Silylium-Ion-Promoted Ring-Opening Hydrosilylation and Disilylation of Unactivated Cyclopropanes

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Supporting Information

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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. Standard solvents and reagents were obtained from ABCR, Acros, Alfa Aesar, Merck, Sigma-Aldrich, or Tokyo Chemical Industry (TCI). Technical grade solvents for extraction or chromatography (cyclohexane, CH_2Cl_2, Et_2O, and *n*-pentane) were distilled prior to use. For reactions performed outside the glovebox: Et_2O and THF were dried over potassium/benzophenone, CH_2Cl_2 was dried over CaH_2, and all of them were freshly distilled prior to use. Acetonitrile (99.9%, extra dry, over molecular sieves, AcroSeal^{TM}) was purchased from Acros Organics. All of the solvents and liquid compounds (including cyclopropanes) were degassed by three freeze-pump-thaw cycles before storing in the glovebox over thermally activated 4 Å molecular sieves. Among the solvents, dry benzene and *n*-pentane were obtained from an *MBraun* solvent purification system (SPS-800). Toluene was dried over sodium/benzophenone, and distilled before the freeze-pump-thaw cycles. All hydrosilanes and dihydrosilanes were distilled, hexamethyldisilane was additionally dried over CaH_2, and distilled before the freeze-pump-thaw cycles. C_6D_6 and C_6D_5Cl were degassed by three freeze-pump-thaw cycles, and stored in the glovebox over thermally activated 4 Å molecular sieves. $Ph_3C^+[B(C_6F_5)_4]^-$ [S1] and $Ph_3C^+[CHB_{11}H_5Br_6]^-$ [S2] were synthesized according to previously reported procedures. 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. ^1H, ^{11}B, ^{13}C, ^{19}F and ^{29}Si NMR spectra were recorded in C_6D_6, C_6D_5Cl, $CDCl_3$ on a *Bruker* AV500 and AV700 instrument, respectively. 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). ^{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.[S3] Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, 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}). High resolution mass spectra (HRMS) were obtained from the *Laboratory of Mass Spectrometry* at the *Institut für Chemie*, *Technische Universität Berlin*.

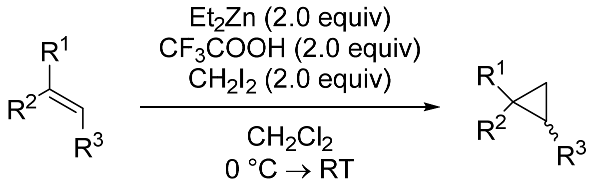
2 General Procedures

2.1 General Procedures for Synthesis of Alkenes

Styrene, all other substituted styrenes, oct-1-ene and *trans*-β-methylstyrene are commercially available and were used as received. 1-Methylene-2,3-dihydro-1*H*-indene[S4] and (*E*)-4-bromostilbene[S5] were synthesized according to literature-reported procedures.

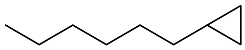
2.2 General Procedures for Synthesis of Cyclopropanes

2.2.1 Simmons–Smith Procedure



According to a literature procedure,[S6] freshly distilled CH_2Cl_2 (10 mL) was added to a flame-dried three-neck flask equipped with a stir bar, reflux condenser, and dropping funnel under N_2. A 0.9 M solution of Et_2Zn in hexane (11.1 mL, 10.0 mmol, 2.0 equiv) was carefully added via syringe, and the solution was stirred and cooled to 0 °C. A solution of TFA (0.76 mL, 10.0 mmol, 2.0 equiv) in CH_2Cl_2 (5 mL) was added very slowly and carefully via the dropping funnel; the reaction mixture was left stirring for 20 min. Next, a solution of CH_2I_2 (0.81 mL, 10.0 mmol, 2.0 equiv) in CH_2Cl_2 (5 mL) was added via the dropping funnel; the reaction mixture was stirred for 20 min. Finally, a solution of the indicated alkene (5.0 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) was added via the dropping funnel. The reaction mixture was gradually warmed to room tempera-ture and stirred for additional 3–16 h depending upon reactivity of the alkene. A general indication for the completion of the reaction was the appearance of a white precipitate. Upon completion, the reaction was quenched with saturated NH_4Cl solution, and the organic phase was separated. The aqueous phase was washed twice with 10 mL of CH_2Cl_2. The combined organic phases were washed with water and brine, dried with $MgSO_4$, and the volatiles were evaporated to dryness. The crude reaction mixture was purified by column chromatography on silica gel, eluting with *n*-pentane. Only the fractions that were free from CH_2I_2 (checked by GLC analysis) were collected [Note: If CH_2I_2 cannot be removed by initial column chromatography due to poor separation, excess CH_2I_2 can be removed by heating the crude sample with five-fold excess of DABCO in Et_2O at reflux].[S7]

The cyclopropanes **1a**[S6], **1b**–**e**, **1g**, **1i**,[S8], **1f**,[S9], **1h**,[S10] **1j**, **1n**,[S11] **1k**, **1o**,[S12], and **1p**[S13] were characterized before.

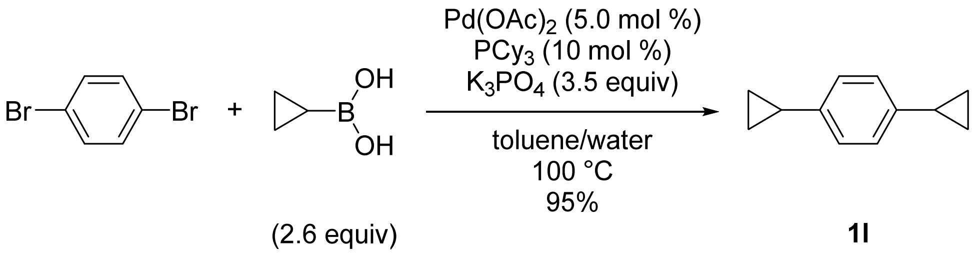


1m
C_9H_{18}
M = 126.24 g/mol

Hexylcyclopropane (1m): Prepared from oct-1-ene (4.14 mL, 26.4 mmol, 1.0 equiv) according to the Simmons–Smith procedure as described above. Purification by column chromatography on silica gel using *n*-pentane afforded **1m** as a colorless oil (0.67 g, 20% yield).

IR (ATR): ṽ = 3075, 2999, 2920, 2852, 1460, 1378, 1322, 1013, 883, 819, 722 cm^{-1}. **^{1}H NMR** (500 MHz, C_6D_6, 298 K): δ = 0.01 (m_c, 2H), 0.36–0.40 (m, 2H), 0.56–0.64 (m, 1H), 0.91 (t, *J* = 7.0 Hz, 3H), 1.16 (dd, J = 14.7, 7.1 Hz, 2H), 1.21–1.32 (m, 6H), 1.36–1.42 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 298 K): δ = 4.9, 11.3, 14.4, 23.1, 29.6, 30.1, 32.3, 35.2 ppm.

2.2.2 Suzuki Coupling Procedure



1l
$C_{12}H_{14}$
M = 158.24 g/mol

According to a modified literature procedure,[S14] 1,4-dibromobenzene (236 mg, 1.00 mmol, 1.0 equiv), cyclopropylboronic acid (223 mg, 2.60 mmol, 2.6 equiv), K_3PO_4 (743 mg, 3.50 mmol, 3.5 equiv), toluene (6.6 mL), and water (0.4 mL) were added to a three-neck flask equipped with a magnetic stir bar, and the resultant mixture was degassed. Cy_3P (28.0 mg, 0.10 mmol, 10 mol %) and $Pd(OAc)_2$ (11.2 mg, 50.0 µmol, 5.0 mol %) were added to the solution. The resultant mixture was degassed again and heated at 100 °C in an oil bath for 12 h. The reaction was cooled to room temperature and diluted with deionized water (2 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with water and brine, dried with $MgSO_4$, and the volatiles evaporated to dryness. The crude reaction mixture was purified by column chromatography on silica gel, eluting with *n*-pentane. After removal of the solvents, 1,4-dicyclopropylbenzene (**1l**, 150 mg, 95%) was obtained as a white solid. The spectroscopic data were in accordance with those reported.[S15]

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.55–0.59 (m, 4H), 0.69–0.73 (m, 4H), 1.69 (tt, J = 8.4, 5.1 Hz, 2H), 6.91 (s, 4H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6, 298 K): δ = 9.0, 15.5, 126.1, 141.1 ppm.

3 Experimental Details for the Synthesis of Deuterated Trialkylsilanes

3.1 Triethylsilane-*d*1 (2a-*d*1)

$$\mathrm{Et_3Si{-}Cl} \xrightarrow[\substack{\mathrm{Et_2O} \\ 0\,°\mathrm{C} \rightarrow \mathrm{reflux} \\ 28\%}]{\mathrm{LiAlD_4}\ (0.8\ \mathrm{equiv})} \mathrm{Et_3Si{-}D}$$

2a-*d*1
$C_6H_{15}DSi$
M = 117.29 g/mol

In a flame-dried Schlenk flask, ethyltrichlorosilane (8.66 mL, 65.6 mmol, 1.0 equiv) was dissolved in 30 mL of anhydrous Et_2O at 0 °C. Then, lithium aluminum deuteride (2.20 g, 52.5 mmol, 0.8 equiv) was added portionwise. The resulting suspension was heated at reflux overnight in an oil bath. The reaction mixture was quenched with 6 mL of deionized water followed by the addition of 20 mL of 50% (v/v) aqueous solution of HCl. The organic phase was separated, and the aqueous phase was washed with Et_2O (3 × 10 mL). The combined organic fractions were dried over anhydrous $MgSO_4$, and the solvent was evaporated under reduced pressure to get the crude product. This was purified by fractional distillation (390 mbar/80 °C) affording triethylsilane-*d*1 (**2a**-*d*1, 2.15 g, 28%) as a colorless liquid.

IR (ATR): ṽ = 2952, 2910, 2874, 2109, 1528, 1460, 1414, 1234, 1013, 967, 731 cm^{-1}. **^{1}H NMR** (500 MHz, C_6D_6, 298 K): δ = 0.54 (q, J = 7.9 Hz, 6H), 0.97 (t, J = 7.9 Hz, 9H) ppm. **^{2}H NMR** (700 MHz, C_6D_6, 298 K): δ = 3.91 (s, 1H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 298 K): δ = 2.7, 8.4 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, C_6D_6, 298 K, optimized for J = 7 Hz): δ = 0.54/–1.0, 0.97/–1.0 ppm. **HRMS** (APCI): calculated for $C_6H_{15}Si^{+\bullet}$ $[M]^{+\bullet}$: 115.0938; found 115.0936.

3.2 Triisopropylsilane-*d*1 (2b-*d*1)

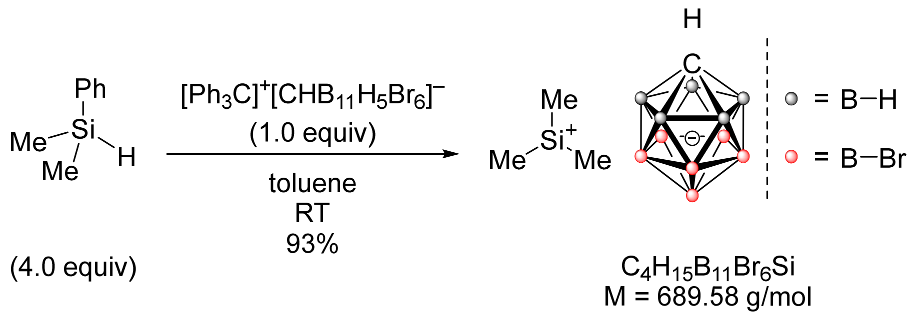
$$^{i}\mathrm{Pr_3Si{-}Cl} \xrightarrow[\substack{\mathrm{CH_3CN} \\ \mathrm{RT} \\ 68\%}]{\mathrm{NaBD_4}\ (2.0\ \mathrm{equiv})} {}^{i}\mathrm{Pr_3Si{-}D}$$

2b-*d*1
$C_9H_{21}DSi$
M = 159.37 g/mol

According to a literature procedure,[S16] in a flame-dried Schlenk flask, chlorotriisopropylsilane (1.07 mL, 5.0 mmol, 1.0 equiv) was dissolved in 1.4 mL of anhydrous acetonitrile at room temperature. Then, sodium tetrahydroborate-*d*4 (419 mg, 10.0 mmol, 2.0 equiv) was added in one portion. The resulting suspension was stirred at room temperature overnight. Before water was added, and two extractions with Et_2O were performed. Combined organic fractions were washed once with water and once with brine, before drying them over anhydrous $MgSO_4$. Crude product was filtered through short pad of silica using *n*-pentane as eluent. The solvent was removed carefully at 100 mbar/40 °C to avoid evaporation of the product, furnishing triisopropylsilane-d_1 (**2b**-d_1, 542 mg, 68%) as a colorless liquid. The compound was characterized before.[S16]

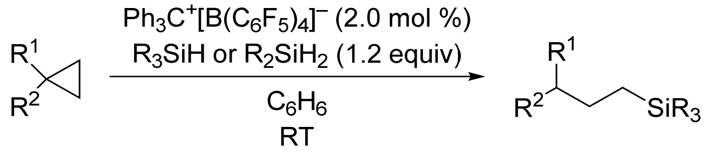
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = 0.97–1.04 (m, 3H), 1.07–1.09 (m, 18H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 298 K): δ = 10.5, 19.6 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, C_6D_6, 298 K, optimized for J = 7 Hz): δ = 0.97–1.04/10.8, 1.07–1.09/10.8 ppm.

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



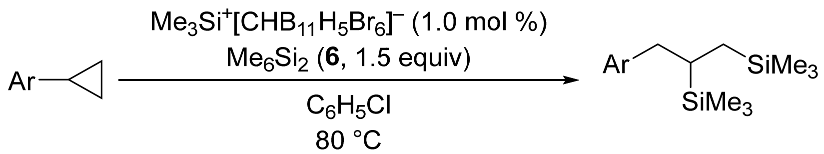
According to a literature procedure,[S17] in an argon-filled glovebox, $Ph_3C^+[CHB_{11}H_5Br_6]^-$ (50 mg, 58 µmol, 1.0 equiv) was suspended in toluene (~10 drops) and treated with dimethylphenylsilane (31 mg, 0.23 mmol, 4.0 equiv). After stirring the reaction mixture at room temperature for 24 h, *n*-pentane (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 $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (37 mg, 93%) as a white solid. This can be stored for several weeks in the glovebox freezer at –30°C without loss in reactivity. The spectroscopic data were in accordance with those reported.[S17]

5 General Procedure for the Catalytic Hydrosilylation of Cyclopropanes with Trialkylsilanes Using $Ph_3C^+[B(C_6F_5)_4]^-$ as Initiator (GP 1)



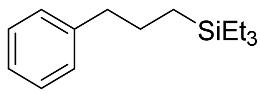
In an argon-filled glovebox, $Ph_3C^+[B(C_6F_5)_4]^-$ (2.0 mol %) was suspended in C_6H_6 (0.2–1.0 mL), and then the desired trialkylsilane or dihydrosilane (1.2 equiv) in C_6H_6 (0.1–0.6 mL) was added dropwise. After stirring at room temperature for ~1 min, the dark yellow colour of the trityl salt's solution faded, indicating the formation of respective silylium ion. Then, the solution of the indicated cyclopropane (0.2–0.5 mmol, 1.0 equiv) in C_6H_6 (0.3–1.4 mL) was added slowly and stirred for 15 min. After completion of the reaction as monitored by NMR spectroscopy, the solvent was evaporated and the oil was purified by flash column chromatography on silica gel with cyclohexane or *n*-pentane as eluent.

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



In an argon-filled glovebox, $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.0 mol %) was suspended in C_6H_5Cl (0.4 mL) in a GC-vial, and hexamethyldisilane (1.5 equiv) was added dropwise. Then, the vial was transferred to a heating reaction block with a preset temperature of 50 °C and stirred for 5 min. A solution of the cyclopropane (1.0 equiv) in C_6H_5Cl (0.4 mL) was added dropwise over a period of 10 min. at this temperature. After addition, the temperature was allowed to reach at 80 °C, and the resulting mixture was stirred for additional 16 h at this temperature. The reaction mixture was allowed to cool to room temperature, and CH_2Br_2 (0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy. Purification by flash column chromatography on silica gel using *n*-pentane as eluent afforded the 1,2-bissilylated alkanes in analytically pure form.

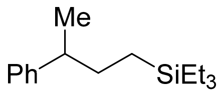
7 Experimental Details for the Catalytic Hydrosilylation of Cyclopropanes with Trialkylsilanes Using $Ph_3C^+[B(C_6F_5)_4]^-$ as Initiator



3aa
$C_{15}H_{26}Si$
M = 234.46 g/mol

Triethyl(3-phenylpropyl)silane (3aa): Prepared from cyclopropylbenzene (**1a**, 128 mg, 1.08 mmol, 1.0 equiv) and triethylsilane (151 mg, 1.30 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (20.3 mg, 22.0 µmol, 2.0 mol %) in benzene (3.0 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using cyclohexane afforded the monosilylated adduct **3aa** as a colorless oil (213 mg, 84% yield).

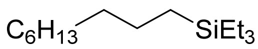
R_f = 0.62 (cyclohexane). **IR** (ATR): ṽ = 3025, 2949, 2909, 2873, 1603, 1494, 1454, 1415, 1342, 1237, 1169, 1069, 1013, 824, 720 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.51 (q, *J* = 8.0 Hz, 6H), 0.58 (m_c, 2H), 0.93 (t, *J* = 7.9 Hz, 9H), 1.60–1.66 (m, 2H), 2.64 (t, *J* = 7.7 Hz, 2H), 7.18–7.20 (m, 3H), 7.27–7.30 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = 3.5, 7.6, 11.5, 26.2, 40.4, 125.7, 128.4, 128.6, 142.9 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = 0.51/6.3, 0.58/6.3, 0.93/6.3 ppm. **HRMS** (APCI): calculated for $C_{13}H_{21}Si^{+\bullet}$ $[M–C_2H_5]^{+\bullet}$: 205.1407; found 205.1404.



3ka
$C_{16}H_{28}Si$
M = 248.49 g/mol

Triethyl(3-phenylbutyl)silane (3ka): Prepared from (1-methylcyclopropyl)benzene (**1k**, 143 mg, 1.08 mmol, 1.0 equiv) and triethylsilane (151 mg, 1.30 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (20.3 mg, 22.0 µmol, 2.0 mol %) in benzene (3.0 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using cyclohexane afforded the monosilylated adduct **3ka** as a colorless oil (204 mg, 76% yield).

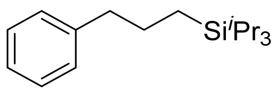
R_f = 0.73 (cyclohexane). **IR** (ATR): ṽ = 3026, 2951, 2909, 2873, 1602, 1452, 1415, 1374, 1236, 1174, 1071, 1010, 965, 905, 721 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.35–0.42 (m, 1H), 0.48–0.56 (m, 7H), 0.91 (t, *J* = 7.9 Hz, 9H), 1.26 (d, *J* = 7.0 Hz, 3H), 1.51–1.64 (m, 2H), 2.61 (m_c, 1H), 7.19–7.21 (m, 3H), 7.29–7.33 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ 3.4, 7.6, 9.4, 21.9, 32.7, 43.5, 125.9, 127.2, 128.4, 148.0 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = 0.49–0.56/6.4, 0.91/6.4 ppm. **HRMS** (APCI): calculated for $C_{14}H_{23}Si^{+\bullet}$ $[M–C_2H_5]^{+\bullet}$: 219.1564; found 219.1567.



3ma
$C_{15}H_{34}Si$
M = 242.52 g/mol

Triethyl(nonyl)silane (3ma): Prepared from hexylcyclopropane (**1m**, 136 mg, 1.08 mmol, 1.0 equiv) and triethylsilane (151 mg, 1.30 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (20.3 mg, 22.0 µmol, 2.0 mol %) in benzene (3.0 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using cyclohexane afforded the monosilylated adduct **3ma** as a colorless oil (162 mg, 62% yield).

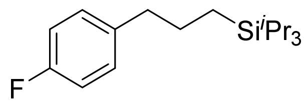
$\mathbf{R_f}$ = 0.82 (cyclohexane). **IR** (ATR): ṽ = 2918, 2873, 2099, 1459, 1414, 1377, 1236, 1171, 1073, 1013, 967, 812, 717 cm^{-1}. **^{1}H NMR** (500 MHz, C_6D_6, 298 K): δ = 0.52–0.60 (m, 8H), 0.89–0.92 (m, 3H), 0.97–1.02 (m, 9H), 1.29–1.37 (m, 14H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 298 K): δ = 3.8, 7.8, 11.8, 14.4, 23.1, 24.4, 29.8, 29.9, 30.1, 32.4, 34.4 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, C_6D_6, 298 K, optimized for *J* = 7 Hz): δ = 0.52–0.60/6.0, 0.97–1.02/6.0 ppm. **HRMS** (APCI): calculated for $C_{13}H_{29}Si^{+\bullet}$ $[M–C_2H_5]^{+\bullet}$: 213.2033; found 213.2036.



3ab
$C_{18}H_{32}Si$
M = 276.54 g/mol

Triisopropyl(3-phenylpropyl)silane (3ab): Prepared from cyclopropylbenzene (**1a**, 128 mg, 1.08 mmol, 1.0 equiv) and triisopropylsilane (206 mg, 1.30 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (20.3 mg, 22.0 µmol, 2.0 mol %) in benzene (3.0 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using cyclohexane afforded the monosilylated adduct **3ab** as a colorless oil (278 mg, 93% yield).

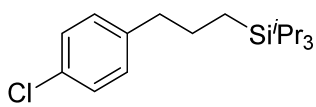
$\mathbf{R_f}$ = 0.66 (cyclohexane). **IR** (ATR): ṽ = 3025, 2935, 2862, 1602, 1458, 1382, 1244, 1174, 1069, 1010, 917, 881, 825, 725, 693 cm^{-1}. **^{1}H NMR** (500 MHz, C_6D_6, 298 K): δ = 0.62 (m_c, 2H), 0.90–0.98 (m, 3H), 1.02 (d, *J* = 6.9 Hz, 18H), 1.67 (m_c, 2H), 2.57 (t, *J* = 7.5 Hz, 2H), 7.07–7.09 (m, 1H), 7.12–7.14 (m, 2H), 7.19–7.21 (m, 2H) ppm. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.66 (m_c, 2H), 1.04 (s, 21H), 1.67–1.73 (m, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 7.18–7.21 (m, 2H), 7.28–7.31 (m, 3H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = 9.5, 11.1, 18.9, 19.0, 26.7, 40.9, 125.7, 128.4, 128.6, 142.8 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = 0.66/5.6, 1.04/5.6 ppm. **HRMS** (APCI): calculated for $C_{18}H_{32}Si^{+\bullet}$ $[M–C_3H_7]^{+\bullet}$: 233.1720; found 233.1728.



3bb
$C_{18}H_{31}FSi$
M = 294.53 g/mol

(3-(4-Fluorophenyl)propyl)triisopropylsilane (3bb): Prepared from 1-cyclopropyl-4-fluorobenzene (**1b**, 68 mg, 0.50 mmol, 1.0 equiv) and triisopropylsilane (95 mg, 0.60 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (9.2 mg, 10.0 µmol, 2.0 mol %) in benzene (1.5 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using cyclohexane afforded the monosilylated adduct **3bb** as a colorless oil (143 mg, 97% yield).

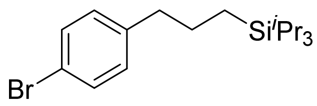
R_f = 0.76 (cyclohexane). **IR** (ATR): ṽ = 2935, 2863, 1600, 1508, 1461, 1382, 1221, 1156, 1086, 1013, 917, 881, 821, 774, 687 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.61 (m_c, 2H), 1.02 (s, 21H), 1.65 (m_c, 2H), 2.60 (t, *J* = 7.7 Hz, 2H), 6.96 (m_c, 2H), 7.12 (m_c, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = 9.3, 11.1, 19.0, 26.8, 39.9, 115.1 (d, *J* = 20.1 Hz), 129.9 (d, *J* = 7.6 Hz), 138.4 (d, *J* = 3.1 Hz), 161.4 (d, *J* = 243.3 Hz) ppm. **^{19}F{^{1}H} NMR** (471 MHz, $CDCl_3$, 298 K): δ = –118.2 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = 0.61/5.6, 1.02/5.6 ppm. **HRMS** (APCI): calculated for $C_{15}H_{24}FSi^{+\bullet}$ $[M–C_3H_7]^{+\bullet}$: 251.1626; found 251.1628.



3cb
$C_{18}H_{31}ClSi$
M = 310.98 g/mol

(3-(4-Chlorophenyl)propyl)triisopropylsilane (3cb): Prepared from 1-chloro-4-cyclopropylbenzene (**1c**, 76 mg, 0.50 mmol, 1.0 equiv) and triisopropylsilane (95 mg, 0.60 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (9.2 mg, 10.0 µmol, 2.0 mol %) in benzene (1.5 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using cyclohexane afforded the monosilylated adduct **3cb** as a colorless oil (129 mg, 83% yield).

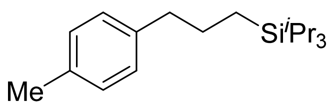
R_f = 0.79 (cyclohexane). **IR** (ATR): ṽ = 3025, 2935, 2862, 1490, 1460, 1406, 1382, 1174, 1092, 1013, 916, 881, 837, 810, 779, 729, 691 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.61 (m_c, 2H), 1.02 (s, 21H), 1.65 (m_c, 2H), 2.59 (t, *J* = 7.7 Hz, 2H), 7.10 (m_c, 2H), 7.24 (m_c, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = 9.3, 11.1, 19.0, 26.6, 40.1, 128.4, 130.0, 131.4, 141.2 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = 0.61/5.6, 1.02/5.6 ppm. **HRMS** (APCI): calculated for $C_{15}H_{24}ClSi^{+\bullet}$ $[M–C_3H_7]^{+\bullet}$: 267.1330; found 267.1331.



3db
$C_{18}H_{31}BrSi$
M = 355.44 g/mol

(3-(4-Bromophenyl)propyl)triisopropylsilane (3db): Prepared from 1-bromo-4-cyclopropylbenzene (**1d**, 98 mg, 0.50 mmol, 1.0 equiv) and triisopropylsilane (95 mg, 0.60 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (9.2 mg, 10.0 µmol, 2.0 mol %) in benzene (1.5 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using cyclohexane afforded the monosilylated adduct **3db** as a colorless oil (174 mg, 98% yield).

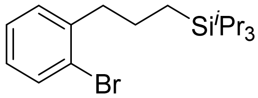
$\mathbf{R_f}$ = 0.76 (cyclohexane). **IR** (ATR): ṽ = 2935, 2862, 1888, 1460, 1243, 1174, 1072, 1010, 916, 880, 806, 772, 727, 690 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.61 (m_c, 2H), 1.02 (s, 21H), 1.65 (m_c, 2H), 2.58 (t, J = 7.5 Hz, 2H), 7.06 (m_c, 2H), 7.39 (m_c, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = 9.4, 11.1, 19.0, 26.5, 40.1, 119.5, 130.4, 131.4, 141.7 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz): δ = 0.61/5.6, 1.02/5.6 ppm. **HRMS** (APCI): calculated for $C_{15}H_{24}BrSi^{+•}$ $[M–C_3H_7]^{+•}$: 311.0825; found 311.0829.



3eb
$C_{19}H_{34}Si$
M = 290.57 g/mol

Triisopropyl(3-(*para*-tolyl)propyl)silane (3eb): Prepared from 1-cyclopropyl-4-methylbenzene (**1e**, 66 mg, 0.50 mmol, 1.0 equiv) and triisopropylsilane (95 mg, 0.60 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (9.2 mg, 10.0 µmol, 2.0 mol %) in benzene (1.5 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using cyclohexane afforded the monosilylated adduct **3eb** as a colorless oil (118 mg, 81% yield).

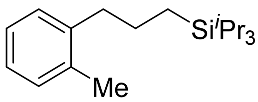
$\mathbf{R_f}$ = 0.74 (cyclohexane). **IR** (ATR): ṽ = 3017, 2933, 2862, 1513, 1460, 1382, 1243, 1173, 1070, 1011, 916, 881, 804, 717, 687 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.66 (m_c, 2H), 1.04 (s, 21H), 1.68 (m_c, 2H), 2.34 (s, 3H), 2.61 (t, J = 7.7 Hz, 2H), 7.08–7.12 (m, 4H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = 9.6, 11.1, 19.0, 21.1, 26.8, 40.5, 128.5, 129.0, 135.1, 139.8 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz): δ = 0.66/5.6, 1.04/5.6 ppm. **HRMS** (APCI): calculated for $C_{16}H_{27}Si^{+•}$ $[M–C_3H_7]^{+•}$: 247.1877; found 247.1877.



3fb
$C_{18}H_{31}BrSi$
M = 355.44 g/mol

(3-(2-Bromophenyl)propyl)triisopropylsilane (3fb): Prepared from 1-bromo-2-cyclopropylbenzene (**1f**, 99 mg, 0.50 mmol, 1.0 equiv) and triisopropylsilane (95 mg, 0.60 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (9.2 mg, 10.0 μmol, 2.0 mol %) in benzene (1.5 mL) at room temperature according to the **GP 1**. 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 cyclohexane afforded the monosilylated adduct **3fb** as a colorless oil (123 mg, 69% yield).

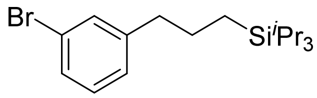
R*f* = 0.77 (cyclohexane). **IR** (ATR): ṽ = 3058, 2937, 2862, 1565, 1467, 1382, 1243, 1174, 1022, 916, 880, 746, 690 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.69 (m_c, 2H), 1.03 (s, 21H), 1.64–1.70 (m, 2H), 2.74 (t, *J* = 7.8 Hz, 2H), 7.04 (ddd, *J* = 8.0, 6.4, 2.7 Hz, 1H), 7.19–7.24 (m, 2H), 7.51–7.53 (m, 1H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = 9.6, 11.1, 19.0, 25.2, 41.1, 124.6, 127.4, 127.5, 130.5, 132.9, 142.0 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = 0.69/5.6, 1.03/5.6 ppm. **HRMS** (APCI): calculated for $C_{15}H_{24}BrSi^{+\bullet}$ $[M–C_3H_7]^{+\bullet}$: 311.0825; found 311.0829.



3gb
$C_{19}H_{34}Si$
M = 290.57 g/mol

Triisopropyl(3-(*ortho*-tolyl)propyl)silane (3gb): Prepared from 1-cyclopropyl-2-methylbenzene (**1g**, 66 mg, 0.50 mmol, 1.0 equiv) and triisopropylsilane (95 mg, 0.60 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (9.2 mg, 10.0 μmol, 2.0 mol %) in benzene (1.5 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using cyclohexane afforded the monosilylated adduct **3gb** as a colorless oil (124 mg, 85% yield).

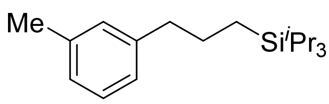
R*f* = 0.71 (cyclohexane). **IR** (ATR): ṽ = 3015, 2936, 2862, 1603, 1459, 1381, 1245, 1174, 1048, 1011, 916, 881, 722, 690 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.72 (m_c, 2H), 1.04 (s, 21H), 1.61–1.67 (m, 2H), 2.32 (s, 3H), 2.63 (t, *J* = 7.9 Hz, 2H), 7.09–7.15 (m, 4H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = 9.9, 11.1, 19.0, 19.4, 25.5, 38.5, 125.9, 126.0, 129.0, 130.2, 135.9, 141.0 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = 0.72/5.6, 1.04/5.6 ppm. **HRMS** (APCI): calculated for $C_{16}H_{27}Si^{+\bullet}$ $[M–C_3H_7]^{+\bullet}$: 247.1877; found 247.1879.



3hb
$C_{18}H_{31}BrSi$
M = 355.44 g/mol

(3-(3-Bromophenyl)propyl)triisopropylsilane (3hb): Prepared from 1-bromo-3-cyclopropylbenzene (**1h**, 99 mg, 0.50 mmol, 1.0 equiv) and triisopropylsilane (95 mg, 0.60 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (9.2 mg, 10.0 µmol, 2.0 mol %) in benzene (1.5 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using cyclohexane afforded the monosilylated adduct **3hb** as a colorless oil (148 mg, 83% yield).

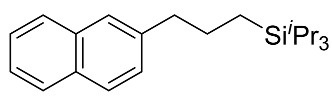
R*f* = 0.77 (cyclohexane). **IR** (ATR): ṽ = 3058, 2935, 2862, 1566, 1462, 1382, 1244, 1167, 1070, 996, 917, 880, 774, 728, 689 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.62 (m_c, 2H), 1.02 (s, 21H), 1.63–1.69 (m, 2H), 2.60 (t, *J* = 7.7 Hz, 2H), 7.09–7.16 (m, 2H), 7.30–7.33 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = 9.4, 11.1, 19.0, 26.5, 40.4, 122.5, 127.3, 128.9, 129.9, 131.7, 145.1 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = 0.62/5.6, 1.02/5.6 ppm. **HRMS** (APCI): calculated for $C_{15}H_{24}BrSi^{+\bullet}$ $[M–C_3H_7]^{+\bullet}$: 311.0825; found 311.0827.



3ib
$C_{19}H_{34}Si$
M = 290.57 g/mol

Triisopropyl(3-(*meta*-tolyl)propyl)silane (3ib): Prepared from 1-cyclopropyl-3-methylbenzene (**1i**, 66 mg, 0.50 mmol, 1.0 equiv) and triisopropylsilane (95 mg, 0.60 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (9.2 mg, 10.0 µmol, 2.0 mol %) in benzene (1.5 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using cyclohexane afforded the monosilylated adduct **3ib** as a colorless oil (116 mg, 80% yield).

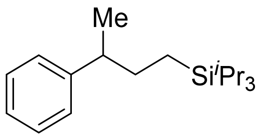
R*f* = 0.74 (cyclohexane). **IR** (ATR): ṽ = 2935, 2862, 1608, 1460, 1382, 1244, 1172, 1070, 1011, 917, 880, 776, 691 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.66 (m_c, 2H), 1.04 (s, 21H), 1.65–1.71 (m, 2H), 2.35 (s, 3H), 2.61 (t, *J* = 7.7 Hz, 2H), 6.99–7.01 (m, 3H), 7.17–7.20 (m, 1H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = 9.6, 11.1, 19.0, 21.6, 26.7, 40.9, 125.6, 126.5, 128.3, 129.4, 137.9, 142.8 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = 0.66/5.6, 1.04/5.6 ppm. **HRMS** (APCI): calculated for $C_{16}H_{27}Si^{+\bullet}$ $[M–C_3H_7]^{+\bullet}$: 247.1877; found 247.1879.



3jb
$C_{22}H_{34}Si$
M = 326.60 g/mol

Triisopropyl(3-(naphthalen-2-yl)propyl)silane (3jb): Prepared from 2-cyclopropylnaphthalene (**1j**, 84 mg, 0.50 mmol, 1.0 equiv) and triisopropylsilane (95 mg, 0.60 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (9.2 mg, 10.0 µmol, 2.0 mol %) in benzene (1.5 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using cyclohexane afforded the monosilylated adduct **3jb** as a colorless oil (155 mg, 95% yield).

$\mathbf{R_f}$ = 0.66 (cyclohexane). **IR** (ATR): ṽ = 3050, 2934, 2861, 1632, 1599, 1507, 1460, 1382, 1242, 1173, 1070, 1012, 880, 850, 812, 739, 704 cm^{-1}. ^{1}**H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.70 (m_c, 2H), 1.03 (s, 21H), 1.78 (m_c, 2H), 2.81 (t, *J* = 7.6 Hz, 2H), 7.34 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.44 (dddd, *J* = 14.6, 8.2, 6.9, 1.4 Hz, 2H), 7.62 (s, 1H), 7.77–7.82 (m, 3H) ppm. ^{13}**C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = 9.6, 11.1, 19.0, 26.5, 41.0, 125.1, 125.9, 126.6, 127.6, 127.7, 127.9, 132.1, 133.8, 140.3 ppm. ^{1}**H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = 0.70/5.6, 1.03/5.6 ppm. **HRMS** (APCI): calculated for $C_{19}H_{27}Si^{+\bullet}$ $[M–C_3H_7]^{+\bullet}$: 283.1877; found 283.1880.

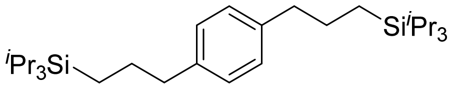


3kb
$C_{19}H_{34}Si$
M = 290.57 g/mol

Triisopropyl(3-phenylbutyl)silane (3kb): Prepared from (1-methylcyclopropyl)benzene (**1k**, 143 mg, 1.08 mmol, 1.0 equiv) and triisopropylsilane (206 mg, 1.30 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (20.3 mg, 22.0 µmol, 2.0 mol %) in benzene (3.0 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using cyclohexane afforded the monosilylated adduct **3kb** as a colorless oil (292 mg, 93% yield).

$\mathbf{R_f}$ = 0.76 (cyclohexane). **IR** (ATR): ṽ = 3026, 2938, 2863, 1602, 1459, 1381, 1243, 1177, 1072, 1011, 881, 729, 695 cm^{-1}. ^{1}**H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.45 (ddd, *J* = 14.6, 12.7, 4.7 Hz, 1H), 0.60 (ddd, *J* = 14.6, 12.9, 4.9 Hz, 1H), 1.00–1.01 (m, 21H), 1.26 (d, *J* = 6.9 Hz, 3H), 1.56–1.69 (m, 2H), 2.59 (sext, *J* = 6.9 Hz, 1H), 7.17–7.19 (m, 3H), 7.28–7.31 (m, 2H) ppm. ^{13}**C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = 7.4, 11.1, 19.0, 21.8, 33.2, 43.9, 125.9, 127.3, 128.4, 147.9 ppm. ^{1}**H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7

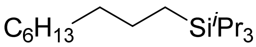
Hz): δ = 0.45/5.8, 0.60/5.8, 1.00–1.01/5.8 ppm. **HRMS** (APCI): calculated for $C_{16}H_{27}Si^{+\bullet}$ [M–C_3H_7]$^{+\bullet}$: 247.1877; found 247.1875.



3lb
$C_{30}H_{58}Si_2$
M = 474.96 g/mol

1,4-Bis(3-(triisopropylsilyl)propyl)benzene (3lb): Prepared from 1,4-dicyclopropylbenzene (**1l**, 32 mg, 0.20 mmol, 1.0 equiv) and triisopropylsilane (38 mg, 0.24 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (3.7 mg, 4.0 µmol, 2.0 mol %) in benzene (0.6 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using cyclohexane afforded the monosilylated adduct **3lb** as a colorless oil (89 mg, 94% yield).

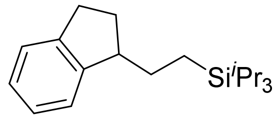
R*f* = 0.82 (cyclohexane). **IR** (ATR): ṽ = 2933, 2862, 1511, 1460, 1382, 1243, 1172, 1048, 1011, 916, 880, 810, 689 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.64 (m_c, 4H), 1.02 (s, 42H), 1.63–1.70 (m, 4H), 2.60 (t, *J* = 7.7 Hz, 4H), 7.09 (s, 4H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = 8.5, 10.1, 18.0, 25.7, 39.5, 127.4, 139.0 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = 0.64/5.5, 1.02/5.5 ppm. **HRMS** (APCI): calculated for $C_{27}H_{51}Si_2^{+\bullet}$ [M–C_3H_7]$^{+\bullet}$: 431.3524; found 431.3529.



3mb
$C_{18}H_{40}Si$
M = 284.60 g/mol

Triisopropyl(nonyl)silane (3mb): Prepared from hexylcyclopropane (**1m**, 136 mg, 1.08 mmol, 1.0 equiv) and triisopropylsilane (206 mg, 1.30 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (20.3 mg, 22.0 µmol, 2.0 mol %) in benzene (3.0 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using cyclohexane afforded the monosilylated adduct **3mb** as a colorless oil (261 mg, 85% yield).

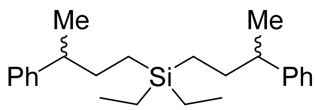
R*f* = 0.82 (cyclohexane). **IR** (ATR): ṽ = 3026, 2921, 2861, 1602, 1460, 1380, 1244, 1171, 1070, 917, 881, 731, 696 cm^{-1}. **^{1}H NMR** (500 MHz, C_6D_6, 298 K): δ = 0.52–0.65 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H), 0.93–1.00 (m, 3H), 1.01–1.06 (m, 18H), 1.14–1.36 (m, 9H), 1.51–1.73 (m, 3H), 1.76–1.83 (m, 1H), 2.40–2.46 (m, 1H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 298 K): δ = 7.6, 11.3, 14.3, 19.1, 23.1, 28.2, 30.0, 32.2, 32.3, 36.9, 50.6 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, C_6D_6, 298 K, optimized for *J* = 7 Hz): δ = 0.52–0.65/5.8, 1.01–1.06/5.8 ppm. **HRMS** (APCI): calculated for $C_{18}H_{40}Si^{+\bullet}$ [M]$^{+\bullet}$: 284.2894; found 284.2848.



3nb
$C_{19}H_{34}Si$
M = 302.58 g/mol

(2-(2,3-Dihydro-1*H*-inden-1-yl)ethyl)triisopropylsilane (3nb): Prepared from 2',3'-dihydrospiro[cyclopropane-1,1'-indene] (**1n**, 72 mg, 0.50 mmol, 1.0 equiv) and triisopropylsilane (95 mg, 0.60 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (9.2 mg, 10.0 µmol, 2.0 mol %) in benzene (1.5 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using cyclohexane afforded the monosilylated adduct **3nb** as a colorless oil (107 mg, 71% yield).

R_f = 0.73 (cyclohexane). **IR** (ATR): ṽ = 3018, 2937, 2862, 1602, 1459, 1382, 1243, 1182, 1048, 1013, 917, 881, 810, 744, 694 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.70 (m_c, 2H), 1.05 (s, 21H), 1.46 (m_c, 1H), 1.71 (m_c, 1H), 1.91 (tt, J = 13.4, 4.5 Hz, 1H), 2.31 (m_c, 1H), 2.80–2.95 (m, 2H), 3.06 (qd, J = 7.8, 4.6 Hz, 1H), 7.12–7.18 (m, 2H), 7.20–7.22 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = 7.1, 11.1, 19.0, 29.7, 31.4, 31.5, 48.6, 123.7, 124.6, 126.1, 126.3, 144.3, 147.7 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = 0.70/6.0, 1.05/6.0 ppm. **HRMS** (APCI): calculated for $C_{17}H_{27}Si^{+\bullet}$ $[M–C_3H_7]^{+\bullet}$: 259.1877; found 259.1878.

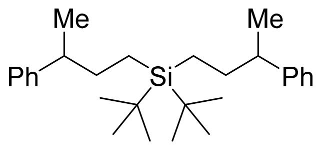


4kf
$C_{24}H_{36}Si$
M = 352.64 g/mol

Diethylbis(3-phenylbutyl)silane (4kf): Prepared from (1-methylcyclopropyl)benzene (**1k**, 90 mg, 0.50 mmol, 1.0 equiv) and diethylsilane (53 mg, 0.60 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (9.2 mg, 10.0 µmol, 2.0 mol %) in benzene (1.5 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using cyclohexane afforded the monosilylated adduct **4kf** as a colorless oil (48 mg, 54% yield).

R_f = 0.49 (cyclohexane). **IR** (ATR): ṽ = 3025, 2952, 2911, 2872, 1738, 1601, 1491, 1451, 1414, 1373, 1233, 1174, 1071, 1008, 959, 905, 757, 722, 696 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.29–0.36 (m, 2H), 0.42–0.49 (m, 6H), 0.84 (t, *J* = 7.9 Hz, 6H, two overlapping triplets Δδ = 0.003 ppm), 1.23 (d, *J* = 6.9, 6H), 1.43–1.56 (m, 4H), 2.57 (sext, *J* = 6.9 Hz, 2H), 7.15–7.20 (m, 6H), 7.29 (t, *J* = 7.5 Hz, 4H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = 3.5, 3.6, 7.5, 9.6, 21.9, 22.0, 32.6, 43.3, 43.4, 125.9, 127.2, 128.4, 147.9 ppm. **^{1}H/^{29}Si HMQC NMR**

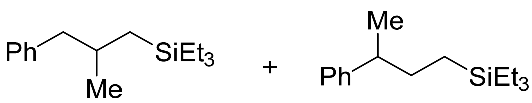
(500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz): δ = 0.29–0.36/5.6, 0.44–0.49/5.6, 0.84/5.6 ppm. **HRMS** (APCI): calculated for $C_{22}H_{31}Si^{+\bullet}$ $[M–C_2H_5]^{+\bullet}$: 323.2190; found 323.2194.



4kg
$C_{28}H_{44}Si$
M = 408.75 g/mol

Di-*tert*-butylbis(3-phenylbutyl)silane (4kg): Prepared from (1-methylcyclopropyl)benzene (**1k**, 26 mg, 0.20 mmol, 1.0 equiv) and di-*tert*-butylsilane (35 mg, 0.24 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (3.7 mg, 4.0 µmol, 2.0 mol %) in benzene (0.6 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using *n*-pentane afforded the monosilylated adduct **4kg** as a colorless oil (15 mg, 37% yield).

R*f* = 0.52 (cyclohexane). **IR** (ATR): ṽ = 3060, 3025, 2926, 2854, 1601, 1451, 1363, 1286, 1182, 1074, 1028, 933, 906, 819, 758, 696 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.42–0.49 (m, 2H), 0.56–0.64 (m, 2H), 0.89–0.92 (m, 18H), 1.25 (d, J = 6.9, 6H), 1.57–1.70 (m, 4H), 2.56 (m_c, 2H), 7.15–7.22 (m, 6H), 7.27–7.31 (m, 4H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = 8.5, 20.1, 20.2, 21.7, 21.9, 29.2, 29.3, 33.9, 34.0, 43.9, 44.0, 125.9, 127.2, 127.3, 128.4, 128.6, 129.1, 147.8 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz): δ = 0.89–0.92/6.3 ppm. **HRMS** (APCI): calculated for $C_{24}H_{35}Si^{+\bullet}$ $[M–C_4H_9]^{+\bullet}$: 351.2503; found 351.2505.

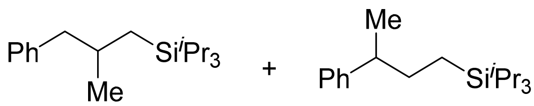


3oa **3oa'**

3oa, 3oa'
$C_{16}H_{28}Si$
M = 248.49 g/mol

Triethyl(2-methyl-3-phenylpropyl)silane (3oa) & triethyl(3-phenylbutyl)silane (3oa'): Prepared from (2-methylcyclopropyl)benzene (**1o** (*trans*:*cis* = 44:56), 81 mg, 0.60 mmol, 1.0 equiv) and triethylsilane (84 mg, 0.72 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (11.1 mg, 12.0 µmol, 2.0 mol %) in benzene (1.5 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using cyclohexane afforded the monosilylated adduct **3oa** & **3oa'** as a colorless oil (65 mg, 43% yield).

R*f* = 0.80 (cyclohexane). **IR** (ATR): ṽ = 3025, 2950, 2908, 2873, 1602, 1454, 1415, 1374, 1236, 1076, 1013, 969, 840, 737 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.49–0.55 (m, 8H), 0.69 (dd, J = 14.8, 4.7 Hz, 1H), 0.87–0.93 (m, 14H), 1.88 (m_c, 1H), 2.40 (dd, J = 13.2, 8.3 Hz, 1H), 2.62 (dd, J = 13.2, 6.0 Hz, 1H), 7.13–7.19 (m, 3H), 7.26–7.31 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): (Only major peaks) δ = 4.2, 7.6, 19.7, 22.9, 31.8, 47.7, 125.8, 128.2, 129.3, 141.9 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz): δ = 0.49–0.55/5.6, 0.69/5.6, 0.87–0.93/5.6 ppm. **HRMS** (APCI): calculated for $C_{14}H_{23}Si^{+•}$ [M–C_2H_5]$^{+•}$: 219.1564; found 219.1566.

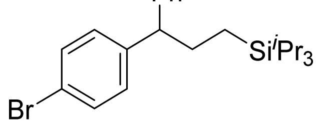


3ob **3ob'**

3ob, 3ob'
$C_{19}H_{34}Si$
M = 290.57 g/mol

Triisopropyl(2-methyl-3-phenylpropyl)silane (3ob) & triisopropyl(3-phenylbutyl)silane (3ob'): Prepared from (2-methylcyclopropyl)benzene (**1o** (*trans*:*cis* = 44:56), 81 mg, 0.60 mmol, 1.0 equiv) and triisopropylsilane (114 mg, 0.72 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (11.1 mg, 12.0 μmol, 2.0 mol %) in benzene (1.5 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using cyclohexane afforded the mixture of monosilylated adducts **3ob** & **3ob'** as a colorless oil (172 mg, 97% yield).

R$_f$ = 0.51 (cyclohexane). **IR** (ATR): ṽ = 3025, 2939, 2863, 1602, 1458, 1381, 1242, 1177, 1073, 1013, 881, 730, 696 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.45 (m$_c$, 1H), 0.54–0.63 (m, 2H), 0.78 (dd, J = 15.0, 4.4 Hz, 1H), 0.93 (d, J = 6.5 Hz, 3H), 1.00 (d, J = 1.1 Hz, 21H), 1.04 (d, J = 2.2 Hz, 17H), 1.26 (d, J = 6.9 Hz, 3H), 1.56–1.69 (m, 2H), 1.98 (m$_c$, 1H), 2.41 (dd, J = 13.2, 8.5 Hz, 1H), 2.59 (sext, J = 6.9 Hz, 1H), 2.68 (dd, J = 13.2, 5.8 Hz, 1H), 7.14–7.20 (m, 5H), 7.26–7.31 (m, 4H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): Peaks for **3ob**: δ = 11.8, 17.8, 19.0, 19.1, 23.2, 31.7, 48.1, 125.8, 128.2, 129.4, 141.9; Peaks for **3ob':** δ = 7.4, 11.1, 18.9, 21.8, 33.2, 43.9, 125.9, 127.3, 128.4, 147.9 ppm. **^{29}Si-DEPT NMR** (99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz): 5.4, 6.0. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz): δ = 0.45/4.9, 0.54–0.63/4.9, 0.78/4.9, 1.00/4.9, 1.04/4.9 ppm. **HRMS** (APCI): calculated for $C_{16}H_{27}Si^{+•}$ [M–C_3H_7]$^{+•}$: 247.1877; found 247.1878.

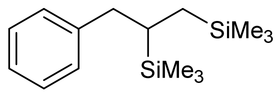


3pb'
$C_{24}H_{35}BrSi$
M = 431.53 g/mol

(3-(4-Bromophenyl)-3-phenylpropyl)triisopropylsilane (3pb'): Prepared from 1-bromo-4-(2-phenylcyclopropyl)benzene (**1p** (*trans*:*cis* ≥ 98:2), 137 mg, 0.50 mmol, 1.0 equiv) and triisopropylsilane (95 mg, 0.60 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (9.2 mg, 10.0 µmol, 2.0 mol %) in benzene (1.5 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using cyclohexane afforded the monosilylated adduct **3pb'** as a colorless oil (151 mg, 70% yield).

R_f = 0.65 (cyclohexane). **IR** (ATR): ṽ = 3024, 2935, 2862, 1598, 1484, 1461, 1382, 1244, 1169, 1072, 1009, 915, 880, 814, 750, 696 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.54 (m_c, 2H), 1.00–1.01 (m, 21H), 2.06 (m_c, 2H), 3.75 (t, *J* = 7.6 Hz, 1H), 7.11 (m_c, 2H), 7.17–7.21 (m, 3H), 7.26–7.30 (m, 2H), 7.40 (m_c, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = 8.2, 11.1, 19.0, 30.6, 55.1, 119.9, 126.4, 128.0, 128.6, 129.8, 131.6, 144.3, 144.7 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = 0.54/5.9, 1.00–1.01/5.9 ppm. **HRMS** (APCI): calculated for $C_{21}H_{28}BrSi^{+\bullet}$ $[M–C_3H_7]^{+\bullet}$: 387.1138; found 387.1147.

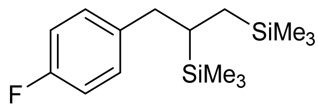
8 Experimental Details for the Catalytic 1,2-Disilylation of Cyclopropanes with Hexamethyldisilane Using $Me_3Si^+[CHB_{11}H_5Br_6]^-$ as Initiator



7a
$C_{15}H_{28}Si_2$
M = 264.56 g/mol

(3-Phenylpropane-1,2-diyl)bis(trimethylsilane) (7a): Prepared from cyclopropylbenzene (**1a**, 24 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (44 mg, 0.30 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 2.0 µmol, 1.0 mol %) in chlorobenzene (0.8 mL) at 80°C for 16 h according to **GP 2**. CH_2Br_2 (7.0 µL, 0.10 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (67%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **7a** as a colorless oil (33 mg, 62% yield).

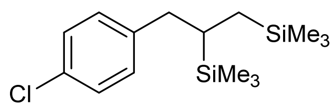
$\mathbf{R_f}$ = 0.81 (cyclohexane). **IR** (ATR): ṽ = 3063, 3025, 2951, 2894, 1937, 1798, 1602, 1494, 1453, 1410, 1245, 1112, 1069, 1030, 976, 828, 742, 696 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = –0.14 (s, 9H), –0.09 (s, 9H), 0.44 (dd, *J* = 15.2, 8.5 Hz, 1H), 0.68 (dd, *J* = 15.2, 3.8 Hz, 1H), 1.07 (m_c, 1H), 2.64 (dd, *J* = 7.8, 4.6 Hz, 2H), 7.14–7.18 (m, 3H), 7.24–7.27 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –2.6, –2.5, –0.8, –0.7, 16.3, 22.6, 39.9, 125.9, 128.3, 129.2, 143.0 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = –0.09/1.5, –0.14/4.0 ppm. **HRMS** (APCI): calculated for $C_{14}H_{25}Si_2^{\bullet+}$ $[M–CH_3]^{+\bullet}$: 249.1489; found 249.1491.



7b
$C_{15}H_{27}FSi_2$
M = 282.55 g/mol

(3-(4-Fluorophenyl)propane-1,2-diyl)bis(trimethylsilane) (7b): Prepared from 1-cyclopropyl-4-fluorobenzene (**1b**, 27 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (44 mg, 0.30 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 2.0 µmol, 1.0 mol %) in chlorobenzene (0.8 mL) at 80°C for 16 h according to **GP 2**. CH_2Br_2 (7.0 µL, 0.10 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (59%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **7b** as a colorless oil (25 mg, 45% yield). The spectroscopic data were in accordance with those reported.[S18]

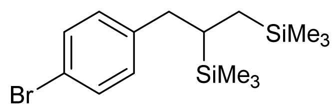
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = –0.14 (s, 9H), –0.09 (s, 9H), 0.40 (dd, *J* = 15.3, 8.4 Hz, 1H), 0.67 (dd, *J* = 15.4, 3.8 Hz, 1H), 1.00 (qd, *J* = 8.0, 3.8 Hz, 1H), 2.60 (d, *J* = 7.8 Hz, 2H), 6.92–6.97 (m, 2H), 7.10–7.13 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –2.6, –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.



7c
$C_{15}H_{27}ClSi_2$
M = 299.00 g/mol

(3-(4-Chlorophenyl)propane-1,2-diyl)bis(trimethylsilane) (7c): Prepared from 1-chloro-4-cyclopropylbenzene (**1c**, 31 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (44 mg, 0.30 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 2.0 µmol, 1.0 mol %) in chlorobenzene (0.8 mL) at 80°C for 16 h according to **GP 2**. CH_2Br_2 (7.0 µL, 0.10 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (53%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **7c** as a colorless oil (29 mg, 48% yield). The spectroscopic data were in accordance with those reported.[S18]

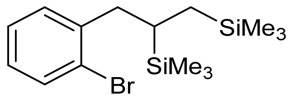
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = –0.14 (s, 9H), –0.09 (s, 9H), 0.39 (dd, *J* = 15.3, 8.4 Hz, 1H), 0.67 (dd, *J* = 15.2, 3.8 Hz, 1H), 1.01 (qd, *J* = 7.9, 3.8 Hz, 1H), 2.59 (d, *J* = 7.9 Hz, 2H), 7.08–7.11 (m, 2H), 7.21–7.23 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –2.5, –0.8, 16.2, 22.6, 39.3, 128.4, 130.5, 131.5, 141.5 ppm.



7d
$C_{15}H_{27}BrSi_2$
M = 343.46 g/mol

(3-(4-Bromophenyl)propane-1,2-diyl)bis(trimethylsilane) (7d): Prepared from 1-bromo-4-cyclopropylbenzene (**1d**, 39 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (44 mg, 0.30 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 2.0 µmol, 1.0 mol %) in chlorobenzene (0.8 mL) at 80°C for 16 h according **GP 2**. CH_2Br_2 (7.0 µL, 0.10 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 **7d** as a colorless oil (54 mg, 79% yield). The spectroscopic data were in accordance with those reported.[S18]

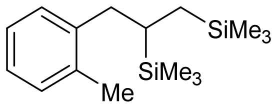
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = –0.14 (s, 9H), –0.10 (s, 9H), 0.39 (dd, *J* = 15.3, 8.4 Hz, 1H), 0.67 (dd, *J* = 15.2, 3.8 Hz, 1H), 1.01 (qd, *J* = 8.0, 3.8 Hz, 1H), 2.57 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –2.5, –0.8, 16.2, 22.5, 39.3, 119.5, 130.9, 131.3, 142.0 ppm.



7f
$C_{15}H_{27}BrSi_2$
M = 343.46 g/mol

(3-(2-Bromophenyl)propane-1,2-diyl)bis(trimethylsilane) (7f): Prepared from 1-bromo-2-cyclopropylbenzene (**1f**, 39 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (44 mg, 0.30 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 2.0 µmol, 1.0 mol %) in chlorobenzene (0.8 mL) at 80°C for 16 h according **GP 2**. CH_2Br_2 (7.0 µL, 0.10 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (76%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **7f** as a colorless oil (50 mg, 72% yield). The spectroscopic data were in accordance with those reported.[S18]

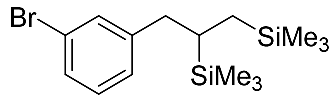
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = –0.22 (s, 9H), –0.05 (s, 9H), 0.44 (dd, *J* = 15.4, 6.8 Hz, 1H), 0.67 (dd, *J* = 15.4, 4.5 Hz, 1H), 1.28 (dtd, *J* = 9.6, 6.5, 4.5 Hz, 1H), 2.52 (dd, *J* = 13.6, 9.6 Hz, 1H), 2.92 (dd, *J* = 13.6, 6.3 Hz, 1H), 7.01–7.06 (m, 1H), 7.19–7.22 (m, 2H), 7.51 (d, *J* = 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.



7g
$C_{16}H_{30}Si_2$
M = 278.59 g/mol

(3-(*ortho*-Tolyl)propane-1,2-diyl)bis(trimethylsilane) (7g): Prepared from 1-cyclopropyl-2-methylbenzene (**1g**, 26 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (44 mg, 0.30 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 2.0 µmol, 1.0 mol %) in chlorobenzene (0.8 mL) at 80°C for 16 h according **GP 2**. CH_2Br_2 (7.0 µL, 0.10 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (79%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **7g** as a colorless oil (41 mg, 74% yield). The spectroscopic data were in accordance with those reported.[S18]

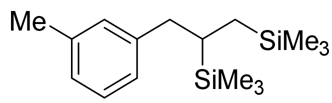
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = –0.19 (s, 9H), –0.08 (s, 9H), 0.46 (dd, *J* = 15.4, 7.2 Hz, 1H), 0.69 (dd, *J* = 15.2, 4.3 Hz, 1H), 1.06 (m_c, 1H), 2.32 (s, 3H), 2.49 (dd, *J* = 13.9, 9.2 Hz, 1H), 2.75 (dd, *J* = 13.9, 6.8 Hz, 1H), 7.06–7.13 (m, 4H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –2.7, –1.0, 15.9, 19.8, 20.2, 37.3, 125.7, 126.0, 130.1, 130.5, 136.2, 140.9 ppm.



7h
$C_{15}H_{27}BrSi_2$
M = 343.46 g/mol

(3-(3-Bromophenyl)propane-1,2-diyl)bis(trimethylsilane) (7h): Prepared from 1-bromo-3-cyclopropylbenzene (**1h**, 39 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (44 mg, 0.30 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 2.0 µmol, 1.0 mol %) in chlorobenzene (0.8 mL) at 80°C for 16 h according **GP 2**. CH_2Br_2 (7.0 µL, 0.10 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (92%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **7h** as a colorless oil (62 mg, 90% yield).

R*f* = 0.75 (cyclohexane). **IR** (ATR): ṽ = 2950, 2893, 1566, 1472, 1422, 1245, 1112, 1070, 827, 773, 686 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = –0.12 (s, 9H), –0.11 (s, 9H), 0.39 (dd, *J* = 15.3, 8.1 Hz, 1H), 0.67 (dd, *J* = 15.3, 3.9 Hz, 1H), 1.02 (qd, *J* = 7.9, 3.9 Hz, 1H), 2.58 (qd, *J* = 13.8, 7.8 Hz, 2H), 7.08–7.14 (m, 2H), 7.29–7.31 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = –2.6, –0.8, 16.1, 22.5, 39.6, 122.4, 127.9, 129.0, 129.8, 132.2, 145.5 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = –0.12/4.8, –0.11/1.5, 0.39/1.5, 0.67/1.5, 1.02/4.8, 2.58/4.8 ppm. **HRMS** (APCI): calculated for $C_{14}H_{24}BrSi_2^{\bullet+}$ $[M–CH_3]^{+\bullet}$: 327.0594; found 327.0598.



7i
$C_{16}H_{30}Si_2$
M = 278.59 g/mol

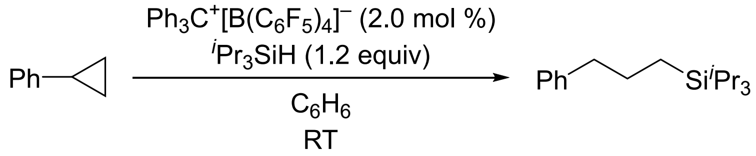
(3-(*meta*-Tolyl)propane-1,2-diyl)bis(trimethylsilane) (7i): Prepared from 1-cyclopropyl-3-methylbenzene (**1i**, 26 mg, 0.20 mmol, 1.0 equiv) and hexamethyldisilane (44 mg, 0.30 mmol, 1.5 equiv) with $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (1.4 mg, 2.0 µmol, 1.0 mol %) in chlorobenzene (0.8 mL) at 80°C for 16 h according **GP 2**. CH_2Br_2 (7.0 µL, 0.10 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (47%). Purification by flash column chromatography on silica gel using *n*-pentane afforded the 1,2-bissilylated adduct **7i** as a colorless oil (23 mg, 42% yield).

R*f* = 0.74 (cyclohexane). **IR** (ATR): ṽ = 3015, 2951, 2894, 1607, 1446, 1410, 1245, 1112, 827, 778, 747, 686 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = –0.14 (s, 9H), –0.10 (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* = 7.9, 3.8 Hz, 1H), 2.32 (s, 3H), 2.59 (d, *J* = 8.2 Hz, 2H), 6.96–6.97 (m, 3H), 7.12–7.15 (m, 1H) ppm. **^{13}C{^{1}H} NMR**

(126 MHz, $CDCl_3$, 298 K): δ –2.6, –0.8, 16.3, 21.5, 22.5, 39.8, 126.2, 126.5, 128.1, 130.0, 137.7, 142.9 ppm. **$^{1}H/^{29}Si$ HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ = –0.14/4.7, –0.10/1.9, 0.42/1.9, 0.66/1.9, 2.59/4.7 ppm. **HRMS** (APCI): calculated for $C_{15}H_{27}Si_2^{\bullet+}$ $[M–CH_3]^{+\bullet}$: 263.1646; found 263.1646.

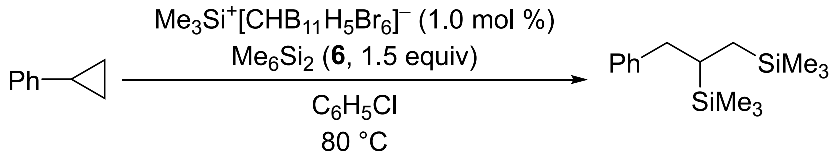
9 Representative Examples at 1 mmol Scale

9.1 Catalytic Hydrosilylation of 1a



In an argon-filled glovebox, $Ph_3C^+[B(C_6F_5)_4]^-$ (20.3 mg, 22.0 μmol, 2.0 mol %) was suspended in C_6H_6 (1.0 mL) in a medium-sized dram vial, and then triisopropylsilane (206 mg, 1.30 mmol, 1.2 equiv) in C_6H_6 (0.6 mL) was added dropwise. After stirring at room temperature for ~2 min, the dark yellow colour of the trityl salt's solution faded, indicating the formation of respective silylium ion. Then, the solution of cyclopropylbenzene (**1a**, 128 mg, 1.08 mmol, 1.0 equiv) in C_6H_6 (1.4 mL) was added dropwise and stirred for 15 min. The solvent was evaporated, and the oil was purified by flash column chromatography on silica gel using cyclohexane as eluent yielding the monosilylated adduct **3ab** as a colorless oil (278 mg, 93% yield).

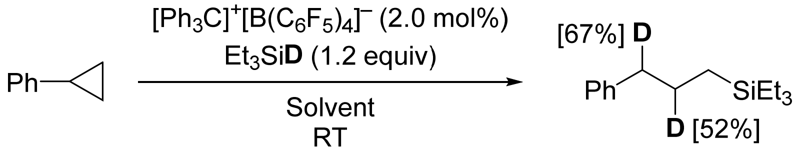
9.2 Catalytic 1,2-Disilylation of 1a



In an argon-filled glovebox, $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (6.9 mg, 10 μmol, 1.0 mol %) was suspended in C_6H_5Cl (2.0 mL) in a medium-sized dram vial, and hexamethyldisilane (220 mg, 1.5 mmol, 1.5 equiv) was added dropwise. Then, the vial was transferred to a heating reaction block with a preset temperature of 50 °C and stirred for ~5 min. A solution of cyclopropylbenzene (**1a**, 118 mg, 1.0 mmol, 1.0 equiv) in C_6H_5Cl (2.0 mL) was added dropwise over a period of 20 min at this temperature. After addition, the temperature was allowed to reach at 80 °C, and the resulting mixture was stirred for additional 24 h at this temperature. The reaction mixture was allowed to cool to room temperature, and CH_2Br_2 (35 μL, 0.5 mmol, 0.5 equiv) was added as internal standard to determine the yield by NMR spectroscopy (56%). Purification by flash column chromatography on silica gel using *n*-pentane as eluent afforded the 1,2-bissilylated adduct **7a** as a colorless oil (138 mg, 52% yield).

10 Control Experiments and Mechanistic Studies for the Catalytic Hydrosilylation of Cyclopropanes with Trialkylsilanes Using $Ph_3C^+[B(C_6F_5)_4]^-$ as Initiator

10.1 Catalytic Hydrosilylation of 1a with Triethylsilane-d_1



1a **3aa**-d_1 $C_{15}H_{25}DSi$ M = 235.46 g/mol

3aa-d_1: Prepared from cyclopropylbenzene (**1a**, 24 mg, 0.20 mmol, 1.0 equiv) and triethylsilane-d_1 (28 mg, 0.24 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (3.7 mg, 4.0 μmol, 2.0 mol %) in benzene (0.6 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using *n*-pentane afforded the monosilylated adduct **3aa**-d_1 as a colorless oil (32 mg, 68% yield). The same reaction was repeated with C_6D_6 as solvent, which resulted **3aa**-d_1 as a colorless oil (33 mg, 69% yield).

$\mathbf{R_f}$ = 0.71 (cyclohexane). **IR** (ATR): ṽ = 3025, 2909, 2093, 1603, 1454, 1342, 1237, 1169, 1069, 1013, 824, 720 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.52 (m_c, 6H), 0.57–0.60 (m, 2H), 0.93 (m_c, 9H), 1.63 (m_c, 1H), 2.61–2.64 (m, 1H), 7.18–7.20 (m, 3H), 7.28–7.31 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 298 K): δ = 3.5, 7.6, 11.4, 11.5, 26.1, 40.3, 125.7, 128.4, 128.6, 142.8, 142.9 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz): δ = 0.52/6.2, 0.57–0.60/6.2, 0.93/6.2 ppm. **HRMS** (APCI): calculated for $C_{13}H_{20}DSi^{+\bullet}$ $[M–C_2H_5]^{+\bullet}$: 206.1470, found 206.1470.

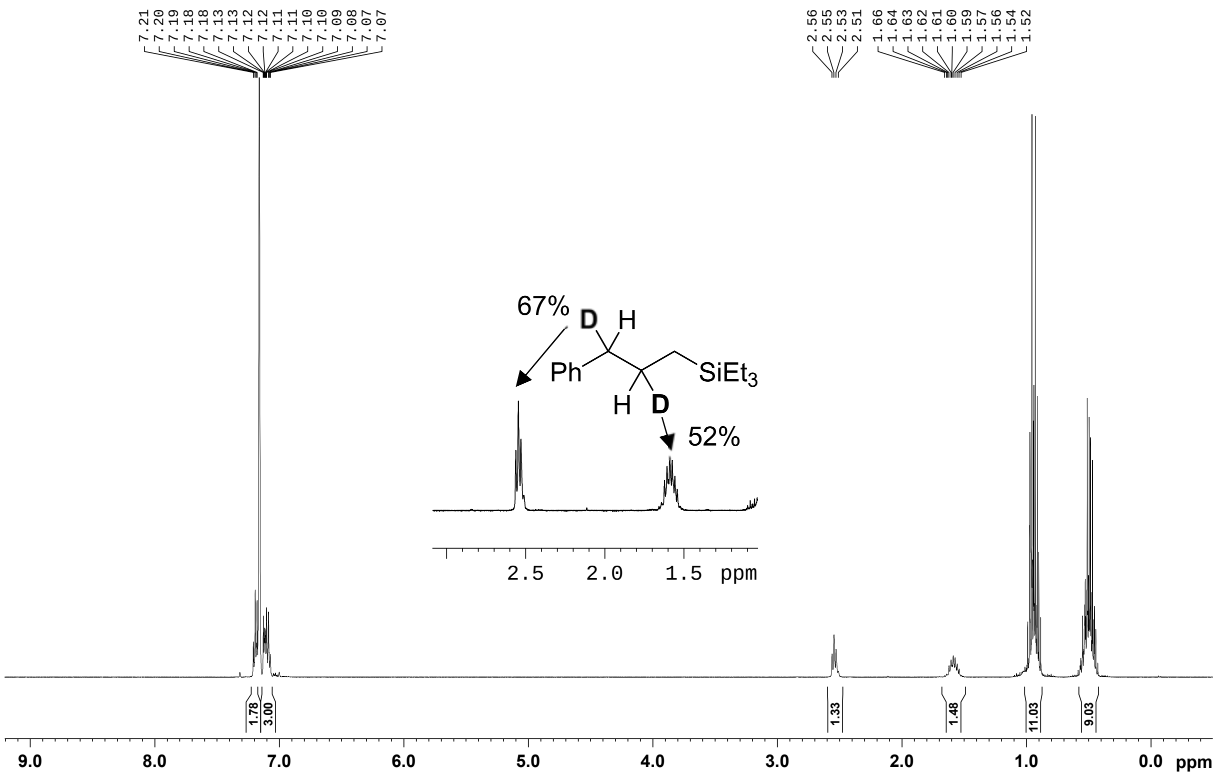
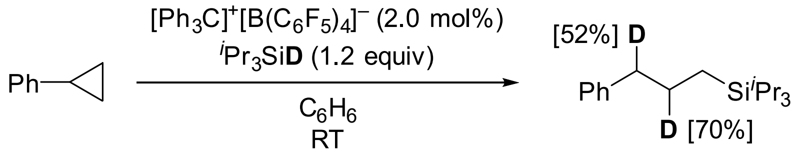


Figure A. Crude ^{1}H NMR spectrum (500 MHz, C_6D_6, 298 K) of the catalytic reaction of cyclopropylbenzene (**1a**) and Et_3SiD using $Ph_3C^+[B(C_6F_5)_4]^-$ in C_6H_6.

10.2 Catalytic Hydrosilylation of 1a with Triisopropylsilane-*d*₁



1a

3ab-d_1
$C_{18}H_{31}DSi$
M = 277.55 g/mol

3ab-d_1**:** Prepared from cyclopropylbenzene (**1a**, 24 mg, 0.20 mmol, 1.0 equiv) and triisopropylsilane-d_1 (38 mg, 0.24 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (3.7 mg, 4.0 μmol, 2.0 mol %) in benzene (0.6 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using *n*-pentane afforded the monosilylated adduct **3ab-**d_1 as a colorless oil (51 mg, 92% yield).

