Supporting Information

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Heterocycles in reactions with boradigermaallyl

Content

Experimental

General procedures: All manipulations were carried out under argon atmosphere using standard Schlenk techniques and gloveboxes. Benzene was dried with activated aluminium oxide, *n*-pentane and *n*-hexane were obtained from a MBraun solvent purification systems (SPS). All other solvents (Et_2O, THF, toluene, benzene-d_6, cyclohexane-d_{12}) were distilled from a sodium-potassium alloy and like the previous mentioned solvents subsequently degassed by three freeze–pump–thaw cycles. Digermaboraallyl was prepared according to a literature procedure.[1] Further chemicals were purchased commercially and used as received.

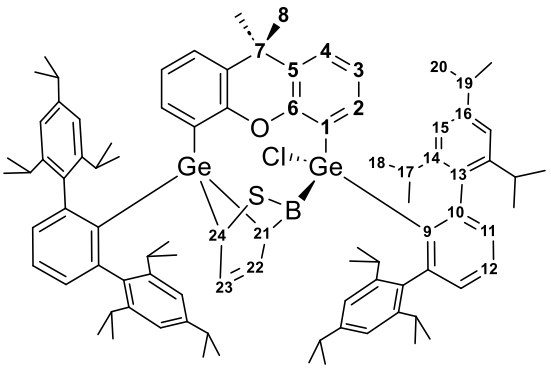
Elemental analysis: Elemental analysis was performed at the Institute of Inorganic Chemistry, University of Tübingen using an *elementar* vario MICRO Cube.

NMR spectroscopy: NMR spectra were recorded with either a Bruker Avance III HD 300 NanoBay spectrometer equipped with a 5 mm BBFO probe head and operating at 300.13 (^{1}H) and 96.29 (^{11}B) MHz, a Bruker Avance III HDX 600 spectrometer equipped with a 5 mm Prodigy BBO cryo probe head operating at 600.13 (^{1}H) and 150.90 (^{13}C) or a Bruker Avance III HDX 700 NMR spectrometer equipped with a 5 mm TXI probe head operating at 700.29 (^{1}H) and 176.9 (^{13}C) MHz. Chemical shifts are reported in δ values in ppm relative to external $SiMe_4$ (^{1}H, ^{13}C) or $BF_3 \cdot OEt_2$ (^{11}B) referenced in most cases on the residual proton signal of the ^{2}H resonance frequency as follows: Ξ = 25.145020 % for ^{13}C, Ξ = 32.083 974 % for ^{11}B. The multiplicity of the signals is indicated as s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet or br = broad/unresolved. For the assignment of proton and carbon signals detailed analysis of ^{1}H, ^{13}C{^{1}H}, ^{1}H–^{1}H COSY, ^{1}H–^{13}C HSQC, ^{1}H–^{13}C HMBC, and ^{13}C{^{1}H} DEPT 135 spectra was done.

Crystallography: X-ray data were collected with a Bruker Smart APEX II diffractometer with graphite-monochromated Mo-K_α radiation. The programs used were Bruker's APEX2 v2011.8-0, including SAINT for data reduction, SADABS for absorption correction, and SHELXS for structure solution, as well as the WinGX suite of programs version 1.70.01 or the GUI ShelXle, including SHELXL for structure refinement. [2-8]

UV/Vis Spectroscopy: Visible UV/Vis absorption spectra were recorded on PerkinElmer Lambda 35 spectrophotometer in gas tight 1 cm quartz cuvettes sealed with Teflon stoppers or Teflon lined screw caps.

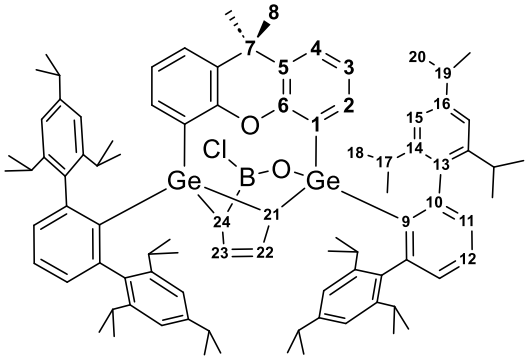
Synthesis



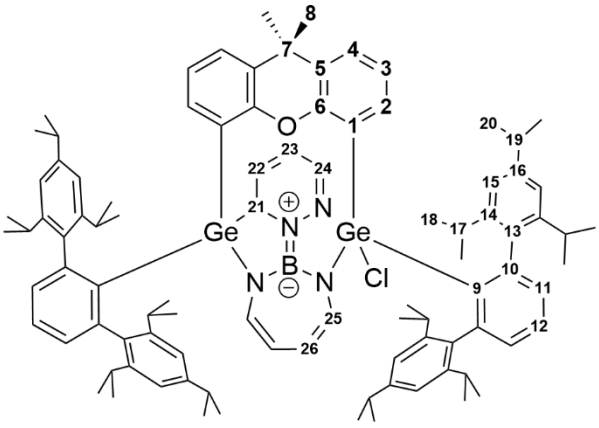
Synthesis of compound **2**: Thiophene (7.05 µl, 88.0 µmol, 1.20 equiv.) was added to a turquoise solution of boradigermaally **1** (100 mg, 73.4 µmol, 1.00 equiv.) in *n*-pentane (15.0 ml) at room temperature. The solution decolorized immediately and was then heated to 40 °C over a period of 4 days, after which a yellow-orange fine suspension was obtained. Small, suspended particles were filtered off and the solution was concentrated under reduced pressure. For purification, the *n*-pentane solution was cooled to −38 °C, causing the product **2** to precipitate as a colorless solid (74.7 mg, 51.6 µmol, 70 %). Colorless crystals of **2** suitable for X-ray crystallography were obtained from a concentrated THF

solution after 3 weeks at room temperature. *Analytical data:* **^{1}H-NMR** (700.29 MHz, C_6D_6): δ [ppm] = 0.13 (d, 3H, $^{3}J_{HH}$ = 6.7 Hz, H-18), 0.44 (d, 3H, $^{3}J_{HH}$ = 6.7 Hz, H-18), 0.86 – 0.90 (m, 9H, H-18 (9H)), 0.93 (d, 3H, $^{3}J_{HH}$ = 6.9 Hz, H-18), 1.04 (d, 3H, $^{3}J_{HH}$ = 6.8 Hz, H-18), 1.08 – 1.10 (m, 6H, H-8 (3H) + H-18 (3H)), 1.11 – 1.14 (m, 6H, H-18 (6H)), 1.17 (d, 3H, $^{3}J_{HH}$ = 6.7 Hz, H-18), 1.20 – 1.24 (m, 6H, H-20), 1.27 (d, 3H, $^{3}J_{HH}$ = 6.9 Hz, H-20), 1.29 (d, 3H, $^{3}J_{HH}$ = 6.9 Hz, H-18), 1.36 (s, 3H, H-8), 1.37 – 1.41 (m, 9H, H-20 (9H)), 1.44 – 1.49 (m, 9H, H-18 (3H) + H-20 (6H)), 1.50 (d, 3H, $^{3}J_{HH}$ = 6.8 Hz, H-18), 1.70 – 1.74 (m, 6H, H-18 (6H)), 2.34 (sept, 1H, $^{3}J_{HH}$ = 6.7 Hz, H-17), 2.52 (sept, 1H, $^{3}J_{HH}$ = 6.8 Hz, H-17), 2.62 (sept, 1H, $^{3}J_{HH}$ = 6.9 Hz, H-17), 2.75 (sept, 1H, $^{3}J_{HH}$ = 6.9 Hz, H-19), 2.84 (d, 1H, $^{3}J_{HH}$ = 5.3 Hz, H-24), 2.88 – 3.00 (m, 3H, H-17 (1H) + H-19 (2H)), 3.08 (sept, 1H, $^{3}J_{HH}$ = 6.9 Hz, H-19), 3.20 (sept, 1H, $^{3}J_{HH}$ = 6.8 Hz, H-17), 3.32 – 3.40 (m, 2H, H-17 (2H)), 3.47 (sept, 1H, $^{3}J_{HH}$ = 6.7 Hz, H-17), 4.25 (d, 1H, $^{3}J_{HH}$ = 5.6 Hz, H-21), 5.67 – 5.71 (m, 1H, H-23), 6.16 – 6.19 (m, 1H, H-22), 6.47 – 6.51 (m , 1H, H-3), 6.62 – 6.65 (m, 1H, H-3), 6.73 (s, br, 1H, H-15), 6.78 (d, br, 1H, $^{3}J_{HH}$ = 7.4 Hz, H-2), 6.93 – 6.97 (m, 2H, H-4 + H-15), 6.98 – 7.01 (m, 2H, H-2 + H-15), 7.01 – 7.03 (m, 2H, H-4 + H-11), 7.06 (t, 1H, $^{3}J_{HH}$ = 7.5 Hz, H-12), 7.08 (t, 1H, $^{3}J_{HH}$ = 7.5 Hz, H-12), 7.12 (d, 1H, $^{4}J_{HH}$ = 1.2 Hz, H-15), 7.17 – 7.19 (m, 1H, H-11), 7.19 – 7.21 (m, 1H, H-11), 7.22 – 7.23 (m, 2H, H-15 (3H)), 7.24 – 7.26 (m, 1H, H-11), 7.28(s, br, 1H, H-15), 7.33 (s, br, 1H, H-15). **^{13}C{^{1}H}-NMR** (176.09 MHz, C_6D_6): δ [ppm] = 21.8 (C-18), 22.1 (C-18), 22.2 (C-18), 23.0 (C-18), 23.3 (C-20), 23.5 (C-18), 23.9 (C-18), 24.2 (C-18), 24.4 (C-20), 24.4 (C-20), 24.5 (C-20), 24.6 (C-20), 24.6 (C-20), 24.7 (C-20), 24.7 (C-18), 24.8 (C-18), 25.1 (C-18), 25.4 (C-18), 25.5 (C-20), 26.1 (C-18), 26.7 (3 x C-18), 27.7 (C-8), 27.7 (C-18), 30.4 (C-17), 30.8 (C-17), 31.0 (C-17), 31.1 (C-17), 31.7 (2 x C-17), 31.8 (2 x C-17), 34.6 (C-19), 34.6 (C-19), 34.7 (C-7), 34.8 (2 x C-19), 35.6 (C-8), 49.1 (C-24), 52.9 (C-21), 120.4 (C-15), 120.4 (C-15), 120.9 (C-15), 121.0 (C-15), 121.1 (C-15), 121.5 (C-15), 121.9 (C-15), 122.7 (C-3), 122.8 (C-3), 122.9 (C-15), 127.1 (C-4), 127.2 (C-1), 127.4 (C-12), 128.0 (C-4, overlapped by solvent signal), 128.3 (C-12), 129.6 (C-1 + C-5 + C-22), 130.5 (C-11), 130.6 (C-11), 130.7 (C-5), 132.4 (C-11), 132.6 (C-23), 132.8 (C-11), 132.8 (C-2), 134.5 (C-2), 136.5 (C-13), 137.5 (C-9), 138.6 (C-13), 138.8 (C-13), 139.5 (C-13), 142.3 (C-9), 145.8 (C-14), 146.0 (C-14), 146.3 (C-14), 146.4 (C-14), 146.5 (C-14), 147.2 (C-10), 147.3 (C-10), 147.4 (C-14), 147.6 (C-16), 147.7 (C-14), 148.1 (C-10), 149.0 (C-16), 149.3 (C-16), 149.5 (C-10), 149.6 (C-14), 149.8 (C-16), 153.4 (C-6), 154.1 (C-6). **^{11}B{^{1}H}-NMR** (96.29 MHz, C_6D_6): δ [ppm] = 82.9. **Elemental analysis calcd (%)** for $C_{91}H_{114}BClGe_2OS$: C 75.51, H 7.94, S 2.22; found: C 75.95, H 8.15, S 1.61.

Synthesisof compound **3**: Furan (6.53 µl, 6.11 mg, 88.0 µmol, 1.50 equiv.) was added to a solution of boradigermaallyl **1** (80.0 mg, 58.7 µmol, 1.00 equiv.) in *n*-pentane (5.00 ml) at room temperature, resulting in a change in colour from turquoise to yellow. Subsequently, the reaction mixture was heated to 50 °C for the duration of 24 hours, after which it was filtered to remove fine suspended particles. Product concentration in solution was increased by partial evaporation of the solvent and colourless crystals of product **3**, suitable for X-ray diffraction were isolated after one day of crystallization at room temperature. For purification on a preparative scale, a solution of **3** in *n*-pentane was cooled to −38 °C, causing product **3** to precipitate as a colorless to pale yellow solid (52.8 mg, 36.9 µmol, 63 %). *Analytical data:* **^{1}H-NMR** (700.21 MHz, C_6D_6): δ [ppm] = 0.04 (d, 3H, $^{3}J_{HH}$ = 6.7 Hz, H-18), 0.54 (d, 3H, $^{3}J_{HH}$ = 6.7 Hz, H-18), 0.58 (d, 3H, $^{3}J_{HH}$ = 6.7 Hz, H-18), 0.78 (d, 3H, $^{3}J_{HH}$ = 6.7 Hz, H-18), 0.87 (d, 3H, $^{3}J_{HH}$ = 6.7 Hz, H-17), 0.98 (d, 3H, $^{3}J_{HH}$ = 6.7 Hz, H-18), 1.00 – 1.05 (m, 7H, H-18 (6H) + H-24 (1H)), 1.08 (d, 3H, $^{3}J_{HH}$ = 6.7 Hz, H-18), 1.21 (d, 3H, $^{3}J_{HH}$ = 6.7 Hz, H-18),

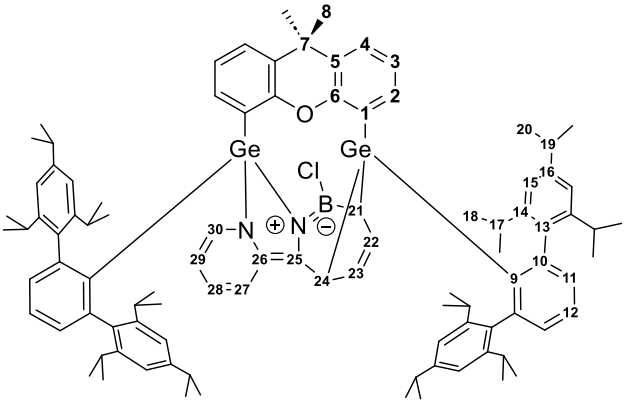


1.25 – 1.33 (m, 24H, H-8 (6H) + H-18 (6H) + H-20 (12H)), 1.42 (d, 3H, $^3J_{HH}$ = 6.7 Hz, H-18), 1.46 (d, 3H, $^3J_{HH}$ = 6.9 Hz, H-20), 1.48 – 1.51 (m, 12H, H-18 (6H) + H-20 (6H)), 1.55 (d, 3H, $^3J_{HH}$ = 6.9 Hz, H-20), 1.58 (d, 3H, $^3J_{HH}$ = 6.9 Hz, H-18), 2.22 (d, 1H, $^3J_{HH}$ = 5.1 Hz, H-21), 2.44 (sept, 1H, $^3J_{HH}$ = 6.7 Hz, H-17), 2.75 (sept, 1H, $^3J_{HH}$ = 6.7 Hz, H-17), 2.84 (sept, 1H, $^3J_{HH}$ = 6.9 Hz, H-19), 2.89 – 2.97 (m, 2H, H-17 (2H)), 2.99 – 3.10 (m, 4H, H-17 (2H) + H-19 (2H)), 3.18 (sept, 1H, $^3J_{HH}$ = 6.9 Hz, H-19), 3.31 (sept, 1H, $^3J_{HH}$ = 6.7 Hz, H-17), 3.42 (sept, 1H, $^3J_{HH}$ = 6.7 Hz, H-17), 5.66 (dd, 1H, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 5.7 Hz, H-23), 6.25 (dd, 1H, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 5.2 Hz, H-22), 6.46 – 6.49 (m, 1H, H-2), 6.55 – 6.59 (m, 1H, H-3), 6.79 – 6.82 (m, 1H, H-3), 6.84 – 6.87 (m, 2H, H-4 (1H) + H-11 (1H)), 6.92 (d, 1H, $^4J_{HH}$ = 1.1 Hz, H-15), 6.93 – 6.97 (m, 4H, H-2 (1H), H-4 (1H) + H-12 (1H) + H-15 (1H)), 6.99 (d, 1H, $^4J_{HH}$ = 1.1 Hz, H-15), 7.2 (d, 1H, $^4J_{HH}$ = 1.2 Hz, H-15), 7.10 (t, 1H, $^3J_{HH}$ = 7.5 Hz, H-12), 7.18 (dd, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.0 Hz, H-11), 7.19 (dd, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.0 Hz, H-11), 7.21 – 7.23 (m, 2H, H-15 (1H) + H-11 (1H)), 7.25 (d, 1H, $^4J_{HH}$ = 1.4 Hz, H-15), 7.28 (d, 1H, $^4J_{HH}$ = 1.4 Hz, H-15), 7.31 (d, 1H, $^4J_{HH}$ = 1.4 Hz, H-15). **^{13}C{^{1}H}-NMR** (176.07 MHz, C_6D_6): δ [ppm] = 22.1 (C-18), 22.3 (C-18), 22.5 (C-18), 22.7 (C-18), 22.8 (C-18), 23.1 (C-18), 23.4 (C-18), 23.8 (C-18), 23.9 (C-18), 24.0 (C-20), 24.3 (C-20), 24.3 (C-8), 24.4 (C-20), 24.5 (C-20), 24.6 (C-20), 24.9 (C-20), 25.2 (C-18), 25.7 (C-18), 25.9 (C-18), 26.3 (C-18), 26.3 (C-20), 26.5 (C-20), 26.6 (C-18), 26.9 (C-18), 27.8 (C-18), 29.6 (C-8), 30.6 (C-17), 30.6 (C-17), 30.8 (C-17), 31.2 (C-17), 31.6 (C-17), 31.7 (C-17), 31.8 (C-17), 32.1 (C-17), 33.8 (C-24), 34.2 (C-19), 34.6 (C-19), 34.9 (C-19), 35.1 (C-19), 35.9 (C-21), 36.5 (C-7), 119.2 (C-15), 120.1 (C-15), 120.3 (C-15), 121.1 (C-15), 121.3 (C-15), 121.9 (C-15), 122.1 (C-15), 122.4 (C-15), 123.5 (C-3), 124.2 (C-3), 125.1 (C-22), 125.6 (C-4), 125.9 (C-4), 126.9 (C-12), 127.5 (C-12), 129.4 (C-1), 130.7 (C-1), 131.7 (C-11), 131.9 (C-11), 132.4 (C-2), 132.7 (C-11), 132.7 (C-11), 132.9 (C-2), 133.2 (C-5), 134.3 (C-5), 137.4 (C-23), 138.1 (C-13), 138.2 (C-9), 138.9 (C-13), 139.2 (C-13), 139.2 (C-13), 140.6 (C-9), 145.3 (C-14), 145.9 (C-14), 146.2 (C-10), 146.6 (C-14), 146.7 (C-14), 146.9 (C-14), 147.2 (C-14), 147.4 (C-16), 147.7 (C-14), 147.8 (C-10), 147.9 (C-10), 148.3 (C-14), 148.4 (C-16), 148.5 (C-16), 149.4 (C-16), 149.4 (C-10), 157.7 (C-6), 158.0 (C-6). **^{11}B-NMR**: A ^{11}B-NMR resonance could not be observed in solution due to severe broadening. **Elemental analysis calcd (%)** for $C_{91}H_{114}BClGe_2O_2$: C 76.36, H 8.03; found: C 76.49, H 7.83.



