

Supporting Information
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Silylium-Ion-Initiated Twofold Halodealkylation of Fully Alkylated Silanes

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Supporting Information

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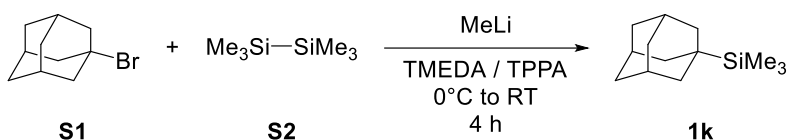
1 General Information

All reactions were performed in flame-dried glassware using an *MBraun* glove box (argon atmosphere, O₂ < 1.0 ppm, H₂O < 1.0 ppm) or conventional Schlenk techniques under a static pressure of nitrogen gas unless otherwise stated. All given temperatures refer to external bath temperatures. Standard solvents and reagents were obtained from commercial suppliers and used as received unless otherwise stated. Liquids and solutions were transferred via syringes. Dry *n*-pentane, *n*-hexane, CH₂Cl₂, and benzene were obtained from an *MBraun* solvent purification system (SPS-800), degassed by three freeze-pump-thaw cycles, and stored in a glovebox over thermally activated 4 Å molecular sieves. Technical grade solvents for extraction or chromatography (CH₂Cl₂, cyclohexane, and *n*-pentane) were distilled prior to use. Et₂O and THF were dried over potassium/ benzophenone and freshly distilled prior to use. Benzene-*d*₆ (C₆D₆) was degassed by three freeze-pump-thaw cycles and stored in a glovebox over thermally activated 4 Å molecular sieves. CDCl₃ was obtained from commercial suppliers and used as received. Trityl salt [Ph₃C]⁺[HCB₁₁H₅Br₆]⁻,^{S1} and carborane-stabilized silylium ion [Me₃Si(HCB₁₁H₅Br₆)]^{S2} were prepared according to reported procedures. 1,2-Dihaloethanes **2a–c** were obtained from commercial suppliers and **2a** and **2b** were stored in the glovebox over thermally activated 4 Å molecular sieves. All tetraalkylsilanes and trialkylhydrosilanes were dried over CaH₂, distilled, degassed by three freeze-pump-thaw cycles, and stored in the glovebox over thermally activated 4 Å molecular sieves. Flash column chromatography was performed on silica gel 60 (40–63 μm, 230–400 mesh ASTM) by *VWR Chemicals* using the indicated solvents. Infrared (IR) spectra were recorded on an *Agilent Technologies* Cary 630 FT-IR spectrometer equipped with an ATR unit or a *Jasco* FT/IR-4100 spectrometer, and the signals are reported in wavenumbers (cm⁻¹). ¹H, ²H, ¹³C, and ²⁹Si NMR spectra were recorded in C₆D₆ or CDCl₃ on *Bruker* AV500 and *Bruker* AV700 instruments, respectively. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard (C₆D₅H: δ = 7.16 ppm for ¹H and ²H NMR and C₆D₆: δ = 128.06 ppm for ¹³C NMR; CHCl₃: δ = 7.28 ppm for ¹H NMR and CDCl₃: δ = 77.00 ppm for ¹³C NMR). ²⁹Si 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 TMS.^{S3} Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sex = sextet, sept = septet, oct = octet, non = nonet, m = multiplet, m_c = centrosymmetric multiplet), coupling constants (Hz) and integration. High resolution mass spectra (HRMS) were obtained from the *Center of Mass Spectrometry* at the *Institut für Chemie, Technische Universität Berlin*. Gas-liquid chromatography mass spectrometry (GLC-MS) measurements were conducted on an *Agilent Technologies* 5975C TAD – GC/MSD-System with electron impact ionization (EI) connected to a fused silica HP-5ms capillary column (length: 30 m, inner diameter: 0.25 mm, thickness of the stationary phase: 0.25 μm).

Measurements were performed using the following protocol: Carrier gas: He, injector temperature: 280°C, detector temperature: 280°C, flow rate: 4 mL/min, temperature program: starting temperature: 40°C, heating rate: 10°C/min, final temperature: 280°C for 10 min.

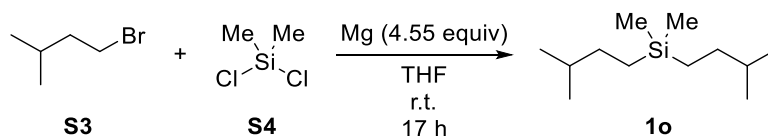
2 Preparation of Tetraalkylsilanes and Trialkylhydrosilanes

2.1 1-Adamantyltrimethylsilane (**1k**)



Prepared according to a modified procedure by Oestreich and Yoshida.^{S4} Hexamethyldisilane (**S2**, 5.00 mL, 3.65 g, 24.9 mmol, 1.00 equiv) was dissolved in TMEDA (20 mL) and TPPA (20 mL) and cooled to -78°C . Methyl lithium (1.6M in diethylether, 15.5 mL, 24.8 mmol, 0.996 equiv) was added at once and the reaction mixture was warmed to 20°C using a water bath. The reaction mixture was stirred for 5 min at 20°C and cooled to -78°C . 1-Bromoadamantane (**S1**, 2.10 g, 9.76 mmol, 0.392 equiv) was dissolved in diethylether (15 mL) and added to the reaction mixture. The reaction mixture was warmed to 20°C using a water bath and stirred for 3 h at room temperature. The reaction mixture was cooled with an ice bath and water (50 mL) was added dropwise. The aqueous layer was extracted with *n*-pentane (1 \times 200 mL) and the combined organic layers were washed with water (3 \times 20 mL). The organic phase was dried over MgSO_4 and filtered. The solvent was removed under reduced pressure and the crude product was recrystallized in methanol. The product was further purified by sublimation (41°C , 33.0 mbar) and collected as a white solid (**1k**, 412 mg, 3%). **¹H NMR** (500 MHz, C_6D_6 , 298 K): δ = 1.86 (m, 3H), 1.74 (m, 6H), 1.61 (m, 6H), -0.06 (s, 9H) ppm. **¹³C{¹H} NMR** (126 MHz, C_6D_6 , 298 K): δ = 38.0, 37.4, 28.7, 20.9, -5.4 ppm. **²⁹Si DEPT NMR** (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 15.0°): δ = 3.4 ppm. **GLC MS** (EI): m/z = 208.1, 193.1, 165.0, 135.1, 73.0. **HRMS** (APCI): calculated for $\text{C}_6\text{H}_{15}^+$ [$\text{M}-\text{SiMe}_3$] † : 135.1168; found: 135.1168.

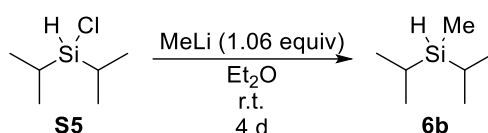
2.2 Diisopentyldimethylsilane (**1o**)



Magnesium turnings (9.98 g, 410 mmol, 4.55 equiv) were heated and stirred in vacuo for 10 min. THF (150 mL) and three small iodine crystals were added. 1-Bromo-3-methylbutane (**S3**, 43.0 mL, 49.0 g, 325 mmol, 3.59 equiv) was added dropwise to the reaction mixture, to maintain gentle reflux. The reaction mixture was stirred for 1 h at 120°C and cooled to room

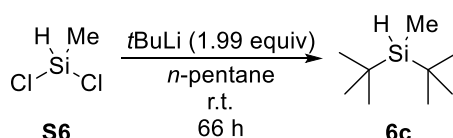
temperature. Dichlorodimethylsilane (11.0 mL, 11.7 g, 90.4 mmol, 1.00 equiv) was added dropwise and the reaction mixture was stirred for 17 h at room temperature. Hydrochloric acid (2.0M 100 mL and 5.0M 50 mL) was added, and the phases were separated. The aqueous layer was extracted with *n*-pentane (2 × 50 mL) and the combined organic layers were dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the crude product was purified by distillation over CaH₂ (b.p. 102°C, 25 mbar). The product **1o** was obtained as a colorless oil (8.49 g, 47%). **IR** (ATR): $\tilde{\nu}$ = 2952, 2908, 1466, 1247, 1186, 1022, 881, 831, 765 cm⁻¹. **¹H NMR** (500 MHz, C₆D₆, 298 K): δ = 1.47 (non, *J* = 6.6 Hz, 2H), 1.23 (m, 4H), 0.92 (d, *J* = 6.6 Hz, 12H), 0.52 (m_c, 4H), 0.03 (s, 6H) ppm. **¹³C{¹H} NMR** (126 MHz, C₆D₆, 298 K): δ = 33.4, 31.4, 22.4, 12.9, -3.4 ppm. **²⁹Si DEPT NMR** (99 MHz, C₆D₆, 298 K, optimized for *J* = 7 Hz, 15.5°): δ = 2.7 ppm. **GLC MS** (EI): *m/z* = 185.1, 129.1, 115.0, 99.0, 86.0, 73.0, 59.0. **HRMS** (APCI): calculated for C₁₁H₂₅Si⁺ [M-CH₃]⁺: 185.1720; found: 185.1719.

2.3 Diisopropyl(methyl)silane (**6b**)



Diisopropylchlorosilane (**S5**, 3.10 mL, 2.70 g, 17.9 mmol, 1.00 equiv) was cooled with an ice bath and methyllithium (1.60M in diethylether, 11.8 mL, 18.9 mmol, 1.06 equiv) was added dropwise over a period of 30 min. The reaction mixture was stirred for 4 days at room temperature. After filtration, the solvent of the filtrate was removed under reduced pressure, and the crude product was purified by distillation at atmospheric pressure (b.p. 122°C). The product **6b** was obtained as a colorless oil (942 mg, 40%). **IR** (ATR): $\tilde{\nu}$ = 2939, 2863, 2096, 1461, 1249, 1000, 873, 820, 725 cm⁻¹. **¹H NMR** (500 MHz, C₆D₆, 298 K): δ = 3.74 (sext, *J* = 3.3 Hz, 1H), 1.02 (d, *J* = 7.3 Hz, 6H), 0.98 (d, *J* = 7.3 Hz, 6H), 0.90–0.81 (m, 2H), -0.04 (d, *J* = 3.7 Hz, 3H) ppm. **¹³C{¹H} NMR** (126 MHz, C₆D₆, 298 K): δ = 19.0, 18.4, 11.2, -10.4 ppm. **²⁹Si{¹H} DEPT NMR** (99 MHz, C₆D₆, 298 K, optimized for *J* = 200 Hz, 90.0°): δ = 4.0 ppm. **HRMS** (APCI): calculated for C₇H₁₇Si⁺ [M-H]⁺: 129.1094; found: 129.1093.

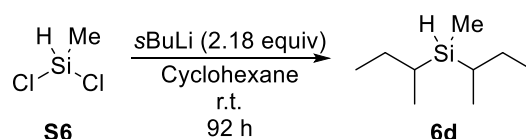
2.4 Di-*tert*-butyl(methyl)silane (**6c**)



Dichloromethylsilane (**S6**, 4.00 mL, 4.40 g, 38.3 mmol, 1.00 equiv) was dissolved in *n*-pentane (10 mL) and cooled with an ice bath. *tert*-Butyllithium (1.90M in *n*-pentane, 40.2 mL, 76.4 mmol, 1.99 equiv) was added dropwise over a period of 30 min. The reaction mixture was stirred for 66 h at room temperature. The mixture was filtered, the solvent was removed under reduced

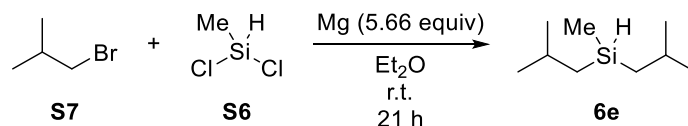
pressure and the crude product was purified by distillation at atmospheric pressure (b.p. 155°C). The product **6c** was obtained as a colorless oil (4.64 g, 77%). **IR** (ATR): $\tilde{\nu}$ = 2929, 2855, 2093, 1467, 1363, 1252, 1009, 870, 831, 720 cm^{-1} . **^1H NMR** (500 MHz, C_6D_6 , 298 K): δ = 3.64 (q, J = 3.7 Hz, 1H), 0.99 (s, 18H), 0.00 (d, J = 3.7 Hz, 3H) ppm. **$^{13}\text{C}\{^1\text{H}\}$ NMR** (126 MHz, C_6D_6 , 298 K): δ = 28.6, 18.3, -9.7 ppm. **^{29}Si DEPT NMR** (99 MHz, C_6D_6 , 298 K, optimized for J = 200 Hz, 90.0°): δ = 10.2 ppm. **HRMS** (APCI): calculated for $\text{C}_9\text{H}_{21}\text{Si}^+$ $[\text{M}-\text{H}]^+$: 157.1407; found: 157.1408.

2.5 Di-sec-butyl(methyl)silane (**6d**)



sec-Butyllithium (1.30M in cyclohexane, 45.0 mL, 58.5 mmol, 2.18 equiv) was cooled with an ice bath and dichloromethylsilane (**S6**, 2.80 mL, 3.08 g, 26.8 mmol, 1.00 equiv) was added dropwise over a period of 10 min. The reaction mixture was stirred for 92 h at room temperature. The mixture was filtered, the solvent was removed under reduced pressure and the residue was purified by distillation at atmospheric pressure (b.p. 157°C). The product **6d** was obtained as a colorless oil (999 mg, 24%). **IR** (ATR): $\tilde{\nu}$ = 2955, 2866, 2097, 1457, 1376, 1249, 1093, 1032, 1000, 965, 850, 820, 724 cm^{-1} . **^1H NMR** (700 MHz, C_6D_6 , 298 K): δ = 3.89–3.79 (m, 1H), 1.54 (m_c , 2H), 1.23 (m_c , 2H), 1.01 (m_c , 3H), 0.98–0.93 (m, 9H), 0.73 (m_c , 2H), 0.00 (m_c , 3H) ppm. **$^{13}\text{C}\{^1\text{H}\}$ NMR** (175 MHz, C_6D_6 , 298 K): δ = 27.25, 26.67, 26.55, 25.93, 18.91, 18.88, 18.71, 18.61, 15.39, 15.29, 14.92, 14.90, 13.50, 13.48, 13.46, 13.43, -9.35, -9.80, -10.19 ppm. **$^{29}\text{Si}\{^1\text{H}\}$ IG NMR** (99 MHz, C_6D_6 , 298 K): δ = 0.9, -0.3, -0.9 ppm. **HRMS** (APCI): calculated for $\text{C}_9\text{H}_{21}\text{Si}^+$ $[\text{M}-\text{H}]^+$: 157.1407; found: 157.1406.

2.6 Diisobutyl(methyl)silane (**6e**)



Magnesium turnings (11.2 g, 460 mmol, 5.66 equiv) were heated and stirred in vacuo for 15 min. Diethylether (60 mL) and three small iodine crystals were added. Isobutyl bromide (**S7**, 20.0 mL, 25.2 g, 184 mmol, 2.26 equiv) was added dropwise over a period of 15 min, to maintain gentle reflux. Diethylether (70 mL) was added, and the solution was heated for 3 h to 70°C. The reaction mixture was cooled to room temperature and dichloromethylsilane (**S6**, 8.50 mL, 9.35 g, 81.3 mmol, 1.00 equiv) was added dropwise over a period of 15 min. The reaction mixture was stirred for 21 h at room temperature and heated for 3 h at 70°C. The reaction mixture was cooled with an ice bath and hydrochloric acid (1.00M) was added slowly

until the magnesium was dissolved. The phases were separated, and the aqueous layer was extracted with diethylether (2 × 10 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and filtered. The solvent was removed under reduced pressure and the crude product was purified by distillation at atmospheric pressure (b.p. 161°C). The product **6e** was obtained as a colorless oil (7.52 g, 58%). **IR** (ATR): $\tilde{\nu}$ = 2952, 2868, 2110, 1462, 1380, 1327, 1251, 1214, 1163, 1089, 1034, 858 cm⁻¹. **¹H NMR** (700 MHz, C₆D₆, 298 K): δ = 4.13 (oct, J = 3.6 Hz, 1H), 1.75 (non, J = 6.7 Hz, 2H), 0.97 (d, J = 6.7 Hz, 12H), 0.59 (ddd, J = 14.6 Hz, 7.2 Hz, 3.1 Hz, 2H), 0.53 (ddd, J = 14.6 Hz, 6.9 Hz, 3.9 Hz, 2H), 0.07 (d, J = 3.8 Hz, 3H) ppm. **¹³C{¹H} NMR** (126 MHz, C₆D₆, 298 K): δ = 26.2, 26.0, 25.7, 24.3, -4.9 ppm. **²⁹Si{¹H} IG NMR** (99 MHz, C₆D₆, 298 K): δ = -14.9 ppm. **HRMS** (APCI): calculated for C₉H₂₁Si⁺ [M-H]⁺: 157.1407; found: 157.1407.

3 Experimental Details for the Silylium-Ion-Initiated Twofold Halodealkylation

3.1 Optimization of the Twofold Chlorodeethylation of Tetraethylsilane (**1a**)

Table S1 Optimization of the reaction conditions for the catalytic twofold chlorodeethylation of tetraethylsilane (**1a**) in the presence of 1,2-dichloroethane **2a** initiated by catalytic amounts [Me₃Si(HCB₁₁H₅Br₆)] (**5**).^a

$$\text{Et-Si(Et)}_3 + \text{Cl-CH}_2\text{-CH}_2\text{-Cl} \xrightarrow[\text{temp., time}]{\text{C}_6\text{D}_6, [\text{Me}_3\text{Si}(\text{HCB}_{11}\text{H}_5\text{Br}_6)] (\mathbf{5})} \text{Et-Si(Et)}_2\text{Cl} + \text{Et-Si(Et)}\text{Cl}_2$$

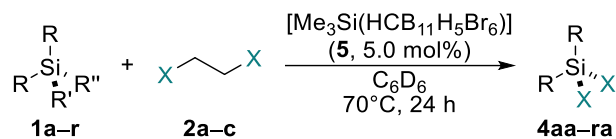
1a
2a
3aa
4aa

Entry	5 / mol%	Temp. / °C	Time / h	3aa ^b / %	4aa ^b / %
1	1.0	r.t.	14	84	16
2	1.0	50	14	68	32
3	1.0	70	14	57	43
4	1.0	70	24	56	44
5	1.0	70	48	48	52
6	5.0	70	48	<5	>95
7	5.0	70	24	<5	>95
8	2.5	70	24	17	83

^aReactions were performed on a 20.0 μmol scale and 1.0 equiv of each **1a** and **2a** were used.

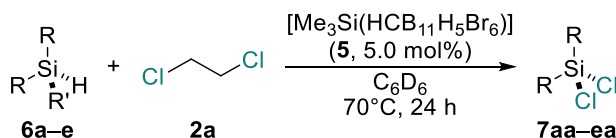
^bYields were determined by quantitative ¹H NMR analysis of the crude reaction mixture using cyclohexane as an internal standard.

3.2 General Procedure for the Twofold Halodealkylation of Tetraalkylsilanes with 1,2-Dihaloethane (GP 1)



In a high-quality glovebox (O_2 , H_2O < 1.0 ppm), $[\text{Me}_3\text{Si}(\text{HCB}_{11}\text{H}_5\text{Br}_6)]$ (**5**, 3.0 mg, 4.35 μmol , 5.00 mol%) was suspended in C_6D_6 (0.6 mL, 0.145M) and the indicated silane (**1a-r**, 87.0 μmol , 1.00 equiv) and the indicated 1,2-dihaloethane (**2a-c**, 87.0 μmol , 1.00 equiv) were added consecutively. The reaction mixture was stirred for 24 h at 70°C and cyclohexane (8.0 μL , 6.2 mg, 74.1 μmol) or the indicated amount of 1,2,4,5-tetrachlorobenzene was added as an internal NMR standard. The reaction mixture was transferred to a J. Young NMR tube and immediately subjected to NMR analysis.

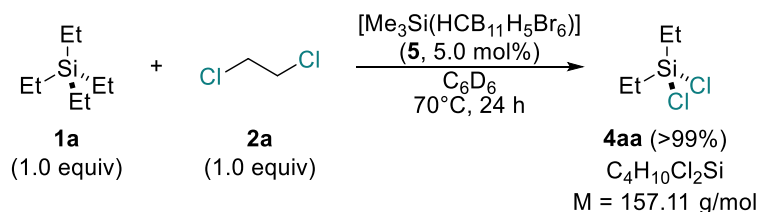
3.3 General Procedure for the Chlorodehydrogenation and Chlorodealkylation of Trialkylhydrosilanes with 1,2-Dichloroethane (GP 2)



In a high-quality glovebox (O_2 , H_2O < 1.0 ppm), $[\text{Me}_3\text{Si}(\text{HCB}_{11}\text{H}_5\text{Br}_6)]$ (**5**, 3.0 mg, 4.35 μmol , 5.00 mol%) was suspended in C_6D_6 (0.6 mL, 0.145M) and the indicated silane (**6a-e**, 87.0 μmol , 1.00 equiv) and 1,2-dichloroethane (**2a**, 87.0 μmol , 1.00 equiv) were added consecutively. The reaction mixture was stirred for 24 h at 70°C and cyclohexane (8.0 μL , 6.2 mg, 74.1 μmol) or the indicated amount of 1,2,4,5-tetrachlorobenzene was added as an internal NMR standard. The reaction mixture was transferred to a J. Young NMR tube and immediately subjected to NMR analysis.

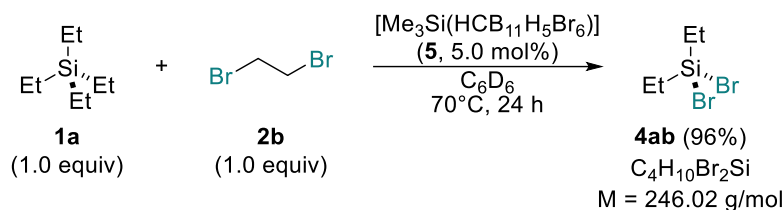
4 Characterization Data of the Halodealkylation Products of Tetraalkylsilanes

4.1 Dichlorodiethylsilane (**4aa**) by Chlorodeethylation of Tetraethylsilane (**1a**) with 1,2-Dichloroethane (**2a**)



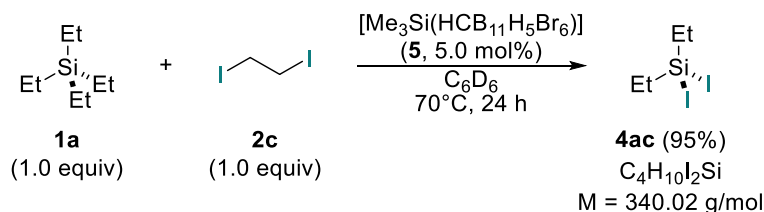
Prepared from tetraethylsilane (**1a**) with 1,2-dichloroethane (**2a**) according to **GP 1**. Quantitative ^1H NMR spectroscopy revealed a yield of >99% of **4aa** with cyclohexane as an internal standard. ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 0.86$ (t, $J = 7.8$ Hz, 6H), 0.70 (q, $J = 7.7$ Hz, 4H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 12.2, 6.1$ ppm. $^{29}\text{Si}\{^1\text{H}\}$ IG NMR (99 MHz, C_6D_6 , 298 K): $\delta = 36.0$ ppm. The NMR spectroscopic data are in accordance with those reported.^{S5}

4.2 Dibromodiethylsilane (**4ab**) by Bromodeethylation of Tetraethylsilane (**1a**) with 1,2-Dibromoethane (**2b**)



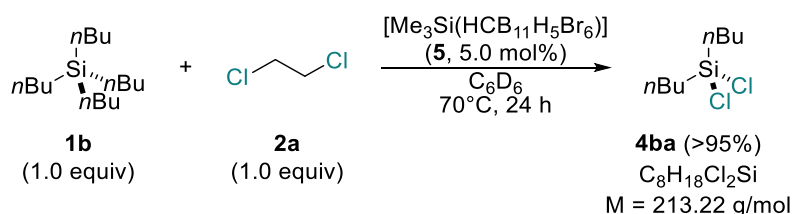
Prepared from tetraethylsilane (**1a**) with 1,2-dibromoethane (**2b**) according to **GP 1**. Quantitative ^1H NMR spectroscopy revealed a yield of 96% of **4ab** with cyclohexane as an internal standard. ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 0.86$ (m, 10H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 14.4, 7.0$ ppm. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 18.4°): $\delta = 31.2$ ppm. The NMR spectroscopic data are in accordance with those reported.^{S6}

4.3 Diethyldiiodosilane (**4ac**) by Iododeethylation of Tetraethylsilane (**1a**) with 1,2-Diiodoethane (**2c**)



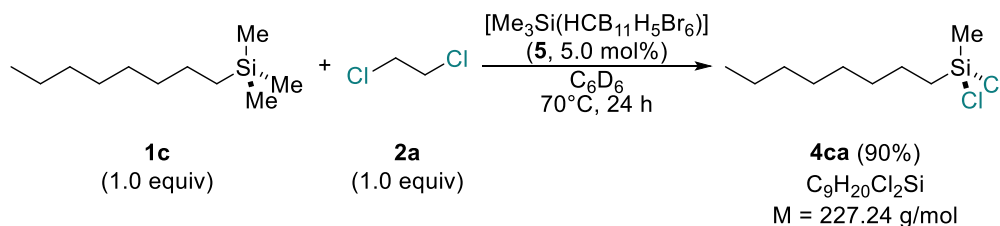
Prepared from tetraethylsilane (**1a**) with 1,2-diiodoethane (**2c**) according to **GP 1**. Quantitative ^1H NMR spectroscopy revealed a yield of 95% of **4ac** with cyclohexane as an internal standard. ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 1.11$ (q, $J = 7.7$ Hz, 4H), 0.79 (t, $J = 7.7$ Hz, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 16.3, 8.8$ ppm. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 18.4°): $\delta = -4.5$ ppm. The NMR spectroscopic data are in accordance with those reported.^{S7}

4.4 Dibutyldichlorosilane (**4ba**) by Chlorodebutylation of Tetrabutylsilane (**1b**) with 1,2-Dichloroethane (**2a**)



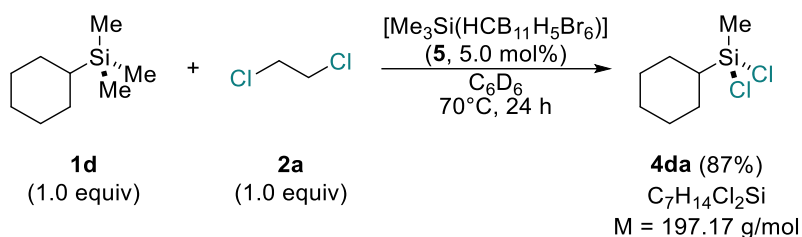
Prepared from tetrabutylsilane (**1b**) with 1,2-dichloroethane (**2a**) according to **GP 1**. Quantitative ^1H NMR spectroscopy revealed a yield of >95% of **4ba** with cyclohexane as an internal standard. ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 1.40$ – 1.33 (m, 4H), 1.19 (sex, $J = 7.4$ Hz, 4H), 0.89–0.82 (m, 4H), 0.79 (t, $J = 7.4$ Hz, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 25.8, 24.9, 20.3, 13.7$ ppm. $^1\text{H},^{29}\text{Si}$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz): $\delta = 1.37/33.4, 0.85/33.4$ ppm. The NMR spectroscopic data are in accordance with those reported.^{S8}

4.5 Dichloro(methyl)(octyl)silane (**4ca**) by Chlorodemethylation of Trimethyl(octyl)silane (**1c**) with 1,2-Dichloroethane (**2a**)



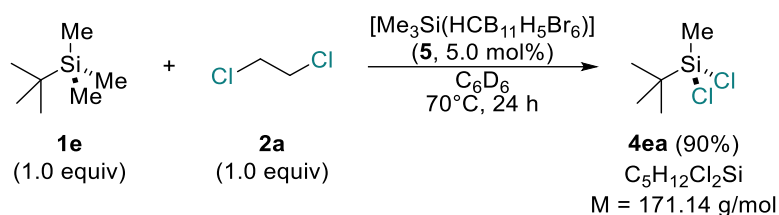
Prepared from trimethyl(octyl)silane (**1c**) with 1,2-dichloroethane (**2a**) according to **GP 1**. Quantitative ^1H NMR spectroscopy revealed a yield of 90% of **4ca** with cyclohexane as an internal standard. ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 1.39$ – 1.11 (m, 11H), 0.91 (t, $J = 7.1$ Hz, 3H), 0.80 (m_c , 2H), 0.40 (s, 3H) ppm. $^1\text{H},^{29}\text{Si}$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz): $\delta = 0.80/32.5, 0.40/32.5$ ppm. The NMR spectroscopic data are in accordance with those reported.^{S9}

4.6 Dichloro(cyclohexyl)(methyl)silane (**4da**) by Chlorodemethylation of Cyclohexyltrimethylsilane (**1d**) with 1,2-Dichloroethane (**2a**)



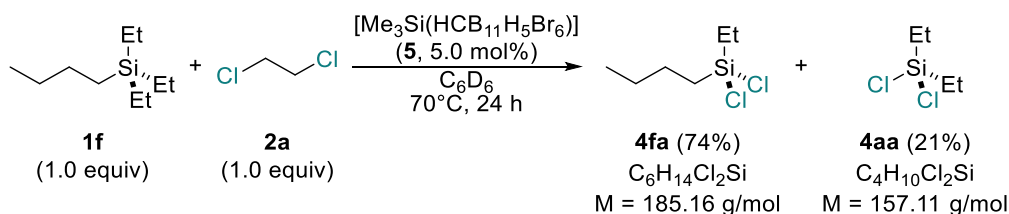
Prepared from cyclohexyltrimethylsilane (**1d**) with 1,2-dichloroethane (**2a**) according to **GP 1**. Quantitative ^1H NMR spectroscopy revealed a yield of 87% of **4da** with cyclohexane as an internal standard. ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 1.71\text{--}1.65$ (m, 2H), 1.60–1.51 (m, 3H), 1.15–0.96 (m, 5H), 0.78 (tt, $J = 12.5$ Hz, $J = 3.1$ Hz, 1H), 0.39 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 30.7, 27.2, 26.5, 25.9, 2.8$ ppm. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 30.0°): $\delta = 32.4$ ppm. The NMR spectroscopic data are in accordance with those reported.^{S10}

4.7 *tert*-Butyldichloro(methyl)silane (**4ea**) by Chlorodemethylation of *tert*-Butyltrimethylsilane (**1e**) with 1,2-Dichloroethane (**2a**)



Prepared from *tert*-butyltrimethylsilane (**1e**) with 1,2-dichloroethane (**2a**) according to **GP 1**. Quantitative ^1H NMR spectroscopy revealed a yield of 90% of **4ea** with cyclohexane as an internal standard. ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 0.89$ (s, 9H), 0.38 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 24.6, 22.4, 1.4$ ppm. $^1\text{H},^{29}\text{Si}$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz): $\delta = 0.89/36.4, 0.38/36.4$ ppm. The NMR spectroscopic data are in accordance with those of a commercially obtained sample.

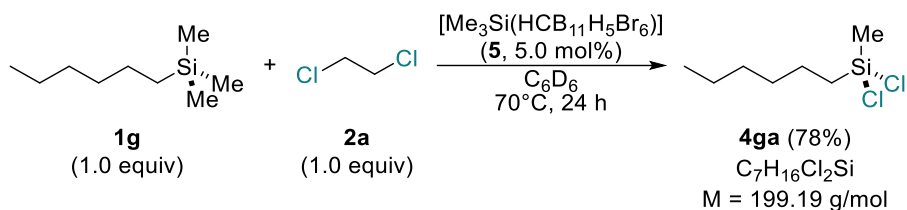
4.8 Butyldichloro(ethyl)silane (**4fa**) by Chloroethylation of Butyltriethylsilane (**1f**) with 1,2-Dichloroethane (**2a**)



Prepared from butyltriethylsilane (**1f**) with 1,2-dichloroethane (**2a**) according to **GP 1**. Quantitative ^1H NMR spectroscopy revealed a yield of 74% of **4fa** and 21% of dichlorodiethylsilane (**4aa**) as a side product with 1,2,4,5-tetrachlorobenzene (15.4 mg) as an internal standard. NMR data for **4fa**: ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 1.36\text{--}1.28$ (m, 2H), 1.15 (sex, $J = 7.4$ Hz, 2H), 0.90 (t, $J = 7.8$ Hz, 3H), 0.82–0.76 (m, 2H), 0.78–0.74 (m, 3H), 0.77–0.72 (m, 2H)

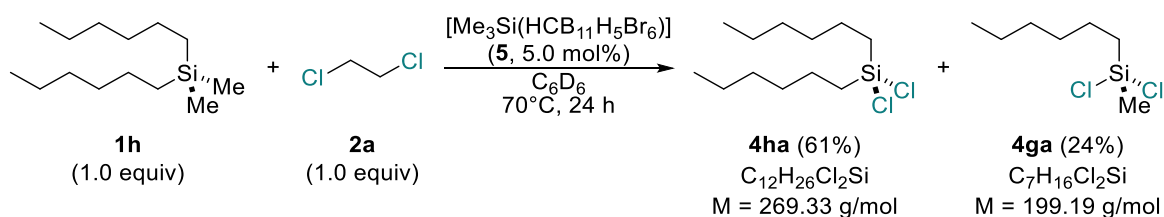
ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 25.7, 24.8, 19.7, 13.7, 12.7, 6.2$ ppm. $^1\text{H},^{29}\text{Si}$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz): $\delta = 1.32/34.7, 0.90/34.7, 0.80/34.7, 0.76/34.7$ ppm. The NMR spectroscopic data are in accordance with those reported.^{S11} NMR data for **4aa**: ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 0.86$ (t, $J = 7.7$ Hz, 6H), 0.70 (q, $J = 7.4$ Hz, 4H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 12.2, 6.1$ ppm. $^1\text{H},^{29}\text{Si}$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz): $\delta = 0.86/36.0, 0.70/36.0$ ppm. The NMR spectroscopic data are in accordance with those reported.^{S5}

4.9 Dichloro(hexyl)(methyl)silane (**4ga**) by Chlorodemethylation of Hexyltrimethylsilane (**1g**) with 1,2-Dichloroethane (**2a**)



Prepared from hexyltrimethylsilane (**1g**) with 1,2-dichloroethane (**2a**) according to **GP 1**. Quantitative ^1H NMR spectroscopy revealed a yield of 78% of **4ga** with cyclohexane as an internal standard. ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 1.36\text{--}1.28$ (m, 2H), 1.21 (sex, $J = 7.0$ Hz, 2H), 1.16–1.06 (m, 4H), 0.87 (t, $J = 7.3$ Hz, 3H), 0.78 (m_c , 2H), 0.40 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 32.3, 31.6, 22.8, 22.6, 21.7, 14.3, 4.9$ ppm. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 22.2°): $\delta = 32.8$ ppm. The NMR spectroscopic data are in accordance with those reported.^{S5,S9}

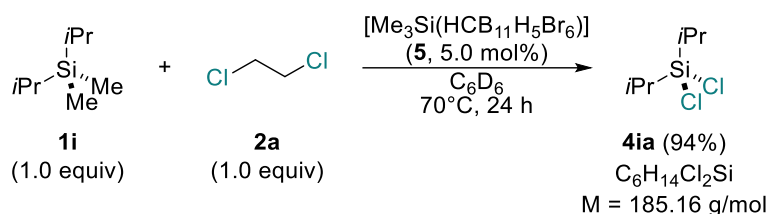
4.10 Dichlorodihexylsilane (**4ha**) by Chlorodemethylation of Dihexyldimethylsilane (**1h**) with 1,2-Dichloroethane (**2a**)



Prepared from dihexyldimethylsilane (**1h**) with 1,2-dichloroethane (**2a**) according to **GP 1**. Quantitative ^1H NMR spectroscopy revealed a yield of 61% of **4ha** and 24% of dichloro(hexyl)(methyl)silane (**4ga**) as a side product with 1,2,4,5-tetrachlorobenzene (19.5 mg, 90.3 μmol) as an internal standard. NMR data for **4ha**: ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 1.46\text{--}1.38$ (m, 4H), 1.28–1.10 (m, 12H), 0.91–0.85 (m, 10H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 32.4, 31.6, 22.9, 22.7, 20.6, 14.3$ ppm. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 20.7°): $\delta = 33.5$ ppm. The NMR spectroscopic data are in accordance with those reported.^{S8} NMR data for **4ga**: ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 1.36\text{--}1.06$ (m, 8H), 0.91–0.84 (m, 3H), 0.78 (m_c , 2H), 0.40 (s, 3H) ppm.

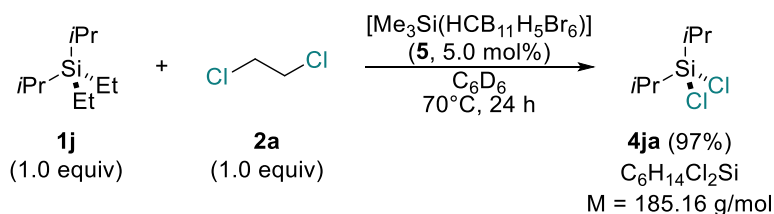
$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 32.3, 31.6, 22.9, 22.7, 21.7, 14.4, 4.9$ ppm.
 $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 20.7°): $\delta = 32.8$ ppm.
 The NMR spectroscopic data are in accordance with those reported.^{S5,S9}

4.11 Dichlorodiisopropylsilane (**4ia**) by Chlorodemethylation of Diisopropyldimethylsilane (**1i**) with 1,2-Dichloroethane (**2a**)



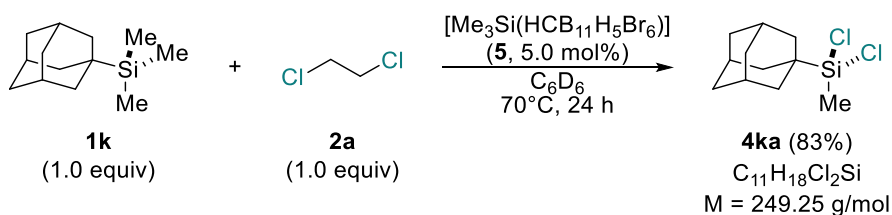
Prepared from diisopropyldimethylsilane (**1i**) with 1,2-dichloroethane (**2a**) according to **GP 1**. Quantitative ^1H NMR spectroscopy revealed a yield of 94% of **4ia** with cyclohexane as an internal standard. ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 1.05\text{--}0.98$ (m, 2H), 0.95 (d, $J = 6.3$ Hz, 12H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 17.4, 16.3$ ppm. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 15.5°): $\delta = 38.0$ ppm. The NMR spectroscopic data are in accordance with those reported.^{S5}

4.12 Dichlorodiisopropylsilane (**4ja**) by Chloroethylation of Diethyldiisopropylsilane (**1j**) with 1,2-Dichloroethane (**2a**)



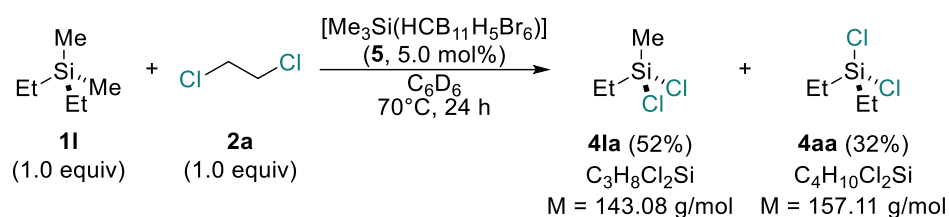
Prepared from diethyldiisopropylsilane (**1j**) with 1,2-dichloroethane (**2a**) according to **GP 1**. Quantitative ^1H NMR spectroscopy revealed a yield of 97% of **4ja** (= **4ia**) with cyclohexane as an internal standard. ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 1.04\text{--}0.98$ (m, 2H), 0.95 (d, $J = 6.4$ Hz, 12H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 17.4, 16.3$ ppm. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 15.5°): $\delta = 38.0$ ppm. The NMR spectroscopic data are in accordance with those reported.^{S5}

4.13 1-Adamantylchloro(methyl)silane (**4ka**) by Chlorodemethylation of 1-Adamantyltrimethylsilane (**1k**) with 1,2-Dichloroethane (**2a**)



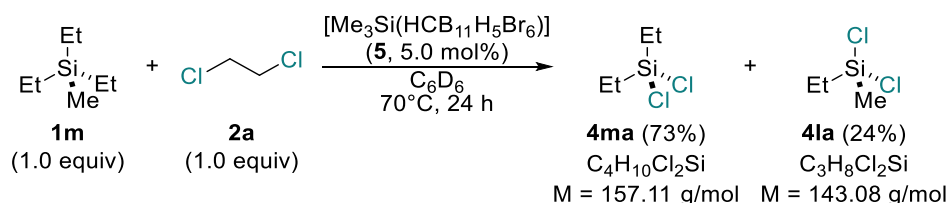
Prepared from 1-adamantyltrimethylsilane (**1k**) with 1,2-dichloroethane (**2a**) according to **GP 1**. Quantitative ^1H NMR spectroscopy revealed a yield of 83% of **4ka** with 1,2,4,5-tetrachlorobenzene (7.2 mg, 33.4 μmol) as an internal standard. ^1H NMR (500 MHz, C_6D_6 , 298 K): δ = 1.77–1.65 (m, 9H), 1.64–1.50 (m, 6H), 0.40 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): δ = 36.8, 35.2, 27.4, 26.9, 0.6 ppm. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, C_6D_6 , 298 K, optimized for J = 7 Hz, 15.5°): δ = 32.1 ppm.

4.14 Dichloro(ethyl)(methyl)silane (**4la**) by Chlorodemethylation and Chlorodeethylation of Diethyldimethylsilane (**1l**) with 1,2-Dichloroethane (**2a**)



Prepared from diethyldimethylsilane (**1l**) with 1,2-dichloroethane (**2a**) according to **GP 1**. Quantitative ^1H NMR spectroscopy revealed a yield of 52% of **4la** and 32% of dichlorodiethylsilane (**4aa**) as a side product with cyclohexane as an internal standard. NMR data for **4la**: ^1H NMR (700 MHz, C_6D_6 , 298 K): δ = 0.82 (t, J = 7.8 Hz, 3H), 0.67 (q, J = 7.8 Hz, 2H), 0.33 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): δ = 13.9, 6.1, 4.2 ppm. $^1\text{H},^{29}\text{Si}$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for J = 7 Hz): δ = 0.82/34.0, 0.67/34.0, 0.33/34.0 ppm. The NMR spectroscopic data are in accordance with those reported.^{S12} NMR data for **4aa**: ^1H NMR (700 MHz, C_6D_6 , 298 K): δ = 0.86 (t, J = 7.8 Hz, 6H), 0.70 (q, J = 7.8 Hz, 4H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): δ = 12.2, 6.1 ppm. $^1\text{H},^{29}\text{Si}$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for J = 7 Hz): δ = 0.86/35.9, 0.70/35.9 ppm. The NMR spectroscopic data are in accordance with those reported.^{S5}

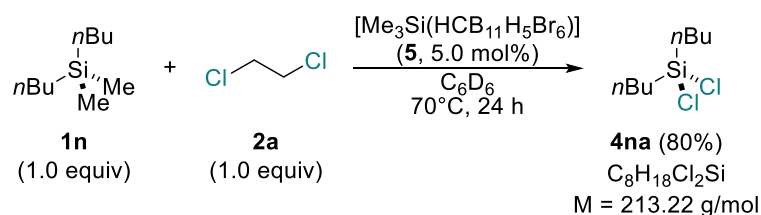
4.15 Dichlorodiethylsilane (**4ma**) by Chlorodemethylation and Chlorodeethylation of Triethyl(methyl)silane (**1m**) with 1,2-Dichloroethane (**2a**)



Prepared from triethyl(methyl)silane (**1m**) with 1,2-dichloroethane (**2a**) according to **GP 1**. Quantitative ^1H NMR spectroscopy revealed a yield of 73% of **4ma** and 24% of dichloro(ethyl)(methyl)silane (**4la**) as a side product with cyclohexane as an internal standard. NMR data for **4ma**: ^1H NMR (500 MHz, C_6D_6 , 298 K): δ = 0.86 (t, J = 7.7 Hz, 6H), 0.70 (q, J = 7.8 Hz, 4H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): δ = 12.2, 6.1 ppm. $^1\text{H},^{29}\text{Si}$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for J = 7 Hz): δ = 0.86/35.9, 0.70/35.9 ppm. The

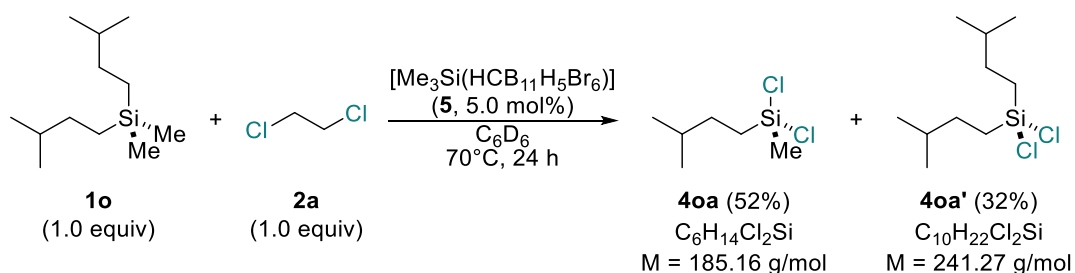
NMR spectroscopic data are in accordance with those reported.^{S5} NMR data for **4la** (24% yield): ¹H NMR (500 MHz, C₆D₆, 298 K): δ = 0.82 (t, *J* = 7.7 Hz, 3H), 0.70–0.64 (m, 2H), 0.33 (s, 3H) ppm. ¹³C{¹H} NMR (126 MHz, C₆D₆, 298 K): δ = 13.9, 6.1, 4.2 ppm. ¹H,²⁹Si HMQC NMR (500/99 MHz, C₆D₆, 298 K, optimized for *J* = 7 Hz): δ = 0.82/34.0, 0.67/34.0, 0.33/34.0 ppm. The NMR spectroscopic data are in accordance with those reported.^{S12}

4.16 Dibutyldichlorosilane (**4na**) by Chlorodemethylation of Dibutyldimethylsilane (**1n**) with 1,2-Dichloroethane (**2a**)



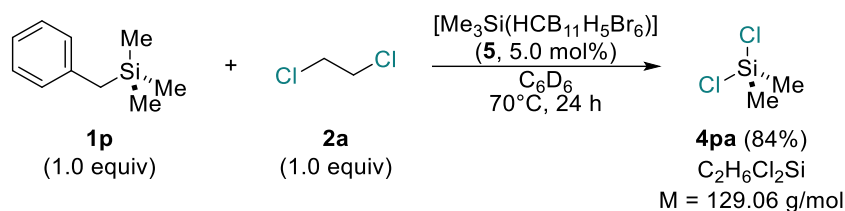
Prepared from dibutyldimethylsilane (**1n**) with 1,2-dichloroethane (**2a**) according to **GP 1**. Quantitative ¹H NMR spectroscopy revealed a yield of 80% of **4na** (= **4ba**) with cyclohexane as an internal standard. ¹H NMR (500 MHz, C₆D₆, 298 K): δ = 1.40–1.32 (m, 4H), 1.18 (sex, *J* = 7.3 Hz, 4H), 0.84 (m_c, 4H), 0.78 (t, *J* = 7.4 Hz, 6H) ppm. ¹³C{¹H} NMR (126 MHz, C₆D₆, 298 K): δ = 25.8, 24.8, 20.2, 13.7 ppm. ²⁹Si{¹H} DEPT NMR (99 MHz, C₆D₆, 298 K, optimized for *J* = 7 Hz, 20.7°): δ = 33.5 ppm. The NMR spectroscopic data are in accordance with those reported.^{S8}

4.17 Dichloro(isopentyl)(methyl)silane (**4oa**) by Chlorodemethylation and Chlorodeisopentylation of Diisopentyldimethylsilane (**1o**) with 1,2-Dichloroethane (**2a**)



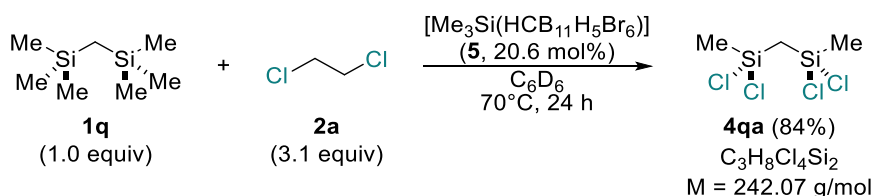
Prepared from diisopentyldimethylsilane (**1o**) with 1,2-dichloroethane (**2a**) according to **GP 1**. Quantitative ¹H NMR spectroscopy revealed a yield of 52% of **4oa** and 32% of dichlorodiiisopentylsilane (**4oa'**) as a side product with 1,2,4,5-tetrachlorobenzene (19.2 mg, 88.9 μmol) as an internal standard. NMR data for **4oa**: ¹H NMR (500 MHz, C₆D₆, 298 K): δ = 1.36–1.31 (m, 1H), 1.26–1.20 (m, 2H), 0.82–0.73 (m, 8H), 0.40 (s, 3H) ppm. ¹³C{¹H} NMR (126 MHz, C₆D₆, 298 K): δ = 31.4, 30.4, 22.0, 19.4, 4.7 ppm. ²⁹Si{¹H} DEPT NMR (99 MHz, C₆D₆, 298 K, optimized for *J* = 7 Hz, 22.2°): δ = 33.3 ppm. NMR data for **4oa'**: ¹H NMR (500 MHz, C₆D₆, 298 K): δ = 1.37–1.30 (m, 6H), 0.92–0.84 (m, 16H) ppm. ¹³C{¹H} NMR (126 MHz, C₆D₆, 298 K): δ = 31.5, 30.3, 22.0, 18.1 ppm. ²⁹Si{¹H} DEPT NMR (99 MHz, C₆D₆, 298 K, optimized for *J* = 7 Hz, 22.2°): δ = 34.5 ppm.

4.18 Dichlorodimethylsilane (**4pa**) by Chlorodemethylation and Chlorodebenzylation of Benzyltrimethylsilane (**1p**) with 1,2-Dichloroethane (**2a**)



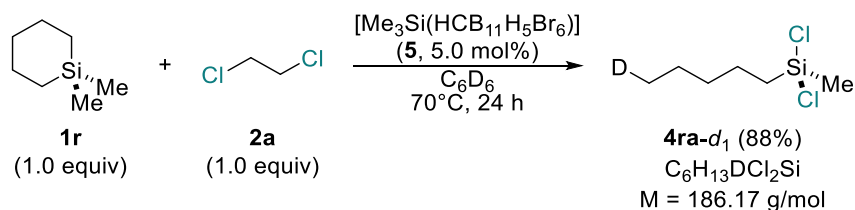
Prepared from benzyltrimethylsilane (**1p**) with 1,2-dichloroethane (**2a**) according to **GP 1**. Quantitative 1H NMR spectroscopy revealed a yield of 84% of **4pa** with cyclohexane as an internal standard. 1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 0.32$ (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 6.1$ ppm. $^{29}Si\{^1H\}$ IG NMR (99 MHz, C_6D_6 , 298 K): $\delta = 32.1$ ppm. The NMR spectroscopic data are in accordance with those reported.^{S13}

4.19 Bis(dichloro(methyl)silyl)methane (**4qa**) by Chlorodemethylation of Bis(trimethylsilyl)methane (**1q**) with 1,2-Dichloroethane (**2a**)



Prepared from bis(trimethylsilyl)methane (**1q**, 4.5 μL , 3.4 mg, 21.1 μmol , 1.00 equiv) with 1,2-dichloroethane (**2a**, 5.3 μL , 6.6 mg, 66.3 μmol , 3.1 equiv) and $[Me_3Si(HCB_{11}H_5Br_6)]$ (**5**, 4.3 mg, 17.7 μmol , 20.6 mol%) according to **GP 1**. Quantitative 1H NMR spectroscopy revealed a yield of 84% of **4qa** with cyclohexane as an internal standard. 1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 0.60$ (s, 2H), 0.46 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 16.8$, 7.1 ppm. $^{29}Si\{^1H\}$ INEPT NMR (99 MHz, $J = 7$ Hz, C_6D_6 , without decoupling in F1 dimension): $\delta = 25.9$ (sex, $J = 7.9$ Hz) ppm. HRMS (APCI): calculated for $C_3H_8Si_2Cl_3^+$ $[M-Cl]^+$: 204.9225; found: 204.9224.

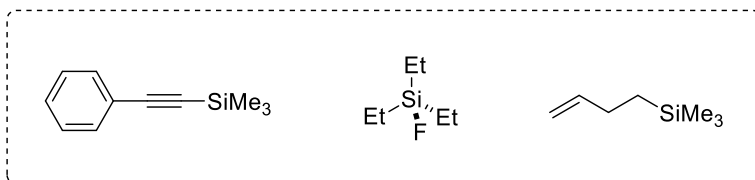
4.20 Dichloro(methyl)(pentyl)silane- d_1 (**4ra-d₁**) by Chlorodemethylation and Ring Opening of 1,1-Dimethylsilinane (**1r**) with 1,2-Dichloroethane (**2a**)



Prepared from 1,1-dimethylsilinane (**1r**) with 1,2-dichloroethane (**2a**) according to **GP 1**. Quantitative 1H NMR spectroscopy revealed a yield of 88% of **4ra-d₁** with cyclohexane as an internal standard. 1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 1.35$ – 1.28 (m, 2H), 1.16–1.07 (m, 4H),

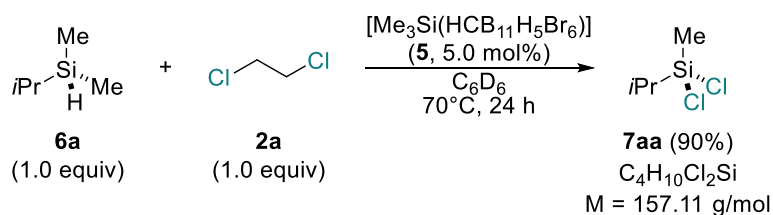
0.80 (tt, $^3J_{\text{HH}} = 6.9$ Hz, $^2J_{\text{HD}} = 2.0$ Hz, 2H), 0.77 (mc, 2H), 0.39 (s, 3H) ppm. $^2\text{H NMR}$ (77 MHz, C_6D_6 , 298 K): $\delta = 0.84\text{--}0.71$ (m) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 34.7, 22.34, 22.32, 21.6, 13.7$ (t, $^1J_{\text{CD}} = 19.2$ Hz), 4.9 ppm. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 20.7°): $\delta = 32.8$ ppm.

4.21 Tested unsuccessful substrates



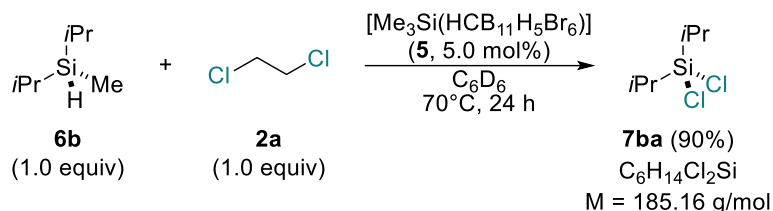
5 Characterization Data of the Chlorodehydrogenation and Chlorodealkylation Products of Trialkylhydrosilanes

5.1 Dichloro(isopropyl)(methyl)silane (**7aa**) by Chlorodehydrogenation and Chlorodemethylation of Isopropyldimethylsilane (**6a**) with 1,2-Dichloroethane (**2a**)



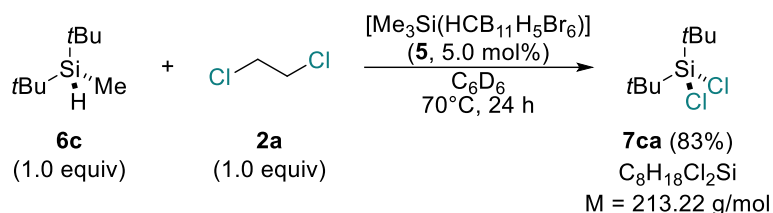
Prepared from isopropyldimethylsilane (**6a**) with 1,2-dichloroethane (**2a**) according to **GP 2**. Quantitative $^1\text{H NMR}$ spectroscopy revealed a yield of 90% of **7aa** with cyclohexane as an internal standard. $^1\text{H NMR}$ (500 MHz, C_6D_6 , 298 K): $\delta = 0.91\text{--}0.84$ (m, 7H), 0.34 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 19.6, 15.9, 2.6$ ppm. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 18.4°): $\delta = 35.2$ ppm.

5.2 Dichlorodiisopropylsilane (**7ba**) by Chlorodehydrogenation and Chlorodemethylation of Diisopropyl(methyl)silane (**6b**) with 1,2-Dichloroethane (**2a**)



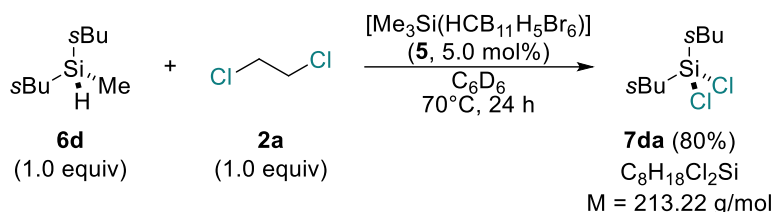
Prepared from diisopropyl(methyl)silane (**6b**) with 1,2-dichloroethane (**2a**) according to **GP 2**. Quantitative $^1\text{H NMR}$ spectroscopy revealed a yield of 90% of **7ba** with cyclohexane as an internal standard. $^1\text{H NMR}$ (500 MHz, C_6D_6 , 298 K): $\delta = 1.05\text{--}0.97$ (m, 2H), 0.95 (d, $J = 6.3$ Hz, 12H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 17.4, 16.3$ ppm. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 15.5°): $\delta = 38.0$ ppm. The NMR spectroscopic data are in accordance with those reported.^{S5}

5.3 Di-*tert*-butyldichlorosilane (**7ca**) by Chlorodehydrogenation and Chlorodemethylation of Di-*tert*-butyl(methyl)silane (**6c**) with 1,2-Dichloroethane (**2a**)



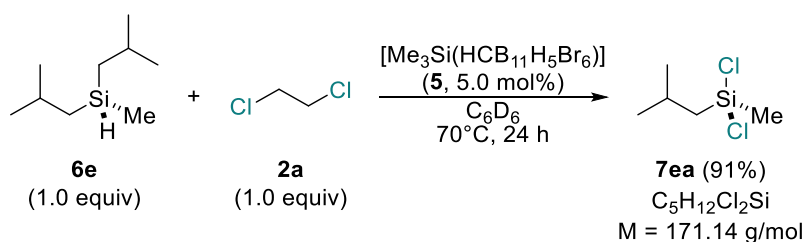
Prepared from di-*tert*-butyl(methyl)silane (**6c**) with 1,2-dichloroethane (**2a**) according to **GP 2**. Quantitative ^1H NMR spectroscopy revealed a yield of 83% of **7ca** with cyclohexane as an internal standard. ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 1.03$ (s, 18H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 26.9, 24.7$ ppm. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 13.6°): $\delta = 39.0$ ppm.

5.4 Di-*sec*-butyldichlorosilane (**7da**) by Chlorodehydrogenation and Chlorodemethylation of Di-*sec*-butyl(methyl)silane (**6d**) with 1,2-Dichloroethane (**2a**)



Prepared from di-*sec*-butyl(methyl)silane (**6d**) with 1,2-dichloroethane (**2a**) according to **GP 2**. Quantitative ^1H NMR spectroscopy revealed a yield of 80% of **7da** with 1,2,4,5-tetrachlorobenzene (18.4 mg, 85.2 μmol) as an internal standard. ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 1.64$ (m_c , 2H), 1.20 (m_c , 2H), 0.99–0.88 (m, 8H), 0.82 (td, $^3J = 7.4$ Hz, $^4J = 1.6$ Hz, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 24.78, 24.76, 23.60, 23.57, 12.89, 12.87, 12.53, 12.48$ ppm. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 13.6°): $\delta = 36.2$ ppm.

5.5 Dichloro(isobutyl)(methyl)silane (**7ea**) by Chlorodehydrogenation and Chlorodeisobutylation of Diisobutyl(methyl)silane (**6e**) with 1,2-Dichloroethane (**2a**)

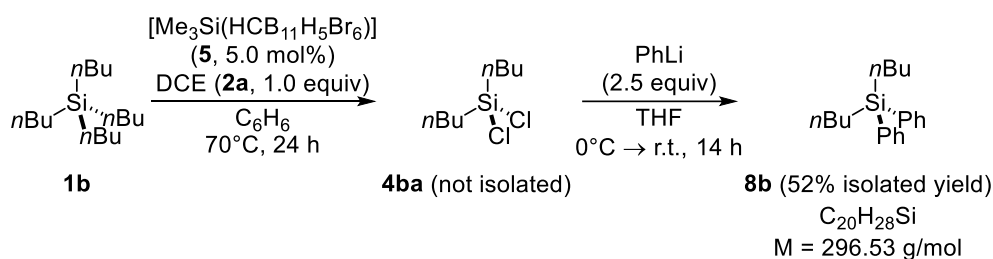


Prepared from diisobutyl(methyl)silane (**6e**) with 1,2-dichloroethane (**2a**) according to **GP 2**. Quantitative ^1H NMR spectroscopy revealed a yield of 91% of **7ea** with cyclohexane as an internal standard. ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 1.79$ (non, $J = 6.7$ Hz, 1H), 0.81 (d,

$J = 6.7$ Hz, 6H), 0.79 (d, $J = 6.9$ Hz, 2H), 0.42 (s, 3 H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 31.6, 25.4, 24.4, 6.1$ ppm. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 24.1°): $\delta = 32.0$ ppm. HRMS (APCI): calculated for $\text{C}_4\text{H}_9\text{SiCl}_2^+$ [M–Me] $^+$: 154.9845; found: 154.9838. The NMR spectroscopic data are in accordance with those reported.^{S5}

6 Synthesis of Heteroleptic Silanes by Successive Twofold Chlorodealkylation of Tetraalkylsilanes and Nucleophilic Substitution

6.1 Dibutyldiphenylsilane (**8b**) by Chlorodebutylation of Tetrabutylsilane (**1b**) and Nucleophilic Substitution with PhLi



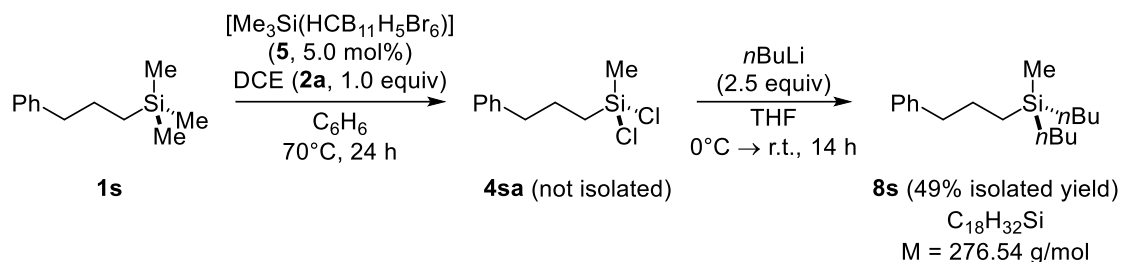
Chlorodemethylation:

The chlorodemethylation of tetrabutylsilane (**1b**, 256 mg, 1.00 mmol, 1.00 equiv) was performed using silylium carborate $[\text{Me}_3\text{Si}(\text{HCB}_{11}\text{H}_5\text{Br}_6)]$ (**5**, 34.5 mg, 0.05 mmol, 5.0 mol%) and 1,2-dichloroethane (**2a**, 79.0 μL , 99.0 mg, 1.00 mmol, 1.00 equiv) in C_6H_6 (2.0 mL) at 70°C for 24 h according to **GP 1**. Complete conversion was observed by $^1\text{H},^{29}\text{Si}$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz): $\delta = 1.37/33.4, 0.84/33.4$ ppm.

Nucleophilic substitution:

To the reaction mixture, anhydrous THF (2.0 mL) was added, followed by the addition of PhLi (1.30 mL of a 1.90M solution in dibutylether, 2.47 mmol, 2.47 equiv) at 0°C . The reaction mixture was then gradually warmed to room temperature and stirred for 12 h. The reaction mixture was quenched by the addition of water (5 mL) and saturated aqueous NH_4Cl solution (10 mL). The organic phase was separated, and the aqueous phase was extracted with Et_2O (3×10 mL). The combined organic layers were dried over MgSO_4 and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using n -pentane as eluent afforded dibutyldiphenylsilane (**8b**, 155 mg, 0.522 mmol, 52%) as a colorless oil. $R_f = 0.60$ (cyclohexane). ^1H NMR (500 MHz, CDCl_3 , 298 K): $\delta = 7.53\text{--}7.48$ (m, 4H), 7.40–7.32 (m, 6H), 1.39–1.28 (m, 8H), 1.13–1.05 (m, 4H), 0.87 (t, $J = 7.0$ Hz, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , 298 K): $\delta = 136.7, 134.8, 129.0, 127.7, 26.7, 25.9, 13.7, 12.3$ ppm. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3 , 298 K, optimized for $J = 7$ Hz, 30.0°): $\delta = -6.7$ ppm. The NMR spectroscopic data are in accordance with those reported.^{S14}

6.2 Dibutyl(methyl)(3-phenylpropyl)silane (**8s**) by Chlorodemethylation of Trimethyl(3-phenylpropyl)silane (**1s**) and Nucleophilic Substitution with *n*BuLi



Chlorodemethylation:

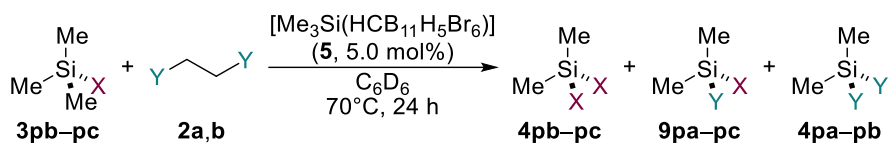
The chlorodemethylation of trimethyl(3-phenylpropyl)silane (**1s**, 192 mg, 1.00 mmol, 1.00 equiv) was performed using silylium carborate [$Me_3Si(HCB_{11}H_5Br_6)$] (**5**, 24.5 mg, 34.5 mmol, 5.0 mol%) and 1,2-dichloroethane (**2a**, 79.2 μ L, 99.0 mg, 99.0 mmol, 1.00 equiv) in C_6H_6 (2.5 mL) at 70°C for 24 h according to **GP 1**. Complete conversion was observed by $^1H,^{29}Si$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz): $\delta = 0.29/32.6, 0.73/32.6$ ppm.

Nucleophilic substitution:

To the reaction mixture, anhydrous THF (2.0 mL) was added, followed by the addition of *n*BuLi (1.00 mL of a 2.50M solution in *n*-hexane, 2.50 mmol, 2.50 equiv) at 0°C. The reaction mixture was then gradually warmed to room temperature and stirred for 12 h. The reaction mixture was quenched by the addition of water (5 mL) and saturated aqueous NH_4Cl solution (10 mL). The organic phase was separated, and the aqueous phase was extracted with Et_2O (3 \times 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using *n*-pentane as eluent afforded dibutyl(methyl)(3-phenylpropyl)silane (**8s**, 135.0 mg, 0.488 mmol, 49%) as a colorless oil. $R_f = 0.75$ (cyclohexane). 1H NMR (500 MHz, $CDCl_3$, 298 K): $\delta = 7.30\text{--}7.26$ (m, 2H), 7.20–7.16 (m, 3H), 2.62 (t, $J = 7.7$ Hz, 2H), 1.65–1.56 (m, 2H), 1.35–1.20 (m, 8H), 0.88 (t, $J = 7.2$ Hz, 6H), 0.55 (m_c , 2H), 0.48 (m_c , 4H), -0.08 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K): $\delta = 142.8, 128.4, 128.2, 125.6, 40.1, 26.7, 26.13, 26.11, 13.81, 13.79, 13.5, -5.2$ ppm. $^{29}Si\{^1H\}$ DEPT NMR (99 MHz, $CDCl_3$, 298 K, optimized for $J = 7$ Hz, 19.5°): $\delta = 2.9$ ppm.

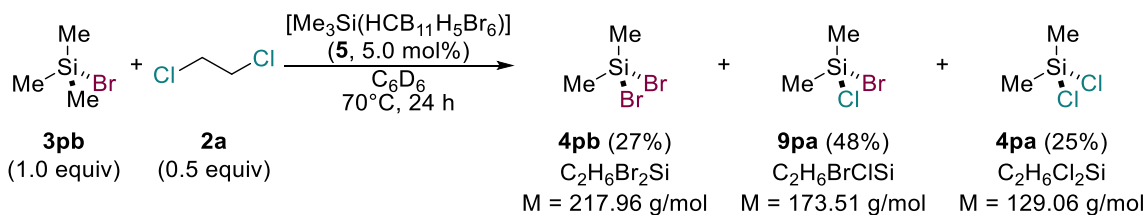
7 Attempted Preparation of Mixed Dihalosilanes by Halodemethylation of Trimethylhalosilanes with 1,2-Dihaloethane

7.1 General Procedure for the Halodemethylation of Trimethylhalosilanes with 1,2-Dihaloethane (GP 3)

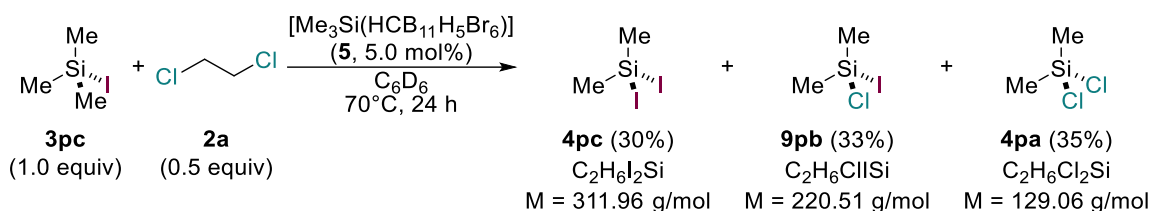


In a high-quality glovebox (O_2 , H_2O < 1.0 ppm), $[\text{Me}_3\text{Si}(\text{HCB}_{11}\text{H}_5\text{Br}_6)]$ (**5**, 3.0 mg, 4.35 μmol , 5.00 mol%) was suspended in C_6D_6 (0.6 mL, 0.145M) and the indicated trimethylhalosilane (**3pb-pc**, 87.0 μmol , 1.00 equiv) and the indicated 1,2-dihaloethane (**2**, 43.5 μmol , 0.50 equiv) were added consecutively. The reaction mixture was stirred for 24 h at 70°C and cyclohexane (8.0 μL , 6.2 mg, 74.1 μmol) was added as an internal NMR standard. The reaction mixture was transferred to a J. Young NMR tube and immediately subjected to NMR analysis.

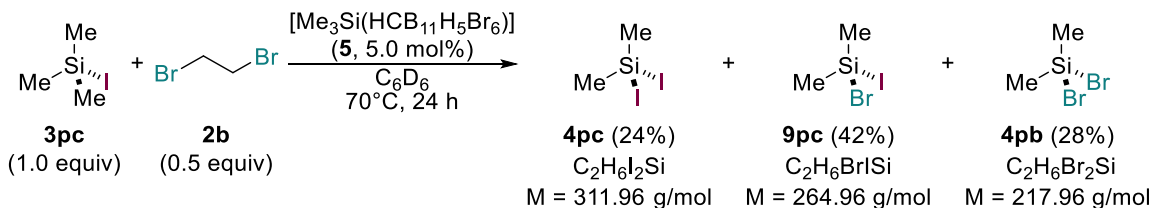
7.1.1 Chlorodemethylation of Bromotrimethylsilane (**3pb**) with 1,2-Dichloroethane (**2a**)



Prepared from bromotrimethylsilane (**3pb**) with 1,2-dichloroethane (**2a**) according to **GP 3**. Quantitative ^1H NMR spectroscopy revealed a yield of 27% of **4pb**, 48% of **9pa** and 25% of **4pa**. NMR data for **4pb**: ^1H NMR (500 MHz, C_6D_6 , 298 K): δ = 0.60 (s, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): δ = 9.0 ppm. $^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR (99 MHz, J = 7 Hz, C_6D_6 , without decoupling in F1 dimension): δ = 19.9 (sept, J = 7.7 Hz) ppm. NMR data for **9pa**: ^1H NMR (500 MHz, C_6D_6 , 298 K): δ = 0.45 (s, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): δ = 7.7 ppm. $^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR (99 MHz, J = 7 Hz, C_6D_6 , without decoupling in F1 dimension): δ = 26.7 (sept, J = 7.4 Hz) ppm. NMR data for **4pa**: ^1H NMR (500 MHz, C_6D_6 , 298 K): δ = 0.32 (s, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): δ = 6.1 ppm. $^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR (99 MHz, J = 7 Hz, C_6D_6 , without decoupling in F1 dimension): δ = 32.1 (sept, J = 7.7 Hz) ppm.

