$B(C_6F_5)_3$-catalyzed hydrogermylation of enones: a facile route to germacycles

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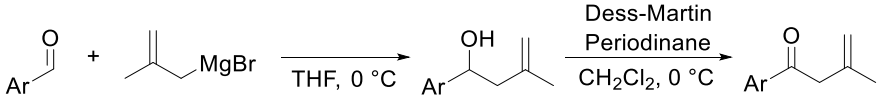
General information

All preparative procedures were performed in an inert atmosphere of dry, deoxygenated (O_2 < 0.5 ppm) argon, using glovebox techniques or standard Schlenk techniques unless otherwise specified. Solvents were stored over activated 3Å molecular sieves following drying procedures. Dichloromethane (DCM), toluene, tetrahydrofuran (THF), ethyl ether (Et_2O) and hexane were purchased from Tedia Company, Inc. Deuterated solvents ($CDCl_3$) were purchased from Cambridge Isotope Laboratories, Inc. and used without further purification. Benzaldehyde and 2-methylallyl magnesium chloride were obtained from Energy Chemical. 2-Chlorobenzaldehyde, 3-chlorobenzaldehyde, 4-chlorobenzaldehyde, 2-bromobenzaldehyde, 3-bromobenzaldehyde, 4-bromobenzaldehyde, 2-fluorobenzaldehyde, 3-fluorobenzaldehyde, 4-fluorobenzaldehyde, 2,4-dichlorobenzaldehyde, 3,5-dichlorobenzaldehyde, 3,4-dichlorobenzaldehyde, 3-(trifluoromethyl)benzaldehyde, 4-(trifluoromethyl)benzaldehyde, 3,5-bis(trifluoromethyl)benzaldehyde, 3-methylbenzaldehyde, 4-bromoanisole, 4-bromophenetole, 4-bromophenoxybenzene, 4-benzyloxybromobenzene, 2,6,10-trimethylundeca-1,9-dien-4-one, *N*-chlorosuccinimide and lithium aluminum hydride were purchased from Adamas-beta. Thin-layer chromatography (TLC) was performed on EMD Silica Gel 60 F254 aluminum plates or EMD basic Aluminium Oxide 60 F254 plastic plates. Silicycle Silia-P Flash Silica Gel was used for all column chromatography.

All NMR spectra were collected at 298 K on Bruker 500 spectrometers in 5 mm diameter NMR tubes. ^{1}H chemical shifts are reported relative to proteo-solvent signals ($CDCl_3$, δ = 7.26 ppm). Data are reported as: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets), coupling constants (Hz), integration and assignment. ^{13}C{^{1}H} chemical shifts are reported relative to proteo-solvent signals ($CDCl_3$, δ = 77.00 ppm). ^{19}F NMR spectra were measured at 376 MHz and $CFCl_3$ (-63.2 ppm) was used as an external standard. Departmental facilities were used for mass spectrometry (FTMS ESI)

Preparation of enones[1]

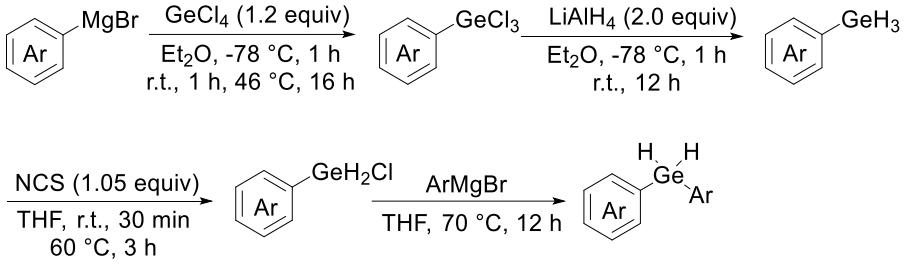


Step 1: To a solution of aldehydes (20.0 mmol) in THF (20 mL) was added 2-methylallyl magnesium chloride (1 M in THF, 28 mL, 28.0 mmol) dropwise at 0 ºC. The reaction mixture was

allowed to stir for 1.5 h at the same temperature. The reaction was quenched with water (30 mL), acidified with conc. HCl (5 mL), and extracted with petroleum ether/EtOAc (9:1) (30 mL × 2). Organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with petroleum ether/EtOAc to give the desired product.

Step 2: To a solution of alcohol (5.0 mmol) in CH_2Cl_2 (20 mL) was added Dess-Martin periodinane (3.2 g, 7.5 mmol) at 0 ºC. The reaction was allowed to stir for overnight at the same temperature. The mixture was diluted with CH_2Cl_2 (50 mL) and saturated aqueous $NaHCO_3$ (50 mL). The organic layer was separated and the aqueous layer was further extracted with CH_2Cl_2 (50 mL × 2). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with petroleum ether/EtOAc to give the desired product.

Preparation of hydrogermane substrates[2]



Step 1: To a solution of Mg (1.2 equiv) and I_2 (two crystals) in anhydrous THF was added aryl bromide (1.0 equiv, 1.0 M in THF) under argon atmosphere at room temperature. The resulting mixture was stirred at room temperature for 3 h to afford Grignard reagent. Under argon atmosphere, a 500 mL Schlenk tube was charged with $GeCl_4$ (1.2 equiv) and anhydrous Et_2O (0.4~0.5 M), and the resulting mixture was cooled to -78 ºC. Then, the Grignard reagent was added dropwise over 1 h to the mixture at -78 ºC. After 1 h, the reaction mixture was stirred at room temperature for 1 h, then refluxed at 46 ºC for 16 h. After being cooled to room temperature, the reaction mixture was filtered off, and the filtrate was concentrated under vacuum.

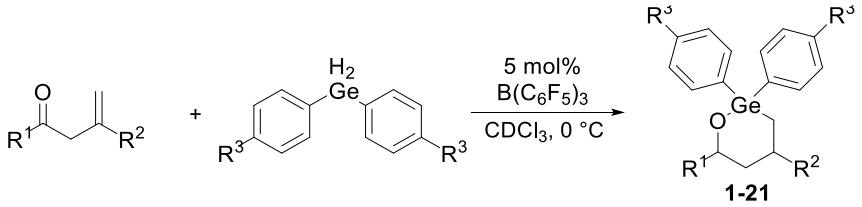
Step 2: The resulting residue was redissolved in anhydrous Et_2O and the resulting mixture was cooled to -78 ºC, $LiAlH_4$ (2.0 equiv, 2.5 M in THF) was added dropwise to the resulting mixture. After 1 h, the reaction mixture was stirred at room temperature overnight. The reaction mixture was quenched with 1 mL H_2O at -78 ºC and dried over anhydrous Na_2SO_4, concentrated under

vacuum, the resulting residue was collected to give crude trihydrogermane, which was used directly without further purification.

Step 3: NCS (1.05 equiv to the trihydrogermane) and anhydrous THF (1.0 M) were added to a 150 mL Schlenk tube under argon atmosphere. The crude trihydrogermane (1.0 M in THF) was rapidly added to the resulting mixture at room temperature. After being stirred at 60 ºC for 3 h-6 h, the solvent was removed under vacuum and the resulting residue was dissolved in *n*-hexane. The resulting mixture was filtered off, and the filtrate was concentrated under vacuum to afford crude chlorogermane, which was used directly without further purification.

Step 4: To a solution of Mg (1.2 equiv) and I_2 (one crystal) in anhydrous THF was added aryl bromide (1.0 equiv, 1.0 M in THF) under argon atmosphere at room temperature. The resulting mixture was stirred at room temperature for 3 h to afford Grignard reagent. Under argon atmosphere, a 500 mL Schlenk tube was charged with crude chlorogermane (1.2 equiv) and anhydrous THF 100 mL, and the resulting mixture was cooled to -78 ºC. Then, the Grignard reagent was added dropwise over 1 h to the mixture at -78 ºC. The resulting mixture was stirred at 60 ºC for 12 h. The reaction mixture was quenched with 1 mL saturated NH_4Cl aqueous solution at room temperature and dried over anhydrous Na_2SO_4, concentrated under vacuum, and the residue was purified by flash chromatography on neutral Al_2O_3 (petroleum ether/EtOAc = 100/0~40/1) to afford dihydrogermane substrates.

General procedure for domino hydrogermylation

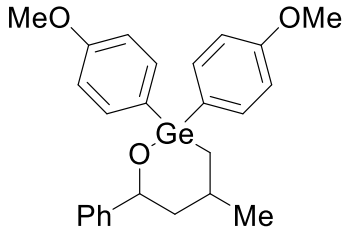


1-21

In an inert atmosphere glovebox, to a solution of enones (0.10 mmol, 1.0 equiv) and dihydrogermanes (0.11 mmol, 1.1 equiv) in $CDCl_3$ (0.5 mL) was added $B(C_6F_5)_3$ (2.5 mg, 0.005 mmol, 5 mol%). The reaction was stirred at room temperature for the indicated time. The residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 50/1 to 5/1) on neutral Al_2O_3 to afford the desired products.

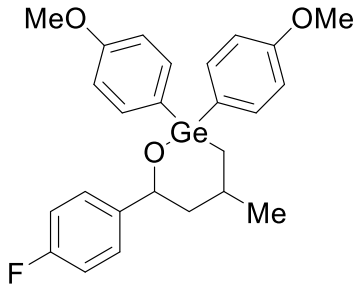
Characterization data

2,2-Bis(4-methoxyphenyl)-4-methyl-6-phenyl-1,2-oxagerminane (1)



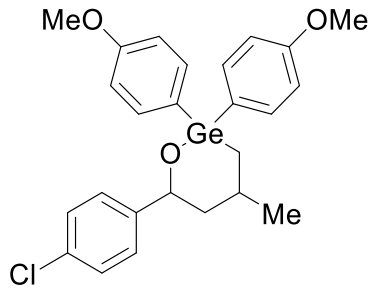
Prepared according to the general procedure (5 h). The compound **1** was obtained as a colorless oil in 87% yield (39.1 mg) with >19:1 dr value. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.59 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 5.22 (dd, *J* = 9.0 Hz, 2.5 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.46 – 2.39 (m, 1H), 2.01 – 1.95 (m, 1H), 1.79 – 1.73 (m, 1H), 1.71 (dd, *J* = 13.5 Hz, 5.5 Hz, 1H), 1.35 (dd, *J* = 13.5 Hz, 5.5 Hz, 1H), 1.14 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 160.94, 160.83, 146.92, 135.15, 134.91, 129.00, 128.94, 128.03, 126.47, 125.75, 114.13, 113.97, 72.66, 55.09, 55.07, 44.66, 26.08, 22.86, 20.40. HRMS (ESI, m/z): Calcd. for $C_{25}H_{29}GeO_3^+$, ($[M+H]^+$): 451.1323; Found: 451.1321.

6-(4-Fluorophenyl)-2,2-bis(4-methoxyphenyl)-4-methyl-1,2-oxagerminane (2)



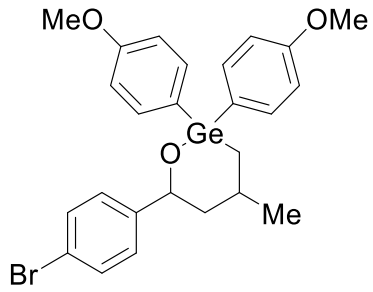
Prepared according to the general procedure (24 h). The compound **2** was obtained as a colorless oil in 77% yield (36.2 mg) with >19:1 dr value. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.58 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.36 – 7.32 (m, 2H), 7.01 – 6.93 (m, 6H), 5.19 (dd, *J* = 9.0 Hz, 3.5 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.45 – 2.39 (m, 1H), 1.97 – 1.91 (m, 1H), 1.77 – 1.68 (m, 2H), 1.35 (dd, *J* = 14.0 Hz, 6.5 Hz, 1H), 1.14 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 161.60 (d, *J* = 244.4 Hz), 160.98, 160.87, 142.61 (d, *J* = 3.2 Hz), 135.11, 134.88, 128.77 (d, *J* = 4.7 Hz), 127.29, 127.22, 114.70, (d, *J* = 21.3 Hz), 114.16, 114.00, 72.09, 55.09, 55.07, 44.65, 26.02, 22.83, 20.30. ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$), δ: -117.01. HRMS (ESI, m/z): Calcd. for $C_{25}H_{28}FGeO_3^+$, ($[M+H]^+$): 469.1229; Found: 469.1228.

6-(4-Chlorophenyl)-2,2-bis(4-methoxyphenyl)-4-methyl-1,2-oxagerminane (3)



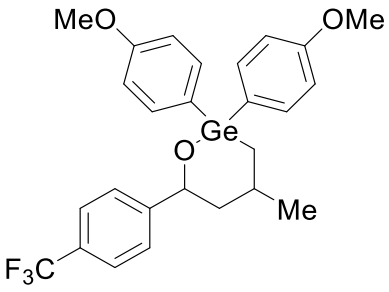
Prepared according to the general procedure (4 h). The compound **3** was obtained as a colorless oil in 91% yield (43.9 mg) with >19:1 dr value. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.52 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 5.14 (dd, *J* = 9.0 Hz, 3.5 Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 2.38 – 2.30 (m, 1H), 1.90 – 1.84 (m, 1H), 1.72 – 1.67 (m, 1H), 1.65 (dd, *J* = 13.5 Hz, 5.5 Hz, 1H), 1.30 (dd, *J* = 13.5 Hz, 6.0 Hz, 1H), 1.08 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 161.00, 160.87, 145.42, 135.09, 134.86, 131.95, 128.73, 128.68, 128.07, 127.15, 114.16, 114.02, 72.14, 55.08, 55.05, 44.54, 25.93, 22.91, 20.36. HRMS (ESI, m/z): Calcd. for $C_{25}H_{28}ClGeO_3^+$, ([M+H]$^+$): 485.0933; Found: 485.0932.

6-(4-Bromophenyl)-2,2-bis(4-methoxyphenyl)-4-methyl-1,2-oxagerminane (4)



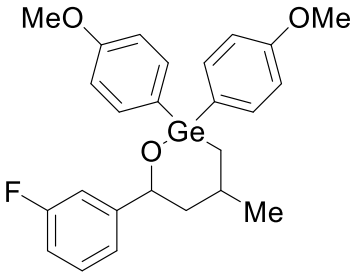
Prepared according to the general procedure (5 h). The compound **4** was obtained as a colorless oil in 89% yield (46.9 mg) with >19:1 dr value. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.58 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.26 (t, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 5.18 (dd, *J* = 8.5 Hz, 3.0 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 2.43 – 2.36 (m, 1H), 1.95 – 1.89 (m, 1H), 1.78 – 1.69 (m, 2H), 1.35 (dd, *J* = 13.5 Hz, 6.5 Hz, 1H), 1.13 (d, *J* = 6.5 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 161.00, 160.87, 145.94, 135.10, 134.86, 131.01, 128.72, 128.66, 127.56, 120.08, 114.16, 114.03, 72.20, 55.09, 55.06, 44.50, 25.91, 22.94, 20.37. HRMS (ESI, m/z): Calcd. for $C_{25}H_{28}BrGeO_3^+$, ([M+H]$^+$): 529.0428; Found: 529.0428.

2,2-Bis(4-methoxyphenyl)-4-methyl-6-(4-(trifluoromethyl)phenyl)-1,2-oxagerminane (5)



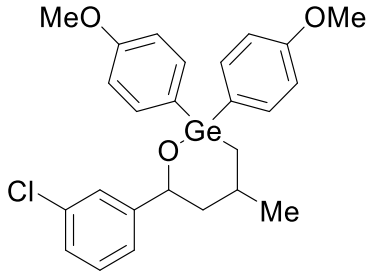
Prepared according to the general procedure (5 h). The compound **5** was obtained as a colorless oil in 99% yield (51.8 mg) with >19:1 dr value. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.58 (d, *J* = 8.5 Hz, 2H), 7.55 – 7.48 (m, 6H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 5.27 (dd, *J* = 8.5 Hz, 3.5 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 2.45 – 2.37 (m, 1H), 1.98 – 1.92 (m, 1H), 1.82 – 1.76 (m, 1H), 1.73 (dd, *J* = 14.0 Hz, 5.5 Hz, 1H), 1.37 (dd, *J* = 14.0 Hz, 7.0 Hz, 1H), 1.15 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 161.06, 160.93, 150.96 (d, *J* = 0.9 Hz), 135.10, 134.86, 128.62 (q, *J* = 32.1 Hz), 128.62, 128.58, 126.03, 124.94 (q, *J* = 6.9 Hz), 124.37 (q, *J* = 272.2 Hz), 114.20, 114.07, 72.31, 55.09, 55.07, 44.48, 25.95, 22.93, 20.37. ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$), δ: -62.23. HRMS (ESI, m/z): Calcd. for $C_{26}H_{28}F_3GeO_3^+$, ([M+H]$^+$): 519.1197; Found: 519.1199.

6-(3-Fluorophenyl)-2,2-bis(4-methoxyphenyl)-4-methyl-1,2-oxagerminane (6)



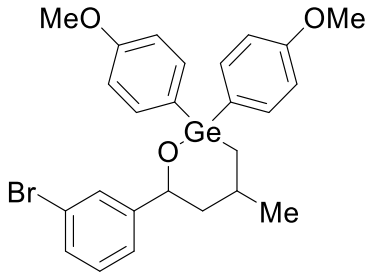
Prepared according to the general procedure (5 h). The compound **6** was obtained as a colorless oil in 91% yield (42.8 mg) with >19:1 dr value. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.58 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.26 – 7.20 (m, 1H), 7.16 – 7.10 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.88 (td, *J* = 8.5 Hz, 3.0 Hz, 1H), 5.20 (dd, *J* = 8.5 Hz, 3.0 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.45 – 2.38 (m, 1H), 1.97 – 1.91 (m, 1H), 1.79 – 1.73 (m, 1H), 1.71 (dd, *J* = 14.0 Hz, 5.5 Hz, 1H), 1.36 (dd, *J* = 14.0 Hz, 6.5 Hz, 1H), 1.14 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 162.93 (d, *J* = 245.2 Hz), 161.02, 160.89, 149.80 (d, *J* = 6.6 Hz), 135.11, 134.88, 129.37 (d, *J* = 8.2 Hz), 128.68 (d, *J* = 11.6 Hz), 121.21(d, *J* = 2.8 Hz), 114.18, 114.05, 113.19 (d, *J* = 21.0 Hz), 112.77 (d, *J* = 22.1 Hz), 72.16 (d, *J* = 245.1 Hz), 55.10, 55.07, 44.51, 26.01, 22.87, 20.36. ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$), δ: -113.79. HRMS (ESI, m/z): Calcd. for $C_{25}H_{28}FGeO_3^+$, ([M+H]$^+$): 469.1229; Found: 469.1230.

6-(3-Chlorophenyl)-2,2-bis(4-methoxyphenyl)-4-methyl-1,2-oxagerminane (7)



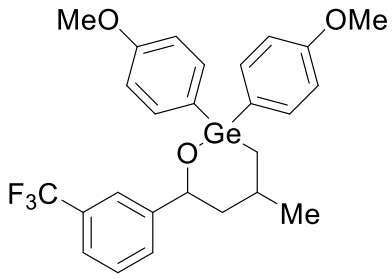
Prepared according to the general procedure (5 h). The compound **7** was obtained as a colorless oil in 95% yield (46.4 mg) with >19:1 dr value. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.59 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.40 (s, 1H), 7.25 – 7.15 (m, 3H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 5.19 (dd, *J* = 9.0 Hz, 3.5 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 2.45 – 2.38 (m, 1H), 1.97 – 1.91 (m, 1H), 1.79 – 1.69 (m, 2H), 1.36 (dd, *J* = 14.0 Hz, 6.5 Hz, 1H), 1.14 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 161.03, 160.89, 149.05, 135.11, 134.86, 133.94, 129.26, 128.64, 128.58, 126.55, 126.06, 123.86, 114.17, 114.06, 72.21, 55.09, 55.06, 44.48, 26.01, 22.89, 20.30. HRMS (ESI, m/z): Calcd. for $C_{25}H_{28}ClGeO_3^+$, ([M+H]$^+$): 485.0933; Found: 485.0929.

6-(3-Bromophenyl)-2,2-bis(4-methoxyphenyl)-4-methyl-1,2-oxagerminane (8)



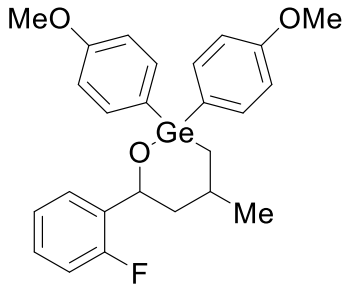
Prepared according to the general procedure (5 h). The compound **8** was obtained as a colorless oil in 93% yield (49.0 mg) with >19:1 dr value. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.58 (d, *J* = 8.5 Hz, 2H), 7.54 (s, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 5.18 (dd, *J* = 8.5 Hz, 3.0 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.44 – 2.37 (m, 1H), 1.97 – 1.91 (m, 1H), 1.78 – 1.69 (m, 2H), 1.35 (dd, *J* = 13.5 Hz, 6.5 Hz, 1H), 1.13 (d, *J* = 6.5 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 161.04, 160.89, 149.31, 135.12, 134.87, 129.59, 129.49, 128.99, 128.62, 128.56, 124.33, 122.30, 114.18, 114.08, 72.22, 55.10, 55.07, 44.49, 25.99, 22.92, 20.32. HRMS (ESI, m/z): Calcd. for $C_{25}H_{28}Br^{78.9183}GeO_3^+$,([M+H]$^+$): 527.0438; Found: 527.0435; $C_{25}H_{28}Br^{80.9163}GeO_3^+$,([M+H]$^+$): 531.0408; Found: 531.0411.

2,2-Bis(4-methoxyphenyl)-4-methyl-6-(3-(trifluoromethyl)phenyl)-1,2-oxagerminane (9)



Prepared according to the general procedure (5 h). The compound **9** was obtained as a colorless oil in 72% yield (37.3 mg) with >19:1 dr value. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.66 (s, 1H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 5.28 (dd, *J* = 8.5 Hz, 3.5 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 2.45 – 2.38 (m, 1H), 1.99 – 1.93 (m, 1H), 1.82 – 1.76 (m, 1H), 1.73 (dd, *J* = 13.5 Hz, 5.5 Hz, 1H), 1.37 (dd, *J* = 14.0 Hz, 6.5 Hz, 1H), 1.16 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 161.07, 160.93, 147.89, 135.09, 134.88, 130.26 (q, *J* = 32.0 Hz), 129.12 (d, *J* = 0.8 Hz), 128.62, 128.51, 128.41, 124.33 (q, *J* = 273.0 Hz), 123.30 (q, *J* = 3.8 Hz), 122.66 (q, *J* = 4.0 Hz), 114.20, 114.10, 72.32, 55.10, 55.07, 44.47, 25.96, 22.92, 20.37. ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$), δ: -62.40. HRMS (ESI, m/z): Calcd. for $C_{26}H_{28}F_3GeO_3^+$, ([M+H]$^+$): 519.1197; Found: 519.1197.

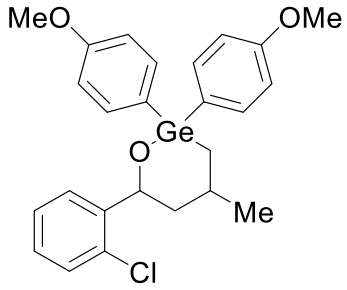
6-(2-Fluorophenyl)-2,2-bis(4-methoxyphenyl)-4-methyl-1,2-oxagerminane (10)



Prepared according to the general procedure (5 h). The compound **10** was obtained as a colorless oil in 87% yield (40.5 mg) with >19:1 dr value. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.75 (t, *J* = 8.5 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.15 (m, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.01 – 6.94 (m, 5H), 5.57 (dd, *J* = 9.0 Hz, 3.0 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 2.46 – 2.40 (m, 1H), 1.95 – 1.89 (m, 1H), 1.84 – 1.79 (m, 1H), 1.74 (dd, J = 13.5 Hz, 6.0 Hz, 1H) 1.38 (dd, *J* = 13.5 Hz, 6.0 Hz, 1H), 1.15 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 161.00, 160.86, 159.07 (d, *J* = 245.1 Hz), 135.12, 134.87, 134.1 (d, *J* = 13.1 Hz), 128.82 (d, *J* = 4.7 Hz), 127.79, 127.74 (d, *J* = 4.2 Hz), 127.72, 123.96 (d, *J* = 3.4 Hz), 114.72 (d, *J* = 21.8 Hz), 114.17, 114.03, 66.60 (d, *J* = 2.3 Hz), 55.09, 55.06, 43.35, 26.16, 22.48, 20.49. ^{19}F{^{1}H} NMR (471 MHz,

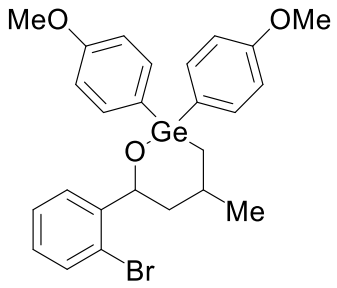
$CDCl_3$), δ: -119.86. HRMS (ESI, m/z): Calcd. for $C_{25}H_{28}FGeO_3^+$, ($[M+H]^+$): 469.1229; Found: 469.1228.

