Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

for

Highly selective α-hydrogermylation of alkynes catalyzed by an *in-situ* generated bulky NHC–cobalt complex

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CONTENTS:

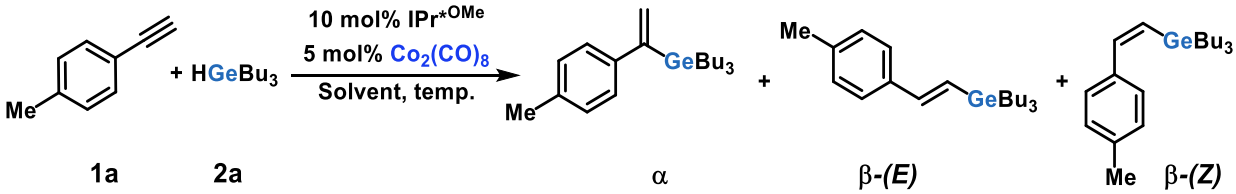
1. General methods and chemicals

All syntheses and catalytic tests were carried out under dry argon, using glove-box, standard Schlenk-line and vacuum techniques. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian 400 operating at 402.6 and 101.2 MHz, respectively. GC-MS analyses were performed on a Varian Saturn 2100T equipped with a DB-1 capillary column (30 m in length and 0.25 mm in internal diameter) and an ion trap detector. Mass spectrum of product **P21** was obtained using Synapt Gs-S HDMS (Waters) mass spectrometer with Electrospray ion source and quadrupole-Time-of-flight analyzer with resolving power FWMH 38000. Acetonitrile was utilized as the sample solvent. The Capillary Voltage was set to 4.5 kV, the sampling was set 40 and the source temperature was equal to 120°C. The most abundant ions in ESI-MS spectra was potassiated ions of desired product. Thin layer chromatography (TLC) was conducted on plates coated with a 250 µm thick silica gel layer and column chromatography was performed on silica gel 60 (70–230 mesh).

NHC carbene precursor was prepared according to literature procedures.[S1] All the other reagents were commercially available and used as received. The solvents were dried over CaH_2 prior to use and stored over 4Å molecular sieves under argon. Dichloromethane was additionally passed through an alumina column and degassed by repeated freeze-pump-thaw cycles.

2. Optimization studies

2.1. Solvent and temperature screening



1a 2a α β-*(E)* β-*(Z)*

Table S1. Optimization of solvent and temperature.

Entry	Solvent	Temperature	Conversion of 1a[a] [%]	Selectivity α:β-(*E*):β-(*Z*)[b]
1	Toluene	100	27	69:28:3
2	Toluene	60	16	74:20:6
3	THF	60	95	89:9:2
4	Acetone	60	<5	-
5	DCM	45	20	68:30:2
6	DCE	60	96	92:8:0
7	DCE	40	54	82:16:2
8	DCE	RT	25	70:24:6

Reaction conditions: [**1a**] : [**2a**] = 1 : 1, [$Co_2(CO)_8$] = 5.0 mol%, [IPr*^{OMe}] = 10.0 mol%, argon. [a] Determined by GC-MS analysis; [b] Determined by GC-MS analysis and confirmed by ^{1}H NMR spectroscopy of the crude reaction mixture.

3. Experimental procedures

3.1. General method for hydrogermylation of acetylenes – optimization studies

An oven-dried 5 mL glass reactor equipped with a magnetic stirring bar was charged with ligand (6.09×10^{-6} mol), octacarbonyl dicobalt(0) (1.0 mg, 3.05×10^{-6} mol) in the glovebox. Then solvent (0.5 mL) was added and reaction mixture was stirred for 30 minutes at room temperature. After this time, alkyne (6.09×10^{-5} mol), germane (6.09×10^{-5} mol) and internal standard (decane or dodecane, 15 µL) were added. The reaction mixture was stirred at set temperature for 18h. Reaction course was monitored by GC-MS.

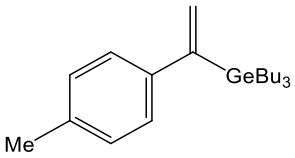
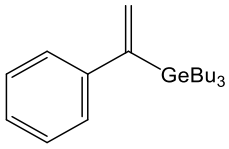
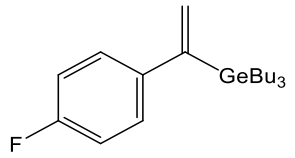
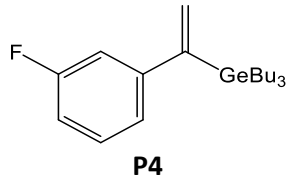
3.2. General method for hydrogermylation of acetylenes

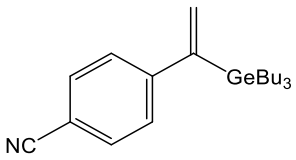
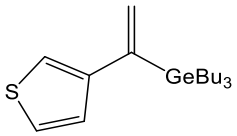
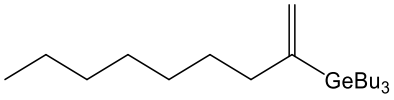
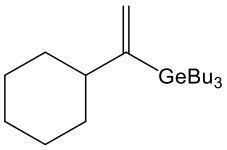
An oven-dried 5 mL glass reactor equipped with a magnetic stirring bar was charged with NHC carbene (5.8 mg, 6.09×10^{-6} mol), octacarbonyl dicobalt(0) (1.0 mg, 3.05×10^{-6} mol) in the glovebox. Then DCE (0.5 mL) was added and reaction mixture was stirred for 30 minutes at room temperature. After this time, alkyne (6.09×10^{-5} mol), germane (6.09×10^{-5} mol) and internal standard (decane or dodecane, 15 µL) were added. The reaction mixture was stirred at 60 °C for 18h. Reaction course was monitored by GC-MS.

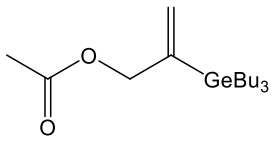
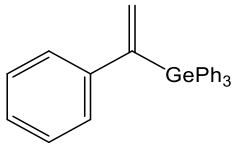
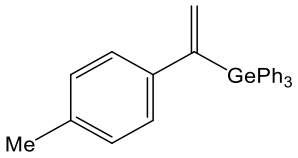
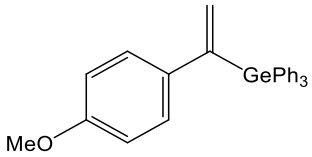
3.3. General procedure for the synthesis of α-vinylgermanes (P1-P24)

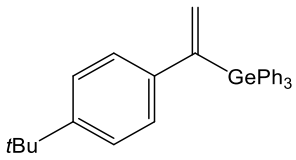
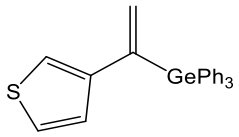
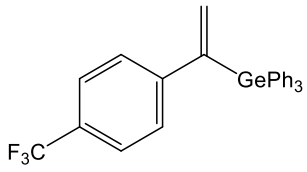
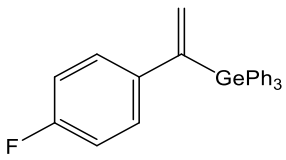
An oven-dried 5 mL glass reactor equipped with a magnetic stirring bar was charged with NHC carbene (28.8 mg, 3.05×10^{-5} mol), octacarbonyl dicobalt(0) (5.2 mg, 1.53×10^{-5} mol) in the glovebox. Then DCE (0.5 mL) was added and reaction mixture was stirred for 30 minutes at room temperature. After this time, alkyne (3.05×10^{-4} mol) and germane (3.05×10^{-4} mol) were added. The reaction mixture was stirred at 60 °C for 18h. Reaction course was monitored by GC-MS. The products were purified by column chromatography on silica gel using hexane or a 10: 1 v/v mixture of *n*-hexane and diethyl ether as eluents. Evaporation of the solvents afforded analytically pure compounds. Purification of **P2**, **P7** – **P17**, **P20** was performed on preparative TLC plates with 10: 1 v/v mixture of *n*-hexane and diethyl ether as eluent.

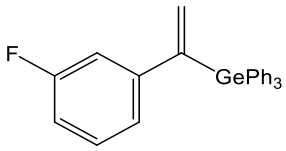
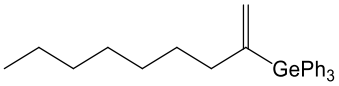
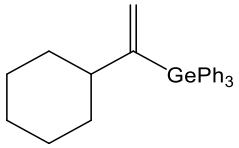
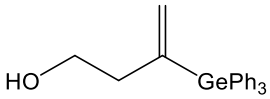
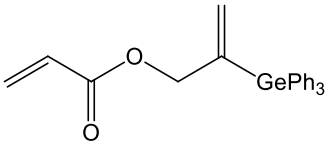
4. Analytical data of isolated products

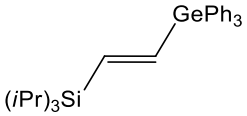
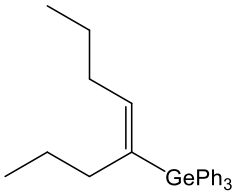
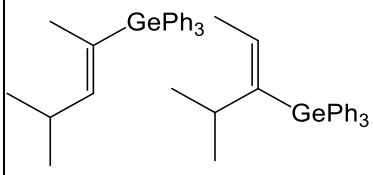
 **P1**	Colourless oil (20.9 mg, 95% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 0.82 – 0.89 (m, 15H, CH_2 and CH_3), 1.26 – 1.34 (m, 12H, CH_2), 2.33 (s, 3H, CH_3), 5.38 (d, 1H, J_{HH} = 2.7 Hz, CH_2=), 5.85 (d, 1H, J_{HH} = 2.7 Hz, CH_2=), 7.05 – 7.12 (m, 4H, CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 13.04, 13.71, 21.06, 26.43, 27.25, 124.78, 126.30, 128.80, 135.80, 142.25, 151.96; **MS** m/z (rel, intensity): 76.00 (10), 102.90 (8), 176.40 (12), 244.90 (80), 271.20 (11), 291.10 (9), 305.20 (100), 347.00 (52), 332.30 (10), 362.40 (8, M^+).
 **P2**	Red oil (17.7 mg, 84% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 0.83 – 0.89 (m, 15H, CH_2 and CH_3), 1.27 – 1.33 (m, 12H, CH_2), 5.42 (d, 1H, J_{HH} = 2.6 Hz, CH_2=), 5.86 (d, 1H, J_{HH} = 2.1 Hz, CH_2=), 7.14 – 7.17 (m, 2H, CH_{Ar}), 7.19 – 7.22 (m, 1H, CH_{Ar}), 7.28 – 7.34 (m, 1H, CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 13.01, 13.71, 26.42, 27.22, 125.40, 126.17, 126.42, 128.08, 128.46, 145.30 (H_2C=); **MS** m/z (rel, intensity): 51.20 (9), 77.20 (15), 103.00 (34), 130.20 (9), 151.00 (15), 176.80 (46), 204.90 (11), 235.30 (100), 243.50 (28), 291.10 (87), 332.90 (5, M^+ - CH_3).
 **P3**	Colourless oil (19.4 mg, 87% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 0.82 – 0.88 (m, 15H, CH_2 and CH_3), 1.25 – 1.32 (m, 12H, CH_2), 5.41 (d, 1H, J_{HH} = 2.6 Hz, CH_2=), 5.83 (d, 1H, J_{HH} = 2.6 Hz, CH_2=), 6.94 – 7.00 (m, 2H, CH_{Ar}), 7.08 – 7.13 (m, 2H, CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 12.98, 13.69, 26.40, 27.21, 114.89 (d, J_{HH} = 21.0 Hz), 125.57, 127.83 (d, J_{HH} = 7.9 Hz), 141.32, 151.37, 161.66 (d, J_{HH} = 244.7 Hz); **MS** m/z (rel, intensity): 95.00 (8), 102.30 (14), 245.20 (47), 309.00 (100), 336.90 (31), 347.10 (12), 351.10 (62), 366.20 (74, M^+).
 **P4**	Colourless oil (19.9 mg, 89% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 0.83 – 0.90 (m, 15H, CH_2 and CH_3), 1.26 – 1.34 (m, 12H, CH_2), 5.44 (d, 1H, J_{HH} = 2.5 Hz, CH_2=), 5.86 (d, 1H, J_{HH} = 2.5 Hz, CH_2=), 6.83 – 6.94 (m, 3H, CH_{Ar}), 7.19 – 7.26 (m, 1H, CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 12.95, 13.68, 26.38, 27.18, 112.92 (d, J = 21.4 Hz), 113.18 (d, J = 21.0 Hz), 122.19, 126.26, 129.44 (d, J = 8.5 Hz), 147.78 (d, J_{HH} = 7.2 Hz), 151.53, 162.70 (d, J = 245.3 Hz); **MS** m/z (rel, intensity): 94.60 (9), 102.90 (7), 245.20 (27), 252.00 (20), 309.20 (100), 337.80 (21), 347.50 (12), 351.10 (62), 366.70 (33, M^+).

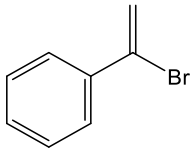
 **P5**	Colourless oil (19.7 mg, 87% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 0.83 – 0.88 (m, 15H, C*H*$_2$ and C*H*$_3$), 1.26 – 1.32 (m, 12H, C*H*$_2$), 5.53 (d, 1H, J_{HH} = 2.3 Hz, C*H*$_2$=), 5.88 (d, 1H, J_{HH} = 2.3 Hz, C*H*$_2$=), 7.22 (dt, 2H, J_{HH} = 8.5, 2.0 Hz, C*H*$_{Ar}$), 7.58 (dt, 2H, J_{HH} = 8.5, 1.6 Hz, C*H*$_{Ar}$); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 12.94, 13.67, 26.34, 27.14, 109.72, 119.20, 127.12, 127.62, 132.02, 150.55, 151.65; **MS** m/z (rel, intensity): 51.10 (11), 128.00 (21), 245.00 (6), 259.20 (44), 301.70 (17), 316.10 (100), 372.20 (15, M^+).
 **P6**	Colourless oil (18.3 mg, 85% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 0.84 – 0.92 (m, 15 H, C*H*$_2$ and C*H*$_3$), 1.28 – 1.35 (m, 12 H, C*H*$_2$), 5.37 (d, 1 H, J_{HH} = 2.5 Hz, C*H*$_2$=), 5.98 (d, 1 H, J_{HH} = 2.6 Hz, C*H*$_2$=),7.02 (dd, 1 H, J_{HH} = 2.9, 1.4 Hz, C*H*$_{tiophene}$), 7.08 (dd, 1 H, J_{HH} = 5.0, 1.4 Hz, C*H*$_{tiophene}$), 7.25 (dd, 1 H, J_{HH} = 5.0, 2.9 Hz, C*H*$_{tiophene}$); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 12.99, 13.71, 26.43, 27.23, 119.78, 124.27, 125.00, 126.22, 145.43,145.55; **MS** m/z (rel, intensity): 83.50 (7), 109.60 (15), 245.20 (62), 296.40 (100), 339.20 (20), 353.30 (14, M^+).
 **P7**	Colourless oil (19.4 mg, 85% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 0.77 – 0.80 (m, 5H, C*H*$_2$), 0.86 – 0.90 (m, 15H, C*H*$_2$ and C*H*$_3$), 1.26 – 1.29 (m, 8H, C*H*$_2$), 1.30 – 1.35 (m, 12H, C*H*$_2$), 2.13 (t, 2H, J_{HH} = 7.7 Hz, C*H*$_2$), 5.12 (d, 1H, J_{HH} = 2.8 Hz, C*H*$_2$=), 5.55 (d, 1H, J_{HH} = 2.8 Hz, C*H*$_2$=); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 12.44, 12.91, 13.74, 13.78, 14.10, 22.68, 26.59, 27.35, 28.82, 29.23, 29.43, 31.88, 37.84, 122.03, 152.36; **MS** m/z (rel, intensity): 55.10 (11), 81.20 (20), 123.20 (34), 155.30 (8), 186.70 (13), 232.30 (13), 243.70 (18), 257.40 (100), 313.20 (46, M^+ - C_4H_9).
 **P8**	Colourless oil (13.6 mg, 90% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 0.86 – 0.92 (m, 15H, C*H*$_2$ and C*H*$_3$), 1.10 – 1.17 (m, 4H, C*H*$_2$), 1.28 – 1.33 (m, 12 H, C*H*$_2$), 1.66 – 1.77 (m, 6H, C*H*$_2$), 1.99 (m, 1H, C*H*), 5.10 (d, 1H, J_{HH} = 2.4 Hz, C*H*$_2$=), 5.56 (dd, 1H, J_{HH} = 2.4, 1.3 Hz, C*H*$_2$=); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 12.84, 13.76, 26.36, 26.60, 26.92, 27.36, 33.09, 44.82, 120.13, 157.51; **MS** m/z (rel, intensity): 55.00 (21), 73.80 (5), 88.80 (15), 104.80 (20), 132.70 (100), 188.80 (65), 240.70 (17, M^+ - 2 C_4H_9).