7.1.2 Chlorodemethylation of Iodotrimethylsilane (**3pc**) with 1,2-Dichloroethane (**2a**)

Prepared from iodotrimethylsilane (**3pc**) with 1,2-dichloroethane (**2a**) according to **GP 3**. Quantitative ^1H NMR spectroscopy revealed a yield of 30% of **4pc**, 33% of **9pb** and 35% of **4pa**. NMR data for **4pc**: ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 1.06$ (s, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 12.3$ ppm. $^1\text{H},^{29}\text{Si}$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz): $\delta = 1.06/-33.9$ ppm. NMR data for **9pb**: ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 0.65$ (s, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 10.2$ ppm. $^1\text{H},^{29}\text{Si}$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz): $\delta = 0.65/5.4$ ppm. NMR data for **4pa**: ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 0.32$ (s, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 6.1$ ppm. $^1\text{H},^{29}\text{Si}$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz): $\delta = 0.32/32.0$ ppm.

7.1.3 Bromodemethylation of Iodotrimethylsilane (**3pc**) with 1,2-Dibromoethane (**2b**)

Prepared from iodotrimethylsilane (**3pc**) with 1,2-dibromoethane (**2b**) according to **GP 3**. Quantitative ^1H NMR spectroscopy revealed a yield of 24% of **4pc**, 42% of **9pc** and 28% of **4pb**. NMR data for **4pc**: ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 1.06$ (s, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 12.3$ ppm. $^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR (99 MHz, $J = 7$ Hz, C_6D_6 , without decoupling in F1 dimension): $\delta = -33.8$ (sept, $J = 7.7$ Hz) ppm. NMR data for **9pc**: ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 0.81$ (s, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 11.1$ ppm. $^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR (99 MHz, $J = 7$ Hz, C_6D_6 , without decoupling in F1 dimension): $\delta = -4.3$ (sept, $J = 7.3$ Hz) ppm. NMR data for **4pb**: ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 0.60$ (s, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 9.0$ ppm. $^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR (99 MHz, $J = 7$ Hz, C_6D_6 , without decoupling in F1 dimension): $\delta = 19.9$ (sept, $J = 7.7$ Hz) ppm.

8 Analytical Spectra

Figure S1. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of 1-adamantyltrimethylsilane (**1k**) (* 1,2,4,5-tetrachlorobenzene)

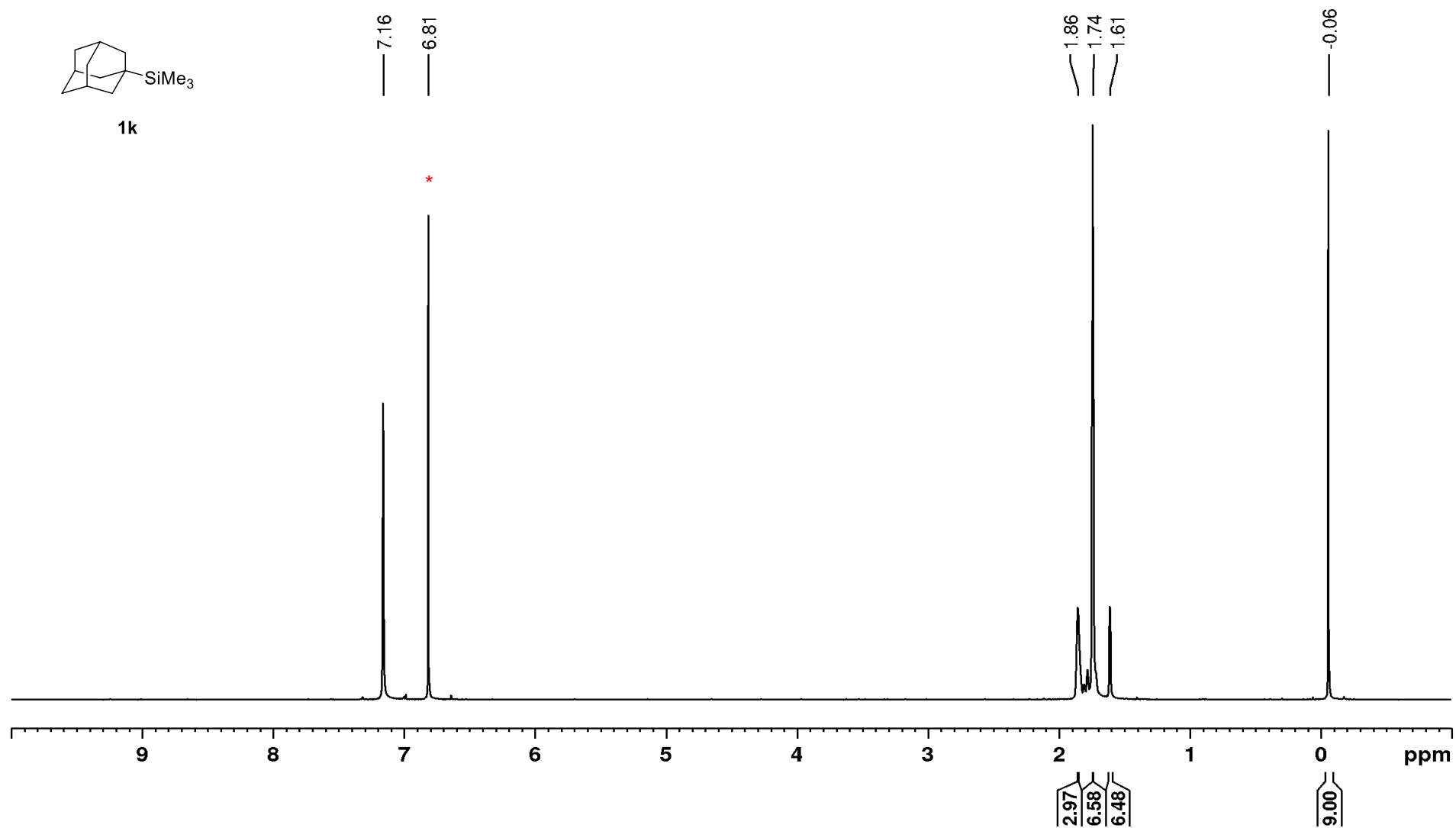


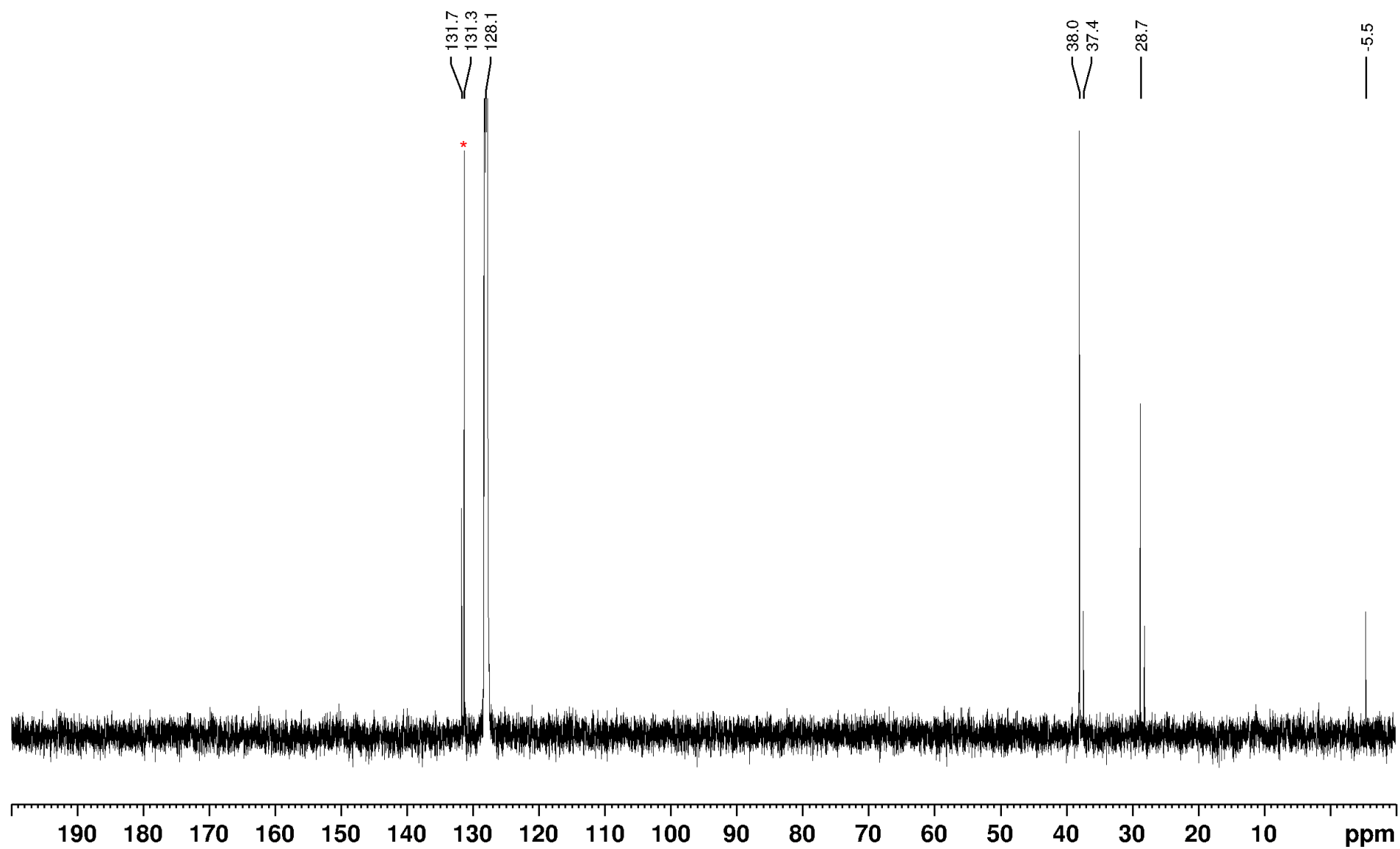
Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of 1-adamantyltrimethylsilane (**1k**) (* 1,2,4,5-tetrachlorobenzene)

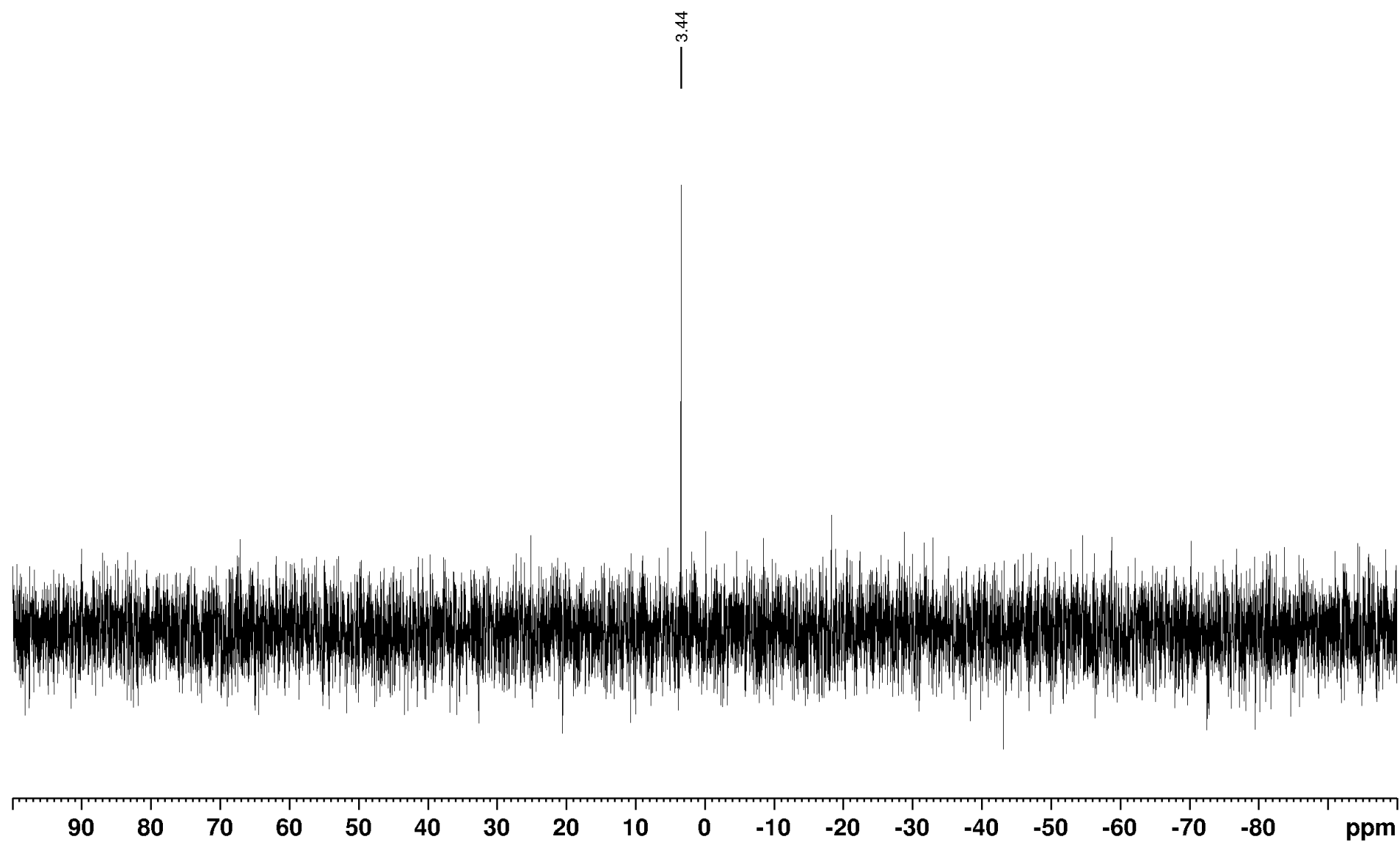
Figure S3. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 15.0°) of 1-adamantyltrimethylsilane (**1k**)

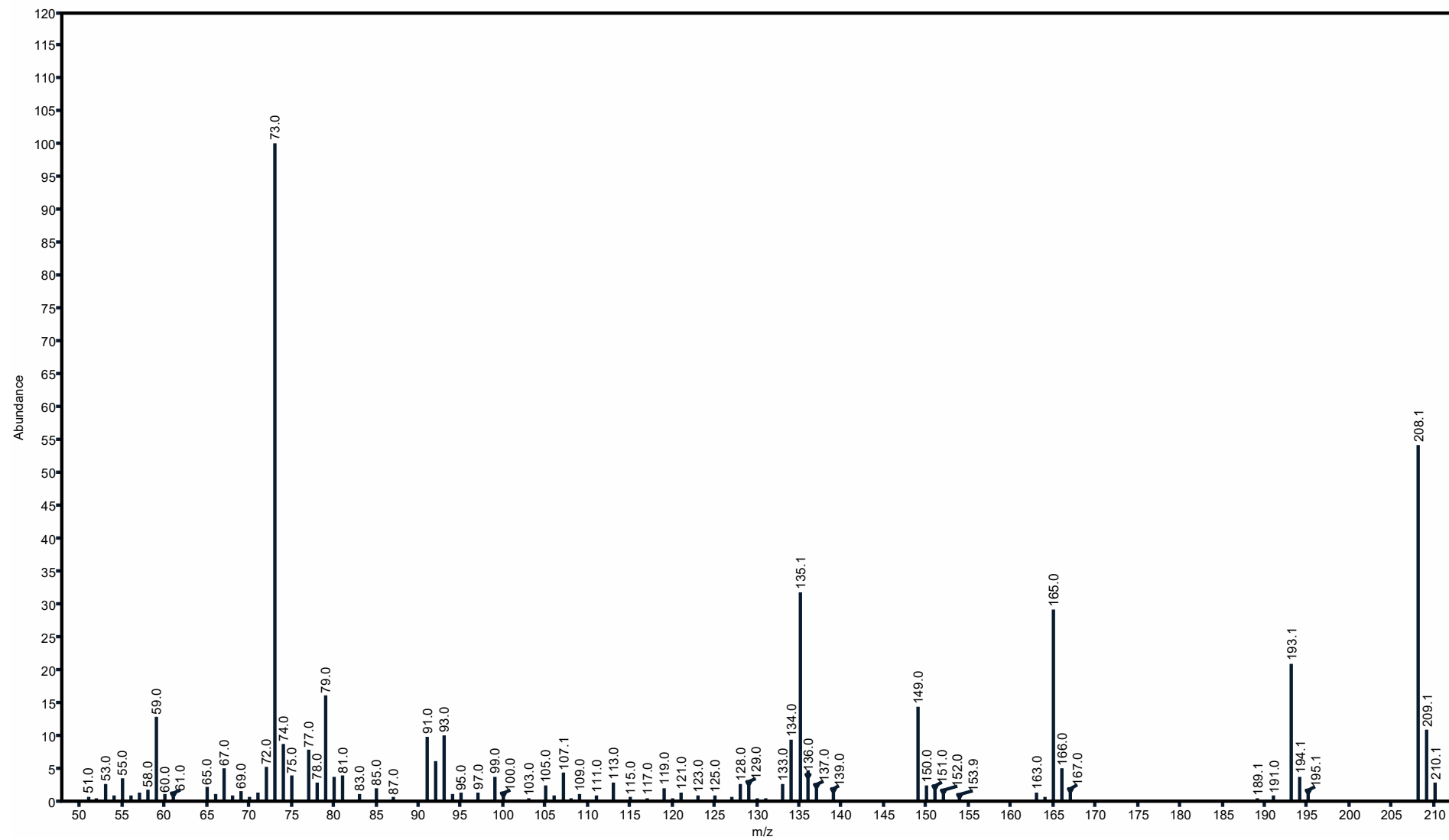
Figure S4. **GLC-MS** spectrum (EI) of 1-adamantyltrimethylsilane (**1k**)

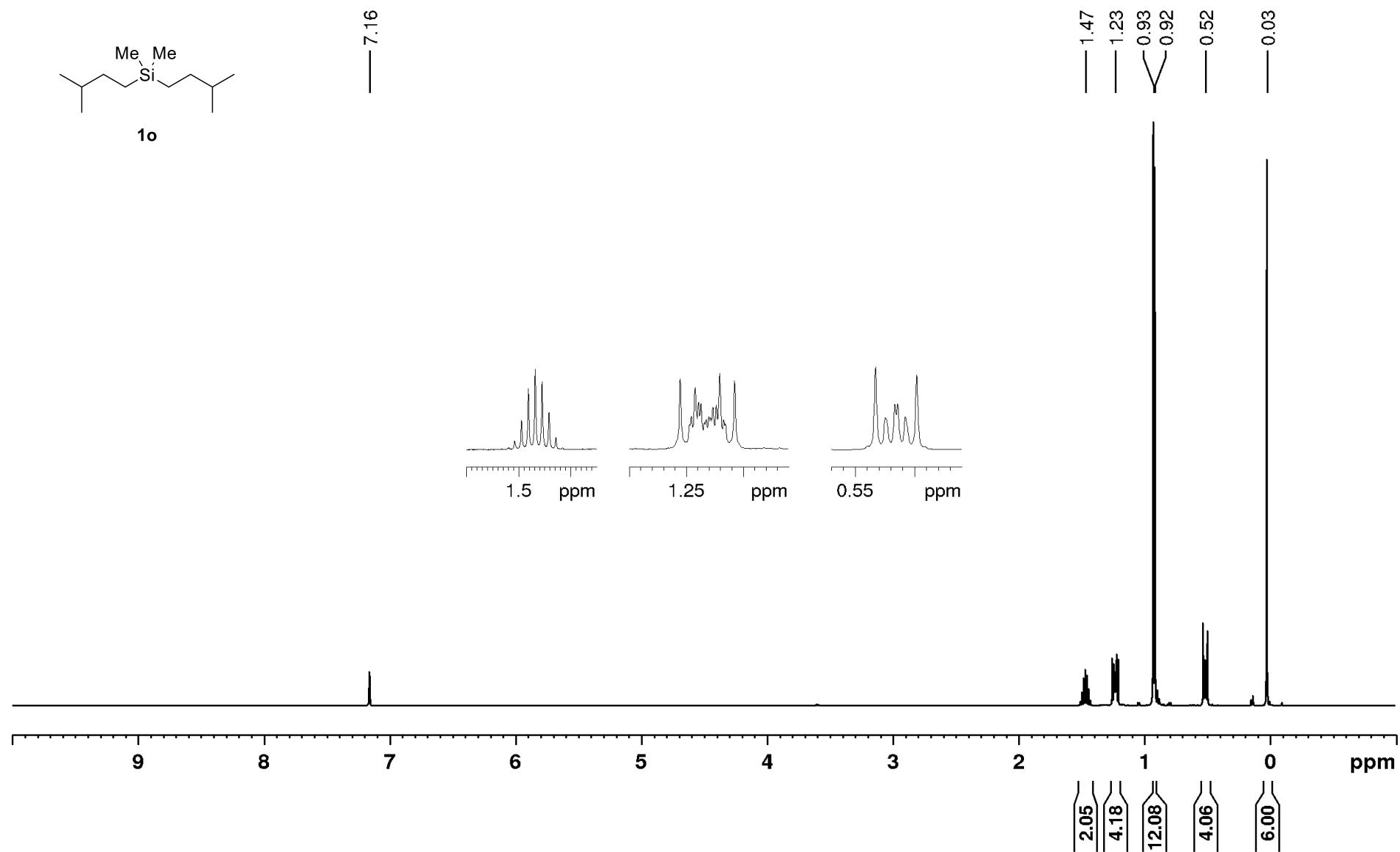
Figure S5. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of diisopentyldimethylsilane (**1o**)

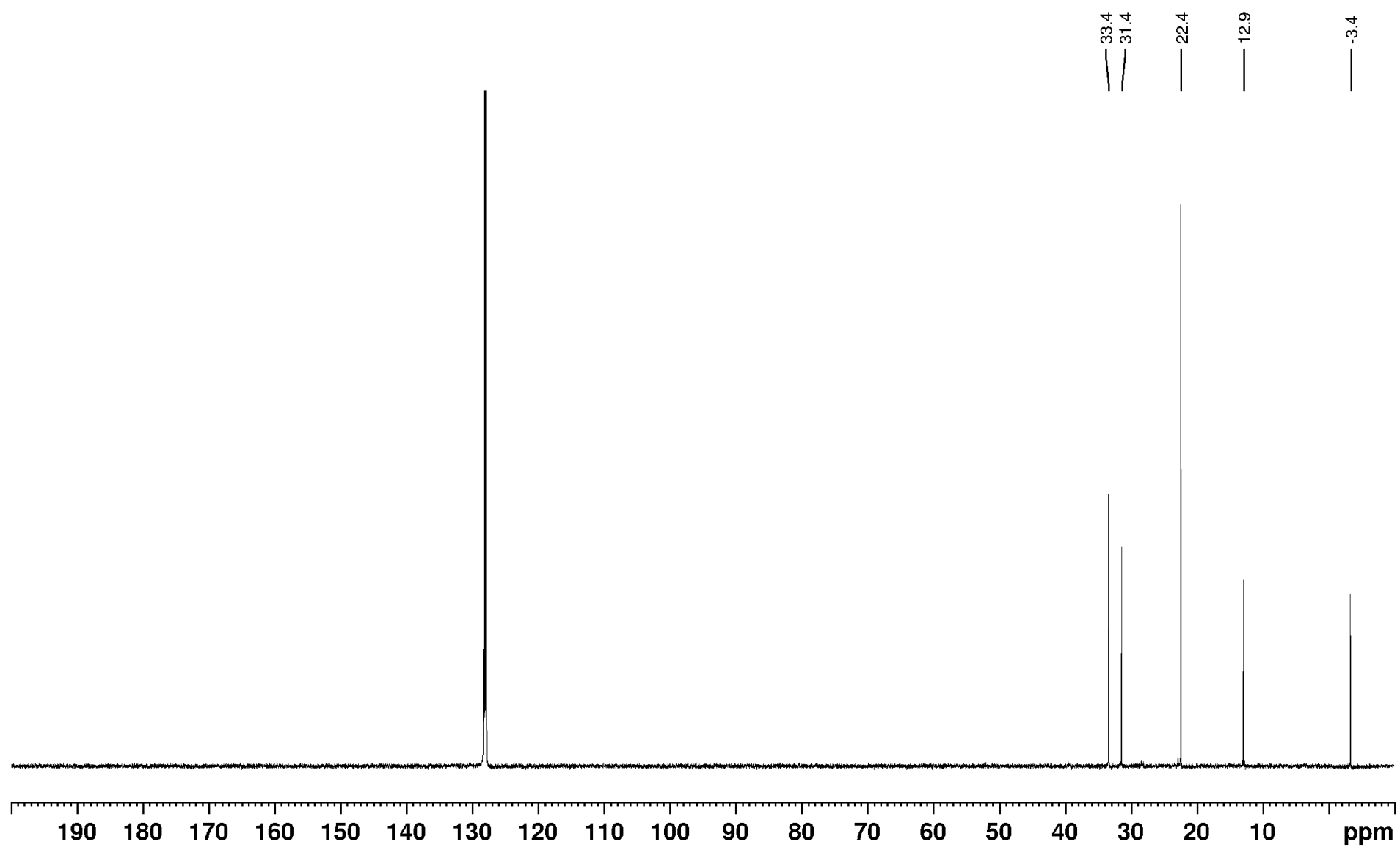
Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of diisopentylidimethylsilane (**1o**)

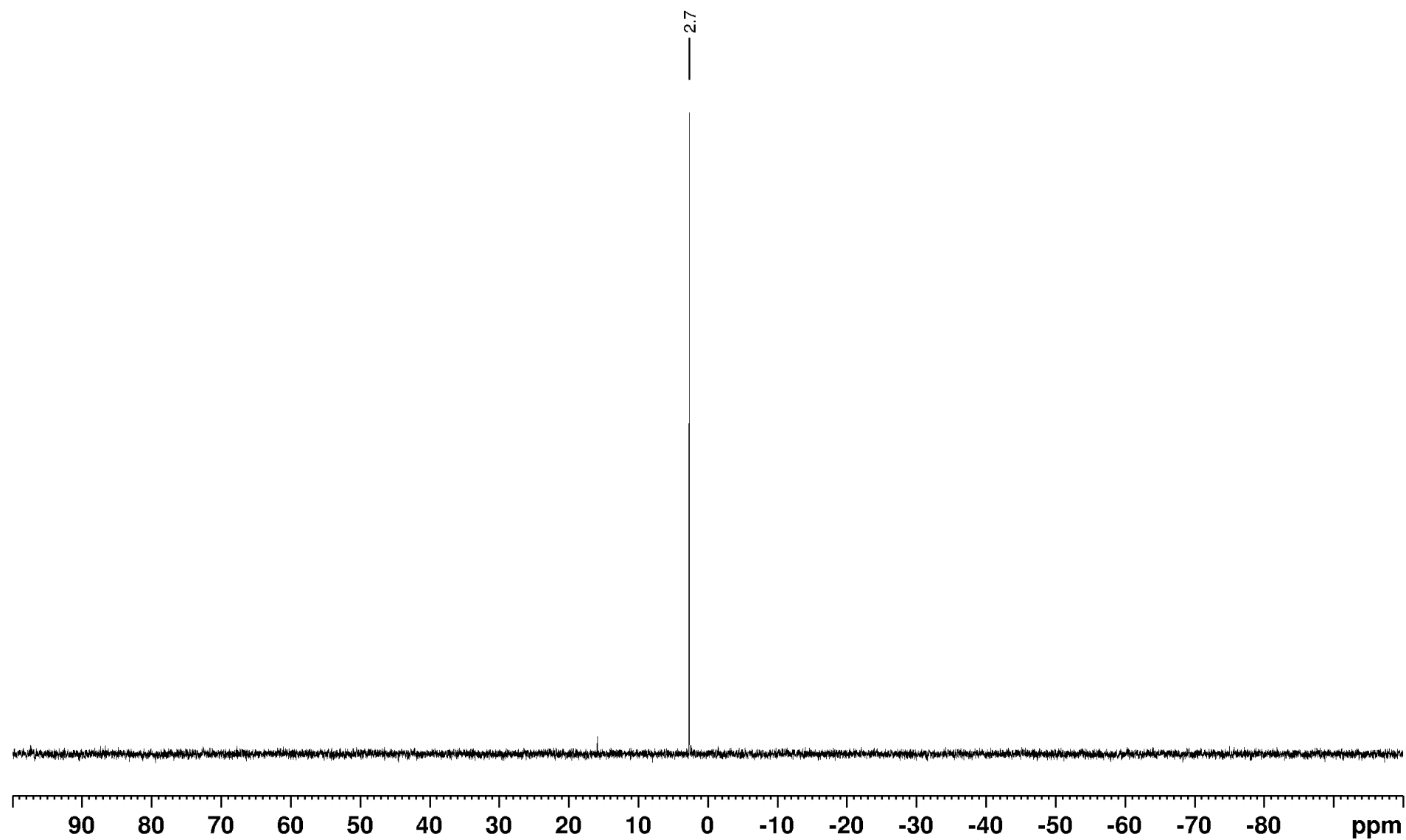
Figure S7. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 15.5°) of diisopentylidimethylsilane (**1o**)

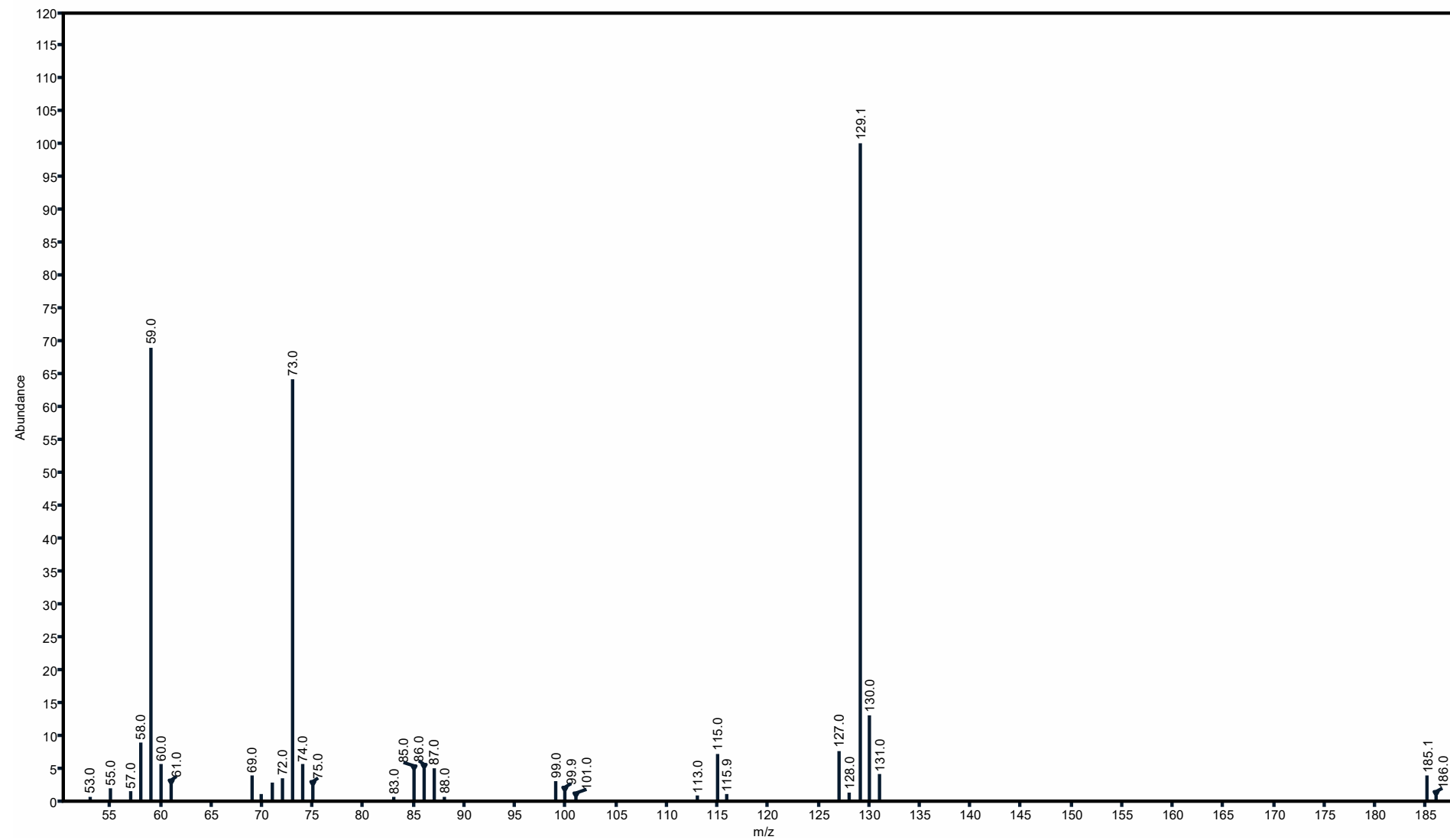
Figure S8. **GLC-MS** spectrum (EI) of diisopentyldimethylsilane (**1o**)

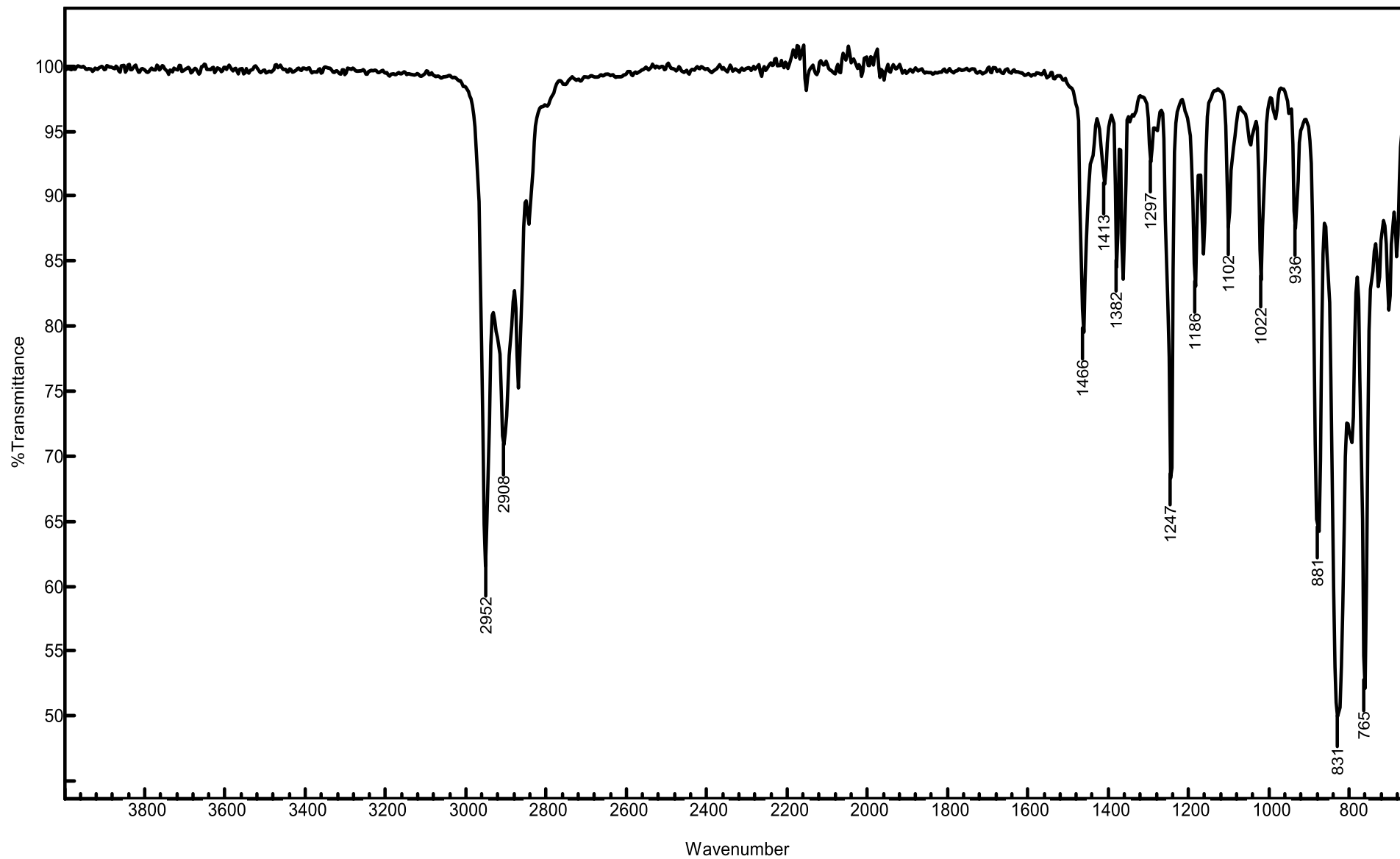
Figure S9. IR spectrum (ATR) of diisopentyldimethylsilane (**1o**)

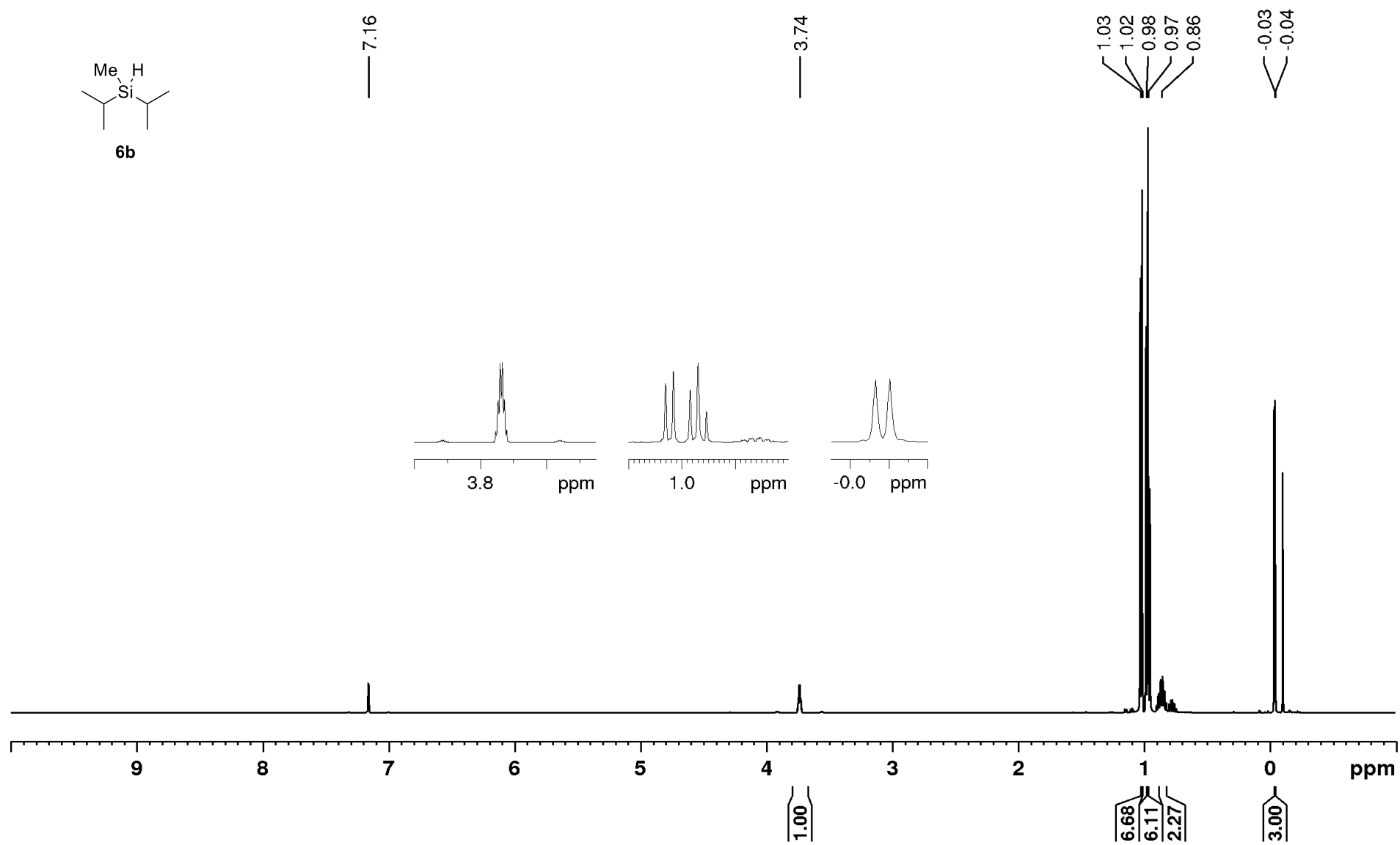
Figure S10. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of diisopropyl(methyl)silane (**6b**)

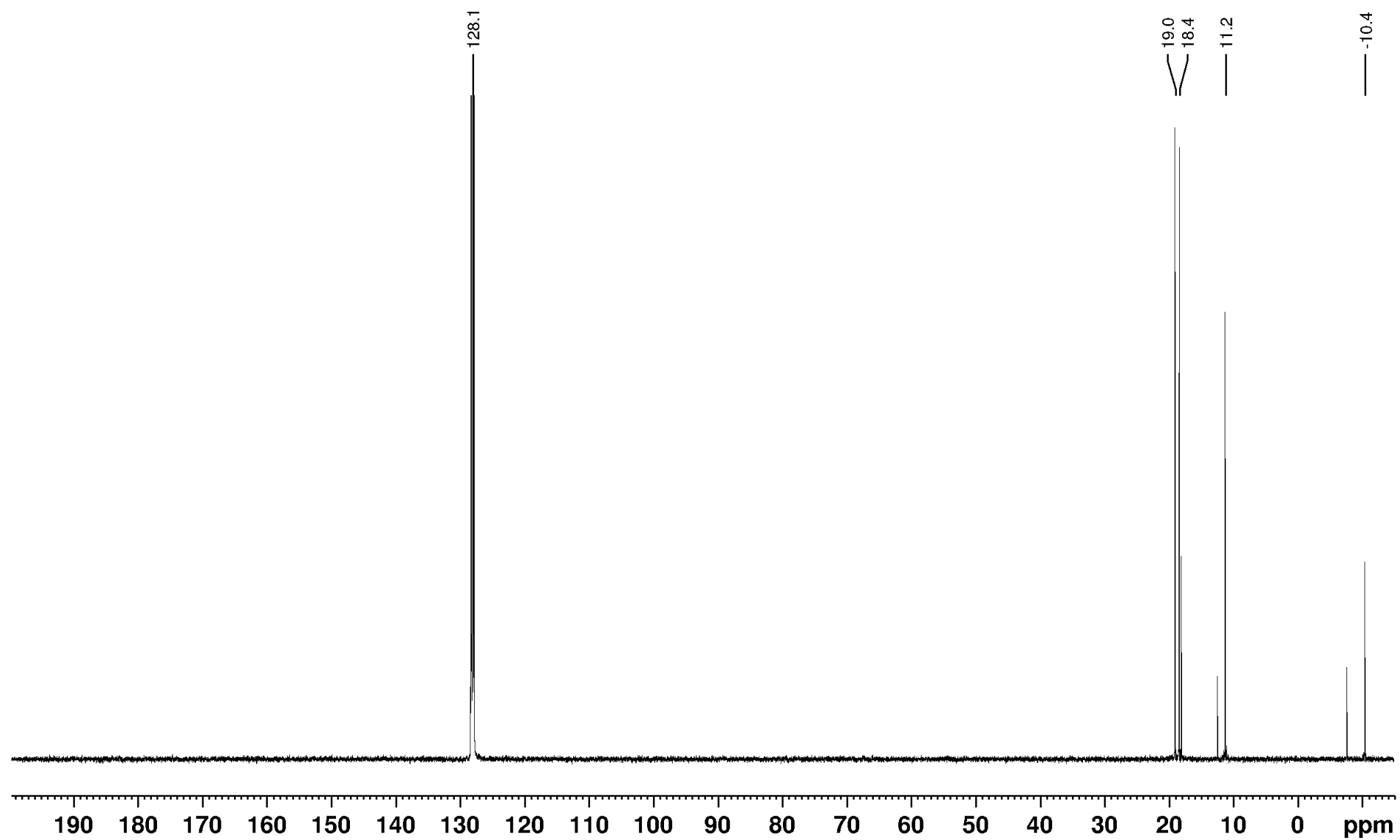
Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of diisopropyl(methyl)silane (**6b**)

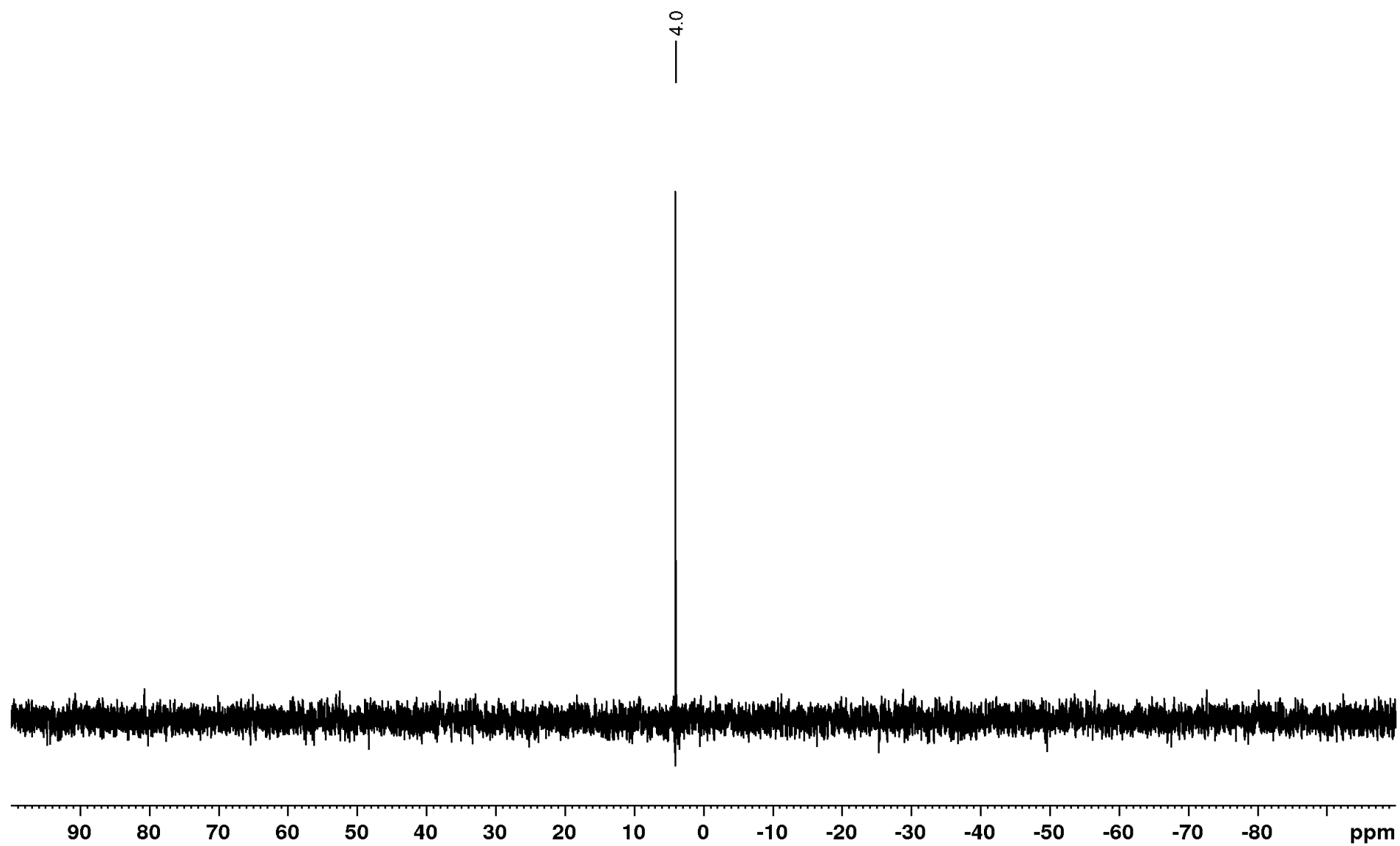
Figure S12. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 12.9°) of diisopropyl(methyl)silane (**6b**)

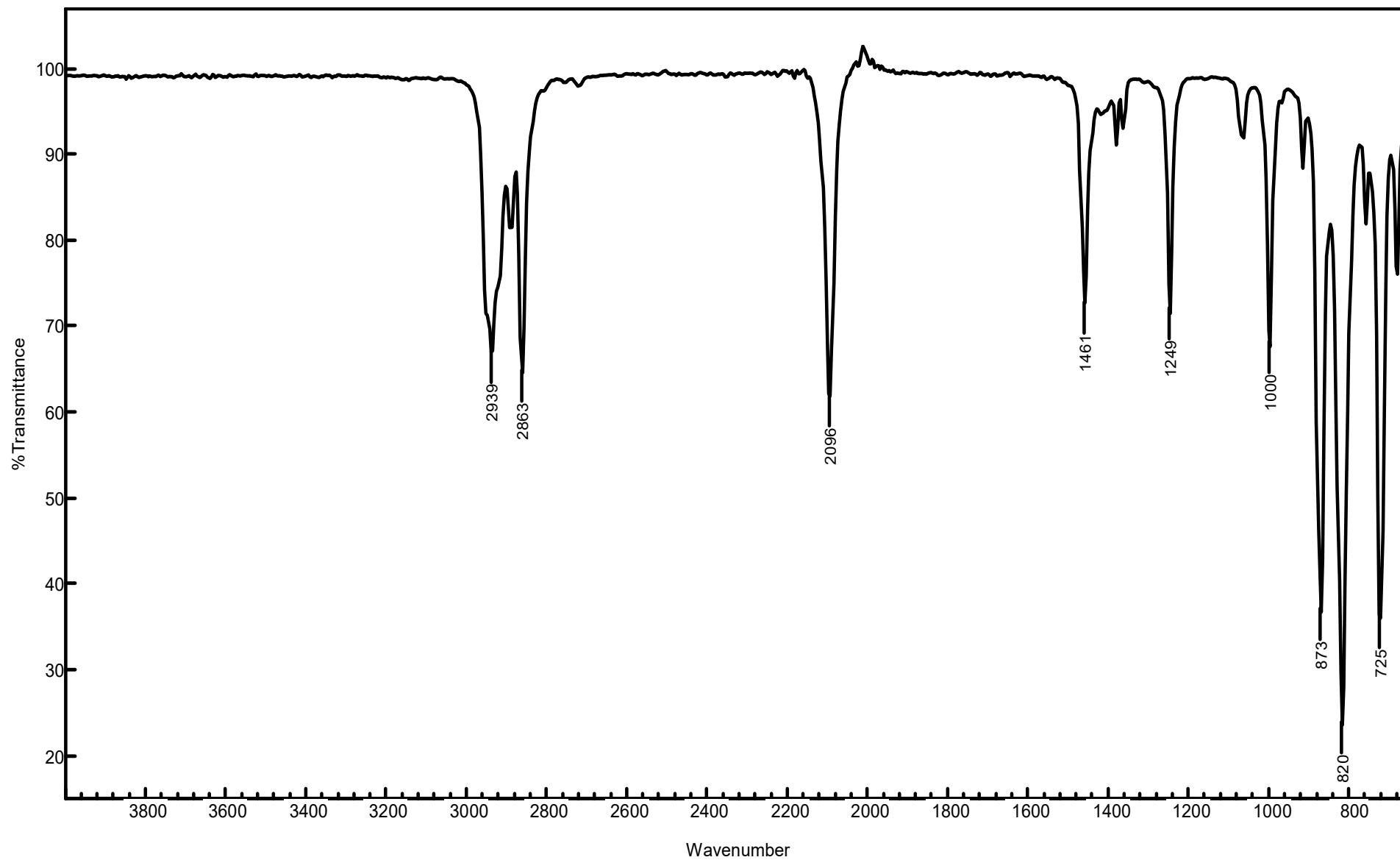
Figure S13. IR spectrum (ATR) of diisopropyl(methyl)silane (**6b**)

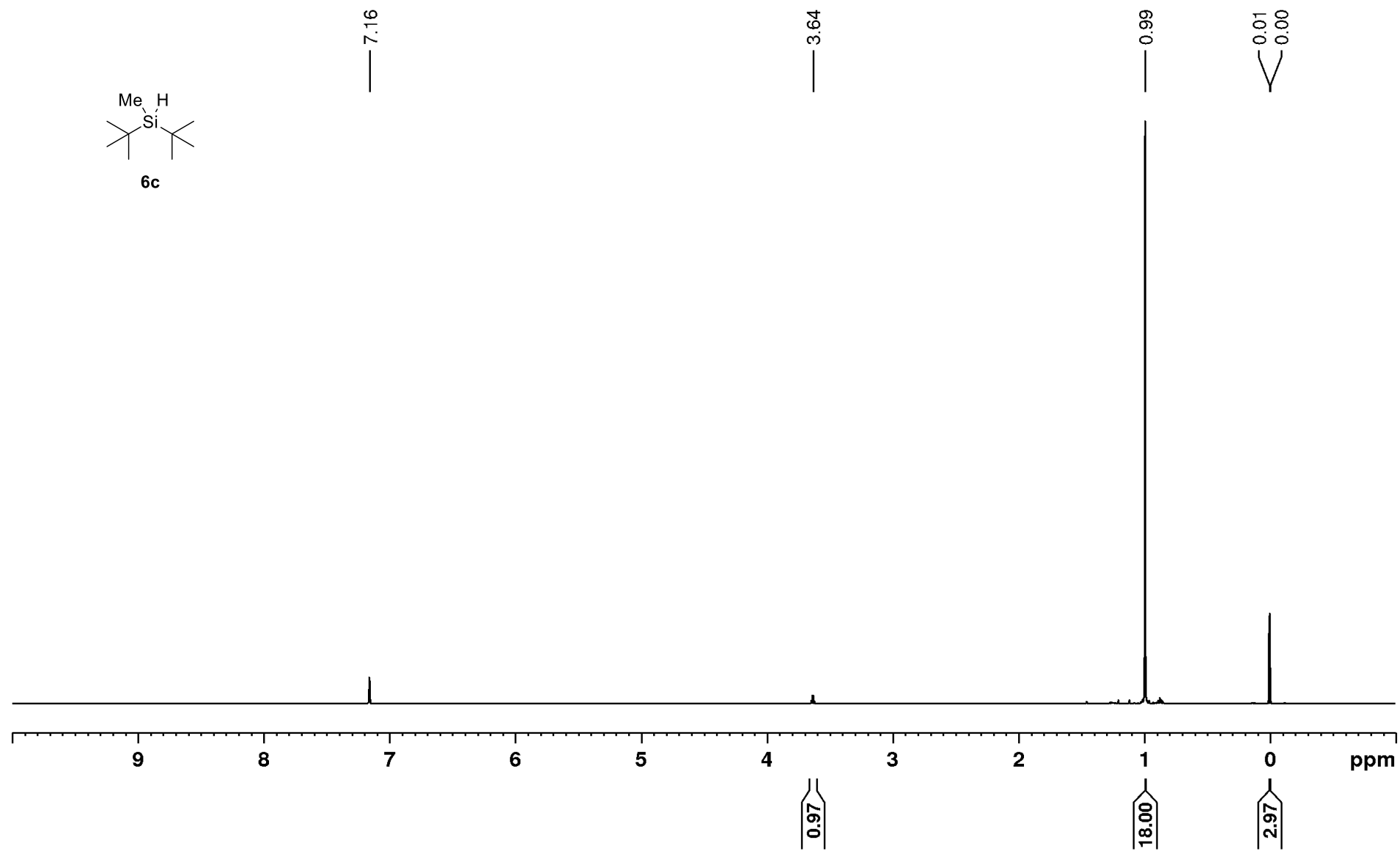
Figure S14. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of di-*tert*-butyl(methyl)silane (**6c**)

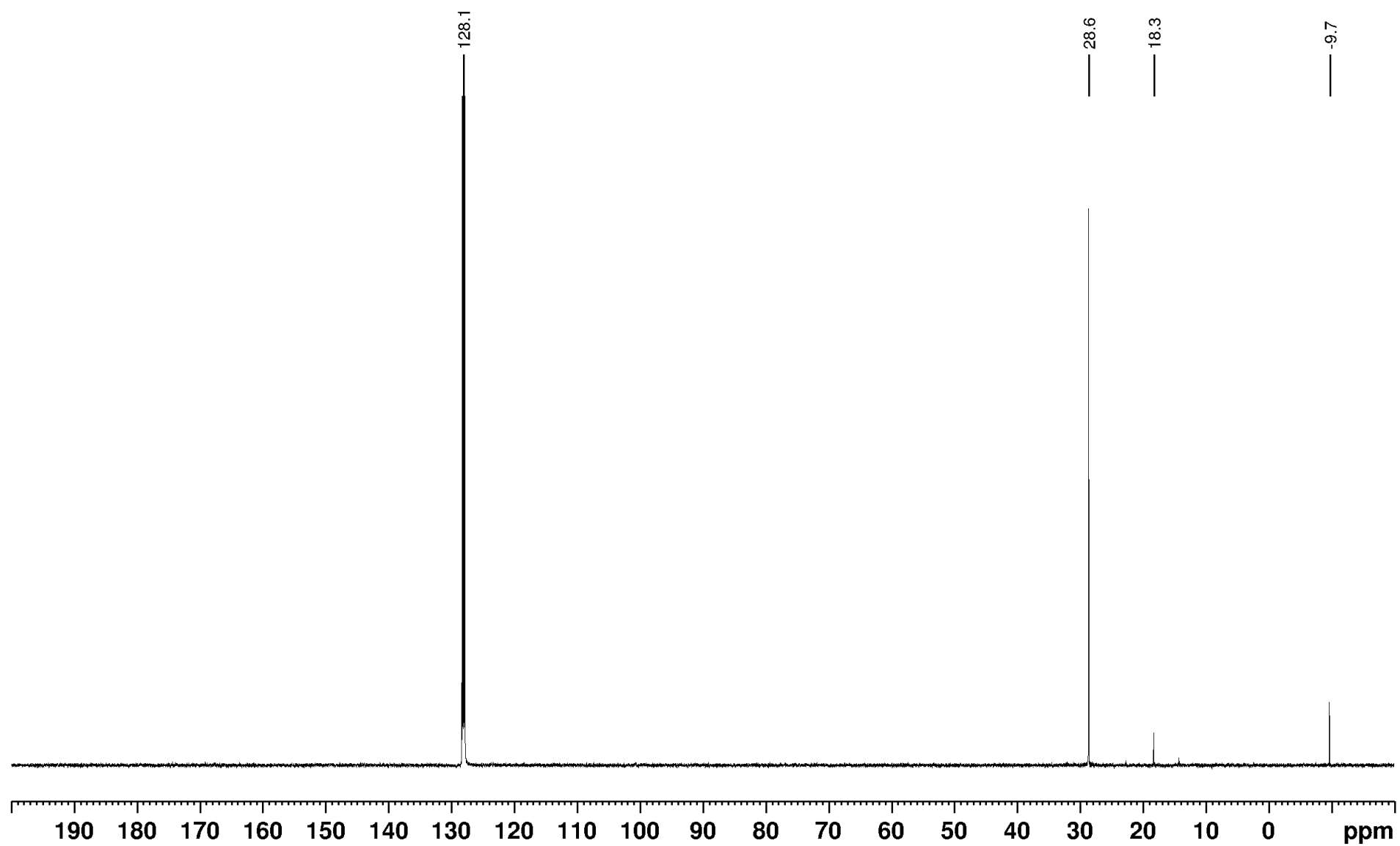
Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of di-*tert*-butyl(methyl)silane (**6c**)

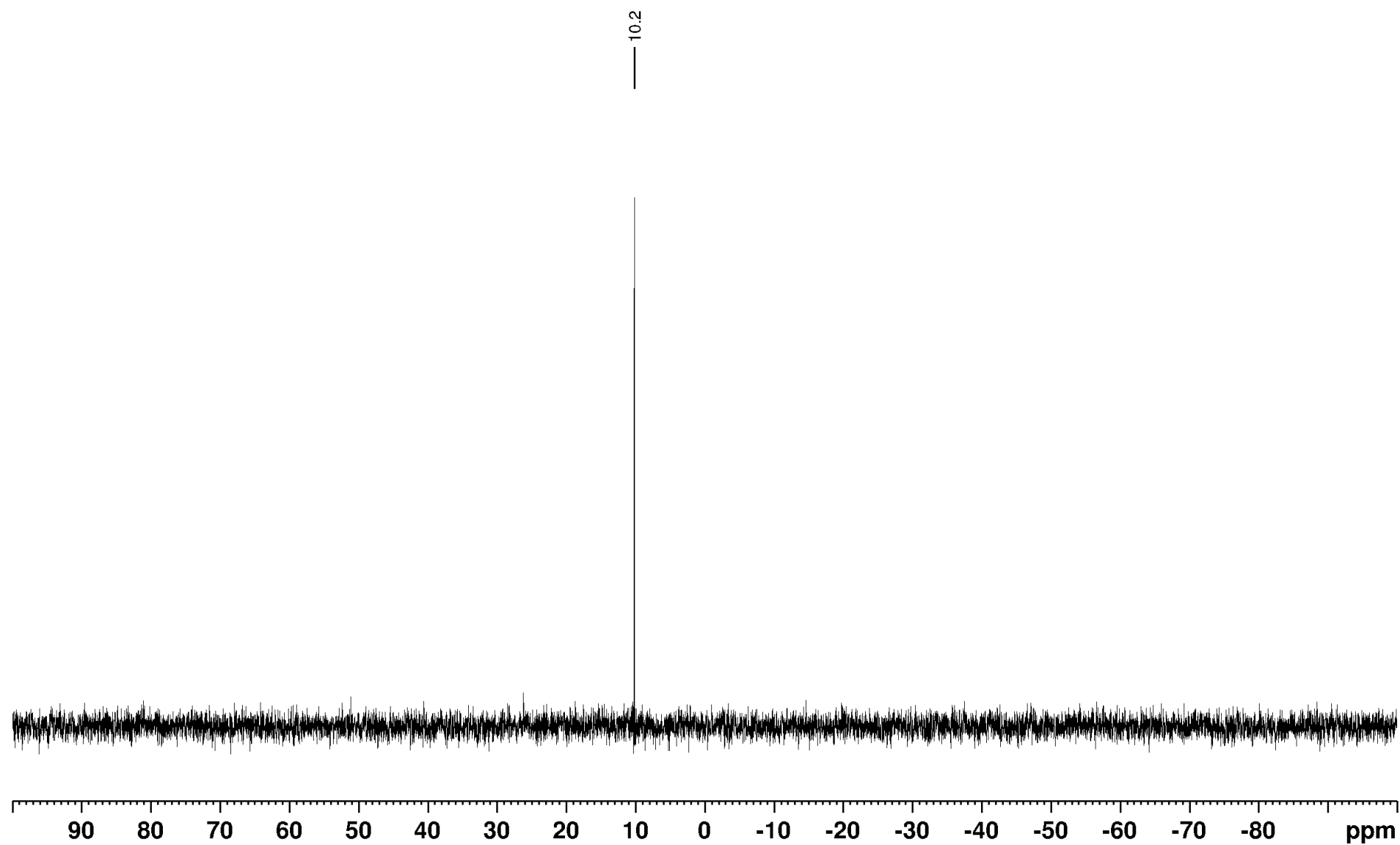
Figure S16. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, C_6D_6 , 298 K, optimized for $J = 200$ Hz, 90.0°) of di-*tert*-butyl(methyl)silane (**6c**)

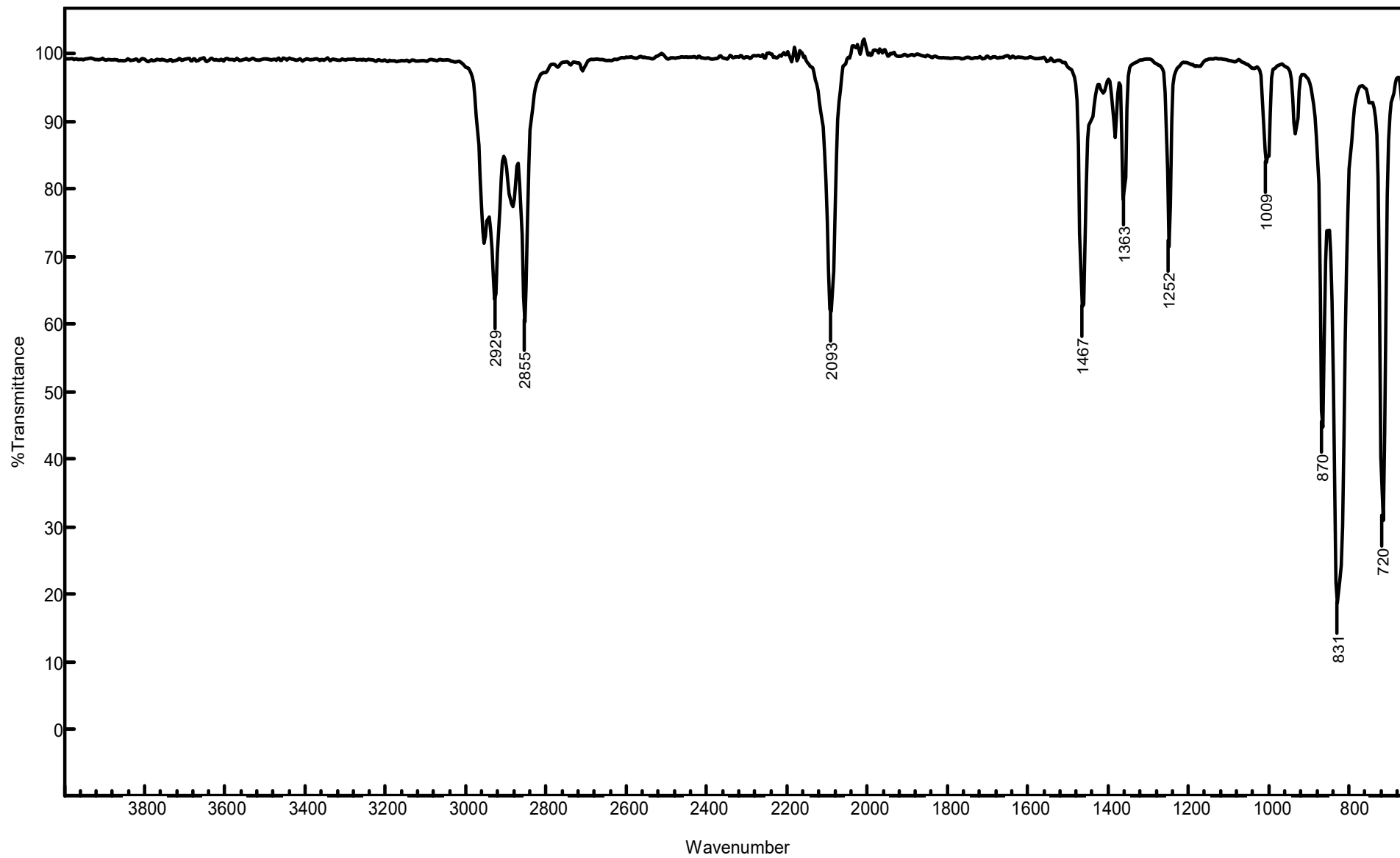
Figure S17. IR spectrum (ATR) of di-*tert*-butyl(methyl)silane (**6c**)

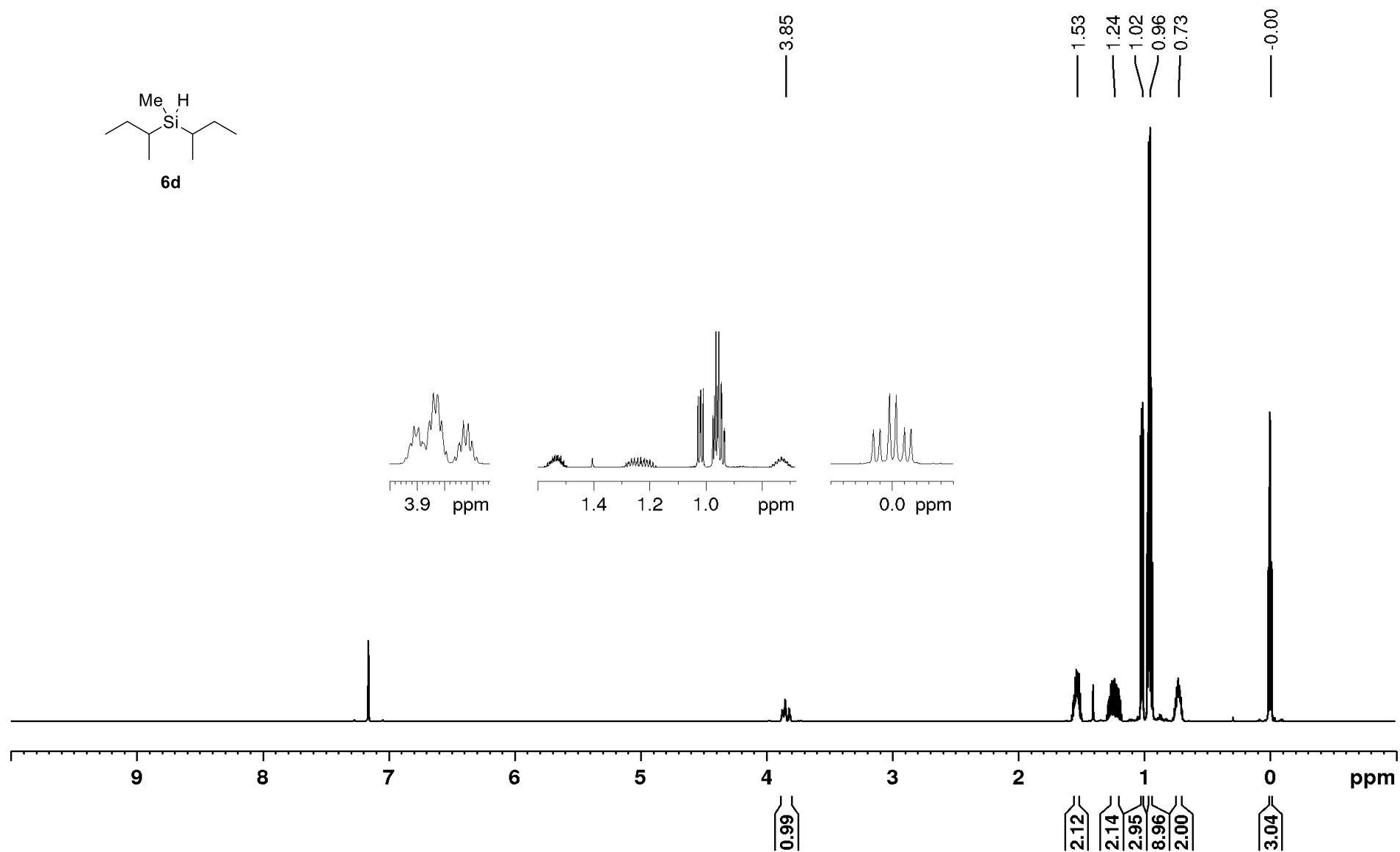
Figure S18. ^1H NMR spectrum (700 MHz, C_6D_6 , 298 K) of di-sec-butyl(methyl)silane (**6d**)

