Modular Access to Substituted Germoles by Intramolecular Germylzincation

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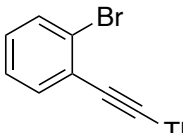
Supporting Information

General Information. Mass spectra were recorded with a quadrupolar MS instrument coupled to a gas chromatograph. Column chromatographies were performed on standard silica gel (230-400 mesh). Analytical thin layer chromatography was performed on silica gel plates (Merck® TLC Silica gel 60 F254) and the spots were visualized by illumination with a UV lamp (λ = 254/365 nm) and/or staining with $KMnO_4$. ^1H NMR spectra were recorded in $CDCl_3$ at 300 MHz, and ^{13}C NMR spectra were recorded at 75 MHz; chemical shift (δ) are given in parts per million (ppm) and the coupling constants (*J*) in hertz. The following abbreviations were used in the spectral description: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), ddd (doublet of doublet of doublet), dt (doublet of triplet), br (broad signal), m (multiplet). IR spectra 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. High-resolution mass spectrometry (HRMS) were recorded either 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 (oa-TOF) mass spectrometer (Waters Micromass) equipped with an ESI source. Melting points (Mp) were measured with a Kofler apparatus from Wagner and Munz. Unless otherwise noted, all chemicals were used as received from commercial sources without further purification. THF was freshly distilled over Na/benzophenone before use, and Hexane was freshly distilled over CaH_2 before use.

General procedure for Sonogashira reaction: To a solution of aryl or vinyl halides (0.2-15 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (0.02 equiv), CuI (0.04 equiv) and Et_3N (2 equiv) in dry THF was added dropwise a solution of terminal alkynes (1.5 equiv) at room temperature. The resulting mixture was stirred at reflux for 4h, then after cooling to room temperature, the reaction mixture was filtered through celite. The filtrate was evaporated under reduced pressure, and the residue was dissolved in Et_2O, washed with a saturated aqueous solution of NH_4Cl and

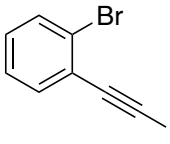
brine. The obtained organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduce pressure before being purified by flash chromatography on silica gel.



((2-bromophenyl)ethynyl)trimethylsilane 1a

Compound **1a** was prepared according to general procedure for **Sonogashira reaction** using 2-bromoiodobenzene (1.36 mL, 10.604 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (150 mg, 0.214 mmol, 0.02 equiv), CuI (82 mg, 0.428 mmol, 0.04 equiv), Et_3N (3 mL, 21.208 mmol, 2 equiv) and trimethylsilyl acetylene (2.2 mL, 15.906 mmol, 1.5 equiv) in dry THF (20 mL). Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 99.5:0.5, 99/1) afforded **1a** (2.607 g, 10.296 mmol, 97%) as a yellow oil.

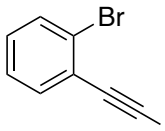
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.49 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.24 (td, *J* = 7.6, 1.2 Hz, 1H), 7.15 (td, *J* = 7.8, 1.8 Hz, 1H), 0.27 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 139.6, 132.4, 129.6, 126.9, 125.8, 125.3, 103.2, 99.6, -0.02 (3C); **IR** (neat)**:** υ_{max} = 2960, 2163, 1465, 1249, 838, 750, 669, 448 cm^{-1}; **MS** (CI, methane): m/z (%) : 253 (100, MH^+).



1-bromo-2-(3,3-dimethylbut-1-yn-1-yl)benzene 1b

Compound **1b** was prepared according to general procedure for **Sonogashira reaction** using 2-bromoiodobenzene (1.36 mL, 10.602 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (149 mg, 0.212 mmol, 0.02 equiv), CuI (81 mg, 0.424 mmol, 0.04 equiv), Et_3N (3 mL, 21.200 mmol, 2 equiv) and *tert*-butyl acetylene (1.293 g, 15.750 mmol, 1.5 equiv) in dry THF (20 mL). Purification of the crude product by flash chromatography on silica gel (Cyclohexane = 100) afforded **1b** (2.345 g, 9.889 mmol, 93%) as a green oil.

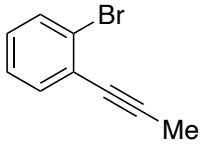
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.41 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.21 (td, *J* = 7.7, 0.8 Hz, 1H), 7.10 (td, *J* = 8.0, 1.6 Hz, 1H), 1.35 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 133.1, 132.3, 128.6, 126.9, 126.1, 125.8, 103.6, 78.2, 30.9, 28.3 (3C); **IR** (neat)**:** υ_{max} = 2968, 2200, 1465, 1433, 1026, 750, 679, 442 cm^{-1}; **HRMS** (IC): calcd for $C_{12}H_{14}{}^{79}Br$ ($M+H^+$) 237.0279, found 237.0274.



1-bromo-2-(but-1-yn-1-yl)benzene 1c

Compound **1c** was prepared according to general procedure for **Sonogashira reaction** using 2-bromoiodobenzene (1.36 mL, 10.602 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (149 mg, 0.212 mmol, 0.02 equiv), CuI (81 mg, 0.424 mmol, 0.04 equiv), Et_3N (3 mL, 21.200 mmol, 2 equiv) and 1-butyne (2.350 g, 43.446 mmol, 4.1 equiv) is bubbled in mixture (mixture turns from yellow to green), dry THF (20 mL). Purification of the crude product by flash chromatography on silica gel (Petroleum ether = 100) afforded **1c** (2.032 g, 9.718 mmol92%) as a brown oil.

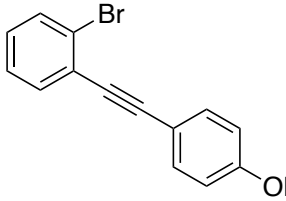
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.43 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.22 (td, *J* = 7.7, 1.2 Hz, 1H), 7.11 (td, *J* = 8.0, 1.7 Hz, 1H), 2.48 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 133.4, 132.4, 128.8, 127.0, 126.1, 125.5, 96.9, 78.8, 13.9, 13.4; **IR** (neat)**:** υ_{max} = 2977, 2937, 2239, 1588, 1470, 1321, 1026, 750, 445 cm^{-1}; **HRMS** (EI): calcd for $C_{10}H_9{}^{79}Br$ (M^+) 207.9888, found 207.9888.



1-bromo-2-(prop-1-yn-1-yl)benzene 1d[1]

To a suspension of $ZnCl_2$ (1.275 g, 9.350 mmol, 1.25 equiv)) in dry THF (10 mL) 1-propynyl-magnesium bromide (0.5 M solution in THF, 17 mL, 8.500 mmol, 1.13 equiv) was added dropwise at 0°C. The mixture was stirred for 20 minutes before adding successively $Pd(PPh_3)_4$ (120 mg, 0.104 mmol, 0.014 equiv) and 2-bromoiodobenzene (0.96 mL, 7.500 mmol, 1 equiv). The resulting mixture was stirred for 23h at room temperature and the reaction was then quenched with saturated NH_4Cl_{aq}. The mixture was dilute with 1 M HCl_{aq} and extracted with Et_2O. The Combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude was purified by flash chromatography on silica gel (Petroleum ether = 100) affording **1d** (1.463 g, 7.500 mmol, 100%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.42 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.22 (td, *J* = 7.6, 1.2 Hz, 1H), 7.11 (td, *J* = 8.0, 1.6 Hz, 1H), 2.11 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 133.3, 132.2, 128.6, 126.8, 125.9, 125.2, 90.9, 77.6, 4.4; **IR** (neat)**:** υ_{max} = 2915, 2231, 1588, 1469, 1432, 1053, 1025, 750 cm^{-1}; **HRMS** (EI): calcd for $C_9H_7{}^{79}Br$ (M^+) 193.9731, found 193.9736.

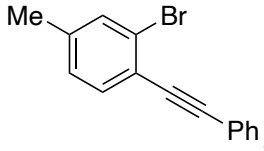


1-Bromo-2-[2-(4-methoxyphenyl)ethynyl]benzene 1e

[1] Ryo, S.; Nana, M.; Ryo, T. ; Kyoto, N. *Chem. Eur. J.* **2017**, *11*, 2660-2665.

Compound **1e** was prepared according to general procedure for **Sonogashira reaction** using 2-bromoiodobenzene (1.25 mL, 6.0 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (84 mg, 0.120 mmol, 0.02 equiv), CuI (45 mg, 0.240 mmol, 0.04 equiv), Et_3N (1.66 mL, 12.0 mmol, 2 equiv) and 4-methoxyphenyl acetylene (1.000 g, 7.566 mmol, 1.26 equiv) in dry THF (20 mL). Purification of the crude product by flash chromatography on silica gel (Petroleum ether/EtOAc = 99/1, 98/2) afforded **1e** (576 mg, 2.006 mmol, 33%) as a white solid.

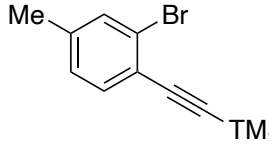
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.55-7.50 (m, 3H), 7.28 (td, *J* = 7.6, 1.2 Hz, 1H), 7.15 (td, *J* = 7.8, 1.8 Hz, 1H), 6.89 (m, 2H), 3.83 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 160.1, 133.3 (2C), 133.2, 132.5, 129.2, 127.1, 125.9, 125.6, 115.2, 114.2 (2C), 94.2, 87.0, 54.5.



2-bromo-4-methyl-1-(phenylethynyl)benzene 1f

Compound **1f** was prepared according to general procedure for **Sonogashira reaction** using 2-bromo-1-iodo-4-methylbenzene (1.597 g, 5.302 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (75 mg, 0.107 mmol, 0.02 equiv), CuI (41 mg, 0.214 mmol, 0.04 equiv), Et_3N (1.5 mL, 10.604 mmol, 2 equiv) and phenylacetylene (0.87 mL, 7.953 mmol, 1.5 equiv) in dry THF (15 mL). Purification of the crude product by flash chromatography on silica gel (Petroleum ether = 100) afforded **1f** (1.437 g, 5.299 mmol, 97%) as a colorless oil.

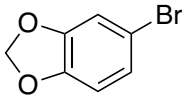
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64-7.61 (m, 2H), 7.49-7.46 (m, 2H), 7.41-7.38 (m, 3H), 7.11 (dd, *J* = 8.0, 1.5 Hz, 1H), 2.36 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 140.1, 133.0, 132.9, 131.7, 128.5 (2C), 128.4, 128.1(2C), 125.5, 123.2, 122.4, 93.2, 88.3, 21.2; **IR** (neat)**:** υ_{max} = 2988, 2102, 1593, 1487, 1441, 1039, 818, 752, 686 cm^{-1}; **HRMS** (EI): calcd for $C_{15}H_{11}{}^{79}Br$ (M^+) 270.0044, found 270.0039.



((2-bromo-4-methylphenyl)ethynyl)trimethylsilane 1g

Compound **1g** was prepared according to general procedure for **Sonogashira reaction** using 2-bromo-1-iodo-4-methylbenzene (1.597 g, 5.302 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (75 mg, 0.106 mmol, 0.02 equiv), CuI (41 mg, 0.212 mmol, 0.04 equiv), Et_3N (1.5 mL, 10.604 mmol, 2 equiv) and trimethylsilylacetylene (1.1 mL, 7.953 mmol, 1.5 equiv) in dry THF (15 mL). Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 99.5:0.5, 99:1) afforded **1g** (1.135 g, 4.247 mmol, 80%) as a yellow oil.

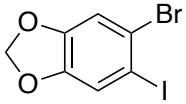
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39-7.35 (m, 2H), 7.04 (dd, *J* = 7.9, 1.0 Hz, 1H), 2.31 (s, 3H), 0.26 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 140.3, 133.4, 133.0, 127.9, 125.6, 122.3, 103.3, 98.7, 21.3, 0.03 (3C); **IR** (neat)**:** υ_{max} = 2959, 2163, 1601, 1484, 1250, 838, 632 cm^{-1}; **HRMS** (EI): calcd for $C_{12}H_{15}{}^{79}BrSi$ (M^+) 266.0126, found 266.0128.



5-bromobenzo[*d*][1,3]dioxole SI1[2]

To a solution of benzodioxole (1.7 mL, 14.777 mmol, 1 equiv) in anhydrous ACN (15 mL) a solution of NBS (2.630 g, 14.777 mmol) in ACN (15 mL) was added at 0°C. The solution was warmed to room temperature and stirred for 48 h before being quenched with water. The mixture was extracted with pentane and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude was purified by flash chromatography on silica gel (cyclohexane :100) affording **SI1** (2.377 g, 11.825 mmol, 80%) as a brown oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.96-6.92 (m, 2H), 6.70-6.67 (m, 1H), 5.96 (s, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 148.7, 147.1, 124.4, 113.2, 112.4, 109.7, 101.7; **IR** (neat)**:** υ_{max} = 2894, 1500, 1469, 1229, 1104, 1034, 796, 573 cm^{-1}; **HRMS** (EI): calcd for $C_7H_5{}^{79}BrO_2$ (M^+) 199.9473, found 199.9468.



5-bromo-6-benzo[*d*][1,3]dioxole SI2

SI2 was synthesized using modified protocols from the literature[3]. NIS (4.680 g, 20.804 mmol, 2 equiv) was added to a mixture of **SI1** (2.091 g, 10.402 mmol, 1 equiv), TFA (1.6 mL, 20.804 mmol, 2 equiv) in anhydrous ACN (40 mL) was added. The resultant mixture was stirred for 40h at room temperature before being hydrolyzed and stirred with saturated $Na_2S_2O_3$ for 15 minutes. The layers were separated, the aqueous layer was extracted with CH_2Cl_2 and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduce pressure. Crystallization of the crude in ethanol afforded **SI2** (3.300 g, 10.094 mmol, 97%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26 (s, 1H), 7.09 (s, 1H), 5.99 (s, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 149.2, 148.0, 120.7, 119.2, 112.8, 102.4, 89.4; **IR** (neat)**:** υ_{max} = 2893, 1498, 1474,

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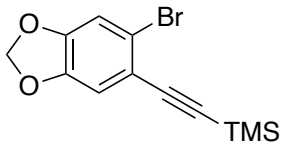
[2] E. Zysman-Colman, K. Arias, J. S. Siegel, *Can. J. Chem*, *87*, **2009**, 440-447

[3] D. Augros, B. Yalcouye, A. Berthelot-Brehier, M. Chesse, S. Choppin, A. Panossian, F. R. Leroux, *Tetrahedron, 72*, **2016**, 5208-5220

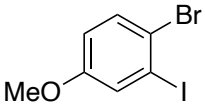
1231, 1033, 844, 411 cm^{-1}; **HRMS** (EI): calcd for $C_7H_4{}^{79}BrIO_2$ (M^+) 325.8439, found 325.8427; **mp**: 67.1-67.8°C.



((6-bromobenzo[*d*][1,3]dioxol-5-yl)ethynyl)trimethylsilane 1h

Compound **1h** was prepared according to general procedure for **Sonogashira reaction** using **SI2** (968 mg, 2.961 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (83 mg, 0.118 mmol, 0.04 equiv), CuI (45 mg, 0.236 mmol, 0.08 equiv), Et_3N (0.8 mL, 5.922 mmol, 2 equiv), trimethylsilylacetylene (0.61 mL, 4.441 mmol, 1.5 equiv) and dry THF (12 mL). Purification of the crude product by flash chromatography on silica gel (Cyclohexane = 100) afforded **1h** (750 mg, 2.521 mmol, 85%) as a colorless oil.

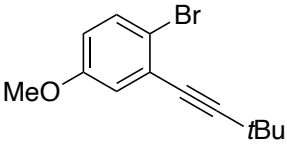
^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.99 (s, 1H), 6.91 (s, 1H), 5.97 (s, 2H), 0.26 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 148.8, 146.9, 118.2, 118.1, 112.7, 112.5, 103.3, 102.2, 98.0, 0.01 (3C); **IR** (neat)**:** υ_{max} = 2957, 2148, 1503, 1473, 1410, 1239, 1191, 1036, 837, 758 cm^{-1}; **HRMS** (EI): calcd for $C_{12}H_{13}{}^{79}BrO_2Si$ (M^+) 295.9868, found 295.9866.



1-bromo-2-iodo-4-methoxybenzene SI3

To a solution of 3-iodoanisole (1.19 mL, 10.0 mmol, 1.0 equiv) in AcOH (20 mL) was added a solution of bromine (0.67 mL, 13.0 mmol, 1.3 equiv) dropwise at 0°C and the reaction mixture was stirred for 24h at room temperature. The resultant mixture was hydrolyzed with saturated solution $Na_2S_2O_3$ before being extracted with pentane and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduce pressure. Purification of the crude product by flash chromatography on silica gel (Petroleum ether / EtOAc = 99.5 / 0.5) afforded **SI3** (2.793 g, 8.925 mmol, 89%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 8.9 Hz, 1H), 7.38 (d, *J* = 2.9 Hz, 1H), 6.77 (dd, *J* = 8.9, 2.9 Hz, 1H), 3.76 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 158.8, 132.7, 125.5, 120.4, 116.1, 101.2, 55.8; **IR** (neat)**:** υ_{max} = 3003, 2934, 1578, 1557, 1458, 1225, 1030, 600 cm^{-1}; **HRMS** (EI): calcd for $C_7H_6{}^{79}BrIO$ (M^+) 311.8647, found 311.8646.

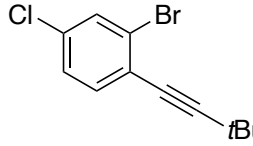


1-bromo-2-(3,3-dimethylbut-1-yn-1-yl)-4-methoxybenzene 1i

Compound **1i** was prepared according to general procedure for **Sonogashira reaction** using **SI3** (2.793 g, 8.952 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (126 mg, 0.179 mmol, 0.02 equiv), CuI (68

mg, 0.358 mmol, 0.04 equiv), Et_3N (2.5 mL, 17.904 mmol, 2 equiv) and tert-butylacetylene (1.65 mL, 13.428 mmol, 1.5 equiv) in dry THF (15 mL). Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 100/0, 99.5/0.5) afforded **1i** (2.019g, 7.557 mmol, 84%) as a colorless oil.

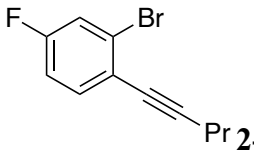
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.8 Hz, 1H), 6.93 (d, *J* = 3.0 Hz, 1H), 6.68 (dd, *J* = 8.8, 3.0 Hz, 1H), 3.77 (s, 3H), 1.35 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 158.4, 132.8, 126.5, 117.6, 116.4, 115.6, 103.3, 78.2, 55.4, 30.9, 28.2 (3C); **IR** (neat)**:** υ_{max} = 2968, 2867, 2222, 1588, 1565, 1464, 1231, 1019, 600 cm^{-1}; **HRMS** (EI): calcd for $C_{13}H_{15}{}^{79}BrO$ (M^+) 266.0306, found 266.0315.



2-bromo-4-chloro-1-(3,3-dimethylbut-1-yn-1-yl)benzene 1j

Compound **1j** was prepared according to general procedure for **Sonogashira reaction** using 4-chloro-2-bromoiodobenzene (1.904 g, 6.000 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (84 mg, 0.120 mmol, 0.02 equiv), CuI (46 mg, 0.240 mmol, 0.04 equiv), Et_3N (1.66 mL, 12.000 mmol, 2 equiv) and *tert*-butylacetylene (1.1 mL, 9.000 mmol, 1.5 equiv) in dry THF (15 mL). Purification of the crude product by flash chromatography on silica gel (Petroleum ether = 100) afforded **1j** (1.532 g, 5.641 mmol, 94%) as a colorless oil.

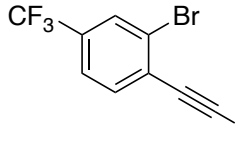
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 2.0 Hz, 1H), 7.33 (d, *J* = 8.4, 1H), 7.20 (dd, *J* = 8.4, 2.0 Hz, 1H), 1.34 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 133.6, 133.5, 132.1, 127.3, 126.2, 124.8, 104.6, 77.3, 30.9, 28.4 (3C); **IR** (neat)**:** υ_{max} = 2969, 2865, 2242, 1581, 1465, 1362, 1095, 813, 735, 563 cm^{-1}; **HRMS** (EI): calcd for $C_{12}H_{12}{}^{79}BrCl$ (M^+) 269.9811, found 269.9820.



2-bromo-4-fluoro-1-(pent-1-yn-1-yl)benzene 1k

Compound **1k** was prepared according to general procedure for **Sonogashira reaction** using 1-bromo-4-fluoro-2-iodobenzene (1.33 mL, 5.919 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (166 mg, 0.236 mmol, 0.04 equiv), CuI (90 mg, 0.473 mmol, 0.08 equiv), Et_3N (1.60 mL, 11.838 mmol, 2 equiv) and pent-1-yne (0.87 mL, 8.878 mmol, 1.5 equiv) in dry THF (15 mL). Purification of the crude product by flash chromatography on silica gel (Petroleum ether = 100) afforded **1k** (1.151 g, 4.774 mmol, 81%) as a brown oil.

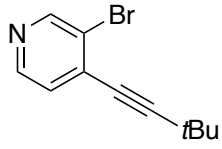
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (dd, *J* = 8.7, 6.0 Hz, 1H), 7.31 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.95 (td, *J* = 8.3, 2.6 Hz, 1H), 2.43 (t, *J* = 7.0 Hz, 2H), 1.6 (sextuplet, *J* = 7.2 Hz, 2H), 1.07 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 161.4 (d, *J* = 252 Hz), 134.3 (d, *J* = 8 Hz), 126.0 (d, *J* = 10 Hz), 122.5 (d, *J* = 4 Hz), 119.8 (d, *J* = 25 Hz), 114.5 (d, *J* = 22 Hz), 95.1 (d, *J* = 2 Hz), 78.6, 22.1, 21.6, 13.6; **^{19}F NMR** (282 MHz, $CDCl_3$): -110.4; **IR** (neat)**:** υ_{max} = 2964, 2869, 2238, 1596, 1484, 1383, 1254, 1196, 816, 423 cm^{-1}; **HRMS** (EI): calcd for $C_{11}H_{10}{}^{79}BrF$ (M^+) 239.9945, found 239.9946.



((2-bromo-4-(trifluoromethyl)phenyl)ethynyl)trimethylsilane 1l

Compound **1l** was prepared according to general procedure for **Sonogashira reaction** using 2-bromo-1-iodo-4-(trifluoromethyl) benzene (0.95 mL, 5.919 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (166 mg, 0.237 mmol, 0.04 equiv), CuI (90 mg, 0.474 mmol, 0.08 equiv), Et_3N (1.6 mL, 11.838 mmol, 2 equiv) and trimethylsilyl acetylene (1.23 mL, 8.878 mmol, 1.5 equiv) in dry THF (15 mL). Purification of the crude product by flash chromatography on silica gel (Cyclohexane = 100) afforded **1l** (1.660 g, 5.168 mmol, 78%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83 (s, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.49 (dd, *J* = 8.1, 1.0 Hz, 1H), 0.29 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 133.8, 131.3 (q, *J* = 33.5 Hz), 129.5 (q, *J* = 3.8 Hz), 129.2, 126.1, 123.9 (q, *J* = 3.8 Hz), 122.9 (q, *J* = 272.7 Hz), 103.1, 101.8, -0.2 (3C); **^{19}F NMR** (282 MHz, $CDCl_3$): -62.9; **IR** (neat)**:** υ_{max} = 2962, 2069, 1607, 1386, 1317, 1130, 832, 759, 691 cm^{-1}; **HRMS** (EI): calcd for $C_{12}H_{12}{}^{79}BrF_3Si$ (M^+) 319.9843, found 319.9858.

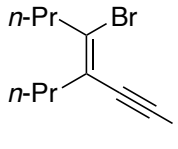


3-bromo-4-(3,3-dimethylbut-1-yn-1-yl)pyridine 1m

Compound **1m** was prepared according to general procedure for **Sonogashira reaction** using 3-bromo-4-iodopyridine (1.000 g, 3.522 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (49 mg, 0.070 mmol, 0.02 equiv), CuI (27 mg, 0.140 mmol, 0.04 equiv), Et_3N (1 mL, 7.044 mmol, 2 equiv) and *tert*-butylacetylene (0.65 mL, 5.283 mmol, 1.5 equiv) in dry THF (12 mL). Purification of the crude product by flash chromatography on silica gel (Cyclohexane = 100) afforded **1m** (748 mg, 3.141 mmol, 89%) as a brown oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.71 (s, 1H), 8.41 (d, *J* = 5.0 Hz, 1H), 7.26 (d, *J* = 5.0, 1H), 1.35 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 151.6, 147.7, 133.9, 126.8, 123.6, 109.2, 76.3,

30.6, 28.6 (3C); **IR** (neat)**:** υ_{max} = 2970, 2868, 2247, 1575, 1469, 1397, 1086, 832, 574 cm^{-1}; **HRMS** (API+): calcd for $C_{11}H_{13}{}^{79}BrN$ (MH^+) 238.0231, found 238.0239.

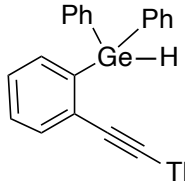


(*Z*)-(4-bromo-3-propylhept-3-en-yn-1-yl)trimethylsilane 1n[4]

In a dry sealed tube, the mixture ACN (10 mL), $Pd(OAc)_2$ (112 mg, 0.500 mmol, 0.05 equiv), 4-octyne (1.46 mL, 10.000 mmol, 1 equiv) and (bromoethynyl)(trimethylsilane (2125 mg, 12 mmol, 1.2 equiv) was stirred for 14 h at 30°C. The resulting mixture was filtered through short column with silica gel and Na_2SO_4 layers. The crude was purified by flash chromatography on silica gel (cyclohexane / EtOAc 99.5:0.5) affording **1n** (900 mg, 3.132 mmol, 31%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.52 (t, *J* = 7.3 Hz, 2H), 2.18 (t, *J* = 7.3 Hz, 2H), 1.65-1.51 (m, 4H), 0.92 (td, *J* = 7.3, 2.3 Hz, 6H), 0.21 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 133.5, 124.5, 105.8, 98.6, 39.1, 35.2, 22.0 (2C), 13.8, 13.4, 0.1 (3C); **IR** (neat)**:** υ_{max} = 2961, 2933, 2873, 2148, 1459, 1380, 1249, 839, 758 cm^{-1}; **HRMS** (EI): calcd for $C_{13}H_{23}{}^{79}BrSi$ (M^+) 286.0752, found 286.0756.

General procedure for germylation of bromoaryls towards arylgermanes synthesis: To a solution of bromoaryls (1 - 10 mmol, 1 equiv) in anhydrous THF (5 - 20 mL) *n*-BuLi (2.4 M in hexane, 1.05 equiv) was added under argon atmosphere at -78°C. After stirring the mixture for 30 minutes, diphenylgermanium dichloride (1.0 - 1.1 equiv) was added and the resulting mixture was stirred at -78°C for 2 h. $LiAlH_4$ (1M in THF, 0.5 equiv) was then added to the mixture at 0°C followed by stirring for 1h at this temperature and subsequently for 1h at room temperature before being quenched with water and HCl (0.5 M, 2 – 20 ml). The mixture was extracted with DCM and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude was purified by flash chromatography on silica gel.



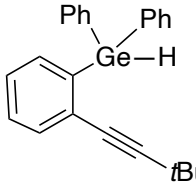
((2-(diphenylgermyl)phenyl)ethynyl)trimethylsilane 2a

Germane **2a** was prepared following the general procedure for **bromoaryls germylation** using **1a** (2.000 g, 7.900 mmol, 1 equiv), *n*-BuLi (2.4 M in hexane, 3.45 mL, 8.300 mmol, 1.05 equiv),

[4] H. Kinoshita, H. Fukumoto, A. Ueda, K. Miura, *Tetrahedron*, *74*, **2018**, 1632-1645

diphenylgermanium dichloride (2.352 g, 7.900 mmol, 1.0 equiv), $LiAlH_4$ (1M in THF, 3.95 mL, 3.950 mmol, 0.5 equiv) in anhydrous THF (20 mL). The crude was purified by flash chromatography on silica gel (Cyclohexane/Et_2O = 99.5:0.5, 99:1) affording **2a** (2.085 g, 5.197 mmol, 66%) as a yellow solid.

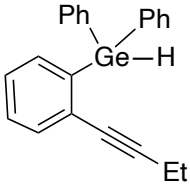
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56-7.51 (m, 5H), 7.39-7.32 (m, 9H), 5.89 (s, 1H), 0.02 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 139.1, 135.8 (2C), 135.5, 135.4 (4C), 132.4, 129.6, 129.2, 129.1 (2C), 128.3 (4C), 128.2, 105.6, 97.8, -0.3 (3C); **IR** (neat)**:** υ_{max} = 2957, 2156, 2046, 1485, 1459, 1431, 1248, 839, 695 cm^{-1}; **HRMS** (EI): calcd for $C_{23}H_{24}{}^{74}GeSi$ (M^+) 402.0859, found 402.0843; **mp**: 63.2-64.1°C.



(2-(3,3-dimethylbut-1-yn-yl)phenyl)diphenylgermane 2b

Germane **2b** was prepared following the general procedure for **bromoaryls germylation** using **1b** (910 mg, 3.837 mmol, 1 equiv), *n*-BuLi (2.5 M in hexane, 1.60 mL, 4.028 mmol, 1.05 equiv), diphenylgermanium dichloride (1.142 g, 3.837 mmol, 1.0 equiv), $LiAlH_4$ (1M in THF, 1.90 mL, 1.918 mmol, 0.5 equiv) in anhydrous THF (12 mL). The crude was purified by flash chromatography on silica gel (Cyclohexane/EtOAc = 99:1) affording **2b** (1.284 g, 3.334 mmol, 87%) as a yellow oil.

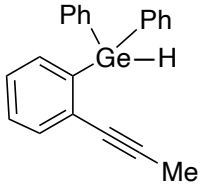
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54-7.46 (m, 5H), 7.37-7.17 (m, 9H), 5.90 (s, 1H), 1.05 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 138.2, 135.7 (3C), 135.4 (4C), 132.0, 130.5, 129.3, 129.1 (2C), 128.3 (4C), 127.3, 101.8, 80.2, 30.6 (3C), 28.0; **IR** (neat)**:** υ_{max} = 2967, 2925, 2044, 1484, 1460, 1431, 1093, 697 cm^{-1}; **HRMS** (EI): calcd for $C_{24}H_{24}{}^{74}Ge$ (M^+) 386.1090, found 386.1094.



(2-(but-1-yn-1-yl)phenyl)diphenylgermane 2c

Germane **2c** was prepared following the general procedure for **bromoaryls germylation** using **1c** (1.200 g, 5.739 mmol, 1.0 equiv), n-BuLi (2.5 M in hexane, 2.30 mL, 5.739 mmol, 1.0 equiv), diphenylgermanium dichloride (1.21 mL, 5.739 mmol, 1.0 equiv), LiAlH4 (1M in THF, 2.87 mL, 2.869 mmol, 0.5 equiv) in anhydrous THF (15 mL). The crude was purified by flash chromatography on silica gel (Cyclohexane/EtOAc = 100/1, 99.5/0.5) affording **2c** (1.220 g, 3.417 mmol, 59%) as a colorless oil.

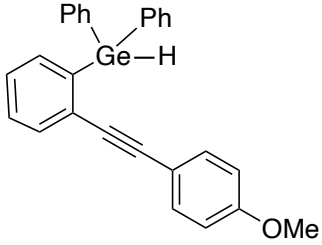
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55-7.51 (m, 4H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.35-7.26 (m, 8H), 7.20 (td, *J* = 7.5, 1.3 Hz, 1H), 5.86 (s, 1H), 2.15 (q, *J* = 7.5 Hz, 2H), 0.92 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 138.6, 135.8 (2C), 135.7, 135.3 (4C), 131.9, 130.4, 129.3, 129.0 (2C), 128.3 (4C), 127.3, 95.4, 81.0, 13.4, 13.1; **IR** (neat)**:** υ_{max} = 3049, 2935, 2041, 1582, 1430, 1092, 695, 462 cm^{-1}; **HRMS** (API+): calcd for $C_{22}H_{21}{}^{74}Ge$ ($M+H^+$) 359.0855, found 359.0859.



Diphenyl(2-(prop-1-yn-yl)phenyl)germane 2d

Germane **2d** was prepared following the general procedure for **bromoaryls germylation** using **1d** (1.057 g, 5.419 mmol, 1.0 equiv), *n*-BuLi (2.5 M in hexane, 2.17 mL, 5.419 mmol, 1.0 equiv), diphenylgermanium dichloride (1.14 mL, 5.419 mmol, 1.0 equiv), $LiAlH_4$ (1M in THF, 2.71 mL, 2.709 mmol, 0.5 equiv) in anhydrous THF (15 mL). The crude was purified by flash chromatography on silica gel (Cyclohexane/EtOAc = 100/1, 99.5/0.5, 99/1) affording **2d** (1.186g, 3.457 mmol, 64%) as a colorless oil.

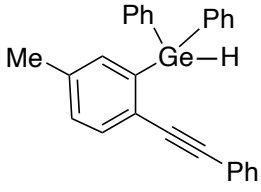
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56-7.53 (m, 4H), 7.44-7.28 (m, 9H), 7.22 (td, *J* = 7.4, 1.4 Hz, 1H), 5.84 (s, 1H), 1.74 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 138.8, 135.8 (2C), 135.7, 135.3 (4C), 131.8, 130.4, 129.3, 129.0 (2C), 128.3 (4C), 127.3, 89.8, 81.0, 4.2; **IR** (neat)**:** υ_{max} = 3049, 2043, 1582, 1484, 1430, 1092, 695 cm^{-1}; **HRMS** (ESI+): calcd for $C_{21}H_{19}{}^{74}GeO$ ($M+OH^+$) 361.0648, found 361.0675.



(2-((4-methoxyphenyl)ethynyl)phenyl)diphenylgermane 2e

Germane **2e** was prepared following the general procedure for **bromoaryls germylation** using **1e** (480 mg, 1.671 mmol, 1.0 equiv), *n*-BuLi (2.5 M in hexane, 0.67 mL, 1.671 mmol, 1.0 equiv), diphenylgermanium dichloride (0.40 mL, 4.425 mmol, 1.0 equiv), $LiAlH_4$ (1M in THF, 0.83 mL, 0.835 mmol, 0.5 equiv) in anhydrous THF (8 mL). The crude was purified by flash chromatography on silica gel (Petroleum ether/Toluene = 90/10, 80/20) affording **2e** (335 mg, 0.770 mmol, 46%) as a colorless oil.

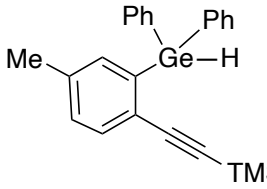
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64-7.57 (m, 5H), 7.45-7.42 (m, 1H), 7.40-7.35 (m, 7H), 7.30 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.06 (d, *J* = 9.0 Hz, 2H), 6.77 (d, *J* = 9.0 Hz, 2H), 5.97 (s, 1H), 3.80 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 159.7, 138.7, 135.9, 135.6 (2C), 135.5 (4C), 133.0 (2C), 132.0, 130.0, 129.4, 129.2 (2C), 128.4 (4C), 127.7, 115.3, 113.9 (2C), 92.8, 89.2, 55.4; **HRMS** (ESI+): calcd for $C_{27}H_{23}{}^{74}GeO$ ($M+H^+$) 437.0961, found 437.0977.



(5-methyl-2-(phenylethynyl)phenyl)diphenylgermane 2f

Germane **2f** was prepared following the general procedure for **bromoaryls germylation** using **1f** (1.200 g, 4.425 mmol, 1.0 equiv), *n*-BuLi (2.5 M in hexane, 1.77 mL, 4.425 mmol, 1.0 equiv), diphenylgermanium dichloride (0.93 mL, 4.425 mmol, 1.0 equiv), $LiAlH_4$ (1M in THF, 2.21 mL, 2.212 mmol, 0.5 equiv) in anhydrous THF (15 mL). The crude was purified by flash chromatography on silica gel (Cyclohexane/EtOAc = 99.5/0.5) affording **2f** (1.331 g, 3.176 mmol, 72%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66-7.56 (m, 4H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.42-7.35 (m, 6H), 7.28 (bs, 1H), 7.26-7.21 (m, 4H), 7.14-7.10 (m, 2H), 5.96 (s, 1H), 2.34 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 138.6, 138.0, 136.6, 135.6 (2C), 135.4 (4C), 132.2, 131.4 (2C), 130.3, 129.1 (2C), 128.4 (4C), 128.2 (2C), 128.1, 126.5, 123.4, 91.9, 90.6, 21.7; **IR** (neat)**:** υ_{max} = 3050, 2038, 1594, 1491, 1470, 1431, 689 cm^{-1}; **HRMS** (API+): calcd for $C_{27}H_{23}{}^{74}Ge$ ($M+H^+$) 421.1012, found 421.1021.

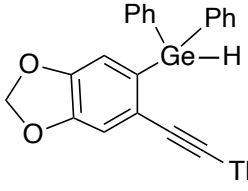


((2-(diphenylgermyl)-4-methylphenyl)ethynyl)trimethylsilane 2g

Germane **2g** was prepared following the general procedure for **bromoaryls germylation** using **1g** (1.135 g, 4.247 mmol, 1.0 equiv), *n*-BuLi (2.5 M in hexane, 1.70 mL, 4.247 mmol, 1.0 equiv), diphenylgermanium dichloride (0.90 mL, 4.247 mmol, 1.0 equiv), $LiAlH_4$ (1M in THF, 2.12 mL, 2.213 mmol, 0.5 equiv) in anhydrous THF (15 mL). The crude was purified by flash chromatography on silica gel (Cyclohexane/EtOAc = 100/0, 99.5/0.5) affording **2g** (869 mg, 2.093 mmol, 49%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57-7.54 (m, 4H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.40-7.35 (m, 6H), 7.19-7.15 (m, 2H), 5.89 (s, 1H), 2.29 (s, 3H), 0.03 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 138.8, 138.2, 136.5 (2C), 135.6, 135.4 (4C), 132.4, 130.1, 129.1 (2C), 128.3 (4C),

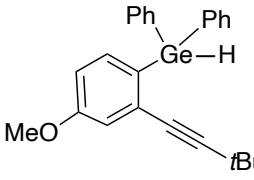
126.5, 105.8, 96.9, 21.7, -0.3 (3C); **IR** (neat)**:** υ_{max} = 3050, 2958, 2155, 1588, 1471, 1432, 1249, 839, 694 cm^{-1}; **HRMS** (API+): calcd for $C_{24}H_{27}{}^{74}GeSi$ ($M+H^+$) 417.1094, found 417.1099.



((6-(diphenylgermyl)benzo[*d*][1,3]dioxol-5-yl)ethynyl)trimethyl-silane 2h

Germane **2h** was prepared following the general procedure for **bromoaryls germylation** using **1h** (750 mg, 2.523 mmol, 1.0 equiv), *n*-BuLi (2.5 M in hexane, 1.01 mL, 2.523 mmol, 1.0 equiv), diphenylgermanium dichloride (0.53 mL, 2.523 mmol, 1.0 equiv), $LiAlH_4$ (1M in THF, 1.26 mL, 1.262 mmol, 0.5 equiv) in anhydrous THF (10 mL). The crude was purified by flash chromatography on silica gel (Cyclohexane/EtOAc = 100/0, 99.5/0.5) affording **2h** (723 mg, 1.624 mmol, 64%) as a yellow oil.

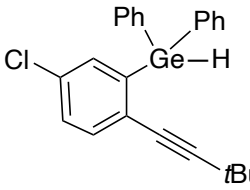
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53-7.48 (m, 4H), 7.39-7.33 (m, 6H), 7.03 (s, 1H), 6.74 (s, 1H), 5.95 (s, 2H), 5.86 (s, 1H), -0.01 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 148.5, 148.1, 135.4 (2C), 135.3 (4C), 133.3, 129.2 (2C), 128.4 (4C), 123.2, 115.1, 112.8, 105.4, 101.3, 96.2, -0.3 (3C); **IR** (neat)**:** υ_{max} = 2958, 2897, 2147, 1501, 1473, 1432, 1243, 1037, 841, 698 cm^{-1}; **HRMS** (ESI+): calcd for $C_{24}H_{25}{}^{74}GeO_2Si$ ($M+H^+$) 447.0836, found 447.0842.



(2-(3,3-dimethylbut-1-yn-1-yl)-4-methoxyphenyl)diphenylgermane 2i

Germane **2i** was prepared following the general procedure for **bromoaryls germylation** using **1i** (1.300 g, 4.866 mmol, 1.0 equiv), *n*-BuLi (2.4 M in hexane, 2.02 mL, 4.866 mmol, 1.0 equiv), diphenylgermanium dichloride (1.02 mL, 4.866 mmol, 1.0 equiv), $LiAlH_4$ (1M in THF, 2.43 mL, 2.433 mmol, 0.5 equiv) in anhydrous THF (15 mL). The crude was purified by flash chromatography on silica gel (Cyclohexane/EtOAc = 99.5/0.5) affording **2i** (1.520 g, 3.662 mmol, 75%) as a colorless oil.

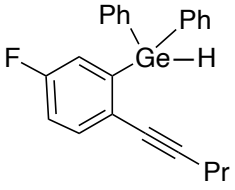
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52-7.49 (m, 4H), 7.34-7.30 (m, 6H), 7.17 (d, *J* = 8.3 Hz, 1H), 7.02 (d, *J* = 2.5 Hz, 1H), 6.77 (dd, *J* = 8.3, 2.5 Hz, 1H), 5.84 (s, 1H), 3.76 (s, 3H), 1.01 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 160.6, 137.0, 136.1 (2C), 135.4 (4C), 131.6, 129.1, 129.0 (2C), 128.2 (4C), 117.1, 114.1, 101.6, 80.1, 55.3, 30.6 (3C), 28.0; **IR** (neat)**:** υ_{max} = 3068, 2967, 2043, 1586, 1556, 1431, 1229, 1064, 698 cm^{-1}; **HRMS** (ESI+): calcd for $C_{25}H_{27}{}^{74}GeO$ ($M+H^+$) 417.1274, found 417.1262.



(5-chloro-2-(3,3-dimethylbut-1-yn-1-yl)phenyl)diphenylgermane 2j

Germane **2j** was prepared following the general procedure for **bromoaryls germylation** using **1j** (923 mg, 3.399 mmol, 1.0 equiv), *n*-BuLi (2.5 M in hexane, 1.35 mL, 3.399 mmol, 1.0 equiv), diphenylgermanium dichloride (0.71 mL, 3.399 mmol, 1.0 equiv), $LiAlH_4$ (1M in THF, 1.70 mL, 1.699 mmol, 0.5 equiv) in anhydrous THF (15 mL). The crude was purified by flash chromatography on silica gel (Cyclohexane/EtOAc = 100/0, 99.5/0.5) affording **2j** (852 mg, 2.031 mmol, 60%) as a yellow oil.

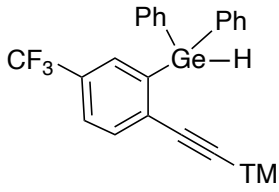
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55-7.51 (m, 4H), 7.43-7.38 (m, 7H), 7.33-7.26 (m, 2H), 5.90 (s, 1H), 1.05 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 140.8, 135.3 (5C), 134.9 (2C), 133.6, 133.3, 129.5, 129.3 (2C), 128.9, 128.5 (4C),102.8, 79.3, 30.5 (3C), 28.0; **IR** (neat)**:** υ_{max} = 3070, 2968, 2051, 1572, 1485, 1432, 698, 460 cm^{-1}; **HRMS** (API+): calcd for $C_{24}H_{24}{}^{74}Ge^{35}Cl$ ($M+H^+$) 421.0778, found 421.0777.



(5-fluoro-2-(pent-1-yn-1-yl)phenyl)diphenylgermane 2k

Germane **2k** was prepared following the general procedure for **bromoaryls germylation** using **1k** (1.050 g, 4.355 mmol, 1.0 equiv), *n*-BuLi (2.5 M in hexane, 1.74 mL, 4.355 mmol, 1.0 equiv), diphenylgermanium dichloride (0.92 mL, 4.355 mmol, 1.0 equiv), $LiAlH_4$ (1M in THF, 2.18 mL, 2.177 mmol, 0.5 equiv) in anhydrous THF (15 mL). The crude was purified by flash chromatography on silica gel (Cyclohexane/EtOAc = 100/0, 99.5/0.5) affording **2k** (882 mg, 2.267 mmol, 52%) as a colorless oil.

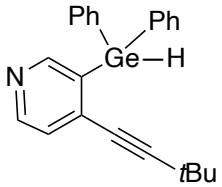
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55-7.52 (m, 4H), 7.48-7.36 (m, 7H), 7.06-6.98 (m, 2H), 5.90 (s, 1H), 2.13 (t, *J* = 7.1 Hz, 2H), 1.35 (sextuplet, *J* = 7.3 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 161.8 (d, *J* = 252 Hz), 141.7 (d, *J* = 5 Hz), 135.3 (4C), 135.0 (2C), 133.8 (d, *J* = 7 Hz), 129.3 (2C), 128.5 (4C), 126.5 (d, *J* = 4 Hz), 122.3 (d, *J* = 20 Hz), 116.4 (d, *J* = 22 Hz), 93.6, 80.8, 21.9, 21.4, 13.7; **^{19}F NMR** (282 MHz, $CDCl_3$): -112.6; **IR** (neat)**:** υ_{max} = 3051, 2962, 2932, 2051, 1589, 1470, 1431, 1202, 824, 695, 461 cm^{-1}; **HRMS** (API+): calcd for $C_{23}H_{22}F^{74}Ge$ ($M+H^+$) 391.0917, found 391.0928.



