Supporting Information

Arylgermylation of alkenes by cooperative photoactivation and hydrogen atom transfer strategy

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1. General Information

All reactions were carried out with standard Schlenk techniques under nitrogen atmosphere-filled reaction vessel. Germyl hydrides, alkenes, (hetero)aryl nitriles, base, photocatalysis, hydrogen transfer reagent were purchased and used without purification. Commercial chemicals were purchased from TCI, Acros, Admas, Sigma-Aldrich, J&K, and Alfa Aesar Chemical Companies and used as received. Anhydrous solvents were purchased from J&K and used as received (water < 30 ppm, J&KSeal). Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminum sheets from Qingdao Haiyang Chemical Co., Ltd. Flash chromatography was performed on silica gel (200–300 mesh, Qingdao Haiyang Chemical Co., Ltd).

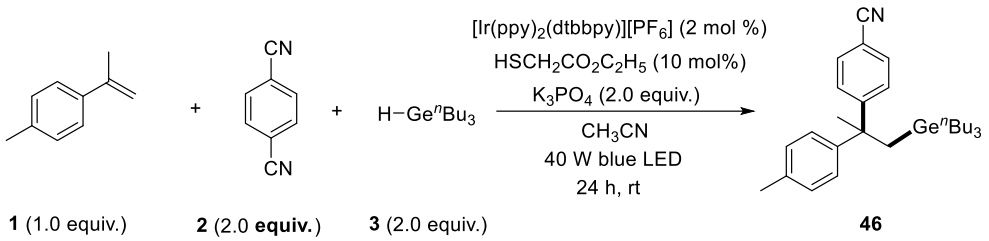
^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ on a Bruker AVANCE Avance III 400 instrument. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm for ^{1}H NMR, and 77.16 ppm for $^{13}C\{^{1}H$ NMR). Data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet), coupling constants (Hz) and integration. Infrared spectra (IR) were recorded on a ThermoFisher Nicolet iS5 FTIR using a neat thin-film technique. Stern-Volmer luminescence quenching analysis was conducted using a HITACHI F-7000 spectrofluorometer. High-resolution mass spectra (HRMS) were recorded on the Thermo Quest Finnigan LCQDECA system equipped with an ESI ionization source and a TOF detector mass spectrometer. All the photochemical reactions were performed with Blue LED (8 W or 40 W, λ = 455 nm).

2. Experimental Details for the Photomediated Arylgermylation of Alkenes

2.1 General procedure for the Photomediated Arylgermylation of Alkenes

Under nitrogen atmosphere conditions, the reaction vessel was evacuated and backfilled with nitrogen for three times. In an oven-dried reaction vial (10 mL) containing a magnetic stir bar was charged with alkene (0.2 mmol, 1.0 equiv.), (hetero)aryl nitrile derivative (0.4 mmol, 2.0 equiv.), germyl hydrides (0.4mmol, 2.0 equiv.), base (0.4 mmol, 2.0 equiv.), photcatalysis (0.004 mmol, 2 mol%) and anhydrous acetonitrile (2 mL). After stirring under 2 × 40 W blue LED light irradiation at room temperature for 24 h (The temperature of the reaction was maintained at room temperature *via* a fan). Upon completion, the reaction mixture was quenched with water and extracted with EtOAc. The combined organic layer was dried over Na_2SO_4. Finally, the filtrate was concentrated under reduced pressure and the resulting crude material was purified by preparative TLC (petroleum ether/ethyl acetate) to afford the desired product.

2.2 Gram scale experiments



1 (1.0 equiv.) **2** (2.0 **equiv.**) **3** (2.0 equiv.) **46**

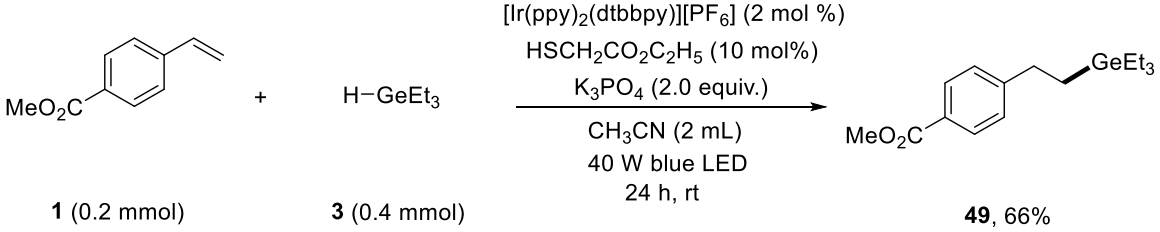
According to the general procedure using 2-(p-methylphenyl)propene (132 mg, 1.0 mmol, 1.0 equiv.), 1,4-dicyanobenzene (255 mg, 2.0 mmol, 2.0 equiv.), ^{n}Bu$_3$GeH (489.5 mg, 2 mmol, 2.0 equiv.), and anhydrous acetonitrile (10 mL) in the presence of [Ir(ppy)$_2$(dtbbpy)][PF$_6$] (2 mol%, 18.5 mg, 0.02 mmol), HSCH$_2$CO$_2$C$_2$H$_5$ (10 mol%, 12.0 mg, 0.1 mmol) and K$_3$PO$_4$ (273.5 mg, 2.0 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **46** (310.8 mg, 65% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1).

According to the general procedure using 2-(p-methylphenyl)propene (4.0 mmol, 1.0 equiv.), 1,4-dicyanobenzene (8.0 mmol, 2.0 equiv.), ^{n}Bu$_3$GeH (8 mmol, 2.0 equiv.), and anhydrous acetonitrile (20 mL) in the presence of [Ir(ppy)$_2$(dtbbpy)][PF$_6$] (2 mol%, 18.5 mg, 0.02 mmol), HSCH$_2$CO$_2$C$_2$H$_5$ (10 mol%, 12.0 mg, 0.1 mmol) and K$_3$PO$_4$ (8.0 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **46** (1.1 g, 58% yield) as colorless oil after purification by chromatography on silica gel (petroleum PE/EA = 20:1).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68 – 7.65 (m, 2H), 7.54 – 7.50 (m, 2H), 7.27 – 7.19 (m, 4H), 2.46 (s, 3H), 1.94 – 1.84 (m, 2H), 1.82 (s, 3H), 1.41 – 1.29 (m, 12H), 1.00 (t, J = 7.1 Hz, 9H), 0.65 – 0.59 (m, 6H) ppm. **^{13}C NMR** (100 MHz, CDCl$_3$) δ 157.8, 146.9, 135.5, 131.7, 128.8, 127.8, 126.8, 119.1, 109.2, 45.7, 30.1, 28.3, 27.2, 26.6, 20.8, 13.7, 13.6 ppm. **IR** (film): 2955, 2923, 2855, 2227, 1922, 1605, 1456, 1375, 1017, 906, 729, 648 cm^{-1}. **HRMS (ESI)**: calculated for C$_{29}$H$_{44}$NGe$^+$ [M+H]$^+$ 480.2680; found 480.2669.

2.3 Experimental Studies on Reaction Mechanism

2.3.1 Control experiment

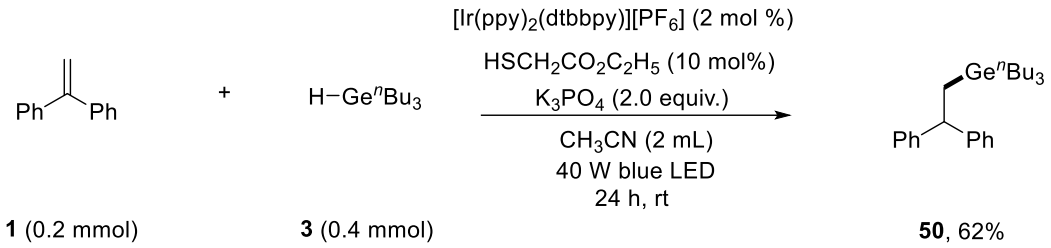


1 (0.2 mmol) **3** (0.4 mmol) **49**, 66%

We performed the reaction of methyl 4-vinylbenzoate and Et$_3$GeH under standard conditions, providing the hydrogermylation of methyl 4-vinylbenzoate product **47** in 66% yield. This result indicated the Et$_3$Ge radical may be involved during the photocatalyzed process.

Experimental procedure: According to the general procedure using methyl 4-vinylbenzoate (32.4 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (84.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **49** (42.6 mg, 66% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 8.2, 1.4 Hz, 2H), 7.30 – 7.25 (m, 2H), 3.90 (s, 3H), 2.74 – 2.68 (m, 2H), 1.03 (t, J = 7.8 Hz, 9H), 0.78 – 0.71 (m, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 151.1, 129.8, 127.9, 127.6, 52.0, 31.5, 13.3, 9.0, 3.9 ppm. **IR** (film): 2948, 2903, 1721, 1608, 1434, 1274, 1108, 1016, 706, 573 cm^{-1}. **HRMS (ESI)**: calculated for $C_{16}H_{27}O_2Ge^+$ $[M+H]^+$ 325.1217; found 327.1209.

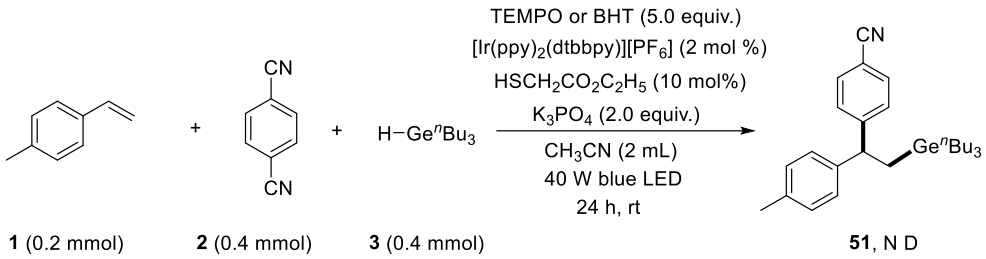
2.3.2 Control experiment



We performed the reaction of 1,1-diphenylethylene and Et_3GeH under standard conditions, providing the hydrogermylation of methyl 4-vinylbenzoate product **52** in 62% yield. This result indicated the Et_3Ge radical may be involved during the photocatalyzed process.

Experimental procedure: According to the general procedure using 1,1-diphenylethylene (36.0 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), ^{n}Bu_3GeH (97.9 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (84.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **50** (52.7 mg, 62% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 8H), 7.21 – 7.10 (m, 2H), 4.12 (t, J = 8.1 Hz, 1H),1.62 – 1.55 (m, 2H), 1.34 – 1.15 (m, 12H), 0.87 (td, J = 6.9, 2.1 Hz, 9H), 0.60 – 0.47 (m, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.3, 128.4, 127.6, 126.1, 48.2, 27.4, 26.7, 20.4, 13.9, 12.7 ppm. **IR** (film): 2954, 2921, 1598, 1492, 1451, 1375, 1081, 882, 697 cm^{-1}. **HRMS (ESI)**: calculated for $C_{26}H_{41}Ge^+$ $[M+H]^+$ 427.2415; found 427.2396.

2.3.3 Radical trapping experiments



When adding the 2,2,6,6-Tetramethyl-1-piperinedinyloxy (TEMPO) or butylated hydroxytoluene（BHT) into the reaction of 4-methylstyrene, 1,4-dicyanobenzene and ^{n}Bu$_3$GeH under standard condition, the desired product **50** was inhibited, indicating a radical mechanism.

Experimental procedure: according to the general procedure, 4-methylstyrene (24 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), TEMPO (or BHT, 5.0 equiv.), ^{n}Bu$_3$GeH (489.5 mg, 2 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of [Ir(ppy)$_2$(dtbbpy)][PF$_6$] (2 mol%, 3.7 mg, 0.004 mmol), HSCH$_2$CO$_2$C$_2$H$_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K$_3$PO$_4$ (84.9 mg, 0.4 mmol, 2.0 equiv.) under 2 × 40 W blue LED light irradiation for 24 hours.

2.3.4 Stern-Volmer luminescence quenching experiments

Stern-Volmer luminescence quenching analysis was conducted using a HITACHI F-7000 spectrofluorometer. All the mixed degassed anhydrous CH$_3$CN solutions were excited at 400 nm. All samples used in the luminescence quenching experiments were freshly prepared under oxygen free conditions (or in a glovebox under a positive pressure of argon) and placed in a 4 mL screw-top quartz cuvette at room temperature. I_0 = emission intensity of the photocatalyst in isolation at the specified wavelength; I = observed emission intensity of the photocatalyst with added quencher.

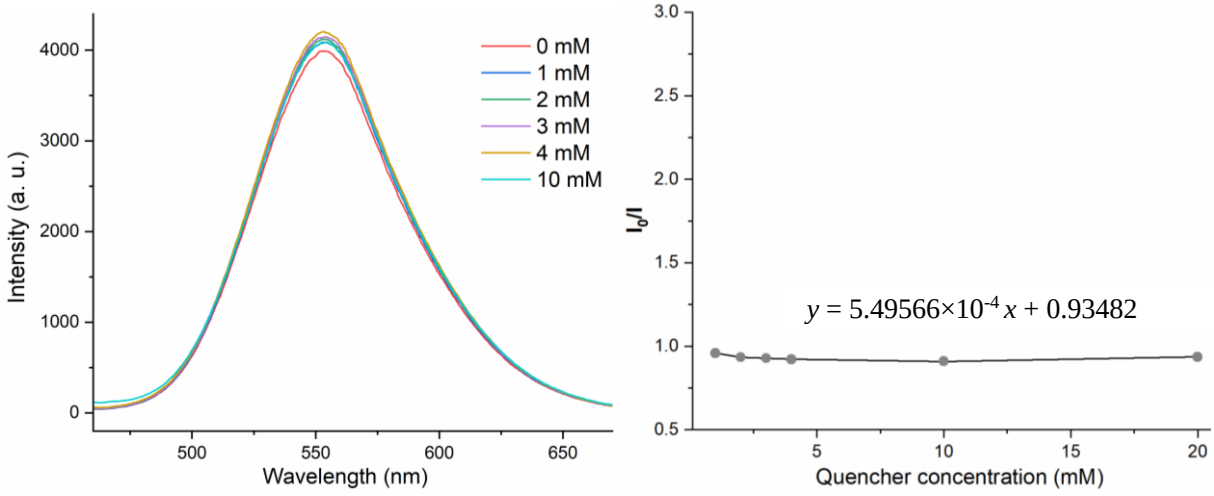


Figure S1. Stern–Volmer plot for the spectrum of [Ir(ppy)$_2$(dtbbpy)][PF$_6$] with tha change of the concentration of K$_3$PO$_4$ in degassed CH$_3$CN with excitation at 400 nm and the emission intensity at 550 nm was observed, [Ir(ppy)$_2$(dtbbpy)][PF$_6$] = 1.5×10^{-5} M.

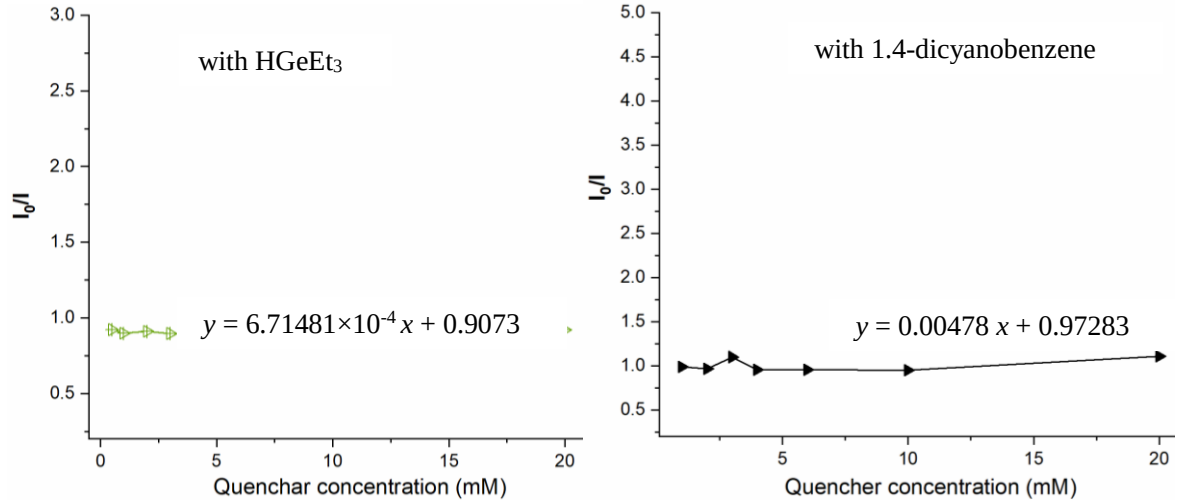


Figure S2. Stern–Volmer plot for the spectrum of $[Ir(ppy)_2(dtbbpy)][PF_6]$ with tha change of the concentration of quenchar in degassed CH_3CN with excitation at 400 nm and the emission intensity at 550 nm was observed, $[Ir(ppy)_2(dtbbpy)][PF_6] = 1.5\times10^{-5}$ M.

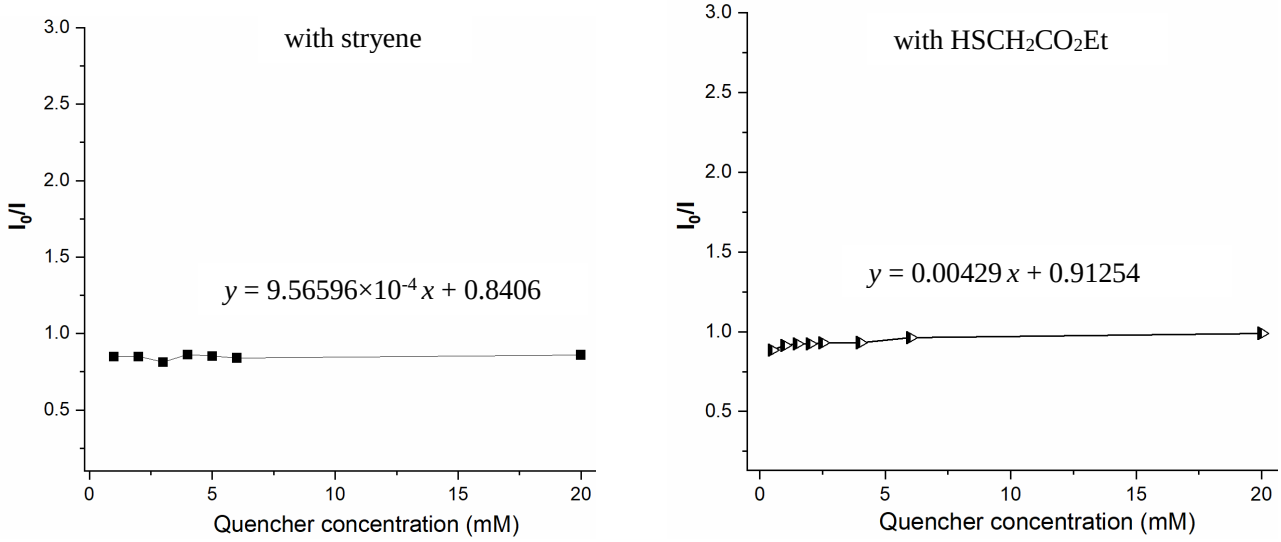


Figure S3. Stern–Volmer plot for the spectrum of $[Ir(ppy)_2(dtbbpy)][PF_6]$ with tha change of the concentration of quenchar in degassed CH_3CN with excitation at 400 nm and the emission intensity at 550 nm was observed, $[Ir(ppy)_2(dtbbpy)][PF_6] = 2\times10^{-5}$ M.

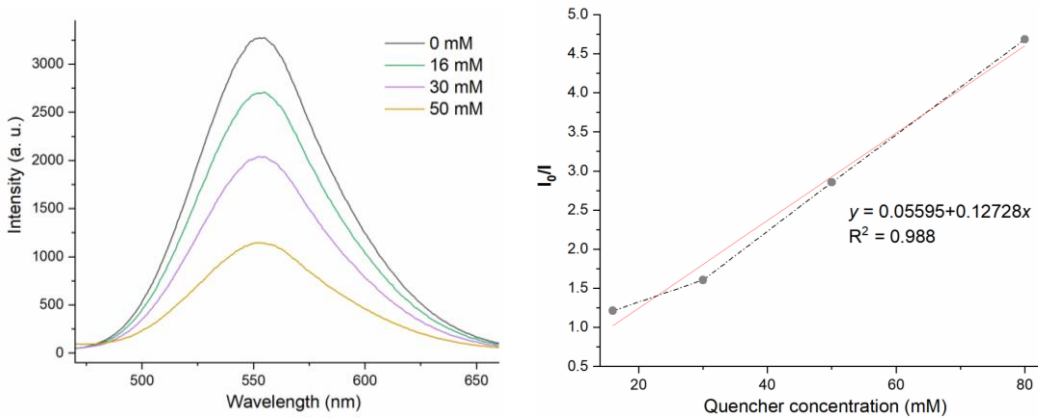
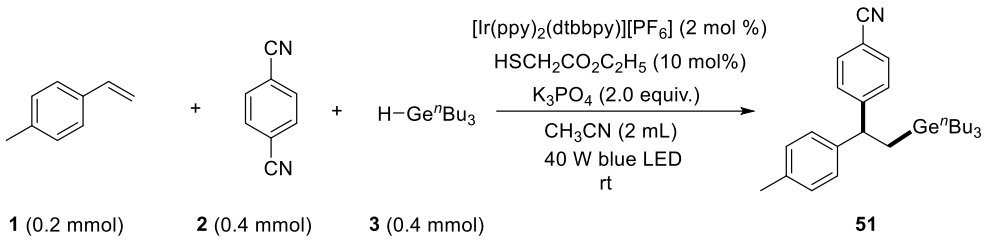


Figure S4. Stern–Volmer plot for the spectrum of $[Ir(ppy)_2(dtbbpy)][PF_6]$ with tha change of the concentration of $HSCH_2CO_2Et$ and K_3PO_4 in degassed CH_3CN with excitation at 400 nm and the emission intensity at 550 nm was observed, $[Ir(ppy)_2(dtbbpy)][PF_6] = 1.5\times10^{-5}$ M.

2.3.5 Light on/off experiment

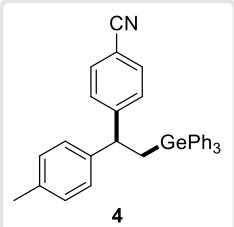


We carried out the light on/off experiments by the reaction of 4-methylstyrene, 1,4-dicyanobenzene and ^{n}Bu$_3$GeH under standard conditions, indicating light irradiation is essential for this protocol.

Experimental procedure: according to the general procedure, four oven-dried reaction vials were charged respectively 4-methylstyrene (24 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), ^{n}Bu$_3$GeH (489.5 mg, 2 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of [Ir(ppy)$_2$(dtbbpy)][PF$_6$] (2 mol%, 3.7 mg, 0.004 mmol), HSCH$_2$CO$_2$C$_2$H$_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K$_3$PO$_4$ (84.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation for 24 hours. The vials were irritated under 2×40 W blue LED irradiation. After 15 minutes, the lamps were turned off, and one vial was removed from the irradiation setup for analysis. The remaining three vials were stirred in the absence of light for an additional 15 minutes. Then, one vial was removed for analysis, and the other lamps were turned back on to irradiate. After an additional 15 minutes of irradiation, the lamps were turned off, and one vial was removed for analysis. The remaining vial was stirred in the absence of light for an additional 15 minutes. Then, the lamps were turned off, and the last vial was removed for analysis. The reaction mixtures were diluted by ethyl acetate, and filtered through a plug of silica (eluting with ethyl acetate). Finally, the filtrate was concentrated under reduced pressure and the resulting crude material was purified by preparative TLC (petroleum ether/ethyl acetate) to afford the corresponding product **51**. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.58 – 7.52 (m, 2H), 7.43 – 7.38 (m, 2H), 7.17 – 7.12 (m, 2H), 7.11 – 7.06 (m, 2H), 4.09 (t, J = 8.0 Hz, 1H), 2.30 (s, 3H), 1.62 – 1.43 (m, 2H), 1.27 – 1.15 (m, 12H), 0.85 (t, J = 7.0 Hz, 9H), 0.57 – 0.49 (m, 6H) ppm. **^{13}C NMR** (100 MHz, CDCl$_3$) δ 153.4, 142.5, 136.3, 132.3, 129.4, 128.3, 127.4, 119.1, 109.7, 48.0, 27.3, 26.7, 21.0, 20.1, 13.8, 12.7 ppm. **IR** (film): 2954, 2922, 2226, 1604, 1511, 1456, 1417, 1081, 809, 569 cm^{-1}. **HRMS (ESI)**: calculated for $C_{28}H_{41}NGe^+$ $[M+H]^+$ 466.2524; found 466.2520.

2.4 Characterization Data of Alkene Arylgermylation Products

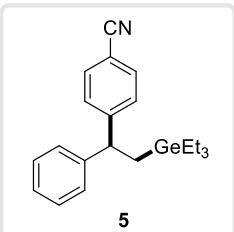
2.4.1 4-(1-(p-tolyl)-2-(triphenylgermyl)ethyl)benzonitrile (**4**)



4
$C_{34}H_{29}NGe$
M = 524.27 g/mol

According to the general procedure using 4-methylstyrene (24 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Ph_3GeH (122 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), iPr_3SiSH (10 mol%, 3.8 mg, 0.02 mmol) and K_3PO_4 (84.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **4** (78 mg, 74% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34 – 7.26 (m, 17H), 7.19 – 7.12 (m, 2H), 7.02 – 6.91 (m, 4H), 4.25 (t, J = 7.8 Hz, 1H), 2.37 – 2.29 (m, 2H), 2.24 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13C NMR (101 MHz, Chloroform-d) δ 151.7, 142.1, 136.5, 136.4, 134.9, 132.2, 129.4, 129.0, 128.5, 128.2, 127.5, 119.1, 109.8, 47.5, 21.9, 21.0 ppm. **IR** (film): 3067, 2920, 2851, 2225, 1604, 1510, 1484, 1429, 1304, 1187, 1089, 1018, 808, 732, 697 cm^{-1}. **HRMS (ESI)**: calculated for $C_{34}H_{29}NaNGe^+$ $[M+Na]^+$ 548.1404; found 548.1401.

2.4.2 4-(1-phenyl-2-(triphenylgermyl)ethyl)benzonitrile (**5**)

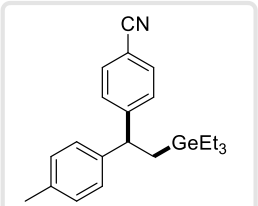


5
$C_{21}H_{27}NGe$
M = 366.08 g/mol

According to the general procedure using styrene (20.8 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (84.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **5** (49 mg, 67% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.2 Hz, 2H),

7.40 (d, J = 8.1 Hz, 2H), 7.31 – 7.20 (m, 5H), 4.13 (t, J = 8.1 Hz, 1H), 1.62 – 1.49 (m, 2H), 0.91 (t, J = 8.0 Hz, 9H), 0.54 (q, J = 7.9 Hz, 6H) ppm. **^{13}C NMR** (100MHz, $CDCl_3$) δ 153.0, 145.5, 132.3, 128.7, 128.3, 127.5, 126.7, 119.1, 109.8, 48.3, 19.0, 8.9, 4.2 ppm. **IR** (film): 3027, 2947, 2929, 2869, 2226, 1604, 1491, 1452, 1377, 1019, 968, 865, 727, 697, 593 cm^{-1}. **HRMS (ESI)**: calculated for $C_{21}H_{27}NGe^+$ $[M+H]^+$ 368.1428; found 368.1422.

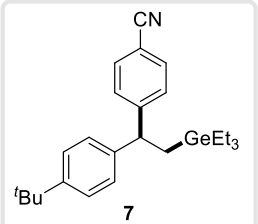
2.4.3 4-(1-(p-tolyl)-2-(triethylgermyl)ethyl)benzonitrile (**6**)



6
$C_{22}H_{29}NGe$
M = 380.11 g/mol

According to the general procedure using 4-methylstyrene (24 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (84.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **6** (42.6 mg, 56% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 8.3 Hz, 2H), 7.14 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 4.09 (t, J = 8.1 Hz, 1H), 2.30 (s, 3H), 1.59 – 1.47 (m, 2H), 0.91 (t, J = 7.9 Hz, 9H), 0.53 (q, J = 7.9 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.3, 142.5, 136.3, 132.3, 129.4, 128.2, 127.4, 119.2, 109.7, 47.9, 21.1, 19.0, 8.9, 4.2 ppm. **IR** (film): 2947, 2093, 2869, 2226, 1604, 1511, 1456, 1424, 1165, 1018, 808, 700, 569 cm^{-1}. **HRMS (ESI)**: calculated for $C_{22}H_{30}NGe^+$ $[M+H]^+$ 382.1585; found 382.1582.

2.4.4 4-(1-(4-(tert-butyl)phenyl)-2-(triethylgermyl)ethyl)benzonitrile (**7**)

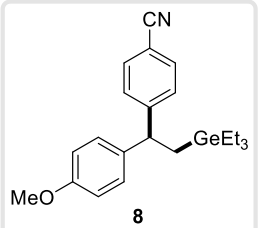


7
$C_{25}H_{35}NGe$
M = 422.19 g/mol

According to the general procedure using 4-tert-butylstyrene (32 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (84.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **7** (58.2 mg, 69% yield) as colorless oil after

purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 2H), 7.46 – 7.38 (m, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.23 – 7.14 (m, 2H), 4.10 (t, J = 8.1 Hz, 1H), 1.60 – 1.48 (m, 2H), 1.29 (s, 9H), 0.90 (t, J = 7.9 Hz, 9H), 0.53 (q, J = 8.0 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.1, 149.6, 142.6, 132.3, 128.4, 127.0, 125.5, 119.2, 109.8, 47.8, 34.4, 31.4, 19.1, 8.9, 4.2 ppm. **IR** (film): 2591, 2903, 2869, 2225, 1604, 1500, 1461, 1424, 1363, 1269, 1017, 809, 703 572 cm^{-1}. **HRMS (ESI)**: calculated for $C_{25}H_{36}NGe^+$ $[M+H]^+$ 424.2054; found 424.2050.

2.4.5 4-(1-(4-methoxyphenyl)-2-(triethylgermyl)ethyl)benzonitrile (**8**)



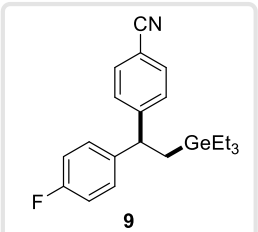
8

$C_{22}H_{29}NGeO$

M = 396.11 g/mol

According to the general procedure using 4-methoxystyrene (26.8 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (84.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **8** (57.0 mg, 72% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 2H), 7.40 – 7.34 (m, 2H), 7.19 – 7.13 (m, 2H), 6.85 – 6.79 (m, 2H), 4.12 – 4.03 (m, 1H), 3.77 (s, 3H), 1.59 – 1.50 (m, 1H), 1.49 – 1.42 (m, 1H), 0.91 (t, J = 7.9 Hz, 9H), 0.54 (q, J = 8.1 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.3, 153.5, 137.5, 132.3, 128.5, 128.2, 119.2, 114.0, 109.7, 55.3, 47.4, 19.2, 8.9, 4.2 ppm. **IR** (film): 2948, 2903, 2869, 2226, 1606, 1508, 1462, 1301, 1245, 1177, 1036, 815, 698 cm^{-1}. **HRMS (ESI)**: calculated for $C_{22}H_{30}NOGe^+$ $[M+H]^+$ 398.1534; found 398.1526.

2.4.6 4-(1-(4-fluorophenyl)-2-(triethylgermyl)ethyl)benzonitrile (**9**)



9

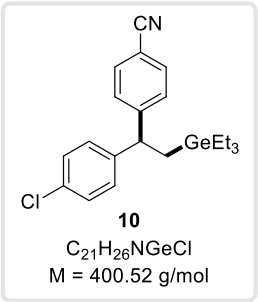
$C_{21}H_{26}NGeF$

M = 384.07 g/mol

According to the general procedure using 4-fluorostyrene (24.4 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol),

$HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (84.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **9** (45.3 mg, 59% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 2H), 7.40 – 7.33 (m, 2H), 7.24 – 7.17 (m, 2H), 7.01 – 6.93 (m, 2H), 4.11 (t, J = 8.1 Hz, 1H), 1.57 – 1.42 (m, 8.1 Hz, 2H), 0.91 (t, J = 7.9 Hz, 9H), 0.53 (q, J = 7.9 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.6 (d, J = 245.2 Hz), 152.8, 141.2, 132.4, 129.0 (d, J = 7.9 Hz), 128.2, 119.1, 115.5 (d, J = 21.2 Hz),110.0, 47.5, 19.2, 8.9, 4.2 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.0 ppm. **IR** (film): 2948, 2929, 2903, 2870, 2226, 1605, 1507, 1459, 1223, 1157, 1014, 819, 699, 568 cm^{-1}. **HRMS (ESI)**: calculated for $C_{21}H_{26}NFGe^+$ $[M+H]^+$ 386.1334; found 386.1331.

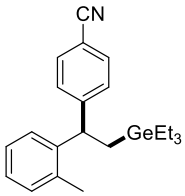
2.4.7 4-(1-(4-chlorophenyl)-2-(triethylgermyl)ethyl)benzonitrile (**10**)



10
$C_{21}H_{26}NGeCl$
M = 400.52 g/mol

According to the general procedure using 4-chlorostyrene (27.6 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (84.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **10** (46.4 mg, 58% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20: 1). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.62 – 7.55 (m, 2H), 7.40 – 7.36 (m, 2H), 7.30 – 7.26 (m, 2H), 7.25 – 7.17 (m, 2H), 4.13 (t, J = 8.1 Hz, 1H), 1.60 – 1.47 (m, 2H), 0.94 (t, J = 7.9 Hz, 9H), 0.57 (q, J = 7.9 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.4, 144.0, 132.4, 132.0, 128.9, 128.8, 128.2, 119.0, 110.1, 47.7, 18.9, 8.9, 4.3 ppm. **IR** (film): 2948, 2929, 2869, 2227, 1605, 1489, 1407, 1090, 1012, 808, 556 cm^{-1}. **HRMS (ESI)**: calculated for $C_{21}H_{26}NClGe^+$ $[M+H]^+$ 402.1038; found 402.1032.

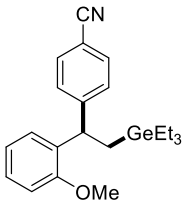
2.4.8 4-(1-(o-tolyl)-2-(triethylgermyl)ethyl)benzonitrile (**11**)



11
$C_{22}H_{29}NGe$
M = 380.11 g/mol

According to the general procedure using 2-methylstyrene (23.6 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (84.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **11** (44.8 mg, 59% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20: 1). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.56 – 7.50 (m, 2H), 7.42 – 7.37 (m, 1H), 7.35 – 7.29 (m, 2H), 7.24 – 7.19 (m, 1H), 7.16 – 7.10 (m, 2H), 4.33 (t, J = 8.0 Hz, 1H), 2.25 (s, 3H), 1.59 – 1.52 (m, 1H), 1.48 – 1.41 (m, 1H), 0.92 (t, J = 7.9 Hz, 9H), 0.56 (q, J = 7.9 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.7, 142.9, 135.6, 132.3, 130.8, 128.6, 126.7, 126.6, 126.3, 119.2, 109.7, 43.8, 20.2, 20.0, 8.9, 4.4 ppm. **IR** (film): 3020, 2947, 2903, 2226, 1603, 1460, 1425, 1019, 837, 735, 559 cm^{-1}. **HRMS (ESI)**: calculated for $C_{22}H_{30}NGe^+$ $[M+H]^+$ 382.1585; found 382.1579.

2.4.9 4-(1-(2-methoxyphenyl)-2-(triethylgermyl)ethyl)benzonitrile (**12**)

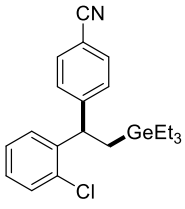


12
$C_{22}H_{29}NGeO$
M = 396.11 g/mol

According to the general procedure using 2-methoxystyrene (26.8 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (41.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **12** (44.8 mg, 53% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.28 – 7.23 (m, 2H), 7.16 – 7.11 (m, 1H), 7.06 – 7.00 (m, 1H), 6.80 – 6.74 (mn, 1H), 6.67 – 6.63(m, 1H), 4.46 (t, J = 8.2 Hz, 1H), 3.63 (s, 3H), 1.41 (dd, J = 13.7, 8.6 Hz, 1H), 1.29 (dd, J = 13.7,

7.8 Hz, 1H), 0.76 (t, J = 7.9 Hz, 9H), 0.38 (q, J = 7.9 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.5, 153.1, 133.9, 132.0, 128.6, 127.7, 127.4, 120.6, 119.4, 110.6, 109.4, 55.3, 40.0, 18.1, 8.9, 4.2 ppm. **IR** (film): 2946, 2869, 2226, 1604, 1489, 1461, 1239, 1051, 751, 571 cm^{-1}. **HRMS (ESI)**: calculated for $C_{22}H_{30}NOGe^+$ $[M+H]^+$ 398.1534; found 398.1530.

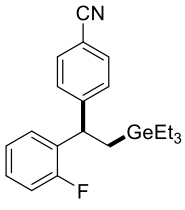
2.4.10 4-(1-(2-chlorophenyl)-2-(triethylgermyl)ethyl)benzonitrile (**13**)



13
$C_{21}H_{26}NGeCl$
M = 400.52 g/mol

According to the general procedure using 2-chlorostyrene (27.6 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (41.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **13** (39.2 mg, 49% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.42 – 7.36 (m, 3H), 7.34 – 7.27 (m, 1H), 7.25 – 7.21 (m, 1H), 7.15 – 7.09 (m, 1H), 4.69 (t, J = 8.1 Hz, 1H), 1.55 – 1.43 (m, 2H), 0.90 (t, J = 8.0 Hz, 9H), 0.55 (q, J = 7.9 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.5, 142.6, 133.7, 132.3, 129.9, 128.6, 128.4, 127.9, 127.2, 119.1, 110.0, 43.6, 19.0, 8.9, 4.3 ppm. **IR** (film): 2947, 2929, 2870, 2226, 1605, 1471, 1019, 747, 574 cm^{-1}. **HRMS (ESI)**: calculated for $C_{21}H_{27}NClGe^+$ $[M+H]^+$ 402.1038; found 402.1035.

2.4.11 4-(1-(2-fluorophenyl)-2-(triethylgermyl)ethyl)benzonitrile (**14**)

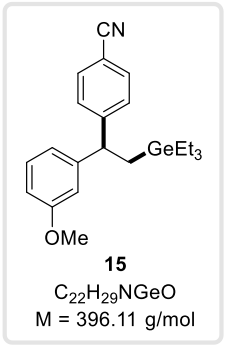


14
$C_{21}H_{26}NGeF$
M = 385.08 g/mol

According to the general procedure using 2-fluorostyrene (24.4 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol),

$HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (41.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **14** (48.3 mg, 63% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.29 – 7.24 (m, 2H), 7.22 – 7.15 (m, 1H), 7.06 –6.99 (m, 1H), 6.97 – 6.91 (m, 1H), 6.86 – 6.78 (m, 1H), 4.33 (t, J = 8.2 Hz, 1H), 1.46 – 1.39 (dd, J = 13.7, 8.7 Hz, 1H), 1.37 – 1.30 (m, 1H), 0.76 (t, J = 8.0 Hz, 9H), 0.40 (q, J = 7.9 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.3 (d, J = 245.3 Hz), 151.8, 132.3, 128.4, 128.3, 128.3, 124.41 (d, J = 3.5 Hz), 119.1, 115.8, 115.6, 110.0, 40.4 (d, J = 2.6 Hz), 17.8, 8.8, 4.2 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.2 ppm. **IR** (film): 2948, 2904, 2870, 2227, 1605, 1487, 1454, 1224, 1019, 757, 558 cm^{-1}. **HRMS (ESI)**: calculated for $C_{21}H_{27}NFGe^+$ $[M+H]^+$ 386.1334; found 386.1324.

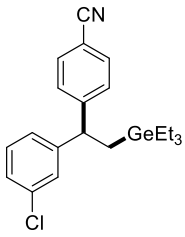
2.4.12 4-(1-(3-methoxyphenyl)-2-(triethylgermyl)ethyl)benzonitrile (**15**)



15
$C_{22}H_{29}NGeO$
M = 396.11 g/mol

According to the general procedure using 3-vinylanisole (26.8 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (41.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **15** (54.6 mg, 69% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2H), 7.48 – 7.42 (m, 2H), 7.28 – 7.23 (m, 1H), 6.93 – 6.88 (m, 1H), 6.86 – 6.83 (m, 1H), 6.81 – 6.76 (m, 1H), 4.15 (t, J = 8.1 Hz, 1H), 3.84 (s, 3H), 1.65 – 1.51 (m, 2H), 0.97 (t, J = 7.9 Hz, 9H), 0.60 (q, J = 7.9 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 152.8, 147.1, 132.3, 129.7, 128.3, 120.0, 119.1, 113.8, 111.4, 109.9, 55.3, 48.3, 18.0, 8.9, 4.2 ppm. **IR** (film): 2947, 2903, 2869, 2226, 1598, 1487, 1455, 1262, 1049, 781, 696, 572 cm^{-1}. **HRMS (ESI)**: calculated for $C_{22}H_{30}NOGe^+$ $[M+H]^+$ 398.1534; found 398.1525.

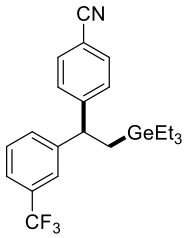
2.4.13 4-(1-(3-chlorophenyl)-2-(triethylgermyl)ethyl)benzonitrile (**16**)



16
$C_{21}H_{26}NGeCl$
M = 400.52 g/mol

According to the general procedure using 3-chlorostyrene (27.6 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (41.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **16** (46.4 mg, 58% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 2H), 7.40 – 7.33 (m, 2H), 7.25 – 7.13 (m, 4H), 4.09 (t, J = 8.1 Hz, 1H), 1.51 (t, J = 8.0 Hz, 2H), 0.91 (t, J = 8.0 Hz, 9H), 0.54 (q, J = 7.9 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.0, 147.6, 134.5, 132.5, 130.0, 128.3, 127.6, 126.9, 125.8, 119.0, 110.2, 48.0, 18.8, 8.9, 4.3 ppm. **IR** (film): 2948, 2903, 2869, 2227, 1592, 1473, 1425, 1092, 1018, 879, 785, 573 cm^{-1}. **HRMS (ESI)**: calculated for $C_{22}H_{27}NClGe^+$ $[M+H]^+$ 402.1038; found 402.1032.

2.4.14 4-(2-(triethylgermyl)-1-(3-(trifluoromethyl)phenyl)ethyl)benzonitrile (**17**)

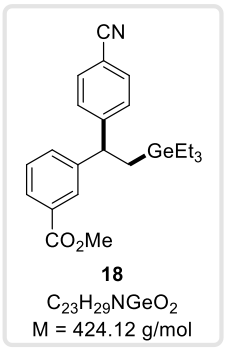


17
$C_{21}H_{26}NGeF_3$
M = 434.08 g/mol

According to the general procedure using 3-(trifluoromethyl)styrene (34.4 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (41.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **17** (52.9 mg, 61% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 3H), 7.48 – 7.37 (m, 5H), 4.19 (t, J = 8.1 Hz, 1H), 1.59 – 1.47 (m, 2H), 0.91 (t, J = 8.0 Hz, 9H),

0.53 (q, J = 7.8 Hz, 6H) ppm. 13C NMR (101 MHz, Chloroform-d) δ 151.91, 146.56, 132.59, 131.20, 131.14, 129.27, 128.32, 125.52, 124.14, 124.11, 124.07, 123.71, 123.67, 122.81, 118.98, 110.41, 48.18, 18.91, 8.88, 4.28 ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.9, 146.5, 132.5, 131.1, 131.04 (q, J = 32.0 Hz), 129.2, 128.3, 125.5, 124.1, 123.6, 118.9, 110.4, 15.5, 48.1, 18.9, 8.8, 4.2 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.4 ppm. **IR** (film): 2950, 2871, 2227, 1605, 1503, 1445, 1325, 1161, 1122, 1073, 1018, 800, 701, 572 cm^{-1}. **HRMS (ESI)**: calculated for $C_2H_{27}NF_3Ge^+$ $[M+H]^+$ 436.1302; found 436.1297.

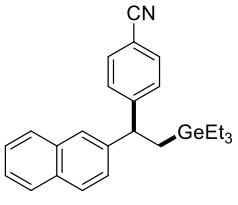
2.4.15 methyl 3-(1-(4-cyanophenyl)-2-(triethylgermyl)ethyl)benzoate (**18**)



18
$C_{23}H_{29}NGeO_2$
M = 424.12 g/mol

According to the general procedure using methyl 4-vinylbenzoate (32.4 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (65.3 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **18** (52.9 mg, 77% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 – 7.94 (m, 1H), 7.89 – 7.84 (m, 1H), 7.57 – 7.53 (m, 2H), 7.46 – 7.34 (m, 4H), 4.18 (t, J = 8.1 Hz, 1H), 3.90 (s, 3H), 1.55 (tt, J = 13.7, 6.5 Hz, 2H), 0.90 (t, J = 7.9 Hz, 9H), 0.52 (q, J = 7.9 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 152.3, 145.9, 132.4, 132.2, 130.5, 128.8, 128.5, 128.2, 128.0, 119.0, 110.1, 52.2, 48.1, 18.9, 8.8, 4.2 ppm. **IR** (film): 2949, 2903, 2870, 2227, 1719, 1604, 1431, 1281, 1195, 1106, 1018, 972, 864, 736, 600 cm^{-1}. **HRMS (ESI)**: calculated for $C_{23}H_{30}NO_2Ge^+$ $[M+H]^+$ 426.1483; found 426.1476.

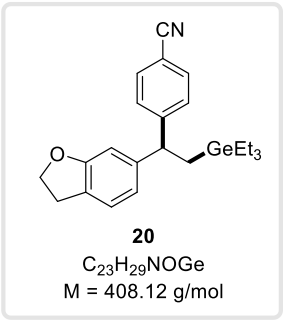
2.4.16 4-(1-(naphthalen-2-yl)-2-(triethylgermyl)ethyl)benzonitrile (**19**)



19
$C_{25}H_{29}NGe$
M = 416.14 g/mol

According to the general procedure using methyl 2-vinylnaphthalene (30.8 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (65.3 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **19** (53.2 mg, 64% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.78 (m, 2H), 7.76 – 7.74 (m, 2H), 7.57 – 7.54 (m, 2H), 7.51 – 7.41 (m, 5H), 7.34 – 7.29 (m, 1H), 4.30 (t, J = 8.1 Hz, 1H), 1.73 – 1.67 (m, 1H), 1.63 – 1.54 (m, 1H), 0.92 (t, J = 7.9 Hz, 9H), 0.56 (q, J = 7.7 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.8, 142.8, 133.5, 132.4, 132.2, 129.2, 128.4, 127.8, 127.7, 126.3, 126.2, 125.8, 125.6, 119.1, 109.9, 48.3, 18.8, 8.9, 4.3 ppm. **IR** (film): 3055, 2928, 2869, 2226, 1604, 1502, 1460, 1424, 1017, 814, 755, 566 cm^{-1}. **HRMS (ESI)**: calculated for $C_{25}H_{30}NGe^+$ $[M+H]^+$ 418.1585; found 418.1584.

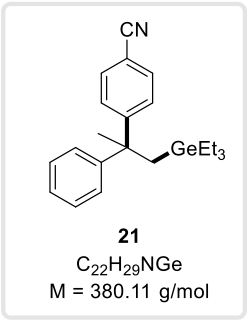
2.4.17 4-(1-(2,3-dihydrobenzofuran-6-yl)-2-(triethylgermyl)ethyl)benzonitrile (**20**)



20
$C_{23}H_{29}NOGe$
M = 408.12 g/mol

According to the general procedure using methyl 6-vinyl-2,3-dihydrobenzofuran (29.2 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (65.3 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **20** (33.4 mg, 41% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 2H), 7.39 – 7.36 (m, 2H), 7.05 (d, J = 1.9 Hz, 1H), 6.99 – 6.96 (m, 1H), 6.69 (d, J = 8.2 Hz, 1H), 4.53 (t, J = 8.7 Hz, 2H), 4.06 (t, J = 8.1 Hz, 1H), 3.15 (t, J = 8.6 Hz, 2H), 1.55 – 1.43 (m, 2H), 0.91 (t, J = 7.9 Hz, 9H), 0.53 (q, J = 7.7 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.8, 153.6, 137.7, 132.3, 128.2, 127.4, 127.1, 124.0, 119.2, 109.7, 109.2, 71.3, 47.7, 29.8, 19.3, 8.9, 4.3 ppm. **IR** (film): 2947, 2902, 2226, 1605, 1489, 1322, 1098, 982, 702, 573 cm^{-1}. **HRMS (ESI)**: calculated for $C_{23}H_{30}NOGe^+$ $[M+H]^+$ 410.1534; found 410.1530.

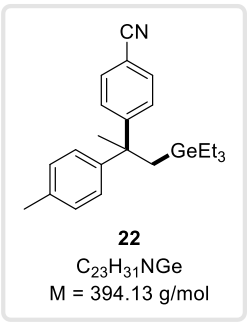
2.4.18 4-(2-phenyl-1-(triethylgermyl)propan-2-yl)benzonitrile (**21**)



21
$C_{22}H_{29}NGe$
M = 380.11 g/mol

According to the general procedure using methyl 2-phenyl-1-propene (23.6 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (54.7 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **21** (54.7 mg, 72% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.29 – 7.23 (m, 2H), 7.20 – 7.09 (m, 5H), 1.70 – 1.62 (m, 2H), 1.59 (s, 3H), 0.79 (t, J = 7.9 Hz, 9H), 0.38 (q, J = 8.1 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6, 149.9, 131.8, 128.2, 127.8, 126.9, 126.2, 119.2, 109.4, 46.0, 30.1, 27.5, 8.9, 5.2 ppm. **IR** (film): 2948, 2870, 2226, 1605, 1460, 1224, 1017, 908, 731, 698, 570 cm^{-1}. **HRMS (ESI)**: calculated for $C_{22}H_{30}NGe^+$ $[M+H]^+$ 382.1585; found 382.1576.

2.4.19 4-(2-(p-tolyl)-1-(triethylgermyl)propan-2-yl)benzonitrile (**22**)

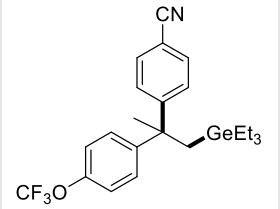


22
$C_{23}H_{31}NGe$
M = 394.13 g/mol

According to the general procedure using 2-(p-methylphenyl)propene (26.4 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (54.7 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **22** (62.2 mg, 79% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.39 – 7.34 (m, 2H), 7.12 – 7.05 (m, 4H), 2.32 (s, 3H), 1.80 – 1.68 (m, 2H), 1.67 (s, 3H), 0.89 (t, J = 7.9 Hz, 9H), 0.48 (q, J = 7.9 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 147.0,

135.7, 131.8, 128.9, 127.8, 126.8, 119.2, 109.3, 45.6, 30.1, 27.6, 21.0, 8.9, 5.3 ppm. **IR** (film): 2947, 2869, 2226, 1604, 1511, 1457, 1375, 1224, 1017, 813, 570 cm^{-1}. **HRMS (ESI)**: calculated for $C_{23}H_{32}NGe^{+}$ $[M+H]^{+}$ 396.1741; found 382.1736.

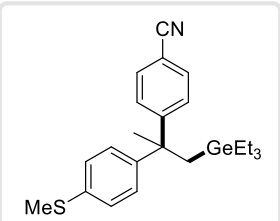
2.4.20 4-(1-(triethylgermyl)-2-(4-(trifluoromethoxy)phenyl)propan-2-yl)benzonitrile (**23**)



23
$C_{23}H_{28}NF_3OGe$
M = 464.10 g/mol

According to the general procedure using 1-(prop-1-en-2-yl)-4-(trifluoromethoxy)benzene (40.4 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (54.7 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **23** (60.3 mg, 65% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.37 – 7.32 (m, 2H), 7.25 – 7.19 (m, 2H), 7.14 – 7.07 (m, 2H), 1.73 – 1.70 (m, 2H), 1.68 (s, 3H), 0.88 (t, J = 7.9 Hz, 9H), 0.47 (q, J = 8.0 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.8, 148.8, 147.5, 132.0, 128.4, 127.8, 120.7, 120.5 (q, J = 256.9 Hz), 119.3, 109.8, 45.8, 30.2, 27.7, 8.8, 5.3 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.8 ppm. **IR** (film): 2951, 2906, 2872, 2227, 1606, 1503, 1462, 1254, 1209, 1159, 1016, 838, 690, 559 cm^{-1}. **HRMS (ESI)**: calculated for $C_{23}H_{29}NOF_3Ge^{+}$ $[M+H]^{+}$ 466.1408; found 466.1404.

2.4.21 4-(2-(4-(methylthio)phenyl)-1-(triethylgermyl)propan-2-yl)benzonitrile (**24**)

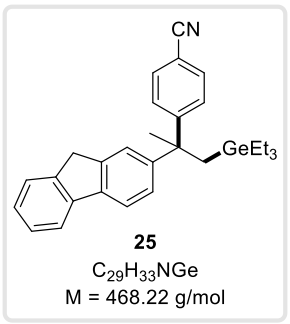


24
$C_{23}H_{31}NSGe$
M = 426.19 g/mol

According to the general procedure using methyl(4-(prop-1-en-2-yl)phenyl)sulfane (32.8 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg,

0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (54.7 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **24** (70.7 mg, 83% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.36 – 7.33 (m, 2H), 7.17 – 7.10 (m, 4H), 2.45 (s, 3H), 1.74 – 1.67 (m, 2H), 1.66 (s, 3H), 0.88 (t, J = 7.9 Hz, 9H), 0.48 (q, J = 7.9 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.3, 147.0, 136.0, 131.8, 127.8, 127.4, 126.5, 119.1, 109.5, 45.6, 30.05, 27.5, 16.0, 8.9, 5.3 ppm. **IR** (film): 2947, 2869, 2226, 1604, 1493, 1397, 1094, 1012, 836, 703, 558 cm^{-1}. **HRMS (ESI)**: calculated for $C_{23}H_{32}NSGe^+$ $[M+H]^+$ 428.1462; found 428.1455.