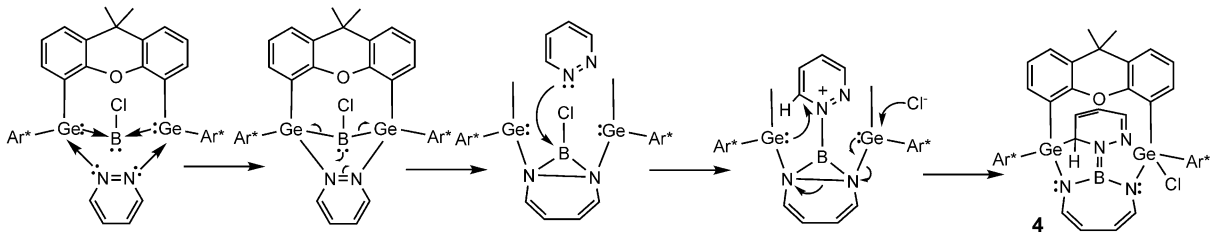
Synthesis of compound **4**: Pyridazine (15.9 µl, 220 µmol, 3.00 equiv.) was added while stirring to a turquoise solution of boradigermaallyl **1** (100 mg, 73.4 µmol, 1.00 equiv.) in cyclohexane (3.00 ml) at room temperature, whereby a color change from green to orange-red was observed within 15 minutes. For complete conversion of the reactants, the orange reaction mixture was stirred at room temperature for three days and volatile components were subsequently removed under reduced pressure. The orange residue was suspended in Et_2O (2.00 ml) and suspended particles were filtered off. The filter was rinsed with Et_2O (2x 1.00 ml) and the volume of the filtrate was reduced under reduced pressure until crystallization occurred. Overnight crystallization at room temperature resulted in a yellow-orange, microcrystalline solid of product **4** (65.1 mg, 42.7 µmol, 58 %). Pale yellow single crystals suitable for X-ray structure analysis were obtained after one week from a concentrated solution of the product **4** in toluene at room temperature. *Analytical data:* **^{1}H-NMR** (700.21 MHz, C_6D_6): δ [ppm] = 0.24 (d, 3H, $^3J_{HH}$ = 6.8 Hz, H-18), 0.35 (d, 3H, $^3J_{HH}$ = 6.7 Hz, H-18), 0.91 (d, 3H, $^3J_{HH}$ = 6.7 Hz, H-18), 0.94 (s, 3H, H-8), 0.98 (d, 3H, $^3J_{HH}$ = 6.8 Hz, H-18), 1.00 (d, 3H, $^3J_{HH}$ = 6.9 Hz,

H-18), 1.02 (d, 3H, $^3J_{HH}$ = 6.7 Hz, H-18), 1.06 (d, 6H, $^3J_{HH}$ = 6.7 Hz, H-18), 1.16 – 1.20 (m, 15H, H-18 (3H) + H-20 (12H)), 1.25 (s, 3H, H-8), 1.34 (d, 3H, $^3J_{HH}$ = 6.9 Hz, H-20), 1.35 – 1.38 (m, 6H, H-18 (3H) + H-20 (3H)), 1.40 (d, 3H, $^3J_{HH}$ = 6.6 Hz, H-18), 1.54 – 1.60 (m, 9H, H-18 (3H) + H-20 (6H)), 1.75 (d, 3H, $^3J_{HH}$ = 6.7 Hz, H-18), 1.77 – 1.81 (m, 6H, H-18), 1.85 (d, 3H, $^3J_{HH}$ = 6.9 Hz, H-18), 2.70 (sept, 1H, $^3J_{HH}$ = 6.9 Hz, H-19), 2.75 (sept, 1H, $^3J_{HH}$ = 6.9 Hz, H-19), 2.88 (sept, 1H, $^3J_{HH}$ = 6.7 Hz, H-17), 2.90 (sept, 1H, $^3J_{HH}$ = 6.8 Hz, H-19), 2.94 (sept, 1H, $^3J_{HH}$ = 6.8 Hz, H-17), 2.97 (sept, 1H, $^3J_{HH}$ = 6.8 Hz, H-17), 3.10 (sept, 1H, $^3J_{HH}$ = 6.8 Hz, H-19), 3.24 (sept, 1H, $^3J_{HH}$ = 6.8 Hz, H-17), 3.28 (sept, 1H, $^3J_{HH}$ = 6.7 Hz, H-17), 3.33 – 3.36 (m, 1H, H-23), 3.44 (sept, 1H, $^3J_{HH}$ = 6.7 Hz, H-17), 3.48 (sept, 1H, $^3J_{HH}$ = 6.7 Hz, H-17), 3.55 (sept, 1H, $^3J_{HH}$ = 6.8 Hz, H-17), 3.65 – 3.70 (m, 1H, H-26), 4.23 – 4.27 (m, 1H, H-21), 4.43 – 4.47 (m, 1H, H-25), 4.54 – 4.58 (m, 1H, H-26), 4.61 – 4.66 (m, 1H, H-25), 4.94 – 4.99 (m, 1H, H-22), 6.03 – 6.08 (m, 1H, H-24), 6.26 (t, 1H, $^3J_{HH}$ = 7.8 Hz, H-3), 6.72 – 6.78 (m, 3H, H-3 (1H) + H-4 (1H) + H-15 (1H)), 6.97 – 6.70 (m, 2H, H-11 (1H) + H-15 (1H)), 7.00 – 7.04 (m, 3H, H-2 (1H) + H-12 (1H) + H-15 (1H), 7.08 (dd, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.4 Hz, H-11), 7.09 – 7.12 (m, 2H, H-4 (1H) + H-12 (1H)), 7.12 (d, 1H, $^4J_{HH}$ = 1.3 Hz, H-15), 7.23 – 7.25 (m, 2H, H-11 (1H) + H-15 (1H)), 7.31 (d, 1H, $^4J_{HH}$ = 0.9 Hz, H-15), 7.38 (dd, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.0 Hz, H-11), 7.40 (d, 1H, $^4J_{HH}$ = 0.9 Hz, H-15), 7.45 (d, 1H, $^4J_{HH}$ = 1.0 Hz, H-15), 7.47 (dd, 1H, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.6 Hz, H-2). **^{13}C{^{1}H}-NMR** (176.07 MHz, C_6D_6): δ [ppm] = 22.6 (C-18), 23.2 (C-18), 23.3 (C-18), 23.4 (C-18), 23.6 (C-18), 23.6 (C-18), 23.7 (C-18), 24.3 (C-20), 24.4 (C-18), 24.4 (C-20), 24.5 (C-20), 24.6 (C-20), 24.6 (C-20), 24.7 (C-20), 24.8 (C-20), 24.9 (C-18), 24.9 (C-8), 25.5 (C-18), 25.9 (C-18), 26.0 (3x C-18), 26.5 (C-20), 26.7 (C-18), 28.1 (C-18), 30.6 (C-17), 30.9 (C-17), 31.0 (C-17), 31.3 (C-17), 31.5 (C-17), 31.6 (C-17), 31.6 (C-17), 31.8 (C-17), 34.2 (C-7), 34.7 (2x C-19), 34.8 (C-19), 35.4 (C-19), 35.8 (C-8), 47.3 (C-21), 110.2 (C-26), 112.2 (C-26), 117.5 (C-22), 121.3 (C-15), 121.4 (2x C-15), 121.4 (C-15), 121.5 (C-3), 121.6 (C-15), 121.6 (C-15), 121.7 (C-1), 122.2 (C-15), 122.7 (C-15), 123.2 (C-3), 123.9 (C-23), 124.7 (C-4), 126.0 (C-12), 127.0 (C-4), 128.7 (C-12), 129.6 (C-5), 130.0 (C-1), 131.5 (C-5), 131.7 (C-11), 133.2 (C-24), 133.2 (C-11), 133.2 (C-11), 133.7 (C-11), 134.0 (C-25), 134.9 (C-2), 136.2 (C-9), 138.3 (C-13 + C-25), 138.9 (C-13), 139.3 (C-13), 139.7 (C-2), 141.2 (C-13), 144.1 (C-10), 145.1 (C-9), 145.2 (C-10), 145.5 (C-14), 146.0 (C-14), 146.6 (C-10), 147.0 (C-14), 147.1 (C-14), 147.8 (C-14), 148.3 (C-10), 148.6 (C-16), 148.6 (C-14), 149.0 (C-14), 149.1 (C-16), 149.5 (C-14), 149.5 (C-16), 150.4 (C-16), 154.9 (C-6), 157.1 (C-6). **^{11}B{^{1}H}-NMR**: A ^{11}B-NMR signal could not be observed in solution due to severe broadening. **Elemental analysis calcd (%)** for $C_{95}H_{118}BClGe_2N_4O$: C 74.89, H 7.81, N 3.68; found: C 74.57, H 7.78, N 3.51.



Synthesis of compound **5**: A mixture of boradigermaallyl **1** (60.0 mg, 44.0 µmol, 1.00 equiv.) and 2,2'-bipyridine (6.87 mg, 44.0 µmol, 1.00 equiv.) was dissolved in *n*-hexane (7.00 ml) at ambient temperature. The turquoise solution was stirred for 2 days at room temperature and underwent a color change to dark purple. In the next step, small, suspended solids in the solution were filtered off and the concentration was increased under reduced pressure. Product **5** was obtained after 3 days of crystallization in *n*-hexane at ambient temperature in the form of intensely red to purple-colored crystals (48.3 mg, 31.8 µmol, 72 %). To obtain a single crystal suitable for X-ray structure analysis, *n*-pentane was diffused into a concentrated Et_2O solution of product **5** at room temperature. *Analytical data:* **^{1}H-NMR** (700.21 MHz, C_6D_6, 342 K): δ [ppm] = 0.40 (d, 3H, $^3J_{HH}$ = 6.7 Hz, H-18),

0.48 (d, 3H, $^3J_{HH}$ = 6.7 Hz, H-18), 0.85 (d, 1H, $^3J_{HH}$ = 5.3 Hz, H-21), 0.93 (d, 6H, $^3J_{HH}$ = 6.7 Hz, H-18 (6H)), 0.95 (d, 6H, $^3J_{HH}$ = 6.8 Hz, H-18 (6H)), 1.08 (d, 6H, $^3J_{HH}$ = 6.6 Hz, H-18), 1.20 – 1.26 (m, very broad, 6H, H-18), 1.16 (d, 3H, $^3J_{HH}$ = 6.7 Hz, H-18), 1.18 (d, 3H, $^3J_{HH}$ = 6.8 Hz, H-18), 1.21 (s, 3H, H-8), 1.31 – 1.40 (m, 33H, H-8 (3H) + H-18 (6H) + H-20 (24H)), 1.49 (d, 3H, $^3J_{HH}$ = 6.8 Hz, H-18), 1.51 (d, 3H, $^3J_{HH}$ = 6.8 Hz, H-18), 2.05 (d, 1H, $^3J_{HH}$ = 5.3 Hz, H-24), 2.77 – 2.92 (m, 6H, H-17 (3H) + H-19 (3H)), 2.95 (sept, 1H, $^3J_{HH}$ = 6.8 Hz, H-19), 3.01 (sept, 2H, $^3J_{HH}$ = 6.7 Hz, H-17 (2H)), 3.15 (sept, 2H, $^3J_{HH}$ = 6.8 Hz, H-17 (2H)), 3.25 (sept, 1H, $^3J_{HH}$ = 6.8 Hz, H-17), 4.29 – 4.36 (m, 1H, H-29), 5.21 – 5.25 (m, 1H, H-27), 5.36 – 5.40 (m, 1H, H-28), 5.43 – 5.47 (m, 1H, H-23), 5.59 (d, br, 1H, $^3J_{HH}$ = 6.7 Hz, H-30), 5.92 – 5.96 (m, 1H, H-22), 6.48 – 6.52 (m, 2H, H-3 (1H)+ H-2 (1H)), 6.54 – 6.58 (m, 1H, H-3), 6.59 – 6.62 (m, 1H, H-2), 6.93 (dd, 1H, $^3J_{HH}$ = 6.7 Hz, $^4J_{HH}$ = 1.4 Hz, H-4), 6.97 – 7.01 (m, 2H, H-15 (2H)), 7.04 – 7.08 (m, 6H, H-4 (1H) + H-11 (2H) + H-12 (1H) + H-15 (2H)), 7.12 – 7.16 (m, 3H, H-15 (2H) + H-12 (1H), overlapped by solvent signal,) 7.19 (d, 1H, $^4J_{HH}$ = 1.5 Hz, H-15), 7.21 – 7.25 (m, 3H, H-15 (1H) + H-11 (2H)). **^{13}C{^{1}H}-NMR** (176.07 MHz, C_6D_6, 342 K): δ [ppm] = 21.5 (C-18), 22.4 (C-18), 22.5 (2 x C-18), 22.6 (C-18), 22.8 (C-18), 23.1 (2 x C-18), 23.4 (C-20), 23.7 (2 x C-20), 23.9 (2 x C-20), 24.0 (2 x C-20), 24.1 (C-20), 25.5 (3 x C-18), 25.7 (C-18), 25.7 (C-18), 25.9 (C-18), 26.3 (2 x C-18), 28.1 (br, C-8), 30.1 (C-17), 30.3 (C-17), 30.6 (C-8), 30.8 (2 x C-17), 31.0 (2 x C-17), 31.1 (C-17), 31.5 (C-17), 32.0 (br, C-21), 34.2 (2 x C-19), 34.2 (C-19), 34.3 (C-19), 34.5 (C-7), 34.8 (C-24), 100.1 (C-29), 110.3 (C-25), 118.9 (C-27), 119.9 (C-15), 120.3 (C-15), 120.6 (2 x C-15), 120.8 (C-15), 121.3 (C-15), 121.7 (2 x C-15), 121.8 (C-3), 122.2 (C-3), 122.3 (C-28), 123.2 (C-1), 125.0 (C-4), 126.1 (C-23), 126.2 (C-4), 126.6 (C-12), 127.4 (C-12), 127.6 (C-26, overlapped by solvent signal), 127.7 (C-1, overlapped by solvent signal), 130.5 (C-5), 130.6 (C-11), 131.0 (C-5), 131.2 (C-2 + C-11), 133.7 (C-9), 133.9 (C-22 + 2x C-11), 135.1 (C-30), 136.8 (C-2), 138.0 (C-13), 138.1 (C-9), 138.4 (C-13), 139.0 (2 x C-13), 146.3 (C-14), 146.5 (2 x C-14), 146.8 (C-14), 147.0 (2 x C-14), 147.6 (2x C-10), 147.8 (C-14), 148.2 (C-16), 148.2 (C-16), 148.5 (2 x C-16 + C-14 + C-10), 148.9 (C-10), 155.9 (C-6), 156.3 (C-6). **^{11}B{^{1}H}-NMR** (192.55 MHz, C_6D_6, 342 K): δ [ppm] = 40.9 (s, br). **UV/Vis** (*n*-pentane, c = 0.053 mmol·L^{-1}): λ [nm] (ε [L·mol^{-1}cm^{-1}]: 660 (960), 610 (1700), 555 (3000), 465 (4400), 345 (4900). **Elemental analysis calcd (%)** for $C_{97}H_{118}BClGe_2N_2O$: C 76.67, H 7.83, N 1.84; found: C 77.01, H 7.89, N 1.79.



Scheme SI1. Possible mechanism for the formation of **4**.

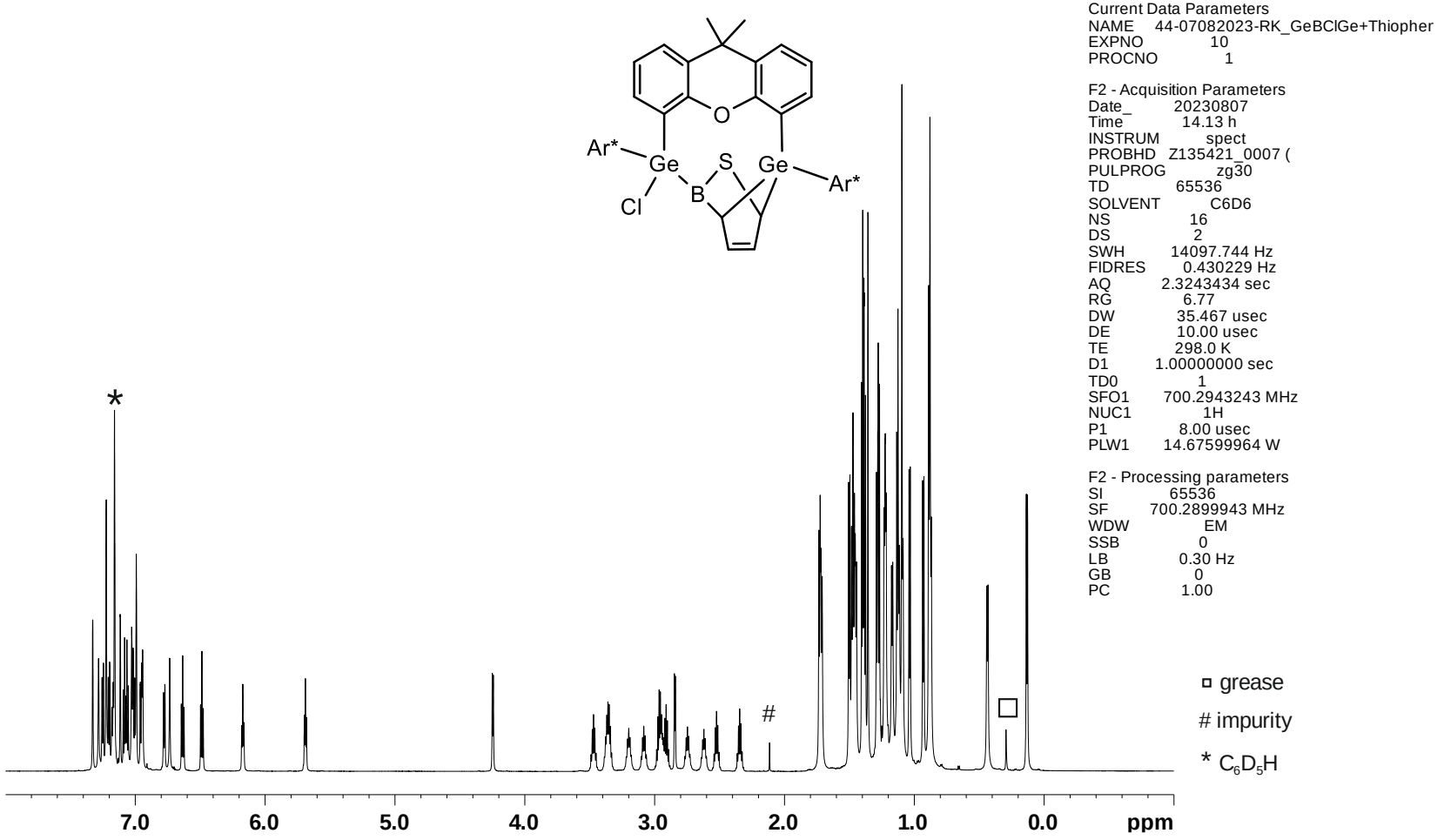
Crystal structure determination

Table SI1: Data of crystal structure determinations.

	2	**3**	**4**	**5**
empirical formula	0.5 x $C_{91}H_{114}BClGe_2OS$ 0.5 x C_4H_8O (THF)	$C_{91}H_{114}BClGe_2O_2$ C_5H_{12} (*n*-pentane)	2 x $C_{95}H_{118}BClGe_2N_4O$ 3 x C_7H_8 (toluene)	$C_{97}H_{118}BClGe_2N_2O$
M [g/mol]	759.71	1503.40	3323.24	1519.42
T [K]	100(2)	100(2)	120 (2)	100(2)
λ [Å]	0.71073	100(2)	0.71073	0.71073
crystal system	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	*P*2/c	$P2_1/n$
Z	4	4	2	4
a [Å]	14.7736(3)	18.6730(4)	22.2383(5)	14.5539(5)
b [Å]	15.1370(3)	21.1109(4)	13.1321(3)	14.7287(5)
c [Å]	20.2706(3)	23.3610(5)	31.4611(7)	44.0318(14)
α [°]	99.6780(10)	106.8640(10)	90	90
β [°]	103.1800(10)	90.2630(10)	93.3240(10)	96.7930(10)
γ [°]	100.5880(10)	106.2950(10)	90	90
V [Å^3]	4232.78(14)	8421.8(3)	9172.3(4)	9372.4(5)
D_c [g/cm^3]	1.192	1.186	1.203	1.077
μ [mm^{-1}]	0.813	0.793	0.735	0.713
F(000)	1620	3216	3540	3232
crystal size [mm]	0.29 x 0.27 x 0.25	0.31 x 0.28 x 0.26	0.32 x 0.29 x 0.27	0.29 x 0.28 x 0.25
θ range [°]	2.946 – 27.729	1.394 – 29.182	1.802 – 26.372	1.966 – 30.575
limiting indices	−19 ≤ h ≤ 18 −19 ≤ k ≤ 19 −26 ≤ l ≤ 25	−25 ≤ h ≤ 25 −28 ≤ k ≤ 28 −32 ≤ l ≤ 32	−27 ≤ h ≤ 27 −16 ≤ k ≤ 16 −39 ≤ l ≤ 39	−20 ≤ h ≤ 20 −21 ≤ k ≤ 21 −61 ≤ l ≤ 62
reflections collected	72401	388583	221629	147541
independent reflections	19557	45311	18739	27996
R_{int}	0.0538	0.0395	0.0940	0.0444
Completeness [%]	98.3	99.5	99.8	97.3
absorption correction	multi-scan	multi-scan	multi-scan	multi-scan
max., min. transmission	0.6910, 0.7456	0.6919, 0.7458	0.6992, 0.7458	0.6636, 0.7461
parameter/restraints	966 / 0	1977 / 399	1153 / 726	1011 / 146
R_1, ωR_2 [I > 2σ(*I*)]	0.0414, 0.0907	0.0379, 0.0940	0.0388, 0.0849	0.0491, 0.1292
R_1, ωR_2 (all data)	0.0674, 0.1002	0.0506, 0.1011	0.0586, 0.0940	0.0676, 0.1376
GooF on F^2	1.019	1.045	1.025	1.039
peak / hole [e·Å^{-3}]	1.342, −0.770	1.389, −0.629	0.785, −0.604	0.475, −0.709
CCDC	2420519	2420521	2420522	2420520

NMR spectroscopy

NMR spectra of compound **2**.



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F2 - Processing parameters
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Figure SI1. ^{1}H NMR of compound **2**.

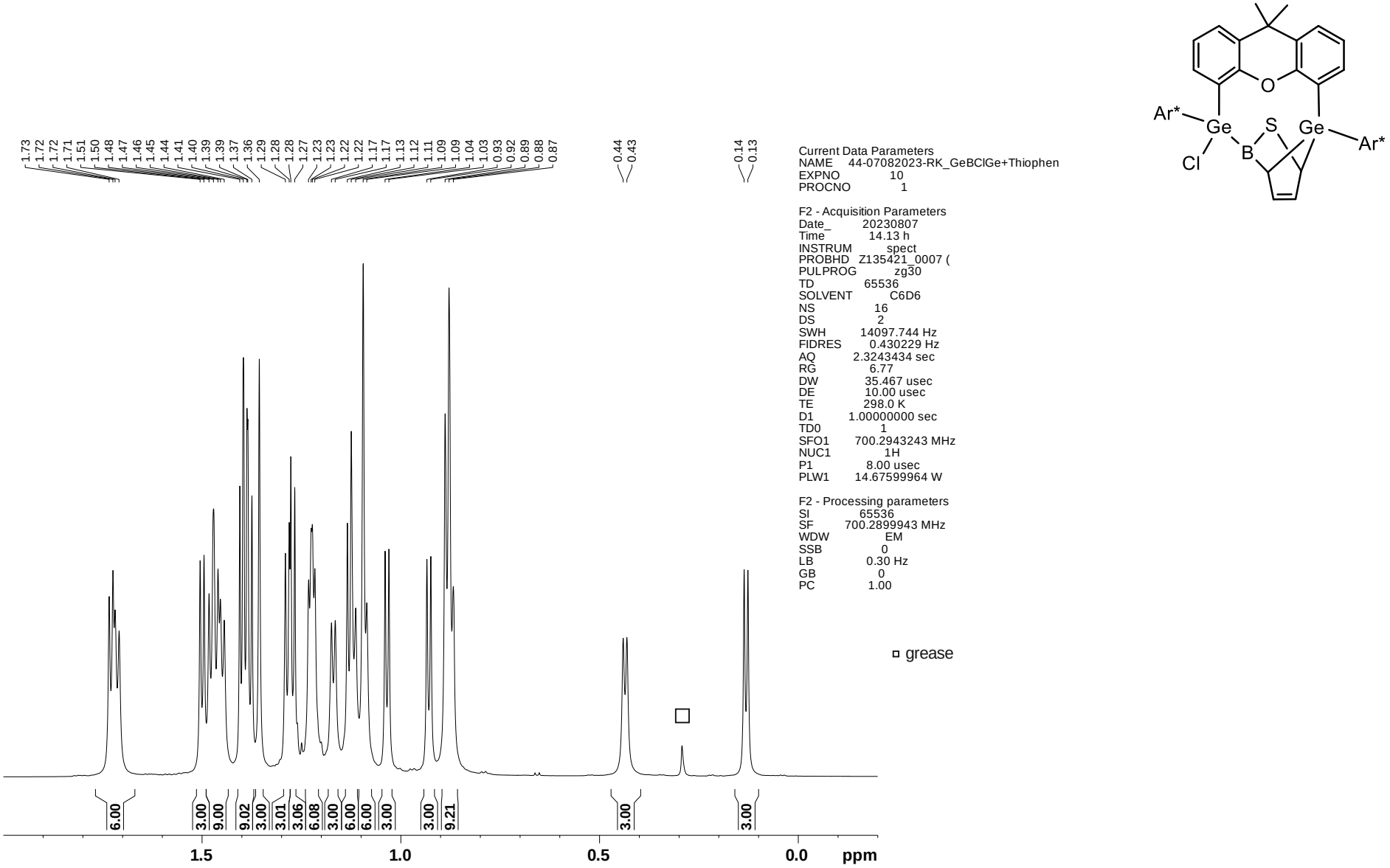


Figure SI2. ^{1}H NMR of compound **2** (0 – 2 ppm).

