Access to Fully Alkylated Germanes by $B(C_6F_5)_3$-catalyzed Transfer Hydrogermylation of Alkenes

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Supporting Information

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1 General Information

Reactions were performed in flame-dried glassware using an *MBraun* glove box or conventional Schlenk techniques under a static pressure of argon (glove box) or nitrogen. Liquids and solutions were transferred with syringes. Solvents (C_6H_6, 1,2-$Cl_2C_6H_4$, CH_2Cl_2, 1,2-$F_2C_6H_4$, *n*-pentane, and THF) were dried and purified following standard procedures. Technical grade solvents for extraction or chromatography (*tert*-butyl methyl ether, cyclohexane, and *n*-pentane) were distilled prior to use. $B(C_6F_5)_3$ was purchased from *Boulder Scientific Company* and sublimed twice before use. Alkenes **3**,[S1] **4**,[S2] and **46**[S3] were prepared according to reported procedures. Methyl cinnamate (**11**), chalcone (**12**), diphenylacetylene (**13**), ethyl 3-phenylpropiolate (**14**), and cyclohexa-1,4-diene (**29**) were purchased from commercial suppliers and used without further purification. All other commercially available alkenes were distilled, degassed, and stored in a glove box over thermally activated 4-Å molecular sieves. Mesitylene was distilled from sodium, degassed, and stored over thermally activated 4-Å molecular sieves in a glove box. All other commercially available reagents and solvents were used as received. *s*BuLi solutions were titrated using *Suffert*'s reagent.[S4] Analytical thin layer chromatography (TLC) was performed on ALUGRAM® Xtra SIL G/UV_{254} TLC-sheets by *Macherey-Nagel*. Flash column chromatography was performed on silica gel 60 (40–63 µm, 230–400 mesh, ASTM) by *Grace* using the indicated solvents. ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded in C_6D_6 or CD_2Cl_2 on *Bruker* AV400, AV500, and AV700 instruments. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard (C_6D_5H: $\delta = 7.16$ ppm for ^1H NMR and C_6D_6 $\delta = 128.06$ ppm for ^{13}C NMR, $CHDCl_2$: $\delta = 5.32$ ppm for ^1H NMR). Data are reported as follows: chemical shift, multiplicity (br s, broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, m_c = centrosymmetric multiplet), coupling constants (Hz), and integration. Gas liquid chromatography (GLC) was performed on an *Agilent Technologies* 7820A gas chromatograph equipped with a FS-SE-54 capillary column (30 m × 0.32 mm, 0.25 µm film thickness) by *CS-Chromatographie Service* using the following program: N_2 carrier gas, injection temperature 240 °C, detector temperature 300 °C, flow rate: 1.74 mL/min; temperature program: start temperature 40 °C, heating rate 10 °C/min, end temperature 280 °C for 10 min. Infrared (IR) spectra were recorded on an *Agilent Technologies* Cary 630 FT-IR spectrometer equipped with an ATR unit and the signals are reported in wavenumbers (cm^{-1}). Melting points (m.p.) were determined with a *Stuart Scientific* SMP20 melting point apparatus and are not corrected. High resolution mass spectrometry (HRMS) analysis was performed by the Analytical Facility at the Institut für Chemie, Technische Universität Berlin.

2 General Procedures

2.1 General Procedure for the Synthesis of Cyclohexa-2,5-dien-1-ylgermanes (GP1)

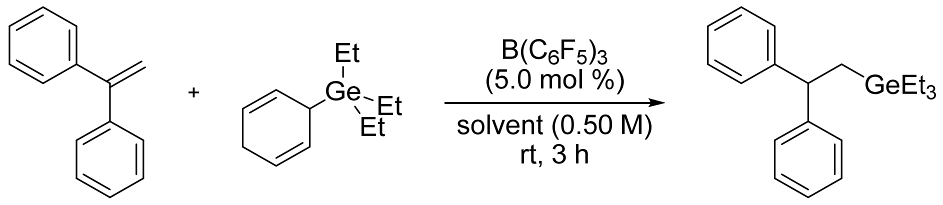
To a flame-dried Schlenk flask purged with N_2 are subsequently added cyclohexa-1,4-diene (1.0–3.2 equiv) and THF (0.32–0.42M). The solution is cooled to –78 °C and *s*BuLi (1.28–1.30 M, 1.1–3.1 equiv) is added dropwise over a period of 30 min. TMEDA (1.1–3.1 equiv) is then added, and the reaction mixture is slowly warmed to –30 °C over a period of 3 h. A solution of the respective chlorogermane (1.00–1.14 equiv) in THF (0.5–1.3 M) is added dropwise over a period of 30 min at –78 °C and the mixture is then slowly warmed to room temperature overnight. Saturated aqueous NH_4Cl solution is added and the aqueous layer is extracted with *tert*-butyl methyl ether (3×). The combined organic layers are washed with saturated aqueous NaCl solution, dried over $MgSO_4$, and all volatiles are removed under reduced pressure. The crude surrogates are purified by flash column chromatography on silica gel.

2.2 General Procedures for the Transfer Hydrogermylation (GP2)

2.2.1 General Procedure for the Optimization of the Transfer Hydrogermylation of 1,1-Diphenylethylene (2) (GP2.1)

In a glove box, a 1.3-mL GLC vial is charged with $B(C_6F_5)_3$ (2.6 mg, 5.0 µmol, 5.0 mol %) and the indicated solvent (20 µL) is added. 1,1-Diphenylethylene (**2**, 18.0 mg, 0.100 mmol, 1.00 equiv) and surrogate **1a** (28.7 mg, 0.120 mmol, 1.20 equiv) are weighed into a separate vial, mesitylene (6 µL, 0.04 mmol, 0.4 equiv, internal standard) and the indicated solvent (80 µL) are added, and an aliquot is taken to measure the t_0 GLC chromatogram. The reagent solution is added to the catalyst solution, and the resulting reaction mixture is stirred in the glove box at room temperature. After 3 h, an aliquot is taken, filtered over a small silica gel column (0.4 cm) using cyclohexane as eluent, and subjected to GLC analysis.

Table S1. Optimization of the Transfer Hydrogermylation



2 + **1a** (1.2 equiv) → **15**

entry	solvent	conversion[a] (%)
1	CH_2Cl_2	83
2	1,2-$F_2C_6H_4$	86
3	1,2-$Cl_2C_6H_4$	77
4	C_6H_6	68
5	*n*-pentane	56
6[b]	1,2-$F_2C_6H_4$	–

[a]Substrate conversion determined by GLC analysis using mesitylene as internal standard. [b]Without catalyst.

2.2.2 General Procedure for the Optimized Reaction (GP2.2)

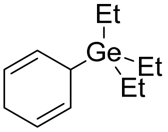
In a glove box, a 1.3-mL GLC vial is charged with $B(C_6F_5)_3$ (5.0–20 µmol, 5.0–10 mol %) and 1,2-$F_2C_6H_4$ (75.0–150 µL) is added. The respective alkene **2**–**14**, **28**–**30**, or **46** or alkyne **13**–**14** (0.100–1.00 mmol, 1.00–5.00 equiv) and surrogate **1a** (0.200–0.320 mmol, 1.00–2.40 equiv), **1b** (0.110 mmol, 0.550 equiv), or **1c** (0.0701 mmol, 0.350 equiv) are weighed into a separate vial and 1,2-$F_2C_6H_4$ (25–50 µL) is added. The catalyst solution is added to the reagent solution, and the reaction mixture is stirred at room temperature (inside the glove box) or transferred into a 1.0-mL Ace pressure tube and heated to 90 °C (outside the glove box). The progress of the reaction is monitored by GLC analysis. The reaction mixture is filtered over a small silica gel column (2.0 cm) using cyclohexane/*tert*-butyl methyl ether mixtures as eluent, and all volatiles are removed under reduced pressure. If necessary, the crude product is further purified by flash column chromatography on silica gel.

2.3 General Procedure for Monitoring the Degradation of 1a–1c (GP3)

In a glove box, a solution of the respective surrogate **1a**–**1c** (0.049–0.10 mmol) in CD_2Cl_2 (0.45 mL) is added to a Wilmad® J-Young NMR tube. The NMR tube is capped, taken out of the glove box to measure the t_0 ^1H NMR spectrum, and then a solution of $B(C_6F_5)_3$ (2.5–5.0 µmol, 5.0 mol %) in CD_2Cl_2 (0.05 mL) is added to the surrogate solution inside the glovebox. The NMR tube is capped immediately and ^1H NMR spectra are measured at time intervals as indicated.

3 Experimental Details for the Preparation of Cyclohexa-2,5-dien-1-yl-germanes

3.1 Cyclohexa-2,5-dien-1-yltriethylgermane (1a)



1a

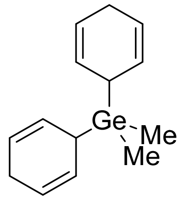
$C_{12}H_{22}Ge$

M = 238.94 g/mol

According to GP1, *s*BuLi (1.30 M in cyclohexane, 4.9 mL, 6.4 mmol, 1.1 equiv) and TMEDA (0.95 mL, 6.3 mmol, 1.1 equiv) were added to a solution of cyclohexa-1,4-diene (0.54 mL, 5.8 mmol, 1.0 equiv) in THF (15 mL). After addition of a solution of $ClGeEt_3$ (1.29 g, 6.61 mmol, 1.14 equiv) in THF (5.0 mL), the reaction mixture was quenched with a saturated aqueous NH_4Cl solution (15 mL). The aqueous layer was extracted with *tert*-butyl methyl ether (3 × 15 mL), and the combined organic layers were washed with saturated aqueous NaCl solution (15 mL) and dried over $MgSO_4$. The crude product was purified by flash column chromatography on silica gel using cyclohexane as eluent to afford cyclohexa-1,4-diene **1a** (1.18 g, 85%) as a colorless oil.

***R*$_f$** = 0.72 (cyclohexane). **GLC** (SE-54): t_R = 13.2 min. **IR** (ATR): $\tilde{\nu}$ = 3022, 2946, 2903, 2870, 2817, 1665, 1621, 1458, 1425, 1376, 1333, 1303, 1231, 1086, 1055, 1014, 968, 891, 754, 699 cm^{-1}. **HRMS** (EI) for $C_{12}H_{22}Ge^{+\bullet}$ $[(M)^{+\bullet}]$: calculated 240.0928, found 240.0937. **^{1}H NMR** (500 MHz, C_6D_6): δ = 0.80 (q, *J* = 7.9 Hz, 6H), 1.05 (t, *J* = 7.9 Hz, 9H), 2.57 (m_c, 1H), 2.65–2.78 (m, 2H), 5.48–5.53 (m, 2H), 5.68–5.74 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 3.6, 9.4, 26.8, 29.1, 121.4, 127.5 ppm.

3.2 Di(cyclohexa-2,5-dien-1-yl)dimethylgermane (1b)



1b

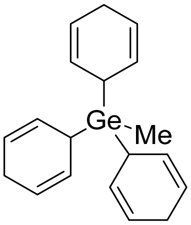
$C_{14}H_{20}Ge$

M = 260.94 g/mol

According to GP1, *s*BuLi (1.30 M in cyclohexane, 2.3 mL, 3.0 mmol, 2.1 equiv) and TMEDA (0.46 mL, 3.0 mmol, 2.1 equiv) were added to a solution of cyclohexa-1,4-diene (0.30 mL, 3.2 mmol, 2.2 equiv) in THF (10 mL). After addition of a solution of Cl_2GeMe_2 (250 mg, 1.44 mmol, 1.00 equiv) in THF (3.0 mL), the reaction mixture was quenched with a saturated aqueous NH_4Cl solution (10 mL). The aqueous layer was extracted with *tert*-butyl methyl ether (3 × 10 mL), and the combined organic layers were washed with saturated aqueous NaCl solution (10 mL) and dried over $MgSO_4$. The crude product was purified by flash column chromatography on silica gel using cyclohexane as eluent to afford cyclohexa-1,4-diene **1b** (301 mg, 80%) as a colorless oil.

***R*$_f$** = 0.50 (cyclohexane). **GLC** (SE-54): t_R = 16.6 min. **IR** (ATR): $\tilde{\nu}$ = 3021, 2969, 2882, 2849, 2815, 1664, 1620, 1431, 1404, 1333, 1303, 1230, 1086, 1054, 930, 889, 822, 794, 726 cm^{-1}. **HRMS** (EI) for $C_{14}H_{20}Ge^{+\bullet}$ $[(M)^{+\bullet}]$: calculated 262.0771, found 262.0760. **^{1}H NMR** (500 MHz, C_6D_6): δ = 0.18 (s, 6H), 2.56–2.62 (m, 2H), 2.63–2.73 (m, 4H), 5.47–5.54 (m, 4H), 5.64–5.72 (m, 4H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = –7.2, 26.8, 30.5, 122.0, 126.9 ppm.

3.3 Tri(cyclohexa-2,5-dien-1-yl)methylgermane (1c)



1c

$C_{19}H_{24}Ge$

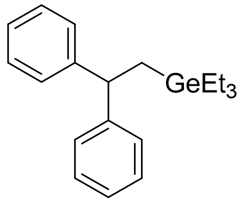
M = 325.03 g/mol

According to GP1, *s*BuLi (1.28 M in cyclohexane, 6.3 mL, 8.1 mmol, 3.1 equiv) and TMEDA (1.2 mL, 8.0 mmol, 3.1 equiv) were added to a solution of cyclohexa-1,4-diene (0.77 mL, 8.3 mmol, 3.2 equiv) in THF (20 mL). After addition of a solution of Cl_3GeMe (500 mg, 2.58 mmol, 1.00 equiv) in THF (3.0 mL), the reaction mixture was quenched with a saturated aqueous NH_4Cl solution (15 mL). The aqueous layer was extracted with *tert*-butyl methyl ether (3 × 15 mL), and the combined organic layers were washed with saturated aqueous NaCl solution (15 mL) and dried over $MgSO_4$. The crude product was purified by flash column chromatography on silica gel using cyclohexane as eluent to afford cyclohexa-1,4-diene **1c** (415 mg, 50%) as a colorless oil that solidifies at –34 °C.

R_f = 0.27 (cyclohexane). m.p. = 38–40°C (cyclohexane). **IR** (ATR): $\tilde{\nu}$ = 3021, 2967, 2881, 2847, 2813, 1663, 1620, 1429, 1333, 1302, 1228, 1160, 1090, 1055, 973, 945, 888, 788, 743, 700 cm^{-1}. **HRMS** (EI) for $C_{13}H_{17}Ge^+$ [$(M\text{-}C_6H_7)^+$]: calculated 247.0537, found 247.0544. **^{1}H NMR** (500 MHz, C_6D_6): δ = 0.24 (s, 3H), 2.58–2.72 (m, 6H), 2.88 (m_c, 3H), 5.50 (m_c, 6H), 5.75 (m_c, 6H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = –9.7, 26.7, 29.9, 122.2, 127.1 ppm.

4 Experimental Details for the Synthesis of Tetraalkylgermanes and Ketone 25 by Transfer Hydrogermylation

4.1 (2,2-Diphenylethyl)triethylgermane (15)



15

$C_{20}H_{28}Ge$

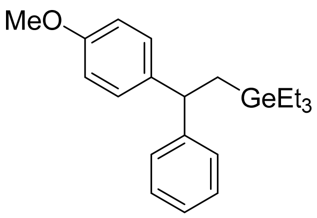
M = 341.07 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of 1,1-diphenylethylene (**2**, 36.0 mg, 0.200 mmol, 1.00 equiv) and surrogate **1a** (57.4 mg, 0.240 mmol, 1.20 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 5 h and subsequently purified by flash column chromatography on silica gel using cyclohexane as eluent. After removal of all volatiles, (2,2-diphenylethyl)triethylgermane (**15**, 64.0 mg, 94%) was obtained as a colorless oil.

R

$\boldsymbol{R_f}$ = 0.45 (*n*-pentane). **GLC** (SE-54): t_R = 21.7 min. **IR** (ATR): $\tilde{\nu}$ = 3024, 2945, 2901, 2868, 1597, 1491, 1450, 1423, 1376, 1129, 1011, 966, 767, 741, 723, 695 cm^{-1}. **HRMS** (EI) for $C_{18}H_{23}Ge^+$ $[(M-C_2H_5)^+]$: calculated 313.1006, found 313.1012. **^{1}H NMR** (500 MHz, C_6D_6): δ = 0.57 (q, *J* = 7.9 Hz, 6H), 0.95 (t, *J* = 7.9 Hz, 9H), 1.54 (d, *J* = 8.2 Hz, 2H), 4.08 (t, *J* = 8.2 Hz, 1H), 7.02 (tt, *J* = 7.3 Hz, J' = 1.5 Hz, 2H), 7.10–7.15 (m, 4H), 7.20–7.25 (m, 4H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 4.6, 9.2, 19.8, 48.5, 126.3, 127.9, 128.7, 147.6 ppm.

4.2 (2-(4-Methoxyphenyl)2-phenylethyl)triethylgermane (16)

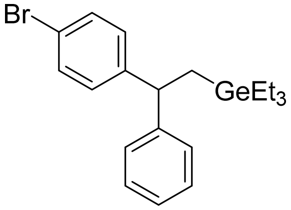


16
$C_{21}H_{30}GeO$
M = 371.10 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of 1-methoxy-4-(1-phenylvinyl)benzene (**3**, 42.1 mg, 0.200 mmol, 1.00 equiv) and surrogate **1a** (57.4 mg, 0.240 mmol, 1.20 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 3 h and subsequently purified by flash column chromatography on silica gel using cyclohexane as eluent. After removal of all volatiles, (2-(4-methoxyphenyl)2-phenylethyl)triethylgermane (**16**, 66.4 mg, 90%) was obtained as a colorless oil.

***R*$_f$** = 0.07 (cyclohexane). **GLC** (SE-54): t_R = 24.0 min. **IR** (ATR): $\tilde{\nu}$ = 3024, 2945, 2901, 2868, 2832, 1608, 1582, 1508, 1453, 1423, 1300, 1244, 1175, 1130, 1036, 1016, 967, 804, 756, 696 cm^{-1}. **HRMS** (EI) for $C_{19}H_{25}GeO^+$ $[(M-C_2H_5)^+]$: calculated 343.1112, found 343.1124. **^{1}H NMR** (500 MHz, C_6D_6): δ = 0.61 (q, *J* = 7.9 Hz, 6H), 0.98 (t, *J* = 7.9 Hz, 9H), 1.54 (dd, *J* = 13.7 Hz, *J* = 7.9 Hz, 1H), 1.57 (dd, *J* = 13.7 Hz, *J* = 8.3 Hz, 1H), 3.31 (s, 3H), 4.08 (t, *J* = 8.2 Hz, 1H), 6.77 (m_c, 2H), 7.04 (tt, *J* = 7.3 Hz, *J* = 1.5 Hz, 1H), 7.13–7.16 (m, 4H), 7.23–7.27 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 4.6, 9.2, 20.0, 47.7, 54.8, 114.1, 126.2, 127.9, 128.6, 128.8, 139.5, 148.2, 158.6 ppm.

4.3 (2-(4-Bromophenyl)2-phenylethyl)triethylgermane (17)

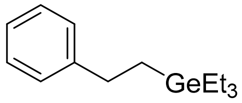


17
$C_{20}H_{27}BrGe$
M = 419.97 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (10.2 mg, 20 µmol, 10.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of 1-bromo-4-(1-phenylvinyl)benzene (**4**, 51.8 mg, 0.200 mmol, 1.00 equiv) and surrogate **1a** (76.5 mg, 0.320 mmol, 1.60 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 24 h and subsequently purified by flash column chromatography on silica gel using *n*-pentane as eluent. After removal of all volatiles, (2-(4-bromophenyl)2-phenylethyl)triethylgermane (**17**, 76.4 mg, 91%) was obtained as a colorless oil.

R_f = 0.59 (*n*-pentane). **GLC** (SE-54): t_R = 24.6 min. **IR** (ATR): $\tilde{\nu}$ = 3024, 2945, 2900, 2868, 1599, 1484, 1451, 1423, 1229, 1164, 1130, 1072, 1008, 996, 909, 795, 757, 696 cm^{-1}. **HRMS** (EI) for $C_{18}H_{22}BrGe^+$ $[(M-C_2H_5)^+]$: calculated 391.0111, found 391.0103. **^{1}H NMR** (500 MHz, C_6D_6): δ = 0.53 (q, *J* = 7.9 Hz, 6H), 0.93 (t, *J* = 8.0 Hz, 9H), 1.35 (dd, *J* = 13.7 Hz, *J* = 7.9 Hz, 1H), 1.42 (dd, *J* = 13.7 Hz, *J* = 8.5 Hz, 1H), 3.90 (t, *J* = 8.1 Hz, 1H), 6.86 (m_c, 2H), 6.99–7.04 (m, 1H), 7.07–7.14 (m, 4H), 7.24 (m_c, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 4.6, 9.1, 19.5, 47.9, 120.2, 126.6, 127.8, 128.7, 129.6, 131.7, 146.6, 146.9 ppm.

4.4 Triethyl(phenylethyl)germane (18)



18

$C_{14}H_{24}Ge$

M = 264.98 g/mol

<u>0.2-mmol scale:</u>

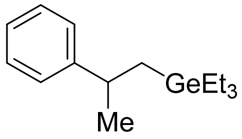
According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of styrene (**5**, 20.8 mg, 0.200 mmol, 1.00 equiv) and surrogate **1a** (57.4 mg, 0.240 mmol, 1.20 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 3 h and subsequently purified by flash column chromatography on silica gel using cyclohexane as eluent. After removal of all volatiles, triethyl(phenylethyl)germane (**18**, 50.3 mg, 95%) was obtained as a colorless oil.

<u>1.0-mmol scale:</u>

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (26 mg, 50 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (750 µL), and a solution of styrene (**5**, 104 mg, 1.00 mmol, 1.00 equiv) and surrogate **1a** (287 mg, 1.20 mmol, 1.20 equiv) in 1,2-$F_2C_6H_4$ (250 µL). The reaction mixture was stirred at room temperature for 3 h and subsequently purified by flash column chromatography on silica gel using cyclohexane as eluent. After removal of all volatiles, triethyl(phenylethyl)germane (**18**, 254 mg, 96%) was obtained as a colorless oil.

***R*$_f$** = 0.67 (cyclohexane). **GLC** (SE-54): t_R = 15.7 min. **IR** (ATR): $\tilde{\nu}$ = 3025, 2946, 2902, 2869, 1601, 1493, 1453, 1424, 1376, 1232, 1160, 1123, 1075, 1017, 966, 745, 695 cm^{-1}. **HRMS** (EI) for $C_{12}H_{19}Ge^+$ $[(M-C_2H_5)^+]$: calculated 237.0693, found 237.0702. **^{1}H NMR** (500 MHz, C_6D_6): δ = 0.70 (q, *J* = 7.8 Hz, 6H), 1.02 (t, *J* = 7.9 Hz, 9H), 1.01–1.06 (m, 2H), 2.64 (m_c, 2H), 7.08–7.12 (m, 1H), 7.13–7.15 (m, 2H), 7.18–7.22 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 4.2, 9.2, 13.9, 31.8, 126.0, 128.2, 128.7, 145.5 ppm.

4.5 Triethyl(2-phenylpropyl)germane (19)



19

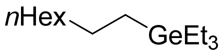
$C_{15}H_{26}Ge$

M = 279.00 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of α-methylstyrene (**6**, 23.6 mg, 0.200 mmol, 1.00 equiv) and surrogate **1a** (57.4 mg, 0.240 mmol, 1.20 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 3 h and subsequently purified by flash column chromatography on silica gel using cyclohexane as eluent. After removal of all volatiles, triethyl(2-phenylpropyl)germane (**22**, 52.9 mg, 95%) was obtained as a colorless oil.

$\boldsymbol{R}_\mathbf{f}$ = 0.71 (cyclohexane). **GLC** (SE-54): t_R = 15.8 min. **IR** (ATR): $\tilde{\nu}$ = 3025, 2949, 2903, 2869, 1601, 1492, 1451, 1425, 1374, 1080, 1014, 969, 759, 723, 696 cm^{-1}. **HRMS** (EI) for $C_{13}H_{21}Ge^+$ $[(M-C_2H_5)^+]$: calculated 251.0850, found 251.0847. **^{1}H NMR** (500 MHz, C_6D_6): δ = 0.62 (m_c, 6H), 0.99 (t, J = 8.0 Hz, 9H), 1.04 (dd, J = 13.8 Hz, J = 7.0 Hz, 1H), 1.15 (dd, J = 13.8 Hz, J = 8.3 Hz, 1H), 1.25 (d, J = 6.9 Hz, 3H), 2.84 (m_c, 1H), 7.05–7.09 (m, 1H), 7.11–7.15 (m, 2H), 7.16–7.20 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 4.7, 9.2, 22.2, 26.7, 37.6, 126.3, 126.9, 128.7, 149.9 ppm.

4.6 Triethyl(octyl)germane (20)



20

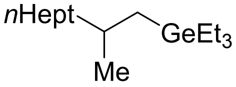
$C_{14}H_{32}Ge$

M = 273.04 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of oct-1-ene (**7**, 22.4 mg, 0.200 mmol, 1.00 equiv) and surrogate **1a** (57.4 mg, 0.240 mmol, 1.20 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 3 h and subsequently purified by flash column chromatography on silica gel using cyclohexane as eluent. After removal of all volatiles, triethyl(octyl)germane (**20**, 54.1 mg, 99%) was obtained as a colorless oil.

***R*$_f$** = 0.97 (cyclohexane). **GLC** (SE-54): t$_R$ = 14.6 min. **IR** (ATR): $\tilde{\nu}$ = 2949, 2920, 2870, 2852, 1459, 1425, 1376, 1017, 967, 699 cm^{-1}. **HRMS** (EI) for $C_{12}H_{27}Ge^+$ [$(M-C_2H_5)^+$]: calculated 245.1319, found 245.1328. **^{1}H NMR** (500 MHz, C_6D_6): δ = 0.76 (q, *J* = 7.8 Hz, 6H), 0.76–0.80 (m, 2H), 0.92 (t, *J* = 7.0 Hz, 3H), 1.08 (t, *J* = 8.0 Hz, 9H), 1.24–1.40 (m, 10H), 1.40–1.49 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 4.3, 9.3, 11.9, 14.4, 23.1, 25.7, 29.8, 29.8, 32.4, 34.2 ppm.

4.7 Triethyl(2-methylnonyl)germane (21)



21

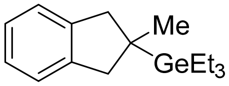
$C_{16}H_{36}Ge$

M = 301.09 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of 2-methylnon-1-ene (**8**, 28.1 mg, 0.200 mmol, 1.00 equiv) and surrogate **1a** (57.4 mg, 0.240 mmol, 1.20 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 3 h and subsequently purified by flash column chromatography on silica gel using cyclohexane as eluent. After removal of all volatiles, triethyl(2-methylnonyl)germane (**21**, 58.1 mg, 97%) was obtained as a colorless oil.

***R*$_f$** = 0.84 (cyclohexane). **GLC** (SE-54): t$_R$ = 16.4 min. **IR** (ATR): $\tilde{\nu}$ = 2950, 2921, 2870, 1458, 1425, 1375, 1016, 968, 740, 700 cm^{-1}. **HRMS** (EI) for $C_{14}H_{31}Ge^+$ [$(M-C_2H_5)^+$]: calculated 273.1632, found 273.1643. **^{1}H NMR** (500 MHz, C_6D_6): δ = 0.68 (dd, *J* = 13.8 Hz, *J* = 8.6 Hz, 1H), 0.78 (q, *J* = 7.9 Hz, 6H), 0.88–0.94 (m, 4H), 0.98 (d, *J* = 6.6 Hz, 3H), 1.09 (t, *J* = 7.9 Hz, 9H), 1.19–1.26 (m, 1H), 1.27–1.40 (m, 11H), 1.66 (m$_c$, 1H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 5.2, 9.3, 14.4, 20.8, 23.1, 23.2, 27.8, 29.9, 30.4, 30.8, 32.4, 41.0 ppm.

4.8 Triethyl(2-methyl-2,3-dihydro-1*H*-inden-2-yl)germane (22)



22

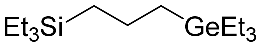
$C_{16}H_{26}Ge$

M = 291.01 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of 2-methylindene (**9**, 26.0 mg, 0.200 mmol, 1.00 equiv) and surrogate **1a** (57.4 mg, 0.240 mmol, 1.20 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 3 h and subsequently purified by flash column chromatography on silica gel using cyclohexane as eluent. After removal of all volatiles, triethyl(2-methyl-2,3-dihydro-1*H*-inden-2-yl)germane (**22**, 50.5 mg, 87%) was obtained as a colorless oil.

***R*$_f$** = 0.66 (cyclohexane). **GLC** (SE-54): t_R = 17.7 min. **IR** (ATR): $\tilde{\nu}$ = 3019, 2944, 2902, 2870, 2832, 1455, 1424, 1374, 1222, 1013, 968, 845, 793, 738, 689 cm^{-1}. **HRMS** (EI) for $C_{14}H_{21}Ge^+$ [$(M-C_2H_5)^+$]: calculated 263.0850, found 263.0854. **^{1}H NMR** (500 MHz, C_6D_6): δ = 0.71 (q, *J* = 8.0 Hz, 6H), 1.03 (t, *J* = 8.0 Hz, 9H), 1.09 (s, 3H), 2.54 (d, *J* = 15.4 Hz, 2H), 3.03 (d, *J* = 15.4 Hz, 2H), 7.09–7.17 (m, 4H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 3.1, 9.7, 25.4, 32.5, 44.9, 125.0, 126.6, 143.4 ppm.

4.9 Triethyl(3-(triethylgermyl)propyl)silane (23)



23

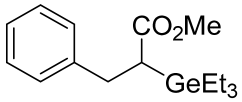
$C_{15}H_{36}GeSi$

M = 317.17 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of allyltriethylsilane (**10**, 31.3 mg, 0.200 mmol, 1.00 equiv) and surrogate **1a** (57.4 mg, 0.240 mmol, 1.20 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 3 h and subsequently filtered over a small silica gel column (2.0 cm) using cyclohexane as eluent. After removal of all volatiles, triethyl(3-(triethylgermyl)propyl)silane (**23**, 62.6 mg, 99%) was obtained as a colorless oil.

***R*~f~** = 0.95 (cyclohexane). **GLC** (SE-54): t_R = 16.5 min. **IR** (ATR): $\tilde{\nu}$ = 2948, 2905, 2871, 1458, 1417, 1376, 1237, 1136, 1078, 1013, 966, 883, 764, 721, 700 cm^{-1}. **HRMS** (EI) for $C_{13}H_{31}GeSi^+$ [$(M-C_2H_5)^+$]: calculated 289.1401, found 289.1404. **^{1}H NMR** (500 MHz, C_6D_6): δ = 0.56 (q, *J* = 8.0 Hz, 6H), 0.68 (m_c, 2H), 0.77 (q, *J* = 8.0 Hz, 6H), 0.89 (m_c, 2H), 1.00 (t, *J* = 8.0 Hz, 9H), 1.09 (t, *J* = 8.0 Hz, 9H), 1.55 (m_c, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 3.9, 4.5, 7.8, 9.3, 16.7, 16.9, 20.3 ppm. **^{1}H,^{29}Si-HMQC NMR** (99 MHz, C_6D_6): δ = 5.9 ppm.

4.10 Methyl 3-phenyl-2-(triethylgermyl)propanoate (24)



24

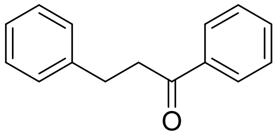
$C_{16}H_{26}GeO_2$

M = 323.01 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of methyl cinnamate (**11**, 32.4 mg, 0.200 mmol, 1.00 equiv) and surrogate **1a** (57.4 mg, 0.240 mmol, 1.20 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 3 h and subsequently filtered over a small silica gel column (2.0 cm) using cyclohexane:*tert*-butyl methyl ether = 9:1 as eluent. After removal of all volatiles, methyl 3-phenyl-2-(triethylgermyl)propanoate (**24**, 64.0 mg, 99%) was obtained as a colorless oil.

***R*~f~** = 0.71 (cyclohexane/*tert*-butyl methyl ether 9:1). **GLC** (SE-54): t_R = 19.1 min. **IR** (ATR): $\tilde{\nu}$ = 2947, 2905, 2871, 1713, 1601, 1493, 1454, 1431, 1348, 1311, 1204, 1144, 1013, 968, 835, 789, 745, 696 cm^{-1}. **HRMS** (EI) for $C_{14}H_{21}GeO_2^+$ [$(M-C_2H_5)^+$]: calculated 295.0748, found 295.0760. **^{1}H NMR** (500 MHz, C_6D_6): δ = 0.78–0.89 (m, 6H), 1.04 (t, *J* = 8.0 Hz, 9H), 2.63–2.70 (m, 2H), 3.29 (s, 3H), 3.36 (dd, *J* = 14.9 Hz, *J* = 12.5 Hz, 1H), 7.05 (tt, *J* = 7.4 Hz, *J* = 1.2 Hz, 1H), 7.14–7.18 (m, 2H), 7.26 (d, *J* = 7.4 Hz, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 4.2, 9.0, 33.7, 36.3, 50.6, 126.4, 128.7, 128.7, 142.8, 175.3 ppm.

4.11 1,3-Diphenylpropan-1-one (25)



25

$C_{15}H_{14}O$

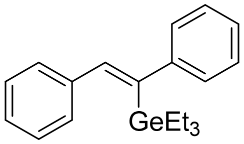
M = 210.28 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of chalcone (**12**, 41.6 mg, 0.200 mmol, 1.00 equiv) and surrogate **1a** (57.4 mg, 0.240 mmol, 1.20 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred outside the glove box at 90 °C for 3 h and subsequently purified by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether = 99:1 as eluent. After removal of all volatiles, 1,3-diphenylpropan-1-one (**25**, 41.0 mg, 97%) was obtained as a white solid.

***R*$_f$** = 0.32 (cyclohexane/*tert*-butyl methyl ether 20:1). **GLC** (SE-54): t_R = 18.7 min. **^{1}H NMR** (500 MHz, C_6D_6): δ = 2.78–2.83 (m, 2H), 2.97 (t, *J* = 7.5 Hz, 2H), 7.01–7.08 (m, 5H), 7.09–7.15 (m, 3H), 7.73–7.77 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 30.4, 40.6, 126.3, 128.3, 128.6, 128.7, 128.8, 132.7, 137.5, 141.9, 197.9 ppm.

The analytical and spectroscopic data are in accordance with those reported.[S5]

4.12 (*Z*)-(1,2-Diphenylvinyl)triethylgermane ((*Z*)-26)



(*Z*)-**26**

$C_{20}H_{26}Ge$

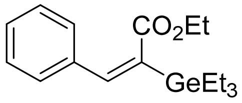
M = 339.06 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of diphenylacetylene (**13**, 35.6 mg, 0.200 mmol, 1.00 equiv) and surrogate **1a** (57.4 mg, 0.240 mmol, 1.20 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 3 h and subsequently purified by flash column chromatography on silica gel using cyclohexane as eluent. After removal of all volatiles, (*Z*)-(1,2-diphenylvinyl)triethylgermane ((*Z*)-**26**, 64.1 mg, 95%) was obtained as a colorless oil.

R**f** = 0.33 (cyclohexane). **GLC** (SE-54): t*R* = 21.7 min. **IR** (ATR): $\tilde{\nu}$ = 3054, 3020, 2947, 2903, 2868, 1594, 1489, 1457, 1442, 1425, 1375, 1230, 1071, 1010, 970, 910, 870, 762, 694 cm^{-1}. **HRMS** (EI) for $C_{18}H_{21}Ge^+$ [$(M-C_2H_5)^+$]: calculated 311.0850, found 311.0850. **^{1}H NMR** (500 MHz, C_6D_6): δ = 0.74 (q, *J* = 7.9 Hz, 6H), 0.94 (t, *J* = 7.9 Hz, 9H), 7.06–7.13 (m, 2H), 7.13–7.18 (m, 2H), 7.19–7.26 (m, 4H), 7.29–7.33 (m, 2H), 7.40 (s, 1H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 6.8, 9.3, 126.1, 127.5, 127.5, 128.2, 128.4, 128.7, 140.4, 143.9, 147.3, 147.7 ppm.

The configuration of the product was determined by comparison of the NMR spectroscopic data in $CDCl_3$ with those reported.[S6]

4.13 Ethyl (*E*)-3-phenyl-2-(triethylgermyl)acrylate ((*E*)-27)



(*E*)-**27**
$C_{17}H_{26}GeO_2$
M = 335.02 g/mol

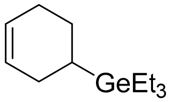
According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (2.6 mg, 5.0 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (75 µL), and a solution of ethyl 3-phenylpropiolate (**14**, 17.4 mg, 0.100 mmol, 1.00 equiv) and surrogate **1a** (47.8 mg, 0.200 mmol, 2.00 equiv) in 1,2-$F_2C_6H_4$ (25 µL). The reaction mixture was stirred at room temperature for 3 h and subsequently purified by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether = 30:1 as eluent. After removal of all volatiles, ethyl (*E*)-3-phenyl-2-(triethylgermyl)acrylate ((*E*)-**27**, 24.9 mg, 74%) was obtained as a yellow oil.

R**f** = 0.62 (cyclohexane/*tert*-butyl methyl ether 30:1). **GLC** (SE-54): t*R* = 19.6 min. **IR** (ATR): $\tilde{\nu}$ = 2949, 2904, 2871, 1700, 1600, 1493, 1458, 1426, 1368, 1205, 1179, 1025, 969, 921, 853, 752, 692 cm^{-1}. **HRMS** (EI) for $C_{15}H_{21}GeO_2^+$ [$(M-C_2H_5)^+$]: calculated 307.0748, found 307.0744. **^{1}H NMR** (500 MHz, C_6D_6): δ = 0.91 (t, *J* = 7.1 Hz, 3H), 0.96–1.01 (m, 6H), 1.10–1.16 (m, 9H), 4.03 (q, *J* = 7.1 Hz, 2H), 6.74 (s, 1H), 6.99–7.05 (m, 1H), 7.07–7.12 (m, 2H), 7.39–7.43 (m, 2H) ppm.

^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ = 4.8, 9.0, 14.2, 60.2, 128.3, 128.5, 128.6, 137.6, 138.1, 140.4, 171.8 ppm.

The configuration of the product was determined by comparison of the NMR spectroscopic data in $CDCl_3$ with those reported.[S6]

4.14 Cyclohex-3-en-1-yltriethylgermane (31)



31
$C_{12}H_{24}Ge$
M = 240.95 g/mol

From cyclohexa-1,3-diene (**28**):

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of cyclohexa-1,3-diene (**28**, 26.8 mg, 0.335 mmol, 1.68 equiv) and surrogate **1a** (47.8 mg, 0.200 mmol, 1.00 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 3 h and subsequently filtered over a small silica gel column (2.0 cm) using cyclohexane as eluent. After removal of all volatiles, cyclohex-3-en-1-yltriethylgermane (**31**, 43.2 mg, 90%) was obtained as a colorless oil.

From cyclohexa-1,4-diene (**29**):

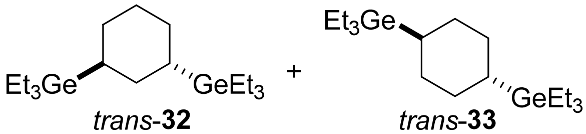
According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of cyclohexa-1,4-diene (**29**, 26.8 mg, 0.335 mmol, 1.68 equiv) and surrogate **1a** (47.8 mg, 0.200 mmol, 1.00 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 3 h and subsequently filtered over a small silica gel column (2.0 cm) using cyclohexane as eluent. After removal of all volatiles, a colorless oil (41.0 mg) was obtained. NMR spectroscopic analysis showed a mixture of cyclohex-3-en-1-yltriethylgermane (**31**, 65%) and *trans*-1,3- (*trans*-**32**) and *trans*-1,4-bis(triethylgermyl)cyclohexane (*trans*-**33**) in a ratio of **31**:(*trans*-**32** + *trans*-**33**) = 0.53:0.47.

Analytical data of an isolated sample of cyclohex-3-en-1-yltriethylgermane (**31**):

R

R_f = 0.94 (cyclohexane). **GLC** (SE-54): t_R = 13.1 min. **IR** (ATR): $\tilde{\nu}$ = 3017, 2946, 2903, 2869, 2828, 1458, 1426, 1138, 1016, 968, 902, 873, 761, 694 cm^{-1}. **HRMS** (EI) for $C_{10}H_{19}Ge^+$ [(M-C_2H_5)$^+$]: calculated 213.0693, found 213.0696. **^{1}H NMR** (500 MHz, C_6D_6): δ = 0.72 (q, *J* = 7.8 Hz, 6H), 1.04 (t, *J* = 7.9 Hz, 9H), 1.26–1.34 (m, 1H), 1.45–1.55 (m, 1H), 1.69–1.77 (m, 1H), 1.95–2.04 (m, 4H), 5.73–5.81 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 2.8, 9.5, 21.2, 25.6, 26.6, 28.1, 127.4, 128.5 ppm.

4.15 *trans*-1,3- (*trans*-32) and *trans*-1,4-Bis(triethylgermyl)cyclohexane (*trans*-33)



trans-**32** *trans*-**33**

$C_{18}H_{40}Ge_2$
M = 401.78 g/mol

From cyclohexa-1,3-diene (**28**):

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (2.6 mg, 5.0 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (75 µL), and a solution of cyclohexa-1,3-diene (**28**, 8.0 mg, 0.100 mmol, 1.00 equiv) and surrogate **1a** (57.3 mg, 0.240 mmol, 2.40 equiv) in 1,2-$F_2C_6H_4$ (25 µL). The reaction mixture was stirred at room temperature for 3 h and subsequently purified by flash column chromatography on silica gel using cyclohexane as eluent. After removal of all volatiles, a mixture of *trans*-1,3- (*trans*-**32**) and *trans*-1,4-bis(triethylgermyl)cyclohexane (*trans*-**33**) (37.3 mg, 93%) was obtained as a colorless oil.

From cyclohexa-1,4-diene (**29**):

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (2.6 mg, 5.0 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (75 µL), and a solution of cyclohexa-1,4-diene (**29**, 8.0 mg, 0.100 mmol, 1.00 equiv) and surrogate **1a** (57.3 mg, 0.240 mmol, 2.40 equiv) in 1,2-$F_2C_6H_4$ (25 µL). The reaction mixture was stirred at room temperature for 3 h and subsequently purified by flash column chromatography on silica gel using cyclohexane as eluent. After removal of all volatiles, a mixture of *trans*-1,3- (*trans*-**32**) and *trans*-1,4-bis(triethylgermyl)cyclohexane (*trans*-**33**) (39.2 mg, 98%) was obtained as a colorless oil.