((2-(diphenylgermyl)-4-(trifluoromethyl)phenylethynyl)trimethyl-silane 2l

Germane **2l** was prepared following the general procedure for **bromoaryls germylation** using **1l** (1.187 g, 3.695 mmol, 1.0 equiv), *n*-BuLi (2.5 M in hexane, 1.48 mL, 3.695 mmol, 1.0 equiv), diphenylgermanium dichloride (0.78 mL, 3.695 mmol, 1.0 equiv), $LiAlH_4$ (1M in THF, 1.85 mL, 1.847 mmol, 0.5 equiv) in anhydrous THF (15 mL). The crude was purified by flash chromatography on silica gel (Cyclohexane/EtOAc = 100/0, 99.5/0.5, 99/1) affording **2l** (967mg, 2.061 mmol, 56%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66-7.61 (m, 3H), 7.55-7.52 (m, 4H), 7.42-7.36 (m, 6H), 5.93 (s, 1H), 0.04 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 140.6, 135.3 (4C), 134.5 (2C), 133.3, 132.6, 132.3 (q, *J* = 3 Hz), 129.8 (q, *J* = 33 Hz), 129.5 (2C), 128.5 (4C), 126.1 (q, *J* = 4 Hz), 124.0 (q, *J* = 272 Hz), 104.3, 100.9, -0.5 (3C); **^{19}F NMR** (282 MHz, $CDCl_3$): -62.9; **IR** (neat)**:** υ_{max} = 3071, 2056, 1602, 1485, 1432, 1320, 1125, 837, 695, 459 cm^{-1}; **HRMS** (ESI+): calcd for $C_{26}H_{25}F_3{}^{74}GeN$ ($M\text{-}H+ACN^+$) 510.0920, found 510.0919.

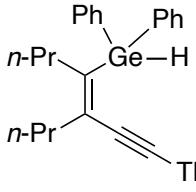


4-(3,3-dimethylbut-1-yn-1-yl)-3-(diphenylgermyl)pyridine 2m

To a solution of bomopyridine **1m** (748 mg, 3.141 mmol, 1 equiv) in dry THF (10 mL) *n*-BuLi (2.5 M in hexane, 1.32 mL, 3.298 mmol, 1.05 equiv) was added, at -105 to -95°C, under argon atmosphere. After stirring the mixture for 15 minutes, diphenylgermanium dichloride (0.79 mL, 3.769 mmol, 1.2 equiv) was added. The resultant mixture was stirred for 2 h. $LiAlH_4$ (1M in THF, 0.5 equiv, 1.57 mL, 1.570 mmol, 0.5 equiv) was then added to the mixture at 0°C followed by stirring for 1h at this temperature and for 1h at room temperature before being quenched with water and HCl (0.5 M, 2 ml). The mixture was extracted with DCM and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude was purified by flash chromatography on silica gel (Cyclohexane/EtOAc = 99/1, 95/5, 90/10) affording **2m** (200 mg, 0,518 mmol, 16%) as a brown oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.55 (d, *J* = 5.0 Hz, 1H), 8.47 (s, 1H), 7.56-7.50 (m, 4H), 7.42-7.36 (m, 6H), 7.31 (d, *J* = 5.0 Hz, 1H), 5.87 (s, 1H), 1.04 (s, 9H); **^{13}C NMR** (75 MHz,

$CDCl_3$): δ = 155.5, 150.3, 138.7, 135.2 (4C), 134.3 (2C), 132.6, 129.3 (2C), 128.4 (4C), 126.1, 106.8, 78.3, 30.2 (3C), 28.1; **IR** (neat)**:** υ_{max} = 3050, 2969, 2048, 1569, 1484, 1460, 1432, 1093, 698 cm^{-1}; **HRMS** (API+): calcd for $C_{23}H_{24}{}^{74}GeN$ ($M+H^+$) 388.1121, found 388.1131.

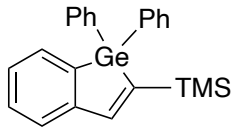


(*Z*)-(4-(diphenylgermyl)-3-propylhep-3-en-1-yn-1-yl)trimethylsilane 2n

Germane **2n** was prepared following the general procedure for **bromoaryls germylation** using **1n** (900 mg, 3.132 mmol, 1.0 equiv), *n*-BuLi (2.4 M in hexane, 1.30 mL, 3.132 mmol, 1.0 equiv), diphenylgermanium dichloride (0.66 mL, 3.132 mmol, 1.0 equiv), $LiAlH_4$ (1M in THF, 1.57 mL, 1.566 mmol, 0.5 equiv) in anhydrous THF (12 mL). The crude was purified by flash chromatography on silica gel (Cyclohexane = 100) affording **2n** (936 mg, 2.150 mmol, 69%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56-7.52 (m, 4H), 7.34-7.31 (m, 6H), 5.56 (s, 1H), 2.32-2.19 (m, 4H), 1.69-1.57 (m, 2H), 1.29-1.18 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.72 (t, *J* = 7.3 Hz, 3H), -0.11 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 147.3, 136.5 (2C), 135.3 (4C), 134.5, 128.7 (2C), 128.1 (4C), 107.2, 96.8, 35.3, 34.3, 23.0, 22.2, 14.2, 14.0, -0.3 (3C); **IR** (neat)**:** υ_{max} = 3069, 2959, 2141, 2043, 1484, 1431,1249, 840, 696 cm^{-1}; **HRMS** (API+): calcd for $C_{25}H_{35}{}^{74}GeSi$ ($M+H^+$) 437.1720, found 437.1708.

General procedure for the germylzincation reaction: In a dry sealed tube under argon atmosphere, germane (0.25-2 mmol) and AIBN (0.15 equiv) were dissolved in dry hexane (1.5 – 5 mL) and the solution was degassed. To this solution, Et_2Zn (1.0 M in hexane, 1.5 equiv) was added at room temperature and the reaction mixture was heated at 80°C for 2 hours. After cooling to room temperature, the reaction mixture was hydrolyzed and stirred with aqueous NH_4Cl for 20 minutes. The layers were separated, the aqueous layer was extracted with Et_2O (x3) and the combined organic layers were washed with brine (x2), dried over anhydrous $MgSO_4$ and concentrated under reduce pressure. The crude was purified by flash chromatography on silica gel.

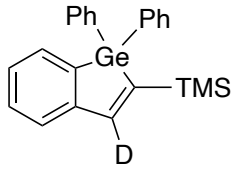


(1,1-diphenyl-1*H*-benzo[*b*]germol-2-yl)trimethylsilane 3a

Compound **3a** was prepared according to **the germylation reaction procedure** from germane **2a** (190 mg, 0.474 mmol, 1 equiv), AIBN (12 mg, 0.071 mmol, 0.15 equiv), Et_2Zn (1 M in hexane, 0.71 mL, 0.711 mmol, 1.5 equiv), hexane (1.5 mL) with reaction time of 2 h at 80 °C.

Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 95.5/0.5) afforded **3a** (175 mg, 0.436 mmol, 92%) as a colorless oil.

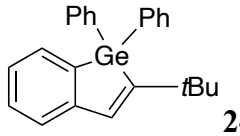
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (s, 1H), 7.60-7.53 (m, 5H), 7.39-7.31 (m, 8H), 7.23 (td, *J* = 7.0, 1.9 Hz, 1H), 0.07 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 150.0, 149.3, 145.7, 139.8, 135.5 (2C), 134.9 (4C), 132.9, 129.7, 129.4 (2C), 128.5 (4C), 127.9, 125.5, 0.02 (3C); **IR** (neat)**:** υ_{max} = 2953, 1571, 1524, 1484, 1431, 1288, 942, 696 cm^{-1}; **HRMS** (API+): calcd for $C_{23}H_{25}{}^{74}GeSi$ ($M+H^+$) 403.0937, found 403.0941.



3a-D

Compound **3a-D** was prepared according to **the germylation reaction procedure** from germane **2a** (174 mg, 0.434 mmol, 1 equiv), AIBN (11 mg, 0.065 mmol, 0.15 equiv), Et_2Zn (1 M in hexane, 0.65 mL, 0.651 mmol, 1.5 equiv), hexane (1.5 mL) with reaction time of 2 h at 80 °C, after hydrolysis with D_2O. Purification of the crude product by flash chromatography on silica gel (Pentane = 100) afforded **3a-D** (149 mg, 0.370 mmol, 85%, 96%D incorporation) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (s, 0.04H), 7.58 (dt, *J* = 7.0, 1.9 Hz, 1H), 7.56-7.50 (m, 4H), 7.39-7.29 (m, 8H), 7.22 (td, *J* = 7.4, 1.0 Hz, 1H), 0.07 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 149.3, 145.6, 139.9, 135.8, 135.5, 135.4 (2C), 134.9 (4C), 132.3, 129.7, 129.4 (2C), 127.9 (4C), 125.5, 0.03 (3C); **IR** (neat)**:** υ_{max} = 2953, 1508, 1483, 1431, 1246, 899, 696 cm^{-1}; **HRMS** (API+): calcd for $C_{23}H_{24}D^{74}GeSi$ ($M+H^+$) 404.1000, found 404.0987.

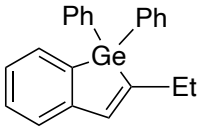


2-(*tert*-butyl)-1,1-diphenyl-1*H*-benzo[*b*]germole 3b

Compound **3b** was prepared according to **the germylation reaction procedure** from germane **3b** (181 mg, 0.470 mmol, 1 equiv), AIBN (12 mg, 0.071 mmol, 0.15 equiv), Et_2Zn (1 M in hexane, 0.70 mL, 0.705 mmol, 1.5 equiv), hexane (1.5 mL) with reaction time of 2 h at 80 °C. Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 99/1) afforded **3b** (169 mg, 0.439 mmol, 93%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75-7.66 (m, 4H), 7.52 (d, *J* = 7.0 Hz 1H), 7.40-7.46 (m, 6H), 7.37-7.33 (m, 2H), 7.22 (td, *J* = 7.0, 1.6 Hz, 1H), 7.17 (s, 1H), 1.22 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 159.4, 149.0, 138.3, 137.9, 135.9 (2C), 135.1 (4C), 132.9, 129.7, 129.4 (2C),

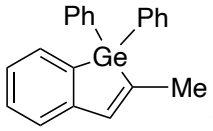
128.5 (4C), 126.9, 124.7, 36.5, 32.0 (3C); **IR** (neat)**:** υ_{max} = 2960, 2860, 1483, 1459, 1430, 1089, 696 cm^{-1}; **HRMS** (EI): calcd for $C_{24}H_{24}{}^{74}Ge$ (M^+) 386.1090, found 386.1084; **mp**: 88°C.



2-ethyl-1,1-diphenyl-1*H*-benzo[*b*]germole 3c

Compound **3c** was prepared according to **the germylation reaction procedure** from germane **2c** (100 mg, 0.280 mmol, 1 equiv), AIBN (7 mg, 0.042 mmol, 0.15 equiv), Et_2Zn (1 M in hexane, 0.42 mL, 0.420 mmol, 1.5 equiv), hexane (1.0 mL) with reaction time of 2 h at 80 °C. Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 100/0, 95.5/0.5) afforded **3c** (65 mg, 0.182 mmol, 65%) as a colorless oil.

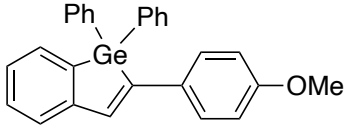
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60-7.51 (m, 5H), 7.41-7.26 (m, 8H), 7.19 (td, *J* = 7.1, 1.1 Hz, 1H), 7.06 (t, *J* = 1.6 Hz, 1H), 2.62 (qd, *J* = 7.4, 1.6 Hz, 2H), 1.12 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 150.6, 149.2, 139.9, 137.5, 135.4 (2C), 134.9 (4C), 133.0, 129.8, 129.5 (2C), 128.6 (4C), 126.7, 124.5, 27.3, 14.5; **IR** (neat)**:** υ_{max} = 3064, 2927, 1580, 1483, 1456, 1430, 1090, 696 cm^{-1}; **HRMS** (API+): calcd for $C_{22}H_{21}{}^{74}Ge$ ($M+H^+$) 359.0855, found 359.0854.



2-methyl-1,1-diphenyl-1*H*-benzo[*b*]germole 3d

Compound **3d** was prepared according to **the germylation reaction procedure** from germane **2d** (145 mg, 0.423 mmol, 1 equiv), AIBN (10 mg, 0.063 mmol, 0.15 equiv), Et_2Zn (1 M in hexane, 0.63 mL, 0.634 mmol, 1.5 equiv), hexane (1.5 mL) with reaction time of 3 h at 80°C. Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 100/0, 95.5/0.5) afforded an inseparable **3d**/**2d** mixture in a 94/6 ratio (114 mg, 0.332 mmol, 79%: 74% **3d** + 5% **2d**) as a colorless oil.

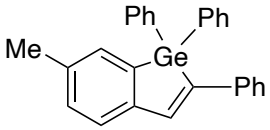
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60-7.54 (m, 5H), 7.43-7.35 (m, 6H), 7.32 (dd, *J* = 7.3 1.2 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.19 (td, *J* = 7.1 1.2 Hz, 1H), 7.06 (q, *J* = 1.4 Hz, 1H), 2.23 (d, *J* =1.4 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 149.2, 143.9, 142.1, 137.5, 135.1 (2C), 134.8 (4C), 133.0, 129.8, 129.6 (2C), 128.6 (4C), 126.7, 124.4, 19.5; **IR** (neat)**:** υ_{max} = 2920, 1581, 1483, 1462, 1430, 1091, 696 cm^{-1}; **HRMS** (API+): calcd for $C_{21}H_{19}{}^{74}Ge$ ($M+H^+$) 345.0699, found 345.0703.



2-(4-methoxyphenyl)-1,1-diphenyl-1*H*-benzo[*b*]germole 3e

Compound **3e** was prepared according to **the germylation reaction procedure** from germane **2e** (93 mg, 0.214 mmol, 1 equiv), AIBN (5 mg, 0.032 mmol, 0.15 equiv), Et_2Zn (1 M in hexane, 0.32 mL, 0.321 mmol, 1.5 equiv), hexane (1.0 mL) with reaction time of 2 h at 80 °C. Purification of the crude product by flash chromatography on silica gel (Petroleum ether/Toluene = 95/5, 90/10, 80/20) afforded compound **3e** (61 mg, 0.140 mmol, 65%) as a colorless oil.

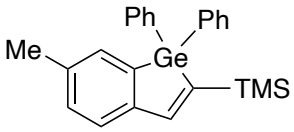
^{1}H NMR (300 MHz, $CDCl_3$): δ =7.62-7.58 (m, 5H), 7.51-7.48 (m, 1H), 7.48 (d, *J* = 8.9 Hz, 2H), 7.39-7.33 (m, 7H), 7.26 (s, 1H), 7.21 (td, *J* = 7.0 1.9 Hz, 1H), 6.84 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 159.3, 149.2, 144.5, 138.1, 137.8, 135.2 (2C), 135.0 (4C), 132.9, 132.0, 130.0, 129.7 (2C), 128.7 (4C), 128.6 (2C), 127.2, 125.3, 114.3 (2C), 55.4; **HRMS** (EsI+): calcd for $C_{27}H_{23}{}^{74}GeO$ ($M+H^+$) 437.0931, found 437.0979.



6-methyl-1,1,2-triphenyl-1*H*-benzo[*b*]germole 3f

Compound **3f** was prepared according to **the germylation reaction procedure** from germane **2f** (120 mg, 0.286 mmol, 1 equiv), AIBN (7 mg, 0.043 mmol, 0.15 equiv), Et_2Zn (1 M in hexane, 0.43 mL, 0.429 mmol, 1.5 equiv), hexane (1.2 mL) with reaction time of 2 h at 80 °C. Purification of the crude product by flash chromatography on silica gel (Cyclohexane/Toluene = 98/2, 95/5, 90/10) afforded **3f** (47 mg, 0.112 mmol, 39%) as a colorless oil.

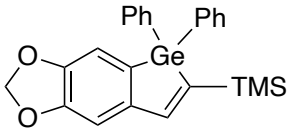
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71 (s, 1H), 7.64-7.60 (m, 4H), 7.55-7.47 (m, 3H), 7.45 (s, 1H), 7.40-7.33 (m, 6H), 7.30 (d, *J* = 7.2 Hz, 2H), 7.19 (d, *J* = 7.2 Hz, 2H), 2.36 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 146.2, 143.7, 140.2, 139.4, 138.2, 137.4, 135.3 (2C), 135.0 (4C), 133.8, 130.6, 129.7 (2C), 128.8 (2C), 128.7 (4C), 128.5, 127.2 (2C), 125.4, 21.6; **IR** (neat)**:** υ_{max} = 2921, 1593, 1537, 1484, 1460, 1431, 1090, 694 cm^{-1}; **HRMS** (API+): calcd for $C_{29}H_{26}{}^{74}GeN$ ($M+H+ACN^+$) 462.1277, found 462.1268.



trimethyl(6-methyl-1,1-diphenyl-1*H*-benzo[*b*]germol-2-yl)silane 3g

Compound **3g** was prepared according to **the germylation reaction procedure** from germane **2g** (180 mg, 0.434 mmol, 1 equiv), AIBN (11 mg, 0.065 mmol, 0.15 equiv), Et_2Zn (1 M in hexane, 0.65 mL, 0.649 mmol, 1.5 equiv), hexane (1.5 mL) with reaction time of 2 h at 80 °C. Purification of the crude product by flash chromatography on silica gel (Cyclohexane = 100) afforded **3g** (158 mg, 0.381 mmol, 88%) as a colorless oil.

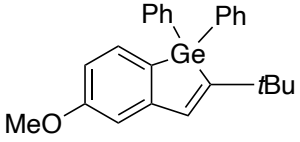
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (s, 1H), 7.57-7.54 (m, 4H), 7.41 (d, *J* = 1.0 Hz, 1H), 7.39-7.29 (m, 7H), 7.15 (td, *J* = 7.7, 1.0 Hz, 1H), 2.33 (s, 3H), 0.07 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 154.9, 146.9, 144.0, 140.0, 137.8, 135.8 (2C), 134.9 (4C), 133.8, 130.3, 129.4 (2C), 128.4 (4C), 125.2, 21.5, 0.05 (3C); **IR** (neat)**:** υ_{max} = 2953, 1518, 1483, 1431, 1247, 830, 696 cm^{-1}; **HRMS** (API+): calcd for $C_{24}H_{27}{}^{74}GeSi$ ($M+H^+$) 417.1094, found 417.1096.



(5,5-diphenyl-5*H*-germolo[2',3'.4,5]benzo[1,2-*d*][1,3]dioxol-6-yl)trimethylsilane 3h

Compound **3h** was prepared according to **the germylation reaction procedure** from germane **2h** (200 mg, 0.449 mmol, 1 equiv), AIBN (11 mg, 0.067 mmol, 0.15 equiv), Et_2Zn (1 M in hexane, 0.67 mL, 0.673 mmol, 1.5 equiv), hexane (1.5 mL) with reaction time of 2 h at 80 °C. Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 95.5/0.5) afforded **3h** (169 mg, 0.380 mmol, 85%) as a colorless oil.

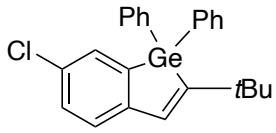
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63-7.59 (m, 5H), 7.44-7.35 (m, 6H), 7.10 (s, 1H), 6.96 (s, 1H), 5.98 (s, 2H), 0.12 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 154.3, 149.3, 148.1, 144.2, 144.0, 135.5 (2C), 134.8 (4C), 133.2, 129.5 (2C), 128.5 (4C), 112.8, 106.8, 101.2, 0.03 (3C); **IR** (neat)**:** υ_{max} = 2956, 2896, 1594, 1501, 1467, 1431, 1245, 1038, 834, 697 cm^{-1}; **HRMS** (ESI+): calcd for $C_{24}H_{25}{}^{74}GeO_2Si$ ($M+H^+$) 447.0836, found 447.0865.



2-(*tert*-butyl)-5-methoxy-1, 1-diphenyl-1H-benzo[*b*]germole 3i

Compound **3i** was prepared according to **the germylation reaction procedure** from germane **2i** (150 mg, 0.361 mmol, 1 equiv), AIBN (9 mg, 0.054 mmol, 0.15 equiv), Et_2Zn (1 M in hexane, 0.54 mL, 0.541 mmol, 1.5 equiv), hexane (1.3 mL) with reaction time of 2 h at 80 °C. Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 95.5/0.5) afforded **3i** (128 mg, 0.308 mmol, 85%) as a white oil.

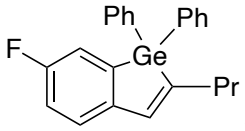
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71-7.64 (m, 4H), 7.42-7.35 (m, 7H), 7.10 (s, 1H), 6.93 (d, *J* = 2.4 Hz, 1H), 6.77 (dd, *J* = 7.8, 2.4 Hz, 1H), 3.86 (s, 3H), 1.19 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 161.6, 161.0, 150.9, 138.0, 136.1 (2C), 135.0 (4C), 133.8, 129.3 (2C), 128.5 (4C), 128.0, 111.9, 111.3, 55.3, 36.6, 31.9 (3C); **IR** (neat)**:** υ_{max} = 2960, 1588, 1552, 1458, 1431, 1230, 1060, 734, 698 cm^{-1}; **HRMS** (ESI+): calcd for $C_{25}H_{27}{}^{74}GeO$ ($M+H^+$) 417.1274, found 417.1271.



2-(*tert*-butyl)-6-chloro-1,1-diphenyl-1*H*-benzo[*b*]germole 3j

Compound **3j** was prepared according to **the germylation reaction procedure** from germane **2j** (212 mg, 0.505 mmol, 1 equiv), AIBN (12 mg, 0.076 mmol, 0.15 equiv), Et_2Zn (1 M in hexane, 0.76 mL, 0.757 mmol, 1.5 equiv), hexane (1.8 mL) with reaction time of 2 h at 80 °C. Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 100/0, 95.5/0.5) afforded **3j** (198 mg, 0.472 mmol, 93%) as a colorless oil.

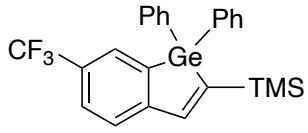
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63-7.58 (m, 4H), 7.40-7.35 (m, 7H), 7.27 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.06 (s, 1H), 1.14 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 160.1, 147.2, 140.5, 137.3, 135.1 (2C), 135.0 (4C), 132.8, 132.7, 129.6 (3C), 128.7 (4C), 125.5, 36.6, 31.9 (3C); **IR** (neat)**:** υ_{max} = 3065, 2958, 1485, 1431, 1403, 1088, 734, 696, 460 cm^{-1}; **HRMS** (API+): calcd for $C_{26}H_{27}{}^{35}Cl^{74}GeN$ ($M+H+ACN^+$) 462.1044, found 462.1035.



6-fluoro-1,1-diphenyl-2-propyl-1*H*-benzo[*b*]germole 3k

Compound **3k** was prepared according to **the germylation reaction procedure** from germane **2k** (197 mg, 0.506 mmol, 1 equiv), AIBN (12 mg, 0.076 mmol, 0.15 equiv), Et_2Zn (1 M in hexane, 0.76 mL, 0.759 mmol, 1.5 equiv), hexane (2 mL) with reaction time of 2 h at 80 °C. Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 100/0, 95.5/0.5) afforded **3k** (149 mg, 0.383 mmol, 76%) as a colorless oil.

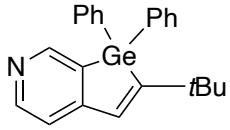
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63-7.53 (m, 4H), 7.46-7.37 (m, 6H), 7.29 (dd, *J* = 7.3, 2.5 Hz, 1H), 7.23 (dd, *J* = 8.0, 4.5 Hz, 1H), 7.07 (s, 1H), 7.02 (td, *J* = 8.7, 2.5 Hz, 1H), 2.59 (t, *J* = 7.7 Hz, 2H), 1.53 (sextuplet, *J* = 7.5 Hz, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 162.2 (d, *J* = 247 Hz), 148.5 (d, *J* = 4 Hz), 144.9 (d, *J* = 3 Hz), 140.4 (d, *J* = 5 Hz), 139.9, 134.8 (6C), 129.7 (2C), 128.7 (4C), 125.2 (d, *J* = 7 Hz), 120.1 (d, *J* = 21 Hz), 116.1 (d, *J* = 22 Hz), 36.7, 23.2, 14.1; **^{19}F NMR** (282 MHz, $CDCl_3$): -116.0; **IR** (neat)**:** υ_{max} = 2986, 2926, 2899, 1570, 1458, 1429, 1188, 736, 697; 473 cm^{-1}; **HRMS** (API+): calcd for $C_{25}H_{23}F^{74}GeN$ ($M-H+ACN^+$) 430.1026, found 430.1042.



(1,1-diphenyl-6-(trifluoromethyl)-1*H*-benzo[*b*]germol-2-yl)tri-methylsilane 3l

Compound **3l** was prepared according to **the germylation reaction procedure** from germane **2l** (207 mg, 0.441 mmol, 1 equiv), AIBN (11 mg, 0.066 mmol, 0.15 equiv), Et_2Zn (1 M in hexane, 0.66 mL, 0.661 mmol, 1.5 equiv), hexane (2 mL) with reaction time of 4 h at 80 °C. Purification of the crude product by flash chromatography on silica gel (Pentane = 100) afforded **3l** (162 mg, 0.345 mmol, 78%) as a colorless oil.

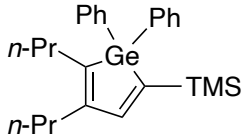
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83 (bs, 1H), 7.76 (s, 1H), 7.64 (dd, *J* = 7.6 1.0 Hz, 1H), 7.58-7.52 (m, 4H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.43-7.36 (m, 6H), 0.11 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 153.7, 152.4, 150.4, 141.1, 134.8 (4C), 134.4 (2C), 129.8 (2C), 129.5 (q, *J* = 37 Hz), 129.2 (q, *J* = 4 Hz), 128.7 (4C), 127.2 (q, *J* = 4 Hz), 124.6 (q, *J* = 273 Hz), 125.2, -0.1 (3C); **^{19}F NMR** (282 MHz, $CDCl_3$): -62.0; **IR** (neat)**:** υ_{max} = 2925, 1598, 1523, 1433, 1405, 1320, 1117, 835, 696, 480 cm^{-1}; **HRMS** (API-): calcd for $C_{24}H_{23}F_3{}^{74}GeSi$ (M^+) 470.0733, found 470.0737.



2-(*tert*-butyl)-1,1-diphenyl-1*H*-germolo[2,3-*c*]pyridine 3m

Compound **3m** was prepared according to **the germylation reaction procedure** from germane **2m** (144 mg, 0.373 mmol, 1 equiv), AIBN (9 mg, 0.056 mmol, 0.15 equiv), Et_2Zn (1 M in hexane, 0.56 mL, 0.559 mmol, 1.5 equiv), hexane (1.5 mL) with reaction time of 2 h at 80 °C. Purification of the crude product by flash chromatography on silica gel (Cyclohexane / EtOAc = 95/5, 90/10) afforded **3m** (79 mg, 0.205 mmol, 55%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.52 (d, *J* = 5.1 Hz, 1H), 8.39 (bs, 1H), 7.49-7.45 (m, 4H), 7.39-7.33 (m, 7H), 7.29 (dd, *J* = 5.1, 1.0 Hz, 1H), 0.95 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 155.8, 150.0, 138.7, 136.7 (2C), 135.5, 135.1 (4C), 133.6, 129.0 (2C), 128.32, 128.26 (4C), 126.9, 30.1 (3C), 28.0; **IR** (neat)**:** υ_{max} = 2967, 2924, 1568, 1484, 1459, 1431, 1090, 698 cm^{-1}; **HRMS** (API+): calcd for $C_{27}H_{32}{}^{74}GeN$ ($M+C_4H_9^+$) 442.1756, found 442.1756.

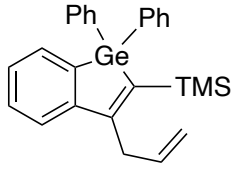


(1,1-diphenyl-4,5-dipropyl-1*H*-germol-2-yl)trimethylsilane 3n

Compound **3n** was prepared according to **the germylation reaction procedure** from germane **2n** (214 mg, 0.492 mmol, 1 equiv), AIBN (12 mg, 0.074 mmol, 0.15 equiv), Et_2Zn (1 M in hexane, 0.74 mL, 0.738 mmol, 1.5 equiv), hexane (2 mL) with reaction time of 2 h at 80 °C. Purification of the crude product by flash chromatography on silica gel (Pentane = 100) afforded **3n** (197 mg, 0.453 mmol, 92%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54-7.50 (m, 4H), 7.37-7.32 (m, 6H), 7.15 (s, 1H), 2.40-2.31 (m, 4H), 1.51 (sextuplet, *J* = 7.5 Hz, 2H), 1.22 (sextuplet, *J* = 7.5 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.65 (t, *J* = 7.4 Hz, 3H), -0.09 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 157, 150.1, 143.5, 141.8, 136.6 (2C), 134.9 (4C), 129.0 (2C), 128.3 (4C), 33.0, 32.6, 24.3, 22.4, 14.4, 14.2, 0.0 (3C); **IR** (neat)**:** υ_{max} = 3069, 2955, 2929, 2870, 1510, 1483, 1431, 1246, 831, 696 cm^{-1}; **HRMS** (API+): calcd for $C_{25}H_{35}{}^{74}GeSi$ ($M+H^+$) 437.1720, found 437.1732.

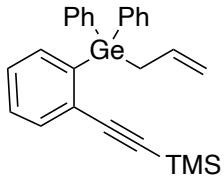
General procedure for the domino germylzincation reaction/CuBrDMS electrophilic trapping of the vinylzinc intermediated: In a dry sealed tube under argon atmosphere, germane (0.25-2 mmol) and AIBN (0.15 equiv) were dissolved in dry hexane and the solution was degassed. To this solution, Et_2Zn (1.0 M in hexane, 1.5 equiv) was added at room temperature and the reaction mixture was heated at 80 °C for 2 h. After cooling to room temperature, CuBrDMS complex salt (0.2 equiv), followed by the allyl chloride (3.6 equiv) were added and the reaction mixture was stirred at room temperature for overnight. The reaction mixture was hydrolyzed and stirred with aqueous NH_4Cl for 20 minutes. The layers were separated, the aqueous layer was extracted with CH_2Cl_2 (x3) and the combined organic layers were washed with brine (x2), dried over anhydrous $MgSO_4$ and concentrated under reduce pressure. The crude was purified by flash chromatography on silica gel.



(3-allyl-1,1-diphenyl-1*H*-benzo[*b*]germol-2-yl)trimethylsilane 5aa

Compound **5aa** was prepared according to the **domino germylzincation/electrophilic coupling with CuBrDMS**, from germane **2a** (205 mg, 0.511 mmol, 1 equiv) using CuBr.DMS (21 mg, 0.102 mmol, 0.20 equiv) and allyl chloride (141 mg, 1.840 mmol, 3.6 equiv). Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 95.5/0.5, 99/1) afforded **5aa** in an 87/13 inseparable mixture with **6aa** (220 mg, 0.434 mmol of **5aa**, 85%) as colorless oil.

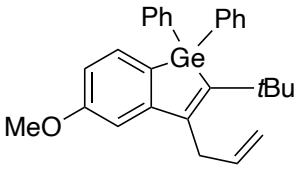
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59-7.52 (m, 5H), 7.37-7.29 (m, 9H), 6.02 (ddt, *J* = 17.0, 10.3, 5.4 Hz, 1H), 5.14 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.11 (dd, *J* = 10.3, 1.5 Hz, 1H), 3.62 (dt, *J* = 5.4, 1.5 Hz, 2H), 0.13 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 163.5, 149.3, 141.2, 139.9, 136.2, 136.0 (2C), 135.0 (4C), 132.3, 129.4 (2C), 128.5 (4C), 128.1, 127.5, 123.8, 116.7, 37.8, 1.4 (3C); **IR** (neat)**:** υ_{max} = 3047, 2954, 1524, 1484, 1431, 1247, 833, 696 cm^{-1}; **HRMS** (API+): calcd for $C_{26}H_{29}{}^{74}GeSi$ ($M+H^+$) 443.1250, found 443.1235.



6aa

Compound **6aa** was obtained with **5aa** (0.065 mmol of **6aa**, 12.7%), or obtained quantitatively when the reaction was run without AIBN), from germane **2a** (90 mg, 0.224 mmol, 1 equiv) Et_2Zn (1.0 M in hexane, 0.34 mL, 0.336 mmol, 1.5 equiv) using allyl chloride (61.7 mg, 0.806 mmol, 3.6 equiv). Product **6aa** (99 mg, 0.224 mmol, 100%) is obtained as colorless oil.

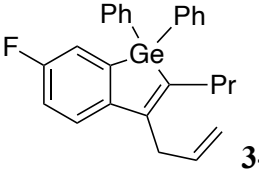
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 7.6 Hz, 1H), 7.50-7.42 (m, 4H), 7.34-7.27 (m, 7H), 7.22-7.17 (m, 2H), 5.94 (ddt, *J* = 16.9, 10.0, 8.2 Hz, 1H), 4.98 (dd, *J* = 16.9, 1.9 Hz, 1H), 4.82 (dd, *J* = 10.0, 1.9 Hz, 1H), 2.66 (d, *J* = 8.2 Hz, 2H), -0.06 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 139.6, 136.9 (2C), 136.1, 135.3 (5C), 133.2, 129.3, 129.0, 128.9 (2C), 128.11 (4C), 128.07, 114.3, 106.3, 97.5, 22.0, -0.5 (3C); **IR** (neat)**:** υ_{max} = 3047, 2900, 2156, 1630, 1485, 1430, 1249, 1091, 697 cm^{-1}; **HRMS** (API+): calcd for $C_{26}H_{29}{}^{74}GeSi$ ($M+H^+$) 443.1250, found 443.1255.



3-allyl-2-(*tert*-butyl)-5-methoxy-1,1-diphenyl-1*H*-benzo[*b*]germole 5ia

Compound **5ia** was prepared according to the **dom ino germylzincation/electrophilic coupling with CuBrDMS**, from germane **2i** (150 mg, 0.361 mmol, 1 equiv) using CuBr.DMS (15 mg, 0.072 mmol, 0.20 equiv) and allyl chloride (99 mg, 1.300 mmol, 3.6 equiv). Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 100/0, 95.5/0.5) afforded **5ia** (139 mg, 0.305 mmol, 85%) as white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66-7.61 (m, 4H), 7.40-7.35 (m, 6H), 7.30 (d, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 2.2 Hz, 1H), 6.71 (dd, *J* = 7.8, 2.2 Hz, 1H), 6.04 (ddt, *J* = 17.8, 9.7, 5.0 Hz, 1H), 5.16 (dd, *J* = 17.8, 1.6 Hz, 1H), 5.15 (dd, *J* = 9.7, 1.4 Hz, 1H), 3.81 (s, 3H), 3.62 (dt, *J* = 5.0, 1.5 Hz, 2H), 1.27 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 161.3, 154.7, 152.3, 146.8, 136.8, 136.2 (2C), 135.0 (4C), 132.6, 129.1 (2C), 128.4 (4C), 127.9, 116.6, 111.0, 110.7, 55.2, 35.9, 33.6, 32.4 (3C); **IR** (neat)**:** υ_{max} = 3067, 2960, 1589, 1548, 1483, 1431, 1229, 1027, 731, 696 cm^{-1}; **HRMS** (ESI+): calcd for $C_{28}H_{31}{}^{74}GeO$ ($M+H^+$) 457.1587, found 457.1588.

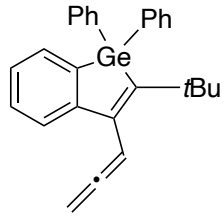


3-allyl-6-fluoro-1,1-diphenyl-2-propyl-1*H*-benzo[*b*]germole 5ka

Compound **5ka** was prepared according to the **domino germylzincation/electrophilic coupling with CuBrDMS**, from germane **2k** (150 mg, 0.385 mmol, 1 equiv) using CuBr.DMS (16 mg, 0.077 mmol, 0.20 equiv) and allyl chloride (106 mg, 1.386 mmol, 3.6 equiv). Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 100/0, 95.5/0.5) afforded **5ka** in an 70/30 inseparable mixture with **3k** (146 mg, 0.245 mmol of **5ka**, 64%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59-7.53 (m, 4H), 7.43-7.37 (m, 6H), 7.34 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.29-7.23 (m, 1H), 7.06-6.97 (m, 1H), 5.97 (ddt, *J* = 17.3, 10.3, 5.9 Hz, 1H), 5.14 (dd, *J* = 17.3, 2.0 Hz, 1H), 5.08 (dd, *J* = 10.3, 1.9 Hz, 1H), 3.42 (dt, *J* = 5.9, 1.9 Hz, 2H), 2.55 (t, *J* = 7.5 Hz, 2H), 1.50-1.35 (m, 2H), 0.85-0.76 (m, 3 H); **IR** (neat)**:** υ_{max} = 3069, 2959, 2928, 1588, 1484, 1459, 1432, 1195, 697 cm^{-1}; **HRMS** (API+): calcd for $C_{26}H_{26}F^{74}Ge$ ($M+H^+$) 431.1230, found 431.1236.

General procedure for the domino germylzincation reaction/CuCN.2LiCl) electrophilic trapping of the vinylzinc intermediated: In a dry sealed tube under argon atmosphere, germane (0.25-2 mmol) and AIBN (0.15 equiv) were dissolved in dry hexane and the solution was degassed. To this solution, Et_2Zn (1.0 M in hexane, 1.2 equiv) was added at room temperature and the reaction mixture was heated at 80 °C for 2 h. After cooling to -30 °C, CuCN.2LiCl (1M in THF, 2-3 equiv) followed by the appropriate electrophile (3-7 equiv) were added and the reaction mixture was allowed to warm slowly to room temperature overnight under stirring. The reaction mixture was hydrolyzed and stirred with aqueous NH_4Cl for 20 minutes. The layers were separated, the aqueous layer was extracted with CH_2Cl_2 (x3) and the combined organic layers were washed with brine (x2), dried over anhydrous $MgSO_4$ and concentrated under reduce pressure. The crude was purified by flash chromatography on silica gel.

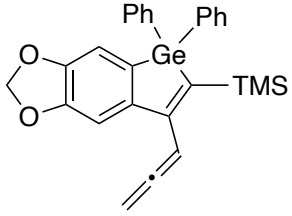


2-(*tert*-butyl)-1,1-diphenyl-3-(propa-1,2-dien-1-yl)-1*H*-benzo[*b*]germole 5bb

Compound **5bb** was prepared according to the **domino germylzincation/electrophilic coupling with CuCN.2LiCl**, from germane **2b** (122 mg, 0.317 mmol, 1 equiv) using CuCN.2LiCl (1M in THF, 0.95 mL, 0.951 mmol, 3 equiv) and propargyl bromide (211µL, 1.902 mmol, 6 equiv). Purification of the crude product by flash chromatography on silica gel

(Cyclohexane/EtOAc = 100/0, 95.5/0.5) afforded **5bb** (119 mg, 0.281 mmol, 89%) as colorless oil.

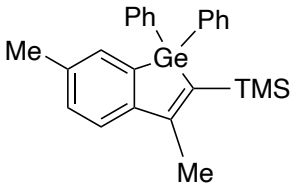
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 7.8 Hz, 1H), 7.64-7.59 (m, 4H), 7.40 (d, *J* = 7.1 Hz, 1H), 7.37-7.30 (m, 7H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.32 (t, *J* = 7.2 Hz, 1H), 4.93 (d, *J* = 7.2 Hz, 2H), 1.30 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 209.4, 154.6, 150.0, 141.7, 137.5, 136.2 (2C), 135.14 (4C), 135.05, 132.3, 129.3 (2C), 128.5 (4C), 127.0, 123.8, 89.1, 75.9, 36.4, 32.1 (3C); **IR** (neat)**:** υ_{max} = 3050, 2960, 2865, 1950, 1581, 1484, 1431, 1089, 733, 697 cm^{-1}; **HRMS** (ESI+): calcd for $C_{27}H_{27}{}^{74}Ge$ ($M+H^+$) 425.1325, found 425.1339.



(5,5-diphenyl-7-(propa-1,2-dien-1-yl)-5*H*-germolo[2',3':4,5]benzo-[1,2-*d*][1,3]dioxol-6-yl)trimethylsilane 5hb

Compound **5hb** was prepared according to the **domino germylzincation/electrophilic coupling with CuCN.2LiCl**, from germane **2h** (137 mg, 0.308 mmol, 1 equiv) using CuCN.2LiCl (1M in THF, 0.92 mL, 0.924 mmol, 3 equiv) and propargyl bromide (205 µL, 1.848 mmol, 6 equiv). Purification of the crude product by flash chromatography on silica gel (Pentane/EtOAc = 95.5/0.5) afforded **5hb** (117 mg, 0.242 mmol of **5hb**, 79%) as yellow oil.

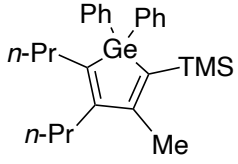
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57-7.53 (m, 4H), 7.49 (s, 1H), 7.38-7.33 (m, 6H), 6.98 (s 1H), 6.38 (t, *J* = 7.1 Hz, 1H), 5.95 (s, 2H), 5.07 (d, *J* = 7.1 Hz, 2H), 0.14 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 210.2, 156.0, 149.0, 147.9, 143.9, 141.0, 135.7 (2C), 135.0 (4C), 134.8, 129.5 (2C), 128.5 (4C), 112.2, 106.2, 101.3, 91.8, 77.3, 1.1 (3C); **IR** (neat)**:** υ_{max} = 3051, 2955, 2894, 1934, 1523, 1501, 1464, 1247, 1039, 835, 697 cm^{-1}; **HRMS** (API+): calcd for $C_{27}H_{27}{}^{74}GeO_2Si$ ($M+H^+$) 485.0992, found 485.0999.



(3,6-dimethyl-1,1-diphenyl-1*H*-benzo[*b*]germol-2-yl)trimethyl-silane 5gc

Compound **5gc** was prepared according to the **domino germylzincation/electrophilic coupling with CuCN.2LiCl**, from germane **2g** (101 mg, 0.243 mmol, 1 equiv) using CuCN.2LiCl (1M in THF, 0.73 mL, 0.729 mmol, 3 equiv) and methyl iodide (241 mg, 1.701

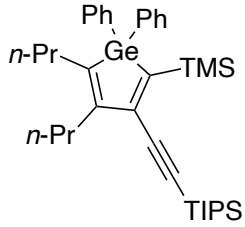
mmol, 7 equiv). Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 100/0, 95.5/0.5) afforded **5gc** (87 mg, 0.203 mmol, 83%) as yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.62-7.58 (m, 4H), 7.44 (s, 1H), 7.41-7.36 (m, 7H), 7.20 (d, *J* = 7.8 Hz, 1H), 2.46 (s, 3H), 2.35 (s, 3H), 0.19 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 162.2, 148.1, 141.0, 137.3 (2C), 136.4, 135.8, 135.1 (4C), 133.1, 130.0, 129.3 (2C), 128.4 (4C), 122.4, 21.4, 20.0, 1.3 (3C); **IR** (neat)**:** υ_{max} = 3068, 2953, 1526, 1483, 1431, 1246, 832, 697 cm^{-1}; **HRMS** (API+): calcd for $C_{25}H_{29}{}^{74}GeSi$ ($M+H^+$) 431.1250, found 431.1257.



Trimethyl(3-methyl-1,1-diphenyl-4,5-dipropyl-1*H*-germol-2-yl)silane 5nc

Compound **5nc** was prepared according to the **domino germylzincation/electrophilic coupling with CuCN.2LiCl**, from germane **2n** (110 mg, 0.253 mmol, 1 equiv) using CuCN.2LiCl (1M in THF, 0.76 mL, 0.759 mmol, 3 equiv) and methyl iodide (251 mg, 1.771 mmol, 7 equiv). Purification of the crude product by flash chromatography on silica gel (Cyclohexane/EtOAc = 100/0, 95.5/0.5) afforded **5nc** in an 70/30 inseparable mixture with **6nc** (97 mg, 0.151 mmol of **5nc**, 60%) as colorless oil.

