Synthesis of 6-membered germacycles by intramolecular germylzincation of alkynes

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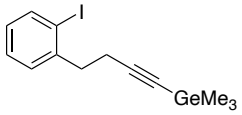
Supporting Information

General Information. Unless otherwise noted, all reagents and solvents were purchased from commercial sources and used as received. THF was freshly distilled over Na/benzophenone before use, and Hexane was freshly distilled over CaH_2 before use. All manipulations were conducted under argon. The reactions were monitored by thin-layer chromatography (TLC) using silica gel gel (60 F254) plates. Compounds were visualized using a UV lamp (254 nm) and/or by potassium permanganate stain. Flash column chromatography was carried out on silica gel 60 (230-400 mesh, 0.040-0.063 mm). Melting points (mp [°C]) were measured with a Kofler apparatus from Wagner and Munz. The infrared spectra of compounds were recorded by transmission on a IRFT spectrometer. Wavelength (ν) were reported in cm^{-1} and only the strongest or structurally most important peaks are listed. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a spectrometer at 300 MHz (^{13}C, 75 MHz). Chemical shifts are given in parts per million. The following abbreviations are used for the proton spectra multiplicities: s: singulet, d: doublet, t: triplet, q: quartet, qt: quintuplet, m: multiplet, br.: broad, dd: double doublet, dt: double triplet. High-resolution mass spectrometry (HRMS) were recorded on a Thermo LTQ Orbitrap XL apparatus equipped with an ESI source or on a LCT Premier XE bench top orthogonal acceleration time-of-flight mass spectrometer (Waters Micromass) equipped with an ESI source.

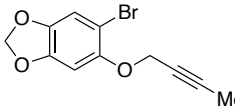


(4-(2-iodophenyl)but-1-yn-1-yl)trimethylgermane 1g

To a solution of 1-(but-3-yn-1-yl)-2-iodobenzene (3 g, 11.715 mmol, 1 equiv.) in anhydrous THF at -70°C under argon atmosphere, a freshly prepared LDA (12.300 mmol, 1.05 equiv.) was added dropwise and the resultant mixture was stirred at this temperature for 1h. Trimethylgermanium chloride (1.974 g, 12.886 mmol, 1.10 equiv.) was then added and the solution was stirred at -70°C for an

additional 1h before being stirred at room temperature for 2h. The reaction was then hydrolyzed with water and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over aqueous anhydrous $MgSO_4$ and concentrated under reduced pressure. Purification of the crude product by flash chromatography on silica gel (Cyclohexane/OEt_2 = 99:1-98:2) afforded **1g** (3.247 g, 74%) as a pale yellow solid; mp 65.5-66.2°C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 7.9 Hz, 1 H), 7.28-7.26 (m, 2 H), 6.93-6.87 (m, 1H), 2.94 (t, *J* = 7.4 Hz, 2 H), 2.51 (t, *J* = 7.4, 2 H), 0.32 (s, 9 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 143.2, 139.5, 130.2, 128.3, 128.2, 104.5, 100.5, 85.5, 40.1, 20.7, -0.04; **IR** (neat): υ_{max} = 2976, 2909, 2171, 1563, 1466, 1435, 1239, 1012, 828, 746 cm^{-1}; **HRMS** (EI): calcd for $C_{13}H_{17}{}^{74}GeI$ (M^+) 373.9587, found 373.9581.



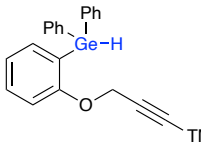
5-bromo-6-(but-2-yn-1-yloxy)benzo[*d*][1,3]dioxole 1k

To a solution of 6-bromobenzo[*d*][1,3]dioxol-5-ol (1.600 g, 7.373 mmol, 1.0 equiv.) in anhydrous DMF (15 mL) under argon atmosphere, was added potassium carbonate (2.038 g, 14.746 mmol, 2 equiv.) followed by 1-bromo-2-butyne (0.71 mL, 8.110 mmol, 1.1 equiv.). After stirring at 60°C for 2h, the mixture was hydrolyzed with water and extracted with Et_2O. The Combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to provide the ether. Purification of the crude product by flash chromatography on silica gel (Cyclohexane / CH_2Cl_2 = 94:6) afforded **1k** (1.302 g, 66%) as a white solid, mp 80.4-81.3 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.99 (s, 1H), 6.73 (s, 1H), 5.96 (s, 2H), 4.64 (q, *J* = 2.3 Hz, 2H), 1.86 (t, *J* = 2.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 149.4, 147.5, 142.6, 112.5, 102.7, 101.8, 98.5, 84.4, 73.7, 58.7, 3.7; **IR** (neat): υ_{max} = 2899, 2241, 1501, 1486, 1415, 1260, 1180, 1013, 844 cm^{-1}; **HRMS** (CI): calcd for $C_{11}H_9{}^{79}BrO_3$ (M^+) 267.9735, found: 267.9731.

General procedure for the synthesis of arylgermanes

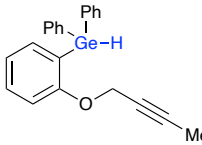
*i*PrMgCl.LiCl (1.3 M in THF, 1.3 equiv.) was added dropwise to a solution of iodoaryls **1**, in anhydrous THF under argon atmosphere at 0°C, and the reaction mixture was stirred for 2 h. Diphenylgermanium dichloride (1.0 - 1.2 equiv.) was then added and the mixture was stirred at room temperature until completion by TLC (for 10–16 h). The resulting mixture was then cooled to 0°C and $LiAlH_4$ (0.5 equiv.) was added and the solution stirred at 0°C for 1 h and at room temperature for additional 2 h. The solution was quenched with water and the aqueous layer was extracted with Et_2O (x3). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel.



(3-(2-(diphenylgermyl)phenoxy)prop-1-yn-1-yl)trimethylsilane 2a

Germane **2a** was prepared following our general procedure for **synthesis of arylgermanes** using ether **1a** (2.064 g, 6.250 mmol, 1 equiv.), *i*PrMgCl.LiCl (1.3 M in THF, 6.7 mL, 8.750 mmol, 1.4 equiv.), diphenylgermanium dichloride (2.047 g, 6.875 mmol, 1.1 equiv.), $LiAlH_4$ (1.0 M in THF, 3.1 mL, 3.125 mmol, 0.5 equiv.) in anhydrous THF (20 mL). Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 100:0-99.5:0.5-99:1) afforded **2a** (2.452 g, 91%) as a colorless oil.

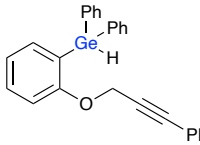
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60-7.56 (m, 4H), 7.42-7.34 (m, 8H), 7.05-6.97 (m, 2H), 5.73 (s, 1 H), 4.57 (s, 2H), 0.18 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 161.5, 136.8, 136.2 (2C), 135.4 (4C), 131.1, 129.0 (2C), 128.2 (4C), 125.0, 121.8, 111.8, 100.4, 92.6, 56.9, -0,1 (3C); **IR** (neat): υ_{max} = 2961, 2913, 2029, 1585, 1438, 1206, 831, 753 cm^{-1}; **HRMS** (API+): calcd for $C_{24}H_{25}{}^{74}GeOSi$ $(M-H)^+$ 431.0886, found: 431.0894.



(2-(but-2-yn-1-yloxy)phenyl)diphenylgermane 2b

Germane **2b** was prepared following our general procedure for **synthesis of arylgermanes** using ether **1b** (840 mg, 3.087 mmol, 1 equiv.), *i*PrMgCl.LiCl (1.3 M in THF, 2.9 mL, 3.704 mmol, 1.2 equiv.), diphenylgermanium dichloride (1.103 g, 3.704 mmol, 1.2 equiv.), $LiAlH_4$ (1.0 M in THF, 1.5 mL, 1.543 mmol, 0.5 equiv.) in anhydrous THF (10 mL). Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 99:1) afforded **2b** (804 mg, 70%) as a colorless oil.

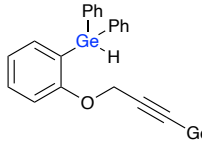
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59-7.56 (m, 4H), 7.38-7.30 (m, 8H), 7.00 (dd, *J* = 8.5, 0.7 Hz, 1H), 6.94 (td, *J* = 7.2, 0.9 Hz, 1H), 5.73 (s, 1H), 4.52 (q, *J* = 2.3 Hz, 2H), 1.77 (t, *J* = 2.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 161.6, 136.8, 136.1 (2C), 135.4 (4C), 131.1, 128.9 (2C), 128.2 (4C), 124.8, 121.6, 111.7, 83.5, 74.3, 56.5, 3.8; **IR** (neat): υ_{max} = 3069; 2901, 2049, 1584, 1470, 1431, 1207, 996, 698 cm^{-1}; **HRMS** (API+): calcd for $C_{22}H_{19}{}^{74}GeO$ $(M-H)^+$ 373.0648, found: 373.0659.



diphenyl(2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)germane 2c

Germane **2c** was prepared following our general procedure for **synthesis of arylgermanes** using ether **1c** (600 mg, 1.800 mmol, 1 equiv.), *i*PrMgCl.LiCl (1.3 M in THF, 1.8 mL, 2.340 mmol, 1.3 equiv.), diphenylgermanium dichloride (643 mg, 2.160 mmol, 1.2 equiv.), $LiAlH_4$ (1.0 M in THF, 0.9 mL, 0.900 mmol, 0.5 equiv.) in anhydrous THF (8 mL). Purification of the crude product by flash chromatography on silica gel (Cyclohexane/Et_2O = 100:0-99:1-98:2) afforded **2c** (480 mg, 61%) as a yellow pale oil.

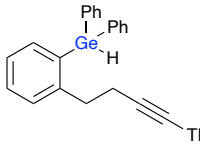
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59-7.52 (m, 4H), 7.35-7.29 (m, 4H), 7.28-7.23 (m, 6H), 7.19-7.16 (m, 3H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.91 (td, *J* = 7.3, 0.9 Hz, 1H), 5.74 (s, 1H), 4.67 (s, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 161.4, 136.8, 136.1 (2C), 135.3 (4C), 131.8 (2C), 131.1, 128.9 (2C), 128.6, 128.3 (2C), 128.2 (4C), 124.9, 122.5, 121.8, 111.7, 87.1, 84.2, 56.6; **IR** (neat): υ_{max} = 3050, 2047, 1584, 1490, 1470, 1431, 1208, 710, 689 cm^{-1}; **HRMS** (IC): calcd for $C_{27}H_{21}{}^{74}GeO$ $(M-H)^+$ 435.0804, found 435.0814.



(3-(2-(diphenylgermyl)phenoxy)prop-1-yn-1-yl)trimethylgermane 2d

Germane **2d** was prepared following our general procedure for **synthesis of arylgermanes** using ether **1d** (1.700 g, 4.536 mmol, 1 equiv.), *i*PrMgCl.LiCl (1.3 M in THF, 4.5 mL, 5.897 mmol, 1.3 equiv.), diphenylgermanium dichloride (1.620 g, 5.443 mmol, 1.2 equiv.), $LiAlH_4$ (1.0 M in THF, 2.3 mL, 2.268 mmol, 0.5 equiv.) in anhydrous THF (15 mL). Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 99.5:0.5- 99:1-98:2) afforded **2d** (1.828 g, 85%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60-7.57 (m, 4H), 7.41-7.32 (m, 8H), 7.03 (dd, *J* = 8.7, 1.0 Hz, 1H), 6.98 (td, *J* = 7.1, 1.0 Hz, 1H), 5.71 (s, 1H), 4.55 (s, 2H), 0.34 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 161.5, 136.8, 136.2 (2C), 135.4 (4C), 131.1, 128.9 (2C), 128.2 (4C), 125.0, 121.7, 111.9, 99.3, 92.8, 56.9, -0.2 (3C); **IR** (neat): υ_{max} = 2977, 2906, 2034, 1584, 1470, 1432, 1211, 1026, 694 cm^{-1}; **HRMS** (API+): calcd for $C_{24}H_{25}{}^{74}Ge_2O$ $(M-H)^+$ 477.0329, found 477.0342.

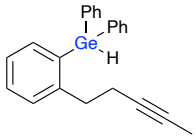


(4-(2-diphenylgermyl)phenyl)but-1-yn-1-yl)trimethylsilane 2e

Germane **2e** was prepared following our general procedure for **synthesis of arylgermanes** using ether **1e** (1.900 g, 5.788 mmol, 1 equiv.), *i*PrMgCl.LiCl (1.3 M in THF (5.8 mL, 7.524 mmol, 1.3 equiv.), diphenylgermanium dichloride (2.068 g, 6.946 mmol, 1.2 equiv.), $LiAlH_4$

(1.0 M in THF, 2.9 mL, 2.894 mmol, 0.5 equiv.) in anhydrous THF (15 mL). Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 99.5:0.5-99:1-98:2) afforded **2e** (1.802 g, 72%) as a colorless oil.

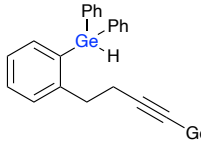
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51-7.48 (m, 4H), 7.42-7.33 (m, 10H), 5.84 (s, 1H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.31 (t, *J* = 7.6 Hz, 2H), 0.13 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 146.5, 136.2, 135.7 (2C), 135.3 (4C), 134.6, 129.7, 129.5, 129.3 (2C), 128.6 (4C), 126.3, 106.6, 85.3, 35.9, 22.1, 0.2 (3C); **IR** (neat): υ_{max} = 3053, 2901, 2173, 2035, 1472, 1432, 1248, 838, 696 cm^{-1}; **HRMS** (API+): calcd for $C_{25}H_{27}{}^{74}GeSi$ $(M-H)^+$ 429.1094, found 429.1092.



(2-(pent-3-yn-1-yl)phenyl)diphenylgermane 2f

Germane **2f** was prepared following our general procedure for **synthesis of arylgermanes** using ether **1f** (1.578 g, 5.842 mmol, 1 equiv.), *i*PrMgCl.LiCl (1.3 M in THF, 5.8 mL, 7.595 mmol, 1.3 equiv.), diphenylgermanium dichloride (1.913 g, 6.426 mmol, 1.1 equiv.), $LiAlH_4$ (1.0 M in THF, 2.92 mL, 2.921mmol, 0.5 equiv.) in anhydrous THF (20 mL). Purification of the crude product by flash chromatography on silica gel (Petroleum ether/DCM = 100:0-99:1) afforded **2f** (1.412 g, 65%) as a colorless oil.

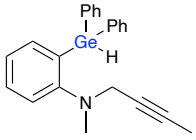
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51-7.48 (m, 4H), 7.41-7.32 (m, 9H), 7.19 (td, *J* = 7.6 Hz, 1.8 Hz, 1H), 5.86 (s, 1H), 2.87 (t, *J* = 7.6 Hz, 2H), 2.31-2.24 (m, 2H), 1.73 (t, *J* = 2.4 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 146.8, 136.2, 135.7 (2C), 135.3 (4C), 134.7, 129.7, 129.23 (2C), 129.19, 128.5 (4C), 126.2, 78.6, 76.3, 36.4, 21.1, 3.6; **IR** (neat): υ_{max} = 3051, 2915, 2034, 1588, 1483, 1431, 1092, 696 cm^{-1}; **HRMS** (ESI+): calcd for $C_{23}H_{21}{}^{74}Ge$ $(M-H)^+$ 371.0855, found 371.0862.



(4-(2-(diphenylgermyl)phenylbut-1-yn-1-yl)trimethylgermane 2g

Germane **2g** was prepared following our general procedure for **synthesis of arylgermanes** using ether **1g** (1.647 g, 4.418 mmol, 1 equiv.), *i*PrMgCl.LiCl (1.3 M in THF, 4.4 mL, 5.743 mmol, 1.3 equiv.), diphenylgermanium dichloride (1.578 g, 5.302 mmol, 1.2 equiv.), $LiAlH_4$ (1.0 M in THF, 2.2 mL, 2.209 mmol, 0.5 equiv.) in anhydrous THF (15 mL). Purification of the crude product by flash chromatography on silica gel (Cyclohexane/Et_2O = 100:0-99:1-98:2-95:5) afforded **2g** (997 mg, 48%) as a colorless oil.

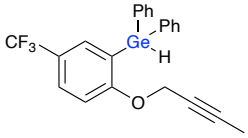
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51-7.48 (m, 4H), 7.39-7.32 (m, 10H), 5.85 (s, 1H), 2.89 (t, *J* = 7.5 Hz, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 0.31 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 146.5, 136.1, 135.6 (2C), 135.3 (4C), 134.6, 129.6, 129.4, 129.2 (2C), 128.4 (4C), 126.1, 105.1, 84.9, 36.1, 22.1, -0.1 (3C); **IR** (neat): υ_{max} = 3050, 2917, 2169, 1692, 1485, 1431, 1092, 827, 734, 696 cm^{-1}; **HRMS** (API+): calcd for $C_{25}H_{27}{}^{74}Ge_2$ $(M-H)^+$ 475.0536, found 475.0536.



***N*-(but-2-yn-1-yl)-2-(diphenylgermyl)-*N*-methylaniline 2h**

Germane **2h** was prepared following our general procedure for **synthesis of arylgermanes** using ether **1h** (752 mg, 2.637 mmol, 1 equiv.), *i*PrMgCl.LiCl (1.3 M in THF, 2.6 mL, 3.428 mmol, 1.3 equiv.), diphenylgermanium dichloride (864 mg, 2.901 mmol, 1.1 equiv.), $LiAlH_4$ (1.0 M in THF, 1.3 mL, 1.318 mmol, 0.5 equiv.) in anhydrous THF (10 mL). Purification of the crude product by flash chromatography on silica gel (Cyclohexane/Et_2O = 99.5:0.5-99:1-98:2) afforded **2h** (665 mg, 65%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54-7.51 (m, 4H), 7.39-7.32 (m, 9H), 7.14-7.09 (m, 1H), 5.79 (s, 1H), 3.45 (q, *J* = 2.5 Hz, 2H), 2.58 (s, 3H), 1.81 (t, *J* = 2.5 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 157.8, 136.9, 136.5 (2C), 135.2 (4C), 134.5, 130.4, 128.8 (2C), 128.2 (4C), 125.1, 122.7, 80.6, 75.0, 47.6, 41.5, 3.6; **IR** (neat): υ_{max} = 3050, 2999, 2789, 2044, 1579, 1471, 1431, 1091, 696 cm^{-1}; **HRMS** (ESI+): calcd for $C_{23}H_{24}N^{74}Ge$ $(M+H)^+$ 388.1121, found: 388.1115.

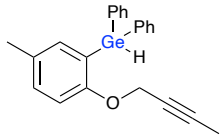


(2-(but-2-yn-1-yloxy)-5-(trifluoromethyl)phenyl)diphenylgermane 2i

Germane **2i** was prepared following our general procedure for **synthesis of arylgermanes** using ether **1i** (1.100 g, 3.234 mmol, 1 equiv.), *i*PrMgCl.LiCl (1.3 M in THF, 3.2 mL, 4.204 mmol, 1.3 equiv.), diphenylgermanium dichloride (1.059 g, 3.557 mmol, 1.1 equiv.), $LiAlH_4$ (1.0 M in THF, 1.6 mL, 1.617 mmol, 0.5 equiv.) in anhydrous THF (10 mL). Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 99.5:0.5-99:1) afforded **2i** (1.065 g, 75%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67-7.62 (m, 2H), 7.57-7.54 (m, 4H), 7.43-7.33 (m, 6H), 7.08 (d, *J* = 9.2 Hz, 1H), 5.72 (s, 1H), 4.59 (q, *J* = 2.2 Hz, 2H), 1.82 (t, *J* = 2.2 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 163.9, 135.24 (4C), 135.19 (2C), 134.1, 133.7 (q, *J* = 4 Hz), 129.3 (2C), 128.6 (q, *J* = 4 Hz), 128.4 (4C), 128.2 (q, *J* = 273 Hz), 123.6 (q, *J* = 32 Hz), 111.3, 84.3, 73.4, 56.6, 3.6; **^{19}F NMR** (282 MHz, $CDCl_3$): -61.4; **IR** (neat): υ_{max} = 3068, 2919, 2229,

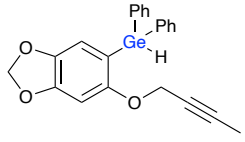
2039, 1596, 1477,1431, 1210, 1004, 695 cm^{-1}; **HRMS** (ESI+): calcd for $C_{23}H_{20}F_3{}^{74}GeO$ $(M+H)^+$ 443.0693, found: 443.0685.



(2-(but-2-yn-1-yloxy)-5-methylphenyl)diphenylgermane 2j

Germane **2j** was prepared following our general procedure for **synthesis of arylgermanes** using ether **1j** (1.224 g, 4.278 mmol, 1 equiv.), *i*PrMgCl.LiCl (1.3 M in THF, 4.3 mL, 5.561 mmol, 1.3 equiv.), diphenylgermanium dichloride (1.401 g, 4.706 mmol, 1.1 equiv.), $LiAlH_4$ (1.0 M in THF, 2.1 mL, 2.139 mmol, 0.5 equiv.) in anhydrous THF (12 mL). Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 99.5:0.5-99:1) afforded **2j** (1.302 g, 79%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58-7.55 (m, 4H), 7.36-7.33 (m, 6H), 7.18-7.17 (m, 1H), 7.16 (s, 1H), 6.93 (d, *J* = 8.9 Hz, 1H), 5.68 (s, 1H), 4.50 (q, *J* = 2.3 Hz, 2H), 2.25 (s, 3H), 1.81 (t, *J* = 2.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 159.5, 137.2, 136.3 (2C), 135.3 (4C), 131.5, 130.7, 128.8 (2C), 128.1 (4C), 124.6, 111.7, 83.2, 74.5, 56.6, 20.5, 3.6; **IR** (neat): υ_{max} = 3068, 2919, 2229, 2041, 1580, 1477, 1431, 1210, 1092, 696 cm^{-1}; **HRMS** (ESI+): calcd for $C_{23}H_{21}{}^{74}GeO$ $(M-H)^+$ 387.0804, found: 387.0817.

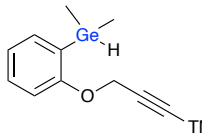


(6-(but-2-yn-1-yloxy)benzo[*d*][1,3]dioxol-5-yl)diphenylgermane 2k

To a mixture of ether **1k** (940 mg, 3.493 mmol, 1 equiv.) and diphenylgermanium dichloride (1.247 g, 4.192 mmol, 1.2 equiv.) in anhydrous THF (15 mL), at -90°C was added under argon atmosphere *t*-BuLi (1.48 M in hexane, 4.70 mL, 6.986 mmol, 2 equiv.) dropwise over 10 min. After stirring the mixture for 3h, $LiAlH_4$ (1M in THF, 2.98 mL, 4.418 mmol, 0.5 equiv.) was then added to the mixture at 0°C followed by stirring for 1h at this temperature and 1h at room temperature before hydrolysis with water. The mixture was extracted with CH_2Cl_2 and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude is purified by flash chromatography on silica gel (Cyclohexane/EtOAc = 99:1) to give **2k** (1.190 g, 82%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58-7.55 (m, 4H), 7.38-7.36 (m, 6H), 6.76 (d, *J* = 2.8 Hz, 2H), 5.93 (s, 2H), 5.70 (s, 1H), 4.44 (q, *J* = 2.2 Hz, 2H), 1.83 (t, *J* = 2.2 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 157.2, 149.9, 142.4, 136.2 (2C), 135.3 (4C), 129.0 (2C), 128.2 (4C), 116.0, 114.7, 101.4, 96.6, 83.7, 74.4, 57.9, 3.8; **IR** (neat): υ_{max} = 3065, 2918, 2035, 1606, 1470, 1430,

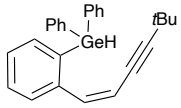
1242, 1170, 694 cm^{-1}; **HRMS** (API+): calcd for $C_{23}H_{21}{}^{74}GeO_3$ $(M+H)^+$: 419.0702, found 419.0709.



(3-(2-(dimethylgermyl)phenoxy)prop-1-yn-1-yl)trimethylsilane 2l

Germane **2l** was prepared following our general procedure for **synthesis of arylgermanes** using ether **1a** (1.000 g, 3.028 mmol, 1 equiv.), *i*PrMgCl**.**LiCl (1.3 M in THF, 3.0 mL, 3.936 mmol, 1.3 equiv.), dimethylgermanium dichloride (578 mg, 3.331 mmol, 1.1 equiv.), $LiAlH_4$ (1.0 M in THF, 1.5 mL, 1.514 mmol, 0.5 equiv.), anhydrous THF (10 mL). Purification of the crude product by flash chromatography on silica gel (Cyclohexane = 100) afforded **2l** (915 mg, 98%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 (dd, *J* = 7.1, 1.7 Hz, 1H), 7.32 (ddd, *J* = 8.0, 7.3, 1.7 Hz, 1H), 6.99 (td, *J* = 7.3, 1.0 Hz, 1H), 6.95 (dd, *J* = 8.0, 1.0 Hz, 1H), 4.68 (s, 2H), 4.47 (heptuplet, *J* = 3.4 Hz, 1H), 0.50 (d, *J* = 3.4 Hz, 6H), 0.18 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 161.8, 135.4, 130.3, 128.5, 121.6, 111.5, 100.7, 92.5, 57.0, -0.2 (3C), -3.7 (2C); **IR** (neat): υ_{max} = 3063, 2961, 2024, 1585, 1470, 1438, 1250, 1206, 1008, 831, 753 cm^{-1}; **HRMS** (ESI+): calcd for $C_{14}H_{21}{}^{74}GeOSi$ $(M-H)^+$ 307.0573, found 307.0578.

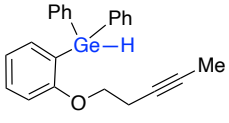


(*Z*)-(2-(5,5-dimethylhex-1-en-3-yn-1-yl)phenyl)diphenylgermane 2m

To a mixture of compound **1m** (802 mg, 3.047 mmol, 1 equiv.) and diphenylgermanium dichloride (1.179 g, 3.961 mmol, 1.3 equiv.) in anhydrous THF (18 mL), at -80°C was added under argon atmosphere *t*-BuLi (1.48 M in hexane, 4.1 mL, 6.094 mmol, 2 equiv.) dropwise over 10 min. After stirring the mixture for 1h, $LiAlH_4$ (1M in THF, 1.5 mL, 1.523 mmol, 0.5 equiv.) was added to the mixture at 0°C followed by stirring 1h at this temperature and 1h at room temperature before being quenched with water. The mixture was extracted with CH_2Cl_2 and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude is purified by flash chromatography on silica gel (Petroleum ether/Et_2O = 99.5:0.5) afforded **2m** (752 mg, 60%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.49 (d, *J* = 8.5 Hz, 1H), 7.50-7.46 (m, 4H), 7.43-7.33 (m, 9H), 6.72 (d, *J* = 11.9 Hz, 1H), 5.82 (s, 1H), 5.59 (d, *J* = 11.9 Hz, 1H), 1.28 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 137.3, 136.9, 135.5, 134.2, 129.7, 129.1, 128.9, 128.7 (4C), 128.4 (2C), 128.22 (2C), 128.16 (4C), 108.3, 105.6, 78.1, 30.9 (3C), 28.8 ; **IR** (neat):): υ_{max} = 3050, 2966,

2100, 2036,1693, 1583, 1484, 1431, 1091, 695 cm^{-1} ; **HRMS** (API+): calcd for $C_{26}H_{25}{}^{74}Ge$ $(M-H)^+$ 411.1168, found 411.1173.



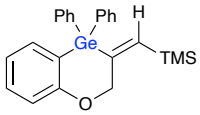
(2-(pent-3-yn-1-yloxy)phenyl)diphenylgermane 2n

Germane **2n** was prepared following our general procedure for **synthesis of arylgermanes** using ether **1n** (1.600 g, 5.592 mmol, 1 equiv.), *i*PrMgCl**.**LiCl (1.3 M in THF, 5.6 mL, 7.270 mmol, 1.3 equiv.), diphenylgermanium dichloride (1.831 g, 6.151 mmol, 1.1 equiv.), $LiAlH_4$ (1.0 M in THF, 2.8 mL, 2.796 mmol, 0.5 equiv.), anhydrous THF (20 mL). Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 99:1, 98:2) afforded **22** (1.702 g, 79%) as a white solid, mp 75.6-76.5 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65-7.56 (m, 4H), 7.43-7.38 (m, 8H), 7.00 (td, *J* = 7.7, 0.8 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 5.75 (s, 1H), 3.99 (t, *J* = 7.4 Hz, 2H), 2.35-2.27 (m, 2H), 1.77 (t, *J* = 2.6 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 162.2, 136.9, 136.3 (2C), 135.3 (4C), 131.3, 128.9 (2C), 128.2 (4C), 124.5, 121.3, 110.9, 77.3, 75.1, 66.7, 19.5, 3.6; **IR** (neat):): υ_{max} = 3059, 2917, 2049, 1583, 1464, 1431, 1237, 691 cm^{-1} ; **HRMS** (API+): calcd for $C_{23}H_{21}{}^{74}GeO$ $(M-H)^+$ 387.0804, found 387.0817.

General procedure for the polar intramolecular germylzincation

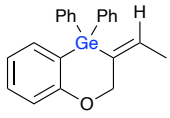
In a dry sealed tube under argon atmosphere, germane **2** (0.25–2 mmol) was dissolved in dry hexane and the solution was degassed. *i*Pr_2Zn (1.0 M in toluene, 1.2 equiv.) was then added at room temperature, and the reaction mixture was heated at 80° C for 1.5 h. After cooling to room temperature, the reaction mixture was hydrolyzed with aqueous NH_4Cl and stirred for 20 min. The layers were separated and the aqueous layer was extracted with ether (x3). The combined organic layers were washed with brine (x2), dried over anhydrous $MgSO_4$ and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel.



(*E*)-((4,4-diphenyl-2*H*-benzo[*b*][1,4]oxagermin-3(4*H*)-ylidene)methyl) trimethylsilane 3a

Prepared according to **germylzincation** procedure from germane **2a** (293 mg, 0.679 mmol, 1 equiv.), hexane (2.6 mL), *i*Pr_2Zn (1 M in toluene, 0.82 mL, 0.815 mmol, 1.2 equiv.). Purification of the crude product (*E* / *Z* = 96:4) by flash chromatography on silica gel (Cyclohexane/EtOAc = 99.5:0.5) afforded **3a** (249 mg, 85%, *E* / *Z* = 96:4) as a colorless oil.

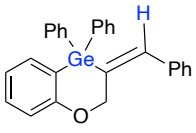
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57-7.54 (m, 4H), 7.42-7.35 (m, 8H), 7.07-7.02 (m, 2H), 6.35 (t, *J* = 1.4 Hz, 1H), 4.90 (d, *J* = 1.4 Hz, 2H), 0.21 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 164.7, 157.0, 145.3, 135.8 (2C), 135.6, 135.0 (4C), 130.9, 129.5 (2C), 128.5 (4C), 123.9, 122.9, 119.0, 75.4, 0.4 (3C); **NMR 2D NOESY:** correlation between 4.90 (d, *J* = 1.4 Hz, 2H) and 0.21 (s, 9H); **IR** (neat): υ_{max} = 3063, 2955, 1589,1465, 1431, 1248, 1091, 838 cm^{-1}; **HRMS** (API+): calcd for $C_{24}H_{27}{}^{74}GeOSi$ $(M+H)^+$ 433.1043, found 433.1051.



(*E*)-3-ethylidene-4,4-diphenyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxagermine 3b

Prepared according to **germylzincation** procedure from germane **2b** (73 mg, 0.195 mmol, 1 equiv.), hexane (0.8 mL), *i*Pr_2Zn (1 M in toluene, 0.23 mL, 0.234 mmol, 1.2 equiv.). Purification of the crude product (*E* / *Z* = 95:5) by flash chromatography on silica gel (Cyclohexane/Et_2O = 99.5:0.5) afforded **3b** (69 mg, 94%, *E* / *Z* = 95:5) as a colorless oil.

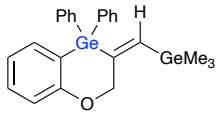
^{1}H NMR (300 MHz, $CDCl_3$): δ =7.59-7.55 (m, 4H), 7.43-7.29 (m, 8H), 7.04 (m, 2H), 6.06 (qt, *J* = 6.7, 1.8 Hz, 1H), 4.90 (bs, 2H), 1.85 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 164.8, 136.6, 136.1, 135.74 (2C), 135.72, 135.0 (4C), 130.8, 129.4 (2C), 128.5 (4C), 123.5, 122.7, 119.1, 70.5, 14.5; **NMR 2D NOESY:** correlation between 4.90 (dq, *J* = 1.8, 1.0 Hz, 2H) and 1.85 (td, *J* = 6.7, 1.0 Hz, 3H); **IR** (neat): υ_{max} = 3067, 2955, 1588, 1464, 1430, 1199, 1090, 697 cm^{-1}; **HRMS** (API+): calcd for $C_{22}H_{21}{}^{74}GeO$ $(M+H)^+$ 375.0804, found 375.0802.



(*E*)-3-benzylidene-4,4-diphenyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxagermine 3c

Prepared according to **germylzincation** procedure from germane **2c** (93.2 mg, 0.214 mmol, 1 equiv.), hexane (0.9 ml), *i*Pr_2Zn (1 M in toluene, 0.26 mL, 0.257 mmol, 1.2 equiv.). Purification of the crude product (*E* / *Z* = 92:8) by flash chromatography on silica gel (Cyclohexane/Toluene = 95:5-90-10, 80-20, 0-100) afforded **3c** (72 mg, 78%, *E* / *Z* = 92:8) as a colorless solid.

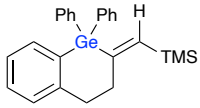
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65-7.62 (m, 4H), 7.46-7.29 (m, 12H), 7.23 (bs, 1H), 7.10-7.05 (m, 2H), 6.97 (bs, 1H), 5.12 (d, *J* = 1.9 Hz, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 164.7, 139.8, 139.7, 136.6, 135.5 (2C), 135.3, 135.1 (4C), 131.0, 129.6 (2C), 129.0 (2C), 128.6 (4C), 128.5 (2C), 127.7, 124.2, 123.1, 119.3, 77.1; **NMR 2D NOESY:** correlation between 7.46-7.29 (m, H_{aryle}) and 5.13 (d, *J* = 1.9 Hz, 2H); **HRMS** (API+): calcd for $C_{27}H_{23}{}^{74}GeO$ $(M+H^+)$ 437.0961, found 437.0969.



(*E*)-4,4-diphenyl-3-((trimethylgermyl)methylene)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxagermine 3d

Prepared according to **germylzincation** procedure from germane **2d** (605 mg, 1.272 mmol, 1 equiv.), hexane (4.5 mL), *i*Pr$_2$Zn (1 M in toluene, 1.53 mL, 1.526 mmol, 1.2 equiv.). Purification of the crude product (*E* / *Z* = 95:5) by flash chromatography on silica gel (Cyclohexane/Et$_2$O = 99.5:0.5) afforded **3d** (488 mg, 81%, *E* / *Z* = 95:5) as a white solid; mp 73.9-75.1°C.

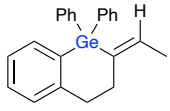
^{1}H NMR (300 MHz, $CDCl_3$): δ =7.61-7.56 (m, 4H), 7.45-7.36 (m, 8H), 7.09-7.03 (m, 2H), 6.52 (t, *J* = 1.4 Hz, 1H), 4.87 (d, *J* = 1.4 Hz, 2H), 0.37 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 164.8, 154.2, 146.4, 135.8 (2C), 135.7, 135.0 (4C), 130.8, 129.5 (2C), 128.5 (4C), 123.6, 122.8, 119.0, 75.6, 0.3 (3C); **NMR 2D NOESY:** correlation between 4.87 (d, *J* = 1.4 Hz, 2H) and 0.37 (s, 9H); **IR** (neat): υ_{max} = 2961, 2906, 1588, 1465, 1430, 1201, 1089, 696 cm^{-1}; **HRMS** (API+): calcd for $C_{24}H_{27}{}^{74}Ge_2O$ $(M+H)^+$ 479.0485, found 479.0471.