6-(2-Chlorophenyl)-2,2-bis(4-methoxyphenyl)-4-methyl-1,2-oxagerminane (11)



Prepared according to the general procedure (5 h). The compound **11** was obtained as a colorless oil in 81% yield (39.3 mg) with >19:1 dr value. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.74 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.14 – 7.10 (m, 1H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 5.56 (dd, *J* = 9.0 Hz, 2.5 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 2.49 – 2.42 (m, 1H), 1.90 – 1.84 (m, 1H), 1.79 – 1.70 (m, 2H), 1.38 (dd, *J* = 13.5 Hz, 4.5 Hz, 1H), 1.17 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 160.98, 160.85, 144.42, 135.08, 134.86, 130.83, 128.93, 128.91, 128.76, 127.71, 127.55, 126.86, 114.17, 114.04, 69.16, 55.08, 55.05, 42.74, 26.47, 21.92, 20.30. HRMS (ESI, m/z): Calcd. for $C_{25}H_{28}ClGeO_3^+$, ($[M+H]^+$): 485.0933; Found: 485.0928.

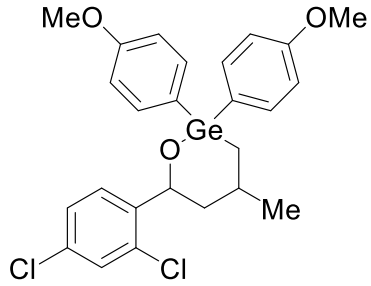
6-(2-Bromophenyl)-2,2-bis(4-methoxyphenyl)-4-methyl-1,2-oxagerminane (12)



Prepared according to the general procedure (5 h). The compound **12** was obtained as a colorless oil in 78% yield (41.0 mg) with >19:1 dr value. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.74 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.46 (dd, *J* = 8.0 Hz, 0.5Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.07 (td, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.00 (d, *J* = 9.0 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 5.14 (dd, *J* = 9.0 Hz, 2.0 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 2.52 – 2.45 (m, 1H), 1.93 – 1.80 (m, 1H), 1.78 – 1.72 (m, 2H), 1.39 (dd, *J* = 13.5 Hz, 4.0 Hz, 1H), 1.20 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 160.99, 160.85, 145.90, 135.08, 134.87, 132.19, 128.95, 128.75, 128.05, 127.98, 127.51, 121.05, 114.18, 114.04, 71.44, 55.10, 55.06, 42.82, 26.58, 21.82,

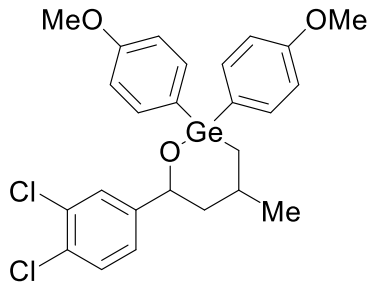
20.26. HRMS (ESI, m/z): Calcd. for $C_{25}H_{28}Br^{78.9183}GeO_3^+$, ([M+H]$^+$): 529.0428; Found: 529.0423; $C_{25}H_{28}Br^{80.9163}GeO_3^+$, ([M+H]$^+$): 531.0408; Found: 531.0413.

6-(2,4-Diclorophenyl)-2,2-bis(4-methoxyphenyl)-4-methyl-1,2-oxagerminane (13)



Prepared according to the general procedure (5 h). The compound **13** was obtained as a colorless oil in 72% yield (37.3 mg) with >19:1 dr value. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.67 (d, *J* = 8.5 Hz, 1H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 9.0 Hz, 2H), 7.28 (d, *J* = 2.0 Hz, 1H), 7.22 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 6.99 (dd, *J* = 8.5 Hz, 2H), 6.96 (dd, *J* = 8.5 Hz, 2H), 5.02 (dd, *J* = 8.5 Hz, 2.5 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 2.49 – 2.42 (m, 1H), 1.88 – 1.82 (m, 1H), 1.76 – 1.69 (m, 2H), 1.39 (dd, *J* = 13.5 Hz, 5.5 Hz, 1H), 1.17 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 161.06, 160.92, 143.14, 135.06, 134.84, 132.42, 131.37, 128.80, 128.72, 128.61, 128.54, 127.13, 114.22, 114.10, 68.92, 55.11, 55.07, 42.62, 26.41, 21.93, 20.23. HRMS (ESI, m/z): Calcd. for $C_{25}H_{27}Cl_2GeO_3^+$, ([M+H]$^+$): 519.0544; Found: 519.0540.

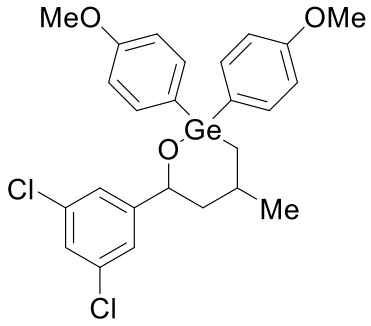
6-(3,4-Diclorophenyl)-2,2-bis(4-methoxyphenyl)-4-methyl-1,2-oxagerminane (14)



Prepared according to the general procedure (5 h). The compound **14** was obtained as a colorless oil in 89% yield (46.1 mg) with >19:1 dr value. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.56 (d, *J* = 8.5 Hz, 2H), 7.50 – 7.47 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 1H), 5.17 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 6.99 (d, *J* = 9.0 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 5.19 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 2.42 – 2.35 (m, 1H), 1.93 – 1.87 (m, 1H), 1.78 – 1.69 (m, 2H), 1.35 (dd, *J* = 13.5 Hz, 6.5 Hz, 1H), 1.13 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 161.10, 160.94, 147.26, 135.09, 134.84, 132.00, 130.03, 129.88, 128.44, 128.40, 127.96, 125.14, 114.21, 114.12, 71.80, 55.11,

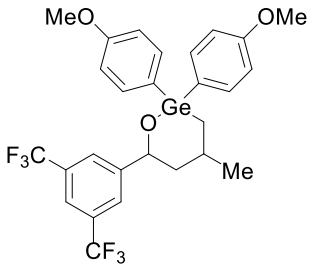
55.08, 44.35, 25.90, 22.99, 20.31. HRMS (ESI, m/z): Calcd. for $C_{25}H_{27}Cl_2GeO_3^+$, ([M+H]$^+$): 519.0544; Found: 519.0536.

6-(3,5-Diclorophenyl)-2,2-bis(4-methoxyphenyl)-4-methyl-1,2-oxagerminane (15)



Prepared according to the general procedure (5 h). The compound **15** was obtained as a colorless oil in 95% yield (49.4 mg) with >19:1 dr value. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.57 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 2.0 Hz, 2H), 7.50 (t, *J* = 1.5 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.66 (d, *J* = 8.5 Hz, 2H), 5.15 (dd, *J* = 8.5 Hz, 3.0 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 2.43 – 2.36 (m, 1H), 1.94 – 1.88 (m, 1H), 1.78 – 1.70 (m, 2H), 1.35 (dd, *J* = 13.5 Hz, 6.5 Hz, 1H), 1.14 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 161.13, 160.96, 150.46, 135.10, 134.83, 134.49, 128.30, 128.27, 126.49, 124.40, 114.23, 114.15, 71.93, 55.11, 55.07, 44.30, 25.98, 22.92, 20.23. HRMS (ESI, m/z): Calcd. for $C_{25}H_{27}Cl_2GeO_3^+$, ([M+H]$^+$): 519.0544; Found: 519.0536.

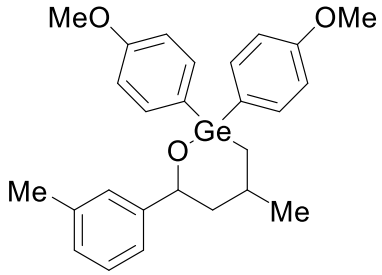
6-(3,5-Bis(trifluoromethyl)phenyl)-2,2-bis(4-methoxyphenyl)-4-methyl-1,2-oxagerminan (16)



Prepared according to the general procedure (5 h). The compound **16** was obtained as a colorless oil in 72% yield (42.1 mg) with >19:1 dr value. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.83 (s, 2H), 7.71 (s, 1H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 5.32 (dd, *J* = 8.5 Hz, 3.0 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 2.44 – 2.37 (m, 1H), 1.98 – 1.92 (m, 1H), 1.85 – 1.79 (m, 1H), 1.75 (dd, *J* = 14.0 Hz, 5.5 Hz, 1H), 1.39 (dd, *J* = 13.5 Hz, 6.5 Hz, 1H), 1.18 (d, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 161.22, 161.05, 149.57, 135.03, 134.86, 131.15 (q, *J* = 33.0 Hz), 128.21, 128.09, 126.05 (d, *J* = 4.0 Hz), 123.51 (q, *J* =

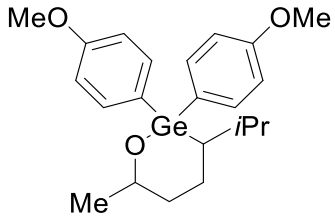
273.2 Hz), 120.52 – 120.39 (m), 114.29, 114.23, 71.99, 55.12, 55.10, 44.31, 25.94, 22.95, 20.30. $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$), δ: -62.70. HRMS (ESI, m/z): Calcd. for $C_{27}H_{27}F_6GeO_3^+$, ($[M+H]^+$): 587.1071; Found: 587.1071.

6-(3-Methylphenyl)-2,2-bis(4-methoxyphenyl)-4-methyl-1,2-oxagerminane (17)



Prepared according to the general procedure (12 h). The compound **17** was obtained as a colorless oil in 47% yield (21.7 mg) with >19:1 dr value. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.59 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.14 (m, 3H), 7.00 (d, *J* = 7.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 5.19 (dd, *J* = 9.0 Hz, 3.0 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.45 – 2.38 (m, 1H), 2.29 (s, 3H), 2.02 – 1.96 (m, 1H), 1.78 – 1.68 (m, 2H), 1.34 (dd, *J* = 13.5 Hz, 6.5 Hz, 1H), 1.13 (d, *J* = 7.0 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 160.94, 160.81, 146.77, 137.54, 135.20, 134.92, 128.99, 127.91, 127.21, 126.57, 122.78, 114.11, 113.95, 72.81, 55.09, 55.07, 44.63, 26.08, 22.96, 21.47, 20.40. HRMS (ESI, m/z): Calcd. for $C_{26}H_{31}GeO_3^+$, ($[M+H]^+$): 465.1479; Found: 465.1478.

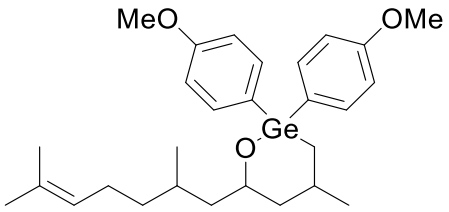
3-Isopropyl-2,2-bis(4-methoxyphenyl)-6-methyl-1,2-oxagerminane (18)



Prepared according to the general procedure (12 h). The compound **18** was obtained as a colorless oil in 88% yield (36.6 mg) with 9:1 dr value. $^{1}H_{mixture}$ NMR (500 MHz, $CDCl_3$), δ: 7.59 (d, *J* = 8.0 Hz, 1.8H), 7.55 (d, *J* = 8.5 Hz, 0.2H), 7.50 (d, *J* = 9.5 Hz, 0.2H), 7.48 (d, *J* = 8.0 Hz, 1.8H), 7.00 (d, *J* = 8.5 Hz, 1.8H), 6.97 (d, *J* = 8.5 Hz, 0.2H), 6.91 (d, *J* = 6.0 Hz, 0.2H), 6.90 (d, *J* = 8.5 Hz, 1.8H), 4.15 – 4.10 (m, 0.1H), 4.05 – 3.98 (m, 0.9H), 3.85 (s, 2.7H), 3.83 (s, 0.3H), 3.80 (s, 0.3H), 3.79 (s, 2.7H), 2.28 – 2.23 (m, 1H), 1.99 – 1.62 (m, 3H), 1.61 – 1.38 (m, 3H), 1.26 (d, *J* = 7.0 Hz, 0.3H), 1.23 (d, *J* = 6.0 Hz, 2.7H), 0.98 (d, *J* = 5.5 Hz, 0.3H), 0.96 (d, *J* = 6.5 Hz, 2.7H),

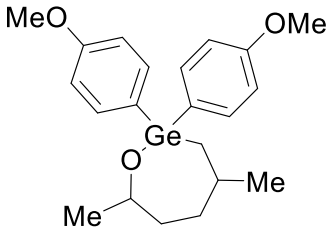
0.90 (d, *J* = 7.0 Hz, 2.7H), 0.82 (d, *J* = 6.5 Hz, 0.3H). $^{13}C\{^{1}H\}_{major}$ NMR (126 MHz, $CDCl_3$), δ: 160.73, 160.70, 136.00, 135.33, 129.83, 126.31, 114.11, 113.90, 72.09, 55.02, 38.78, 38.59, 30.45, 29.12, 25.68, 25.08, 21.67. $^{13}C\{^{1}H\}_{minor}$ NMR (126 MHz, $CDCl_3$), δ: 160.73, 160.70, 135.65, 135.35, 128.86, 128.13, 113.99, 113.88, 69.71, 53.40, 36.39, 34.63, 28.88, 24.69, 24.39, 24.18, 21.62. HRMS (ESI, m/z): Calcd. for $C_{22}H_{31}GeO_3^+$, ($[M+H]^+$): 417.1479; Found: 417.147.

6-(2,6-Dimethylhept-5-en-1-yl)-2,2-bis(4-methoxyphenyl)-4-methyl-1,2-oxagerminane (19)



Prepared according to the general procedure at 50 ºC (12 h). The compound **19** was obtained as a colorless oil in 53% yield (26.3 mg) with 1.3 :1 dr value. $^{1}H_{mixture}$ NMR (500 MHz, $CDCl_3$), δ: 7.51 – 7.48 (m, 4H), 6.95 – 6.92 (m, 4H), 5.08 – 5.01 (m, 1H), 4.21 – 4.16 (m, 1H), 3.81 (s, 3H), 3.81 (s, 3H), 2.35 – 2.25 (m, 1H), 1.99 – 1.76 (m, 2H), 1.64 – 1.55 (m, 7H), 1.47 – 1.26 (m, 2H), 1.21 – 1.35 (m, 1H), 1.07 – 0.94 (m, 5H), 0.83 (d, *J* = 6.5 Hz, 1.7H), 0.77(d, *J* = 7.0 Hz, 1.3H). $^{13}C\{^{1}H\}_{mixture}$ NMR (126 MHz, $CDCl_3$), δ: 160.83, 160.77, 135.05, 135.00, 134.94, 130.79, 130.62, 129.10, 129.09, 129.02, 128.97, 125.20, 125.10, 113.99, 113.97, 69.84, 69.79, 55.06, 55.04, 55.01, 45.56, 45.33, 43.33, 42.25, 37.80, 36.82, 29.23, 28.82, 25.70, 25.45, 25.12, 24.79, 20.69, 20.59, 19.95, 18.94, 17.60, 17.60. HRMS (ESI, m/z): Calcd. for $C_{28}H_{40}GeO_3^+$, ($[M+H]^+$): 499.2262; Found: 499.2258.

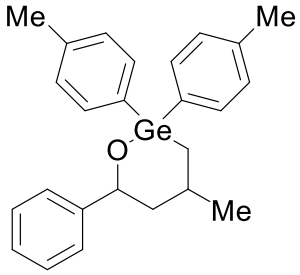
2,2-Bis(4-methoxyphenyl)-4,7-dimethyl-1,2-oxagermepane (20)



Prepared according to the general procedure (5 h). The compound **20** was obtained as a colorless oil in 99% yield with 3:1 dr value. $^{1}H_{mixture}$ NMR (500 MHz, $CDCl_3$), δ: 7.52 – 7.47 (m, 4H), 6.96 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 4.14 – 4.08 (m, 0.75H), 3.95 – 3.90 (m, 0.25H), 3.82 (s, 3H), 3.80 (s, 3H), 2.27 – 2.20 (m, 0.75H), 2.13 – 2.05 (m, 0.25H), 1.81 – 1.48 (m, 5H), 1.41 – 1.35 (m, 1H), 1.24 (d, *J* = 6.0 Hz, 0.0.75H), 1.20 (d, *J* = 6.5 Hz, 2.25H), 1.12 (d, *J* = 7.0 Hz, 2.25H),

1.11 (d, *J* = 7.5 Hz, 0.75H). $^{13}C\{^{1}H\}_{major}$ NMR (126 MHz, $CDCl_3$), δ: 160.68, 160.68,134.94, 134.90, 129.62, 129.01, 114.03, 113.90, 70.93, 55.03, 36.88, 35.22, 29.66, 25.82, 25.46, 24.55. $^{13}C\{^{1}H\}_{minor}$ NMR (126 MHz, $CDCl_3$), δ: 160.75, 160.72, 135.03, 134.97, 128.96, 128.74, 114.03, 113.94, 72.71, 55.03, 39.74, 39.17, 31.48, 28.18, 26.07, 25.25. HRMS (ESI, m/z): Calcd. for $C_{21}H_{29}GeO_3^+$, ($[M+H]^+$): 403.1323; Found: 403.1317.

4-Methyl-6-phenyl-2,2-di-*p*-tolyl-1,2-oxagerminane (21)



Prepared according to the general procedure (24 h). The compound **21** was obtained as a colorless oil in 73% yield (30.6 mg) with >19:1 dr value. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.44 (d, *J* = 7.5 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.5 Hz, 3H), 5.31 (dd, *J* = 8.5 Hz, 3.0 Hz, 1H), 2.54 – 2.46 (m, 1H), 2.47 (s, 3H), 2.44 (s, 3H), 2.08 – 2.02 (m, 1H), 1.87 – 1.81 (m, 1H), 1.80 (dd, *J* = 14.0 Hz, 6.0 Hz, 1H), 1.50 (dd, *J* = 13.5 Hz, 6.0 Hz, 1H), 1.21 (d, *J* = 7.0 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$), δ: 146.96, 139.65, 139.45, 134.59, 134.33, 133.69, 133.48, 129.17, 129.01, 128.01, 126.46, 125.74, 72.63, 44.70, 26.06, 22.83, 21.53, 21.51, 20.28. HRMS (ESI, m/z): Calcd. for $C_{25}H_{29}GeO^+$, ($[M+H]^+$): 419.1425; Found: 419.1423.

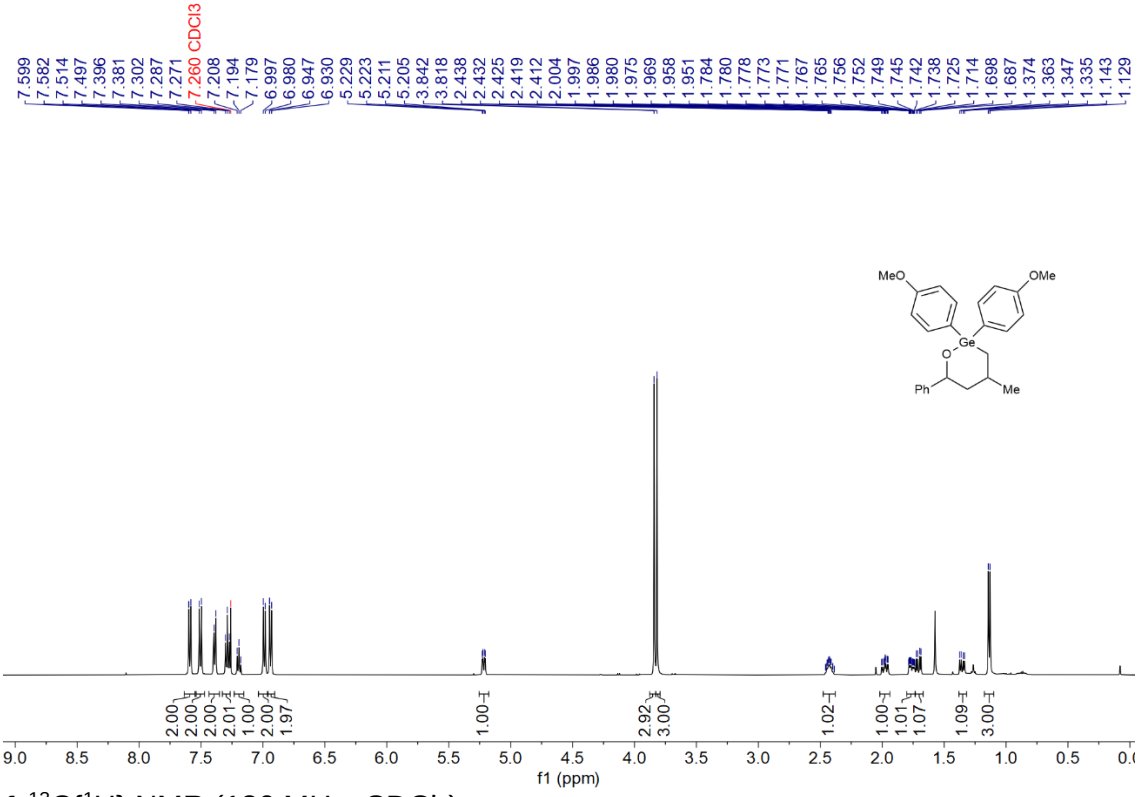
References

1 K. Shin, S. Joung, Y. Kim, S. Changa, *Adv. Synth. Catal.*, 2017, **359**, 3428 – 3436.

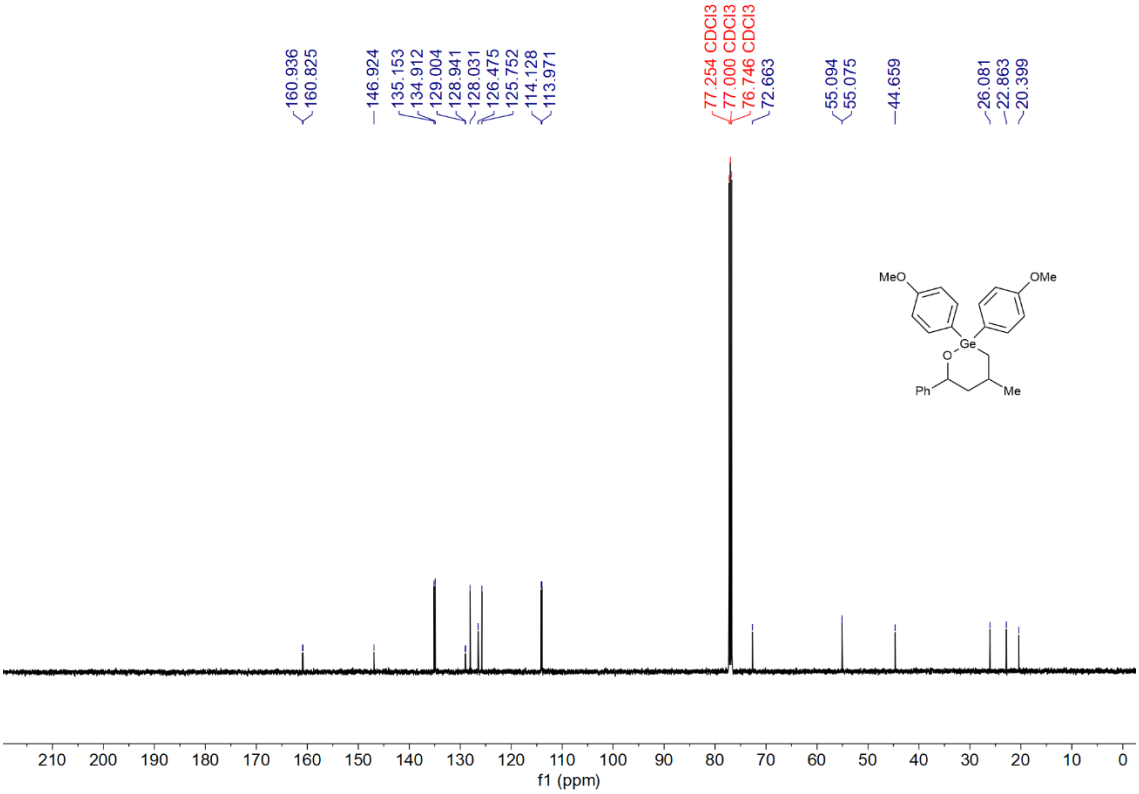
2 W. Lin, L. You, W. Yuan, C. He, *ACS Catal.*, 2022, **12**, 14592 – 114600.