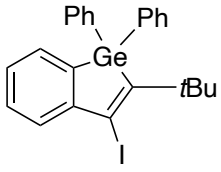
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60-7.53 (m, 4H), 7.40-7.34 (m, 6H), 2.41-2.31 (m, 4H), 2.24 (s, 3H), 1.52-1.42 (m, 2H), 1.29-1.20 (m, 2H), 1.00 (t, *J* = 7.1 Hz, 3H), 0.70 (t, *J* = 7.3 Hz, 3H), 0.04 (s, 9H); **IR** (neat)**:** υ_{max} = 3068, 3051, 2956, 2871, 1483, 1455, 1431, 1246, 833, 697 cm^{-1}; **HRMS** (API+): calcd for $C_{26}H_{37}{}^{74}GeSi$ ($M+H^+$) 451.1876, found 451.1887.



((1,1-diphenyl-4,5-dipropyl-2-(trimethylsilyl)-1*H*-germol-3-yl)ethynyl)triisopropylsilane 5nd

Compound **5nd** was prepared according to the **domino germylzincation/electrophilic coupling with CuCN.2LiCl**, from germane **2n** (160 mg, 0.367 mmol, 1 equiv) using CuCN.2LiCl (1M in THF, 1.10 mL, 1.101 mmol, 3 equiv) and (2-bromoethynyl)tris(1-methylethyl) silane (386 µL, 1.468 mmol, 4 equiv). Purification of the crude product by flash chromatography on silica gel (Pentane = 100) afforded **5nd** (160 mg, 0.260 mmol, 71%) as colorless oil.

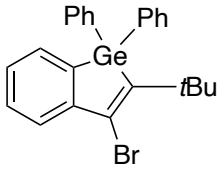
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61-7.54 (m, 4H), 7.42-7.36 (m, 6H), 2.67-2.56 (t, *J* = 7.7 Hz, 2H), 2.43-2.37 (t, *J* = 7.7 Hz, 2H), 1.64 (sextuplet, *J* = 7.5 Hz, 2H), 1.20 (s, 18H), 1.15-1.10 (m, 2H), 1.01 (t, *J* = 7.2 Hz, 3H), 0.94-0.86 (m, 3H), 0.73 (t, *J* = 7.2 Hz, 3H), 0.14 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 150.4, 149.5, 148.8, 143.6, 136.0 (2C), 135.1 (4C), 129.2 (2C), 128.5 (4C), 107.0, 95.8, 33.6, 29.9, 24.2, 23.5, 18.9 (6C), 14.5,14.3, 11.8 (3C), -0.1 (3C); **IR** (neat)**:** υ_{max} = 2925, 2866, 2131, 1463, 1432, 1243, 1089, 835, 697 cm^{-1}; **HRMS** (ESI+): calcd for $C_{36}H_{55}{}^{74}GeSi_2$ ($M+H^+$) 617.3054, found 617.3055.



2-(*tert*-butyl)-3-iodo-1,1-diphenyl-1*H*-benzo[*b*]germole 5be

Compound **5be** was prepared according to the **domino germylzincation/electrophilic coupling with CuCN.2LiCl**, from germane **2b** (157 mg, 0.408 mmol, 1 equiv) using CuCN.2LiCl (1M in THF, 1.22 mL, 1.220 mmol, 3 equiv) and iodine crystals (207 mg, 0.816 mmol, 2 equiv). Purification of the crude product by flash chromatography on silica gel (Cyclohexane / EtOAc = 99/1) afforded **5be** (201 mg, 0.393 mmol, 96%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 7.8 Hz, 1H), 7.64-7.59 (m, 4H), 7.40-7.32 (m, 7H), 7.27 (dd, *J* = 7.1, 1.3 Hz, 1H), 7.16 (td, *J* = 7.4, 1.3 Hz, 1H), 1.39 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 159.7, 149.8, 136.4, 135.2 (2C), 134.9 (4C), 131.5, 130.0, 129.8 (2C), 129.3, 128.8 (4C), 128.3, 109.6, 37.3, 30.7 (3C); **IR** (neat)**:** υ_{max} = 3050, 2961, 1579, 1519, 1483, 1431, 1089, 732, 696 cm^{-1}; **HRMS** (API+): calcd for $C_{24}H_{24}{}^{74}GeI$ ($M+H^+$) 513.0135, found 513.0135.

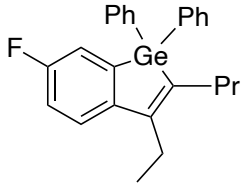


3-bromo-2-(tert-butyl)-1,1-diphenyl-1*H*-benzo[*b*]germole 5bf

Compound **5bf** was prepared according to the **domino germylzincation/electrophilic coupling with CuCN.2LiCl**, from germane **2b** (100 mg, 0.260 mmol, 1 equiv) using CuCN.2LiCl (1M in THF, 0.52 mL, 0.520 mmol, 2 equiv) and N-bromosuccinimide (92.5 mg, 0.520 mmol, 2 equiv). Purification of the crude product by flash chromatography on silica gel (Cyclohexane / EtOAc = 100/0, 99.5/0.5) afforded **5bf** (95 mg, 0.205 mmol, 79%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.6 Hz, 1H), 7.67-7.61 (m, 4H), 7.46-7.36 (m, 8H), 7.25 (td, *J* = 7.7, 1.0 Hz, 1H), 1.40 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 152.6, 148.1,

136.4, 135.0 (4C), 134.9 (2C), 131.7, 129.9, 129.8 (2C), 128.8 (4C), 128.7, 128.1, 125.3, 36.9, 30.6 (3C); **IR** (neat)**:** υ_{max} = 2965, 2906, 1536, 1431, 1054, 695 cm^{-1}; **HRMS** (API+): calcd for $C_{24}H_{24}{}^{79}Br^{74}Ge$ ($M+H^+$) 465.0273, found 465.0278.

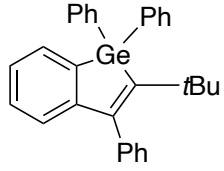


5kg

Compound **5kg** was prepared according to the **domino germylzincation/electrophilic coupling with CuCN.2LiCl**, from germane **2k** (83 mg, 0.213 mmol, 1 equiv) using CuCN.2LiCl (1M in THF, 0.42 mL, 0.420 mmol, 2 equiv) alone. Purification of the crude product by flash chromatography on silica gel (Cyclohexane / EtOAc = 100/0, 99.5/0.5) afforded **5kg** (73 mg, 0.175 mmol, 82%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (dd, *J* = 7.2, 2.1 Hz, 4H), 7.40-7.30 (m, 7H), 7.23 (dd, *J* = 7.4, 2.3 Hz, 1H), 7.02 (td, *J* = 8.9, 2.7 Hz, 1H), 2.64 (q, *J* = 7.5 Hz, 2H), 2.53 (t, *J* = 7.6 Hz, 2H), 1.42 (qint, *J* = 7.4 Hz, 2H), 1.17 (t, *J* = 7.5 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 162.2 (d, *J* = 249 Hz), 151.2, 145.2 (d, *J* = 3 Hz), 140.7 (d, *J* = 5 Hz), 140.4 (d, *J* = 4 Hz), 135.3 (2C), 134.8 (4C), 129.5 (2C), 128.5 (4C), 123.1 (d, *J* = 7 Hz), 119.6 (d, *J* = 20 Hz), 115.7 (d, *J* = 22 Hz), 33.3, 24.2, 20.7, 14.4, 13.8.

Functionalization of germole 5be (Scheme 7):

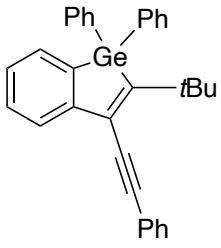


2-(tert-butyl)-1,1,3-triphenyl-1*H*-benzo[*b*]germole 7

Compound **7** was prepared according to a **Suzuki reaction** from germane **5be** (174 mg, 0.341 mmol, 1 equiv) using phenylboronic acid (62 mg, 0.76 mL, 0.511 mmol, 1.5 equiv), $Pd(OAc)_2$ (1.5 mg, $6.8x10^{-3}$ mmol, 0.02 equiv), SPhos (5.6 mg, $13.6x10^{-3}$ mmol, 0.04 equiv), K_3PO_4 (145 mg, 0.682 mmol, 2 equiv), toluene (3 mL) during 10 h at 80 °C. Purification of the crude product by flash chromatography on silica gel (Petroleum ether/Toluene = 98/2, 94/6, 90/10) afforded **7** (122 mg, 0.265 mmol, 78%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79-7.73 (m, 4H), 7.50-7.48 (m, 1H), 7.48-7.45 (m, 3H), 7.45-7.40 (m, 6H), 7.34-7.30 (m, 2H), 7.22-7.15 (m, 2H), 6.60-6.53 (m, 1H), 1.06 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 153.2, 152.6, 151.3, 141.0, 136.7, 136.4 (2C), 135.2 (4C), 132.0, 130.3 (2C), 129.41, 129.37 (2C), 128.6 (4C), 128.2 (2C), 126.9, 126.8, 124.7, 37.0, 33.2 (3C);

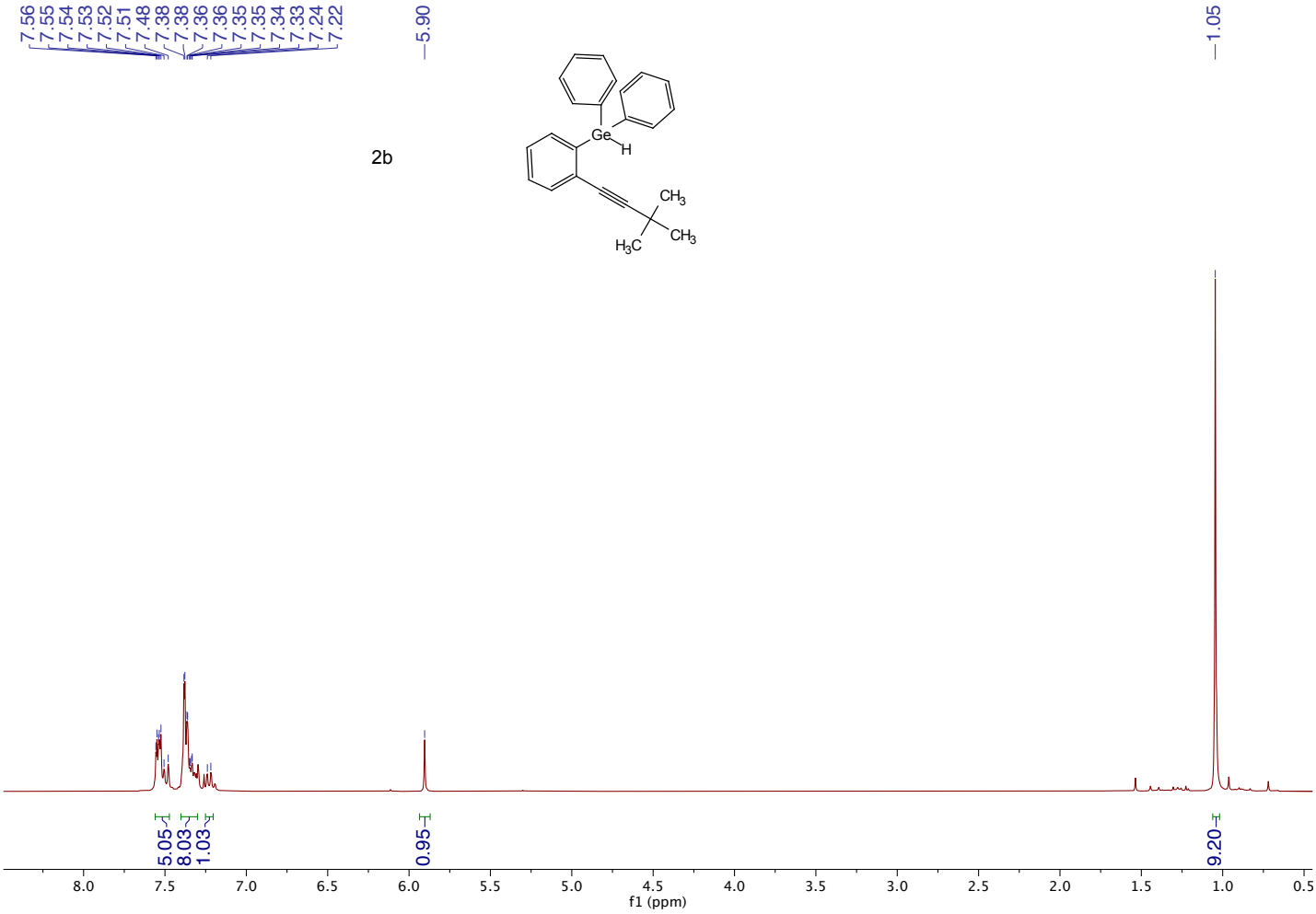
IR (neat)**:** υ_{max} = 2957, 2925, 1589, 1484, 1471, 1431, 1089, 697 cm^{-1}; **HRMS** (API+): calcd for $C_{30}H_{29}{}^{74}Ge$ ($M+H^+$) 463.1481, found 463.1493.



2-(tert-butyl)-1,1-diphenyl-3-(phenylethynyl)-1*H*-benzo[*b*]germole 8

Compound **8** was prepared according to **general procedure for Sonogashira reaction** using germane **5be** (174 mg, 0.341 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (14 mg, 0.020 mmol, 0.06 equiv), CuI (2 mg, 0.010 mmol, 0.03 equiv), Et_3N (94 µL, 0.0682 mmol, 0.2 equiv) and phenylacetylene (52 mg, 0.511 mmol, 1.5 equiv) in dry THF (5 mL). Purification of the crude product by flash chromatography on silica gel (Petroleum ether / Toluene = 99/1, 98/2, 95/5) afforded **8** (103 mg, 0.212 mmol, 62%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.67-7.60 (m, 6H), 7.45-7.38 (m, 11H), 7.23-7.17 (m, 1H), 1.44 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 165.0, 148.4, 136.0, 135.4 (2C), 135.1 (4C), 132.1, 131.4 (2C), 129.8, 129.6 (2C), 129.2, 128.65 (4C), 128.63 (2C), 127.5, 126.7, 123.7, 116.2, 99.6, 86.8, 36.8, 31.1 (3C); **IR** (neat)**:** υ_{max} = 3022, 2959, 2198, 1596, 1523, 1484, 1460, 1431, 1089, 689 cm^{-1}; **HRMS** (API+): calcd for $C_{32}H_{29}{}^{74}Ge$ ($M+H^+$) 487.1481, found 487.1471.


7.56
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7.33
7.24
7.22
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1.05
2b
Ge
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CH3
H3C
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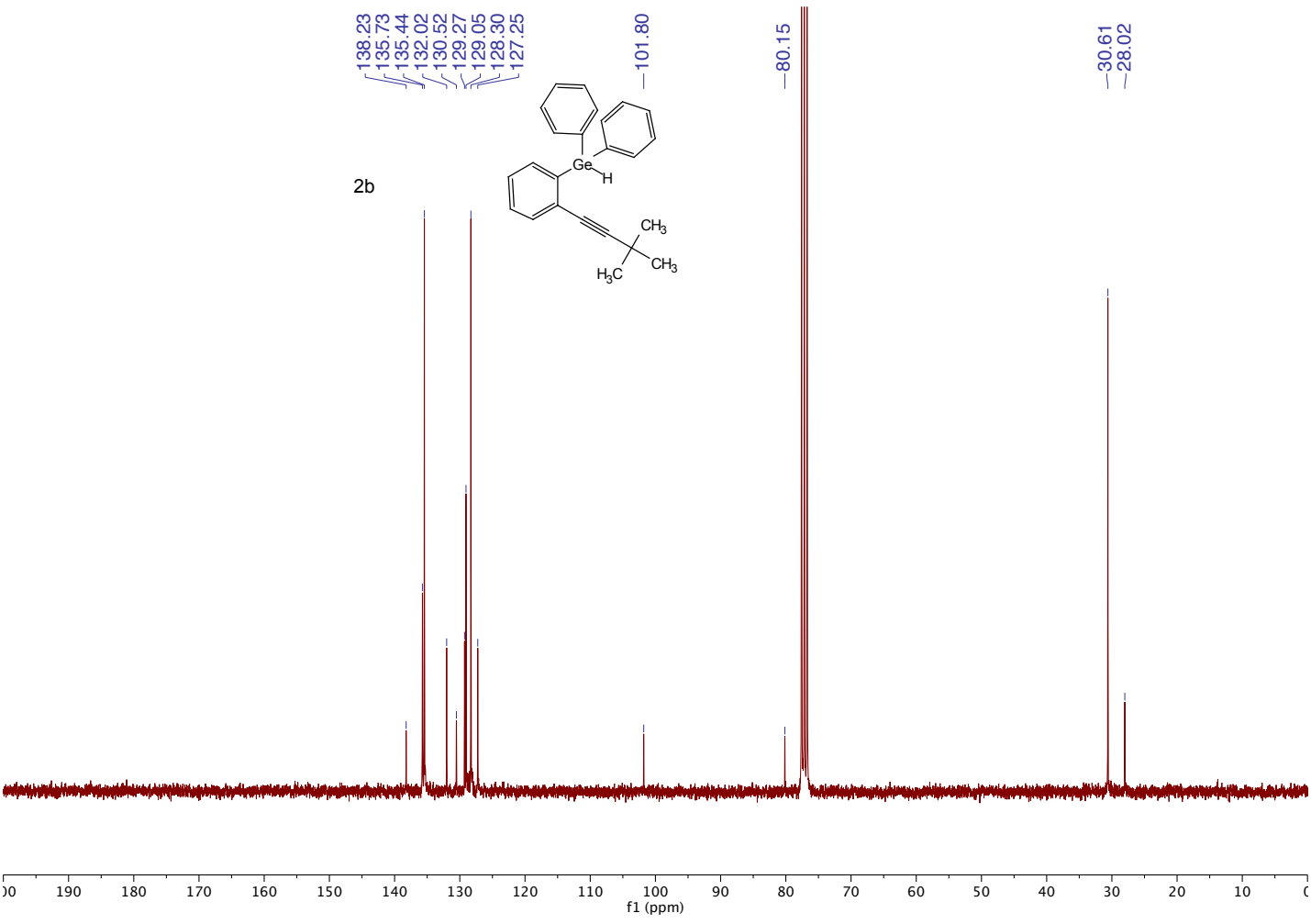
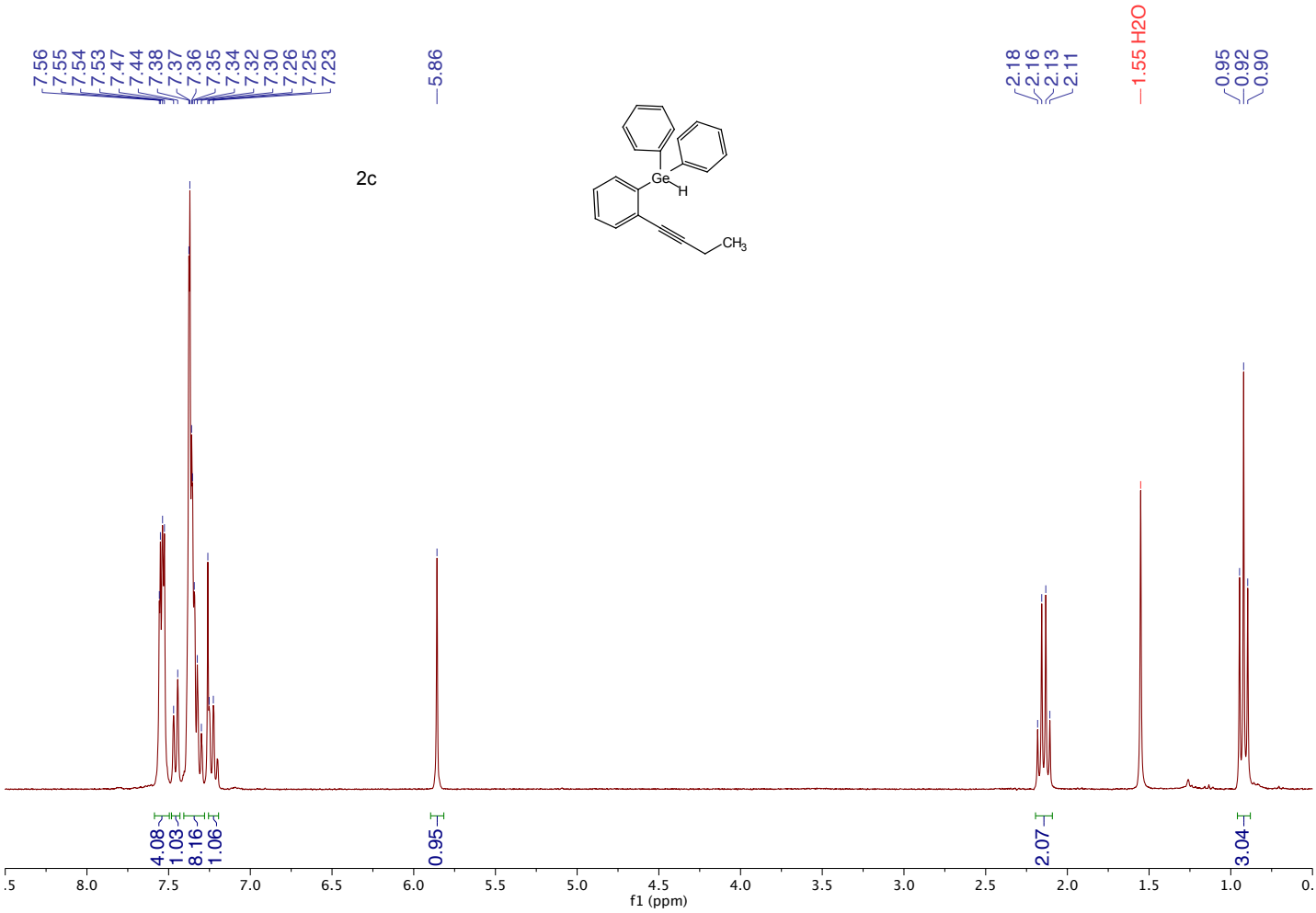
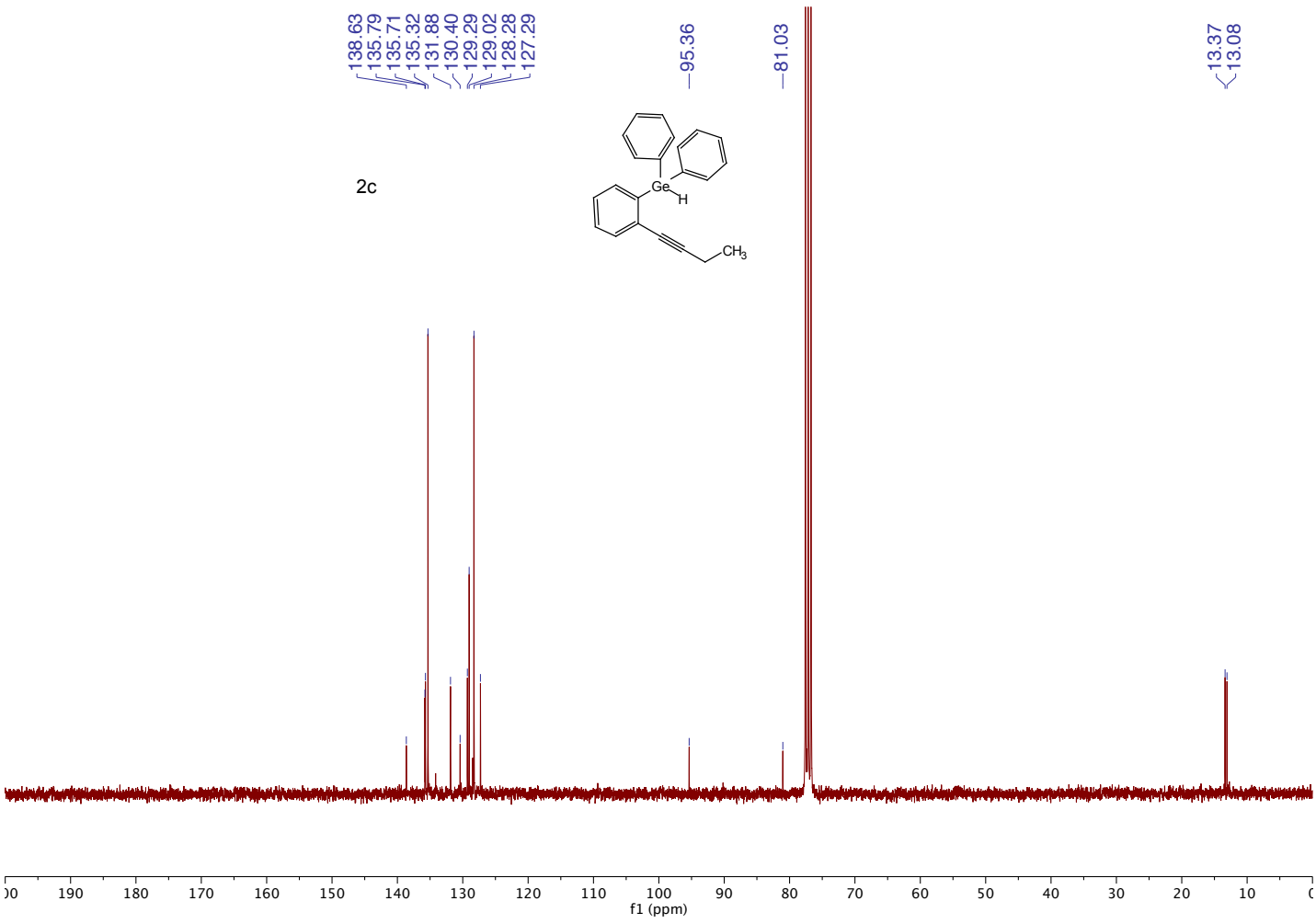
8.03
1.03
0.95
9.20
f1 (ppm)


138.23
135.73
135.44
132.02
130.52
129.27
129.05
128.30
127.25
101.80
80.15
30.61
28.02
2b
Ge
H
CH3
CH3
H3C
f1 (ppm)

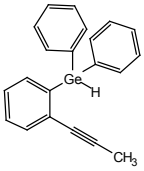

7.56
7.55
7.54
7.53
7.47
7.44
7.38
7.37
7.36
7.35
7.34
7.32
7.30
7.26
7.25
7.23
5.86
2.18
2.16
2.13
2.11
1.55 H2O
0.95
0.92
0.90
2c
Ge
H
CH3
4.08
1.03
8.16
1.06
0.95
2.07
3.04
f1 (ppm)

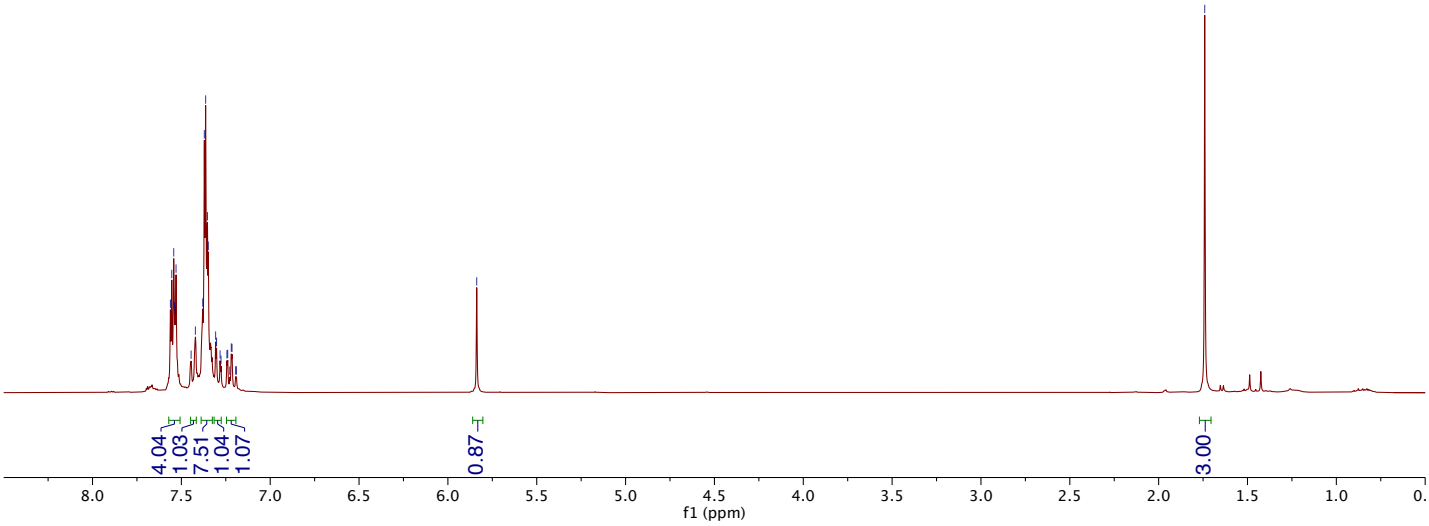

138.63
135.79
135.71
135.32
131.88
130.40
129.29
129.02
128.28
127.29
95.36
81.03
13.37
13.08
2c
Ge
H
CH3
f1 (ppm)


7.56
7.55
7.54
7.54
7.53
7.53
7.45
7.42
7.38
7.37
7.36
7.35
7.35
7.31
7.30
7.28
7.28
7.24
7.24
7.23
7.22
7.21
7.19
7.19
5.84


1.74

2d


Ge
H
CH3

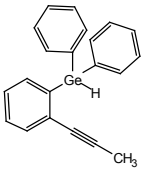

4.04
1.03
7.51
1.04
1.07
0.87
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