(*E*)-((1,1-diphenyl-3,4-dihydrobenzo[*b*]germin-2(1*H*)-ylidene)methyl)trimethylsilane 3e

Prepared according to **germylzincation** procedure from germane **2e** (202 mg, 0.471 mmol, 1 equiv.), hexane (1.5 mL), *i*Pr$_2$Zn (1 M in toluene, 0.56 mL, 0.565 mmol, 1.2 equiv.). Purification of the crude product (*E* / *Z* = 94:6) by flash chromatography on silica gel (Cyclohexane/EtOAc = 99.5:0.5) afforded **2e** (157 mg, 78%, *E* / *Z* = 94:6) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54-7.43 (m, 4H), 7.42-7.22 (m, 8H), 7.19-7.16 (m, 2H), 6.15 (t, *J* = 1.6 Hz, 1H), 2.96-2.79 (m, 4H), 0.14 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 160.4, 148.0, 142.8, 136.9, 135.80, 135.76 (2C), 135.1 (4C), 129.14, 129.08 (2C), 128.6, 128.3 (4C), 126.2, 36.6, 35.5, 0.4 (3C); **NMR 2D NOESY:** correlation between 2.86-2.81 (m, 2H) and 0.14 (s, 9H); **IR** (neat): υ_{max} = 3051, 2951, 1573, 1484, 1431, 1246, 1090, 834 cm^{-1}; **HRMS** (API+): calcd for $C_{25}H_{29}Si^{74}Ge$ $(M+H)^+$ 431.1250, found 431.1262.

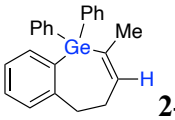


(*E*)-2-ethylidene-1,1-diphenyl-1,2,3,4-tetrahydrobenzo[*b*]germine 3f

Prepared according to **germylzincation** procedure from germane **2f** (225 mg, 0.606 mmol, 1 equiv.), hexane (2.0 mL), *i*Pr$_2$Zn (1 M in toluene, 0.73 mL, 0.728 mmol, 1.2 equiv.). Purification of the crude product (*E* / *Z* / 7-*endo-dig* = 66:13:21) by flash chromatography on

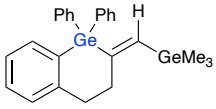
silica gel (Cyclohexane/EtOAc = 99.5:0.5) afforded an inseparable **3f/3f'** mixture in a 76/24 ratio (195 mg, 87%: 66% **3f** *E* / *Z* = 83:17 + 21% **3'f**) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43-7.40 (m, 4H), 7.29-7.24 (m, 10H), 5.85-5.79 (m, 1H), 2.79-2.73 (m, 2H), 2.68-2.60 (m, 2H), 1.68 (dt, *J* = 6.7, 1.0 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ =148.3, 138.2, 137.0, 135.3 (2C), 135.2 (4C), 134.9, 129.2, 129.03 (2C), 128.98, 128.6, 128.3 (4C), 126.1, 34.8, 29.8, 14.6; **NMR 2D NOESY:** correlation between 2.65-2.62 (m, 2H) and 1.68 (dt, *J* = 6.7, 1.0 Hz, 3H); **IR** (neat): υ_{max} = 3050, 2907, 1483, 1430, 1090, 697cm^{-1}; **HRMS** (API+): calcd for $C_{23}H_{23}{}^{74}Ge$ (M+H$^+$) 373.1012, found 373.1015.



2-methyl-1,1-diphenyl-4,5-dihydro-1*H*-benzo[*b*]germepine 3'f

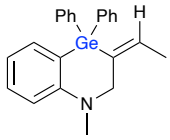
^{1}H NMR (300 MHz, $CDCl_3$): δ =7.44-7.37 (m, 4H), 7.30-7.25 (m, 5H), 7.20 (td, *J* = 7.5, 1.6 Hz, 1H), 7.15-7.07 (m, 3H), 7.02 (td, *J* = 7.2, 1.2 Hz, 1H), 6.43 (m, 1H), 2.89-2.82 (m, 2H), 2.50-2.43 (m, 2H), 1.77 (q, *J* = 1.9 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 149.7, 143.2, 137.0, 135.9, 135.3 (4C), 135.1 (2C), 134.8, 131.0, 129.7, 129.0 (2C), 128.4 (4C), 125.5, 35.8, 32.7, 26.2; **IR** (neat): υ_{max} = 3048, 2906, 1633, 1483, 1430, 1090, 698; **HRMS** (API+): calcd for $C_{23}H_{23}{}^{74}Ge$ (M+H$^+$) 373.1012, found 373.1021.



(*E*)-1,1-diphenyl-2-((trimethylgermyl)methylene)-1,2,3,4-tetrahydro-benzo[*b*]germine 3g

Prepared according to **germylzincation** procedure from germane **2g** (369 mg, 0.779 mmol, 1 equiv.), hexane (2.7 mL), *i*Pr_2Zn (1 M in toluene, 0.94 mL, 0.935 mmol, 1.2 equiv.). Purification of the crude product (*E* / *Z* = 99:1) by flash chromatography on silica gel (Cyclohexane/EtOAc = 99:1) afforded **3g** (297 mg, 80%, *E* / *Z* = 97:3) as a colorless oil.

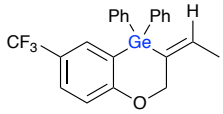
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57-7.52 (m, 4H), 7.41-7.37 (m, 7H), 7.32-7.29 (m, 1H), 7.25-7.23 (m, 1H), 7.16-7.13 (m, 1H), 6.32 (t, *J* = 1.7 Hz, 1H), 2.99-2.94 (m, 2H), 2.88-2.83 (m, 2H), 0.34 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 157.3, 156.6, 149.6, 148.0, 143.6, 136.9, 135.7 (2C), 135.3, 135.1 (4C), 129.1 (2C), 128.3 (4C), 126.2, 36.7, 35.6, 0.1 (3C); **NMR 2D NOESY:** correlation between 2.88-2.83 (m, 2H) and 0.34 (s, 9H); **IR** (neat): υ_{max} = 3051, 2906, 1576, 1484, 1430, 1090, 697 cm^{-1}; **HRMS** (API+): calcd for $C_{25}H_{29}{}^{70}Ge^{72}Ge$ (M+H$^+$) 471.0733, found 471.0716.



(*E*)-3-ethylidene-1-methyl-4,4-diphenyl-1,2,3,4-tetrahydrobenzo[*b*][1,4]-azagermine 3h

Prepared according to **germylzincation** procedure from germane **2h** (135 mg, 0.350 mmol, 1 equiv.), hexane (1.2 mL), *i*Pr_2Zn (1 M in toluene, 0.42 mL, 0.420 mmol, 1.2 equiv.). Purification of the crude product (conversion 75%) (*E* / *Z* = 70:30) by flash chromatography on silica gel (Cyclohexane/CH_2Cl_2 = 98:2-96:4-90:10) afforded **3h** (52 mg, 39%, 51% BRSM) as a colorless oil.

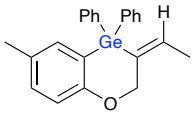
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54-7.51 (m, 4H), 7.39-7.35 (m, 6H), 7.30 (d, *J* = 7.3 Hz, 2H), 6.92-6.84 (m, 2H), 5.89 (qt, *J* = 6.7, 2.0 Hz, 1H), 3.93 (dq, *J* = 2.0, 1.2 Hz, 2H), 2.93 (s, 3H), 1.79 (dt, *J* = 6.7, 1.2 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 157.4, 138.8, 136.5, 135.4 (2C), 135.2 (4C), 133.6, 130.2, 129.1 (2C), 128.3 (4C), 125.8, 119.9,115.0, 57.6, 42.1, 14.6; **NMR 2D NOESY:** correlation between 3.93 (dq, *J* = 2.0, 1.2 Hz, 2H) and 1.79 (dt, *J* = 6.7, 1.2 Hz, 3H); **IR** (neat): υ_{max} = 3049, 2794, 1736, 1583, 1430, 1266, 1090, 697 cm^{-1}; **HRMS** (API+): calcd for $C_{23}H_{24}N^{72}Ge$ ($M+H^+$) 386.1130, found 386.1123.



(*E*)-3-ethylidene-4,4-diphenyl-6-(trifluoromethyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxagermine 3i

Prepared according to **germylzincation** procedure from germane **2i** (260 mg, 0.589 mmol, 1 equiv.), hexane (2.0 mL), *i*Pr_2Zn (1 M in toluene, 0.71 mL, 0.707 mmol, 1.2 equiv.). Purification of the crude product (*E* / *Z* = 95:5) by flash chromatography on silica gel (Cyclohexane/AcOEt = 99:1) afforded **3i** (217 mg, 83%, *E* / *Z* = 95:5) as a colorless oil.

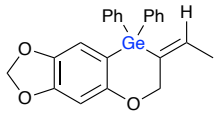
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 1.9 Hz, 1H), 7.60-7.55 (m, 5H), 7.46-7.42 (m, 6H), 7.11 (d, *J* = 8.6 Hz, 1H), 6.12 (qt, *J* = 6.9, 1.8 Hz, 1H), 4.96 (q, *J* = 0.8 Hz, 2H), 1.90 (dt, *J* = 6.9, 0.8. Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 167.3 (q, *J* = 1.5 Hz), 137.8 (2C), 134.9 (4C), 134.7, 134.5, 132.8 (q, *J* = 4 Hz), 129.8 (2C), 128.7 (4C), 128.0 (q, *J* = 4 Hz), 124.5 (q, *J* = 32 Hz), 124.6 (q, *J* = 273 Hz), 123.8, 119.3, 70.3, 14.5; **^{19}F NMR** (282 MHz, $CDCl_3$): -61.4; **NMR 2D NOESY:** correl ation between 4.96 (dq, *J* = 1.8, 1.0 Hz, 2H) and 1.90 (dt, *J* = 6.9, 1.0. Hz, 3H); **IR** (neat): υ_{max} = 3050, 1483, 1431, 1320, 1074, 697 cm^{-1}; **HRMS** (API-): calcd for $C_{23}H_{19}F_3{}^{74}GeO$ (M^+) 442.0600, found 442.0595.



(*E*)-3-ethylidene-6-methyl-4,4-diphenyl-3,4-dihydro-2*H*-benzo[*b*][1,4]-oxagermine 3j

Prepared according to **germylzincation** procedure from germane **2j** (230 mg, 0.594 mmol, 1 equiv.), hexane (2.0 mL), *i*Pr$_2$Zn (1 M in toluene, 0.71 mL, 0.712 mmol, 1.2 equiv.). Purification of the crude product (*E* / *Z* = 98:2) by flash chromatography on silica gel (Cyclohexane/AcOEt = 99:1) afforded **3j** (219 mg, 95%, *E* / *Z* = 98:2) as a colorless oil.

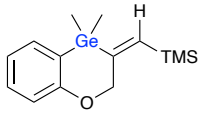
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68-7.65 (m, 4H), 7.50-7.44 (m, 6H), 7.29 (d, *J* = 2.4 Hz, 1H), 7.20 (ddd, *J* = 8.3, 2.3, 0.7 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.12 (qt, *J* = 6.9, 1.9 Hz, 1H), 4.96 (dq, *J* = 1.9, 1.0 Hz, 2H), 2.34 (s, 3H), 1.91 (dt, *J* = 6.9, 1.0. Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 162.7, 136.6, 136.2, 135.8, 135.7 (2C), 135.0 (4C), 131.9, 131.6, 129.4 (2C), 128.4 (4C), 123.3, 118.8, 70.7, 20.8, 14.5; **NMR 2D NOESY:** correlation between 4.96 (dq, *J* = 1.9, 1.0 Hz, 2H) and 1.91 (dt, *J* = 6.9, 1.0. Hz, 3H); **IR** (neat): υ_{max} = 3048, 2919, 1600, 1470, 1203, 696 cm^{-1}; **HRMS** (API+): calcd for $C_{23}H_{23}{}^{72}GeO$ ($M+H^+$) 387.0970, found 387.0983.



(*E*)-7-ethylidene-8,8-diphenyl-7,8-dihydro-6*H*-[1,3]dioxolo[4',5':4,5]-benzo[1,2-b][1,4]oxagermine 3k

Prepared according to **germylzincation** procedure from germane **2k** (220 mg, 0.527 mmol, 1 equiv.), hexane (1.8 mL), *i*Pr$_2$Zn (1 M in toluene, 0.63 mL, 0.632 mmol, 1.2 equiv.). Purification of the crude product (*E* / *Z* = 97:3) by flash chromatography on silica gel (Cyclohexane/AcOEt = 99:1) afforded **3k** (172 mg, 78%, *E* / *Z* = 95:5) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55-7.52 (m, 4H), 7.40-7.35 (m, 6H), 6.75 (s, 1H), 6.61 (s, 1H), 6.00 (qt, *J* = 6.8, 1.8 Hz, 1H), 5.91 (s, 2H), 4.84-4.83 (m, 2H), 1.81 (dt, *J* = 6.8, 1.0 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 160.2, 149.6, 143.5, 136.5, 136.1 (2C), 135.8, 134.9 (4C), 129.4 (2C), 128.5 (4C), 114.7, 112.6, 101.6, 101.2, 71.3, 14.6; **NMR 2D NOESY:** correlation between 4.83 (dq, *J* = 1.8, 1.0 Hz, 2H) and 1.81 (dt, *J* = 6.8, 1.0. Hz, 3H); **IR** (neat): υ_{max} = 3067, 2888, 1606, 1469, 1430, 1026, 696cm^{-1}; **HRMS** (API+): calcd for $C_{23}H_{21}{}^{74}GeO_3$ ($M+H^+$) 419.0702, found 419.0708.



(*E*)-((4,4-dimethyl-2*H*-benzp[*b*][1,4]oxagermin-3(4*H*)-ylidene)methyl)-trimethylsilane 3l

Prepared according to **germylzincation** procedure from germane **2l** (120 mg, 0.391 mmol, 1 equiv.), hexane (1.5 mL), *i*Pr_2Zn (1 M in toluene, 0.47 mL, 0.469 mmol, 1.2 equiv.). Purification of the crude product (*E* / *Z* = 68:32) by flash chromatography on silica gel (Cyclohexane/AcOEt = 100:0-99.5:0.5-99:1) afforded **3l** (49 mg, 41%, *E* / *Z* = 65:35, 75% BRSM) as a colorless oil.

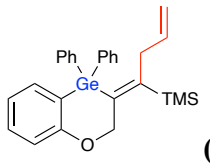
(*E*) isomer :^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36-7.32 (m, 1H), 7.29-7.22 (m, 1H), 7.04 (td, *J* = 7.2, 1.2 Hz, 1H), 6.92 (dd, *J* = 8.5, 0.8 Hz, 1H), 6.16 (t, *J* = 1.5 Hz, 1H), 4.73 (d, *J* = 1.5 Hz, 2H), 0.46 (s, 6H), 0.19 (s, 9H), **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 164.0, 161.4, 141.6, 134.5, 130.2, 127.7, 122.7, 118.7, 75.0, 0.4 (3C), 0.2 (2C); **NMR 2D NOESY:** correlation between 4.73 (d, *J* = 1.5 Hz, 2H) and 0.19 (s, 9H).

(*Z*) isomer :^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36-7.32 (m, 1H), 7.29-7.22 (m, 1H), 7.02 (td, *J* = 7.3, 1.1 Hz, 1H), 6.97-6.90 (dd, *J* = 8.2, 0.7 Hz, 1H), 6.52 (t, *J* = 1.3 Hz, 1H), 4.54 (d, *J* = 1.3 Hz, 2H), 0.58 (s, 6H), 0.18 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 164.2, 157.7, 144.1, 134.3, 130.0, 126.7, 122.4, 118.0, 82.1, 0.2 (3C), -2.2 (2C); **NMR 2D NOESY:** correlation between 6.52 (t, *J* = 1.3 Hz, 1H) and 4.54 (d, *J* = 1.3 Hz, 2H*Z*).

IR (neat): υ_{max} = 3061, 2955, 1590, 1433, 1247, 1002, 836, 693 cm^{-1}; **HRMS** (API+): calcd for $C_{14}H_{23}{}^{74}GeOSi$ ($M+H^+$) 309.0730, found 309.0740.

General procedure for the Domino polar germylzincation / Cu(I)-mediated electrophilic trapping

The general procedure GP2 was followed. Instead of hydrolysis, the appropriate Cu(I)-salt (0.2 equiv.) and electrophile (3.6 equiv.) were consecutively added and the resulting mixture stirred at room temperature for 2 h or overnight. The mixture was hydrolyzed with aqueous NH_4Cl and stirred for 20 min. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (x3). The combined organic layers washed with brine (x2), dried over anhydrous $MgSO_4$ and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel.

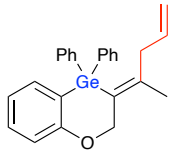


(*E*)-(1-(4,4-diphenyl-2*H*-benzo[*b*][1,4]oxagermin-3(4*H*)-ylidene)but-3-en-1-yl)trimethylsilane 4aa

Prepared according to **domino germylzincation** procedure from germane **2a** (93 mg, 0.214 mmol, 1 equiv.), hexane (1.0 mL), *i*Pr_2Zn (1M in toluene, 0.26 mL, 0.257 mmol, 1.2 equiv.),

$CuBr.SMe_2$ (9 mg, 0.043 mmol, 0.2 equiv.) and allyl chloride (59 mg, 0.770 mmol, 3.6 equiv.) with reaction time of 90 minutes at 80°C and 14h at room temperature. Purification of the crude product by flash chromatography on silica gel (Petroleum ether/CH_2Cl_2 = 99:1-98:2-95:5) afforded an inseparable **4aa/2a** mixture in a 94/6 ratio (76 mg, 76%: 71% **4aa** *E* / *Z* = 95:5 + 5% **2a**) as a colorless oil.

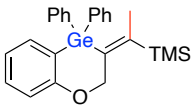
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56-7.53 (m, 4H), 7.37-7.29 (m, 8H), 7.01-6.94 (m, 2H), 5.30 (ddt, *J* = 16.3, 10.4, 5.9 Hz, 1H), 4.92 (t, *J* = 1.7 Hz, 2H), 4.73-4.63 (m, 2H), 2.99 (dt, *J* = 5.9, 1.7 Hz, 2H), 0.25 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 165.3, 154.5, 149.3, 136.4 (2C), 135.7,135.0 (4C), 130.5, 129.2 (2C), 128.5 (4C), 128.4, 124.3, 122.7, 118.2, 116.1, 75.6, 43.2, 1.2 (3C); **NMR 2D NOESY:** correlation between 4.92 (t, *J* = 1.7 Hz, 2H) and 0.25 (s, 9H); **IR** (neat): υ_{max} = 3063, 2955,1588, 1465, 1431, 1249, 1090, 837 cm^{-1};**HRMS** (API+): calcd for $C_{27}H_{31}{}^{74}GeOSi$ $(M+H)^+$ 473.1356, found: 473.1357.



(*Z*)-3-(pent-4-en-2-ylidene)-4,4-diphenyl-3,4-dihydro-2*H*-benzo[*b*][1,4]-oxagermine 4ba

Prepared according to domino germylzincation procedure from germane **2b** (160 mg, 0.429 mmol, 1 equiv.), hexane (1.5 ml), *i*Pr_2Zn (1 M in toluene, 0.52 mL, 0.515 mmol, 1.2 equiv.), $CuBr.SMe_2$ (18 mg, 0.086 mmol, 0.2 equiv.) and allyl chloride (118 mg, 1.544 mmol, 3.6 equiv.) with reaction time of 90 minutes at 80°C and 14h at room temperature. Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 99.8:0.2-99.5:0.5) afforded an inseparable **4ba/3b** mixture in a 78/22 ratio (164 mg, 76% **4ba** *Z* / *E* = 96:4 + 19% **3b**) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59-7.55 (m, 4H), 7.39-7.35 (m, 8H), 7.00-6.94 (m, 2H), 5.31 (ddt, *J* = 16.9, 10.0, 6.9 Hz, 1H), 4.81 (s, 2H), 4.80 (dt, *J* = 10.0, 1.5 Hz, 1H), 4.73 (dt, *J*= 16.9, 1.5 Hz, 1H), 2.83 (dt, *J* = 6.9, 1.5 Hz, Hz, 2H), 1.85 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 165.2, 145.9, 136.4, 135.6 (2C), 135.2, 135.0 (4C), 130.6, 130.5, 129.3 (2C), 128.5 (4C), 124.5, 122.7, 118.5, 117.0, 72.8, 45.6, 17.3; **NMR 2D NOESY:** correlation between 4.81 (s, 2H) and 1.85 (s, 3H); **IR** (neat): υ_{max} = 3069, 3045, 1587, 1465, 1431, 1205, 1089, 696 cm^{-1}; **HRMS** (API+): calcd for $C_{25}H_{25}{}^{74}GeO$ $(M+H)^+$ 415.1117, found: 415.1130.



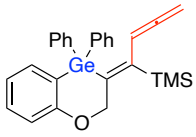
(*E*)-(1-(4,4-diphenyl-2*H*-benzo[*b*][1,4]oxagermin-3(4*H*)-ylidene)ethyl)trimethylsilane 4ab

Prepared according to domino germylzincation procedure from germane **2a** (207 mg, 0.480 mmol, 1 equiv.), hexane (1.5 ml), *i*Pr$_2$Zn (1 M in toluene, 0.58 mL, 0.58 mmol, 1.2 equiv.), CuCN.2LiCl (1 M in THF, 1.44 mL, 1.44 mmol, 3 equiv.) and methyl iodide (204 mg, 1.44 mmol, 3.0 equiv.) with reaction time of 90 minutes at 80°C and 14h at room temperature. Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 99.8:0.2-99.5:0.5) afforded **4ab** (143.8 mg, 67% **4ab** *E* / *Z* = 7:3) as a colorless oil.

(*E*) isomer : ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60-7.55 (m, 4H), 7.40-7.36 (m, 6H), 7.34-7.28 (m, 1H), 7.24-7.18 (m, 1H), 7.02-6.90 (m, 2H), 4.95 (s, 2H), 2.05 (s, 3H), -0.17 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 164.7, 151.4, 146.7, 135.9 (2C), 135.0, 134.4 (4C), 129.9, 128.6 (2C), 127.9 (4C), 124.2, 122.1, 117.7, 75.1, 25.1, -0.0 (3C); **NMR 2D NOESY:** correlation between 4.95 (s, 2H) and -0.17 (s, 3H).

(*Z*) isomer : ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67-7.64 (m, 4H), 7.40-7.36 (m, 6H), 7.34-7.28 (m, 1H), 7.24-7.18 (m, 1H), 7.02-6.90 (m, 2H), 4.89 (s, 2H), 1.86 (s, 3H), 0.26 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 163.7, 152.1, 144.4, 136.5 (2C), 134.69 (4C), 134.66, 129.6, 128.7 (2C), 127.8 (4C), 126.6, 122.1, 117.3, 72.9, 18.6, -0.7 (3C); **NMR 2D NOESY:** correlation between 4.89 (s, 2H) and 1.86 (s, 3H).

IR (neat): υ_{max} = 3068, 2955, 1587, 1466, 1431, 1257, 1089, 834, 696 cm^{-1}; **HRMS** (ESI+): calcd for $C_{25}H_{28}{}^{74}GeOSi$ $(M)^+$ 446.1121, found: 446.1123.

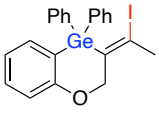


4ac

Prepared according to domino germylzincation procedure from germane **2a** (213 mg, 0.495 mmol, 1 equiv.), hexane (1.5 ml), *i*Pr$_2$Zn (1 M in toluene, 0.60 mL, 0.600 mmol, 1.2 equiv.), CuCN.2LiCl (1 M in THF, 1.49 mL, 1.49 mmol, 3 equiv.) and propargyl bromide (330 µL, 2.97 mmol, 6 equiv.) with reaction time of 90 minutes at 80°C and 14h at room temperature. Purification of the crude product by flash chromatography on silica gel (Cyclohexane/DCM = 99:1) afforded **4ac** (160.5 mg, 69%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65-7.59 (m, 4H), 7.44-7.39 (m, 6H), 7.37-7.34 (m, 1H), 7.32-7.29 (m, 1H), 7.07-6.99 (m, 2H), 6.01 (tt, *J* = 6.8, 0.9 Hz, 1H), 5.01 (d, *J* = 0.9 Hz, 2H), 4.62 (d, *J* = 6.8 Hz, 2H), 0.36 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 210.1, 165.1, 150.9,

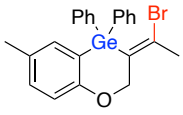
148.9, 136.1, 135.7 (2C), 135.1 (4C), 130.6, 129.3 (2C), 128.52, 128.47 (4C), 124.6, 122.8, 118.3, 96.8, 75.3, 1.8 (3C); **NMR 2D NOESY:** correlation between 4.62 (d, *J* = 6.8 Hz, 2H) and 0.36 (s, 9H); **IR** (neat): υ_{max} = 3050, 2955, 1934, 1693, 1588, 1566, 1466, 1431, 1251, 1089, 837, 696 cm^{-1}; **HRMS** (ESI+): calcd for $C_{27}H_{29}{}^{72}GeOSi$ $(M+H)^+$ 469.1208, found: 469.1210.



(*Z*)-3-(1-iodoethylidene)-4,4-diphenyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxa-germine 4bd

Prepared according to domino germylzincation procedure from germane **2b** (233 mg, 0.623 mmol, 1 equiv.), hexane (2.0 ml), *i*Pr_2Zn (1 M in toluene, 0.74 mL, 0.74 mmol, 1.2 equiv.), and iodide (317 mg, 1.25 mmol, 2.0 equiv.) with reaction time of 90 minutes at 80°C and 14h at room temperature. Purification of the crude product by flash chromatography on silica gel (Cyclohexane/DCM = 8: 2) afforded **4bd** (251.1 mg, 82%) as a white solid; mp 119.1°C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77-7.66 (m, 4H), 7.44-7.37 (m, 6H), 7.32-7.26 (m, 2H), 7.03 (dd, *J* = 7.6, 1.1 Hz, 1H), 6.99 (td, *J* = 7.3, 1.0 Hz, 1H), 4.79 (q, *J* = 0.9 Hz, 2H), 2.75 (t, *J* = 0.9 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 164.6, 145.8, 135.8 (2C), 135.7 (4C), 134.1, 130.7, 129.5 (2C), 128.5 (4C), 125.5, 123.2, 118.3, 110.3, 72.8, 31.5; **NMR 2D NOESY:** correlation between 4.79 (q, *J* = 0.9 Hz, 2H) and 2.75 (t, *J* = 0.9 Hz, 3H); **IR** (neat): υ_{max} = 2917, 1619, 1599, 1472, 1430, 1205, 1091, 1067, 986, 697 cm^{-1}; **HRMS** (API+): calcd for $C_{22}H_{20}{}^{74}GeIO$ $(M+H)^+$ 500.9771, found: 500.9760.

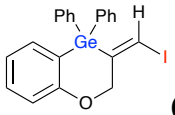


(*Z*)-3-(1-bromoethylidene)-6-methyl-4,4-diphenyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxagermine 4je

Prepared according to domino germylzincation procedure from germane **2j** (237 mg, 0.613 mmol, 1 equiv.), hexane (1.5 ml), *i*Pr_2Zn (1 M in toluene, 0.74 mL, 0.74 mmol, 1.2 equiv.), CuCN.2LiCl (1 M in THF, 1.83 mL, 1.83 mmol, 3 equiv.) and NBS (220 mg, 1.24 mmol, 2.0 equiv.) with reaction time of 90 minutes at 80°C and 14h at room temperature. Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 99.8:0.2-99.5:0.5) afforded **4je** (209 mg, 73% *Z* / *E* = 98:2) as a colorless solid; mp 88.5°C.

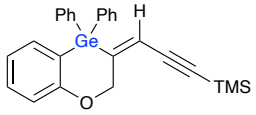
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74-7.66 (m, 4H), 7.45-7.40 (m, 6H), 7.13-7.08 (m, 2H), 6.96 (d, *J* = 9.0 Hz, 1H), 4.78 (q, *J* = 0.8 Hz, 2H), 2.15 (t, *J* = 0.8 Hz, 3H), 2.25 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 162.7, 138.0, 135.7 (2C), 135.4 (4C), 134.7, 132.4, 132.3, 131.5,

129.4 (2C), 128.4 (4C), 124.4, 118.2, 73.1, 26.0, 20.3; **NMR 2D NOESY:** correlation between 4.78 (q, *J* = 0.8 Hz, 2H) and 2.15 (t, *J* = 0.8 Hz, 3H); **IR** (neat): υ_{max} = 2917, 1619, 1599, 1472, 1430, 1205, 1091, 1067, 731, 697 cm^{-1}; **HRMS** (API+): calcd for $C_{23}H_{22}{}^{79}Br^{70}GeIO$ $(M+H)^+$ 463.0097, found: 463.0097.



((*E*)-3-(iodomethylene)-4,4-diphenyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxa-germine 5d

To a solution of vinylgermane **3d** (*E*/*Z* = 95:5) (126 mg, 0.265 mmol, 1 equiv.) in anhydrous CH_2Cl_2 (1.5 mL) under argon atmosphere, was added *N*-iodosuccinimide (78 mg, 0.346 mmol, 1.3 equiv.) at room temperature. The reaction mixture was stirred at room temperature for 3h before being quenched with water and extracted with CH_2Cl_2. The organic layer was washed with $Na_2S_2O_3$ and brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Purification of the crude product (*E*/*Z* = 95:5) by flash chromatography on silica gel (Cyclohexane/EtOAc = 99.8:0.2, 99.5:0.5, 99:1) afforded **5d** (112 mg, 87%) as a white solid. **^{1}H NMR** (300 MHz, $CDCl_3$): δ =7.54-7.49 (m, 4H), 7.44-7.36 (m, 8H), 7.12-7.04 (m, 2H), 6.59 (t, *J* = 1.8 Hz, 1H), 4.76 (d, *J* = 1.8 Hz, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 164.3, 149.6, 135.1 (2C), 134.8 (4C), 133.9, 131.5, 130.0 (2C), 128.8 (4C), 123.5, 123.2, 119.7, 87.8, 79.6; **NMR 2D NOESY:** correlation between 7.45-7.35 (m, 8H) and 6.61 (t, *J* =1.8 Hz, 1H); **IR** (neat): υ_{max} = 3333, 2974, 1583, 1430, 1202, 1047, 879, 695 cm^{-1}; **HRMS** (API+): calcd for $C_{21}H_{18}{}^{72}GeIO$ $(M+H^+)$ 484.9623, found 484.9618.

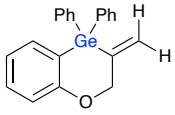


(*E*)-(3-(4,4-diphenyl-2*H*-benzo[*b*][1,4]oxagermin-3(4*H*)-ylidene) prop-1-yn-1-yl)trimethylsilane 6

To a mixture of vinyl iodide **5d** (*E*/*Z* = 95:5) (71 mg, 0.149 mmol, 1 equiv.), $PdCl_2(PPh_3)_2$ (2 mg, 0.003 mmol, 0.02 equiv.), CuI (1 mg, 0.005 mmol, 0.04 equiv.), Et_3N (0.04 mL, 0.268 mmol, 1.8 equiv.) in dry THF (4 mL) was added dropwise a solution of trimethylsilylacetylene (19.7 mg, 0.201 mmol, 1.4 equiv.) at room temperature. The resulting mixture was stirred at reflux for 4h, and after cooling it down to ambient temperature, the reaction mixture was filtered over celite. The filtrate was evaporated under reduced pressure, and the residue was dissolved in Et_2O, washed with a satured aqueous solution of NH_4Cl and brine. The obtained organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduce pressure. Purification

of the crude product (*E*/*Z* = 97:3) by flash chromatography on silica gel (Cyclohexane/EtOAc = 99.5:0.5, 99:1) afforded **6** (61 mg, 90%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57-7.51 (m, 4H), 7.42-7.35 (m, 8H), 7.11-7.04 (m, 2H), 5.98 (t, *J* = 1.8 Hz, 1H), 5.07 (d, *J* = 1.8 Hz, 2H), 0.23 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 164.6, 153.6, 135.5 (2C), 134.9 (4C), 134.5, 131.2, 129.8 (2C), 128.7 (4C), 123.2, 122.9, 119.4, 118.4, 102.4, 100.3, 73.5, 0.0 (3C); **NMR 2D NOESY:** correlation between 7.42-7.35 (m, 8H) and 5.97 (t, *J* =1.8 Hz, 1H); **IR** (neat): υ_{max} = 2961, 2155, 1587, 1465, 1443, 1431, 1250, 1092, 839, 696 cm^{-1}; **HRMS** (API+): calcd for $C_{26}H_{27}{}^{74}GeOSi$ ($M+H^+$) 457.1043, found 457.1047.



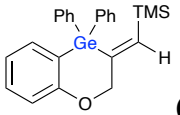
3-methylene-4,4-diphenyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxagermine 7

A solution of **5d** (*E*/*Z* = 95:5) (80 mg, 0.165 mmol, 1 equiv.), Bu_3SnH (0.1 ml, 0.330 mmol, 2 equiv.) and AIBN (6 mg, 0.033 mmol, 0.2 equiv.) in toluene/hexane (1 mL/1 mL) was stirred and heated at 100°C for 1h. The reaction mixture was quenched by NH_4Cl and extracted with DCM. The organic layer was washed with water and brine, dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 99.8:0.2, 99.5:0.5, 99:1) afforded **7** (54 mg, 91%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65-7.56 (m, 4H), 7.47-7.33 (m, 8H), 7.09-7.03 (m, 2H), 6.04 (q, *J* = 1.4 Hz, 1H), 5.64 (dt, *J* = 1.4, 1.2 Hz, 1H), 4.78 (t, *J* = 1.2 Hz, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 164.7, 145.9, 135.9 (2C), 135.3, 134.8 (4C), 130.9, 129.6 (2C), 128.6 (4C), 126.5, 122.6, 122.1, 119.0, 77.0; **IR** (neat): υ_{max} = 2923, 1589, 1464, 1432, 1202, 1091, 697 cm^{-1}; **HRMS** (API+): calcd for $C_{21}H_{19}{}^{72}GeO$ ($M+H^+$) 359.0657, found 359.0665.

General procedure for the radical intramolecular hydrogermylation

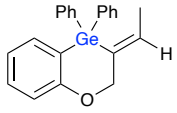
In a dry sealed tube under argon atmosphere, AIBN (0.15 equiv.) was added to a solution of germane **2** (0.25–2 mmol) in dry hexane and the mixture was stirred 1 h at 100° C. After cooling at room temperature, the reaction mixture was hydrolyzed with aqueous NH_4Cl and stirred for 20 minutes. The layers were separated and the aqueous layer was extracted with ether (x3). The combined organic layers were washed with brine (x2), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel.



(*Z*)-((4,4-diphenyl-2*H*-benzo[*b*][1,4]oxagermin-3(4*H*)-ylidene)methyl)trimethylsilane (*Z*)-3a

Prepared according to the general procedure for **hydrogermylation** using germane **2a** (160 mg, 0.371 mmol, 1 equiv.), hexane (1.5 mL), AIBN (12 mg, 0.074 mmol, 0.2 equiv.). Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtO_2 = 100:0, 99:1) afforded **(*Z*)-3a** (123 mg, 77%,) as a colorless oil.

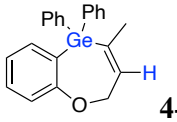
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65-7.59 (m, 4H), 7.41-7.36 (m, 6H), 7.30 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.24 (td, *J* = 7.7, 1.6 Hz, 1H), 6.98-6.91 (m, 2H), 6.79 (t, *J* = 1.2 Hz, 1H), 4.73 (d, *J* = 1.2 Hz, 2H), -0.21 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 164.5, 153.0, 147.5, 135.9, 135.6 (2C), 135.3 (4C), 130.5, 129.6 (2C), 128.5 (4C), 124.5, 122.6, 118.1, 82.6, -0.3 (3C); **NMR 2D NOESY:** correlation between 6.77 (t, *J* = 1.2 Hz, 1H) and 4.71 (d, *J* = 1.2 Hz, 2H); **IR** (neat): υ_{max} = 3063, 2955, 1589,1465, 1431, 1248, 1091, 838 cm^{-1}; **HRMS** (API+): calcd for $C_{24}H_{27}{}^{74}GeOSi$ $(M+H)^+$ 433.1043, found 433.1051.



(*Z*)-3-ethylidene-4,4-diphenyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxagermine 3b

Prepared according to the general procedure for **hydrogermylation** using germane **2b** (120 mg, 0.322 mmol, 1 equiv.), hexane (1.5 ml), AIBN (8 mg, 0.048 mmol, 0.15 equiv.). Purification of the crude product (*Z* / 7-*endo-dig* = 82:18) by flash chromatography on silica gel (Cyclohexane/AcOEt = 99:1) afforded an inseparable **(*Z*)-3b/3'b** mixture in a 82/18 ratio (109 mg, 91%: 75% **(*Z*)-3b** + 16% **3'b**) as a colorless oil.

