

Supporting Information

Metal Triflates-mediated Coupling of Allylgermanes with Thiols: A Facile Route to Thiogermanes

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1. Preparation of (2-methylallyl)germanes

1.1. Preparation of (2-methylallyl)triethylgermane

In two-necked round bottom flask (100 mL) equipped with condenser, THF (15 mL) and 2.84 g of chlorotriethylgermane (14.5 mmol) were placed. Next, 22 mL of 1M solution of 2-methylallyl magnesium chloride was added. The system was stirred by 3 hours in inert atmosphere (Ar). After that, the solvent was evaporated. The reaction mixture was extracted with hexane. Next, hexane was evaporated and the crude product was distilled under reduced pressure to obtain 3 g of (2-methylallyl)triethylgermane (Yield = 95%).

1.2. Preparation of (2-methylallyl)tributylgermane

In two-necked round bottom flask (100 mL) equipped with condenser, THF (15 mL) and 2.03 g of chlorotributylgermane (7.25 mmol) were placed. Next, 11 mL of 1M solution of 2-methylallyl magnesium chloride was added. The system was stirred by 3 hours in inert atmosphere (Ar). After that, the solvent was evaporated. The reaction mixture was extracted with hexane. Next, hexane was evaporated and the crude product was distilled under reduced pressure to obtain 2 g of (2-methylallyl)tributylgermane (Yield = 92%).

1.3. Preparation of di(2-methylallyl)diethylgermane

In two-necked round bottom flask (100 mL) equipped with condenser, THF (15 mL) and 2 g of dichlorodiethylgermane (9.95 mmol) were placed. Next, 30 mL of 1M solution of 2-methylallyl magnesium chloride was added. The system was stirred by 3 hours in inert atmosphere (Ar). After that, the solvent was evaporated. The reaction mixture was extracted with hexane. Next, hexane was evaporated and the crude product was distilled under reduced pressure to obtain 2.1 g of di(2-methylallyl)diethylgermane (Yield = 87.5%).

2. Characterization data of 2-methylallylgermanes

2.1. (2-Methylallyl)triethylgermane

(2-Methylallyl)triethylgermane was obtained as a colorless liquid in 95% yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 0.65-0.84 (m, 6H), 1.02 (t, *J* = 7.9 Hz, 9H), 1.54 (s, 3H), 1.61-1.75 (m, 2H), 4.60-4.81 (m, 2H). **¹³C NMR** (101 MHz, C₆D₆): δ (ppm) = 4.3, 8.8, 22.9, 24.7, 108.0, 144.2.

MS (EI) m/z (rel.int.): 187(100%, (M-C₂H₅)⁺), 159 (25), 131 (15), 103 (20), 75 (5).

2.2. (2-Methylallyl)tributylgermane

(2-Methylallyl)tributylgermane was obtained as a colorless liquid in 92% yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 0.78-0.87 (m, 6H), 0.93 (t, *J* = 7.1 Hz, 8H), 1.29-1.46 (m, 11H), 1.54 (s, 3H), 1.71-1.76 (m, 4H), 4.69-4.76 (m, 2H). **¹³C NMR** (101 MHz, C₆D₆): δ (ppm) = 12.9, 13.6, 24.0, 24.8, 26.7, 27.5, 108.1, 144.3.

MS (EI) m/z (rel.int.): 243(50%, (M-C₄H₉)⁺), 189 (100), 133 (90), 103 (20), 89 (15), 55 (25).

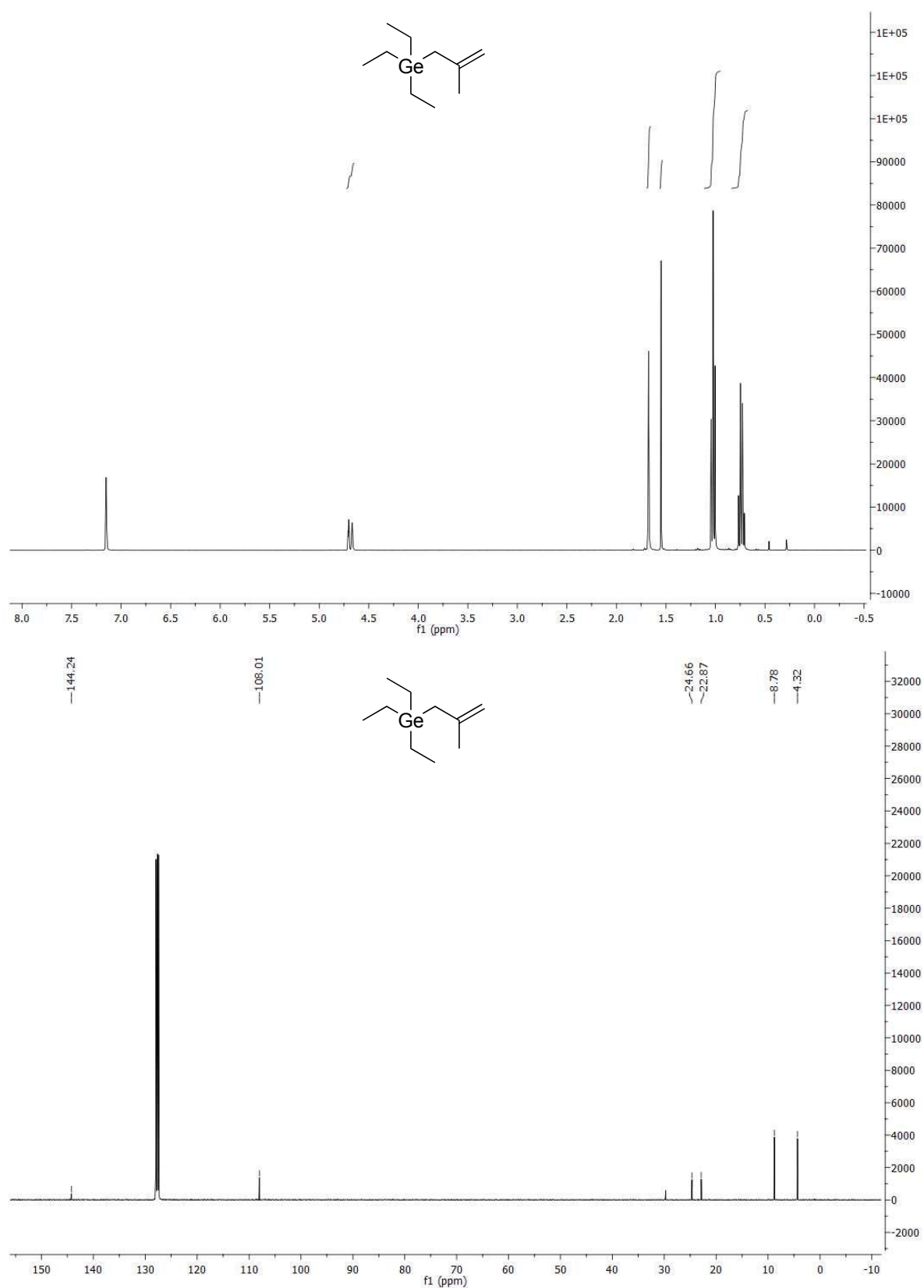
2.3. Di(2-methylallyl)diethylgermane

Di(2-methylallyl)diethylgermane was obtained as a colorless liquid in 87.5% yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 0.71-0.83 (m, 4H), 0.98-1.07 (m, 6H), 1.63-1.69 (m, 6H), 1.71 (d, *J* = 0.9 Hz, 4H), 4.57-4.82 (m, 4H). **¹³C NMR** (101 MHz, C₆D₆): δ (ppm) = 5.3, 8.7, 23.5, 24.7, 108.6, 143.9.

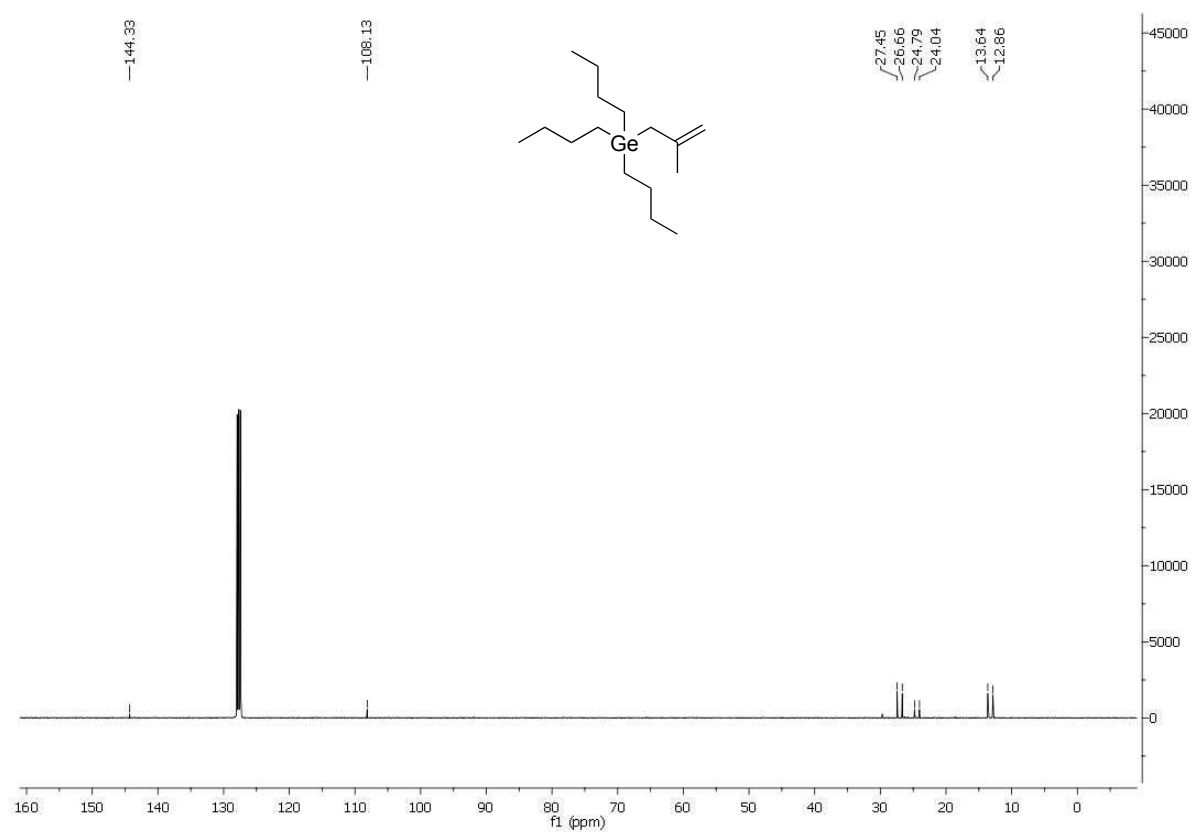
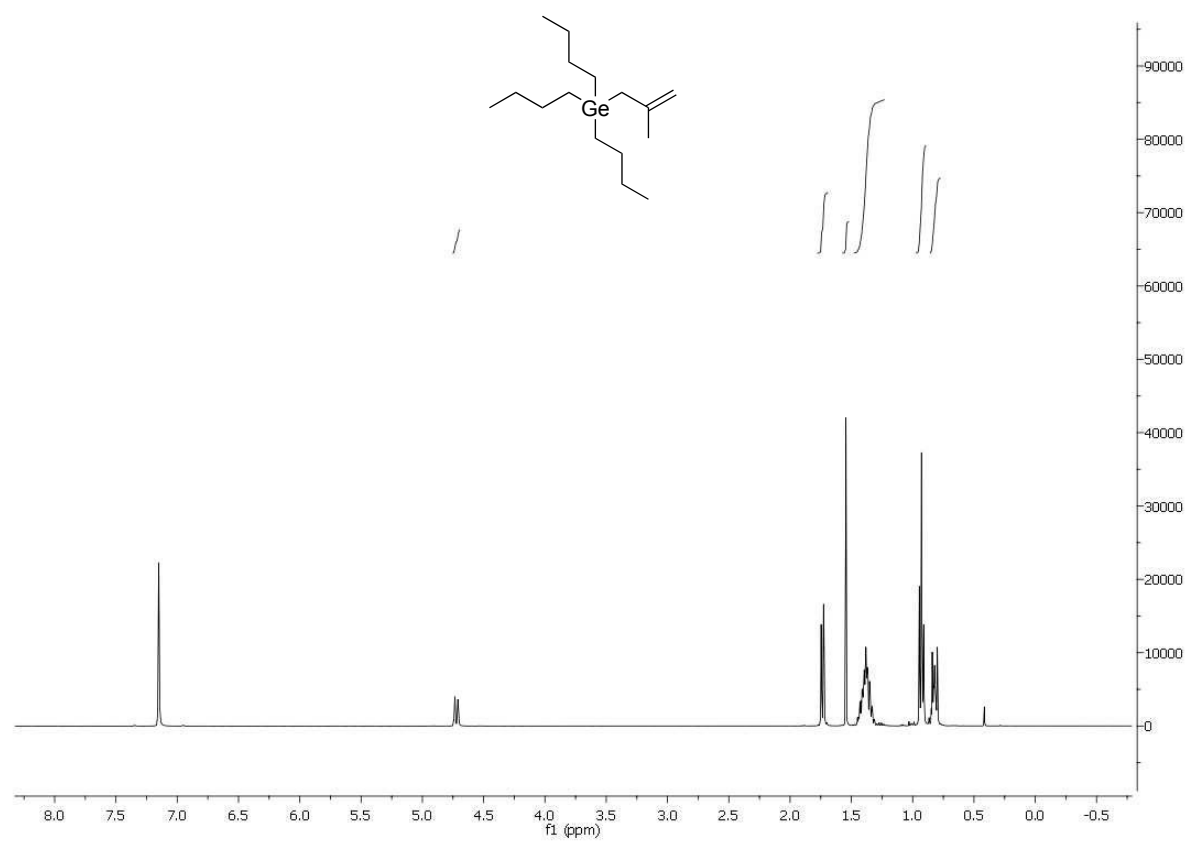
MS (EI) m/z (rel.int.): 213 (15%, (M-C₂H₅)⁺), 187 (100), 157 (10), 129 (15), 103 (30).