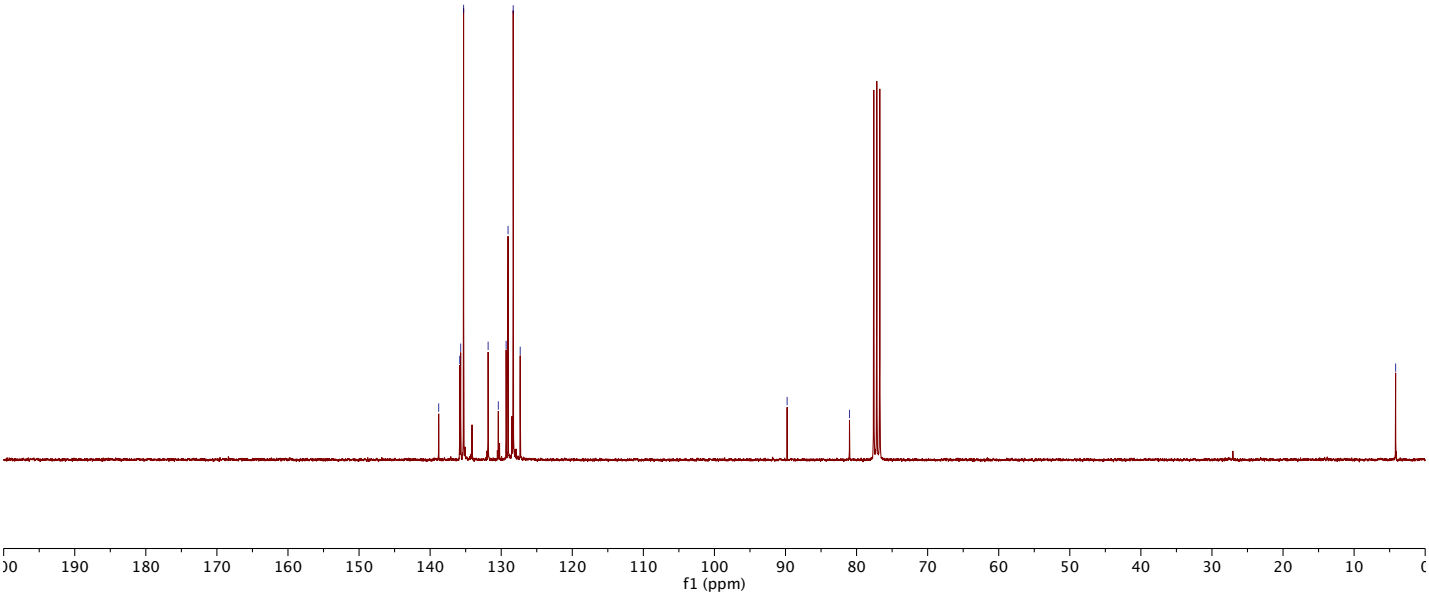

138.80
135.83
135.70
135.29
131.84
130.40
129.30
129.03
128.31
127.32

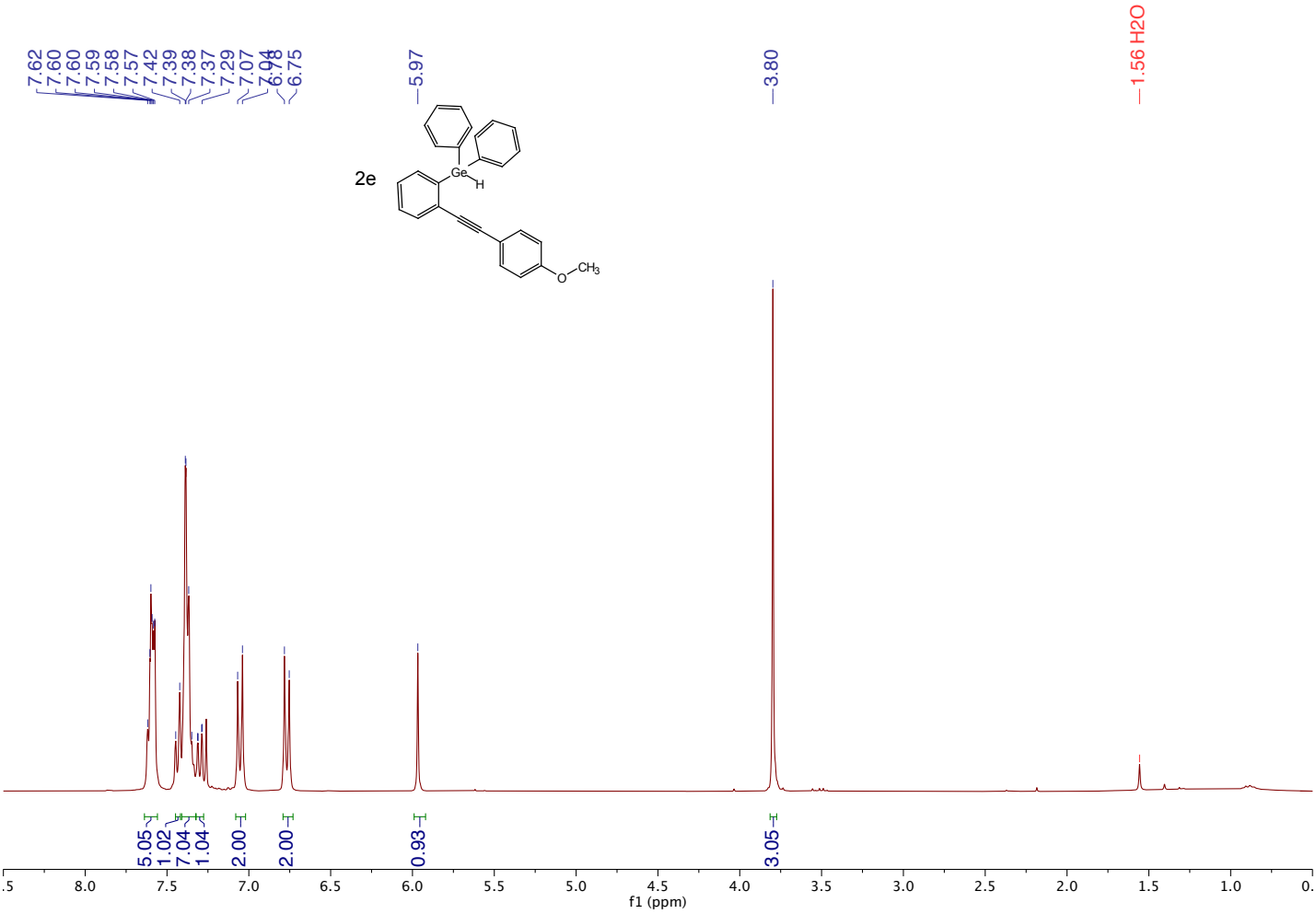

89.77
81.00

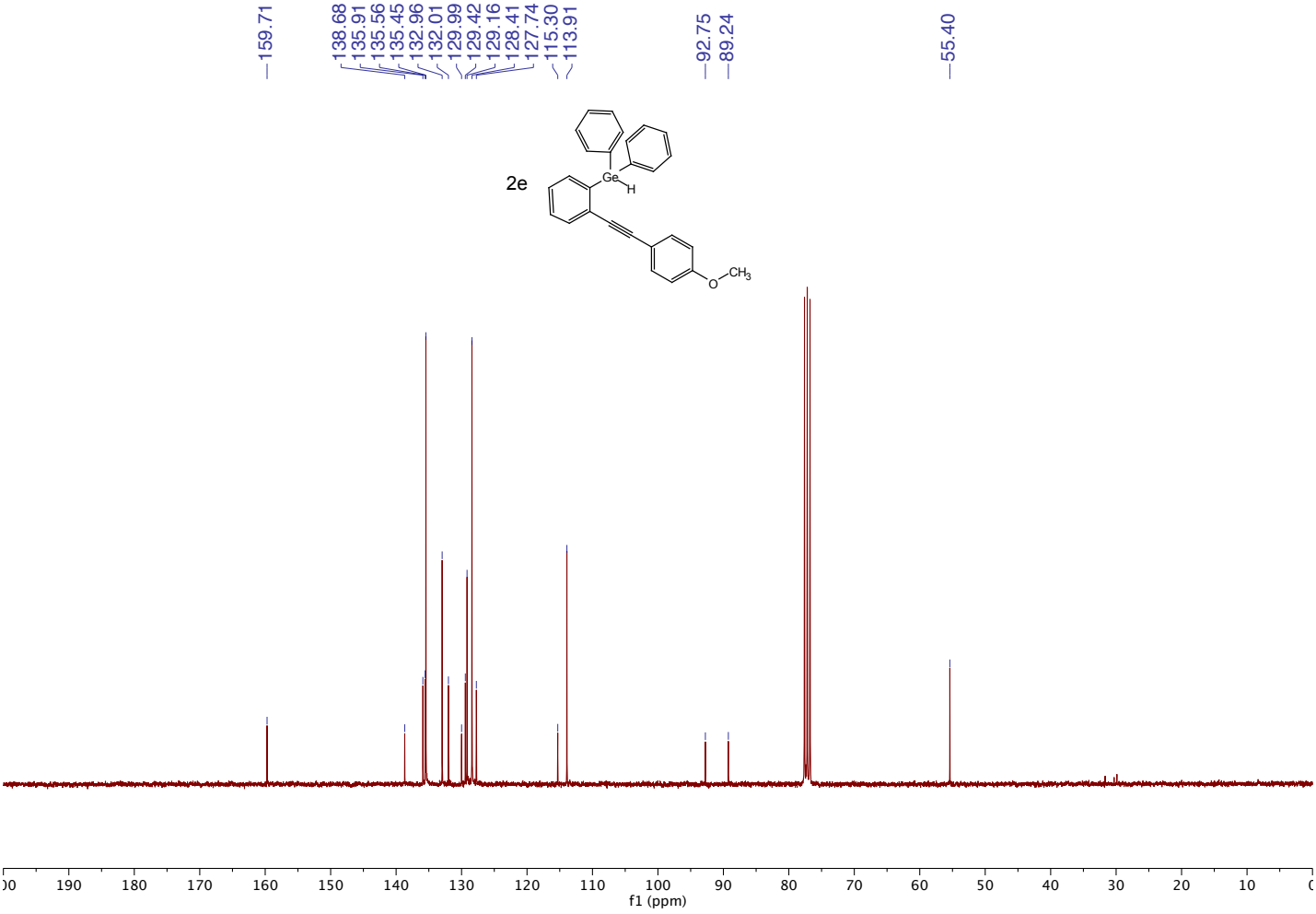

4.16

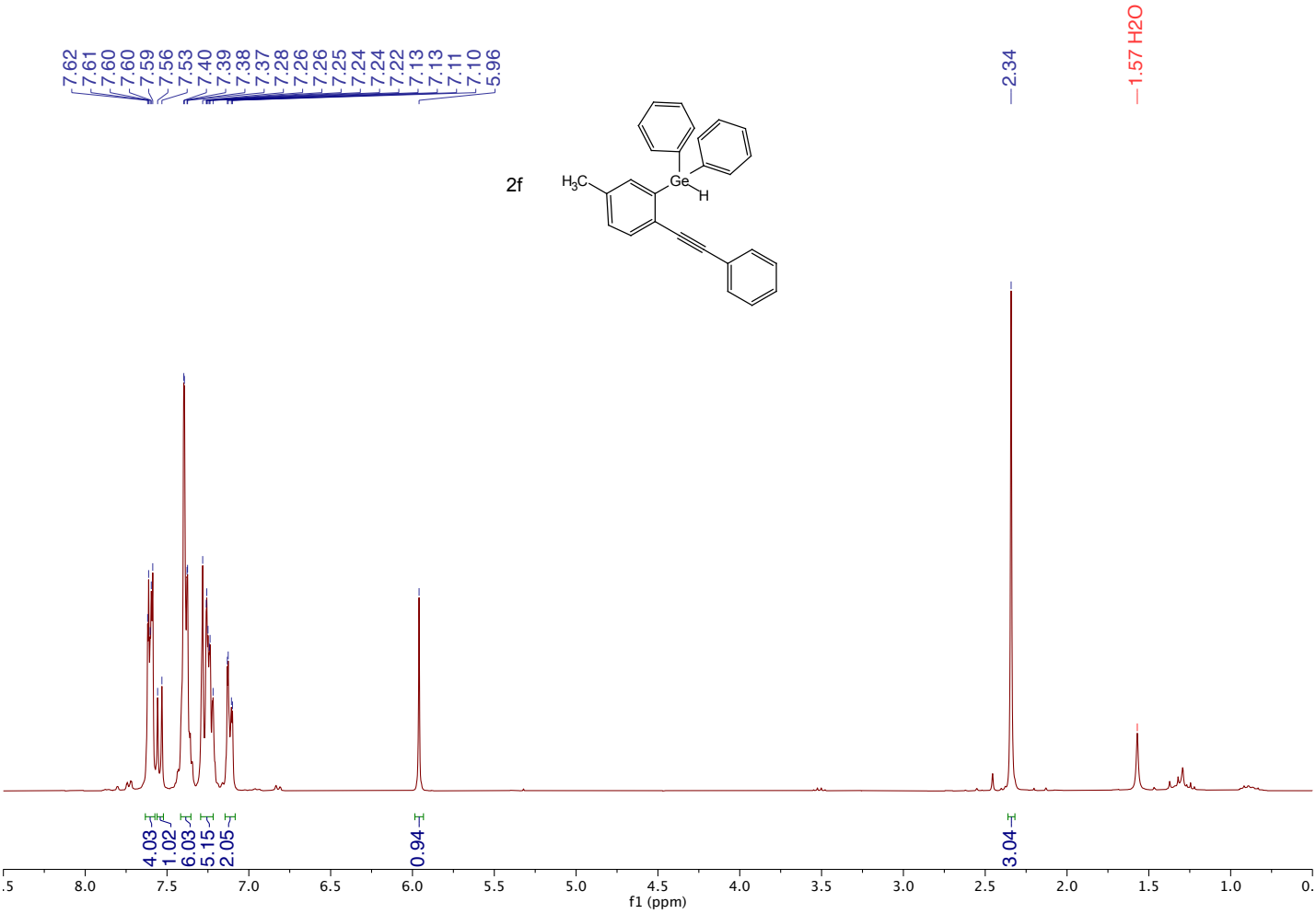
2d

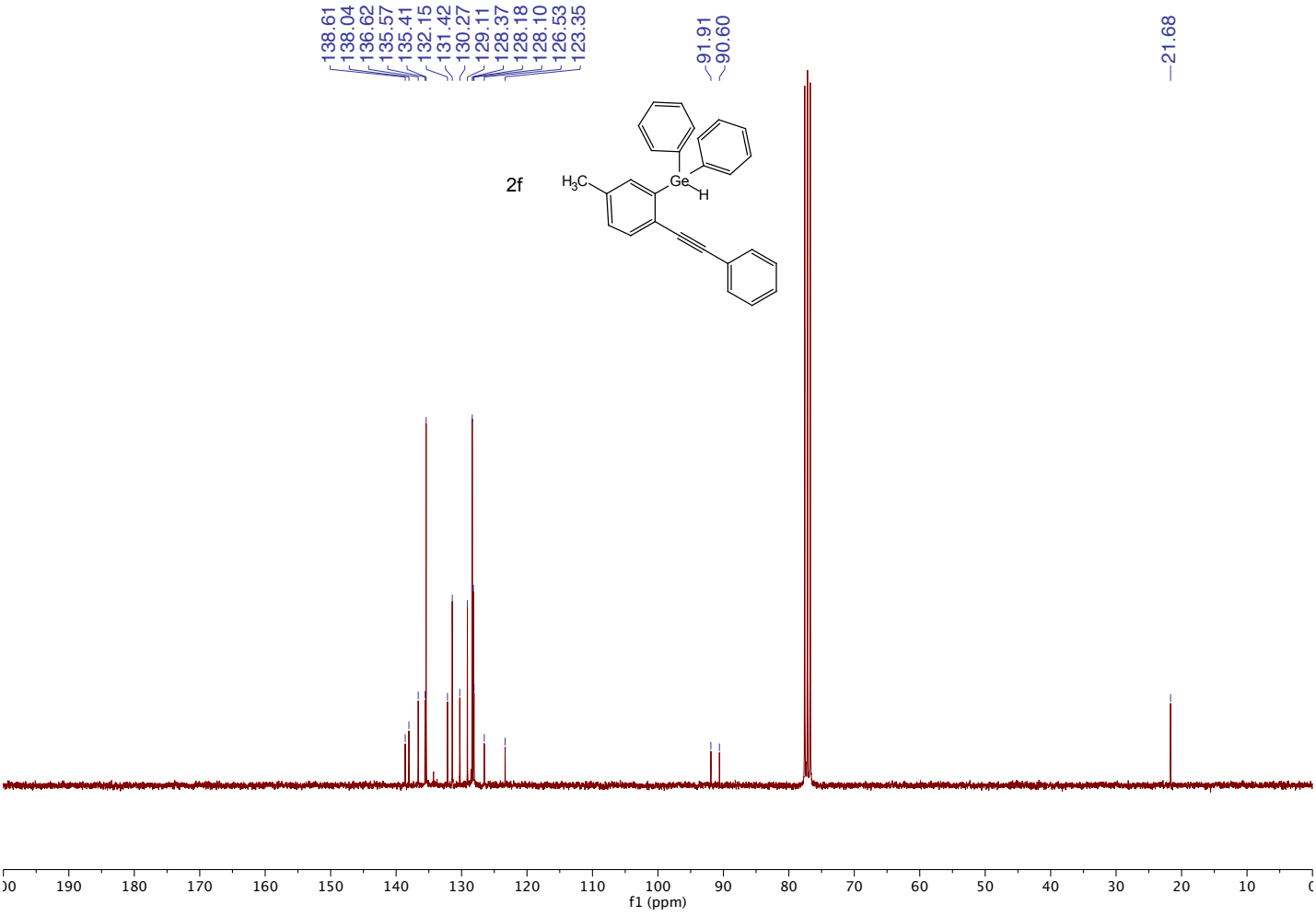

Ge
H
CH3

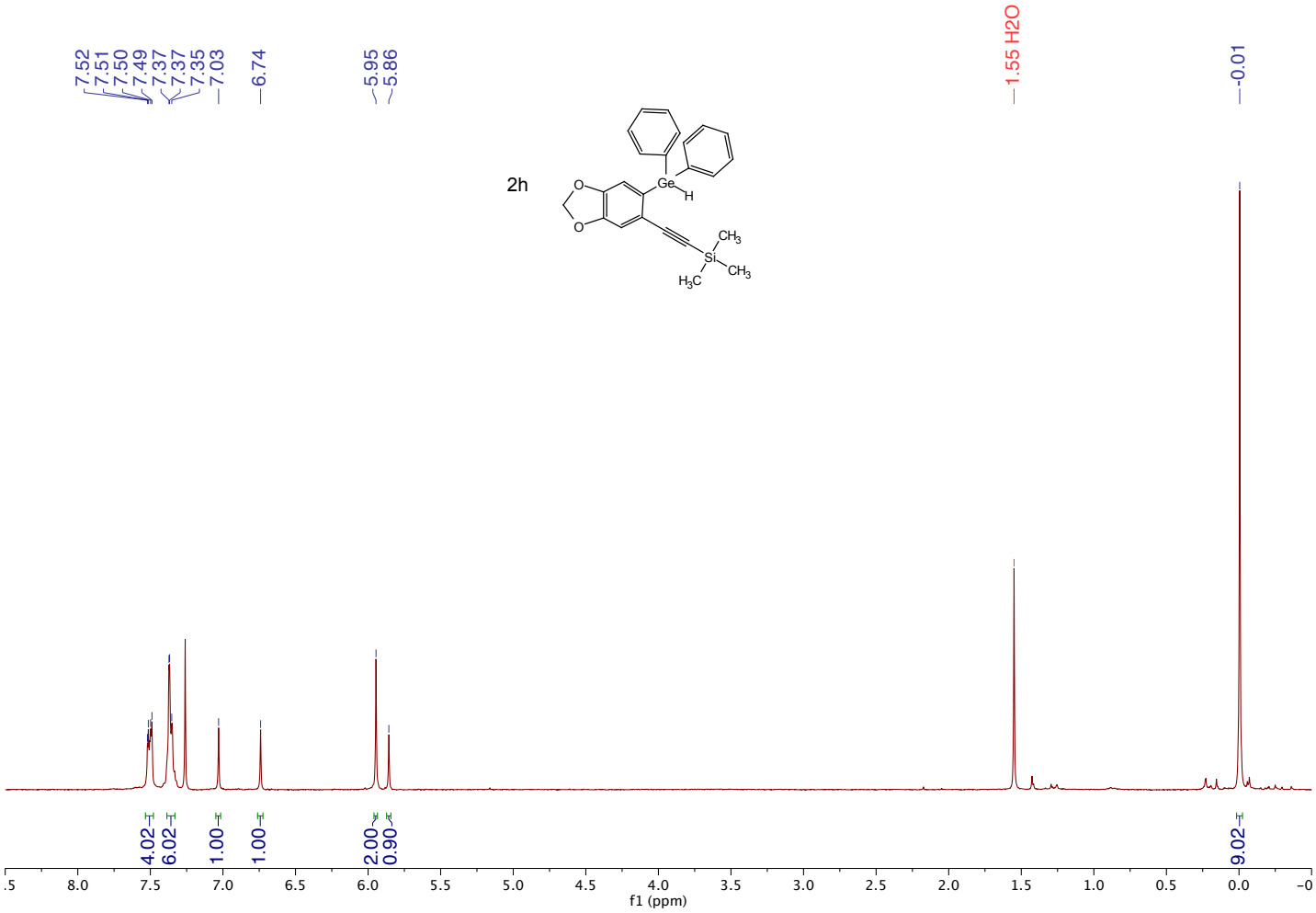

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

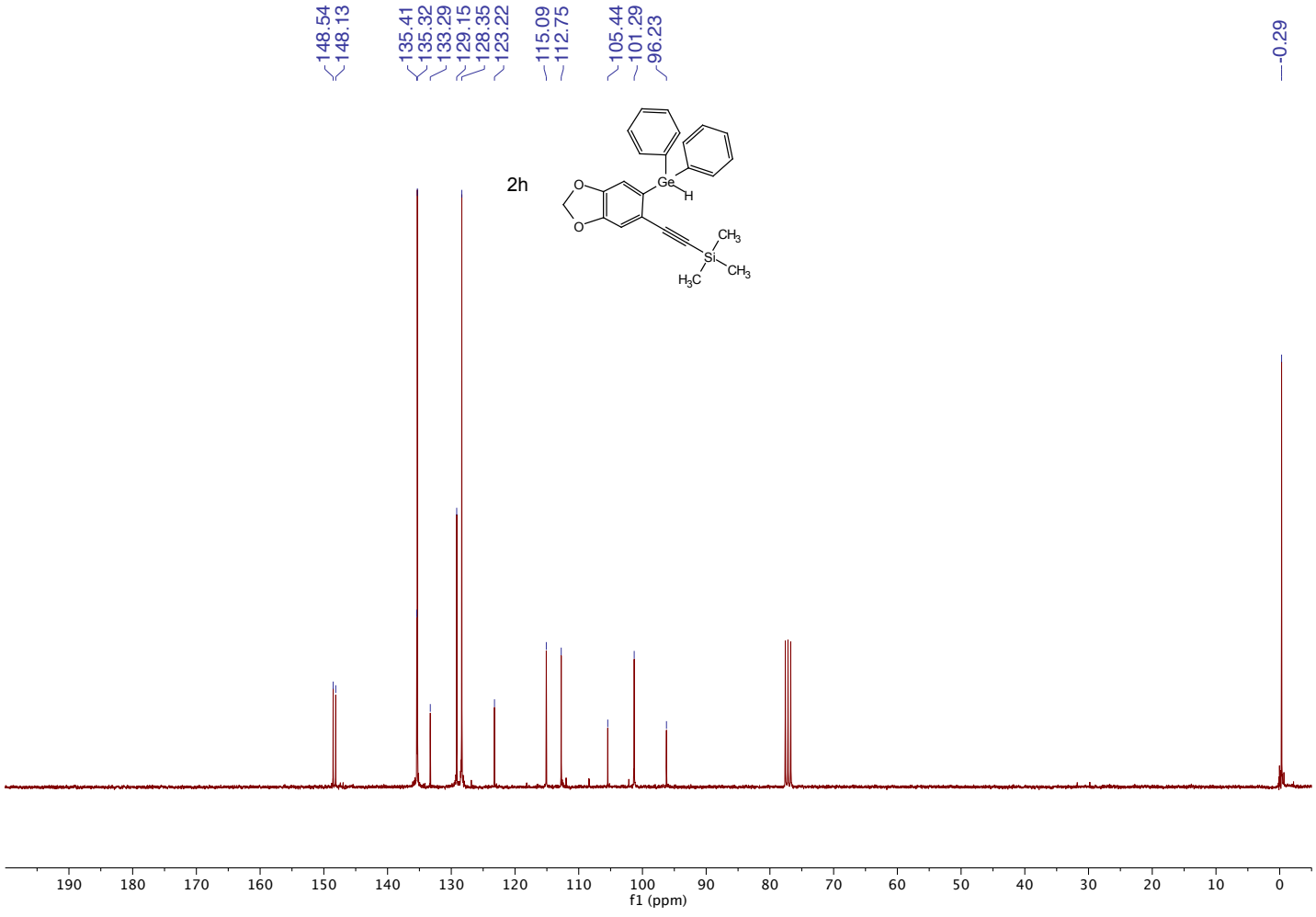

7.62
7.60
7.60
7.59
7.58
7.57
7.42
7.39
7.38
7.37
7.29
7.07
6.94
6.78
6.75
5.97
3.80
1.56 H2O
2e
Ge
H
O
CH3
5.05
1.02
7.04
1.04
2.00
2.00
0.93
3.05
f1 (ppm)

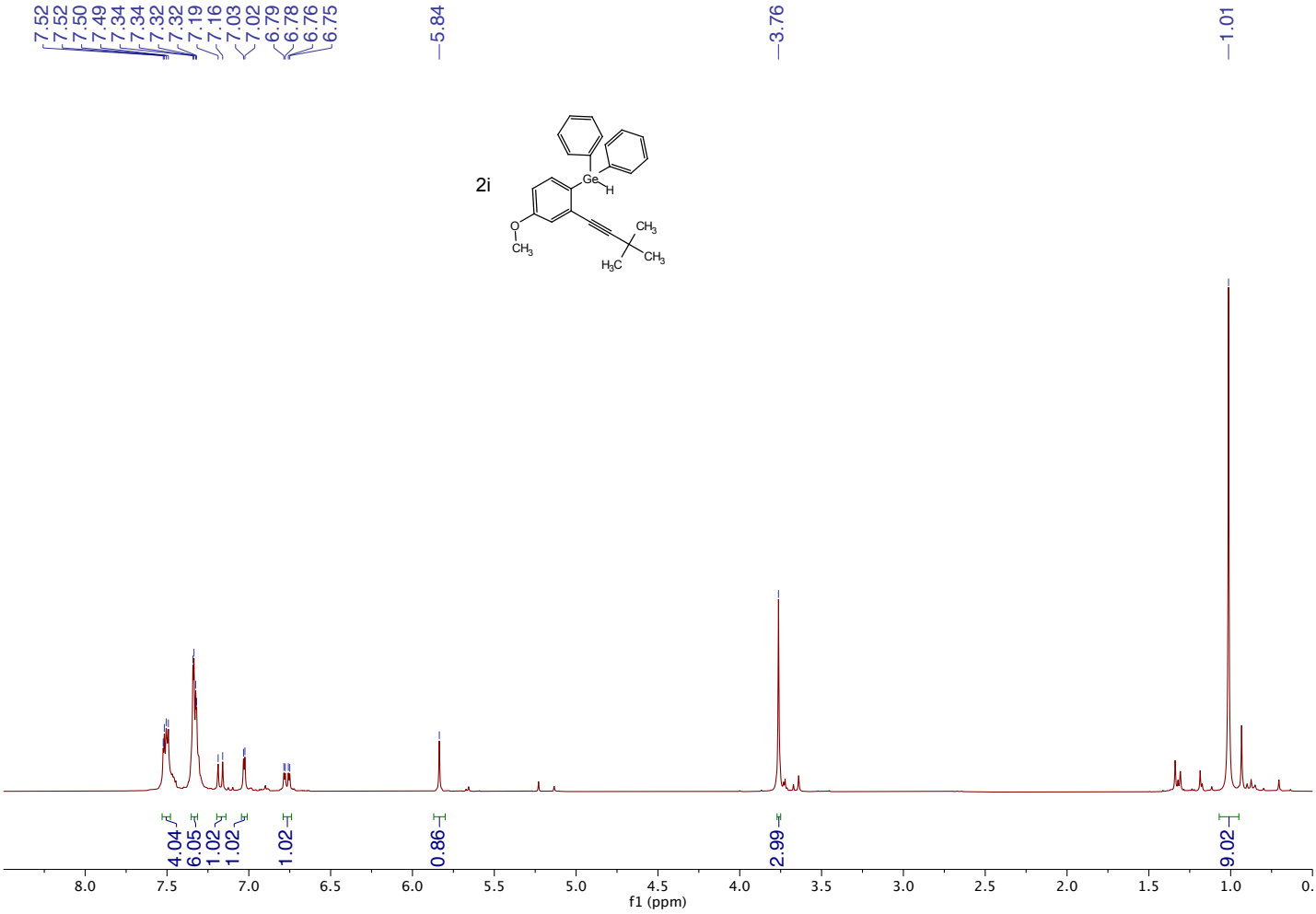

159.71
138.68
135.91
135.56
135.45
132.96
132.01
129.99
129.42
129.16
128.41
127.74
115.30
113.91
92.75
89.24
55.40
2e
Ge
H
O
CH3
f1 (ppm)

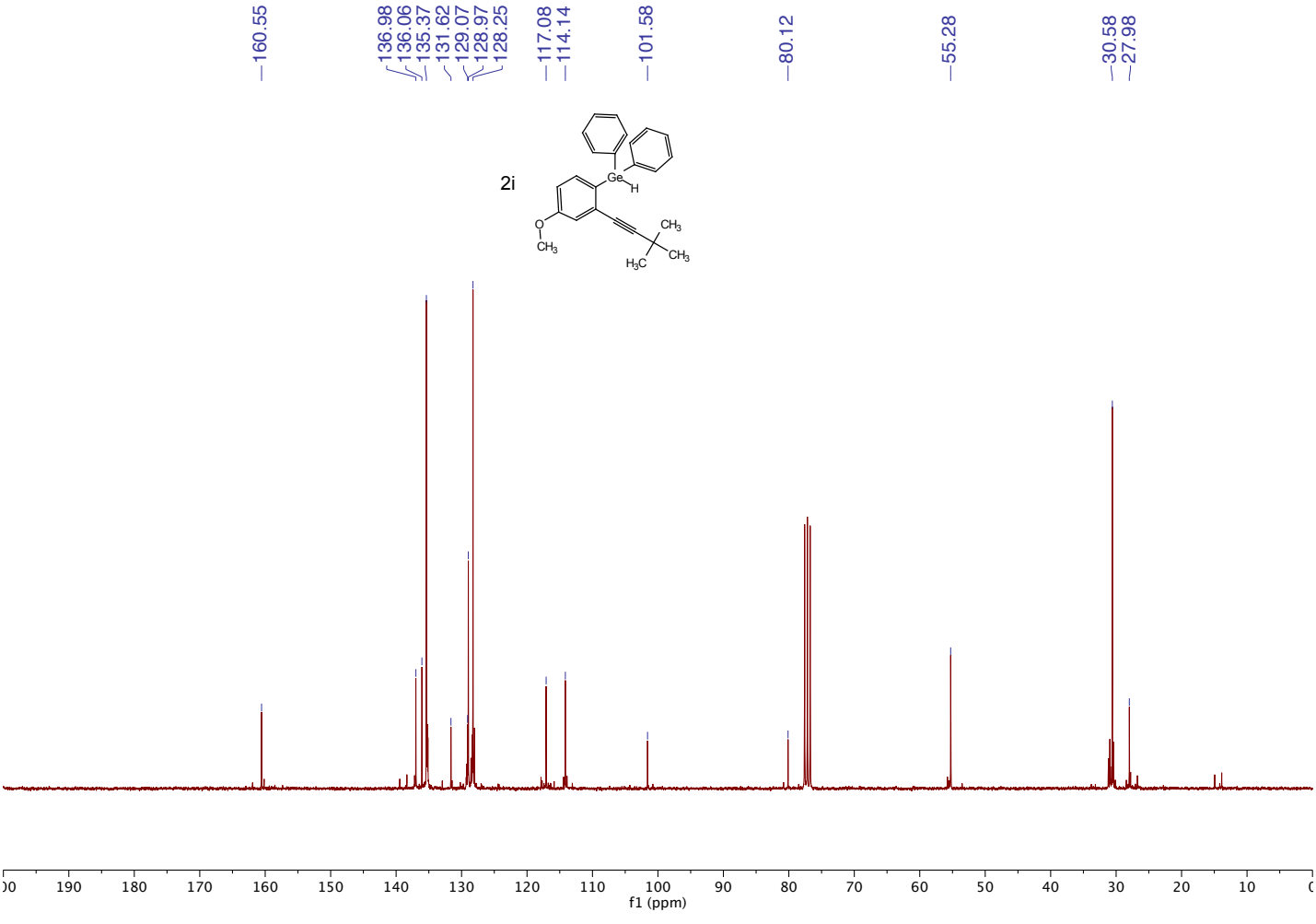

7.62
7.61
7.60
7.60
7.59
7.56
7.53
7.40
7.39
7.38
7.37
7.28
7.26
7.26
7.25
7.24
7.24
7.22
7.13
7.13
7.11
7.10
5.96
2.34
1.57 H2O
2f
H3C
Ge
H
4.03
1.02
6.03
5.15
2.05
0.94
3.04
f1 (ppm)


138.61
138.04
136.62
135.57
135.41
132.15
131.42
130.27
129.11
128.37
128.18
128.10
126.53
123.35
91.91
90.60
21.68
2f
H3C
Ge
H
f1 (ppm)


7.52
7.51
7.50
7.49
7.37
7.37
7.35
7.03
6.74
5.95
5.86
1.55 H2O
-0.01
2h
Ge
H
O
O
CH3
Si
CH3
H3C
4.02
6.02
1.00
1.00
2.00
0.90
9.02
f1 (ppm)

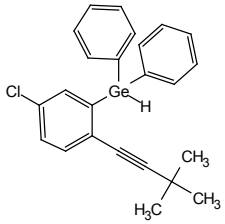

148.54
148.13
135.41
135.32
133.29
129.15
128.35
123.22
115.09
112.75
105.44
101.29
96.23
-0.29
2h
Ge
H
O
O
CH3
Si
CH3
H3C
f1 (ppm)

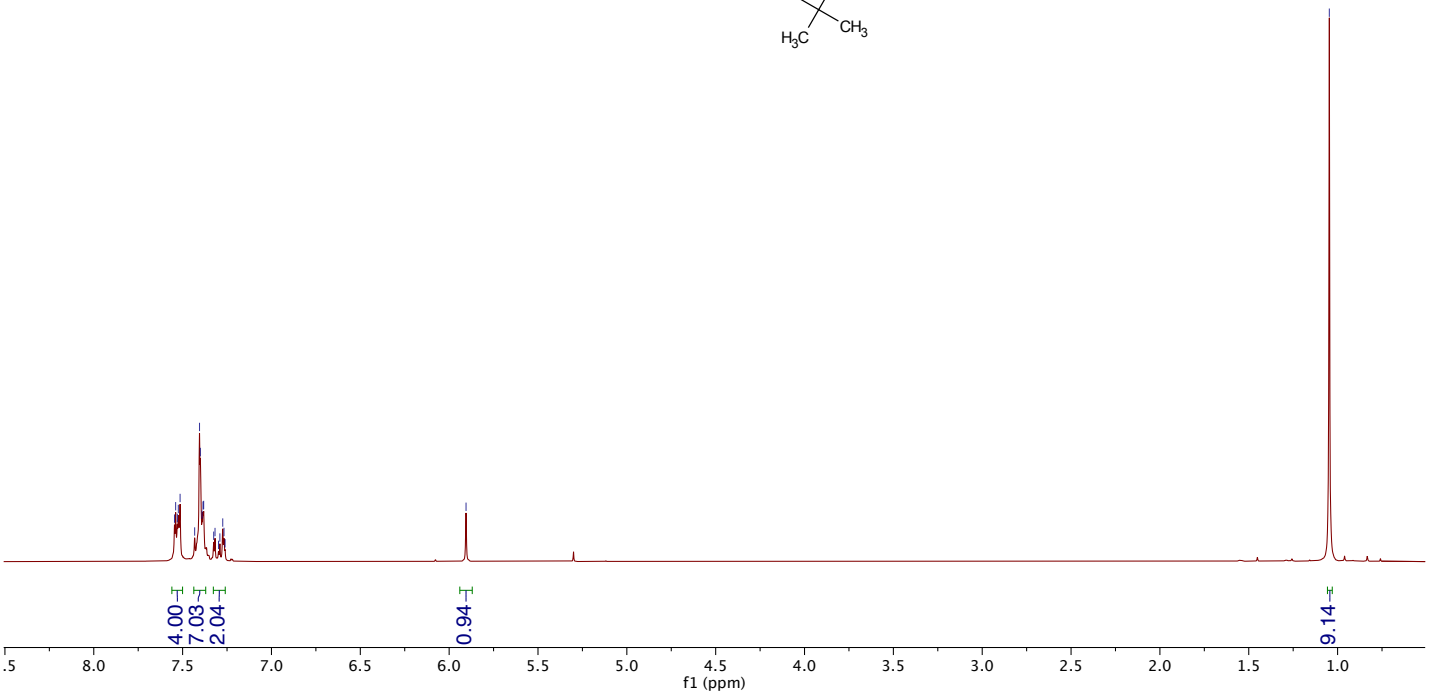

7.52
7.52
7.50
7.49
7.34
7.34
7.32
7.32
7.19
7.16
7.03
7.02
6.79
6.78
6.76
6.75
5.84
3.76
1.01
2i
Ge
H
O
CH3
CH3
H3C
CH3
4.04
6.05
1.02
1.02
1.02
0.86
2.99
9.02
f1 (ppm)


160.55
136.98
136.06
135.37
131.62
129.07
128.97
128.25
117.08
114.14
101.58
80.12
55.28
30.58
27.98
2i
Ge
H
O
CH3
CH3
H3C
CH3
f1 (ppm)

7.55 7.54 7.53 7.52 7.51 7.43 7.40 7.40 7.39 7.39 7.38 7.33 7.32 7.30 7.29 7.27 7.27 7.26 — 5.90 — 1.05

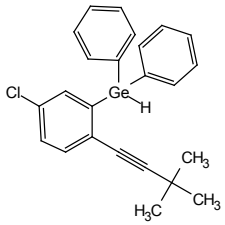
2j

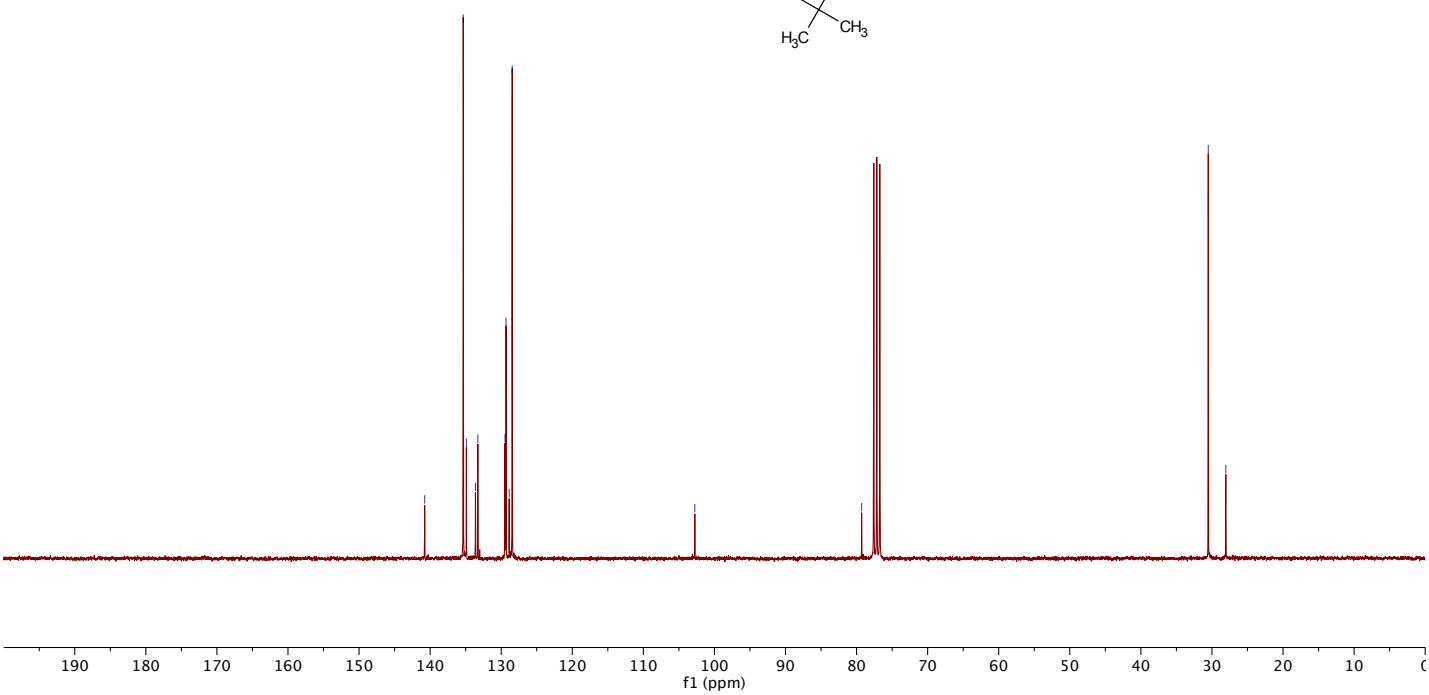


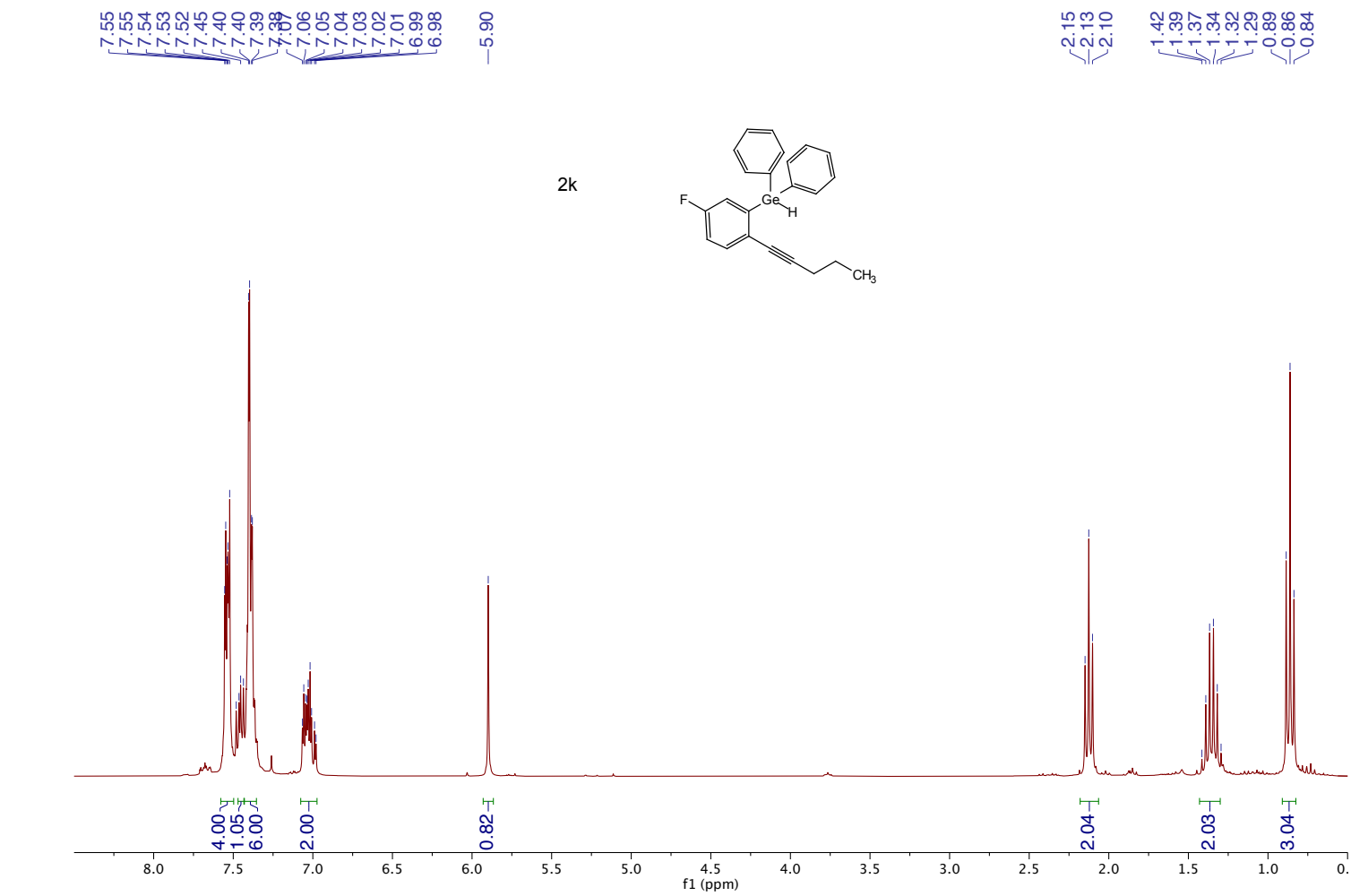


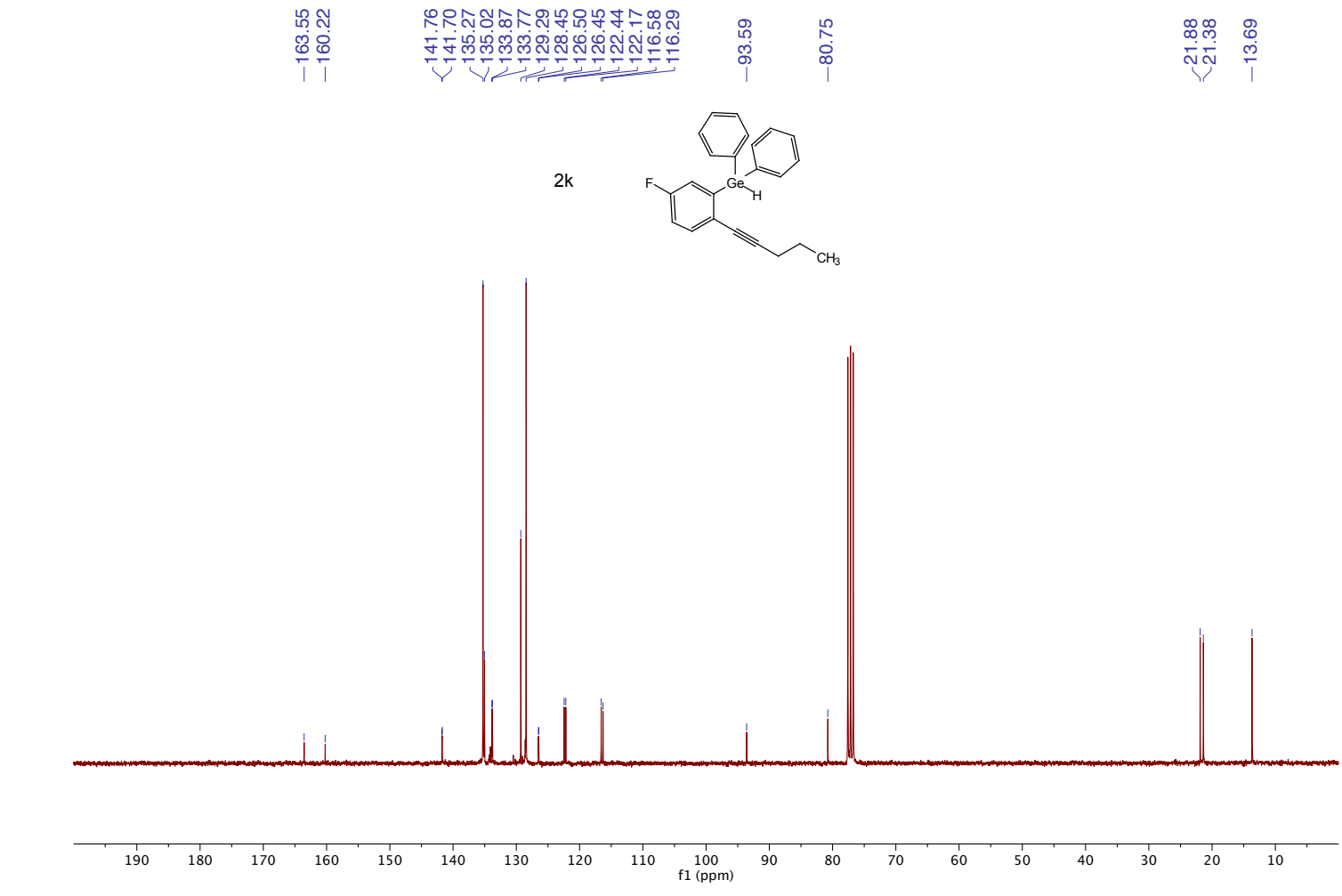
140.77 135.34 134.90 133.62 133.28 129.46 129.32 128.87 128.45 — 102.76 — 79.29 — 30.52 — 28.05

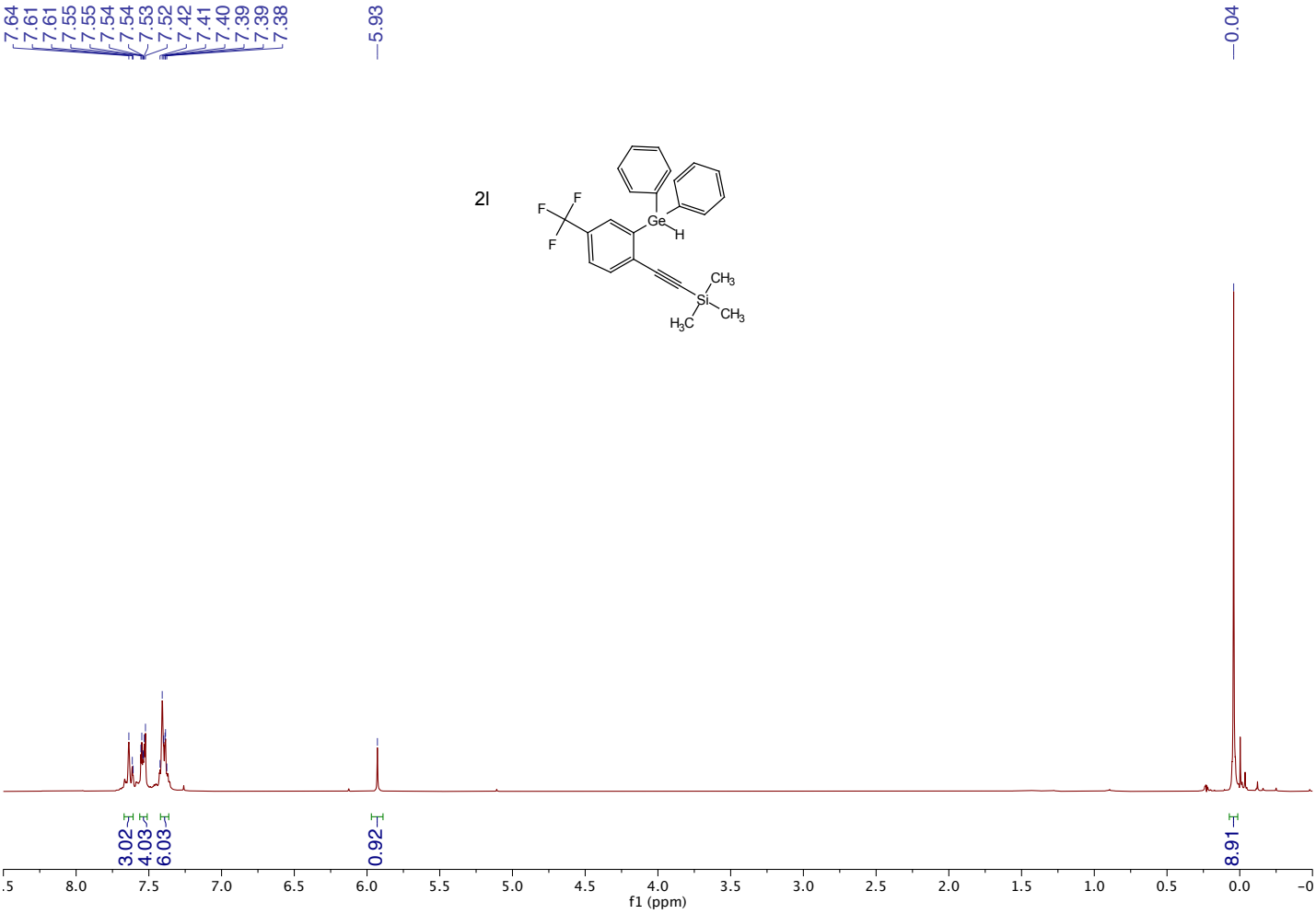
2j

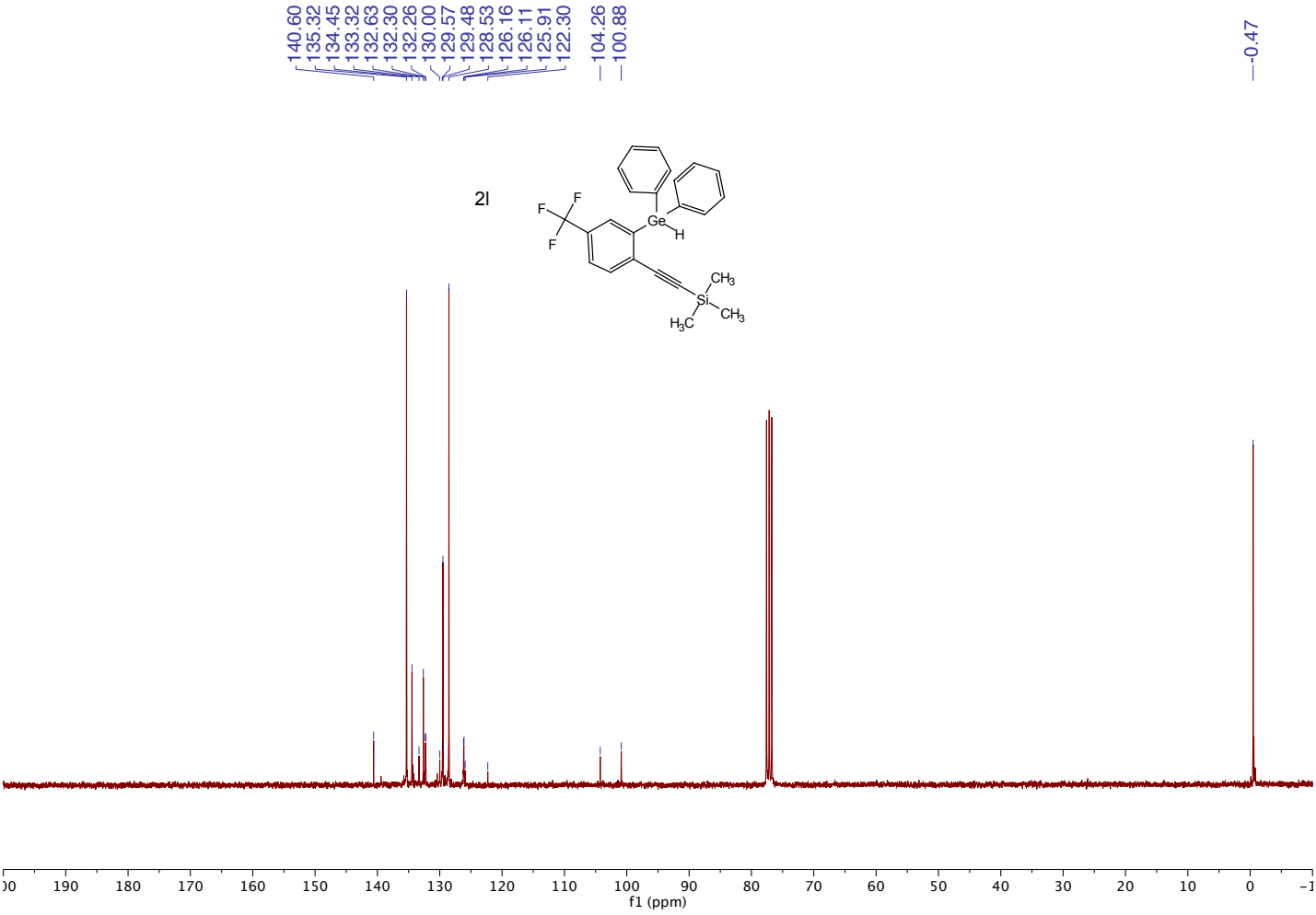


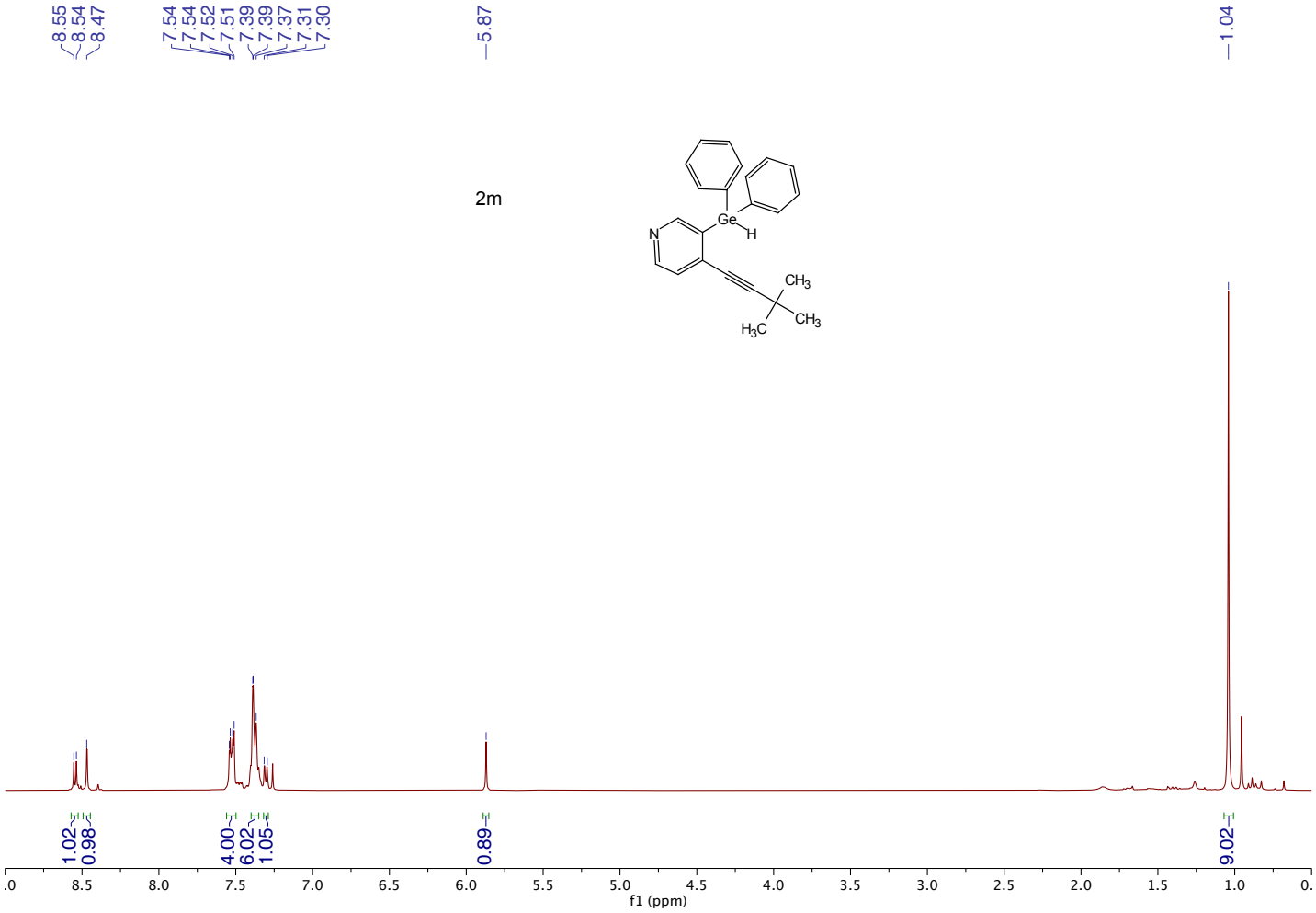


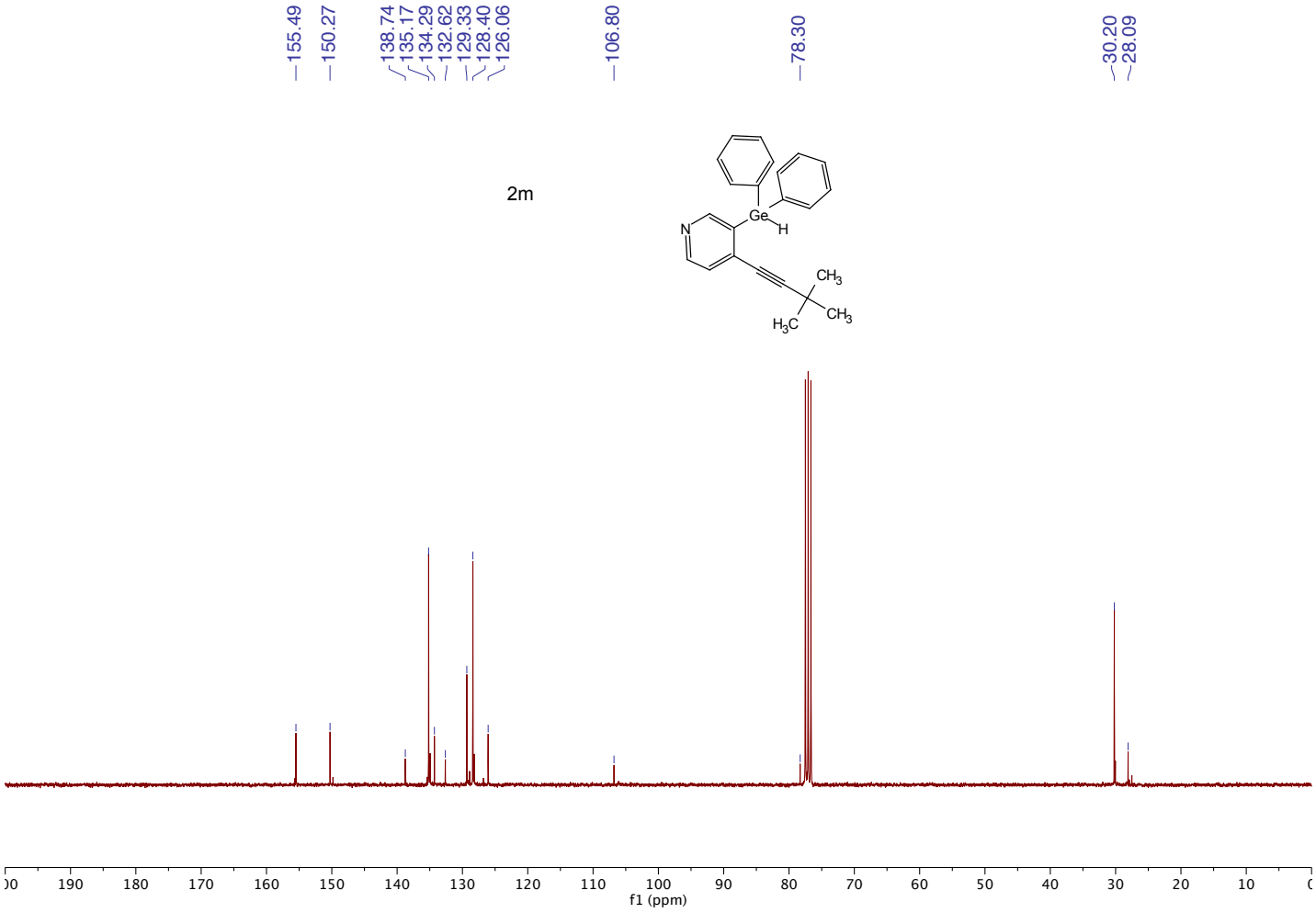

7.55
7.55
7.54
7.53
7.52
7.45
7.40
7.40
7.39
7.38
7.07
7.06
7.05
7.04
7.03
7.02
7.01
6.99
6.98
5.90
2.15
2.13
2.10
1.42
1.39
1.37
1.34
1.32
1.29
0.89
0.86
0.84
2k
F
Ge
H
CH3
4.00
1.05
6.00
2.00
0.82
2.04
2.03
3.04
f1 (ppm)