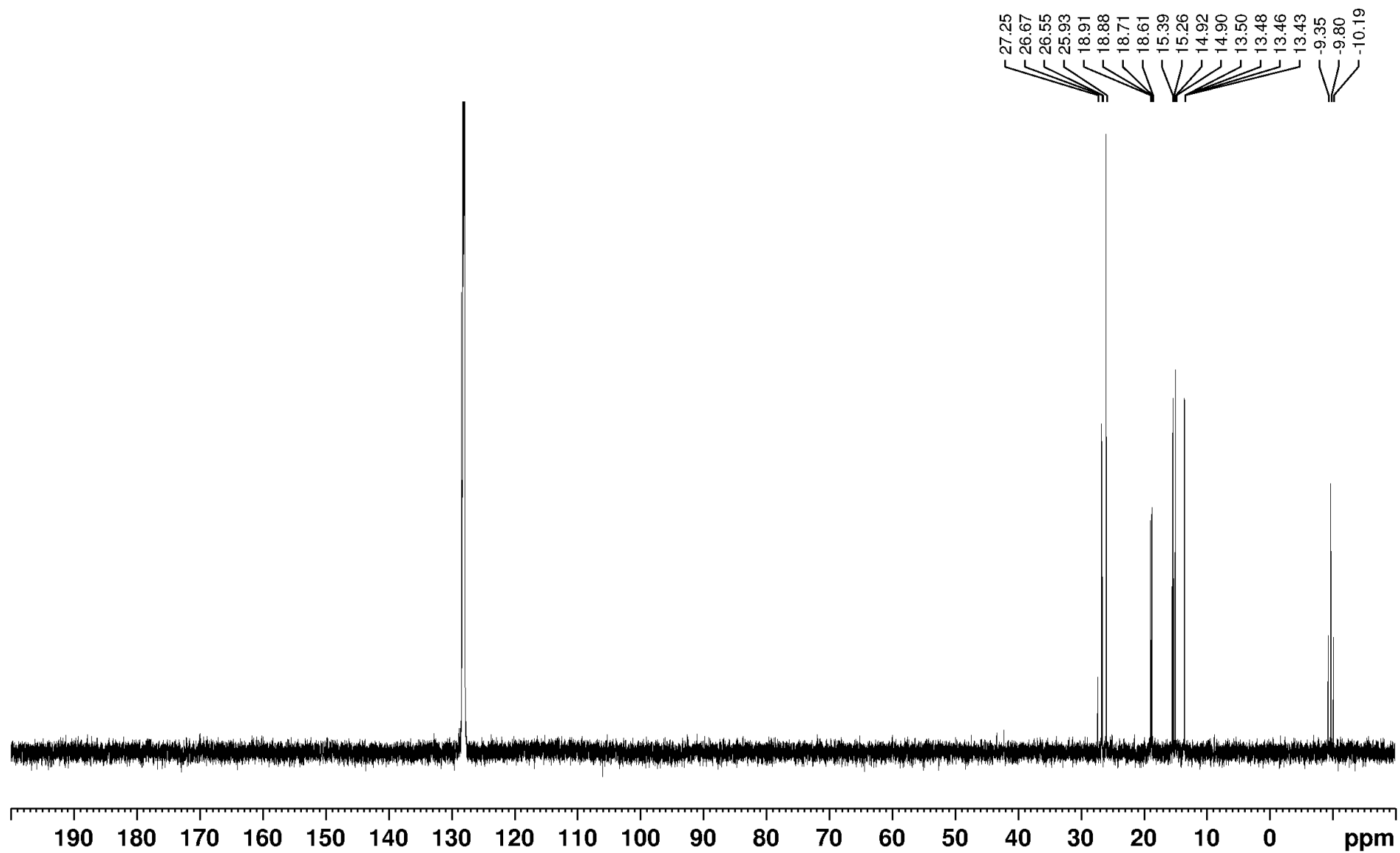
Figure S19. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (175 MHz, C_6D_6 , 298 K) of di-sec-butyl(methyl)silane (**6d**)

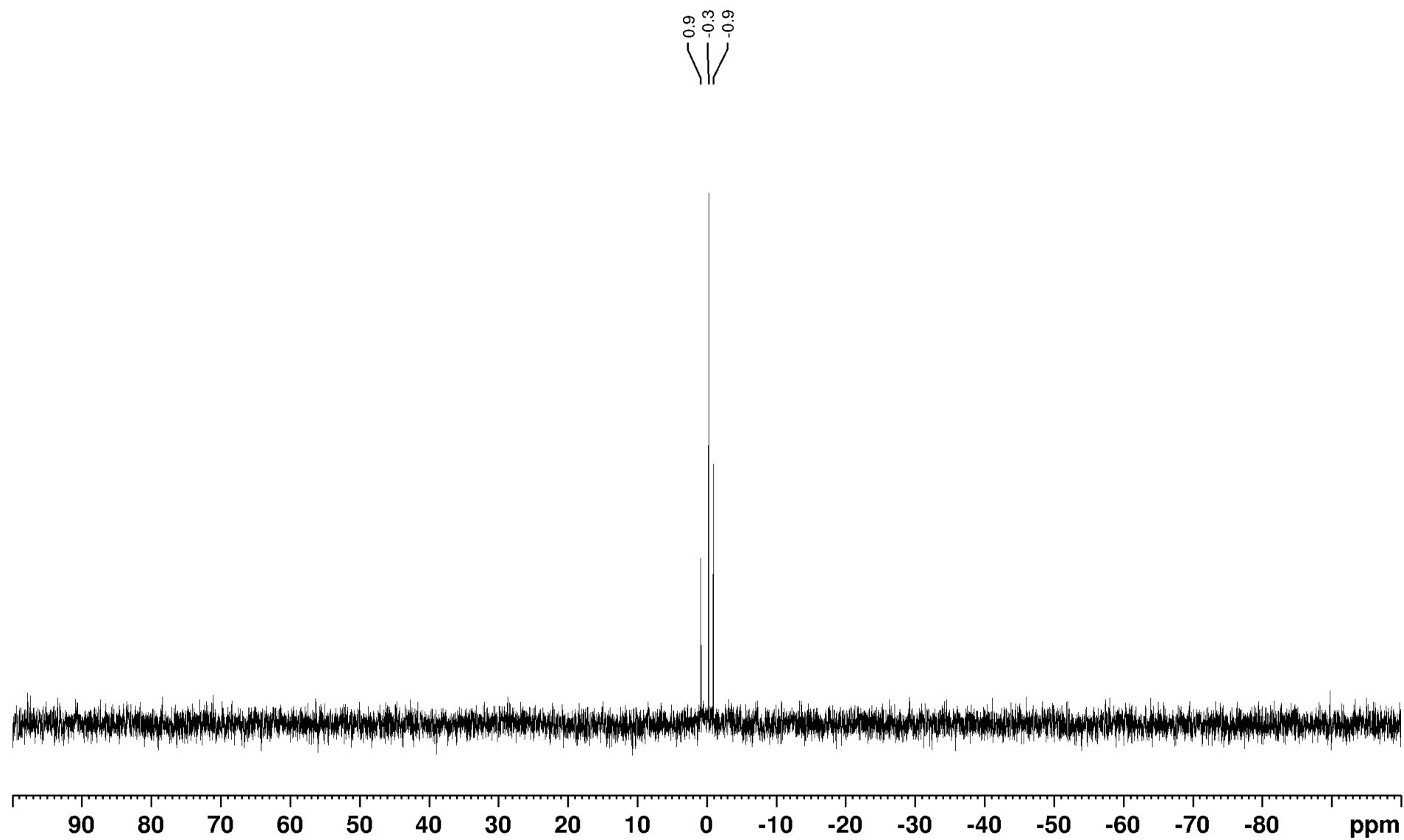
Figure S20. $^{29}\text{Si}\{^1\text{H}\}$ IG NMR spectrum (99 MHz, C_6D_6 , 298 K) of di-sec-butyl(methyl)silane (**6d**)

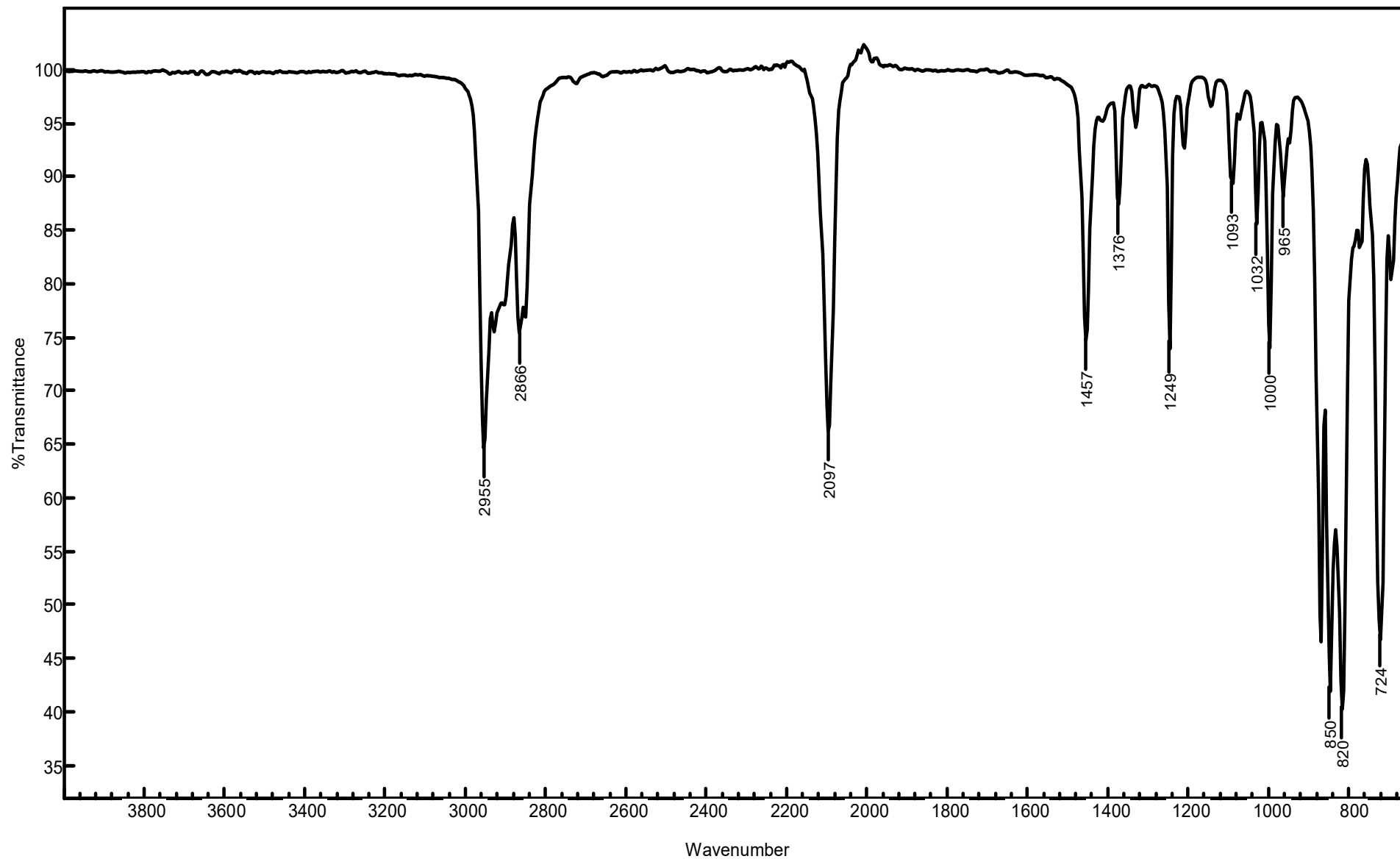
Figure S21. IR spectrum (ATR) of di-sec-butyl(methyl)silane (**6d**)

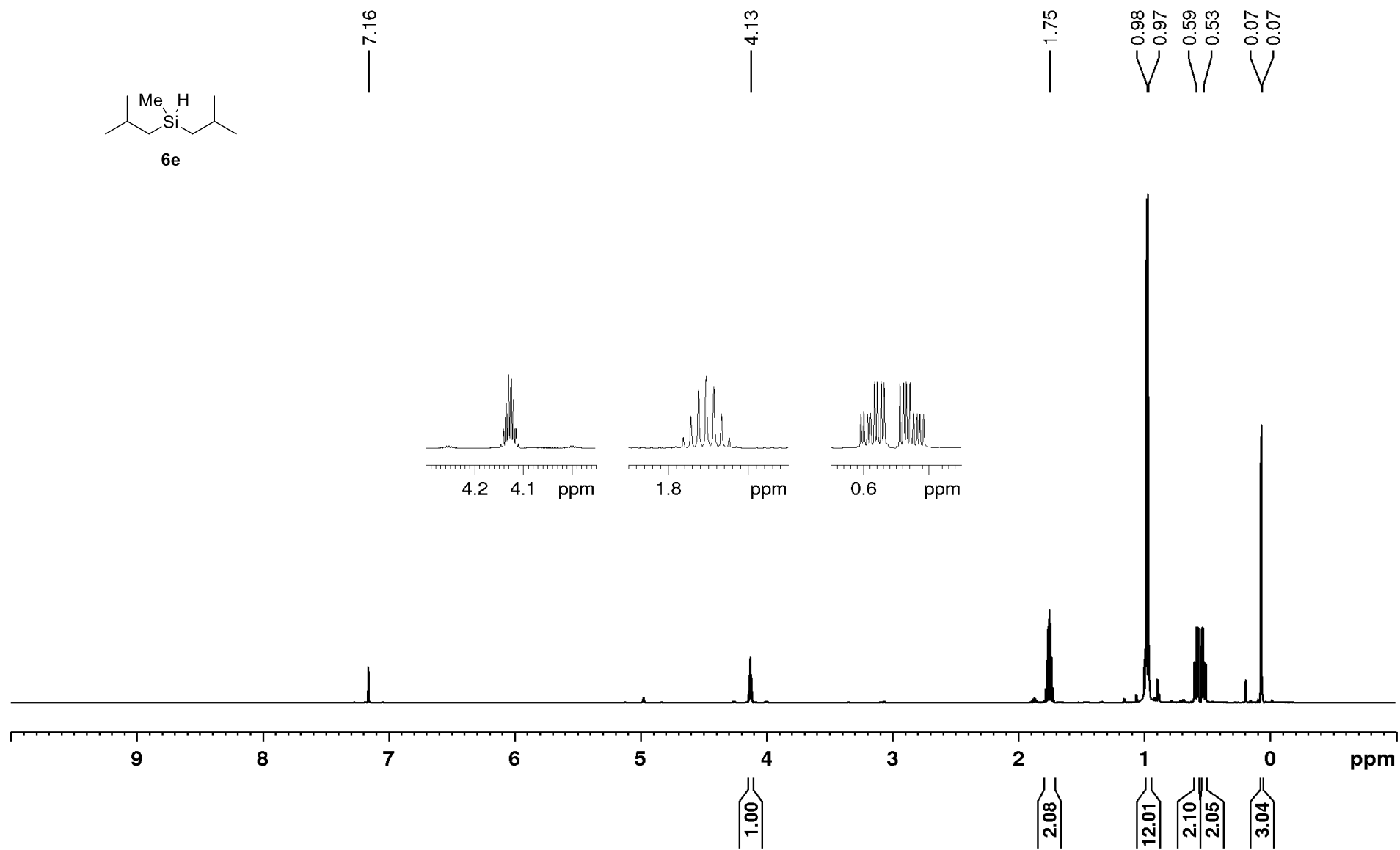
Figure S22. ^1H NMR spectrum (700 MHz, C_6D_6 , 298 K) of diisobutyl(methyl)silane (**6e**)

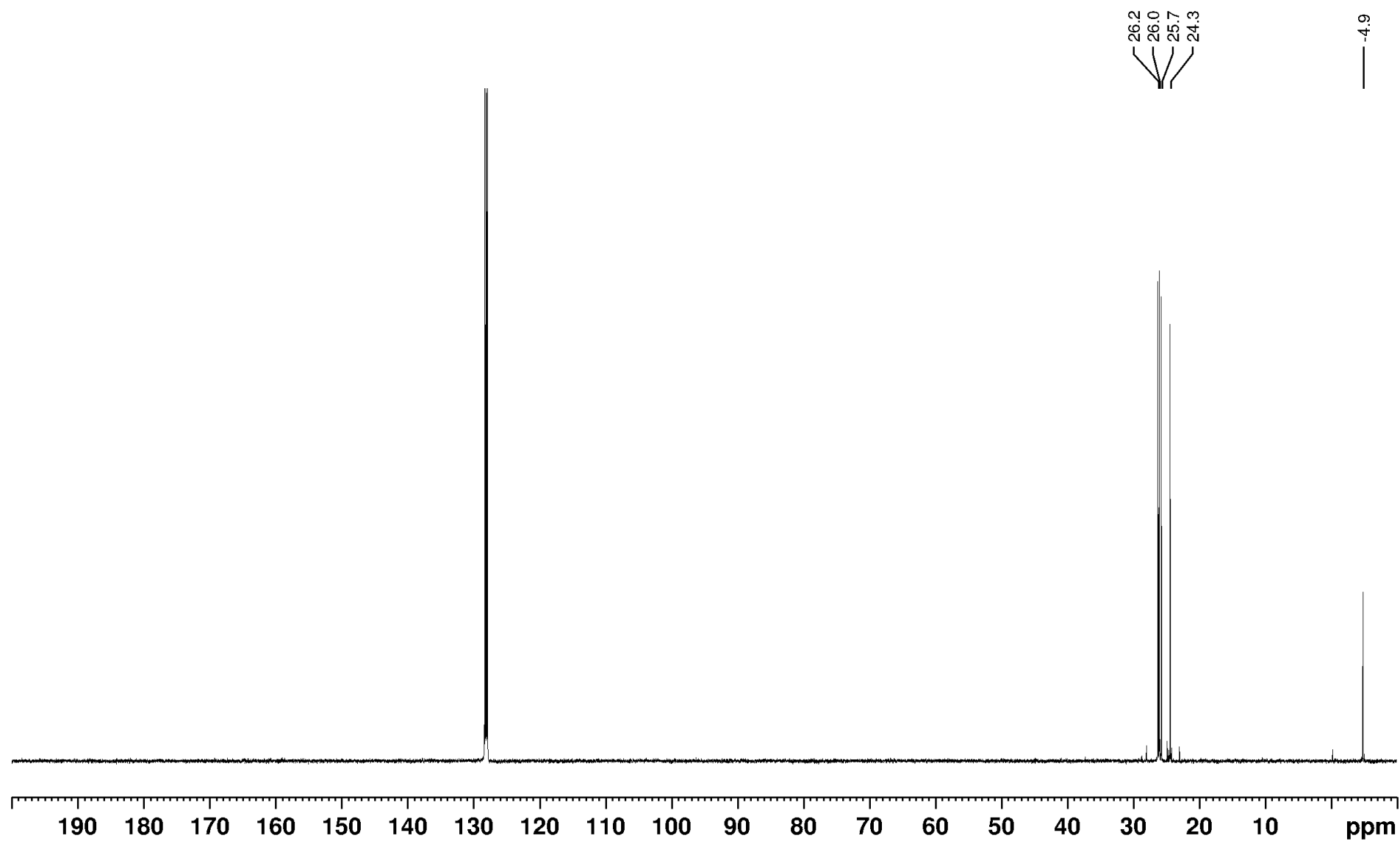
Figure S23. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of diisobutyl(methyl)silane (**6e**)

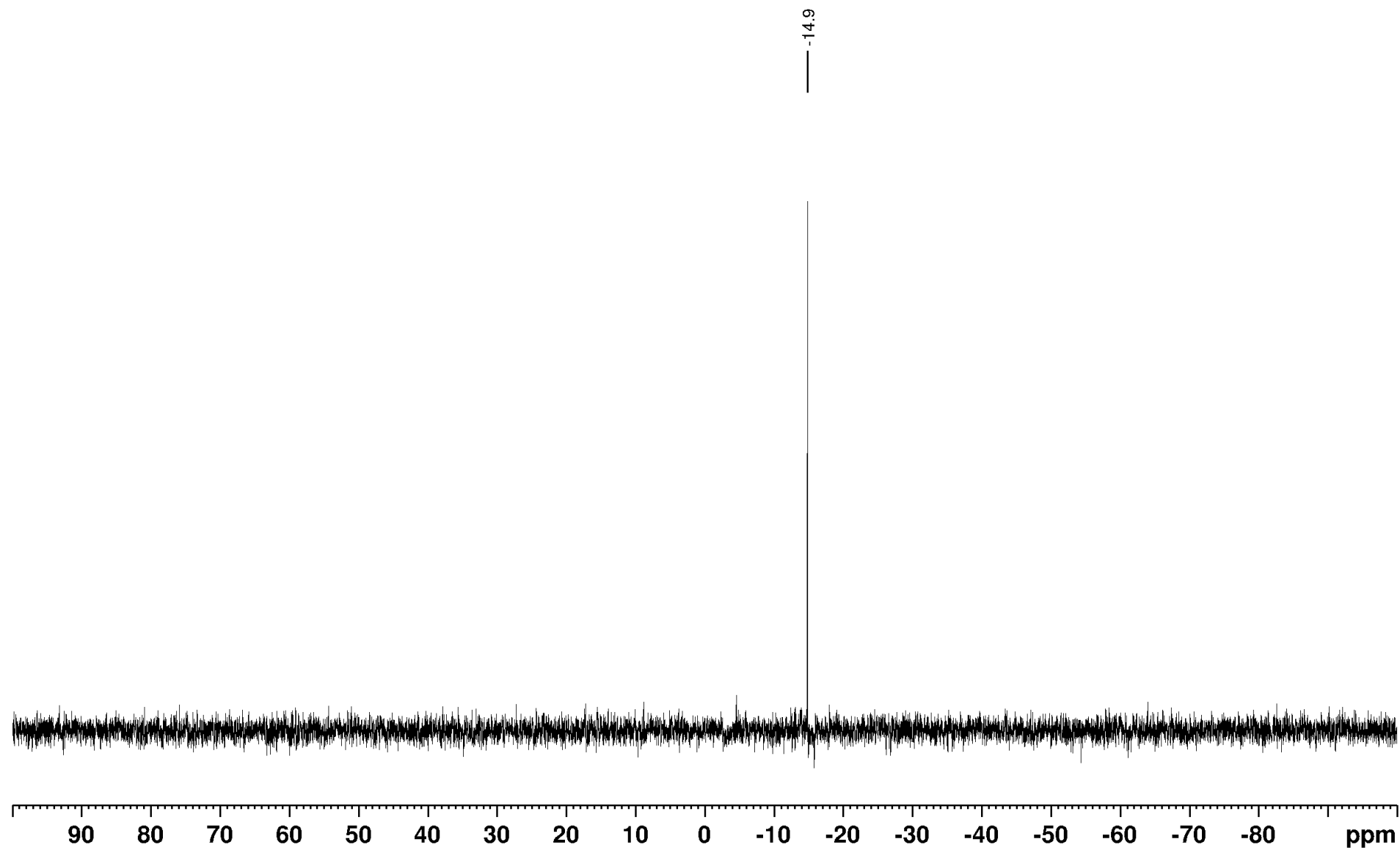
Figure S24. $^{29}\text{Si}\{^1\text{H}\}$ IG NMR spectrum (99 MHz, C_6D_6 , 298 K) of diisobutyl(methyl)silane (**6e**)

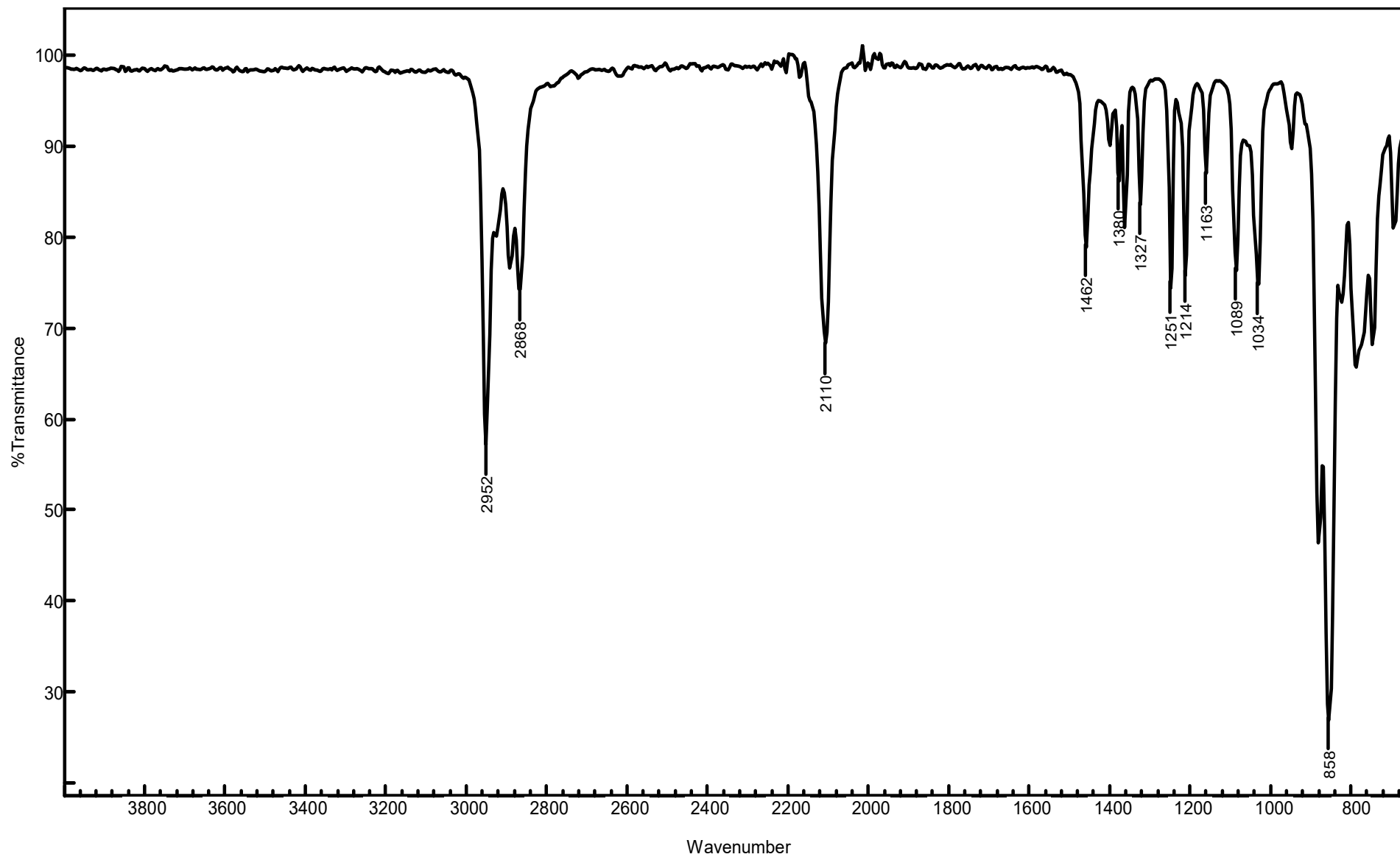
Figure S25. IR spectrum (ATR) of diisobutyl(methyl)silane (**6e**)

Figure S26. $^1\text{H NMR}$ spectrum (500 MHz, C_6D_6 , 298 K) of dichlorodiethylsilane (**4aa**) by chlorodeethylation of tetraethylsilane (**1a**) with 1,2-dichloroethane (**2a**)
(* 1,2-diphenylethane- d_{10} ; ^ cyclohexane)

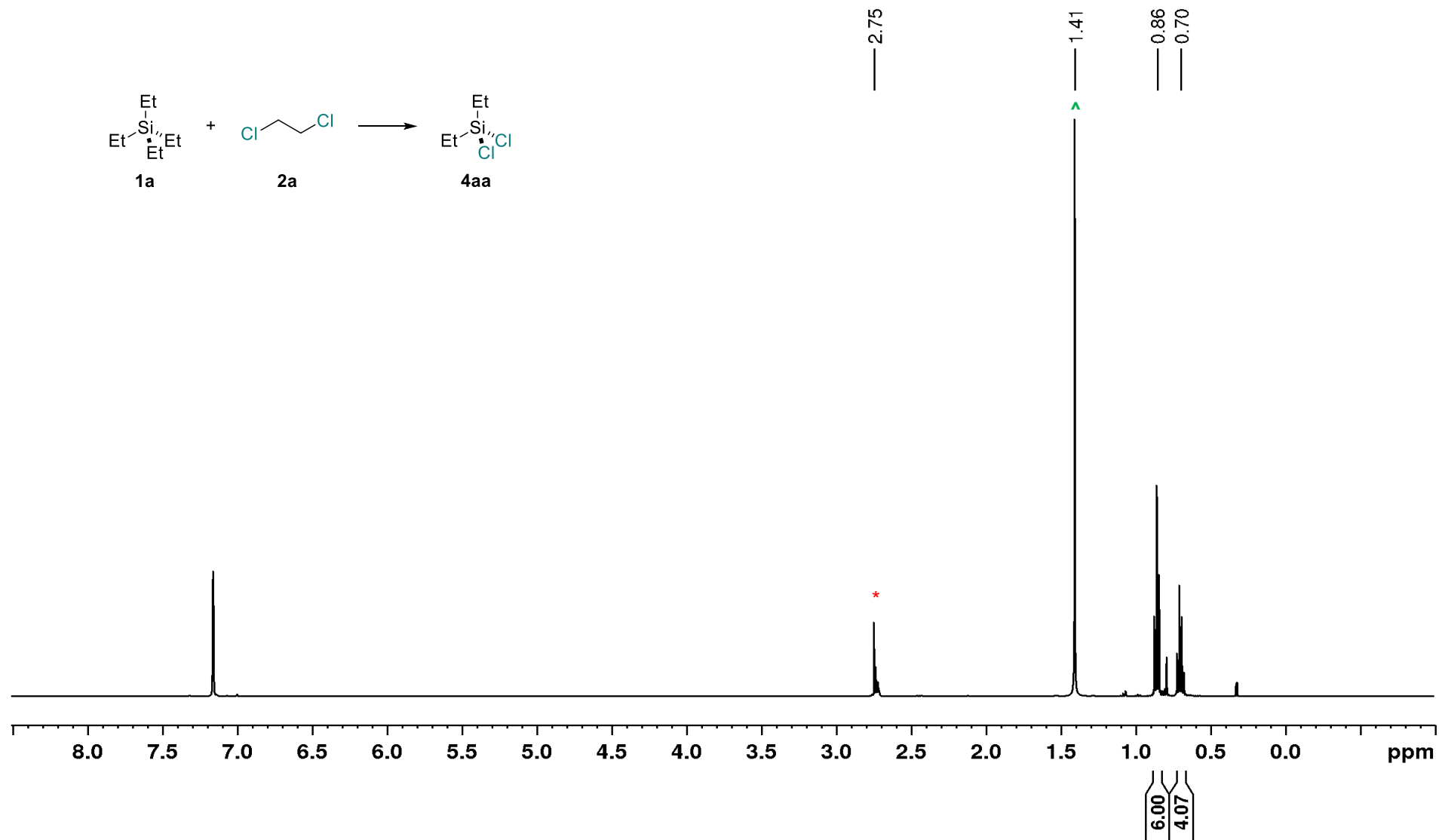


Figure S27. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of dichlorodiethylsilane (**4aa**) by chloroethylation of tetraethylsilane (**1a**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane)

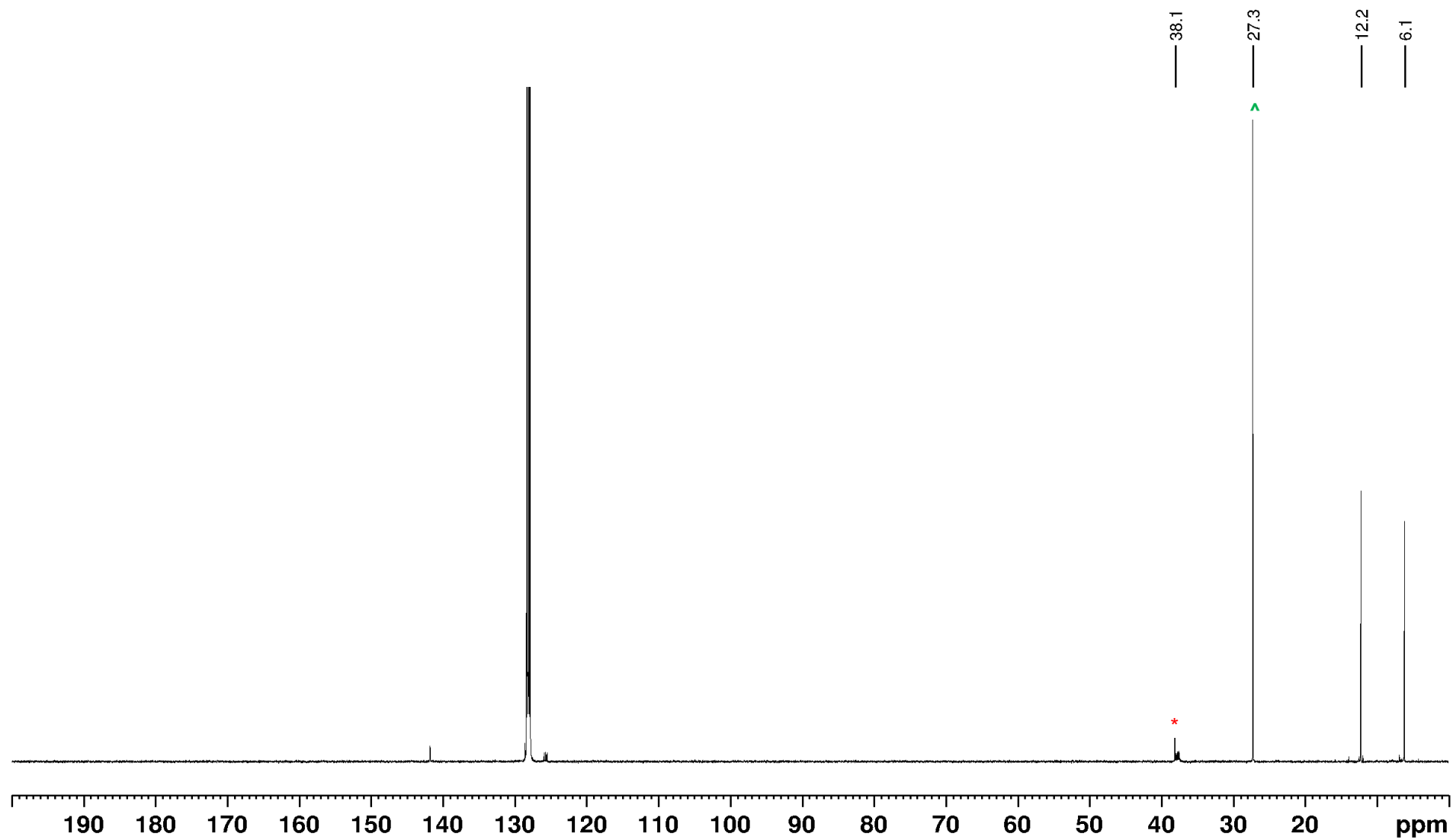


Figure S28. $^{29}\text{Si}\{^1\text{H}\}$ IG NMR spectrum (99 MHz, C_6D_6 , 298 K) of dichlorodiethylsilane (**4aa**) by chloroethylation of tetraethylsilane (**1a**) with 1,2-dichloroethane (**2a**)

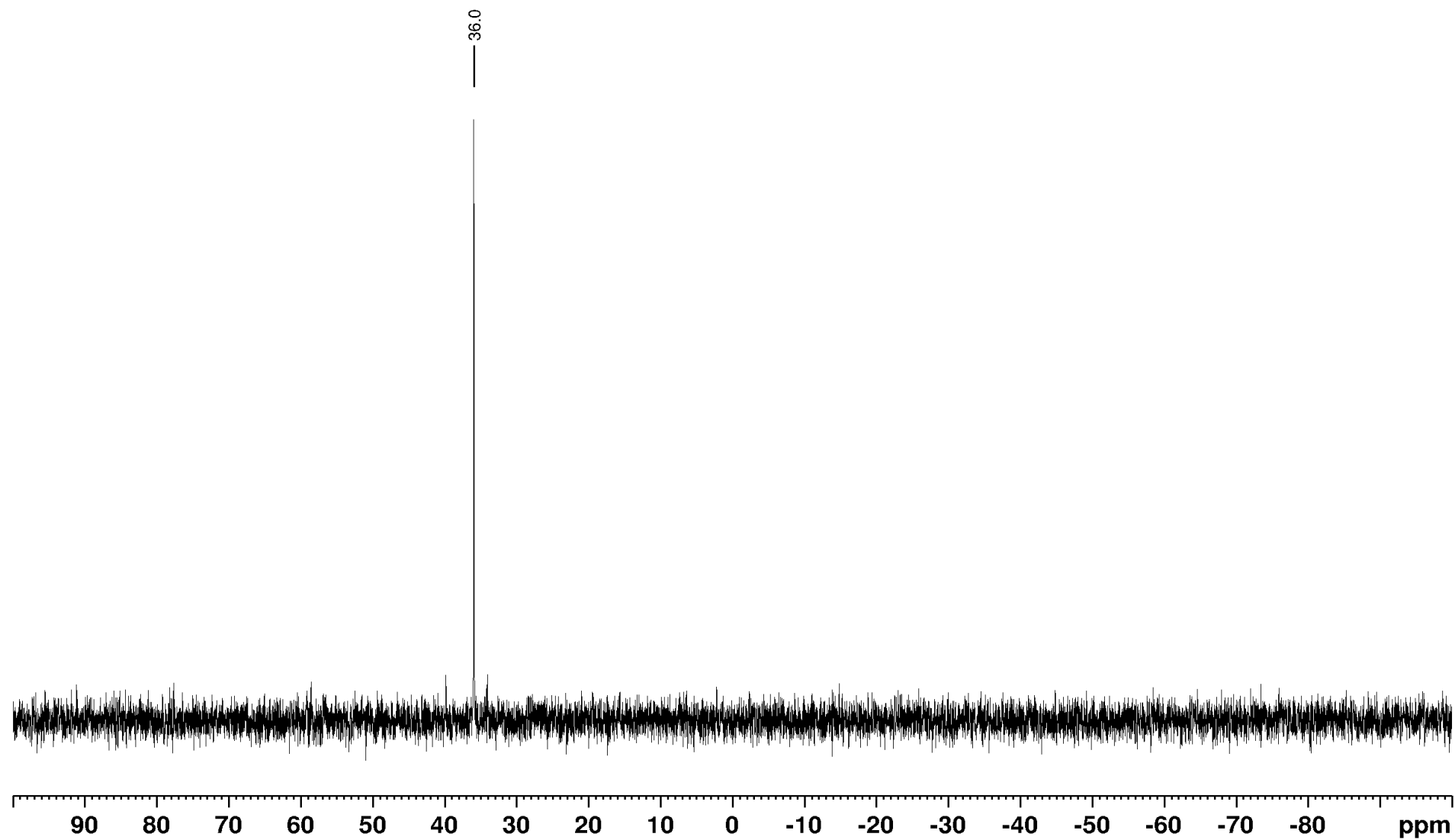


Figure S29. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of dibromodiethylsilane (**4ab**) by bromodeethylation of tetraethylsilane (**1a**) with 1,2-dibromoethane (**2b**)
(* 1,2-diphenylethane- d_{10} ; ^ cyclohexane)

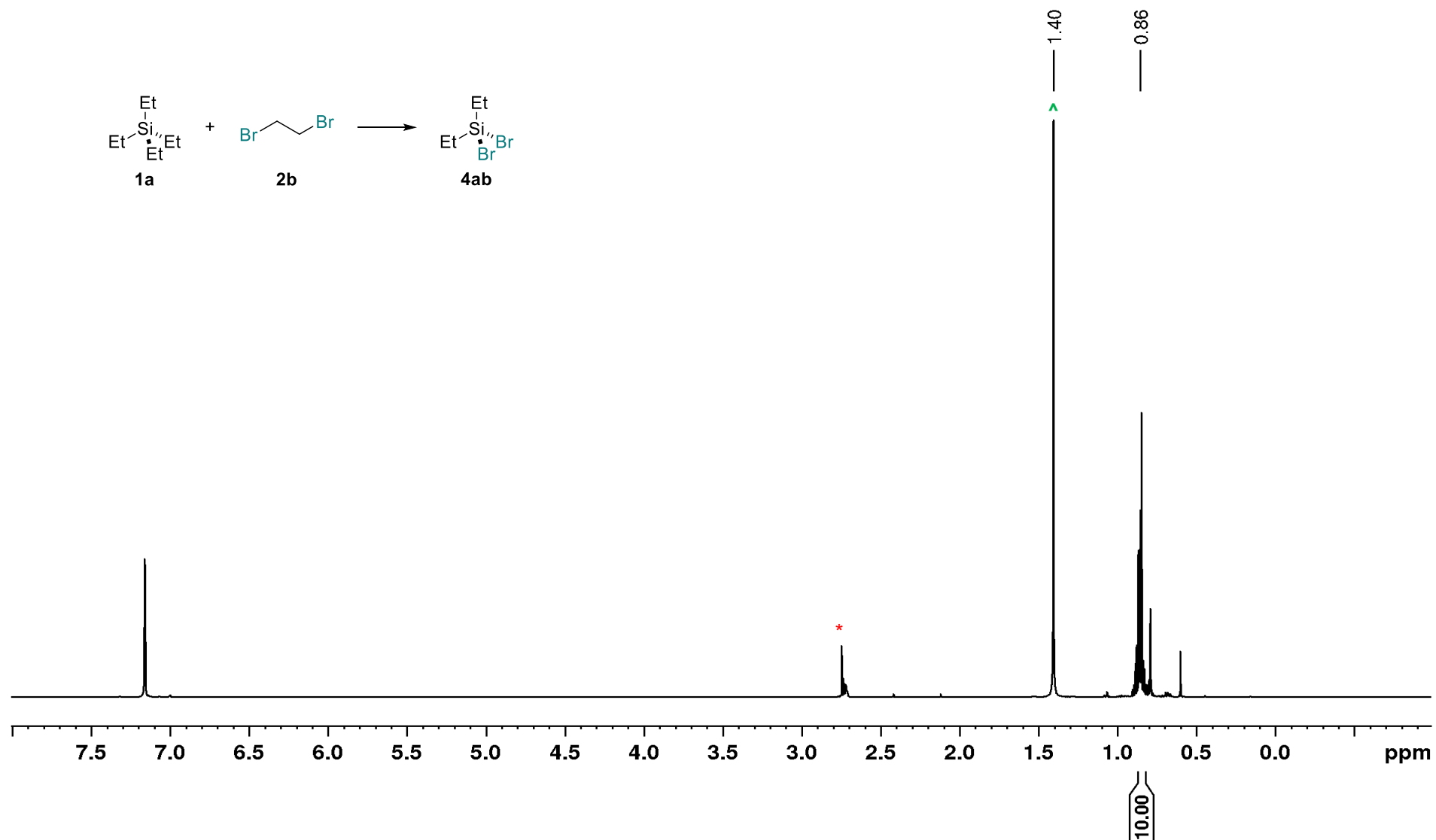


Figure S30. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of dibromodiethylsilane (**4ab**) by bromodeethylation of tetraethylsilane (**1a**) with 1,2-dibromoethane (**2b**) (* 1,2-diphenylethane- d_{10} ; ^ cyclohexane)

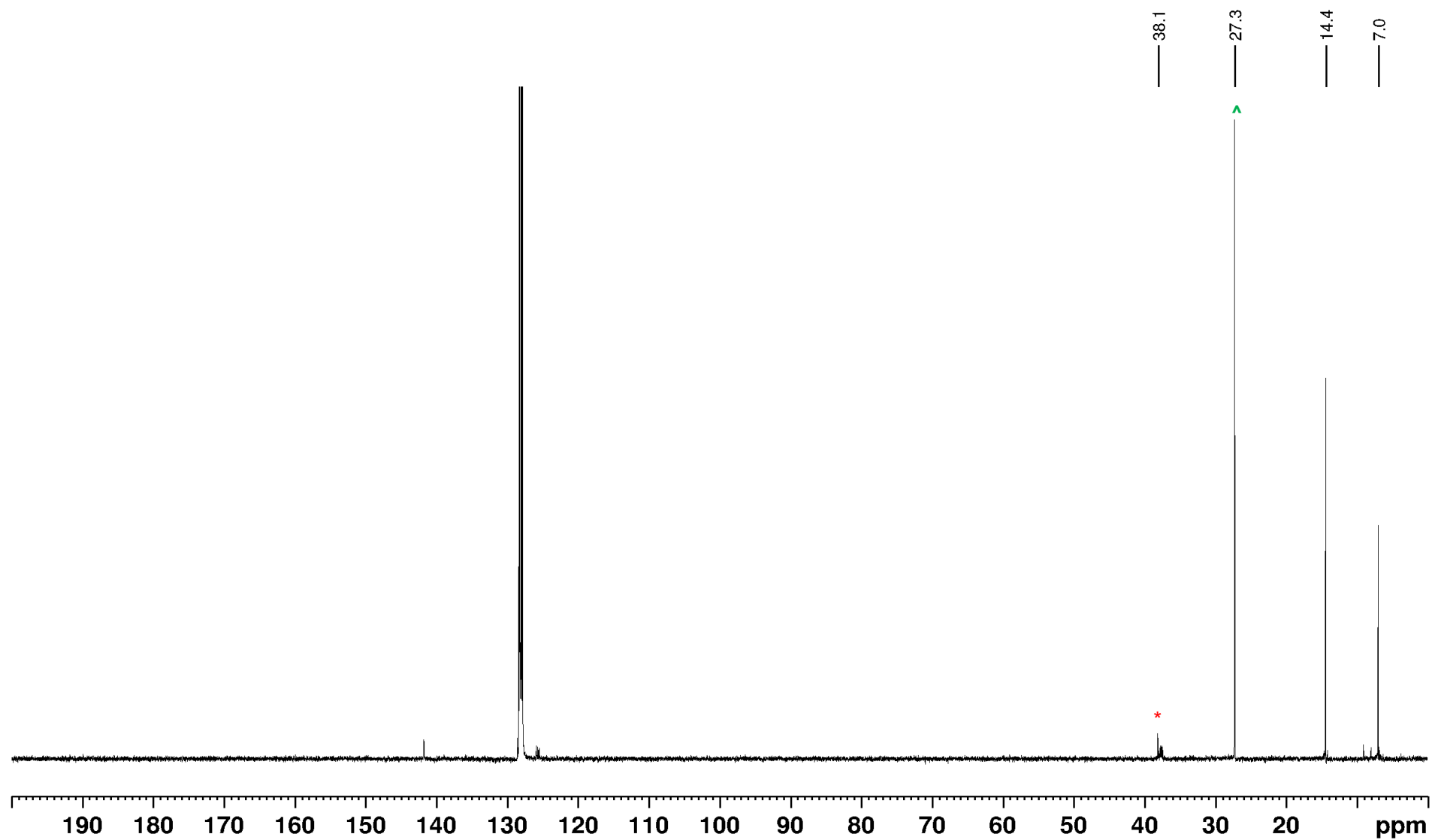


Figure S31. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 18.4°) of dibromodiethylsilane (**4ab**) by bromodeethylation of tetraethylsilane (**1a**) with 1,2-dibromoethane (**2b**)

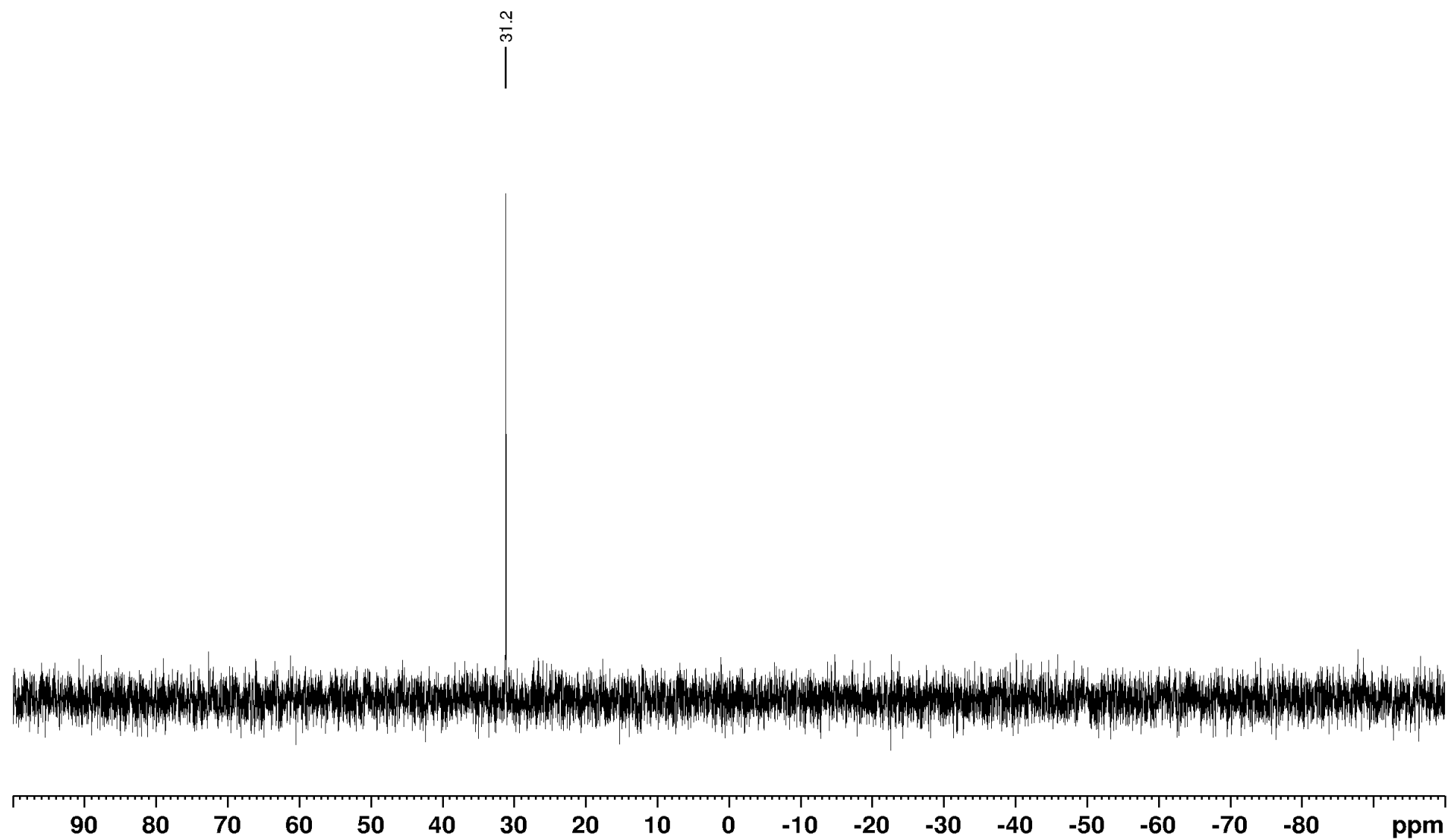


Figure S32. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of diethyldiiodosilane (**4ac**) by iododeethylation of tetraethylsilane (**1a**) with 1,2-diiodoethane (**2c**)
(* 1,2-diphenylethane- d_{10} ; ^ cyclohexane)

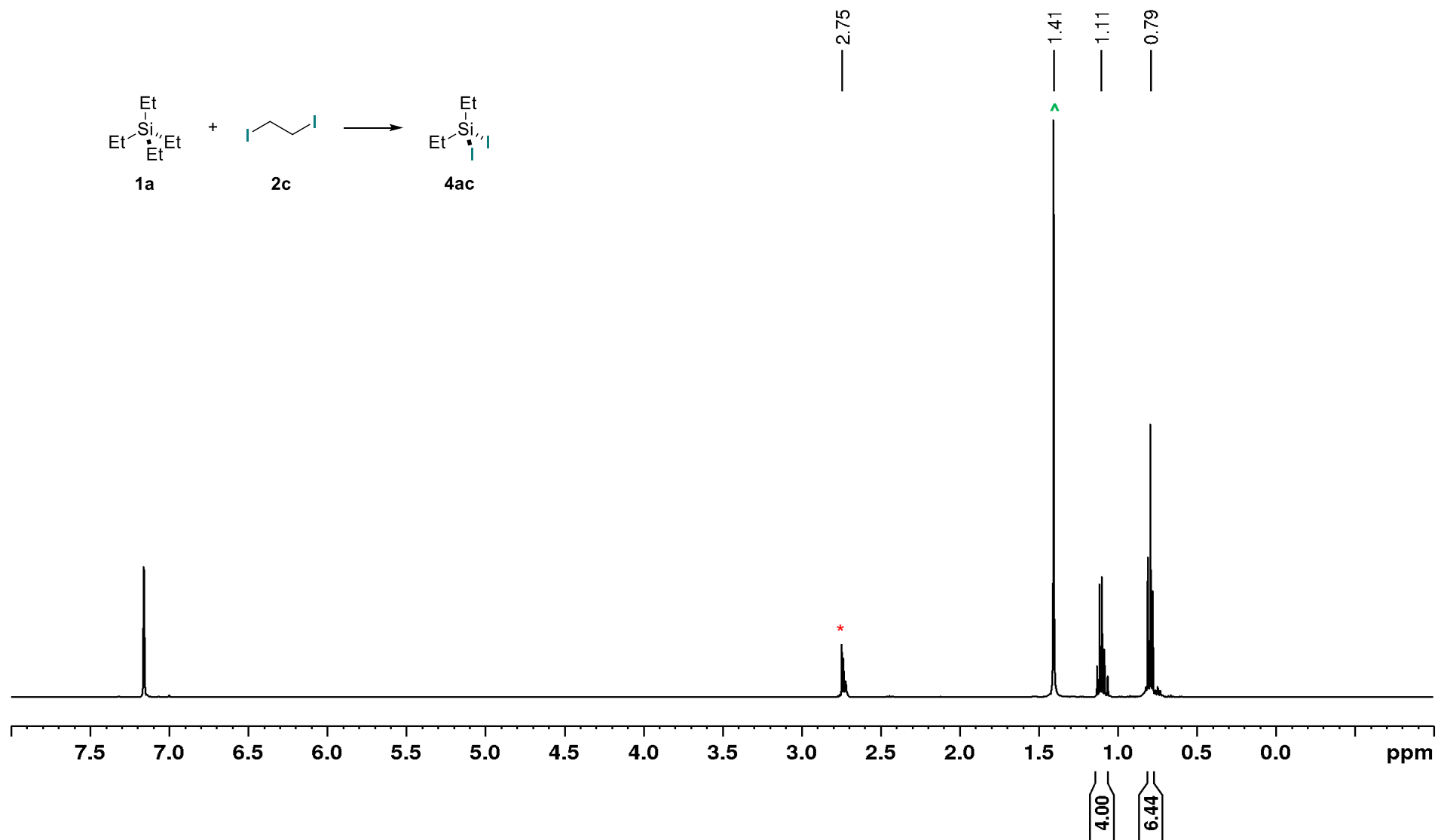


Figure S33. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of diethyldiiodosilane (**4ac**) by iododeethylation of tetraethylsilane (**1a**) with 1,2-diiodoethane (**2c**)
(* 1,2-diphenylethane- d_{10} ; ^ cyclohexane)

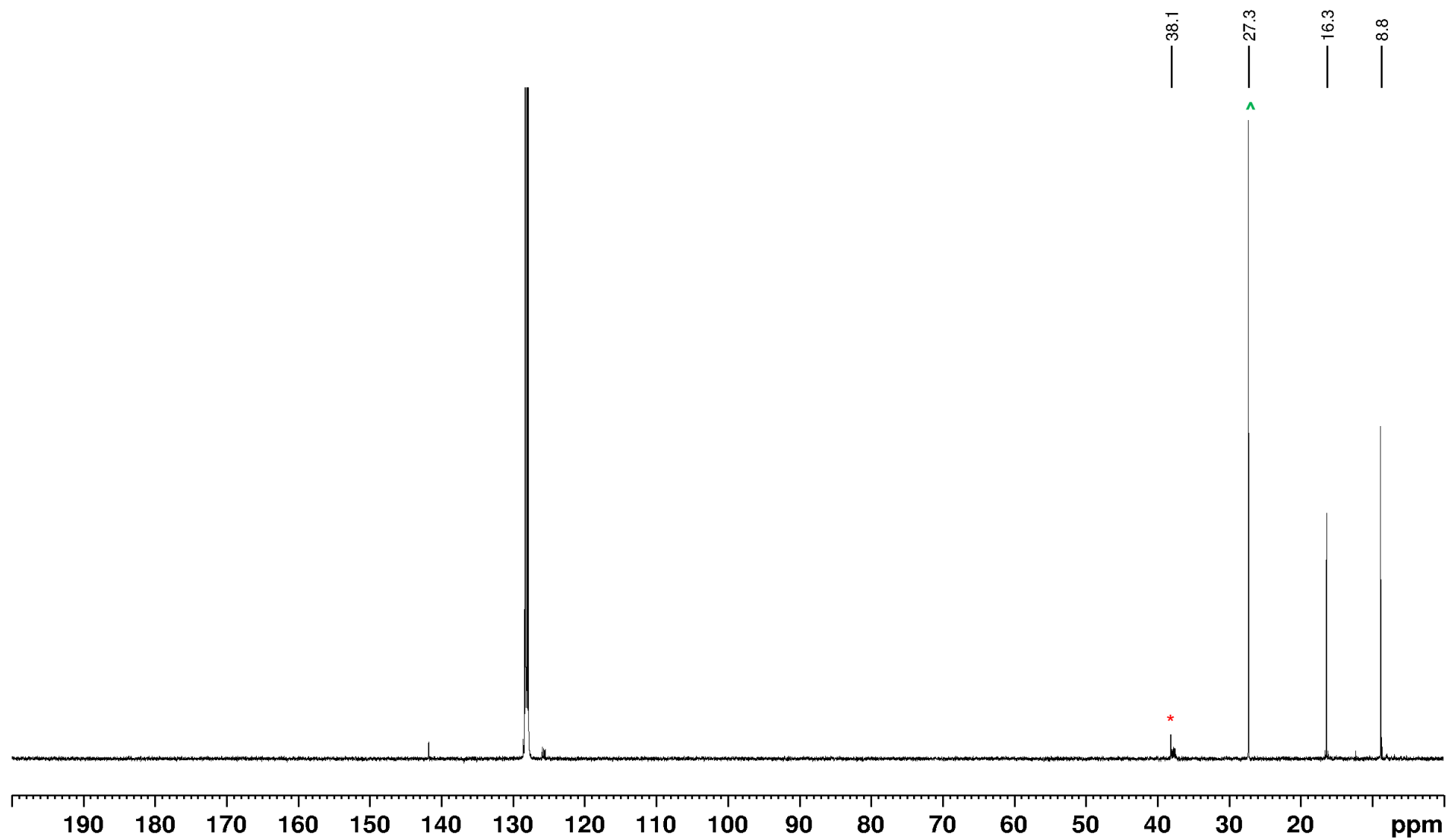


Figure S34. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 18.4°) of diethyldiiodosilane (**4ac**) by iododeethylation of tetraethylsilane (**1a**) with 1,2-diiodoethane (**2c**)

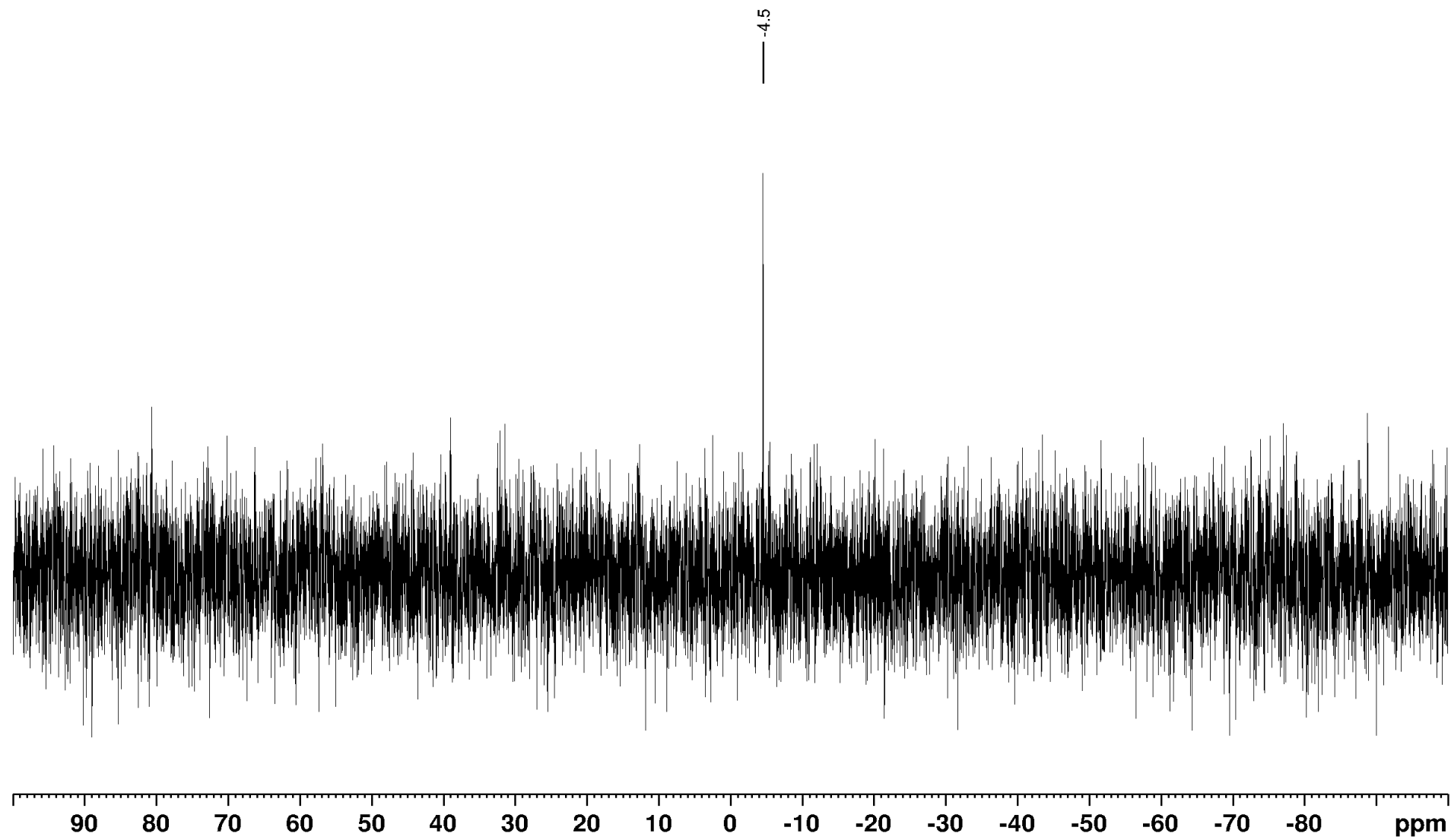


Figure S35. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of dibutyldichlorosilane (**4ba**) by chlorodebutylation of tetrabutylsilane (**1b**) with 1,2-dichloroethane (**2a**)
(* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane)

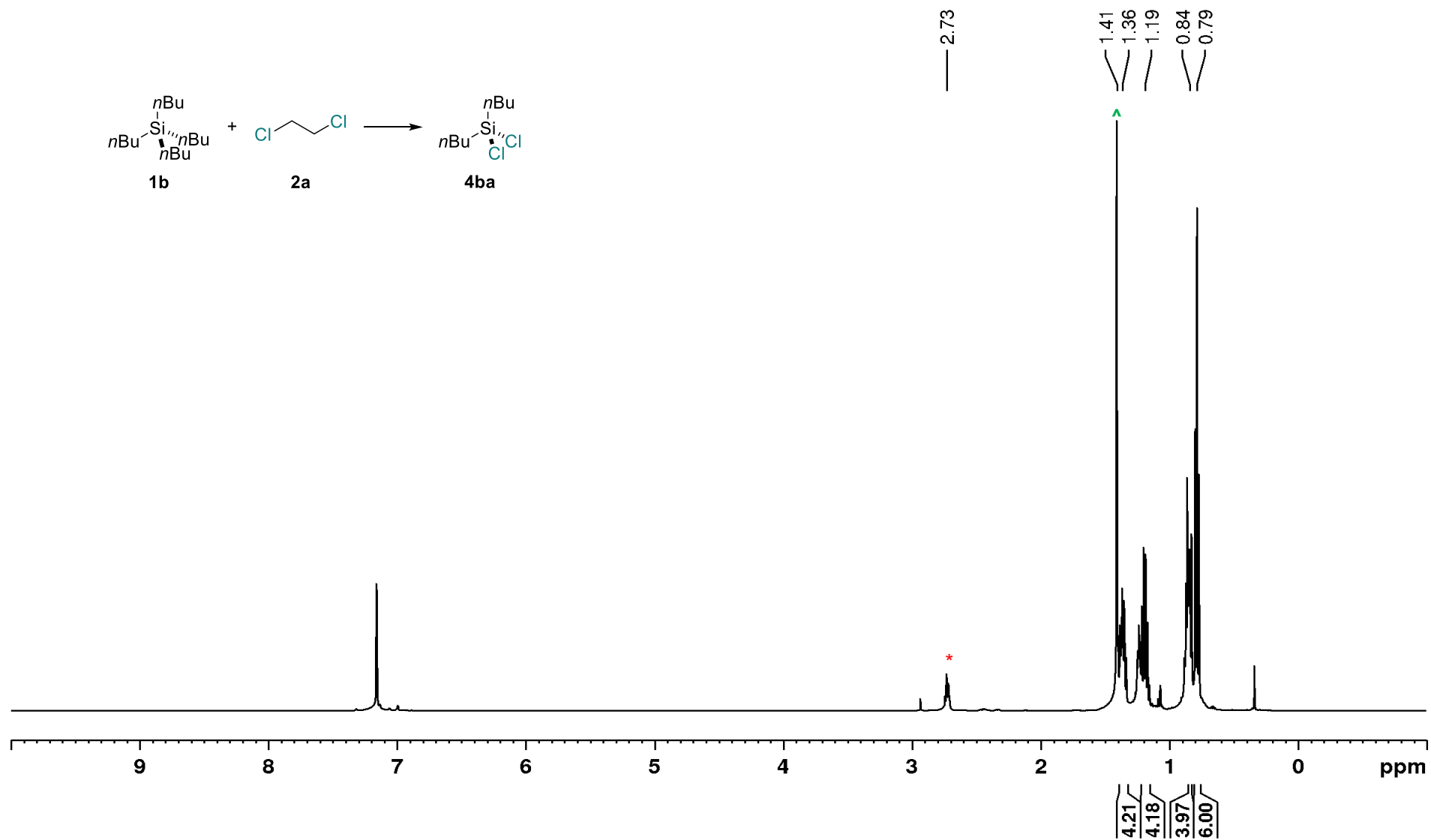


Figure S36. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of dibutyldichlorosilane (**4ba**) by chlorodebutylation of tetrabutylsilane (**1b**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane)

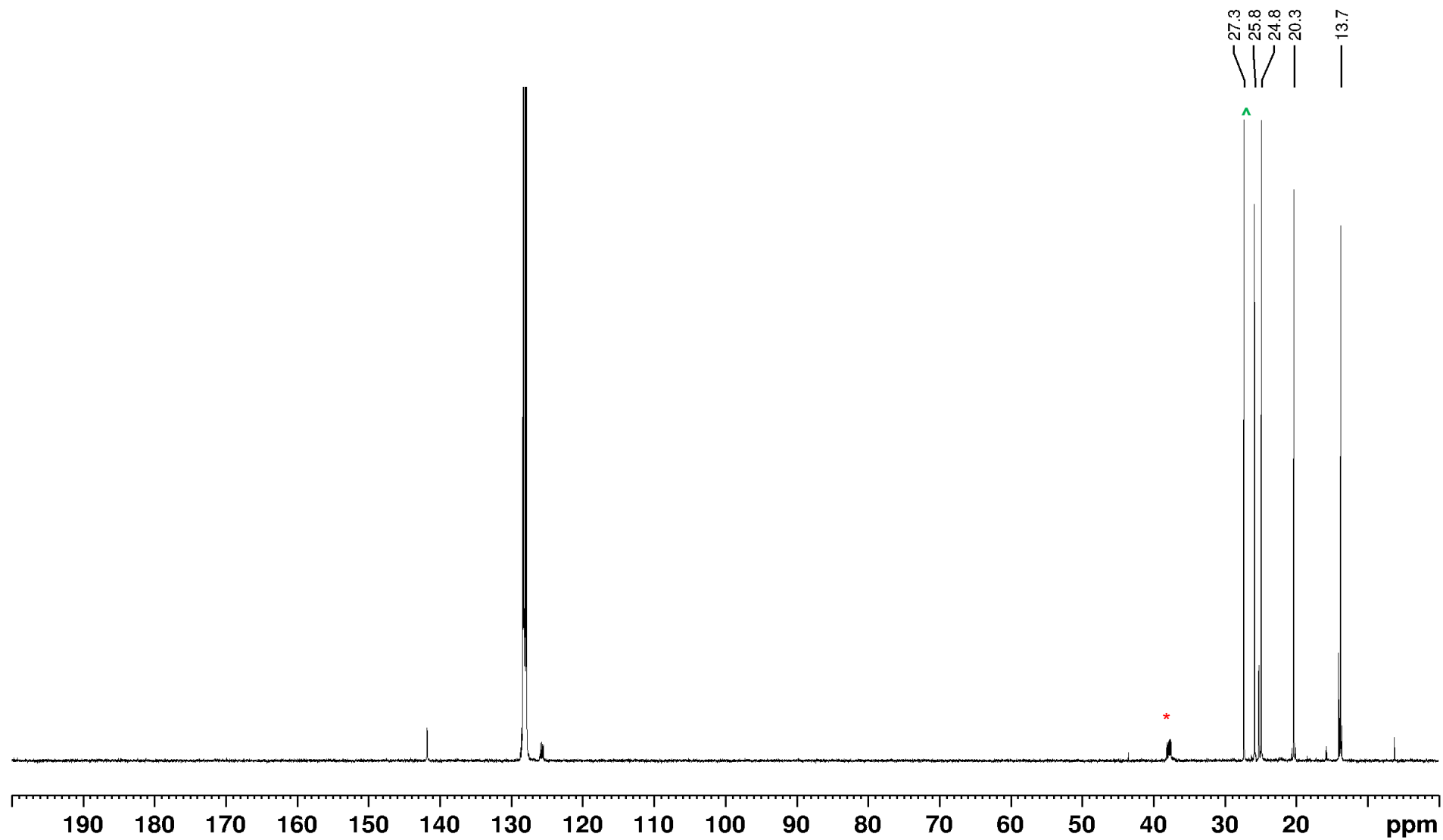


Figure S37. $^1\text{H},^{29}\text{Si}$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz) of dibutyldichlorosilane (**4ba**) by chlorodebutylation of tetrabutylsilane (**1b**) with 1,2-dichloroethane (**2a**)

