Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Data about

Iridium complex catalyzed germylative coupling reaction between alkynes and iodogermanes - a new route to alkynylgermaniumand alkynylgermasilicon compounds

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1. Experimental procedures

1.1. Nuclear Magnetic Resonance spectroscopy

Liquid state NMR spectra were recorded in $CDCl_3$ or benzene-d6 using a Brucker Ultra Shield spectrometer (600 MHz) and Varian Mercury spectrometer (300 HMz), Bruker Avance II (400 MHz), Bruker Avance III (500 MHz) and referred to the residual protonated solvent peaks (^{1}H δ = 7.26 ppm, ^{13}C δ = 77.0 ppm for $CDCl_3$ and ^{1}H δ = 7.16 ppm, ^{13}C δ = 128.05 ppm for benzene-d6) or external $Si(CH_3)_4$ (^{29}Si δ = 0.00 ppm).

1.2. Gas phase analyses

Gas phase analyses were performed on Varian CP-3380 gas chromatography (GC) apparatus equipped with a TCD detector and capillary column J&W DB5 (30 m × 0.53 mm).

1.3. GC/MS analyses

Products were identified by GC/MS (Varian Saturn 2100T) equipped with a CP-SIL 6CB column (30 m × 0.25 mm).

1.4. HR/MS analyses

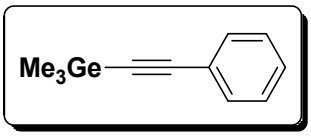
High resolution mass spectra (HRMS) were obtained by electron impact ionization (EI) using AMD Intectra Mass AMD 402 instrument. Some of the products have significant fragmentation which made them difficult to analyze by HRMS method. For a few of them HRMS analysis were impossible to do or have been obtained for fragmented ions.

2. Procedures and NMR data and HR/MS analyses of synthesized compounds

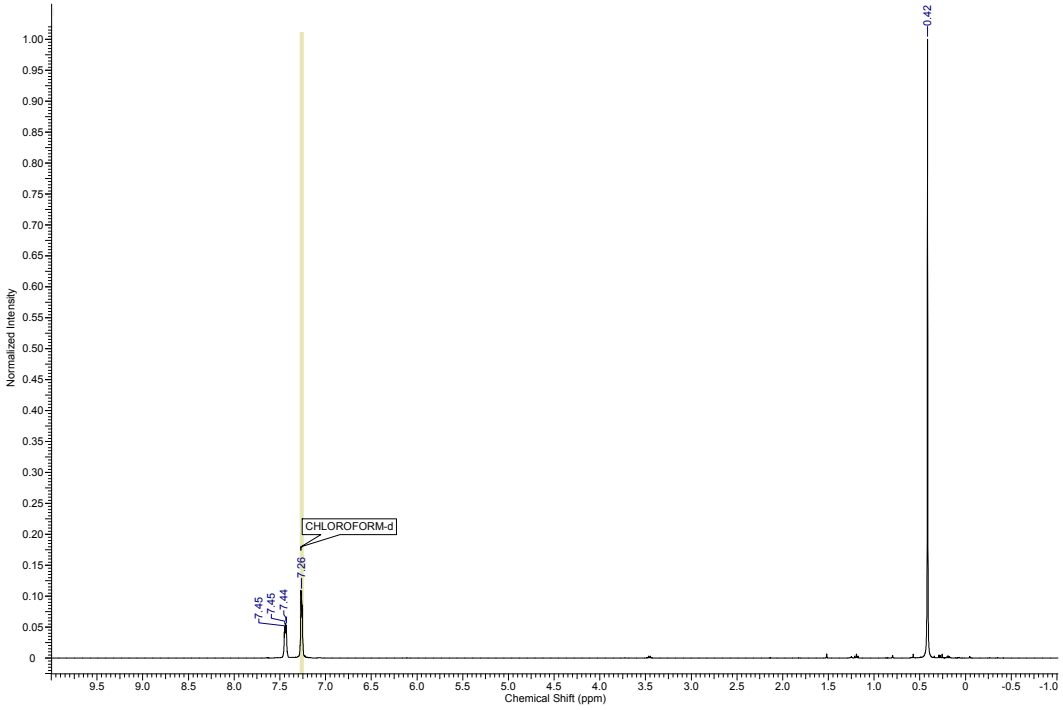
Procedure for germylative coupling of terminal tlkynes 1-21

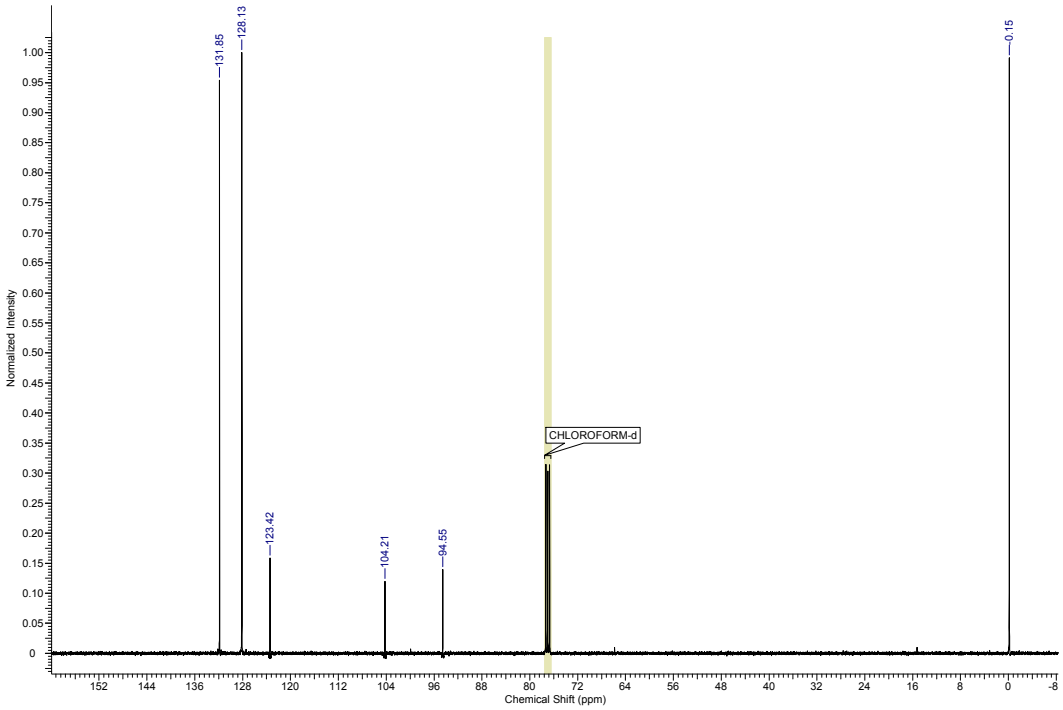
The glass Schlenk reactor equipped with a magnetic stirring bar was evacuated and flushed with argon. The calculated amount of the complex $[\{Ir(\mu\text{-}Cl)(CO)_2\}_2]$ (0.014 mmol) was placed in the reactor in the flow of argon; then toluene and a calculated amount of $NEt(^iPr)_2$ (2.22 mmol) were added. The mixture obtained was stirred for 10 min. In the next step, appropriate amounts of terminal alkyne (1.41 mmol) and Me_3GeI (1.48 mmol) were added. The reaction was conducted in a closed system at 80ºC upon stirring for 24 hours (or 48 hours). After the reaction completion, toluene and the excess of other reagents were evaporated under reduced pressure. The crude product was isolated by purification using column chromatography (SiO_2 or SiO_2 modified with 15% of Et_3N) with hexane as eluent.

Trimethyl(phenylethynyl)germane (1)

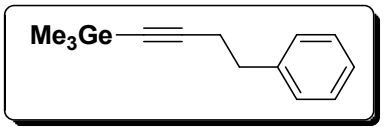


^{1}H NMR (400 MHz, $CDCl_3$, 25˚C): δ = 7.47-7.44 (m, 2H), 7.29-7.28 (*m*, 3H), 0.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C): δ = 131.85, 128.13, 123.42, 104.21, 94.55, -0.15; MS m/z (rel. int.%): 205.20 (100), 175.20 (7), 115 (11); HRMS (EI) calcd for $C_{11}H_{14}Ge$: 220.03073, found $[M]^{+}$: 220.03037. This spectral data are analogous to reported. [1]

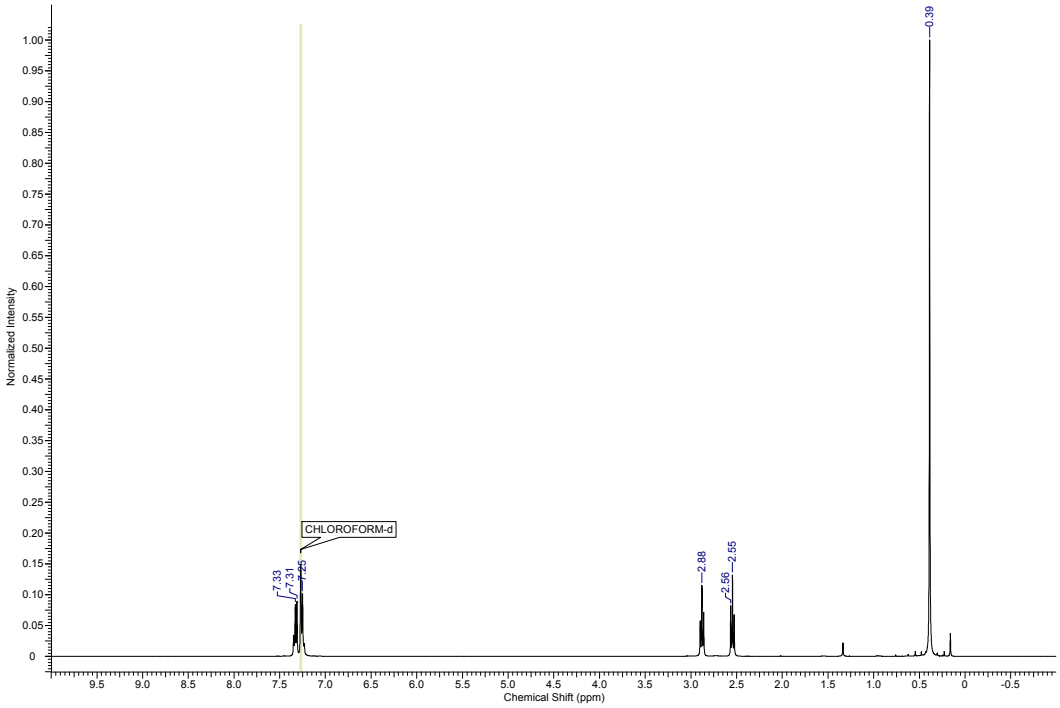


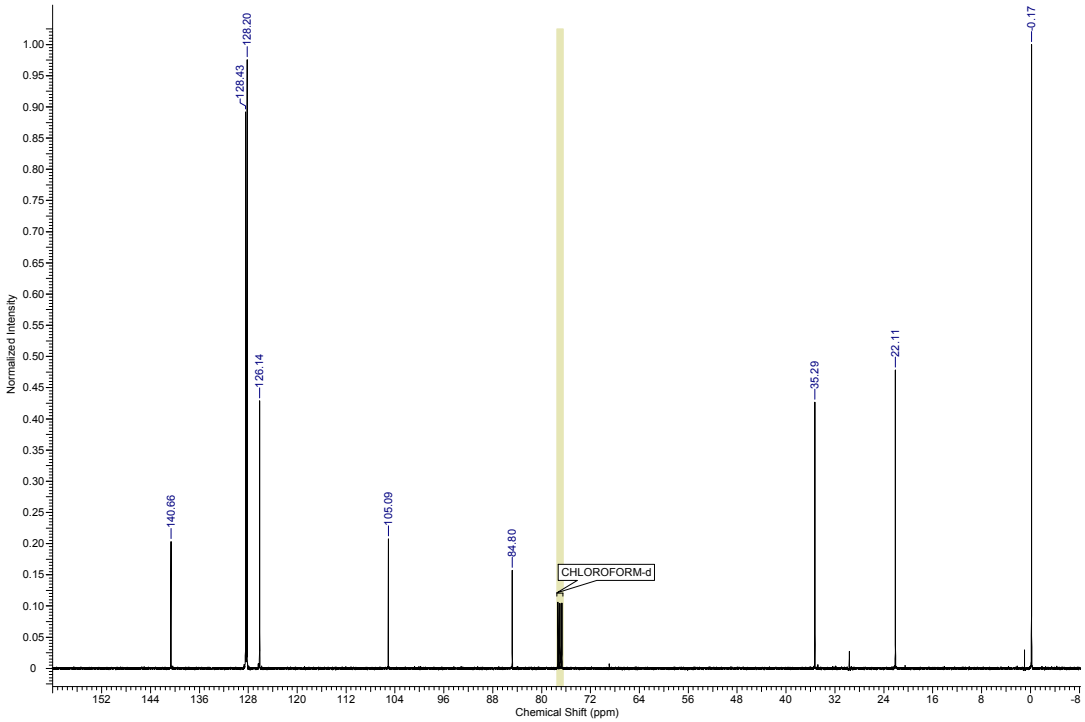


Trimethyl(4-phenylbut-1-yn-1-yl)germane (2)

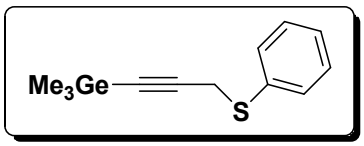


^{1}H NMR (400 MHz, $CDCl_3$, 25˚C): δ = 7.33-7.25 (m, 5H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.55 (t, *J* = 7.6 Hz, 2H), 0.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C): δ = 140.66, 128.43, 128.20, 126.14, 105.09, 84.80, 35.29, 22.11, -0.17; MS (EI) m/z (rel. int.%): 248.5 (2), 233.50 (100), 129.30 (18), 91.20 (34), 105.20 (12); HRMS (EI): *m*/*z* calcd for $C_{13}H_{18}Ge$: 248.06203, found $[M]^+$: 248.06215.

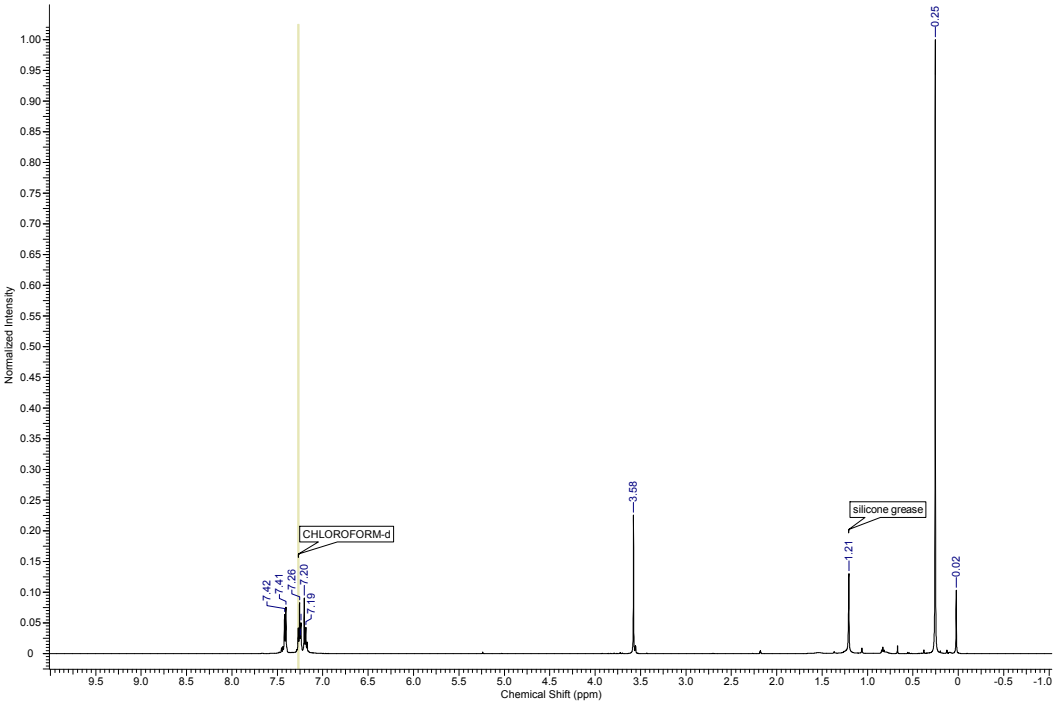


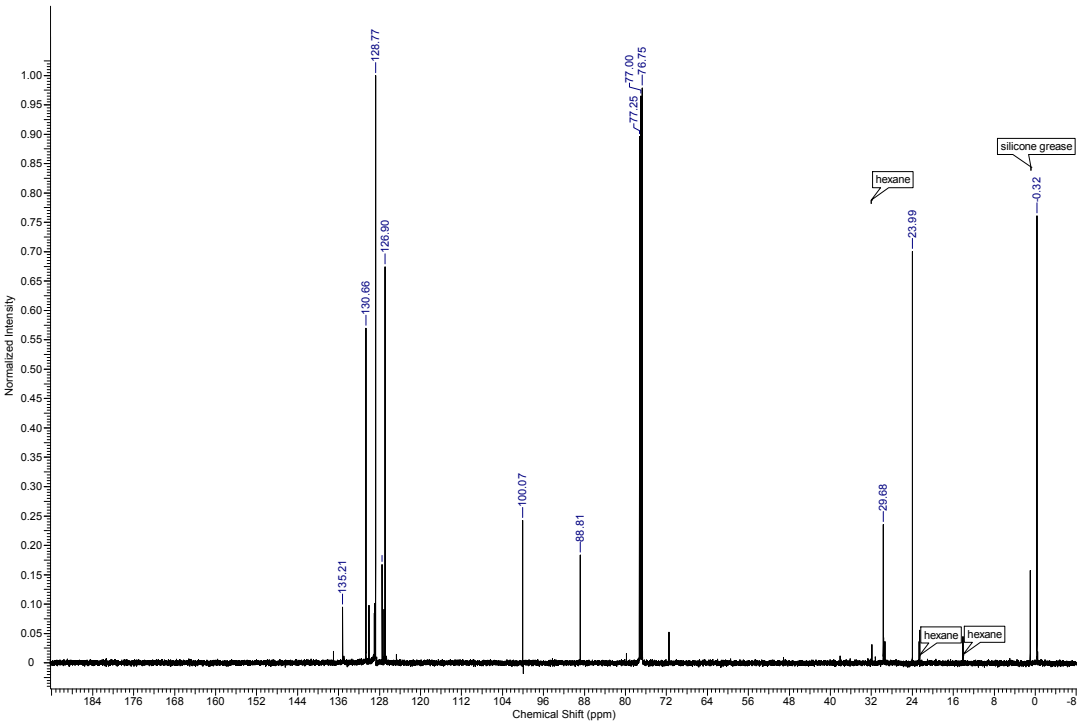


Trimethyl(3-(phenylthio)prop-1-ynyl)germane (3)

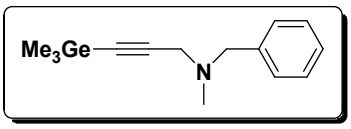


^{1}H NMR (500 MHz, $CDCl_3$, 25˚C): δ = 7.42-7.19 (m, 5H), 3.58 (s, 2H), 0.25 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, 25˚C): δ = 135.21, 130.65, 128.77, 126.90, 100.07, 88.81, 23.99, -0.32; MS (EI) m/z (rel. int.%): 266 (7), 251 (19),147.1 (100), 119.20 (38) 109.20 (25); HRMS (EI) *m/z* calcd for $C_{12}H_{16}GeS$: 266.01845, found $[M]^+$: 266.01835.