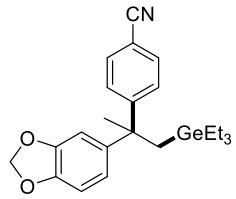
2.4.22 4-(2-(9H-fluoren-2-yl)-1-(triethylgermyl)propan-2-yl)benzonitrile (**25**)



25
$C_{29}H_{33}NGe$
M = 468.22 g/mol

According to the general procedure using 2-(prop-1-en-2-yl)-9H-fluorene (41.2 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (59.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **25** (70.7 mg, 64% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.61 (m, 1H), 7.57 – 7.52 (m, 1H), 7.43 – 7.38 (m, 3H), 7.29 – 7.25 (m, 3H), 7.24 – 7.14 (m, 2H), 7.10 – 7.06 (m, 1H), 3.72 (s, 1H), 1.70 (d, J = 13.3 Hz, 1H), 1.60 (s, 3H), 0.76 (t, J = 7.9 Hz, 9H), 0.39 – 0.30 (m, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.0, 148.6, 143.4, 143.3, 141.5, 139.8, 131.9, 127.8, 126.8, 126.6, 125.7, 125.1, 123.7, 119.9, 119.5, 119.2, 109.3, 46.1, 37.0, 30.4, 27.7, 8.9, 5.3 ppm. **IR** (film): 2947, 2869, 2226, 1603, 1500, 1455, 1403, 1017, 908, 836, 731, 570 cm^{-1}. **HRMS (ESI)**: calculated for $C_{29}H_{34}NGe^+$ $[M+H]^+$ 470.1898; found 470.1900.

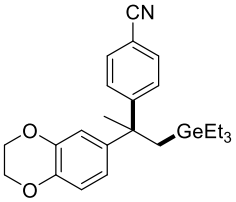
2.4.23 4-(2-(benzo[d][1,3]dioxol-5-yl)-1-(triethylgermyl)propan-2-yl)benzonitrile (**26**)



26
$C_{23}H_{29}NGeO_2$
M = 424.12 g/mol

According to the general procedure using 5-(prop-1-en-2-yl)benzo[d][1,3]dioxole (32.4 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (59.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **26** (50.0 mg, 59% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.38 – 7.33 (m, 2H), 6.73 – 6.67 (m, 2H), 6.62 – 6.59 (m, 1H), 5.92 (s, 2H), 1.67 (s, 2H), 1.63 (s, 3H), 0.89 (t, J = 7.9 Hz, 9H), 0.49 (q, J = 7.9 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6, 147.6, 145.8, 144.1, 131.9, 127.7, 119.7, 119.2, 109.4, 108.0, 107.6, 101.0, 45.8, 30.3, 27.8, 8.9, 5.3 ppm. **IR** (film): 2948, 2870, 2226, 1604, 1484, 1430, 1231, 1038, 935, 868, 539 cm^{-1}. **HRMS (ESI)**: calculated for $C_{23}H_{30}NGeO_2^+$ $[M+H]^+$ 426.1483; found 426.1478.

2.4.24 4-(2-(benzo[d][1,3]dioxol-5-yl)-1-(triethylgermyl)propan-2-yl)benzonitrile (**27**)

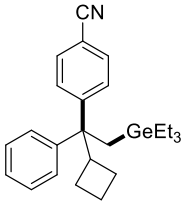


27
$C_{24}H_{31}NGeO_2$
M = 438.14 g/mol

According to the general procedure using 6-(prop-1-en-2-yl)-2,3-dihydrobenzo[b][1,4]dioxine (35.2 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (59.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **27** (75.3 mg, 86% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 2H), 7.38 – 7.32 (m, 2H), 6.76 – 6.72 (m, 1H), 6.71 (d, J = 2.3 Hz, 1H), 6.65 – 6.61 (m, 1H), 4.23 (s, 4H), 1.67 (d, J = 2.4 Hz, 2H), 1.62 (s, 3H), 0.88 (t, J = 7.9 Hz, 9H), 0.48 (q, J = 7.7 Hz,

6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6, 143.6, 143.0, 141.8, 131.8, 127.7, 120.0, 119.2, 116.8, 116.0, 109.3, 64.5, 64.4, 45.4, 30.1, 27.7, 8.9, 5.3 ppm. **IR** (film): 2946, 2870, 2226, 1604, 1500, 1457, 1308, 1284, 1069, 900, 731 cm^{-1}. **HRMS (ESI)**: calculated for $C_{24}H_{32}NGeO_2^+$ $[M+H]^+$ 440.1639; found 440.1636.

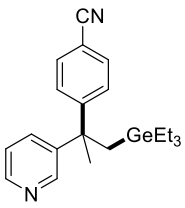
2.4.25 4-(1-cyclobutyl-1-phenyl-2-(triethylgermyl)ethyl)benzonitrile (**28**)



28
$C_{25}H_{33}NGe$
M = 420.17 g/mol

According to the general procedure using (1-cyclobutylvinyl)benzene (31.6 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (59.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **28** (40.3 mg, 48% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.26 – 7.16 (m, 5H), 7.08 – 7.03 (m, 2H), 3.22 – 3.09 (m, 1H), 1.99 – 1.88 (m, 2H), 1.72 – 1.62 (m, 1H), 1.58 (s, 2H), 1.54 – 1.44 (m, 2H), 1.31 – 1.19 (m, 1H), 0.82 (t, J = 7.9 Hz, 9H), 0.36 (q, J = 7.7 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.9, 147.6, 131.2, 130.0, 128.9, 127.7, 126.2, 119.3, 109.5, 52.2, 43.1, 25.0, 24.8, 24.1, 17.6, 8.9, 5.1 ppm. **IR** (film): 2944, 2903, 2869, 2226, 1604, 1500, 1457, 1250, 1018, 910, 820, 701, 565 cm^{-1}. **HRMS (ESI)**: calculated for $C_{25}H_{34}NGe^+$ $[M+H]^+$ 422.1898; found 422.1891.

2.4.26 4-(1-cyclobutyl-1-phenyl-2-(triethylgermyl)ethyl)benzonitrile (**29**)

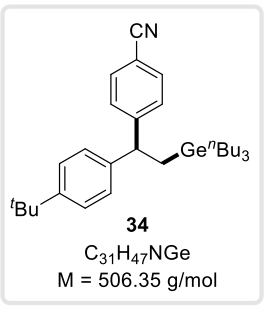


29
$C_{21}H_{28}N_2Ge$
M = 381.09 g/mol

According to the general procedure using 3-(1-methylethenyl)pyridine (23.8 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004

mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (59.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **29** (53.3 mg, 70% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 – 8.47 (m, 1H), 8.44 (d, J = 4.1 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.50 – 7.45 (m, 1H), 7.35 – 7.32 (m, 2H), 7.21 – 7.16 (m, 1H), 1.73 (d, J = 3.1 Hz, 2H), 1.70 (s, 3H), 0.87 (t, J = 7.9 Hz, 9H), 0.46 (q, J = 7.9 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.0, 148.6, 147.5, 145.3, 134.4, 132.1, 127.8, 123.1, 118.9, 109.9, 44.9, 29.8, 27.3, 8.8, 5.3 ppm. **IR** (film): 2948, 2904, 2870, 2227, 1605, 1501, 1413, 1018, 835, 713, 570 cm^{-1}. **HRMS (ESI)**: calculated for $C_{21}H_{29}N_2Ge^+$ $[M+H]^+$ 383.1537; found 383.1526.

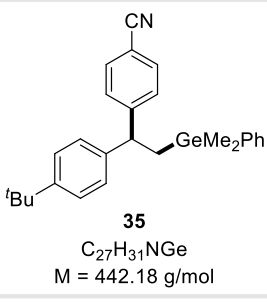
2.4.27 4-(1-(4-(tert-butyl)phenyl)-2-(tributylgermyl)ethyl)benzonitrile (**34**)



34
$C_{31}H_{47}NGe$
M = 506.35 g/mol

According to the general procedure using 4-tert-butylstyrene (32 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), ^{n}Bu_3GeH (97.9 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (59.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **34** (69.8 mg, 69% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.37 – 7.32 (m, 2H), 7.24 – 7.21 (m, 2H), 7.13 – 7.06 (m, 2H), 4.02 (t, J = 8.0 Hz, 1H), 1.21 (s, 9H), 1.16 – 1.06 (m, 12H), 0.77 (t, J = 6.9 Hz, 9H), 0.47 – 0.40 (m, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.3, 149.5, 142.4, 132.3, 128.3, 127.2, 125.6, 119.2, 109.7, 47.9, 34.4, 31.4, 27.3, 26.7, 20.1, 13.8, 12.7 ppm. **IR** (film): 2954, 2922, 2869, 2227, 1604, 1463, 1416, 1269, 1081, 809, 692, 574 cm^{-1}. **HRMS (ESI)**: calculated for $C_{31}H_{48}NGe^+$ $[M+H]^+$ 508.2993; found 508.2986.

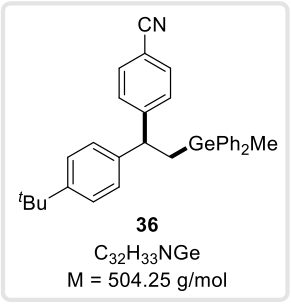
2.4.28 4-(1-(4-(tert-butyl)phenyl)-2-(dimethyl(phenyl)germyl)ethyl)benzonitrile (**35**)



35
$C_{27}H_{31}NGe$
M = 442.18 g/mol

According to the general procedure using 4-tert-butylstyrene (32 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), dimethyl(phenyl)germane (73.6 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (59.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **35** (55.7 mg, 63% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H), 7.34 – 7.29 (m, 7H), 7.28 – 7.25 (m, 2H), 7.14 – 7.09 (m, 2H), 4.08 (t, J = 8.2 Hz, 1H), 1.85 – 1.73 (m, 2H), 1.29 (s, 9H), 0.17 (d, J = 13.7 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.4, 149.6, 141.9, 140.8, 133.2, 132.3, 128.4, 128.4, 128.0, 127.1, 125.6, 119.1, 109.8, 47.7, 34.4, 31.4, 23.6, -3.2, -3.3 ppm. **IR** (film): 2963, 2904, 2227, 1604, 1500, 1429, 1363, 1268, 1092, 907, 819, 727, 574 cm^{-1}. **HRMS (ESI)**: calculated for $C_{27}H_{32}NGe^+$ $[M+H]^+$ 444.1741; found 444.1735.

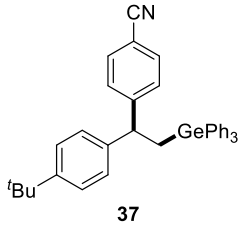
2.4.29 4-(1-(4-(tert-butyl)phenyl)-2-(methyldiphenylgermyl)ethyl)benzonitrile (**36**)



36
$C_{32}H_{33}NGe$
M = 504.25 g/mol

According to the general procedure using 4-tert-butylstyrene (32 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), methyldiphenylgermane (97.1 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (59.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **36** (53.4 mg, 53% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 2H), 7.36 – 7.31 (m, 10H), 7.29 – 7.24 (m, 4H), 7.12 – 7.05 (m, 2H), 2.12 – 2.02 (m, 2H), 1.29 (s, 9H), 0.30 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.0, 149.6, 141.8, 138.8, 138.7, 133.8, 132.8, 132.2, 129.2, 128.8, 128.5, 128.2, 1281, 127.2, 125.6, 119.1, 109.9, 47.5, 34.4, 31.4, 22.3, -5.0 ppm. **IR** (film): 2962, 2904, 2867, 2226, 1604, 1430, 1268, 1091, 907, 728, 574 cm^{-1}. **HRMS (ESI)**: calculated for $C_{32}H_{34}NGe^+$ $[M+H]^+$ 506.1898; found 506.1896.

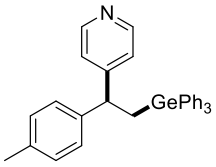
2.4.30 4-(1-(4-(tert-butyl)phenyl)-2-(triphenylgermyl)ethyl)benzonitrile (**37**)



37
$C_{37}H_{35}NGe$
M = 566.32 g/mol

According to the general procedure using 4-tert-butylstyrene (32 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), triphenylgermane (121.9 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (59.9 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **37** (66.8 mg, 59% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 5H), 7.32 – 7.27 (m, 12H), 7.22 – 7.17 (m, 4H), 7.06 – 7.02 (m, 2H), 4.27 (t, J = 7.8 Hz, 1H), 2.44 – 2.30 (m, 2H), 1.28 (s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.8, 149.6, 141.9, 136.5, 134.9, 132.2, 129.0, 128.6, 128.2, 127.2, 125.6, 119.1, 109.8, 47.4, 34.4, 31.4, 22.0 ppm. **IR** (film): 2962, 2866, 2227, 1604, 1420, 1090, 906, 727 cm^{-1}. **HRMS (ESI)**: calculated for $C_{37}H_{36}NGe^+$ $[M+H]^+$ 568.2054; found 568.2047.

2.4.31 4-(1-(p-tolyl)-2-(triphenylgermyl)ethyl)pyridine (**39**)

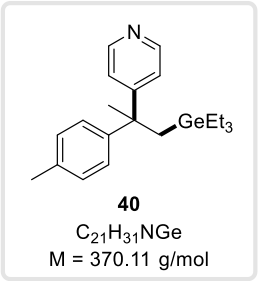


39
$C_{32}H_{29}NGe$
M = 500.22 g/mol

According to the general procedure using 4-methylstyrene (24 mg, 0.2 mmol, 1.0 equiv.), 4-canopyridine (41.2 mg, 0.4 mmol, 2.0 equiv.), triphenylgermane (121.9 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (70.0 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **39** (65.0 mg, 65% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 – 8.24 (m, 2H), 7.41 – 7.33 (m, 4H), 7.32 – 7.27 (m, 11H), 7.07 (d, J = 5.0 Hz, 2H), 7.02 – 6.94 (m, 4H), 4.19 (t, J = 7.8 Hz, 1H), 2.41 – 2.32 (m, 2H), 2.28 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.2, 149.6, 141.6, 136.5, 136.4, 134.9, 129.3, 128.9, 128.2, 127.6, 123.0, 46.8, 21.5, 21.0 ppm. **IR** (film): 3069, 2922,

2247, 1597, 1430, 1090, 904, 724, 697, 648 cm^{-1}. **HRMS (ESI)**: calculated for $C_{32}H_{30}NGe^{+}$ $[M+H]^{+}$ 502.1585; found 502.1580.

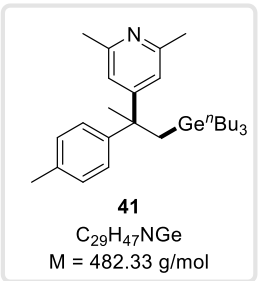
2.4.32 4-(2-(p-tolyl)-1-(triethylgermyl)propan-2-yl)pyridine (**40**)



40
$C_{21}H_{31}NGe$
M = 370.11 g/mol

According to the general procedure using 2-(p-methylphenyl)propene (26.4 mg, 0.2 mmol, 1.0 equiv.), 4-canopyridine (41.2 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (70.0 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **40** (46.6 mg, 63% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 – 8.41 (m, 2H), 7.18 – 7.14 (m, 2H), 7.11 – 7.06 (m, 4H), 2.31 (s, 3H), 1.76 – 1.66 (m, 2H), 1.65 (s, 3H), 0.88 (t, J = 7.9 Hz, 9H), 0.52 – 0.45 (m, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) 161.1, 149.5, 146.5, 135.7, 128.9, 126.8, 122.3, 45.1, 29.7, 27.2, 21.0, 8.9, 5.3 ppm. **IR** (film): 2947, 2869, 1594, 1511, 1408, 1374, 1018, 821, 693, 570 cm^{-1}. **HRMS (ESI)**: calculated for $C_{21}H_{32}NGe^{+}$ $[M+H]^{+}$ 372.1741; found 372.1730.

2.4.33 2,6-dimethyl-4-(2-(p-tolyl)-1-(tributylgermyl)propan-2-yl)pyridine (**41**)

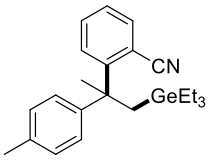


41
$C_{29}H_{47}NGe$
M = 482.33 g/mol

According to the general procedure using 2-(p-methylphenyl)propene (26.4 mg, 0.2 mmol, 1.0 equiv.), 2,6-dimethylpyridine-4-carbonitrile (52.8 mg, 0.4 mmol, 2.0 equiv.), ^{n}Bu_3GeH (97.9 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (70.0 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **41** (77.1 mg, 80% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 – 7.02 (m, 4H), 6.85 – 6.81 (m, 2H), 2.46 (s, 6H), 2.30 (s, 3H), 1.67 (s, 2H), 1.61 (s, 3H), 1.25 – 1.12 (m, 12H), 0.84 (t, J = 7.1 Hz, 9H), 0.51 – 0.42 (m, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.3, 157.2, 147.1, 135.4, 128.8, 126.8, 118.9, 45.0, 29.8, 28.1, 27.3, 26.7, 24.7, 20.9, 13.9, 13.8 ppm. **IR**

(film): 2955, 2922, 2870, 2194, 1715, 1601, 1561, 1456, 1375, 1190, 1081, 906, 821, 729 cm^{-1}. **HRMS (ESI)**: calculated for $C_{29}H_{48}NGe^{+}$ $[M+H]^{+}$ 484.2993; found 484.2981.

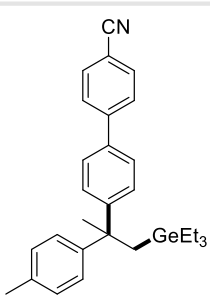
2.4.34 2-(2-(p-tolyl)-1-(tributylgermyl)propan-2-yl)benzonitrile (**42**)



42
$C_{23}H_{31}NGe$
M = 394.13 g/mol

According to the general procedure using 2-(p-methylphenyl)propene (26.4 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (70.0 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **42** (28.3 mg, 36% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.67 (m, 1H), 7.61 – 7.52 (m, 2H), 7.32 – 7.25 (m, 1H), 7.13 – 7.04 (m, 4H), 2.31 (s, 3H), 2.21 – 2.14 (m, 1H), 1.89 – 1.66 (m, 4H), 0.90 (t, J = 7.9 Hz, 9H), 0.51 – 0.40 (m, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.2, 147.1, 135.7, 135.6, 132.2, 128.7, 127.2, 127.1, 126.5, 118.9, 112.7, 45.9, 31.0, 26.1, 21.1, 8.9, 8.8, 5.1 ppm. **IR** (film): 2948, 2904, 2870, 2221, 1595, 1511, 1456, 1225, 1018, 908, 731, 571 cm^{-1}. **HRMS (ESI)**: calculated for $C_{23}H_{32}NGe^{+}$ $[M+H]^{+}$ 396.1741; found 396.1741.

2.4.35 4'-(2-(p-tolyl)-1-(triethylgermyl)propan-2-yl)-[1,1'-biphenyl]-4-carbonitrile (**43**)

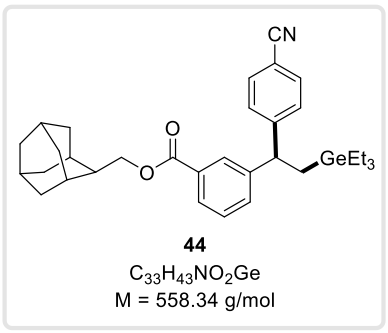


43
$C_{29}H_{35}NGe$
M = 470.23 g/mol

According to the general procedure using 2-(p-methylphenyl)propene (26.4 mg, 0.2 mmol, 1.0 equiv.), 4,4′ -Biphenyldicarbonitrile (81.6 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (70.0 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **43** (28.2 mg, 30% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$)

δ 7.72 – 7.66 (m, 4H), 7.49 – 7.46 (m, 2H), 7.38 – 7.35 (m, 2H), 7.18 – 7.15 (m, 2H), 7.09 – 7.06 (m, 2H), 2.32 (s, 3H), 1.79 – 1.75 (m, 2H), 1.71 (s, 3H), 0.90 (t, J = 7.9 Hz, 9H), 0.50 (q, J = 7.8 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.9, 148.2, 145.5, 136.2, 135.3, 132.6, 128.7, 127.8, 127.6, 126.9, 126.7, 119.2, 110.6, 45.1, 30.4, 28.0, 21.0, 9.0, 5.4 ppm. **IR** (film): 2947, 2927, 2869, 2226, 1606, 1491, 1456, 1104, 1018, 907, 822, 570 cm^{-1}. **HRMS (ESI)**: calculated for $C_{29}H_{36}NGe^+$ $[M+H]^+$ 472.2054; found 472.2050.

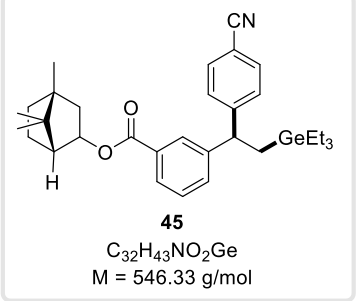
2.4.36 (Adamantan-2-yl)methyl 3-(1-(4-cyanophenyl)-2-(triethylgermyl)ethyl)benzoate (**44**)



44
$C_{33}H_{43}NO_2Ge$
M = 558.34 g/mol

According to the general procedure using adamantan-2-yl)methyl 3-vinylbenzoate (59.2 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (70.0 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **44** (75.9 mg, 68% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 1H), 7.91 – 7.84 (m, 1H), 7.57 – 7.54 (m, 2H), 7.43 – 7.35 (m, 4H), 4.19 (t, J = 8.1 Hz, 1H), 3.93 – 3.87 (m, 2H), 2.03 – 1.99 (m, 3H), 1.75 – 1.57 (m, 14H), 0.90 (t, J = 7.9 Hz, 9H), 0.53 (q, J = 7.9 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 152.3, 145.9, 132.4, 132.1, 131.0, 128.8, 128.6, 128.3, 127.9, 119.0, 110.2, 74.5, 48.1, 39.5, 37.0, 33.6, 28.1, 19.0, 8.9, 4.3 ppm. **IR** (film): 2903, 2871, 2848, 2228, 1715, 1605, 1454, 1276, 1182, 1104, 906, 728, 573 cm^{-1}. **HRMS (ESI)**: calculated for $C_{33}H_{44}NO_2Ge^+$ $[M+H]^+$ 560.2578; found 560.2571.

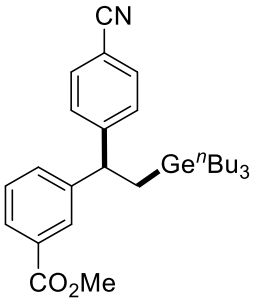
2.4.37 4,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3-((R)-1-(4-cyanophenyl)-2-triethylgermyl)ethyl)benzoate (**45**)



45
$C_{32}H_{43}NO_2Ge$
M = 546.33 g/mol

According to the general procedure using 4,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3-vinylbenzoate (56.8 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), Et_3GeH (64.3 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $[Ir(ppy)_2(dtbbpy)][PF_6]$ (2 mol%, 3.7 mg, 0.004 mmol), $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (70.0 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **45** (68.8 mg, 63% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 1H), 7.91 – 7.85 (m, 1H), 7.59 – 7.53 (m, 2H), 7.46 – 7.32 (m, 4H), 5.12 – 5.04 (m, 1H), 4.19 (t, J = 8.1 Hz, 1H), 2.51 – 2.43 (m, 1H), 2.14 – 2.02 (m, 1H), 1.88 – 1.70 (m, 3H), 1.62 – 1.52 (m, 2H), 1.45 – 1.36 (m, 1H), 1.33 – 1.23 (m, 2H), 1.14 – 1.02 (m, 2H), 0.96 (s, 3H), 0.94 – 0.87 (m, 12H), 0.54 (q, J = 7.7 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 152.3, 145.9, 132.4, 132.0, 131.2, 128.8, 128.6, 128.3, 127.8, 119.0, 110.2, 80.7, 49.2, 48.1, 47.9, 45.0, 37.0, 28.1, 27.4, 19.8, 19.0, 13.7, 8.9, 4.3 ppm. **IR** (film): 2951, 2871, 2228, 1711, 1605, 1455, 1284, 1185, 1114, 1017, 729, 573 cm^{-1}. **HRMS (ESI)**: calculated for $C_{32}H_{44}NO_2Ge^+$ $[M+H]^+$ 548.2578; found 548.2576.

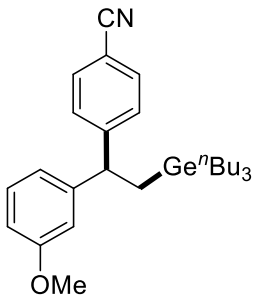
2.4.38 methyl (R)-3-(1-(4-cyanophenyl)-2-(tributylgermyl)ethyl)benzoate (**47**)



47
$C_{29}H_{41}NO_2Ge$
M = 508.28 g/mol

According to the general procedure using methyl 4-vinylbenzoate (32.4 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), ^{n}Bu_3GeH (97.9 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (65.3 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **47** (71.1 mg, 70% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 1H), 7.90 – 7.84 (m, 1H), 7.58 – 7.52 (m, 2H), 7.45 – 7.32 (m, 4H), 4.18 (t, J = 8.0 Hz, 1H), 3.90 (s, 3H), 1.61 – 1.44 (m, 2H), 1.27 – 1.11 (m, 12H), 0.83 (t, J = 6.9 Hz, 9H), 0.55 – 0.45 (m, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 152.4, 145.9, 132.4, 132.3, 130.5, 128.8, 128.6, 128.3, 128.0, 119.0, 110.1, 52.2, 48.2, 27.3, 26.6, 19.8, 13.8, 12.8 ppm. **IR** (film): 2953, 2923, 2870, 2227, 1722, 1605, 1444, 1282, 1195, 1107, 846, 736 cm^{-1}. **HRMS (ESI)**: calculated for $C_{29}H_{42}NO_2Ge^+$ $[M+H]^+$ 510.2422; found 510.2415.

2.4.39 4-(1-(3-methoxyphenyl)-2-(tributylgermyl)ethyl)benzonitrile (**48**)



48
$C_{28}H_{41}NOGe$
M = 480.27 g/mol

According to the general procedure using 3-vinylanisole (26.8 mg, 0.2 mmol, 1.0 equiv.), 1,4-dicyanobenzene (51 mg, 0.4 mmol, 2.0 equiv.), $^nBu_3GeH$ (97.9 mg, 0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2 mL) in the presence of $HSCH_2CO_2C_2H_5$ (10 mol%, 2.4 mg, 0.02 mmol) and K_3PO_4 (65.3 mg, 0.4 mmol, 2.0 equiv.) under 2×40 W blue LED light irradiation provided the product **48** (65.3 mg, 68% yield) as colorless oil after purification by preparative TLC (petroleum PE/EA = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.43 – 7.37 (m, 2H), 7.20 (t, J = 7.9 Hz, 1H), 6.84 (d, J = 7.9 Hz, 1H), 6.81 – 6.77 (m, 1H), 6.75 – 6.69 (m, 1H), 4.09 (t, J = 8.0 Hz, 1H), 3.77 (s, 3H), 1.60 – 1.52 (m, 1H), 1.49 – 1.42 (m, 1H), 1.26 – 1.16 (m, 12H), 0.85 (t, J = 6.9 Hz, 9H), 0.57 – 0.49 (m, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 152.9, 147.1, 132.3, 129.7, 128.3, 120.1, 119.1, 113.9, 111.3, 109.9, 55.2, 48.3, 27.3, 26.6, 19.9, 13.8, 12.8 ppm. **IR** (film): 2954, 2922, 2853, 2226, 1598, 1488, 1455, 1261, 1146, 1049, 873, 780, 693, 545 cm^{-1}. **HRMS (ESI)**: calculated for $C_{28}H_{42}NOGe^+$ $[M+H]^+$ 482.2473; found 482.2464.

3. Computational Investigations

3.1 DFT calculations

All calculations were performed with the Gaussian 16 package.[1] Geometry optimizations and frequencies calculations were performed at UM06-2X[2] level of theory. The SDD basis set is employed for the germanium atom and Iridium atom,[3] and the 6-31+G(d,p) basis set is used for all the other atoms. Intrinsic reaction coordinate calculations are performed to confirm that each transition state connects with the desired reactants and products.[4] To obtain more accurate energies, single-point energy calculations were done with the UM06-2X functional. The SDD basis set is employed for the germanium atom and Iridium atom, and the cc-PVTZ basis set is used for all the other atoms in conjugation with the polarizable continuum model (SMD) solvation model for acetonitrile.[5] The 3D structures of the optimized species were generated using CYLview.[6]

3.2 Macus theory calculations

The barrier heights of single electron transfer steps were calcualted by using Marcus-Hush theory.[7] The free energy barrier of a single electron transfer process of outer-sphere electron transfer can be applied according to the following equation:

$$\Delta G_{ET}^{\dagger} = \frac{(\Delta G_{\mathrm{r}} + \lambda)^2}{4\lambda}$$

Where ΔG_{r} is the Gibbs free energy change of the studied single electron transfer step, λ is the reorganization energy which includes two components, inner reorganization energy (λ_i) and outer reorganization energy (λ_0). The outer-sphere electron transfer model is applicable and the activation barrier may be estimated from the outer-sphere Marcus-Hush model. Since the inner reorganization energies are usually small and could be neglected. Thus, the total reorganization energy $\lambda \approx \lambda_0$.

$$\lambda = \lambda_{\mathrm{o}} = 332\left(\frac{1}{2\mathrm{a}_1} + \frac{1}{2\mathrm{a}_2} - \frac{1}{R}\right)\left(\frac{1}{\varepsilon_{opt}} - \frac{1}{\varepsilon}\right)$$

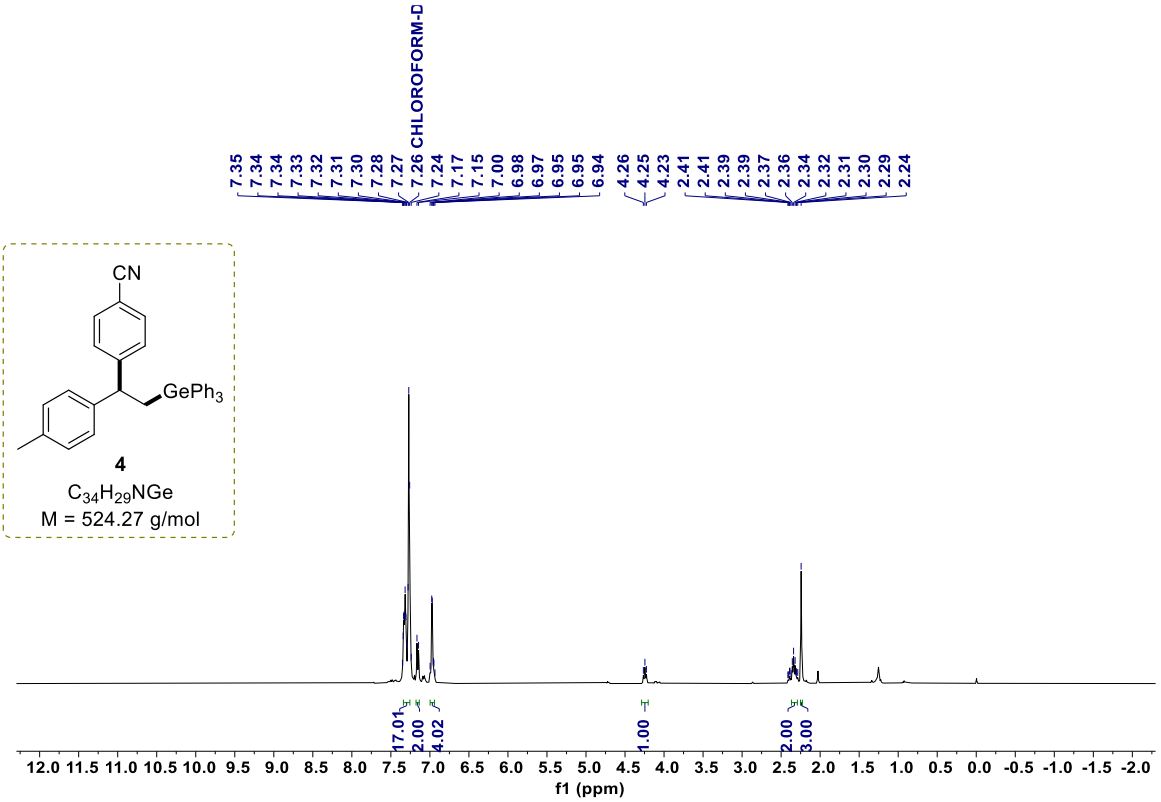
Where, a_1 and a_2 are the radii of donor and acceptor, R is the sum of a_1 and a_2, ε_{opt} and ε is the optical dielectric constant and static dielectric constant of solvent respectively (for CH_3CN ε_{opt} = 1.80, ε = 35.68). a_1 and a_2 are calculated by using Multiwfn package.[8]

Table S2. Calculated free energy barriers ($\Delta G_{ET}^{\dagger}$, kcal/mol) of single electron transfer steps and their relevant parameters.

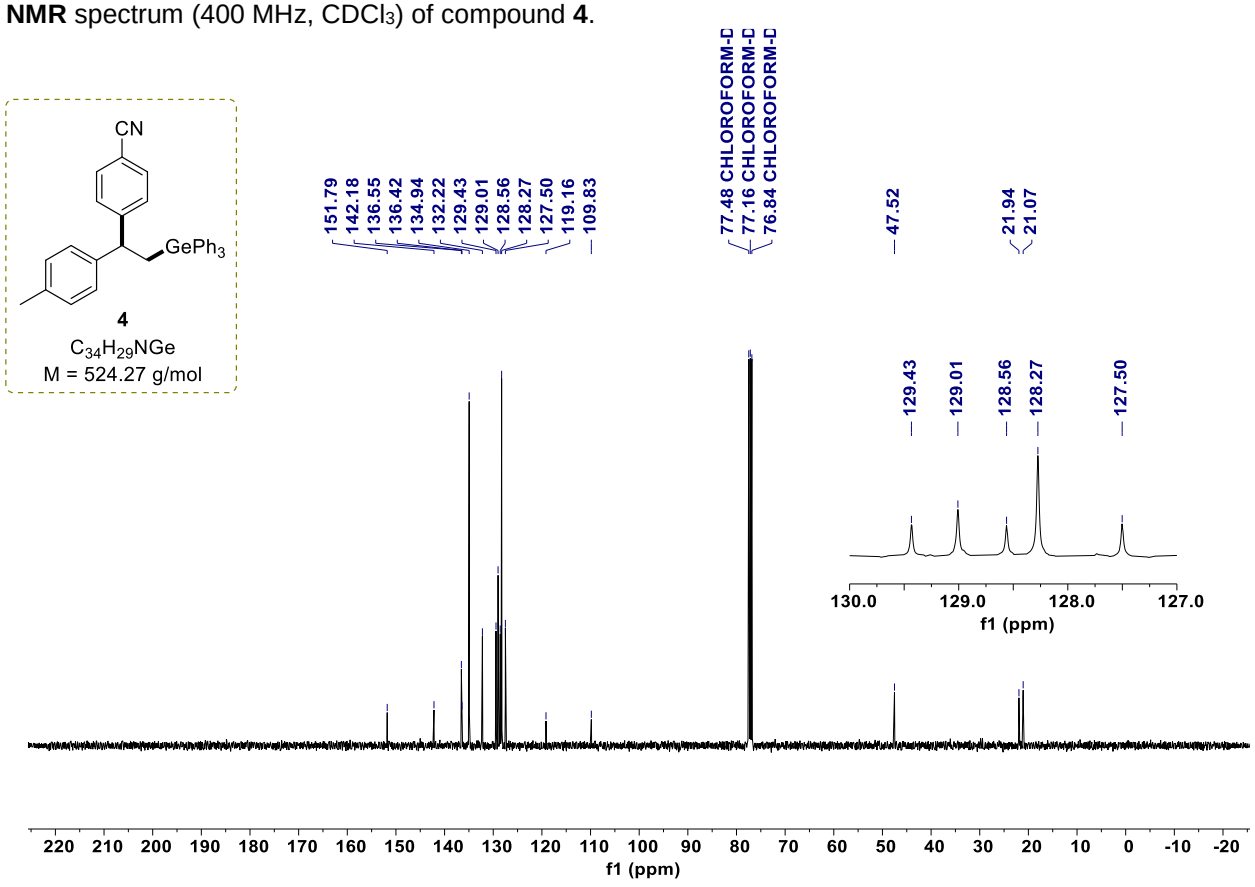
entry	a_1 (Å)	a_2 (Å)	R (Å)	λ	ΔG_r	$\Delta G_{ET}^{\dagger}$
SET1	8.18	5.53	13.71	13.70	-2.94	2.11
SET2	4.85	8.58	13.43	15.14	-31.90	4.63

4. NMR Spectra

4.1 4-(1-(p-tolyl)-2-(triphenylgermyl)ethyl)benzonitrile (**4**)

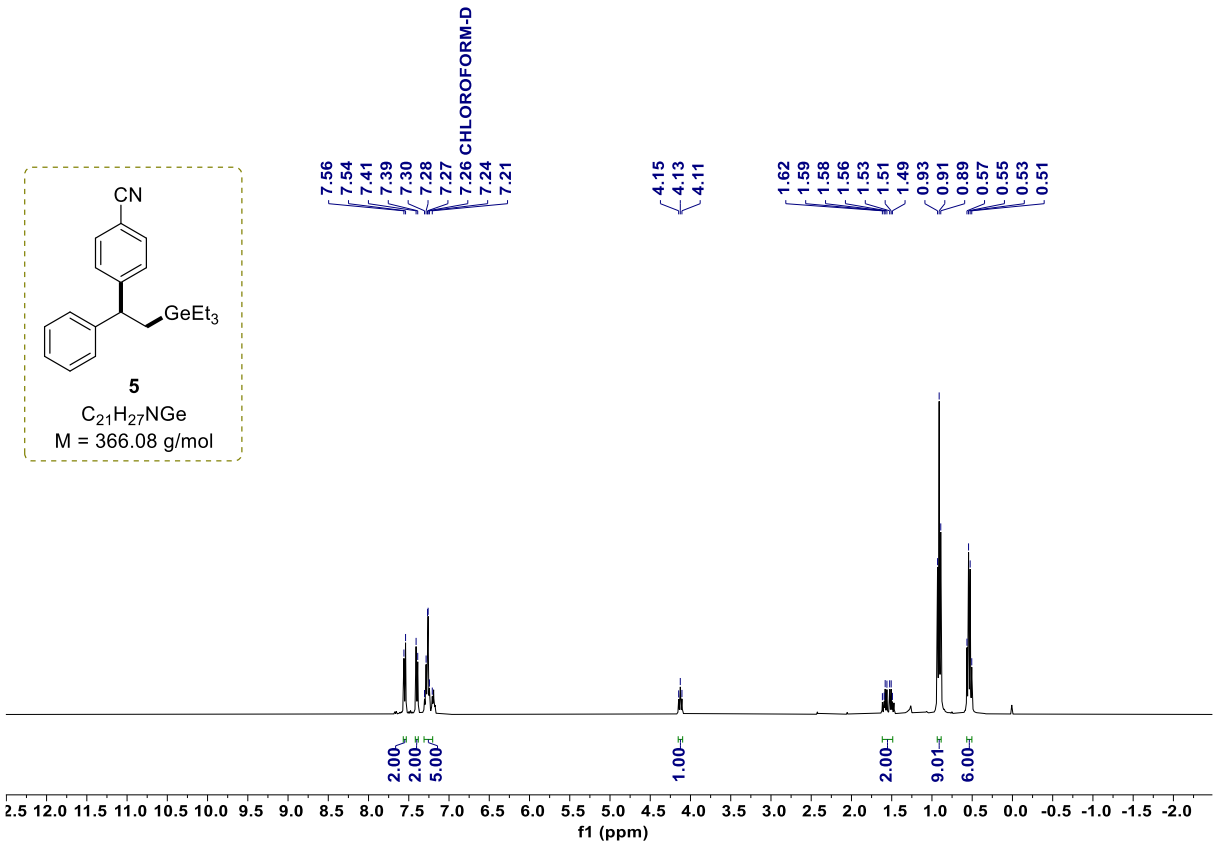


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4**.

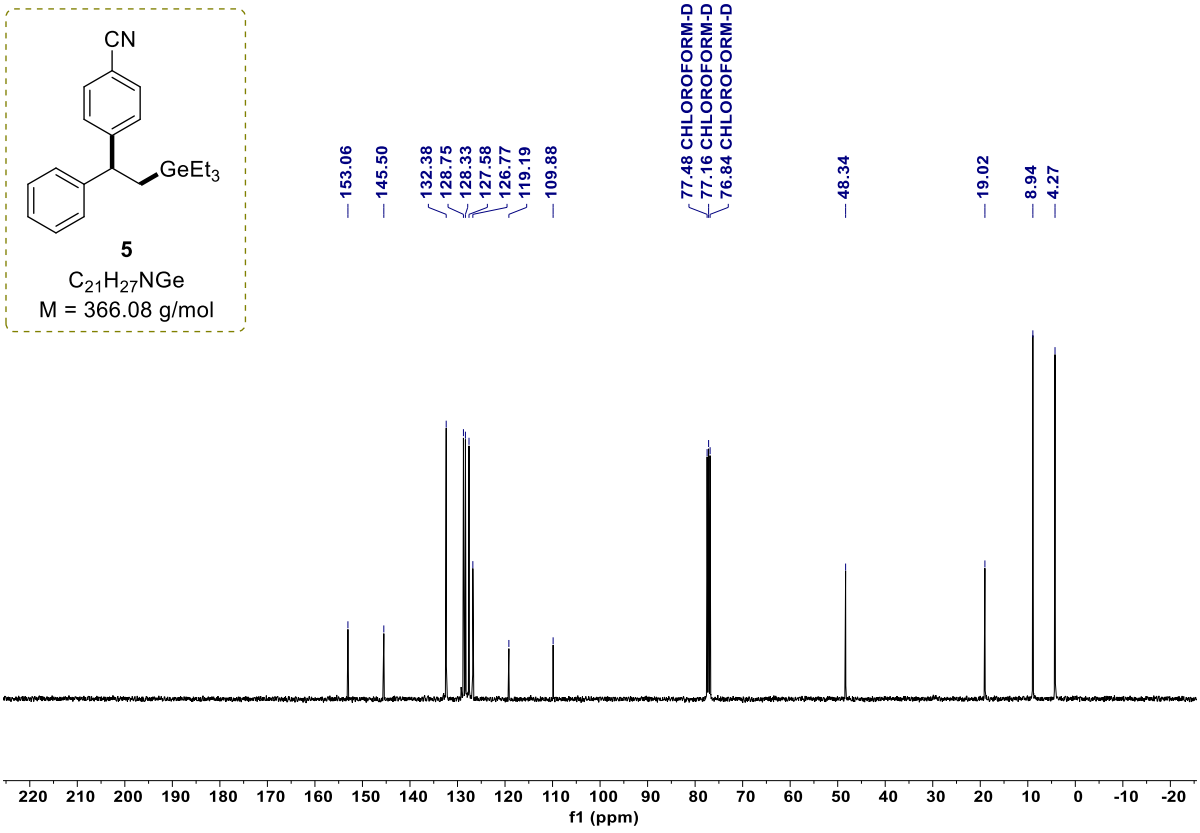


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4**.

4.2 4-(1-phenyl-2-(triphenylgermyl)ethyl)benzonitrile (**5**)

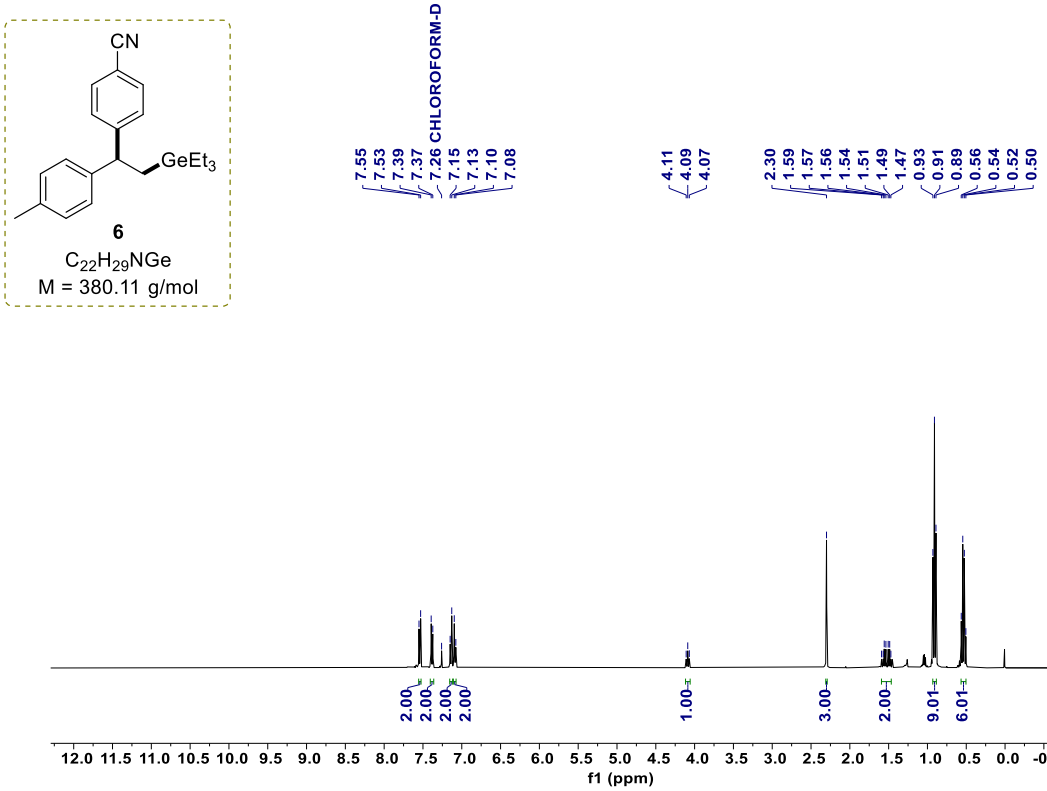


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5**.

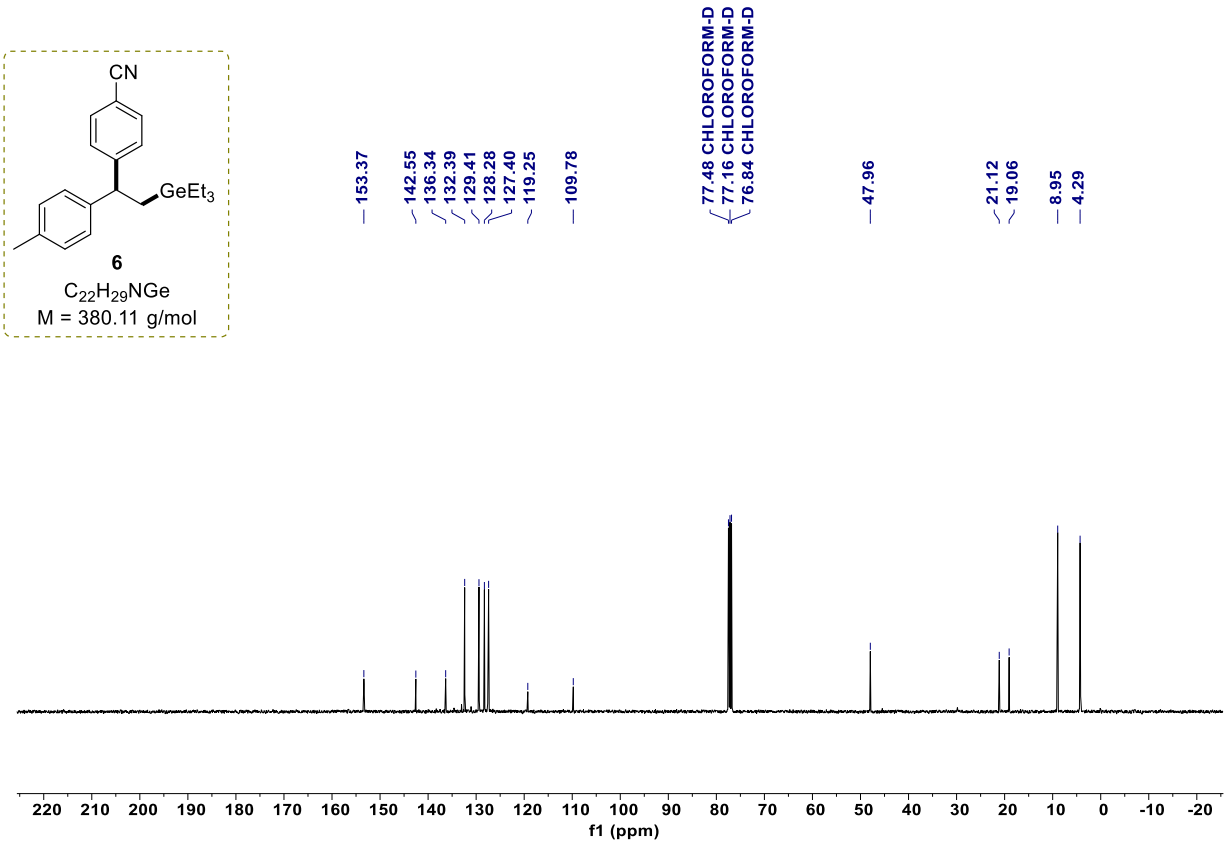


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **5**.

4.3 4-(1-(p-tolyl)-2-(triethylgermyl)ethyl)benzonitrile (**6**)

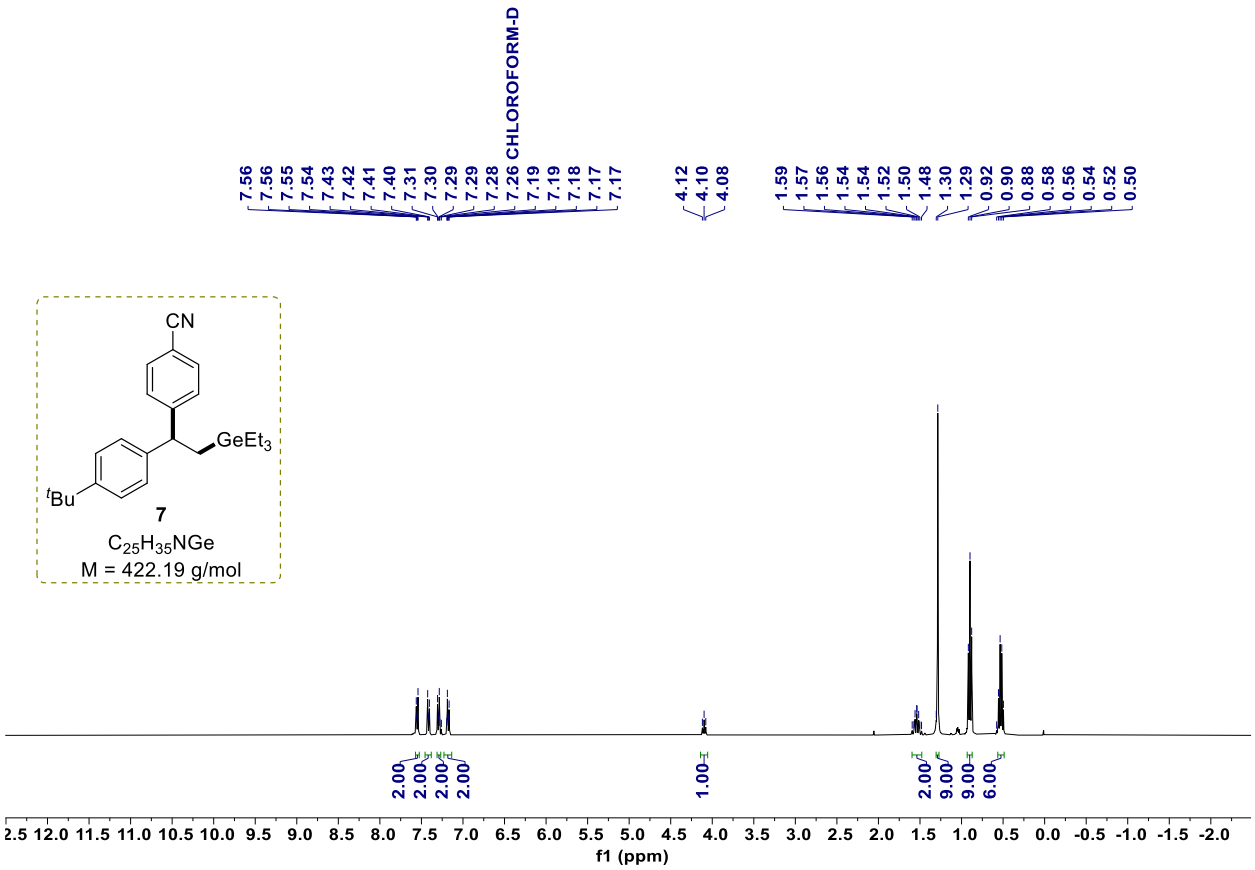


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **6**.