3. Copies of ^1H and ^{13}C NMR spectra of (2-methylallyl)germanes

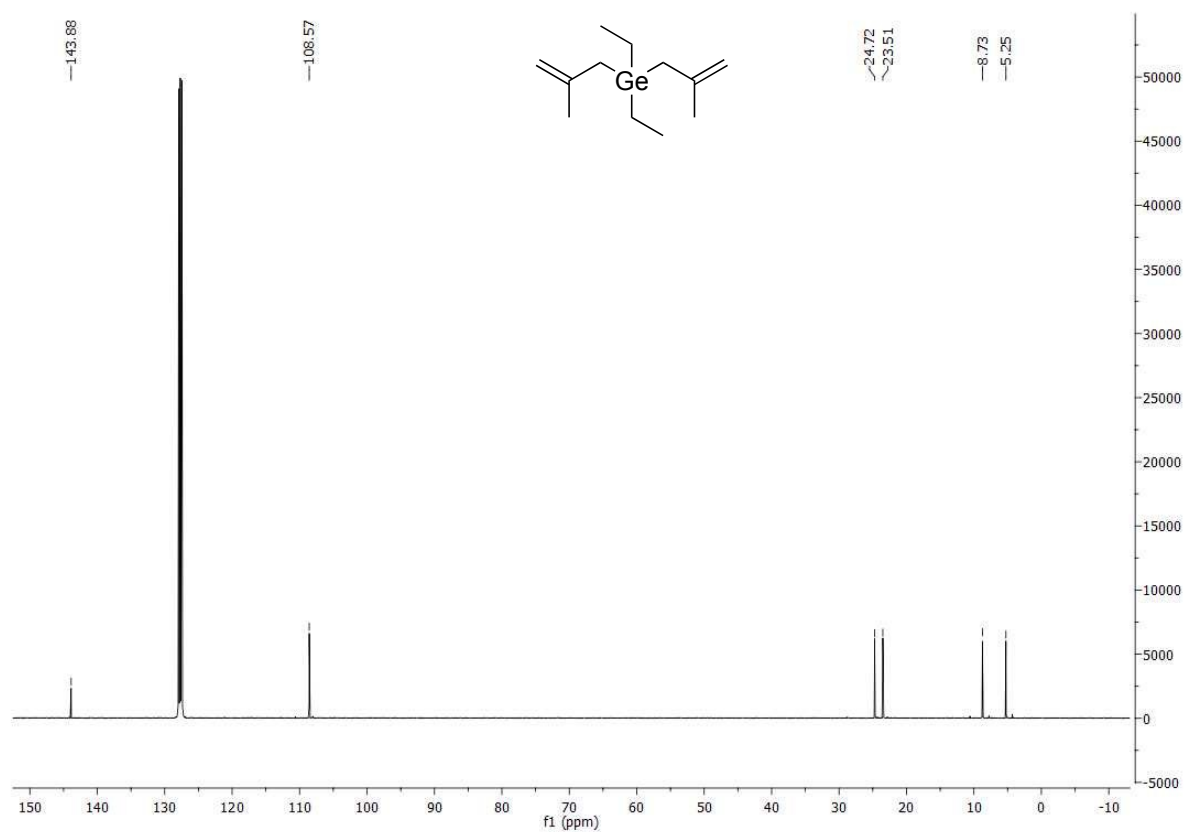
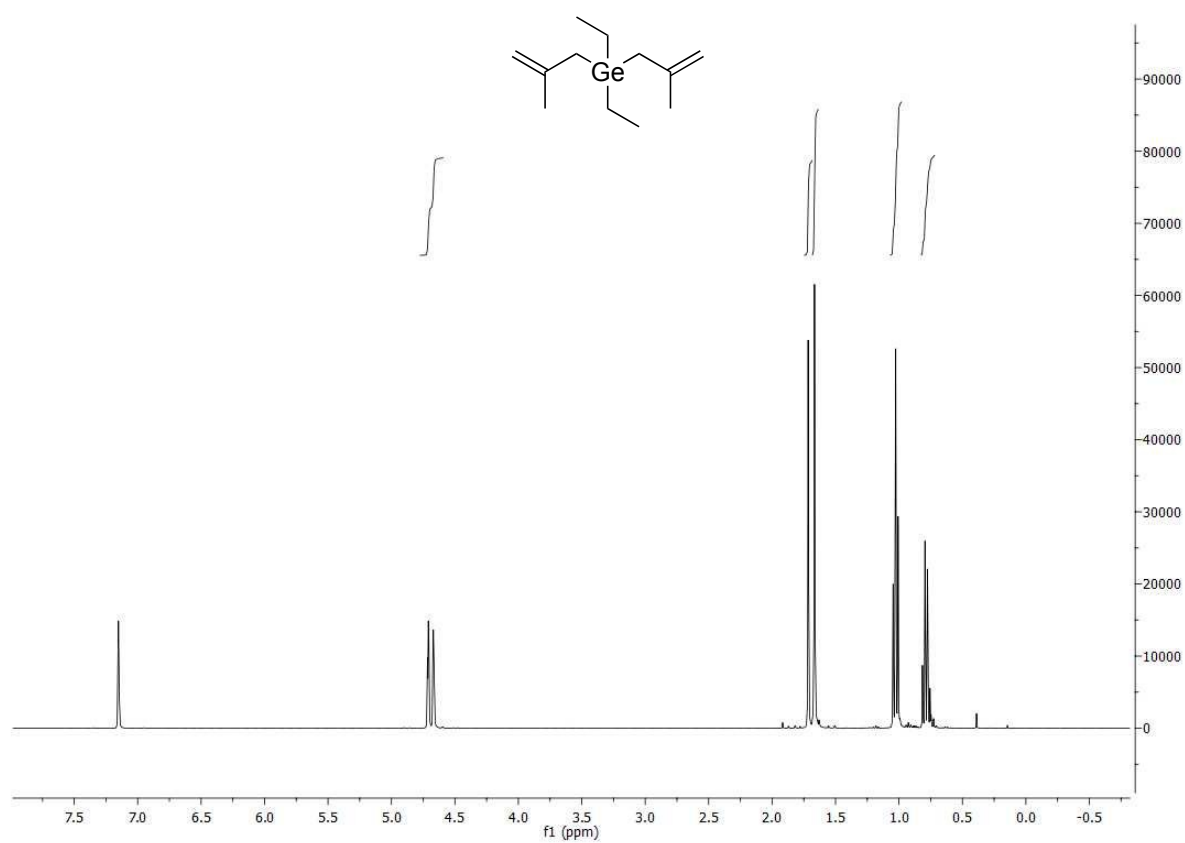
3.1. (2-methylallyl)triethylgermane



3.2. (2-methylallyl)tributylgermane



3.3. Di(2-methylallyl)diethylgermane



4. Characterization data of products

4.1. Triethyl[(*p*-chlorophenyl)thio]germane (**1**)

The product **1** was obtained as a colorless liquid in 91 % yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 0.74-0.83 (m, 6H), 0.89-1.02 (m, 9H), 6.89-6.94 (m, 2H), 7.20-7.25 (m, 2H). **¹³C NMR** (101 MHz, C₆D₆): δ (ppm) = 7.5, 8.4, 128.6, 132.4, 132.5, 136.3.

MS (EI) m/z (rel. int.): 304 (10% M⁺), 275 (100, (M-C₂H₅)⁺), 247 (15), 217 (10), 161 (20), 133 (25), 105 (15).

HRMS calcd for C₁₃H₁₉ClGeS[(M-C₂H₅)⁺]: 274.97165, found: 274.97147

4.2. Triethyl(cyclohexylthio)germane (**2**)

The product **2** was obtained as a colorless liquid in 93 % yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 0.89-0.97 (m, 6H), 1.05-1.12 (m, 9H), 1.13-1.27 (m, 3H), 1.35-1.44 (m, 1H), 1.46-1.59 (m, 2H), 1.63-1.76 (m, 2H), 1.95-2.06 (m, 2H), 2.69-2.81 (m, 1H). **¹³C NMR** (101 MHz, C₆D₆): δ (ppm) = 7.7, 8.7, 25.5, 26.3, 38.3, 40.1.

MS (EI) m/z (rel. int.): 247 (100%, (M-C₂H₅)⁺), 161 (30), 137 (20), 105 (15), 55 (30).

HRMS calcd for C₁₂H₂₆GeS: 276.09671, found: 276.09492

4.3. Triethyl[(*p*-methoxyphenyl)thio]germane (**3**)

The product **3** was obtained as a colorless liquid in 95 % yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 0.83-0.94 (m, 6H), 1.03 (t, *J* = 7.8 Hz, 9H), 3.22 (s, 3H), 6.60-6.65 (m, 2H), 7.42-7.49 (m, 2H). **¹³C NMR** (101 MHz, C₆D₆): δ (ppm) = 7.4, 8.5, 54.4, 114.3, 114.6, 123.6, 132.3, 136.4, 158.9.

MS (EI) m/z (rel. int.): 300 (30% M⁺), 271 (100 (M-C₂H₅)⁺), 256 (10), 213 (15), 133 (25), 109 (40), 77 (20).

HRMS calcd for C₁₃H₂₂GeOS: 300.06030, found: 300.06127

4.4. 3,3,9,9-Tetraethyl-4,8-dithia-3,9-digermaundecane (**4**)

The product **4** was obtained as a colorless liquid in 90 % yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 0.87-0.95 (m, 6H), 1.07 (t, *J* = 7.7 Hz, 9H), 1.94 (p, *J* = 6.9 Hz, 2H), 2.64 (t, *J* = 6.9 Hz, 4H). **¹³C NMR** (101 MHz, C₆D₆): δ (ppm) 7.2, 8.6, 25.0, 37.0.

MS (EI) m/z (rel. int.): 426 (2% M⁺), 397 (100, (M-C₂H₅)⁺), 235 (55), 209 (20), 161 (45), 133 (60), 103 (40).

HRMS calcd for C₁₅H₃₆Ge₂S₂: 426.06909, found: 426.07191

4.5. Triethyl(phenylthio)germane (**5**)

The product **5** was obtained as a colorless liquid in 92 % yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 0.81-0.90 (m, 6H), 0.95-1.03 (m, 9H), 6.90-7.02 (m, 3H), 7.49-7.56 (m, 2H). **¹³C NMR** (101 MHz, C₆D₆): δ (ppm) = 7.5, 8.4, 126.2, 128.5, 133.9, 135.1.

MS (EI) m/z (rel. int.): 267 (10% M⁺), 241 (100 (M-C₂H₅)⁺), 213 (100), 183 (12), 159 (17), 133 (15), 103 (10), 77 (25).

HRMS calcd for C₁₂H₂₀GeS: 270.04974, found: 270.05082

4.6. Triethyl[(3-methylbutyl)thio]germane (**6**)

The product **6** was obtained as a colorless liquid in 91 % yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 0.83 (d, *J* = 6.6 Hz, 6H), 0.87-0.96 (m, 6H), 1.03-1.14 (m, 9H), 1.47-1.57 (m, 2H), 1.65-1.79 (m, 1H), 2.46-2.54 (m, 2H).

¹³C NMR (101 MHz, C₆D₆): δ (ppm) = 7.2, 8.6, 22.0, 24.3, 27.0, 42.8.

MS (EI) m/z (rel. int.): 235 (100%, (M-C₂H₅)⁺), 149 (40), 133 (25), 103 (20), 71 (15).

HRMS calcd for C₁₁H₂₆GeS: 264.09671, found: 264.09721

4.7. Triethyl[(p-fluorophenyl)thio]germane (**7**)

The product **7** was obtained as a colorless liquid in 93 % yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 0.76-0.85 (m, 6H), 0.92-1.03 (m, 9H), 6.58-6.68 (m, 2H), 7.23-7.33 (m, 2H). **¹³C NMR** (101 MHz, C₆D₆): δ (ppm) = 7.6, 8.4, 115.5 (d, *J* = 21.6 Hz), 128.6 (d, *J* = 3.4 Hz), 136.7 (d, *J* = 7.8 Hz), 162.0 (d, *J* = 245.6 Hz).

MS (EI) m/z (rel. int.): 288 (10% M⁺), 259 (100, (M-C₂H₅)⁺), 231 (25), 201 (15), 161 (15), 133 (30), 103 (20), 75 (15).

HRMS calcd for C₁₂H₁₉FGeS: 288.04034, found: 288.04110

4.8. Triethyl[(o-fluorophenyl)thio]germane (**8**)

The product **8** was obtained as a colorless liquid in 92 % yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 0.84-0.93 (m, 6H), 0.95-1.04 (m, 9H), 6.54-6.68 (m, 1H), 6.69-6.82 (m, 2H), 7.39-7.50 (m, 1H). **¹³C NMR** (101 MHz, C₆D₆): δ (ppm) = 7.8, 8.3, 115.5 (d, *J* = 24 Hz), 121.0 (d, *J* = 19.9 Hz), 123.8 (d, *J* = 3.9 Hz), 128.2 (d, *J* = 7.6 Hz), 137.8, 163.7 (d, *J* = 243.6 Hz).

MS (EI) m/z (rel. int.): 259 (100%, (M-C₂H₅)⁺), 231 (15), 183 (10), 133 (5), 105 (12), 93 (7).

HRMS calcd for C₁₂H₁₉FGeS: 288.04034, found: 288.03954

4.9. Triethyl[(3-methylphenyl)thio]germane (**9**)

The product **9** was obtained as a colorless liquid in 95 % yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 0.85-0.95 (m, 6H), 0.97-1.09 (m, 9H), 2.03 (s, 3H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.42 (s, 1H). **¹³C NMR** (101 MHz, C₆D₆): δ (ppm) = 7.6, 8.5, 20.8, 127.0, 128.3, 132.2, 133.5, 135.8, 138.0.

MS (EI) m/z (rel. int.): 284 (5% M⁺), 255 (100, (M-C₂H₅)⁺), 227 (5), 197 (10), 133 (15), 103 (10), 91 (25), 65 (10).

HRMS calcd for C₁₃H₂₂GeS: 284.06540, found: 284.06594

4.10. Triethyl(benzylthio)germane (**10**)

The product **10** was obtained as a colorless liquid in 92 % yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 0.78-0.87 (m, 6H), 1.01 (t, *J* = 7.8 Hz, 9H), 3.61 (s, 2H), 7.00-7.06 (m, 1H), 7.07-7.14 (m, 2H), 7.28-7.36 (m, 2H).

¹³C NMR (101 MHz, C₆D₆): δ (ppm) = 7.2, 8.6, 30.6, 126.6, 128.2, 128.5, 141.7.

MS (EI) m/z (rel. int.): 283 (3%, M⁺), 255 (100, (M-C₂H₅)⁺), 159 (7), 133 (3), 103 (5), 91 (30).

HRMS calcd for C₁₃H₂₂GeS: 284.06540, found: 284.06687

4.11. Tributyl(benzylthio)germane (**11**)

The product **11** was obtained as a colorless liquid in 89 % yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 0.84-0.91 (m, 9H), 0.91-1.00 (m, 6H), 1.24-1.36 (m, 6H), 1.38-1.49 (m, 6H), 3.68 (s, 2H), 6.99-7.05 (m, 1H), 7.09-7.14 (m, 2H), 7.33-7.38 (m, 2H). **¹³C NMR** (101 MHz, C₆D₆): δ (ppm) = 13.6, 15.6, 26.2, 27.1, 30.9, 126.5, 128.2, 128.6, 141.8.

MS (EI) m/z (rel. int.): 311 (75%, (M-C₄H₉)⁺), 255 (100), 199 (20), 189 (15), 91 (90), 65 (20).

HRMS calcd for C₁₉H₃₄GeS: 368.15930, found: 368.16106

4.12. Tributyl(phenylthio)germane (**12**)

The product **12** was obtained as a colorless liquid in 94 % yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 0.86 (t, *J* = 7.3 Hz, 9H), 0.96-1.03 (m, 6H), 1.21-1.34 (m, 6H), 1.39-1.50 (m, 6H), 6.91-7.03 (m, 3H), 7.54-7.61 (m, 2H). **¹³C NMR** (101 MHz, C₆D₆): δ (ppm) = 13.5, 16.0, 26.1, 26.9, 126.2, 128.5, 134.1, 135.2.

MS (EI) m/z (rel. int.): 297 (100%, (M-C₄H₉)⁺), 241 (30), 189 (60), 131 (20), 79 (95).

HRMS calcd for C₁₈H₃₂GeS: 354.14365, found: 354.14305

4.13. Tributyl(cyclohexylthio)germane (**13**)

The product **13** was obtained as a colorless liquid in 91 % yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 0.91 (t, *J* = 7.3 Hz, 9H), 1.01-1.09 (m, 6H), 1.12-1.27 (m, 3H), 1.30-1.37 (m, 6H), 1.38-1.52 (m, 1H), 1.47-1.56 (m, 6H), 1.57-1.62 (m, 2H), 1.65-1.75 (m, 2H), 1.99-2.09 (m, 2H), 2.77-2.88 (m, 1H). **¹³C NMR** (101 MHz, C₆D₆): δ (ppm) = 13.6, 16.2, 25.5, 26.3, 26.5, 27.2, 38.3, 40.3.

MS (EI) m/z (rel. int.): 361 (5%, M⁺), 303 (100, (M-C₄H₉)⁺), 247 (20), 189 (25), 165 (35), 131 (20), 55 (45).