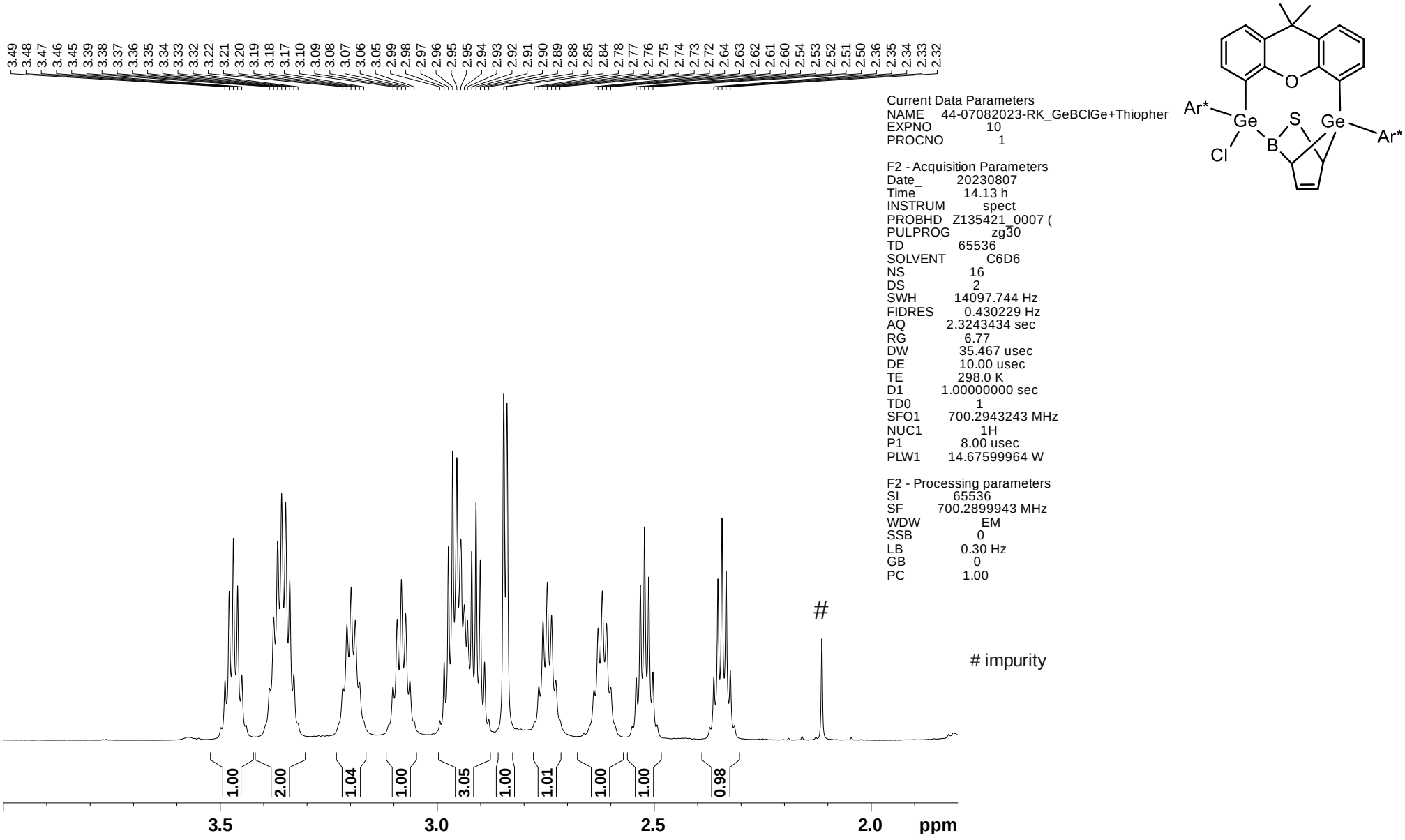
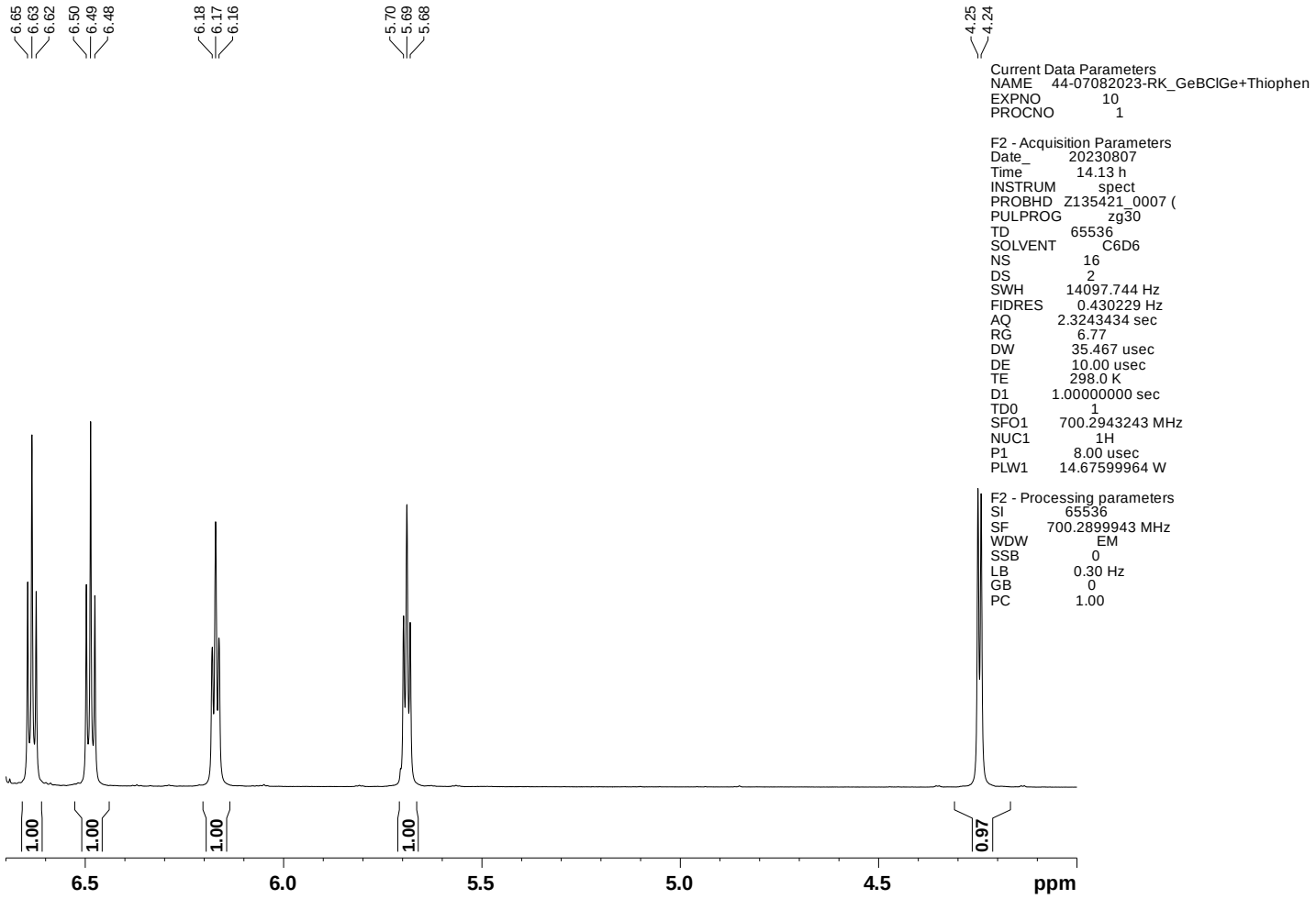


Figure SI3. ^{1}H NMR of compound **2** (1.8 – 4 ppm).



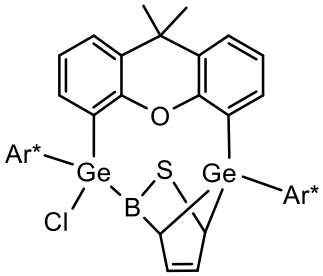
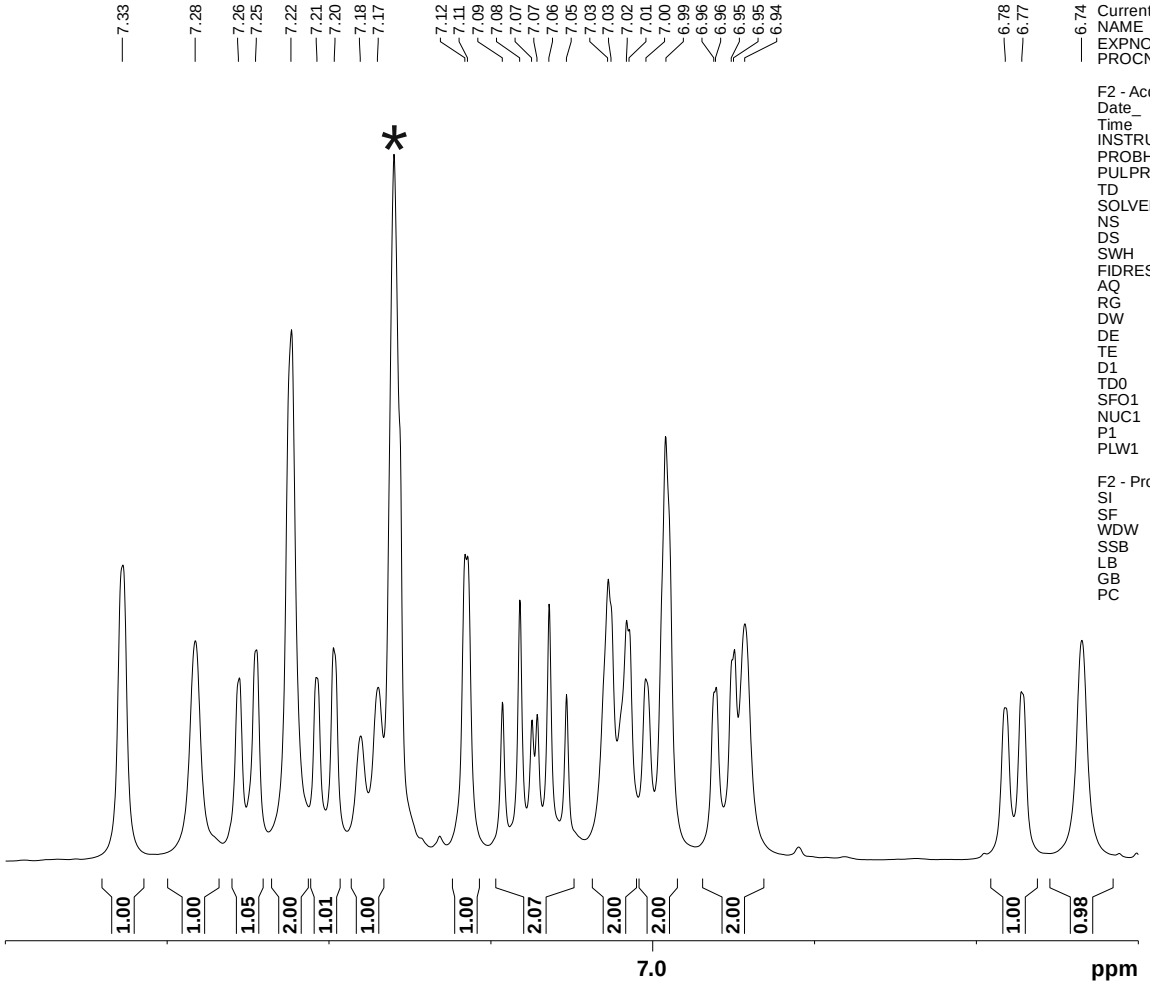


Figure SI4. ^{1}H NMR of compound **2** (4 – 6.7 ppm).



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F2 - Processing parameters
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* C_6D_5H

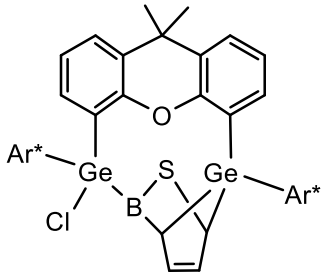
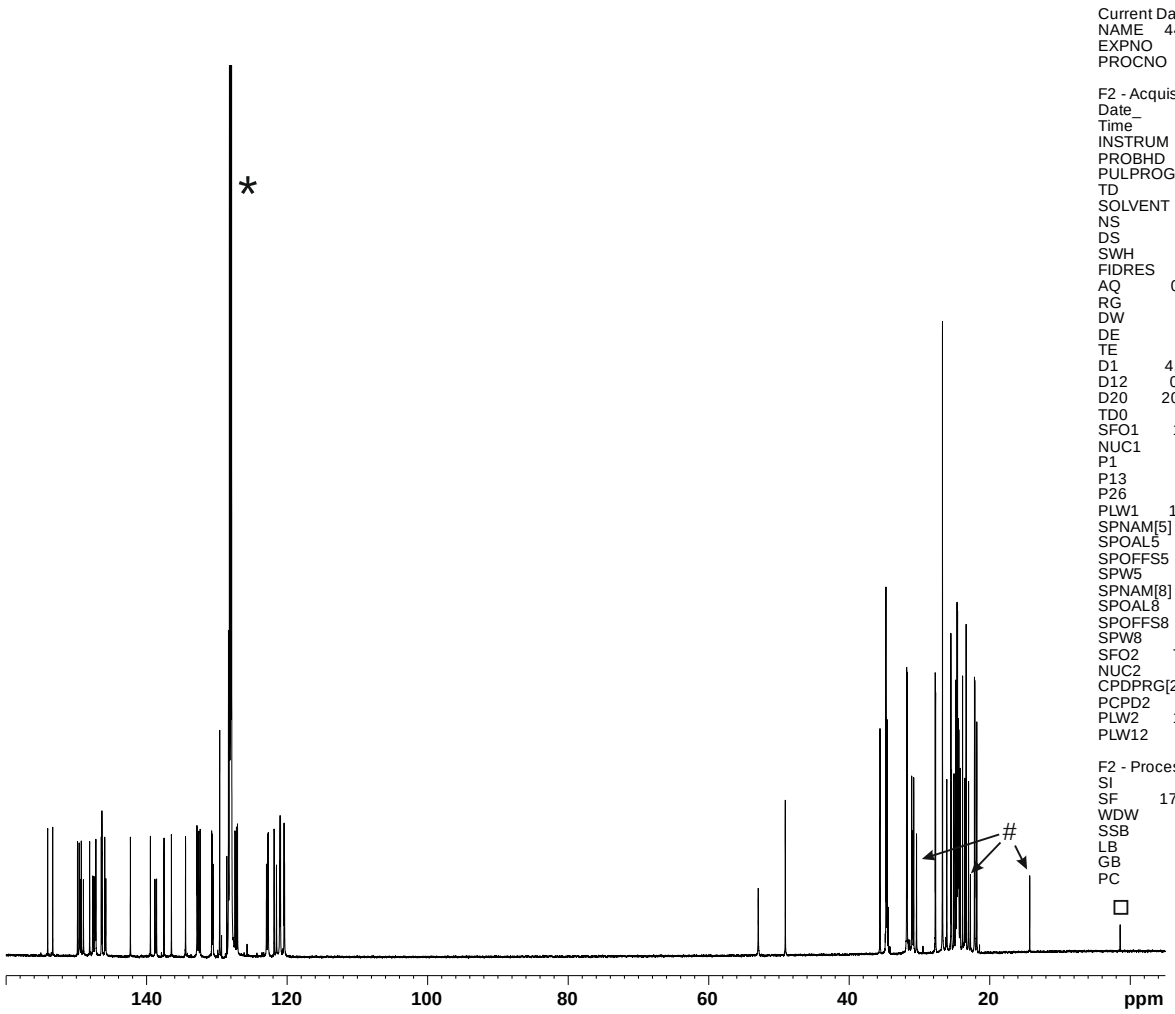


Figure SI5. ^{1}H NMR of compound **2** (6.7 – 7.4 ppm).



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SPOFFS5 0 Hz
SPW5 42.94699860 W
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SPOFFS8 0 Hz
SPW8 42.94699860 W
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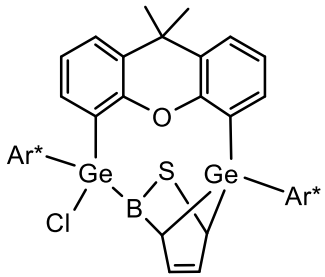
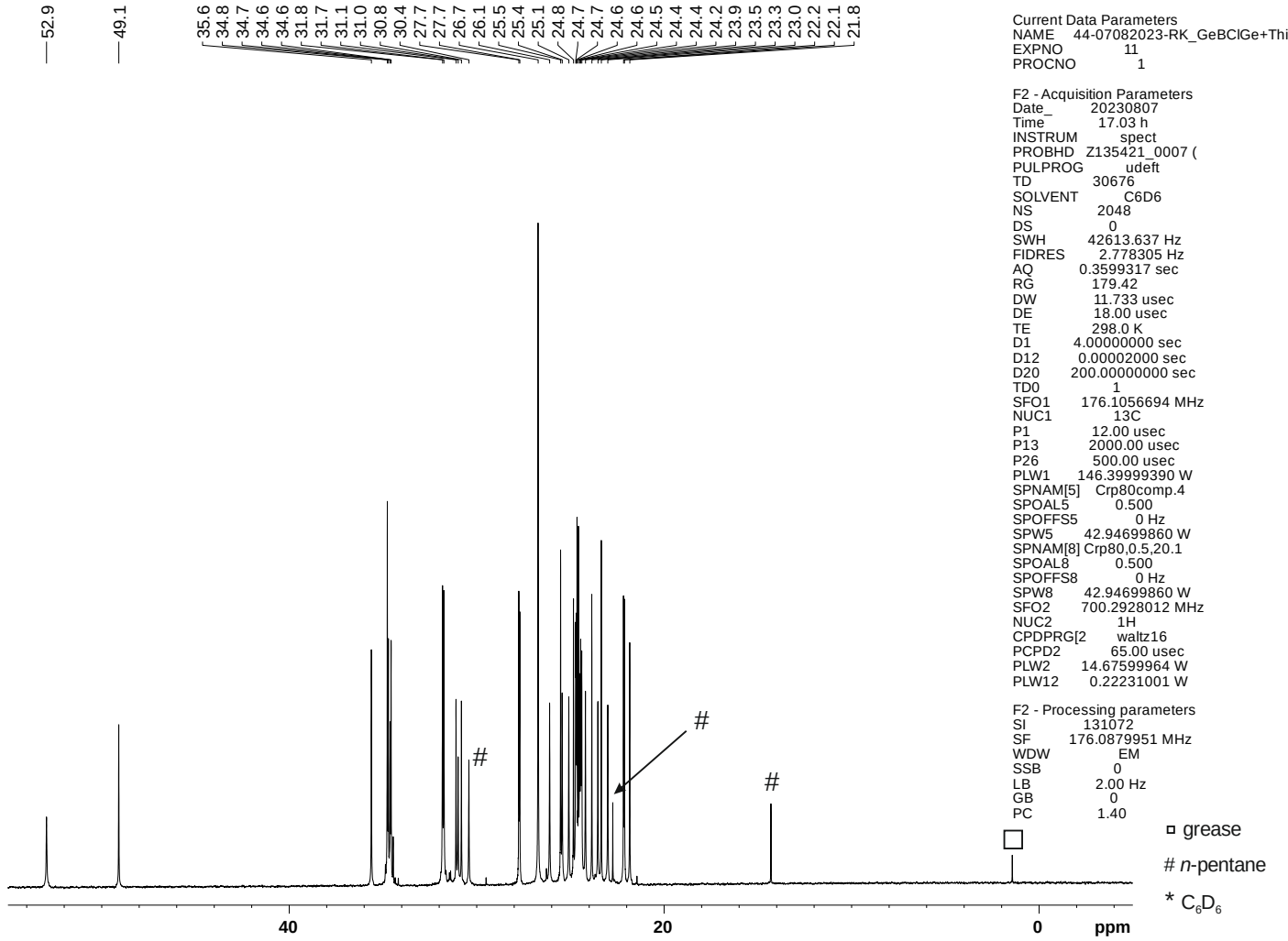


▫ grease
n-pentane
* C_6D_6

Figure SI6. $^{13}C\{^1H\}$ NMR of compound **2**.

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SPOFFS5            0 Hz
SPW5       42.94699860 W
SPNAM[8] Crp80,0.5,20.1
SPOAL8           0.500
SPOFFS8            0 Hz
SPW8       42.94699860 W
SFO2       700.2928012 MHz
NUC2              1H
CPDPRG[2        waltz16
PCPD2          65.00 usec
PLW2       14.67599964 W
PLW12       0.22231001 W

F2 - Processing parameters
SI            131072
SF         176.0879951 MHz
WDW               EM
SSB                0
LB              2.00 Hz
GB                 0
PC              1.40
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▫ grease

n-pentane

* C_6D_6

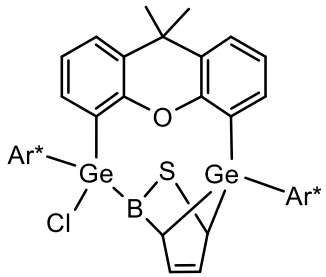


Figure SI7. $^{13}C\{^{1}H\}$ NMR of compound **2** (0-50 ppm).