163.55
160.22
141.76
141.70
135.27
135.02
133.87
133.77
129.29
128.45
126.50
126.45
122.44
122.17
116.58
116.29
93.59
80.75
21.88
21.38
13.69
2k
F
Ge
H
CH3
f1 (ppm)

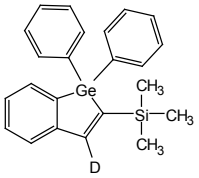

7.64
7.61
7.61
7.55
7.55
7.54
7.54
7.53
7.52
7.42
7.41
7.40
7.39
7.39
7.38
5.93
0.04
2l
F
F
F
Ge
H
CH3
Si
CH3
H3C
3.02
4.03
6.03
0.92
8.91
f1 (ppm)

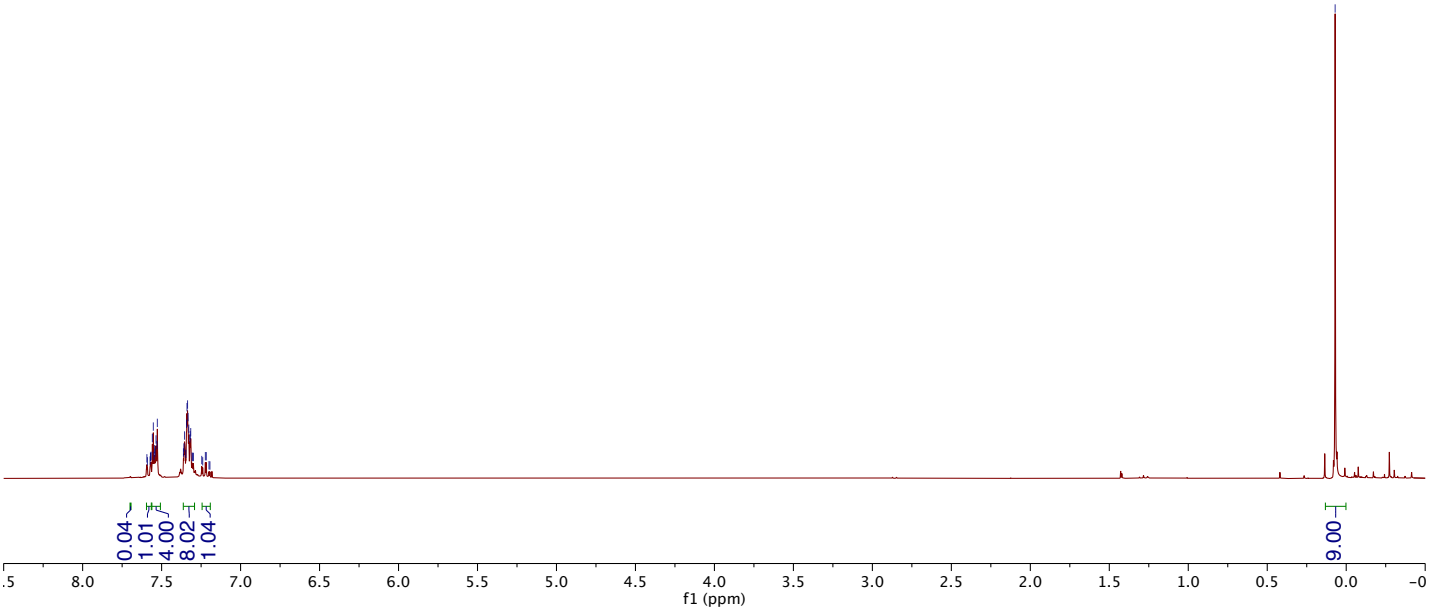

140.60
135.32
134.45
133.32
132.63
132.30
132.26
130.00
129.57
129.48
128.53
126.16
126.11
125.91
122.30
104.26
100.88
-0.47
2l
F
F
F
Ge
H
CH3
Si
CH3
H3C
f1 (ppm)


8.55
8.54
8.47
7.54
7.54
7.52
7.51
7.39
7.39
7.37
7.31
7.30
5.87
1.04
2m
Ge
H
N
CH3
CH3
H3C
1.02
0.98
4.00
6.02
1.05
0.89
9.02
f1 (ppm)

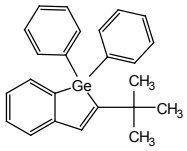

155.49
150.27
138.74
135.17
134.29
132.62
129.33
128.40
126.06
106.80
78.30
30.20
28.09
2m
Ge
H
N
CH3
CH3
H3C
f1 (ppm)

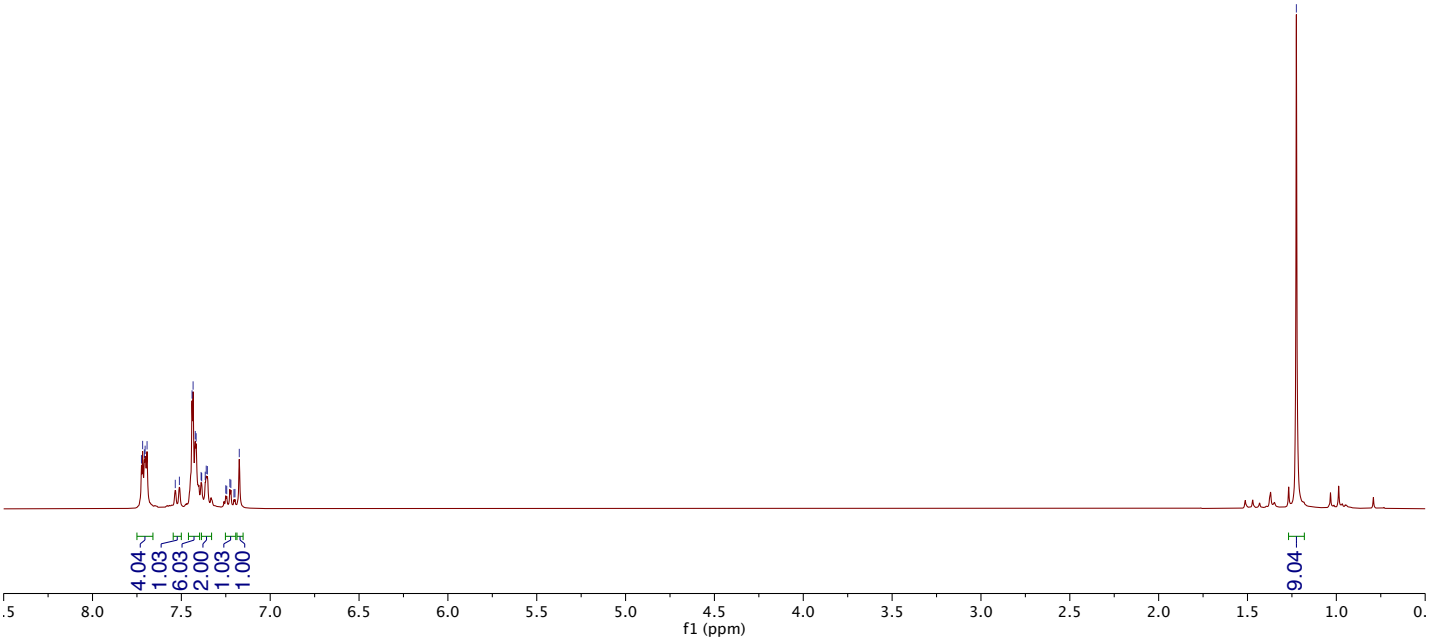
3a-D, 96%D incorporation





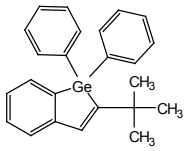
3b

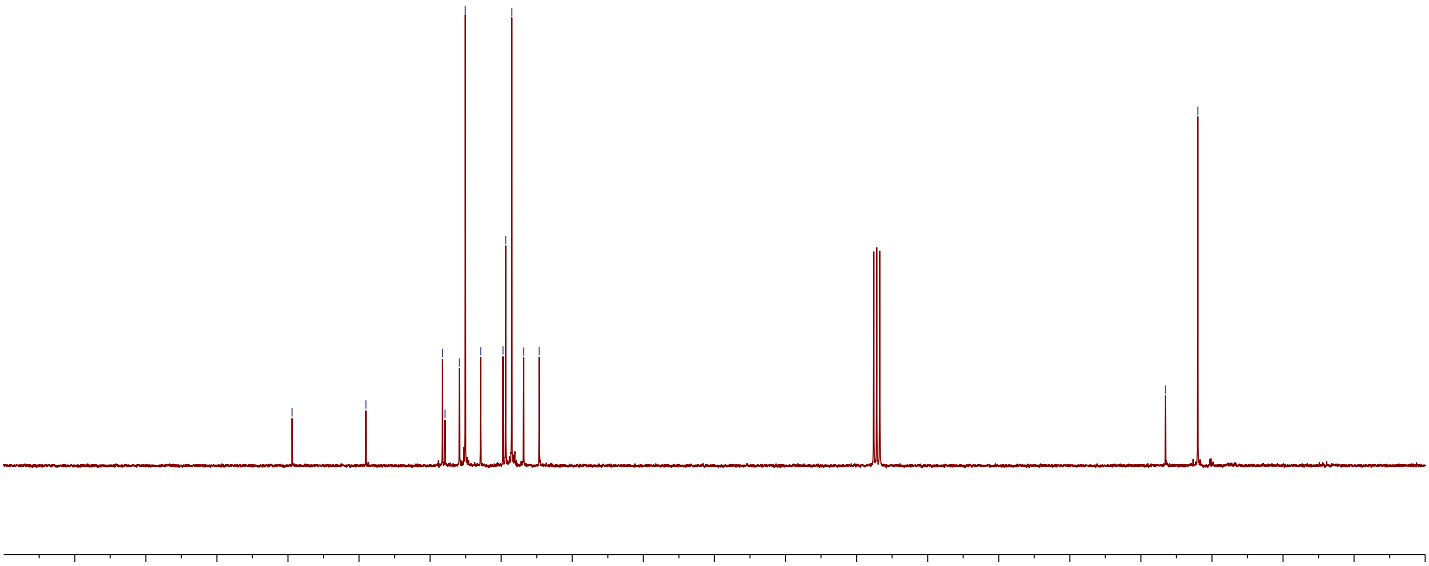




159.42
149.04
138.27
137.90
135.88
135.06
132.89
129.74
129.36
128.51
126.85
124.65
36.54
31.99

3b





190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

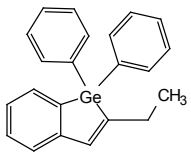
7.57
7.55
7.55
7.38
7.36
7.33
7.31
7.30
7.27
7.21
7.19
7.16
7.06

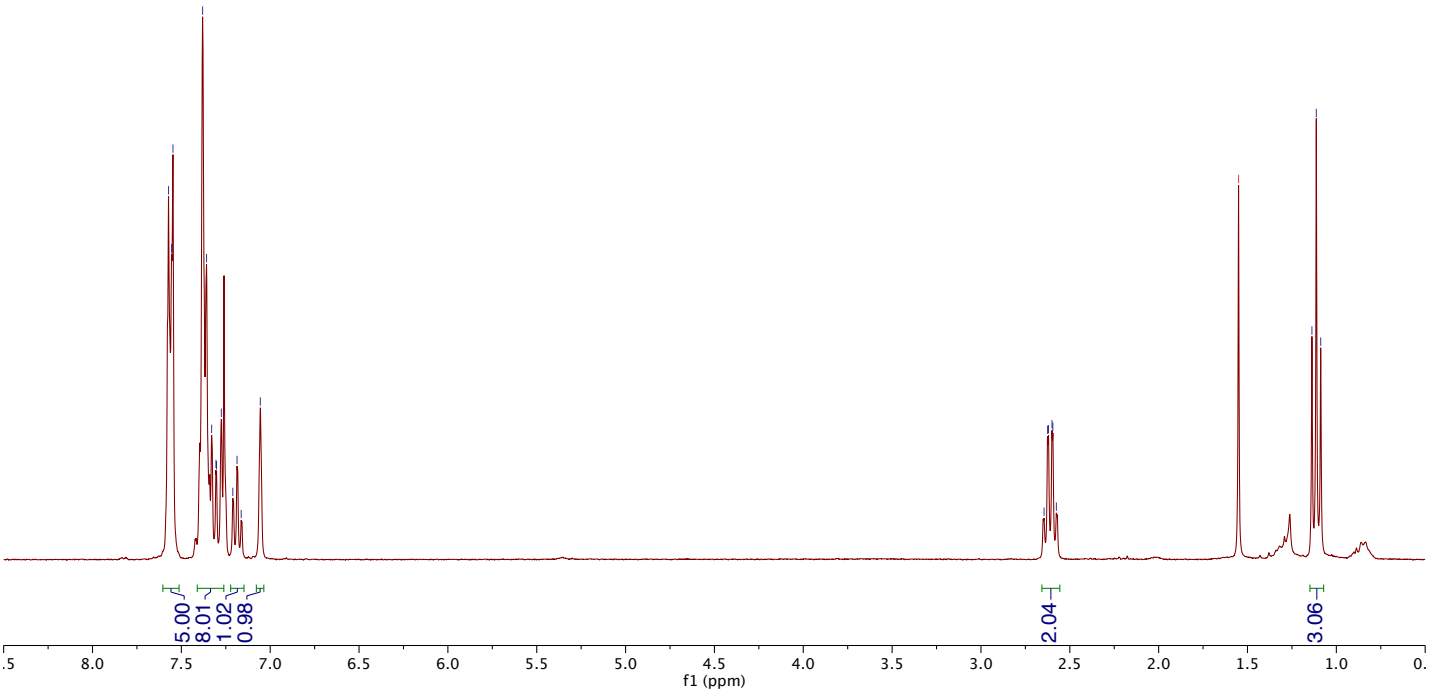
2.64
2.63
2.62
2.60
2.60
2.58

1.55 H2O

1.14
1.11
1.09

3c





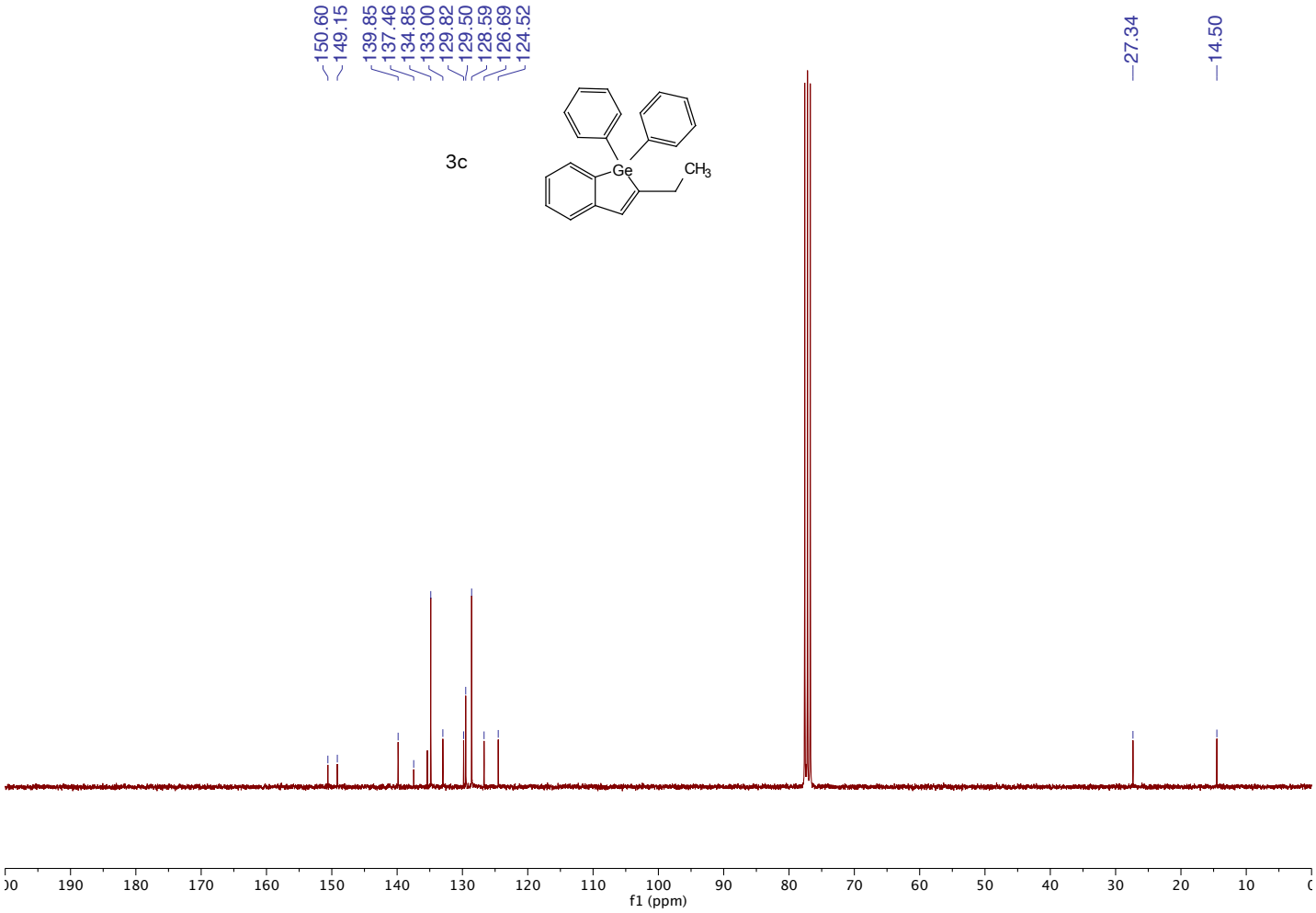
5.00
8.01
1.02
0.98

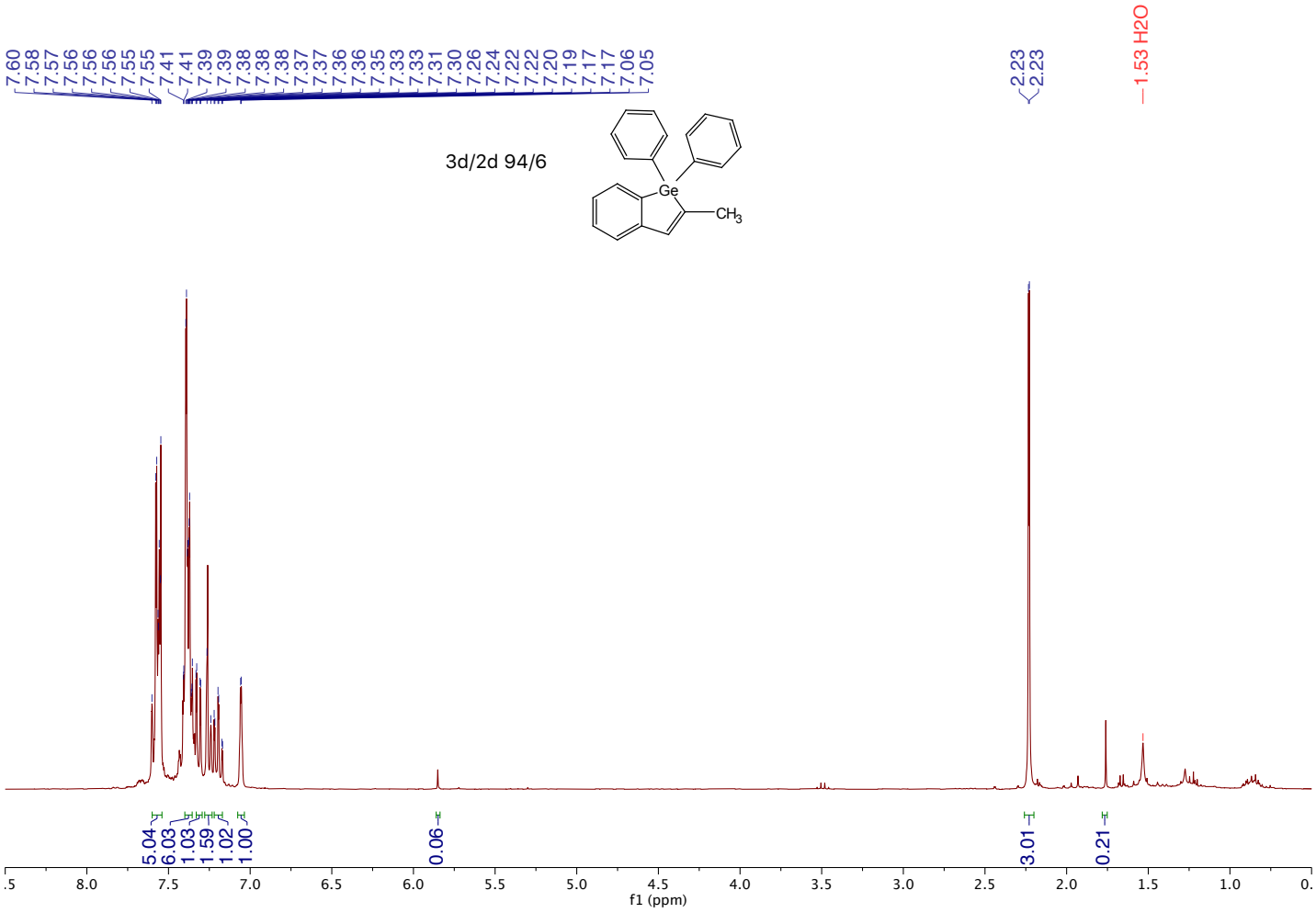
2.04

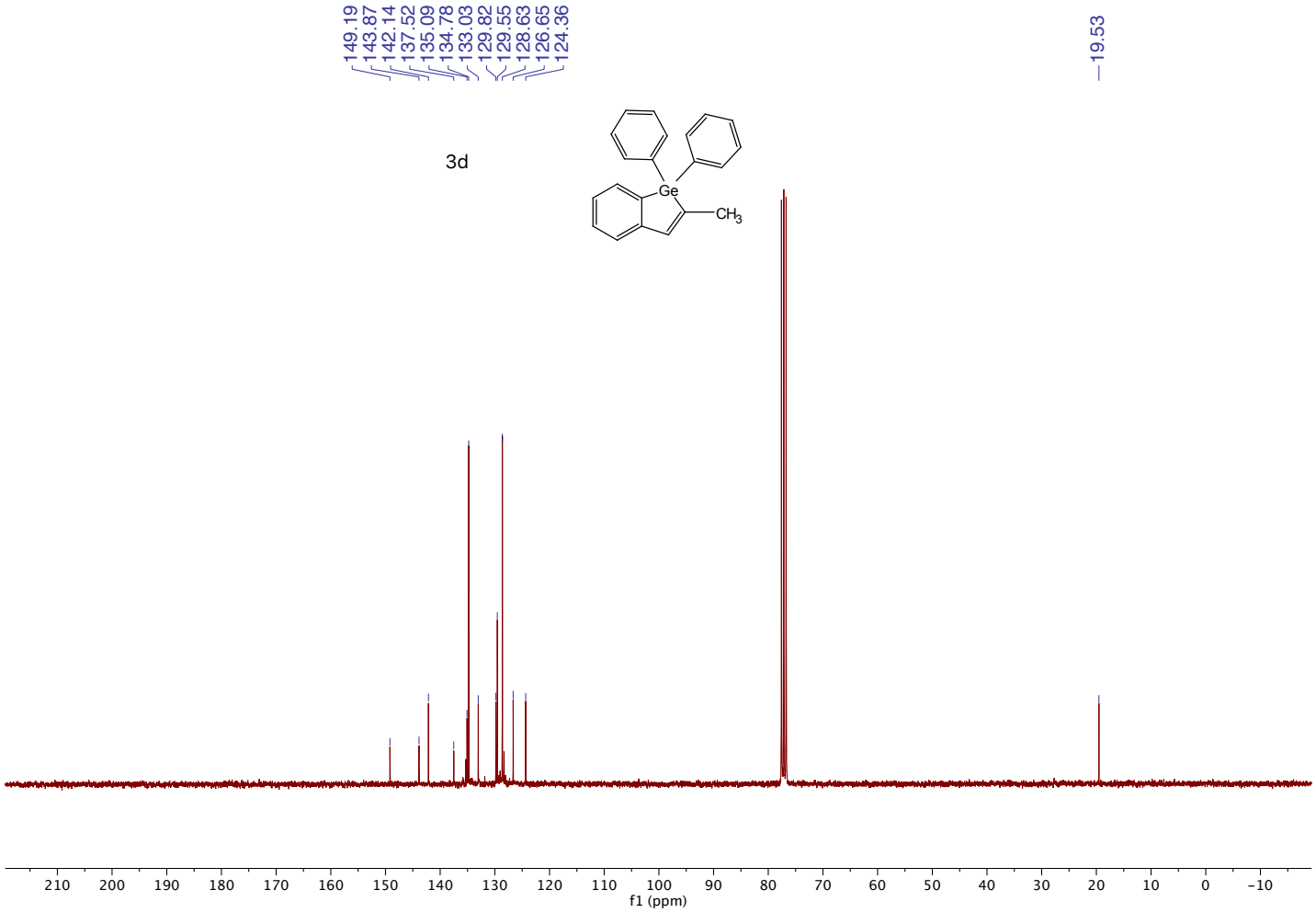
3.06

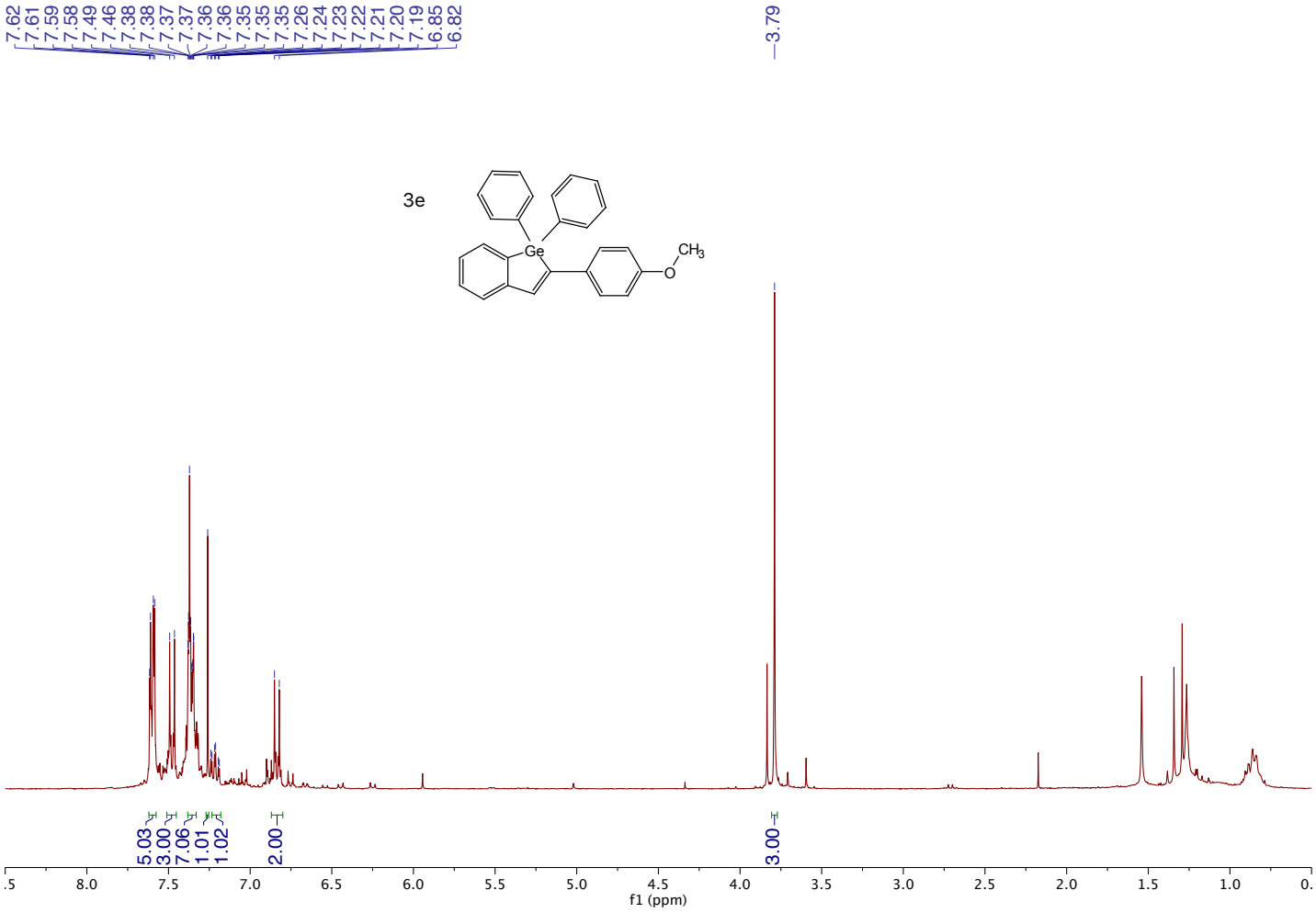
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.

f1 (ppm)


150.60
149.15
139.85
137.46
134.85
133.00
129.82
129.50
128.59
126.69
124.52
27.34
14.50
3c
Ge
CH3
f1 (ppm)


7.60
7.58
7.57
7.56
7.56
7.56
7.55
7.55
7.41
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.33
7.33
7.31
7.30
7.26
7.24
7.22
7.22
7.20
7.19
7.17
7.17
7.06
7.05
2.23
2.23
1.53 H2O
3d/2d 94/6
Ge
CH3
5.04
6.03
1.03
1.59
1.02
1.00
0.06
3.01
0.21
f1 (ppm)


149.19
143.87
142.14
137.52
135.09
134.78
133.03
129.82
129.55
128.63
126.65
124.36
19.53
3d
Ge
CH3
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)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7.37
7.36
7.36
7.35
7.35
7.35
7.26
7.24
7.23
7.22
7.21
7.20
7.19
6.85
6.82
3.79
3e
Ge
CH3
O
5.03
3.00
7.06
1.01
1.02
2.00
3.00
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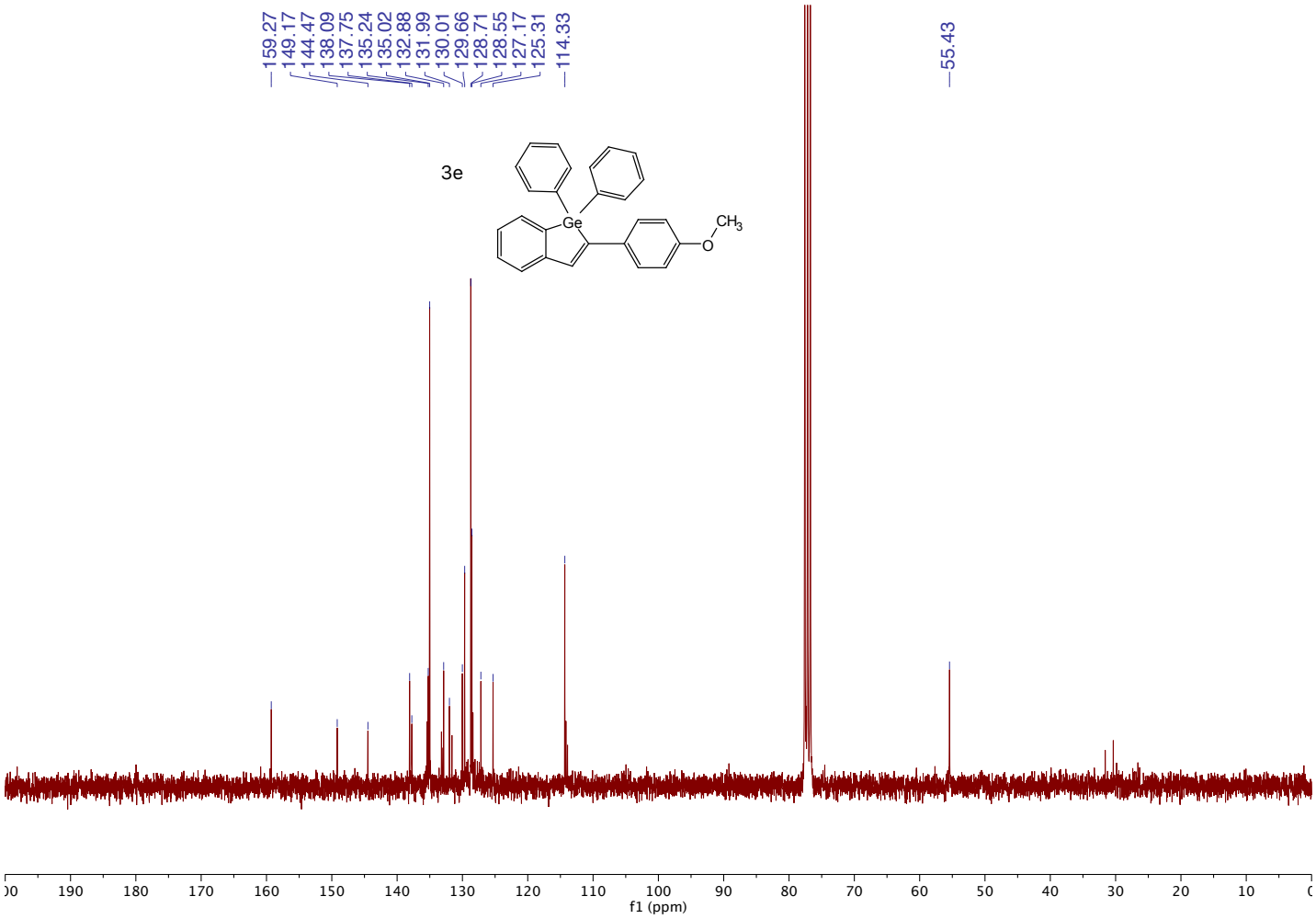
f1 (ppm)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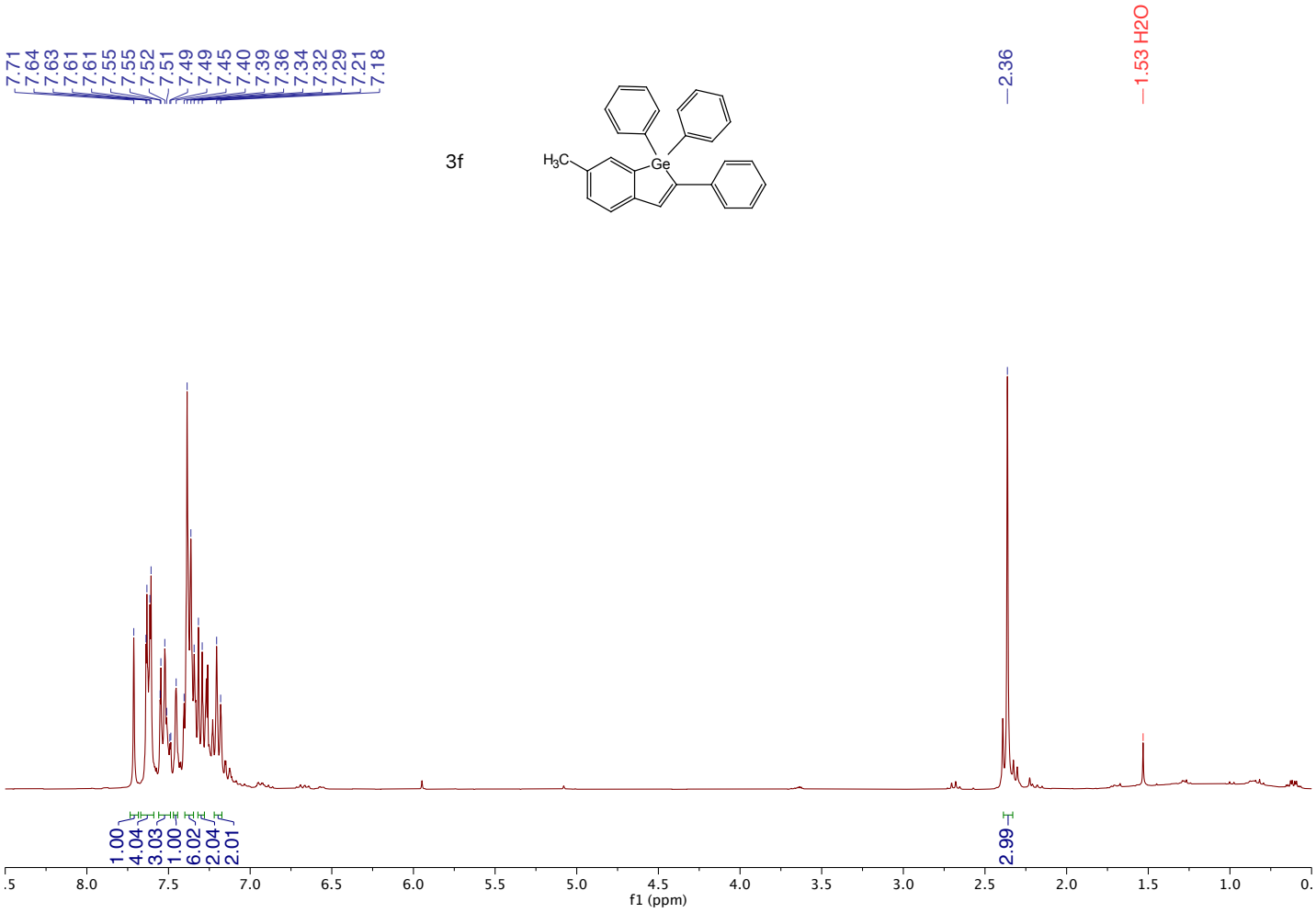
135.02
132.88
131.99
130.01
129.66
128.71
128.55
127.17
125.31
114.33
55.43
3e
Ge
CH3
O
f1 (ppm)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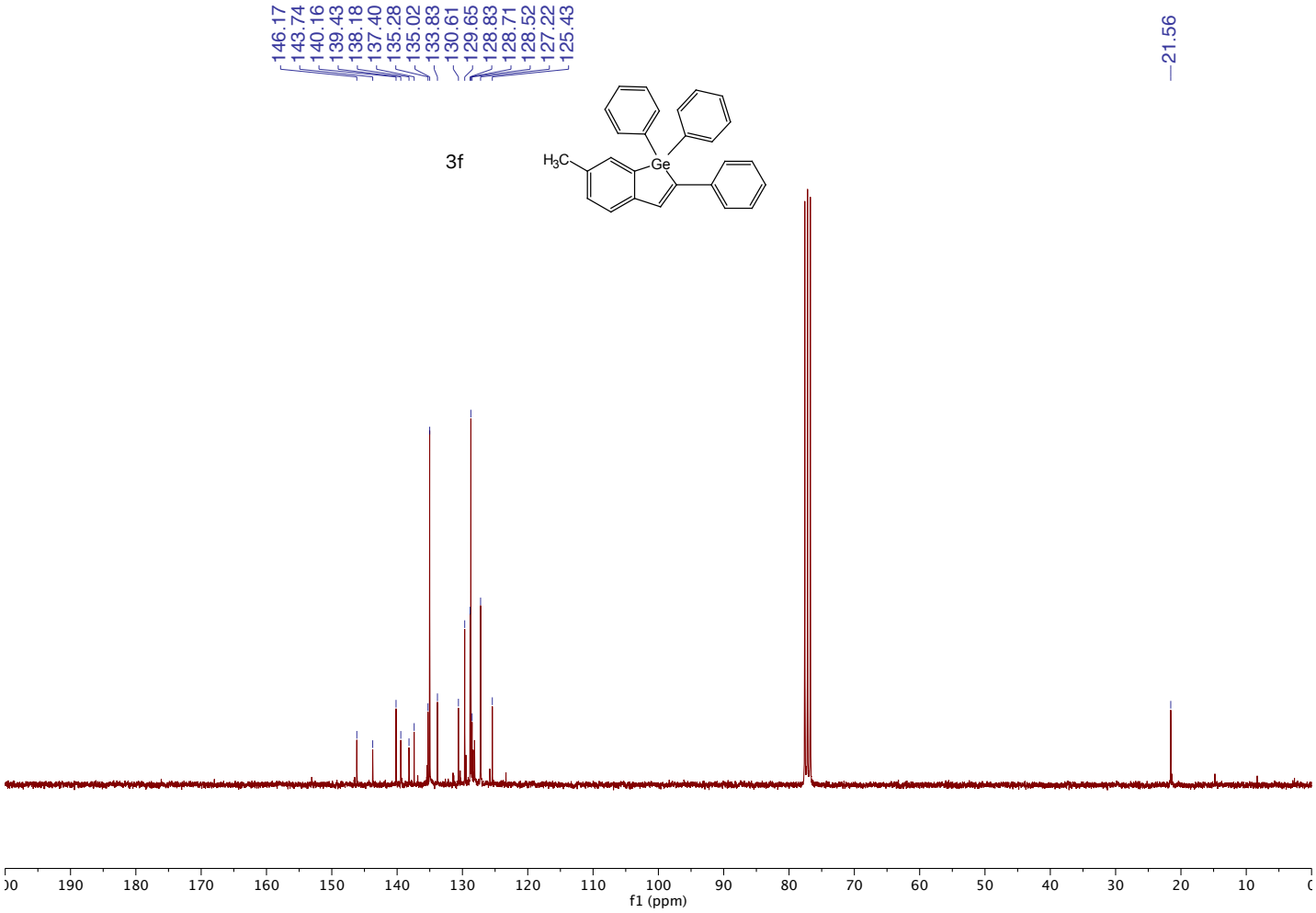
7.55
7.52
7.51
7.49
7.49
7.45
7.40
7.39
7.36
7.34
7.32
7.29
7.21
7.18
2.36
1.53 H2O
3f
H3C
Ge
1.00
4.04
3.03
1.00
6.02
2.04
2.01
2.99
f1 (ppm)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143.74
140.16
139.43
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137.40
135.28
135.02
133.83
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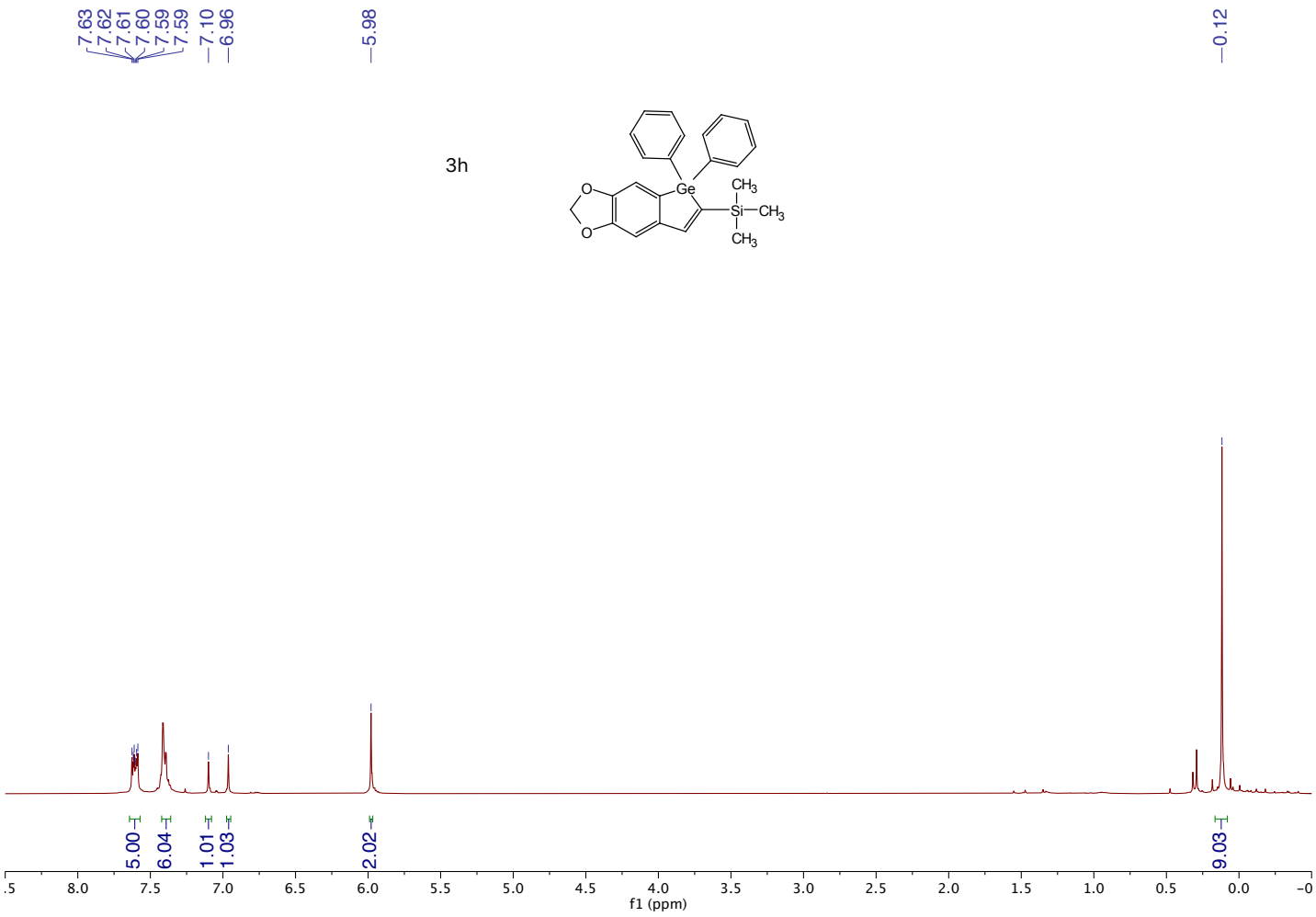
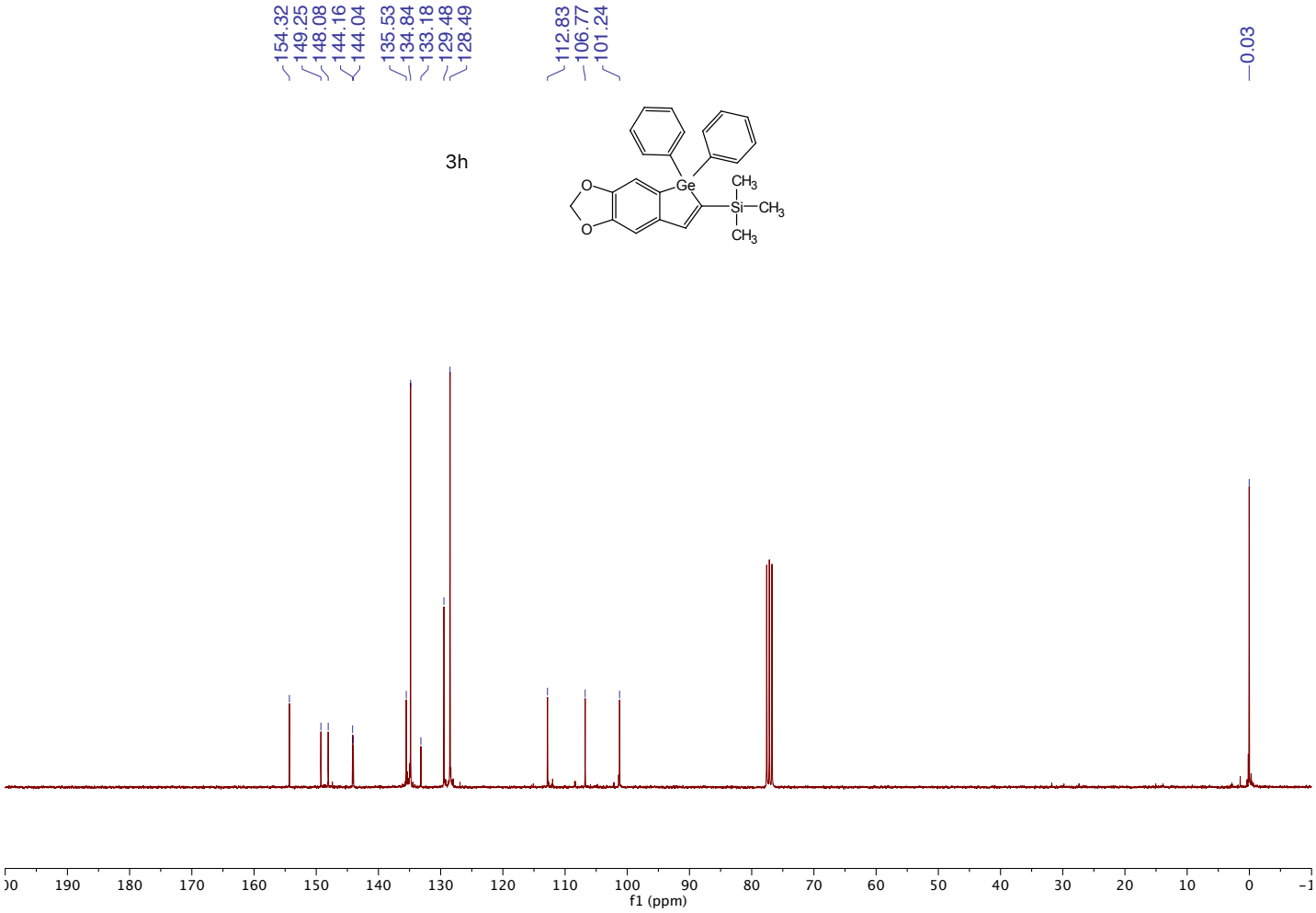
128.83
128.71
128.52
127.22
125.43
21.56
3f
H3C
Ge
f1 (ppm)