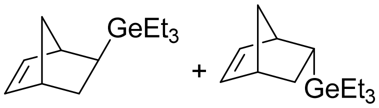
***R*_f** = 0.86 (cyclohexane). **GLC** (SE-54): t$_R$ = 20.8, 21.2 min. **IR** (ATR): $\tilde{\nu}$ = 2945, 2904, 2869, 1457, 1424, 1376, 1346, 1014, 968, 881, 719, 690 cm^{-1}. **HRMS** (EI) for $C_{18}H_{40}Ge_2^{+\bullet}$ [(M)$^{+\bullet}$]: calculated 404.1548, found 404.1566.

NMR spectroscopic data for *trans*-1,3-bis(triethylgermyl)cyclohexane (*trans*-**32**):
^{1}H NMR (700 MHz, C_6D_6): δ = 0.82 (q, *J* = 7.9 Hz, 12H), 1.11 (t, *J* = 7.9 Hz, 18H), 1.36 (m$_c$, 2H), 1.48 (m$_c$, 2H), 1.58 (m$_c$, 2H), 1.69–1.75 (m, 2H), 1.80 (t, *J* = 6.0 Hz, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 4.1, 9.5, 25.3, 27.0, 29.7, 31.9 ppm.

NMR spectroscopic data for *trans*-1,4-bis(triethylgermyl)cyclohexane (*trans*-**33**):
^{1}H NMR (700 MHz, C_6D_6): δ = 0.82 (q, *J* = 7.9 Hz, 12H), 1.11 (t, *J* = 7.9 Hz, 18H), 1.34 (m$_c$, 2H), 1.58–1.70 (m, 8H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 4.1, 9.5, 25.6, 29.5 ppm.

The relative configuration of *trans*-**32** was verified by NMR spectroscopy, and we assume the same for *trans*-**33**, for which unambiguous assignment by NMR spectroscopic analysis was not possible.

4.16 Bicyclo[2.2.1]hept-5-en-2-yltriethylgermane (*exo*-34 + *endo*-34)



exo-**34** *endo*-**34**

$C_{13}H_{24}Ge$
M = 252.97 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of norborna-2,5-diene (**30**, 92.3 mg, 1.00 mmol, 5.00 equiv) and surrogate **1a** (47.8 mg, 0.200 mmol, 1.00 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 3 h and subsequently purified by flash column chromatography on silica gel using *n*-pentane as eluent. After removal of all volatiles, bicyclo[2.2.1]hept-5-en-2-yltriethylgermane (*exo*-**34**:*endo*-**34** = 87:13, 46.9 mg, 93%) was obtained as a colorless oil.

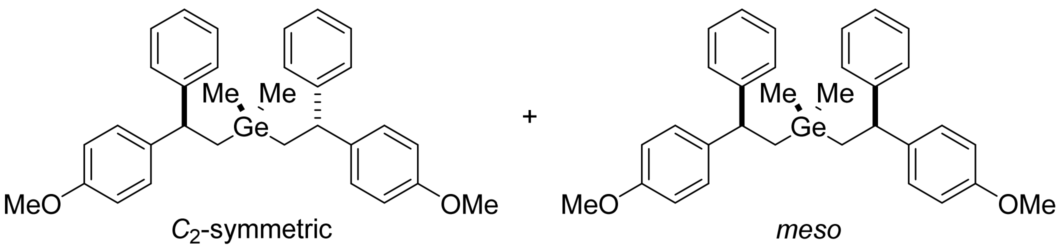
***R*~f~** = 0.85 (cyclohexane). **GLC** (SE-54): t$_R$ = 13.6 min. **IR** (ATR): $\tilde{\nu}$ = 3056, 2945, 2902, 2868, 1565, 1458, 1424, 1376, 1330, 1127, 1099, 1016, 969, 882, 802, 720, 686 cm^{-1}. **HRMS** (EI) for $C_{13}H_{24}Ge^{+\bullet}$ [(M)$^{+\bullet}$]: calculated 254.1084, found 254.1094.

NMR spectroscopic data for *exo*-bicyclo[2.2.1]hept-5-en-2-yltriethylgermane (*exo*-**32**):
^{1}H NMR (500 MHz, C_6D_6): δ = 0.65–0.71 (m, 1H), 0.71–0.78 (m, 6H), 1.03–1.08 (m, 1H), 1.06 (t, *J* = 7.9 Hz, 9H), 1.09–1.19 (m, 1H), 1.34 (m$_c$, 1H), 1.59 (ddd, *J* = 11.4 Hz, *J* = 5.5 Hz, *J* = 3.6 Hz, 1H), 2.77 (br s, 1H), 2.87 (br s, 1H), 5.93 (dd, *J* = 5.6 Hz, *J* = 2.9 Hz, 1H), 6.13 (dd, *J* = 5.6 Hz, *J* = 2.9 Hz, 1H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 4.2, 9.4, 23.3, 28.1, 43.0, 44.2, 47.8, 133.4, 137.8 ppm.

Representative NMR spectroscopic data for *endo*-bicyclo[2.2.1]hept-5-en-2-yltriethylgermane (*endo*-**32**):
^{1}H NMR (500 MHz, C_6D_6): δ = 1.30 (m$_c$, 1H), 1.51 (m$_c$, 1H), 1.80 (ddd, *J* = 11.3 Hz, *J* = 9.6 Hz, *J* = 3.8 Hz, 1H), 2.90 (br s, 1H), 5.88–5.92 (m, 1H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 4.7, 9.5, 23.9, 42.5, 45.7, 51.3, 134.7, 135.9 ppm.

The configuration was determined by comparison of the NMR spectroscopic data in $CDCl_3$ with those reported.[S7]

4.17 Bis(2-(4-methoxyphenyl)-2-phenylethyl)dimethylgermane (35)

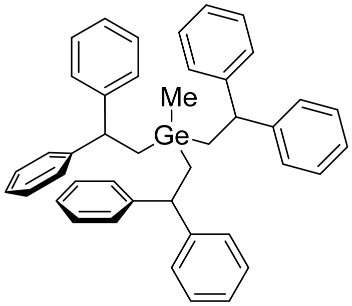


35
$C_{32}H_{36}GeO_2$
M = 525.27 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 μmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 μL), and a solution of 1-methoxy-4-(1-phenylvinyl)benzene (**3**, 42.1 mg, 0.200 mmol, 1.00 equiv) and surrogate **1b** (28.7 mg, 0.110 mmol, 0.550 equiv) in 1,2-$F_2C_6H_4$ (50 μL). The reaction mixture was stirred at room temperature for 72 h and subsequently purified by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether = 99:1 as eluent. After removal of all volatiles, bis(2-(4-methoxyphenyl)-2-phenylethyl)-dimethylgermane (**35**, 32.6 mg, 62%) was obtained as an inseparable 1:1 mixture of C_2-symmetric and *meso* compounds in form of a colorless oil.

***R*$_f$** = 0.42 (cyclohexane/*tert*-butyl methyl ether 20:1). **GLC** (SE-54): t_R = 18.0 min. **IR** (ATR): $\tilde{\nu}$ = 3023, 2901, 2832, 1606, 1507, 1450, 1330, 1300, 1243, 1175, 1033, 819, 778, 697 cm^{-1}. **HRMS** (APCI) for $C_{31}H_{33}GeO_2^+$ [(M-CH$_3$)$^+$]: calculated 511.1687, found 511.1686. **^{1}H NMR** (500 MHz, C_6D_6): δ = {–0.14 (s, GeMe$_{meso}$), –0.13 (s, GeMe$_{C2}$), –0.13 (s, GeMe$_{meso}$), 6H}, 1.33–1.43 (m, 4H), 3.31 (s, 6H), 3.97 (t, *J* = 8.2 Hz, 2H), 6.75 (m$_c$, 4H), 7.04 (m$_c$, 2H), 7.09 (m$_c$, 4H), 7.12–7.18 (m, 4H), 7.19–7.23 (m, 4H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = {–2.8 (C$_{meso}$), –2.8 (C$_{C2}$), –2.8 (C$_{meso}$)}, 24.0, 47.5, 54.8, 114.2, 126.2, 127.9, 128.6, 129.0, 139.3, 148.0, 158.6 ppm.

4.18 Tris(2,2-diphenylethyl)methylgermane (36)



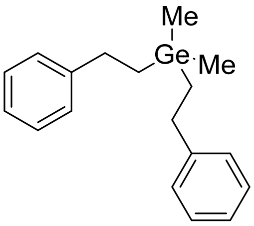
36
$C_{43}H_{42}Ge$
M = 631.44 g/mol

According to GP2.2, the reaction vial was charged with B(C_6F_5)$_3$ (10.2 mg, 20.0 µmol, 10.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of 1,1-diphenylethylene (**2**, 36.1 mg, 0.200 mmol, 1.00 equiv) and surrogate **1c** (22.8 mg, 0.0701 mmol, 0.350 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 72 h and subsequently purified by flash column chromatography on silica gel using cyclohexane → cyclohexane:*tert*-butyl methyl ether = 50:1 as eluent. After removal of all volatiles, tris(2,2-diphenylethyl)methylgermane (**36**, 39.0 mg, 93%) was obtained as a colorless oil.

***R*$_f$** = 0.13 (cyclohexane/*tert*-butyl methyl ether 50:1). **IR** (ATR): $\tilde{\nu}$ = 3056, 3022, 2985, 1596, 1490, 1448, 1412, 1236, 1167, 1130, 1071, 1029, 861, 765, 741, 696 cm^{-1}. **HRMS** (EI) for

$C_{29}H_{29}Ge^+$ [$(M-C_{14}H_{13})^+$]: calculated 451.1476, found 451.1480. **^{1}H NMR** (500 MHz, C_6D_6): δ = –0.41 (s, 3H), 1.27 (d, *J* = 8.1 Hz, 6H), 3.89 (t, *J* = 8.1 Hz, 3H), 6.99–7.04 (m, 6H), 7.08–7.15 (m, 24H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = –4.3, 22.8, 48.2, 126.4, 128.1, 128.7, 147.4 ppm.

4.19 Dimethyldiphenethylgermane (37)



37

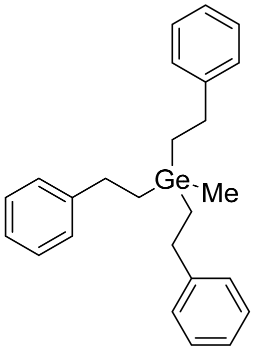
$C_{18}H_{24}Ge$

M = 313.02 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of styrene (**5**, 20.8 mg, 0.200 mmol, 1.00 equiv) and surrogate **1b** (28.7 mg, 0.110 mmol, 0.550 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 5 h and subsequently purified by flash column chromatography on silica gel using cyclohexane as eluent. After removal of all volatiles, dimethyldiphenethylgermane (**37**, 30.1 mg, 96%) was obtained as a colorless oil.

***R*$_f$** = 0.29 (cyclohexane). **GLC** (SE-54): t_R = 20.9 min. **IR** (ATR): $\tilde{\nu}$ = 3060, 3023, 2966, 2926, 2899, 2847, 1601, 1493, 1451, 1416, 1233, 1158, 1123, 1028, 897, 821, 787, 744, 695 cm^{-1}. **HRMS** (EI) for $C_{17}H_{21}Ge^+$ [$(M-CH_3)^+$]: calculated 299.0850, found 299.0854. **^{1}H NMR** (500 MHz, C_6D_6): δ = 0.05 (s, 6H), 0.97 (m_c, 4H), 2.59 (m_c, 4H), 7.07–7.13 (m, 6H), 7.17–7.22 (m, 4H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = –4.1, 17.5, 31.6, 126.0, 128.3, 128.7, 145.0 ppm.

4.20 Methyltriphenethylgermane (38)



38

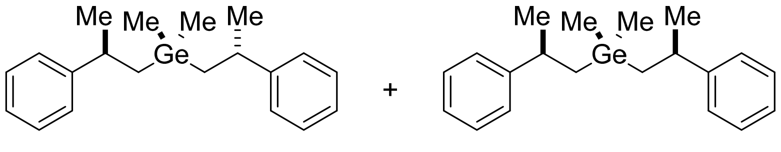
$C_{25}H_{30}Ge$

M = 403.15 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of styrene (**5**, 20.8 mg, 0.200 mmol, 1.00 equiv) and surrogate **1c** (22.8 mg, 0.0701 mmol, 0.350 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 72 h and subsequently purified by flash column chromatography on silica gel using cyclohexane as eluent. After removal of all volatiles, methyltriphenethylgermane (**38**, 23.6 mg, 88%) was obtained as a colorless oil.

***R*$_f$** = 0.18 (cyclohexane). **GLC** (SE-54): t_R = 29.1 min. **IR** (ATR): $\tilde{\nu}$ = 3023, 2924, 2899, 2847, 1600, 1493, 1451, 1235, 1157, 1123, 1028, 1000, 897, 826, 775, 744, 695 cm^{-1}. **HRMS** (EI) for $C_{24}H_{27}Ge^+$ $[(M-CH_3)^+]$: calculated 389.1319, found 389.1311. **^{1}H NMR** (500 MHz, C_6D_6): δ = 0.04 (s, 3H), 0.98 (m_c, 6H), 2.58 (m_c, 6H), 7.08–7.14 (m, 9H), 7.18–7.23 (m, 6H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = –6.1, 16.2, 31.6, 126.1, 128.2, 128.7, 145.1 ppm.

4.21 Dimethylbis(2-phenylpropyl)germane (39)



39

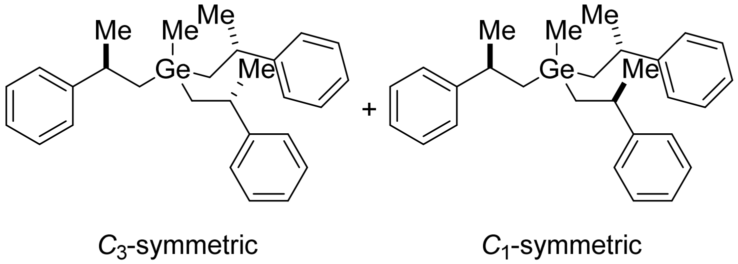
$C_{20}H_{28}Ge$

M = 341.07 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of α-methylstyrene (**6**, 23.6 mg, 0.200 mmol, 1.00 equiv) and surrogate **1b** (28.7 mg, 0.110 mmol, 0.550 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 5 h and subsequently purified by flash column chromatography on silica gel using cyclohexane as eluent. After removal of all volatiles, dimethylbis(2-phenylpropyl)germane (**39**, 31.3 mg, 92%) was obtained as an inseparable 1:1 mixture of C_2-symmetric and *meso* compounds in form of a colorless oil.

***R*_f** = 0.39 (cyclohexane). **GLC** (SE-54): t_R = 21.0, 21.0 min. **IR** (ATR): $\tilde{\nu}$ = 3024, 2956, 2910, 1600, 1491, 1449, 1410, 1369, 1233, 1179, 1145, 1082, 1003, 906, 814, 759, 696 cm^{-1}. **HRMS** (EI) for $C_{19}H_{25}Ge^+$ $[(M-CH_3)^+]$: calculated 327.1163, found 327.1170. **^{1}H NMR** (500 MHz, C_6D_6): δ = {–0.12 (s, $GeMe_{meso}$), –0.09 (s, $GeMe_{C2}$), –0.07 (s, $GeMe_{meso}$), 6H}, {0.87 (dd, *J* = 13.7 Hz, *J* = 6.9 Hz), 0.89 (dd, *J* = 13.7 Hz, *J* = 6.9 Hz), 2H}, {1.02 (dd, *J* = 13.7 Hz, *J* = 6.7 Hz), 1.03 (dd, *J* = 13.7 Hz, *J* = 6.5 Hz), 2H}, {1.20 (d, *J* = 6.9 Hz), 1.21 (d, *J* = 6.9 Hz), 6H}, 2.75 (m_c, 2H), 7.04–7.12 (m, 6H), 7.15–7.16 (m, 2H), 7.17–7.19 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = {–2.8 (C_{meso}), –2.6 (C_{C2}), –2.6 (C_{meso})}, {26.5, 26.5 (C_{C2} + C_{meso})}, 26.6, 37.6, 126.3, {127.0, 127.0 (C_{C2} + C_{meso})}, 128.7, 149.5 ppm.

4.22 Methyltris(2-phenylpropyl)germane (40)



40

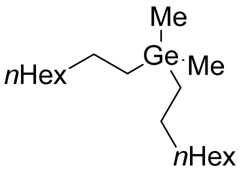
$C_{28}H_{36}Ge$

M = 445.23 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of α-methylstyrene (**6**, 23.6 mg, 0.200 mmol, 1.00 equiv) and surrogate **1c** (22.8 mg, 0.0701 mmol, 0.350 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 72 h and subsequently purified by flash column chromatography on silica gel using cyclohexane:*tert*-butyl methyl ether = 50:1 as eluent. After removal of all volatiles, methyltris(2-phenylpropyl)germane (**40**, 24.3 mg, 82%) was obtained as an inseparable 3:1 mixture of C_3- and C_1-symmetric compounds in form of a colorless oil.

***R*$_f$** = 0.50 (cyclohexane/*tert*-butyl methyl ether 50:1). **GLC** (SE-54): t_R = 28.4 min. **IR** (ATR): $\tilde{\nu}$ = 3024, 2954, 2916, 1600, 1491, 1449, 1408, 1369, 1082, 1003, 906, 811, 758, 696 cm^{-1}. **HRMS** (EI) for $C_{19}H_{25}Ge^+$ [(M-C_9H_{11})$^+$]: calculated 327.1163, found 327.1167. **^{1}H NMR** (500 MHz, C_6D_6): δ = {–0.23 (s, GeMe$_{C3}$), –0.21 (s, GeMe$_{C1}$), 3H}, {0.76 (dd, *J* = 13.7 Hz, *J* = 6.5 Hz), 0.80 (dd, *J* = 13.7 Hz, *J* = 6.7 Hz), 0.82 (dd, *J* = 13.8 Hz, *J* = 6.7 Hz), 0.84 (dd, *J* = 13.8 Hz, *J* = 7.0 Hz), 3H}, 0.92–1.03 (m, 3H), {1.16 (d, *J* = 6.9 Hz), 1.18 (d, *J* = 6.9 Hz), 1.19 (d, *J* = 6.9 Hz), 1.20 (d, *J* = 6.9 Hz), 9H}, 2.62–2.76 (m, 3H), 7.04–7.12 (m, 9H), 7.14–7.20 (m, 6H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = {–3.9 (C$_{C3}$), –3.8 (C$_{C1}$)}, {25.5, 25.6, 25.6, 25.7 (C$_{C3}$ + C$_{C1}$)}, {26.7, 26.7, 26.7 (C$_{C3}$ + C$_{C1}$)}, {37.5, 37.5 (C$_{C3}$ + C$_{C1}$)}, {126.2, 126.3 (C$_{C3}$ + C$_{C1}$)}, {127.1, 127.1, 127.1 (C$_{C3}$ + C$_{C1}$)}, {128.7, 128.7 (C$_{C3}$ + C$_{C1}$)}, {149.6, 149.7 (C$_{C3}$ + C$_{C1}$)} ppm.

4.23 Dimethyldioctylgermane (41)



41

$C_{18}H_{40}Ge$

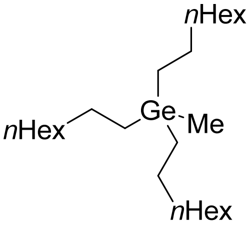
M = 329.15 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of oct-1-ene (**7**, 22.4 mg, 0.200 mmol, 1.00 equiv) and surrogate **1b** (28.7 mg, 0.110 mmol, 0.550 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 5 h and subsequently purified by flash column chromatography on silica gel using cyclohexane as eluent. After removal of all volatiles, dimethyldioctylgermane (**41**, 29.7 mg, 90%) was obtained as a colorless oil.

***R*$_f$** = 0.83 (cyclohexane). **GLC** (SE-54): t_R = 18.6 min. **IR** (ATR): $\tilde{\nu}$ = 2956, 2919, 2851, 1460, 1377, 1233, 1013, 819, 791, 737 cm^{-1}. **HRMS** (EI) for $C_{17}H_{37}Ge^+$ [(M-CH_3)$^+$]: calculated 315.2102, found 315.2108. **^{1}H NMR** (500 MHz, C_6D_6): δ = 0.19 (s, 6H), 0.78 (m$_c$, 4H), 0.89–0.96

(m, 6H), 1.25–1.41 (m, 20H), 1.41–1.51 (m, 4H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = –3.9 (2C), 14.4 (2C), 15.9 (2C), 23.1 (2C), 25.7 (2C), 29.8 (4C), 32.4 (2C), 33.9 (2C) ppm.

4.24 Methyltrioctylgermane (42)



42

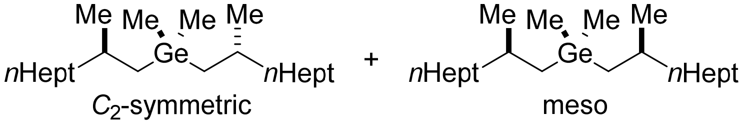
$C_{25}H_{54}Ge$

M = 427.34 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of oct-1-ene (**7**, 22.4 mg, 0.200 mmol, 1.00 equiv) and surrogate **1c** (22.8 mg, 0.0701 mmol, 0.350 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 72 h and subsequently purified by flash column chromatography on silica gel using *n*-pentane as eluent. After removal of all volatiles, methyltrioctylgermane (**42**, 21.5 mg, 75%) was obtained as a colorless oil.

***R*$_f$** = 0.90 (*n*-pentane). **GLC** (SE-54): t_R = 24.5 min. **IR** (ATR): $\tilde{\nu}$ = 2955, 2918, 2850, 1460, 1376, 1234, 1165, 1013, 831, 777, 722, 689 cm^{-1}. **HRMS** (EI) for $C_{24}H_{51}Ge^+$ [(M-CH$_3$)$^+$]: calculated 413.3197, found 413.3187. **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.22 (s, 3H), 0.85 (m$_c$, 6H), 0.89–0.96 (m, 9H), 1.22–1.46 (m, 30H), 1.46–1.61 (m, 6H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = –5.8 (1C), 14.4 (3C), 14.7 (3C), 23.1 (3C), 25.8 (3C), 29.8 (6C), 32.4 (3C), 34.1 (3C) ppm.

4.25 Dimethylbis(2-methylnonyl)germane (43)



43

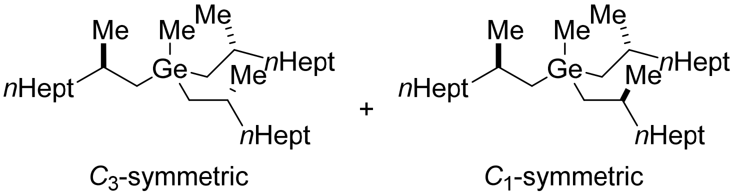
$C_{22}H_{48}Ge$

M = 385.26 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of 2-methylnon-1-ene (**8**, 28.1 mg, 0.200 mmol, 1.00 equiv) and surrogate **1b** (28.7 mg, 0.110 mmol, 0.550 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 5 h and subsequently purified by flash column chromatography on silica gel using cyclohexane as eluent. After removal of all volatiles, dimethylbis(2-methylnonyl)germane (**43**, 35.8 mg, 93%) was obtained as an inseparable 1:1 mixture of C_2-symmetric and *meso* compounds in form of a colorless oil.

***R*$_f$** = 0.82 (cyclohexane). **GLC** (SE-54): t_R = 21.5 min. **IR** (ATR): $\tilde{\nu}$ = 2955, 2920, 2852, 1459, 1374, 1234, 1208, 799, 722 cm^{-1}. **HRMS** (EI) for $C_{12}H_{27}Ge^+$ [$(M-C_{10}H_{21})^+$]: calculated 245.1319, found 245.1326. **^{1}H NMR** (500 MHz, C_6D_6): δ = {0.27 (s, GeMe$_{C2}$), 0.27 (s, GeMe$_{meso}$), 0.27 (s, GeMe$_{C2}$), 6H}, {0.70 (dd, *J* = 13.7 Hz, *J* = 8.6 Hz), 0.71 (dd, *J* = 13.7 Hz, *J* = 8.6 Hz), 2H}, 0.89–0.97 (m, 8H), {0.99 (d, *J* = 6.6 Hz), 0.99 (d, *J* = 6.6 Hz), 6H}, 1.19–1.42 (m, 24H), 1.69 (m$_c$, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = {–1.7 (C$_{meso}$), –1.6 (C$_{C2}$), –1.4 (C$_{meso}$)}, 14.4, 23.1, 23.1, 25.8, 27.7, 29.9, 30.4, 30.9, 32.4, {40.8, 40.9 (C$_{C2}$ + C$_{meso}$)} ppm.

4.26 Methyltris(2-methylnonyl)germane (44)



44

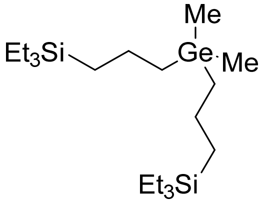
$C_{31}H_{66}Ge$

M = 511.50 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of 2-methylnon-1-ene (**8**, 28.1 mg, 0.200 mmol, 1.00 equiv) and surrogate **1c** (22.8 mg, 0.0701 mmol, 0.350 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 72 h and subsequently purified by flash column chromatography on silica gel using cyclohexane as eluent. After removal of all volatiles, methyltris(2-methylnonyl)germane (**44**, 22.0 mg, 65%) was obtained as an inseparable 3:1 mixture of C_3- and C_1-symmetric compounds in form of a colorless oil.

***R*f** = 0.93 (cyclohexane). **GLC** (SE-54): t_R = 28.5 min. **IR** (ATR): $\tilde{\nu}$ = 2954, 2919, 2852, 1458, 1373, 1236, 1208, 791, 755, 722 cm^{-1}. **HRMS** (EI) for $C_{21}H_{45}Ge^+$ [$(M-C_{10}H_{21})^+$]: calculated 371.2728, found 371.2732. **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.35 (s, 3H), 0.79 (dd, *J* = 13.8 Hz, *J* = 8.7 Hz, 3H), 0.89–0.96 (m, 9H), 1.04 (m_c, 12H), 1.20–1.50 (m, 36H), 1.76 (m_c, 3H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = {–2.3 (C_{C3}), –2.2 (C_{C1})}, 14.4, 23.2, {23.3, 23.3, 23.4 (C_{C3} + C_{C1})}, {25.2, 25.2, 25.3, 25.3 (C_{C3} + C_{C1})}, {27.8, 27.8 (C_{C3} + C_{C1})}, 29.9, 30.5, 30.9, 32.4, {41.0, 41.0, 41.1 (C_{C3} + C_{C1})} ppm.

4.27 Dimethylbis(3-(triethylsilyl)propyl)germane (45)



45

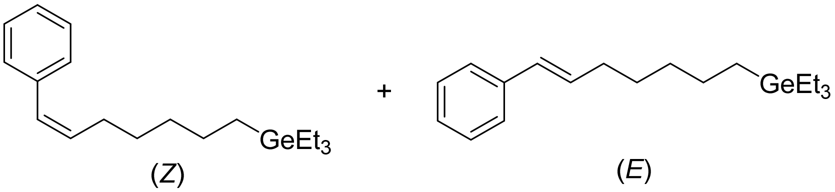
$C_{20}H_{48}GeSi_2$

M = 417.40 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of allyltriethylsilane (**10**, 31.3 mg, 0.200 mmol, 1.00 equiv) and surrogate **1b** (28.7 mg, 0.110 mmol, 0.550 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 5 h and subsequently purified by flash column chromatography on silica gel using cyclohexane as eluent. After removal of all volatiles, dimethylbis(3-(triethylsilyl)propyl)germane (**45**, 28.1 mg, 67%) was obtained as a colorless oil.

***R*f** = 0.86 (cyclohexane). **GLC** (SE-54): t_R = 21.9 min. **IR** (ATR): $\tilde{\nu}$ = 2950, 2906, 2873, 1457, 1414, 1331, 1235, 1136, 1013, 966, 889, 763, 720 cm^{-1}. **HRMS** (EI) for $C_{11}H_{27}GeSi^+$ [$(M-C_9H_{21}Si)^+$]: calculated 261.1088, found 261.1077. **^{1}H NMR** (500 MHz, C_6D_6): δ = 0.23 (s, 6H), 0.57 (q, *J* = 8.0 Hz, 12H), 0.68 (m$_c$, 4H), 0.92 (m$_c$, 4H), 1.01 (t, *J* = 8.0 Hz, 18 H), 1.57 (m$_c$, 4H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = –3.6, 3.8, 7.8, 16.3, 20.3, 20.9 ppm. **^{1}H,^{29}Si-HMQC NMR** (99 MHz, C_6D_6): δ = 6.0 ppm.

4.28 Triethyl(7-phenylhept-6-en-1-yl)germane (48)



48
$C_{19}H_{32}Ge$
M = 333.10 g/mol

According to GP2.2, the reaction vial was charged with $B(C_6F_5)_3$ (5.1 mg, 10 µmol, 5.0 mol %) dissolved in 1,2-$F_2C_6H_4$ (150 µL), and a solution of hepta-1,6-dien-1-ylbenzene (**46**, *Z*:*E* = 55:45, 34.5 mg, 0.200 mmol, 1.00 equiv) and surrogate **1a** (50.2 mg, 0.210 mmol, 1.10 equiv) in 1,2-$F_2C_6H_4$ (50 µL). The reaction mixture was stirred at room temperature for 3 h and subsequently purified by flash column chromatography on silica gel using cyclohexane as eluent. After removal of all volatiles, triethyl(7-phenylhept-6-en-1-yl)germane (**48**, 65.1 mg, 98%) was obtained as a mixture of (Z)- and (*E*)-**48** (*Z*:*E* = 55:45) in form of a colorless oil.

***R*$_f$** = 0.68 (cyclohexane). **GLC** (SE-54): t_R = 21.4 (major), 22.2 (minor) min. **IR** (ATR): $\tilde{\nu}$ = 3023, 2920, 2868, 1492, 1457, 1425, 1376, 1072, 1017, 962, 912, 767, 741, 693 cm^{-1}. **HRMS** (EI) for $C_{17}H_{27}Ge^+$ [$(M\text{-}C_2H_5)^+$]: calculated 305.1319, found 305.1327.

NMR spectroscopic data for (*Z*)-**48**:

^{1}H NMR (500 MHz, C_6D_6): δ = 0.67–0.74 (m, 2H), 0.72 (q, *J* = 8.0 Hz, 6H), 1.05 (t, *J* = 8.0 Hz, 9H), 1.25–1.48 (m, 6H), 2.33 (dq, *J* = 7.3 Hz, *J* = 1.8 Hz, 2H), 5.65 (dt, *J* = 11.6 Hz, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 11.6 Hz, 1H), 7.06 (m$_c$, 1H), 7.14–7.21 (m, 2H), 7.27–7.33 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 4.3, 9.3, 11.8, 25.5,*[1] 28.9, 30.0, 33.6, 126.8,*[2] 128.5,*[3] 129.2, 129.5, 133.3, 138.3 ppm.

NMR spectroscopic data for (*E*)-**48**:

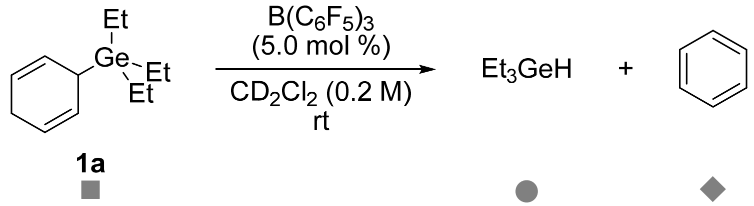
^{1}H NMR (500 MHz, C_6D_6): δ = 0.67–0.74 (m, 2H), 0.75 (q, *J* = 8.0 Hz, 6H), 1.07 (t, *J* = 8.0 Hz, 9H), 1.25–1.48 (m, 6H), 2.14 (dq, *J* = 7.1 Hz, *J* = 1.3 Hz, 2H), 6.17 (dt, *J* = 15.8 Hz, *J* = 7.0 Hz, 1H), 6.39 (d, *J* = 15.8 Hz, 1H), 7.06 (m_c, 1H), 7.14–7.21 (m, 2H), 7.27–7.33 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 4.3, 9.3, 11.8, 25.6,^{*1} 29.4, 33.4, 33.6, 126.4, 127.1,^{*2} 128.8,^{*3} 130.6, 131.1, 138.4 ppm.

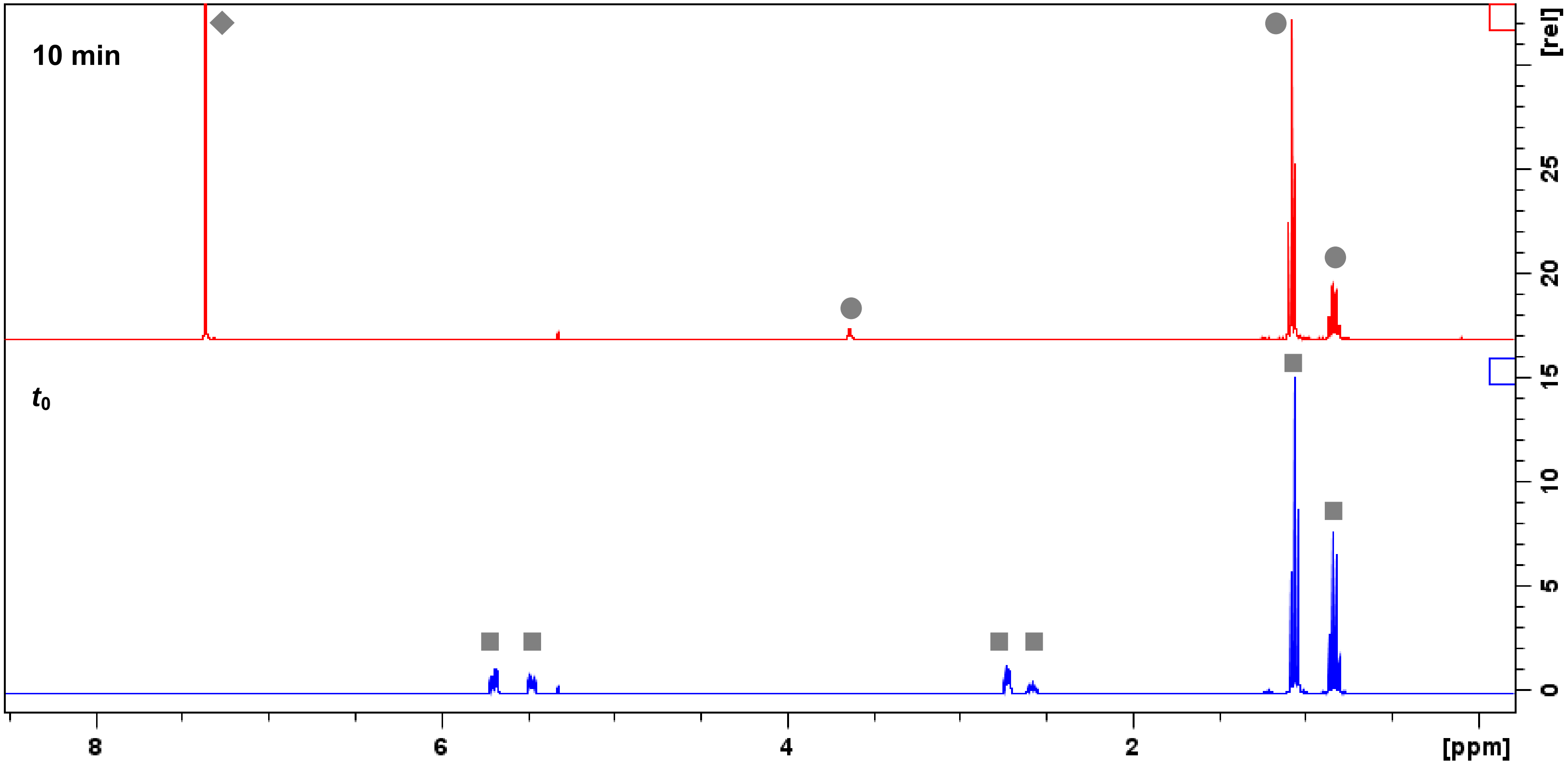
Signals indicated with "*" could not be assigned and can be exchanged, respectively.

5 Time-Dependent NMR Experiments

5.1 Degradation of Surrogate 1a

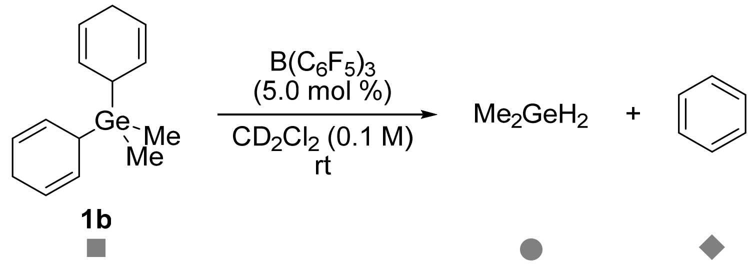
According to GP3, cyclohexa-2,5-dien-1-yltriethylgermane (**1a**, 24 mg, 0.10 mmol, 1.0 equiv) and $B(C_6F_5)_3$ (2.6 mg, 5.0 µmol, 5.0 mol %) were dissolved in CD_2Cl_2 (0.5 mL) and subjected to NMR spectroscopic analysis.



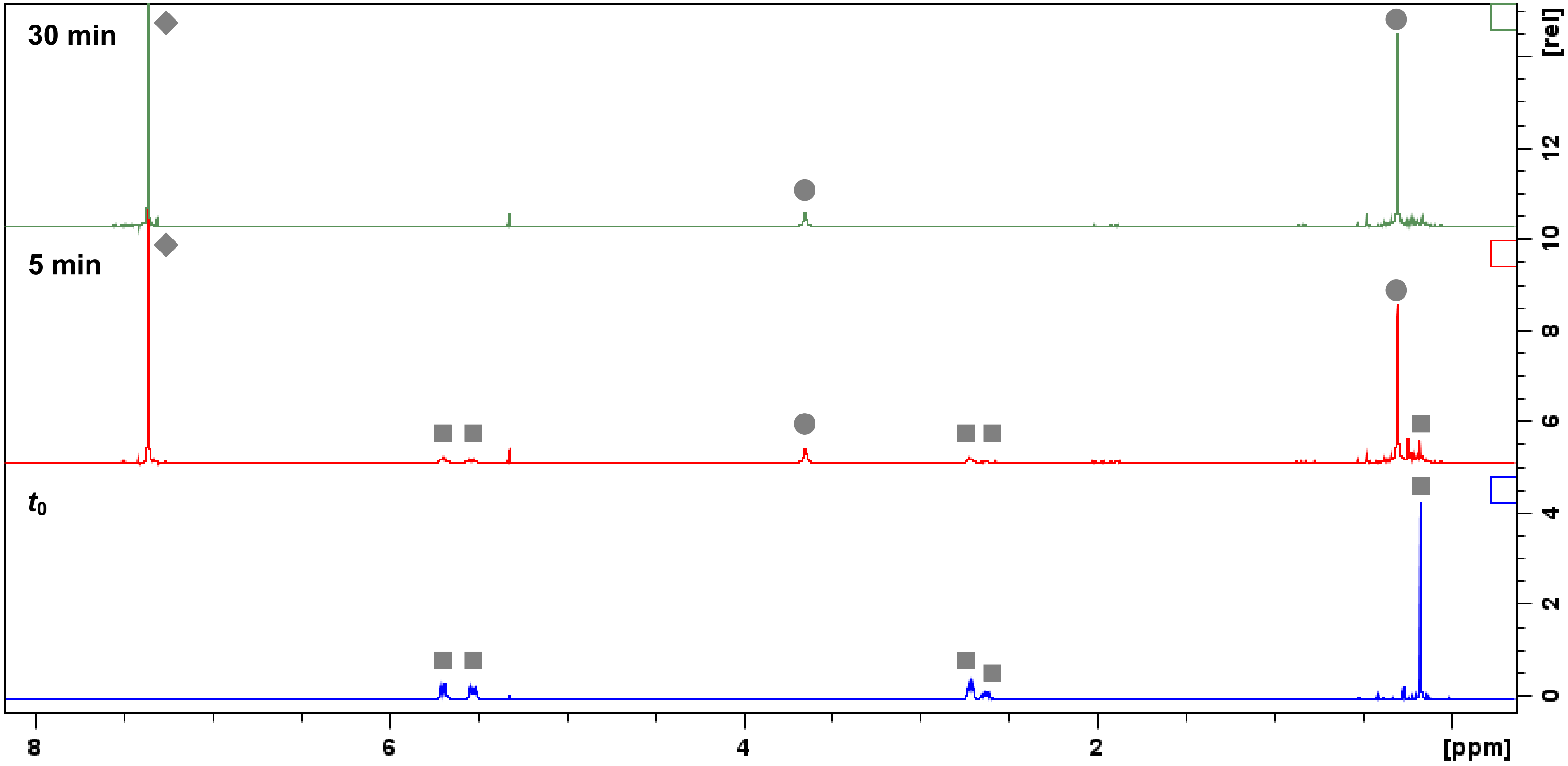


5.2 Degradation of Surrogate 1b

According to GP3, di(cyclohexa-2,5-dien-1-yl)dimethylgermane (**1b**, 13 mg, 0.050 mmol, 1.0 equiv) and $B(C_6F_5)_3$ (1.3 mg, 2.5 µmol, 5.0 mol %) were dissolved in CD_2Cl_2 (0.5 mL) and subjected to NMR spectroscopic analysis.