 **P9**	Colourless oil (16.7 mg, 80% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 0.82 – 0.90 (m, 15H, CH_2 and CH_3), 1.30 – 1.35 (m, 12H, CH_2), 2.09 (s, 3H, CH_3), 4.67 (s, 2H, OCH_2), 5.30 (d, 1H, J_{HH} = 1.8 Hz, CH_2=), 5.78 (d, 1H, J_{HH} = 1.8 Hz, CH_2=); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 12.33, 13.72, 20.96, 26.49, 27.21, 68.88, 123.88, 146.03, 170.70; **MS** m/z (rel, intensity): 73.70 (11), 99.50 (8), 245.90 (10), 286.90 (83), 301.00 (12), 329.10 (100), 344.40 (34, M^+).
 **P10**	Colourless oil (22.8 mg, 92% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 5.60 (d, 1H, J_{HH} = 2.2 Hz, CH_2=), 6.26 (d, 1H, J_{HH} = 2.2 Hz, CH_2=), 7.17 – 7.21 (m, 3H, CH_{Ar}), 7.33 – 7.40 (m, 10H, CH_{Ar}), 7.47 – 7.51 (m, 6H, CH_{Ar}), 7.63 – 7.66 (m, 1H, CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 127.18, 128.18, 128.48, 129.00, 130.08, 134.10, 135.37, 136.36, 143.48, 147.95; **MS** m/z (rel, intensity): 51.20 (16), 77.20 (13), 103.20 (10), 150.30 (5), 221.80 (13), 305.70 (100), 329.50 (18), 406.50 (50, M^+).
 **P11**	Colourless oil (19.2 mg, 75% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 2.29 (s, 3H, CH_3), 5.53 (d, 1H, J_{HH} = 2.2 Hz, CH_2=), 6.24 (d, 1H, J_{HH} = 2.1 Hz, CH_2=), 7.00 (dt, 2H, J_{HH} = 7.9, 0.7 Hz, CH_{Ar}), 7.17 (d, 2H, J_{HH} = 8.0 Hz, CH_{Ar}), 7.34 – 7.40 (m, 10H, CH_{Ar}), 7.47 – 7.50 (m, 5H, CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 21.08 (CH_3), 127.03, 128.15, 128.24, 128.95, 134.82, 135.12, 135.38, 136.51, 146.69, 148.21; **MS** m/z (rel, intensity): 51.00 (9), 91.00 (7), 115.20 (12), 151.00 (6), 226.10 (7), 305.30 (100), 345.20 (13), 422.00 (50, M^+).
 **P12**	Pale yellow oil (16.8 mg, 63% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 3.76 (s, 3H, OCH_3), 5.50 (d, 1H, J_{HH} = 2.1 Hz, CH_2=), 6.22 (d, 1H, J_{HH} = 2.1 Hz, CH_2=), 6.75 (d, 2H, J_{HH} = 8.8 Hz, CH_{Ar}), 7.24 (d, 2H, J_{HH} = 8.6 Hz, CH_{Ar}), 7.34 – 7.41 (m, 10H, CH_{Ar}), 7.48 – 7.52 (m, 5H, CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 55.17 (OCH_3), 113.60, 128.17, 128.49, 128.96, 134.81, 135.12, 135.37, 136.54, 146.20, 146.75 (H_2C=), 158.73 (*C*-OCH_3); **MS** m/z (rel, intensity): 51.20 (8), 77.20 (6), 133.10 (10), 224.220 (8), 305.50 (75), 361.50 (20), 438.30 (100, M^+).

 **P13**	Yellow oil (13.6 mg, 48% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 1.28 (s, 9H, C(CH_3)$_3$), 5.54 (d, 1H, J_{HH} = 2.2 Hz, CH_2=), 6.26 (d, 1H, J_{HH} = 2.2 Hz, CH_2=), 6.91 – 6.97 (m, 2H, CH_{Ar}), 7.28 – 7.31 (m, 2H, CH_{Ar}), 7.38 – 7.43 (m, 10H, CH_{Ar}), 7.48 – 7.50 (m, 5H, CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 31.14 (C(CH_3)$_3$), 31.29 (C(CH_3)$_3$), 124.42, 125.11, 125.48, 126.31, 126.81, 128.15, 128.93, 134.85, 135.13, 135.42, 146.66, 148.17; **MS** m/z (rel, intensity): 51.00 (6), 129.10 (8), 234.20 (7), 305.50 (100), 387.30 (19), 464.10 (60, M^+).
 **P14**	Colourless oil (18.1 mg, 72% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 5.51 (d, J_{HH} = 2.1 Hz, CH_2=), 6.33 (d, J_{HH} = 2.1 Hz, CH_2=), 6.83 – 6.91 (m, 1H, C$H_{tiophene}$), 6.98 (d, 1H, J_{HH} = 1.6 Hz, C$H_{tiophene}$), 7.15 – 7.20 (m, 1H, C$H_{tiophene}$), 7.34 – 7.42 (m, 10H, CH_{Ar}), 7.51 – 7.57 (m, 5H, CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 122.25, 125.17, 126.28, 128.25, 129.08, 134.78, 135.34, 136.14, 141.20, 144.05; **MS** m/z (rel, intensity): 65.10 (12), 109.10 (10), 184.00 (33), 225.60 (10), 305.30 (100), 337.10 (10), 414.00 (12, M^+).
 **P15**	Pale yellow oil (22.0 mg, 76% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 5.69 (d, 1H, J_{HH} = 2.0 Hz, CH=), 6.27 (d, 1H, J_{HH} = 2.1 Hz, CH=), 7.37 – 7.42 (m, 10H, CH_{Ar}), 7.46 – 7.48 (m, 5H, CH_{Ar}), 7.53 – 7.55 (m, 4H, CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 125.14 (q, J = 3.8 Hz), 126.74, 128.34, 128.18 (q, J = 31.7 Hz), 128.32 (q, J = 279.6 Hz), 134.71, 135.09, 135.14, 135.29, 135.66, 145.20, 147.35; **MS** m/z (rel, intensity): 51.00 (7), 152.20 (19), 225.50 (6), 305.20 (100), 399.10 (3), 456.80 (7), 476.00 (5, M^+).
 **P16**	Colourless oil (19.7 mg, 76% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 5.58 (d, 1H, J_{HH} = 2.1 Hz, CH_2=), 6.21 (d, 1H, J_{HH} = 2.1 Hz, CH_2=), 6.88 (t, 2H, J_{HH} = 8.8 Hz, CH_{Ar}), 7.18 – 7.22 (m, 2H, CH_{Ar}), 7.34 – 7.42 (m, 10H, CH_{Ar}), 7.46 – 7.49 (m, 5H, CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 115.04 (d, J = 21.5 Hz), 128.25, 128.69 (d, J = 7.7 Hz), 129.11, 134.76, 135.10, 135.32, 145.48, 147.01 (d, J = 8.5 Hz), 162.00 (d, J = 245.9 Hz); **MS** m/z (rel, intensity): 51.10 (5), 101.00 (8), 121.00 (5), 222.60 (11), 305.50 (100), 349.30 (29), 426.10 (73, M^+).

 **P17**	Pale yellow solid (23.3 mg, 90% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 5.63 (d, 1H, J_{HH} = 2.0 Hz, CH_2=), 6.25 (d, 1H, J_{HH} = 2.0 Hz, CH_2=), 6.85 – 6.90 (m, 1H, CH_{Ar}), 6.94 – 7.00 (m, 2H, CH_{Ar}), 7.08 – 7.16 (m, 1H, CH_{Ar}), 7.35 – 7.42 (m, 9H, CH_{Ar}), 7.46 – 7.50 (m, 5H, CH_{Ar}), 7.54 – 7.58 (m, 1H, CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 113.58 (dd, *J* = 21.5, 11.5 Hz), 123.13 (d, *J* = 2.6 Hz), 128.27, 129.15, 129.56 (d, *J* = 8.4 Hz), 130.89, 135.08, 135.30, 135.88, 145.92 (d, *J* = 7.4 Hz), 147.18, 162.62 (d, *J* = 245.7 Hz); **MS** m/z (rel, intensity): 51.20 (2), 101.20 (4), 221.70 (11), 305.70 (100), 349.50 (41), 426.20 (42, M^+).
 **P18**	Colourless oil (23.6 mg, 90% isolated yield). **H NMR** (400 MHz, $CDCl_3$, ppm): 0.86 (t, 3H, J_{HH} = 7.1 Hz, CH_3), 1.13 – 1.21 (m, 6H, CH_2), 1.28 – 1.32 (m, 2H, CH_2), 1.34 – 1.39 (m, 2H, CH_2), 2.30 (t, 2H, J_{HH} = 7.8 Hz, CH_2C=), 5.41 (dt, 1H, J_{HH} = 2.3, 1.0 Hz, =CH_2), 5.92 (q, 1H, J_{HH} = 2.4, =CH_2), 7.36 – 7.41 (m, 10H, CH_{Ar}), 7.52 – 7.56 (m, 5H, CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 14.07 (*C*H_3), 22.60, 28.68, 29.01, 29.20, 31.73, 37.39, 126.75, 128.15, 128.87, 135.29, 136.41, 148.33 (H_2*C*=); **MS** m/z (rel, intensity): 51.00 (4), 150.50 (4), 223.20 (12), 305.70 (93), 353.20 (100), 430.00 (4, M^+).
 **P19**	White solid (22.4 mg, 89% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 1.04 -1.17 (m, 6H, CH_2), 1.62 – 1.67 (m, 2H, CH_2), 1.69 – 1.74 (m, 2H, CH_2), 2.11 – 2.19 (m, 1H, C*H*), 5.37 (d, 1H, J_{HH} = 1.8 Hz, CH_2=), 5.93 (d, 1H, J_{HH} = 1.6 Hz, CH_2=), 7.36 – 7.40 (m, 10H, CH_{Ar}), 7.51 – 7.54 (m, 5H, CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 26.18, 26.65, 33.08, 44.05, 124.75, 128.05, 128.33, 128.81, 135.06, 135.34, 136.81, 153.53 (H_2*C*=); **MS** m/z (rel, intensity): 51.20 (10), 150.90 (10), 177.20 (5), 223.60 (23), 305.70 (100), 336.30 (56), 414.10 (10, M^+).
 **P20**	White solid (18.1 mg, 93% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 2.60 (t, 2H, J_{HH} = 6.5 Hz, CH_2C=), 3.58 (q, 2H, J_{HH} = 4.7 Hz, CH_2OH), 5.56 (d, 1H, J_{HH} = 2.2 Hz, CH_2=), 6.02 (d, 1H, J_{HH} = 2.2 Hz, CH_2=), 7.38 – 7.43 (m, 8H, CH_{Ar}), 7.44 – 7.47 (m, 1H, CH_{Ar}), 7.53 – 7.56 (m, 5H, CH_{Ar}), 7.64 – 7.67 (m, 1H, CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 40.53 (*C*H_2CH$_2$OH), 61.24 (*C*H_2OH), 128.28, 129.11, 130.05, 134.07, 135.18, 144.71 (H_2*C*=); **MS** m/z (rel, intensity): 51.10 (13), 77.20 (5), 150.80 (8), 223.20 (11), 244.80 (4), 299.80 (64), 305.30 (100), 375.30 (3, M^+).
 **P21**	White solid (22.2 mg, 91% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 4.88 (t, 2H, J_{HH} = 1.6 Hz, OCH_2C=), 5.55 (q, 1H, J_{HH} = 1.5 Hz, CH_2=), 5.66 (dd, 1H, J_{HH} = 10.6, 1.5 Hz, CH_2=CHCO), 5.89 (dd, 1H, J_{HH} = 17.3, 10.4 Hz, CH$_2$=C*H*CO), 6.10 (dd, 1H, J_{HH} = 14.6, 1.6 Hz, CH_2=CHCO), 6.13 (d, 1H, J_{HH} = 1.5 Hz, CH_2=), 7.36 – 7.41 (m, 10H, CH_{Ar}), 7.50 – 7.53(m, 5H, CH_{Ar});

	^{13}C NMR (100 MHz, $CDCl_3$, ppm): 68.40 (CH_2O), 128.04, 128.30, 128.71, 129.19, 130.74, 135.13, 135.19, 142.58 (H_2C=), 165.57 (C=O); **MS (ESI+)** m/z 439 $[M+K]^+$.
 **P22**	White solid (28.8 mg, 97% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 1.05 (s, 6H, $CH(CH_3)_2$), 1.06 (s, 12H, $CH(CH_3)_2$), 1.11 – 1.18 (m, 3H, $CH(CH_3)_2$), 6.62 (d, 1H, J_{HH} = 22.2 Hz, C*H*=), 7.14 (d, 1H, J_{HH} = 22.2 Hz, C*H*=), 7.34 – 7.39 (m, 10H, CH_{Ar}), 7.47 – 7.50 (m, 5H, CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 10.73 $CH(CH_3)_2$, 18.64 $CH(CH_3)_2$, 128.16, 128.90, 135.09, 136.70, 145.66, 150.03 (H_2C=); **MS** m/z (rel, intensity): 59.00 (9), 151.00 (5), 223.50 (8), 262.50 (5), 305.50 (100), 331.30 (4), 411.20 (24), 445.20 (6, M^+ - $CH(CH_3)_2$).
 **P23**	Colourless oil (23.6 mg, 93% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 0.73 (t, 3H, J_{HH} = 7.3 Hz, CH_3), 0.93 (t, 3H, J_{HH} = 7.3 Hz, CH_3), 1.14 – 1.22 (m, 2H, CH_2), 1.37 – 1.47 (m, 2H, CH_2), 2.17 - 2.29 (m, 4H, CH_2), 5.80 (t, 1H, J_{HH} = 7.2 Hz, C*H*=), 7.34 – 7.40 (m, 10H, CH_{Ar}), 7.48 – 7.52 (m, 5H, CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 13.93, 14.13, 22.77, 23.17, 30.75, 33.09, 127.98, 128.14, 128.69, 135.34, 137.16, 143.75 (H*C*=); **MS** m/z (rel, intensity): 177.00 (2), 221.20 (3), 303.00 (12), 339.50 (100), 373.20 (1), 416.10 (5, M^+).
 **P24**	Yellow oil (19.4 mg, 82% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 0.98 (d, 6H, J_{HH} = 6.6 Hz, $CH(CH_3)_2$), 1.89 (d, 3H, J_{HH} = 1.8 Hz, $=CCH_3$), 1.14 – 1.22 (m, 2H, CH_2), 2.79 – 2.88 (m, 1H, $CH(CH_3)_2$), 5.65 (dq, J_{HH} = 8.9, 1.7 Hz, C*H*=), 7.35 – 7.39 (m, 10H, CH_{Ar}), 7.48 – 7.52 (m, 5H, CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 16.76, 22.66, 27.58, 128.07, 128.77, 135.36, 135.52, 136.58 (H*C*=), 150.86 (H*C*=); **MS** m/z (rel, intensity): 157.10 (2), 222.90 (4), 311.30 (100), 345.20 (2), 388.20 (2, M^+). These data are in accordance with the literature.[S2]

 **P25**	**^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 5.68 (d, 1H, J_{HH} = 2.1 Hz, CH_2=), 6.01 (d, 1H, J_{HH} = 2.1 Hz, CH_2=), 7.20 – 7.26 (m, 3H, CH_{Ar}), 7.47 – 7.52 (m, 2H, CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 138.73, 131.25, 129.23, 128.48, 127.51, 117.84. These data are in accordance with the literature.[S3]