NMR spectra of isolated compounds

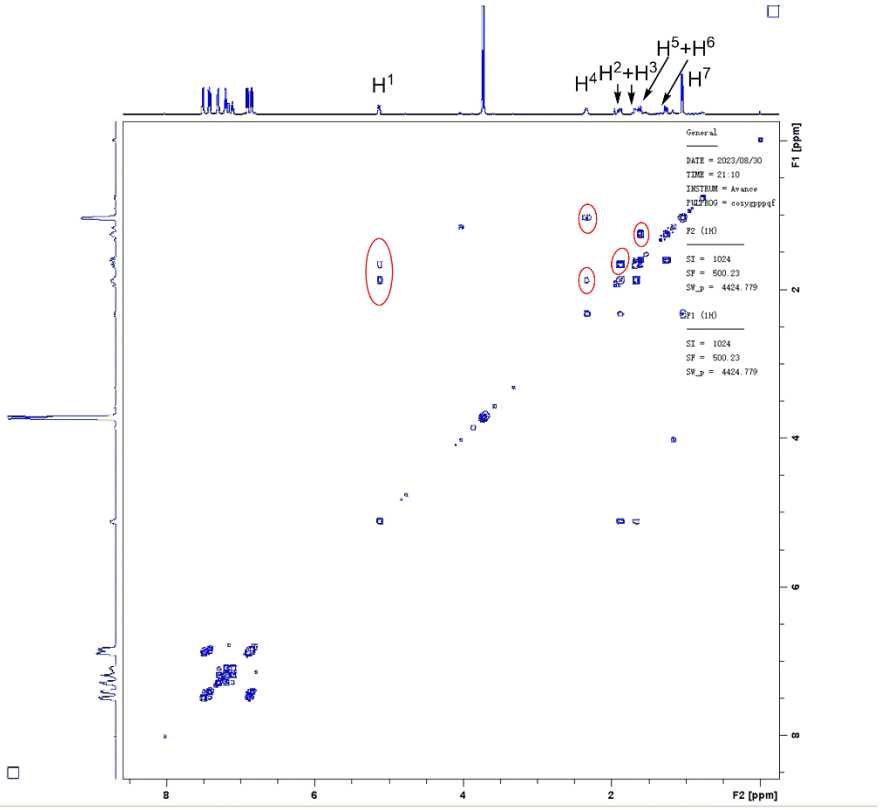
1 ^{1}H NMR (500 MHz, $CDCl_3$)

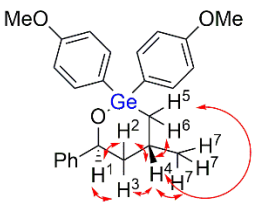


1 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

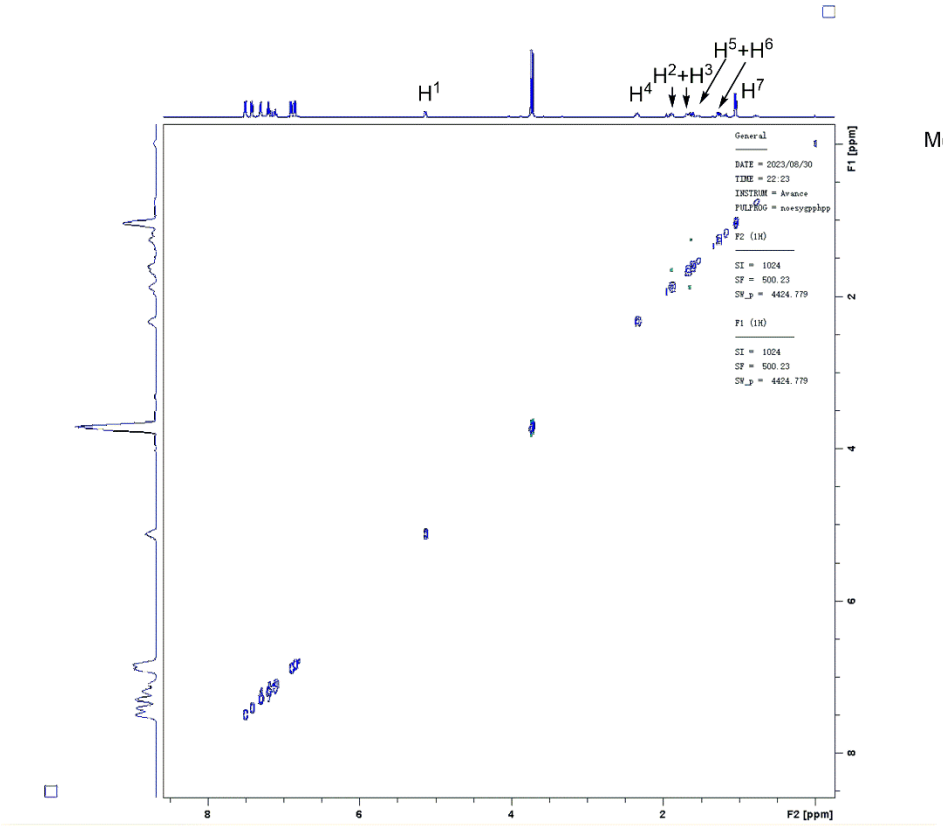


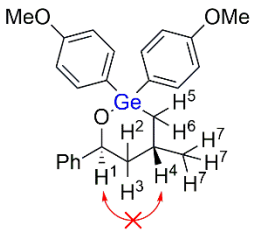
COSY



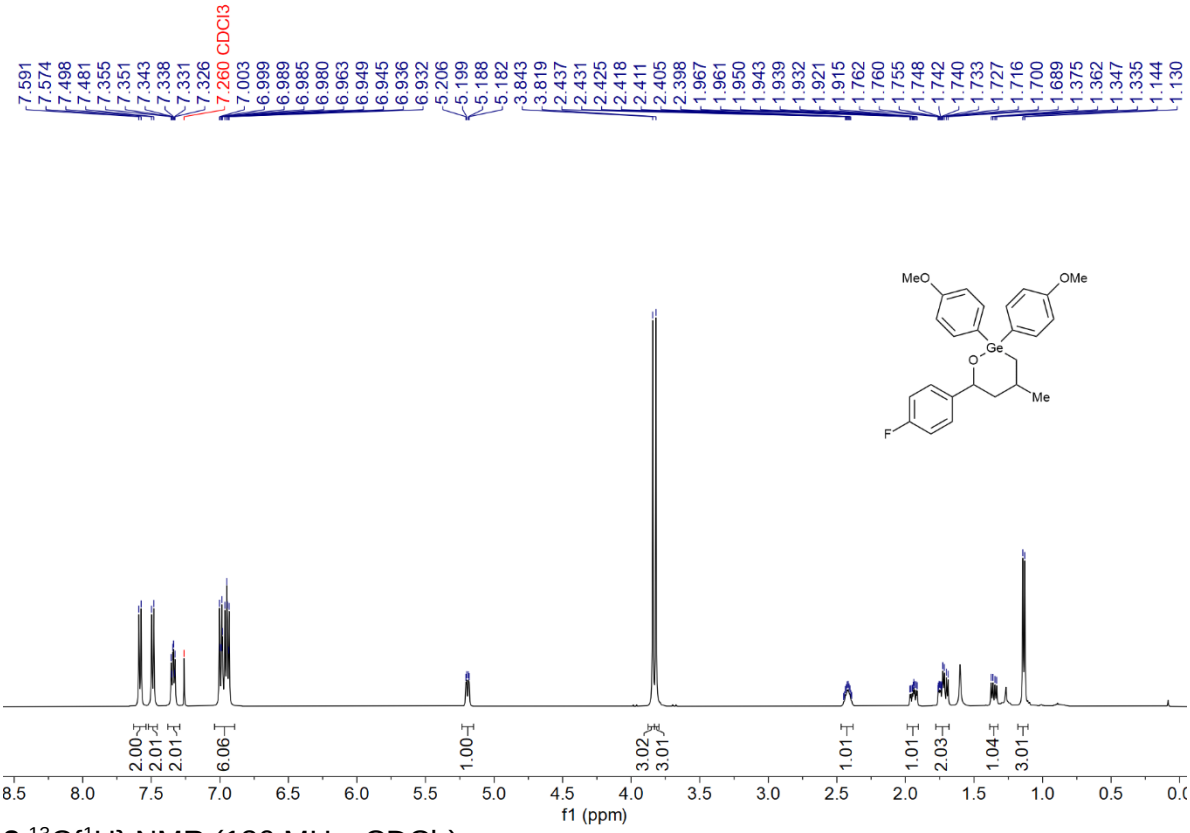


NOESY (No obvious signal)

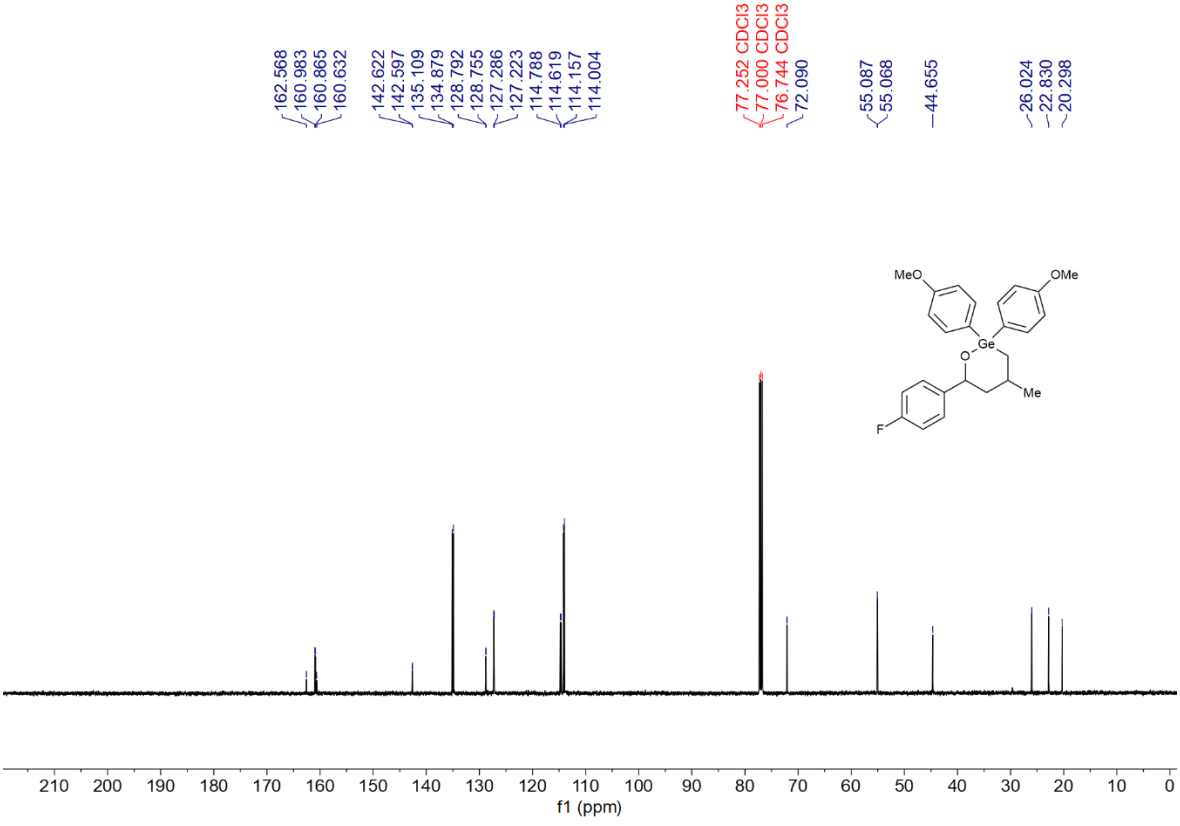




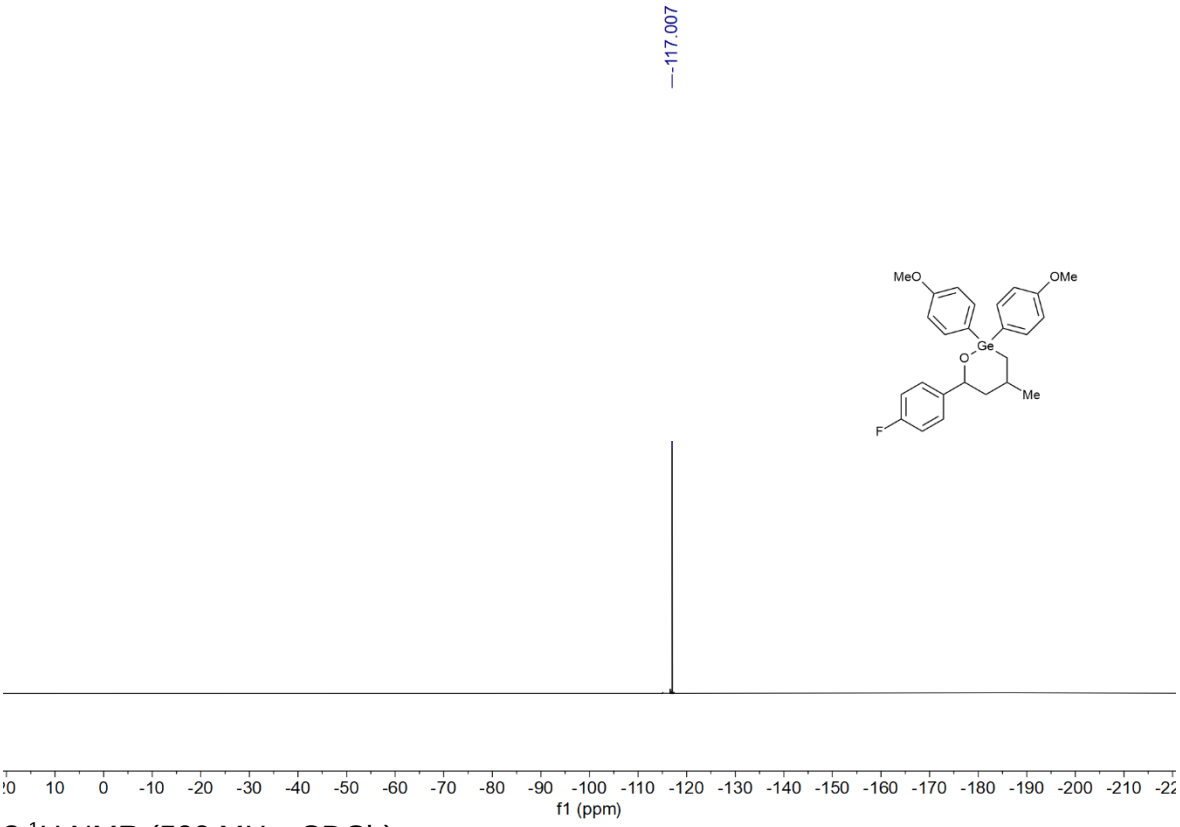
2 ^{1}H NMR (500 MHz, $CDCl_3$)



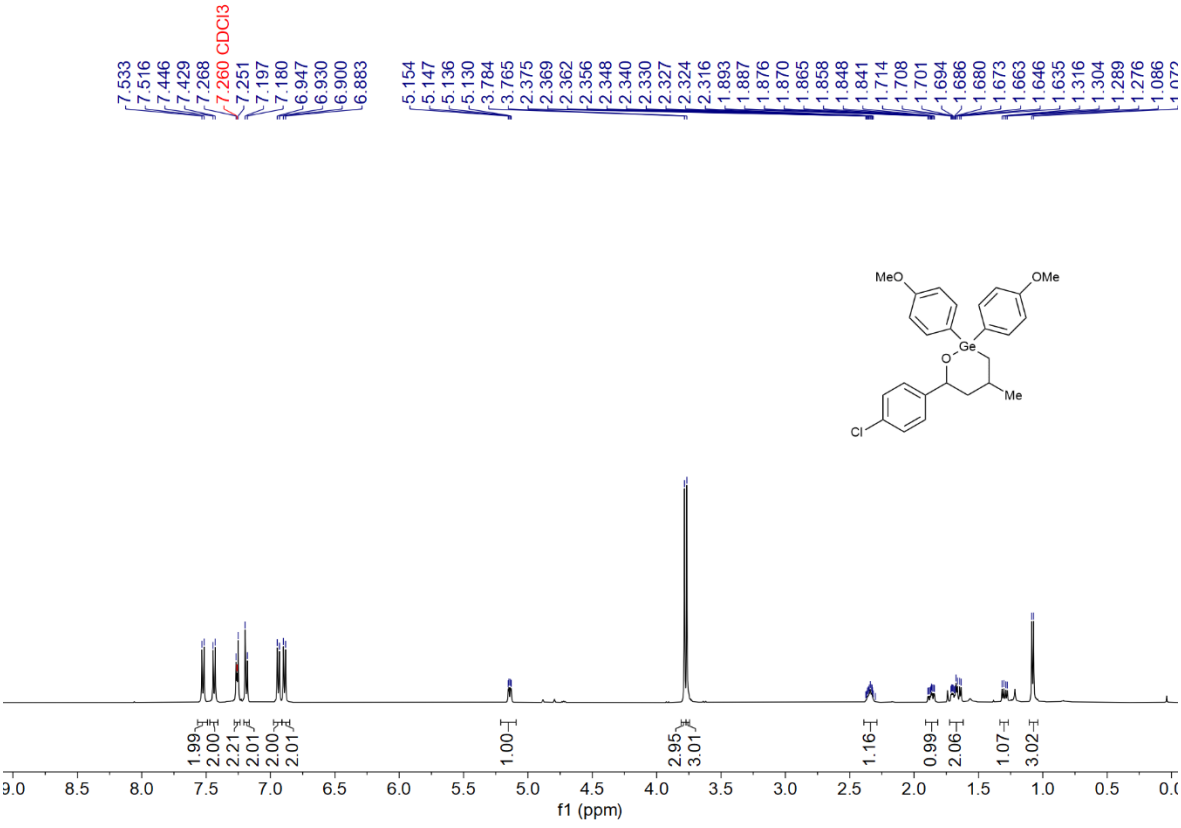
2 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



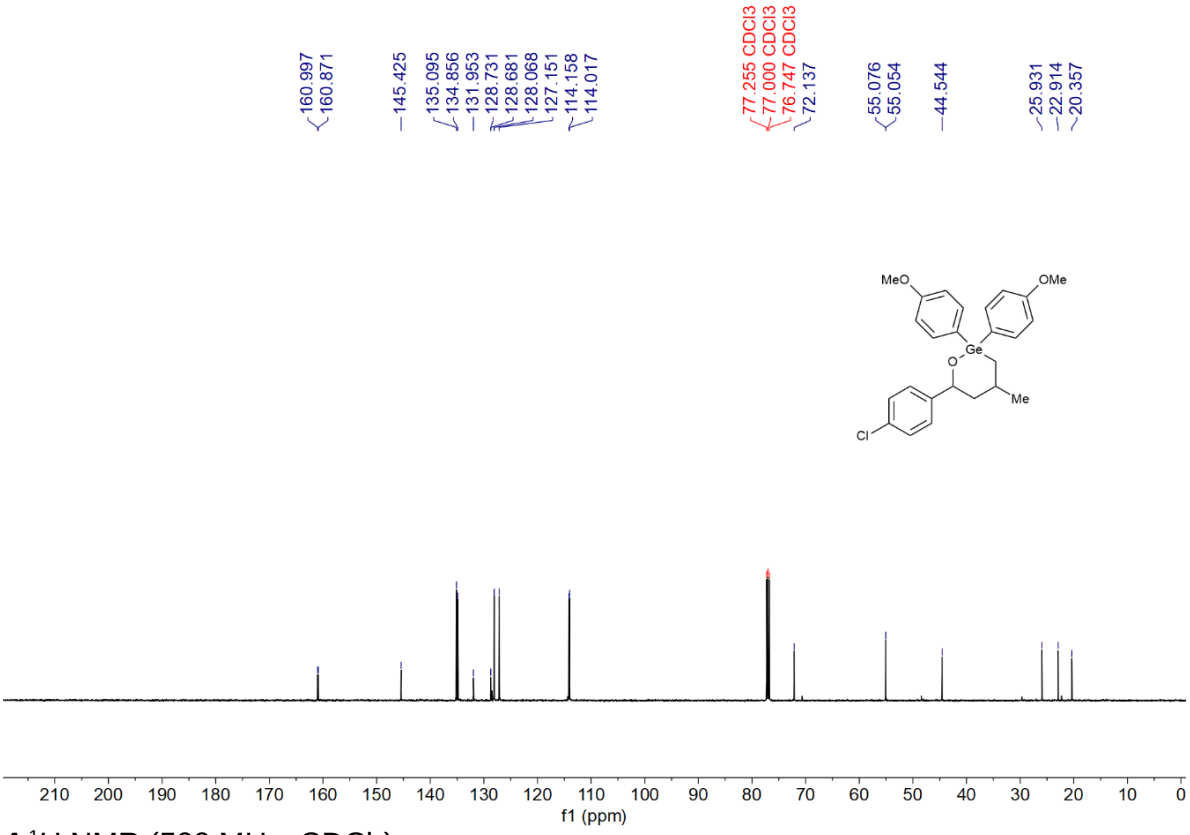
2 $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



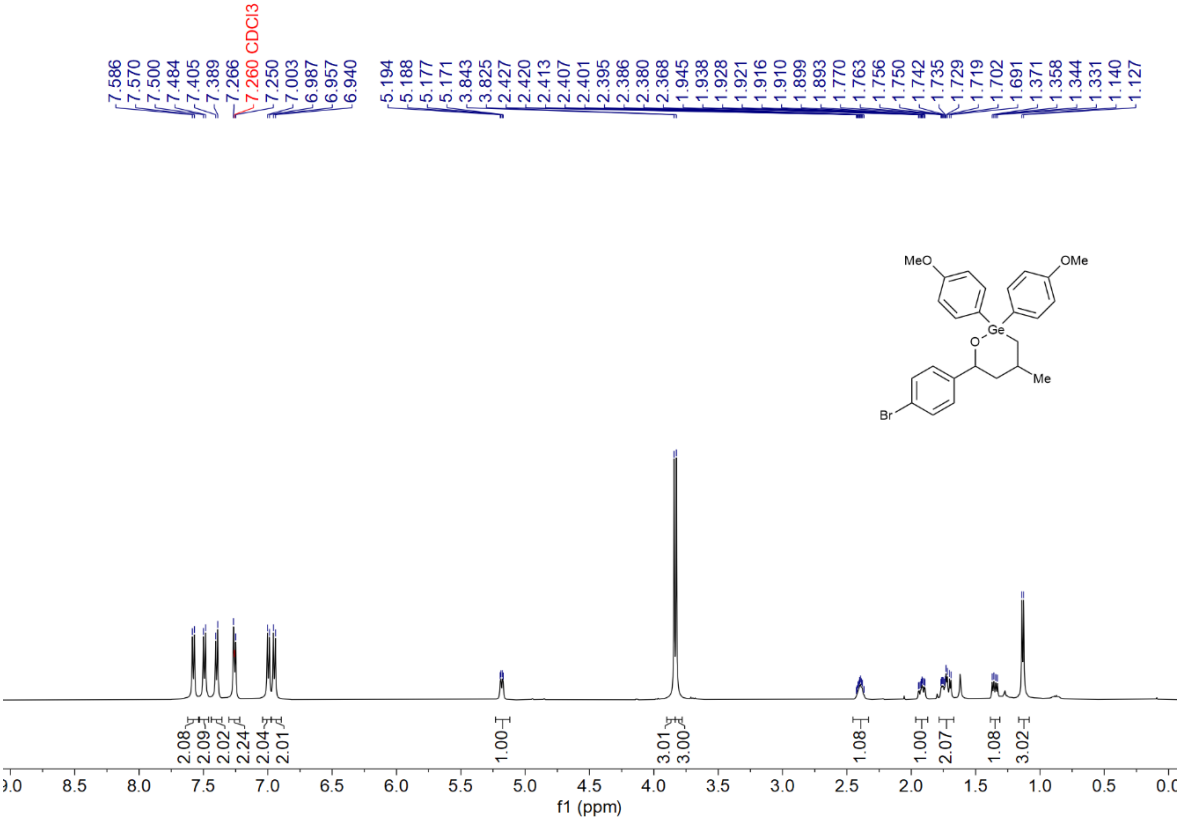
3 ^{1}H NMR (500 MHz, $CDCl_3$)