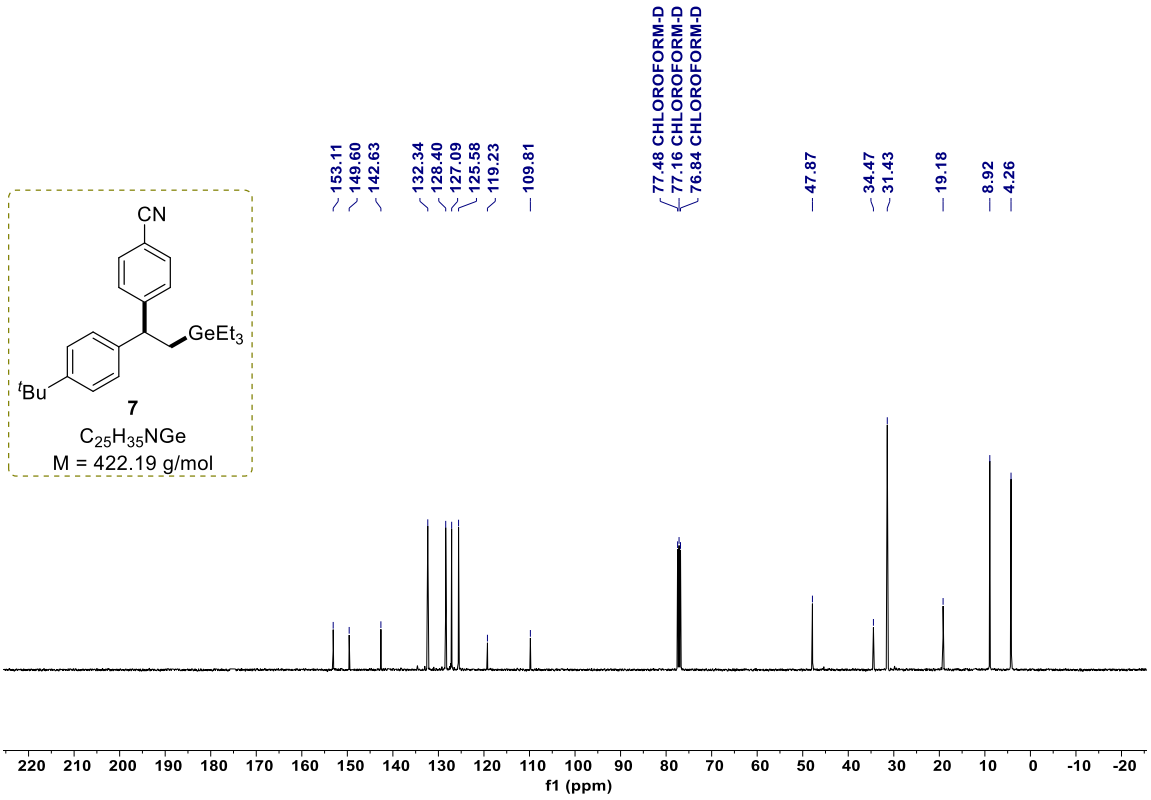


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **6**.

4.4 4-(1-(4-(tert-butyl)phenyl)-2-(triethylgermyl)ethyl)benzonitrile (**7**)

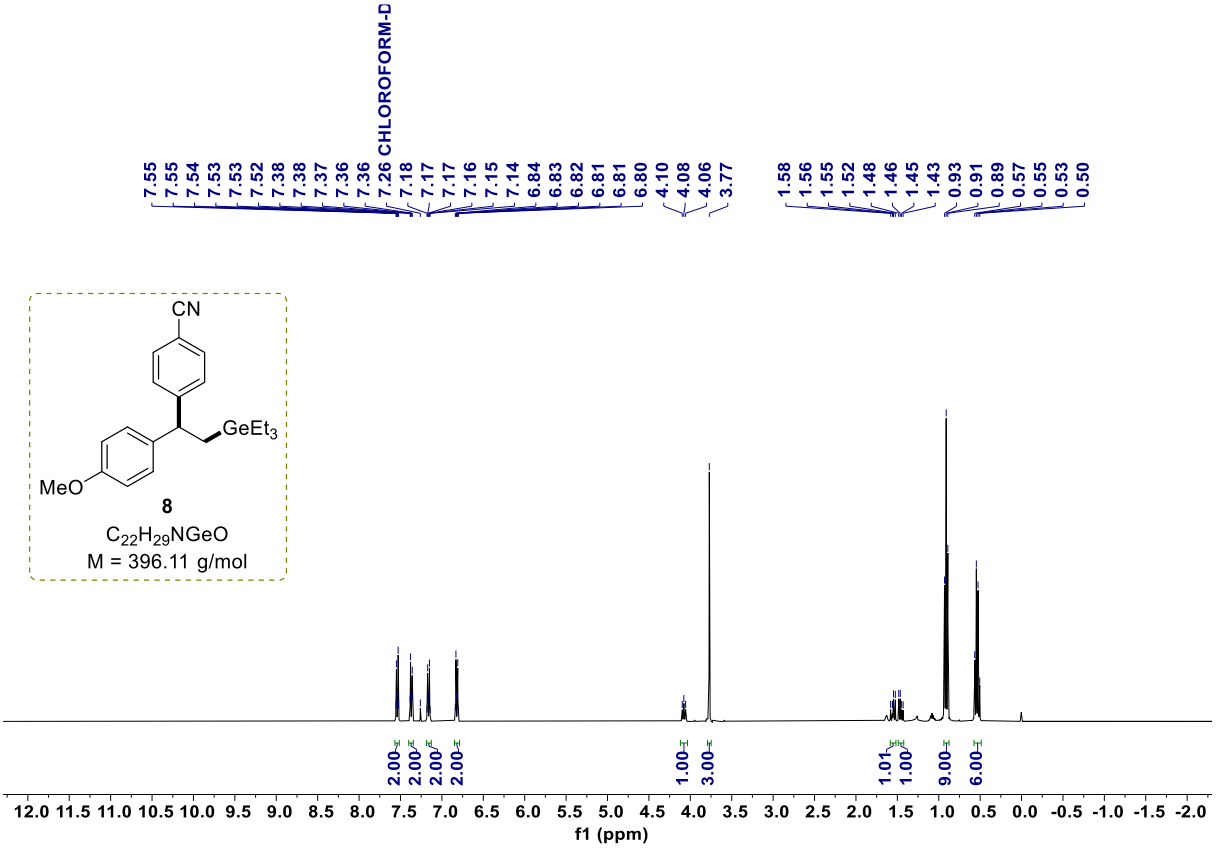


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **7**.

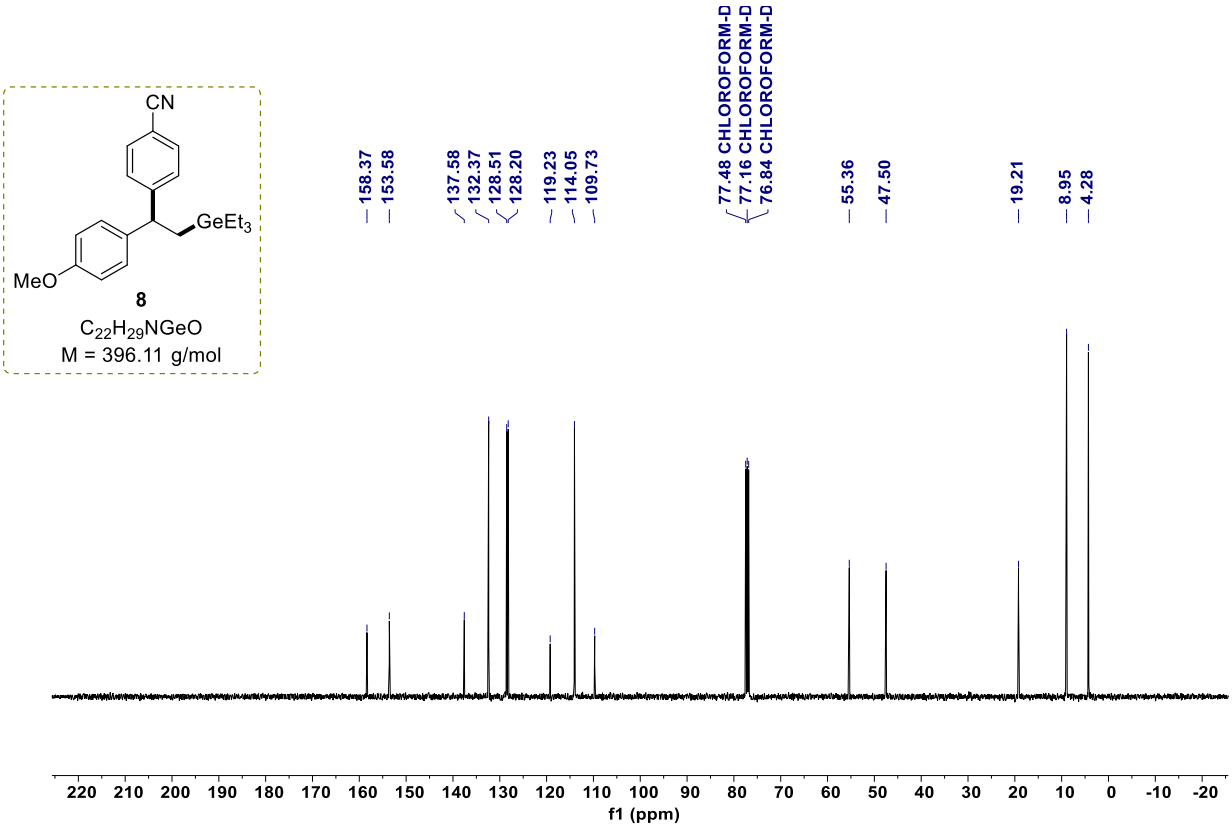


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **7**.

4.5 4-(1-(4-methoxyphenyl)-2-(triethylgermyl)ethyl)benzonitrile (**8**)

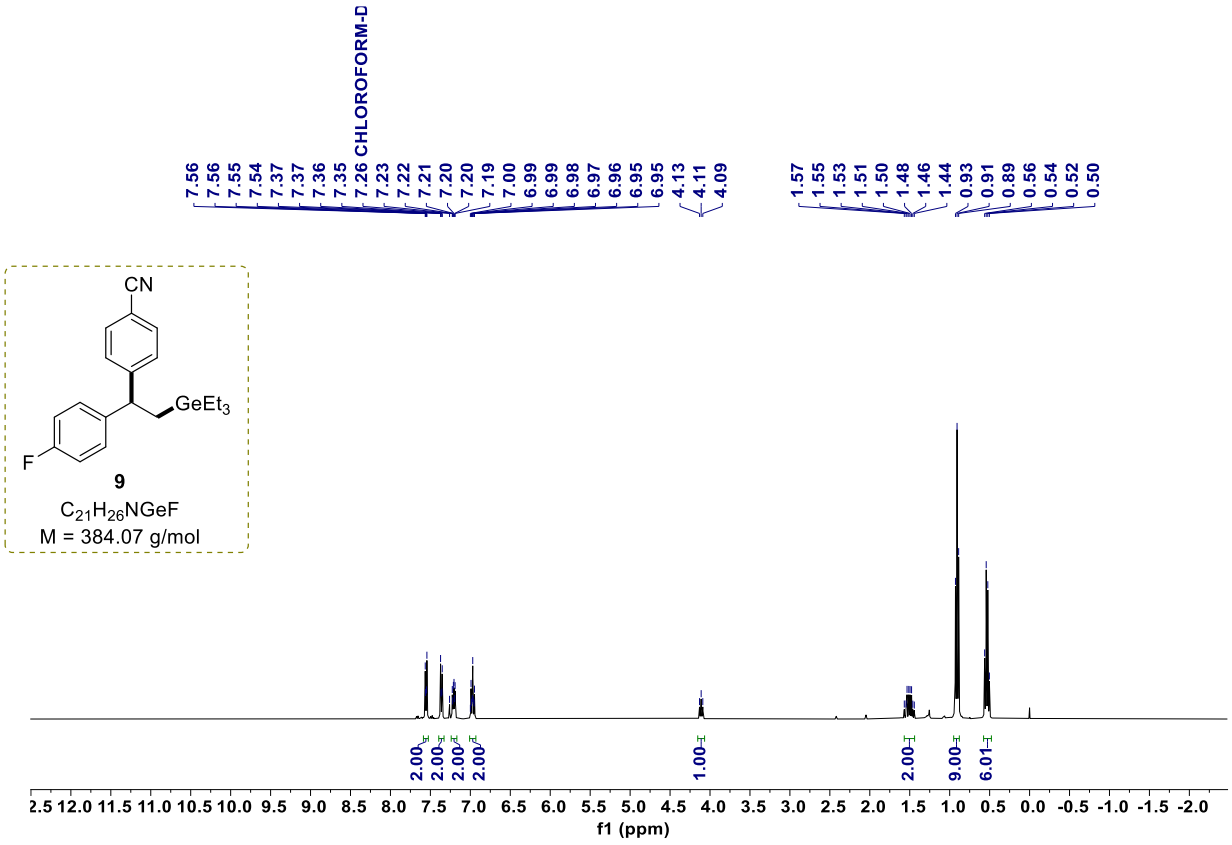


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **8**.

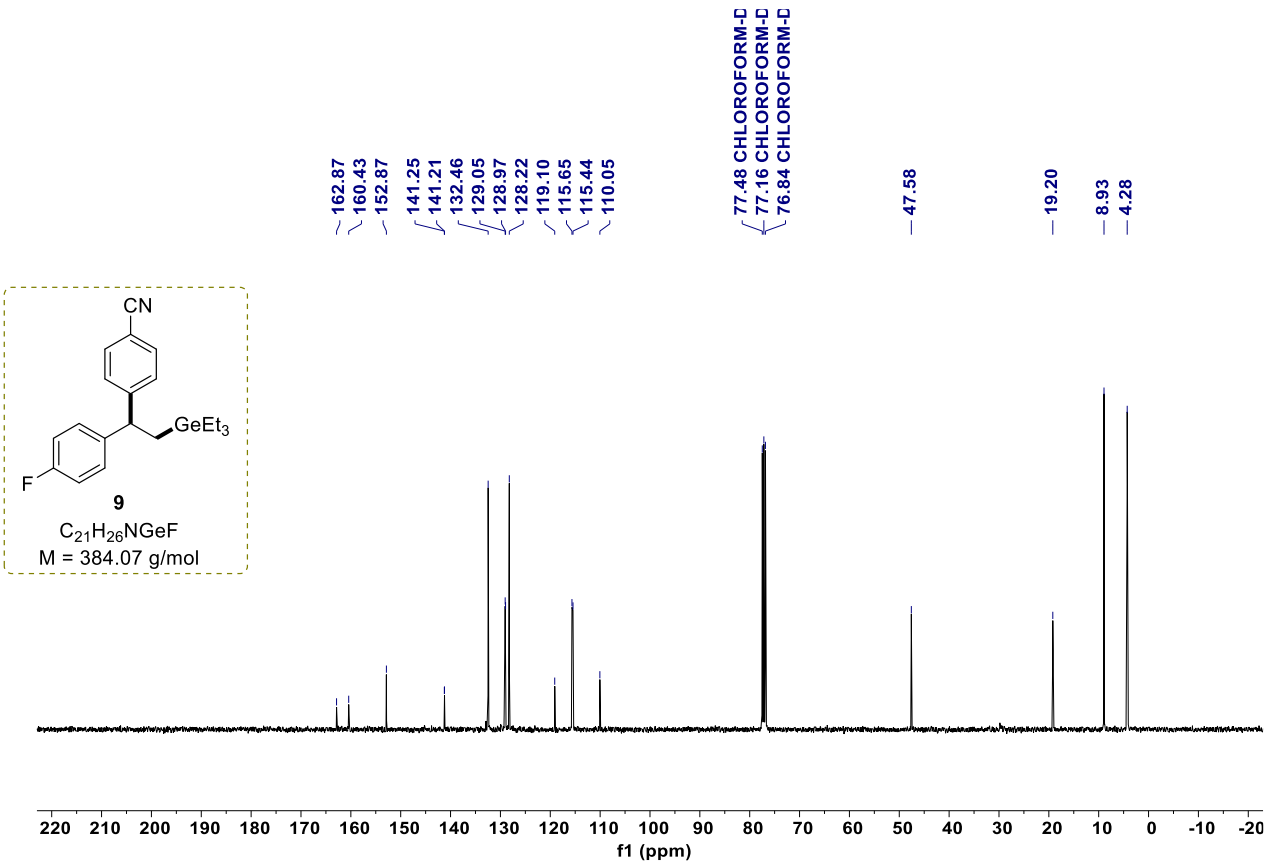


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **8**.

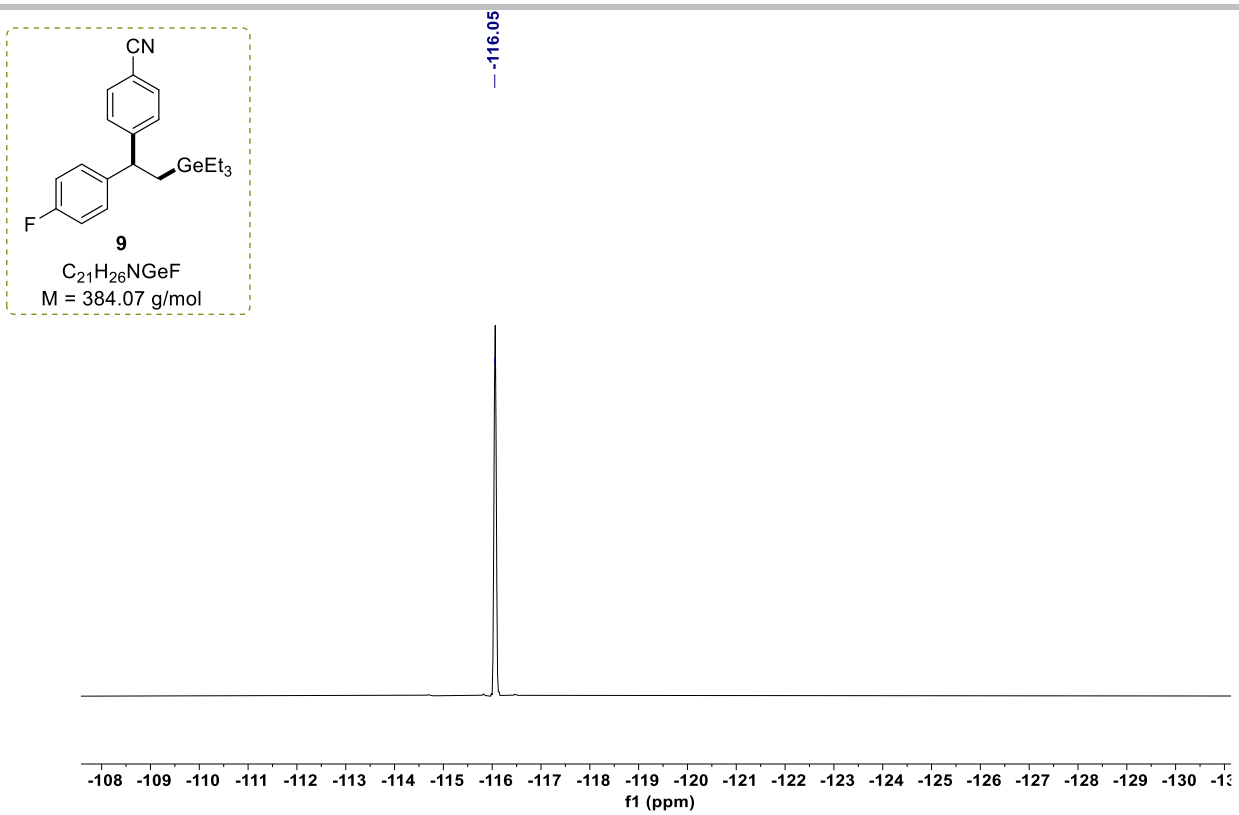
4.6 4-(1-(4-fluorophenyl)-2-(triethylgermyl)ethyl)benzonitrile (**9**)



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **9**.

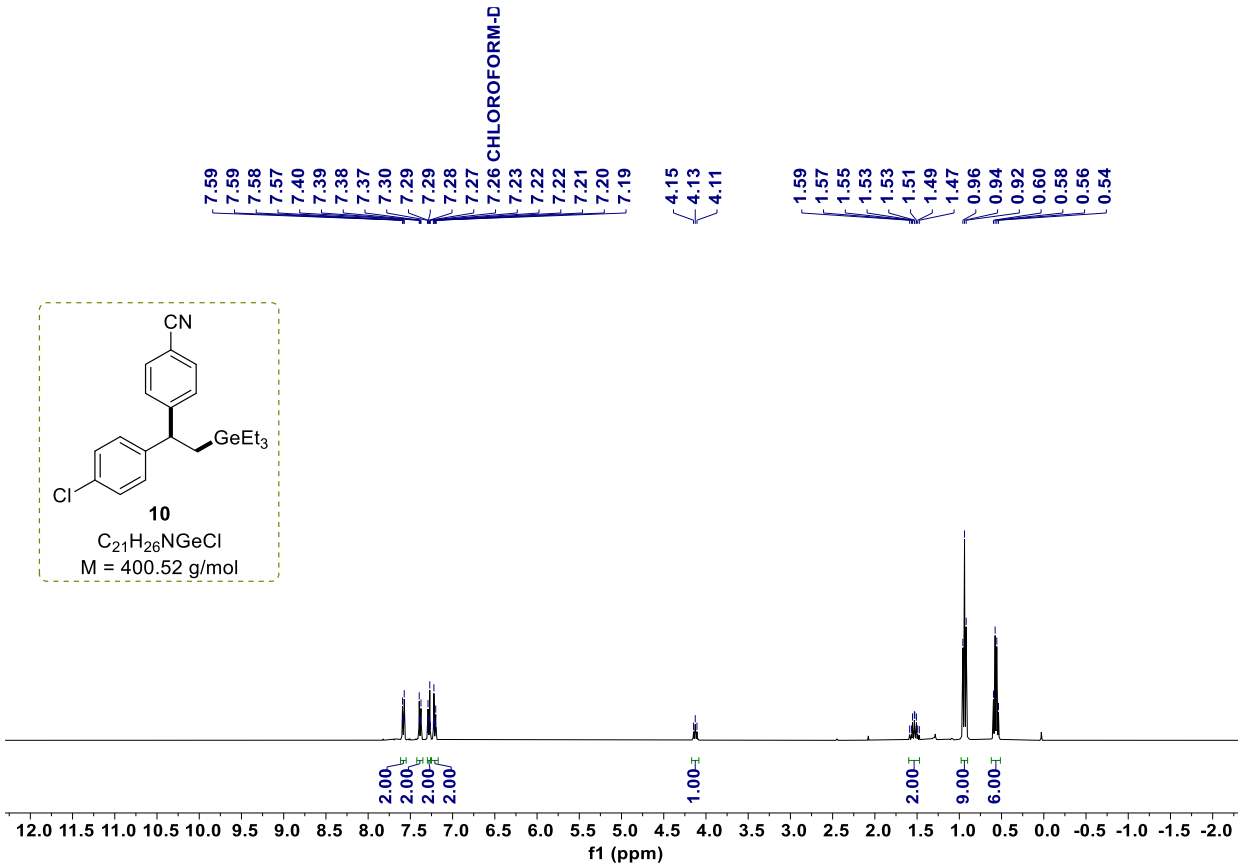


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **9**.

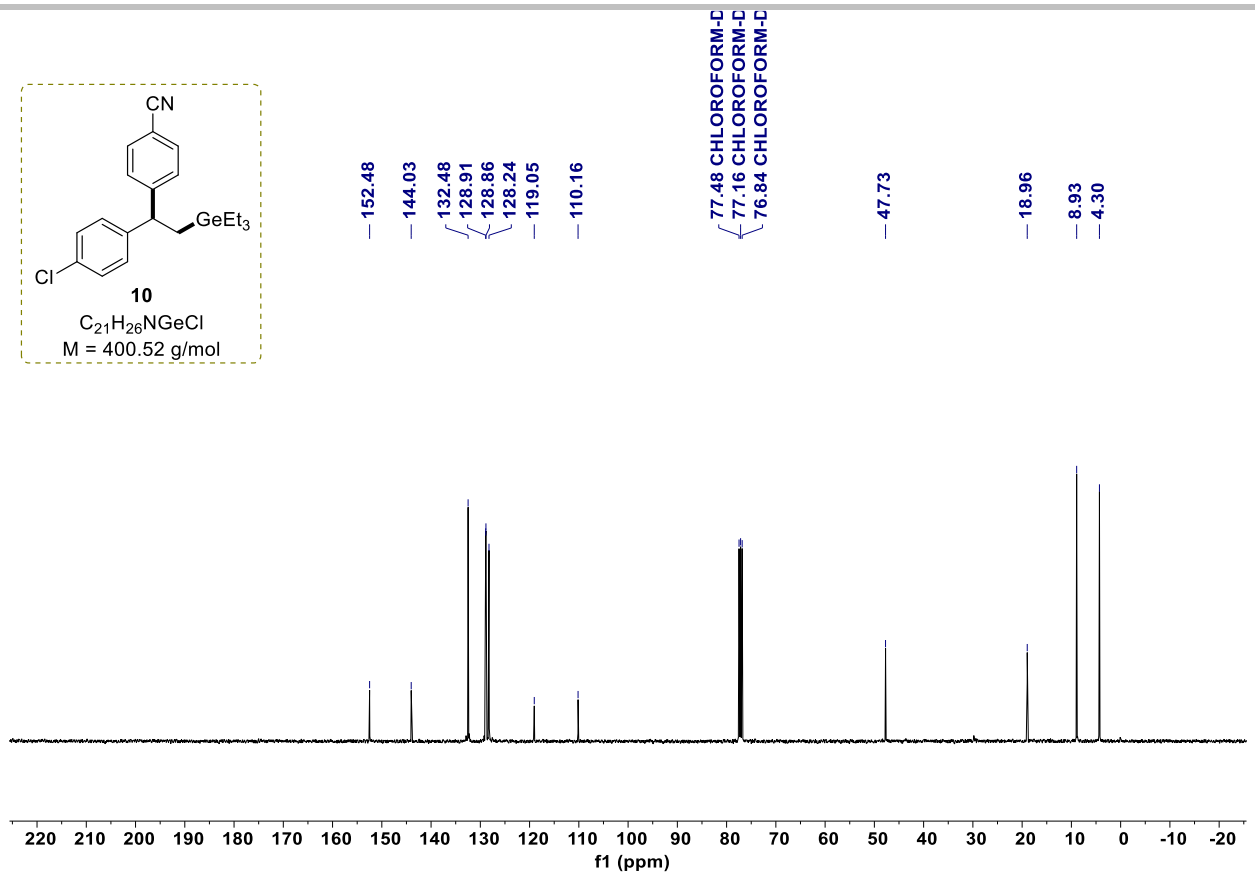


^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **9**.

4.7 4-(1-(4-chlorophenyl)-2-(triethylgermyl)ethyl)benzonitrile (**10**)

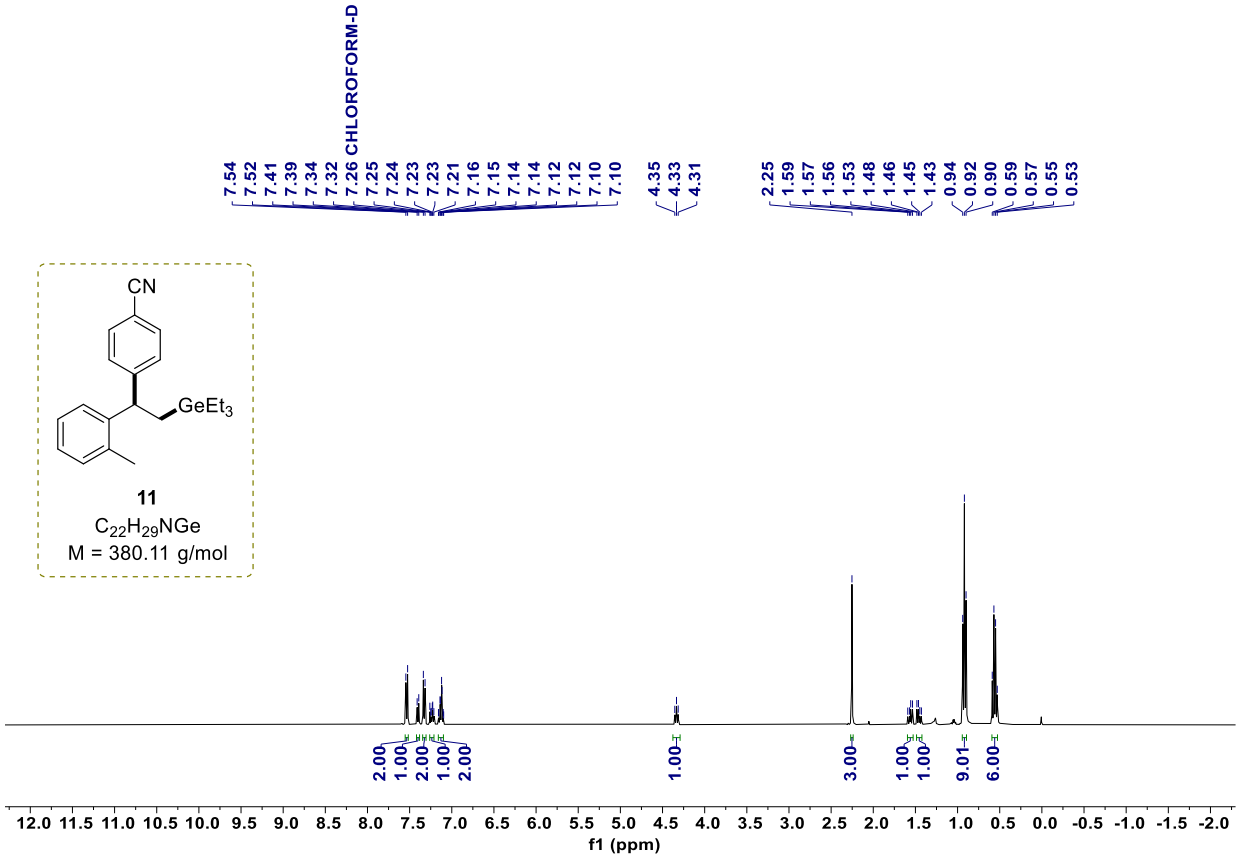


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **10**.

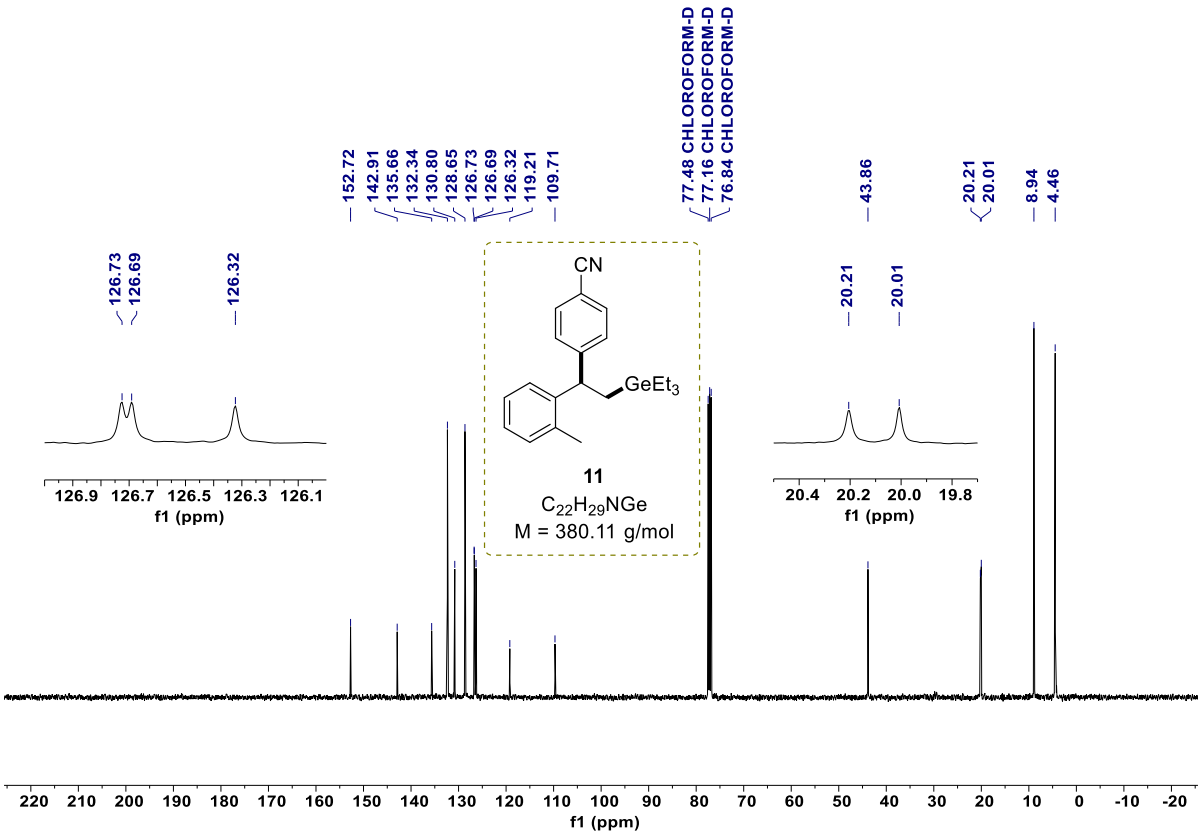


$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **10**.

4.8 4-(1-(o-tolyl)-2-(triethylgermyl)ethyl)benzonitrile (**11**)

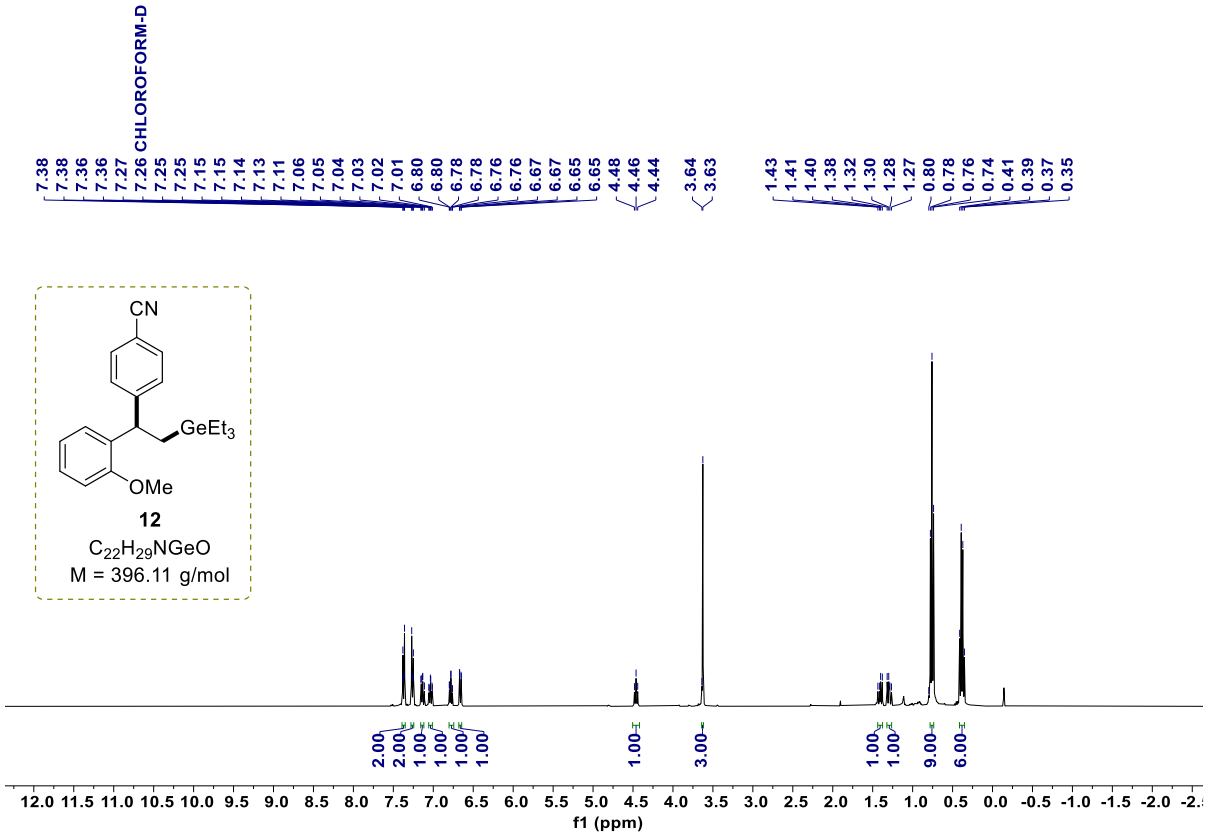


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **11**.

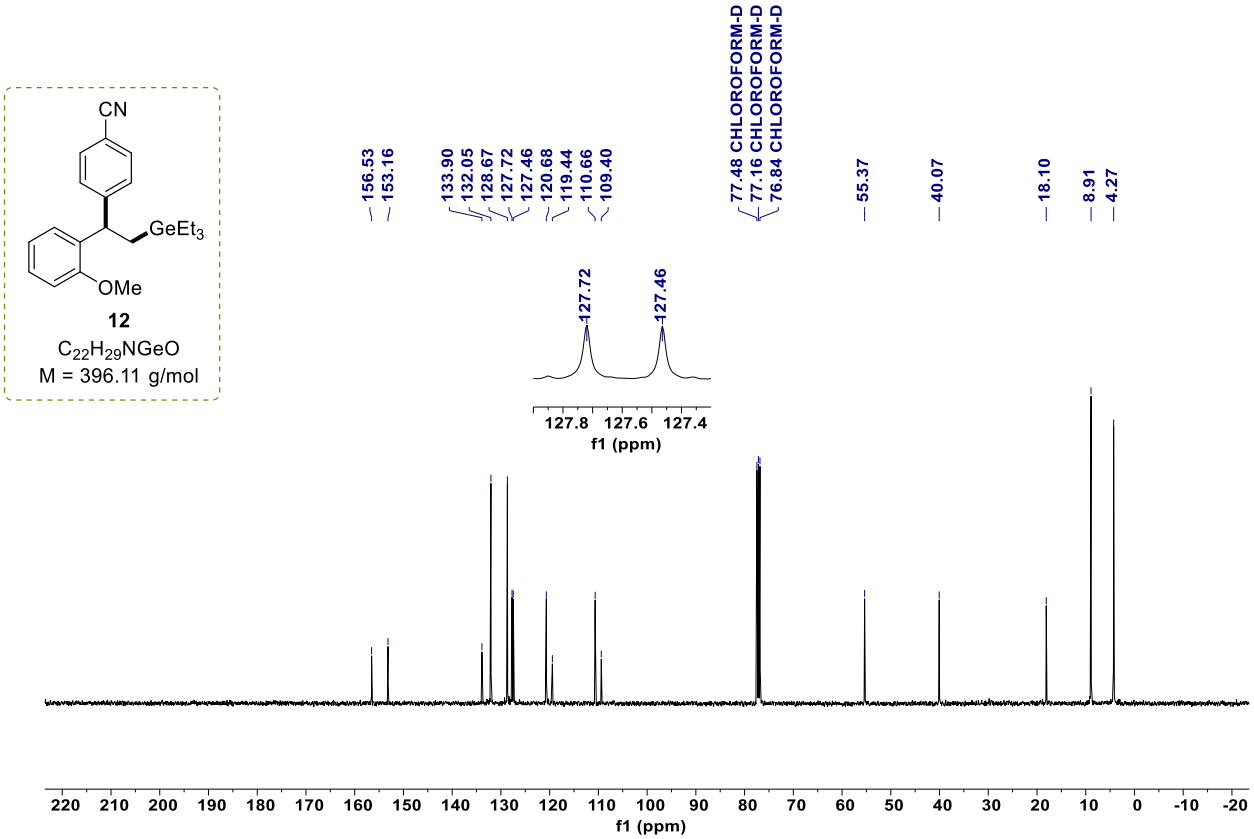


$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **11**.

4.9 4-(1-(2-methoxyphenyl)-2-(triethylgermyl)ethyl)benzonitrile (**12**)

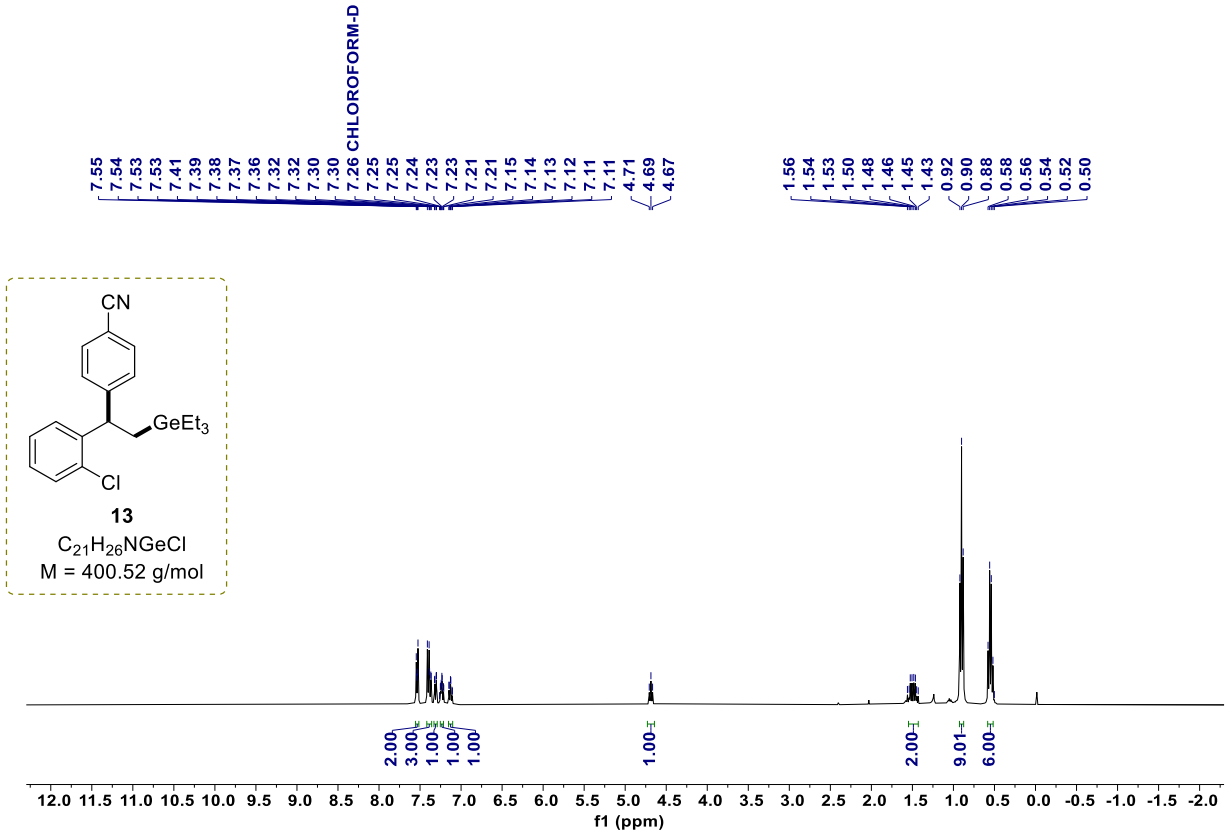


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **12**.

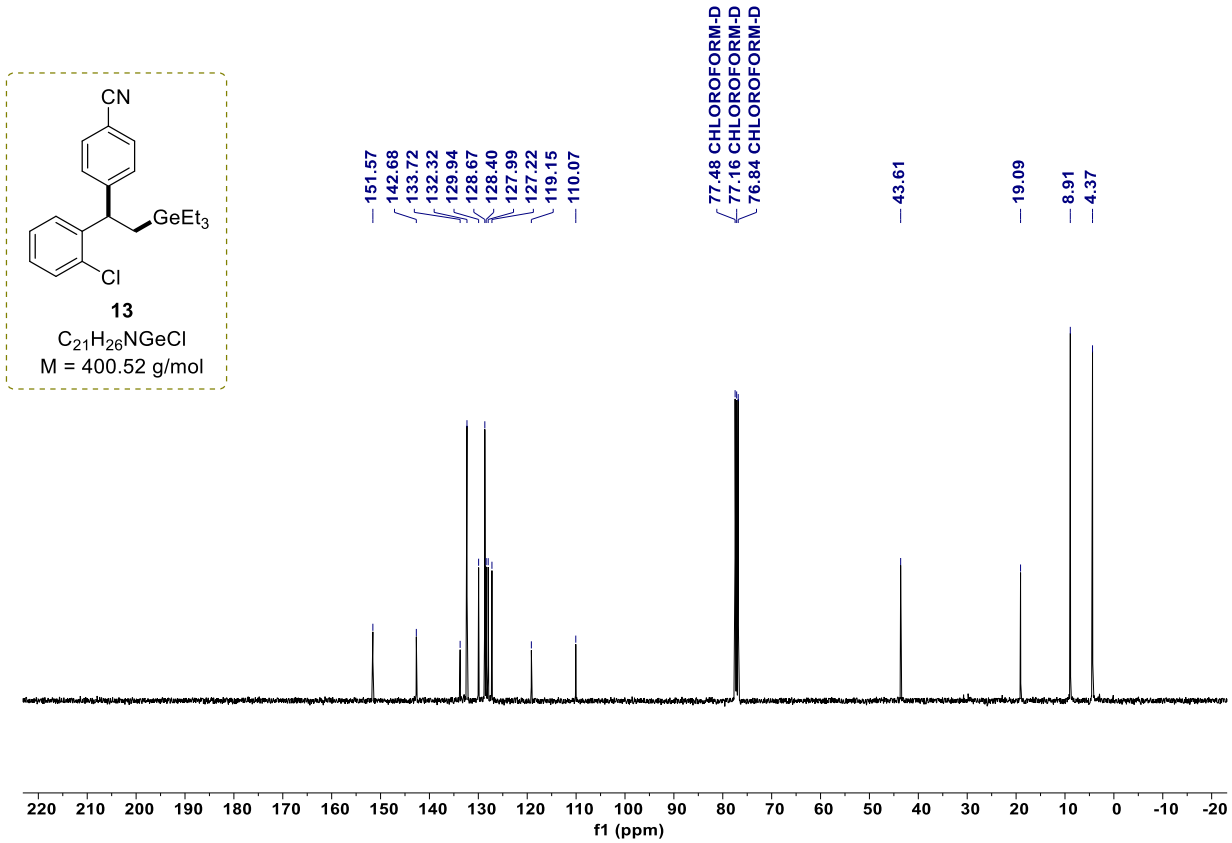


$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **12**.

4.10 4-(1-(2-chlorophenyl)-2-(triethylgermyl)ethyl)benzonitrile (**13**)

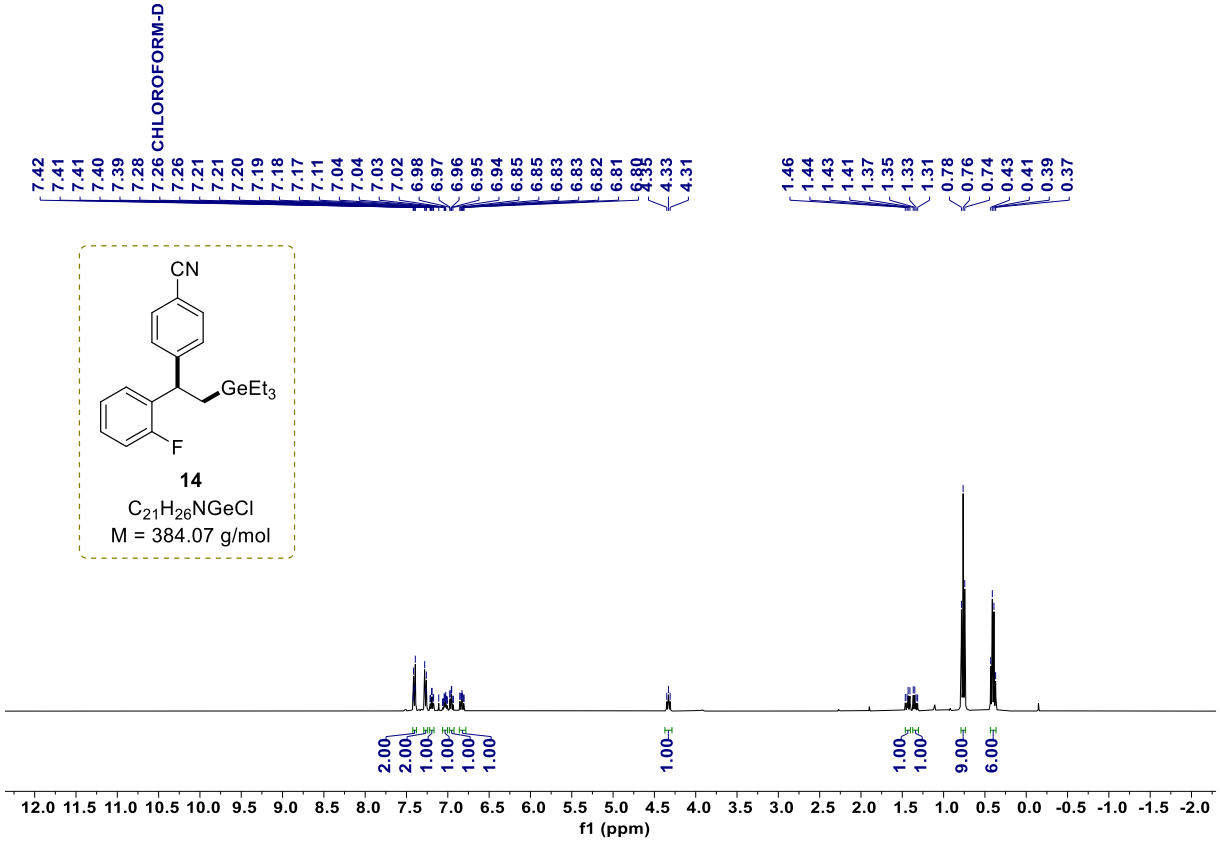


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **13**.

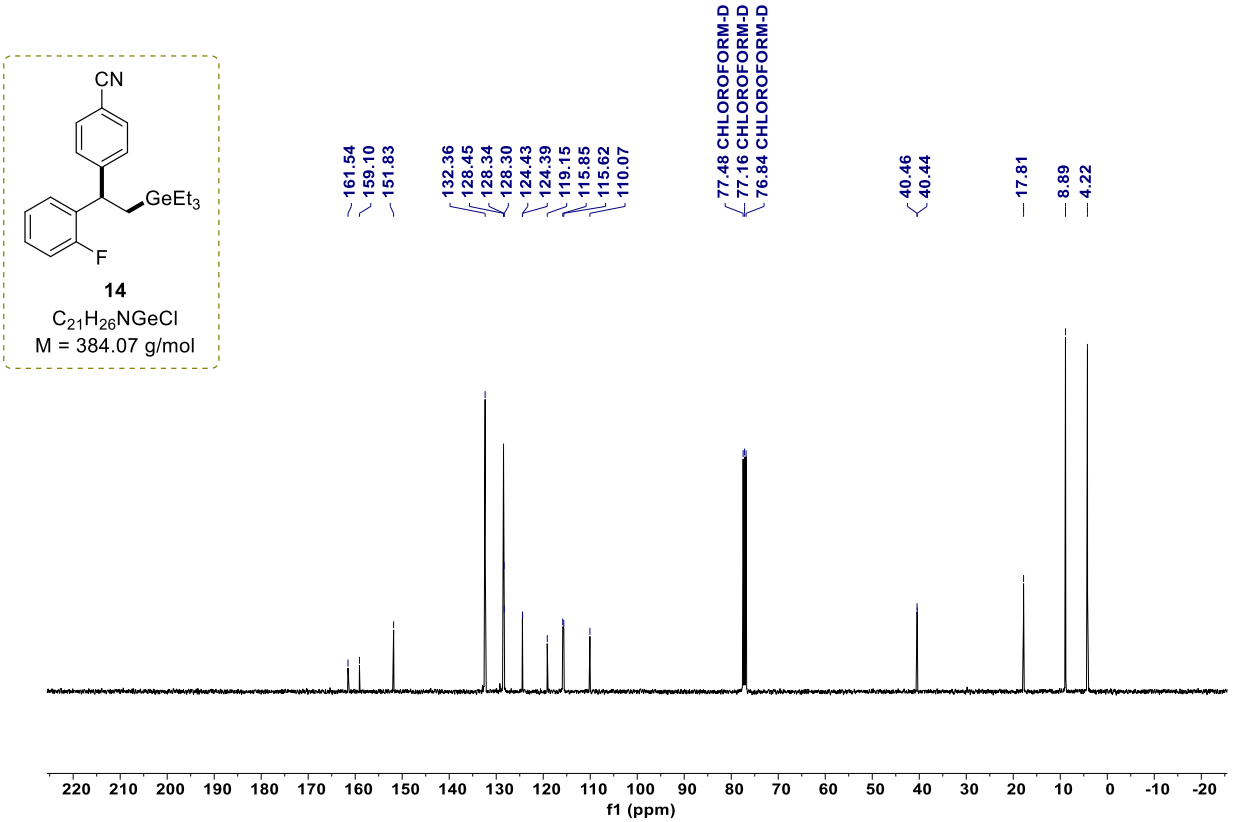


$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **13**.