7.63
7.62
7.61
7.60
7.59
7.59
7.10
6.96
5.98
0.12
3h
O
O
Ge
CH3
Si
CH3
CH3
5.00
6.04
1.01
1.03
2.02
9.03
f1 (ppm)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144.04
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112.83
106.77
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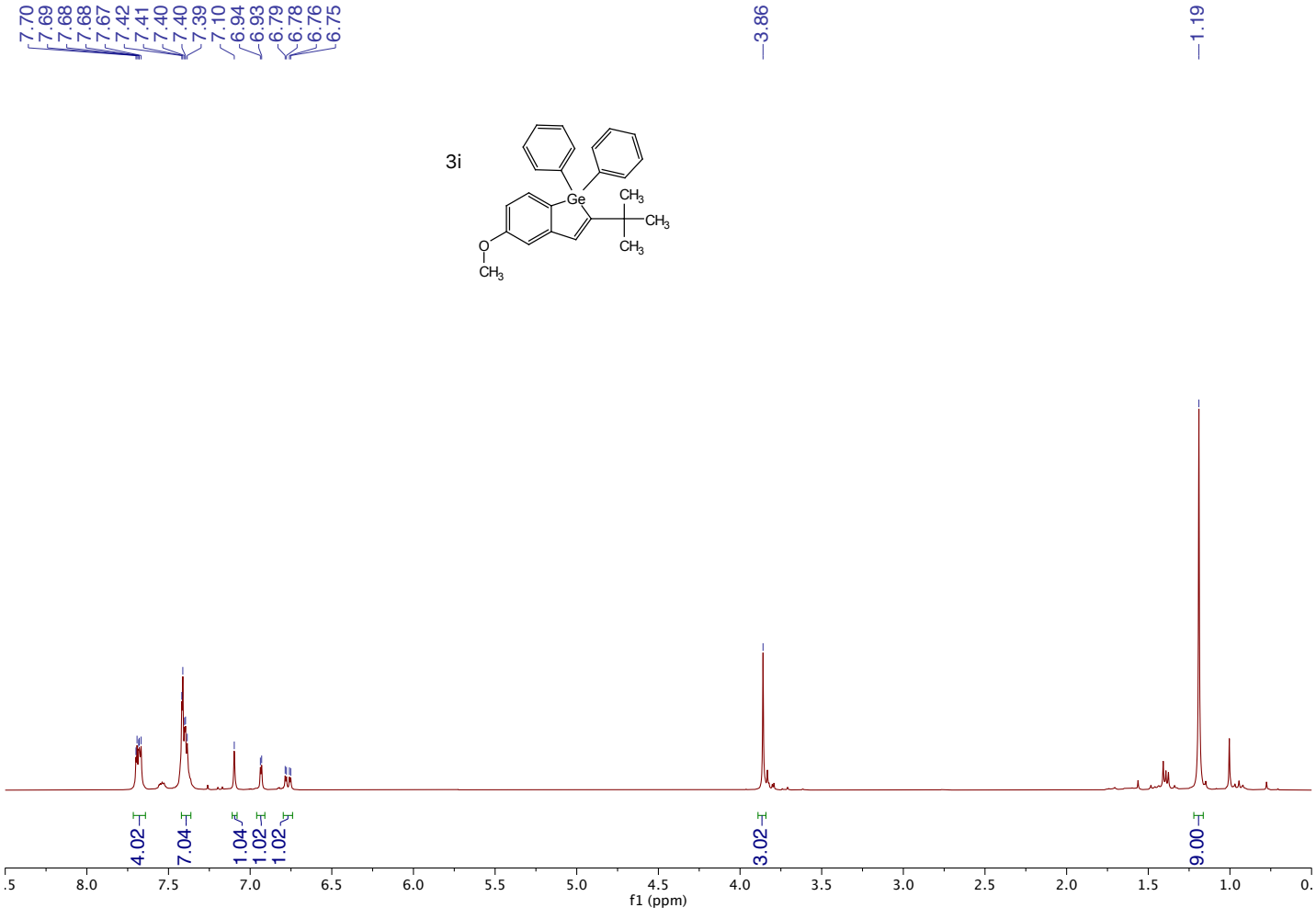
0.03
3h
Ge
Si
CH3
O
f1 (ppm)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7.40
7.40
7.39
7.10
6.94
6.93
6.79
6.78
6.76
6.75
3.86
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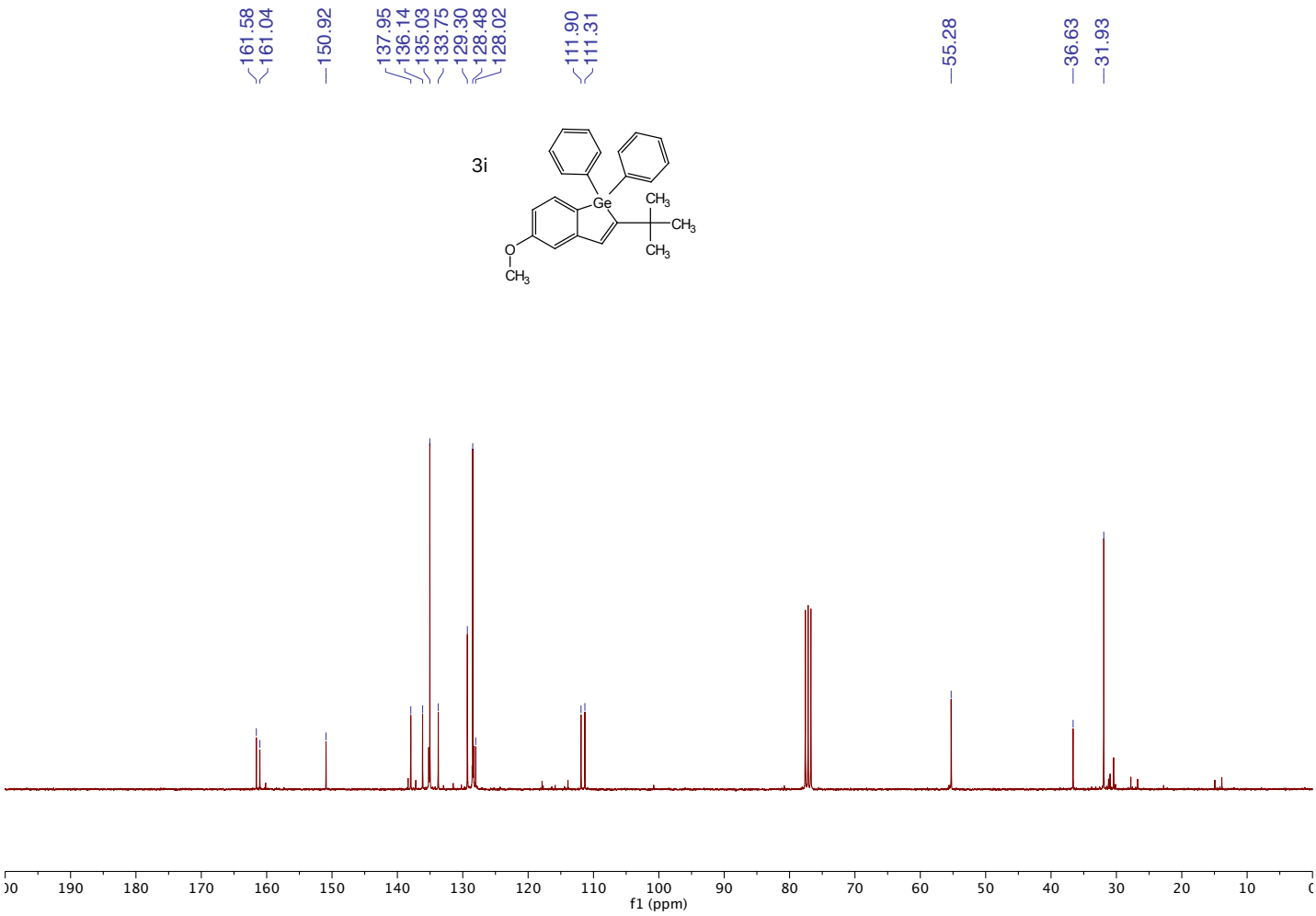
3i
Ge
CH3
O
4.02
7.04
1.04
1.02
1.02
3.02
9.00
f1 (ppm)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161.04
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135.03
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129.30
128.48
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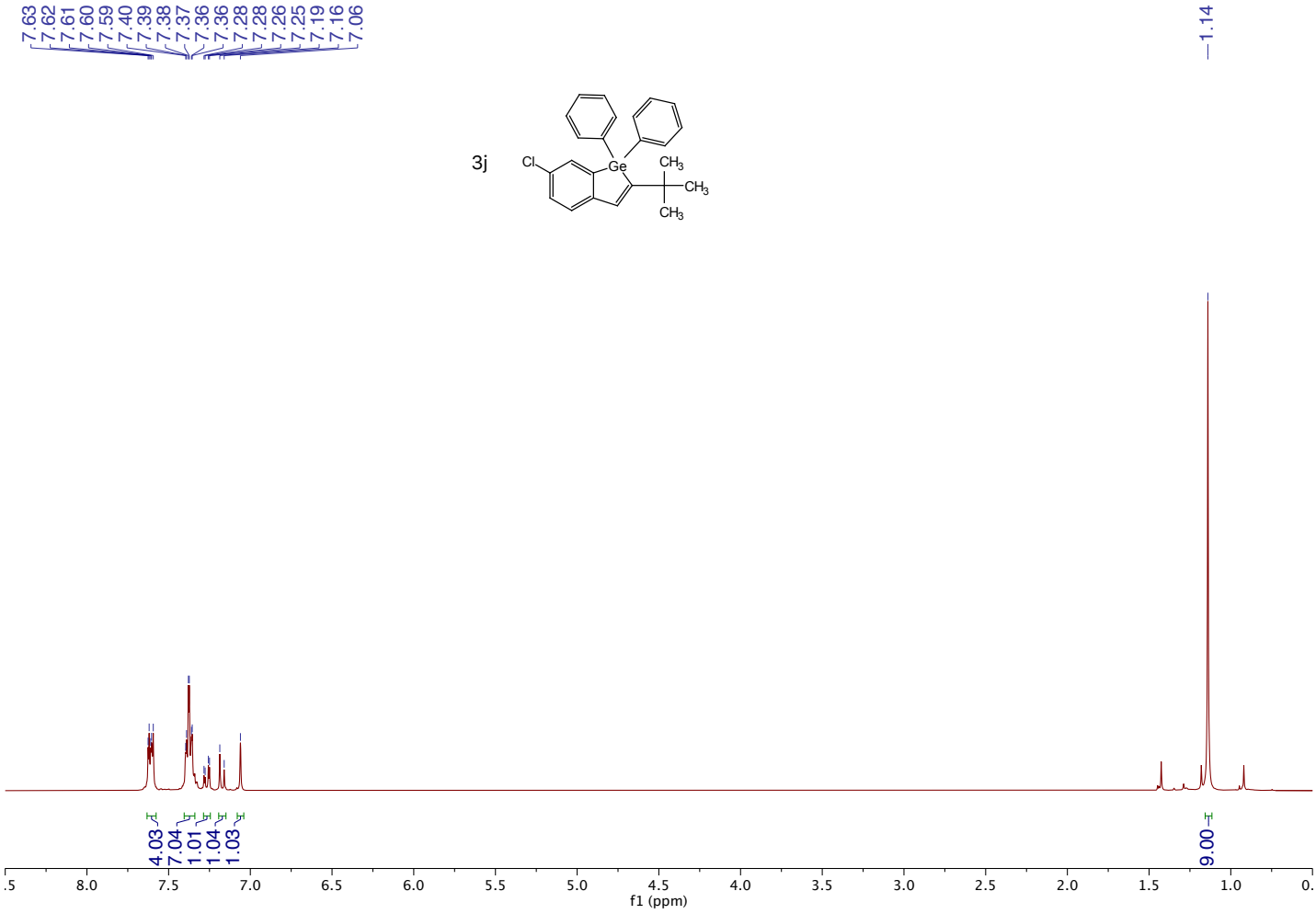
111.31
55.28
36.63
31.93
3i
Ge
CH3
CH3
CH3
O
CH3
f1 (ppm)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7.62
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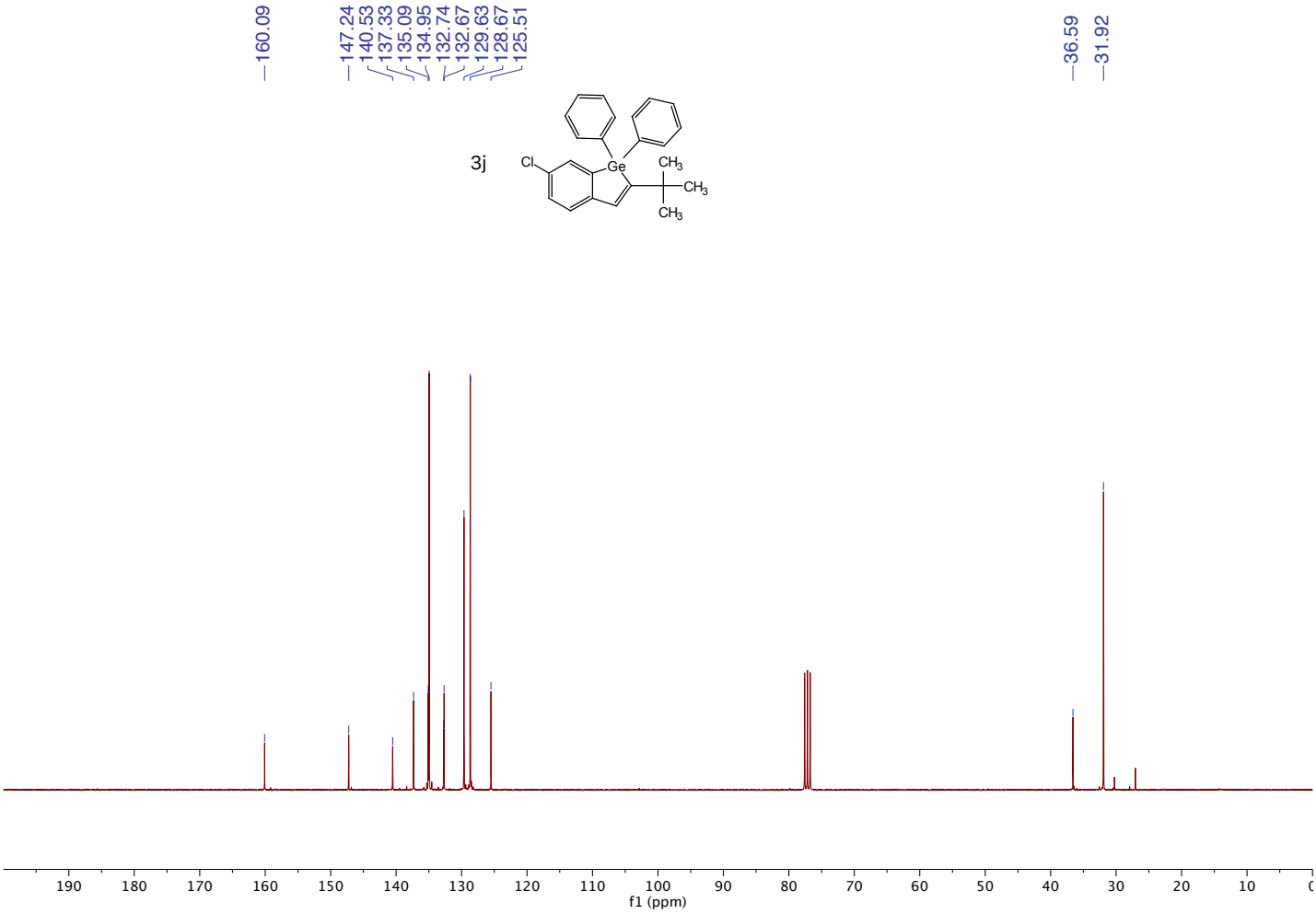
7.59
7.40
7.39
7.38
7.37
7.36
7.36
7.28
7.28
7.26
7.25
7.19
7.16
7.06
1.14
3j
Cl
Ge
CH3
CH3
CH3
4.03
7.04
1.01
1.04
1.03
9.00
f1 (ppm)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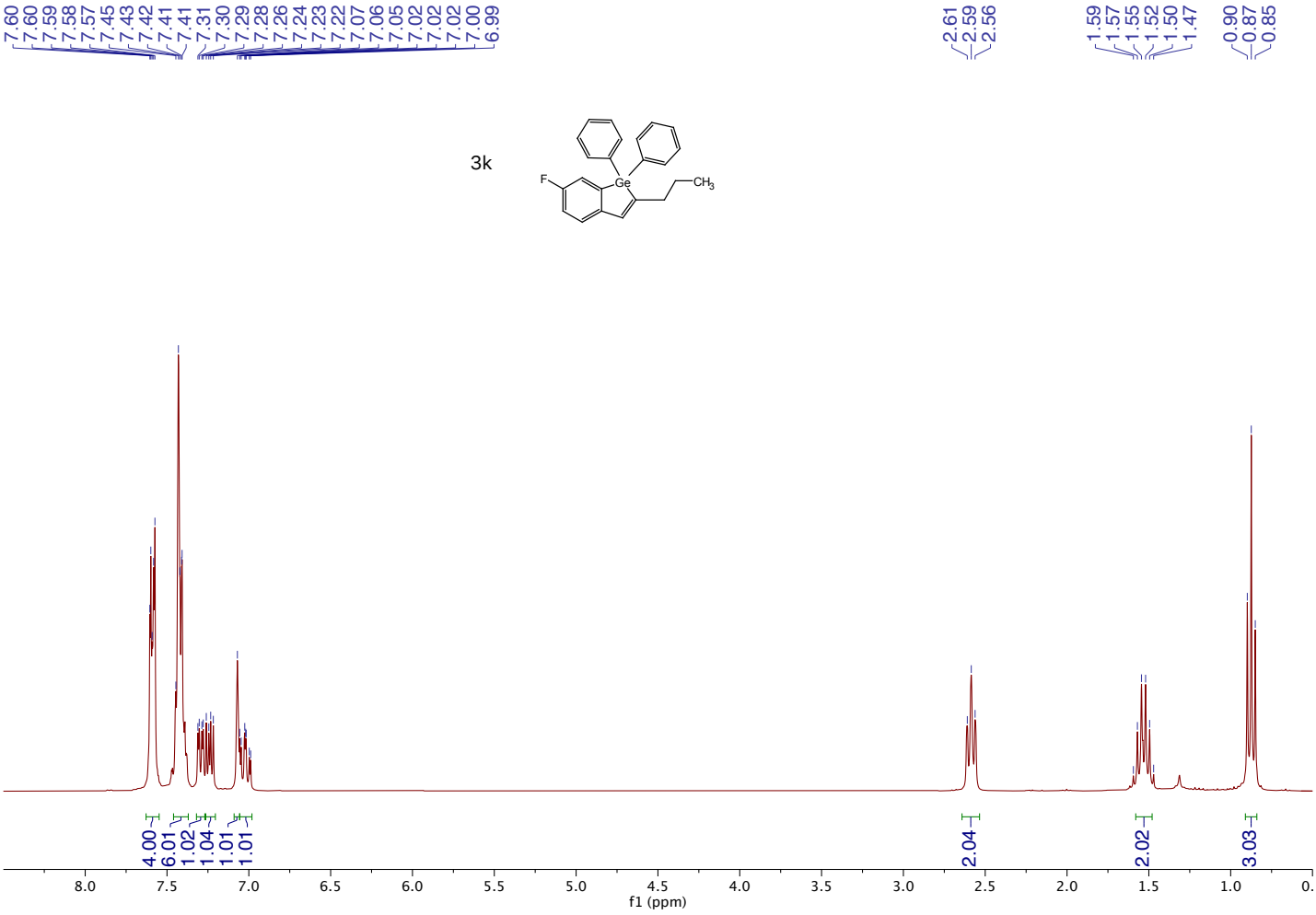
147.24
140.53
137.33
135.09
134.95
132.74
132.67
129.63
128.67
125.51
36.59
31.92
3j
Cl
Ge
CH3
CH3
CH3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.60
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7.29
7.28
7.26
7.24
7.23
7.22
7.07
7.06
7.05
7.02
7.02
7.02
7.00
6.99
2.61
2.59
2.56
1.59
1.57
1.55
1.52
1.50
1.47
0.90
0.87
0.85
3k
F
Ge
CH3
4.00
6.01
1.02
1.04
1.01
1.01
2.04
2.02
3.03
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
f1 (ppm)

163.90
160.61
148.54
148.49
144.89
144.85
140.48
140.42
139.93
134.76
129.70
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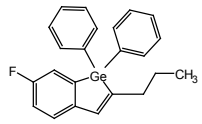
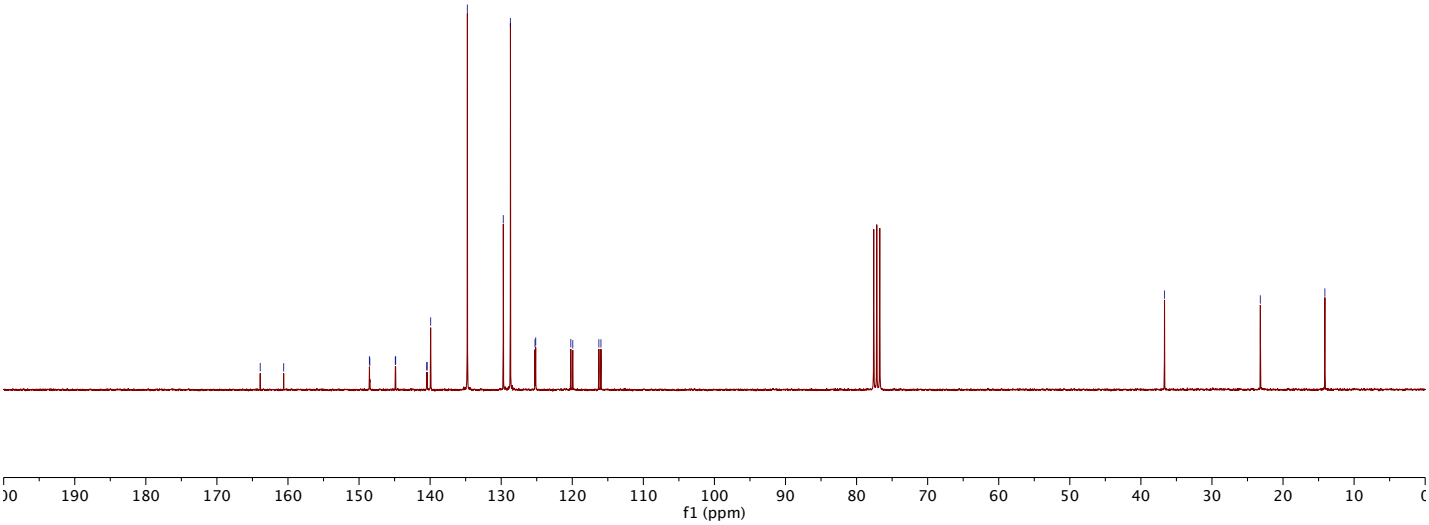
125.24
125.15
120.21
119.93
116.26
115.97
36.68
23.19
14.11

3k





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7.76
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7.63
7.57
7.56
7.56
7.55
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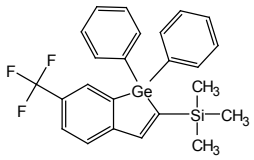
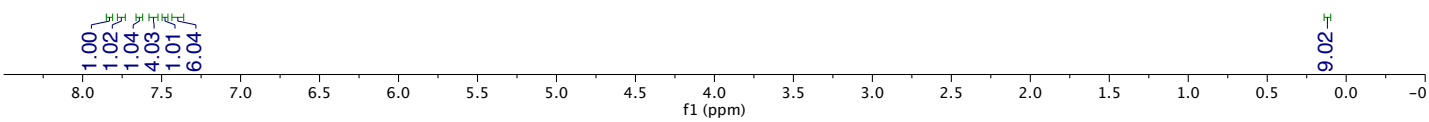
7.50
7.47
7.44
7.42
7.42
7.41
7.40
7.39
0.11

3l





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150.36
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134.40
129.84
129.74
129.32
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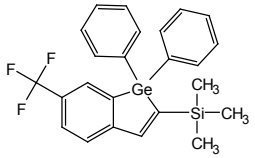
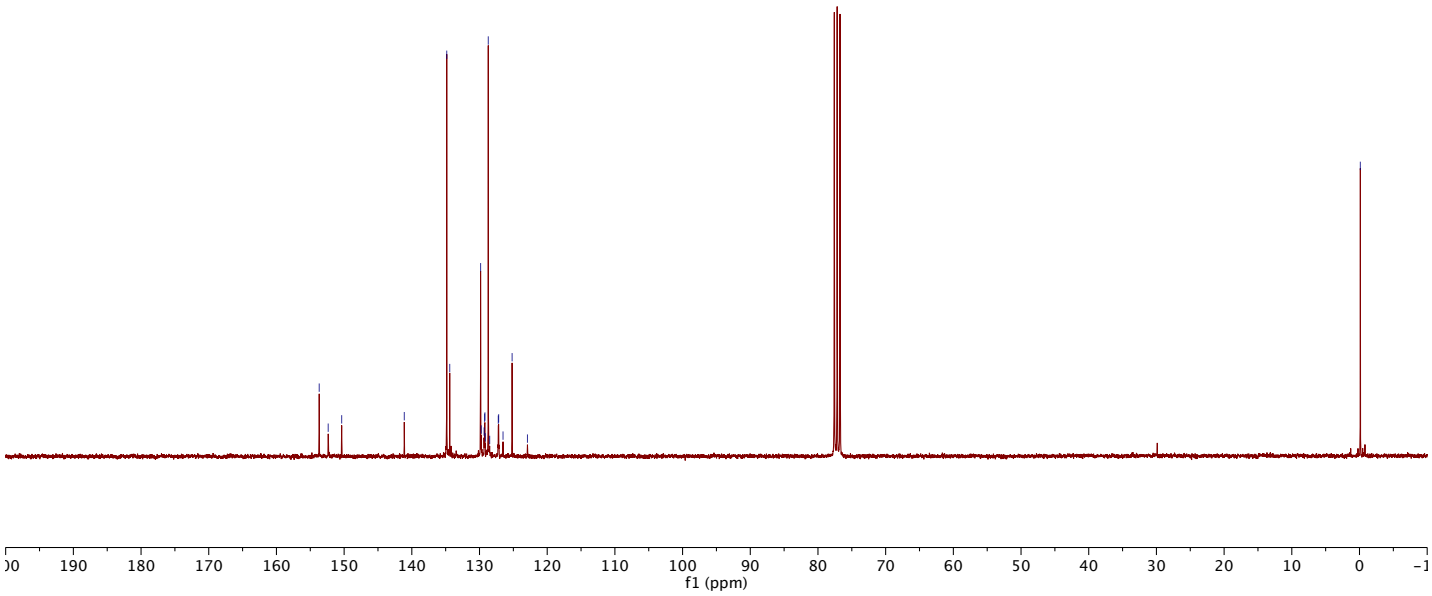
129.15
128.70
128.50
127.22
127.17
126.52
125.18
122.91
-0.12

3l





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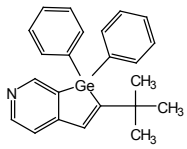
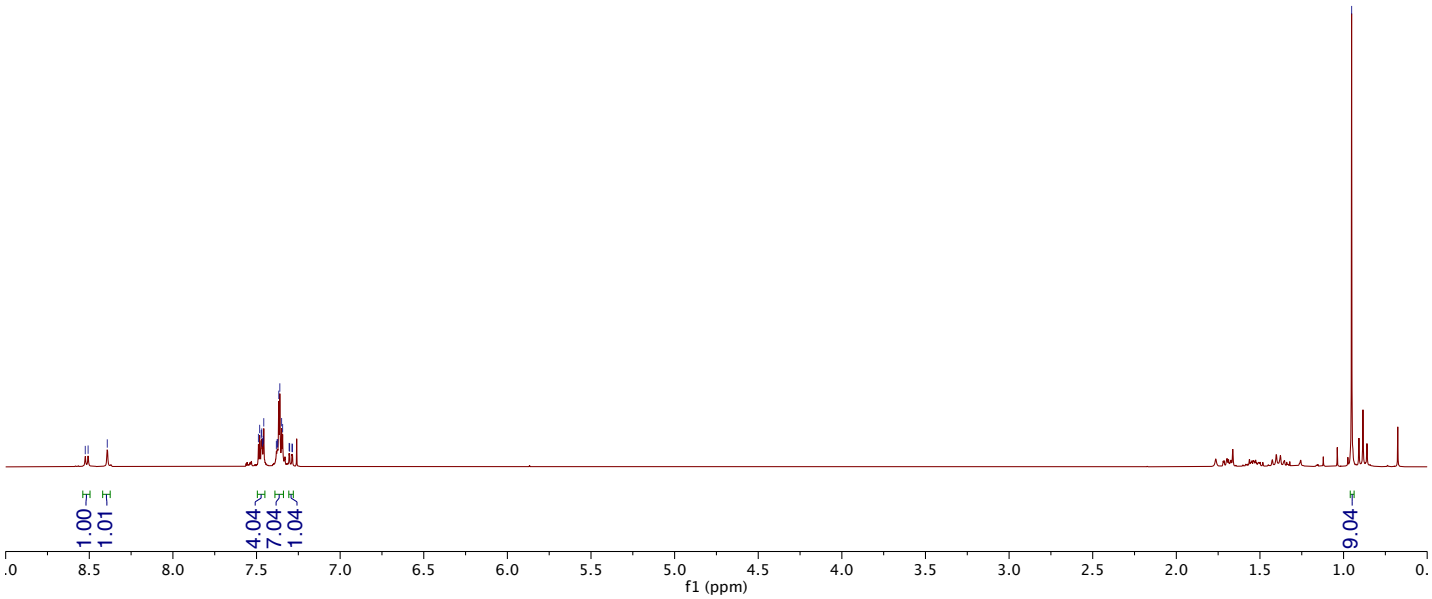
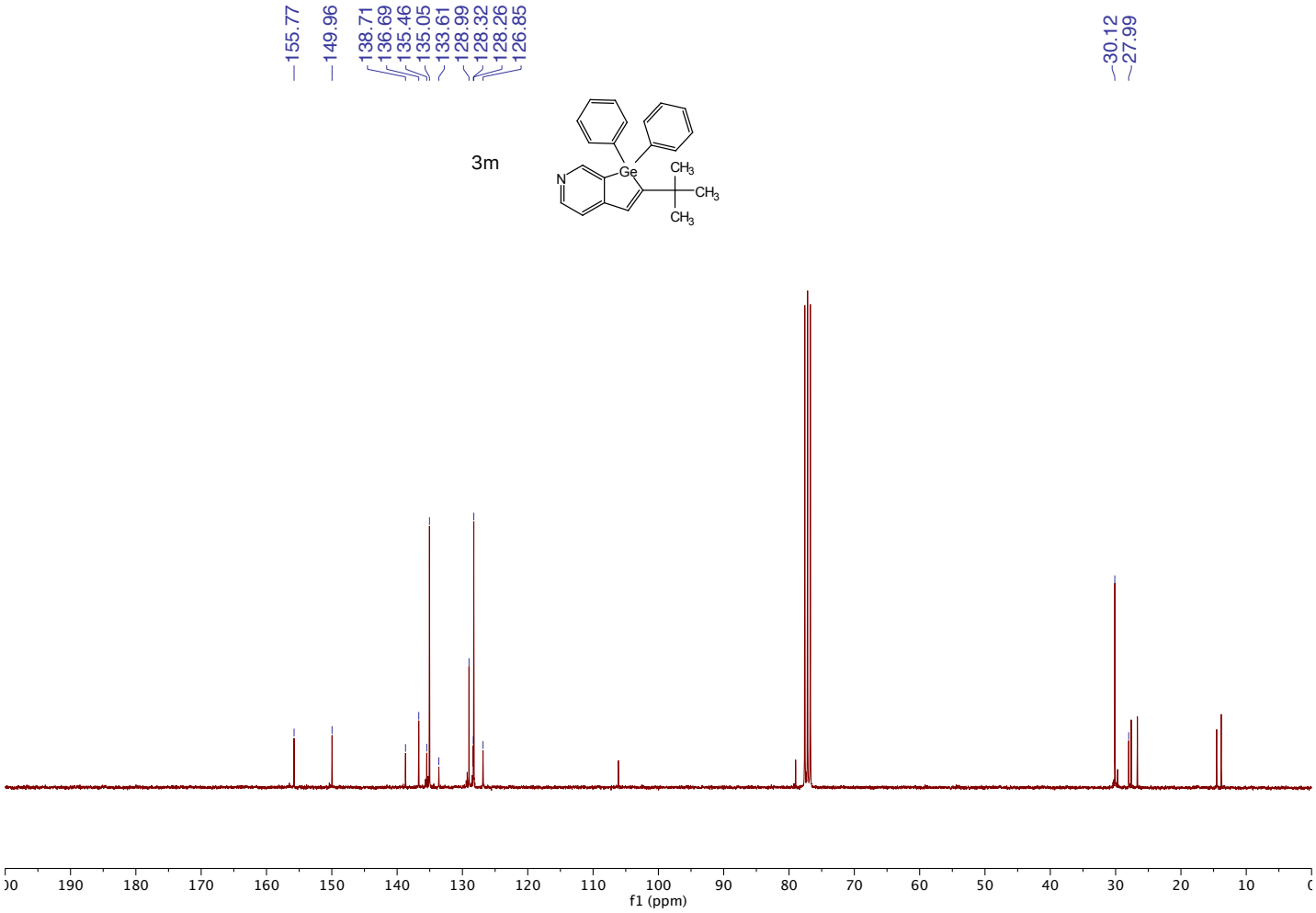
8.51
8.39
7.49
7.48
7.47
7.47
7.46
7.46
7.46
7.38
7.38
7.37
7.37
7.36
7.35
7.34
7.30
7.30
7.29
7.29
0.95