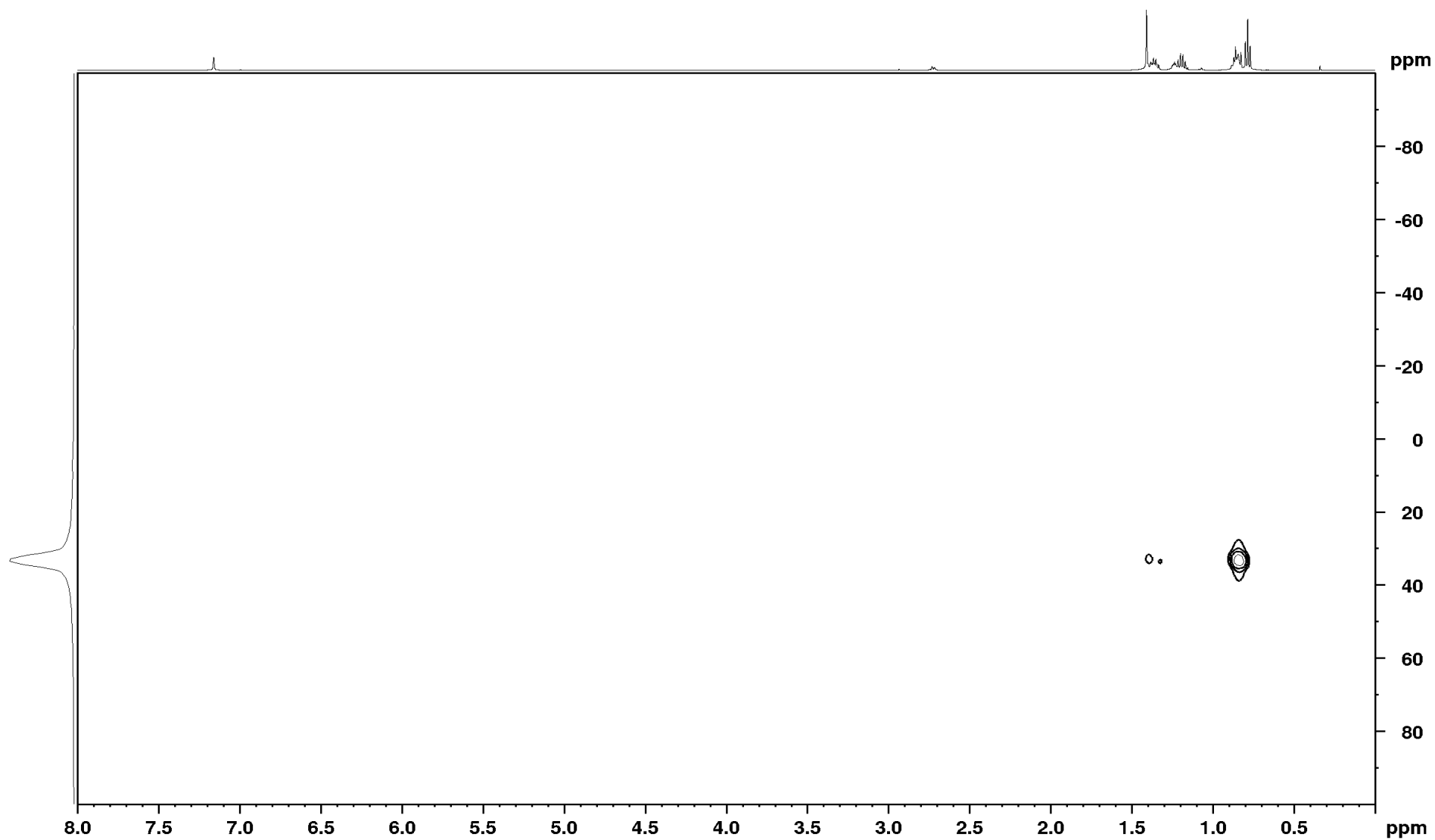


Figure S38. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of dichloro(methyl)(octyl)silane (**4ca**) by chlorodemethylation of trimethyl(octyl)silane (**1c**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10})

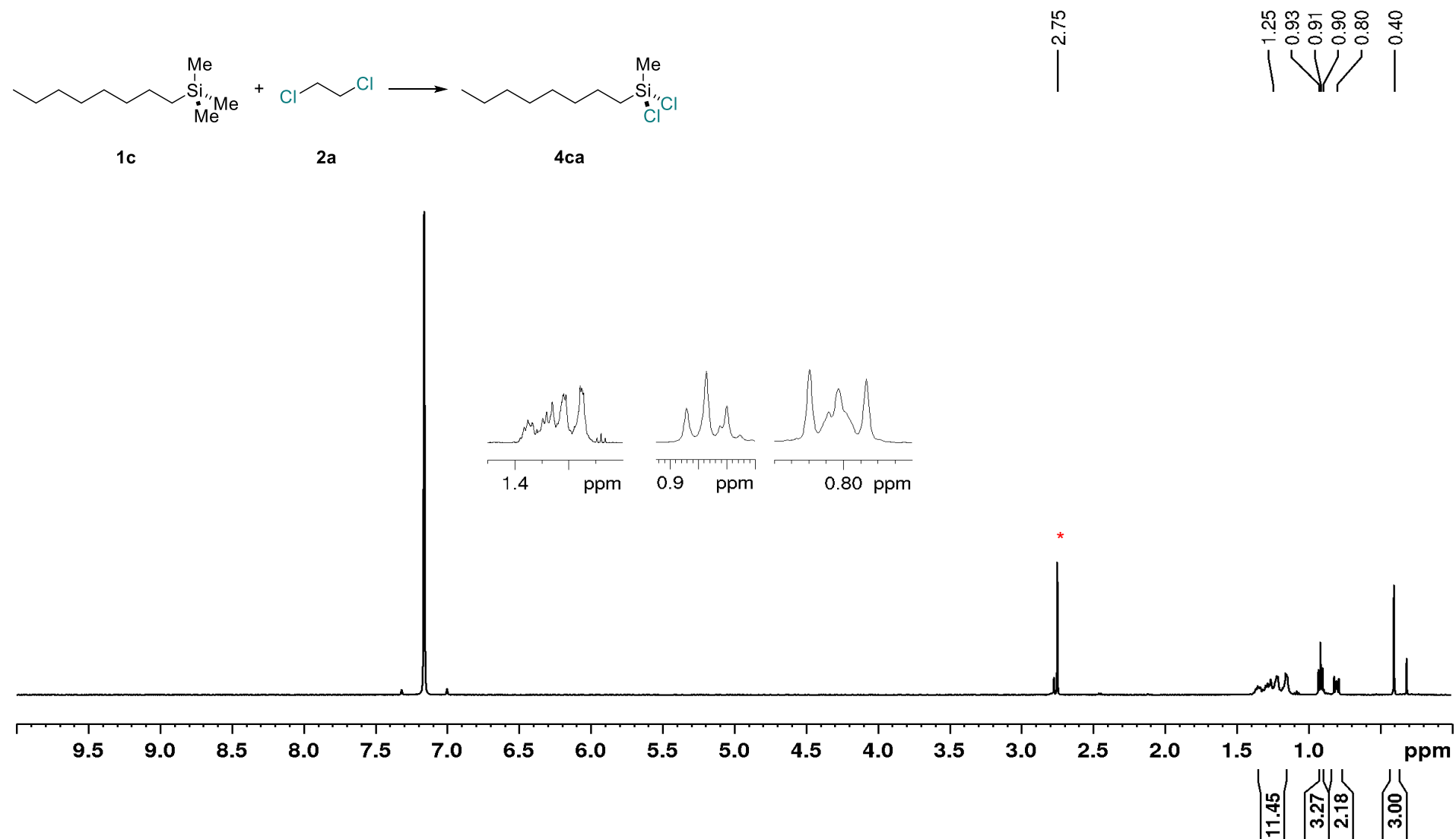


Figure S39. $^1\text{H},^{29}\text{Si}$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz) of dichloro(methyl)(octyl)silane (**4ca**) by chlorodemethylation of trimethyl(octyl)silane (**1c**) with 1,2-dichloroethane (**2a**)

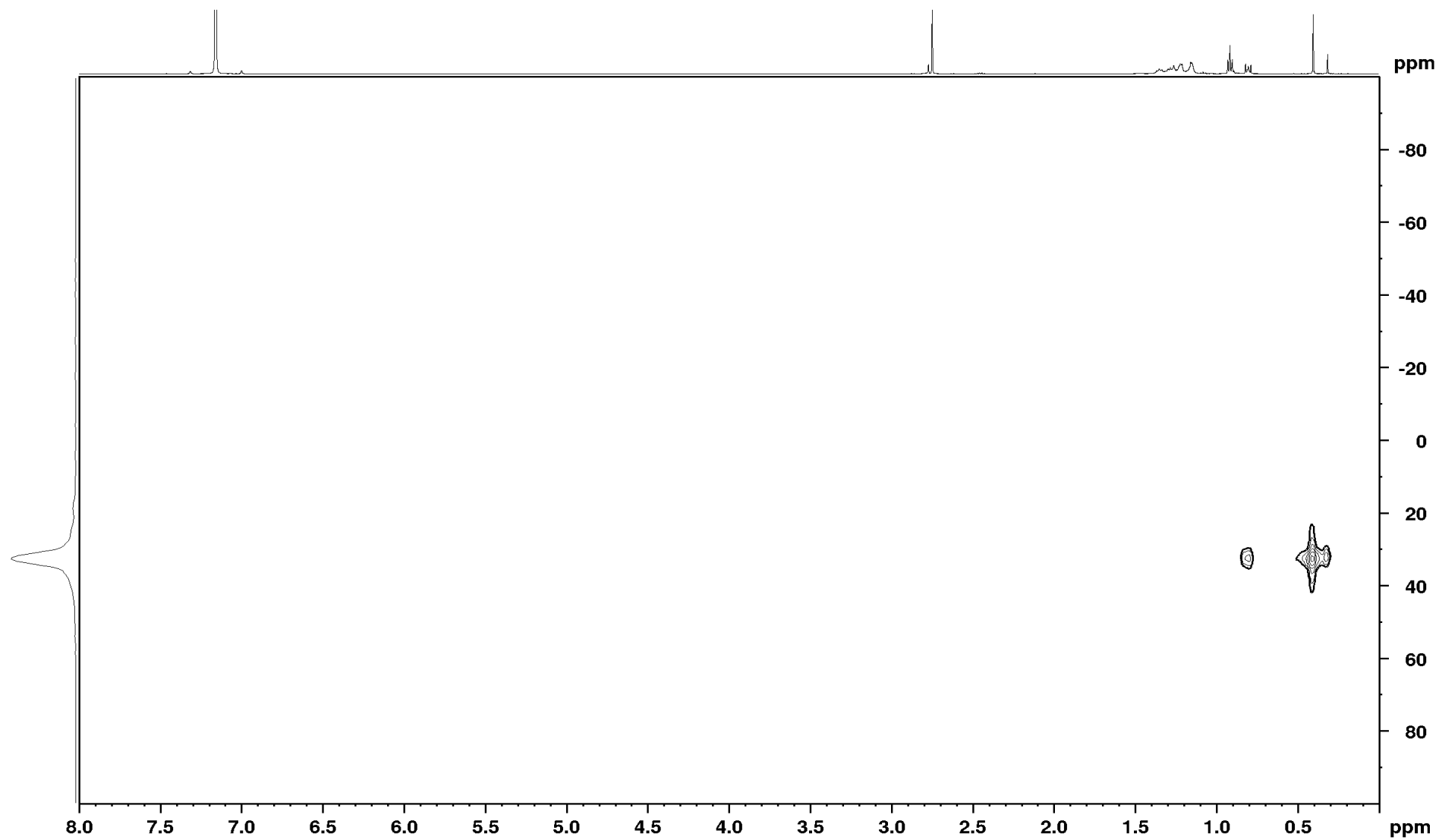


Figure S40. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of dichloro(cyclohexyl)(methyl)silane (**4da**) by chlorodemethylation of cyclohexyltrimethylsilane (**1d**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane)

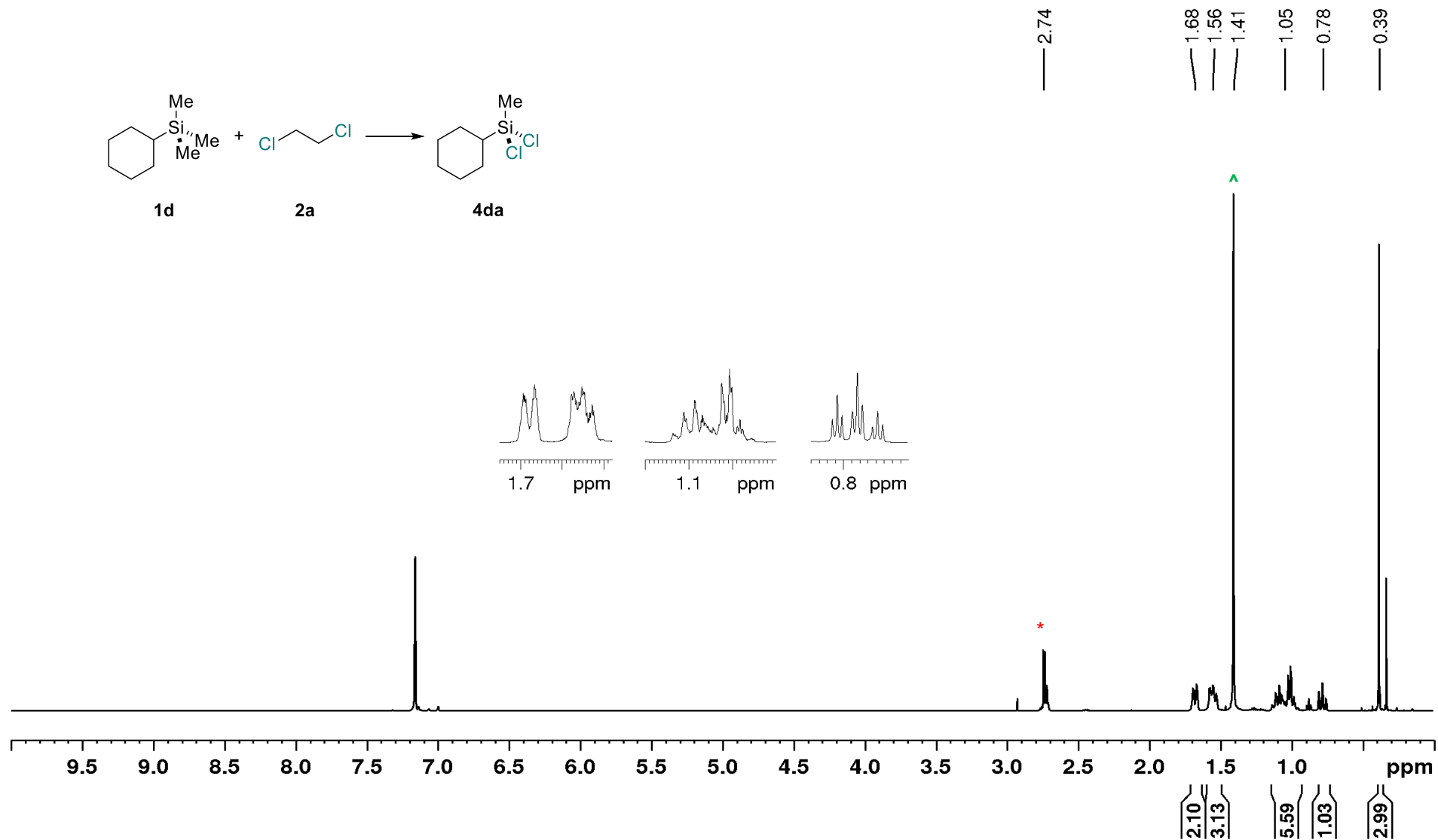


Figure S41. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of dichloro(cyclohexyl)(methyl)silane (**4da**) by chlorodemethylation of cyclohexyltrimethylsilane (**1d**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; ^ cyclohexane)

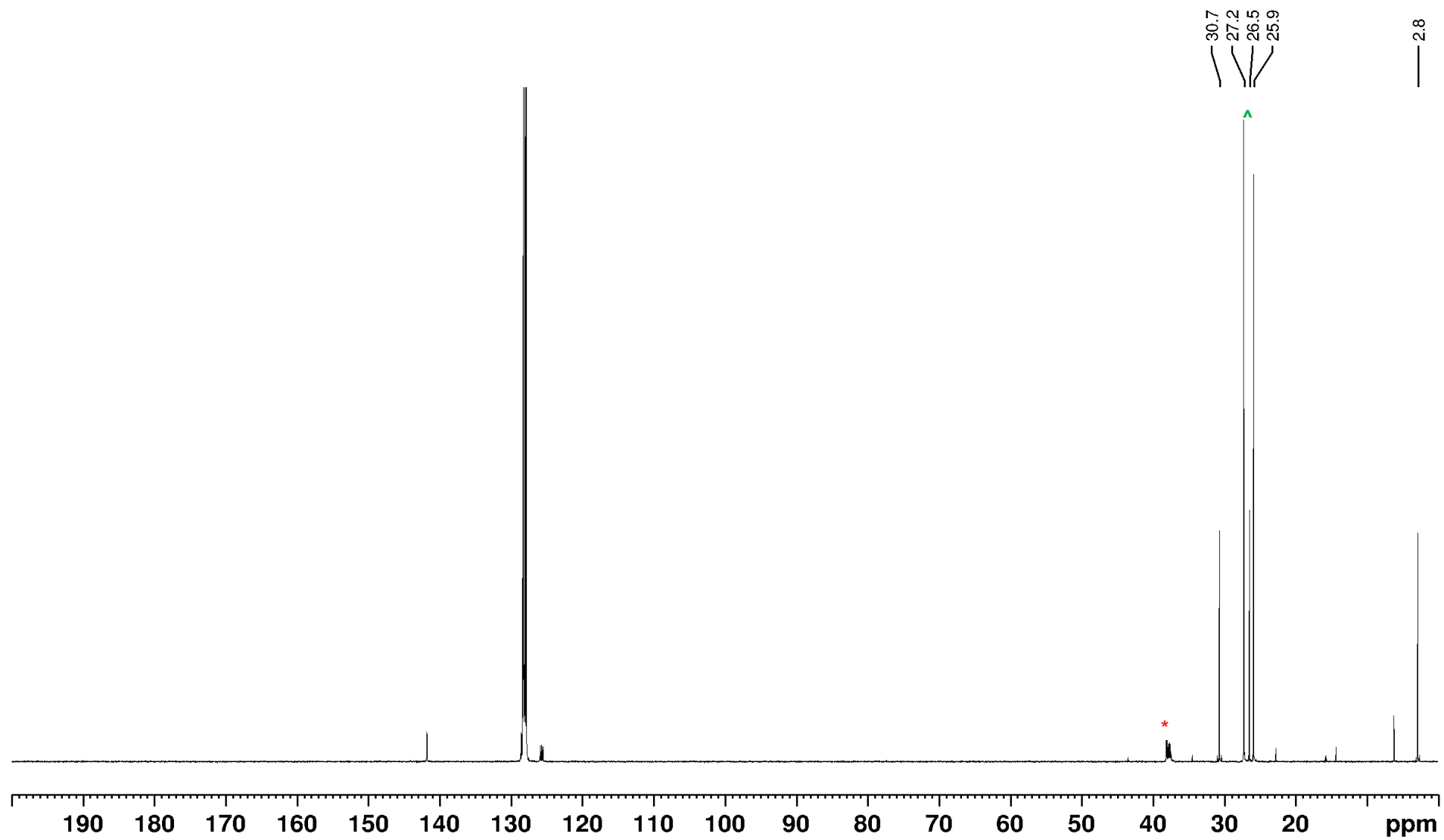


Figure S42. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 30.0°) of dichloro(cyclohexyl)(methyl)silane (**4da**) by chlorodemethylation of cyclohexyltrimethylsilane (**1d**) with 1,2-dichloroethane (**2a**)

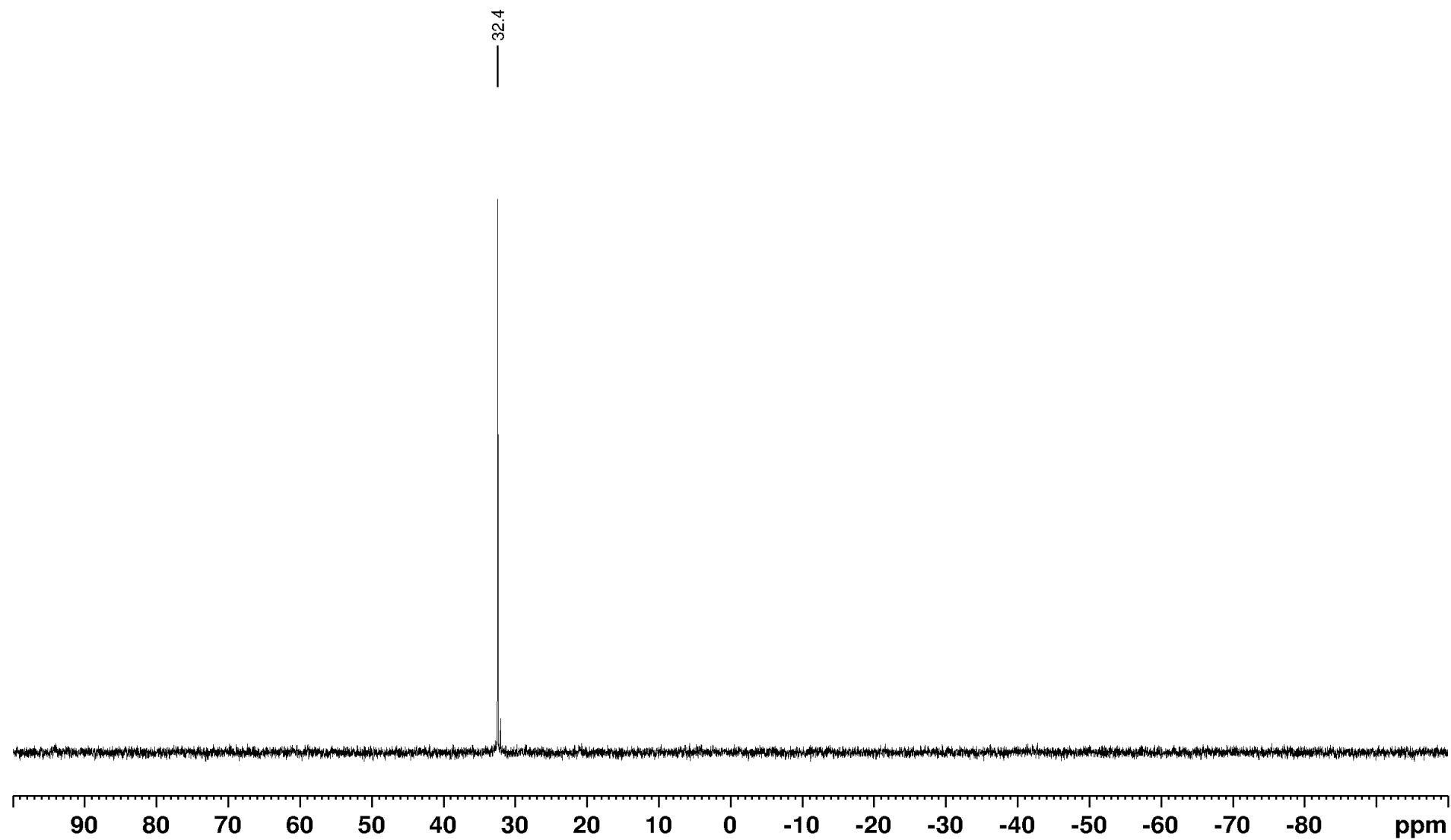


Figure S43. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of *tert*-butylmethyldichlorosilane (**4ea**) by chlorodemethylation of *tert*-butyltrimethylsilane (**1e**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane)

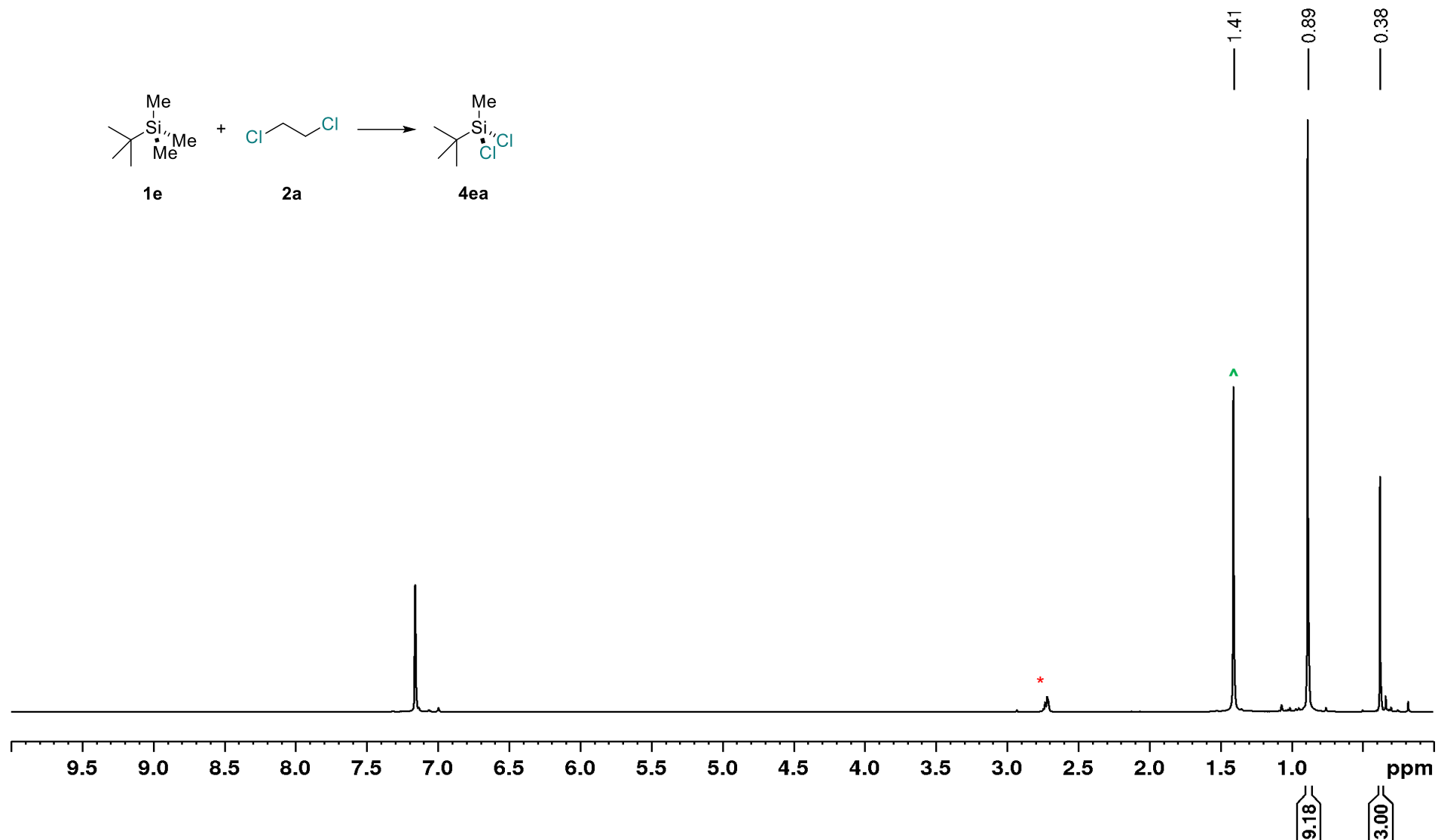


Figure S44. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of *tert*-butylmethyldichlorosilane (**4ea**) by chlorodemethylation of *tert*-butyltrimethylsilane (**1e**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane)

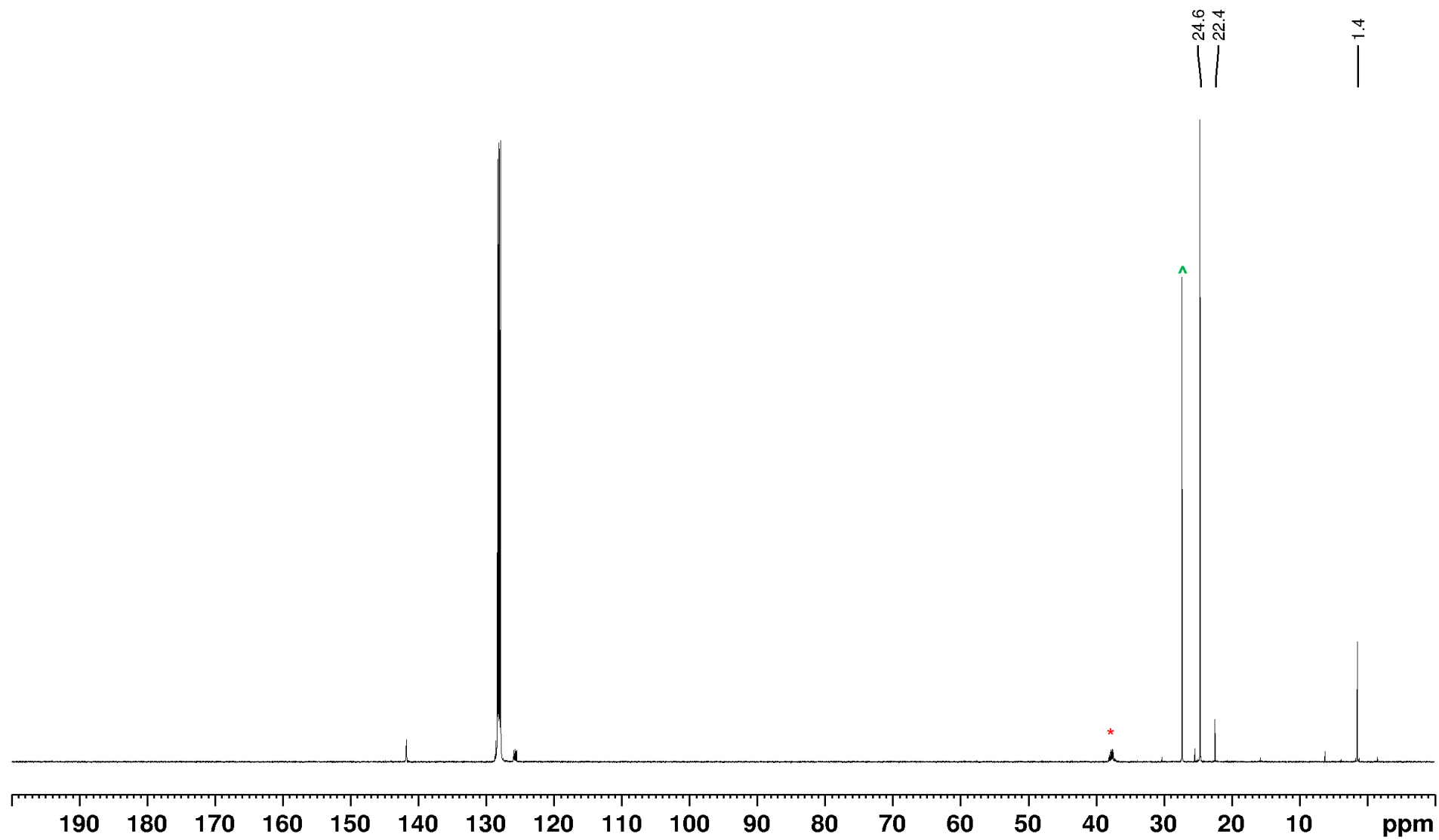


Figure S45. $^1\text{H},^{29}\text{Si}$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz) of *tert*-butylmethyldichlorosilane (**4ea**) by chlorodemethylation of *tert*-butyltrimethylsilane (**1e**) with 1,2-dichloroethane (**2a**)

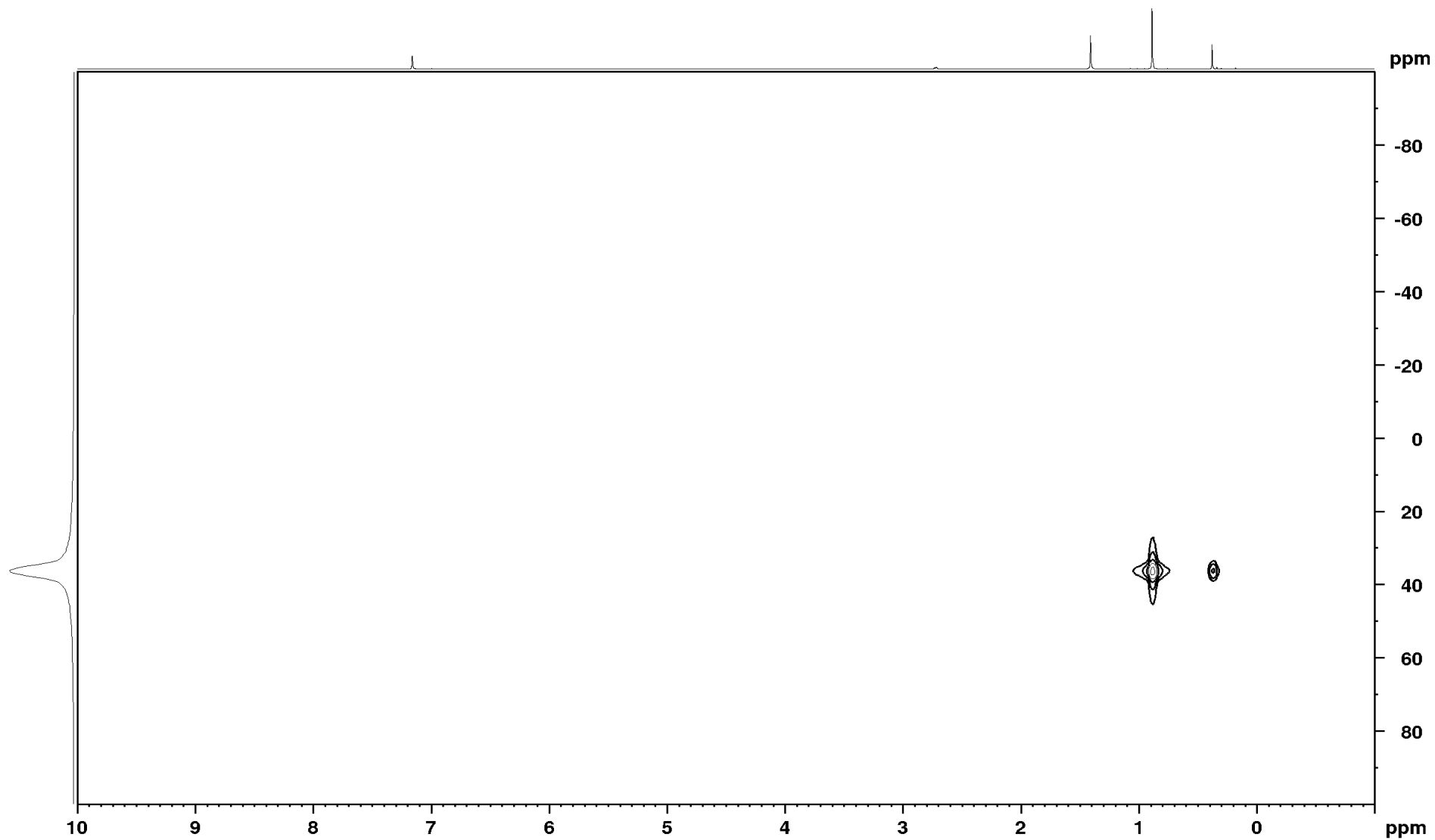


Figure S46. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of butyldichloro(ethyl)silane (**4fa**) by chlorodeethylation of butyltriethylsilane (**1f**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle 1,2,4,5-tetrachlorobenzene)

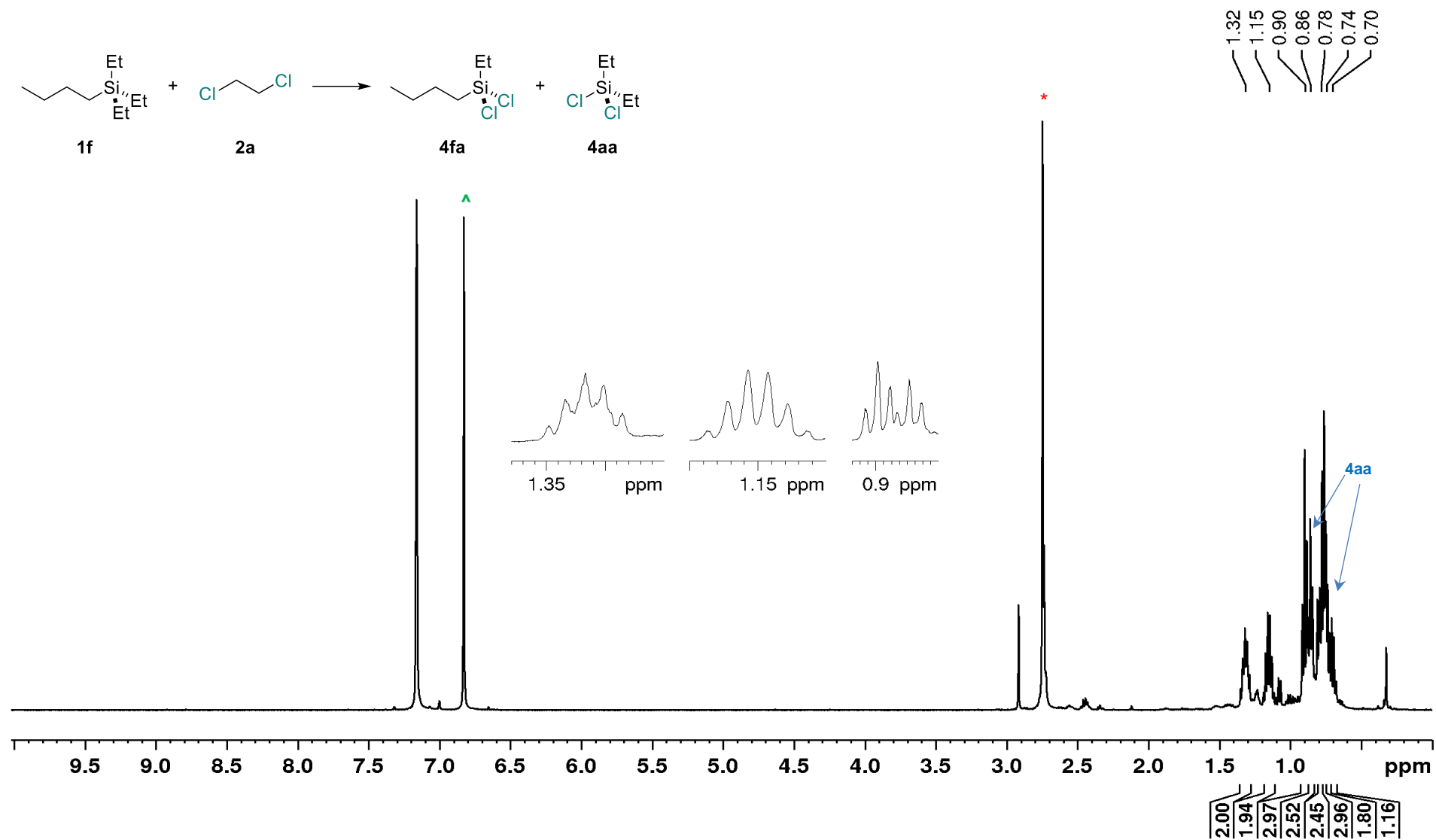


Figure S47. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of butyldichloro(ethyl)silane (**4fa**) by chloroethylation of butyltriethylsilane (**1f**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; ^ 1,2,4,5-tetrachlorobenzene)

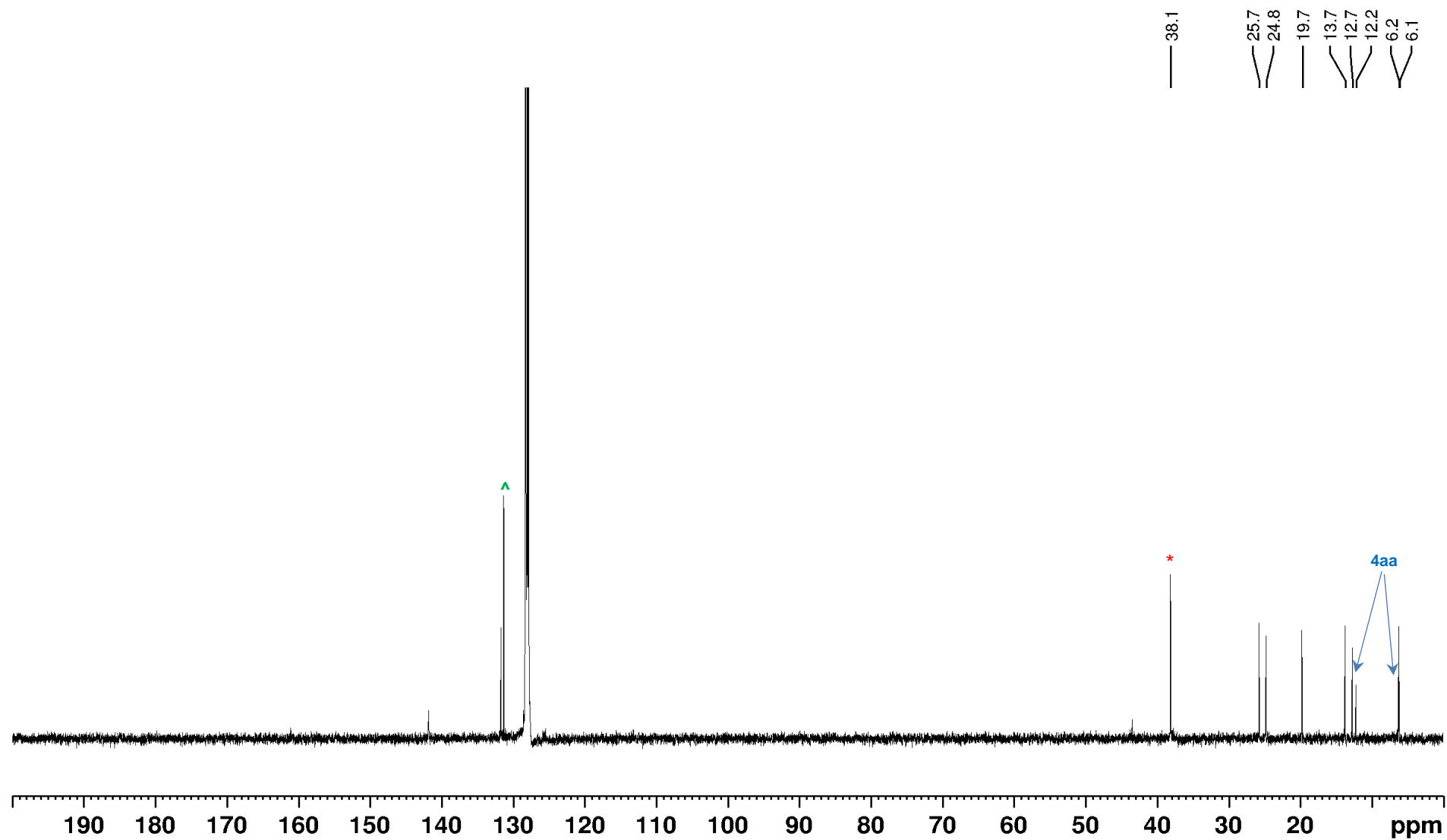


Figure S48. $^1\text{H},^{29}\text{Si}$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz) of butyldichloro(ethyl)silane (**4fa**) by chlorodeethylation of butyltriethylsilane (**1f**) with 1,2-dichloroethane (**2a**)

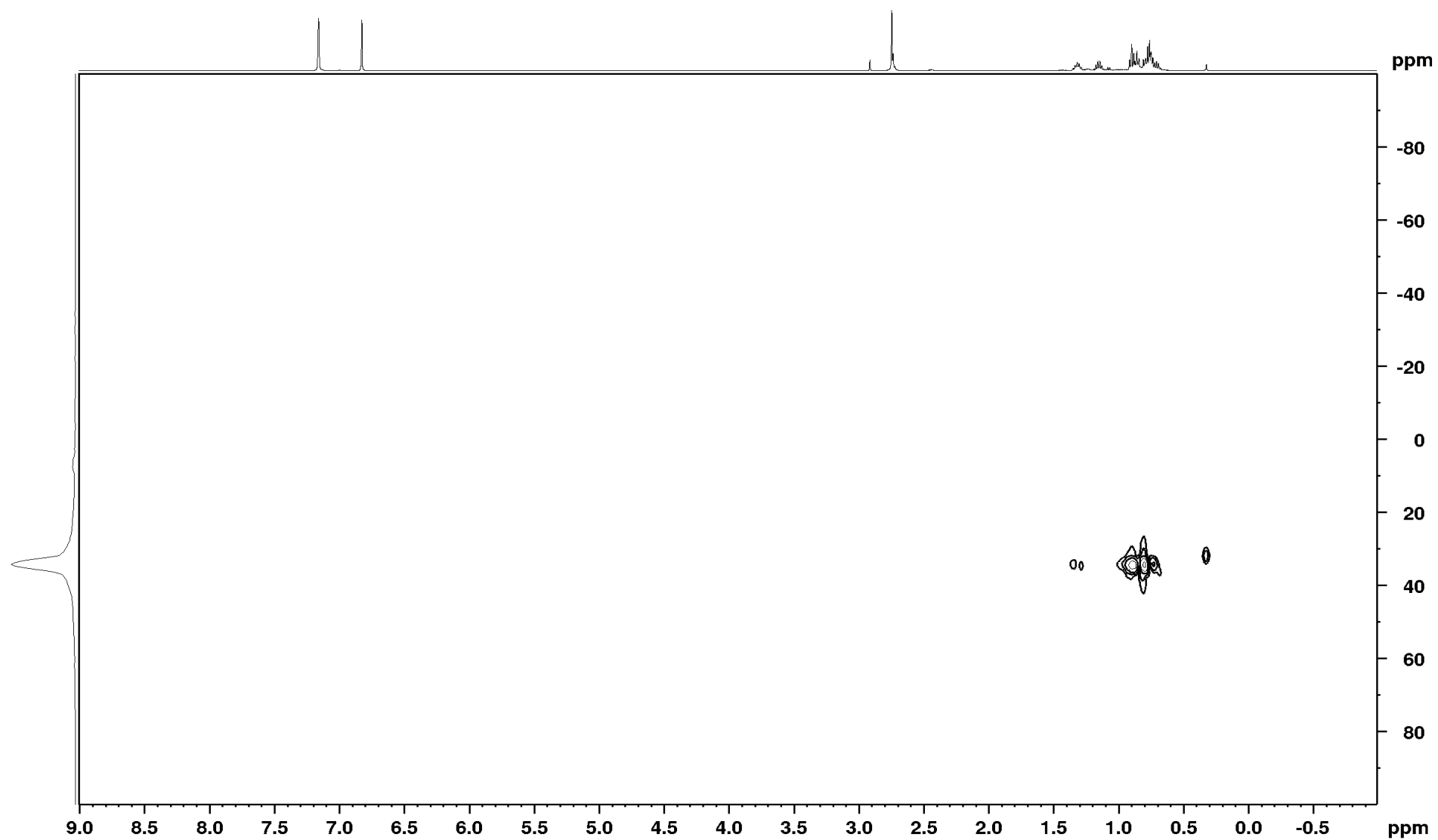


Figure S49. $^1\text{H},^{13}\text{C}$ HSQC NMR (500/126 MHz, C_6D_6 , 298 K) of butyldichloro(ethyl)silane (**4fa**) by chlorodeethylation of butyltriethylsilane (**1f**) with 1,2-dichloroethane (**2a**)

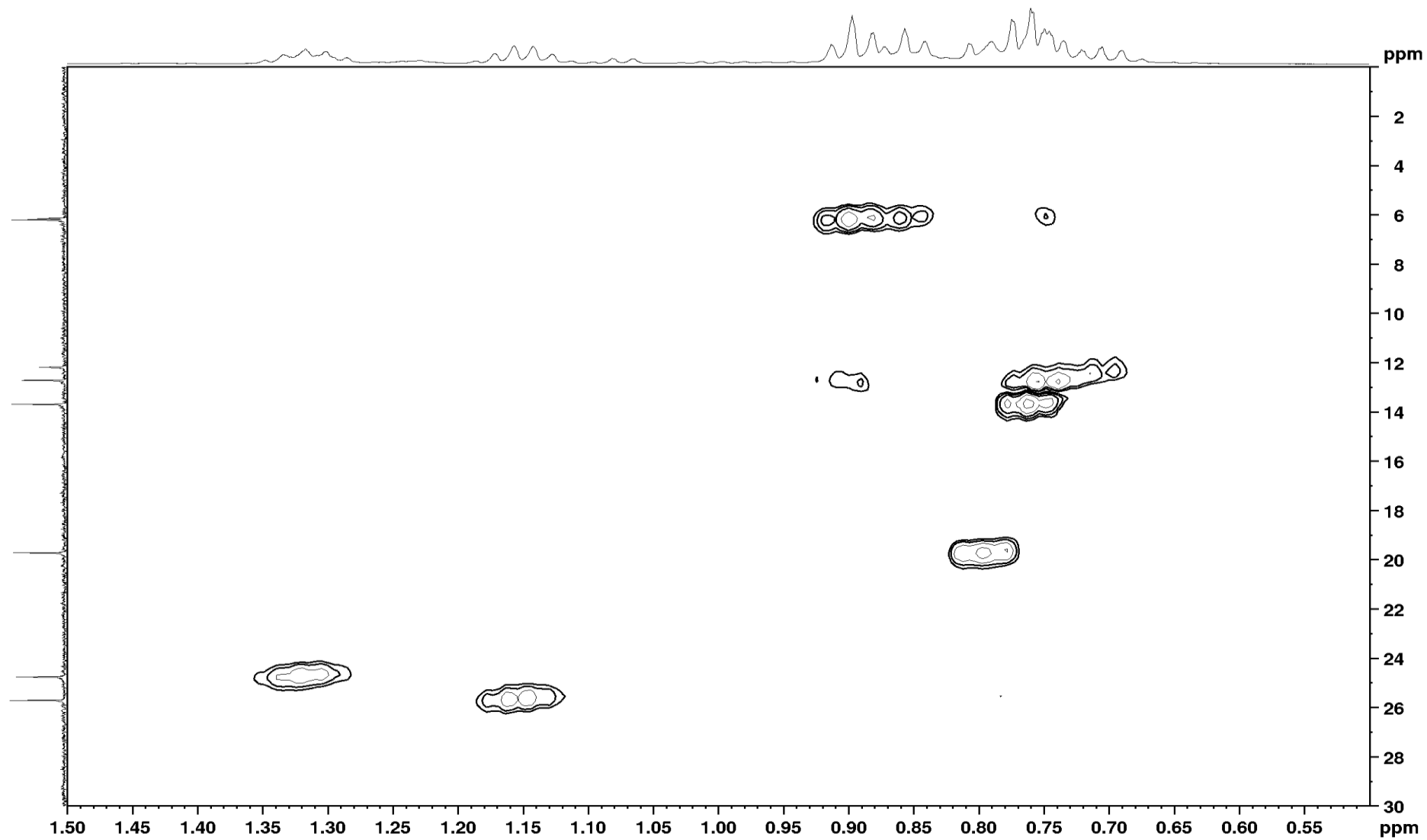


Figure S50. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of dichloro(hexyl)(methyl)silane (**4ga**) by chlorodemethylation of hexyltrimethylsilane (**1g**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane)

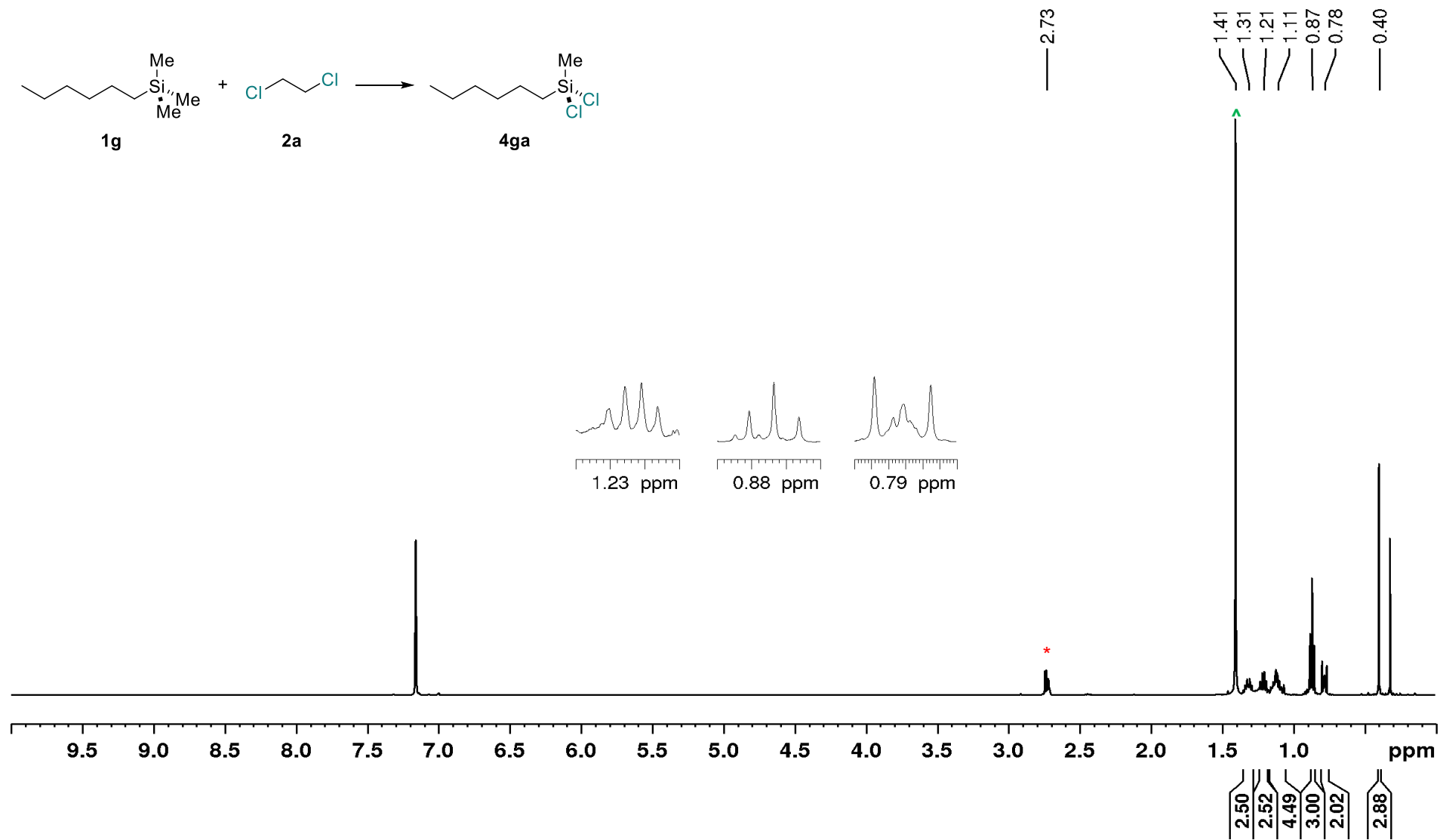


Figure S51. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of dichloro(hexyl)(methyl)silane (**4ga**) by chlorodemethylation of hexyltrimethylsilane (**1g**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; ^ cyclohexane)

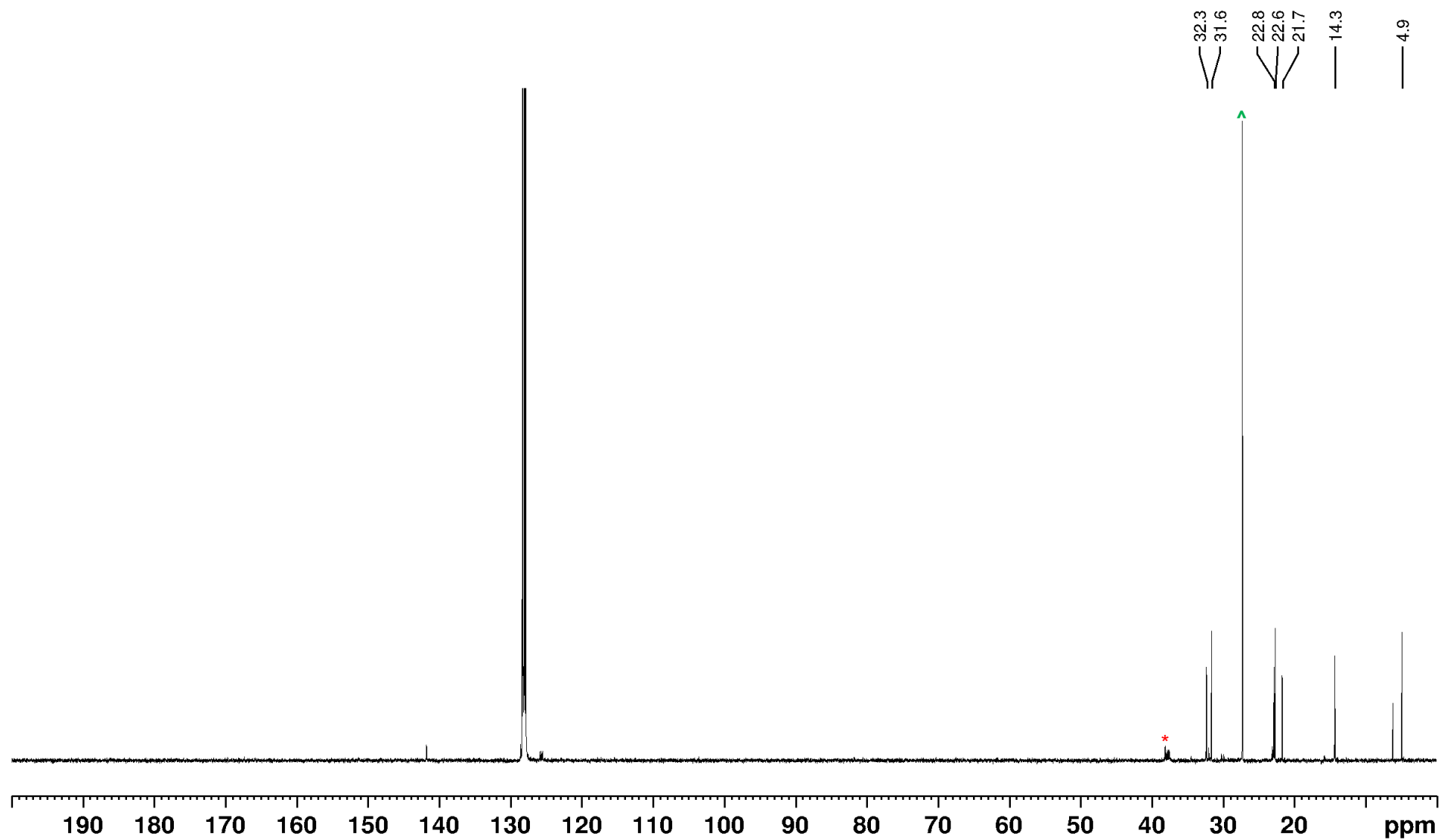


Figure S52. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 22.2°) of dichloro(hexyl)(methyl)silane (**4ga**) by chlorodemethylation of hexyltrimethylsilane (**1g**) with 1,2-dichloroethane (**2a**)

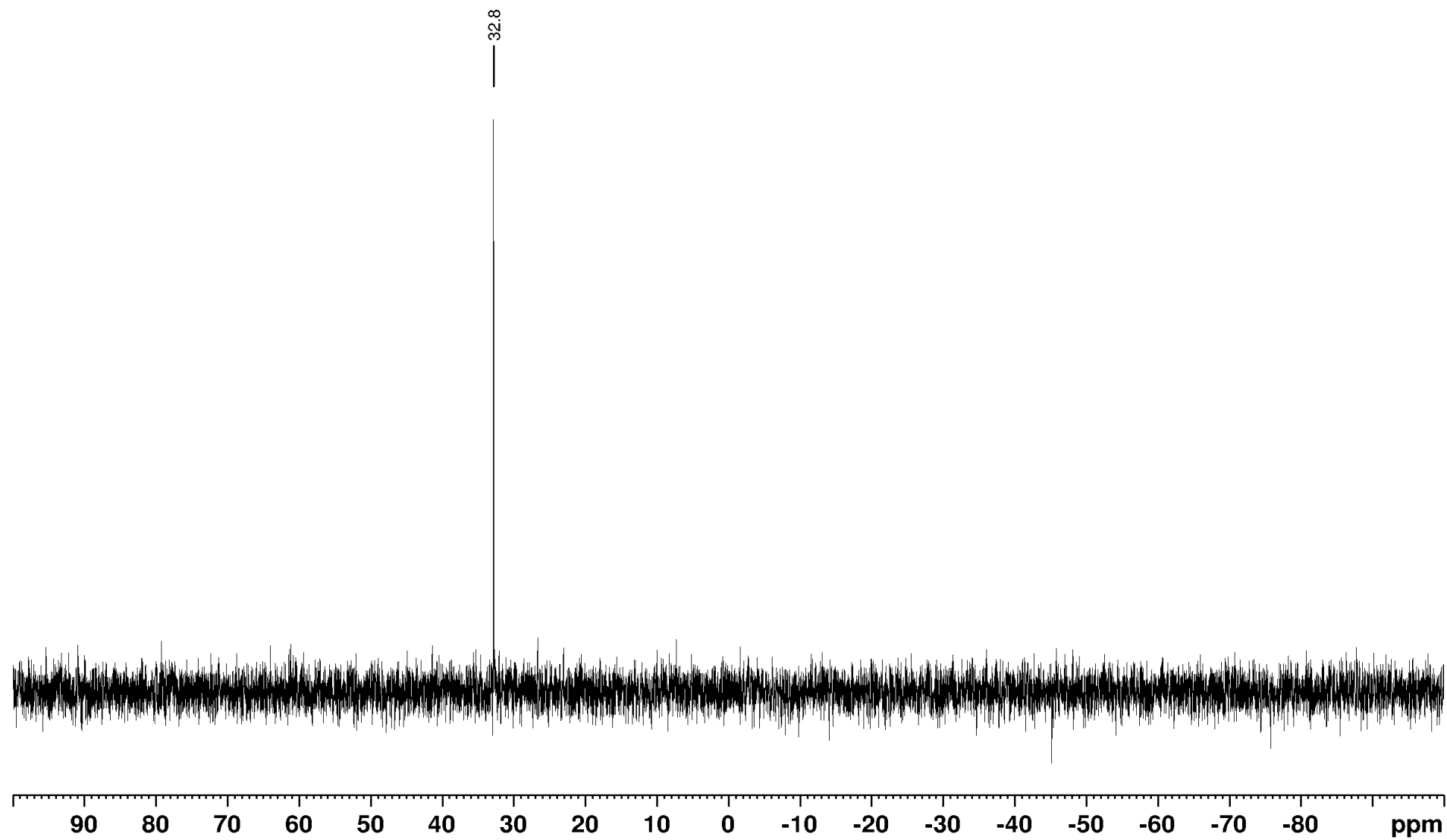


Figure S53. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of dichloro(hexyl)(methyl)silane (**4ga**) by chlorodemethylation of hexyltrimethylsilane (**1g**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle 1,2,4,5-tetrachlorobenzene)

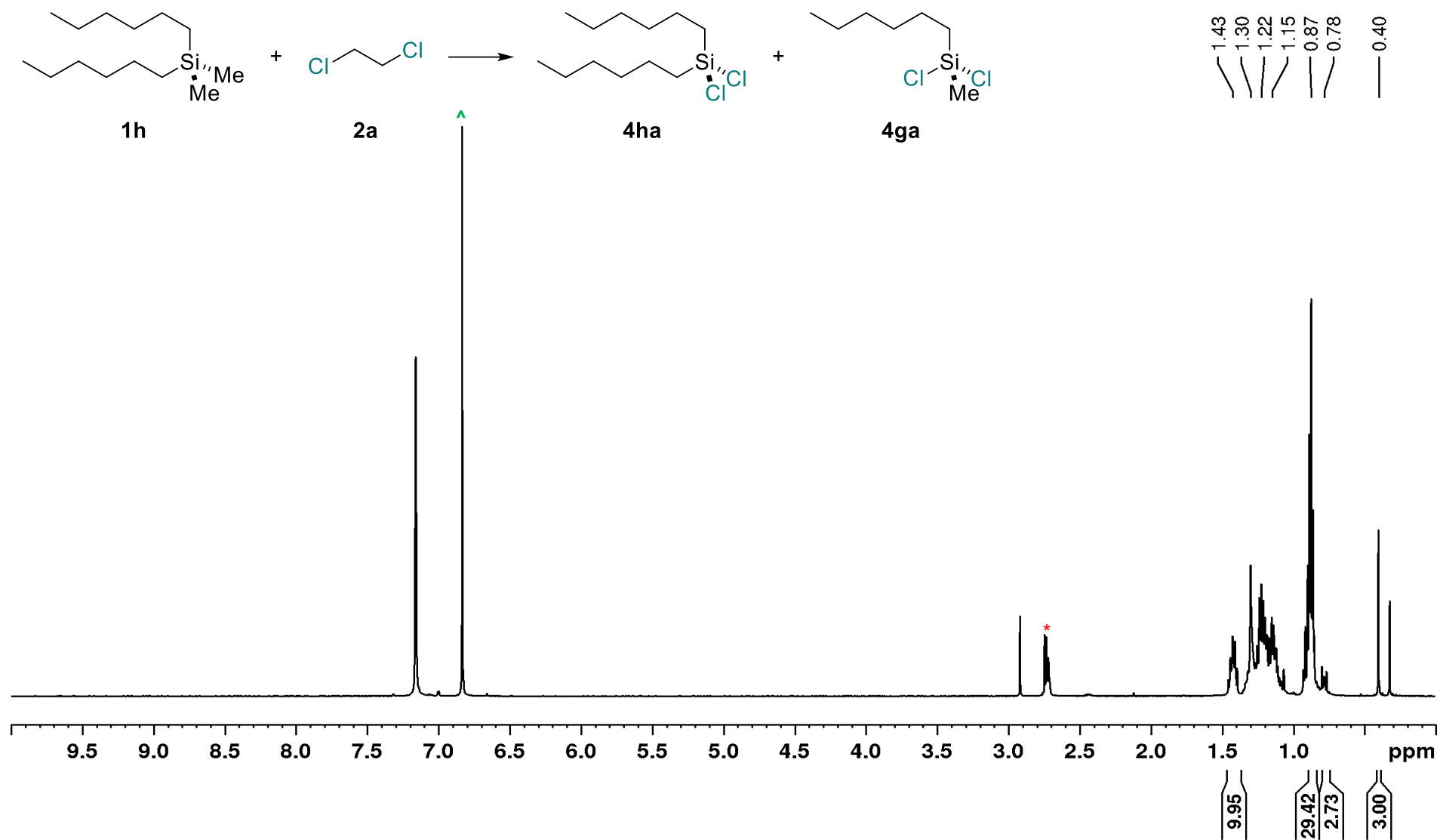


Figure S54. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of dichloro(hexyl)(methyl)silane (**4ga**) by chlorodemethylation of hexyltrimethylsilane (**1g**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; ^ 1,2,4,5-tetrachlorobenzene)

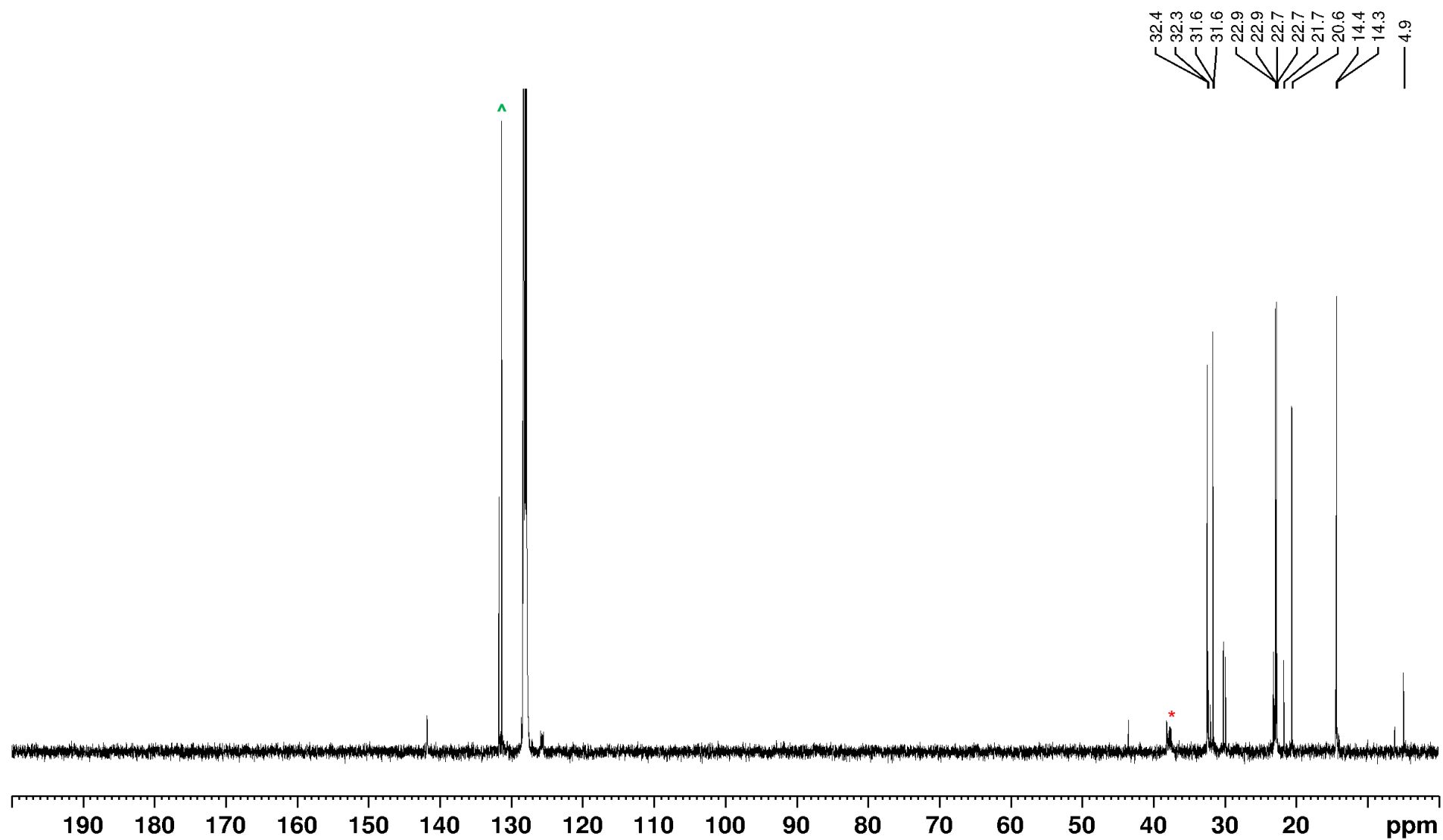


Figure S55. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 20.7°) of dichloro(hexyl)(methyl)silane (**4ga**) by chlorodemethylation of hexyltrimethylsilane (**1g**) with 1,2-dichloroethane (**2a**)

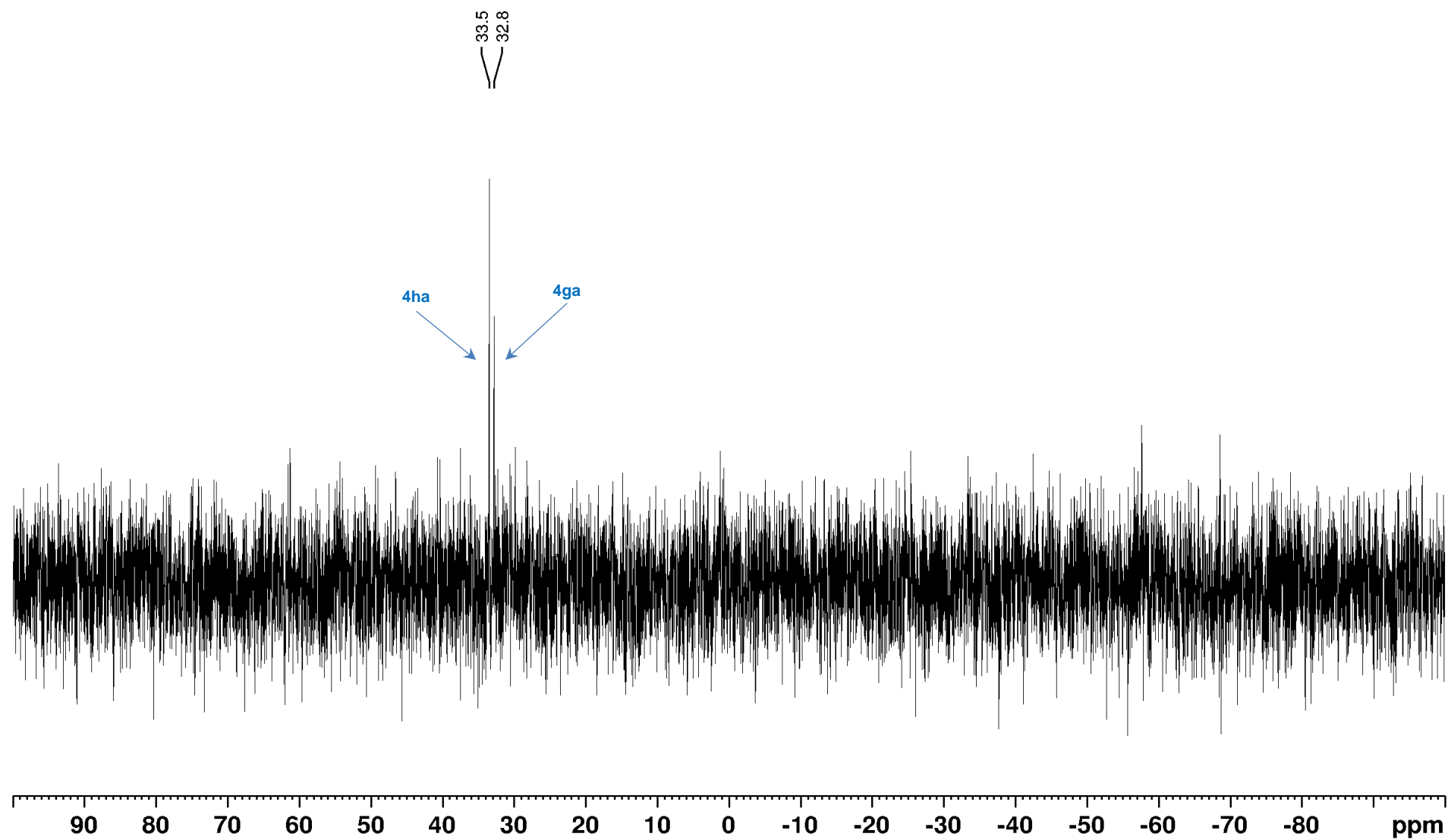


Figure S56. $^1\text{H},^{13}\text{C}$ HSQC NMR (500/126 MHz, C_6D_6 , 298 K) of dichloro(hexyl)(methyl)silane (**4ga**) by chlorodemethylation of hexyltrimethylsilane (**1g**) with 1,2-dichloroethane (**2a**)