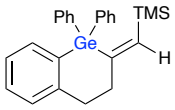
^{1}H NMR (300 MHz, $CDCl_3$): δ =7.62-7.55 (m, 4H), 7.40-7.35 (m, 7H), 7.28 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.01-6.93 (m, 2H), 6.48 (qt, *J* = 6.8, 1.3 Hz, 1H), 4.69 (bs, 2H), 1.70 (d, *J* = 6.8, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 165.2, 137.9, 136.3, 135.8, 135.7 (2C), 135.0 (4C), 130.6, 129.4 (2C), 128.6 (4C), 124.0, 122.5, 118.7, 77.5, 18.8; **NMR 2D NOESY:** correlation between 6.48 (qt, *J* = 6.8, 1.3 Hz, 1H) and 4.69 (bs, 2H); **IR** (neat): υ_{max} = 3067, 2955, 1588, 1464, 1430, 1199, 1090; **HRMS** (API+): calcd for $C_{22}H_{21}{}^{74}GeO$ $(M+H)^+$ 375.0804, found 375.0810.



4-methyl-5,5-diphenyl-2,5-dihydrobenzo[*b*][1,4]oxagermepine 3'b

^{1}H NMR (300 MHz, $CDCl_3$): δ =7.52-7.48 (m, 4H), 7.40-7.35 (m, 6H), 7.29-7.20 (m, 2H), 7.08-7.04 (m, 2H), 6.38-6.33 (m, 1H), 4.69 (bs, 2H), 1.90 (d, *J* = 1.8 Hz, 3H); **^{13}C NMR** (75

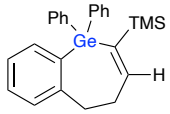
MHz, $CDCl_3$): δ = 165.7, 138.5, 136.5, 136.0, 135.5 (2C), 135.1 (4C), 131.3, 129.1 (2C), 128.4 (4C), 124.0, 123.0, 120.8, 72.9, 18.8; **IR** (neat): υ_{max} = 3067, 2955, 1588, 1464, 1430, 1199, 1090; **HRMS** (API+): calcd for $C_{22}H_{21}{}^{70}GeO$ $(M+H)^+$ 371.0835, found 371.0839.



(*Z*)-((1,1-diphenyl-3,4-dihydrobenzo[*b*]germin-2(1*H*)-ylidene)methyl)trimethylsilane 3e

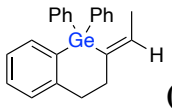
Prepared according to the general procedure for **hydrogermylation** using germane **2e** (177 mg, 0.412 mmol, 1 equiv.), hexane (1.5 mL), AIBN (10 mg, 0.062 mmol, 0.15 equiv.). Purification of the crude product by flash chromatography on silica gel (Cyclohexane/AcOEt = 99:1) afforded an inseparable **(*Z*)-3e/3'e** mixture in a 80/20 ratio (142 mg, 80%: 64% **(*Z*)-3e** + 16% **3'e**) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91-7.84 (m, 4H), 7.62-7.56 (m, 7H), 7.45-7.40 (m, 1H), 7.39-7.31 (m, 2H), 6.91 (t, *J* = 1.6 Hz, 1H), 3.21-3.09 (m, 4H), 0.00 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 157.0, 147.8, 144.5, 137.5, 137.3, 135.8 (2C), 135.4 (4C), 129.2 (2C), 128.7, 128.3 (4C), 128.1, 126.1, 45.8, 35.5, 0.1 (3C); **NMR 2D NOESY:** correlation between 6.91 (t, *J* = 1.6 Hz, 1H) and 3.21-3.09 (m, 4H); **IR** (neat): υ_{max} = 3051, 2951, 1573, 1484, 1431, 1246, 1090, 834 cm^{-1}; **HRMS** (API+): calcd for $C_{25}H_{29}Si^{74}Ge$ $(M+H)^+$ 431.1250, found 431.1262.



3'e

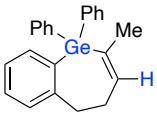
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78-7.74 (m, 4H), 7.62-7.56 (m, 8H), 7.45-7.40 (m, 1H), 7.39-7.31 (m, 2H), 3.15-3.09 (m, 2H), 3.02-2.95 (m, 2H), 0.11 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 158.9, 149.6, 140.1, 138.3, 136.0 (2C), 134.9 (4C), 134.8, 129.5 (2C), 128.9, 128.4 (4C), 128.2, 125.3, 36.2, 34.9, 0.6 (3C); **HRMS** (API+): calcd for $C_{25}H_{29}Si^{74}Ge$ $(M+H)^+$ 431.1250, found 431.1262.



(*Z*)-2-ethylidene-1,1-diphenyl-1,2,3,4-tetrahydrobenzo[*b*]germine 3f

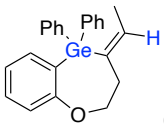
Prepared according to the general procedure for **hydrogermylation** using germane **2f** (205 mg, 0.552 mmol, 1 equiv.), hexane (1.5 ml), AIBN (15 mg, 0.083 mmol, 0.15 equiv.). Purification of the crude product (*Z* / 7-*endo-dig* = 41:59) by flash chromatography on silica gel (Cyclohexane/AcOEt = 99:1) afforded an inseparable **(*Z*)-3f/3'f** mixture in a 37/63 ratio (184 mg, 89%: 33% **(*Z*)-3f** + 56% **3'f**) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50-7.44 (m, 4H), 7.30-7.23 (m, 10H), 6.26 (qt, *J* = 6.7, 1.6 Hz, 1H), 2.86-2.76 (m, 2H), 2.65-2.59 (m, 2H), 1.55 (dt, *J* = 6.8, 1.4 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ =148.7, 138.2, 138.0, 137.1, 135.3 (2C), 135.1 (4C), 129.0 (2C), 128.9, 128.5, 128.4 (4C), 126.2, 38.3, 35.7, 19.0; **NMR 2D NOESY:** correlation between 6.26 (qt, *J* = 6.7, 1.6 Hz, 1H) and 2.65-2.59 (m, 2H); **IR** (neat): υ_{max} = 3050, 2907, 1483, 1430, 1090, 697cm^{-1}; **HRMS** (API+): calcd for $C_{23}H_{23}{}^{74}Ge$ ($M+H^+$) 373.1012, found 373.1015.



2-methyl-1,1-diphenyl-4,5-dihydro-1*H*-benzo[*b*]germepine 3'f

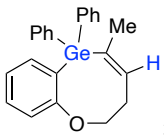
^{1}H NMR (300 MHz, $CDCl_3$): δ =δ = 7.44-7.34 (m, 4H), 7.30-7.23 (m, 4H), 7.18 (td, *J* = 7.5, 1.6 Hz, 1H), 7.15-7.04 (m, 4H), 7.01 (td, *J* = 7.2, 1.2 Hz, 1H), 6.45-6.38 (m, 1H), 2.86-2.76 (m, 2H), 2.50-2.41 (m, 2H), 1.77 (q, *J* = 1.9 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 149.7, 143.2, 137.0, 135.9, 135.3 (4C), 135.1 (2C), 134.8, 131.0, 129.7, 129.0 (2C), 128.4 (4C), 125.5, 35.8, 32.7, 26.2; **IR** (neat): υ_{max} = 3048, 2906, 1633, 1483, 1430, 1090, 698; **HRMS** (API+): calcd for $C_{23}H_{23}{}^{74}Ge$ ($M+H^+$) 373.1012, found 373.1021.



(*Z*)-4-ethylidene-5,5-diphenyl-2,3,4,5-tetrahydrobenzo[*b*][1,4]oxagermepine 3n

Prepared according to the general procedure for **hydrogermylation** using germane **2n** (168 mg, 0.434 mmol, 1 equiv.), hexane (1.5 ml), AIBN (11 mg, 0.065 mmol, 0.15 equiv.). Purification of the crude product (*Z* / 8-*endo-dig* = 28:72) by flash chromatography on silica gel (Cyclohexane/AcOEt = 99:1) afforded an inseparable **(*Z*)-3n/3'n** mixture in a 31/69 ratio (163 mg, 99%: 31% **(*Z*)-3n** + 68% **3'n**) as a colorless oil.

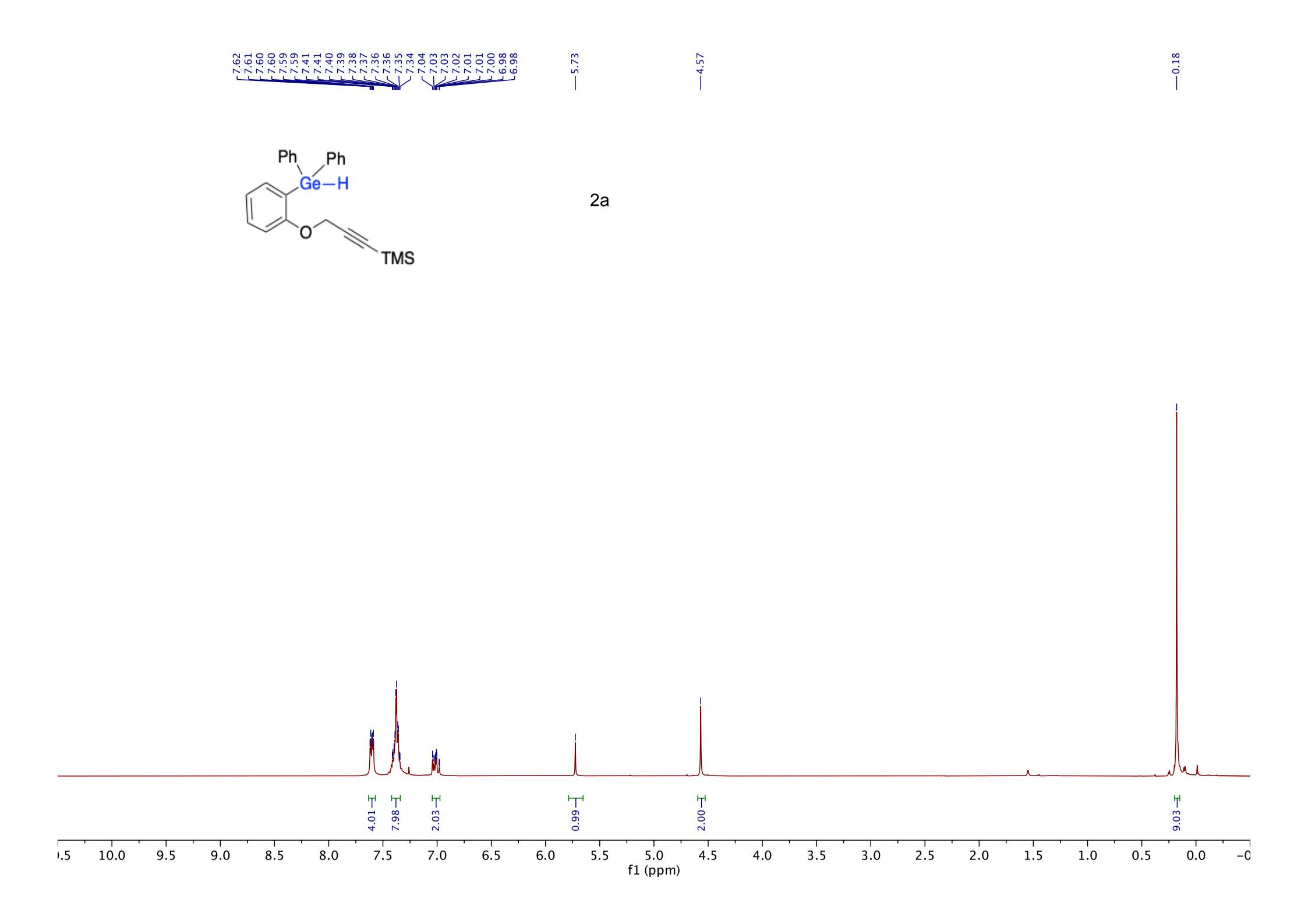
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83-7.77 (m, 4H), 7.54-7.47 (m, 9H), 7.35-7.28 (m, 1H), 6.63-6.44 (m, 1H), 4.32 (t, *J* = 5.9 Hz, 2H), 2.70 (t, *J* = 5.9 Hz, 2H), 1.78 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ =160.8, 136.4 (2C), 135.2 (4C), 134.9, 134.6, 134.2, 134.1, 131.3, 129.0 (2C), 128.3 (4C), 124.7, 121.5, 74.6, 25.2, 19.4; **NMR 2D NOESY:** correlation between 2.70 (t, *J* = 5.9 Hz, 2H) and 6.63-6.44 (m, 1H); **HRMS** (API+): calcd for $C_{25}H_{26}{}^{74}GeNO$ $(M+H+ACN)^+$ 430.1226, found 430.1219.



5-methyl-6,6-diphenyl-3,6-dihydro-2*H*-benzo[*b*][1, 4]oxagermocine 3'n

^{1}H NMR (300 MHz, $CDCl_3$): δ =7.72-7.66 (m, 4H), 7.54-7.46 (m, 6H), 7.35-7.28 (m, 2H), 7.22 (dd, *J* = 8.0, 3.4 Hz, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.63-6.44 (m, 1H), 4.22 (t, *J* = 5.3 Hz, 2H),

2.39 (dt, *J* = 7.5, 5.3 Hz, 2H), 2.05 (brs, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 161.4, 139.9, 137.3,136.7, 136.6 (2C), 135.4 (4C), 134.8, 131.5, 128.9 (2C), 128.3 (4C), 124.4, 122.1, 73.8, 38.4, 24.9; **IR** (neat): υ_{max} = 3041, 2865, 1583, 1466, 1431, 1089, 697; **HRMS** (API+): calcd for $C_{25}H_{26}{}^{72}GeNO$ $(M+H+ACN)^+$ 428.1235, found 428.1237.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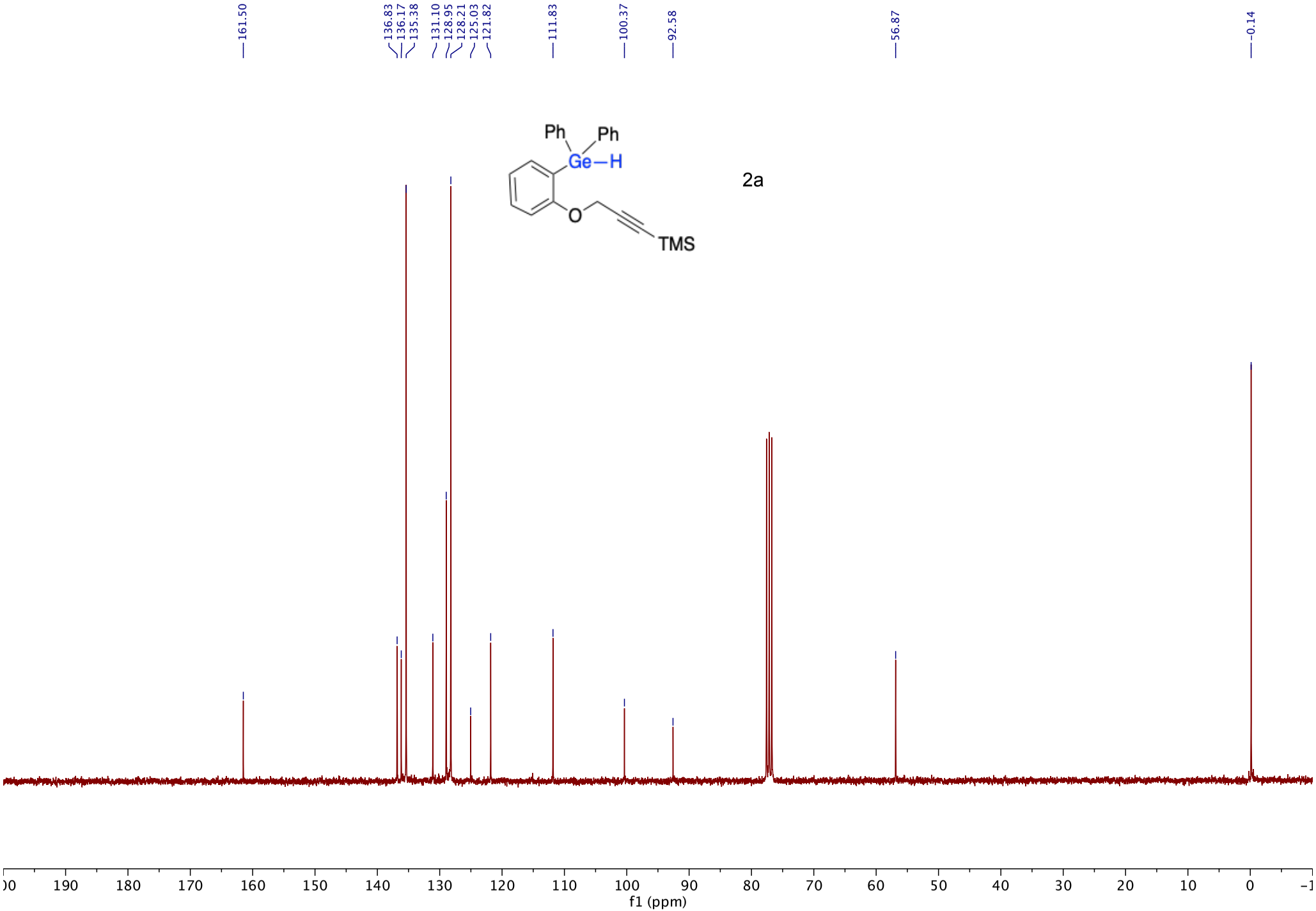
7.60
7.59
7.59
7.41
7.41
7.40
7.39
7.38
7.37
7.36
7.36
7.35
7.34
7.04
7.03
7.03
7.02
7.01
7.01
7.00
6.98
6.98
5.73
4.57
0.18
Ph
Ph
Ge—H
O
TMS
2a
4.01
7.98
2.03
0.99
2.00
9.03
f1 (ppm)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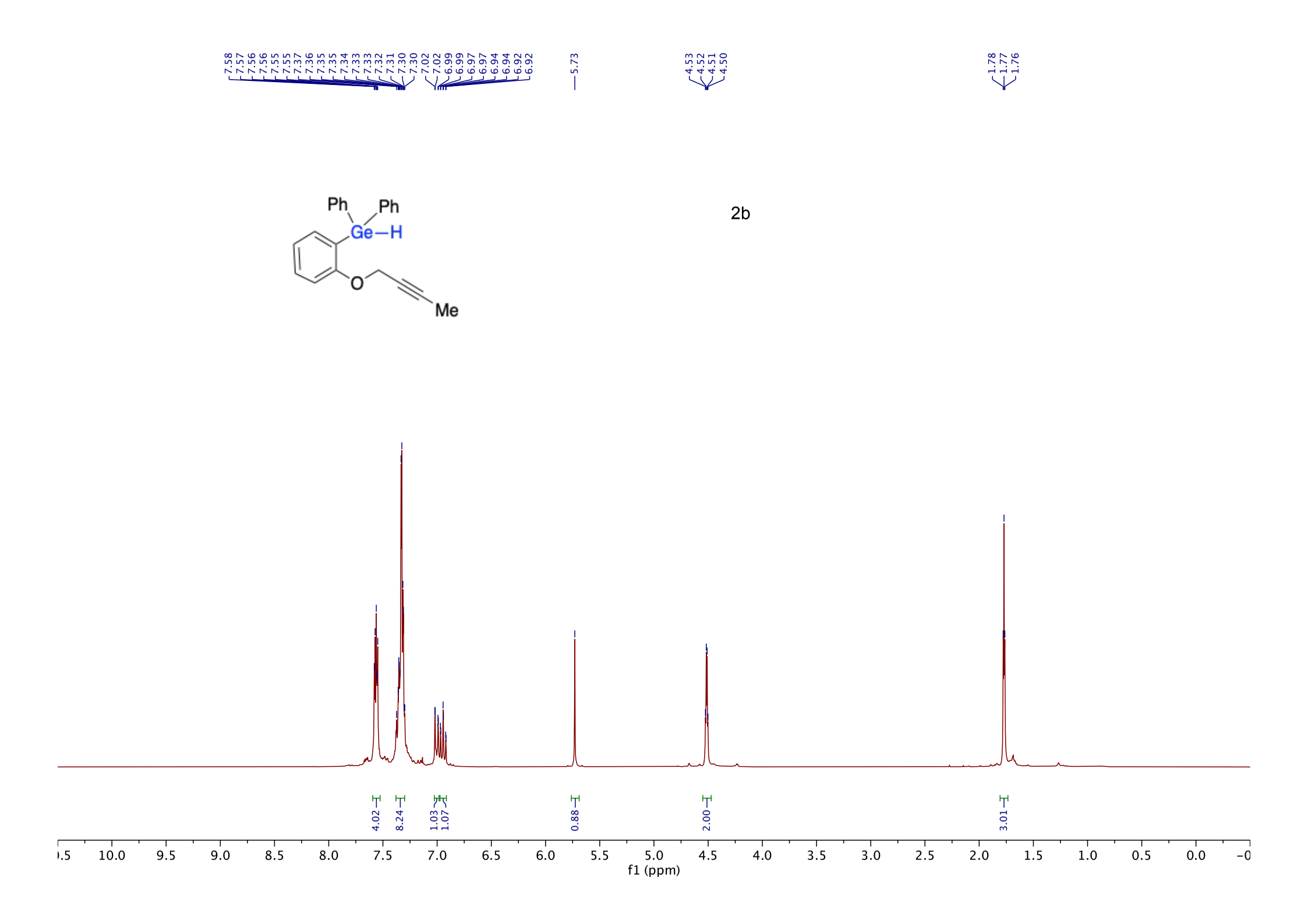
136.83
136.17
135.38
131.10
128.95
128.21
125.03
121.82
111.83
100.37
92.58
56.87
-0.14
Ph
Ph
Ge—H
O
TMS
2a
f1 (ppm)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7.57
7.56
7.56
7.55
7.55
7.37
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.30
7.02
7.02
6.99
6.99
6.97
6.97
6.94
6.94
6.92
6.92
5.73
4.53
4.52
4.51
4.50
1.78
1.77
1.76
Ph
Ph
Ge—H
O
Me
2b
4.02
8.24
1.03
1.07
0.88
2.00
3.01
f1 (ppm)

Ph
Ge—H
Ph
O
Me
2b
161.55
136.76
136.14
135.35
131.10
128.90
128.16
124.77
121.58
111.69
83.45
74.27
56.49
3.76
f1 (ppm)


7.57
7.56
7.55
7.55
7.54
7.34
7.33
7.33
7.32
7.31
7.30
7.29
7.27
7.26
7.25
7.25
7.24
7.23
7.18
7.18
7.17
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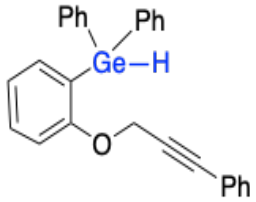
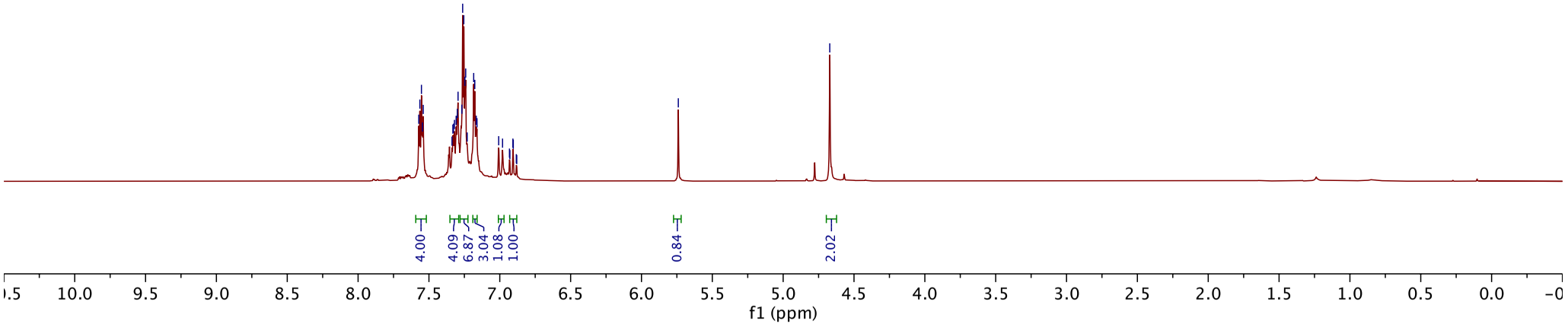
6.93
6.93
6.91
6.90
6.88
6.88
5.74
4.67

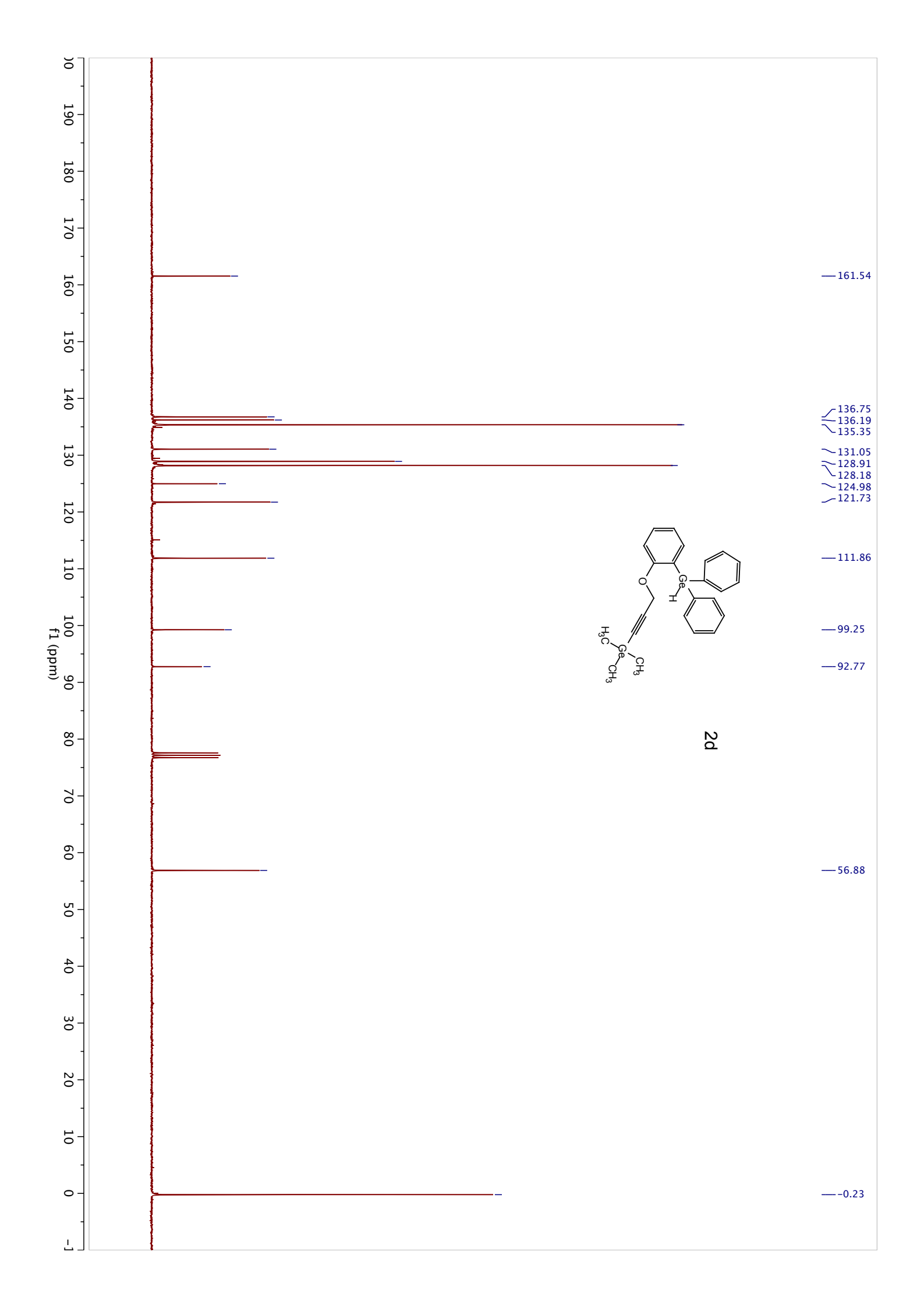

Ph
Ph
Ge—H
O
Ph

2c


4.00
4.09
6.87
3.04
1.08
1.00
0.84
2.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

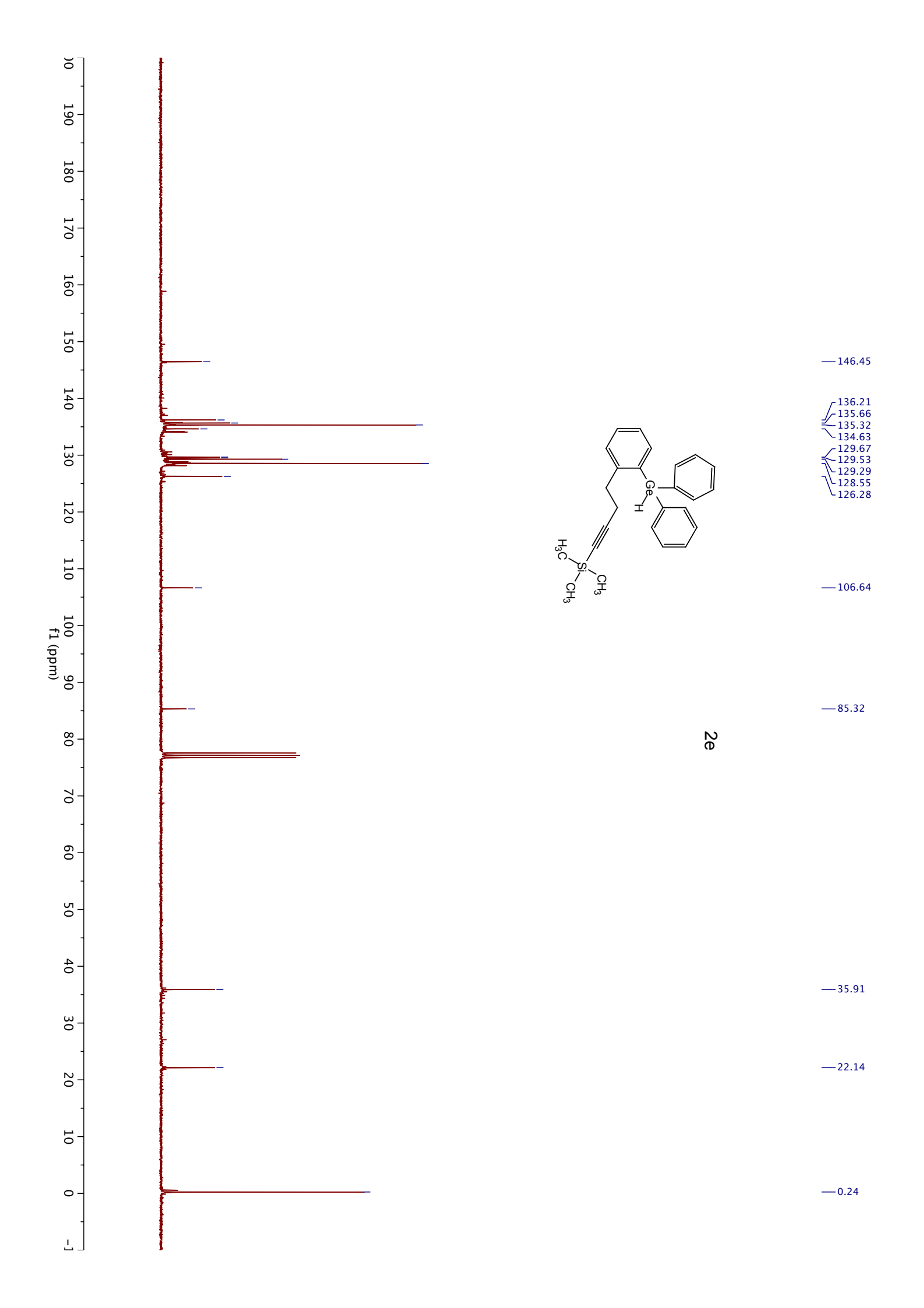
f1 (ppm)
161.40
136.82
136.05
135.30
131.76
131.13
128.90
128.61
128.32
128.18
124.91
122.46
121.80
111.73
87.08
84.19
56.62
Ph
Ge—H
Ph
O
Ph
2c

10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
4.03
8.00
1.03
1.05
0.96
2.00
9.03
7.60
7.59
7.58
7.58
7.58
7.57
7.57
7.40
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.35
7.34
7.34
7.34
7.34
7.33
7.32
7.05
7.04
7.02
7.02
7.01
7.00
6.98
6.98
6.96
6.95
5.71
4.55
1.53
0.34
O
Ge
H
H3C
Ge
CH3
CH3
2d


f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
161.54
136.75
136.19
135.35
131.05
128.91
128.18
124.98
121.73
111.86
99.25
92.77
56.88
-0.23
O
Ge
H
H3C
Ge
CH3
CH3
2d

10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
4.00
10.03
0.91
2.02
2.01
9.02
7.52
7.51
7.51
7.50
7.50
7.49
7.49
7.48
7.48
7.39
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.33
5.84
2.91
2.89
2.86
2.34
2.31
2.29
0.13
Ge
H
H3C
Si
CH3
CH3

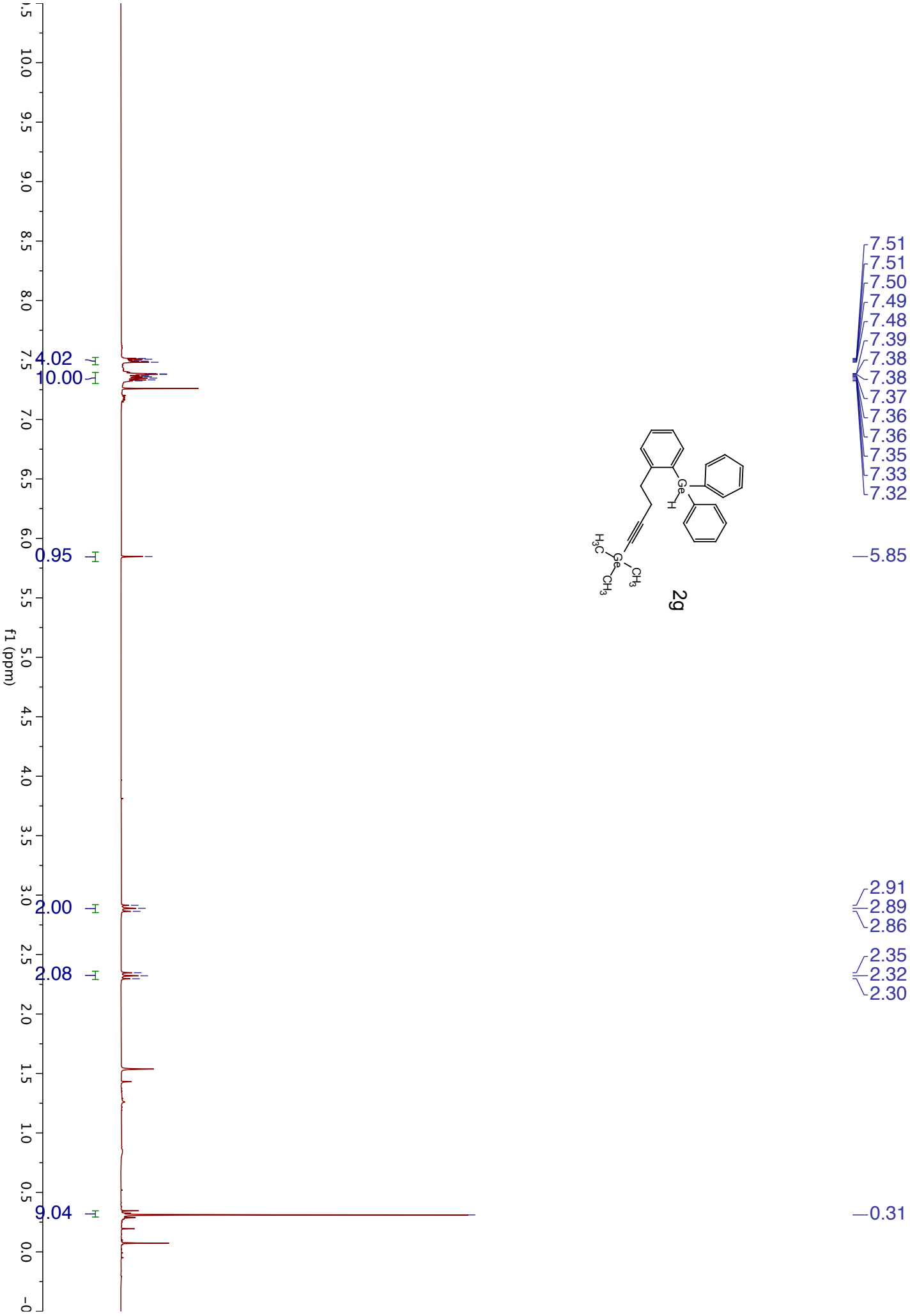
2e


f1 (ppm)
210
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
146.45
136.21
135.66
135.32
134.63
129.67
129.53
129.29
128.55
126.28
106.64
85.32
35.91
22.14
0.24
Ge
H
Si
H3C
CH3
CH3
2e

f1 (ppm)
3.99
9.02
0.98
0.94
2.00
2.03
3.02
7.51
7.50
7.49
7.49
7.48
7.40
7.38
7.37
7.36
7.36
7.34
7.33
7.33
7.32
7.26
7.20
7.19
7.18
7.17
7.15
7.15
5.86
2.89
2.87
2.84
2.29
2.28
2.27
2.26
2.25
2.24
2.24
2.23
1.74
1.73
1.73
1.54
Ge
H
CH3