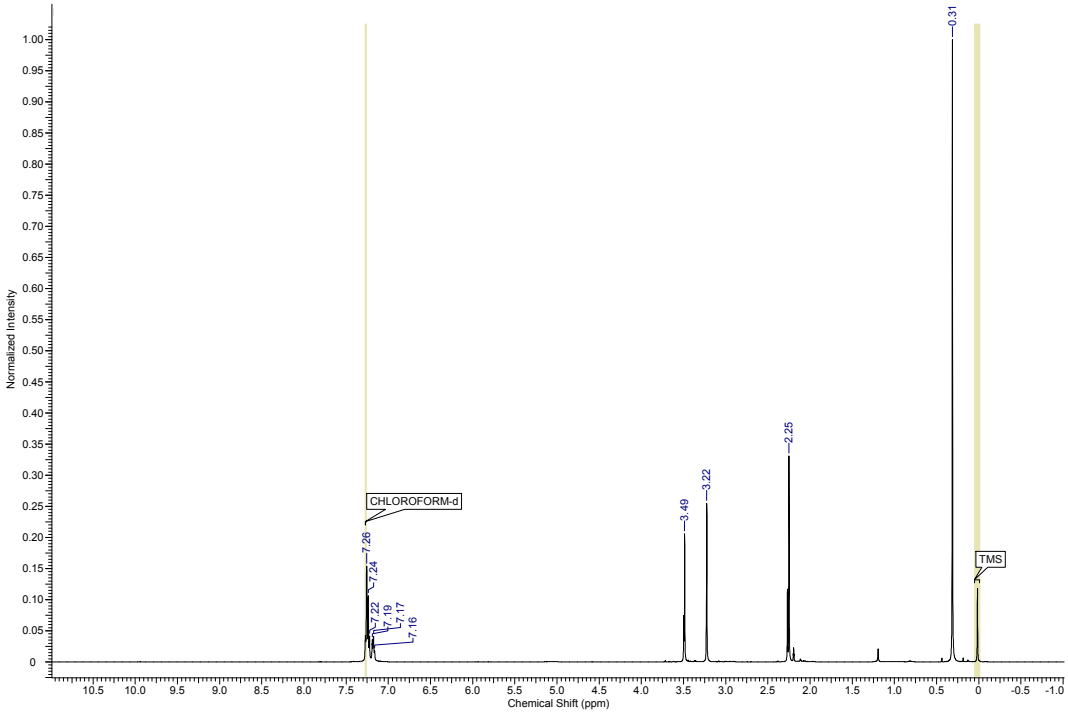


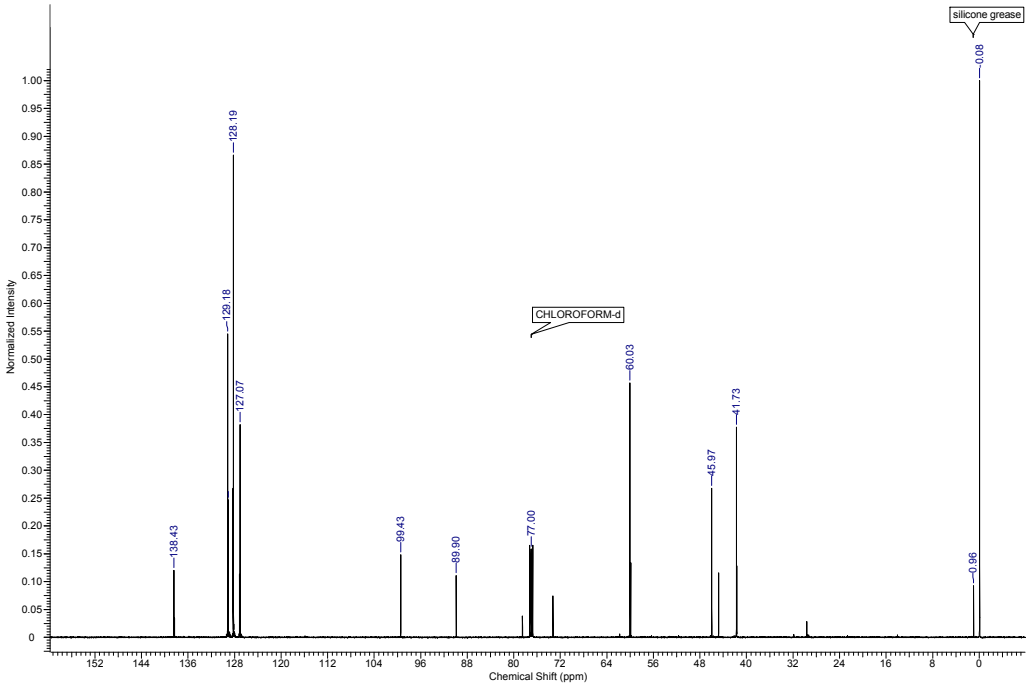


N-benzyl-N-methyl-3-(trimethylgermyl)prop-2-yn-1-amine (4)

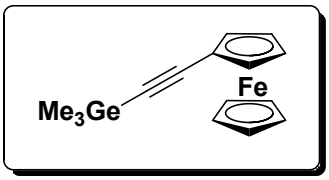


^{1}H NMR (500 MHz, $CDCl_3$, 25˚C): δ = 7.26-7.17 (m, 5H), 3.49 (s, 2H), 3.22 (s, 2H), 2.25 (s, 3H), 0.31 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, 25˚C): δ = 138.51, 129.26, 128.27, 127.15, 99.52, 89.98, 60.11, 46.06; 41.81, -0.08; MS (EI) m/z (rel. int.%): 276 (25), 262.00 (12), 200.10 (17), 158.10 (99), 134.20 (23), 91.20 (100); HRMS (EI) *m*/*z* calcd for $C_{14}H_{21}GeN$: 277.08859, found $[M]^+$: 277.08691.

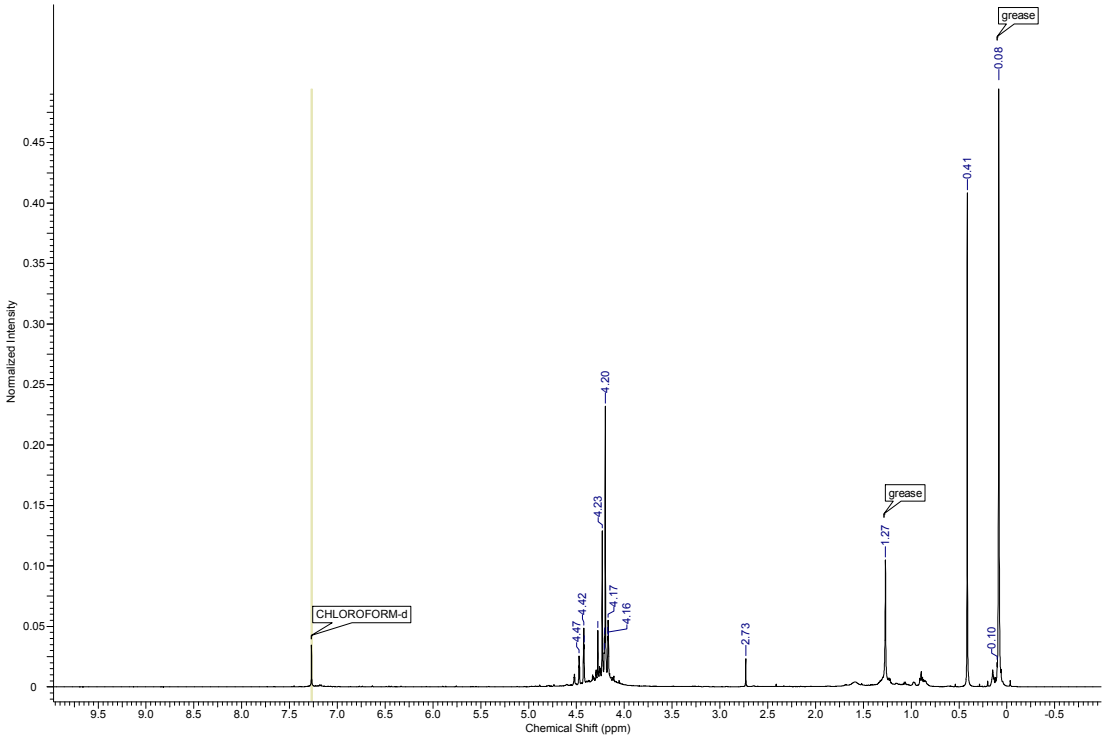


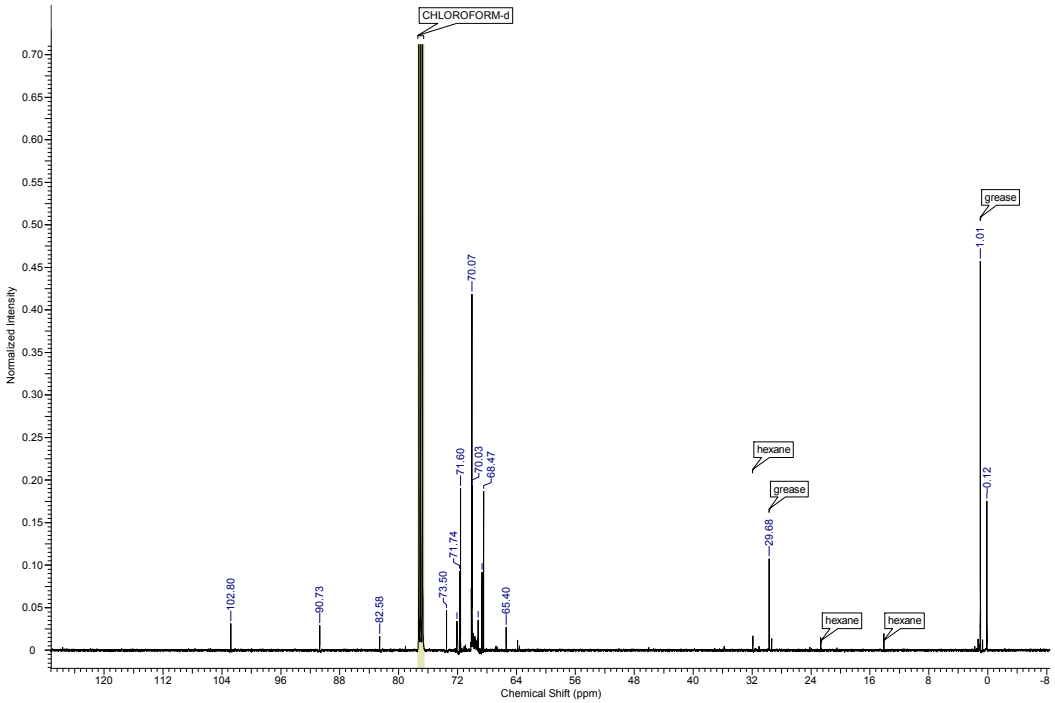


1-ferrocenyl-2-trimethylgermylethyne (5)

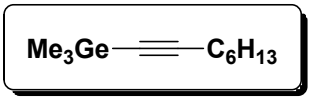


^{1}H NMR (500 MHz, $CDCl_3$, 25˚C): δ = 4.41 (t, J=1.7 Hz, 2H), 4.18 (s, 5H), 4.15 (t, J=1.7 Hz, 2H), 0.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C): δ = 102.8, 90.7, 71.6, 70.1, 68.5, 65.4, 0.12; MS (EI) m/z (rel. int.%): 328.20 (100), 327.40 (30), 313.40 (24), 298.30 (15); HRMS (EI) m/z calcd for $C_{15}H_{18}GeFe$: 327.99697, found $[M]^+$: 327.99571.

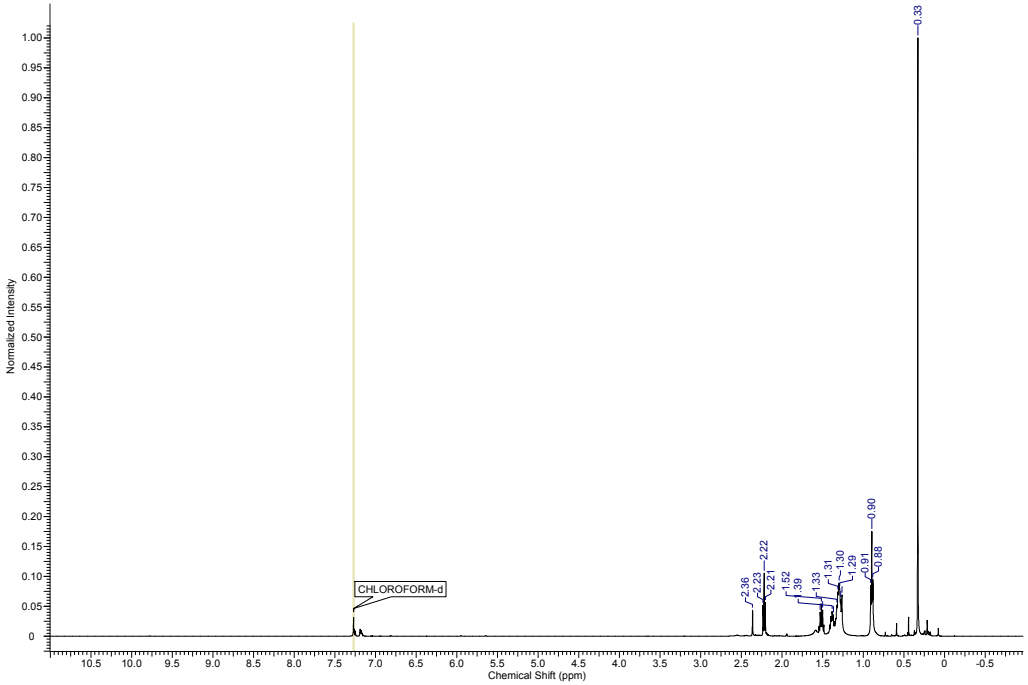


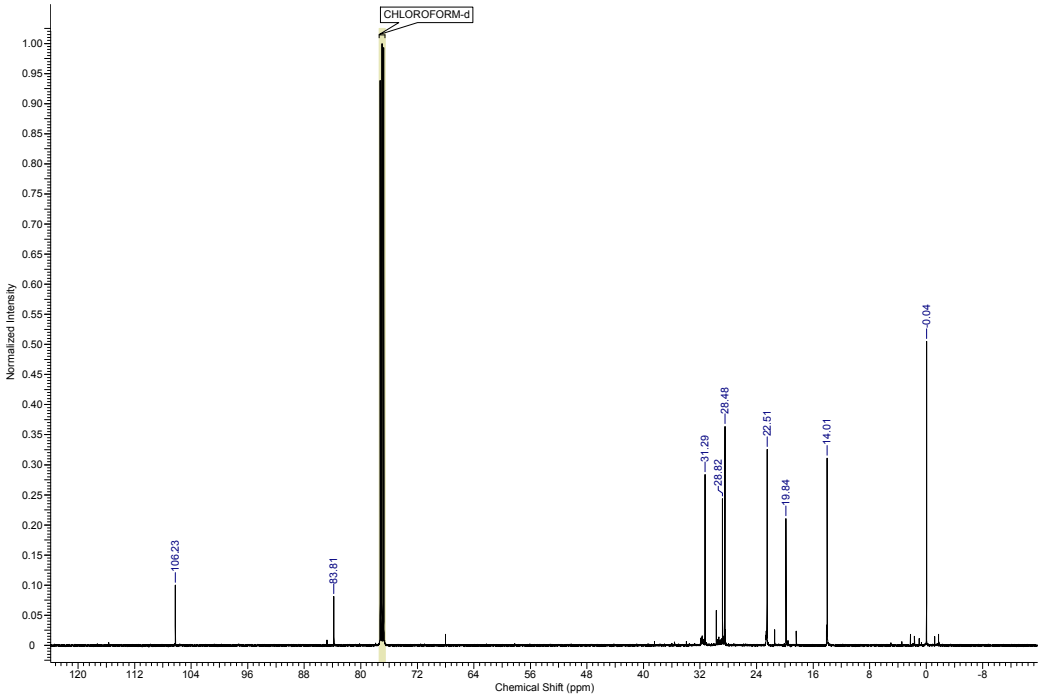


Trimethyl(oct-1-ynyl)germane (6)

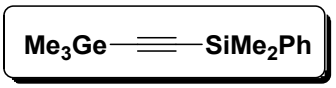


^{1}H NMR (500 MHz, $CDCl_3$, 25˚C): δ = 2.22 (t, *J*=7.3 Hz, 2H), 1.49–1.55 (m, 4H), 1.26 -1.41 (m, 12H), 0.90 (t, *J*=7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, 25˚C): δ = 107.64, 88.77, 31.92, 31.76, 29.70, 29.36, 22.69, 22.64, 14.12, -1.73; MS (EI) m/z (rel. int.%): 213.20 (100), 127.00 (5), 119.10 (13), 104.20 (11), 85.00 (4); HRMS (EI) *m*/*z* calcd for $C_{11}H_{22}Ge$: 228.09333; found $[M - CH_3]^+$: 213.06907.