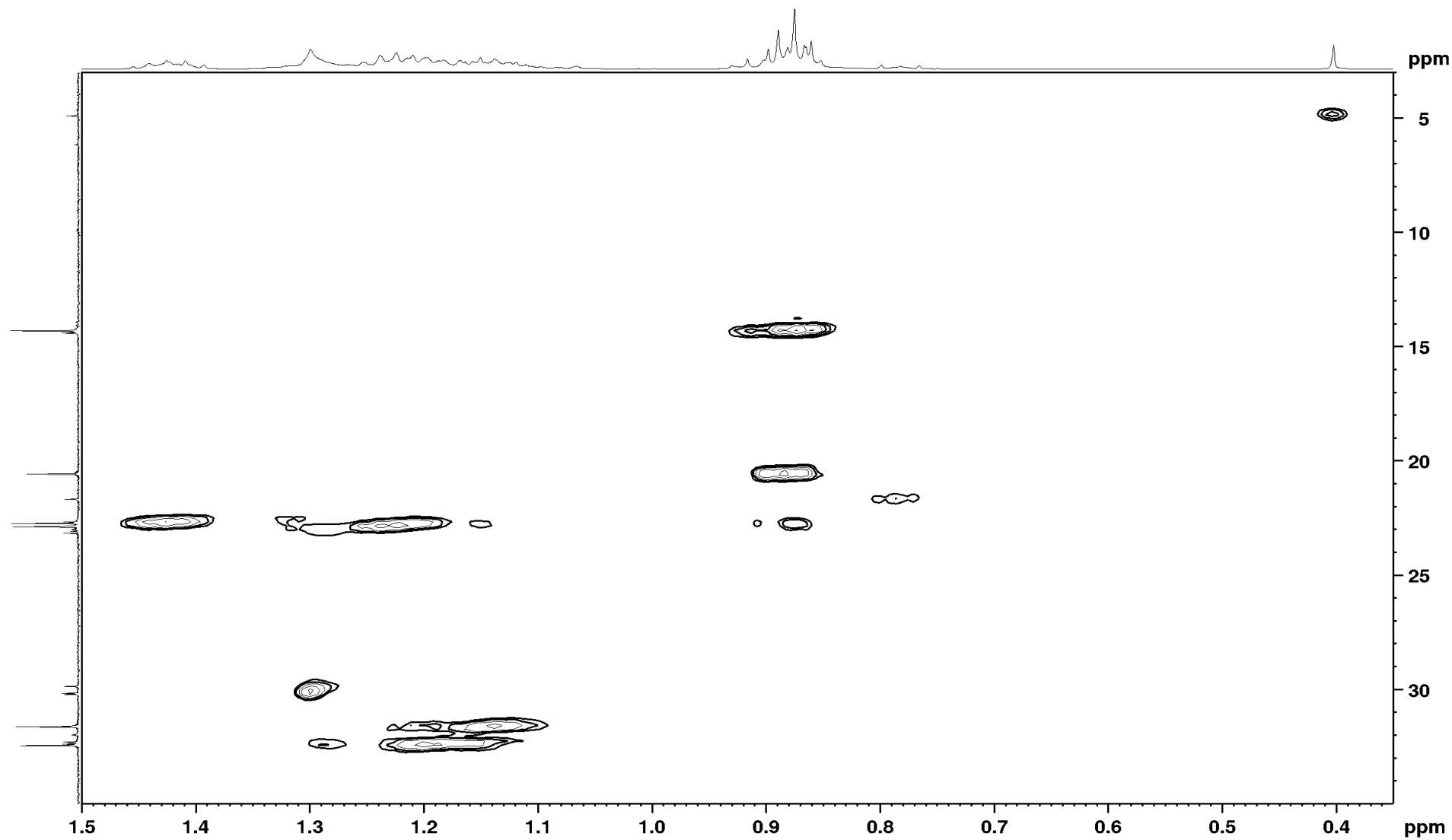


Figure S57. $^1\text{H},^{29}\text{Si}$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz) of dichloro(hexyl)(methyl)silane (**4ga**) by chlorodemethylation of hexyltrimethylsilane (**1g**) with 1,2-dichloroethane (**2a**) (* Me_2SiCl_2)

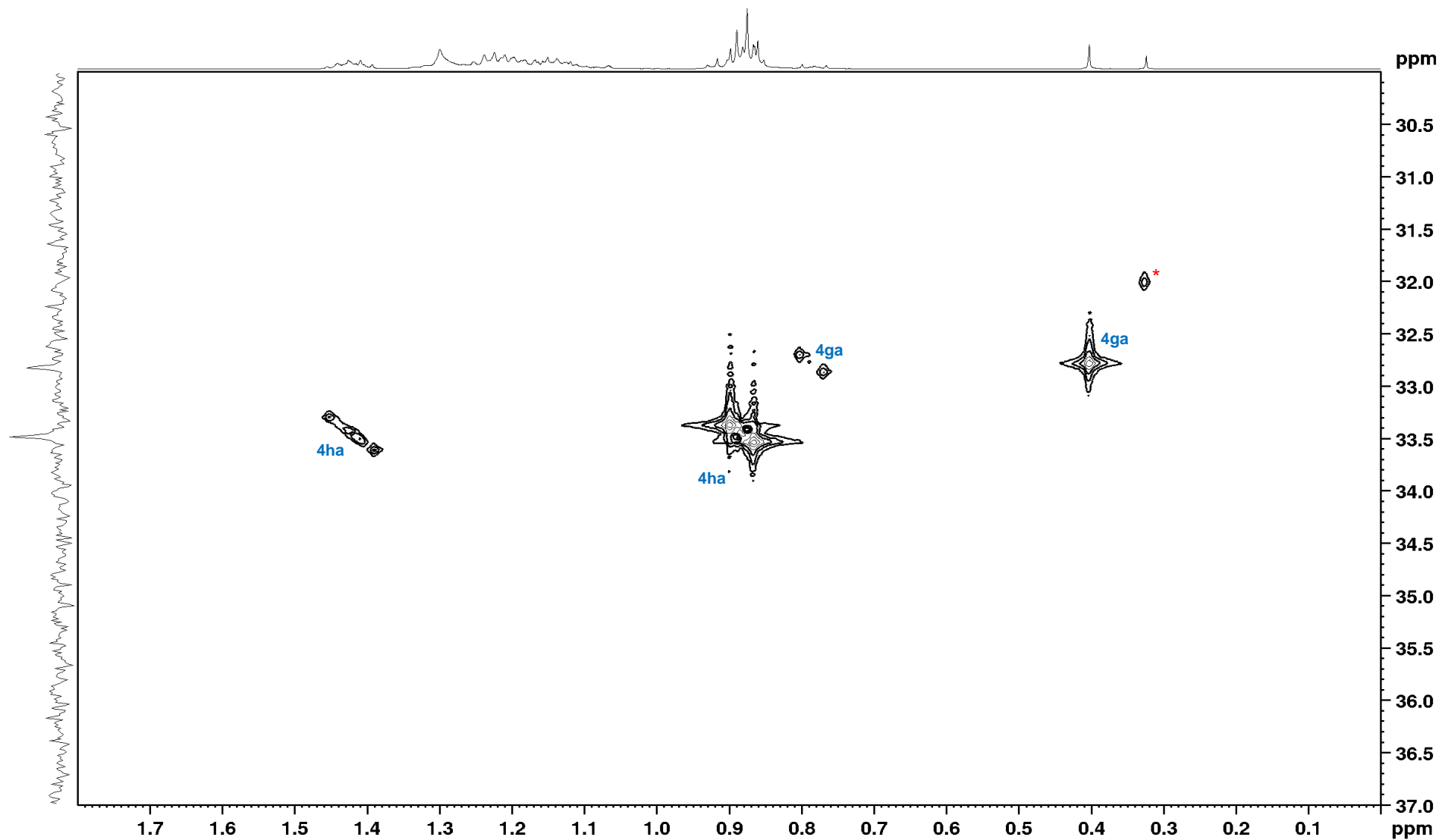


Figure S58. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of dichlorodiisopropylsilane (**4ia**) by chlorodemethylation of diisopropyldimethylsilane (**1i**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane)

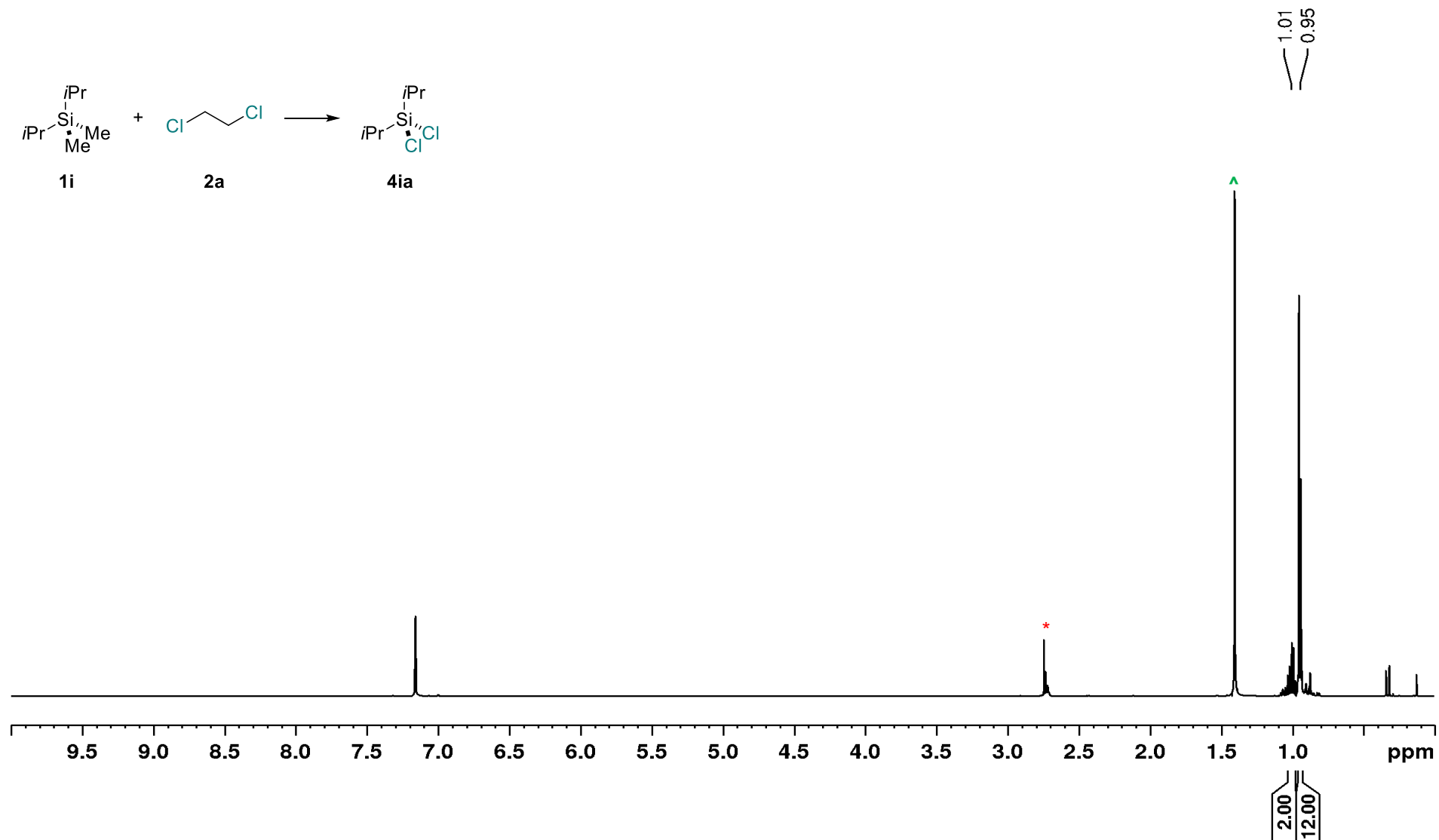


Figure S59. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of dichlorodiisopropylsilane (**4ia**) by chlorodemethylation of diisopropyldimethylsilane (**1i**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane)

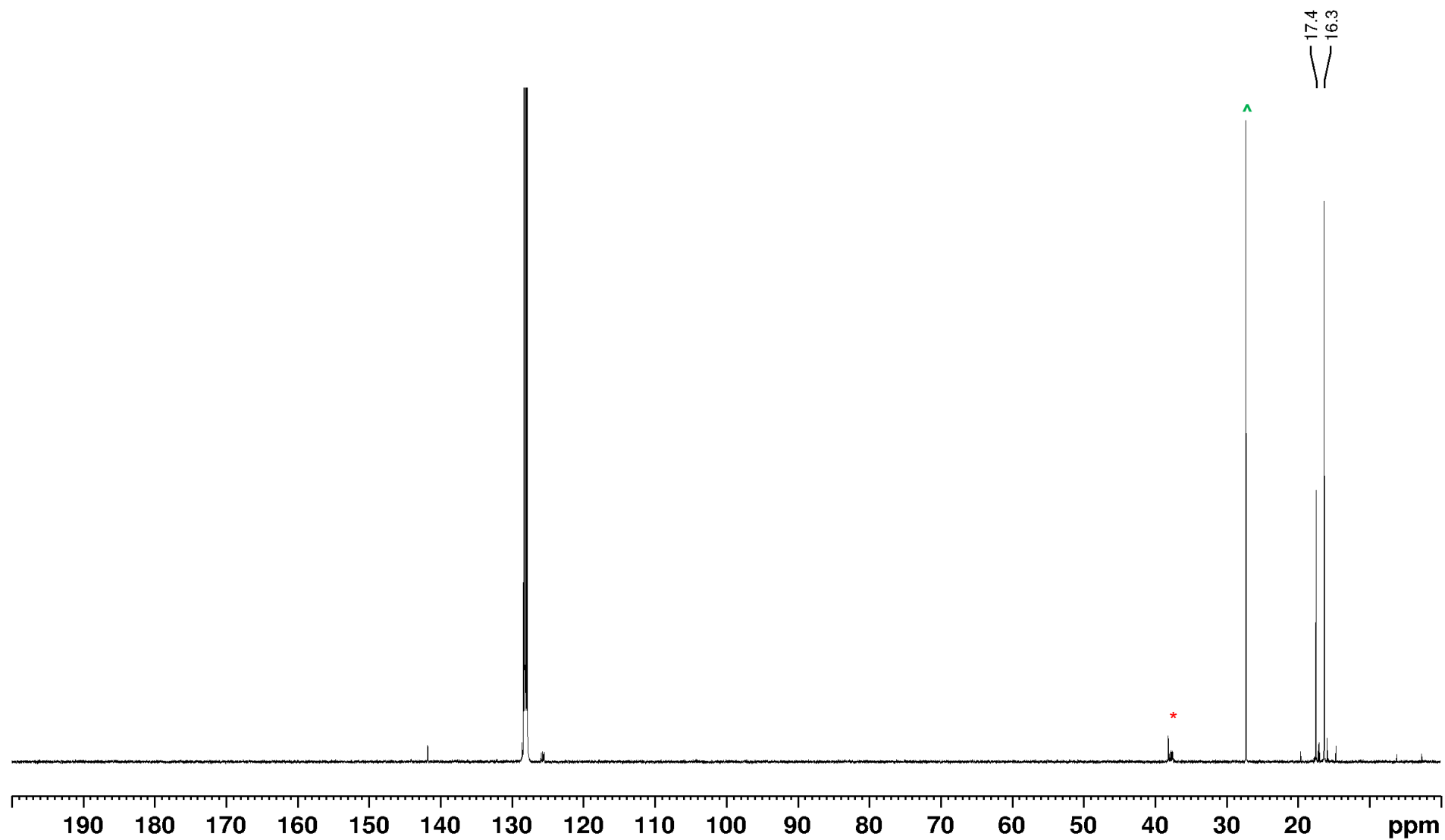


Figure S60. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 20.7°) of dichlorodiisopropylsilane (**4ia**) by chlorodemethylation of diisopropyldimethylsilane (**1i**) with 1,2-dichloroethane (**2a**)

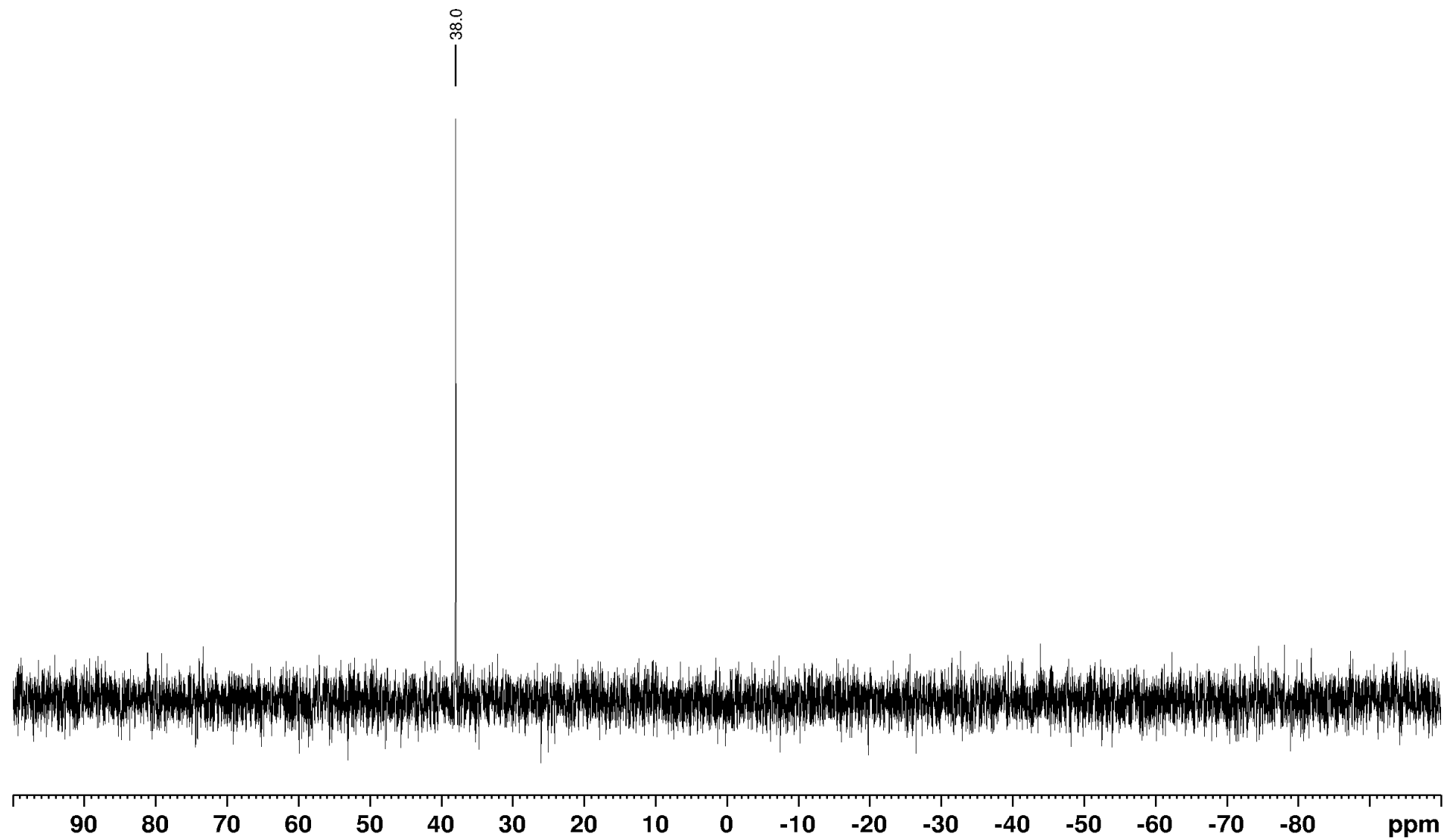


Figure S61. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of dichlorodiisopropylsilane (**4ja**) by chlorodeethylation of diethyldiisopropylsilane (**1j**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane)

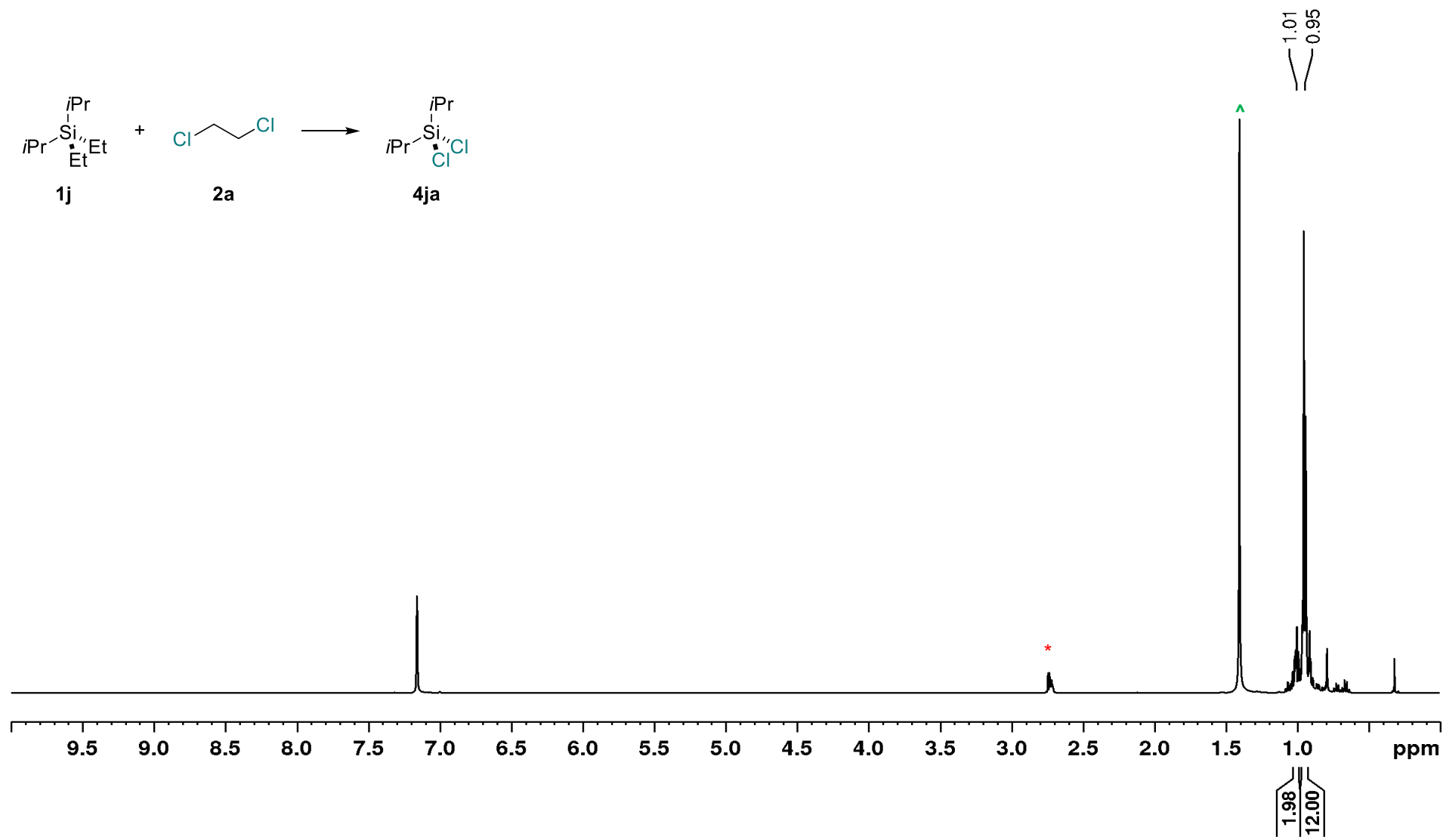


Figure S62. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of dichlorodiisopropylsilane (**4ja**) by chlorodeethylation of diethyldiisopropylsilane (**1j**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane)

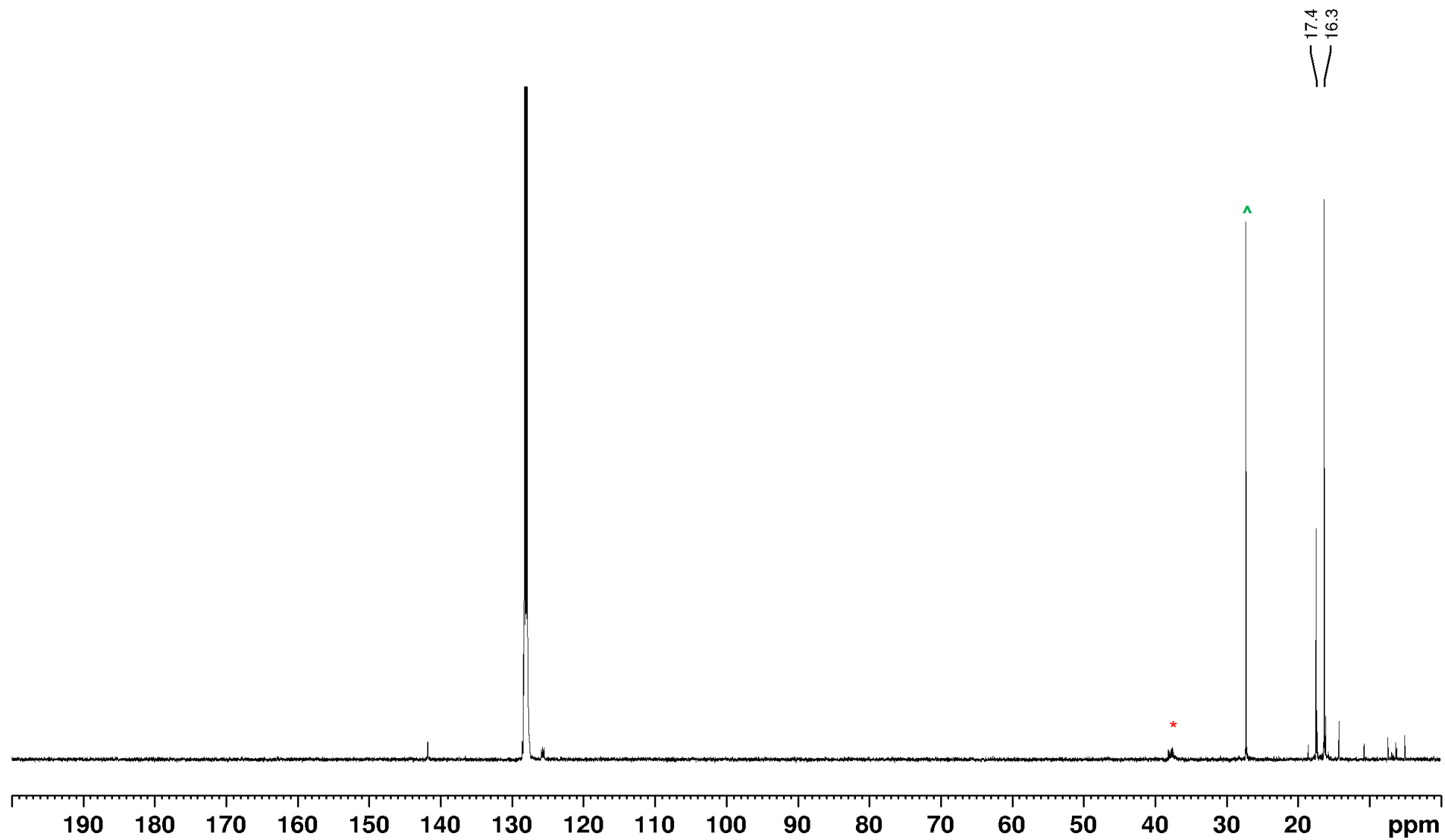


Figure S63. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 20.7°) of dichlorodiisopropylsilane (**4ja**) by chloroethylation of diethyldiisopropylsilane (**1j**) with 1,2-dichloroethane (**2a**)

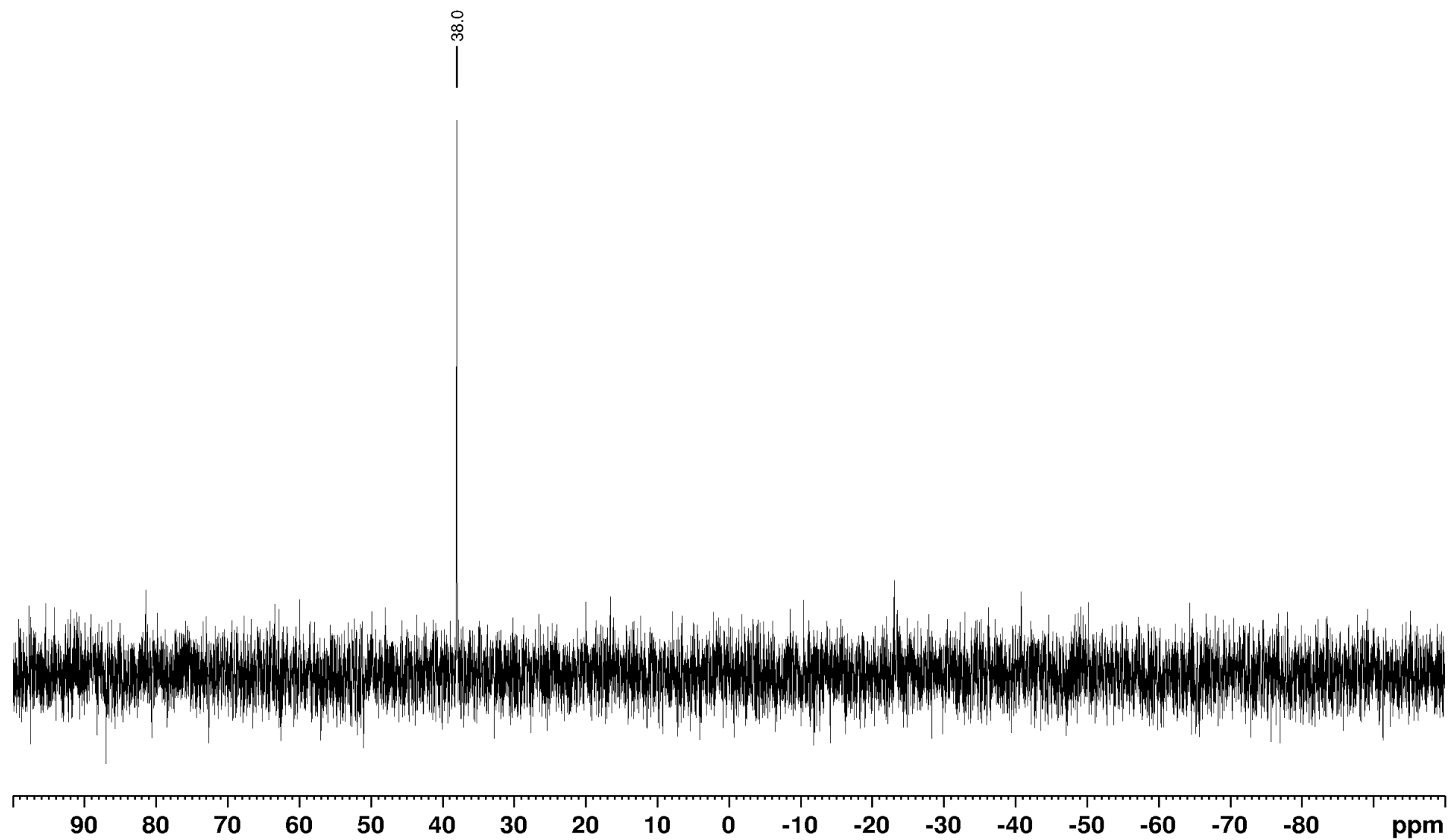


Figure S64. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of 1-adamantylchloro(methyl)silane (**4ka**) by chlorodemethylation of 1-adamantyltrimethylsilane (**1k**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; ^ 1,2,4,5-tetrachlorobenzene)

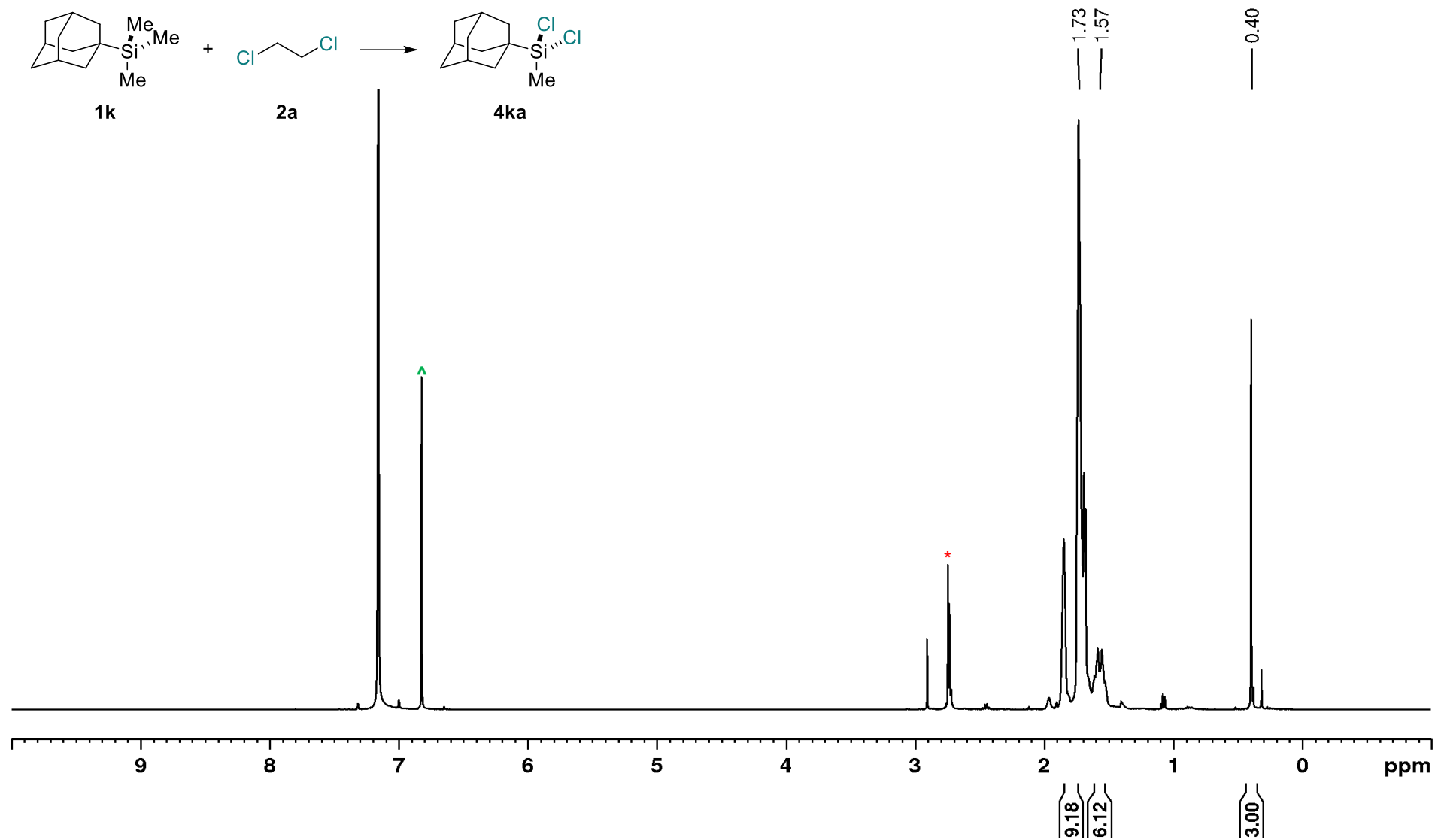


Figure S65. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of 1-adamantyldichloro(methyl)silane (**4ka**) by chlorodemethylation of 1-adamantyltrimethylsilane (**1k**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; ^ 1,2,4,5-tetrachlorobenzene)

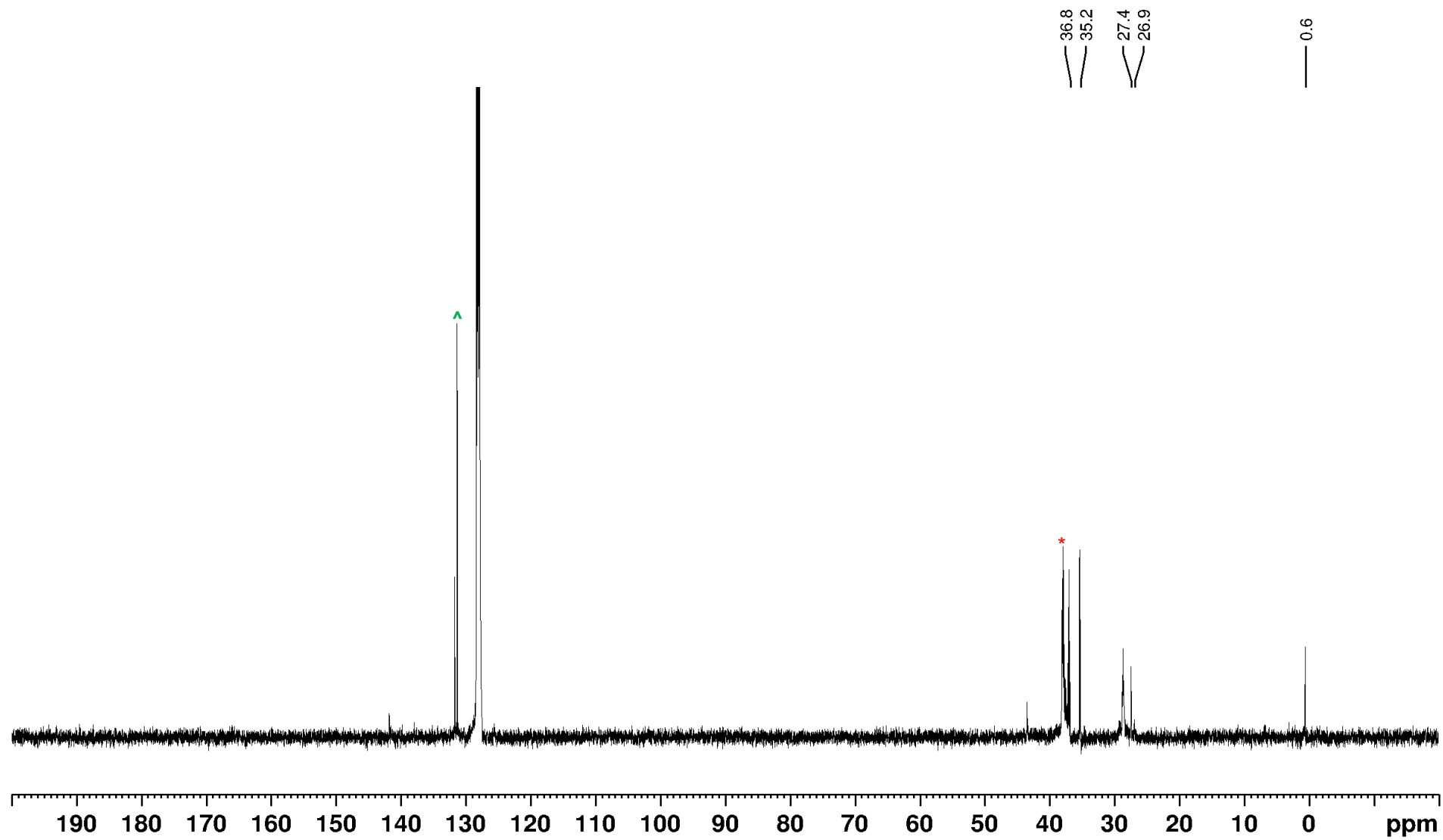


Figure S66. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 19.5°) of 1-adamantylidichloro(methyl)silane (**4ka**) by chlorodemethylation of 1-adamantyltrimethylsilane (**1k**) with 1,2-dichloroethane (**2a**)

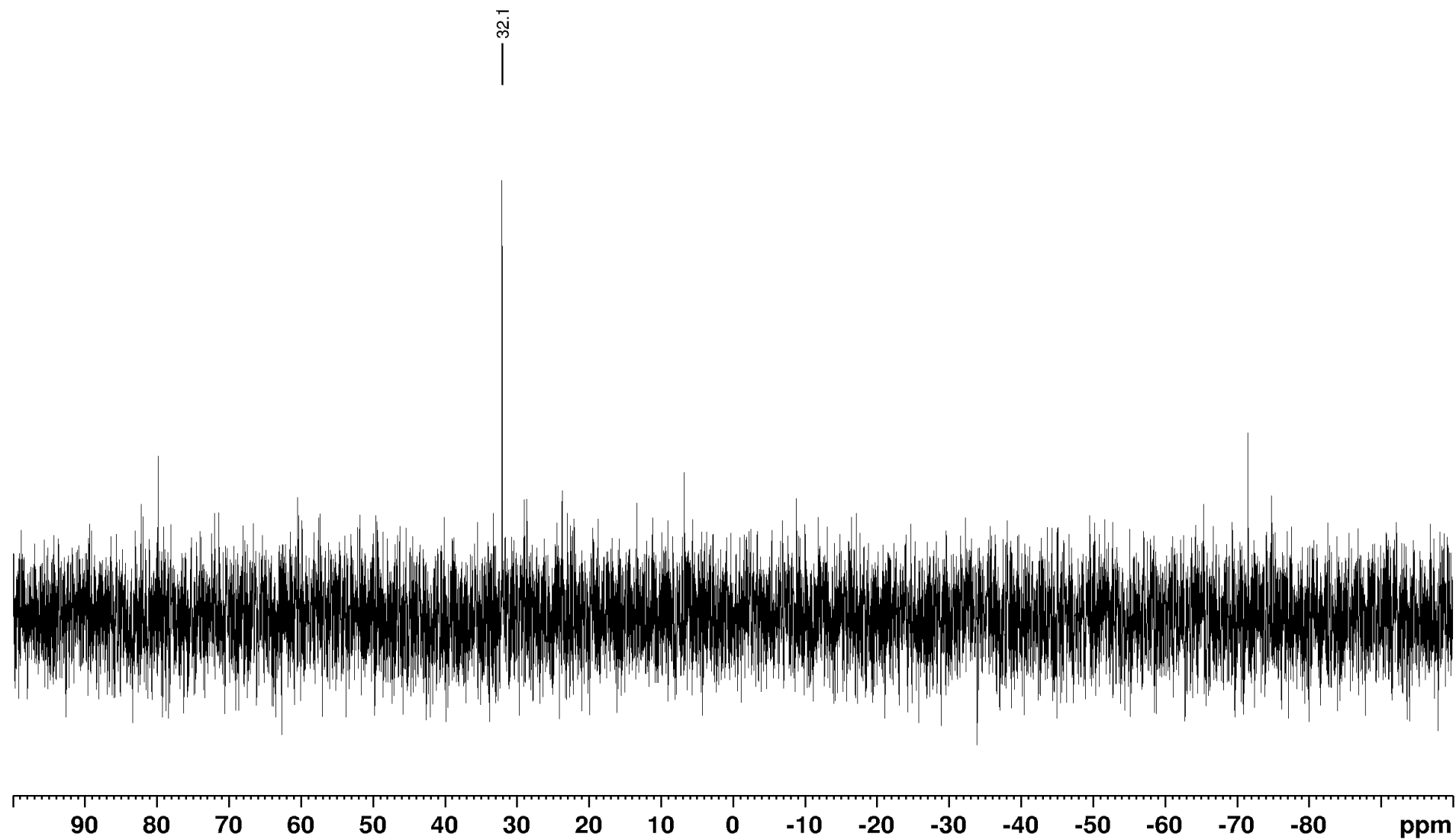


Figure S67. $^1\text{H NMR}$ spectrum (700 MHz, C_6D_6 , 298 K) of dichloro(ethyl)(methyl)silane (**4la**) by chlorodemethylation and chlorodeethylation of diethyldimethylsilane (**1l**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane)

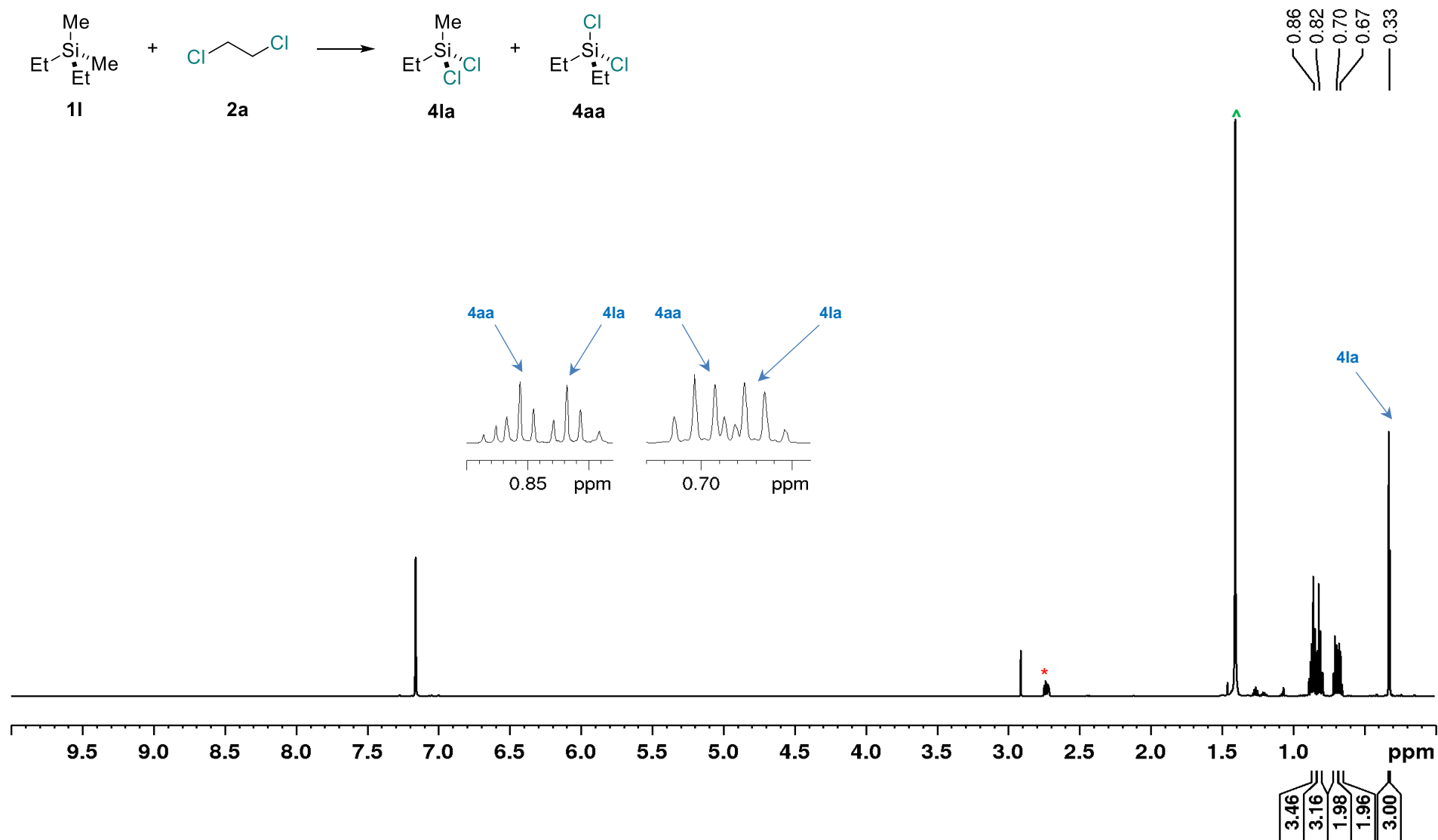


Figure S68. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of dichloro(ethyl)(methyl)silane (**4la**) by chlorodemethylation and chloroethylolation of diethyldimethylsilane (**1I**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; ^ cyclohexane)

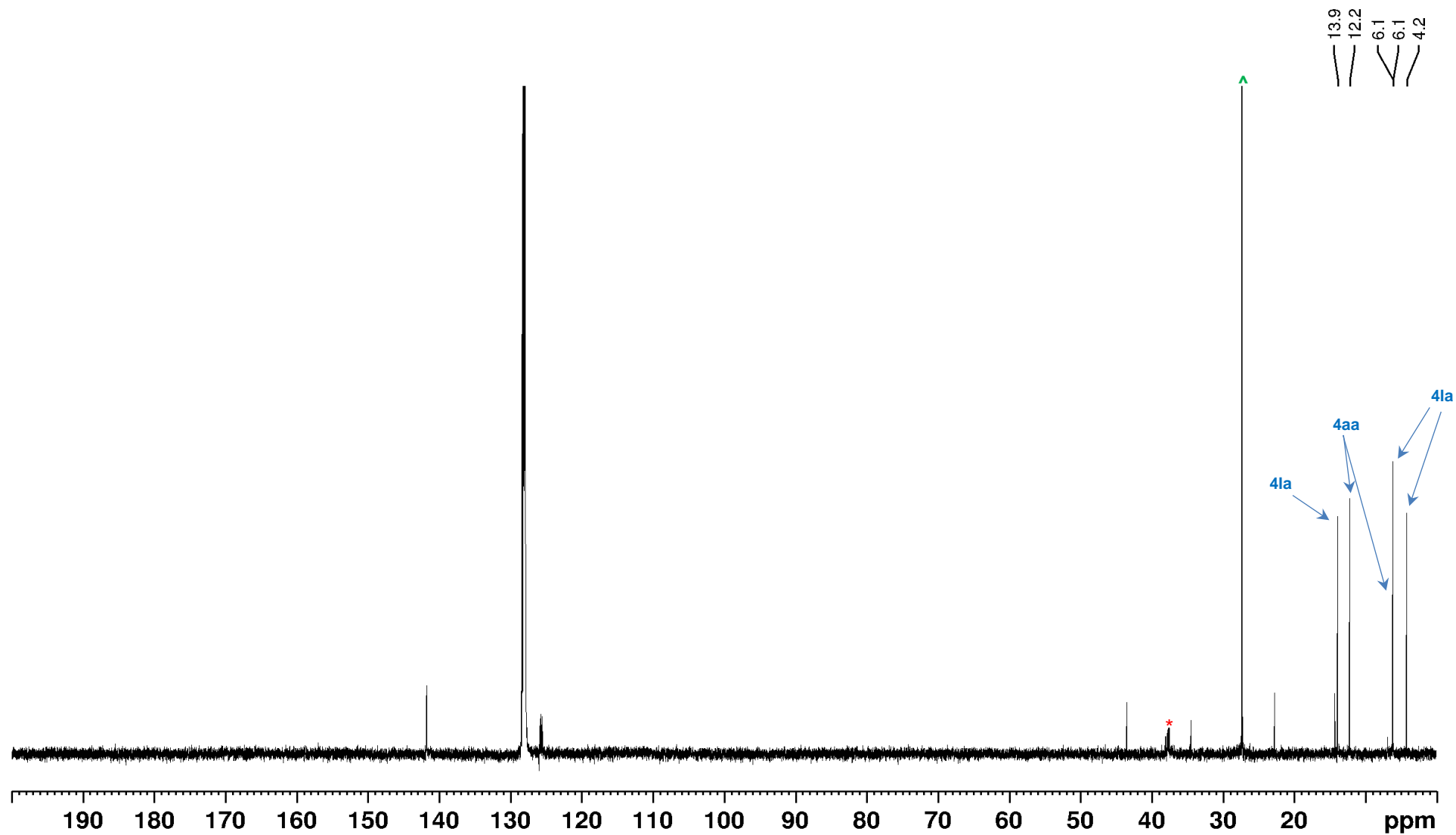


Figure S69. $^1\text{H},^{29}\text{Si}$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz) of dichloro(ethyl)(methyl)silane (**4la**) by chlorodemethylation and chloroethylolation of diethyldimethylsilane (**1I**) with 1,2-dichloroethane (**2a**) (+ Me_2SiCl_2)

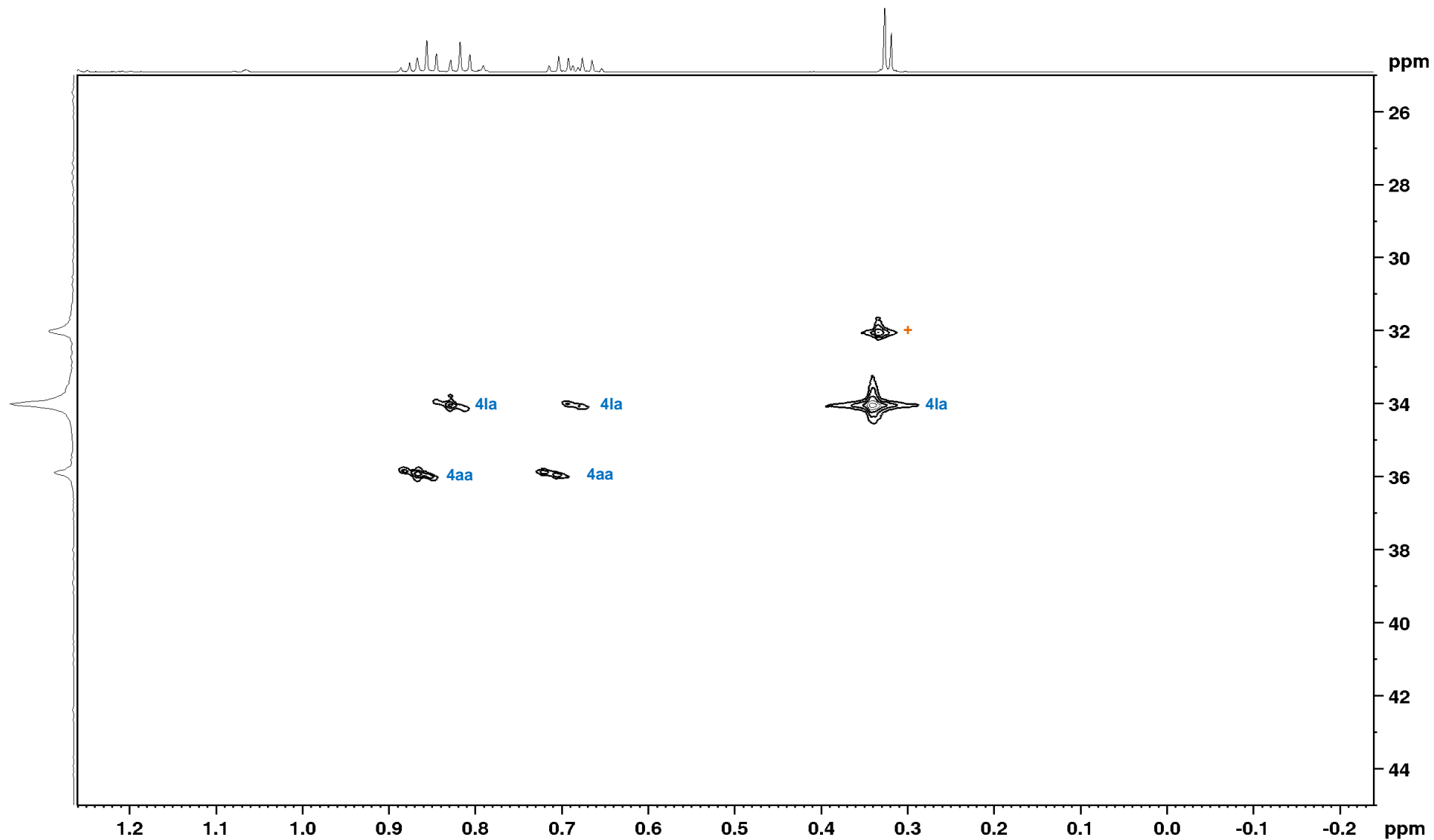


Figure S70. ^1H NMR spectrum (700 MHz, C_6D_6 , 298 K) of dichlorodiethylsilane (**4ma**) by chlorodemethylation and chlorodeethylation of triethyl(methyl)silane (**1m**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane)

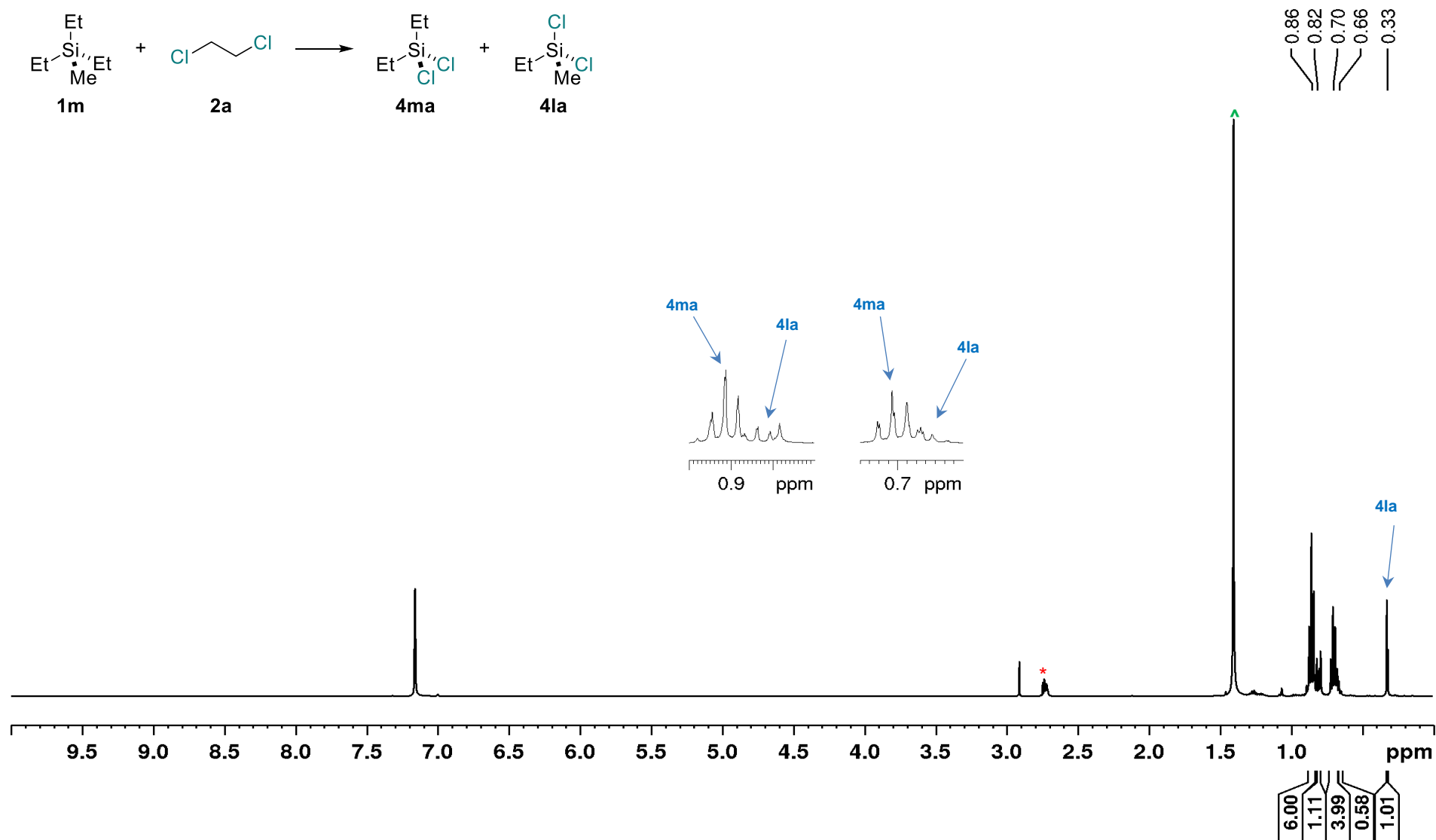


Figure S71. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of dichlorodiethylsilane (**4ma**) by chlorodemethylation and chlorodeethylation of triethyl(methyl)silane (**1m**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; ^ cyclohexane)

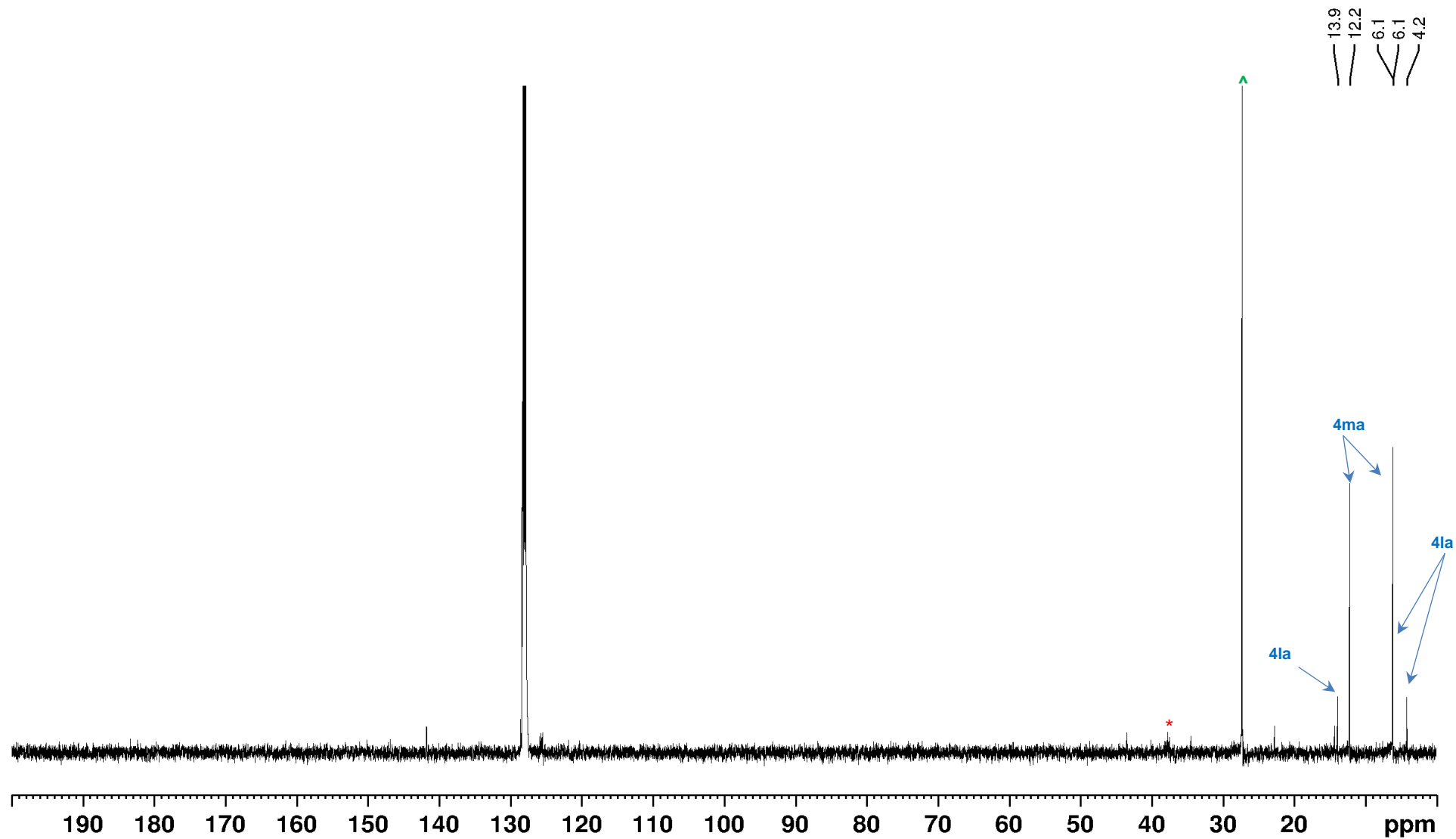


Figure S72. $^1\text{H},^{29}\text{Si}$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz) of dichlorodiethylsilane (**4ma**) by chlorodemethylation and chlorodeethylation of triethyl(methyl)silane (**1m**) with 1,2-dichloroethane (**2a**) (+ Me_2SiCl_2)

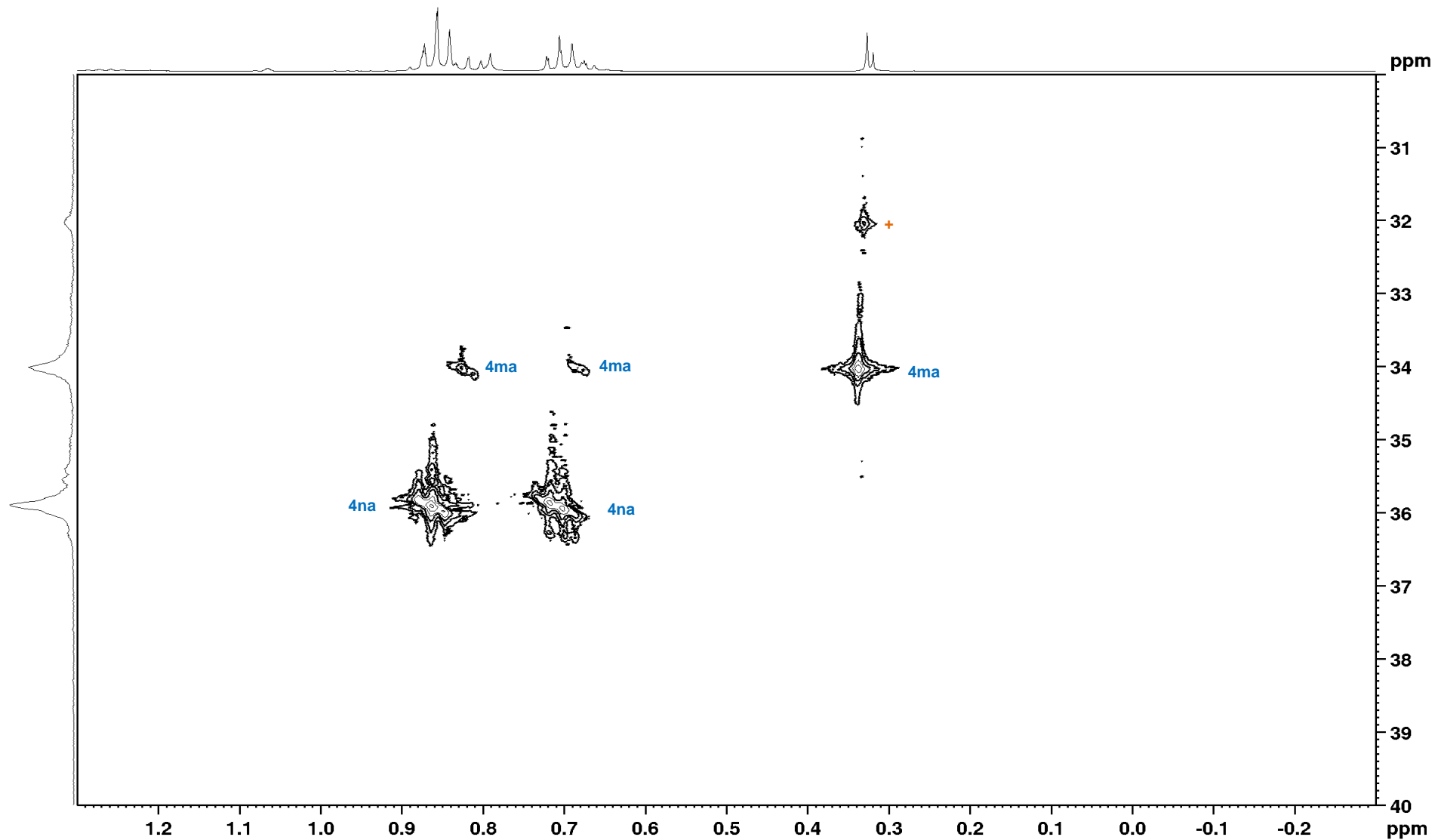


Figure S73. ^1H NMR spectrum (700 MHz, C_6D_6 , 298 K) of dibutyldichlorosilane (**4na**) by chlorodemethylation of dibutyldimethylsilane (**1n**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane; + Me_2SiCl_2)

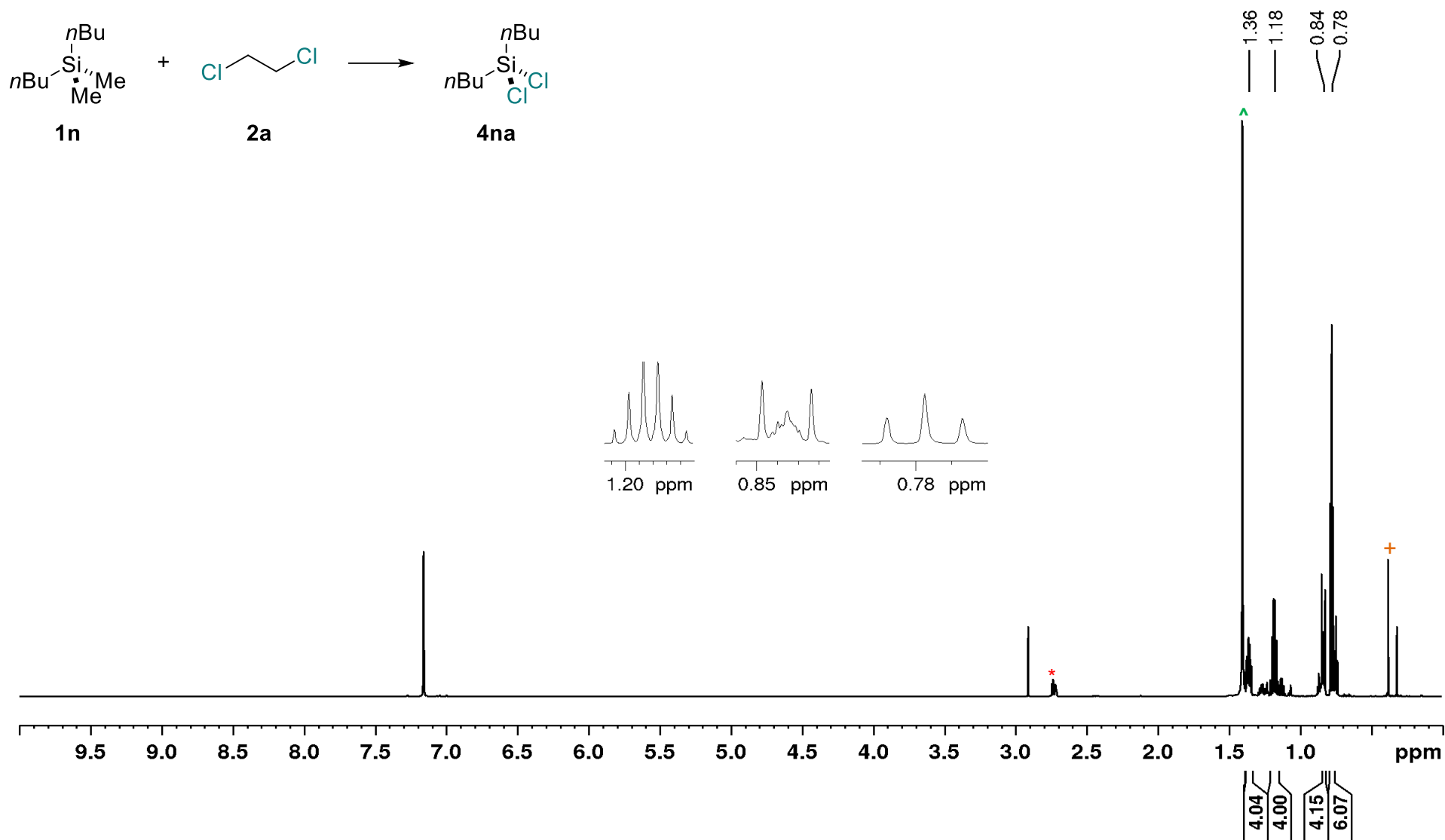


Figure S74. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of dibutyldichlorosilane (**4na**) by chlorodemethylation of dibutyldimethylsilane (**1n**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane)