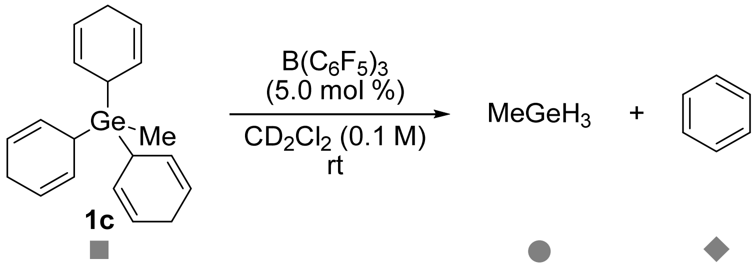


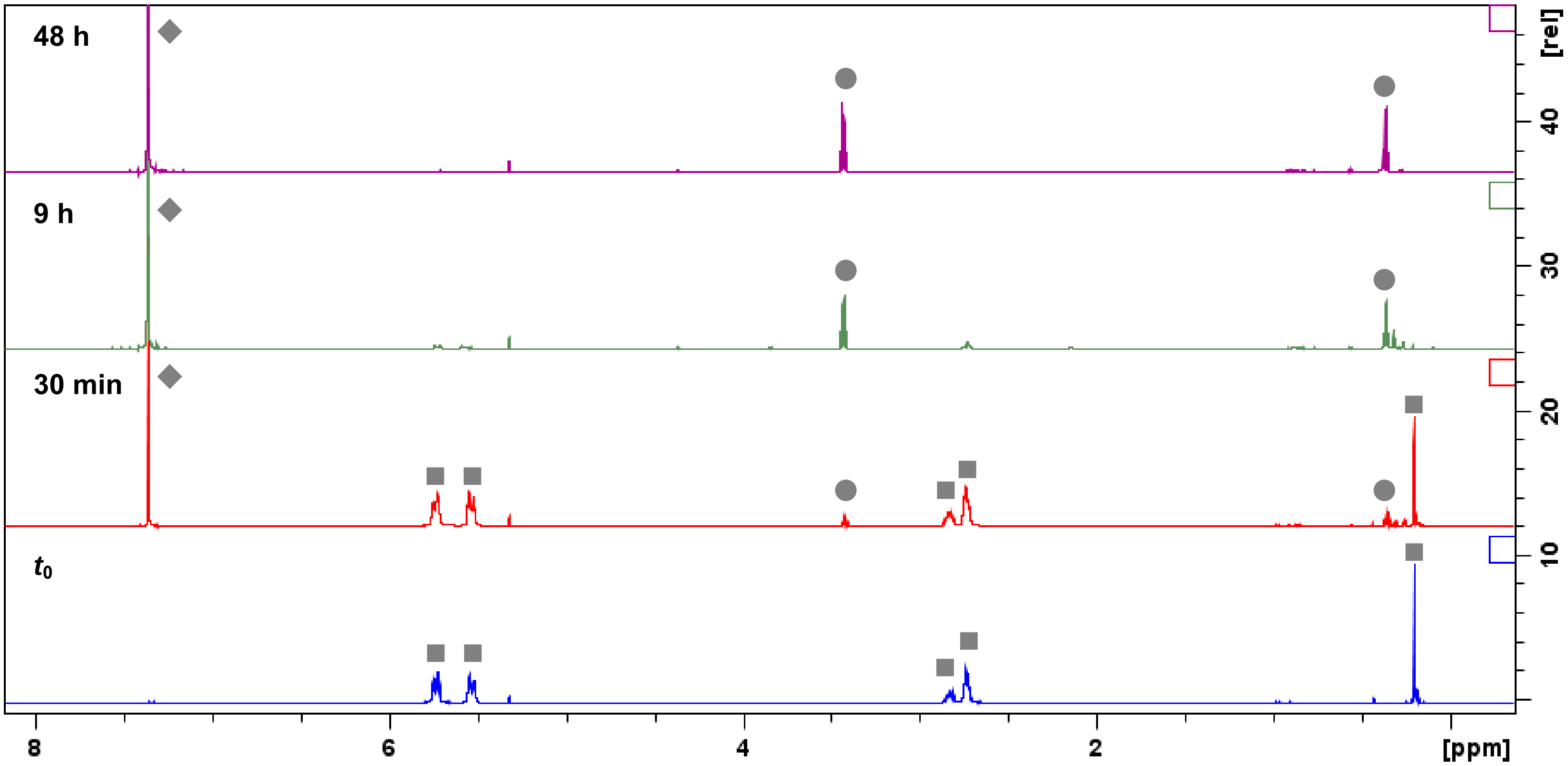
1b



5.3 Degradation of Surrogate 1c

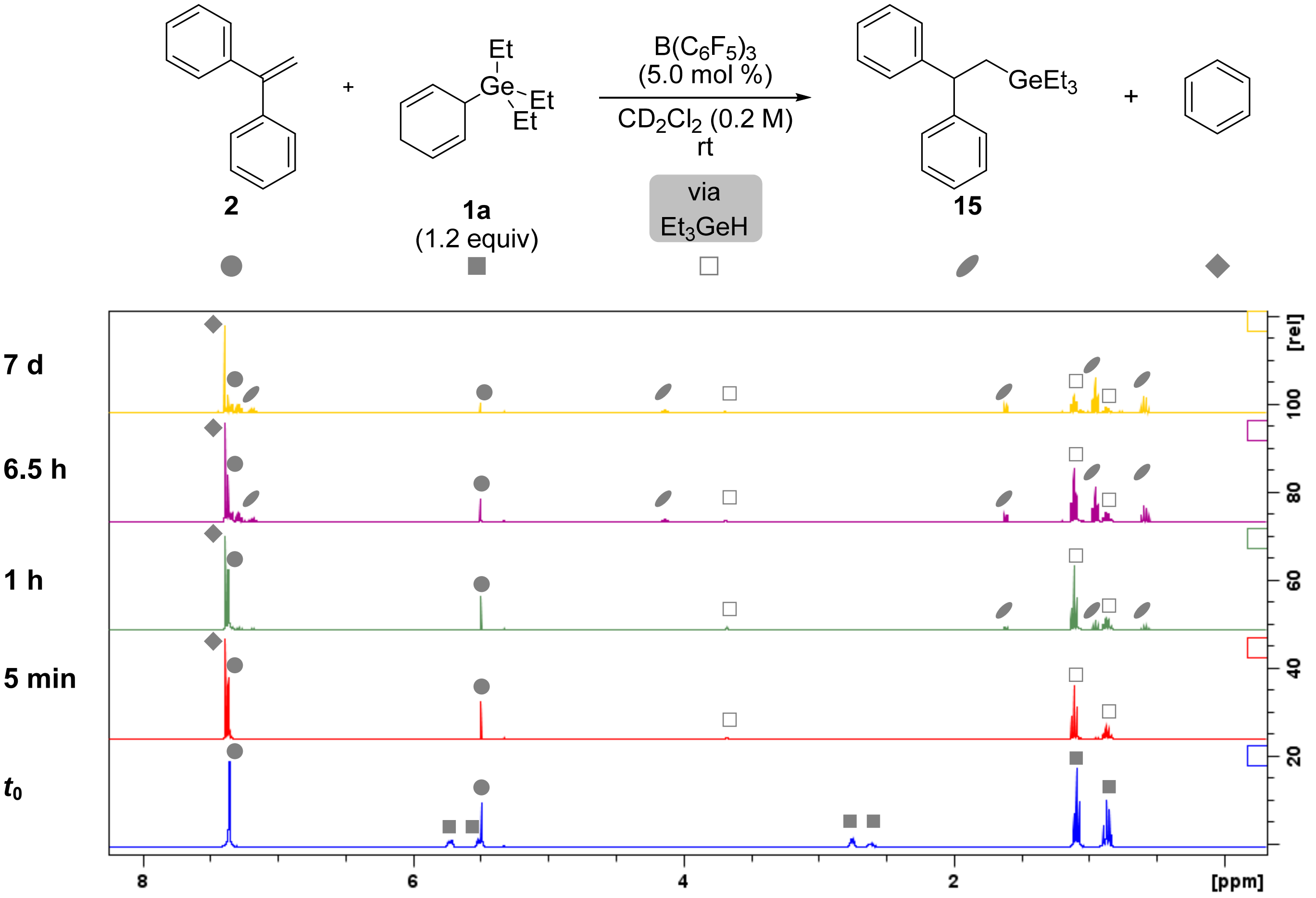
According to GP3, tri(cyclohexa-2,5-dien-1-yl)methylgermane (**1c**, 16 mg, 0.049 mmol, 1.0 equiv) and $B(C_6F_5)_3$ (1.3 mg, 2.5 µmol, 5.0 mol %) were dissolved in CD_2Cl_2 (0.5 mL) and subjected to NMR spectroscopic analysis.





5.4 Reaction of 1,1-Diphenylethylene (2) with Surrogate 1a

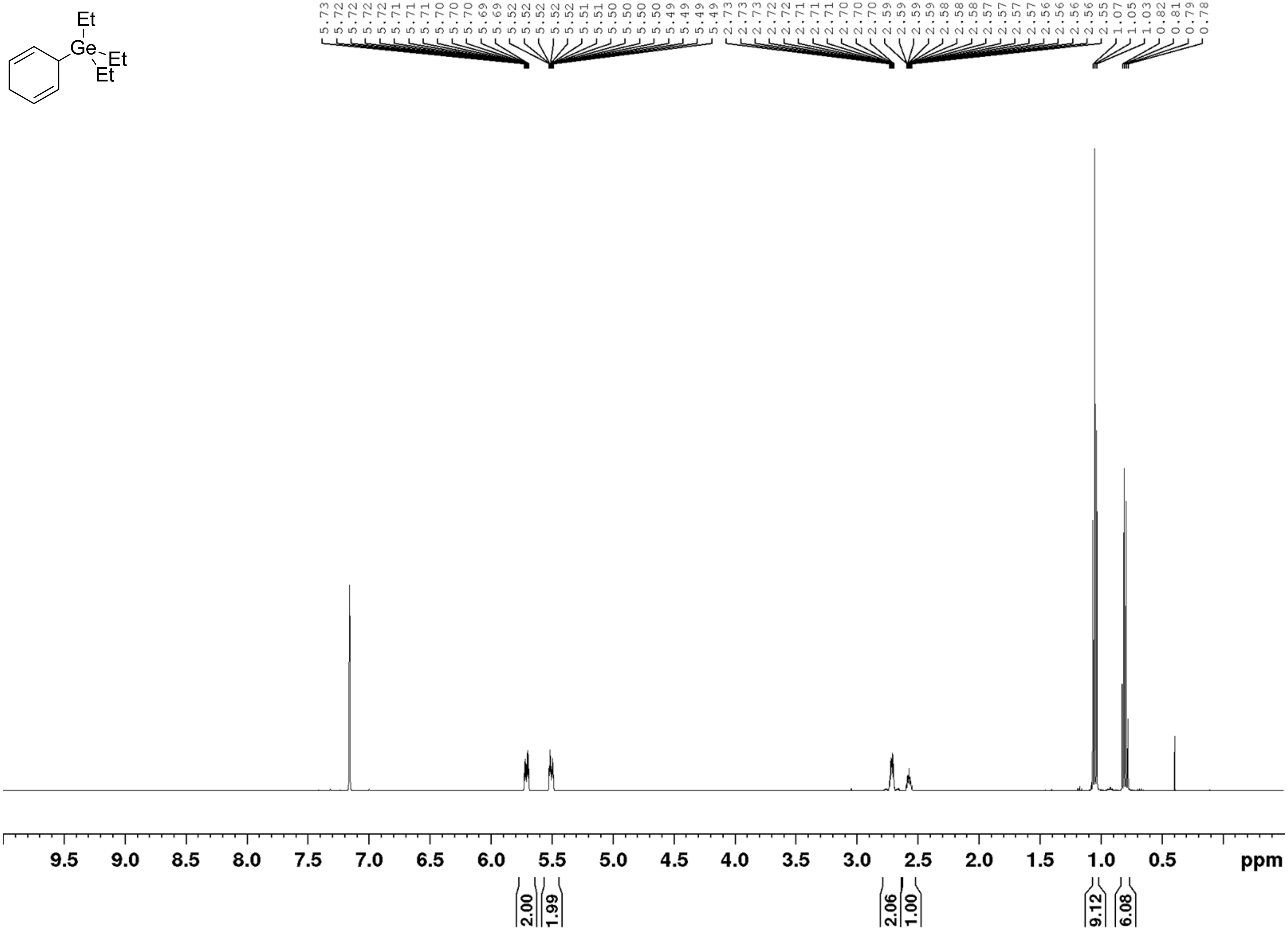
In a glove box, a solution of 1,1-diphenylethylene (**2**, 18.0 mg, 0.100 mmol, 1.00 equiv) and surrogate **1a** (23.9 mg, 0.120 mmol, 1.20 equiv) in CD_2Cl_2 (0.45 mL) was added to a Wilmad® J-Young NMR tube. The NMR tube was capped, taken out of the glove box to measure the t_0 ^{1}H NMR spectrum, and then a solution of $B(C_6F_5)_3$ (2.6 mg, 5.0 µmol, 5.0 mol %) in CD_2Cl_2 (0.05 mL) was added to the reagent solution inside the glovebox. The NMR tube was capped immediately and ^{1}H NMR spectra were measured in the time interval as indicated.



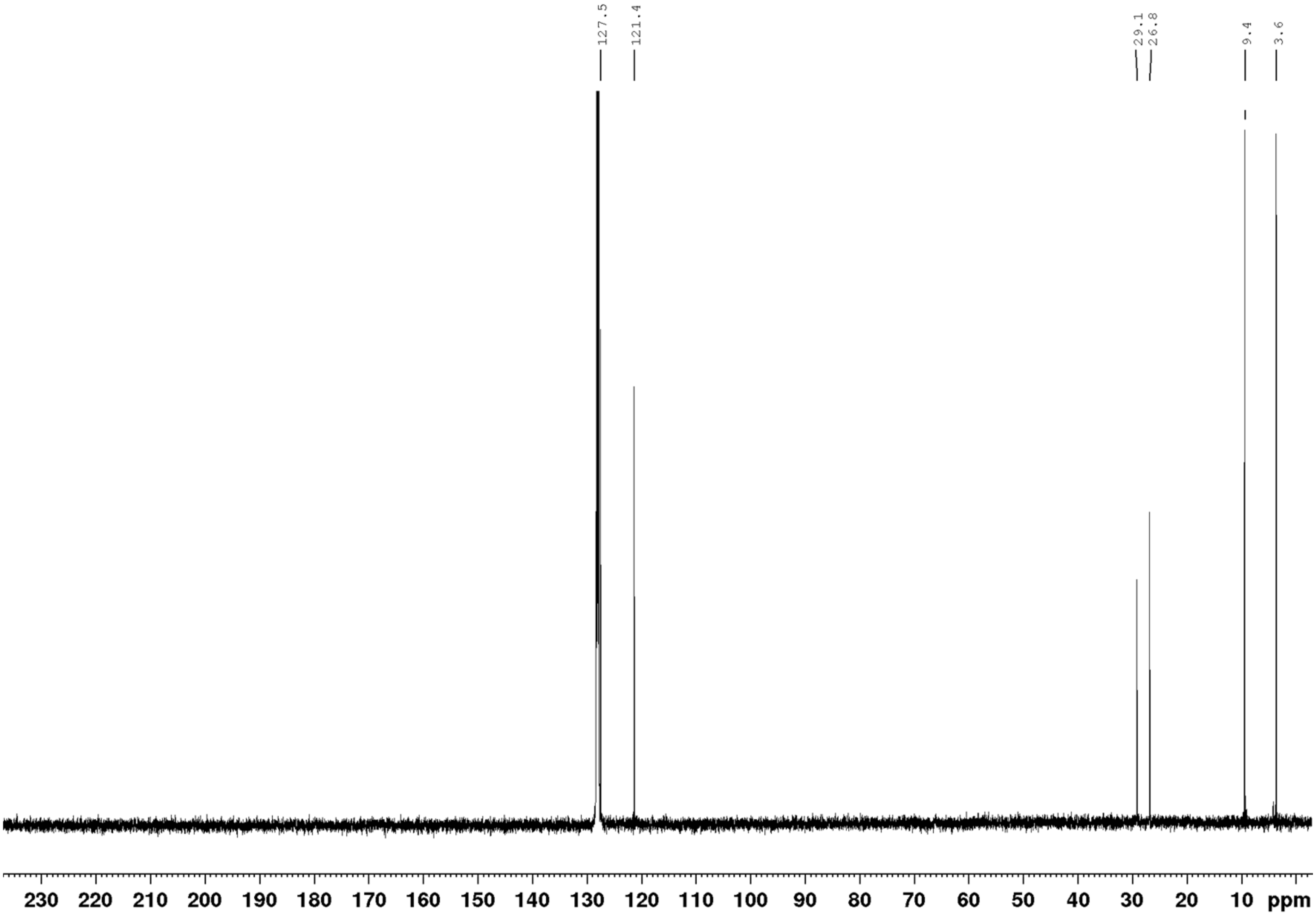
6 NMR Spectra

Cyclohexa-2,5-dien-1-yltriethylgermane (1a)

^{1}H NMR (500 MHz, C_6D_6):

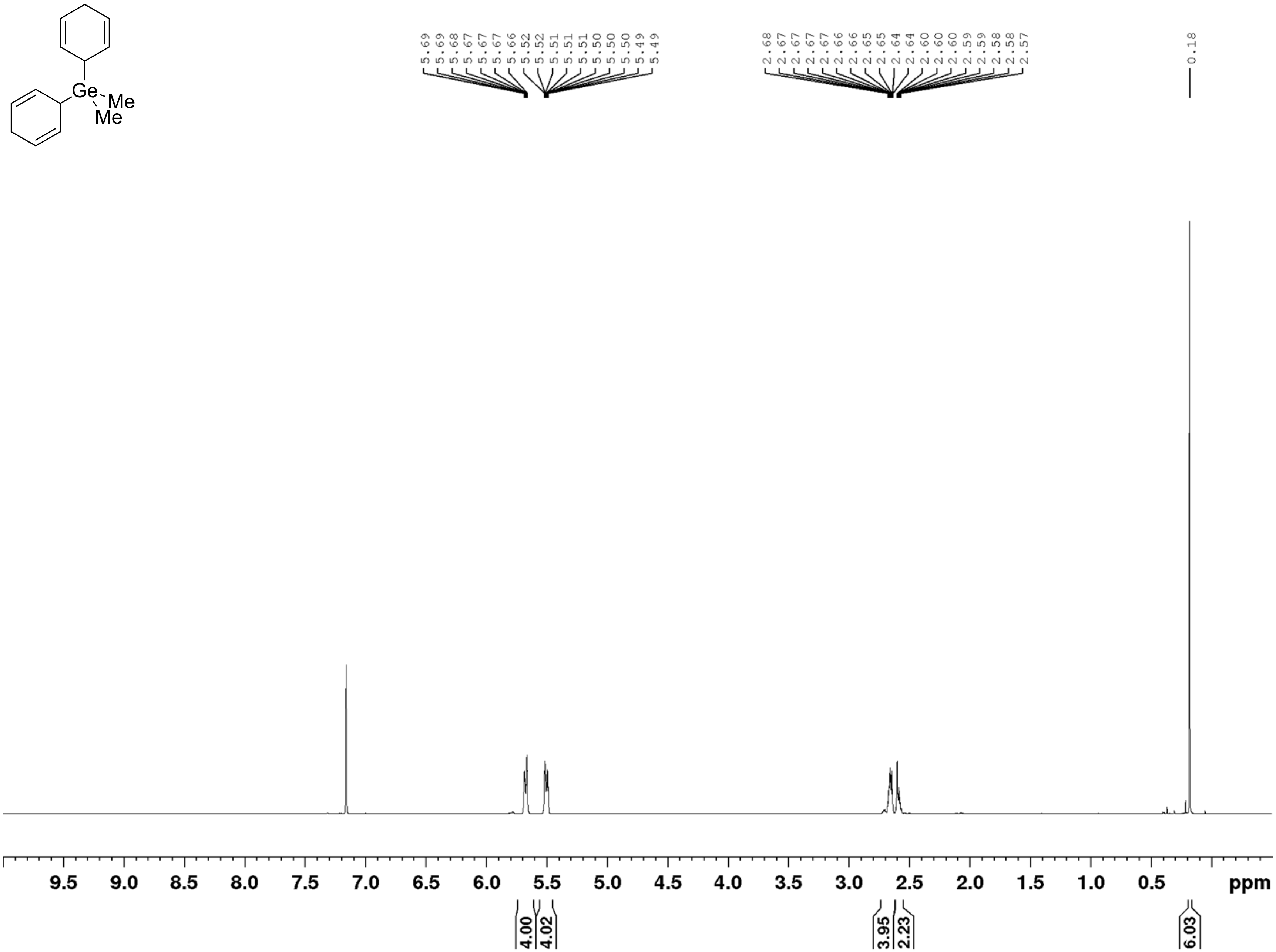


$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6)

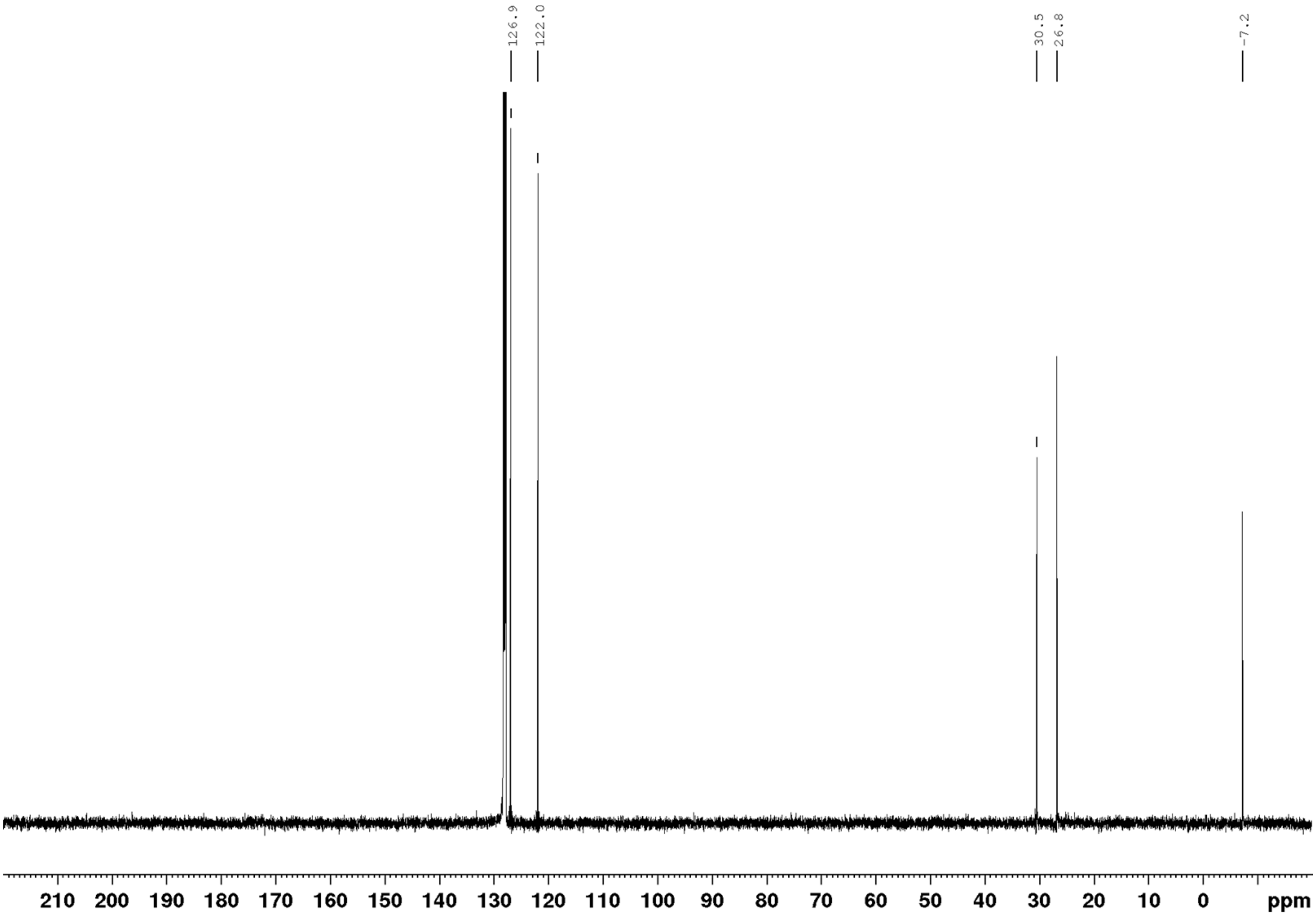


Di(cyclohexa-2,5-dien-1-yl)dimethylgermane (1b)

^{1}H NMR (500 MHz, C_6D_6):

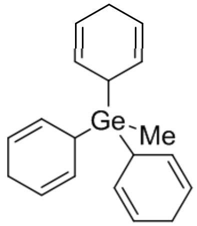


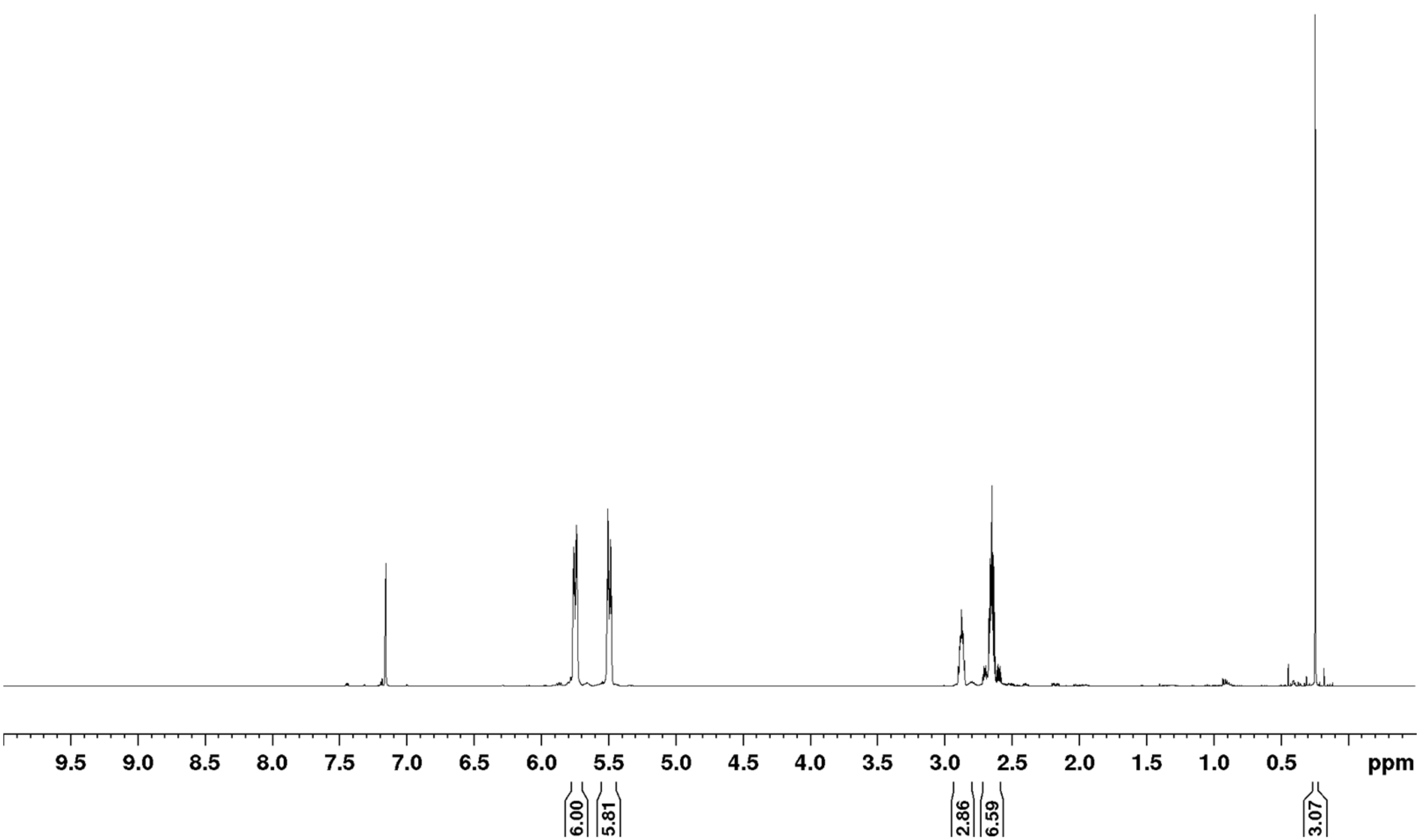
$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6):



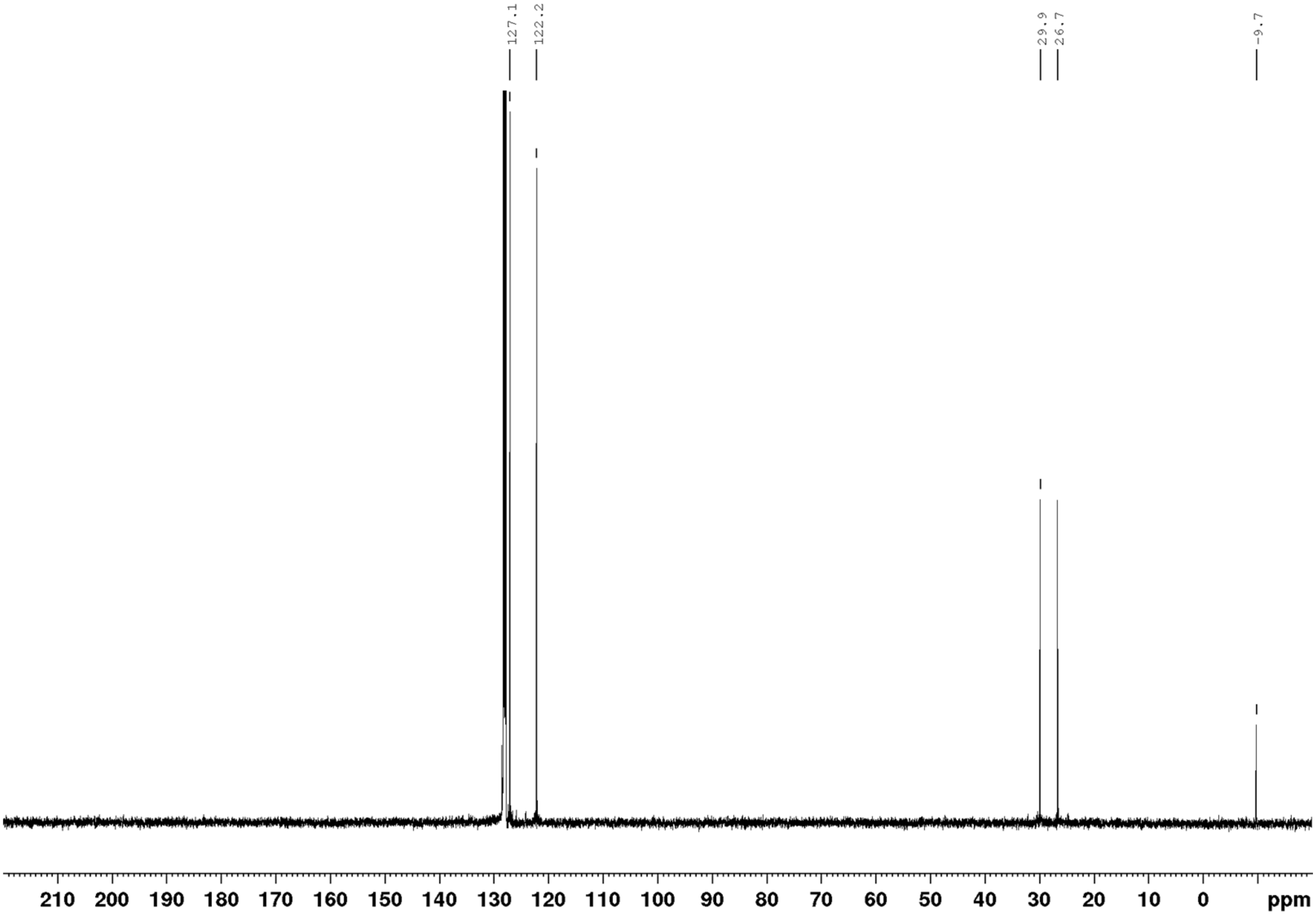
Tri(cyclohexa-2,5-dien-1-yl)methylgermane (1c)

^{1}H NMR (500 MHz, C_6D_6):



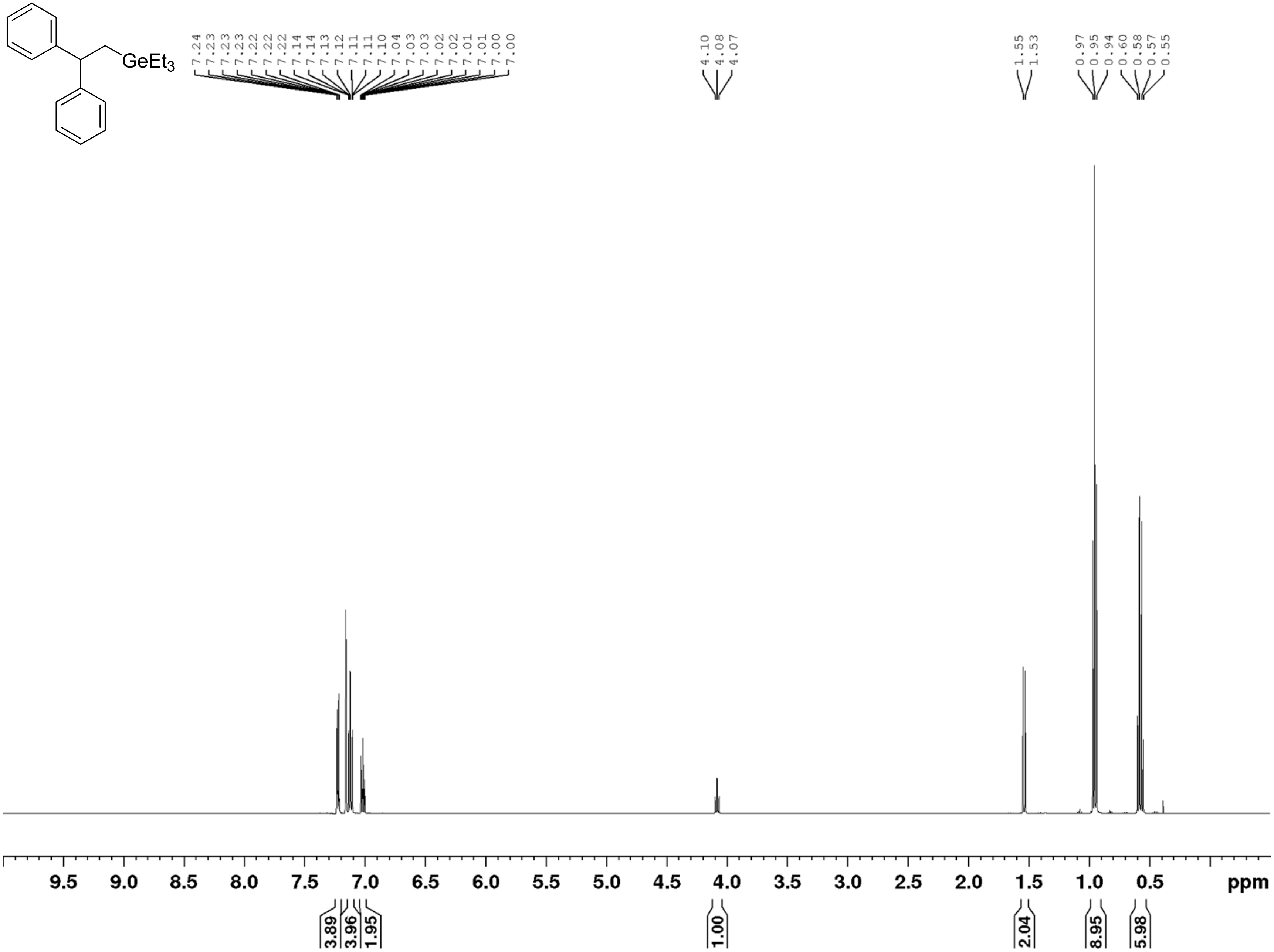


$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6):

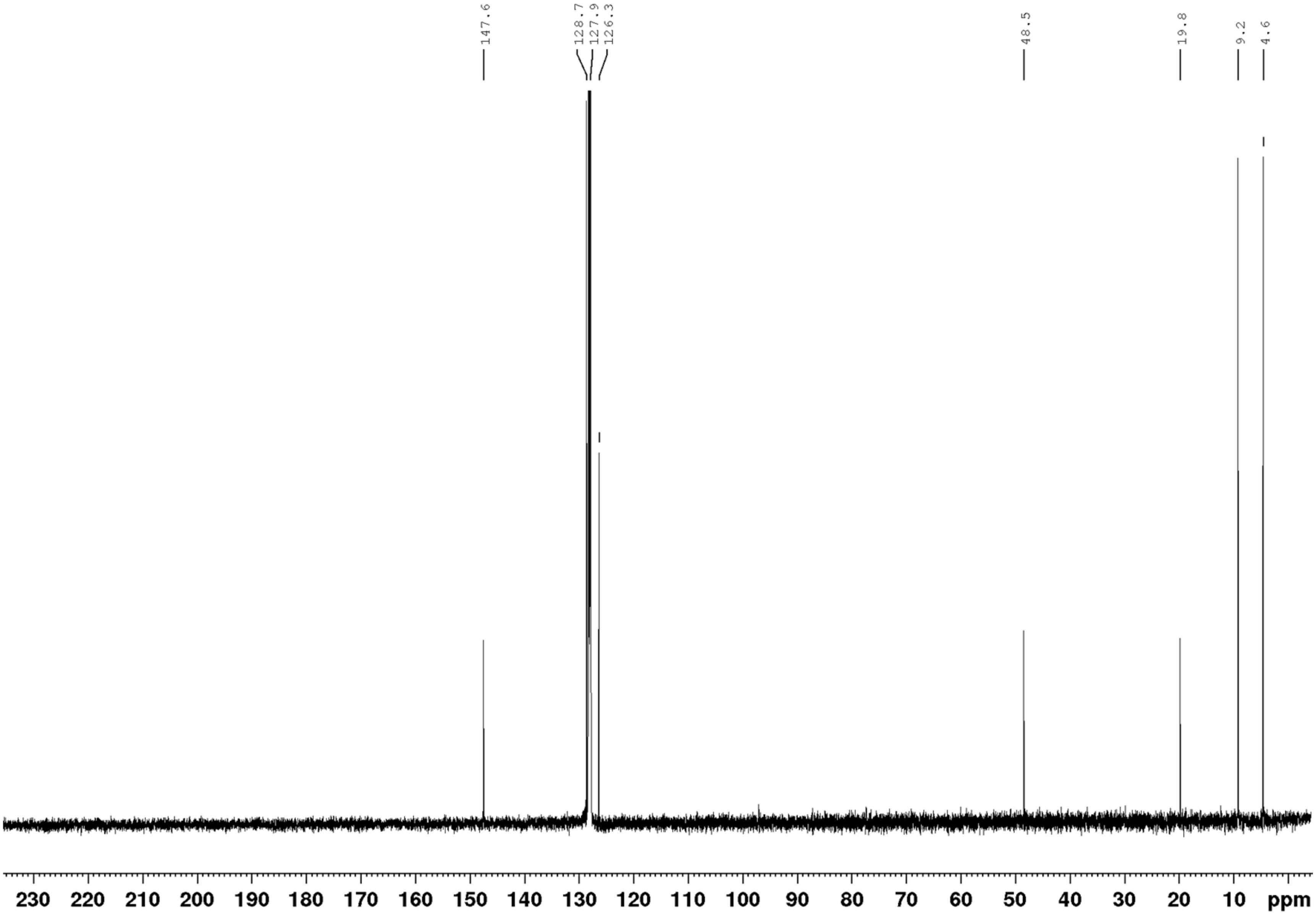


(2,2-Diphenylethyl)triethylgermane (15)

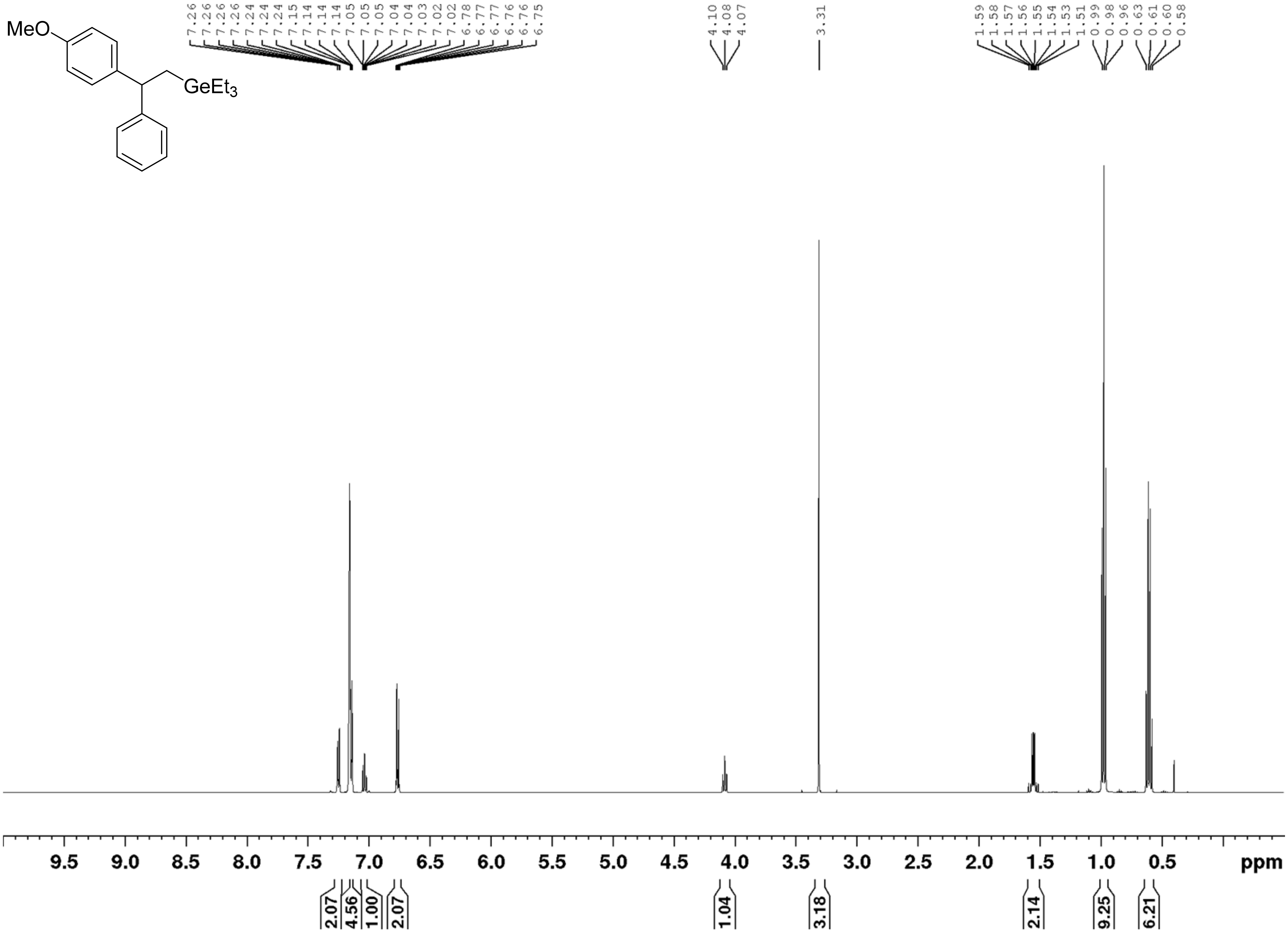
^{1}H NMR (500 MHz, C_6D_6):