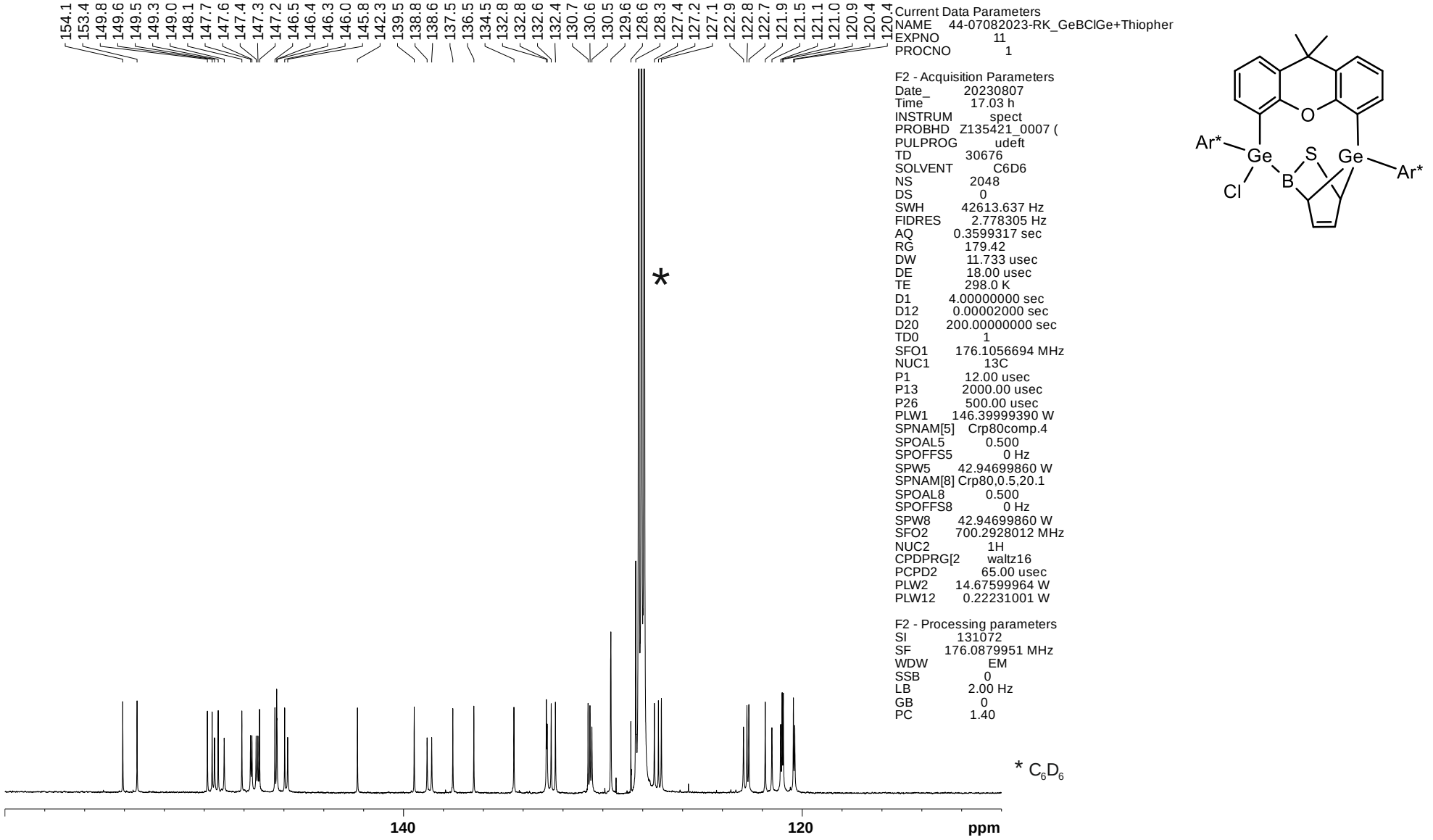
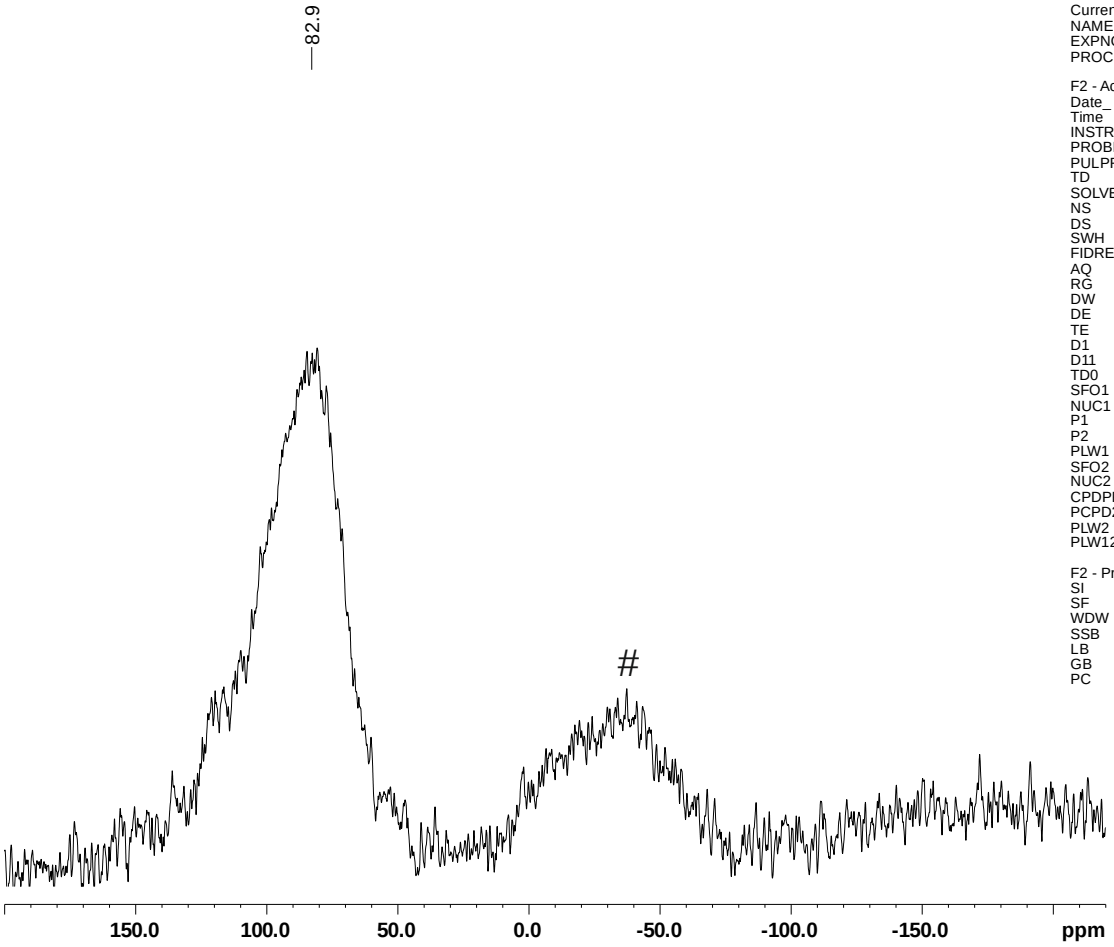


Figure SI8. $^{13}C\{^{1}H\}$ NMR of compound **2** (110-160 ppm).



Current Data Parameters
NAME RK328_300
EXPNO 32
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230901
Time 11.14 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgbsig
TD 8192
SOLVENT C6D6
NS 4096
DS 0
SWH 48076.922 Hz
FIDRES 11.737530 Hz
AQ 0.0851968 sec
RG 130.23
DW 10.400 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
D11 0.03000000 sec
TD0 1
SFO1 96.2936310 MHz
NUC1 11B
P1 5.75 usec
P2 11.50 usec
PLW1 70.00000000 W
SFO2 300.1314106 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 8.26509953 W
PLW12 0.20000000 W

F2 - Processing parameters
SI 32768
SF 96.2936310 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 1.40

glass

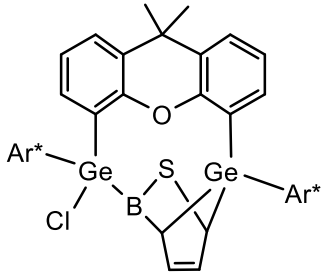
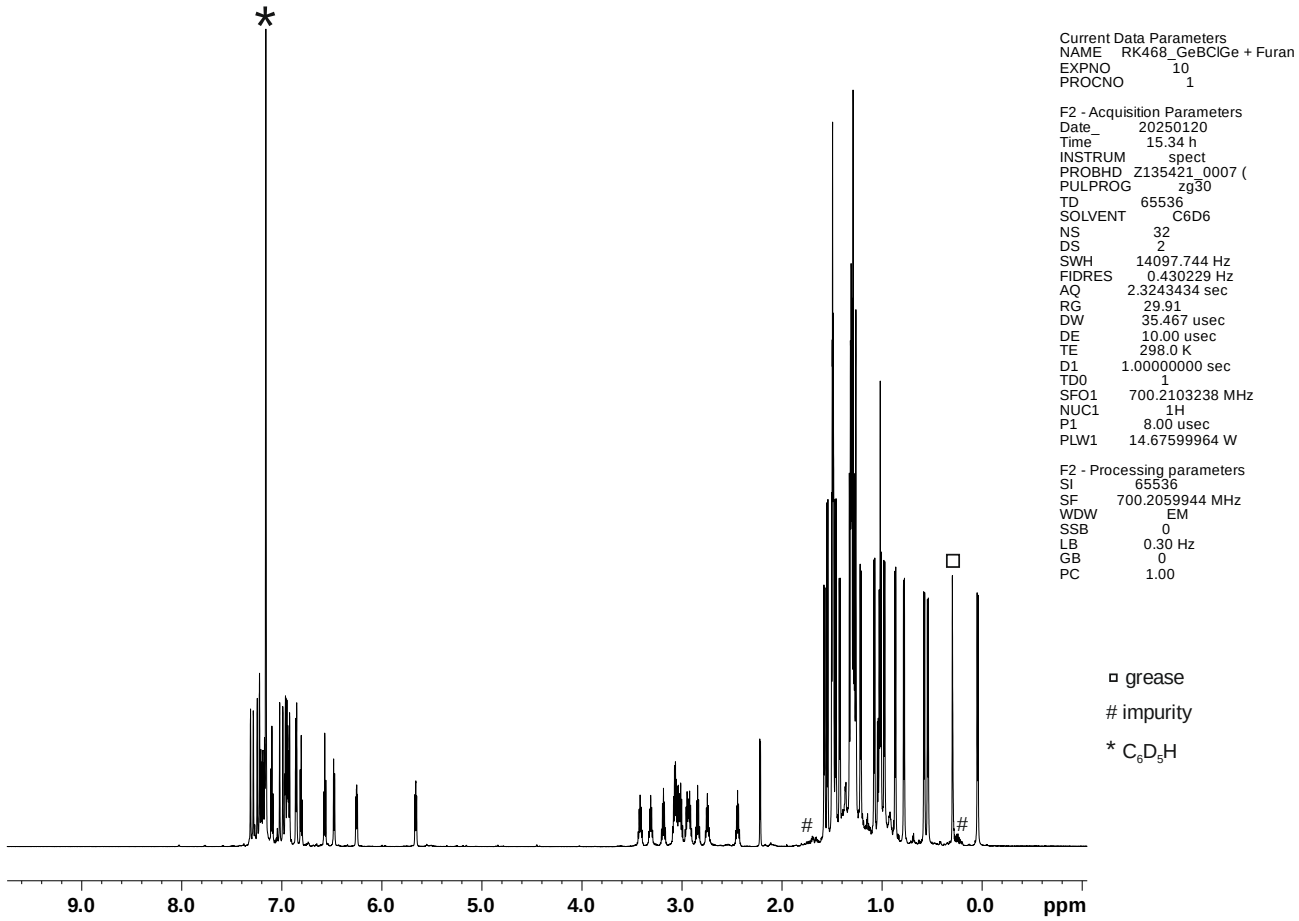


Figure SI9. $^{11}B\{^{1}H\}$ NMR of compound **2**.

NMR spectra of compound **3**.



Current Data Parameters
NAME RK468_GeBClGe + Furan
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20250120
Time 15.34 h
INSTRUM spect
PROBHD Z135421_0007 (
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 32
DS 2
SWH 14097.744 Hz
FIDRES 0.430229 Hz
AQ 2.3243434 sec
RG 29.91
DW 35.467 usec
DE 10.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 700.2103238 MHz
NUC1 1H
P1 8.00 usec
PLW1 14.67599964 W

F2 - Processing parameters
SI 65536
SF 700.2059944 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

▫ grease
impurity
* C_6D_5H

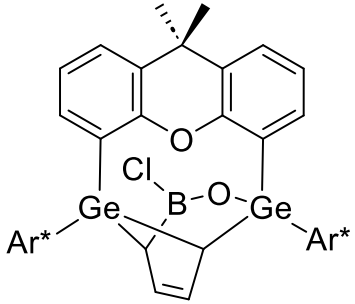
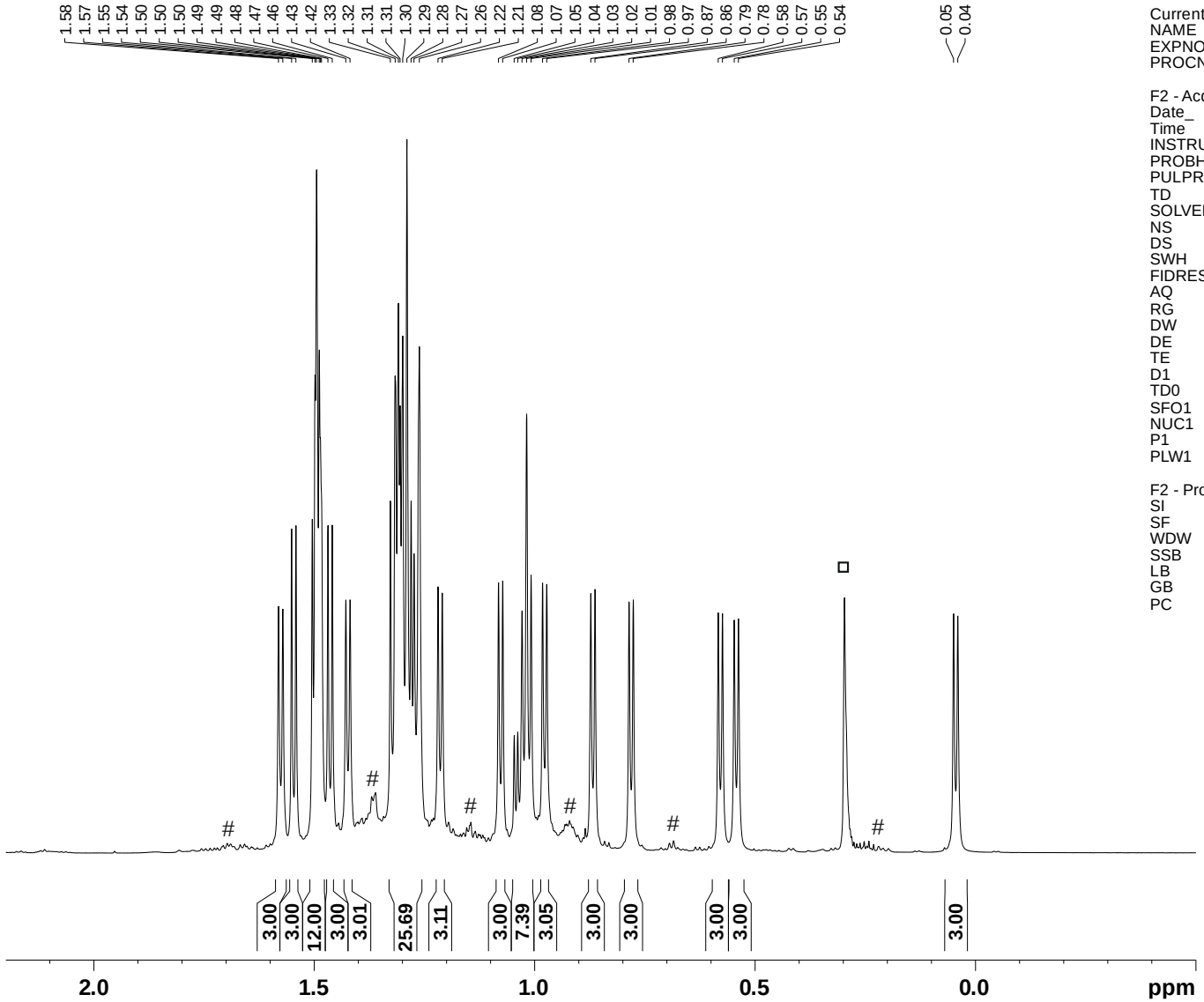


Figure SI10. ^{1}H NMR of compound **3**.



Current Data Parameters
NAME RK468_GeBClGe + Furan
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20250120
Time 15.34 h
INSTRUM spect
PROBHD Z135421_0007 (
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 32
DS 2
SWH 14097.744 Hz
FIDRES 0.430229 Hz
AQ 2.3243434 sec
RG 29.91
DW 35.467 usec
DE 10.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 700.2103238 MHz
NUC1 1H
P1 8.00 usec
PLW1 14.67599964 W

F2 - Processing parameters
SI 65536
SF 700.2059944 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

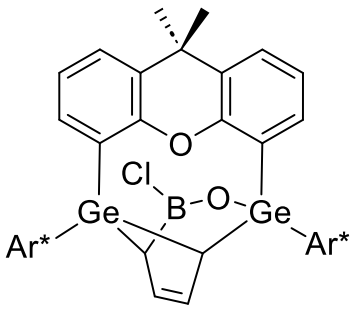


Figure SI11. ^{1}H NMR of compound **3** (0.5 – 2.2 ppm).

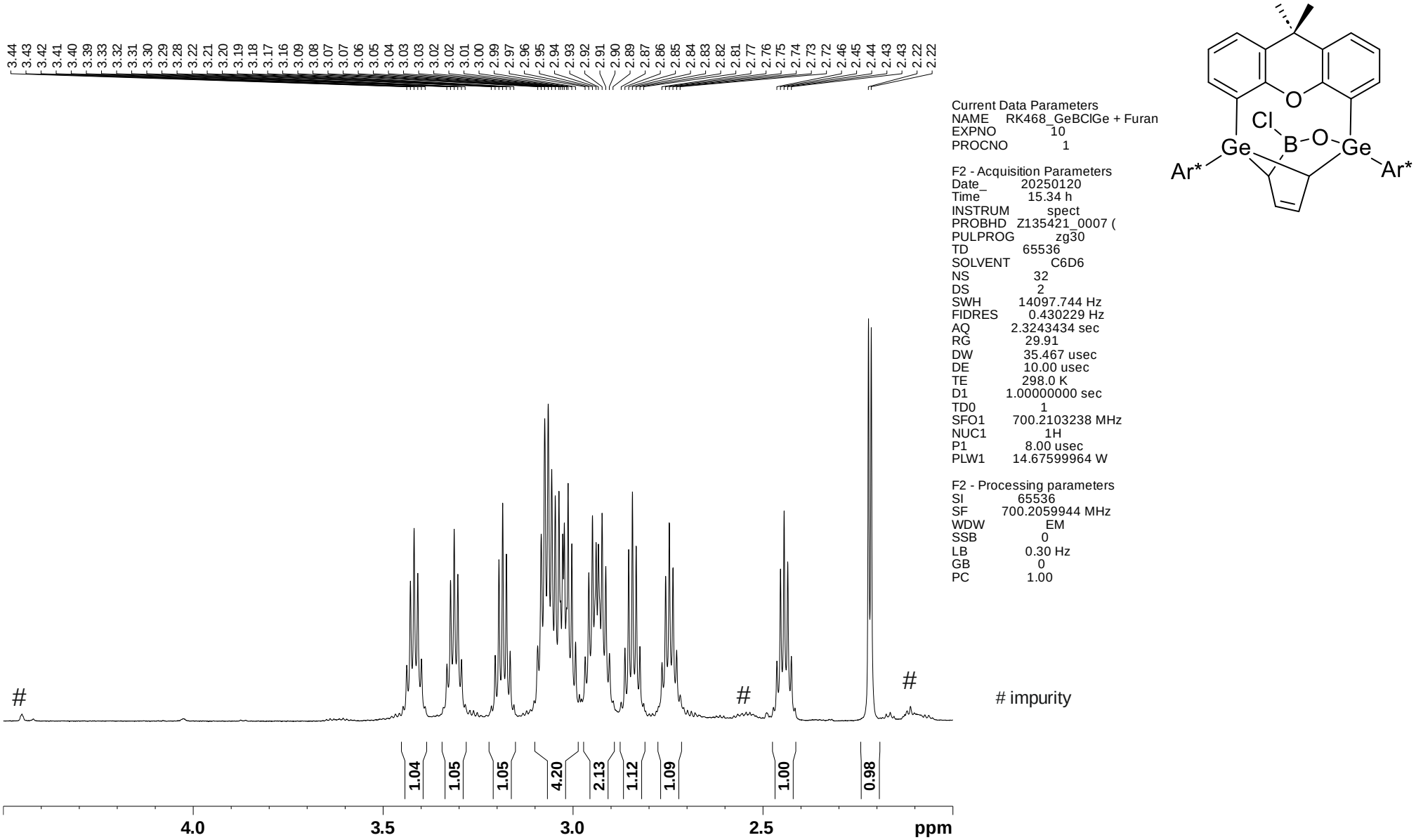


Figure SI12. ^{1}H NMR of compound **3** (2 – 4.5 ppm).

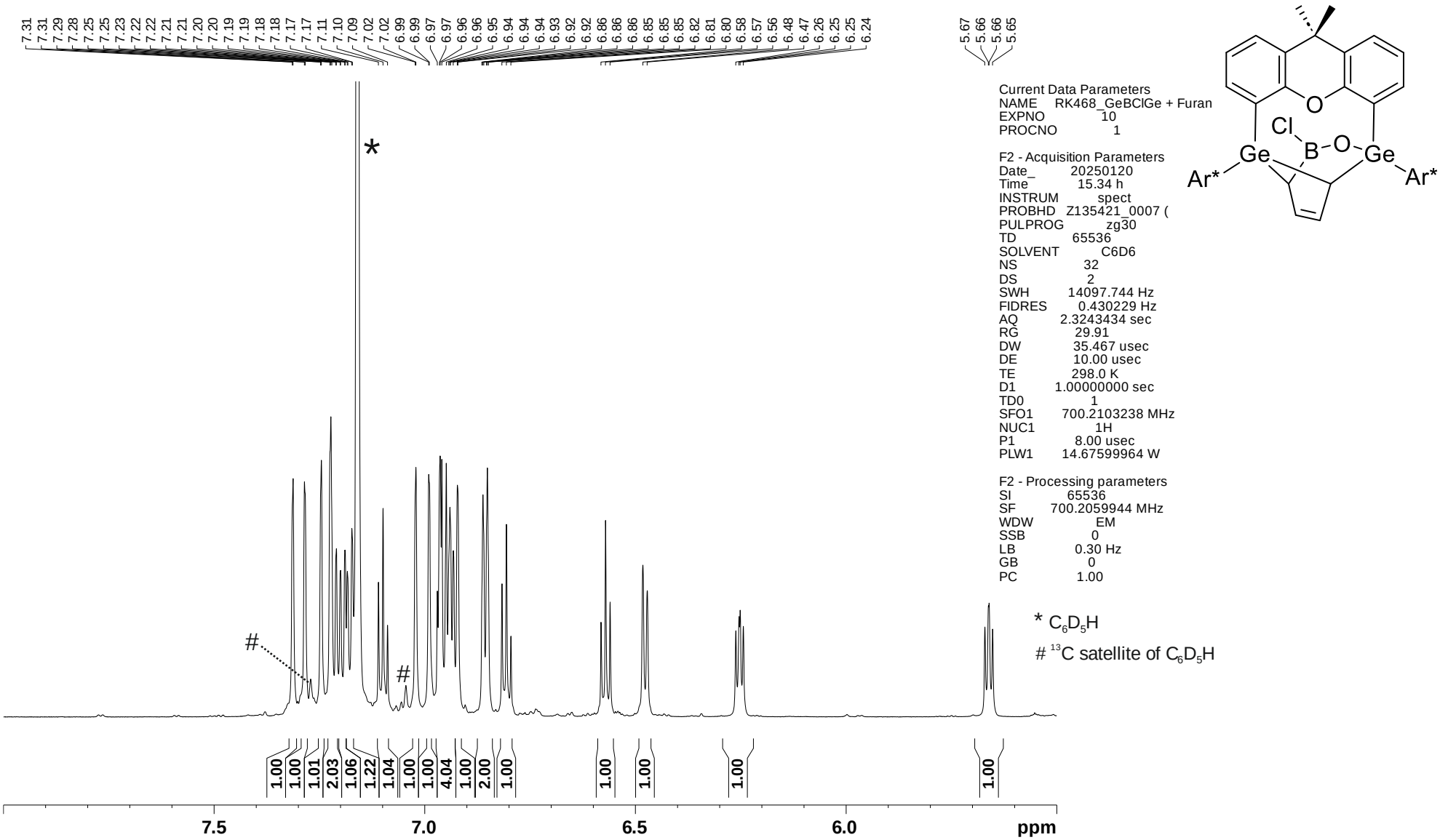


Figure SI13. ^{1}H NMR of compound **3** (5.5 – 8 ppm).