$\mathbf{R_f}$ = 0.71 (cyclohexane). **IR** (ATR): ṽ = 3025, 2935, 2862, 2255, 2102, 1937, 1602, 1458, 1382, 1244, 1169, 1010, 917, 881, 825, 725, 693 cm^{-1}. $\mathbf{^{1}H}$ **NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.63–0.67 (m, 2H), 1.03 (s, 21H), 1.64–1.71 (m, 1H), 2.61–2.64 (m, 2H), 7.17–7.20 (m, 3H), 7.27–7.30 (m, 2H) ppm. $\mathbf{^{13}C\{^{1}H\}}$ **NMR** (126 MHz, $CDCl_3$, 298 K): δ = 9.4, 11.1, 19.0, 26.6, 40.8, 125.7, 128.4, 128.6, 142.8 ppm. $\mathbf{^{1}H/^{29}Si}$ **HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz): δ = 0.63–0.67/5.6, 1.03/5.6 ppm. **HRMS** (APCI): calculated for $C_{15}H_{24}DSi^{+•}$ [M–C_3H_7]$^{+•}$: 234.1783; found 234.1786.

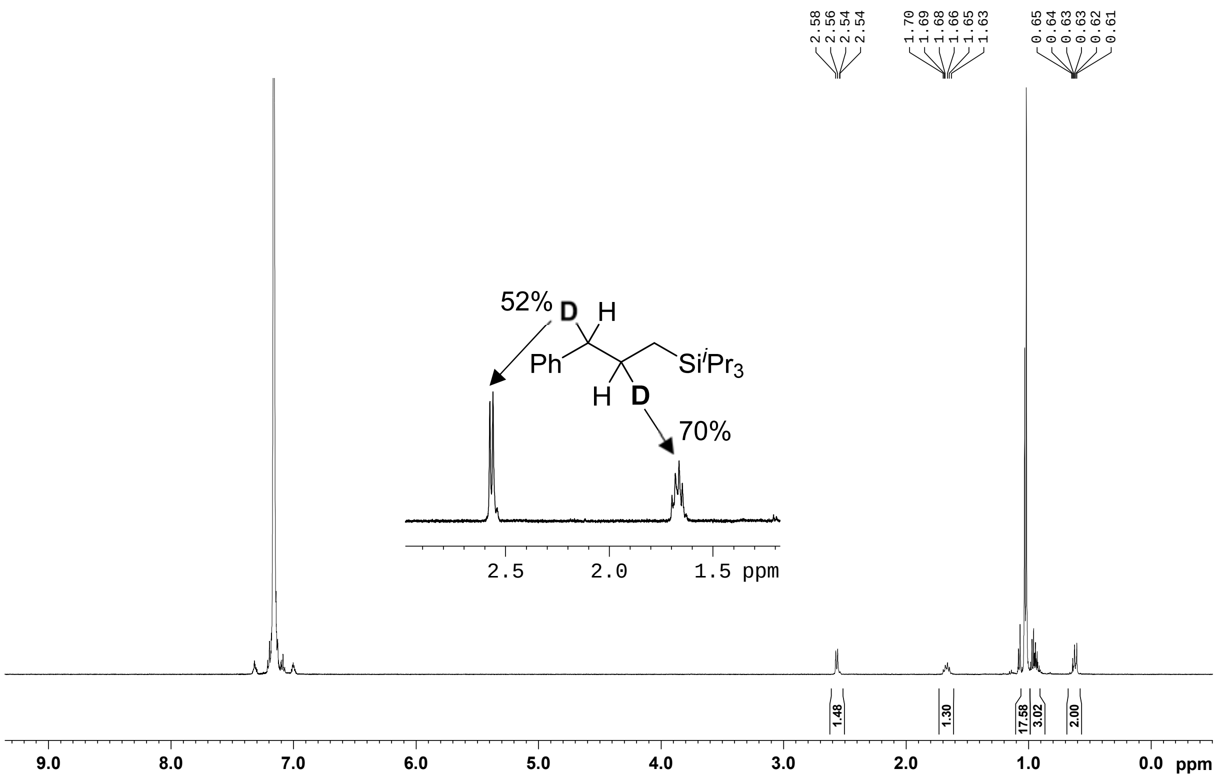
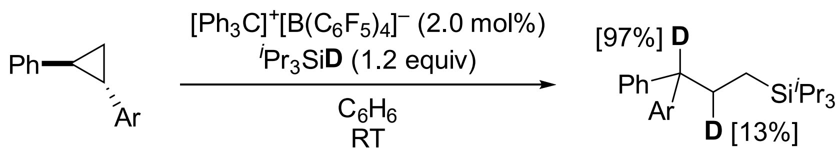


Figure B. Crude ^{1}H NMR spectrum (500 MHz, C_6D_6, 298 K) of the catalytic reaction of cyclopropylbenzene (**1a**) and ^{i}Pr$_3$SiD using $Ph_3C^+[B(C_6F_5)_4]^-$.

10.3 Catalytic Hydrosilylation of 1p with Triisopropylsilane-d_1



1p
(Ar = 4-BrC$_6$H$_4$)

3pb'-d_1
$C_{24}H_{34}DBrSi$
M = 432.53 g/mol

3pb'-d_1: Prepared from 1-bromo-4-(2-phenylcyclopropyl)benzene (**1p** (*trans*:*cis* ≥ 98:2), 55 mg, 0.20 mmol, 1.0 equiv) and triisopropylsilane-*d*1 (38 mg, 0.24 mmol, 1.2 equiv) with $Ph_3C^+[B(C_6F_5)_4]^-$ (3.7 mg, 4.0 µmol, 2.0 mol %) in benzene (0.6 mL) at room temperature according to the **GP 1**. Purification by flash column chromatography on silica gel using *n*-pentane afforded the monosilylated adduct **3pb'**-d_1 as a colorless oil (52 mg, 60% yield).

R*f* = 0.59 (cyclohexane). **IR** (ATR): ṽ = 3025, 2909, 2093, 1603, 1454, 1342, 1237, 1169, 1069, 1013, 824, 720 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 0.53 (m$_c$, 2H), 1.00–1.01 (m, 21H), 2.05 (m$_c$, 2H), 7.11 (m$_c$, 2H), 7.16–7.21 (m, 3H), 7.26–7.30 (m, 2H), 7.39 (m$_c$, 2H) ppm. **^{13}C{^{1}H}**

NMR (126 MHz, $CDCl_3$, 298 K): δ = 8.1, 11.1, 19.0, 30.5, 120.0, 126.4, 127.9, 128.6, 129.8, 131.6, 144.3, 144.6 ppm. **$^1H/^{29}Si$ HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz): δ = 0.53/5.9, 1.00–1.01/5.9 ppm. **HRMS** (APCI): calculated for $C_{21}H_{27}DBrSi^{+\bullet}$ $[M–C_3H_7]^{+\bullet}$: 388.1201; found 388.1207.

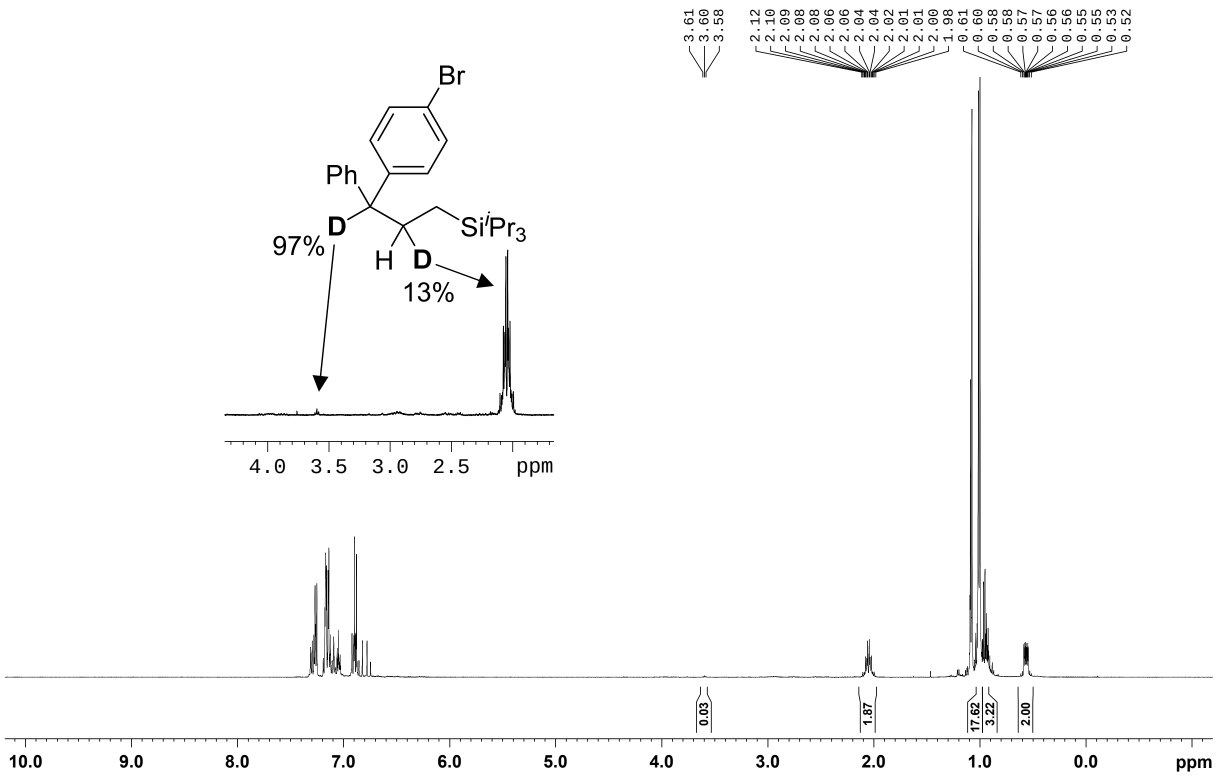
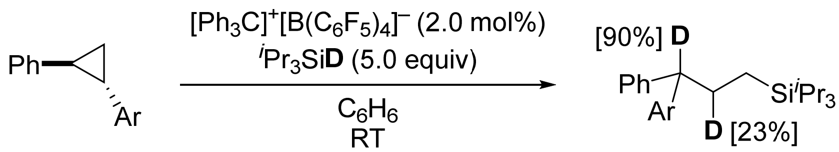


Figure C. Crude ^1H NMR spectrum (500 MHz, C_6D_6, 298 K) of the catalytic reaction of 1-bromo-4-(2-phenylcyclopropyl)benzene (**1p**) and $^iPr_3SiD$ (1.2 equiv) using $Ph_3C^+[B(C_6F_5)_4]^–$.

10.4 Catalytic Hydrosilylation of 1p with Excess of Triisopropylsilane-d_1



1p
(Ar = 4-BrC$_6$H$_4$)

3pb'-d_1
$C_{24}H_{34}DBrSi$
M = 432.53 g/mol

The same reaction was repeated with 1-bromo-4-(2-phenylcyclopropyl)benzene (**1p** (*trans*:*cis* ≥ 98:2), 27 mg, 0.10 mmol, 1.0 equiv) and triisopropylsilane-*d*1 (80 mg, 0.50 mmol, 5.0 equiv) with $Ph_3C^+[B(C_6F_5)_4]^–$ (1.8 mg, 2.0 µmol, 2.0 mol %) in benzene (0.3 mL). After 15 min., NMR spectroscopic analysis was conducted with the crude reaction mixture. However, purification step was not performed in this case.

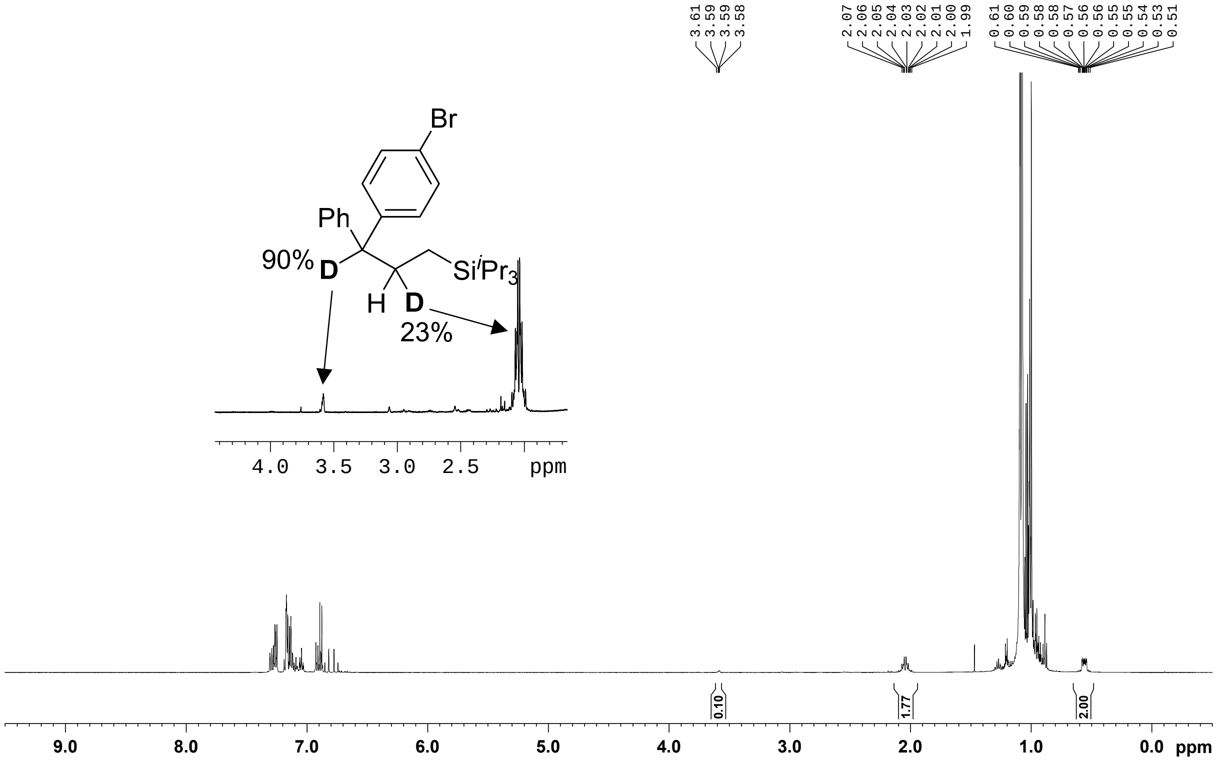
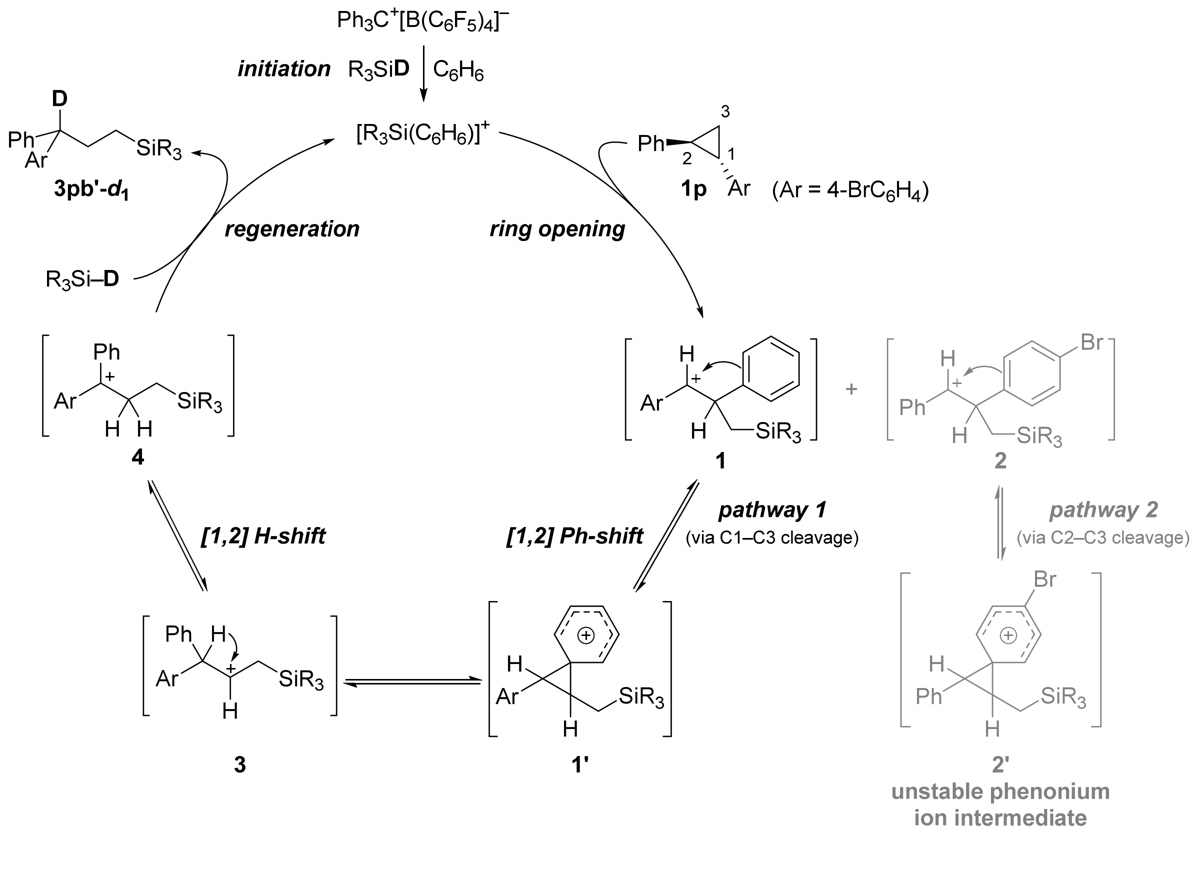


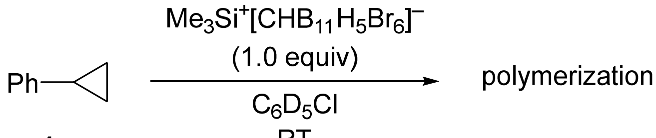
Figure D. Crude [1]H NMR spectrum (500 MHz, C_6D_6, 298 K) of the catalytic reaction of 1-bromo-4-(2-phenylcyclopropyl)benzene (**1p**) and $^{i}Pr_3SiD$ (5.0 equiv) using $Ph_3C^+[B(C_6F_5)_4]^-$.

10.5 Proposed Catalytic Cycle for Hydrosilylation of 1p



11 Control Experiments and Mechanistic Studies for the Ring-Opening Isomerization of Cyclopropylbenzene to Allylbenzene

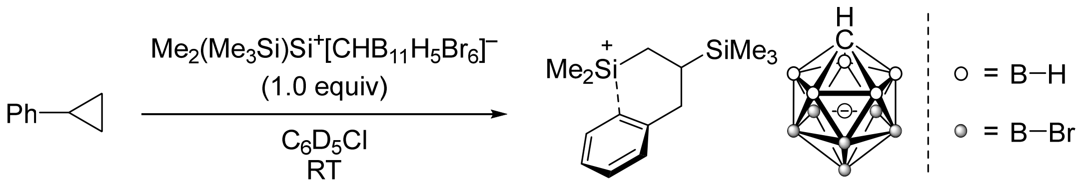
11.1 Stoichiometric Reaction of 1a with $Me_3Si^+[CHB_{11}H_5Br_6]^-$



1a

In a valved NMR tube, $Me_3Si^+[CHB_{11}H_5Br_6]^-$ (6.9 mg, 10.0 μmol, 1.0 equiv) was suspended in 0.6 mL of C_6D_5Cl, and then cyclopropylbenzene (**1a**, 1.2 mg, 0.01 mmol, 1.0 equiv) in C_6D_5Cl was added at room temperature. NMR spectroscopic analysis was conducted immediately, and the polymerization of cyclopropylbenzene was observed.

11.2 Stoichiometric Reaction of 1a with $Me_2(Me_3Si)Si^+[CHB_{11}H_5Br_6]^-$

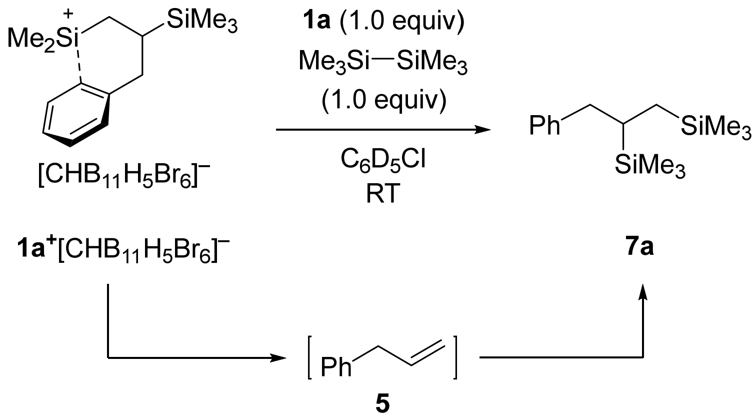


1a$^+[CHB_{11}H_5Br_6]^-$
$C_{15}H_{30}B_{11}Br_6Si_2$
M = 865.92 g/mol

In a valved NMR tube, $Me_2(Me_3Si)Si^+[CHB_{11}H_5Br_6]^-$ (7.5 mg, 10.0 μmol, 1.0 equiv) was suspended in 0.6 mL of C_6D_5Cl, and then cyclopropylbenzene (**1a**, 1.2 mg, 0.01 mmol, 1.0 equiv) was added at room temperature. NMR spectroscopic analysis was conducted immediately, and the formation of a new intramolecular phenyl group-stabilized silylium ion species **1a**$^+[CHB_{11}H_5Br_6]^-$ was observed. The spectroscopic data were in accordance with those reported.[S18]

Selected NMR spectroscopic data for **1a**$^+[CHB_{11}H_5Br_6]^-$:
^{1}H NMR (500 MHz, C_6D_5Cl, 298 K): δ = 0.03 (s, 9H), 0.59–0.65 (m, 1H), 0.69–0.74 (m, 2H), 1.99 (t, *J* = 12.6 Hz, 1H), 2.37 (s, 1H, $[CHB_{11}H_5Br_6]^-$), 2.69 (dd, *J* = 12.6, 2.6 Hz, 1H), 6.81 (d, *J* = 6.0 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.81 (t, *J* = 7.2 Hz, 2H) 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, 16.1, 30.6, 38.7, 41.5 ($[CHB_{11}H_5Br_6]^-$), 132.6, 150.1, 170.6 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.

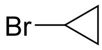
11.3 Stoichiometric Reaction of $1a^+[CHB_{11}H_5Br_6]^-$ with 1a and Hexamethyldisilane



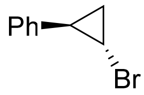
In a valved NMR tube, intramolecular phenyl group-stabilized silylium ion **1a**$^+[CHB_{11}H_5Br_6]^-$ (8.6 mg, 10.0 μmol, 1.0 equiv) was suspended in 0.6 mL of C_6D_5Cl, and then a solution of cyclopropylbenzene **1a** (1.2 mg, 0.01 mmol, 1.0 equiv) and hexamethylsilane (1.5 mg, 0.01 mmol, 1.0 equiv) in C_6D_5Cl (0.6 mL) was added. After shaking the NMR tube vigorously for ~10 min., NMR spectroscopic analysis was conducted. The formation of allylbenzene **5** was detected (**Figure S112 & 113**) along with the silylium ion **1a**$^+[CHB_{11}H_5Br_6]^-$. This experiment supported the isomerization of cyclopropylbenzene to allylbenzene in presence of stoichiometric amount of silylium ion **1a**$^+[CHB_{11}H_5Br_6]^-$. However, when more than 2.0 equiv of cyclopropylbenzene was added, the polymerization was observed. Incomplete conversion of allylbenzene (**5**) to 1,2-bissilylated adduct (**7a**) was observed after stirring the reaction mixture at room temperature for ~18 h.

12 Unsuccessful Cyclopropanes

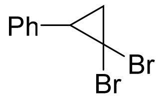
12.1 For Catalytic Hydrosilylation



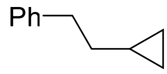
1q



1r



1s



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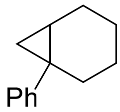

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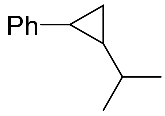

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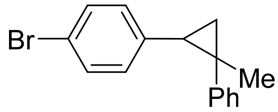
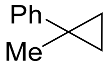


1w[a]

[a] Complex mixture of hydrosilylated products as detected by NMR and GC-MS analysis

12.2 For Catalytic Disilylation



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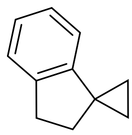

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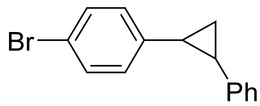

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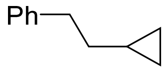

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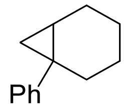


1u

13 NMR Spectra

Figure S1. [1]H NMR (500 MHz, C_6D_6, 298 K) of **hexylcyclopropane (1m)**.

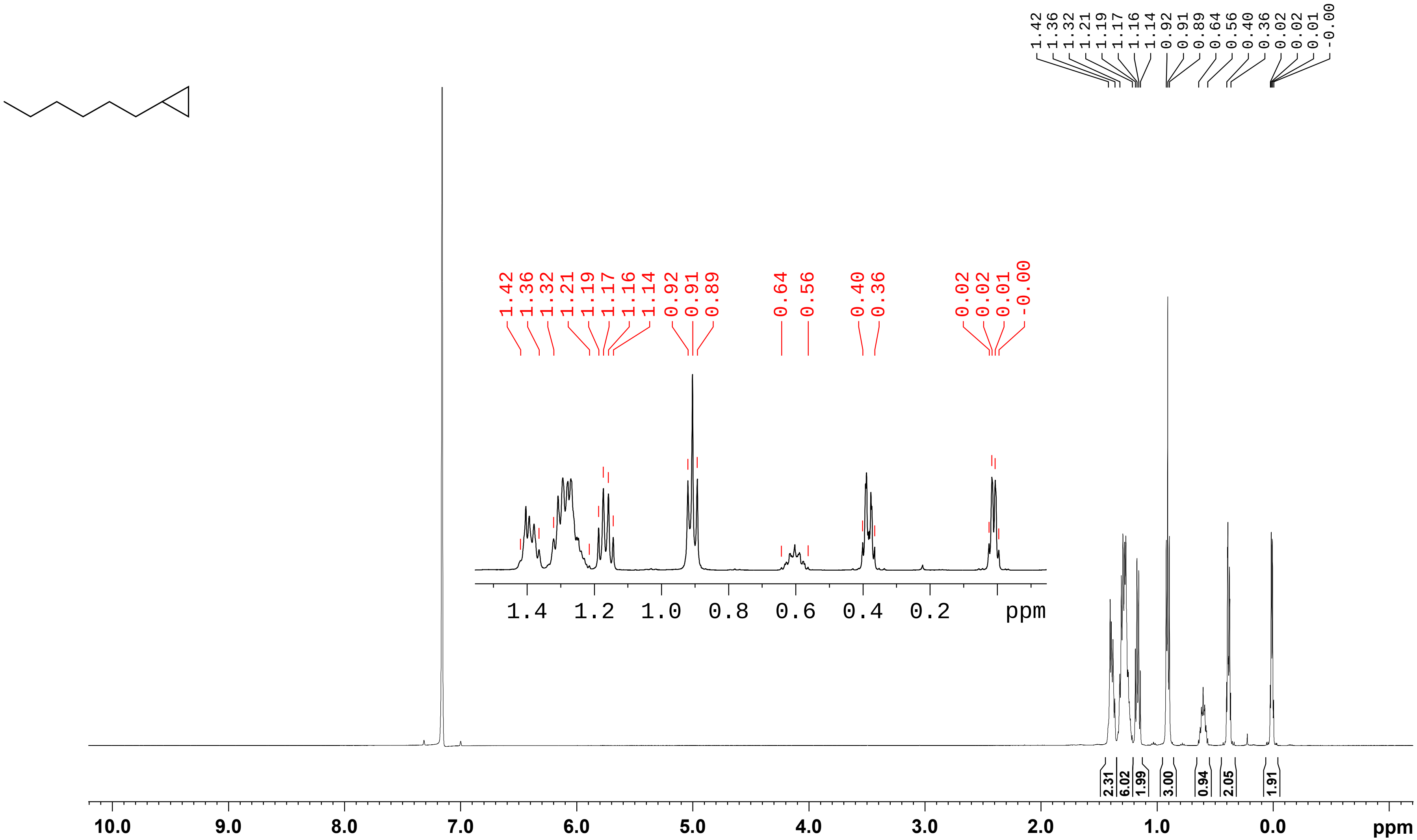


Figure S2. $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 298 K) of **hexylcyclopropane (1m)**.

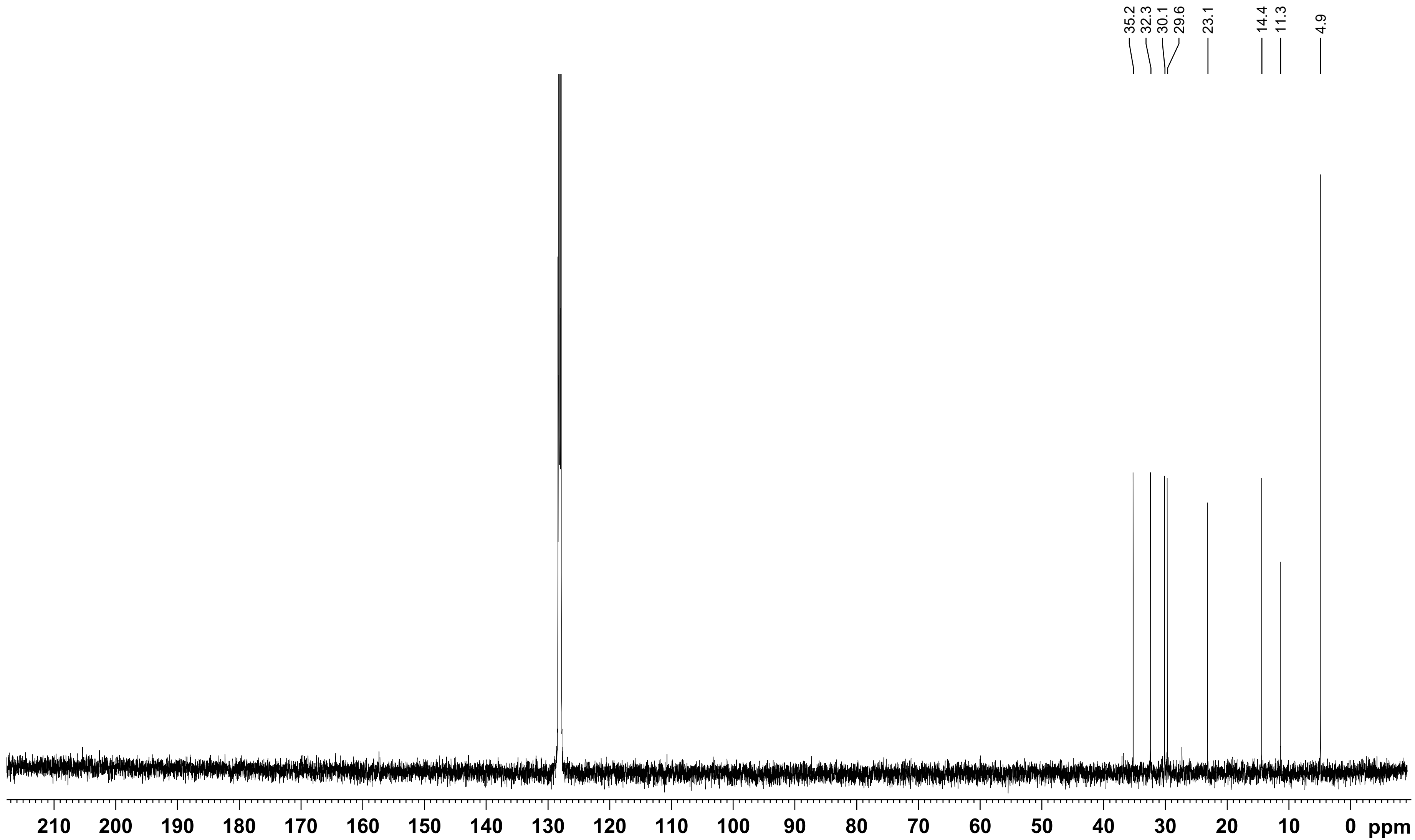


Figure S3. ^{1}H NMR (400 MHz, C_6D_6, 298 K) of **1,4-dicyclopropylbenzene (1l)**.

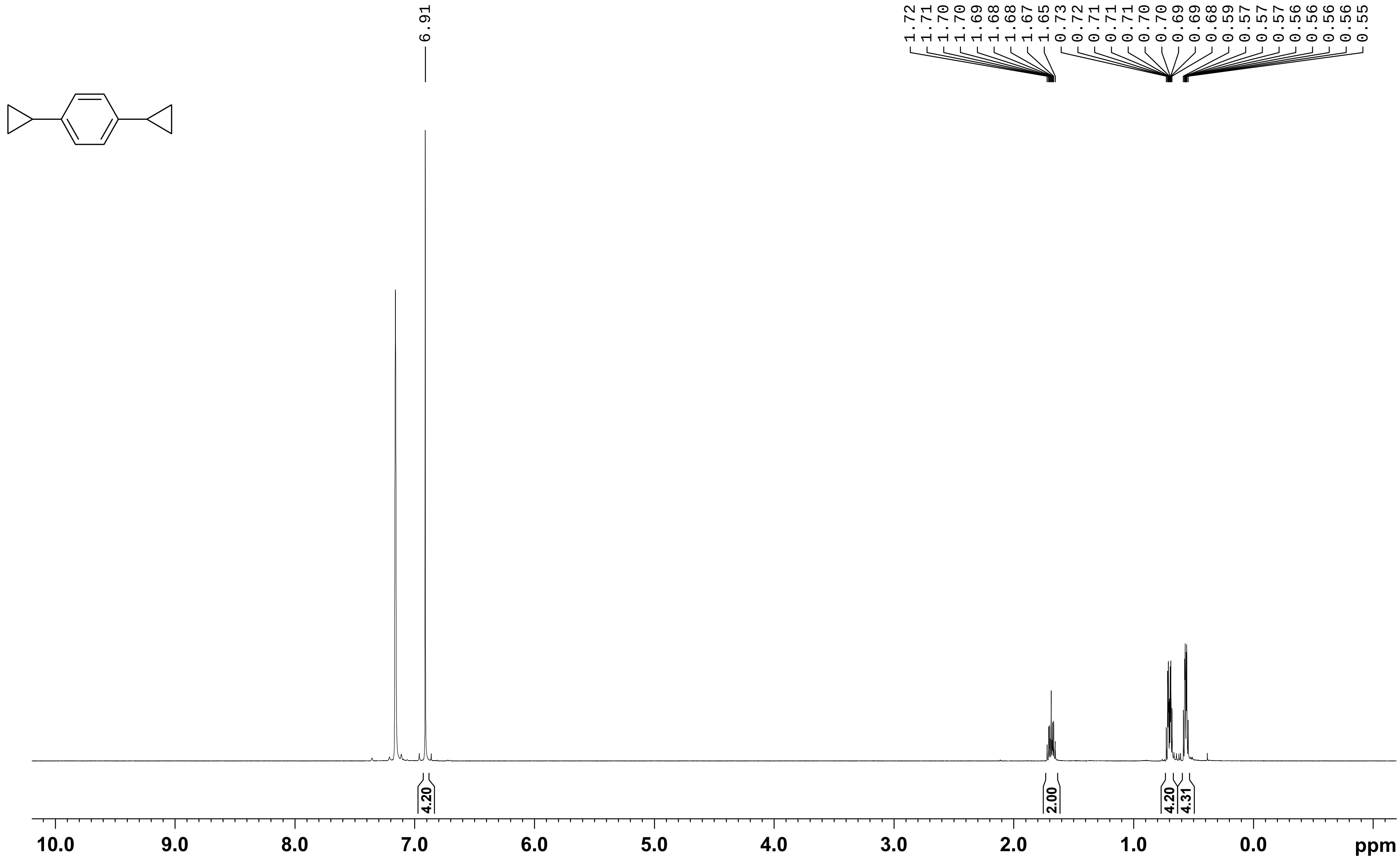


Figure S4. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K) of **1,4-dicyclopropylbenzene (1l)**.

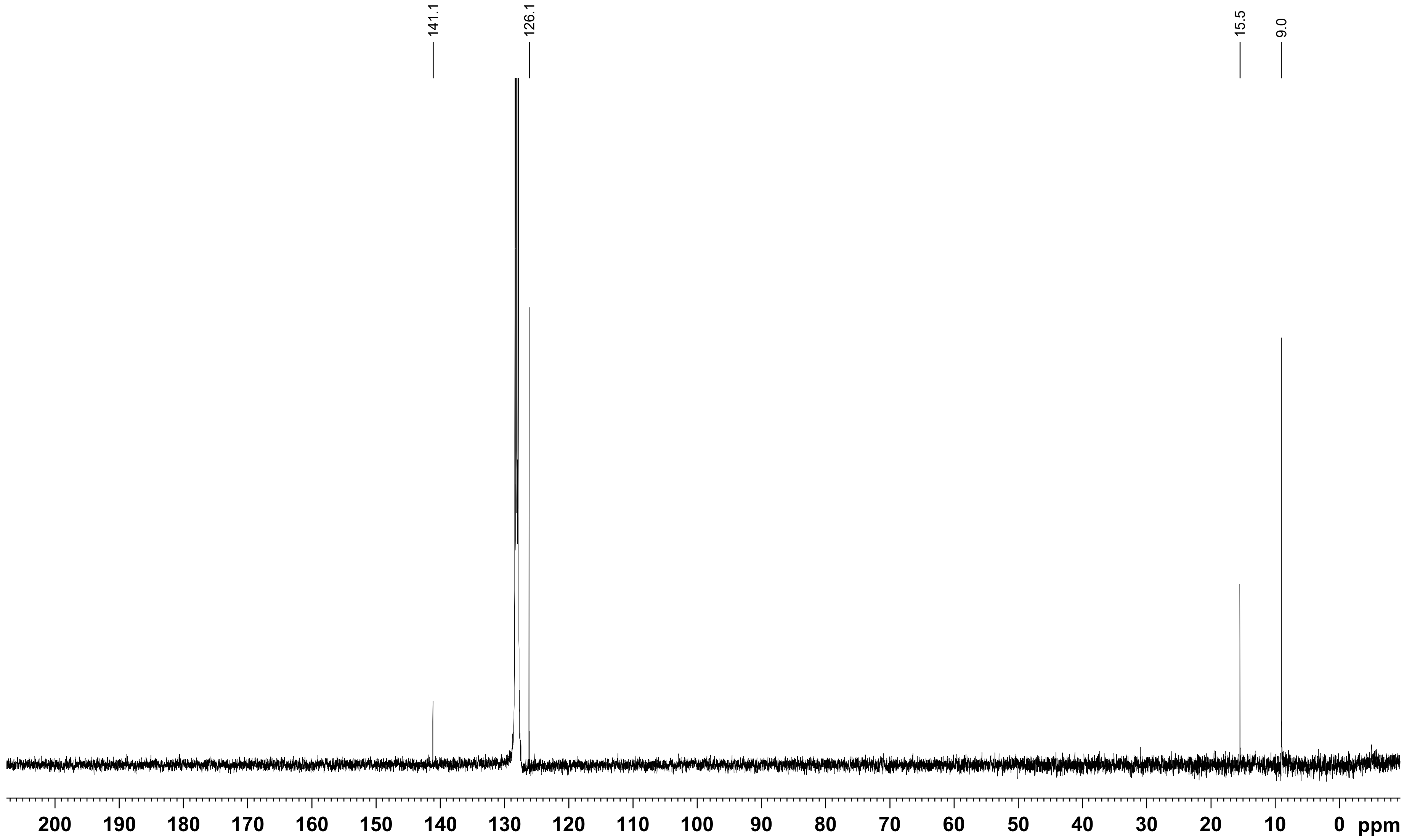


Figure S5. [1]H NMR (500 MHz, C_6D_6, 298 K) of **triethylsilane-*d*$_1$ (2a**-*d*$_1$**)**.

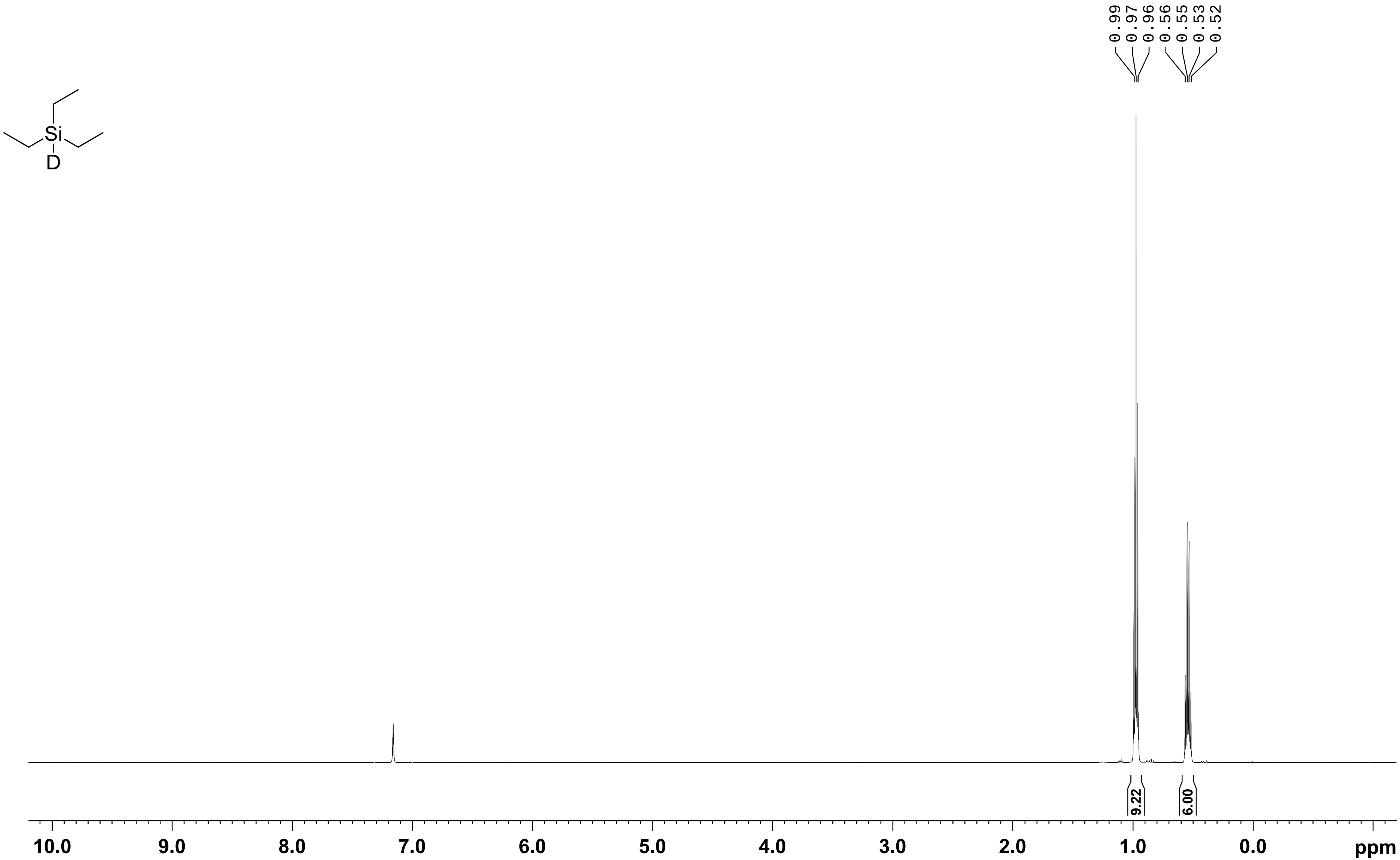


Figure S6. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K) of **triethylsilane-*d*₁ (2a-*d*₁).**

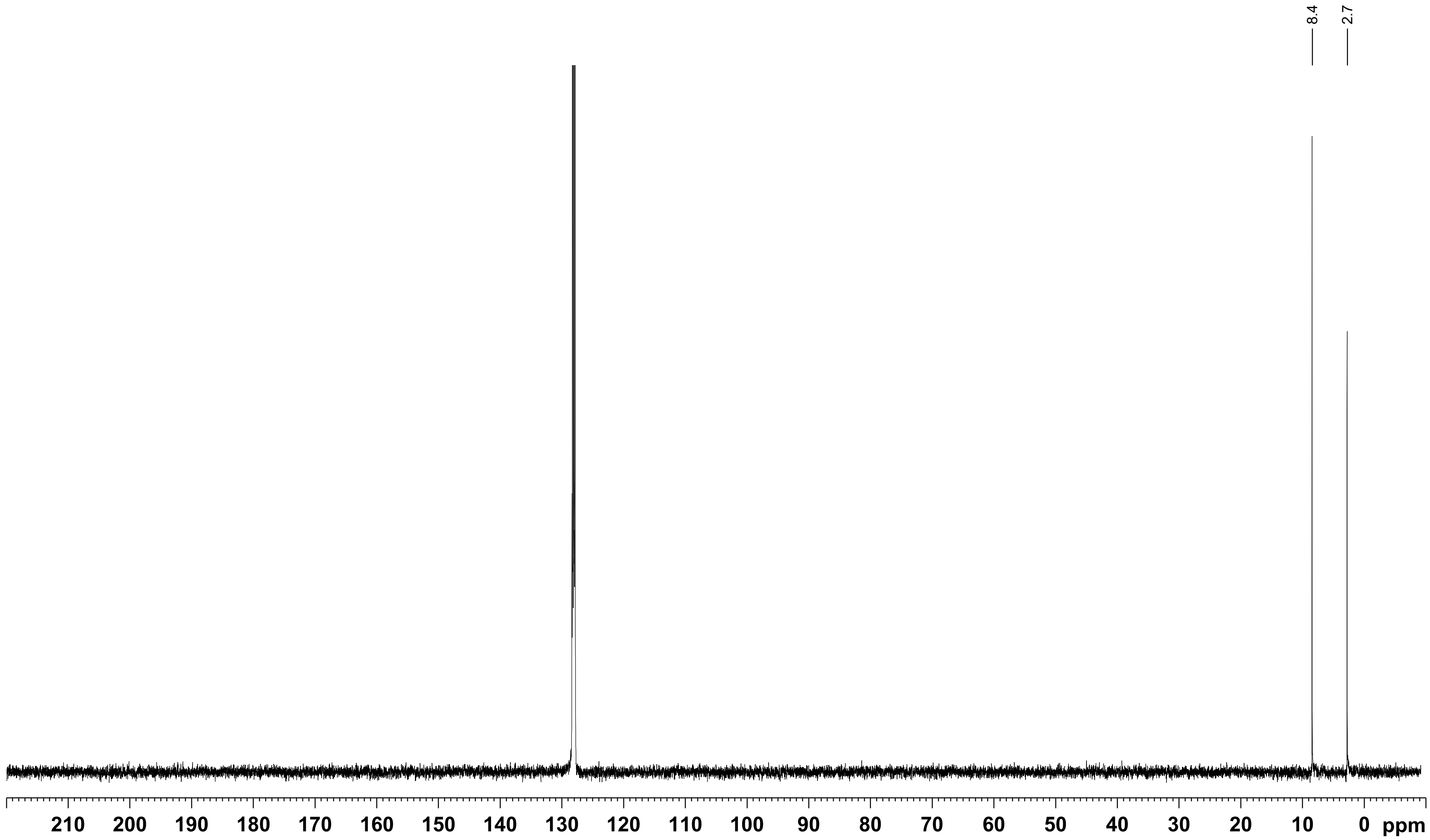


Figure S7. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, C_6D_6, 298 K, optimized for *J* = 7 Hz) of **triethylsilane-*d*$_1$ (2a-*d*$_1$).**

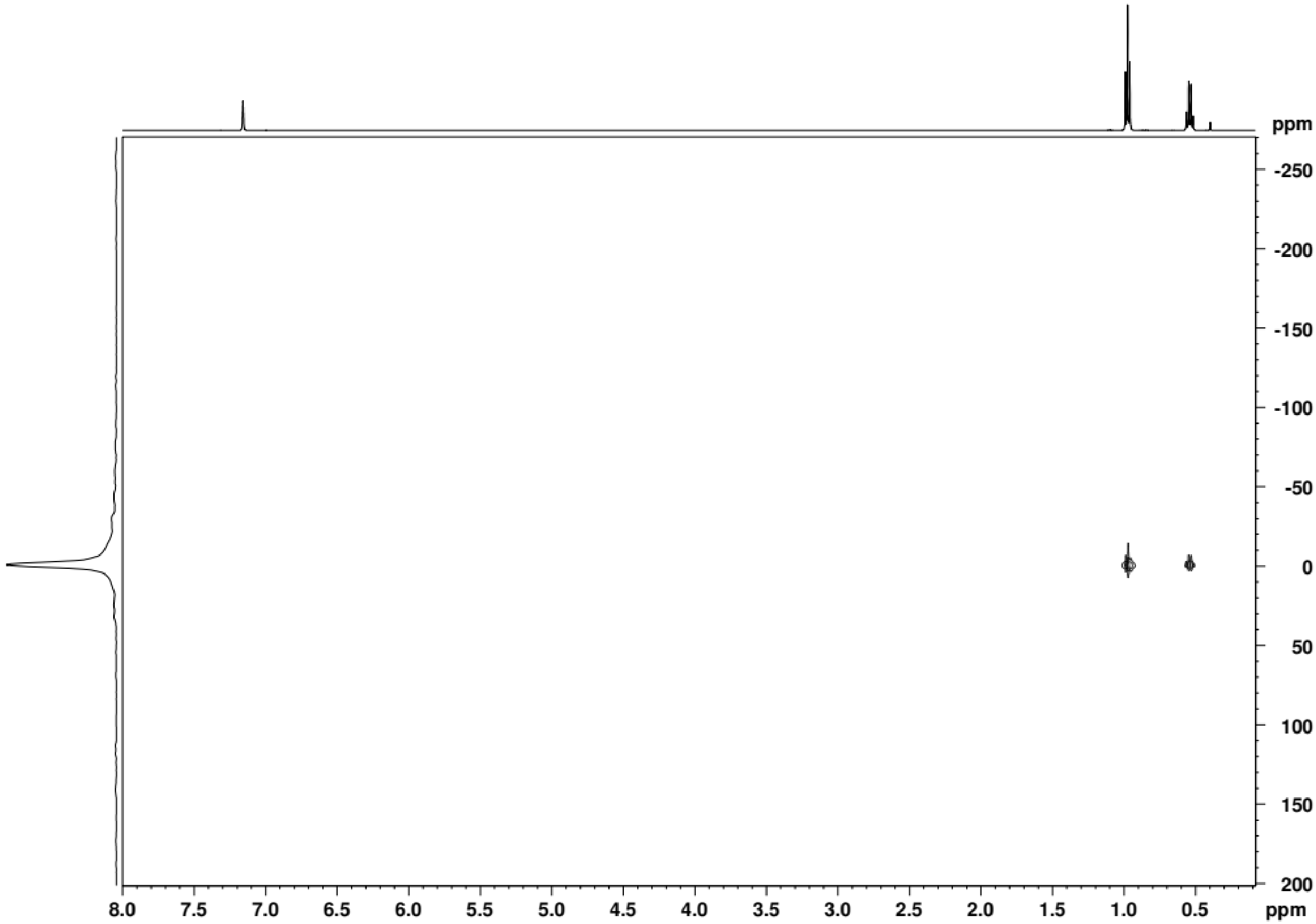
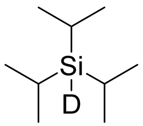


Figure S8. [1]H NMR (500 MHz, C_6D_6, 298 K) of **triisopropylsilane-*d*$_1$ (2b-*d*$_1$).**



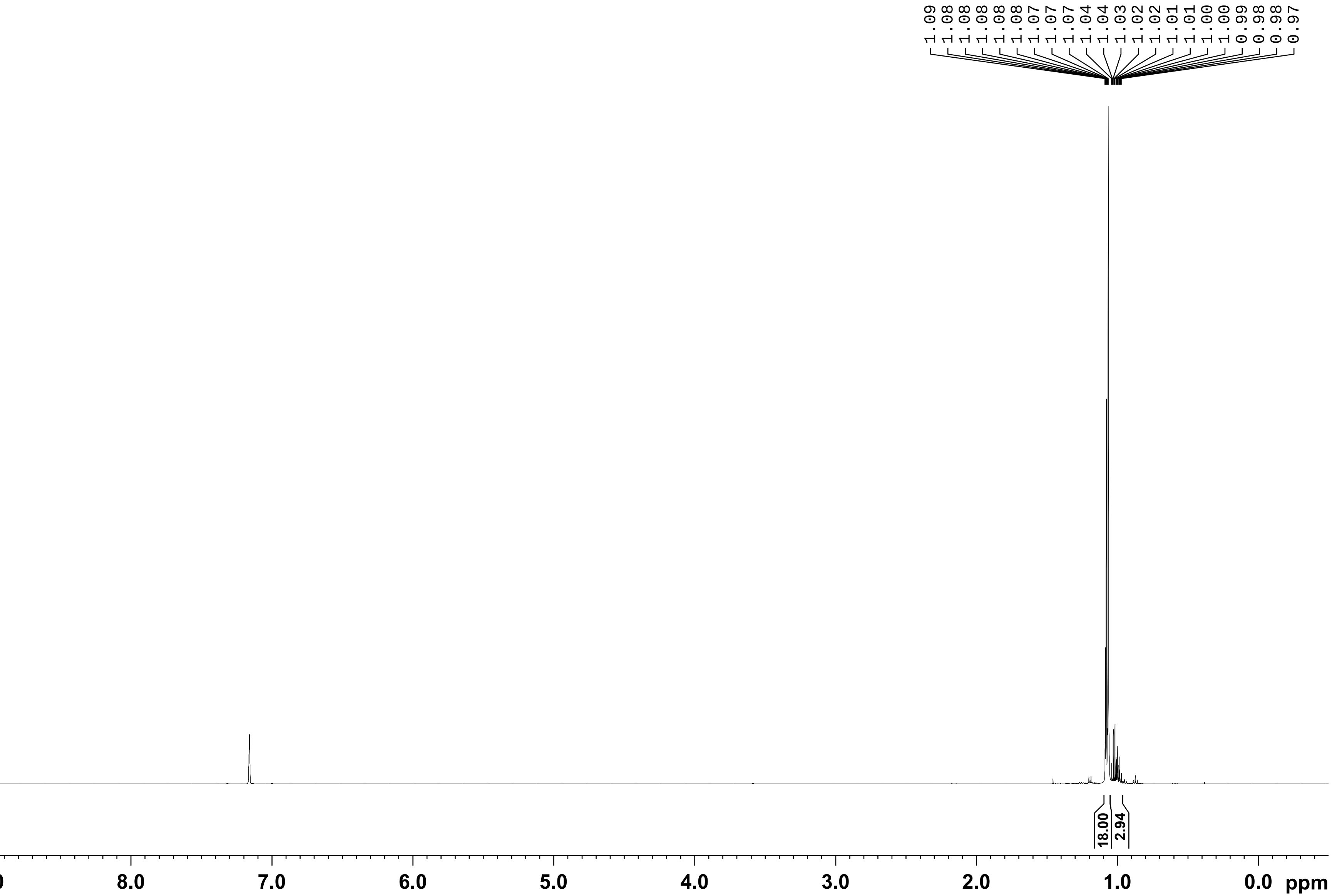


Figure S9. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K) of **triisopropylsilane-*d*$_1$ (2b-*d*$_1$).**

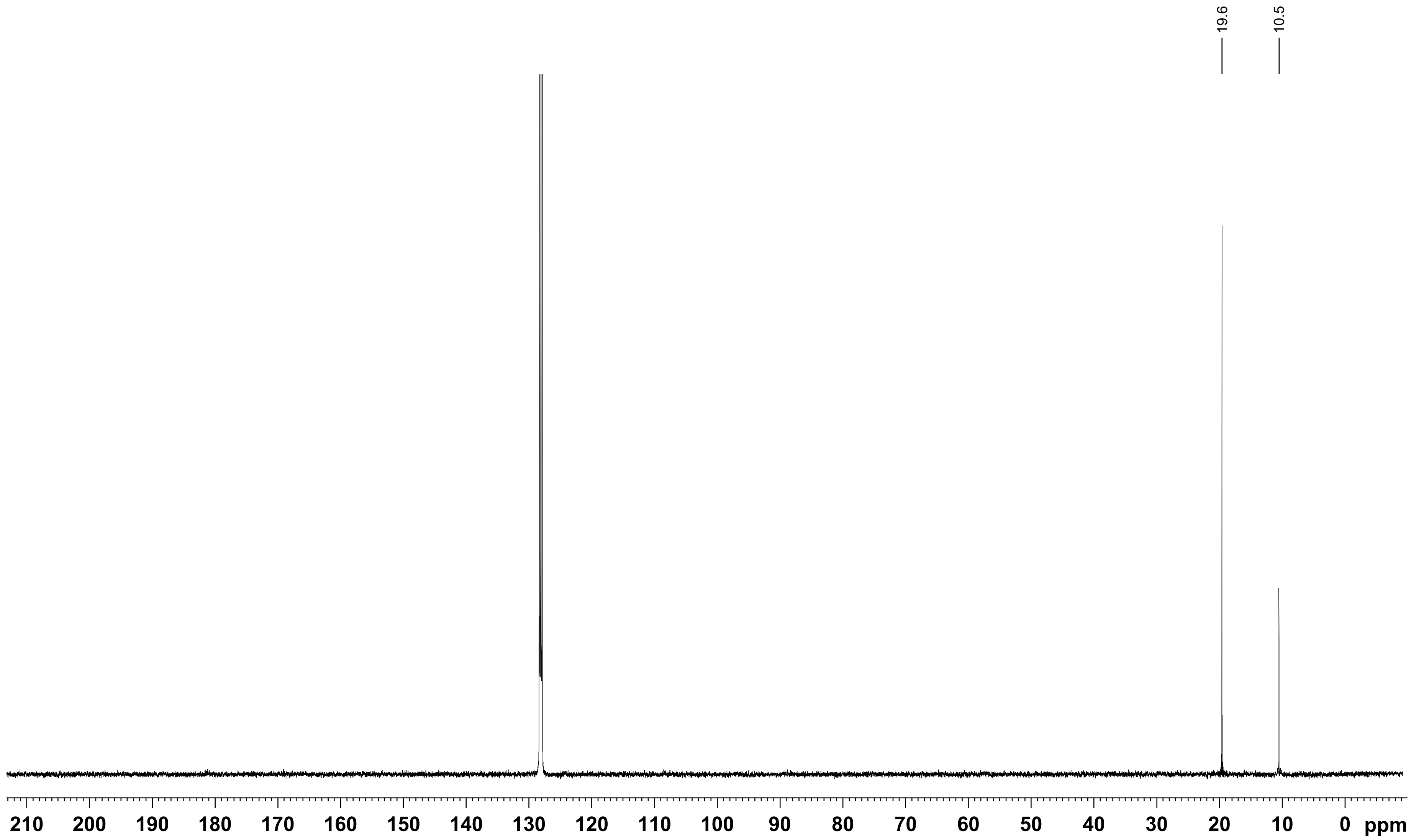


Figure S10. [1]H/[29]Si HMQC NMR (500/99 MHz, C_6D_6, 298 K, optimized for *J* = 7 Hz) of **triisopropylsilane-*d*₁ (2b-*d*₁).**

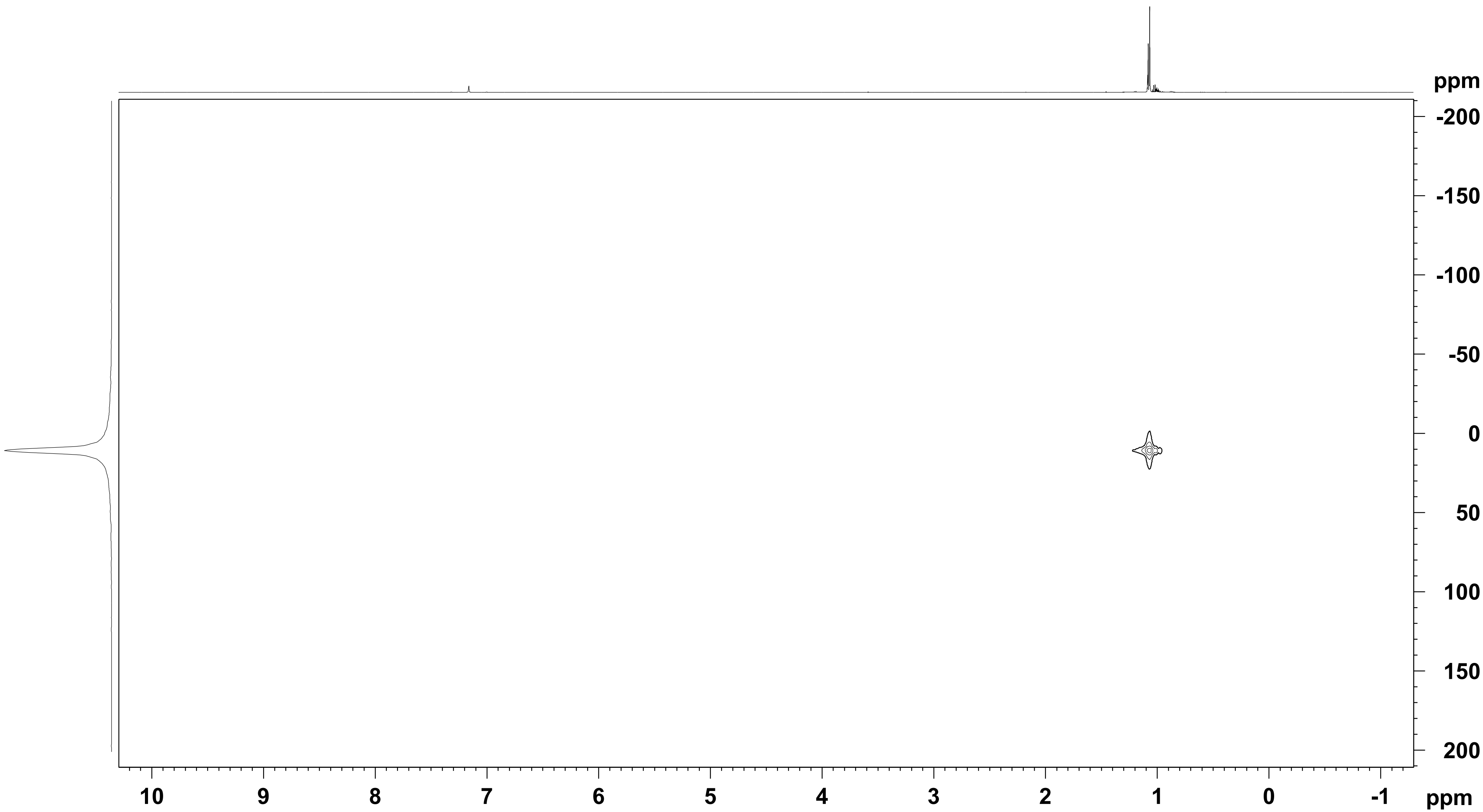
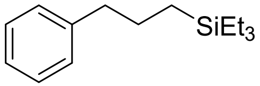


Figure S11. [1]H NMR (500 MHz, $CDCl_3$, 298 K) of **3aa** from the catalytic reaction of cyclopropylbenzene (**1a**) and Et_3SiH using $Ph_3C^+[B(C_6F_5)_4]^-$.



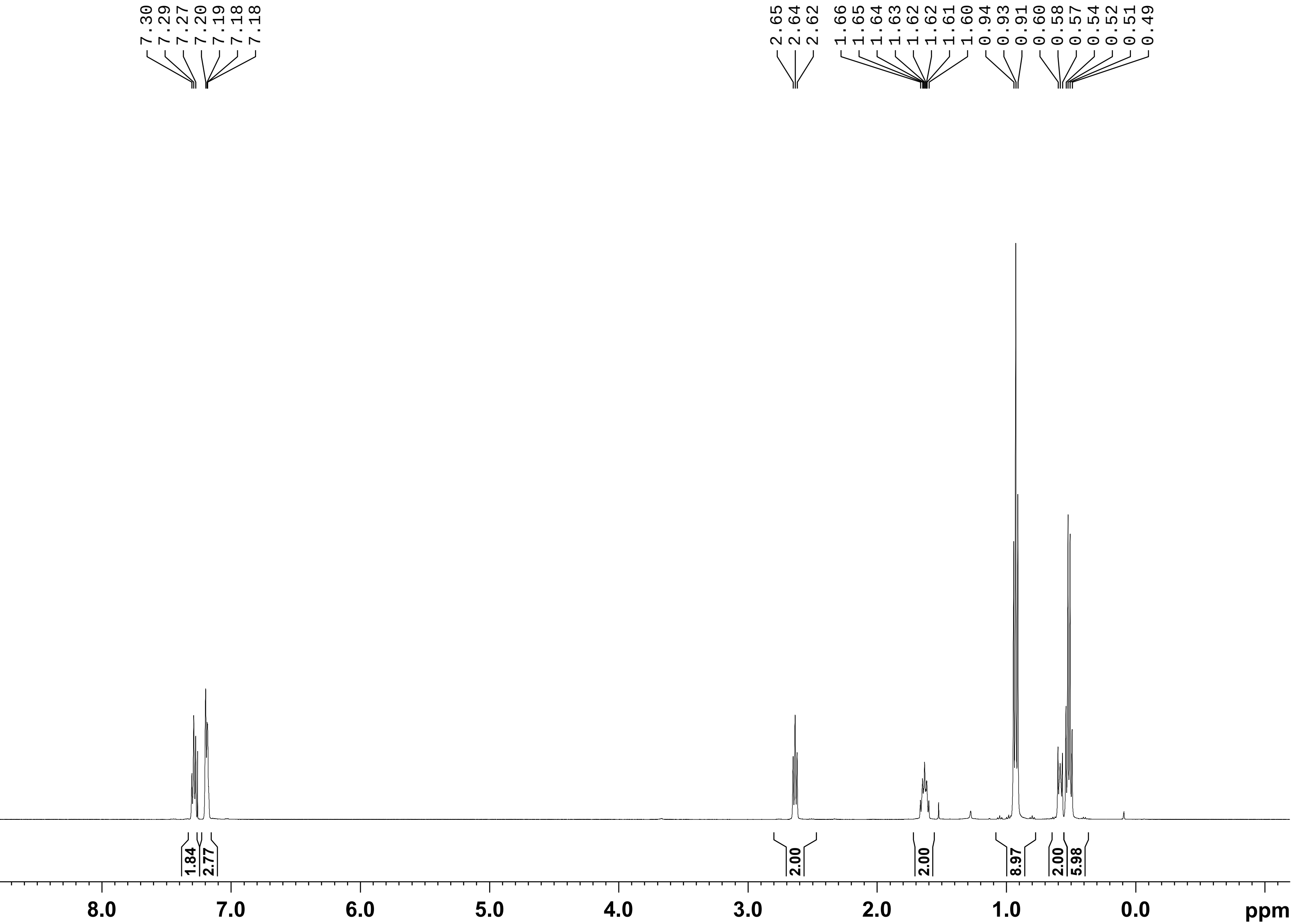


Figure S12. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **3aa** from the catalytic reaction of cyclopropylbenzene (**1a**) and Et_3SiH using $Ph_3C^+[B(C_6F_5)_4]^-$.

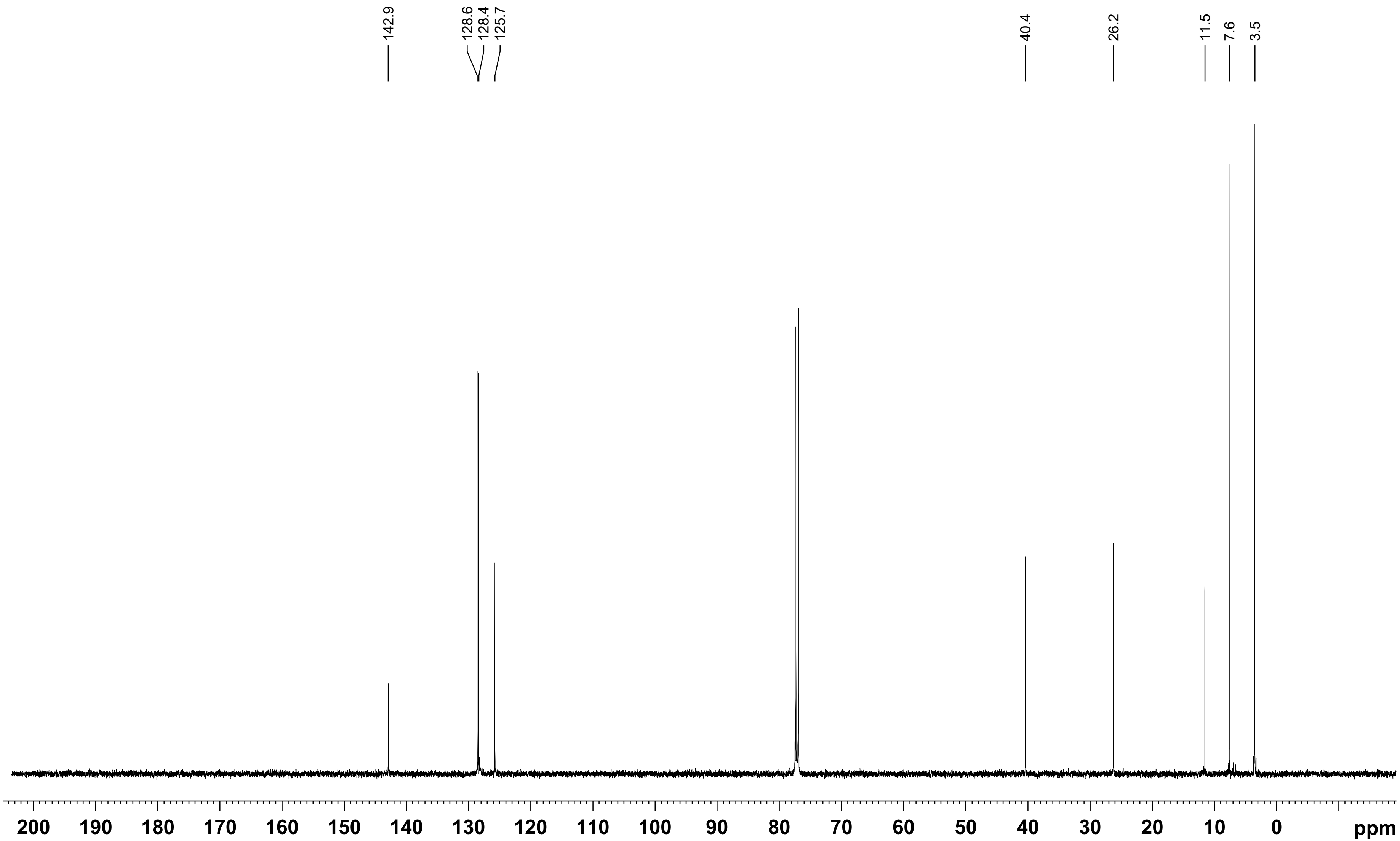


Figure S13. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz) of **3aa** from the catalytic reaction of cyclopropylbenzene (**1a**) and Et_3SiH using $Ph_3C^+[B(C_6F_5)_4]^-$.

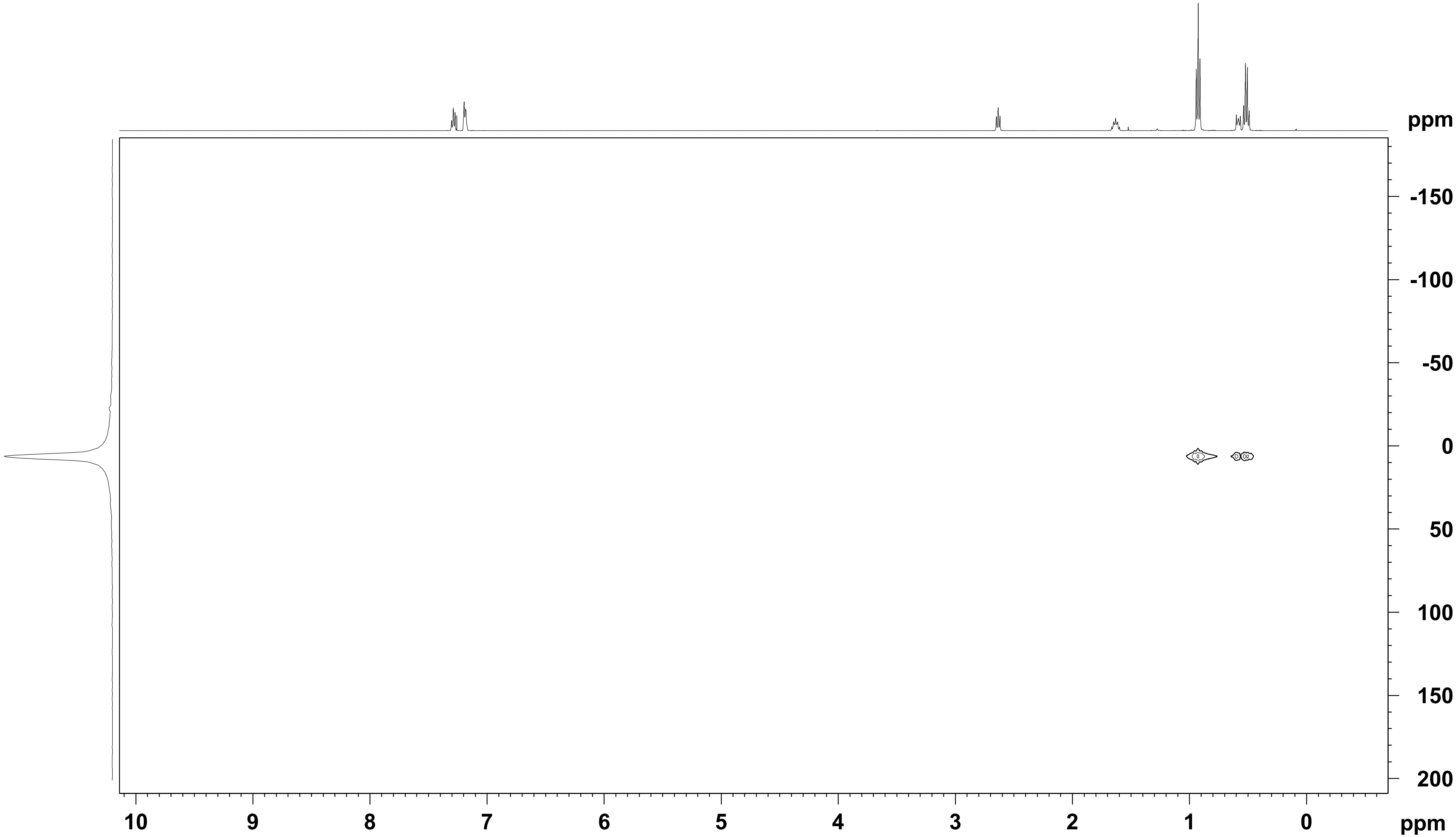


Figure S14. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **3ka** from the catalytic reaction of (1-methylcyclopropyl)benzene (**1k**) and Et_3SiH using $Ph_3C^+[B(C_6F_5)_4]^-$.