HRMS calcd for C₁₈H₃₈GeS: 360.19061, found: 360.19160

4.14. Tributyl[*p*-methoxyphenylthio]germane (**14**)

The product **14** was obtained as a colorless liquid in 88 % yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 0.88-0.91 (m, 9H), 0.93-1.04 (m, 6H), 1.25-1.37 (m, 6H), 1.38-1.52 (m, 6H), 3.21 (s, 3H), 6.62-6.69 (m, 2H), 7.46-7.54 (m, 2H). **¹³C NMR** (101 MHz, C₆D₆): δ (ppm) = 13.6, 15.9, 26.2, 27.0, 54.4, 114.3, 123.9, 136.5, 158.9.

MS (EI) m/z (rel. int.): 384 (90%, M⁺), 327 (100, (M-C₄H₉)⁺), 271 (60), 189 (50), 131 (40), 109 (90), 57 (60).

HRMS calcd for C₁₉H₃₄GeOS: 384.15421, found: 384.15459

4.15. Diethyl-di[(3-methylbutyl)thio]germane (**15**)

The product **15** was obtained as a colorless liquid in 90 % yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 0.79-0.89 (m, 12H), 1.02-1.13 (m, 6H), 1.14-1.20 (m, 4H), 1.53-1.61 (m, 4H), 1.62-1.79 (m, 2H), 2.65-2.80 (m, 4H). **¹³C NMR** (101 MHz, C₆D₆): δ (ppm) = 8.7, 12.3, 25.5, 26.2, 37.8, 41.4.

MS (EI) m/z (rel. int.): 309 (100%, (M-C₂H₅)⁺), 236 (30), 205 (10), 167 (3), 149 (3), 135 (3), 107 (5), 71 (5).

HRMS calcd for C₁₄H₃₂GeS₂: 338.11572, found: 338.11740

4.16. Diethyl-bis(tert-butylthio)germane (**16**)

The product **16** was obtained as a colorless liquid in 88 % yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 1.11-1.16 (m, 4H), 1.17-1.22 (m, 6H), 1.47 (s, 18H).

¹³C NMR (101 MHz, C₆D₆): δ (ppm) = 8.7, 14.6, 35.3, 45.5.

MS (EI) m/z (rel. int.): 295 (2%, (M-CH₃)⁺), 219 (5), 197 (15), 169 (100), 135 (7), 107 (5), 57 (20).

HRMS calcd for C₁₂H₂₈GeS₂: 310.08441, found: 310.08495

4.17. Diethyl-bis(n-butylthio)germane (**17**)

The product **17** was obtained as a colorless liquid in 93 % yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 0.91 (t, *J* = 7.4 Hz, 6H), 1.09-1.19 (m, 4H), 1.18-1.27 (m, 6H), 1.38-1.53 (m, 4H), 1.61-1.75 (m, 4H), 2.62-2.84 (m, 4H).

¹³C NMR (101 MHz, C₆D₆): δ (ppm) = 8.7, 11.6, 13.5, 21.9, 27.1, 35.3.

MS (EI) m/z (rel. int.): 281 (100%, (M-C₂H₅)⁺), 221 (30), 167 (2), 135 (5), 105 (5), 57 (5).

HRMS calcd for C₁₂H₂₈GeS₂: 310.08441, found: 310.08299

4.18. Diethyl-bis(cyclohexylthio)germane (**18**)

The product **18** was obtained as a colorless liquid in 89 % yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 1.07-1.15 (m, 6H), 1.16-1.19 (m, 4H), 1.20-1.31 (m, 6H), 1.33-1.44 (m, 2H), 1.50-1.62 (m, 4H), 1.63-1.73 (m, 4H), 2.02-2.17 (m, 4H), 3.02-3.18 (m, 2H).

¹³C NMR (101 MHz, C₆D₆): δ (ppm) = 8.7, 12.3, 25.5, 26.2, 37.8, 41.4.

MS (EI) m/z (rel. int.): 333 (100%, (M-C₂H₅)⁺), 251 (40), 167 (15), 135 (5), 107 (5), 83 (5), 55 (35).

HRMS calcd for C₁₆H₃₂GeS₂: 362.11572, found: 362.11434

4.19. Diethyl-bis[(p-fluorophenyl)thio]germane (**19**)

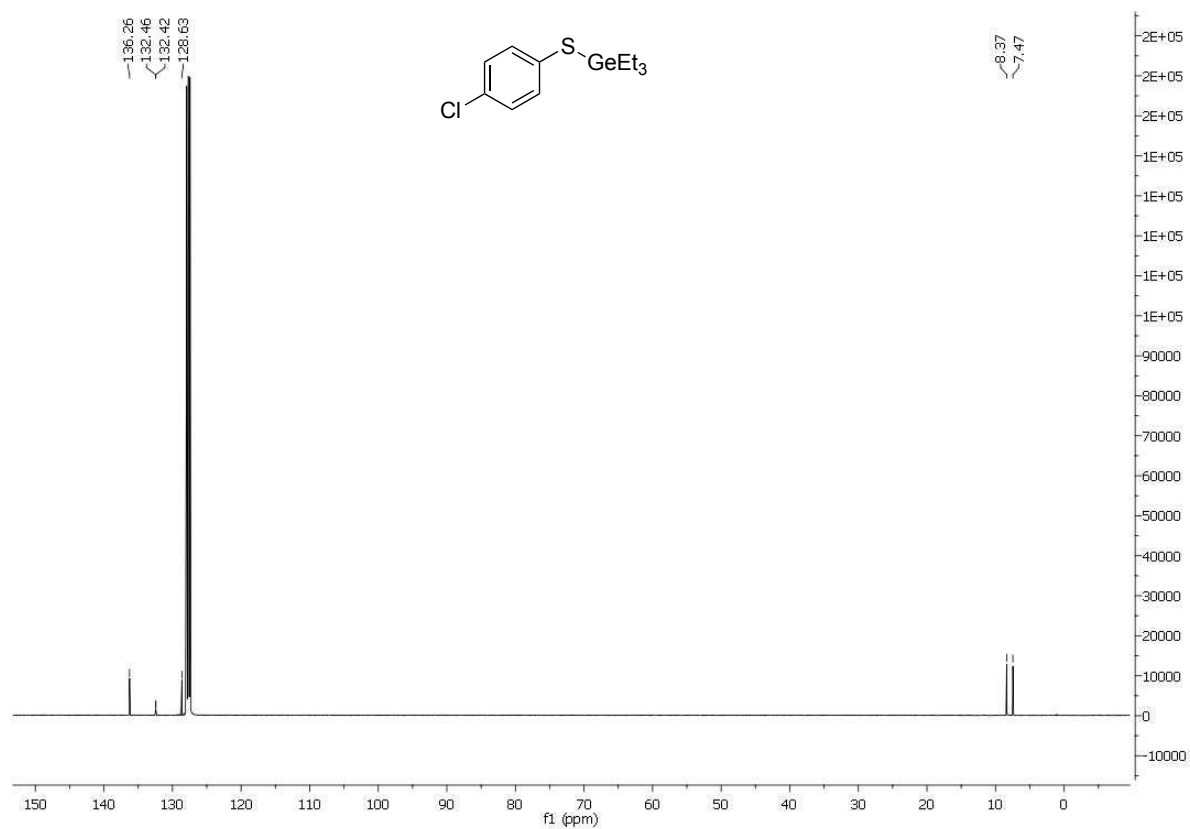
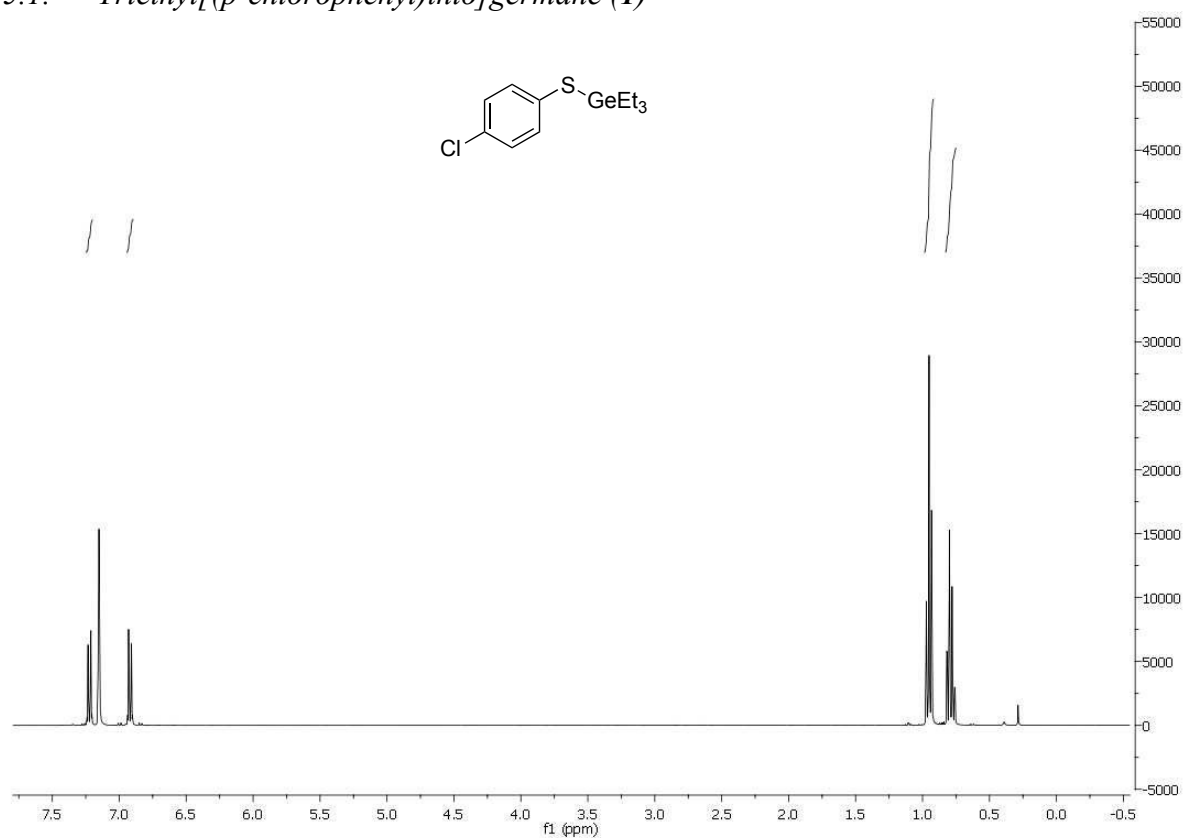
The product **19** was obtained as a colorless liquid in 85 % yield. **¹H NMR** (400 MHz, C₆D₆): δ (ppm) = 0.77-0.99 (m, 10H), 6.47-6.58 (m, 1H), 6.59-6.66 (m, 3H), 7.05-7.12 (m, 1H), 7.30-7.36 (m, 3H). **¹³C NMR** (101 MHz, C₆D₆): δ (ppm) = 8.2, 11.4, 115.8 (d, *J* = 21.8 Hz), 136.8 (d, *J* = 8.0 Hz), 161.3 (d, *J* = 12.3 Hz), 163.7 (d, *J* = 13.2 Hz).

MS (EI) m/z (rel. int.): 357 (10%, (M-C₂H₅)⁺), 259 (100), 229 (15), 201 (5), 127 (10), 83 (7).

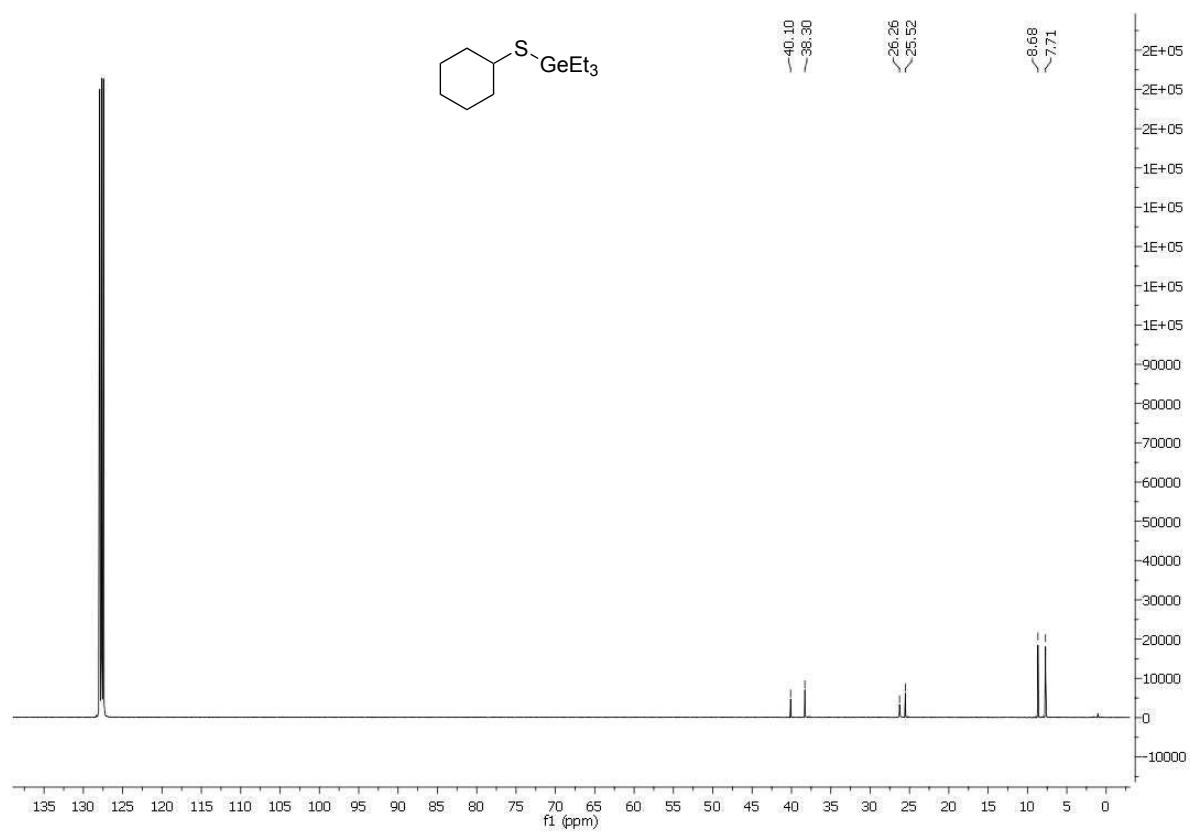
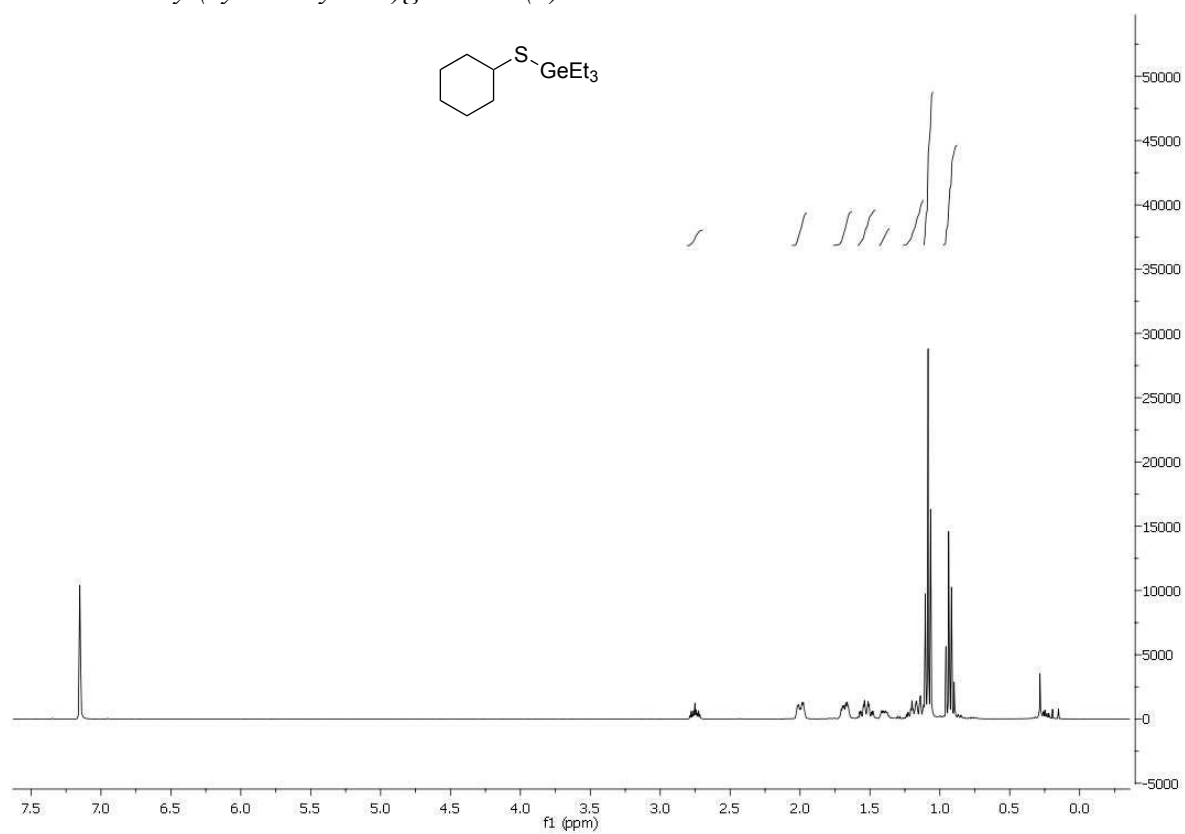
HRMS calcd for C₁₆H₁₈F₂GeS₂: 386.00299, found: 386.00200.