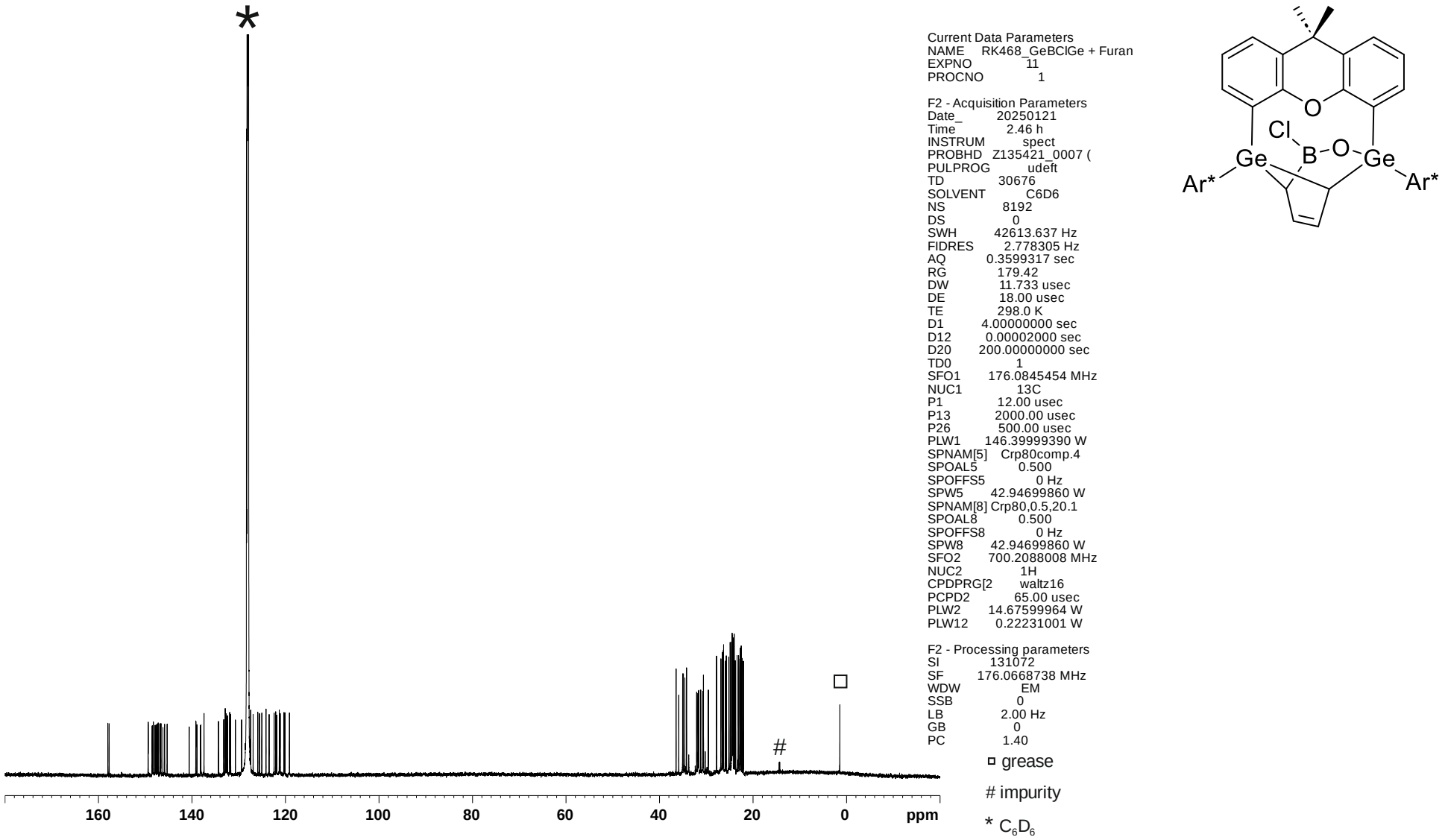


Figure SI14. $^{13}C\{^{1}H\}$ NMR of compound **3**.

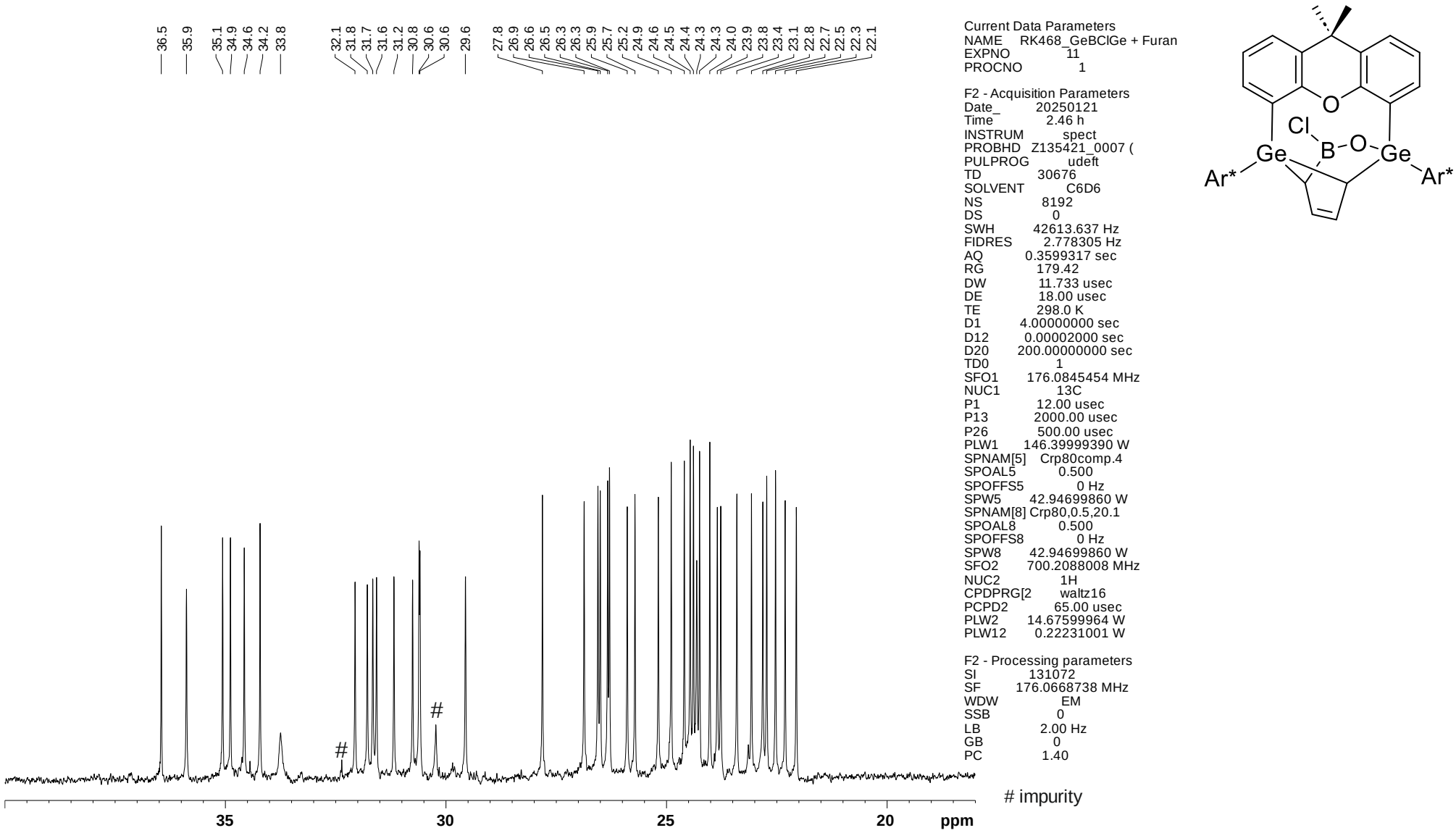


Figure SI15. $^{13}C\{^{1}H\}$ NMR of compound **3** (18-40 ppm).

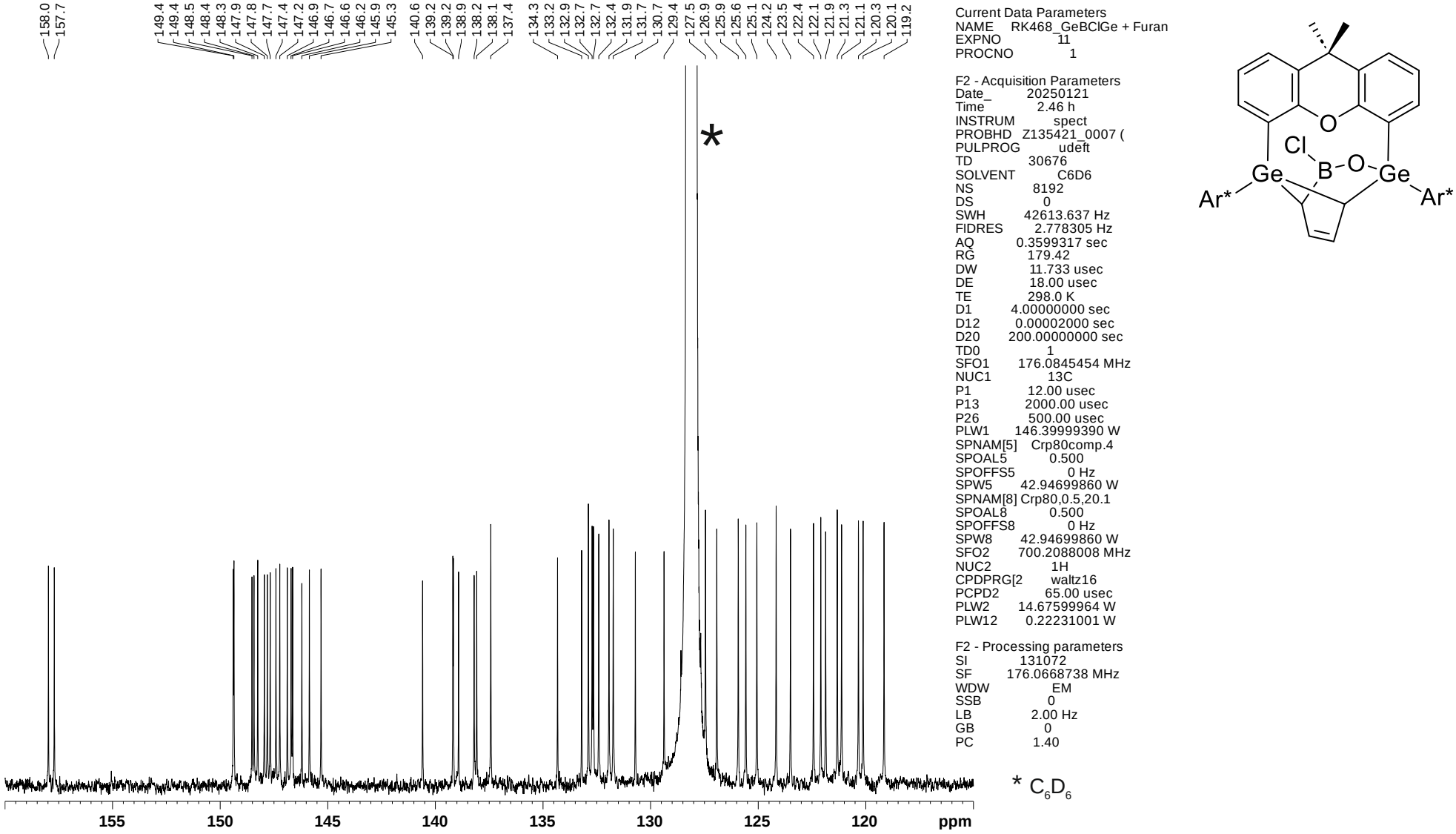
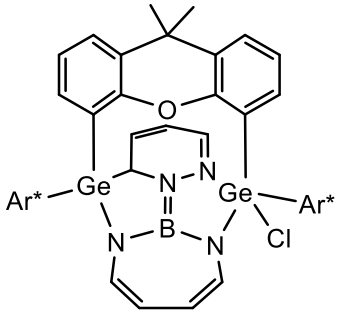
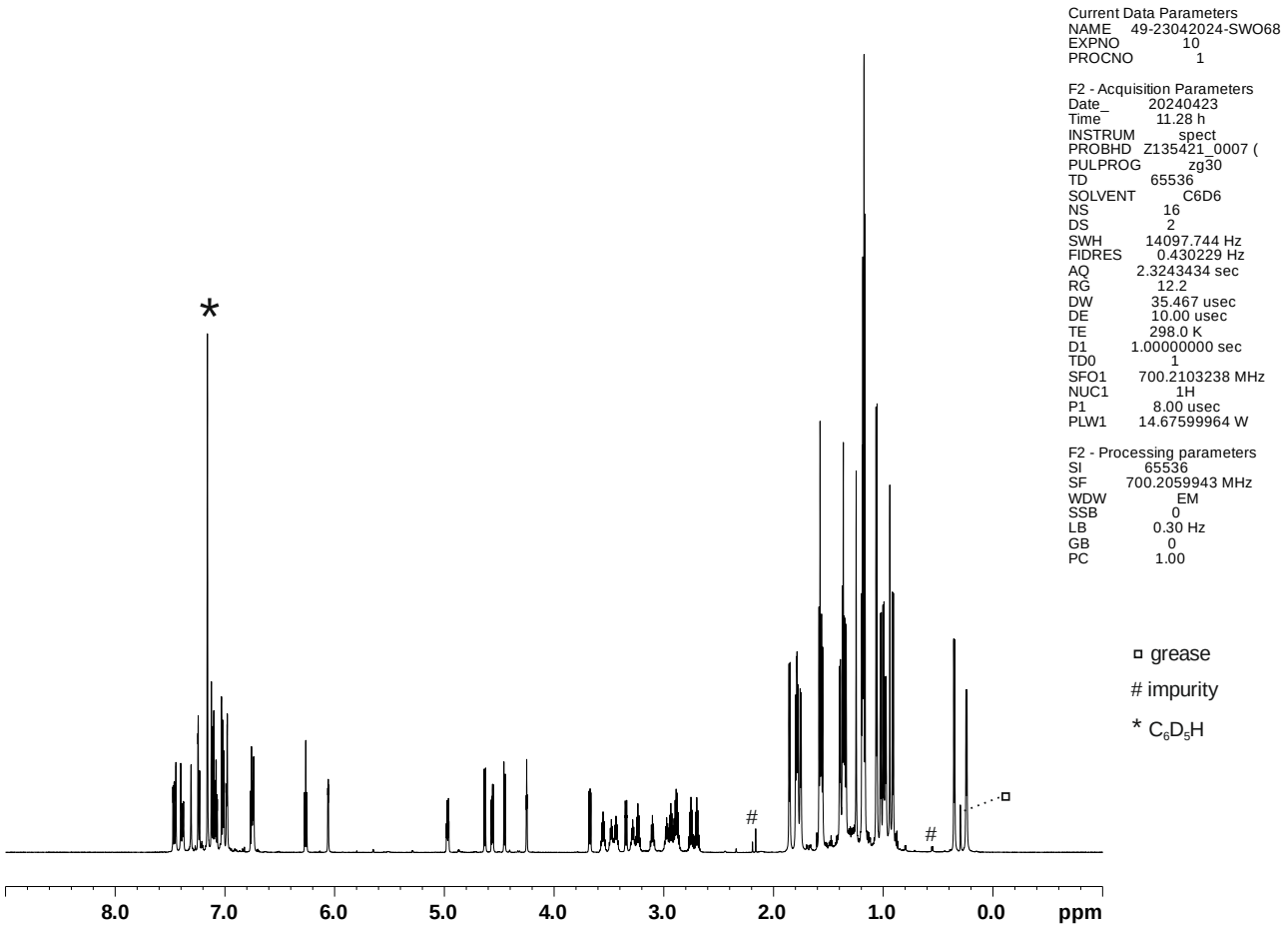


Figure SI16. $^{13}C\{^{1}H\}$ NMR of compound **3** (115-160 ppm).

NMR spectra of compound **4**.





Current Data Parameters
NAME 49-23042024-SWO68
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
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Time 11.28 h
INSTRUM spect
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PULPROG zg30
TD 65536
SOLVENT C6D6
NS 16
DS 2
SWH 14097.744 Hz
FIDRES 0.430229 Hz
AQ 2.3243434 sec
RG 12.2
DW 35.467 usec
DE 10.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 700.2103238 MHz
NUC1 1H
P1 8.00 usec
PLW1 14.67599964 W

F2 - Processing parameters
SI 65536
SF 700.2059943 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

▫ grease

impurity

* C_6D_5H

Figure SI17. ^{1}H NMR of compound **4**.

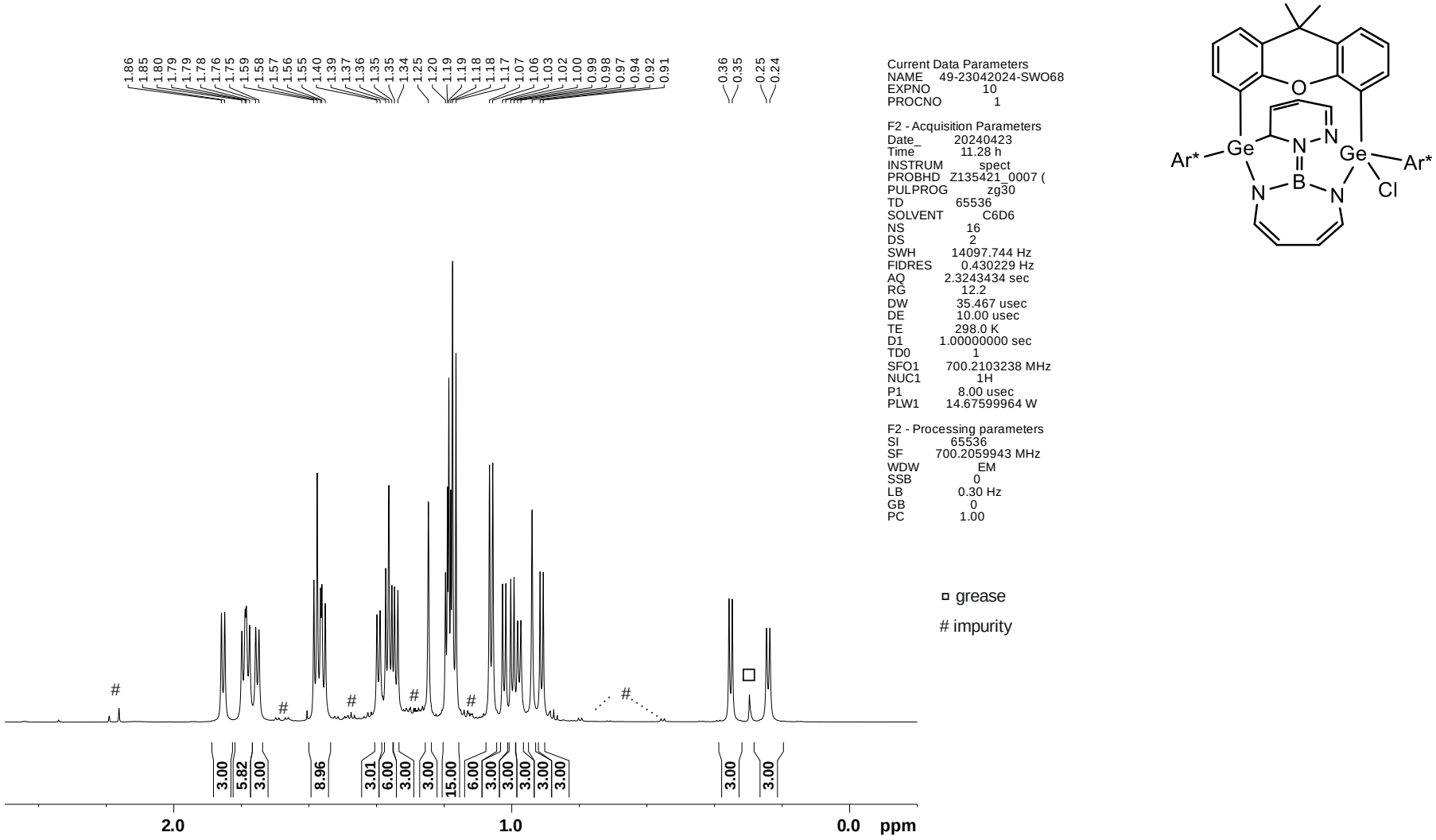
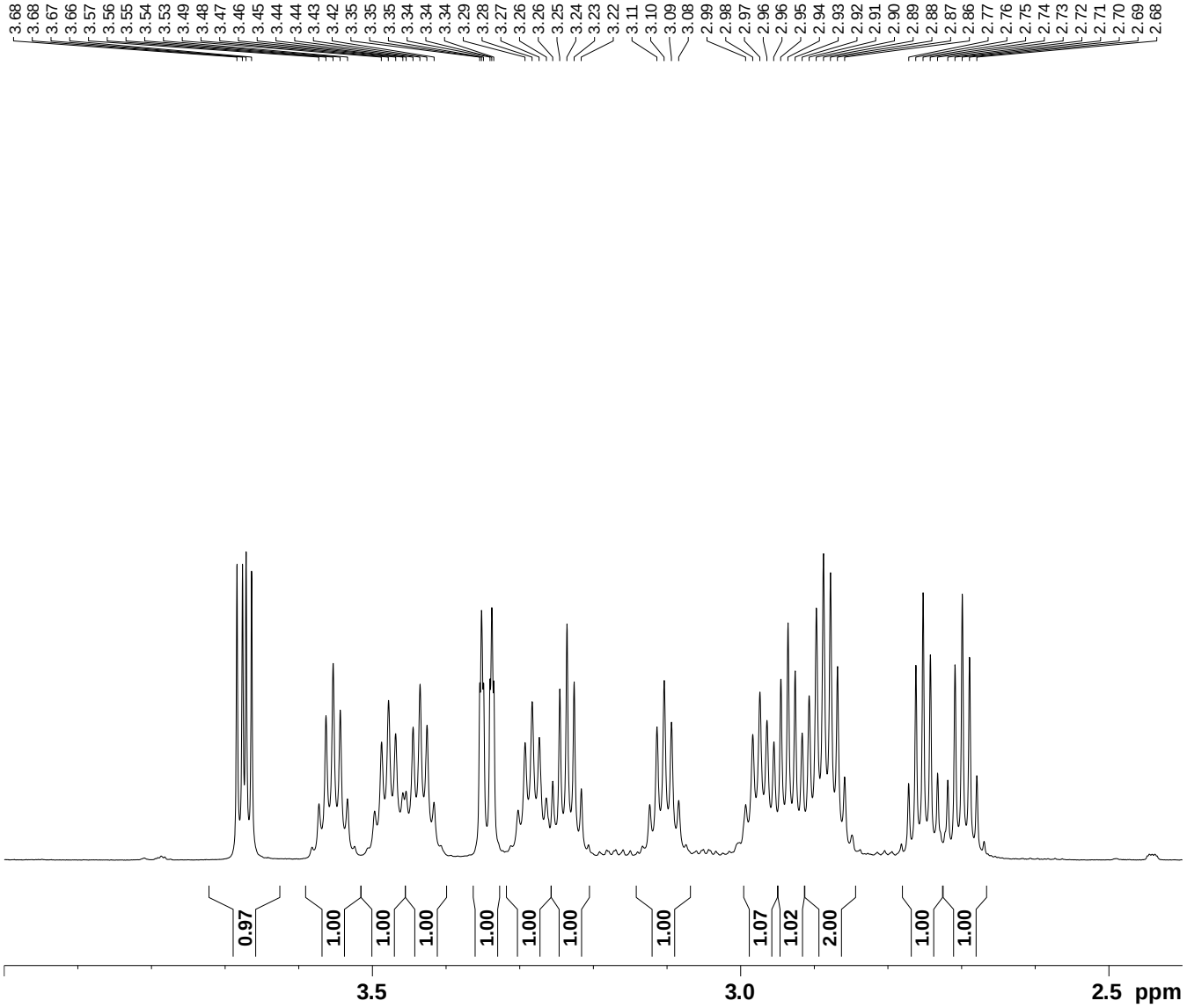


Figure SI18. ^{1}H NMR of compound **4** (0-2.4 ppm).