3m



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135.46
135.05
133.61
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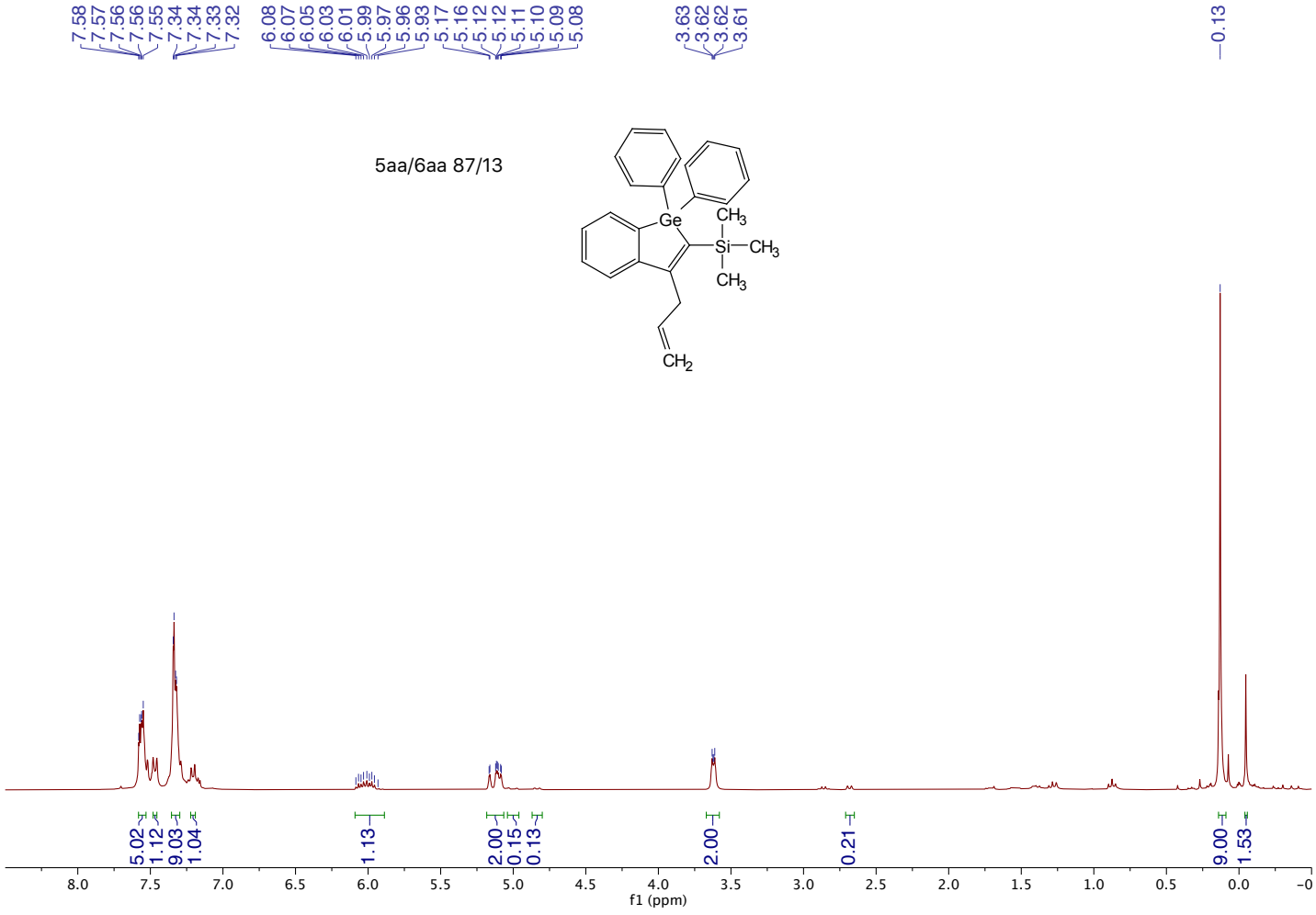
128.26
126.85
30.12
27.99
3m
Ge
N
CH3
CH3
CH3
f1 (ppm)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7.34
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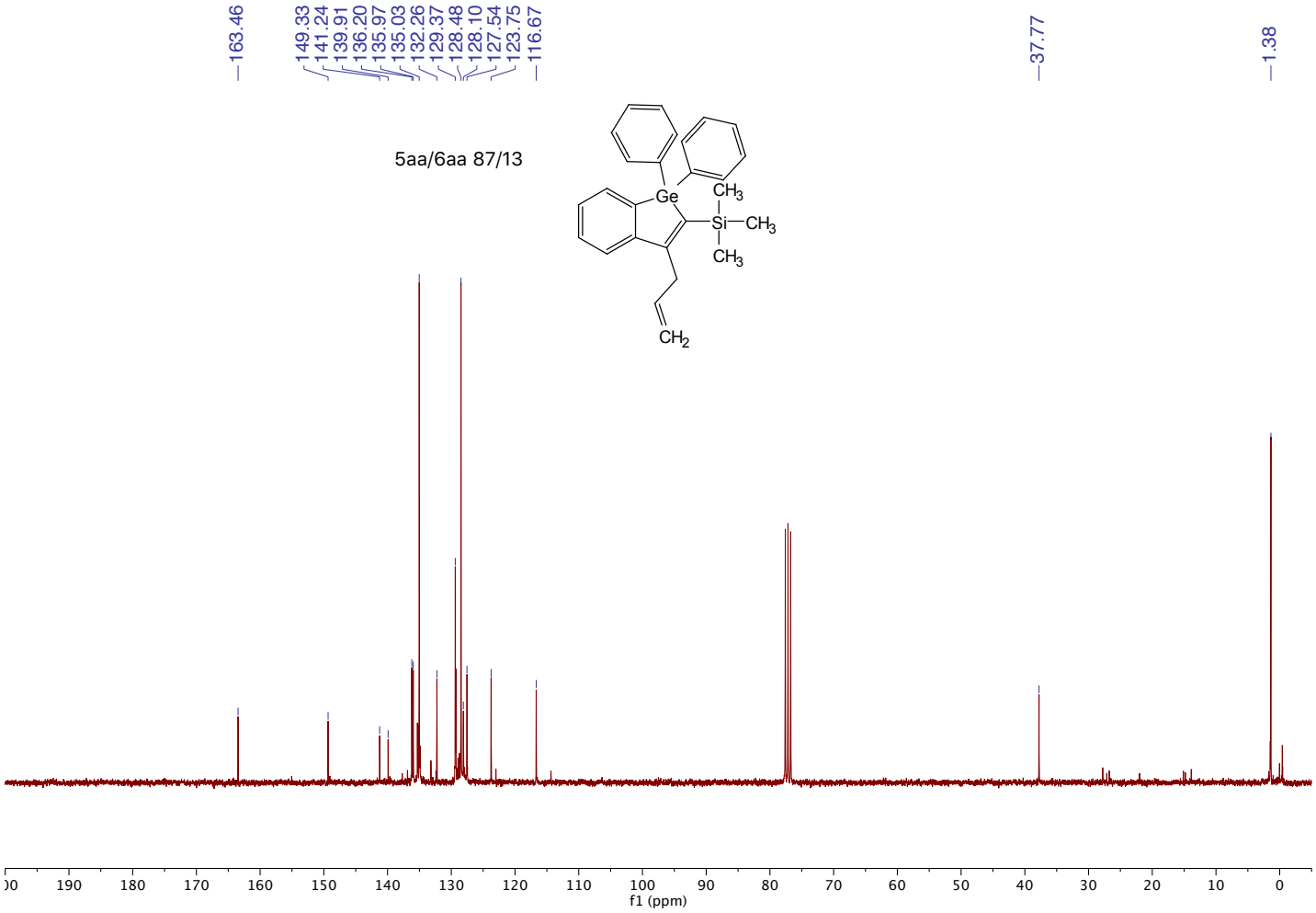
7.32
6.08
6.07
6.05
6.03
6.01
5.99
5.97
5.96
5.93
5.17
5.16
5.12
5.12
5.11
5.10
5.09
5.08
3.63
3.62
3.62
3.61
0.13
5aa/6aa 87/13
Ge
Si
CH3
CH3
CH3
CH3
CH2
5.02
1.12
9.03
1.04
1.13
2.00
0.15
0.13
2.00
0.21
9.00
1.53
f1 (ppm)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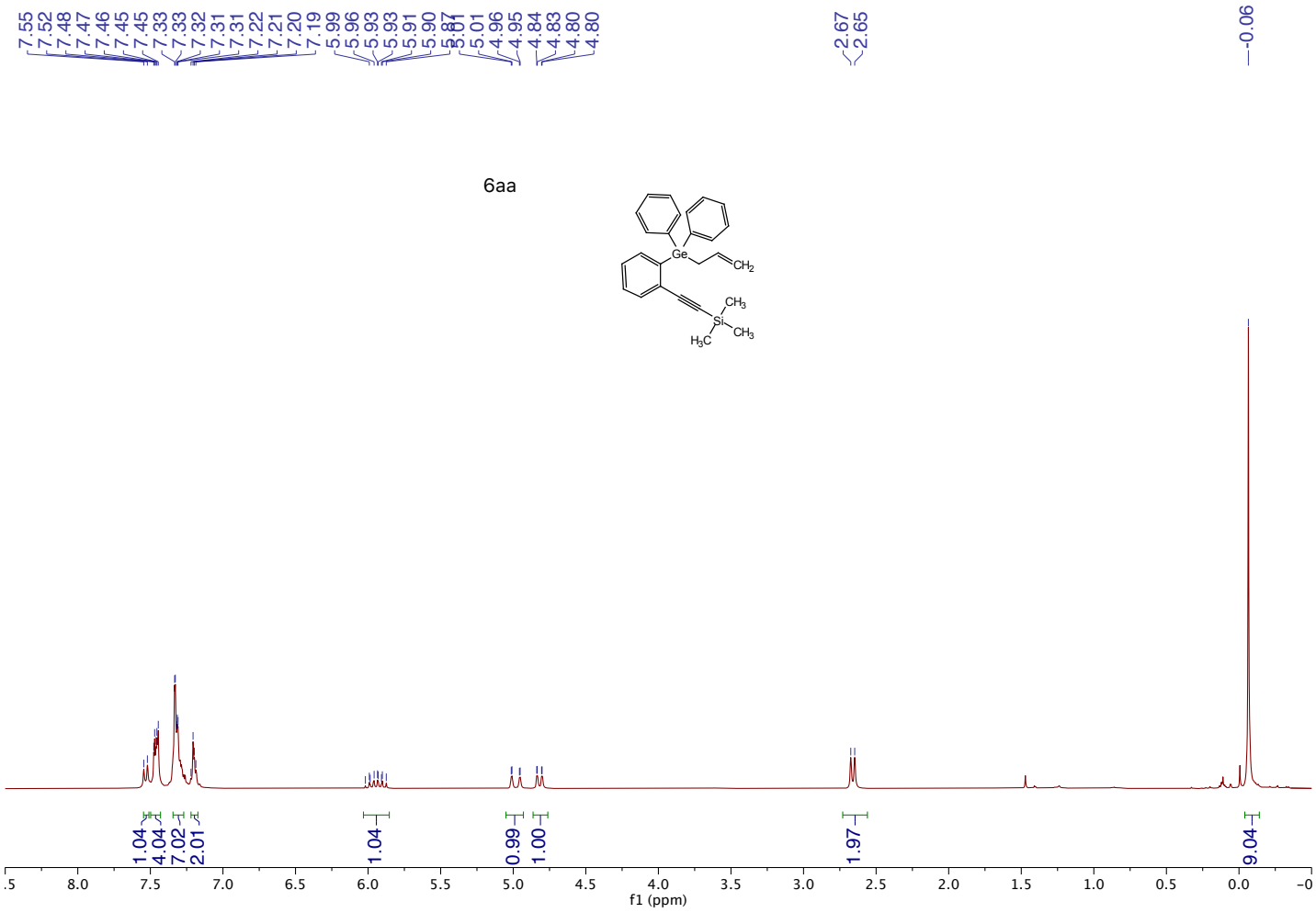
135.97
135.03
132.26
129.37
128.48
128.10
127.54
123.75
116.67
37.77
1.38
5aa/6aa 87/13
Ge
CH3
Si
CH3
CH3
CH2
f1 (ppm)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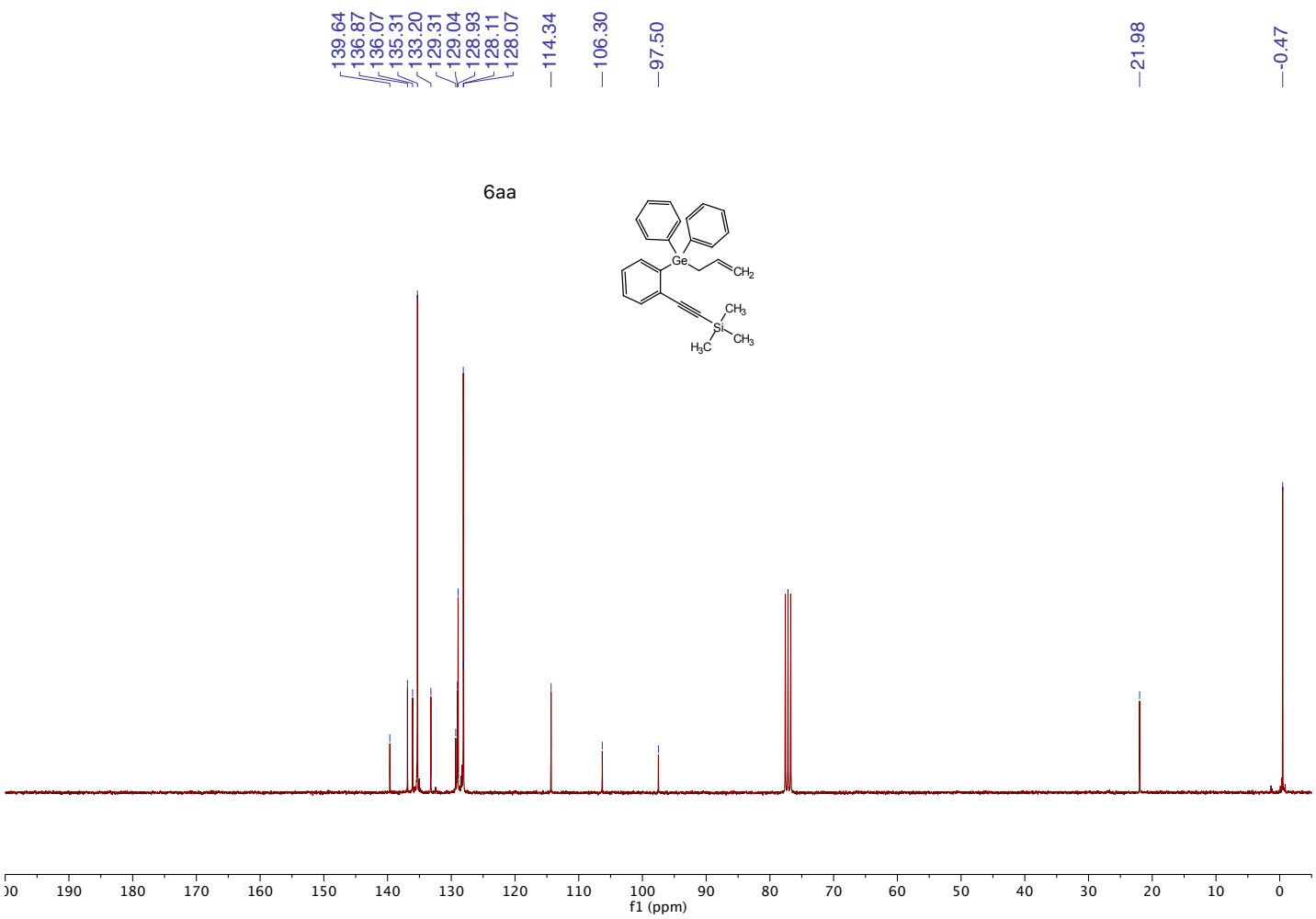
7.31
7.22
7.21
7.20
7.19
5.99
5.96
5.93
5.93
5.91
5.90
5.87
5.01
4.96
4.95
4.84
4.83
4.80
4.80
2.67
2.65
0.06
6aa
Ge
CH2
CH3
Si
CH3
H3C
1.04
4.04
7.02
2.01
1.04
0.99
1.00
1.97
9.04
f1 (ppm)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129.04
128.93
128.11
128.07
114.34
106.30
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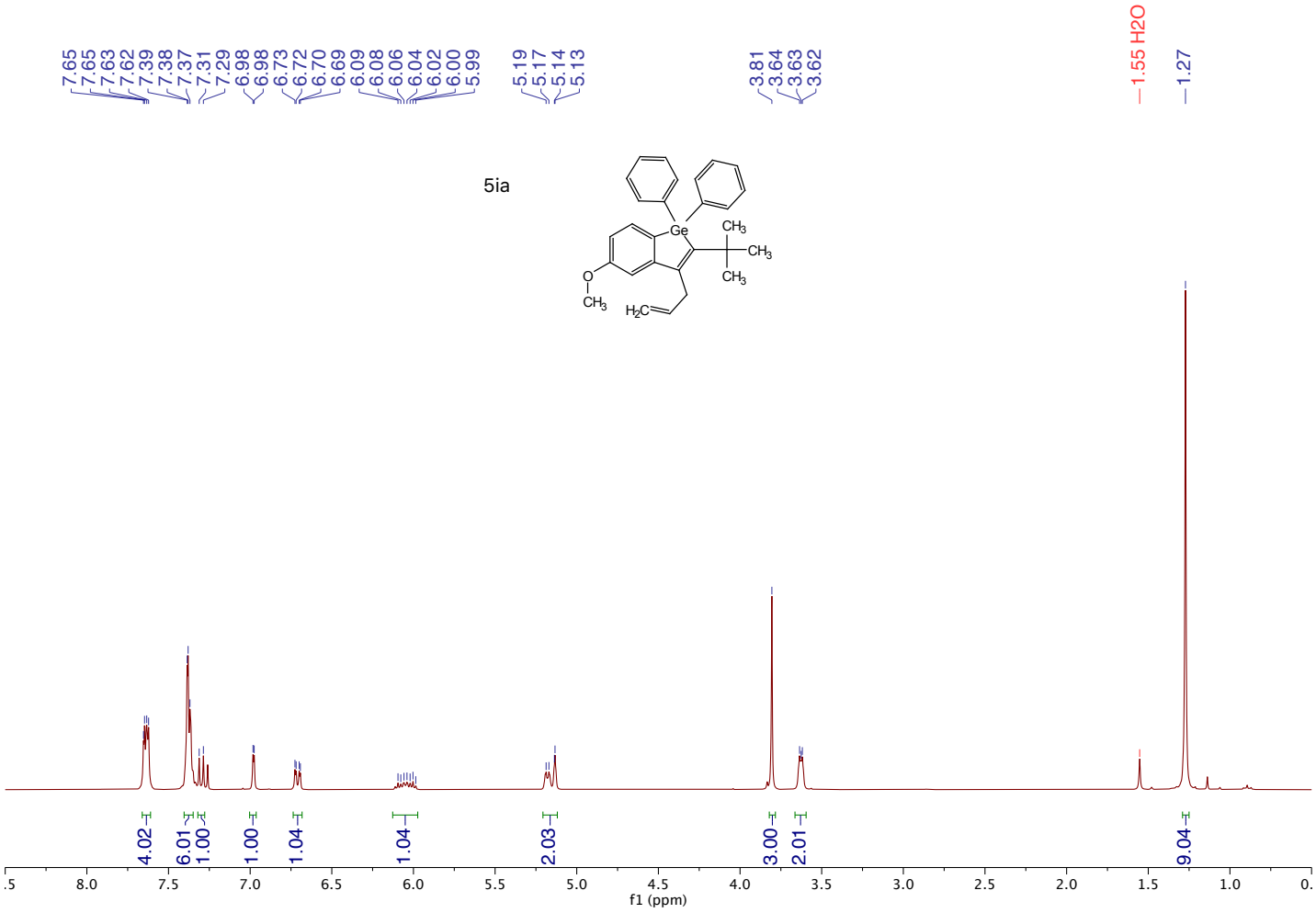
21.98
-0.47
6aa
Ge
CH2
CH3
Si
H3C
CH3
f1 (ppm)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7.65
7.63
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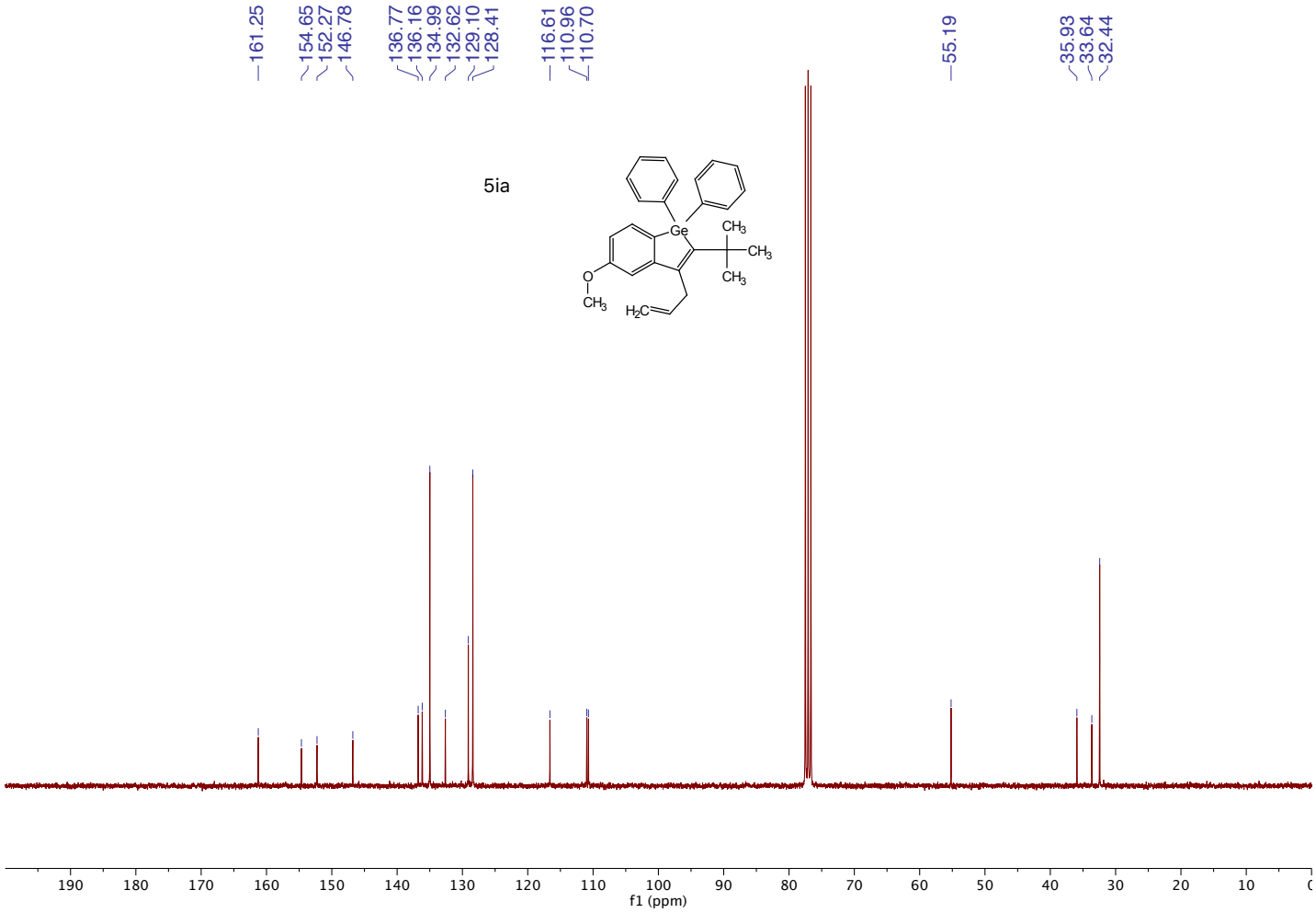
7.31
7.29
6.98
6.98
6.73
6.72
6.70
6.69
6.09
6.08
6.06
6.04
6.02
6.00
5.99
5.19
5.17
5.14
5.13
3.81
3.64
3.63
3.62
1.55 H2O
1.27
5ia
Ge
CH3
CH3
CH3
O
CH3
H2C
4.02
6.01
1.00
1.00
1.04
1.04
2.03
3.00
2.01
9.04
f1 (ppm)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136.16
134.99
132.62
129.10
128.41
116.61
110.96
110.70
55.19
35.93
33.64
32.44
5ia
Ge
CH3
CH3
CH3
O
CH3
H2C
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.57
7.56
7.55
7.41
7.39
7.34
7.33
7.31
7.27
7.26
7.24
7.24
7.05
7.03
7.02
7.01
6.03
6.01
6.00
5.98
5.96
5.94
5.92
5.91
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5.10
5.06
5.06
3.43
3.42
2.58
2.55
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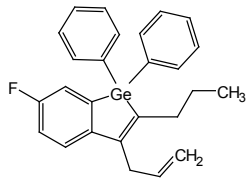
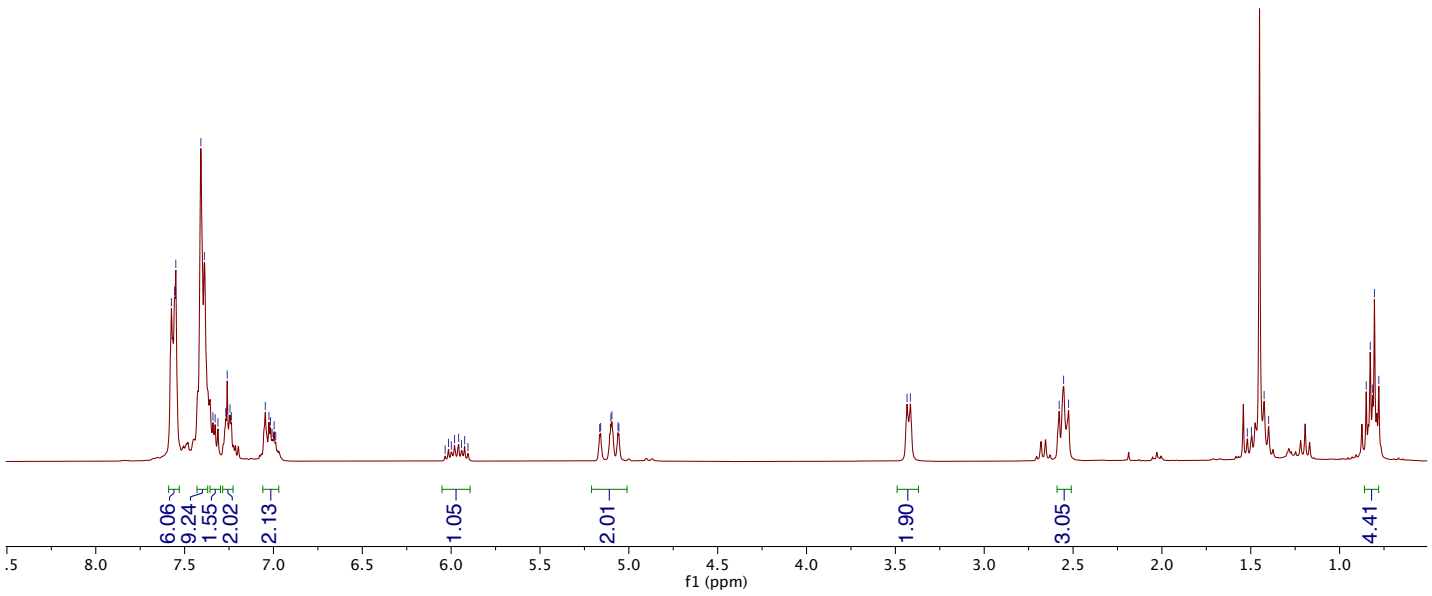
1.42
1.40
0.85
0.83
0.81
0.80
0.78

5ka/3k 70/30


F
Ge
CH3
CH2


6.06
9.24
1.55
2.02
2.13
1.05
2.01
1.90
3.05
4.41
.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
f1 (ppm)

7.70
7.67
7.64
7.63
7.62
7.62
7.61
7.42
7.39
7.38
7.36
7.36
7.35
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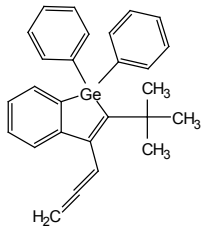
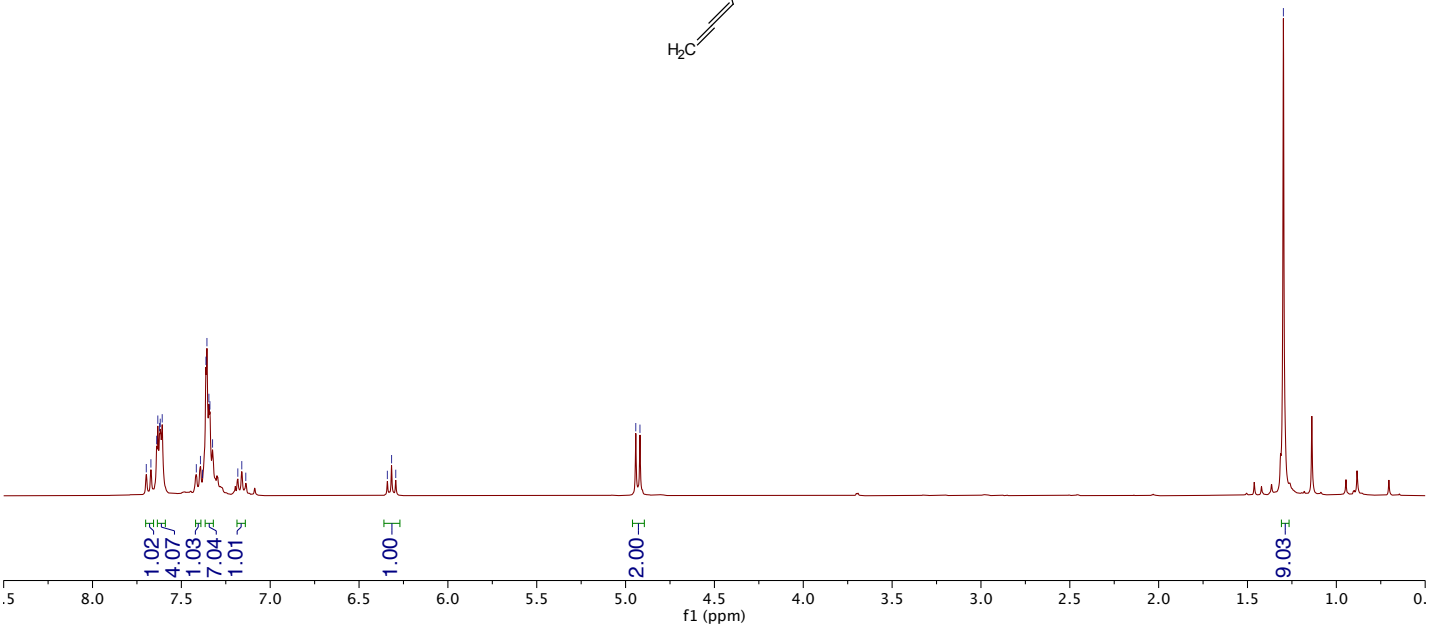
7.32
7.18
7.16
6.34
6.32
6.29

4.94
4.92

1.30

5bb





209.42

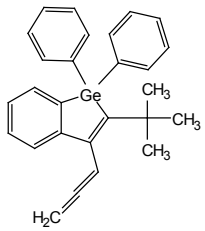
154.58
149.97
141.65
137.45
136.19
135.14
135.05
132.25
129.34
128.53
127.00
123.76

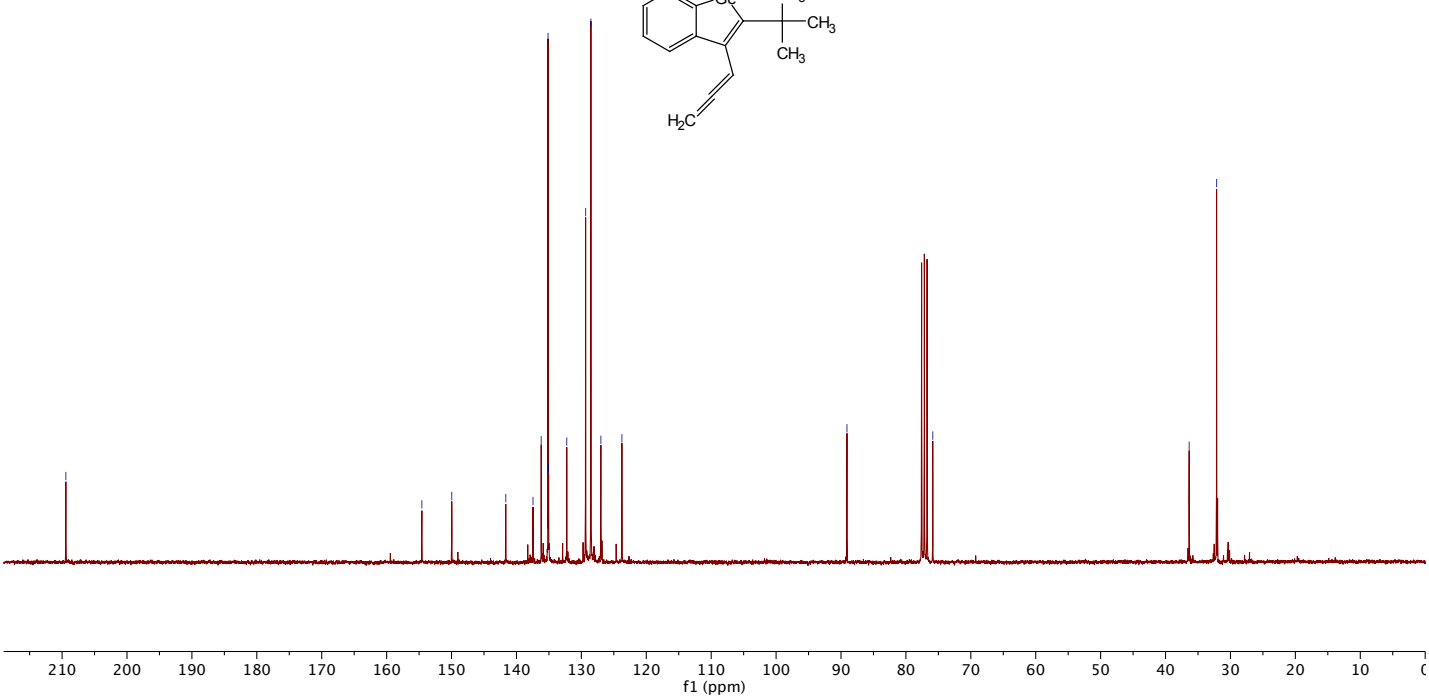
89.08

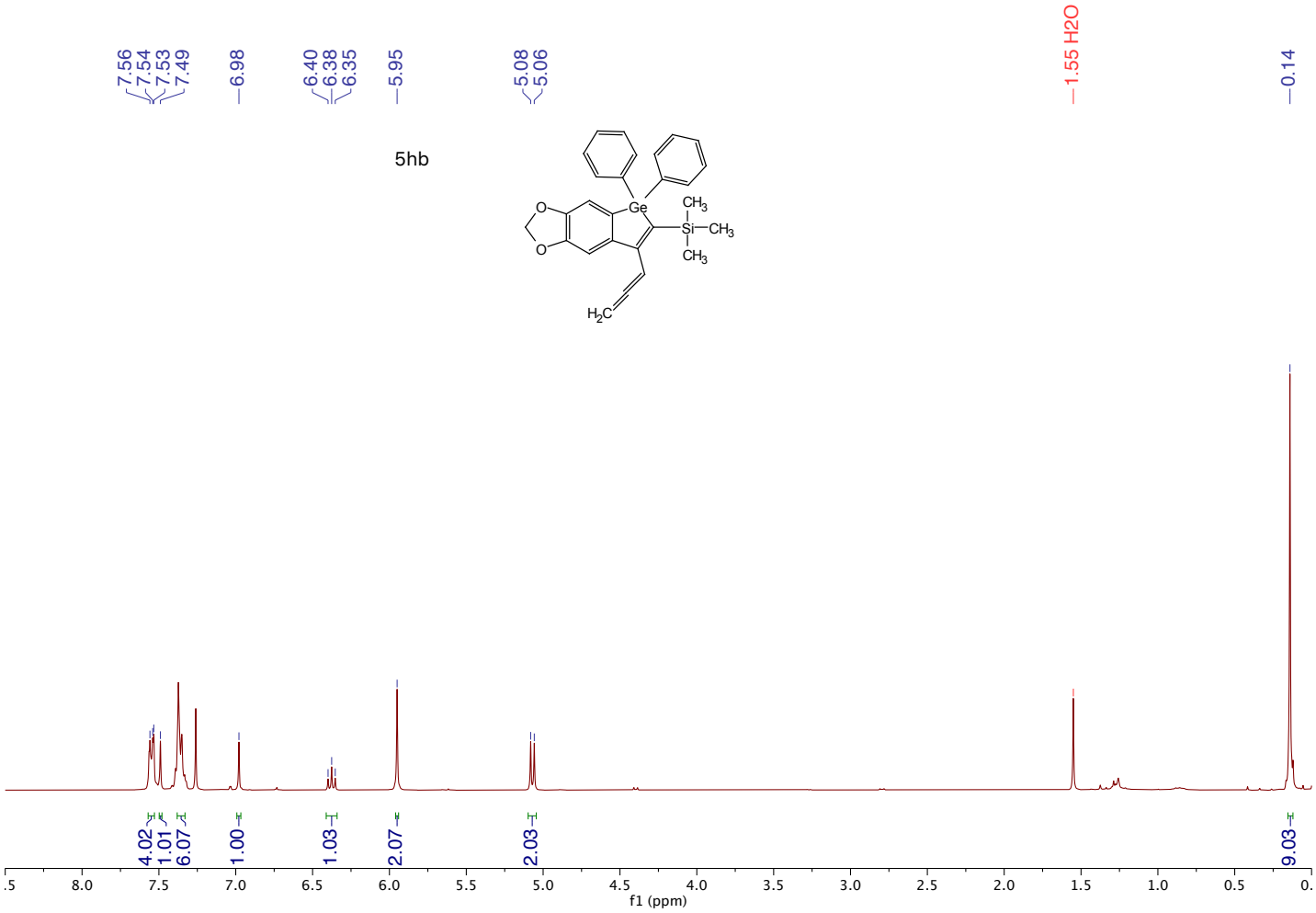
75.86

36.36
32.13

5bb



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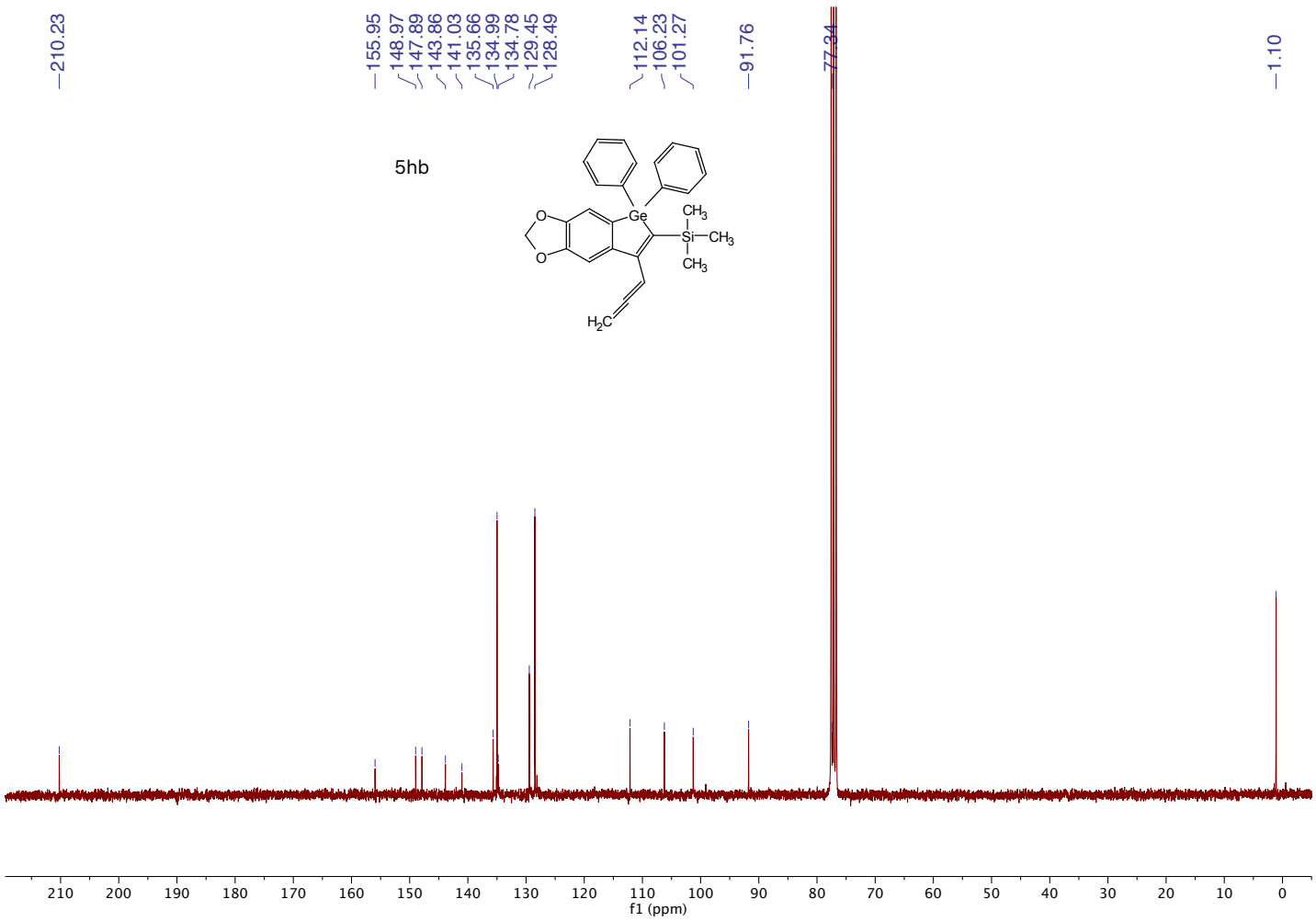
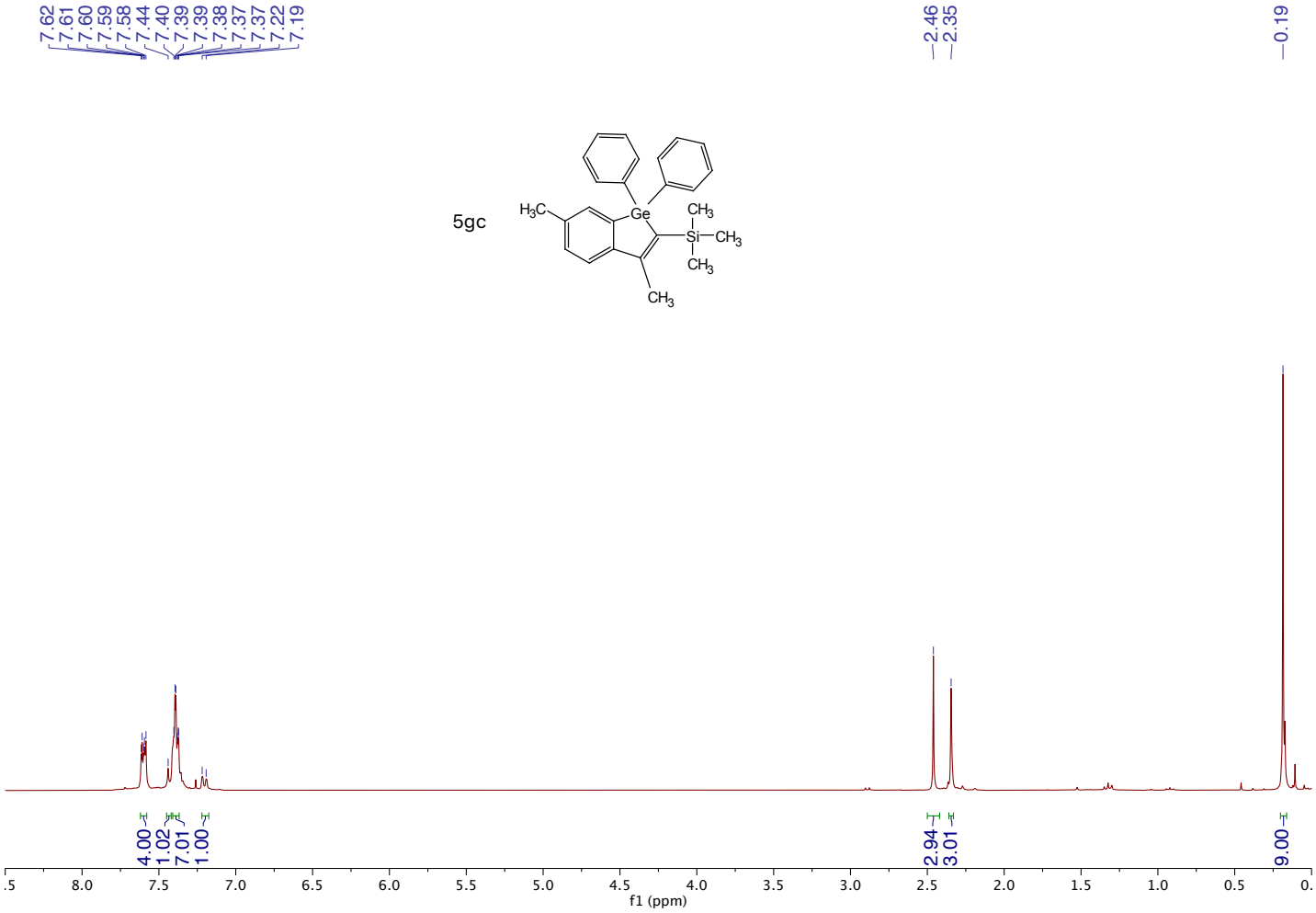
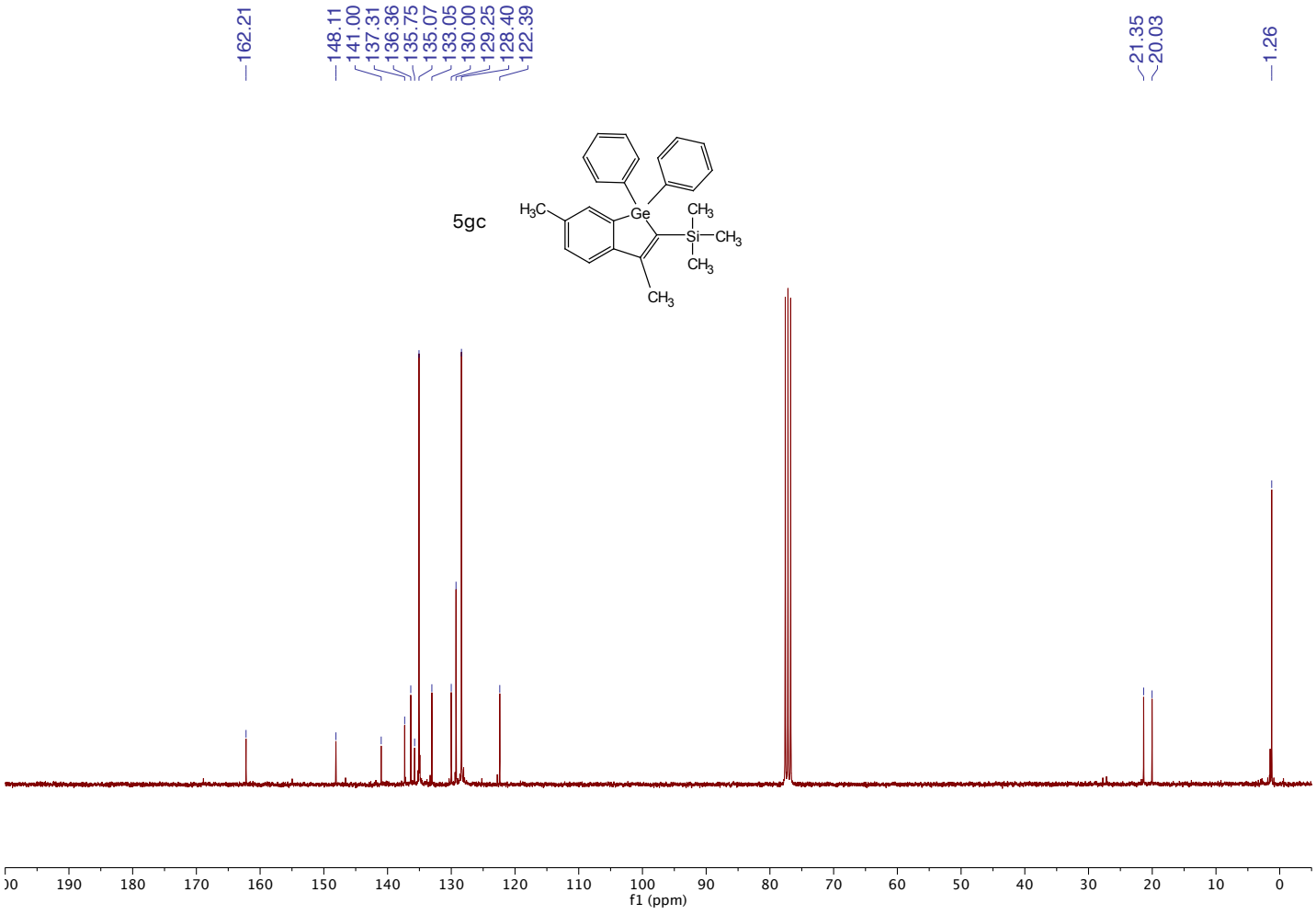
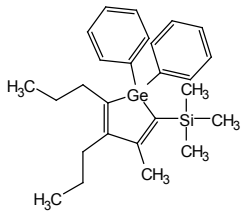
7.54
7.53
7.49
6.98
6.40
6.38
6.35
5.95
5.08
5.06
1.55 H2O
0.14
5hb
Ge
O
O
Si
CH3
CH3
CH3
H2C
4.02
1.01
6.07
1.00
1.03
2.07
2.03
9.03
f1 (ppm)