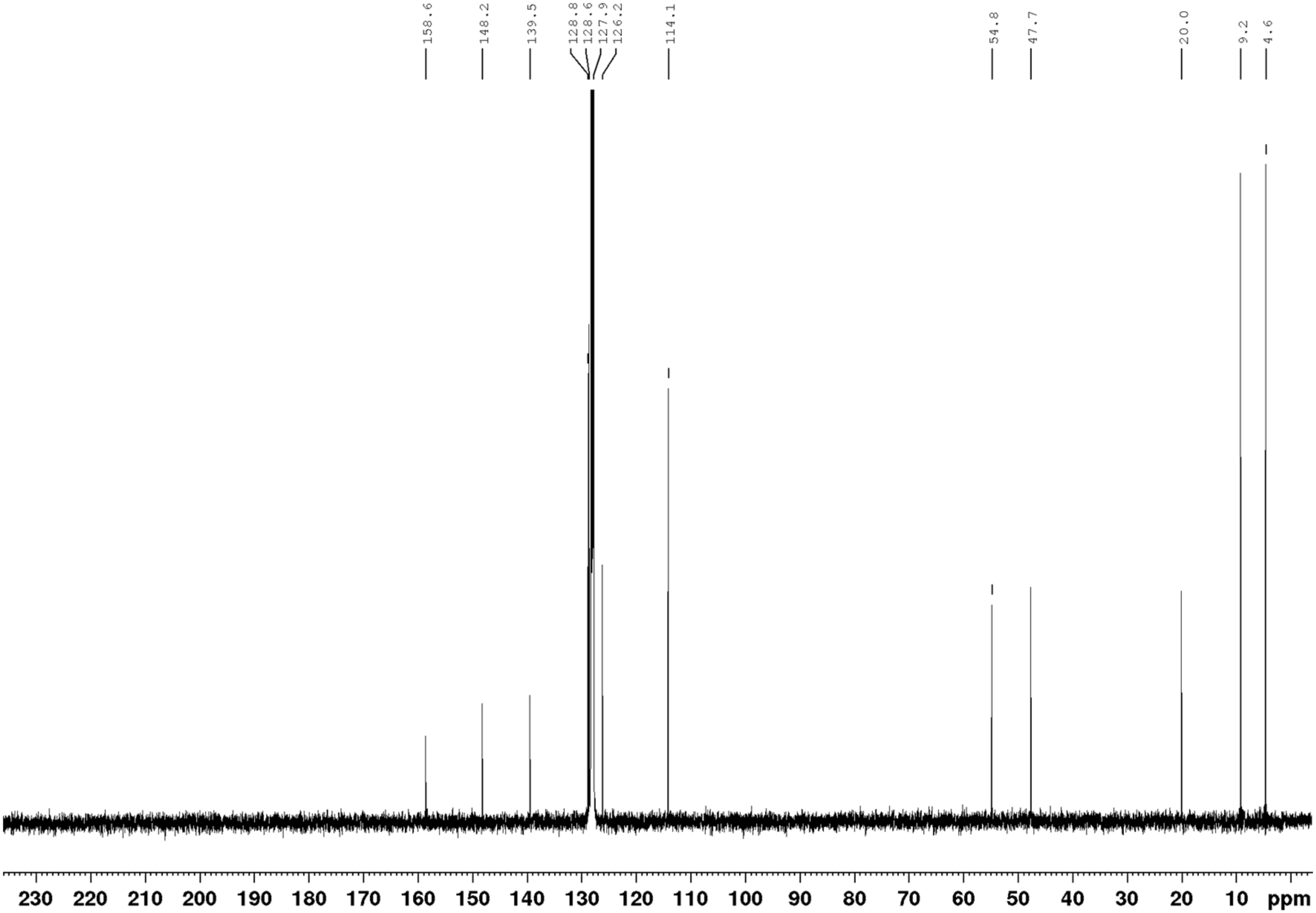
$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6):



(2-(4-Methoxyphenyl)-2-phenylethyl)triethylgermane (16)
^{1}H NMR (500 MHz, C_6D_6):

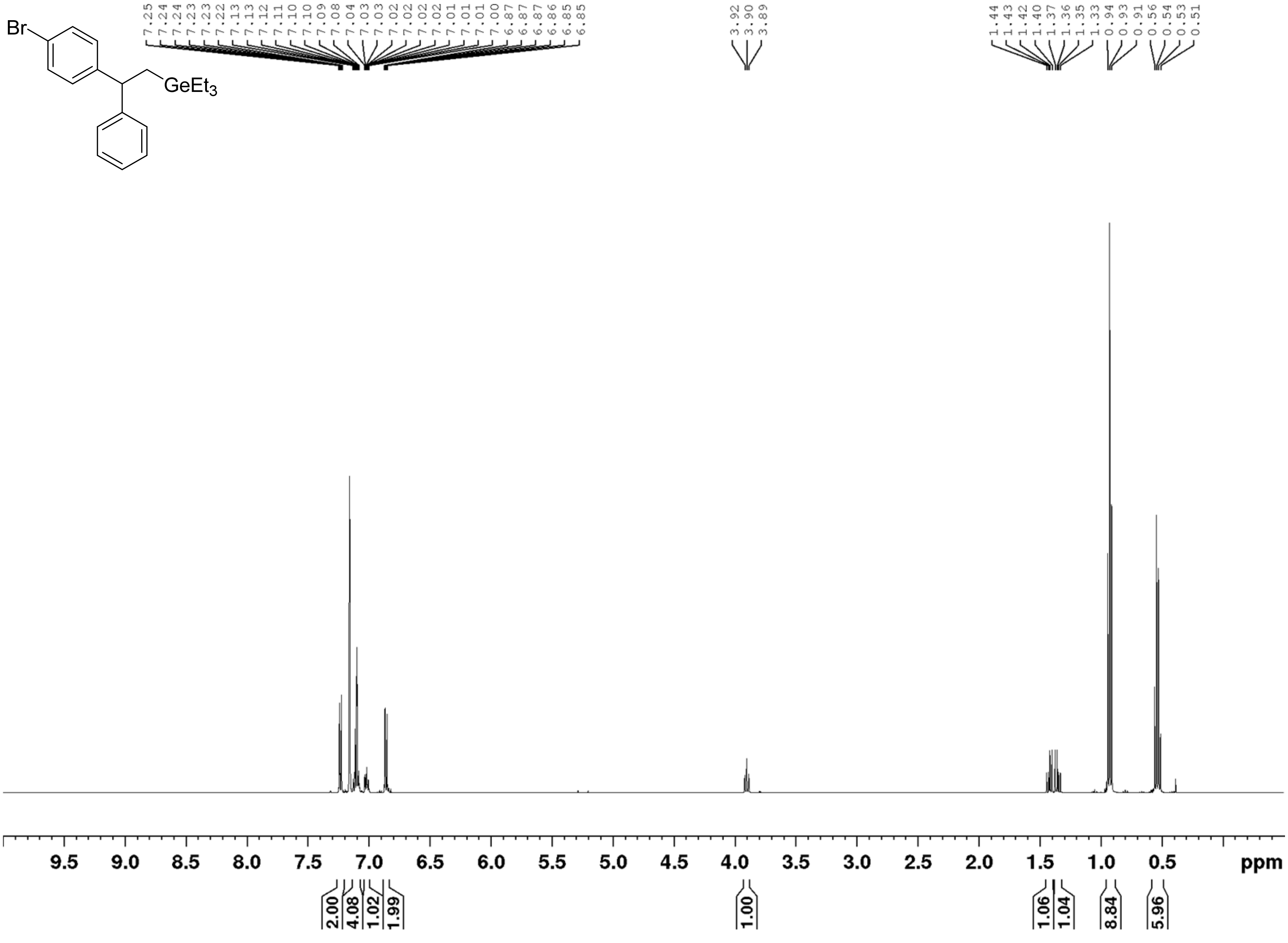


$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6):

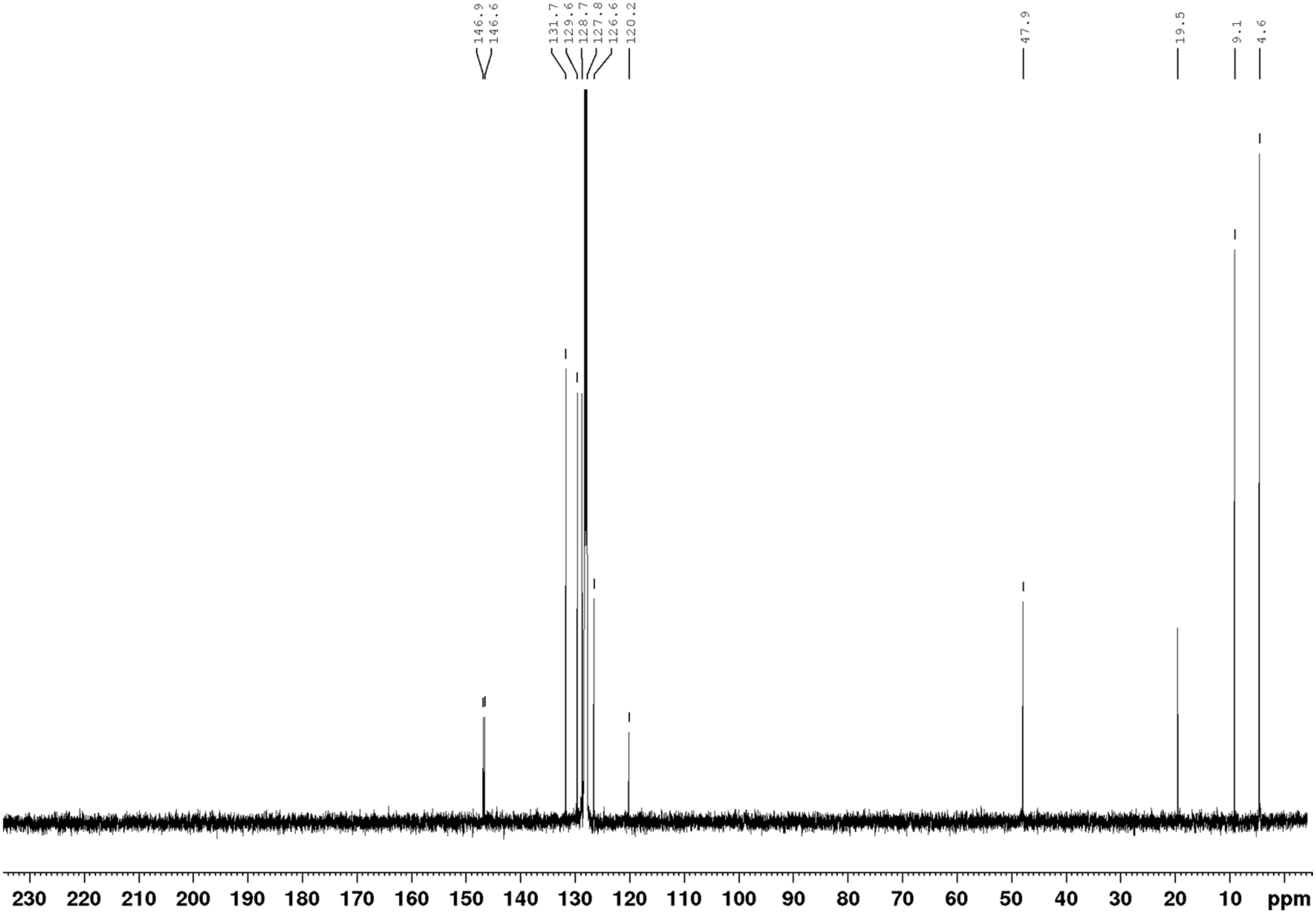


(2-(4-Bromophenyl)-2-phenylethyl)triethylgermane (17)

^{1}H NMR (500 MHz, C_6D_6):

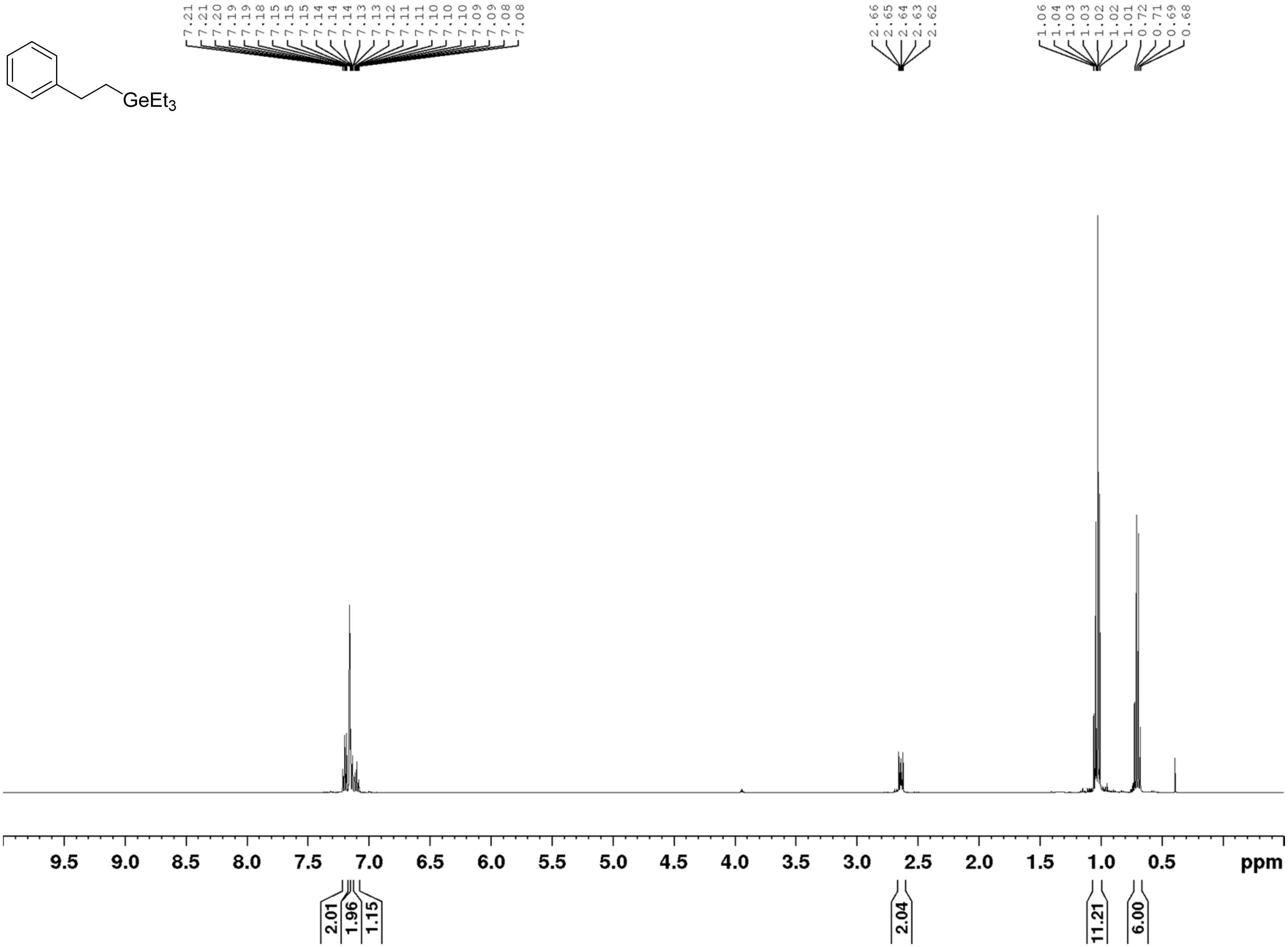


$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6):

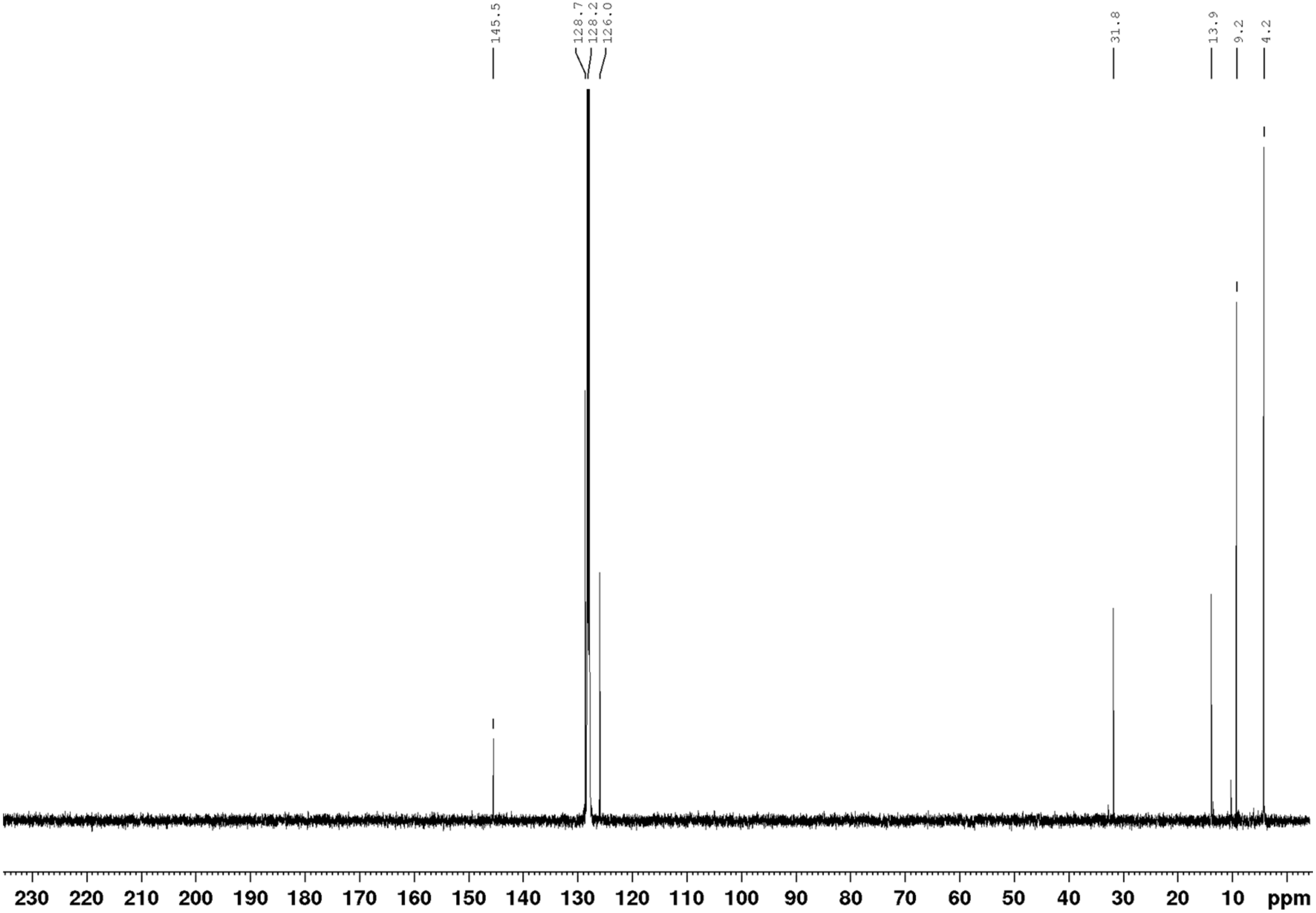


Triethyl(phenylethyl)germane (18)

^{1}H NMR (500 MHz, C_6D_6):

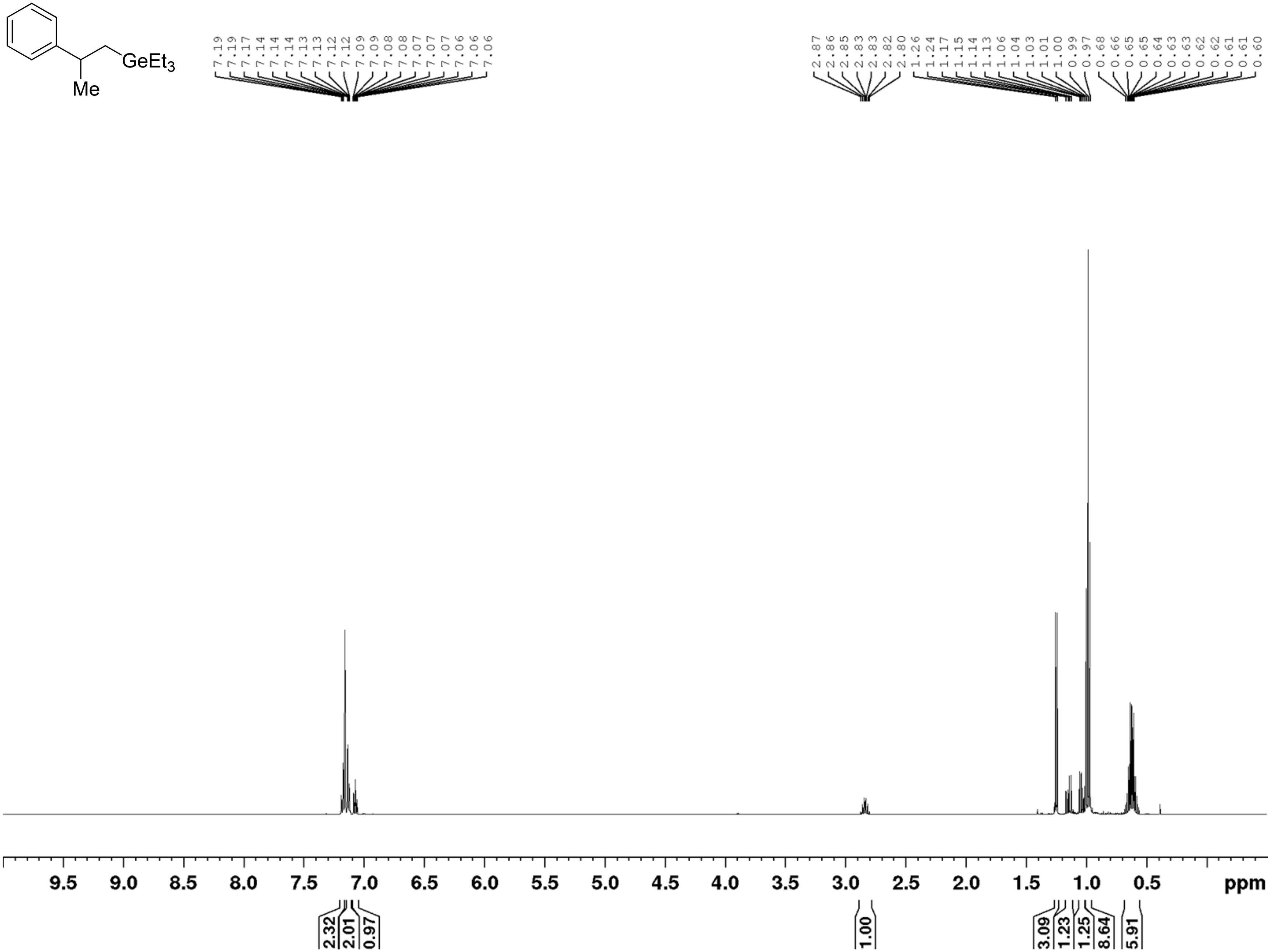


$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6):

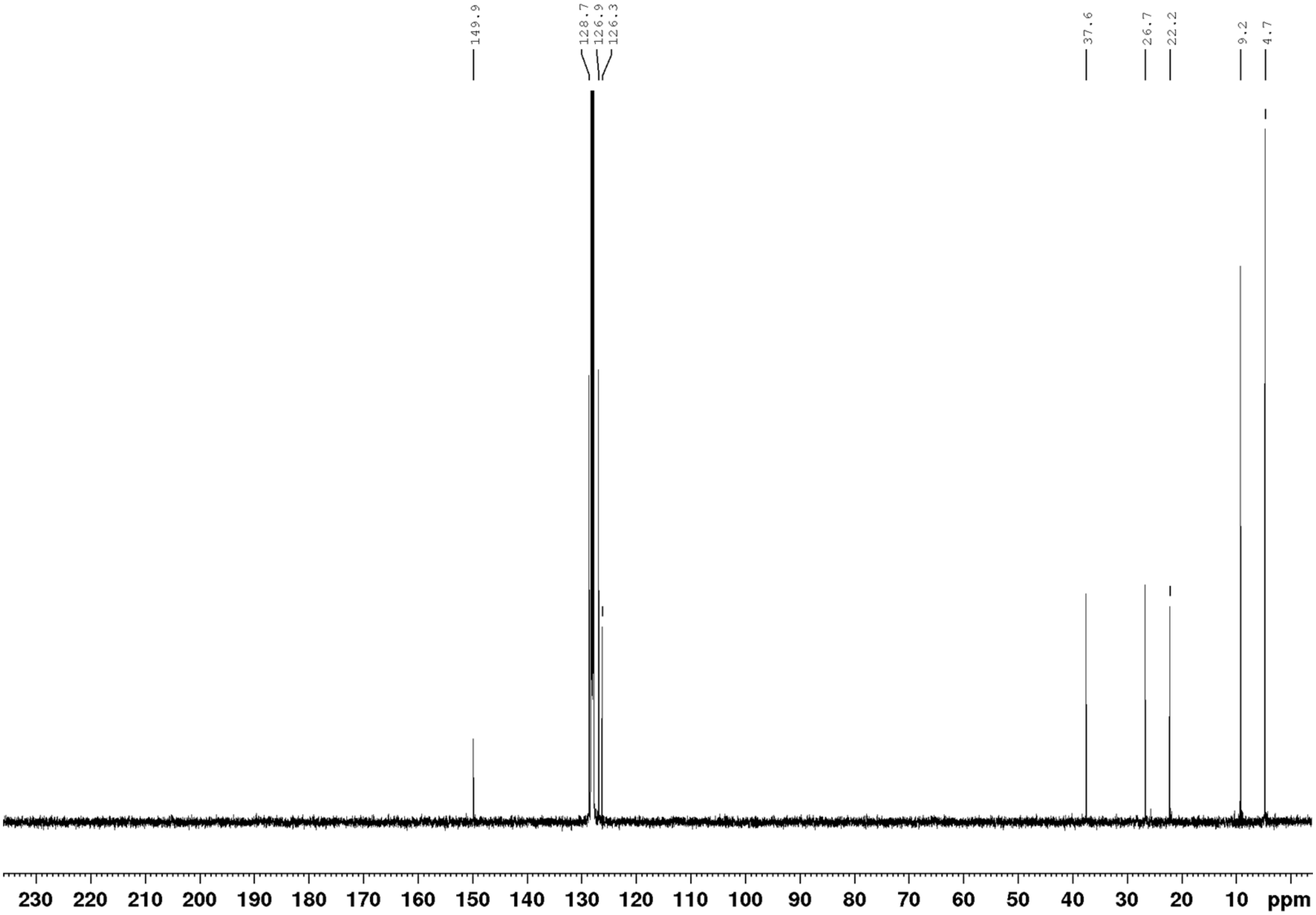


Triethyl(2-phenylpropyl)germane (19)

^{1}H NMR (500 MHz, C_6D_6):

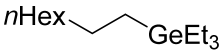


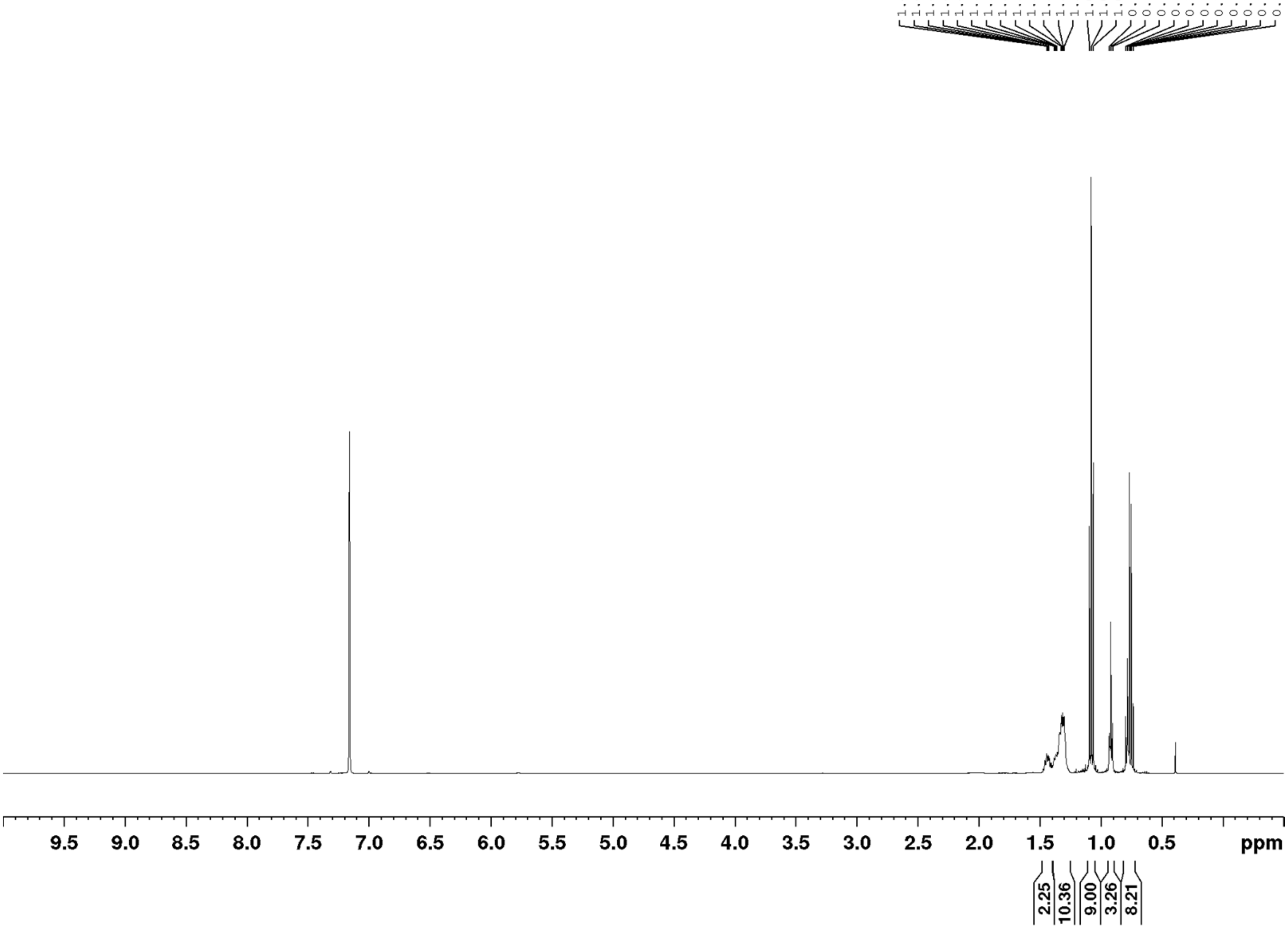
$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6):



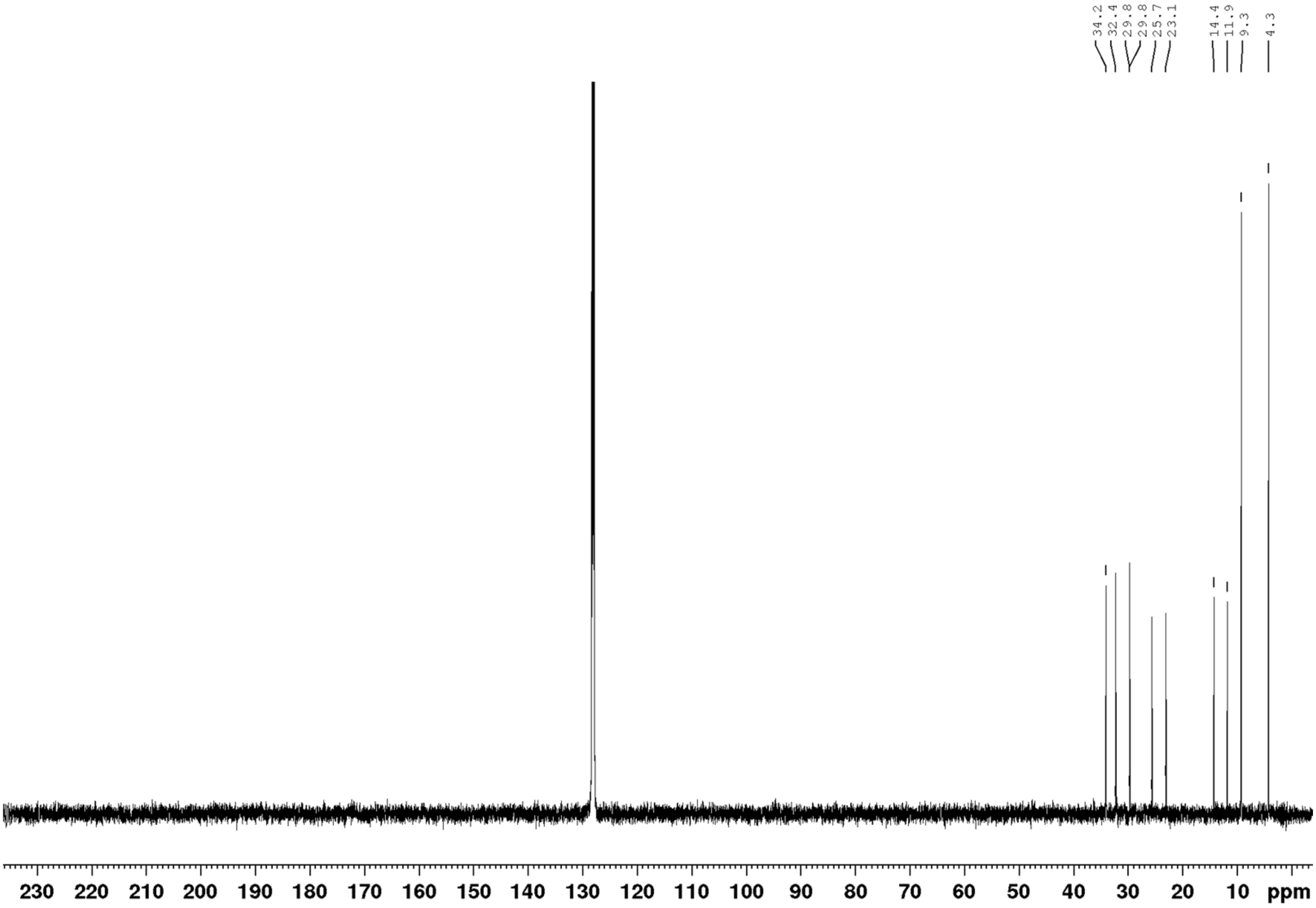
Triethyl(octyl)germane (20)

^{1}H NMR (500 MHz, C_6D_6):



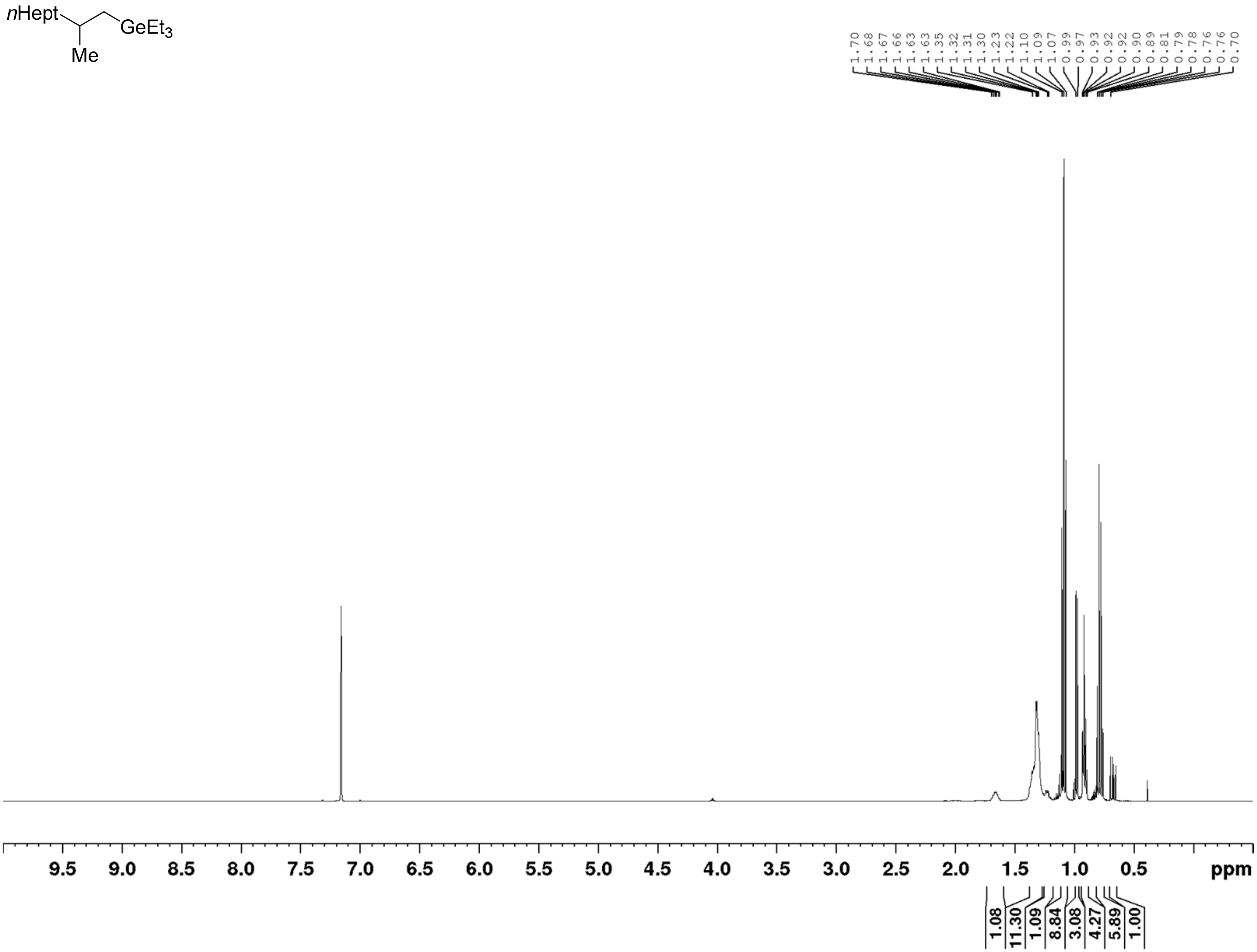


$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6):

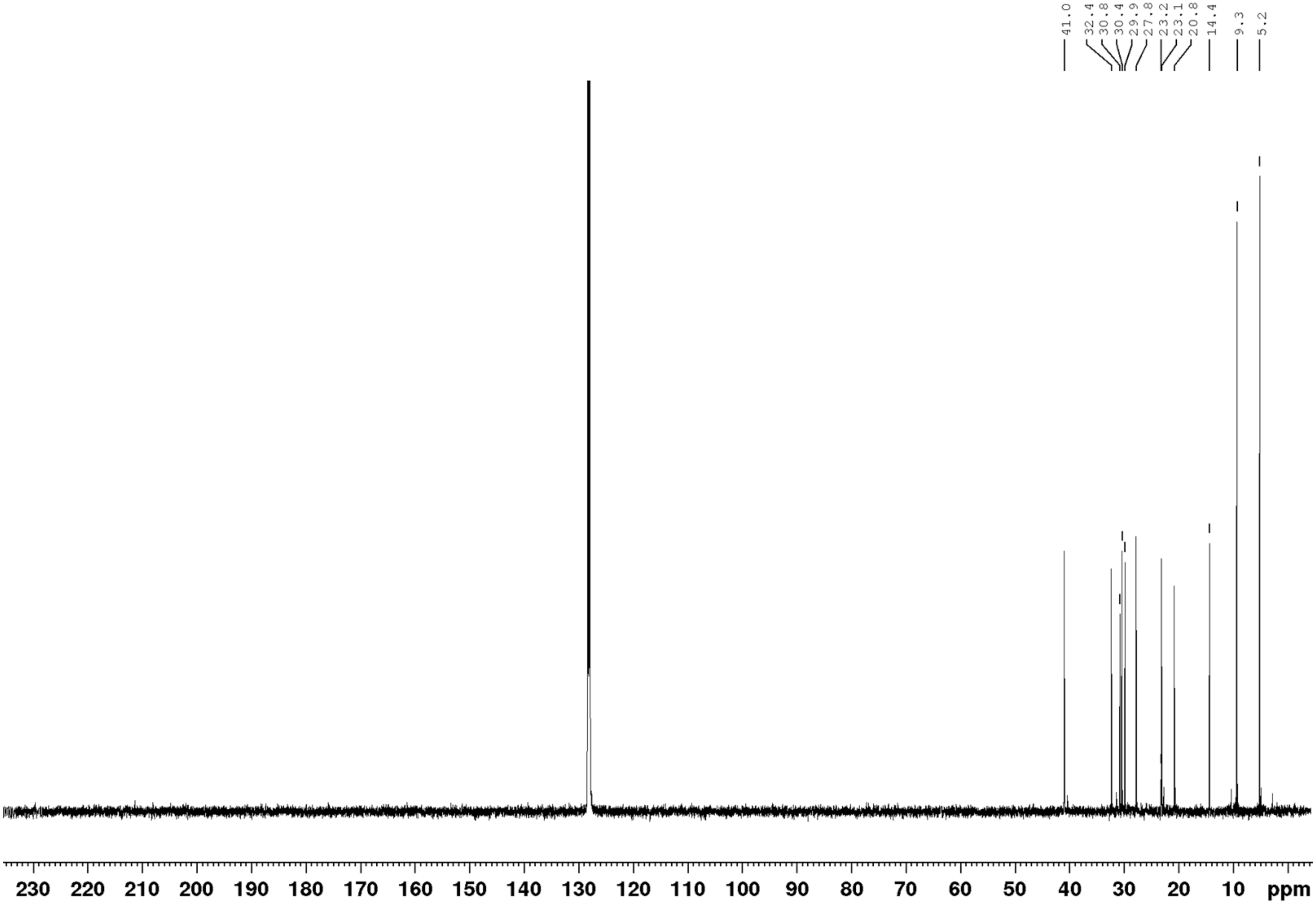


Triethyl(2-methylnonyl)germane (21)