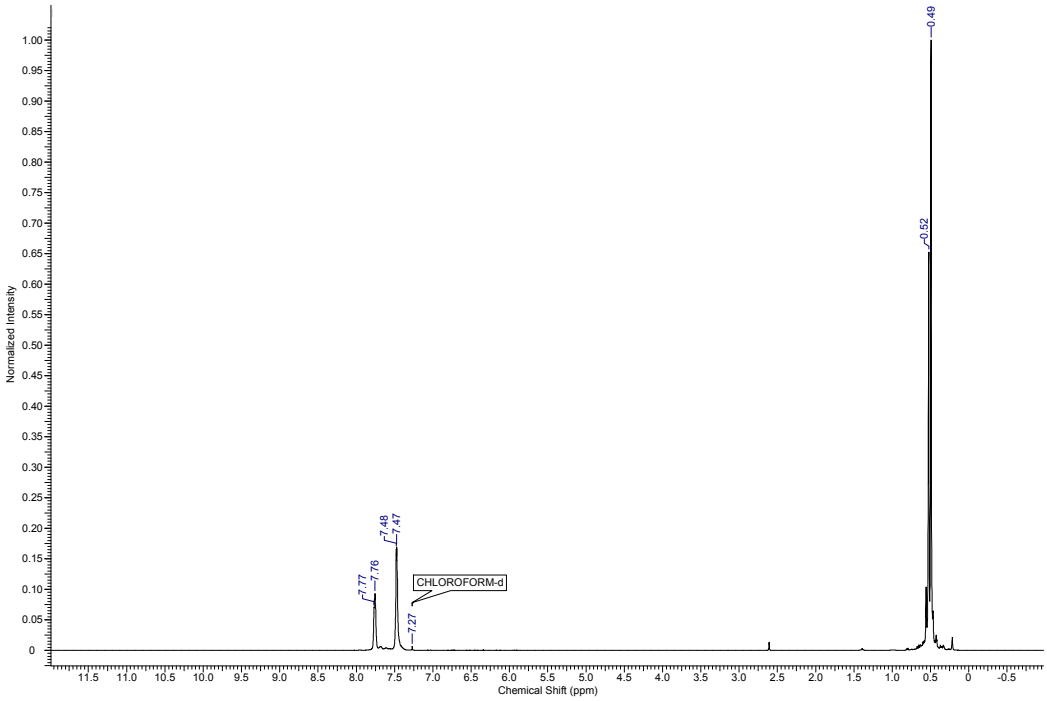


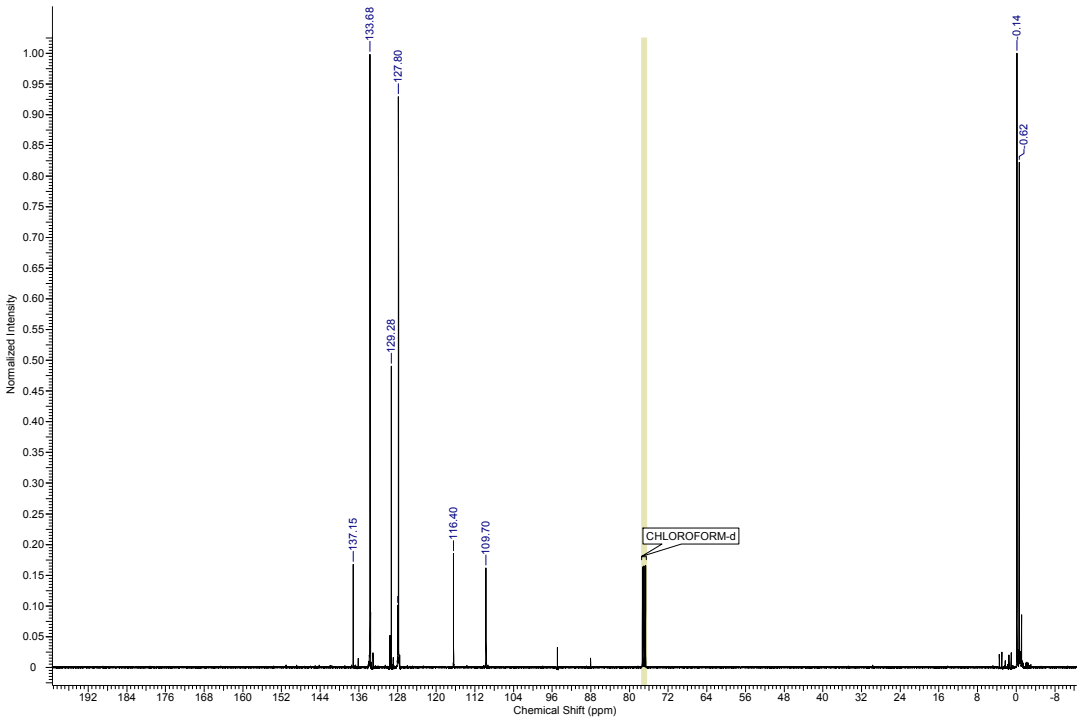


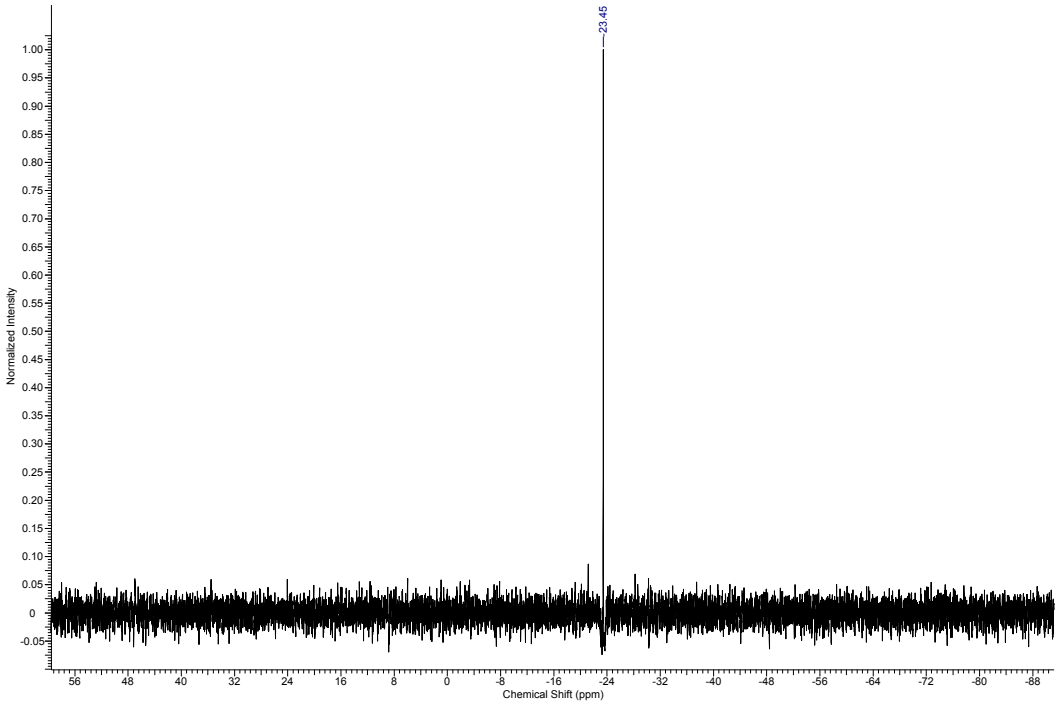
Dimethyl(phenyl)((trimethylgermyl)ethynyl)silane (7)



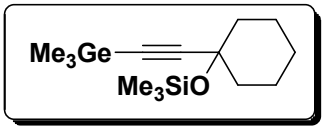
^{1}H NMR (400 MHz, $CDCl_3$, 25˚C): δ = 7.77-7.76 (m, 2H), 7.48-7.47 (m, 3H); 0.52 (s, 6H), 0.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C): δ = 137.15, 133.68, 129.28, 127.80, 116.40, 109.70, -0.14, -0.62; ^{29}Si NMR (79 MHz, $CDCl_3$, 25˚C): δ = -23.45 ($SiMe_2Ph$); MS (EI) m/z (rel. int.%): 278.20 (8), 263.5 (100), 159.30 (9); HRMS (EI) *m*/*z* calcd for $C_{13}H_{20}GeSi$: 278.05460, found $[M]^+$: 278.05565.



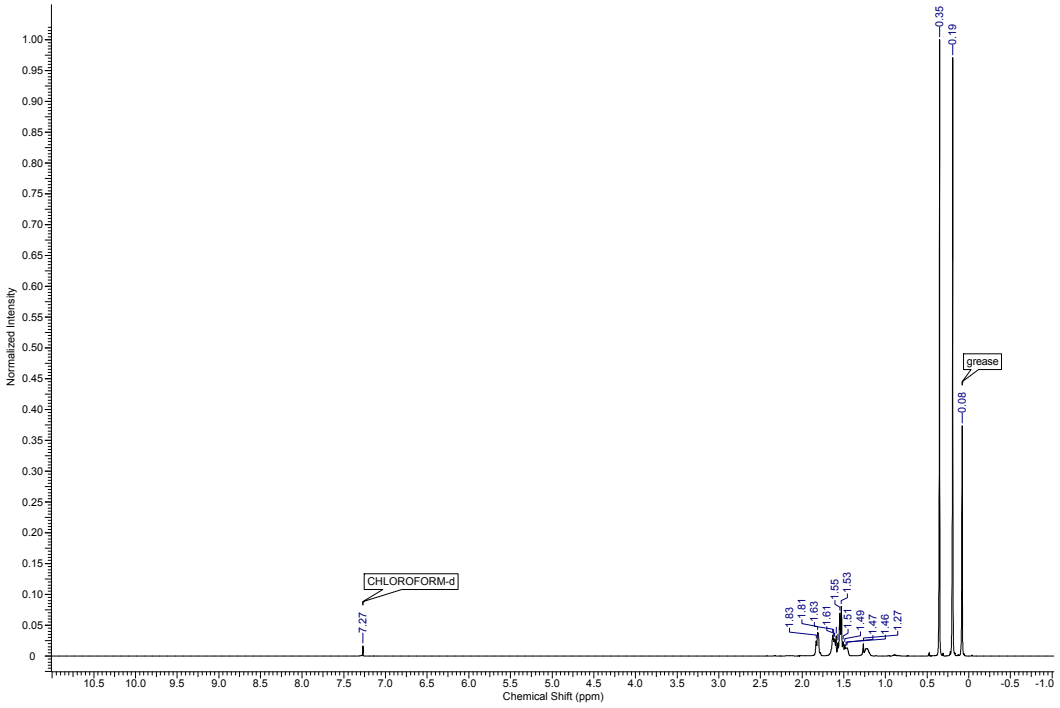


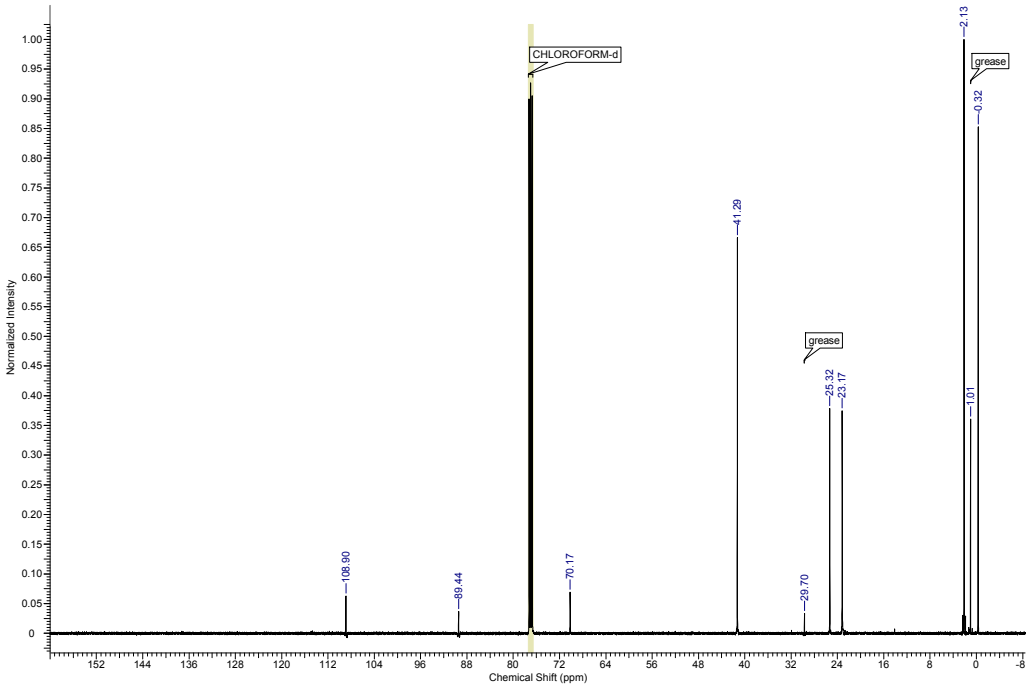


1-trimethylgermylethynyl-1-trimethylsiloxy-cyclohexane (8)

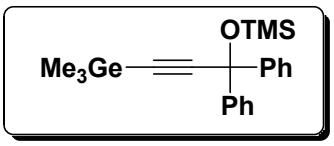


^{1}H NMR (300 MHz, $CDCl_3$, 25˚C): δ = 1.83-1.81 (m, 2H), 1.63-1.46 (m, 6H), 1.27-1.22 (m, 2H), 0.35 (s, 9H), 0.19 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, 25˚C): δ = 108.90, 89.44, 70.17, 41.29, 25.32, 23.17, 2.13, -0.32; ^{29}Si NMR (99 MHz, $CDCl_3$, 25˚C): δ = 12.78; MS (EI) m/z (rel. int.%): 299.1 (22), 285.1 (9), 269.20 (27), 195.30 (100), 119.20 (31); HRMS (EI) *m*/z calcd for $C_{14}H_{28}GeOSi$: 314.11212, found $[M - CH_3]^+$: 299.08670.

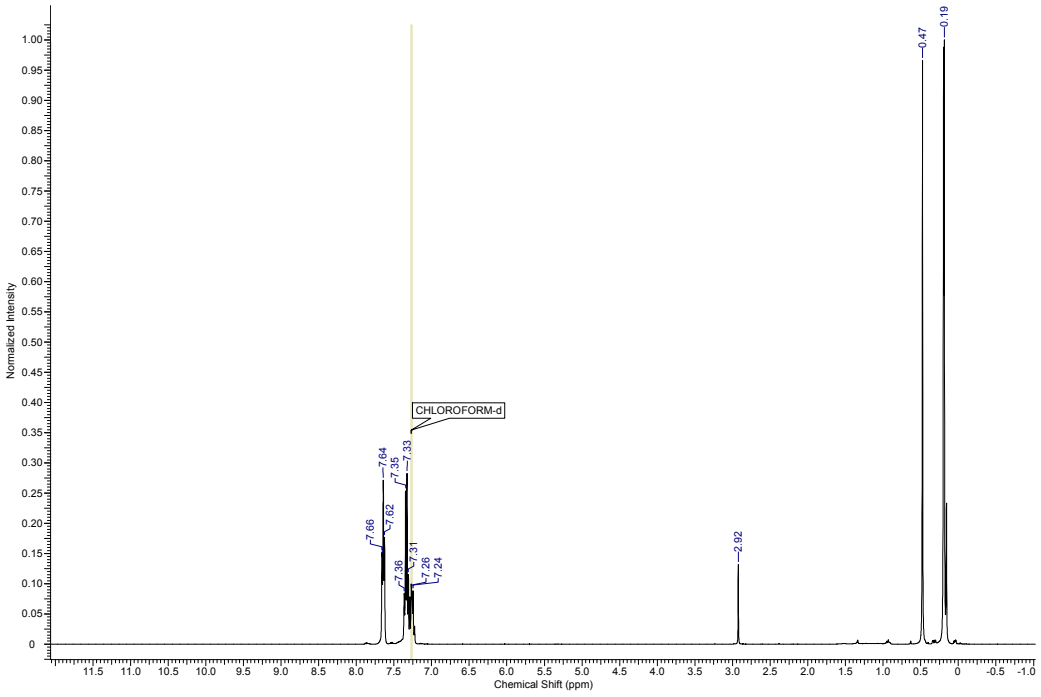




1-trimethylgermyl-3,3-diphenyl-3-trimethylsiloxy-1-propyne (9)



^{1}H NMR (400 MHz, $CDCl_3$, 25˚C): δ = 7.66-7.62 (m, 4H), 7.36-7.24 (m, 6H), 0.47 (s, 9H), 0.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C): δ = 146.81, 127.97, 127.08, 125.93, 107.00, 93.17, 75.80, 1.54, -0.40; ^{29}Si NMR (79 MHz, $CDCl_3$, 25˚C): δ = 17.81; MS (EI) m/z (rel. int.%): 279.2 (100), 105.20 (35), 280.30 (25), 321.20 (10), 383.10 (5); HRMS (EI) *m*/*z* calcd for $C_{21}H_{28}GeOSi$: 398.11212, found $[M]^+$: 398.11016.


