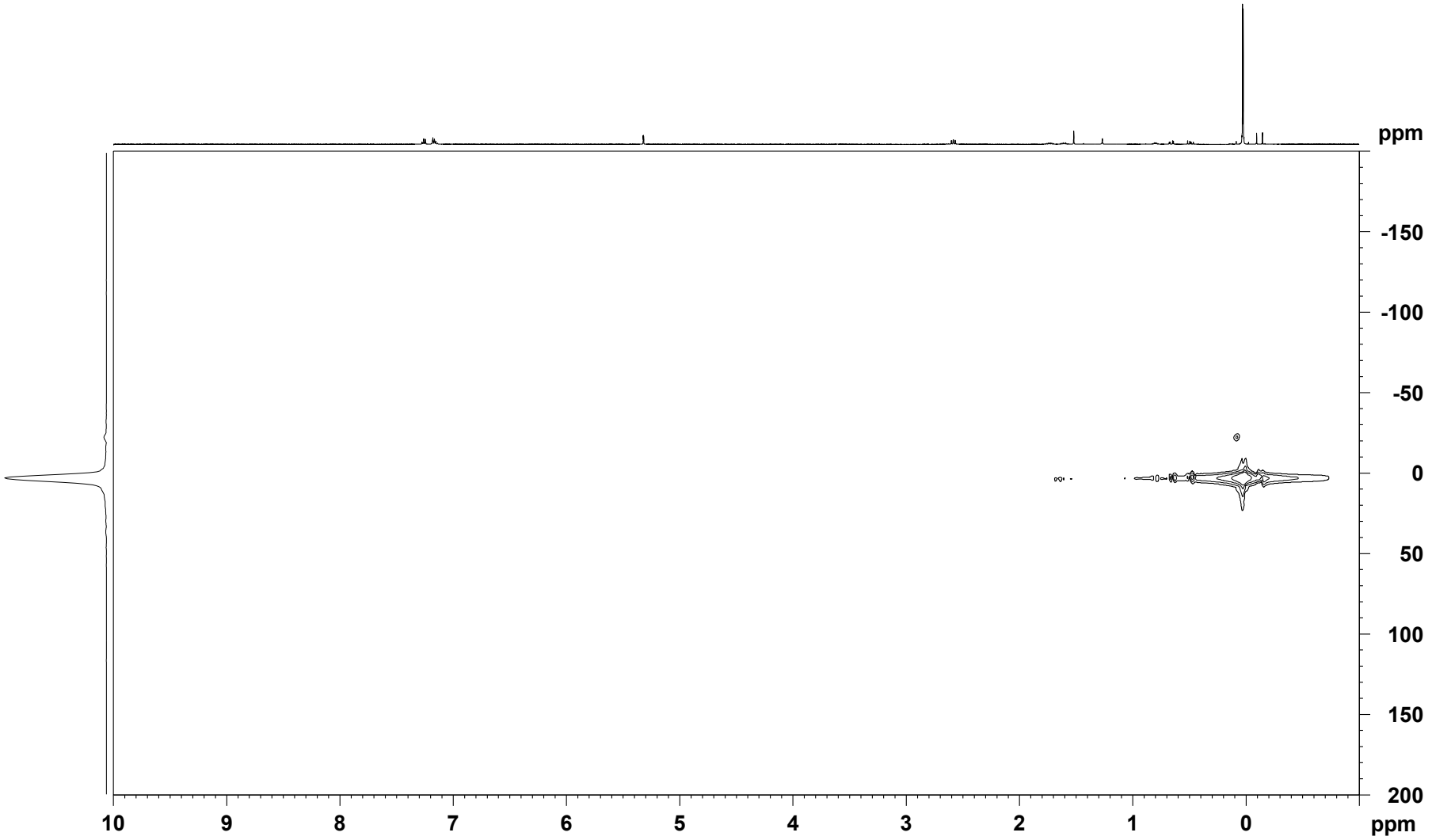


Figure S71. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4p** from the catalytic 1,2-disilylation of oct-1-ene (**1p**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

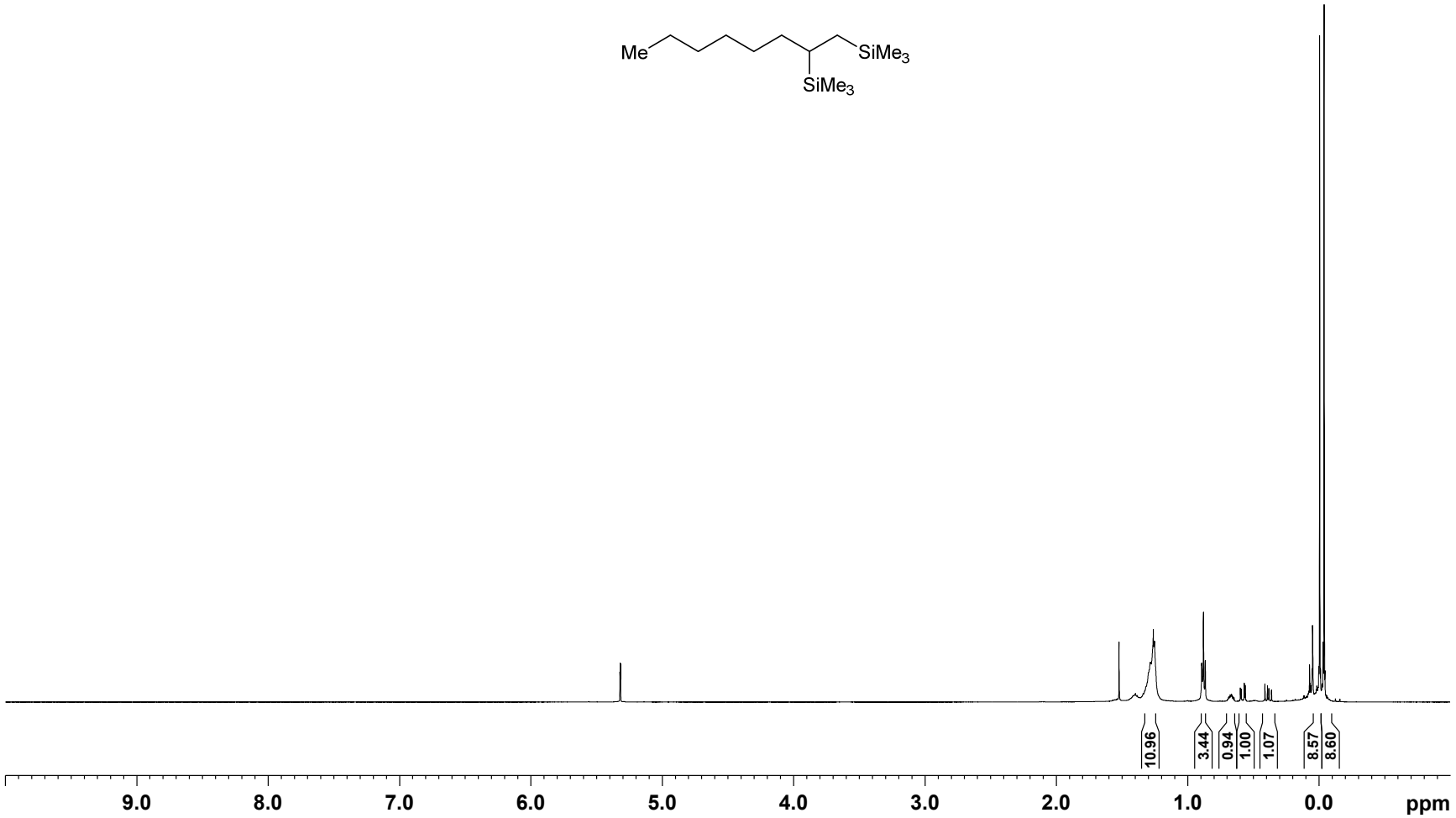


Figure S72. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298 K) of **4p** from the catalytic 1,2-disilylation of oct-1-ene (**1p**) with $Me_3SiSiMe_3$ using $Me_3Si^+[CHB_{11}H_5Br_6]^-$ as initiator.

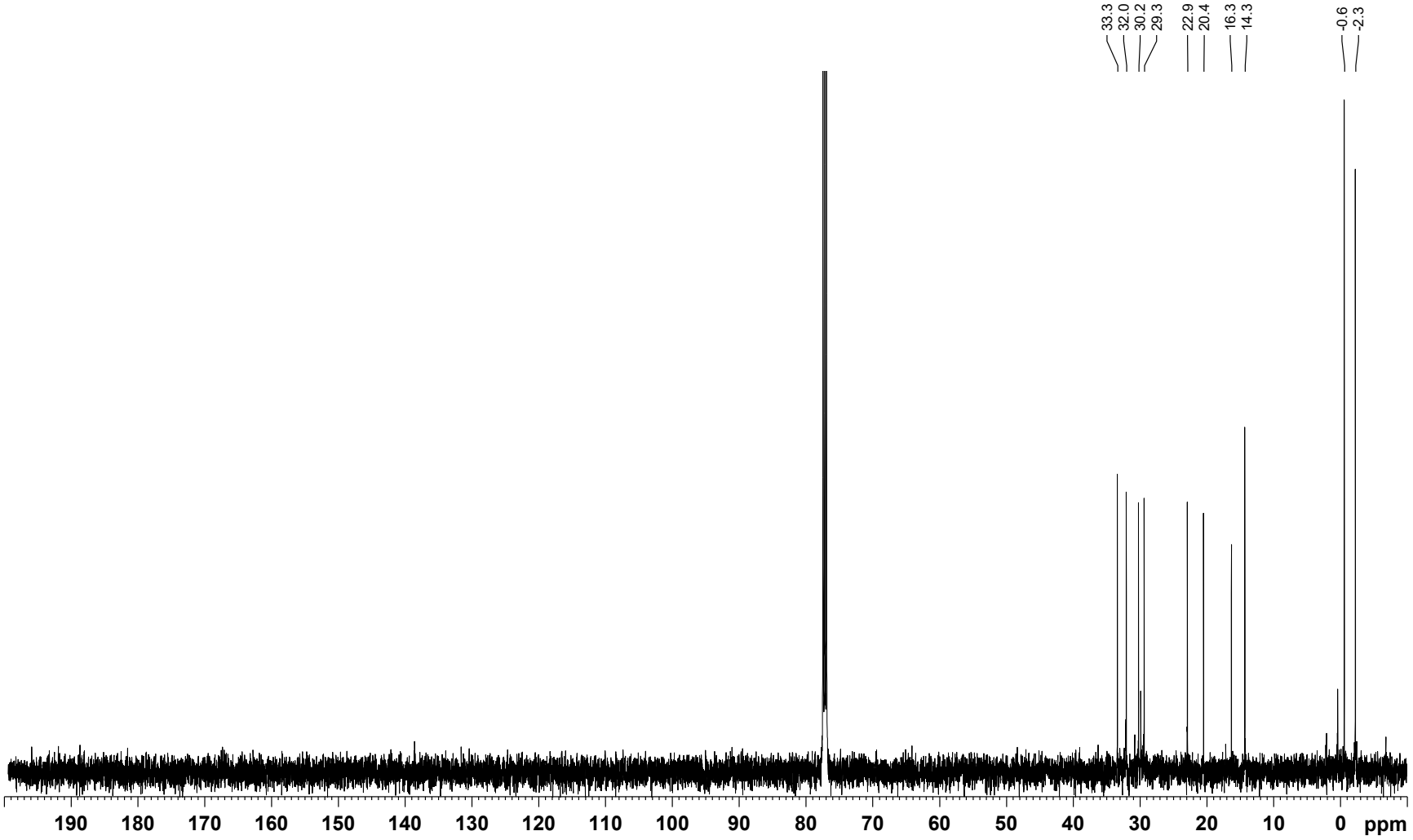


Figure S73. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **4p** from the catalytic 1,2-disilylation of oct-1-ene (**1p**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

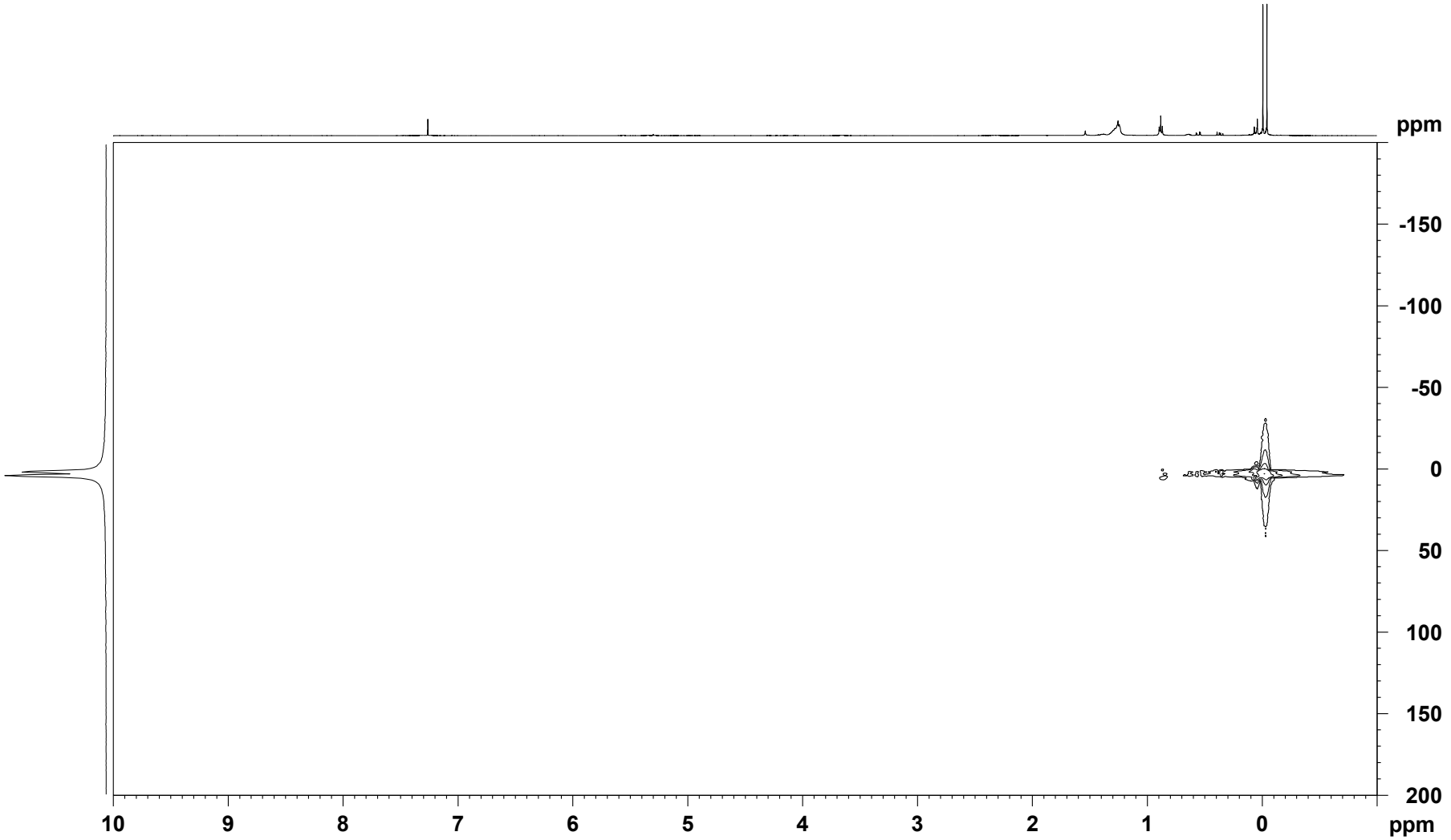


Figure S74. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4q** from the catalytic 1,2-disilylation of 3,3-dimethylbut-1-ene (**1q**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

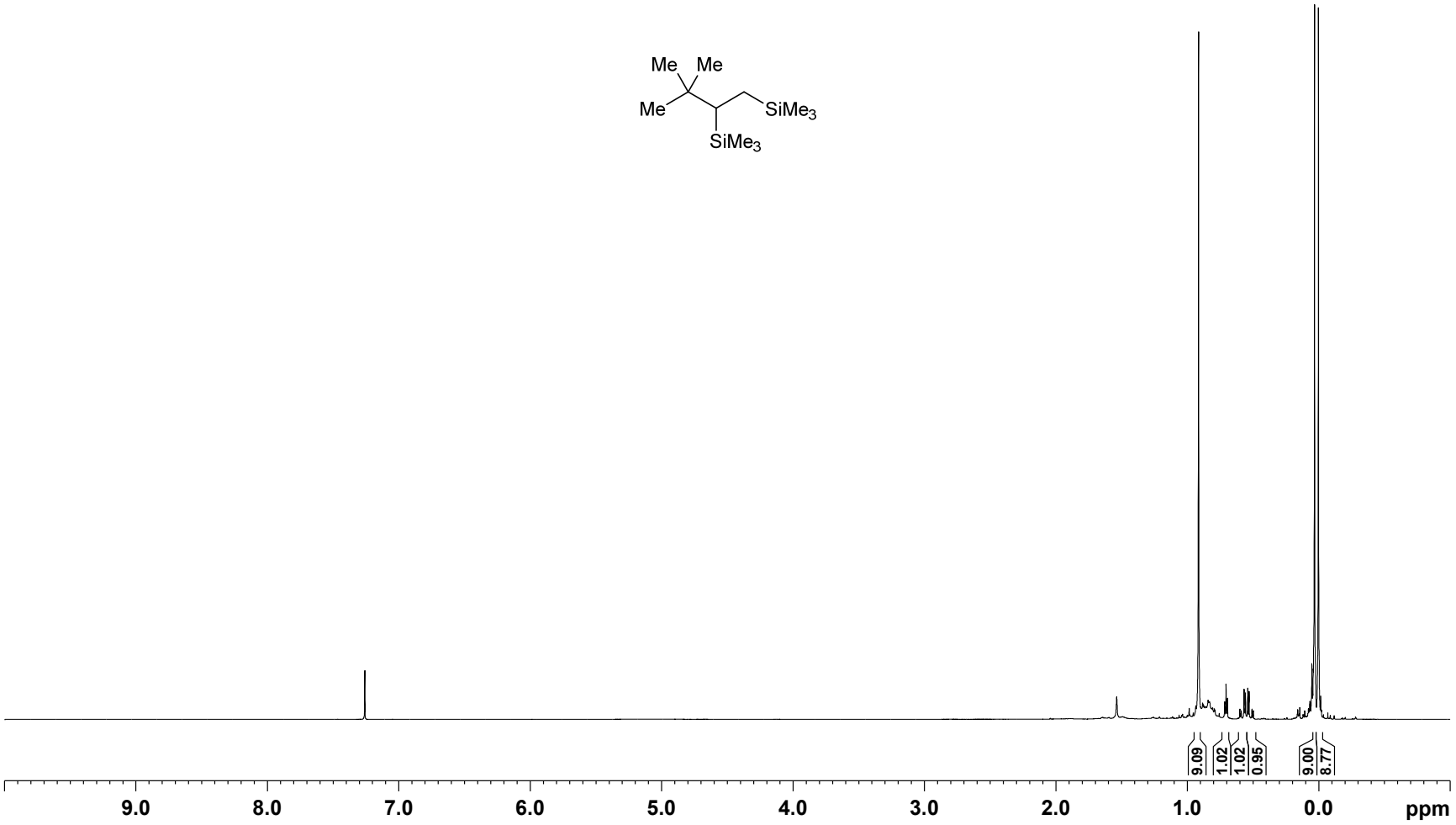


Figure S75. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298 K) of **4q** from the catalytic 1,2-disilylation of 3,3-dimethylbut-1-ene (**1q**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

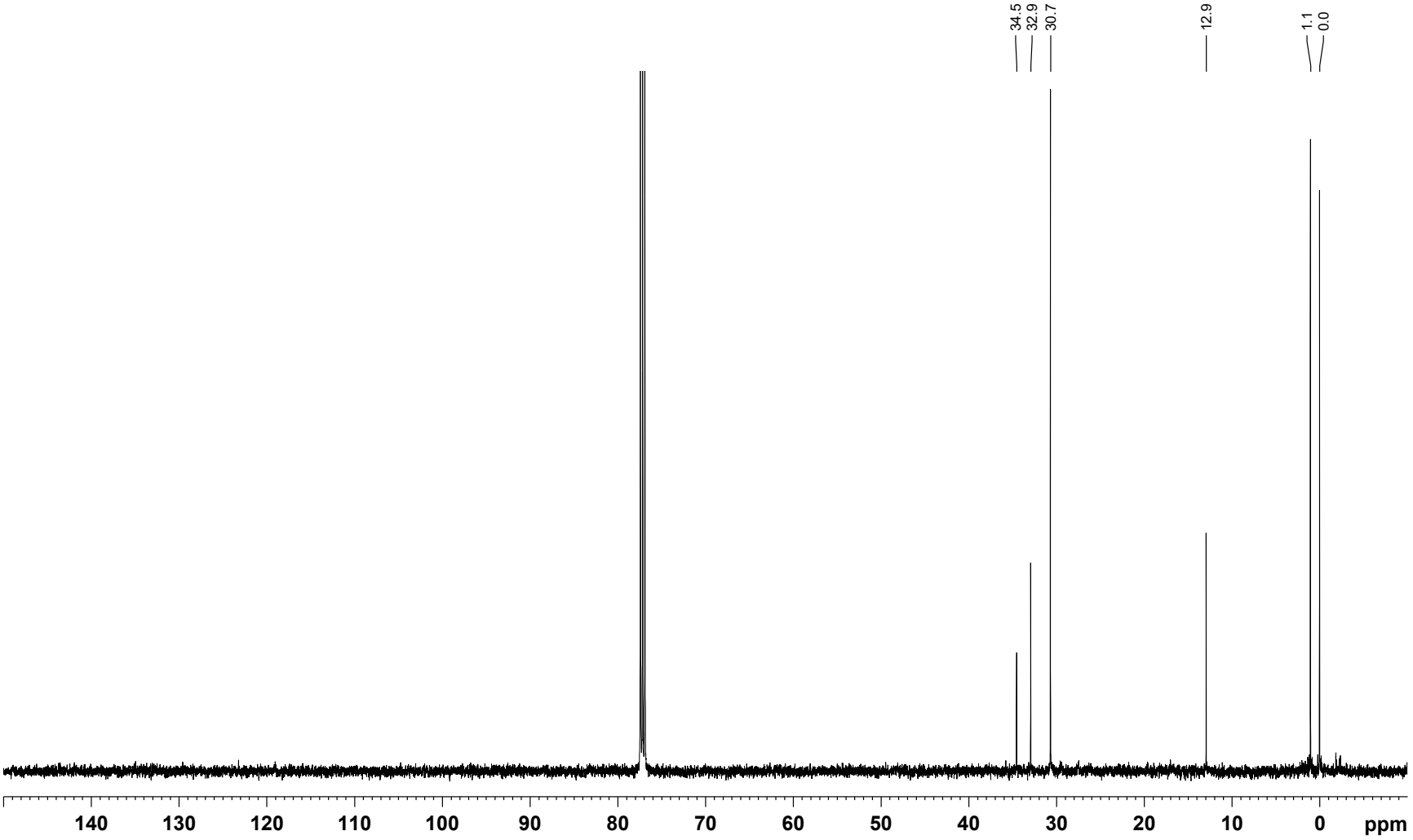


Figure S76. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **4q** from the catalytic 1,2-disilylation of 3,3-dimethylbut-1-ene (**1q**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

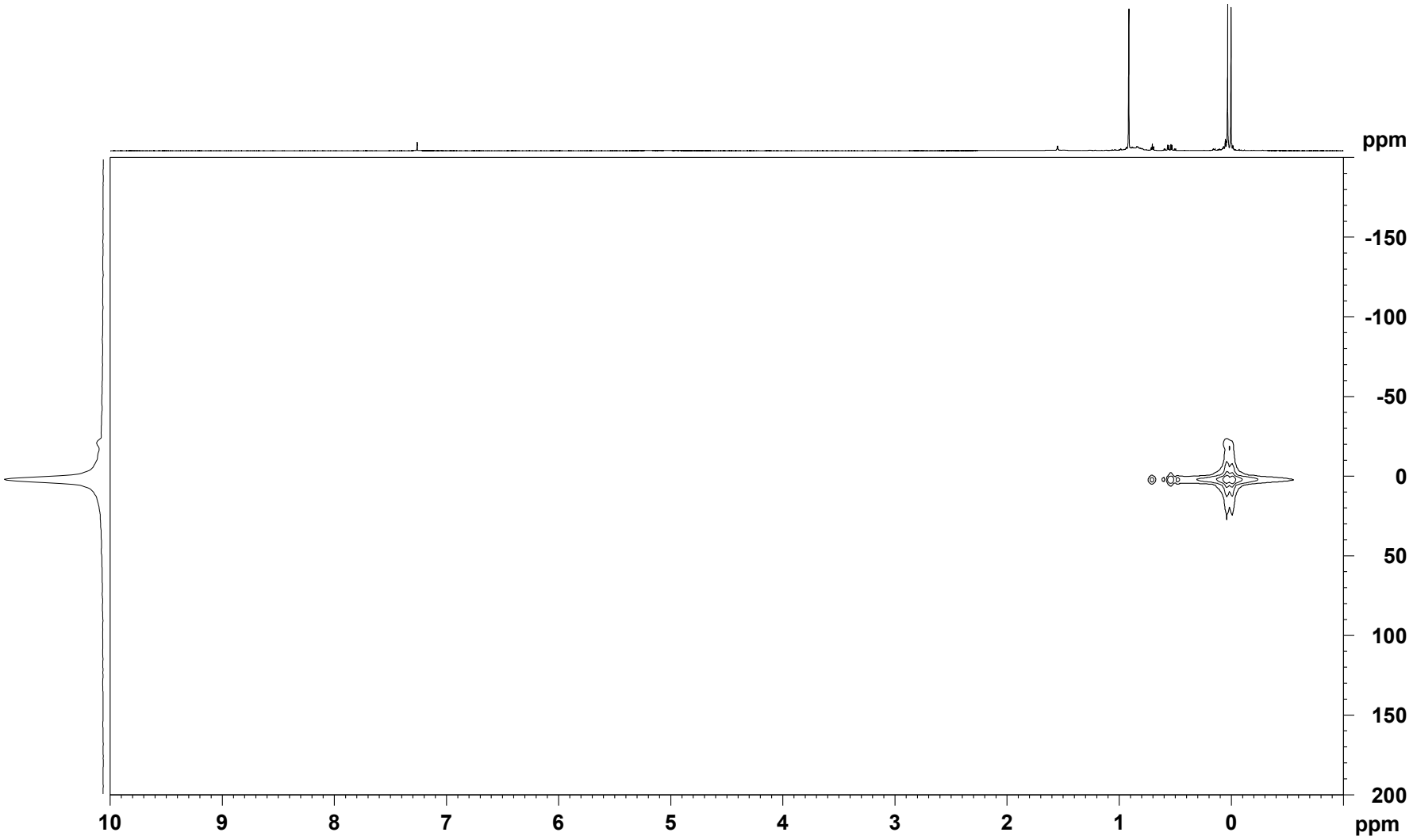


Figure S77. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of *cis*-**6a** from the catalytic 1,2-disilylation of 1,2-dihydronaphthalene (**5a**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