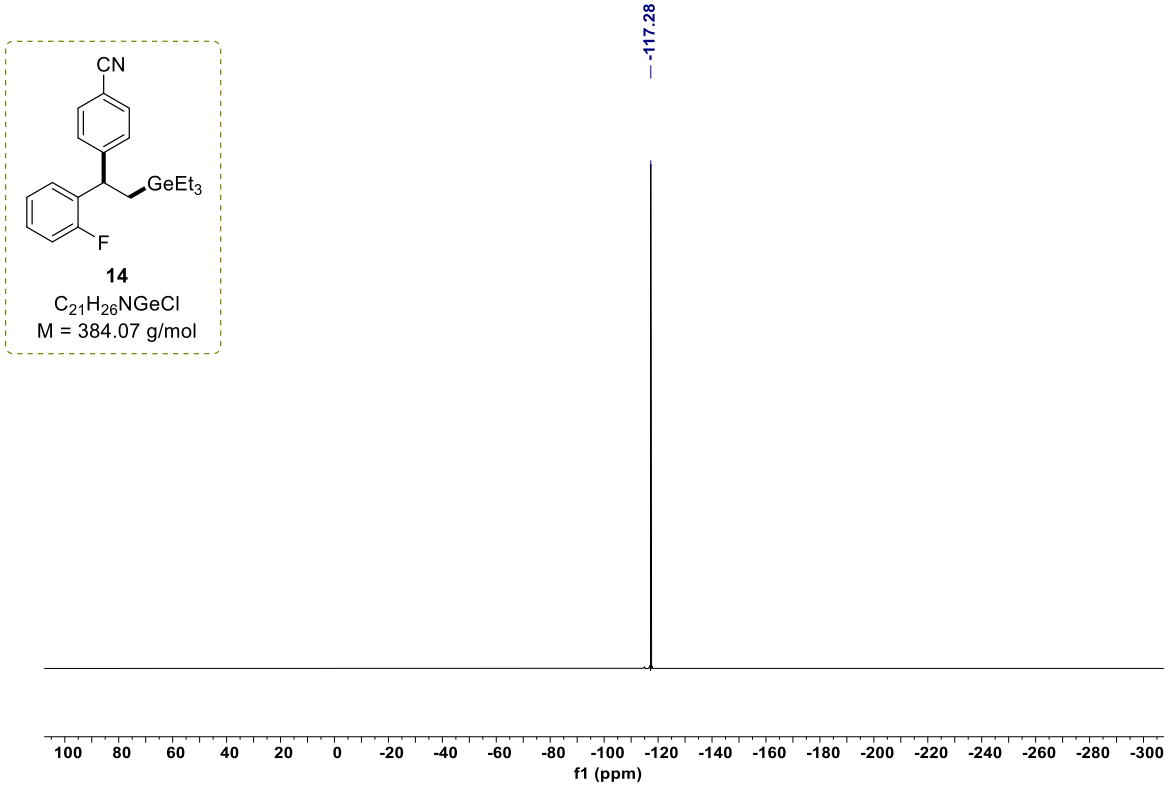
4.11 4-(1-(2-fluorophenyl)-2-(triethylgermyl)ethyl)benzonitrile (**14**)



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **14**.

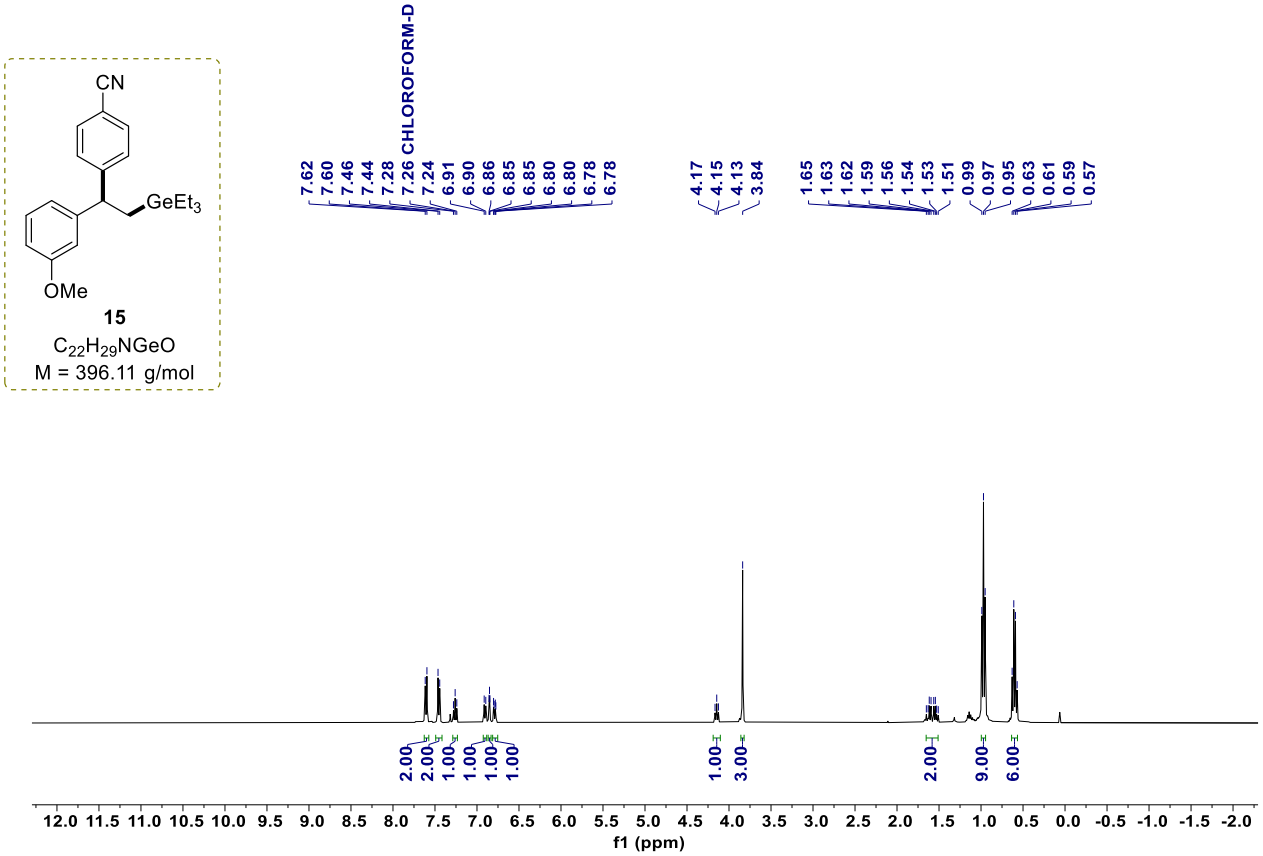


$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **14**.

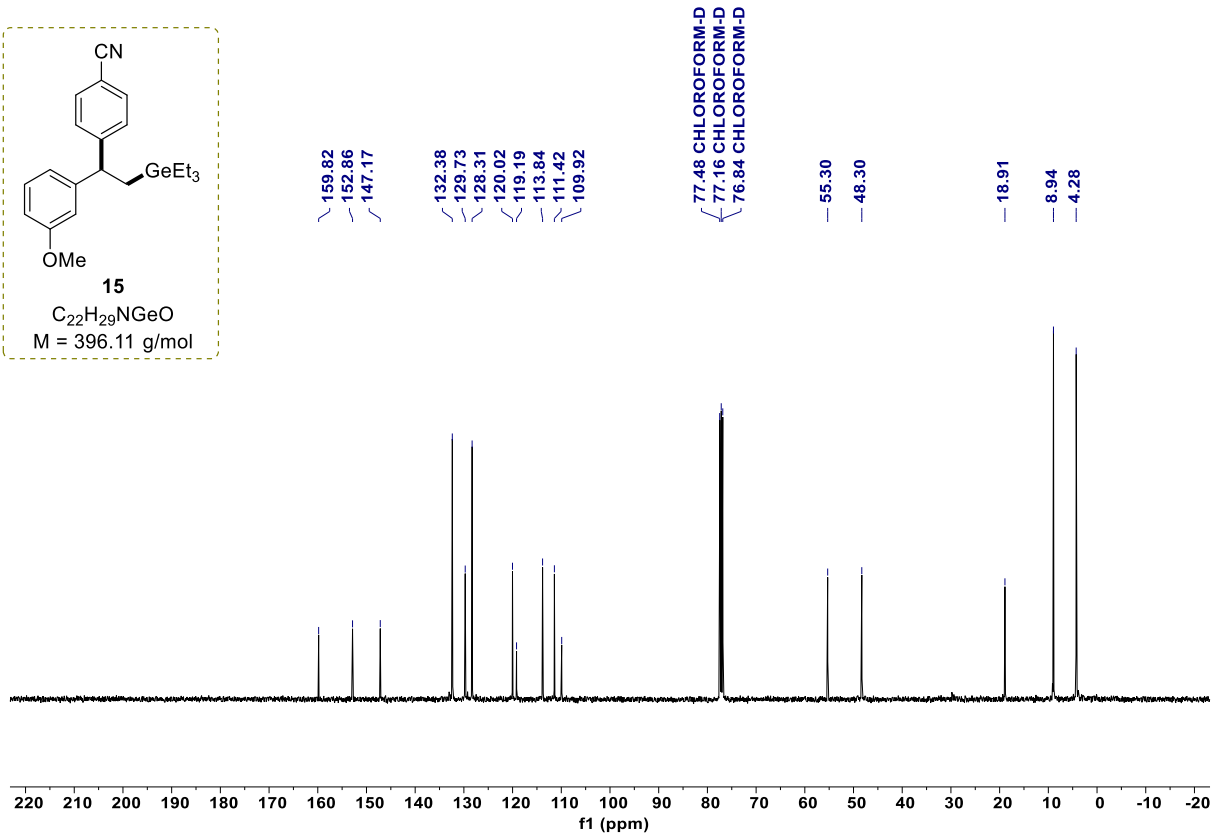


^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **14**.

4.12 4-(1-(3-methoxyphenyl)-2-(triethylgermyl)ethyl)benzonitrile (**15**)

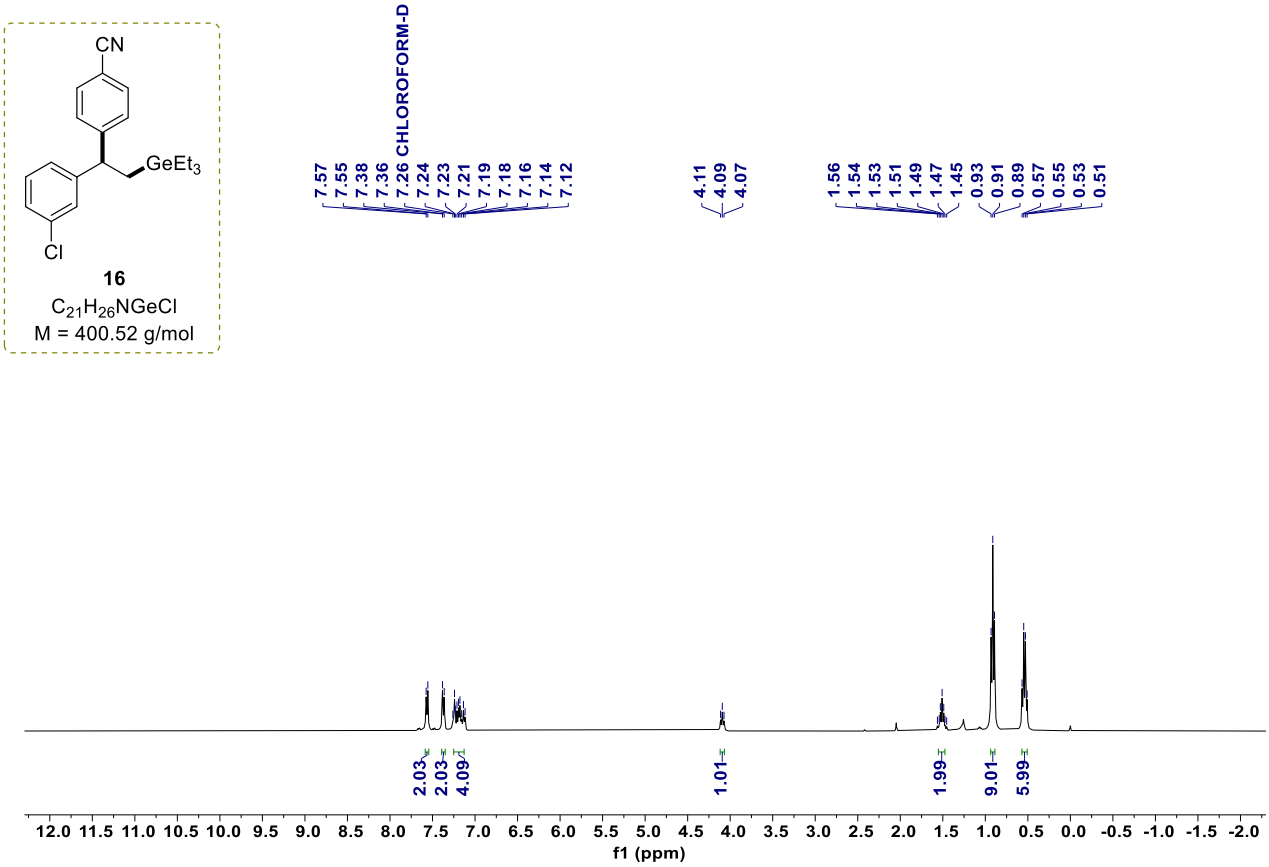


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **15**.

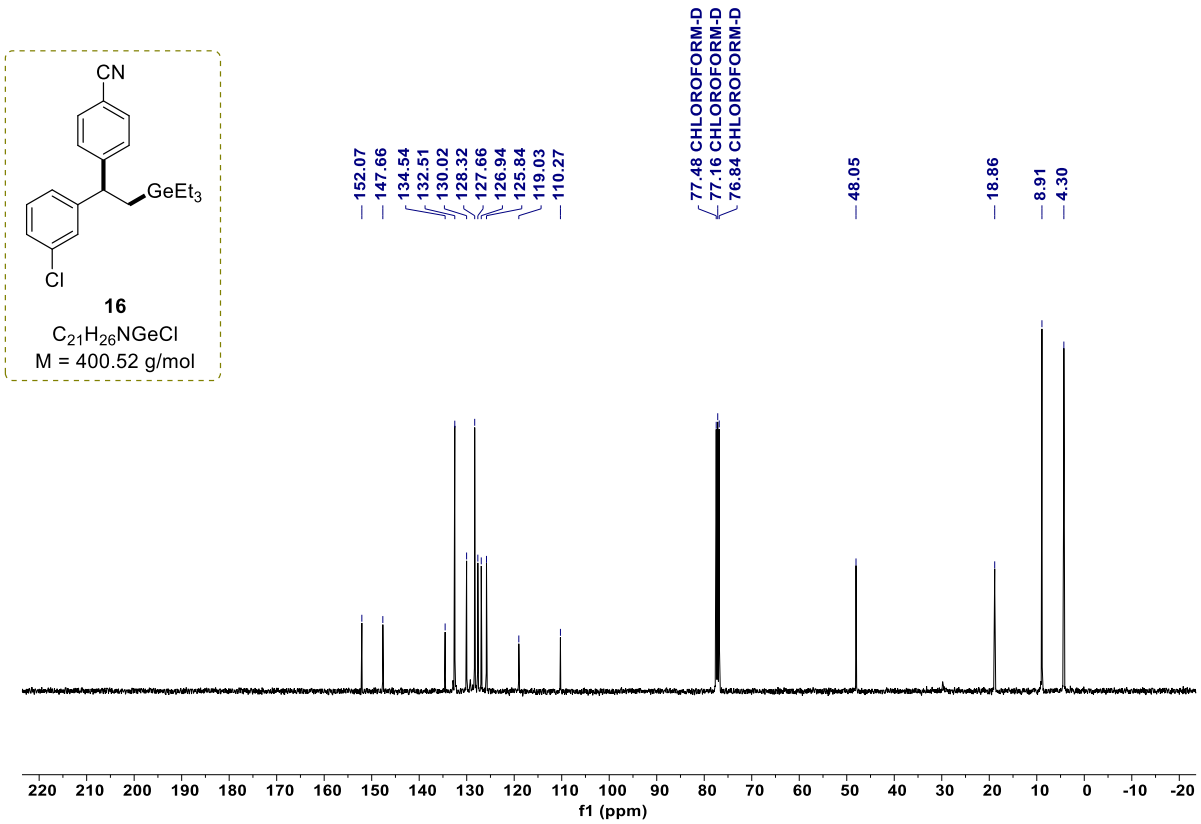


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **15**.

4.13 4-(1-(3-chlorophenyl)-2-(triethylgermyl)ethyl)benzonitrile (**16**)

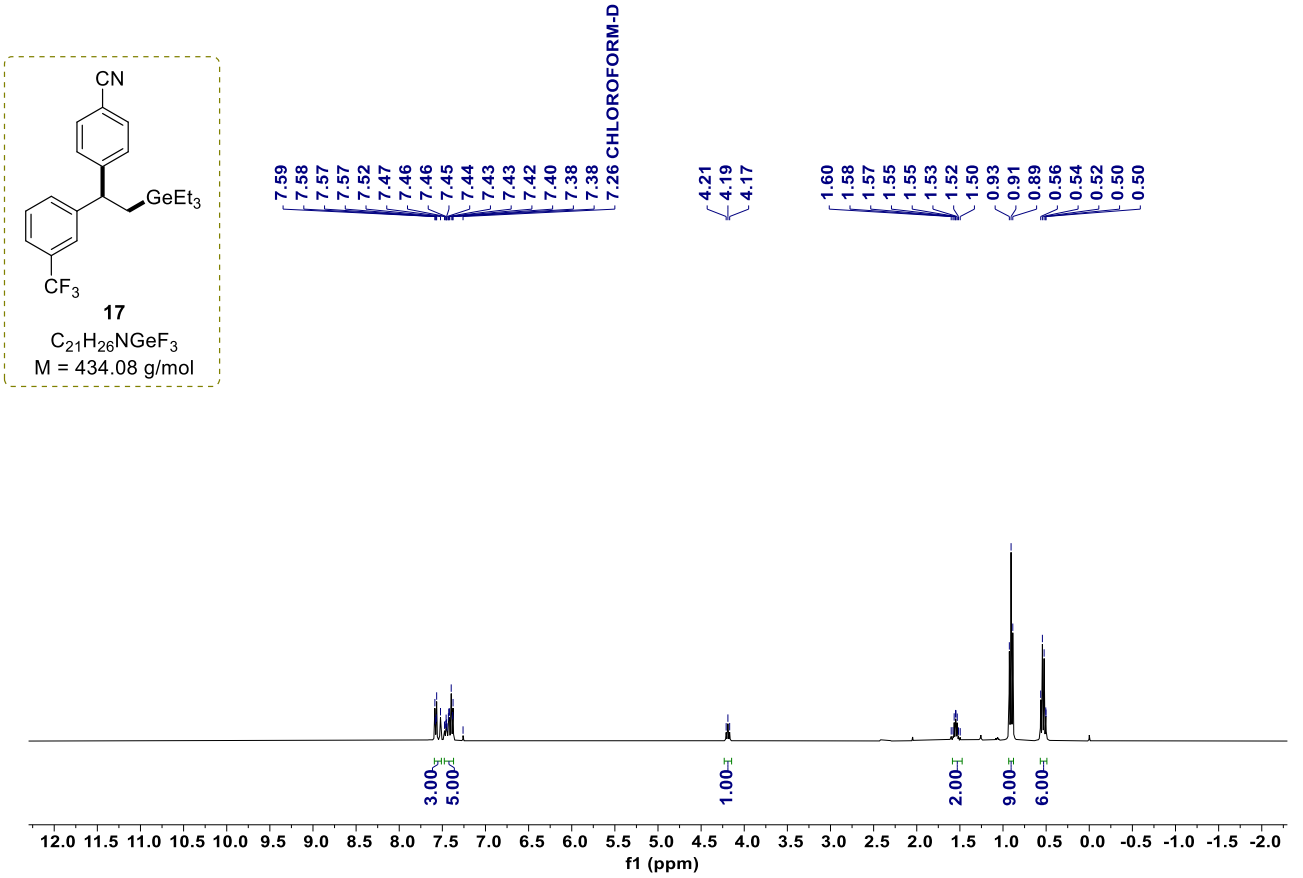


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **16**.

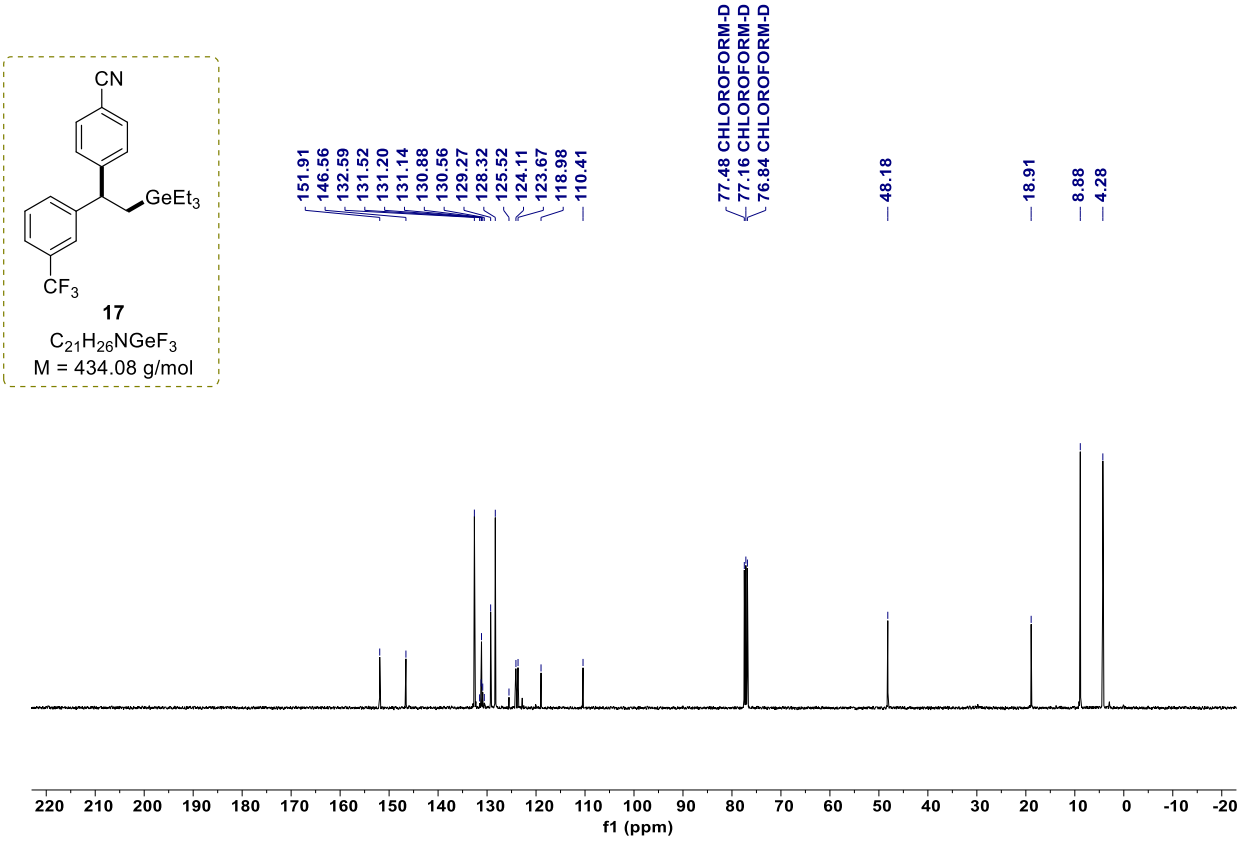


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **16**.

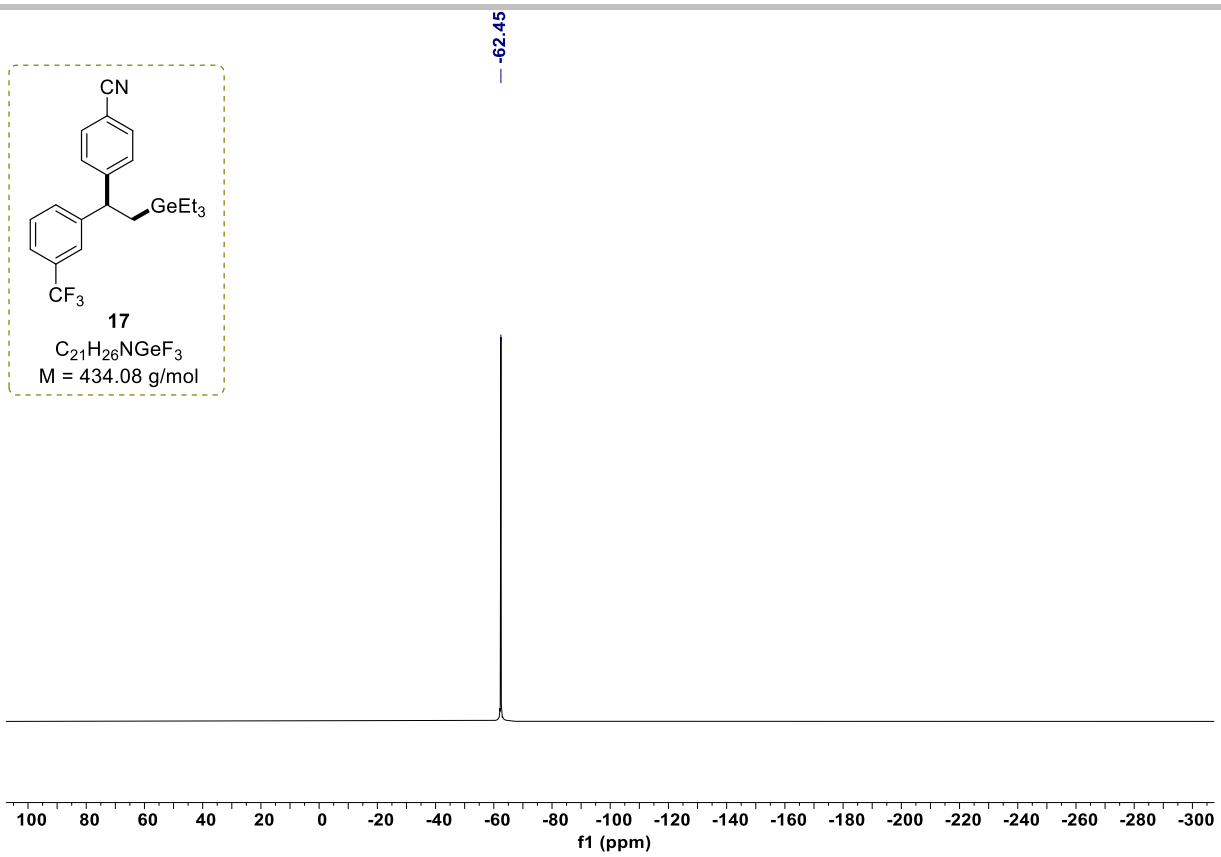
4.14 4-(2-(triethylgermyl)-1-(3-(trifluoromethyl)phenyl)ethyl)benzonitrile (**17**)



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **17**.

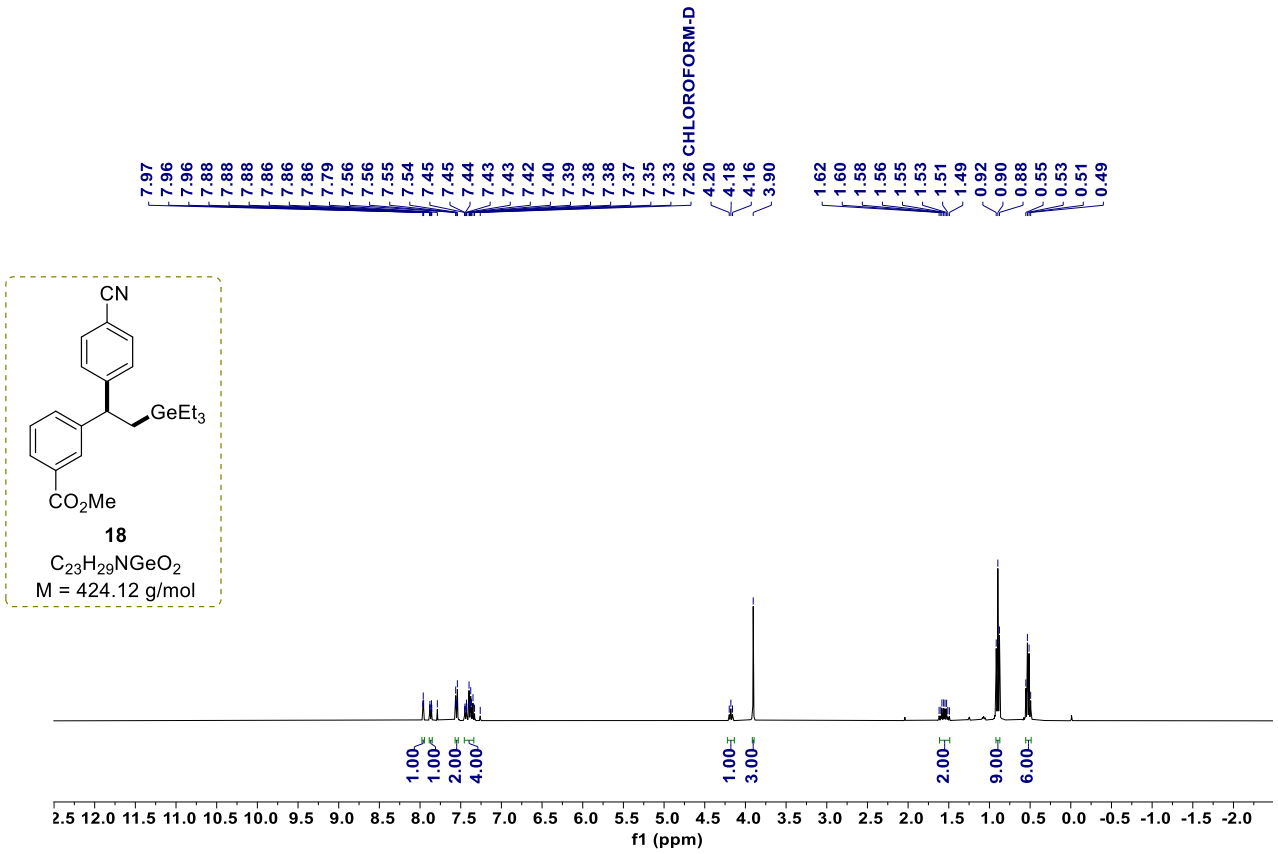


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **17**.

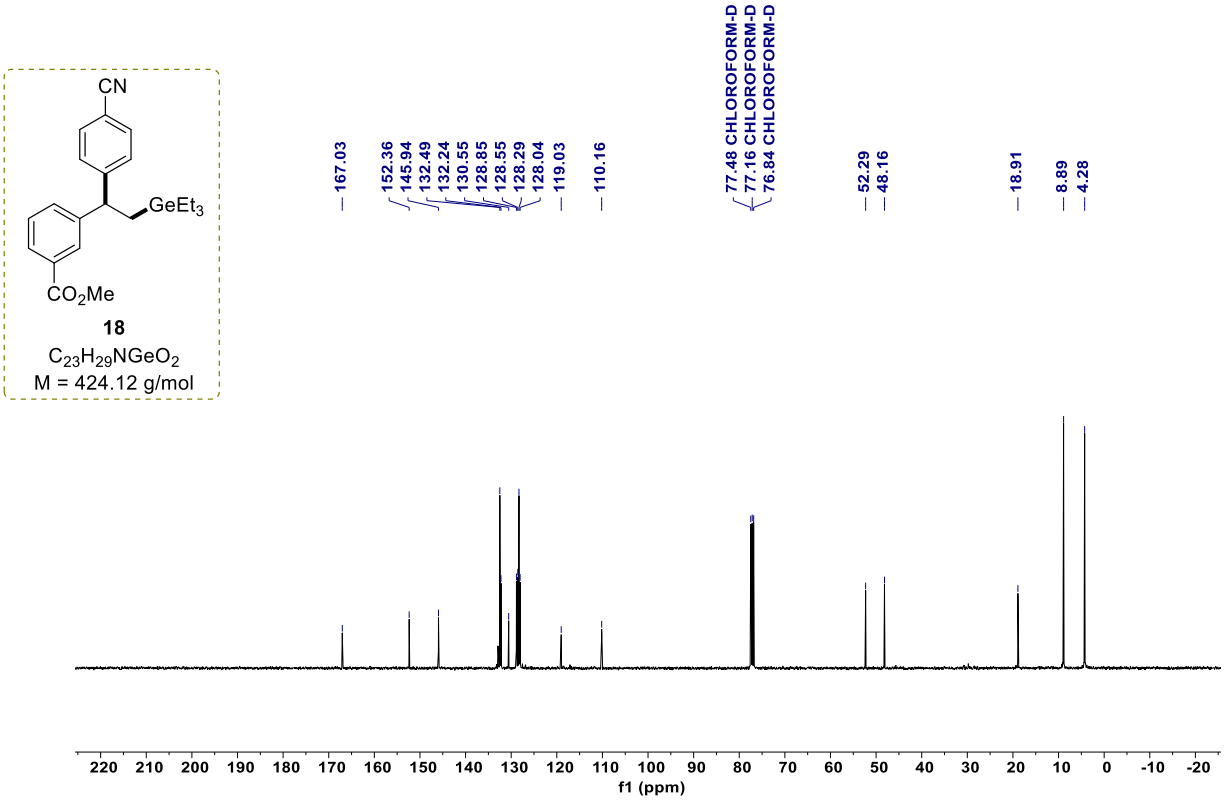


^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **17**.

4.15 methyl 3-(1-(4-cyanophenyl)-2-(triethylgermyl)ethyl)benzoate (**18**)

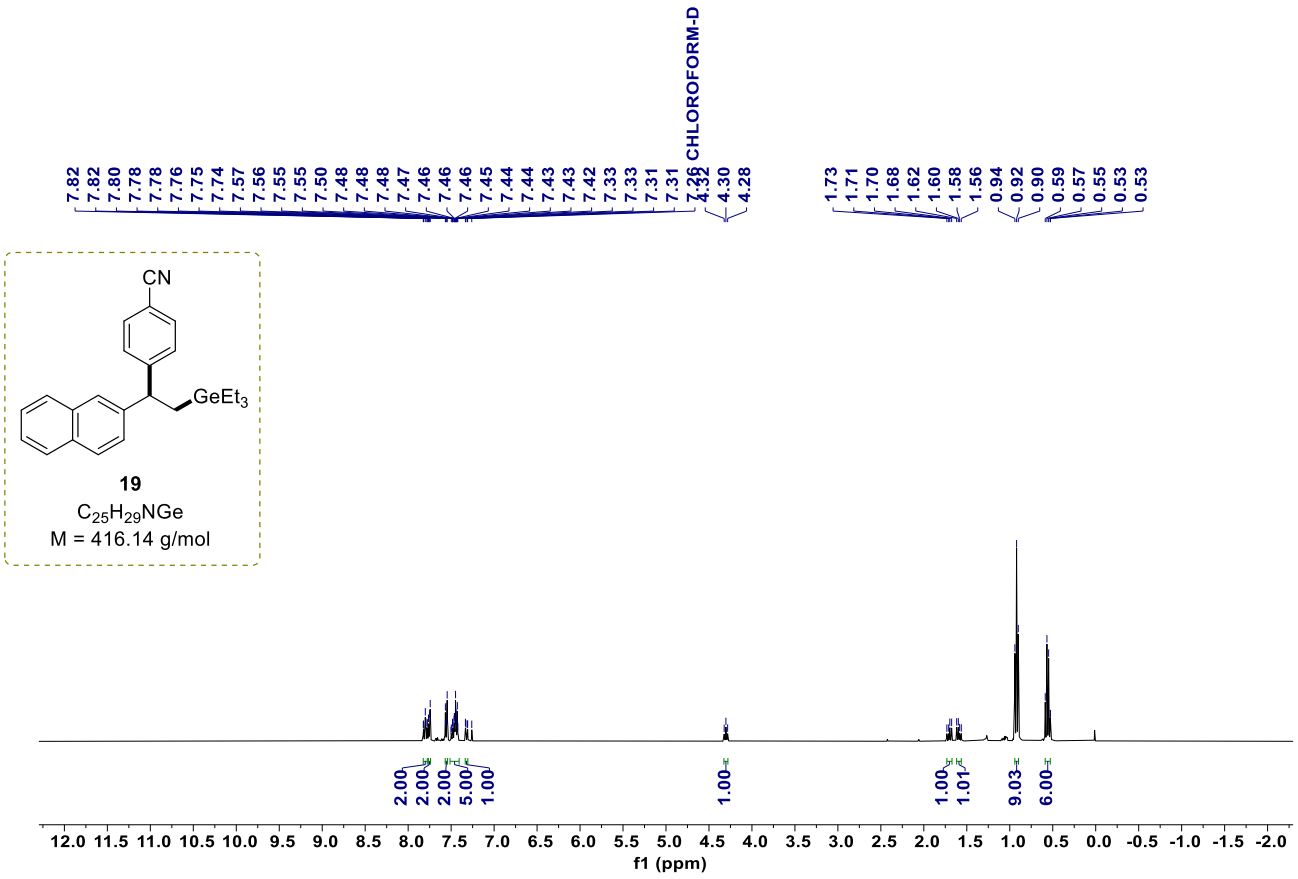


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **18**.

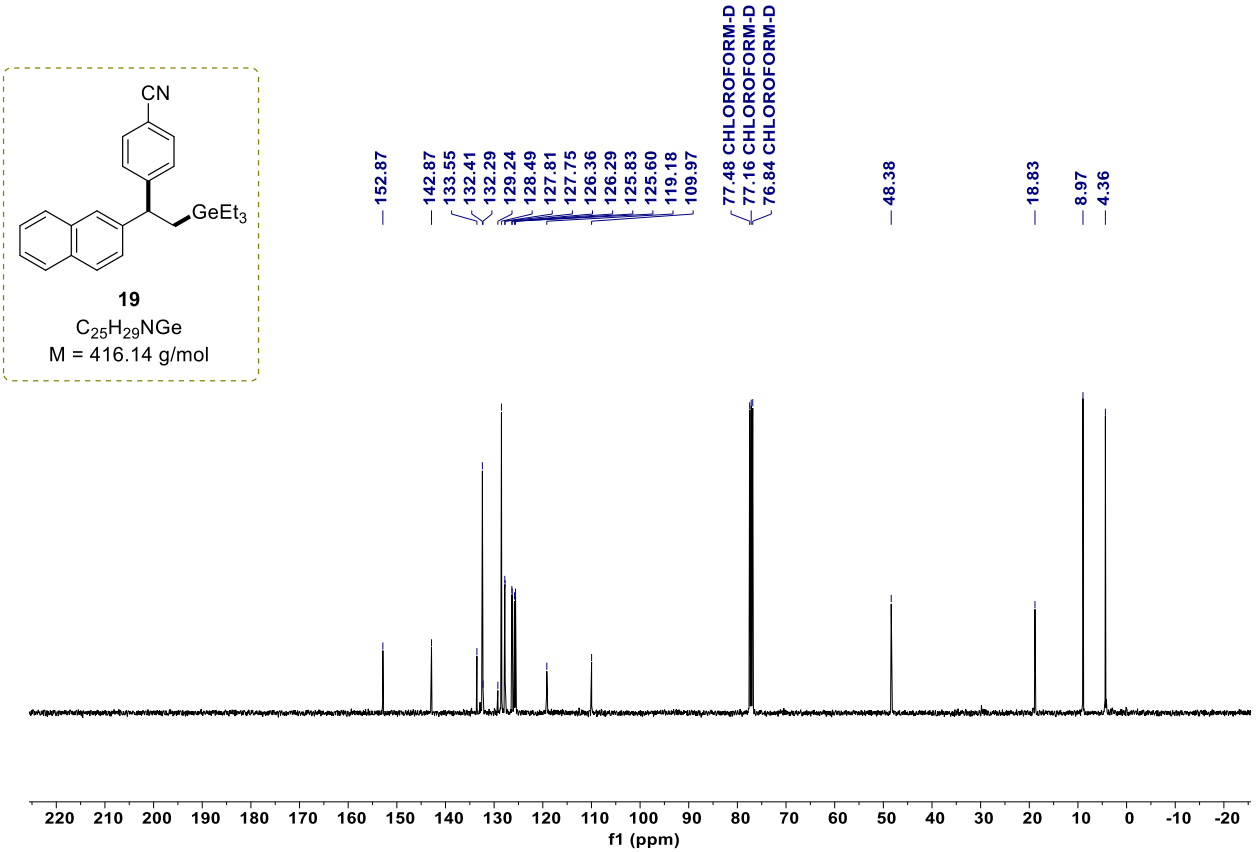


$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **18**.

4.16 4-(1-(naphthalen-2-yl)-2-(triethylgermyl)ethyl)benzonitrile (**19**)

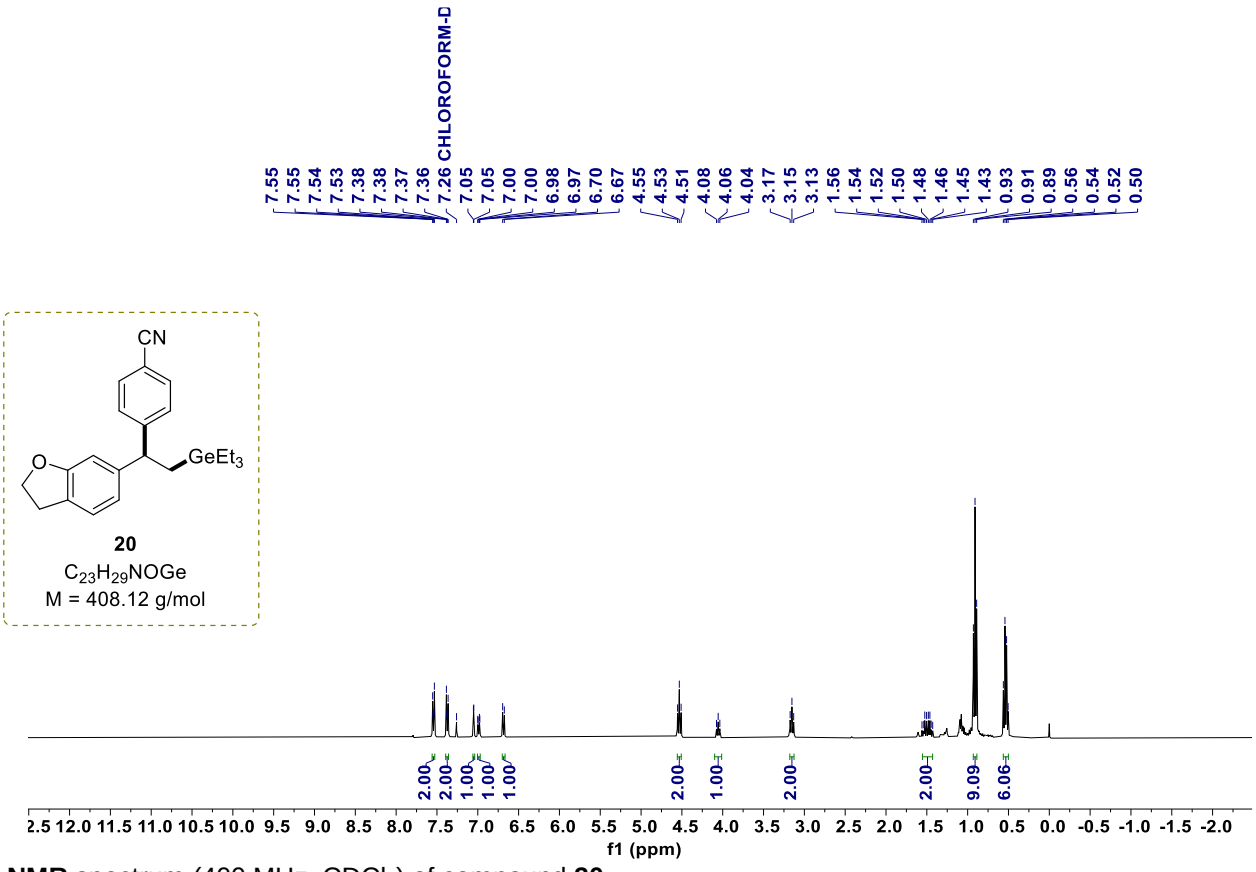


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **19**.

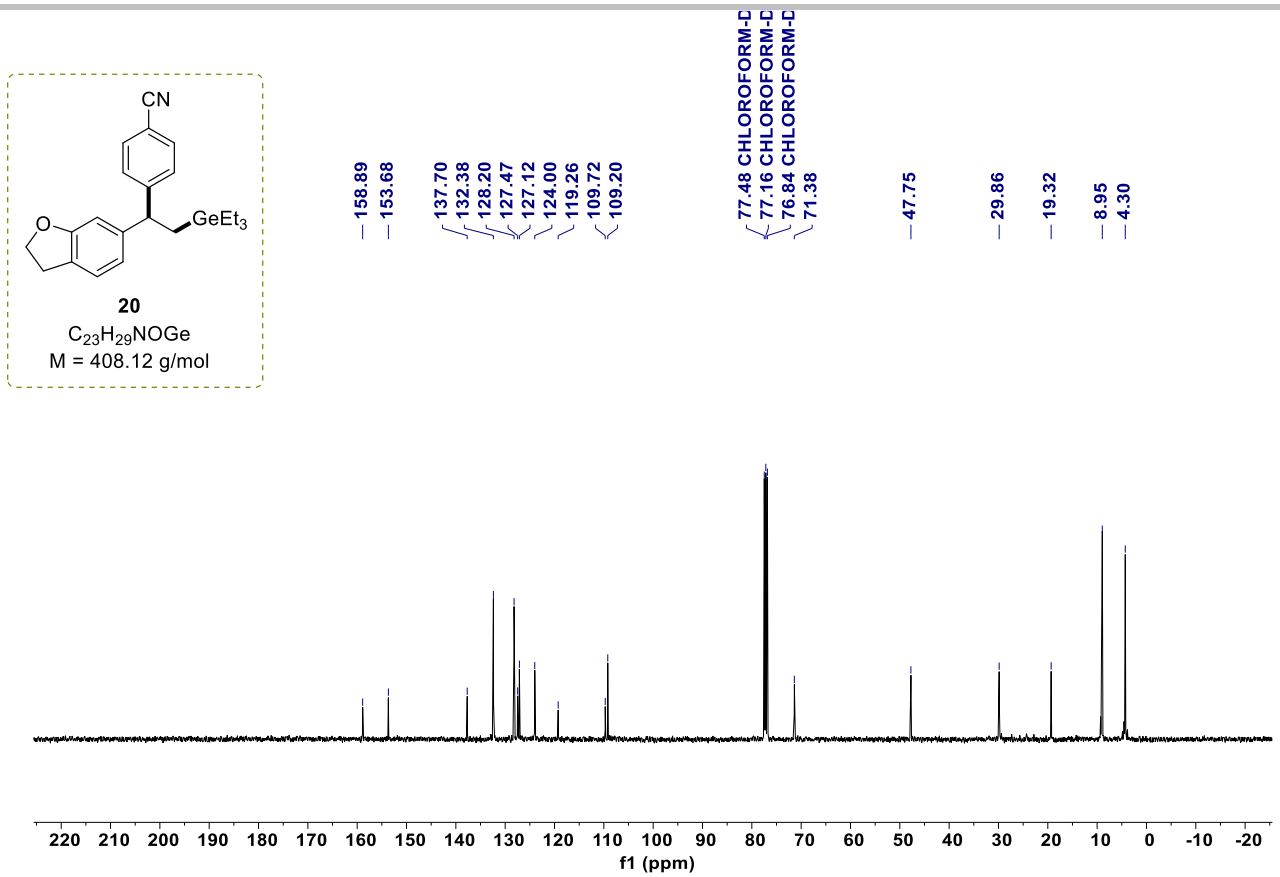


$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **19**.

4.17 4-(1-(2,3-dihydrobenzofuran-6-yl)-2-(triethylgermyl)ethyl)benzonitrile (**20**)

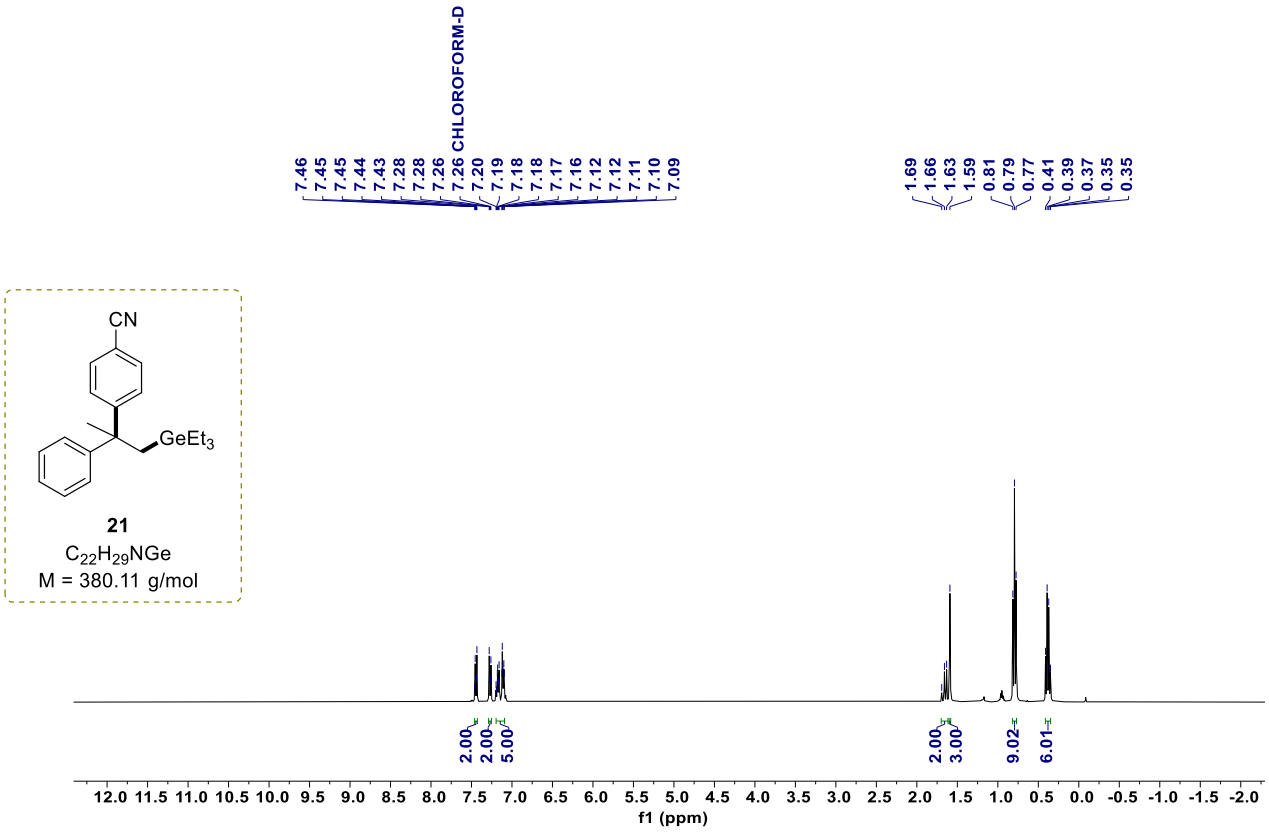


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20**.

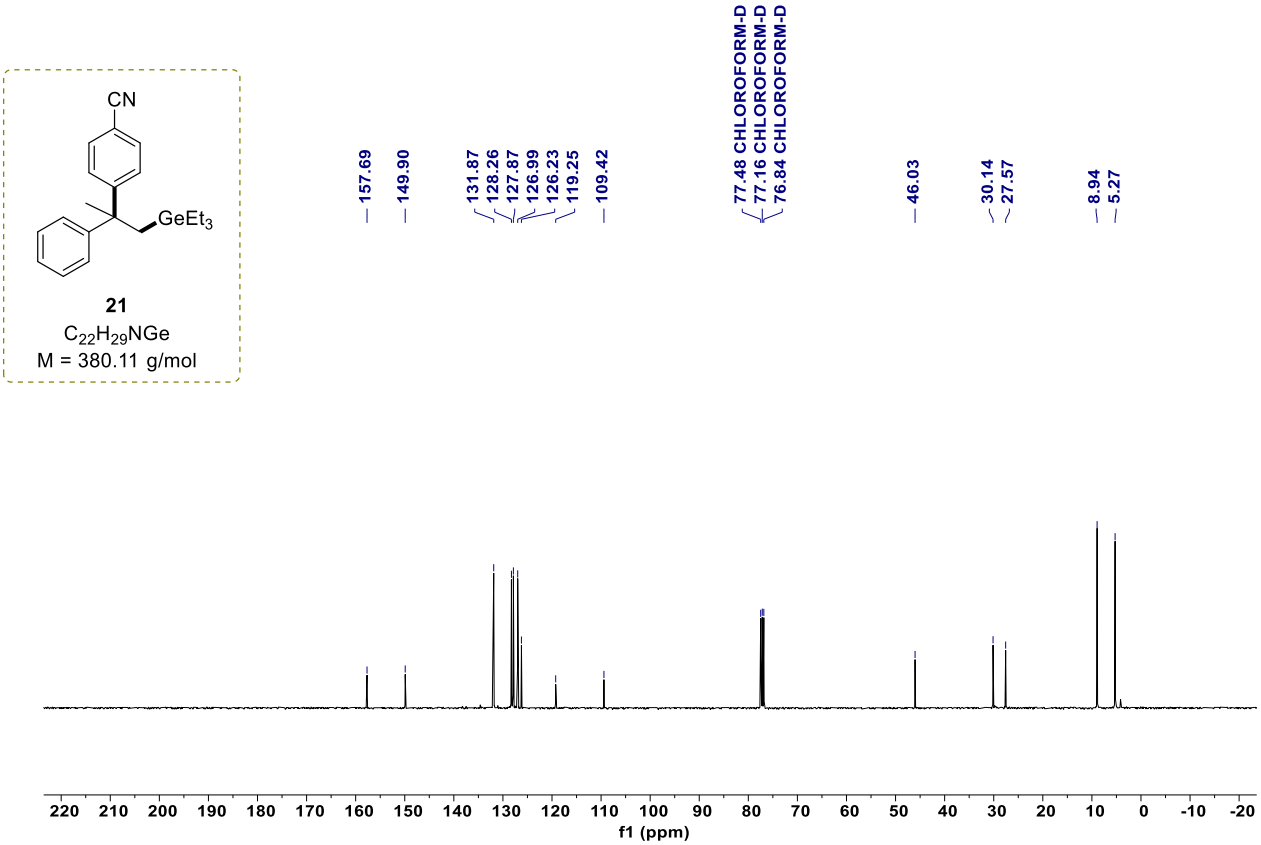


$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **20**.