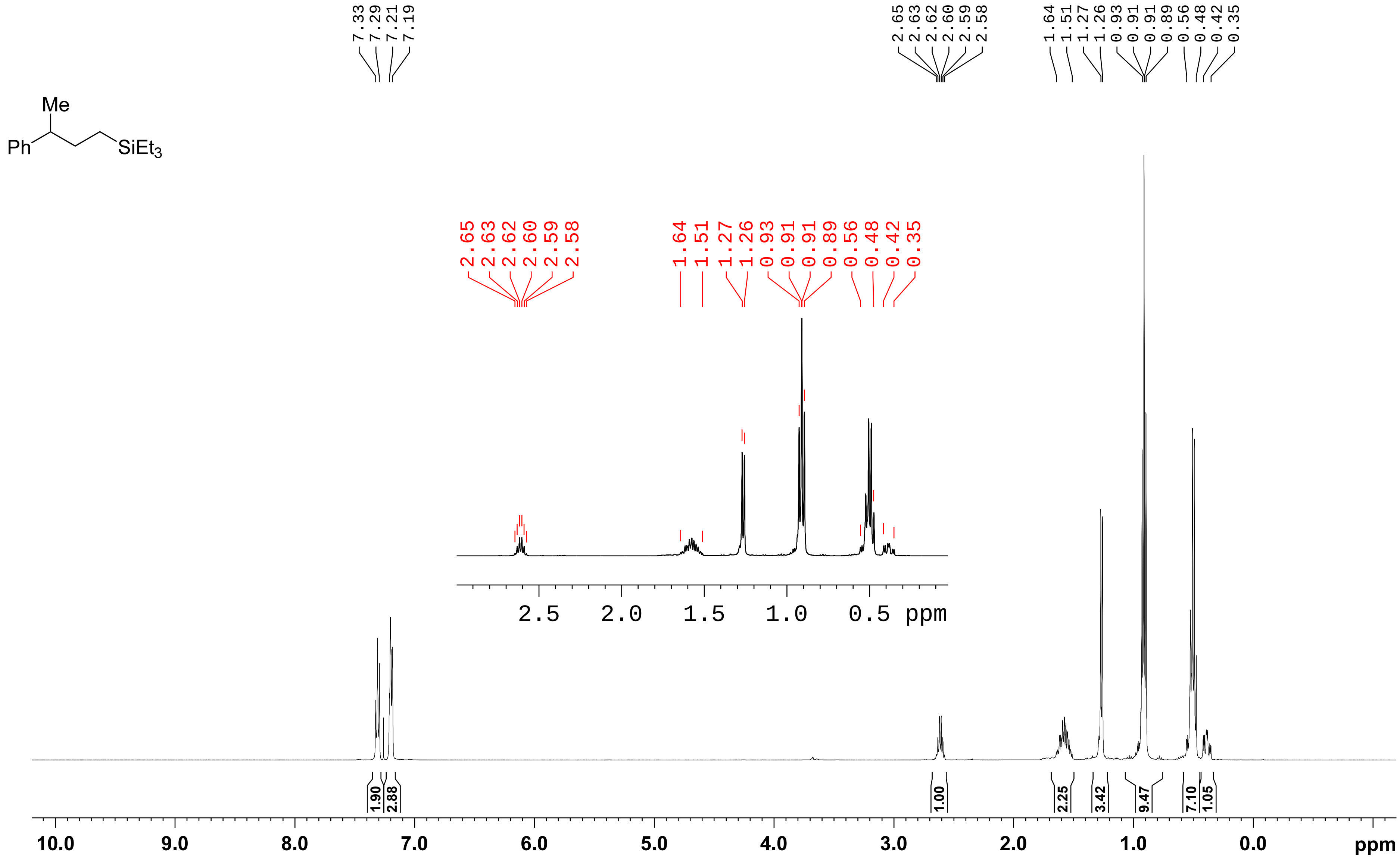


Figure S15. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **3ka** from the catalytic reaction of (1-methylcyclopropyl)benzene (**1k**) and Et_3SiH using $Ph_3C^+[B(C_6F_5)_4]^-$.

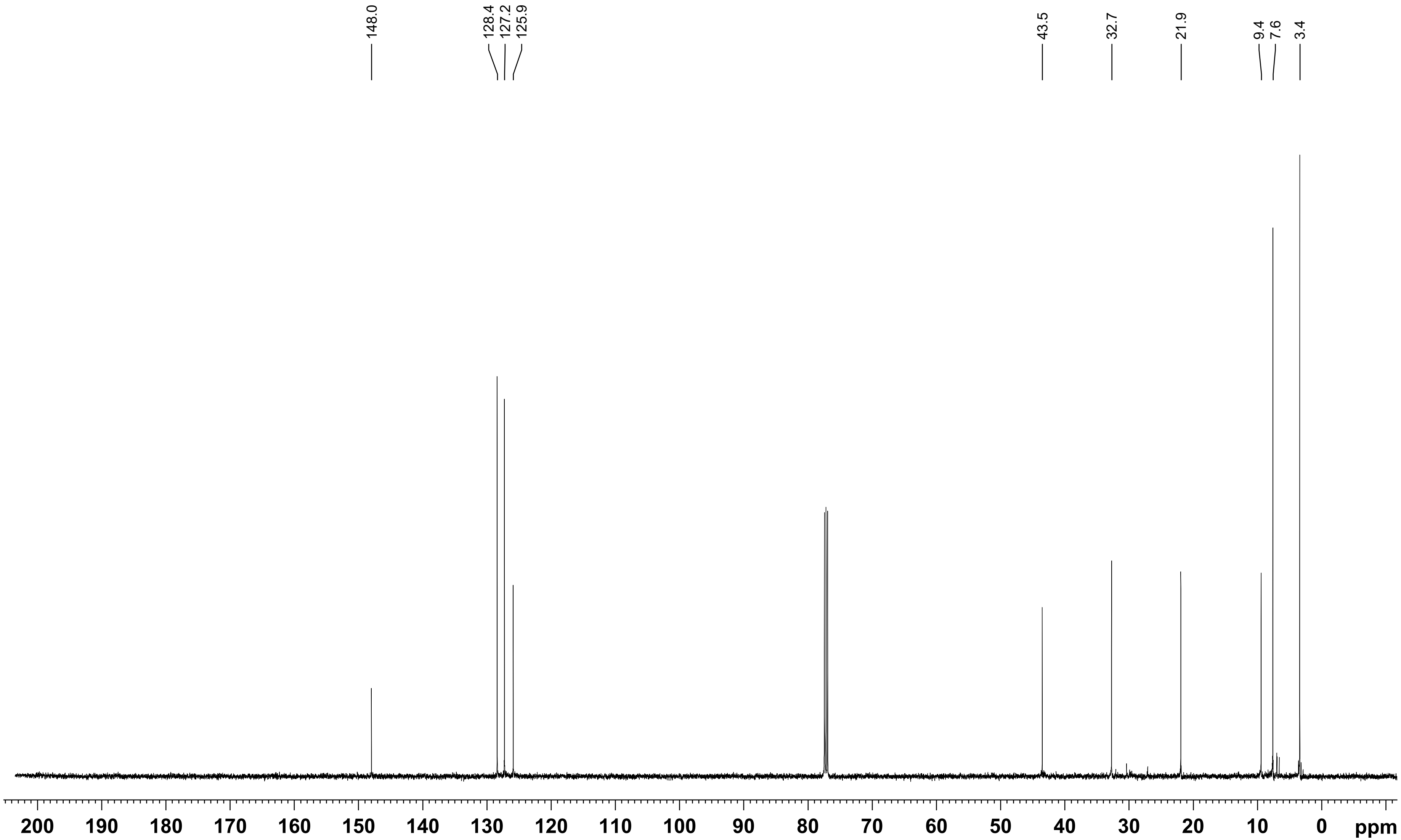


Figure S16. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz) of **3ka** from the catalytic reaction of (1-methylcyclopropyl)benzene (**1k**) and Et_3SiH using $Ph_3C^+[B(C_6F_5)_4]^-$.

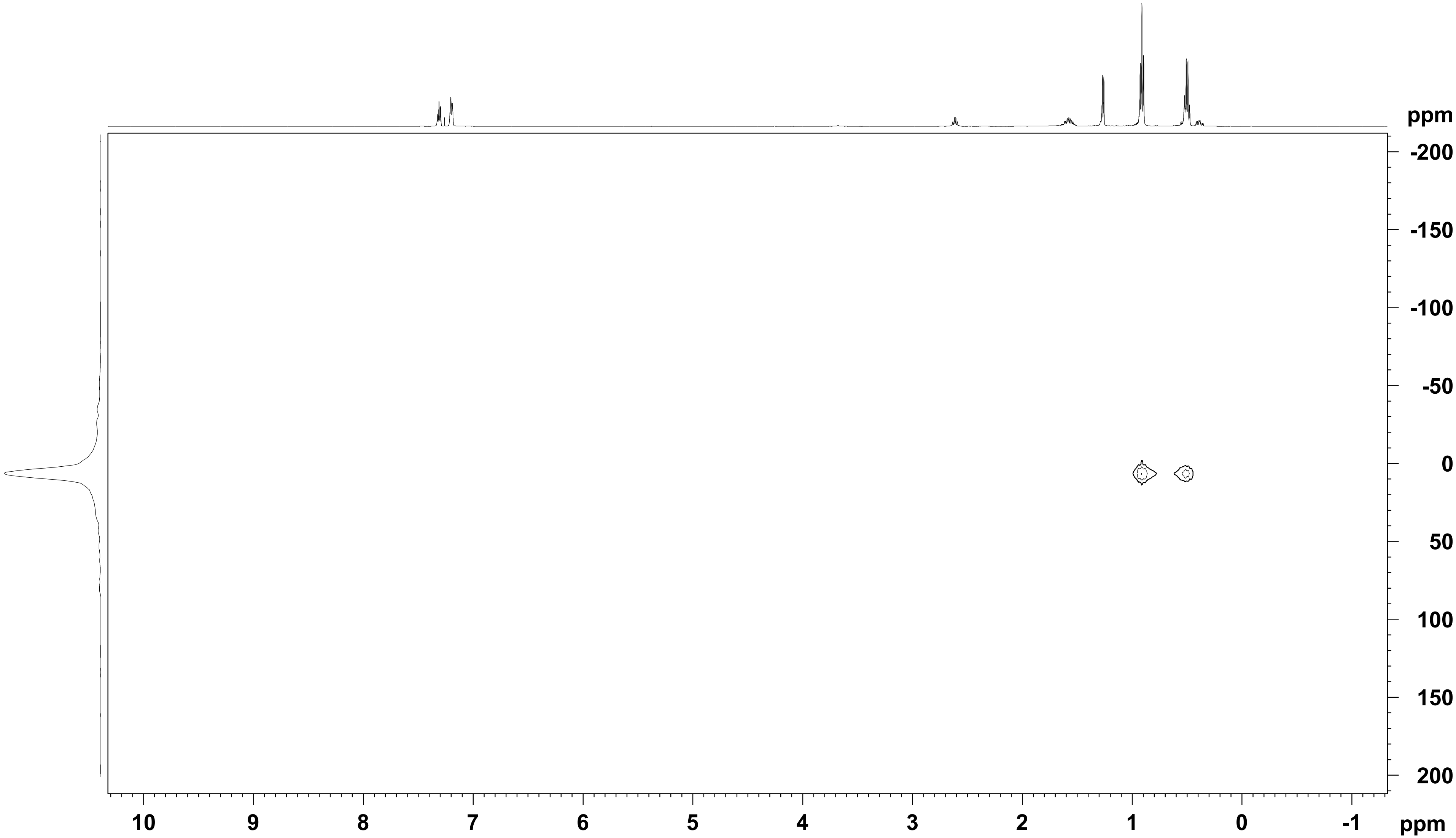
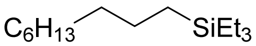


Figure S17. [1]H NMR (500 MHz, C_6D_6, 298 K) of **3ma** from the catalytic reaction of hexylcyclopropane (**1m**) and Et_3SiH using $Ph_3C^+[B(C_6F_5)_4]^-$.



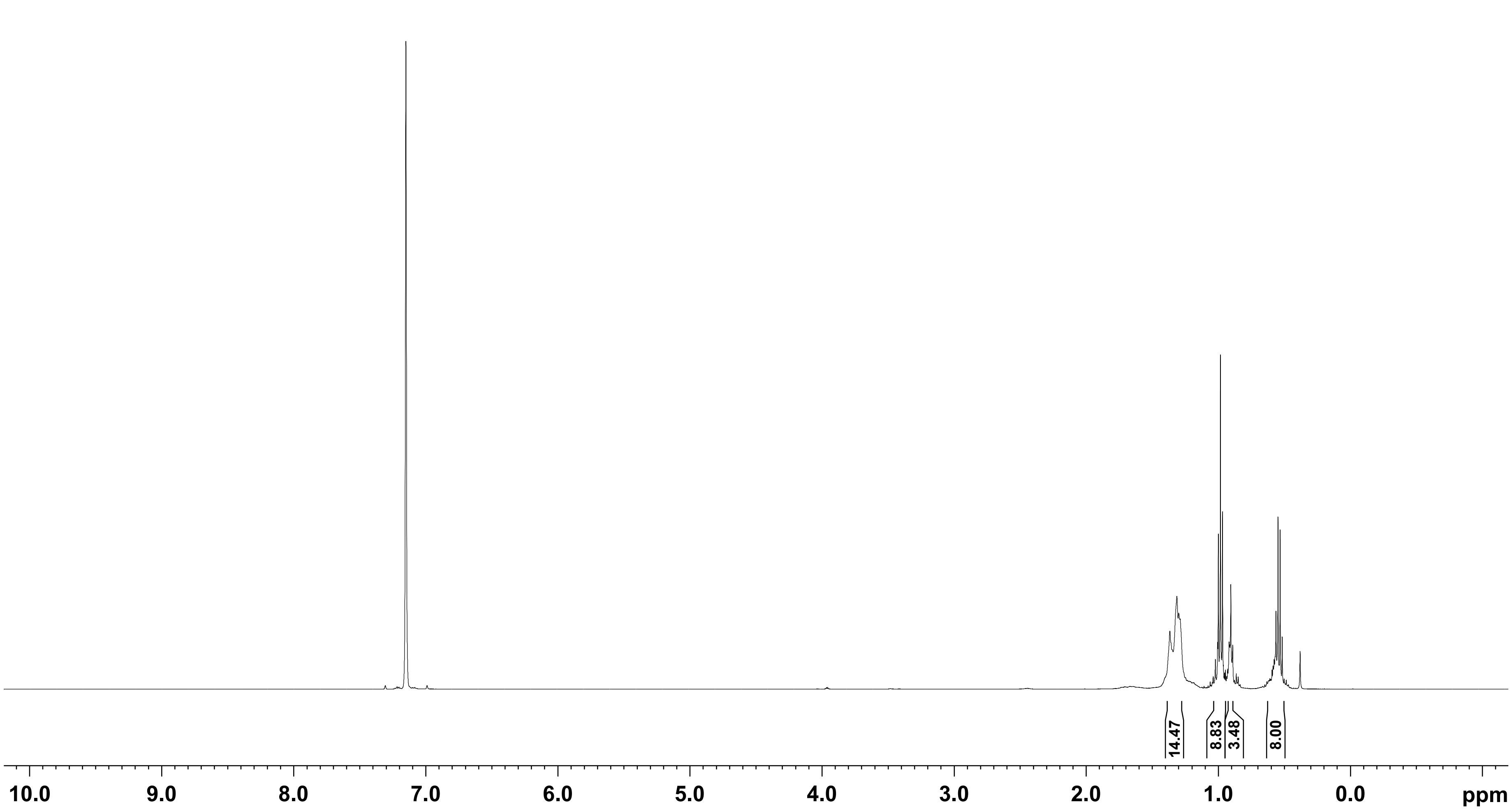


Figure S18. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K) of **3ma** from the catalytic reaction of hexylcyclopropane (**1m**) and Et_3SiH using $Ph_3C^+[B(C_6F_5)_4]^-$.

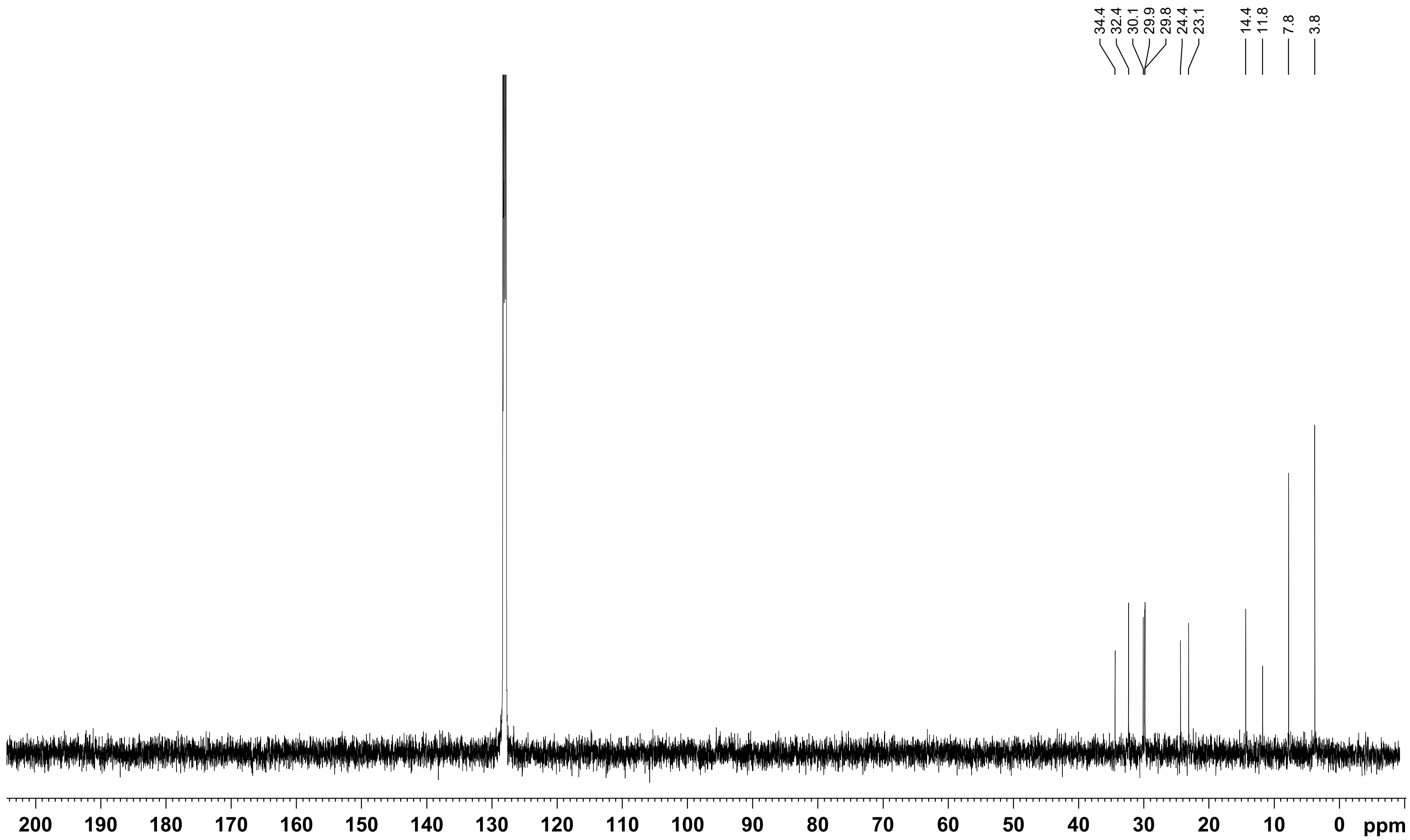


Figure S19. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, C_6D_6, 298 K, optimized for *J* = 7 Hz) of **3ma** from the catalytic reaction of hexylcyclopropane (**1m**) and Et_3SiH using $Ph_3C^{+}[B(C_6F_5)_4]^{-}$.

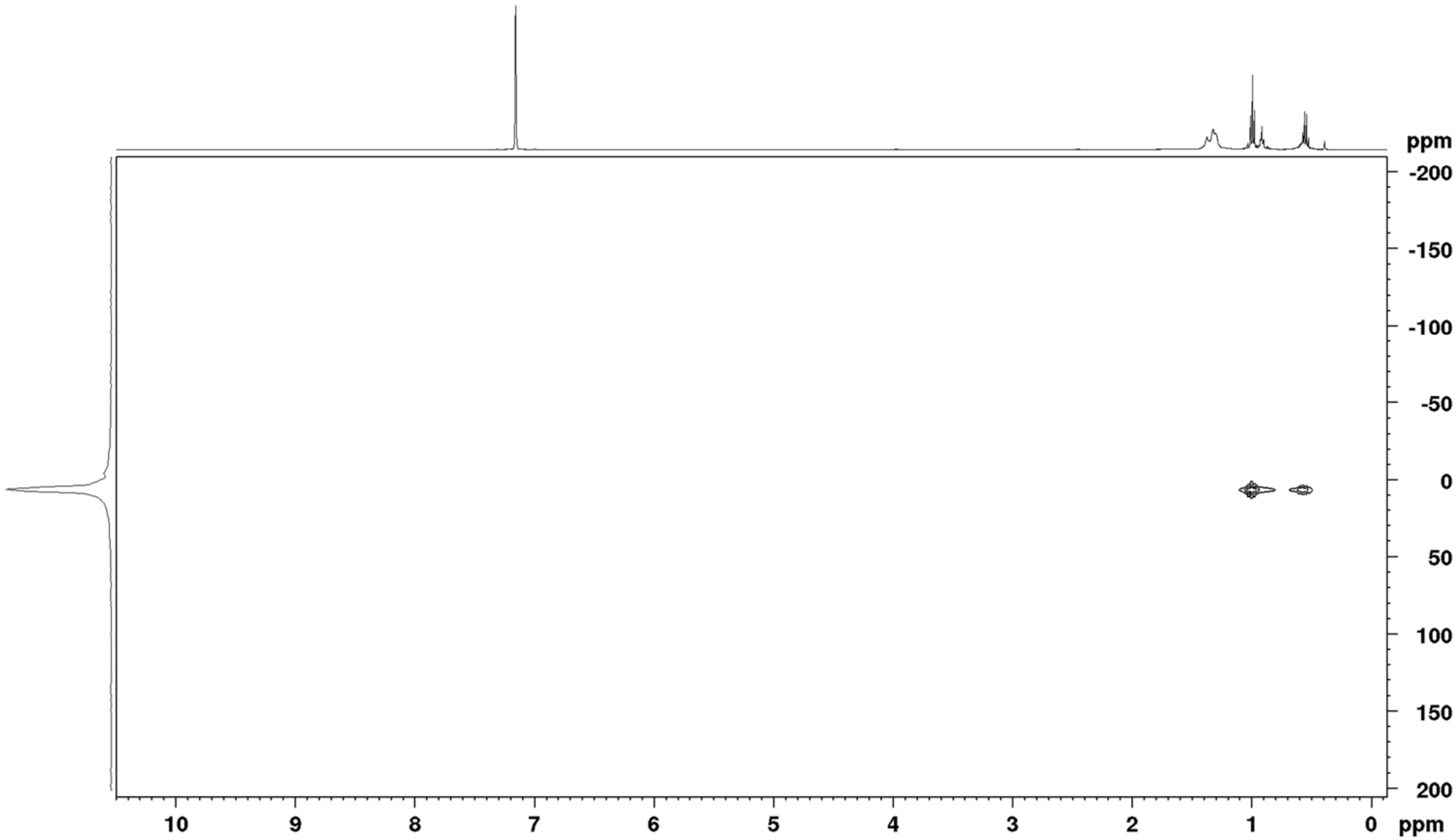


Figure S20. ^{1}H NMR (500 MHz, C_6D_6, 298 K) of **3ab** from the catalytic reaction of cyclopropylbenzene (**1a**) and $^i Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

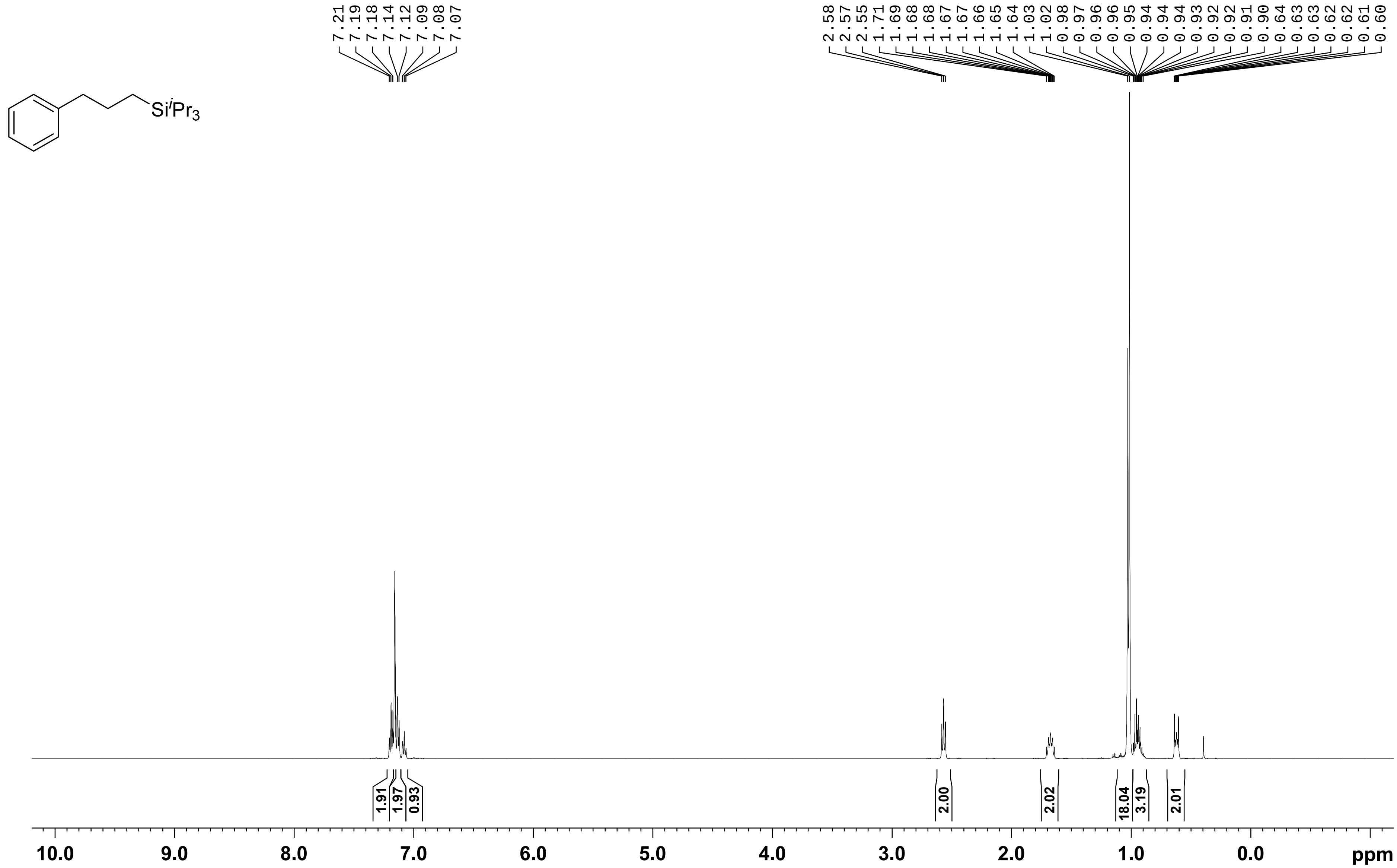


Figure S21. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **3ab** from the catalytic reaction of cyclopropylbenzene (**1a**) and $^{i}Pr_3SiH$ using $Ph_3C^{+}[B(C_6F_5)_4]^{-}$.

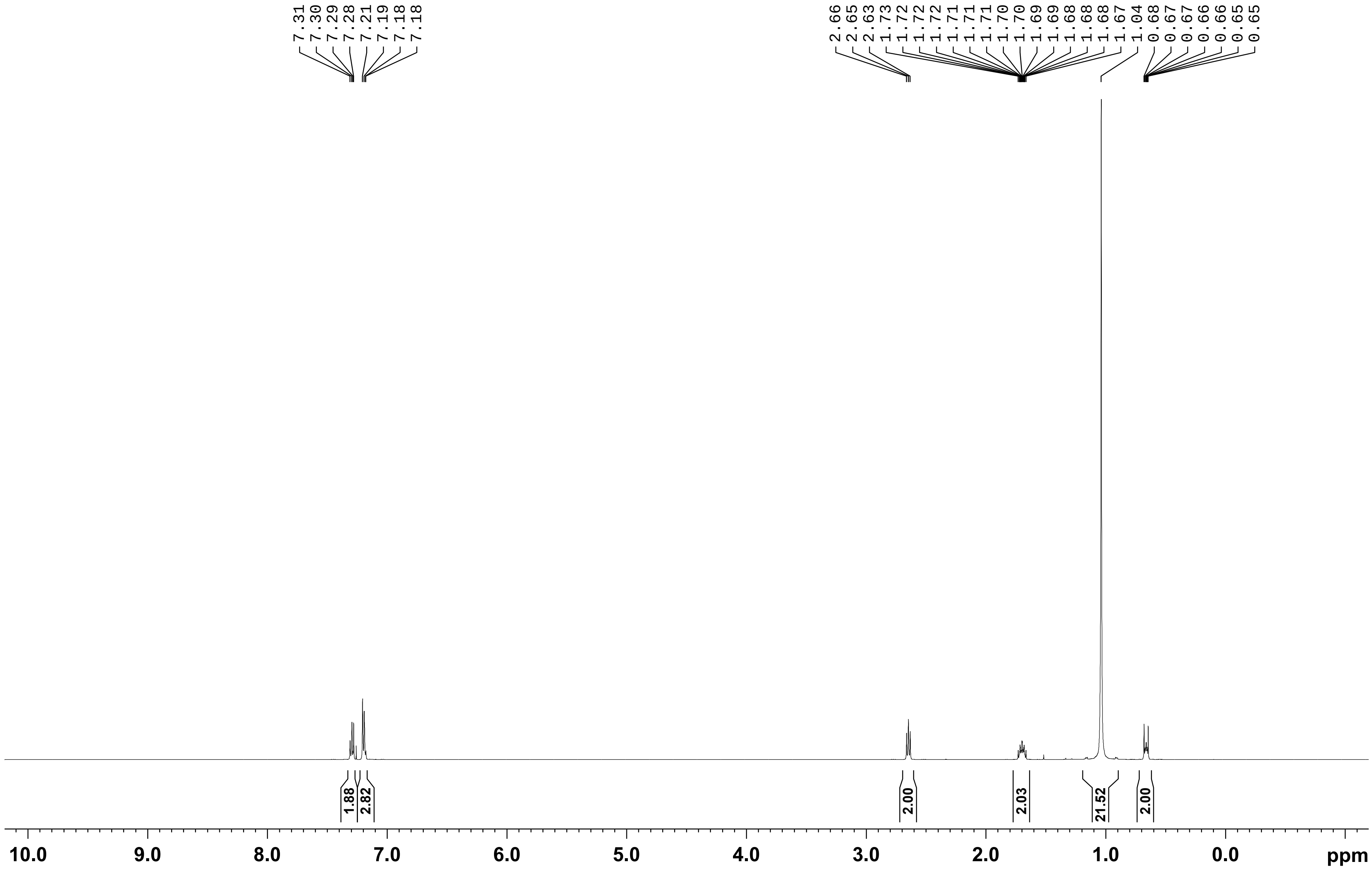


Figure S22. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **3ab** from the catalytic reaction of cyclopropylbenzene (**1a**) and $^{i}Pr_3SiH$ using $Ph_3C^{+}[B(C_6F_5)_4]^{-}$.

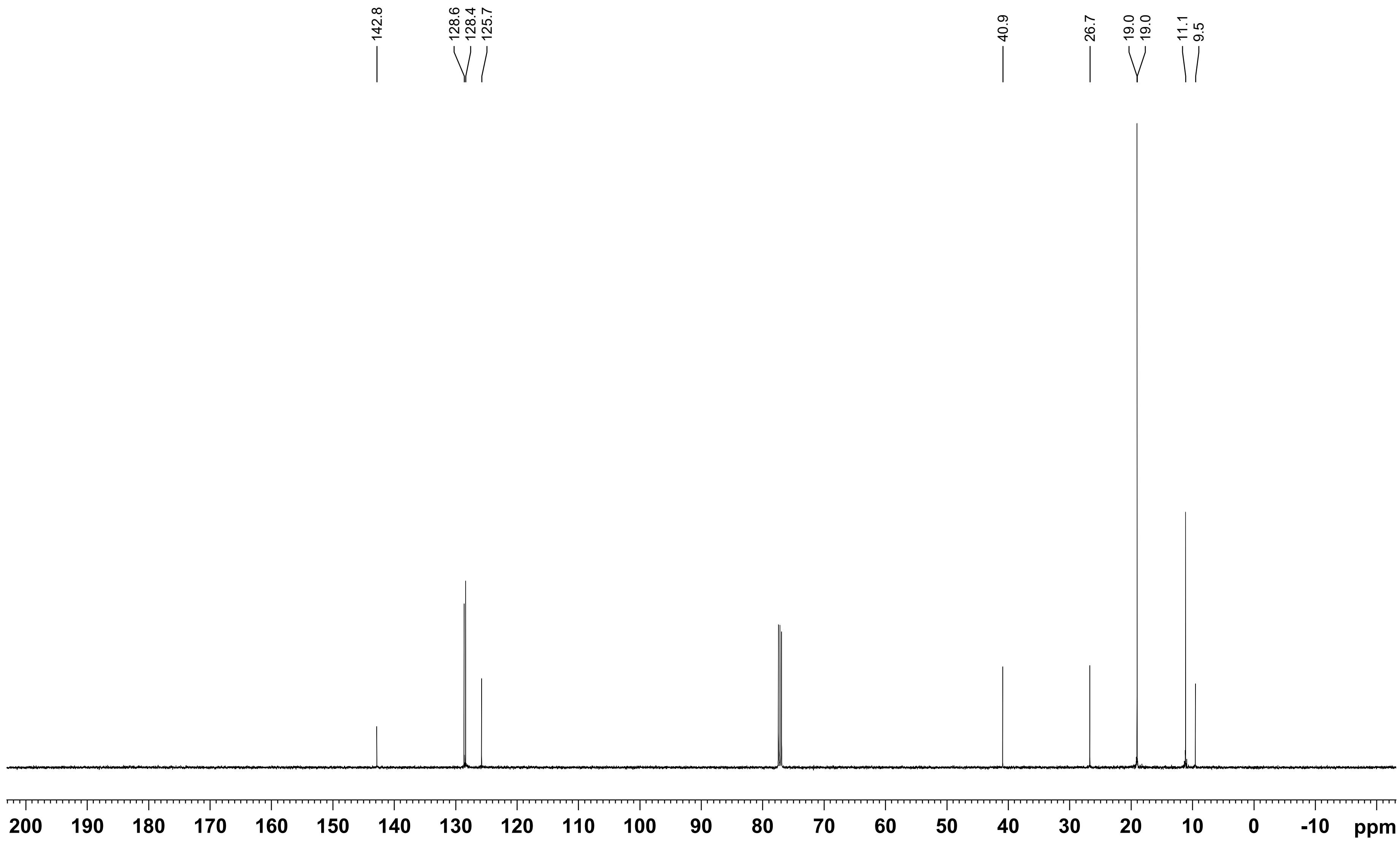


Figure S23. $^1H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz) of **3ab** from the catalytic reaction of cyclopropylbenzene (**1a**) and $^iPr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

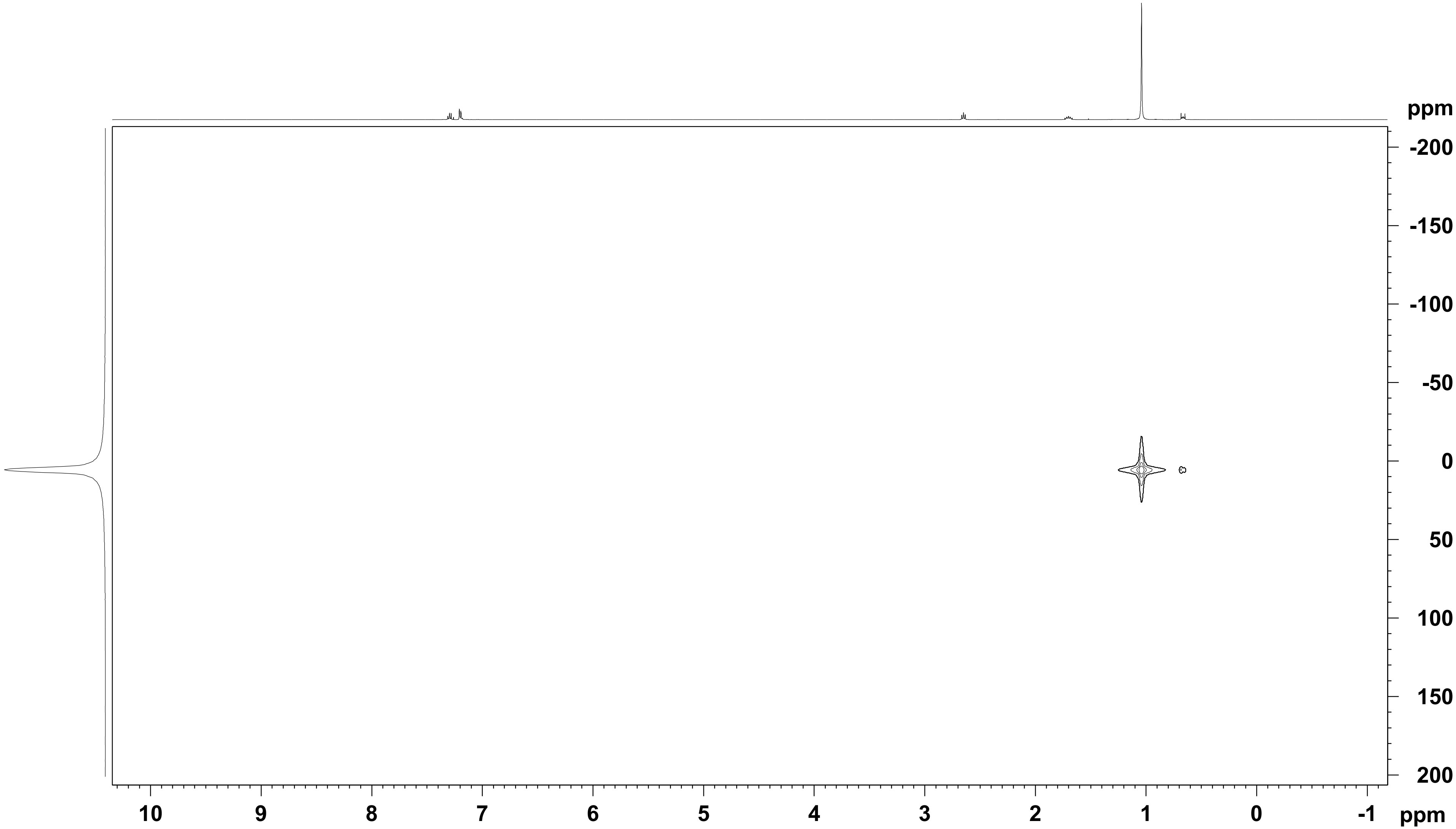


Figure S24. [1]H NMR (500 MHz, $CDCl_3$, 298 K) of **3bb** from the catalytic reaction of 1-cyclopropyl-4-fluorobenzene (**1b**) and $^{i}Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

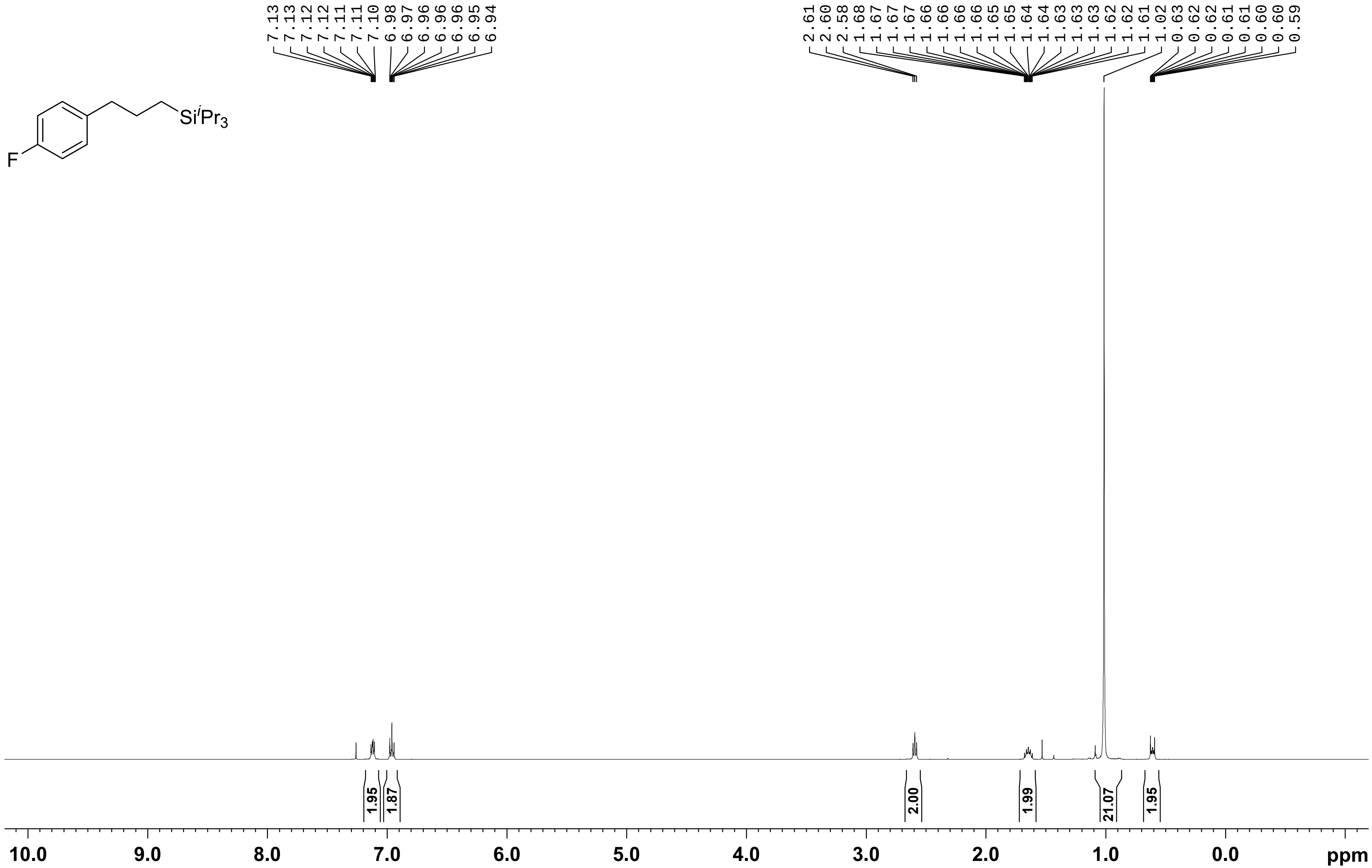


Figure S25. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **3bb** from the catalytic reaction of 1-cyclopropyl-4-fluorobenzene (**1b**) and $^{i}Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

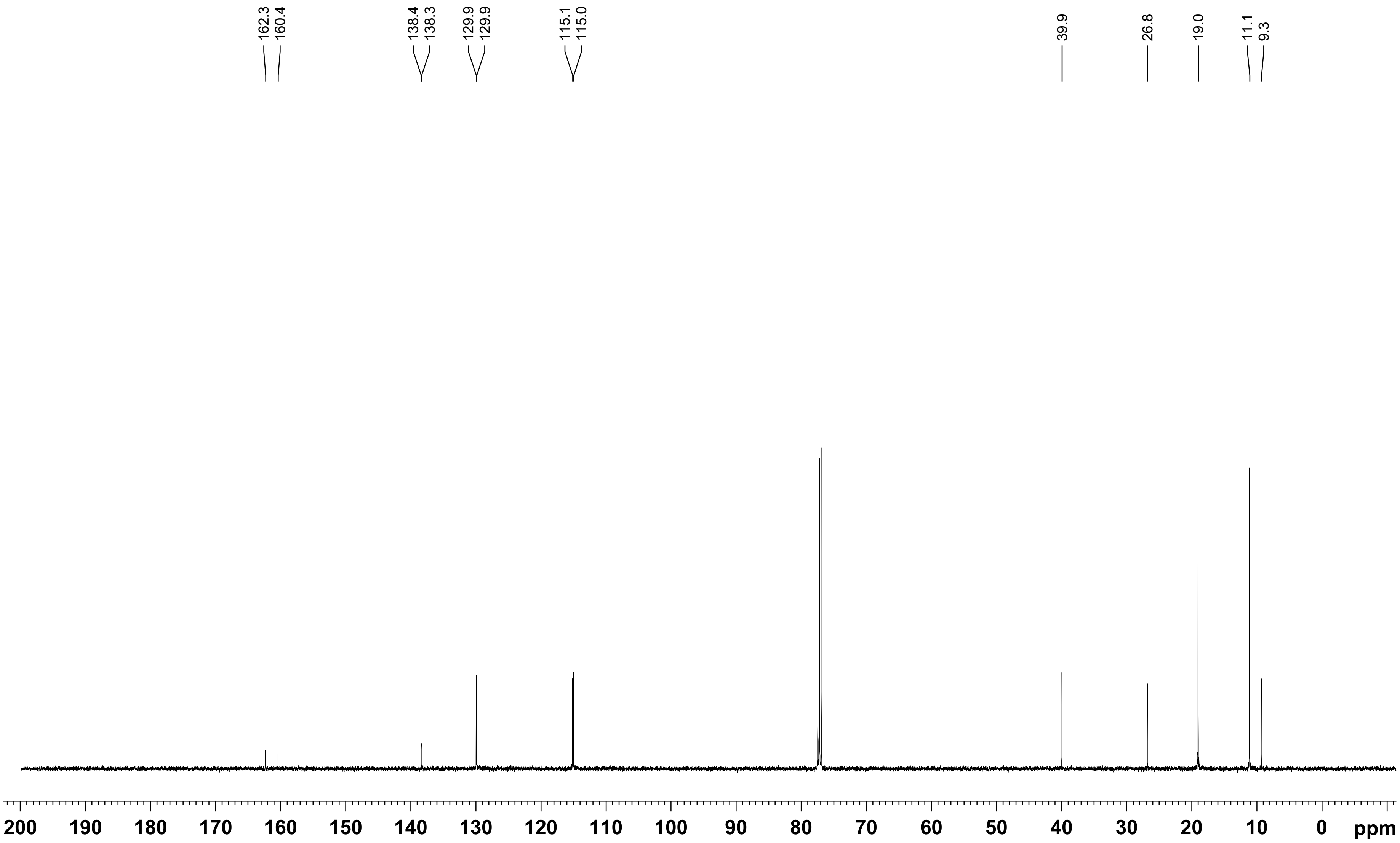


Figure S26. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **3bb** from the catalytic reaction of 1-cyclopropyl-4-fluorobenzene (**1b**) and $^{i}Pr_3SiH$ using $Ph_3C^{+}[B(C_6F_5)_4]^{-}$.

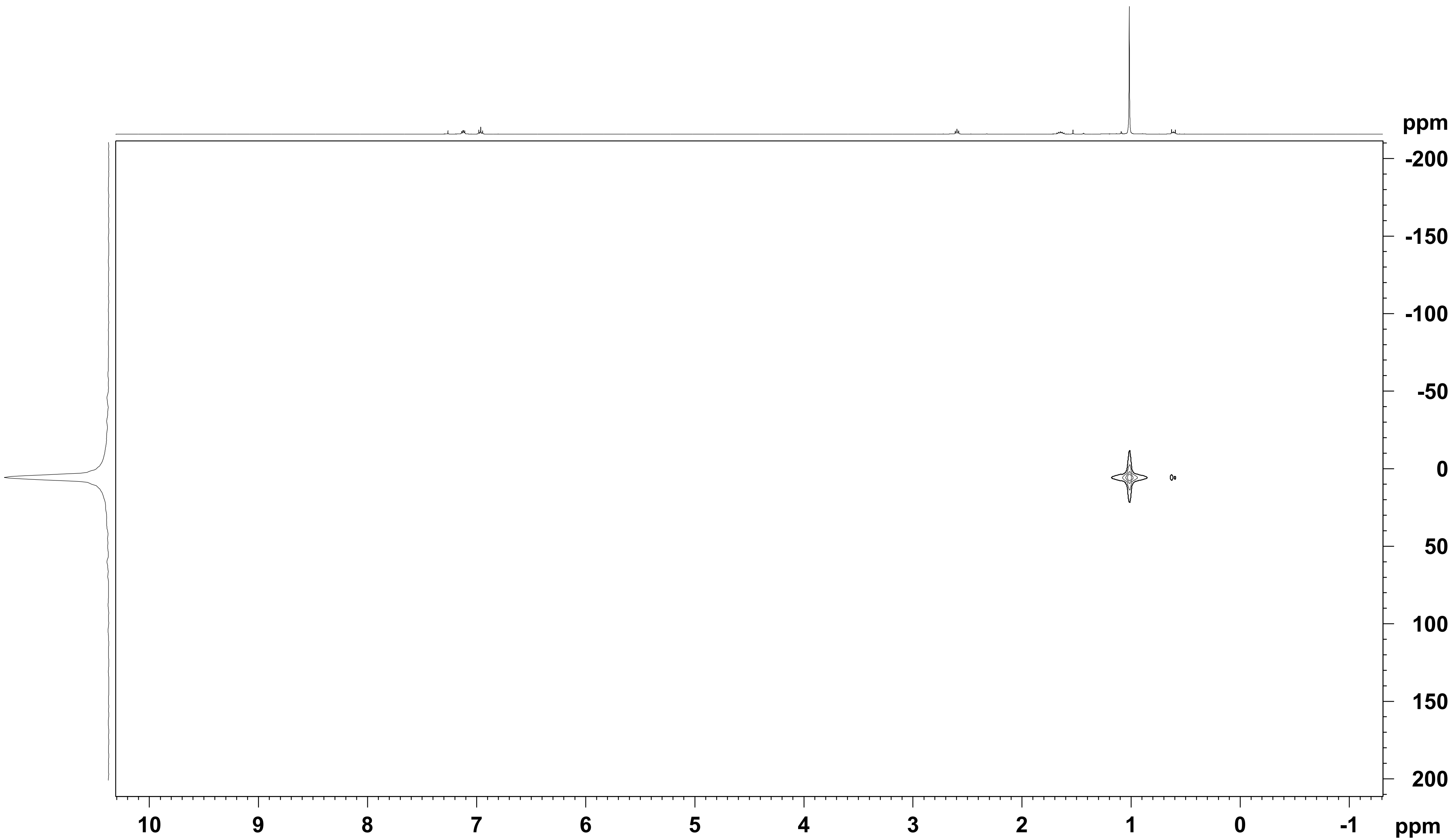


Figure S27. $^{19}F\{^{1}H\}$ NMR (500 MHz, $CDCl_3$, 298 K) of **3bb** from the catalytic reaction of 1-cyclopropyl-4-fluorobenzene (**1b**) and $^{i}Pr_3SiH$ using $Ph_3C^{+}[B(C_6F_5)_4]^{-}$.

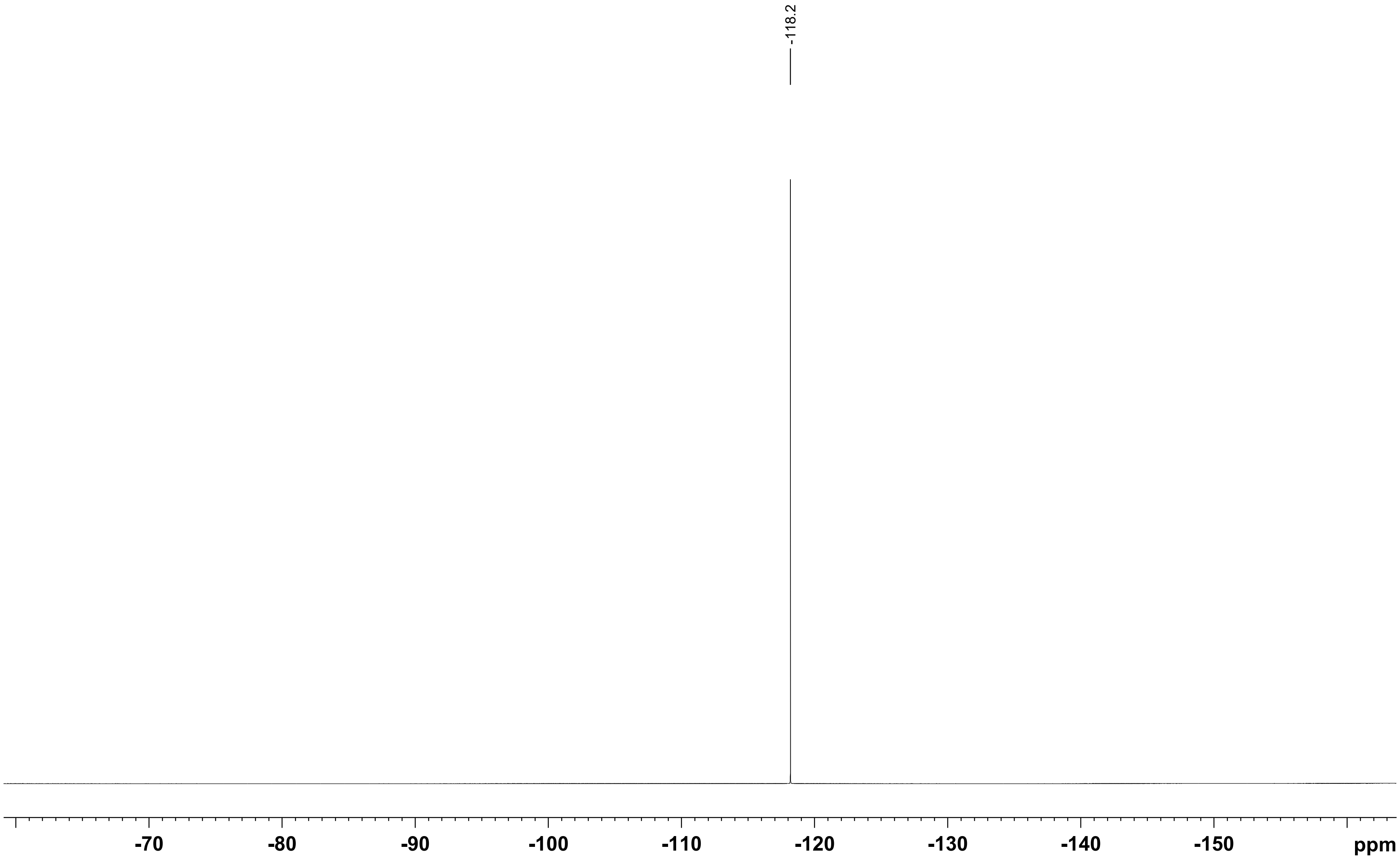


Figure S28. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **3cb** from the catalytic reaction of 1-chloro-4-cyclopropylbenzene (**1c**) and $^i Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

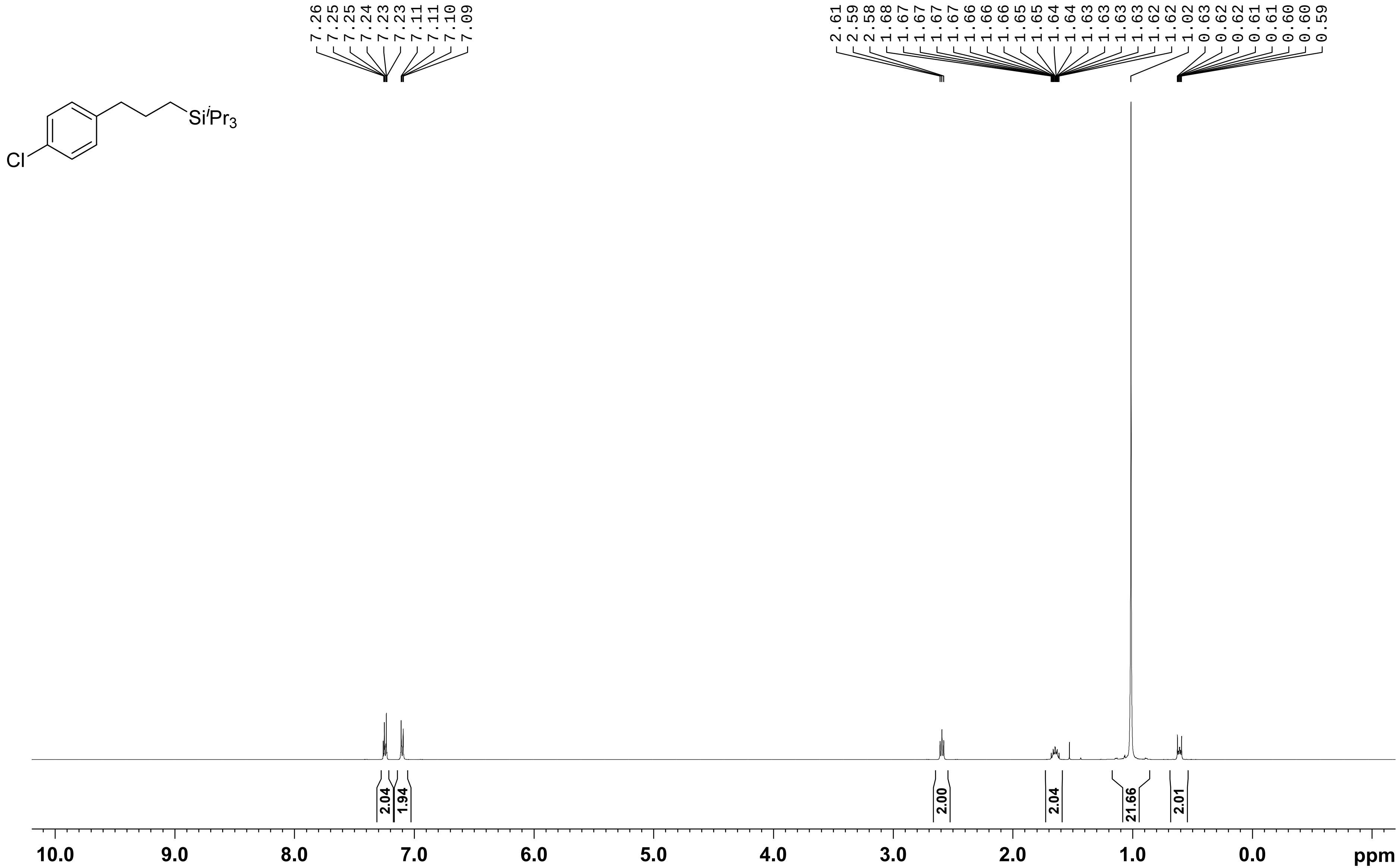


Figure S29. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **3cb** from the catalytic reaction of 1-chloro-4-cyclopropylbenzene (**1c**) and $^{i}Pr_3SiH$ using $Ph_3C^{+}[B(C_6F_5)_4]^{-}$.

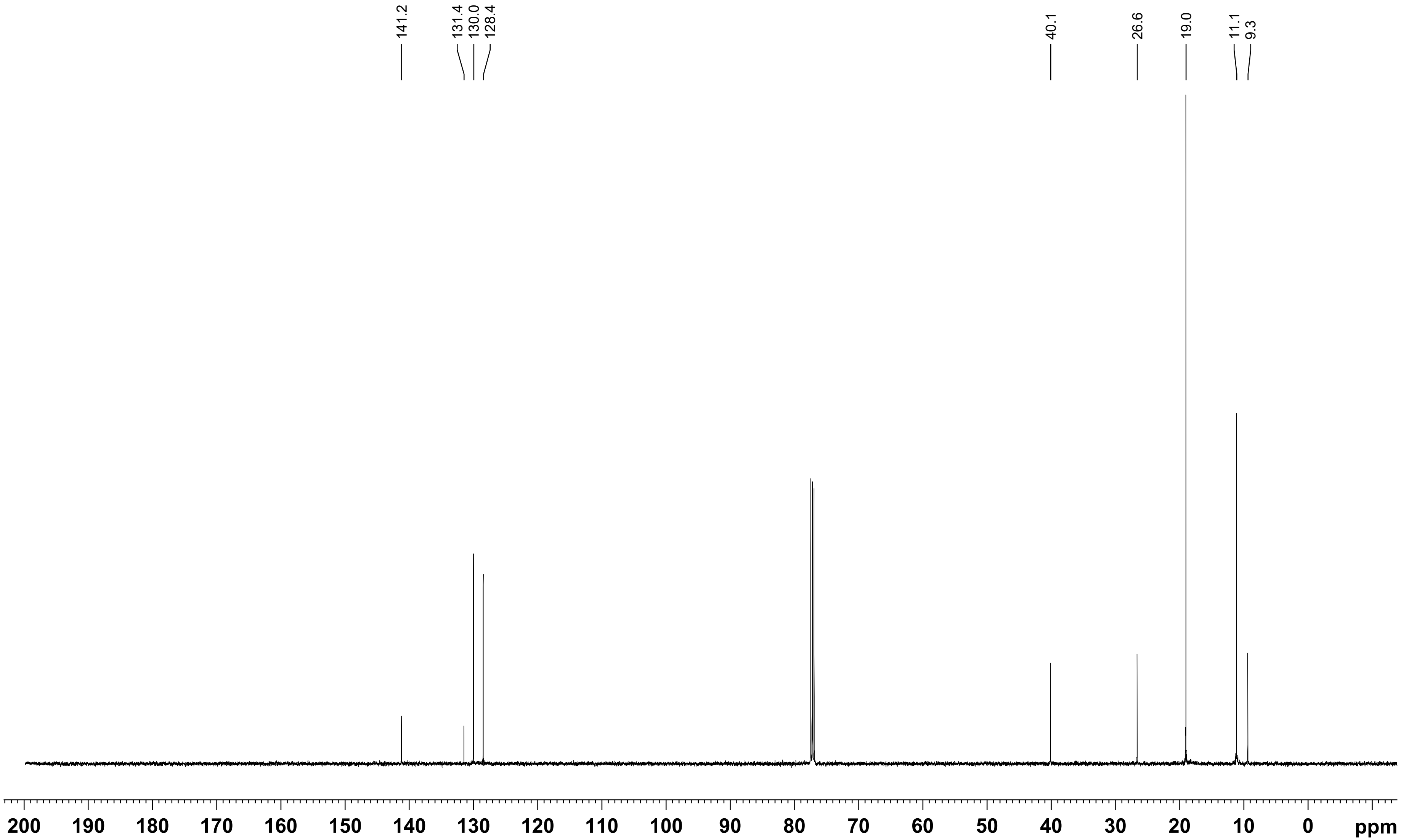


Figure S30. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **3cb** from the catalytic reaction of 1-chloro-4-cyclopropylbenzene (**1c**) and $^{i}Pr_3SiH$ using $Ph_3C^{+}[B(C_6F_5)_4]^{-}$.

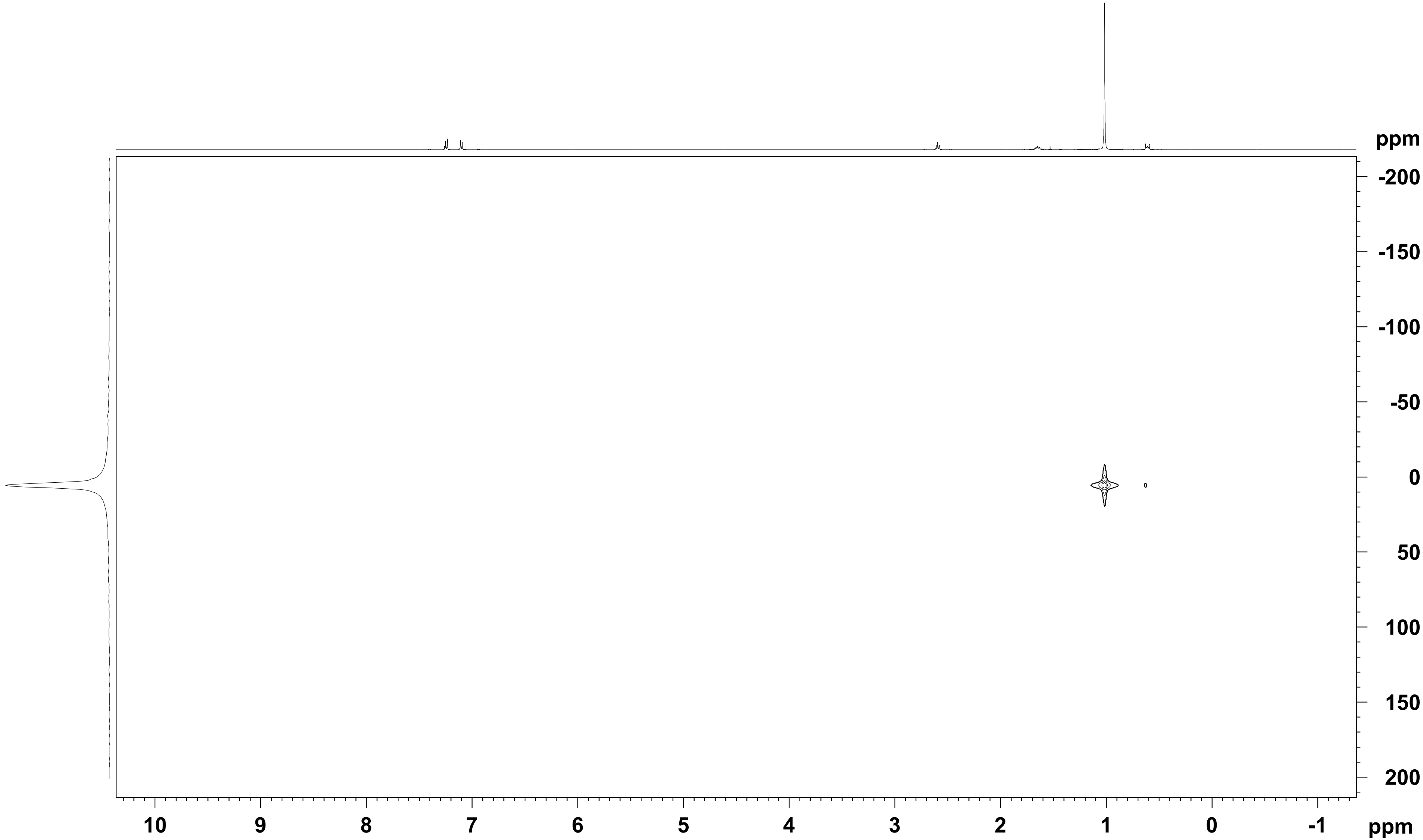


Figure S31. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **3db** from the catalytic reaction of 1-bromo-4-cyclopropylbenzene (**1d**) and $^i Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

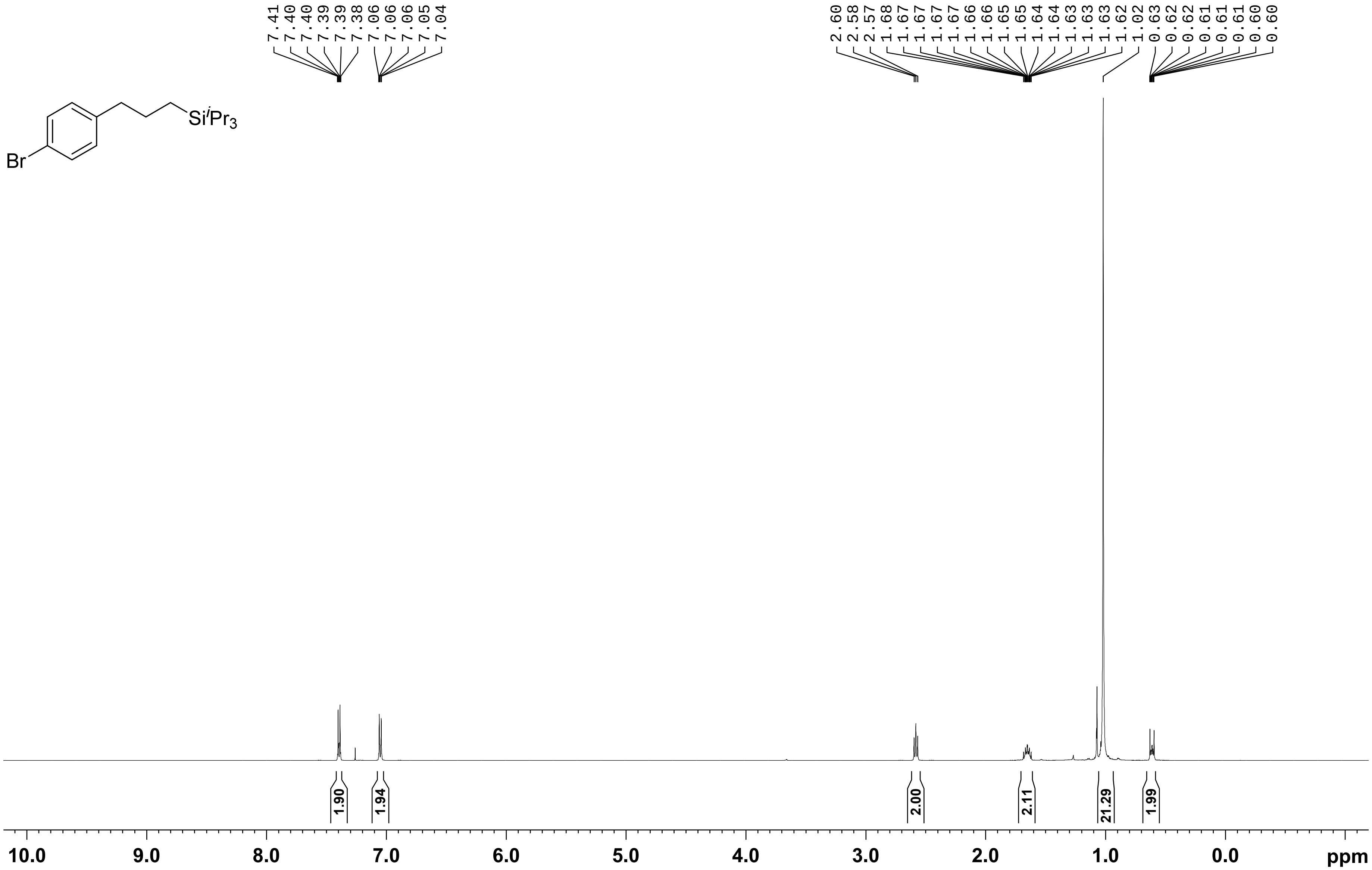


Figure S32. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **3db** from the catalytic reaction of 1-bromo-4-cyclopropylbenzene (**1d**) and $^{i}Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

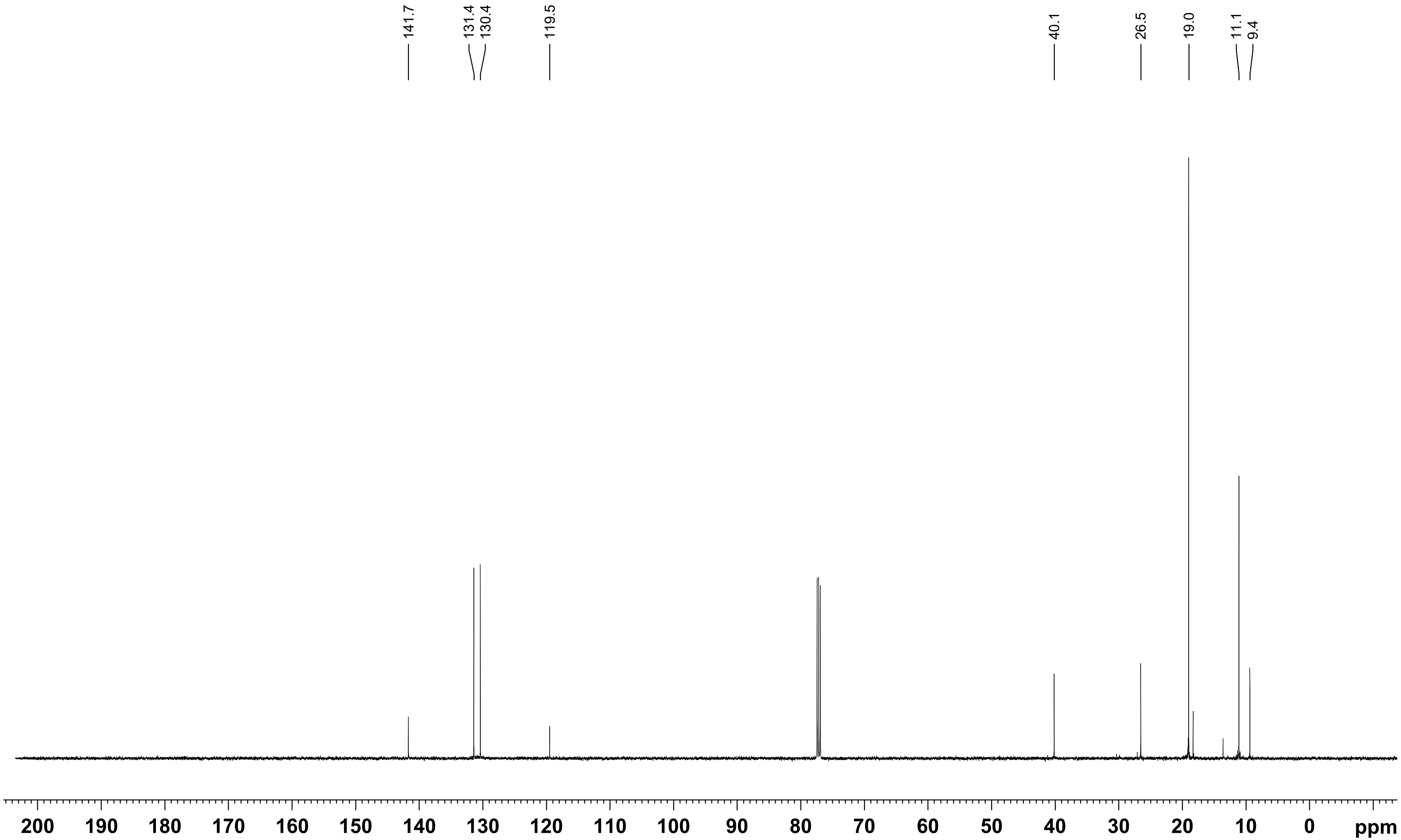


Figure S33. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **3db** from the catalytic reaction of 1-bromo-4-cyclopropylbenzene (**1d**) and $^{i}Pr_3SiH$ using $Ph_3C^{+}[B(C_6F_5)_4]^{-}$.