Current Data Parameters
NAME 49-23042024-SWO68
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240423
Time 11.28 h
INSTRUM spect
PROBHD Z135421_0007 (
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 16
DS 2
SWH 14097.744 Hz
FIDRES 0.430229 Hz
AQ 2.3243434 sec
RG 12.2
DW 35.467 usec
DE 10.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 700.2103238 MHz
NUC1 1H
P1 8.00 usec
PLW1 14.67599964 W

F2 - Processing parameters
SI 65536
SF 700.2059943 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

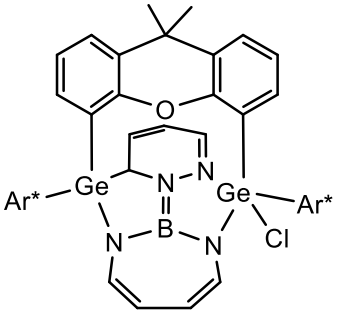
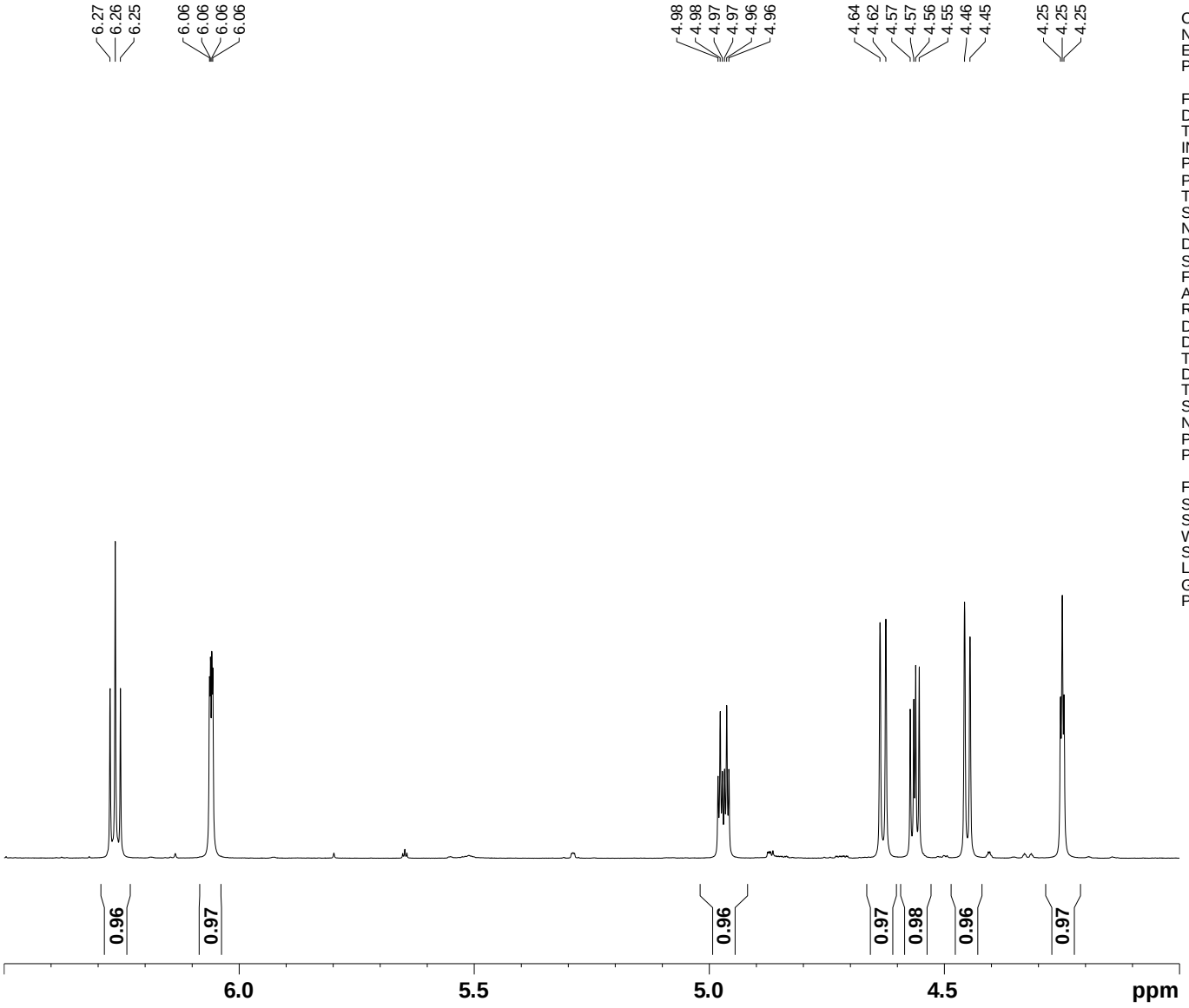


Figure SI19. ^{1}H NMR of compound **4** (2.5-4 ppm).



Current Data Parameters
NAME 49-23042024-SWO68
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240423
Time 11.28 h
INSTRUM spect
PROBHD Z135421_0007 (
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 16
DS 2
SWH 14097.744 Hz
FIDRES 0.430229 Hz
AQ 2.3243434 sec
RG 12.2
DW 35.467 usec
DE 10.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 700.2103238 MHz
NUC1 1H
P1 8.00 usec
PLW1 14.67599964 W

F2 - Processing parameters
SI 65536
SF 700.2059943 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

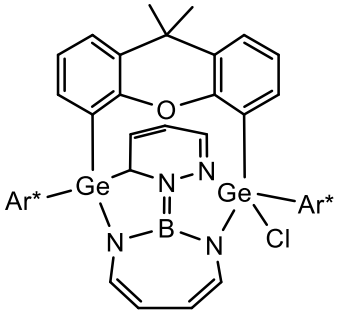
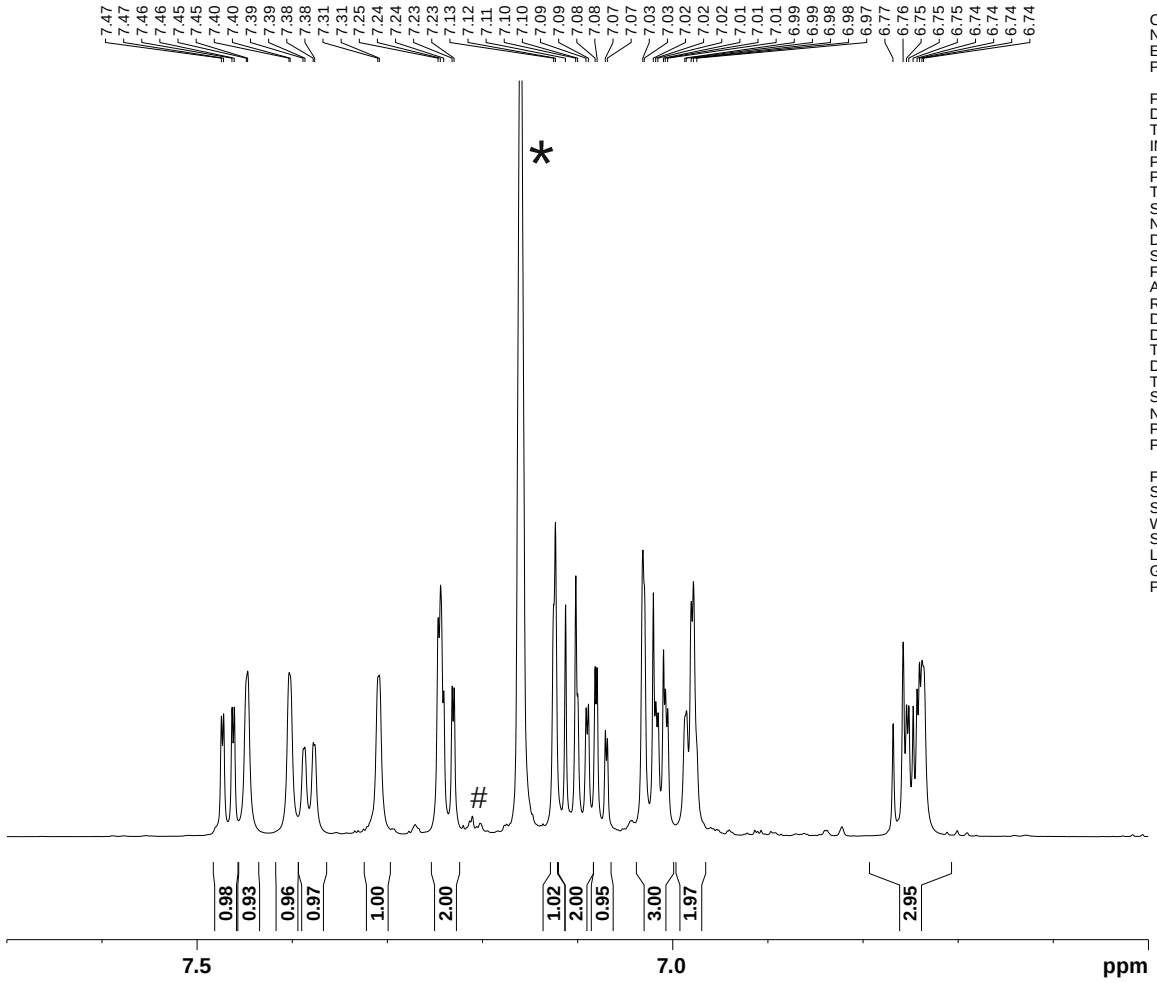


Figure SI20. ^{1}H NMR of compound **4** (4-6.5 ppm).



Current Data Parameters
NAME 49-23042024-SWO68
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240423
Time 11.28 h
INSTRUM spect
PROBHD Z135421_0007 (
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 16
DS 2
SWH 14097.744 Hz
FIDRES 0.430229 Hz
AQ 2.3243434 sec
RG 12.2
DW 35.467 usec
DE 10.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 700.2103238 MHz
NUC1 1H
P1 8.00 usec
PLW1 14.67599964 W

F2 - Processing parameters
SI 65536
SF 700.2059943 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

impurity

* C_6D_5H

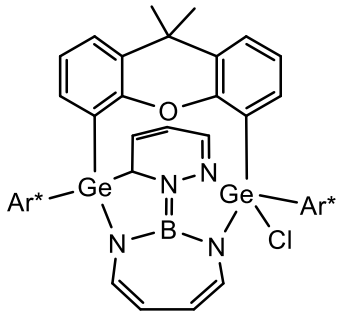
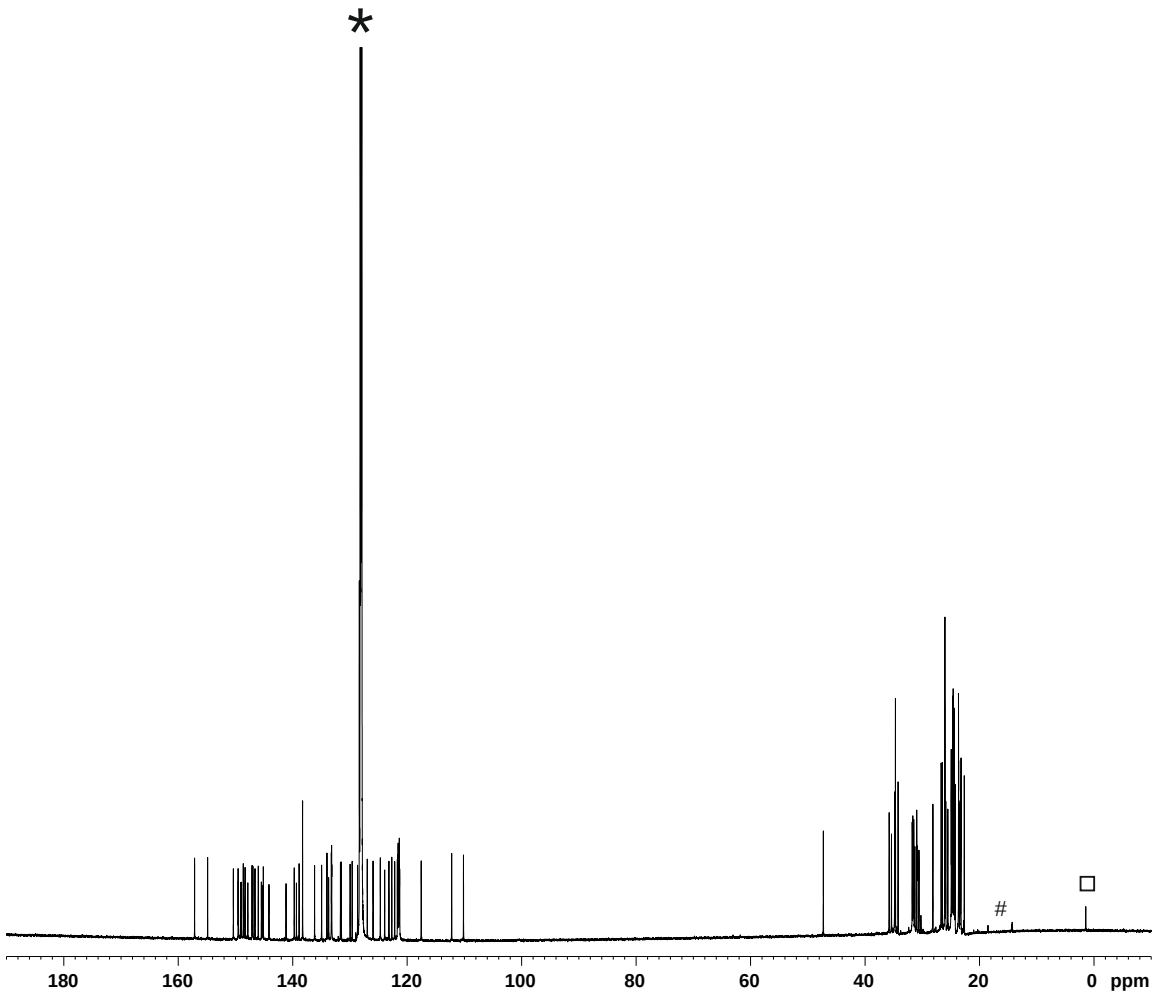


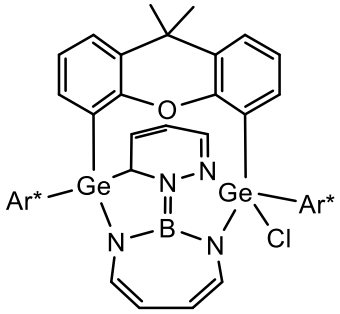
Figure SI21. ^{1}H NMR of compound **4** (6.5-7.7 ppm).



Current Data Parameters
NAME 49-23042024-SWO68
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240423
Time 18.21 h
INSTRUM spect
PROBHD Z135421_0007 (
PULPROG udeft
TD 30676
SOLVENT C6D6
NS 5120
DS 0
SWH 42613.637 Hz
FIDRES 2.778305 Hz
AQ 0.3599317 sec
RG 179.42
DW 11.733 usec
DE 18.00 usec
TE 298.0 K
D1 4.00000000 sec
D12 0.00002000 sec
D20 200.00000000 sec
TD0 1
SFO1 176.0845454 MHz
NUC1 13C
P1 12.00 usec
P13 2000.00 usec
P26 500.00 usec
PLW1 146.39999390 W
SPNAM[5] Crp80comp.4
SPOAL5 0.500
SPOFFS5 0 Hz
SPW5 42.94699860 W
SPNAM[8] Crp80,0.5,20.1
SPOAL8 0.500
SPOFFS8 0 Hz
SPW8 42.94699860 W
SFO2 700.2088008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 65.00 usec
PLW2 14.67599964 W
PLW12 0.22231001 W

F2 - Processing parameters
SI 131072
SF 176.0668736 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

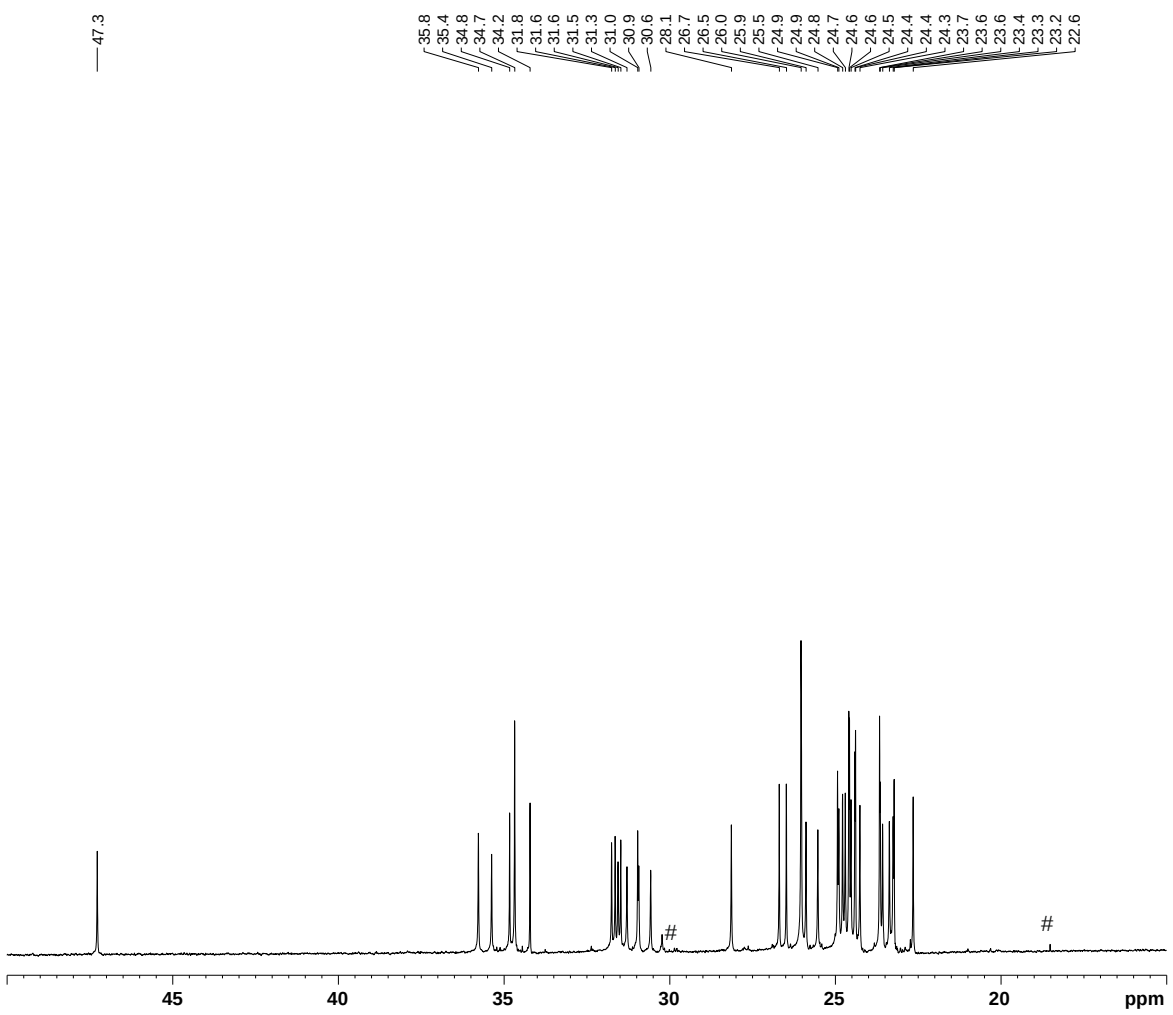


▫ grease

impurity

* C_6D_6

Figure SI22. $^{13}C\{^1H\}$ NMR of compound **4**.