5. NMR spectra of isolated products

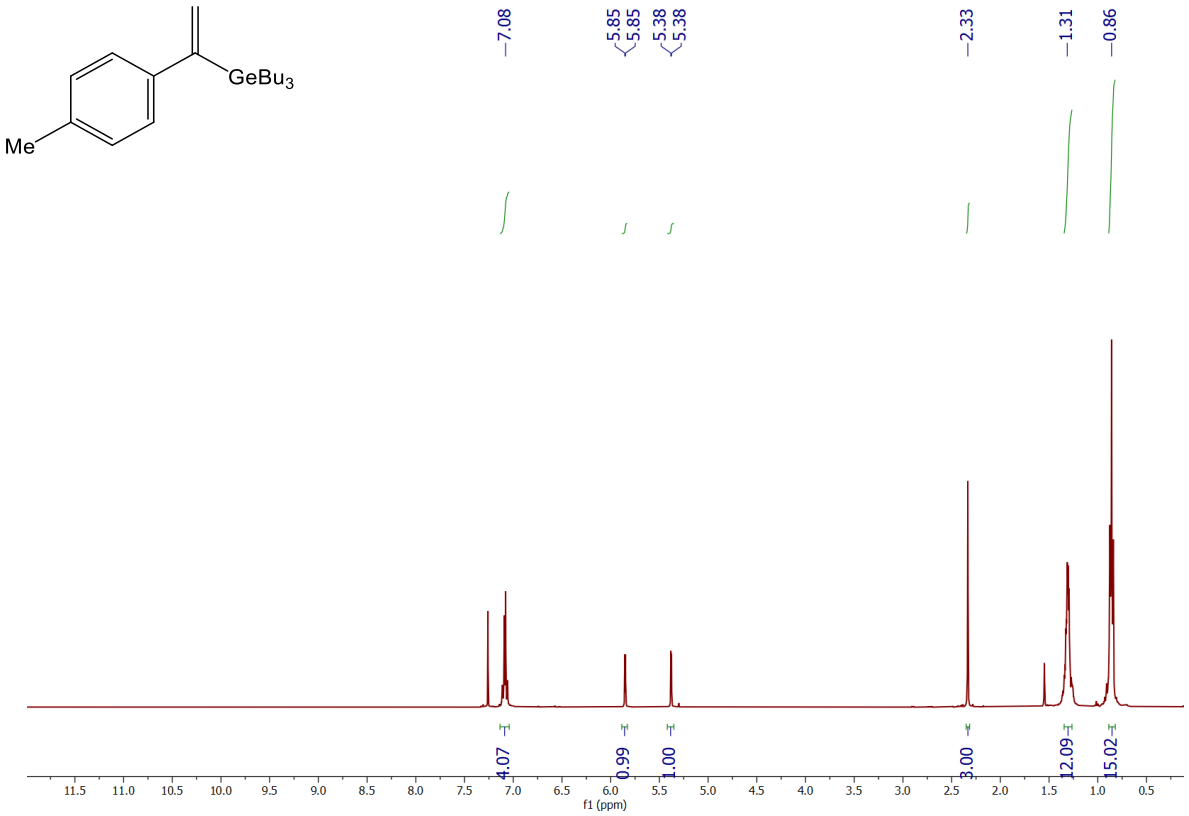


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P1**

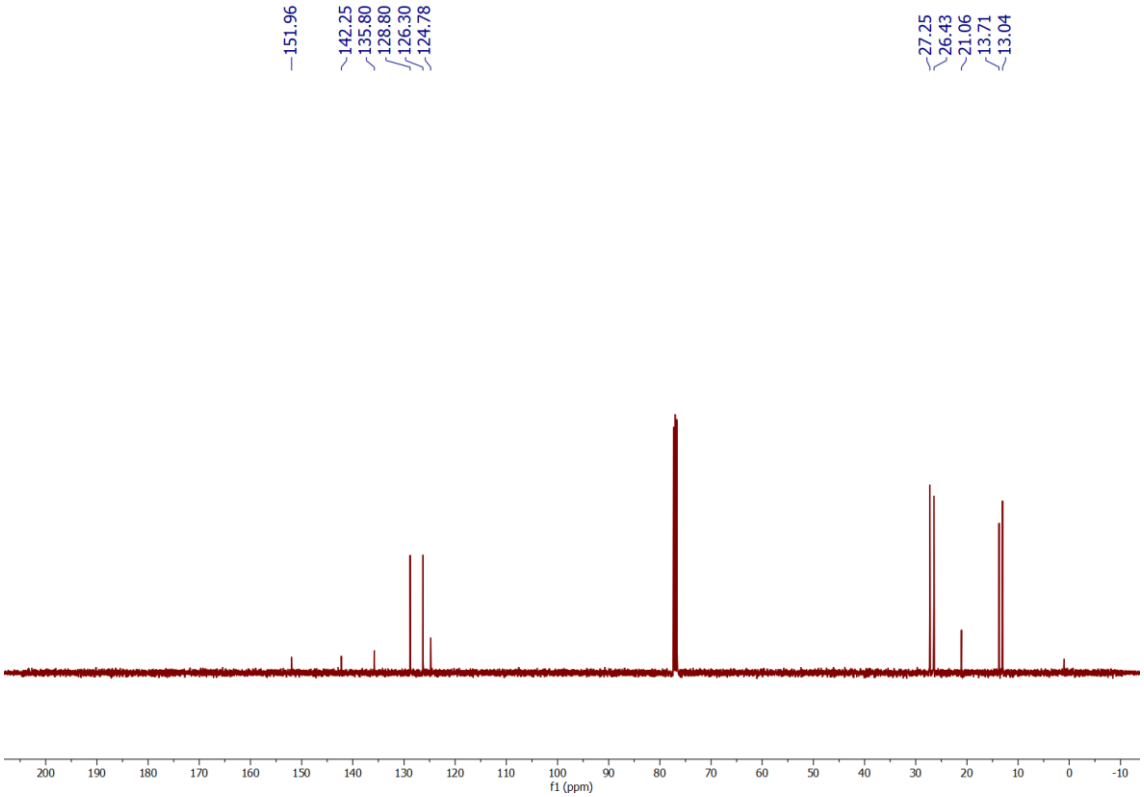


Figure S2. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P1**

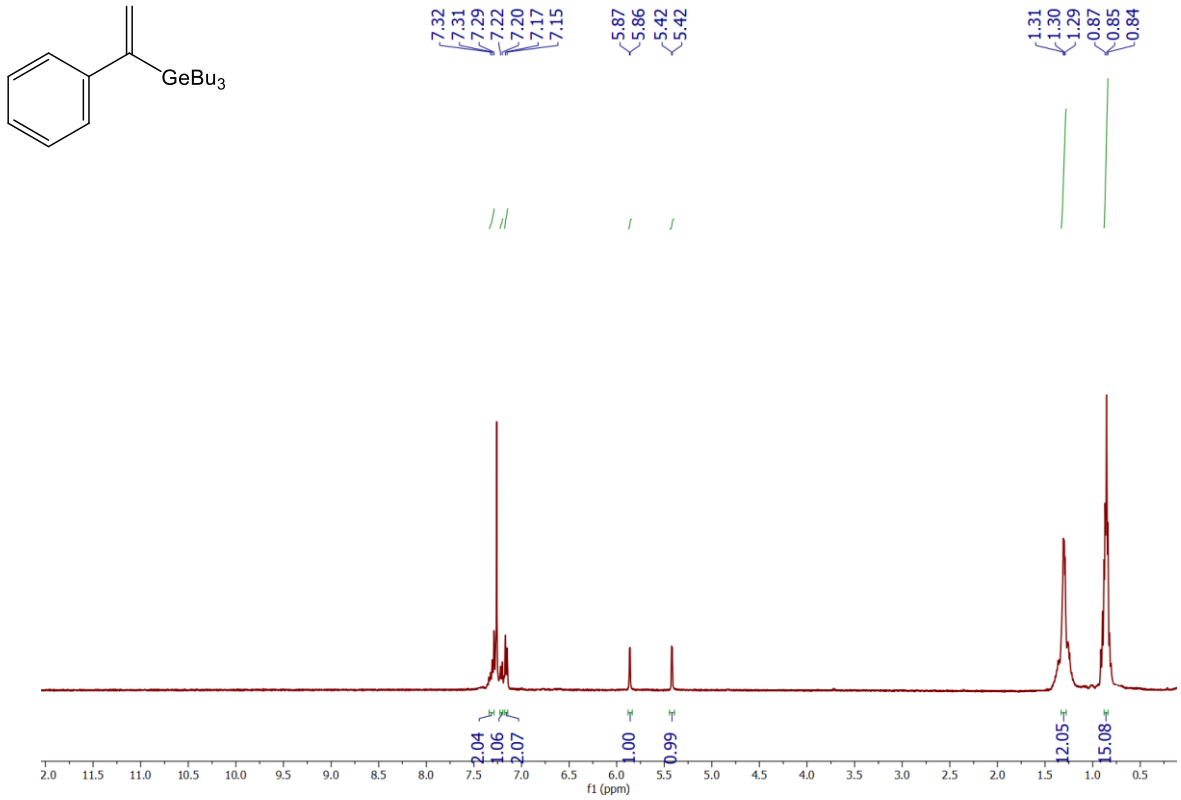


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P2**

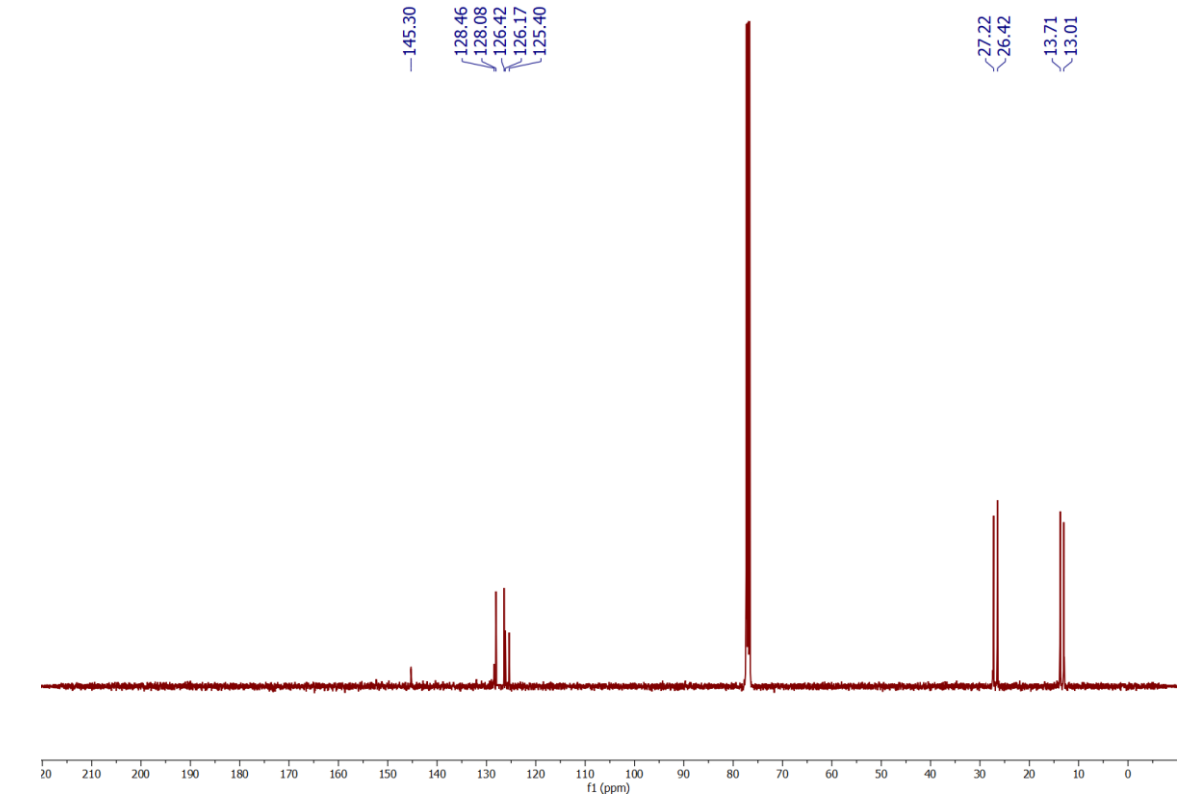


Figure S4. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P2**

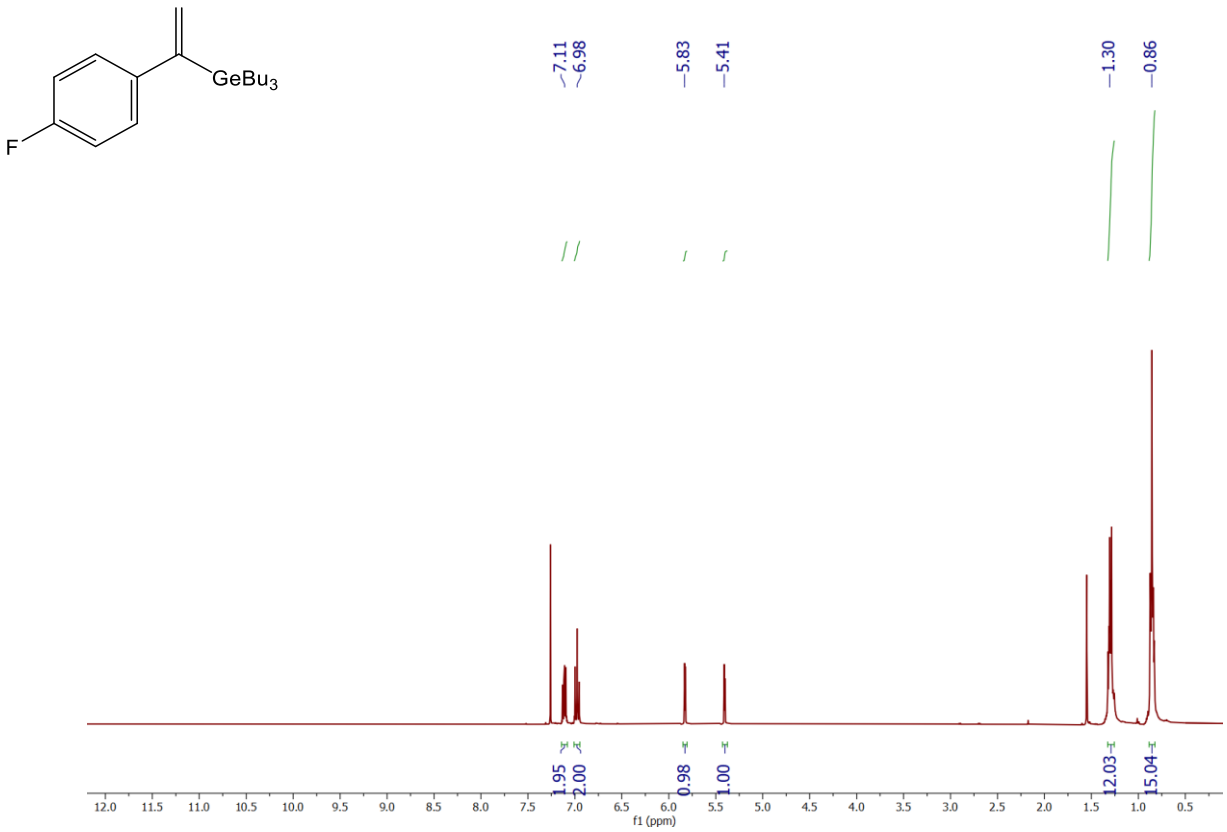


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P3**