Normalized Intensity
Chemical Shift (ppm)
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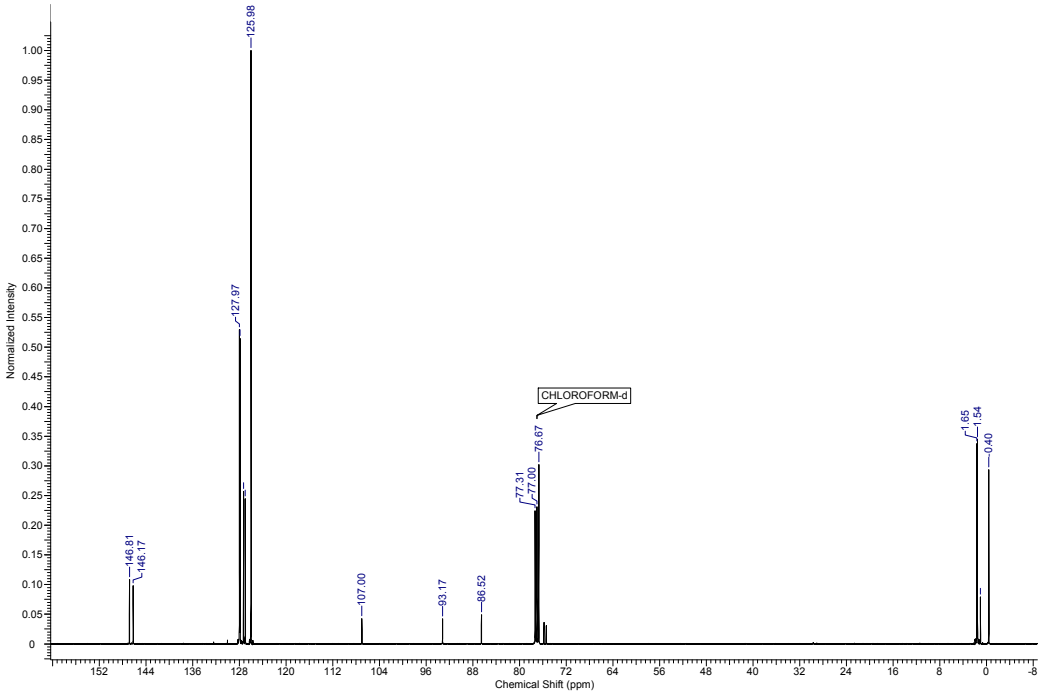
7.33
7.66
7.62
7.36
7.31
7.26
7.24
2.92
0.47
0.19


Normalized Intensity
Chemical Shift (ppm)
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1.65
1.54
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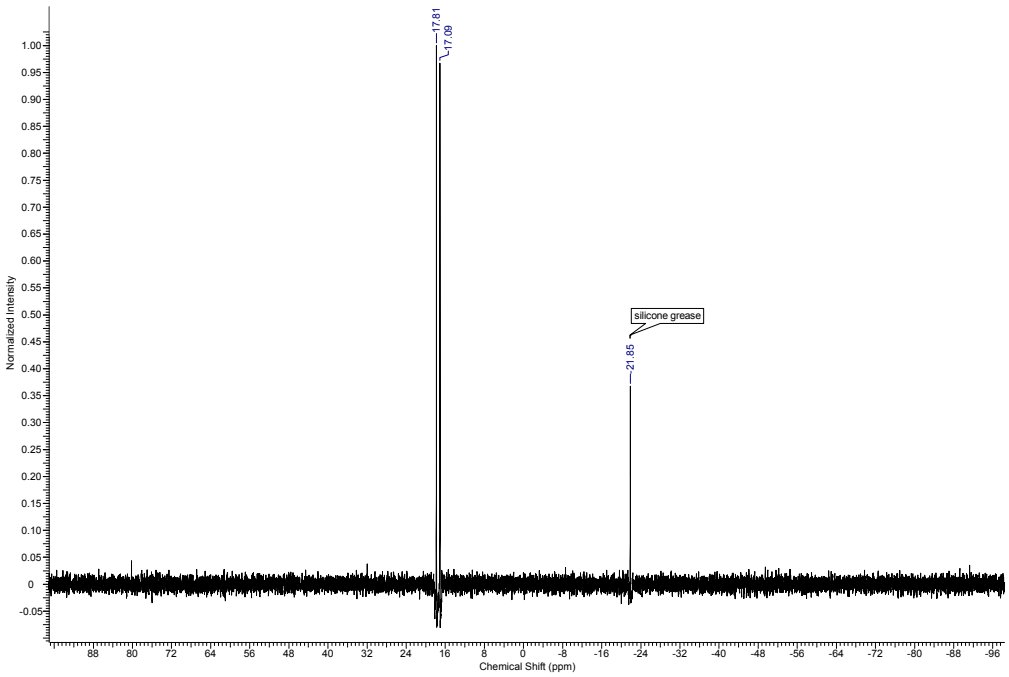
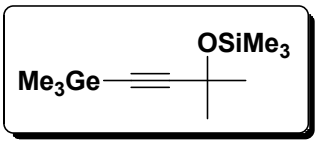
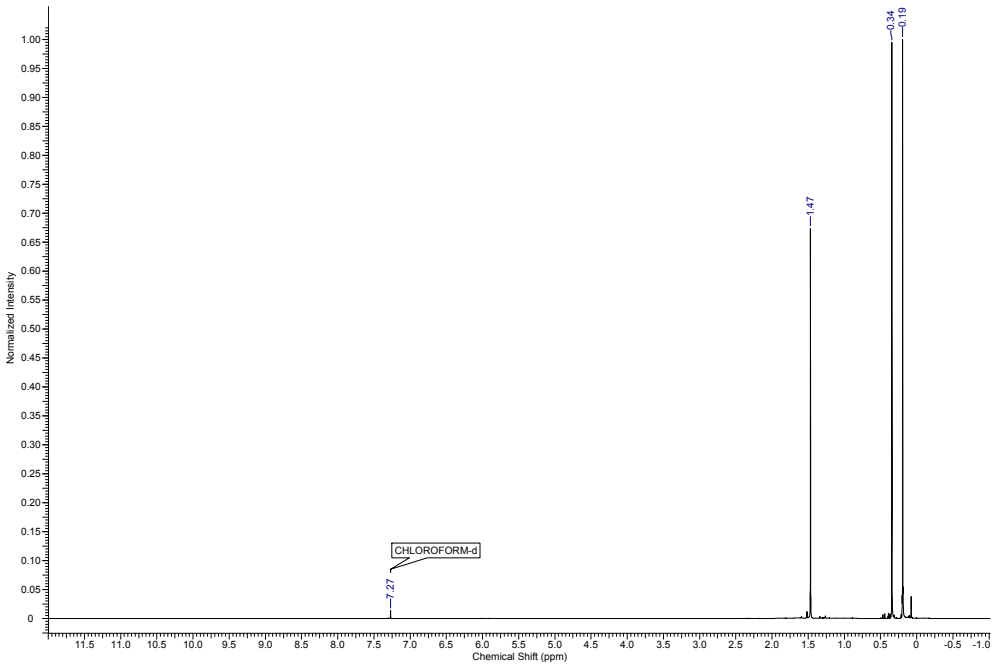
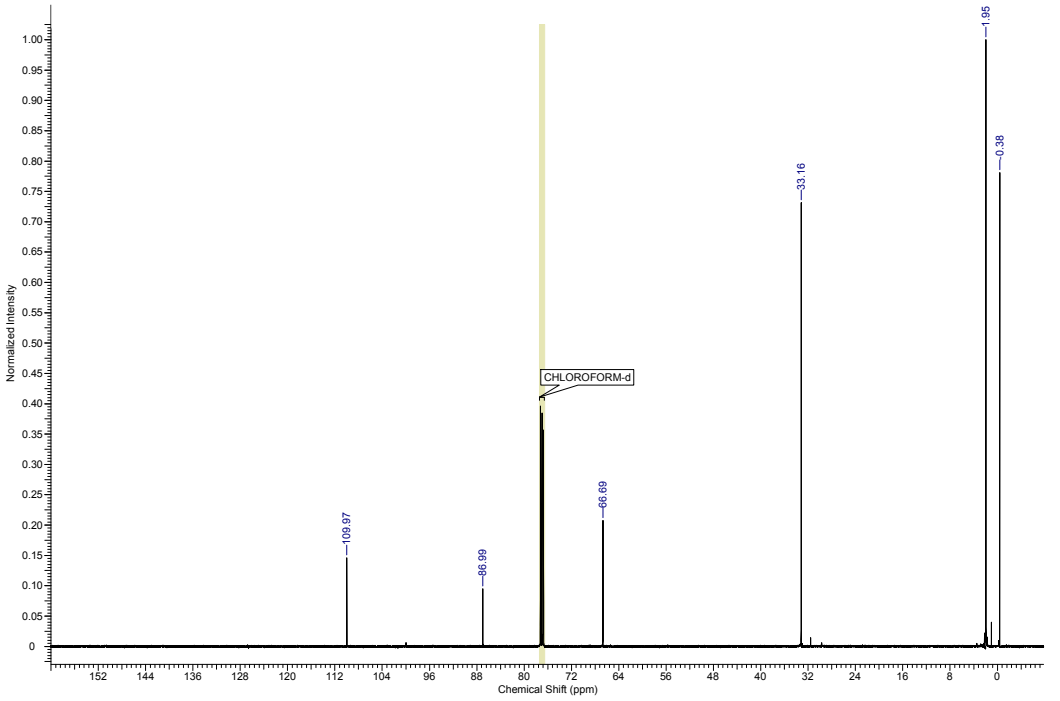


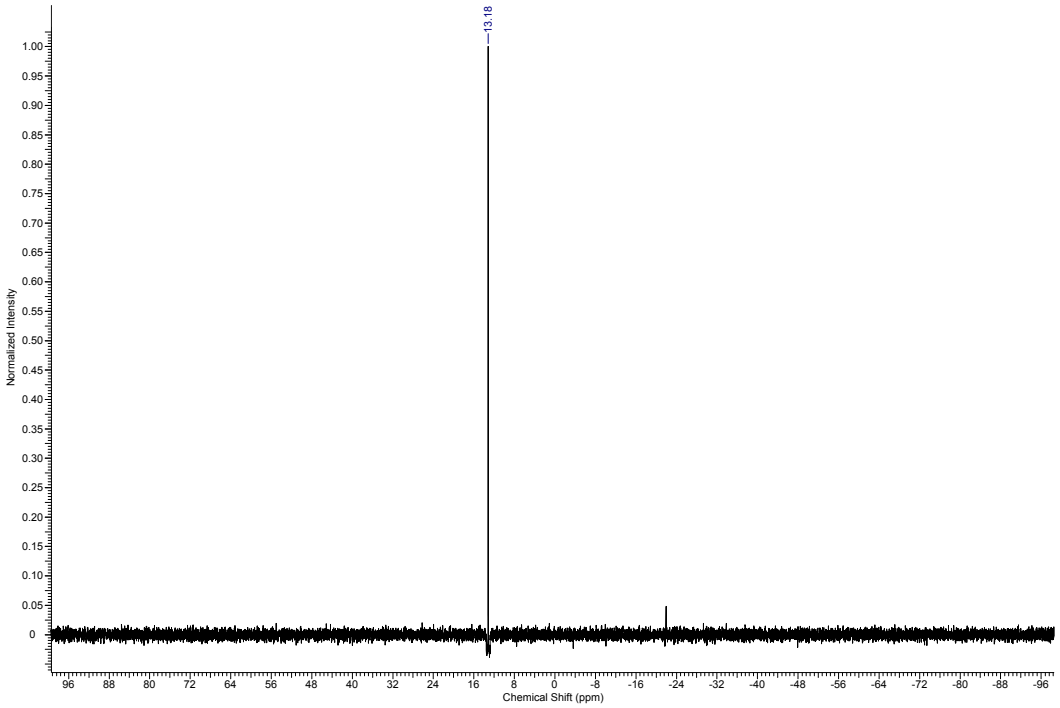
Trimethyl(2-methyl-4-(trimethylgermyl)but-3-yn-2-yloxy)silane (10)



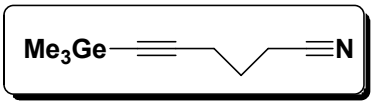
^{1}H NMR (500 MHz, $CDCl_3$, 25˚C): δ = 1.47 (s, 6H), 0.34 (s, 9H), 0.19 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, 25˚C): δ = 109.97, 86.99, 66.69, 33.16, 1.95, -0.38; ^{29}Si NMR (99 MHz, $CDCl_3$, 25˚C): δ = 13.18; MS(EI) m/z (rel. int.%): 259.10 (100), 215.30 (2), 201.20 (19), 199.30 (13), 185.30 (14), 119.20 (50); HRMS – neither molecular nor fragmentary ions were observed.



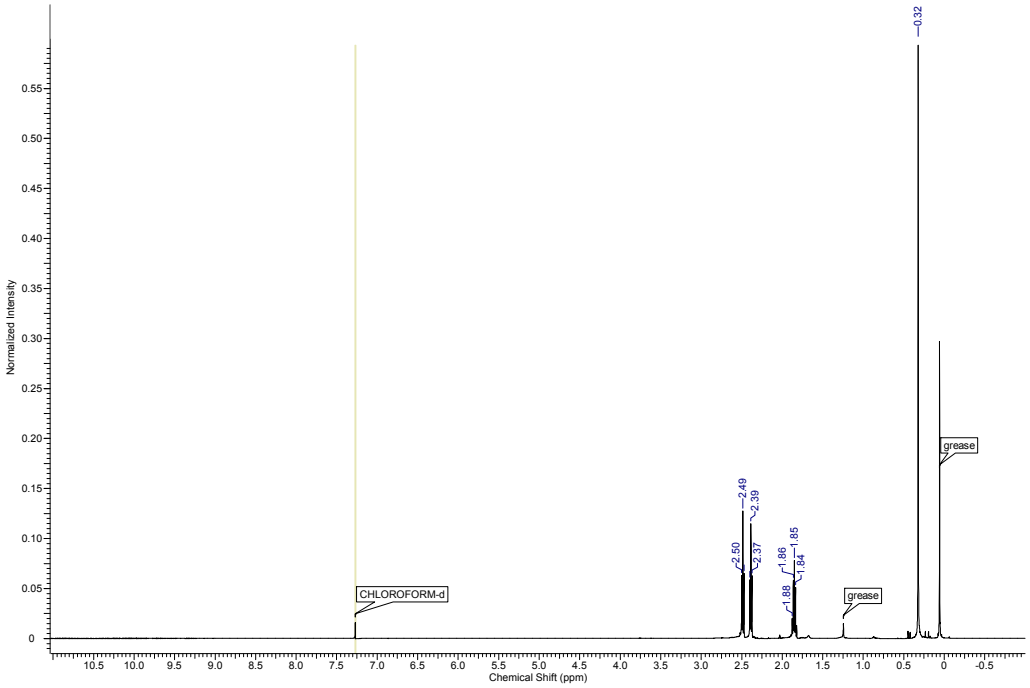


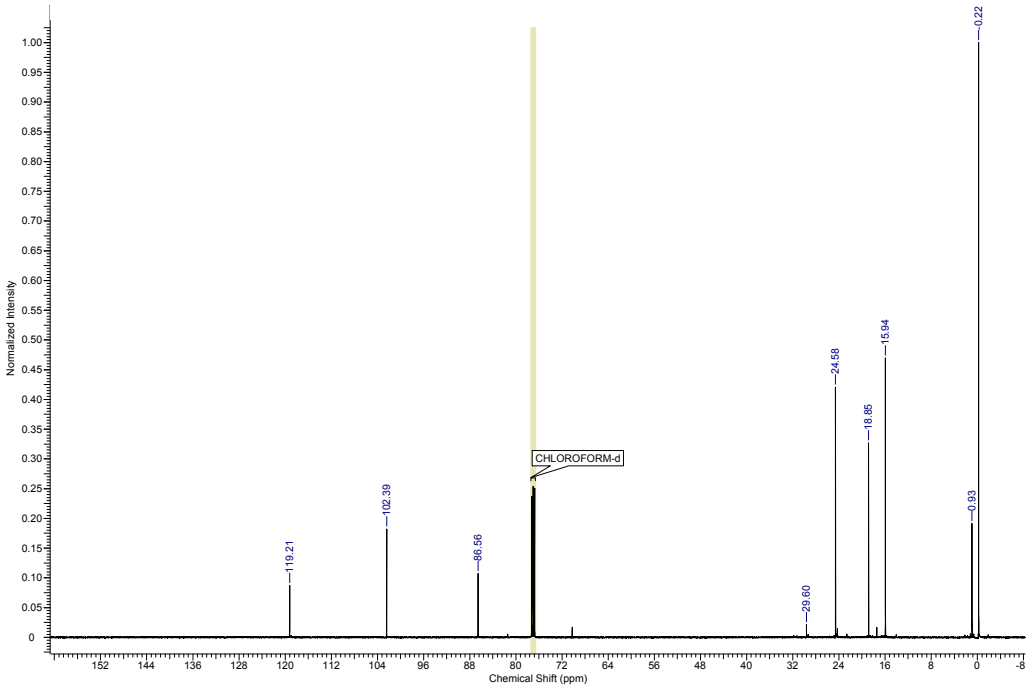


6-(trimethylgermyl)hex-5-ynenitrile (11)

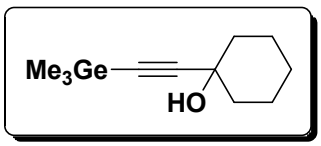


^{1}H NMR (500 MHz, $CDCl_3$, 25˚C): δ = 2.49 (t, *J* = 7.2 Hz, 2H), 2.39 (t, *J*=6.7 Hz, 2H), 1.88-1.82 (m, 2H), 0.32 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, 25˚C): δ = 119.21, 102.39, 86.56, 24.58, 18.85, 15.94; -0.22; MS (EI) m/z (rel. int.%): 196.20 (100), 143.20 (9), 89.10 (5); HRMS (EI) *m*/*z* calcd for $C_9H_{15}GeN$: 211.04163, found $[M - CH_3]^+$: 196.01767.