Current Data Parameters
NAME 49-23042024-SWO68
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240423
Time 18.21 h
INSTRUM spect
PROBHD Z135421_0007 (
PULPROG udeft
TD 30676
SOLVENT C6D6
NS 5120
DS 0
SWH 42613.637 Hz
FIDRES 2.778305 Hz
AQ 0.3599317 sec
RG 179.42
DW 11.733 usec
DE 18.00 usec
TE 298.0 K
D1 4.00000000 sec
D12 0.00002000 sec
D20 200.00000000 sec
TD0 1
SFO1 176.0845454 MHz
NUC1 13C
P1 12.00 usec
P13 2000.00 usec
P26 500.00 usec
PLW1 146.39999390 W
SPNAM[5] Crp80comp.4
SPOAL5 0.500
SPOFFS5 0 Hz
SPW5 42.94699860 W
SPNAM[8] Crp80,0.5,20.1
SPOAL8 0.500
SPOFFS8 0 Hz
SPW8 42.94699860 W
SFO2 700.2088008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 65.00 usec
PLW2 14.67599964 W
PLW12 0.22231001 W

F2 - Processing parameters
SI 131072
SF 176.0668736 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

impurity

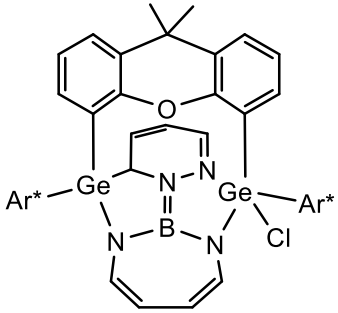
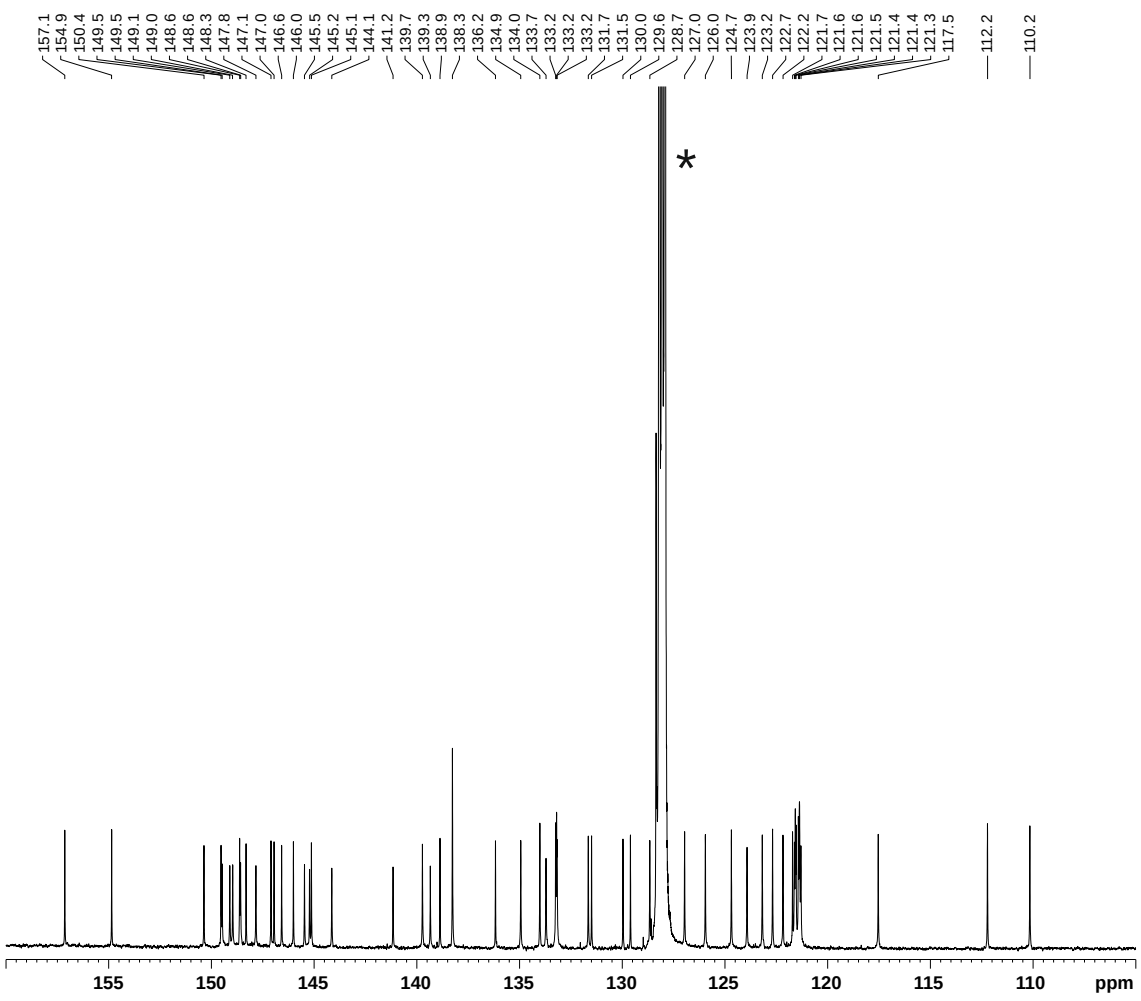


Figure SI23. $^{13}C\{^{1}H\}$ NMR of compound **4** (15-50 ppm).



Current Data Parameters
NAME 49-23042024-SWO68
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240423
Time 18.21 h
INSTRUM spect
PROBHD Z135421_0007 (
PULPROG udeft
TD 30676
SOLVENT C6D6
NS 5120
DS 0
SWH 42613.637 Hz
FIDRES 2.778305 Hz
AQ 0.3599317 sec
RG 179.42
DW 11.733 usec
DE 18.00 usec
TE 298.0 K
D1 4.00000000 sec
D12 0.00002000 sec
D20 200.00000000 sec
TD0 1
SFO1 176.0845454 MHz
NUC1 13C
P1 12.00 usec
P13 2000.00 usec
P26 500.00 usec
PLW1 146.39999390 W
SPNAM[5] Crp80comp.4
SPOAL5 0.500
SPOFFS5 0 Hz
SPW5 42.94699860 W
SPNAM[8] Crp80,0.5,20.1
SPOAL8 0.500
SPOFFS8 0 Hz
SPW8 42.94699860 W
SFO2 700.2088008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 65.00 usec
PLW2 14.67599964 W
PLW12 0.22231001 W

F2 - Processing parameters
SI 131072
SF 176.0668736 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

* C_6D_6

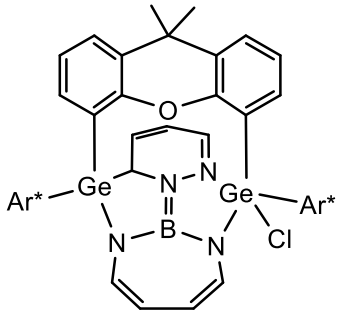
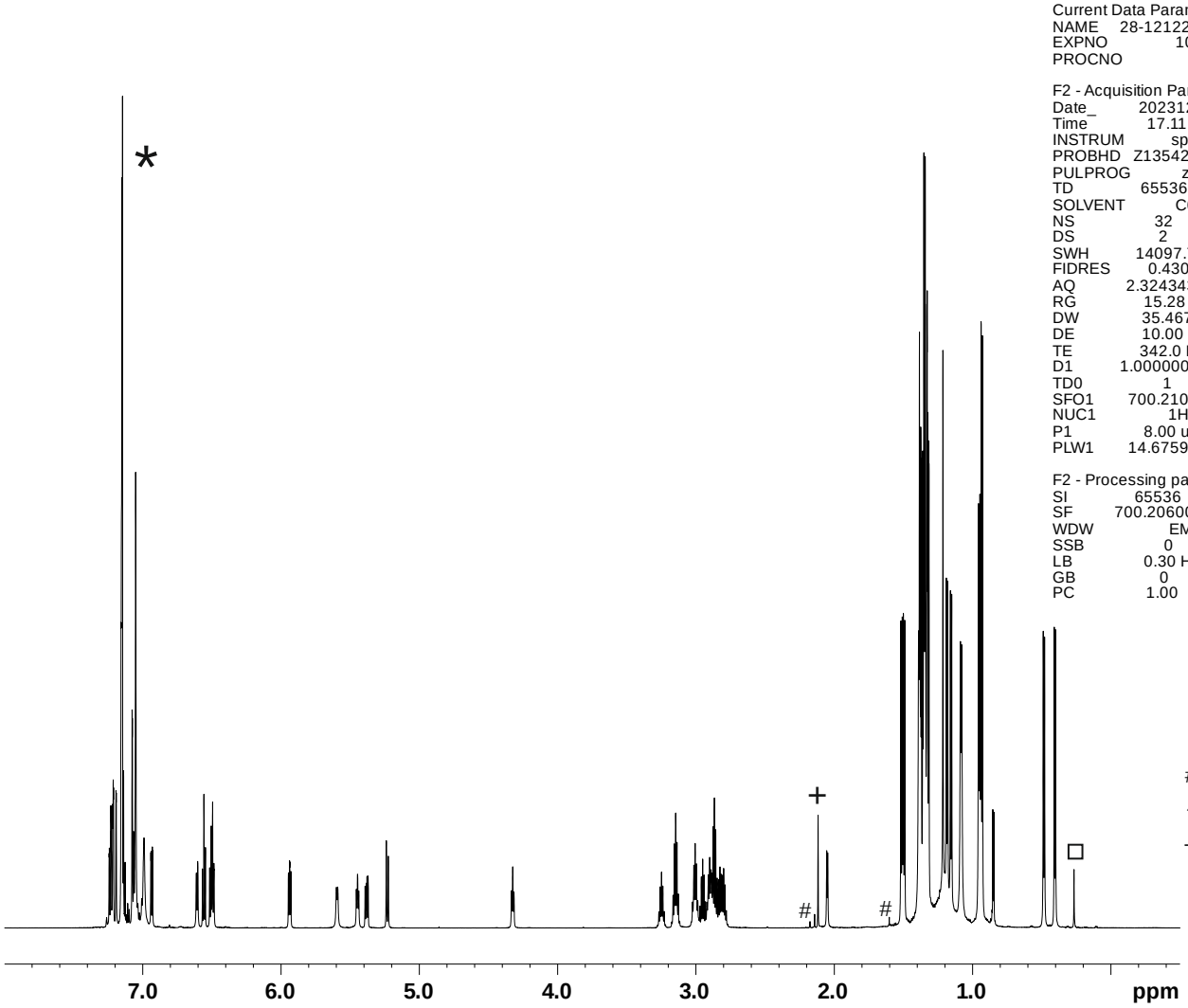


Figure SI24. $^{13}C\{^1H\}$ NMR of compound **4** (105-160 ppm).

NMR spectra of compound **5**.



Current Data Parameters
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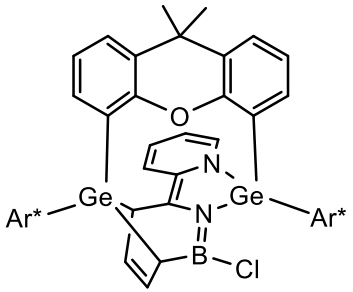
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20231212
Time 17.11 h
INSTRUM spect
PROBHD Z135421_0007 (
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 32
DS 2
SWH 14097.744 Hz
FIDRES 0.430229 Hz
AQ 2.3243434 sec
RG 15.28
DW 35.467 usec
DE 10.00 usec
TE 342.0 K
D1 1.00000000 sec
TD0 1
SFO1 700.2103238 MHz
NUC1 1H
P1 8.00 usec
PLW1 14.67599964 W

F2 - Processing parameters
SI 65536
SF 700.2060000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



▫ grease

impurity

* C_6D_5H

+ residual toluene contamination

Figure SI25. ^{1}H NMR of compound **5**.

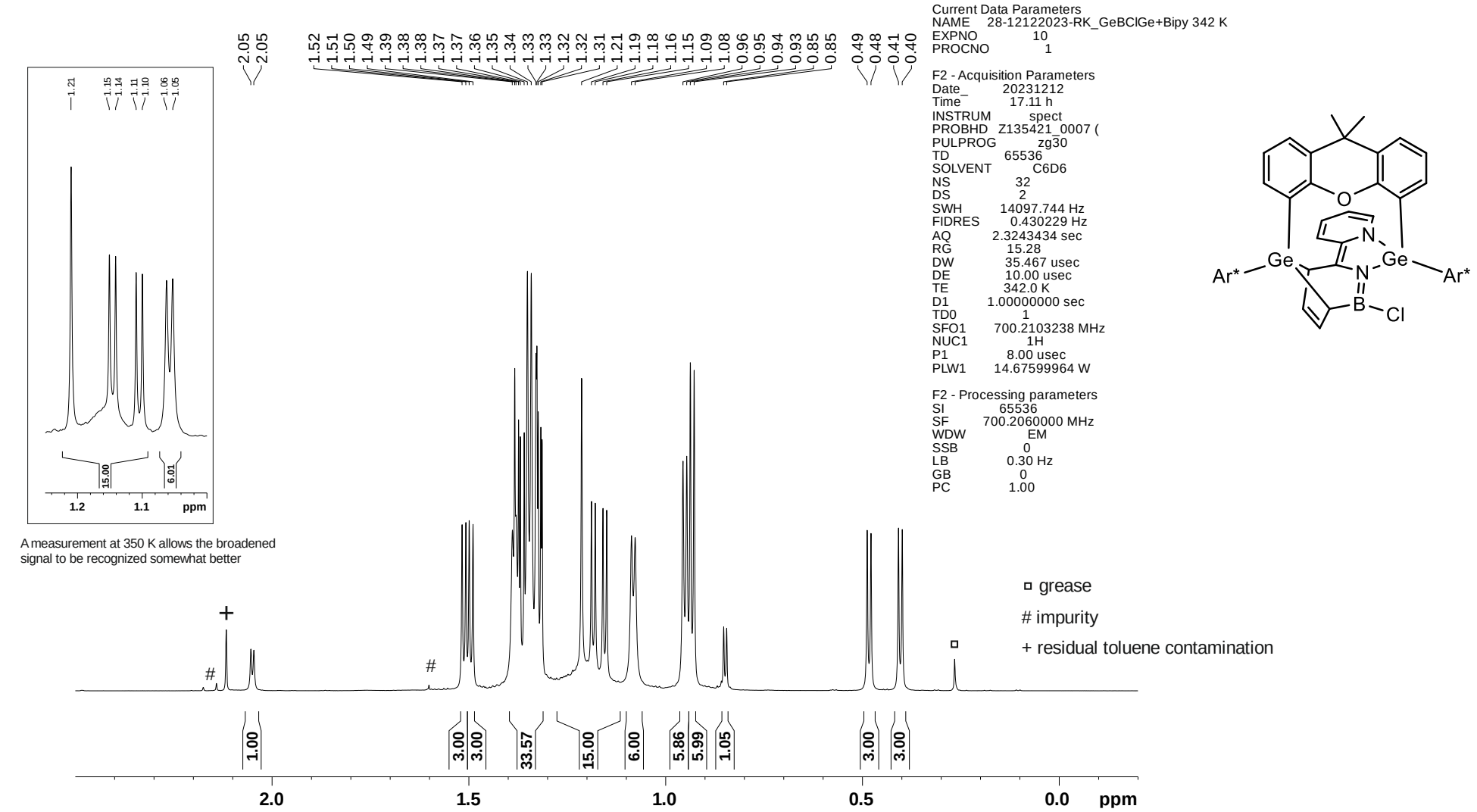


Figure SI26. ^{1}H NMR of compound **5** (-0.2-2.5 ppm).

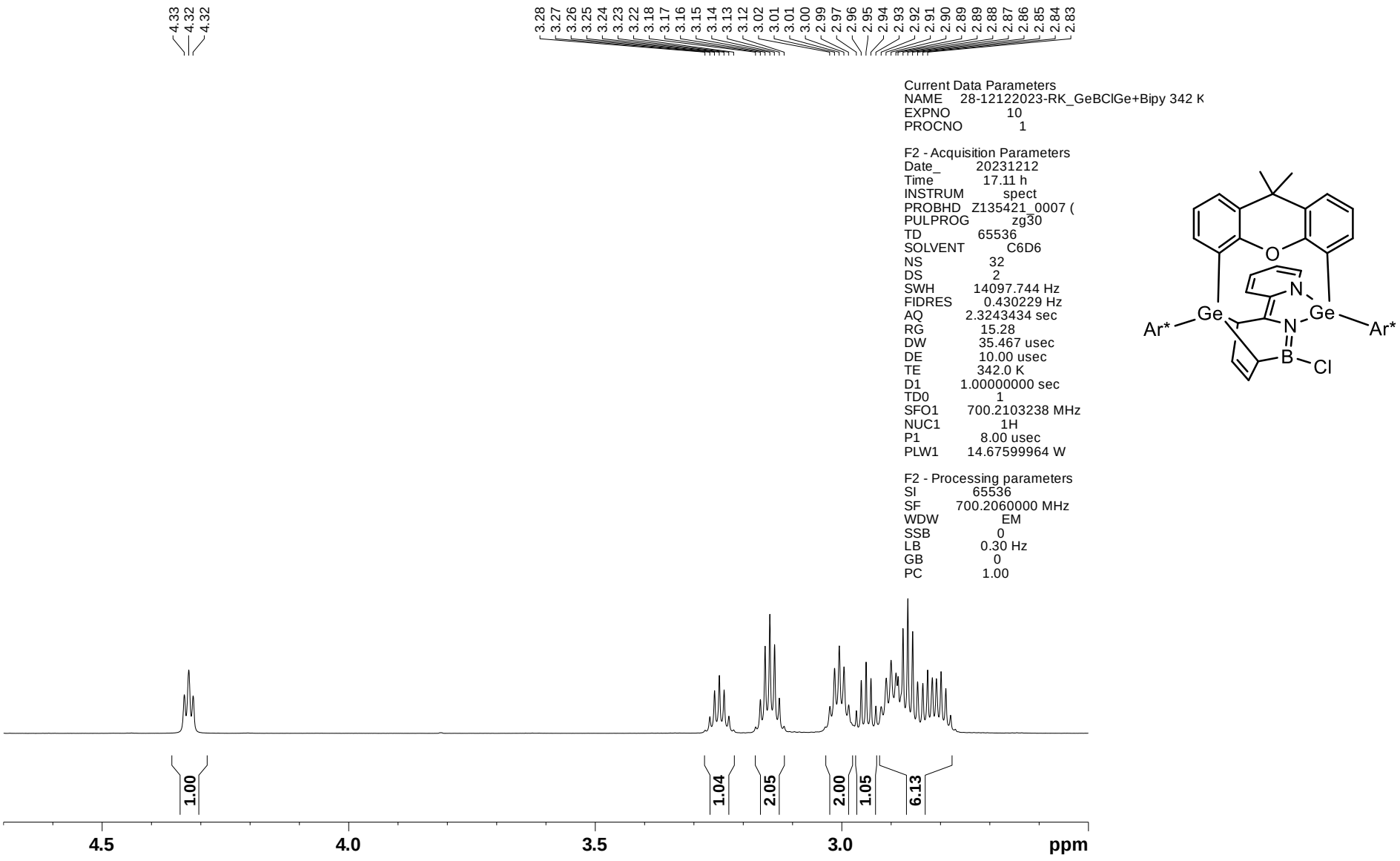


Figure SI27. ^{1}H NMR of compound **5** (2.5-4.7 ppm).

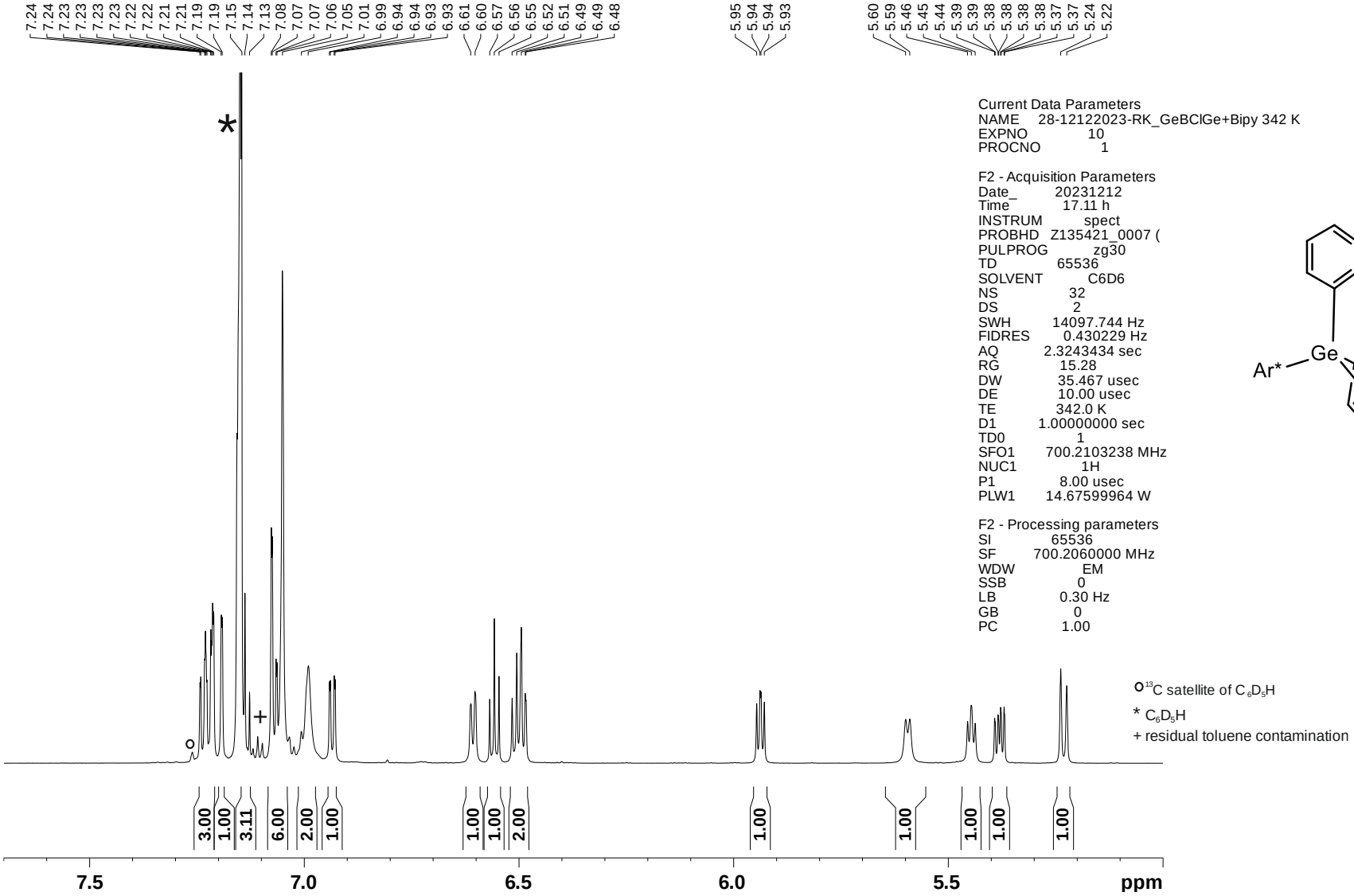
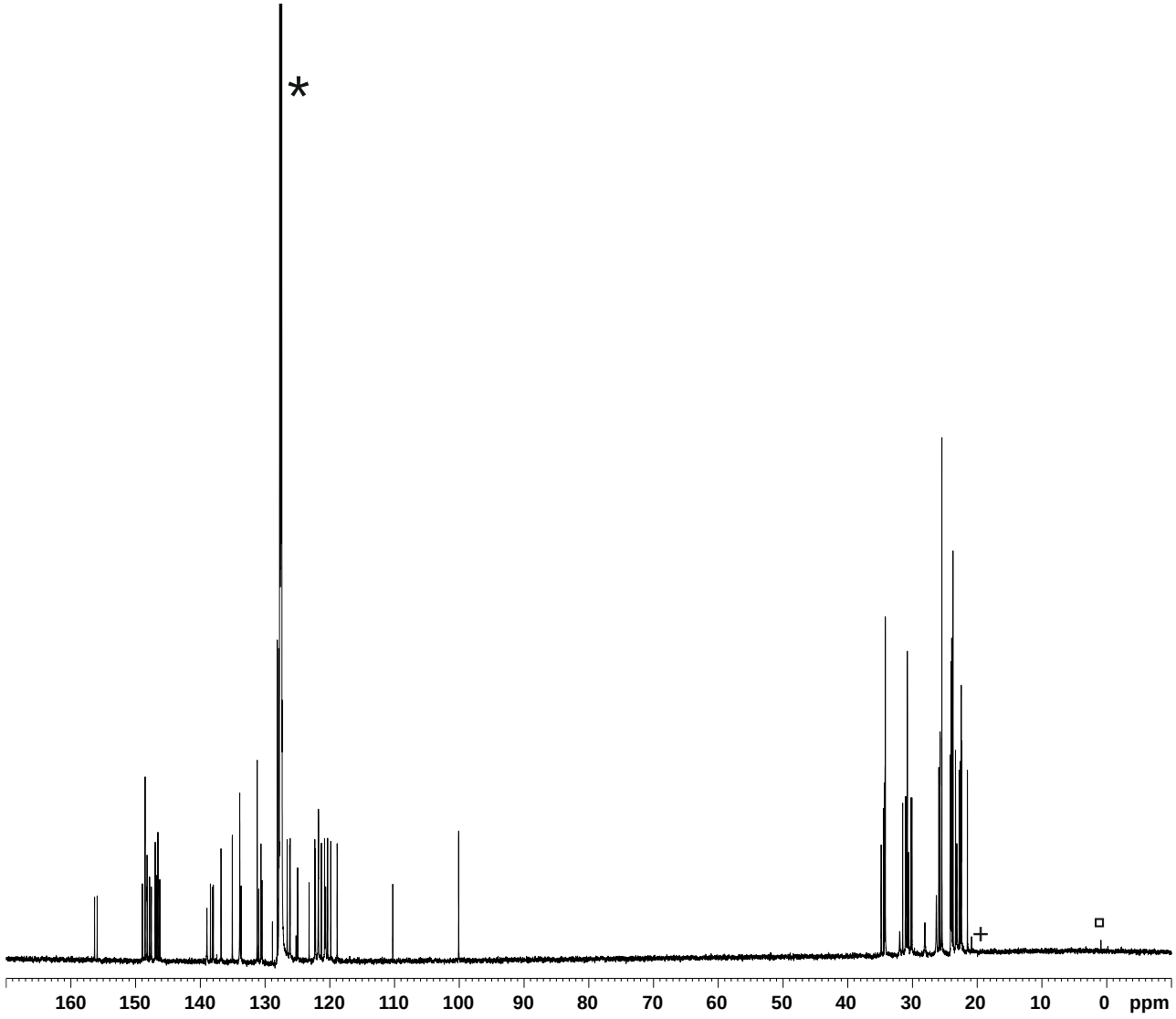