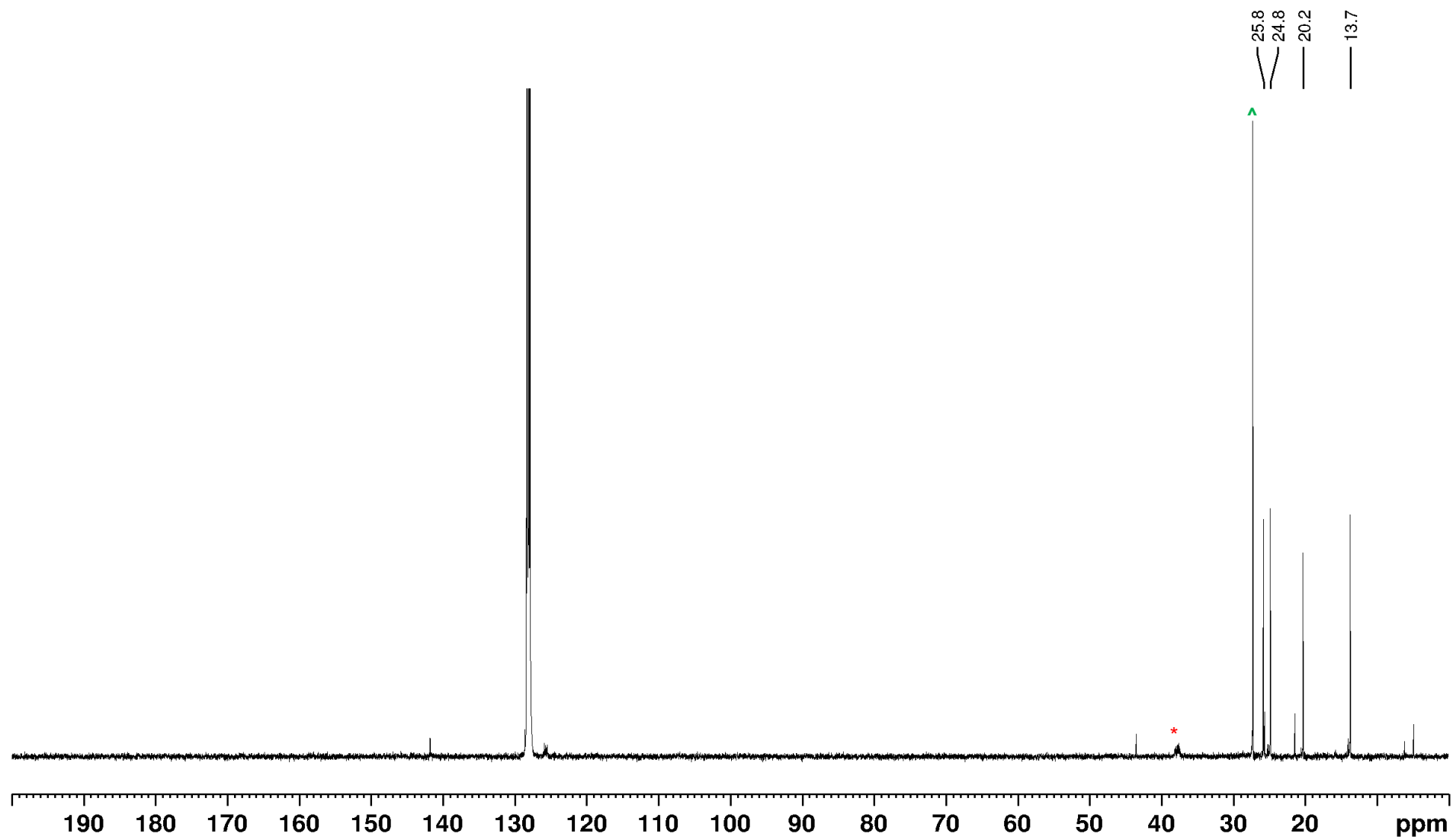


Figure S75. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 20.7°) of dibutyldichlorosilane (**4na**) by chlorodemethylation of dibutyldimethylsilane (**1n**) with 1,2-dichloroethane (**2a**)

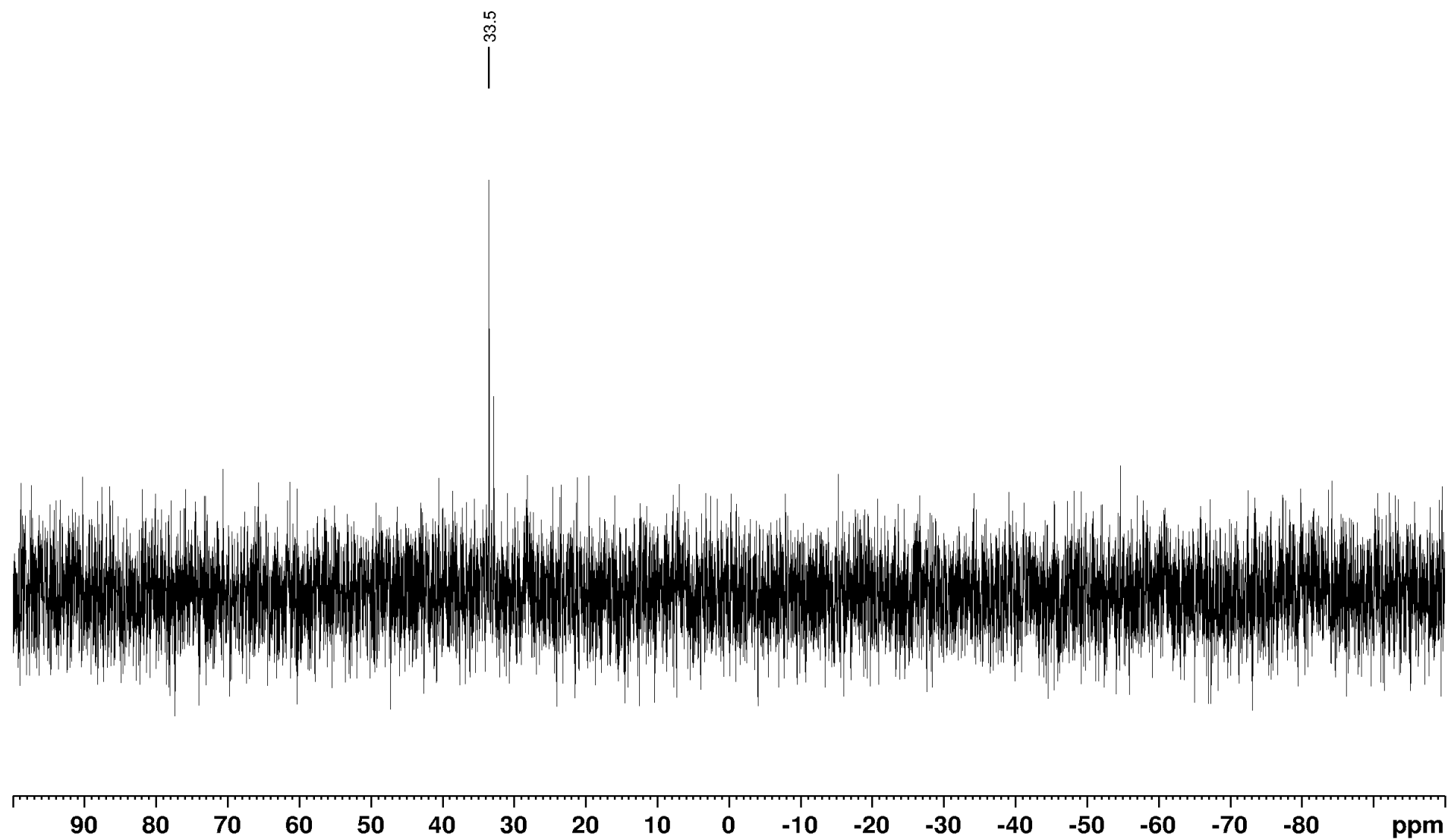


Figure S76. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of dichloro(isopentyl)(methyl)silane (**4oa**) by chlorodemethylation and chlorodeisopentylation of diisopentyl dimethylsilane (**1o**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; ^ 1,2,4,5-tetrachlorobenzene; + Me_2SiCl_2)

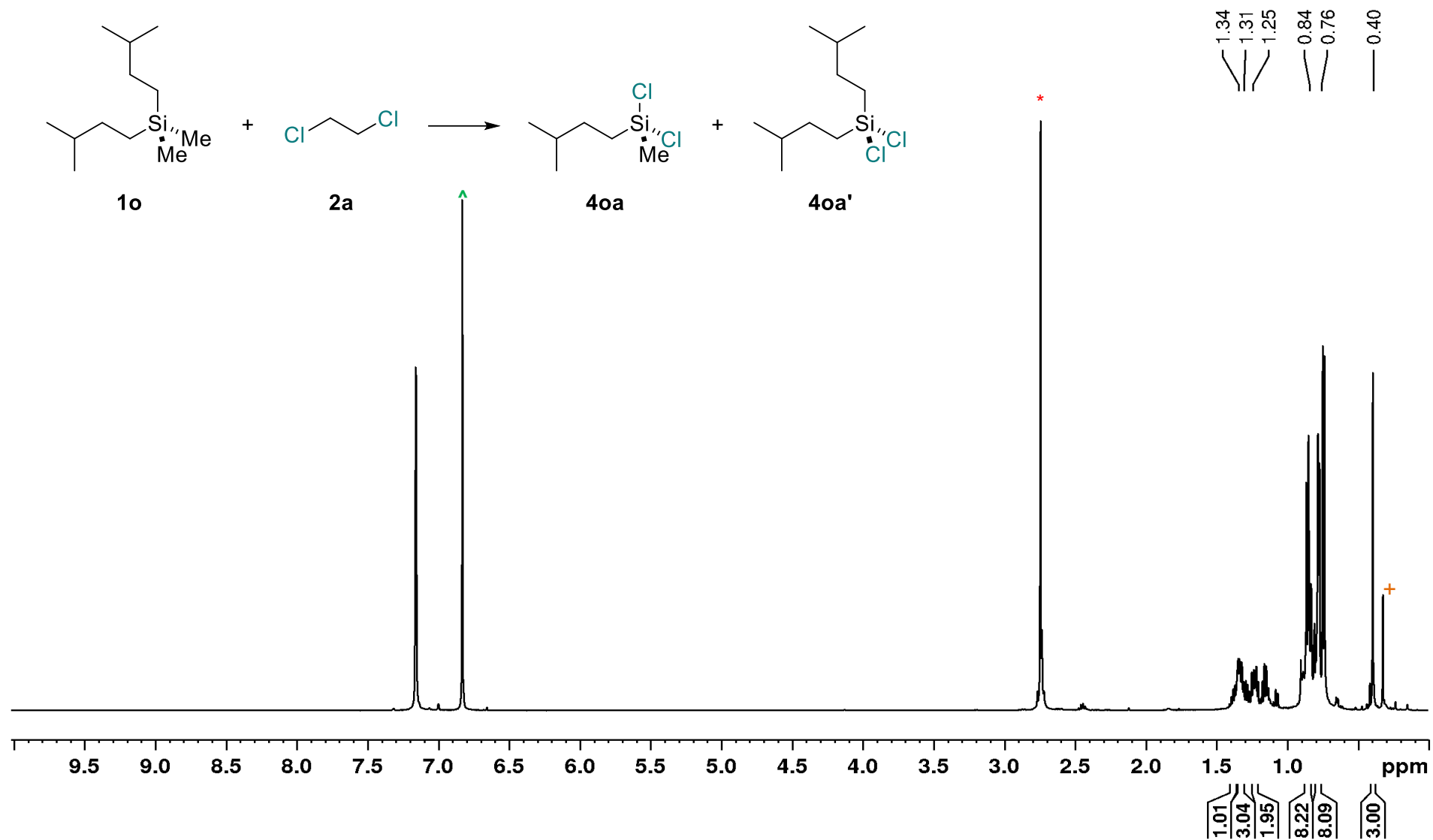


Figure S77. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of dichloro(isopentyl)(methyl)silane (**4oa**) by chlorodemethylation and chlorodeisopentylation of diisopentyl dimethylsilane (**1o**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; ^ 1,2,4,5-tetrachlorobenzene)

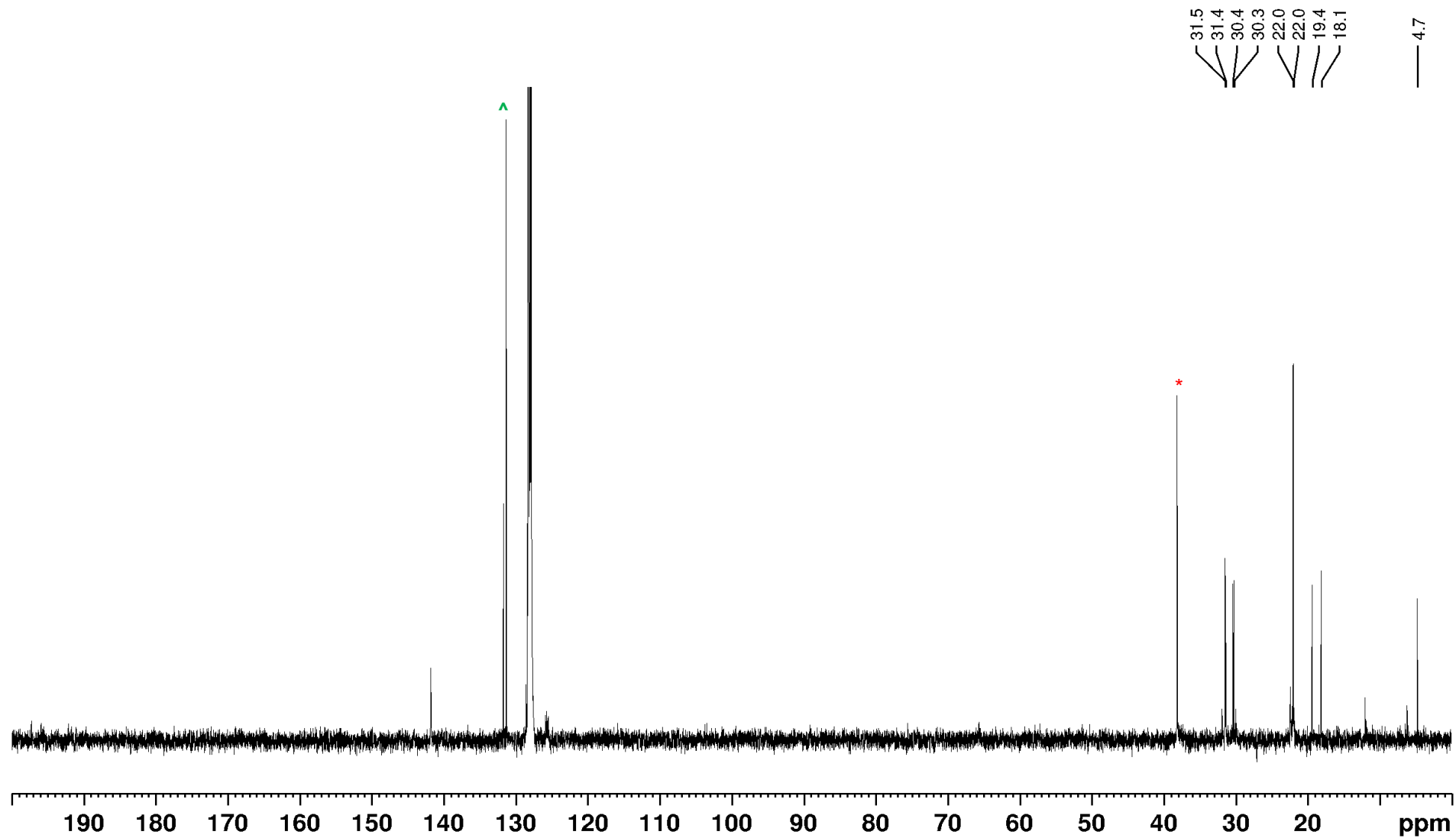


Figure S78. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 20.7°) of dichloro(isopentyl)(methyl)silane (**4oa**) by chlorodemethylation and chlorodeisopentylation of diisopentyl(dimethyl)silane (**1o**) with 1,2-dichloroethane (**2a**)

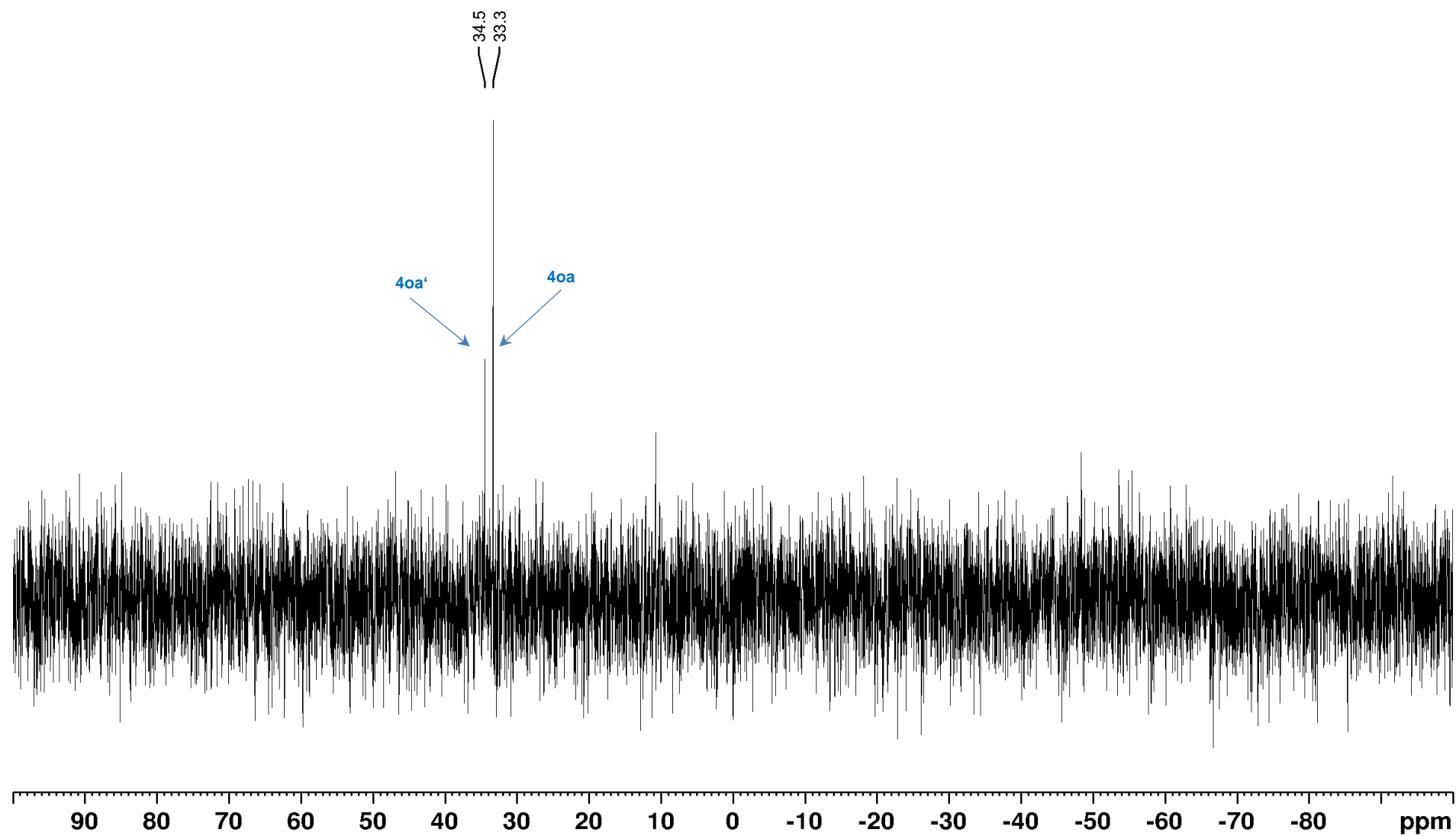


Figure S79. $^1\text{H},^{29}\text{Si}$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz) of dichloro(isopentyl)(methyl)silane (**4oa**) by chlorodemethylation and chlorodeisopentylation of diisopentyldimethylsilane (**1o**) with 1,2-dichloroethane (**2a**) (+ Me_2SiCl_2)

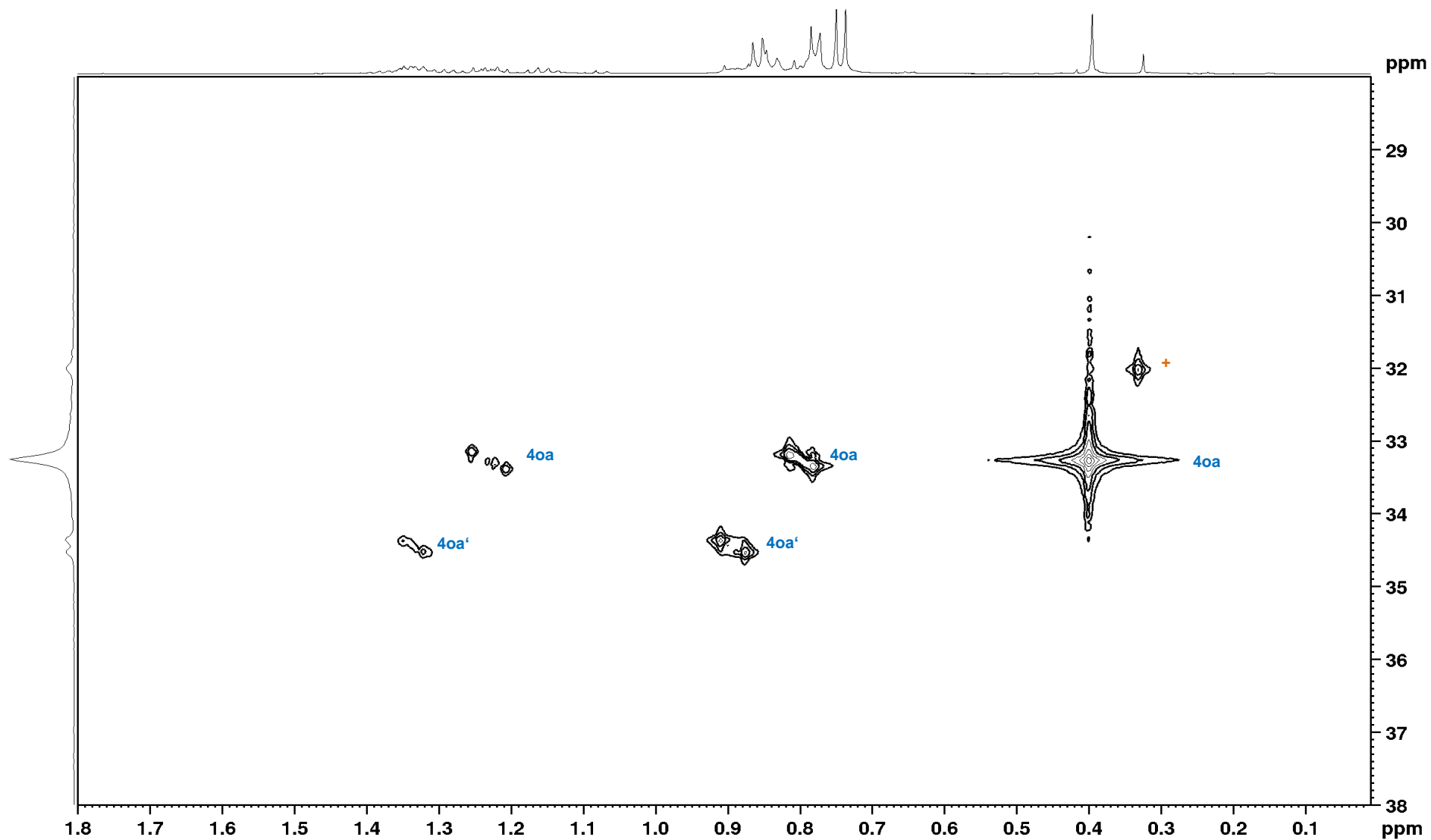


Figure S80. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of dichlorodimethylsilane (**4pa**) by chlorodemethylation and chlorodebenzylation of benzyltrimethylsilane (**1p**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; ^ cyclohexane; # toluene- d_6 ; + 1,2-dichloroethane)

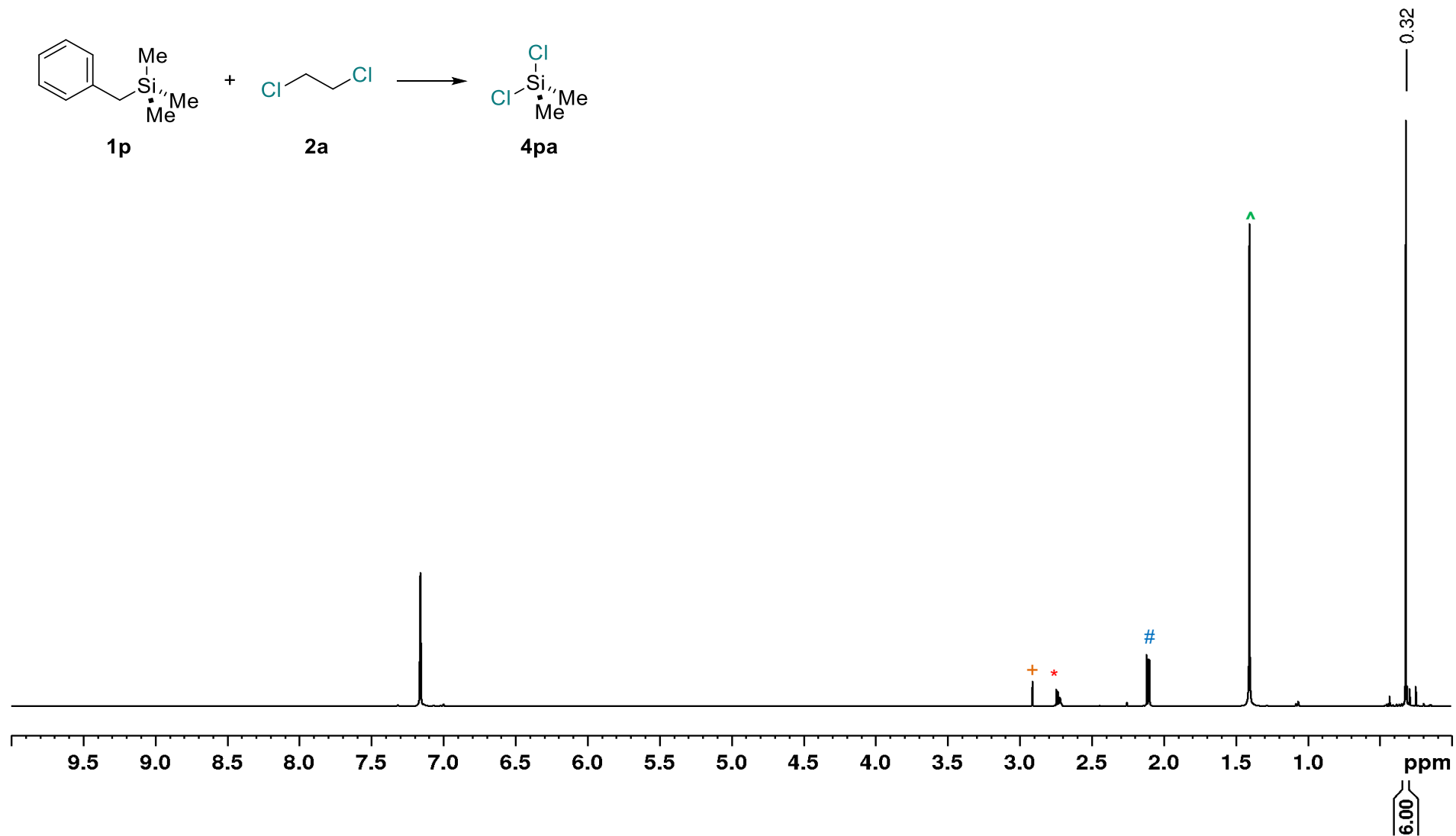


Figure S81. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of dichlorodimethylsilane (**4pa**) by chlorodemethylation and chlorodebenzylation of benzyltrimethylsilane (**1p**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; ^ cyclohexane; # toluene- d_6 ; + 1,2-dichloroethane)

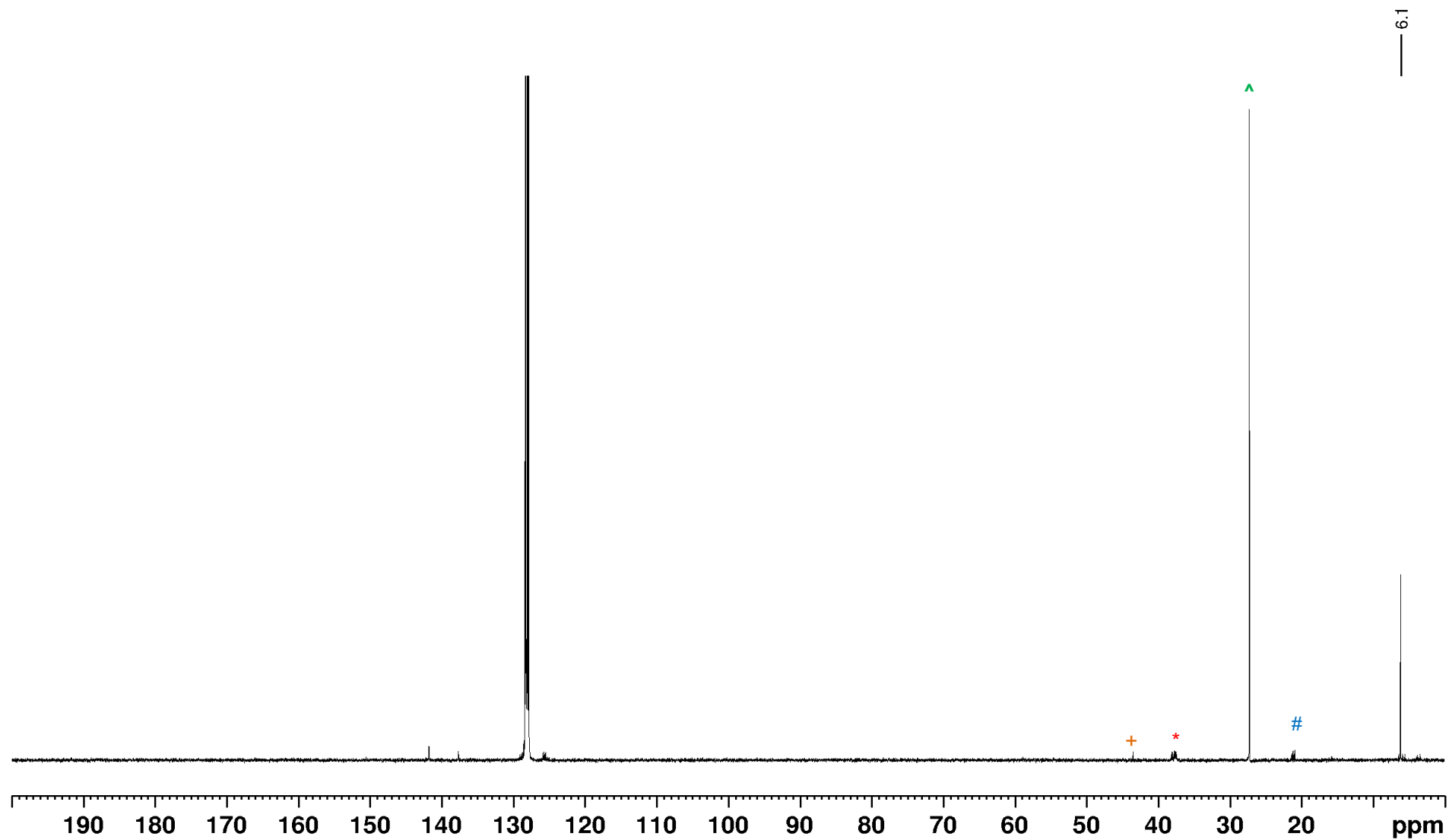


Figure S82. $^{29}\text{Si}\{^1\text{H}\}$ IG NMR spectrum (99 MHz, C_6D_6 , 298 K) of dichlorodimethylsilane (**4pa**) by chlorodemethylation and chlorodebenzylation of benzyltrimethylsilane (**1p**) with 1,2-dichloroethane (**2a**)

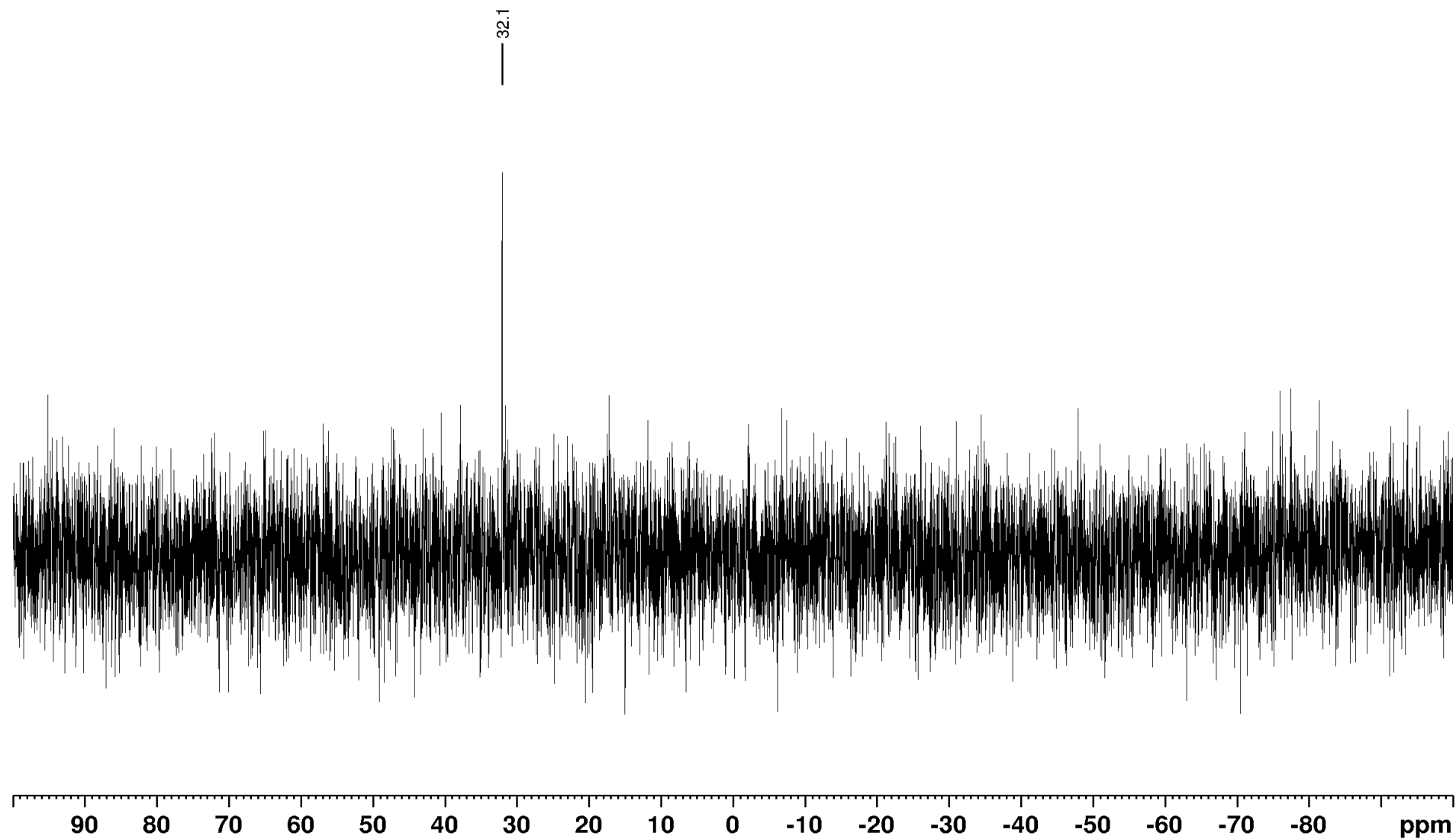


Figure S83. $^1\text{H NMR}$ spectrum (500 MHz, C_6D_6 , 298 K) of bis(dichloro(methyl)silyl)methane (**4qa**) by chlorodemethylation of bis(trimethylsilyl)methane (**1q**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; ^ cyclohexane; # 1,2-dichloroethane; + Me_2SiCl_2)

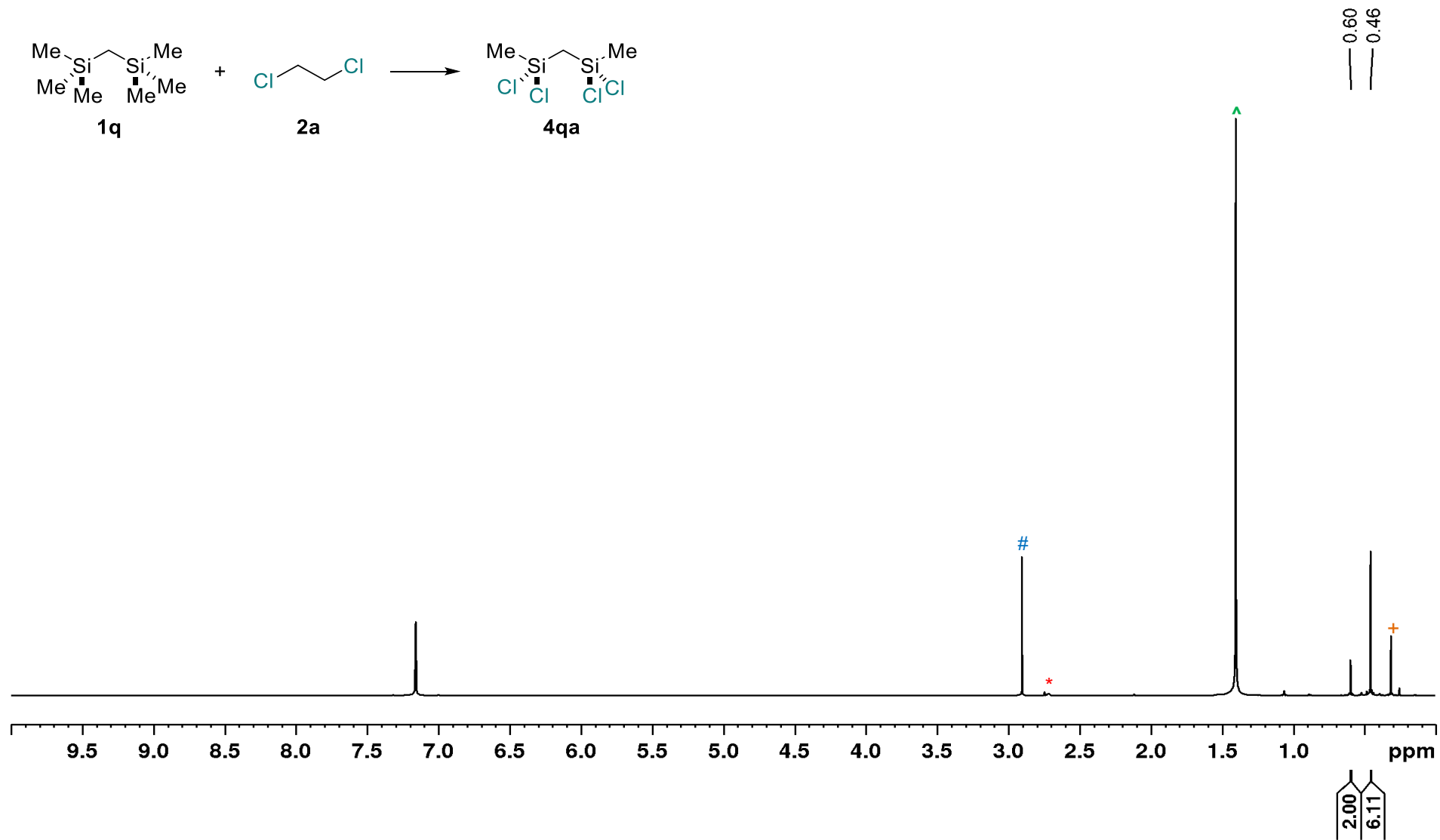


Figure S84. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of bis(dichloro(methyl)silyl)methane (**4qa**) by chlorodemethylation of bis(trimethylsilyl)methane (**1q**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; ^ cyclohexane; # 1,2-dichloroethane; + Me_2SiCl_2)

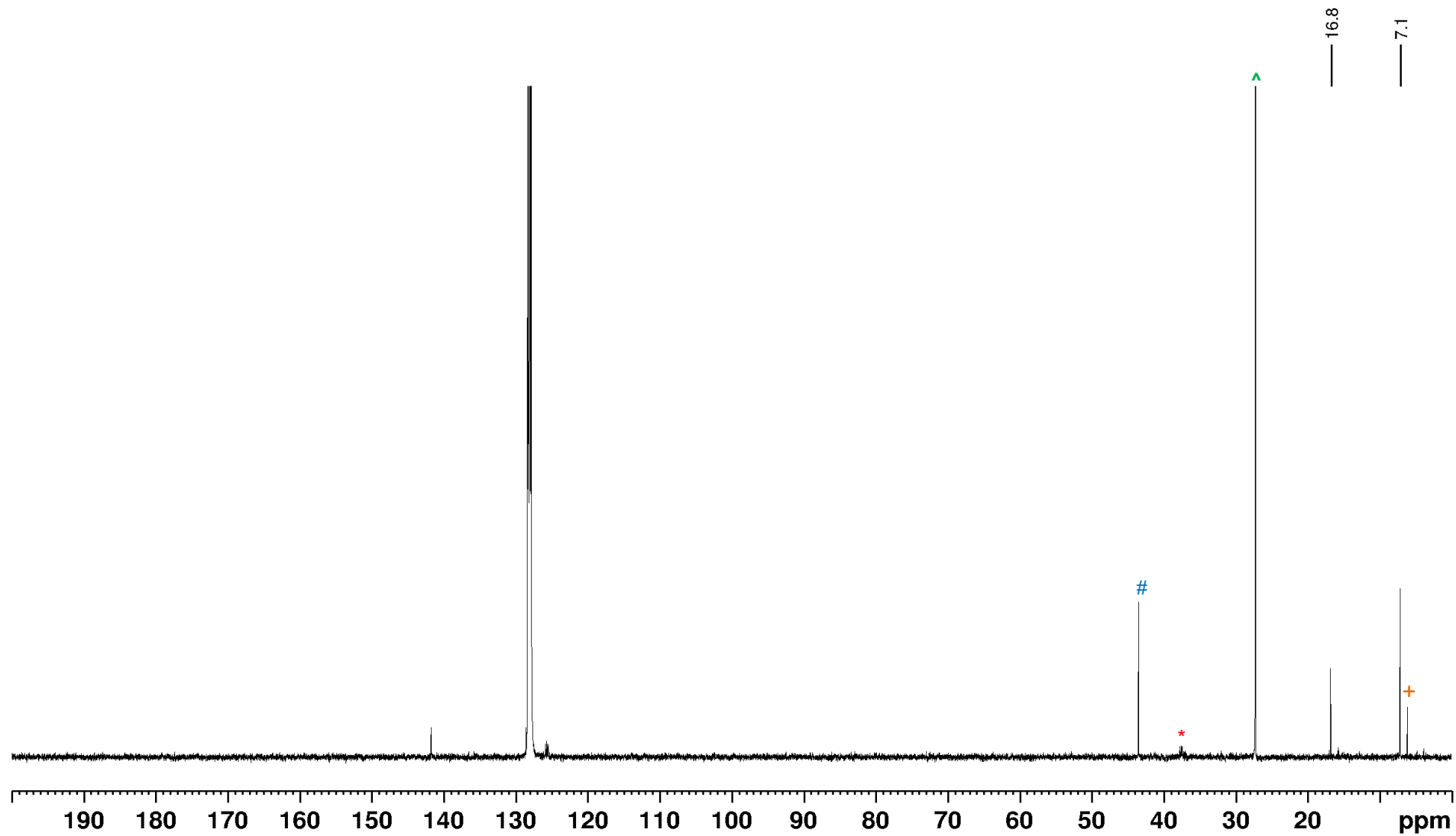


Figure S85. $^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR spectrum (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz) of bis(dichloro(methyl)silyl)methane (**4qa**) by chlorodemethylation of bis(trimethylsilyl)methane (**1q**) with 1,2-dichloroethane (**2a**) (+ Me_2SiCl_2)

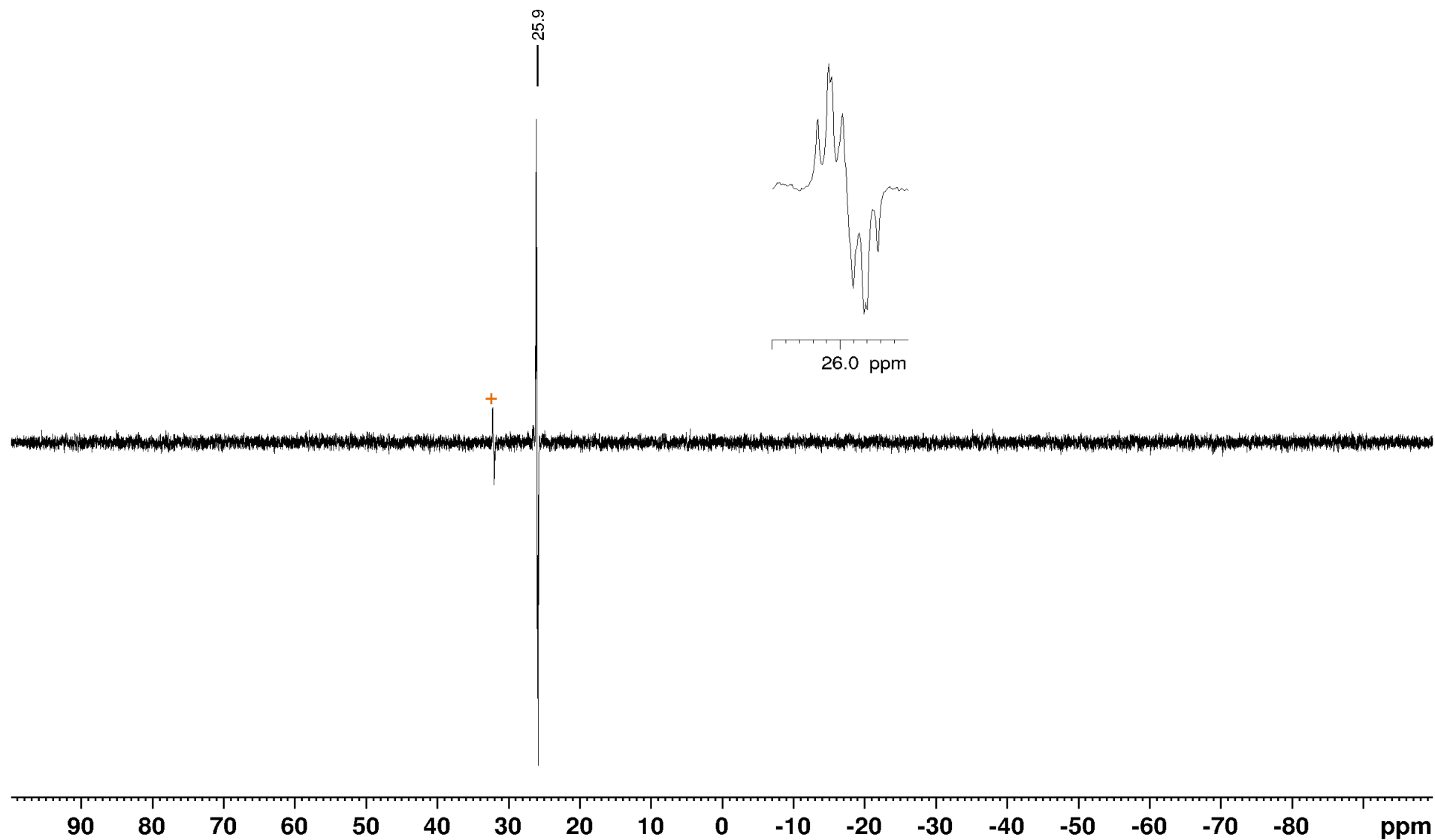


Figure S86. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of dichloro(methyl)(pentyl)silane- d_1 (**4ra- d_1**) by chlorodemethylation and ring opening of 1,1-dimethylsilinane (**1r**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane; + Me_2SiCl_2)

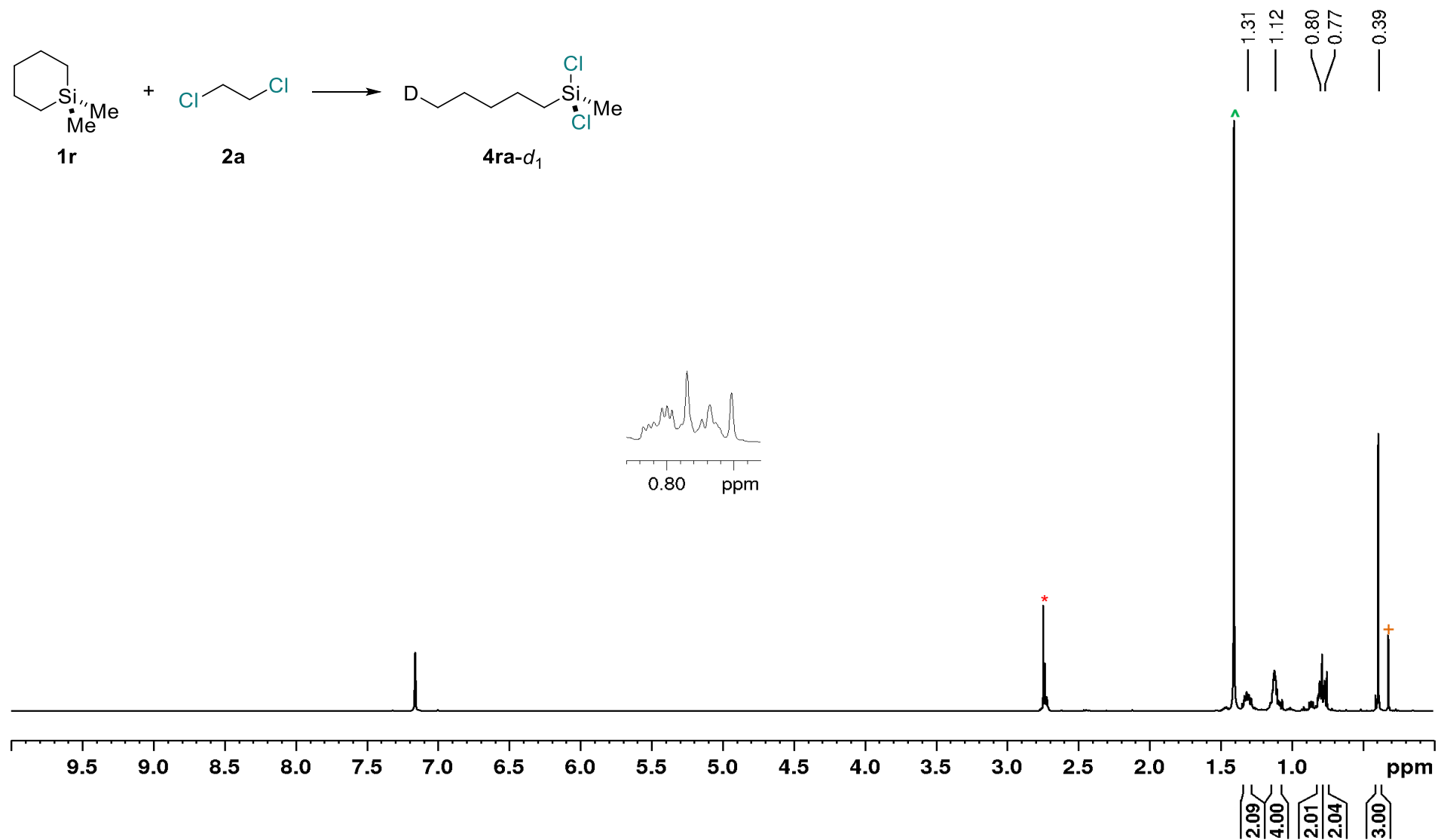


Figure S87. ^2H NMR spectrum (77 MHz, C_6D_6 , 298 K) of dichloro(methyl)(pentyl)silane- d_1 (**4ra-d₁**) by chlorodemethylation and ring opening of 1,1-dimethylsilinane (**1r**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10})

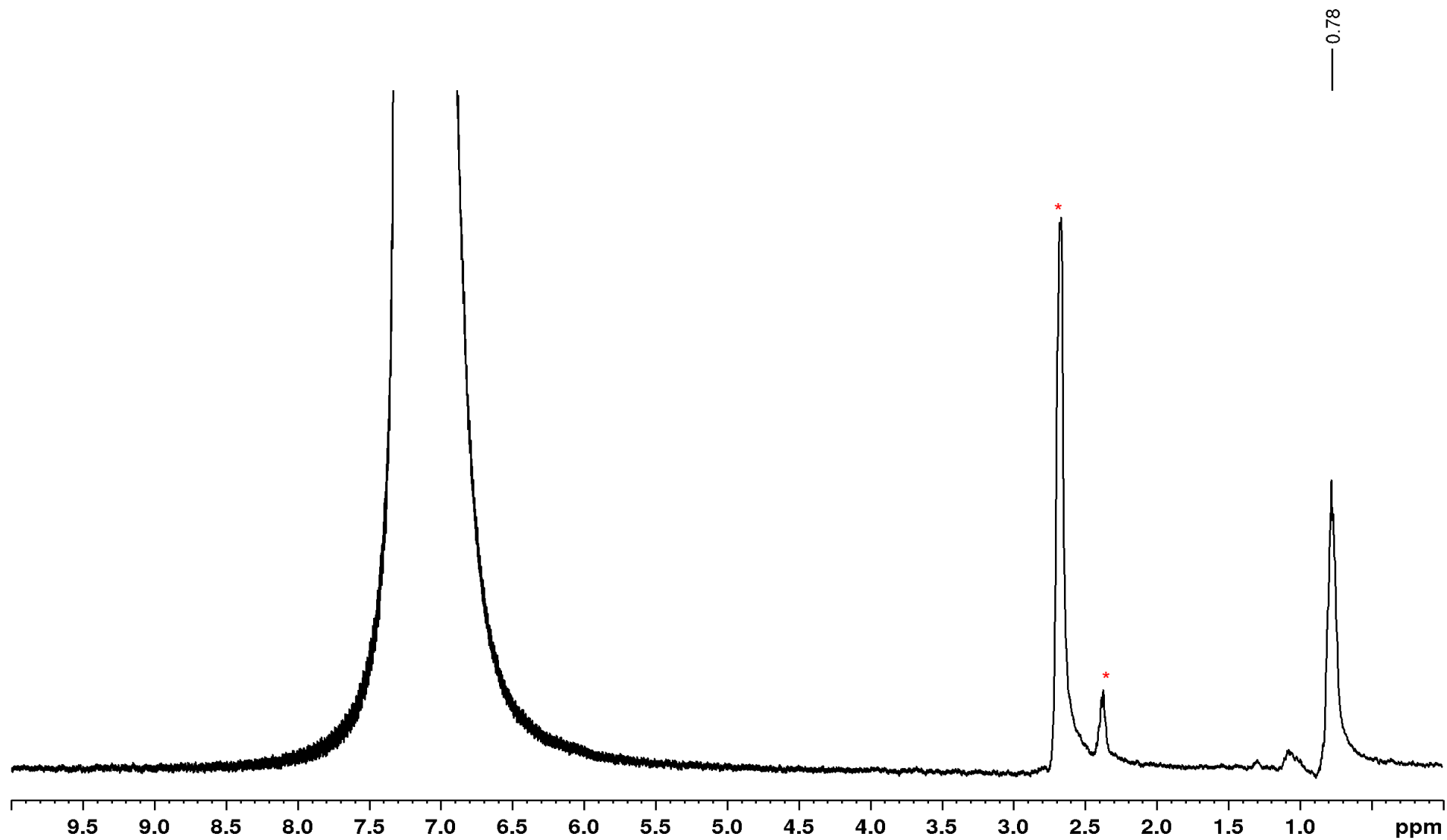


Figure S88. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of dichloro(methyl)(pentyl)silane- d_1 (**4ra-d₁**) by chlorodemethylation and ring opening of 1,1-dimethylsilinane (**1r**) with 1,2-dichoroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; ^ cyclohexane; + Me_2SiCl_2)

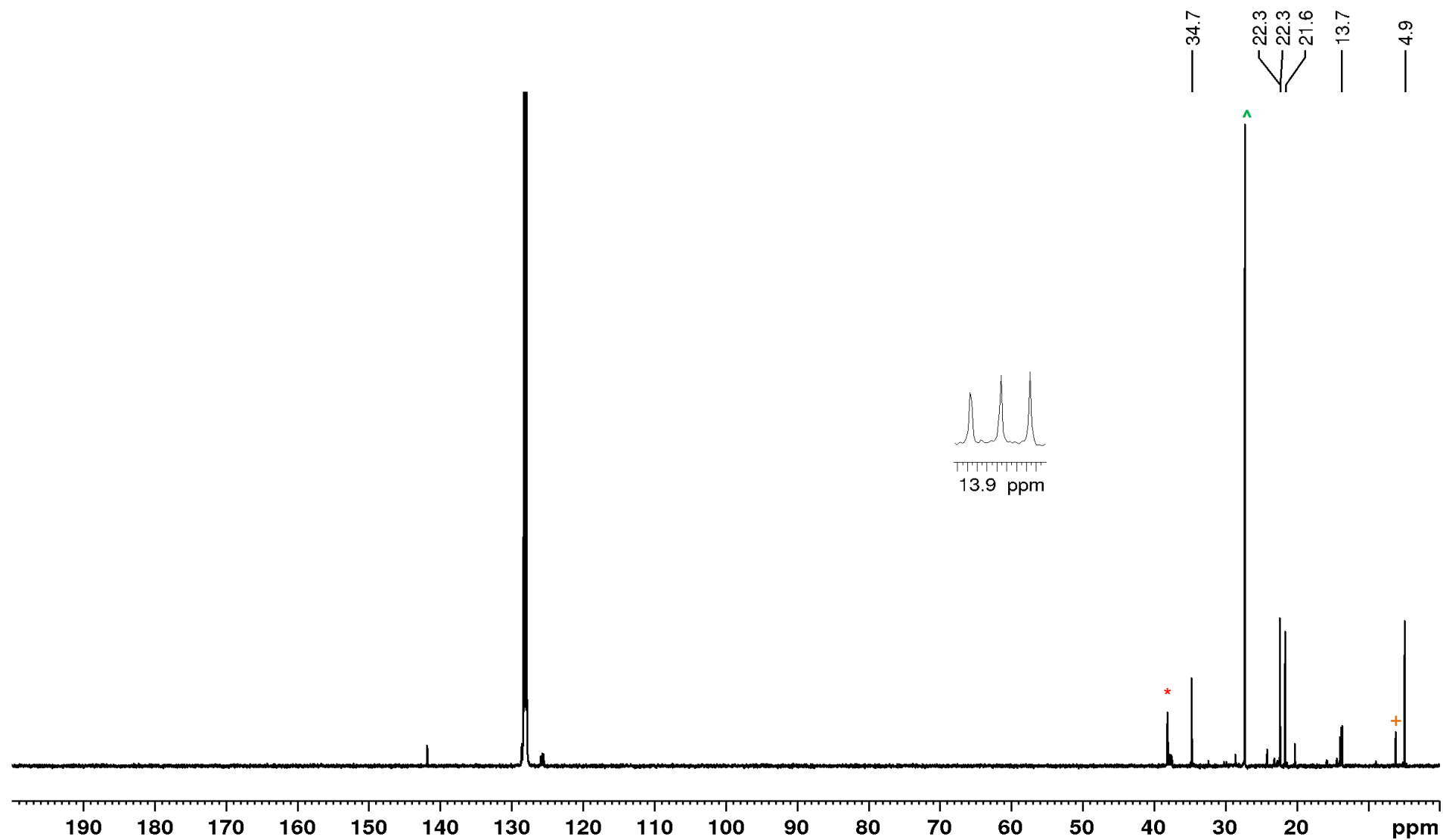


Figure S89. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 20.7°) of dichloro(methyl)(pentyl)silane- d_1 (**4ra-d₁**) by chlorodemethylation and ring opening of 1,1-dimethylsilinane (**1r**) with 1,2-dichloroethane (**2a**)

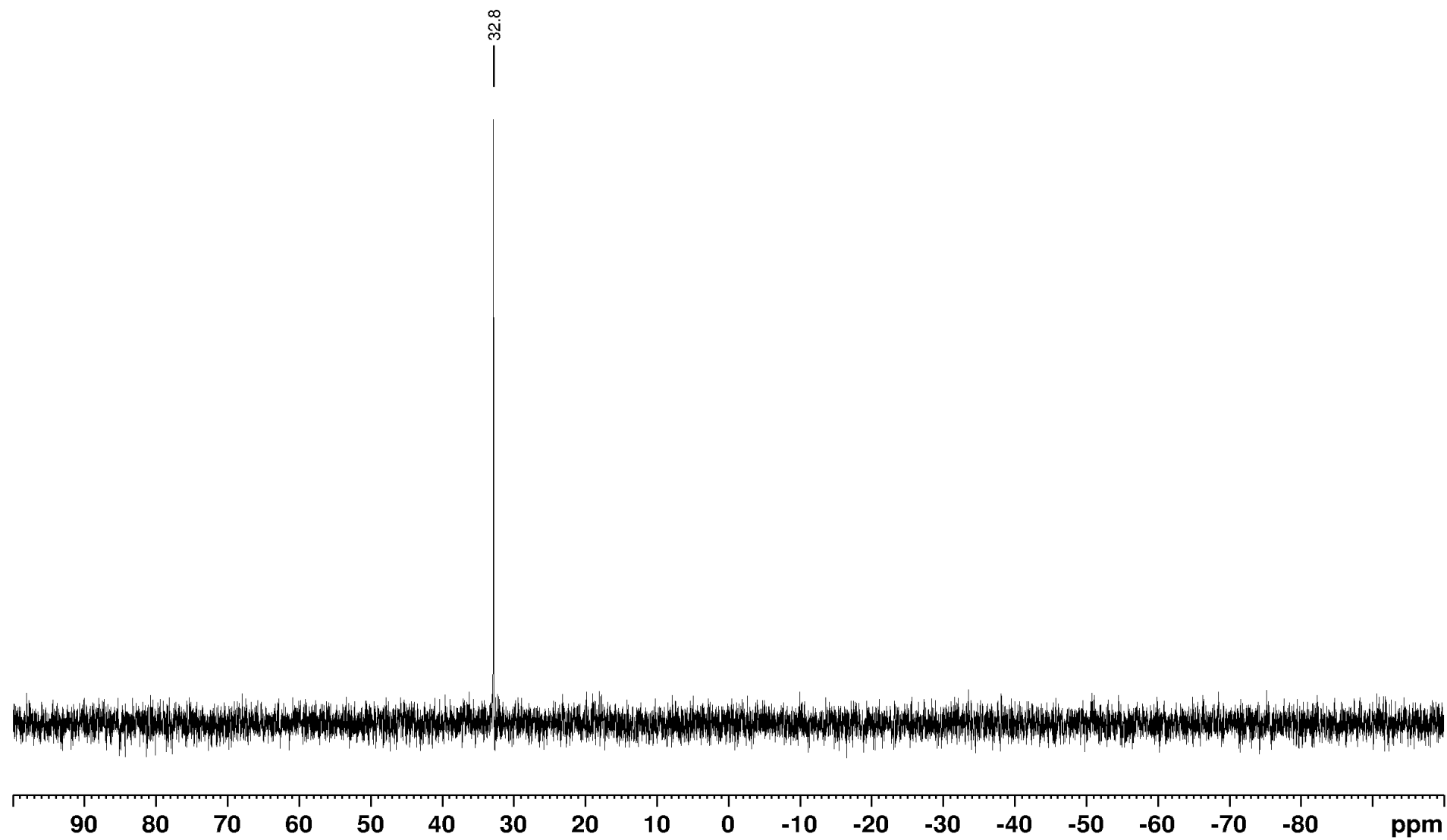


Figure S90. $^1\text{H},^{29}\text{Si}$ HMQC NMR (500/99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz) of dichloro(methyl)(pentyl)silane- d_1 (**4ra-d₁**) by chlorodemethylation and ring opening of 1,1-dimethylsilinane (**1r**) with 1,2-dichoroethane (**2a**) (+ Me_2SiCl_2)

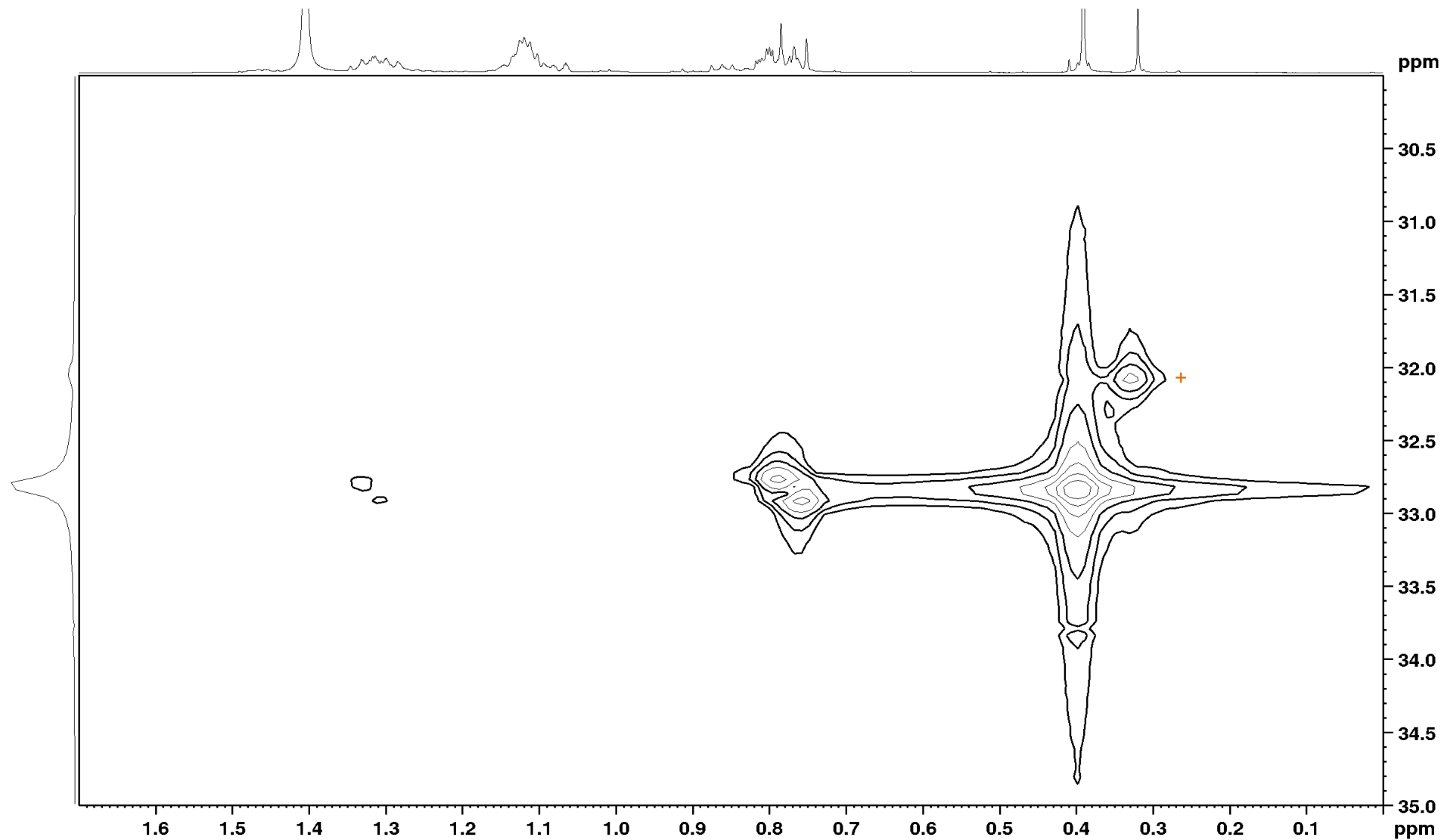


Figure S91. ^1H , ^1H COSY NMR (500 MHz, C_6D_6 , 298 K) of dichloro(methyl)(pentyl)silane- d_1 (**4ra-d₁**) by chlorodemethylation and ring opening of 1,1-dimethylsilinane (**1r**) with 1,2-dichloroethane (**2a**)

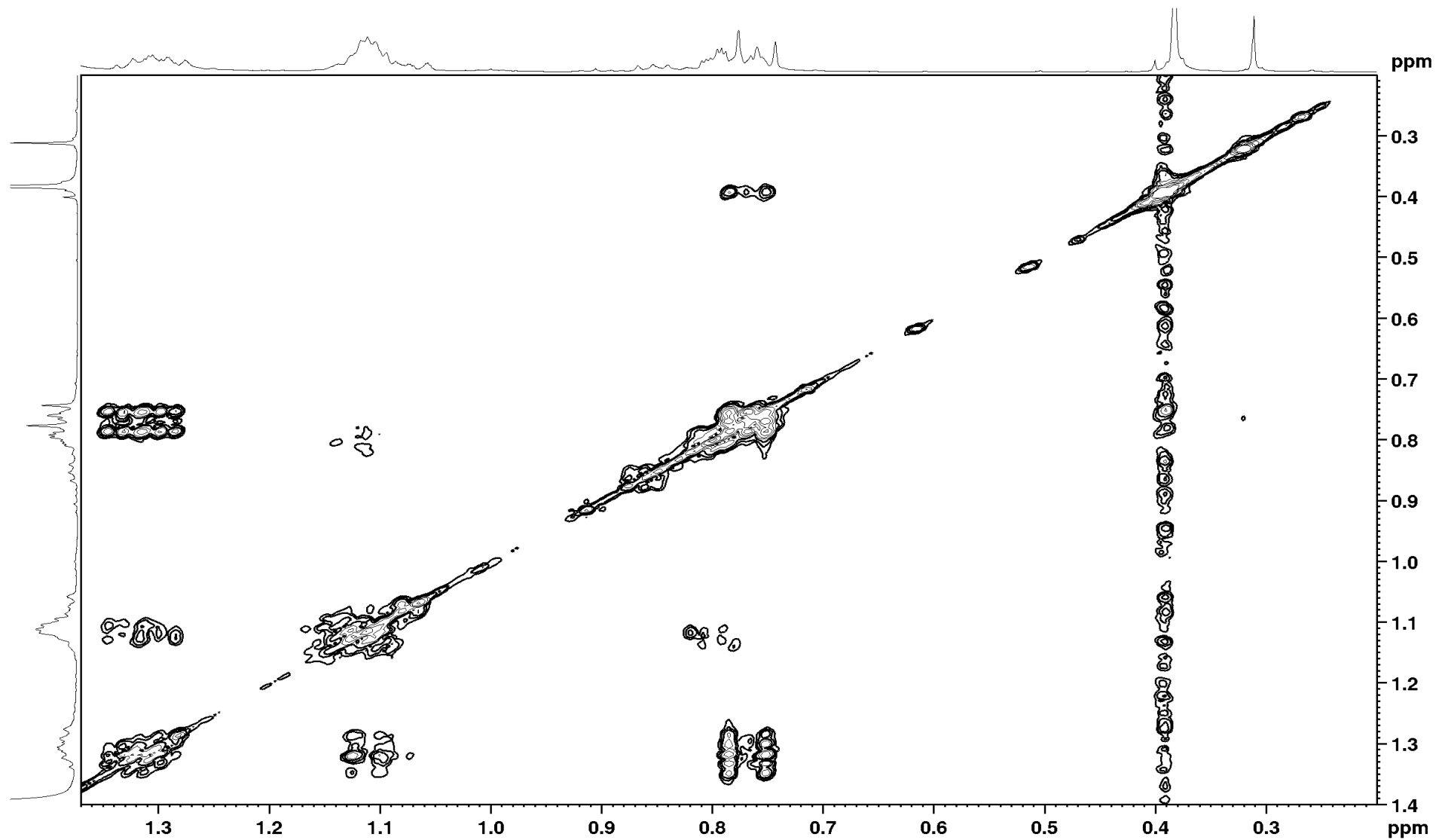


Figure S92. ^1H , ^{13}C HSQC NMR (500 MHz, C_6D_6 , 298 K) of dichloro(methyl)(pentyl)silane- d_1 (**4ra-d₁**) by chlorodemethylation and ring opening of 1,1-dimethylsilinane (**1r**) with 1,2-dichloroethane (**2a**) (\blacktriangle cyclohexane; $+$ Me_2SiCl_2)