^{1}H NMR (500 MHz, C_6D_6):

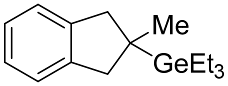


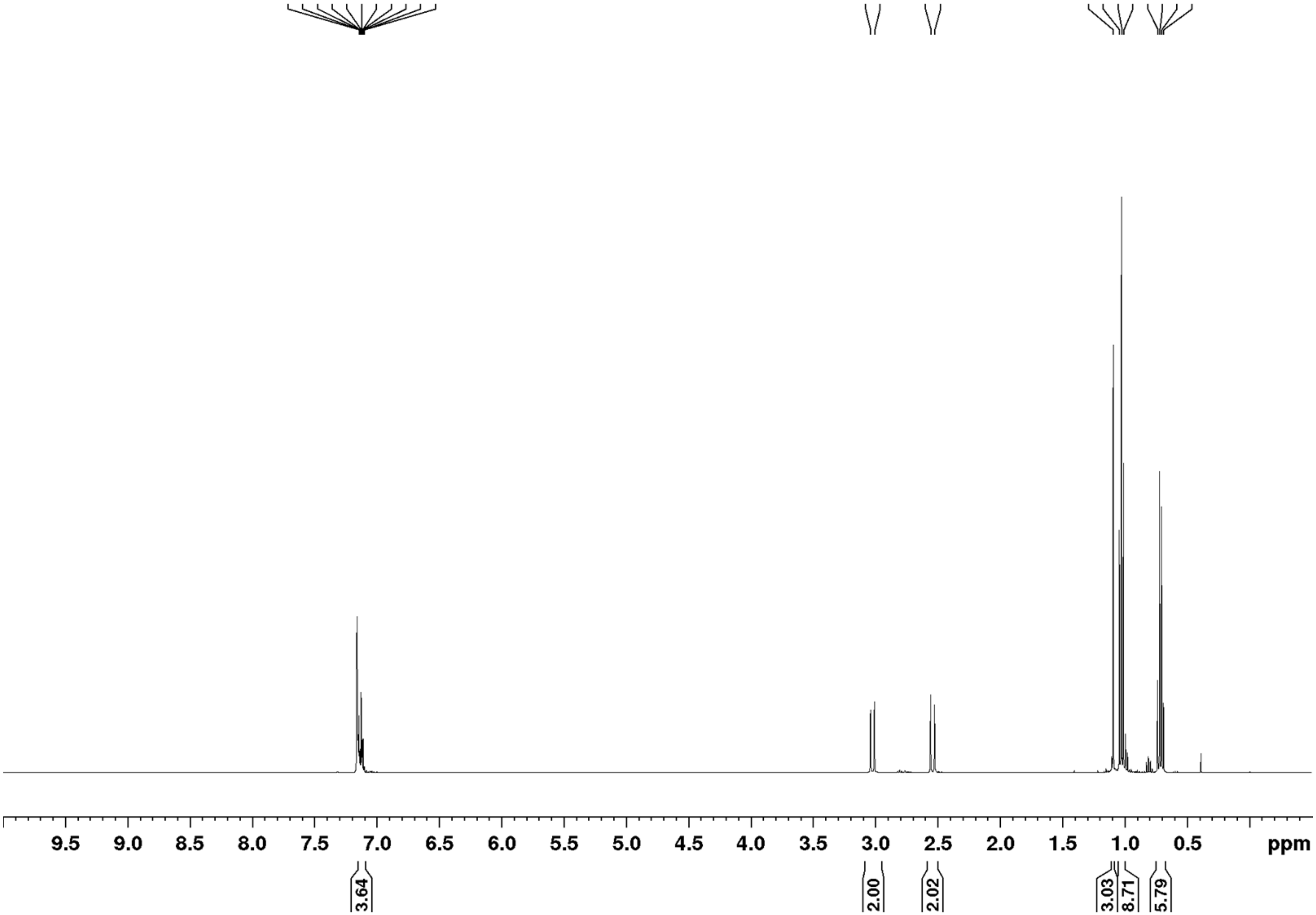
$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6):



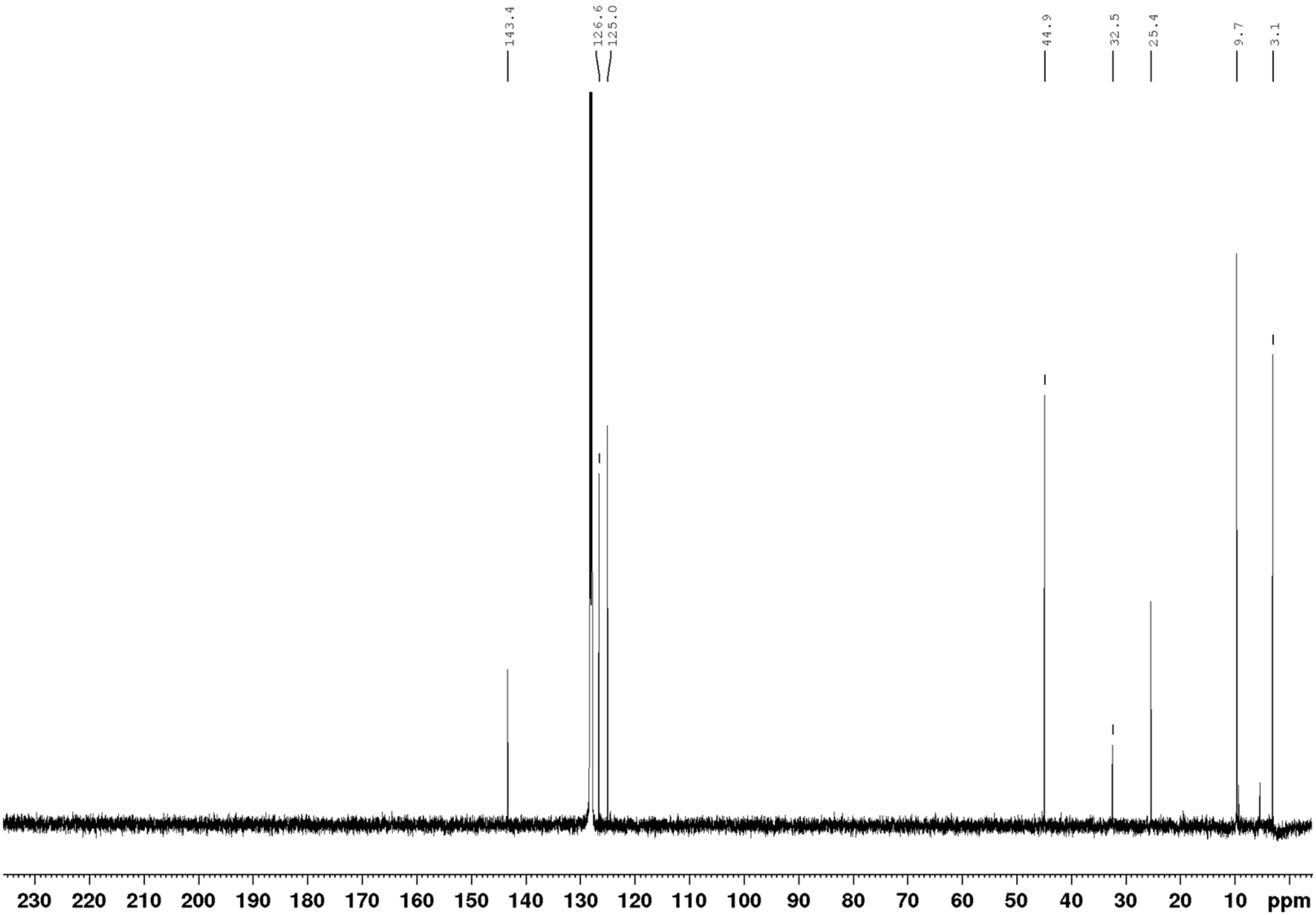
Triethyl(2-methyl-2,3-dihydro-1*H*-inden-2-yl)germane (22)

^{1}H NMR (500 MHz, C_6D_6):



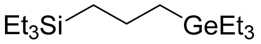


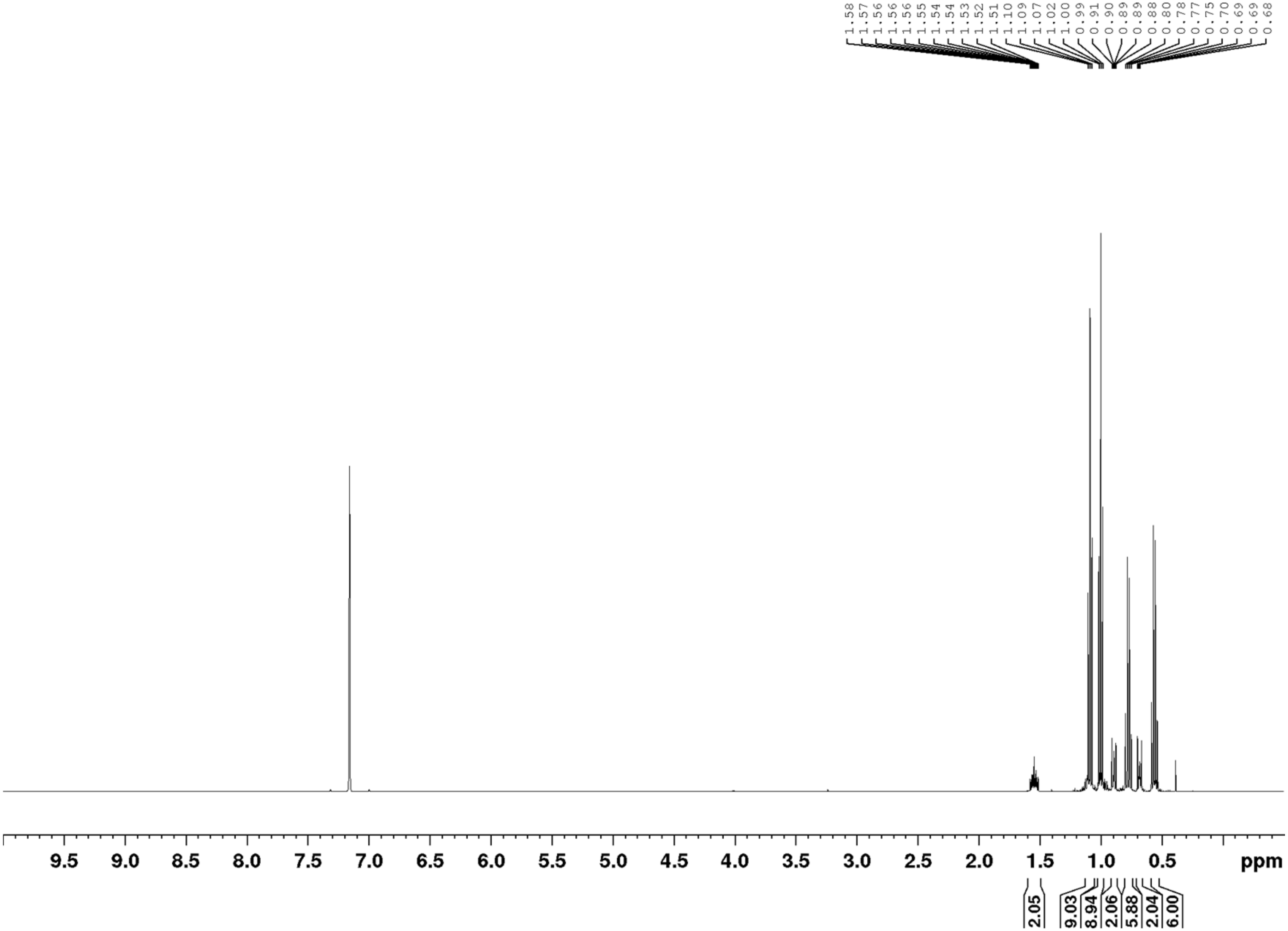
$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6):



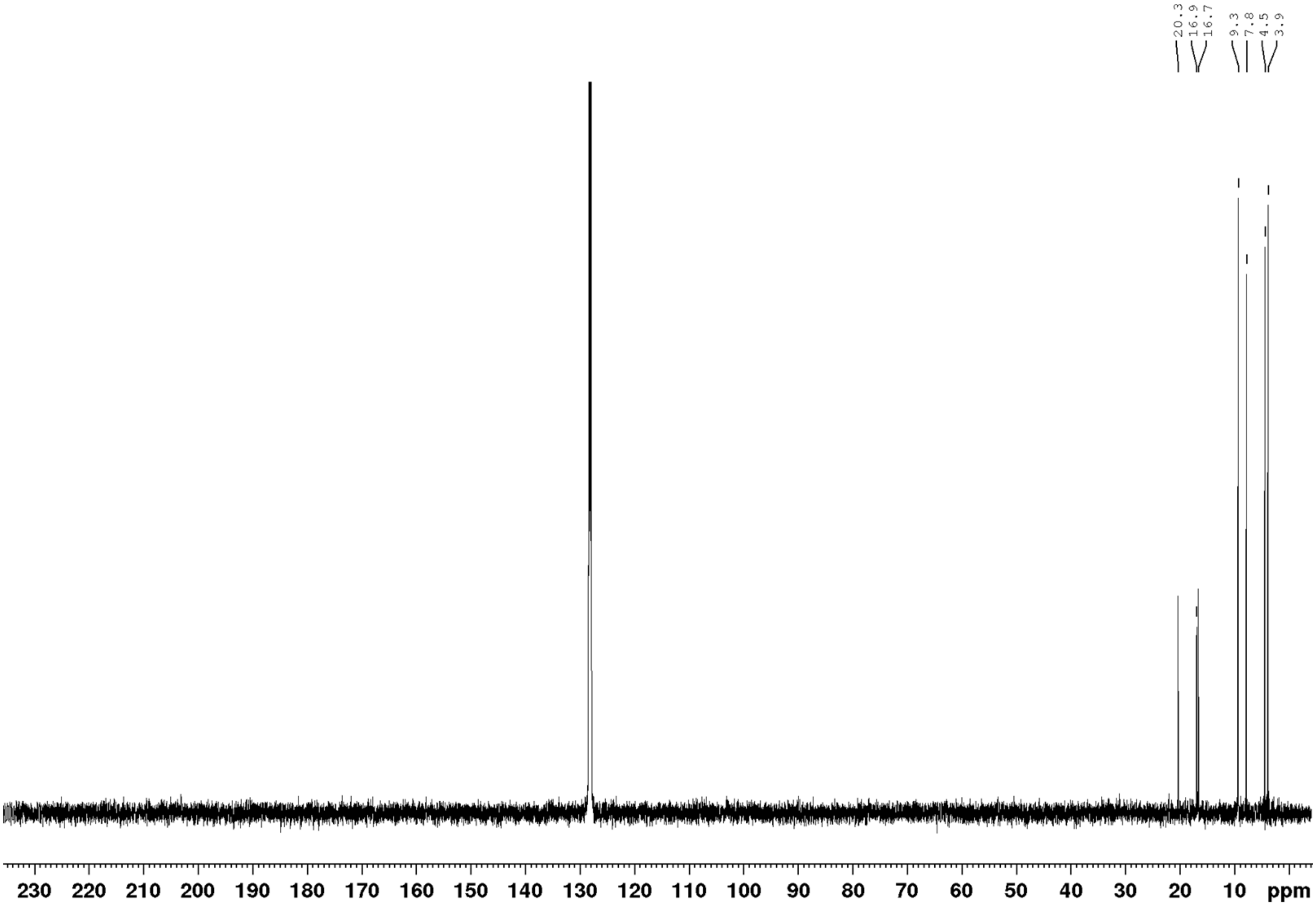
Triethyl(3-(triethylgermyl)propyl)silane (23)

^{1}H NMR (500 MHz, C_6D_6):

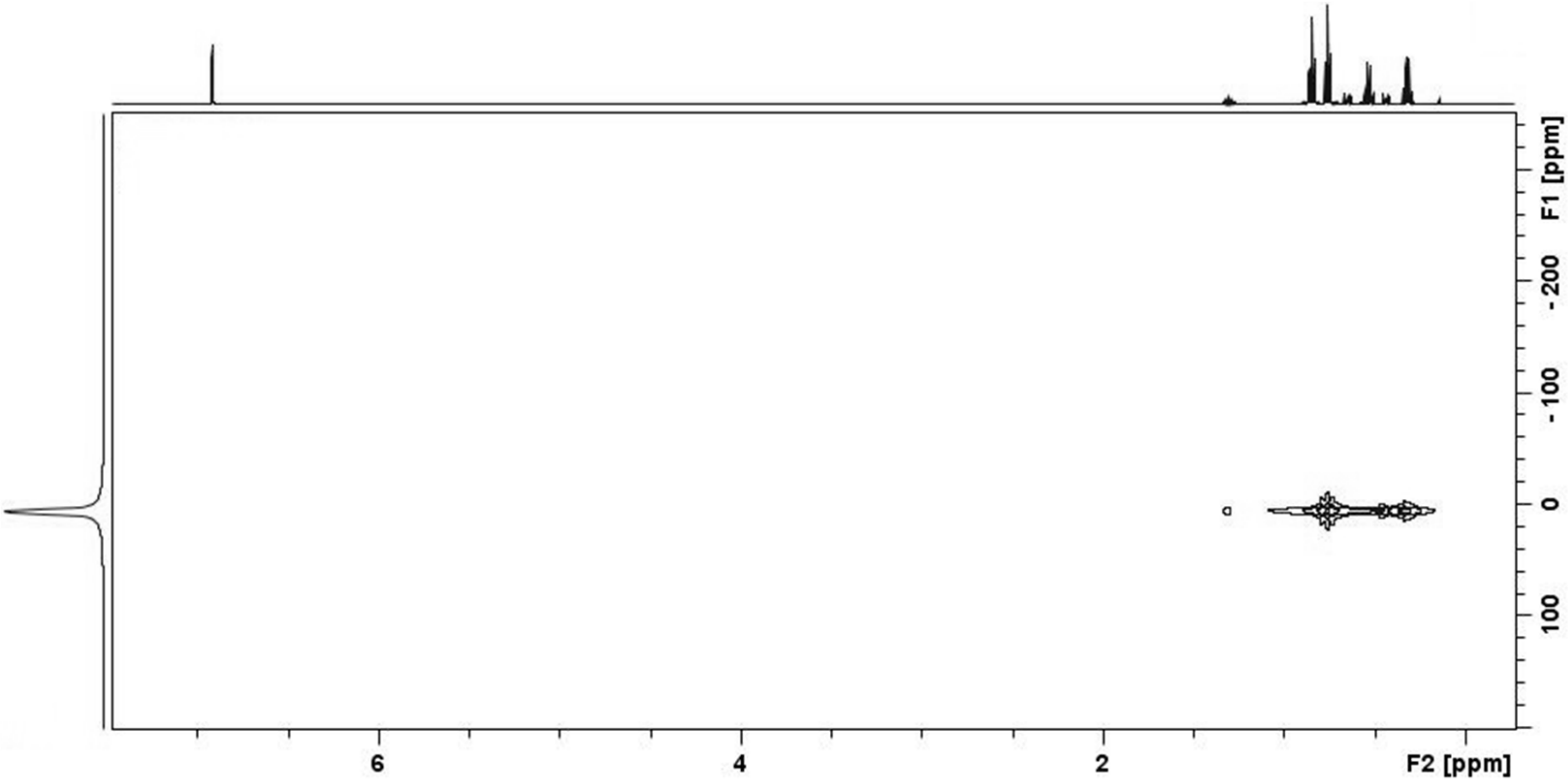




$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6):

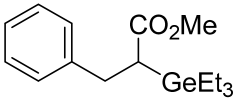


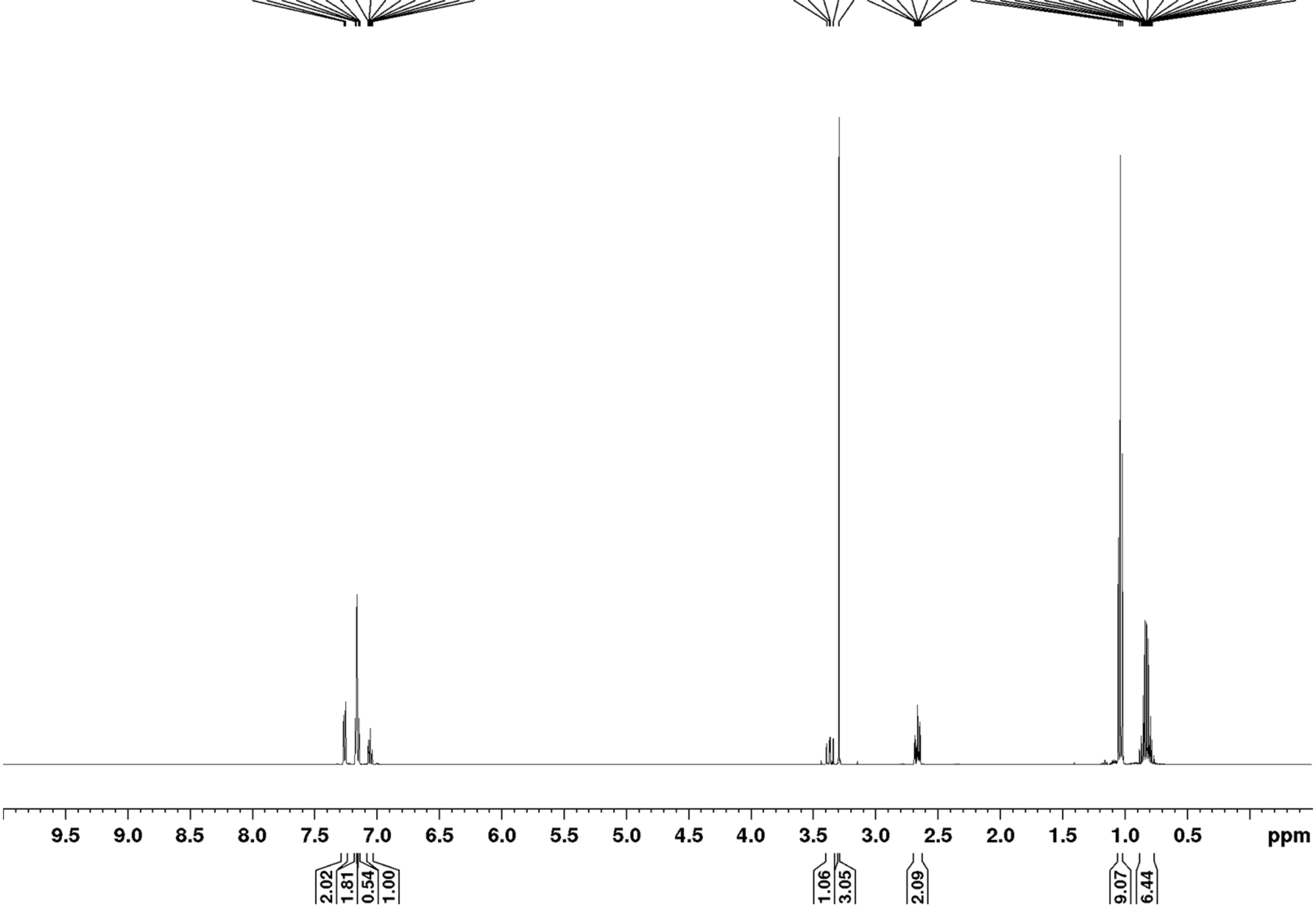
$^{1}H,^{29}Si$-HMQC 2D NMR (C_6D_6, SFO1 500 MHz, SFO2 99 MHz):



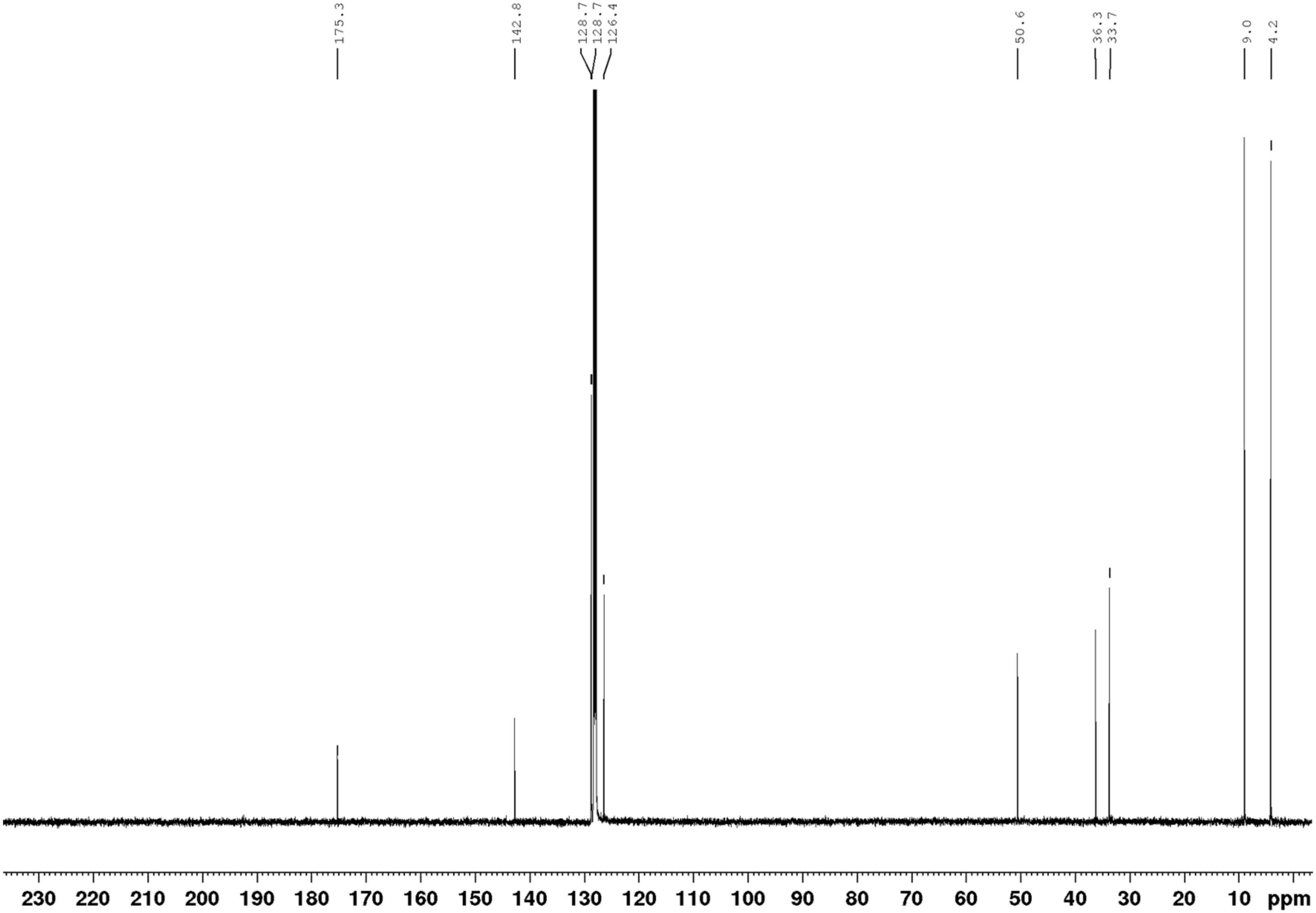
Methyl 3-phenyl-2-(triethylgermyl)propanoate (24)

^{1}H NMR (500 MHz, C_6D_6):



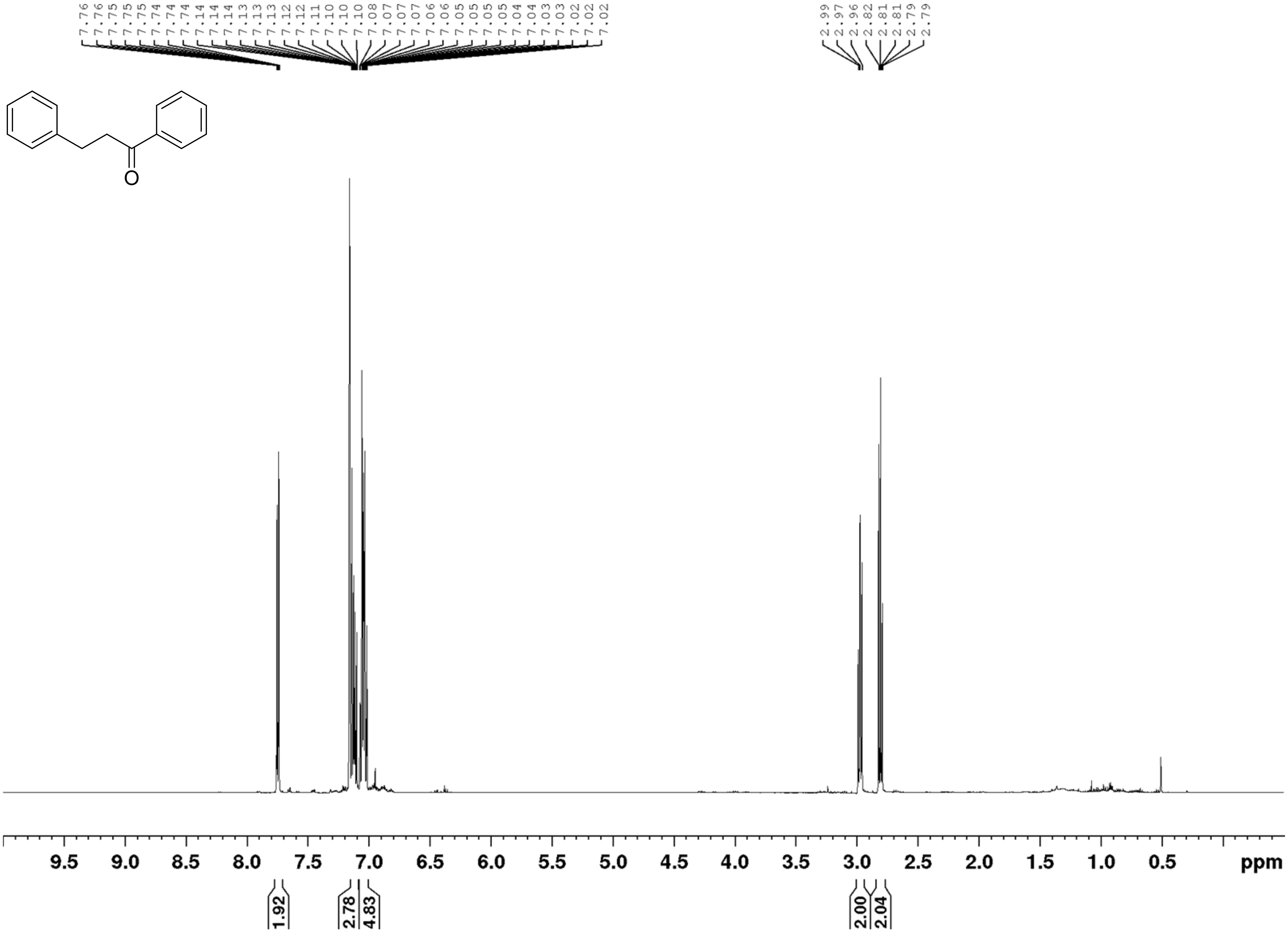


$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6):

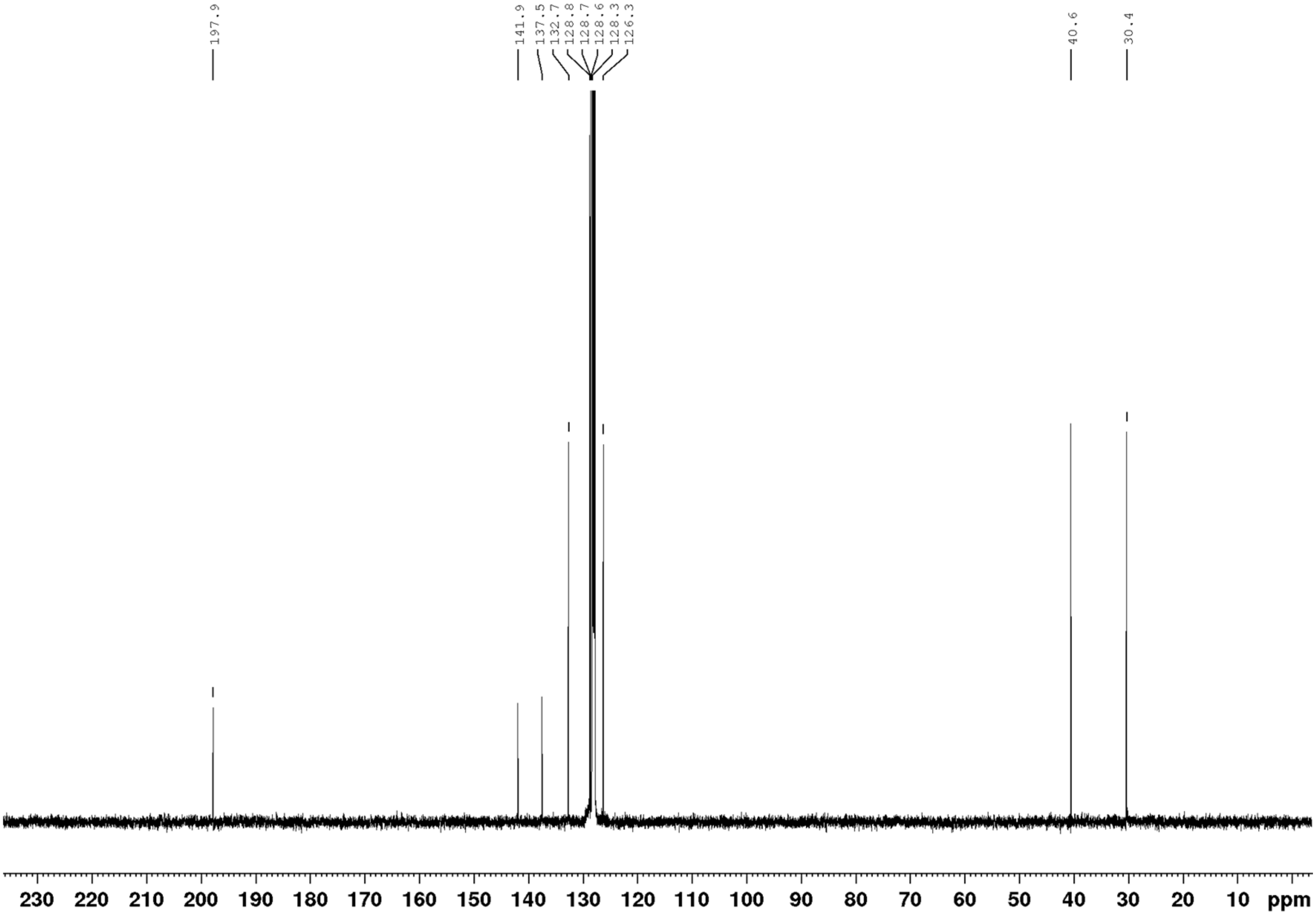


1,3-Diphenylpropan-1-one (25)

^{1}H NMR (500 MHz, C_6D_6):

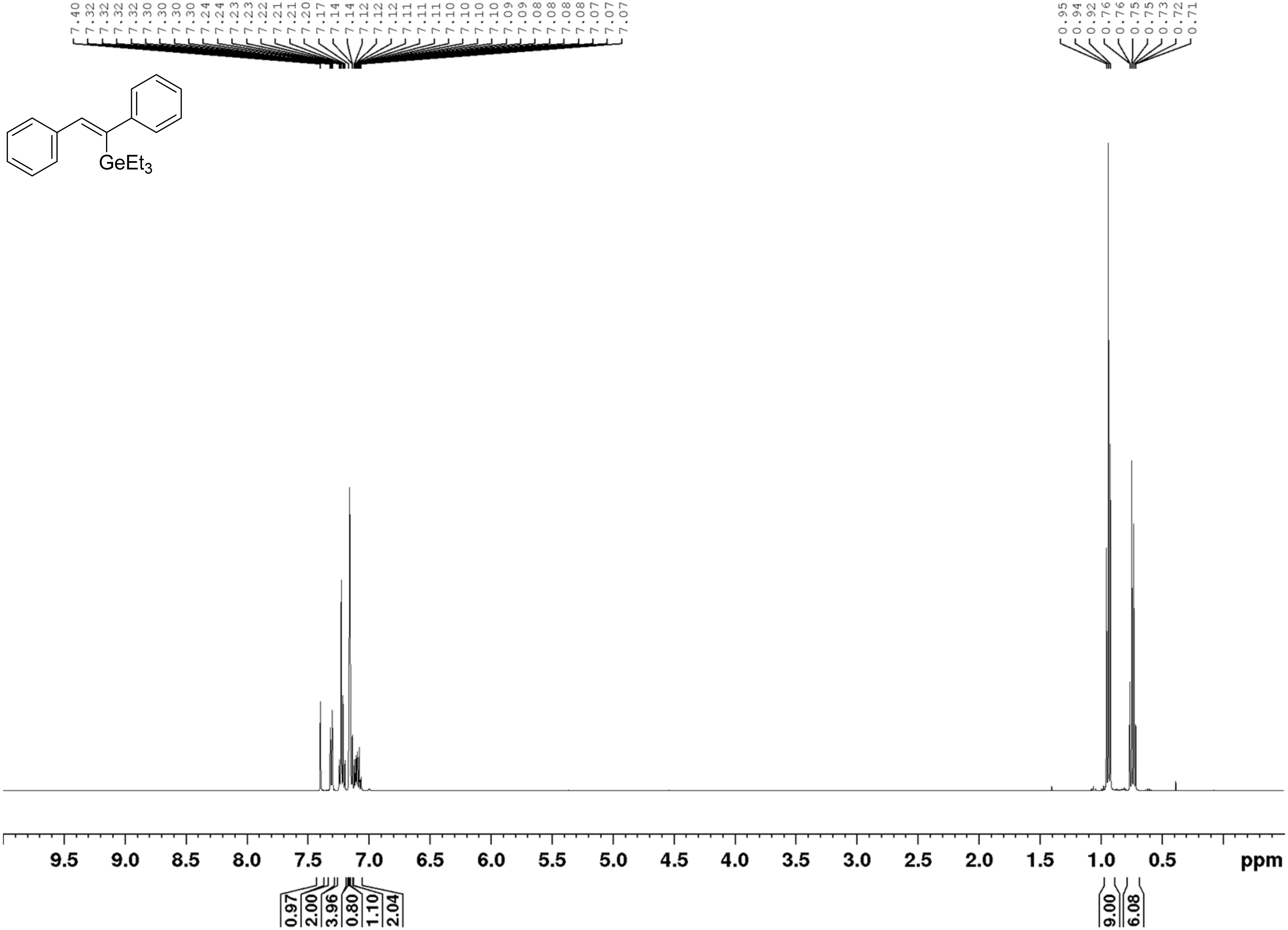


$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6):

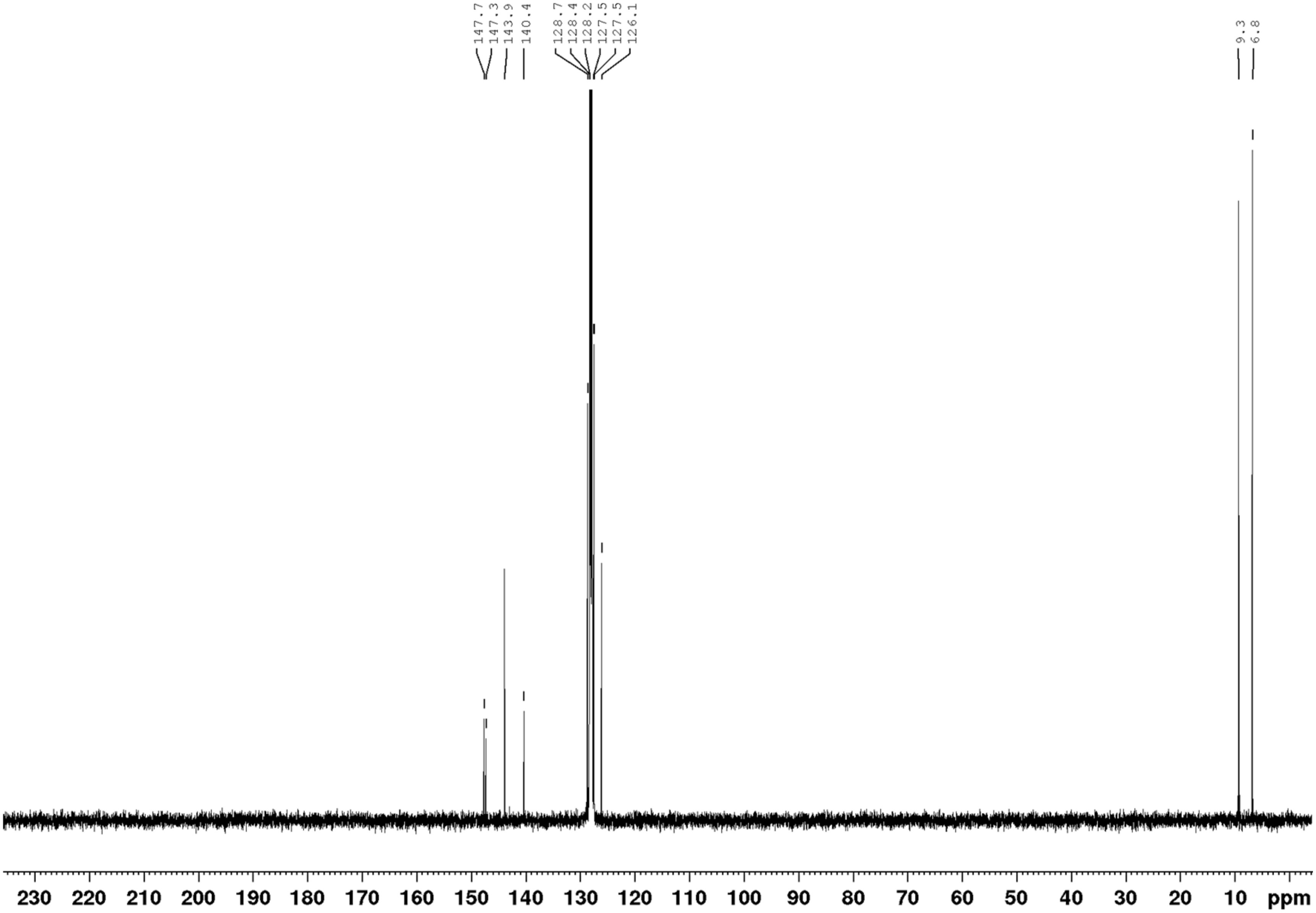


(*Z*)-(1,2-Diphenylvinyl)triethylgermane ((*Z*)-26)