4.18 4-(2-phenyl-1-(triethylgermyl)propan-2-yl)benzonitrile (**21**)

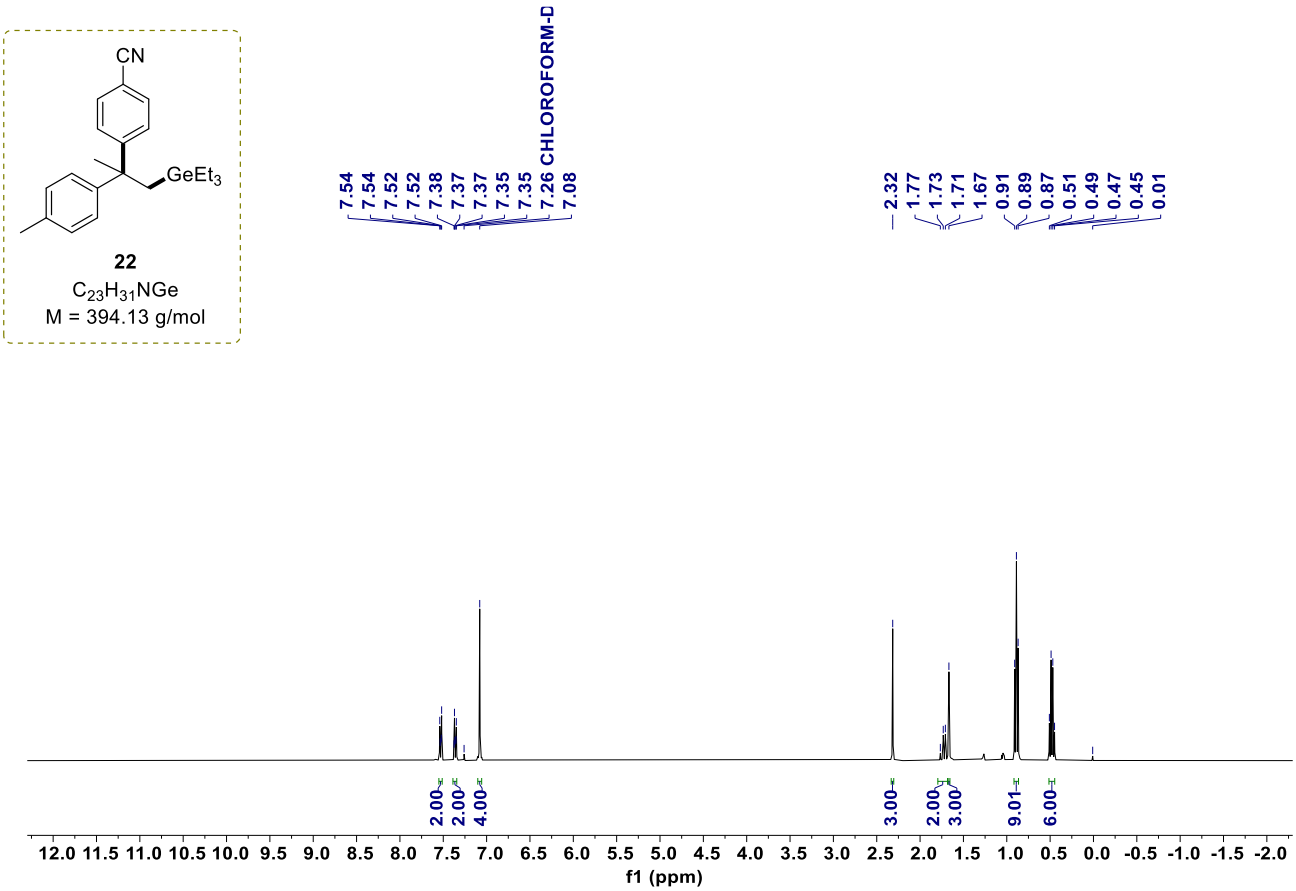


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **21**.

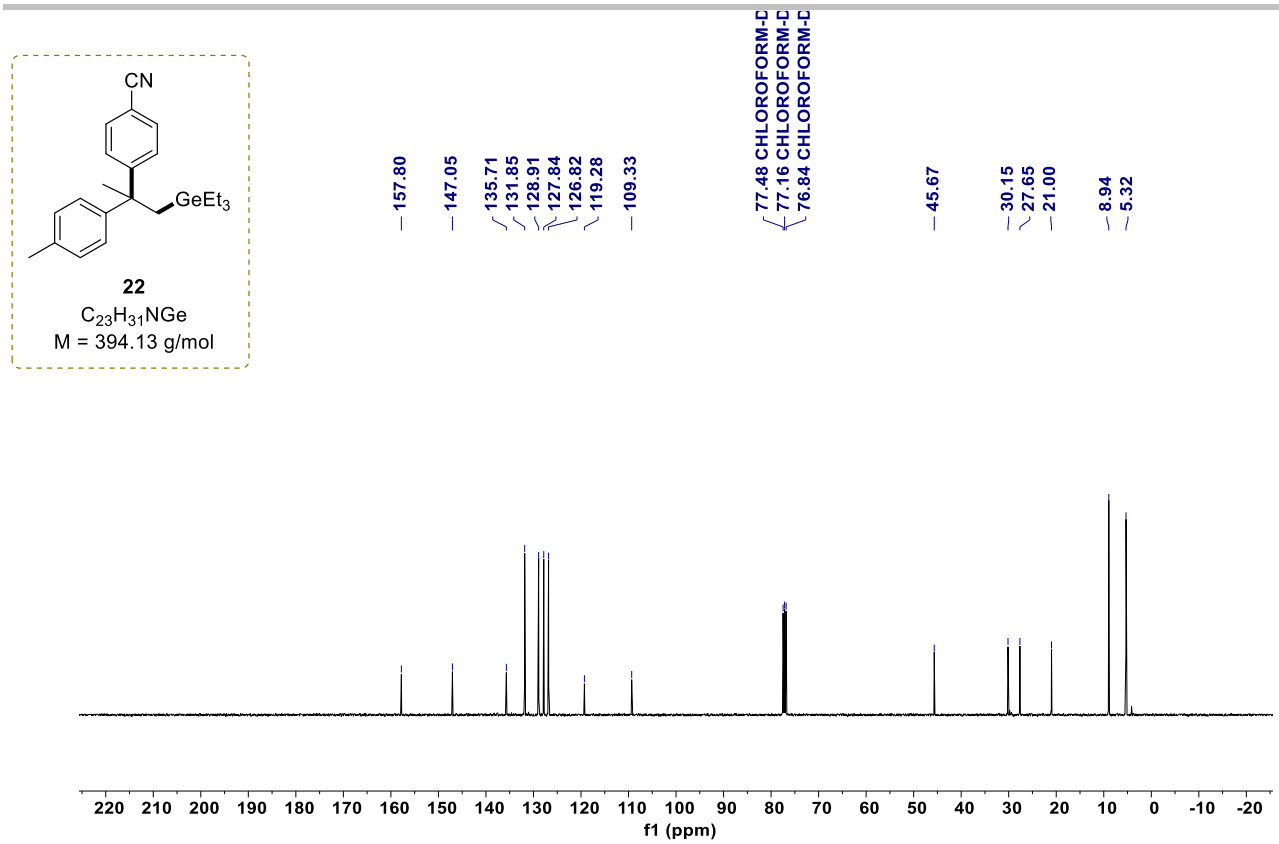


$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **21**.

4.19 4-(2-(p-tolyl)-1-(triethylgermyl)propan-2-yl)benzonitrile (**22**)

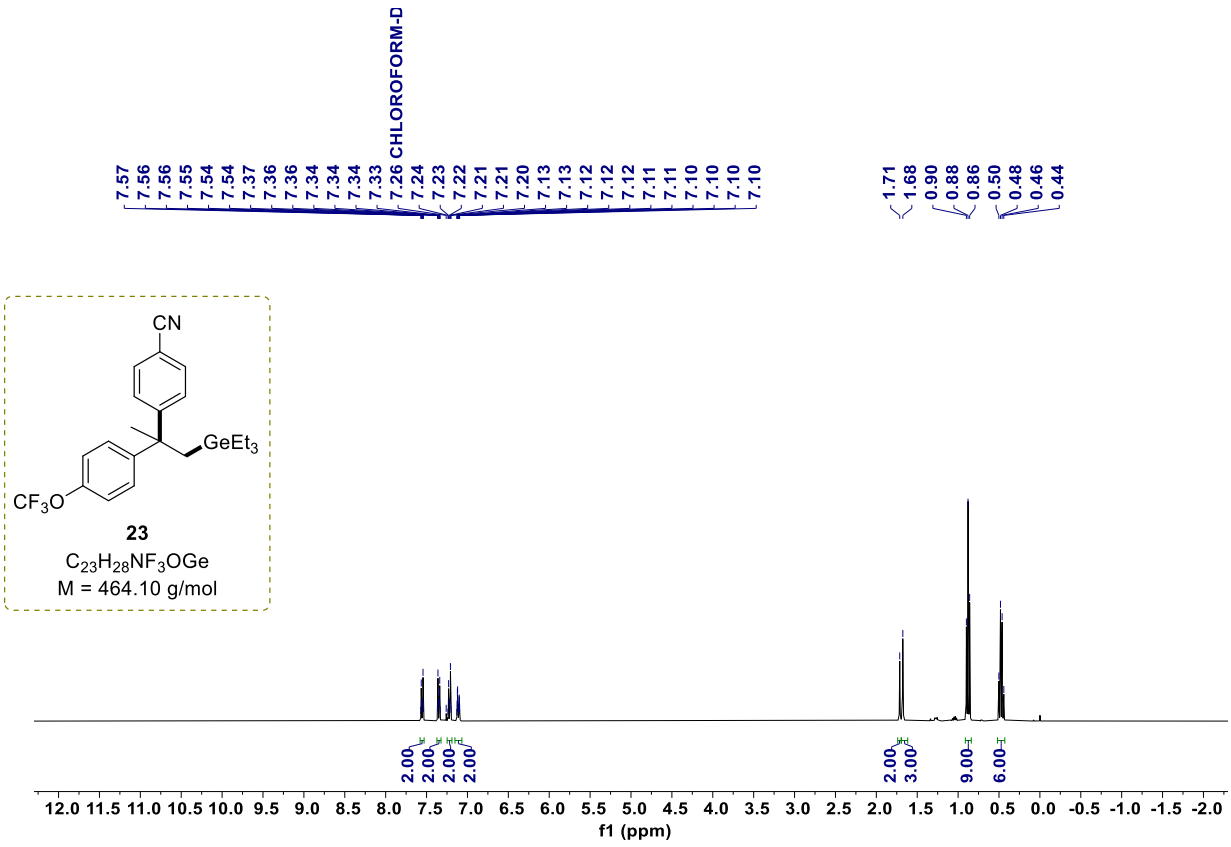


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **22**.

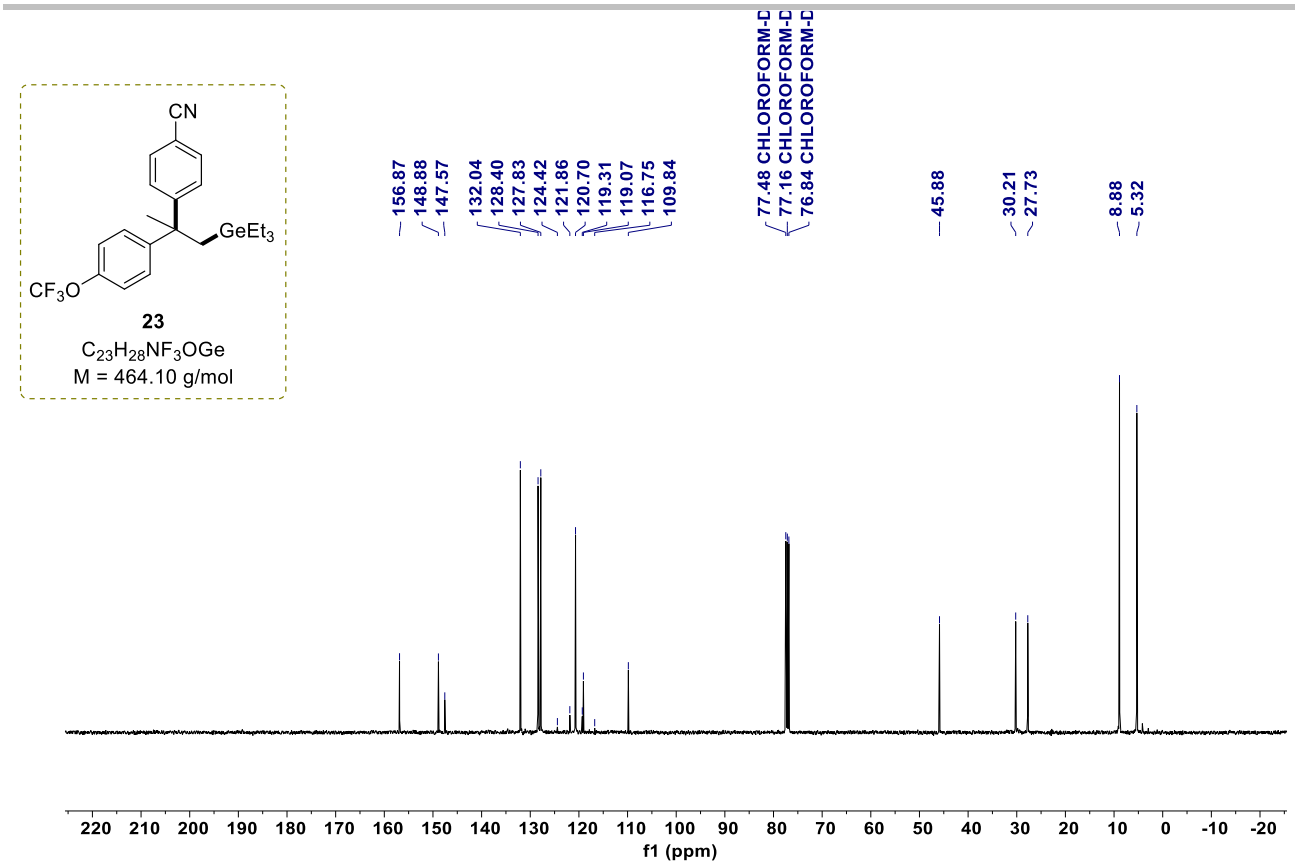


$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **22**.

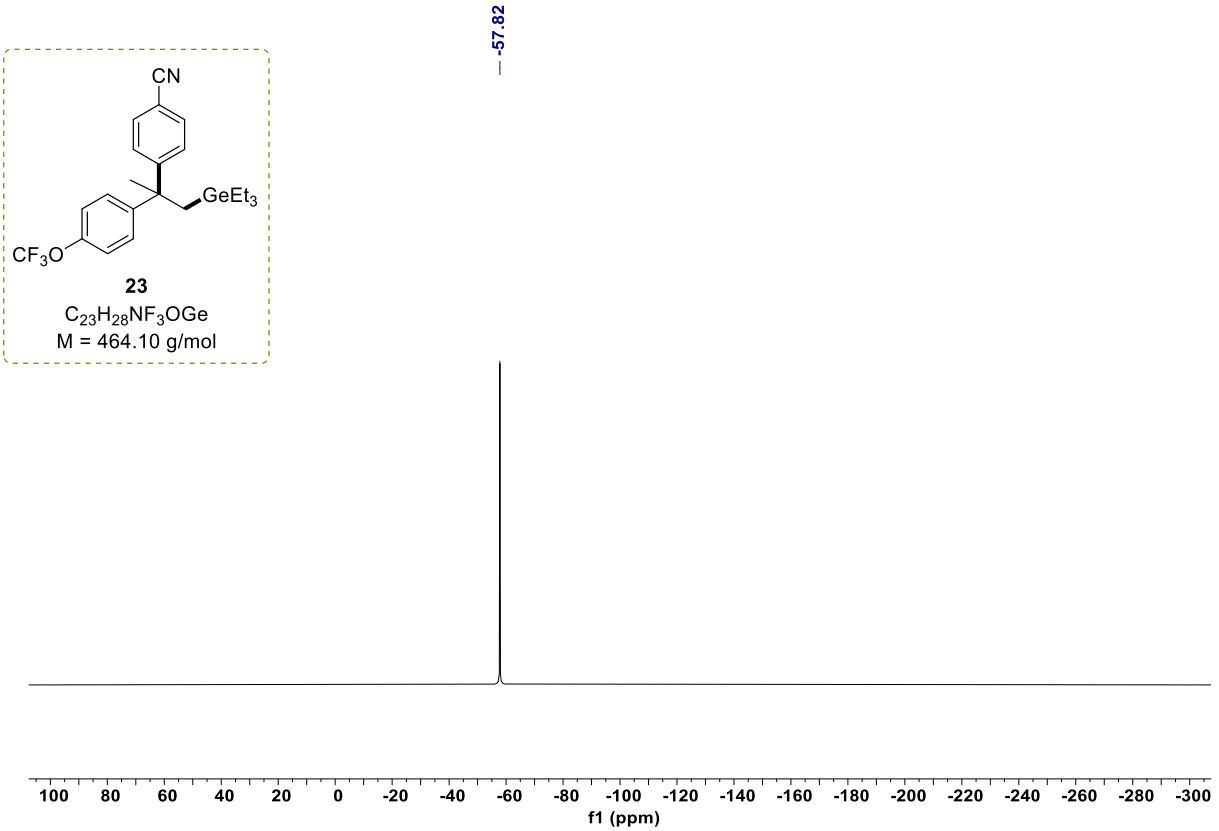
4.20 4-(1-(triethylgermyl)-2-(4-(trifluoromethoxy)phenyl)propan-2-yl)benzonitrile (**23**)



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4**.

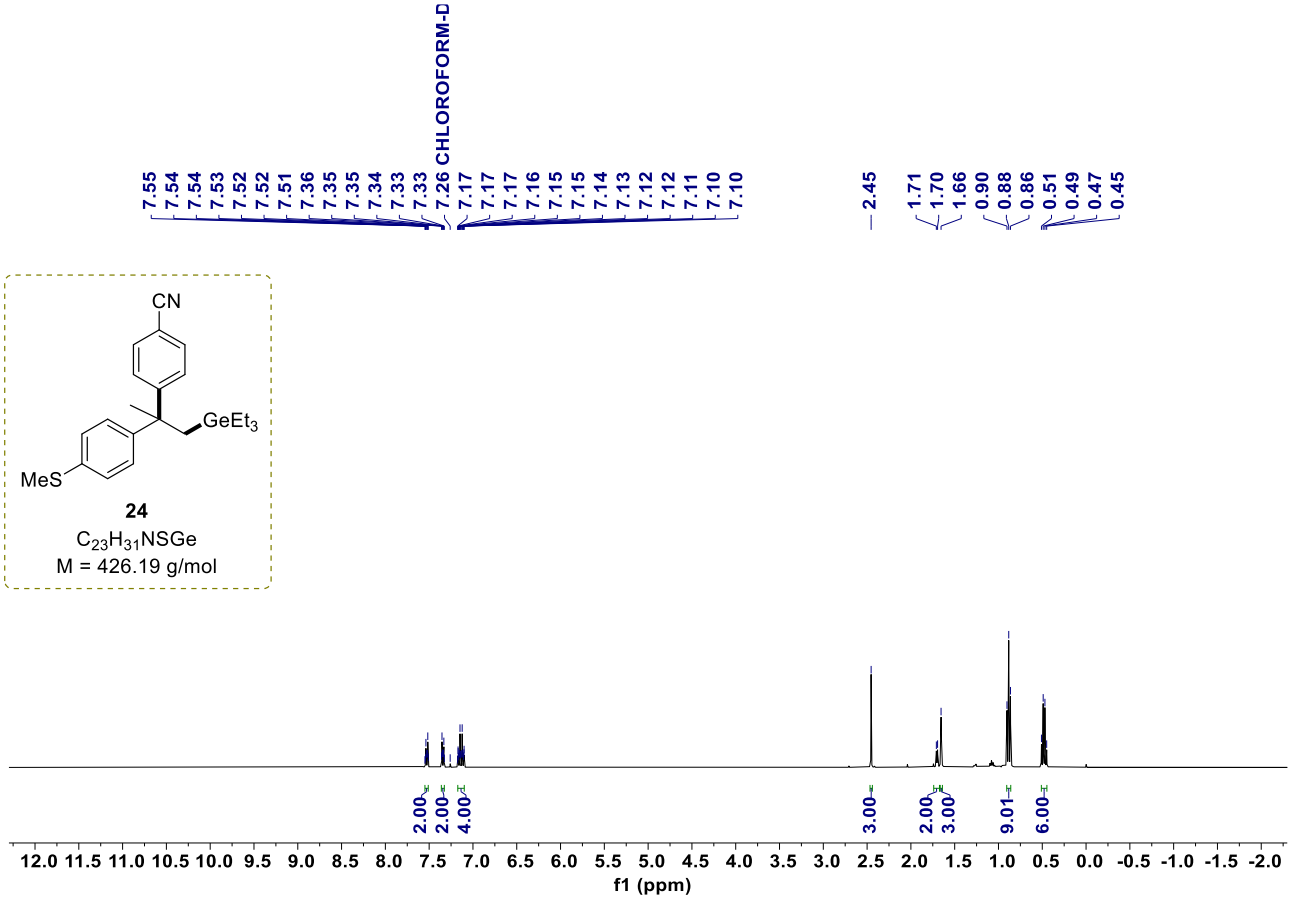


$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **23**.

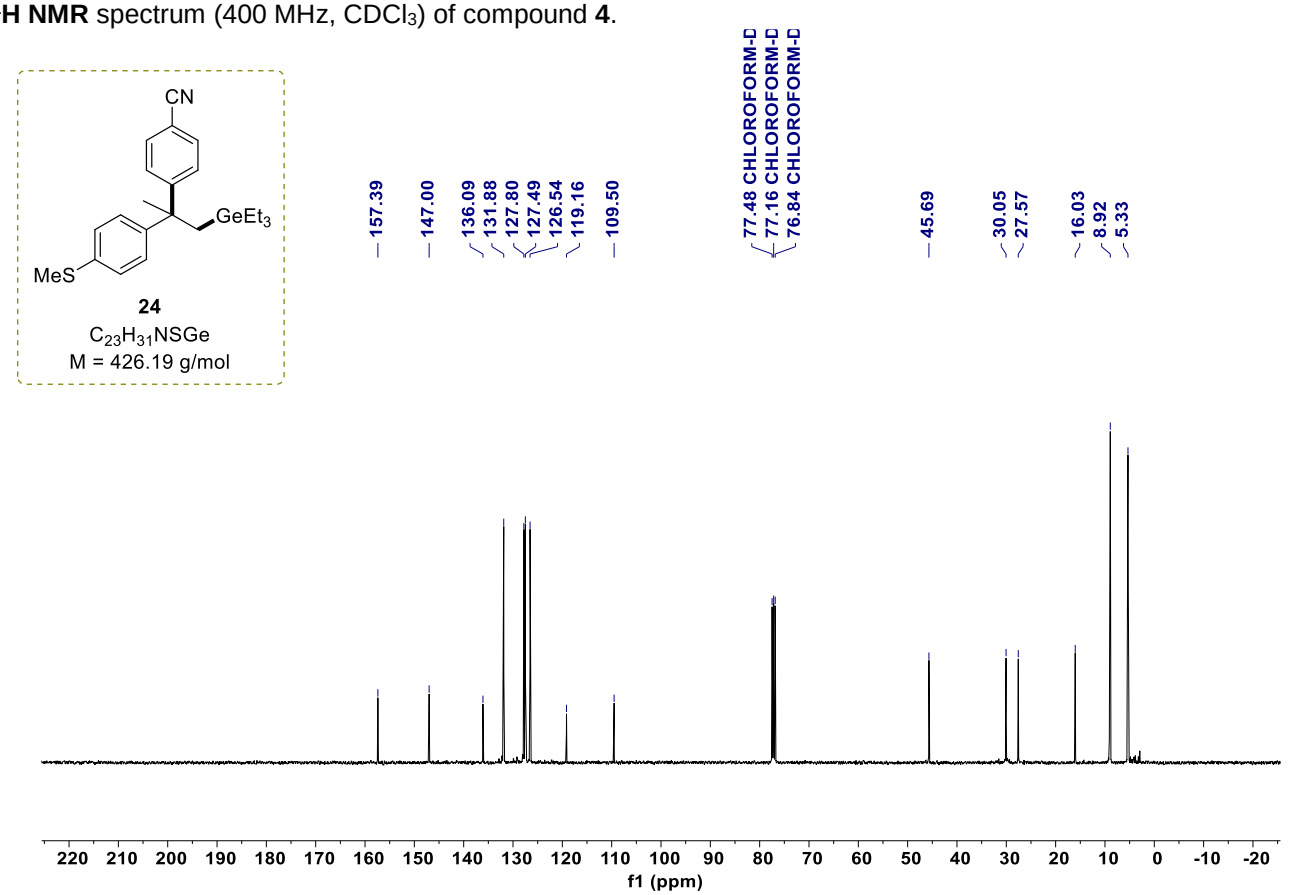


^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **23**.

4.21 4-(2-(4-(methylthio)phenyl)-1-(triethylgermyl)propan-2-yl)benzonitrile (**24**)

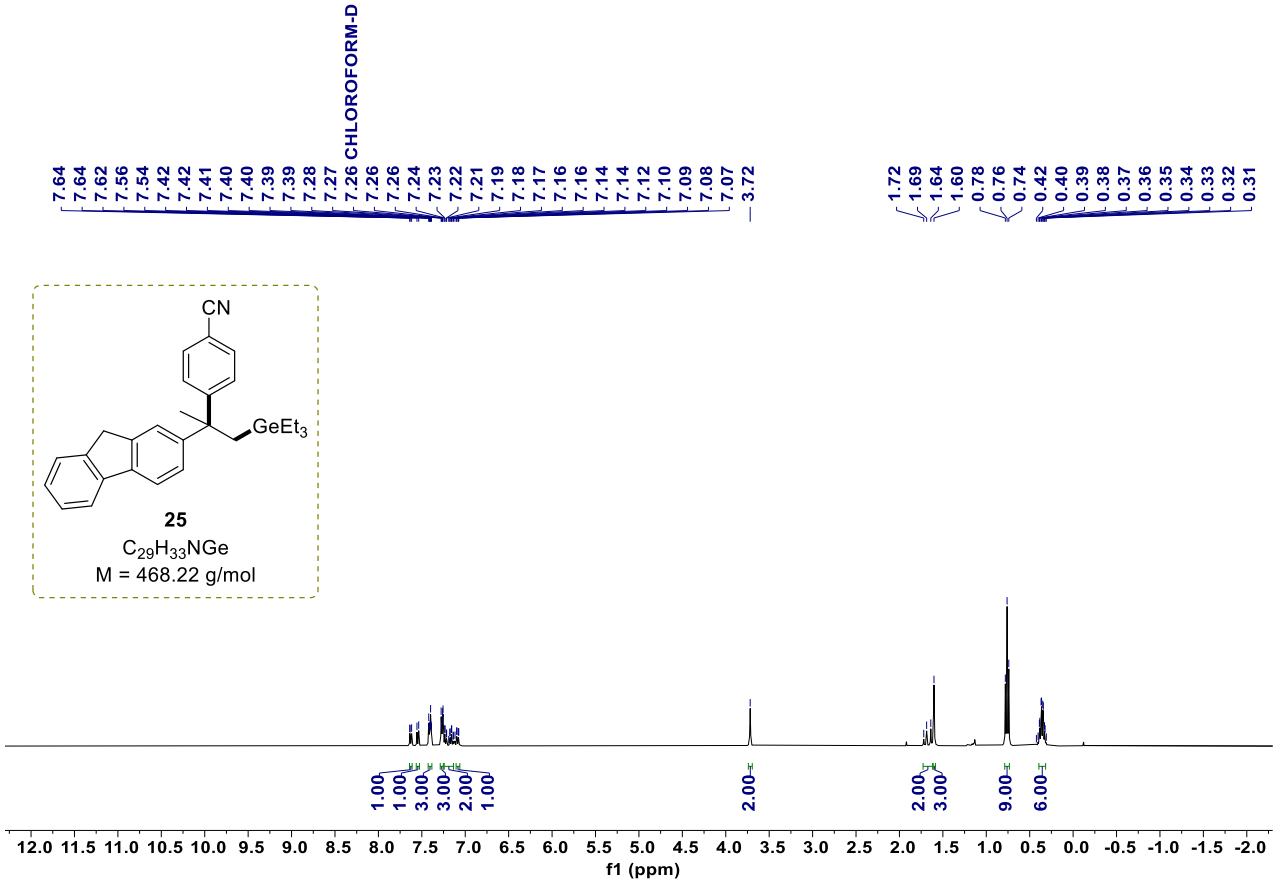


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4**.

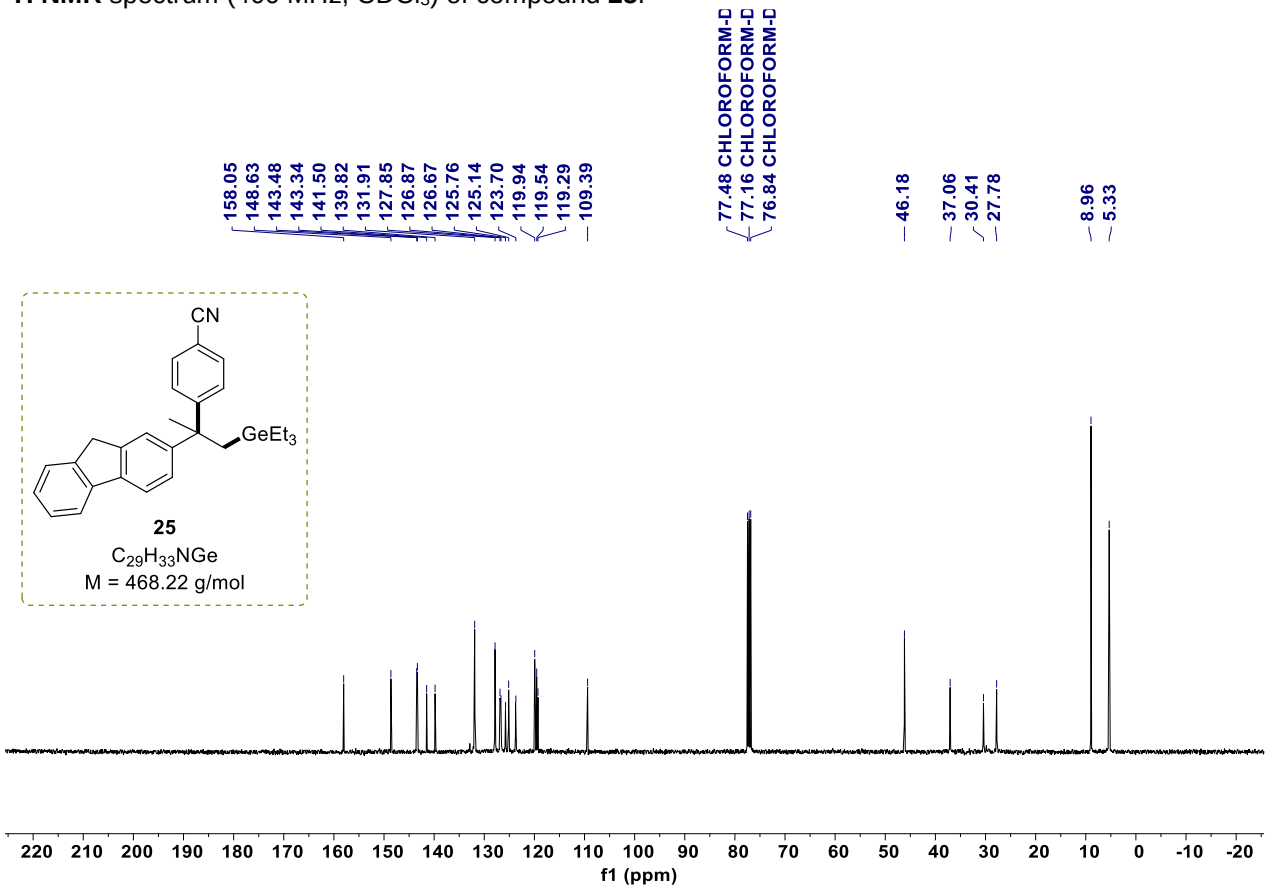


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4**.

4.22 4-(2-(9H-fluoren-2-yl)-1-(triethylgermyl)propan-2-yl)benzonitrile (**25**)

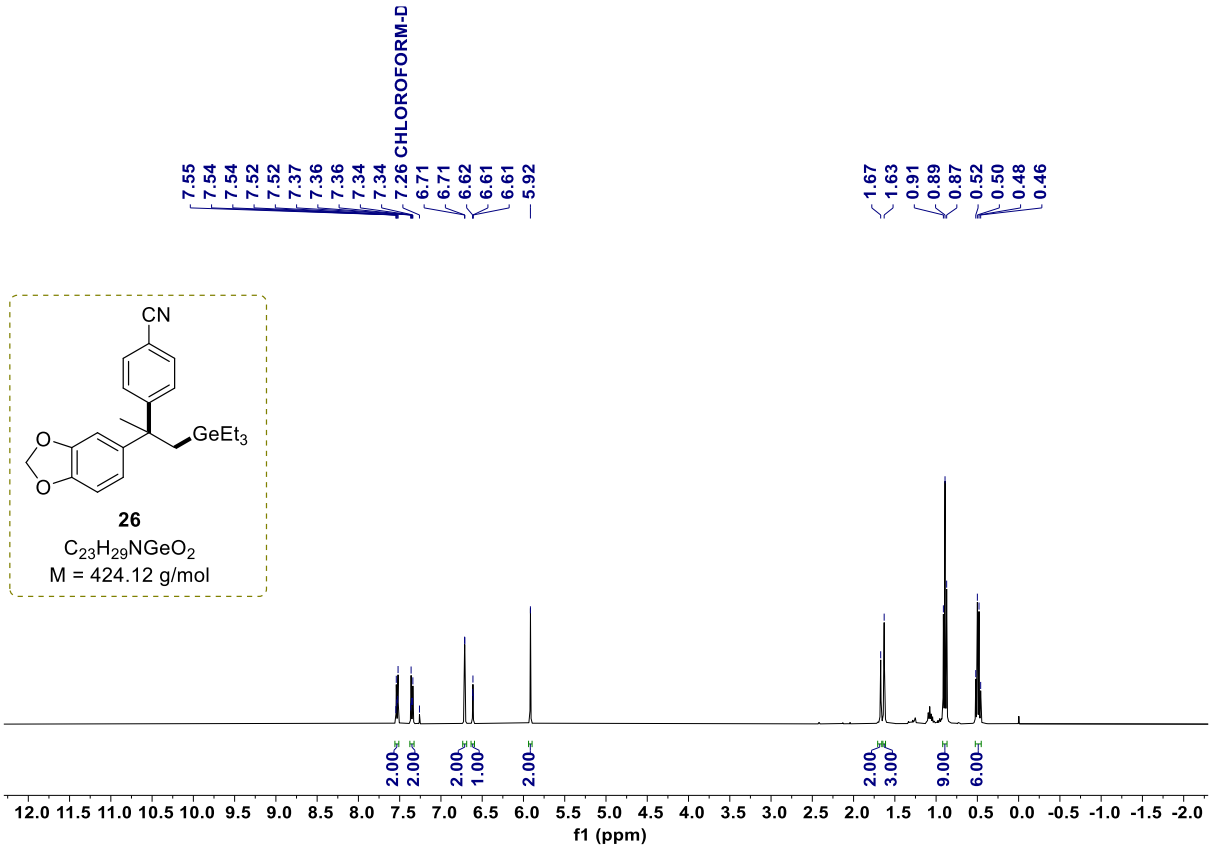


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25**.

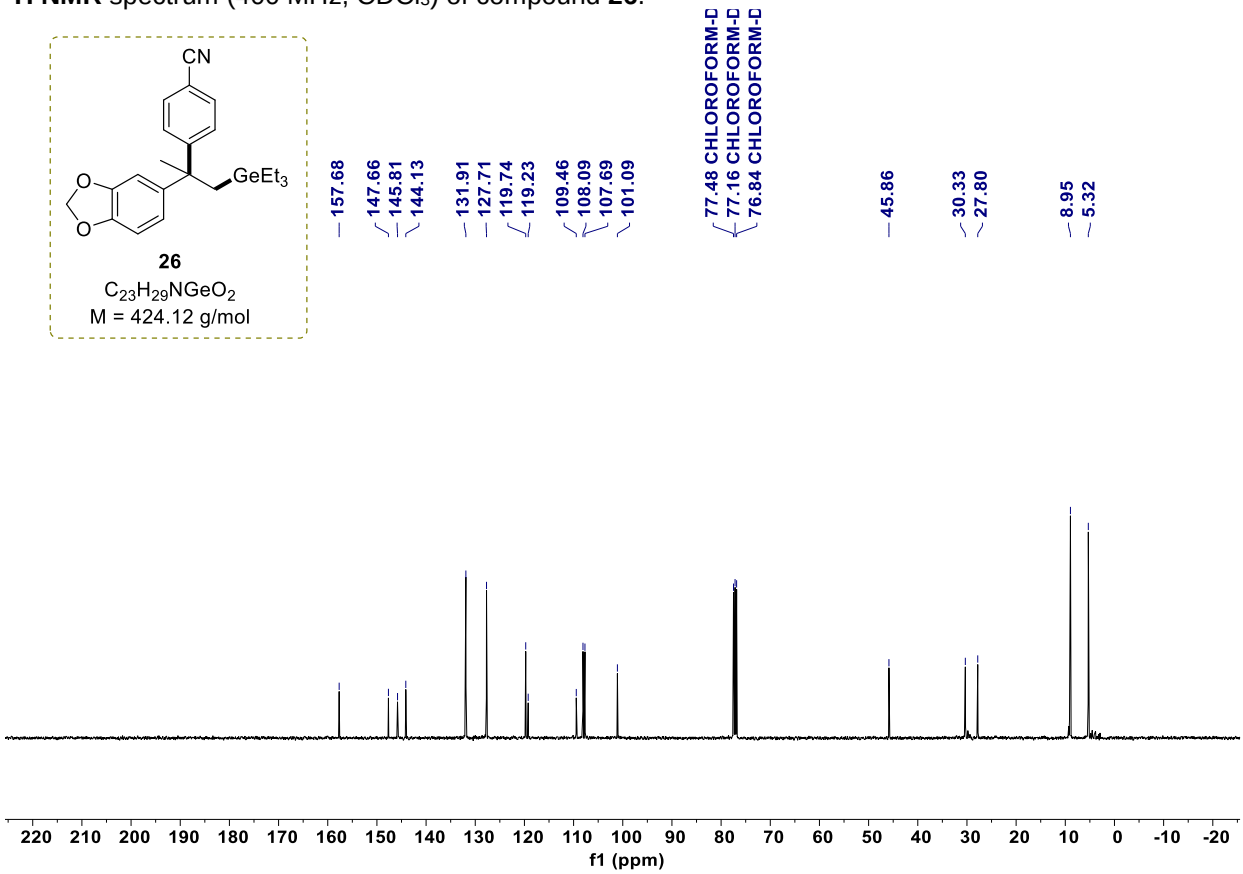


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **25**.

4.23 4-(2-(benzo[d][1,3]dioxol-5-yl)-1-(triethylgermyl)propan-2-yl)benzonitrile (**26**)

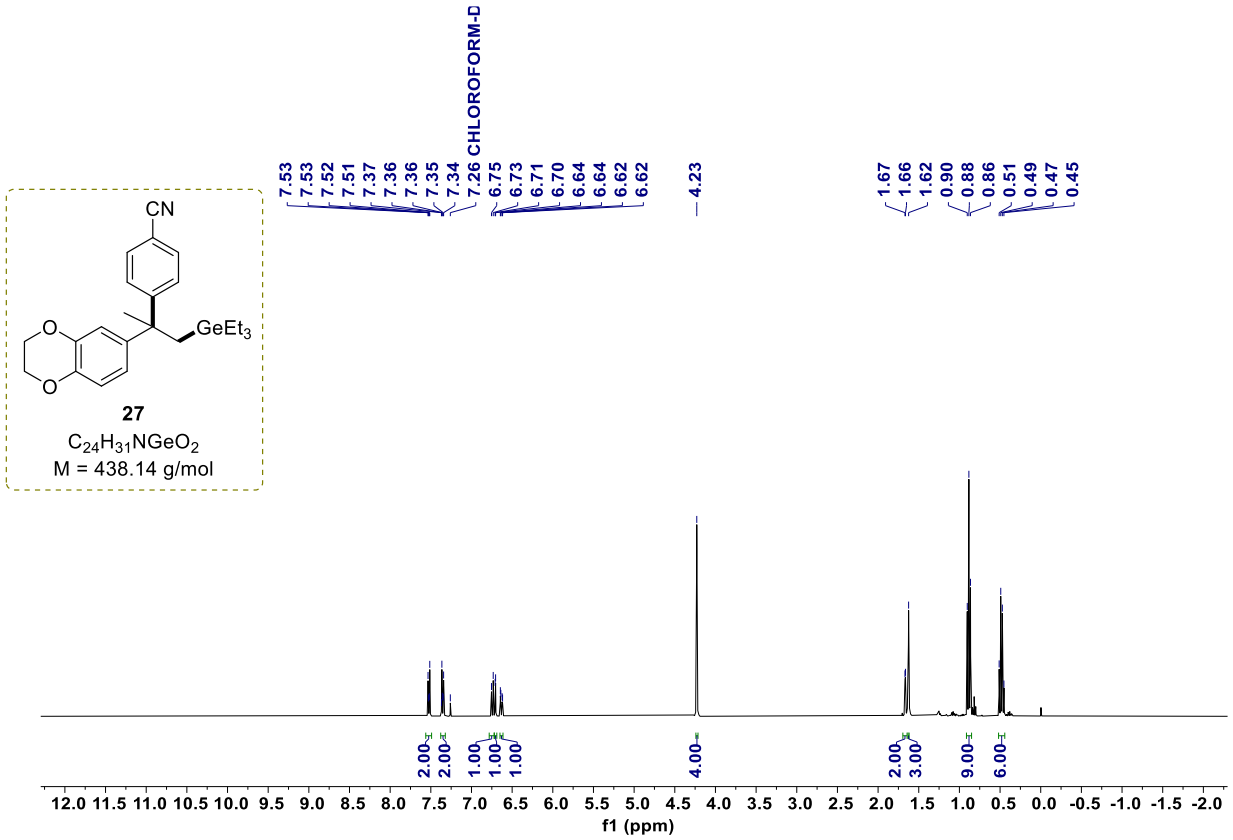


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **26**.

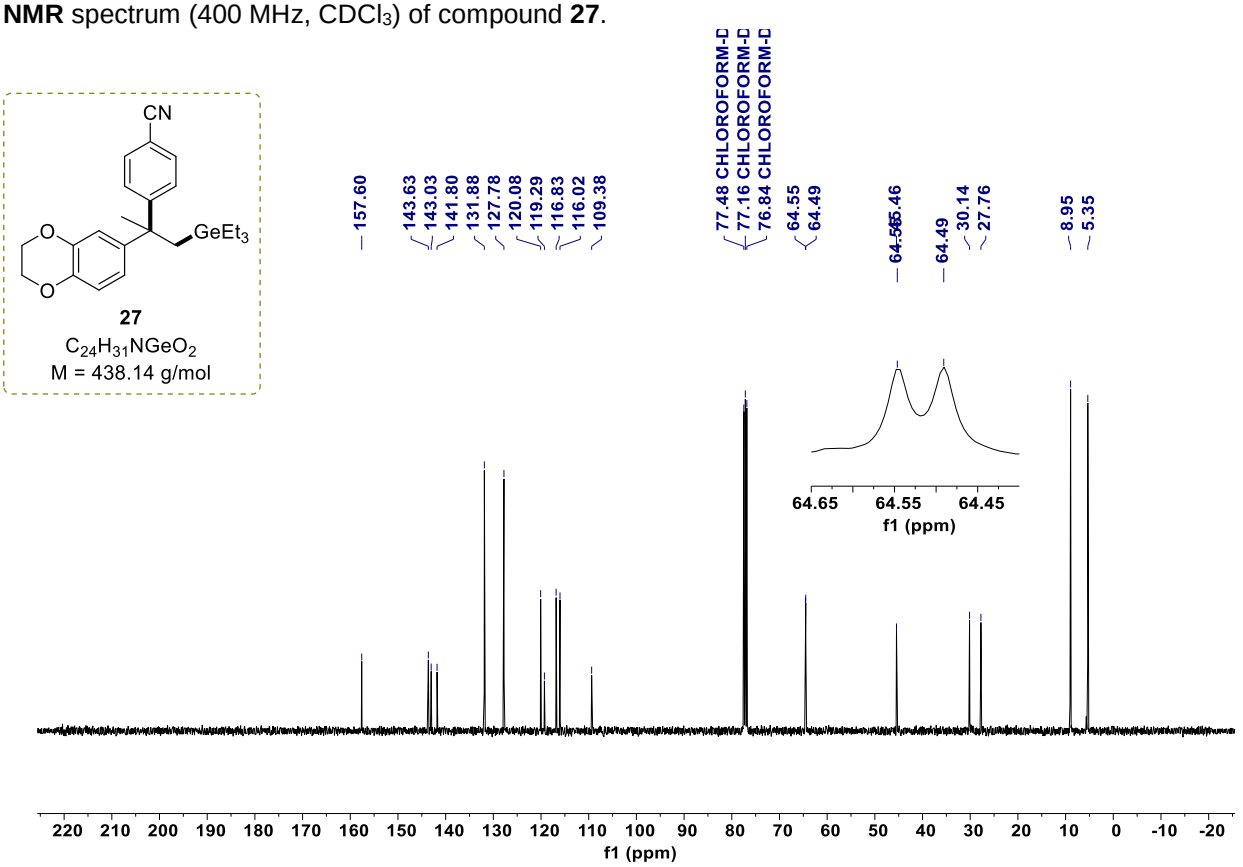


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **26**.

4.24 4-(2-(benzo[d][1,3]dioxol-5-yl)-1-(triethylgermyl)propan-2-yl)benzonitrile (**27**)

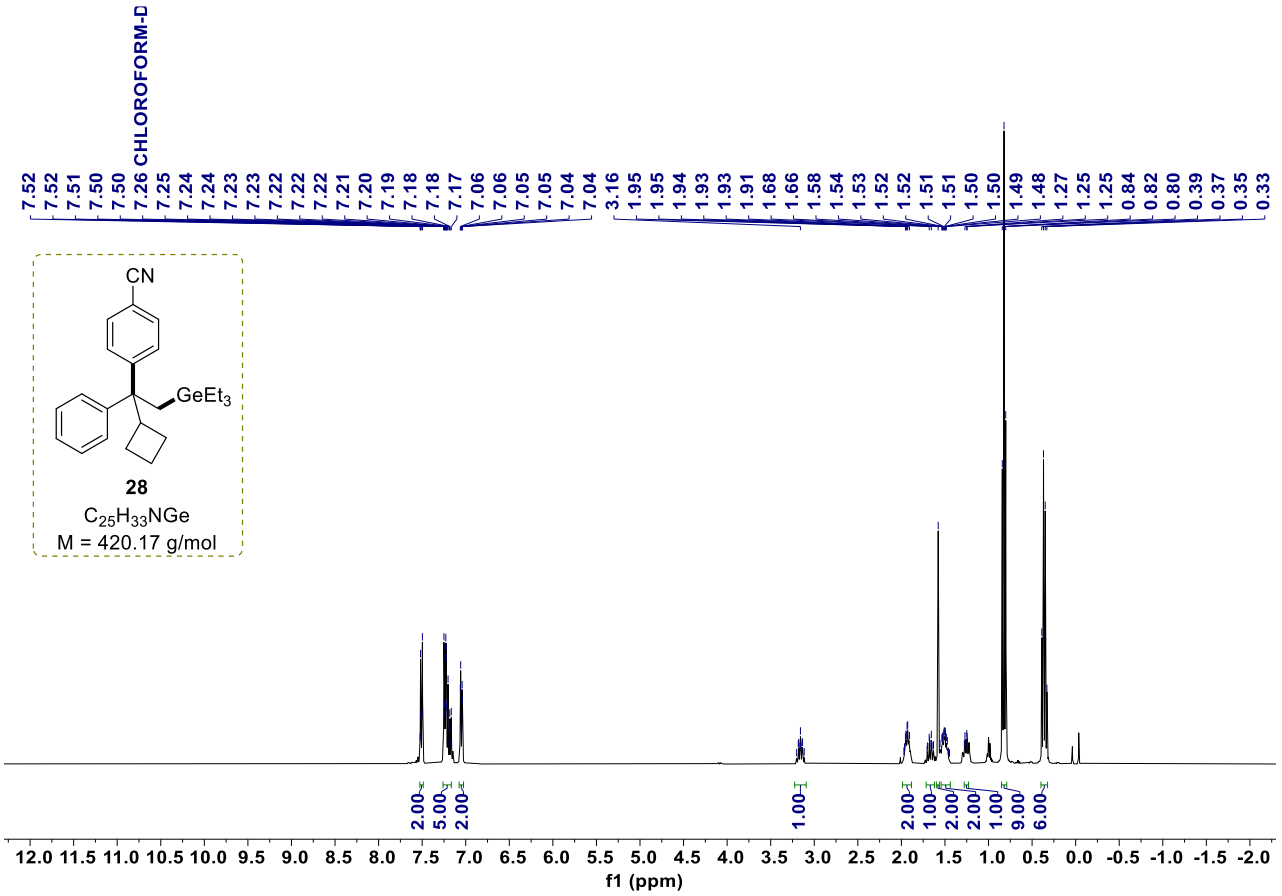


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **27**.

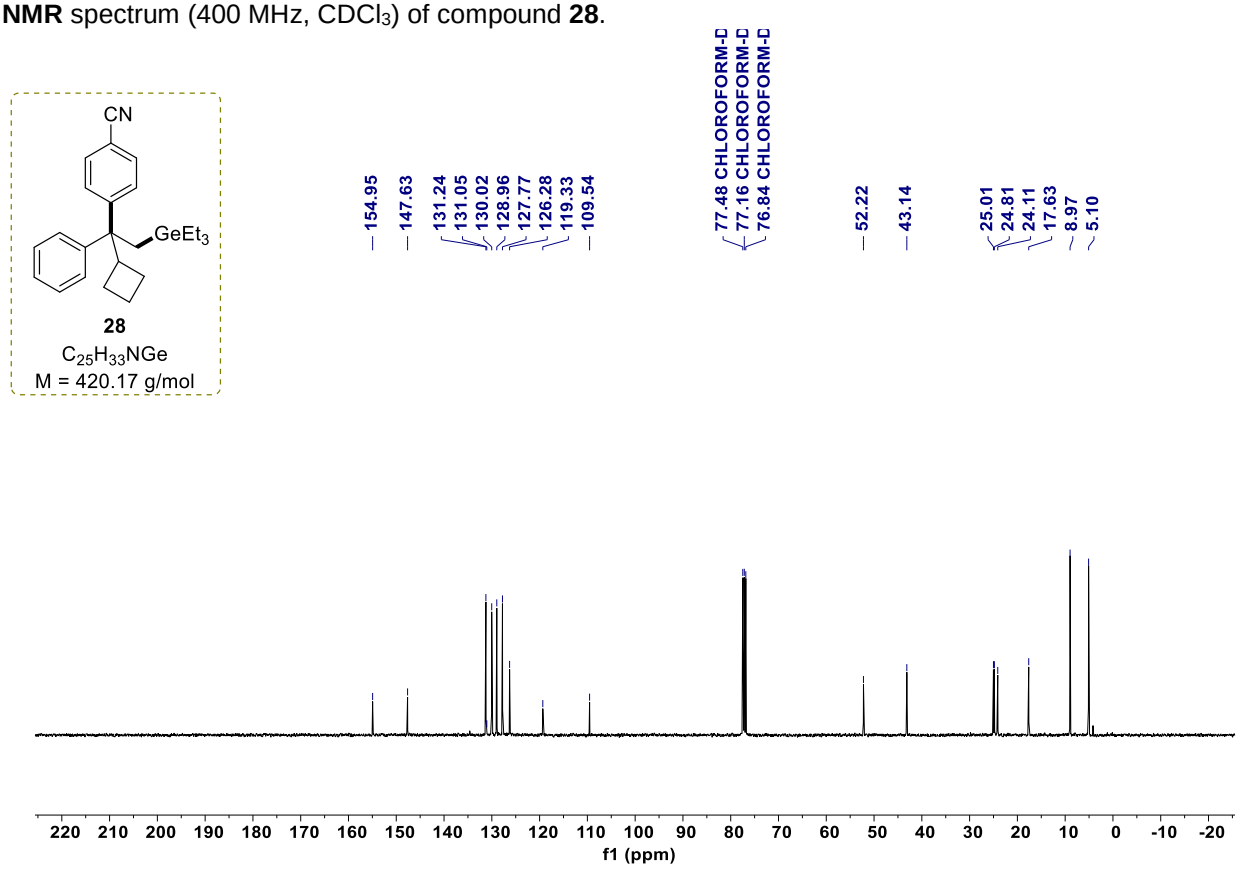


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **27**.