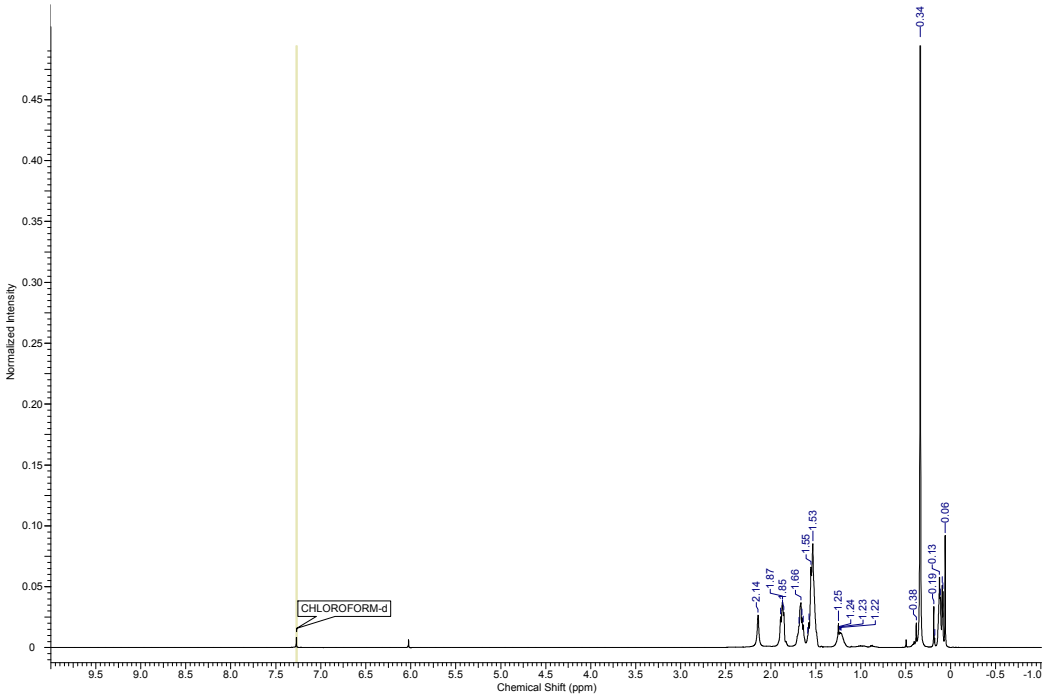


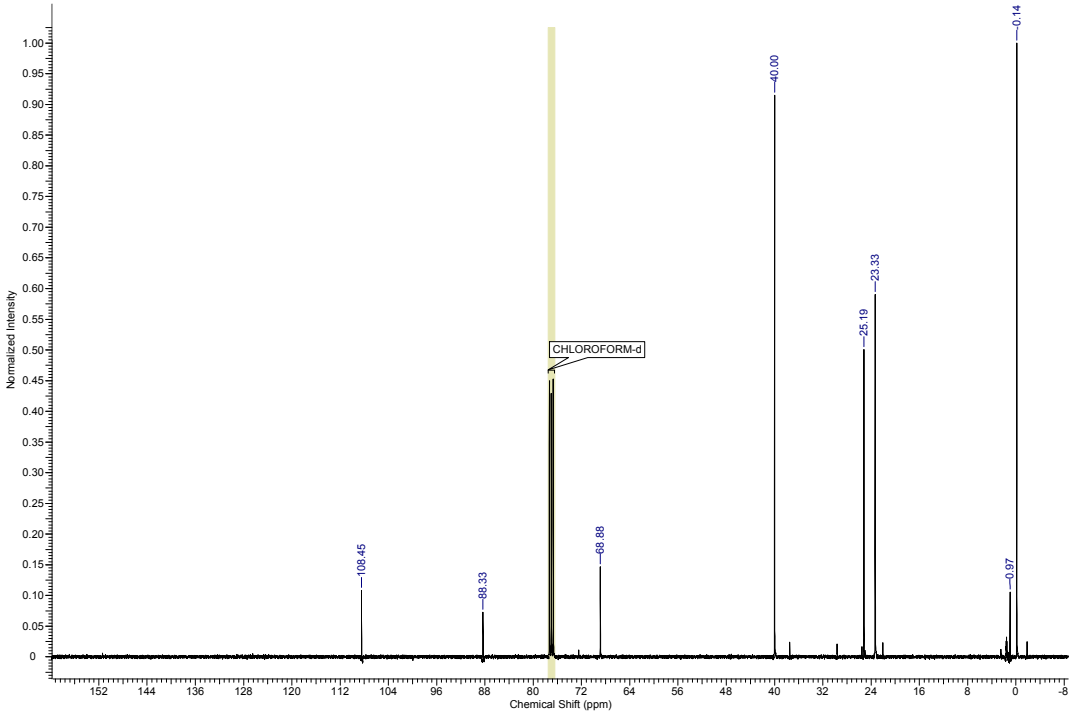


1-((trimethylgermyl)ethynyl)cyclohexanol (12)

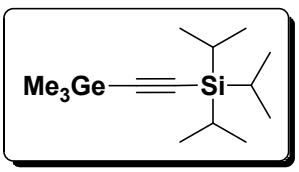


^{1}H NMR (400 MHz, $CDCl_3$, 25˚C): δ = 2.14 (s, 1H), 1.89-1.85 (m, 2H), 1.69-1.53 (m, 6H), 1.25-1.22 (m, 2H), 0.34 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C): δ = 108.45, 88.33, 68.88, 40.00, 25.19, 23.33, -0.14; MS (EI) m/z (rel. int.%): 226.90 (100), 211.00 (33), 197.20 (26), 143.20 (7), 123.00 (14), 119.10 (50), 105.30 (37); HRMS (EI) *m*/*z* calcd for $C_{10}H_{17}OGe$: 242.07259, found $[M + H]^+$: 227.04782.

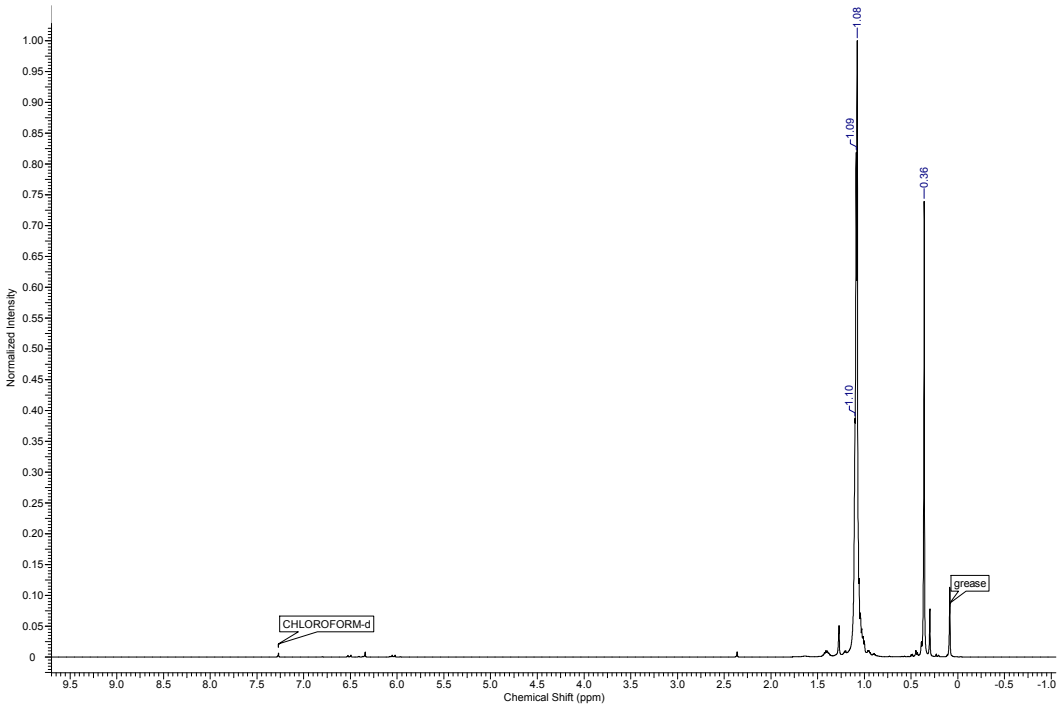


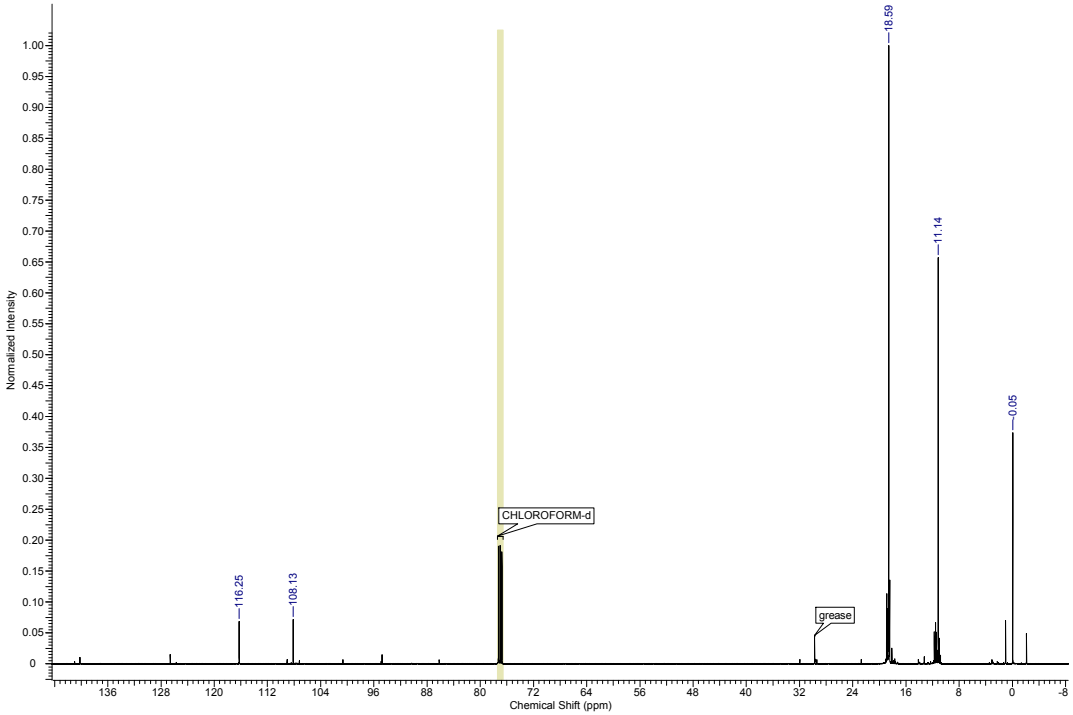


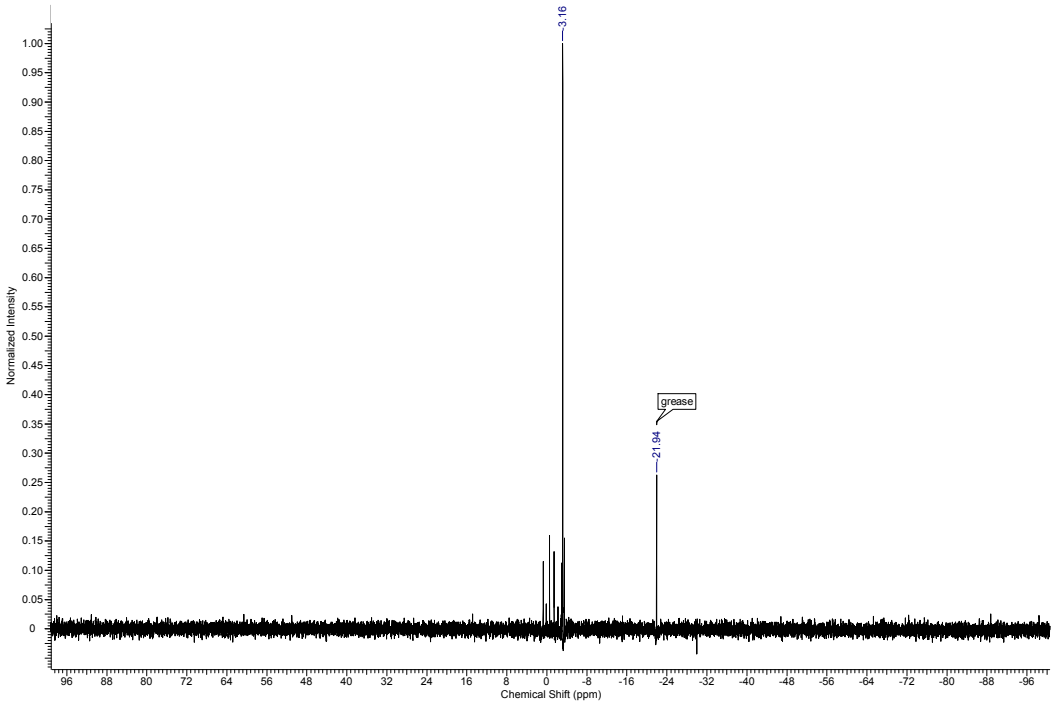
1-tri-iso-propylsilyl-2-trimethylgermylethyne (13)



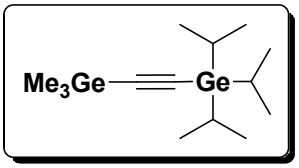
^{1}H NMR (400 MHz, $CDCl_3$, 25˚C): δ = 1.10-1.05 (m, 21H), 0.36 (s, 9H), ^{13}C NMR (101 MHz, $CDCl_3$, 25˚C): δ = 116.25, 108.12, 18.59, 11.11, -0.04; ^{29}Si NMR (79 MHz, $CDCl_3$, 25˚C): δ = -3.16; MS(EI) m/z (rel. int.%): 284.8 (88), 256.60 (61), 215.00 (93), 199.00 (22), 118.9 (30); HRMS – neither molecular nor fragmentary ions were observed.


1.08
1.09
0.36
1.10
CHLOROFORM-d
grease
Normalized Intensity
Chemical Shift (ppm)

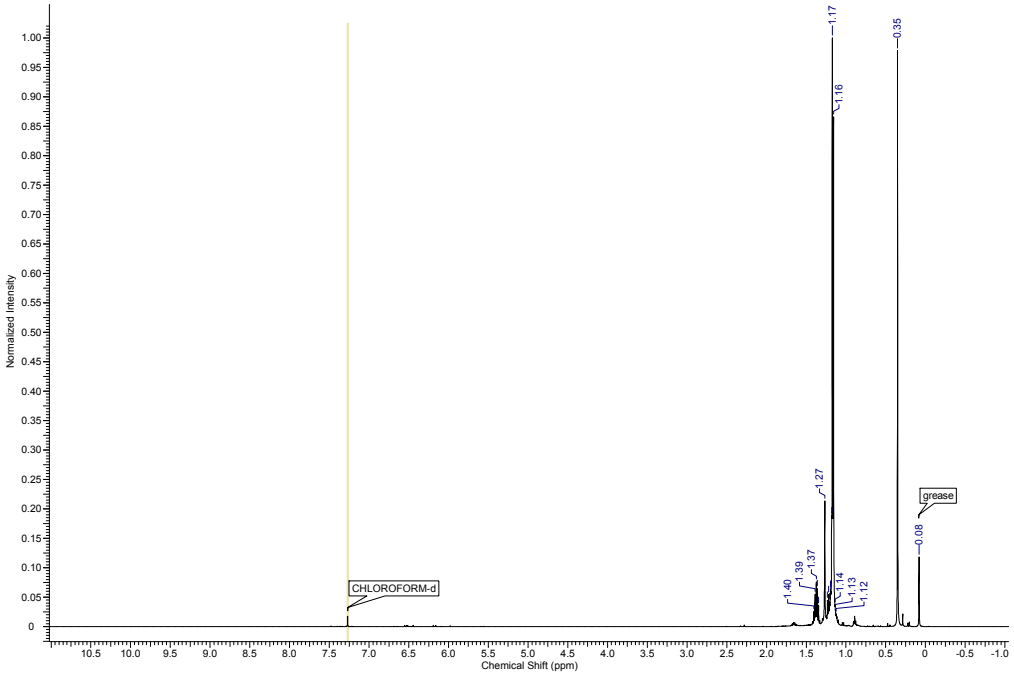

18.59
11.14
0.05
116.25
108.13
CHLOROFORM-d
grease
Normalized Intensity
Chemical Shift (ppm)

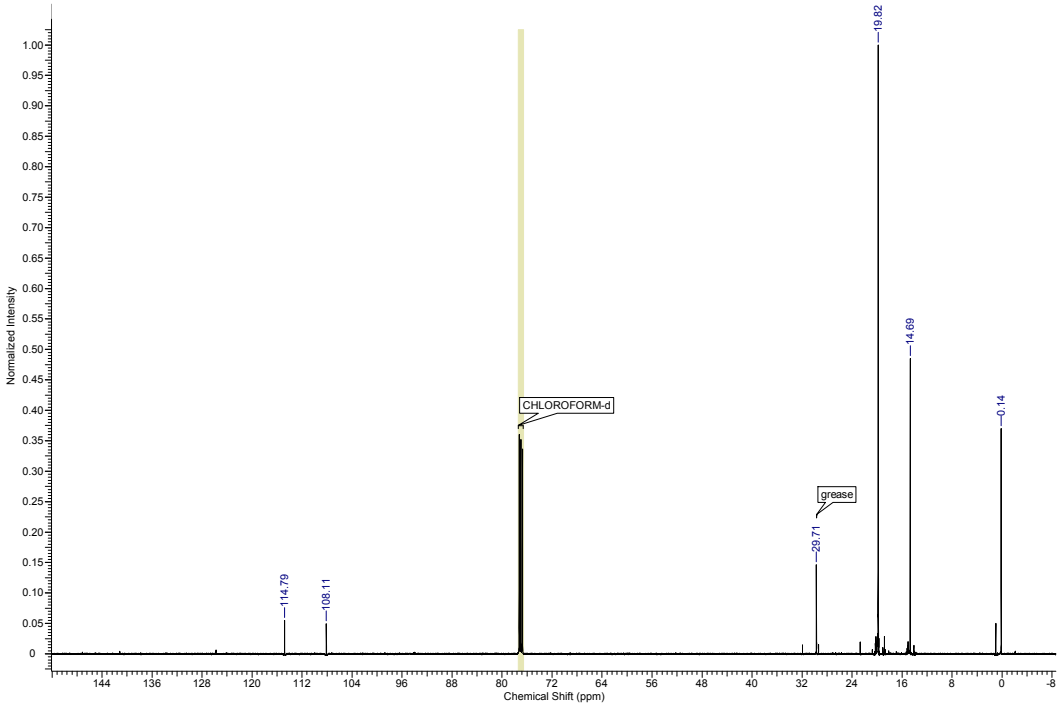


1-tri-iso-propylgermyl-2-trimethylgermylethyne (14)

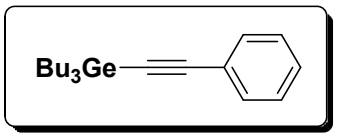


^{1}H NMR (500 MHz, $CDCl_3$, 25˚C): δ = 1.40-1.16 (m, 21H), 0.35 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, 25˚C): δ = 114.79, 108.11, 19.82, 14.69, 0.14; MS(EI) m/z (rel. int.%): 303.30 (31), 299.40 (47), 259.20 (32), 201.50 (100), 198.30 (62); HRMS – neither molecular nor fragmentary ions were observed.