^{1}H NMR (500 MHz, C_6D_6):

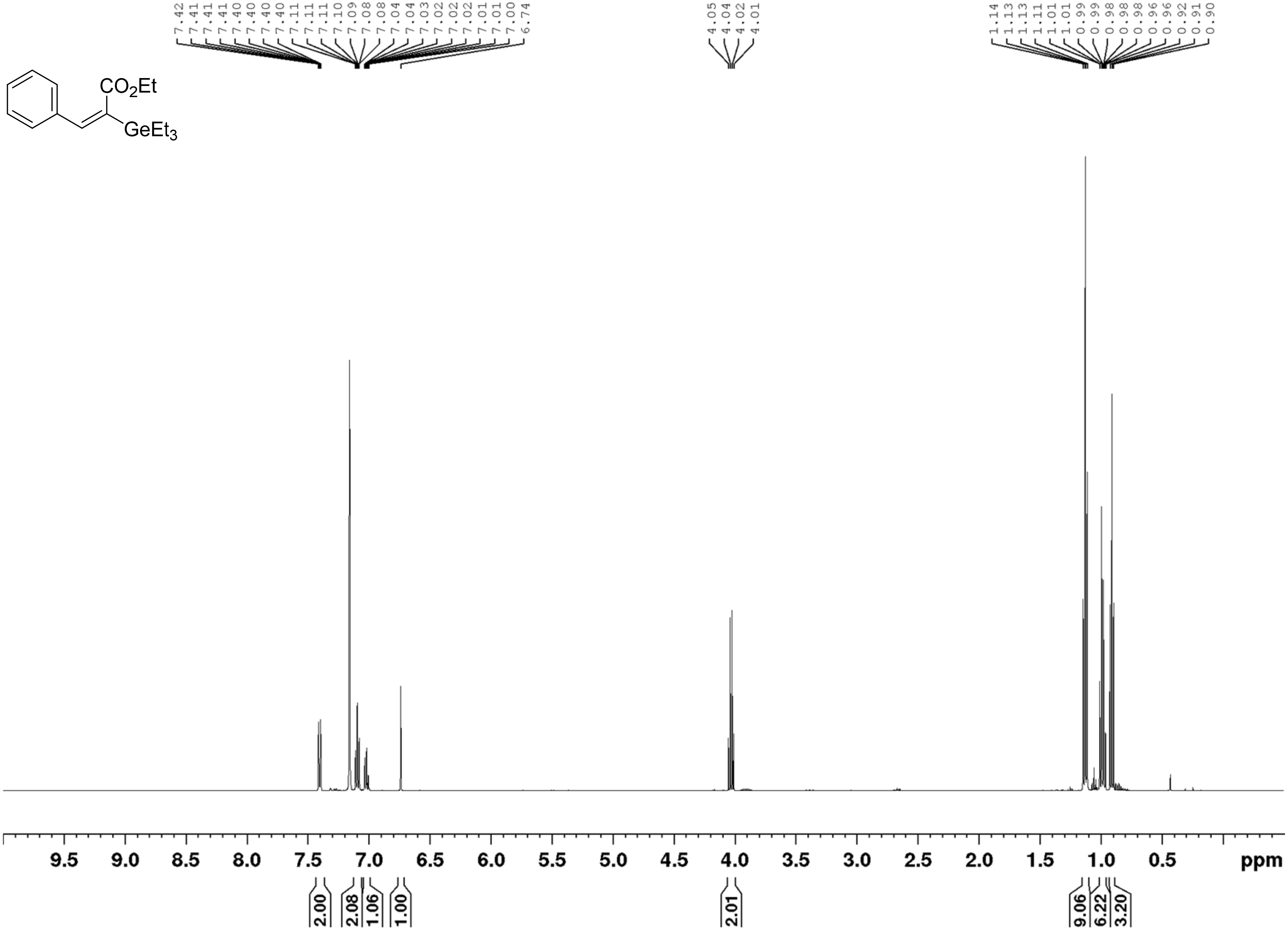


^{13}C{^{1}H} NMR (126 MHz, C_6D_6):

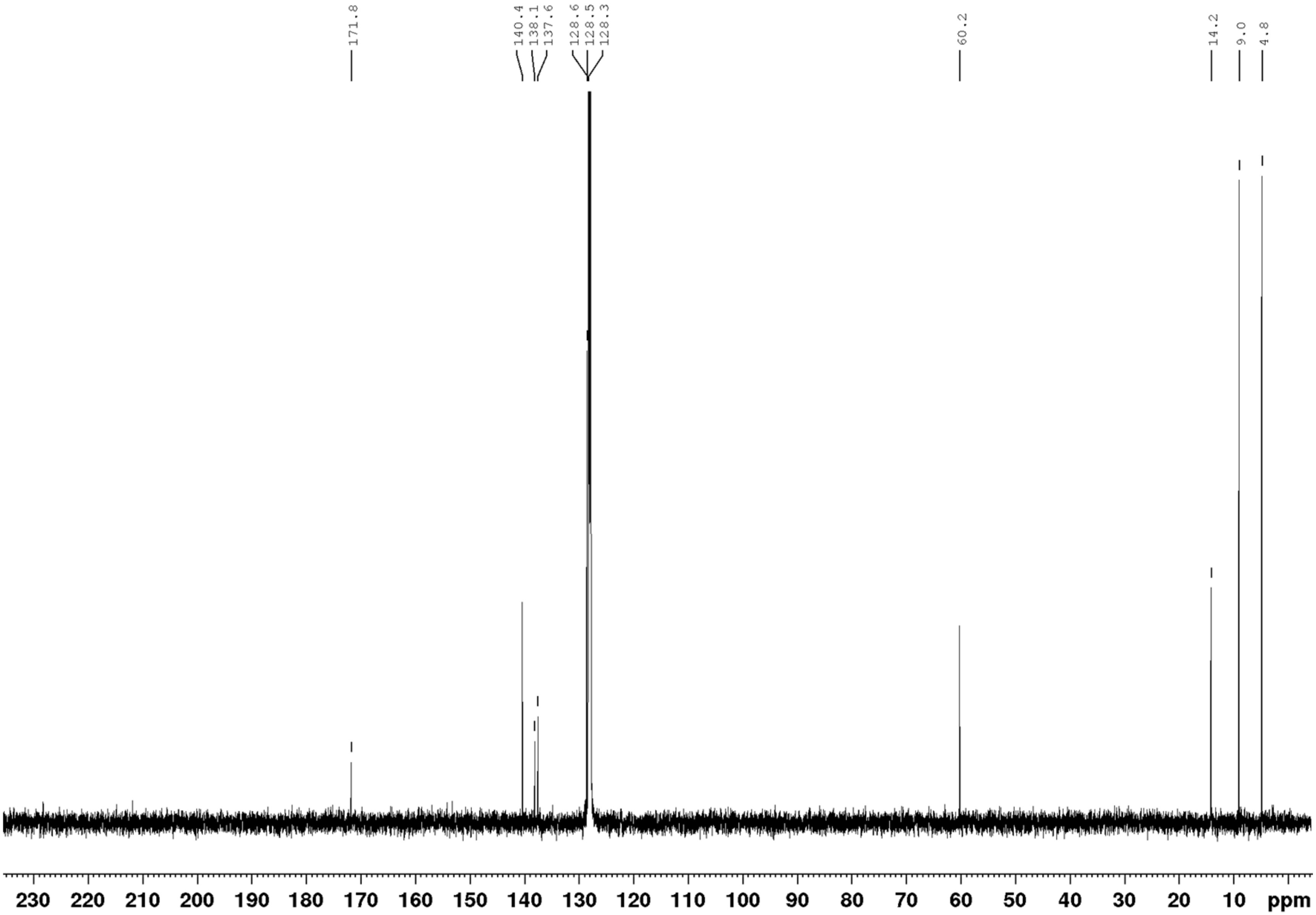


Ethyl (*E*)-3-phenyl-2-(triethylgermyl)acrylate ((*E*)-27)

^{1}H NMR (500 MHz, C_6D_6):

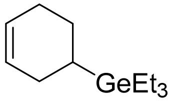


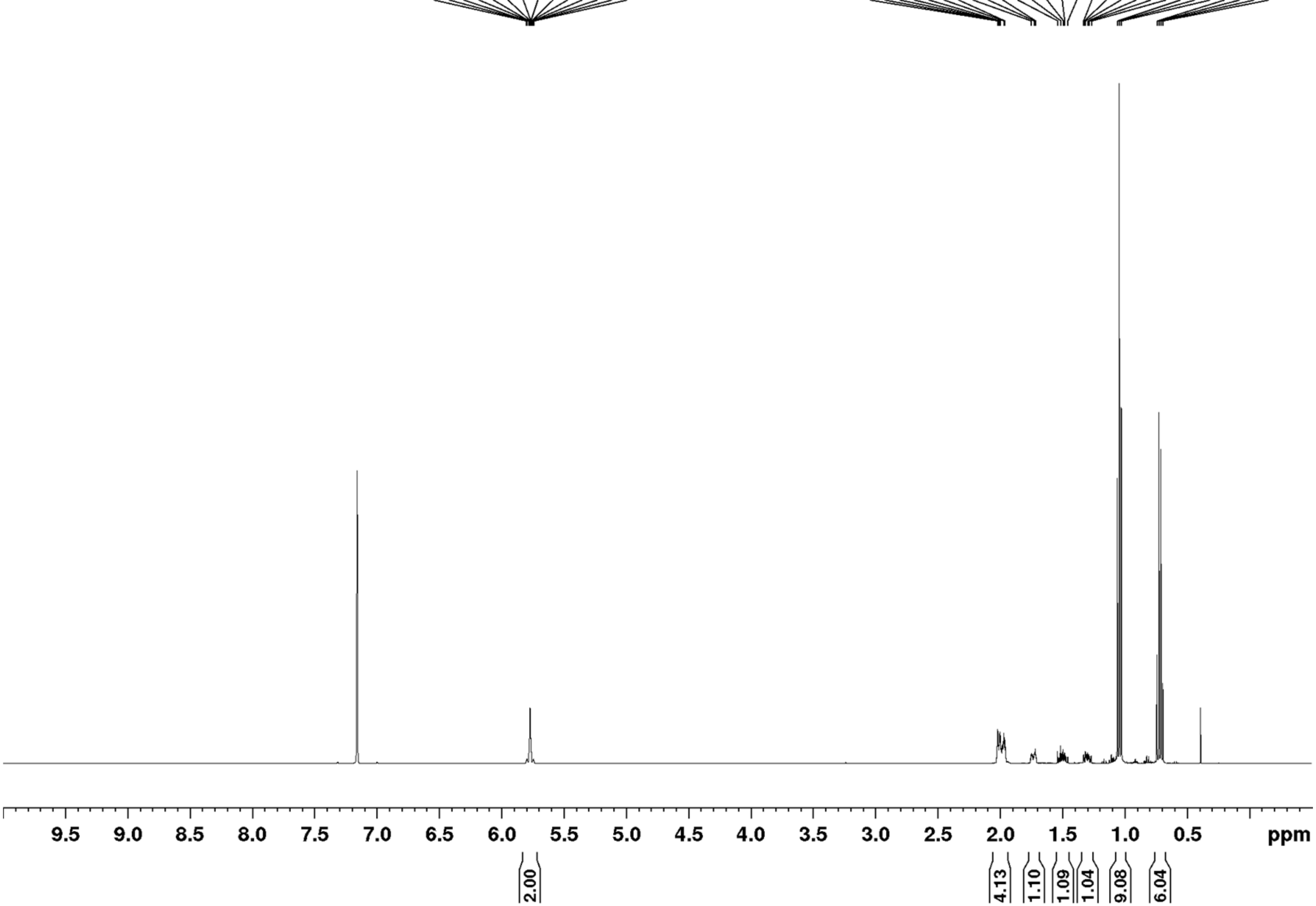
$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6):



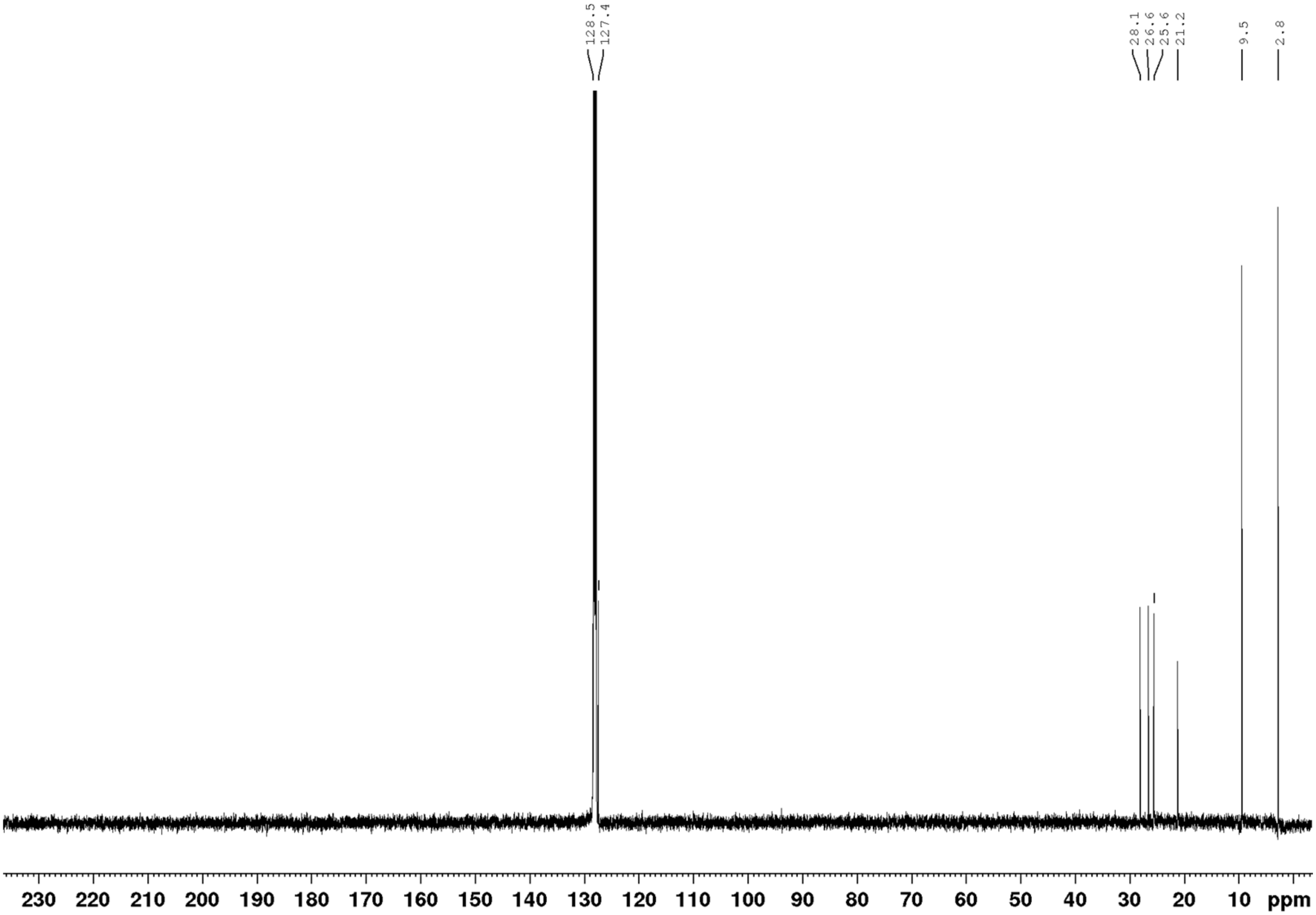
Cyclohex-3-en-1-yltriethylgermane (31)

^{1}H NMR (500 MHz, C_6D_6):



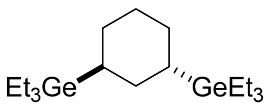


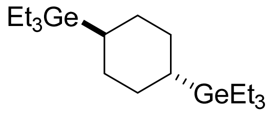
$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6):

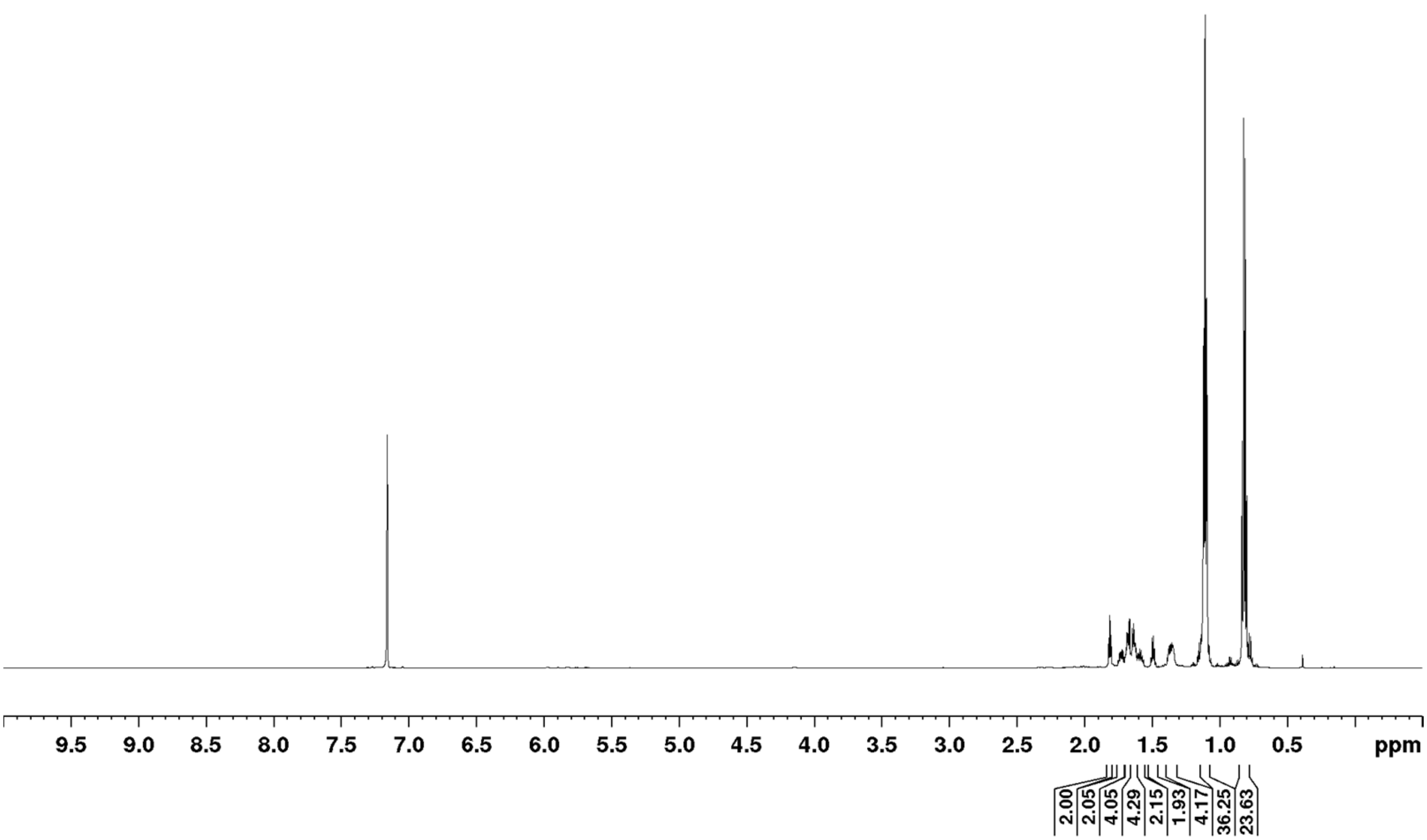


trans-1,3-Bis(triethylgermyl)cyclohexane (_trans_-32) + _trans_-1,4-bis(triethylgermyl)cyclohexane (_trans_-33)

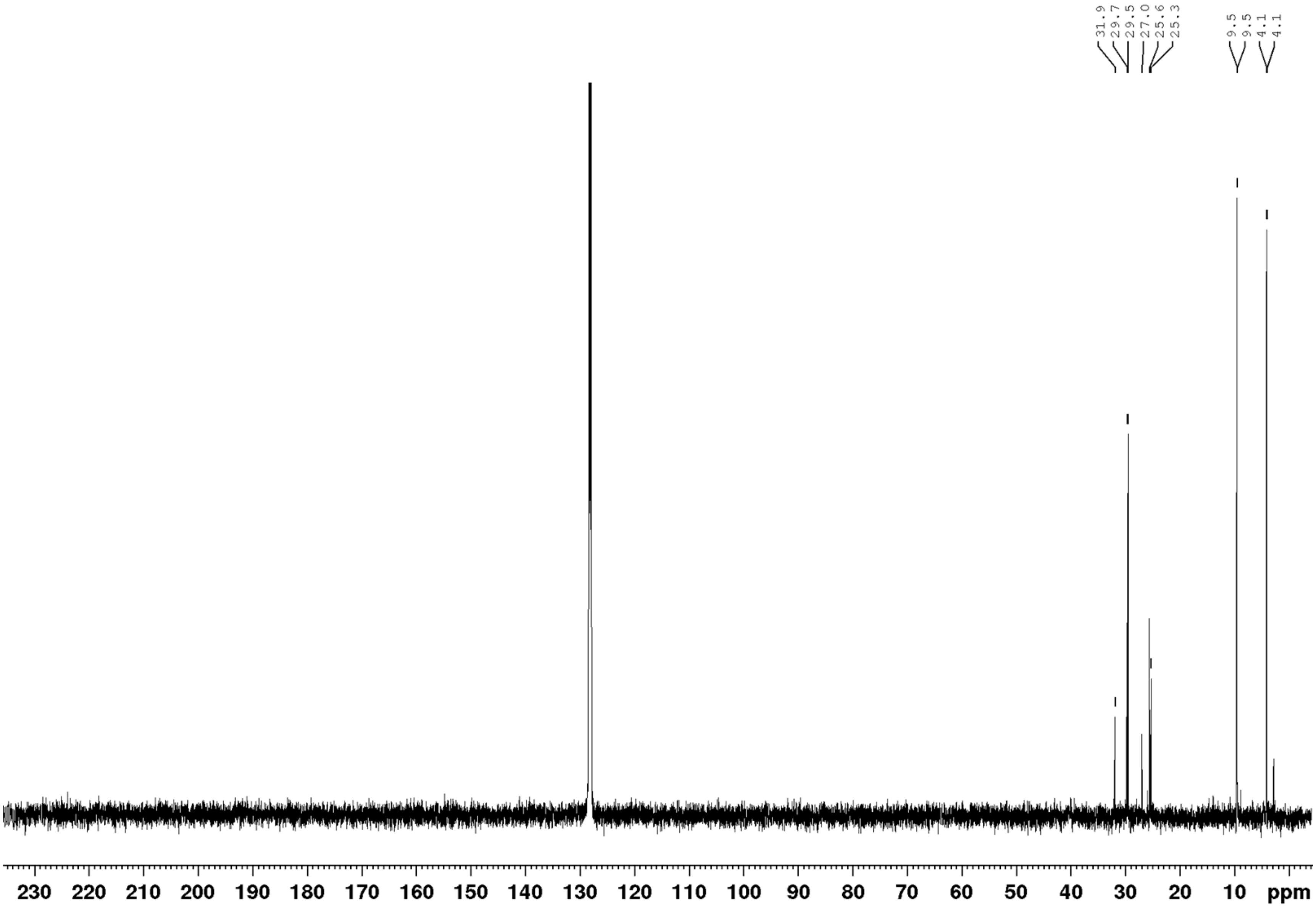
^{1}H NMR (700 MHz, C_6D_6):





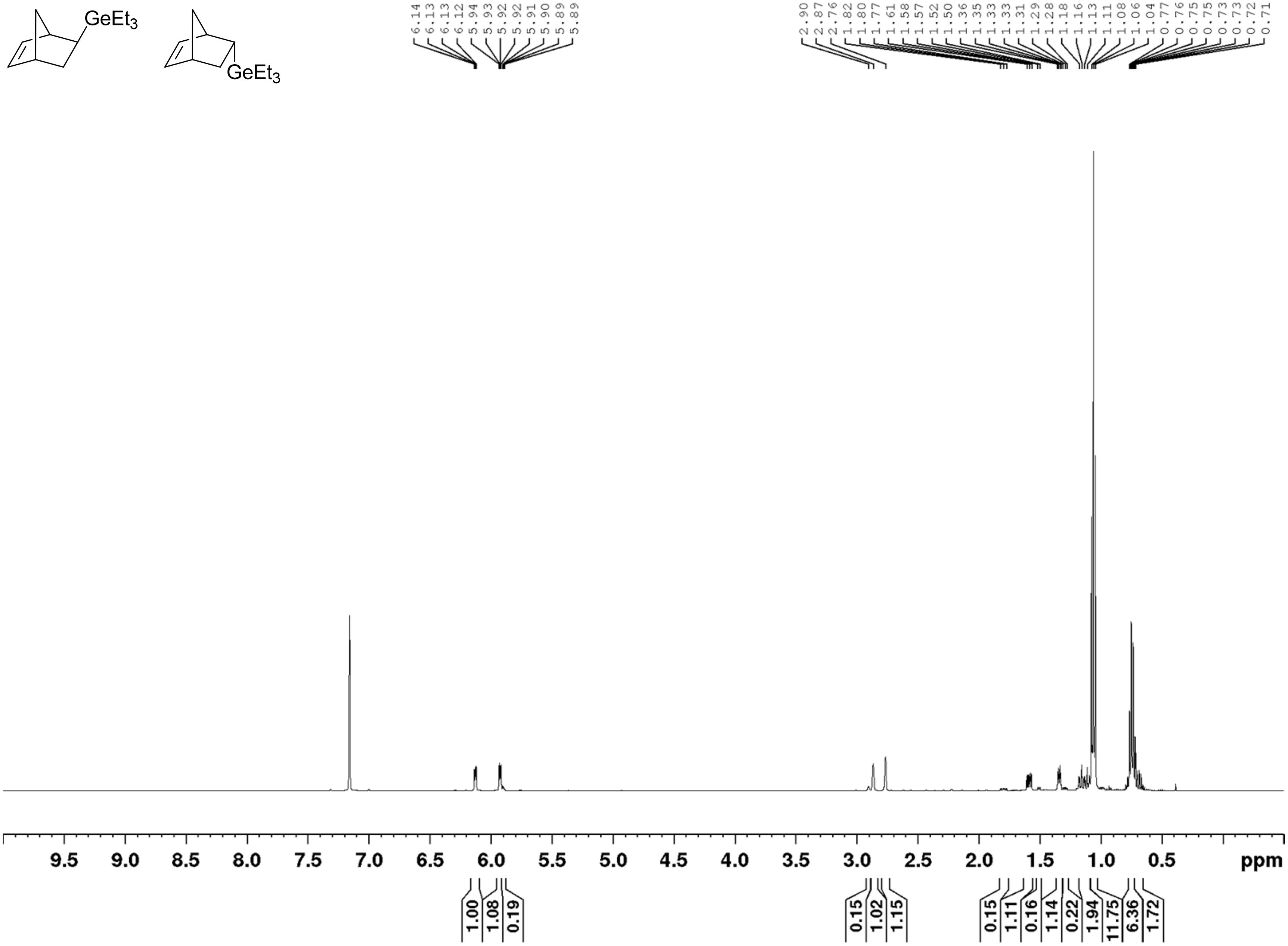


$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6):

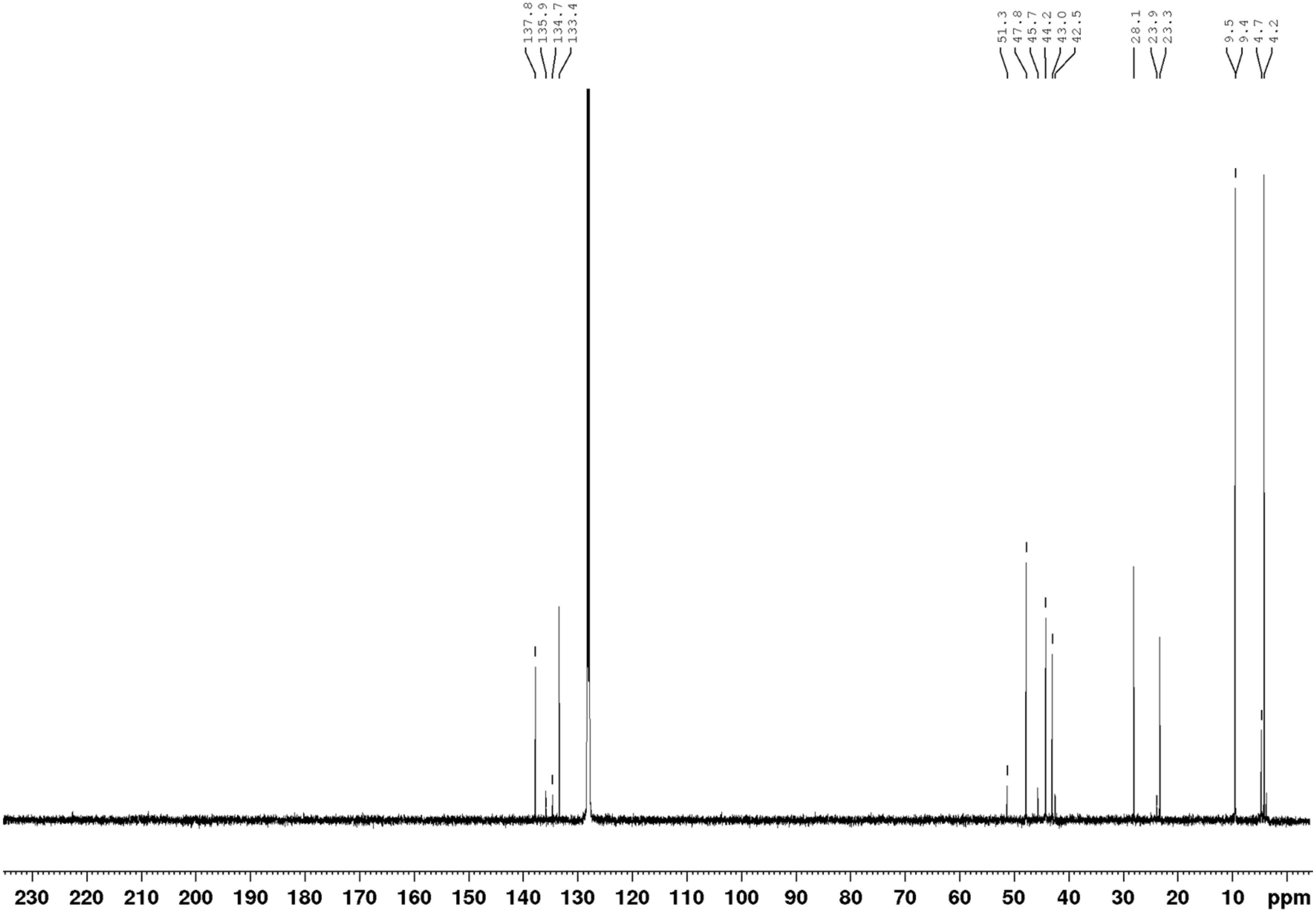


Bicyclo[2.2.1]hept-5-en-2-yltriethylgermane (*exo*-34 + *endo*-34)

^{1}H NMR (500 MHz, C_6D_6):

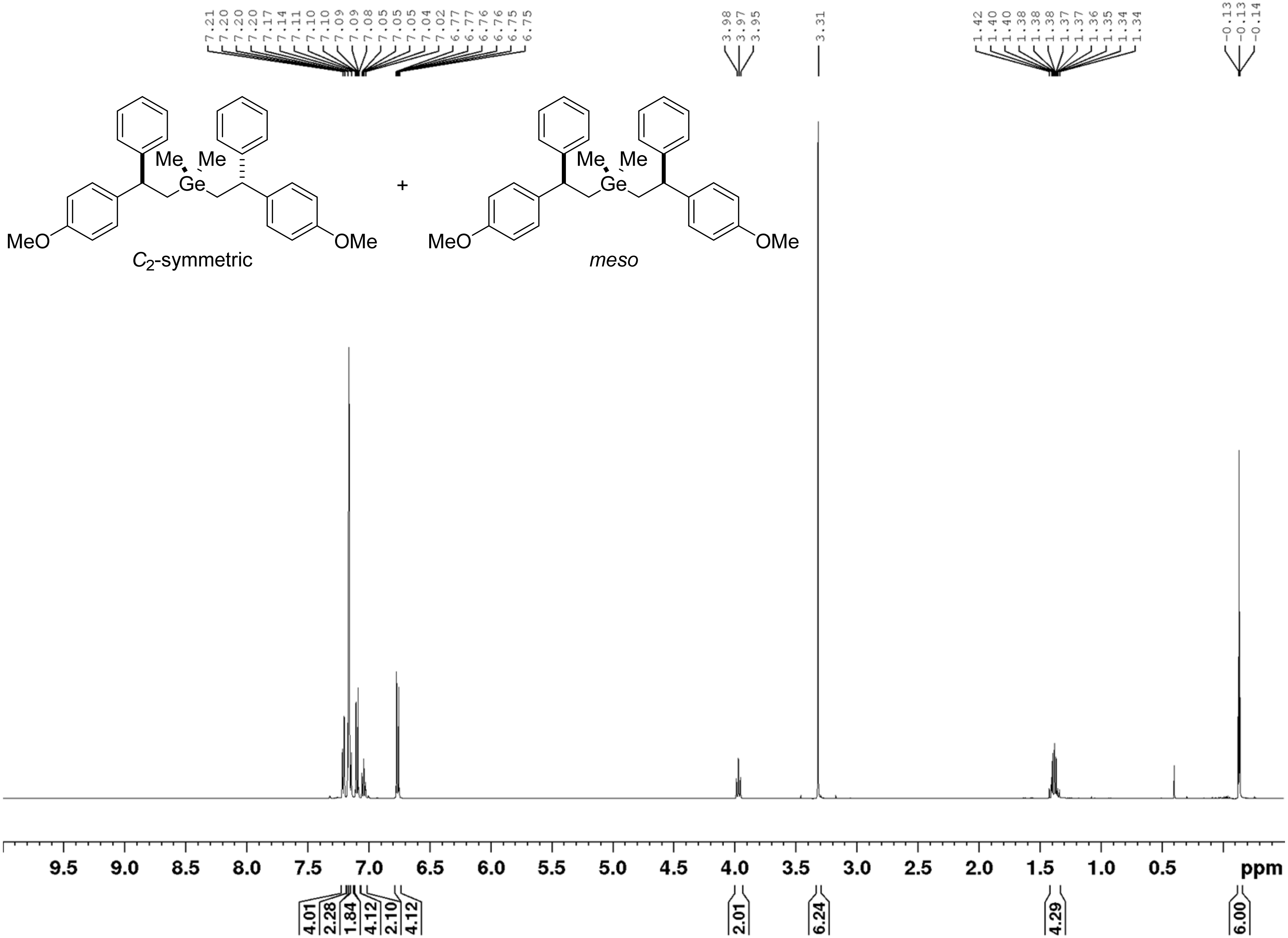


$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6):

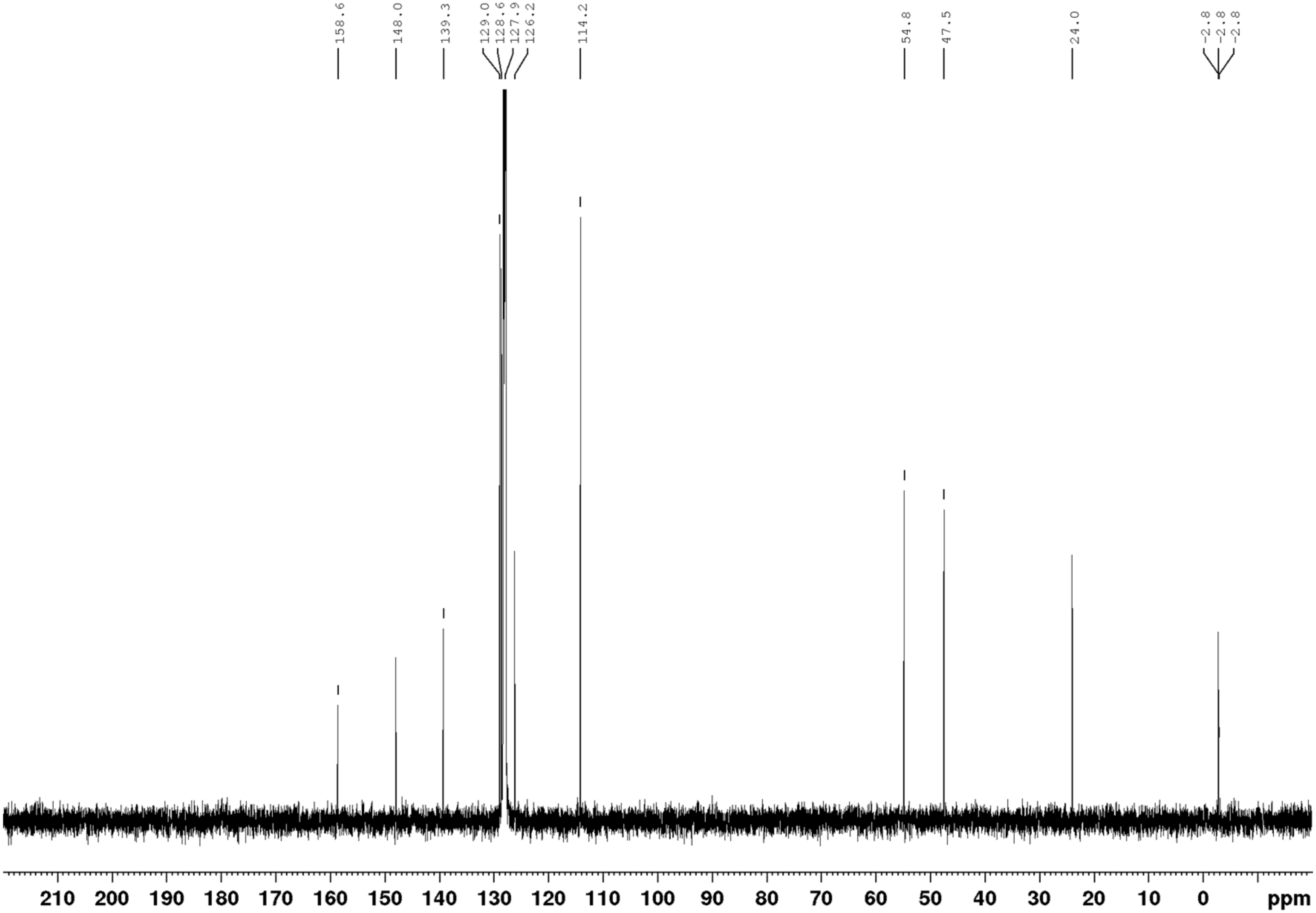


Bis(2-(4-methoxyphenyl)-2-phenylethyl)dimethylgermane (35)

^{1}H NMR (500 MHz, C_6D_6):

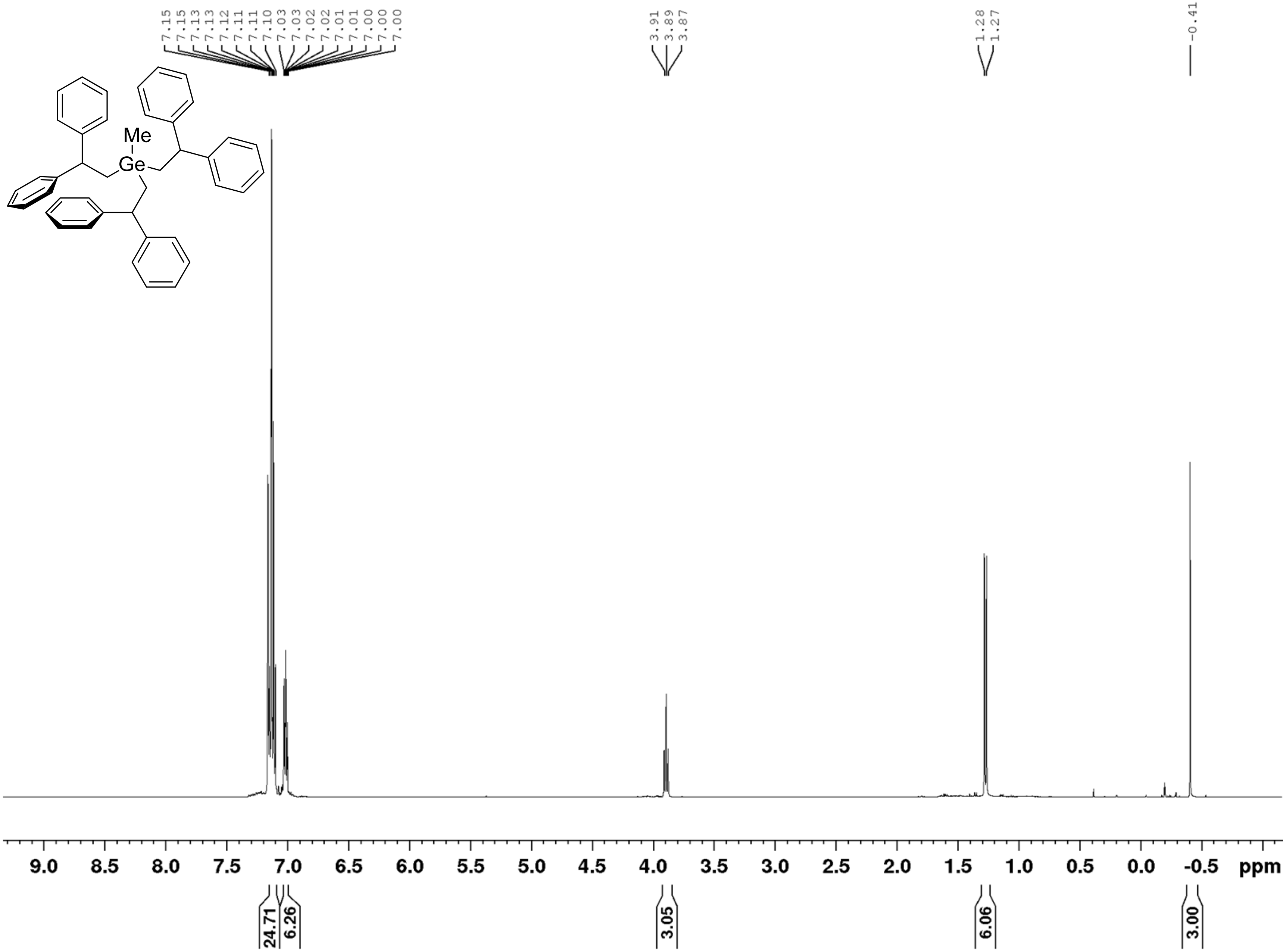


$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6):