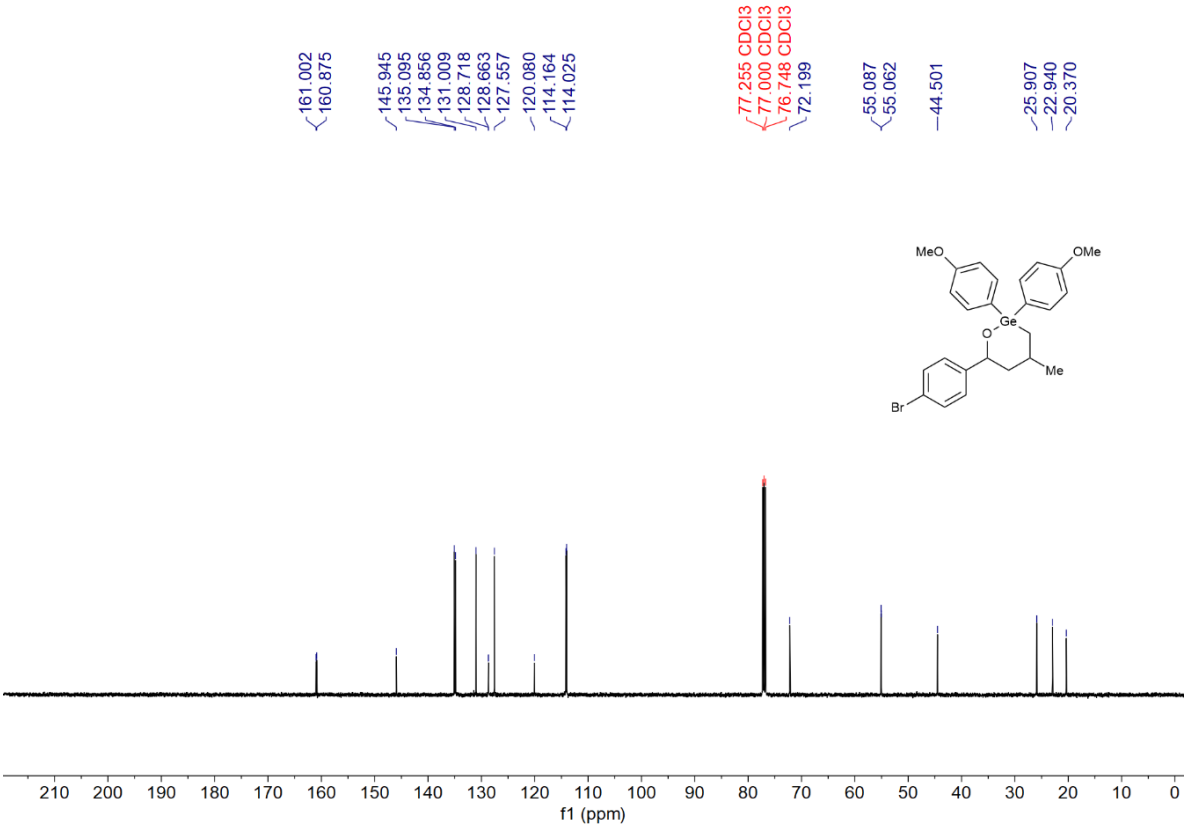
3 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



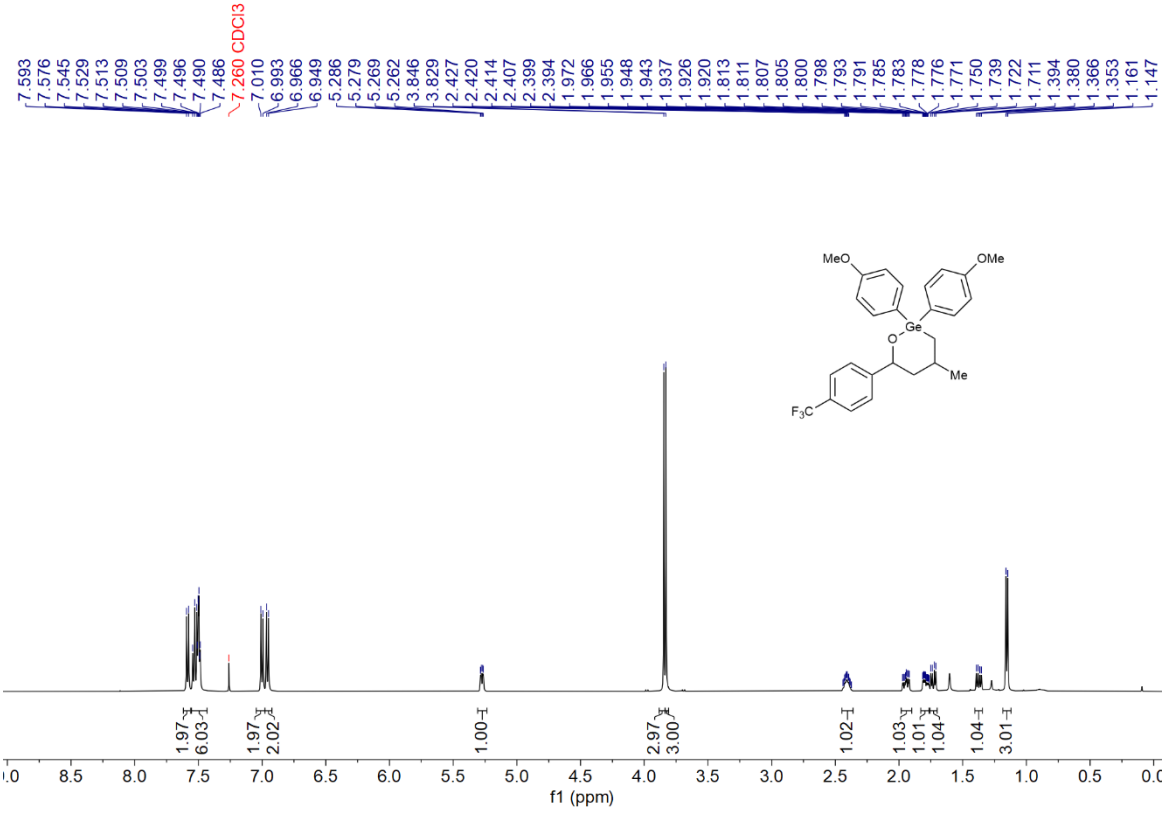
4 ^{1}H NMR (500 MHz, $CDCl_3$)



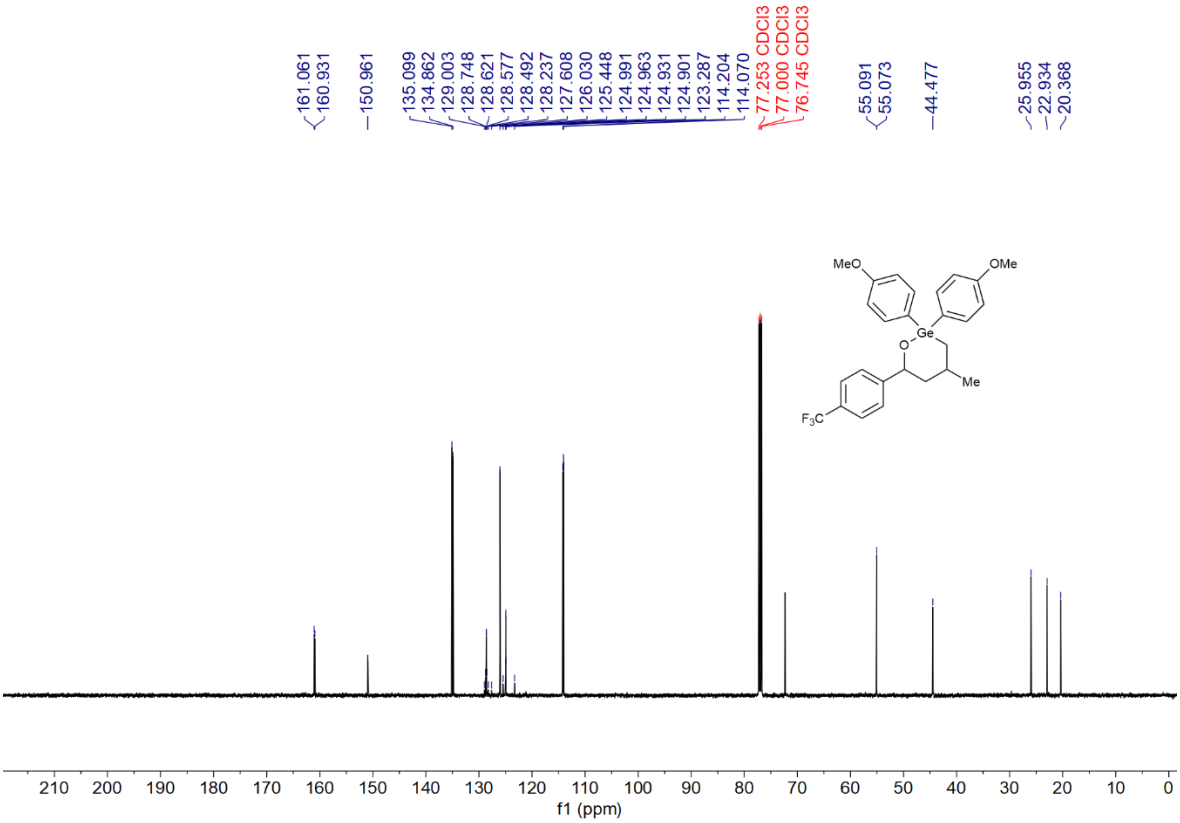
4 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



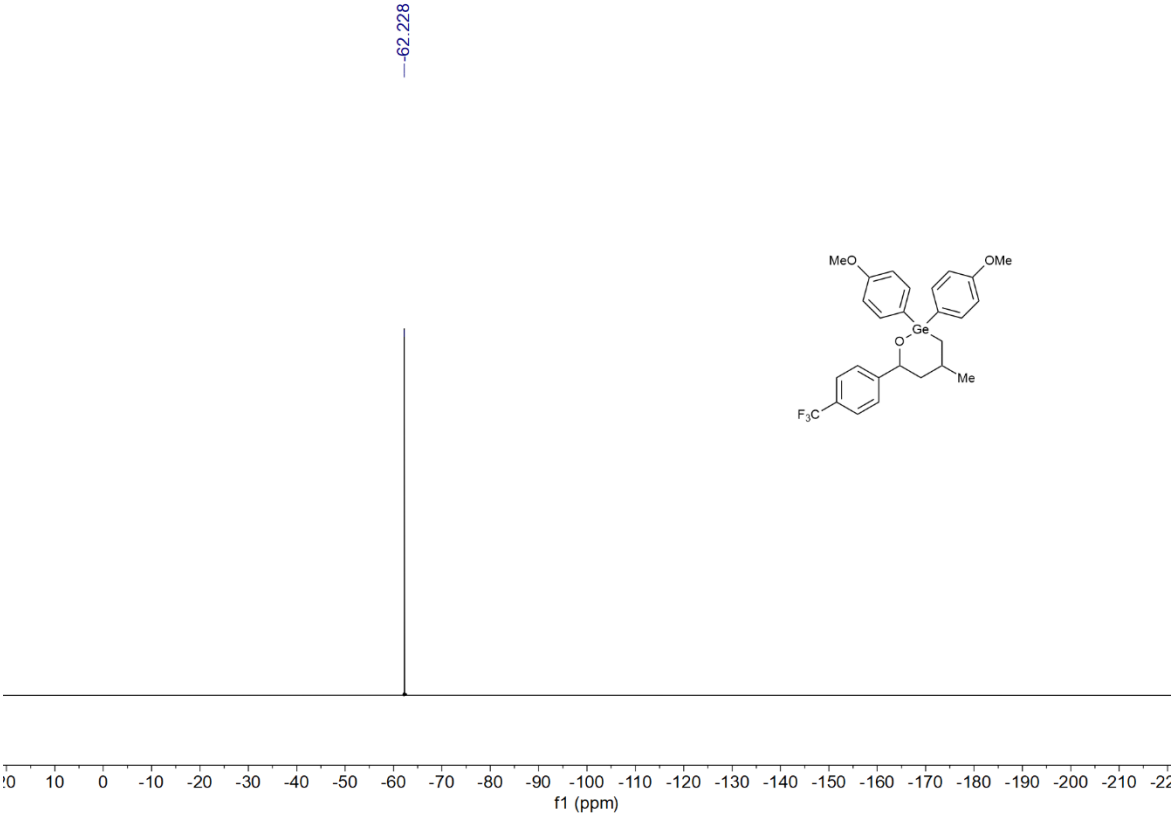
5 ^{1}H NMR (500 MHz, $CDCl_3$)



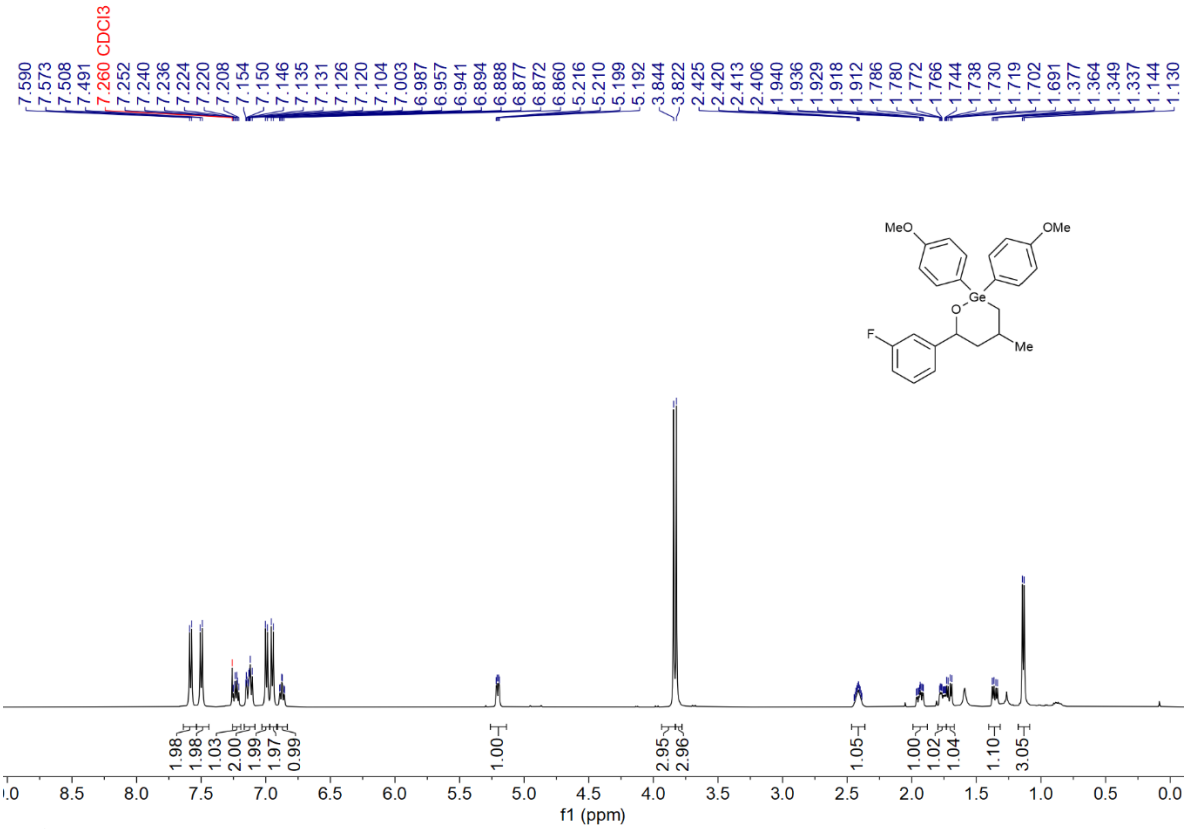
5 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



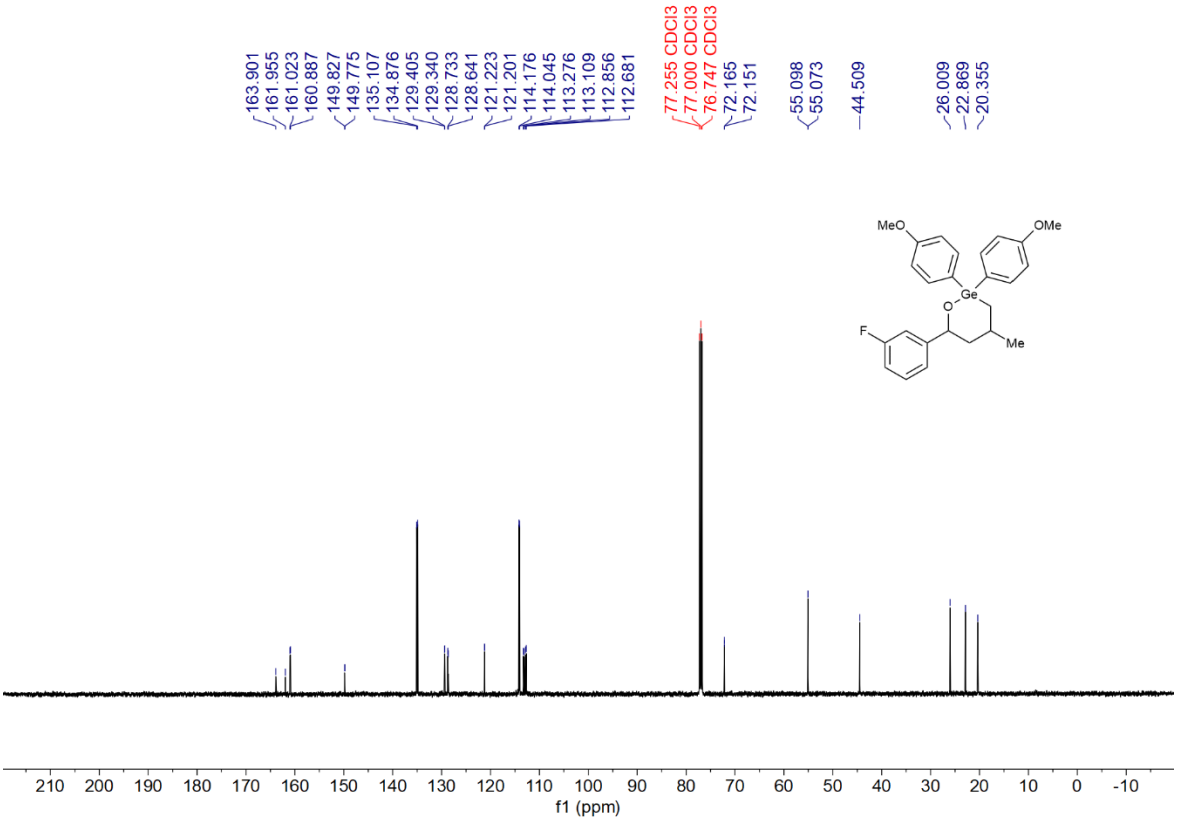
5 $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



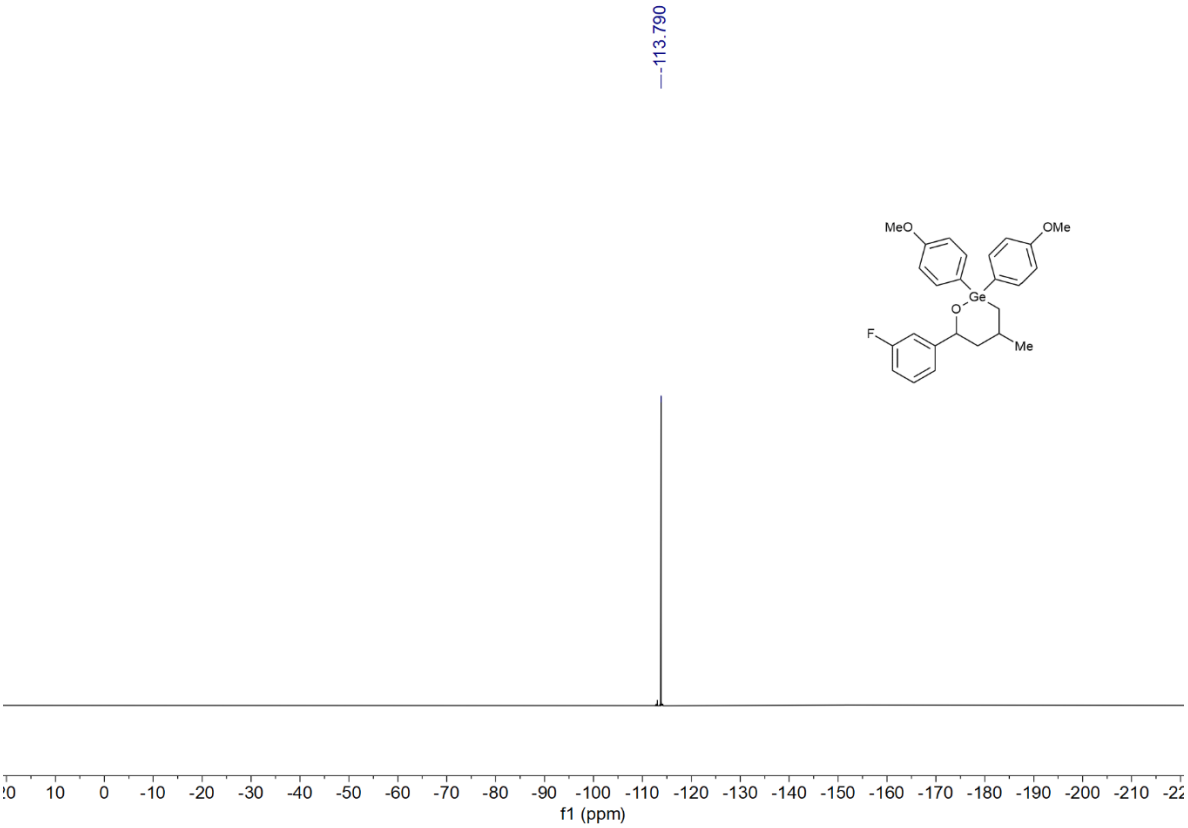
6 ^{1}H NMR (500 MHz, $CDCl_3$)



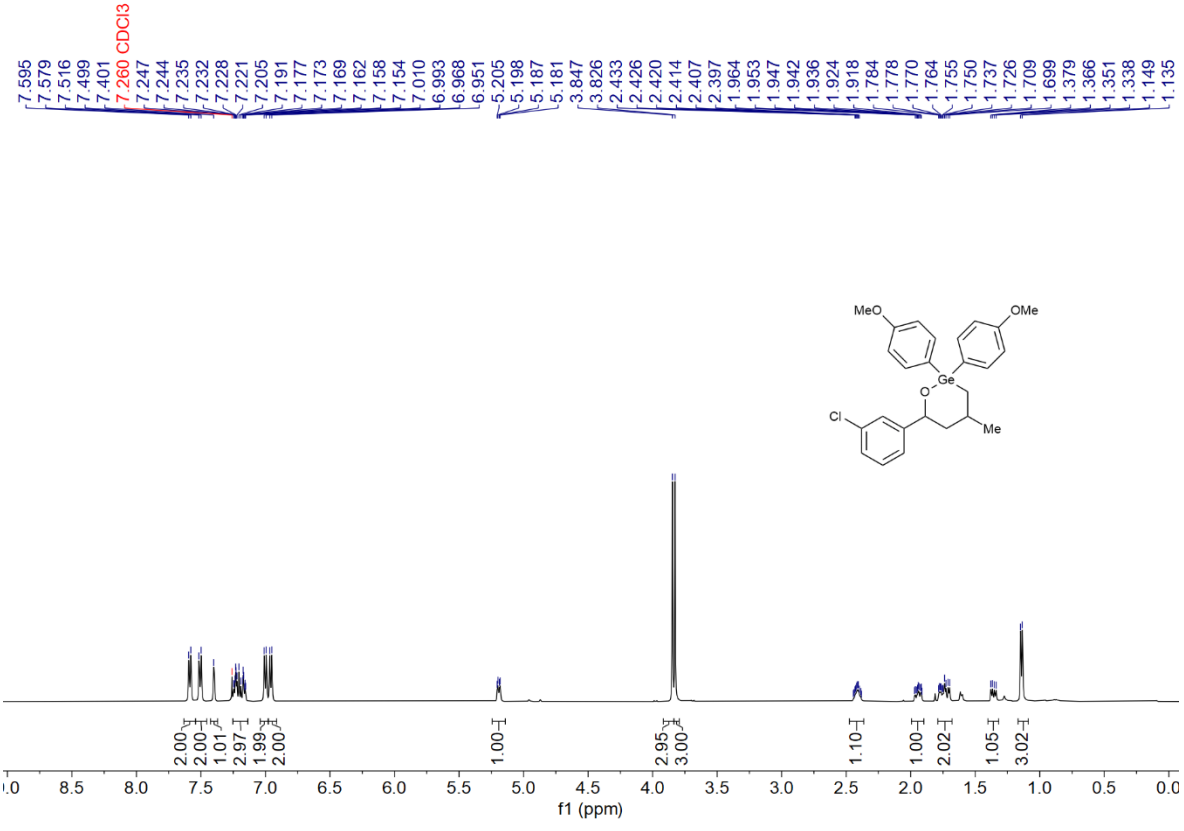
6 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