4.25 4-(1-cyclobutyl-1-phenyl-2-(triethylgermyl)ethyl)benzonitrile (**28**)

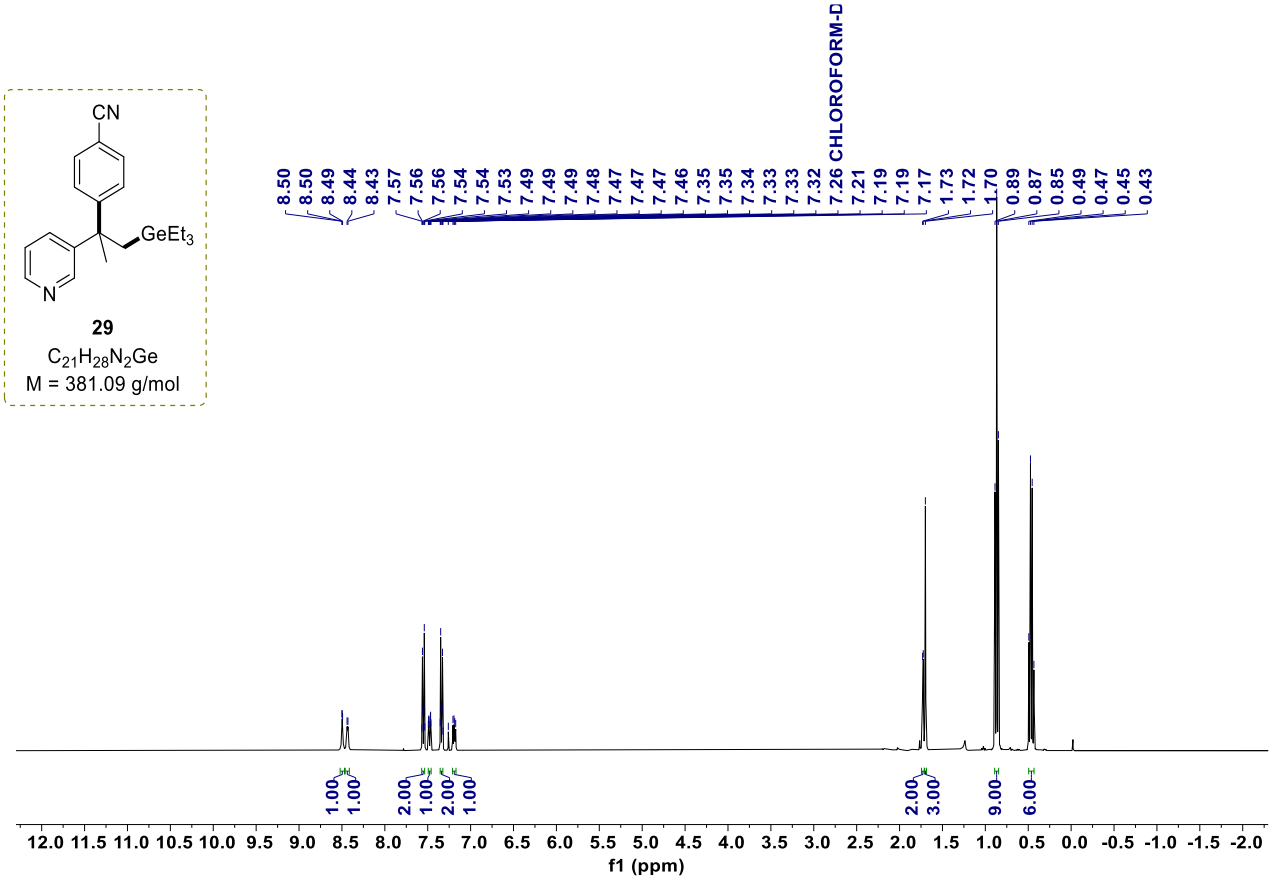


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **28**.

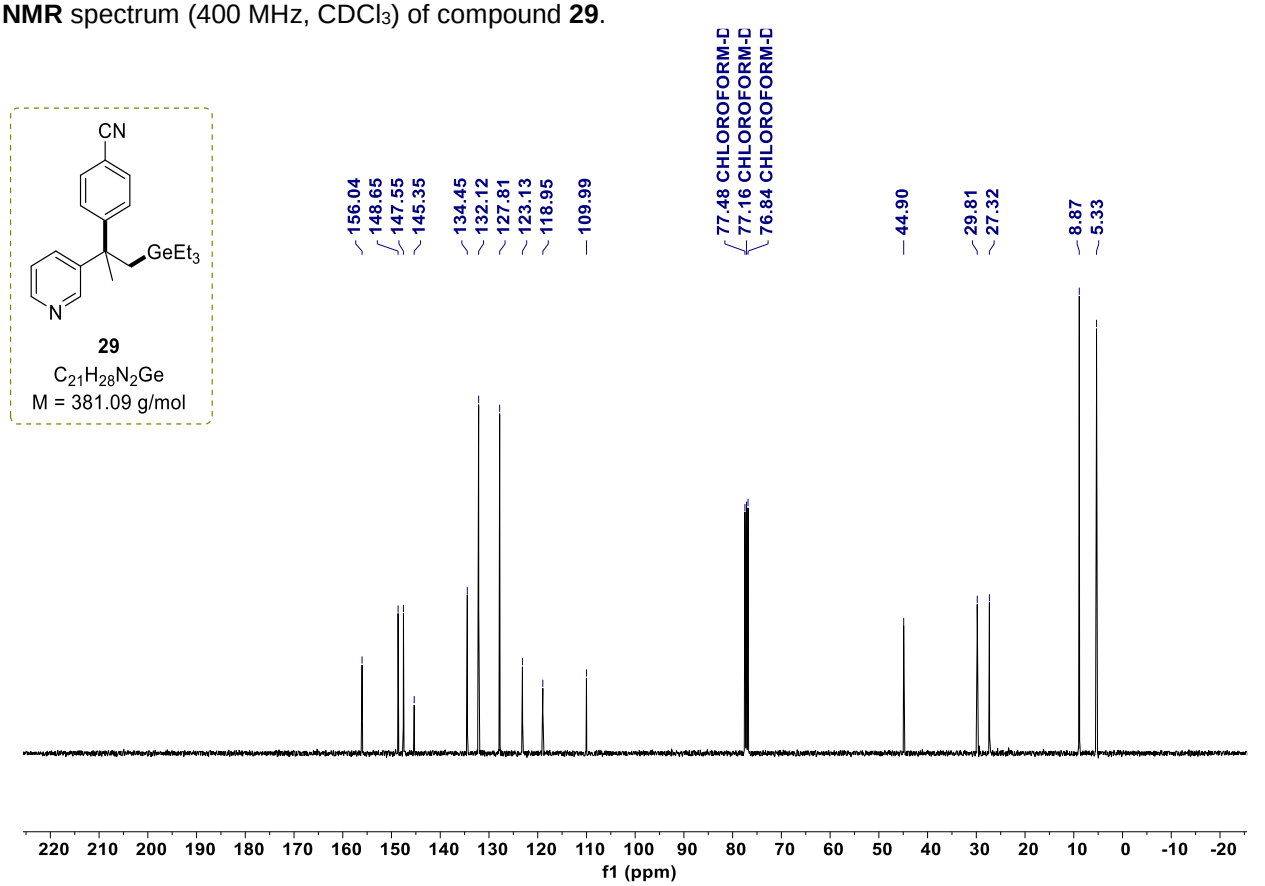


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **28**.

4.26 4-(1-cyclobutyl-1-phenyl-2-(triethylgermyl)ethyl)benzonitrile (**29**)

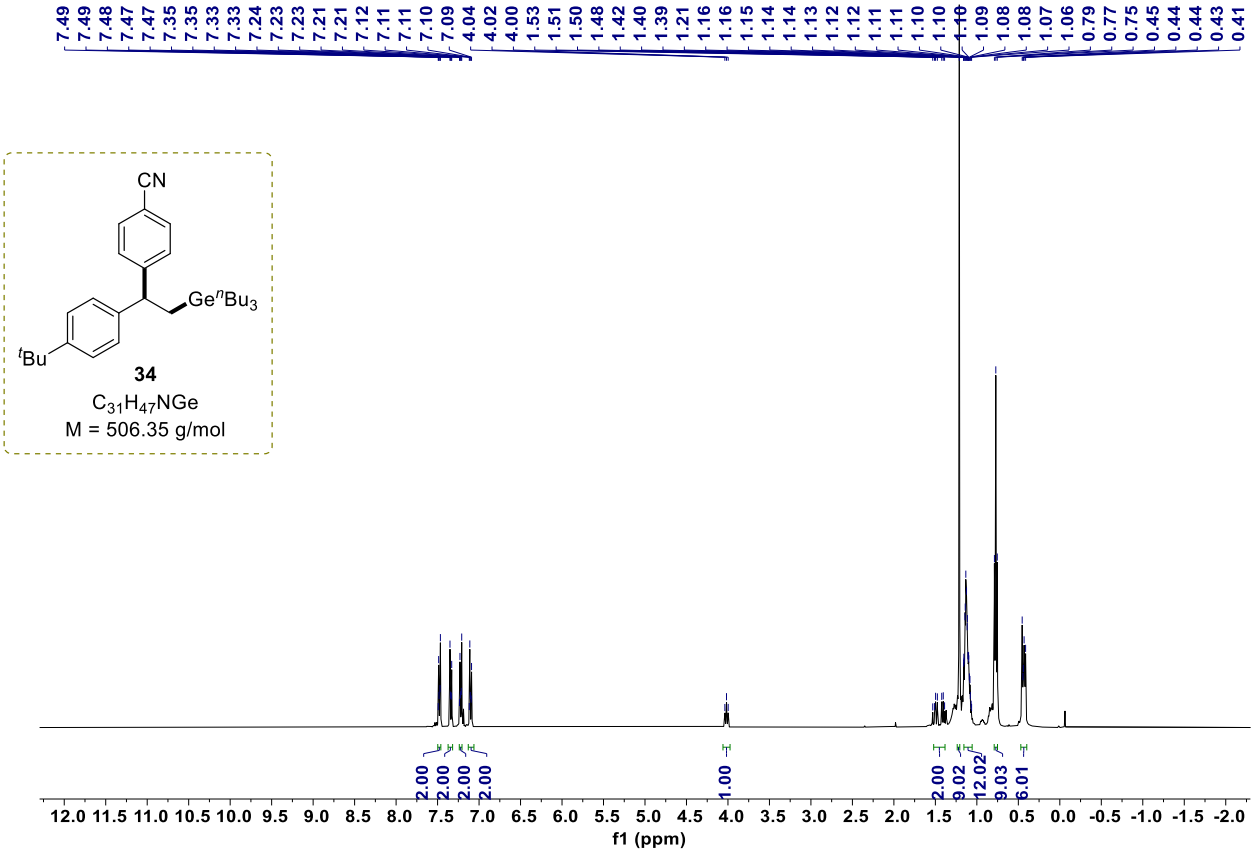


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **29**.

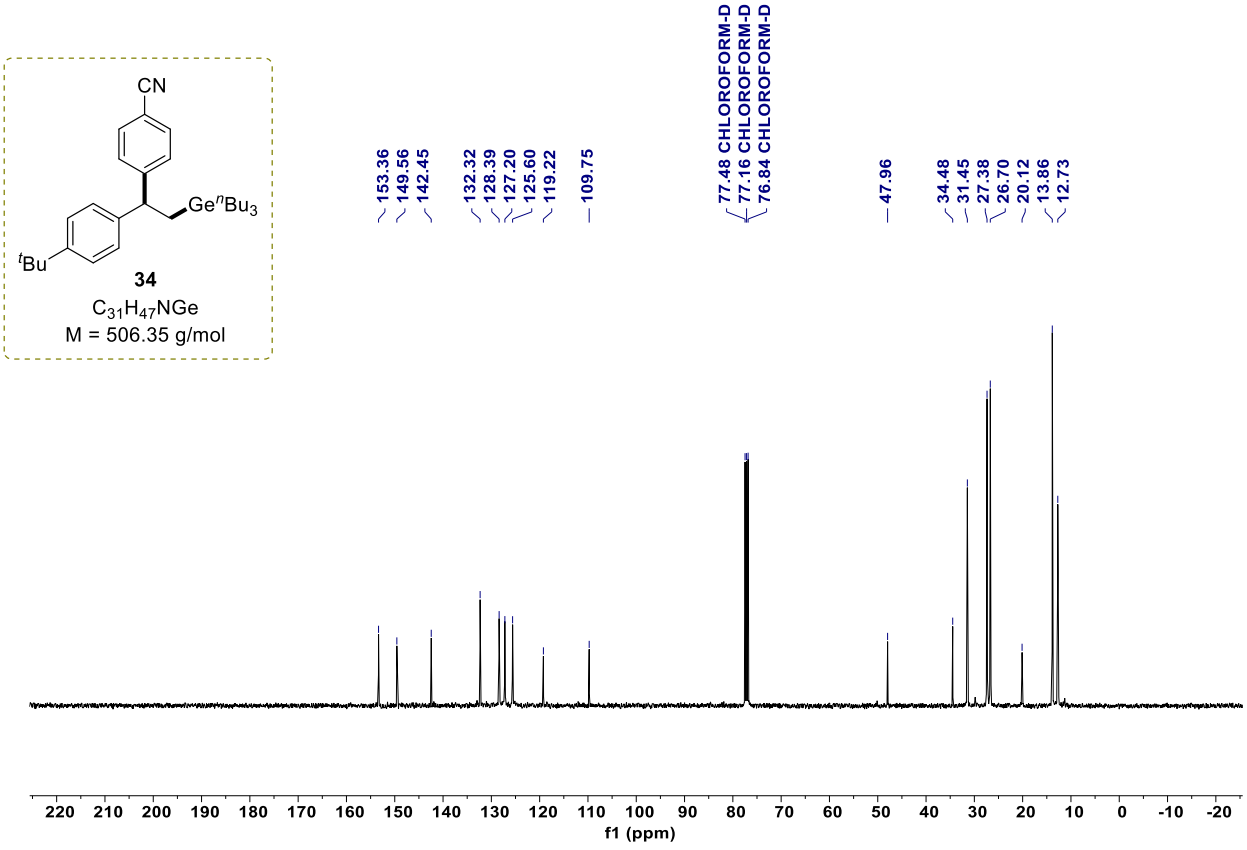


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **29**.

4.27 4-(1-(4-(tert-butyl)phenyl)-2-(tributylgermyl)ethyl)benzonitrile (**34**)

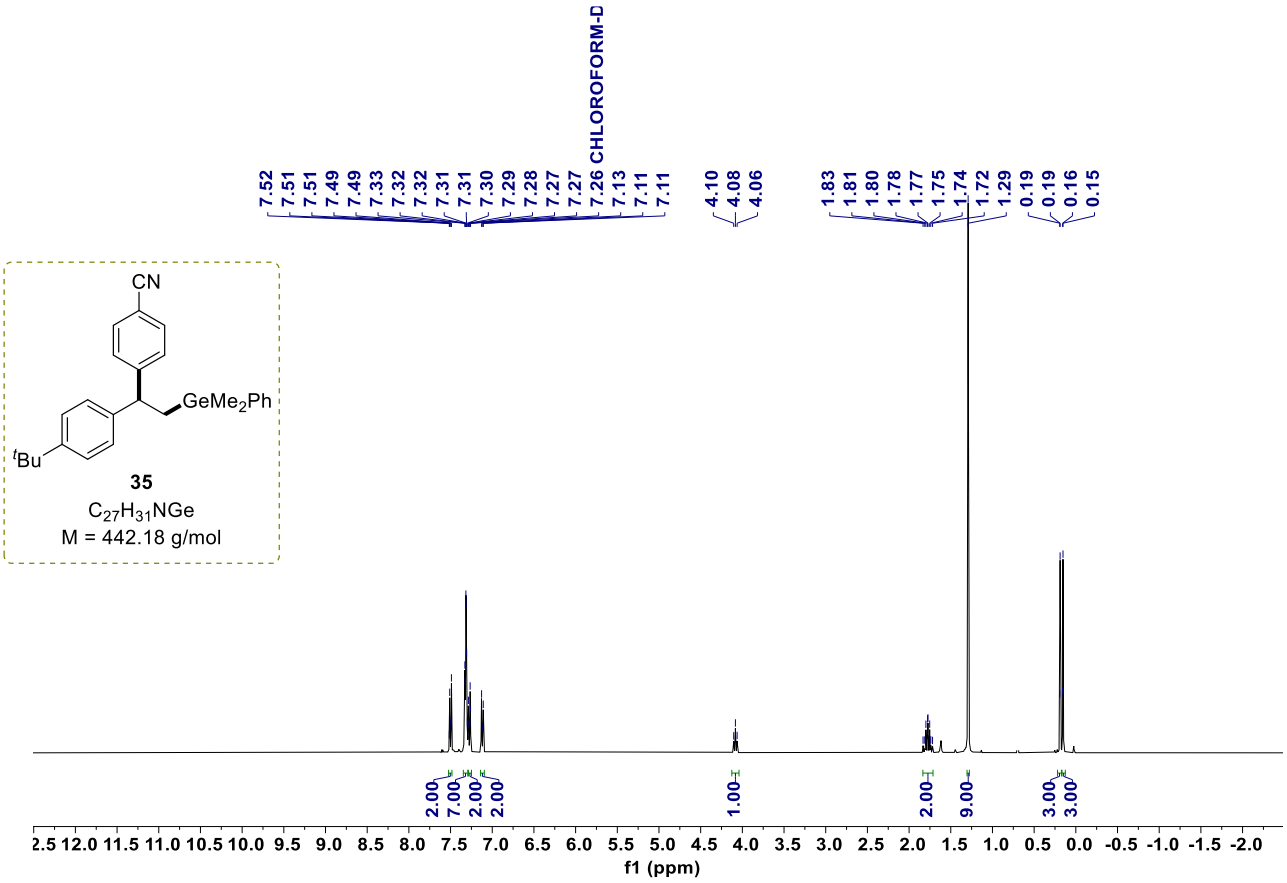


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **34**.

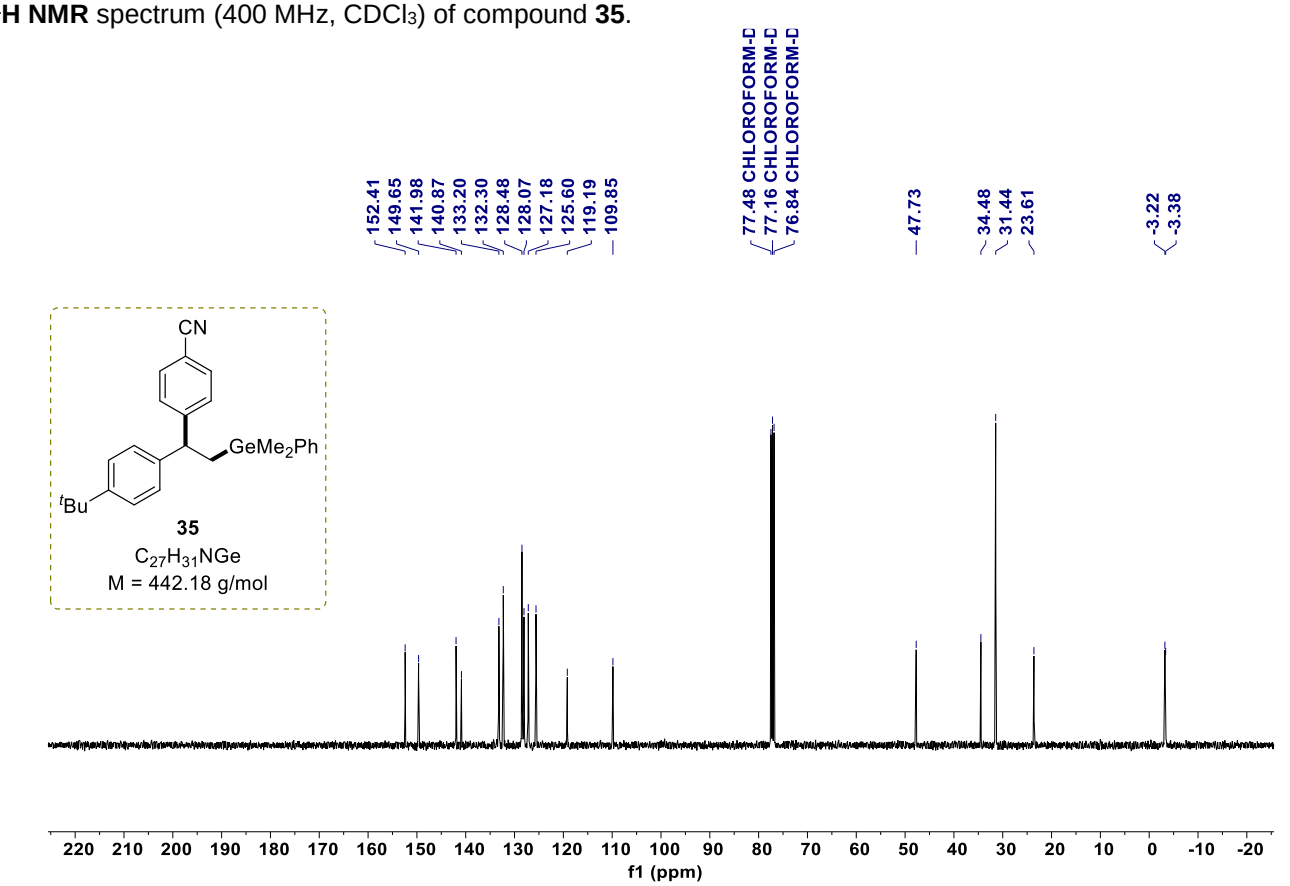


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **34**.

4.28 4-(1-(4-(tert-butyl)phenyl)-2-(dimethyl(phenyl)germyl)ethyl)benzonitrile (**35**)

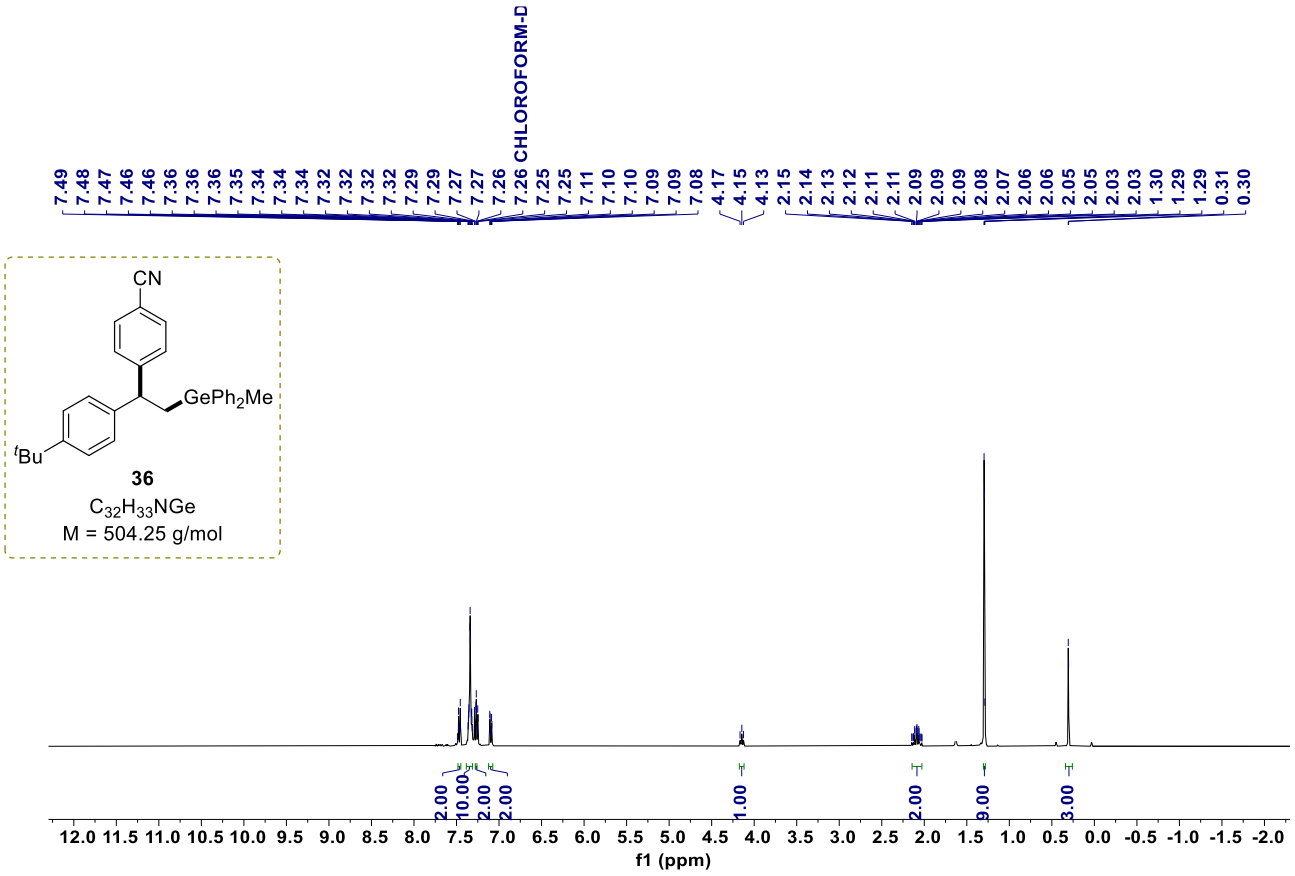


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **35**.

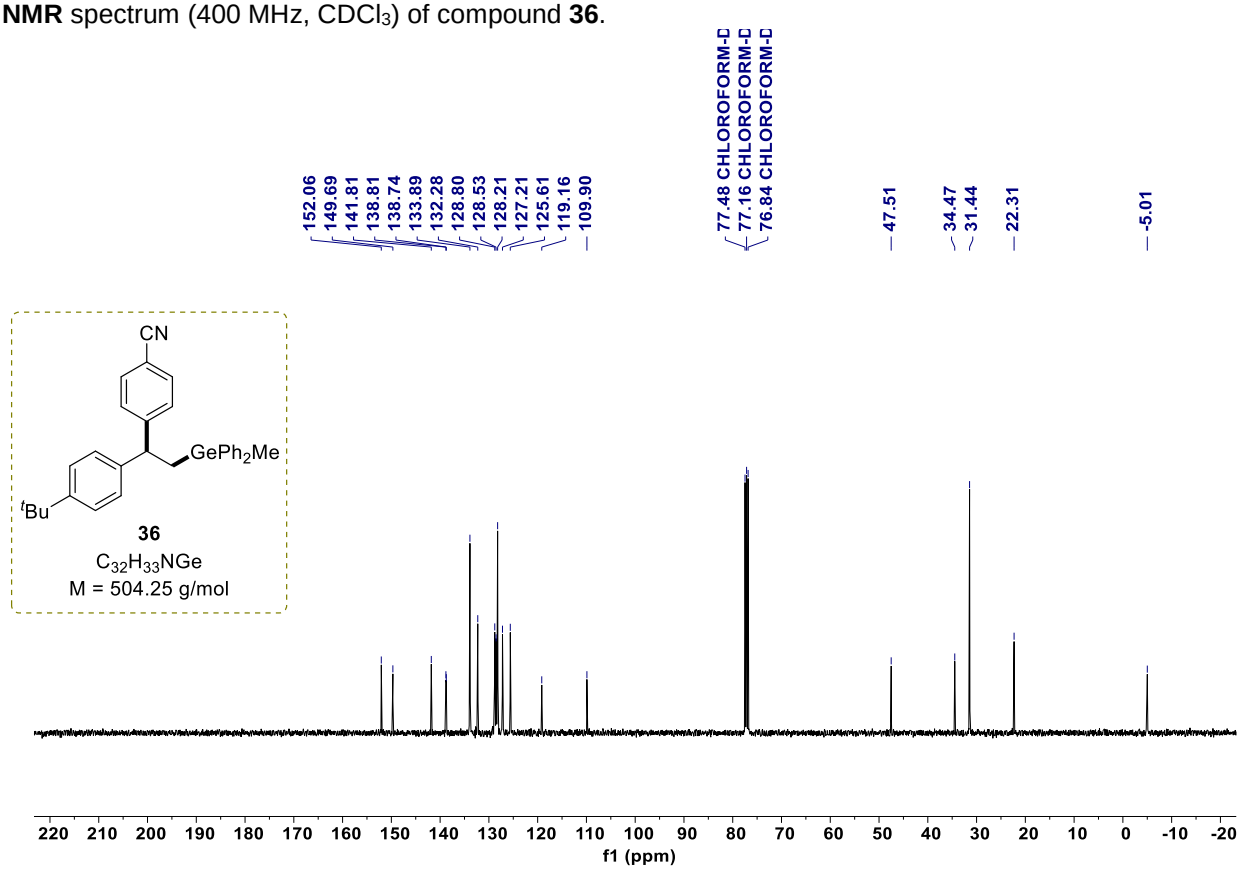


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **35**.

4.29 4-(1-(4-(tert-butyl)phenyl)-2-(methyldiphenylgermyl)ethyl)benzonitrile (**36**)

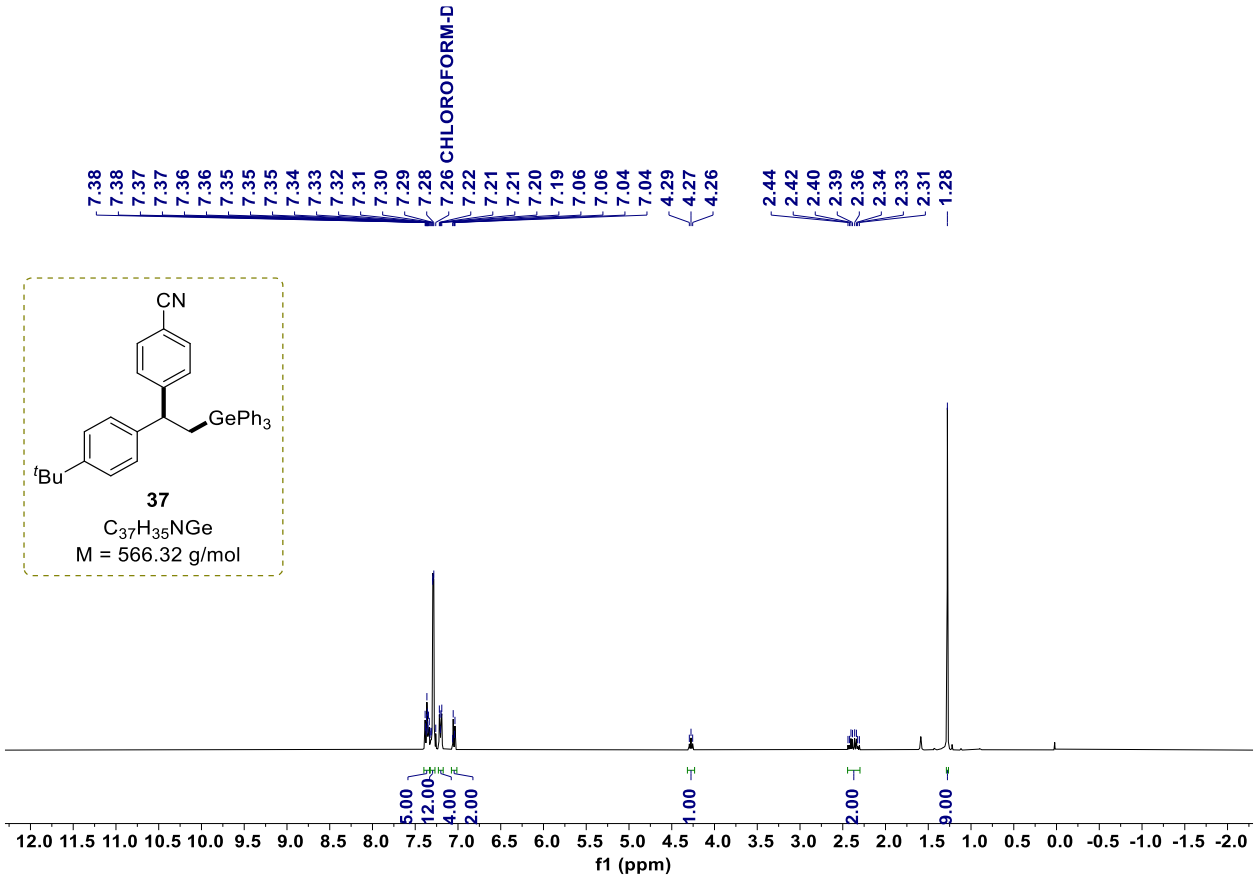


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **36**.

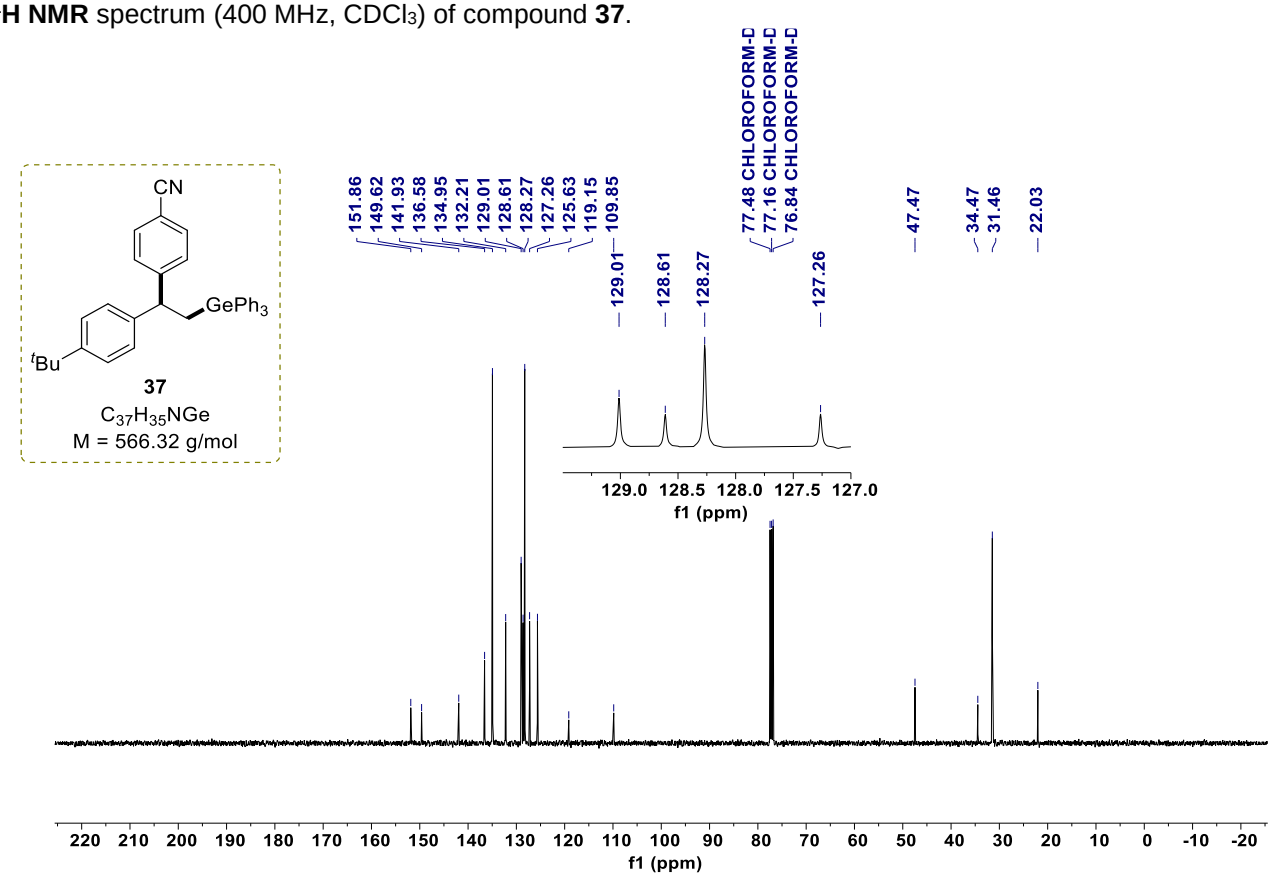


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **36**.

4.30 4-(1-(4-(tert-butyl)phenyl)-2-(triphenylgermyl)ethyl)benzonitrile (**37**)

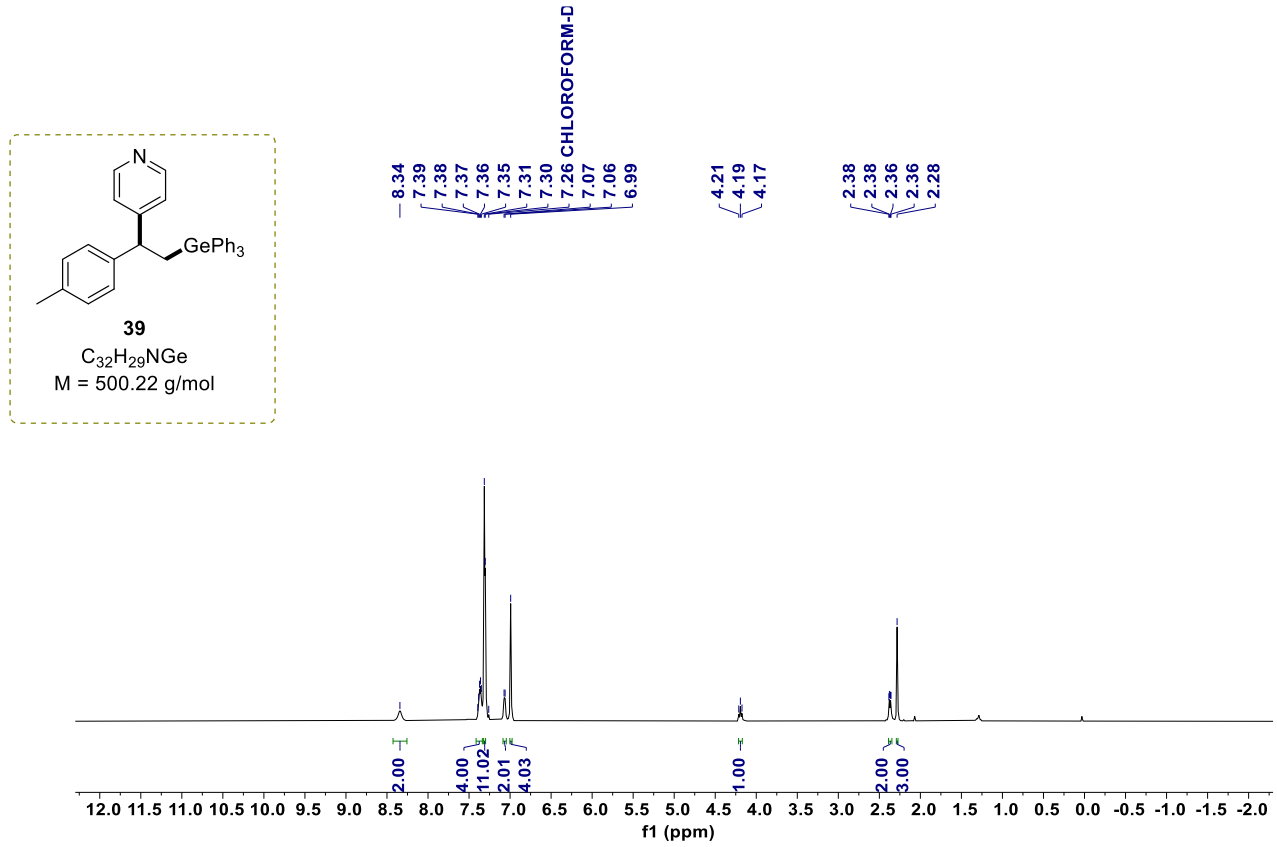


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **37**.

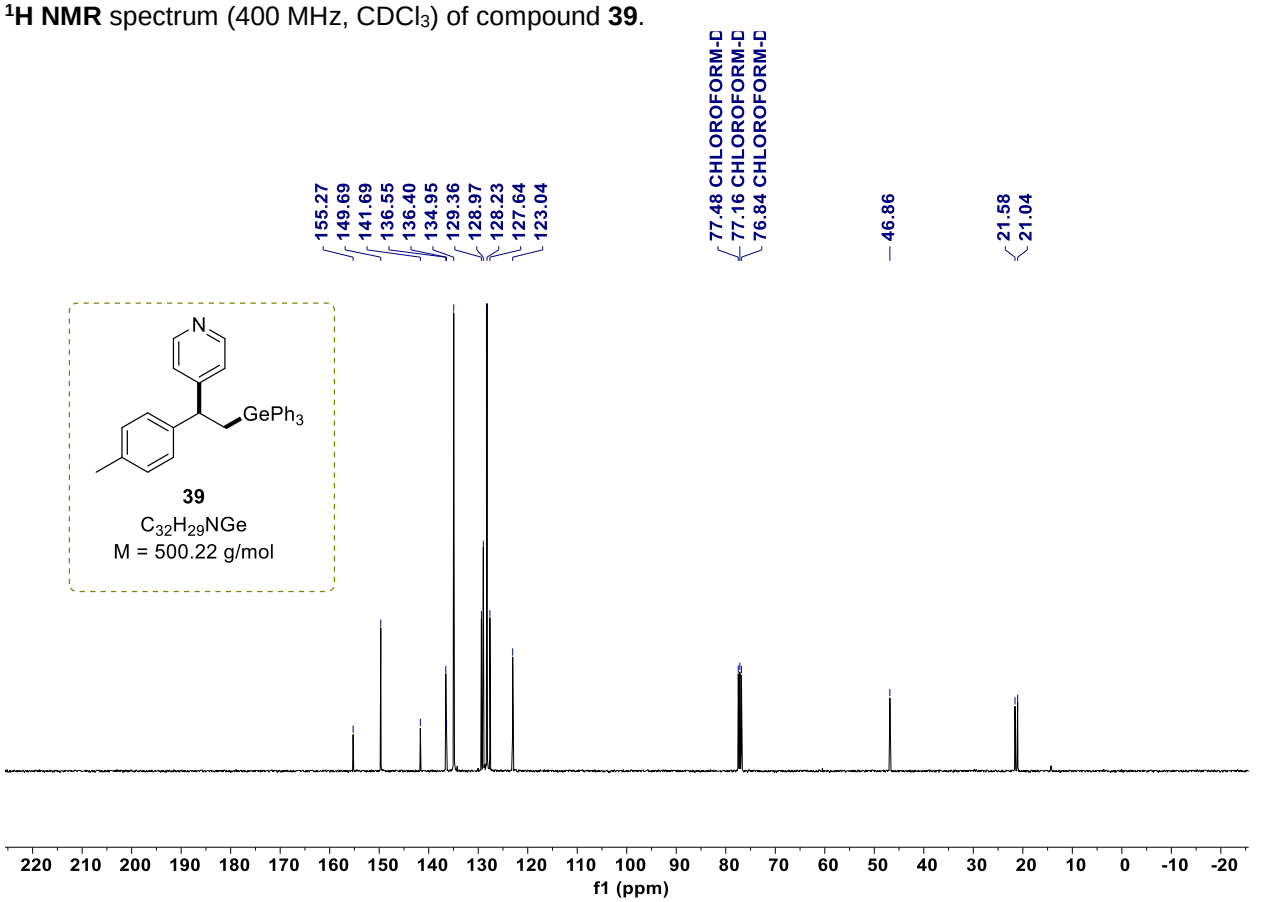


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **37**.

4.31 4-(1-(p-tolyl)-2-(triphenylgermyl)ethyl)pyridine (**39**)

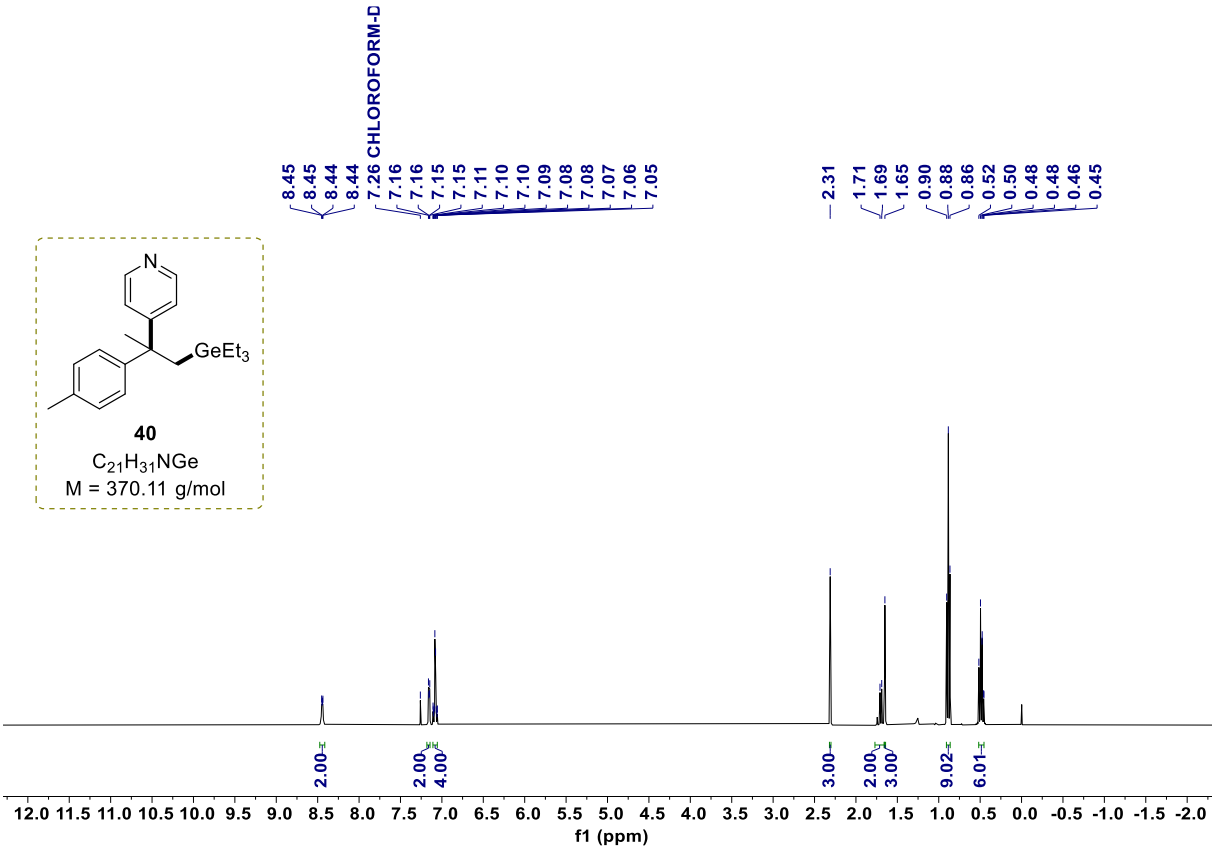


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **39**.

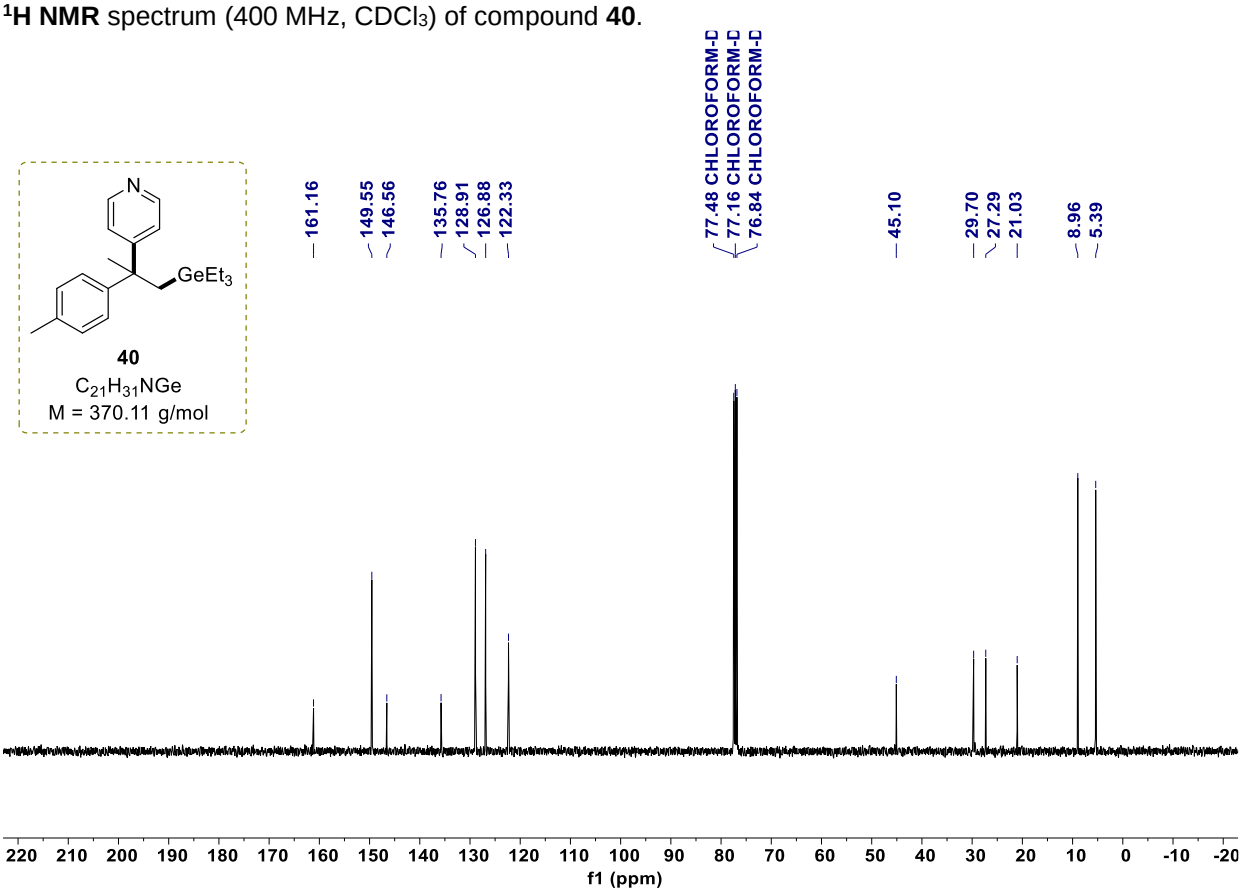


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **39**.

4.32 4-(2-(p-tolyl)-1-(triethylgermyl)propan-2-yl)pyridine (**40**)

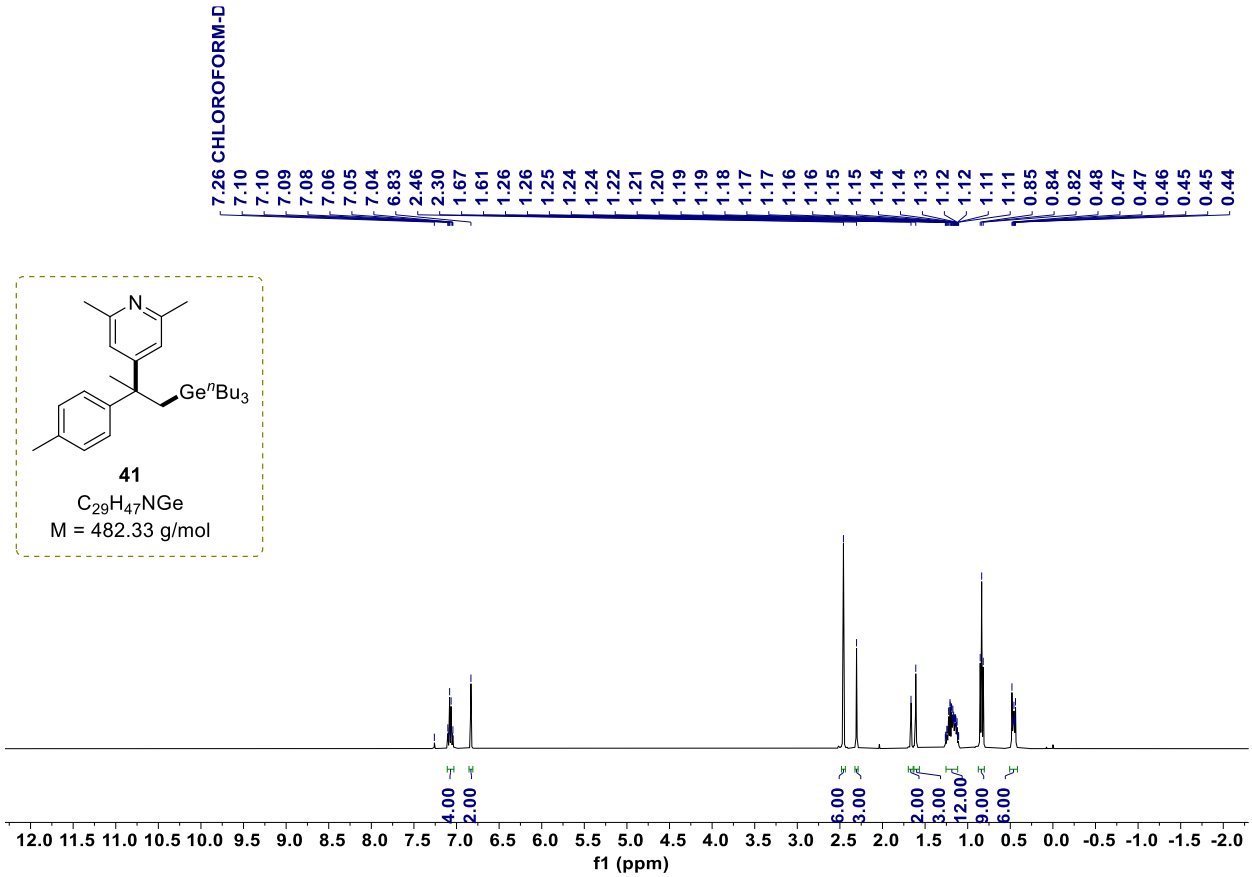


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **40**.