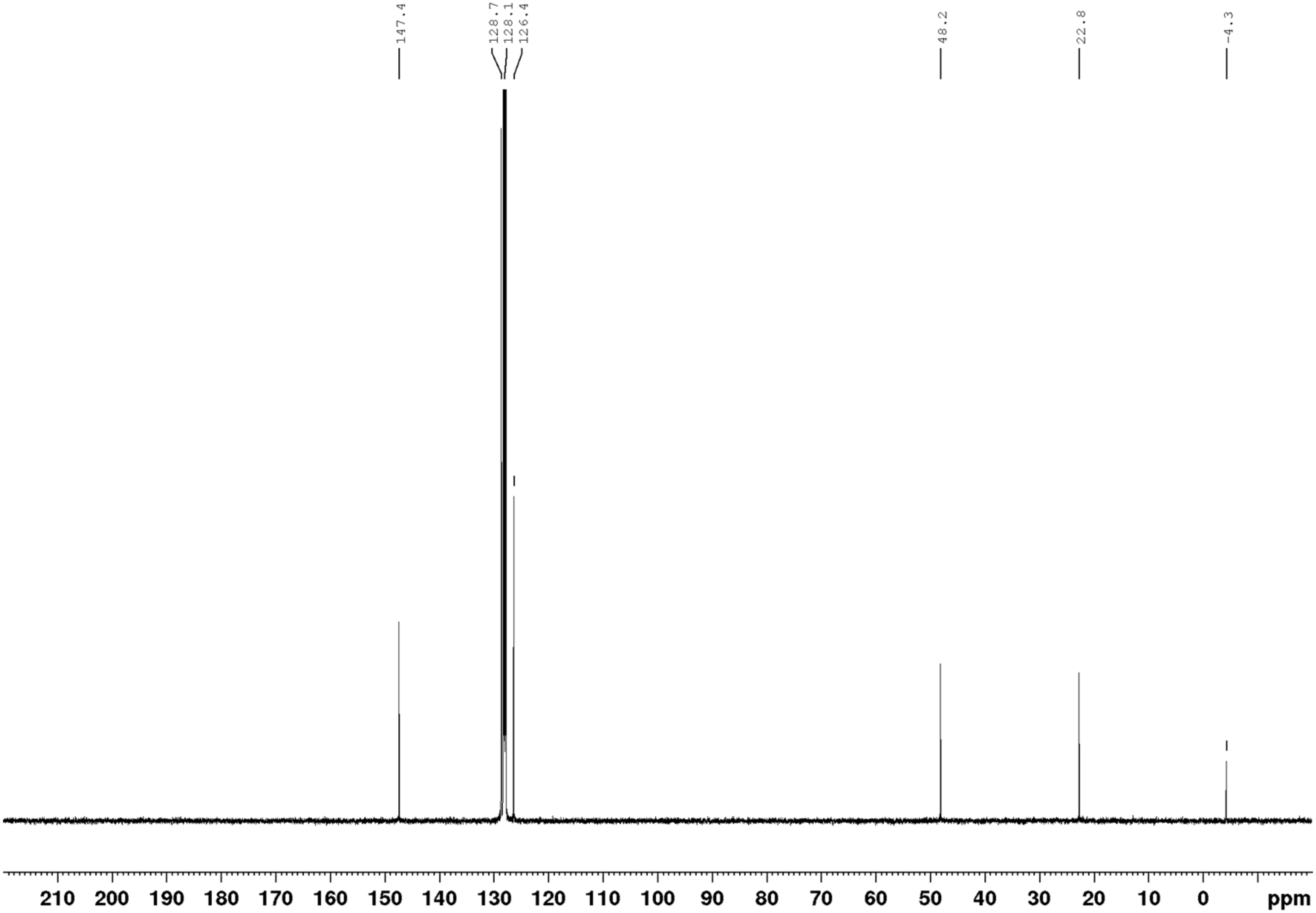


Tris(2,2-diphenylethyl)methylgermane (36)

^{1}H NMR (500 MHz, C_6D_6):

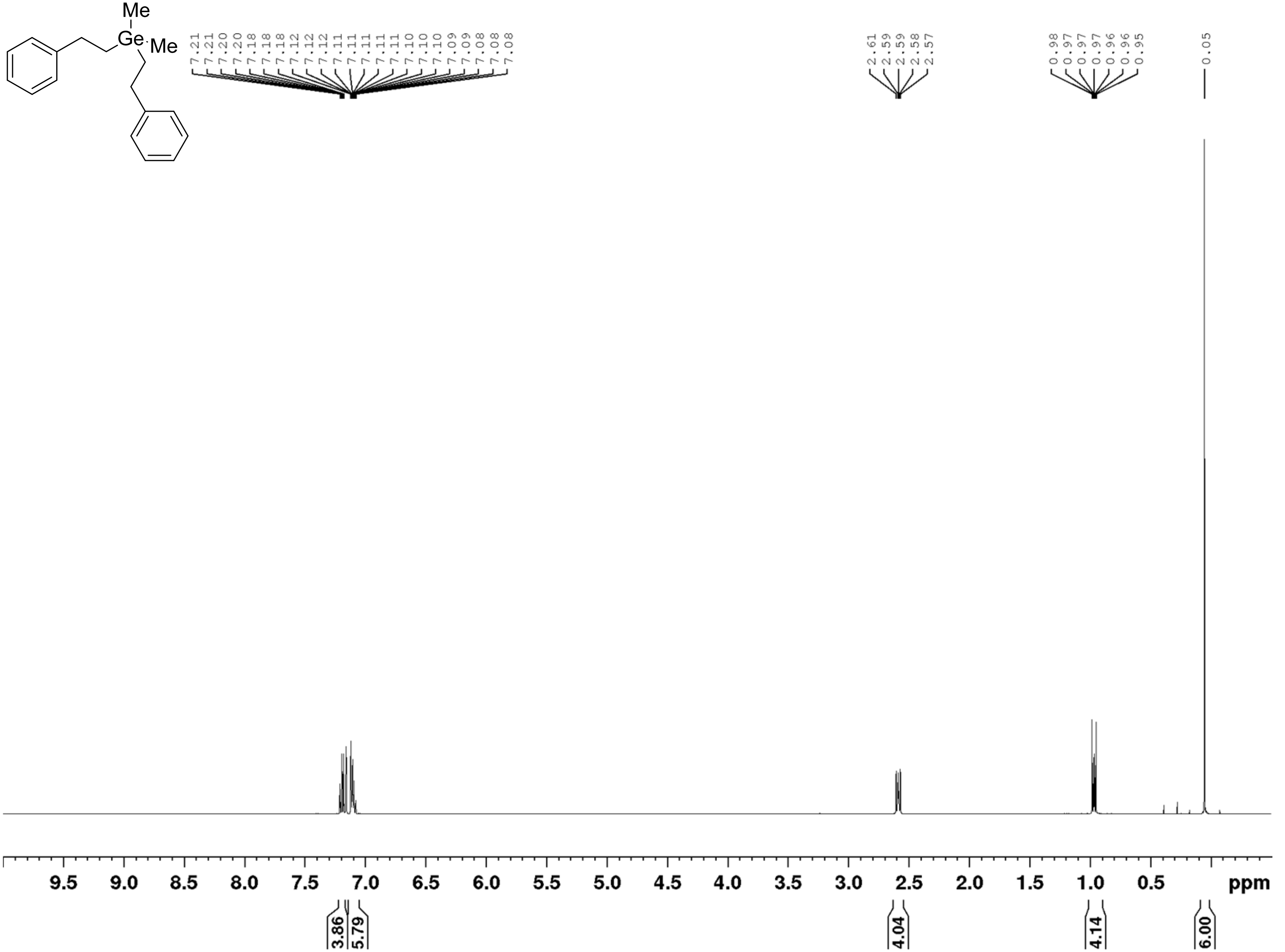


$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6):

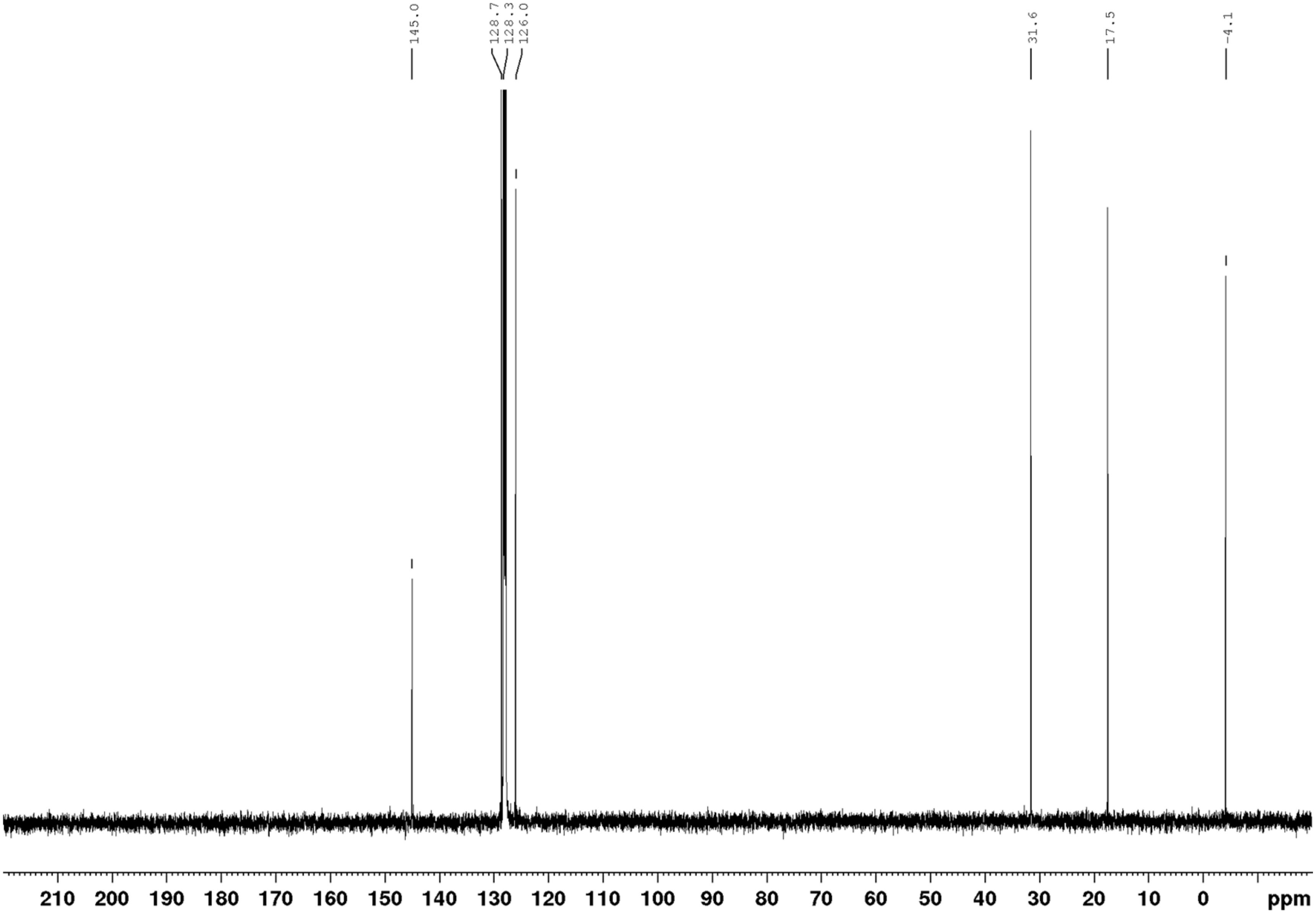


Dimethyldiphenethylgermane (37)

^{1}H NMR (500 MHz, C_6D_6):

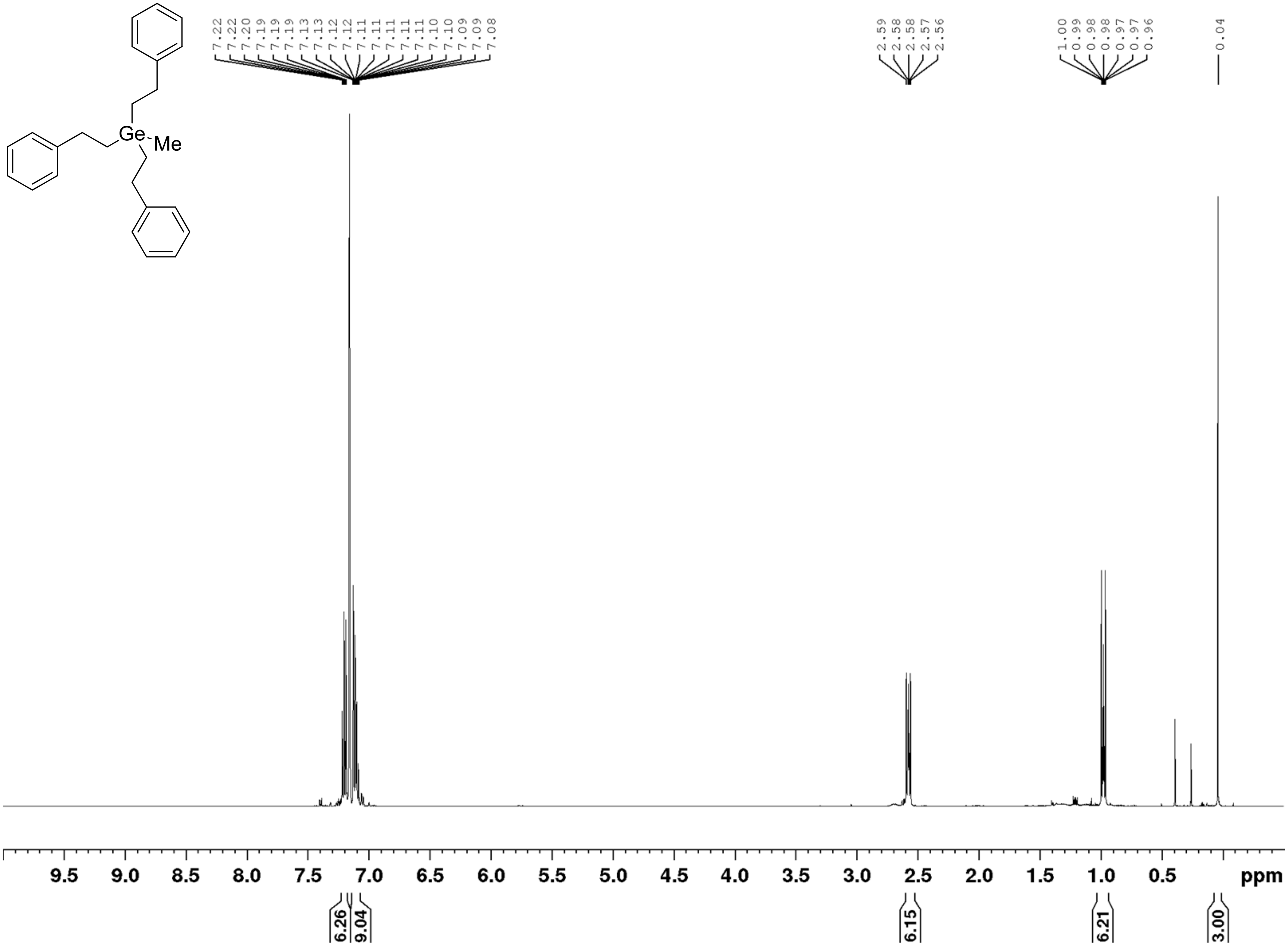


$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6):

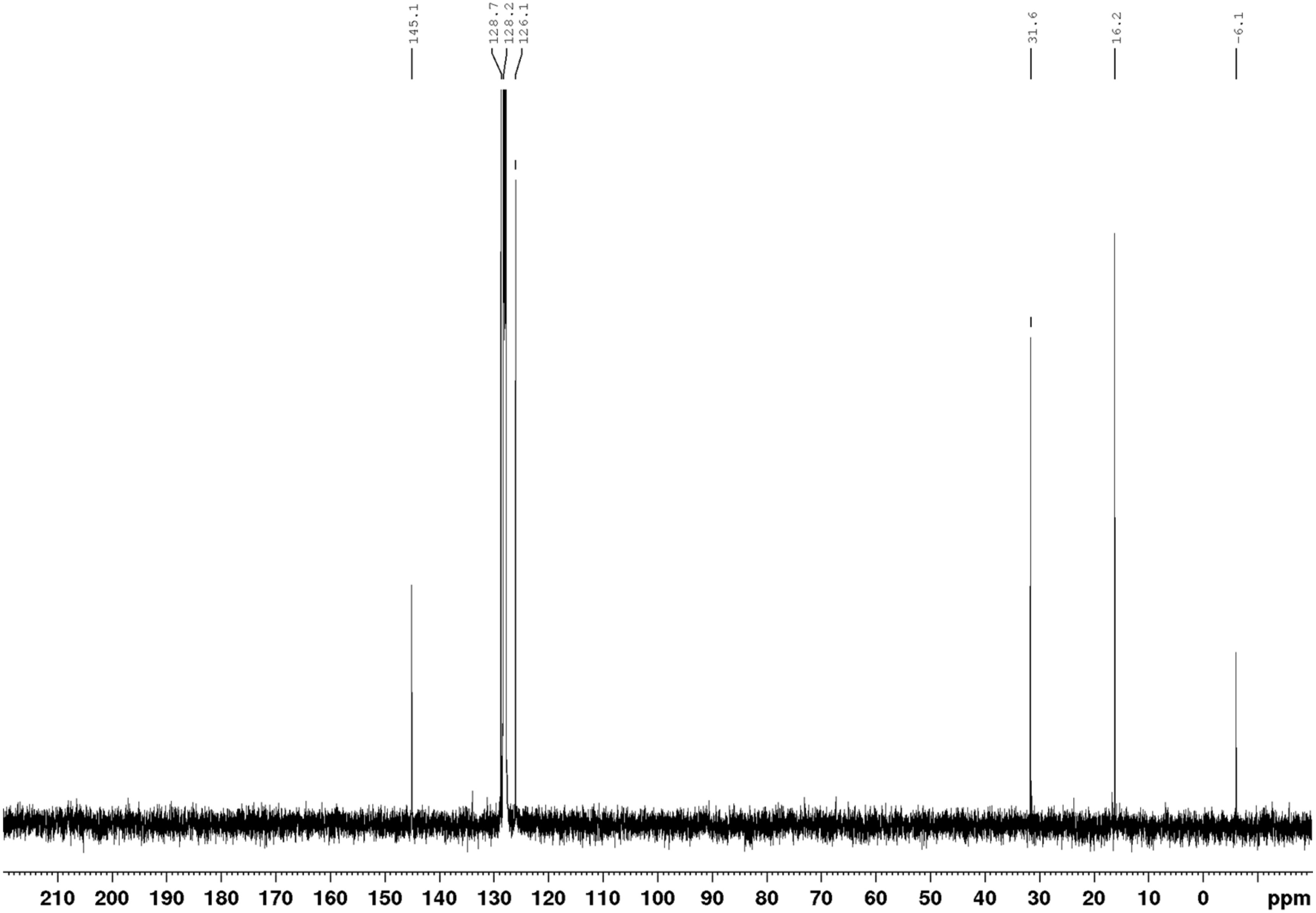


Methyltriphenethylgermane (38)

^{1}H NMR (500 MHz, C_6D_6):

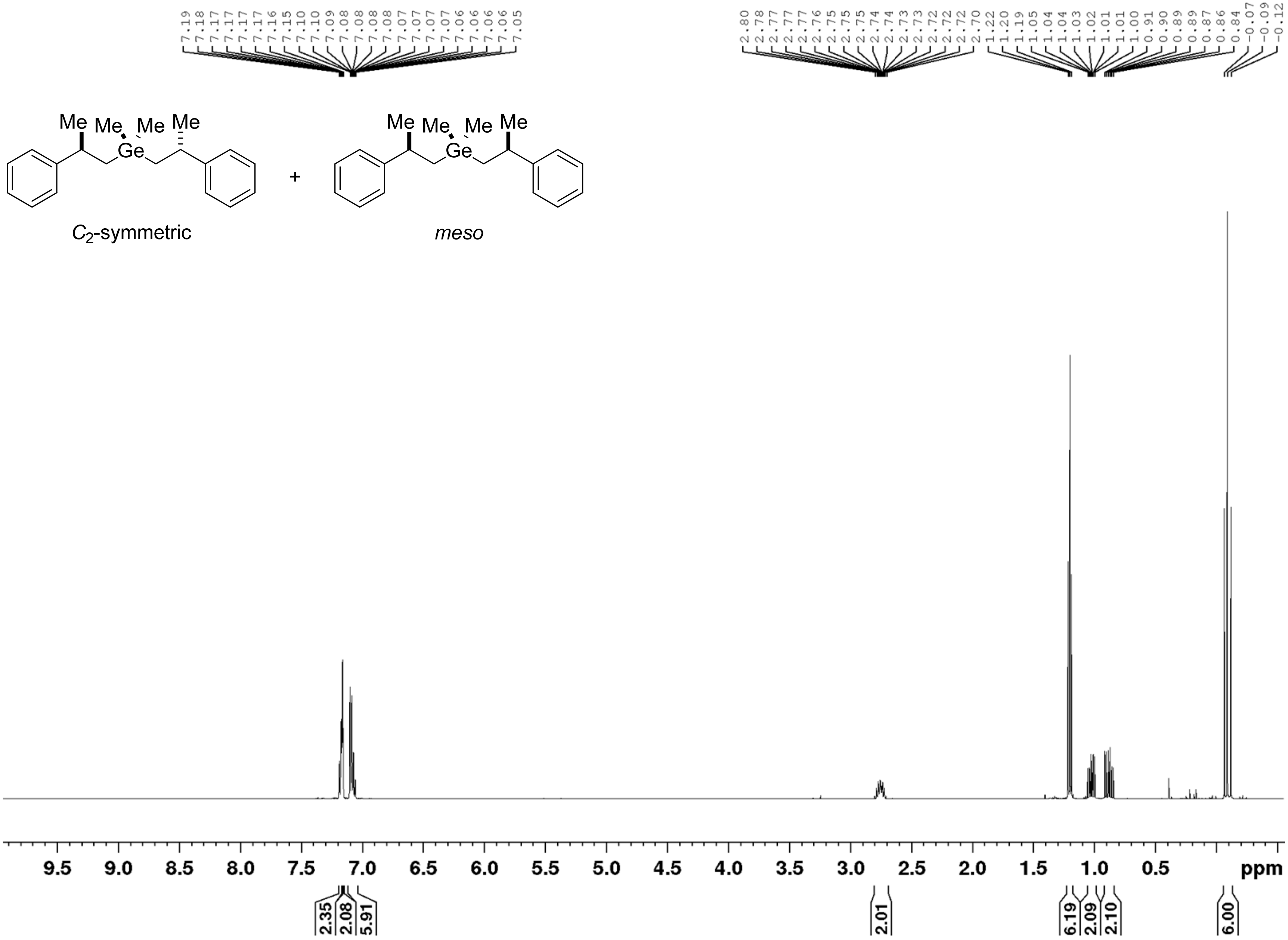


$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6):

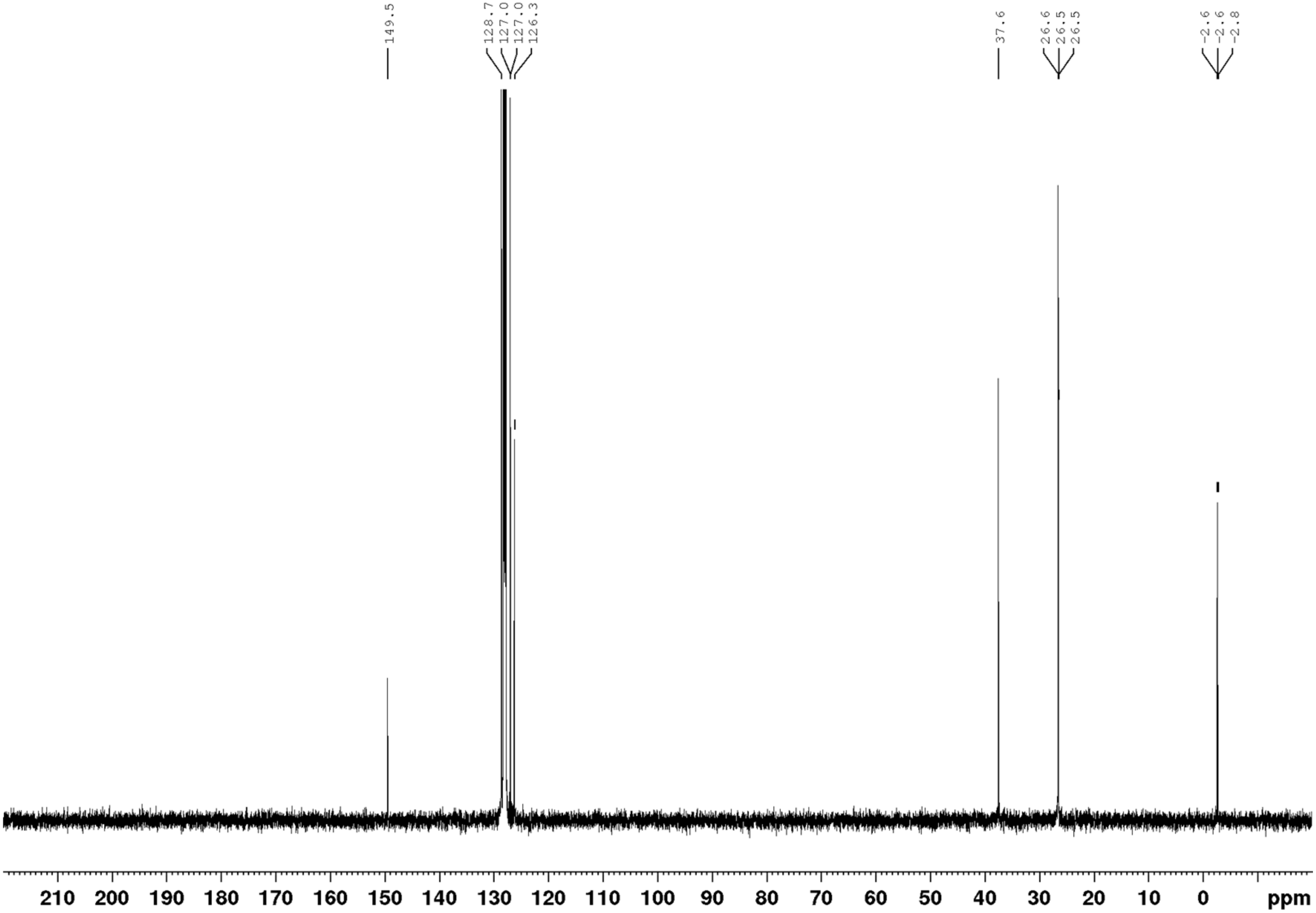


Dimethylbis(2-phenylpropyl)germane (39)

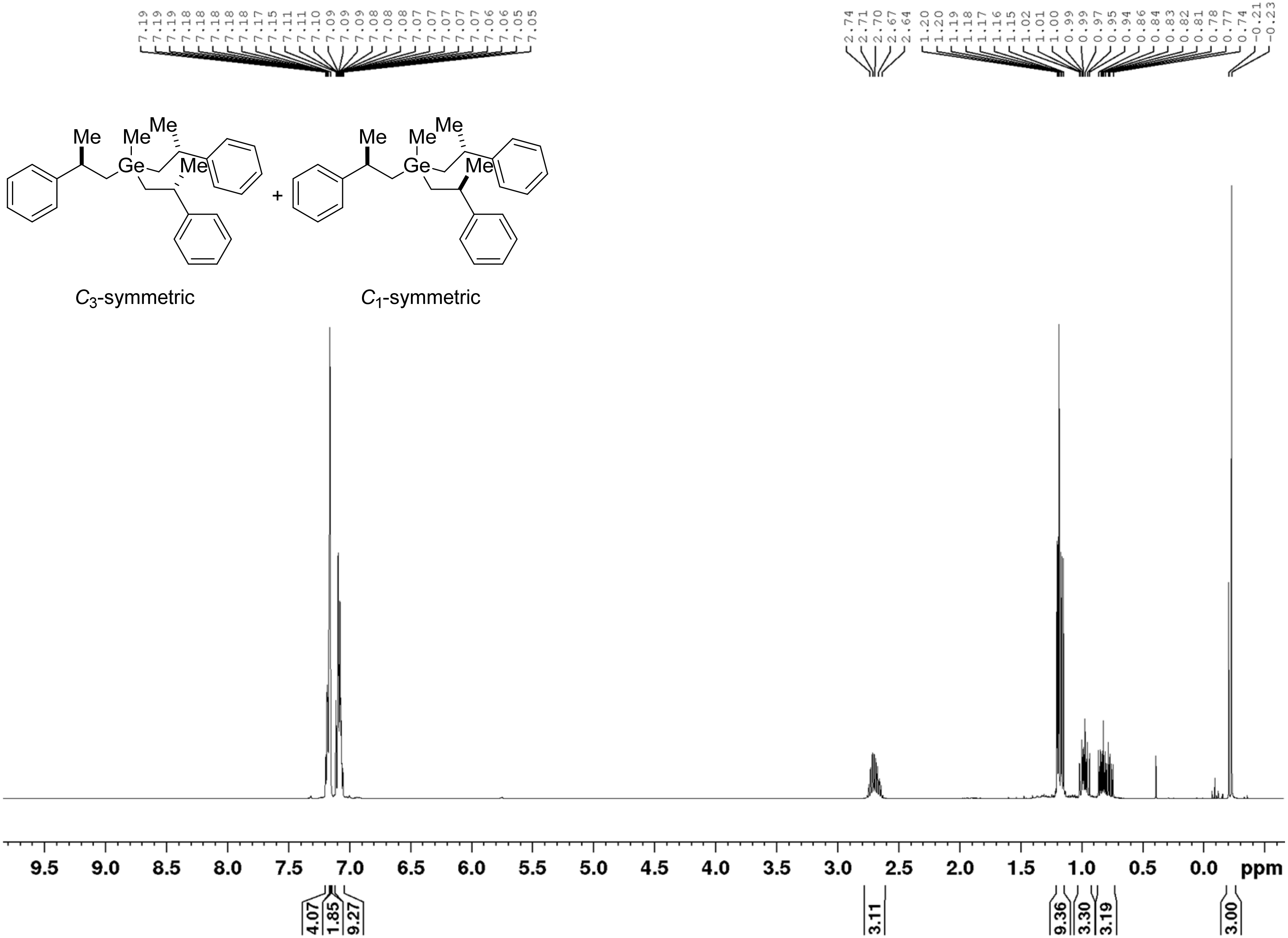
^{1}H NMR (500 MHz, C_6D_6):



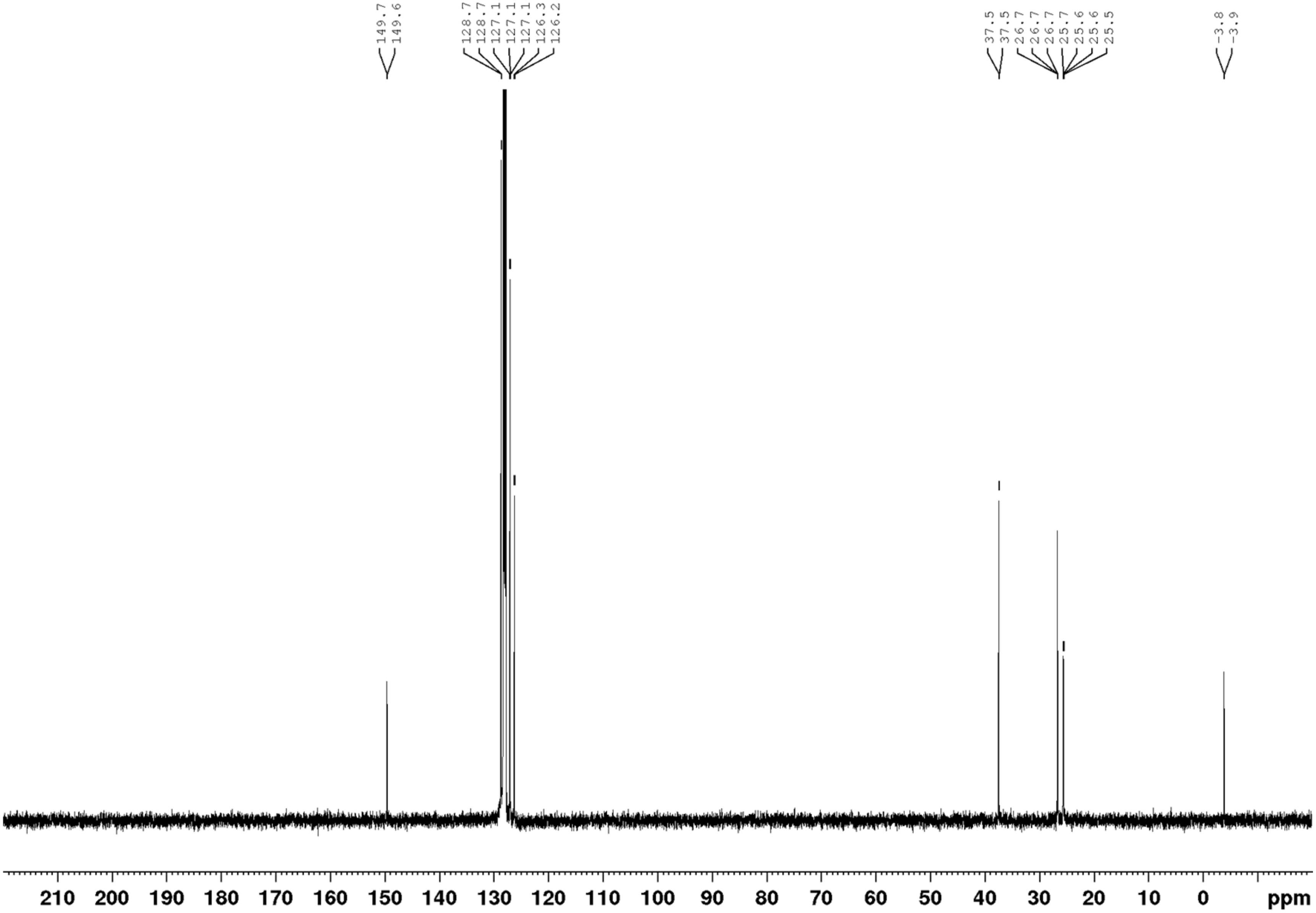
$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6):



Methyltris(2-phenylpropyl)germane (40)
^{1}H NMR (500 MHz, C_6D_6):

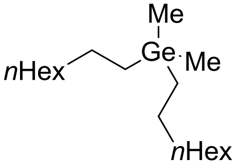


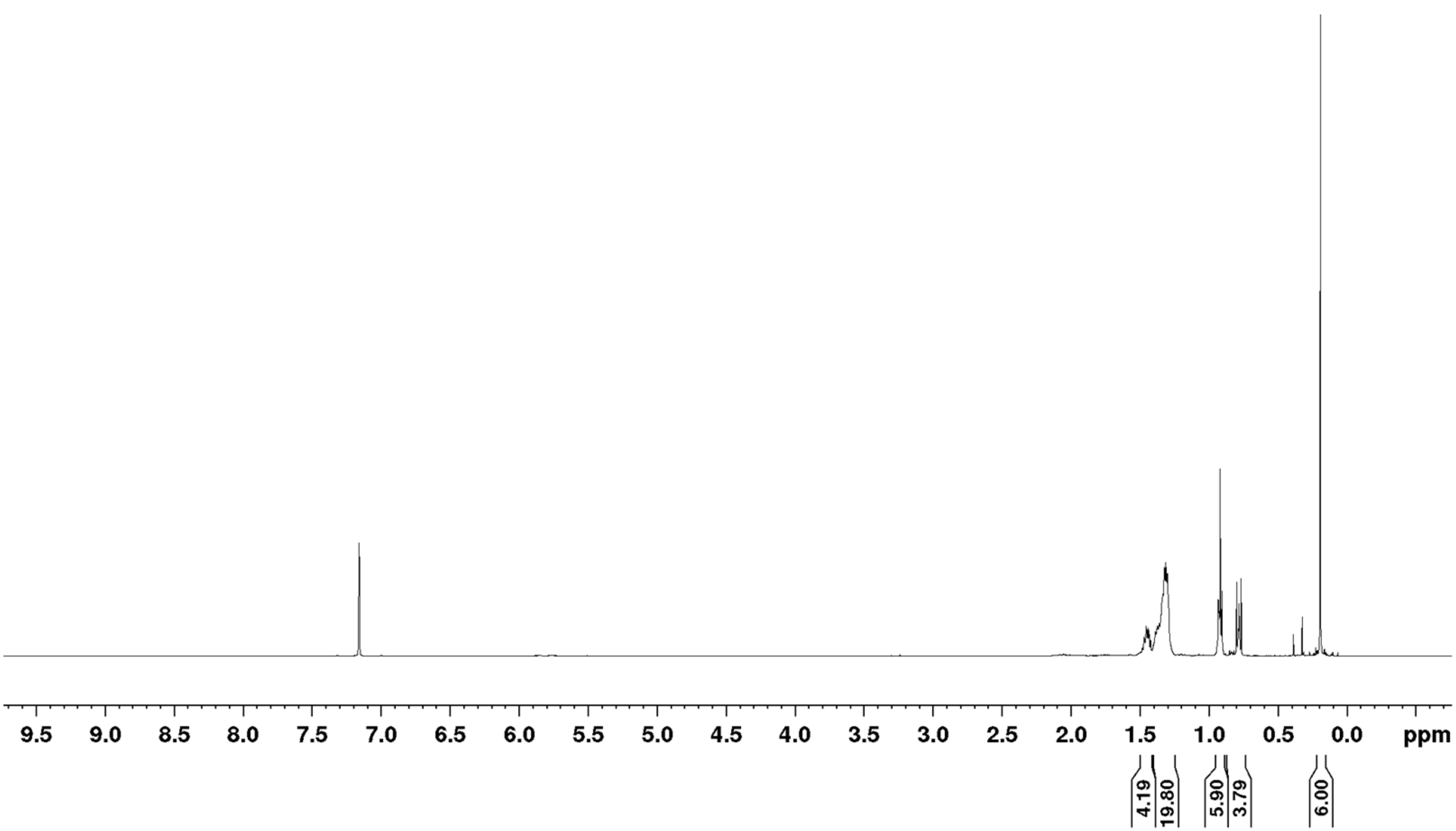
$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6):



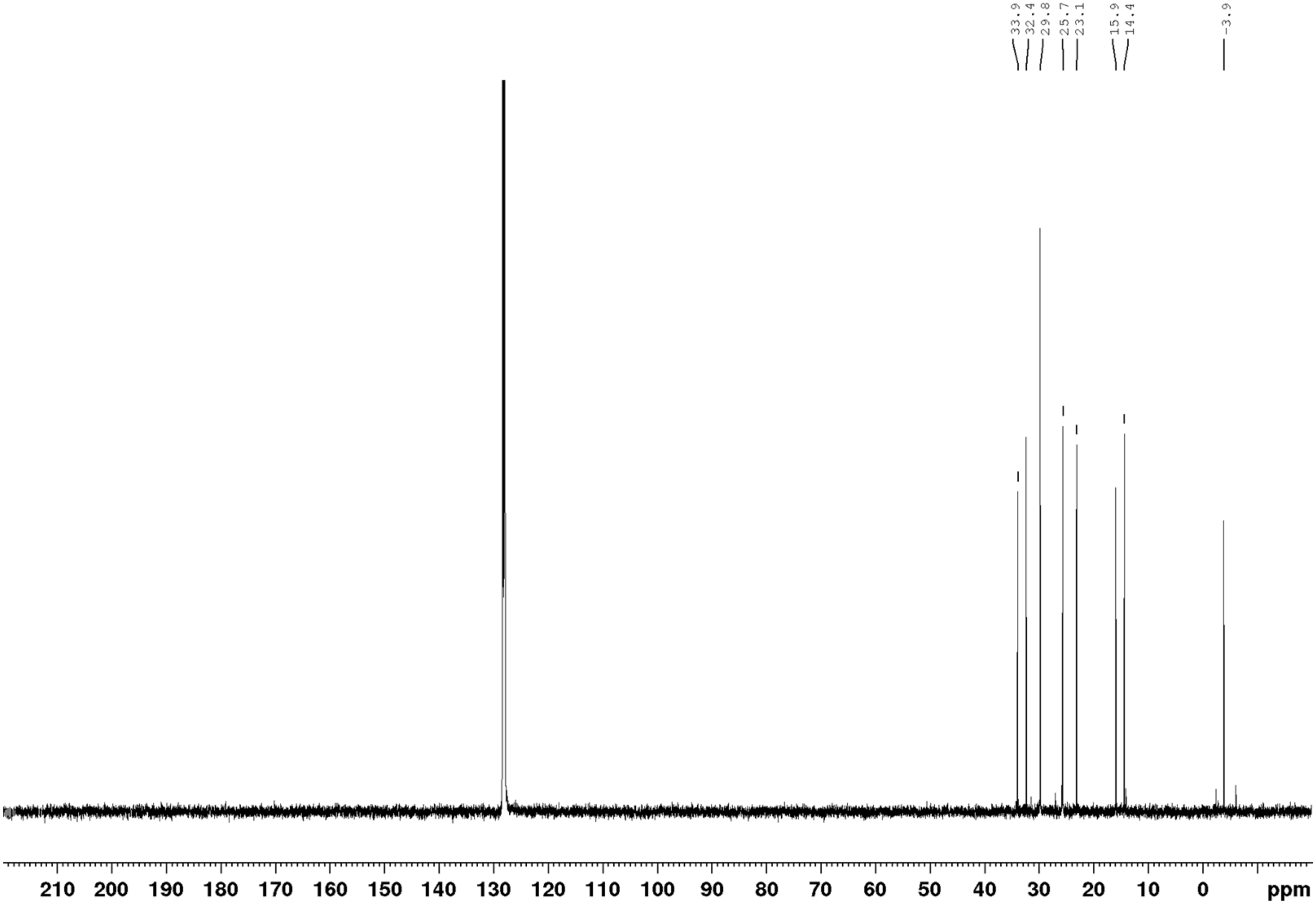
Dimethyldioctylgermane (41)