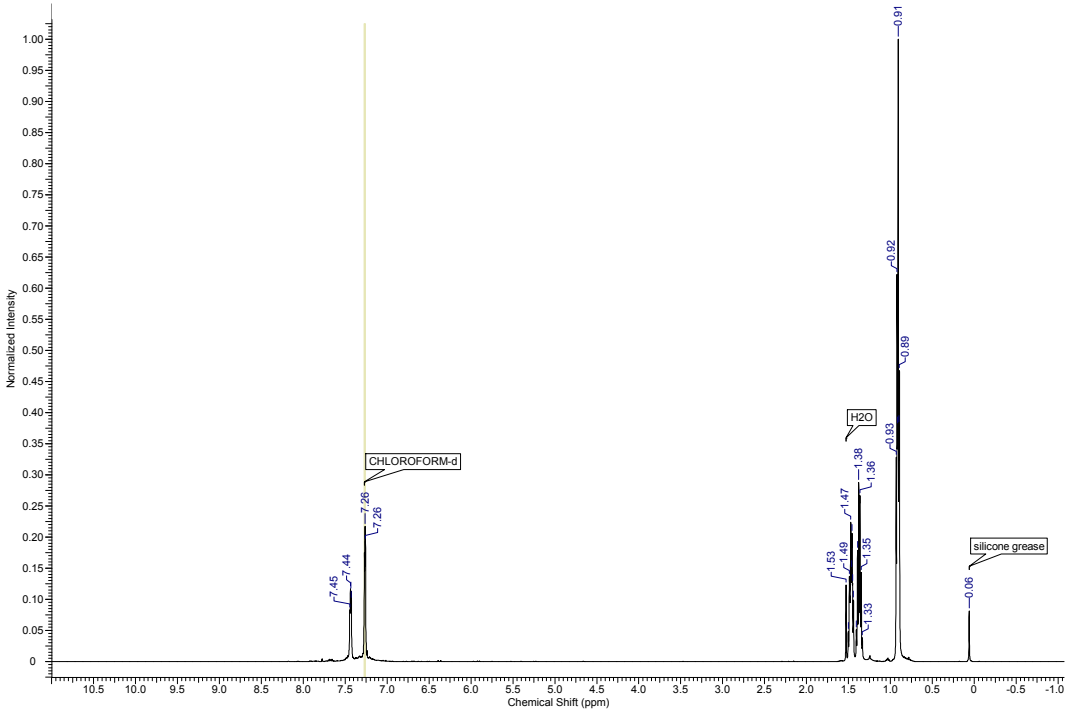


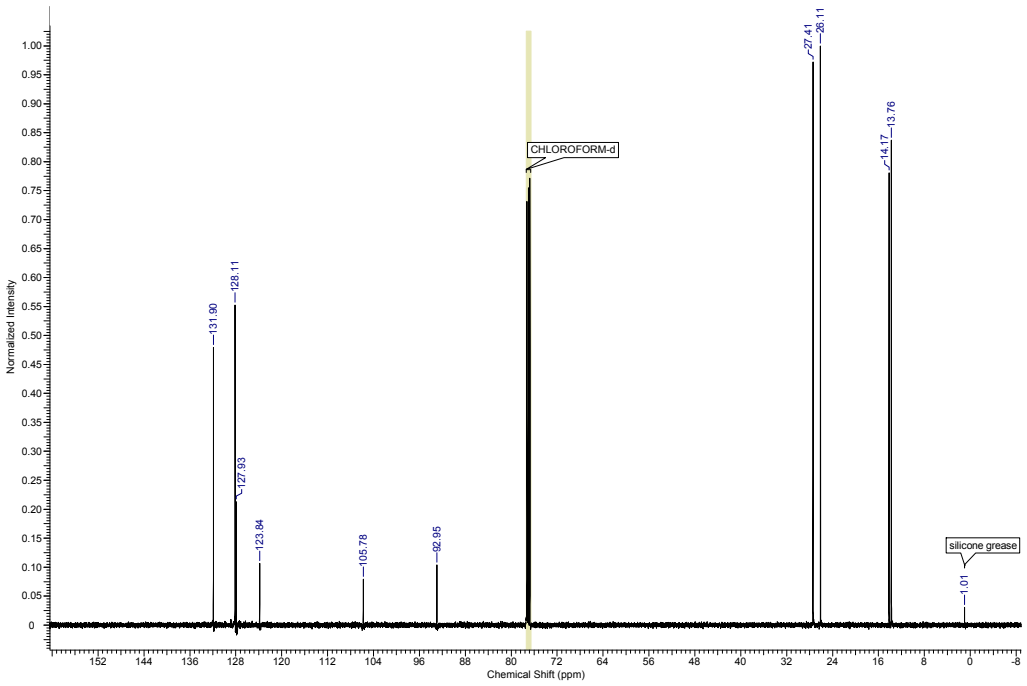


Tributyl(phenylethynyl)germane (15)

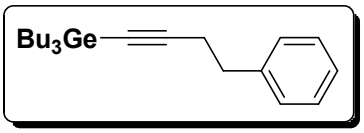


^{1}H NMR (500 MHz, $CDCl_3$, 25˚C): δ = 7.45-7.43 (m, 2H), 7.26 (m, 3H); 1.50-1.44 (m, 6H), 1.41-1.33 (m, 6H), 0.93-0.89 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$, 25˚C): δ = 131.90, 128.11, 127.93, 123.84, 105.78, 92.95, 27.41, 26.11, 14.17, 13.76; MS (EI) m/z (rel. int.%): 347.5 (4), 289.30 (100), 232.8 (40), 203.5 (83), 189.50 (82) 101.3 (13); HRMS (EI) *m*/*z* calcd for $C_{20}H_{32}Ge$ 346.17158, found $[M - C_4H_9]^+$: 289.10009.

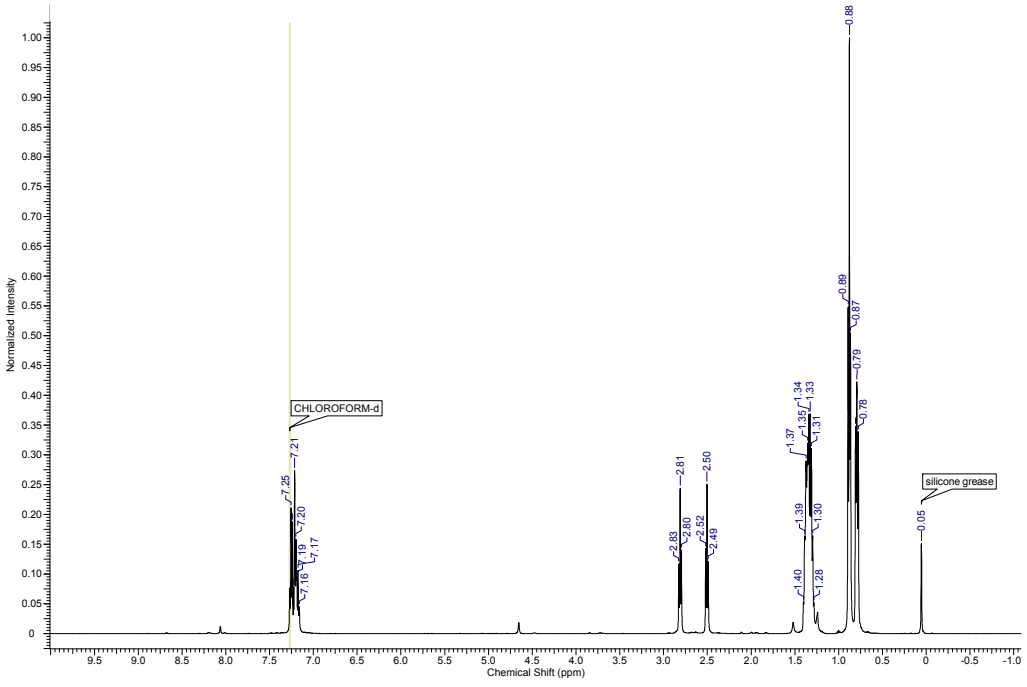


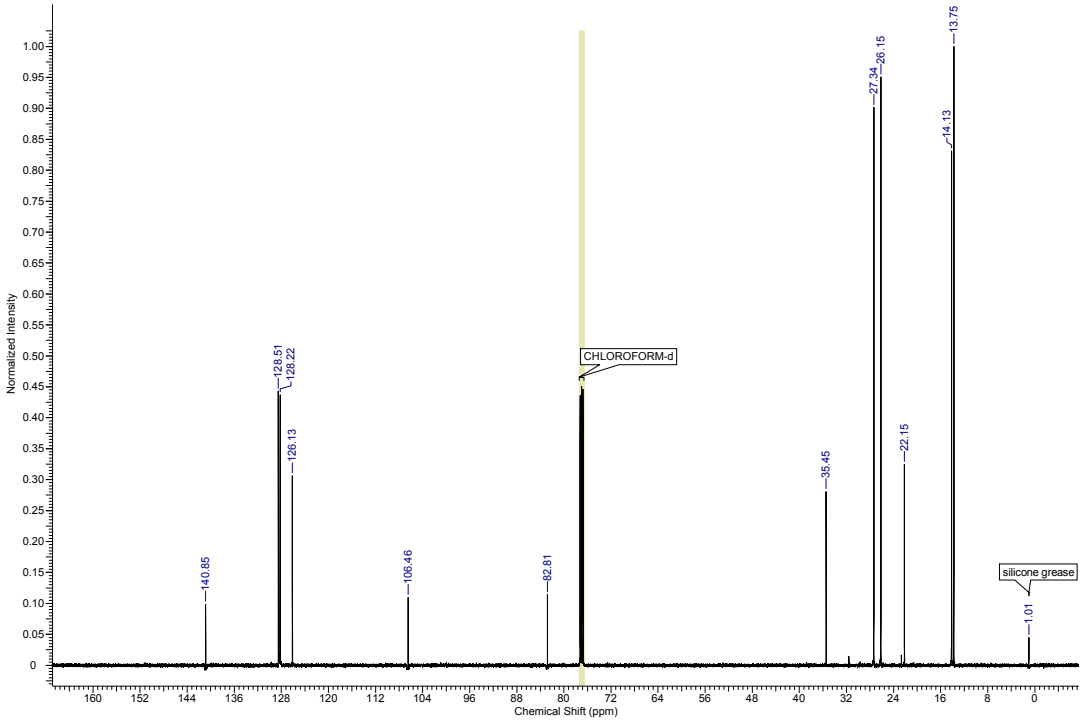


Tributyl(4-phenylbut-1-ynyl)germane (16)

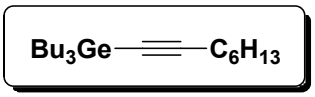


^{1}H NMR (500 MHz, $CDCl_3$, 25˚C): δ = 7.25-7.16 (m, 5H), 2.81 (t, J=7.5, 2H), 2.50 (t, J=7.5, 2H), 1.40-1.28 (m, 12H), 0.88 (t, J=6.7, 9H), 0.81-0.78 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, 25˚C): δ =140.85, 128.51, 128.22, 126.13, 106.46, 82.81, 35.45, 27.34, 26.15, 22.15, 14.13, 13.75; MS (EI) m/z (rel. int.%): 373.00 (4), 317.00 (29), 259.10 (82), 187.20 (45), 129.10 (28); HRMS–FAB: *m*/*z* calcd for $C_{22}H_{36}Ge$: 374.20288, found $[M - C_4H_9]^+$: 317.13179.

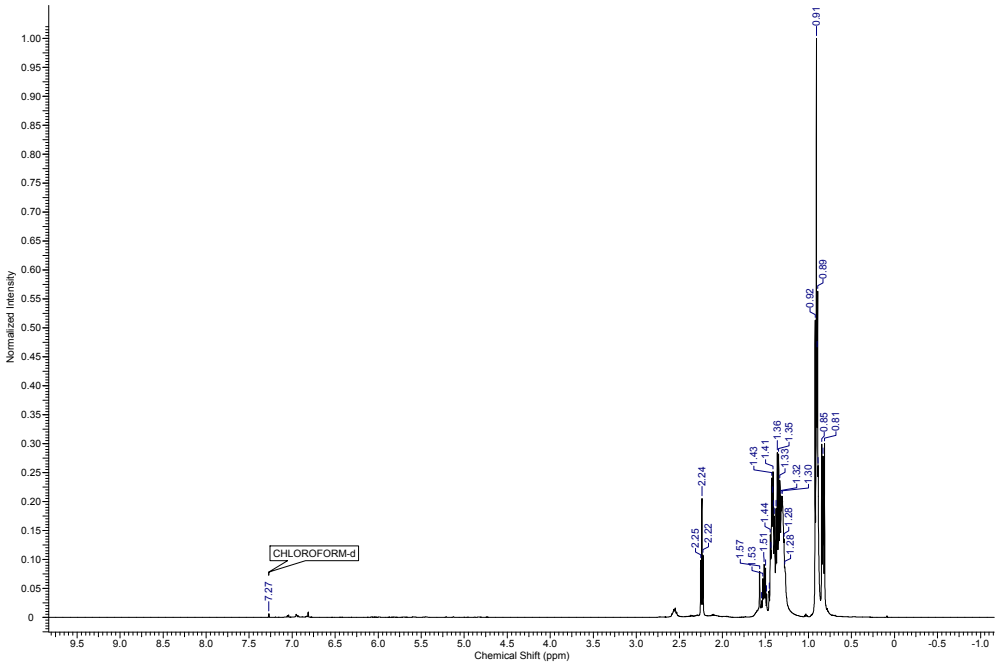


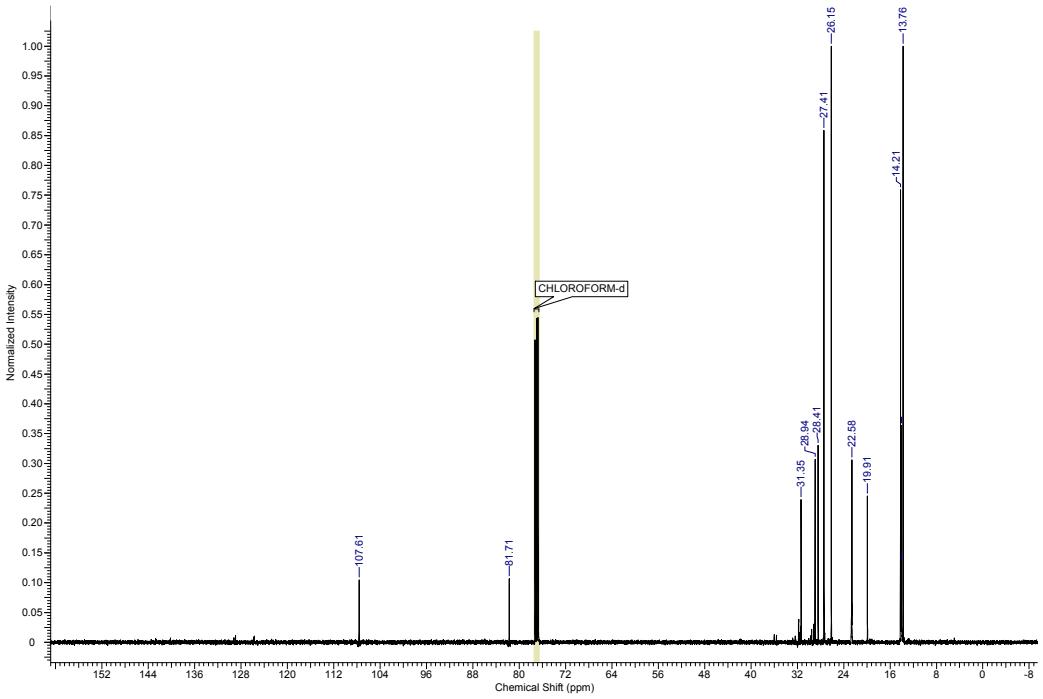


Tributyl(oct-1-ynyl)germane (17)

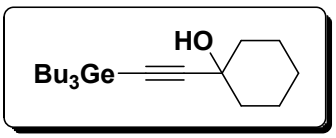


^{1}H NMR (500 MHz, $CDCl_3$, 25˚C): δ = 2.24 (t, J=7 Hz, 2H), 1.54-1.50 (m, 6H), 1.46-1.28 (m, 17H), 0.92-0.89 (m, 9H), 0.83 (t, J=7, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 25˚C): δ = 107.61, 81.71, 31.35, 28.94, 28.41, 27.41, 26.15, 22.58, 19.91, 14.21, 14.03, 13.76; MS (EI) m/z (rel. int.%): 297.30 (50), 241.30 (56), 199.20 (25), 183.20 (80), 169.20 (47), 153.20 (45), 109.20 (55); HRMS–FAB: *m*/*z* calcd for $C_{20}H_{40}Ge$: 354.23418, found $[M - C_4H_9]^+$: 297.16344.