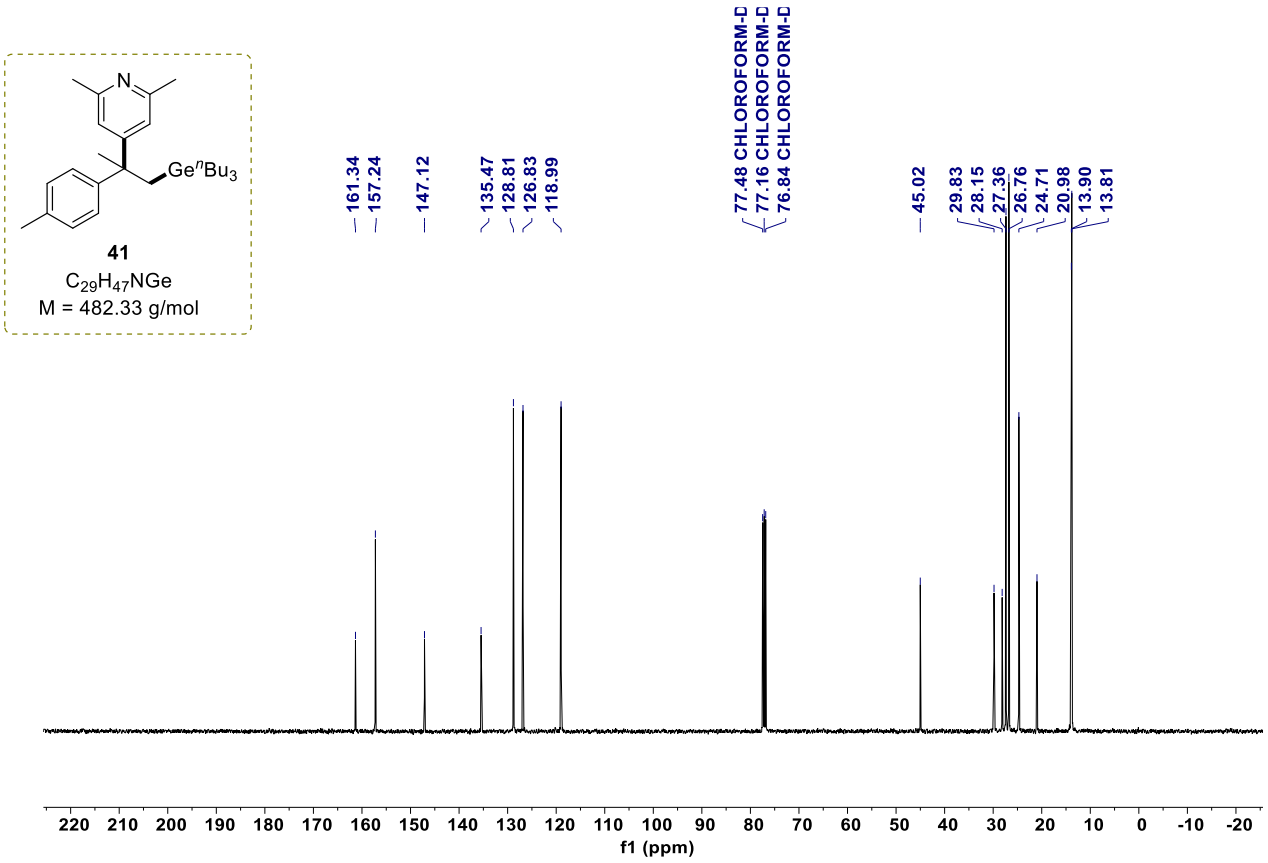


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **40**.

4.33 2,6-dimethyl-4-(2-(p-tolyl)-1-(tributylgermyl)propan-2-yl)pyridine (**41**)

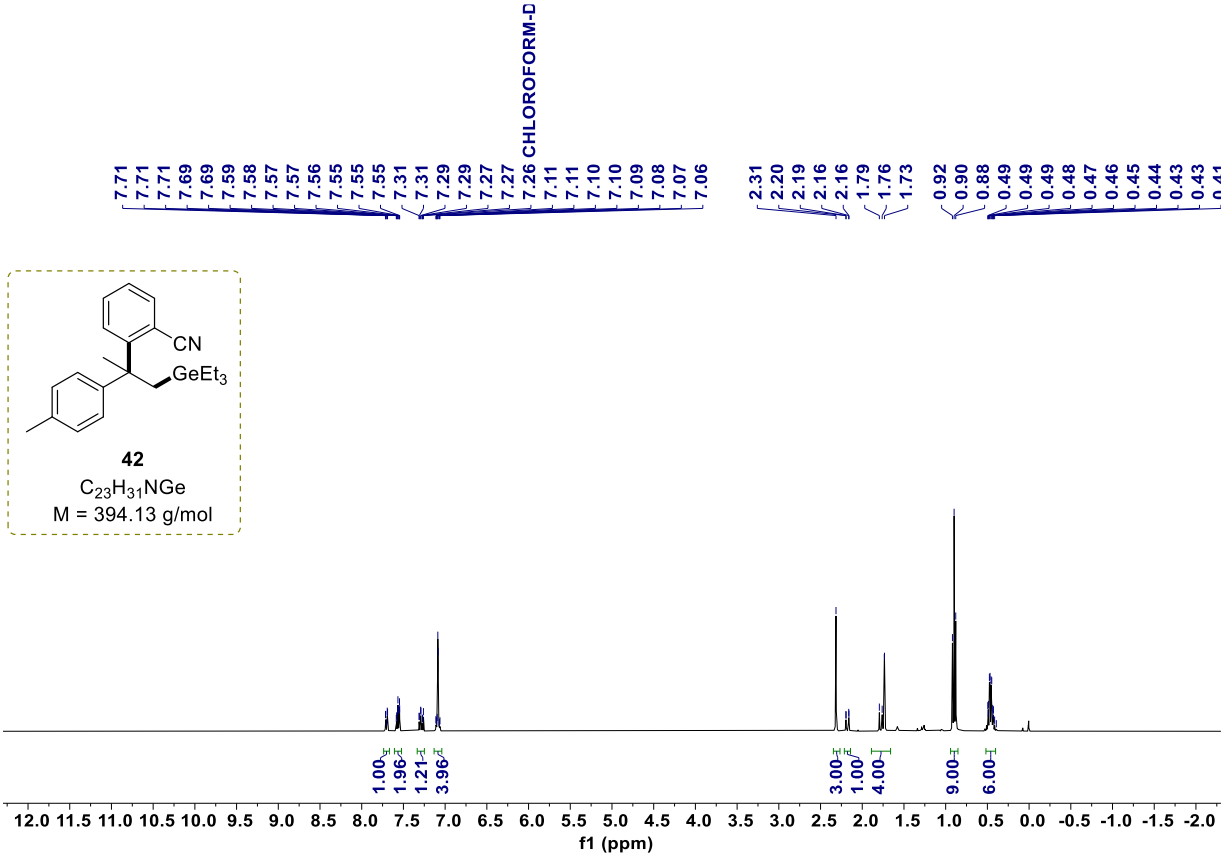


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **41**.

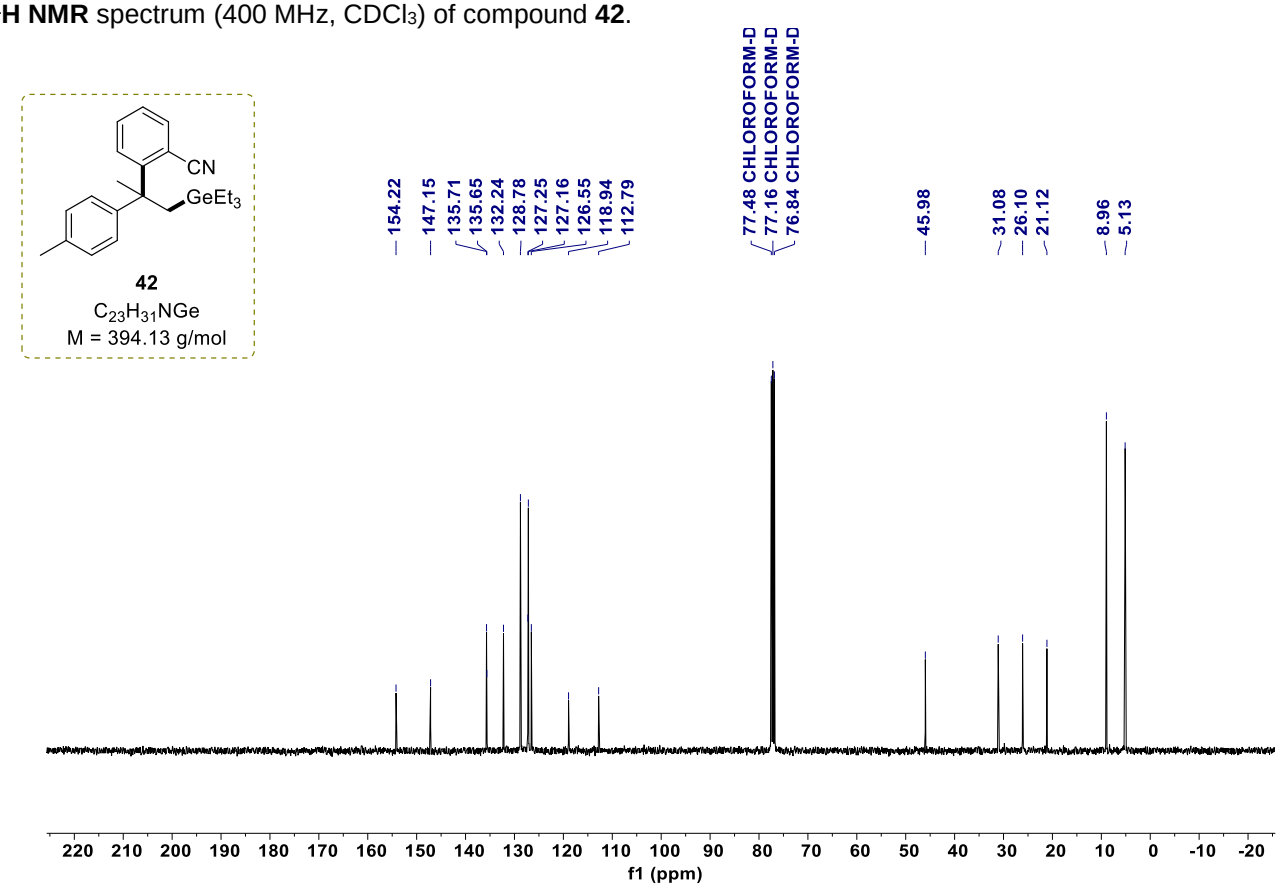


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **41**.

4.34 2-(2-(p-tolyl)-1-(tributylgermyl)propan-2-yl)benzonitrile (**42**)

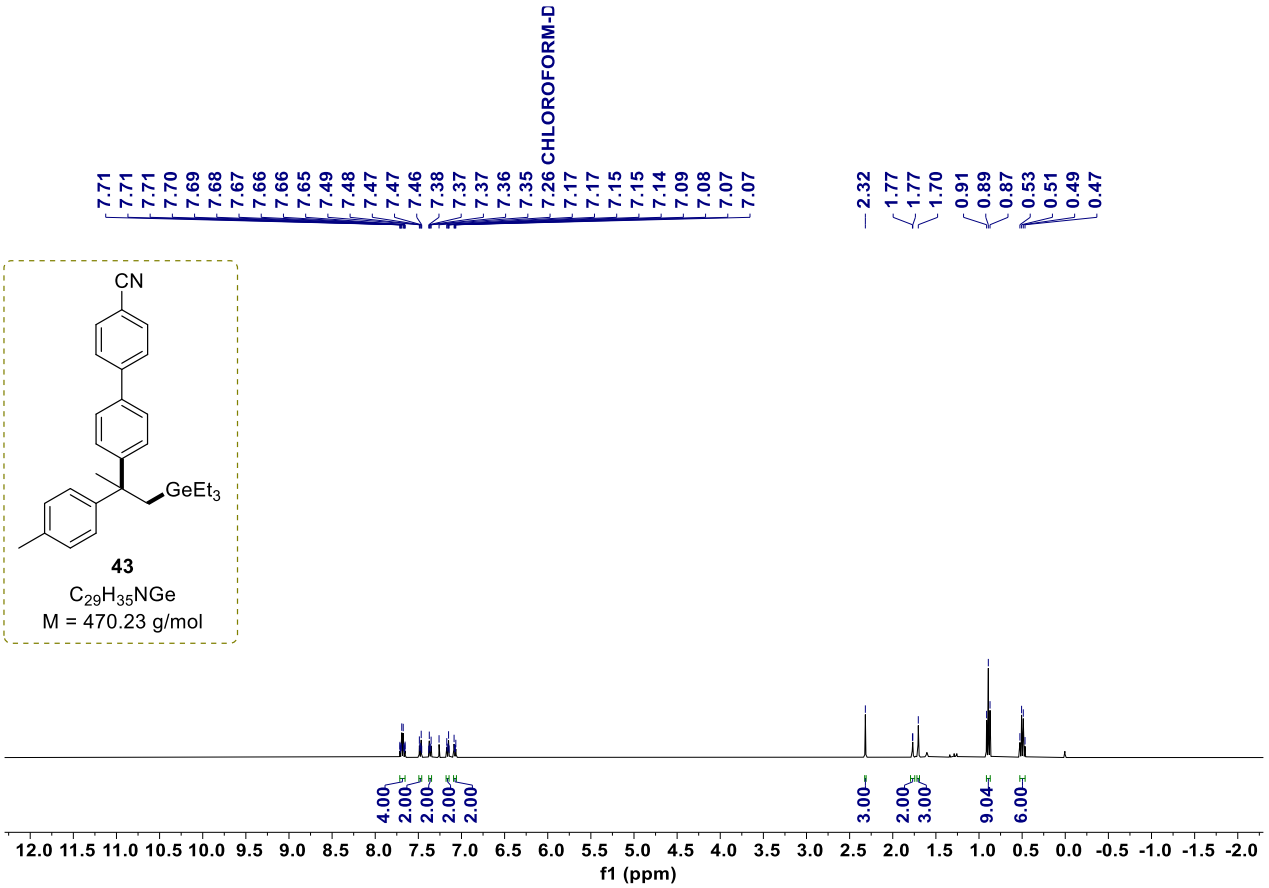


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **42**.

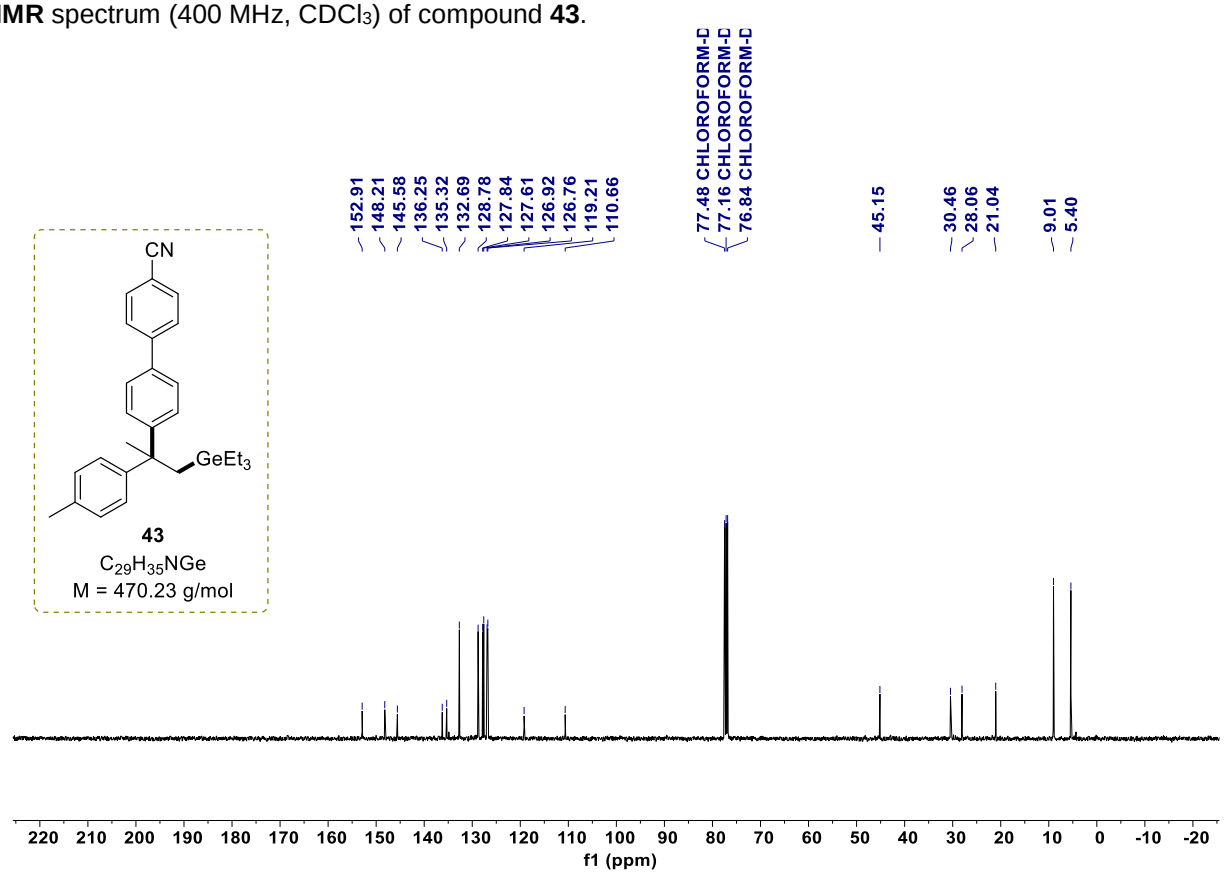


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **42**.

4.35 4'-(2-(p-tolyl)-1-(triethylgermyl)propan-2-yl)-[1,1'-biphenyl]-4-carbonitrile (**43**)

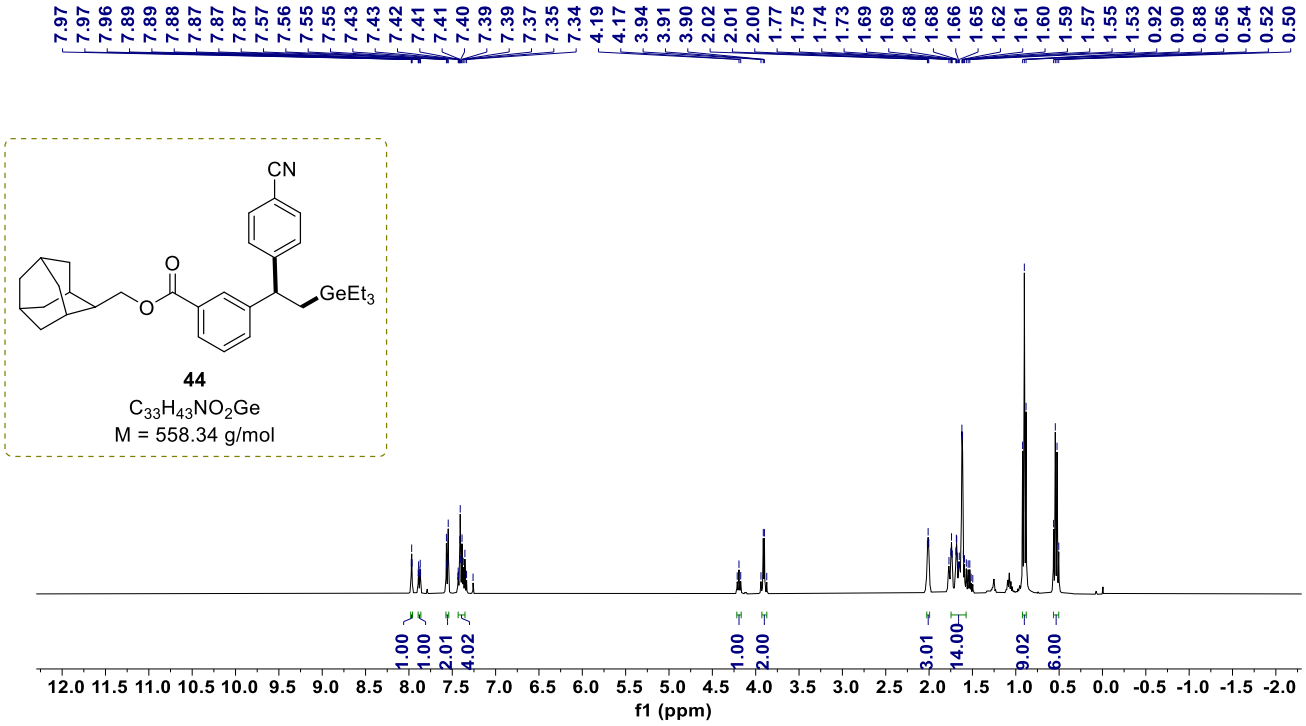


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **43**.

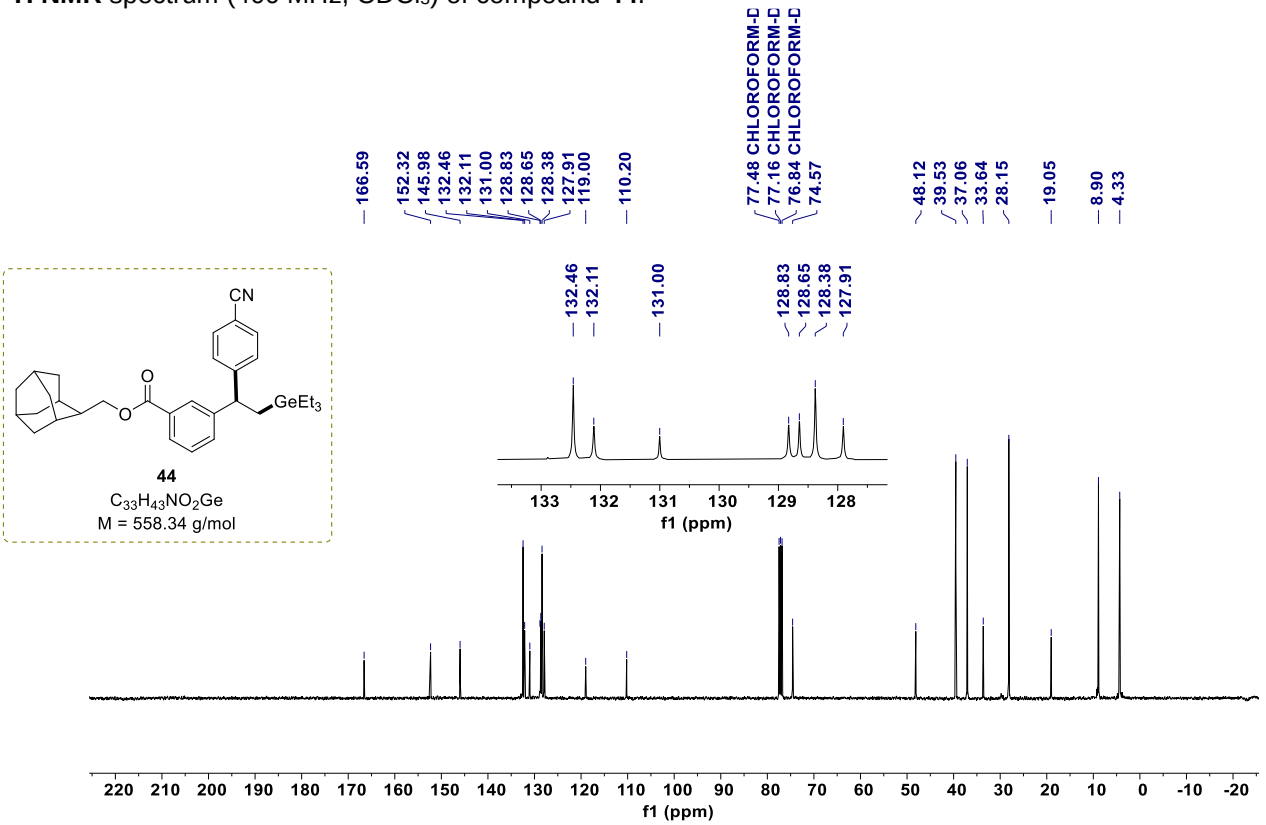


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **43**.

4.36 (Adamantan-2-yl)methyl 3-(1-(4-cyanophenyl)-2-(triethylgermyl)ethyl)benzoate (**44**)

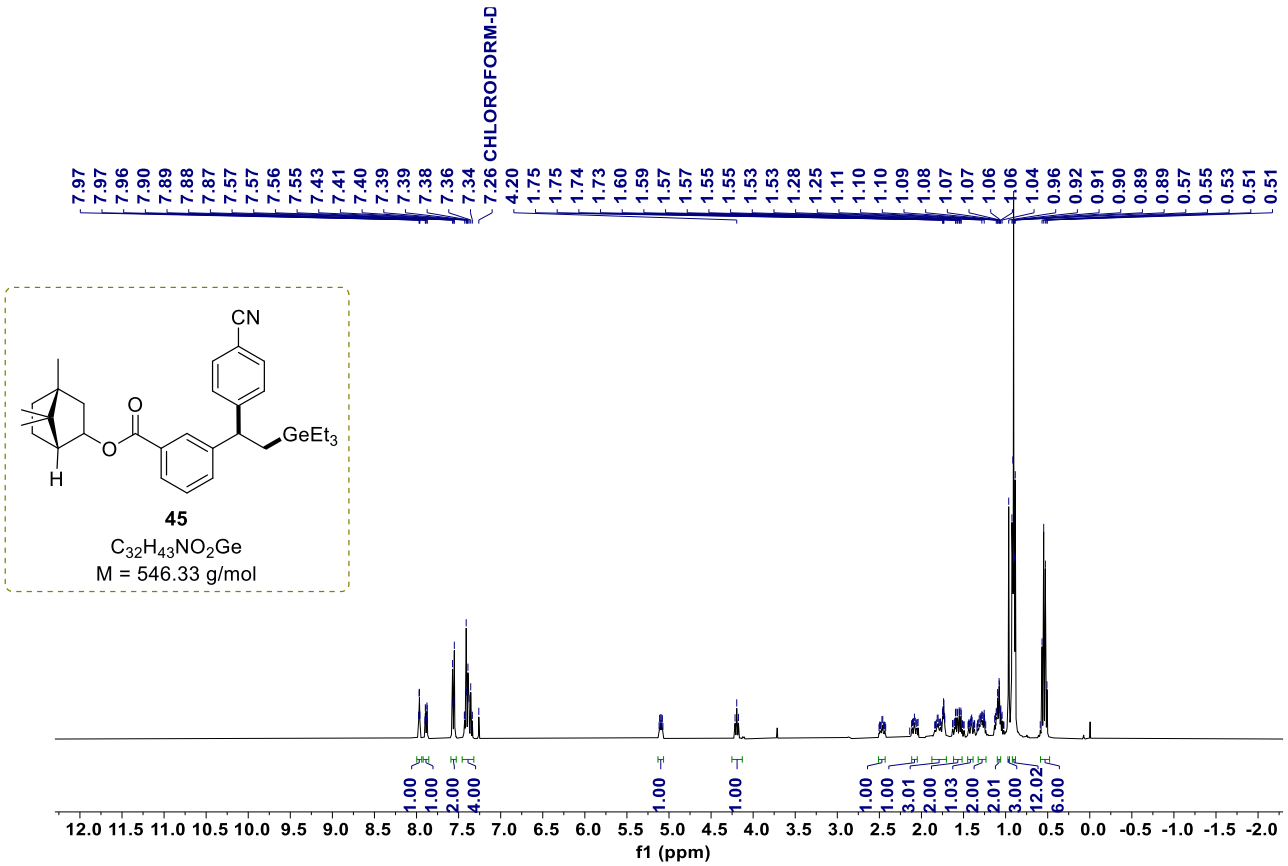


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **44**.

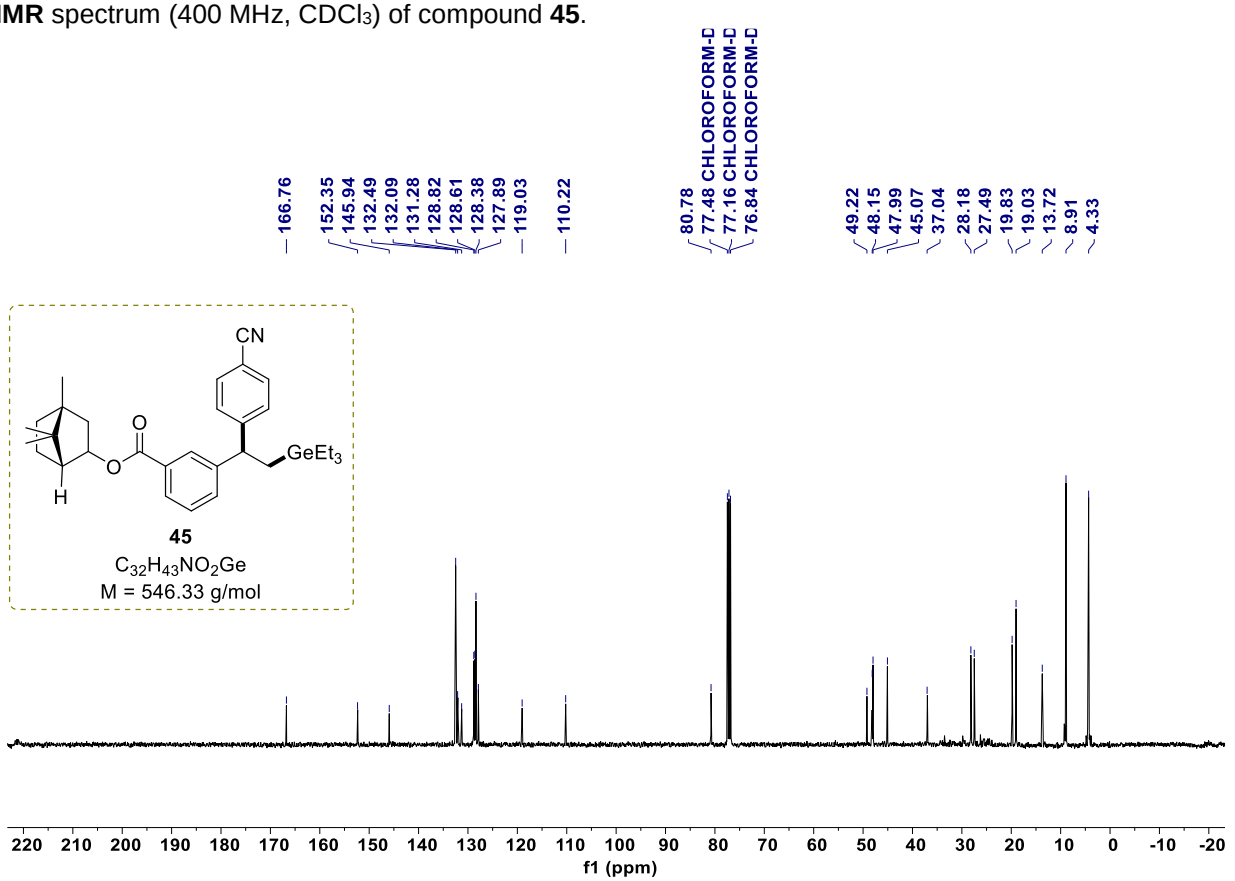


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **44**.

4.37 4,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3-((R)-1-(4-cyanophenyl)-2-triethylgermyl)ethyl)benzoate (**45**)

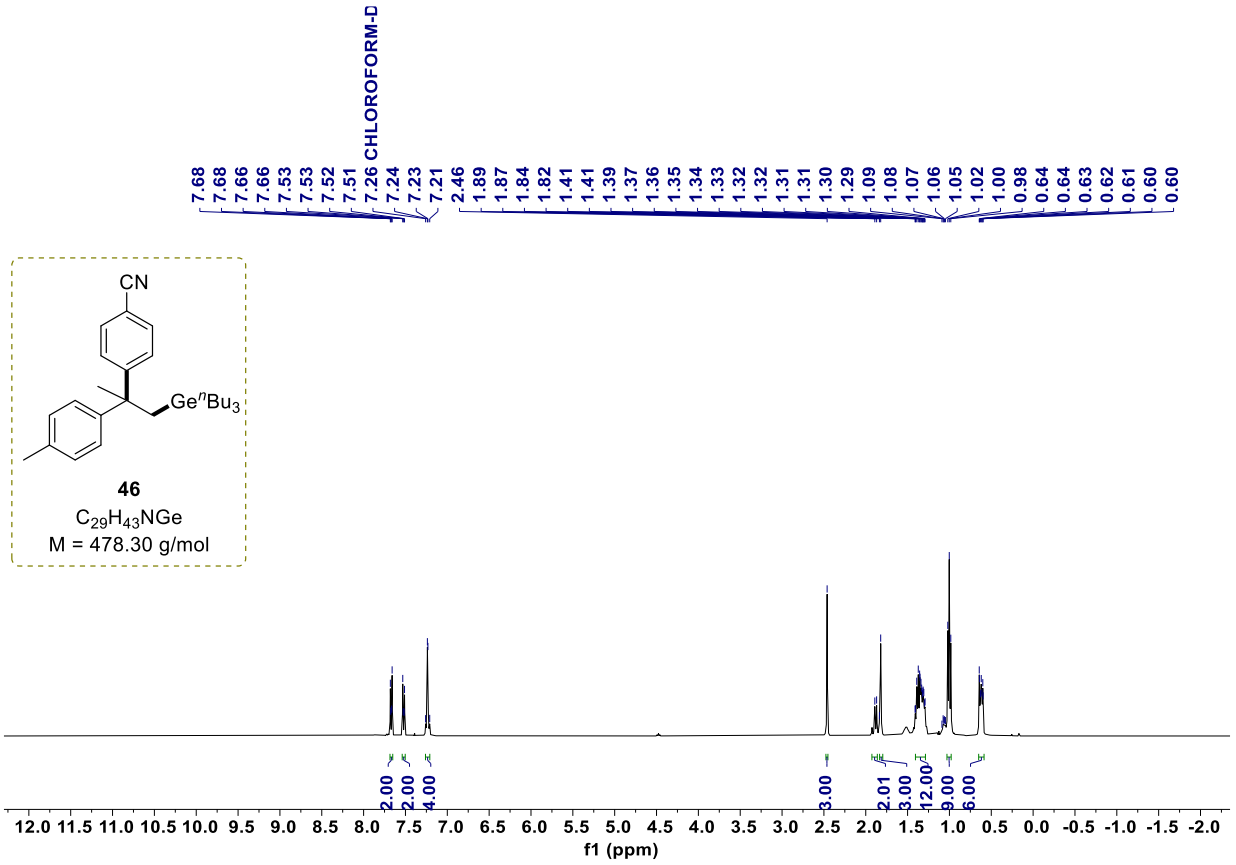


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **45**.

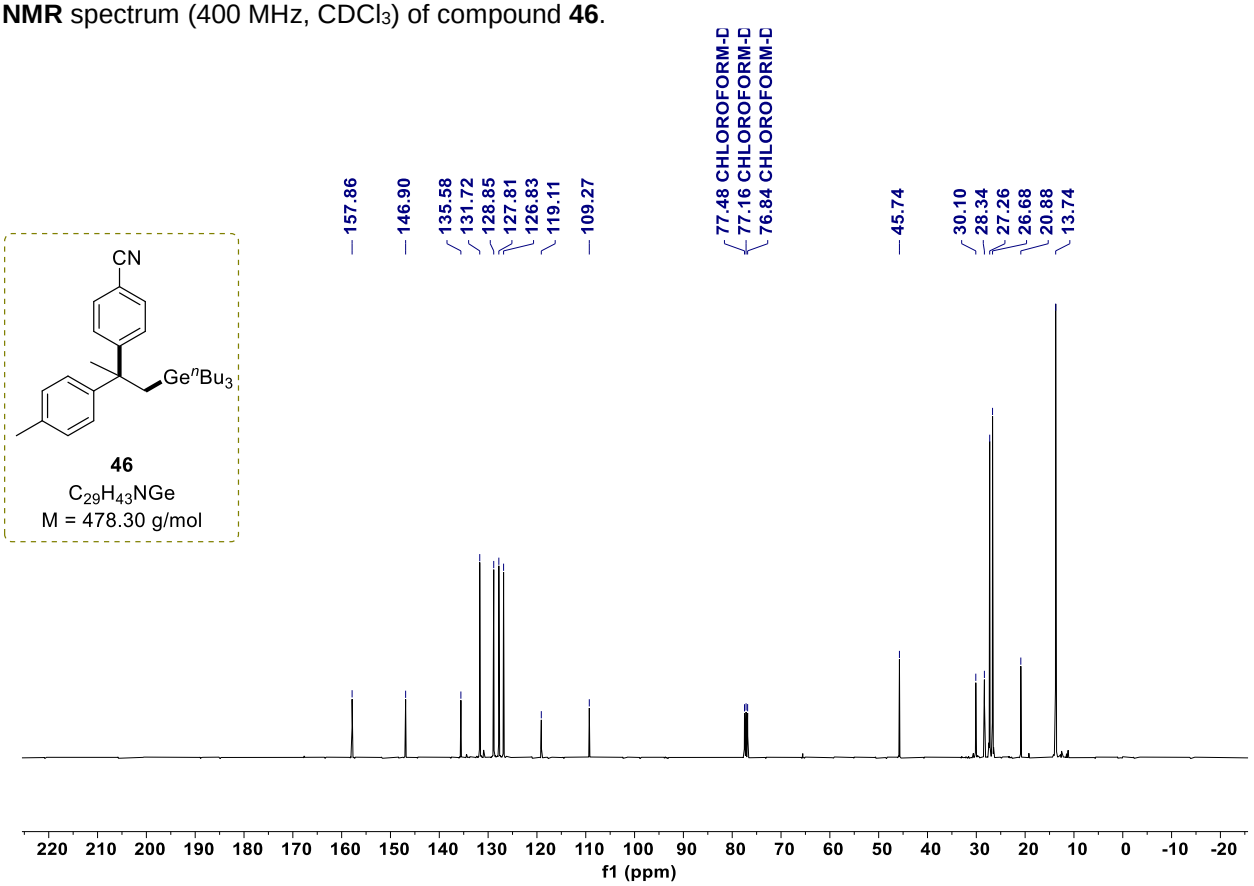


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **45.**

4.38 4-(2-(p-tolyl)-1-(tributylgermyl)propan-2-yl)benzonitrile (**46**)

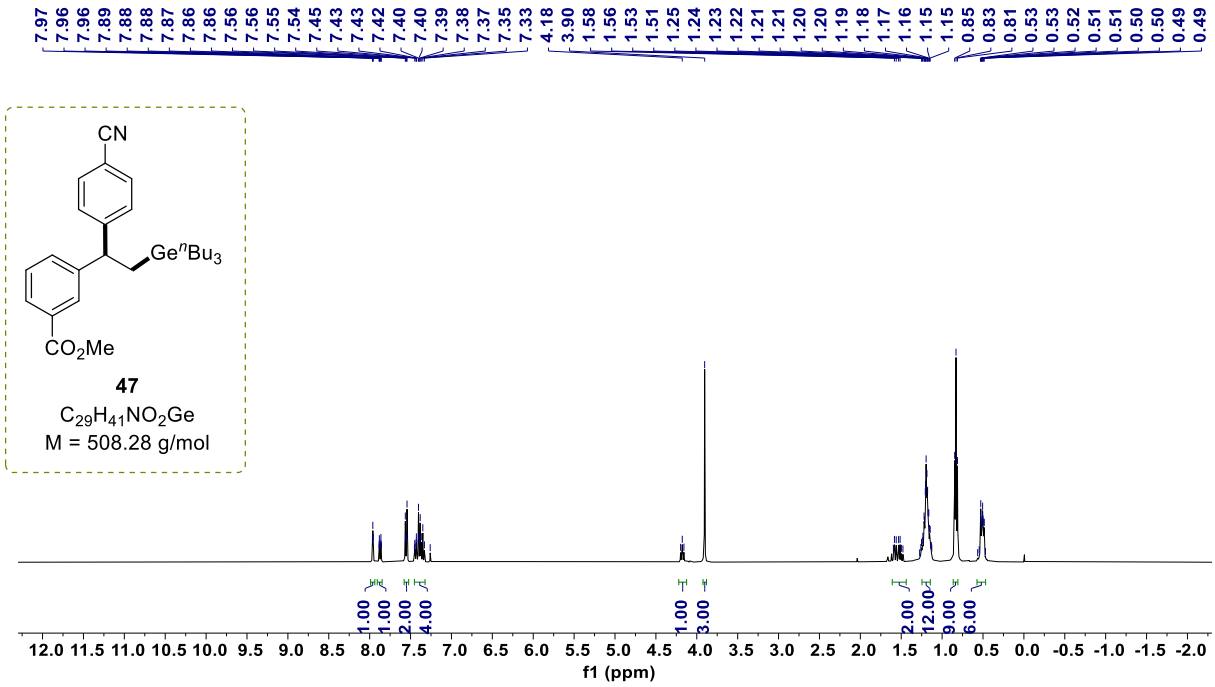


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **46**.

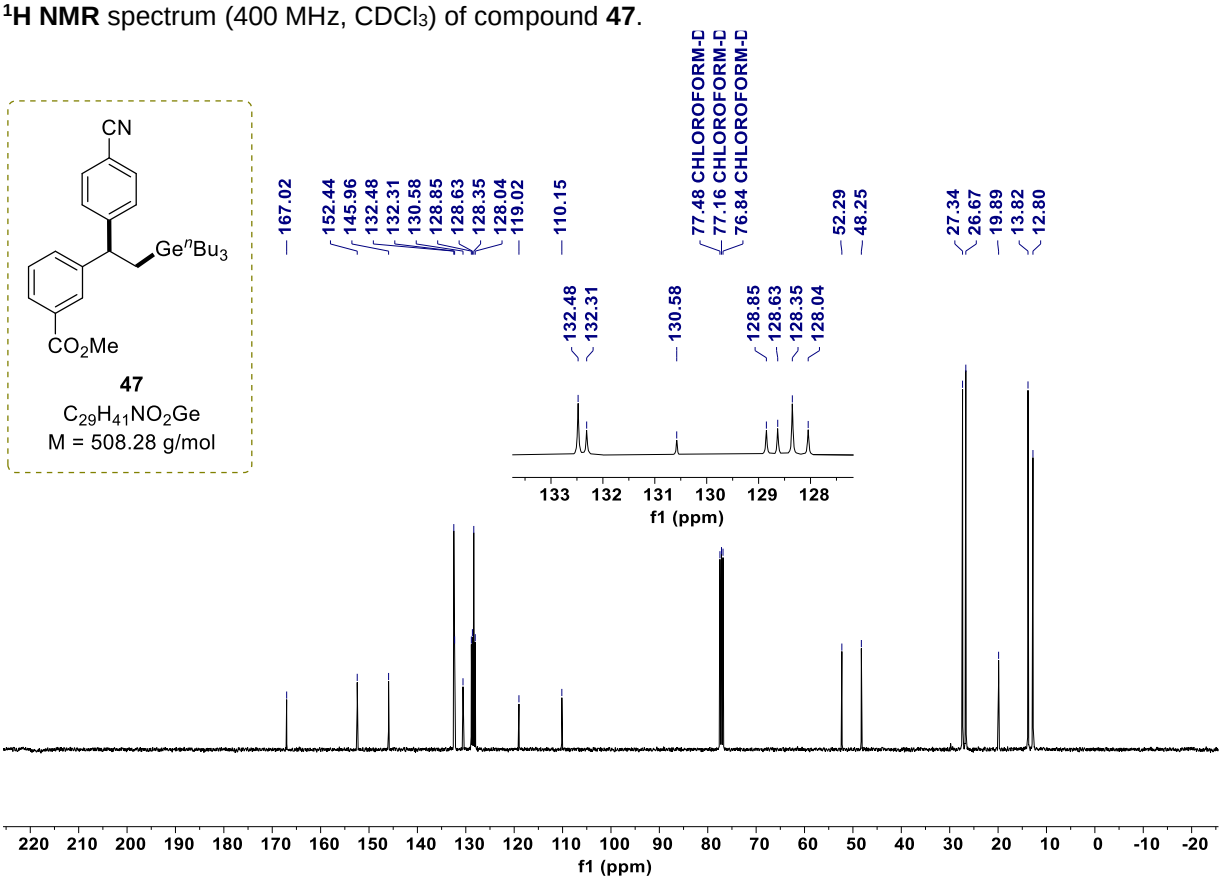


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **46**.

4.39 methyl (R)-3-(1-(4-cyanophenyl)-2-(tributylgermyl)ethyl)benzoate (**47**)

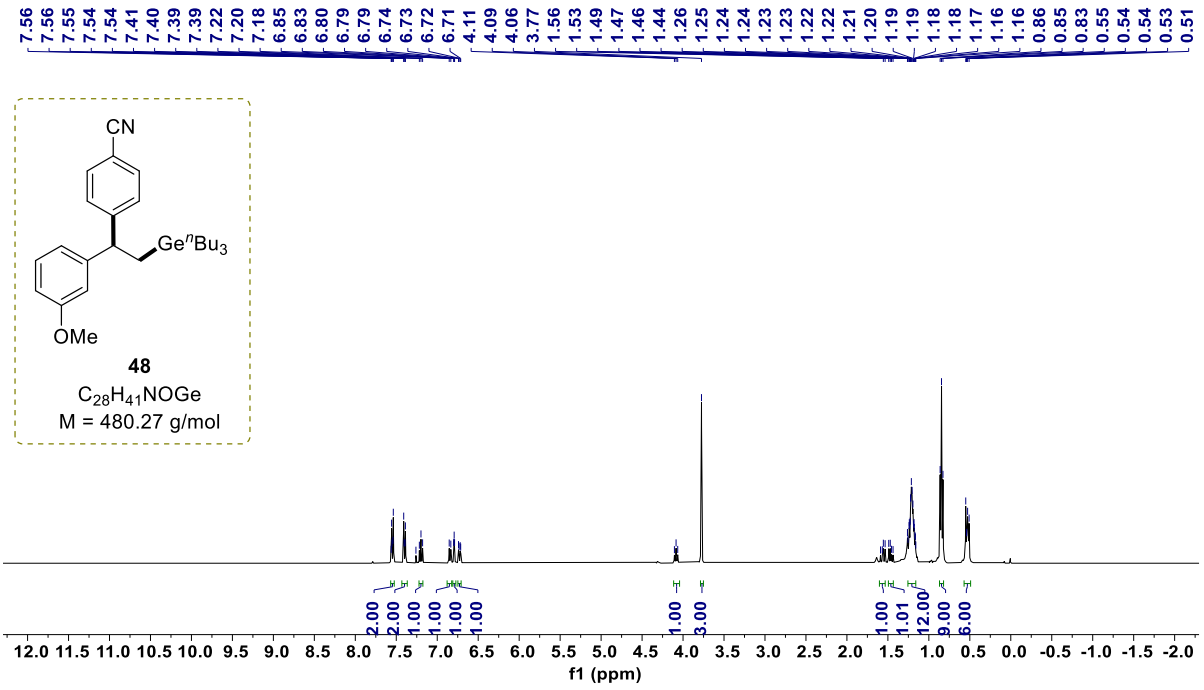


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **47**.

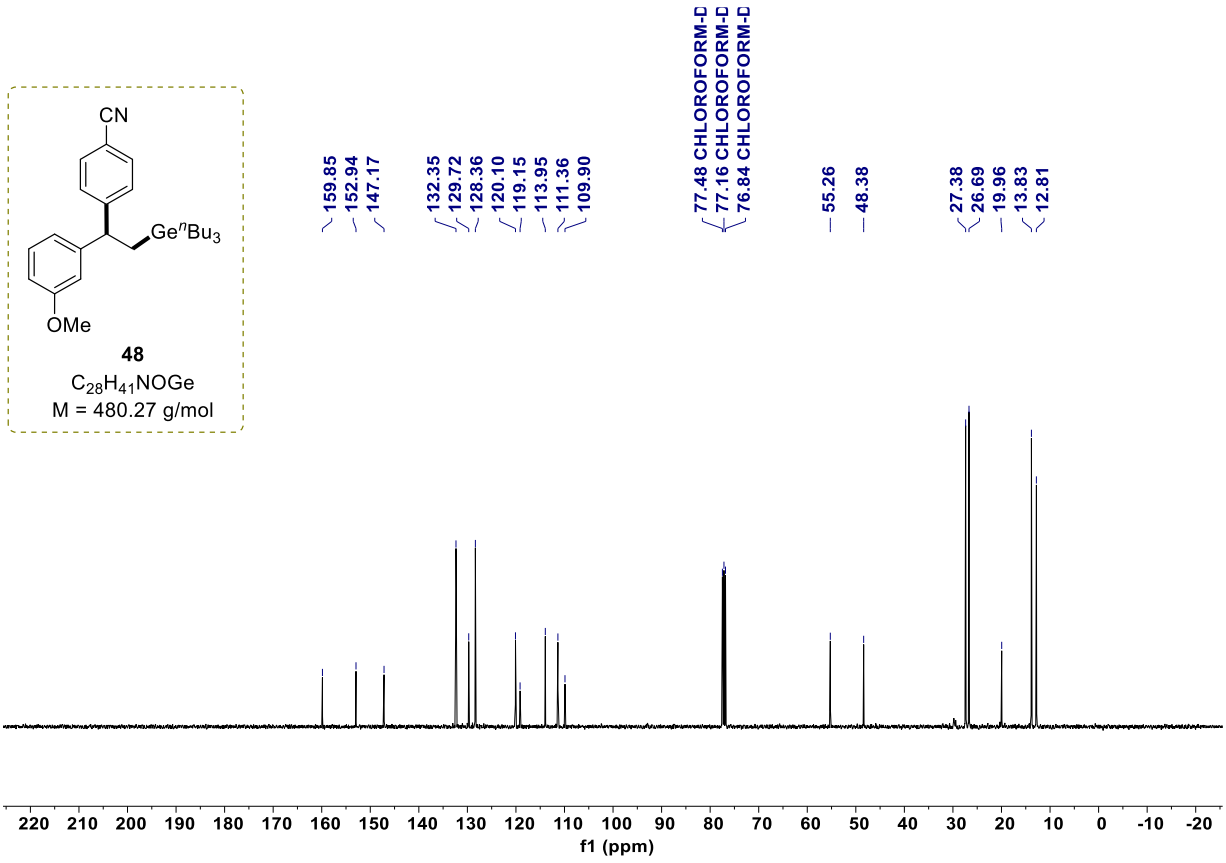


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **47**.

4.40 4-(1-(3-methoxyphenyl)-2-(tributylgermyl)ethyl)benzonitrile (**48**)

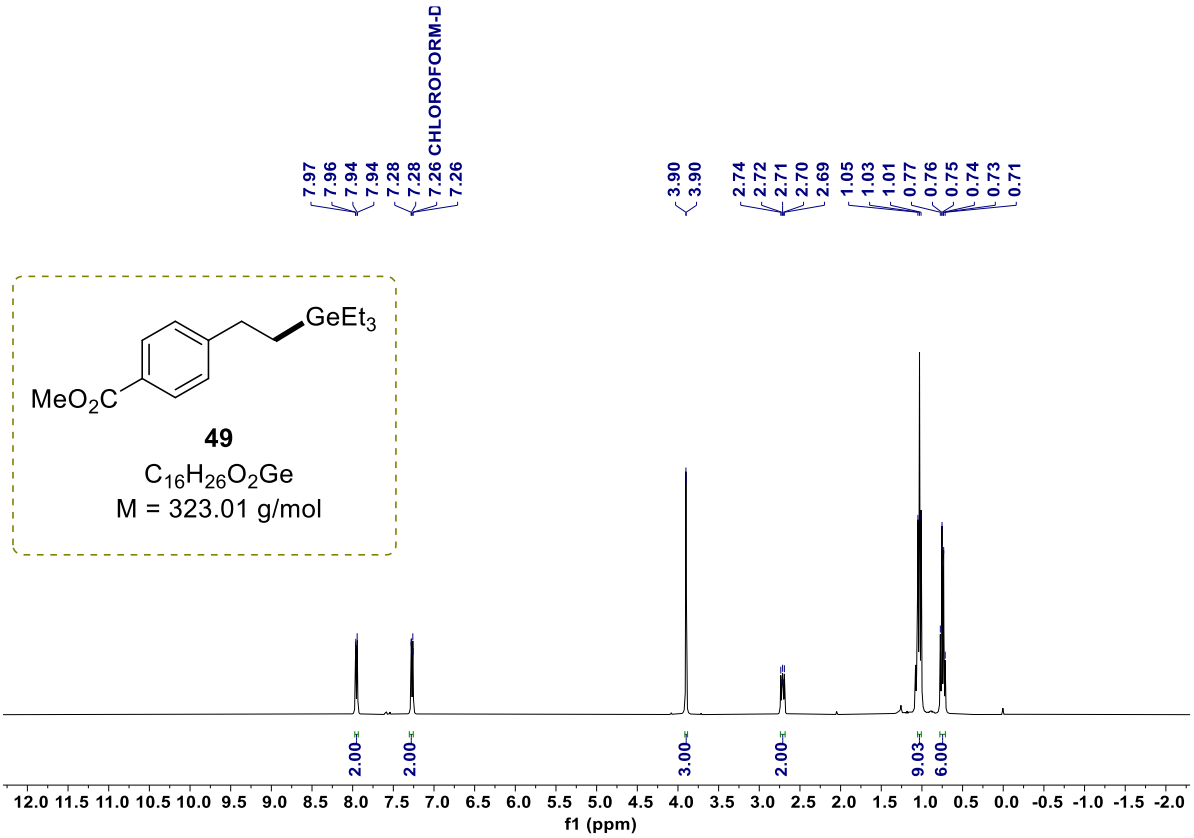


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **48**.