^{1}H NMR (500 MHz, C_6D_6):



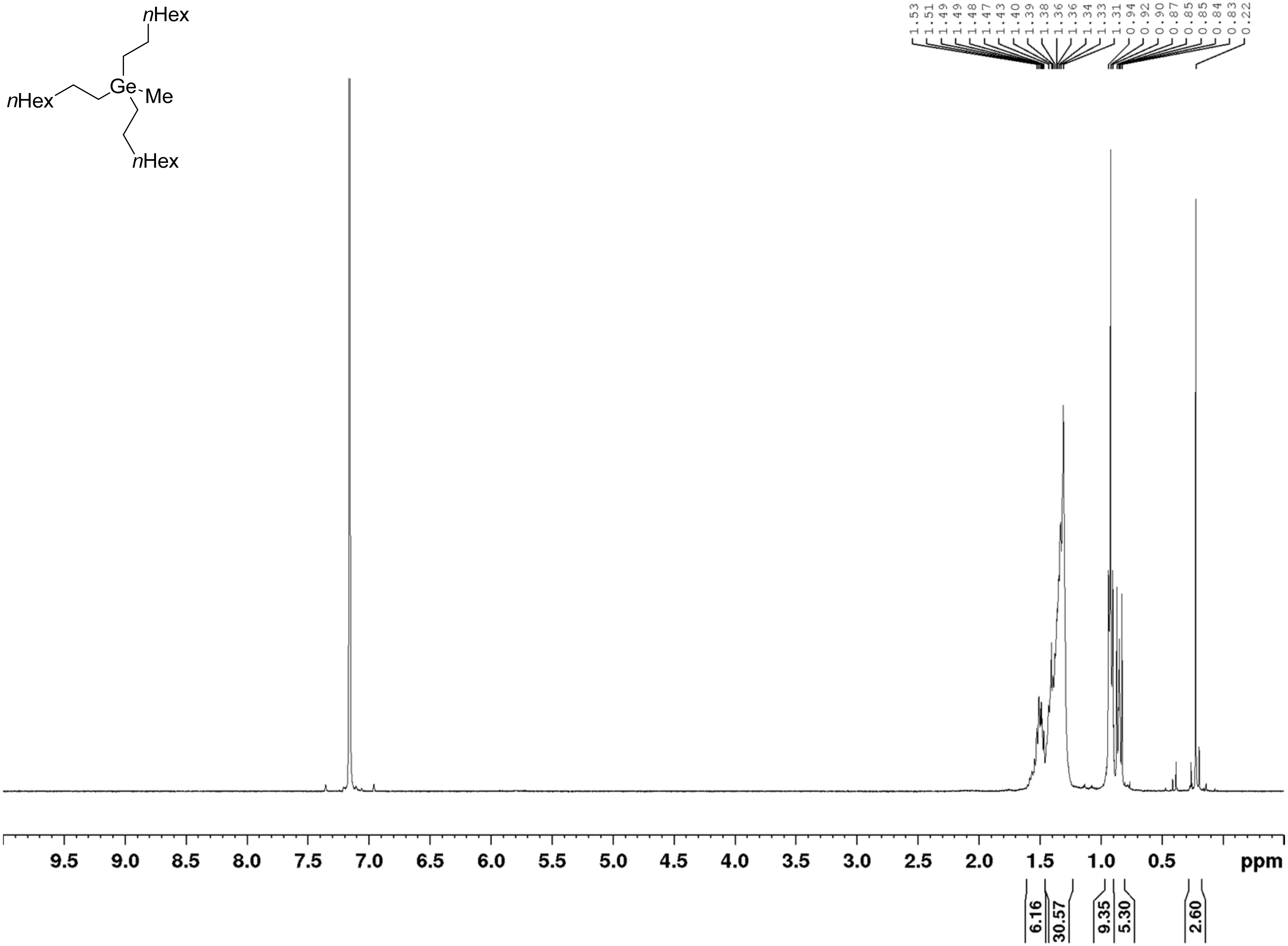


$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6):

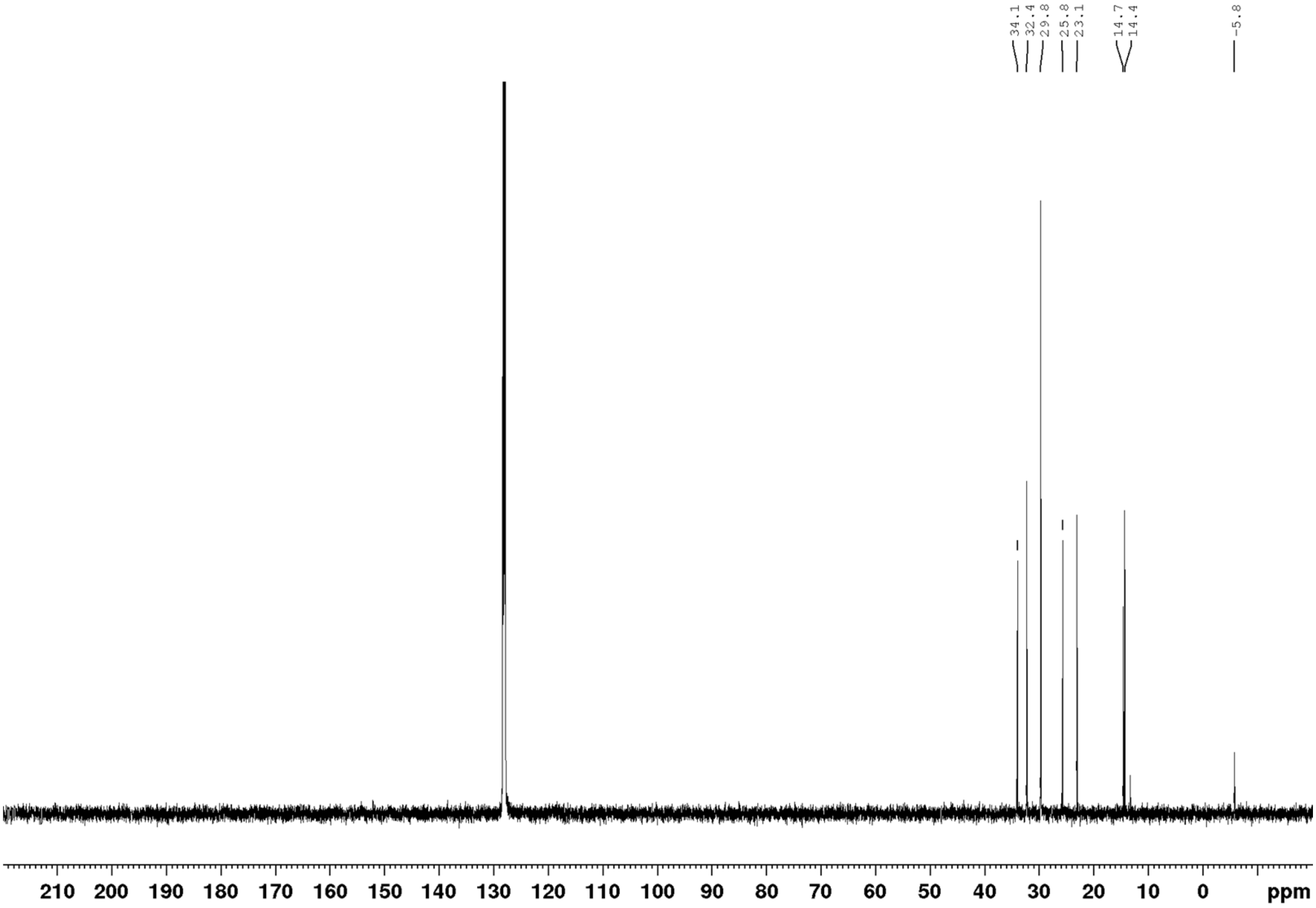


Methyltrioctylgermane (42)

^{1}H NMR (400 MHz, C_6D_6):

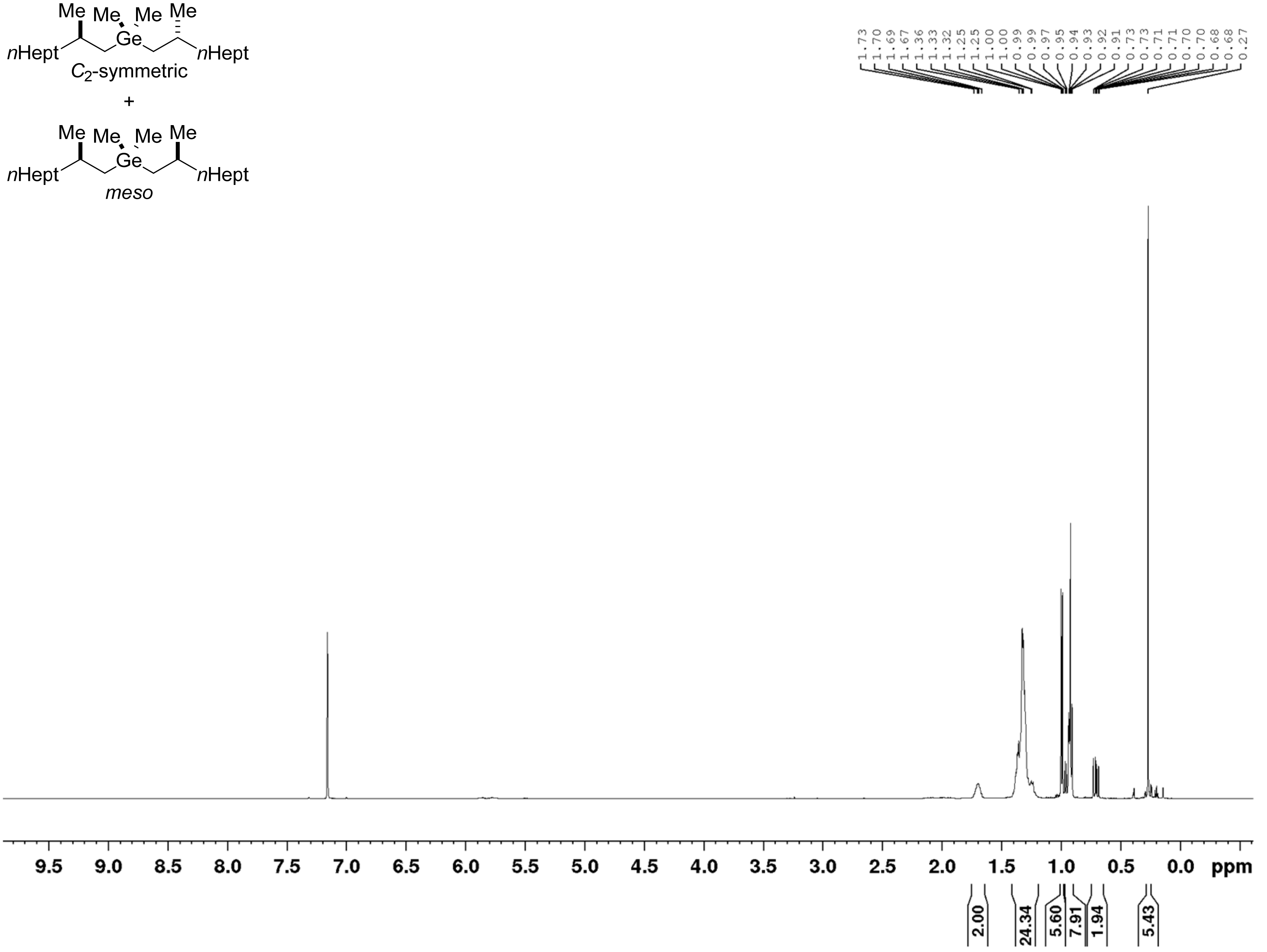


$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6):

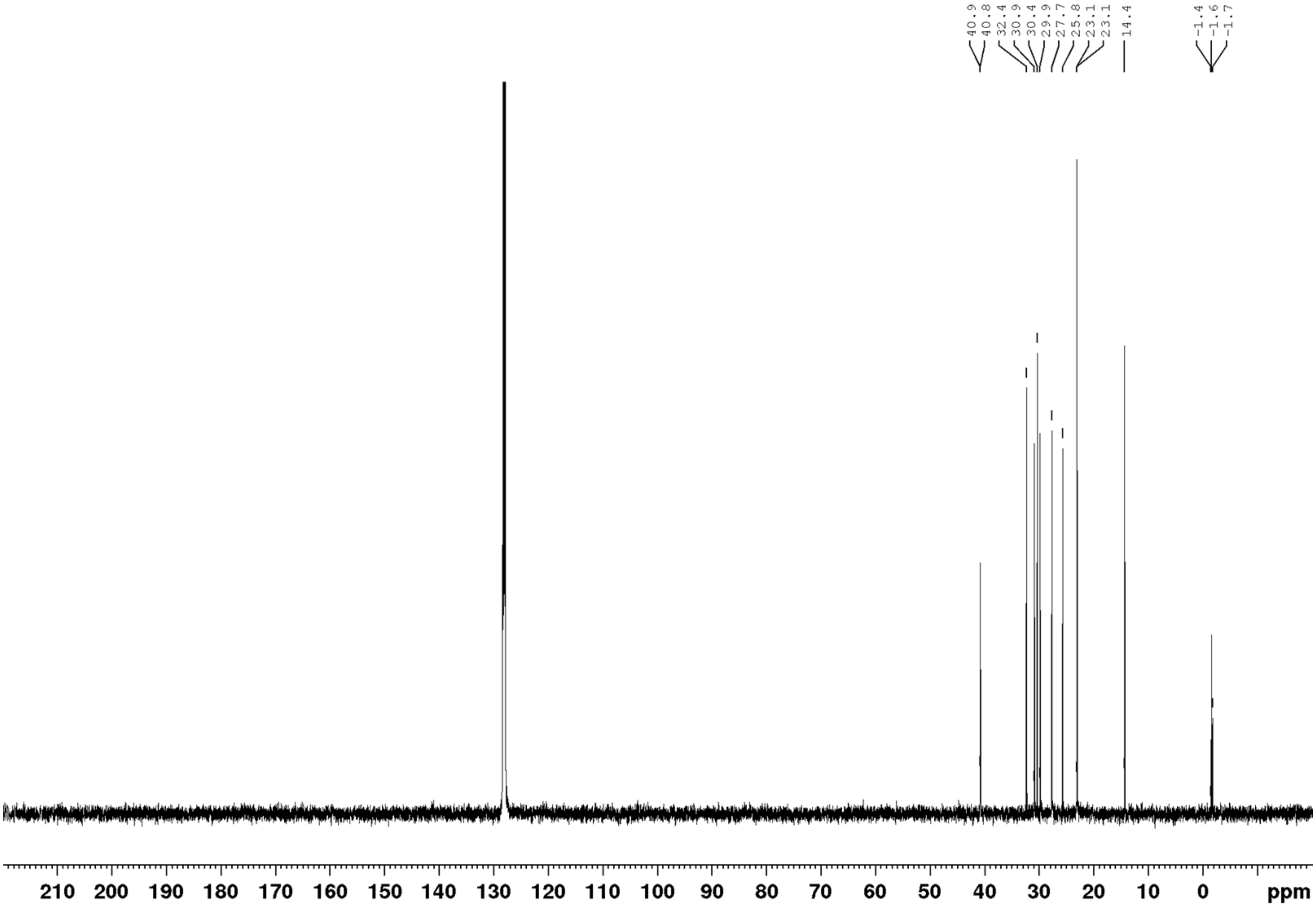


Dimethylbis(2-methylnonyl)germane (43)

^{1}H NMR (500 MHz, C_6D_6):

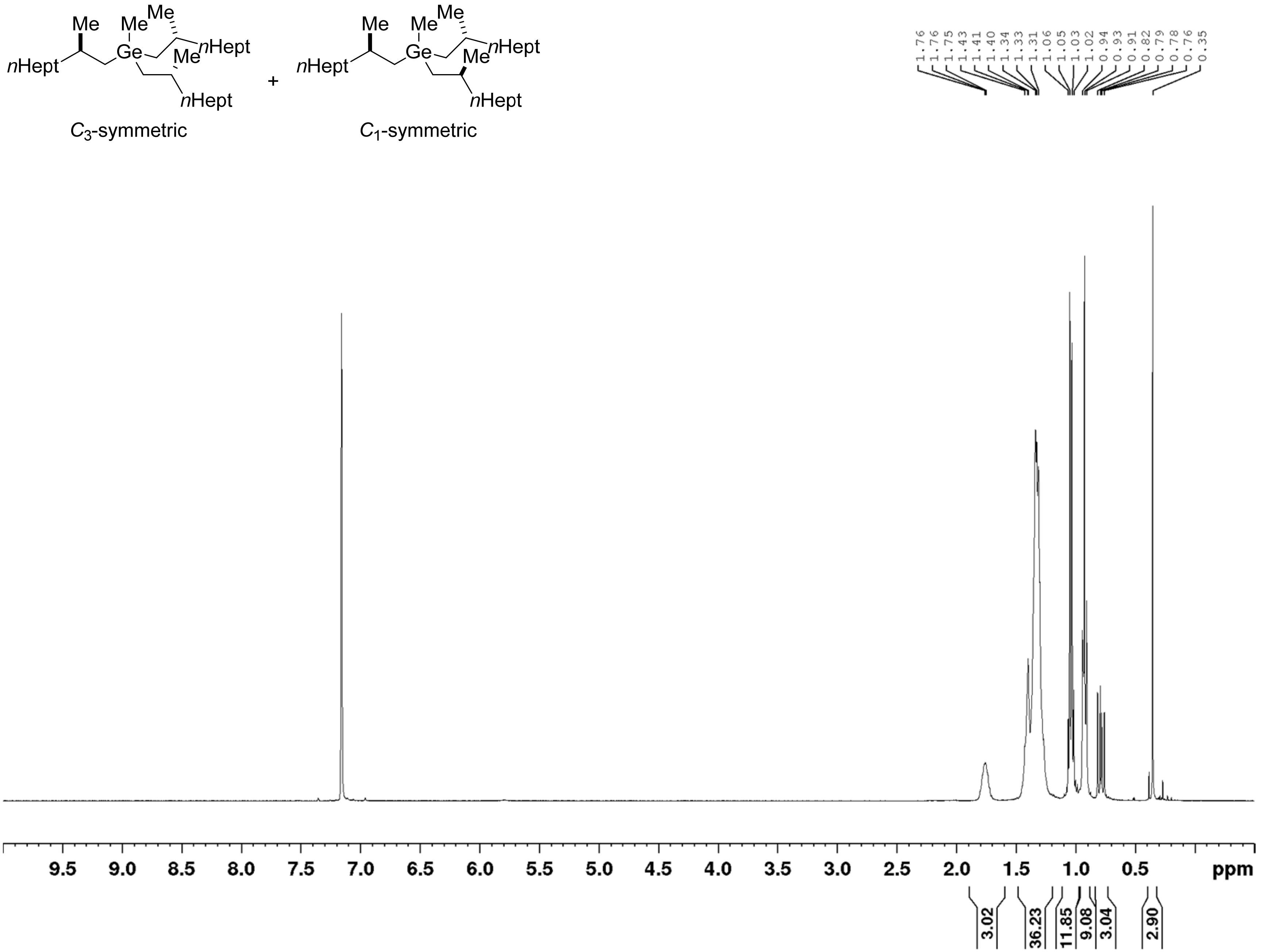


$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6):

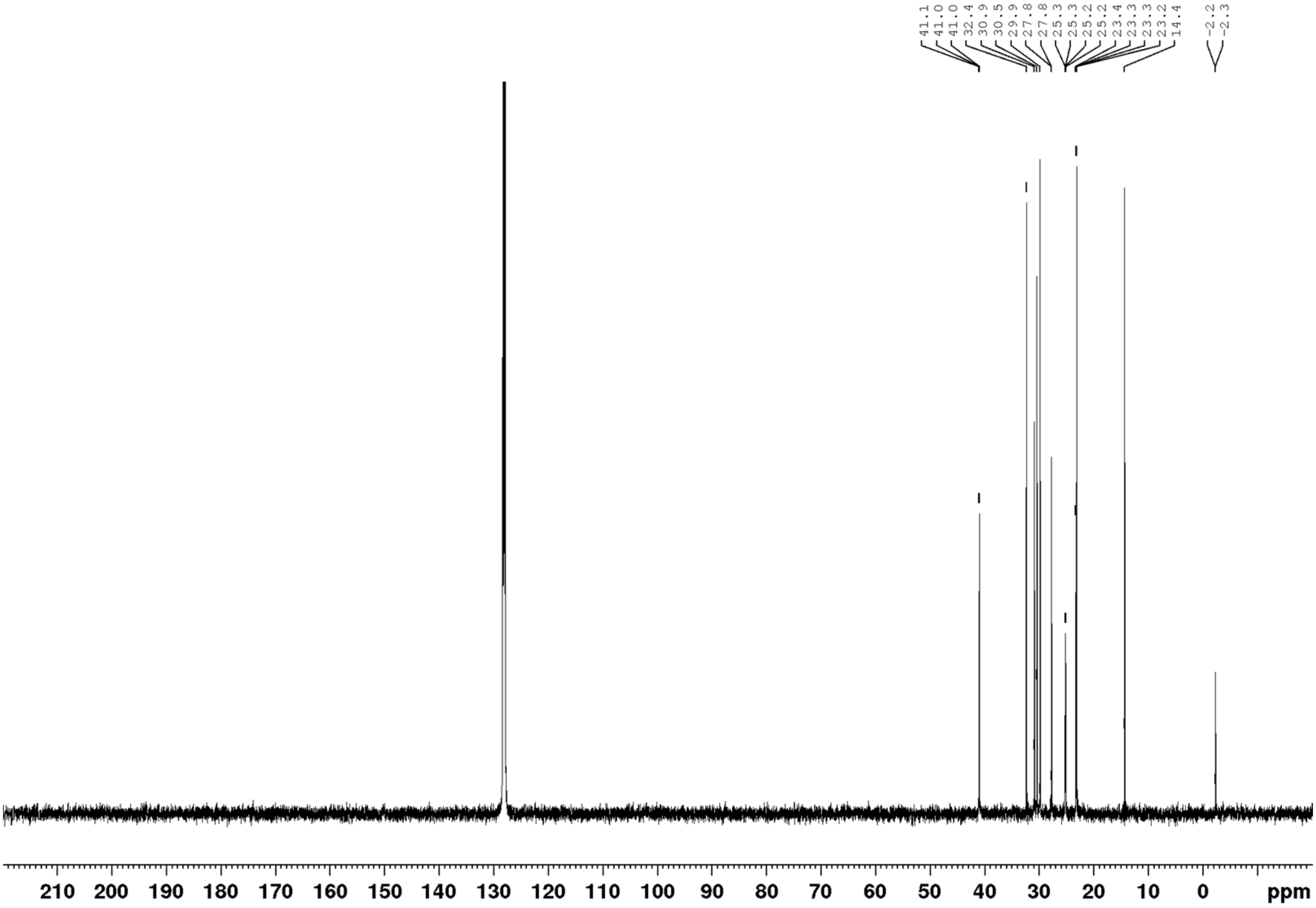


Methyltris(2-methylnonyl)germane (44)

^{1}H NMR (400 MHz, C_6D_6):

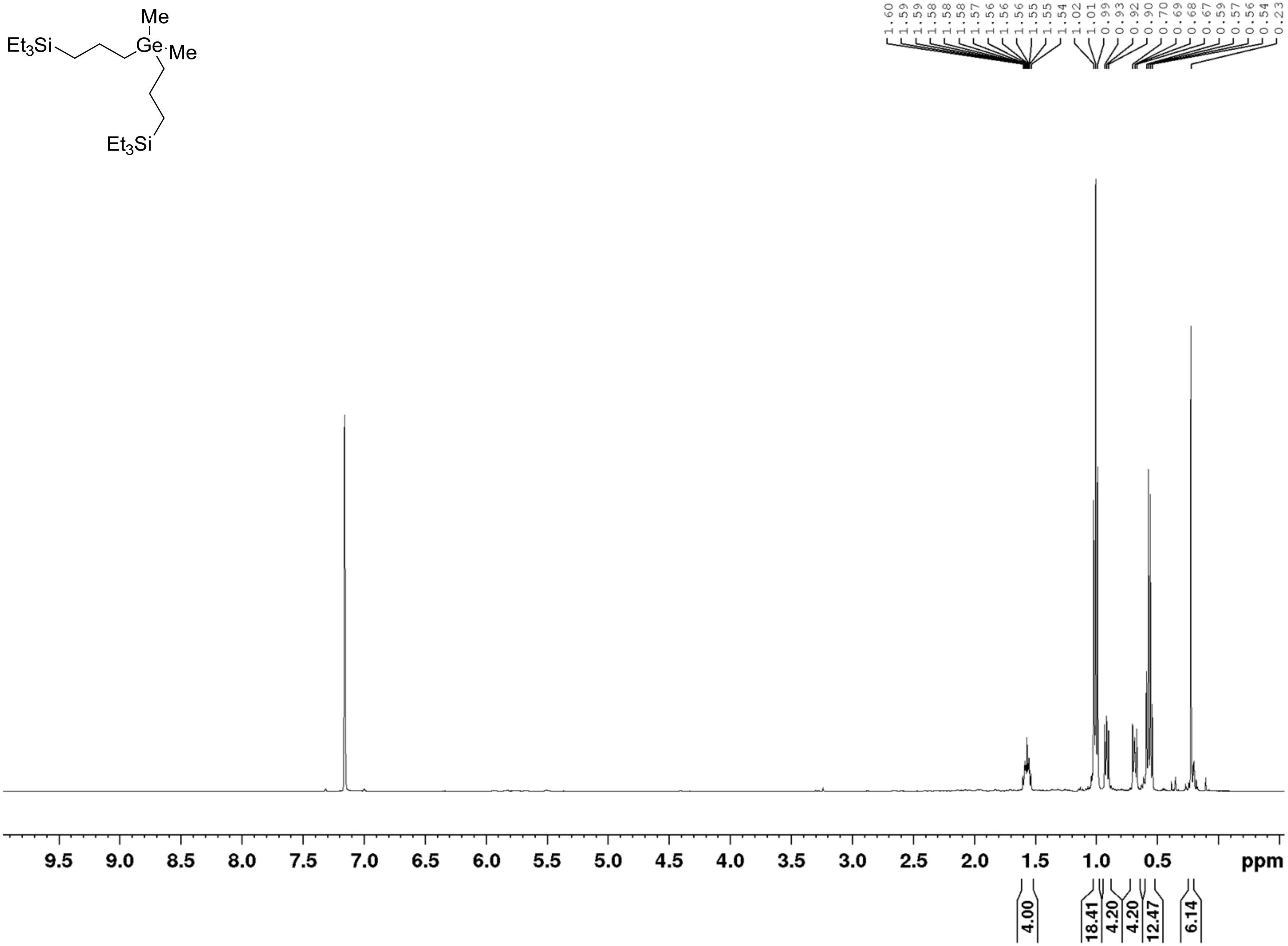


$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6):

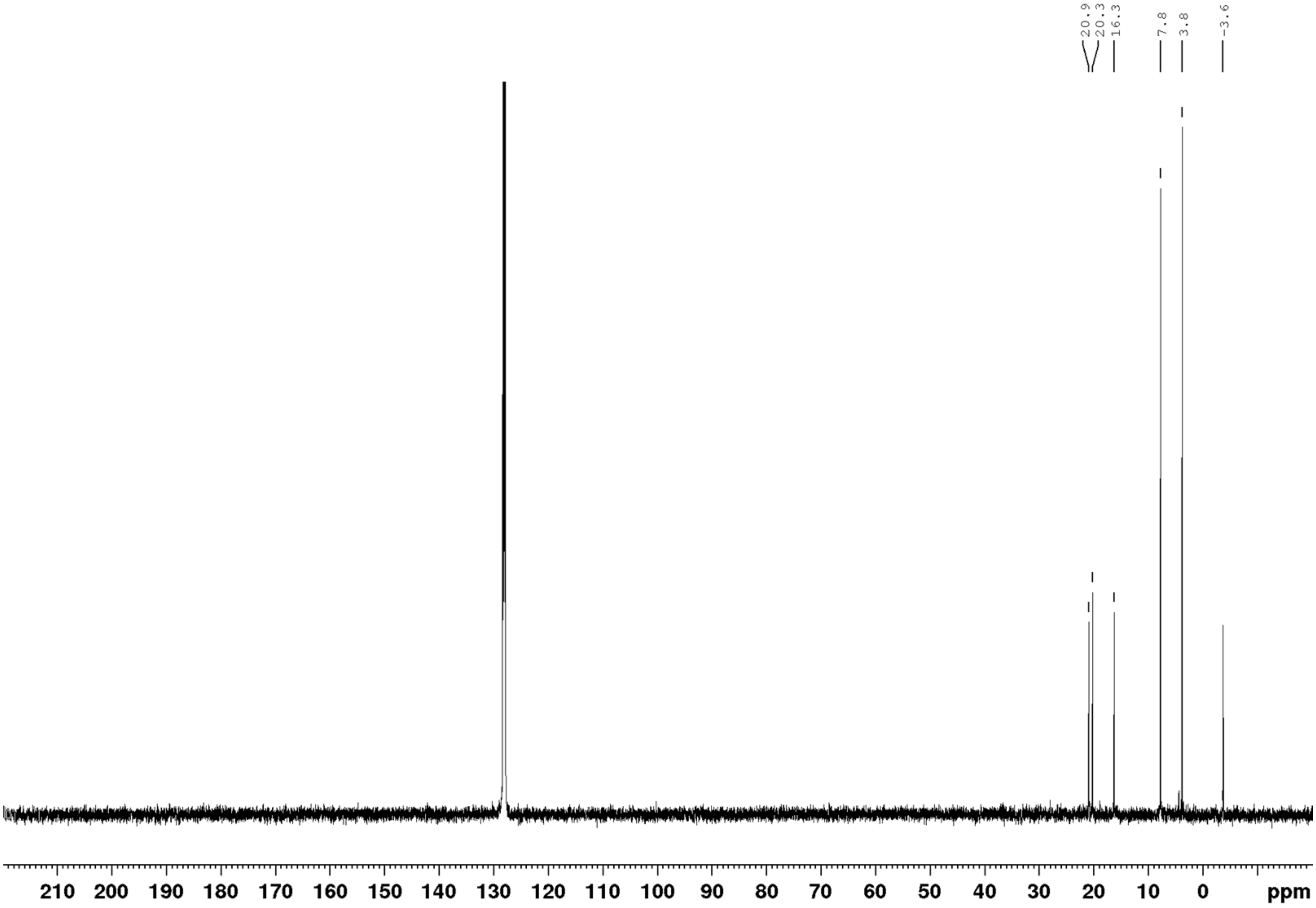


Dimethylbis(3-(triethylsilyl)propyl)germane (45)

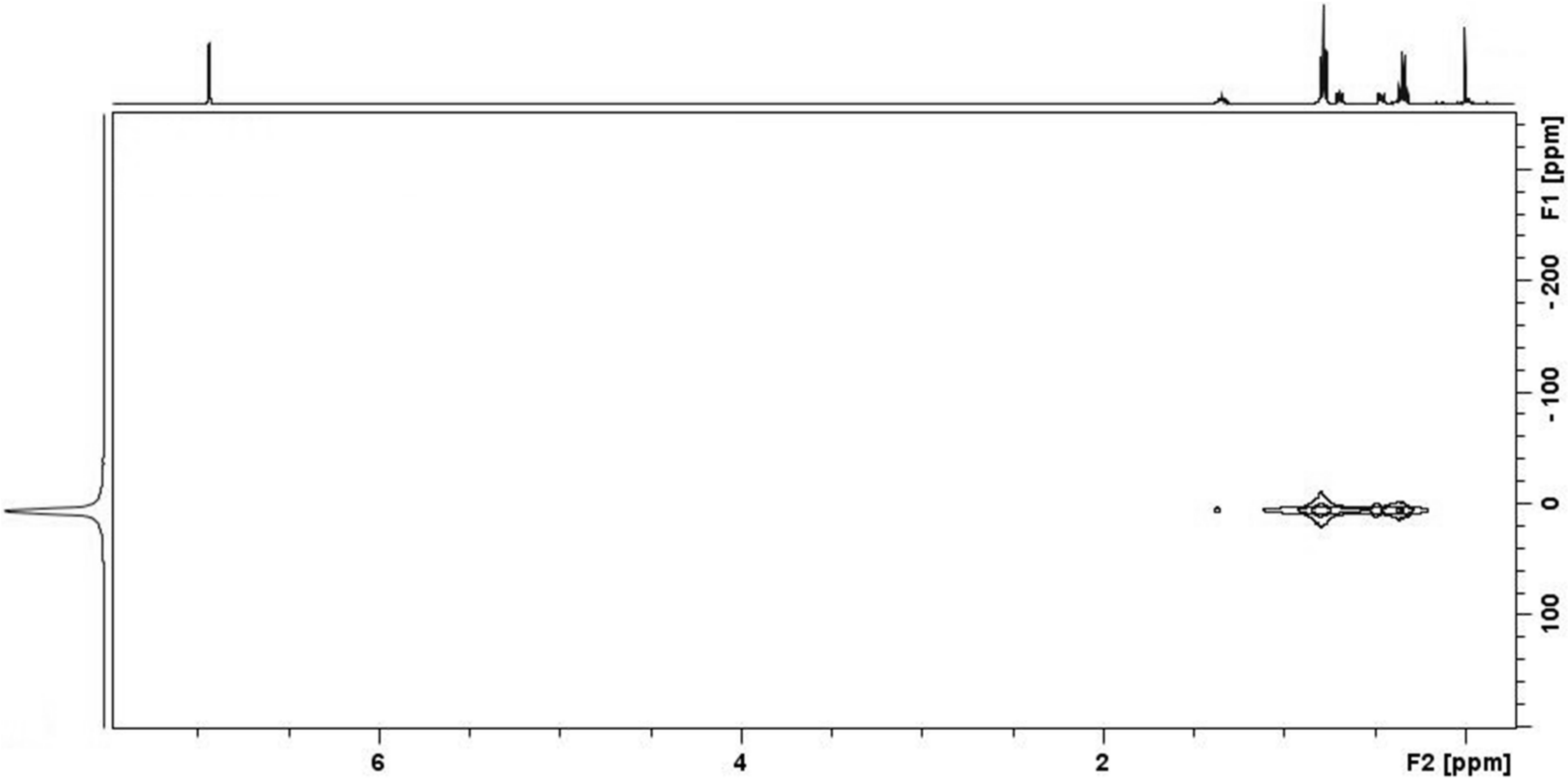
^{1}H NMR (500 MHz, C_6D_6):



$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6):



^{1}H,^{29}Si-HMQC 2D NMR (C_6D_6, SFO1 500 MHz, SFO2 99 MHz):



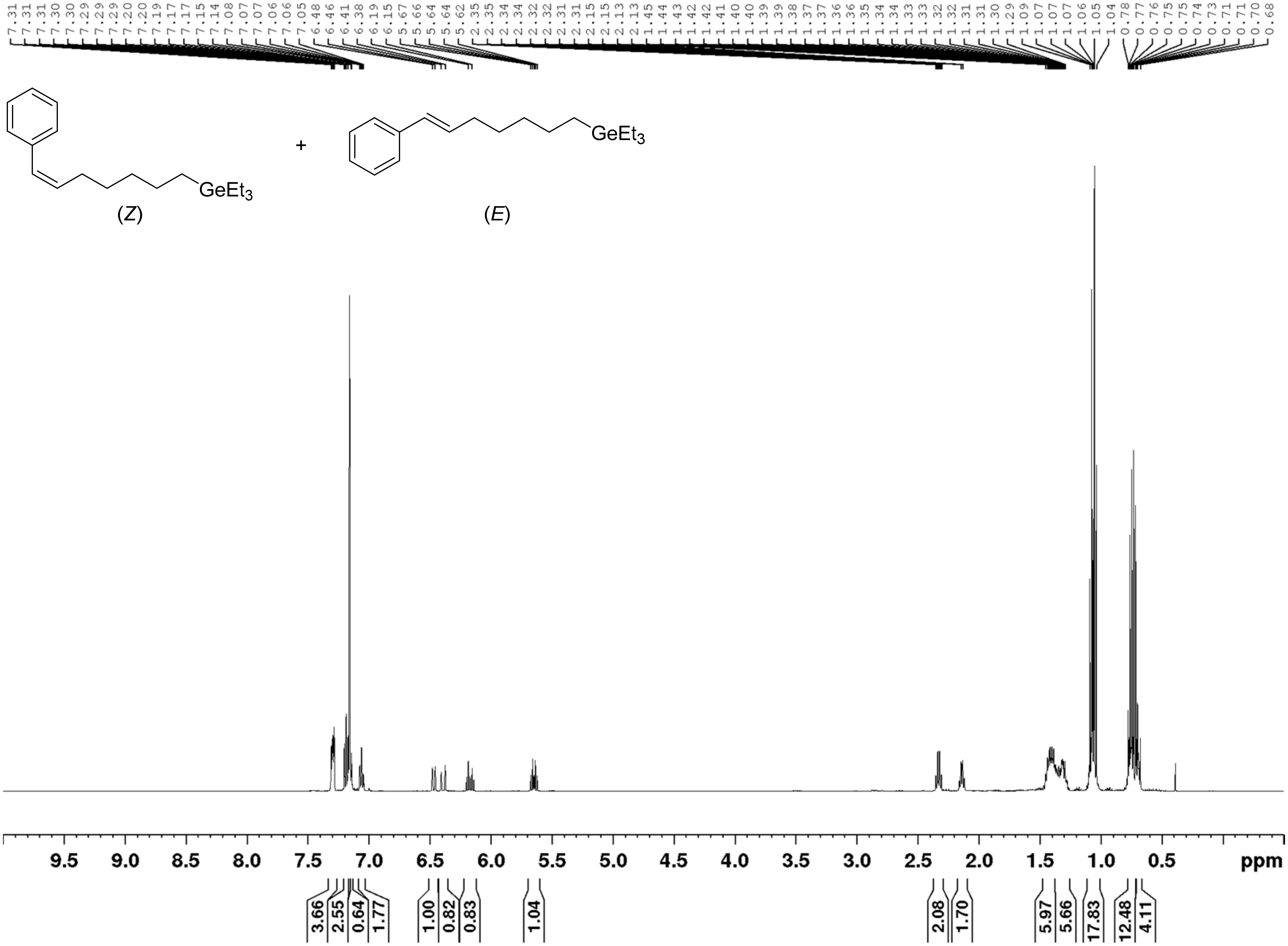
Triethyl(7-phenylhept-6-en-1-yl)germane (48)

^{1}H NMR (500 MHz, C_6D_6):

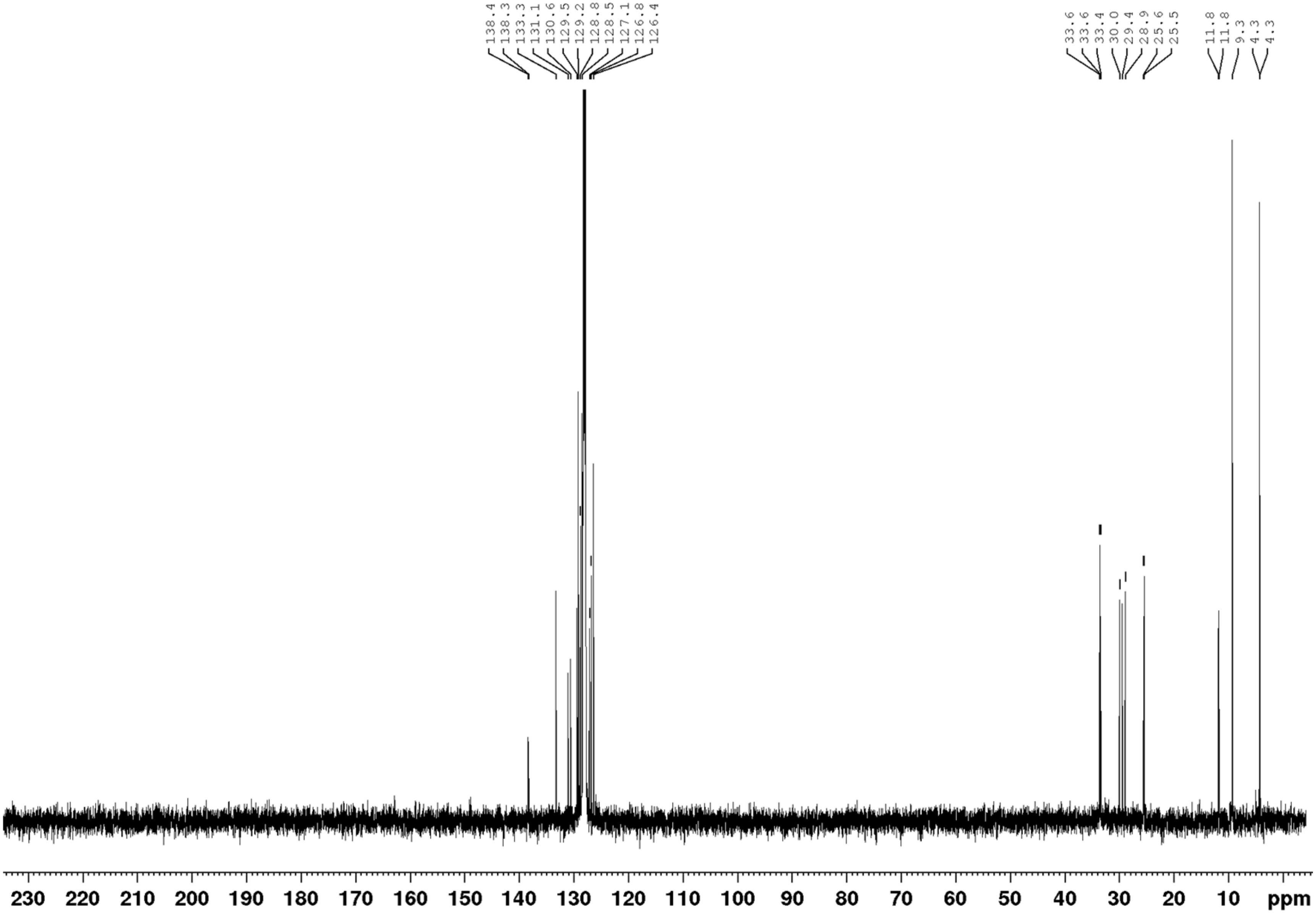
(*Z*)

\+

(*E*)



$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6):



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[S7] Zyder, M.; Szymańska-Buzar, T. *J. Organomet. Chem.* **2009**, *694*, 2110–2113.