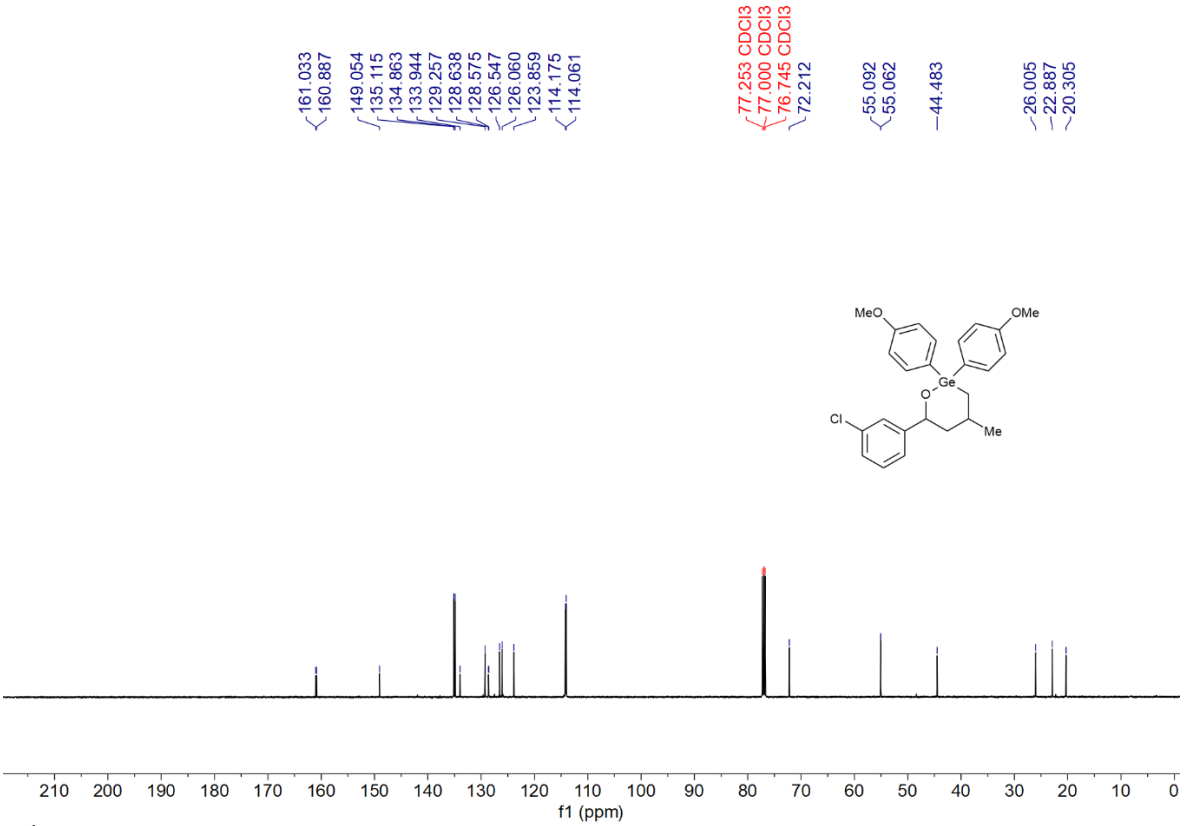
6 $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



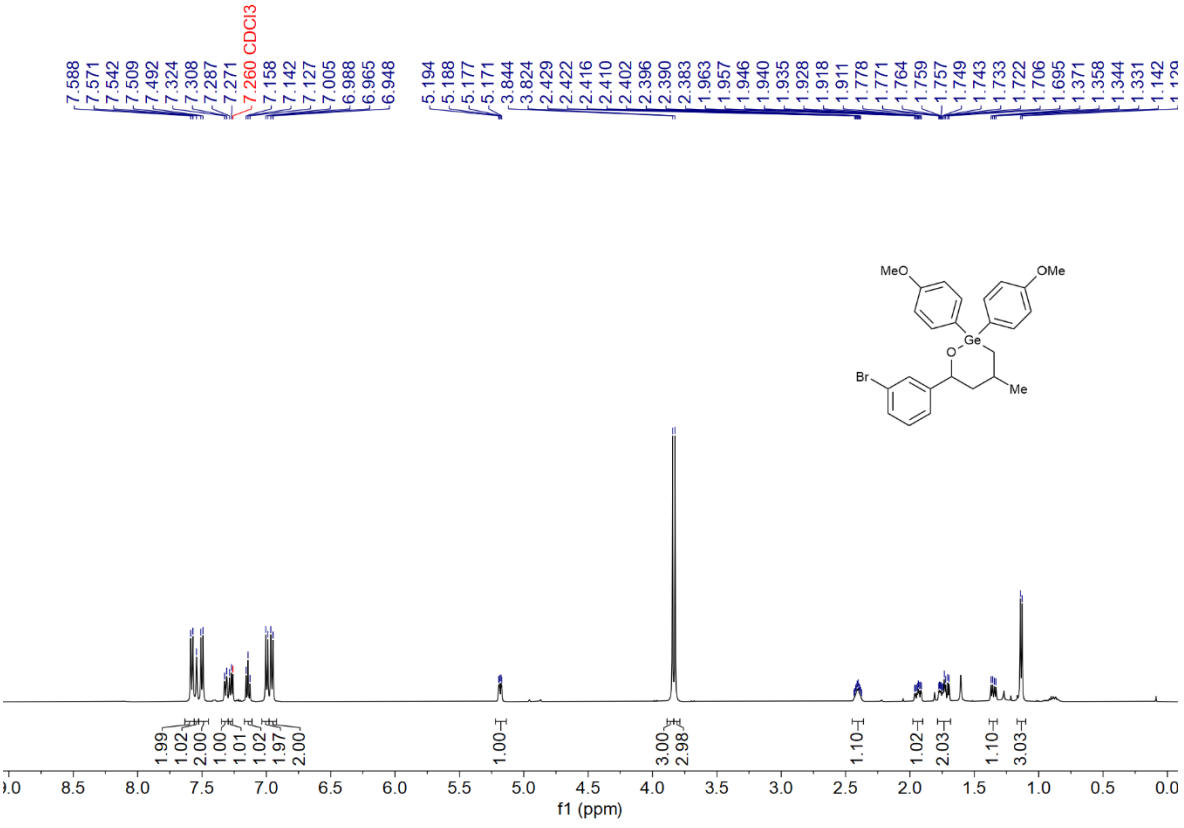
7 ^{1}H NMR (500 MHz, $CDCl_3$)



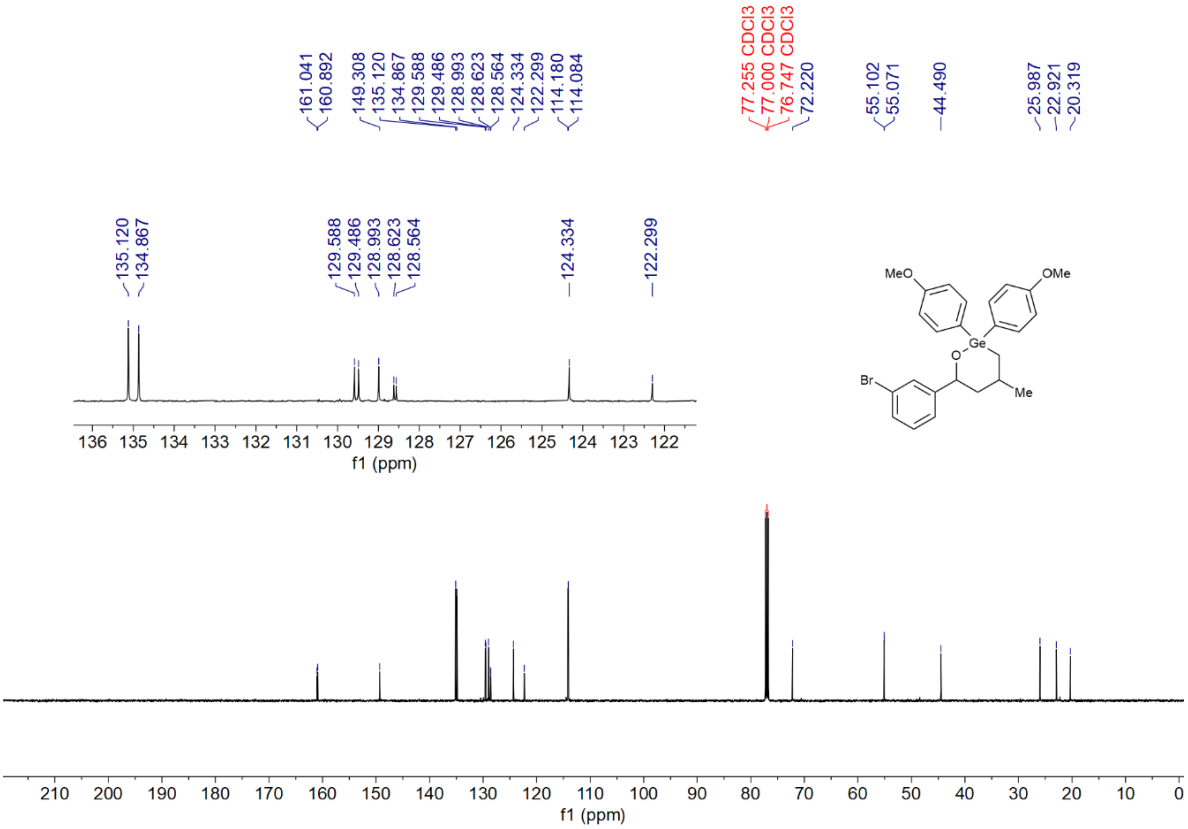
7 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



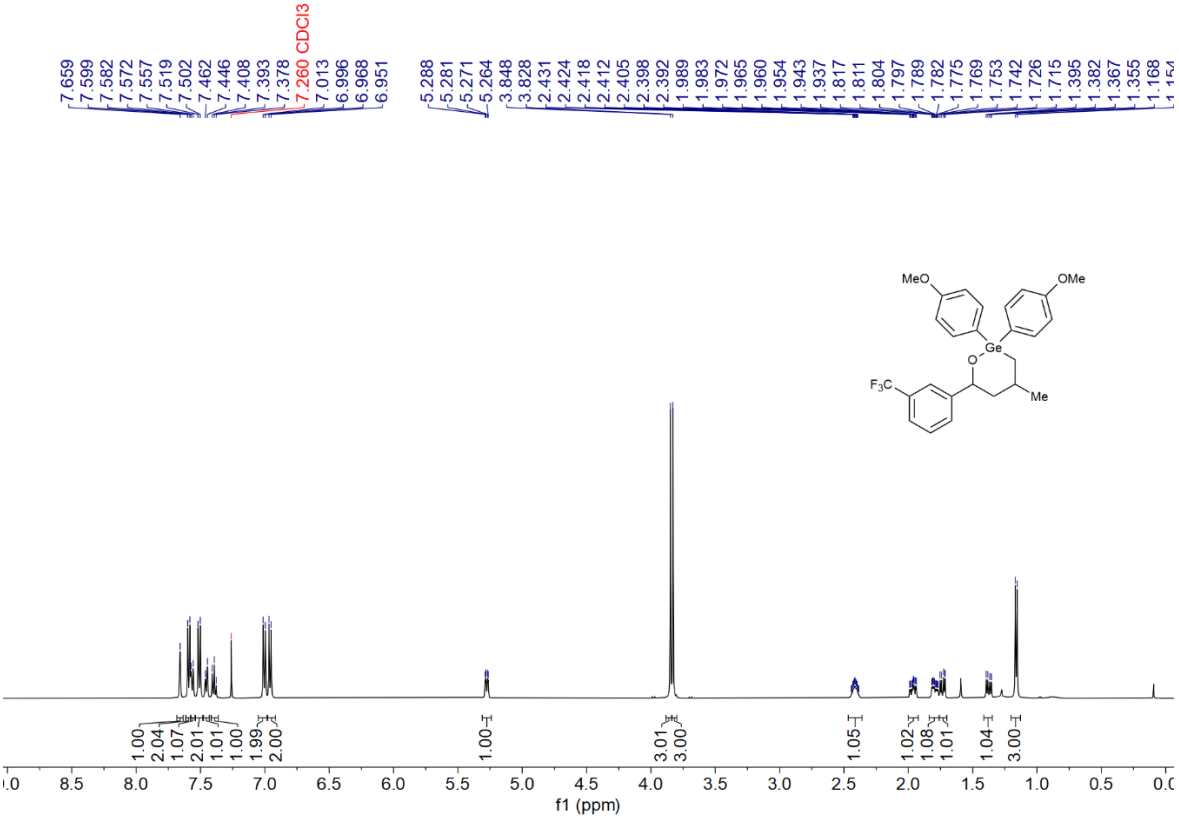
8 ^{1}H NMR (500 MHz, $CDCl_3$)



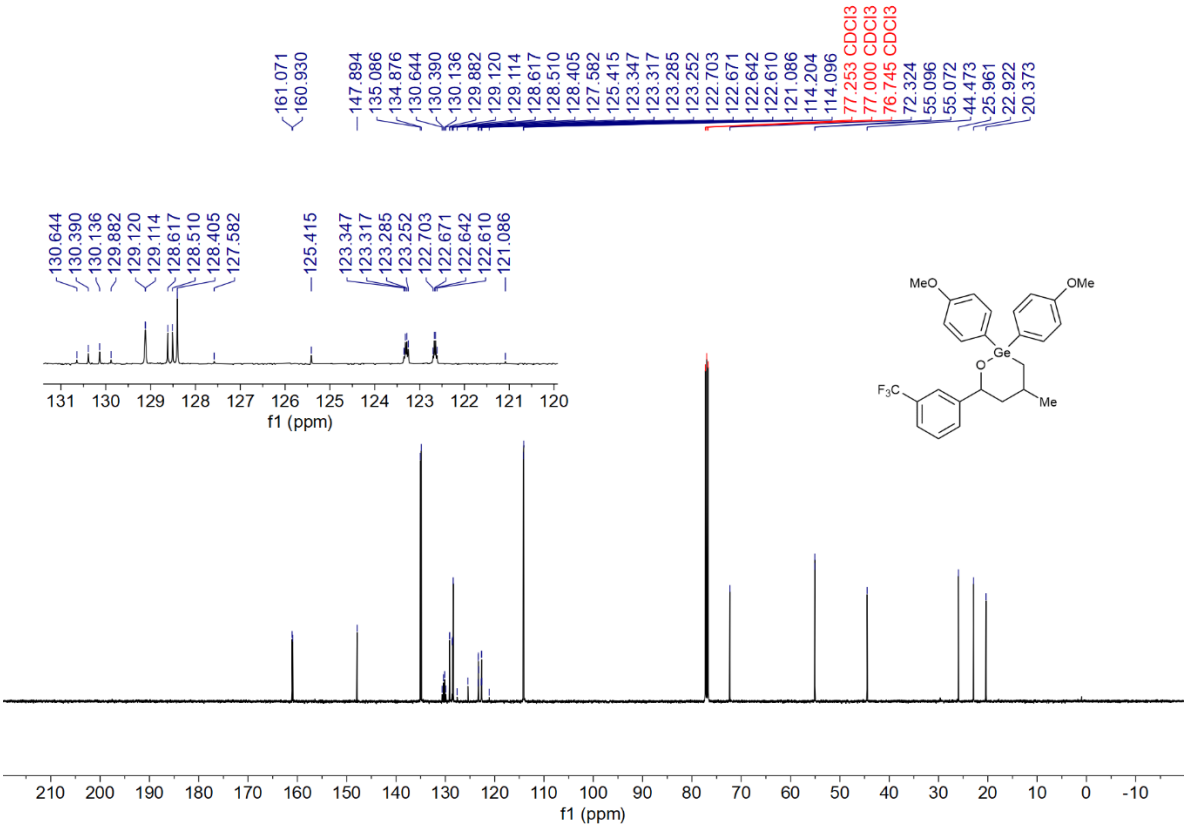
8 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



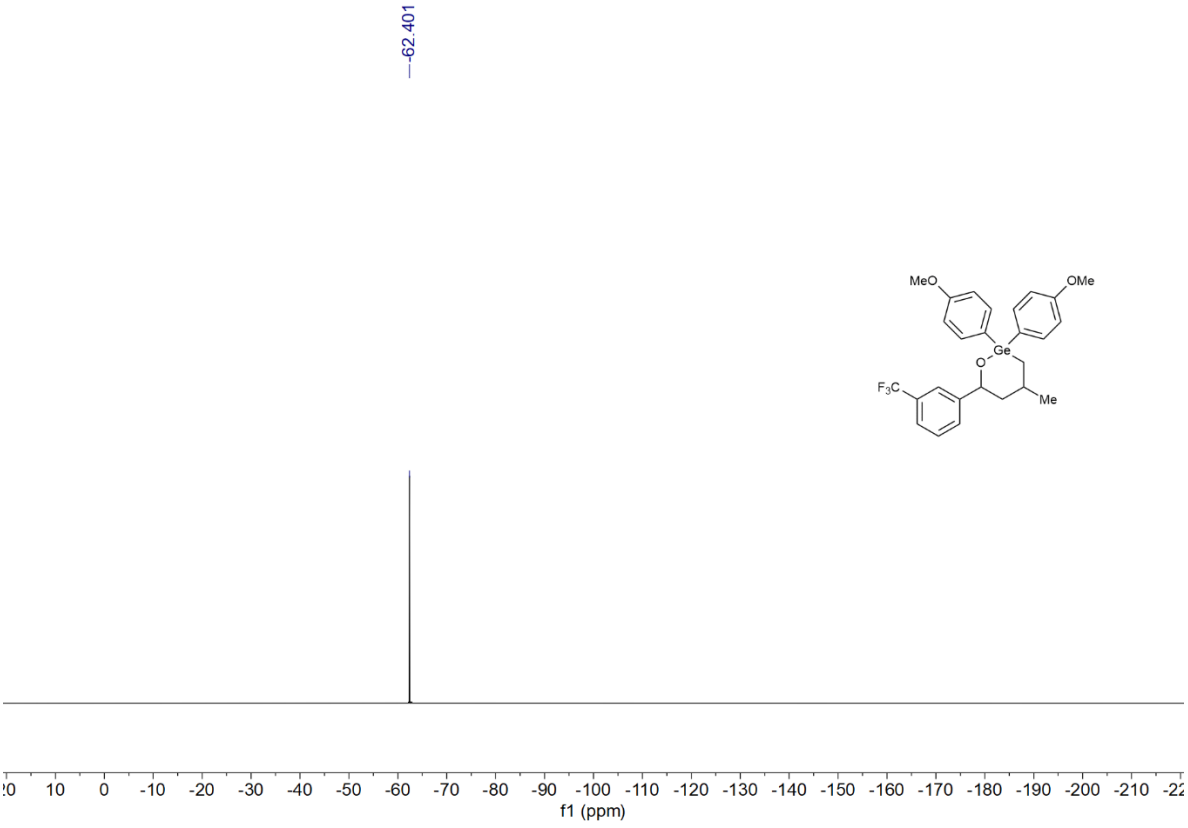
9 ^{1}H NMR (500 MHz, $CDCl_3$)



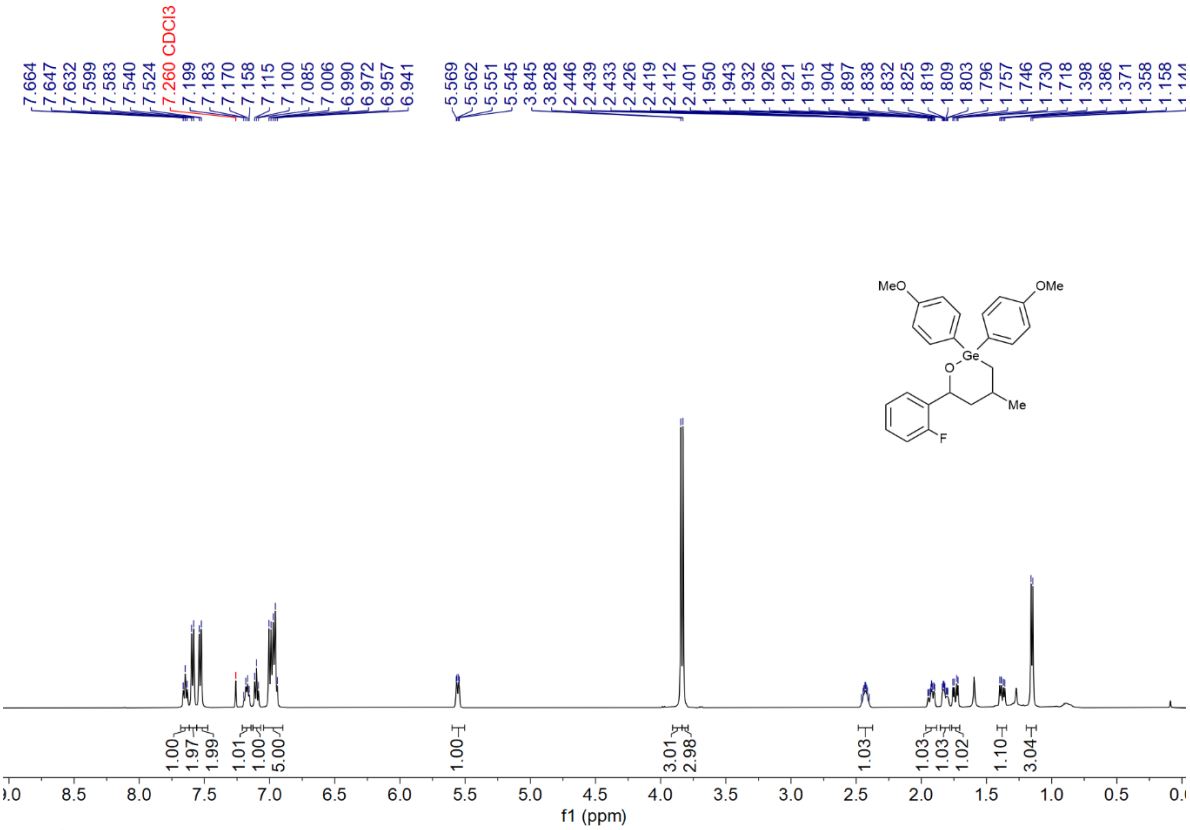
9 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



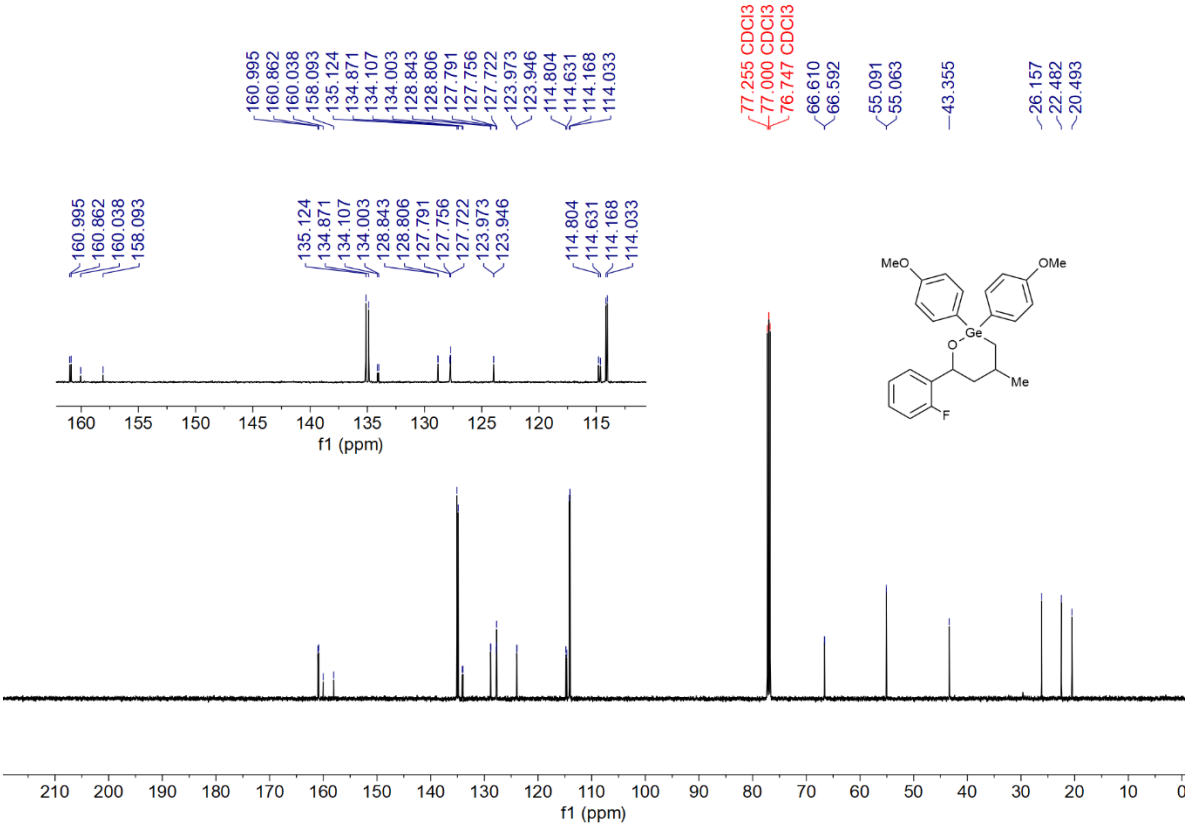
9 $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