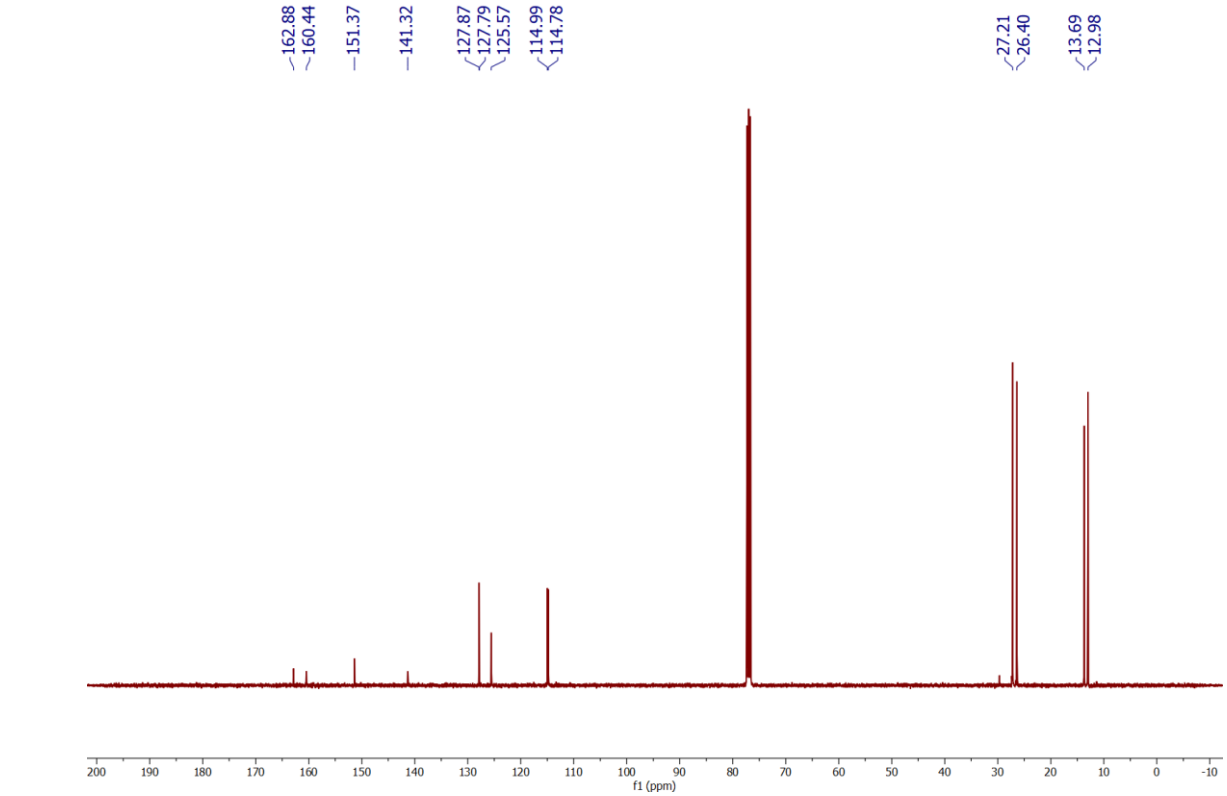


Figure S6. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P3**

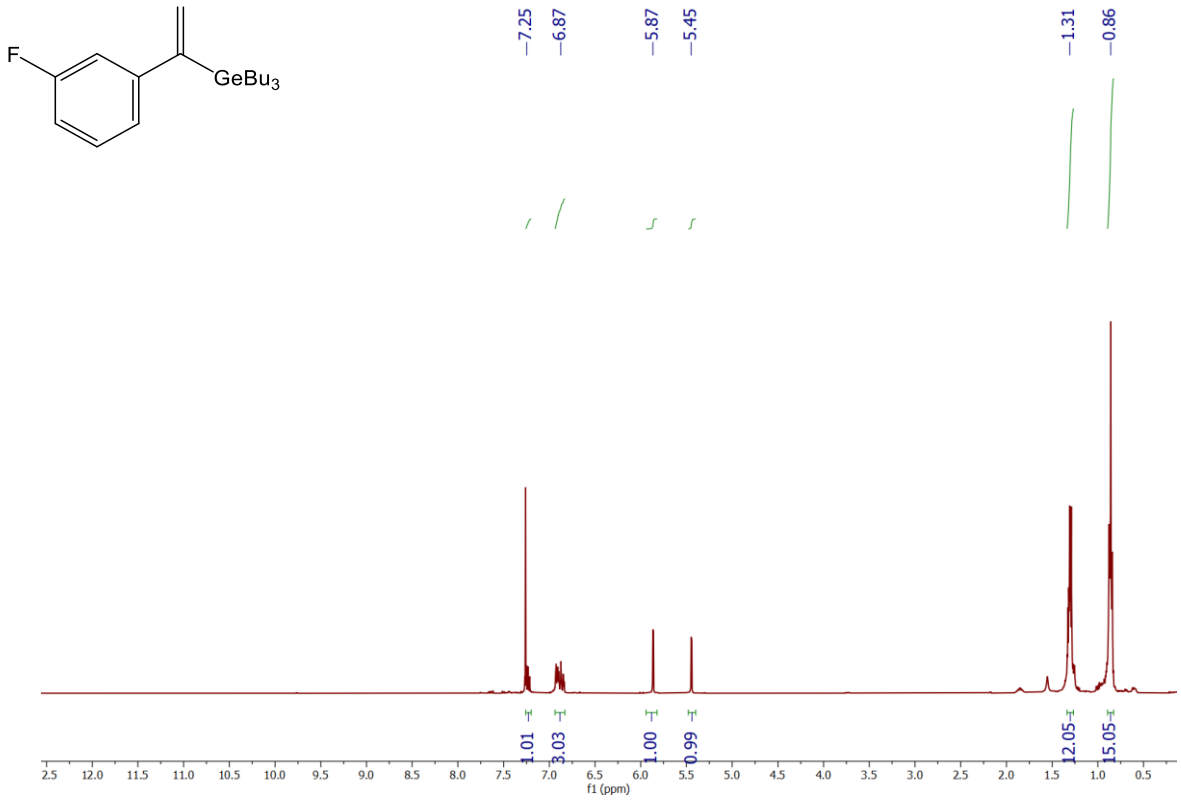


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P4**

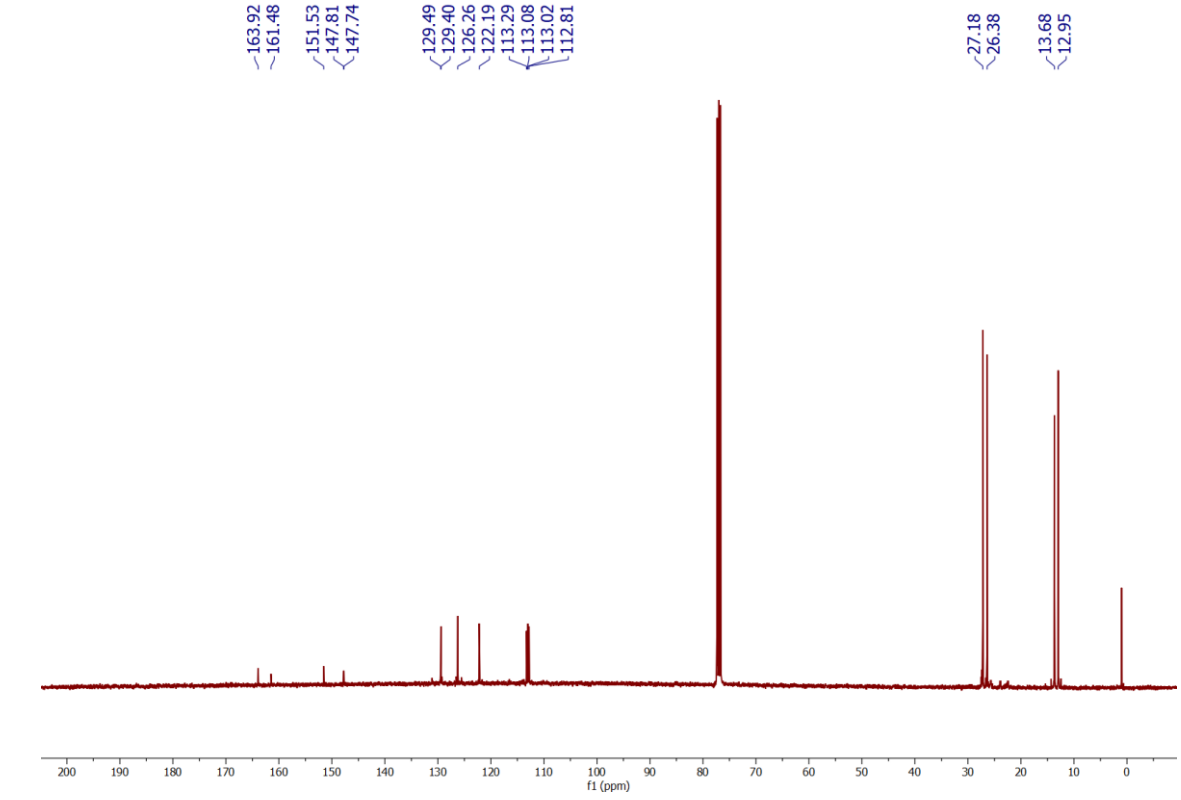


Figure S8. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P4**

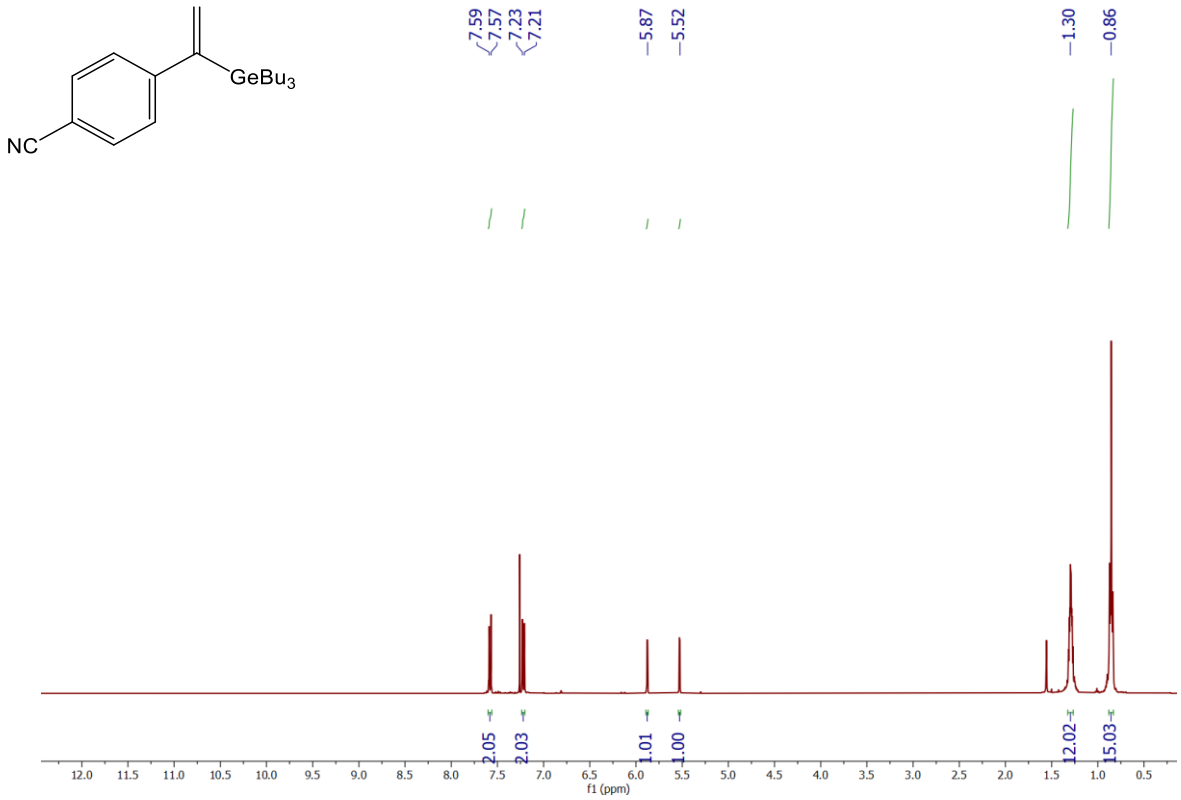


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P5**

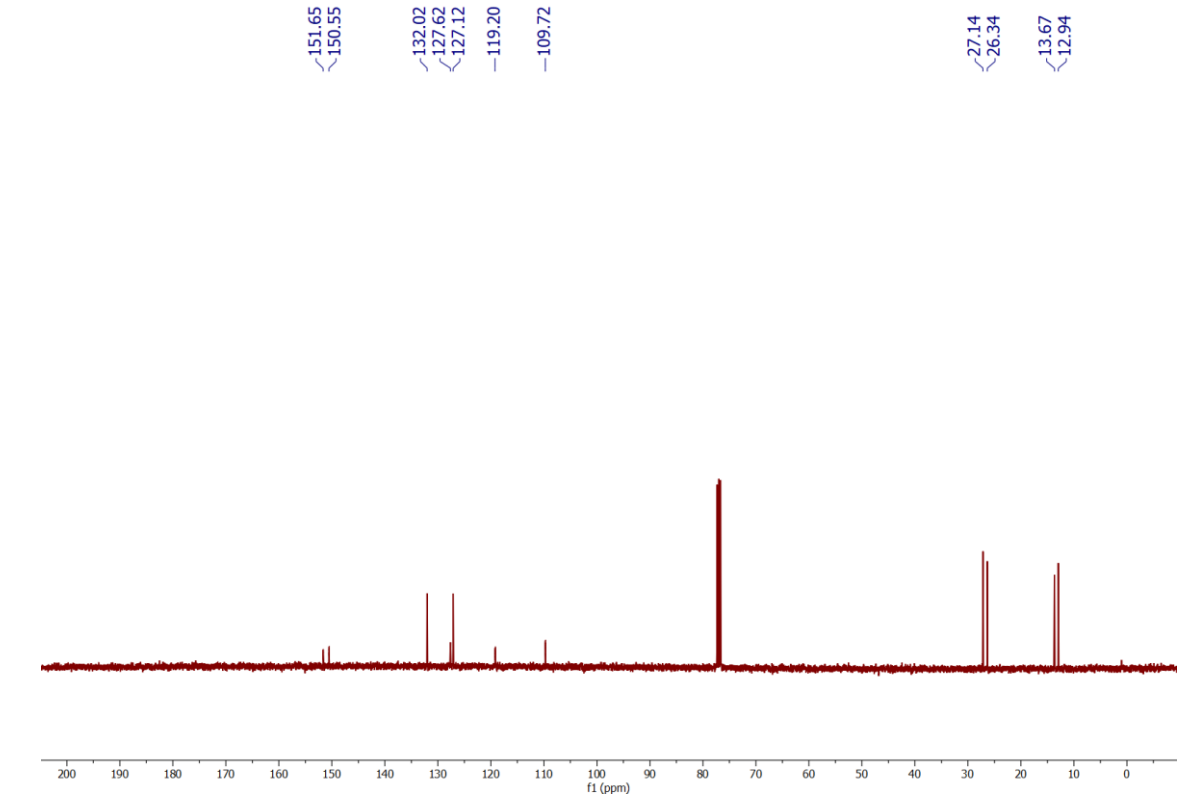


Figure S10. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P5**