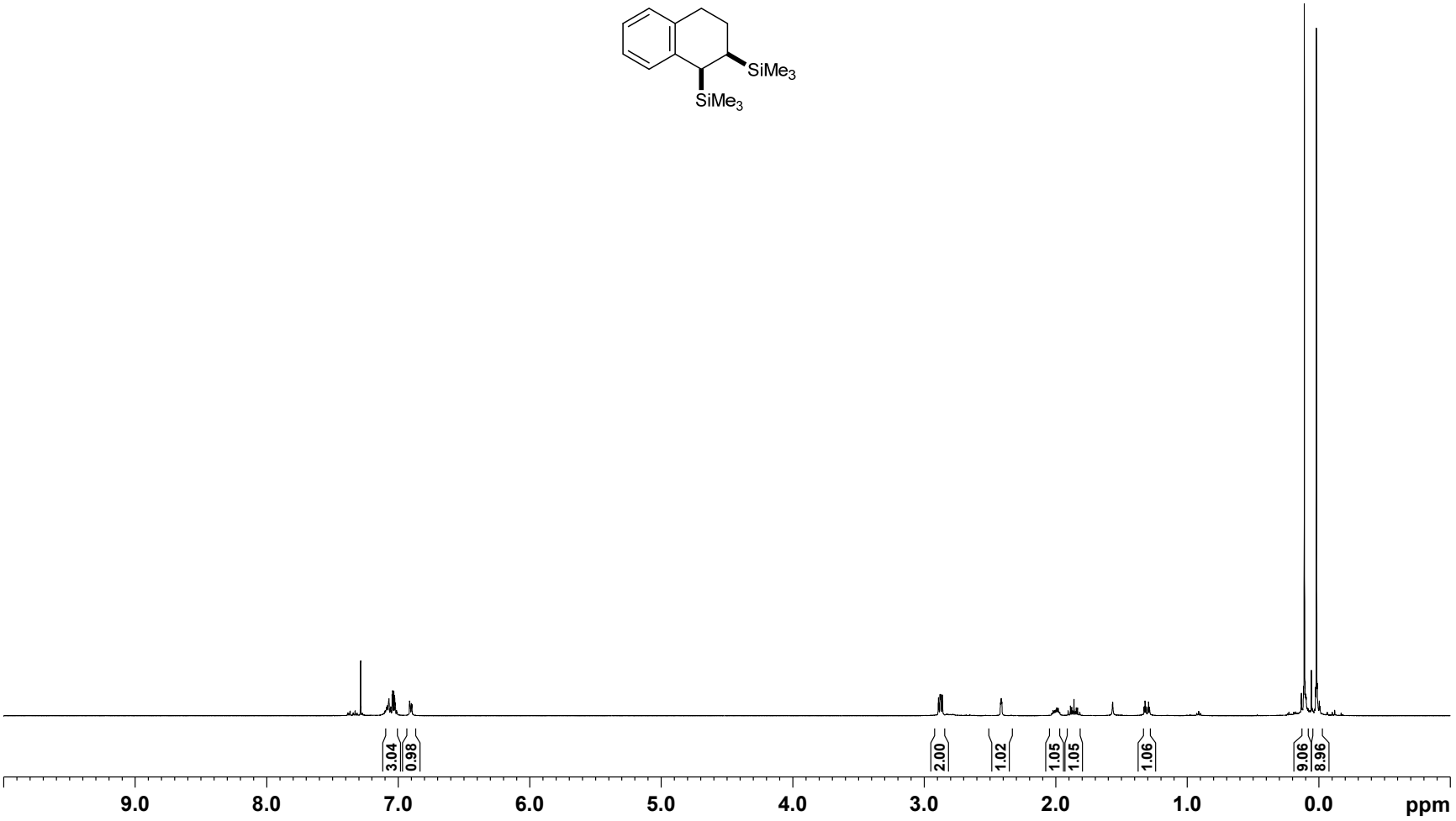


Figure S78. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298 K) of *cis*-**6a** from the catalytic 1,2-disilylation of 1,2-dihydronaphthalene (**5a**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

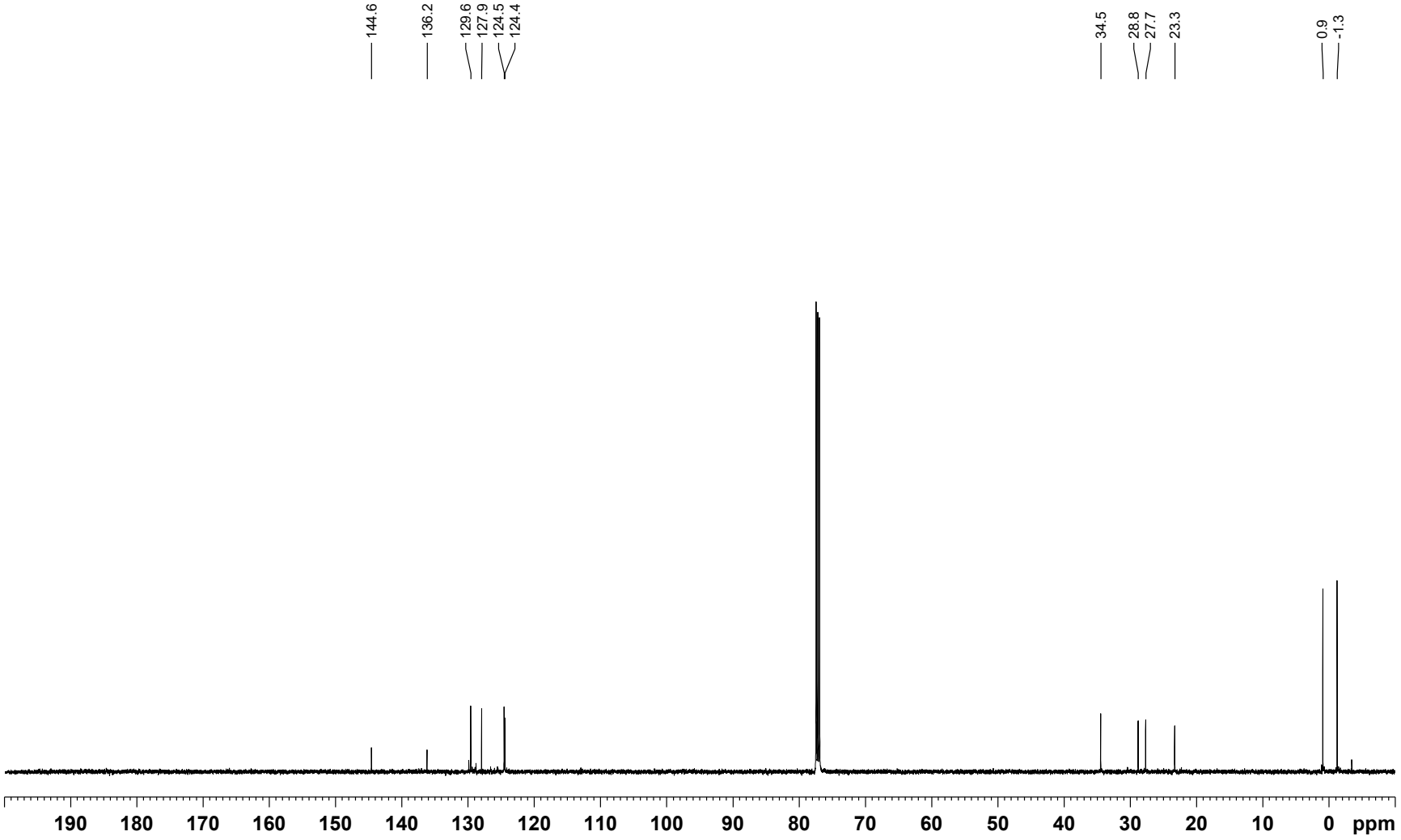


Figure S79. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of *cis*-**6a** from the catalytic 1,2-disilylation of 1,2-dihydronaphthalene (**5a**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

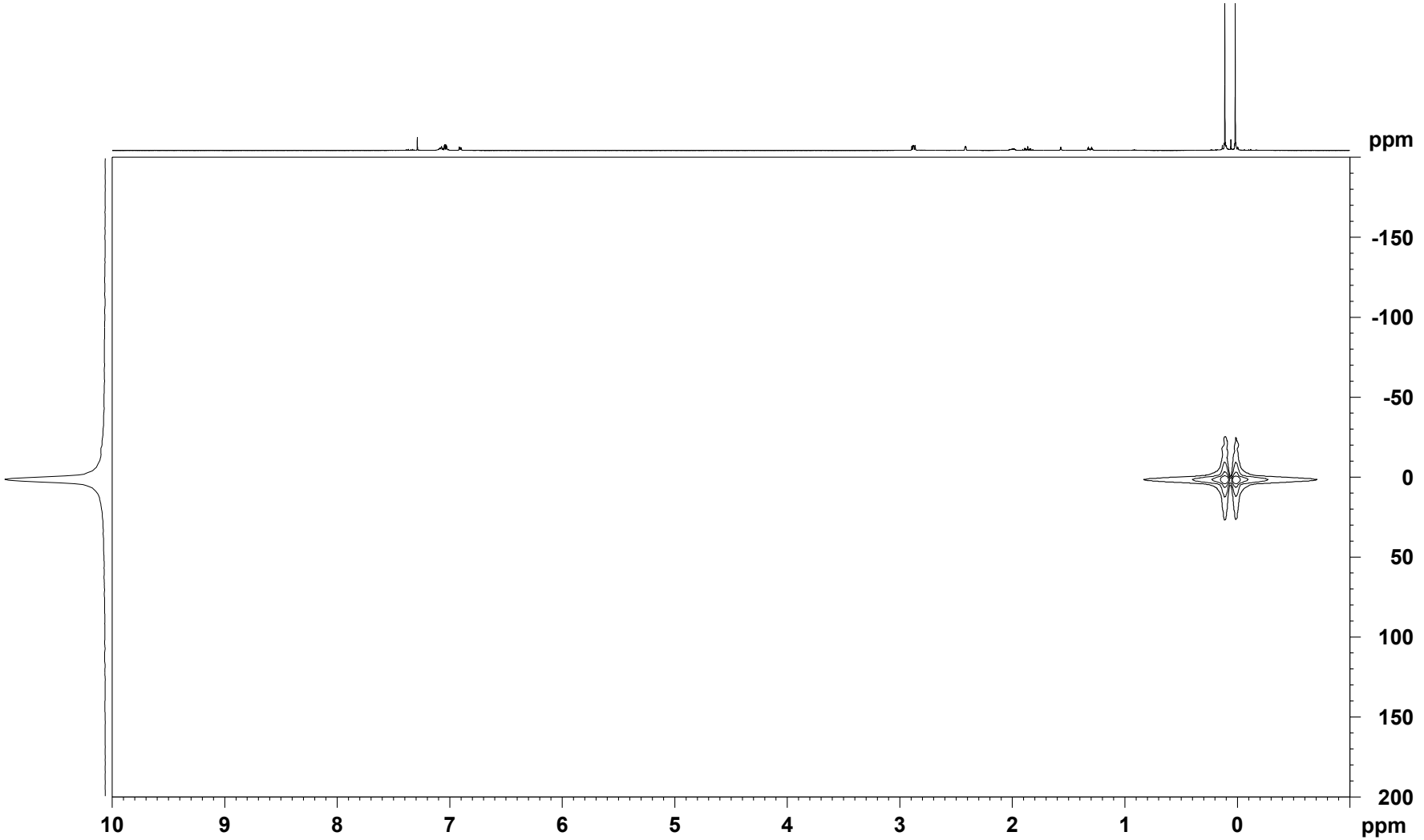


Figure S80. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of *cis*-**6b** from the catalytic 1,2-disilylation of cycloheptene (**5b**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

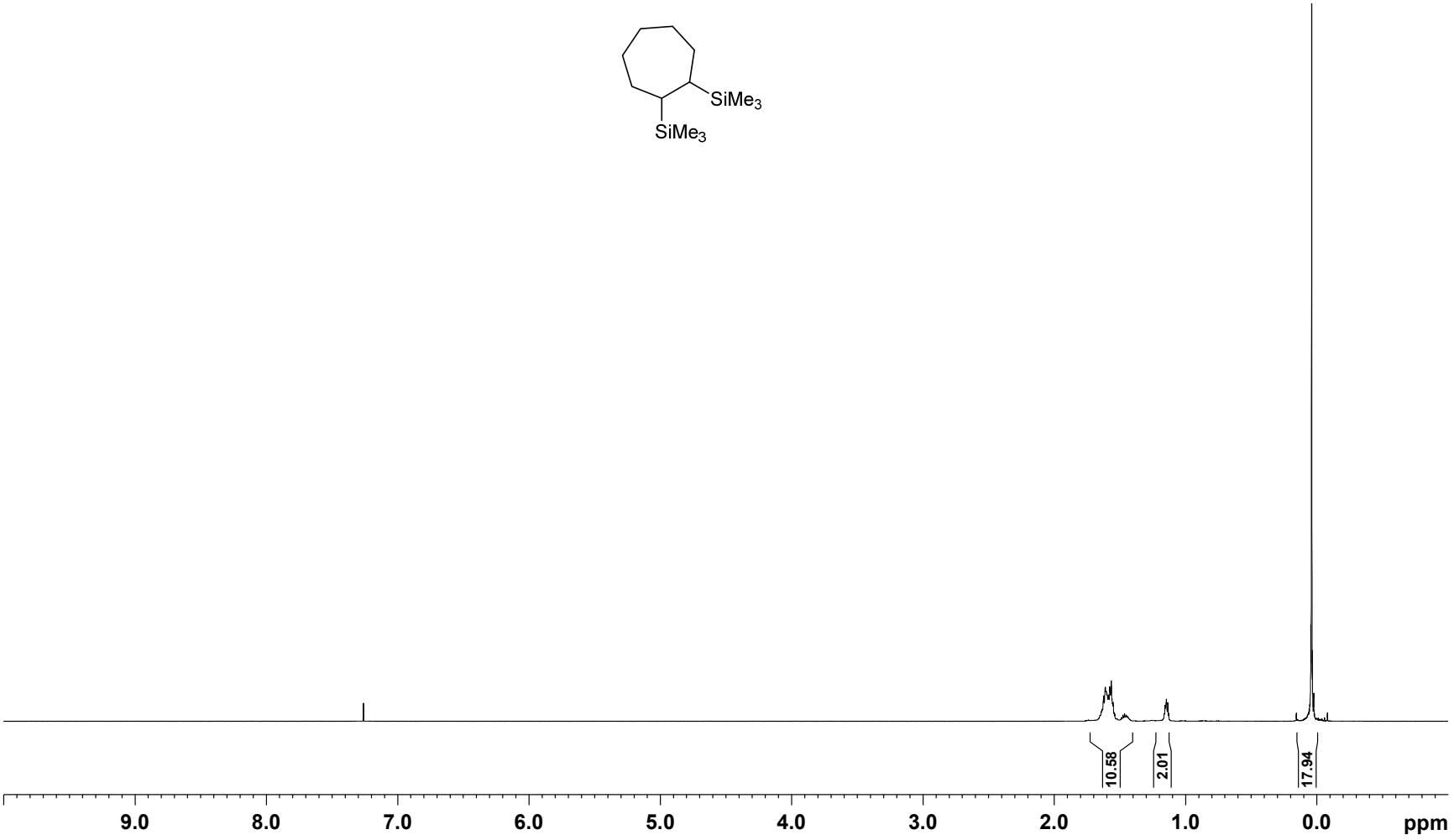


Figure S81. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 298 K) of *cis*-**6b** from the catalytic 1,2-disilylation of cycloheptene (**5b**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

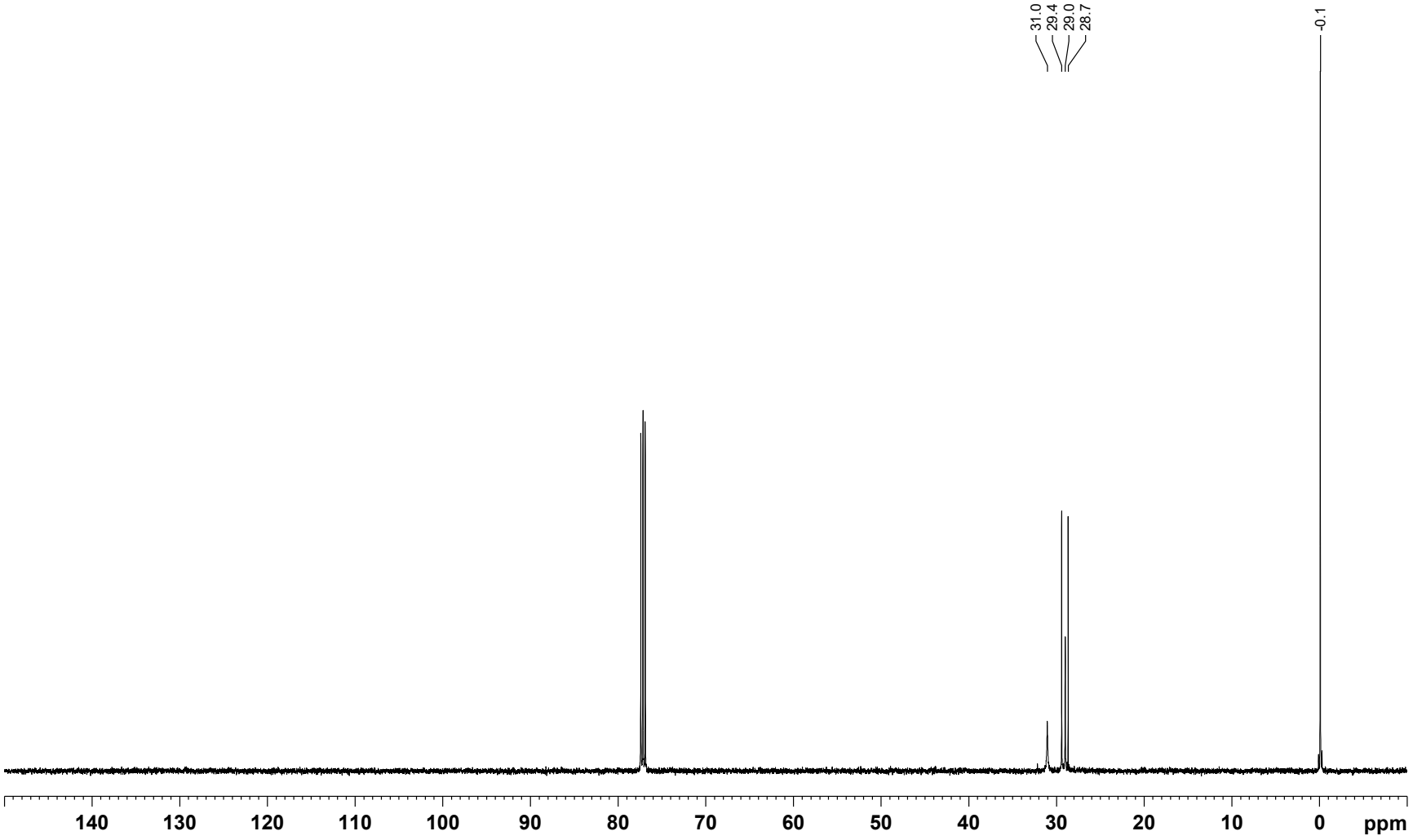


Figure S82. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of *cis*-**6b** from the catalytic 1,2-disilylation of cycloheptene (**5b**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

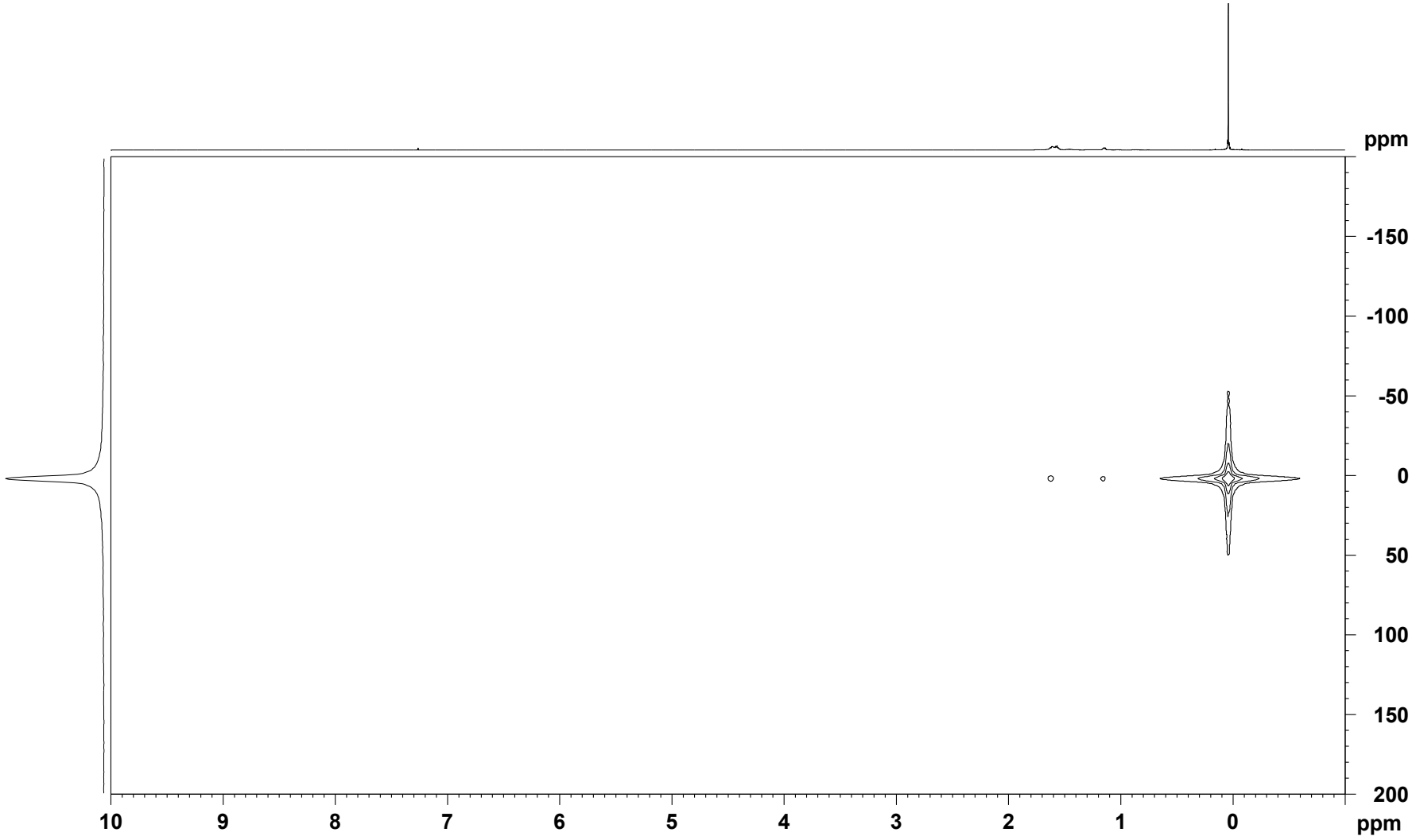


Figure S83. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of *cis*-**6c** from the catalytic 1,2-disilylation of *cis*-cyclooctene (*cis*-**5c**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

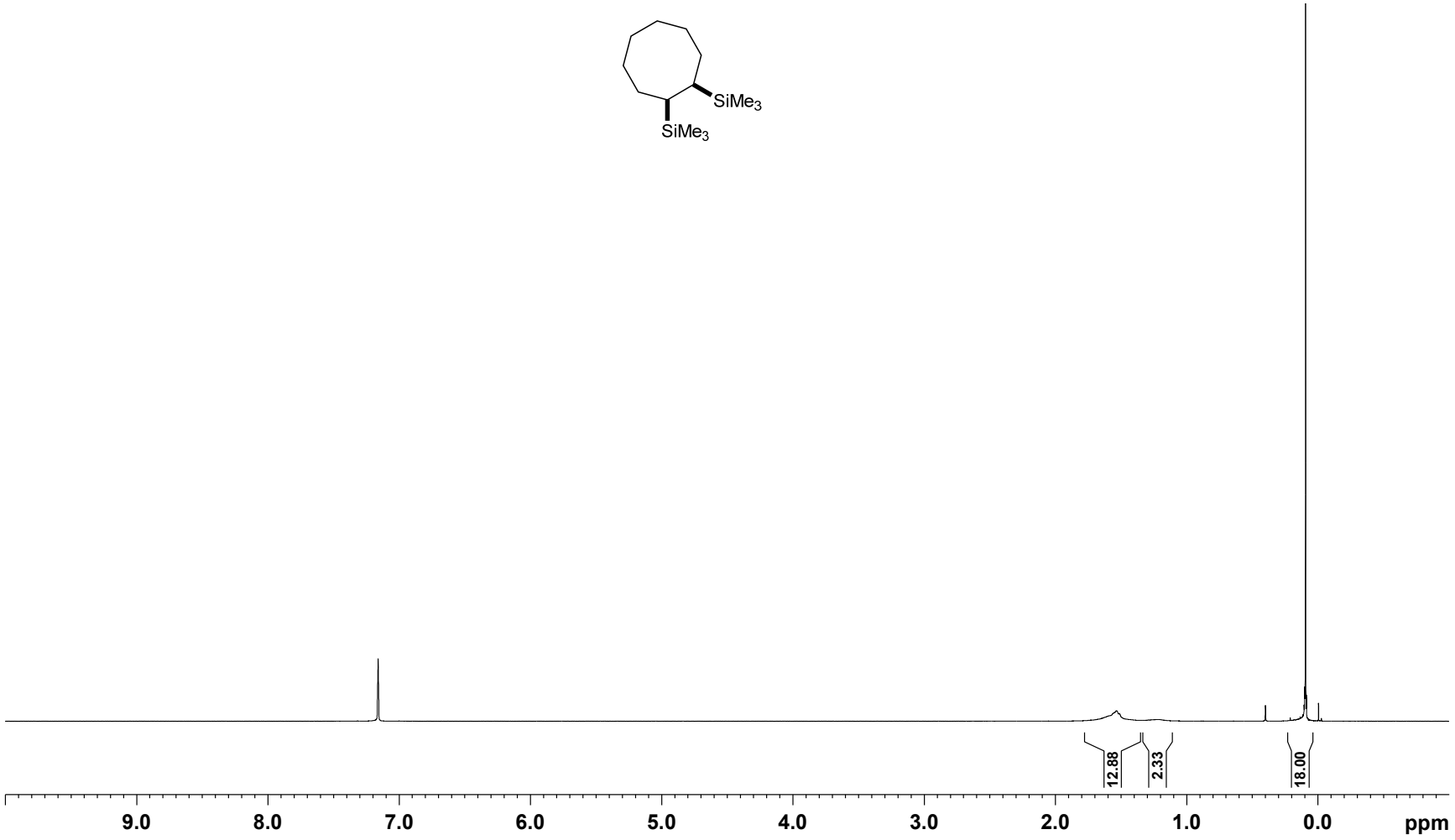


Figure S84. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 338 K) of *cis*-**6c** from the catalytic 1,2-disilylation of *cis*-cyclooctene (*cis*-**5c**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