5. Copies of ^1H and ^{13}C NMR spectra of products

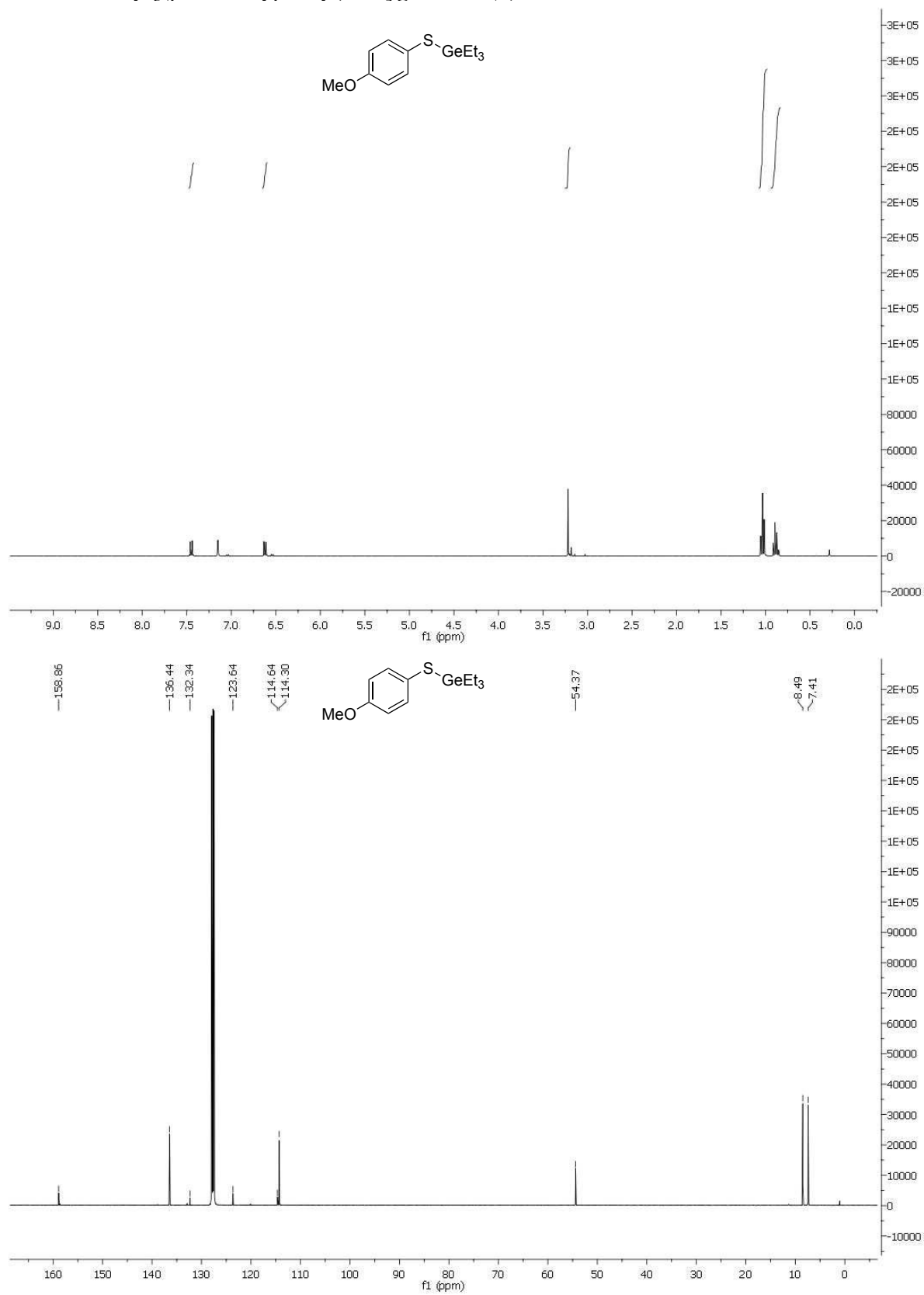
5.1. Triethyl[(p-chlorophenyl)thio]germane (**1**)



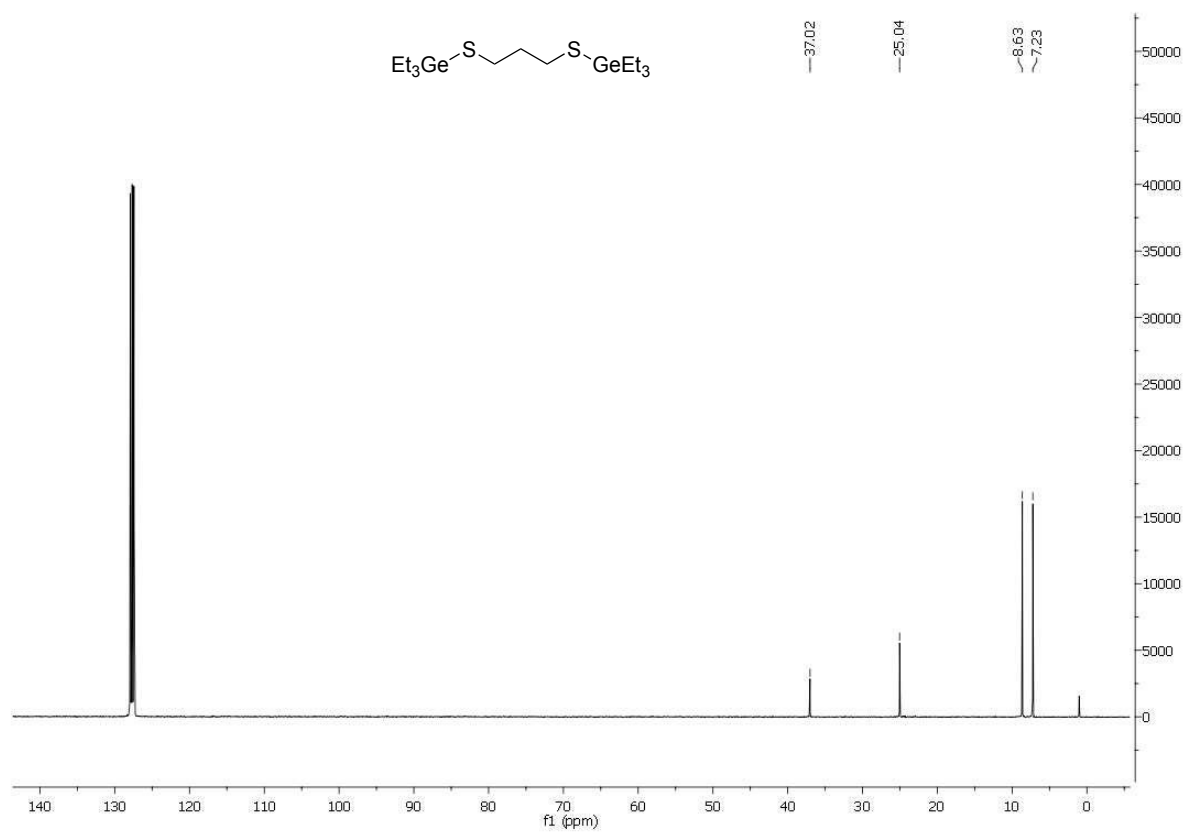
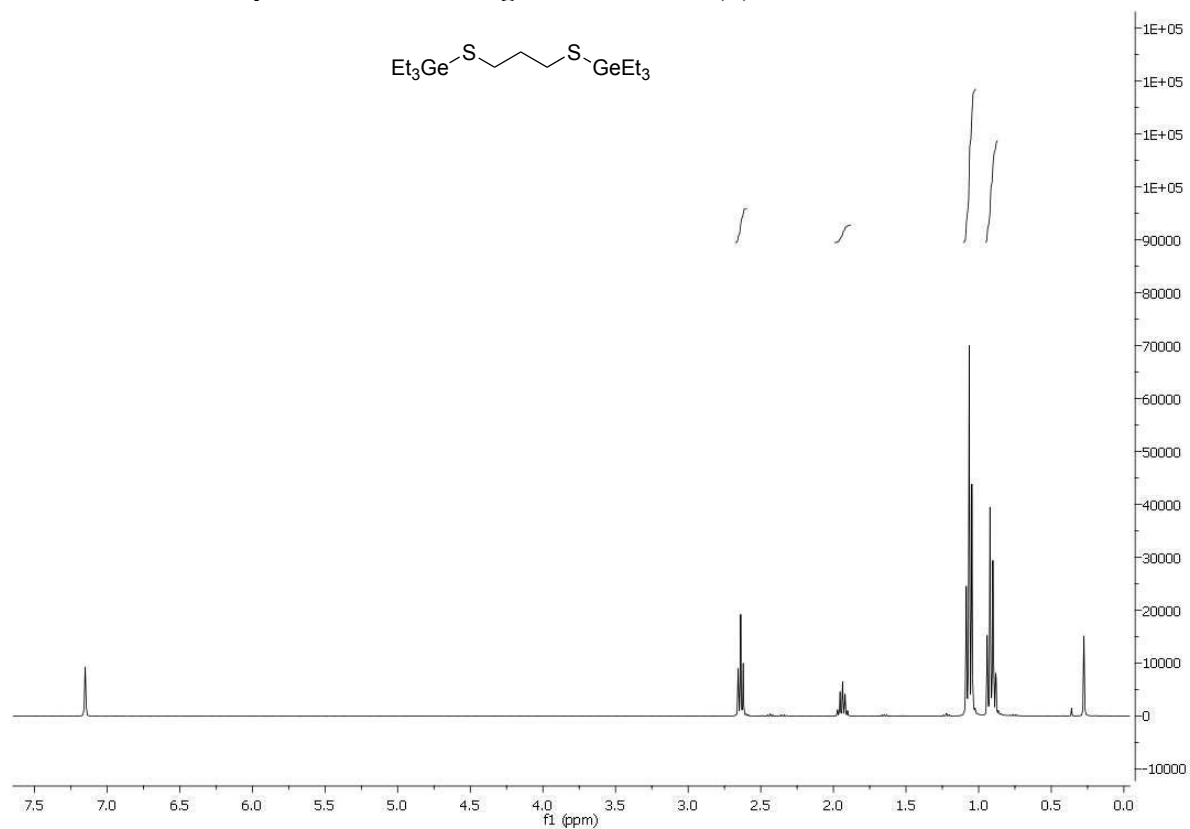
5.2. Triethyl(cyclohexylthio)germane (2)



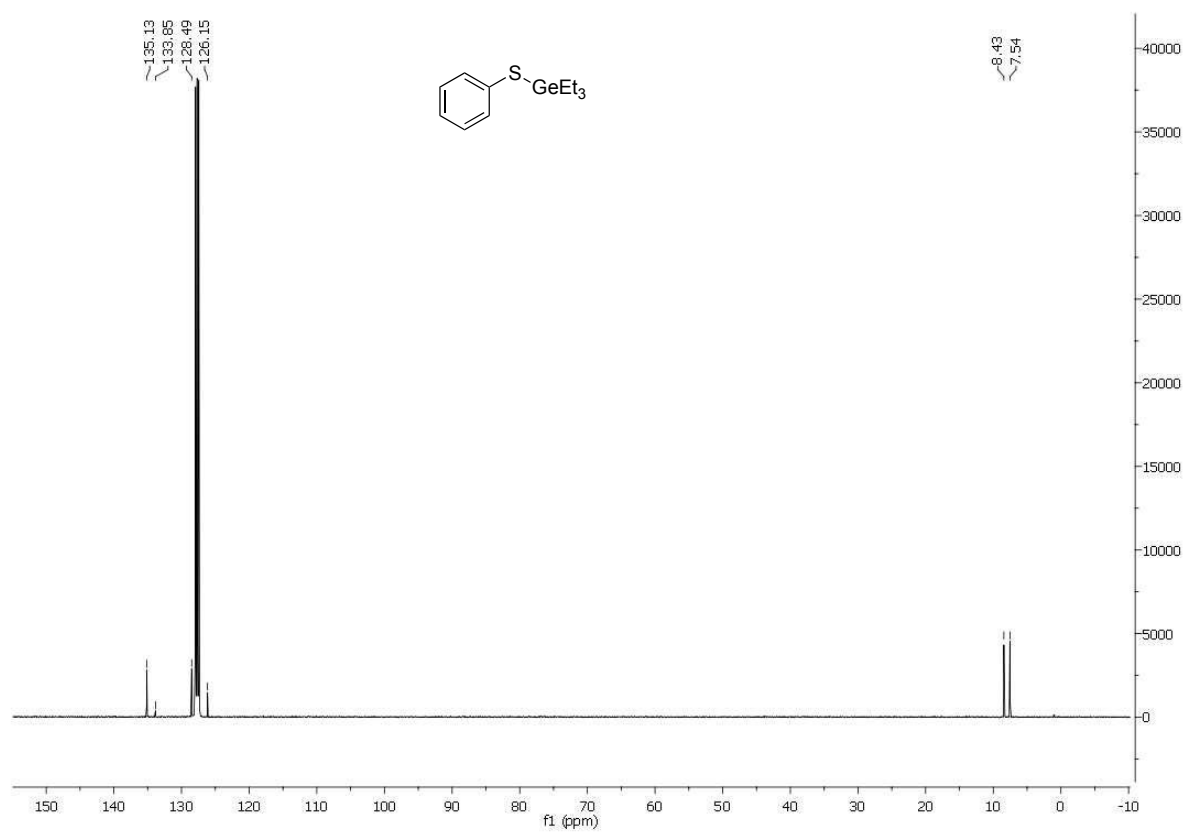
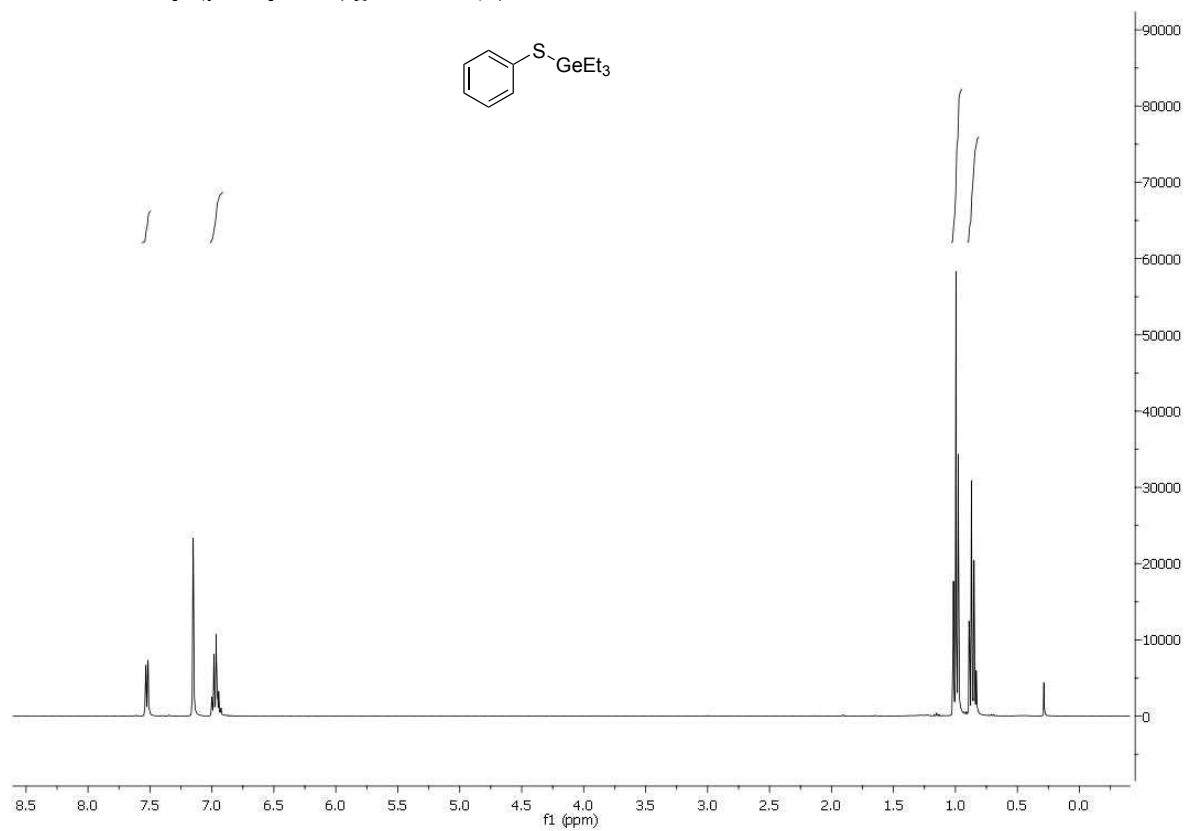
5.3. Triethyl[(p-methoxyphenyl)thio]germane (3)