2f

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)
146.83
136.16
135.71
135.32
134.69
129.71
129.23
129.19
128.49
126.15
78.55
76.28
36.36
21.10
3.61
Ge
H
CH3
2f


f1 (ppm)
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2.00
2.08
9.04
7.51
7.51
7.50
7.49
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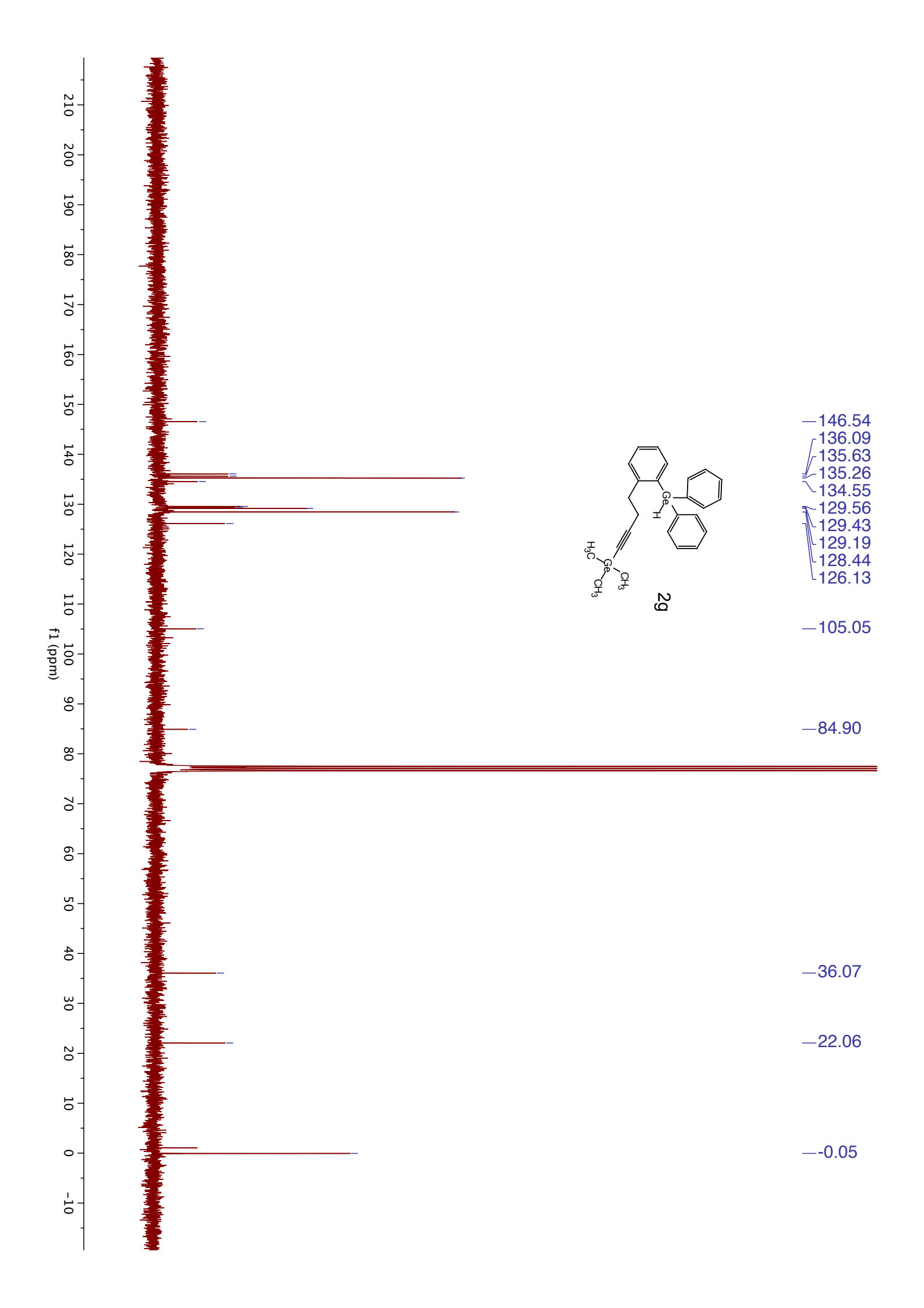
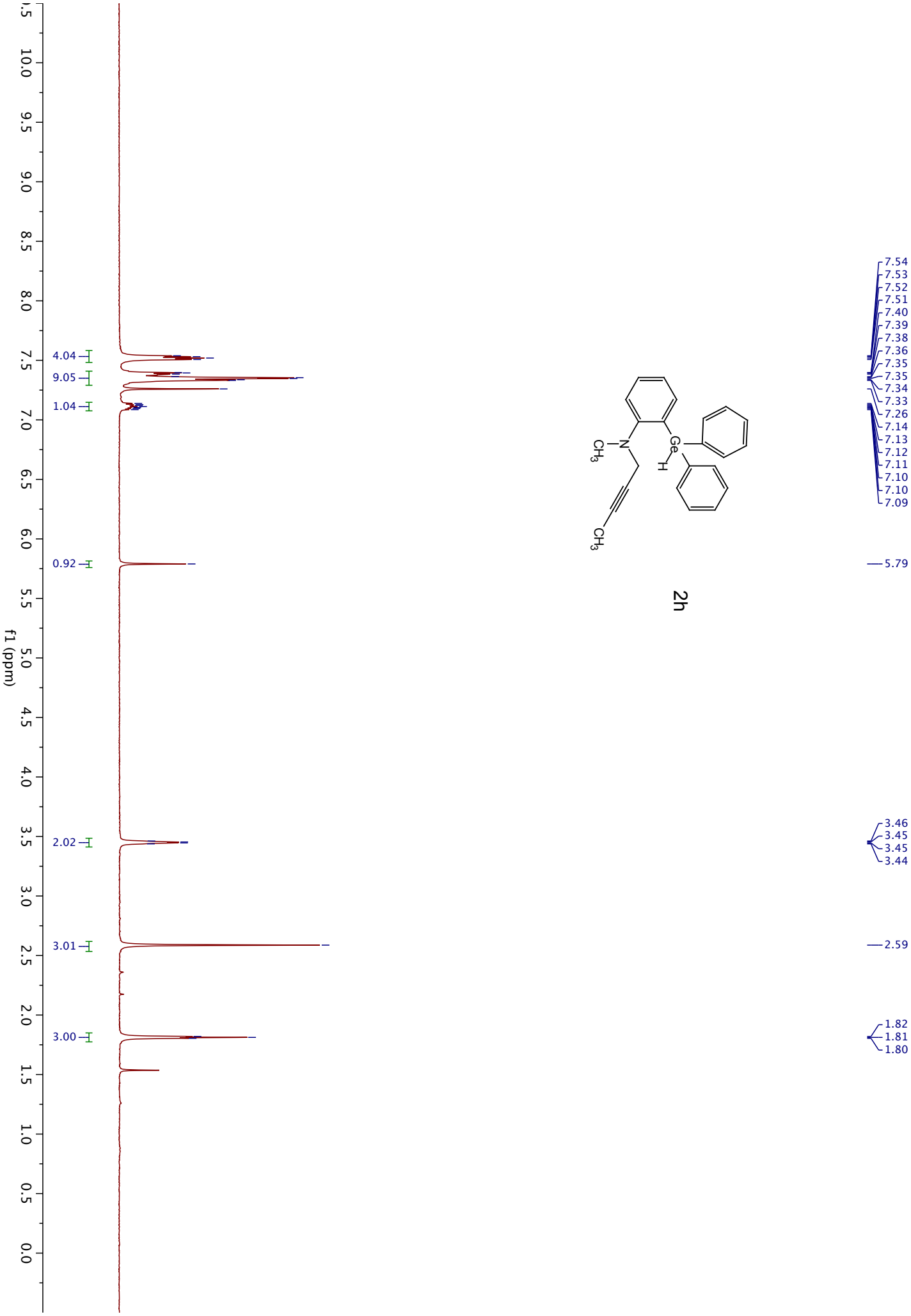
7.38
7.38
7.37
7.36
7.36
7.35
7.33
7.32
5.85
2.91
2.89
2.86
2.35
2.32
2.30
0.31
2g


f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
146.54
136.09
135.63
135.26
134.55
129.56
129.43
129.19
128.44
126.13
105.05
84.90
36.07
22.06
-0.05
Ge
H
H3C
Ge
CH3
CH3
2g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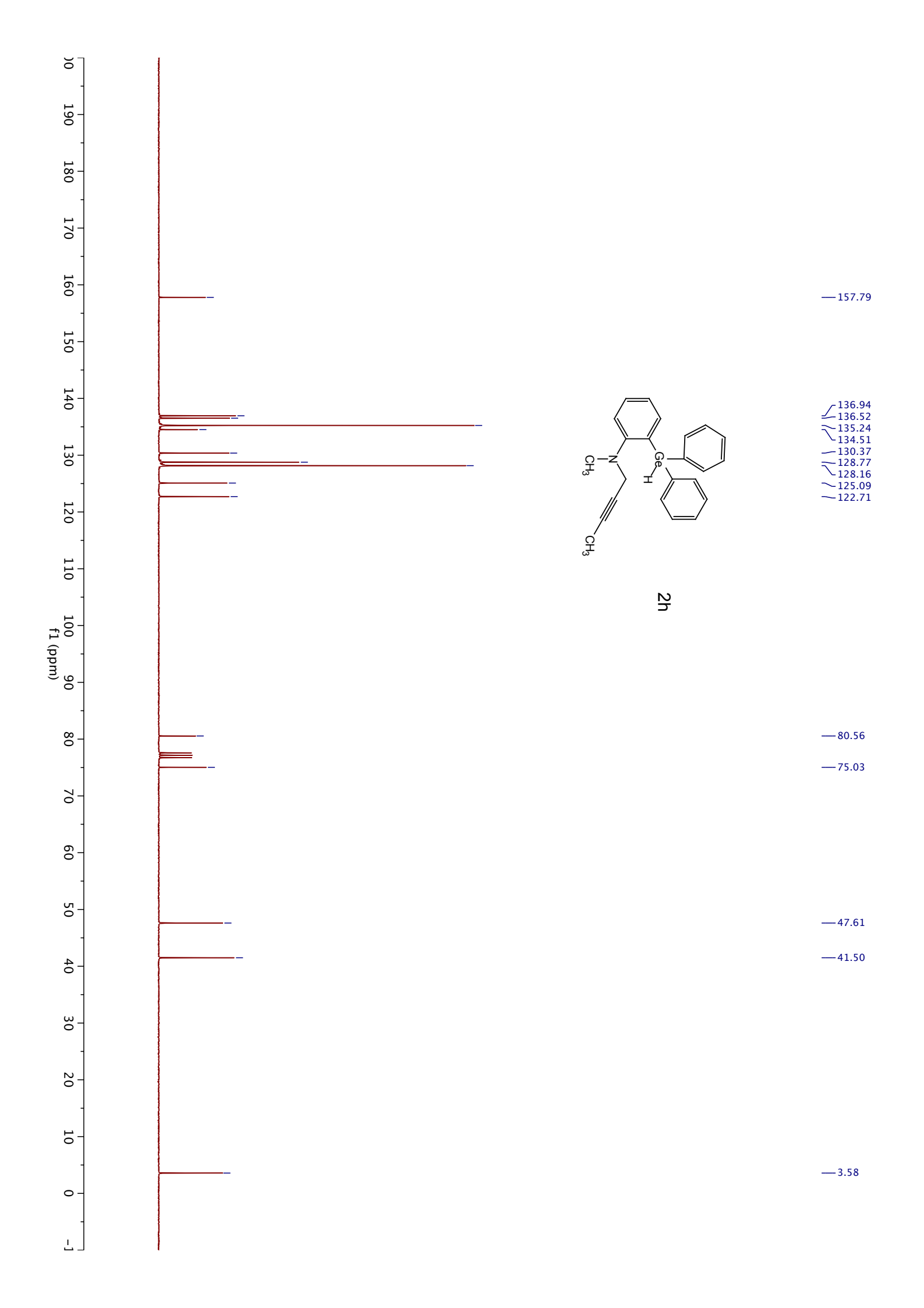
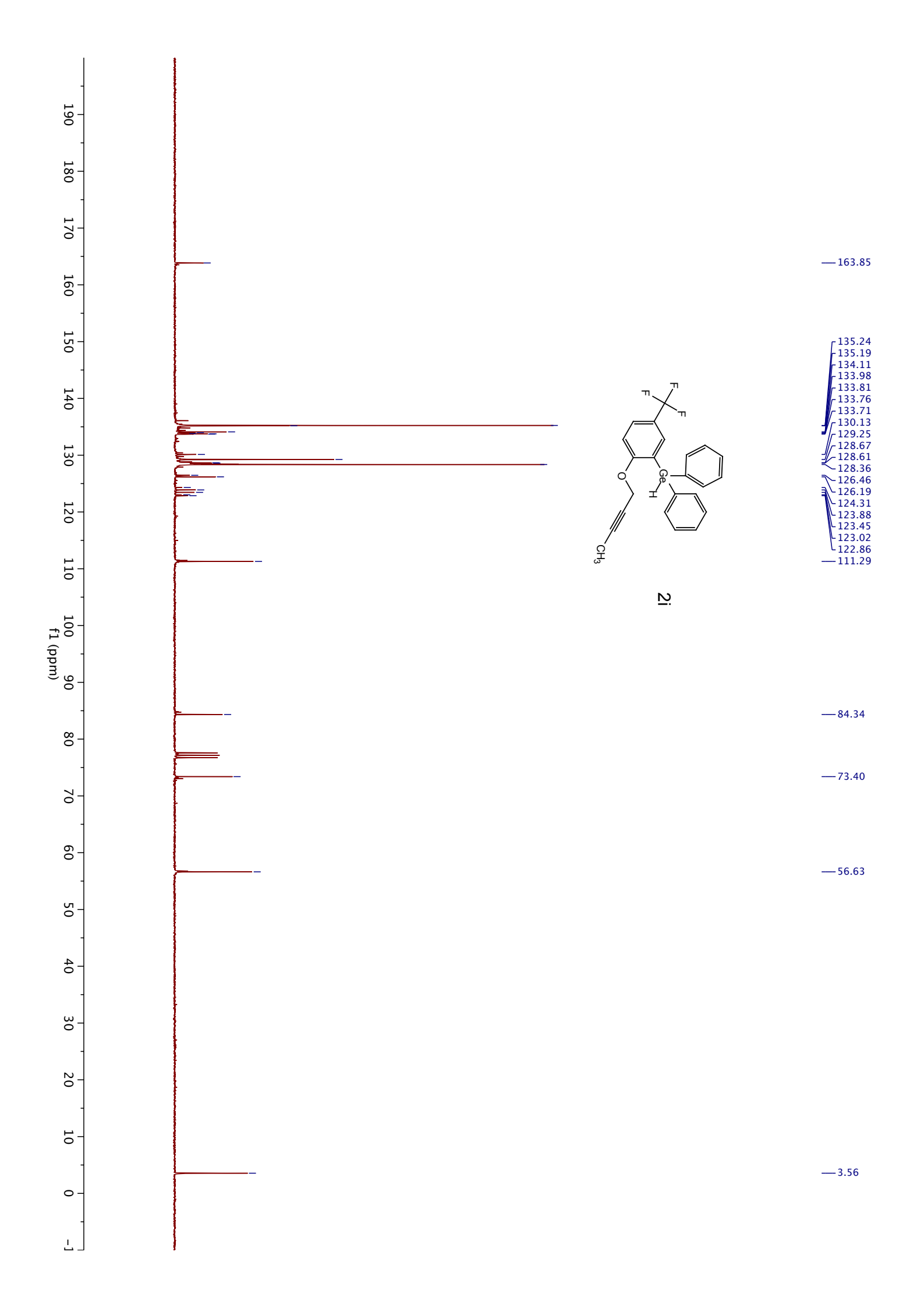
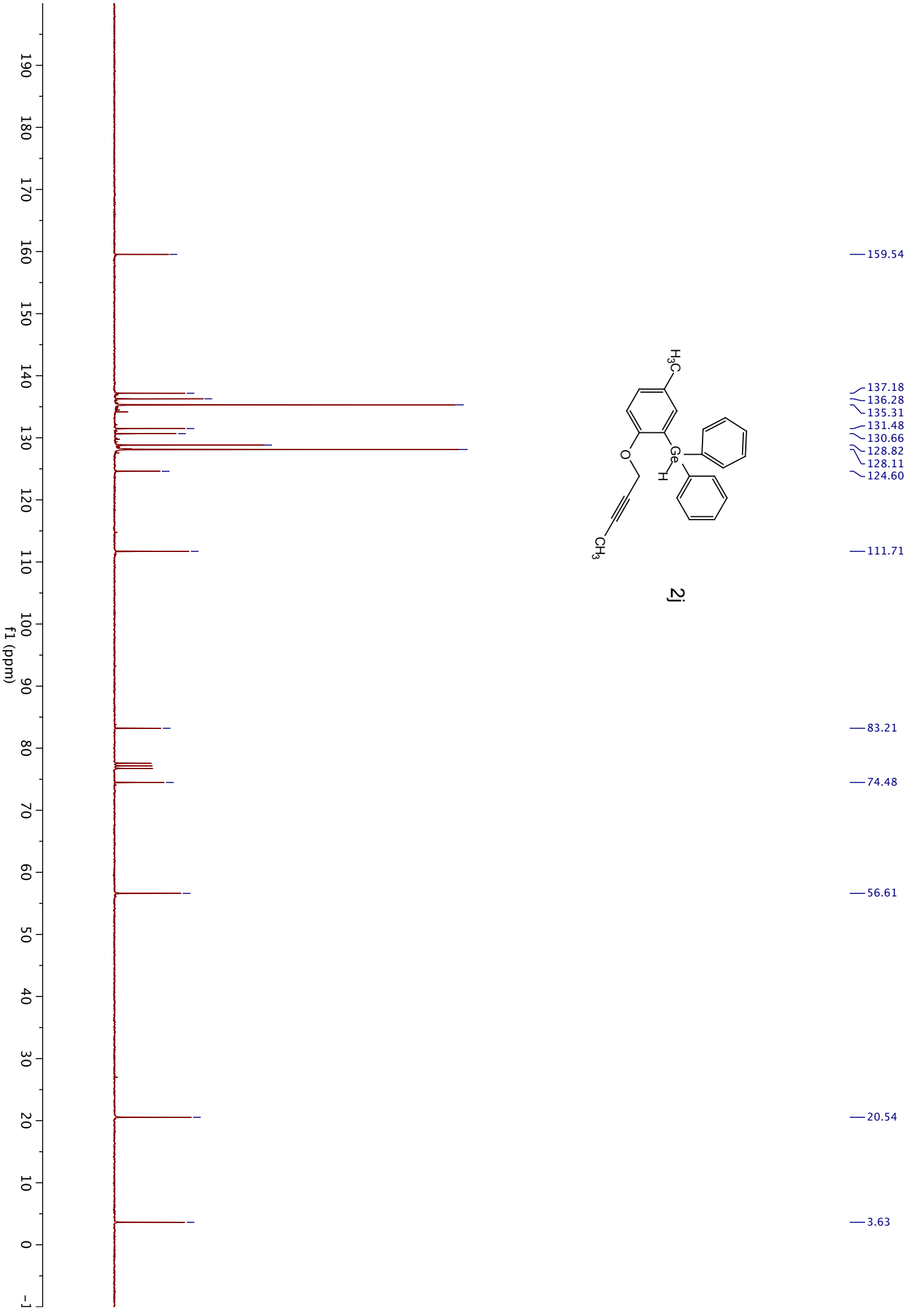
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
4.04
9.05
1.04
0.92
2.02
3.01
3.00
7.54
7.53
7.52
7.51
7.40
7.39
7.38
7.36
7.35
7.35
7.34
7.33
7.26
7.14
7.13
7.12
7.11
7.10
7.10
7.09
5.79
3.46
3.45
3.45
3.44
2.59
1.82
1.81
1.80
N
CH3
Ge
H
CH3
2h


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)
157.79
136.94
136.52
135.24
134.51
130.37
128.77
128.16
125.09
122.71
80.56
75.03
47.61
41.50
3.58
N
CH3
Ge
H
CH3
2h

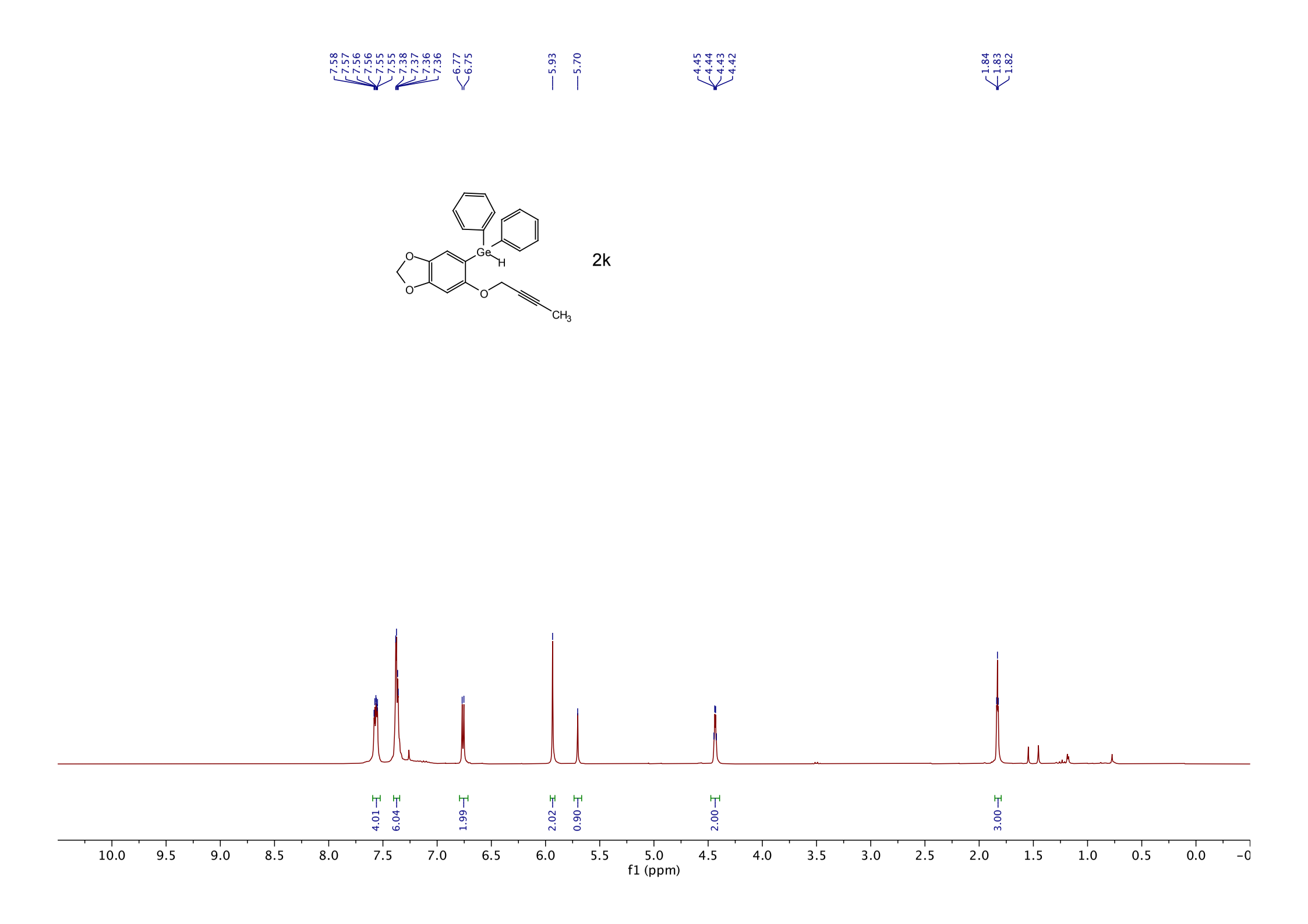
f1 (ppm)
2.04
3.96
6.03
1.05
0.82
2.01
3.00
7.65
7.63
7.57
7.56
7.55
7.55
7.54
7.42
7.39
7.38
7.37
7.37
7.36
7.35
7.34
7.26
7.09
7.06
5.72
4.60
4.59
1.83
1.82
1.81
F
F
F
O
Ge
H
CH3
2i

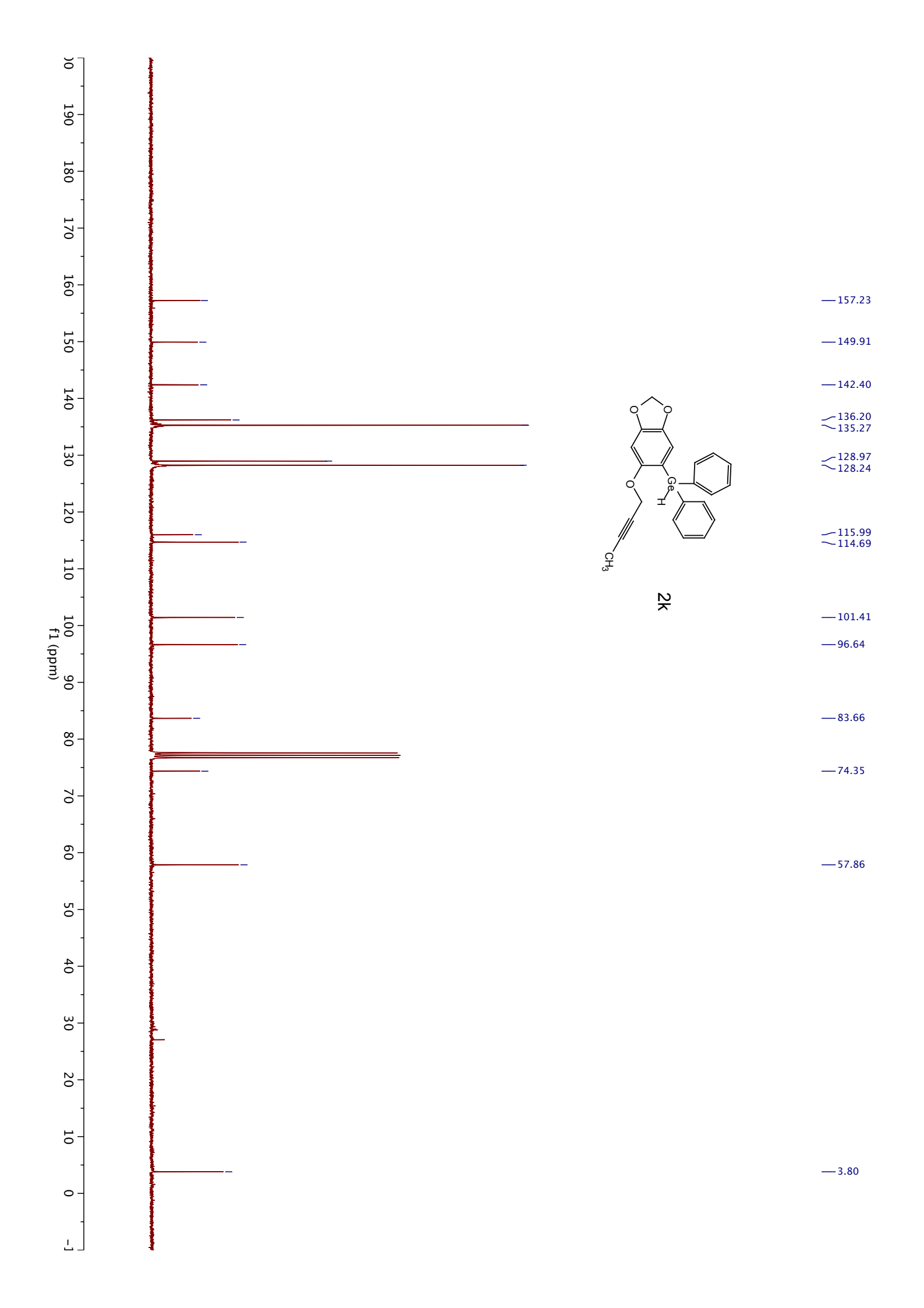

f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
163.85
135.24
135.19
134.11
133.98
133.81
133.76
133.71
130.13
129.25
128.67
128.61
128.36
126.46
126.19
124.31
123.88
123.45
123.02
122.86
111.29
84.34
73.40
56.63
3.56
F
F
F
O
Ge
H
CH3
2i

f1 (ppm)
4.03
6.08
2.00
0.99
0.88
2.00
3.00
3.02
7.58
7.58
7.57
7.56
7.56
7.55
7.37
7.36
7.35
7.34
7.33
7.26
7.16
6.95
6.92
5.68
4.50
4.49
2.25
1.81
H3C
O
Ge
H
CH3
2j

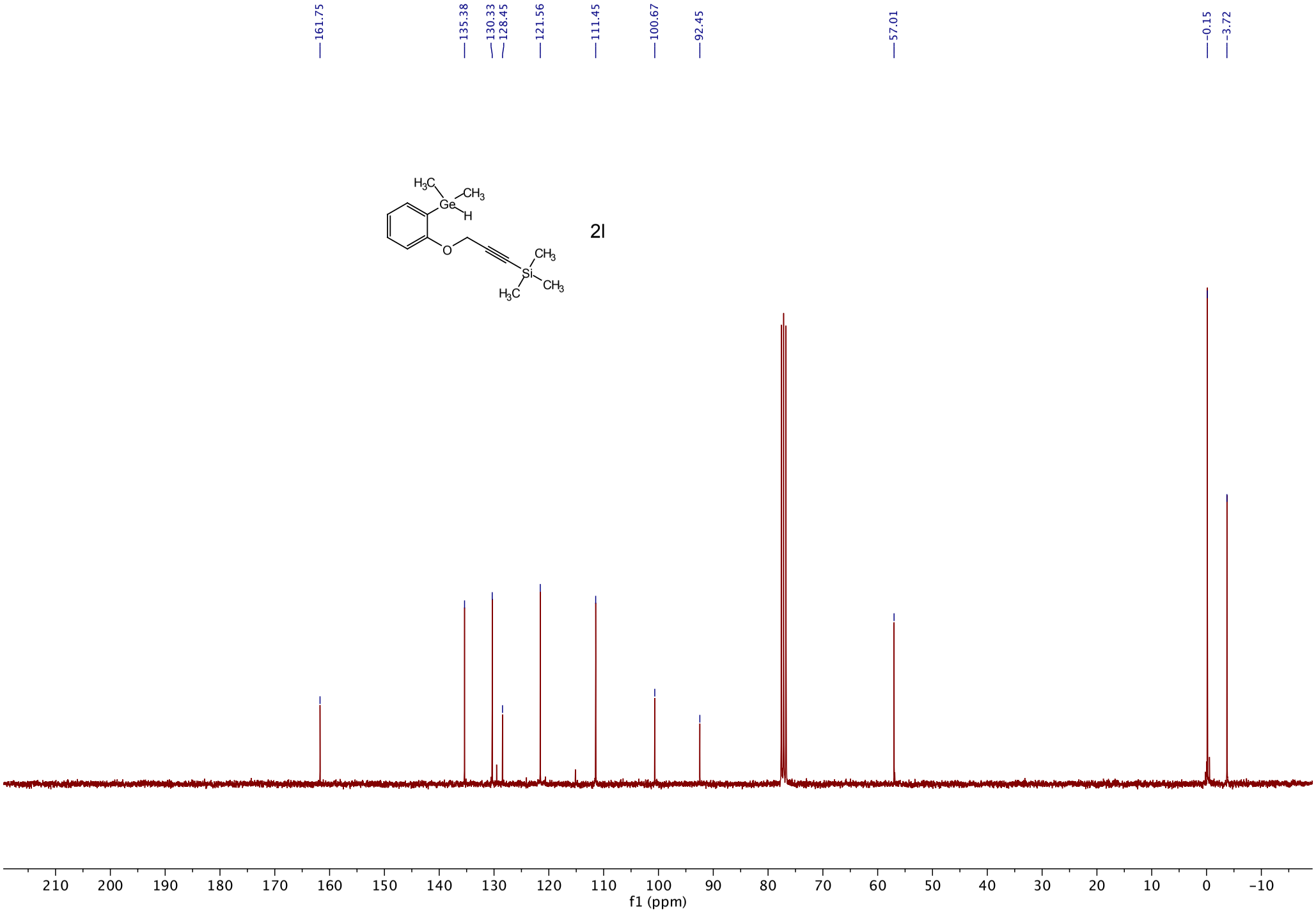

159.54
137.18
136.28
135.31
131.48
130.66
128.82
128.11
124.60
111.71
83.21
74.48
56.61
20.54
3.63
f1 (ppm)
H3C
O
Ge
H
CH3