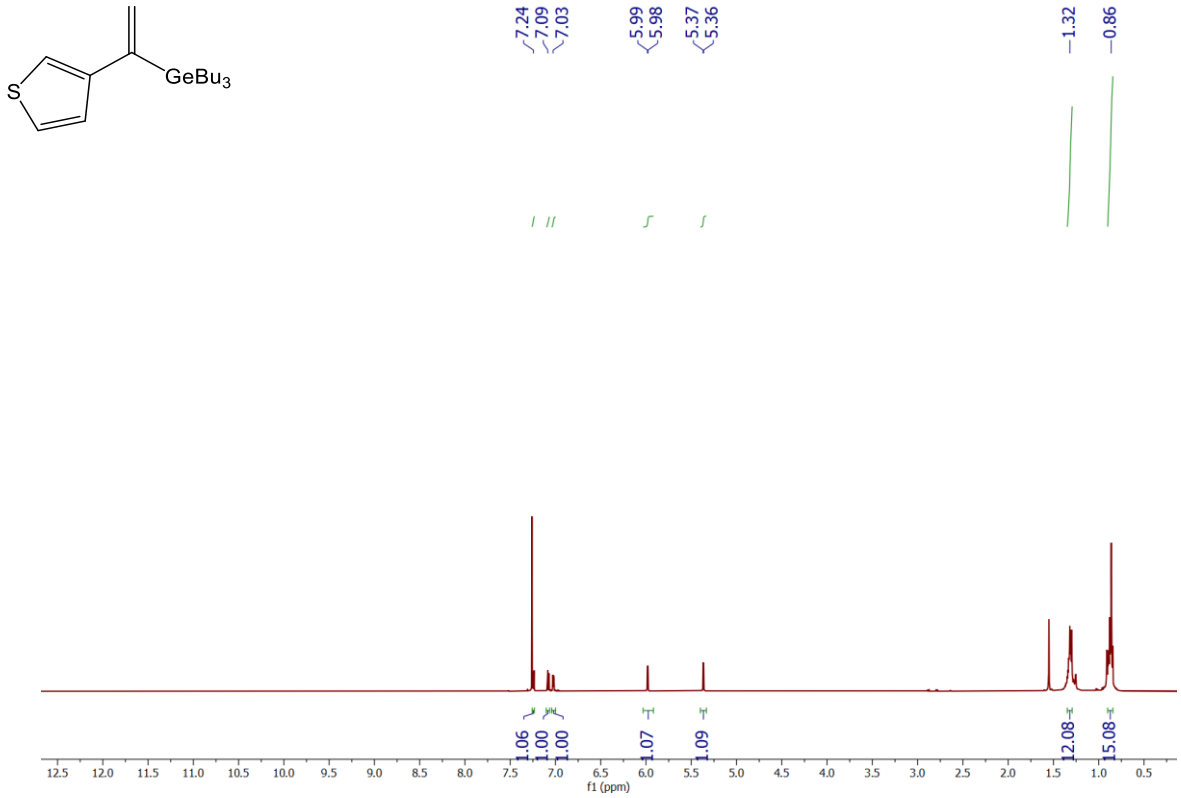


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P6**

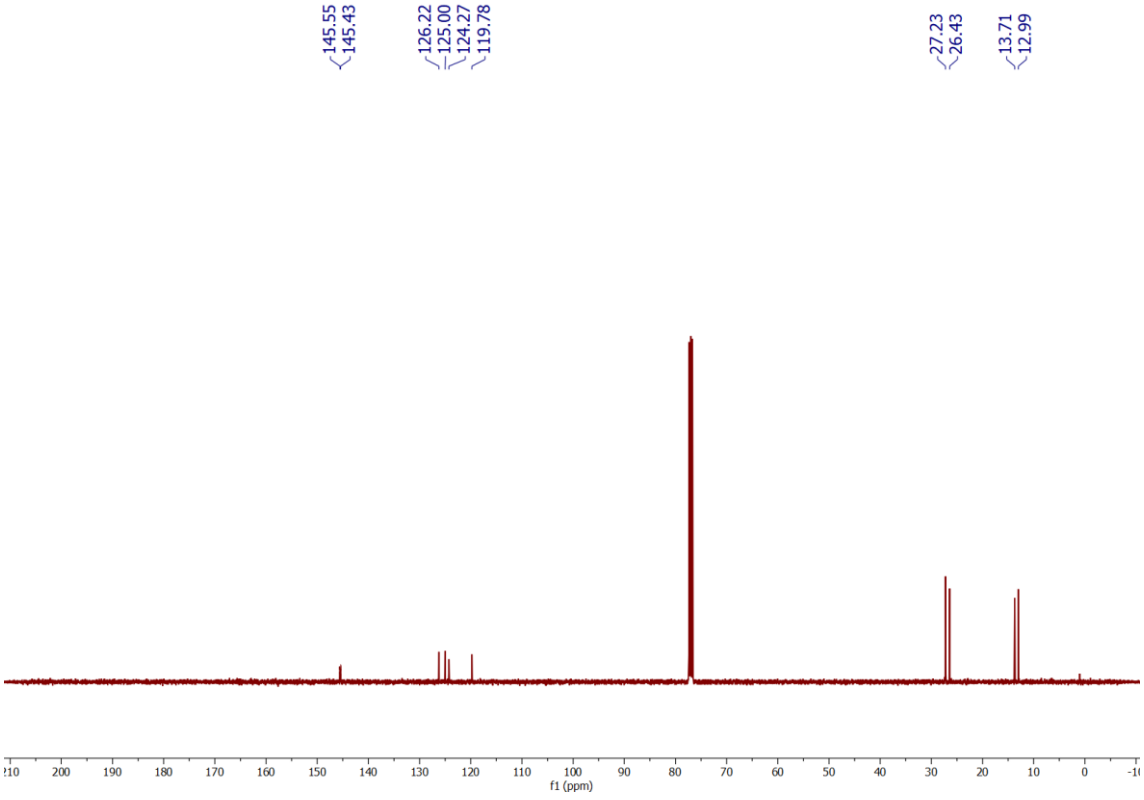


Figure S12. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P6**

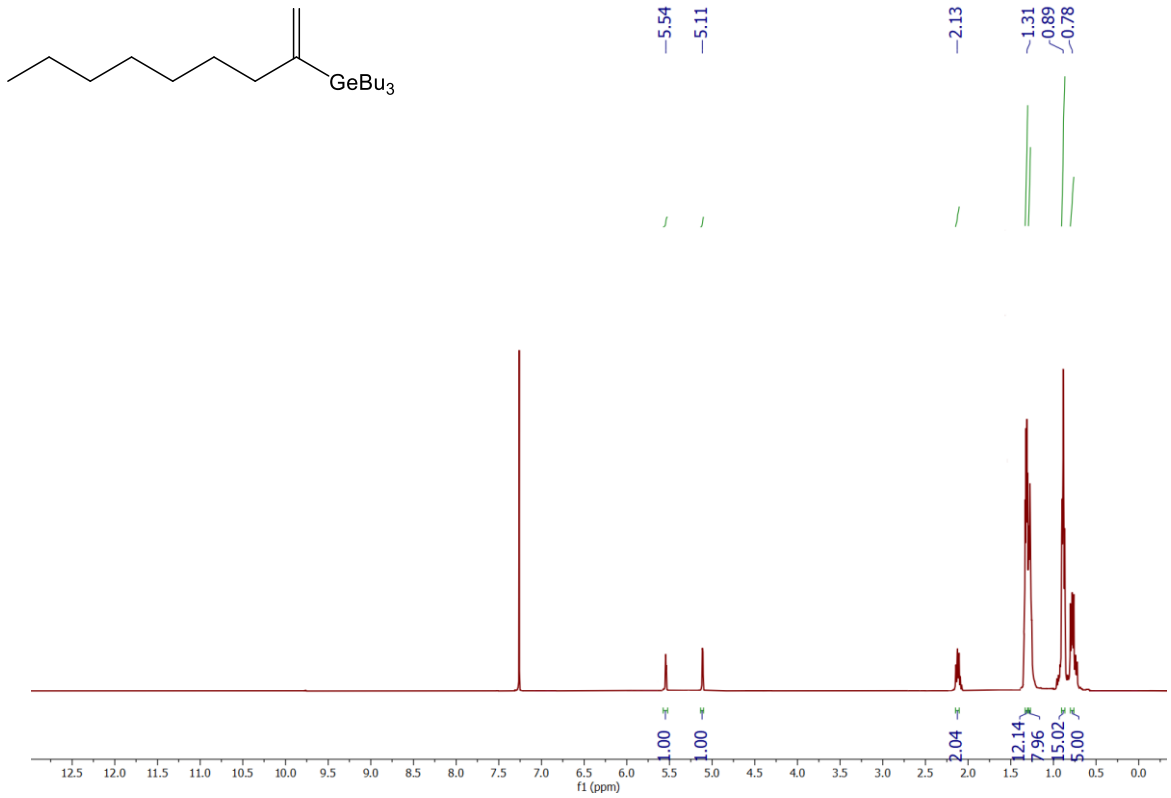


Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P7**

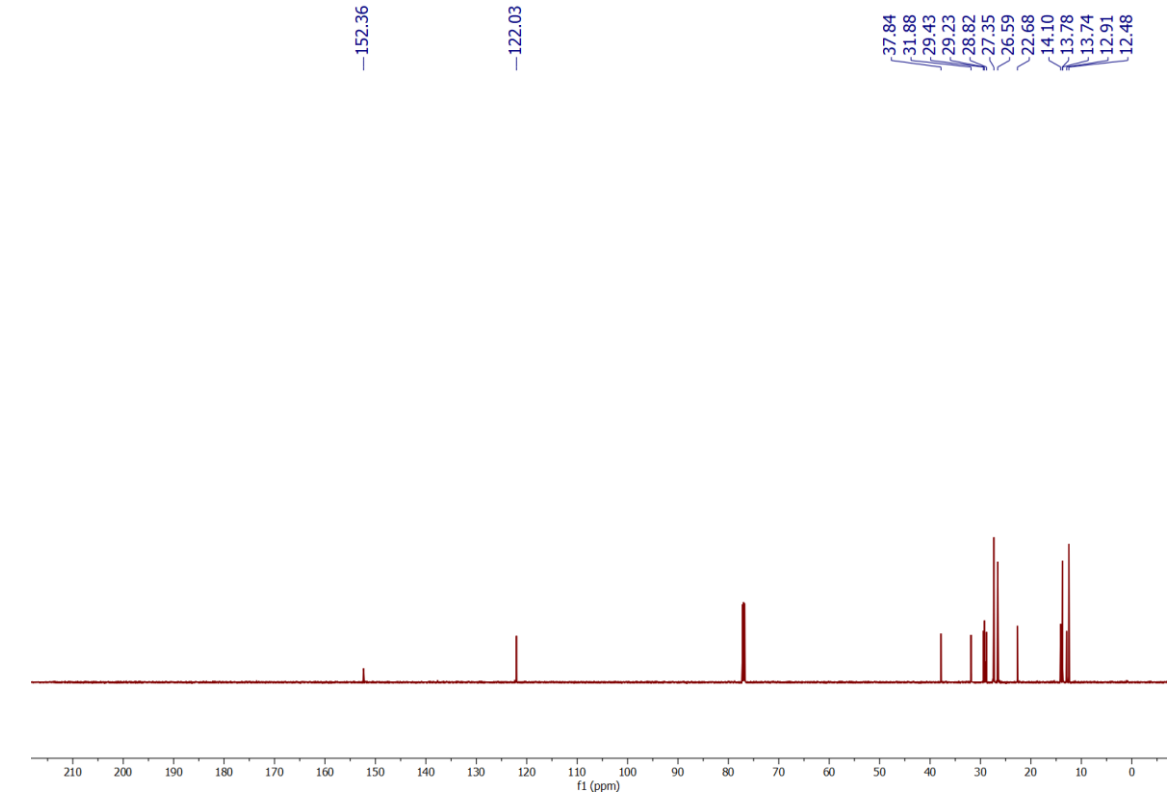


Figure S14. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P7**

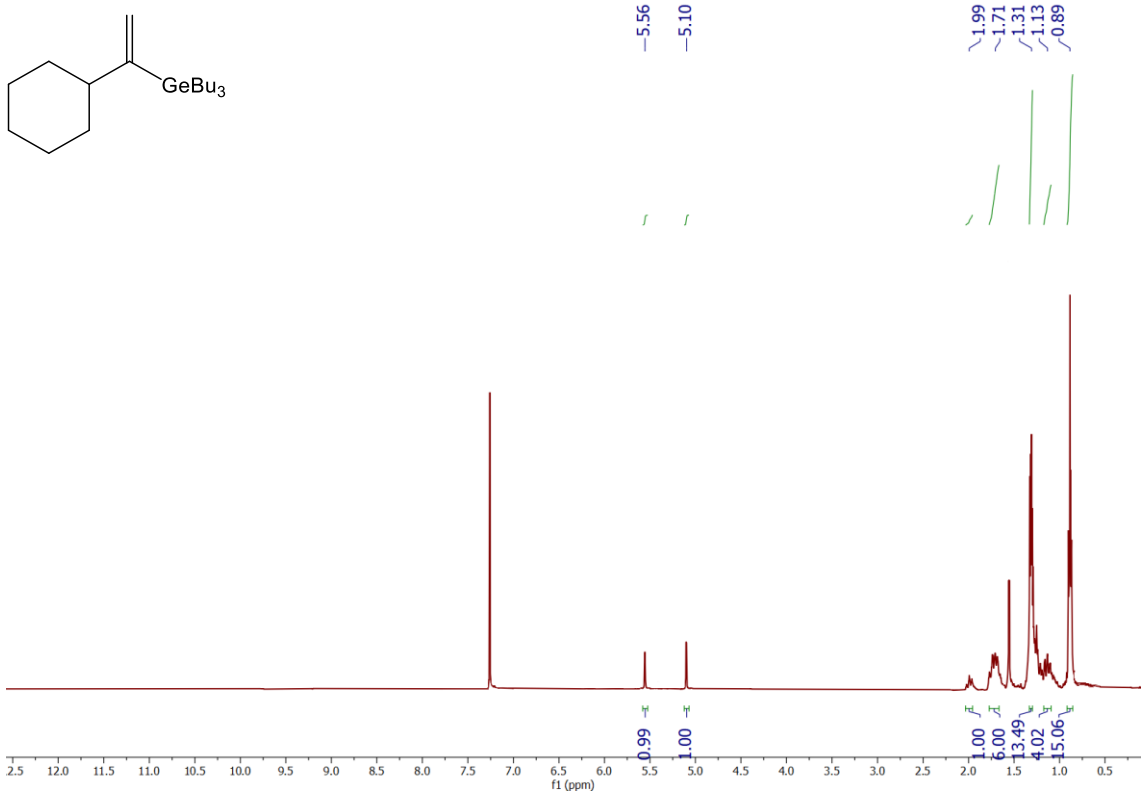


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P8**. Signal at 1.56 ppm derives from water from $CDCl_3$