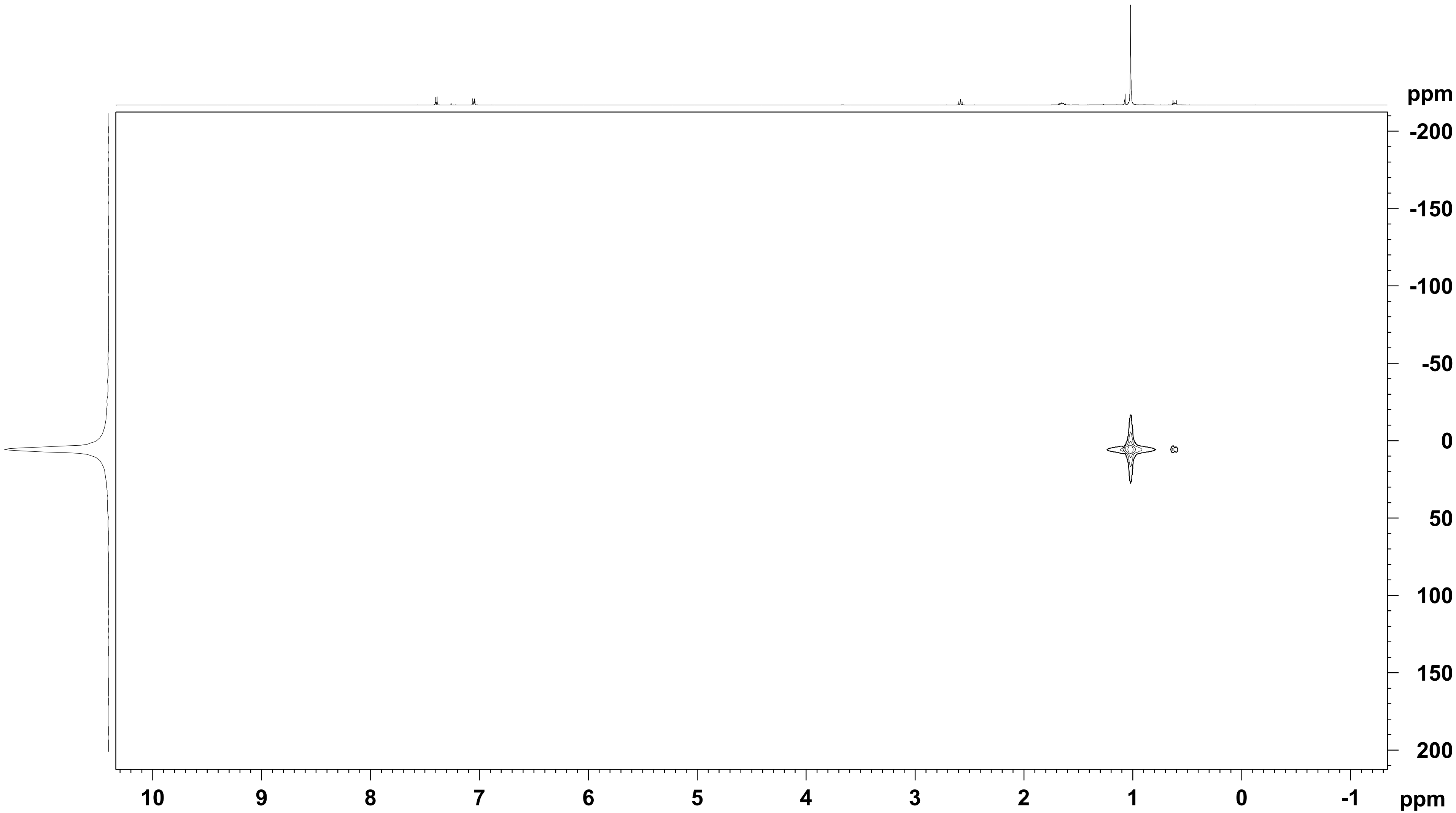


Figure S34. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **3eb** from the catalytic reaction of 1-cyclopropyl-4-methylbenzene (**1e**) and $^{i}Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

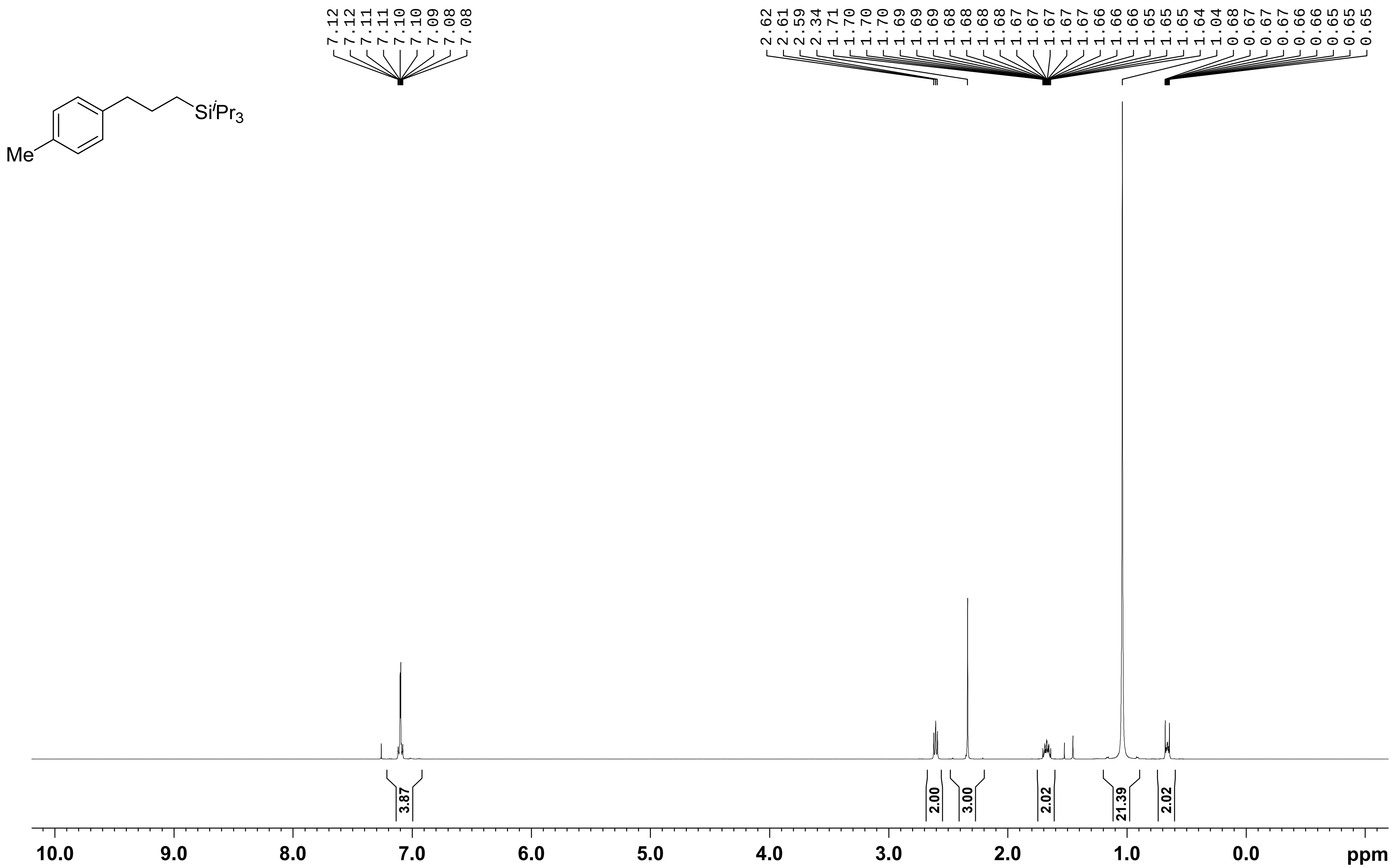


Figure S35. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **3eb** from the catalytic reaction of 1-cyclopropyl-4-methylbenzene (**1e**) and $^iPr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

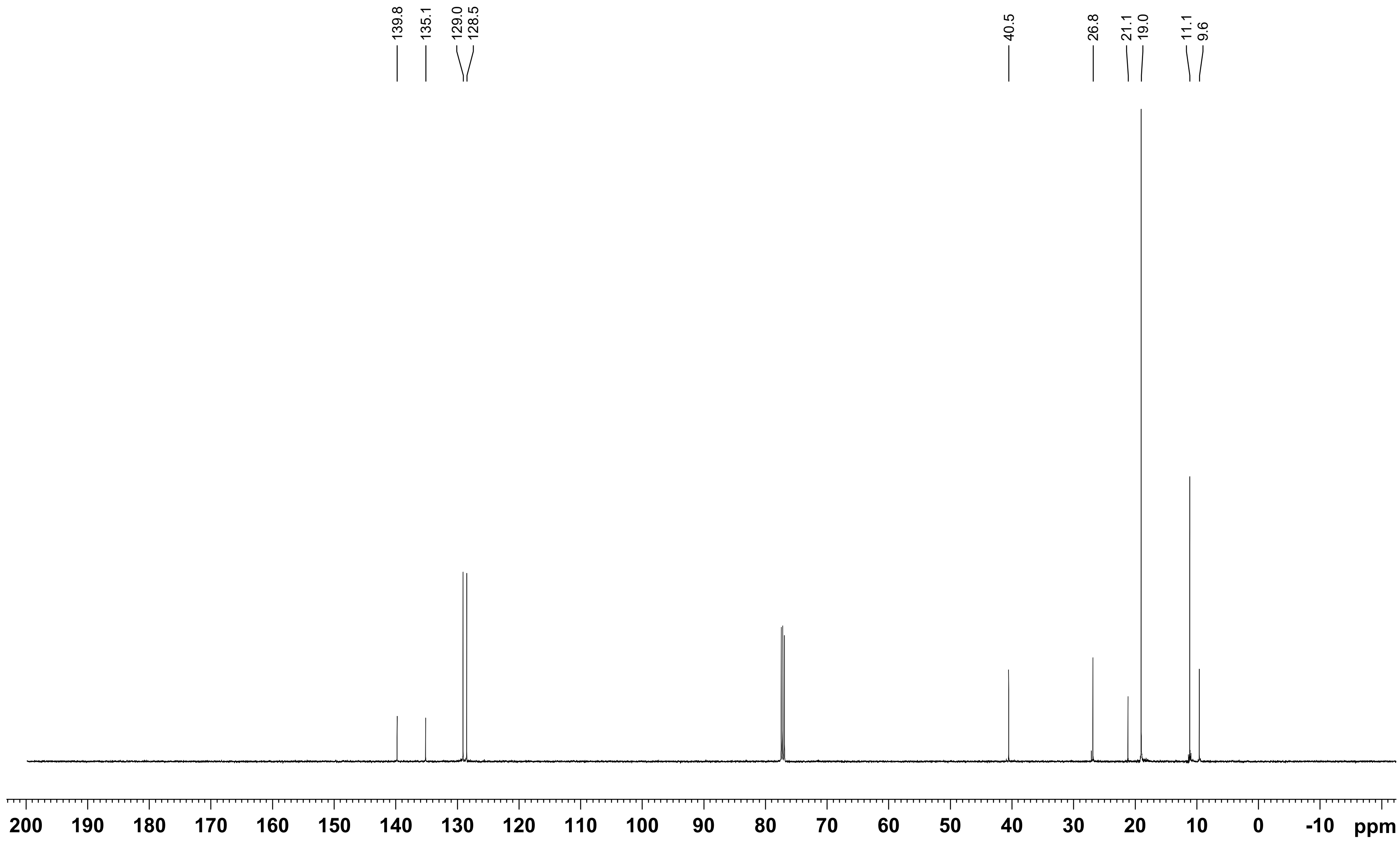


Figure S36. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **3eb** from the catalytic reaction of 1-cyclopropyl-4-methylbenzene (**1e**) and $^{i}Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

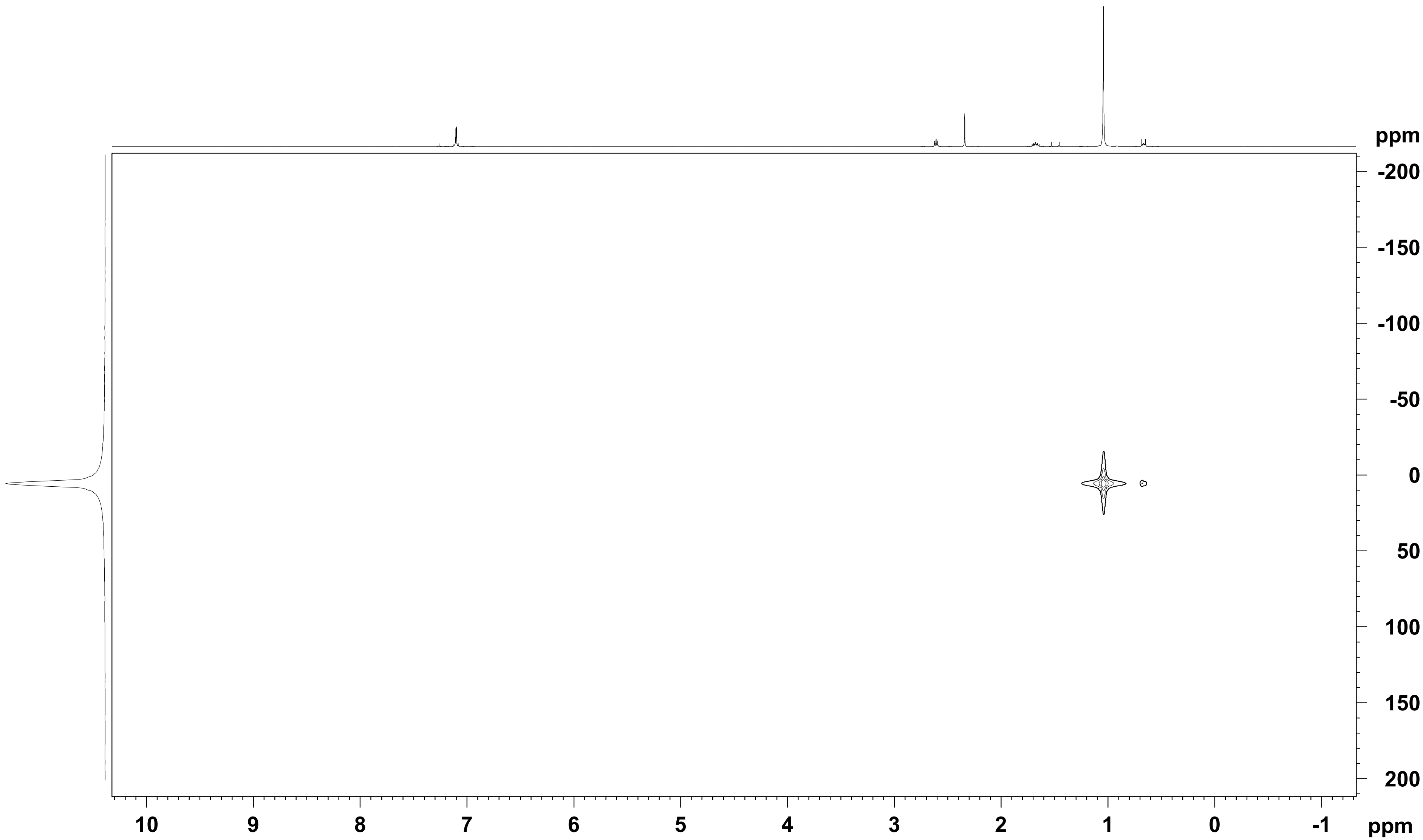


Figure S37. [1]H NMR (500 MHz, $CDCl_3$, 298 K) of **3fb** from the catalytic reaction of 1-bromo-2-cyclopropylbenzene (**1f**) and $^{i}Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

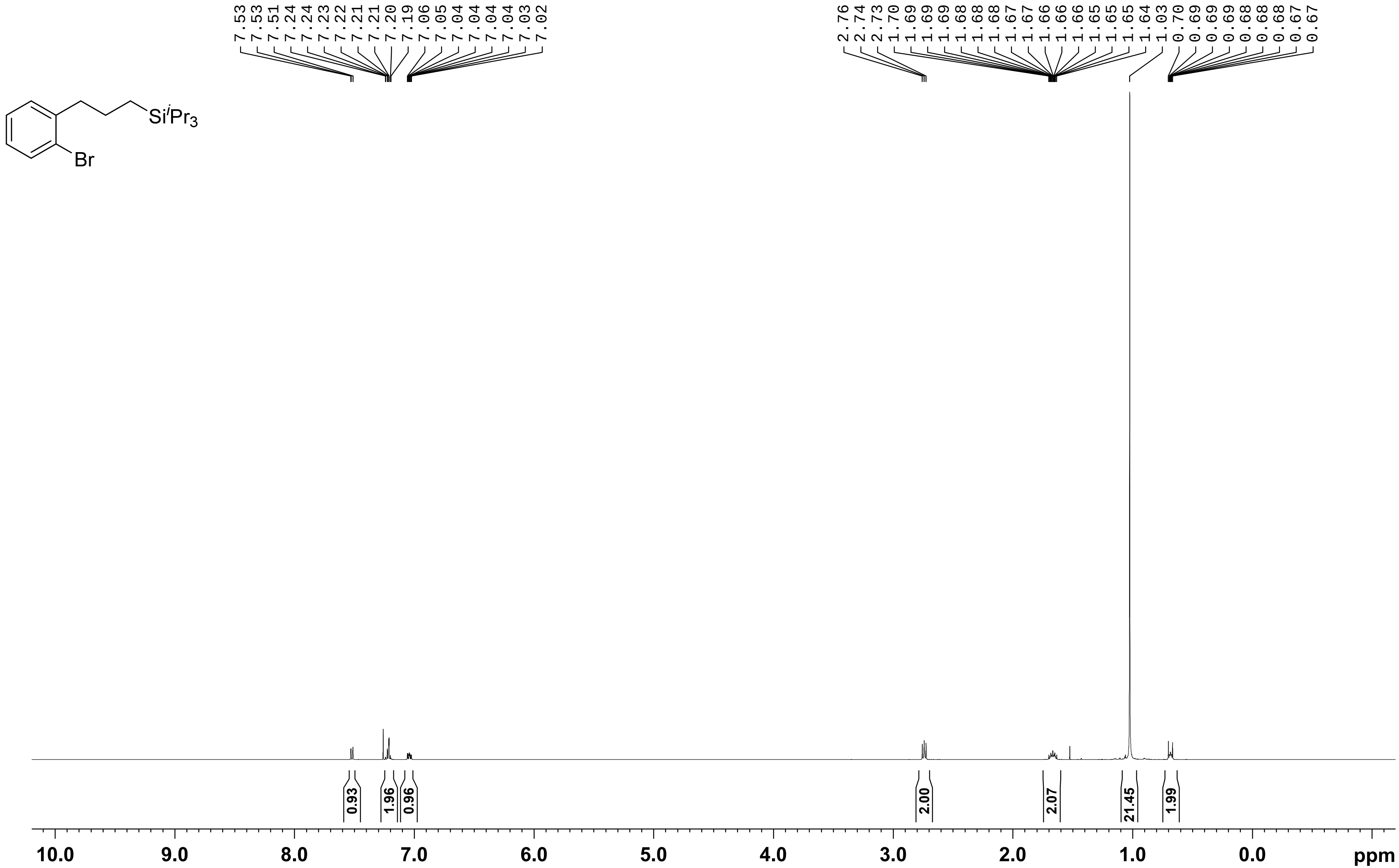


Figure S38. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **3fb** from the catalytic reaction of 1-bromo-2-cyclopropylbenzene (**1f**) and $^iPr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

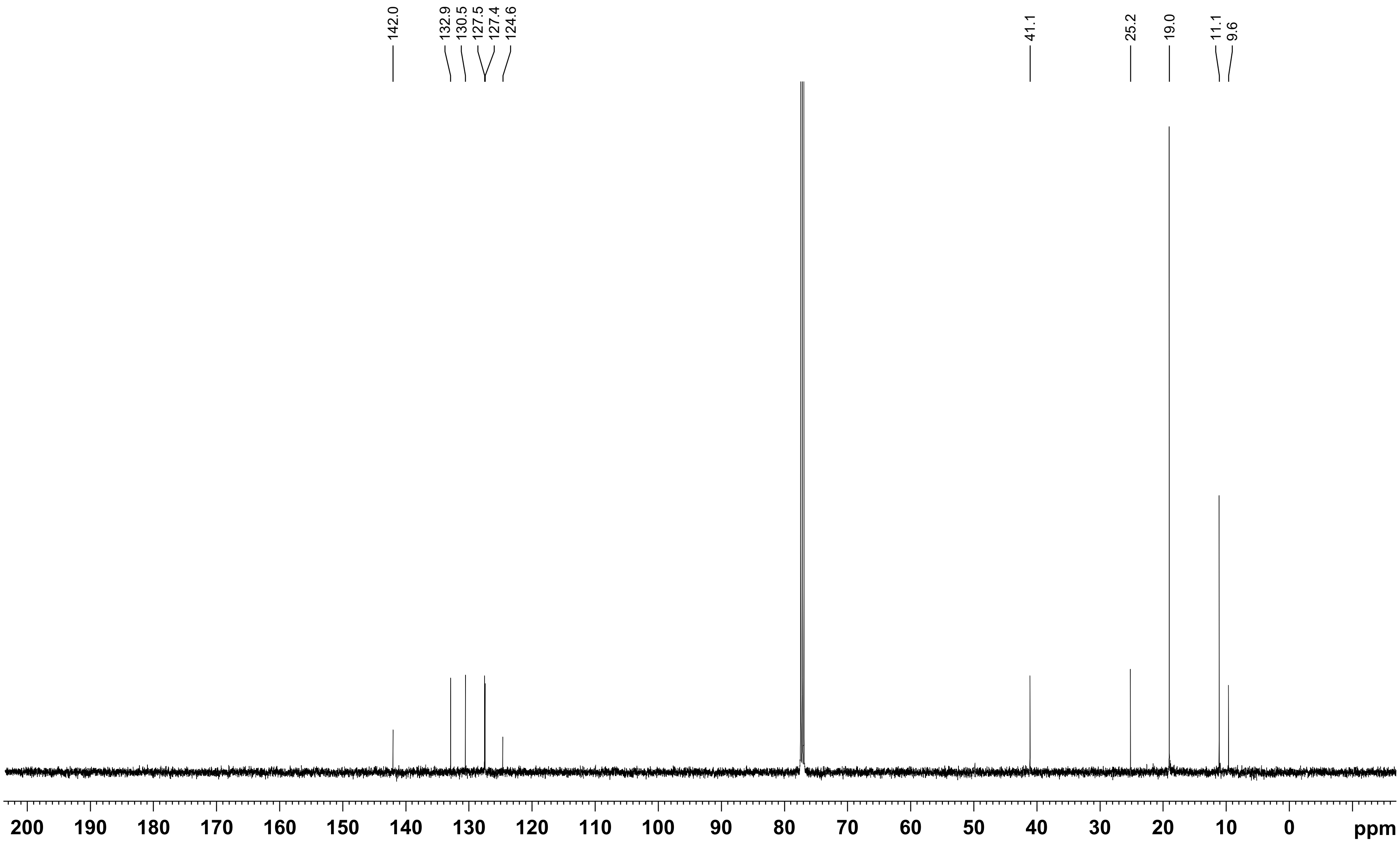


Figure S39. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **3fb** from the catalytic reaction of 1-bromo-2-cyclopropylbenzene (**1f**) and $^{i}Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

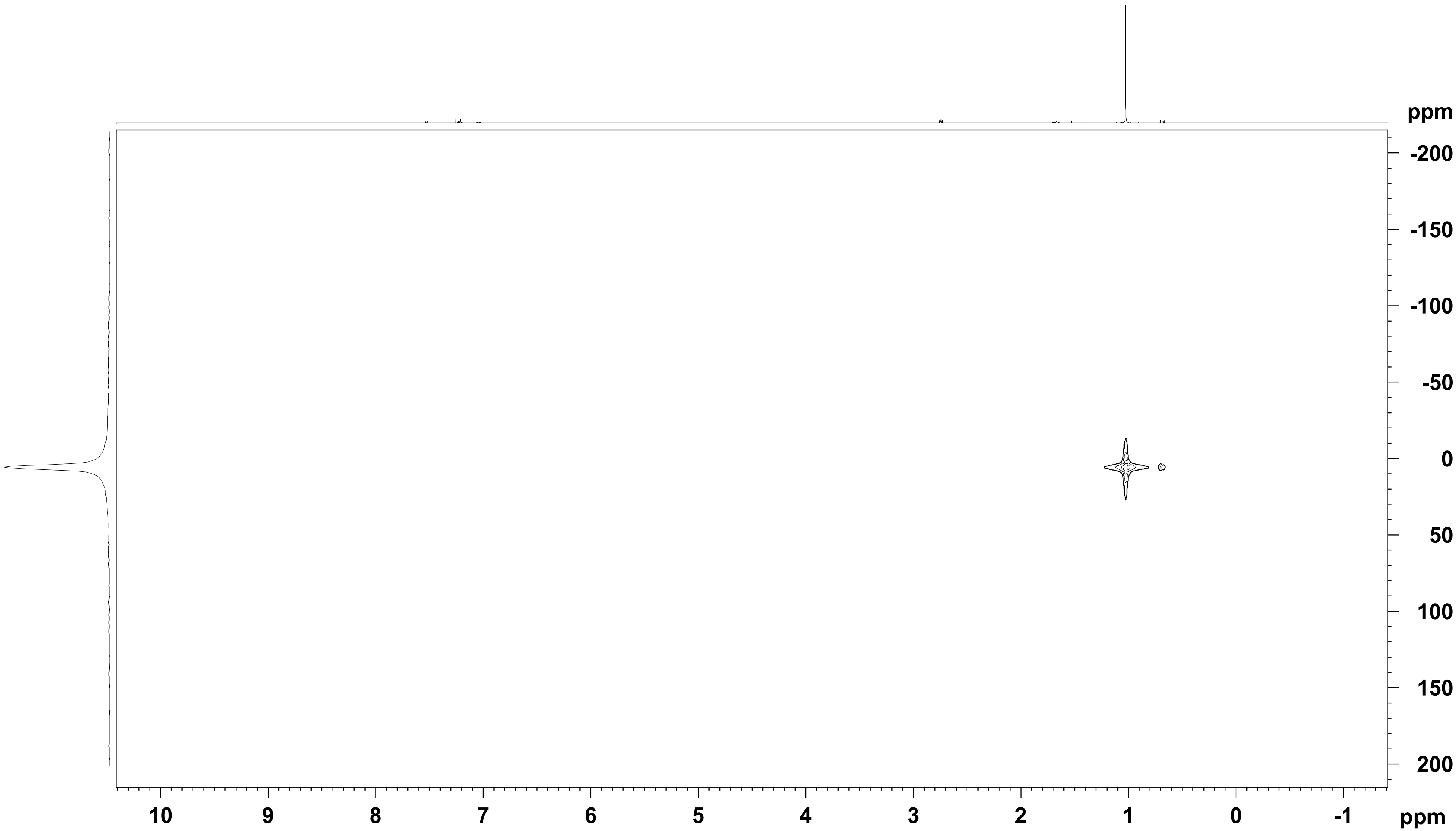


Figure S40. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **3gb** from the catalytic reaction of 1-cyclopropyl-2-methylbenzene (**1g**) and $^{i}Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

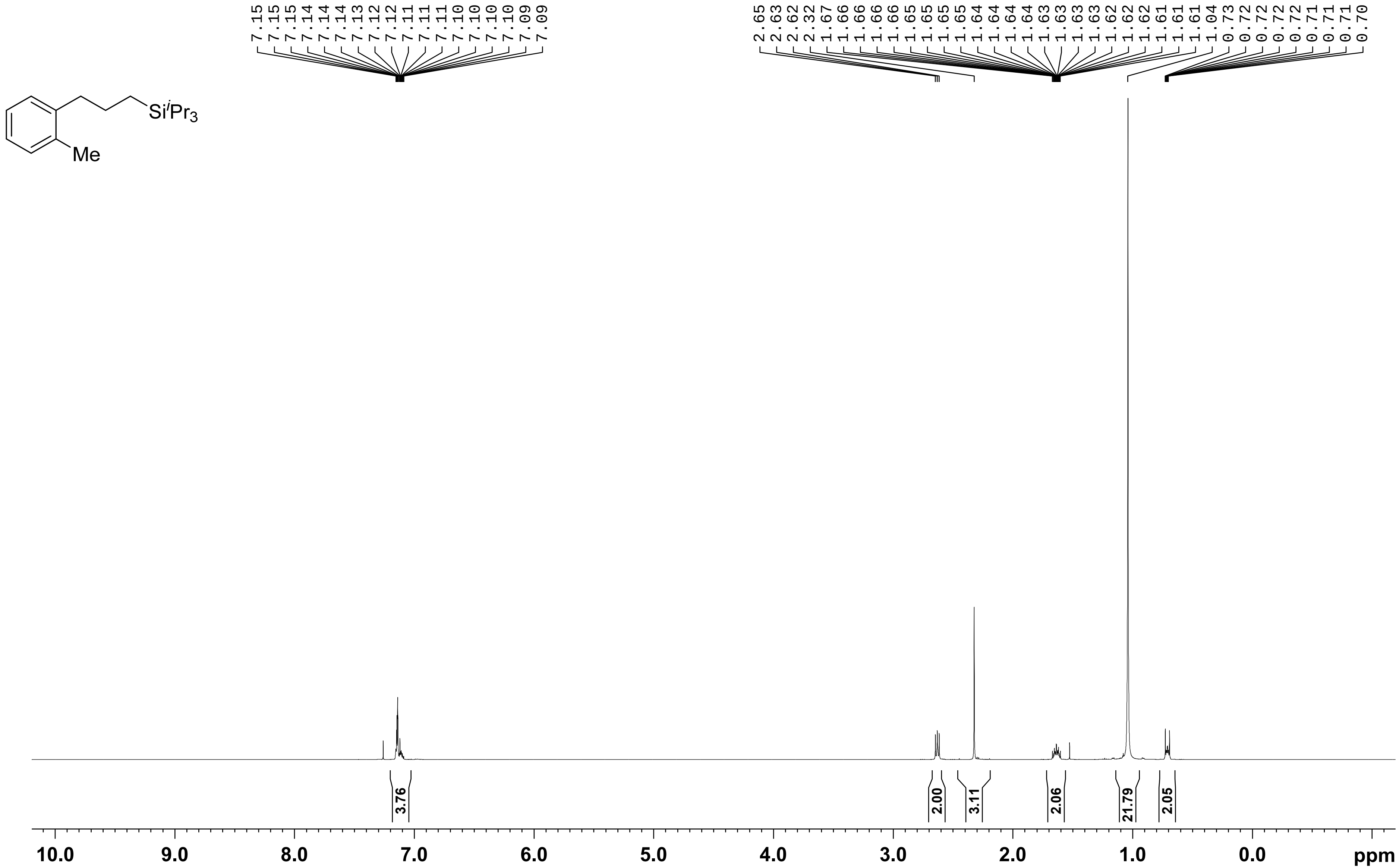


Figure S41. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **3gb** from the catalytic reaction of 1-cyclopropyl-2-methylbenzene (**1g**) and $^iPr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

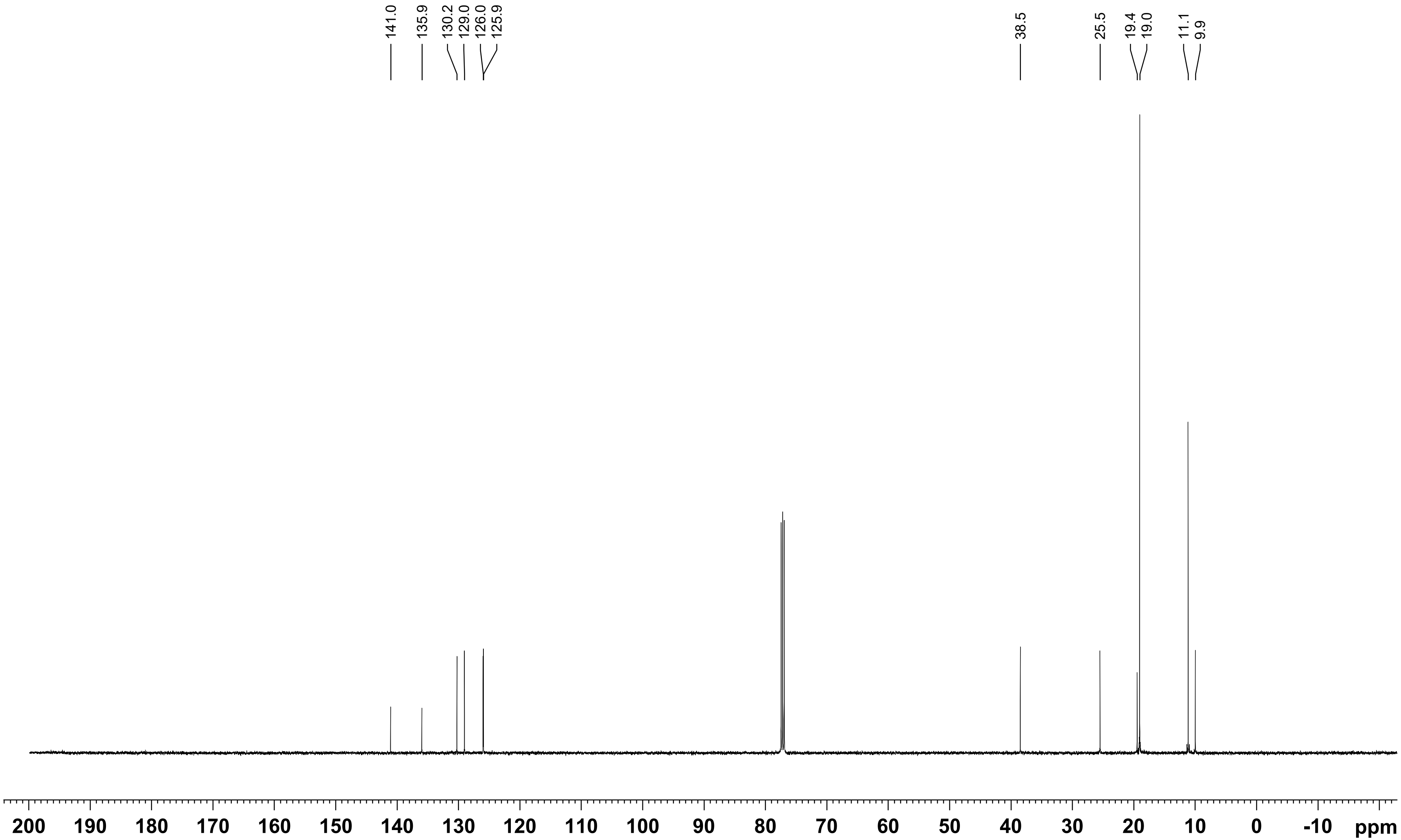


Figure S42. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **3gb** from the catalytic reaction of 1-cyclopropyl-2-methylbenzene (**1g**) and $^{i}Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

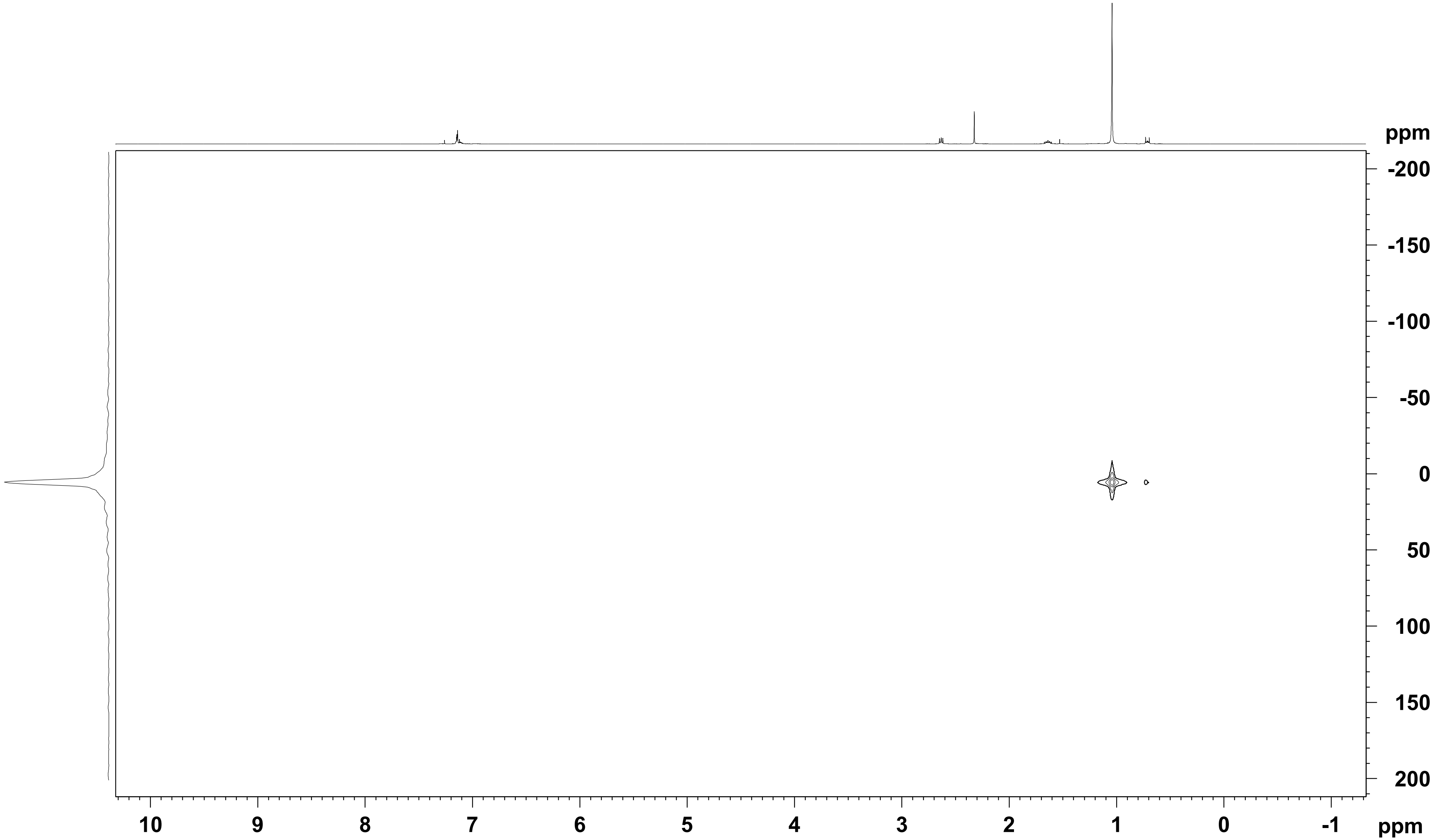


Figure S43. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **3hb** from the catalytic reaction of 1-bromo-3-cyclopropylbenzene (**1h**) and ^{i}Pr$_3$SiH using $Ph_3C^+[B(C_6F_5)_4]^-$.

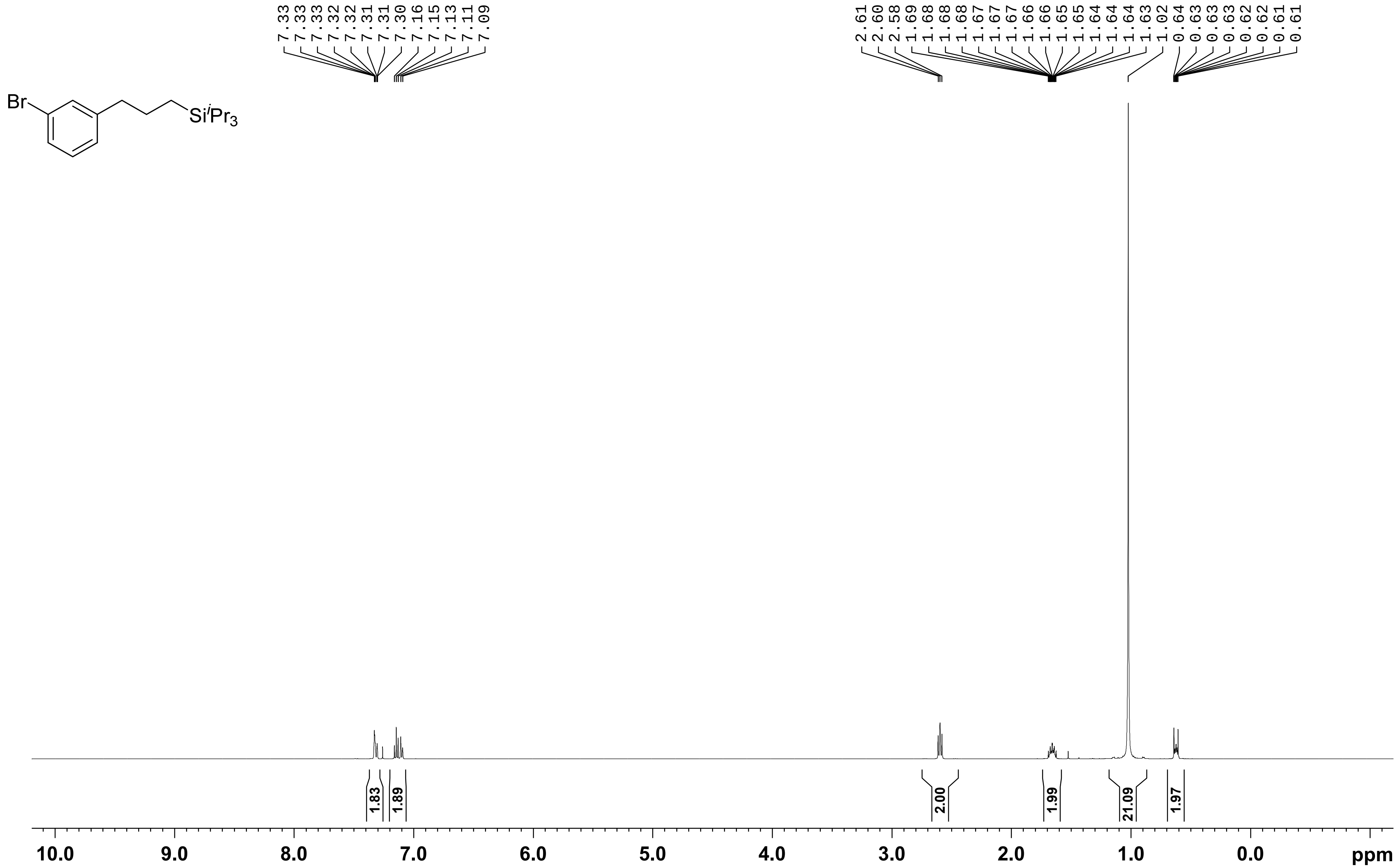


Figure S44. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **3hb** from the catalytic reaction of 1-bromo-3-cyclopropylbenzene (**1h**) and $^iPr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

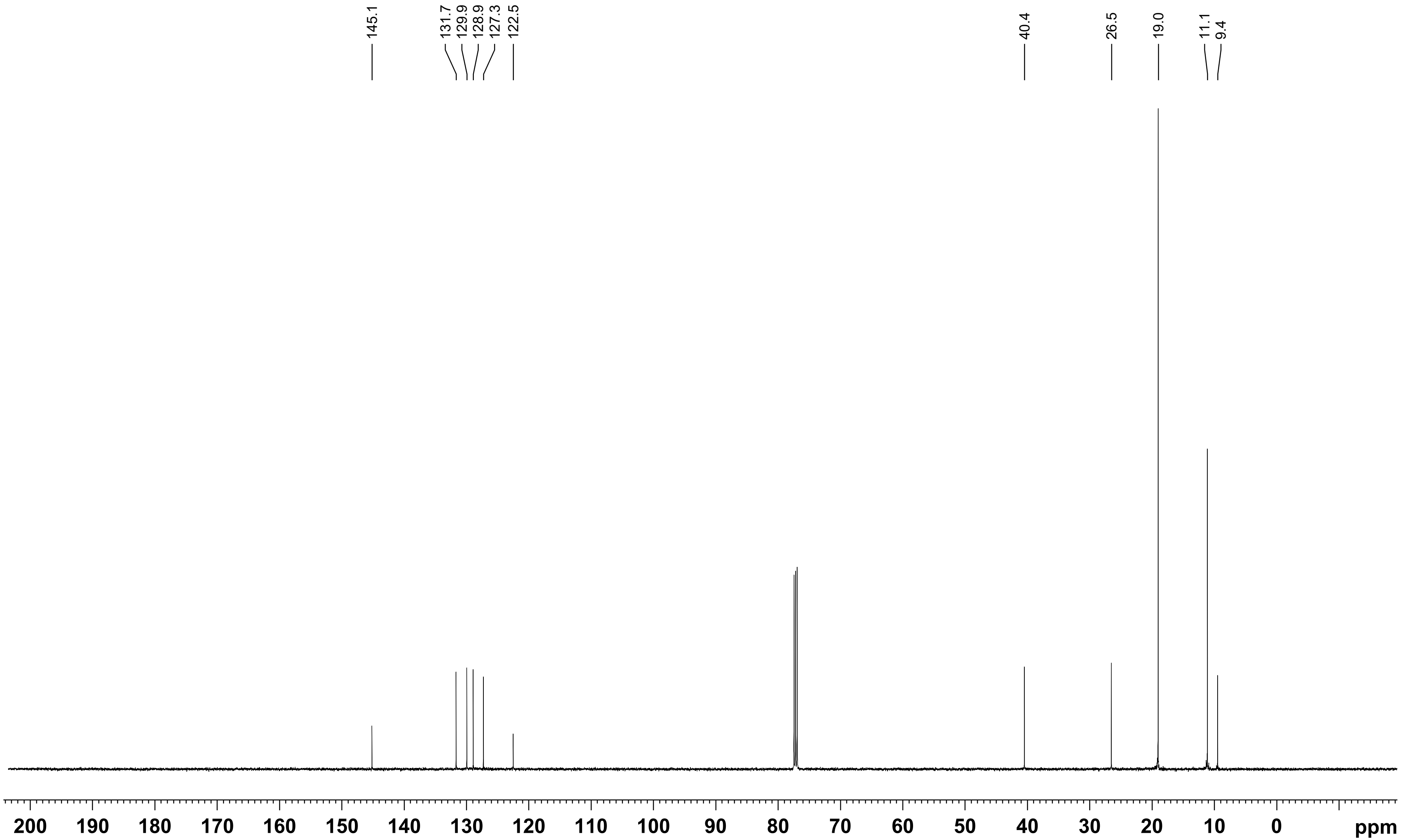


Figure S45. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz) of **3hb** from the catalytic reaction of 1-bromo-3-cyclopropylbenzene (**1h**) and $^{i}Pr_3SiH$ using $Ph_3C^{+}[B(C_6F_5)_4]^{-}$.

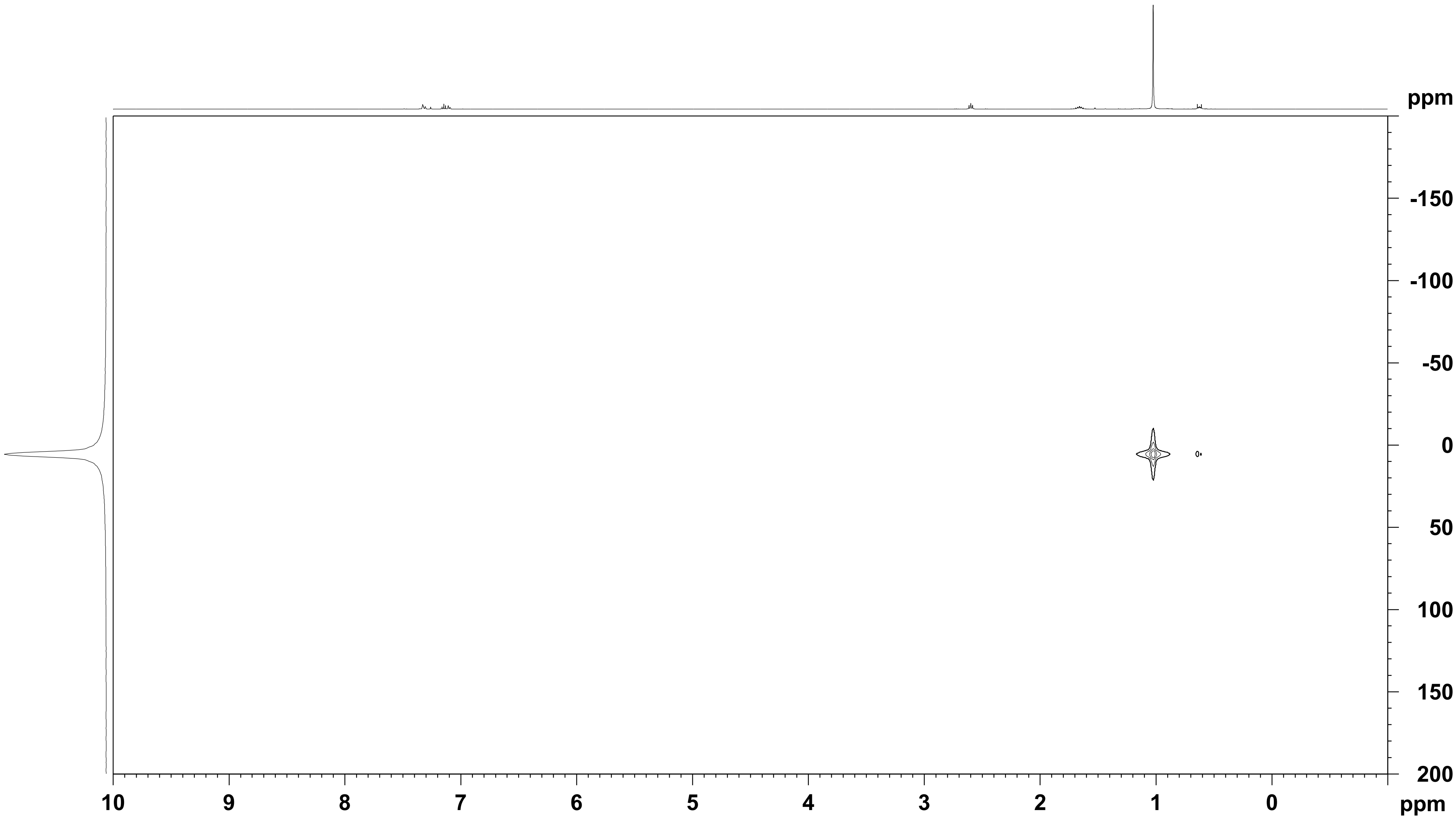
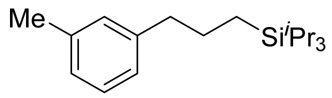


Figure S46. [1]H NMR (500 MHz, $CDCl_3$, 298 K) of **3ib** from the catalytic reaction of 1-cyclopropyl-3-methylbenzene (**1i**) and $^{i}Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.



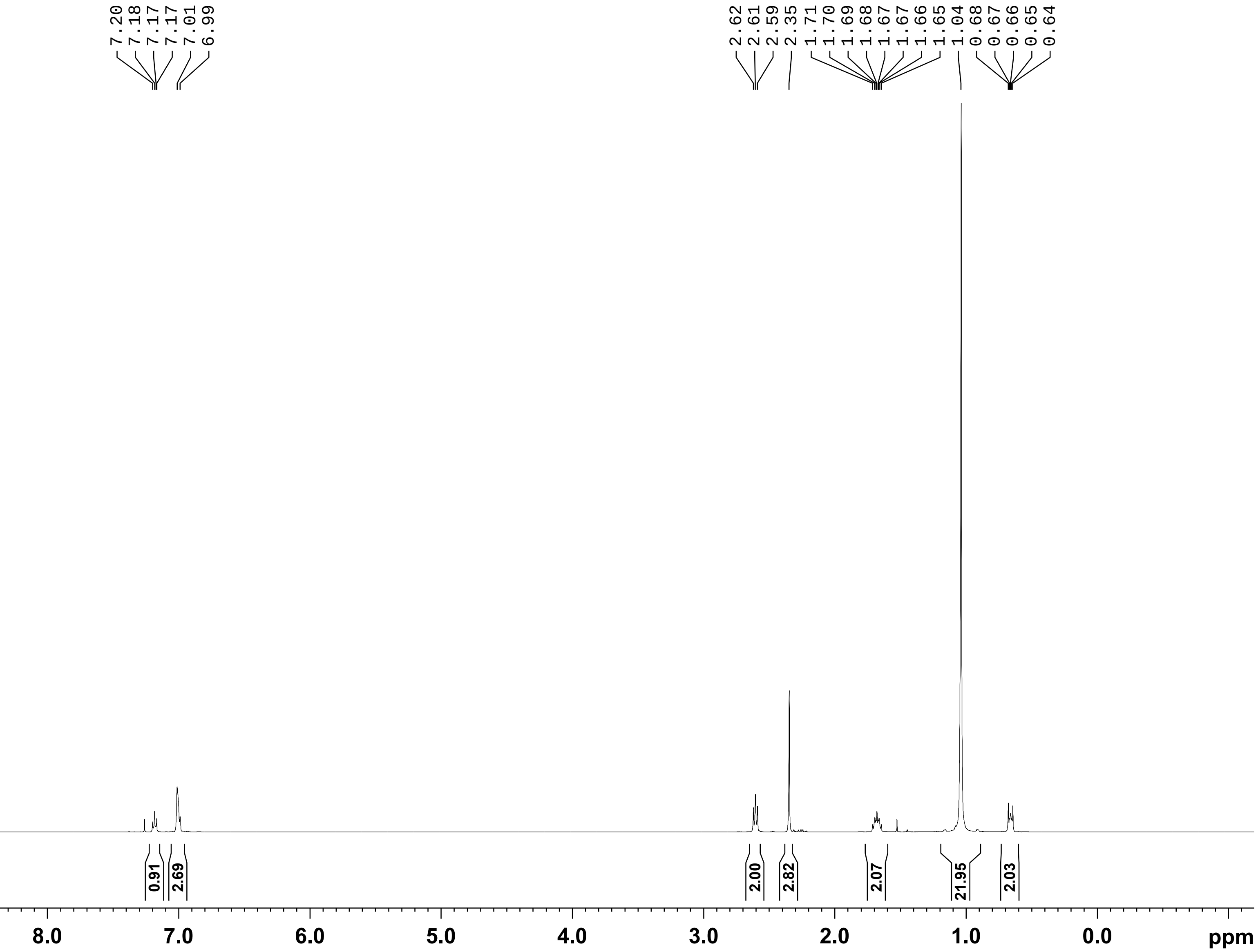


Figure S47. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **3ib** from the catalytic reaction of 1-cyclopropyl-3-methylbenzene (**1i**) and $^{i}Pr_3SiH$ using $Ph_3C^{+}[B(C_6F_5)_4]^{-}$.

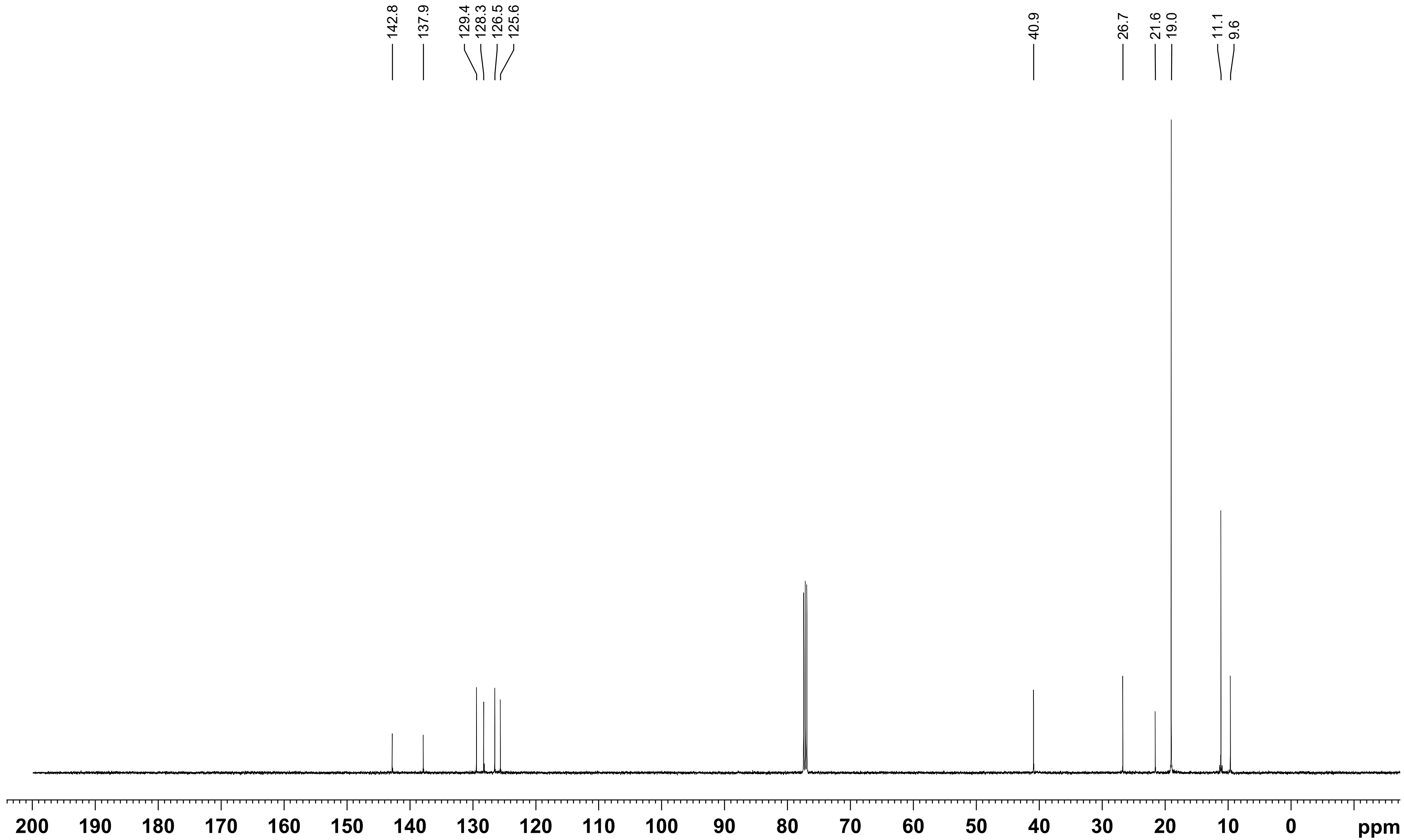


Figure S48. $^1H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **3ib** from the catalytic reaction of 1-cyclopropyl-3-methylbenzene (**1i**) and $^iPr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

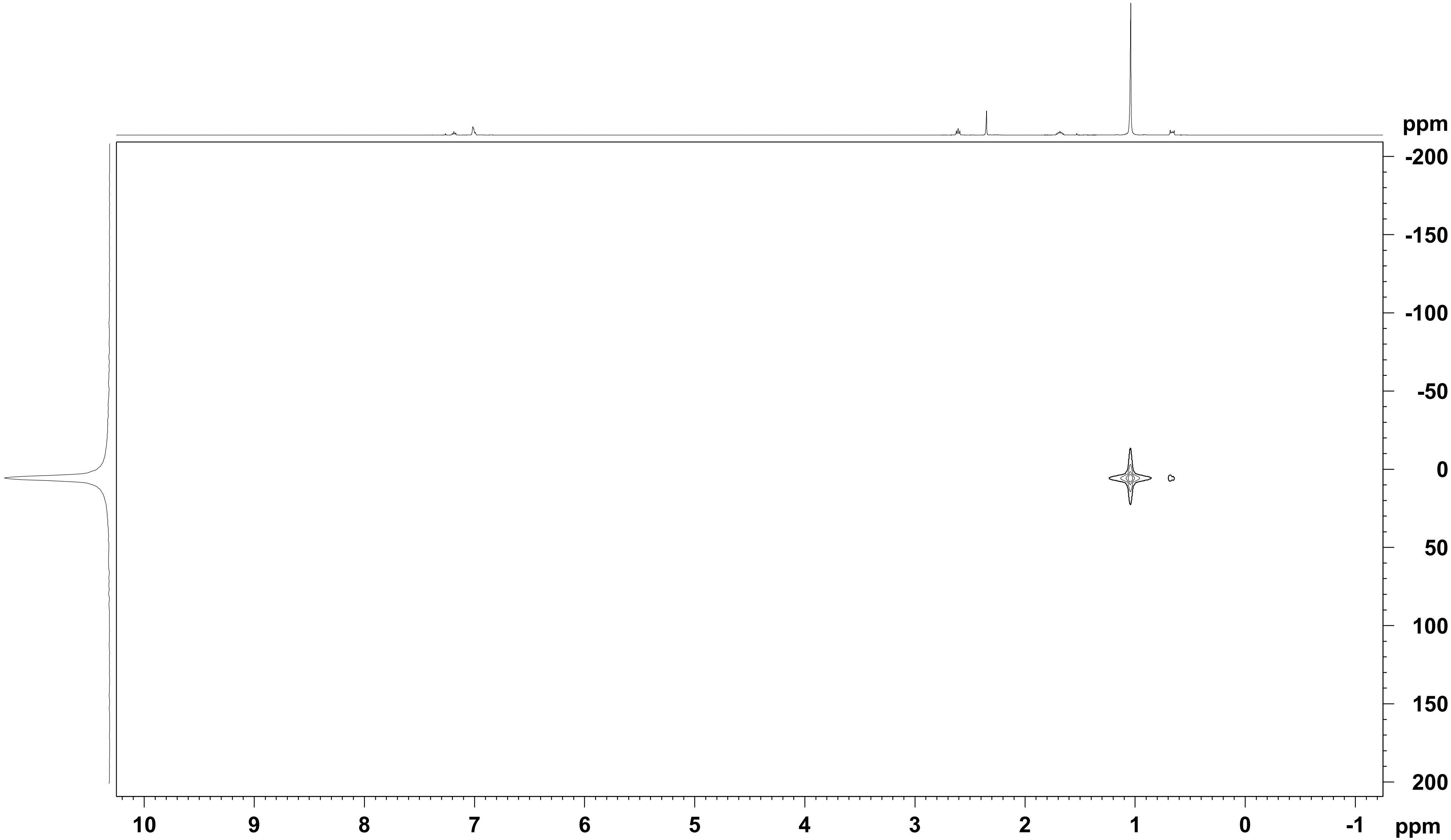


Figure S49. [1]H NMR (500 MHz, $CDCl_3$, 298 K) of **3jb** from the catalytic reaction of 2-cyclopropylnaphthalene (**1j**) and $^{i}Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

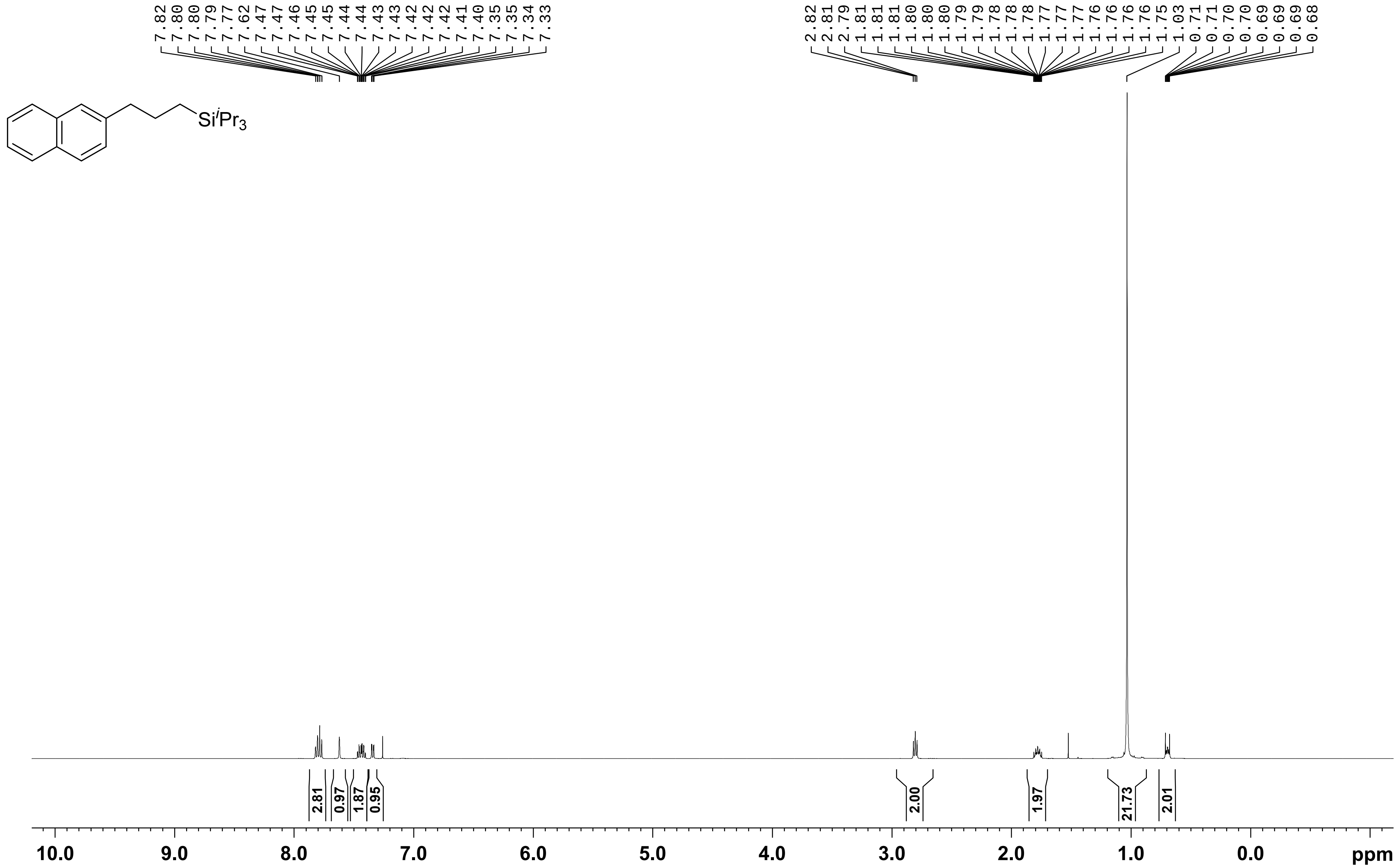


Figure S50. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **3jb** from the catalytic reaction of 2-cyclopropylnaphthalene (**1j**) and $^{i}Pr_3SiH$ using $Ph_3C^{+}[B(C_6F_5)_4]^{-}$.