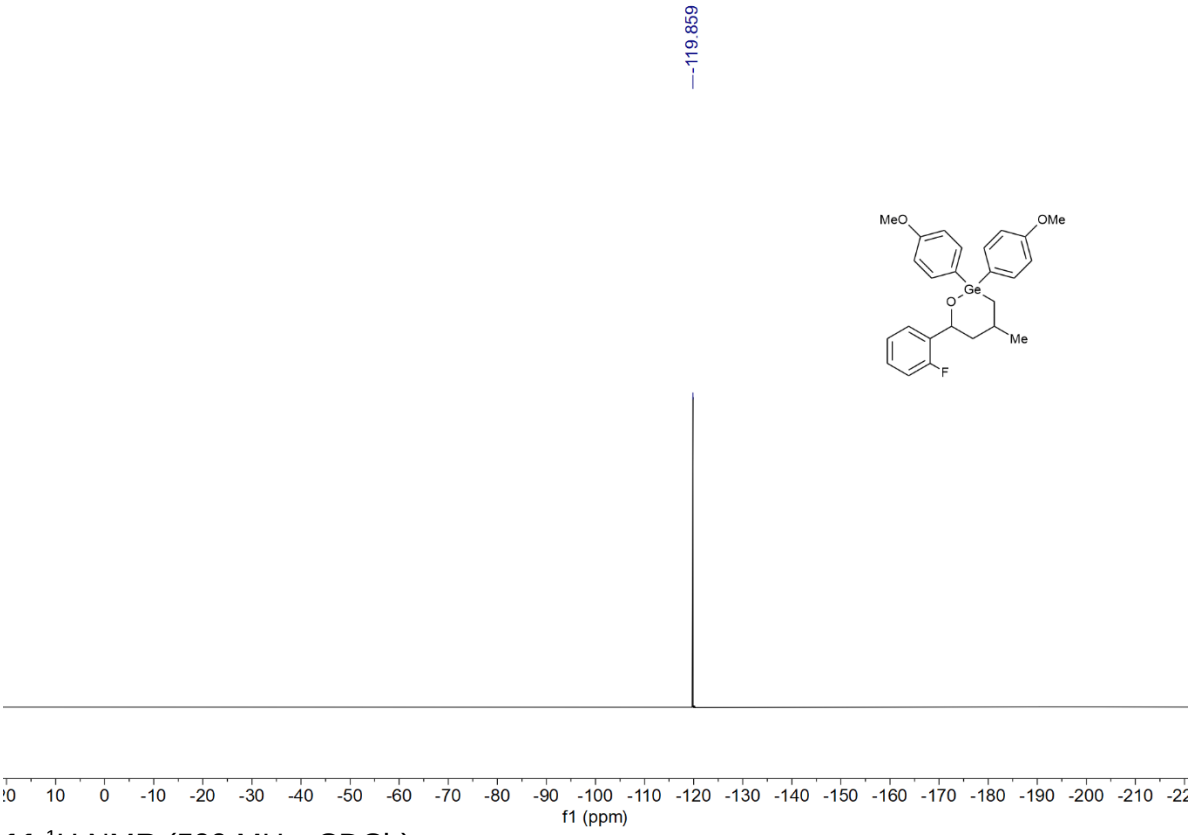
10 ^{1}H NMR (500 MHz, $CDCl_3$)



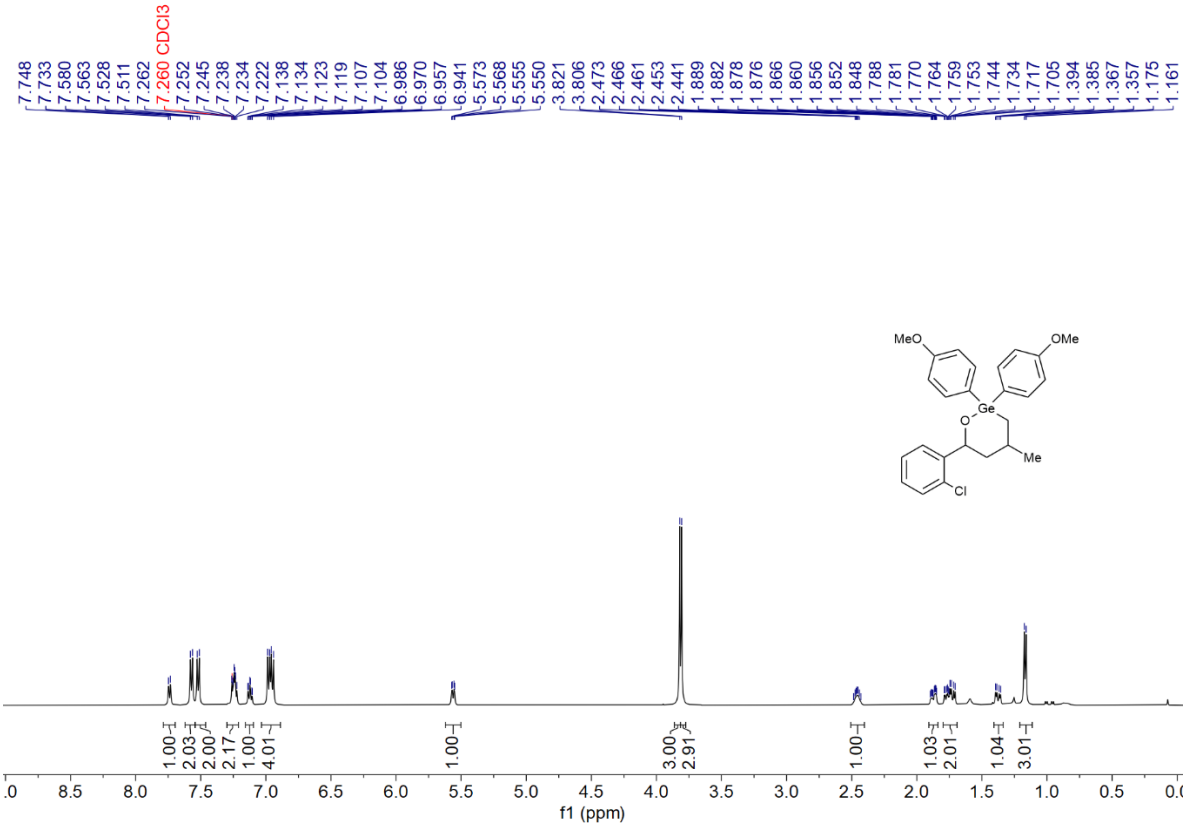
10 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



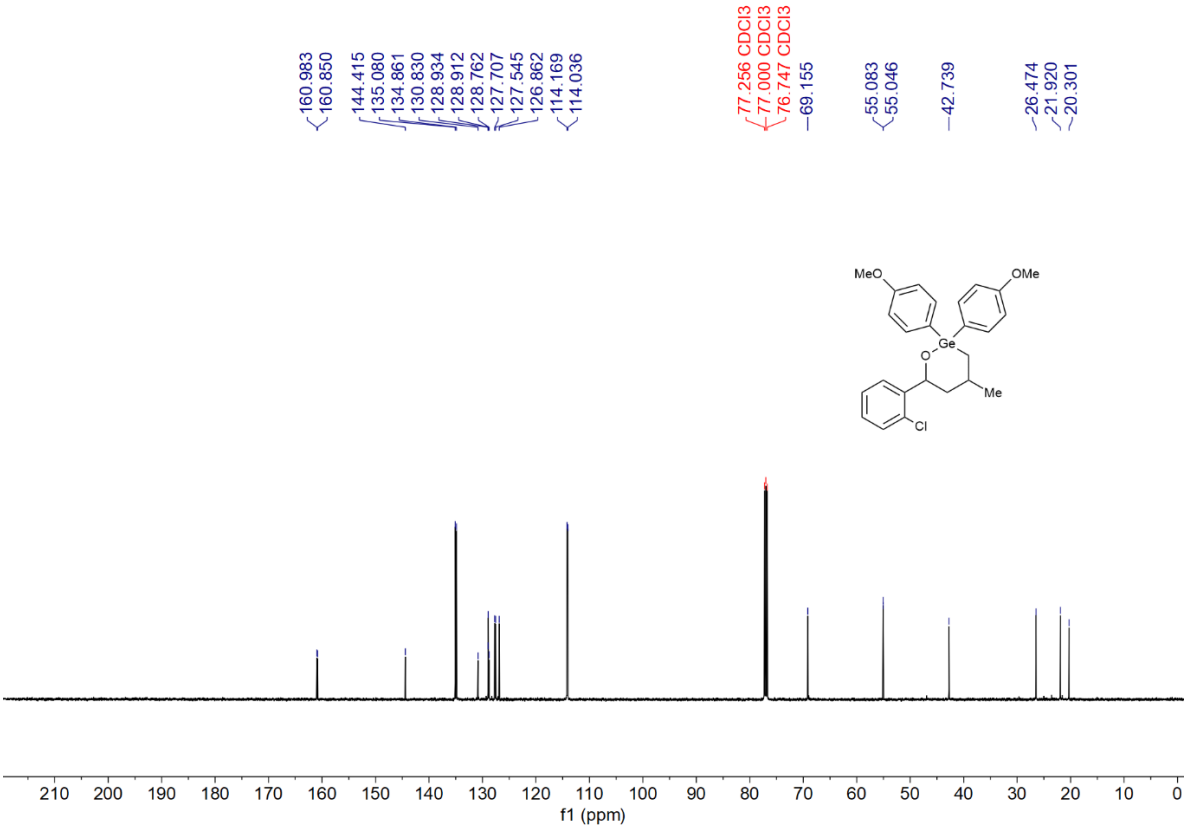
10 $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



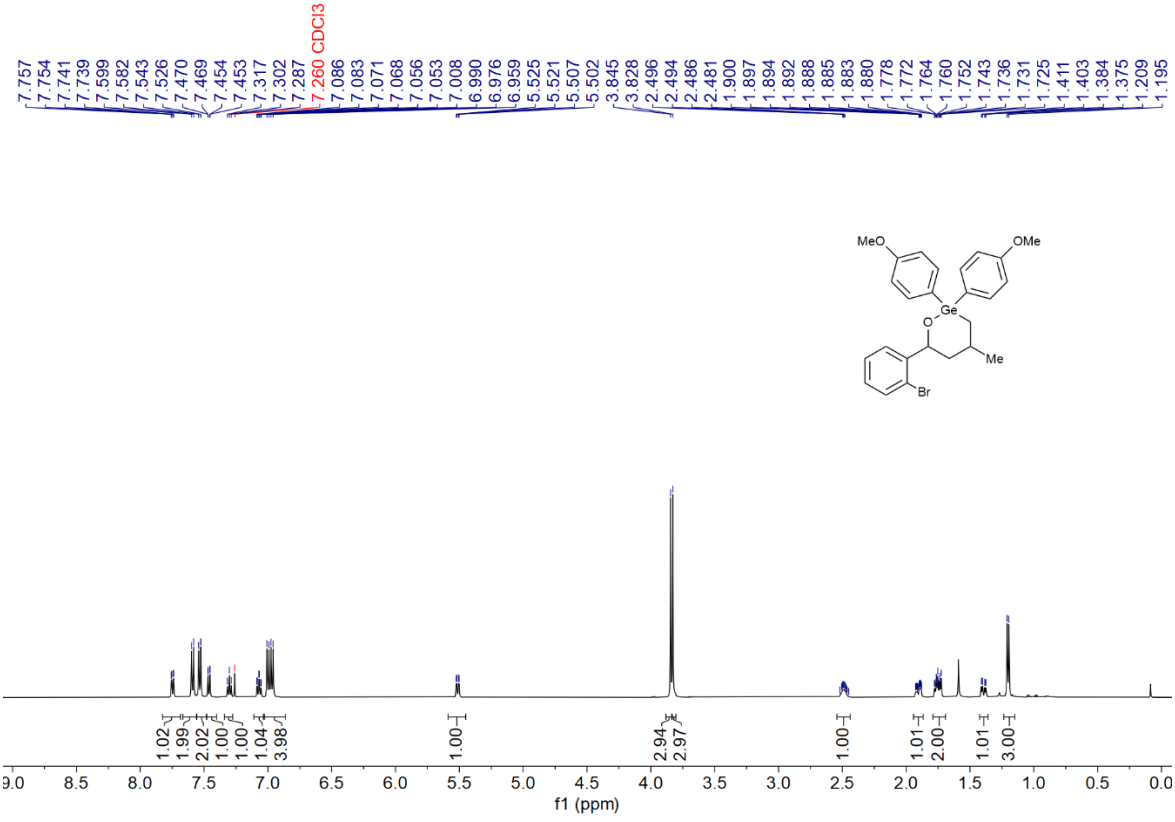
11 ^{1}H NMR (500 MHz, $CDCl_3$)



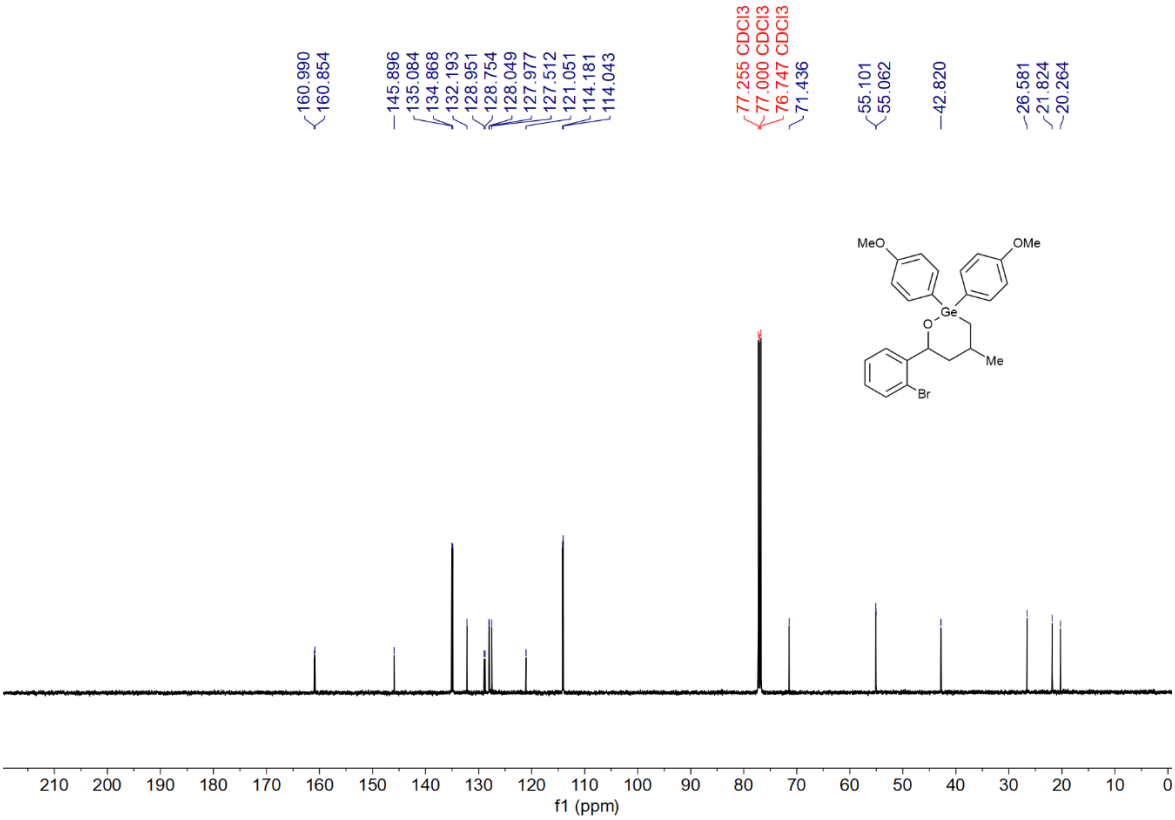
11 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



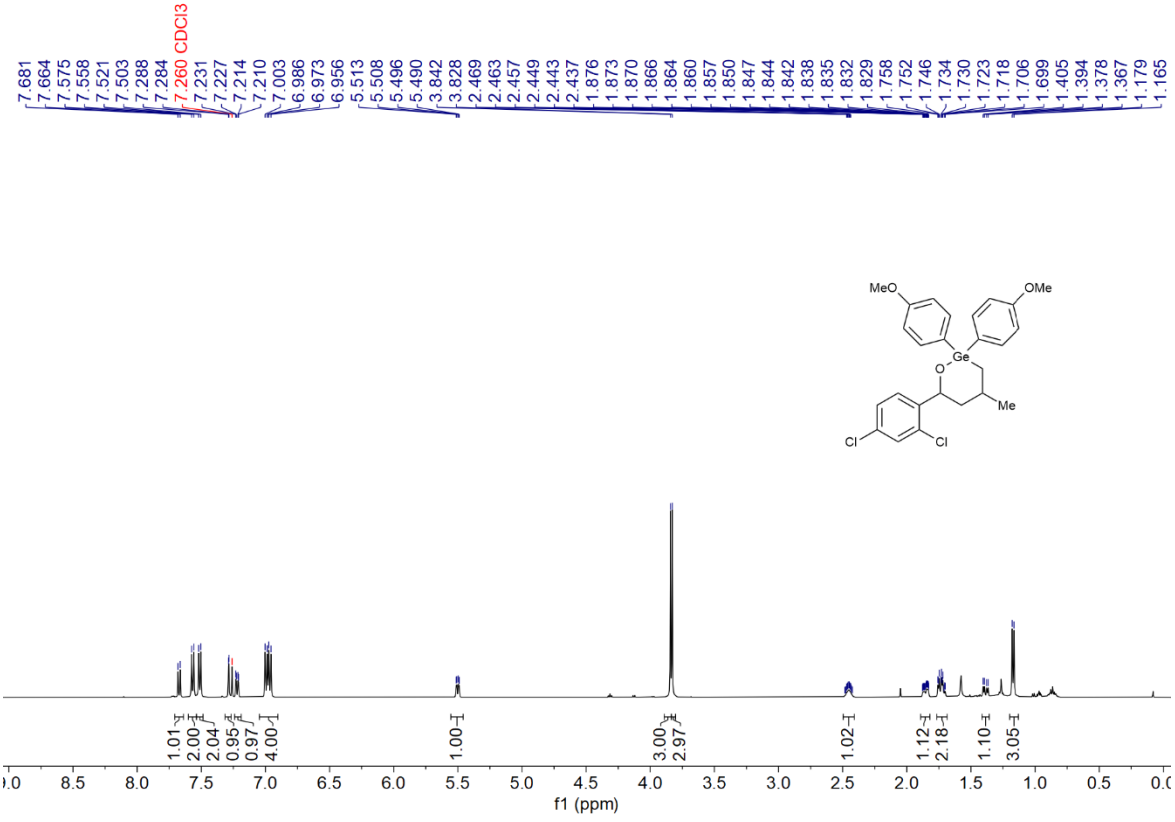
12 ^{1}H NMR (500 MHz, $CDCl_3$)



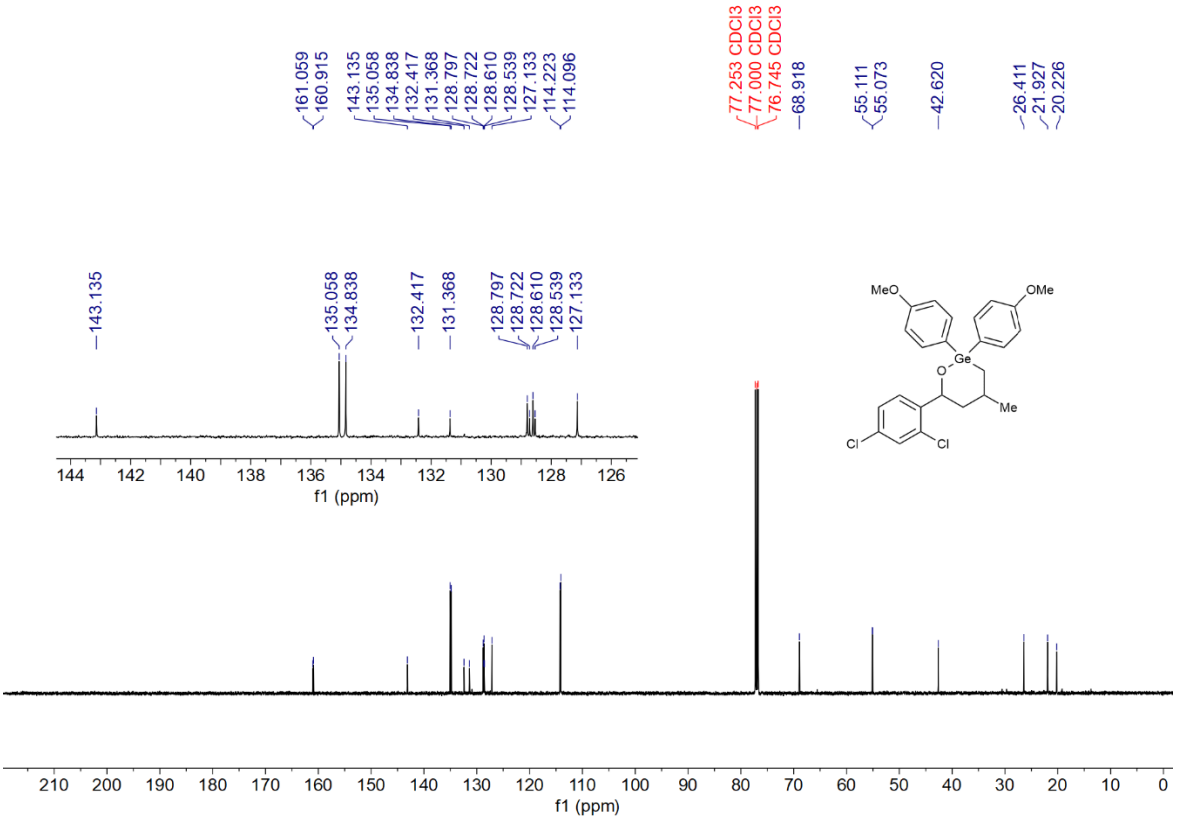
12 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