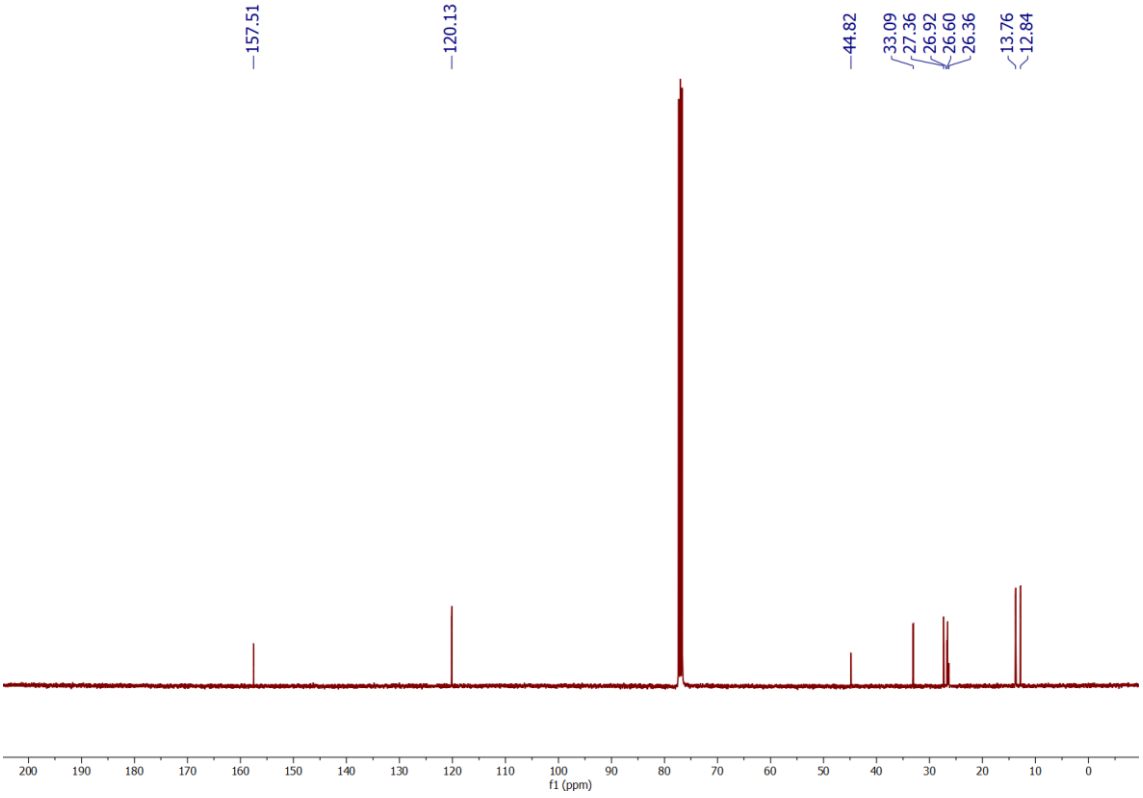


Figure S16. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P8**

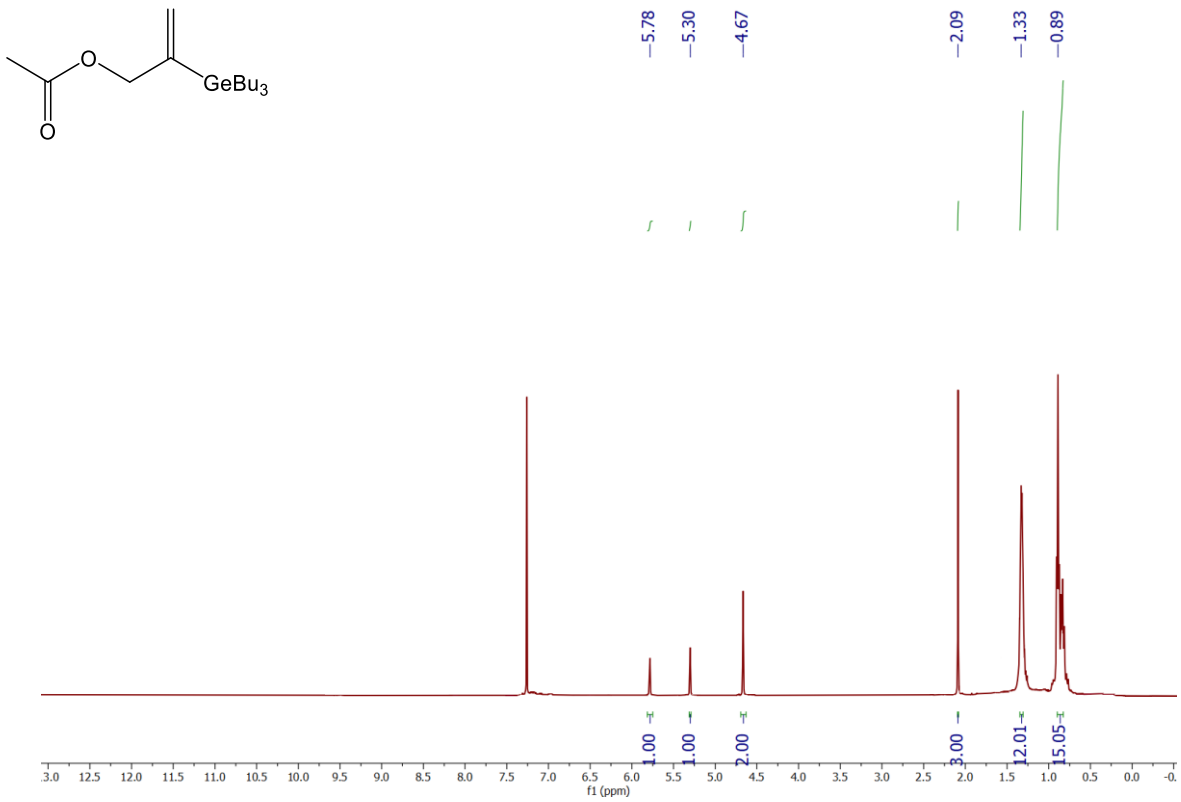


Figure S17. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P9**

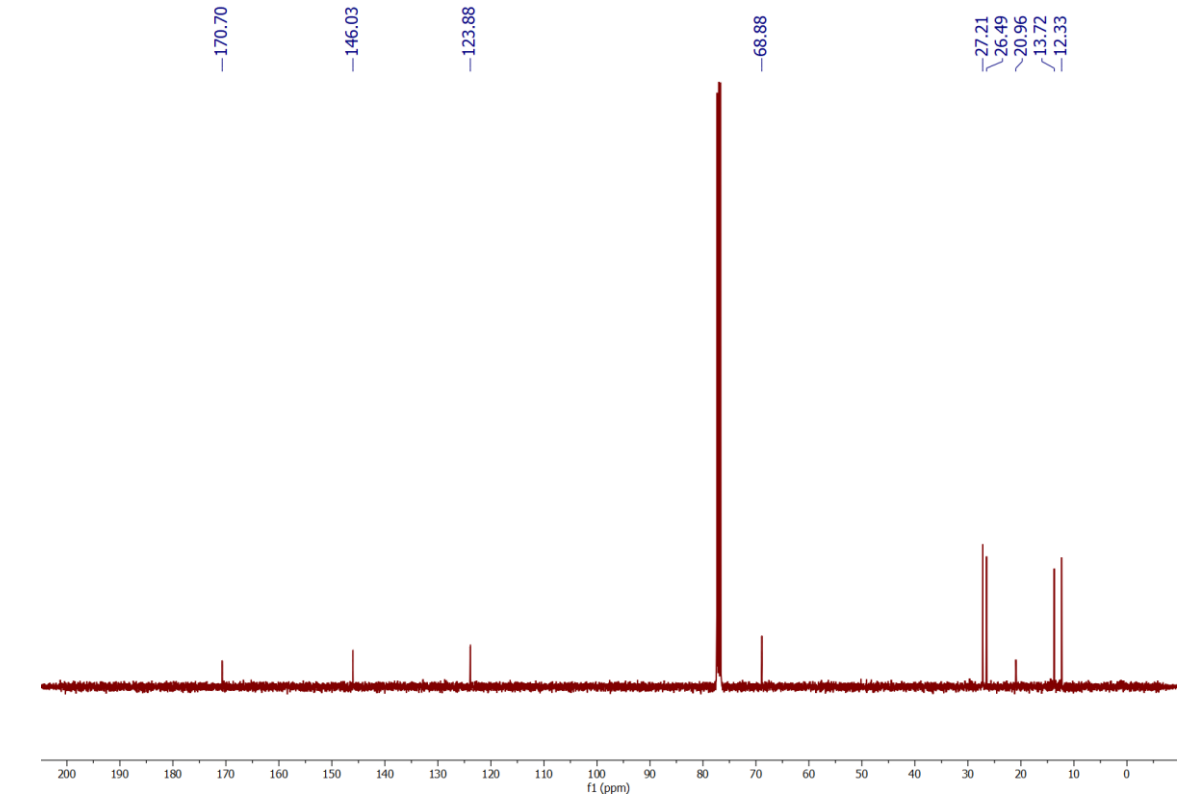


Figure S18. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P9**

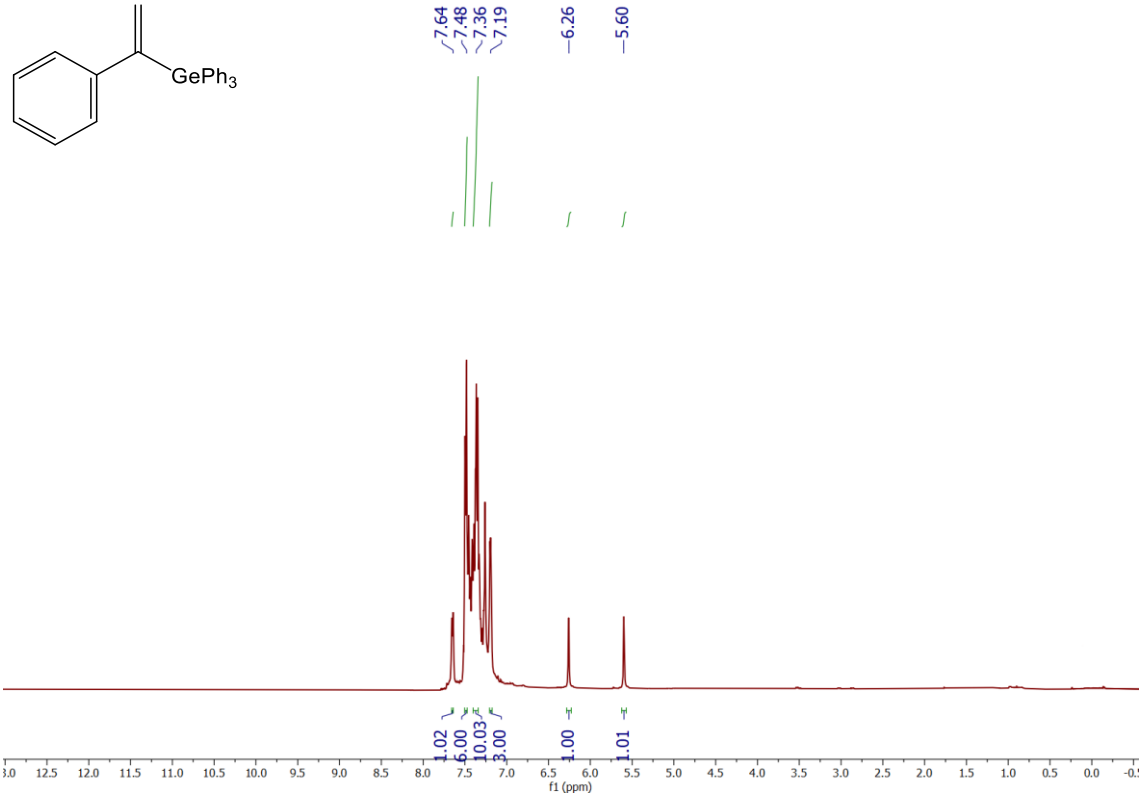


Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P10**

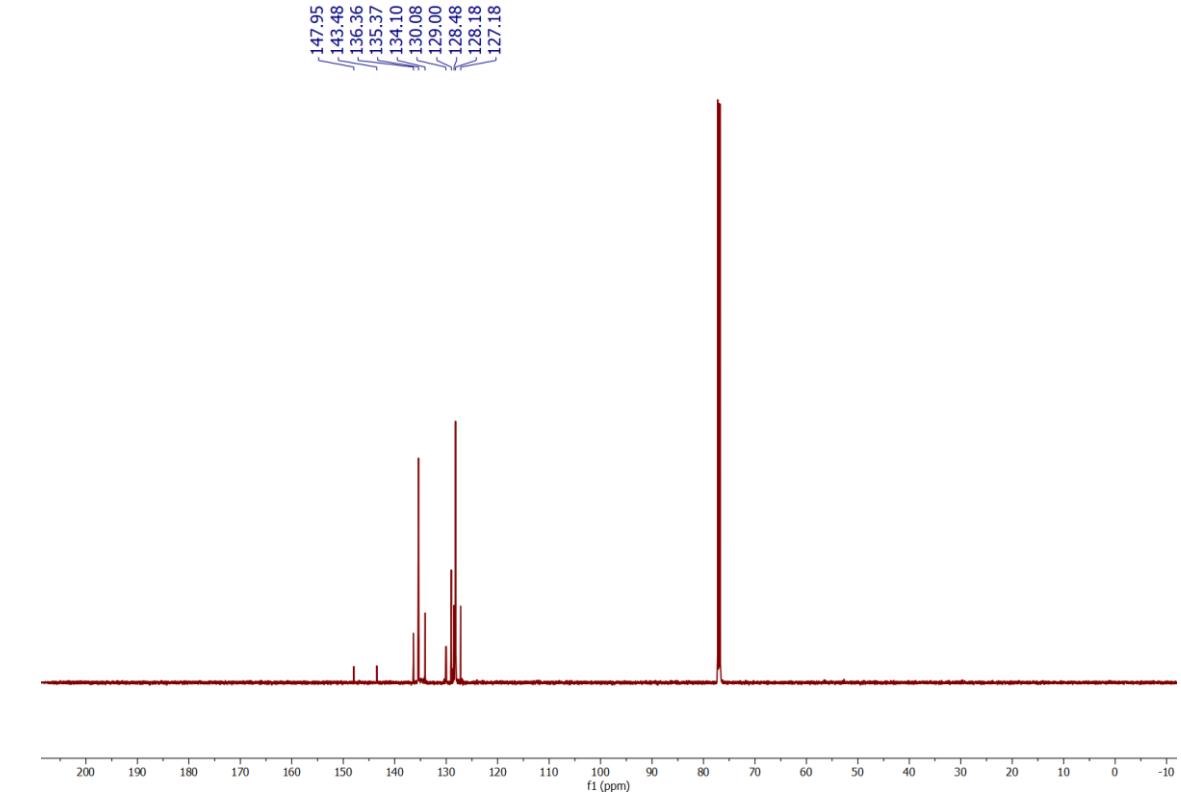


Figure S20. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P10**

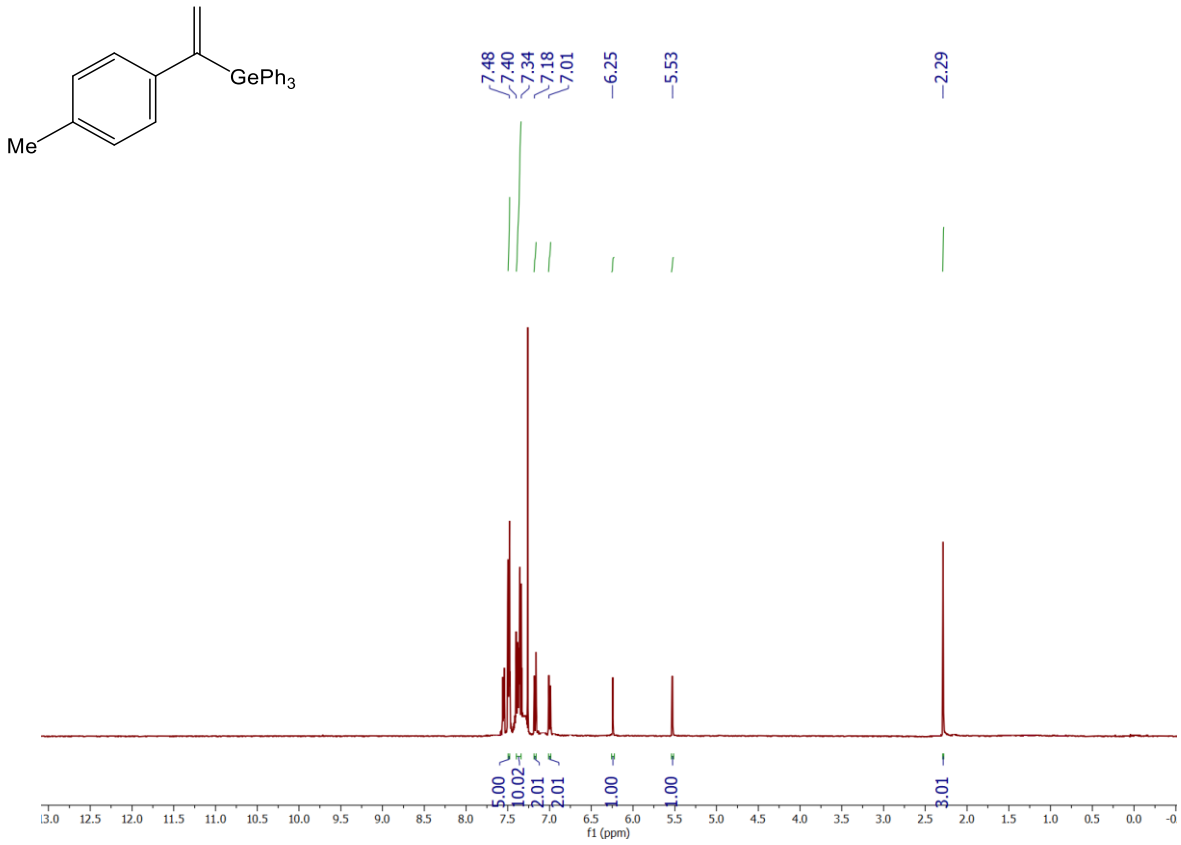


Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P11**

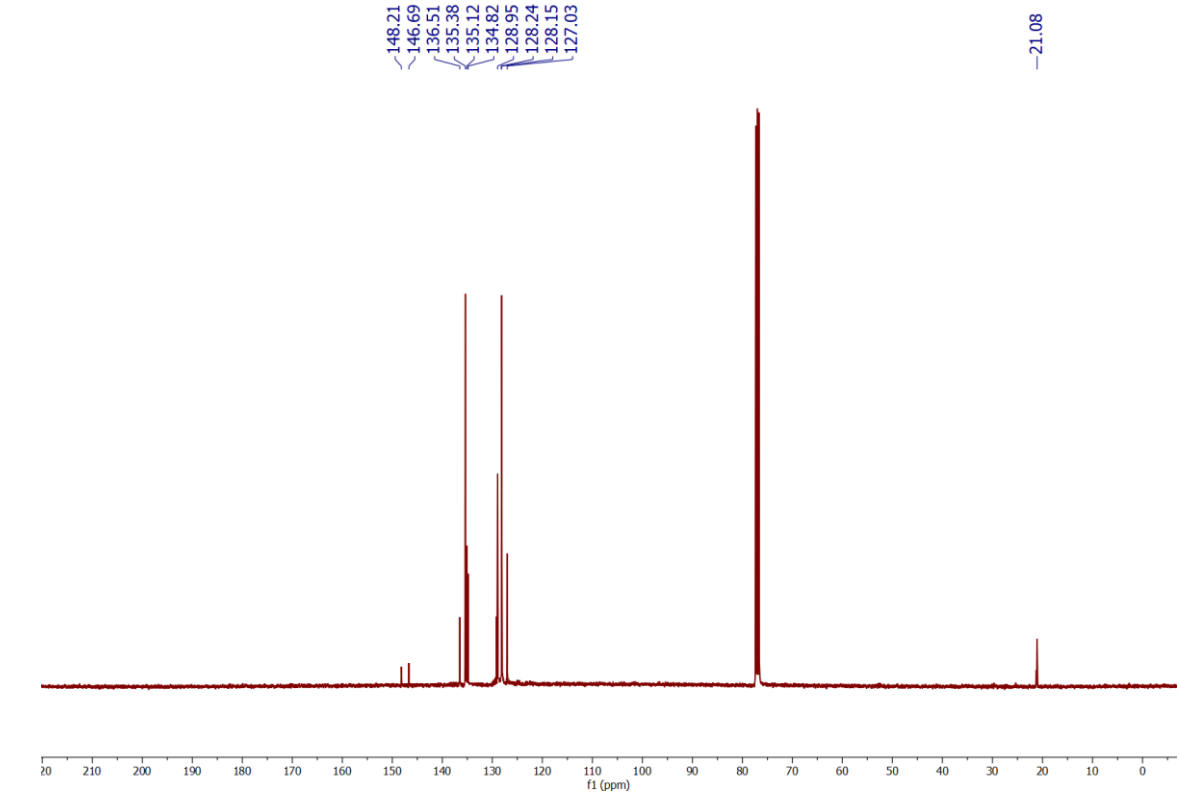