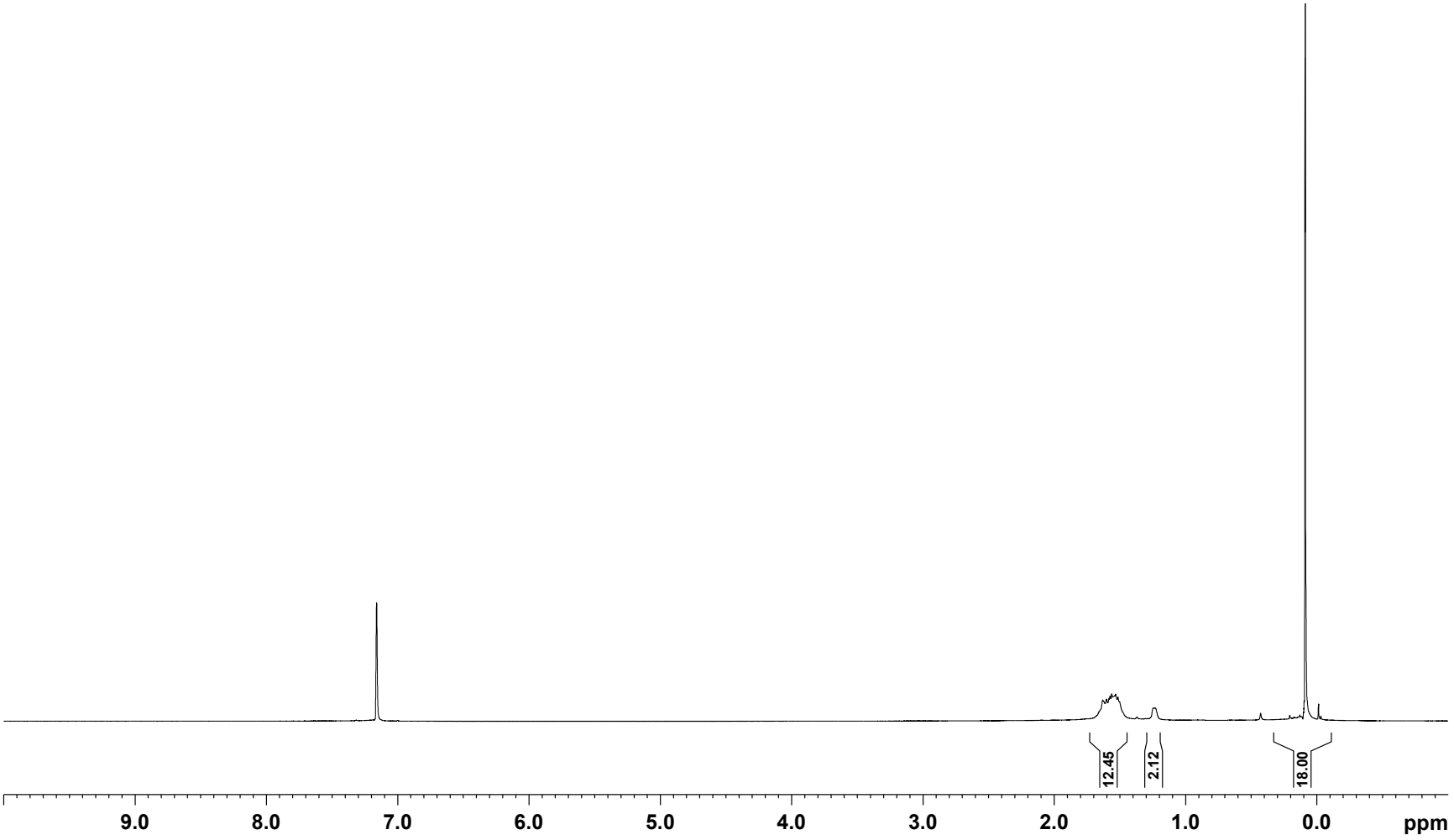


Figure S85. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$, 338 K) of *cis*-**6c** from the catalytic 1,2-disilylation of *cis*-cyclooctene (*cis*-**5c**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

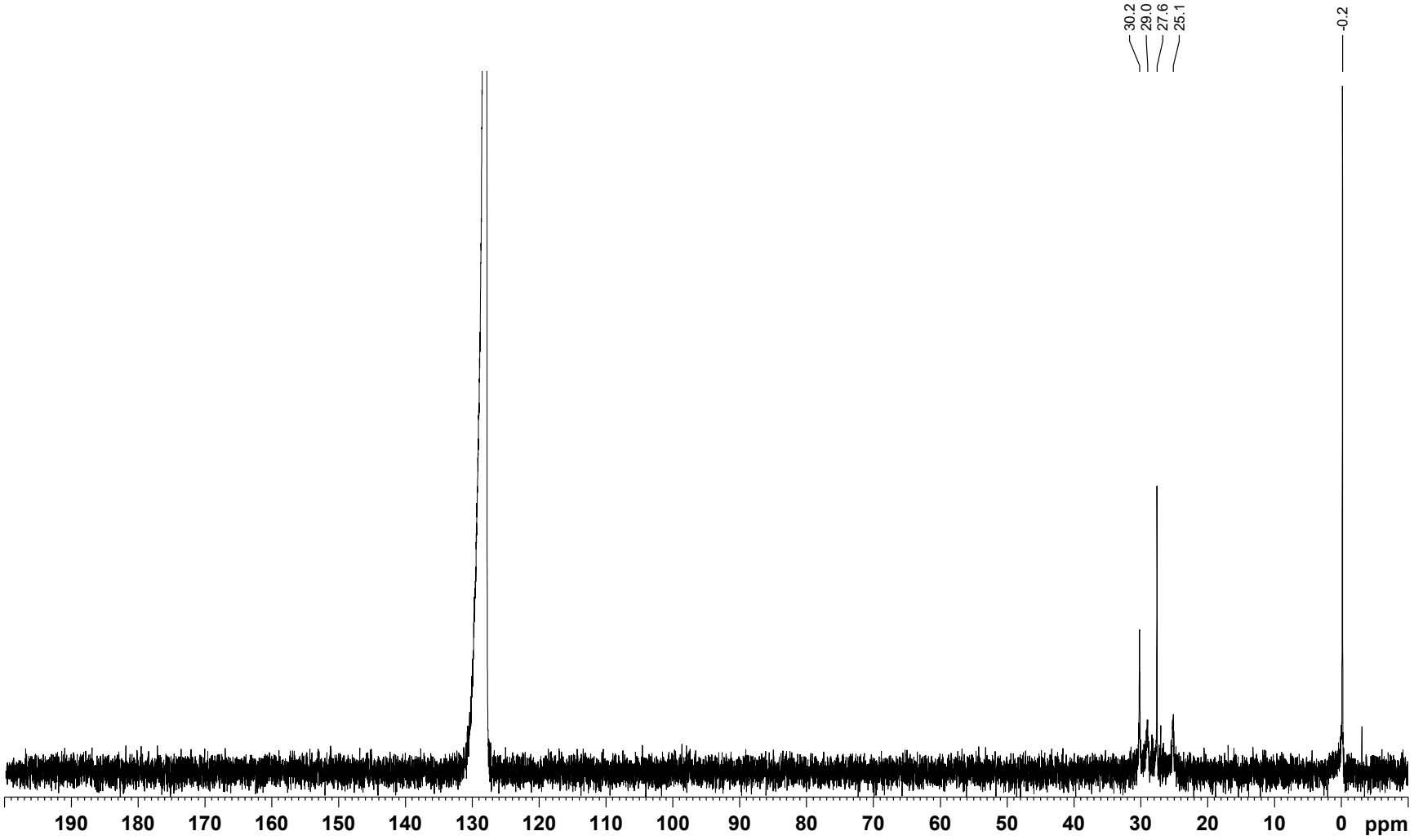


Figure S86. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, $CDCl_3$, 338 K, optimized for J = 7 Hz) of *cis*-**6c** from the catalytic 1,2-disilylation of *cis*-cyclooctene (*cis*-**5c**) with $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

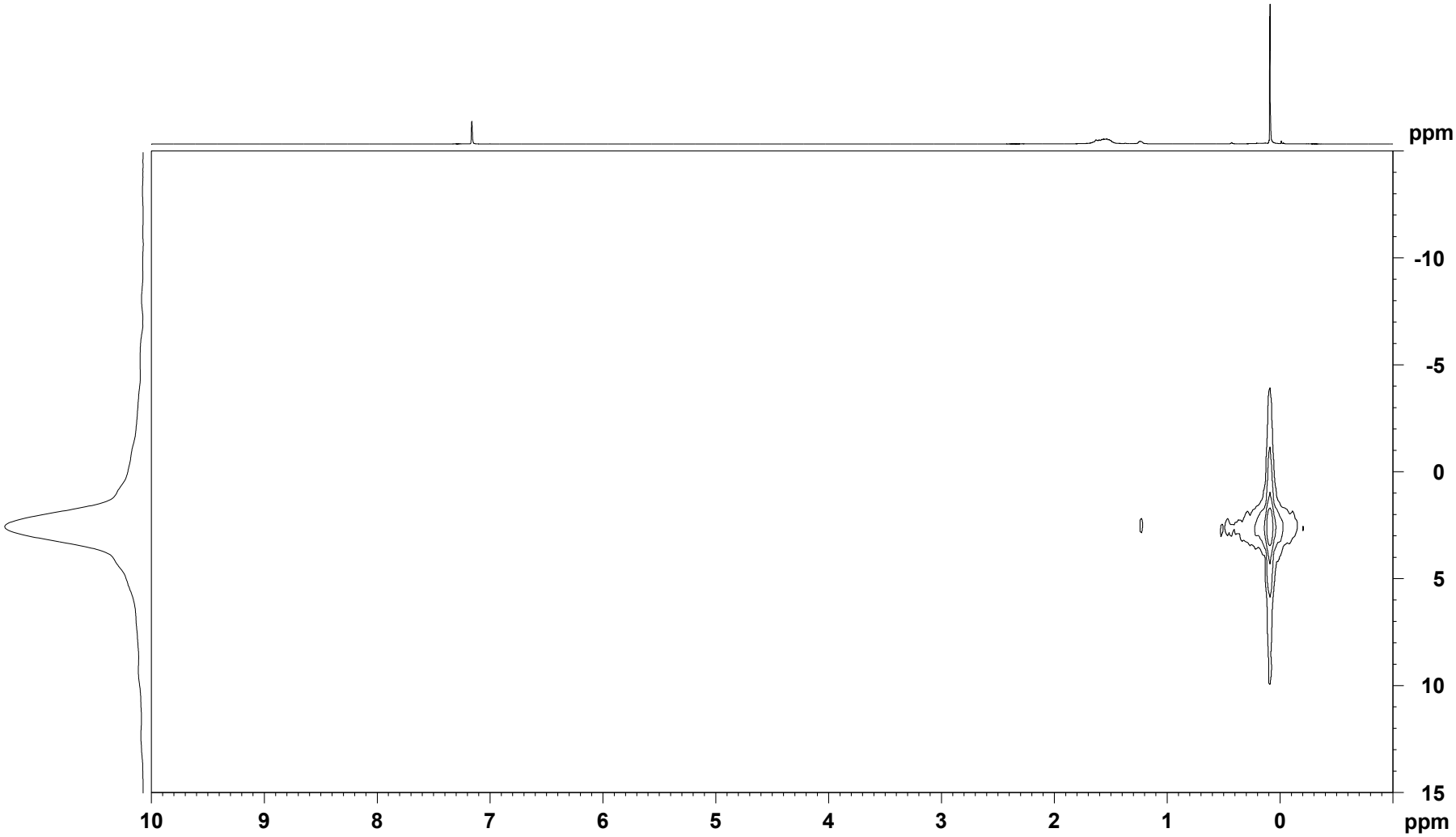


Figure S87. ^{1}H NMR spectrum (500 MHz, C_6D_5Cl, 338 K) for the dealkyative silylation of unsymmetrically substituted 1-isopropyl-1,1,2,2,2-pentamethyldisilane with $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$.

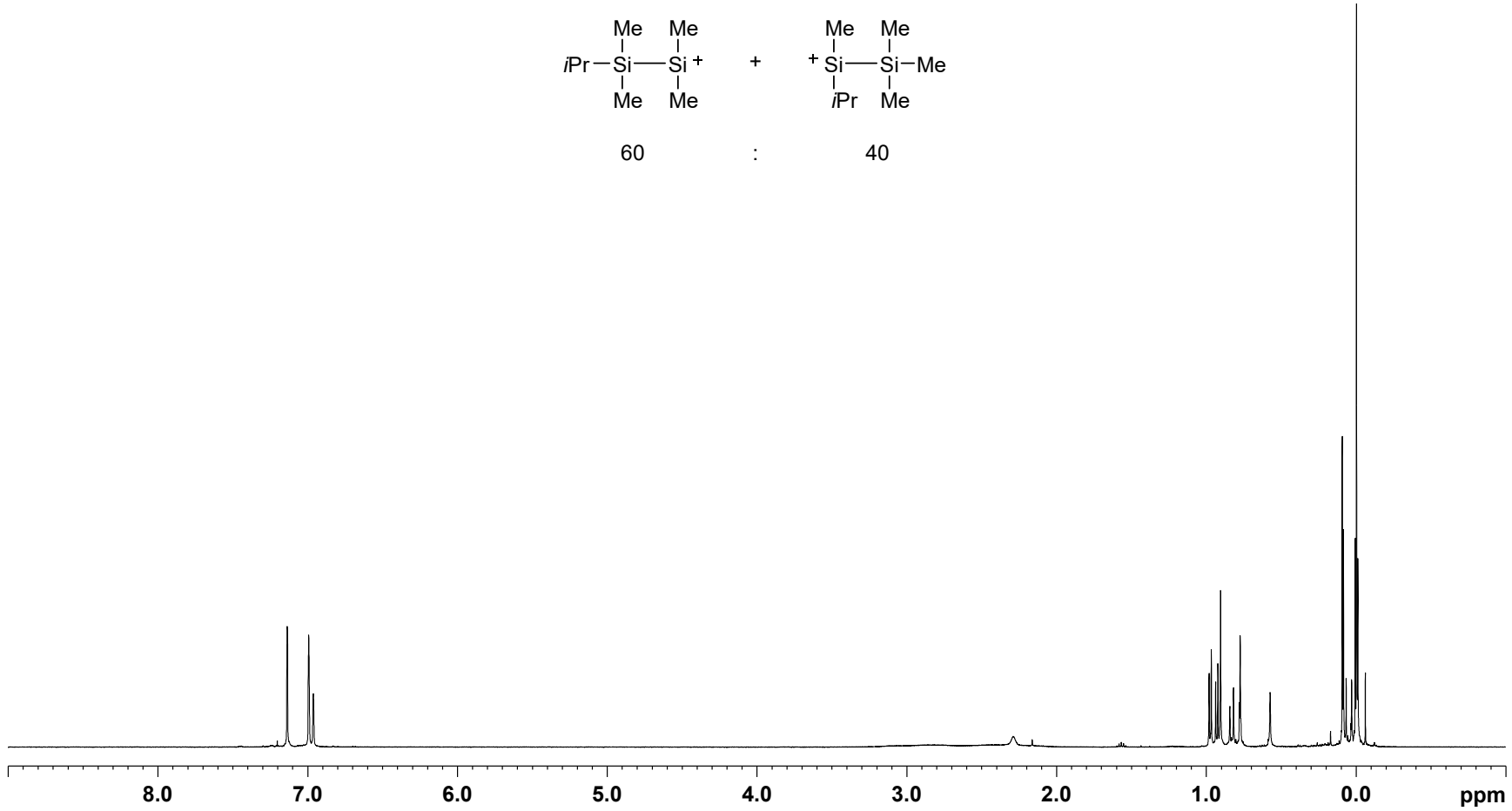


Figure S88. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, C_6D_5Cl, 338 K, optimized for J = 7 Hz) for the dealkyative silylation of unsymmetrically substituted 1-isopropyl-1,1,2,2,2-pentamethyldisilane with $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$.

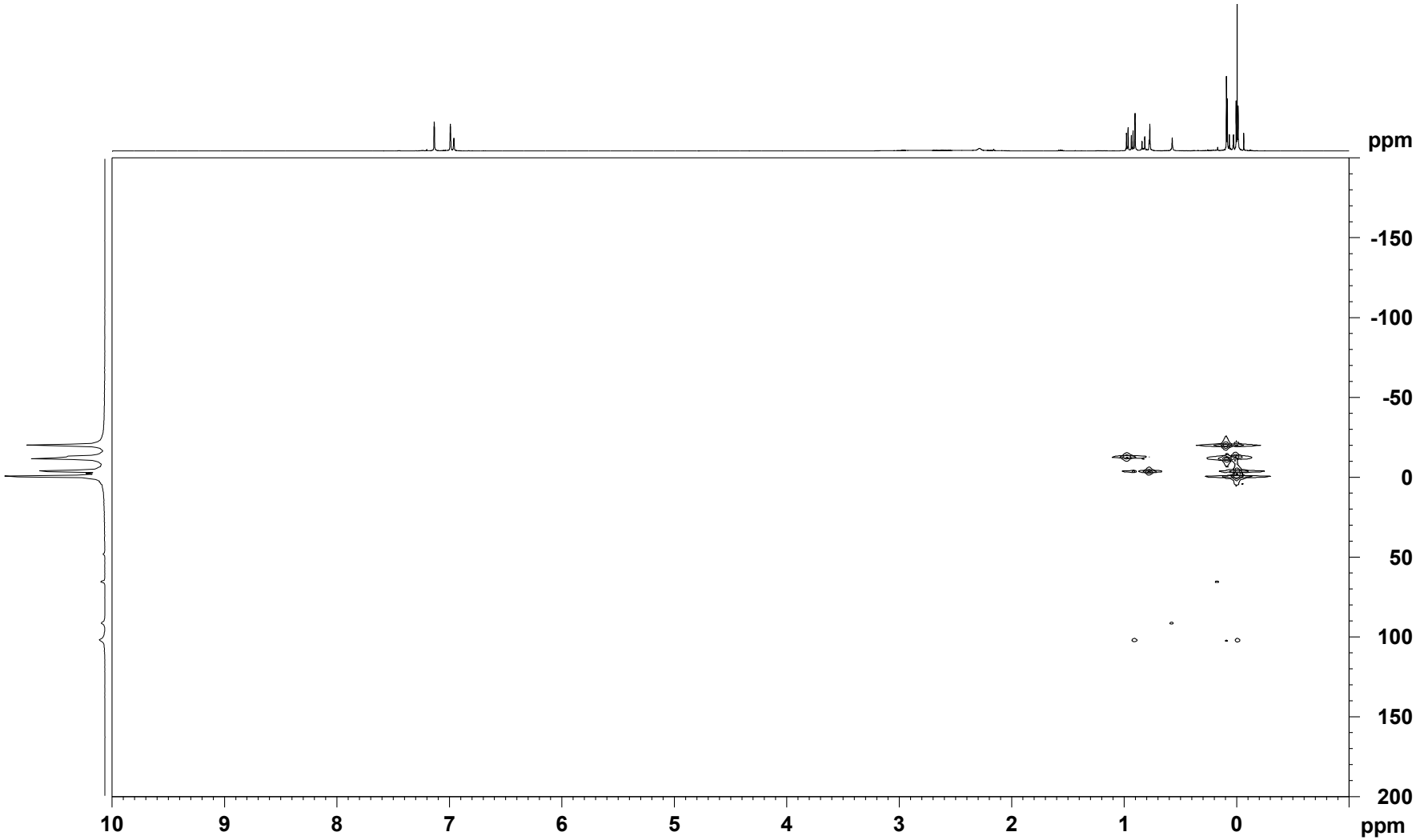


Figure S89. ^{1}H NMR spectrum (500 MHz, C_6D_6, 338 K) of the catalytic 1,2-disilylation of allylbenzene (**1a**) with 1-isopropyl-1,1,2,2,2-pentamethyldisilane using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.

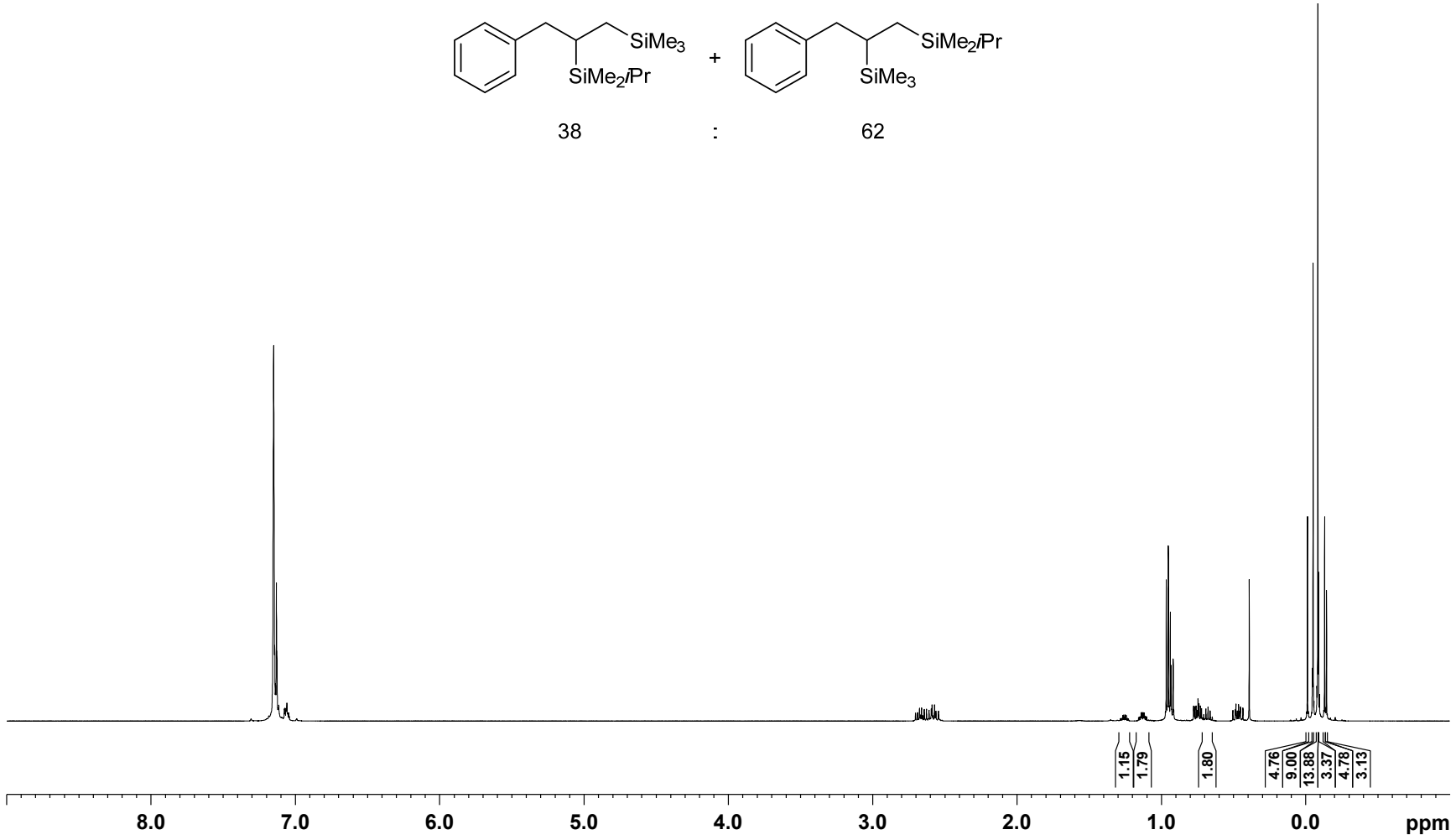


Figure S90. ^{13}C NMR spectrum (126 MHz, C_6D_6, 338 K) of the catalytic 1,2-disilylation of allylbenzene (**1a**) with 1-isopropyl-1,1,2,2,2-pentamethyldisilane using $Me_3Si^+[CHB_{11}H_5Br_6]^-$ as initiator.

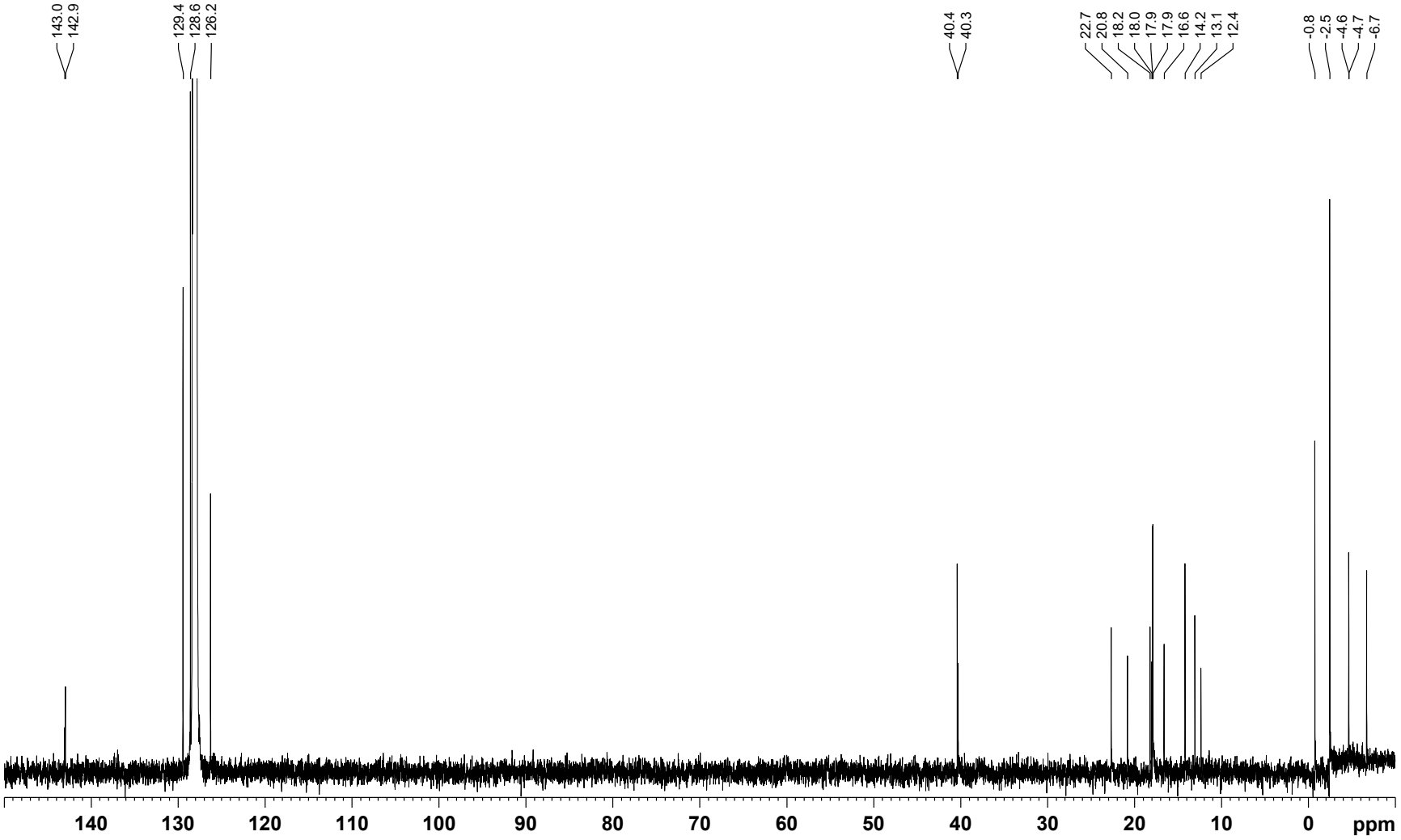
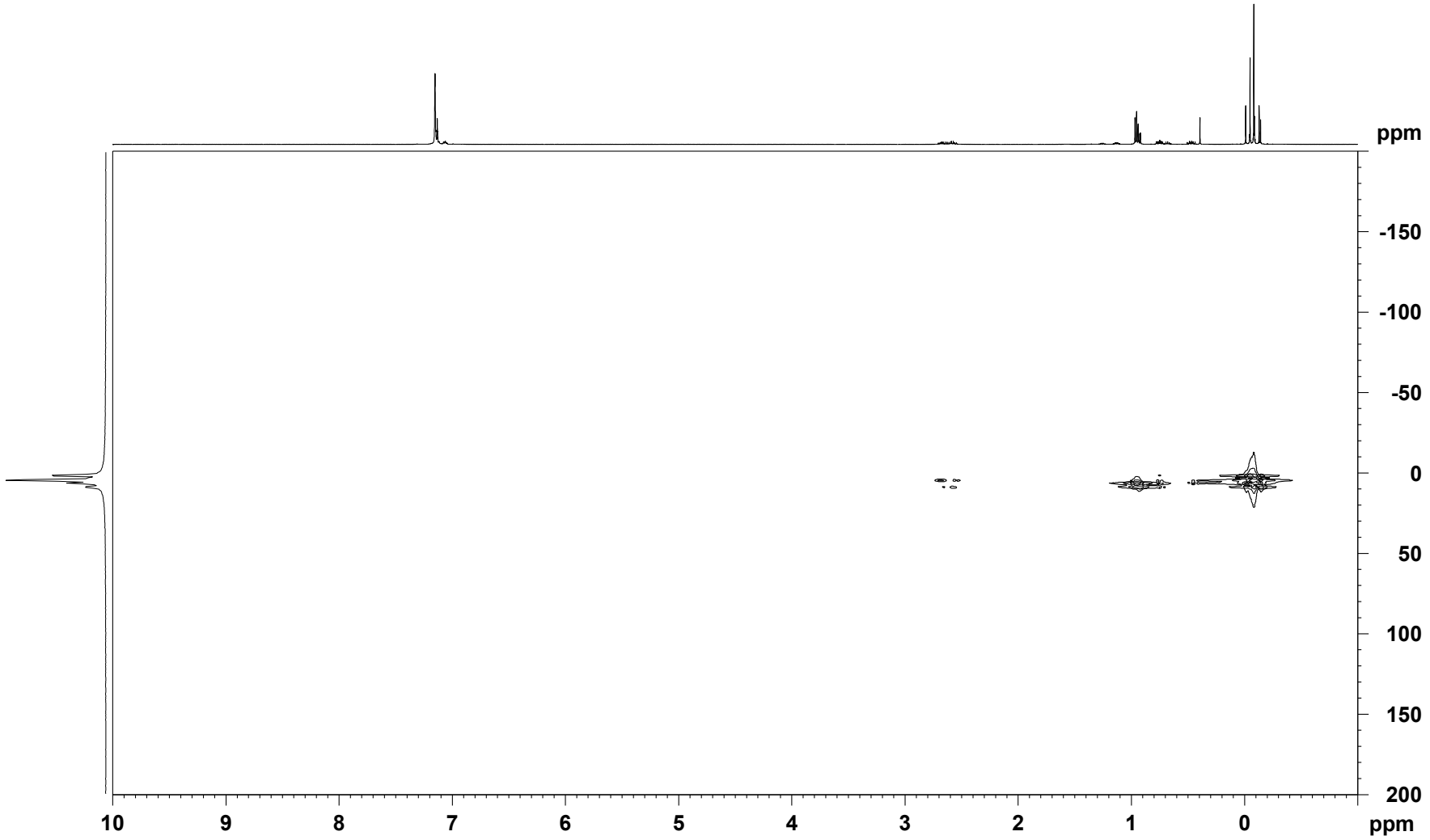


Figure S91. $^{1}H/^{29}Si$ HMQC NMR spectrum (500/99 MHz, C_6D_6, 338 K, optimized for J = 7 Hz) of the catalytic 1,2-disilylation of allylbenzene (**1a**) with 1-isopropyl-1,1,2,2,2-pentamethyldisilane using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$ as initiator.