5.4. 3,3,9,9-tetraethyl-4,8-dithia-3,9-digermaundecane (**4**)

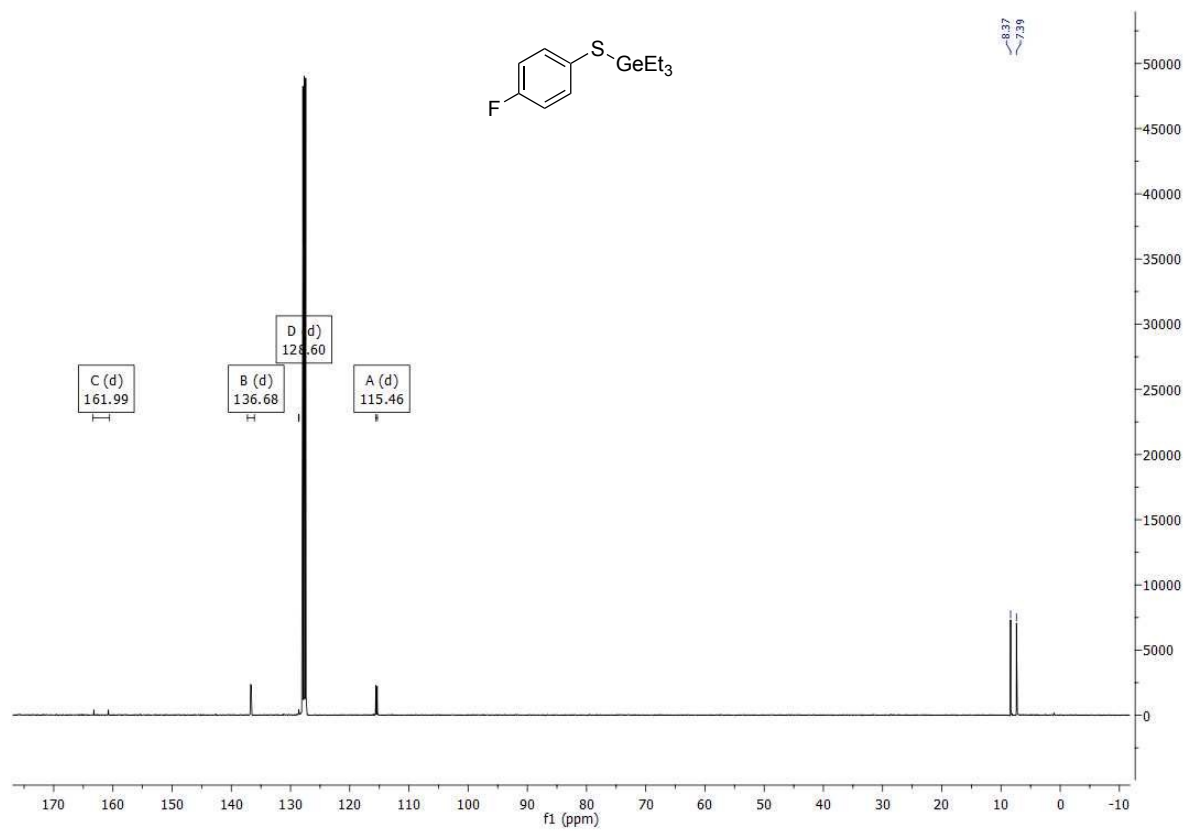
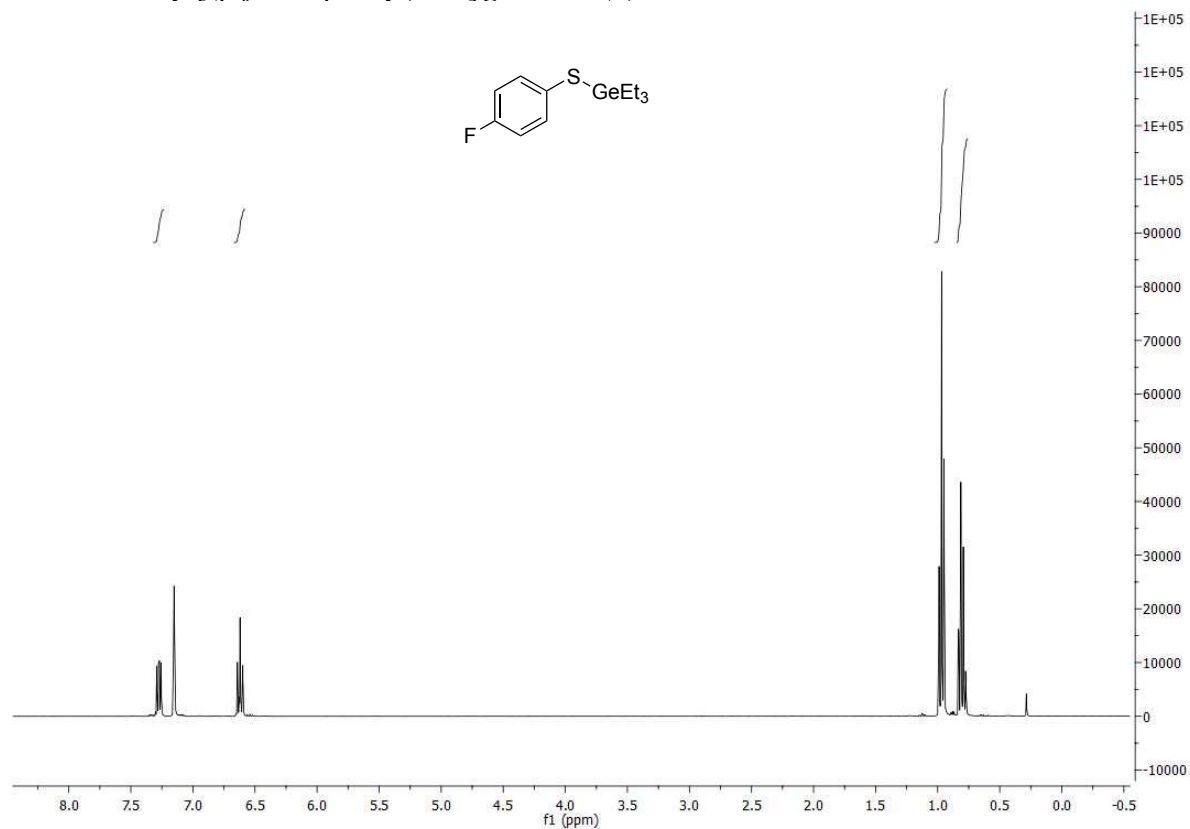


5.5. Triethyl(phenylthio)germane (**5**)

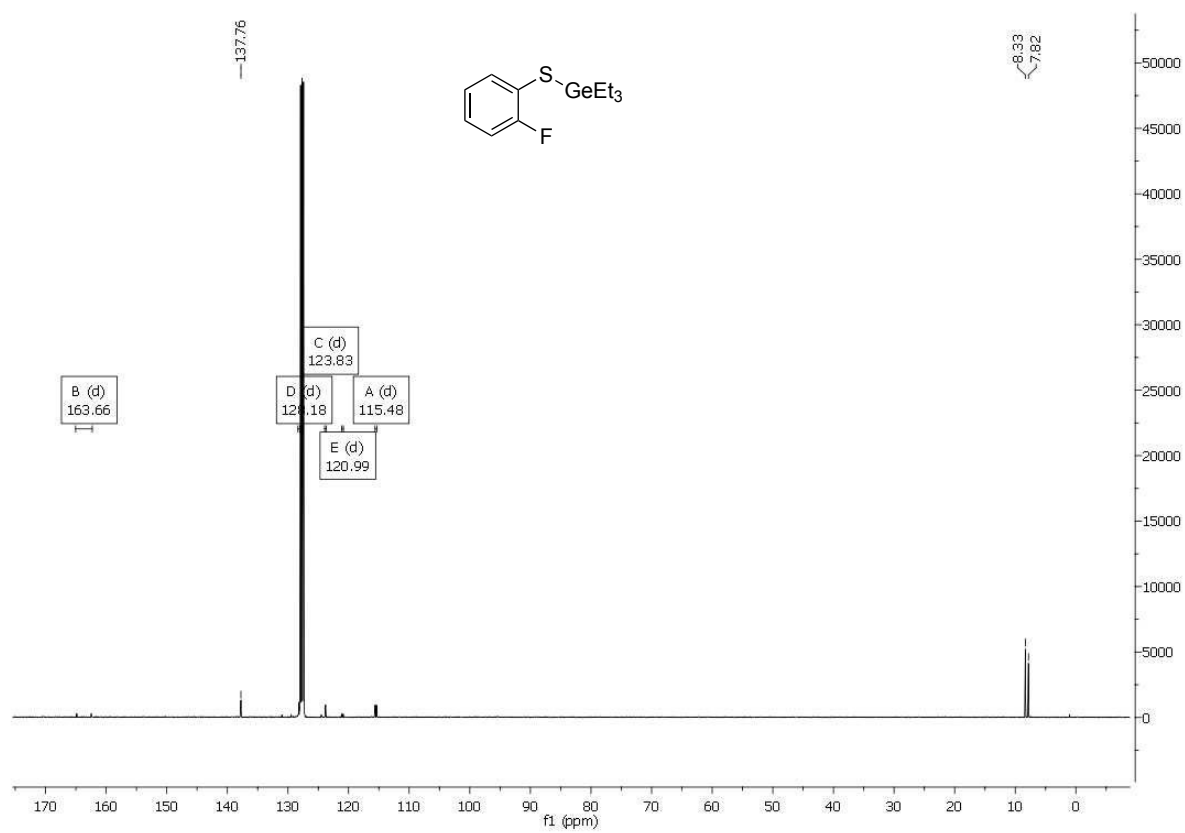
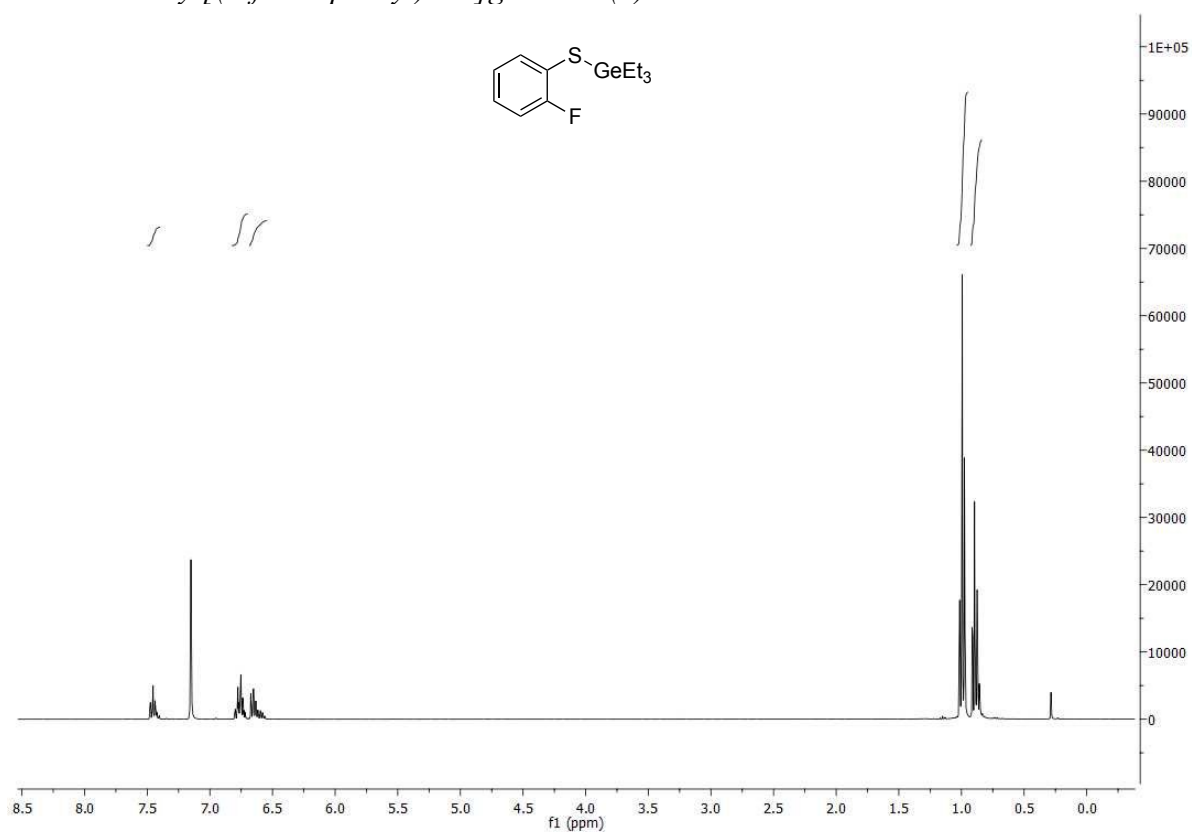