2j


7.58
7.57
7.56
7.56
7.55
7.55
7.38
7.37
7.36
7.36
6.77
6.75
5.93
5.70
4.45
4.44
4.43
4.42
1.84
1.83
1.82
Ge
H
O
O
O
CH3
2k
4.01
6.04
1.99
2.02
0.90
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
157.23
149.91
142.40
136.20
135.27
128.97
128.24
115.99
114.69
101.41
96.64
83.66
74.35
57.86
3.80
O
O
O
Ge
H
CH3
2k

f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
1.03
1.04
1.03
1.02
2.01
0.94
6.00
9.10
7.43
7.43
7.41
7.40
7.36
7.36
7.34
7.34
7.33
7.33
7.31
7.31
7.02
7.02
7.00
6.99
6.97
6.97
6.97
6.96
6.94
6.94
4.68
4.50
4.49
4.48
4.47
4.46
4.45
4.44
0.50
0.49
0.18
H3C
Ge
CH3
H
O
H3C
Si
CH3
CH3
2l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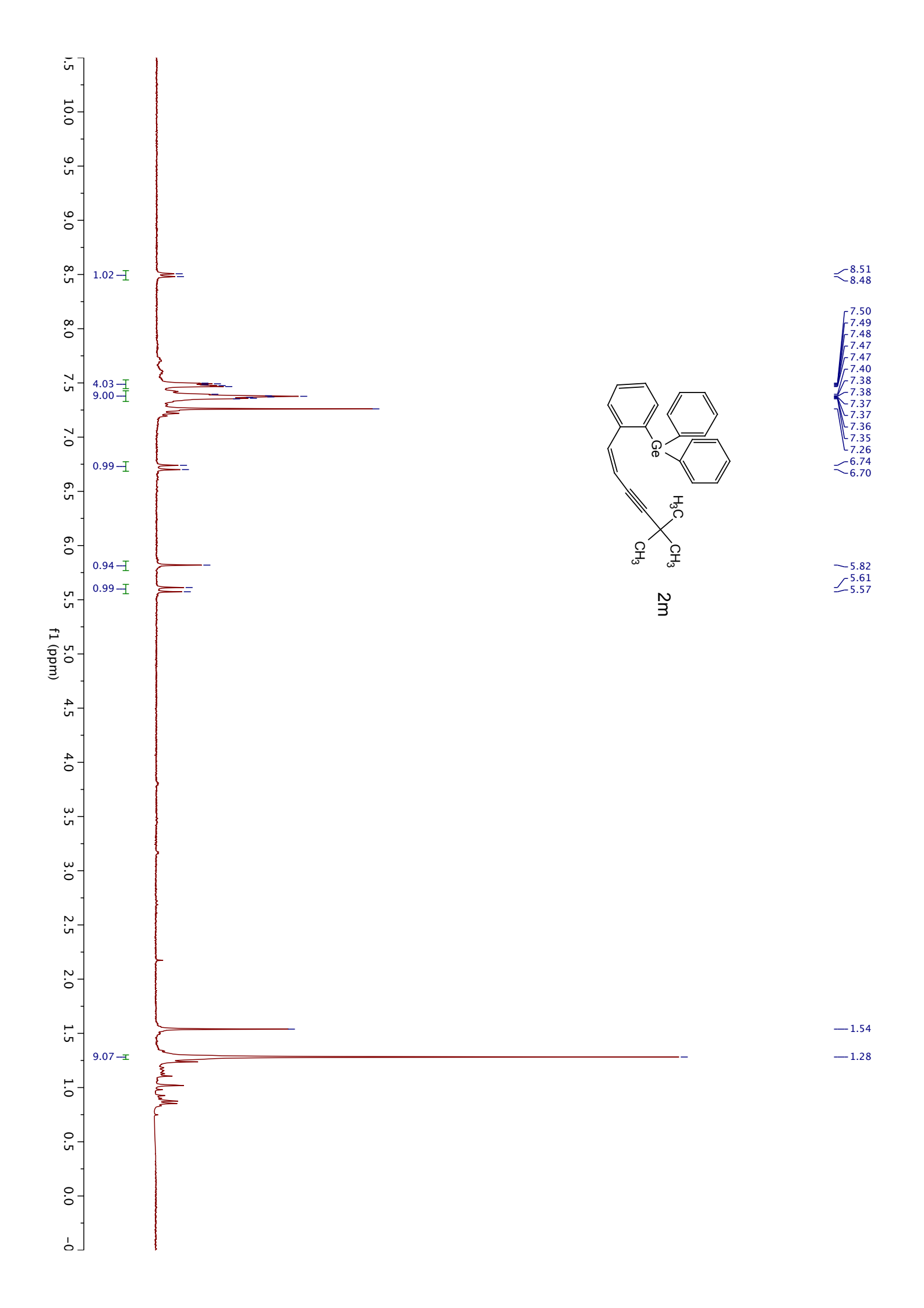
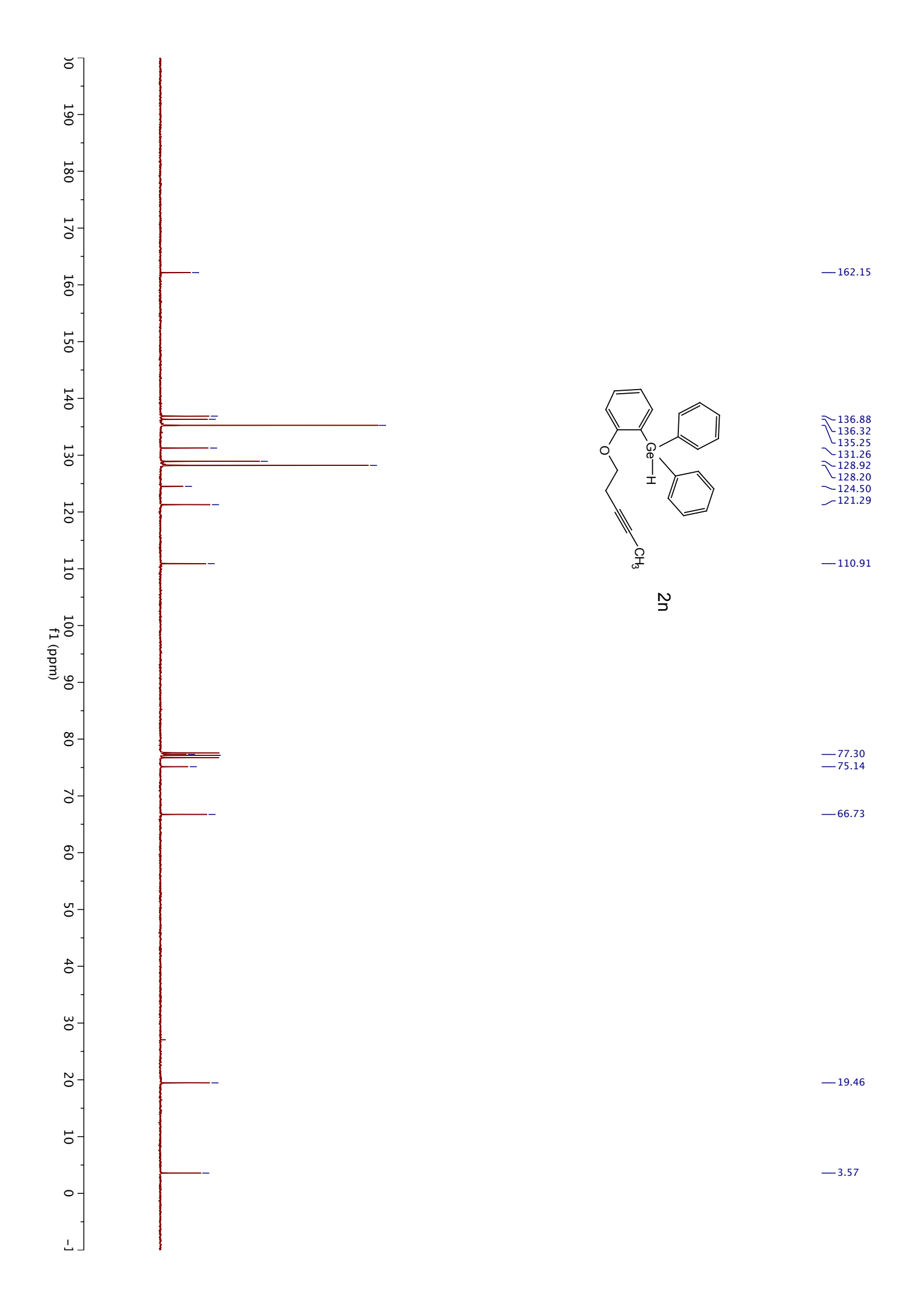
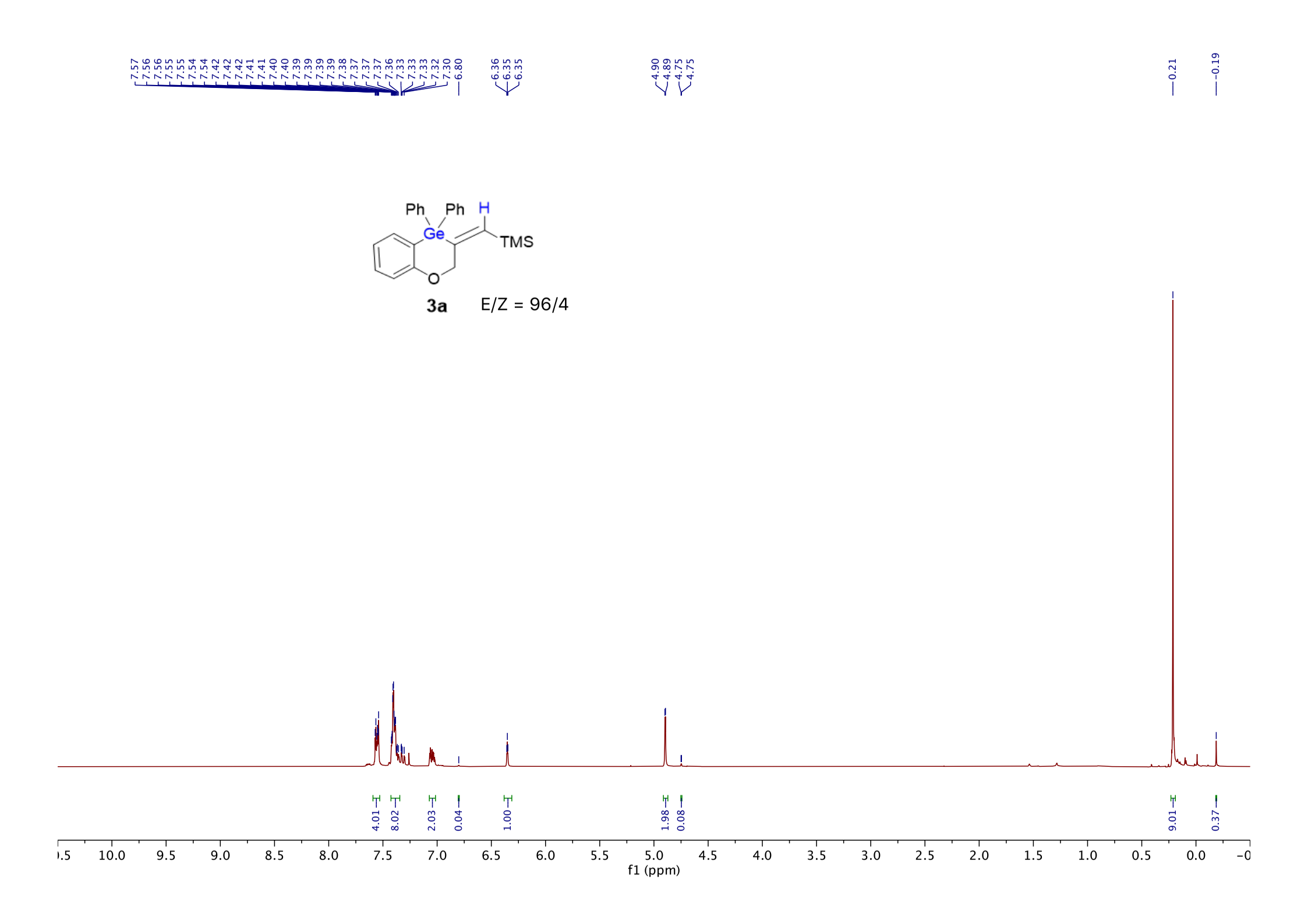
135.38
130.33
128.45
121.56
111.45
100.67
92.45
57.01
-0.15
-3.72
H3C
CH3
Ge
H
O
CH3
Si
CH3
H3C
2l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


f1 (ppm)
1.02
4.03
9.00
0.99
0.94
0.99
9.07
8.51
8.48
7.50
7.49
7.48
7.47
7.47
7.40
7.38
7.38
7.37
7.37
7.36
7.35
7.26
6.74
6.70
5.82
5.61
5.57
1.54
1.28
Ge
H3C
CH3
CH3
2m

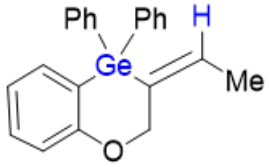
Ge
H3C
CH3
CH3
2m
137.30
136.88
135.48
134.20
129.71
129.13
128.86
128.65
128.39
128.22
128.16
108.33
105.64
78.09
30.89
28.79
f1 (ppm)

f1 (ppm)
4.01
8.00
1.02
1.02
0.86
2.04
1.99
2.95
7.62
7.62
7.61
7.60
7.59
7.43
7.42
7.41
7.41
7.41
7.40
7.39
7.38
7.38
7.03
7.02
7.00
7.00
6.98
6.97
6.92
6.90
5.75
4.02
3.99
3.97
2.34
2.33
2.32
2.31
2.31
2.30
2.29
2.28
1.77
1.77
1.76
O
Ge
H
CH3
2n

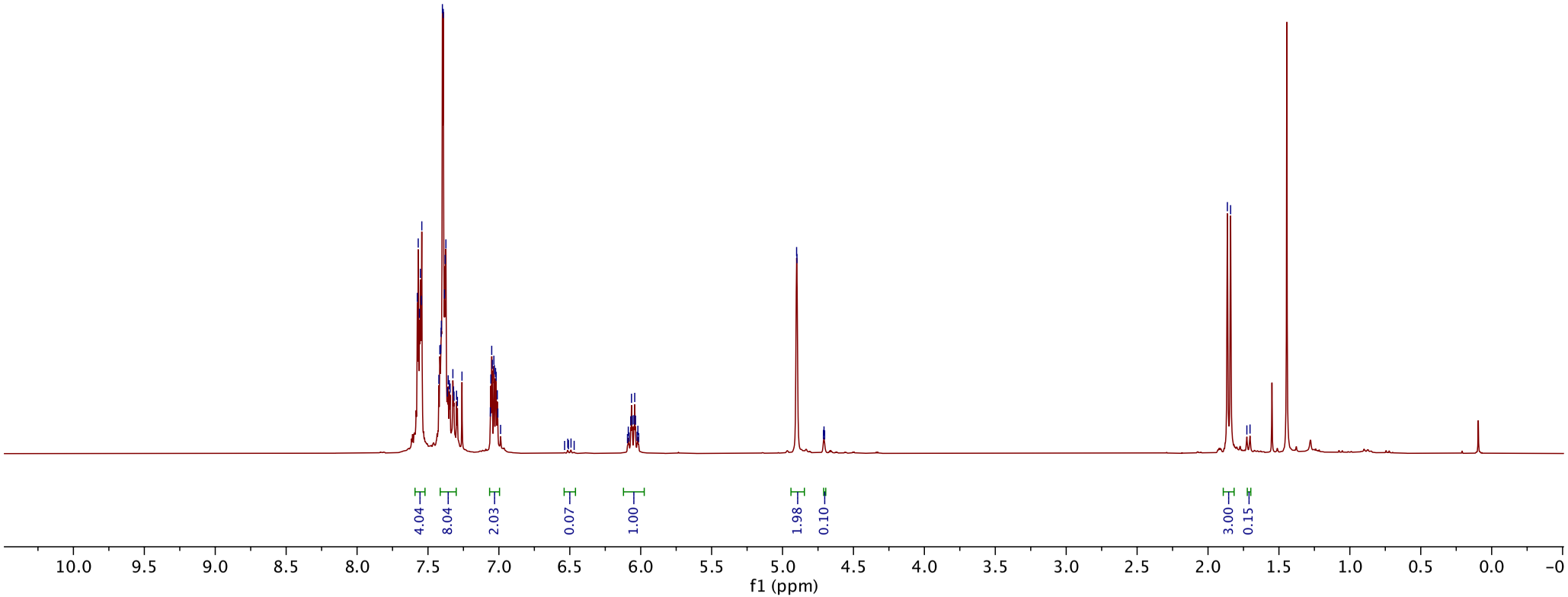

f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
162.15
136.88
136.32
135.25
131.26
128.92
128.20
124.50
121.29
110.91
77.30
75.14
66.73
19.46
3.57
O
Ge
H
CH3
2n

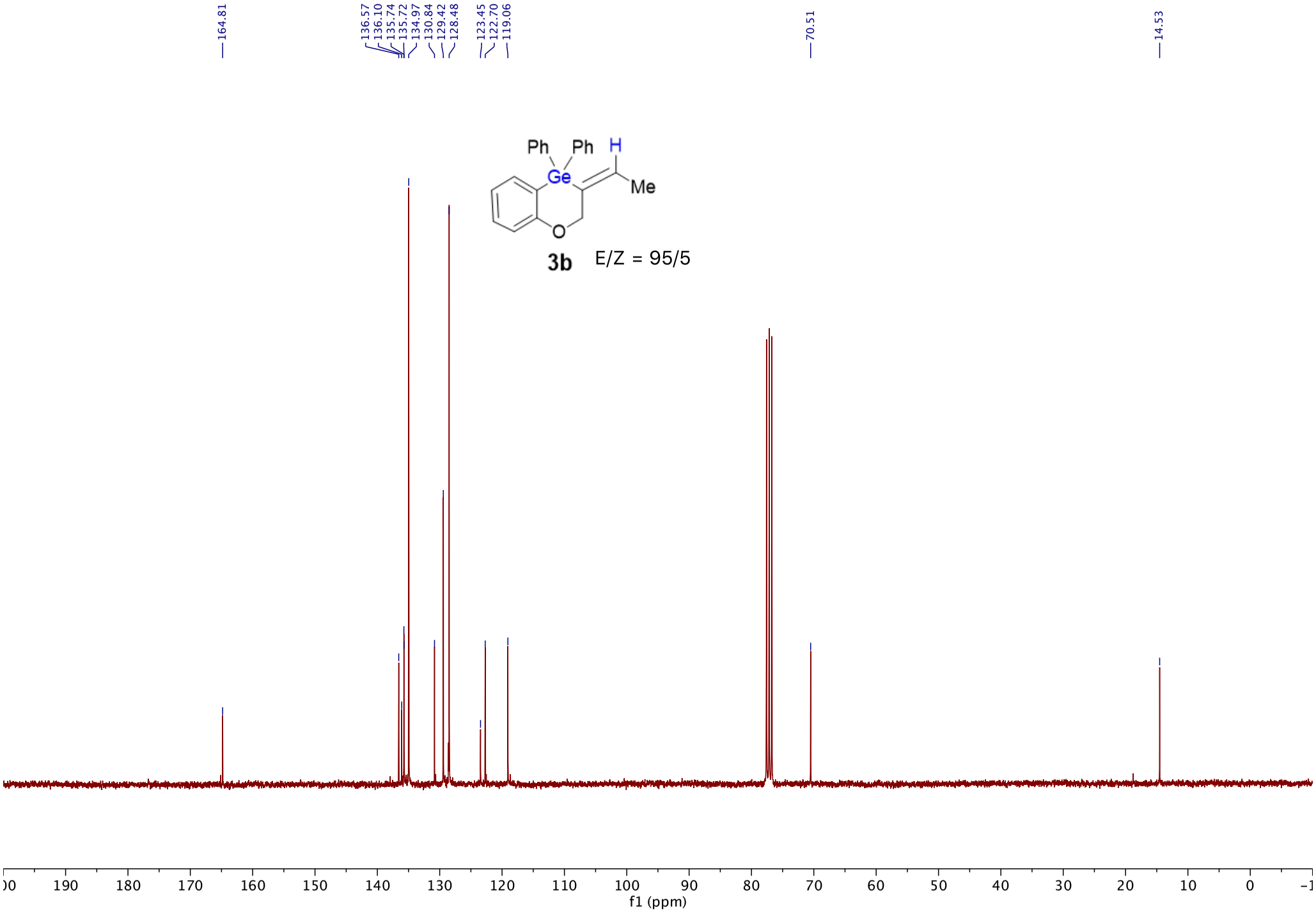

7.57
7.56
7.56
7.55
7.55
7.54
7.54
7.42
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.39
7.39
7.38
7.37
7.37
7.37
7.36
7.33
7.33
7.32
7.30
6.80
6.36
6.35
6.35
4.90
4.89
4.75
4.75
0.21
-0.19
Ph
Ph
H
Ge
TMS
O
3a
E/Z = 96/4
4.01
8.02
2.03
0.04
1.00
1.98
0.08
9.01
0.37
f1 (ppm)

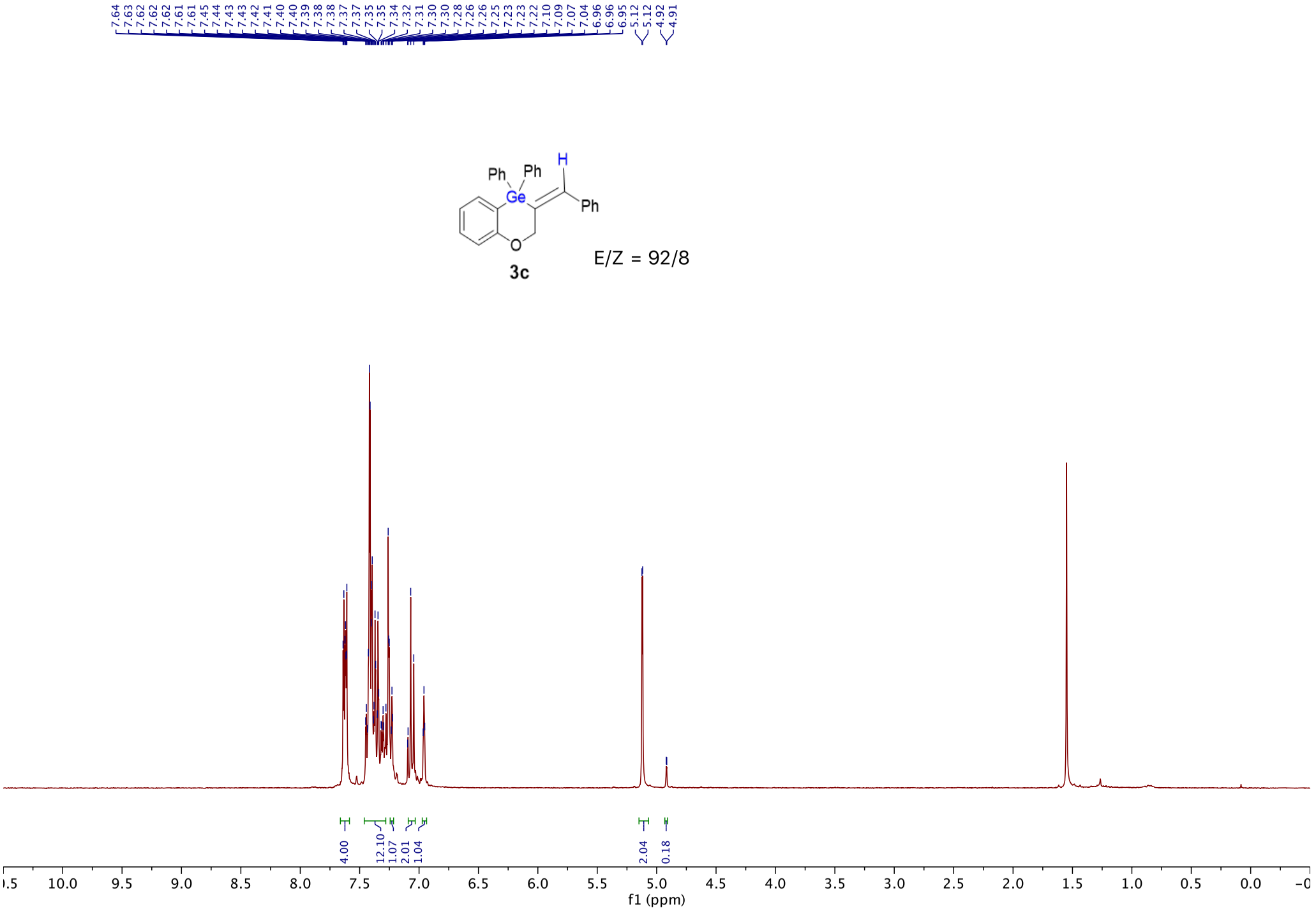
164.73
156.99
145.25
135.79
135.55
134.99
130.85
129.45
128.52
123.87
122.88
119.02
75.41
0.44
Ph
Ph
Ge
O
H
TMS
3a
E/Z = 96/4
f1 (ppm)



3b *E*/*Z* = 95/5



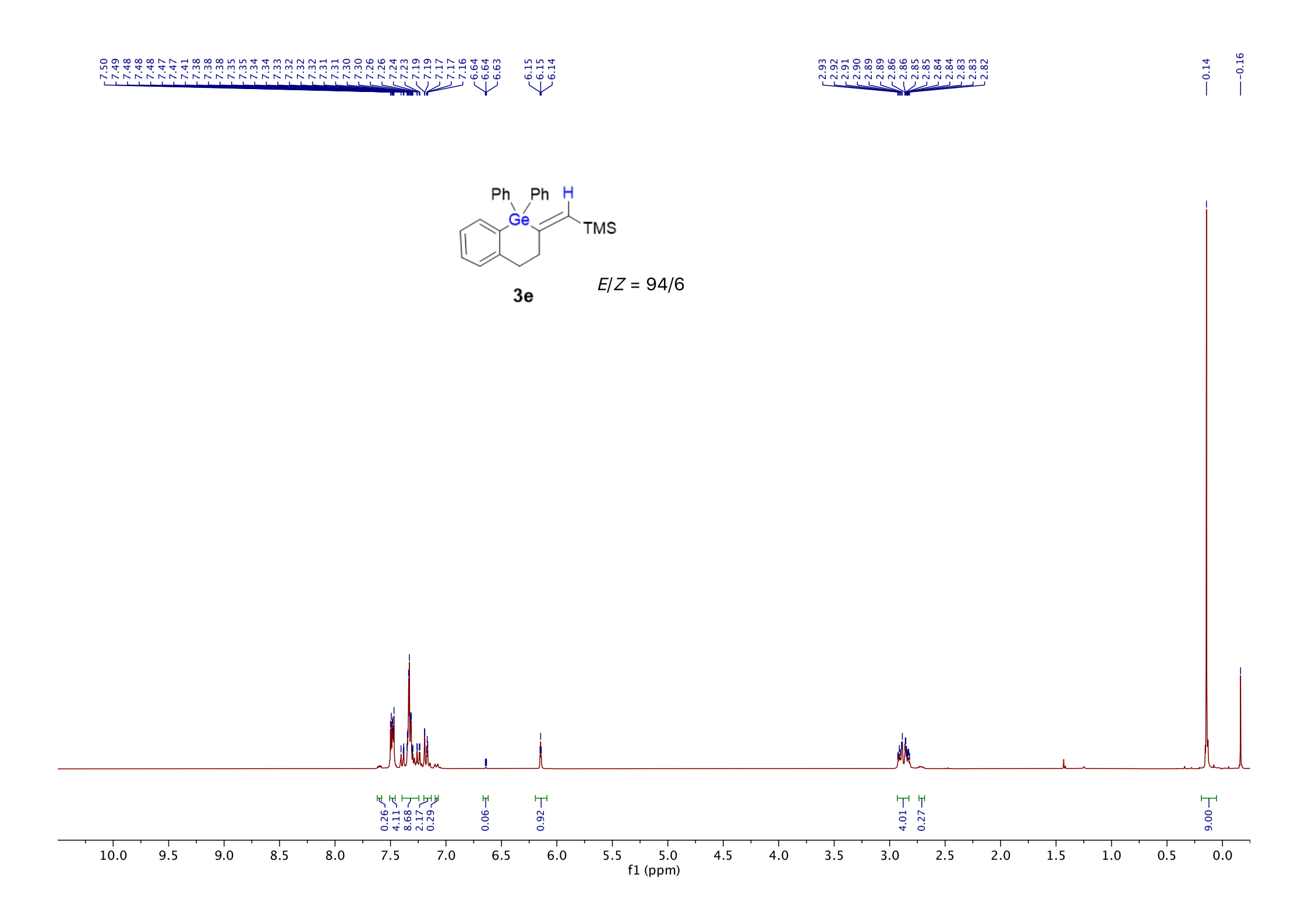

164.81
136.57
136.10
135.74
135.72
134.97
130.84
129.42
128.48
123.45
122.70
119.06
70.51
14.53
Ph
Ph
H
Ge
Me
O
3b
E/Z = 95/5
f1 (ppm)

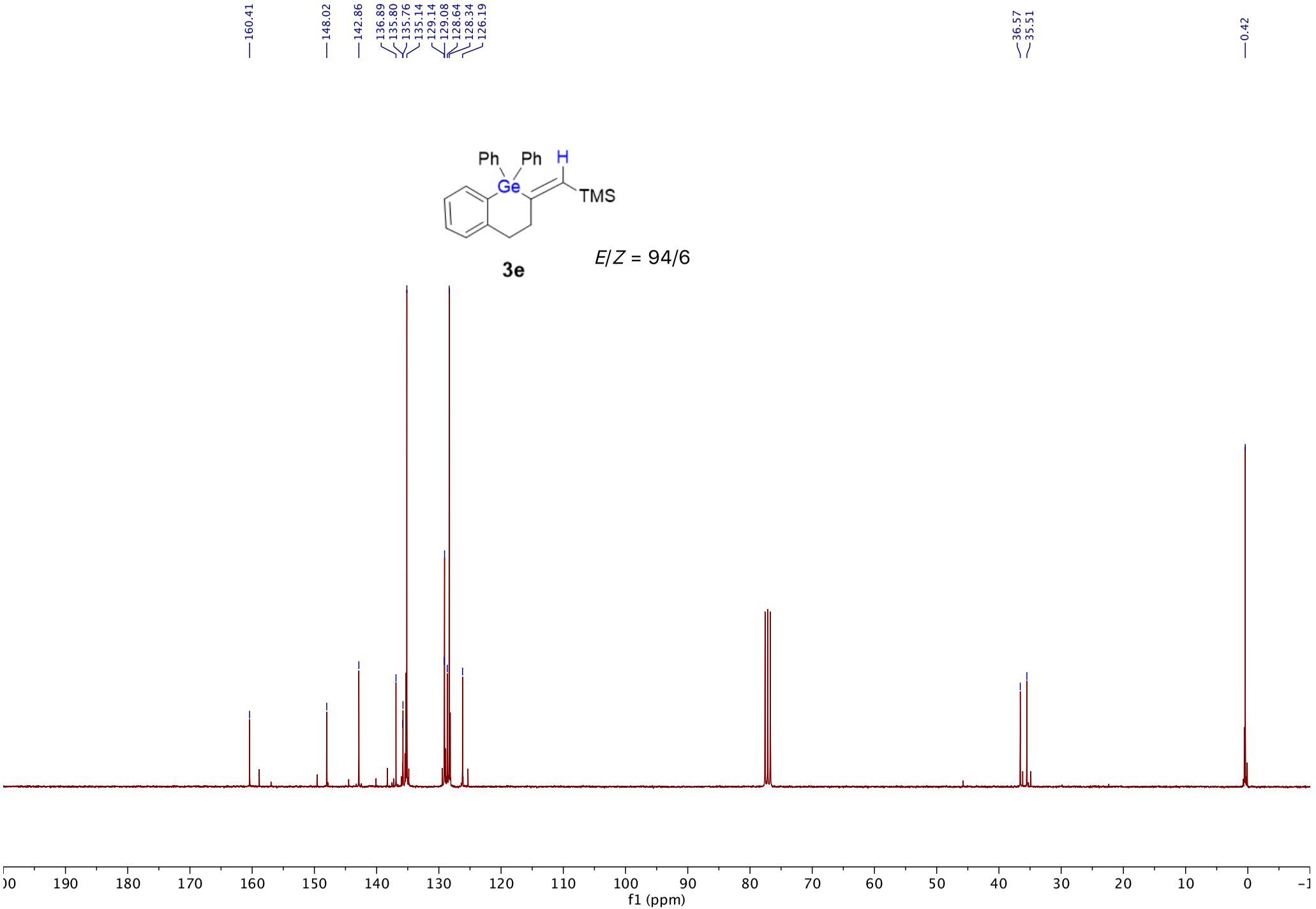

7.64
7.63
7.62
7.62
7.62
7.61
7.61
7.45
7.44
7.43
7.43
7.42
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.37
7.35
7.35
7.34
7.32
7.31
7.30
7.30
7.28
7.26
7.26
7.25
7.23
7.23
7.22
7.10
7.09
7.07
7.04
6.96
6.96
6.95
5.12
5.12
4.92
4.91
Ph
Ph
Ge
H
Ph
O
3c
E/Z = 92/8
4.00
12.10
1.07
2.01
1.04
2.04
0.18
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

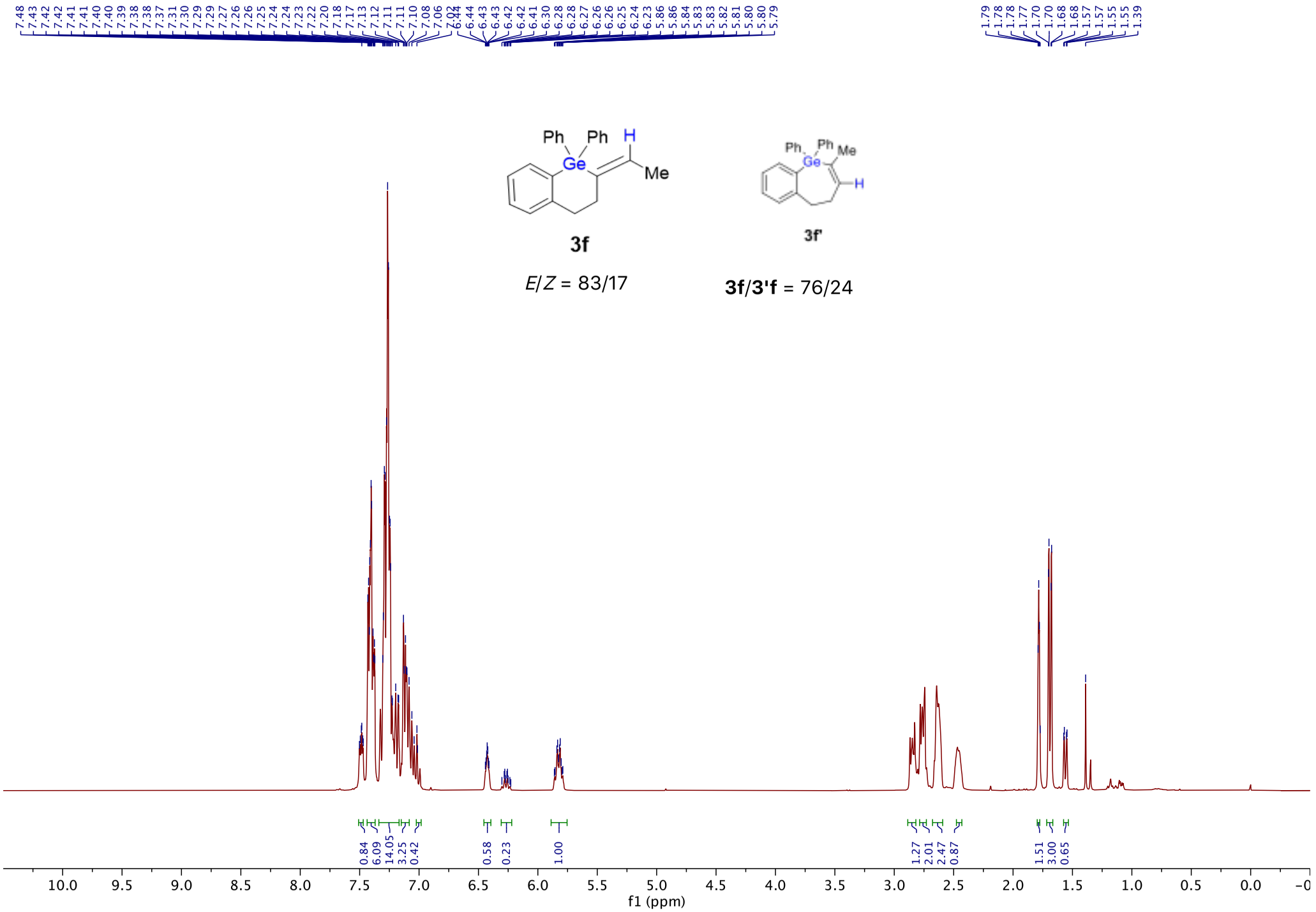
164.69
139.84
139.70
136.59
135.49
135.31
135.07
131.03
129.59
129.01
128.60
128.48
127.70
124.21
123.14
119.28
72.12
Ph
Ge
Ph
O
H
Ph
3c
f1 (ppm)