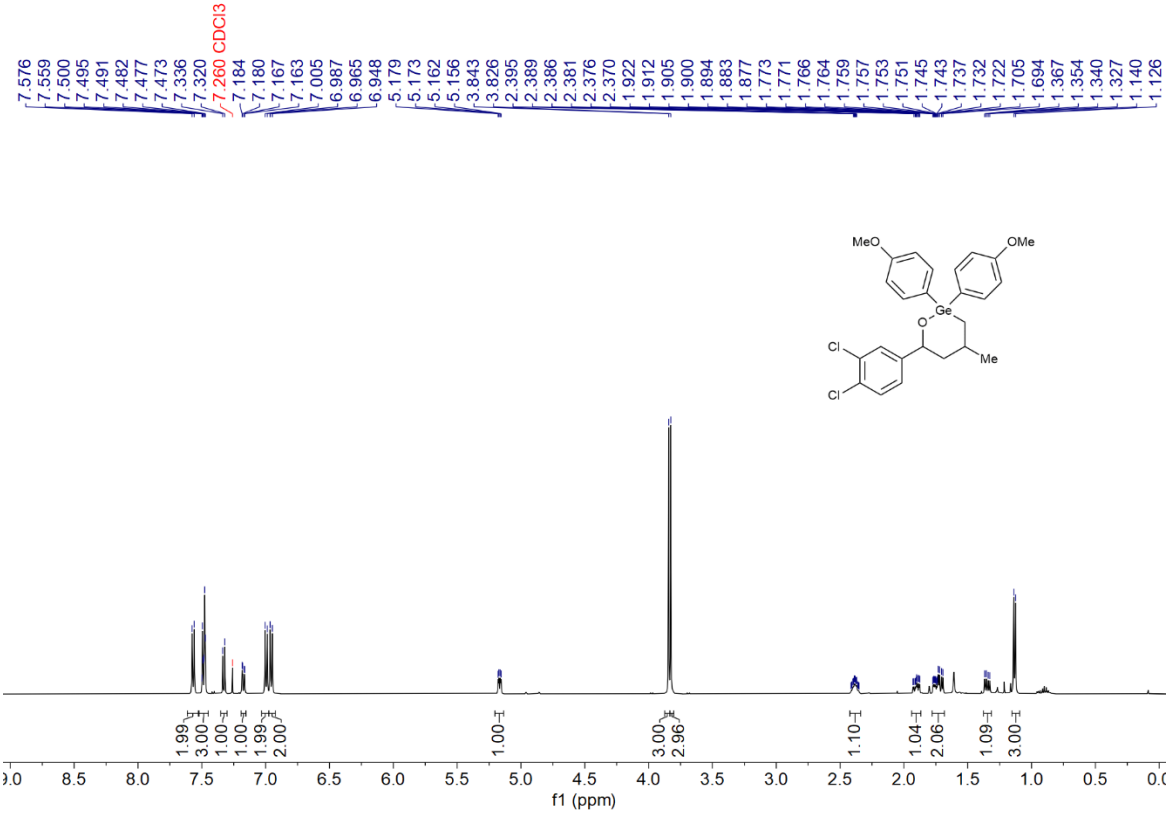
13 ^{1}H NMR (500 MHz, $CDCl_3$)



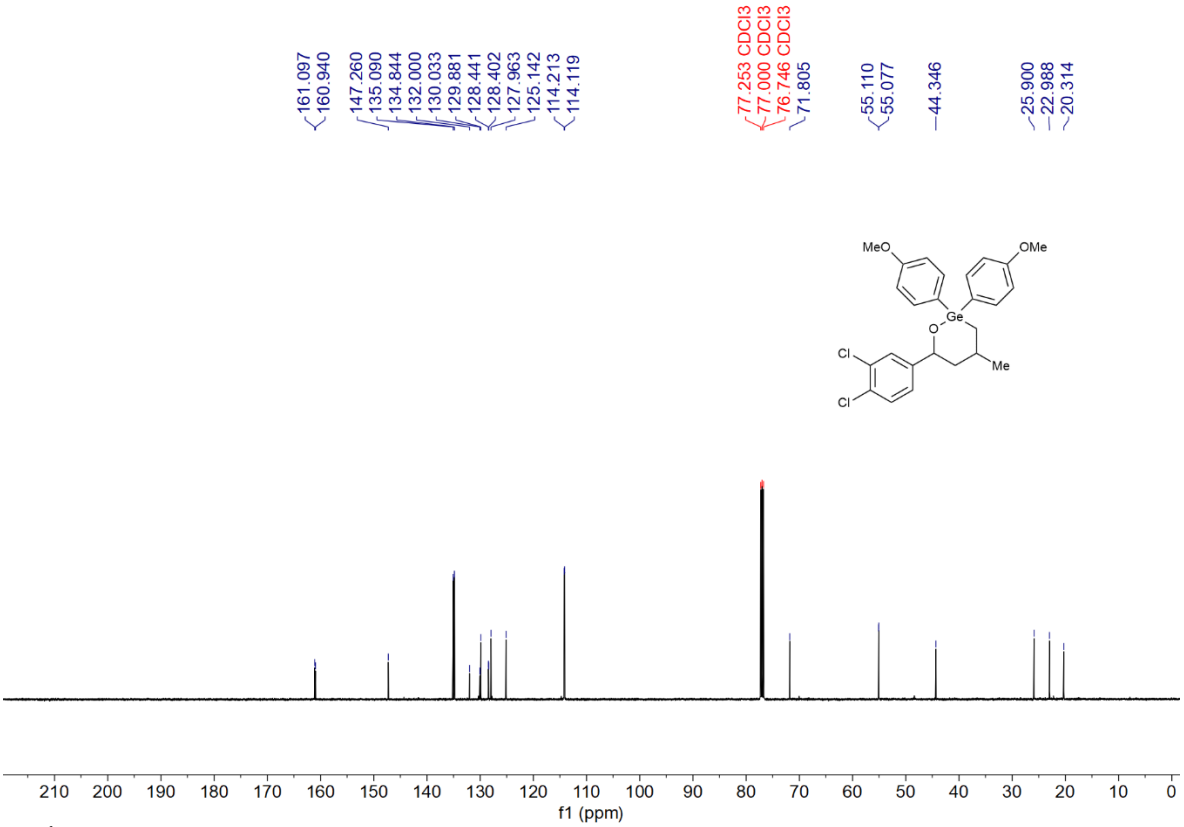
13 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



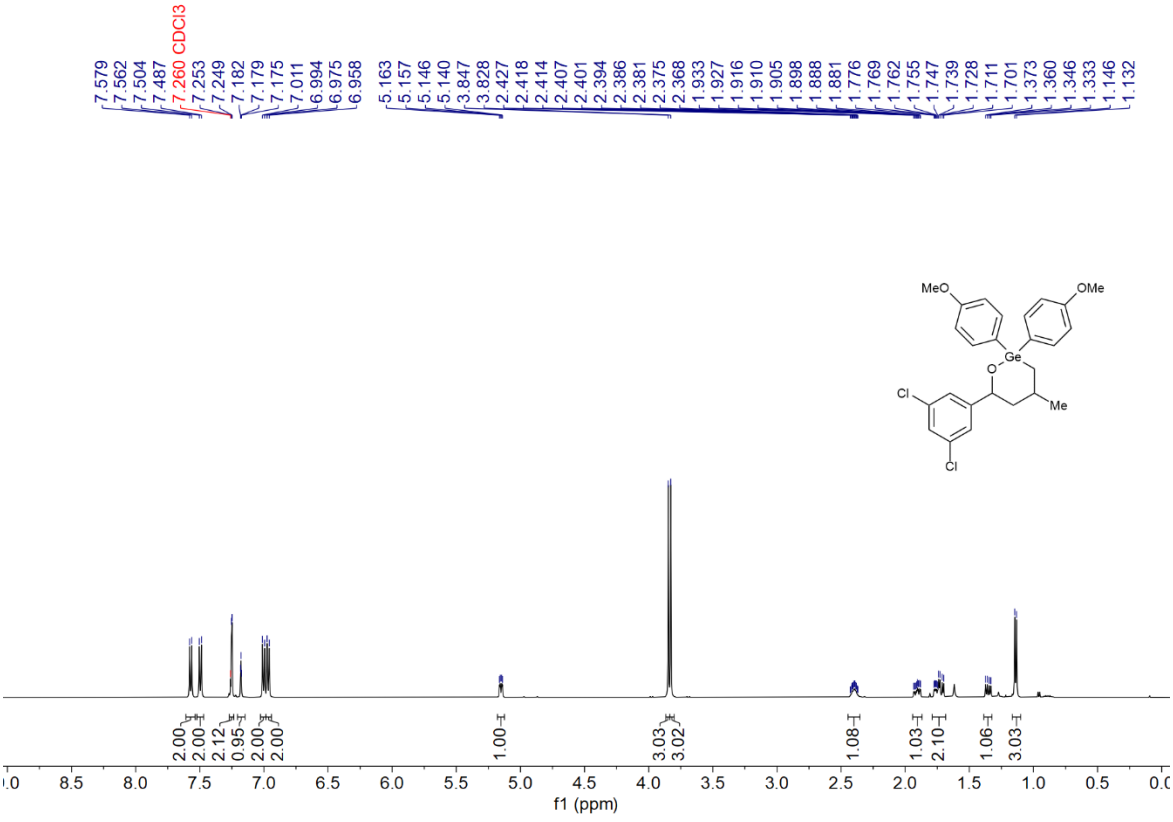
14 ^{1}H NMR (500 MHz, $CDCl_3$)



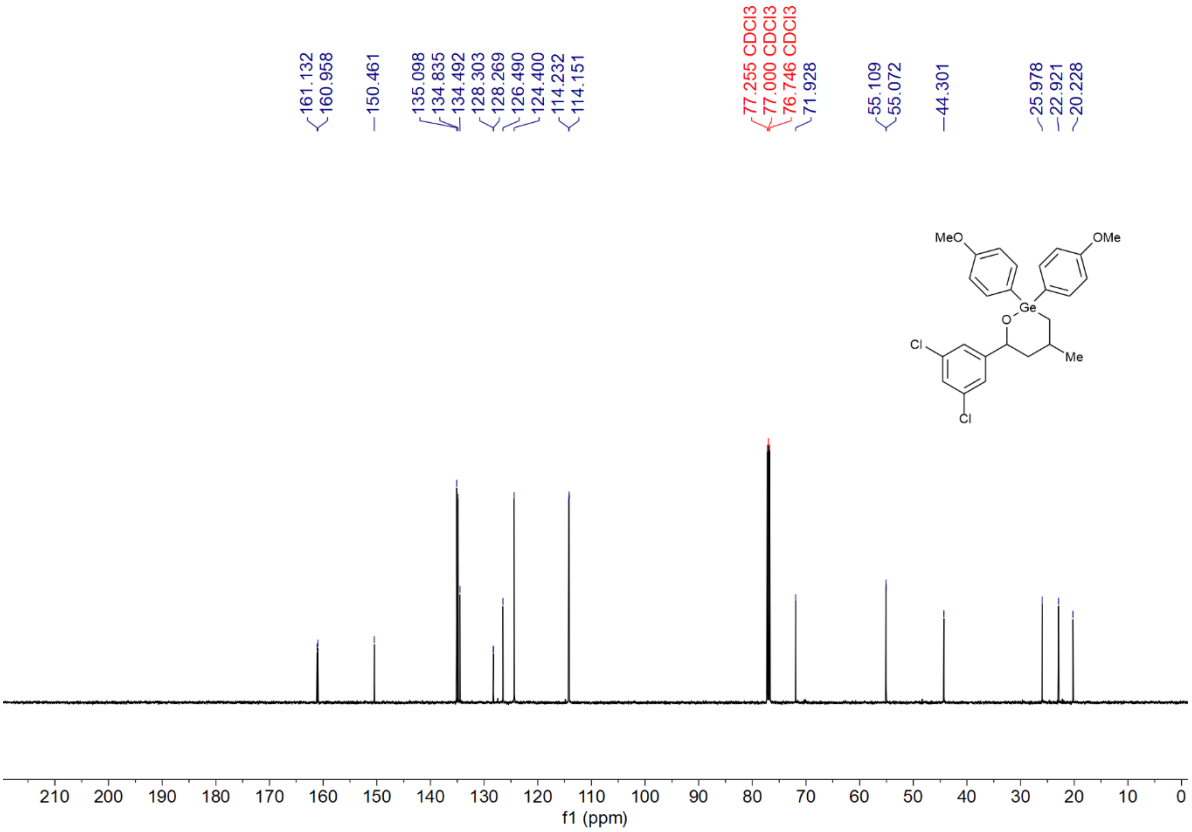
14 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



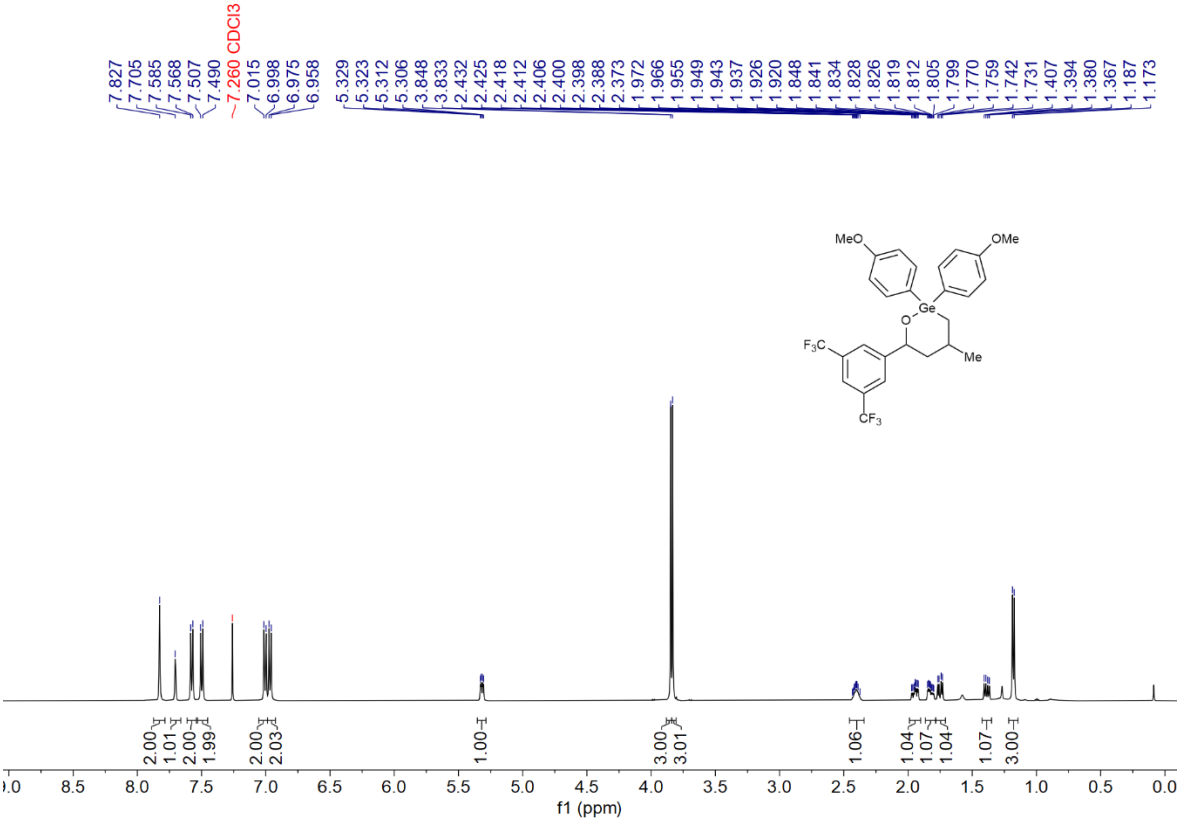
15 ^{1}H NMR (500 MHz, $CDCl_3$)



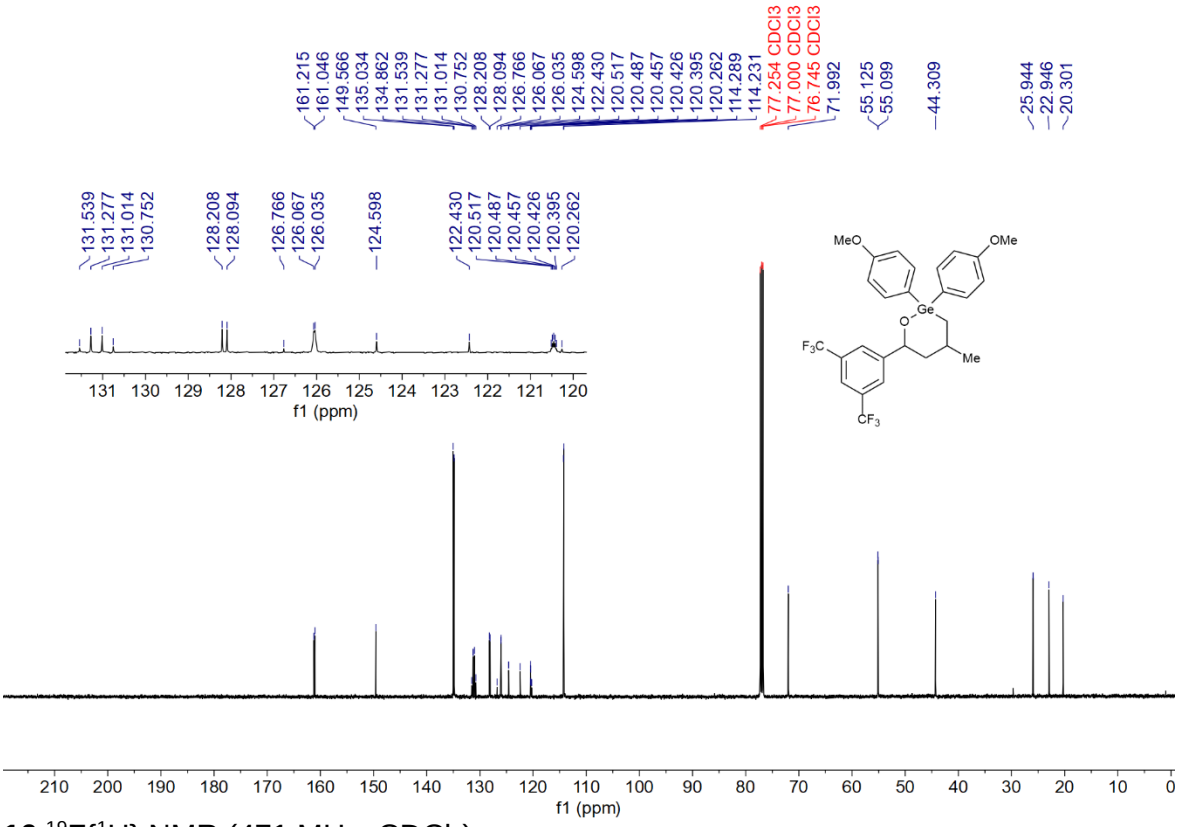
15 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



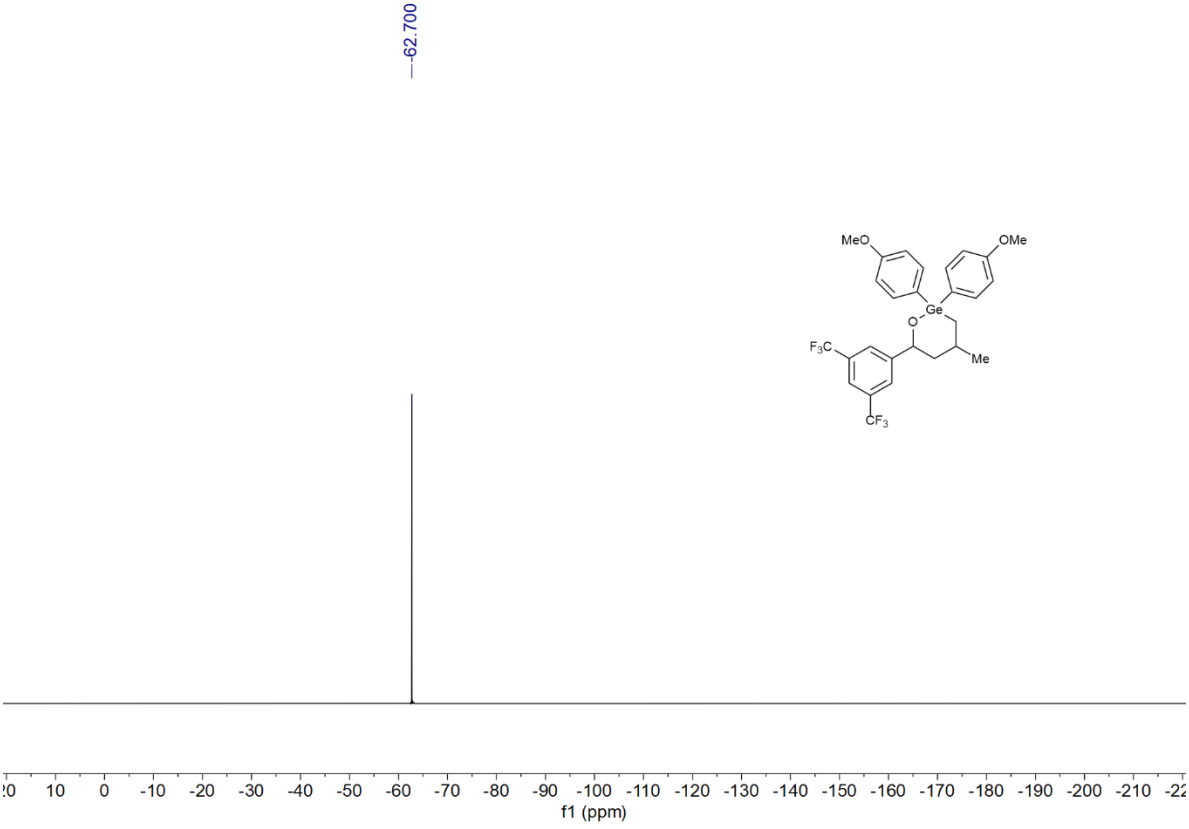
16 ^{1}H NMR (500 MHz, $CDCl_3$)



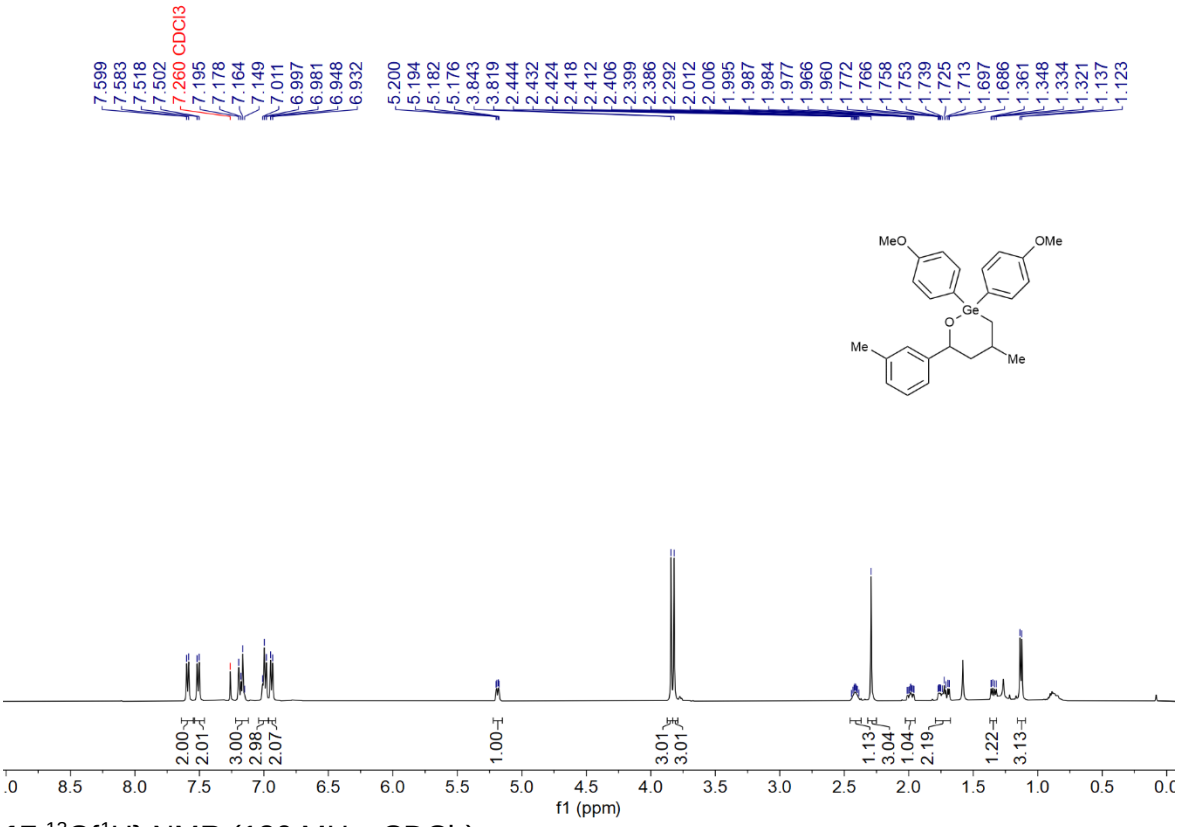
16 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