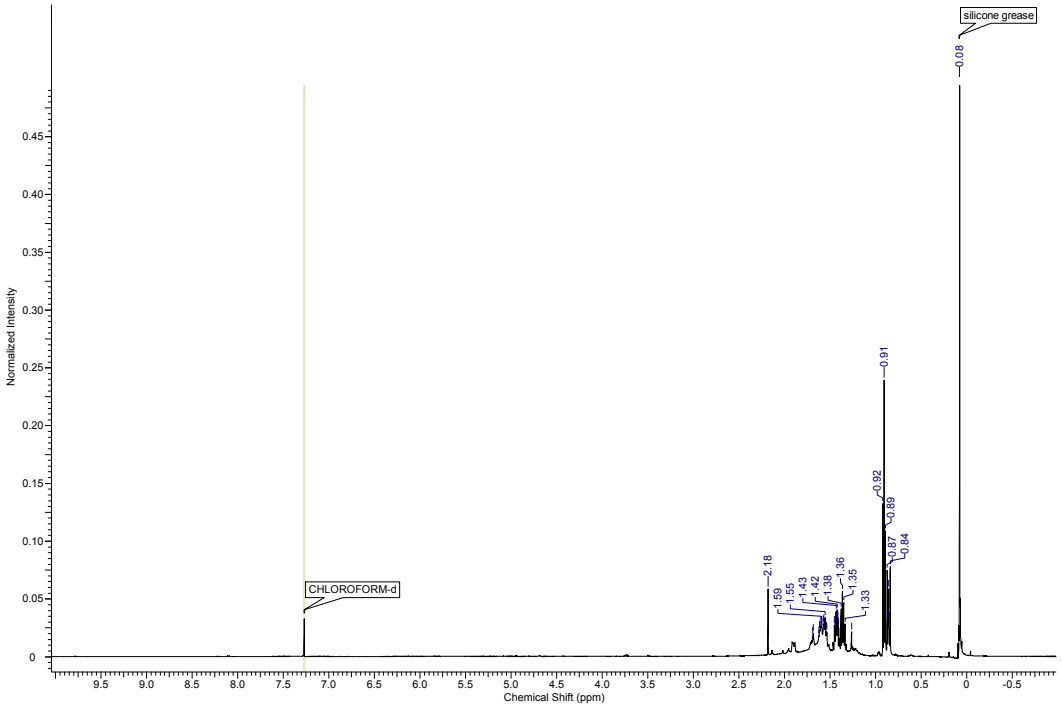


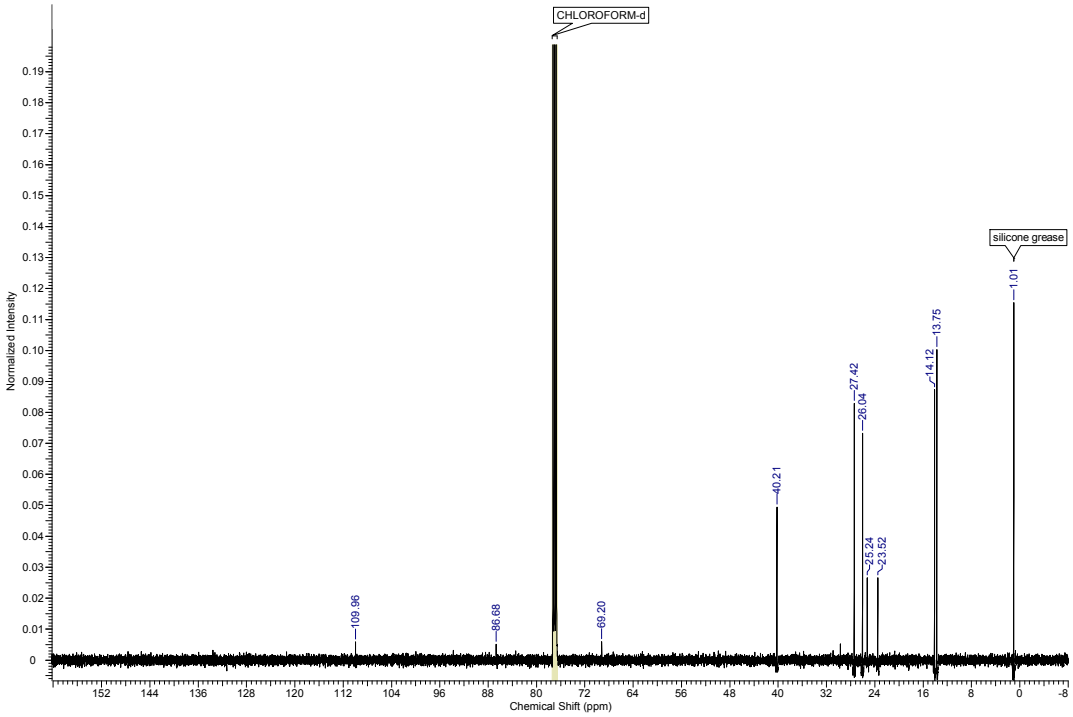


1-((tributylgermyl)ethynyl)cyclohexanol (18)

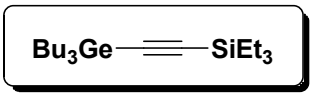


^{1}H NMR (500 MHz, $CDCl_3$, 25˚C): δ = 2.18 (s, 1H), 1.69-1.54 (m, 11H), 1.45-1.34 (m, 12H), 0.92-0.84 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$, 25˚C): δ = 109.96, 86.68, 69.20, 40.21, 27.42, 26.04, 25.24, 23.52, 14.12, 13.75; MS (EI) m/z (rel. int.%): 367.5 (2), 293.3 (9), 255.30 (100), 181.30 (43); HRMS – neither molecular nor fragmentary ions were observed.

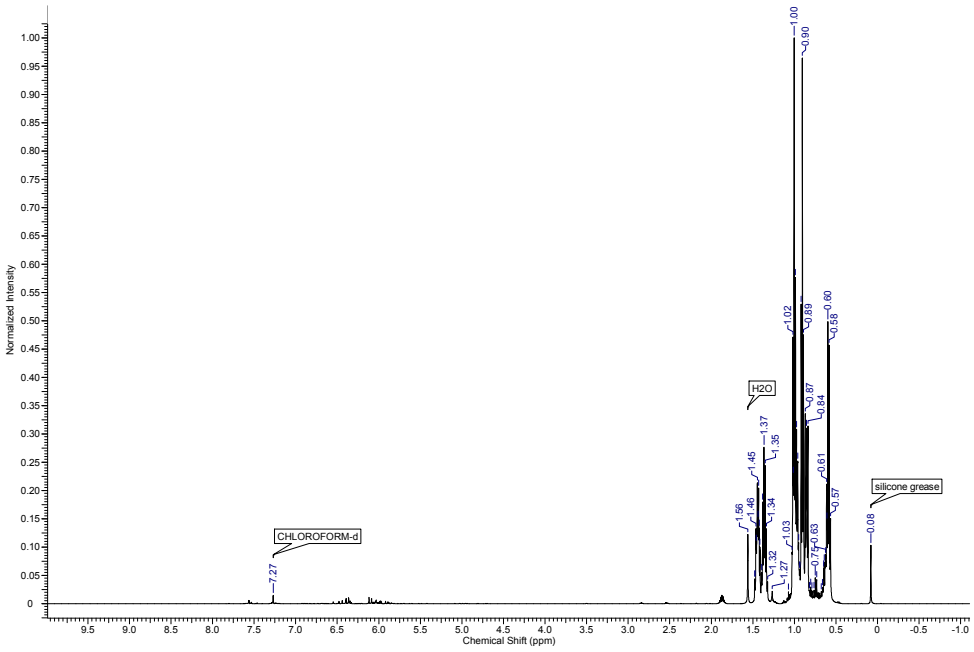


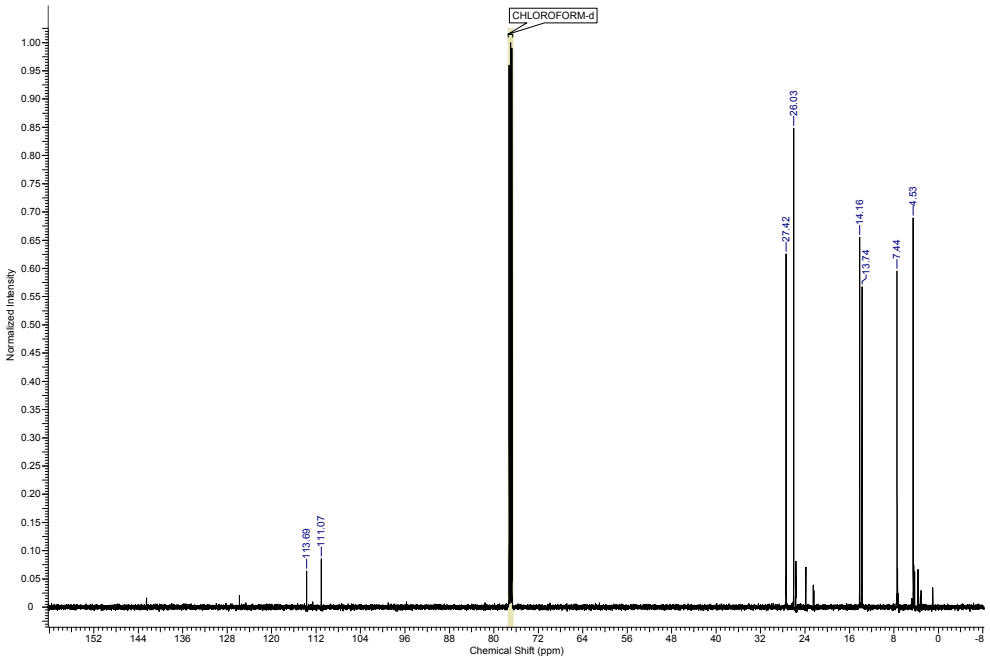


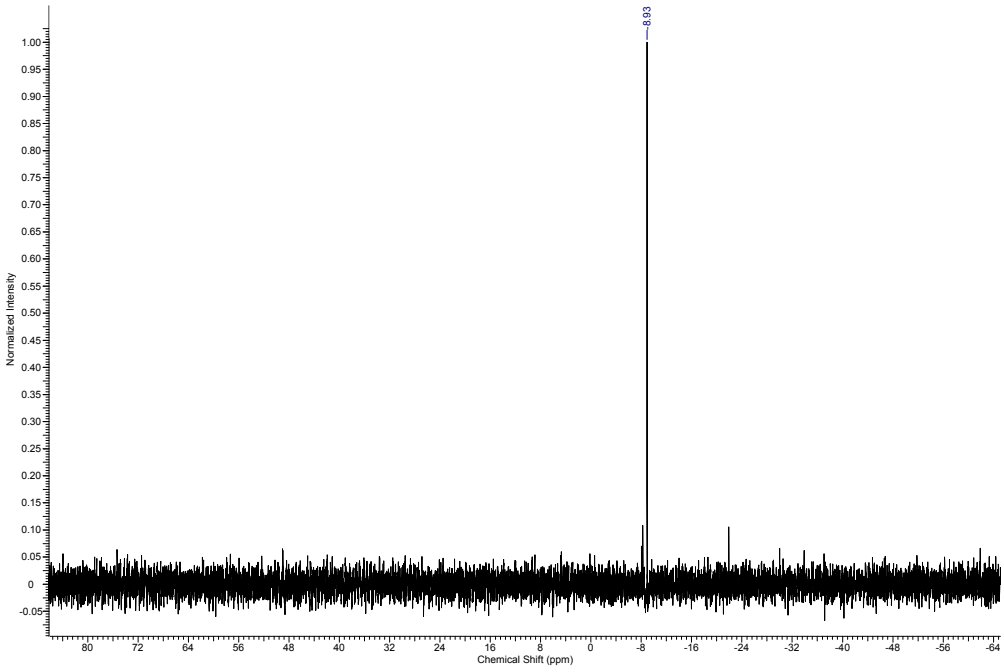
Triethyl((tributylgermyl)ethynyl)silane (19)



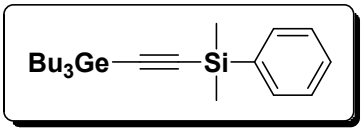
^{1}H NMR (500 MHz, $CDCl_3$, 25˚C): δ = 1.48-1.32 (m, 12H), 1.00 (t, J=8, 3H), 0.92-0.84 (m, 15H), 0.61-0.57 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, 25˚C): δ = 113.69, 111.07, 27.42, 26.03, 14.16, 13.74, 7.44, 4.53; ^{29}Si NMR (99 MHz, $CDCl_3$, 25˚C): δ = -8.91; MS (EI) m/z (rel. int.%): 299.20 (20), 271.30 (100), 269.30 (85), 209.50 (16); HRMS–FAB: *m*/*z* calcd for $C_{20}H_{42}GeSi$: 384.22676, found $[M - C_4H_9]^+$: 327.15482.



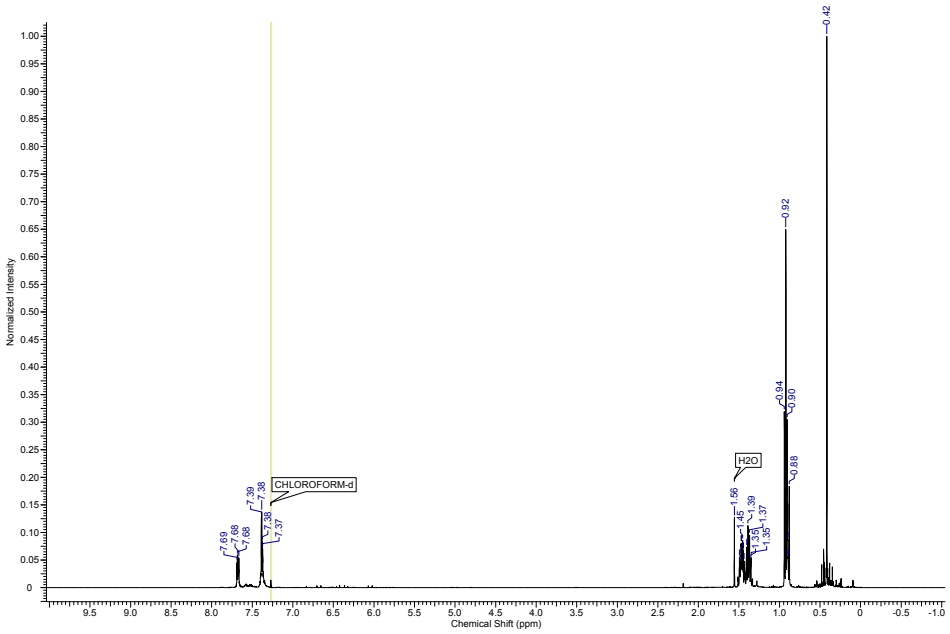


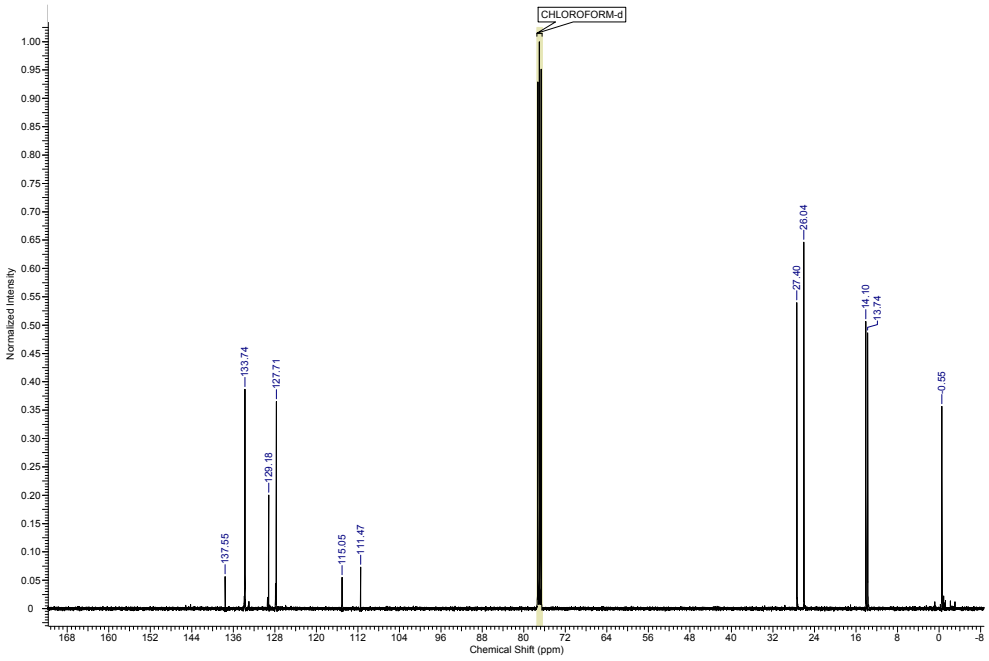


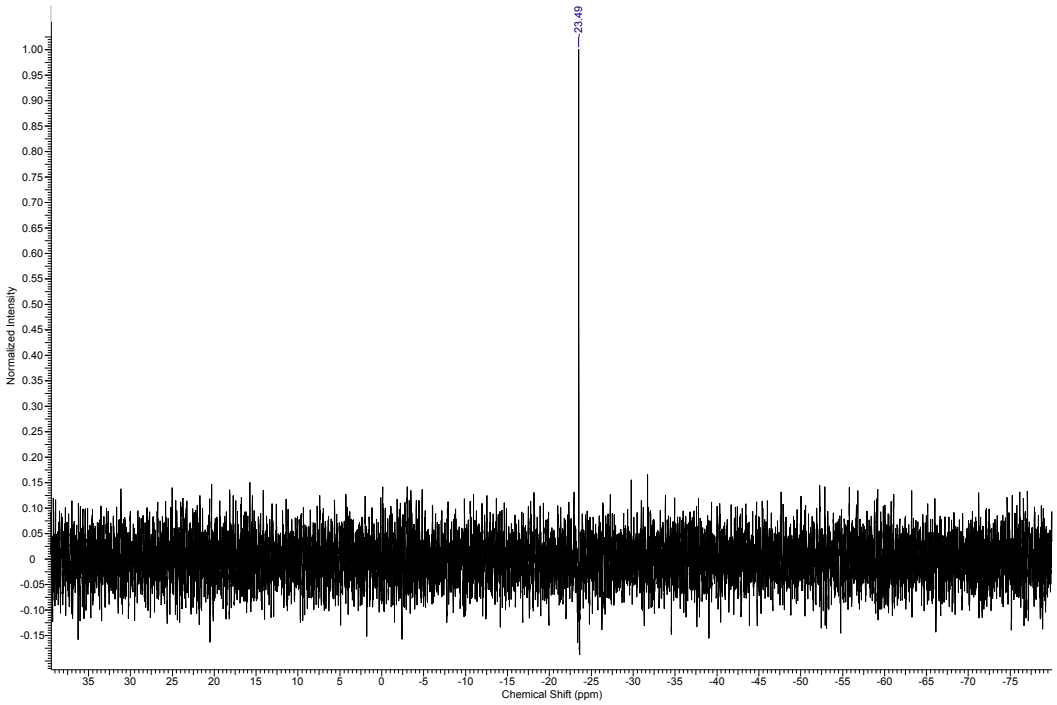
Dimethyl(phenyl)((tributylgermyl)ethynyl)silane (20)