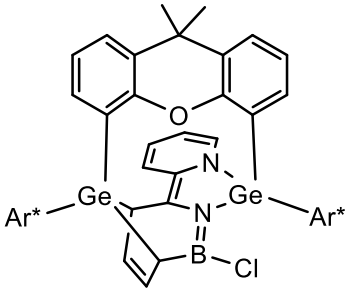
Figure SI28. ^{1}H NMR of compound **5** (5-7.7 ppm).



Current Data Parameters
NAME 28-12122023-RK_ GeBClGe+Bipy 342 K
EXPNO 11
PROCNO 1

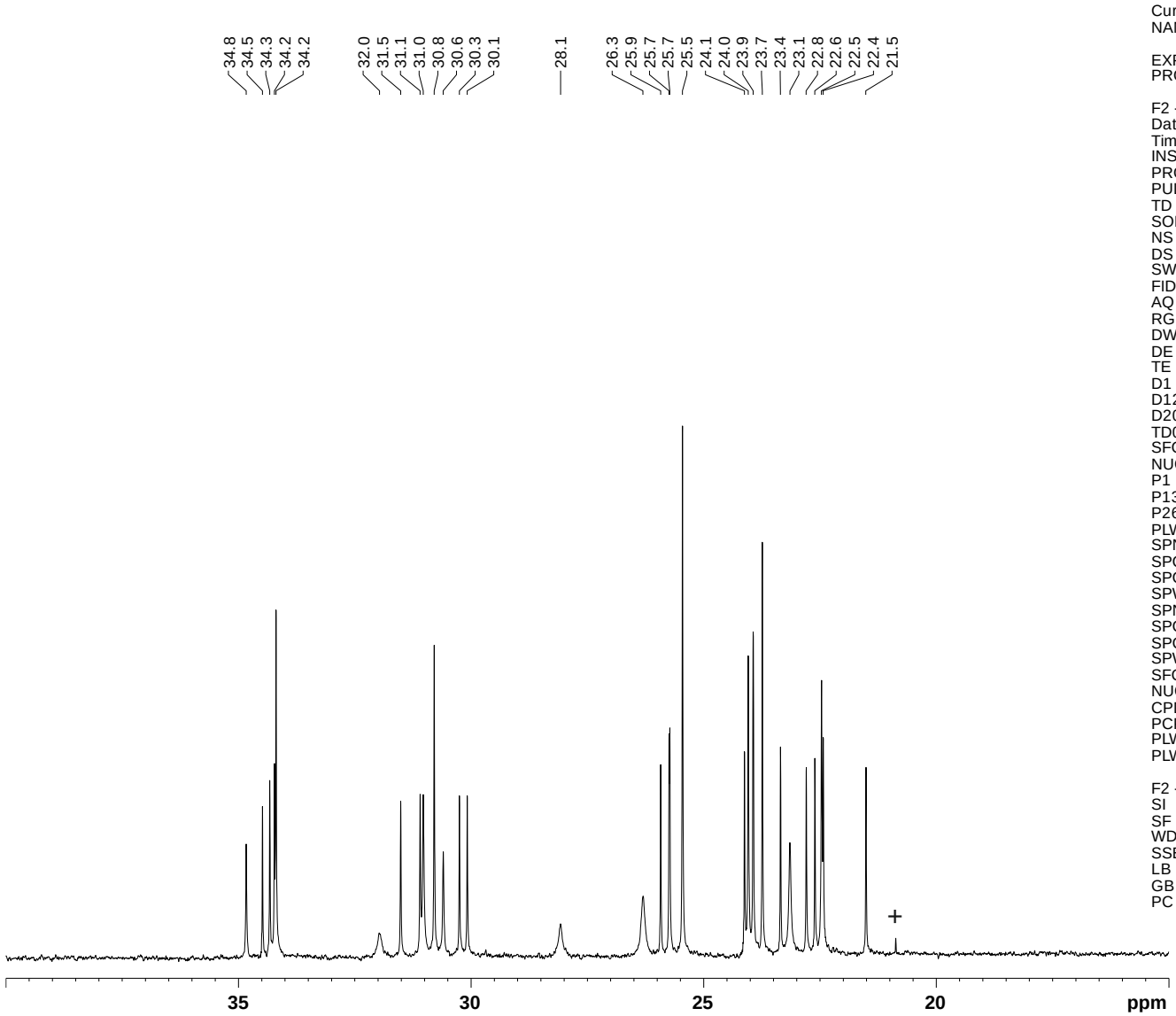
F2 - Acquisition Parameters
Date_ 20231212
Time 19.38 h
INSTRUM spect
PROBHD Z135421_0007 (
PULPROG udeft
TD 30676
SOLVENT C6D6
NS 1750
DS 0
SWH 42613.637 Hz
FIDRES 2.778305 Hz
AQ 0.3599317 sec
RG 179.42
DW 11.733 usec
DE 18.00 usec
TE 342.0 K
D1 4.00000000 sec
D12 0.00002000 sec
D20 200.00000000 sec
TD0 1
SFO1 176.0845454 MHz
NUC1 13C
P1 12.00 usec
P13 2000.00 usec
P26 500.00 usec
PLW1 146.39999390 W
SPNAM[5] Crp80comp.4
SPOAL5 0.500
SPOFFS5 0 Hz
SPW5 42.94699860 W
SPNAM[8] Crp80,0.5,20.1
SPOAL8 0.500
SPOFFS8 0 Hz
SPW8 42.94699860 W
SFO2 700.2088008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 65.00 usec
PLW2 14.67599964 W
PLW12 0.22231001 W

F2 - Processing parameters
SI 131072
SF 176.0669387 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40



▫ grease
* C_6D_6
+ residual toluene contamination

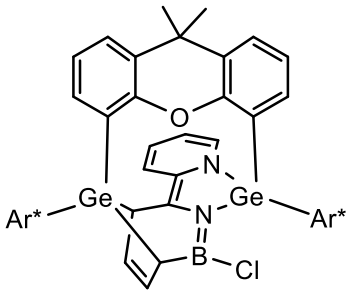
Figure SI29. $^{13}C\{^1H\}$ NMR of compound **5**.



Current Data Parameters
NAME 28-12122023-RK_
GeBClGe+Bipy 342 K
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20231212
Time 19.38 h
INSTRUM spect
PROBHD Z135421_0007 (
PULPROG udeft
TD 30676
SOLVENT C6D6
NS 1750
DS 0
SWH 42613.637 Hz
FIDRES 2.778305 Hz
AQ 0.3599317 sec
RG 179.42
DW 11.733 usec
DE 18.00 usec
TE 342.0 K
D1 4.00000000 sec
D12 0.00002000 sec
D20 200.00000000 sec
TD0 1
SFO1 176.0845454 MHz
NUC1 13C
P1 12.00 usec
P13 2000.00 usec
P26 500.00 usec
PLW1 146.39999390 W
SPNAM[5] Crp80comp.4
SPOAL5 0.500
SPOFFS5 0 Hz
SPW5 42.94699860 W
SPNAM[8] Crp80,0.5,20.1
SPOAL8 0.500
SPOFFS8 0 Hz
SPW8 42.94699860 W
SFO2 700.2088008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 65.00 usec
PLW2 14.67599964 W
PLW12 0.22231001 W

F2 - Processing parameters
SI 131072
SF 176.0669387 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40



+ residual toluene contamination

Figure SI30. $^{13}C\{^{1}H\}$ NMR of compound **5** (15-40 ppm).

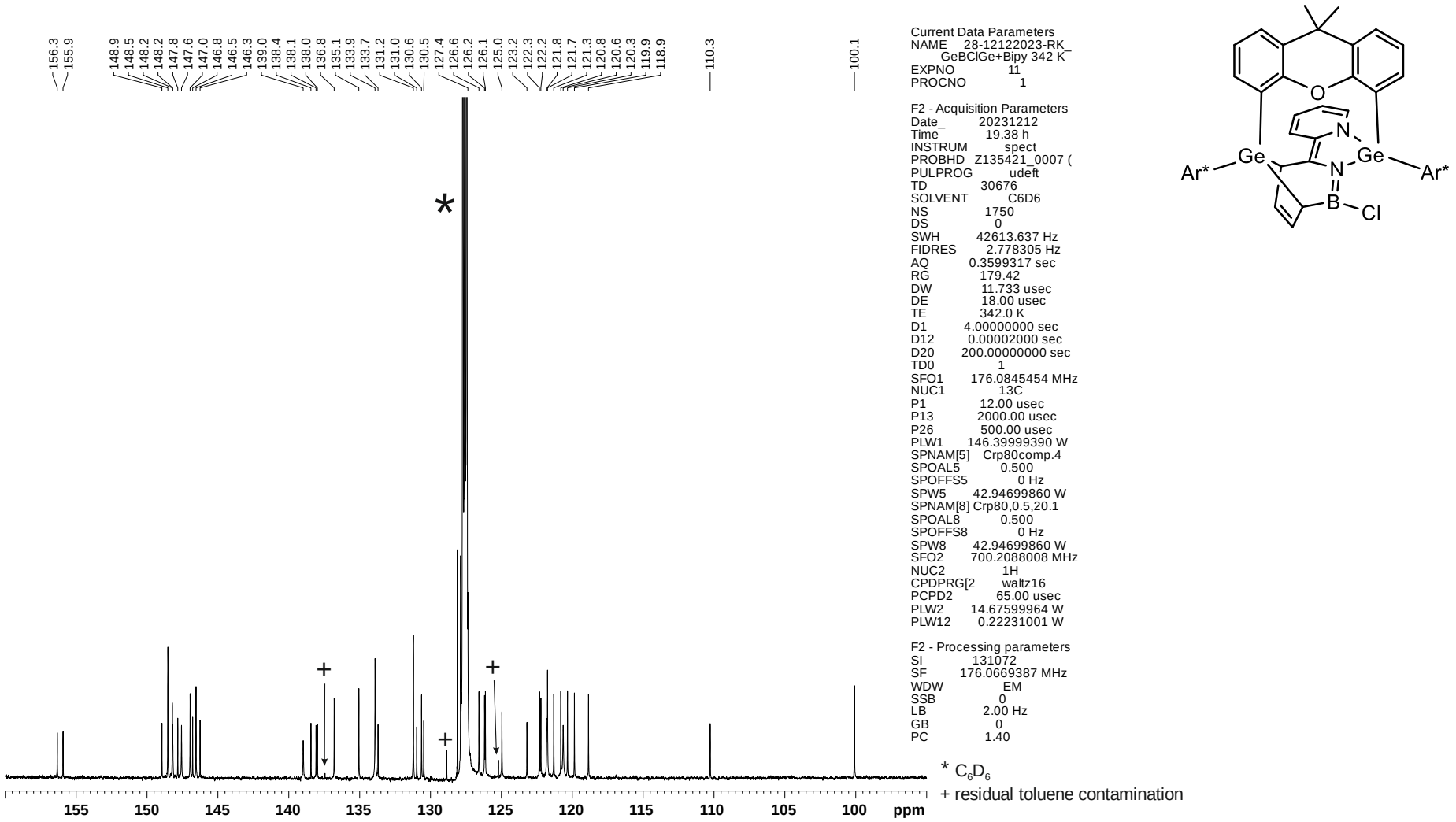
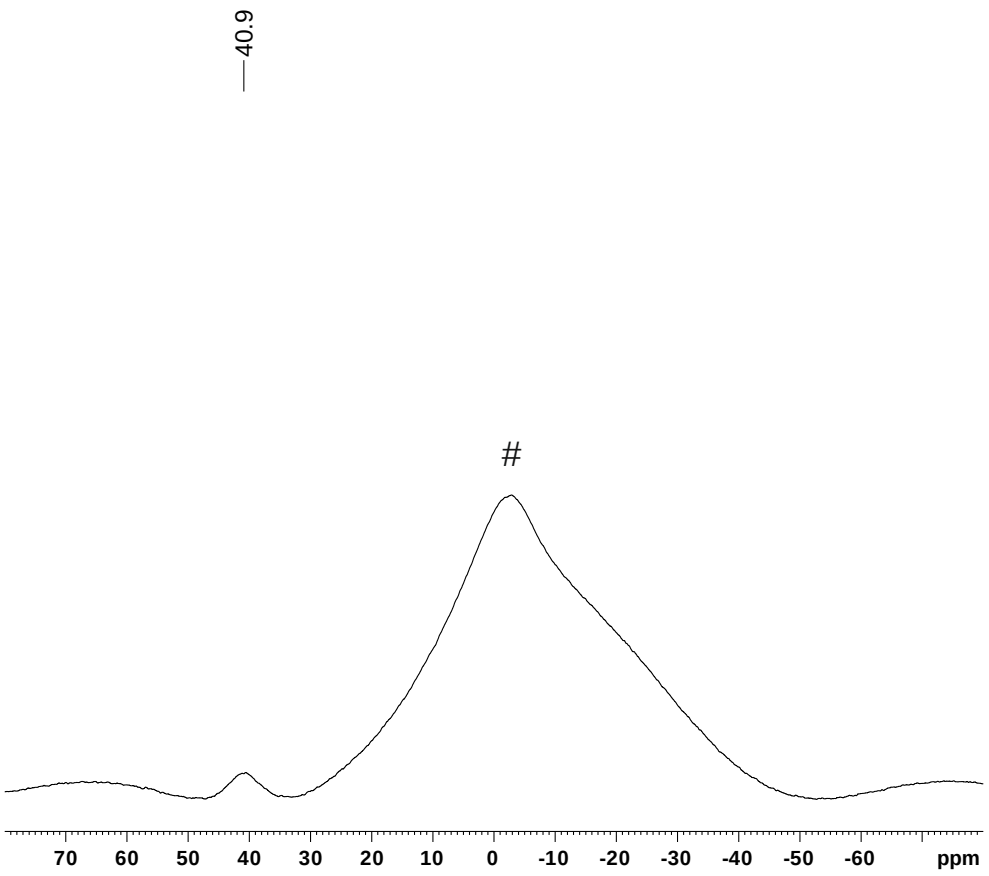


Figure SI31. $^{13}C\{^{1}H\}$ NMR of compound **5** (95-160 ppm).



Current Data Parameters
NAME 28-13122023-RK362
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20231214
Time 9.11 h
INSTRUM spect
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PULPROG zgbsig
TD 16384
SOLVENT C6D6
NS 10240
DS 4
SWH 38461.539 Hz
FIDRES 4.695012 Hz
AQ 0.2129920 sec
RG 189.6
DW 13.000 usec
DE 18.00 usec
TE 342.0 K
D1 0.10000000 sec
D11 0.03000000 sec
TD0 1
SFO1 192.5455530 MHz
NUC1 11B
P1 19.80 usec
P2 39.60 usec
PLW1 50.00000000 W
SFO2 600.1328206 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 23.41200066 W
PLW12 1.95930004 W

F2 - Processing parameters
SI 16384
SF 192.5455530 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 1.40

glass

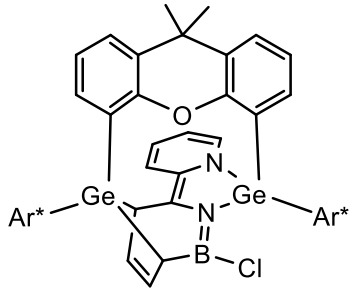
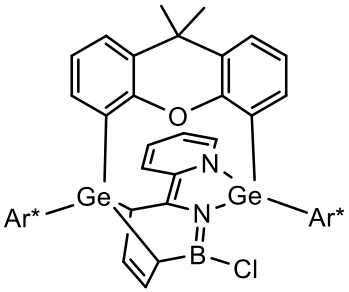


Figure SI32. $^{11}B\{^{1}H\}$ NMR of compound **5**.

UV-Vis spectroscopy



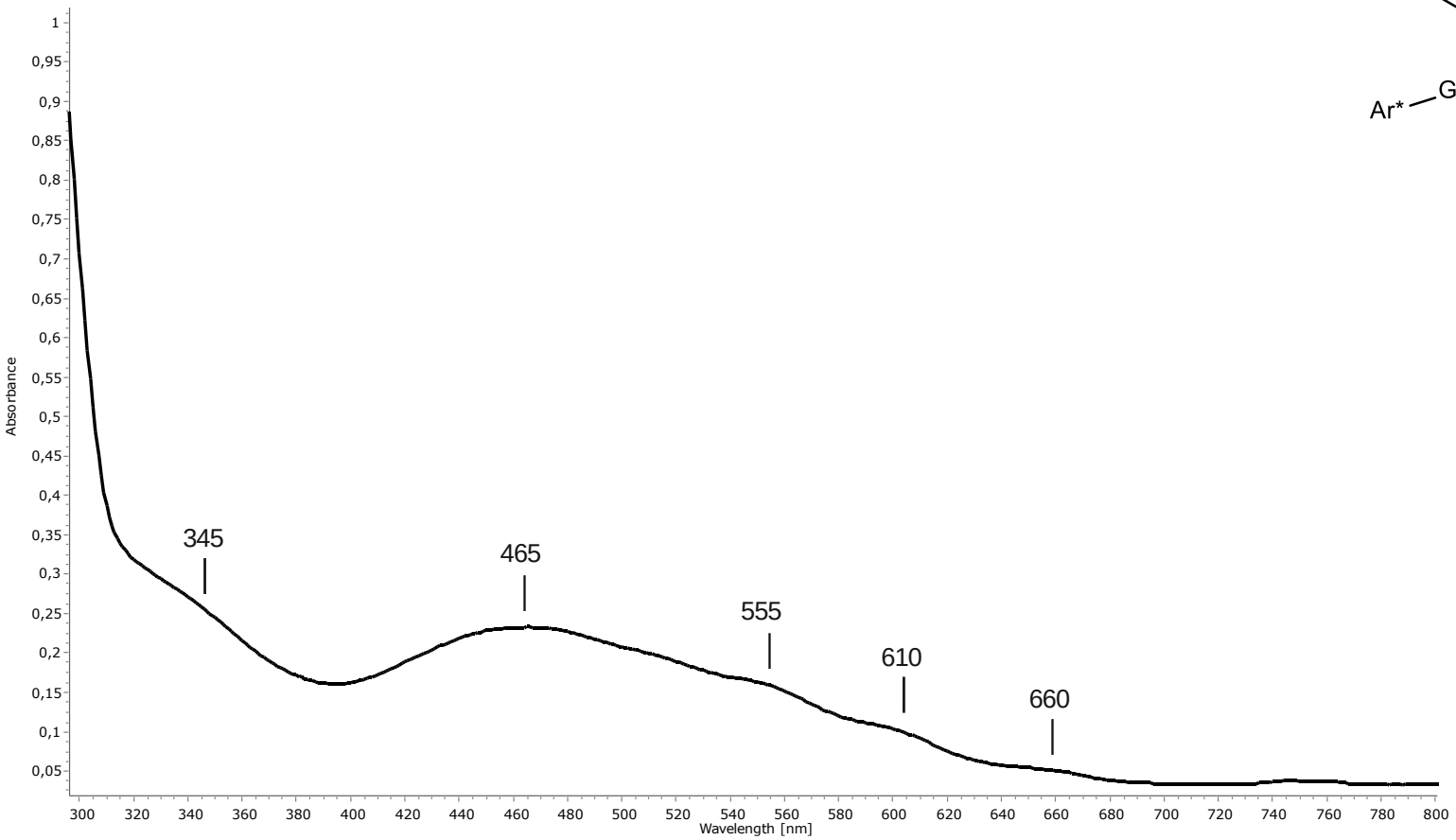


Figure SI33. UV-Vis spectrum of compound **5**.

Quantum chemistry

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