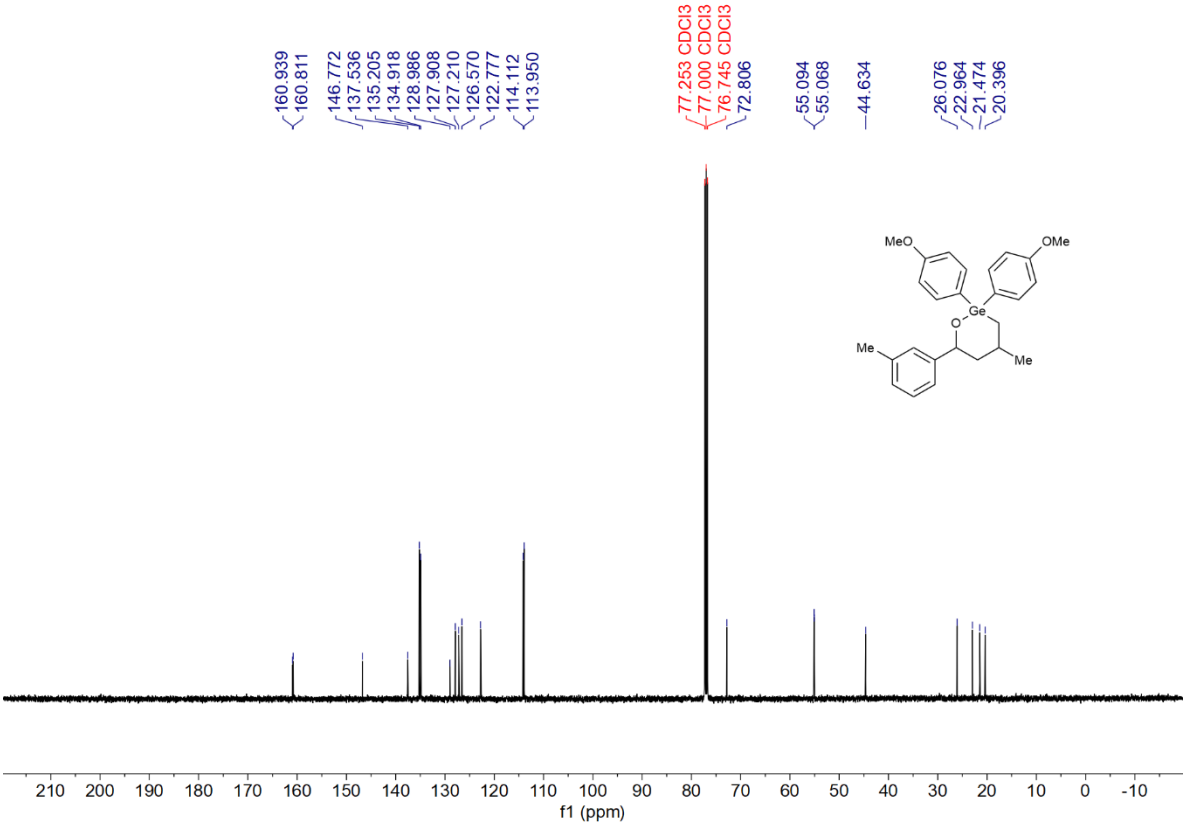
16 $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$)



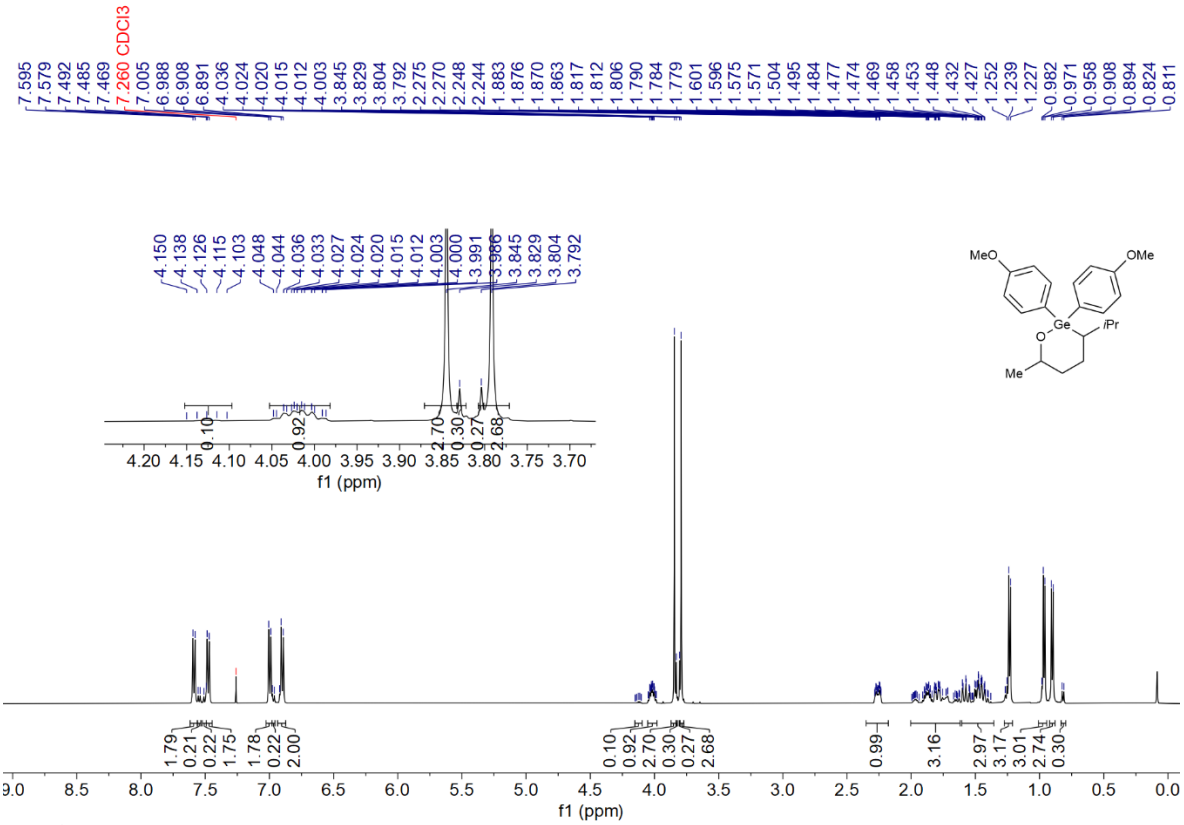
17 ^{1}H NMR (500 MHz, $CDCl_3$)



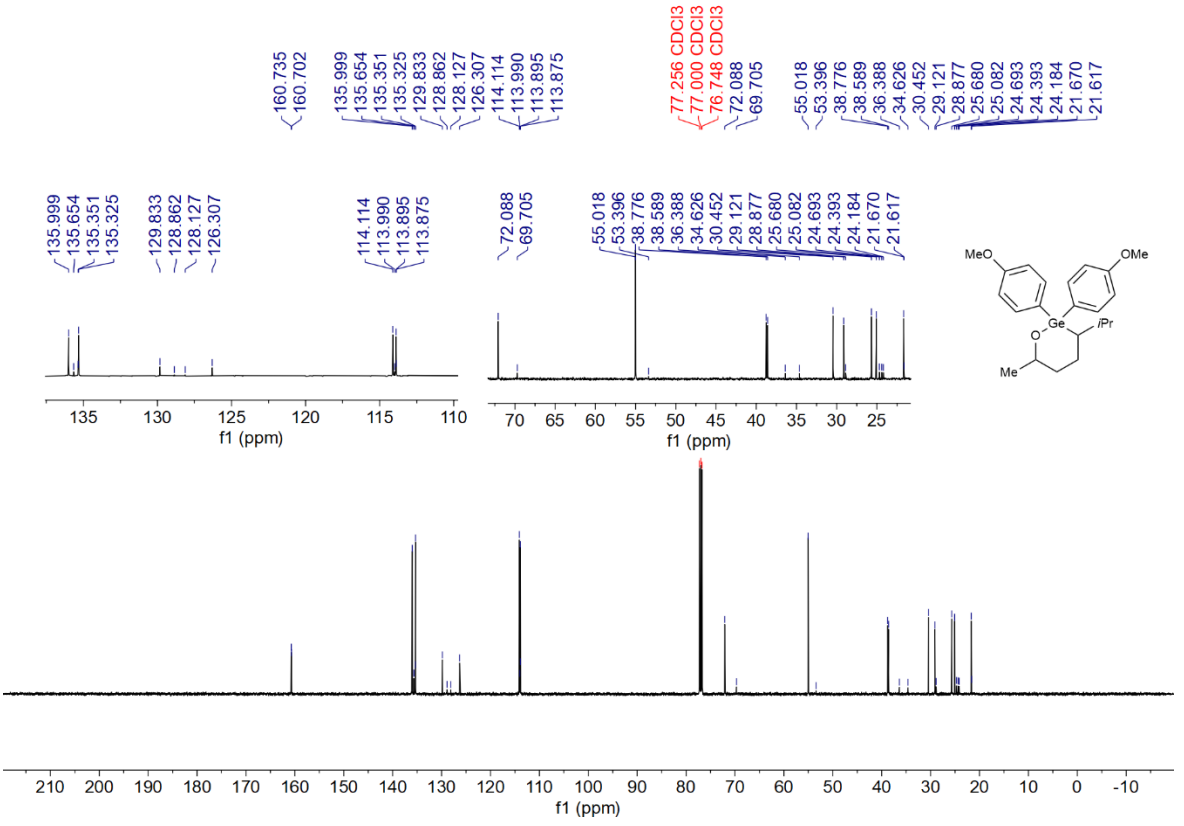
17 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



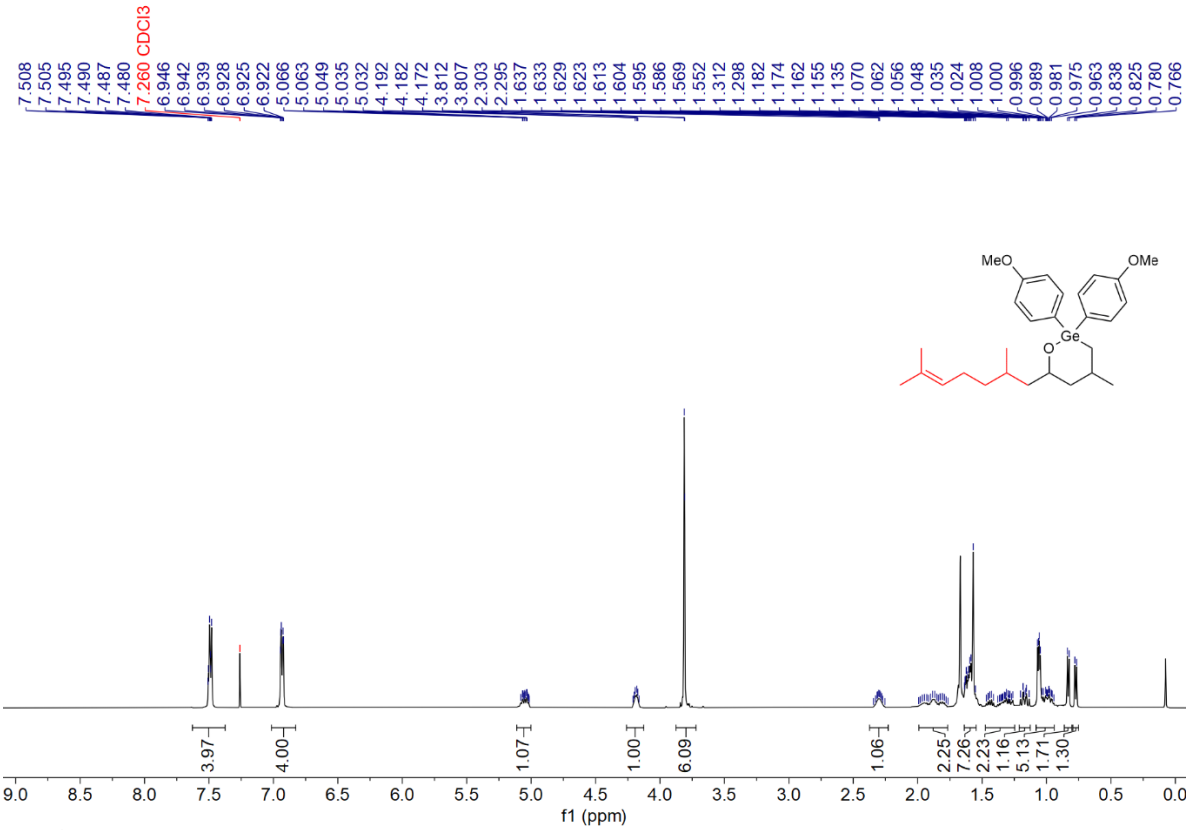
18 ^{1}H NMR (500 MHz, $CDCl_3$)



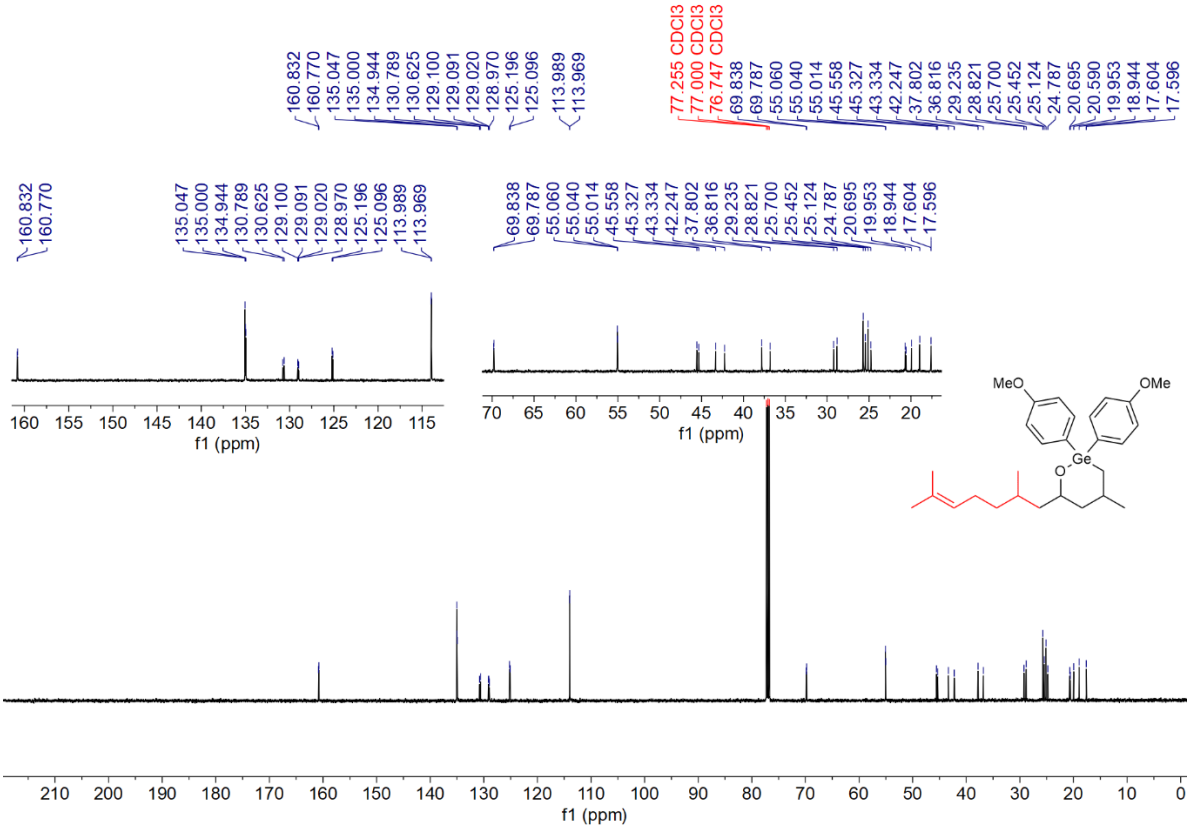
18 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



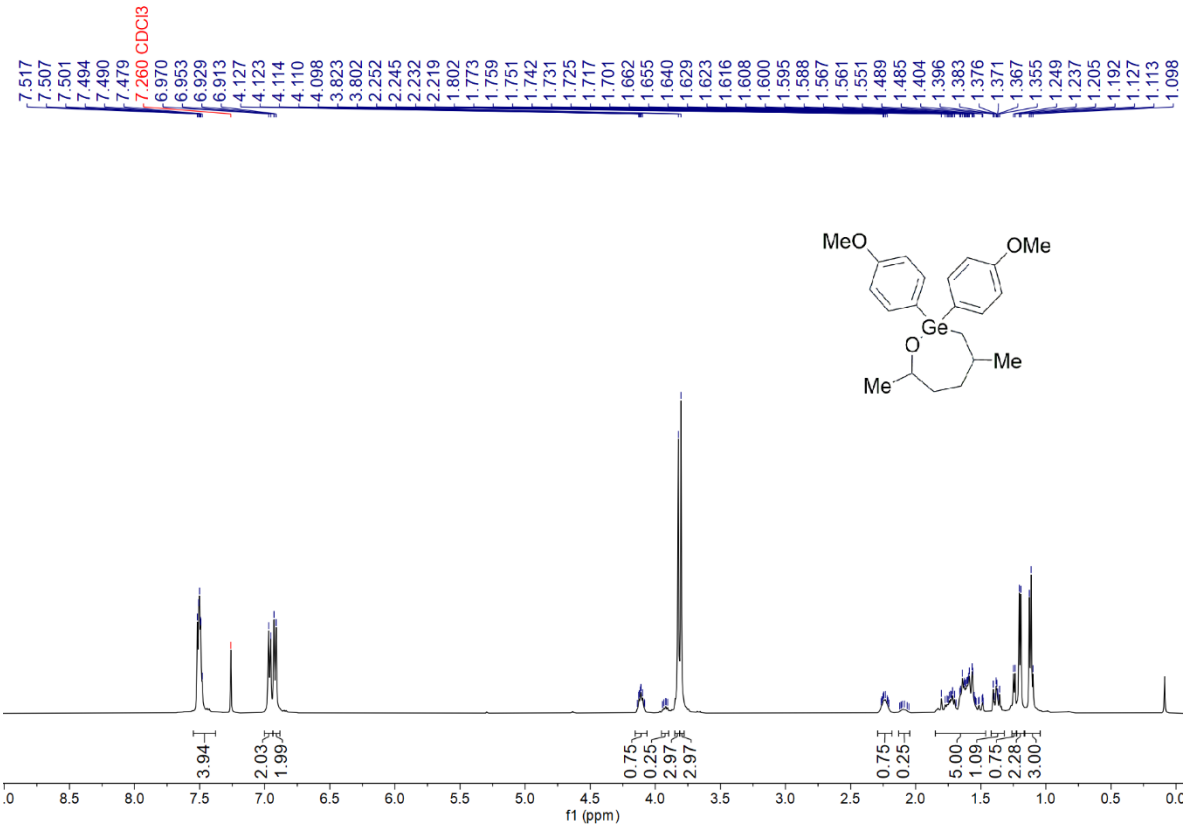
19 ^{1}H NMR (500 MHz, $CDCl_3$)



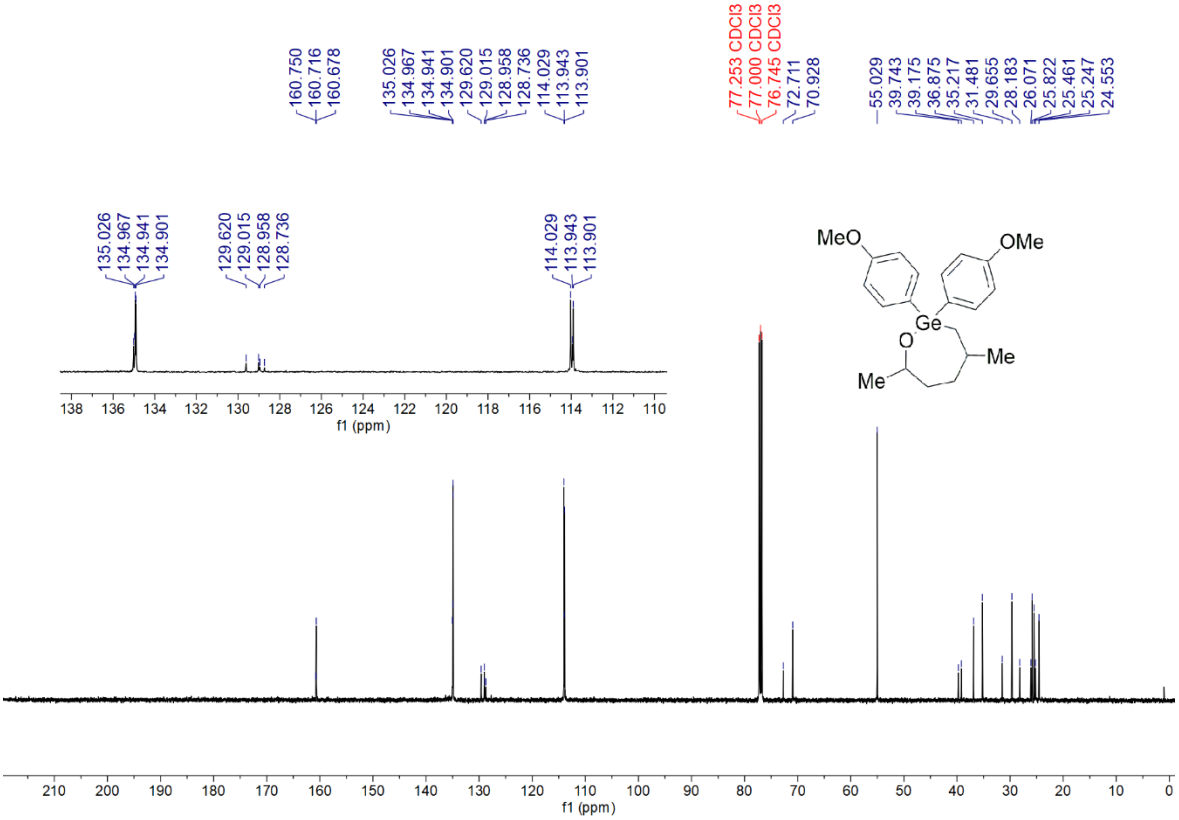
19 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



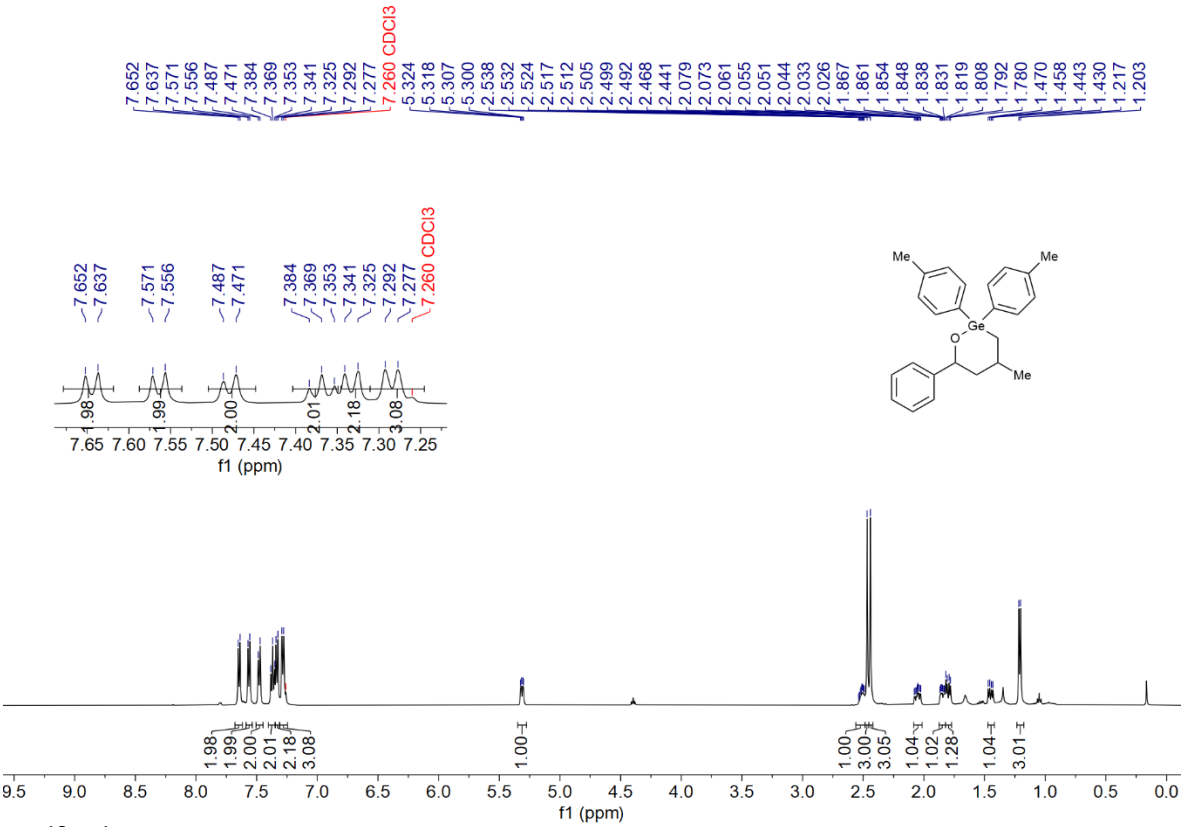
20 ^{1}H NMR (500 MHz, $CDCl_3$)



20^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



21 ^{1}H NMR (500 MHz, $CDCl_3$)



21 ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)