11 Crystallographic Data

Data for the single-crystal structure determination were collected with an *Agilent* SuperNova diffractometer equipped with a CCD area Atlas detector and a mirror monochromator by utilizing Cu-K_α radiation (λ = 1.5418 Å). Software packages used: CrysAlis PRO for data collection, cell refinement, and data reduction,[S7] SHELXS-97 for structure solution,[S8] SHELXL-97 for structure refinement,[S9] and Mercury[S10] for graphics.

Molecular Structure of $3a^+[CHB_{11}H_5Br_6]^-$ (CCDC 1951131)

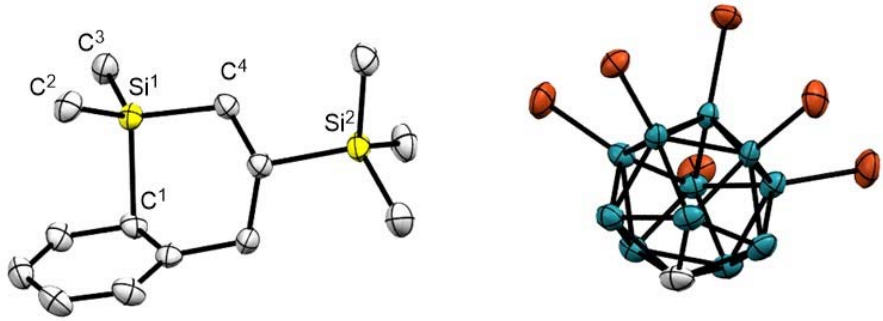


Figure S92. Molecular structure of **3a**$^+$[$CHB_{11}H_5Br_6$]$^-$ (thermal ellipsoids are shown at 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths [Å]: Si^1–C^1 2.106(5), Si^1–C^2 1.848(5), Si^1–C^3 1.845(5), Si^1–C^4 1.859(4). Selected bond angles [°]: C^2–Si^1–C^3 114.9(2), C^2–Si^1–C^4 115.0(2), C^3–Si^1–C^4 113.3(2), Si^1–C^1–C_{para} 106.5.

Empirical formula	C15 H31 B11 Br6 Si2	
Formula weight	865.95	
Temperature	150.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 20.30186(15) Å	α = 90°
	b = 25.92719(16) Å	β = 109.7901(8)°
	c = 25.38493(19) Å	γ = 90°
Volume	12572.70(15) Å^3	
Z	16	
Density (calculated)	1.830 Mg/m^3	
Absorption coefficient	9.998 mm^{-1}	
F(000)	6624	
Crystal size	0.22 × 0.10 × 0.04 mm^3	
Theta range for data collection	2.52 to 67.50°	
Index ranges	–17<=h<=24, –31<=k<=31, –30<=l<=29	
Reflections collected	85674	
Independent reflections	22667 [R(int) = 0.0396]	
Completeness to theta = 67.50°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6788 and 0.2129	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	22667 / 0 / 1318	
Goodness-of-fit on F^2	1.012	
Final R indices [I>2sigma(I)]	R1 = 0.0392, wR2 = 0.0947	
R indices (all data)	R1 = 0.0493, wR2 = 0.1021	
Largest diff. peak and hole	2.311 and –1.482 e.Å^3	

12 Computational Data

The quantum chemical DFT calculations have been performed with the TURBOMOLE 7.3 suite of programs[S11] The structures are fully optimized at the TPSS-D3/def2-TZVP + COSMO(chlorobenzene) level of theory, which combines the TPSS meta-GGA density functional[S12] with the BJ-damped DFT-D3 dispersion correction[S13,S14] and the def2-TZVP basis set,[S15,S16] using the Conductor-like Screening Model (COSMO) continuum solvation model[S17] for chlorobenzene solvent (dielectric constant ε = 5.7 and solvent diameter R_{solv} = 3.5 Å). The density-fitting RI-J approach[S15,S18,S19] is used to accelerate the geometry optimization and numerical harmonic frequency calculations[S20] in solution. The optimized structures are characterized by frequency analysis to identify the nature of located stationary points (no imaginary frequency for true minima and only one imaginary frequency for transition state) and to provide thermal corrections (at 298.15 K and 1 atm) according to the modified ideal gas–rigid rotor–harmonic oscillator model.[S21]

The final solvation free energies in chlorobenzene are computed with the COSMO-RS solvation model[S22] (parameter file: BP_TZVP_C30_1601.ctd) using the COSMOtherm program package[S23] on the above TPSS-D3 optimized structures, and corrected by +1.89 kcal·mol^{-1} to account for higher reference solute concentration of 1 mol·L^{-1} usually used in solution. To check the effects of the chosen DFT functional on the reaction energies and barriers, single-point calculations at the TPSS-D3[S12] and hybrid PW6B95-D3[S24] levels are performed using a larger def2-QZVP basis set.[S16,S25] The final reaction Gibbs free energies (ΔG) are determined from the electronic single-point energies plus TPSS-D3 thermal corrections and COSMO-RS solvation free energies. As expected, the computed reaction free energies and barriers from both DFT functionals are in good mutual agreement of –0.4 ± 1.2 kcal/mol (average and standard deviations, see Table S1 below). In our discussion, the final PW6B95-D3 Gibbs free energies (in kcal/mol, at 298.15 K and 1 mol/L standard state concentration) will be used in our discussion unless specified otherwise.

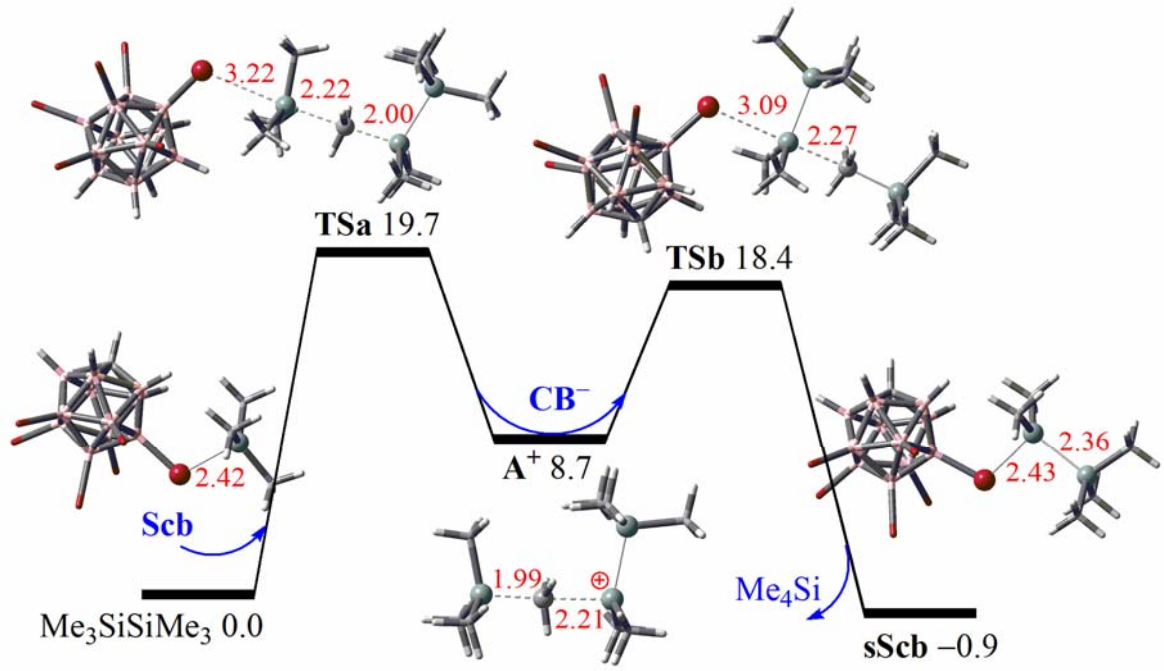


Figure S93. Gibbs free energy profile (in kcal/mol at 298 K and 1 mol/L in chlorobenzene solution) for the generation of $Me_2(Me_3Si)Si^+[CHB_{11}H_5Br_6]^-$ (sScb) via methyl transfer from hexamethyldisilane to silylium carborate $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (Scb) computed at the PW6B95-D3/def2-QZVP + COSMO-RS // TPSS-D3/def2-P + COSMO level of theory.

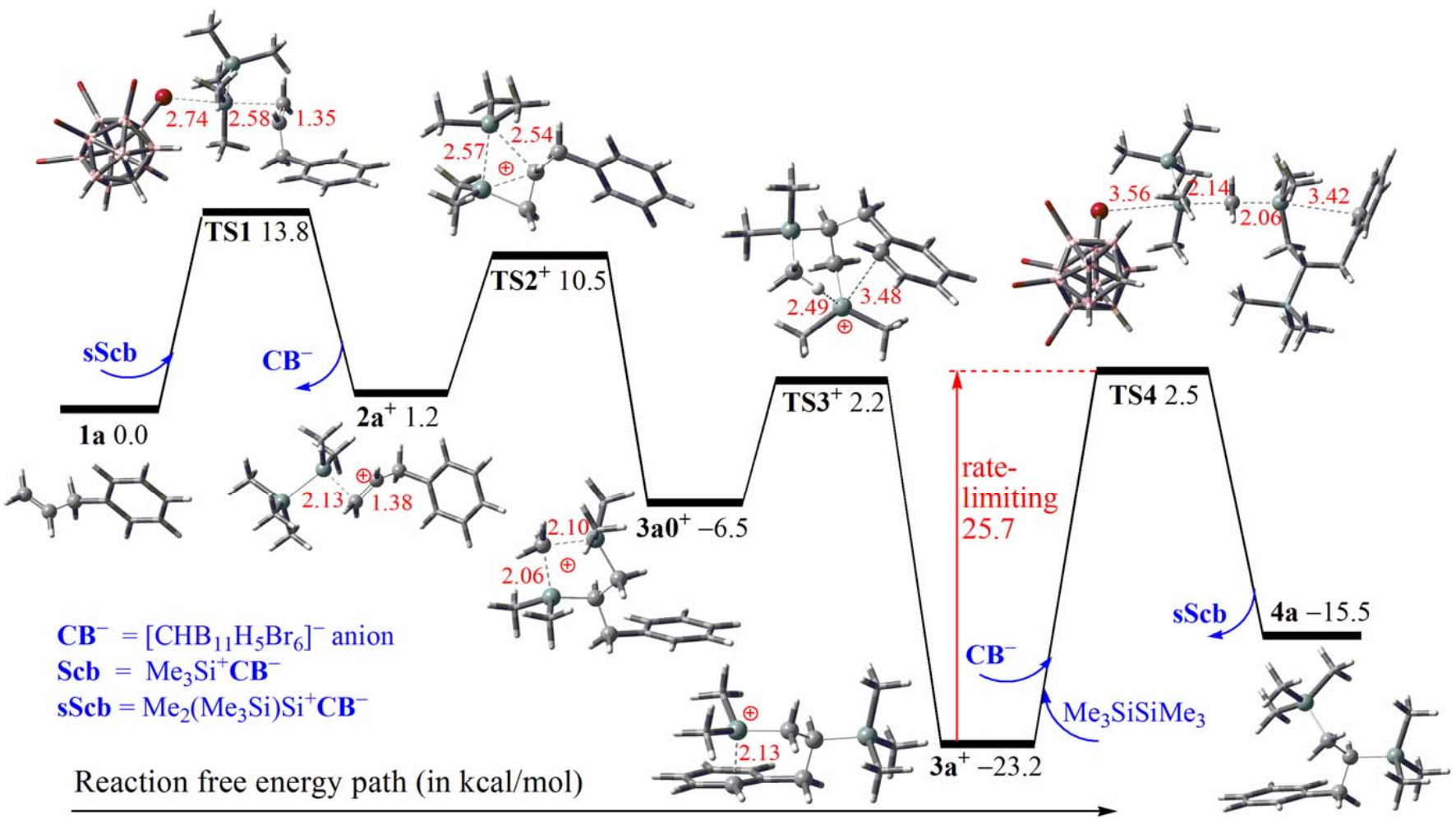


Figure S94. Gibbs free energy profile (in kcal/mol at 298 K and 1 M in chlorobenzene solution) for the catalytic 1,2-disilylation of allylbenzene (**1a**) with $Me_2(Me_3Si)Si^+[CHB_{11}H_5Br_6]^-$ (sScb) computed at the PW6B95-D3/def2-QZVP + COSMO-RS // TPSS-D3/def2-P + COSMO level of theory.

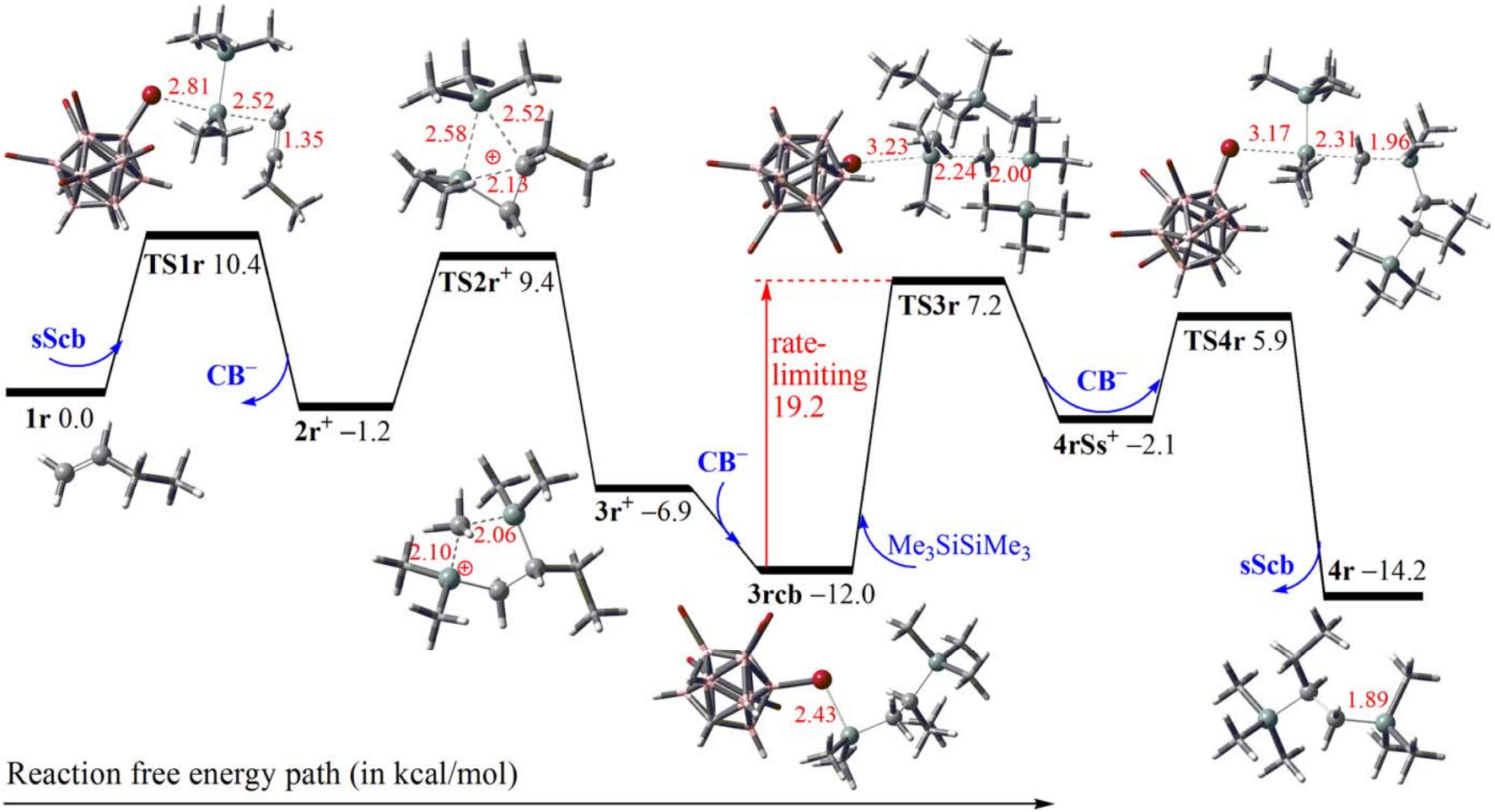


Figure S95. Gibbs free energy profile (in kcal/mol at 298 K and 1 M in chlorobenzene solution) for the catalytic 1,2-disilylation of but-1-ene (**1r**) with $Me_2(Me_3Si)Si^+[CHB_{11}H_5Br_6]^-$ (sScb) computed at the PW6B95-D3/def2-QZVP + COSMO-RS // TPSS-D3/def2-P + COSMO level of theory.

Table S1. TPSS-D3/def2-TZVP + COSMO computed lowest imaginary frequency (ImF), zero-point energies (ZPE), gas-phase enthalpic (Hc) and Gibbs free-energy (Gc) corrections; the COSMO-RS computed solvation enthalpic (Hsol) and Gibbs free-energy (Gsol) corrections in Chlorobenzene solution; TPSS-D3/def2-QZVP and PW6B95-D3/def2-QZVP single-point energies (TPSS-D3 and PW6B95-D3); the relative electronic energies (ΔET and ΔEP) and Gibbs free-energies (ΔGT and ΔGP) at the TPSS-D3 and PW6B95-D3 levels. Each structure is labeled either by its molecular formula or a specific name in bold. Transition structures (with only one imaginary frequency) are indicated by the "**TS**" prefix. See also Figures S93–S95 for labellings.

Reaction	ImF	ZPE	Hc	Gc	Hsol	Gsol	TPSS-D3	PW6B95-D3	ΔET	ΔEP	ΔGP	ΔGT
	cm^{-1}	kcal/mol	kca/mol	kcal/mol	kcal/mol	kcal/mol	E_h	E_h	kcal/mol	kcal/mol	kcal/mol	kcal/mol
*Catalyst formation via methyl transfer from $Me_3SiSiMe_3$ (**sSMe**) to $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (**Scb**)*												
Scb + **sSMe**	0	284.14	311.49	226.69	-41.90	-28.71	-16988.72517	-16997.54058	0.0	0.0	0.0	0.0
TSa	-73	284.74	311.86	241.12	-51.67	-39.17	-16988.69739	-16997.51252	17.4	17.6	19.7	19.5
$\mathbf{A^+}$ (or $\mathbf{INT^+}$) + $\mathbf{CB^-}$	0	284.51	311.68	225.39	-105.72	-91.02	-16988.60950	-16997.42538	72.6	72.3	8.7	9.0
TSb	-105	284.92	312.26	241.22	-47.96	-36.01	-16988.70592	-16997.51970	12.1	13.1	18.4	17.4
sScb + Me_4Si	0	284.05	311.55	227.65	-40.39	-27.64	-16988.72982	-16997.54532	-2.9	-3.0	-0.9	-0.9
*Unfavorable silylium ion transfer from $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (**Scb**) to allylbenzene (**1a**)*												
Scb + **1a**	0	245.88	268.91	191.37	-45.32	-32.20	-16519.10931	-16527.58830	0.0	0.0	0.0	0.0
TSc	-26	247.31	270.30	207.38	-49.28	-37.16	-16519.10403	-16527.57985	3.3	5.3	14.5	12.5
$\mathbf{1aS^+}$ + $\mathbf{CB^-}$	0	246.93	269.36	192.40	-111.58	-96.83	-16519.00329	-16527.48203	66.5	66.7	3.1	2.9
1aScb	0	247.31	270.76	206.44	-59.95	-47.09	-16519.09219	-16527.56985	10.7	11.6	9.9	9.0

*Catalytic 1,2-disilylation of allylbenzene (**1a**) with $Me_3SiSiMe_3$ (**sSMe**) promoted by $Me_2(Me_3Si)Si^+[CHB_{11}H_5Br_6]^-$ (**sScb**)*

1a + **sScb**	0	292.49	319.47	234.10	-45.81	-32.17	-16888.56613	-16897.36269	0.0	0.0	0.0	0.0
TS1	-9	294.10	320.85	250.86	-47.12	-34.85	-16888.56601	-16897.36015	0.1	1.6	13.8	12.3
2a$^+$ + **CB**$^-$	0	293.66	320.04	234.87	-110.26	-94.68	-16888.46776	-16897.26236	61.7	63.0	1.2	0.0
2a$^+$	0	217.31	231.81	187.55	-49.70	-42.95	-1127.82425	-1128.87850	0.0	0.0	1.2	0.0
TS2$^+$ (or **7a**$^{+‡}$)	-136	217.49	231.15	188.81	-49.64	-43.07	-1127.80930	-1128.86551	9.4	8.2	10.5	10.5
3a0$^+$ (or **8a**$^+$)	0	217.29	231.08	188.55	-52.05	-45.31	-1127.82825	-1128.88857	-2.5	-6.3	-6.5	-3.9
TS3$^+$ (or **9a**$^{+‡}$)	-86	217.31	230.62	189.11	-49.66	-43.41	-1127.81964	-1128.87863	2.9	-0.1	2.2	4.0
3a$^+$	0	217.90	231.62	189.28	-48.90	-42.73	-1127.86276	-1128.92049	-24.2	-26.4	-23.2	-22.2
3a$^+$ + **CB**$^-$ + **sSMe**	0	432.38	468.01	351.34	-116.38	-97.67	-17707.31124	-17716.82720	0.0	0.0	-23.2	0.0
3acb + **sSMe**	0	433.01	469.43	367.11	-49.17	-33.90	-17707.41847	-17716.93460	-67.3	-67.4	-12.9	10.4
TS4	-46	433.07	470.26	379.33	-51.89	-37.70	-17707.40538	-17716.92045	-59.1	-58.5	2.5	25.1
4a	0	432.39	469.05	364.11	-49.33	-33.99	-17707.41647	-17716.93371	-66.0	-66.8	-15.5	8.5

*Catalytic 1,2-disilylation of but-1-ene (**1r**) with $Me_3SiSiMe_3$ (**sSMe**) promoted by* $Me_2(Me_3Si)Si^+[CHB_{11}H_5Br_6]^-$ *(**sScb**)*

1r + **sScb**	0	259.68	284.82	204.61	-40.26	-27.89	-16696.70325	-16705.28392	0.0	0.0	0.0	0.0
TS1r	0	261.39	286.76	219.38	-43.48	-32.38	-16696.70220	-16705.28077	0.7	2.0	10.4	9.1
TS1r0	-28	260.72	285.83	218.98	-39.05	-28.25	-16696.70728	-16705.28776	-2.5	-2.4	9.7	9.6
2r$^+$ + **CB$^-$**	0	261.04	285.41	204.68	-107.72	-93.33	-16696.60176	-16705.18161	63.7	64.2	-1.2	-1.7
2r$^+$	0	184.69	197.18	157.37	-47.16	-41.60	-935.95826	-936.79776	0.0	0.0	-1.2	0.0
TS2r$^+$	-139	185.34	196.77	159.48	-46.51	-41.20	-935.94381	-936.78499	9.1	8.0	9.4	11.6
3r$^+$	0	184.80	196.51	158.66	-47.88	-42.41	-935.96294	-936.80770	-2.9	-6.2	-6.9	-2.5
TS2r0$^+$	-78	184.02	195.57	157.81	-49.19	-43.61	-935.94374	-936.78803	9.1	6.1	3.4	7.5
3r0$^+$	0	184.18	196.04	157.60	-50.05	-44.22	-935.96096	-936.80354	-1.7	-3.6	-7.2	-4.1
3r0$^+$ + **CB$^-$**	0	260.52	284.27	204.92	-110.60	-95.95	-16696.60447	-16705.18739	0.0	0.0	-7.2	0.0
3rcb0	0	261.54	286.29	220.29	-38.59	-27.63	-16696.74196	-16705.32435	-86.3	-86.0	-11.3	-4.5
3rcb	0	261.68	286.26	220.81	-37.20	-26.60	-16696.74465	-16705.32790	-88.0	-88.2	-12.0	-4.6
3rcb + **sSMe**	0	399.82	434.42	335.56	-44.12	-29.81	-17515.54962	-17524.85075	0.0	0.0	-12.0	0.0
TS3r	-33	400.25	434.71	350.05	-52.42	-38.97	-17515.52473	-17524.82567	15.6	15.7	7.2	19.1
4rSs$^+$ + **CB$^-$**	0	400.08	434.49	333.99	-106.68	-90.62	-17515.43370	-17524.73558	72.8	72.3	-2.1	10.4
TS4r	-41	400.75	435.51	350.38	-50.85	-37.55	-17515.52959	-17524.83042	12.6	12.8	6.0	17.8
4r + **sScb**	0	399.93	434.49	334.08	-44.90	-30.48	-17515.54939	-17524.85077	0.2	0.0	-14.2	-2.0

*Potential complexes of Me_3Si^+ (**S**$^+$) and $Me_2(Me_3Si)Si^+$ (**sS**$^+$)*												
PhHS$^+$	0	132.65	141.03	109.63	-49.42	-44.36	-641.56542	-642.17716	0.0	0.0	0.0	0.0
PhH + **S**$^+$	0	130.54	138.98	96.71	-61.96	-54.48	-641.51245	-642.12791	33.2	30.9	9.8	12.1
PhClS$^+$	0	126.31	135.57	101.96	-49.56	-43.95	-1101.21731	-1102.16340	0.0	0.0	0.0	0.0
PhCl + **S**$^+$	0	124.62	133.76	88.29	-63.63	-55.67	-1101.16271	-1102.11214	34.3	32.2	8.7	10.8
Scb	0	146.00	163.33	111.94	-34.98	-25.50	-16169.92020	-16178.01772	0.0	0.0	0.0	0.0
Scb0	0	145.79	163.17	111.68	-29.79	-20.84	-16169.92570	-16178.02315	-3.5	-3.4	1.0	0.9
S$^+$ + **CB**$^-$	0	144.53	161.51	97.43	-115.06	-101.59	-16169.75385	-16177.85442	104.4	102.5	13.8	15.7
1aS$^+$	0	170.59	181.13	145.09	-51.02	-45.09	-758.35978	-759.09817	0.0	0.0	0.0	0.0
1a + **S**$^+$	0	168.06	178.86	129.54	-64.85	-56.56	-758.29945	-759.04114	37.9	35.79	10.7	12.7
sScb	0	192.61	213.88	154.68	-35.46	-25.48	-16539.37701	-16547.79211	0.0	0	0.0	0.0
sScb0	0	192.38	213.72	154.47	-29.86	-20.57	-16539.38241	-16547.79733	-3.4	-3.3	1.4	1.3
sS$^+$ + **CB**$^-$	0	191.53	212.21	139.18	-110.27	-96.25	-16539.21895	-16547.63677	99.2	97.5	13.1	14.8

Table S2. The TPSS-D3/def2-TZVP + COSMO optimized atomic Cartesian coordinates (in Å) in chlorobenzene solution. Each structure is labeled by the specific name (see also Figures S93–S95 and Table S1 for labellings), followed by the number of atoms, the total energy, and the detailed atomic coordinates (in double-column text list).