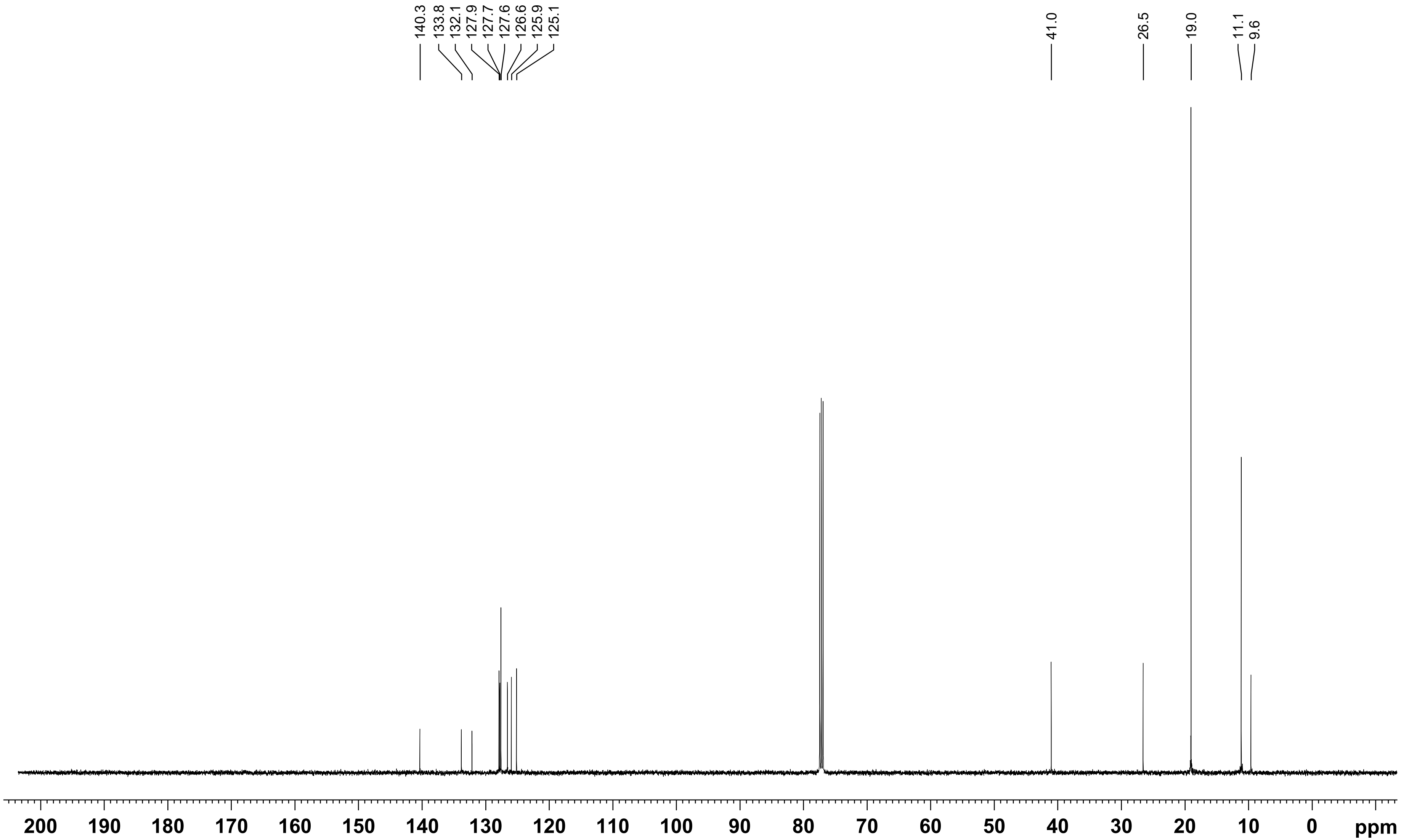


Figure S51. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **3jb** from the catalytic reaction of 2-cyclopropylnaphthalene (**1j**) and $^{i}Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

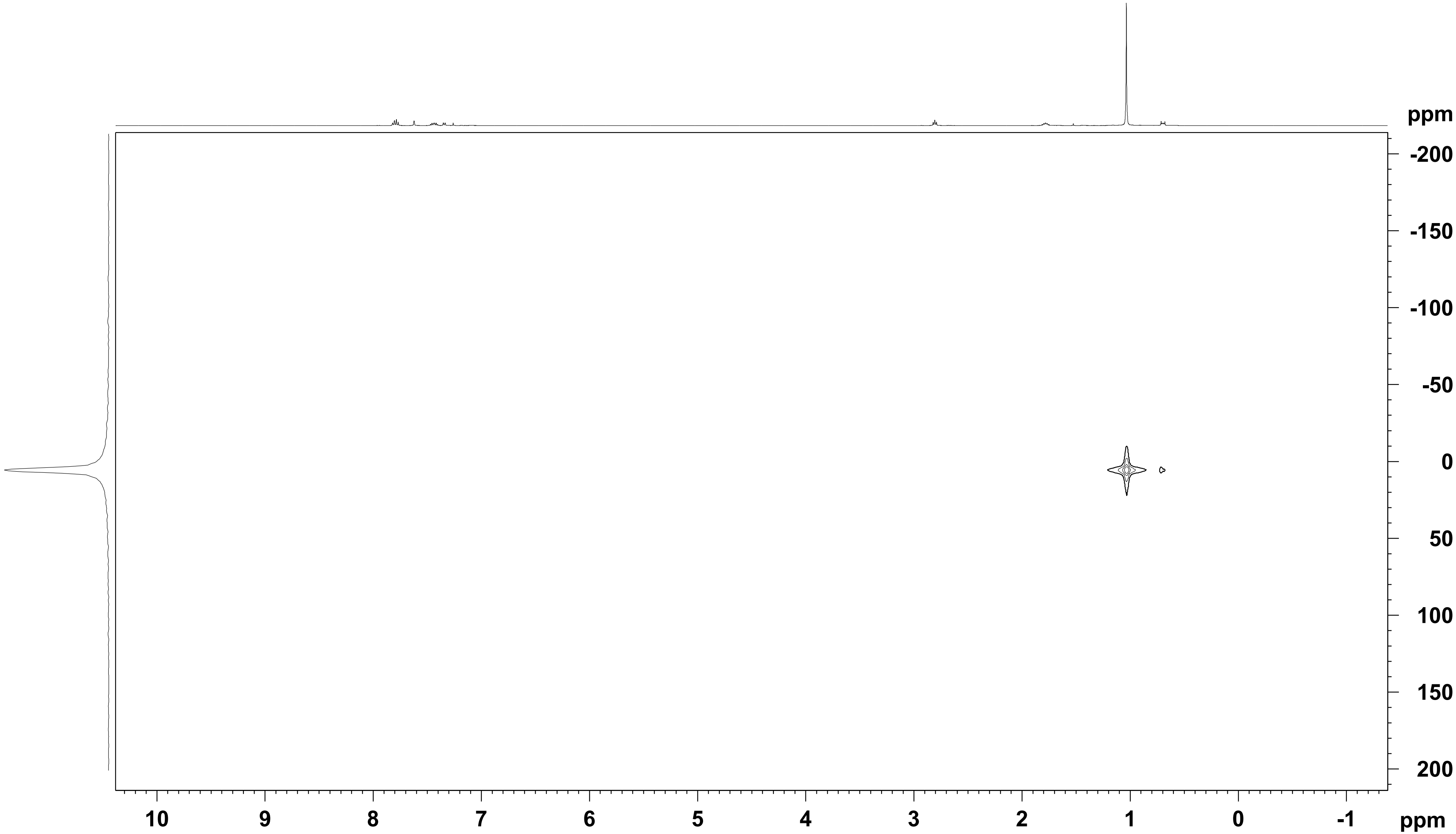


Figure S52. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **3kb** from the catalytic reaction of (1-methylcyclopropyl)benzene (**1k**) and ^{i}Pr_3SiH using $Ph_3C^+[B(C_6F_5)_4]^-$.

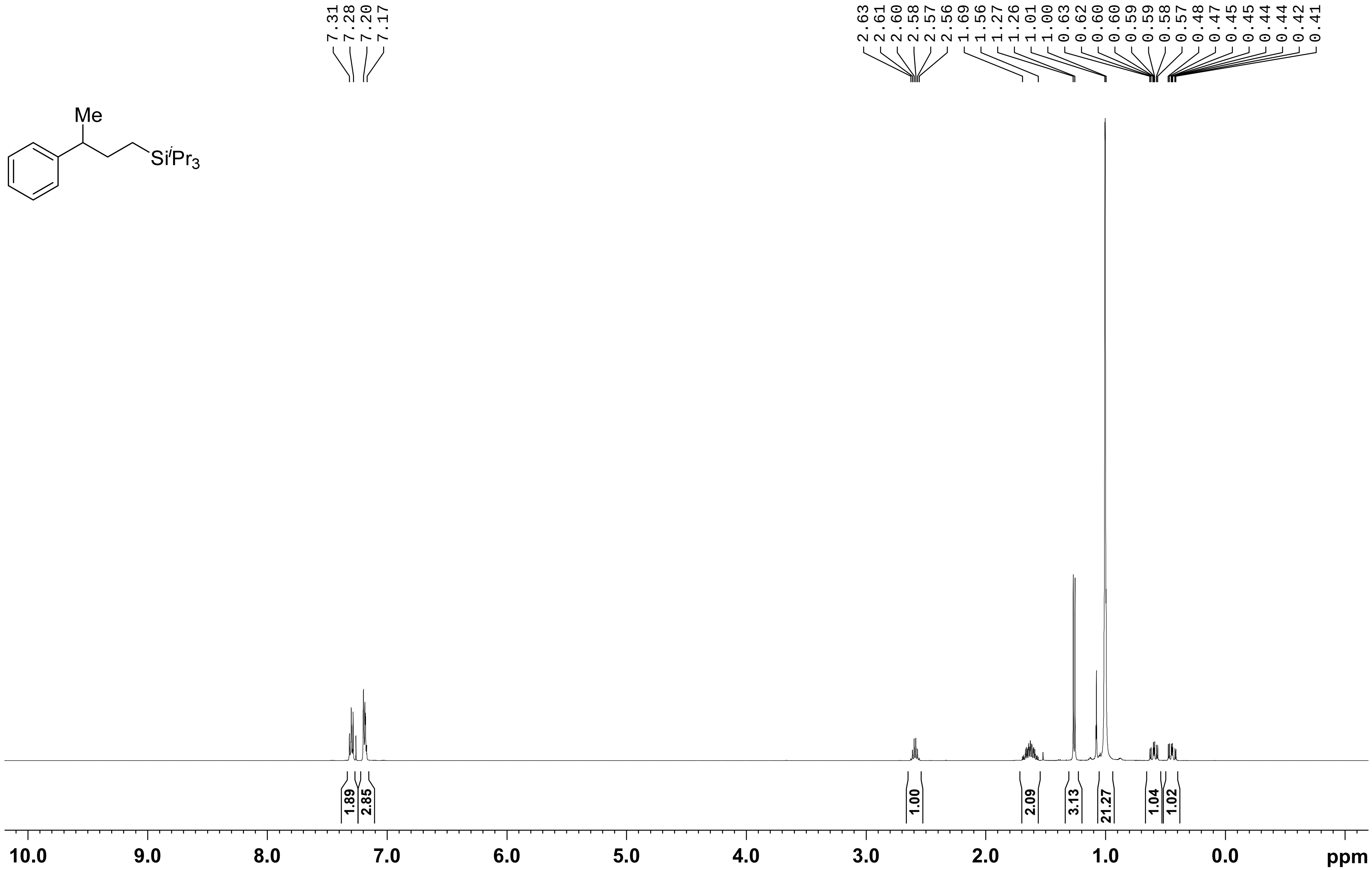


Figure S53. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **3kb** from the catalytic reaction of (1-methylcyclopropyl)benzene (**1k**) and $^iPr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

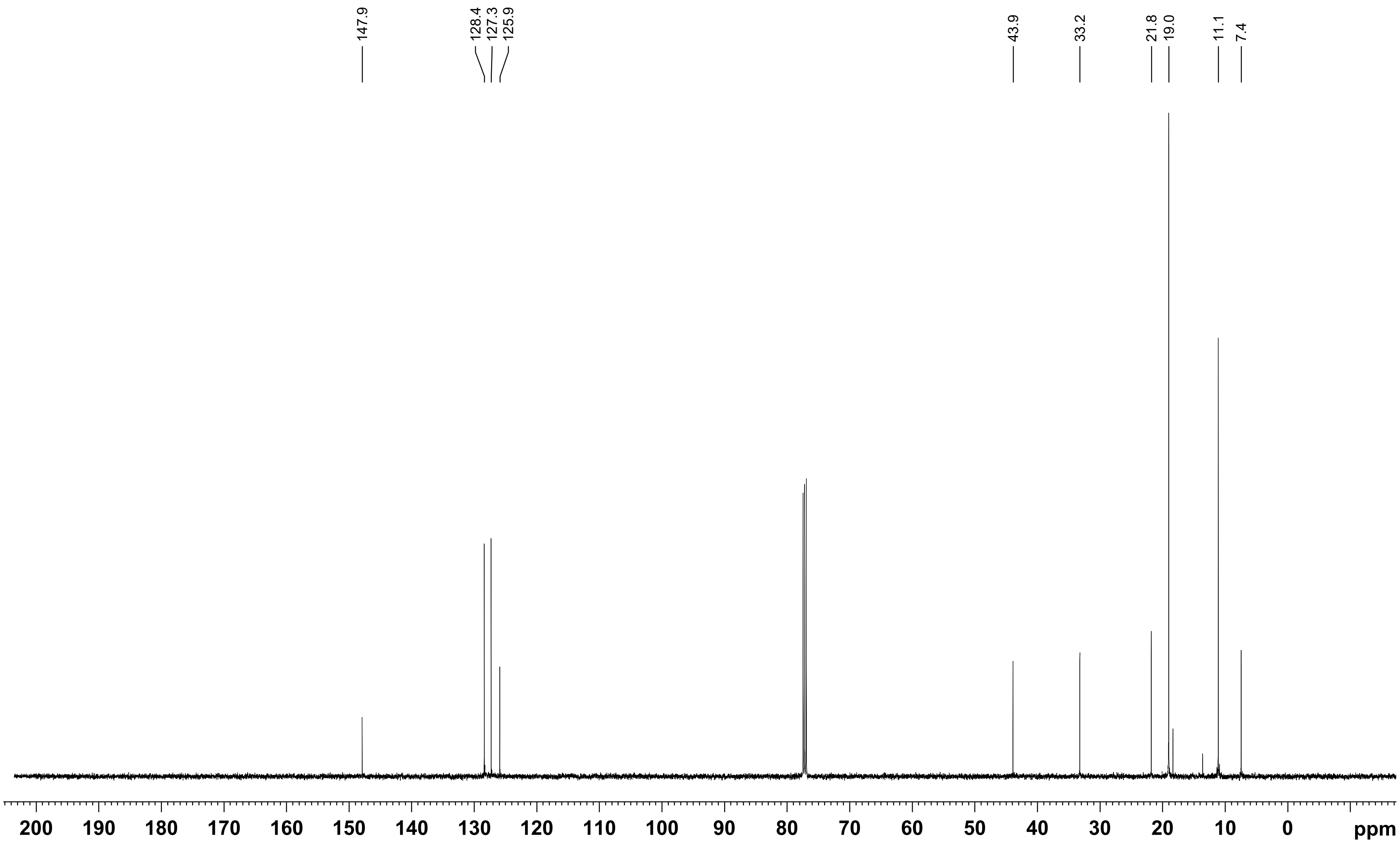


Figure S54. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **3kb** from the catalytic reaction of (1-methylcyclopropyl)benzene (**1k**) and $^{i}Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

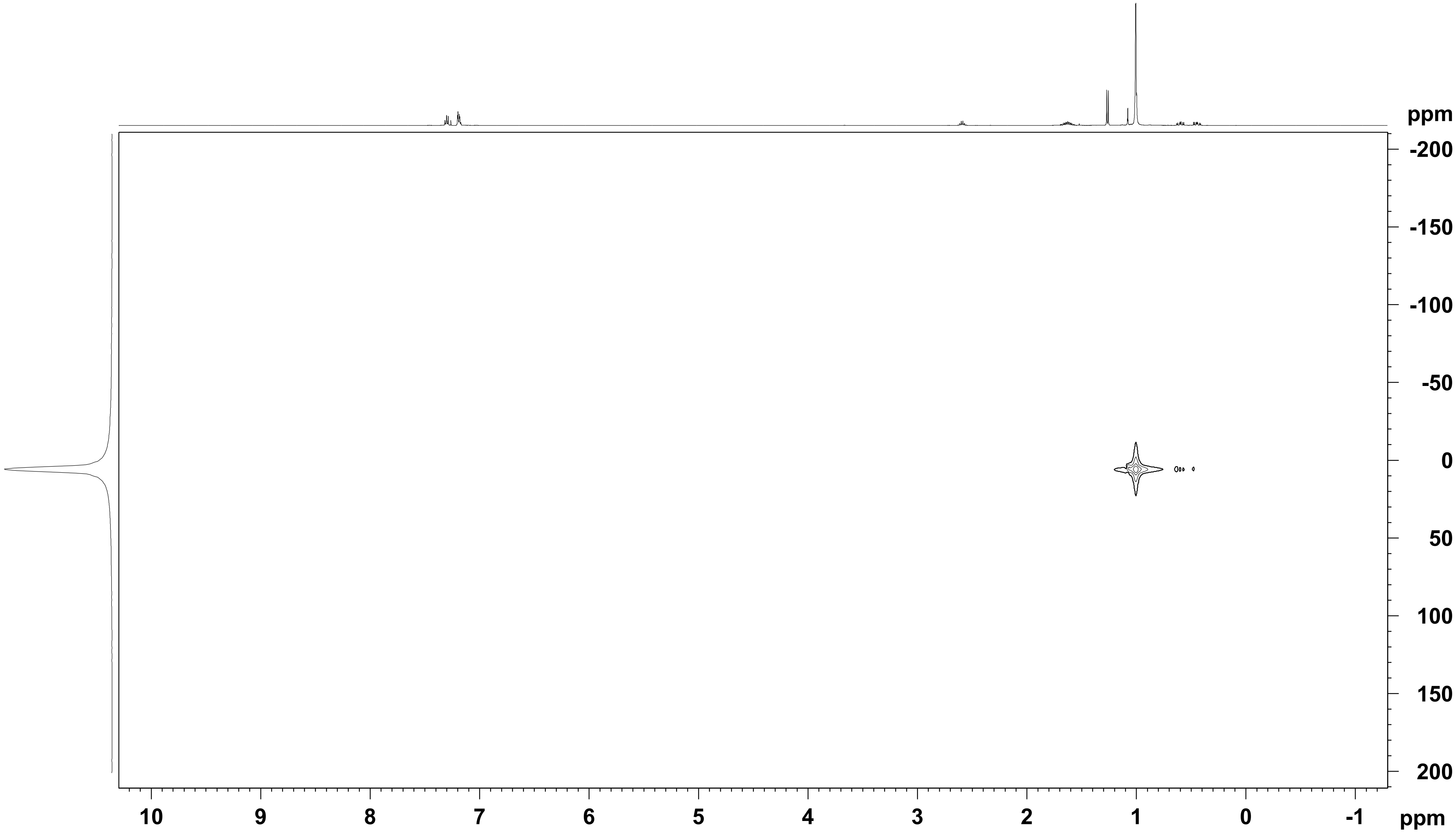


Figure S55. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **3lb** from the catalytic reaction of 1,4-dicyclopropylbenzene (**1l**) and $^{i}Pr_3SiH$ using $Ph_3C^{+}[B(C_6F_5)_4]^{-}$.

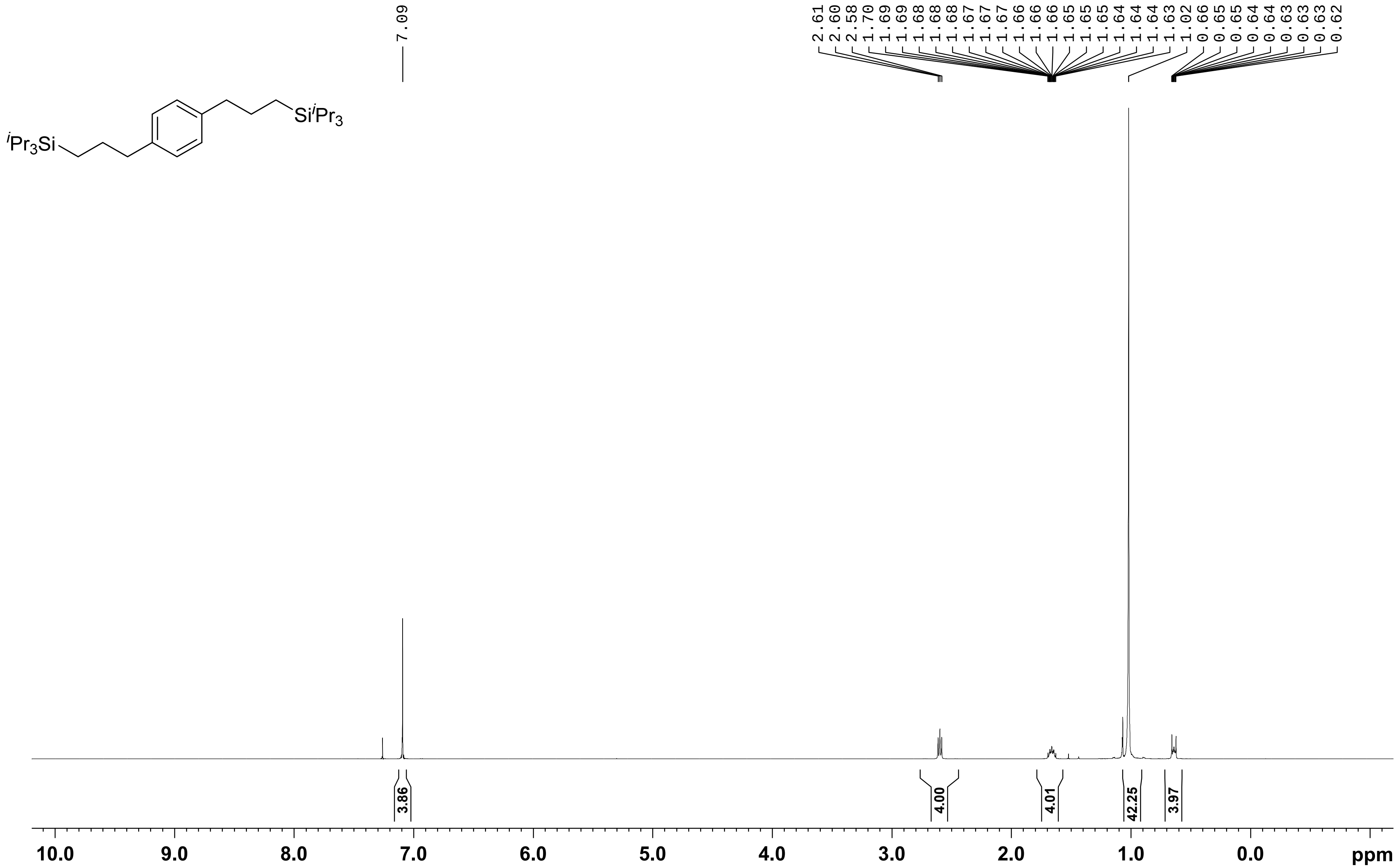


Figure S56. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **3lb** from the catalytic reaction of 1,4-dicyclopropylbenzene (**1l**) and $^{i}Pr_3SiH$ using $Ph_3C^{+}[B(C_6F_5)_4]^{-}$.

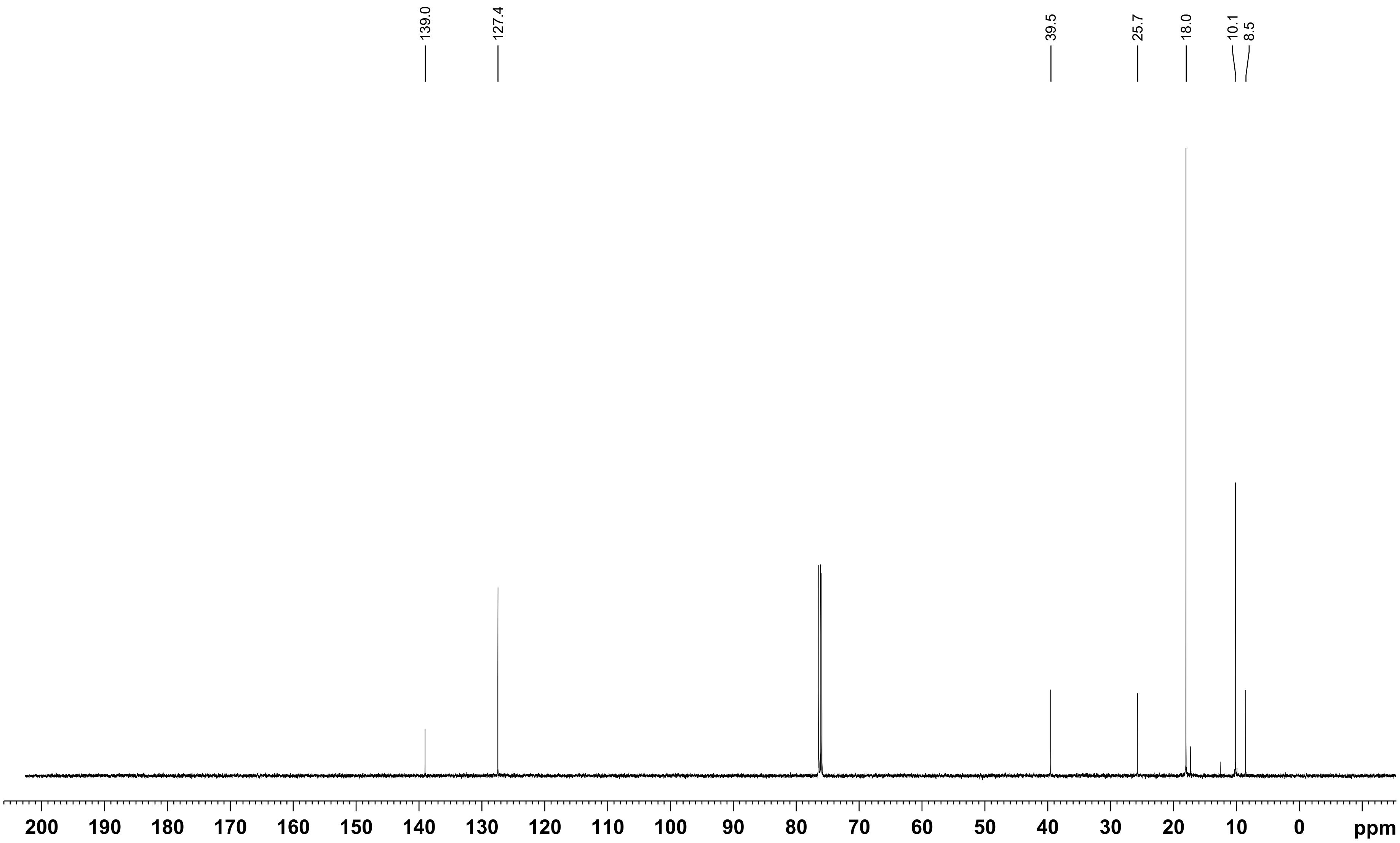


Figure S57. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz) of **3lb** from the catalytic reaction of 1,4-dicyclopropylbenzene (**1l**) and $^{i}Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

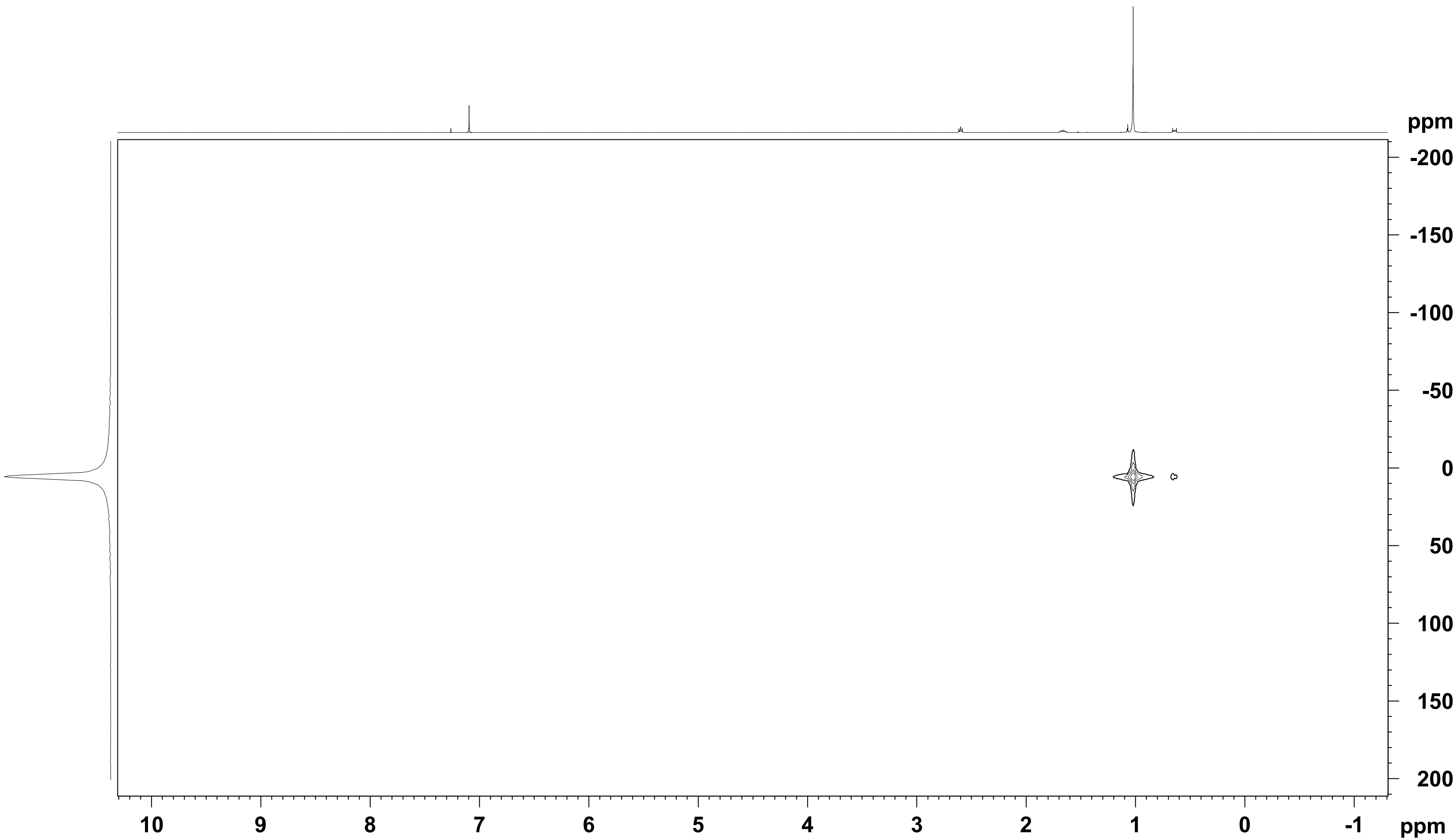


Figure S58. ^{1}H NMR (500 MHz, C_6D_6, 298 K) of **3mb** from the catalytic reaction of hexylcyclopropane (**1m**) and $^i Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

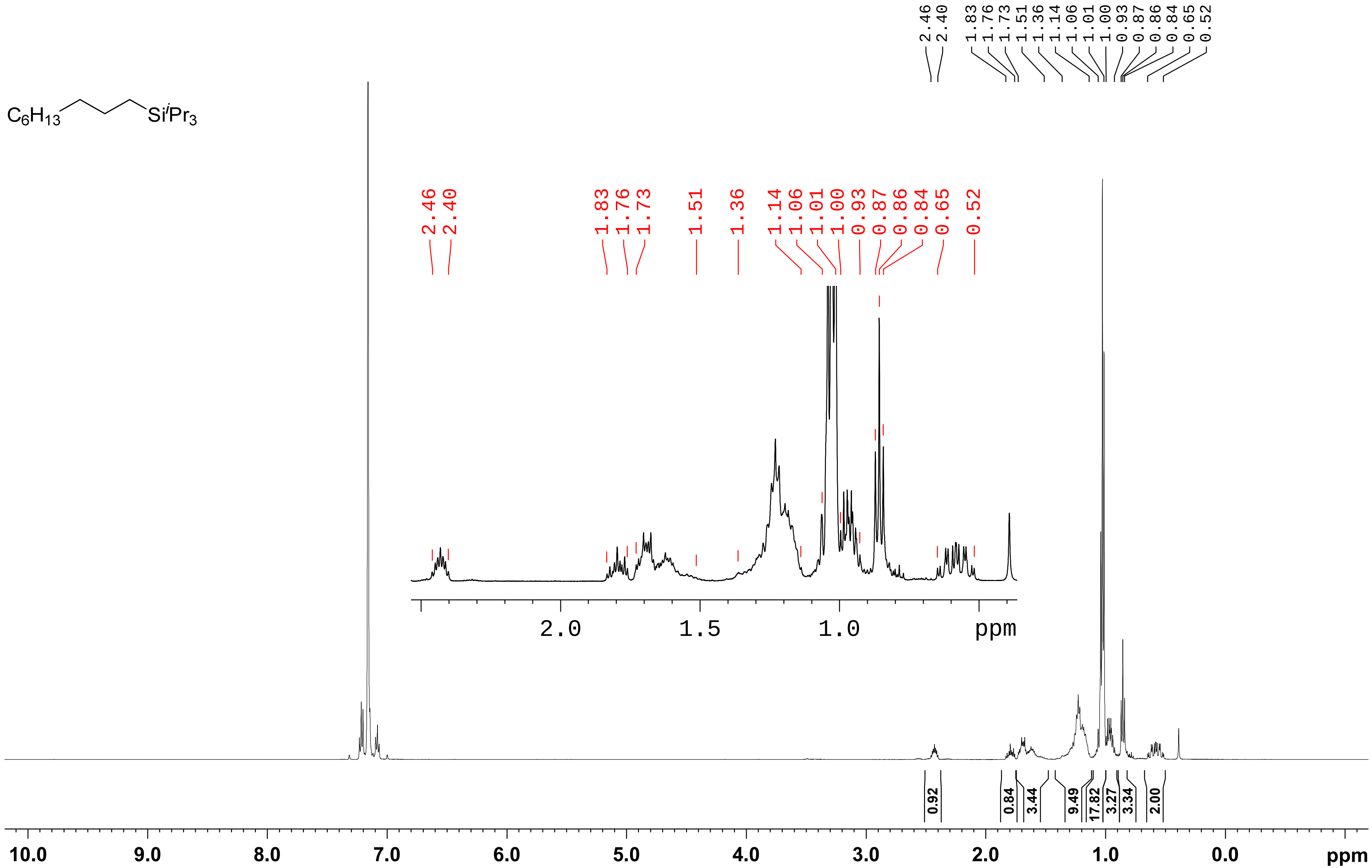


Figure S59. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K) of **3mb** from the catalytic reaction of hexylcyclopropane (**1m**) and $^iPr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

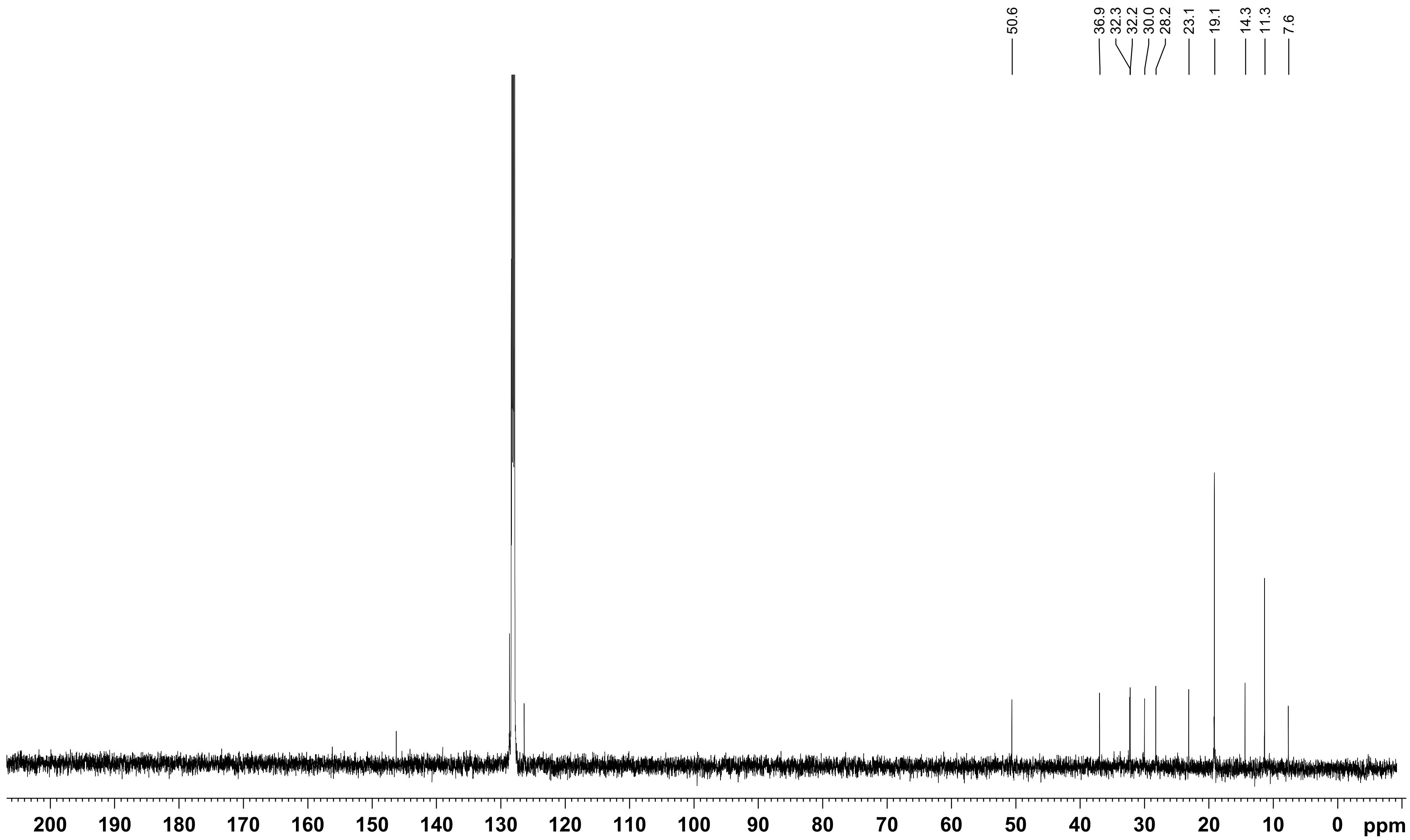


Figure S60. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, C_6D_6, 298 K, optimized for J = 7 Hz) of of **3mb** from the catalytic reaction of hexylcyclopropane (**1m**) and $^{i}Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

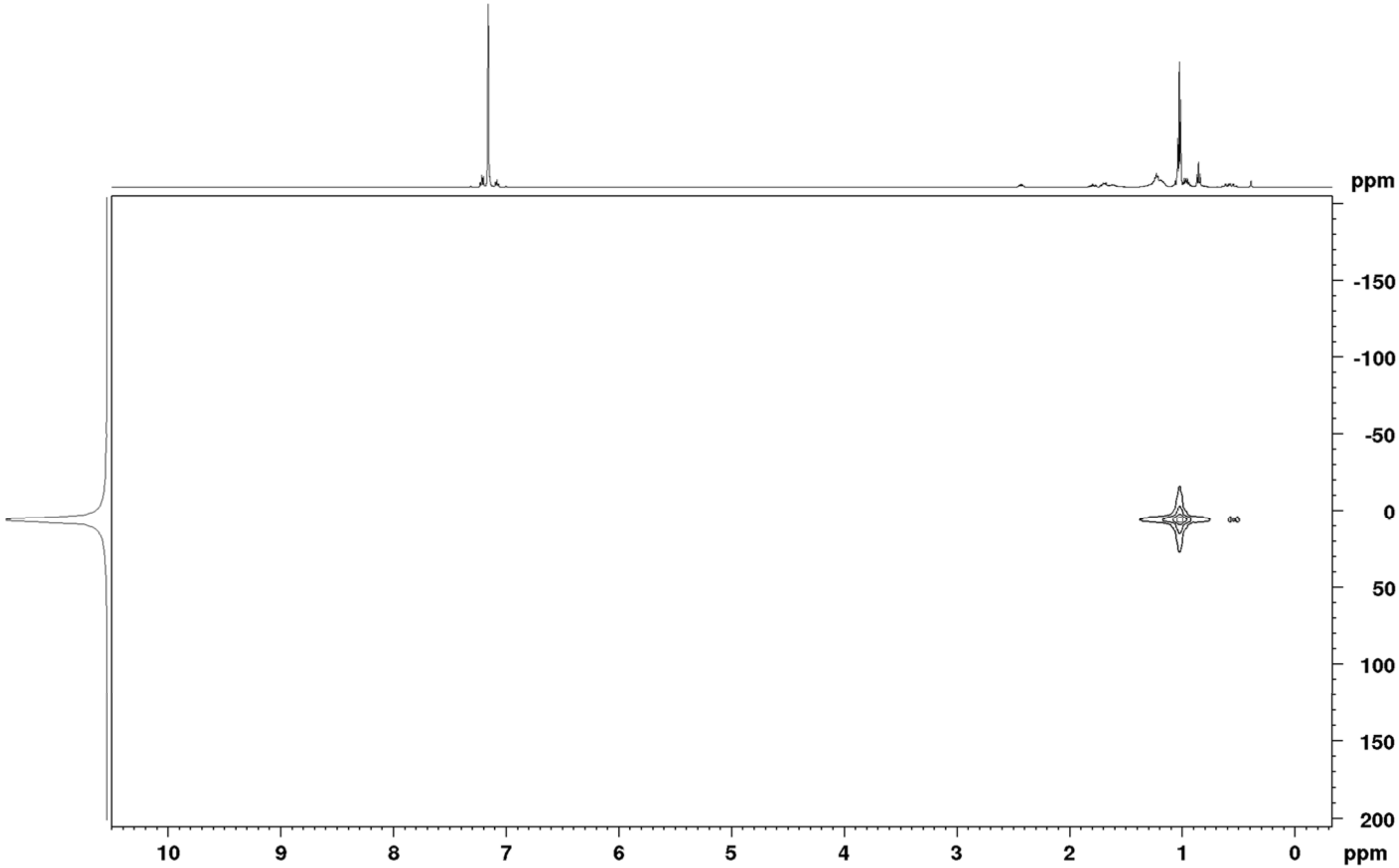
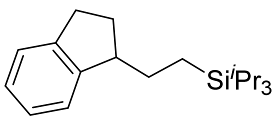


Figure S61. [1]H NMR (500 MHz, $CDCl_3$, 298 K) of **3nb** from the catalytic reaction of 2',3'-dihydrospiro[cyclopropane-1,1'-indene] (**1n**) and $^{i}Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.



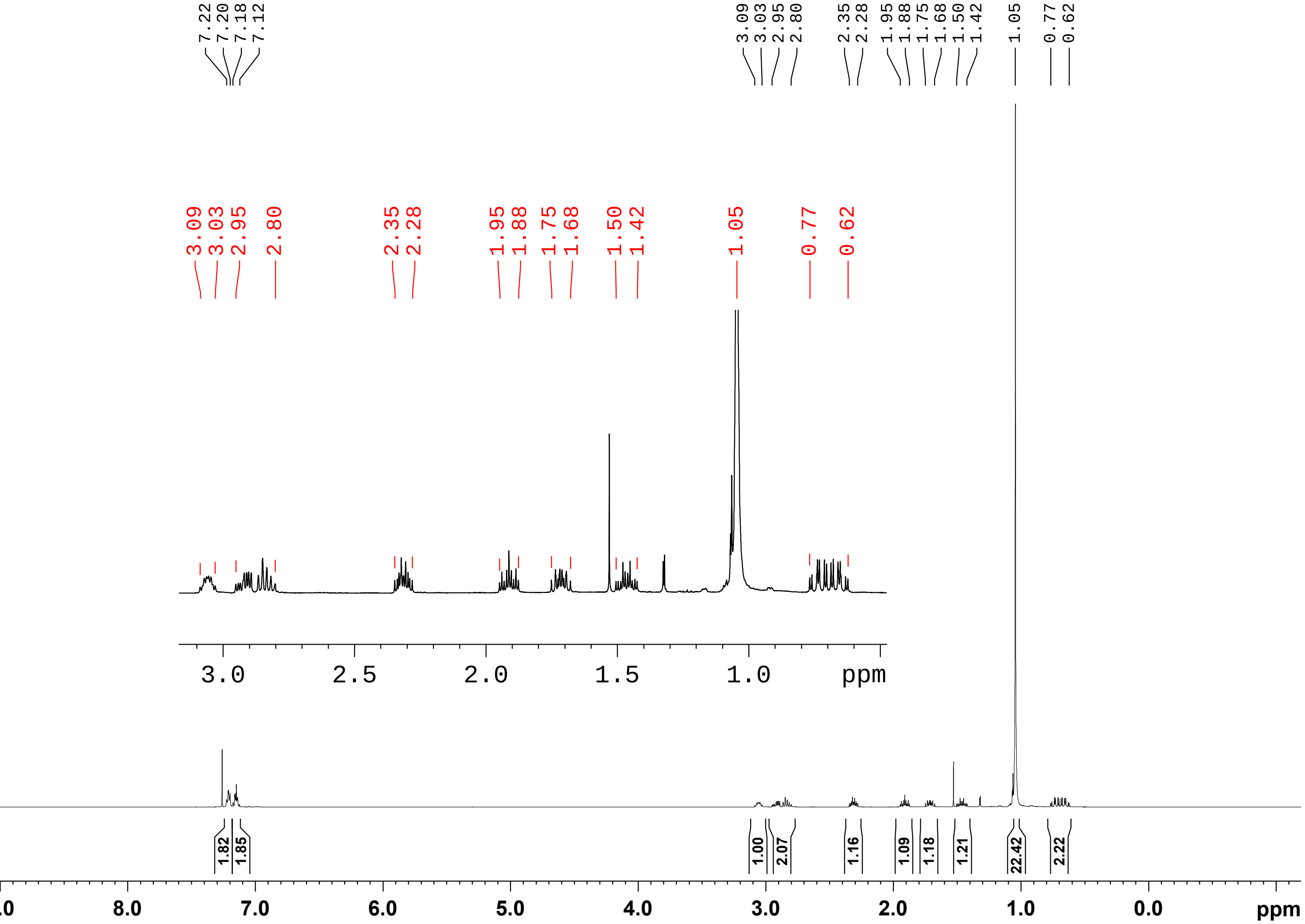


Figure S62. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **3nb** from the catalytic reaction of 2',3'-dihydrospiro[cyclopropane-1,1'-indene] (**1n**) and $^{i}Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

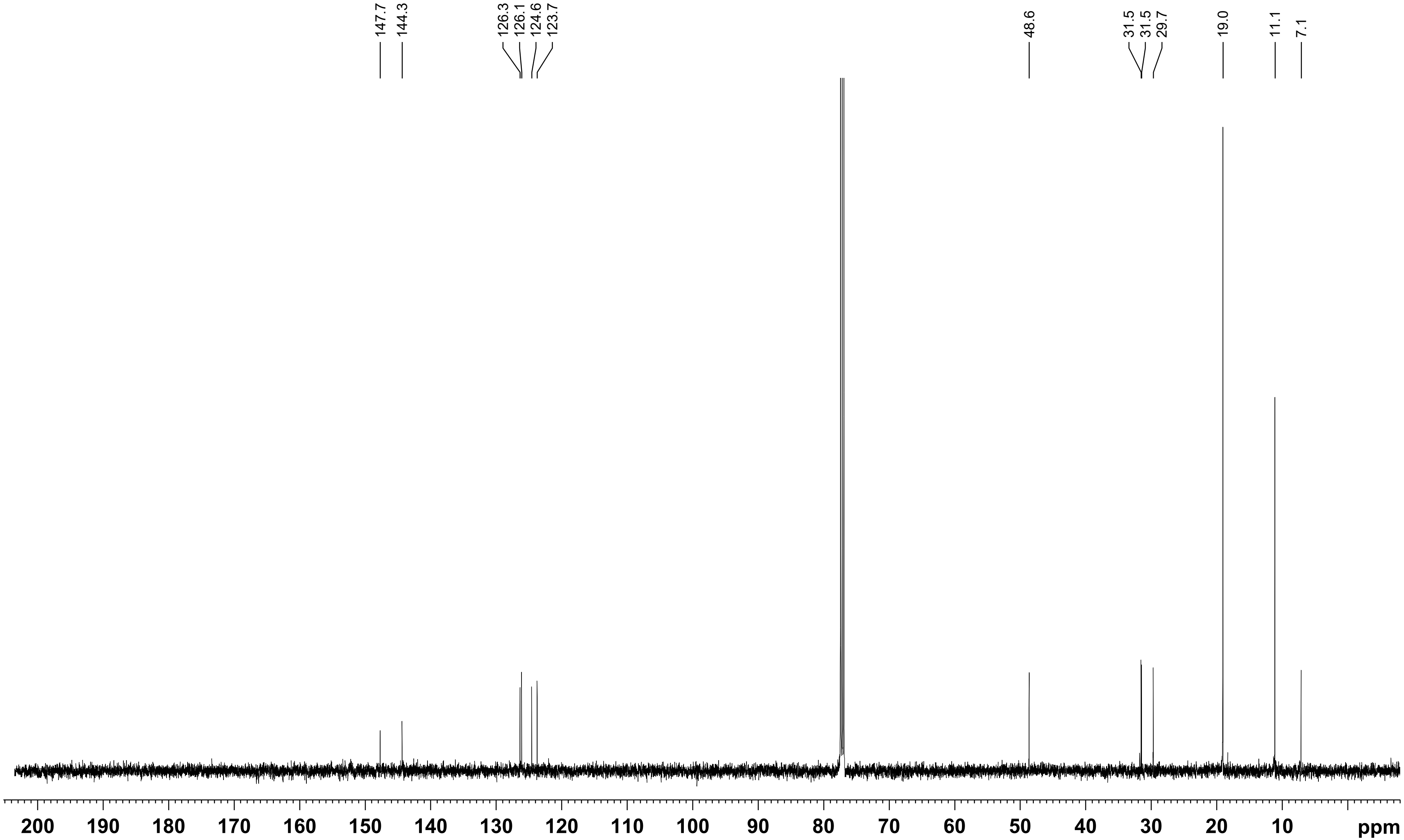


Figure S63. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **3nb** from the catalytic reaction of 2',3'-dihydrospiro[cyclopropane-1,1'-indene] (**1n**) and $^{i}Pr_3SiH$ using $Ph_3C^{+}[B(C_6F_5)_4]^{-}$.

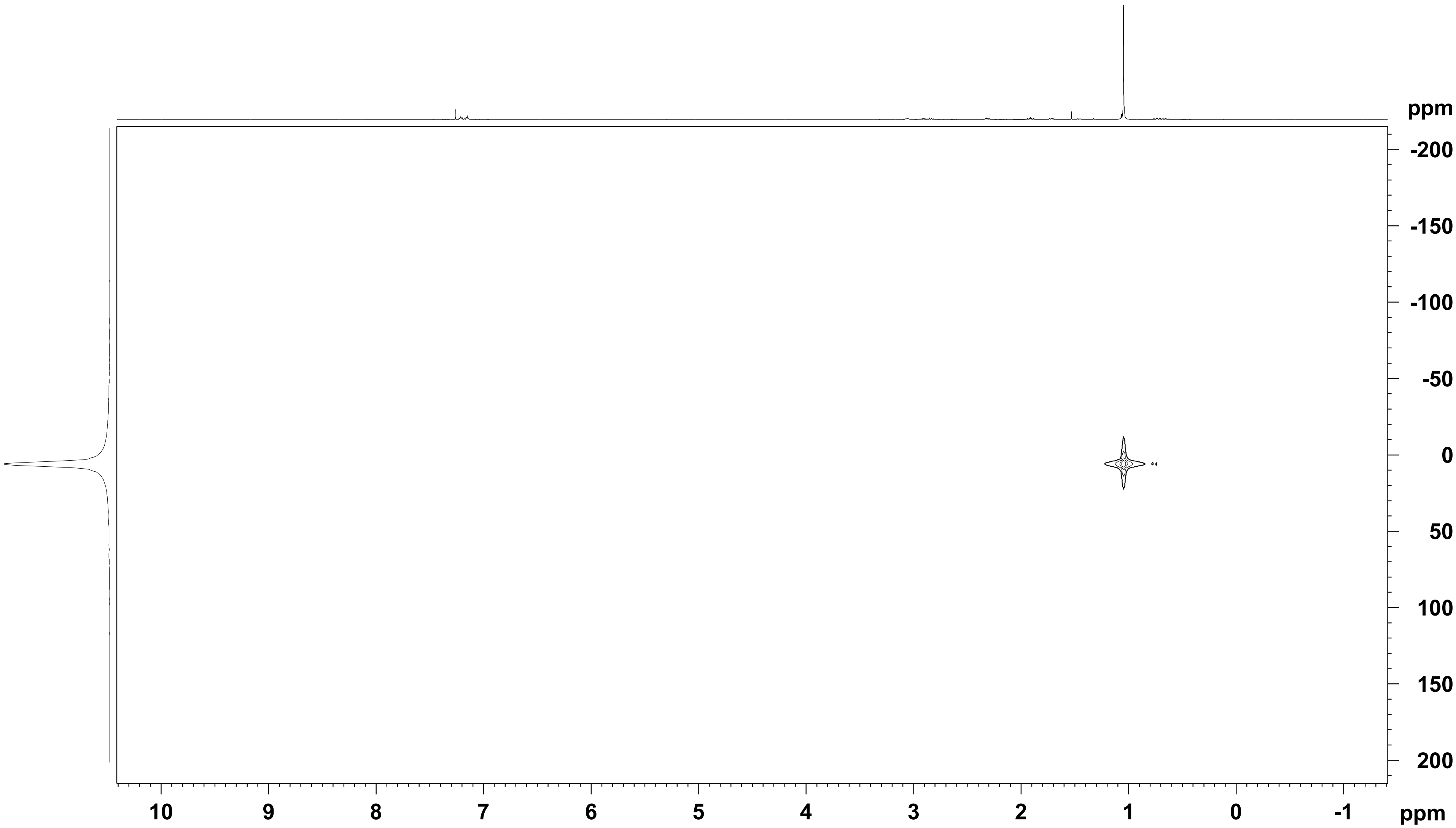
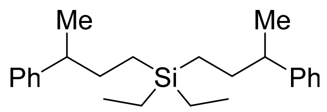


Figure S64. [1]H NMR (500 MHz, $CDCl_3$, 298 K) of **4kf** from the catalytic reaction of (1-methylcyclopropyl)benzene (**1k**) and Et_2SiH_2 using $Ph_3C^+[B(C_6F_5)_4]^-$.



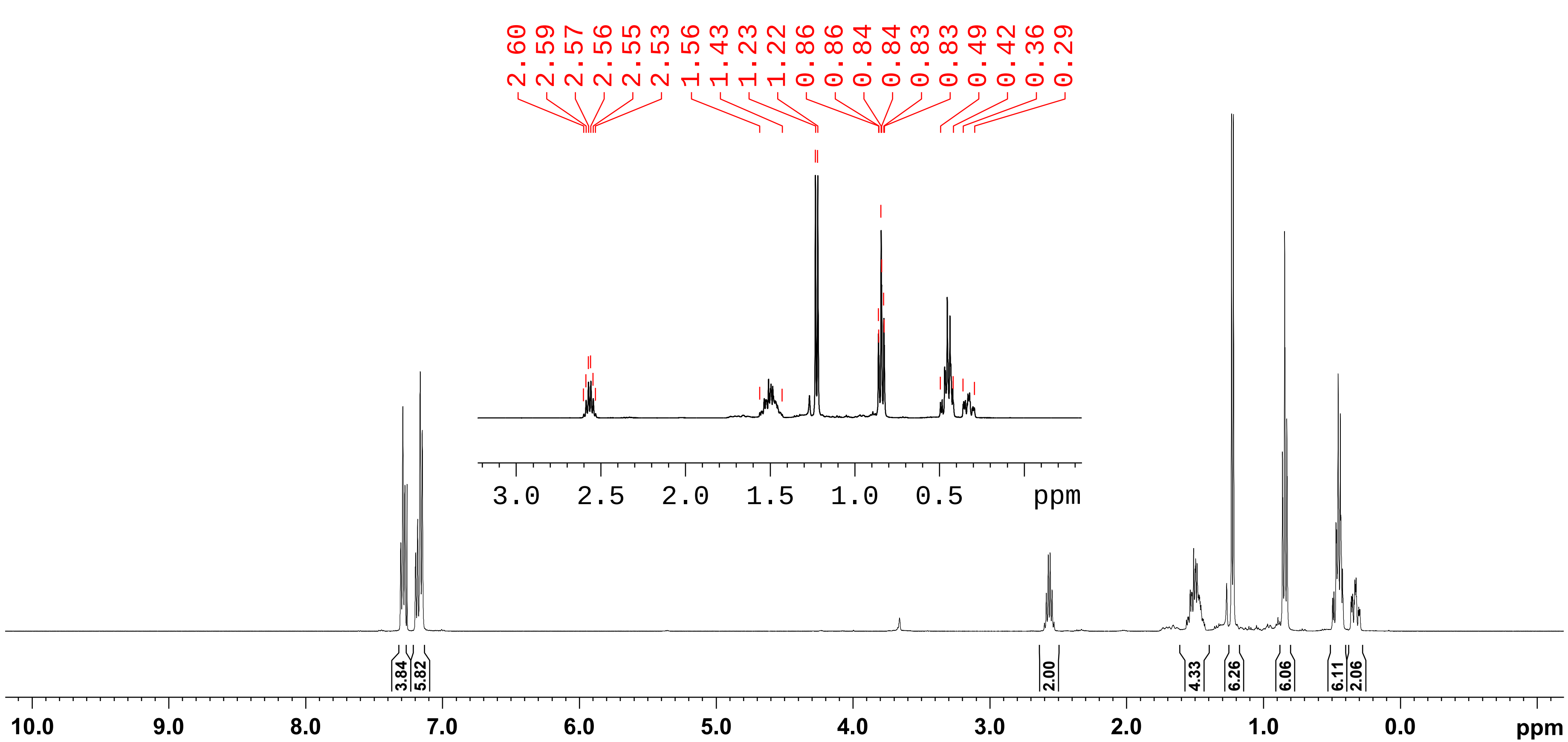


Figure S65. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **4kf** from the catalytic reaction of (1-methylcyclopropyl)benzene (**1k**) and Et_2SiH_2 using $Ph_3C^+[B(C_6F_5)_4]^-$.

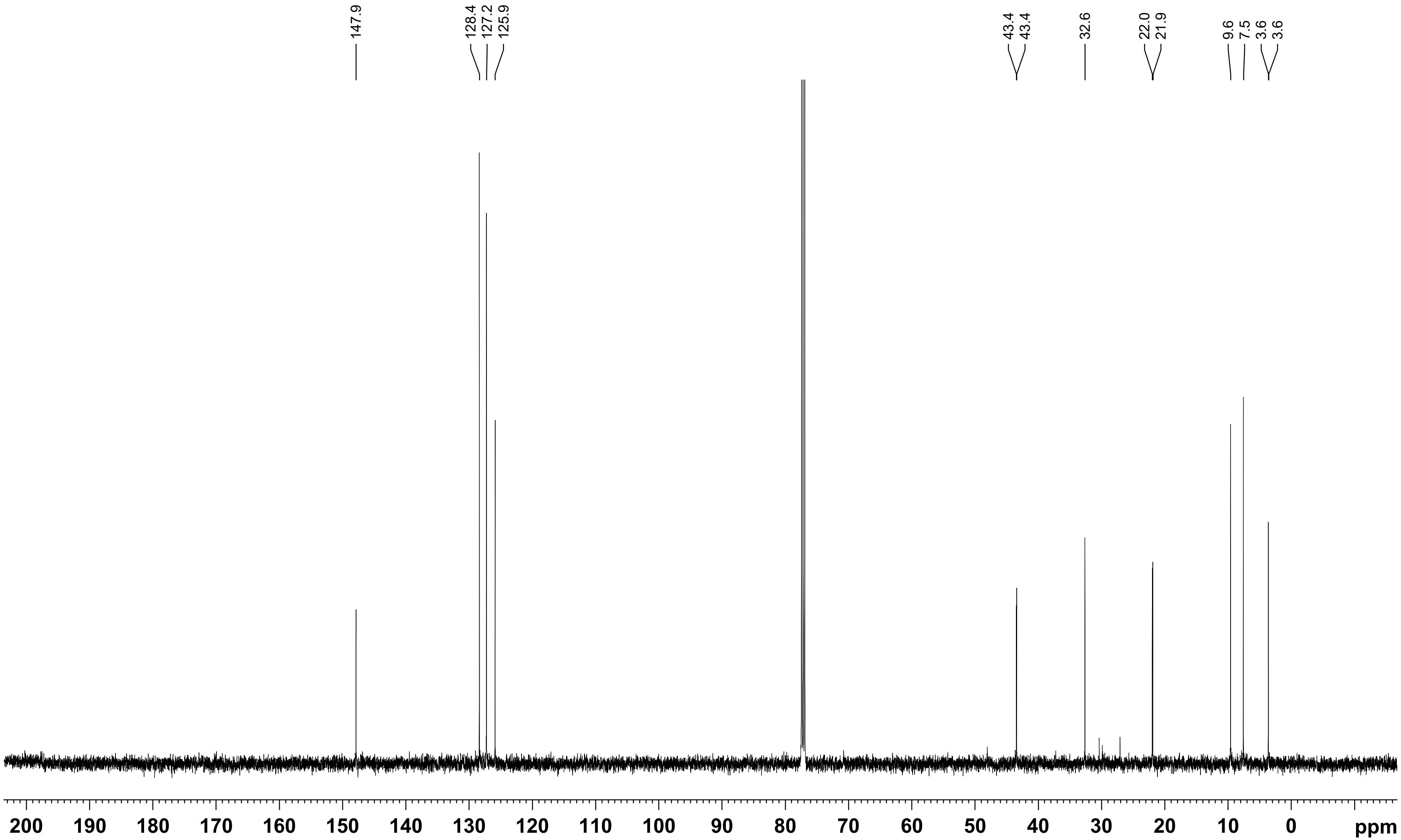


Figure S66. $^1H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **4kf** from the catalytic reaction of (1-methylcyclopropyl)benzene (**1k**) and Et_2SiH_2 using $Ph_3C^+[B(C_6F_5)_4]^-$.

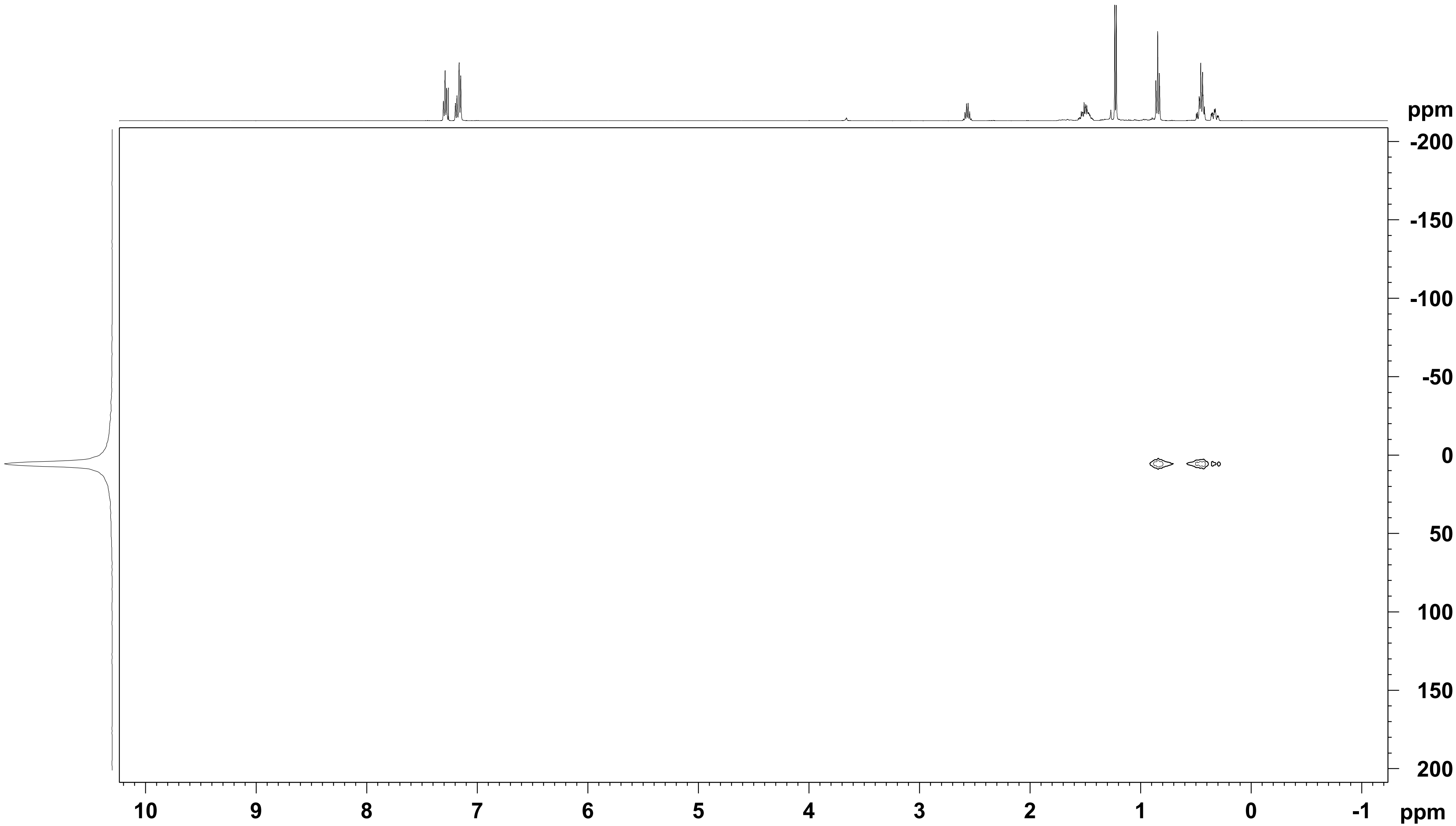


Figure S67. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **4kg** from the catalytic reaction of (1-methylcyclopropyl)benzene (**1k**) and $^tBu_2SiH_2$ using $Ph_3C^+[B(C_6F_5)_4]^-$. (# = Ph_2CH_2)

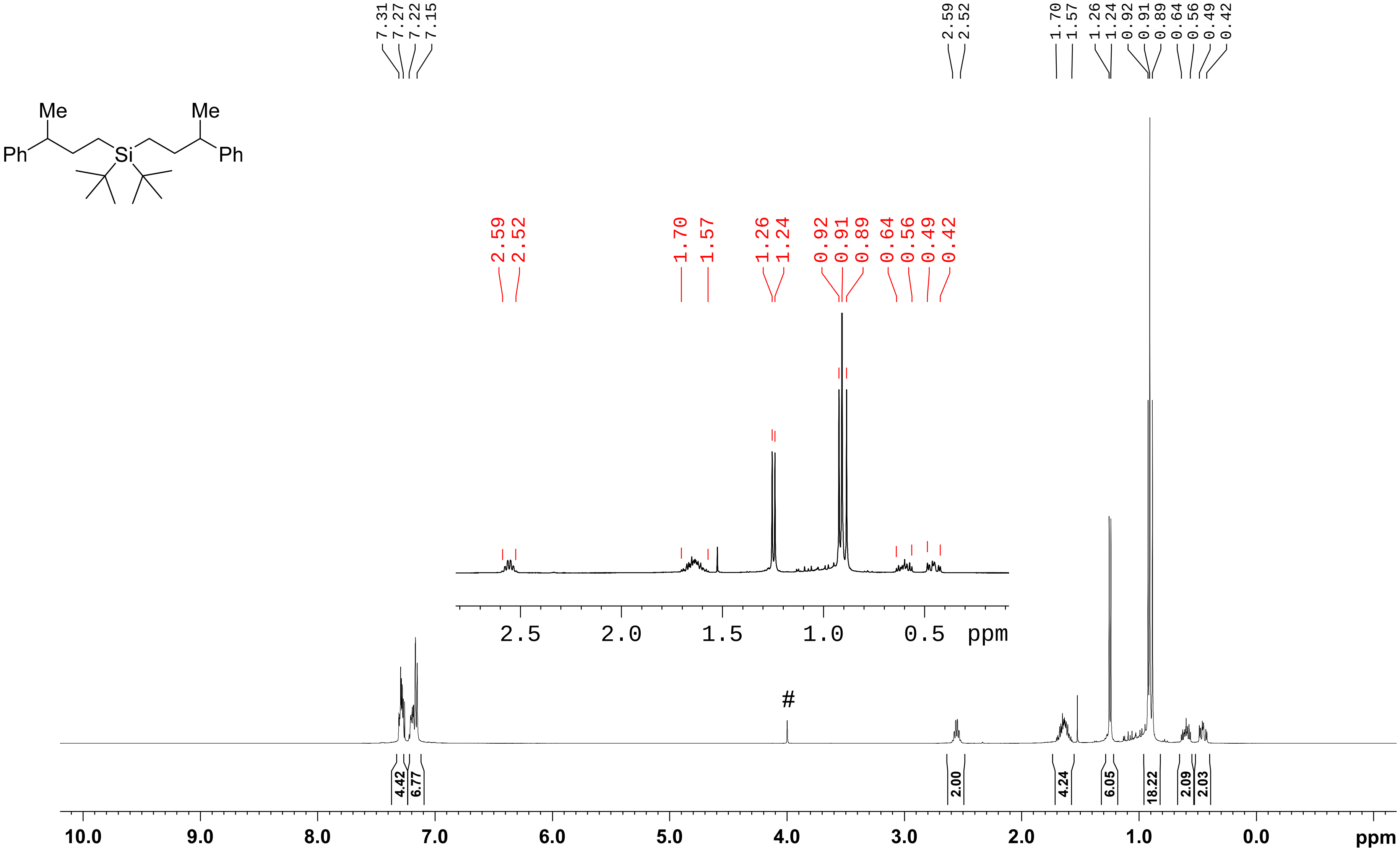


Figure S68. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **4kg** from the catalytic reaction of (1-methylcyclopropyl)benzene (**1k**) and $^tBu_2SiH_2$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

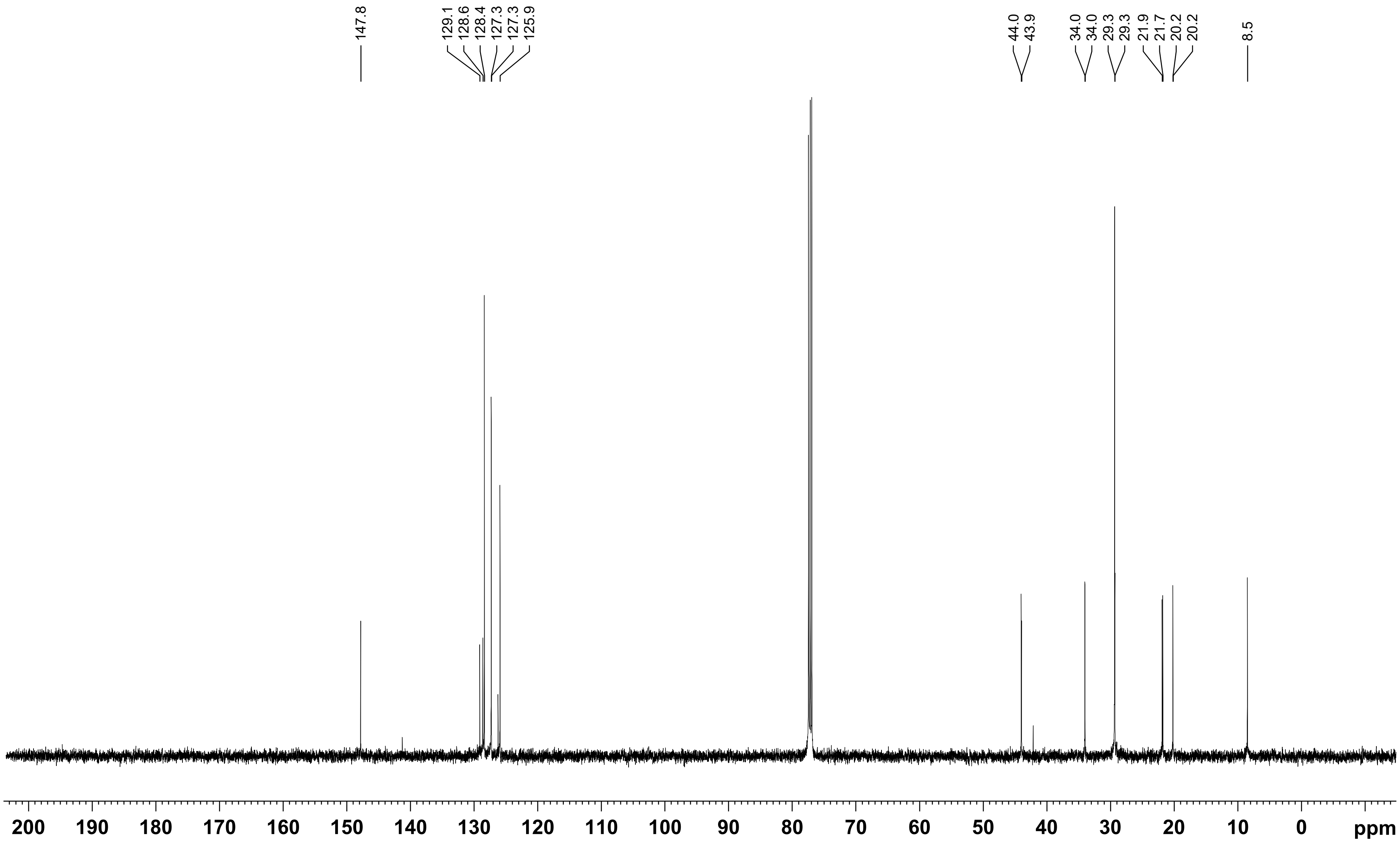


Figure S69. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz) of **4kg** from the catalytic reaction of (1-methylcyclopropyl)benzene (**1k**) and $^{t}Bu_2SiH_2$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

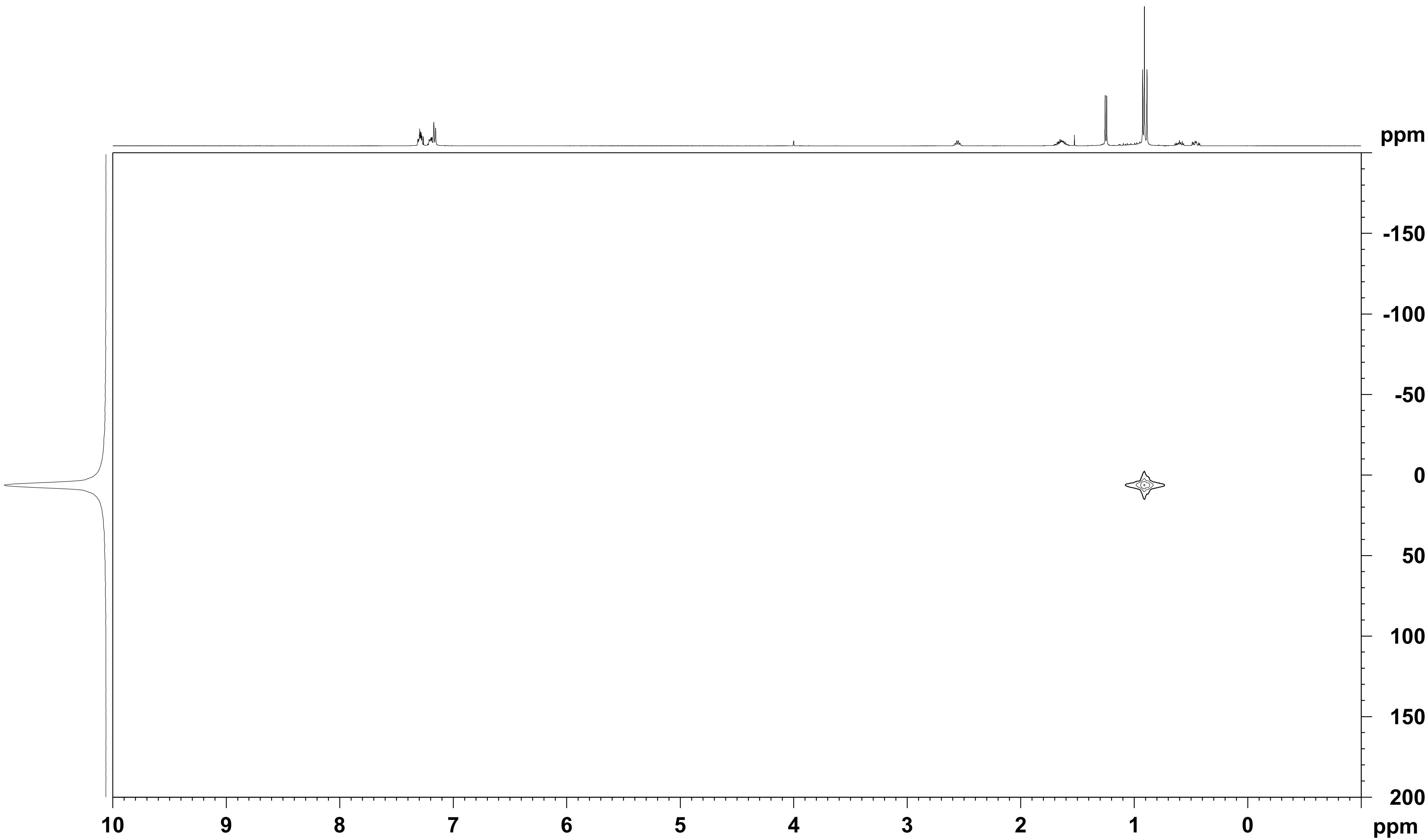


Figure S70. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **3oa & 3oa'** from the catalytic reaction of (2-methylcyclopropyl)benzene (**1o**) and Et_3SiH using $Ph_3C^+[B(C_6F_5)_4]^-$.