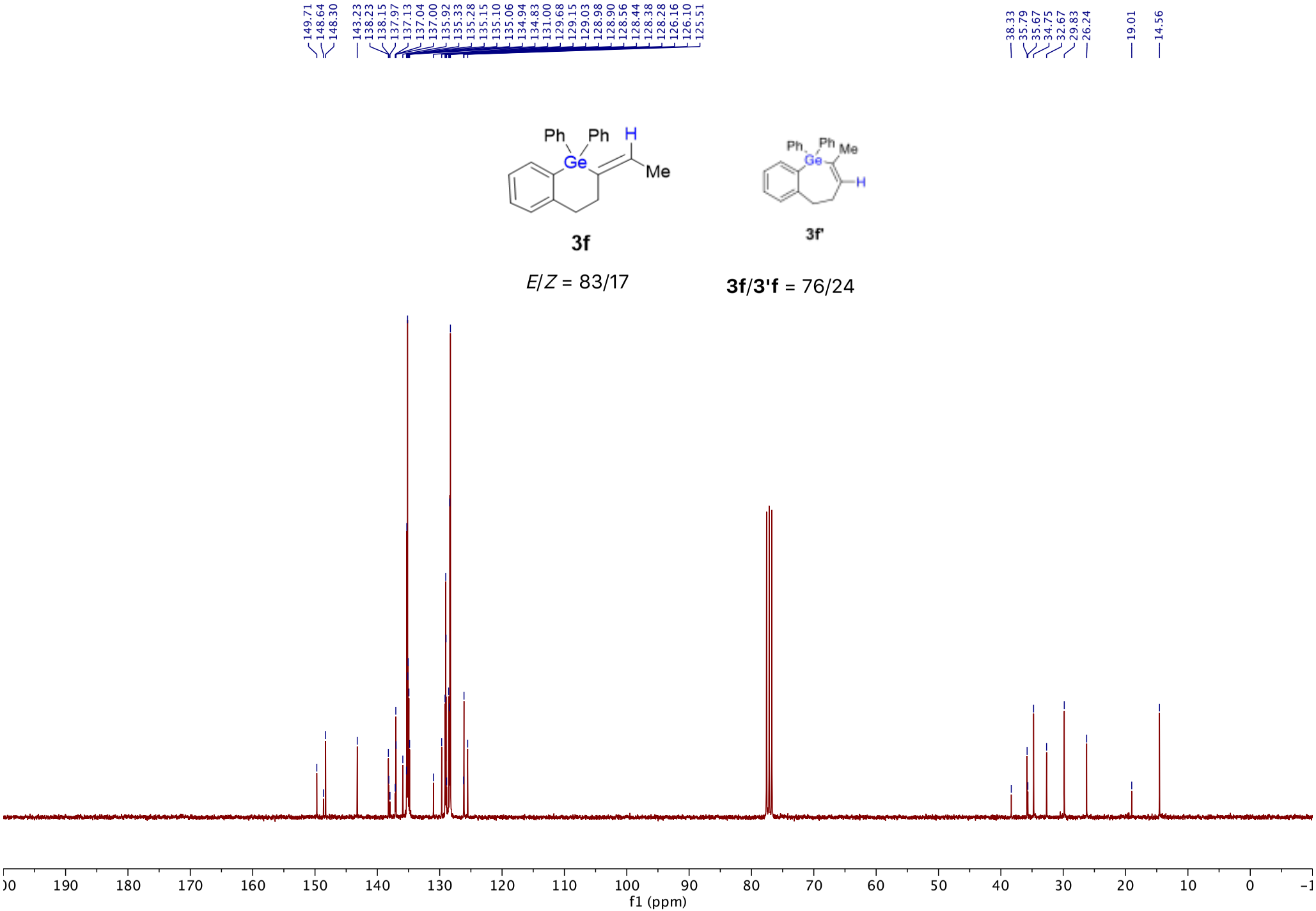
0.23
4.00
8.07
0.50
2.06
0.97
2.01
0.11
9.06
0.45
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
7.60
7.59
7.58
7.58
7.58
7.57
7.57
7.57
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.40
7.39
7.39
7.38
7.37
7.34
7.34
7.34
7.32
7.08
7.08
7.08
7.06
7.06
7.05
7.05
7.04
7.03
6.53
6.52
6.52
4.87
4.87
0.38
-0.06
Ph
Ph
Ge
O
H
GeMe3
3d
E/Z = 95/5

164.79
154.23
146.42
135.82
135.67
134.98
130.84
129.45
128.52
123.63
122.80
119.02
75.59
0.27
Ph
Ph
Ge
O
H
GeMe3
3d
E/Z = 95/5
f1 (ppm)


7.50 7.49 7.48 7.48 7.48 7.47 7.47 7.41 7.38 7.38 7.38 7.35 7.35 7.34 7.34 7.33 7.32 7.32 7.32 7.31 7.31 7.30 7.30 7.26 7.26 7.24 7.23 7.19 7.19 7.17 7.17 7.16 6.64 6.64 6.63 6.15 6.15 6.14
2.93 2.92 2.91 2.90 2.89 2.89 2.86 2.86 2.85 2.85 2.84 2.84 2.83 2.83 2.82
0.14 -0.16
Ph Ph H
Ge
TMS
3e
E/Z = 94/6
0.26 4.11 8.68 2.17 0.29 0.06 0.92 4.01 0.27 9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


160.41
148.02
142.86
136.89
135.80
135.76
135.14
129.14
129.08
128.64
128.34
126.19
36.57
35.51
0.42
Ph
Ph
H
Ge
TMS
3e
E/Z = 94/6
f1 (ppm)


7.48 7.43 7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.38 7.38 7.37 7.31 7.30 7.29 7.29 7.27 7.26 7.26 7.25 7.24 7.24 7.23 7.22 7.20 7.18 7.17 7.13 7.12 7.11 7.11 7.10 7.08 7.06 7.04 6.44 6.43 6.43 6.42 6.42 6.41 6.30 6.28 6.28 6.27 6.26 6.26 6.25 6.24 6.23 5.86 5.86 5.84 5.83 5.83 5.82 5.81 5.80 5.80 5.79
1.79 1.78 1.78 1.77 1.70 1.70 1.68 1.68 1.57 1.57 1.55 1.55 1.39
Ph Ph H Ge Me
3f
E/Z = 83/17
Ph Ph Me Ge H
3f'
3f/3'f = 76/24
0.84 6.09 14.05 3.25 0.42 0.58 0.23 1.00 1.27 2.01 2.47 0.87 1.51 3.00 0.65
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

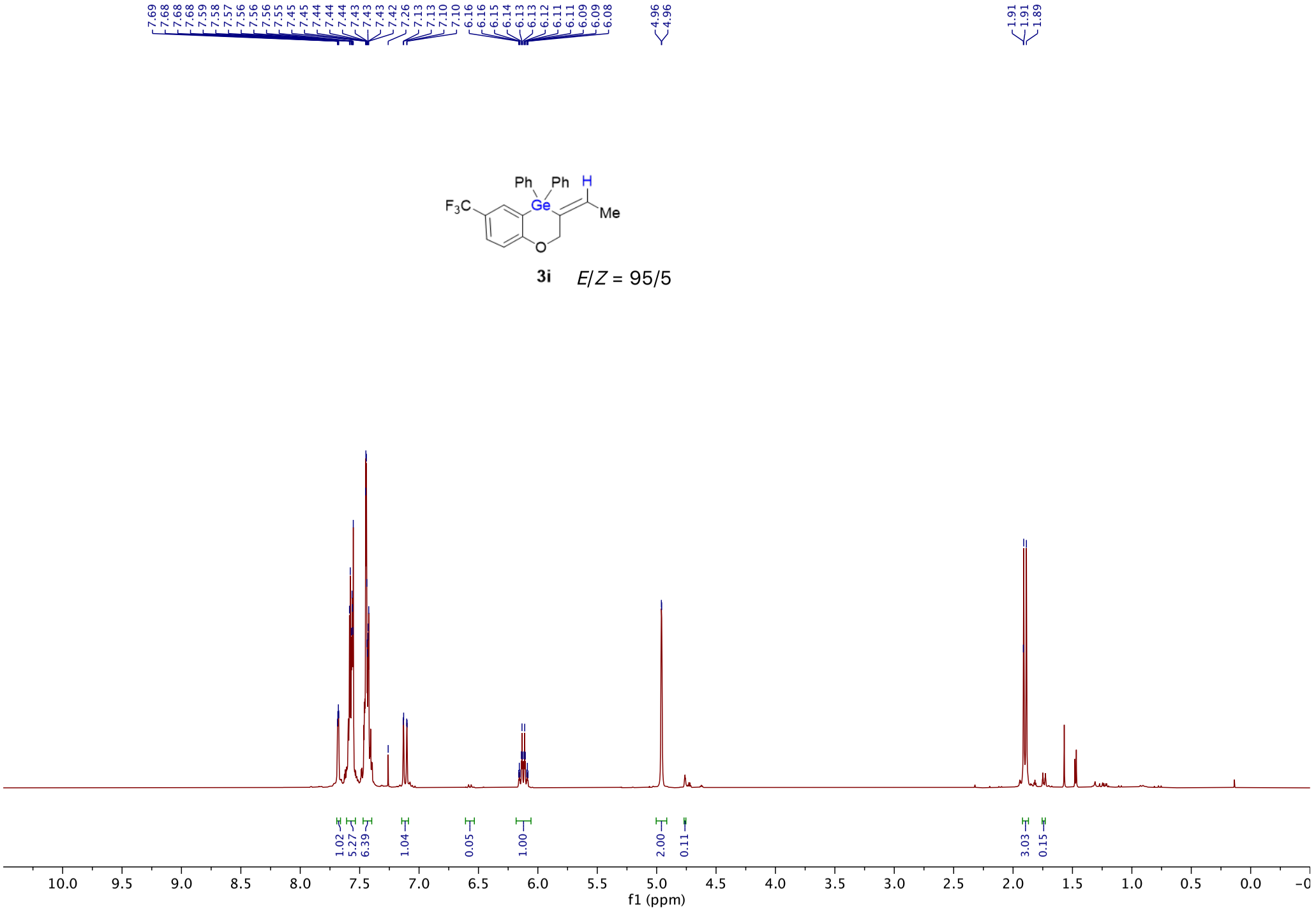

149.71
148.64
148.30
143.23
138.23
138.15
137.97
137.13
137.04
137.00
135.92
135.33
135.28
135.15
135.10
135.06
134.94
134.83
131.00
129.68
129.15
129.03
128.98
128.90
128.56
128.44
128.38
128.28
126.16
126.10
125.51
38.33
35.79
35.67
34.75
32.67
29.83
26.24
19.01
14.56
Ph
Ph
H
Ge
Me
3f
Ph
Ph
Me
Ge
H
3f'
E/Z = 83/17
3f/3'f = 76/24
f1 (ppm)

7.57
7.56
7.55
7.55
7.55
7.54
7.54
7.53
7.52
7.45
7.41
7.41
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.38
7.38
7.37
7.36
7.32
7.30
7.30
7.29
7.26
7.25
7.23
7.23
7.23
7.14
6.82
6.82
6.81
6.33
6.32
6.31
2.99
2.98
2.97
2.96
2.95
2.94
2.88
2.88
2.87
2.87
2.86
2.86
2.85
2.85
2.84
0.34
0.16
4.33
7.48
1.24
1.19
1.04
0.04
0.94
2.28
2.00
8.95
0.31
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)
Ph
Ph
Ge
H
GeMe3
3g
E/Z = 97/3

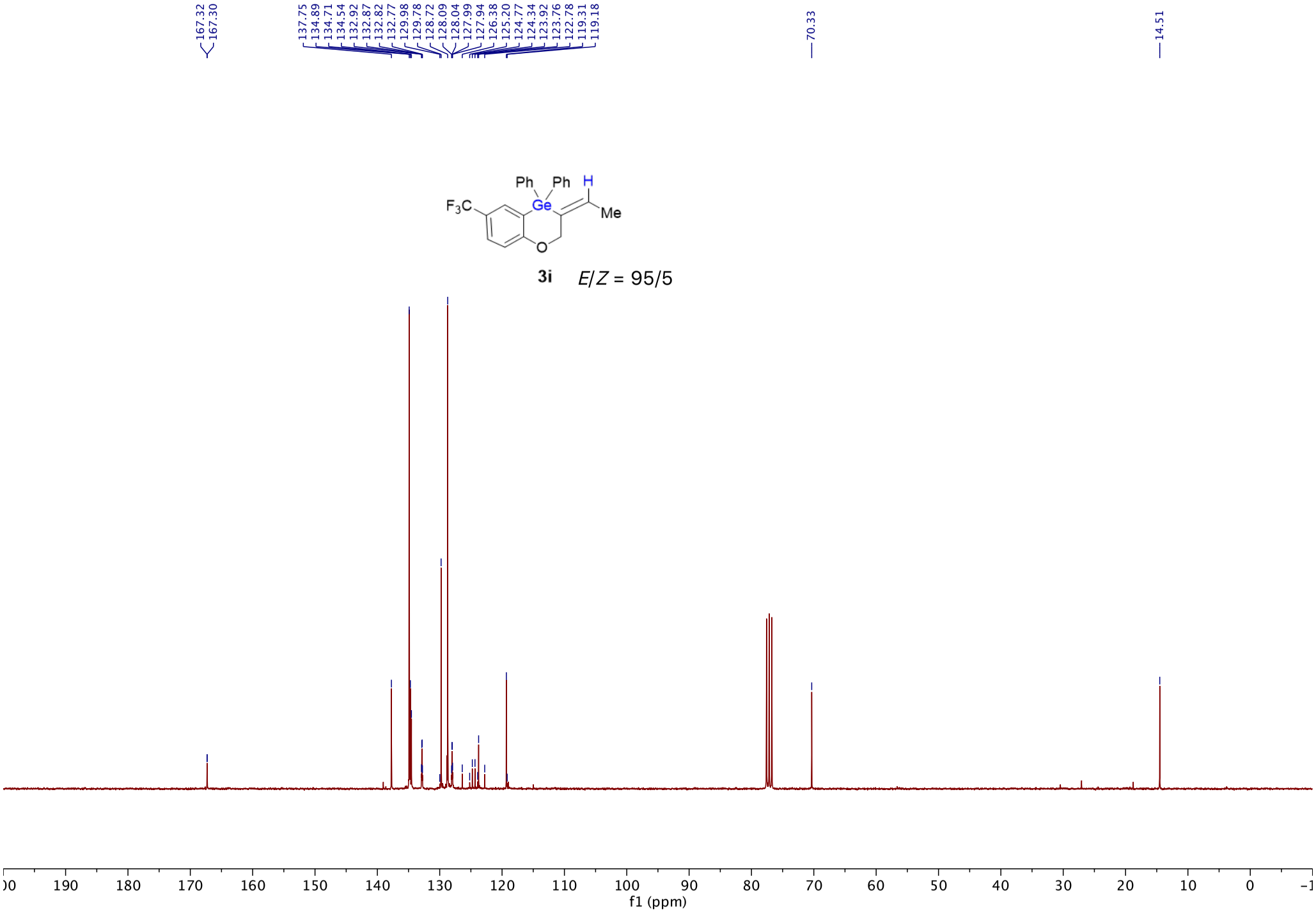
157.25
156.57
149.55
148.03
143.57
136.94
135.65
135.30
135.12
129.08
128.33
126.17
36.69
35.62
0.13
Ph
Ph
Ge
H
GeMe3
3g
E/Z = 97/3
f1 (ppm)

f1 (ppm)
4.05
6.18
2.08
2.10
0.97
2.00
2.99
3.00
7.55
7.54
7.53
7.52
7.52
7.51
7.37
7.37
7.37
7.36
7.36
7.35
7.35
7.35
7.35
7.32
7.32
7.29
6.93
6.92
6.90
6.89
6.89
6.87
6.86
6.84
6.84
5.93
5.92
5.91
5.91
5.90
5.89
5.88
5.88
5.87
5.86
5.85
5.85
3.94
3.94
3.93
3.93
2.93
1.80
1.78
Ph
Ph
H
Ge
N
Me
Me
3h

157.42
138.77
136.47
135.43
135.18
133.62
130.23
129.09
128.28
125.81
119.93
114.97
57.59
42.11
14.59
3h
Ph
Ph
Ge
N
Me
H
Me
f1 (ppm)

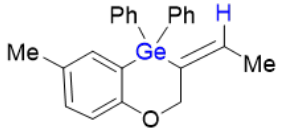

7.69
7.68
7.68
7.68
7.59
7.58
7.57
7.56
7.56
7.56
7.55
7.45
7.45
7.44
7.44
7.44
7.43
7.43
7.43
7.42
7.26
7.13
7.13
7.10
7.10
6.16
6.16
6.15
6.14
6.13
6.13
6.12
6.11
6.11
6.09
6.09
6.08
4.96
4.96
1.91
1.91
1.89
Ph
Ph
H
F3C
Ge
Me
O
1.02
5.27
6.39
1.04
0.05
1.00
2.00
0.11
3.03
0.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3i *E*/*Z* = 95/5

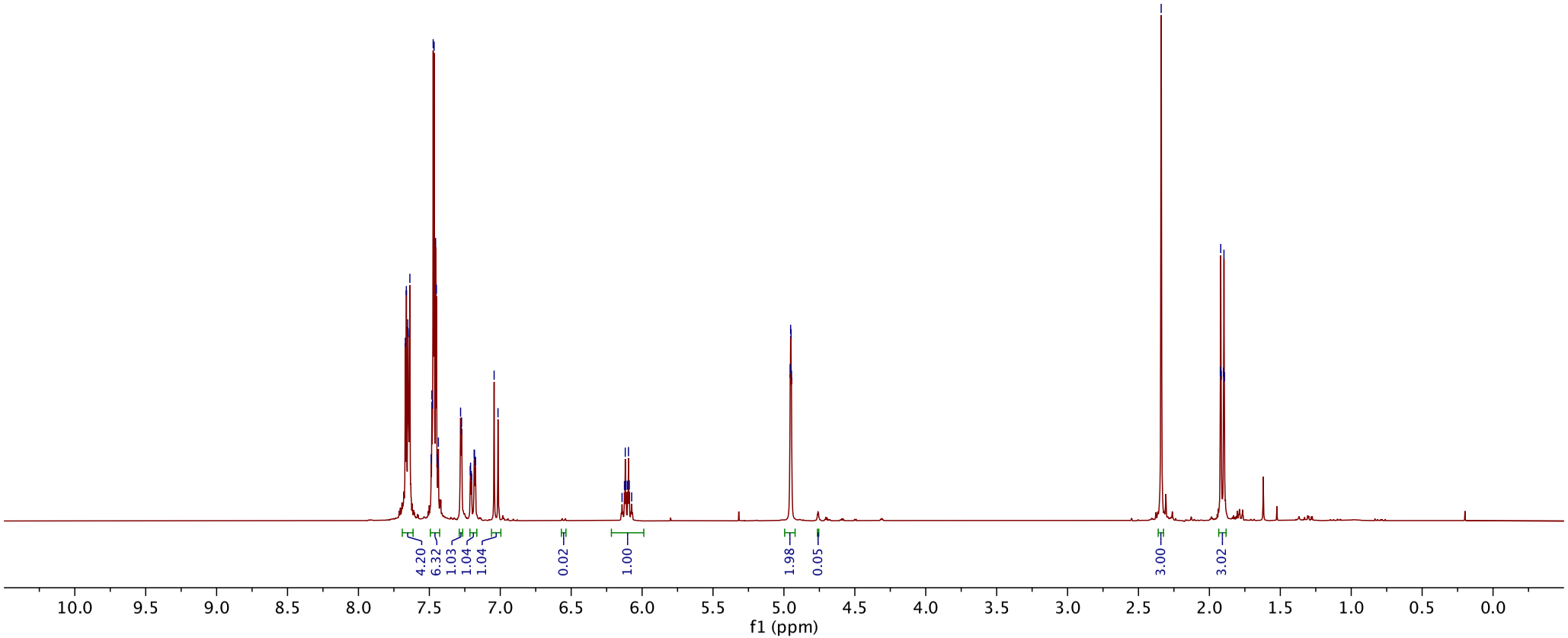

167.32
167.30
137.75
134.89
134.71
134.54
132.92
132.87
132.82
132.77
129.98
129.78
128.72
128.09
128.04
127.99
127.94
126.38
125.20
124.77
124.34
123.92
123.76
122.78
119.31
119.18
70.33
14.51
Ph
Ph
H
F3C
Ge
Me
O
f1 (ppm)

3i *E*/*Z* = 95/5


7.67
7.66
7.65
7.65
7.64
7.49
7.48
7.48
7.47
7.47
7.46
7.45
7.44
7.44
7.44
7.28
7.27
7.27
7.21
7.21
7.20
7.20
7.18
7.18
7.18
7.17
7.04
7.02
6.14
6.12
6.12
6.11
6.10
6.10
6.09
6.07
4.96
4.95
4.95
4.95
2.34
1.92
1.92
1.92
1.90
1.90
1.89

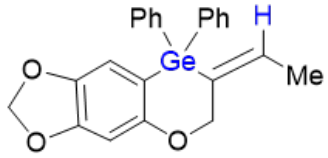

Ph
Ph
H
Me
Ge
Me
O

3j *E*/*Z* = 98/2


4.20
6.32
1.03
1.04
1.04
0.02
1.00
1.98
0.05
3.00
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

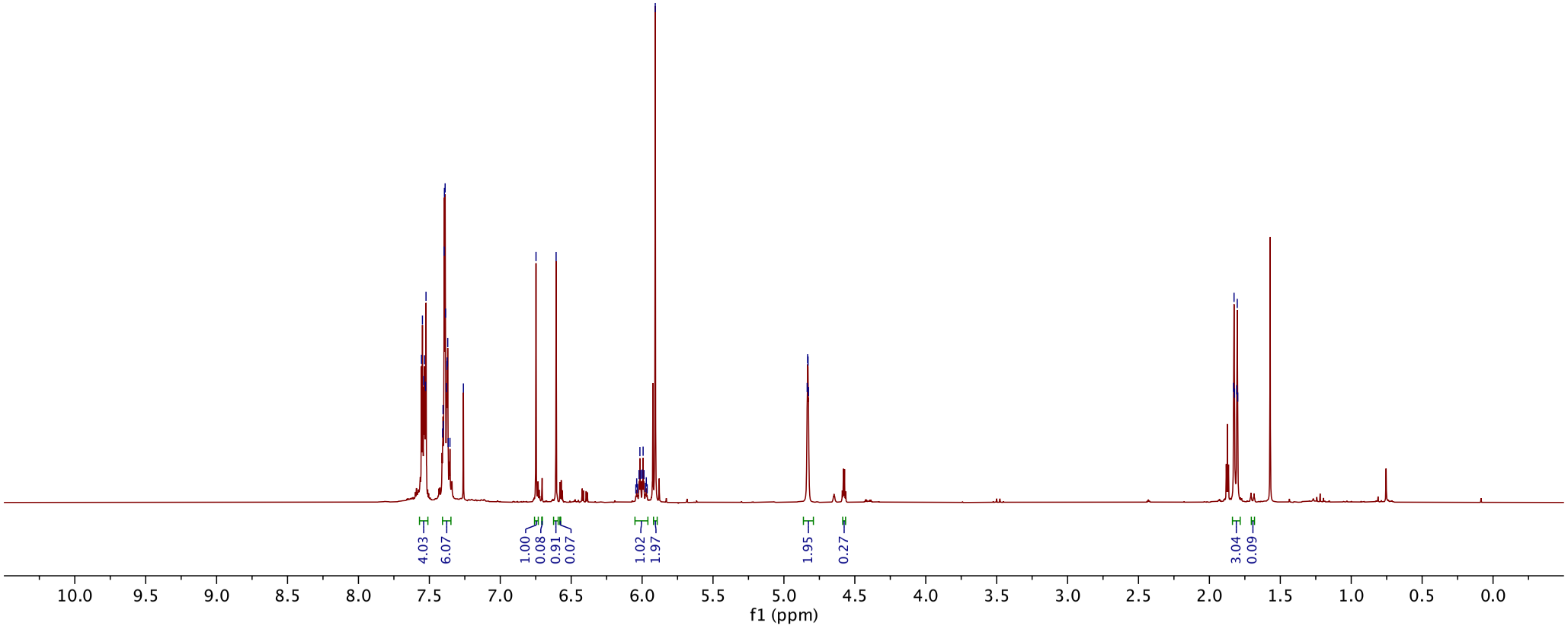
162.73
136.57
136.24
135.86
135.73
134.99
131.87
131.58
129.37
128.46
123.34
118.79
70.67
20.78
14.51
Me
Ph
Ge
Ph
H
O
Me
3j E/Z = 98/2
f1 (ppm)

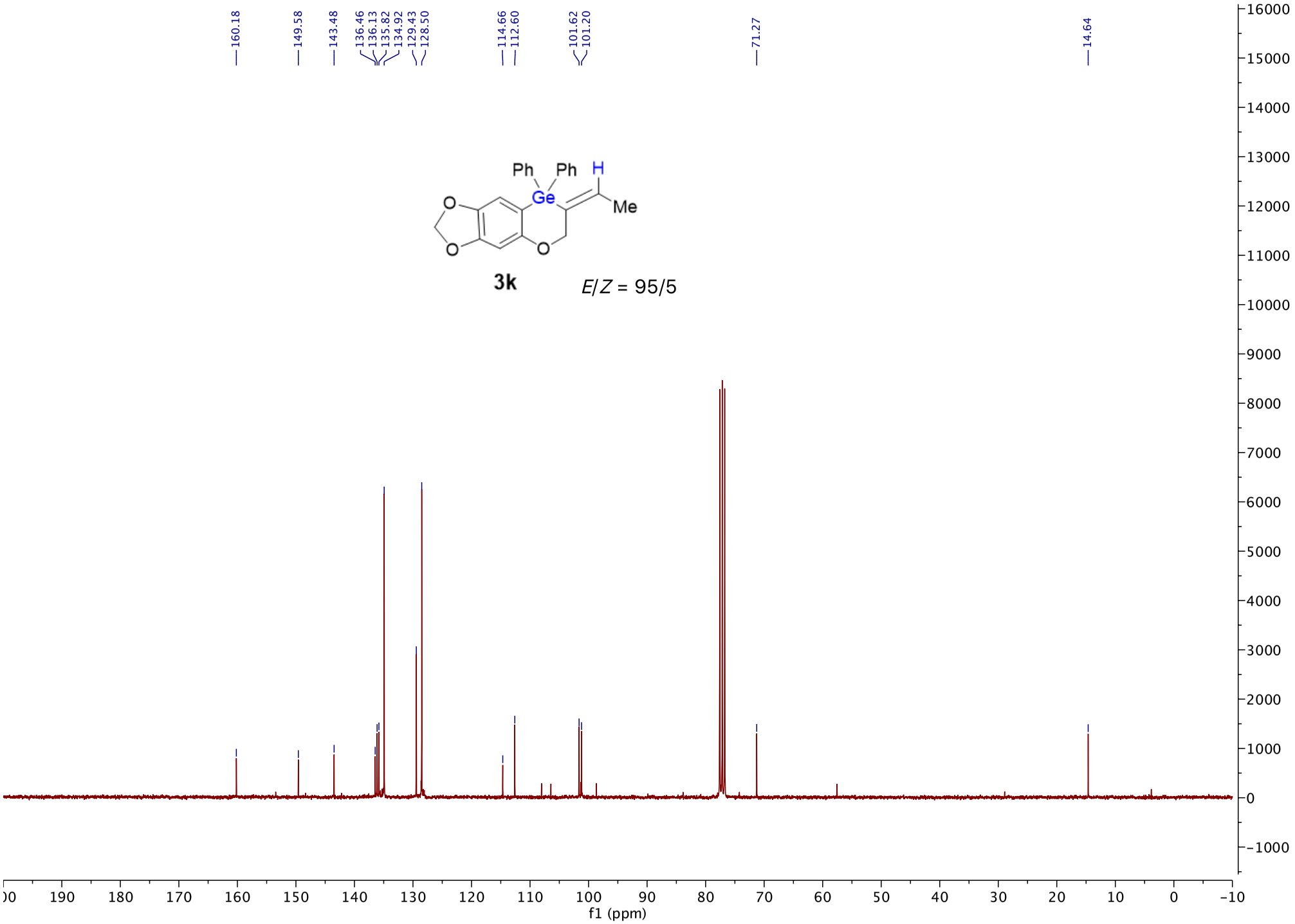

7.56
7.55
7.54
7.53
7.53
7.52
7.41
7.40
7.40
7.40
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.35
7.26
6.75
6.61
6.04
6.04
6.03
6.02
6.02
6.01
6.00
5.99
5.99
5.98
5.97
5.96
5.91
4.84
4.83
4.83
4.83
1.83
1.83
1.82
1.81
1.80
1.80

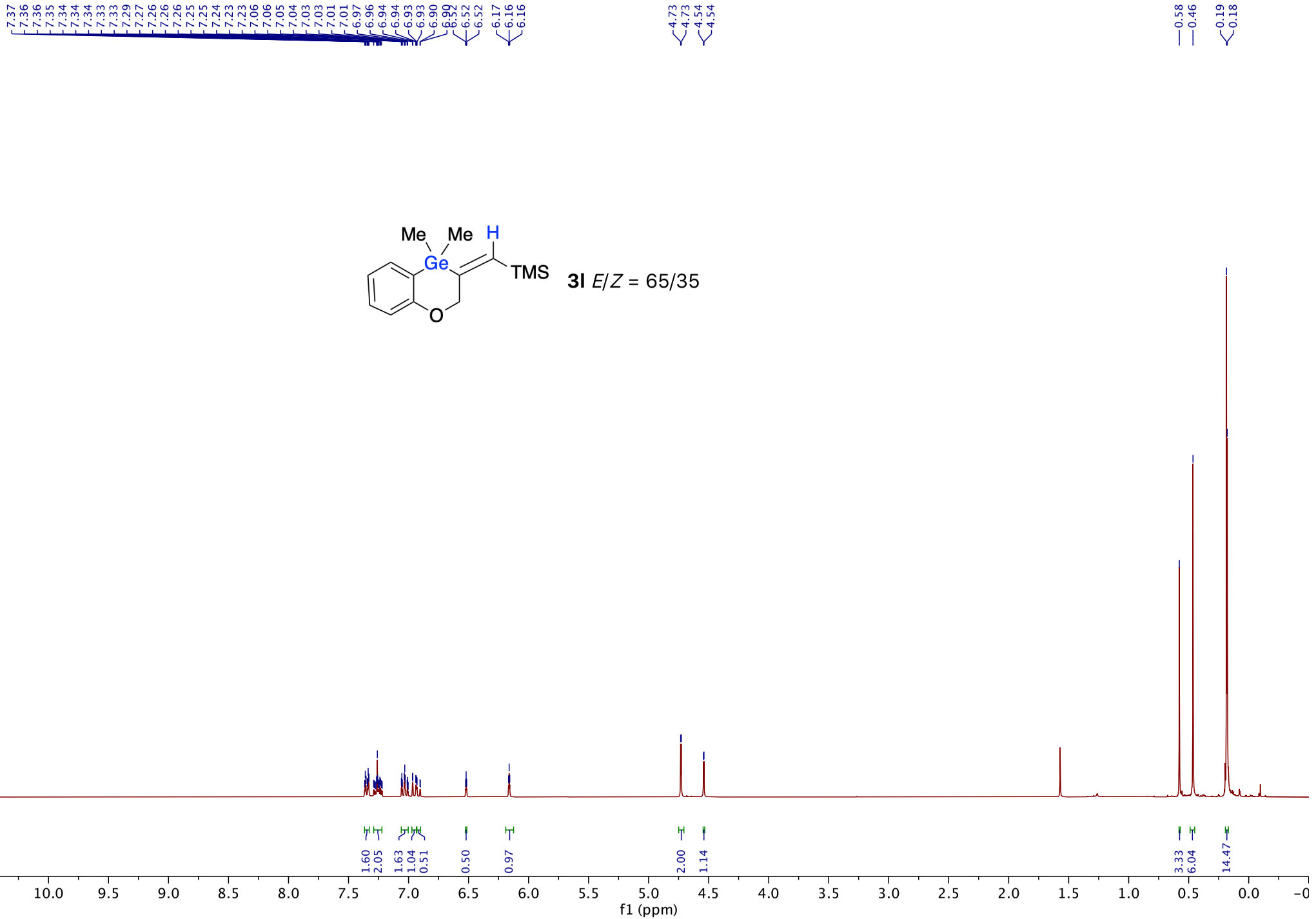

Ph
Ph
H
Ge
Me
O
O
O

3k

E/*Z* = 95/5


4.03
6.07
1.00
0.08
0.91
0.07
1.02
1.97
1.95
0.27
3.04
0.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


160.18
149.58
143.48
136.46
136.13
135.82
134.92
129.43
128.50
114.66
112.60
101.62
101.20
71.27
14.64
Ph
Ph
H
Ge
Me
O
O
O
O
3k
E/Z = 95/5
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

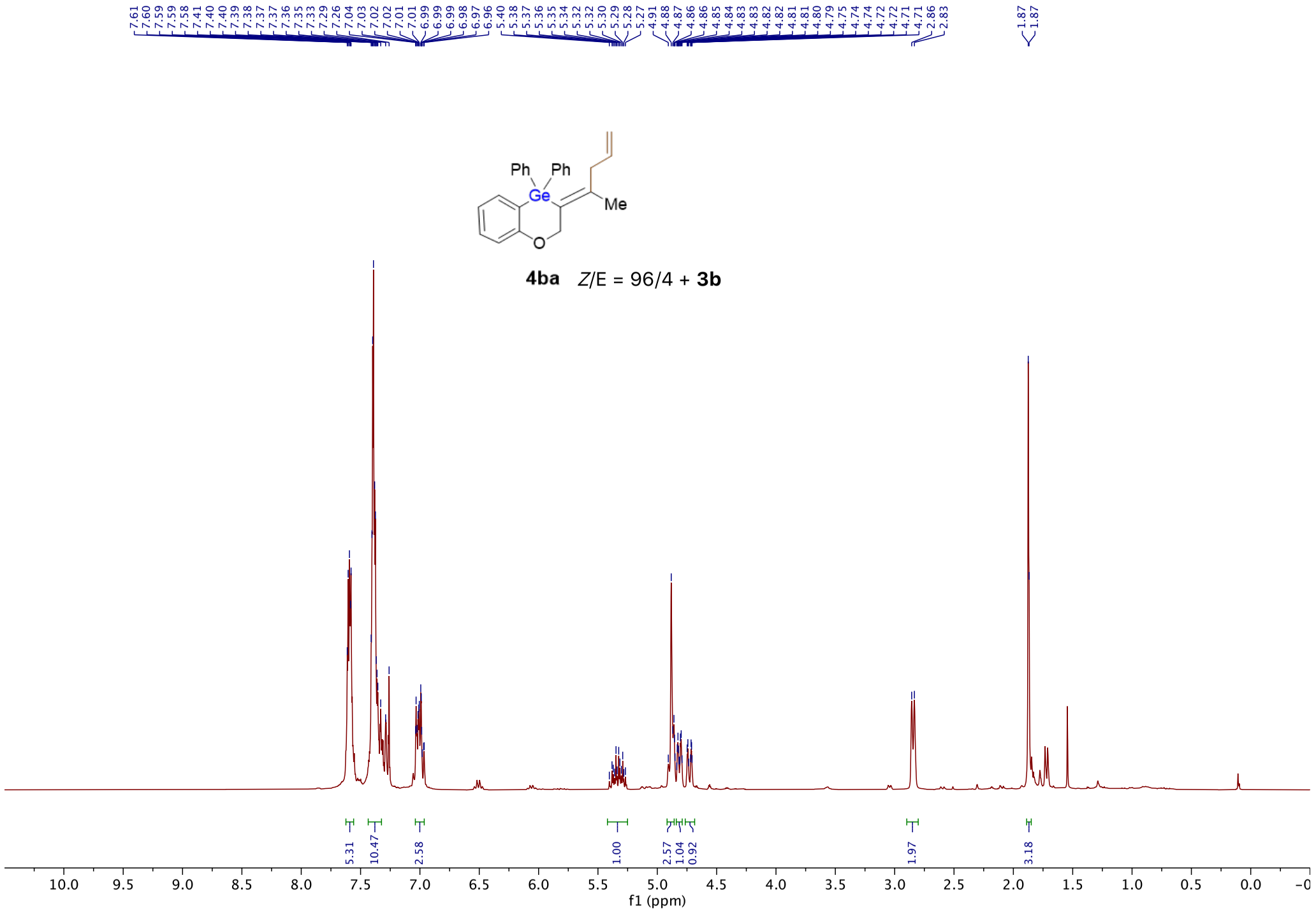

7.37
7.36
7.36
7.35
7.34
7.34
7.34
7.33
7.33
7.29
7.27
7.26
7.26
7.26
7.25
7.25
7.24
7.23
7.23
7.06
7.06
7.05
7.04
7.03
7.03
7.01
7.01
6.97
6.96
6.94
6.94
6.93
6.93
6.90
6.52
6.52
6.17
6.16
6.16
4.73
4.73
4.54
4.54
0.58
0.46
0.19
0.18
Me
Me
H
Ge
TMS
O
3l E/Z = 65/35
1.60
2.05
1.63
1.04
0.51
0.50
0.97
2.00
1.14
3.33
6.04
14.47
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