1aScb

56

Energy = -16518.75388637

B	-1.2987695	1.5971971	-0.9993095
B	-0.7174912	3.0186255	-0.0980618
B	-2.5364435	2.1351244	-2.1618805
B	-1.1011151	3.1600272	-1.8416112
B	-3.0135949	1.3749841	-0.6358087
B	-1.8950707	1.9192498	0.6334987
Br	-0.1257861	0.0696908	-1.4052186
B	-1.6000165	4.4472481	-0.7021425
B	-2.0836366	3.6745904	0.8165681
Br	1.1227703	3.1350107	0.5739091
B	-2.7244844	3.9009769	-1.9791488
B	-3.8940094	2.7956909	-1.2383531
Br	-2.8051403	1.2247899	-3.8759791
Br	0.2880144	3.4364921	-3.1806835
C	-3.3956139	2.6792747	0.3851108
H	-3.5648502	0.3353098	-0.5272735
H	-1.7071199	1.2484702	1.5883537
B	-3.3175656	4.2166436	-0.3407818
Br	-0.7880920	6.2299409	-0.7249492
H	-2.0215962	4.1636322	1.8899776
Br	-3.2181515	5.0497511	-3.4868371
H	-5.0350111	2.7027252	-1.5302036
Si	0.2963192	-2.0293134	1.7028478
H	-4.1661456	2.5208305	1.1282172
H	-4.0776979	5.0673555	-0.0352289

C	1.1151293	-3.0458585	0.3693553
C	1.1930308	-0.4763063	2.1824291
C	-1.5559530	-1.9353985	1.5884041
C	0.7398736	-3.4917006	3.2638384
H	0.6481892	-4.0295900	0.2674436
H	0.9943696	-2.5087810	-0.5788418
H	2.1845486	-3.1703848	0.5625818
H	0.6947671	0.0557570	2.9987841
H	2.2254198	-0.6921145	2.4784767
H	1.2202628	0.1978127	1.3186566
H	-2.0081235	-1.4061152	2.4316786
H	-1.8010092	-1.3773074	0.6777869
H	-2.0061590	-2.9298988	1.5055161
H	1.8131417	-3.5425315	3.0926134
H	0.1467511	-4.3328990	2.9092832
C	-1.1166287	-2.7433603	4.8290438
H	-1.7515295	-3.4439815	4.2825308
C	-0.9005783	-3.2011291	6.2721531
C	-0.7884619	-4.5652963	6.5647913
C	-0.7778119	-2.2587233	7.2993008
C	-0.5934436	-4.9838479	7.8807326
H	-0.8700657	-5.2998856	5.7675518
C	-0.5759465	-2.6789789	8.6131379
H	-0.8578050	-1.1984285	7.0730870
C	-0.4886114	-4.0416555	8.9061875
H	-0.5231927	-6.0439383	8.1045866
H	-0.4947994	-1.9446646	9.4084296
H	-0.3426686	-4.3677344	9.9315966
C	0.2502700	-2.6759570	4.2508682
H	0.9145481	-1.9271131	4.6809686
H	-1.5857128	-1.7540288	4.8338772

1aS^{+} $PhCH_2CH=CH_2.Me_3Si^{+}$

32

Energy = -758.3748389480

Si	2.1898970	0.2958745	0.1279644
C	4.0335611	0.1494849	0.3544934
C	1.2452861	0.4180531	1.7256471
C	1.6743860	1.5073015	-1.1815472
C	1.9218601	-1.6405342	-0.7970903
H	4.3895742	1.1135335	0.7418240
H	4.2933441	-0.6274205	1.0794683
H	4.5471635	-0.0515594	-0.5900222
H	0.1636584	0.4687886	1.5679664
H	1.4697785	-0.4166028	2.3973490
H	1.5584352	1.3427852	2.2268709
H	0.5884273	1.5716235	-1.2824114
H	2.0376516	2.4968516	-0.8743793
H	2.1162528	1.2779833	-2.1559144
H	2.6587552	-2.1914393	-0.2169716
H	2.1896968	-1.3854994	-1.8217330
C	-0.5595299	-1.3028071	-1.2565917
H	-1.0222596	-2.2578722	-1.5643601
C	-1.5870960	-0.4770424	-0.4945274
C	-2.1461997	-0.9448535	0.7004764
C	-1.9746788	0.7719909	-0.9870921
C	-3.0692406	-0.1670153	1.3983823
H	-1.8709792	-1.9225735	1.0888968
C	-2.8978010	1.5523330	-0.2878229
H	-1.5694817	1.1306240	-1.9297876
C	-3.4414127	1.0873707	0.9095013
H	-3.5034324	-0.5444877	2.3192211
H	-3.1925148	2.5198370	-0.6829554
H	-4.1557153	1.6950562	1.4565685

C 0.6024041 -1.7141773 -0.4305430

H 0.3729473 -2.1110275 0.5579132

H -0.2386976 -0.8030047 -2.1742546

1a $PhCH_2CH=CH_2$

19

Energy = -349.1714759221

C 3.4140251 0.6436484 -0.2463944

C 2.4053371 -0.1971788 -0.4837856

H 3.6246641 1.0085046 0.7572454

H 4.0656232 0.9921354 -1.0432649

H 2.2163135 -0.5371909 -1.5029204

C 1.4591303 -0.7203727 0.5652754

H 1.5171414 -1.8158332 0.5976164

H 1.7678598 -0.3468143 1.5493568

C 0.0186612 -0.3217268 0.2904794

C -0.9614461 -1.2864340 0.0323546

C -0.3517136 1.0298798 0.2843424

C -2.2837427 -0.9132404 -0.2211268

H -0.6863128 -2.3387765 0.0339387

C -1.6710263 1.4070530 0.0362391

H 0.4032449 1.7895810 0.4734093

C -2.6426954 0.4351956 -0.2191682

H -3.0323396 -1.6760330 -0.4181872

H -1.9421251 2.4594238 0.0401759

H -3.6703312 0.7281057 -0.4156137

1r $MeCH_2CH=CH_2$

12

Energy = -157.3162145890

C 3.4206945 0.6440792 -0.2483101

C 2.4091503 -0.1966259 -0.4767990

H	3.6383014	1.0112468	0.7529789
H	4.0661114	0.9918820	-1.0506929
H	2.2235934	-0.5365340	-1.4979082
C	1.4642365	-0.7201613	0.5668235
H	1.5270754	-1.8177843	0.5906231
H	1.7694135	-0.3590836	1.5563058
C	0.0039436	-0.3199554	0.2892279
H	-0.3218804	-0.6830425	-0.6922259
H	-0.6635370	-0.7439658	1.0469536
H	-0.1091596	0.7694755	0.3015240

2a^{+} $PhCH_2CH{=}CH_2.Me_2(Me_3Si)Si^{+}$

41

Energy = -1127.817631318

Si	2.2156704	-1.1237698	1.1288460
C	0.9691932	-0.4014000	2.3227964
H	0.5453238	-1.1650484	2.9827097
H	1.5000175	0.3224264	2.9544673
H	0.1547793	0.1325116	1.8245442
C	2.7340357	0.0698236	-0.2219624
H	3.4250534	0.7988464	0.2188050
H	3.2653303	-0.4427981	-1.0305082
H	1.8910505	0.6240064	-0.6453095
C	1.3917415	-2.8900562	0.2709606
H	2.2588846	-3.3131727	-0.2315225
H	1.0337283	-3.4228468	1.1511142
C	0.5181045	-2.0917671	-0.4420439
H	0.8466544	-1.6999348	-1.4034680
C	-0.8810497	-1.7797451	-0.0473027
H	-1.0913137	-2.0944503	0.9769378
H	-1.0954082	-0.7123004	-0.1551227
Si	4.0371101	-2.2390817	2.1629710

C	-1.7224904	-2.5723122	-1.0502702
C	-2.2595846	-1.9452258	-2.1800004
C	-1.9223918	-3.9446472	-0.8574783
C	-3.0185999	-2.6791076	-3.0911869
H	-2.1002736	-0.8814158	-2.3360354
C	-2.6850601	-4.6758299	-1.7666302
H	-1.4922342	-4.4375194	0.0105996
C	-3.2338802	-4.0436348	-2.8848026
H	-3.4464751	-2.1844665	-3.9579774
H	-2.8496214	-5.7366011	-1.6032582
H	-3.8267985	-4.6131921	-3.5941177
C	3.3743097	-3.6391197	3.2254587
H	4.2023448	-4.1038344	3.7749731
H	2.6466954	-3.2777106	3.9600613
H	2.8988491	-4.4210766	2.6232895
C	5.1838247	-2.8628765	0.8114136
H	6.0667339	-3.3254128	1.2700436
H	4.7055243	-3.6201776	0.1804002
H	5.5296386	-2.0469806	0.1676196
C	4.8597102	-0.9057327	3.2084279
H	5.2076554	-0.0660503	2.5972295
H	4.1828379	-0.5177191	3.9770468
H	5.7324884	-1.3377585	3.7146952

2r^{+} $MeCH_2CH{=}CH_2.Me_2(Me_3Si)Si^{+}$

34

Energy = -935.9631807774

Si	2.2123091	-1.1349388	1.1289938
C	0.9524794	-0.4286340	2.3165125
H	0.5267951	-1.1994867	2.9666885
H	1.4750265	0.2923582	2.9583715
H	0.1405052	0.1053418	1.8145712

C	2.7290226	0.0629296	-0.2178705
H	3.3950047	0.8074030	0.2358161
H	3.2876056	-0.4402110	-1.0137067
H	1.8821892	0.5970319	-0.6586014
C	1.4236281	-2.9351354	0.2725654
H	2.3117749	-3.3409177	-0.2067437
H	1.0633641	-3.4574495	1.1575326
C	0.5626054	-2.1422510	-0.4545332
H	0.9116131	-1.7623599	-1.4146298
C	-0.8314316	-1.8057231	-0.0775738
H	-1.0489940	-2.1157980	0.9474334
H	-0.9917728	-0.7244844	-0.1655520
Si	4.0396110	-2.2354205	2.1699673
C	3.3915186	-3.6266682	3.2527649
H	4.2251318	-4.0730332	3.8090546
H	2.6596204	-3.2635594	3.9824809
H	2.9255902	-4.4231201	2.6622638
C	5.1865447	-2.8659379	0.8219401
H	6.0717355	-3.3208639	1.2838251
H	4.7116293	-3.6308677	0.1976763
H	5.5286899	-2.0540723	0.1711511
C	4.8551127	-0.8820946	3.1950079
H	5.1891686	-0.0444177	2.5734309
H	4.1802062	-0.4944672	3.9655537
H	5.7365546	-1.2999091	3.6982417
C	-1.7924974	-2.5186371	-1.0671264
H	-2.8192466	-2.2434442	-0.8139913
H	-1.5925103	-2.2135371	-2.0978847
H	-1.6884407	-3.6040969	-0.9935383

3a0^{+}

41

Energy = -1127.825381061

Si	1.9348564	-1.4228905	-0.1210596
C	1.8377803	-2.3202034	-1.7465050
H	1.2567936	-1.7544968	-2.4823073
H	2.8279854	-2.5265912	-2.1647240
H	1.3301467	-3.2786920	-1.5831612
C	3.0029573	-2.2259622	1.1712169
H	3.9600812	-2.5663255	0.7623350
H	3.2018798	-1.5511288	2.0103516
H	2.4727740	-3.1008021	1.5669167
C	0.2656230	-0.8141469	0.4787048
H	-0.5087603	-1.5343848	0.1846156
H	0.2509565	-0.7598736	1.5736490
C	0.0062129	0.5820622	-0.1340192
H	-0.1373285	0.4703007	-1.2192003
C	-1.2397484	1.2986463	0.4460816
H	-1.1064348	1.4430004	1.5246664
H	-1.3281613	2.2920214	-0.0098631
Si	1.6320081	1.4756682	0.1268842
C	-2.5005280	0.5038660	0.1933905
C	-3.1018692	0.5129844	-1.0722148
C	-3.0598847	-0.2947072	1.1973824
C	-4.2345668	-0.2589002	-1.3289543
H	-2.6839016	1.1348823	-1.8613825
C	-4.1937009	-1.0698463	0.9446983
H	-2.6070890	-0.3058485	2.1862527
C	-4.7831866	-1.0548746	-0.3200934
H	-4.6926369	-0.2357622	-2.3138604
H	-4.6174054	-1.6813243	1.7365180
H	-5.6670546	-1.6543348	-0.5180795
C	1.8648113	3.0560783	-0.8247008
H	2.8604461	3.4858065	-0.6738459

H	1.7038891	2.9076103	-1.8973926
H	1.1261032	3.7867207	-0.4720050
C	2.1329411	1.5899158	1.9169794
H	3.1594769	1.9576655	2.0182347
H	1.4723114	2.3031561	2.4246136
H	2.0552374	0.6342743	2.4441990
C	3.0118413	0.2552523	-0.7840487
H	3.7625641	-0.5504414	-0.6767945
H	2.8709411	0.4066859	-1.8565430
H	3.6810078	1.0478266	-0.4011981

3acb or **3a**$^{+}$**CB**$^{-}$

65

Energy = -16888.23770538

Si	-1.4974313	1.0002634	-1.3311108
C	-1.4717428	1.5738688	-3.0901699
H	-2.3633056	2.1769031	-3.2932346
H	-0.5860479	2.1881353	-3.2733436
H	-1.4536534	0.7319613	-3.7871767
C	-1.3161920	2.2947751	-0.0094720
H	-2.2332354	2.8903032	0.0458940
H	-1.1429075	1.8340137	0.9677691
H	-0.4866861	2.9710135	-0.2332121
C	-2.4227399	-0.5660208	-0.8538687
H	-1.6677504	-1.2561034	-0.4518681
H	-3.0602096	-0.3241783	0.0062019
C	-3.2644453	-1.2623586	-1.9567178
H	-2.7971248	-1.0883565	-2.9386708
C	-4.6979451	-0.6746168	-2.0120131
H	-5.2862975	-1.2271975	-2.7521239
H	-5.1780326	-0.8222386	-1.0370090
Si	-3.2564154	-3.1556963	-1.7145793

C	-4.7102512	0.7914368	-2.3677524
C	-4.5644364	1.7815938	-1.3824656
C	-4.8295282	1.1967947	-3.7043020
C	-4.5276845	3.1369543	-1.7264252
H	-4.5276100	1.4933443	-0.3346269
C	-4.8006798	2.5471378	-4.0498618
H	-4.9488131	0.4436336	-4.4795239
C	-4.6417998	3.5234623	-3.0611557
H	-4.4232369	3.8890070	-0.9493638
H	-4.8990883	2.8402718	-5.0911991
H	-4.6166235	4.5750638	-3.3303167
C	-3.9796909	-3.5713560	-0.0267576
H	-3.9505279	-4.6534473	0.1490594
H	-3.4169521	-3.0898329	0.7819924
H	-5.0249690	-3.2499912	0.0530081
C	-4.2697485	-3.9576149	-3.0829850
H	-3.8925104	-3.6751204	-4.0734555
H	-4.2194224	-5.0505781	-3.0076000
H	-5.3262023	-3.6704572	-3.0295636
C	-1.4678726	-3.7422519	-1.8200394
H	-1.4220163	-4.8371695	-1.7794482
H	-0.9984927	-3.4260758	-2.7596555
H	-0.8538989	-3.3637642	-0.9942265
B	2.2167400	1.2344153	-1.4085382
B	3.5641739	1.1491415	-0.2616614
B	5.0348719	1.6043406	-1.1651399
B	4.5662441	1.9499153	-2.8587901
B	2.8037608	1.7059696	-3.0094895
B	3.7804538	0.6121468	-1.9673931
B	4.8328013	3.2764970	-1.7160700
B	3.4634692	3.3387350	-2.8463621
B	1.9982974	2.8856846	-1.9527835

B	2.4678947	2.5427208	-0.2626001
B	4.2200260	2.7861163	-0.1233520
C	3.2716744	3.7122078	-1.1932113
H	3.1036881	4.7500130	-0.9374599
H	5.6889671	4.0855333	-1.7903191
H	3.4087042	4.1849892	-3.6673368
H	0.9749374	3.4289967	-2.1785101
H	1.7500715	2.8454138	0.6236155
H	4.6666665	3.2645214	0.8587677
Br	0.7311314	-0.1054526	-1.2108068
Br	3.5731208	-0.1185377	1.2279149
Br	6.7880889	0.8745141	-0.7041311
Br	5.7760977	1.6173087	-4.3570042
Br	1.9624450	1.0707427	-4.6571127
Br	4.0324075	-1.2637312	-2.4168014

3r0^{+}

34

Energy = -935.9690259072

Si	0.2274850	1.5186409	0.2439047
C	0.3361260	0.8923859	1.9755122
H	1.2855595	0.3787991	2.1568344
H	0.2973623	1.7636684	2.6439373
H	-0.4946373	0.2283474	2.2291801
C	1.6384051	2.5386734	-0.3775176
H	2.6048577	2.1386036	-0.0571494
H	1.6203279	2.6407646	-1.4661595
H	1.5271320	3.5418397	0.0587587
C	-1.4346260	1.6195463	-0.5645814
H	-2.0745030	2.2391601	0.0784814
H	-1.3393073	2.1460163	-1.5224728
C	-2.0617603	0.2070631	-0.7597293

H	-2.2111888	-0.2423521	0.2347627
C	-1.0890405	-0.6941659	-1.5419432
H	-1.5099189	-1.7008464	-1.6408273
H	-0.9417574	-0.3098184	-2.5577799
Si	-3.7968527	0.3201419	-1.5645758
C	-3.6295478	1.0969668	-3.2705325
H	-4.6146644	1.1741220	-3.7465396
H	-3.2102950	2.1089409	-3.2206819
H	-2.9914705	0.4974980	-3.9305627
C	-4.4998559	-1.4191934	-1.6974545
H	-4.5442439	-1.9075466	-0.7164544
H	-5.5195386	-1.3885437	-2.1001337
H	-3.9014246	-2.0512996	-2.3639418
C	-4.8845688	1.3856229	-0.4606127
H	-5.9044743	1.4312682	-0.8611431
H	-4.9449519	0.9764588	0.5551782
H	-4.5139883	2.4151730	-0.3903566
C	0.2626942	-0.8393520	-0.8543871
H	0.8541123	0.1377322	-0.8431495
H	0.1906179	-1.2301585	0.1629880
H	0.9833930	-1.4439021	-1.4147454

3rcb0 or **3r0^{+}CB^{-}**

58

Energy = -16696.37432651

Si	-2.0965693	-4.7768745	-0.7615796
C	-3.7048706	-4.4233275	0.1012995
H	-3.7393907	-3.3801552	0.4300923
H	-4.5377543	-4.5869422	-0.5915794
H	-3.8507362	-5.0737755	0.9670719
C	-1.5881536	-6.5510417	-0.9646418
H	-2.2559751	-7.0440681	-1.6806334

H	-0.5649629	-6.6189572	-1.3463529
H	-1.6410490	-7.0945571	-0.0179207
C	-1.6048432	-3.6343469	-2.1612334
H	-1.9432762	-2.6194796	-1.9116367
H	-0.5060741	-3.6004948	-2.1543191
C	-2.0878563	-4.0172910	-3.5909735
H	-1.7078052	-5.0242547	-3.8243207
C	-3.6304424	-4.0381029	-3.7265715
H	-4.0584067	-3.2649484	-3.0752436
H	-3.9205326	-3.7574494	-4.7469502
Si	-1.2885762	-2.8518574	-4.8761041
C	-1.6783541	-3.5034137	-6.6001111
H	-1.2199820	-2.8632674	-7.3637491
H	-1.2863595	-4.5186122	-6.7363931
H	-2.7566728	-3.5297354	-6.7951501
C	-1.9951614	-1.1190255	-4.6592277
H	-1.5573010	-0.4297459	-5.3912931
H	-3.0822289	-1.1097061	-4.8018943
H	-1.7832007	-0.7169901	-3.6611226
C	0.5783679	-2.8269764	-4.6204222
H	0.8588264	-2.3652075	-3.6664851
H	0.9982563	-3.8401581	-4.6433885
H	1.0636652	-2.2497292	-5.4168689
C	-4.2646402	-5.3993916	-3.4226879
H	-4.0280834	-5.7546839	-2.4121376
H	-5.3562995	-5.3571780	-3.4992006
H	-3.8998066	-6.1579973	-4.1234352
B	-0.7622425	-4.7194720	2.6344912
B	-0.0188087	-6.2662379	3.0650431
B	0.4082952	-6.1626074	4.7960996
B	-0.0647491	-4.5403337	5.3922119
B	-0.7898666	-3.6355849	4.0333869

B	0.6143545	-4.7273995	3.7488455
B	-1.0927752	-5.9481847	5.7110781
B	-1.8271823	-4.3997316	5.2451082
B	-2.2575371	-4.4936778	3.5261642
B	-1.7834853	-6.1114175	2.9294297
B	-1.0656432	-7.0055914	4.2836984
C	-2.3113619	-5.8654177	4.5235273
H	-3.2886808	-6.2488428	4.7854521
H	-1.3200420	-6.4073879	6.7742732
H	-2.5388758	-3.8296449	5.9942837
H	-3.2418486	-3.9802082	3.1275030
H	-2.4620642	-6.6715945	2.1428106
H	-1.2744656	-8.1617366	4.3959259
Br	-0.4425800	-3.9059975	0.8168041
Br	1.0089946	-7.3193446	1.7772276
Br	1.9384344	-7.1300479	5.5305003
Br	0.9189926	-3.6348827	6.8167492
Br	-0.6438001	-1.6958957	3.8356167
Br	2.3532043	-4.0244019	3.2266772

3rcb or **3r^{+}CB^{-}**

58

Energy = -16696.37633192

Si	-2.0152981	6.3546027	4.9712368
C	-3.4477226	5.5151518	5.7980434
H	-3.6135544	6.0017075	6.7679563
H	-4.3648396	5.6050517	5.2111363
H	-3.2490252	4.4542040	5.9692809
C	-2.2563989	8.1465280	4.5502006
H	-2.2153693	8.7183453	5.4865933
H	-1.4620797	8.5118850	3.8925962
H	-3.2246391	8.3344587	4.0795468

C	-0.3127715	5.8827152	5.5708240
H	0.4021758	6.2508870	4.8206792
H	-0.1010665	6.4624098	6.4798230
C	-0.1489949	4.3600105	5.8707205
H	-0.8119379	3.7893570	5.1987094
C	-0.5900010	4.0536339	7.3218509
H	0.2356623	4.2673095	8.0140503
H	-1.3961309	4.7446226	7.6068195
Si	1.6356414	3.8410857	5.4305761
C	2.8283440	4.9691590	6.3569393
H	2.6923769	6.0213511	6.0810302
H	2.6966648	4.8869035	7.4425368
H	3.8659231	4.6978006	6.1276233
C	1.9988326	2.0483798	5.8766417
H	1.9733304	1.8818154	6.9593916
H	1.2855193	1.3599207	5.4087123
H	3.0019203	1.7771491	5.5241849
C	1.8466432	4.0577477	3.5687652
H	1.6727940	5.0899313	3.2420017
H	2.8655280	3.7888155	3.2653196
H	1.1558963	3.4099132	3.0149797
C	-1.0864804	2.6197170	7.5238357
H	-0.3135307	1.8855509	7.2811154
H	-1.3948967	2.4549371	8.5613261
H	-1.9494915	2.4160642	6.8784963
B	-3.4212658	5.6527482	1.7101077
B	-3.1444774	6.1288027	0.0274225
B	-4.4980775	5.4506902	-0.9197051
B	-5.5722756	4.5545767	0.2009923
B	-4.8849507	4.6741080	1.8465923
B	-3.7979500	4.4963538	0.4228868
B	-5.9952225	6.1926117	-0.3276560

B	-6.2319936	5.7172434	1.3681085
B	-4.8897110	6.3900461	2.3145256
B	-3.8186579	7.2832025	1.1953087
B	-4.5089653	7.1578501	-0.4351474
C	-5.4963656	7.1994543	0.9521382
H	-6.0682855	8.1009962	1.1277185
H	-6.9285354	6.4801283	-0.9902658
H	-7.3169633	5.6894013	1.8316625
H	-5.0781214	6.8070193	3.4020687
H	-3.2924804	8.2787574	1.5477866
H	-4.4514296	8.0819578	-1.1668237
Br	-1.8004335	5.2351252	2.8307683
Br	-1.3417626	6.3699000	-0.6902942
Br	-4.2737990	4.9187612	-2.7861338
Br	-6.5900073	2.9871212	-0.3682442
Br	-5.0656938	3.2570187	3.1819760
Br	-2.7346925	2.8887052	0.1533562

3r^{+}

34

Energy = -935.9692729355

Si	1.9484376	-1.4283771	-0.1169244
C	1.8799588	-2.3522906	-1.7299115
H	1.3084011	-1.8023043	-2.4848990
H	2.8785376	-2.5595496	-2.1276190
H	1.3752715	-3.3111970	-1.5595810
C	3.0164555	-2.2079063	1.1911733
H	3.9799391	-2.5406023	0.7907821
H	3.2025721	-1.5248883	2.0264540
H	2.4940655	-3.0859840	1.5901423
C	0.2655523	-0.8343318	0.4603552
H	-0.4852271	-1.5698548	0.1443735