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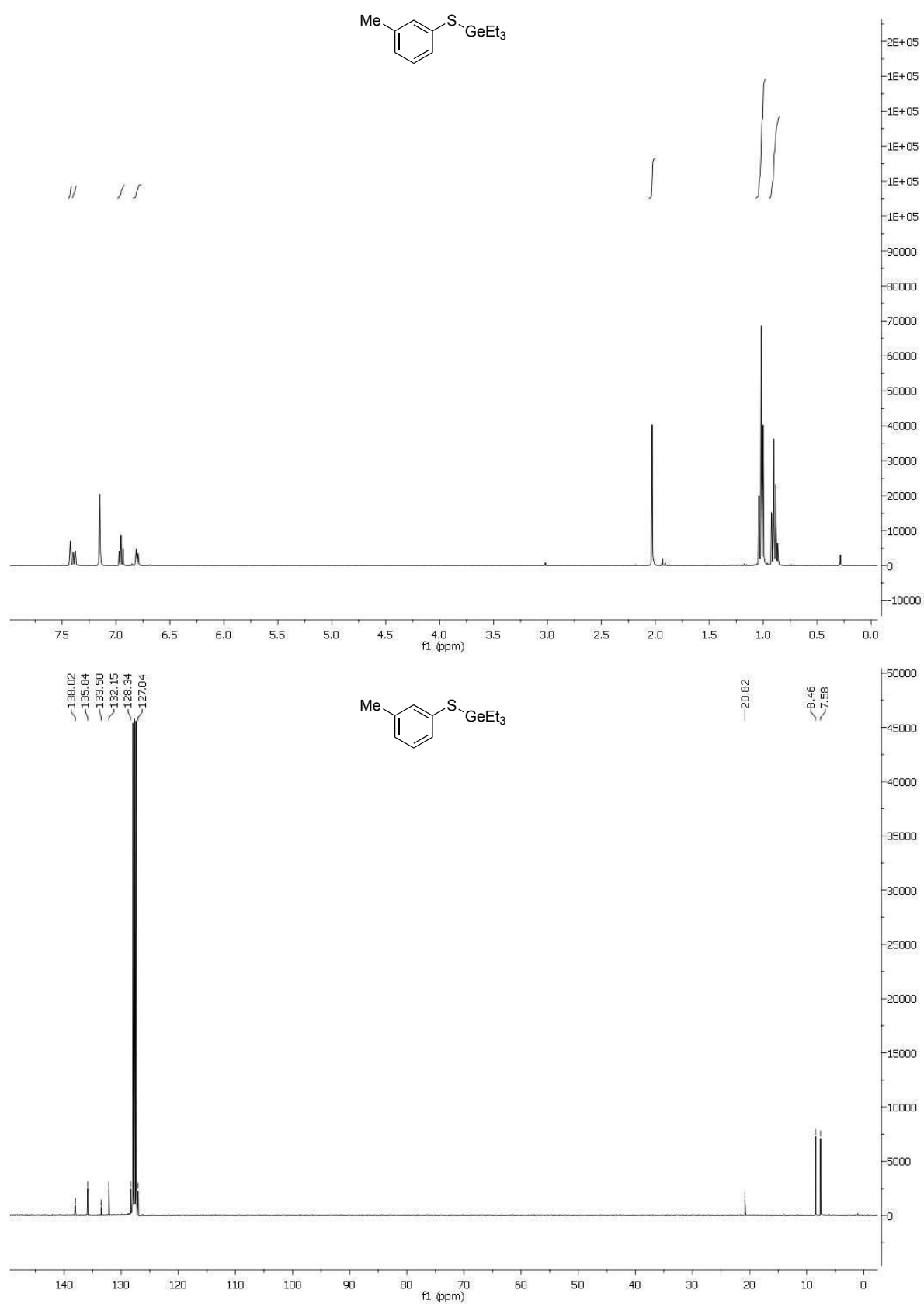
5.7. Triethyl[(p-fluorophenyl)thio]germane (7)



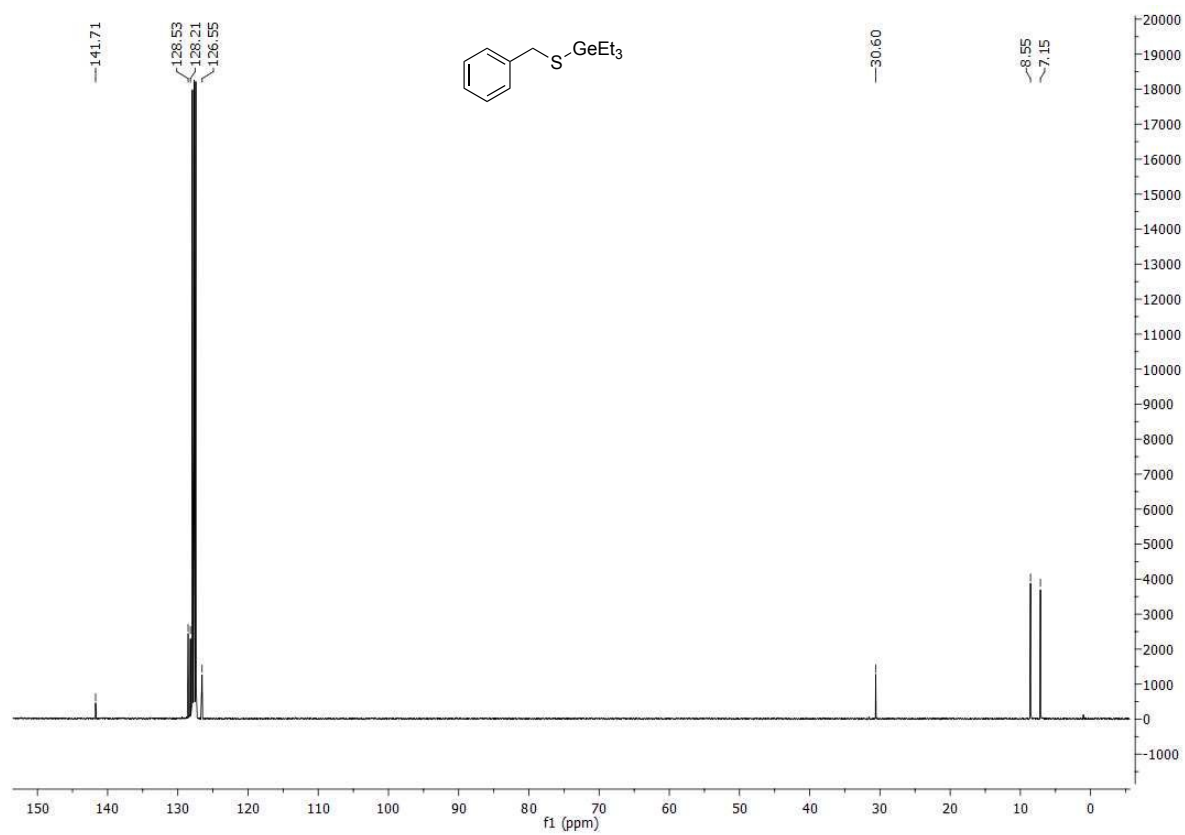
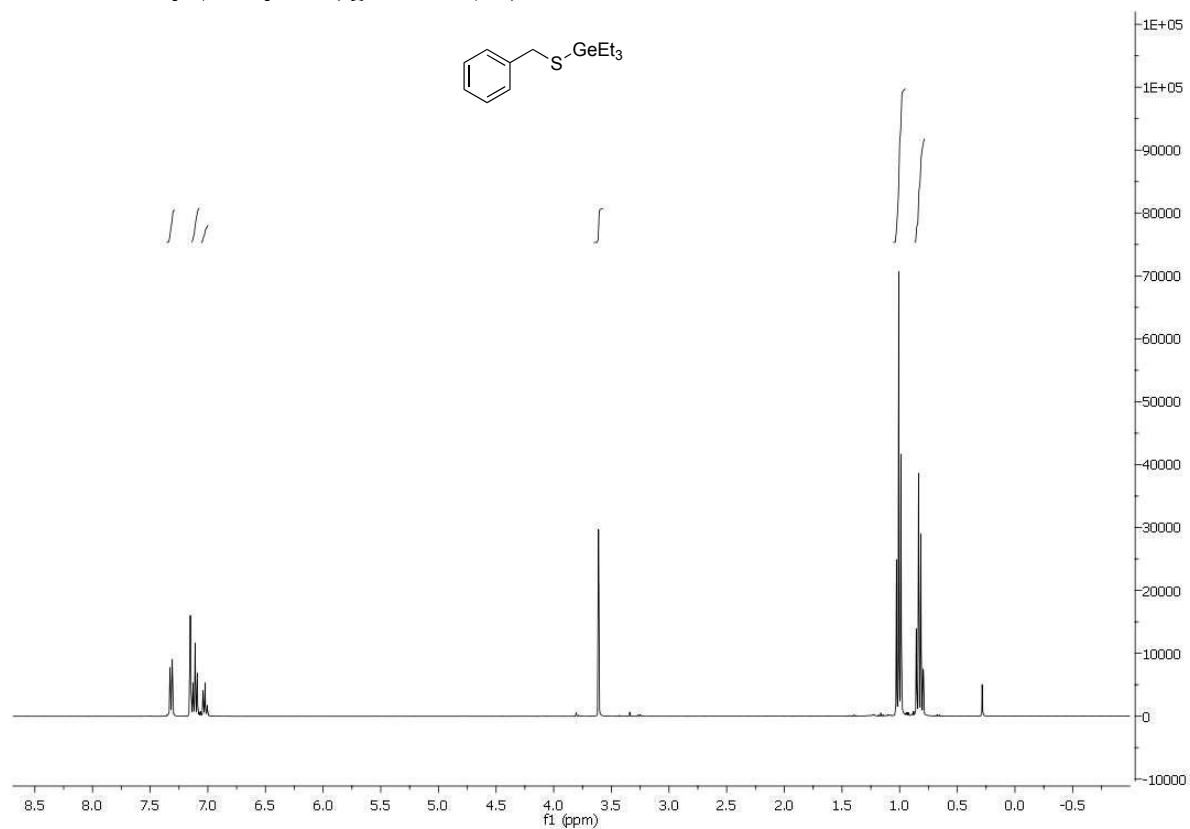
5.8. Triethyl[(*o*-fluorophenyl)thio]germane (**8**)



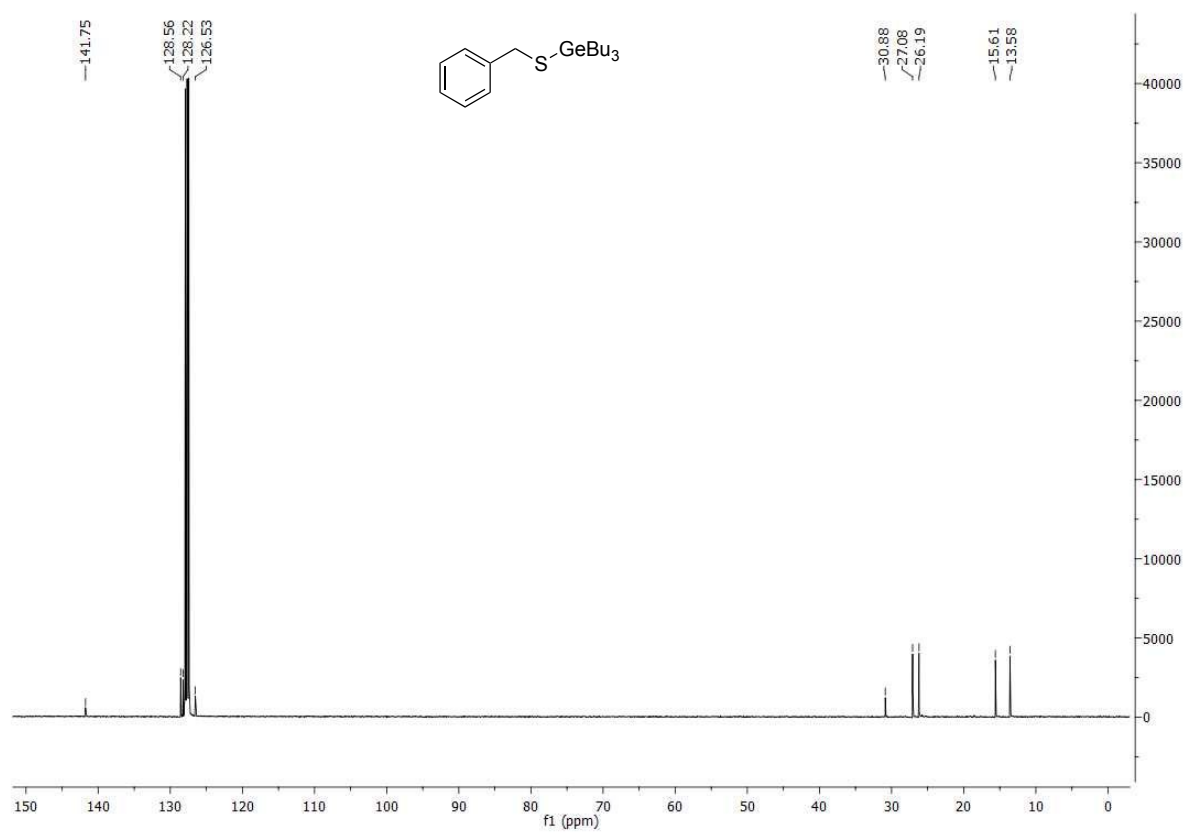
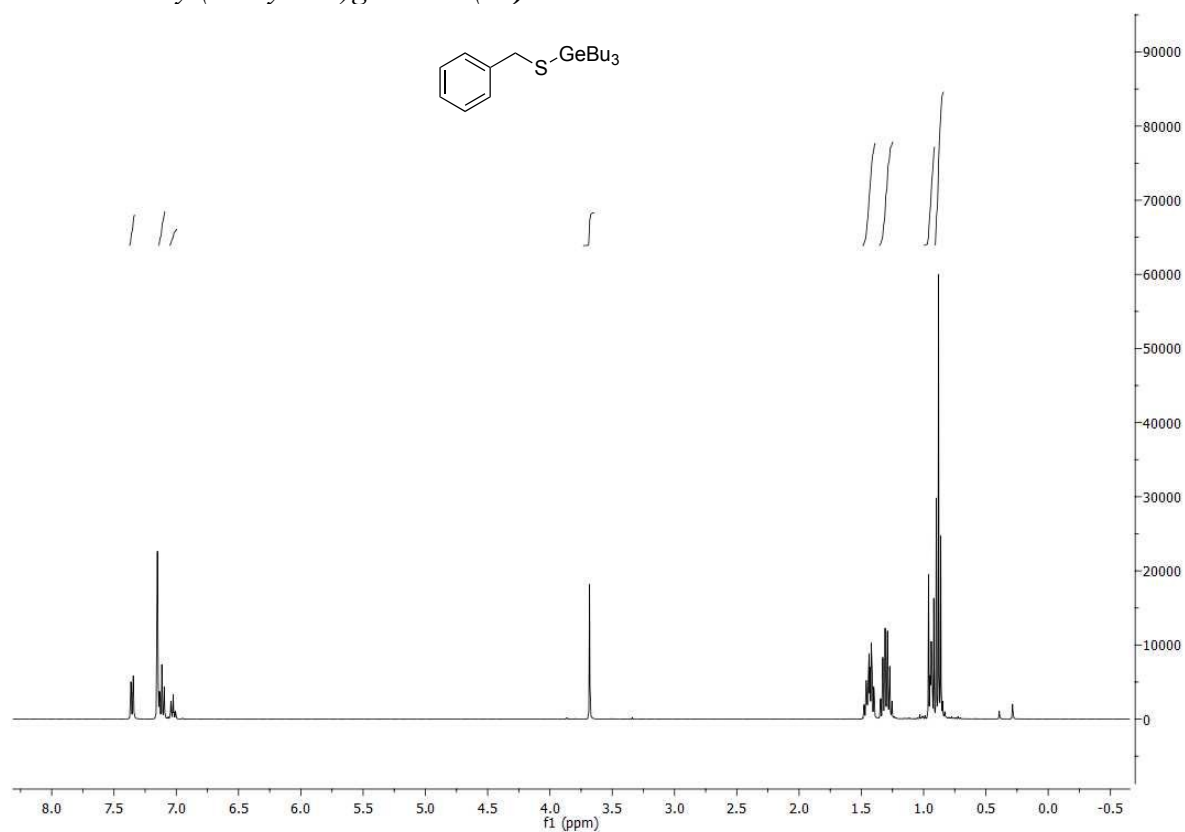
5.9. Triethyl[(3-methylphenyl)thio]germane (9)