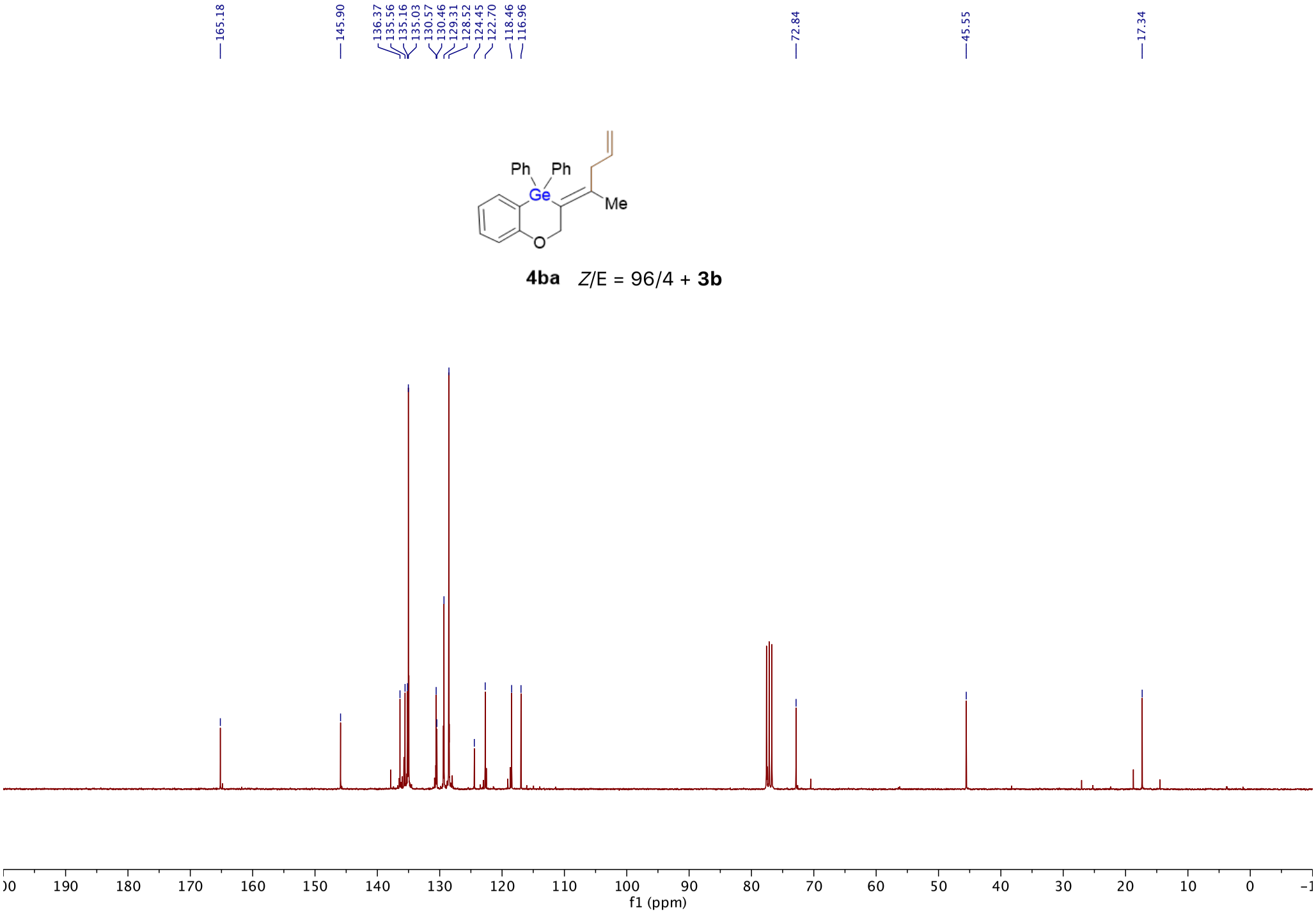
164.20
164.04
161.43
157.66
144.12
141.59
134.52
134.38
130.22
130.04
127.71
126.71
122.68
122.42
118.65
117.96
82.12
74.99
0.44
0.20
0.15
-2.18
Me
Me
Ge
H
O
TMS
3l E/Z = 65/35
f1 (ppm)

10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
4.00
9.21
2.64
1.04
1.94
2.31
2.07
7.56
7.55
7.54
7.54
7.54
7.53
7.53
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.35
7.34
7.33
7.33
7.32
7.30
7.30
7.30
7.26
7.02
7.01
7.01
7.00
7.00
6.99
6.99
6.98
6.97
6.97
6.95
6.94
5.37
5.35
5.34
5.33
5.32
5.31
5.30
5.29
5.28
5.27
5.26
5.24
4.93
4.73
4.72
4.72
4.71
4.71
4.70
4.70
4.69
4.68
4.68
4.65
4.64
3.01
3.01
3.00
2.99
2.99
2.98
1.56

Ph
Ph
Ge
O
TMS

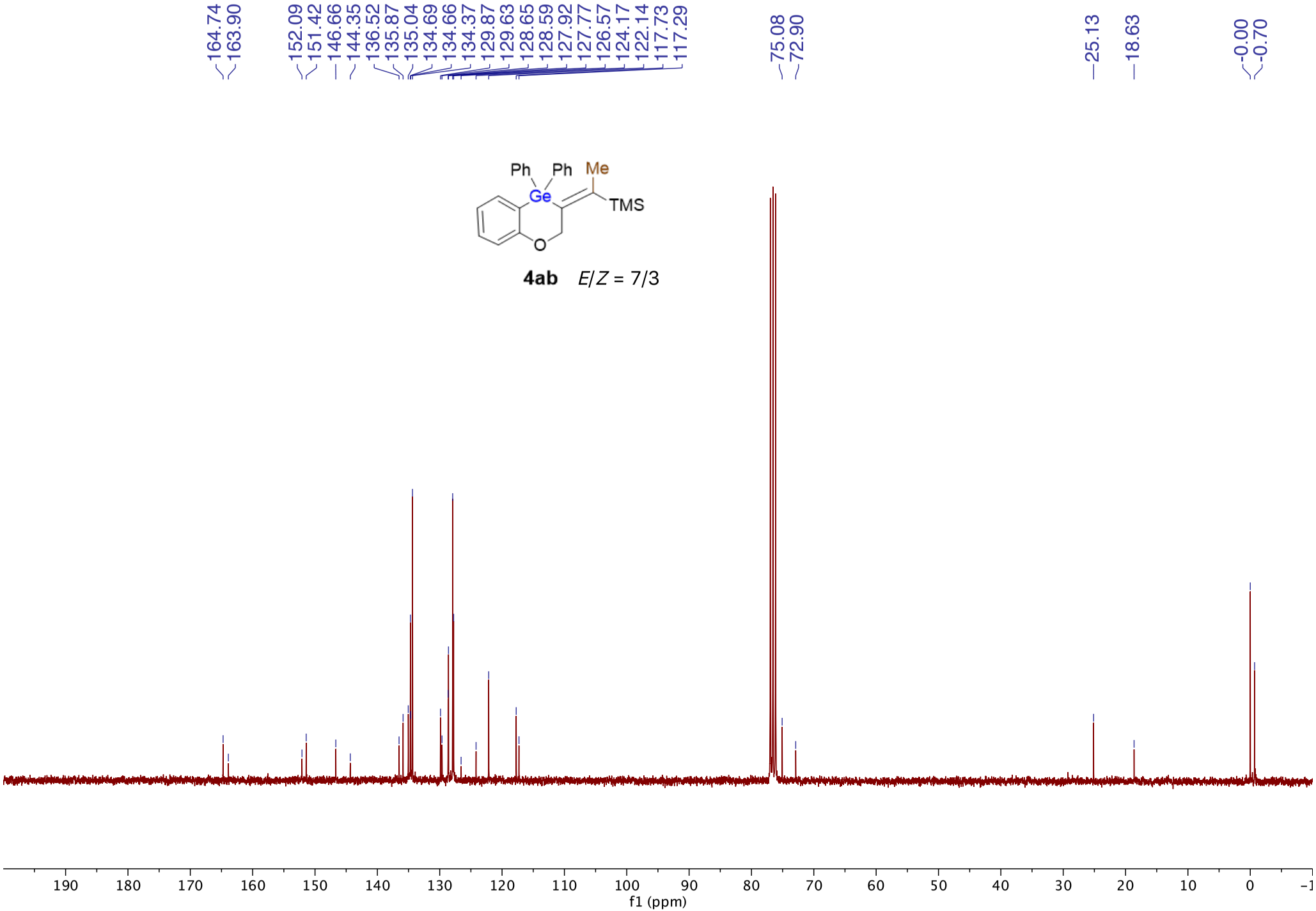
4aa

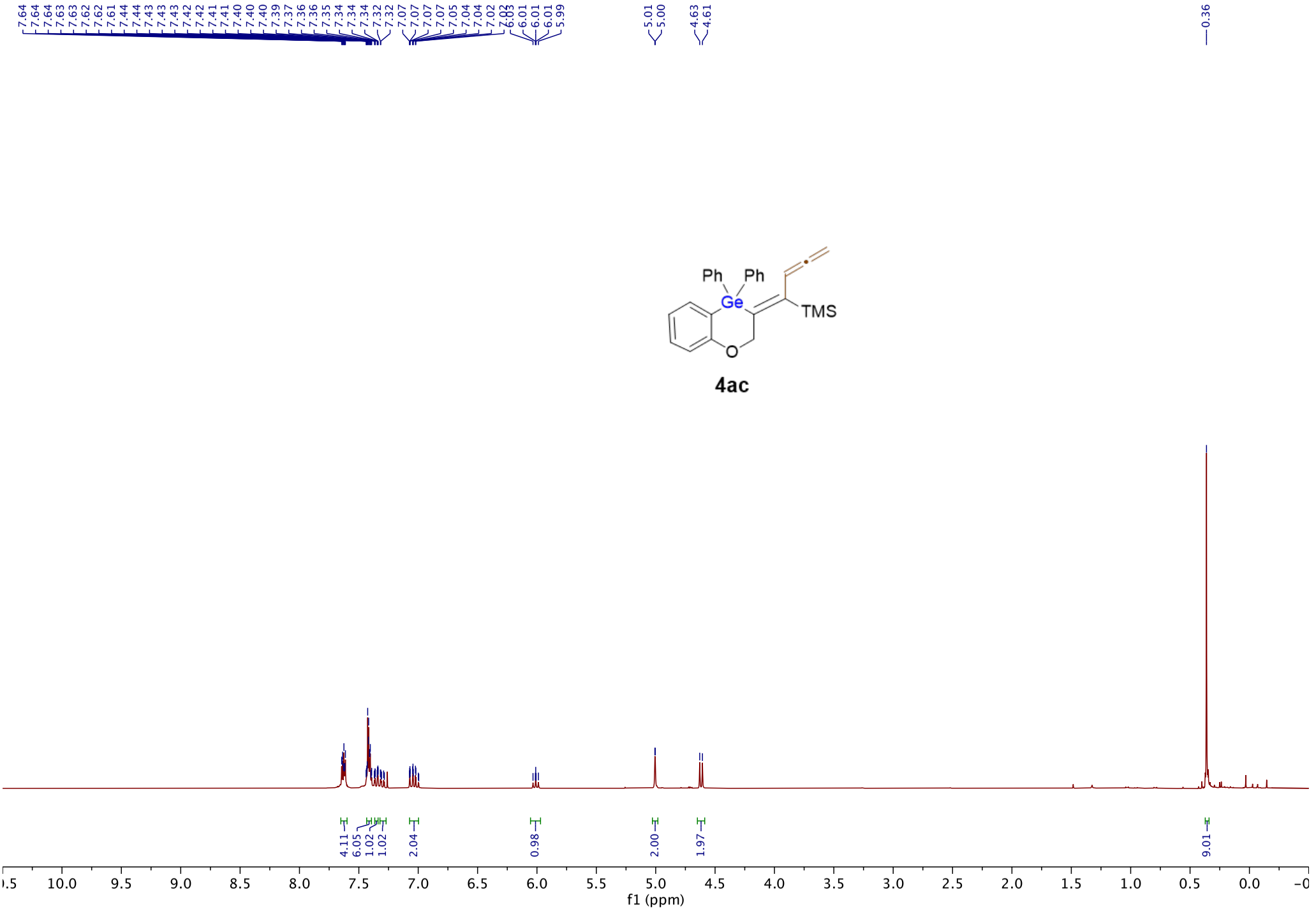

7.61 7.60 7.59 7.59 7.58 7.41 7.40 7.40 7.39 7.38 7.37 7.37 7.36 7.35 7.33 7.29 7.26 7.04 7.03 7.02 7.02 7.01 7.01 6.99 6.99 6.99 6.98 6.97 6.96
5.40 5.38 5.37 5.36 5.35 5.34 5.32 5.32 5.30 5.29 5.28 5.27
4.91 4.88 4.87 4.86 4.86 4.85 4.84 4.83 4.83 4.82 4.82 4.81 4.81 4.80 4.79 4.75 4.74 4.74 4.72 4.72 4.71 4.71
2.86 2.83
1.87 1.87
Ph
Ph
Ge
Me
O
4ba Z/E = 96/4 + 3b
5.31
10.47
2.58
1.00
2.57
1.04
0.92
1.97
3.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


165.18
145.90
136.37
135.56
135.16
135.03
130.57
130.46
129.31
128.52
124.45
122.70
118.46
116.96
72.84
45.55
17.34
Ph
Ph
Ge
Me
O
f1 (ppm)

4ba *Z*/E = 96/4 + **3b**

1.77
4.02
9.20
1.52
1.42
1.62
1.40
0.95
2.00
1.45
3.01
9.05
4.39
7.67
7.66
7.65
7.64
7.60
7.59
7.58
7.58
7.57
7.57
7.39
7.38
7.37
7.35
7.32
7.29
7.22
7.19
7.01
7.00
6.98
6.96
6.95
6.93
6.93
4.95
4.89
2.05
1.86
0.26
-0.17
Ph
Ph
Me
Ge
O
TMS
4ab E/Z = 7/3
f1 (ppm)


164.74
163.90
152.09
151.42
146.66
144.35
136.52
135.87
135.04
134.69
134.66
134.37
129.87
129.63
128.65
128.59
127.92
127.77
126.57
124.17
122.14
117.73
117.29
75.08
72.90
25.13
18.63
-0.00
-0.70
Ph
Ph
Me
Ge
TMS
O
4ab E/Z = 7/3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

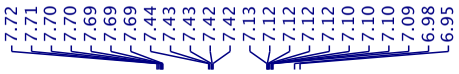

7.64
7.64
7.64
7.63
7.63
7.62
7.62
7.61
7.44
7.44
7.43
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.40
7.39
7.37
7.36
7.36
7.35
7.34
7.34
7.34
7.32
7.07
7.07
7.07
7.05
7.04
7.04
7.02
6.01
6.01
6.01
5.99
5.01
5.00
4.63
4.61
0.36
Ph
Ph
Ge
TMS
O
4ac
4.11
6.05
1.02
1.02
2.04
0.98
2.00
1.97
9.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

210.12
165.13
150.86
148.93
136.06
135.69
135.13
130.56
129.27
128.52
128.47
124.62
122.83
118.33
96.83
75.26
1.83
f1 (ppm)
4ac
Ph
Ph
Ge
O
TMS

4.00
6.02
2.00
1.00
1.00
2.00
3.00
7.72
7.72
7.71
7.70
7.70
7.69
7.44
7.43
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.39
7.39
7.29
7.28
7.27
7.27
7.04
7.04
7.02
7.01
7.01
6.99
6.99
6.97
6.97
4.79
4.79
2.76
2.75
2.75
f1 (ppm)

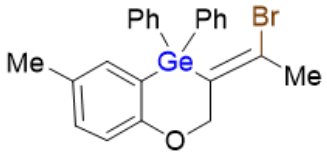
4bd

164.63
145.83
135.79
135.66
134.10
130.67
129.47
128.47
125.45
123.23
118.29
110.25
72.78
31.52
4bd
Ph
Ge
Ph
O
I
Me
f1 (ppm)

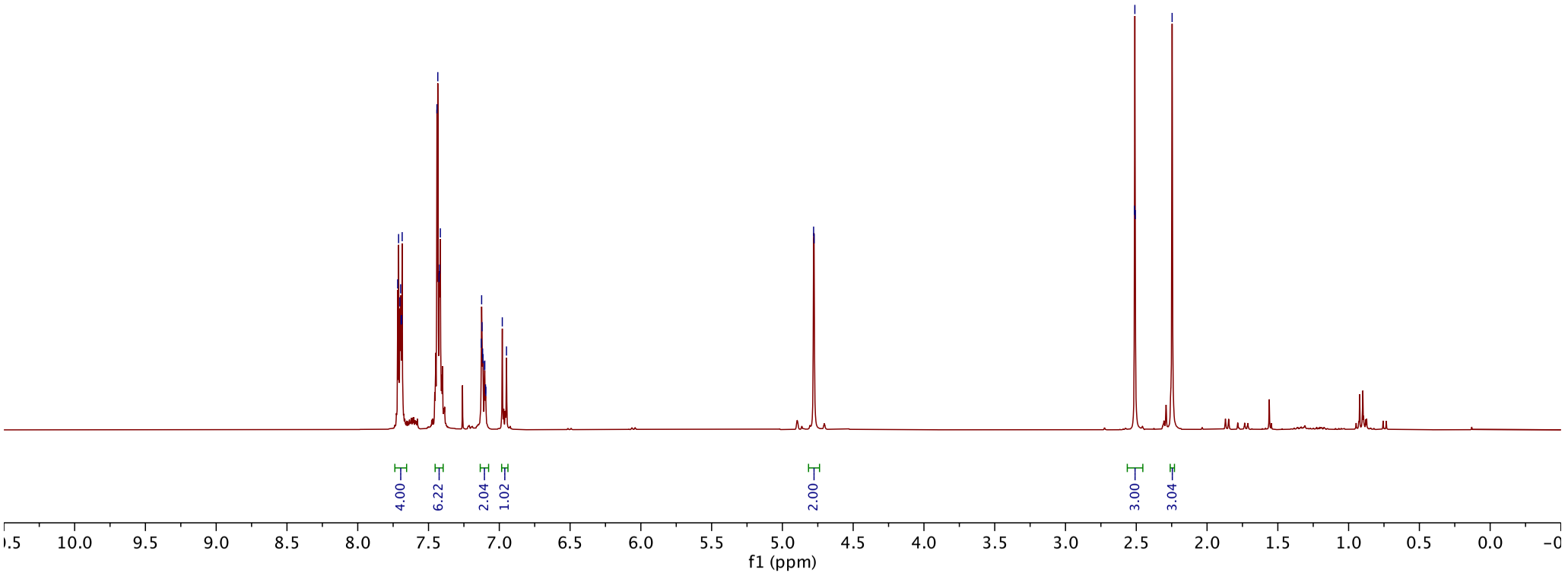

7.72
7.71
7.70
7.70
7.69
7.69
7.69
7.44
7.43
7.43
7.42
7.42
7.13
7.12
7.12
7.12
7.12
7.10
7.10
7.10
7.09
6.98
6.95

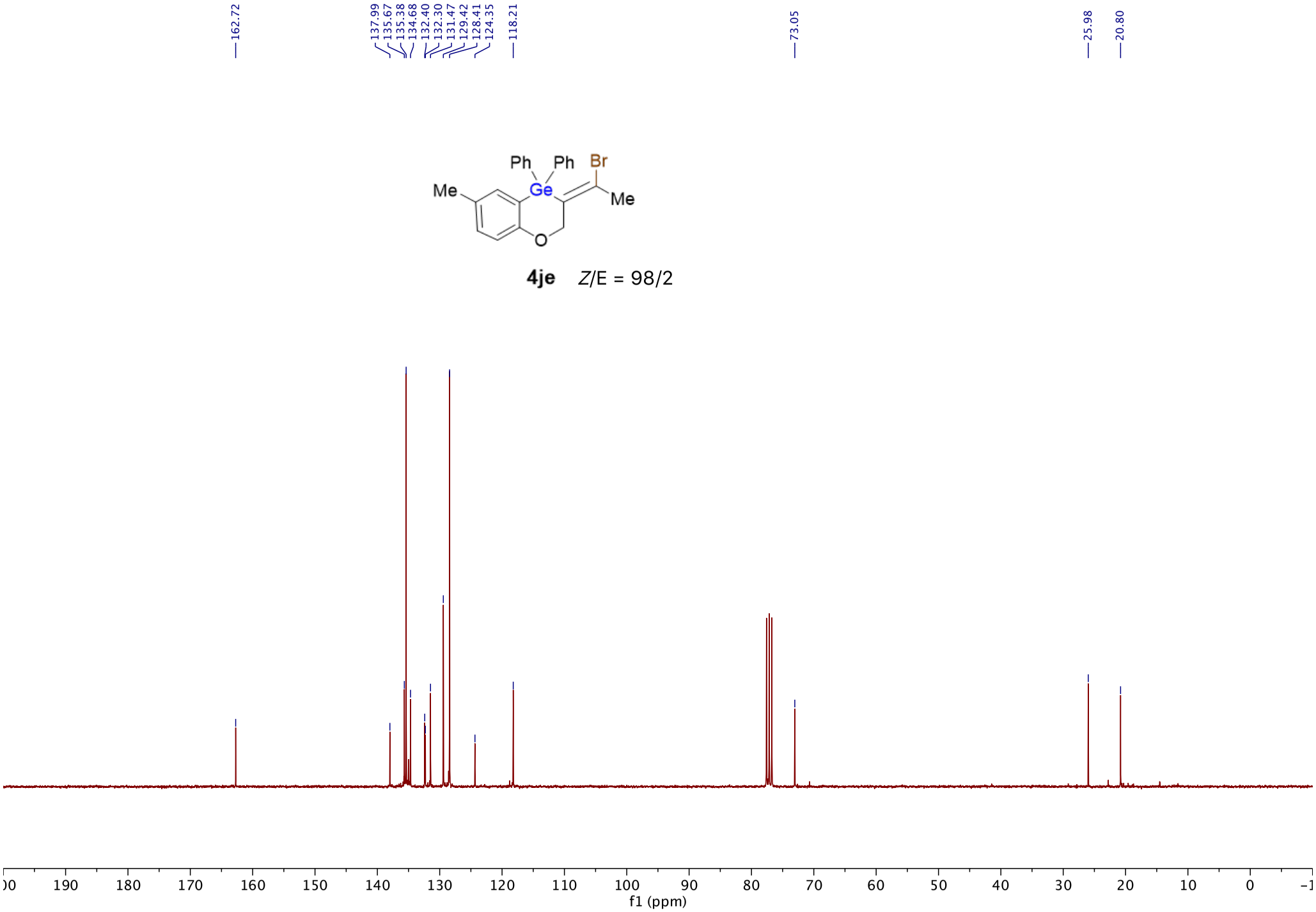

4.78
4.78


2.51
2.51
2.51
2.25


Ph
Ph
Br
Me
Ge
Me
O

4je *Z*/E = 98/2

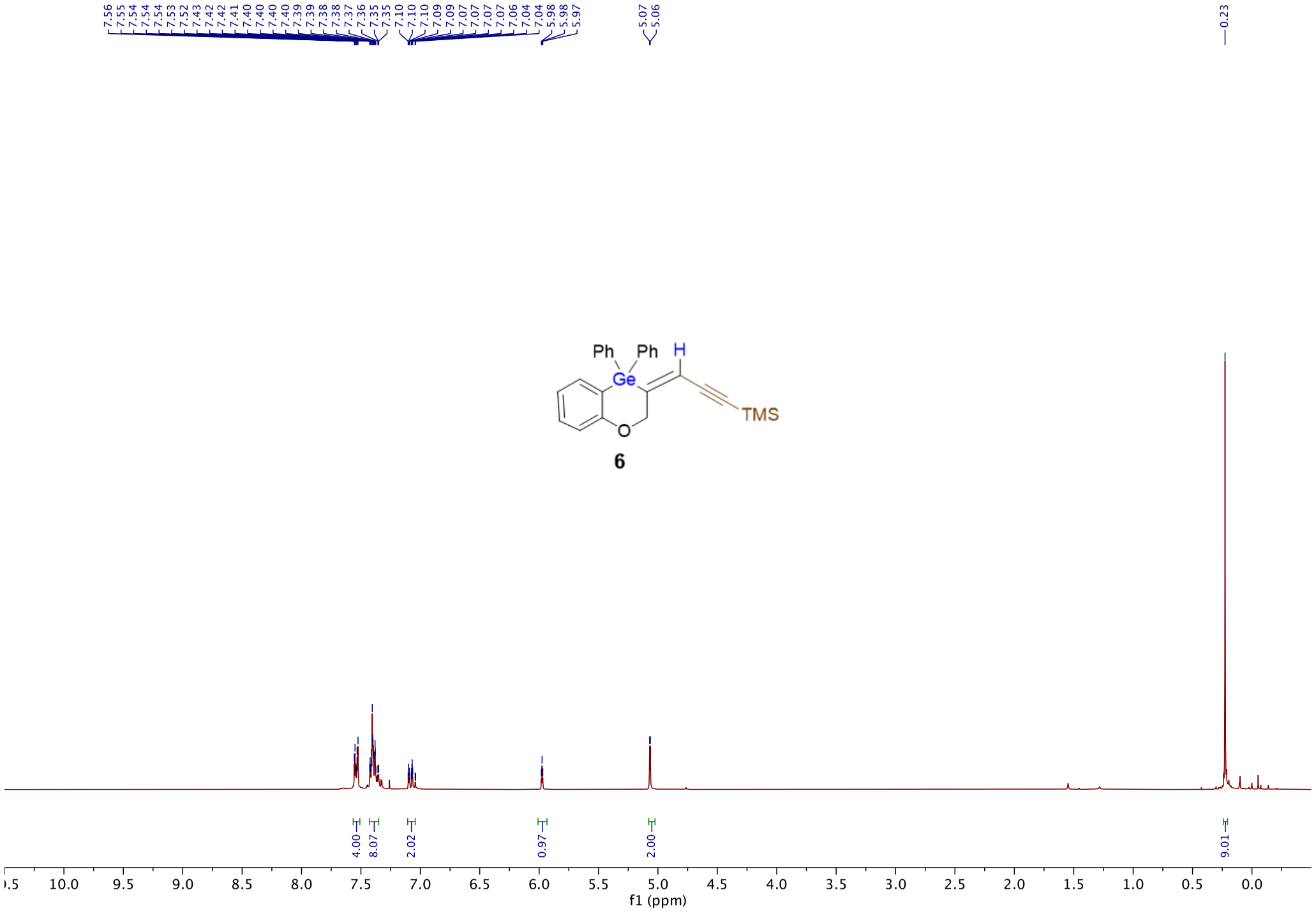

4.00
6.22
2.04
1.02
2.00
3.00
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

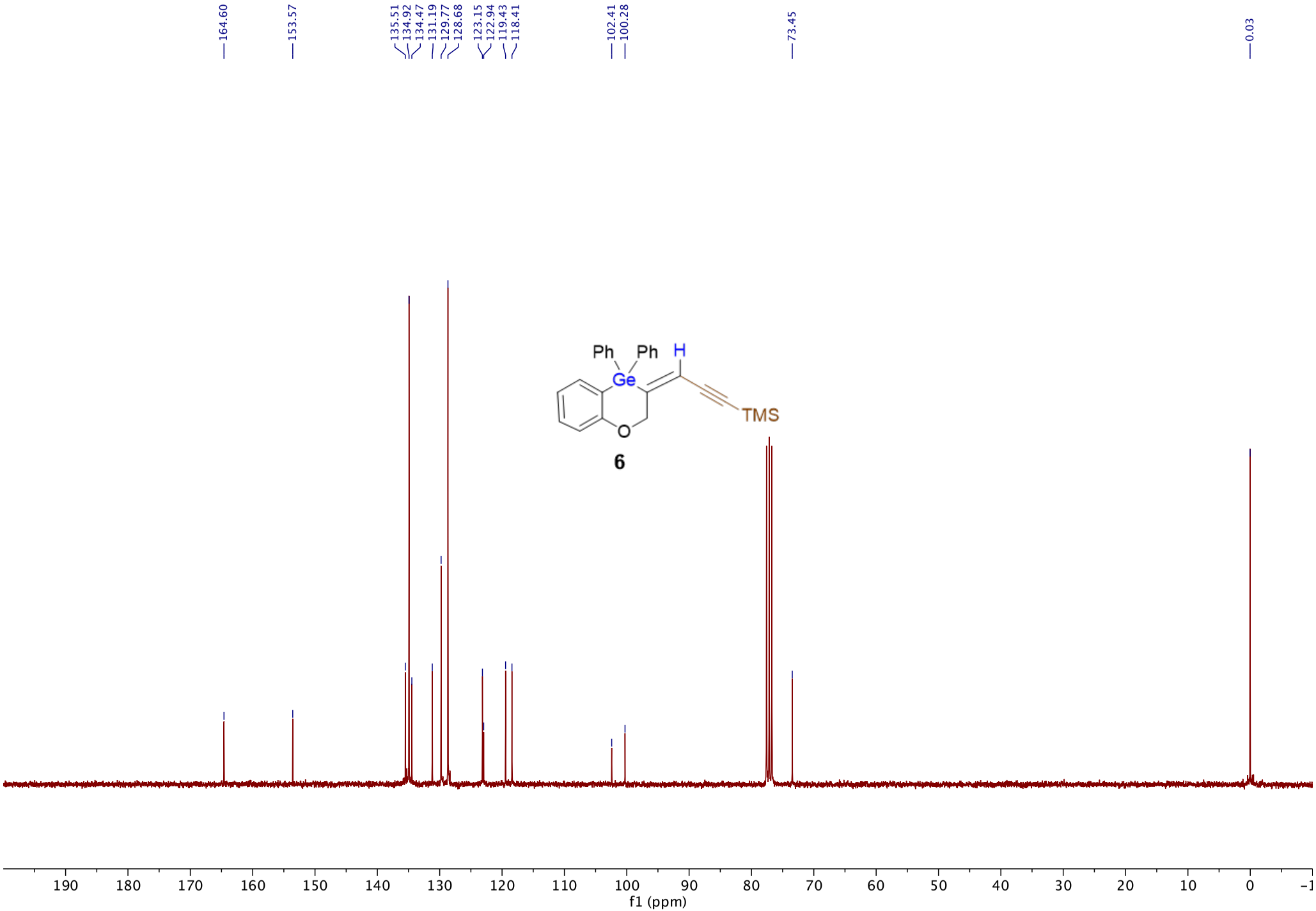

162.72
137.99
135.67
135.38
134.68
132.40
132.30
131.47
129.42
128.41
124.35
118.21
73.05
25.98
20.80
Ph
Ph
Br
Me
Ge
Me
O
f1 (ppm)

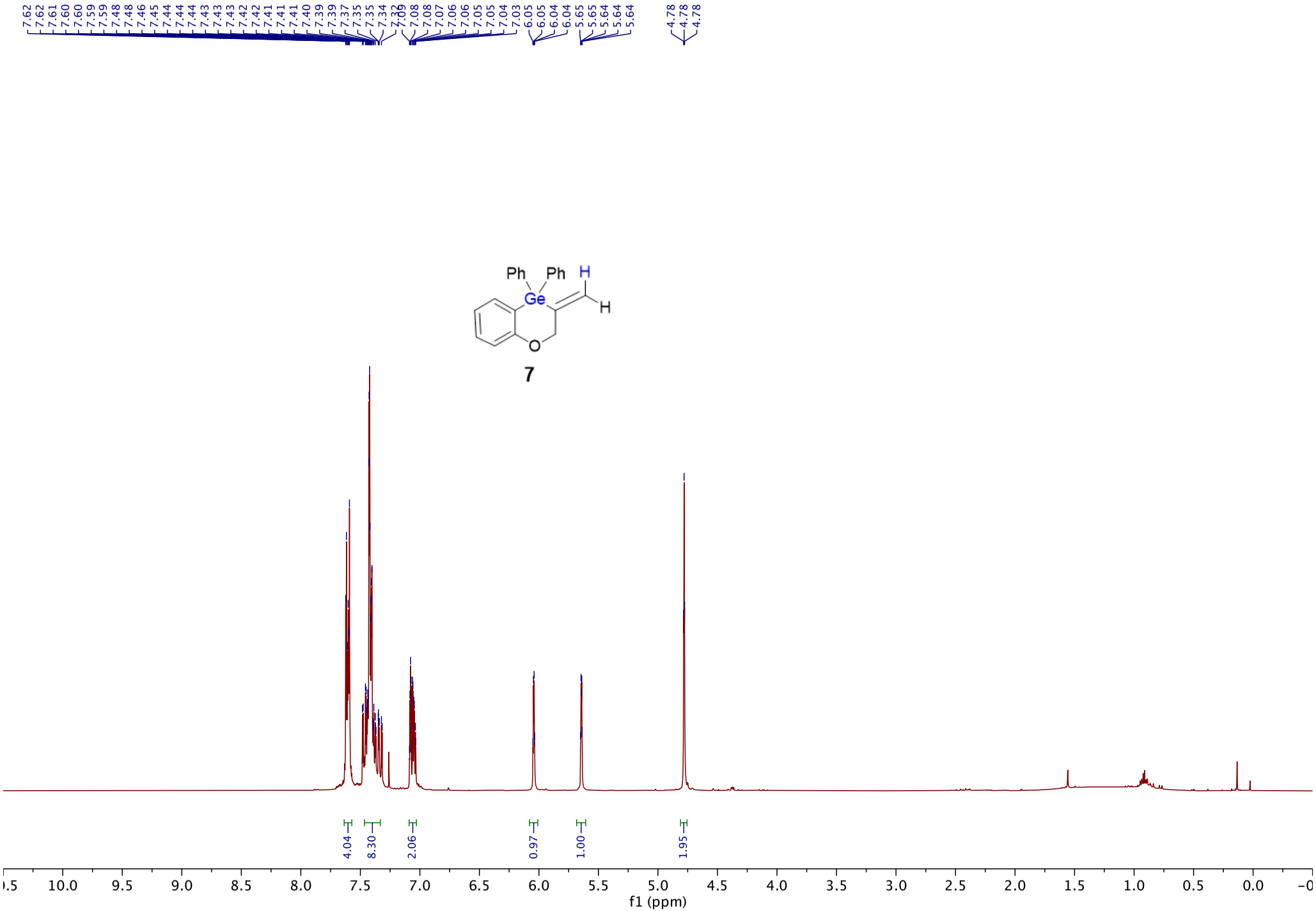
4je *Z*/E = 98/2

7.53
7.53
7.52
7.51
7.50
7.44
7.42
7.42
7.41
7.40
7.39
7.37
7.36
7.34
7.11
7.11
7.09
7.09
7.09
7.08
7.07
7.07
6.60
6.59
6.59
4.76
4.75
4.00
8.02
2.07
0.99
2.01
f1 (ppm)
Ph
Ge
Ph
H
O
I
5d

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
164.32
149.56
135.05
134.84
133.91
131.45
129.97
128.77
123.45
123.17
119.69
87.75
79.63
Ph
Ge
Ph
H
O
I
5d