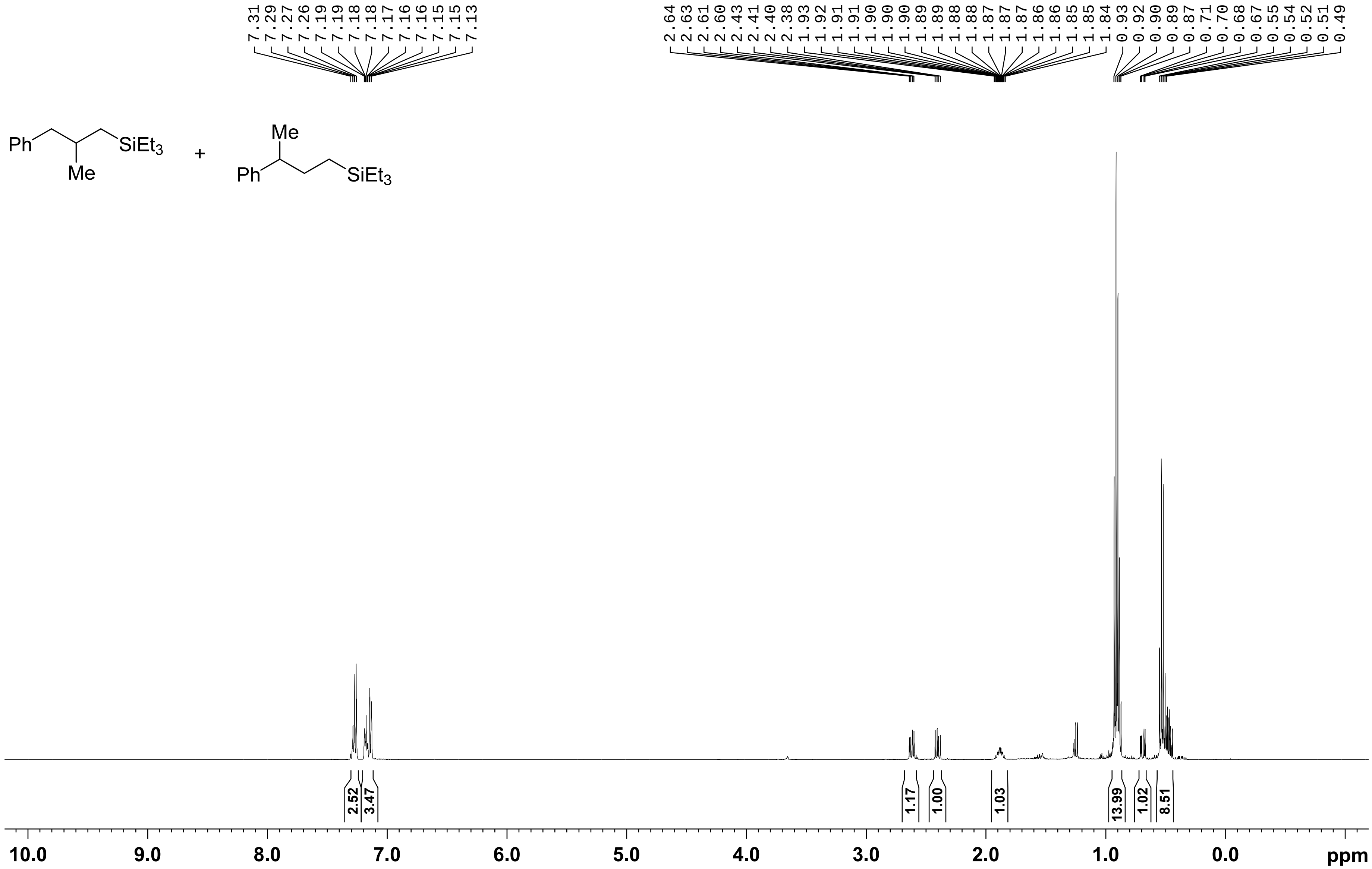


Figure S71. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **3oa & 3oa'** from the catalytic reaction of (2-methylcyclopropyl)benzene (**1o**) and Et_3SiH using $Ph_3C^+[B(C_6F_5)_4]^-$.

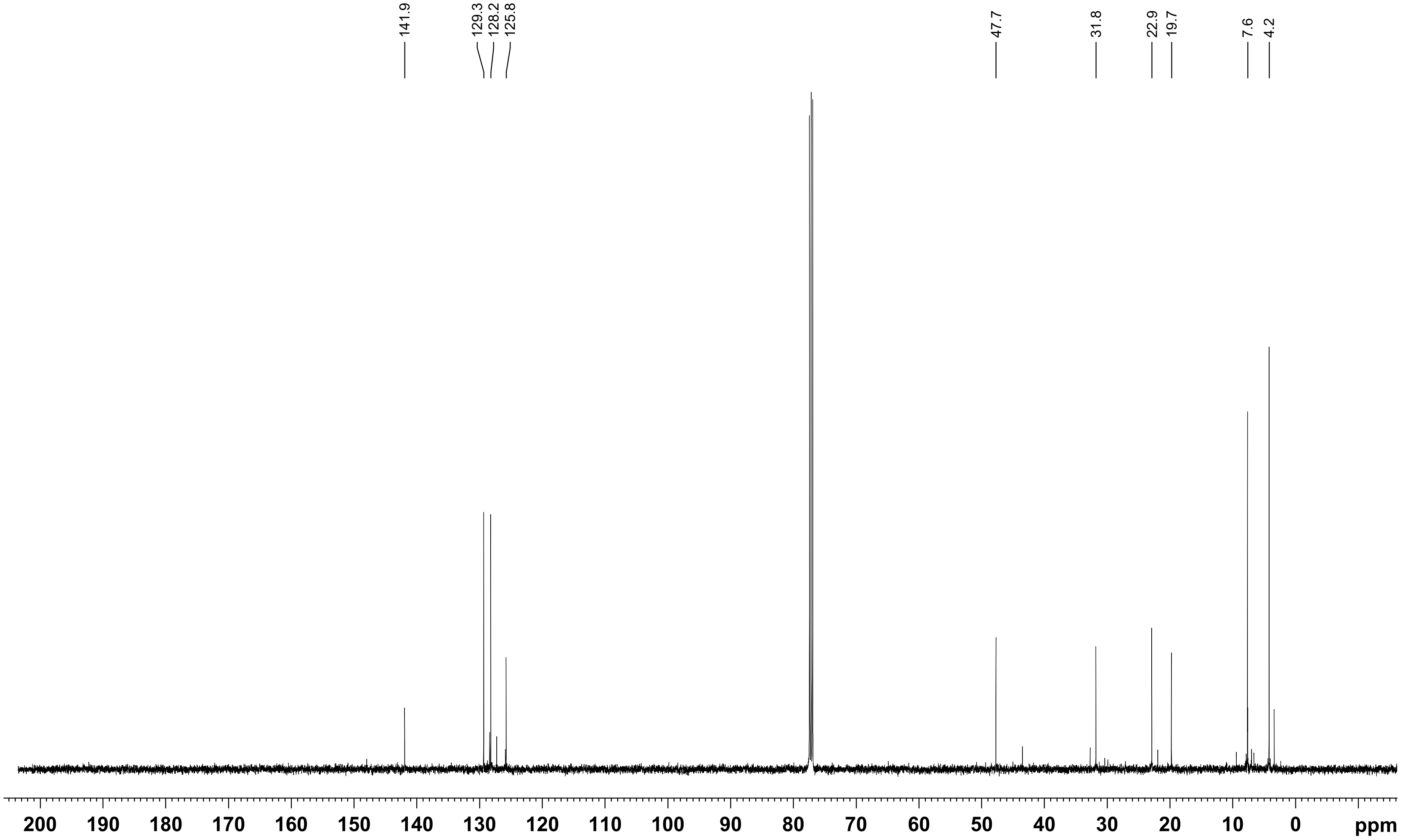


Figure S72. [1]H/[29]Si HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **3oa & 3oa'** from the catalytic reaction of (2-methylcyclopropyl)benzene (**1o**) and Et_3SiH using $Ph_3C^+[B(C_6F_5)_4]^-$.

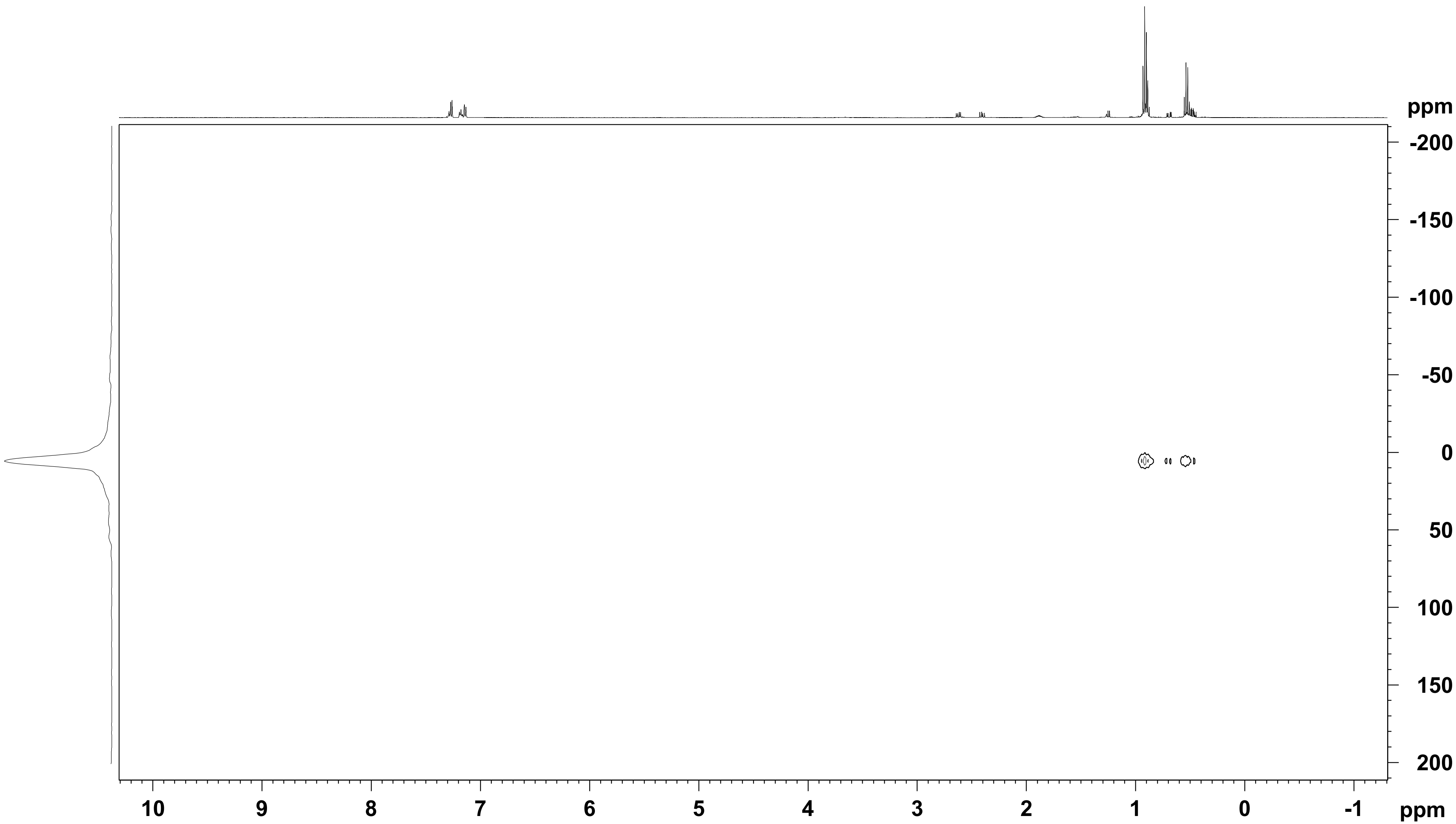


Figure S73. [1]H NMR (500 MHz, $CDCl_3$, 298 K) of **3ob & 3ob'** from the catalytic reaction of (2-methylcyclopropyl)benzene (**1o**) and $^{i}Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$

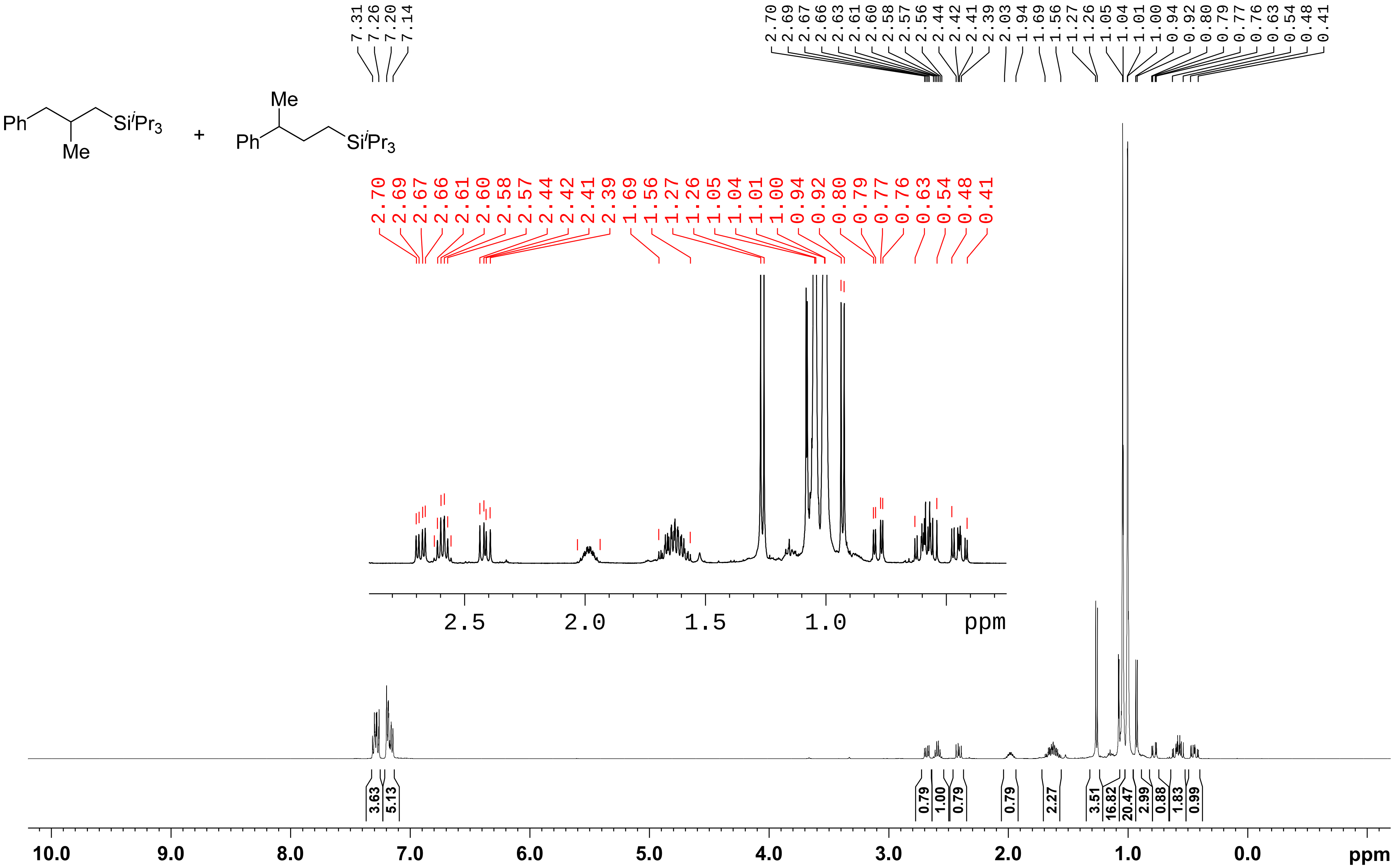


Figure S74. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **3ob & 3ob'** from the catalytic reaction of (2-methylcyclopropyl)benzene (**1o**) and $^iPr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

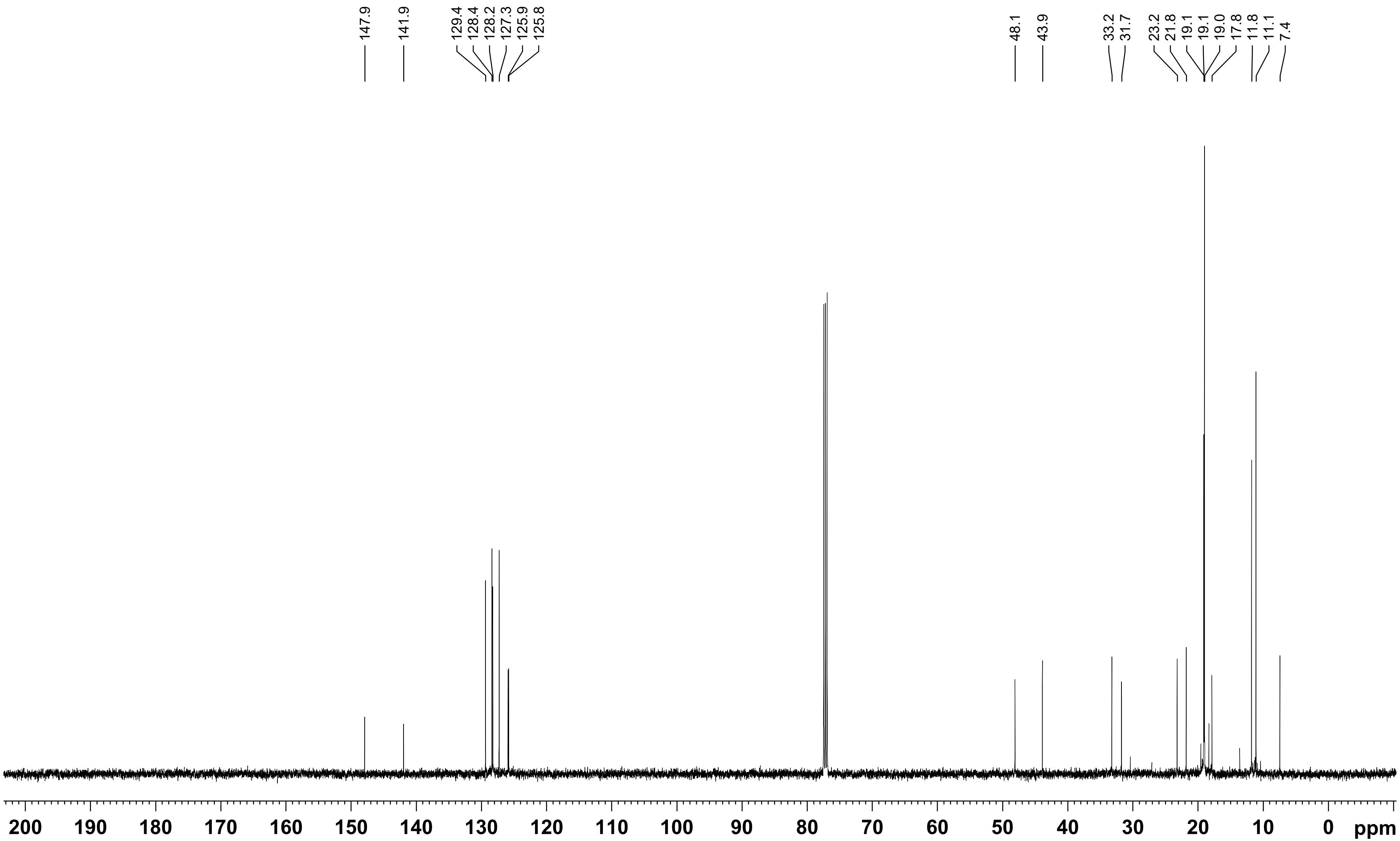


Figure S75. ^{29}Si-DEPT NMR (99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz) of **3ob & 3ob'** from the catalytic reaction of (2-methylcyclopropyl)benzene (**1o**) and $^{i}Pr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

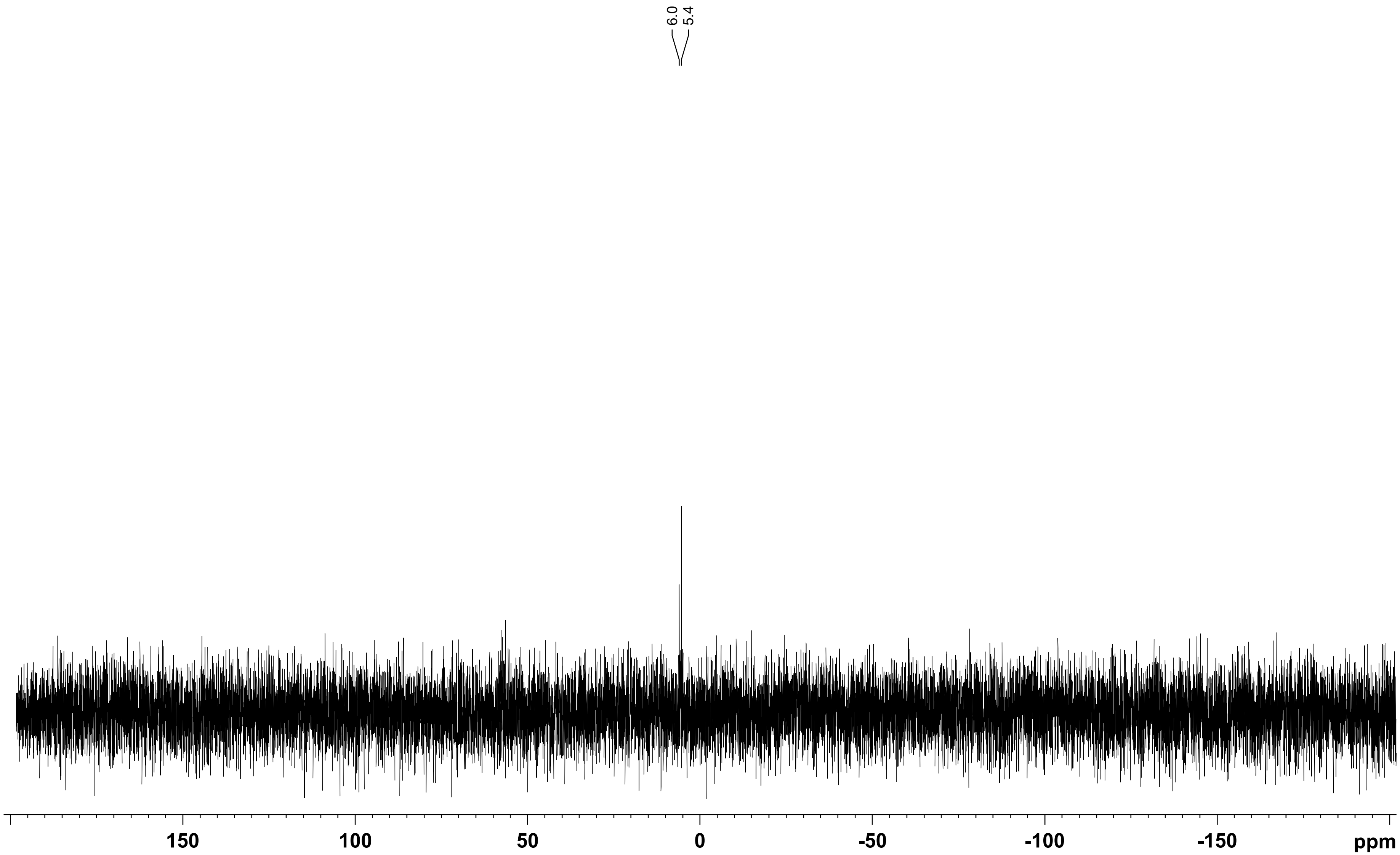


Figure S76. $^1H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz) of **3ob & 3ob'** from the catalytic reaction of (2-methylcyclopropyl)benzene (**1o**) and $^iPr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

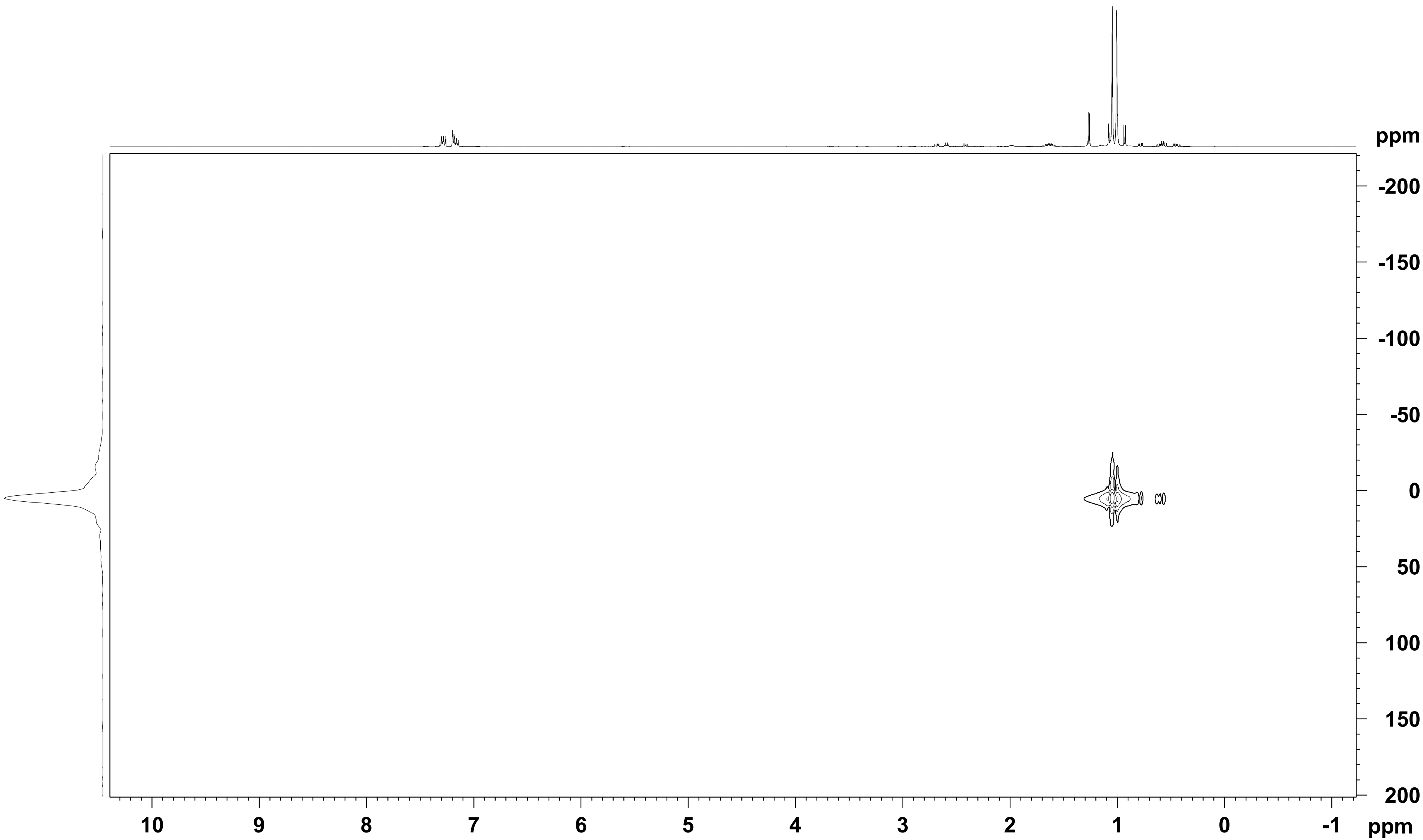


Figure S77. [1]H NMR (500 MHz, $CDCl_3$, 298 K) of **3pb'** from the catalytic reaction of 1-bromo-4-(2-phenylcyclopropyl)benzene (**1p**) and $^iPr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

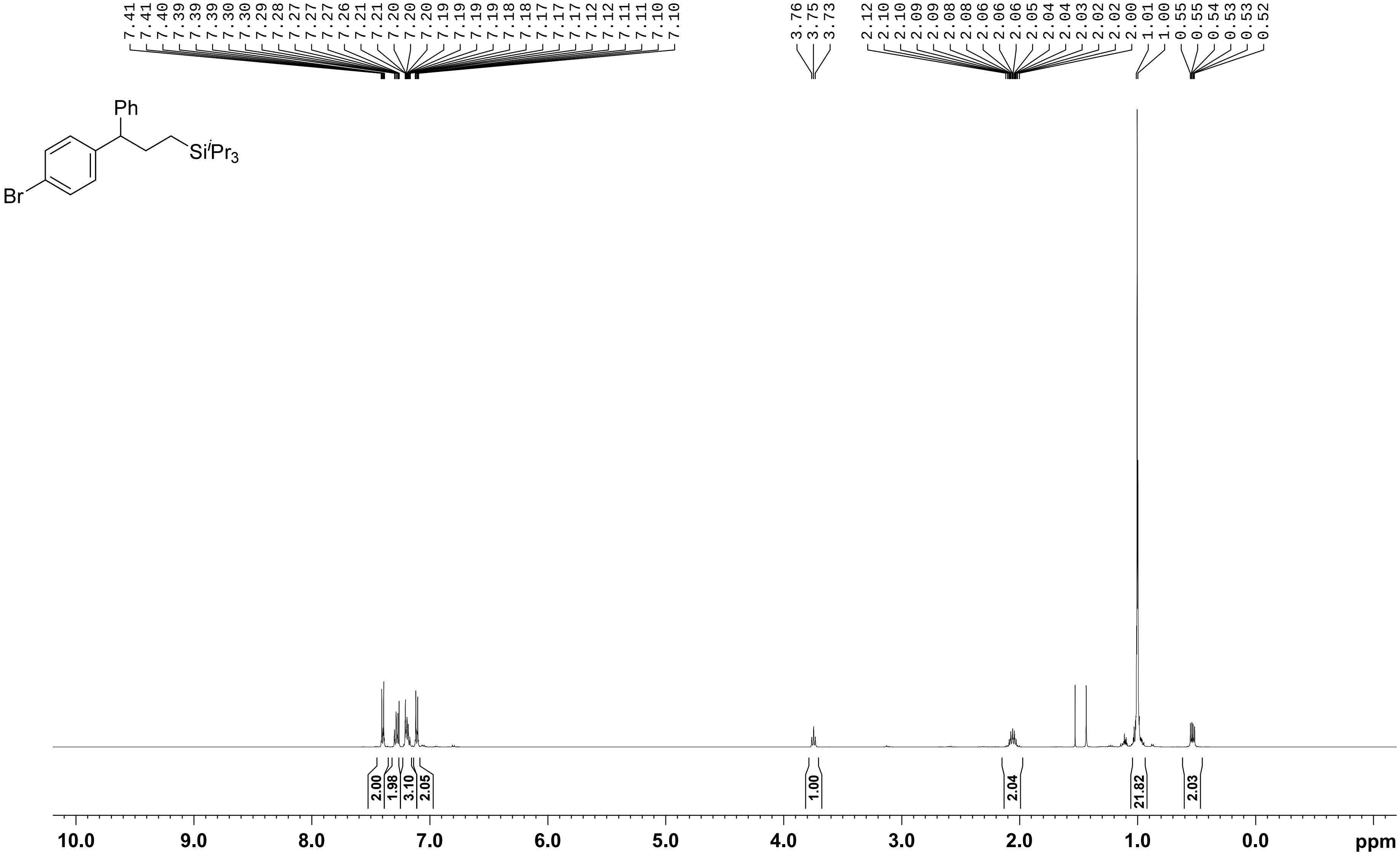


Figure S78. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **3pb'** from the catalytic reaction of 1-bromo-4-(2-phenylcyclopropyl)benzene (**1p**) and $^iPr_3SiH$ using $Ph_3C^+[B(C_6F_5)_4]^-$. (# = cyclohexane)

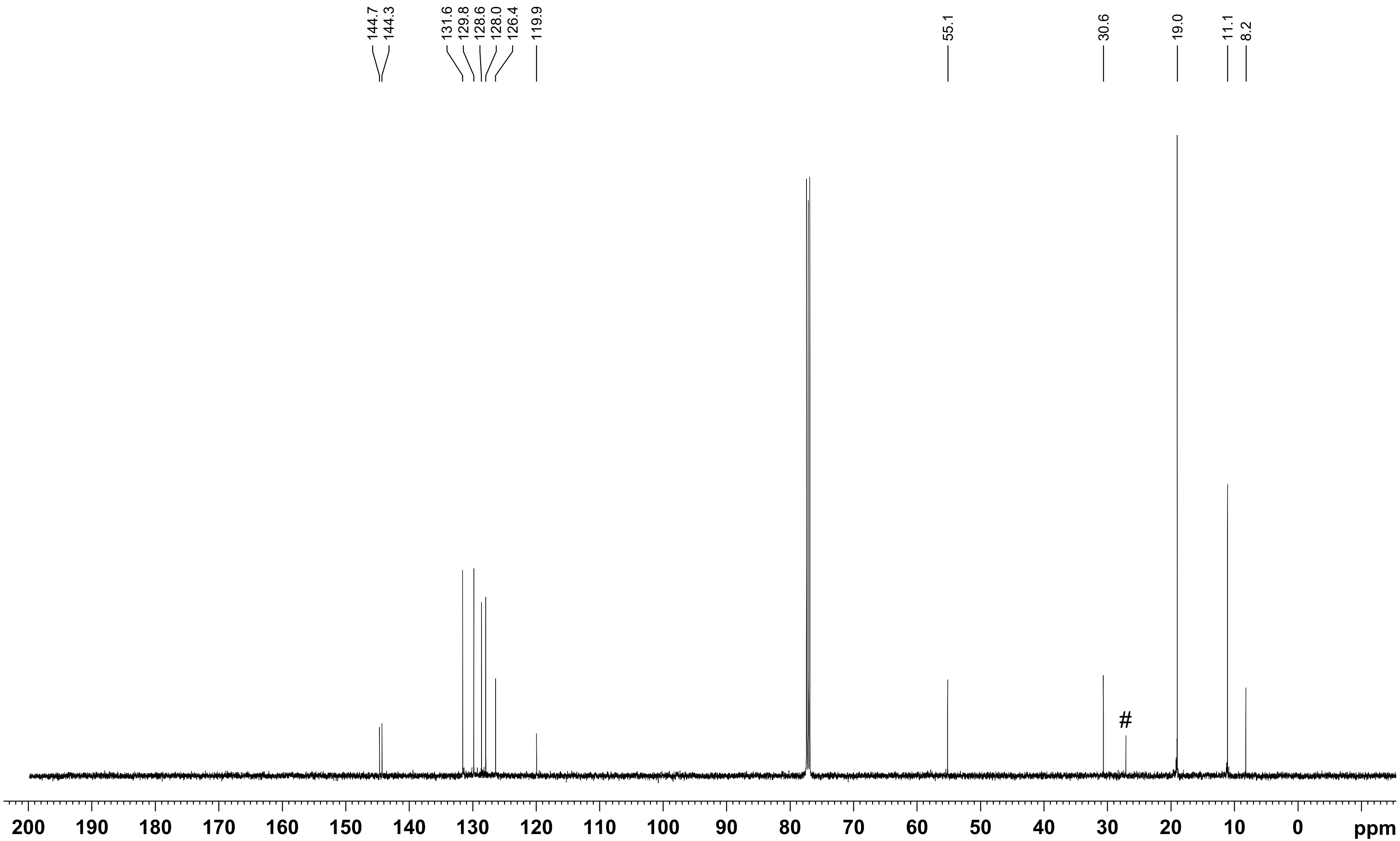


Figure S79. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **3pb'** from the catalytic reaction of 1-bromo-4-(2-phenylcyclopropyl)benzene (**1p**) and $^{i}Pr_3SiH$ using $Ph_3C^{+}[B(C_6F_5)_4]^{-}$.

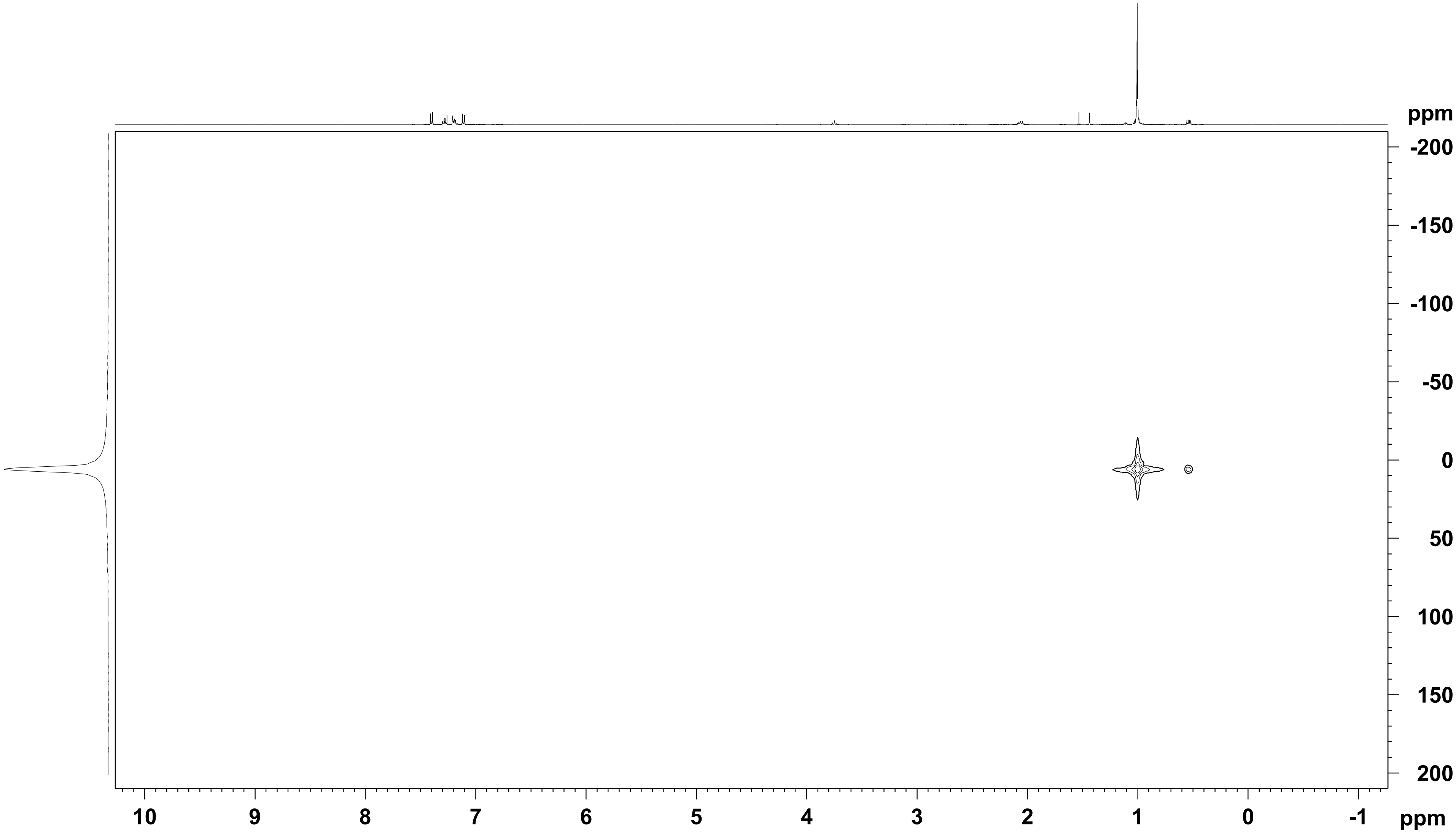


Figure S80. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **7a** from the catalytic reaction of cyclopropylbenzene (**1a**) and $Me_3SiSiMe_3$ using $Me_3Si^+[CHB_{11}H_5Br_6]^-$.

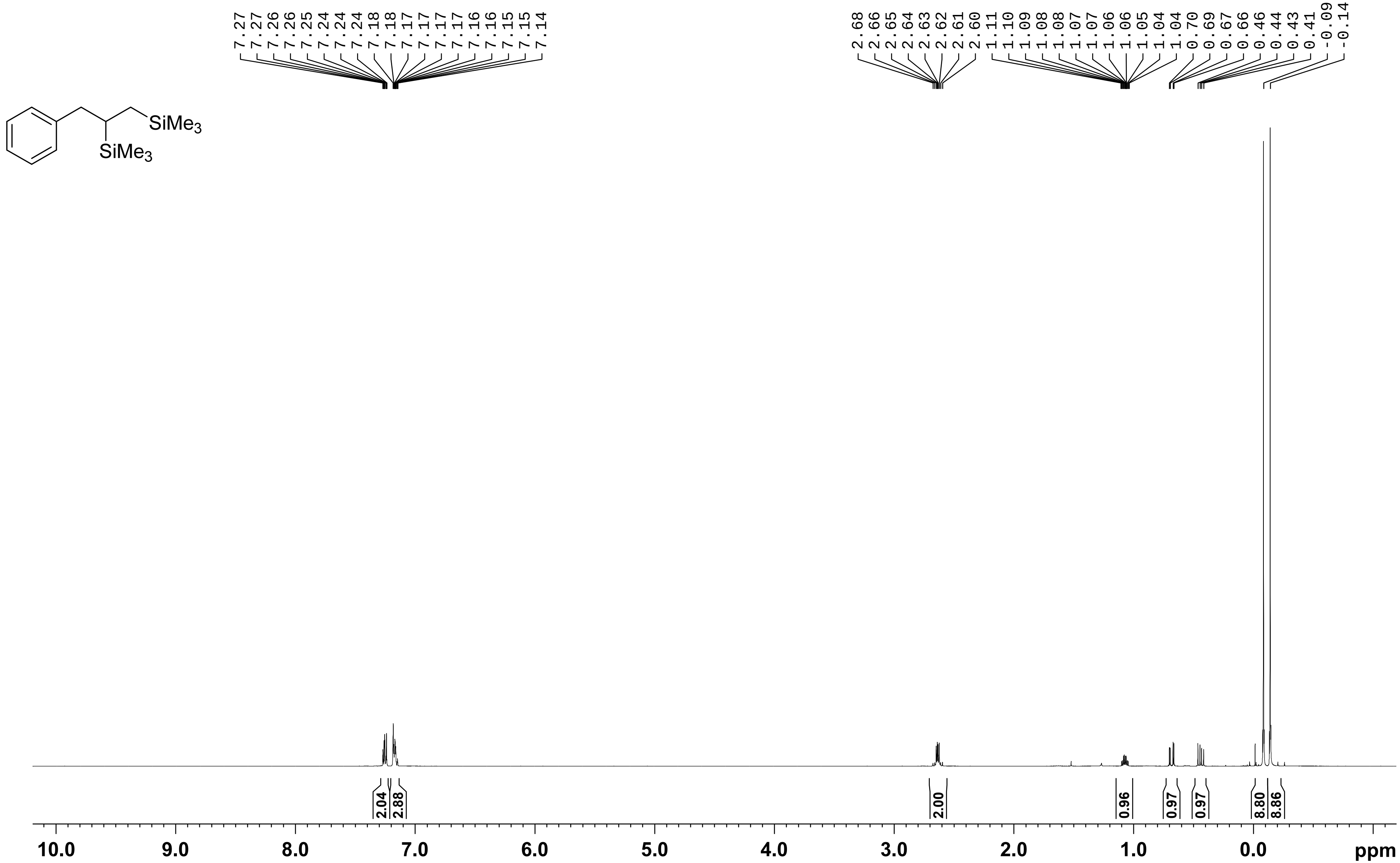


Figure S81. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **7a** from the catalytic reaction of cyclopropylbenzene (**1a**) and $Me_3SiSiMe_3$ using $Me_3Si^+[CHB_{11}H_5Br_6]^-$.

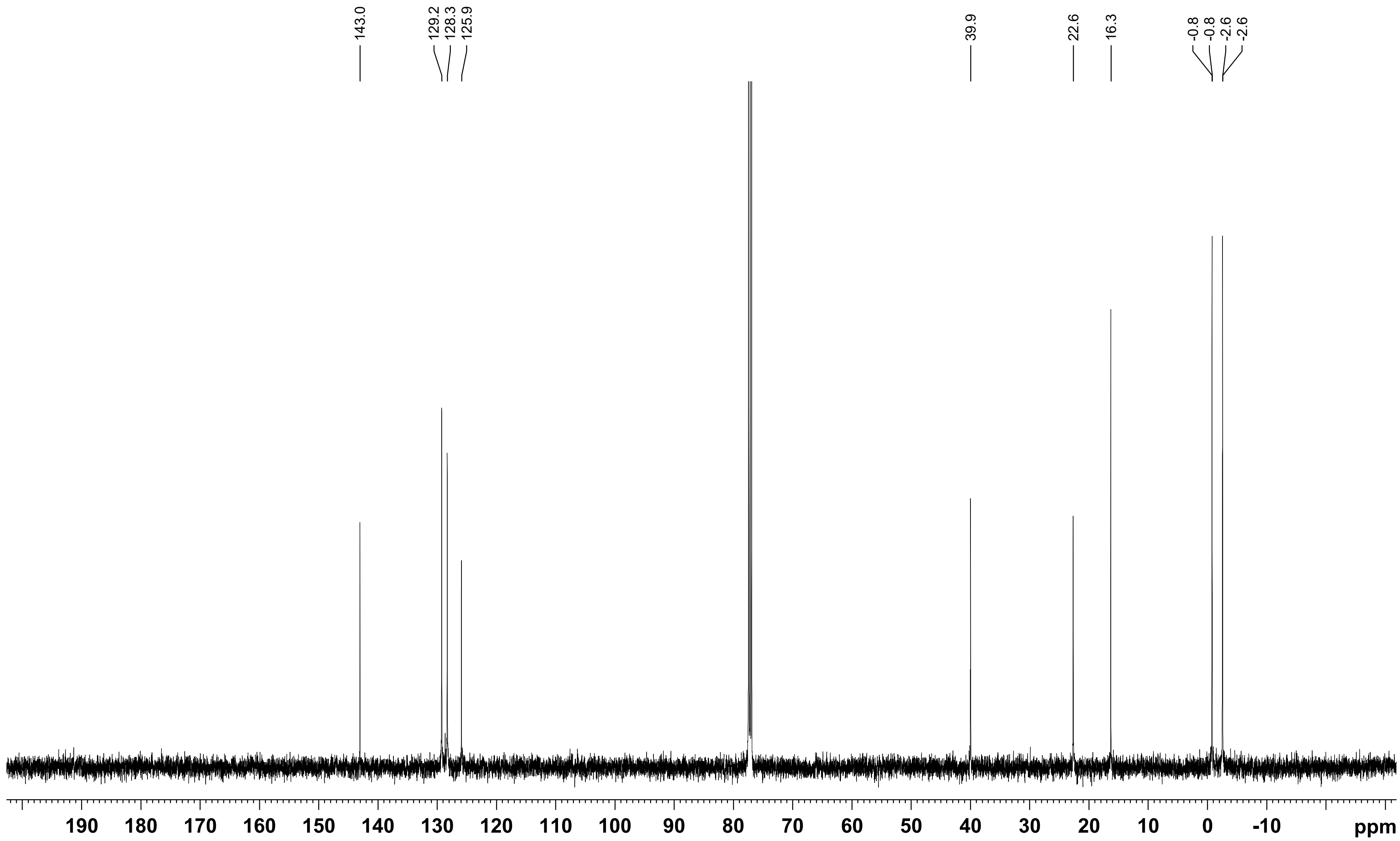


Figure S82. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz) of **7a** from the catalytic reaction of cyclopropylbenzene (**1a**) and $Me_3SiSiMe_3$ using $Me_3Si^+[CHB_{11}H_5Br_6]^-$.

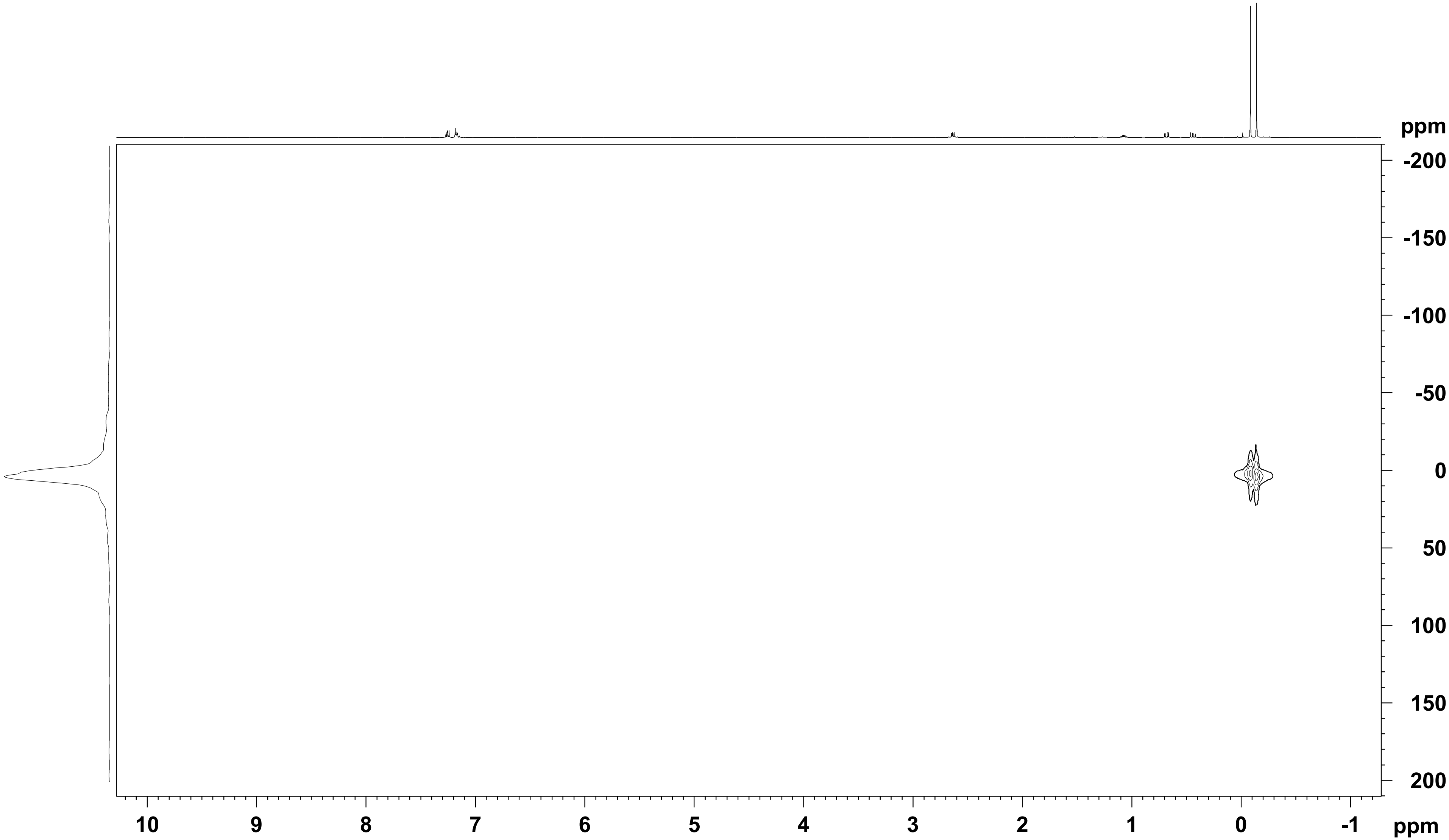


Figure S83. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **7b** from the catalytic reaction of 1-cyclopropyl-4-fluorobenzene (**1b**) and $Me_3SiSiMe_3$ using $Me_3Si^+[CHB_{11}H_5Br_6]^-$.

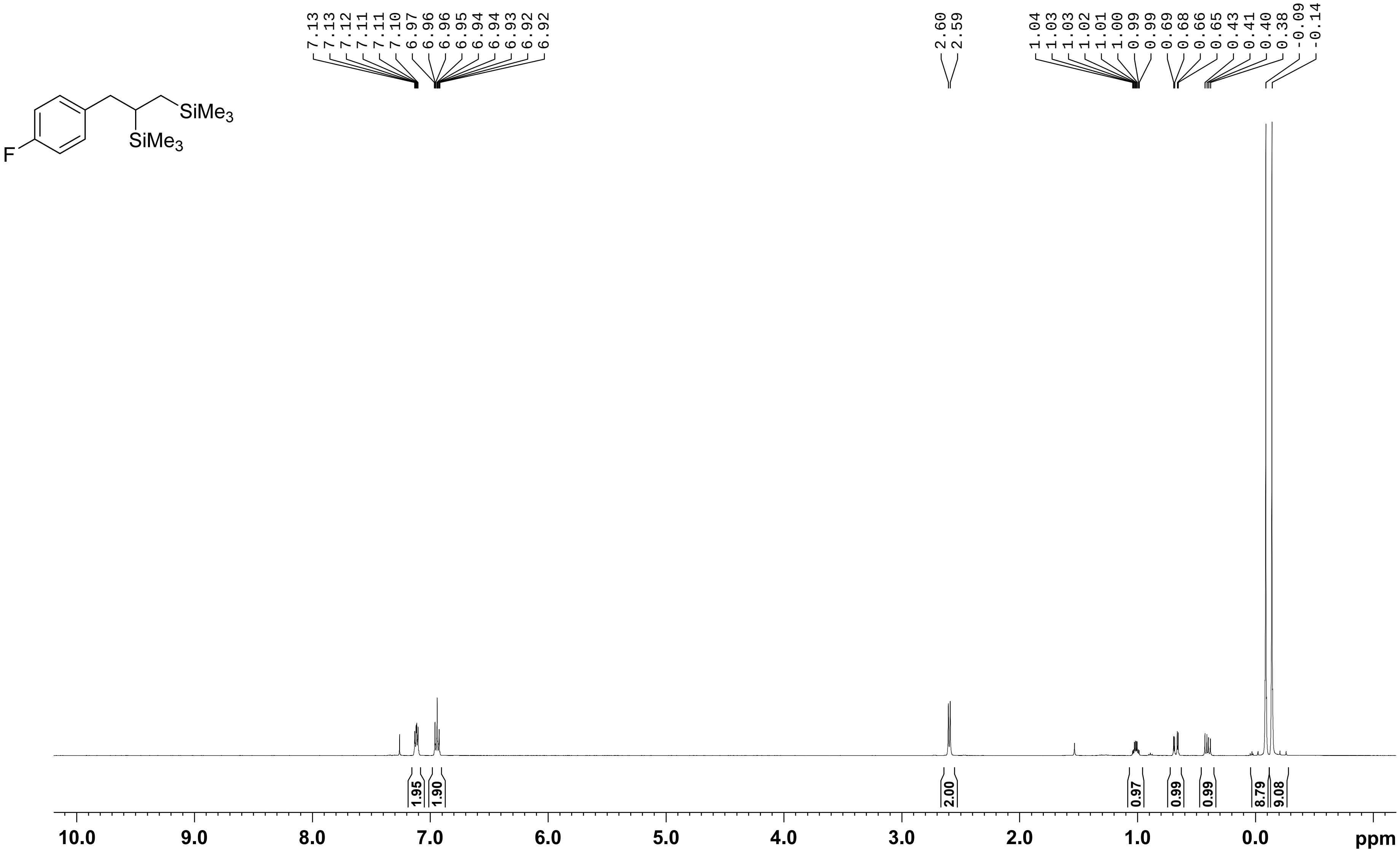


Figure S84. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **7b** from the catalytic reaction of 1-cyclopropyl-4-fluorobenzene (**1b**) and $Me_3SiSiMe_3$ using $Me_3Si^+[CHB_{11}H_5Br_6]^-$.

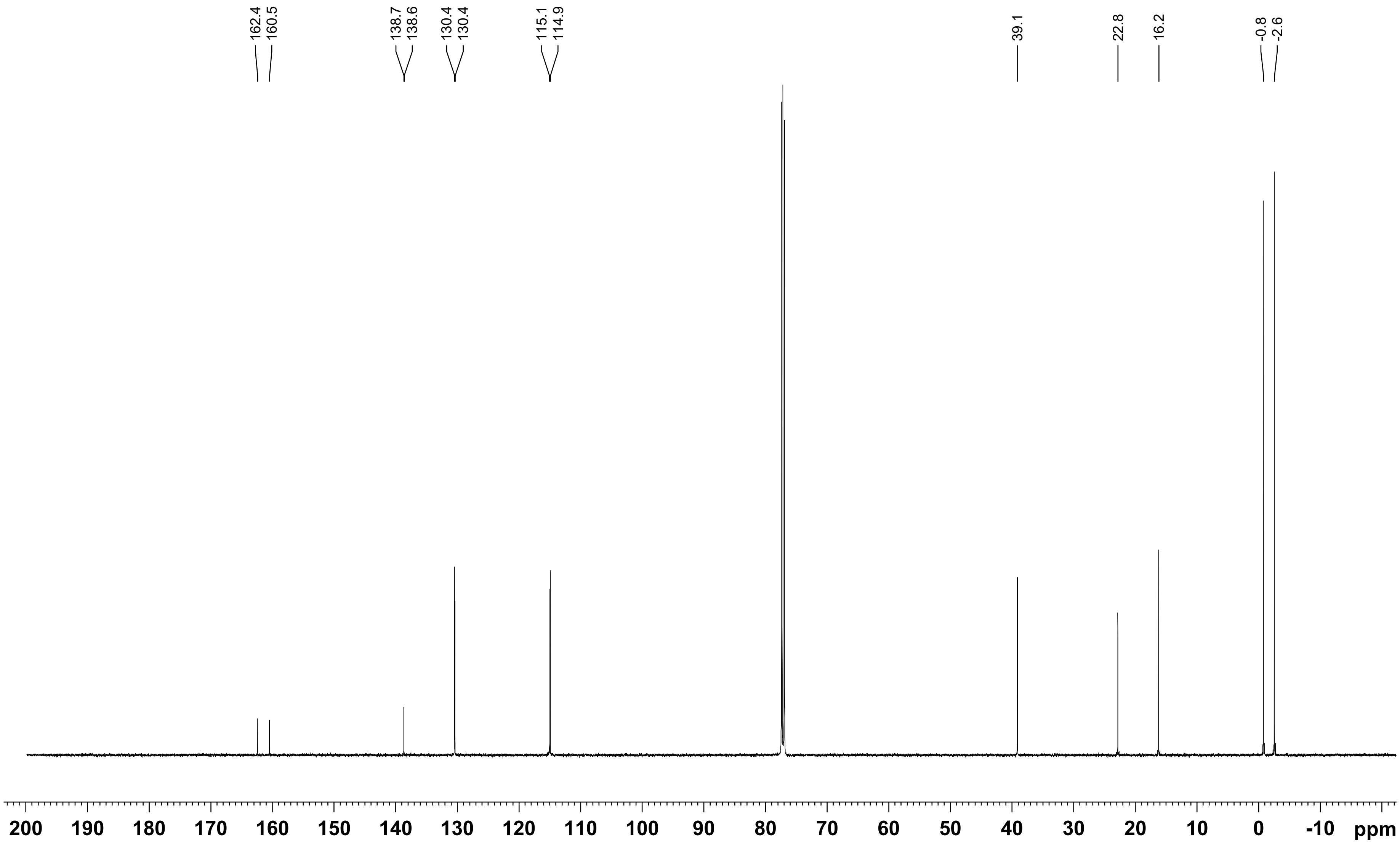


Figure S85. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **7c** from the catalytic reaction of 1-chloro-4-cyclopropylbenzene (**1c**) and $Me_3SiSiMe_3$ using $Me_3Si^+[CHB_{11}H_5Br_6]^-$.

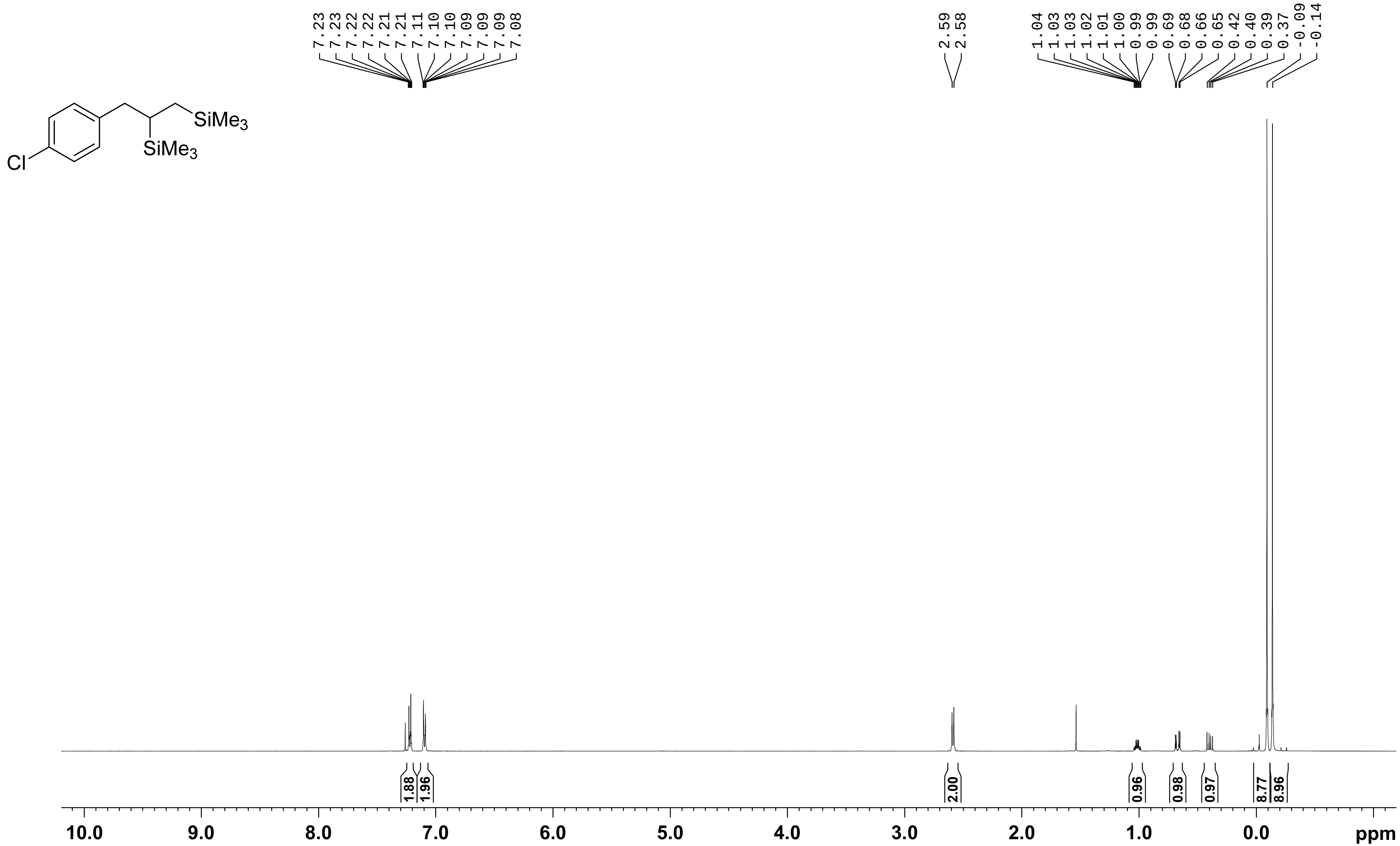


Figure S86. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **7c** from the catalytic reaction of 1-chloro-4-cyclopropylbenzene (**1c**) and $Me_3SiSiMe_3$ using $Me_3Si^+[CHB_{11}H_5Br_6]^-$.

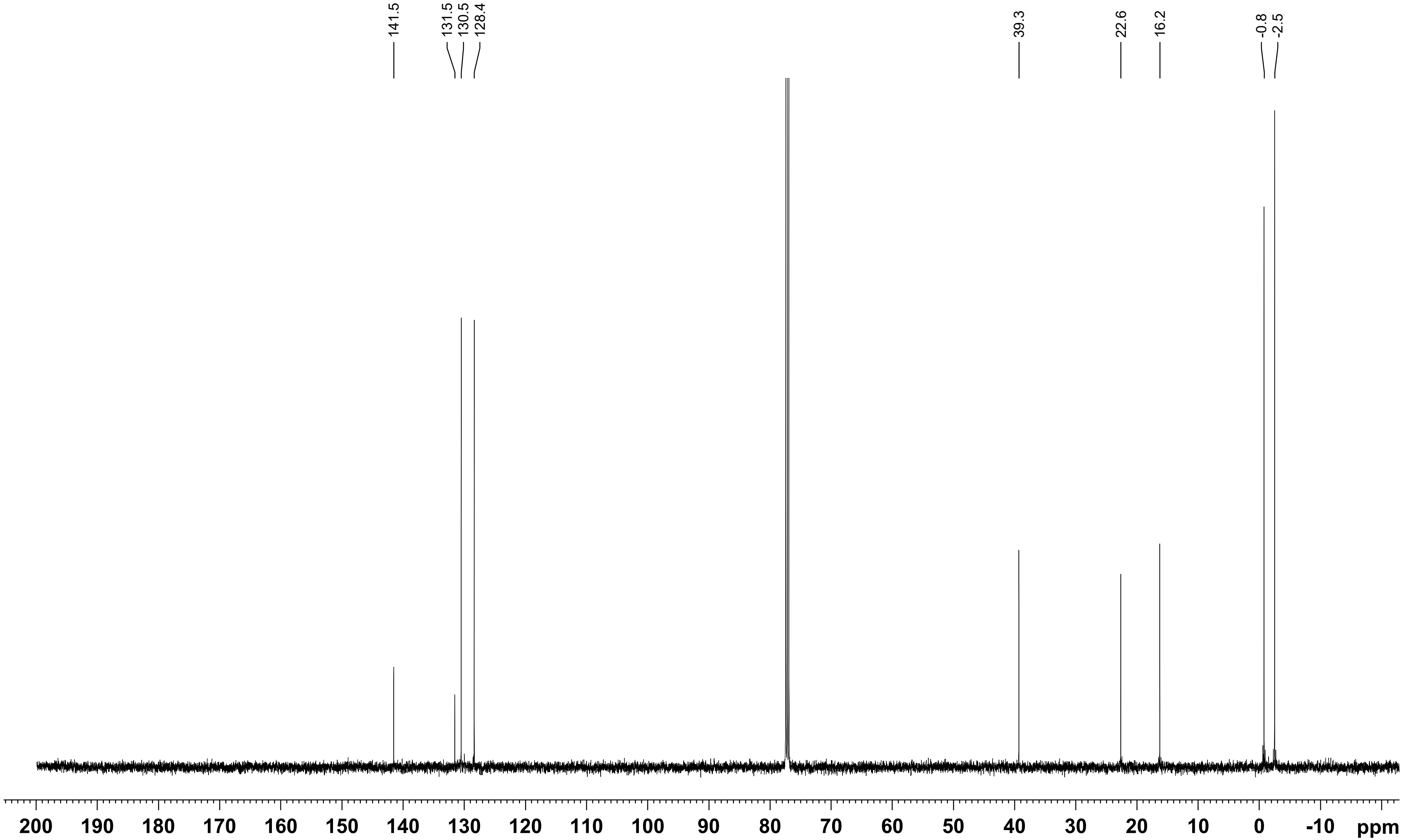
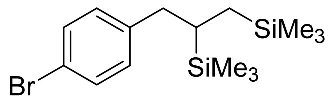


Figure S87. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **7d** from the catalytic reaction of 1-bromo-4-cyclopropylbenzene (**1d**) and $Me_3SiSiMe_3$ using $Me_3Si^+[CHB_{11}H_5Br_6]^-$.



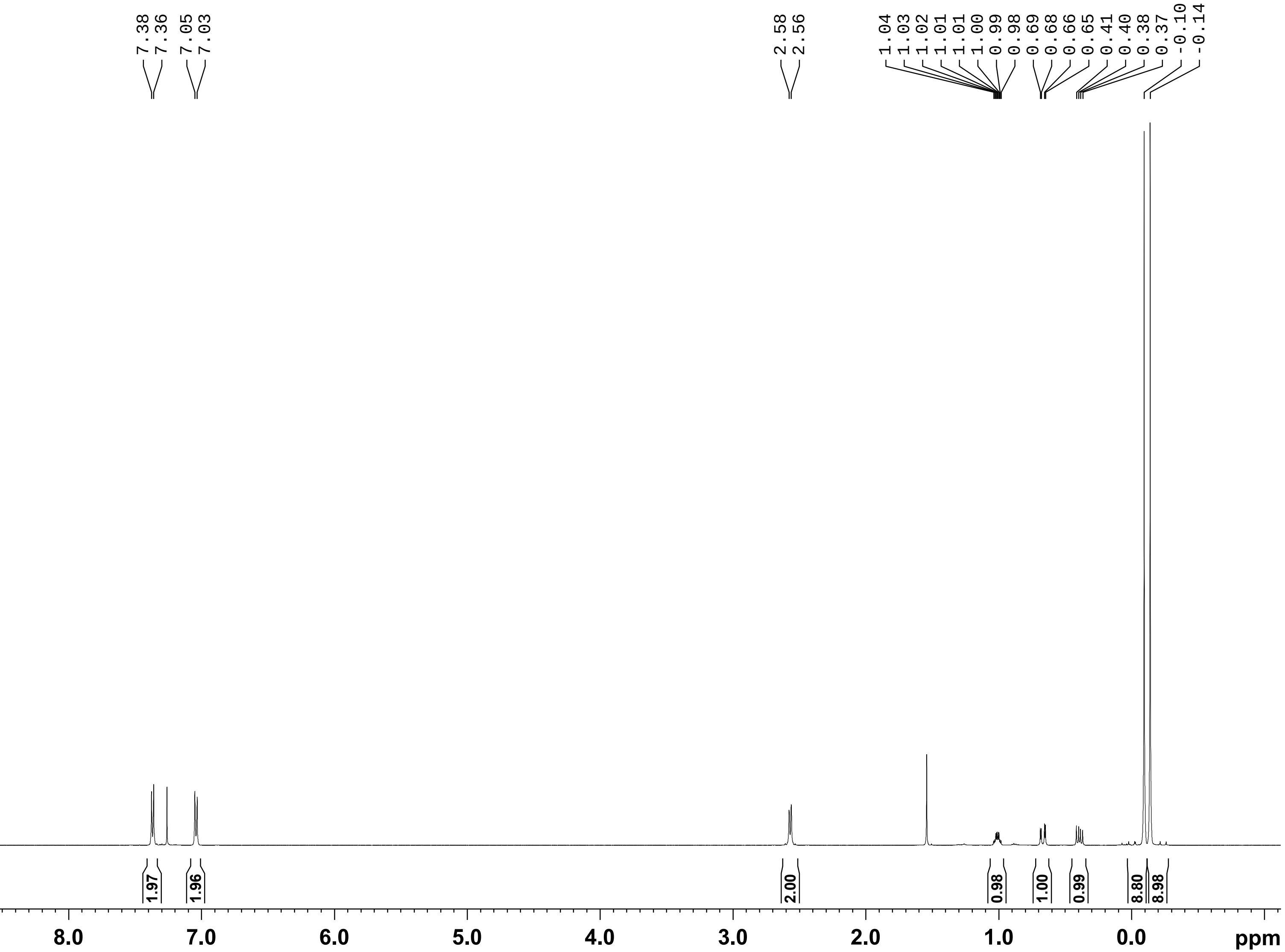


Figure S88. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **7d** from the catalytic reaction of 1-bromo-4-cyclopropylbenzene (**1d**) and $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$.