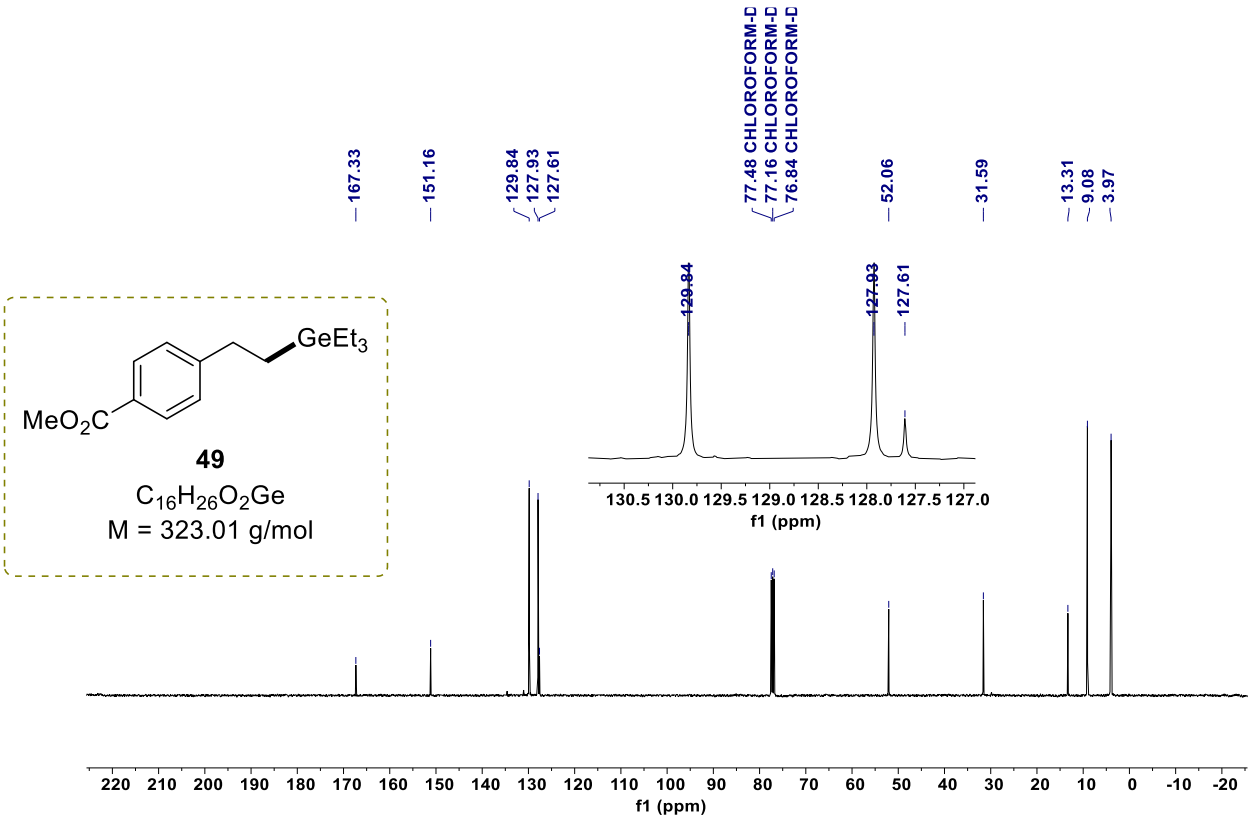


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **48**.

4.41 methyl 4-(2-(triethylgermyl)ethyl)benzoate (**49**)

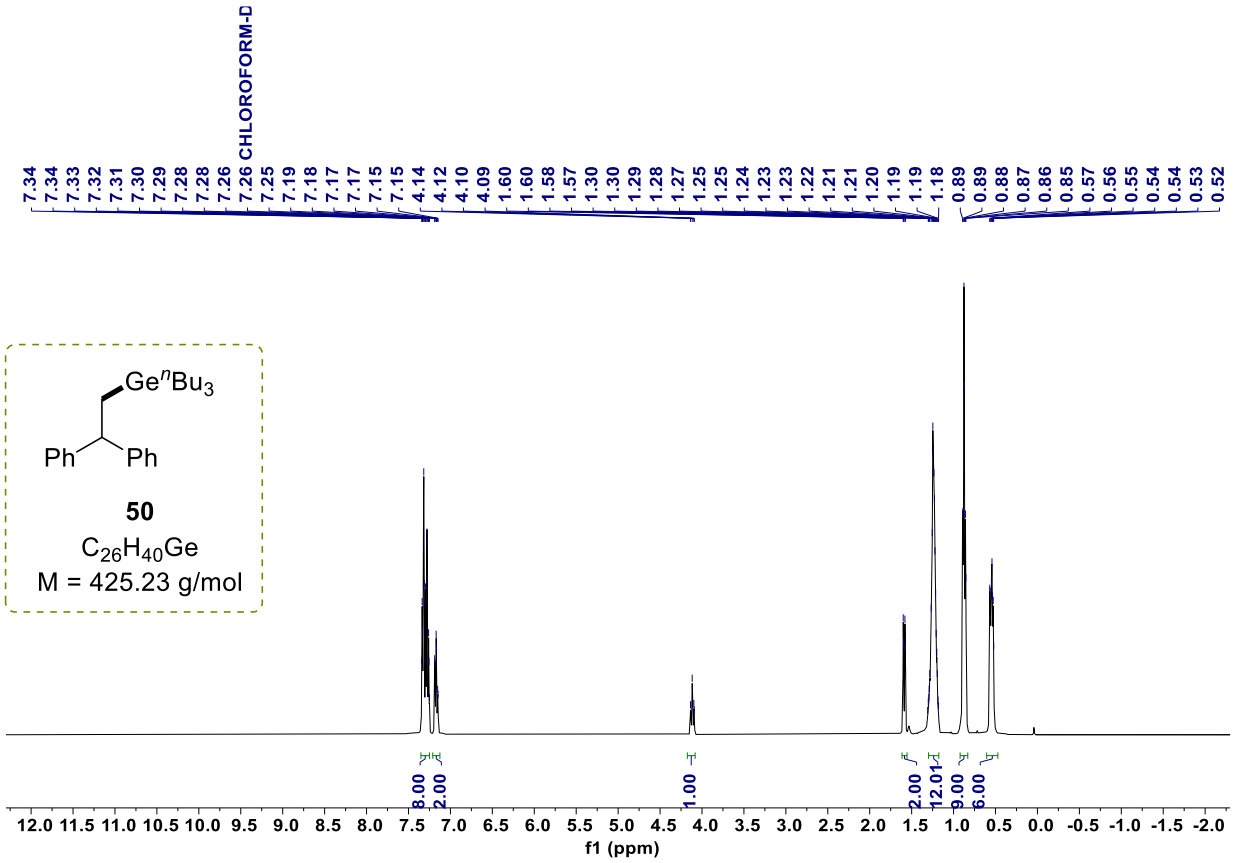


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **49**.

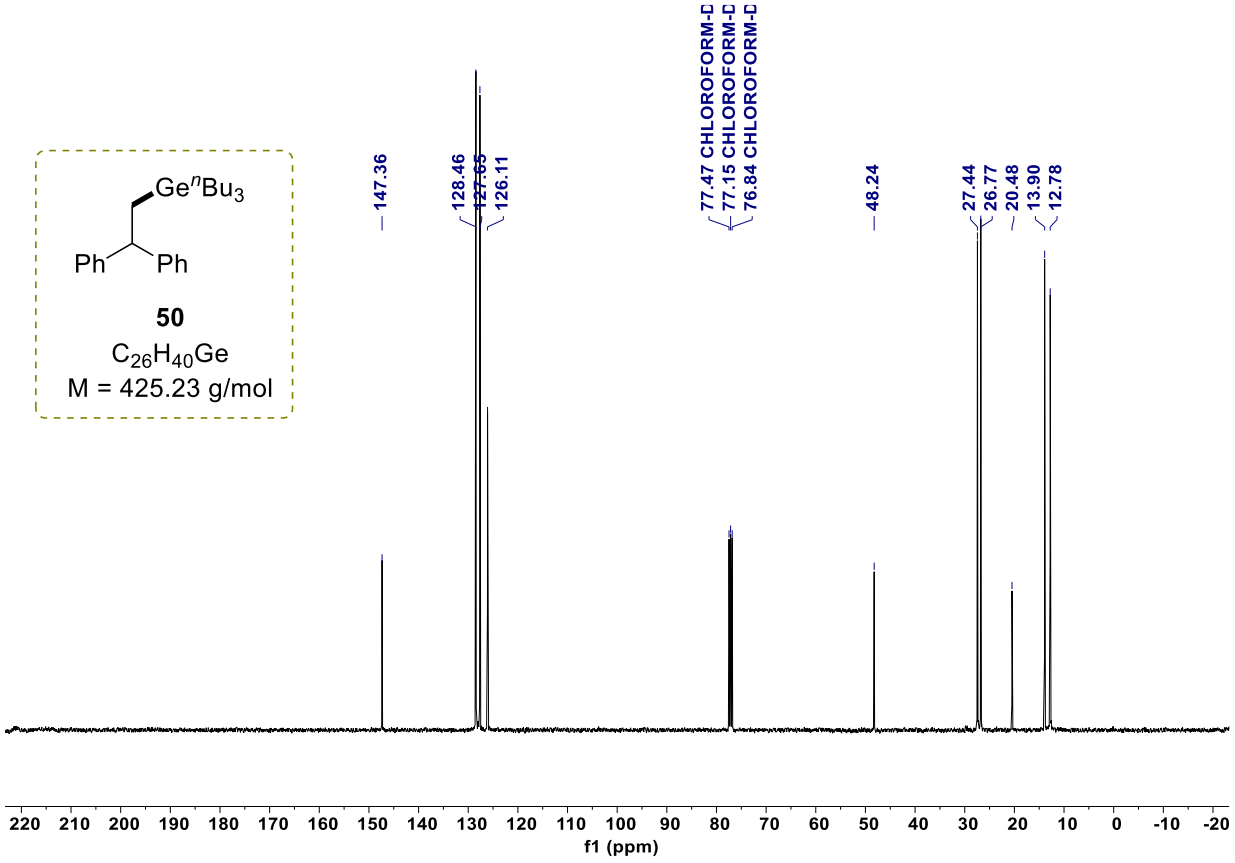


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **49**.

4.42 tributyl(2,2-diphenylethyl)germane (**50**)

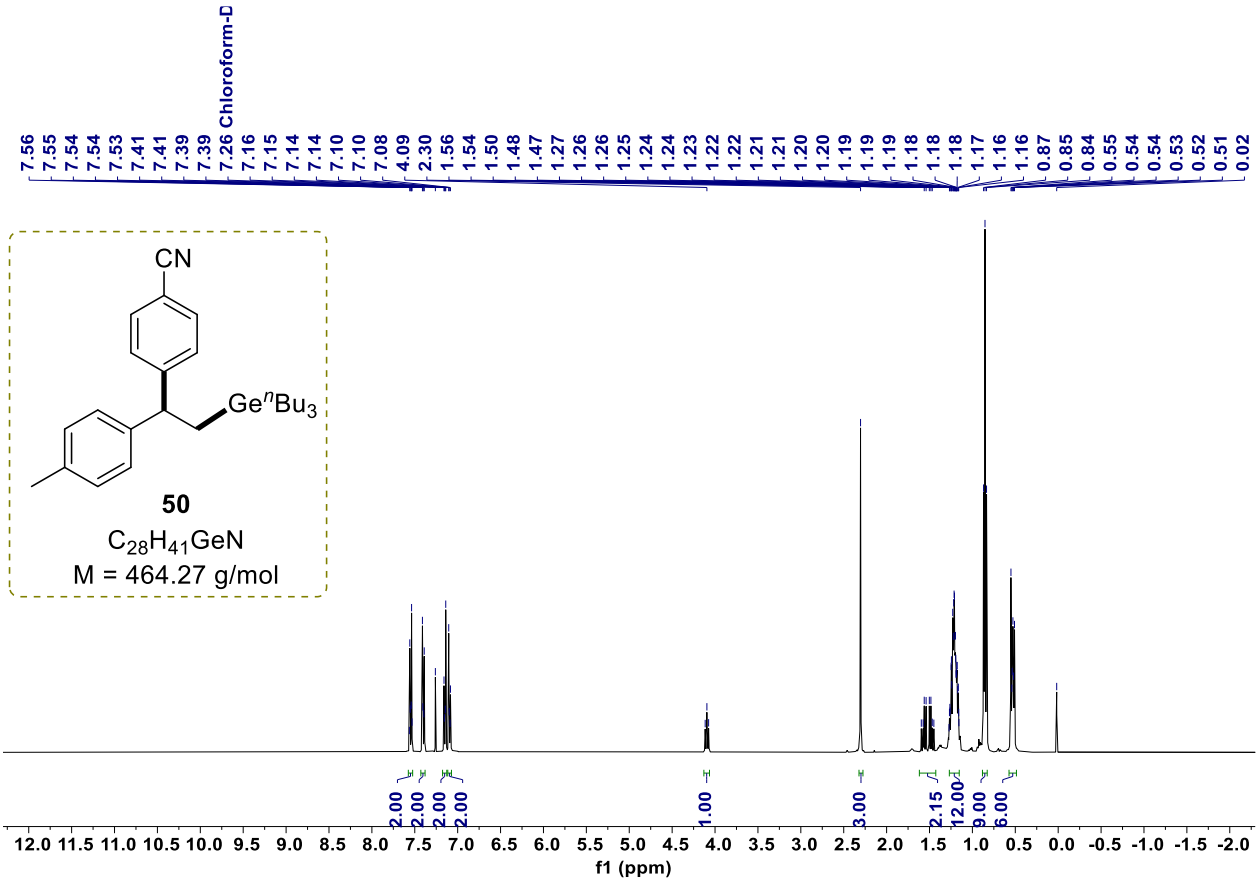


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **50**.

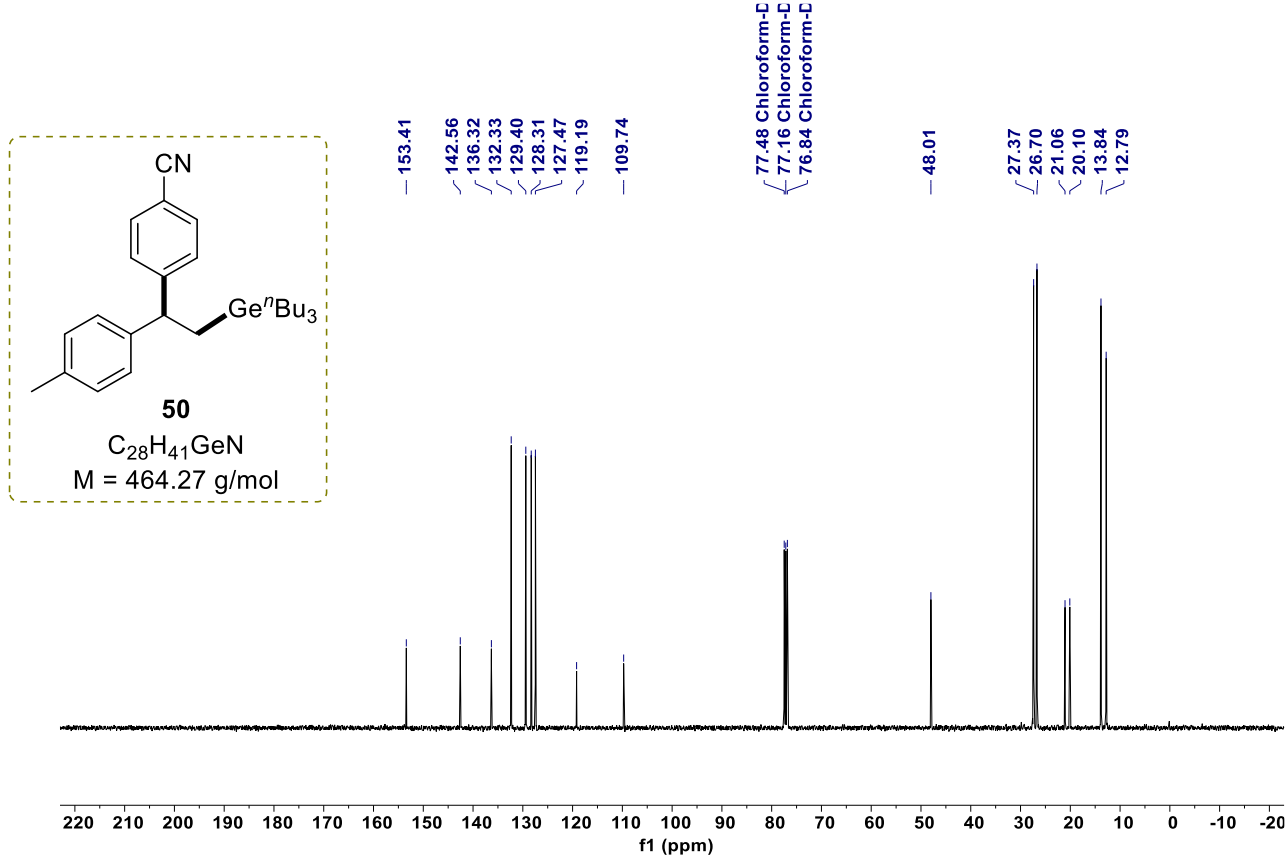


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **50**.

4.43 4-(1-(p-tolyl)-2-(tributylgermyl)ethyl)benzonitrile (**43**)



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **51**.



^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **50**.

5. Energies and Cartesian Coordinates of the Optimized Structures

Et_3GeH

M06-2X/6-31+G(d,p) Electronic Energy: -241.9340902 a.u

M06-2X/6-31G(d,p) Gibbs free Energy: -242.0158473 a.u

M06-2X(SMD, CH_3CN)/cc-pvtz Electronic Energy: -241.768047 a. u

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.775233	0.489233	-0.723238
2	6	0	2.008790	1.957892	-1.091225
3	1	0	2.525614	-0.149464	-1.201636
4	1	0	1.884265	0.344199	0.358175
5	1	0	3.012880	2.292300	-0.810576
6	1	0	1.897963	2.120644	-2.168666
7	1	0	1.291680	2.612971	-0.585708
8	6	0	-1.420976	1.106105	-0.592160
9	6	0	-2.841091	0.569856	-0.798542
10	1	0	-1.295802	2.066081	-1.104664
11	1	0	-1.233843	1.292630	0.472062
12	1	0	-3.598068	1.278715	-0.447408
13	1	0	-3.042042	0.372730	-1.857035
14	1	0	-2.993942	-0.368803	-0.255909
15	6	0	-0.351737	-1.970207	-0.523187
16	6	0	0.790851	-2.939979	-0.840864
17	1	0	-1.297254	-2.346377	-0.928631
18	1	0	-0.488710	-1.883217	0.561293
19	1	0	0.593157	-3.943019	-0.448908
20	1	0	0.944022	-3.034144	-1.921288
21	1	0	1.735162	-2.597765	-0.404876
22	32	0	-0.030060	-0.149966	-1.251030
23	1	0	-0.105232	-0.210948	-2.799236

Et_3Ge radical

M06-2X/6-31+G(d,p) Electronic Energy: -241.2976483 a.u

M06-2X/6-31G(d,p) Gibbs free Energy: -241.140744 a.u

M06-2X(SMD, CH_3CN)/cc-pvtz Electronic Energy: -241.3770483 a. u

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	32	0	-0.042103	-0.160216	-1.370603
2	6	0	1.782953	0.457293	-0.802995
3	6	0	2.001650	1.948457	-1.065957
4	1	0	2.536473	-0.144212	-1.321029
5	1	0	1.880218	0.232971	0.268297
6	1	0	2.998415	2.273903	-0.750338
7	1	0	1.900656	2.181969	-2.131121

8	1	0	1.270595	2.559507	-0.526341
9	6	0	-1.418183	1.116466	-0.655734
10	6	0	-2.839848	0.561704	-0.763632
11	1	0	-1.329404	2.067322	-1.190479
12	1	0	-1.157646	1.317164	0.392731
13	1	0	-3.580522	1.265049	-0.368938
14	1	0	-3.105817	0.353015	-1.805272
15	1	0	-2.945681	-0.374204	-0.205172
16	6	0	-0.383388	-1.986792	-0.607864
17	6	0	0.787317	-2.943821	-0.840450
18	1	0	-1.304814	-2.385212	-1.043992
19	1	0	-0.571923	-1.857046	0.466876
20	1	0	0.590654	-3.935005	-0.418593
21	1	0	0.986245	-3.074203	-1.909436
22	1	0	1.706835	-2.567610	-0.380069

1.4-dicyanobenzene

M06-2X/6-31+G(d,p) Electronic Energy: -416.5755436 a.u

M06-2X/6-31G(d,p) Gibbs free Energy: -416.509853 a.u

M06-2X(SMD, CH_3CN)/cc-pvtz Electronic Energy: -416.7243417 a. u

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.386306	0.000005	0.000012
2	6	0	-0.694128	-1.216732	0.000010
3	6	0	0.694154	-1.216719	0.000008
4	6	0	1.386306	0.000030	0.000006
5	6	0	0.694130	1.216765	0.000003
6	6	0	-0.694156	1.216752	0.000006
7	1	0	-1.245451	-2.150269	0.000013
8	1	0	1.245497	-2.150245	0.000006
9	1	0	1.245449	2.150304	-0.000001
10	1	0	-1.245494	2.150280	0.000004
11	6	0	2.827014	0.000031	-0.000003
12	7	0	3.984091	0.000102	-0.000009
13	6	0	-2.827014	-0.000012	0.000016
14	7	0	-3.984091	-0.000055	0.000018

1.4-dicyanobenzene anion radical

M06-2X/6-31+G(d,p) Electronic Energy: -416.6174972 a.u

M06-2X/6-31G(d,p) Gibbs free Energy: -416.555826 a.u

M06-2X(SMD, CH_3CN)/cc-pvtz Electronic Energy: -416.8265903 a. u

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.428096	-0.000001	0.000014

2	6	0	-0.684613	-1.227467	0.000016
3	6	0	0.684671	-1.227431	0.000004
4	6	0	1.428096	0.000074	-0.000003
5	6	0	0.684615	1.227530	0.000004
6	6	0	-0.684674	1.227494	0.000008
7	1	0	-1.226940	-2.168867	0.000027
8	1	0	1.227045	-2.168804	0.000002
9	1	0	1.226929	2.168938	0.000001
10	1	0	-1.227034	2.168875	0.000011
11	6	0	2.836398	0.000094	-0.000004
12	7	0	4.008411	-0.000096	-0.000009
13	6	0	-2.836398	-0.000054	0.000008
14	7	0	-4.008411	-0.000046	0.000009

$CH_3CH_2CO_2CH_2SH$

M06-2X/6-31+G(d,p) Electronic Energy: -705.7240144 a.u

M06-2X/6-31G(d,p) Gibbs free Energy: -705.639415 a.u

M06-2X(SMD, CH_3CN)/cc-pvtz Electronic Energy: -705.8843518 a. u

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.324523	3.001427	0.023672
2	8	0	-1.130967	2.834292	0.022860
3	8	0	-2.914409	4.205049	0.024852
4	6	0	-2.023390	5.335334	0.025129
5	6	0	-2.879482	6.582373	0.025994
6	1	0	-1.382930	5.273099	-0.859378
7	1	0	-1.382419	5.272244	0.909209
8	1	0	-2.240492	7.469082	0.026276
9	1	0	-3.516691	6.614277	-0.861005
10	1	0	-3.516218	6.613372	0.913365
11	6	0	-3.365293	1.903871	0.023330
12	1	0	-3.993975	2.032214	-0.861124
13	1	0	-3.993298	2.031004	0.908439
14	16	0	-2.530890	0.286236	0.021905
15	1	0	-3.674794	-0.415702	0.021930

$CH_3CH_2CO_2CH_2S^-$

M06-2X/6-31+G(d,p) Electronic Energy: -705.1699998 a.u

M06-2X/6-31G(d,p) Gibbs free Energy: -705.093733 a.u

M06-2X(SMD, CH_3CN)/cc-pvtz Electronic Energy: -705.4116701 a. u

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.316376	2.984340	0.023362
2	8	0	-1.114882	2.899297	0.022268

3	8	0	-2.918791	4.229632	0.025081
4	6	0	-2.028170	5.334855	0.024995
5	6	0	-2.869747	6.596979	0.026422
6	1	0	-1.378837	5.284546	-0.856803
7	1	0	-1.377414	5.283532	0.905691
8	1	0	-2.228259	7.484122	0.026470
9	1	0	-3.511197	6.629211	-0.858734
10	1	0	-3.509825	6.628125	0.912609
11	6	0	-3.374534	1.903106	0.023131
12	1	0	-4.002224	2.140611	-0.848586
13	1	0	-4.003764	2.141481	0.893464
14	16	0	-2.827392	0.174550	0.024391

$CH_3CH_2CO_2CH_2S$ radical

M06-2X/6-31+G(d,p) Electronic Energy: -705.0912545 a.u

M06-2X/6-31G(d,p) Gibbs free Energy: -705.016419 a.u

M06-2X(SMD, CH_3CN)/cc-pvtz Electronic Energy: -705.2417925 a. u

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.183975	0.689770	0.031598
2	8	0	-0.112153	1.533040	-0.829083
3	8	0	0.836507	-0.089128	0.409357
4	6	0	2.061533	0.084025	-0.325497
5	6	0	3.065572	-0.896994	0.237351
6	1	0	2.388935	1.121946	-0.216118
7	1	0	1.856030	-0.094961	-1.384829
8	1	0	4.014332	-0.802000	-0.296912
9	1	0	3.243816	-0.702517	1.297699
10	1	0	2.705679	-1.922584	0.126801
11	6	0	-1.440714	0.359980	0.802019
12	1	0	-2.141895	1.194488	0.715071
13	1	0	-1.217148	0.200199	1.861839
14	16	0	-2.251679	-1.127945	0.180224

$[Ir(ppy)_2(dtbbpy)][PF_6]$

M06-2X/6-31+G(d,p) Electronic Energy: -2811.4821698 a.u

M06-2X/6-31G(d,p) Gibbs free Energy: -2810.830093 a.u

M06-2X(SMD, CH_3CN)/cc-pvtz Electronic Energy: -2812.3525827 a. u

Total Energy, E(TD-HF/TD-DFT): -2812.23488332 a.u

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	0.117448	0.091699	-0.119095
2	6	0	1.092018	-1.320445	0.931594
3	6	0	0.914688	-2.655264	0.483529

4	6	0	1.933235	-1.119743	2.035908
5	6	0	1.558347	-3.722156	1.124561
6	6	0	0.000099	-2.864371	-0.660387
7	6	0	2.568941	-2.185240	2.673101
8	1	0	2.091109	-0.111064	2.408362
9	6	0	2.385606	-3.491354	2.217422
10	1	0	1.419758	-4.741065	0.775115
11	6	0	-0.360392	-4.106725	-1.187675
12	1	0	3.212009	-1.995238	3.527987
13	1	0	2.881529	-4.321752	2.709455
14	6	0	-1.416145	-1.790183	-2.182632
15	6	0	-1.276883	-4.169257	-2.232395
16	1	0	0.055928	-5.016713	-0.772841
17	6	0	-1.827664	-2.996340	-2.738285
18	1	0	-1.830766	-0.846627	-2.527856
19	1	0	-1.572590	-5.132619	-2.636095
20	1	0	-2.582307	-2.988976	-3.515235
21	6	0	0.837110	1.641949	0.910777
22	6	0	2.075547	2.146545	0.446127
23	6	0	0.259627	2.279870	2.017546
24	6	0	2.706442	3.232059	1.067527
25	6	0	2.637045	1.439502	-0.709931
26	6	0	0.886353	3.359344	2.637355
27	1	0	-0.690477	1.922483	2.407762
28	6	0	2.112153	3.839650	2.166024
29	1	0	3.658812	3.607029	0.702802
30	6	0	3.846159	1.737398	-1.349051
31	1	0	0.418693	3.832960	3.496149
32	1	0	2.596085	4.679741	2.652865
33	6	0	2.274199	-0.326231	-2.208764
34	6	0	4.258752	0.981577	-2.435330
35	1	0	4.454298	2.557557	-0.987066
36	6	0	3.460483	-0.073257	-2.878773
37	1	0	1.609616	-1.134160	-2.497359
38	1	0	5.196008	1.208957	-2.932890
39	1	0	3.746677	-0.691868	-3.720583
40	6	0	-2.731099	0.689488	0.358647
41	6	0	-1.975514	-0.910622	1.855051
42	6	0	-4.034379	0.513305	0.799444
43	6	0	-2.387128	1.611248	-0.749423
44	6	0	-3.259095	-1.117135	2.344628
45	1	0	-1.123921	-1.463352	2.238249
46	6	0	-4.336221	-0.420227	1.793557
47	1	0	-4.831161	1.041462	0.290795
48	6	0	-3.288088	2.531281	-1.277892
49	1	0	-3.397075	-1.851137	3.128886
50	6	0	-0.790228	2.212008	-2.303454
51	6	0	-2.952593	3.273783	-2.407432
52	1	0	-4.272353	2.619308	-0.842734
53	6	0	-1.659007	3.100084	-2.915102
54	1	0	0.224709	2.068068	-2.664103

55	1	0	-1.322681	3.640673	-3.793088
56	7	0	-1.148218	1.472270	-1.249906
57	7	0	1.872834	0.411391	-1.162848
58	7	0	-0.523615	-1.730985	-1.186446
59	7	0	-1.712535	-0.043719	0.870314
60	6	0	-5.792083	-0.672728	2.167252
61	6	0	-6.438220	0.644603	2.630681
62	6	0	-6.518678	-1.195353	0.912447
63	6	0	-5.921139	-1.705625	3.290658
64	1	0	-5.924233	1.048728	3.509193
65	1	0	-6.421745	1.402690	1.842650
66	1	0	-7.484944	0.465720	2.896263
67	1	0	-6.066589	-2.125609	0.555871
68	1	0	-7.569788	-1.387351	1.152549
69	1	0	-6.480209	-0.483064	0.083504
70	1	0	-6.979089	-1.850234	3.528057
71	1	0	-5.514368	-2.677635	2.993371
72	1	0	-5.415283	-1.377807	4.205730
73	6	0	-3.952048	4.176112	-3.122706
74	6	0	-5.278217	4.276585	-2.361552
75	6	0	-3.360078	5.585759	-3.285367
76	6	0	-4.229411	3.554145	-4.505345
77	1	0	-5.763839	3.299297	-2.279716
78	1	0	-5.137947	4.694596	-1.358039
79	1	0	-5.954440	4.941624	-2.906846
80	1	0	-2.437177	5.577796	-3.872920
81	1	0	-4.078102	6.227287	-3.806208
82	1	0	-3.141263	6.035634	-2.311270
83	1	0	-4.962451	4.166821	-5.040957
84	1	0	-3.319144	3.507409	-5.111798
85	1	0	-4.625232	2.539306	-4.403856
86	15	0	-4.952374	-0.439652	-2.902213
87	9	0	-6.303563	-1.247234	-2.548463
88	9	0	-4.211451	-1.099496	-1.598986
89	9	0	-4.424180	-1.666916	-3.825276
90	9	0	-5.658669	0.256388	-4.177226
91	9	0	-5.450087	0.808455	-1.951930
92	9	0	-3.568607	0.383974	-3.230045

{[Ir(ppy)$_2$(dtbbpy)][PF$_6$]}$^+$

M06-2X/6-31+G(d,p) Electronic Energy: -2811.2157413 a.u

M06-2X/6-31G(d,p) Gibbs free Energy: -2810.565005 a.u

M06-2X(SMD, CH_3CN)/cc-pvtz Electronic Energy: -2812.1319566 a. u

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	0.082202	0.127401	-0.094747
2	6	0	1.070597	-1.358211	0.887352
3	6	0	0.888338	-2.670682	0.407832

4	6	0	1.907660	-1.150171	1.989926
5	6	0	1.525934	-3.743396	1.042271
6	6	0	0.009451	-2.843334	-0.764220
7	6	0	2.533490	-2.228627	2.616905
8	1	0	2.064269	-0.149498	2.379761
9	6	0	2.344125	-3.525656	2.144598
10	1	0	1.386521	-4.756475	0.679762
11	6	0	-0.285455	-4.061871	-1.370988
12	1	0	3.169889	-2.049338	3.477889
13	1	0	2.831495	-4.363304	2.631384
14	6	0	-1.361583	-1.718594	-2.289780
15	6	0	-1.143302	-4.089764	-2.466775
16	1	0	0.142603	-4.980278	-0.988738
17	6	0	-1.695979	-2.904012	-2.935192
18	1	0	-1.792727	-0.775237	-2.609058
19	1	0	-1.386449	-5.034556	-2.941860
20	1	0	-2.400658	-2.872845	-3.756381
21	6	0	0.770385	1.630564	0.958119
22	6	0	2.026887	2.140940	0.515899
23	6	0	0.155803	2.225322	2.077667
24	6	0	2.635324	3.199420	1.183871
25	6	0	2.604161	1.471177	-0.658751
26	6	0	0.772230	3.279103	2.740964
27	1	0	-0.801289	1.852346	2.430077
28	6	0	2.007744	3.763765	2.295781
29	1	0	3.591809	3.594904	0.857700
30	6	0	3.814498	1.792095	-1.272450
31	1	0	0.297341	3.729685	3.606229
32	1	0	2.483938	4.587021	2.817784
33	6	0	2.253565	-0.262239	-2.197486
34	6	0	4.238470	1.059213	-2.374140
35	1	0	4.417576	2.605869	-0.888345
36	6	0	3.448569	0.013104	-2.846602
37	1	0	1.596539	-1.066095	-2.513306
38	1	0	5.178878	1.299763	-2.858530
39	1	0	3.746671	-0.585226	-3.698927
40	6	0	-2.747475	0.696552	0.377629
41	6	0	-1.988588	-0.898574	1.891101
42	6	0	-4.042385	0.553179	0.845932
43	6	0	-2.406308	1.566160	-0.770732
44	6	0	-3.267875	-1.077960	2.397937
45	1	0	-1.140346	-1.457868	2.272008
46	6	0	-4.342741	-0.365569	1.858111
47	1	0	-4.838813	1.087841	0.343654
48	6	0	-3.274443	2.515439	-1.291664
49	1	0	-3.408730	-1.801403	3.191235
50	6	0	-0.847367	2.024371	-2.431221
51	6	0	-2.957989	3.191403	-2.471329
52	1	0	-4.227482	2.679746	-0.810856
53	6	0	-1.700895	2.926078	-3.035971
54	1	0	0.139425	1.814093	-2.833434

55	1	0	-1.385409	3.410247	-3.953214
56	7	0	-1.192845	1.351690	-1.323138
57	7	0	1.845537	0.455382	-1.141460
58	7	0	-0.523668	-1.692183	-1.242524
59	7	0	-1.732813	-0.041910	0.893498
60	6	0	-5.793536	-0.591141	2.258636
61	6	0	-6.413259	0.744138	2.708362
62	6	0	-6.540069	-1.122643	1.017598
63	6	0	-5.919113	-1.606034	3.398460
64	1	0	-5.885438	1.154882	3.575246
65	1	0	-6.401421	1.490178	1.908700
66	1	0	-7.457611	0.581871	2.990036
67	1	0	-6.103331	-2.061825	0.665452
68	1	0	-7.587748	-1.303067	1.276964
69	1	0	-6.512137	-0.418524	0.181257
70	1	0	-6.974654	-1.729520	3.654323
71	1	0	-5.536433	-2.590218	3.109394
72	1	0	-5.396405	-1.273519	4.302169
73	6	0	-3.941136	4.116334	-3.173169
74	6	0	-5.226558	4.306681	-2.361529
75	6	0	-3.284126	5.487178	-3.409943
76	6	0	-4.302938	3.459173	-4.521579
77	1	0	-5.755043	3.358105	-2.224114
78	1	0	-5.027492	4.757242	-1.382393
79	1	0	-5.893827	4.981530	-2.904064
80	1	0	-2.390114	5.413933	-4.036195
81	1	0	-3.991934	6.143808	-3.924055
82	1	0	-3.004786	5.961548	-2.463523
83	1	0	-5.026126	4.091867	-5.045308
84	1	0	-3.424254	3.348976	-5.164750
85	1	0	-4.744907	2.469998	-4.371789
86	15	0	-4.857519	-0.474155	-2.823197
87	9	0	-6.154450	-1.306804	-2.373016
88	9	0	-4.027102	-1.057299	-1.525277
89	9	0	-4.319525	-1.713948	-3.717227
90	9	0	-5.626509	0.157017	-4.085268
91	9	0	-5.340945	0.795367	-1.893793
92	9	0	-3.502331	0.378968	-3.233088

Styrene

M06-2X/6-31+G(d,p) Electronic Energy: -309.5163385 a.u

M06-2X/6-31G(d,p) Gibbs free Energy: -309.413724 a.u

M06-2X(SMD, CH_3CN)/cc-pvtz Electronic Energy: -309.6175472 a. u

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.180249	1.344471	0.005429
2	6	0	-1.024531	0.228317	-0.044486
3	6	0	-0.440607	-1.046526	-0.074244

4	6	0	0.941206	-1.196013	-0.038250
5	6	0	1.770813	-0.074544	0.022280
6	6	0	1.204842	1.197862	0.041996
7	1	0	-0.618836	2.339017	0.020990
8	1	0	-1.070922	-1.928115	-0.138376
9	1	0	1.375133	-2.190759	-0.064464
10	1	0	1.840079	2.077018	0.084130
11	6	0	-2.484733	0.437812	-0.068392
12	6	0	-3.427170	-0.495274	0.091710
13	1	0	-2.797103	1.470054	-0.221252
14	1	0	-4.478660	-0.232936	0.056436
15	1	0	-3.189396	-1.539602	0.270536
16	1	0	2.849003	-0.194235	0.047806

IM1

M06-2X/6-31+G(d,p) Electronic Energy: -550.8553053 a.u

M06-2X/6-31G(d,p) Gibbs free Energy: -550.573497 a.u

M06-2X(SMD, CH_3CN)/cc-pvtz Electronic Energy: -551.0361613 a. u

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	32	0	-1.063149	-0.252969	-0.072963
2	6	0	2.213919	0.631661	-1.562297
3	6	0	2.698106	-0.661857	-1.233335
4	6	0	4.031554	-0.865177	-0.908371
5	6	0	4.934528	0.201553	-0.895890
6	6	0	4.479878	1.486403	-1.216571
7	6	0	3.151093	1.699331	-1.541808
8	1	0	2.016186	-1.506489	-1.230912
9	1	0	4.373907	-1.865424	-0.659933
10	1	0	5.172134	2.322972	-1.210481
11	1	0	2.806294	2.699947	-1.790182
12	6	0	-0.223385	-0.123152	-1.911454
13	1	0	-1.025740	0.163149	-2.599169
14	1	0	0.120650	-1.122703	-2.198379
15	6	0	0.857643	0.881609	-1.904601
16	1	0	0.586354	1.913536	-2.116850
17	1	0	5.975866	0.035791	-0.640752
18	6	0	-1.630847	1.584263	0.426786
19	6	0	-2.608421	2.199412	-0.579382
20	1	0	-0.730197	2.202698	0.519130
21	1	0	-2.087289	1.544247	1.422681
22	1	0	-2.894315	3.218509	-0.299403
23	1	0	-2.172585	2.247892	-1.583822
24	1	0	-3.529366	1.610381	-0.649802
25	6	0	-2.651330	-1.457361	-0.168807
26	6	0	-3.283150	-1.533332	-1.563008
27	1	0	-3.385239	-1.101667	0.564473
28	1	0	-2.343018	-2.456295	0.161056

29	1	0	-4.167398	-2.178947	-1.571503
30	1	0	-3.595314	-0.545918	-1.919698
31	1	0	-2.577516	-1.934269	-2.297863
32	6	0	0.242755	-0.934835	1.252968
33	6	0	-0.358150	-0.994128	2.662284
34	1	0	1.129089	-0.291046	1.234234
35	1	0	0.574188	-1.931121	0.937448
36	1	0	0.356841	-1.392263	3.389337
37	1	0	-0.656584	0.000468	3.009677
38	1	0	-1.247313	-1.633735	2.693927

IM2

M06-2X/6-31+G(d,p) Electronic Energy: -967.5259416 a.u

M06-2X/6-31G(d,p) Gibbs free Energy: -967.154205 a.u

M06-2X(SMD, CH_3CN)/cc-pvtz Electronic Energy: -967.9048922 a. u

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	32	0	1.430964	-0.471769	-0.113895
2	6	0	-1.368377	1.257913	-0.452455
3	6	0	-0.854790	2.270014	-1.273752
4	6	0	-0.841017	3.597815	-0.850963
5	6	0	-1.338888	3.941988	0.405558
6	6	0	-1.866566	2.947457	1.228067
7	6	0	-1.885564	1.621837	0.796829
8	1	0	-0.467558	2.020489	-2.257662
9	1	0	-0.436877	4.365088	-1.505314
10	1	0	-2.269546	3.202884	2.204033
11	1	0	-2.316361	0.847921	1.427924
12	6	0	-0.039286	-0.662990	-1.433694
13	1	0	-0.115719	-1.724413	-1.699323
14	1	0	0.224154	-0.123817	-2.353191
15	6	0	-2.694273	-2.017246	-2.095115
16	6	0	-3.911561	-0.035904	-1.256373
17	6	0	-3.374976	-2.786058	-1.203205
18	1	0	-2.141923	-2.454238	-2.920210
19	6	0	-4.569261	-0.838861	-0.380039
20	1	0	-4.224546	0.986364	-1.440960
21	6	0	-4.229008	-2.218944	-0.206967
22	1	0	-3.328993	-3.870011	-1.290909
23	1	0	-5.425841	-0.444373	0.163420
24	6	0	-4.922908	-3.034846	0.712906
25	7	0	-5.488436	-3.708622	1.483590
26	6	0	-2.608358	-0.517439	-1.866687
27	6	0	-2.349559	0.167117	-3.150212
28	7	0	-2.107113	0.703718	-4.148277
29	6	0	-1.391176	-0.190200	-0.886983
30	1	0	-1.647319	-0.796678	-0.008172
31	1	0	-1.321706	4.976175	0.737312

32	6	0	2.151476	1.388515	-0.017284
33	6	0	3.604515	1.459541	0.464772
34	1	0	1.490488	1.972943	0.635005
35	1	0	2.060496	1.840984	-1.011718
36	1	0	3.960298	2.494409	0.529229
37	1	0	3.727557	1.009305	1.455631
38	1	0	4.277041	0.924460	-0.215056
39	6	0	2.938593	-1.650562	-0.680498
40	6	0	3.395285	-1.337884	-2.109811
41	1	0	2.604476	-2.692316	-0.606679
42	1	0	3.772214	-1.537447	0.023468
43	1	0	4.236313	-1.966137	-2.425234
44	1	0	2.581081	-1.494255	-2.825379
45	1	0	3.712155	-0.292632	-2.207696
46	6	0	0.794152	-1.042251	1.681762
47	6	0	1.827334	-0.826916	2.791923
48	1	0	0.507923	-2.098686	1.617189
49	1	0	-0.122745	-0.487609	1.910432
50	1	0	1.473928	-1.208606	3.756401
51	1	0	2.774980	-1.330715	2.567453
52	1	0	2.044799	0.238653	2.923567

P

M06-2X/6-31+G(d,p) Electronic Energy: -874.6864979 a.u

M06-2X/6-31G(d,p) Gibbs free Energy: -874.323843 a.u

M06-2X(SMD, CH_3CN)/cc-pvtz Electronic Energy: -875.0374661 a. u

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	32	0	1.624023	-0.533451	0.271096
2	6	0	-1.304487	0.890012	0.062295
3	6	0	-1.272397	1.598926	-1.149129
4	6	0	-1.214943	2.986631	-1.168110
5	6	0	-1.201948	3.711817	0.030131
6	6	0	-1.265387	3.023789	1.239471
7	6	0	-1.318134	1.628440	1.252628
8	1	0	-1.308889	1.045229	-2.084622
9	1	0	-1.184095	3.511157	-2.119249
10	1	0	-1.273251	3.572003	2.178105
11	1	0	-1.369602	1.099995	2.202501
12	6	0	-0.050781	-1.196359	-0.563743
13	1	0	-0.076066	-2.292801	-0.519629
14	1	0	-0.006011	-0.929147	-1.627197
15	6	0	-2.760549	-1.456390	-1.923768
16	6	0	-3.797069	-1.222511	0.253387
17	6	0	-3.971128	-1.813025	-2.472404
18	1	0	-1.891018	-1.425873	-2.578645
19	6	0	-5.016855	-1.578896	-0.267572
20	1	0	-3.726773	-0.983529	1.315302

21	6	0	-5.157282	-1.895075	-1.664381
22	1	0	-4.038768	-2.052873	-3.530178
23	1	0	-5.891167	-1.634123	0.375365
24	6	0	-6.395114	-2.266689	-2.213209
25	7	0	-7.430295	-2.581646	-2.672034
26	6	0	-2.615247	-1.157097	-0.539888
27	6	0	-1.337717	-0.632895	0.071962
28	1	0	-1.340135	-0.931892	1.132514
29	1	0	-1.158776	4.796769	0.015401
30	6	0	2.068731	1.318288	-0.325813
31	6	0	3.555481	1.673124	-0.220837
32	1	0	1.452890	2.024468	0.244760
33	1	0	1.729901	1.410869	-1.364824
34	1	0	3.753165	2.690351	-0.578679
35	1	0	3.915275	1.615553	0.811888
36	1	0	4.175048	0.992109	-0.815559
37	6	0	3.126857	-1.705404	-0.327988
38	6	0	3.244148	-1.746131	-1.855429
39	1	0	2.955108	-2.713916	0.067169
40	1	0	4.062251	-1.348260	0.121071
41	1	0	4.083421	-2.364978	-2.193585
42	1	0	2.332881	-2.152149	-2.307349
43	1	0	3.388758	-0.741675	-2.270677
44	6	0	1.519998	-0.631000	2.260625
45	6	0	2.540009	0.265286	2.968648
46	1	0	1.661676	-1.679541	2.550052
47	1	0	0.505356	-0.357662	2.568074
48	1	0	2.473235	0.180191	4.059510
49	1	0	3.567194	0.010086	2.682813
50	1	0	2.379326	1.317993	2.710633

CN^-

M06-2X/6-31+G(d,p) Electronic Energy: -92.8246895 a.u

M06-2X/6-31G(d,p) Gibbs free Energy: -92.838755 a.u

M06-2X(SMD, CH_3CN)/cc-pvtz Electronic Energy: -92.9576435 a. u

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.816671	0.000017	0.000009
2	7	0	-3.994434	-0.000007	0.000011

TS1

M06-2X/6-31+G(d,p) Electronic Energy: -947.0280343 a.u

M06-2X/6-31G(d,p) Gibbs free Energy: -946.770459 a.u

M06-2X(SMD, CH_3CN)/cc-pvtz Electronic Energy: -947.2656073 a. u

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Center	Atomic	Atomic	Coordinates (Angstroms)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.979239	0.859856	0.111172
2	8	0	-1.464878	0.437041	1.117840
3	8	0	-3.160711	0.420451	-0.352393
4	6	0	-3.770118	-0.641631	0.400612
5	6	0	-5.028203	-1.049196	-0.333484
6	1	0	-3.977244	-0.280362	1.412185
7	1	0	-3.052876	-1.465824	0.477811
8	1	0	-5.527785	-1.857074	0.207267
9	1	0	-5.718882	-0.206498	-0.414419
10	1	0	-4.788877	-1.400730	-1.340215
11	6	0	-1.404937	1.897833	-0.834156
12	1	0	-2.122952	2.720530	-0.909034
13	1	0	-1.352204	1.444591	-1.829352
14	16	0	0.184340	2.591831	-0.331391
15	6	0	0.185090	-1.984329	-0.025163
16	6	0	-0.638148	-2.021312	-1.314937
17	1	0	-0.461953	-1.865915	0.848822
18	1	0	0.738143	-2.924191	0.099378
19	1	0	-1.337013	-2.865099	-1.321645
20	1	0	-1.230622	-1.108341	-1.443213
21	1	0	0.000174	-2.120192	-2.199087
22	6	0	2.919670	-0.745922	-1.380072
23	6	0	3.899866	0.429666	-1.423029
24	1	0	2.416952	-0.863804	-2.345834
25	1	0	3.448460	-1.686975	-1.182265
26	1	0	4.652393	0.298291	-2.207126
27	1	0	3.378197	1.372040	-1.619226
28	1	0	4.432804	0.539230	-0.473041
29	6	0	2.319941	-0.279186	1.831585
30	6	0	1.263734	0.021695	2.899208
31	1	0	3.048843	0.536120	1.769860
32	1	0	2.882388	-1.189120	2.076960
33	1	0	1.724645	0.157405	3.883051
34	1	0	0.702197	0.927025	2.652676
35	1	0	0.534648	-0.790532	2.980924
36	32	0	1.528807	-0.520270	0.027147
37	1	0	0.835751	1.070949	-0.285334

TS2

M06-2X/6-31+G(d,p) Electronic Energy: -550.8202283 a.u

M06-2X/6-31G(d,p) Gibbs free Energy: -550.540223 a.u

M06-2X(SMD, CH_3CN)/cc-pvtz Electronic Energy: -550.9998679 a. u

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	32	0	-1.386761	0.250806	0.127896
2	6	0	2.304844	-0.833512	0.420841

3	6	0	2.313557	0.450179	0.993717
4	6	0	3.326166	1.356044	0.693962
5	6	0	4.350673	1.004843	-0.185677
6	6	0	4.350723	-0.262809	-0.768582
7	6	0	3.336395	-1.166972	-0.472000
8	1	0	1.518713	0.747215	1.672155
9	1	0	3.312754	2.343807	1.144850
10	1	0	5.140218	-0.544751	-1.458290
11	1	0	3.336009	-2.151449	-0.933302
12	6	0	0.242185	-1.645095	1.585957
13	1	0	-0.522639	-2.406586	1.701276
14	1	0	0.270170	-0.875747	2.350474
15	6	0	1.235858	-1.798023	0.680380
16	1	0	1.215637	-2.665941	0.023051
17	1	0	5.138449	1.714104	-0.418187
18	6	0	-0.746631	-0.415965	-1.646449
19	6	0	-1.301035	-1.799471	-1.989440
20	1	0	0.349038	-0.427236	-1.621339
21	1	0	-1.039276	0.316271	-2.410164
22	1	0	-0.912568	-2.169170	-2.944481
23	1	0	-1.037557	-2.534753	-1.220105
24	1	0	-2.393907	-1.783572	-2.065110
25	6	0	-3.372640	-0.051534	0.274197
26	6	0	-3.737533	-1.424701	0.844530
27	1	0	-3.802408	0.076921	-0.728194
28	1	0	-3.786210	0.745455	0.902355
29	1	0	-4.822128	-1.571076	0.888811
30	1	0	-3.319668	-2.235122	0.238009
31	1	0	-3.345186	-1.544096	1.859893
32	6	0	-0.993432	2.217360	0.257851
33	6	0	-1.906895	3.041187	-0.658396
34	1	0	0.059269	2.359563	-0.010647
35	1	0	-1.106057	2.535702	1.299637
36	1	0	-1.681457	4.111852	-0.593747
37	1	0	-1.792174	2.746375	-1.706746
38	1	0	-2.961414	2.911738	-0.393506

TS3

M06-2X/6-31+G(d,p) Electronic Energy: -967.5020289 a.u

M06-2X/6-31G(d,p) Gibbs free Energy: -967.130897 a.u

M06-2X(SMD, CH_3CN)/cc-pvtz Electronic Energy: -967.8848319 a. u

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	32	0	-2.191175	-0.885627	-0.246641
2	6	0	0.124321	1.407509	-0.025654
3	6	0	-0.166168	1.933112	1.240563
4	6	0	-0.675784	3.223039	1.374743
5	6	0	-0.915392	4.013218	0.250267

6	6	0	-0.624318	3.505756	-1.014406
7	6	0	-0.105227	2.217348	-1.143650
8	1	0	0.022341	1.332048	2.124543
9	1	0	-0.890200	3.610392	2.366725
10	1	0	-0.795809	4.110719	-1.900327
11	1	0	0.135981	1.831283	-2.131664
12	6	0	-0.324435	-1.031983	0.412080
13	1	0	0.011297	-2.052690	0.194824
14	1	0	-0.312709	-0.928353	1.502969
15	6	0	2.694901	-1.500367	-0.115159
16	6	0	3.016886	0.900368	-0.155966
17	6	0	4.038083	-1.679530	-0.333604
18	1	0	2.057092	-2.375187	-0.043512
19	6	0	4.359317	0.710807	-0.372306
20	1	0	2.623959	1.911553	-0.120301
21	6	0	4.922247	-0.582860	-0.428579
22	1	0	4.430062	-2.684998	-0.464689
23	1	0	5.002800	1.572286	-0.532195
24	6	0	6.309079	-0.774549	-0.684433
25	7	0	7.443034	-0.932146	-0.898250
26	6	0	2.128625	-0.197051	0.156914
27	6	0	1.923456	-0.164199	2.169056
28	7	0	2.085351	-0.242175	3.324622
29	6	0	0.636819	-0.010772	-0.216580
30	1	0	0.638843	-0.186325	-1.302677
31	1	0	-1.319800	5.015405	0.359636
32	6	0	-3.199568	0.631724	0.564635
33	6	0	-4.717540	0.422286	0.585162
34	1	0	-2.934741	1.548963	0.023318
35	1	0	-2.823325	0.772183	1.584371
36	1	0	-5.236792	1.279073	1.029928
37	1	0	-5.124322	0.280347	-0.421788
38	1	0	-4.990553	-0.463768	1.169068
39	6	0	-3.146127	-2.562083	0.261857
40	6	0	-3.093742	-2.811084	1.773516
41	1	0	-2.683771	-3.397422	-0.277952
42	1	0	-4.185831	-2.503136	-0.083494
43	1	0	-3.636491	-3.717977	2.063904
44	1	0	-2.060806	-2.919520	2.120000
45	1	0	-3.531166	-1.974396	2.330747
46	6	0	-2.209089	-0.735856	-2.235391
47	6	0	-3.590141	-0.404714	-2.808987
48	1	0	-1.839069	-1.684649	-2.643189
49	1	0	-1.488108	0.033294	-2.532664
50	1	0	-3.584698	-0.381565	-3.904867
51	1	0	-4.342373	-1.140417	-2.500865
52	1	0	-3.931058	0.577292	-2.463149

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