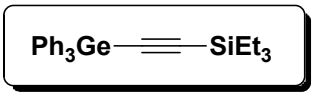
^{1}H NMR (400 MHz, $CDCl_3$, 25˚C): δ = 7.69-7.66 (m, 2H), 7.39-7.36 (m, 3H), 1.49-1.35 (m, 12H), 0.94-0.88 (m, 15H), 0.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C): δ = 137.55, 133.74, 129.18, 127.71, 115.05, 111.47, 27.40, 26.04, 14.10, 13.74, -0.55; ^{29}Si NMR (79 MHz, $CDCl_3$, 25˚C): δ = -23.49; MS (EI) m/z (rel. int.%): 347.5 (9), 291.5 (100), 288.5 (79), 243 (23), 219.5 (10), 189.5 (55); HRMS–FAB: *m*/*z* calcd for $C_{22}H_{38}GeSi$: 404.19546, found $[M - C_4H_9]^+$: 347.12482.


Normalized Intensity
Chemical Shift (ppm)
CHLOROFORM-d
H2O
7.69
7.68
7.68
7.39
7.38
7.38
7.37
1.56
1.45
1.39
1.37
1.35
1.35
0.94
0.92
0.90
0.88
0.42

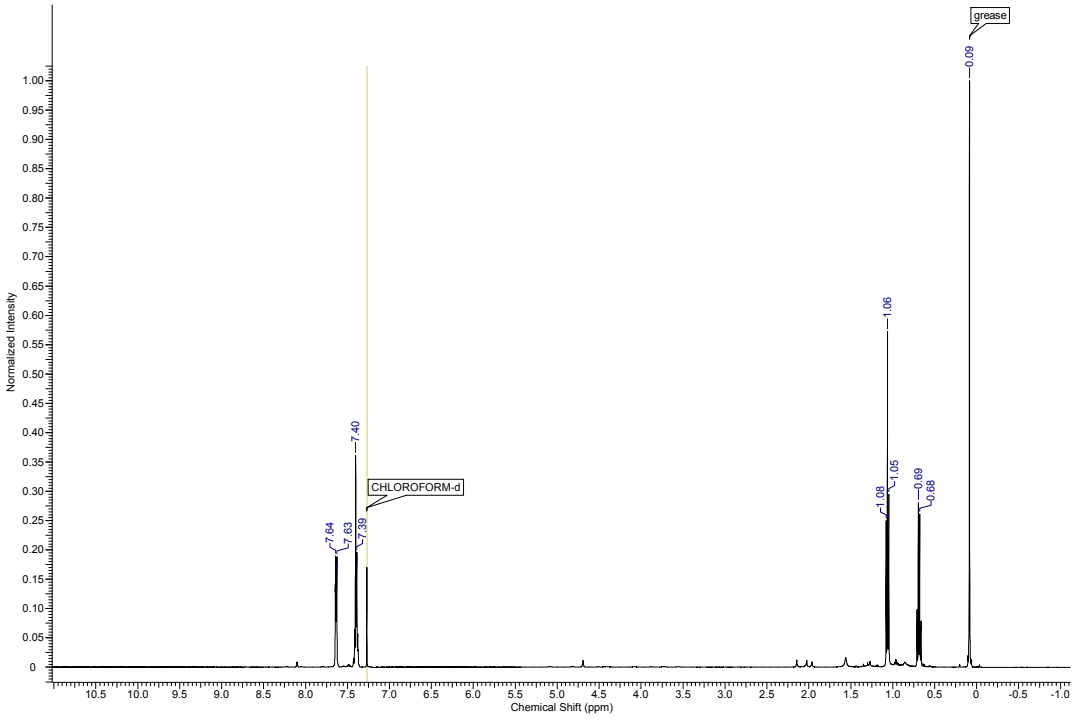

Normalized Intensity
Chemical Shift (ppm)
CHLOROFORM-d
137.55
133.74
129.18
127.71
115.05
111.47
77.48
77.16
76.84
27.40
26.04
14.10
13.74
0.55

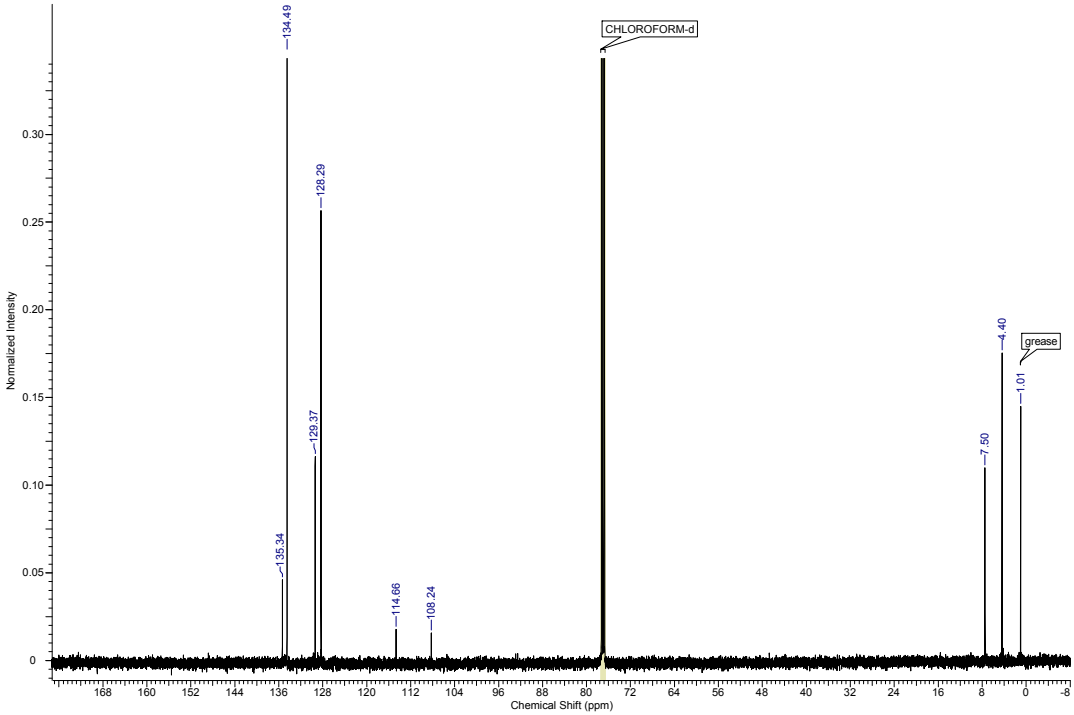


Triethyl((triphenylgermyl)ethynyl)silane (21)



^{1}H NMR (400 MHz, $CDCl_3$, 25˚C): δ = 7.65-7.63 (m, 6H), 7.41-7.38 (m, 9H), 1.06 (t, J=7.9 Hz, 9H), 0.71-0.66 (q, J=7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25˚C): δ = 135.34, 134.49, 129.37, 128.29, 114.66, 108.24, 7.50, 4.40; MS (EI) m/z (rel. int.%): 415 (100), 387 (13), 367 (27), 305 (27); HRMS–FAB: *m*/*z* calcd for $C_{26}H_{30}GeSi$: 444.13286, found $[M - C_2H_5]^+$: 415.09420.




134.49
CHLOROFORM-d
128.29
129.37
135.34
114.66
108.24
7.50
4.40
grease
1.01
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
-8
Chemical Shift (ppm)

3. NMR spectra of stoichiometric reactions

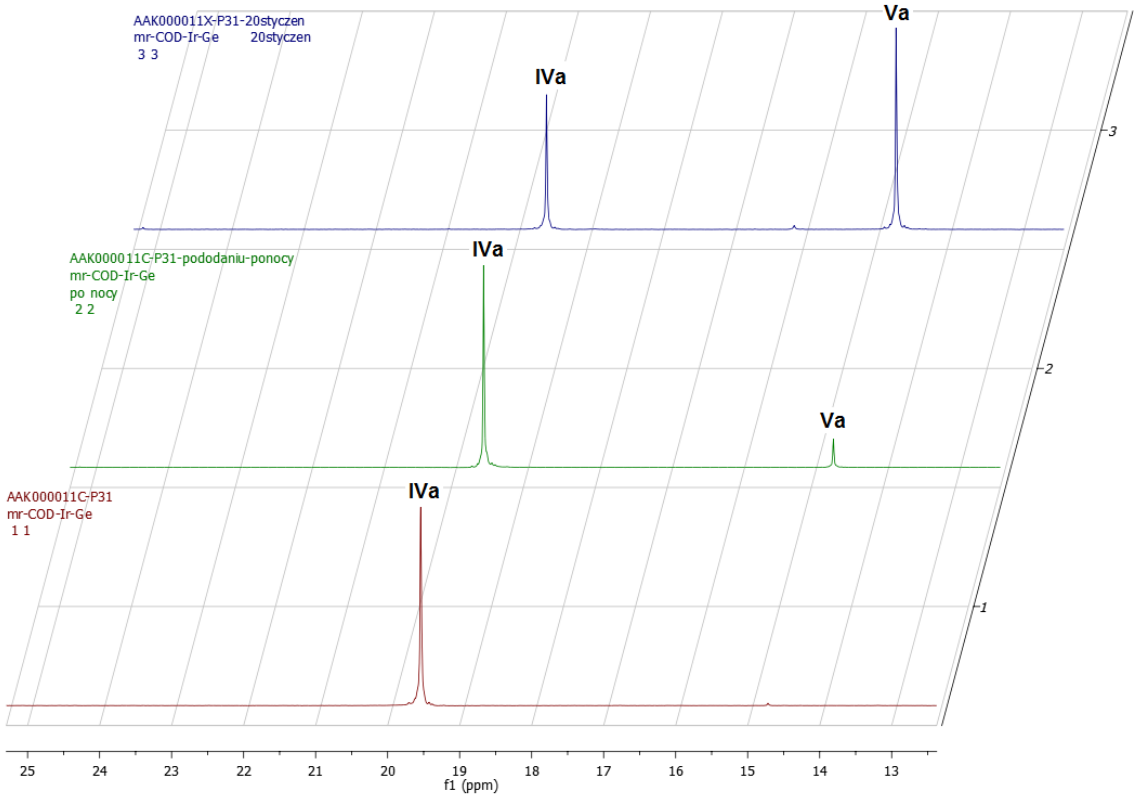


Fig. 1 ^{31}P NMR spectra of **IVa** and after the reaction of **IVa** with iodotrimethylgermane 12 hours and 36 hours.

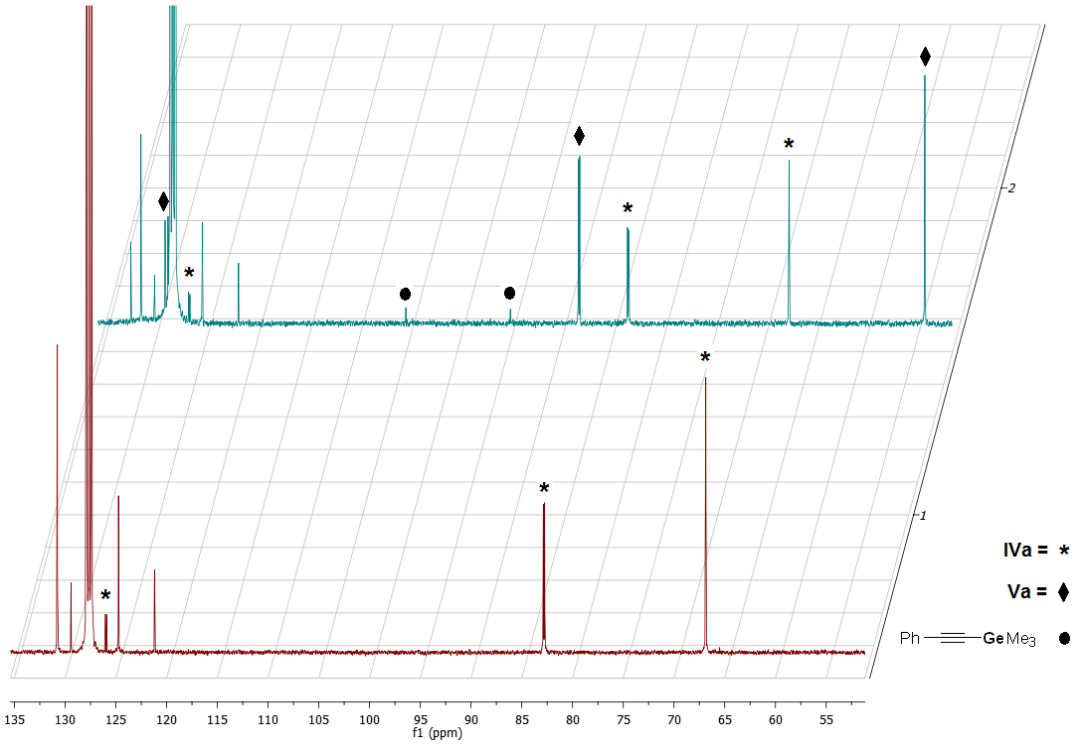


Fig. 2 ^{13}C NMR spectra of **IVa** and after 36 hours of reaction **IVa** with iodotrimethylgermane

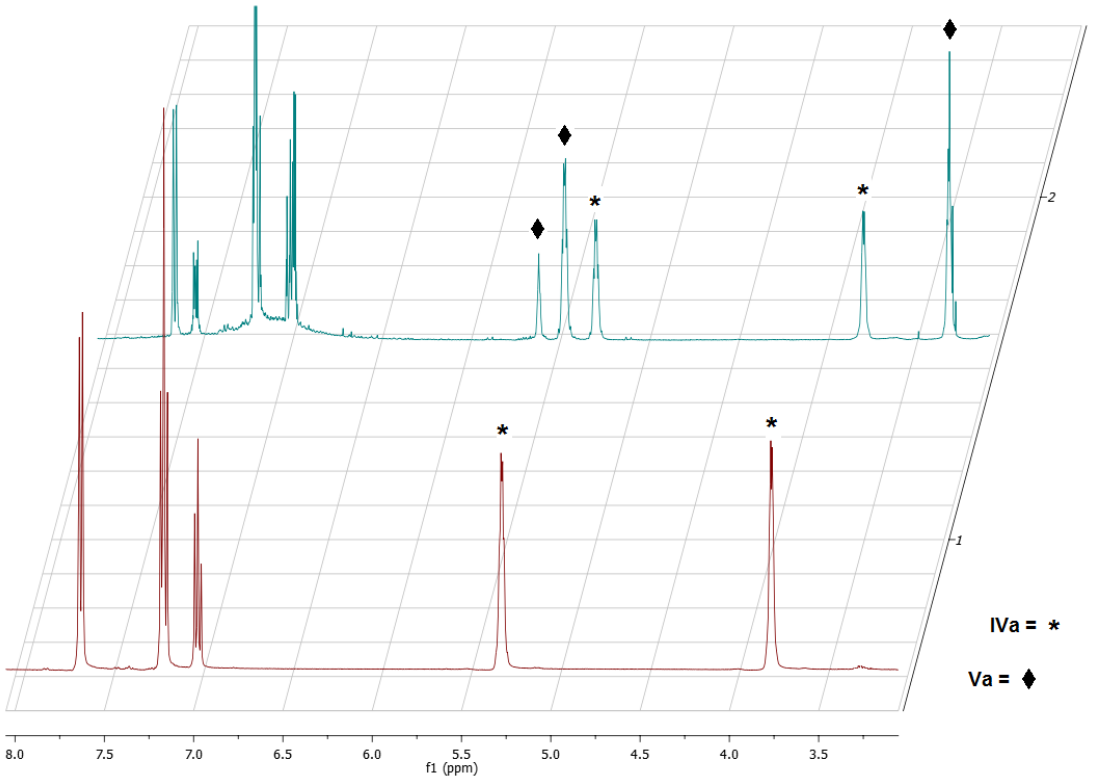


Fig. 3 ^{1}H NMR spectra of **IVa** and after 36 hours of reaction **IVa** with iodotrimethylgermane

4. References

[1] G. Billeb, *J. Organomet. Chem*. **1989**, *373(1)*, 11-19. CAPLUS (^{1}HNMR and GMCS)