H	0.2302685	-0.7905655	1.5553878
C	-0.0048798	0.5678523	-0.1414715
H	-0.1543678	0.4645891	-1.2272641
C	-1.2293567	1.2928685	0.4554414
H	-1.0852556	1.4115639	1.5375098
H	-1.2900632	2.3034525	0.0318912
Si	1.6191712	1.4637353	0.1152106
C	1.8542239	3.0464728	-0.8342597
H	2.8488452	3.4768172	-0.6782106
H	1.6978994	2.8996651	-1.9079760
H	1.1134696	3.7760006	-0.4837288
C	2.1244337	1.5842395	1.9047475
H	3.1523487	1.9494016	2.0018689
H	1.4665559	2.3028891	2.4084426
H	2.0438410	0.6328403	2.4391579
C	3.0115902	0.2486732	-0.7908290
H	3.7722050	-0.5471667	-0.6801550
H	2.8670292	0.3924207	-1.8640679
H	3.6703746	1.0521830	-0.4134214
C	-2.5471577	0.5563184	0.1918669
H	-2.5475923	-0.4368599	0.6528371
H	-3.3914542	1.1173346	0.6047113
H	-2.7140067	0.4325875	-0.8842102

3a^{+}

41

Energy = -1127.856506269

Si	0.4196753	1.4097330	0.1171141
C	0.3558915	0.8059024	1.8743423
H	1.3505408	0.6146936	2.2854592
H	-0.1027367	1.6059821	2.4706065
H	-0.2560392	-0.0918734	1.9919710

C	1.5219856	2.8887563	-0.1392195
H	2.4970331	2.7603857	0.3404571
H	1.6738491	3.1057739	-1.2013853
H	1.0351118	3.7605919	0.3163257
C	-1.2660190	1.5165336	-0.6982061
H	-1.8550183	2.2105453	-0.0815570
H	-1.1620087	1.9904118	-1.6835055
C	-1.9902531	0.1600611	-0.8179547
H	-2.1134364	-0.2632679	0.1913106
C	-1.1306532	-0.8488268	-1.6443694
H	-1.6523203	-1.8067433	-1.7168215
H	-0.9876346	-0.4596925	-2.6585044
Si	-3.7542705	0.3379895	-1.5480213
C	0.1920838	-1.0466864	-0.9763476
C	1.2375064	-0.0818904	-1.1578938
C	0.4105297	-2.0844818	-0.0673268
C	2.5006669	-0.2603623	-0.5151462
H	1.1980635	0.5518712	-2.0459249
C	1.6340799	-2.2139992	0.5889946
H	-0.3761221	-2.8119942	0.1096363
C	2.6813923	-1.3051302	0.3722627
H	3.3021772	0.4411106	-0.7219450
H	1.7819055	-3.0417147	1.2759997
H	3.6298106	-1.4352252	0.8816734
C	-3.6250238	1.0718231	-3.2752400
H	-4.6244657	1.1822046	-3.7130569
H	-3.1611714	2.0650838	-3.2622145
H	-3.0407496	0.4324526	-3.9474837
C	-4.5467179	-1.3665955	-1.6102953
H	-4.5570837	-1.8382773	-0.6202430
H	-5.5861095	-1.2896122	-1.9515777
H	-4.0238039	-2.0383686	-2.3008599

C -4.7344247 1.4741714 -0.4147501

H -5.7693561 1.5621841 -0.7665266

H -4.7639881 1.0862360 0.6105911

H -4.3096347 2.4841745 -0.3834285

4rSs^{+}

60

Energy = -1754.746388902

Si -0.5074976 0.3908309 -1.7858680

C -0.5410285 -1.2057573 -2.7418779

H 0.4667506 -1.4815961 -3.0725633

H -0.9541132 -2.0328305 -2.1563082

H -1.1618288 -1.0850053 -3.6365303

C 0.4105710 1.7618688 -2.6487948

H 1.4137872 1.4523219 -2.9610681

H -0.1424726 2.0490425 -3.5514614

H 0.4982028 2.6517586 -2.0163860

C -2.1027350 0.9291920 -0.9825317

H -1.8463040 1.6764753 -0.2167957

H -2.6348590 1.5063149 -1.7541247

C -3.0370092 -0.1926306 -0.4270419

H -2.5182762 -1.1661327 -0.4686177

C -4.3221580 -0.3280995 -1.2770017

H -4.9864474 -1.0603056 -0.8024455

H -4.8553395 0.6317207 -1.2611251

Si -3.4621698 0.1016404 1.4074846

C -4.3357948 1.7581662 1.5891239

H -4.5553722 1.9616663 2.6440361

H -3.7225003 2.5860935 1.2137171

H -5.2859584 1.7704467 1.0428915

C -4.5485054 -1.2975360 2.0401213

H -4.0773634 -2.2741036 1.8745013

H	-4.7218470	-1.1901817	3.1177414
H	-5.5269534	-1.3081440	1.5470396
C	-1.8552284	0.1247886	2.3973795
H	-2.0578350	0.3067896	3.4593215
H	-1.3336410	-0.8385271	2.3297706
H	-1.1715037	0.9142941	2.0634068
Si	2.2857145	-0.5837858	1.1332218
Si	4.2016331	0.2769569	0.0714087
C	0.7816440	-0.0739119	-0.1742429
H	1.3720782	-0.4874149	-0.9937338
H	-0.0043878	-0.6753498	0.2808388
H	0.8271053	0.9936762	0.0369541
C	2.1665228	-2.4529800	1.2037893
H	2.9468759	-2.8417328	1.8689160
H	1.1982422	-2.7786026	1.6009685
H	2.3113590	-2.9097776	0.2188887
C	1.8436823	0.2198264	2.7655780
H	2.6597760	0.0282091	3.4738290
H	1.7367810	1.3054978	2.6707732
H	0.9236312	-0.1878244	3.1946491
C	5.7184243	-0.1799201	1.0881504
H	6.6231941	0.2112048	0.6068721
H	5.6651480	0.2427726	2.0976144
H	5.8281279	-1.2663229	1.1787117
C	4.0125121	2.1487897	-0.0602567
H	4.8903235	2.5791261	-0.5577020
H	3.1314500	2.4349231	-0.6469012
H	3.9258554	2.6139084	0.9279634
C	4.2906130	-0.4958221	-1.6493789
H	5.1883294	-0.1409213	-2.1703810
H	4.3445215	-1.5891456	-1.6004657
H	3.4311104	-0.2252134	-2.2752462

C -4.0867033 -0.7534312 -2.7301451

H -3.4583080 -0.0334266 -3.2675392

H -3.5988469 -1.7332716 -2.7759149

H -5.0355162 -0.8231493 -3.2721969

4r

38

Energy = -976.1219787573

Si -0.4556944 0.3936108 -1.7286582

C -0.6198726 -1.0052688 -2.9837769

H 0.3734341 -1.3263535 -3.3219712

H -1.1218539 -1.8788048 -2.5521085

H -1.1907879 -0.6947443 -3.8662028

C 0.3695727 1.8754709 -2.5566250

H 1.3649450 1.6142385 -2.9368213

H -0.2266859 2.2376535 -3.4032251

H 0.4895022 2.7080554 -1.8524282

C -2.1512737 0.9373960 -1.0908246

H -1.9797121 1.7521667 -0.3699570

H -2.6749878 1.4174363 -1.9306008

C -3.0660860 -0.1734598 -0.4806953

H -2.5560162 -1.1500940 -0.5410724

C -4.3950032 -0.3138501 -1.2609415

H -5.0587581 -1.0119177 -0.7335431

H -4.9063550 0.6584348 -1.2629991

Si -3.4171782 0.1359008 1.3607720

C -4.3954303 1.7395294 1.5465711

H -4.5778761 1.9610235 2.6053826

H -3.8528206 2.5906568 1.1177784

H -5.3688012 1.6767479 1.0460136

C -4.4213514 -1.2962957 2.0723409

H -3.9026117 -2.2525869 1.9304226

H	-4.5801311	-1.1606275	3.1494833
H	-5.4073538	-1.3768458	1.6000710
C	-1.8128826	0.2860460	2.3413504
H	-2.0353605	0.4851266	3.3972783
H	-1.2235353	-0.6368223	2.2927157
H	-1.1831256	1.1042252	1.9746156
C	0.6360197	-0.2087122	-0.3133431
H	1.6155247	-0.5214517	-0.6964232
H	0.1921000	-1.0671843	0.2037508
H	0.8033127	0.5787726	0.4305046
C	-4.2291824	-0.8005933	-2.7052553
H	-3.5993939	-0.1203461	-3.2882718
H	-3.7613732	-1.7912979	-2.7290971
H	-5.2001065	-0.8703960	-3.2090676

4Ss^{+}

67

Energy = -1946.607534170

Si	-0.2683091	0.3246363	-0.9845092
C	-0.8029880	-1.2594561	-1.8055413
H	-0.0013904	-1.6292751	-2.4561901
H	-1.0443402	-2.0430243	-1.0798010
H	-1.6900937	-1.0917210	-2.4240118
C	0.2479113	1.6511745	-2.1942334
H	0.9991210	1.2864375	-2.9038304
H	-0.6245367	1.9753443	-2.7723888
H	0.6521303	2.5311494	-1.6811757
C	-1.2800339	0.9776851	0.4620413
H	-0.5496710	1.2700653	1.2315129
H	-1.7413776	1.9225813	0.1497478
C	-2.3715217	0.0425043	1.0621964
H	-2.1539829	-1.0036177	0.7921637

C	-3.7719993	0.3782726	0.4822269
H	-4.5262817	-0.2352613	0.9873284
H	-4.0021540	1.4267778	0.7063524
Si	-2.3485485	0.0925600	2.9661731
C	-3.8662526	0.1428169	-1.0064645
C	-3.5423829	1.1490518	-1.9282304
C	-4.2475430	-1.1125951	-1.5000452
C	-3.5733499	0.9008136	-3.3027187
H	-3.2872619	2.1432819	-1.5692012
C	-4.2914164	-1.3622774	-2.8713671
H	-4.5150679	-1.9008166	-0.7997318
C	-3.9450531	-0.3573208	-3.7789343
H	-3.3197058	1.6939687	-4.0007676
H	-4.5921549	-2.3415380	-3.2332532
H	-3.9765748	-0.5504521	-4.8472085
C	-2.7000894	1.8433270	3.5591378
H	-2.6394661	1.9016599	4.6525564
H	-1.9799753	2.5610102	3.1480219
H	-3.7043994	2.1696924	3.2643900
C	-3.6258635	-1.1107039	3.6443072
H	-3.4588041	-2.1253825	3.2624975
H	-3.5720081	-1.1538835	4.7388397
H	-4.6460147	-0.8136320	3.3752866
C	-0.6241666	-0.4389149	3.5253762
H	-0.5763246	-0.5149418	4.6180295
H	-0.3582452	-1.4227393	3.1174001
H	0.1451427	0.2807687	3.2207236
Si	3.3819380	-0.8491974	0.7160307
Si	4.8739248	0.3804334	-0.6289675
C	1.4738445	-0.2206312	-0.1045480
H	1.9160573	-0.6217882	-1.0178722
H	1.0573652	-0.9139582	0.6268045

```
H     1.7774735    0.7704516    0.2326441
C     3.3139658   -2.7007222    0.4708208
H     4.2397110   -3.1392956    0.8645611
H     2.4758818   -3.1541813    1.0116562
H     3.2412480   -2.9724230   -0.5873103
C     3.2436016   -0.3526742    2.5122158
H     4.1832805   -0.6201624    3.0127411
H     3.1019755    0.7263044    2.6327989
H     2.4315858   -0.8780303    3.0250093
C     6.6246123    0.0313893   -0.0370539
H     7.3397811    0.5937320   -0.6499631
H     6.7640848    0.3346265    1.0064045
H     6.8725811   -1.0323910   -0.1211199
C     4.4309566    2.2018792   -0.4354575
H     5.1341417    2.8145435   -1.0129302
H     3.4252424    2.4249972   -0.8112954
H     4.4877419    2.5267167    0.6093947
C     4.6205535   -0.1837202   -2.4085558
H     5.3113835    0.3561865   -3.0677746
H     4.8153179   -1.2553252   -2.5264219
H     3.6049894    0.0209177   -2.7685432
```

4a

```
45
Energy = -1167.981120672
Si   -0.1258075    2.2971349   -0.0910048
C     1.0256067    2.7818126   -1.5053258
H     1.1555027    1.9577920   -2.2171702
H     0.6102663    3.6337963   -2.0582753
H     2.0190118    3.0691698   -1.1425150
C    -1.8286240    1.9287159   -0.8020641
H    -1.7934830    1.1117583   -1.5307021
```

H	-2.5336281	1.6308191	-0.0183004
H	-2.2322796	2.8153270	-1.3072408
C	0.5431169	0.7939314	0.8422135
H	1.4613839	1.1048383	1.3636976
H	-0.1769124	0.5802939	1.6452179
C	0.7855629	-0.5009610	0.0065435
H	0.4895340	-0.3329062	-1.0417026
C	-0.0735319	-1.6913038	0.5225284
H	0.2359755	-2.6109826	0.0100442
H	0.1257256	-1.8341045	1.5911037
Si	2.6207572	-0.9946492	-0.0234419
C	-1.5553066	-1.4972753	0.3065450
C	-2.4007366	-1.0858538	1.3438370
C	-2.1138195	-1.7028894	-0.9633600
C	-3.7631181	-0.8727345	1.1188357
H	-1.9892491	-0.9364966	2.3396468
C	-3.4726648	-1.4967624	-1.1932664
H	-1.4725037	-2.0278696	-1.7803529
C	-4.3034512	-1.0758653	-0.1513023
H	-4.4014903	-0.5499526	1.9372633
H	-3.8852360	-1.6650784	-2.1846236
H	-5.3628915	-0.9129666	-0.3285817
C	3.1644170	-1.4623480	1.7218497
H	4.2304958	-1.7202081	1.7387083
H	3.0114584	-0.6344103	2.4244593
H	2.6059136	-2.3276301	2.0978710
C	2.8584585	-2.4703445	-1.1761895
H	2.5052149	-2.2403191	-2.1891243
H	3.9195081	-2.7398377	-1.2475092
H	2.3156695	-3.3559705	-0.8255594
C	3.6855227	0.4330028	-0.6421478
H	4.7450284	0.1479883	-0.6285950

H	3.4258039	0.7076547	-1.6708251
H	3.5743278	1.3279785	-0.0195484
C	-0.2492033	3.7340566	1.1277379
H	-0.6370000	4.6370438	0.6398573
H	-0.9217327	3.4905045	1.9598158
H	0.7321874	3.9796692	1.5523142

A$^+$ $Me_3SiMe.$**Ss**$^+$

39

Energy = -1227.954495997

Si	-2.8387077	0.0019661	-0.2716310
C	-2.5891258	-0.0070797	-2.1235295
C	-3.6294729	1.5705888	0.3584143
C	-3.6437216	-1.5537522	0.3718824
C	-1.0007986	-0.0029639	0.4868997
H	-2.0452635	-0.8989790	-2.4548819
H	-3.5624055	-0.0071791	-2.6284452
H	-2.0414337	0.8796704	-2.4623448
H	-4.6562908	1.6461729	-0.0187990
H	-3.6728299	1.5850710	1.4529911
H	-3.0836338	2.4587217	0.0210607
H	-3.6894886	-1.5574837	1.4664152
H	-4.6704111	-1.6237189	-0.0068396
H	-3.1051292	-2.4498168	0.0441352
H	-0.6390250	0.9295627	0.0453702
H	-0.6440160	-0.9382659	0.0472066
H	-1.2151017	-0.0015313	1.5580579
Si	1.0876587	-0.0057866	1.2258564
Si	2.2810583	0.0007711	-0.8064703
C	1.1133825	-1.5669554	2.2480934
C	1.1164350	1.5517326	2.2536721
C	1.7701603	1.5447543	-1.7559220

C	1.8100872	-1.5605500	-1.7476594
C	4.1130738	0.0257430	-0.3801129
H	2.1099733	-1.6646149	2.6981277
H	0.3804524	-1.5348041	3.0608826
H	0.9338133	-2.4590029	1.6396535
H	0.9381599	2.4464535	1.6487895
H	0.3843635	1.5183267	3.0671701
H	2.1137144	1.6457936	2.7030447
H	2.3368957	1.6022420	-2.6932871
H	0.7063283	1.5356823	-2.0209800
H	1.9740001	2.4580800	-1.1865246
H	2.3735750	-1.6057262	-2.6876251
H	2.0430728	-2.4647841	-1.1749753
H	0.7450314	-1.5835956	-2.0069990
H	4.7047778	0.0300212	-1.3037966
H	4.3801128	0.9193196	0.1945636
H	4.4034075	-0.8561748	0.2012099

CB$^-$ cage anion $CHB_{11}H_5Br_6^-$

24

Energy = -15760.35344947

B	0.0000035	1.5177695	-0.7541042
B	1.4433183	0.4690104	-0.7539884
B	0.8921364	-1.2279680	-0.7541667
B	-0.8921376	-1.2279590	-0.7541694
B	-1.4433171	0.4690188	-0.7539912
B	-0.0000011	-0.0001119	0.1971951
B	-0.0000035	-1.5112435	-2.2561153
B	-1.4371957	-0.4670143	-2.2560389
B	-0.8882165	1.2224541	-2.2560325
B	0.8882299	1.2224452	-2.2560302
B	1.4371972	-0.4670272	-2.2560374

C	0.0000019	-0.0001833	-3.0359164
H	0.0000026	-0.0000815	-4.1180767
H	-0.0000168	-2.5149921	-2.8797225
H	-2.3916817	-0.7771889	-2.8796593
H	-1.4781784	2.0342722	-2.8797334
H	1.4781825	2.0342715	-2.8797294
H	2.3916759	-0.7771971	-2.8796687
Br	-0.0000074	3.2854587	0.0966947
Br	3.1234946	1.0160923	0.0977532
Br	1.9315510	-2.6577318	0.0963668
Br	-1.9315299	-2.6577396	0.0963812
Br	-3.1235031	1.0160776	0.0977443
Br	-0.0000051	-0.0004312	2.1454774

sSMe or $Me_3SiSiMe_3$

26

Energy = -818.7660634856

Si	-0.4323589	-0.4897019	-2.5682553
Si	1.3210804	0.5267612	-1.3714003
C	-2.0687316	-0.2705306	-1.6391121
H	-2.3136043	0.7902927	-1.5093025
H	-2.8946792	-0.7413334	-2.1877286
H	-2.0240364	-0.7276189	-0.6433233
C	-0.5940028	0.2977257	-4.2834200
H	0.3294241	0.1786399	-4.8626714
H	-1.4095830	-0.1678540	-4.8516530
H	-0.8067228	1.3709115	-4.2091412
C	-0.0916884	-2.3416807	-2.7766083
H	0.8421879	-2.5152161	-3.3245192
H	-0.0060292	-2.8409836	-1.8040826
H	-0.9028784	-2.8278882	-3.3337428
C	2.9572390	0.3097224	-2.3010883

```
H     3.7832938    0.7789522   -1.7513944
H     3.2013898   -0.7512114   -2.4326720
H     2.9127498    0.7687558   -3.2959205
C     1.4840591   -0.2628579    0.3428253
H     2.2994769    0.2024712    0.9115023
H     0.5607076   -0.1455183    0.9226641
H     1.6976570   -1.3357644    0.2677901
C     0.9795859    2.3782314   -1.1605306
H     1.7910373    2.8640169   -0.6035305
H     0.8923905    2.8790377   -2.1321654
H     0.0461762    2.5500896   -0.6112166
```

Me_4Si

```
17
Energy = -449.3300287374
Si   -0.0000025    0.0000001    0.0000000
C     1.0891193   -1.0891248    1.0891137
H     1.7351314   -0.4823324    1.7356273
H     0.4823374   -1.7356330    1.7351410
H     1.7356541   -1.7351469    0.4823301
C    -1.0891233    1.0891140    1.0891237
H    -0.4823348    1.7356393    1.7351253
H    -1.7356400    1.7351282    0.4823349
H    -1.7351413    0.4823309    1.7356638
C     1.0891195    1.0891248   -1.0891137
H     1.7351320    0.4823325   -1.7356265
H     0.4823376    1.7356324   -1.7351411
H     1.7356541    1.7351478   -0.4823298
C    -1.0891232   -1.0891139   -1.0891237
H    -0.4823349   -1.7356394   -1.7351250
H    -1.7356402   -1.7351278   -0.4823350
H    -1.7351413   -0.4823308   -1.7356643
```

PhClS$^+$ complex PhCl.Me_3Si^+

25

Energy = -1101.224516507

Si	-1.6550565	0.3021888	-4.2354029
C	-1.4420186	-1.5348299	-4.2306916
H	-2.4064276	-1.9846670	-4.5005901
H	-0.6994016	-1.8602073	-4.9649719
H	-1.1658196	-1.9096442	-3.2407462
C	-1.8341610	1.1200939	-5.8853085
H	-2.8271092	0.8687812	-6.2800400
H	-1.7687139	2.2095351	-5.8072133
H	-1.0870444	0.7610304	-6.5995196
C	-2.6406256	1.0104313	-2.8399671
H	-2.5628481	2.1007754	-2.7992606
H	-2.3442649	0.5864983	-1.8760669
H	-3.6940219	0.7510832	-3.0085659
C	1.4027830	-0.9359845	-2.0978363
C	1.6672440	-1.4767595	-0.8378683
C	1.3463254	-0.7627183	0.3180510
C	0.7638394	0.5031211	0.2323659
C	0.4899236	1.0712058	-1.0134868
C	0.8174660	0.3210503	-2.1332868
H	1.6468828	-1.4722995	-3.0070965
H	2.1283457	-2.4564359	-0.7693951
H	1.5562391	-1.1932267	1.2916630
H	0.5216288	1.0595088	1.1317183
H	0.0479940	2.0565360	-1.1019237
Cl	0.4817901	1.0397800	-3.7467495

PhCl

12

Energy = -692.0290627841

C	0.0000178	1.2176812	-0.1847604
C	0.0000008	1.2081998	-1.5807588
C	-0.0000025	-0.0000022	-2.2804544
C	-0.0000131	-1.2082007	-1.5807520
C	-0.0000321	-1.2176717	-0.1847557
C	-0.0000080	0.0000061	0.4931112
H	0.0000962	2.1507779	0.3683473
H	0.0000136	2.1517284	-2.1186541
H	0.0000170	-0.0000100	-3.3662067
H	-0.0000109	-2.1517295	-2.1186463
H	-0.0001068	-2.1507665	0.3683532
Cl	0.0000065	0.0000044	2.2484092

PhHS^{+} complex PhH.Me_3Si^{+}

25

Energy = -641.5882397446

Si	-1.2839105	0.0007357	0.1892434
C	-2.1869037	-1.5542046	-0.2927939
H	-3.1665984	-1.5340555	0.2025530
H	-2.3605572	-1.6111756	-1.3720767
H	-1.6606815	-2.4557598	0.0335373
C	-2.1901021	1.5524685	-0.2971621
H	-3.1682918	1.5335442	0.2012209
H	-1.6641099	2.4562351	0.0233457
H	-2.3669983	1.6042745	-1.3761665
C	-0.6248487	0.0036818	1.9243215
H	-0.0443167	0.9007555	2.1535336
H	-0.0270566	-0.8828125	2.1504319
H	-1.5006812	-0.0062780	2.5878008
C	0.9759181	-1.2272603	-0.8123040
C	2.0553872	-1.2216818	0.0596555

C 2.5875534 -0.0033928 0.4983857

C 2.0563230 1.2175886 0.0661415

C 0.9774430 1.2286623 -0.8065490

C 0.3856295 0.0020256 -1.2176879

H 0.5653476 -2.1619184 -1.1787875

H 2.4954176 -2.1569828 0.3880138

H 3.4329344 -0.0054927 1.1795597

H 2.4964015 2.1508197 0.4002139

H 0.5684139 2.1655356 -1.1691978

H -0.2929166 0.0043785 -2.0717139

PhH

12

Energy = -232.3911849400

C 0.0000279 1.2099696 -0.1295934

C 0.0000248 1.2099188 -1.5266164

C -0.0000013 0.0000148 -2.2250746

C -0.0000310 -1.2099410 -1.5266030

C -0.0000357 -1.2098580 -0.1295551

C -0.0000076 -0.0000442 0.5689539

H 0.0000513 2.1510168 0.4138359

H 0.0000639 2.1509844 -2.0700265

H 0.0000096 -0.0000084 -3.3117459

H -0.0000412 -2.1509739 -2.0699991

H -0.0000480 -2.1509550 0.4138395

H -0.0000081 0.0000018 1.6555003

Scb0 higher **S^{+}CB^{-}** via central Br

37

Energy = -16169.58054257

B 0.3538310 -2.4965489 1.6393750

B 1.3568945 -1.8097586 0.3155170

B	2.8068229	-2.8523384	0.1156265
B	2.6932519	-4.1904107	1.3062799
B	1.1772726	-3.9706237	2.2479319
B	2.1229443	-2.5579566	1.7241288
B	2.2480257	-4.4602866	-0.3827623
B	1.2527163	-5.1438103	0.9261217
B	-0.1822623	-4.1080579	1.1271369
B	-0.0717663	-2.7855852	-0.0545605
B	1.4304975	-3.0033416	-0.9879413
C	0.5516914	-4.3310187	-0.3914774
H	0.0152176	-4.9308072	-1.1150733
H	2.8089851	-5.1774798	-1.1335032
H	1.1569971	-6.3139251	1.0449616
H	-1.2293733	-4.5926098	1.3750856
H	-1.0431012	-2.3875265	-0.5938052
H	1.4451746	-2.7481444	-2.1400213
Br	-0.7047896	-1.3538429	2.8198258
Br	1.3754275	0.1018383	-0.1036514
Br	4.5319262	-2.1139938	-0.4311419
Br	4.2893302	-4.9797017	2.1140197
Br	1.0553033	-4.5104916	4.1229859
Br	3.1684818	-1.6633425	3.2011891
Si	3.5034476	0.7523440	3.1862265
C	4.4832397	0.7719101	4.7686520
H	4.7493070	1.8171589	4.9770975
H	3.9025907	0.3976103	5.6170847
H	5.4116405	0.1988095	4.6854974
C	4.5138964	1.1230519	1.6794399
H	3.9712199	0.9177455	0.7548499
H	4.7695598	2.1912081	1.7072378
H	5.4430416	0.5456448	1.6854812
C	1.8226594	1.5134821	3.3431037