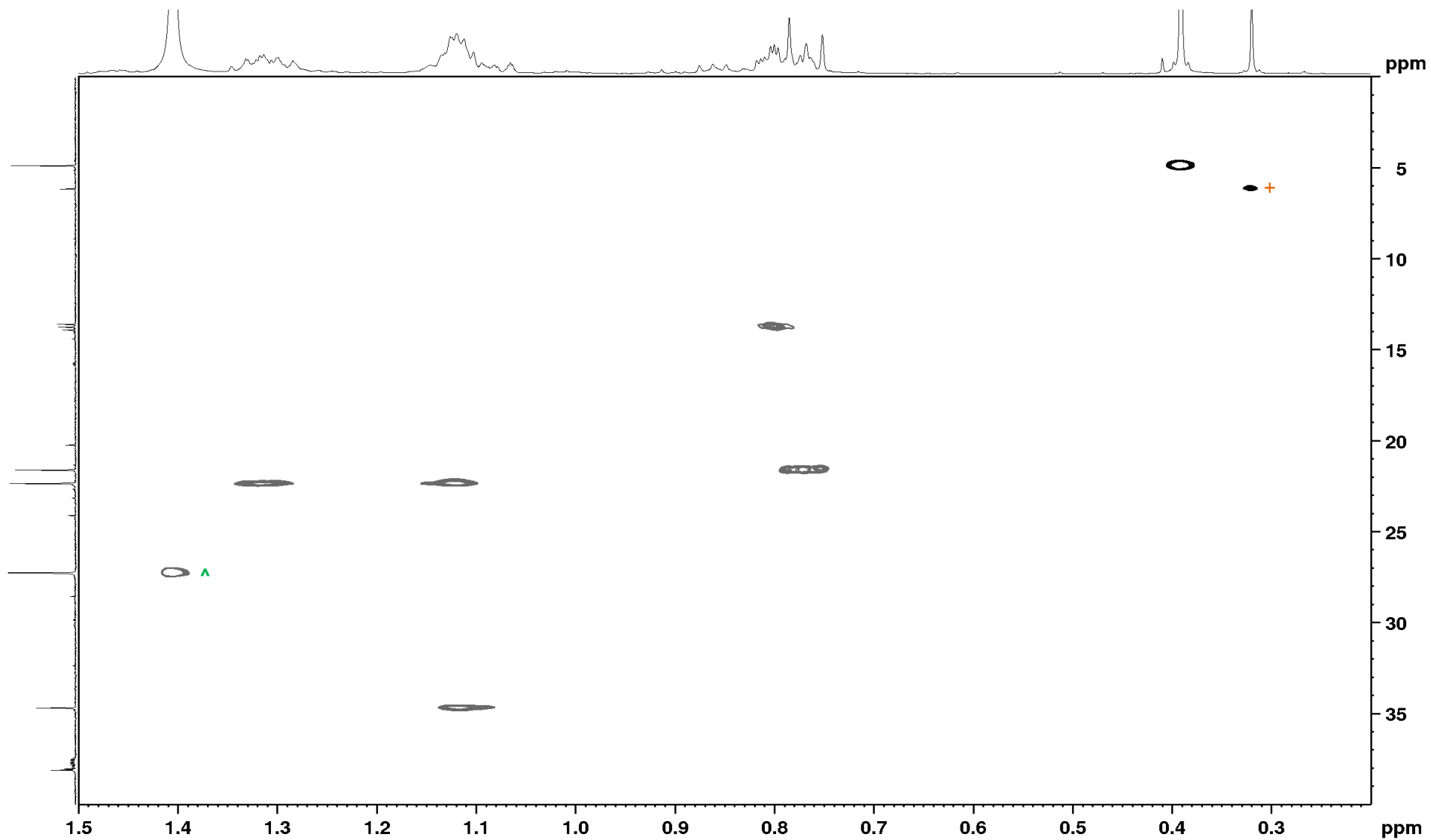


Figure S93. $^1\text{H NMR}$ spectrum (500 MHz, C_6D_6 , 298 K) of dichloro(isopropyl)(methyl)silane (**7aa**) by chlorodemethylation of isopropyldimethylsilane (**6a**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane; + Me_2SiCl_2)

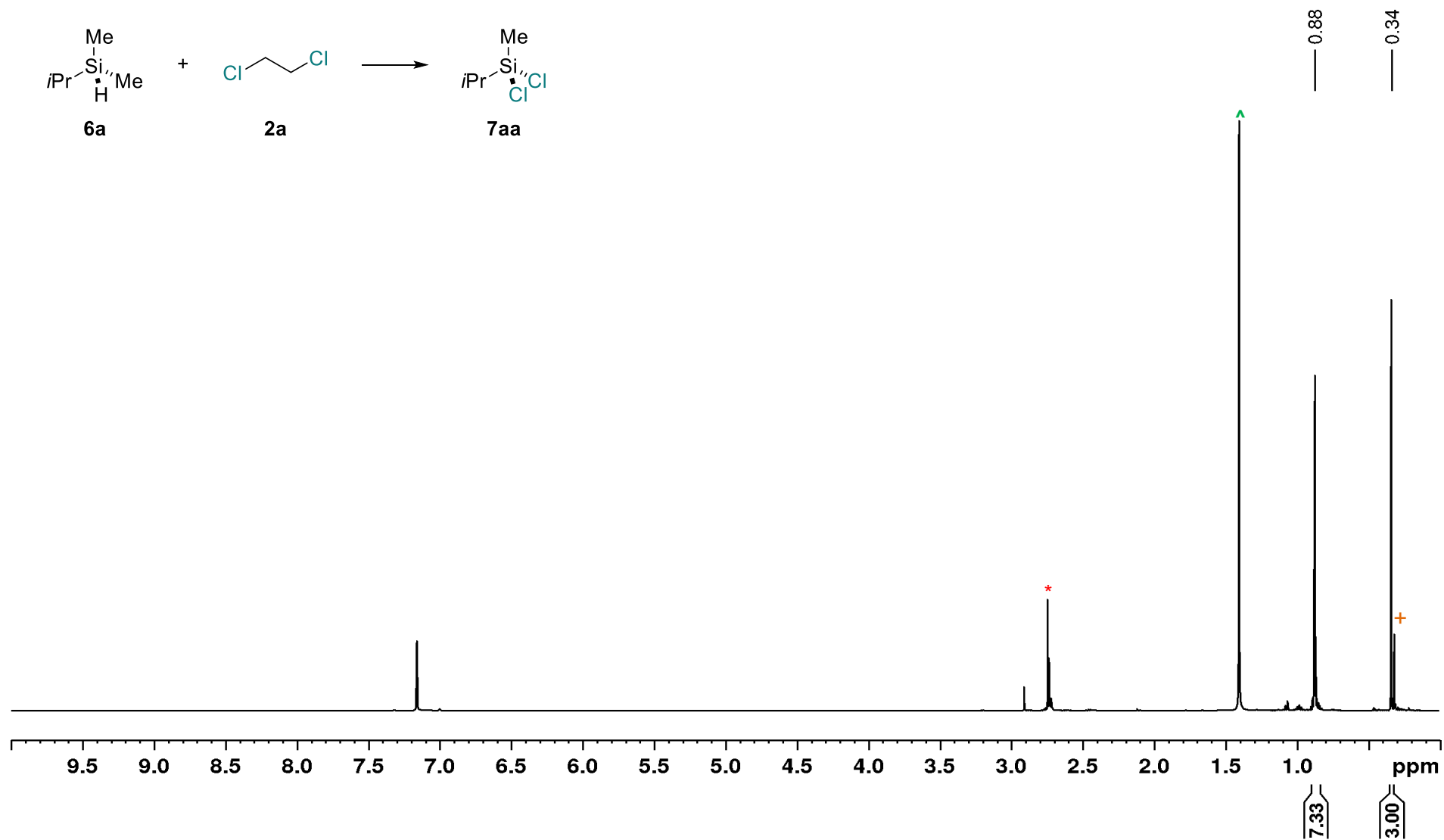


Figure S94. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of dichloro(isopropyl)(methyl)silane (**7aa**) by chlorodemethylation of isopropyldimethylsilane (**6a**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; ^ cyclohexane; + Me_2SiCl_2)

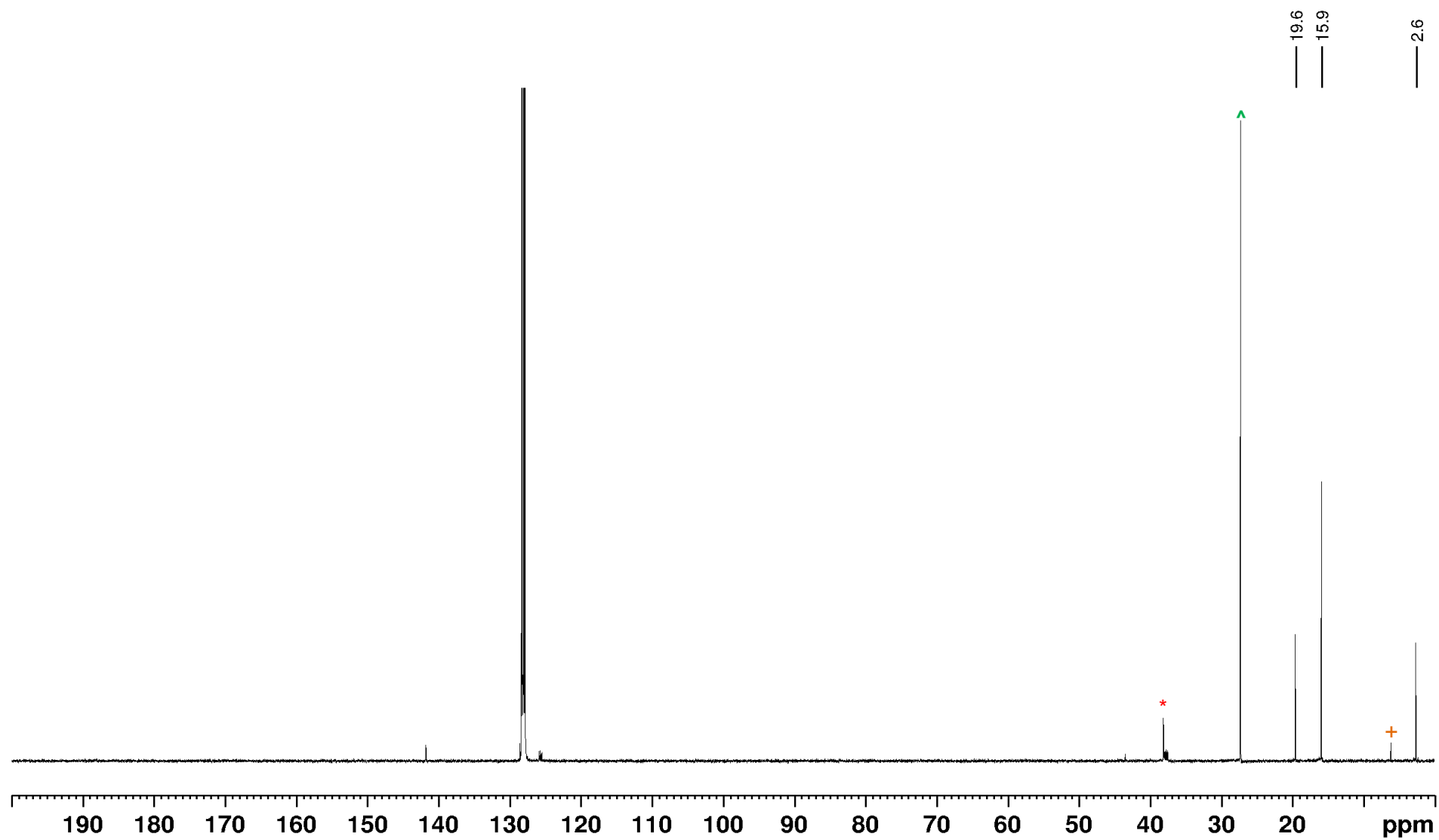


Figure S95. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 18.4°) of dichloro(isopropyl)(methyl)silane (**7aa**) by chlorodemethylation of isopropyldimethylsilane (**6a**) with 1,2-dichloroethane (**2a**)

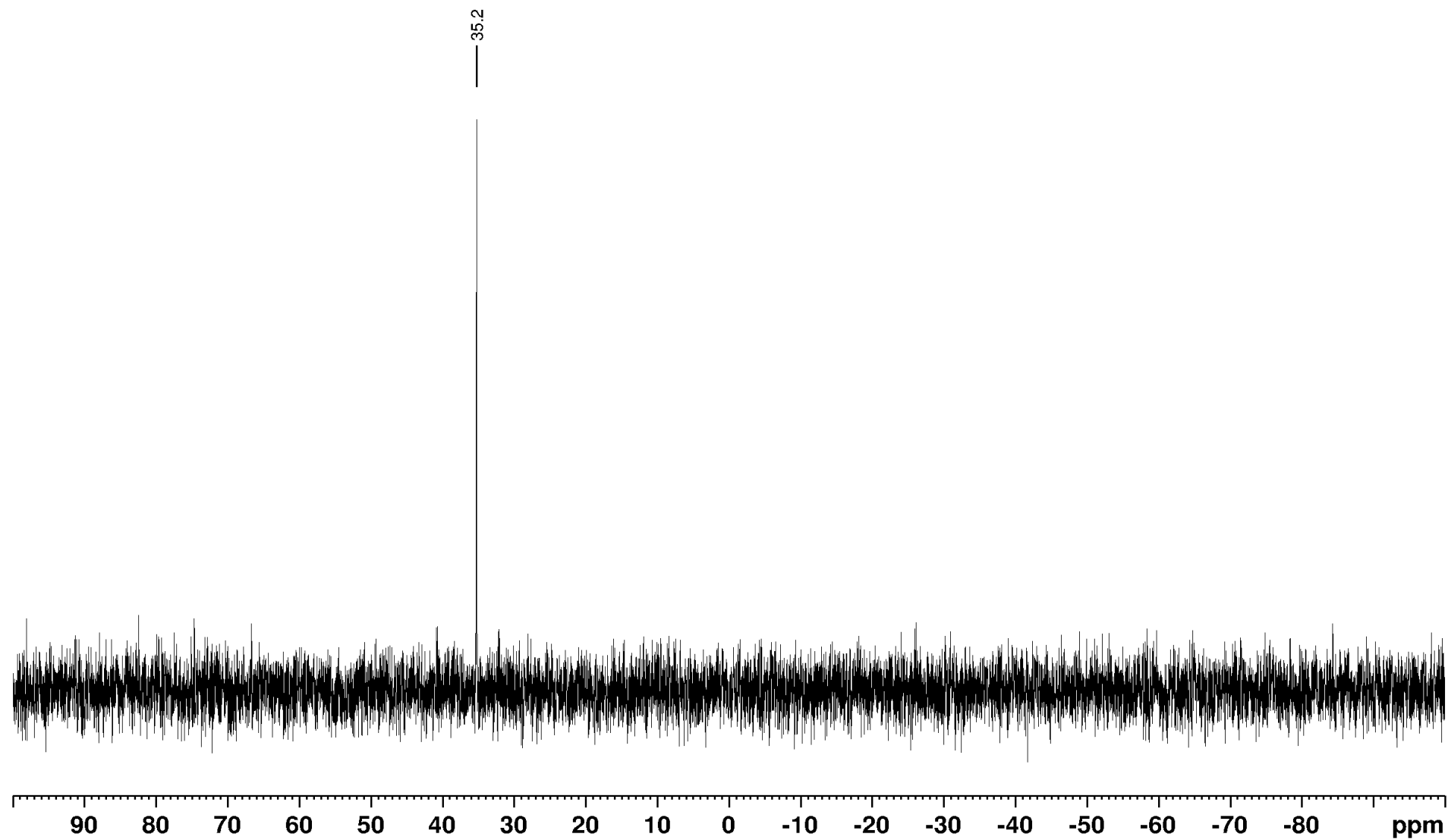


Figure S96. $^1\text{H NMR}$ spectrum (500 MHz, C_6D_6 , 298 K) of dichlorodiisopropylsilane (**7ba**) by chlorodemethylation of diisopropyl(methyl)silane (**6b**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane)

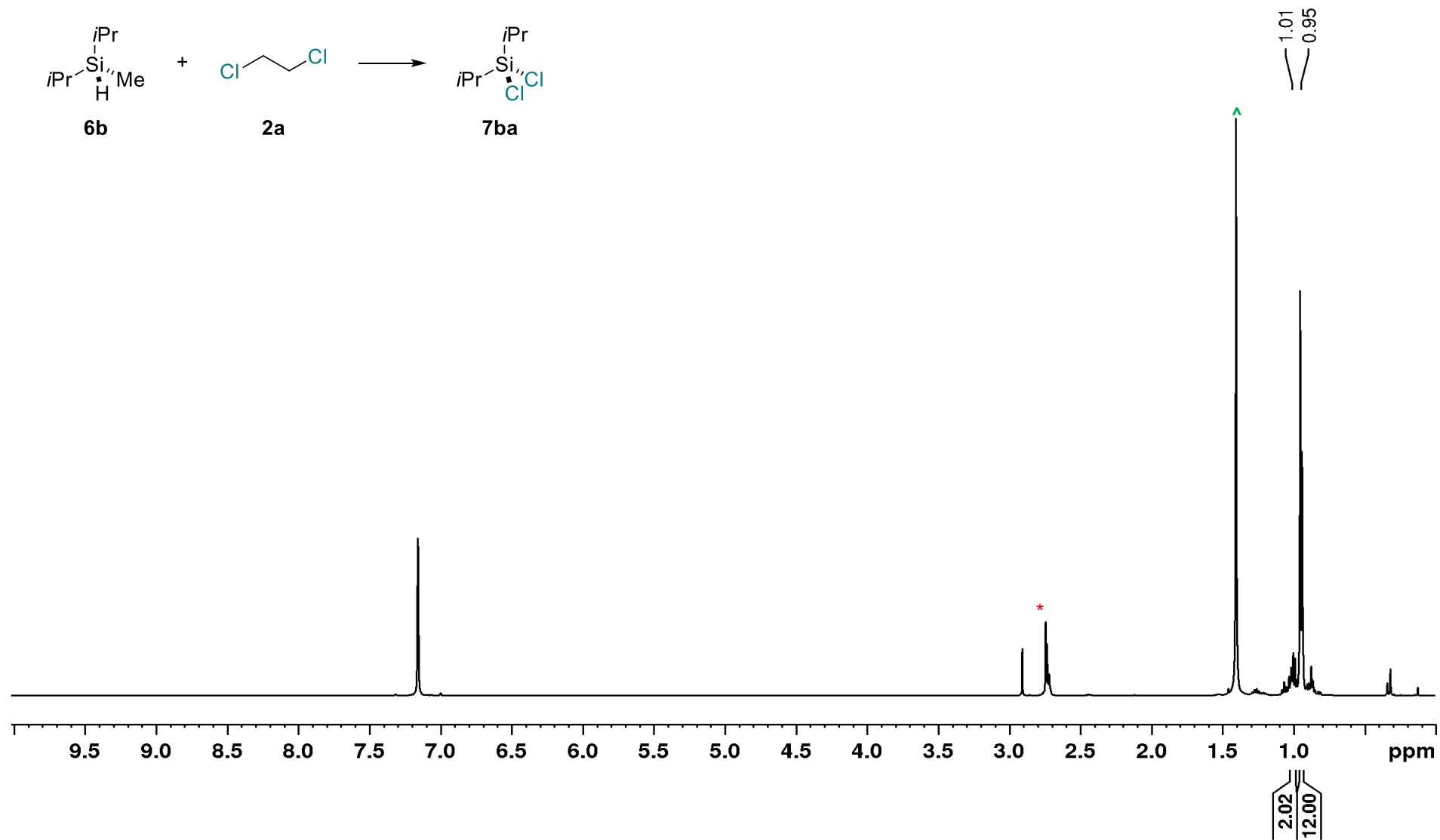


Figure S97. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of dichlorodiisopropylsilane (**7ba**) by chlorodemethylation of diisopropyl(methyl)silane (**6b**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; ^ cyclohexane)

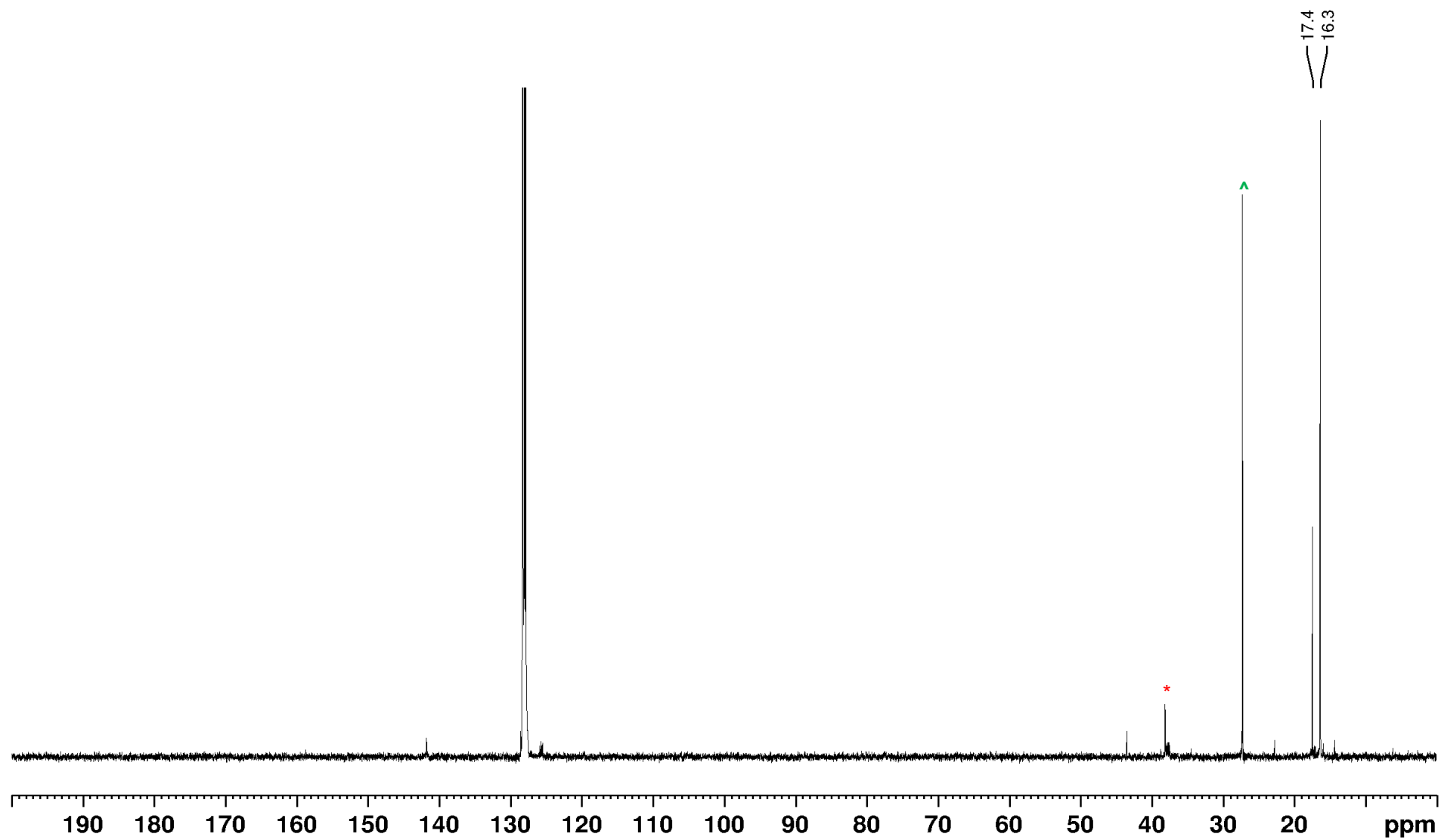


Figure S98. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 15.5°) of dichlorodiisopropylsilane (**7ba**) by chlorodemethylation of diisopropyl(methyl)silane (**6b**) with 1,2-dichloroethane (**2a**)

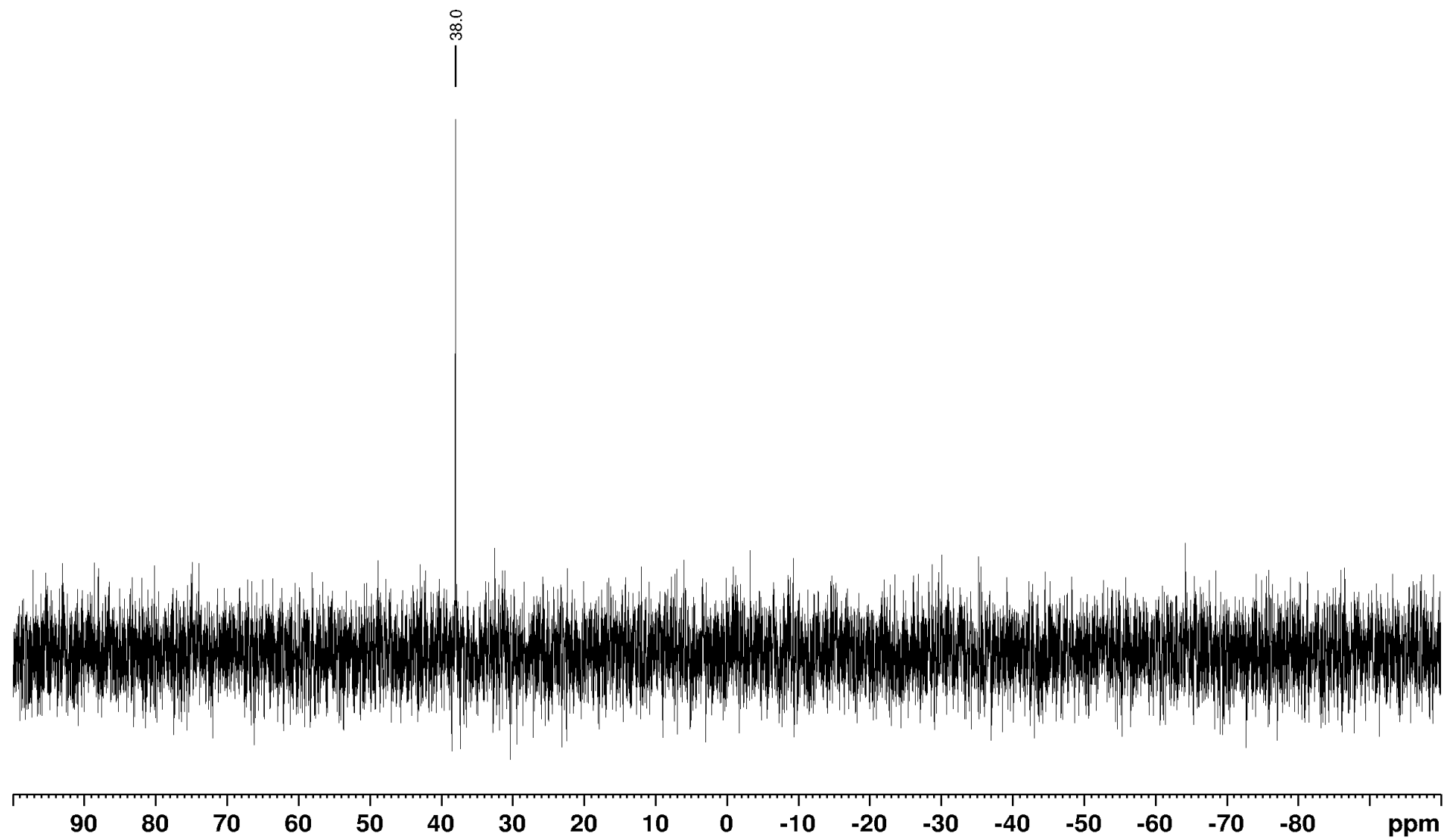


Figure S99. $^1\text{H NMR}$ spectrum (500 MHz, C_6D_6 , 298 K) of di-*tert*-butyldichlorosilane (**7ca**) by chlorodemethylation of di-*tert*-butyl(methyl)silane (**6c**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane; + $t\text{Bu}_2\text{SiMeCl}$)

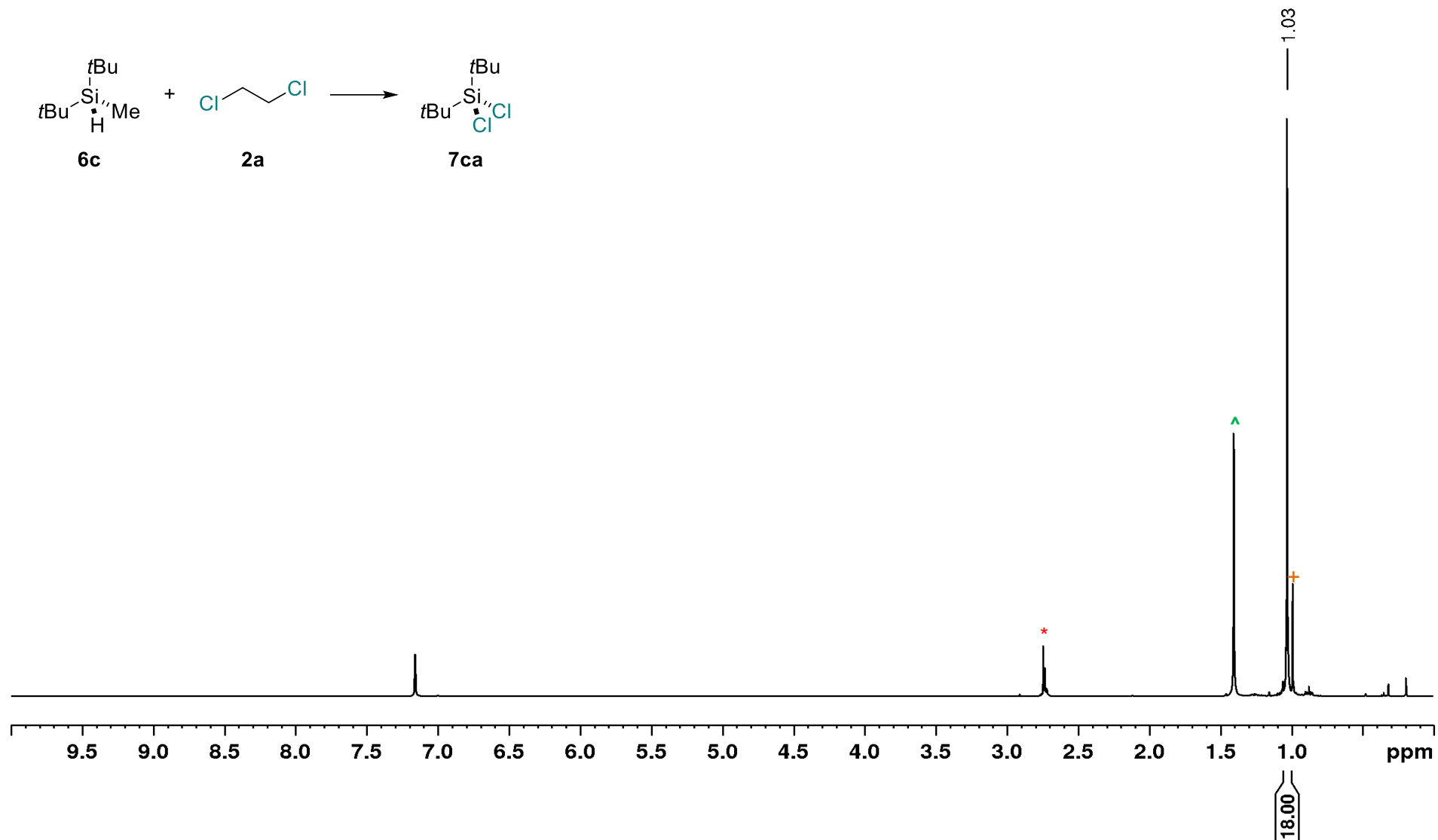


Figure S100. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of di-*tert*-butyldichlorosilane (**7ca**) by chlorodemethylation of di-*tert*-butyl(methyl)silane (**6c**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane)

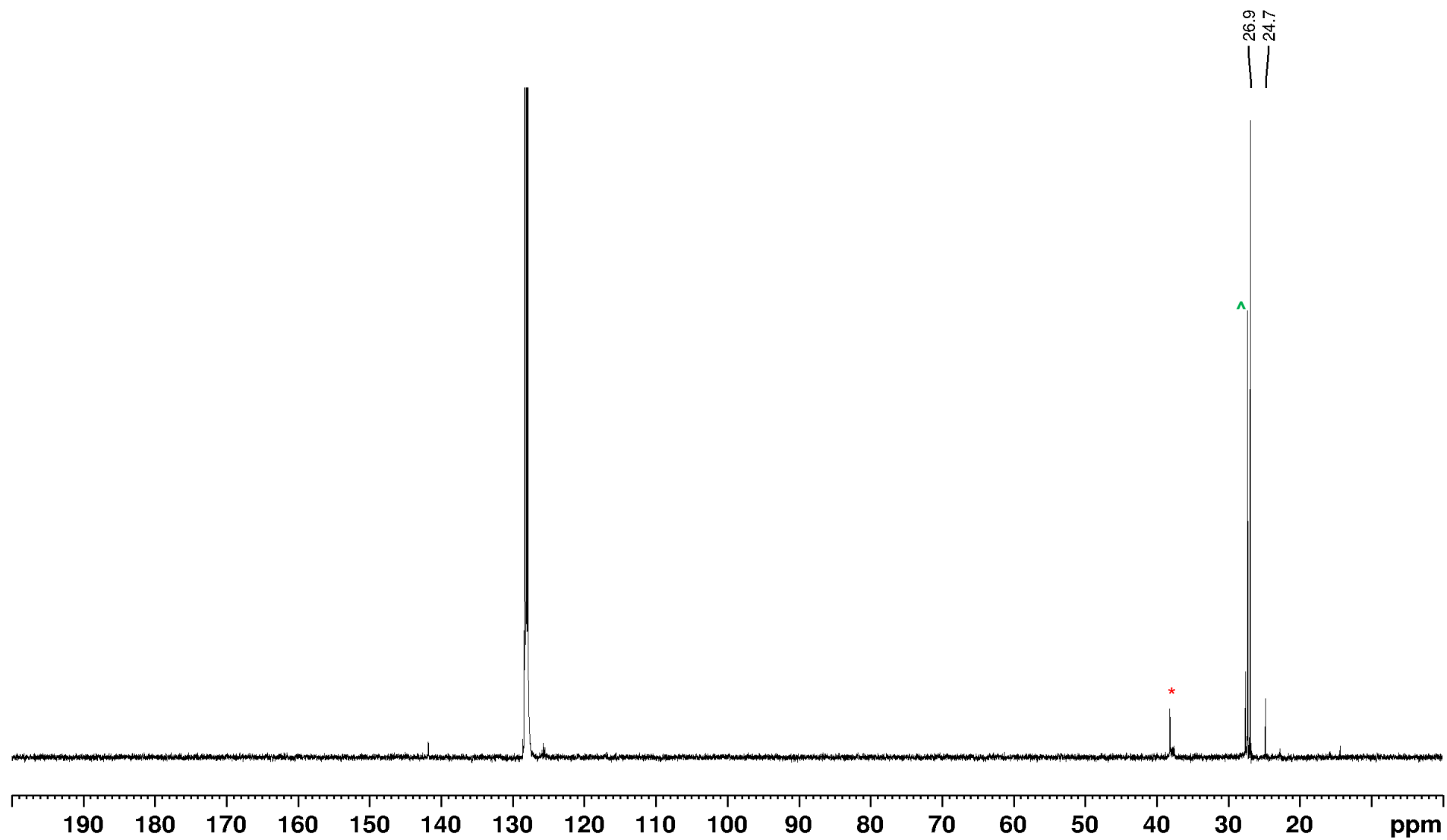


Figure S101. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 15.5°) di-*tert*-butyldichlorosilane (**7ca**) by chlorodemethylation of di-*tert*-butyl(methyl)silane (**6c**) with 1,2-dichloroethane (**2a**) (+ $t\text{Bu}_2\text{SiMeCl}$)

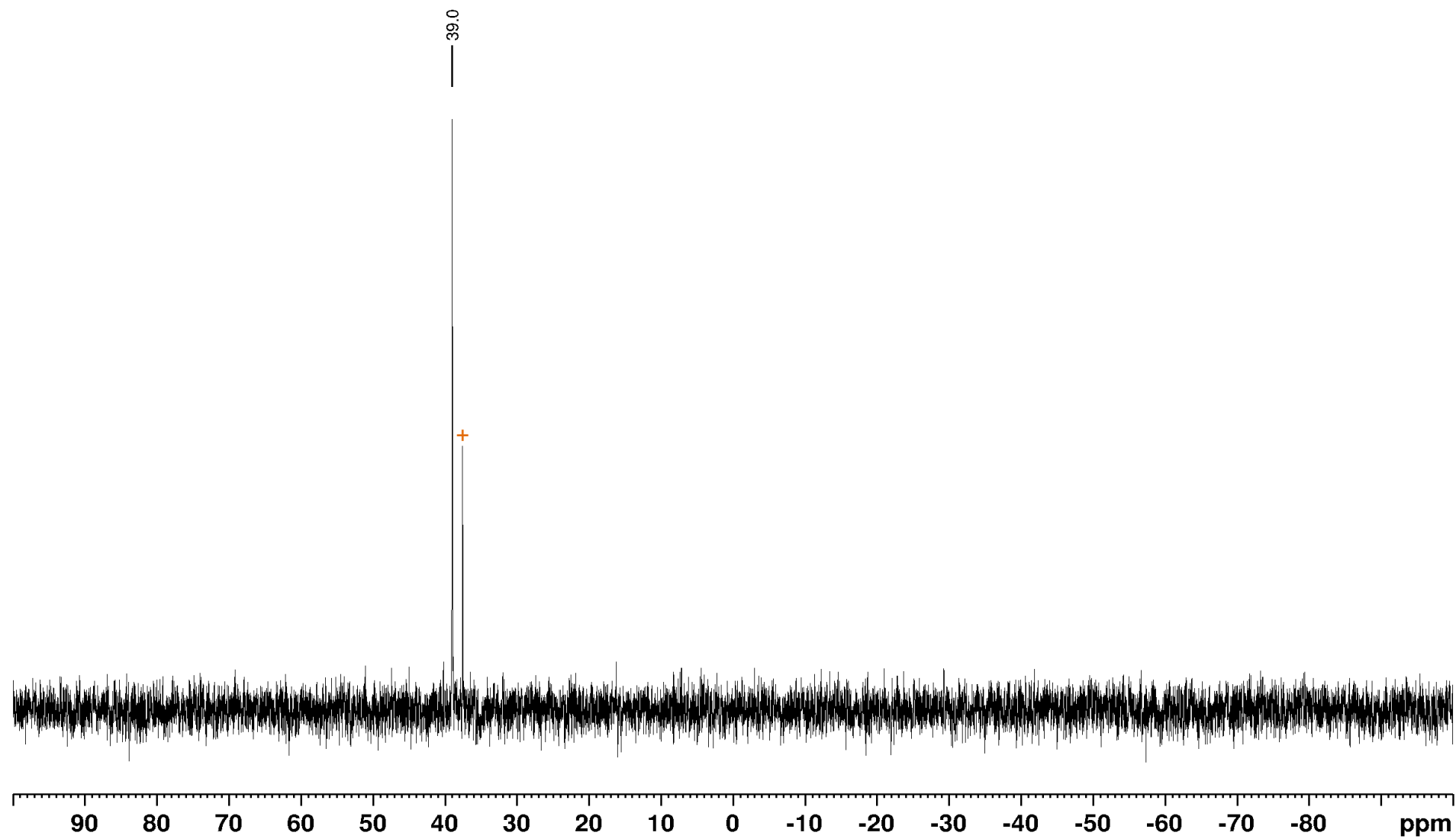


Figure S102. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of di-sec-butyldichlorosilane (**7da**) by chlorodemethylation of di-sec-butyl(methyl)silane (**6d**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle 1,2,4,5-tetrachlorobenzene; # $\text{sBu}_2\text{SiMeCl}$ + Me_2SiCl_2)

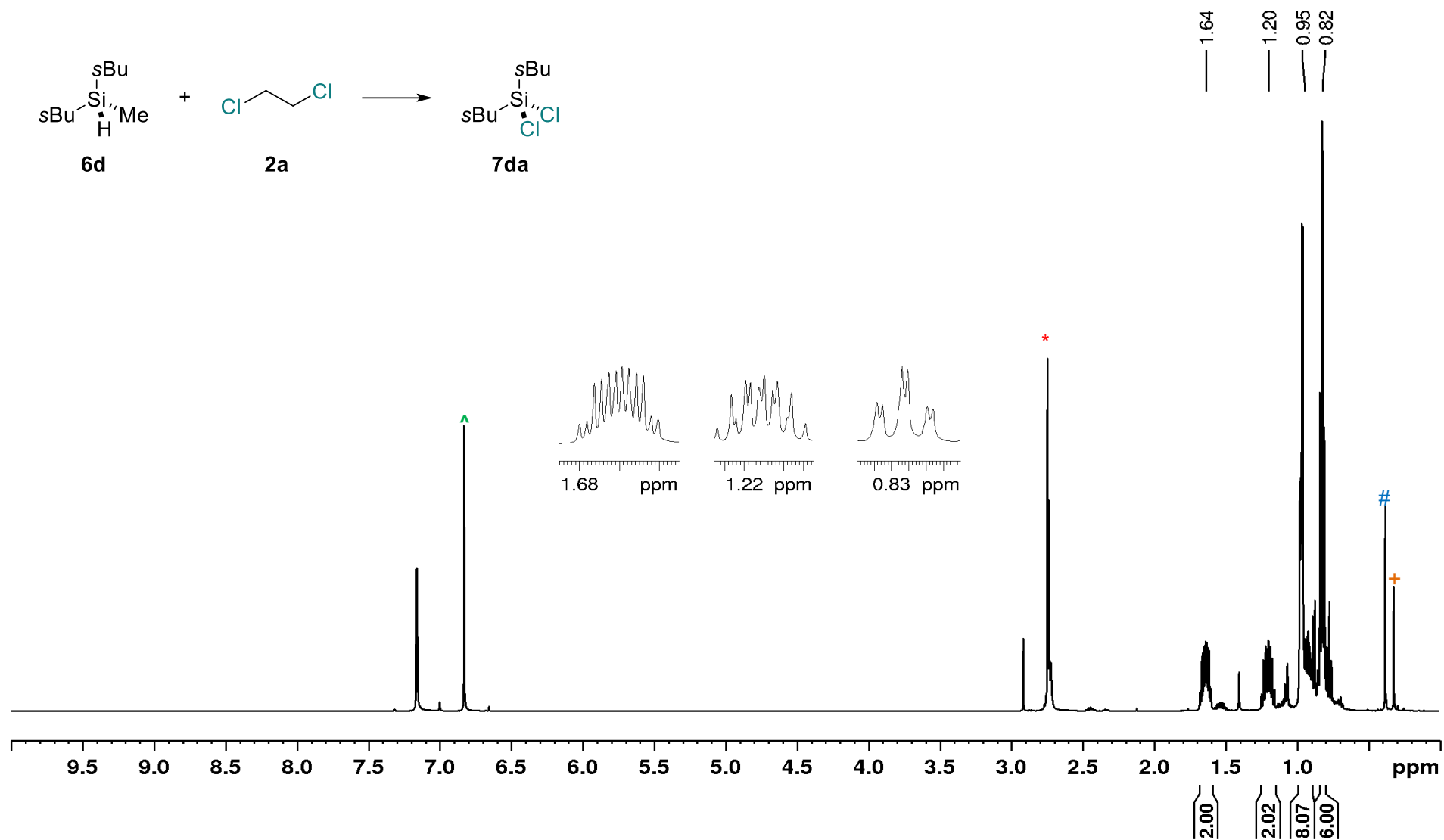


Figure S103. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of di-sec-butyldichlorosilane (**7da**) by chlorodemethylation of di-sec-butyl(methyl)silane (**6d**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; \blacktriangle 1,2,4,5-tetrachlorobenzene; # sBu₂SiMeCl + Me₂SiCl₂)

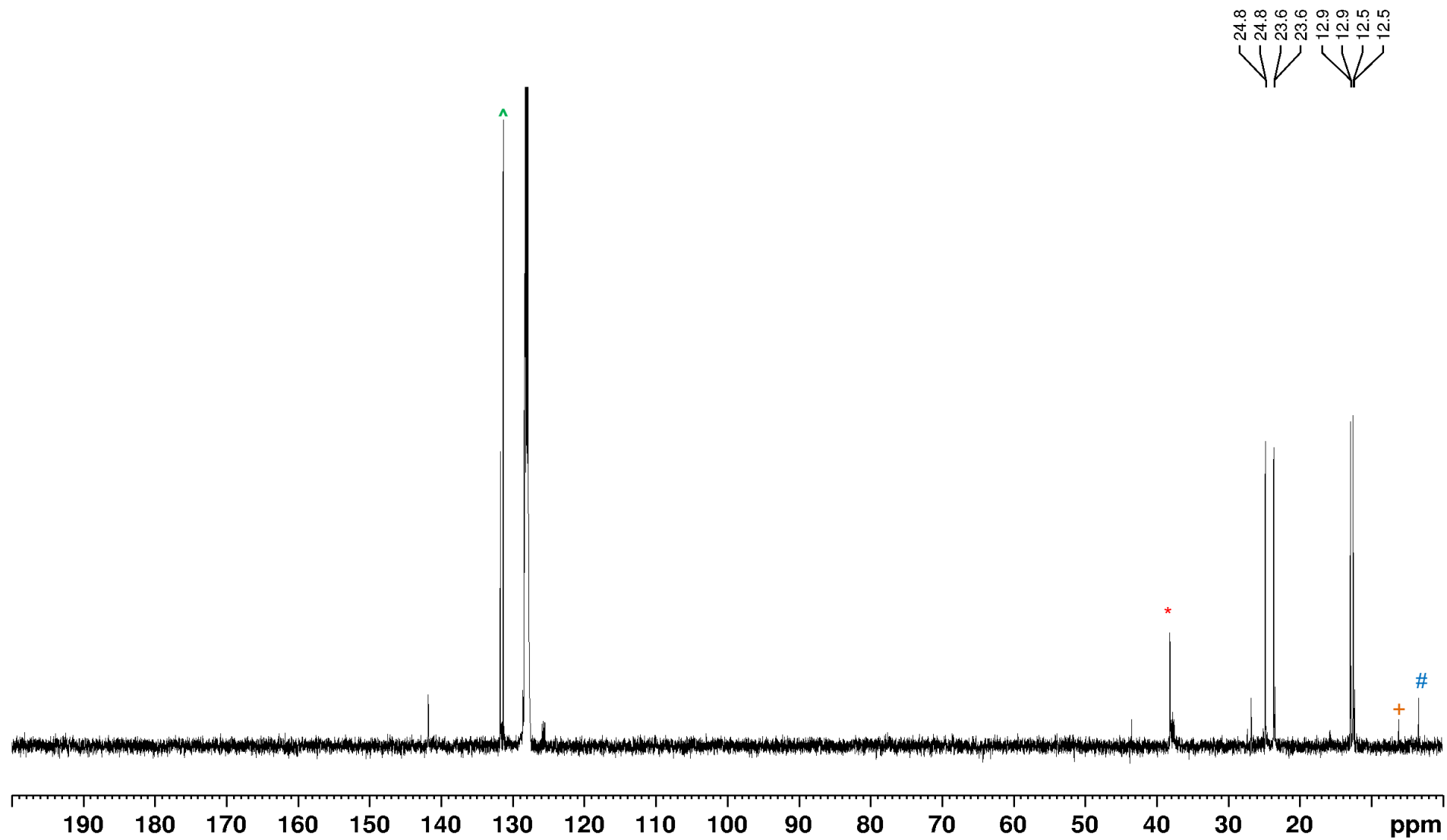


Figure S104. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 13.6°) of di-*sec*-butyldichlorosilane (**7da**) by chlorodemethylation of di-*sec*-butyl(methyl)silane (**6d**) with 1,2-dichloroethane (**2a**)

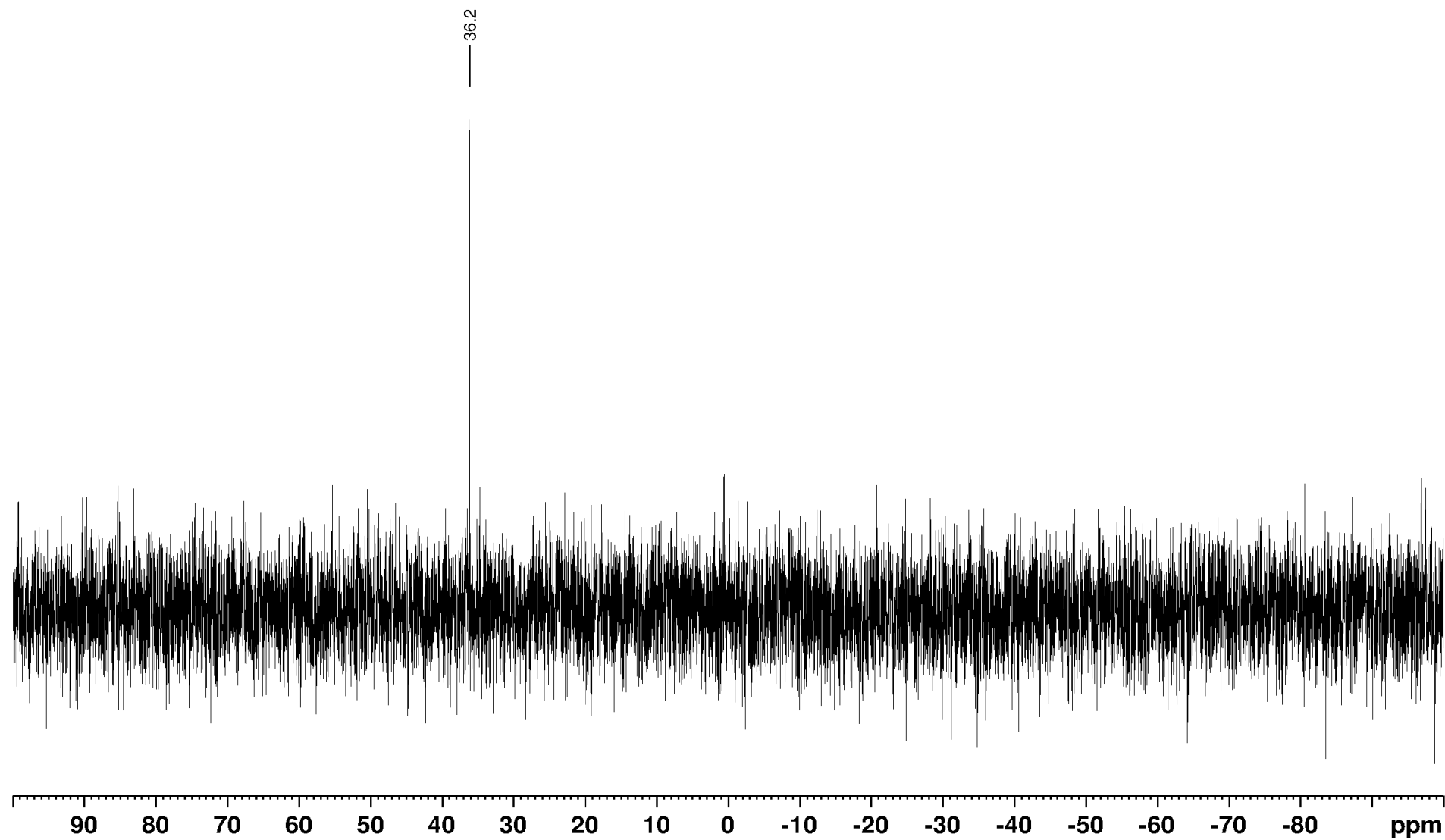


Figure S105. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of dichloro(isobutyl)(methyl)silane (**7ea**) by chlorodemethylation and chlorodeisobutylation of diisobutyl(methyl)silane (**6e**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; ^ cyclohexane; # *t*BuD)

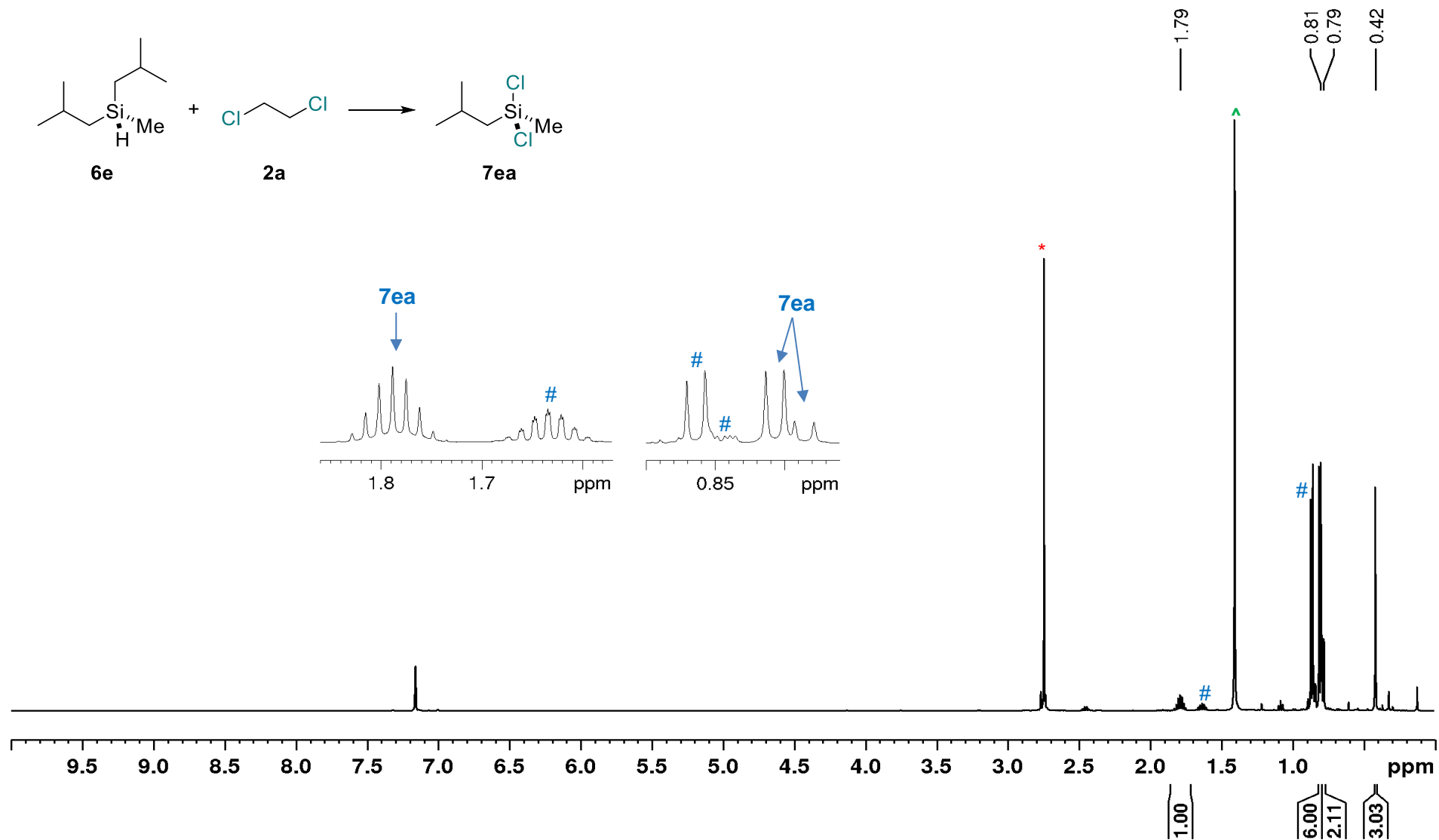


Figure S106. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of dichloro(isobutyl)(methyl)silane (**7ea**) by chlorodemethylation and chlorodeisobutylation of diisobutyl(methyl)silane (**6e**) with 1,2-dichloroethane (**2a**) (* 1,2-diphenylethane- d_{10} ; ^ cyclohexane; # *t*BuD)

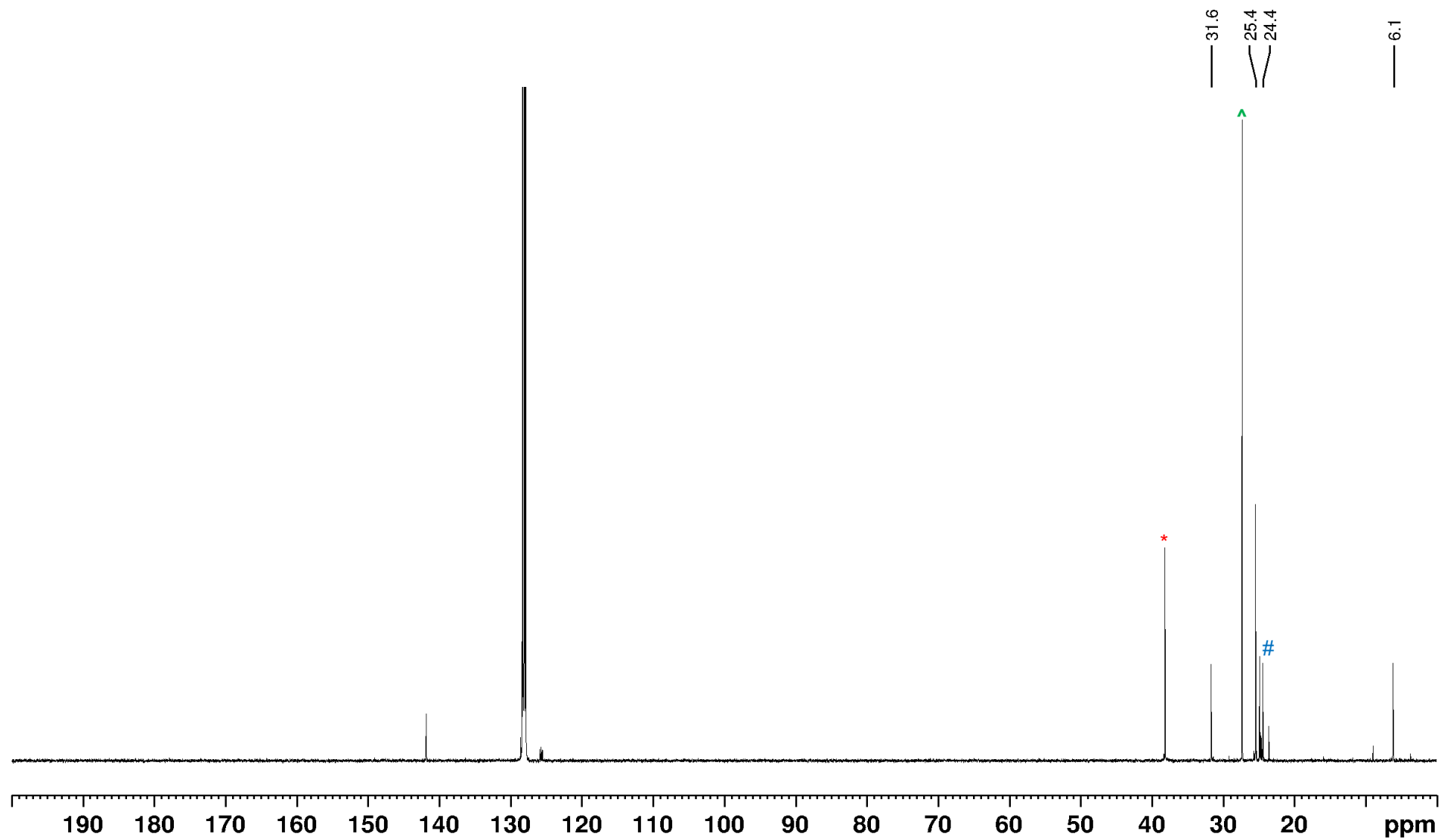


Figure S107. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz, 24.1°) of dichloro(isobutyl)(methyl)silane (**7ea**) by chlorodemethylation and chlorodeisobutylation of diisobutyl(methyl)silane (**6e**) with 1,2-dichloroethane (**2a**)

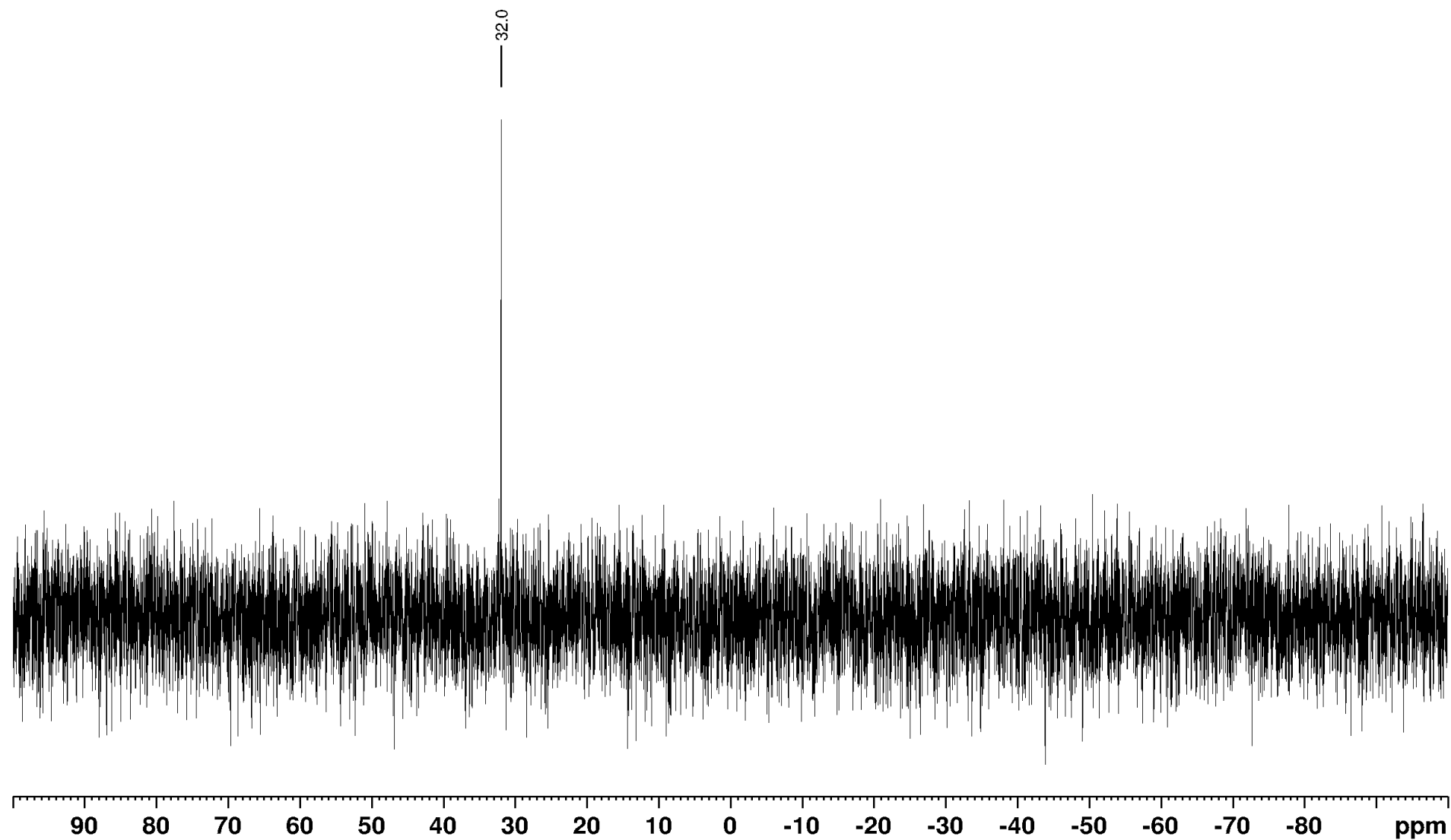


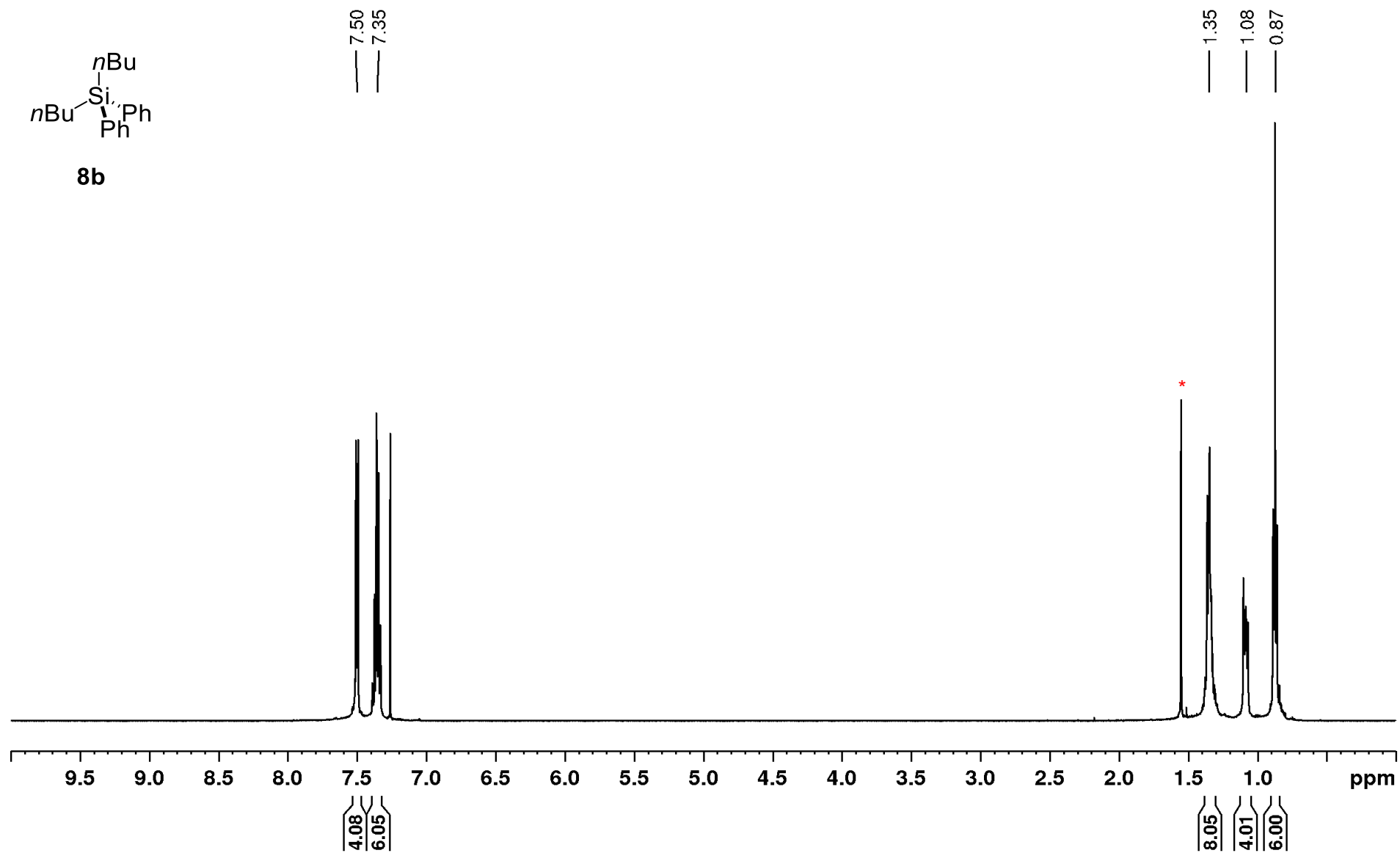
Figure S108. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of dibutyldiphenylsilane (**8b**) (* water)

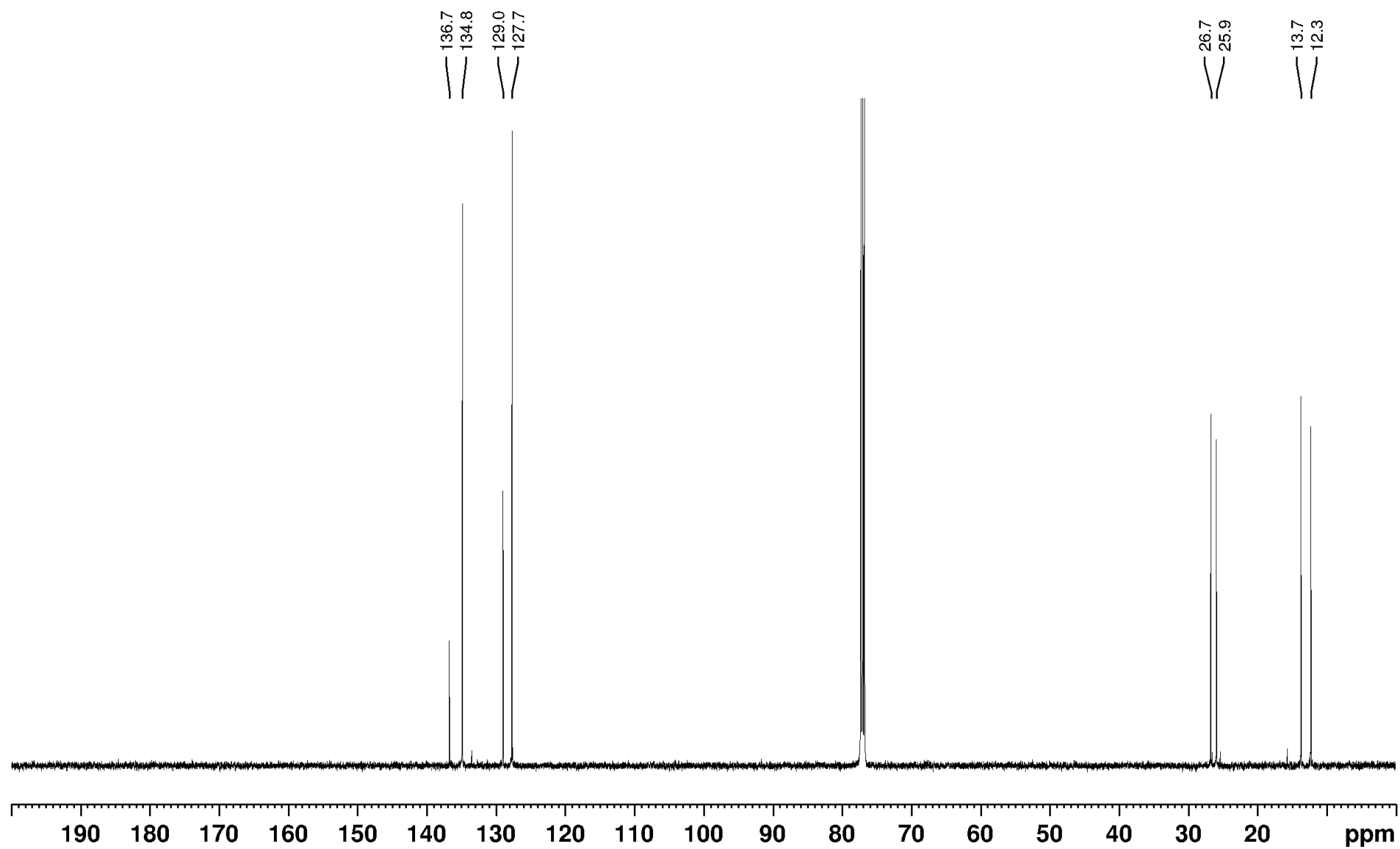
Figure S109. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CDCl_3 , 298 K) of dibutyldiphenylsilane (**8b**)