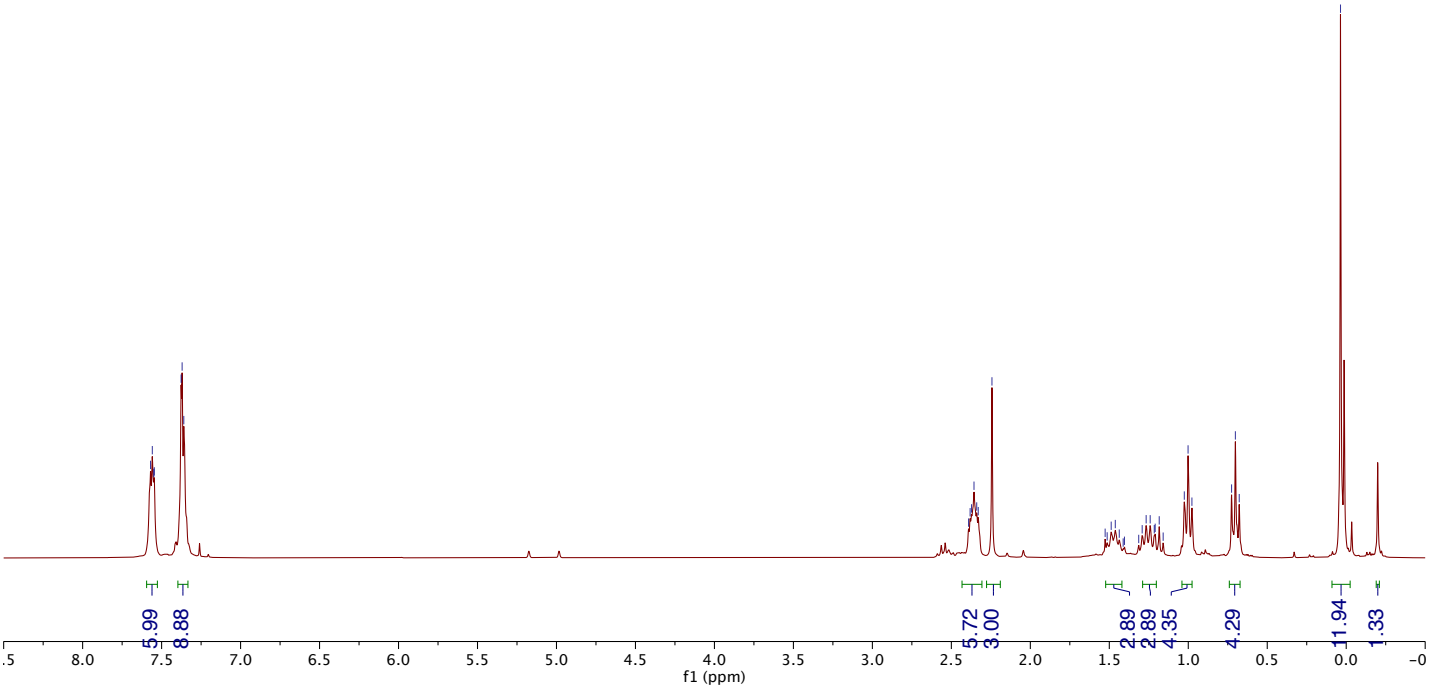

210.23
155.95
148.97
147.89
143.86
141.03
135.66
134.99
134.78
129.45
128.49
112.14
106.23
101.27
91.76
77.34
1.10
5hb
Ge
O
O
Si
CH3
CH3
CH3
H2C
f1 (ppm)


7.62
7.61
7.60
7.59
7.58
7.44
7.40
7.39
7.39
7.38
7.37
7.37
7.22
7.19
2.46
2.35
0.19
5gc
Ge
Si
4.00
1.02
7.01
1.00
2.94
3.01
9.00
f1 (ppm)

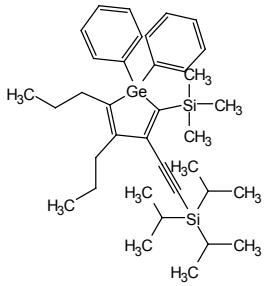

162.21
148.11
141.00
137.31
136.36
135.75
135.07
133.05
130.00
129.25
128.40
122.39
21.35
20.03
1.26
5gc
Ge
Si
f1 (ppm)

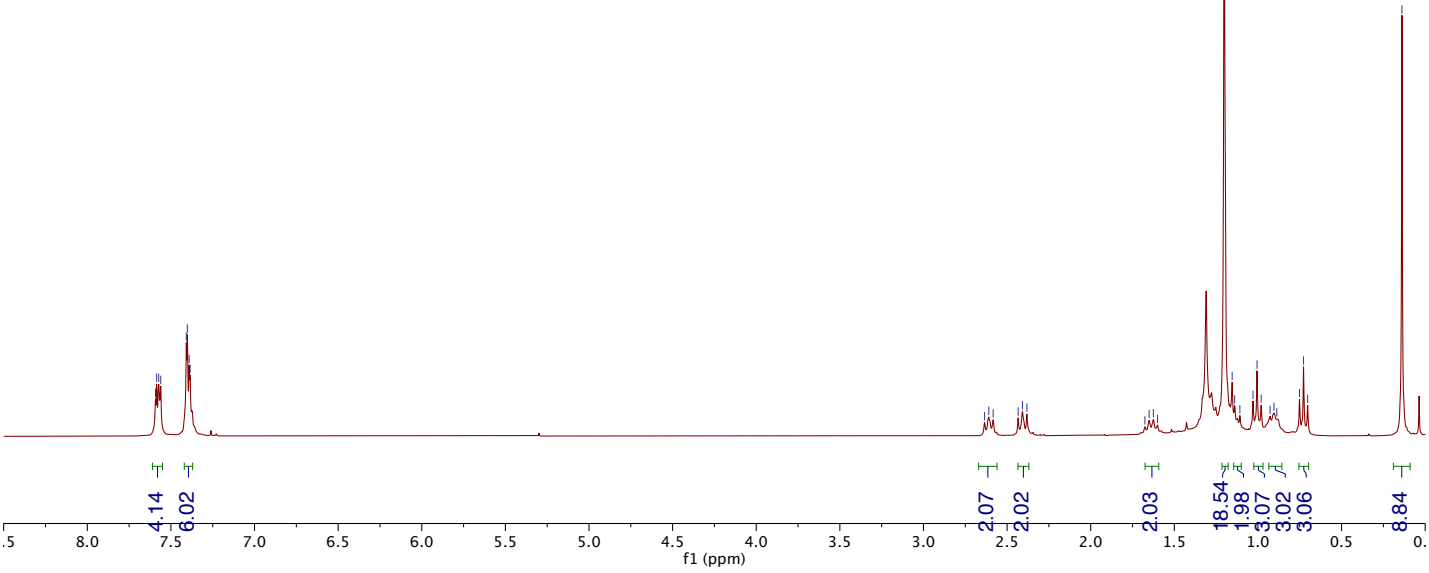
5nc/6nc 70/30





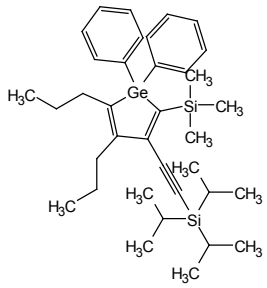
5nd





150.35
149.48
148.81
143.57
136.02
135.06
129.23
128.45
107.03
95.81
33.59
29.89
24.19
23.47
18.88
14.46
14.31
11.79
-0.08

5nd

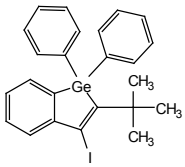


f1 (ppm)

7.89
7.87
7.63
7.62
7.61
7.61
7.60
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.28
7.26
7.26
7.19
7.18
7.16
7.16
7.14
7.14

1.39

5be

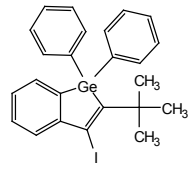


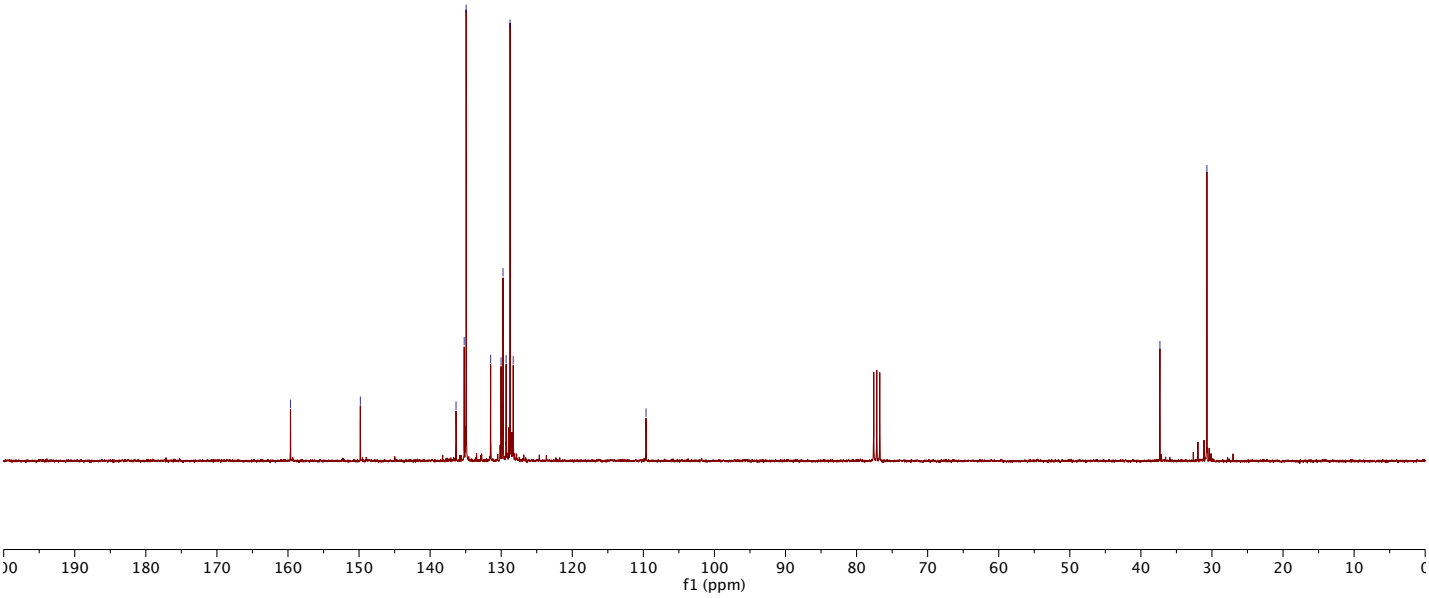
0.95
4.00
7.03
1.04
1.04
8.97

f1 (ppm)

159.65
149.82
136.35
135.21
134.93
131.48
130.02
129.75
129.31
128.75
128.31
109.62
37.32
30.71

5be

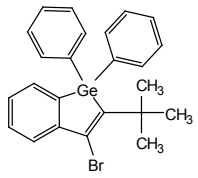


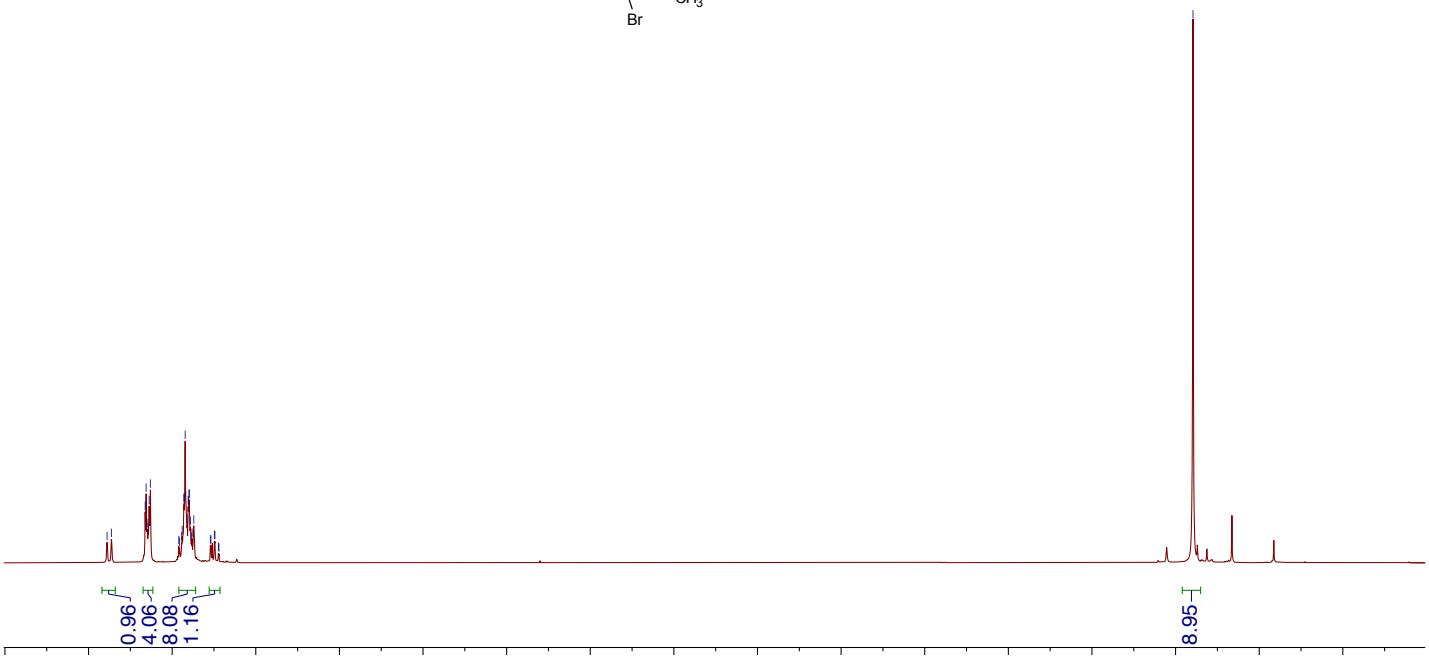


f1 (ppm)

7.89
7.86
7.66
7.66
7.65
7.64
7.64
7.63
7.46
7.44
7.44
7.43
7.42
7.41
7.40
7.40
7.40
7.39
7.39
7.38
7.37
7.27
7.25
7.24
7.22
7.22
1.40

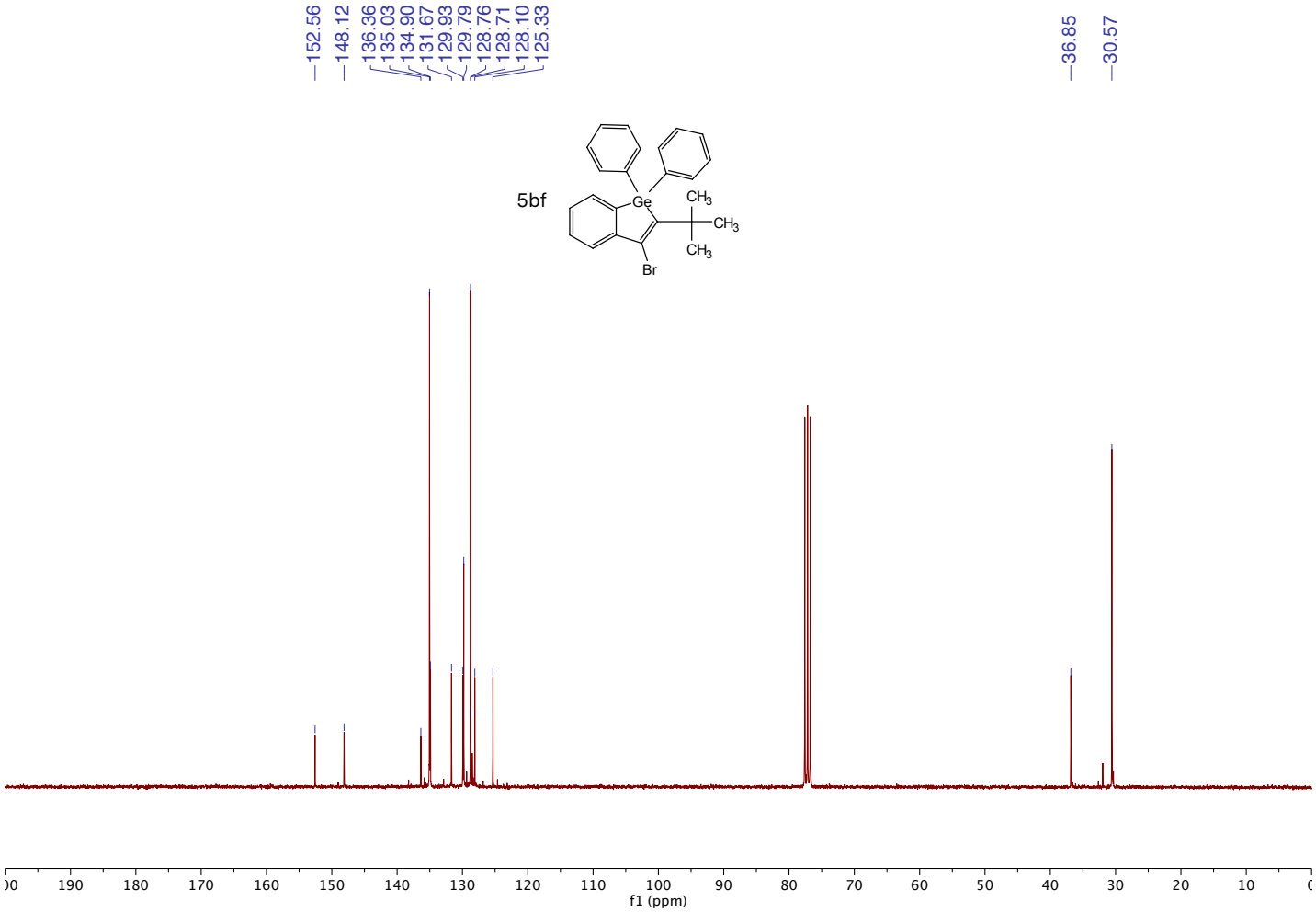
5bf

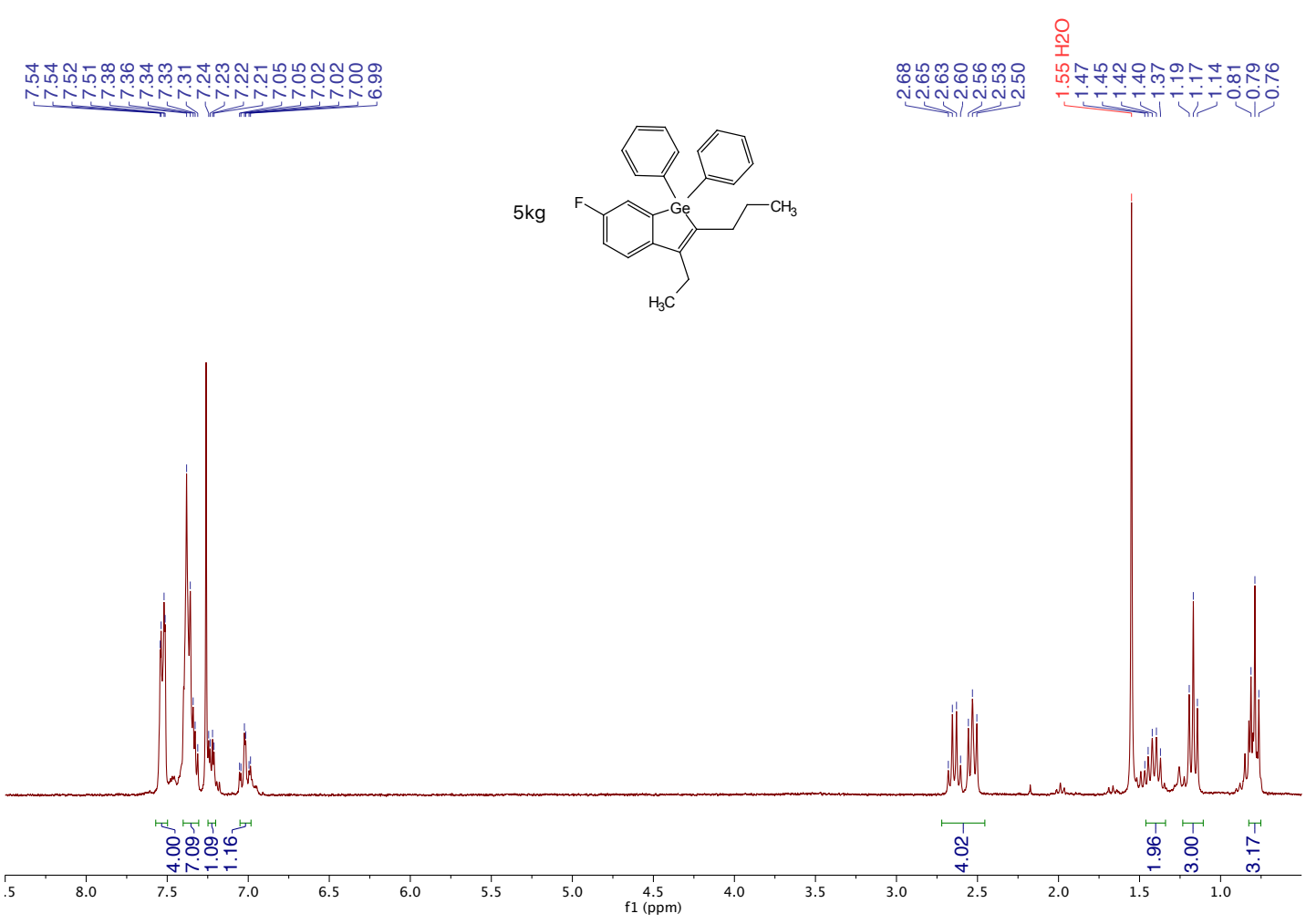


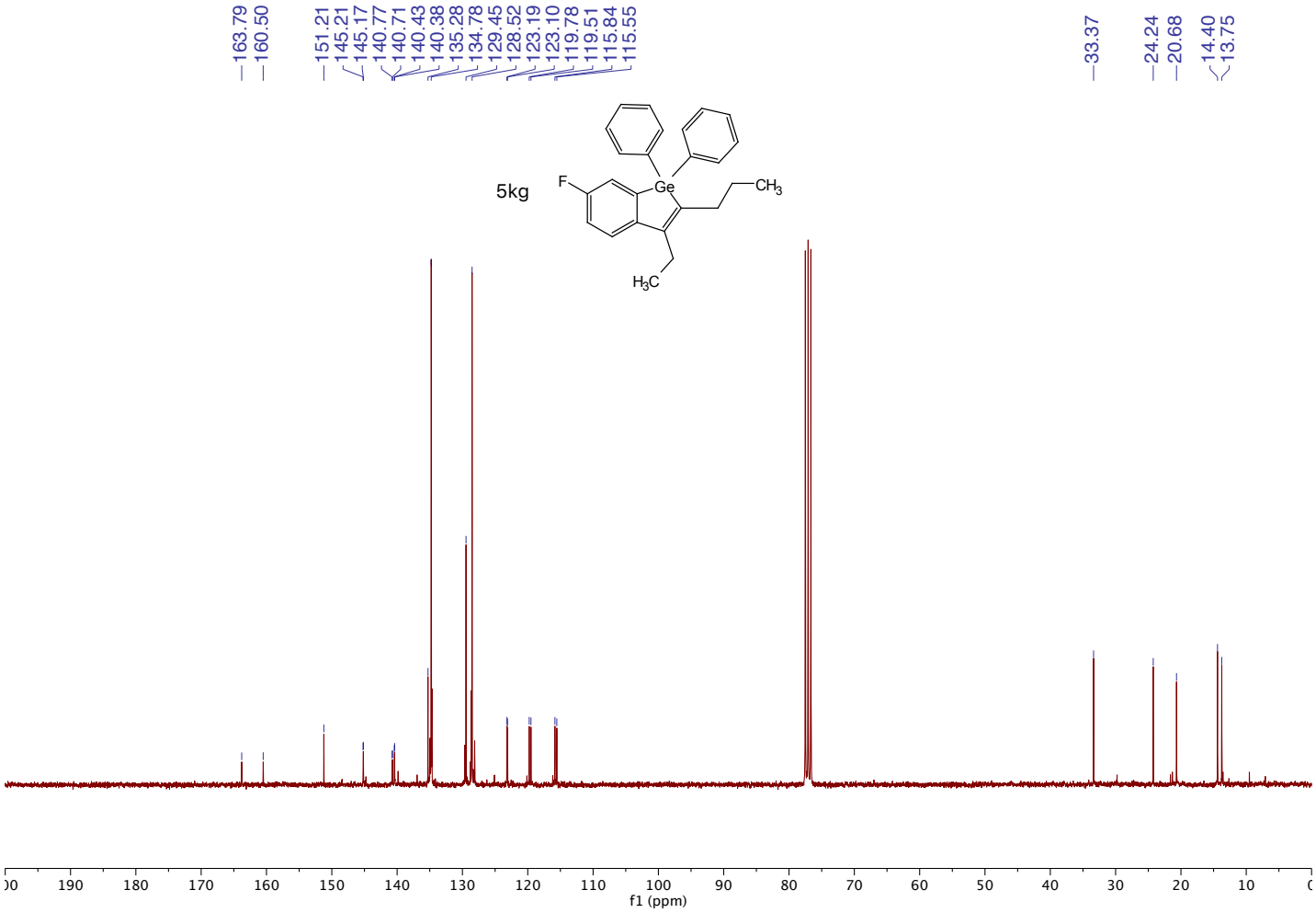


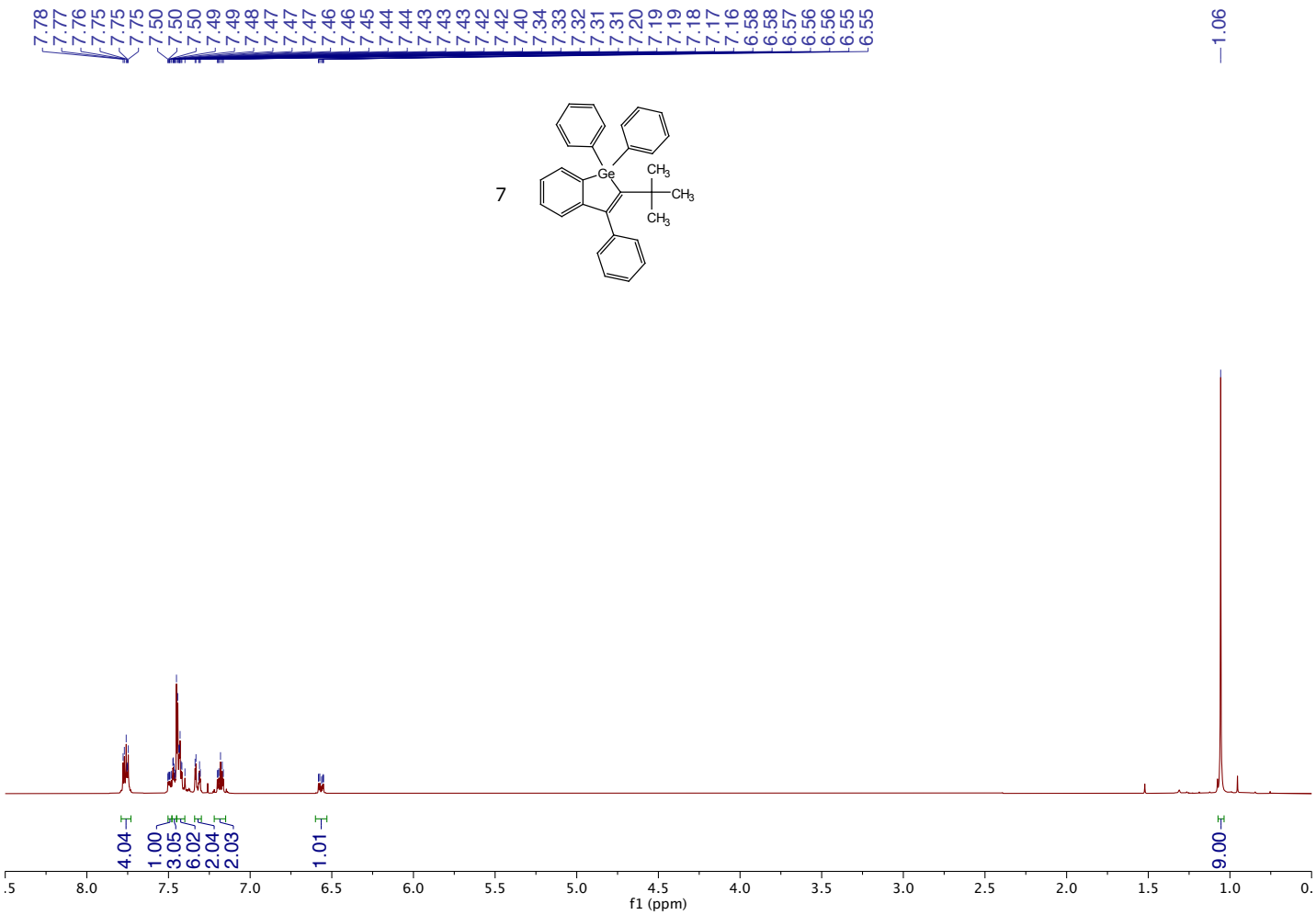
0.96
4.06
8.08
1.16
8.95

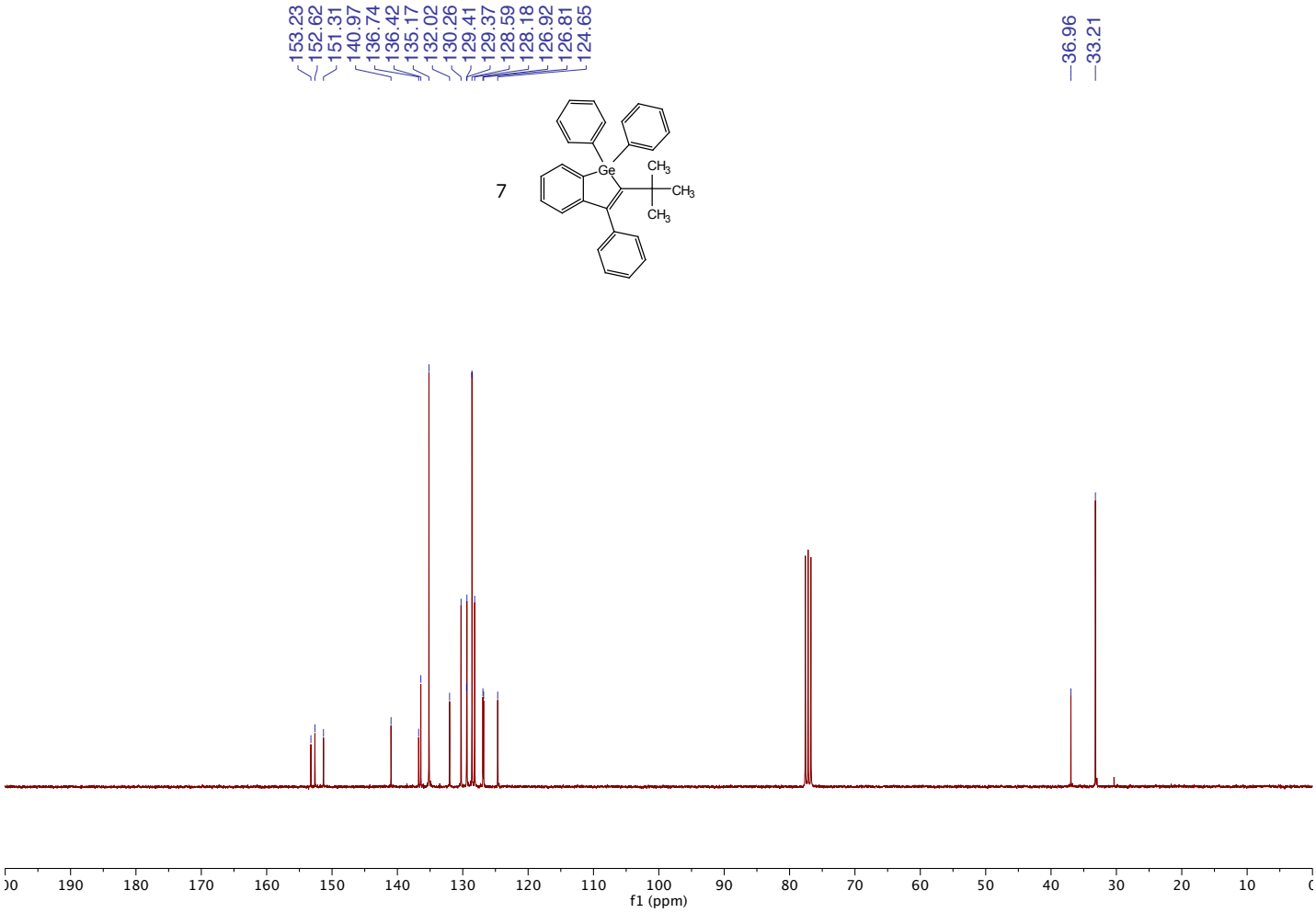
f1 (ppm)


152.56
148.12
136.36
135.03
134.90
131.67
129.93
129.79
128.76
128.71
128.10
125.33
36.85
30.57
5bf
Ge
CH3
CH3
CH3
Br
f1 (ppm)

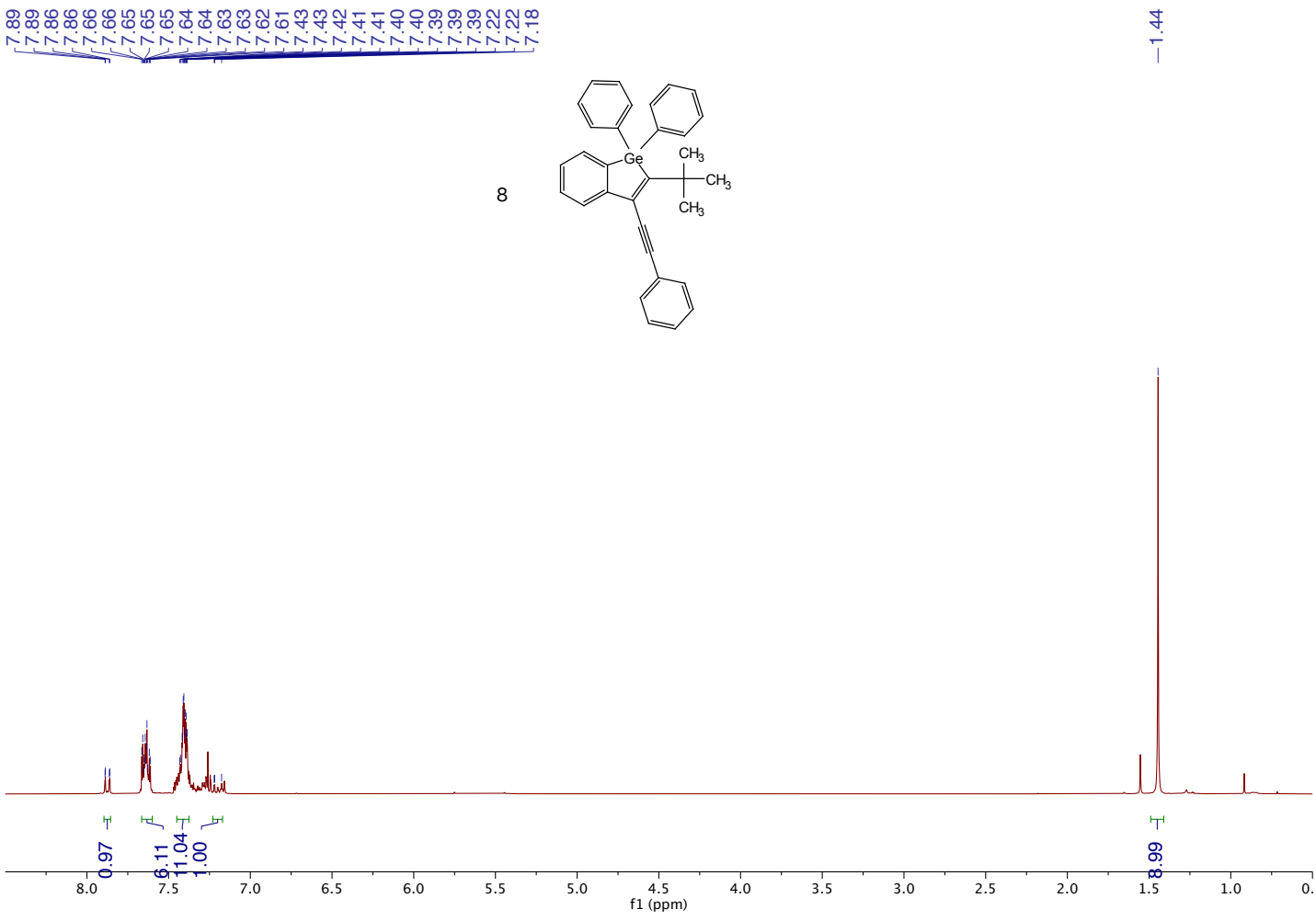

7.54
7.54
7.52
7.51
7.38
7.36
7.34
7.33
7.31
7.24
7.23
7.22
7.21
7.05
7.05
7.02
7.02
7.00
6.99
2.68
2.65
2.63
2.60
2.56
2.53
2.50
1.55 H2O
1.47
1.45
1.42
1.40
1.37
1.19
1.17
1.14
0.81
0.79
0.76
5kg
F
Ge
CH3
H3C
4.00
7.09
1.09
1.16
4.02
1.96
3.00
3.17
f1 (ppm)


163.79
160.50
151.21
145.21
145.17
140.77
140.71
140.43
140.38
135.28
134.78
129.45
128.52
123.19
123.10
119.78
119.51
115.84
115.55
33.37
24.24
20.68
14.40
13.75
5kg
F
Ge
CH3
H3C
f1 (ppm)

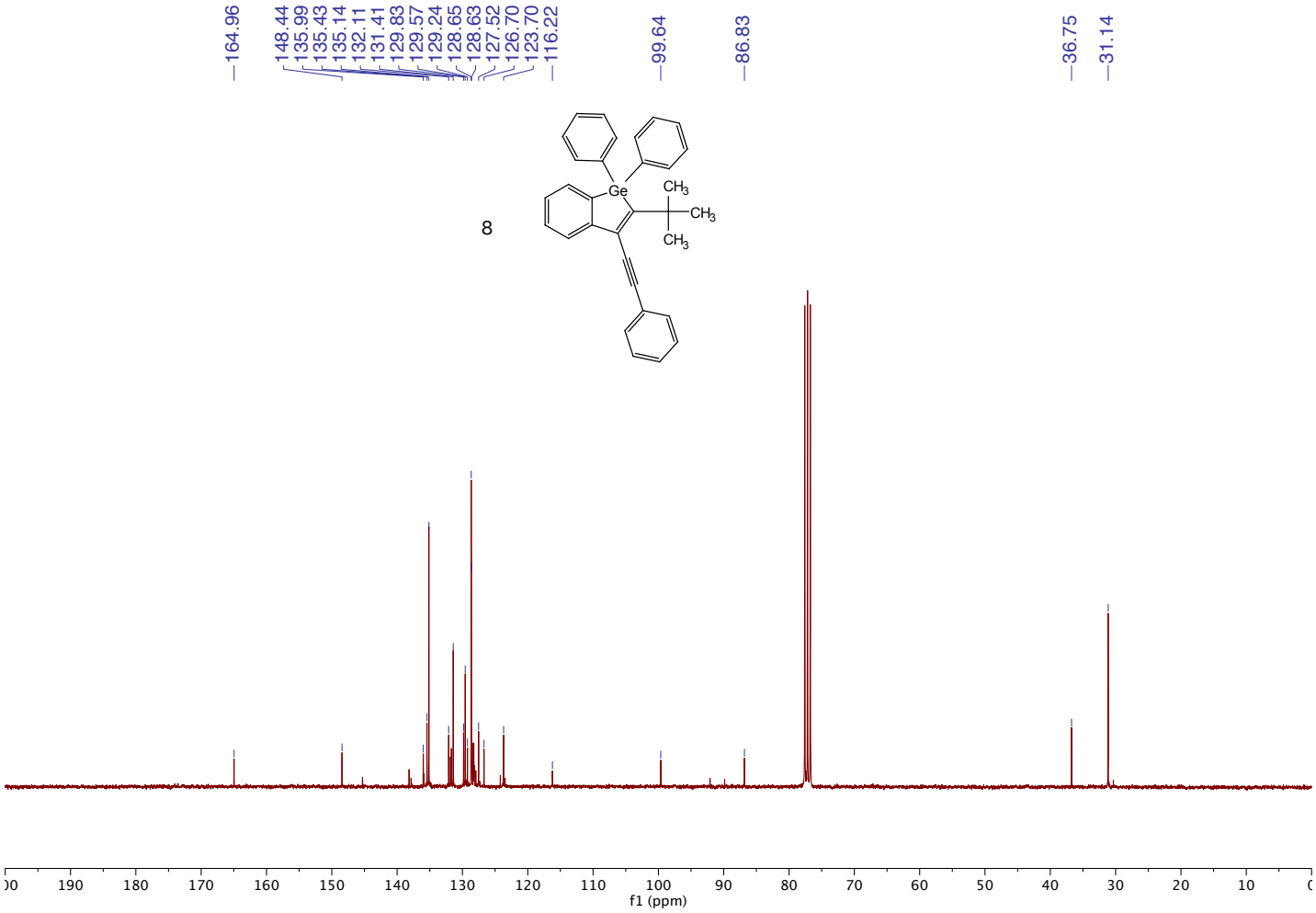

7.78
7.77
7.76
7.75
7.75
7.75
7.50
7.50
7.50
7.49
7.49
7.48
7.47
7.47
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.43
7.43
7.42
7.42
7.40
7.34
7.33
7.32
7.31
7.31
7.20
7.19
7.19
7.18
7.17
7.16
6.58
6.58
6.57
6.56
6.56
6.55
6.55
1.06
7
Ge
CH3
CH3
CH3
4.04
1.00
3.05
6.02
2.04
2.03
1.01
9.00
f1 (ppm)


153.23
152.62
151.31
140.97
136.74
136.42
135.17
132.02
130.26
129.41
129.37
128.59
128.18
126.92
126.81
124.65
36.96
33.21
Ge
CH3
CH3
CH3
f1 (ppm)

7


7.89
7.89
7.86
7.86
7.66
7.66
7.65
7.65
7.65
7.64
7.64
7.63
7.63
7.62
7.61
7.43
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.39
7.22
7.22
7.18
1.44
Ge
CH3
CH3
CH3
0.97
6.11
11.04
1.00
8.99
f1 (ppm)

8


164.96
148.44
135.99
135.43
135.14
132.11
131.41
129.83
129.57
129.24
128.65
128.63
127.52
126.70
123.70
116.22
99.64
86.83
36.75
31.14
Ge
CH3
CH3
CH3
8
f1 (ppm)