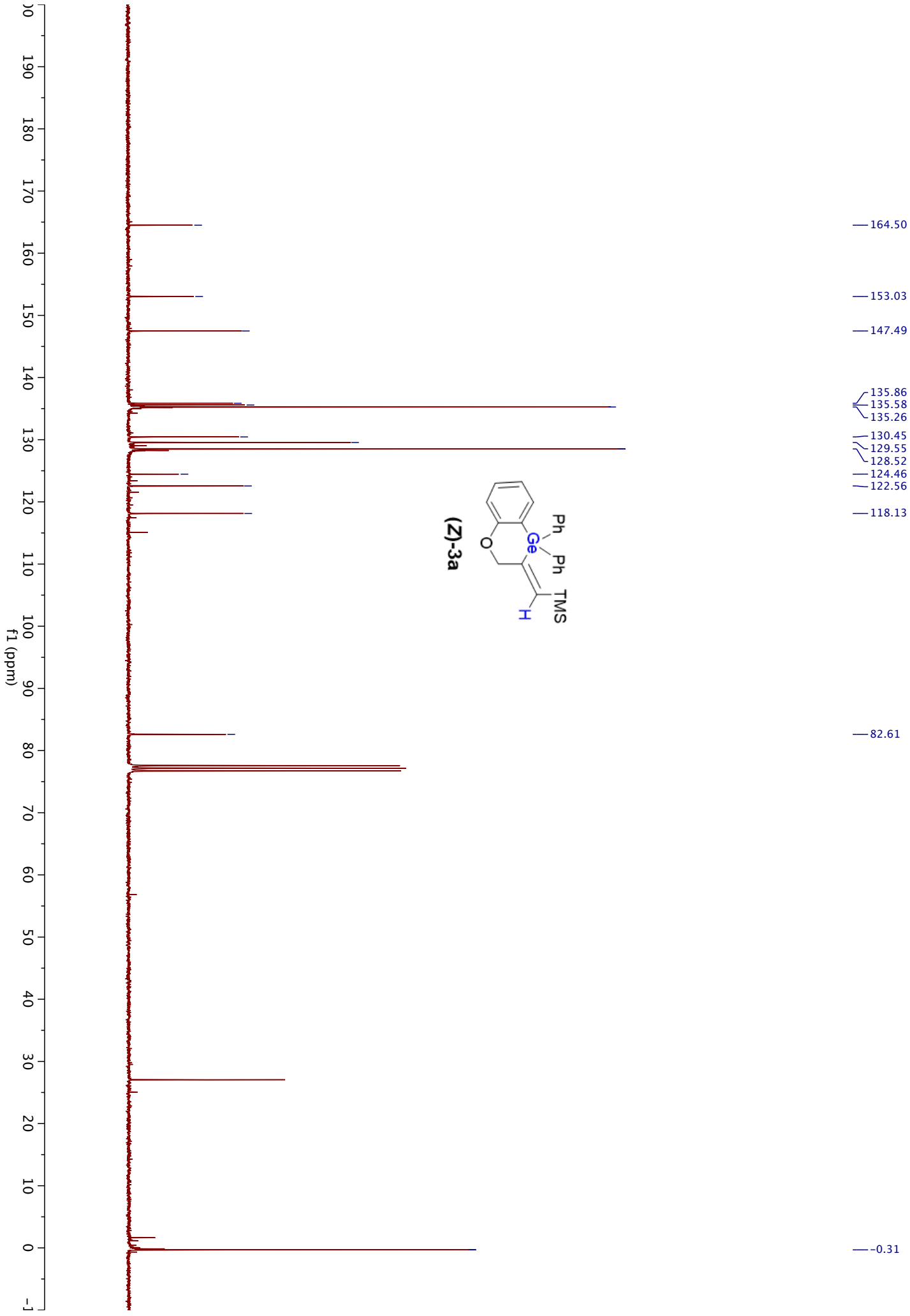

7.56
7.55
7.54
7.54
7.54
7.53
7.52
7.43
7.42
7.42
7.41
7.40
7.40
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.36
7.35
7.35
7.10
7.10
7.09
7.09
7.07
7.07
7.07
7.07
7.06
7.04
7.04
5.98
5.98
5.97
5.07
5.06
0.23
Ph
Ph
H
Ge
TMS
O
6
4.00
8.07
2.02
0.97
2.00
9.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

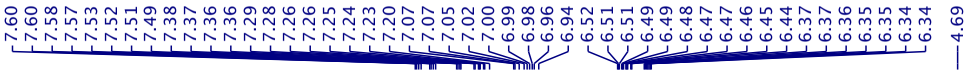

164.60
153.57
135.51
134.92
134.47
131.19
129.77
128.68
123.15
122.94
119.43
118.41
102.41
100.28
73.45
0.03
Ph
Ph
H
Ge
TMS
O
6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

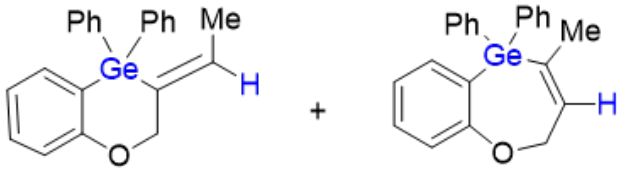

7.62 7.62 7.61 7.60 7.60 7.59 7.59 7.48 7.48 7.46 7.45 7.44 7.44 7.44 7.43 7.43 7.43 7.42 7.42 7.41 7.41 7.41 7.40 7.39 7.39 7.37 7.35 7.35 7.34 7.32 7.08 7.08 7.07 7.06 7.06 7.05 7.05 7.04 7.03 6.05 6.05 6.04 6.04 5.65 5.65 5.64 5.64 5.64 4.78 4.78 4.78
Ph
Ph
H
Ge
H
O
7
4.04
8.30
2.06
0.97
1.00
1.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

164.74
145.85
135.90
135.25
134.84
130.93
129.58
128.59
126.54
122.64
122.11
119.04
77.01
f1 (ppm)
7
Ph
Ge
Ph
H
O
H

(Z)-3a
Ph
Ph
TMS
H
O
Ge
f1 (ppm)
4.03
6.07
1.05
1.02
2.02
0.98
2.00
9.00
7.64
7.63
7.62
7.62
7.62
7.61
7.61
7.41
7.41
7.40
7.39
7.38
7.37
7.36
7.36
7.32
7.31
7.30
7.29
7.24
6.97
6.96
6.96
6.95
6.95
6.94
6.93
6.91
6.91
6.79
6.79
6.78
4.74
4.73
-0.21

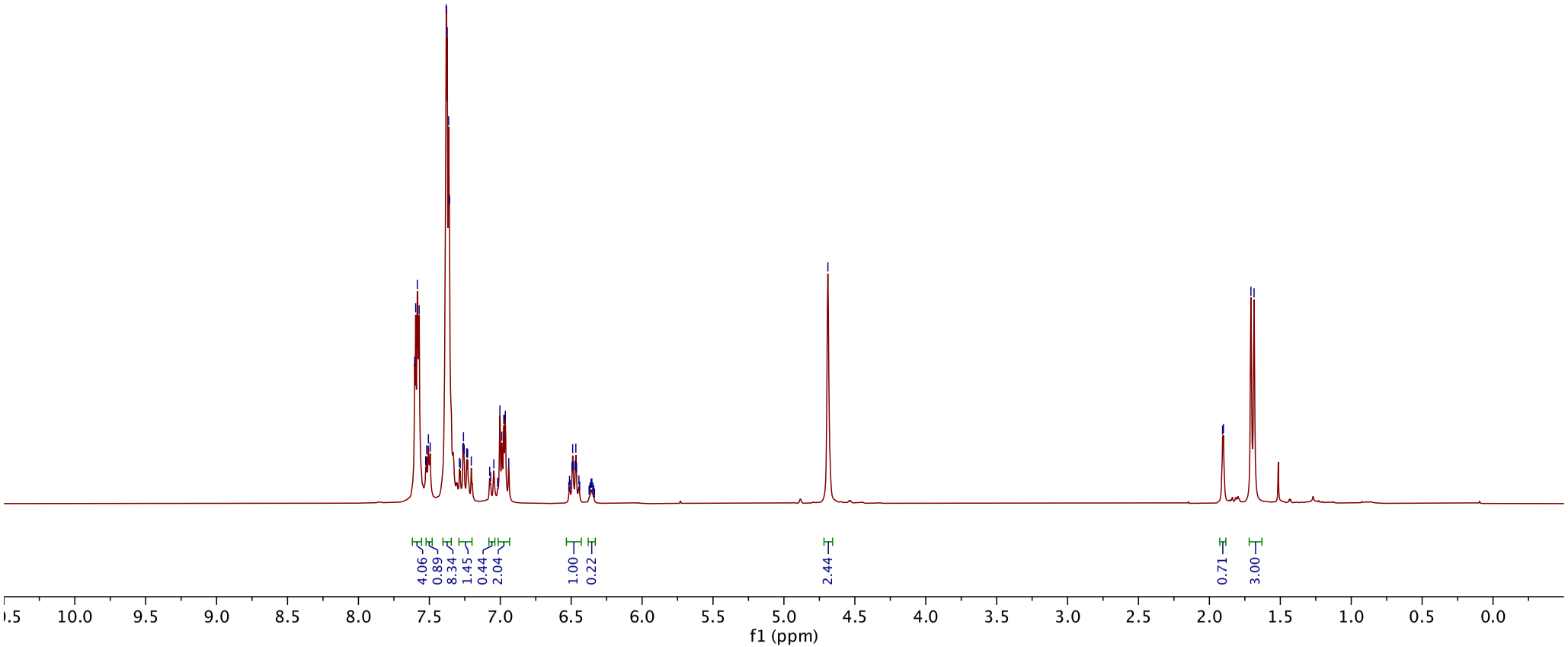

164.50
153.03
147.49
135.86
135.58
135.26
130.45
129.55
128.52
124.46
122.56
118.13
82.61
-0.31
f1 (ppm)
(Z)-3a
Ph
Ph
TMS
Ge
O
H

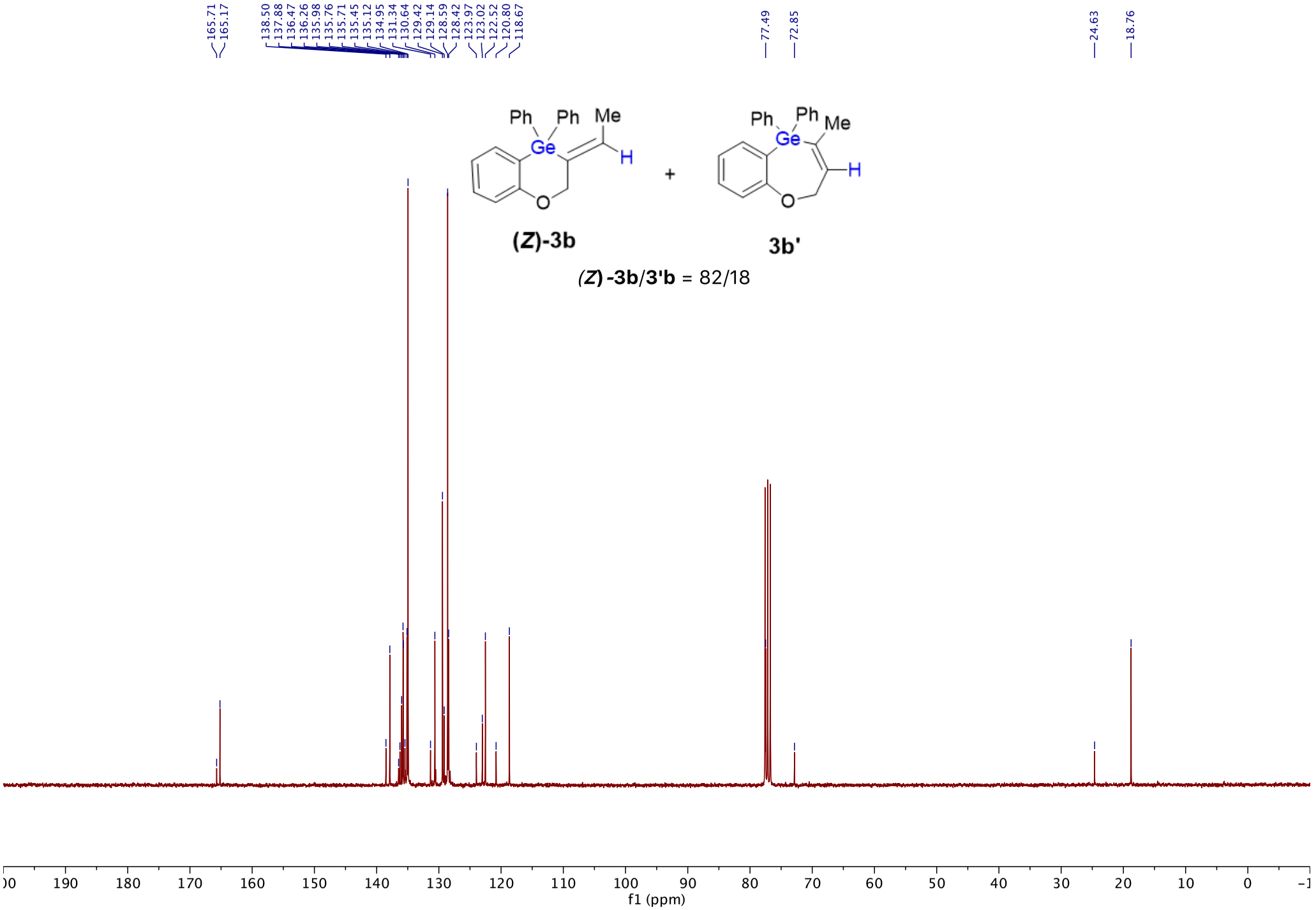


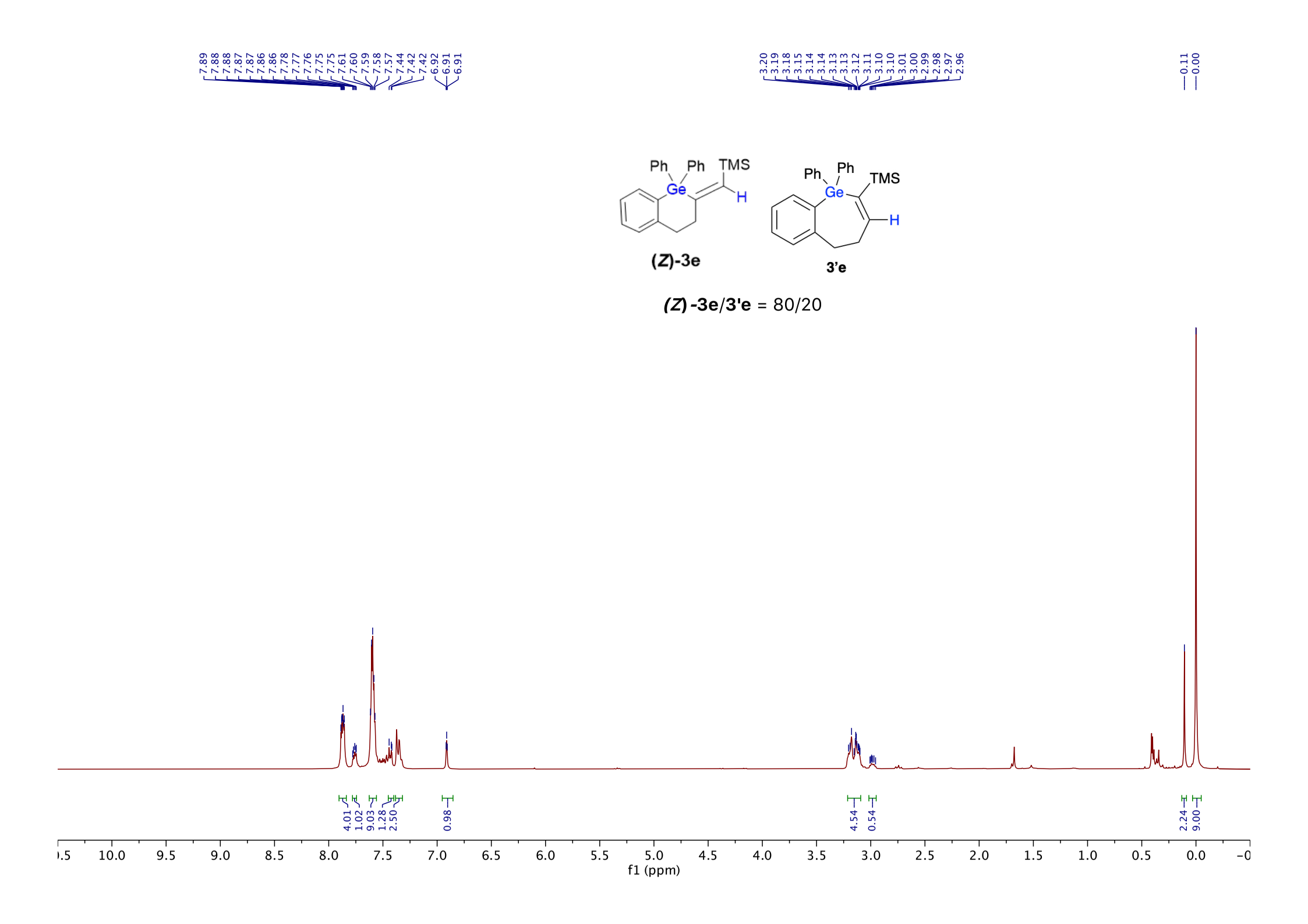


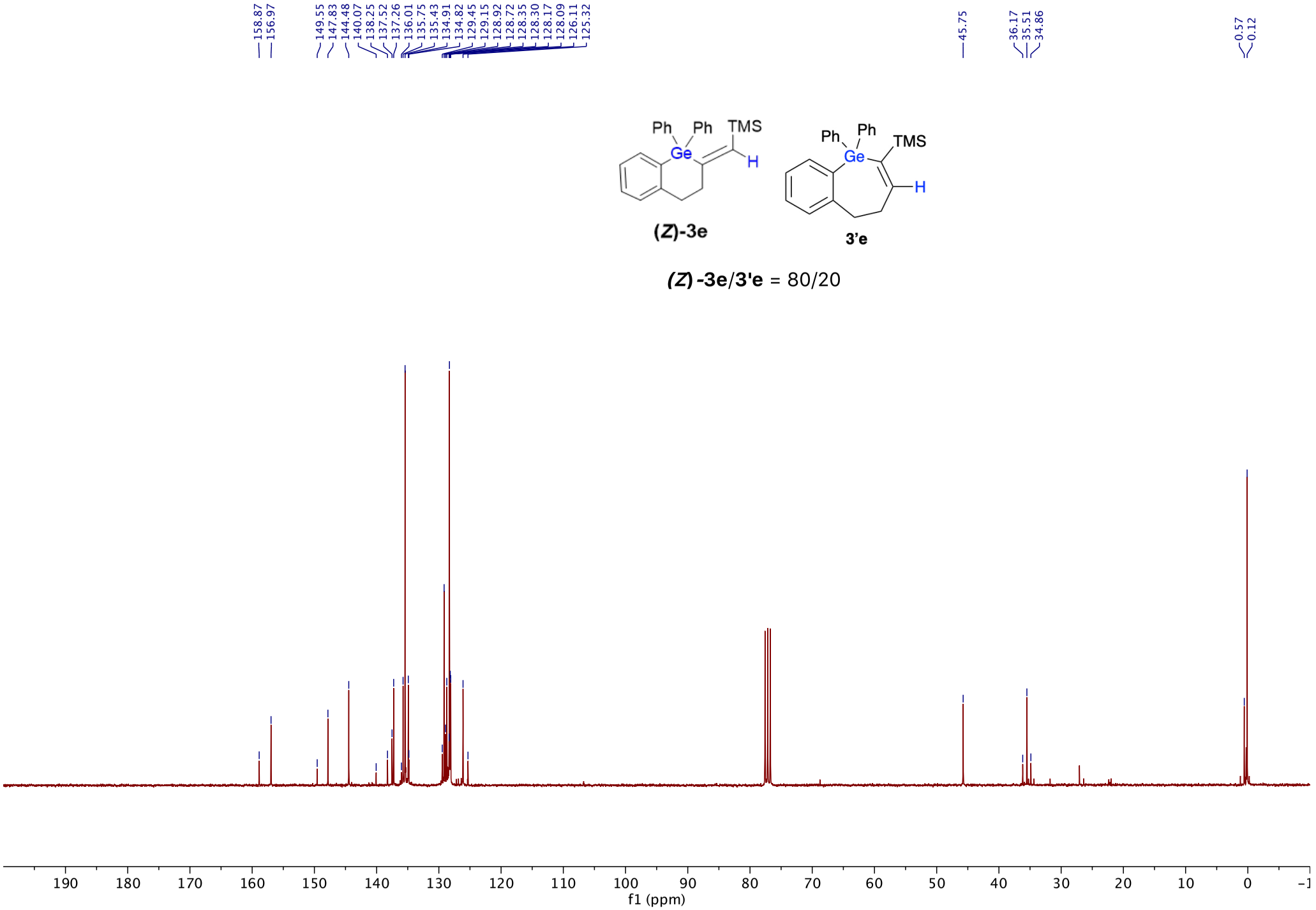
(*Z*)-3b **3b'**

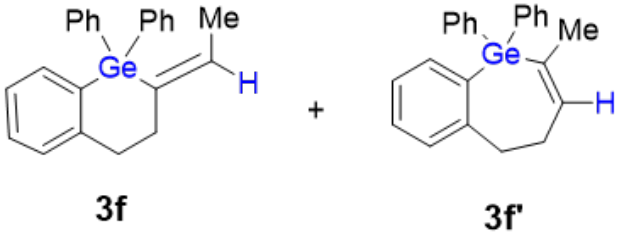
***(Z)*-3b/3'b** = 82/18




165.71
165.17
138.50
137.88
136.47
136.26
135.98
135.76
135.71
135.45
135.12
134.95
131.34
130.64
129.42
129.14
128.59
128.42
123.97
123.02
122.52
120.80
118.67
77.49
72.85
24.63
18.76
Ph
Ph
Me
Ge
H
O
+
Ph
Ph
Me
Ge
H
O
(Z)-3b
3b'
(Z)-3b/3'b = 82/18
f1 (ppm)

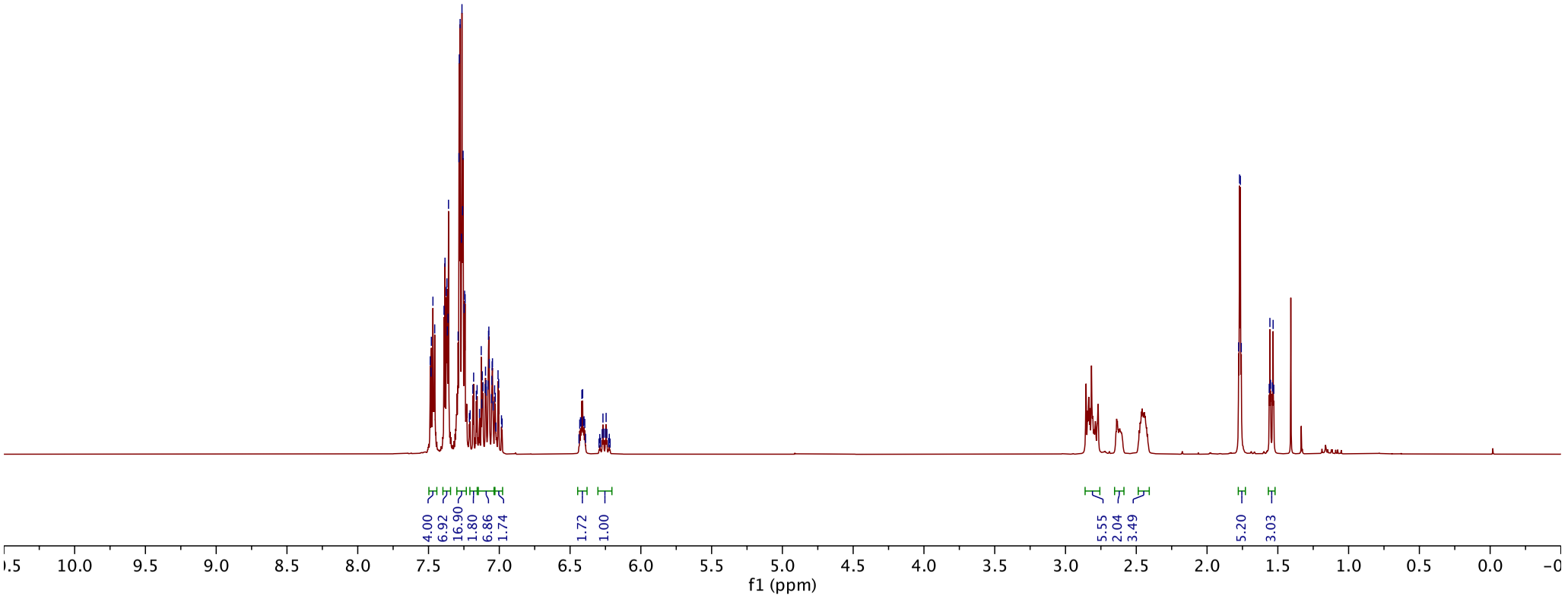

7.89
7.88
7.88
7.87
7.87
7.86
7.86
7.78
7.77
7.76
7.75
7.75
7.61
7.60
7.59
7.58
7.57
7.44
7.42
7.42
6.92
6.91
6.91
3.20
3.19
3.18
3.15
3.14
3.14
3.13
3.13
3.12
3.11
3.10
3.10
3.01
3.00
2.99
2.98
2.97
2.96
0.11
0.00
Ph
Ph
TMS
Ge
H
(Z)-3e
Ph
Ph
TMS
Ge
H
3'e
(Z)-3e/3'e = 80/20
4.01
1.02
9.03
1.28
2.50
0.98
4.54
0.54
2.24
9.00
f1 (ppm)

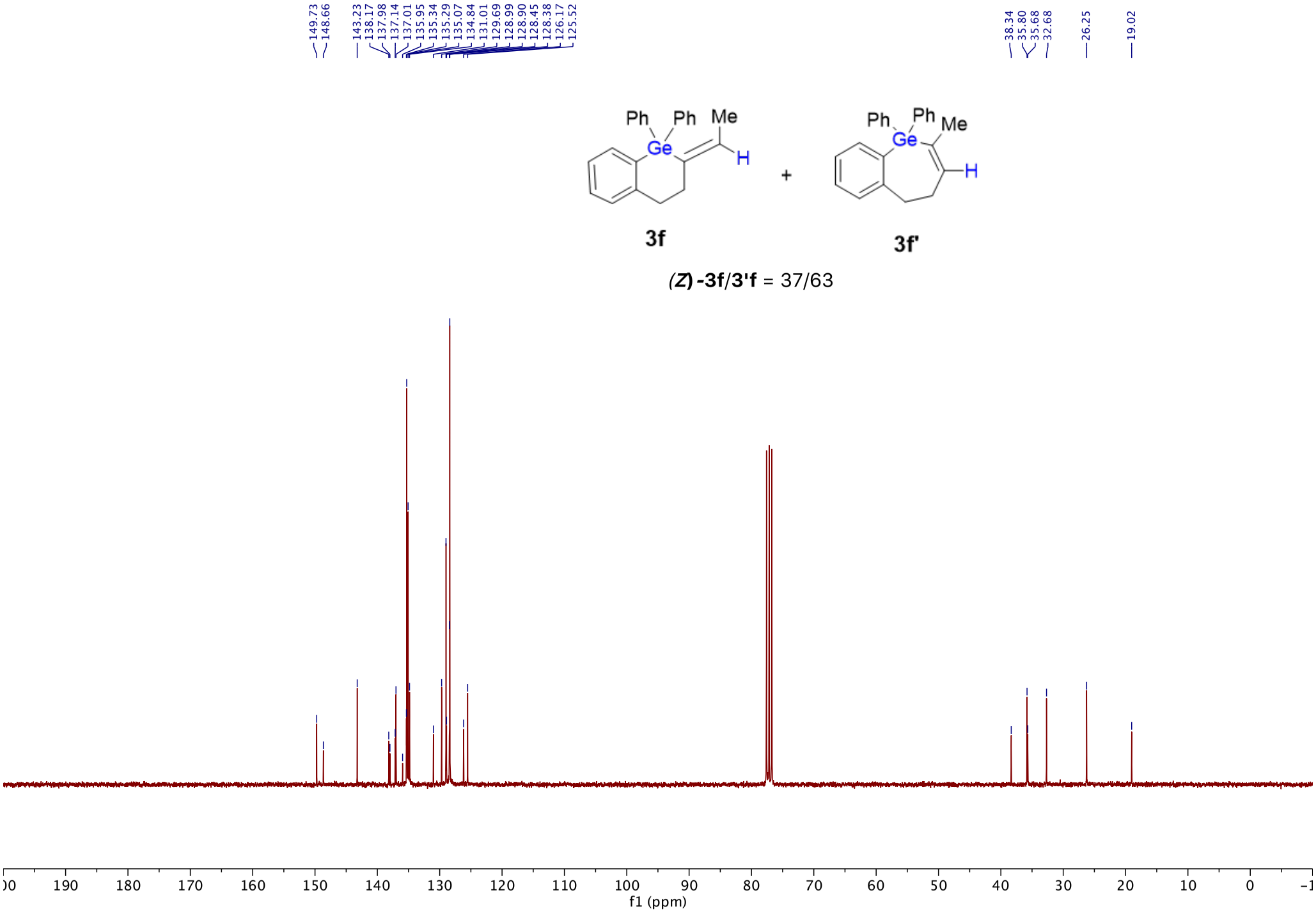

158.87
156.97
149.55
147.83
144.48
140.07
138.25
137.52
137.26
136.01
135.75
135.43
134.91
134.82
129.45
129.15
128.92
128.72
128.35
128.30
128.17
128.09
126.11
125.32
45.75
36.17
35.51
34.86
0.57
0.12
Ph
Ph
TMS
Ge
H
(Z)-3e
Ph
Ph
TMS
Ge
H
3'e
(Z)-3e/3'e = 80/20
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

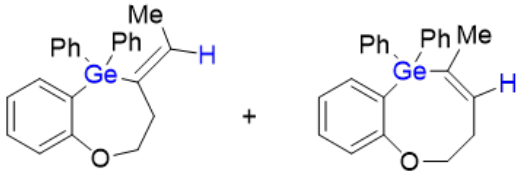


3f **3f'**

***(Z)*-3f/3'f** = 37/63

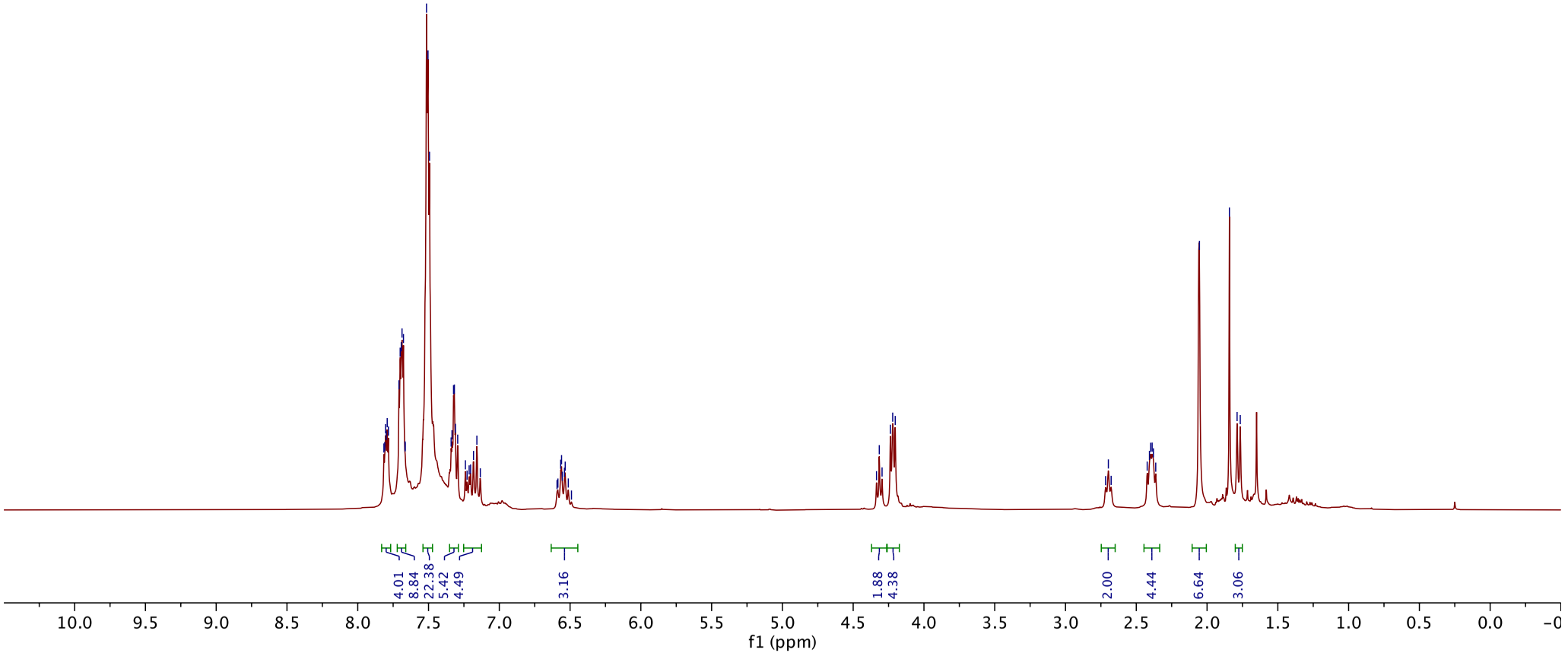


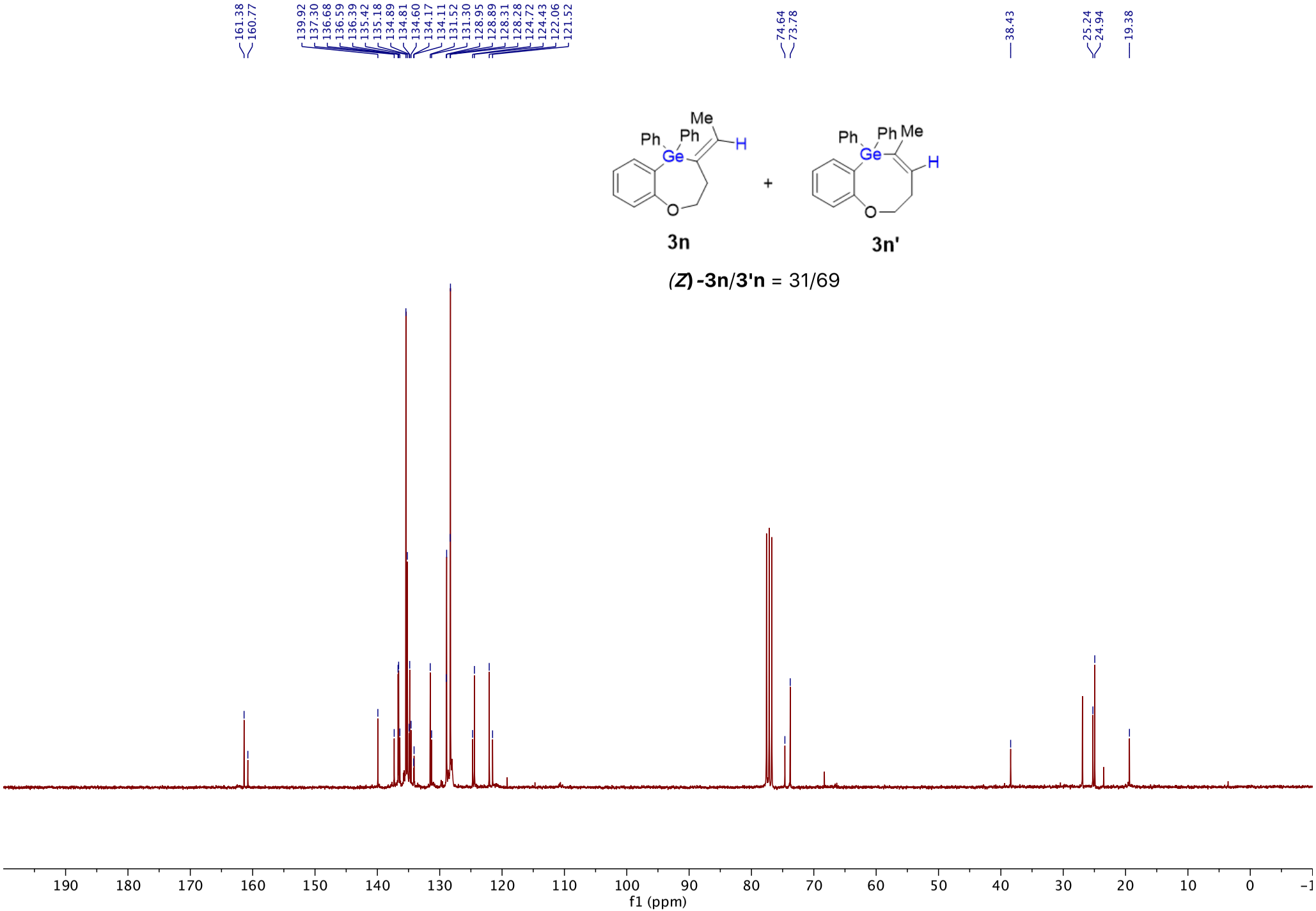

149.73
148.66
143.23
138.17
137.98
137.14
137.01
135.95
135.34
135.29
135.07
134.84
131.01
129.69
128.99
128.90
128.45
128.38
126.17
125.52
38.34
35.80
35.68
32.68
26.25
19.02
Ph
Ph
Me
Ge
H
+
Ph
Ph
Me
Ge
H
3f
3f'
(Z)-3f/3'f = 37/63
f1 (ppm)



3n **3n'**

***(Z)*-3n/3'n** = 31/69




161.38
160.77
139.92
137.30
136.68
136.59
136.39
135.42
135.18
134.89
134.81
134.60
134.17
134.11
131.52
131.30
128.95
128.89
128.31
128.28
124.72
124.43
122.06
121.52
74.64
73.78
38.43
25.24
24.94
19.38
Me
Ph
Ph
Ge
H
O
+
Ph
Ph
Me
Ge
H
O
3n
3n'
(Z)-3n/3'n = 31/69
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)