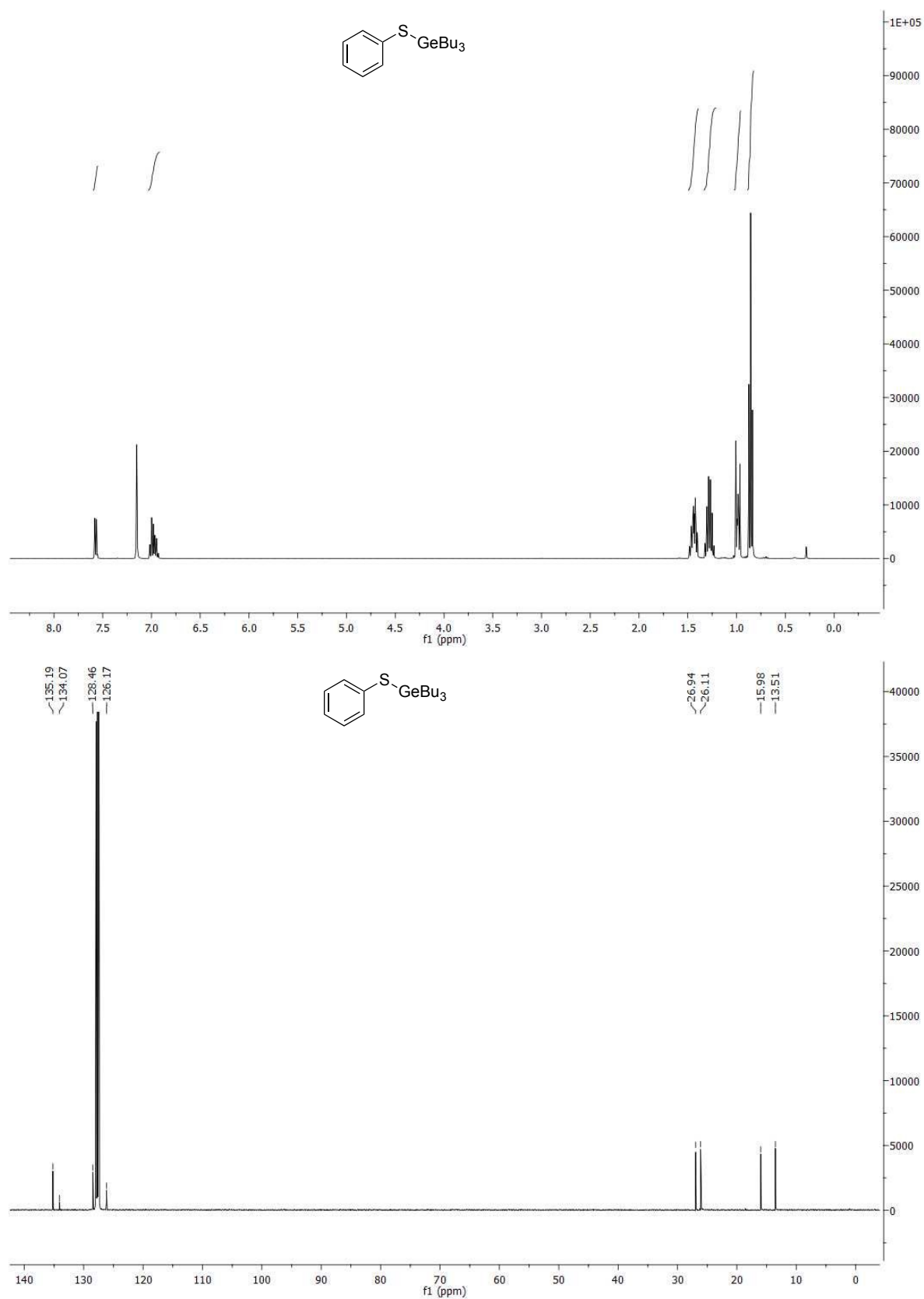
5.10. Triethyl(benzylthio)germane (**10**)



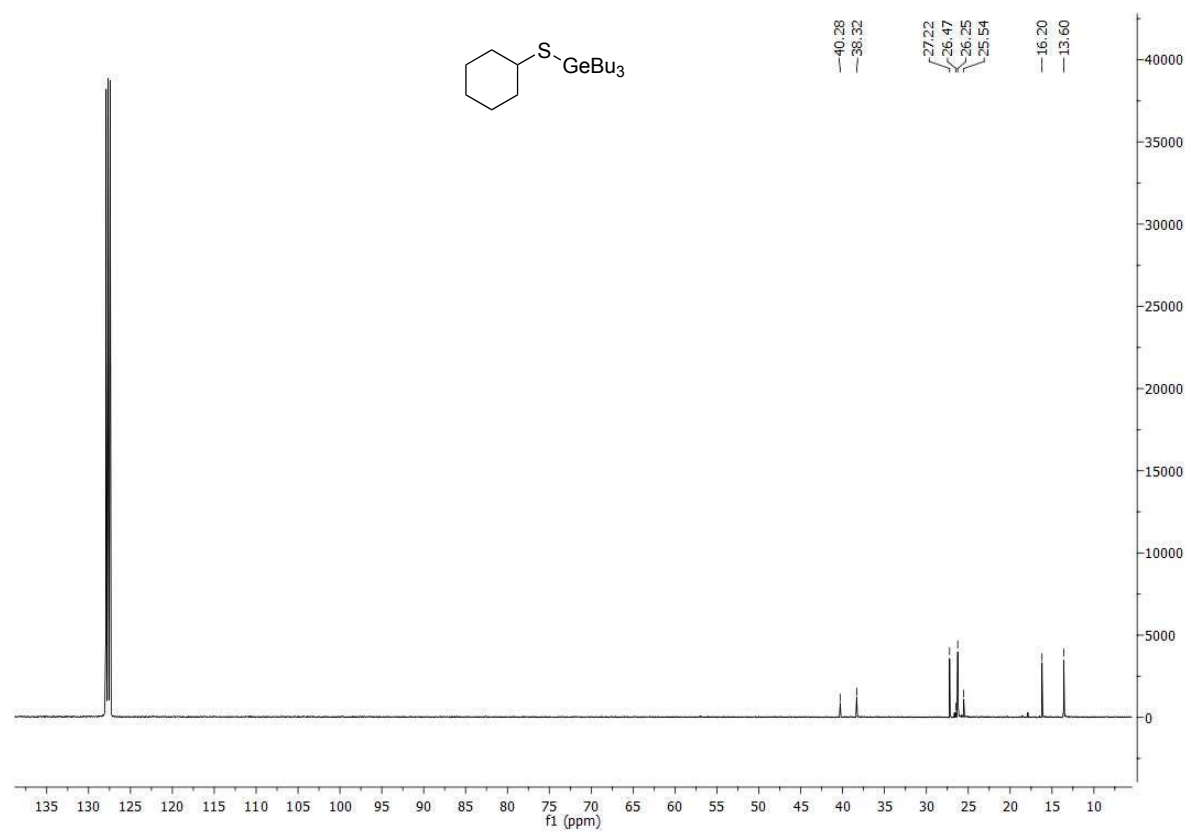
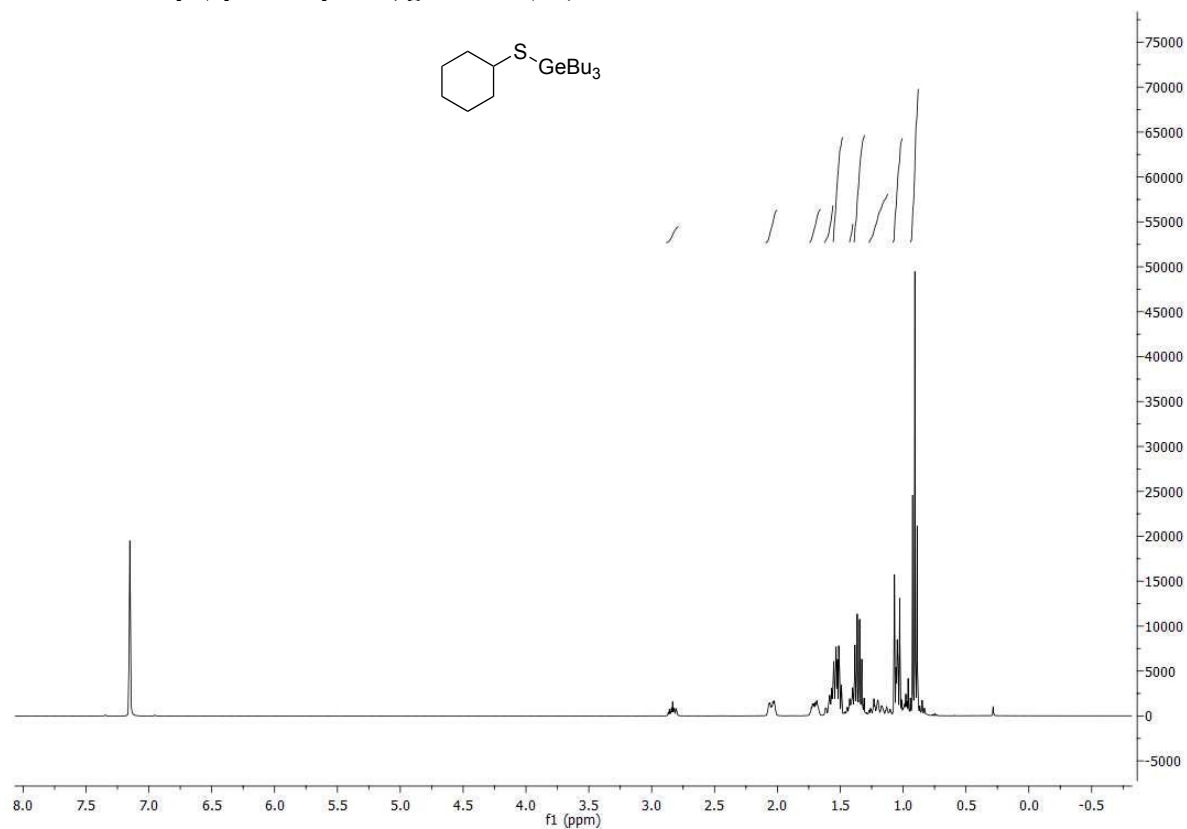
5.11. Tributyl(benzylthio)germane (**11**)



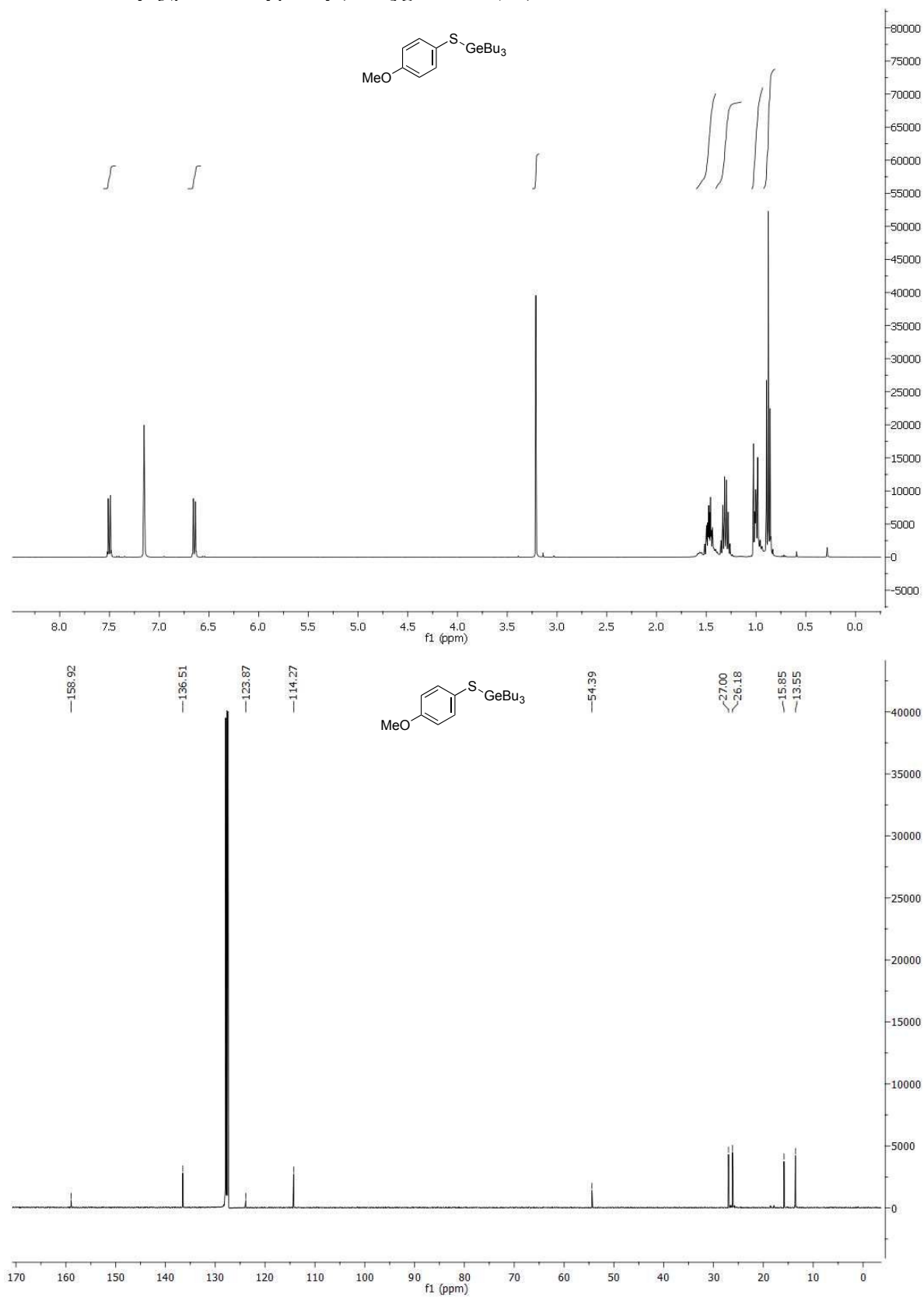
5.12. *Tributyl(phenylthio)germane (12)*