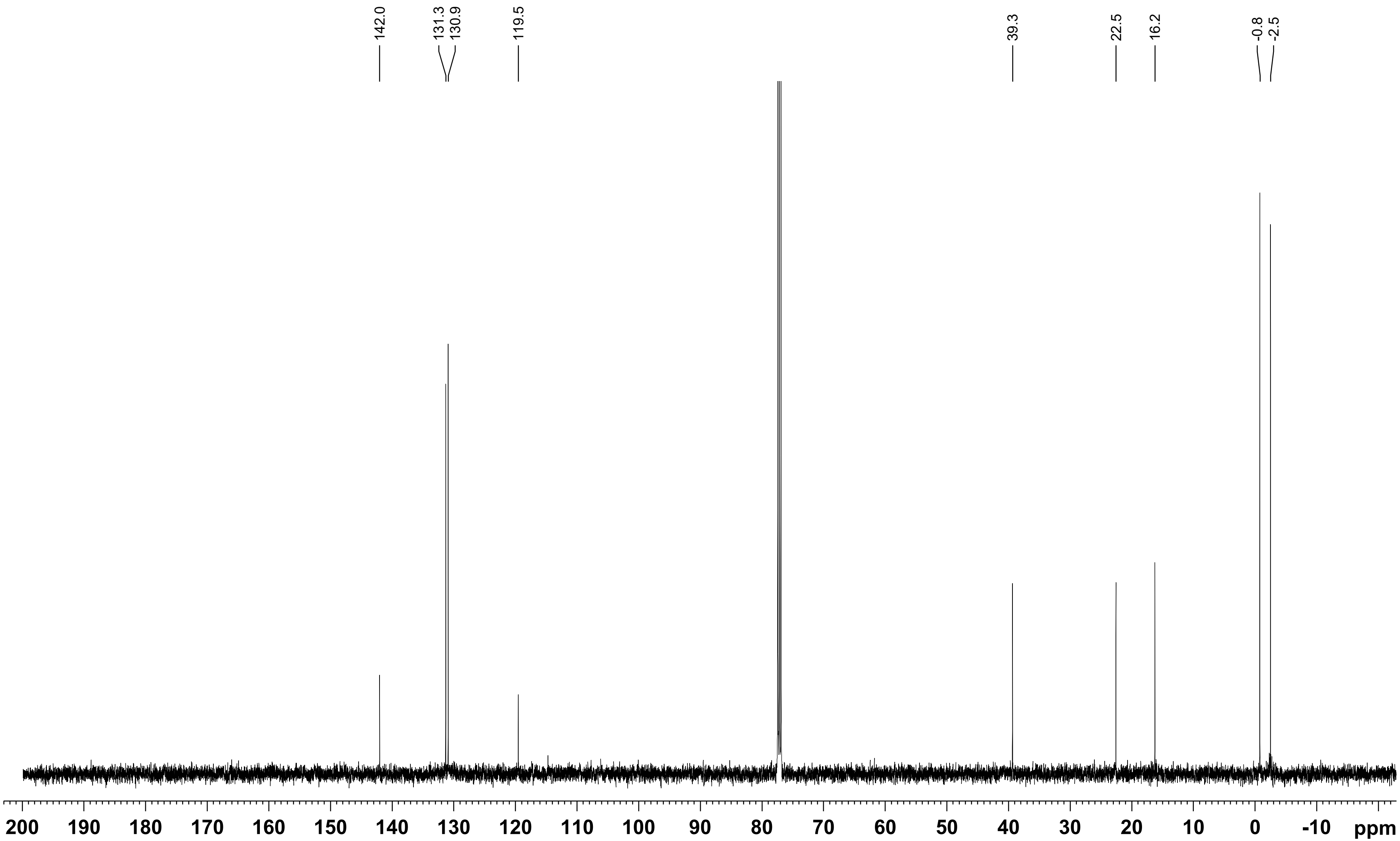
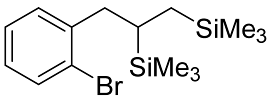


Figure S89. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **7f** from the catalytic reaction of 1-bromo-2-cyclopropylbenzene (**1f**) and $Me_3SiSiMe_3$ using $Me_3Si^+[CHB_{11}H_5Br_6]^-$



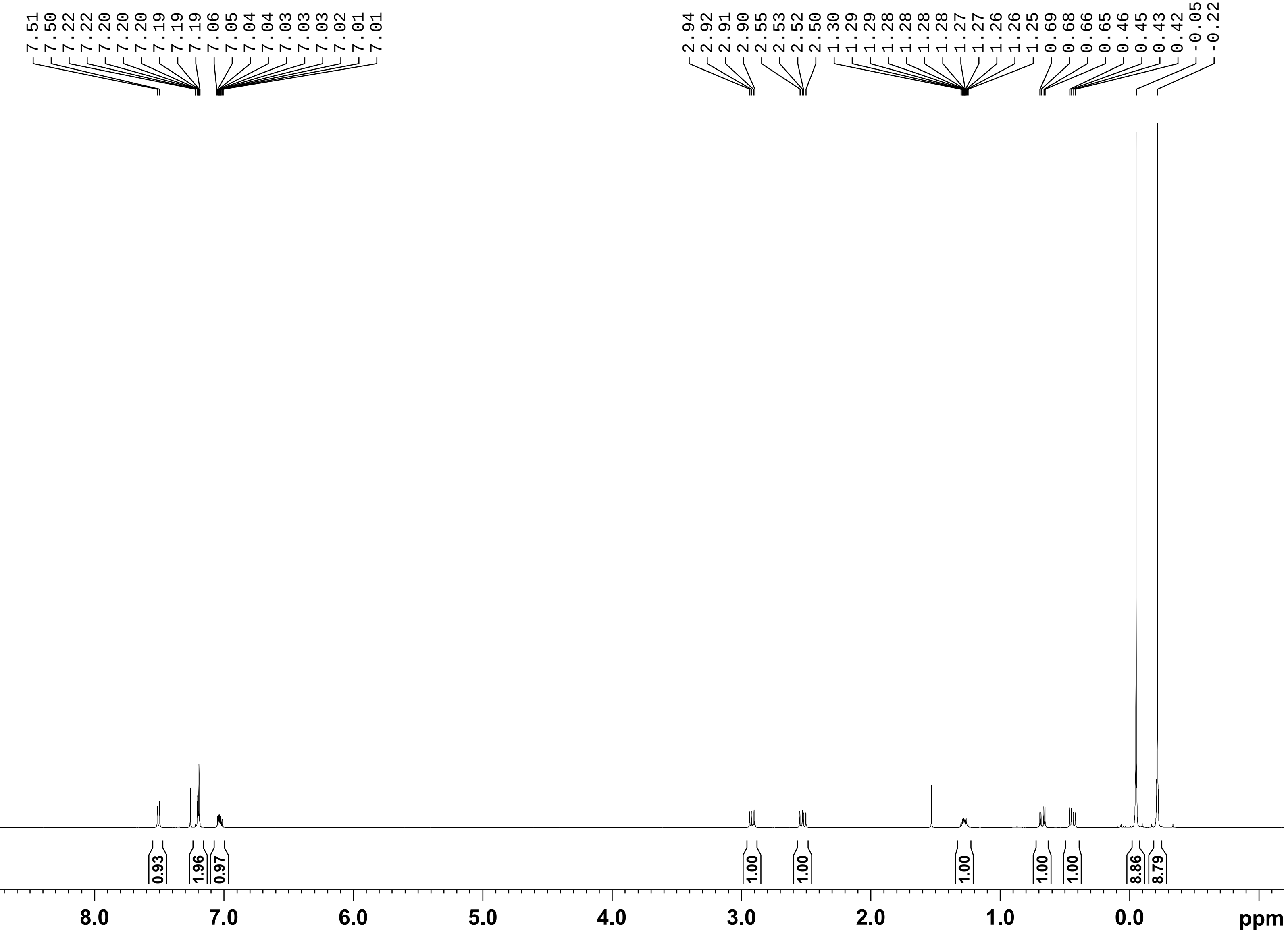


Figure S90. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **7f** from the catalytic reaction of 1-bromo-2-cyclopropylbenzene (**1f**) and $Me_3SiSiMe_3$ using $Me_3Si^+[CHB_{11}H_5Br_6]^-$.

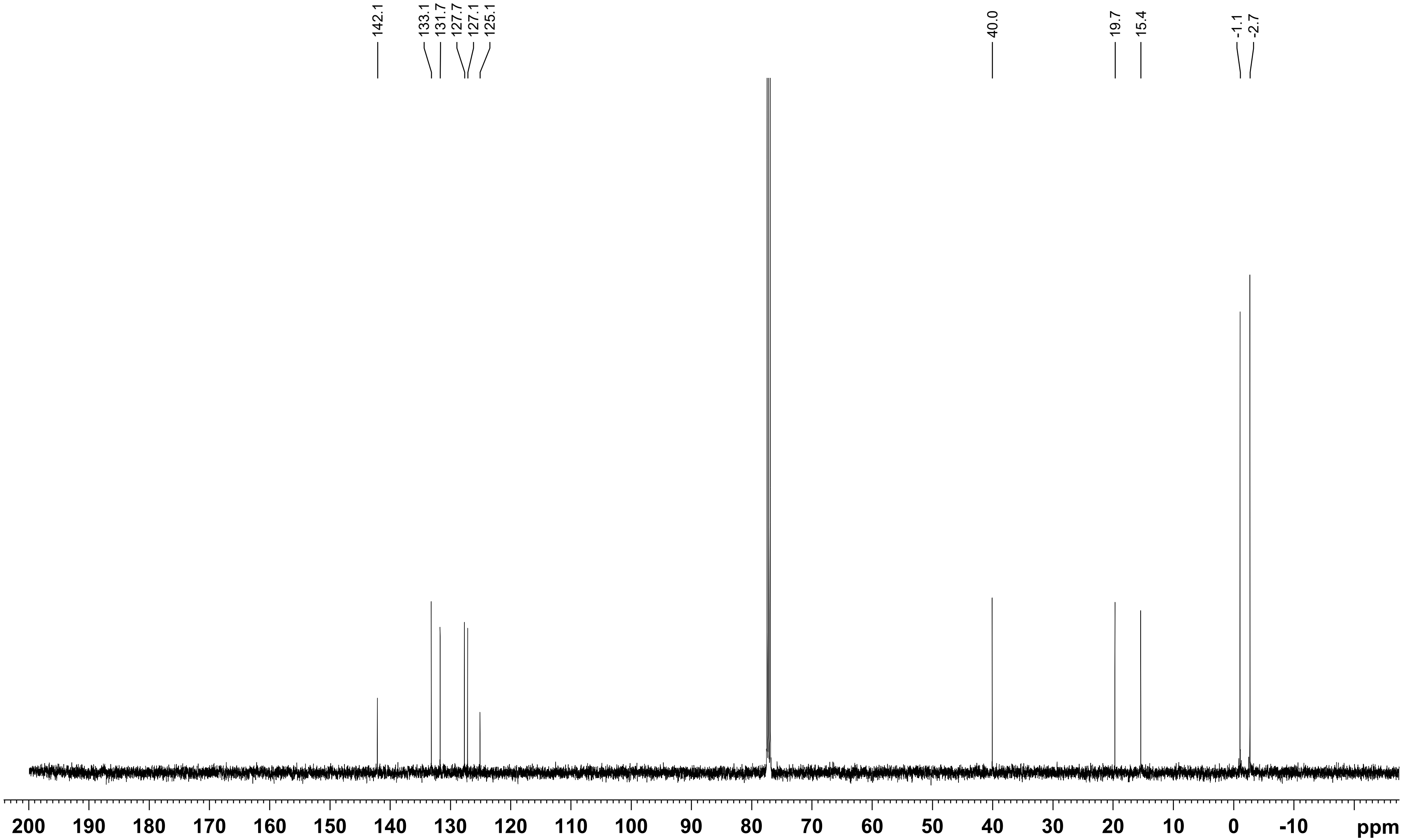


Figure S91. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **7g** from the catalytic reaction of 1-cyclopropyl-2-methylbenzene (**1g**) and $Me_3SiSiMe_3$ using $Me_3Si^+[CHB_{11}H_5Br_6]^-$.

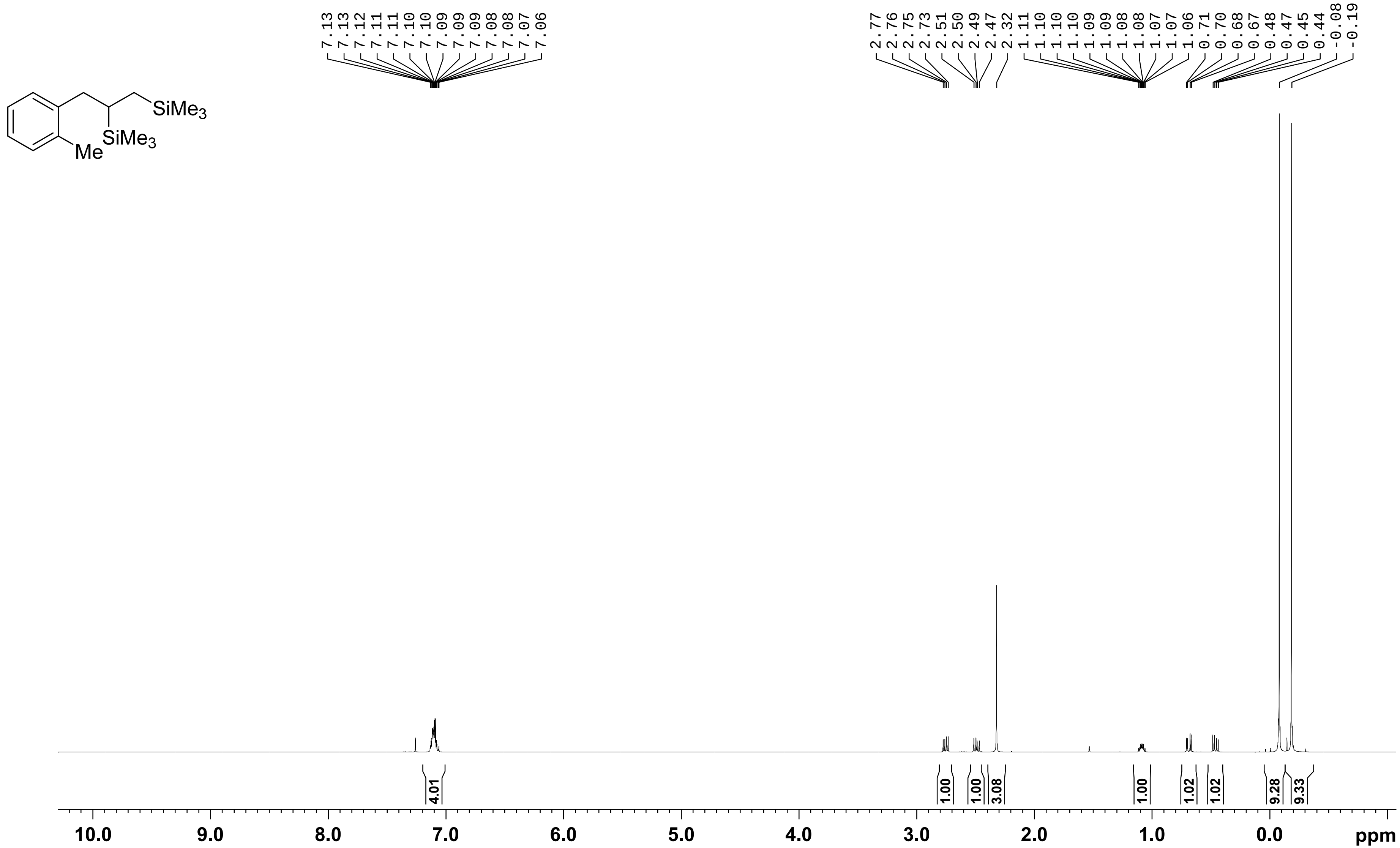


Figure S92. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **7g** from the catalytic reaction of 1-cyclopropyl-2-methylbenzene (**1g**) and $Me_3SiSiMe_3$ using $Me_3Si^+[CHB_{11}H_5Br_6]^-$.

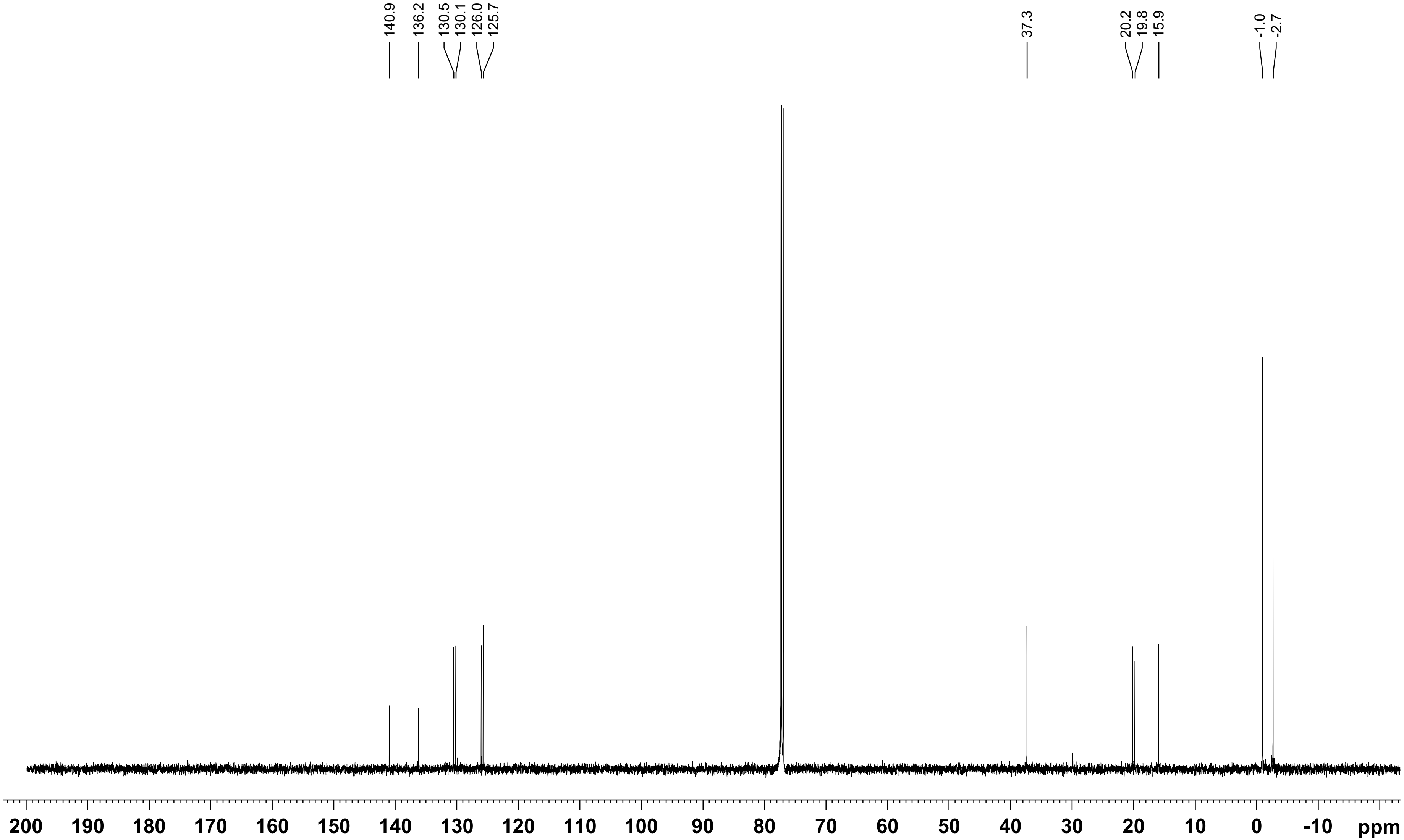
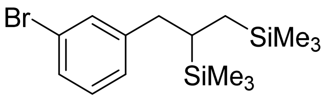


Figure S93. ¹H NMR (500 MHz, $CDCl_3$, 298 K) of **7h** from the catalytic reaction of 1-bromo-3-cyclopropylbenzene (**1h**) and $Me_3SiSiMe_3$ using $Me_3Si^+[CHB_{11}H_5Br_6]^-$.



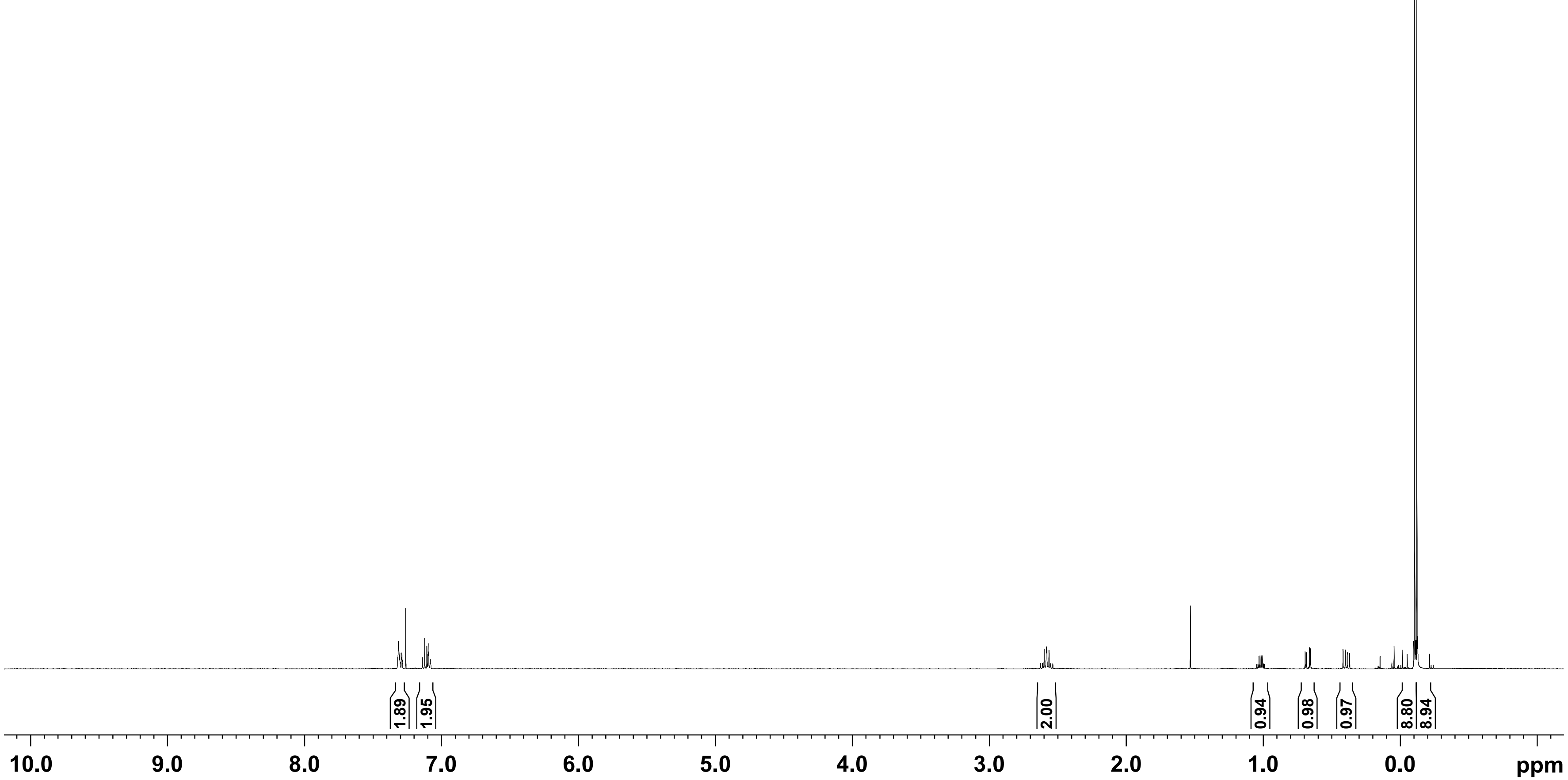


Figure S94. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **7h** from the catalytic reaction of 1-bromo-3-cyclopropylbenzene (**1h**) and $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$.

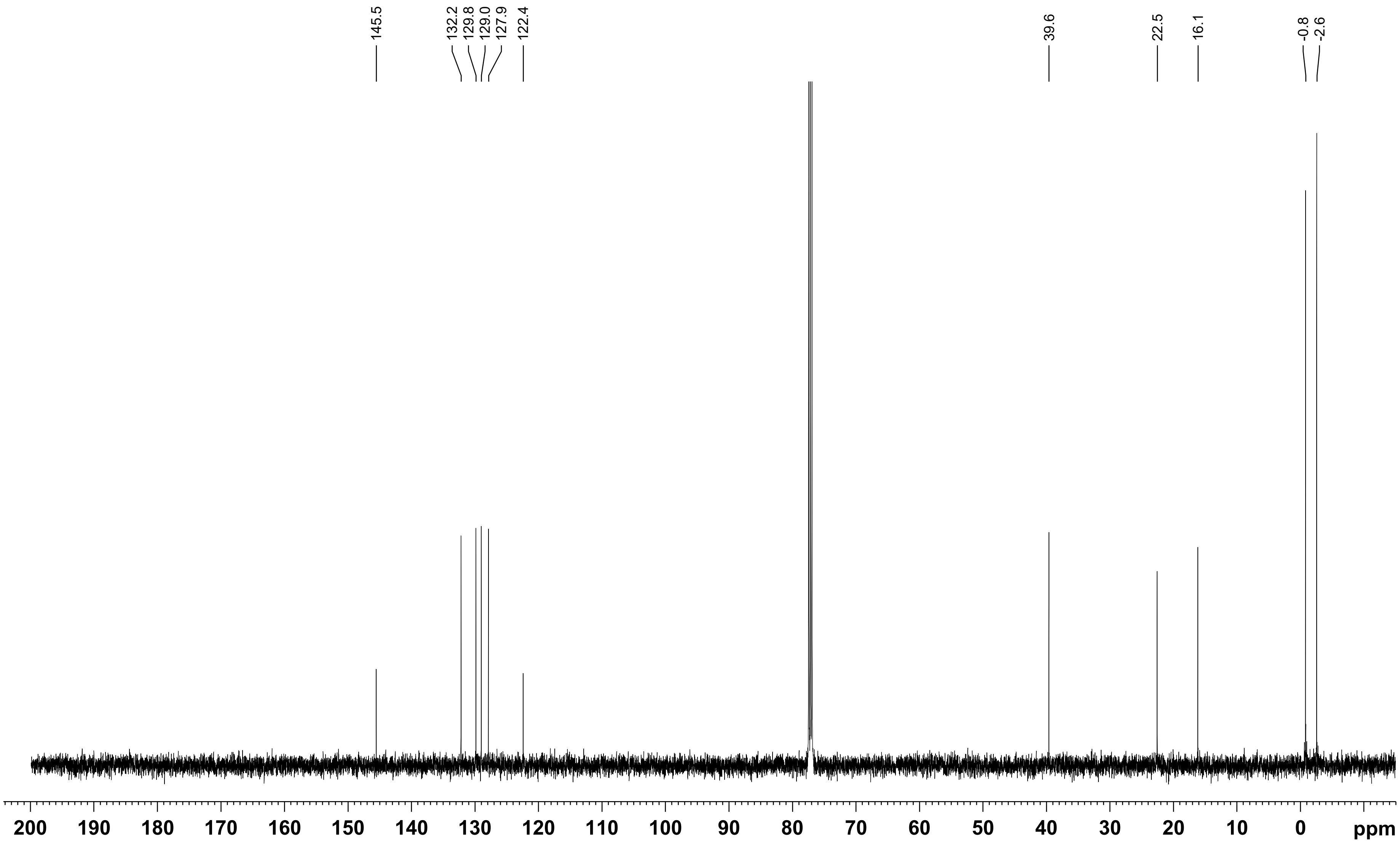


Figure S95. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **7h** from the catalytic reaction of 1-bromo-3-cyclopropylbenzene (**1h**) and $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$.

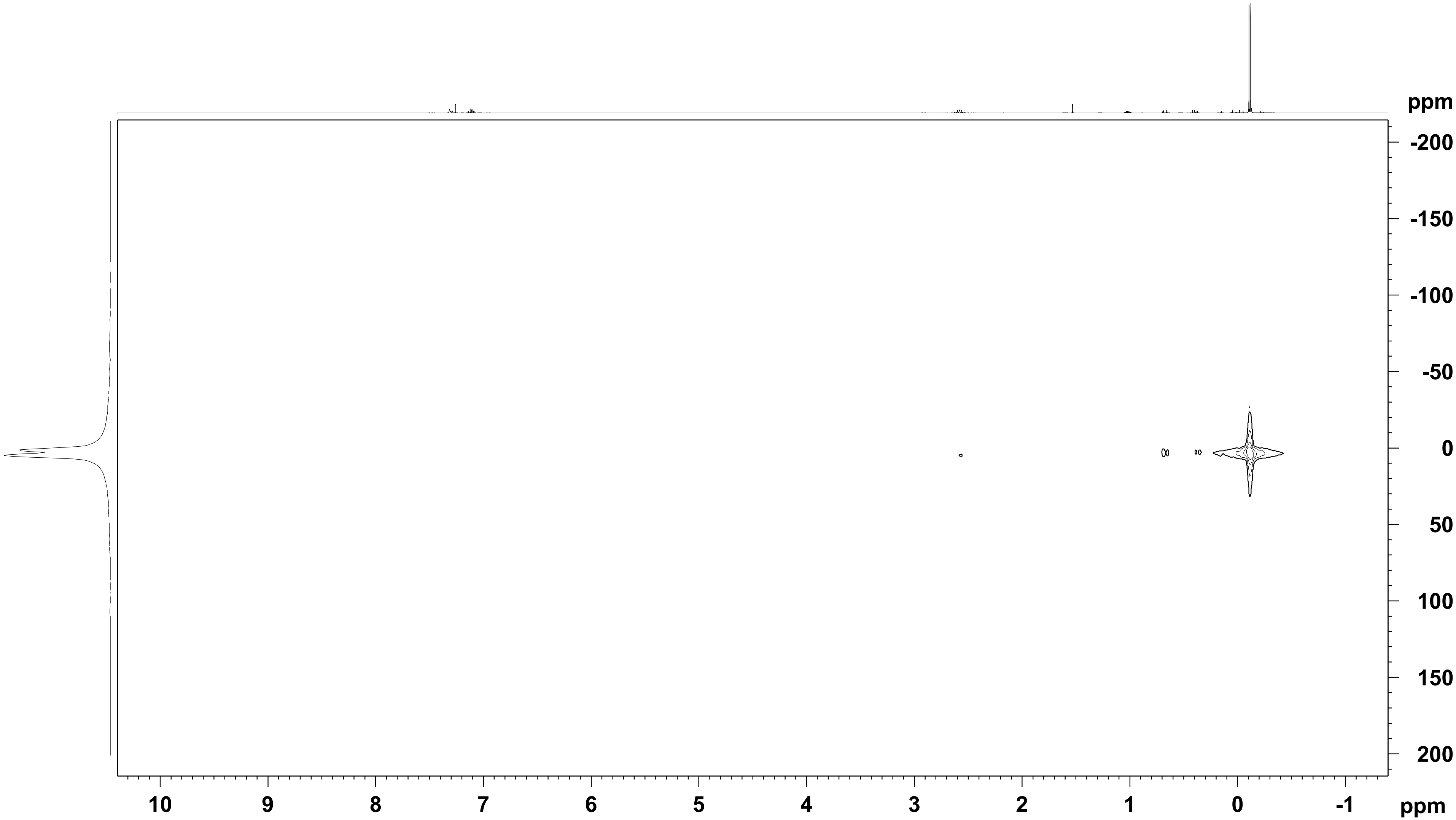
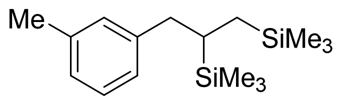


Figure S96. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **7i** from the catalytic reaction of 1-cyclopropyl-3-methylbenzene (**1i**) and $Me_3SiSiMe_3$ using $Me_3Si^{+}[CHB_{11}H_5Br_6]^{-}$



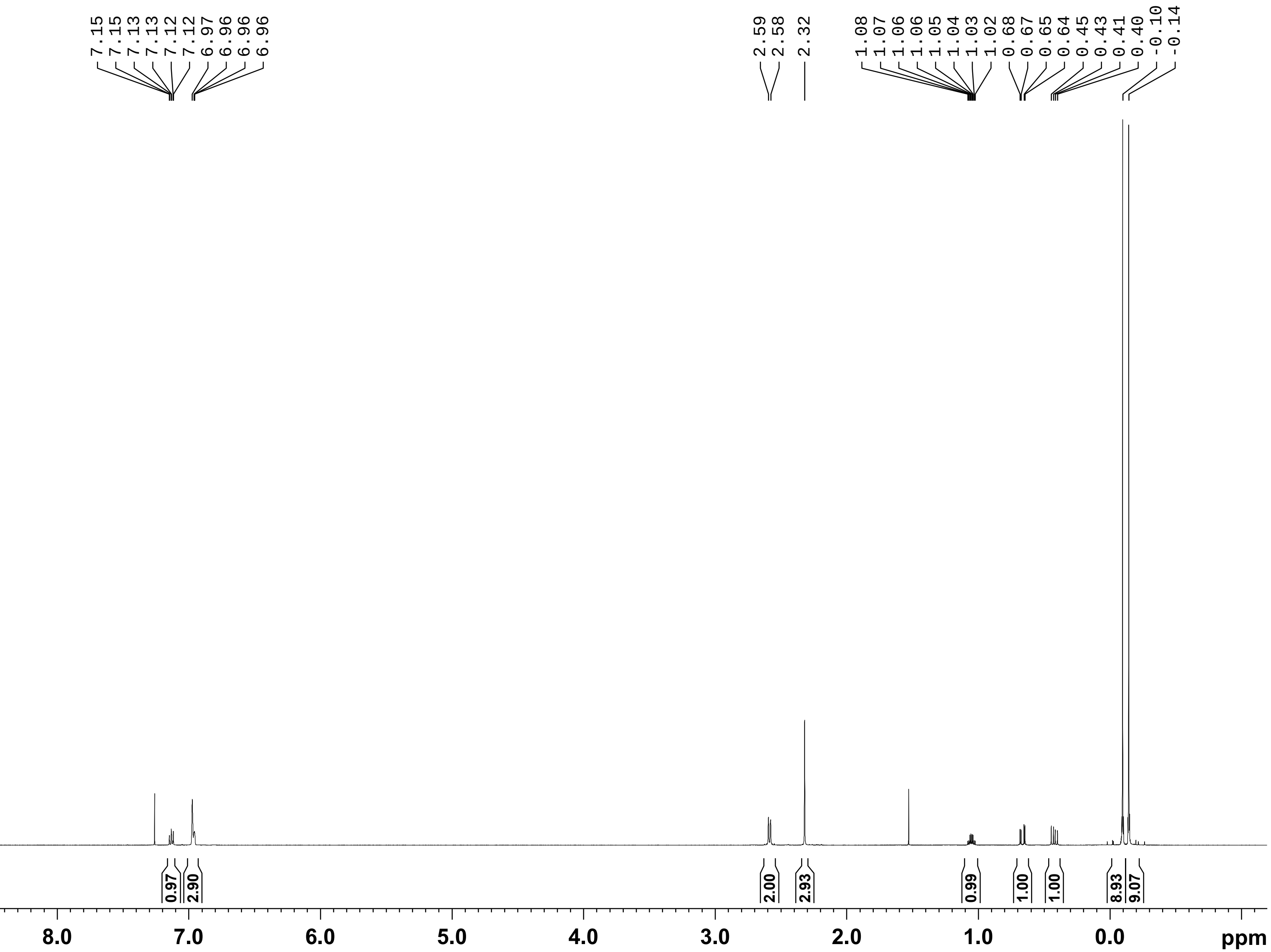


Figure S97. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **7i** from the catalytic reaction of 1-cyclopropyl-3-methylbenzene (**1i**) and $Me_3SiSiMe_3$ using $Me_3Si^+[CHB_{11}H_5Br_6]^-$.

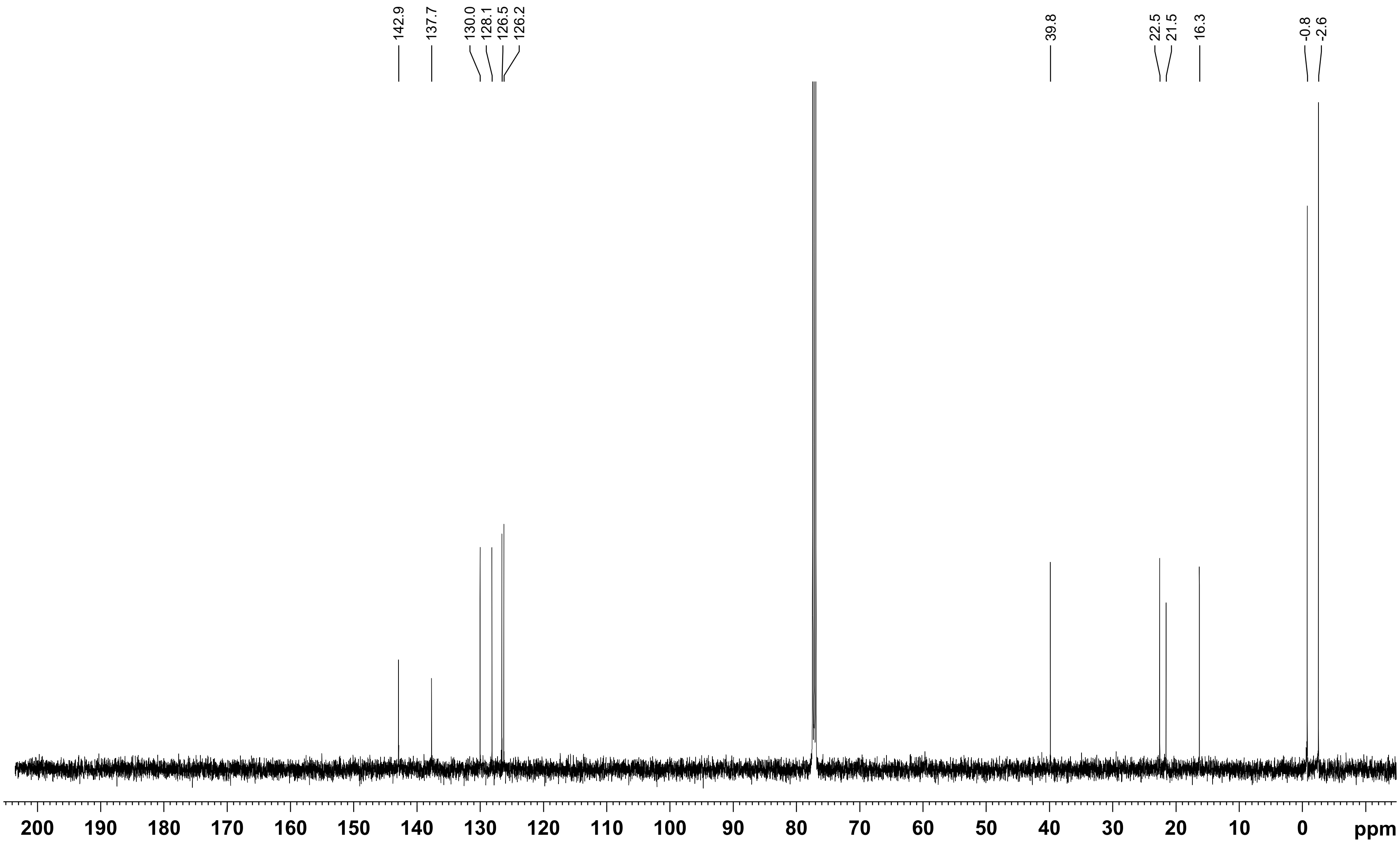


Figure S98. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz) of **7i** from the catalytic reaction of 1-cyclopropyl-3-methylbenzene (**1i**) and $Me_3SiSiMe_3$ using $Me_3Si^+[CHB_{11}H_5Br_6]^-$.

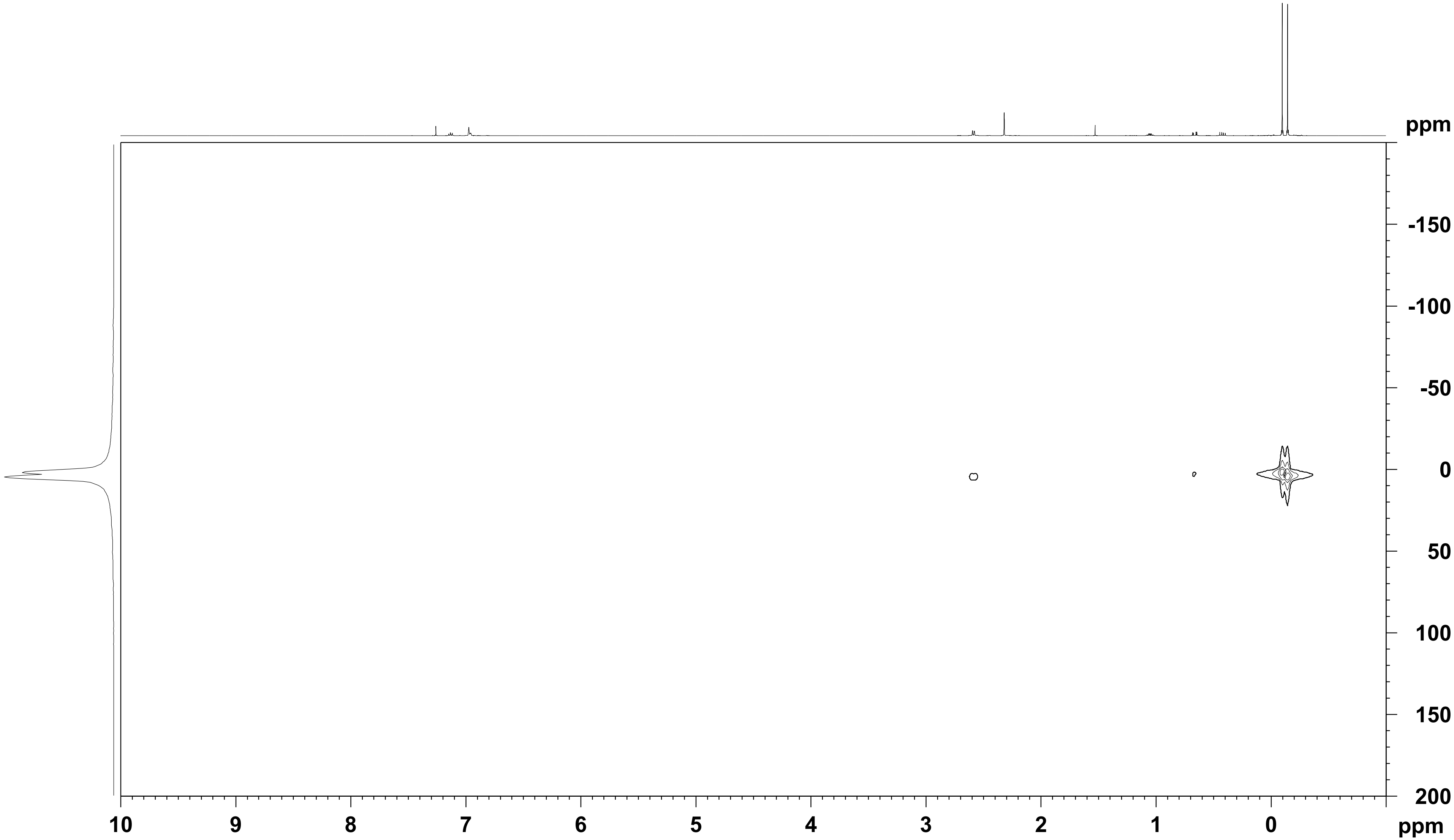


Figure S99. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **3aa**-d_1 from the catalytic reaction of cyclopropylbenzene (**1a**) and Et_3SiD using $Ph_3C^+[B(C_6F_5)_4]^-$.

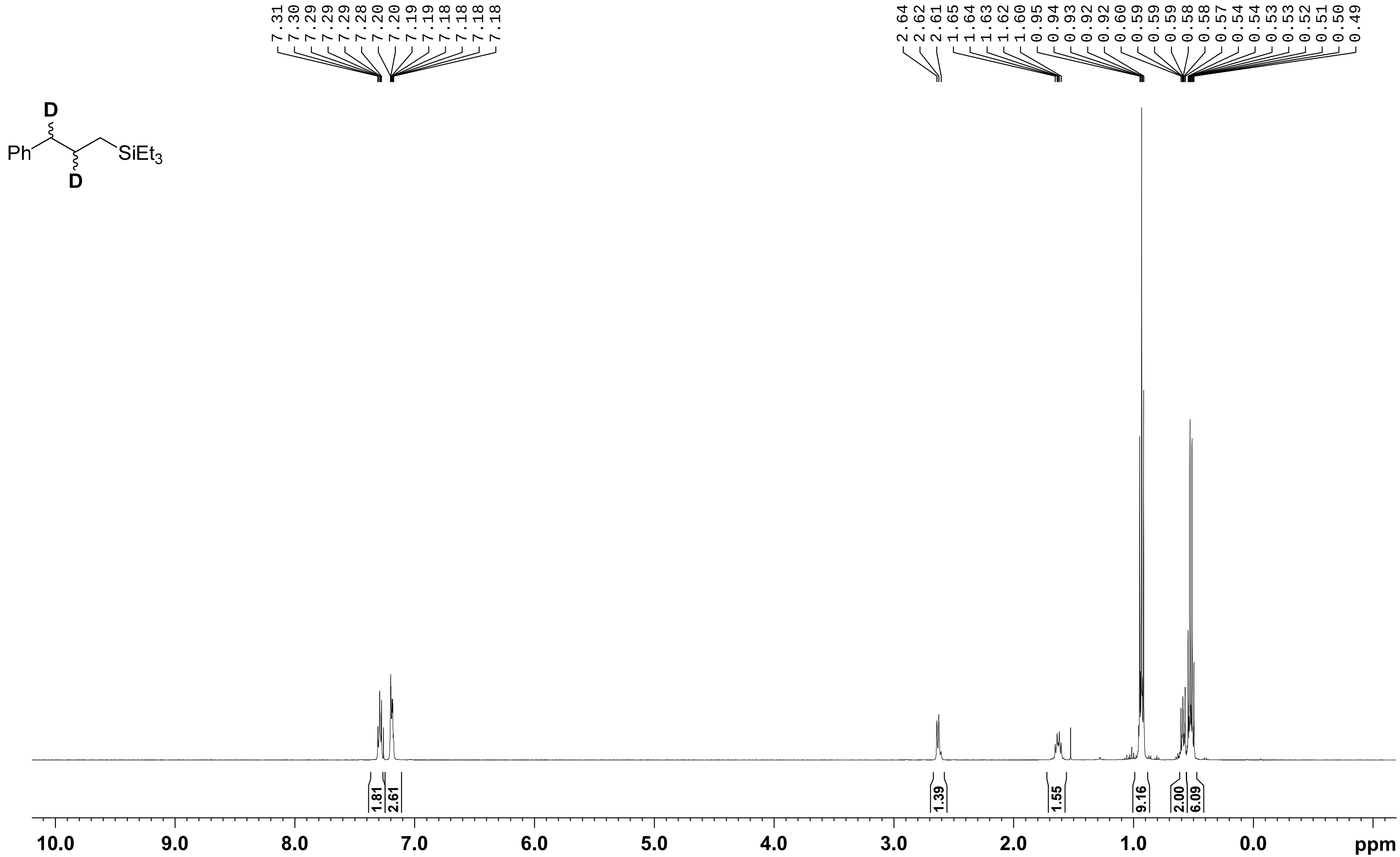


Figure S100. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **3aa**-d_1 from the catalytic reaction of cyclopropylbenzene (**1a**) and Et_3SiD using $Ph_3C^+[B(C_6F_5)_4]^-$.

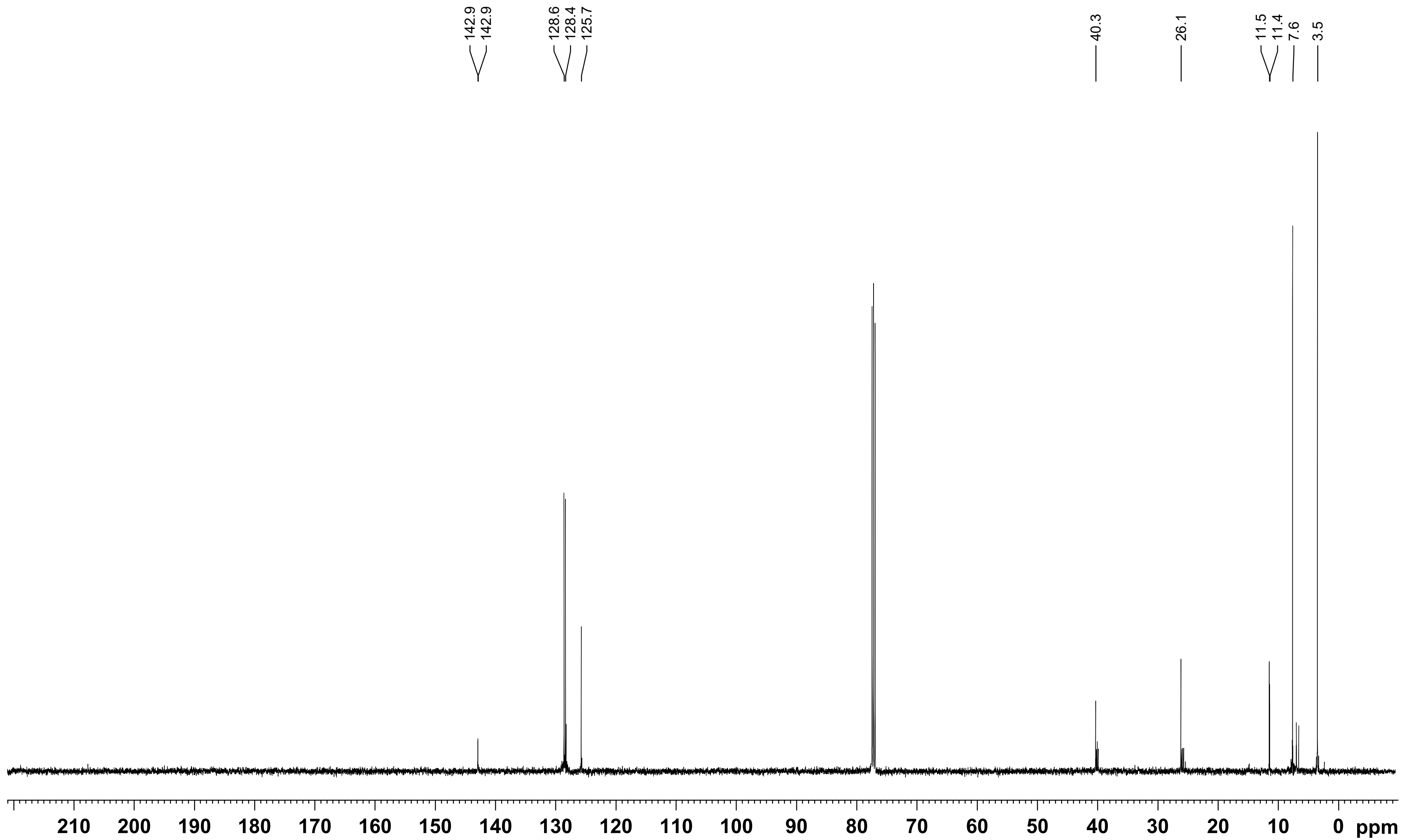


Figure S101. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **3aa**-d_1 from the catalytic reaction of cyclopropylbenzene (**1a**) and Et_3SiD using $Ph_3C^{+}[B(C_6F_5)_4]^{-}$.

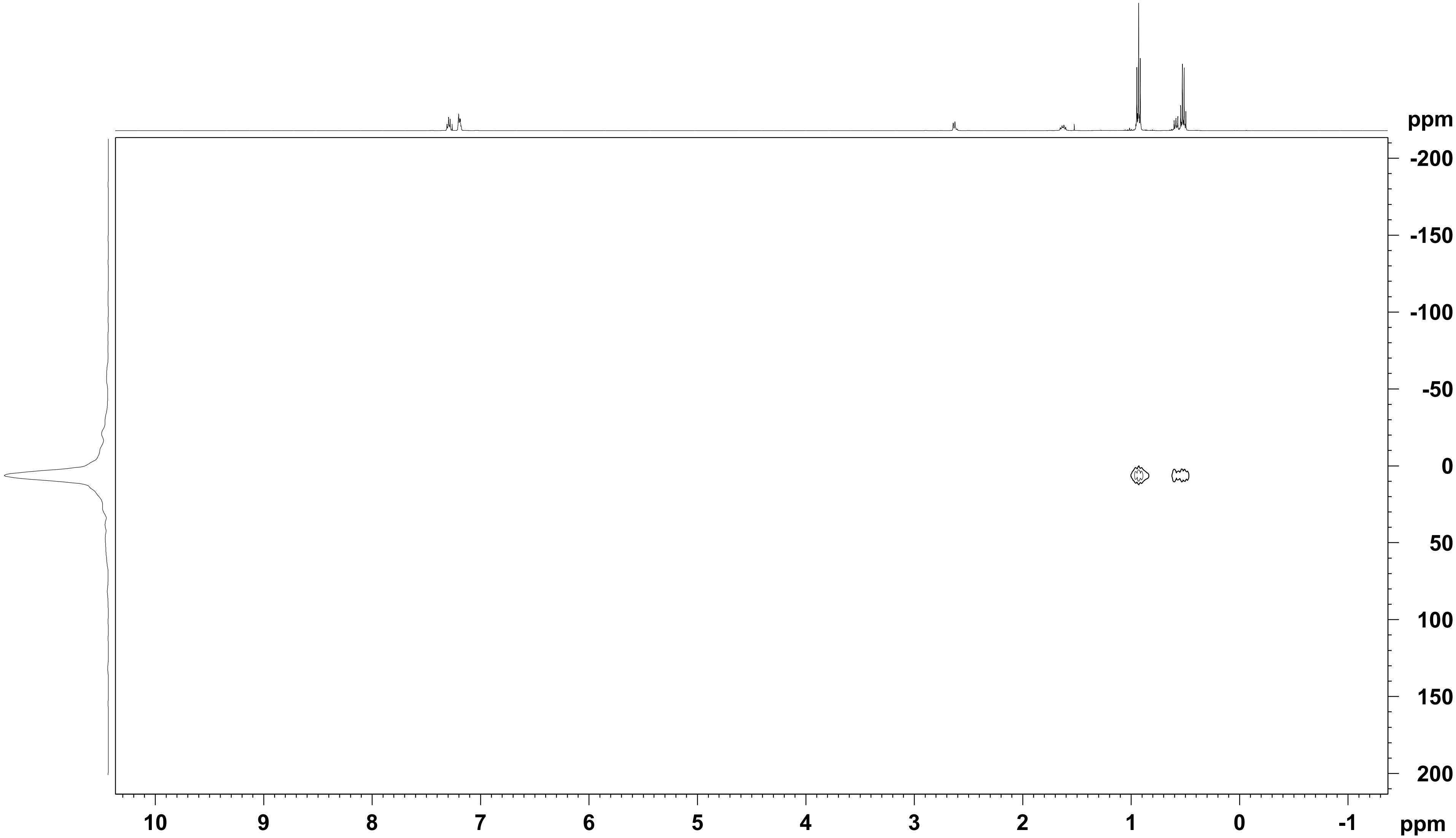
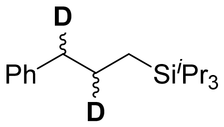


Figure S102. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **3ab**-d_1 from the catalytic reaction of cyclopropylbenzene (**1a**) and ^{i}Pr$_3$SiD using $Ph_3C^+[B(C_6F_5)_4]^-$.



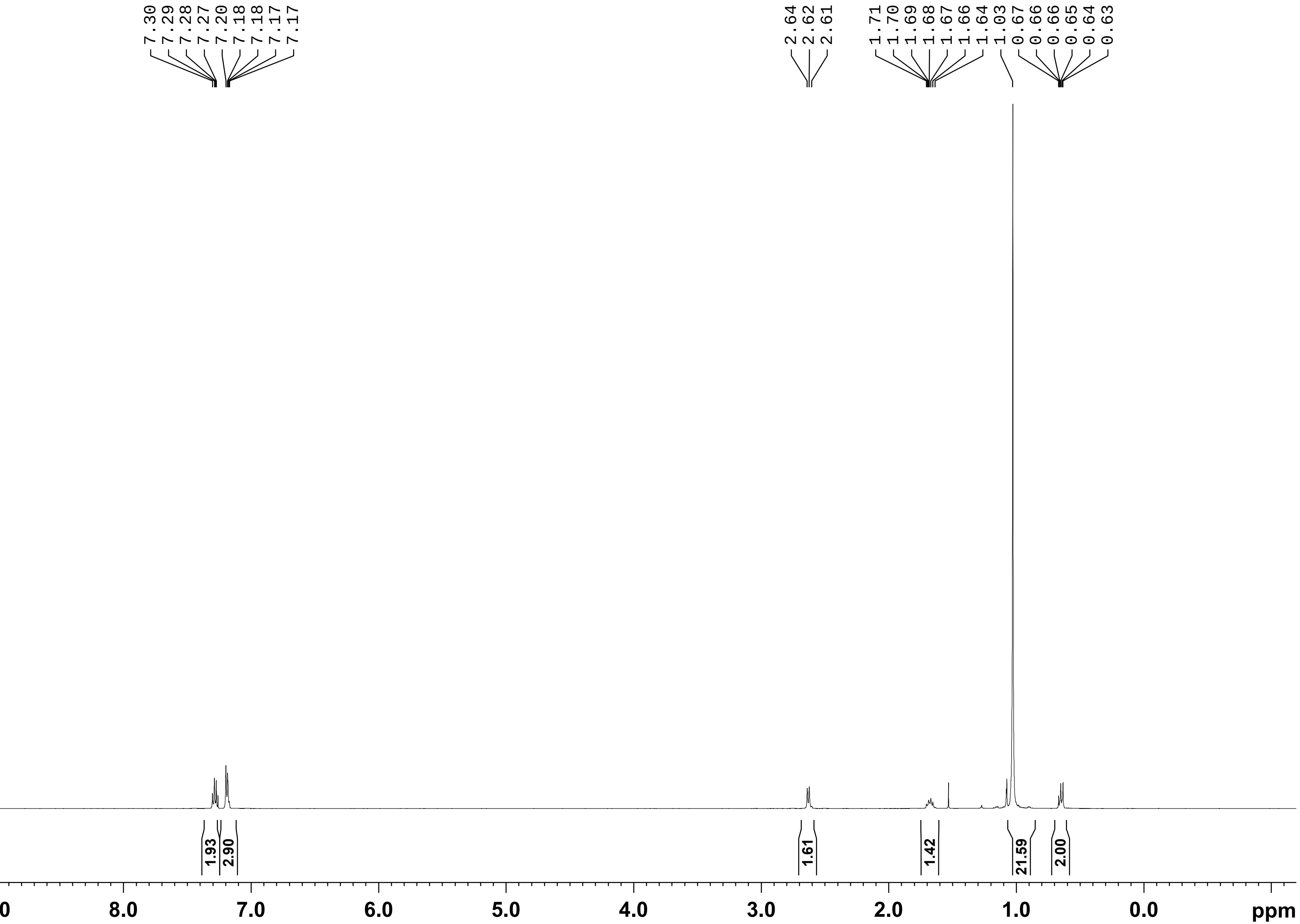


Figure S103. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **3ab**-d_1 from the catalytic reaction of cyclopropylbenzene (**1a**) and $^{i}Pr_3SiD$ using $Ph_3C^{+}[B(C_6F_5)_4]^{-}$.

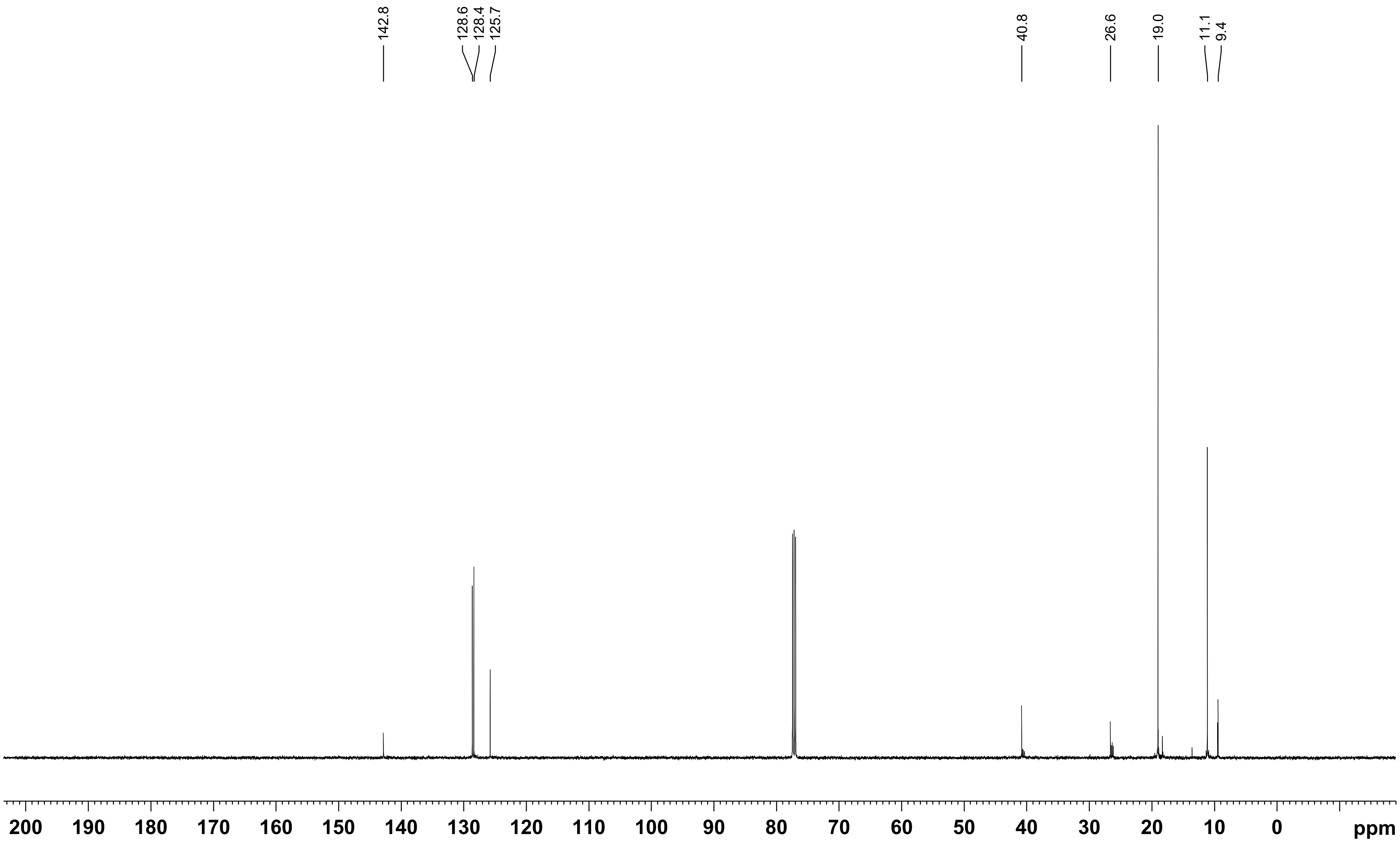


Figure S104. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **3ab**-d_1 from the catalytic reaction of cyclopropylbenzene (**1a**) and $^{i}Pr_3SiD$ using $Ph_3C^{+}[B(C_6F_5)_4]^{-}$.

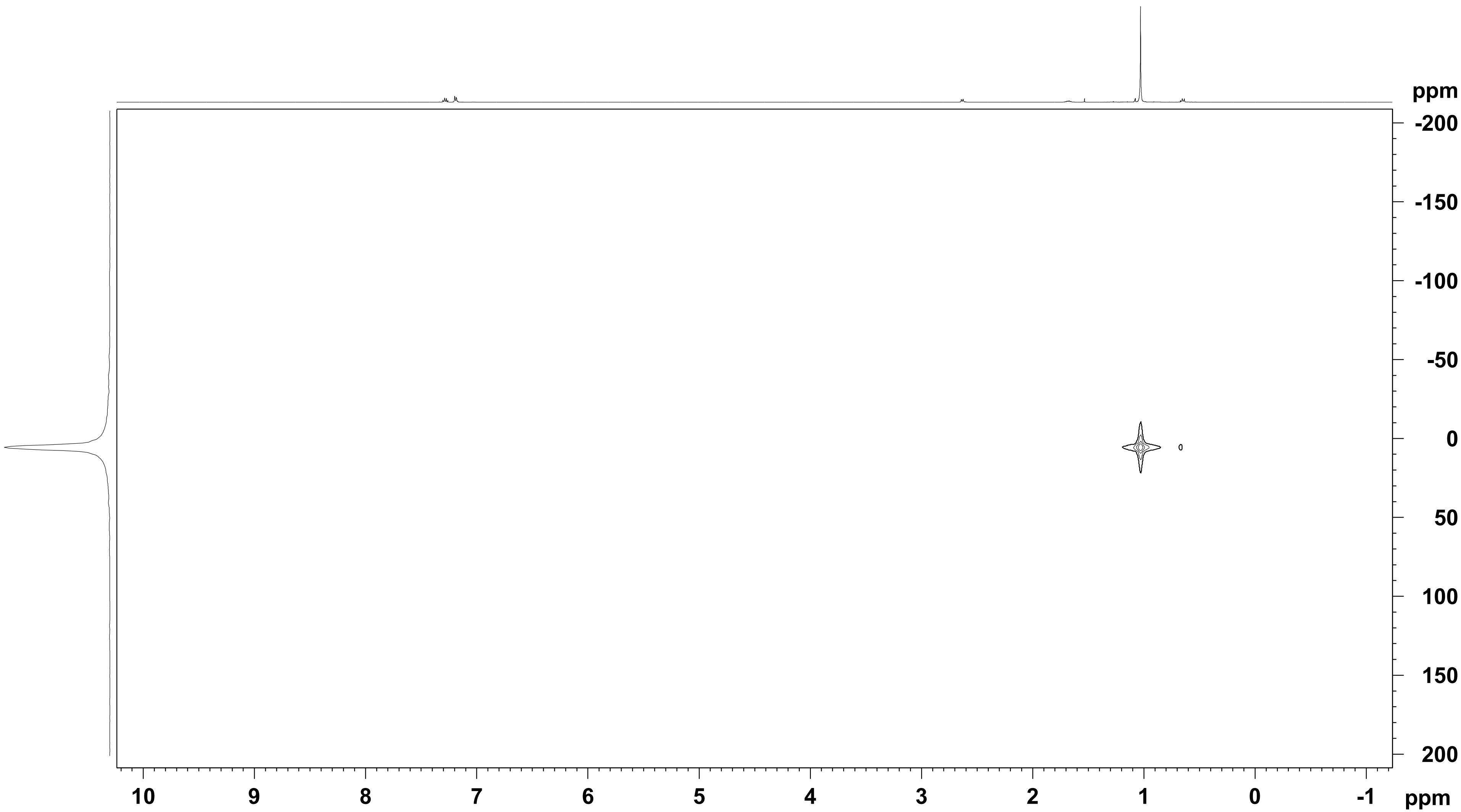


Figure S105. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **3pb'**-d_1 from the catalytic reaction of 1-bromo-4-(2-phenylcyclopropyl)benzene (**1p**) and ^{i}Pr$_3$SiD using $Ph_3C^+[B(C_6F_5)_4]^-$.

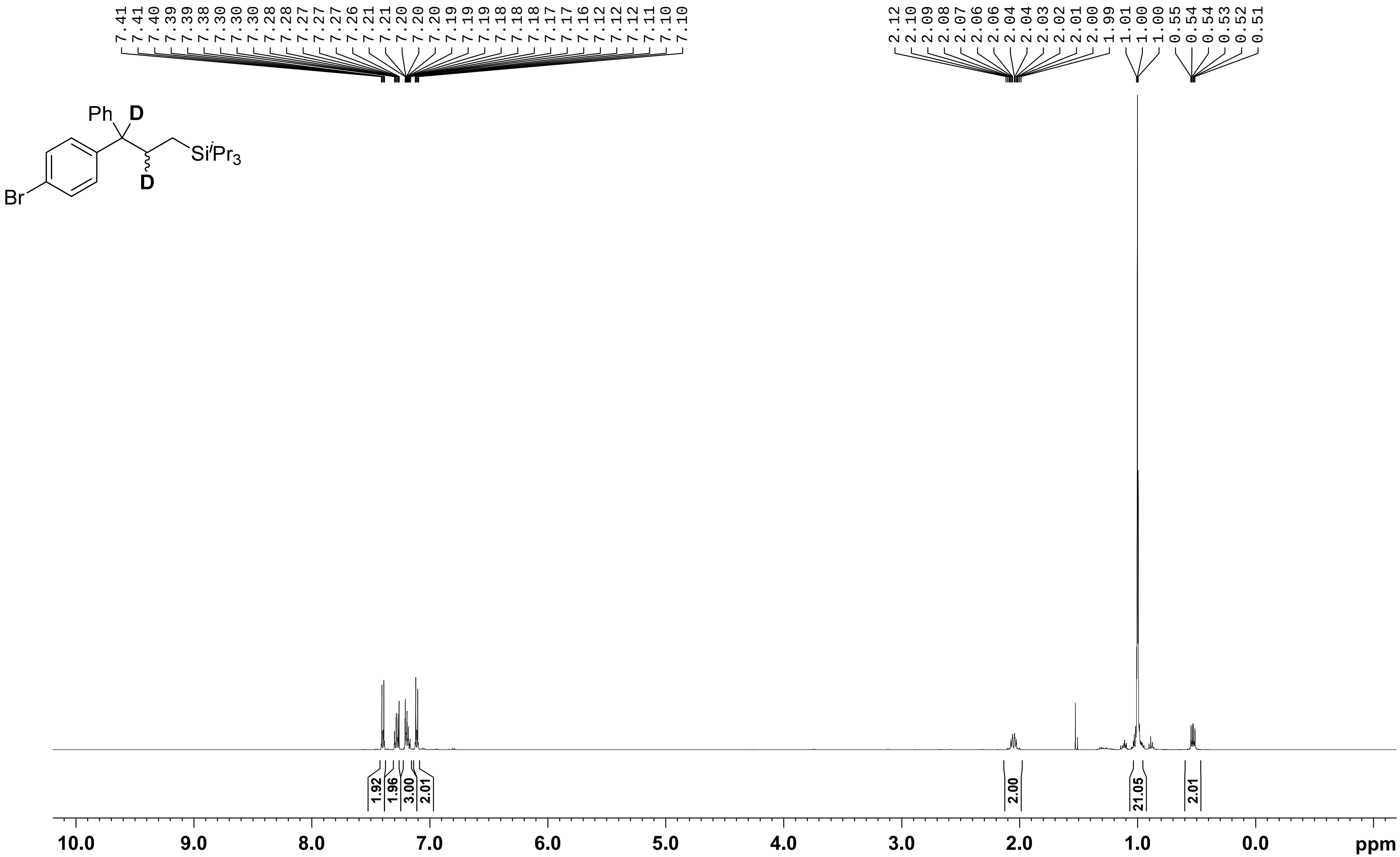


Figure S106. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) of **3pb'**-d_1 from the catalytic reaction of 1-bromo-4-(2-phenylcyclopropyl)benzene (**1p**) and $^{i}Pr_3SiD$ using $Ph_3C^+[B(C_6F_5)_4]^-$.

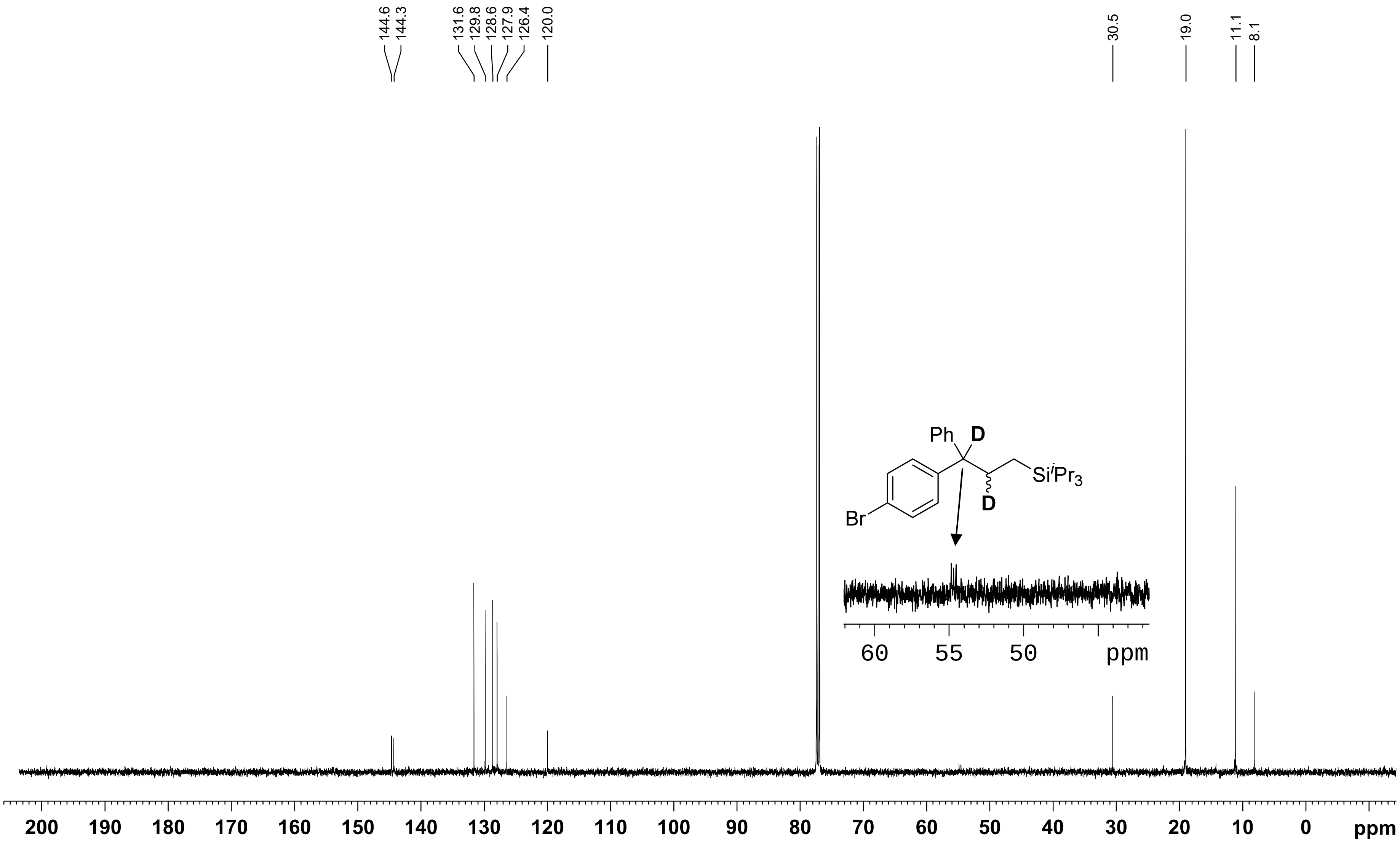


Figure S107. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **3pb'**-d_1 from the catalytic reaction of 1-bromo-4-(2-phenylcyclopropyl)benzene (**1p**) and $^{i}Pr_3SiD$ using $Ph_3C^{+}[B(C_6F_5)_4]^{-}$.