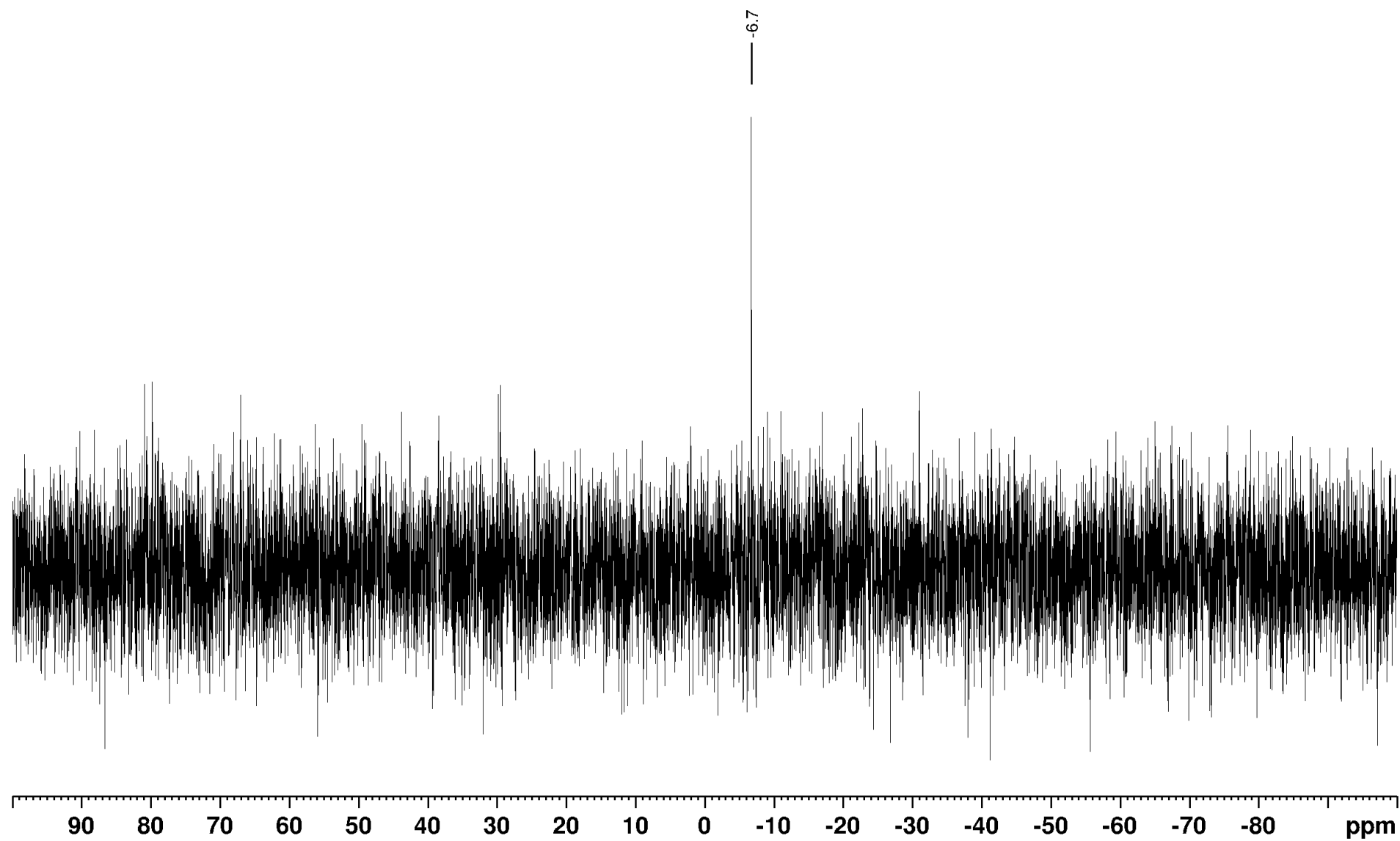
Figure S110. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, CDCl_3 , 298 K, optimized for $J = 7$ Hz, 30.0°) of dibutyldiphenylsilane (**8b**)

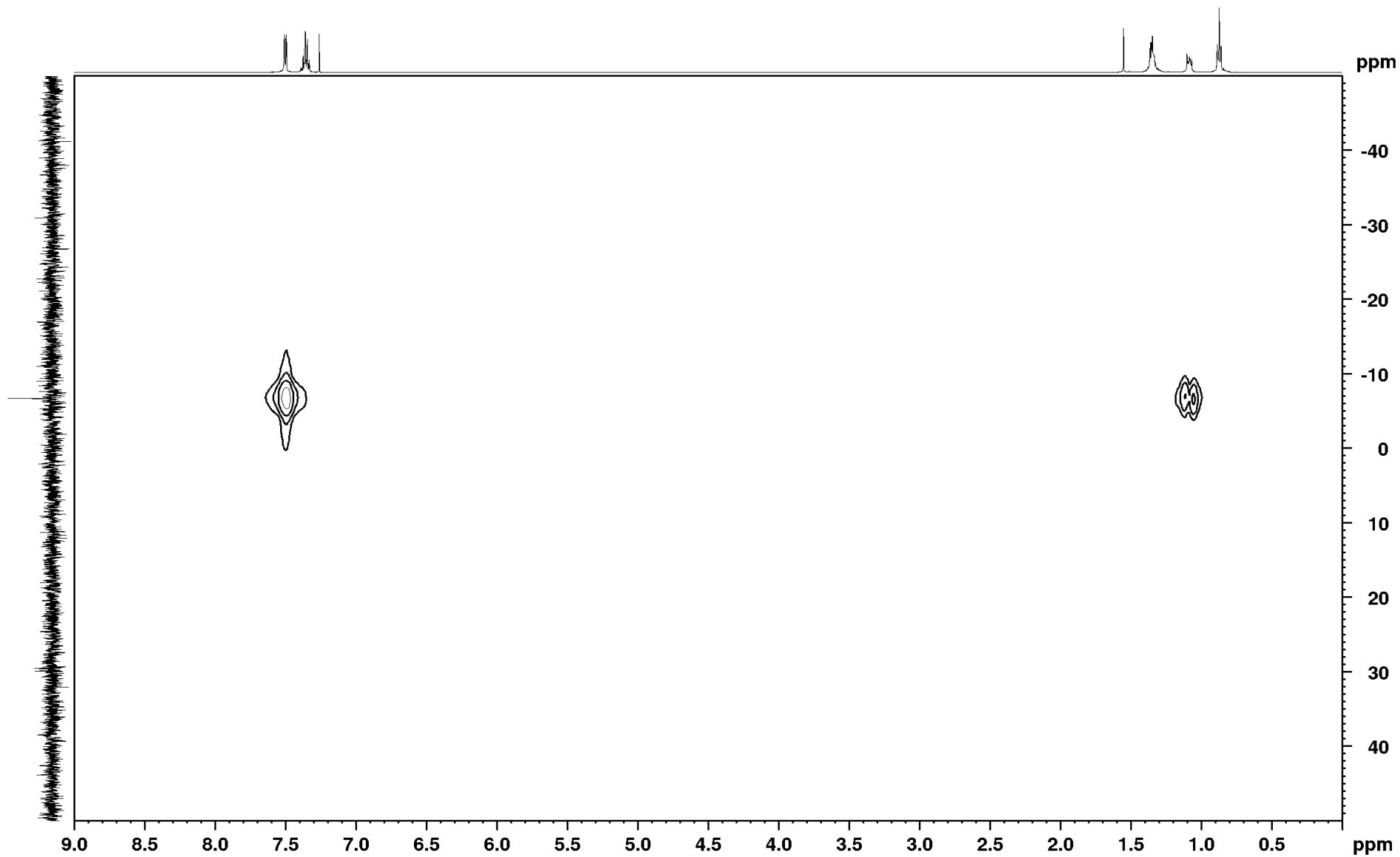
Figure S111. ^1H , ^{29}Si HMQC NMR (500/99 MHz, CDCl_3 , 298 K, optimized for $J = 7$ Hz) of dibutyldiphenylsilane (**8b**)

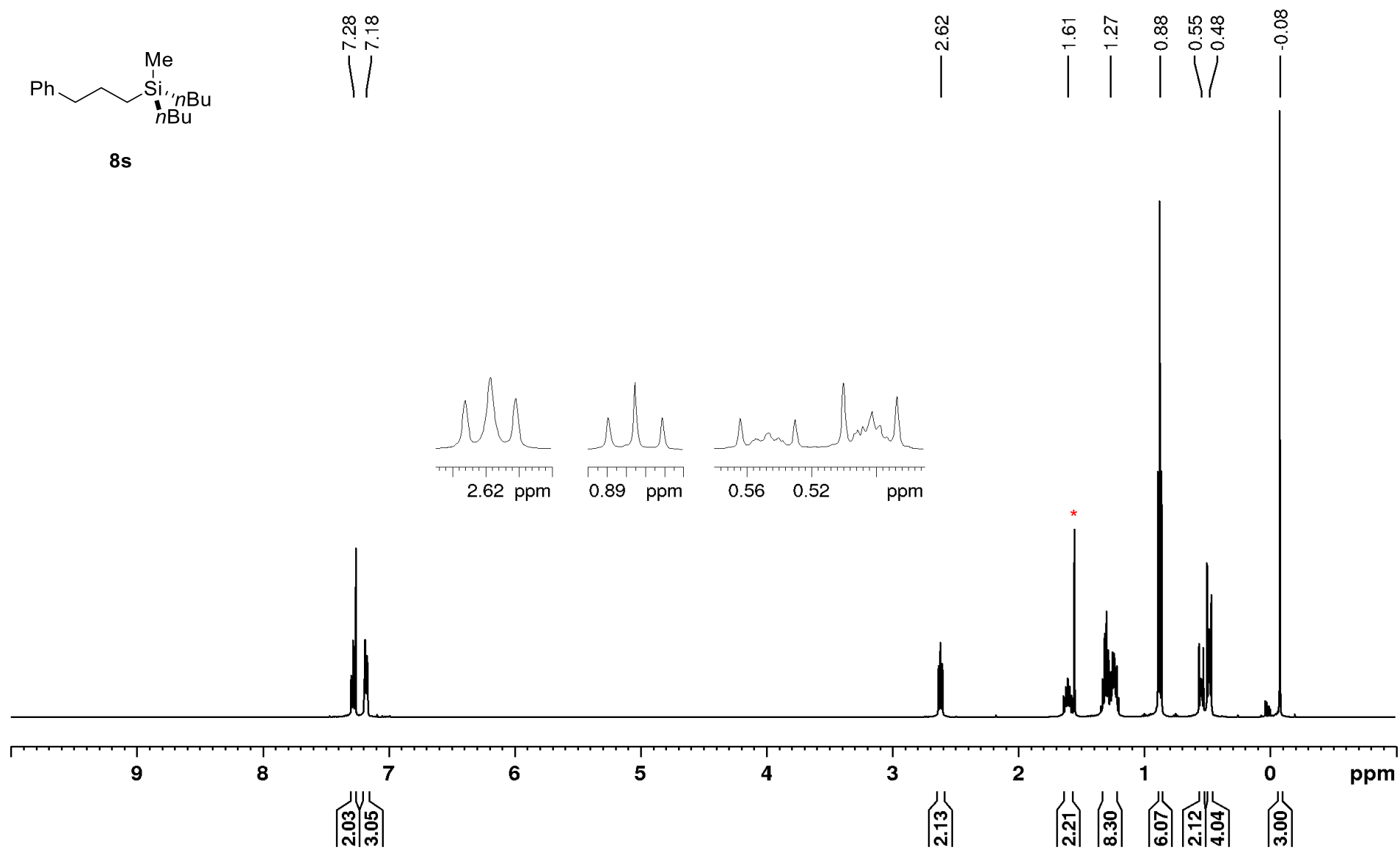
Figure S112. ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K) of dibutyl(methyl)(3-phenylpropyl)silane (**8s**) (* water)

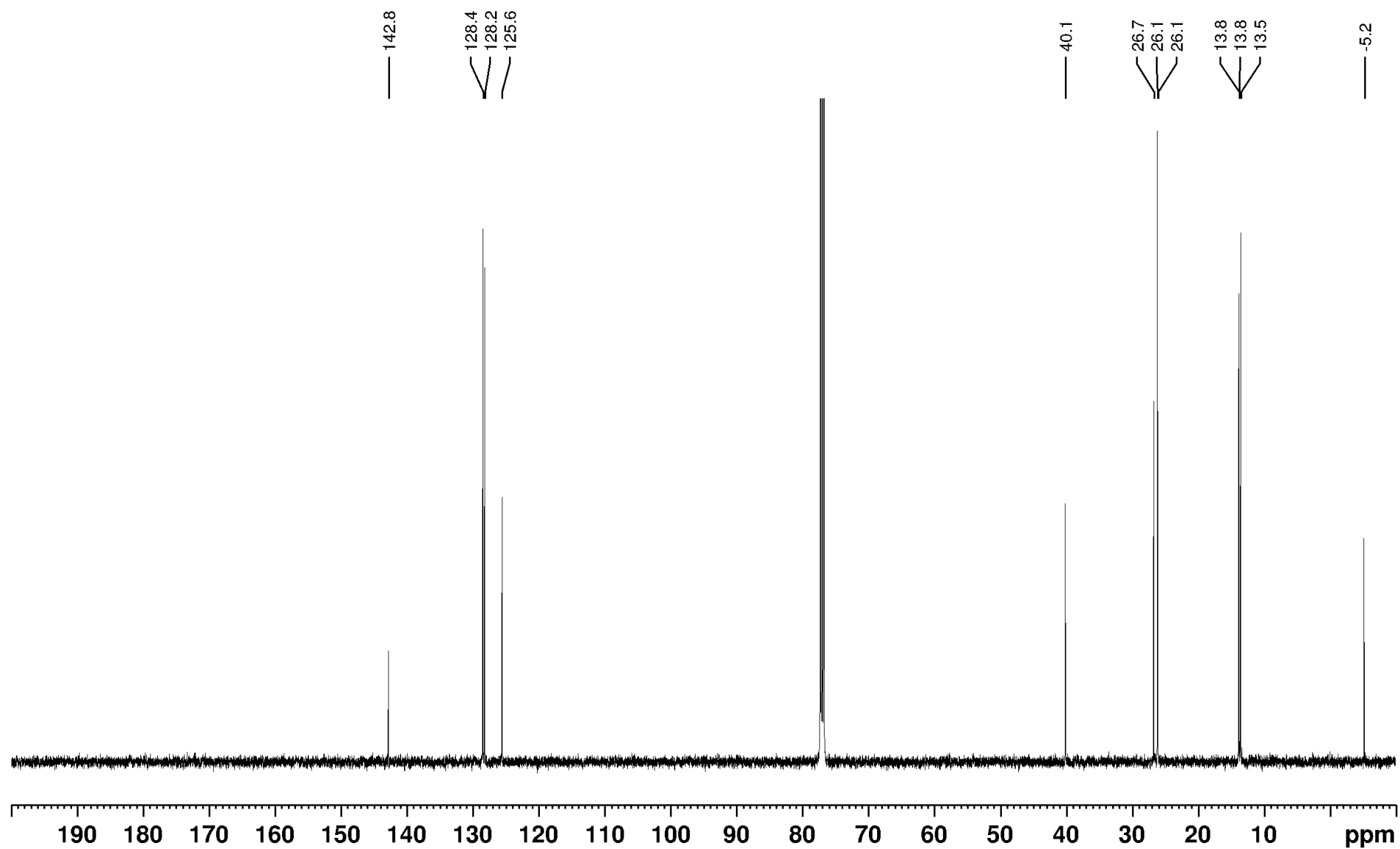
Figure S113. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CDCl_3 , 298 K) of dibutyl(methyl)(3-phenylpropyl)silane (**8s**)

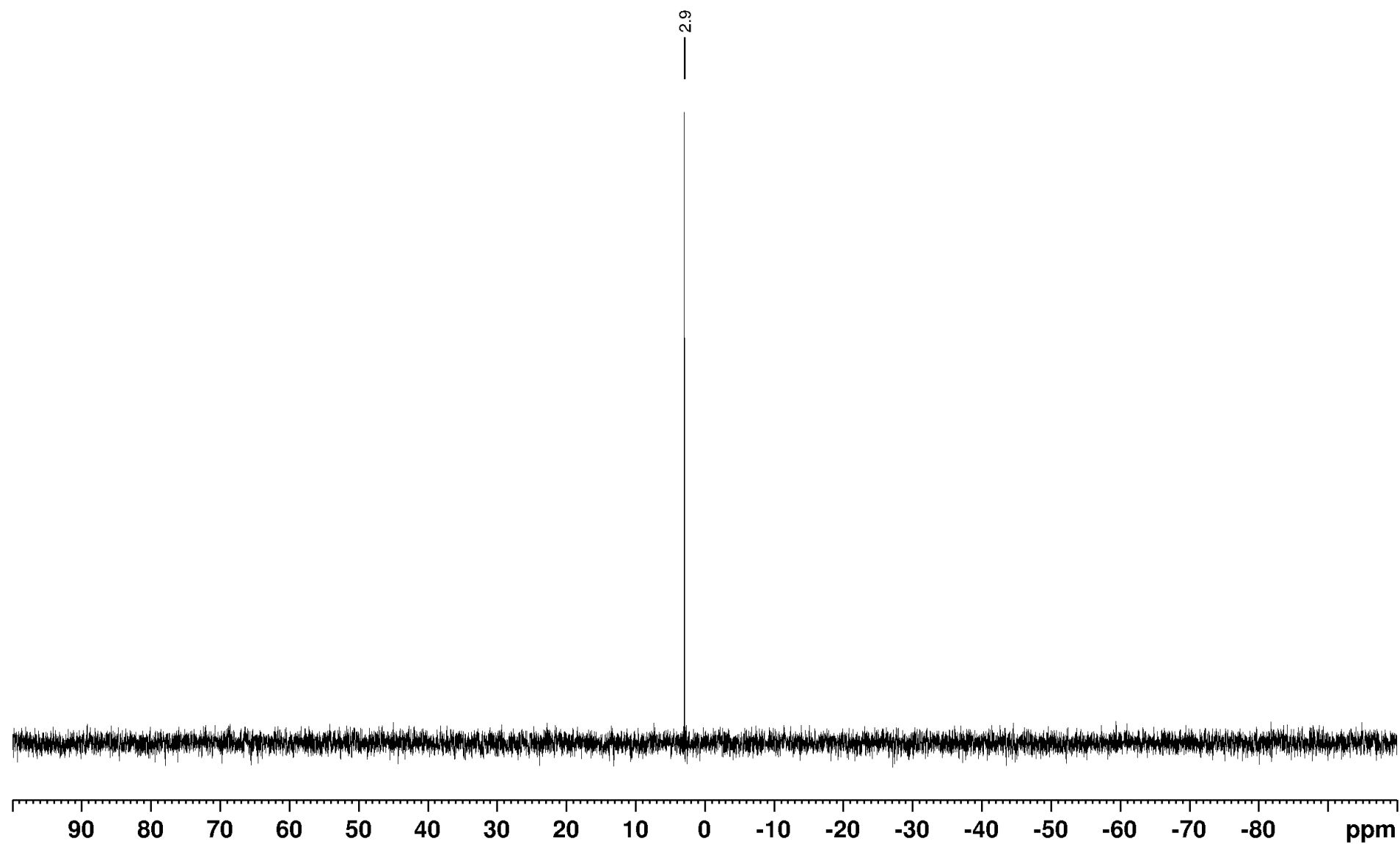
Figure S114. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectrum (99 MHz, CDCl_3 , 298 K, optimized for $J = 7$ Hz, 19.5°) of dibutyl(methyl)(3-phenylpropyl)silane (**8s**)

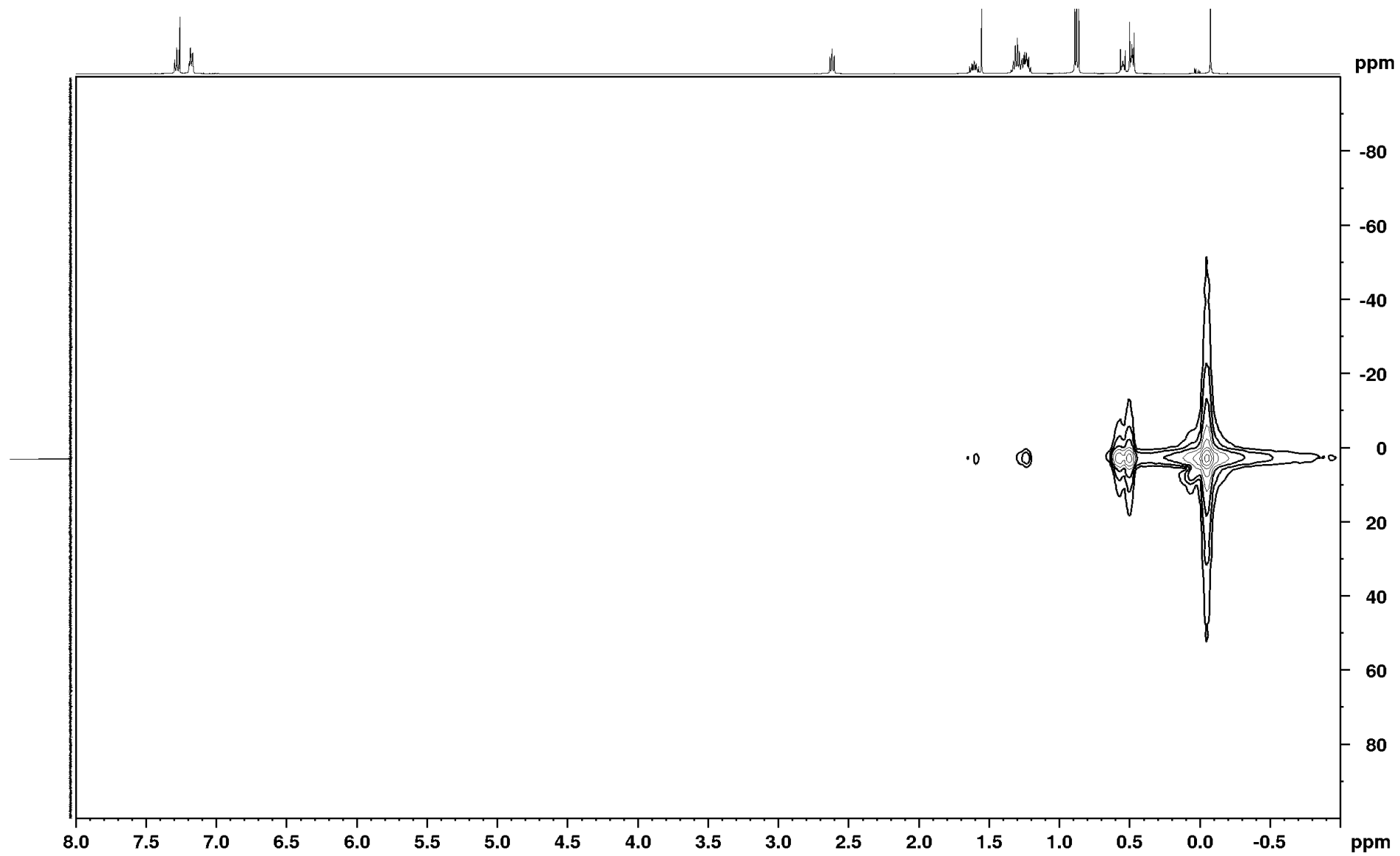
Figure S115. ^1H , ^{29}Si HMQC NMR (500/99 MHz, CDCl_3 , 298 K, optimized for $J = 7$ Hz) of dibutyl(methyl)(3-phenylpropyl)silane (**8s**)

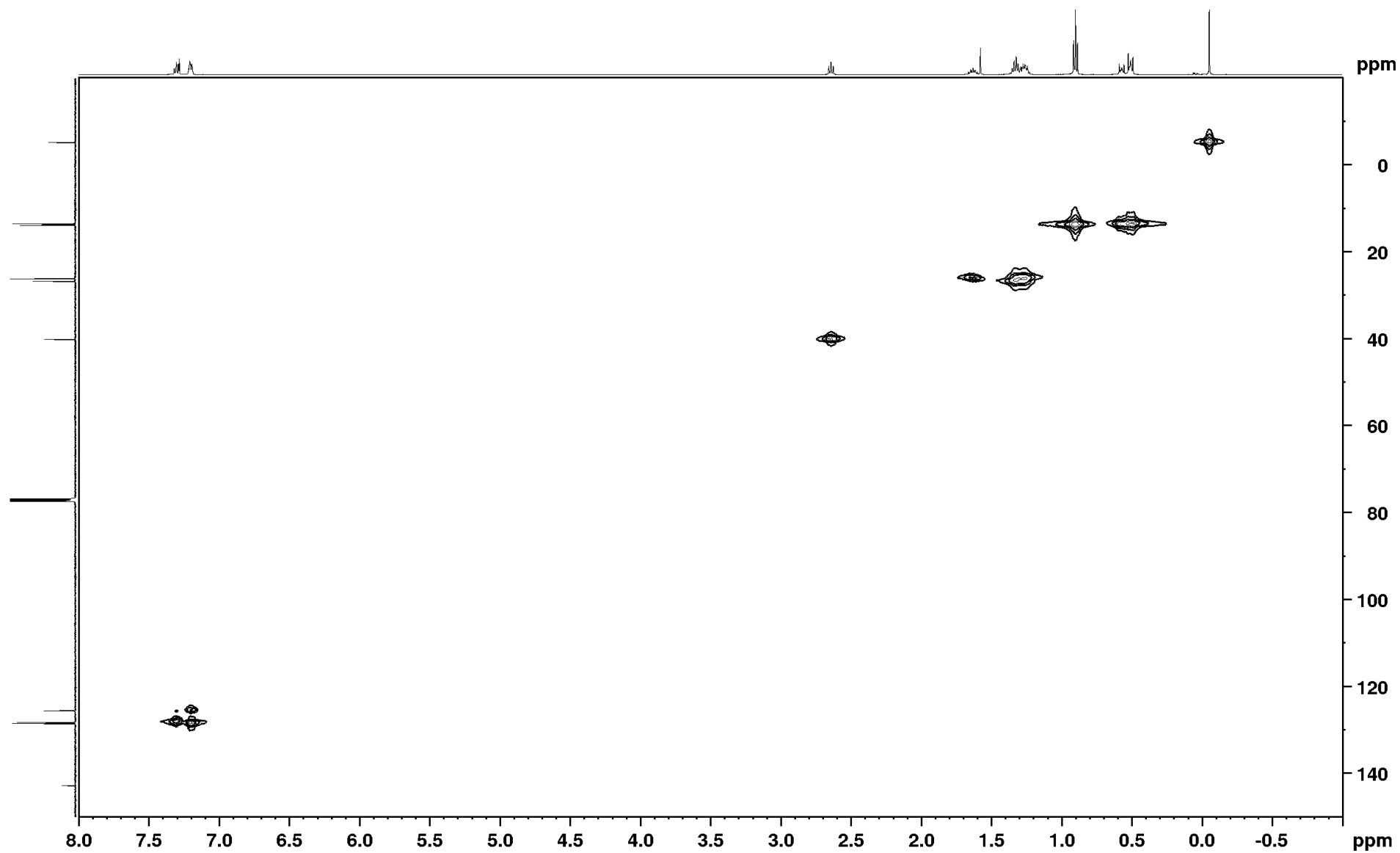
Figure S116. ^1H , ^{13}C HMQC NMR (500/126 MHz, CDCl_3 , 298 K) of dibutyl(methyl)(3-phenylpropyl)silane (**8s**)

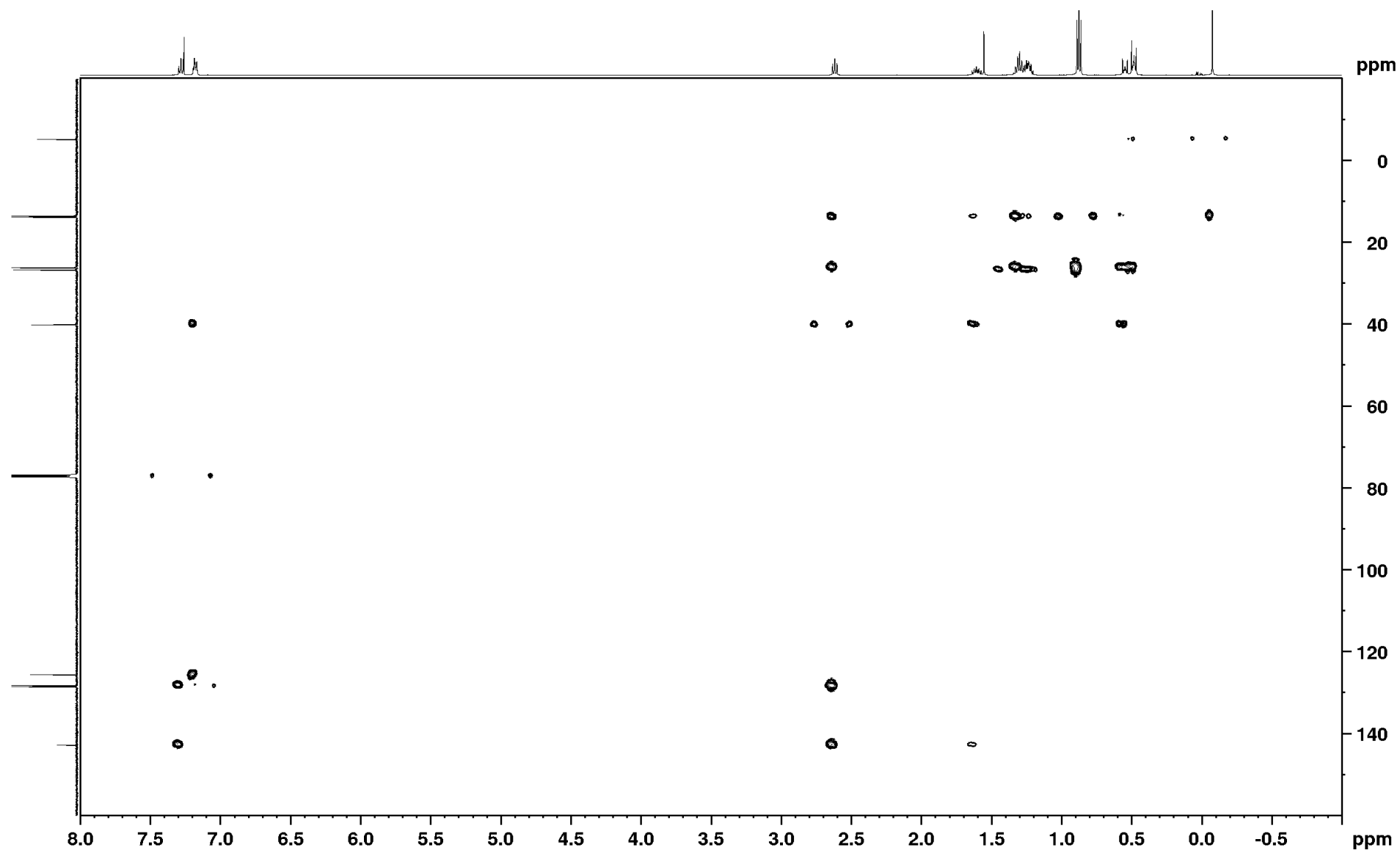
Figure S117. ^1H , ^{13}C HMBC NMR (500/126 MHz, CDCl_3 , 298 K) of dibutyl(methyl)(3-phenylpropyl)silane (**8s**)

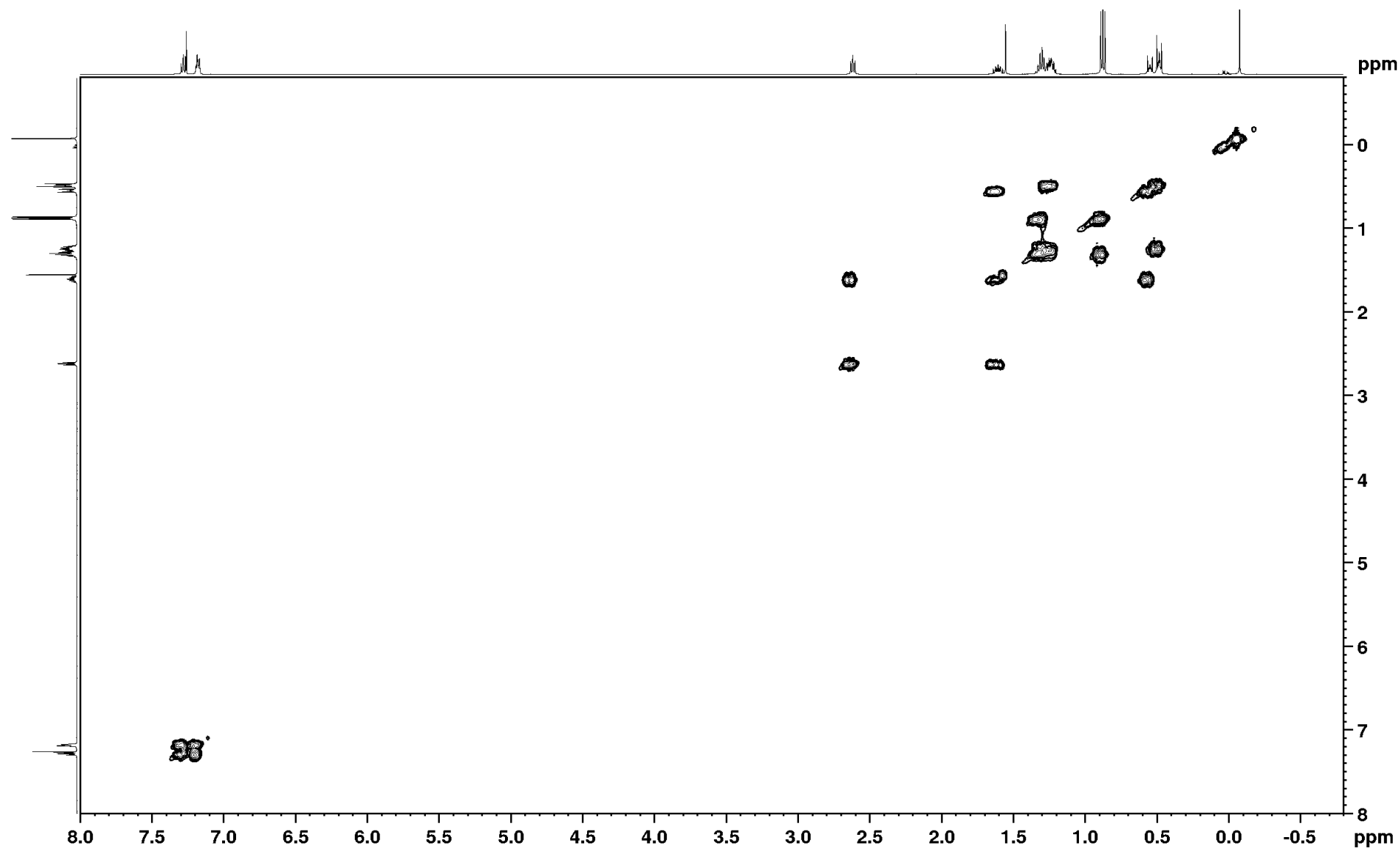
Figure S118. $^1\text{H}, ^1\text{H}$ COSY NMR (500 MHz, CDCl_3 , 298 K) of dibutyl(methyl)(3-phenylpropyl)silane (**8s**)

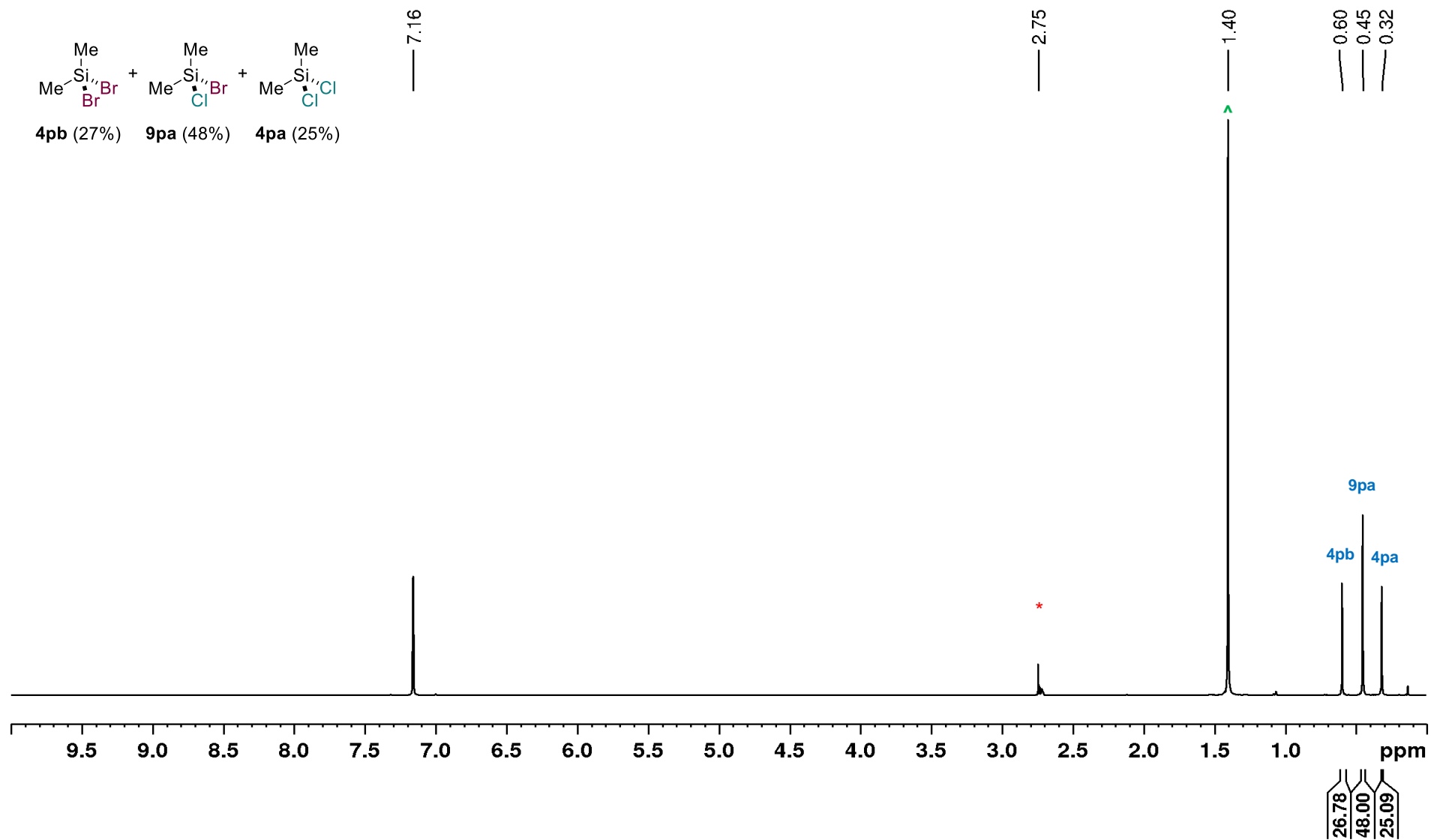
Figure S119. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of the chlorodemethylation of bromotrimethylsilane (**3pb**) with 1,2-dichloroethane (**2a**)(* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane)

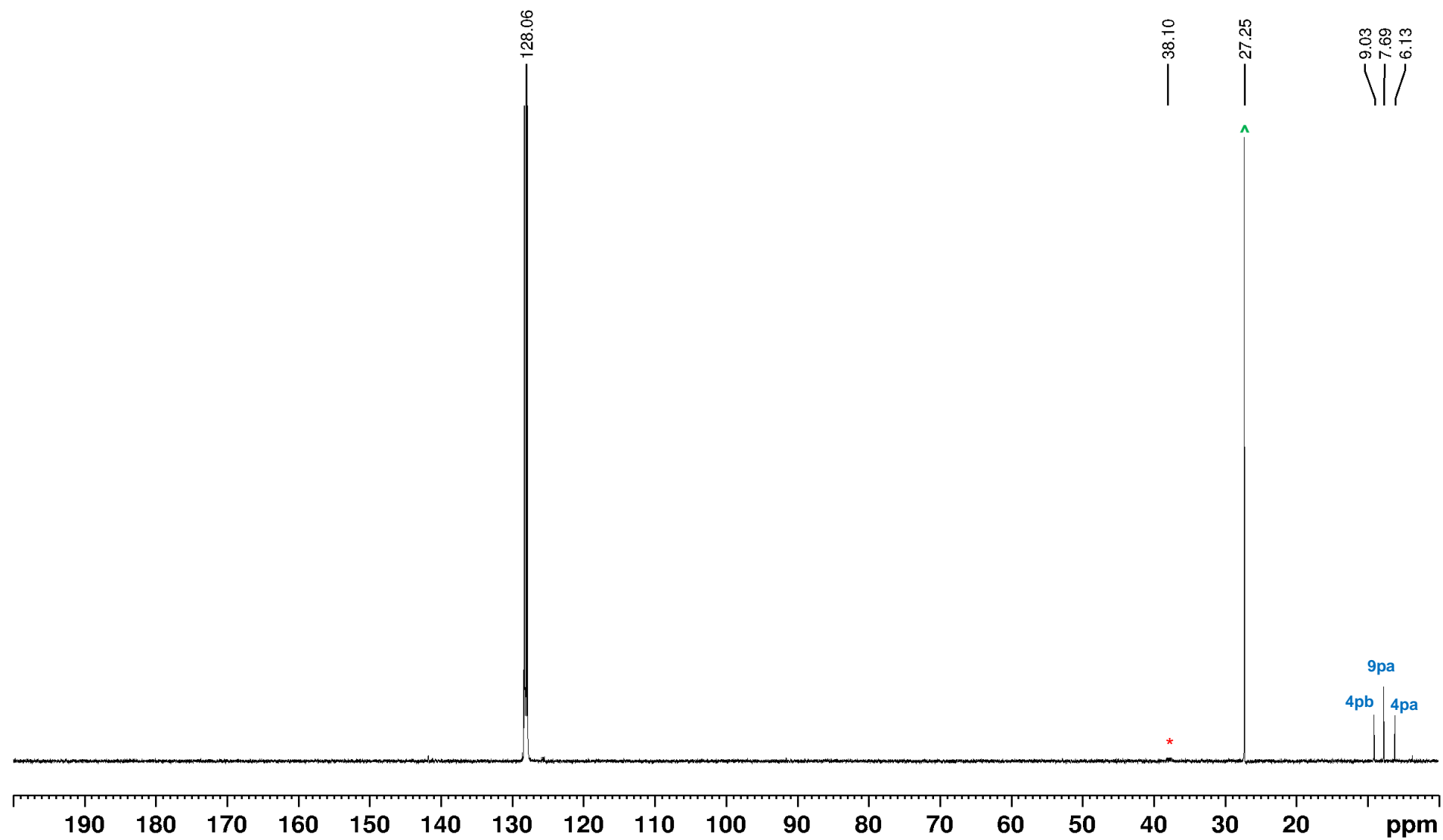
Figure S120. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of the chlorodemethylation of bromotrimethylsilane (**3pb**) with 1,2-dichloroethane (**2a**)(* 1,2-diphenylethane- d_{10} ; ^ cyclohexane)

Figure S121. $^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR spectrum (126 MHz, C_6D_6 , 298 K, without decoupling in F1 dimension) of the chlorodemethylation of bromotrimethylsilane (**3pb**) with 1,2-dichloroethane (**2a**)

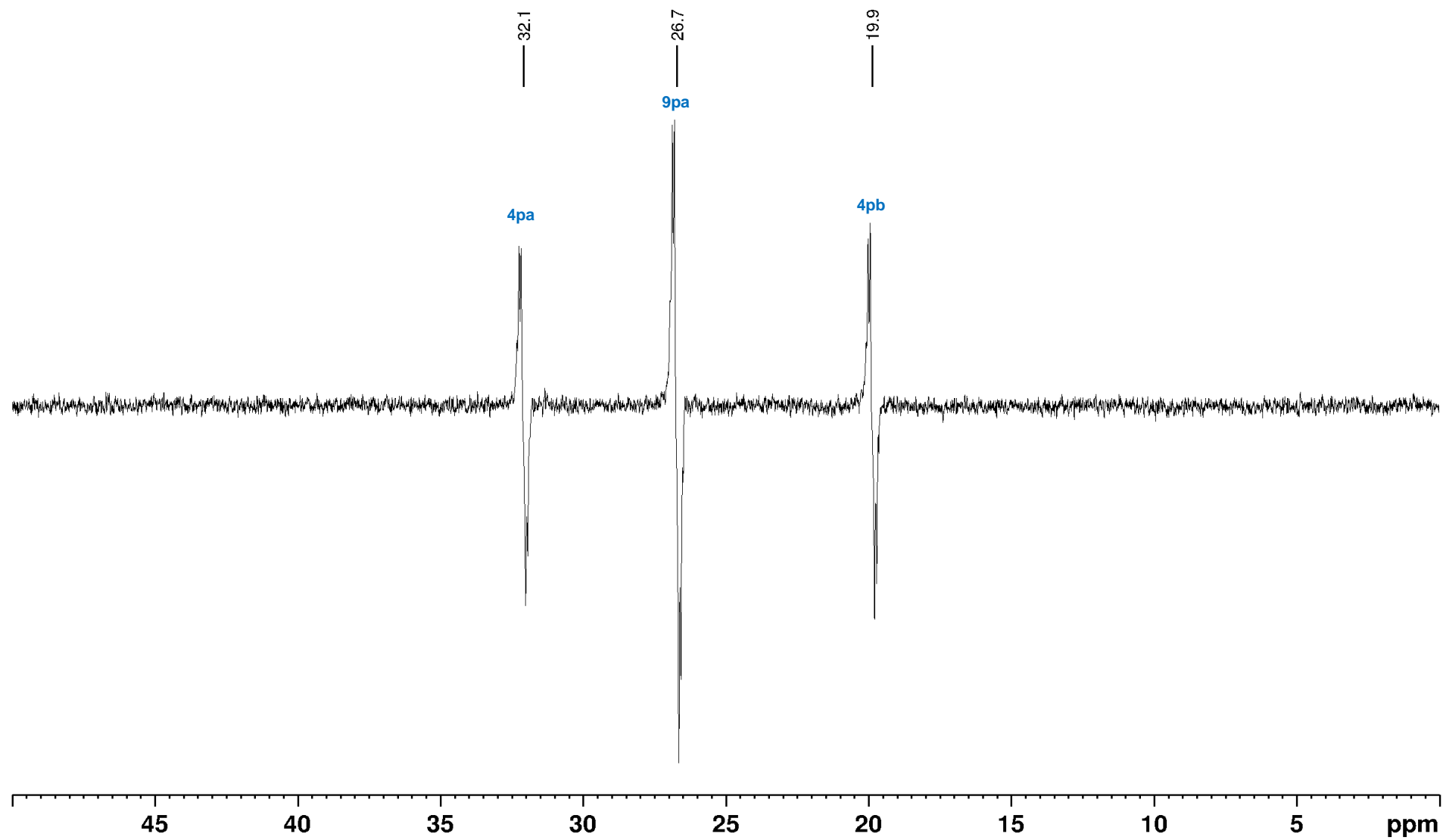


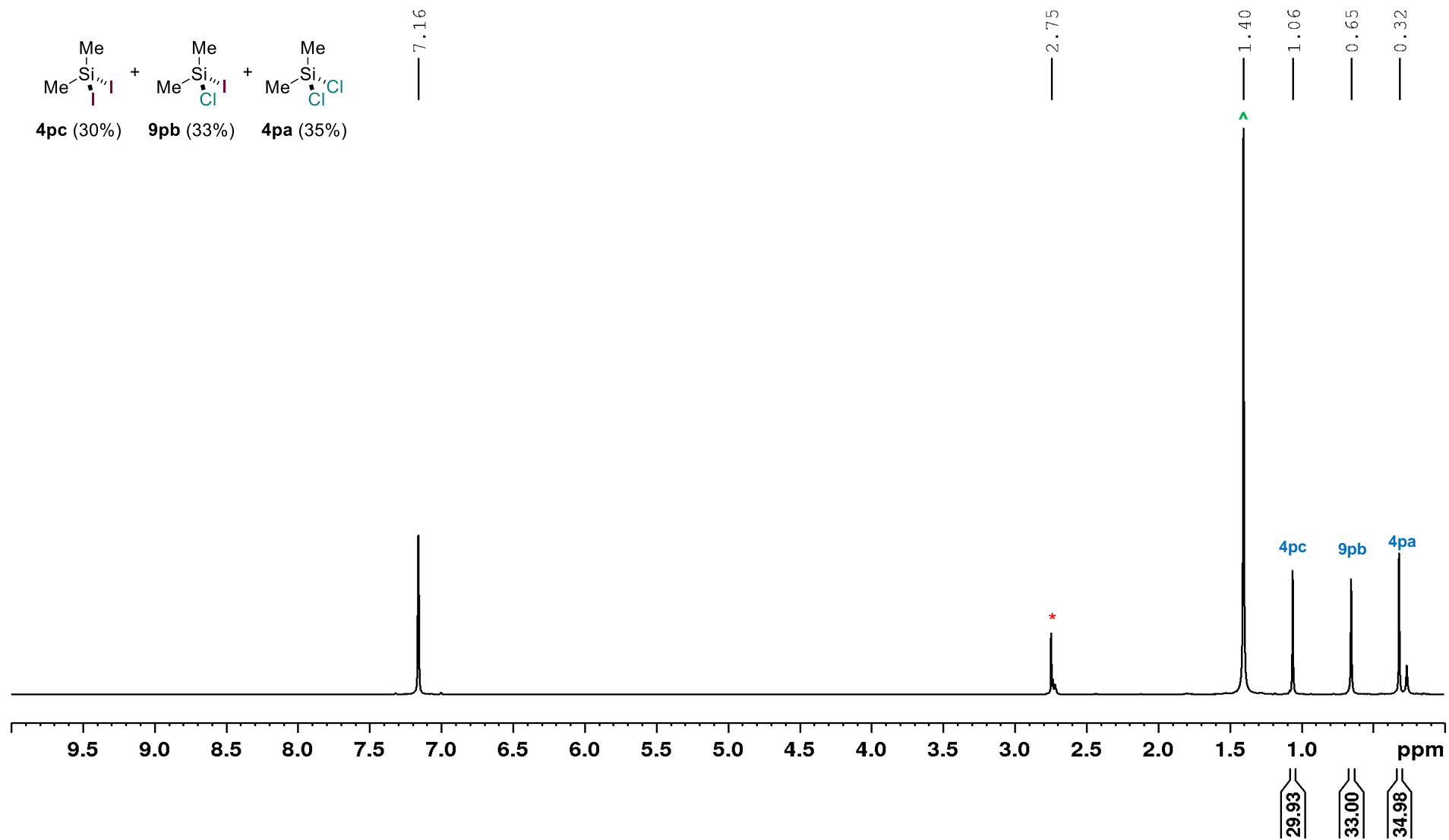
Figure S122. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of the chlorodemethylation of iodotrimethylsilane (**3pc**) with 1,2-dichloroethane (**2a**)(* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane)

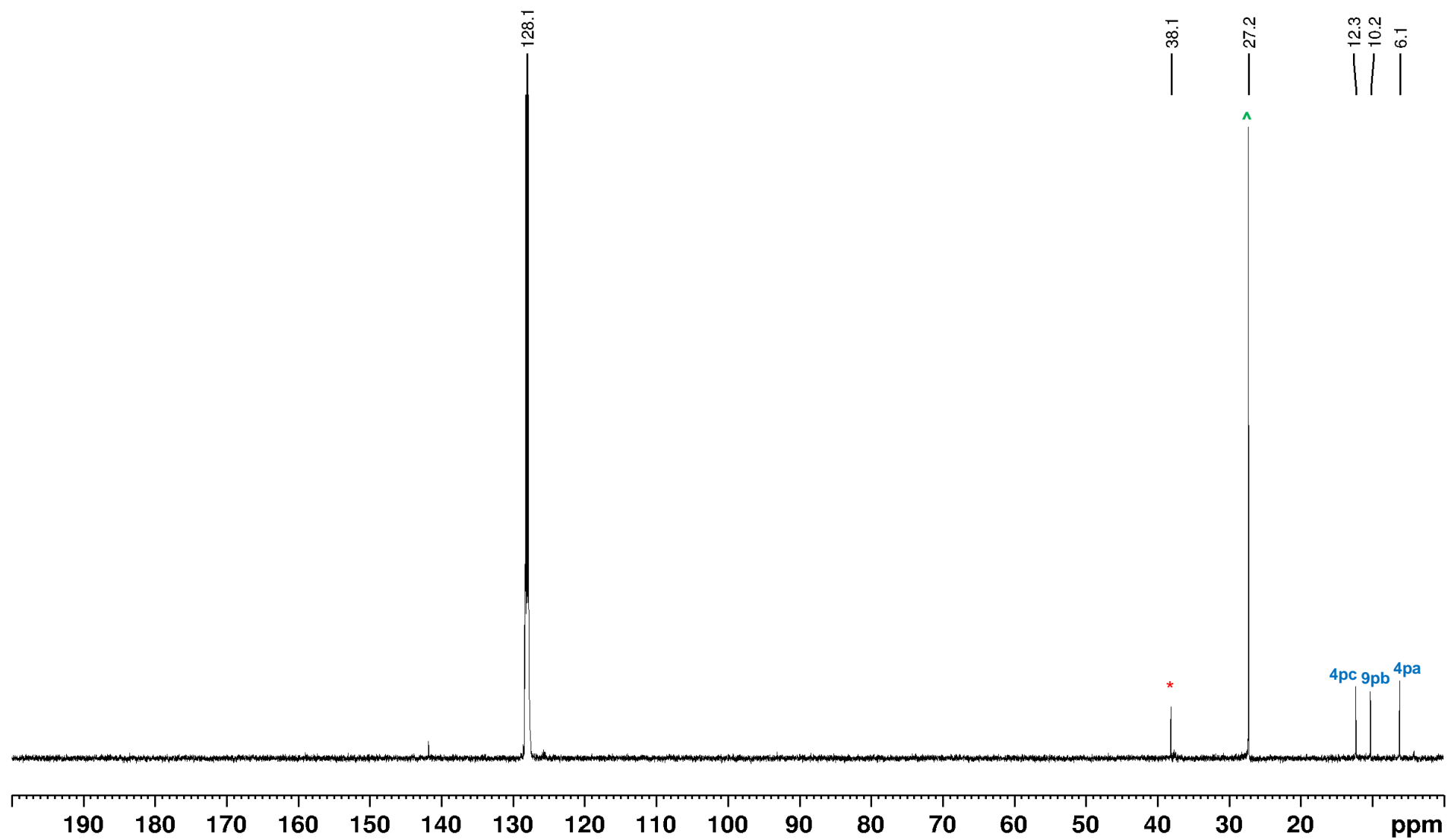
Figure S123. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of the chlorodemethylation of bromotrimethylsilane (**3pc**) with 1,2-dichloroethane (**2a**)(* 1,2-diphenylethane- d_{10} ; ^ cyclohexane)

Figure S124. ^1H , ^{29}Si HMQC NMR spectrum (500/99 MHz, C_6D_6 , 298 K, optimized for $J = 7$ Hz) of the chlorodemethylation of bromotrimethylsilane (**3pc**) with 1,2-dichloroethane (**2a**)

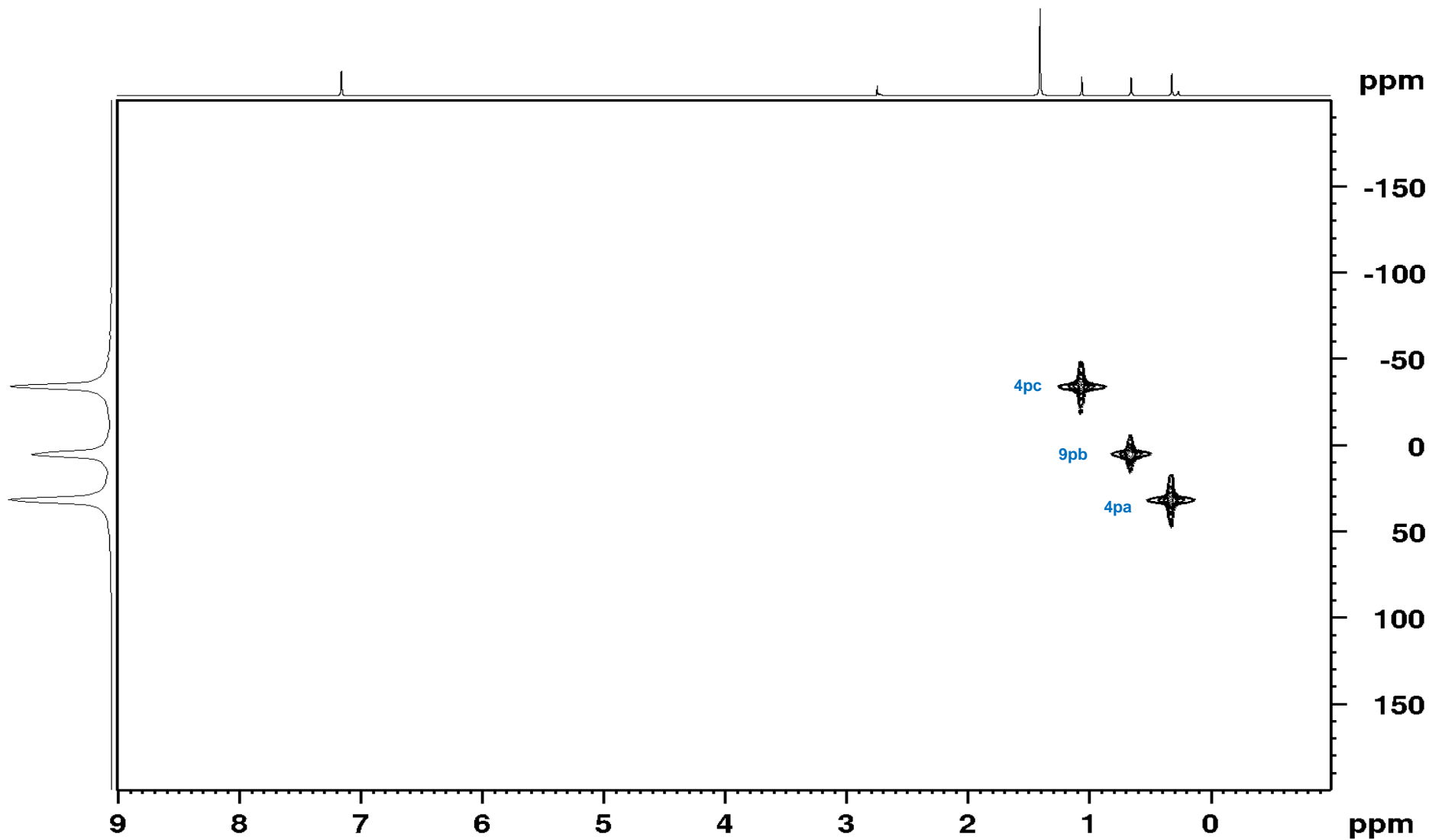


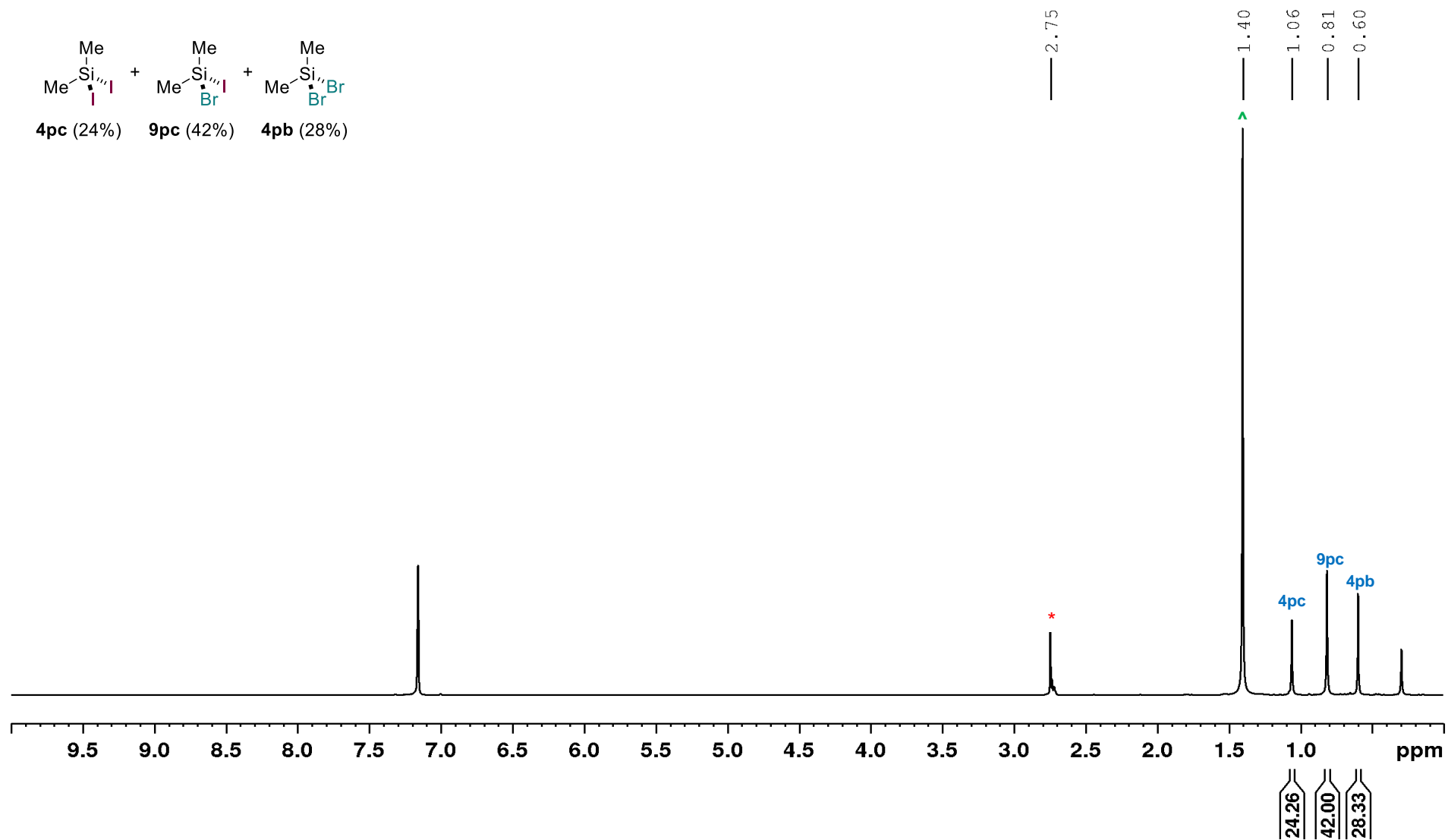
Figure S125. ^1H NMR spectrum (500 MHz, C_6D_6 , 298 K) of the bromodemethylation of iodotrimethylsilane (**3pc**) with 1,2-dibromoethane (**2b**)(* 1,2-diphenylethane- d_{10} ; \blacktriangle cyclohexane)

Figure S126. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6 , 298 K) of the bromodemethylation of iodotrimethylsilane (**3pc**) with 1,2-dibromoethane (**2b**)

(* 1,2-diphenylethane- d_{10} ; ^ cyclohexane)

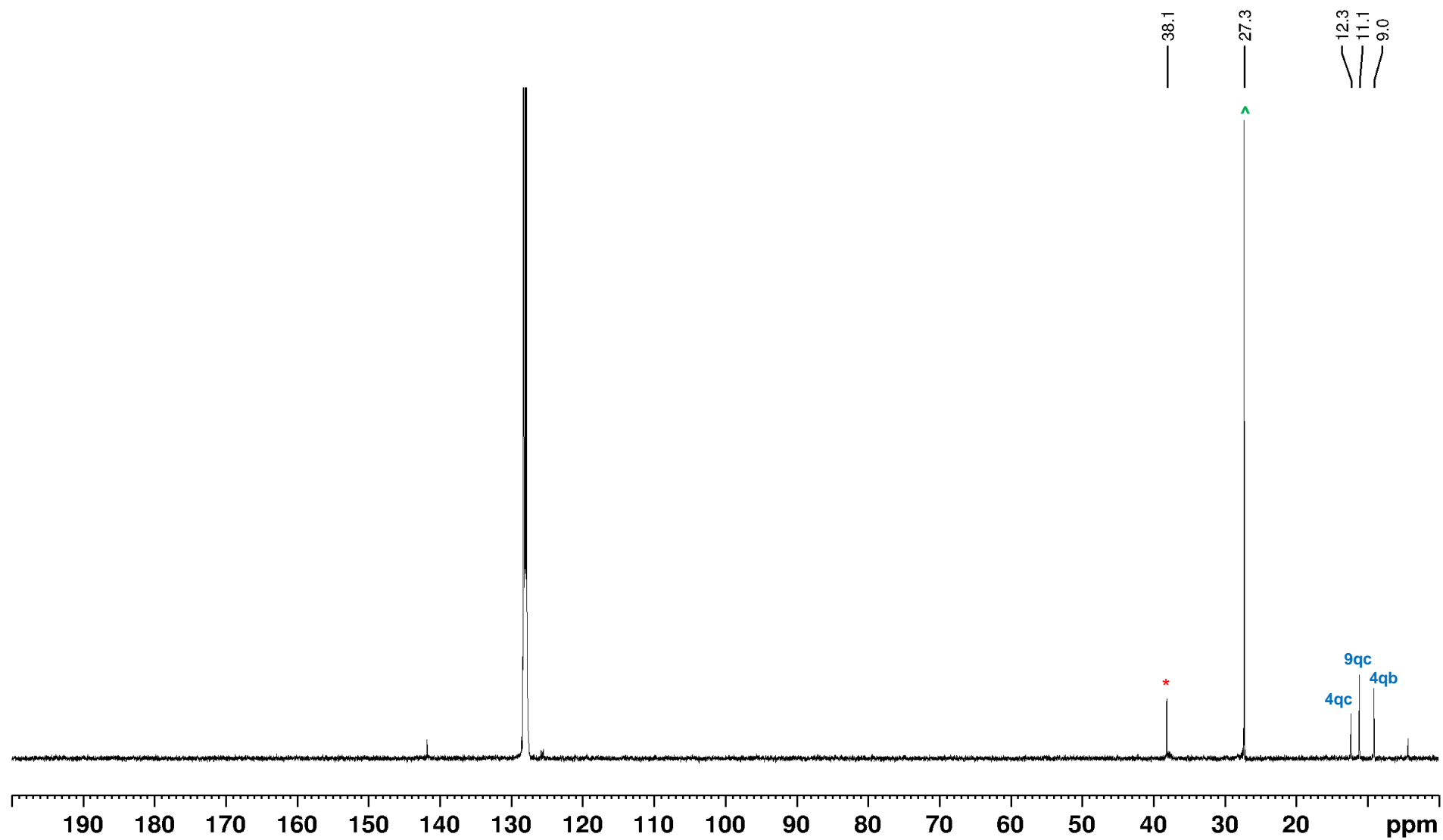
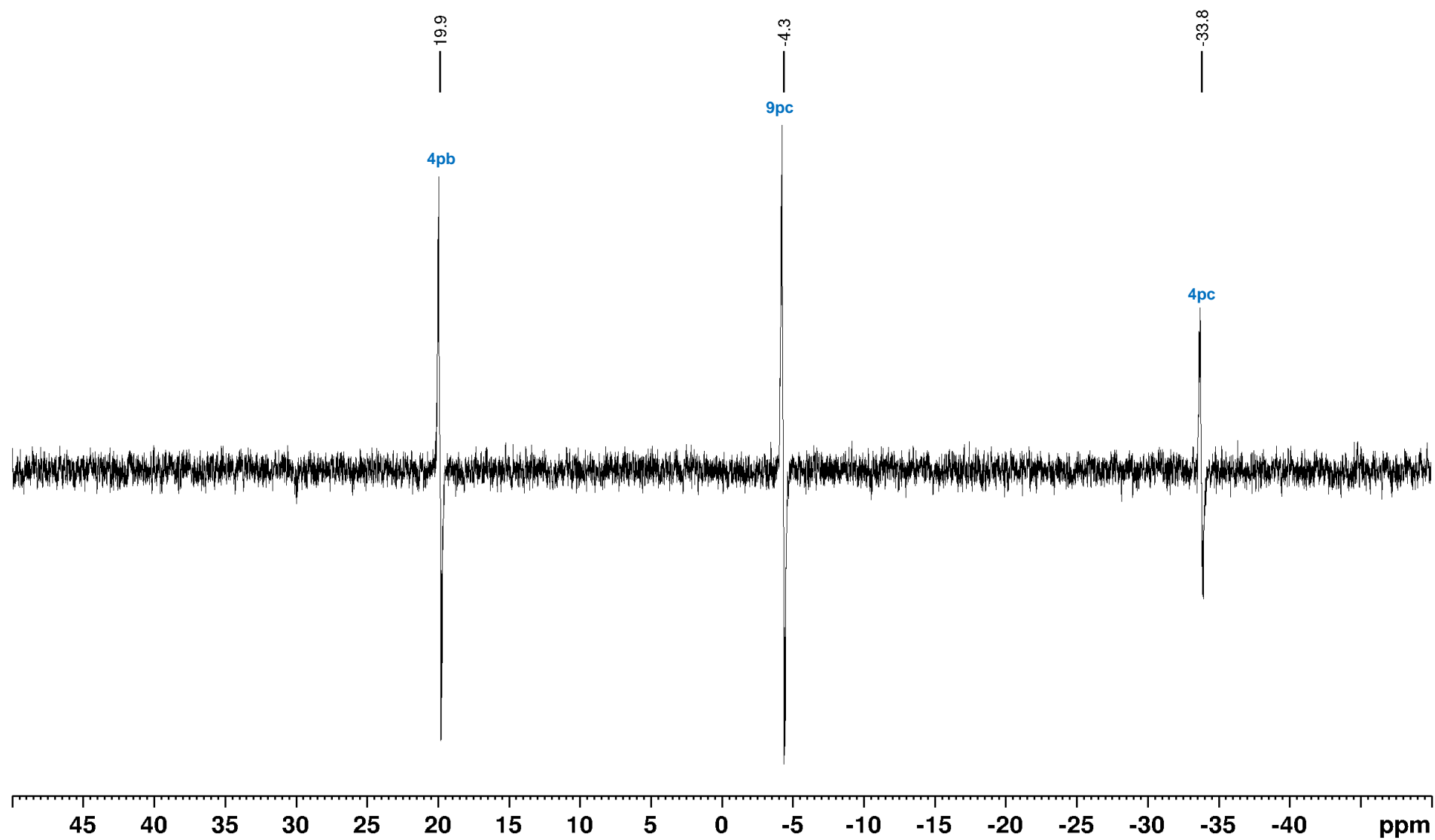


Figure S127. $^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR spectrum (126 MHz, C_6D_6 , 298 K, without decoupling in F1 dimension) of the bromodemethylation of iodotrimethylsilane (**3pc**) with 1,2-dibromoethane (**2b**)



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