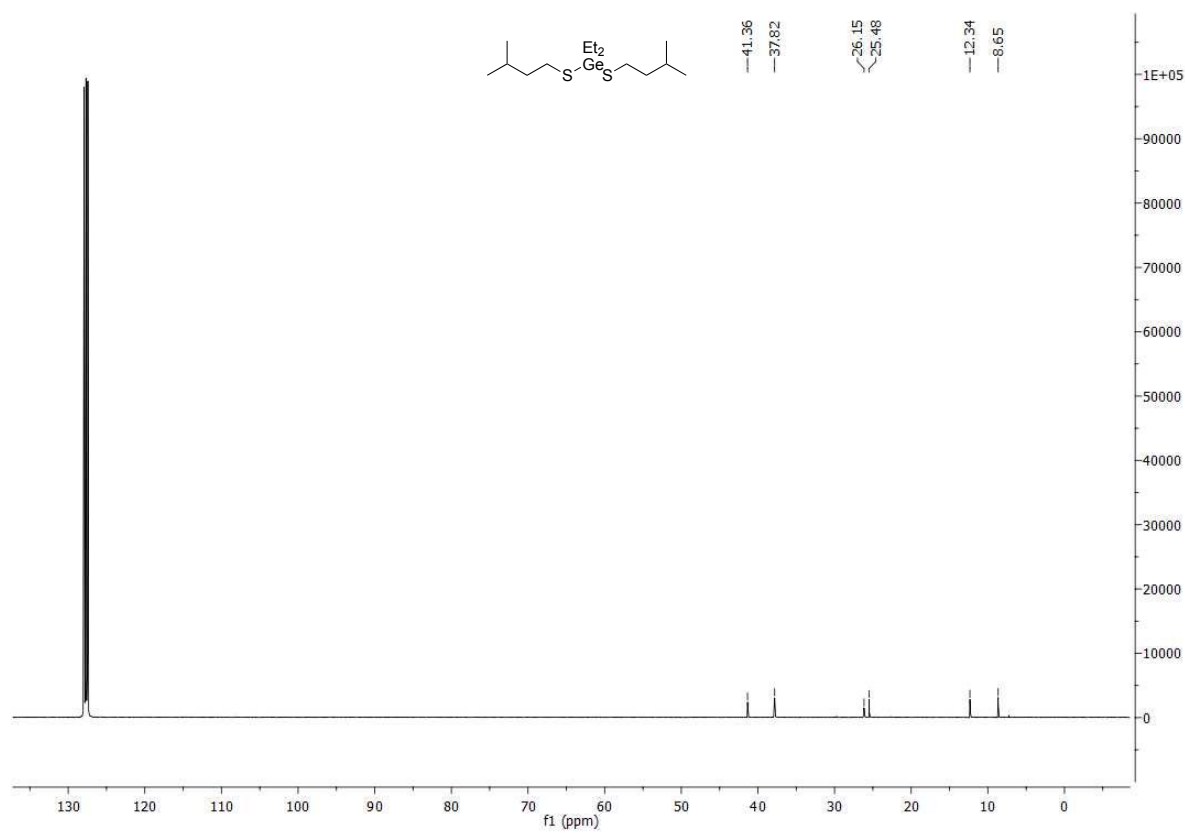
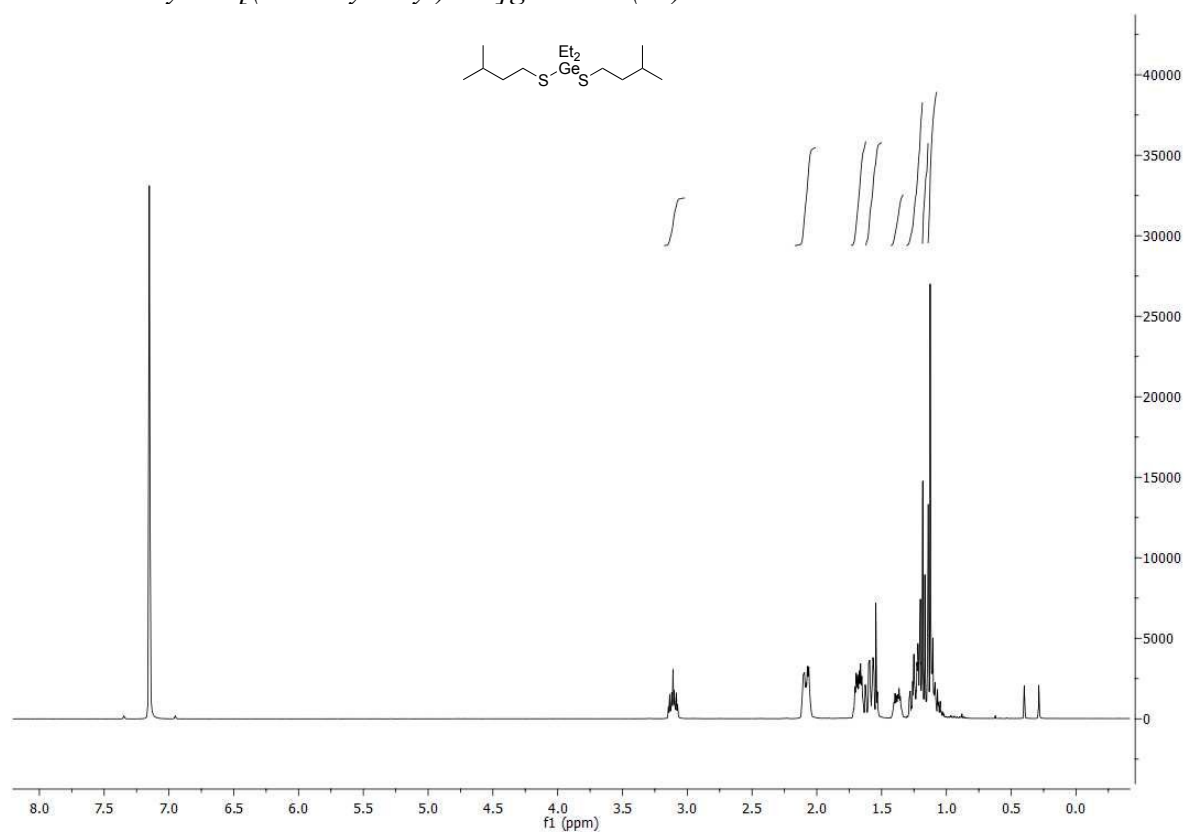
5.13. *Tributyl(cyclohexylthio)germane (13)*



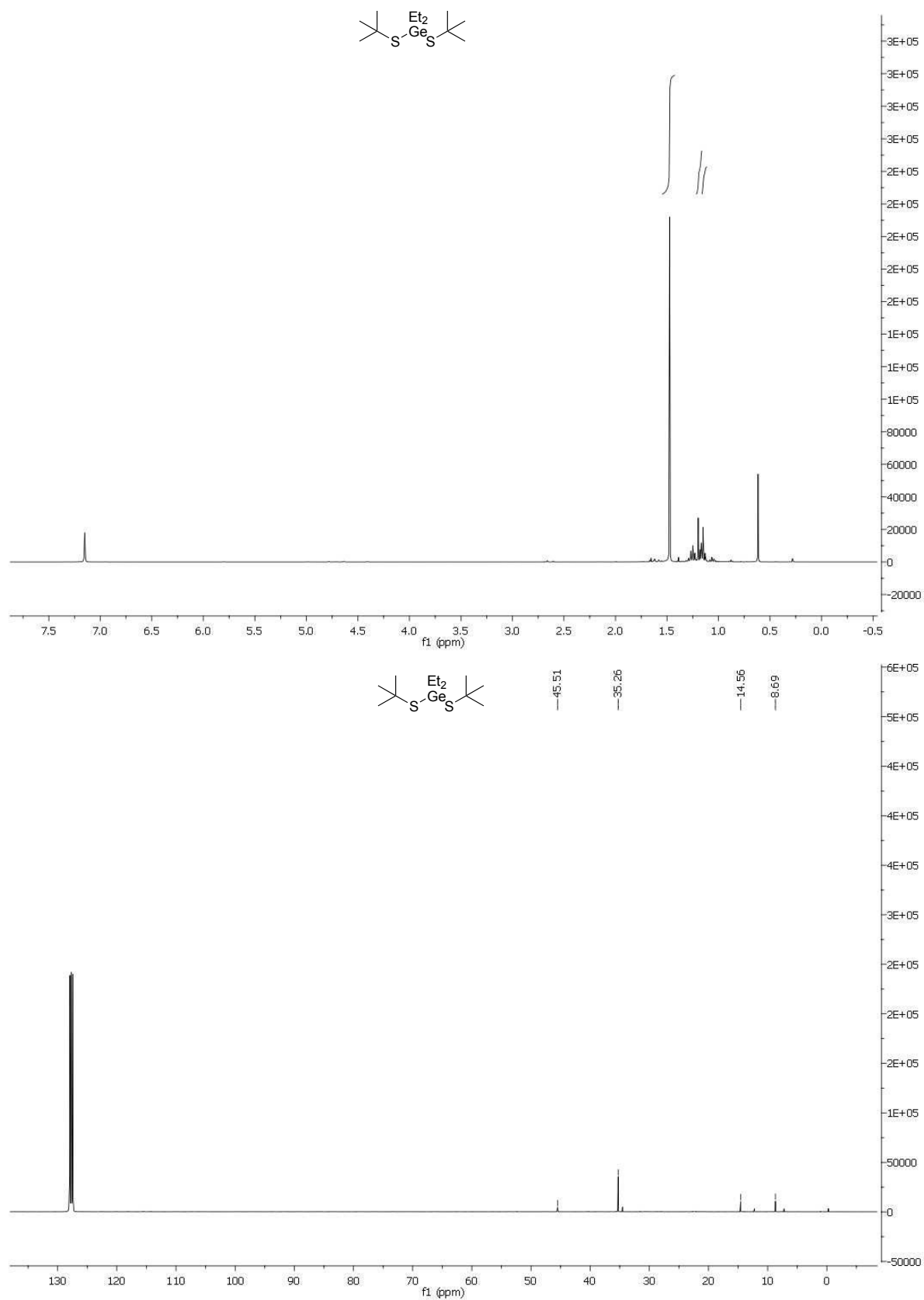
5.14. Tributyl[(*p*-methoxyphenyl)thio]germane (**14**)



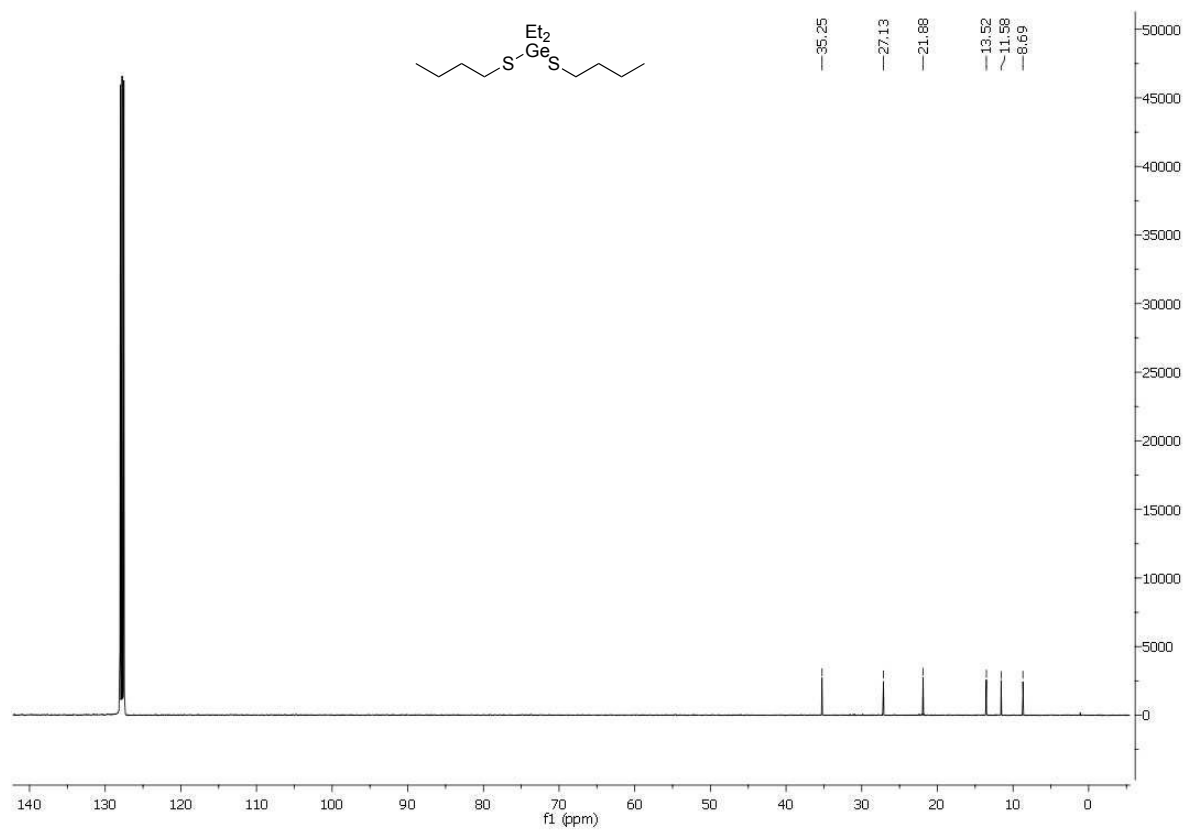
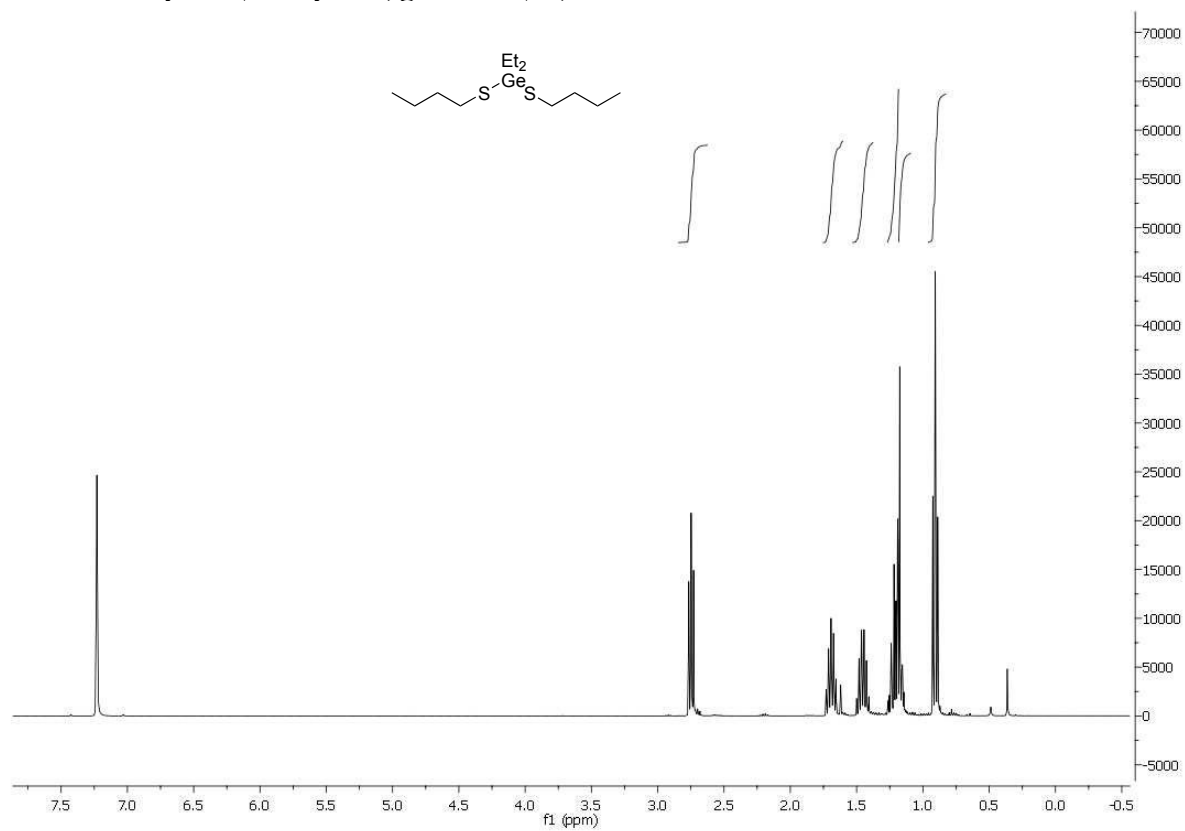
5.15. Diethyl-bis[(3-methylbutyl)thio]germane (**15**)



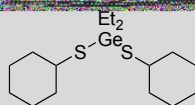
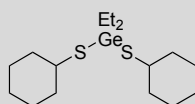
5.16. Diethyl-bis(tert-butylthio)germane (**16**)



5.17. Diethyl-bis(*n*-butylthio)germane (**17**)



5.18. *Diethyl-bis(cyclohexylthio)germane (18)*



5.19. Diethyl-bis[(p-fluorophenyl)thio]germane (**19**)