H 1.9599924 2.5992021 3.4400859

H 1.1950587 1.3177107 2.4717894

H 1.3148472 1.1488598 4.2408617

Scb

37

Energy = -16169.58217050

B -0.1370864 -2.3455440 -0.4270780

B 0.9452720 -1.3750922 -1.4656729

B 1.1140114 -2.2633231 -2.9865780

B 0.1979238 -3.7761542 -2.9257902

B -0.5944966 -3.8264134 -1.3263971

B 1.0628884 -3.1694778 -1.4666386

B -0.4338251 -2.3711675 -3.8064444

B -1.5056174 -3.3291586 -2.7653642

B -1.7098834 -2.4517304 -1.2353259

B -0.7658046 -0.9492494 -1.3216359

B 0.0270473 -0.8937034 -2.9080319

C -1.4917516 -1.6260678 -2.7094741

H -2.3476876 -1.1090043 -3.1227985

H -0.6132522 -2.3225086 -4.9714312

H -2.4143507 -3.9125591 -3.2410783

H -2.7601702 -2.4517507 -0.6970029

H -1.1851639 0.0453128 -0.8444003

H 0.1396533 0.1343131 -3.4762626

Br 0.0278848 -2.3262450 1.5192721

Br 2.3760951 -0.2509293 -0.7497794

Br 2.8619323 -2.2804249 -3.9939882

Br 0.7886559 -5.3791437 -3.8769488

Br -0.9556809 -5.5170496 -0.4173148

Br 2.6340229 -4.0849639 -0.7686165

Si 2.9266951 -0.3276819 -5.4280814

```
C     4.4242848   -0.8073515   -6.4177507
H     4.6355602    0.0014711   -7.1296732
H     5.3071772   -0.9379548   -5.7841351
H     4.2535273   -1.7253122   -6.9888626
C     1.3372369   -0.3454327   -6.3844604
H     0.4684405   -0.1403004   -5.7552677
H     1.4053256    0.4497934   -7.1394596
H     1.1883345   -1.2958183   -6.9051474
C     3.1782775    1.0935552   -4.2657262
H     2.3420375    1.2189094   -3.5734575
H     4.0968449    0.9678942   -3.6851684
H     3.2702932    2.0084525   -4.8661416
```

sScb0 higher **sS⁺CB⁻** via central Br

```
46
Energy = -16539.02020840
Si    4.6276771   -0.7790513    0.1239208
Si    2.9547983    0.8501623   -0.2305275
C     2.8192131    2.1616197    1.0853630
H     3.6873047    2.8266911    0.9786882
H     1.9092199    2.7567880    0.9825913
H     2.8465698    1.7187939    2.0851119
C     2.7551613    1.4207579   -1.9924758
H     3.6211795    2.0530875   -2.2326909
H     2.7486188    0.5723173   -2.6827375
H     1.8448423    2.0066145   -2.1369708
C     4.3353826   -2.2120510   -1.0604577
H     3.3829898   -2.7154291   -0.8619063
H     4.3318047   -1.8759530   -2.1031829
H     5.1358217   -2.9536324   -0.9479275
C     6.2647493    0.0800015   -0.2472637
H     6.4320192    0.9380629    0.4130518
```

H	7.0897419	-0.6276023	-0.0960268
H	6.3081718	0.4303357	-1.2844185
C	4.5404681	-1.3374788	1.9186708
H	3.5750095	-1.8012652	2.1499981
H	5.3240354	-2.0788800	2.1176889
H	4.6878800	-0.4972623	2.6061574
B	-1.9265128	-1.3730748	-0.5088772
B	-1.8901943	-0.9473615	1.2377412
B	-1.5918012	0.8170735	1.3736481
B	-1.4506912	1.4829292	-0.2894505
B	-1.6506551	0.1279735	-1.4528198
B	-0.8141618	-0.1219433	0.0886745
B	-2.9595795	1.6483003	0.6187223
B	-2.9956893	1.2264757	-1.1119538
B	-3.2882764	-0.5214442	-1.2464580
B	-3.4314094	-1.1821429	0.4014528
B	-3.2298058	0.1610894	1.5536411
C	-3.9444308	0.3947890	0.0277330
H	-5.0109635	0.5767023	0.0058580
H	-3.4236592	2.6707698	0.9815046
H	-3.4835519	1.9721554	-1.8856039
H	-3.9728693	-0.9401833	-2.1115848
H	-4.2092919	-2.0404673	0.6271197
H	-3.8757987	0.1938185	2.5406668
Br	-1.2960954	-3.1102646	-1.1471830
Br	-1.2204224	-2.2030671	2.5781119
Br	-0.5843529	1.5747086	2.8671800
Br	-0.3683468	3.0617886	-0.6963984
Br	-0.7088717	0.1025623	-3.1653050
Br	1.1175854	-0.7008554	0.1877711

sScb

46

Energy = -16539.02096204

Si	-0.0697289	5.8951920	-0.9350116
Si	0.2025228	3.8023234	0.1193143
C	0.4698635	3.8183281	1.9646145
H	-0.4759651	4.1242561	2.4323743
H	0.7429046	2.8348365	2.3548760
H	1.2414029	4.5378630	2.2520751
C	-0.9015807	2.4232190	-0.4818055
H	-1.9307537	2.6801910	-0.1964855
H	-0.8679269	2.3233126	-1.5703732
H	-0.6539057	1.4622898	-0.0243140
C	-0.0877662	5.6106052	-2.7950058
H	0.8520435	5.1711000	-3.1471250
H	-0.9063957	4.9451261	-3.0906626
H	-0.2257764	6.5660520	-3.3159425
C	-1.7176964	6.5818213	-0.3319187
H	-1.7239340	6.7205147	0.7548075
H	-1.8979023	7.5593312	-0.7966662
H	-2.5522735	5.9243049	-0.5992477
C	1.3595920	7.0047394	-0.4180684
H	2.3261456	6.6029443	-0.7416958
H	1.2420618	7.9959651	-0.8731270
H	1.3923284	7.1357732	0.6691579
B	4.7393115	-0.7074825	-0.8931327
B	4.8521599	-0.2975840	0.8474674
B	3.6991948	1.0237155	1.1841243
B	2.8890095	1.3858292	-0.3441090
B	3.5141918	0.3561423	-1.6385944
B	4.6161297	0.9969001	-0.3644411
B	2.0625879	0.4154894	0.8559527
B	1.9491794	0.0043998	-0.8808740

B	3.0993092	-1.3075757	-1.2055714
B	3.9186819	-1.7067522	0.3183394
B	3.2804194	-0.6451221	1.5913529
C	2.3032842	-1.1675419	0.2942369
H	1.5330130	-1.8939152	0.5174665
H	1.0899591	0.7065400	1.4572041
H	0.9046964	0.0362983	-1.4288473
H	2.8103534	-2.1622197	-1.9667134
H	4.1721454	-2.8320798	0.5688503
H	3.1089624	-1.0618638	2.6823792
Br	6.2774728	-1.3647316	-1.9027426
Br	6.5204669	-0.4793021	1.8476479
Br	4.0136940	2.3951195	2.5420913
Br	2.3920729	3.2845782	-0.8109455
Br	3.6120229	0.9758165	-3.4909700
Br	5.9611182	2.3421661	-0.7718954

sS^{+} cation $Me_2(Me_3Si)Si^{+}$

22

Energy = -778.5986558018

Si	0.3962010	-1.0834272	-0.0014619
Si	-0.1227093	1.2292579	-0.0031708
C	-0.3353611	-1.8070708	1.5651967
H	-1.4272738	-1.7297656	1.5768605
H	-0.0713951	-2.8706286	1.6191588
H	0.0598389	-1.3175416	2.4614574
C	-0.3193341	-1.8108795	-1.5733953
H	0.0871217	-1.3250950	-2.4666666
H	-0.0575417	-2.8752450	-1.6211713
H	-1.4108654	-1.7308046	-1.5975753
C	2.2788273	-1.0973002	0.0087347
H	2.6992946	-0.6166230	-0.8802137

H 2.6901511 -0.6127029 0.8998640

H 2.6050148 -2.1455818 0.0126396

C -0.3583499 2.2049658 -1.5501950

H -1.4305565 2.4467373 -1.6248805

H 0.1792843 3.1588796 -1.4947043

H -0.0650474 1.6582846 -2.4492845

C -0.3309594 2.2045465 1.5481220

H -1.4055856 2.4238461 1.6537886

H -0.0028823 1.6638285 2.4389051

H 0.1859897 3.1686656 1.4779911

S^{+} cation Me_3Si^{+}

13

Energy = -409.1603043219

Si -0.0002004 0.0000170 0.0002183

C -0.0179752 1.8305508 0.0000793

H 0.5297909 2.1915813 0.8813766

H 0.5286394 2.1912325 -0.8820935

C -1.5763471 -0.9310343 0.0001505

H -2.1631955 -0.6373460 0.8812660

H -2.1619782 -0.6386217 -0.8822273

C 1.5941859 -0.8994424 0.0000202

H 1.6332427 -1.5545118 0.8811708

H 1.6336841 -1.5529473 -0.8822939

H -1.4274137 -2.0129618 0.0009584

H 2.4567379 -0.2295752 0.0007638

H -1.0291726 2.2430598 0.0006106

TS1r0

58

Energy = -16696.34110188

B -0.4983064 0.0777455 -0.1265430

B	0.1259170	-1.3978117	0.6257744
B	-1.4274391	1.0177385	1.0535006
B	0.0623472	0.1408007	1.5557721
B	-2.2550450	0.0339223	-0.1667217
B	-1.2986557	-1.4514980	-0.4335626
Br	0.6059982	1.0642965	-1.4813729
B	-0.4463718	-1.3972327	2.3165096
B	-1.2782293	-2.3680658	1.0873138
Br	1.8299274	-2.2000731	0.0931158
B	-1.4030338	0.0934932	2.5811027
B	-2.8183081	0.0268188	1.5156250
Br	-1.5022234	2.9711731	0.9820542
Br	1.6818521	1.0931630	2.0602205
C	-2.6185568	-1.4173114	0.6339207
H	-2.9499664	0.4532551	-1.0218805
H	-1.3678614	-2.0161529	-1.4672876
B	-2.2159195	-1.4539056	2.2881122
Br	0.5906749	-2.2302271	3.7487044
H	-1.3363114	-3.5467471	1.0610222
Br	-1.4761776	0.9829869	4.3201153
H	-3.8958234	0.4350144	1.7717707
Si	0.1012176	0.1873877	-3.7982792
H	-3.5155278	-1.9401897	0.3291808
H	-2.8973905	-2.0308751	3.0601078
C	0.7510526	-1.5578802	-3.5888198
C	-1.7444284	0.5035089	-3.7772947
C	-0.4844838	-0.8549733	-6.6932972
H	-0.0609463	-2.2704602	-3.4238979
H	1.3011860	-1.8555355	-4.4864418
H	1.4333046	-1.6106453	-2.7349930
H	-2.2909114	-0.3036055	-3.2831937
H	-1.9553070	1.4405436	-3.2535209

```
H    -2.1124589    0.5982394   -4.8024761
H     0.5934133   -0.9189700   -6.8061112
H    -0.9634706    0.0575011   -7.0412179
C    -2.6956623   -1.9329935   -6.1310790
H    -3.1202999   -0.9603628   -6.4039112
C    -1.2019309   -1.8884268   -6.2342880
H    -0.6799406   -2.7969823   -5.9314277
H    -2.9789239   -2.1339168   -5.0883496
Si    1.5152975    1.8550204   -4.7291179
C     0.7725227    3.5110196   -4.2226430
H    -0.2307127    3.6408281   -4.6439831
H     0.7014437    3.6238135   -3.1359904
H     1.4044950    4.3229512   -4.6035705
C     3.2175765    1.5897580   -3.9651342
H     3.2087257    1.6758336   -2.8737135
H     3.6190123    0.6035389   -4.2240997
H     3.9095048    2.3470592   -4.3543872
C     1.6553801    1.7798881   -6.6039363
H     2.1102248    0.8463231   -6.9486811
H     0.6878863    1.9025244   -7.0997709
H     2.3038459    2.6058349   -6.9238076
C    -3.2956106   -3.0383771   -7.0209082
H    -4.3822621   -3.0788691   -6.8974533
H    -3.0731815   -2.8491881   -8.0758808
H    -2.8846434   -4.0185599   -6.7561646
```

TS1r

```
58
Energy = -16696.34158211
B    -0.4436967    0.1948618   -0.4285529
B    -0.9239703   -1.2412558    0.4989515
B    -1.6728490    0.5328209   -1.6669049
```

B	-2.1639721	-0.0599737	-0.0432628
B	-0.1573358	-0.2695721	-2.1050026
B	0.3065754	-1.3592855	-0.7730428
Br	0.4950190	1.7120134	0.4518820
B	-2.4702897	-1.8186019	-0.1810788
B	-0.9468680	-2.6073931	-0.6246972
Br	-0.4845323	-1.4627453	2.3953016
B	-2.9339703	-0.7226536	-1.5165599
B	-1.6948611	-0.8458824	-2.7759963
Br	-2.0552895	2.3568265	-2.2666343
Br	-3.1147385	1.0765569	1.2174231
C	-0.5436686	-1.9225301	-2.1313833
H	0.6770629	0.1607889	-2.8184944
H	1.4474138	-1.6294684	-0.6345717
B	-2.1820487	-2.2891648	-1.8628068
Br	-3.8035352	-2.7266973	0.9261901
H	-0.6429675	-3.7182715	-0.3640364
Br	-4.8052364	-0.3616560	-1.9589559
H	-1.8840605	-0.7888510	-3.9400407
Si	3.2714203	1.2522413	0.4383466
H	-0.0017769	-2.5460149	-2.8302543
H	-2.6970810	-3.1924012	-2.4222060
C	3.0358889	-0.2120983	1.5911363
C	3.2002652	1.1368418	-1.4338133
C	5.7800486	1.0784958	0.5105072
H	3.1193039	-1.1738431	1.0787720
H	3.8002560	-0.1666231	2.3748252
H	2.0537759	-0.1696377	2.0678786
H	2.9882330	0.1275889	-1.7923743
H	2.4234578	1.8040526	-1.8157140
H	4.1573292	1.4661470	-1.8481879
H	5.8013206	1.3273956	1.5670742

H	6.0268224	1.8726806	-0.1896183
C	5.9089507	-0.7238819	-1.2775854
H	6.0430016	0.0987785	-1.9857845
C	5.7210426	-0.2130022	0.1109476
H	5.5607960	-0.9801747	0.8682886
H	5.0122744	-1.2833612	-1.5768618
Si	3.3996235	3.4365985	1.3888055
C	2.6370081	4.6148402	0.1323195
H	3.1987858	4.6037402	-0.8086147
H	1.5933185	4.3755332	-0.0919502
H	2.6727883	5.6360086	0.5322967
C	2.4327257	3.3772964	3.0045461
H	1.3849425	3.0964680	2.8618915
H	2.8826248	2.6649864	3.7053788
H	2.4566119	4.3696351	3.4723245
C	5.1560097	4.0102464	1.7560253
H	5.6582222	3.3817772	2.4983766
H	5.7763905	4.0536359	0.8552499
H	5.0955223	5.0258189	2.1678062
C	7.1159766	-1.6839400	-1.3375124
H	7.1906025	-2.1198251	-2.3374938
H	8.0459920	-1.1518050	-1.1172588
H	7.0035992	-2.4976943	-0.6140362

TS1

65

Energy = -16888.19556456

B	-0.4358939	0.1899516	-0.4353108
B	-0.9206423	-1.2392521	0.4992163
B	-1.6649277	0.5370348	-1.6695803
B	-2.1546703	-0.0494192	-0.0424198
B	-0.1569381	-0.2776191	-2.1115293

B	0.3040312	-1.3675738	-0.7775092
Br	0.5148083	1.7033829	0.4460420
B	-2.4731509	-1.8066434	-0.1749452
B	-0.9559037	-2.6075179	-0.6214187
Br	-0.4796973	-1.4571888	2.3950840
B	-2.9338365	-0.7096897	-1.5114496
B	-1.7002909	-0.8441693	-2.7753450
Br	-2.0352947	2.3634063	-2.2685022
Br	-3.0903519	1.0973127	1.2201072
C	-0.5540116	-1.9277844	-2.1315248
H	0.6849389	0.1378937	-2.8250537
H	1.4492326	-1.6231436	-0.6510833
B	-2.1933358	-2.2823601	-1.8565529
Br	-3.8093124	-2.7018492	0.9385177
H	-0.6599021	-3.7203327	-0.3603154
Br	-4.8040308	-0.3369749	-1.9469983
H	-1.8937087	-0.7894911	-3.9386810
Si	3.2210959	1.2453156	0.4320724
H	-0.0187764	-2.5557955	-2.8314550
H	-2.7167968	-3.1830274	-2.4120435
C	3.0323734	-0.2193836	1.5943668
C	3.1924717	1.1311346	-1.4421098
C	5.7984272	1.0657257	0.4981705
H	3.1242442	-1.1897211	1.0994650
H	3.8046845	-0.1544382	2.3687080
H	2.0562622	-0.1865628	2.0848636
H	2.9948060	0.1234662	-1.8141328
H	2.4184897	1.7970230	-1.8326360
H	4.1549344	1.4733687	-1.8324878
H	5.8103459	1.3194661	1.5532579
H	6.0432714	1.8576579	-0.2047664
C	5.9213775	-0.7284571	-1.2949109

H	6.0615492	0.1002901	-1.9950695
C	7.1307598	-1.6527135	-1.3171584
C	8.4237083	-1.1173987	-1.2700562
C	6.9695468	-3.0413420	-1.3532336
C	9.5370390	-1.9571727	-1.2708486
H	8.5587993	-0.0388942	-1.2362870
C	8.0824468	-3.8841392	-1.3521298
H	5.9693161	-3.4666300	-1.3910914
C	9.3685771	-3.3434978	-1.3101520
H	10.5354251	-1.5301293	-1.2404653
H	7.9436661	-4.9609425	-1.3873119
H	10.2353962	-3.9979774	-1.3111306
C	5.7236933	-0.2227878	0.1020132
H	5.5607806	-0.9921083	0.8548374
H	5.0387123	-1.2969124	-1.6115908
Si	3.3866406	3.4254837	1.3865204
C	2.6240841	4.6132952	0.1384568
H	3.1788421	4.6008378	-0.8066145
H	1.5766116	4.3846701	-0.0793067
H	2.6714126	5.6327622	0.5415380
C	2.4260319	3.3697522	3.0064034
H	1.3753324	3.0975478	2.8679007
H	2.8732169	2.6529905	3.7043969
H	2.4589039	4.3610726	3.4757338
C	5.1463589	3.9920486	1.7463048
H	5.6513340	3.3639598	2.4869280
H	5.7628609	4.0353483	0.8430762
H	5.0881681	5.0079038	2.1579263

TS2r0^{+}

34

Energy = -935.9521624137

Si	-1.9014973	0.4988527	-0.3041726
C	-3.4879773	-0.2560633	0.2424066
H	-4.2976523	0.4473410	0.0076807
H	-3.6870707	-1.2220624	-0.2263907
H	-3.4823850	-0.3835447	1.3328134
C	-1.7708608	2.3021040	0.0419313
H	-2.4109672	2.7888046	-0.7126969
H	-2.1840040	2.5537596	1.0237293
H	-0.7613081	2.7025591	-0.0562981
C	-0.7107529	-0.3267085	-1.4507520
H	-1.2785288	-1.0986892	-1.9908034
H	-0.4562109	0.4619059	-2.1743428
C	0.6199603	-0.9432659	-0.8945426
H	1.2228787	-1.1564002	-1.7890448
C	0.3609930	-2.2910583	-0.1852024
H	0.1150404	-3.0543861	-0.9342735
H	1.2896074	-2.6185521	0.2958321
Si	1.6938053	0.2754020	0.1094081
C	0.8556787	0.7234057	1.7479997
H	1.3137746	1.6265797	2.1695374
H	-0.2232565	0.9366947	1.6929816
H	0.9759652	-0.0861311	2.4764388
C	3.3393481	-0.5445960	0.4887622
H	3.8472544	-0.8533235	-0.4323703
H	3.9994612	0.1545550	1.0158877
H	3.2195481	-1.4295902	1.1234984
C	1.9855994	1.8127610	-0.9372218
H	2.5875763	2.5433080	-0.3840610
H	2.5365176	1.5502219	-1.8484872
H	1.0632808	2.3159859	-1.2478304
C	-0.7652120	-2.2422080	0.8499162
H	-1.7468037	-2.2587818	0.3657640

H -0.7354945 -3.1050780 1.5221521

H -0.6957211 -1.3501226 1.4900835

TS2r^{+}

34

Energy = -935.9483933946

Si 0.5054442 -1.3889991 0.0603651

C 1.6492804 -1.9268142 -1.3100414

H 1.3394710 -1.5038574 -2.2708166

H 2.6858245 -1.6451469 -1.1154563

H 1.5871283 -3.0187030 -1.3824155

C 0.9923894 -1.5678453 1.8514199

H 1.9203579 -1.0398024 2.0847457

H 0.1974687 -1.2088702 2.5109675

H 1.1435922 -2.6367557 2.0434712

C -1.2647577 -1.8194707 -0.3138818

H -1.4035711 -2.3990188 -1.2242260

H -1.8581674 -2.1688560 0.5289765

C -1.2619684 -0.3354736 -0.4915139

H -1.1822144 -0.0016516 -1.5244461

C -2.2047103 0.4657531 0.3792296

H -2.1226790 0.1370856 1.4202512

H -1.9853936 1.5348974 0.3447394

Si 0.7062913 1.1790672 -0.0390065

C 0.0590731 2.2442934 -1.4346527

H 0.6046730 3.1957788 -1.4025982

H 0.2641301 1.7798217 -2.4055130

H -1.0087792 2.4686360 -1.3720537

C 0.4278640 1.8573461 1.6836816

H 0.8443735 2.8738148 1.6840214

H -0.6145544 1.9262832 1.9972953

H 0.9805682 1.2767335 2.4278757

C	2.5678368	0.9983301	-0.2975825
H	3.0575858	0.3197591	0.4057474
H	2.8232972	0.7070430	-1.3190952
H	2.9695579	2.0065436	-0.1211846
C	-3.6427908	0.2370740	-0.1299140
H	-3.9184756	-0.8193930	-0.0724285
H	-4.3372773	0.8133251	0.4878347
H	-3.7464137	0.5681962	-1.1677610

TS2^{+}

41

Energy = -1127.803357795

Si	1.8120427	-1.3565548	-0.2545831
C	2.8052208	-1.5788570	-1.8169573
H	2.4045866	-0.9635355	-2.6286549
H	3.8593620	-1.3348791	-1.6724918
H	2.7217856	-2.6307547	-2.1133677
C	2.4694566	-1.9164436	1.3985494
H	3.4265848	-1.4501121	1.6447113
H	1.7512720	-1.7061451	2.1960984
H	2.6145490	-3.0018565	1.3434348
C	0.0069621	-1.7265043	-0.5250907
H	-0.2365537	-2.0920239	-1.5205307
H	-0.4901152	-2.2726011	0.2739304
C	-0.0154450	-0.2441579	-0.3678747
H	-0.0535405	0.3154338	-1.2999019
C	-0.8484372	0.3351352	0.7643504
H	-0.6468545	-0.1999214	1.6964046
H	-0.6416090	1.3951377	0.9217883
Si	2.0212835	1.1691389	0.1796312
C	-2.3011161	0.1525518	0.3587332
C	-2.8912731	1.0394513	-0.5501880

```
C    -3.0517846   -0.9175951    0.8572205
C    -4.2158526    0.8634921   -0.9487960
H    -2.3179886    1.8775281   -0.9401567
C    -4.3774279   -1.0938531    0.4600027
H    -2.6050877   -1.6046608    1.5715612
C    -4.9606389   -0.2055193   -0.4457646
H    -4.6668937    1.5618530   -1.6475489
H    -4.9552183   -1.9212257    0.8614373
H    -5.9927248   -0.3425521   -0.7543778
C     1.2350280    2.4976180   -0.8791965
H     1.7946922    3.4262396   -0.7112434
H     1.3178741    2.2502272   -1.9431694
H     0.1856960    2.6955348   -0.6457569
C     1.9261149    1.4686348    2.0256038
H     2.3747235    2.4563631    2.1986608
H     0.9198965    1.4842979    2.4467989
H     2.5247582    0.7366158    2.5754318
C     3.8458508    1.0810197   -0.3010907
H     4.4017634    0.2798724    0.1932439
H     3.9931435    1.0104755   -1.3812745
H     4.2677392    2.0378432    0.0384907
```

TS3r

```
84
Energy = -17515.14132663
Si   -2.5874861    0.3486502    0.1164445
C    -2.5812765    0.1008927   -1.7346687
H    -2.6832124   -0.9624116   -1.9730222
H    -3.4134428    0.6445775   -2.1906465
H    -1.6554363    0.4624073   -2.1841757
C    -2.4484784   -1.1638800    1.1978070
H    -3.3112295   -1.8254714    1.0831616
```

H	-1.5421886	-1.7277936	0.9577131
H	-2.3852741	-0.8615000	2.2480779
C	-3.4460680	1.8181846	0.9184022
H	-4.1481014	1.3286212	1.6104778
H	-2.7151594	2.3104062	1.5751349
C	-4.1820047	2.9006260	0.0817337
H	-4.7009141	2.4238416	-0.7651482
C	-3.2380920	3.9826725	-0.4879857
H	-3.8451921	4.8179056	-0.8565033
H	-2.6293872	4.3867172	0.3322428
Si	-5.5538861	3.6931272	1.1555932
C	-4.7741347	4.4127890	2.7116265
H	-5.5416575	4.8618002	3.3535202
H	-4.2605922	3.6432270	3.3001184
H	-4.0440458	5.1941084	2.4695783
C	-6.4255137	5.0460922	0.1766316
H	-6.8356703	4.6567755	-0.7633387
H	-7.2607623	5.4541475	0.7590122
H	-5.7551645	5.8777041	-0.0673331
C	-6.8260070	2.3838532	1.6309466
H	-7.5933584	2.8299576	2.2754871
H	-7.3331494	1.9757677	0.7490466
H	-6.3852397	1.5457511	2.1823296
Si	-6.7632098	-1.6611770	-0.9734714
Si	-6.0011699	-3.8644409	-0.6580241
C	-5.4689623	-0.4748191	-0.2290961
H	-4.4838113	-0.8365435	-0.5454044
H	-5.5996047	0.5411266	-0.6130919
H	-5.5091294	-0.4575522	0.8630818
C	-6.8767157	-1.2670010	-2.8195891
H	-7.5989036	-1.9212763	-3.3214538
H	-7.1973615	-0.2295773	-2.9785363

H	-5.9077920	-1.3993845	-3.3157987
C	-8.4258864	-1.3293262	-0.1413021
H	-9.1952228	-2.0161684	-0.5129872
H	-8.3571003	-1.4579910	0.9449770
H	-8.7666517	-0.3054652	-0.3393218
C	-7.1248122	-5.0821954	-1.5681237
H	-6.7672565	-6.1112244	-1.4363563
H	-8.1531263	-5.0331176	-1.1910734
H	-7.1510439	-4.8704682	-2.6434428
C	-5.9651125	-4.2929416	1.1843054
H	-5.5861573	-5.3110199	1.3388608
H	-5.3176362	-3.6081946	1.7451800
H	-6.9678842	-4.2367799	1.6237649
C	-4.2461376	-4.0056933	-1.3608266
H	-3.8845736	-5.0389634	-1.2872146
H	-4.2129017	-3.7157019	-2.4176570
H	-3.5355938	-3.3728910	-0.8163171
C	-2.3203040	3.5271674	-1.6270316
H	-1.6269775	2.7435239	-1.3088642
H	-2.9058172	3.1446594	-2.4705668
H	-1.7109256	4.3615016	-1.9898213
B	1.1112874	0.1718491	-0.4682518
B	2.3628059	1.0835001	-1.3328636
B	3.8568175	0.1073187	-1.2575046
B	3.5019999	-1.3859108	-0.3351068
B	1.7896295	-1.3362226	0.1668746
B	2.7700158	0.1696344	0.1616047
B	3.5459646	-1.4190196	-2.1047091
B	2.2759632	-2.3029659	-1.2313541
B	0.7876097	-1.3359193	-1.3000984
B	1.1480093	0.1517088	-2.2254853
B	2.8508449	0.0945981	-2.7170139

C	1.9112675	-1.3209797	-2.5756377
H	1.6277737	-1.8211642	-3.4922757
H	4.3257497	-2.0138229	-2.7612254
H	2.2115566	-3.4790232	-1.3057745
H	-0.2616840	-1.8659266	-1.4114368
H	0.3529839	0.6241212	-2.9587652
H	3.1633176	0.5091213	-3.7768758
Br	-0.2651845	1.2031389	0.5685393
Br	2.3562308	3.0385478	-1.3816114
Br	5.6250652	0.9384524	-1.2407182
Br	4.8583906	-2.2795246	0.7509088
Br	1.1704048	-2.1504496	1.8342996
Br	3.2375035	1.0849811	1.8166574