Figure S22. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P11**

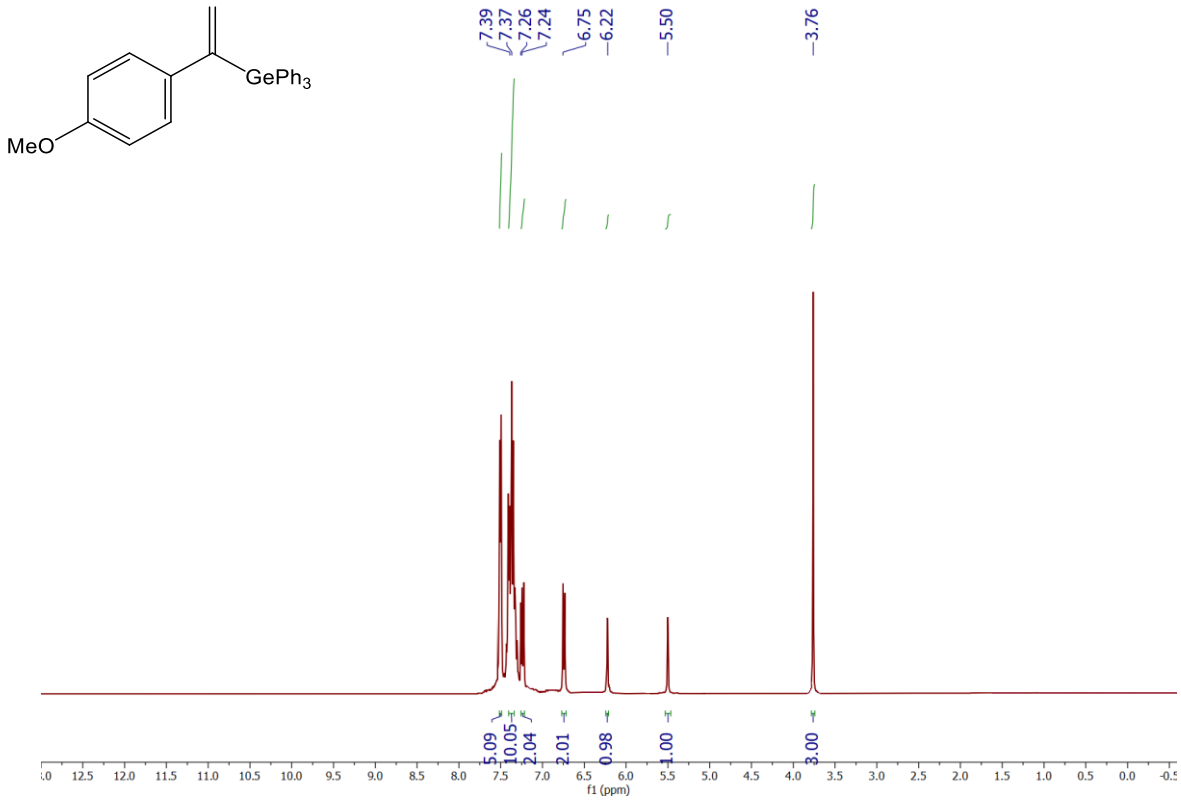


Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P12**

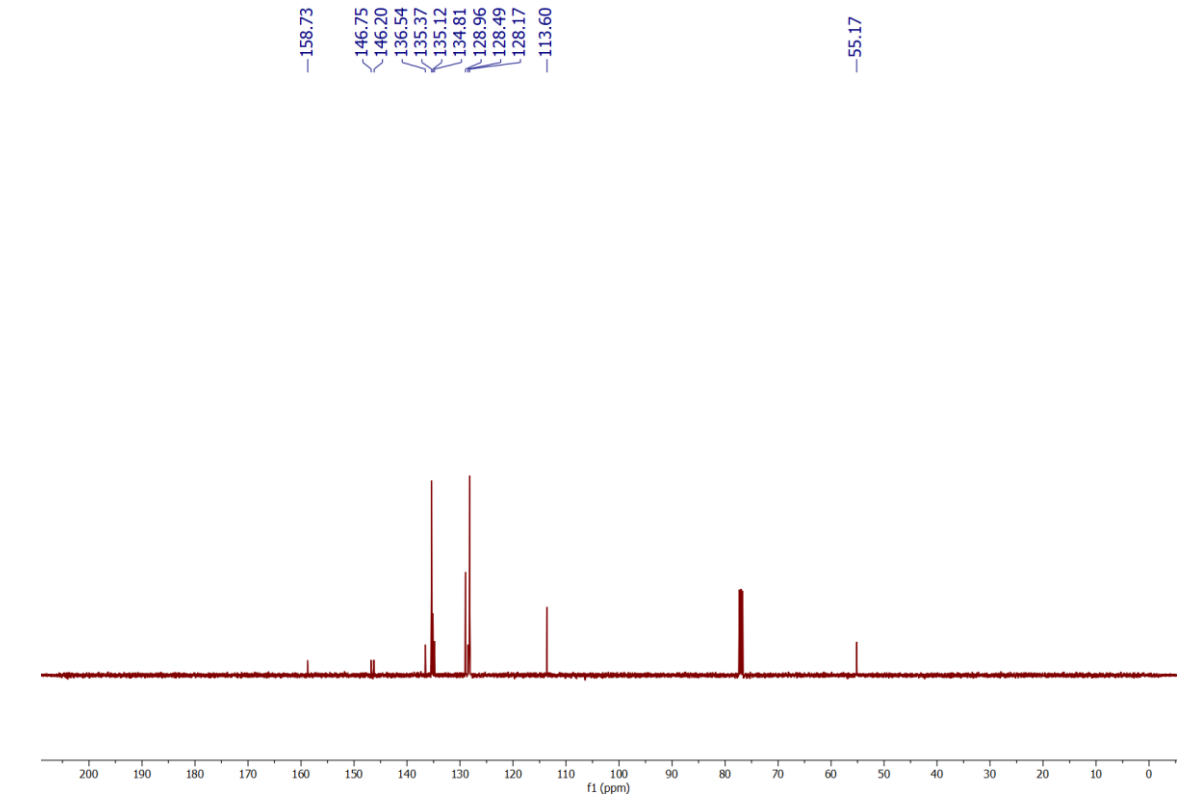


Figure S24. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P12**

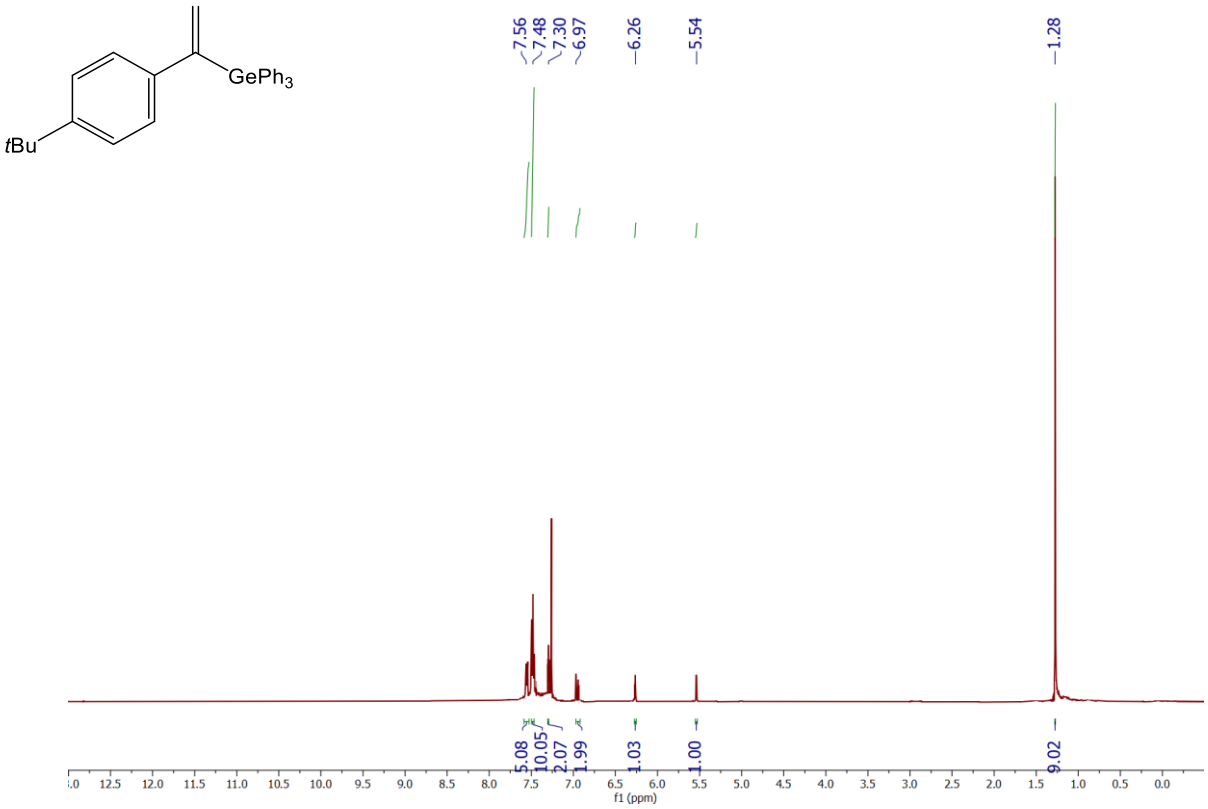


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P13**

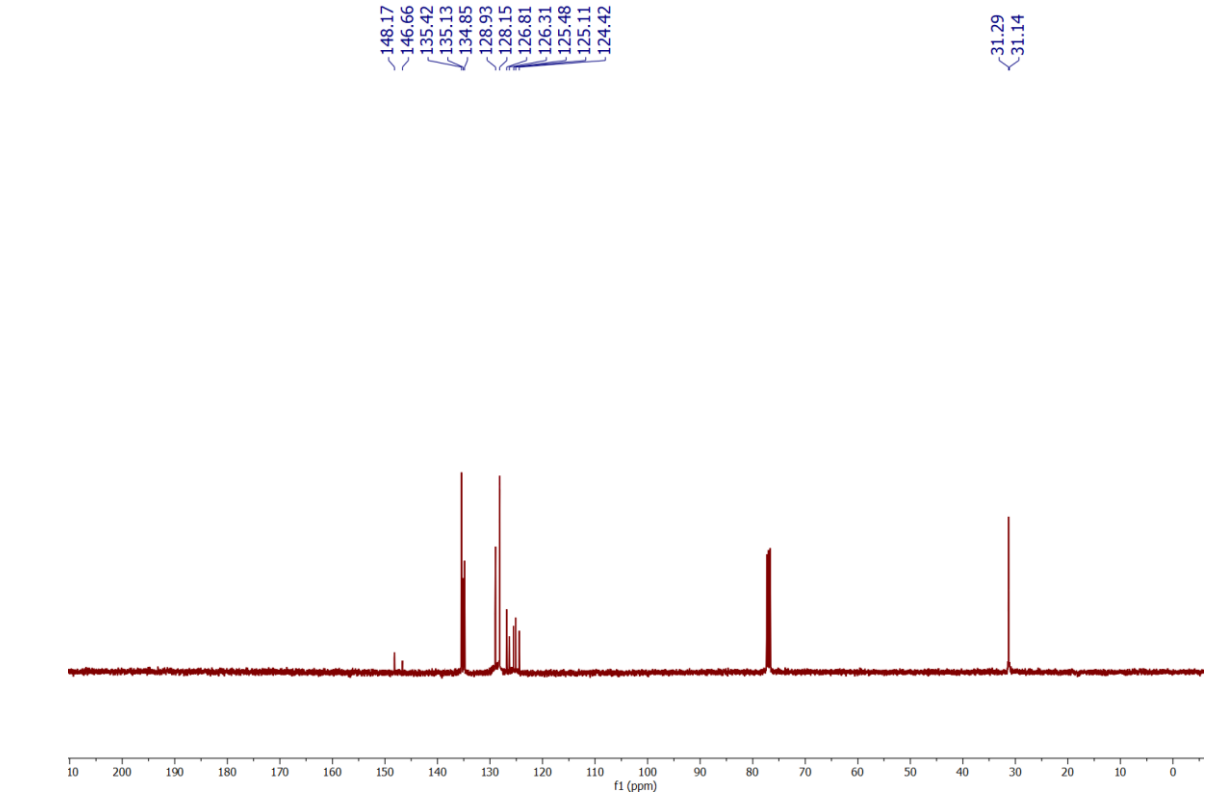


Figure S26. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P13**

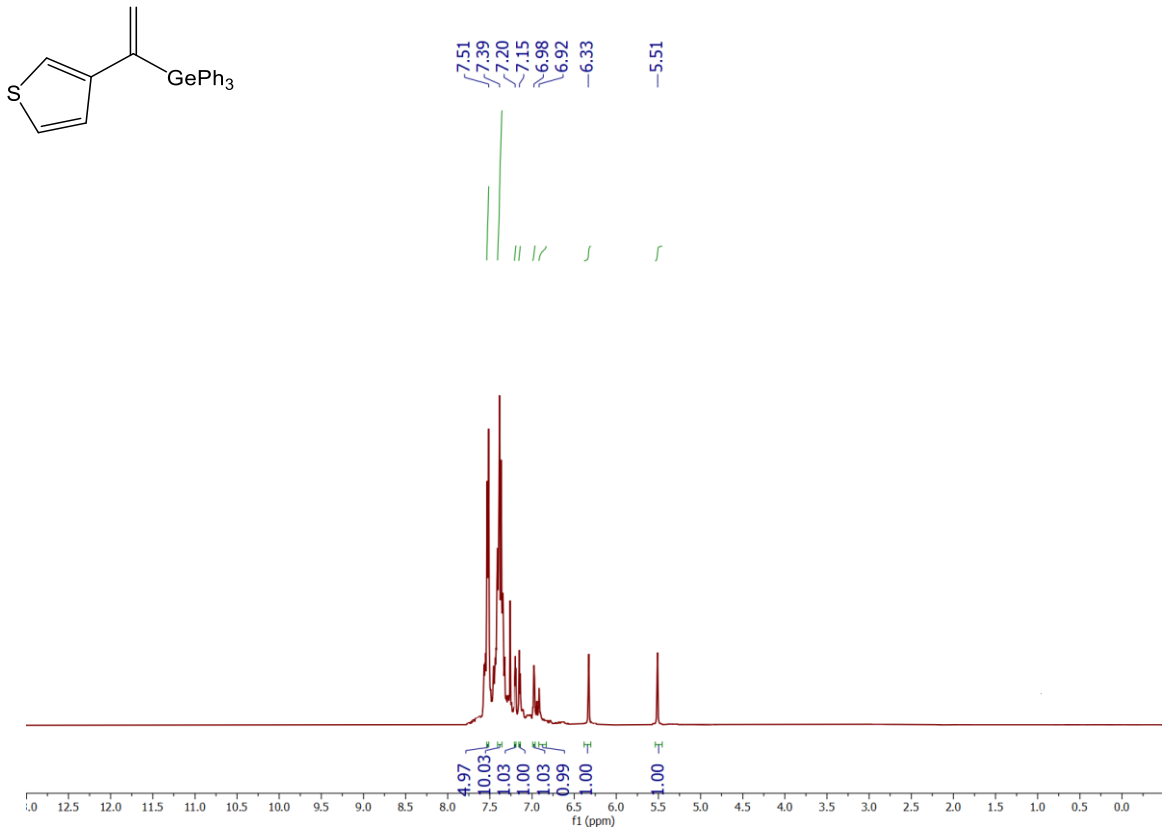


Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P14**

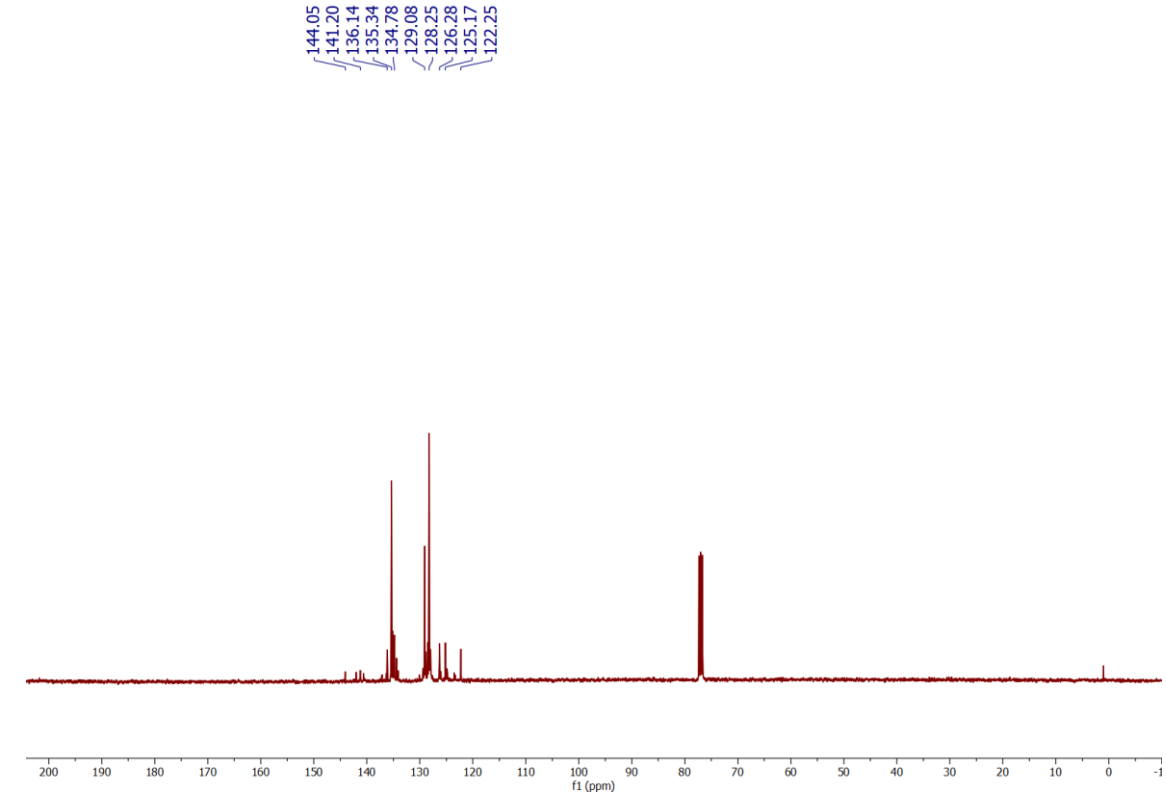


Figure S28. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P14**