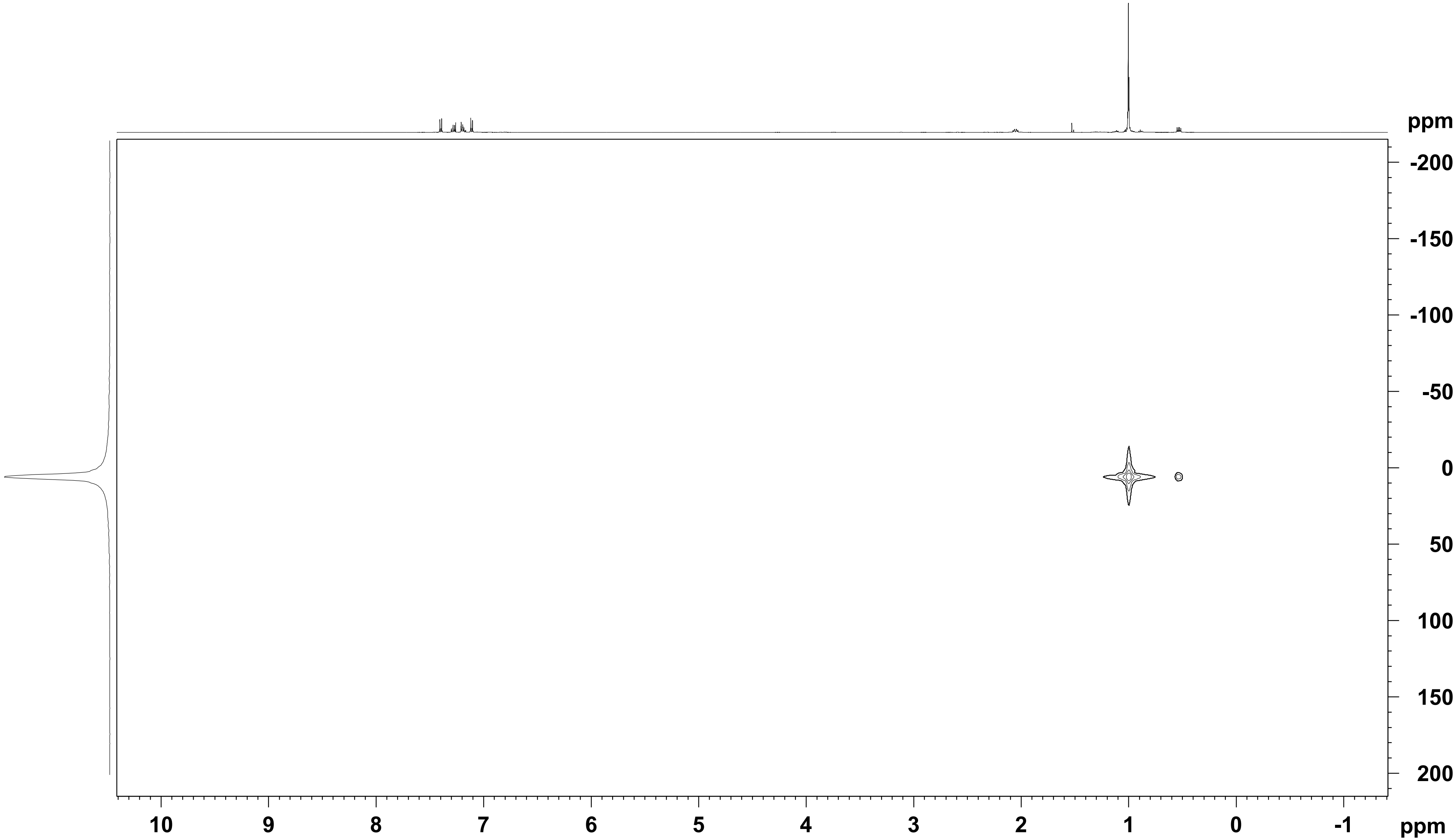


Figure S108. ^{1}H NMR (500 MHz, C_6D_5Cl, 298 K) of **1a**$^+$[$CHB_{11}H_5Br_6$]$^-$ from the reaction of $Me_2(Me_3Si)Si^+$[$CHB_{11}H_5Br_6$]$^-$ and cyclopropylbenzene (**1a**).

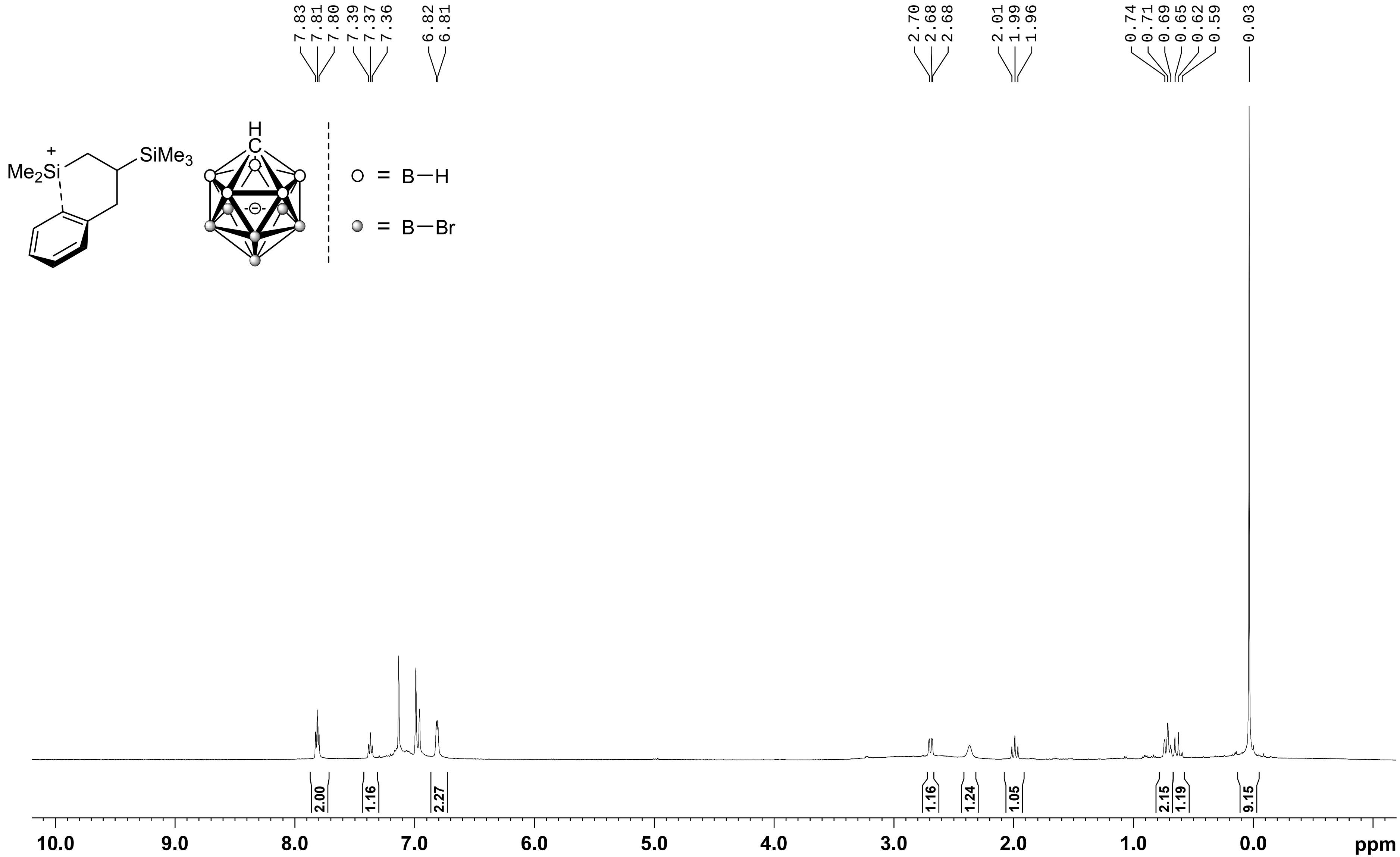


Figure S109. ^{11}B NMR (161 MHz, C_6D_5Cl, 298 K) of **1a**$^+[CHB_{11}H_5Br_6]^-$ from the reaction of $Me_2(Me_3Si)Si^+[CHB_{11}H_5Br_6]^-$ and cyclopropylbenzene (**1a**).

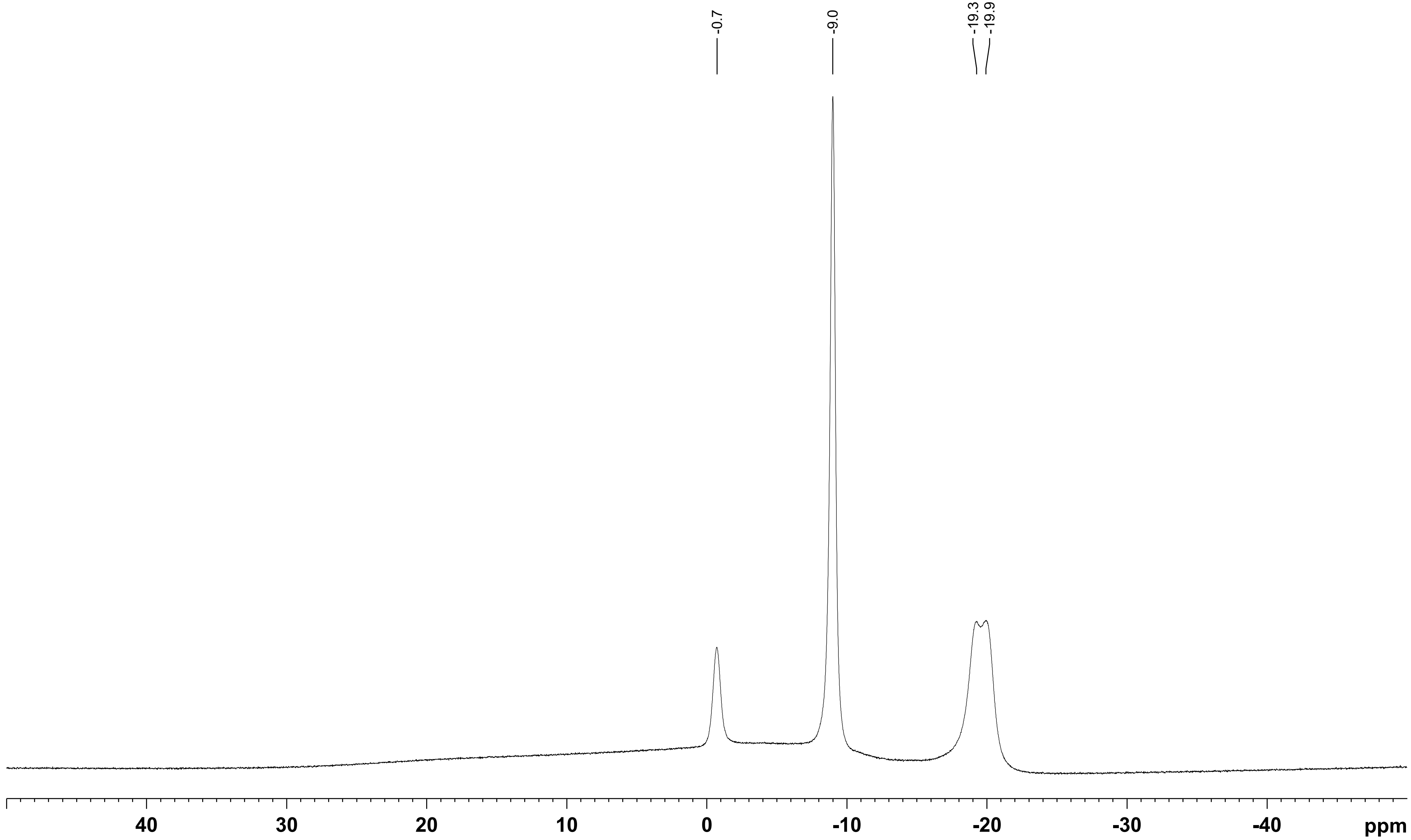


Figure S110. $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_5Cl, 298 K) of **1a**$^+[CHB_{11}H_5Br_6]^-$ from the reaction of $Me_2(Me_3Si)Si^+[CHB_{11}H_5Br_6]^-$ and cyclopropylbenzene (**1a**).

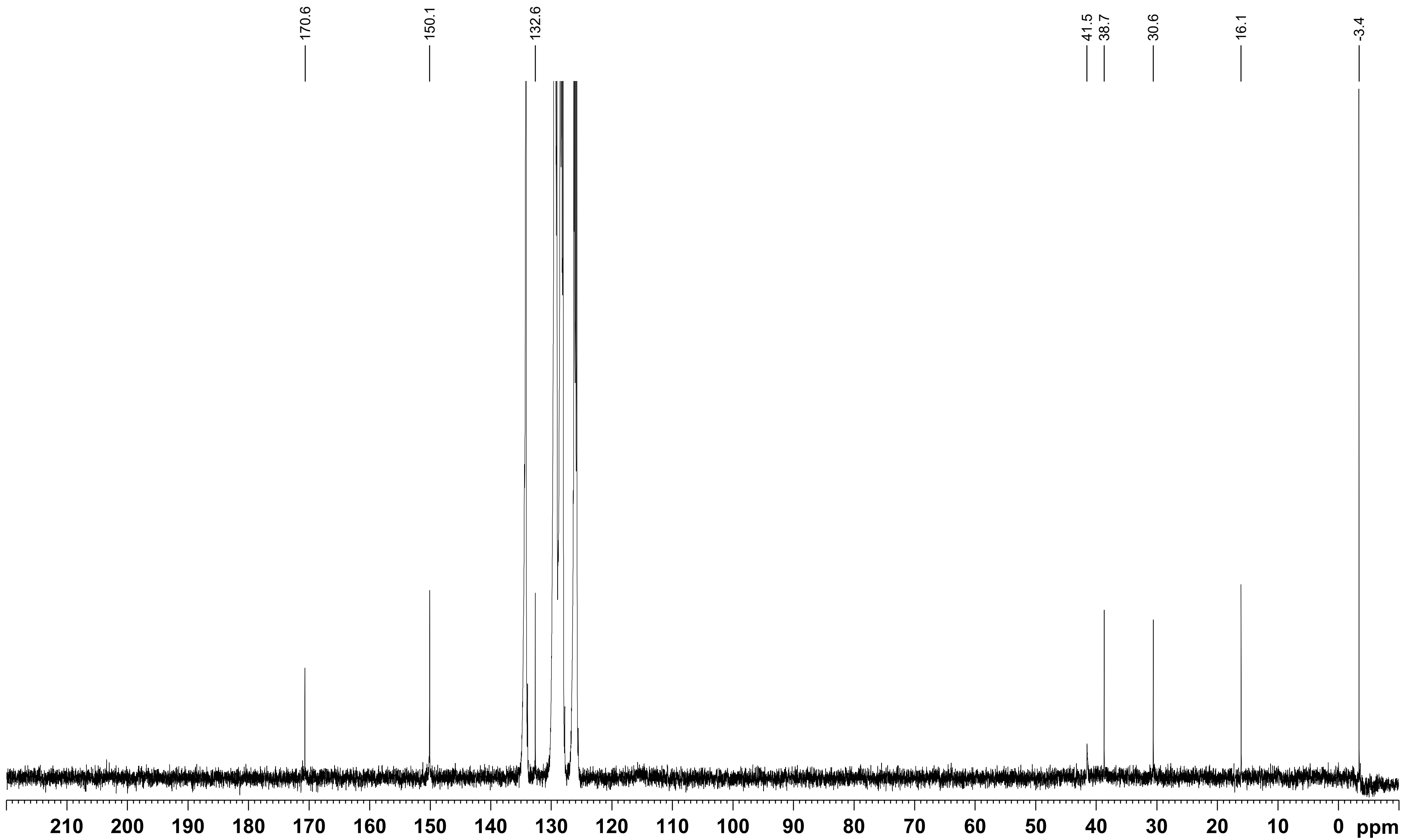


Figure S111. [1]H/[29]Si HMQC NMR (500/99 MHz, C_6D_5Cl, 298 K, optimized for *J* = 7 Hz) of **1a**$^+$[$CHB_{11}H_5Br_6$]$^-$ from the reaction of $Me_2(Me_3Si)Si^+$[$CHB_{11}H_5Br_6$]$^-$ and cyclopropylbenzene (**1a**).

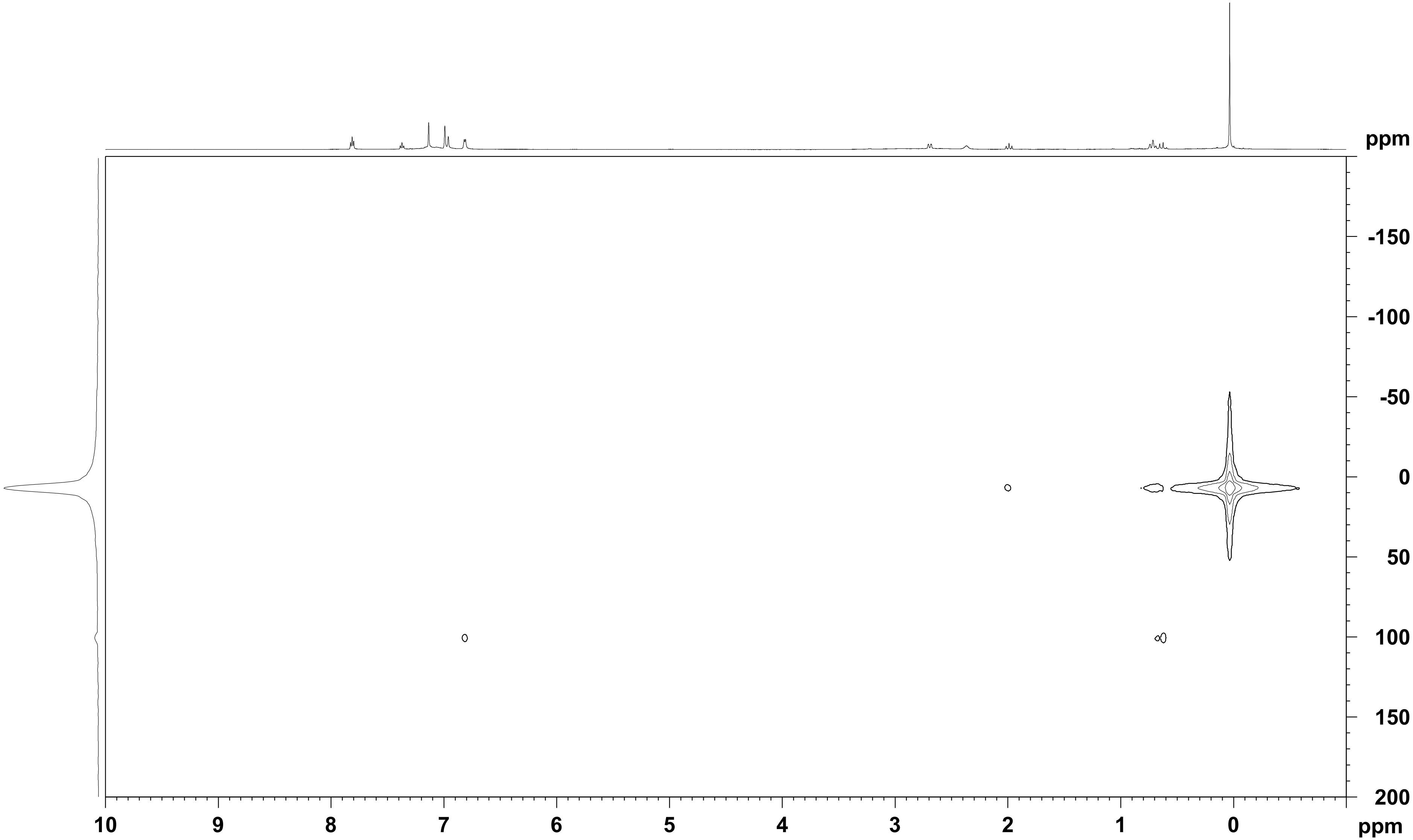


Figure S112. ^{1}H NMR (500 MHz, C_6D_5Cl, 298 K) of **crude mixture** from the reaction of **1a**$^{+}$[$CHB_{11}H_5Br_6$]$^{-}$ with cyclopropylbenzene (**1a**) and hexamethyldisilane. (# = allylbenzene, + = **1a**$^{+}$[$CHB_{11}H_5Br_6$]$^{-}$)

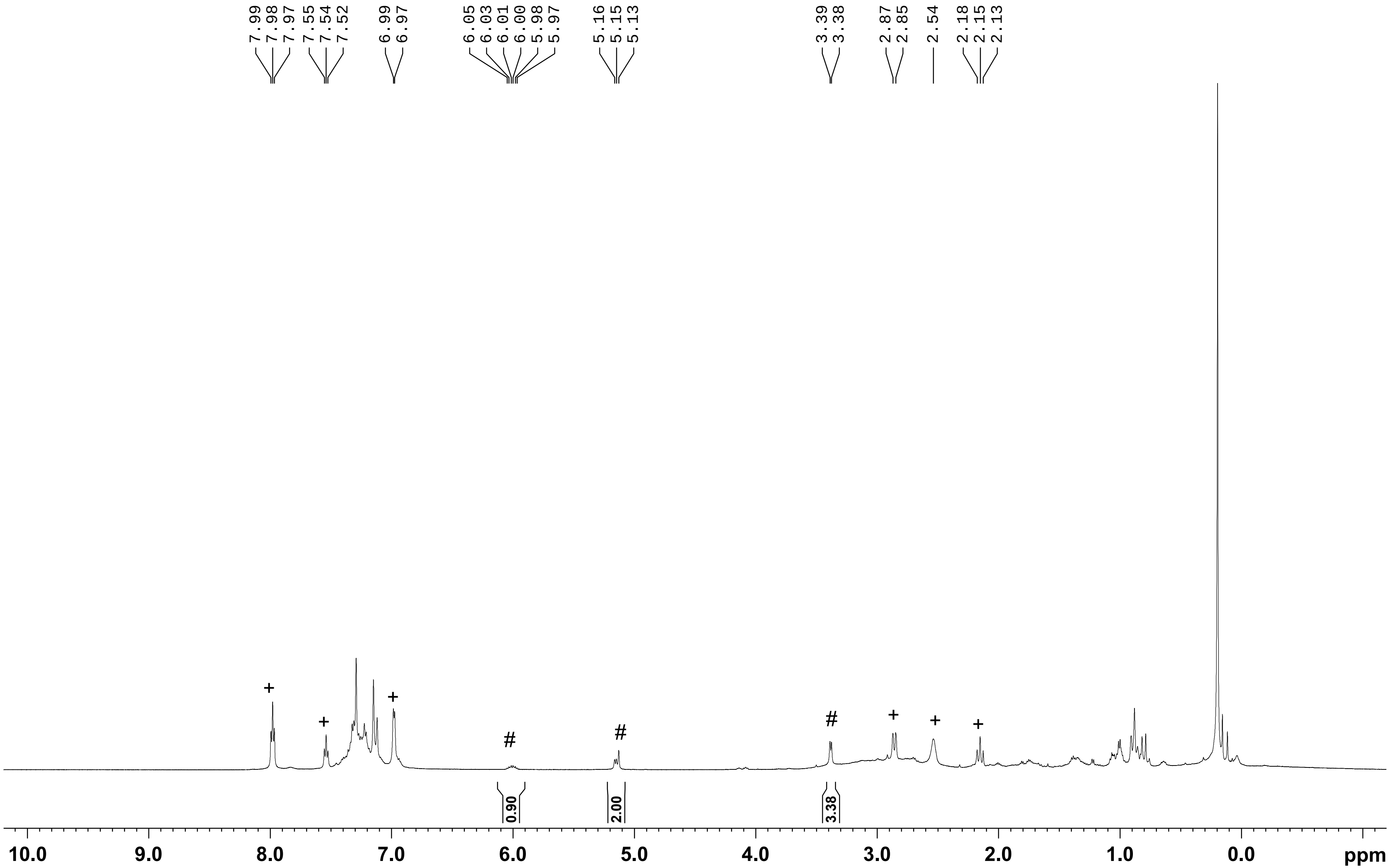
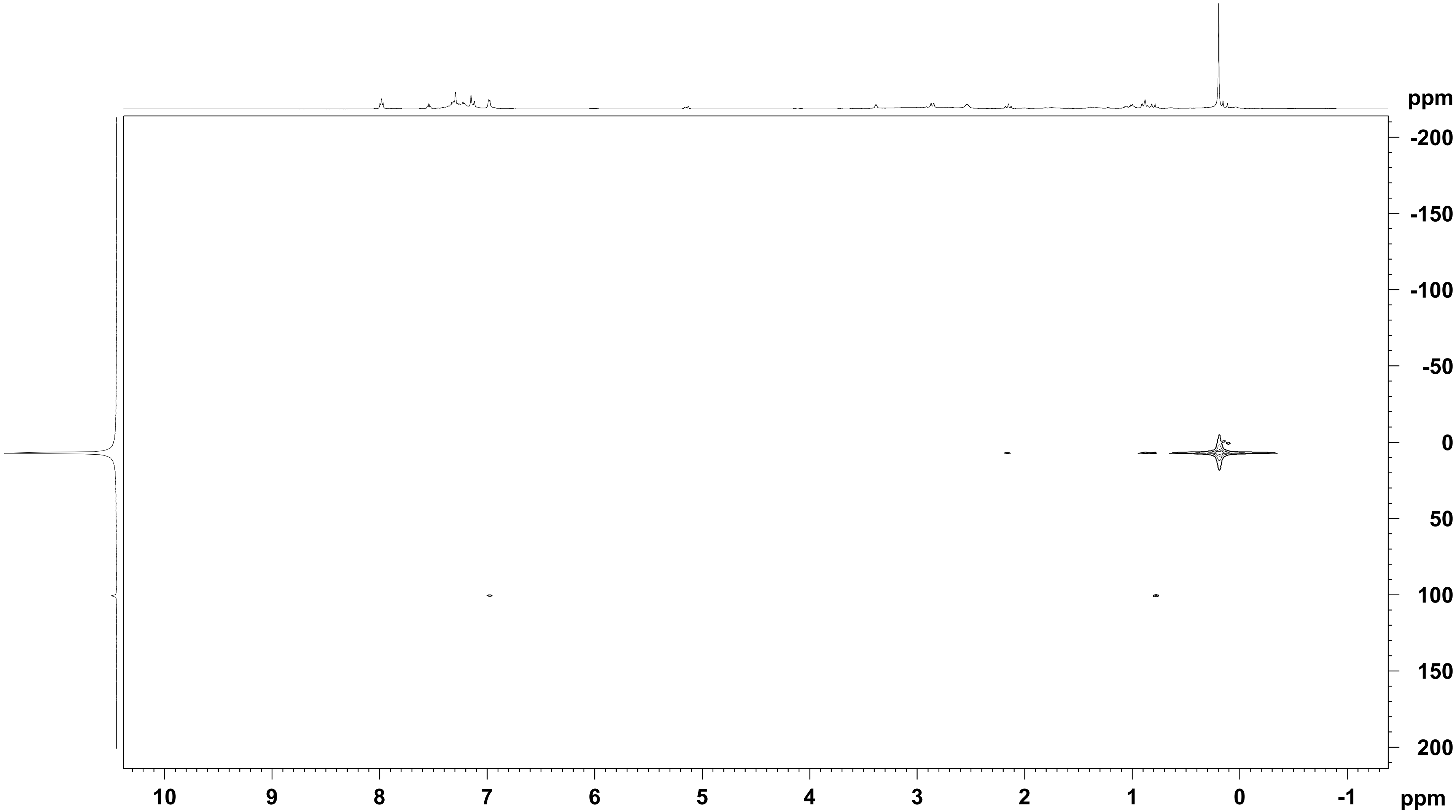


Figure S113. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, C_6D_5Cl, 298 K, optimized for J = 7 Hz) of **crude mixture** from the reaction of **1a**$^{+}[CHB_{11}H_5Br_6]^{-}$ with cyclopropylbenzene (**1a**) and hexamethyldisilane.



14 Computational Studies

14.1 Computational Details

All density functional theory (DFT) calculations were performed with the Gaussian 16 package.[S19] Geometry optimization and vibrational frequency calculations of all stationary points involved were carried out with M06-2X functional, [S20] with 6-311G(d,p) basis set. To get more accurate energies, single point calculations at M06-2X/cc-PVTZ level were performed for all the species along the reaction pathway. The Solvent effect was estimated using the polarizable continuum model (PCM) in both geometry optimizations and single-point calculations, with benzene as solvent.[S21] For saving computational cost, counterion effect was neglected and the reaction between phenyl cyclopropane and benzene-stabilized silylium ion $[Et_3Si(C_6F_5)_3]^+$ was selected as the model reaction.

Activation free energy barriers here are defined as the free energy difference between the transition state and the lowest-energy stationary point before it alone the reaction pathways.

14.2 Results of DFT Calculations

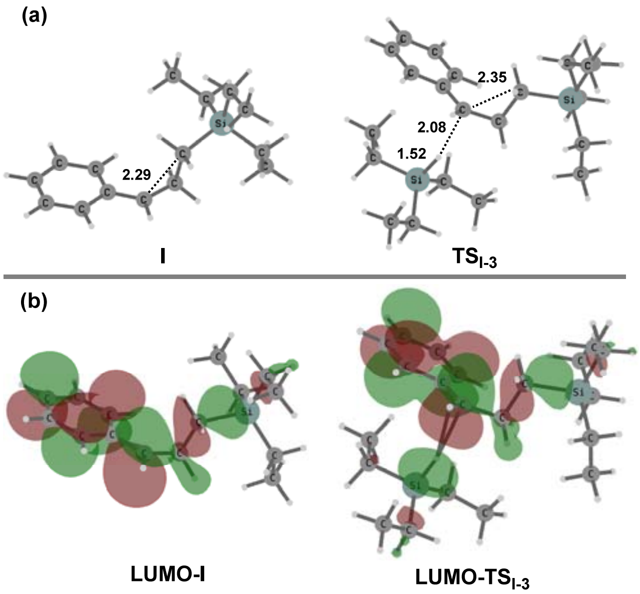


Figure S114. (a) 3D structures of intermediate **I** and the direct hydride transfer transition state **TS$_{I-3}$**. (b) Calculated LUMOs of intermediate **I** and **TS$_{I-3}$** (computed at M06-2X/cc-PVTZ level, with an isodensity value of 0.02).

Analysis of the optimized structures and LUMOs of intermediate **I** and **TS$_{I-3}$** provided an additional insight into the role of γ-silicon effect in the silylium-ion-promoted ring-opening hydrosilylation of cyclopropane. As shown in **Figure S114**, the calculated distance between in C_α and C_γ in carbenium ion **I** and **TS$_{I-3}$** are almost in equal lengths (ca. 2.29 and 2.35 Å), which are much shorter than the sum of the van der Waals radii of two carbon atoms (rvdW,C = 1.70

Å). Further comparison of the unoccupied molecular orbitals (LUMOs, **Figure S114**) in intermediate **I** and **TS$_{I\text{-}3}$** confirms the contribution of γ-silicon effect in **TS$_{I\text{-}3}$**.

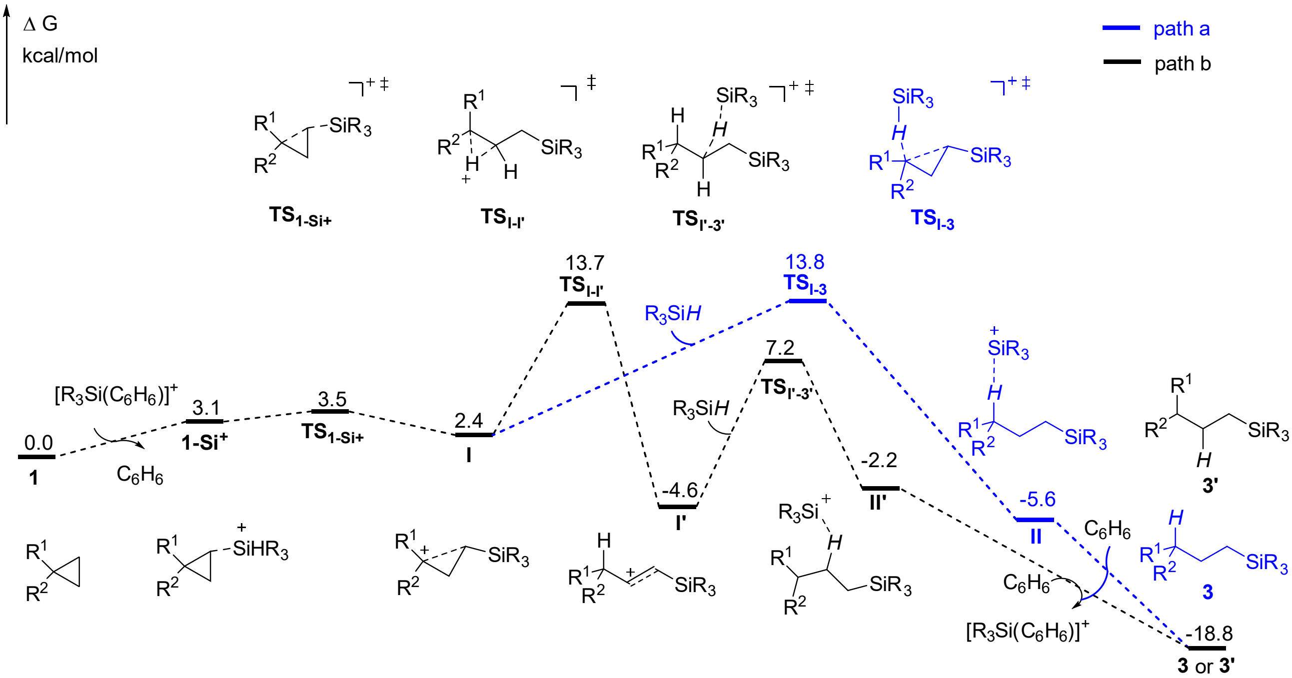


Figure S115. Gibbs free energy profile of silylium-ion-promoted ring-opening hydrosilylation of cyclopropane (for **1a** w/ R^1 = Ph and R^2 = H and **2a** w/ R = Et)

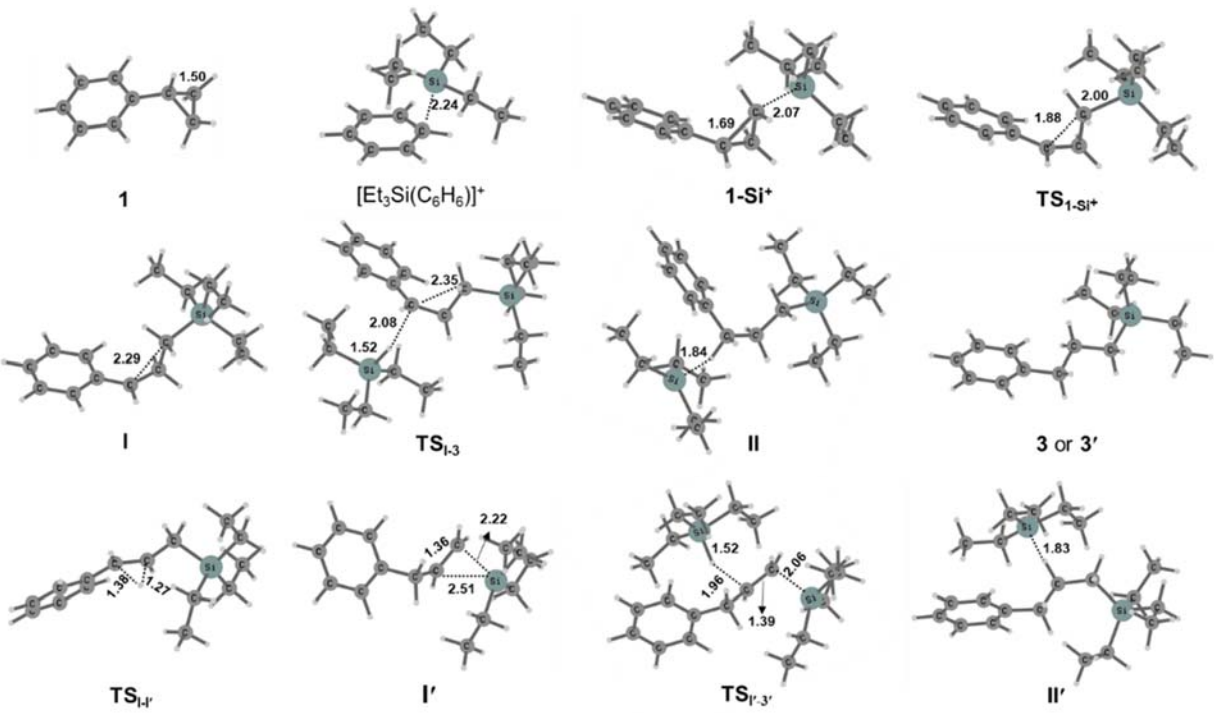


Figure S116. 3D structures of relevant intermediates and transition states (distances are given in Å, optimized at M06-2X/6-311g(d,p) (PCM, benzene) level of theory).

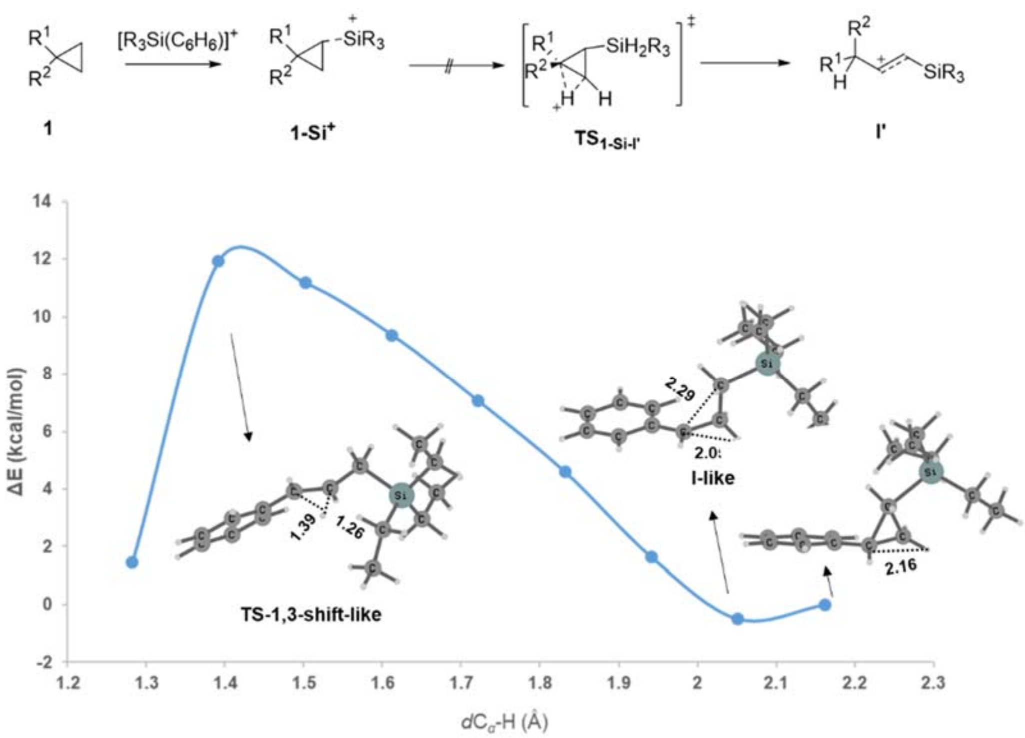


Figure S117. Relaxed potential energy scan for identification of the direct conversion of 1-silylium ion adduct (**1-Si⁺**) to **I′** (performed at M06-2X/6-311g(d,p) (PCM, benzene) level of theory)

No transition state for the direct isomerization of **1-Si⁺** to **I′** (*via* **$TS_{1\text{-}Si\text{-}I'}$**) could be located. As shown in **Figure S117**, a relaxed potential energy scan by fixing the C_α…H distance from 2.16 (in **1-Si⁺**) to 1.28 Å further confirmed the involvement of a γ-silicon stabilized intermediate **I** before the formation of *β*-silicon stabilized carbenium ion **I′**.

Table S1. M06-2X/6-31G(d,p) computed free energies in benzene (G, in a.u.), M06-2X/cc-pVTZ calculated single point energies in benzene (E_{sol}, in a.u.), and corrected free energies (G_c, in a.u.) for all stationary points involved.

Species	G	E_{sol}	G_c
1	-348.74829	-348.91576	-348.78596
$[Et_3Si(C_6H_6)]^+$	-758.85084	-759.167890	-758.90561
Et_3SiH	-527.53615	-527.735606	-527.56560
$1–Si^+$	-875.46921	-875.855243	-875.53655
$TS_{1–Si+}$	-875.46911	-875.854548	-875.53593
I	-875.47142	-875.855657	-875.53781

TS_{I-3}	-1402.99098	-1403.59859	-1403.08516
II	-1403.02206	-1403.63018	-1403.11613
3	-876.31625	-876.705069	-876.38151
$TS_{I-I'}$	-875.45254	-875.83601	-875.51968
I′	-875.48131	-875.870239	-875.54884
$TS_{I'-3'}$	-1403.00072	-1403.60878	-1403.09562
II′	-1403.01686	-1403.63525	-1403.11063

14.3 Cartesian Coordinates of Stationary Points

1

C 1.93238900 -1.19940900 -0.07448700

C 0.56134200 -1.20263400 0.15838300

C -0.14536900 -0.00496900 0.27747000

C 0.55072500 1.19825200 0.15504400

C 1.92195900 1.20623400 -0.07813000

C 2.61672600 0.00633500 -0.19292700

H 2.46652200 -2.13785100 -0.16701700

H 0.02511500 -2.14179800 0.24546700

H 0.00668100 2.13301700 0.24052000

H 2.44788900 2.14904800 -0.17320800

H 3.68433000 0.01073800 -0.37773700

C -1.61518700 -0.01292100 0.56081300

C -2.55682600 0.75628200 -0.32131900

C -2.55340500 -0.74839100 -0.35386900

H -1.87086300 -0.03707200 1.61545500

H -2.12506200 1.27099600 -1.17059900

H -3.39794400 1.25636500 0.13969000

H -3.39194200 -1.27170800 0.08557500

H	-2.11885600	-1.22441200	-1.22401800

[$Et_3Si(C_6H_6)_3$]$^+$

Si	0.90980400	0.06054800	0.27385800
C	2.05385600	-1.34790100	-0.14982800
H	2.84482500	-1.26473200	0.60971300
C	2.67922100	-1.31408500	-1.55053600
H	3.10765400	-0.33553400	-1.77987500
H	3.47961200	-2.04994400	-1.62959900
H	1.94752600	-1.55343100	-2.32541400
C	0.00257400	-0.11891600	1.88752100
H	-0.98291500	0.35247100	1.82710700
C	-0.09517800	-1.55458900	2.42215700
H	-0.66696700	-2.20005100	1.75307500
H	0.89361600	-1.99893300	2.55040600
H	-0.59039300	-1.56530300	3.39359600
C	1.64733800	1.74625900	-0.05057600
H	2.69435000	1.66343200	0.26798900
C	0.96979000	2.90707000	0.69071700
H	1.06720300	2.79676600	1.77171300
H	1.42995400	3.85623800	0.41452900
H	-0.09615100	2.97762300	0.46293600
C	-1.14245500	-1.30718200	-0.99650600
C	-0.55365000	-0.09398200	-1.41931300
C	-1.24139500	1.12360100	-1.21270800
C	-2.44459400	1.13234900	-0.52854500
C	-2.99151300	-0.07205700	-0.08156300
C	-2.34900700	-1.28755600	-0.31469900
H	-0.64483400	-2.24721500	-1.20816100
H	0.26744200	-0.11747700	-2.13362000

H	-2.96793800	2.06471700	-0.35962800
H	-3.93762600	-0.06320100	0.44654800
H	-2.79919800	-2.21320500	0.02002300
H	0.57227500	0.49986700	2.59239000
H	1.68907800	1.93481800	-1.12755600
H	1.56307800	-2.30587300	0.04159500
H	-0.81777200	2.04323500	-1.59850500

Et_3SiH

Si	-0.18245200	-0.01425400	0.58508800
C	-1.77367900	-0.73312000	-0.12560300
H	-1.55495000	-1.17218300	-1.10510500
H	-2.10015200	-1.56015400	0.51344100
C	0.38807700	1.45446500	-0.45223300
H	0.41235600	1.15145800	-1.50533200
H	-0.36178600	2.24890800	-0.38303200
C	-2.89646500	0.30581800	-0.25998900
H	-2.61482100	1.10391100	-0.95133300
H	-3.81947000	-0.14249200	-0.63426800
H	-3.12239300	0.77100000	0.70322300
C	1.76171200	1.99087200	-0.02527700
H	2.53898100	1.23180700	-0.14794500
H	2.05754900	2.86241200	-0.61338600
H	1.75973400	2.28794400	1.02697700
C	1.18261200	-1.31487100	0.62932700
H	2.03765100	-0.91000000	1.18051400
H	0.83259400	-2.17761900	1.20518800
C	1.62513600	-1.75957000	-0.77255700
H	2.42005200	-2.50721900	-0.72720200
H	0.79458400	-2.19785700	-1.33188600

H	2.00174300	-0.91464200	-1.35590300
H	-0.45170000	0.46271400	1.97280100

1-Si⁺

Si	-2.12356200	0.03075500	0.29916700
C	-1.79786500	-1.54021400	1.25143100
H	-2.71549100	-1.72135200	1.82566800
C	-0.59556400	-1.48511800	2.20449800
H	-0.67889000	-0.65605000	2.91033800
H	-0.52054400	-2.40395300	2.78667700
H	0.34954900	-1.36833600	1.66484600
C	-3.29448600	-0.16013400	-1.15002100
H	-2.96348600	0.46931200	-1.98331200
C	-3.52445700	-1.60804500	-1.61340400
H	-2.60331300	-2.09203700	-1.94597100
H	-3.93880200	-2.21667400	-0.80738200
H	-4.22906200	-1.63772300	-2.44503500
C	-2.51088800	1.49795400	1.38688000
H	-3.46549900	1.24764300	1.86664400
C	-2.63102700	2.84211900	0.65559400
H	-3.01247600	3.61343200	1.32527500
H	-1.66151100	3.18835200	0.28989000
H	-3.31196700	2.78009600	-0.19680900
C	4.42406500	1.12899200	-0.07370100
C	3.20094700	1.21557400	-0.72357900
C	2.33128700	0.12219400	-0.73733700
C	2.70720000	-1.06557300	-0.10629900
C	3.93228800	-1.14887000	0.54390500
C	4.78853000	-0.05262100	0.56489300
H	5.09316400	1.98012300	-0.06831400

H	2.91527900	2.13391400	-1.22483100
H	2.06787700	-1.93983500	-0.13898300
H	4.22300600	-2.07476900	1.02393000
H	5.74388700	-0.12271100	1.06990900
C	1.03715600	0.26825100	-1.44156300
C	-0.05067000	-0.65102700	-1.36509400
C	-0.29659900	0.63071900	-0.46350700
H	1.02802400	0.96767500	-2.26865500
H	0.05776700	-1.56557300	-0.79472400
H	-0.74118200	-0.70087800	-2.19772200
H	-0.66816500	1.54471600	-0.91613600
H	0.18448700	0.73380400	0.50455100
H	-4.24914700	0.27038900	-0.82611300
H	-1.77822100	1.56273000	2.19706400
H	-1.71492500	-2.38807400	0.56467000

TS_{1-Si+}

Si	-2.15598400	0.02155900	0.28472700
C	-1.84639000	-1.60912700	1.14958000
H	-2.77427500	-1.85188100	1.68144000
C	-0.67147100	-1.59325300	2.13785600
H	-0.78810200	-0.81092200	2.89104800
H	-0.58965300	-2.54486400	2.66434500
H	0.28337100	-1.42197800	1.63055100
C	-3.28923700	-0.11437400	-1.20690100
H	-2.93848900	0.55903800	-1.99700500
C	-3.47610800	-1.53879700	-1.75377700
H	-2.53383000	-1.98654300	-2.07901100
H	-3.90216100	-2.19764700	-0.99452100
H	-4.15224900	-1.54049700	-2.60957900

C	-2.65451300	1.39569200	1.45307600
H	-3.62381700	1.09130100	1.86681300
C	-2.77603400	2.77813600	0.79675700
H	-3.20580600	3.50251700	1.48954900
H	-1.79985800	3.16362500	0.49339700
H	-3.41679000	2.74903400	-0.08812400
C	4.52675700	1.11094800	-0.05293200
C	3.31329700	1.23266600	-0.71215600
C	2.40214500	0.16830600	-0.71507900
C	2.73050700	-1.02840700	-0.06191300
C	3.94577700	-1.14567300	0.59274700
C	4.84048500	-0.07663900	0.60143000
H	5.22757300	1.93570600	-0.05191200
H	3.06304600	2.15322600	-1.22757700
H	2.05754900	-1.87699200	-0.08554900
H	4.20390500	-2.07275000	1.08824100
H	5.78971800	-0.17507600	1.11357100
C	1.15141700	0.33769000	-1.44191300
C	0.02117400	-0.51999200	-1.39911200
C	-0.37503300	0.64013300	-0.38308100
H	1.11901000	1.15395500	-2.15575500
H	0.10975300	-1.48373500	-0.90951900
H	-0.64572200	-0.50984000	-2.25404800
H	-0.61368700	1.60368200	-0.82858300
H	0.20228900	0.72488300	0.53495800
H	-4.26177000	0.28529000	-0.89893800
H	-1.96373700	1.43256900	2.30061700
H	-1.71911500	-2.40778800	0.41191400

I

Si	-2.25082200	0.12873500	-0.15650800
C	-1.95727600	1.95249800	0.19182000
H	-2.93900800	2.43187500	0.28001700
C	-1.12871100	2.66047100	-0.89009400
H	-1.62619500	2.61572000	-1.86138200
H	-0.97418000	3.71362600	-0.64935800
H	-0.14211200	2.20246900	-1.00901000
C	-3.25105900	-0.69625300	1.21089300
H	-2.99247600	-1.76076900	1.25080800
C	-3.11840200	-0.05945500	2.60368700
H	-2.09196900	-0.08671900	2.97867500
H	-3.42905600	0.98743900	2.58899000
H	-3.74312900	-0.57774400	3.33317800
C	-3.03960600	-0.13104800	-1.84164200
H	-3.94218000	0.49067400	-1.87184100
C	-3.40030800	-1.59248300	-2.14459200
H	-3.89593200	-1.68509100	-3.11234500
H	-2.51180100	-2.22815200	-2.17276900
H	-4.07593400	-2.00088200	-1.38930100
C	4.89798500	-0.82684800	-0.50764600
C	3.71049000	-1.40859500	-0.11489700
C	2.64094300	-0.60286000	0.35145700
C	2.79943000	0.80637400	0.40980100
C	3.98622600	1.37645200	0.00974900
C	5.03039000	0.56103700	-0.44617500
H	5.71823800	-1.43680900	-0.86165100
H	3.58303800	-2.48441500	-0.15661700
H	1.99376000	1.43286700	0.77173200
H	4.11833300	2.44945800	0.04931100
H	5.96204600	1.01955700	-0.75647500
C	1.45983600	-1.24487800	0.75968900

C	0.20524500	-0.63176000	1.13985700
C	-0.52257900	-0.72606900	-0.25415200
H	1.45504300	-2.33162100	0.69444300
H	0.28237600	0.40009100	1.47544300
H	-0.34514700	-1.23468400	1.86161600
H	-0.66851900	-1.77135200	-0.53970000
H	0.06538100	-0.24030900	-1.03718600
H	-4.30187000	-0.66529700	0.90126600
H	-2.37556900	0.26422700	-2.61715800
H	-1.48726900	2.07406000	1.17389300

$TS_{I\text{–}3}$

Si	-3.64555900	-0.29410600	-0.03206000
C	-3.52370300	0.07547100	1.80917700
H	-4.42446700	-0.32331700	2.28926900
C	-3.37686400	1.56844100	2.13545600
H	-4.23318700	2.14102500	1.77210700
H	-3.30255600	1.73808200	3.21115300
H	-2.48241800	1.99761700	1.67326400
C	-3.71534100	-2.15170000	-0.35142500
H	-3.26675600	-2.36354100	-1.32875200
C	-3.06372200	-3.02028900	0.73582500
H	-2.00660800	-2.78043100	0.87696700
H	-3.55673000	-2.87667000	1.69963900
H	-3.12723500	-4.08113200	0.48718100
C	-5.10133100	0.58502700	-0.83121900
H	-6.00100500	0.30174300	-0.27271300
C	-5.27976700	0.24431400	-2.31821400
H	-6.16126800	0.73430300	-2.73524100
H	-4.41851800	0.56669600	-2.90901900

H	-5.40031300	-0.83153400	-2.46822500
C	2.30755000	3.54302700	-1.11032800
C	1.71931000	2.34772800	-1.47669400
C	0.88852000	1.65634700	-0.56594600
C	0.66964000	2.19010300	0.72571200
C	1.25347700	3.38863100	1.07958000
C	2.06846000	4.06171100	0.16257700
H	2.94364400	4.07583200	-1.80474400
H	1.88723900	1.93119700	-2.46401100
H	0.04225000	1.66524200	1.43597300
H	1.08480300	3.80821400	2.06273900
H	2.52458000	5.00212300	0.44854500
C	0.27574300	0.45337000	-0.99496100
C	-0.78075200	-0.27444900	-0.29945300
C	-2.06568700	0.42032300	-0.86266200
H	0.45494200	0.16339100	-2.02815300
H	-0.73050400	-0.18673700	0.78588600
H	-0.78877100	-1.32561600	-0.58756300
H	-2.13782500	0.26462100	-1.94339300
H	-2.03298200	1.49910600	-0.68607100
H	-4.77105200	-2.42816500	-0.44895400
H	-4.99196400	1.66652100	-0.70112800
H	-2.69156100	-0.49284500	2.24047200
Si	3.00966900	-1.36018800	0.03714100
C	4.34554000	-0.07548700	-0.30835700
H	5.31016800	-0.59522200	-0.31180700
C	4.38485900	1.07866400	0.70401200
H	4.62343400	0.71428200	1.70547600
H	5.13886000	1.82045400	0.43286200
H	3.42370200	1.59342500	0.76883500
C	3.48912800	-3.05930400	-0.60088600

H	2.65634500	-3.75143900	-0.44347100
C	3.89760900	-3.04782600	-2.08088800
H	3.08217000	-2.68877400	-2.71443600
H	4.75931400	-2.39782000	-2.25158900
H	4.16713900	-4.04703200	-2.42723000
C	2.48404300	-1.37230900	1.84207100
H	3.37529800	-1.50154400	2.46573200
C	1.45588500	-2.46652900	2.16181400
H	1.11540200	-2.40880100	3.19727400
H	0.57463400	-2.38856100	1.51861700
H	1.87899900	-3.46160100	2.00977800
H	4.31507000	-3.43076500	0.01604000
H	2.08442600	-0.38347400	2.09766500
H	4.21766400	0.31298300	-1.32447800
H	1.77252000	-0.96331000	-0.74677800

II

Si	-3.46373300	-0.13326200	-0.02626500
C	-3.30556500	0.46559500	1.75676200
H	-4.21091600	0.16842100	2.29813900
C	-3.10070200	1.98320100	1.87556200
H	-3.94066700	2.52955200	1.43994100
H	-3.01109500	2.29828800	2.91742500
H	-2.19594100	2.30956800	1.35373600
C	-3.79217200	-1.99456200	-0.05967400
H	-3.50810100	-2.38625800	-1.04322700
C	-3.09391600	-2.79192200	1.05239200
H	-2.00764500	-2.66900000	1.02091300
H	-3.42705600	-2.46273700	2.03928900
H	-3.30419400	-3.86056400	0.97310900

C	-4.84812200	0.78145700	-0.91512100
H	-5.74182300	0.74878600	-0.28186900
C	-5.16878800	0.20044600	-2.30054400
H	-5.97638500	0.74948800	-2.78866800
H	-4.30002900	0.24160800	-2.96296400
H	-5.47827600	-0.84526300	-2.22915300
C	2.28850500	3.41085700	-1.09417200
C	1.85198500	2.14207500	-1.45787100
C	1.10645300	1.36310500	-0.57032500
C	0.78088800	1.89068300	0.68184400
C	1.21203500	3.16232300	1.04510500
C	1.97285300	3.92137400	0.16111500
H	2.86412800	4.00422100	-1.79386300
H	2.08135400	1.75533900	-2.44585100
H	0.16884300	1.32397700	1.37475800
H	0.94465200	3.56258400	2.01539500
H	2.30549900	4.91225400	0.44458200
C	0.67655800	-0.01872900	-0.98047800
C	-0.63251600	-0.54745100	-0.40408300
C	-1.83230600	0.25818700	-0.91823500
H	0.68694400	-0.11257800	-2.07002100
H	-0.59054600	-0.52689700	0.68998100
H	-0.73940400	-1.59831100	-0.69073800
H	-1.95008500	0.08228900	-1.99315700
H	-1.64091700	1.33134000	-0.80230100
H	-4.87515800	-2.14419100	0.01502600
H	-4.57889600	1.83928200	-1.00517900
H	-2.48244300	-0.06621900	2.24930600
Si	2.97229700	-1.39361300	0.18871900
C	4.22837100	-0.15707600	-0.36925000
H	5.15072200	-0.73167200	-0.53001700

C	4.47337900	1.01028700	0.59930000
H	4.86097700	0.65716700	1.55647500
H	5.20833600	1.69575000	0.17654800
H	3.56040300	1.57685000	0.78724700
C	2.82641300	-2.99315500	-0.73301400
H	1.82832000	-3.40568600	-0.55112400
C	3.12639800	-2.88635900	-2.23520900
H	2.41748000	-2.22356700	-2.73564800
H	4.13291100	-2.50591800	-2.41871500
H	3.05051400	-3.86618800	-2.70609000
C	2.31251800	-1.30007100	1.91201300
H	3.19302400	-1.34442700	2.56712500
C	1.31230100	-2.40596600	2.27920900
H	0.96336300	-2.27487600	3.30346600
H	0.43818500	-2.39808900	1.62564900
H	1.77104900	-3.39357500	2.20863400
H	3.52660600	-3.68590900	-0.24646200
H	1.89958400	-0.29673200	2.06743200
H	3.94017500	0.20293900	-1.36364200
H	1.47918300	-0.78059500	-0.69181200

3

Si	-2.44768400	0.00768800	0.14301700
C	-2.25902900	1.48551900	1.30367200
H	-3.13095100	1.52304500	1.96673100
C	-2.10108900	2.82048700	0.56182500
H	-2.95330000	3.01658400	-0.09433400
H	-2.01920500	3.66200600	1.25346700
H	-1.20229300	2.81931200	-0.06140900
C	-2.47367700	-1.60172700	1.14161100

H	-2.14734800	-2.41923500	0.48849100
C	-1.62425500	-1.58094600	2.42164400
H	-0.57878000	-1.34170700	2.21124700
H	-1.99242800	-0.82847900	3.12308800
H	-1.64420500	-2.54625700	2.93283600
C	-4.05860500	0.14980600	-0.83139300
H	-4.88392800	0.25552700	-0.11806800
C	-4.31411200	-1.05336900	-1.75142100
H	-5.26344600	-0.96297700	-2.28422700
H	-3.52554000	-1.15218000	-2.50185500
H	-4.34411900	-1.98694500	-1.18285200
C	4.71171800	1.11736700	0.37213100
C	3.49296000	1.16735100	-0.29590100
C	2.87930100	0.00098900	-0.75615900
C	3.51637400	-1.21990900	-0.52815700
C	4.73534200	-1.27581400	0.13932300
C	5.33727100	-0.10592900	0.59175000
H	5.17555400	2.03375700	0.71822100
H	3.00967200	2.12415100	-0.46834000
H	3.05158600	-2.13476900	-0.88261700
H	5.21747600	-2.23257500	0.30317700
H	6.28829000	-0.14682000	1.10917500
C	1.53122400	0.05413900	-1.42826700
C	0.37965800	-0.03982200	-0.41587900
C	-1.00234400	0.00753100	-1.07661900
H	1.43319900	0.98750800	-1.99156400
H	0.48523800	0.77698600	0.30851000
H	0.49264000	-0.96968200	0.15289900
H	-1.11089400	-0.84544000	-1.75752700
H	-1.08093800	0.90554000	-1.70300300
H	-3.51513500	-1.82552600	1.40019600

H	-4.04485400	1.07280400	-1.42109400
H	-1.39394500	1.31968900	1.95497300
H	1.44081800	-0.76599200	-2.14730700

TS$_{I\text{–}I'}$

Si	-2.42047600	0.00987600	0.13030300
C	-2.49009000	1.74887500	0.83975500
H	-3.21816300	1.73851000	1.65877600
C	-2.87789500	2.82576900	-0.18510800
H	-3.84431800	2.60827700	-0.64504800
H	-2.95197600	3.80827600	0.28367800
H	-2.14091300	2.90550600	-0.98913300
C	-1.89421900	-1.25660900	1.43128900
H	-1.34072700	-2.06944100	0.94334700
C	-1.10003000	-0.70370800	2.62641000
H	-0.14622500	-0.24886800	2.33878600
H	-1.66677200	0.06811600	3.15058500
H	-0.87064000	-1.49186100	3.34531000
C	-4.02237100	-0.48981000	-0.70419900
H	-4.82757800	-0.35487900	0.02659700
C	-4.02639000	-1.93512900	-1.22441600
H	-4.99471700	-2.19632700	-1.65396500
H	-3.27623900	-2.08498100	-2.00474000
H	-3.82034400	-2.64841500	-0.42270400
C	4.96428100	-1.06451200	0.14504200
C	3.63973500	-1.31207100	-0.17999400
C	2.76931500	-0.24359400	-0.43555700
C	3.24338300	1.07631400	-0.38605100
C	4.56723100	1.31528200	-0.06285800
C	5.42403300	0.24740200	0.20708000

H	5.63661500	-1.88835700	0.34567400
H	3.27157000	-2.33031400	-0.23467800
H	2.59416100	1.90972400	-0.62572100
H	4.94066100	2.33053200	-0.03138300
H	6.45963700	0.44283000	0.45700500
C	1.39224800	-0.55964600	-0.77796100
C	0.29376500	0.31566300	-0.77148200
C	-1.06859900	-0.01428300	-1.25294700
H	1.17338600	-1.59238300	-1.04831600
H	0.48575700	1.34513500	-0.47393600
H	0.54868100	-0.34130700	0.28616600
H	-1.08223800	-0.98300100	-1.75795100
H	-1.35315200	0.75314900	-1.97996700
H	-2.81023200	-1.72587700	1.80668800
H	-4.23520000	0.20790200	-1.52048300
H	-1.53074700	2.00013100	1.30714900

I′

Si	2.25358400	0.08451000	-0.02603500
C	2.96478500	1.02824300	1.41516400
H	3.73410500	1.67704500	0.97778300
C	3.58588100	0.15780500	2.51657800
H	4.36554000	-0.49301000	2.11587700
H	4.03998800	0.78270100	3.28584500
H	2.84464100	-0.47453100	3.01035700
C	1.89899800	1.14923600	-1.51804100
H	1.27816800	0.61321100	-2.24073200
C	1.35709500	2.55779600	-1.24064800
H	0.34854300	2.54002200	-0.82015400
H	1.99669400	3.09949700	-0.54106600

H	1.31305000	3.13723900	-2.16318200
C	3.09734300	-1.51962600	-0.46892900
H	4.14099500	-1.24141900	-0.66670300
C	2.50411000	-2.23137000	-1.69253400
H	3.05623100	-3.14667500	-1.90671900
H	1.45909400	-2.51208000	-1.53768600
H	2.55094900	-1.60105000	-2.58232100
C	-4.49950600	1.11015100	0.21962300
C	-3.19833200	1.10007200	-0.26959400
C	-2.49705300	-0.10104200	-0.36639700
C	-3.09901100	-1.28865800	0.04626700
C	-4.40152200	-1.27774400	0.53082900
C	-5.10206200	-0.07857900	0.61861800
H	-5.04380200	2.04424600	0.28347900
H	-2.73039300	2.02637200	-0.58796600
H	-2.55444900	-2.22464800	-0.02415500
H	-4.86985100	-2.20481300	0.83739400
H	-6.11725100	-0.07101500	0.99563400
C	-1.06011000	-0.10792700	-0.86894100
C	-0.22634300	0.07843100	0.35355200
C	0.51781200	-0.89790000	0.94031400
H	-0.82142900	-1.05109800	-1.36468800
H	-0.30228900	1.04730900	0.84749900
H	-0.91398900	0.71481100	-1.57148200
H	0.51281100	-1.90398800	0.53125100
H	0.88700900	-0.77382800	1.95422700
H	2.88676400	1.22823100	-1.99412200
H	3.12329900	-2.17819200	0.40344200
H	2.21288800	1.70919900	1.82751400

$TS_{I'\text{–}3'}$

Si	3.26838800	-0.38441700	-0.08108400
C	3.50996000	0.18208200	-1.84640300
H	4.34607000	-0.40365000	-2.24717400
C	3.80715200	1.68097200	-1.99641200
H	4.70899700	1.96353500	-1.44999800
H	3.95978800	1.94261800	-3.04412500
H	2.98666300	2.30194600	-1.62738200
C	3.21725100	-2.24467100	0.08743500
H	2.72925200	-2.53078600	1.02508400
C	2.60213700	-2.97038500	-1.11830900
H	1.58558600	-2.63116800	-1.33743800
H	3.19371300	-2.79902600	-2.01913300
H	2.55611100	-4.04707900	-0.94994100
C	4.40090000	0.43880900	1.15752100
H	5.41758400	0.32160600	0.76276300
C	4.31679000	-0.15023600	2.57197600
H	4.99843700	0.36659700	3.24840400
H	3.31190600	-0.06082200	2.99280100
H	4.58437900	-1.20871800	2.57712500
C	-2.97065900	-2.97430900	-1.22330700
C	-1.69920100	-2.55098600	-0.85087700
C	-1.50077100	-1.91477200	0.37367800
C	-2.58757200	-1.70423400	1.21980900
C	-3.85894300	-2.13038900	0.84860400
C	-4.05193800	-2.76750900	-0.37212800
H	-3.11384800	-3.47570400	-2.17259400
H	-0.85829000	-2.74030200	-1.51154400
H	-2.43860700	-1.21769000	2.17867500
H	-4.69662800	-1.96808800	1.51615200
H	-5.04049000	-3.10420700	-0.65884200

C	-0.11774100	-1.47704700	0.80445500
C	0.48934200	-0.38403700	-0.00796400
C	1.47546800	0.47013800	0.47815900
H	-0.09474900	-1.21174100	1.86300400
H	0.30315700	-0.40752300	-1.08177200
H	0.56773100	-2.33124900	0.68648300
H	1.53899700	0.58563400	1.55910000
H	1.63976400	1.38741700	-0.08945000
H	4.26146200	-2.55801700	0.20733600
H	4.20436700	1.51548000	1.16732100
H	2.63967900	-0.10163800	-2.44836500
Si	-1.91974200	1.96777700	0.01889300
C	-0.59249500	3.28773800	-0.16450800
H	-1.03847600	4.26891400	0.02849200
C	0.06569800	3.27557000	-1.55294800
H	-0.64231800	3.58120800	-2.32537700
H	0.91802700	3.95664100	-1.60392200
H	0.42047700	2.27533100	-1.82998600
C	-2.68914600	1.94567500	1.73023200
H	-3.44214700	1.15198400	1.76485400
C	-1.65094100	1.74528300	2.84316400
H	-1.09425600	0.81342200	2.69950200
H	-0.92501000	2.56150600	2.86429300
H	-2.11945700	1.69687500	3.82780100
C	-3.17561100	1.98633900	-1.37216600
H	-3.76532900	2.90634100	-1.29338400
C	-4.09242500	0.75503200	-1.35101800
H	-4.80243000	0.77378800	-2.18001500
H	-3.51220600	-0.16837400	-1.42688100
H	-4.66852200	0.70060800	-0.42414000
H	-3.22931700	2.88629700	1.88225800

H	-2.64644400	2.04424400	-2.32840700
H	0.15823100	3.14830500	0.62132800
H	-1.16641400	0.65407800	-0.10619100

II′

Si	3.09482500	-0.56369200	-0.03668000
C	3.51991800	0.39328100	-1.60438600
H	4.25044700	-0.19381700	-2.17210100
C	4.09056900	1.79215200	-1.32687900
H	5.04981900	1.72286800	-0.80943000
H	4.25204000	2.35183400	-2.25049300
H	3.42669000	2.39092300	-0.69550600
C	2.84099100	-2.38219000	-0.46212300
H	2.38425200	-2.91375000	0.37876200
C	2.05658300	-2.62317800	-1.76118300
H	1.07232700	-2.14504900	-1.74587800
H	2.59380800	-2.21650800	-2.62058400
H	1.89722100	-3.68749200	-1.94408700
C	4.45747400	-0.37581900	1.24599400
H	5.41865000	-0.56262600	0.75422200
C	4.29499800	-1.31685500	2.44882200
H	5.08267000	-1.16091500	3.18815500
H	3.33820800	-1.16311900	2.95622600
H	4.33723500	-2.36363800	2.13884700
C	-3.42190900	-2.40298500	-1.30907700
C	-2.11690200	-2.07005000	-0.96503700
C	-1.79265300	-1.72277700	0.34963600
C	-2.80708900	-1.69870100	1.30786900
C	-4.11592600	-2.03342500	0.96650400
C	-4.42356500	-2.39235000	-0.34109700

H	-3.65527000	-2.68746200	-2.32799000
H	-1.33460700	-2.11590100	-1.71705200
H	-2.55869700	-1.45682200	2.33723100
H	-4.88881900	-2.02967500	1.72556100
H	-5.43758700	-2.66566400	-0.60575500
C	-0.36440800	-1.43434600	0.74090900
C	0.18155500	-0.10700600	0.20744700
C	1.55042400	0.27021800	0.74560700
H	-0.27057500	-1.43574100	1.83015600
H	0.11761800	-0.06546300	-0.88451300
H	0.28588300	-2.23017200	0.36835700
H	1.57077600	0.08848200	1.82489800
H	1.73894900	1.34124800	0.61310100
H	3.84319900	-2.81514800	-0.56460800
H	4.48855600	0.66681700	1.58150900
H	2.63576400	0.45738000	-2.25015900
Si	-1.55770000	2.06734400	-0.00048500
C	-0.13867200	3.22899200	-0.25204100
H	-0.60307600	4.22566000	-0.24453200
C	0.63795200	3.01903000	-1.56093900
H	-0.02335400	3.04752400	-2.42900500
H	1.38772100	3.80009300	-1.68920600
H	1.15917300	2.05949000	-1.56913300
C	-2.45355400	2.10317800	1.62114300
H	-3.11289800	1.23094300	1.66510300
C	-1.53937900	2.17969300	2.85250000
H	-0.86389500	1.32361100	2.90720000
H	-0.93165100	3.08607800	2.84541900
H	-2.13503500	2.18767000	3.76528300
C	-2.47957800	1.52197600	-1.51108900
H	-2.46953300	2.38324300	-2.19127800

C	-3.91600800	1.06402100	-1.22181700
H	-4.39444900	0.72450300	-2.14091100
H	-3.93355900	0.23502700	-0.51422800
H	-4.51827600	1.87744500	-0.81250400
H	-3.11264600	2.98126800	1.57483100
H	-1.91259000	0.73716100	-2.02185300
H	0.52003900	3.21409400	0.62108400
H	-0.57920000	0.64732500	0.62060800

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