TS3^{+}

41

Energy = -1127.814491283

Si	-0.3358627	1.9237986	-0.2240039
C	-2.1624186	2.1095784	-0.1950784
H	-2.4189868	3.1138281	0.1583364
H	-2.5907492	1.9321224	-1.1850791
H	-2.6129884	1.3789842	0.4921827
C	0.5683967	3.1757978	0.7847132
H	0.3756352	4.1394013	0.2856488
H	0.1675717	3.2553025	1.7998625
H	1.6468775	3.0137320	0.8203558
C	0.6030628	1.0224585	-1.5413952
H	-0.0583942	0.9764444	-2.4193653
H	1.4254158	1.7109640	-1.7869295
C	1.1920562	-0.3939386	-1.2592108
H	1.8898033	-0.5880598	-2.0878953
C	0.0893658	-1.4734677	-1.3935636

```
H    -0.2070085   -1.5319359   -2.4474245
H     0.5199097   -2.4484755   -1.1343906
Si    2.3470838   -0.4795736    0.2647187
C    -1.1562504   -1.2460702   -0.5711809
C    -1.1334055   -1.2981290    0.8337099
C    -2.3938041   -1.0510604   -1.2042479
C    -2.3032535   -1.1461308    1.5804100
H    -0.2045240   -1.5218378    1.3472494
C    -3.5674656   -0.9193368   -0.4637195
H    -2.4347052   -1.0268649   -2.2904162
C    -3.5254336   -0.9573809    0.9331060
H    -2.2619442   -1.1995543    2.6642883
H    -4.5157522   -0.7822798   -0.9749769
H    -4.4391537   -0.8534625    1.5103185
C     1.5646763    0.2673404    1.8313324
H     2.1498550    1.1110709    2.2089188
H     0.5246202    0.6181825    1.7178695
H     1.5140307   -0.4872711    2.6252031
C     2.7910762   -2.2768174    0.5758705
H     3.2168584   -2.7399033   -0.3220040
H     3.5368185   -2.3503643    1.3762311
H     1.9202571   -2.8693551    0.8796496
C     3.8817941    0.5205422   -0.1592855
H     4.5898702    0.5111137    0.6778155
H     4.3932751    0.1093330   -1.0372643
H     3.6421106    1.5694979   -0.3734422
```

TS4r

```
84
Energy = -17515.13052441
Si   -0.0584233    1.0636030   -7.0401585
C     1.5681038    1.9802975   -7.1974904
```

H	1.4632928	3.0058487	-6.8231804
H	2.3716511	1.4947466	-6.6332767
H	1.8850033	2.0416956	-8.2437026
C	-1.4471286	1.9810747	-7.8987792
H	-1.5127604	3.0209390	-7.5580646
H	-1.2753361	1.9980807	-8.9816218
H	-2.4153133	1.5001963	-7.7203860
C	0.0210904	-0.7427300	-7.5490729
H	-0.9051742	-1.2191436	-7.1931478
H	-0.0614515	-0.7687420	-8.6451745
C	1.2913563	-1.5389236	-7.1045949
H	1.9240460	-0.9043556	-6.4602294
C	2.1577644	-1.9515427	-8.3185719
H	2.9845644	-2.5840175	-7.9713384
H	1.5490148	-2.5753582	-8.9866900
Si	0.8428615	-3.0696845	-6.0670266
C	-0.2154397	-4.2371918	-7.0978069
H	-0.5301000	-5.1019377	-6.5013270
H	-1.1214719	-3.7397670	-7.4642403
H	0.3347640	-4.6139119	-7.9677731
C	2.4127731	-3.9344649	-5.4879075
H	3.0634962	-3.2422843	-4.9390132
H	2.1679283	-4.7649081	-4.8144638
H	2.9900551	-4.3450385	-6.3237905
C	-0.1319156	-2.5287355	-4.5440786
H	-0.4449601	-3.3979891	-3.9536928
H	0.4822898	-1.8997766	-3.8871630
H	-1.0389730	-1.9730084	-4.8081699
Si	-0.5171641	1.4384191	-2.8331549
Si	-1.2504415	3.6871137	-2.9675953
C	-0.4830437	1.1167788	-5.1251357
H	-0.0928830	2.1135079	-4.8942327

H	0.0925192	0.2835408	-4.7187621
H	-1.5648172	1.0123682	-5.0470790
C	1.3131578	1.0837182	-2.6247297
H	1.5402668	0.0267589	-2.7955351
H	1.9036198	1.6899621	-3.3203312
H	1.6117159	1.3350670	-1.6066519
C	-1.7674586	0.0959936	-2.4883403
H	-1.4242219	-0.8933298	-2.8018999
H	-1.9822644	0.0563927	-1.4167371
H	-2.7054459	0.3185428	-3.0097410
C	-1.7428518	4.4539924	-1.3265383
H	-2.1636173	5.4482261	-1.5233148
H	-2.5042706	3.8612117	-0.8096305
H	-0.8862153	4.5769402	-0.6568088
C	-2.7409012	3.6656148	-4.1258341
H	-3.1388062	4.6835447	-4.2199637
H	-2.4900679	3.3182957	-5.1337786
H	-3.5438048	3.0298580	-3.7361239
C	0.1749918	4.6518811	-3.7414263
H	-0.1323100	5.6930375	-3.8987010
H	1.0532162	4.6558284	-3.0865041
H	0.4840389	4.2565131	-4.7161311
B	0.2967969	0.1576818	1.1098528
B	1.5479752	0.2146609	2.3769035
B	1.2761790	-1.1699430	3.4701830
B	-0.1432889	-2.0750309	2.8740528
B	-0.7505915	-1.2492245	1.4146516
B	-0.1240760	-0.2855451	2.7896069
B	1.4925241	-2.6553511	2.5287471
B	0.2458518	-2.7029530	1.2640165
B	0.5156932	-1.3241892	0.1779023
B	1.9318063	-0.4265320	0.7734950

B	2.5325128	-1.2491843	2.2252539
C	1.8099644	-2.1114401	0.9475220
H	2.4581034	-2.7227272	0.3335553
H	1.9645463	-3.6620215	2.9266875
H	-0.1105919	-3.7382485	0.8211280
H	0.3401417	-1.4513920	-0.9829834
H	2.7037965	0.0507912	0.0180018
H	3.6952721	-1.3184158	2.4197649
Br	-0.4201547	1.8191867	0.3129342
Br	2.3114056	1.9106168	2.9916519
Br	1.7311494	-1.0881132	5.3727164
Br	-1.3402229	-3.0448718	4.0827218
Br	-2.6555714	-1.2552492	0.9482496
Br	-1.2914725	0.8218231	3.8842860
C	2.7436680	-0.7811930	-9.1157985
H	1.9576755	-0.1322432	-9.5178974
H	3.3985651	-0.1694665	-8.4859087
H	3.3335178	-1.1465159	-9.9635577

TS4

91

Energy = -17706.98597465

Si	-0.2935310	0.9042690	-6.0944310
C	1.4495540	1.4477940	-6.4642920
H	1.5951650	2.4794210	-6.1227380
H	2.1914320	0.8147600	-5.9663730
H	1.6468930	1.4156440	-7.5400660
C	-1.6049050	2.0237690	-6.8144150
H	-1.4542610	3.0638830	-6.5037580
H	-1.5665090	1.9941650	-7.9081840
H	-2.6087490	1.7112910	-6.5052390
C	-0.6988910	-0.9358930	-6.1759050

H	-1.1794260	-1.1751300	-5.2155180
H	-1.4887620	-1.0819810	-6.9231960
C	0.4697450	-1.9242770	-6.4619000
H	1.4238050	-1.4651690	-6.1563780
C	0.5816540	-2.2430430	-7.9764990
H	1.3546000	-3.0049470	-8.1255760
H	-0.3686230	-2.6738090	-8.3150530
Si	0.3125460	-3.5049160	-5.4075070
C	0.9192090	-1.0348910	-8.8159470
C	-0.0824850	-0.1950270	-9.3239310
C	2.2570040	-0.7060790	-9.0754820
C	0.2436960	0.9520930	-10.0519450
H	-1.1272780	-0.4546390	-9.1714450
C	2.5874890	0.4324920	-9.8095700
H	3.0461710	-1.3518940	-8.6970100
C	1.5801430	1.2718500	-10.2939180
H	-0.5467630	1.5884310	-10.4405720
H	3.6305080	0.6672560	-10.0028180
H	1.8355390	2.1608340	-10.8630810
C	-1.3123510	-4.3699100	-5.7988540
H	-1.4404550	-5.2569930	-5.1670690
H	-2.1713490	-3.7112150	-5.6234510
H	-1.3487110	-4.6978610	-6.8444050
C	1.7721340	-4.6394300	-5.7598420
H	2.7256010	-4.1229980	-5.5944100
H	1.7478540	-5.5130060	-5.0972140
H	1.7627320	-5.0071420	-6.7923660
C	0.3415410	-2.9873990	-3.5925400
H	0.3661410	-3.8659180	-2.9372860
H	1.2260390	-2.3806250	-3.3606170
H	-0.5497380	-2.4108640	-3.3192390
Si	-0.5482520	1.5945220	-1.9580580

Si	-1.8217930	3.5807110	-2.0105060
C	-0.4365380	1.2821760	-4.0757050
H	-0.0239760	2.2836700	-4.1731640
H	0.2199230	0.4490770	-3.8309090
H	-1.5148960	1.1398590	-4.0716770
C	1.2871600	1.7050340	-1.5966400
H	1.7529520	2.4857440	-2.2086870
H	1.4488570	1.9543270	-0.5450680
H	1.7927900	0.7544060	-1.7998440
C	-1.4144140	0.0101520	-1.4714860
H	-0.8049850	-0.8664530	-1.7115840
H	-1.6098050	-0.0073000	-0.3957740
H	-2.3759140	-0.0772030	-1.9908000
C	-2.1874860	4.3029810	-0.3158120
H	-2.7922040	5.2103500	-0.4386360
H	-2.7502420	3.6023070	0.3093450
H	-1.2701830	4.5748910	0.2160990
C	-3.4335500	3.1392420	-2.8911170
H	-4.0740410	4.0276510	-2.9532320
H	-3.2682330	2.7889610	-3.9170230
H	-3.9900460	2.3647430	-2.3515800
C	-0.8401880	4.8188730	-3.0467660
H	-1.3758090	5.7757270	-3.0786730
H	0.1517680	5.0079050	-2.6212370
H	-0.7091760	4.4897940	-4.0846990
B	0.5707220	0.3874550	2.2493250
B	1.8028690	0.6469310	3.5112660
B	1.9197510	-0.8483840	4.4782010
B	0.7585090	-2.0290690	3.8110350
B	-0.0763450	-1.2627200	2.4326260
B	0.3231880	-0.2933220	3.8858500
B	2.4786700	-2.1449270	3.4096780

```
B     1.2508340   -2.3997770    2.1520780
B     1.1358110   -0.9118560    1.1917370
B     2.2901880    0.2633180    1.8548330
B     3.1211470   -0.4993510    3.2257160
C     2.6063990   -1.4069070    1.8826410
H     3.3703160   -1.7797440    1.2131650
H     3.2005990   -3.0282450    3.7161280
H     1.1559690   -3.4504700    1.6202860
H     0.9715960   -0.9905610    0.0253250
H     2.8882400    0.9795160    1.1304760
H     4.2688710   -0.2884530    3.4093730
Br   -0.5361740    1.8772160    1.5944770
Br    2.1355750    2.4196020    4.2778130
Br    2.3922230   -0.8170320    6.3796090
Br   -0.1211630   -3.3724460    4.9345520
Br   -1.9264170   -1.7102660    1.9591480
Br   -1.0519720    0.3791000    5.0874990
```

TSa

```
63
Energy = -16988.33218460
B    -0.3341034    0.8414104   -0.3738389
B    -0.4201694    1.4253907    1.3059304
B    -0.7542302    2.1868399   -1.4634497
B     0.2090035    2.4967601    0.0159197
B    -1.9479716    0.9374181   -1.0827239
B    -1.7442074    0.4680425    0.6212886
Br    0.9597782   -0.5420302   -0.9348954
B    -0.9042574    3.1420879    1.2602599
B    -2.0981542    1.8851379    1.6270440
Br    0.7397619    0.7195131    2.7205950
B    -1.1100524    3.6138456   -0.4505720
```

B	-2.4305154	2.6469937	-1.1246915
Br	0.0148829	2.3388471	-3.2587281
Br	2.0884548	3.0088271	-0.0681387
C	-2.8997360	1.6199795	0.1499764
H	-2.4216874	0.1877507	-1.8637173
H	-2.0679810	-0.6108513	0.9783493
B	-2.5225123	3.2320395	0.5467448
Br	-0.3128993	4.4159641	2.6246038
H	-2.6624923	1.7559872	2.6563602
Br	-0.7554493	5.4357629	-1.0737093
H	-3.2151483	3.0062117	-1.9307385
Si	-0.0255831	-3.4697734	-0.1786433
H	-3.9408732	1.3286095	0.1929623
H	-3.3701967	3.9882873	0.8690092
C	1.4281140	-3.8232200	-1.3046445
C	0.3218204	-2.8455006	1.5440007
C	-1.6388913	-3.0176242	-0.9904442
C	-0.5736394	-5.5616987	0.3276808
H	1.5803078	-4.8957977	-1.4653719
H	1.2667057	-3.3592054	-2.2826786
H	2.3492875	-3.4130349	-0.8791129
H	-0.4053462	-2.0773681	1.8222634
H	0.2767997	-3.6452021	2.2909298
H	1.3138657	-2.3888186	1.5868218
H	-2.4749193	-3.1545194	-0.2970798
H	-1.6181883	-1.9708941	-1.3002483
H	-1.8118811	-3.6350122	-1.8785950
H	0.4476465	-5.5402320	0.7096485
H	-0.7162066	-5.6156335	-0.7514941
H	-1.3488229	-5.0718983	0.9173442
Si	-0.9965494	-7.4667578	0.7752170
Si	0.5611196	-8.7204393	-0.4633435

```
C    -2.7883972   -7.6926718    0.2587987
C    -0.7921568   -7.5777134    2.6392152
C     2.2957587   -8.2136818    0.0835736
C     0.3184844   -8.3200825   -2.2928361
C     0.2826485  -10.5582028   -0.1483750
H    -3.1156811   -8.7133009    0.4901988
H    -3.4470896   -6.9995213    0.7949195
H    -2.9223691   -7.5354798   -0.8171272
H     0.2354834   -7.3537896    2.9458634
H    -1.4663510   -6.8850857    3.1563240
H    -1.0283420   -8.5927310    2.9801236
H     3.0479962   -8.7847115   -0.4746777
H     2.4921464   -7.1502658   -0.0986789
H     2.4529303   -8.4069573    1.1507128
H     1.0239827   -8.8981173   -2.9024190
H    -0.6949251   -8.5681461   -2.6280591
H     0.4951438   -7.2593197   -2.5088575
H     0.9999521  -11.1538736   -0.7265066
H     0.4158678  -10.8063659    0.9106954
H    -0.7263799  -10.8662435   -0.4448402
```

TSb0

```
63
Energy = -16988.34284739
Si    1.4725426   -0.8848205   -7.7395730
C     3.1275838   -0.0251842   -7.9440006
H     3.0337476    1.0578241   -7.8009872
H     3.8627048   -0.4006188   -7.2225427
H     3.5294414   -0.1951485   -8.9499925
C     0.1914126   -0.1865542   -8.9208780
H     0.0321634    0.8854778   -8.7545057
H     0.5200061   -0.3157594   -9.9591324
```

H	-0.7738543	-0.6951564	-8.8141615
C	1.6284407	-2.7454428	-7.9166875
H	0.6659053	-3.2426420	-7.7486946
H	1.9697712	-3.0095071	-8.9247916
Si	0.1383469	0.0455637	-3.5974796
Si	-1.7286670	1.2137025	-4.5204856
C	0.8662238	-0.5244737	-5.9508399
H	0.7859486	0.5640937	-5.8607993
H	1.6090825	-0.9331527	-5.2610508
H	-0.1063867	-1.0038841	-5.8195128
C	1.7624334	0.9244153	-3.2375381
H	1.5561267	1.9371092	-2.8791408
H	2.2740565	0.3826936	-2.4372340
H	2.4486419	0.9992071	-4.0856325
C	0.0302498	-1.7796489	-3.1748908
H	1.0036030	-2.2759733	-3.2466805
H	-0.3292388	-1.9013912	-2.1489042
H	-0.6723318	-2.3041710	-3.8312229
C	-3.0105024	1.7077385	-3.2347466
H	-3.8653373	2.1345596	-3.7753824
H	-3.3735548	0.8537088	-2.6542977
H	-2.6425676	2.4680200	-2.5394272
C	-2.5837525	0.0933519	-5.7752019
H	-3.5131058	0.5838102	-6.0909201
H	-1.9903685	-0.0918820	-6.6750052
H	-2.8560100	-0.8735562	-5.3366031
C	-1.0494603	2.7646625	-5.3494555
H	-1.8846043	3.3336824	-5.7767964
H	-0.5405535	3.4118533	-4.6265666
H	-0.3488414	2.5506803	-6.1638262
B	0.4450799	0.2189969	0.3942174
B	0.8815447	1.3656989	1.6799516

```
B     0.9606687    0.4449338    3.2074284
B     0.5634792   -1.2603391    2.8488583
B     0.2348975   -1.3955235    1.1014540
B    -0.3056859    0.0579044    2.0037899
B     2.2498283   -0.7605820    3.0458274
B     1.8034994   -1.8906609    1.7501305
B     1.7231048   -0.9766274    0.2294165
B     2.1227524    0.7238264    0.5918027
B     2.4453034    0.8518154    2.3311365
C     2.8234012   -0.5589806    1.4550455
H     3.8699823   -0.7659004    1.2746084
H     2.9754007   -1.1134314    3.9077981
H     2.2300221   -2.9917054    1.7497383
H     2.0860012   -1.4743772   -0.7779897
H     2.7572193    1.3773649   -0.1584506
H     3.2983346    1.5727574    2.7139543
Br   -0.7058079    0.8319965   -1.1117343
Br    0.3548854    3.2496497    1.6006405
Br    0.5344325    1.2681256    4.9303856
Br   -0.3262963   -2.4154722    4.1534166
Br   -1.0507150   -2.6933365    0.3910107
Br   -2.1906816    0.4360704    2.3024161
H     2.3513120   -3.1535860   -7.2006807
```

TSb

```
63
Energy = -16988.33644882
Si    1.5190260   -0.9156000   -7.6677080
C     3.1730150   -0.0370930   -7.7213080
H     3.0552290    1.0464590   -7.5946680
H     3.8375930   -0.4049090   -6.9295870
H     3.6720100   -0.2096880   -8.6835380
```

C	0.2980710	-0.2401640	-8.9191020
H	0.1274290	0.8347010	-8.7788630
H	0.6844400	-0.3859110	-9.9362290
H	-0.6687390	-0.7547770	-8.8547380
C	1.6847690	-2.7786400	-7.7582910
H	0.7115340	-3.2717990	-7.6433640
H	2.0982630	-3.0741930	-8.7313640
Si	0.0967100	0.0336570	-3.8046030
Si	-1.7880790	1.2404950	-4.5974670
C	0.7753050	-0.5152620	-5.8964510
H	0.7225710	0.5778400	-5.9346540
H	1.5430200	-0.9372900	-5.2420020
H	-0.1831350	-1.0386020	-5.8958190
C	1.6601510	0.9746120	-3.3386720
H	1.3988170	1.9754430	-2.9798880
H	2.1768200	0.4567860	-2.5262130
H	2.3604620	1.0829000	-4.1752320
C	-0.0656490	-1.7439100	-3.2307660
H	0.9029790	-2.2581450	-3.2524570
H	-0.4485880	-1.7864070	-2.2059680
H	-0.7638180	-2.2905000	-3.8771550
C	-3.0364690	1.7390130	-3.2828110
H	-3.8966050	2.1965000	-3.7908510
H	-3.3984180	0.8775660	-2.7105840
H	-2.6290810	2.4746040	-2.5811180
C	-2.6501010	0.1395030	-5.8713150
H	-3.5709120	0.6384010	-6.2019780
H	-2.0414500	-0.0419780	-6.7651840
H	-2.9353970	-0.8302950	-5.4444910
C	-1.0758510	2.7757570	-5.4387720
H	-1.8966130	3.3732870	-5.8577970
H	-0.5322930	3.4069440	-4.7253150

```
H    -0.3954000    2.5365690   -6.2668450
B     0.3842050    0.2563790    0.4632660
B     0.9017960    1.3542860    1.7708740
B     1.0799800    0.3760150    3.2571380
B     0.6634290   -1.3187110    2.8603270
B     0.2268880   -1.3885030    1.1296570
B    -0.2603520    0.0284630    2.1171170
B     2.3622480   -0.8184940    2.9704120
B     1.8370140   -1.9028560    1.6632920
B     1.6572950   -0.9310060    0.1870930
B     2.0741170    0.7572910    0.5838600
B     2.5089180    0.8222450    2.3037920
C     2.8336190   -0.5549540    1.3542370
H     3.8680290   -0.7507520    1.0997740
H     3.1452910   -1.2000170    3.7719580
H     2.2689040   -3.0029430    1.5943580
H     1.9537570   -1.3913340   -0.8603780
H     2.6529140    1.4350600   -0.1934620
H     3.3875840    1.5308310    2.6604740
Br   -0.8062390    0.8970210   -0.9826470
Br    0.3634530    3.2372080    1.8058010
Br    0.7546410    1.1326720    5.0335810
Br   -0.1459420   -2.5228300    4.1754530
Br   -1.0951640   -2.6630180    0.4391110
Br   -2.1236190    0.3822870    2.5555190
H     2.3568770   -3.1584090   -6.9788550
```

TSc

```
56
Energy = -16518.75386076
B    -0.0180326    0.2566026    0.4839678
B    -0.7771638    1.5932243    1.3781300
```

B	-0.0880698	0.6062750	-1.2568613
B	0.2091756	1.9290872	-0.0832223
B	-1.2351886	-0.5257414	-0.5173390
B	-1.6606791	0.0841126	1.1020850
Br	1.5296352	-0.7104277	1.2704046
B	-1.3393110	2.7866471	0.1732787
B	-2.4810999	1.6443926	0.9013553
Br	-0.1819292	2.1001290	3.1727542
B	-0.9150272	2.1756093	-1.4539768
B	-1.7957621	0.6598398	-1.7142865
Br	1.3022523	0.0070398	-2.5016995
Br	1.9364302	2.8251567	0.0328101
C	-2.6331189	0.4020376	-0.2533745
H	-1.3104594	-1.6817482	-0.7464047
H	-2.0148403	-0.6617931	1.9453567
B	-2.5647671	1.9997866	-0.8364245
Br	-1.4106726	4.6995403	0.5752601
H	-3.3832784	1.9258508	1.6088922
Br	-0.4925198	3.3787893	-2.9373439
H	-2.2432583	0.2891902	-2.7421046
Si	1.1783953	-3.4866517	1.0896118
H	-3.5858787	-0.1075325	-0.3113031
H	-3.5255059	2.5193072	-1.2845069
C	2.8673970	-3.5313508	1.8998445
C	-0.3380428	-3.2855437	2.1606429
C	1.1313049	-3.4289796	-0.7703484
C	1.1787279	-5.9930123	1.2537032
H	3.2894344	-4.5347259	1.9935620
H	3.5614042	-2.9303465	1.3021844
H	2.8022927	-3.0939931	2.9017247
H	-1.1548454	-2.8507943	1.5772504
H	-0.6869344	-4.2280250	2.5912707

H	-0.1110646	-2.5991185	2.9811759
H	0.1314592	-3.6285150	-1.1638395
H	1.4458668	-2.4474913	-1.1355586
H	1.8195324	-4.1790695	-1.1745148
H	1.1932940	-5.8918194	2.3360700
H	2.1245460	-6.2067700	0.7623442
C	-0.1291347	-6.5138280	-0.8495776
H	0.8471936	-6.5298325	-1.3420920
C	-0.7746771	-7.8939455	-0.8925623
C	-0.0117455	-9.0343608	-0.6139633
C	-2.1368787	-8.0357995	-1.1758419
C	-0.5990496	-10.2989130	-0.6348614
H	1.0468423	-8.9327634	-0.3869250
C	-2.7271408	-9.3006231	-1.1936937
H	-2.7359379	-7.1550793	-1.3945746
C	-1.9592540	-10.4345229	-0.9233516
H	0.0043833	-11.1777698	-0.4264584
H	-3.7843714	-9.3991902	-1.4228145
H	-2.4170945	-11.4192744	-0.9394374
C	0.0101913	-6.1135444	0.5858409
H	-0.9239329	-5.9640220	1.1259011
H	-0.7755046	-5.8049913	-1.3782218

13 References

[S1] S. Lin, C.-X. Song, G.-X. Cai, W.-H. Wang, Z.-J. Shi, *J. Am. Chem. Soc.* **2008**, *130*, 12901–12903.

[S2] B. Reiter, K. Hassler, *J. Organomet. Chem.* **1994**, *467*, 21–29.

[S3] M. Weidenbrauch, W. Peter, *J. Organomet. Chem.* **1975**, *84*, 151–163.

[S4] C. A. Reed, *Acc. Chem. Res.* **2010**, *43*, 121–128.

[S5] R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow, P. Granger, *Pure Appl. Chem.* **2001**, *73*, 1795–1818.

[S6] L. Omann, B. Pudasaini, E. Irran, H. F. T. Klare, M.-H. Baik, M. Oestreich, *Chem. Sci.* **2018**, *9*, 5600–5607.

[S7] *Agilent CrysAlis PRO*, **2012**, Agilent Technologies, Yarnton, UK.

[S8] G. M. Sheldrick, *Acta Crystallogr., Sect. A.* **1990**, *46*, 467–473.

[S9] G. M. Sheldrick, *Acta Crystallogr., Sect. A.* **2008**, *64*, 112–122.

[S10] Mercury 3.9; Cambrige Crystallographic Data Center: https://www.ccdc.cam.ac.uk/solutions/csd-system/components/mercury/.

[S11] *TURBOMOLE V7.3*, 2018, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.

[S12] J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett*. **2003**, *91*, 146401.

[S13] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104–154119.

[S14] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.

[S15] F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Lett.* **1998**, *294*, 143–152.

[S16] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

[S17] A. Klamt, G. Schüürmann, *J. Chem. Soc., Perkin Trans. 2*, **1993**, 799–805.

[S18] K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119–124.

[S19] F. Weigend, *Phys. Chem. Chem. Phys.*, **2006**, *8*, 1057–1065.

[S20] P. Deglmann, K. May, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* **2004**, *384*, 103–107.

[S21] S. Grimme, *Chem. Eur. J.* **2012**, *18*, 9955–9964.

[S22] F. Eckert, A. Klamt, *AIChE J.* **2002**, *48*, 369–385.

[S23] F. Eckert and A. Klamt, COSMOtherm, Version C3.0, Release 16.01; COSMOlogic GmbH & Co. KG, Leverkusen, Germany 2015.

[S24] Y. Zhao, D. G. Truhlar, *J. Phys. Chem. A*, **2005**, *109*, 5656–5667.

[S25] F. Weigend, F. Furche, R. Ahlrichs, *J. Chem. Phys.* **2003**, *119*, 12753–12762.