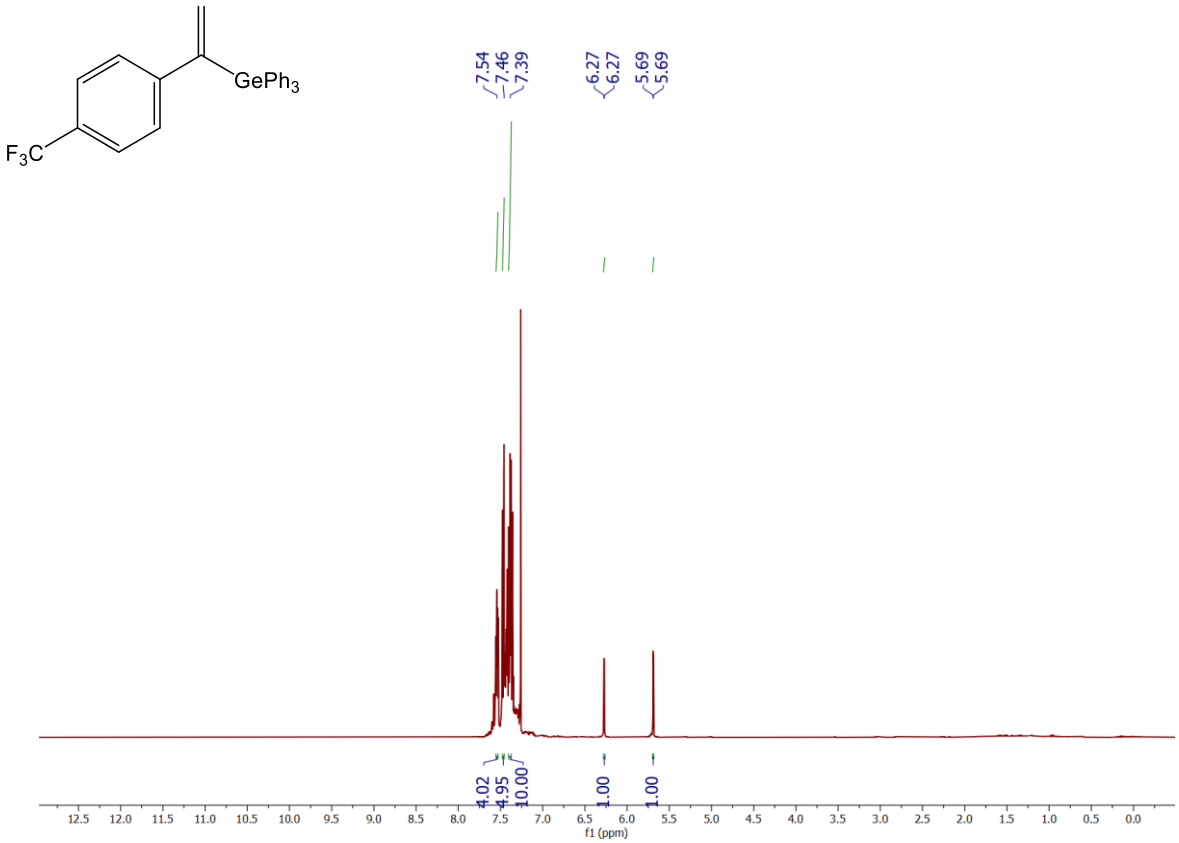


Figure S29. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P15**

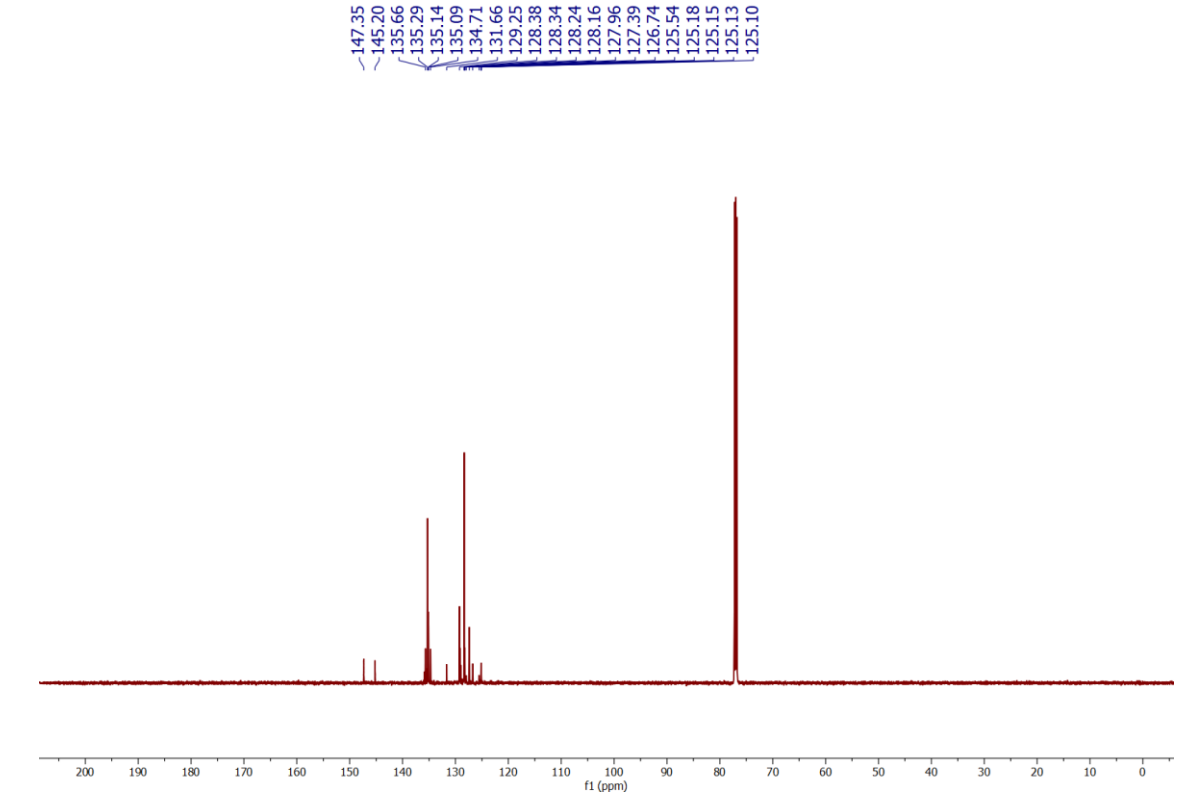


Figure S30. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P15**

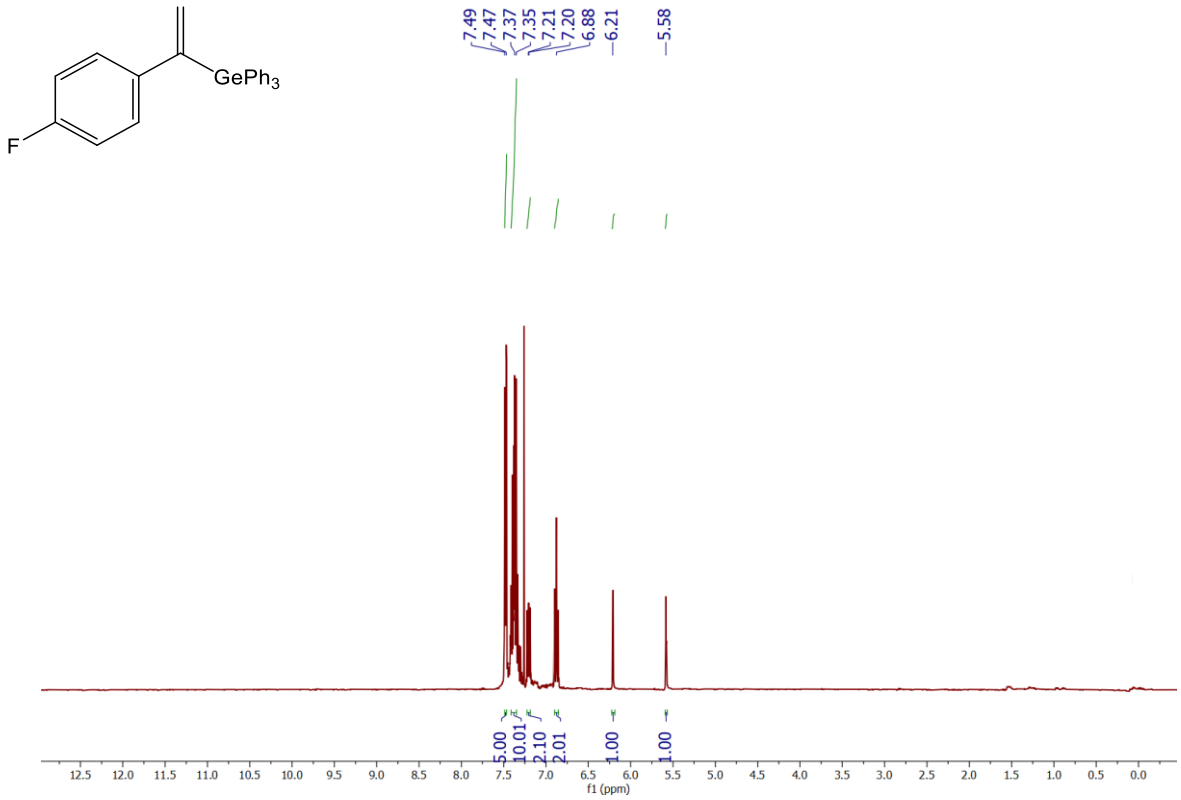


Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P16**

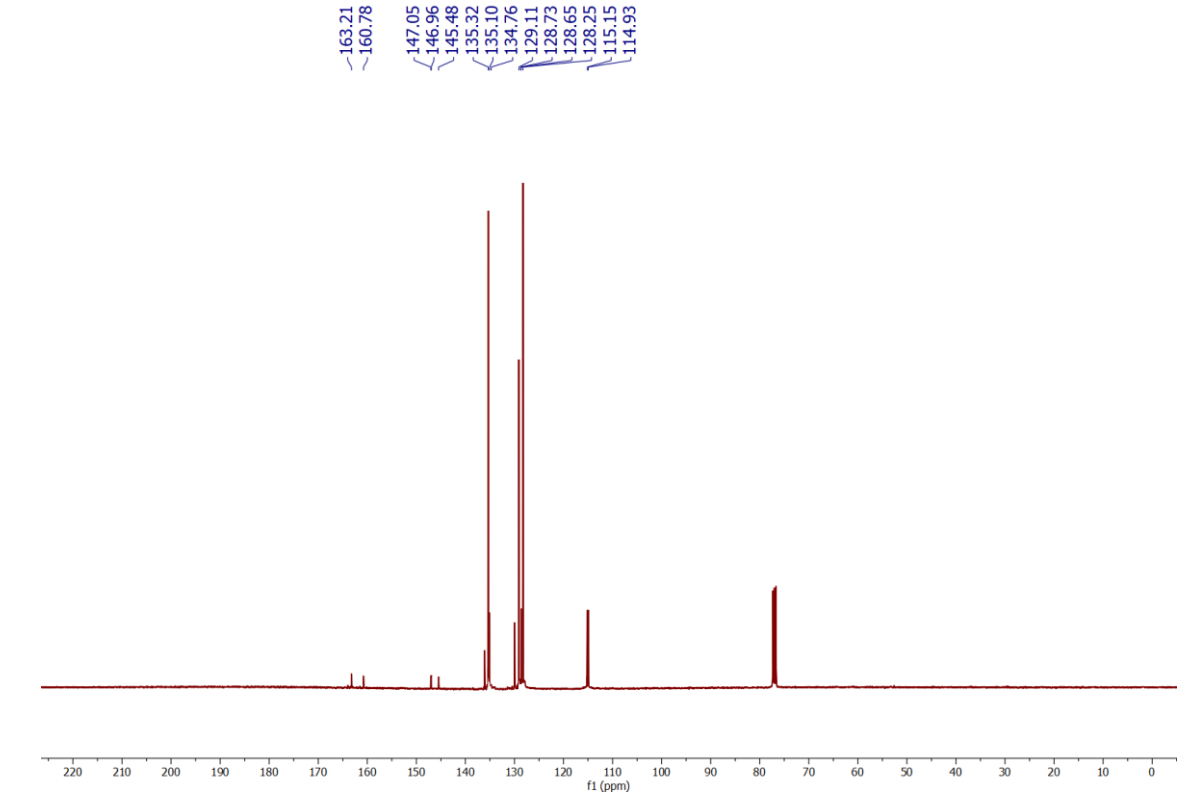


Figure S32. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P16**

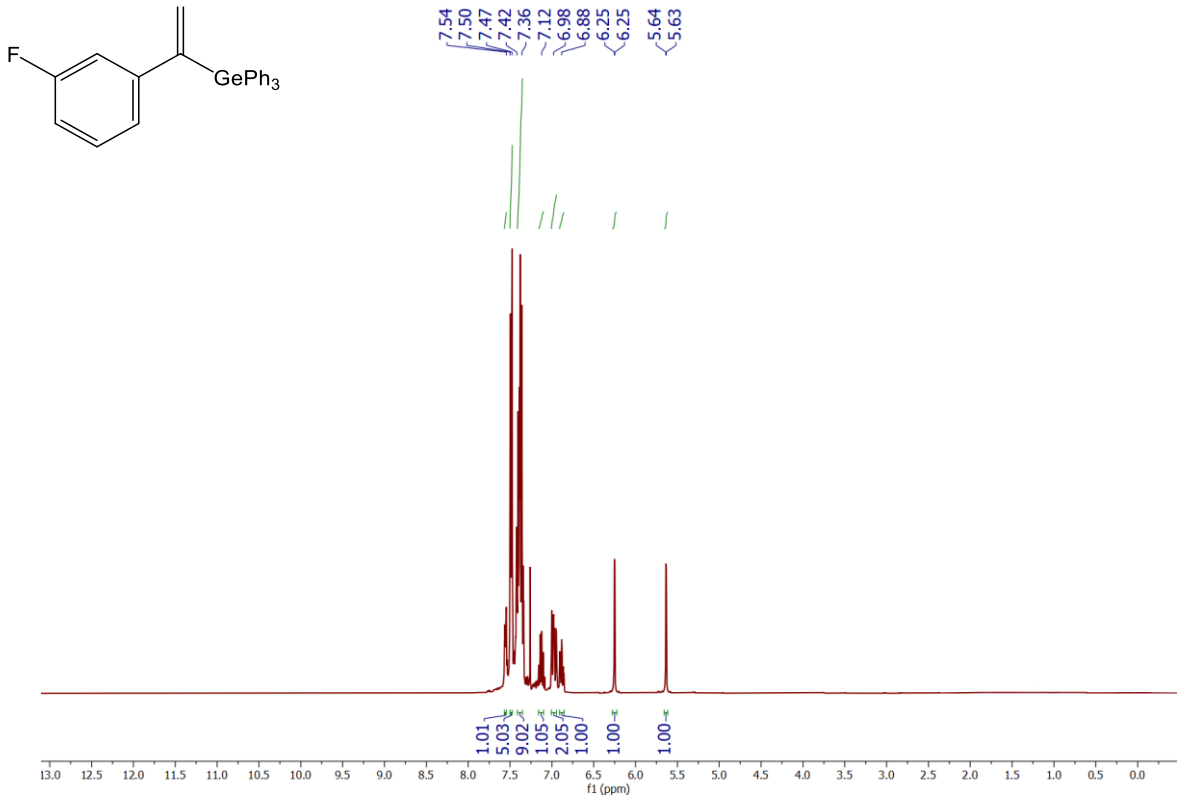


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P17**

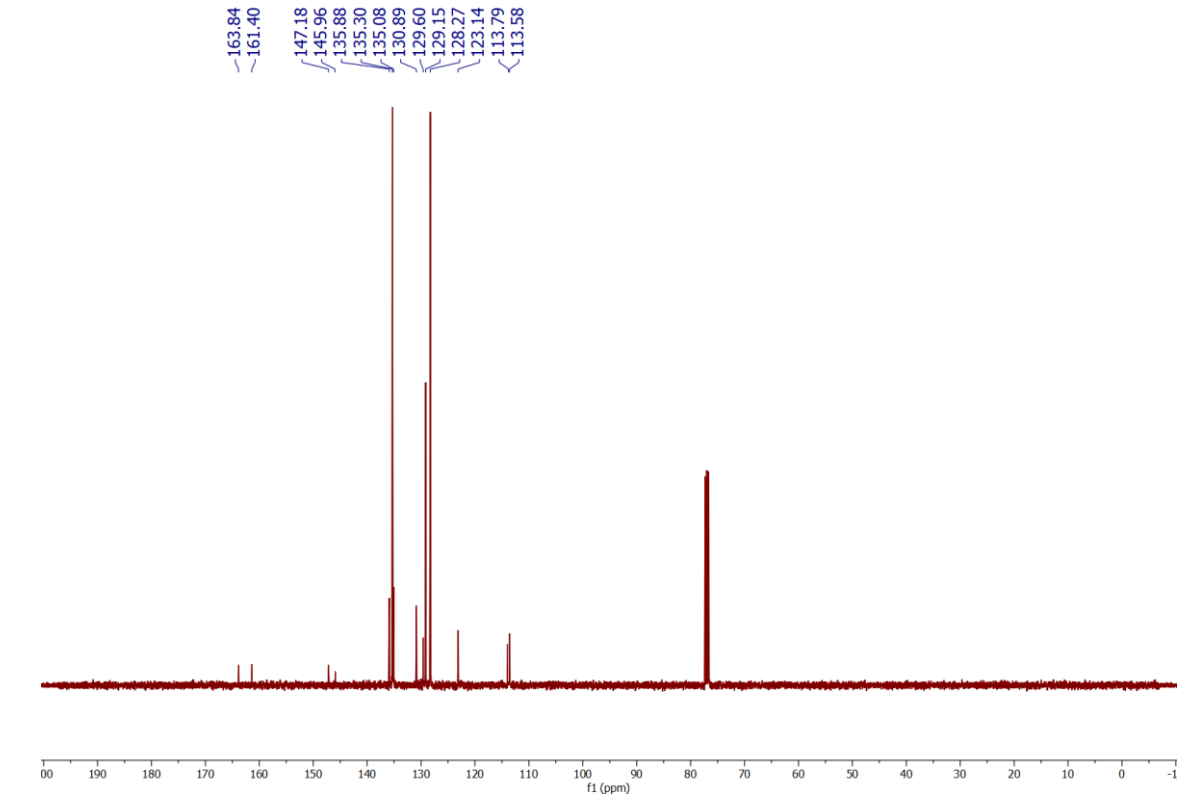


Figure S34. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P17**

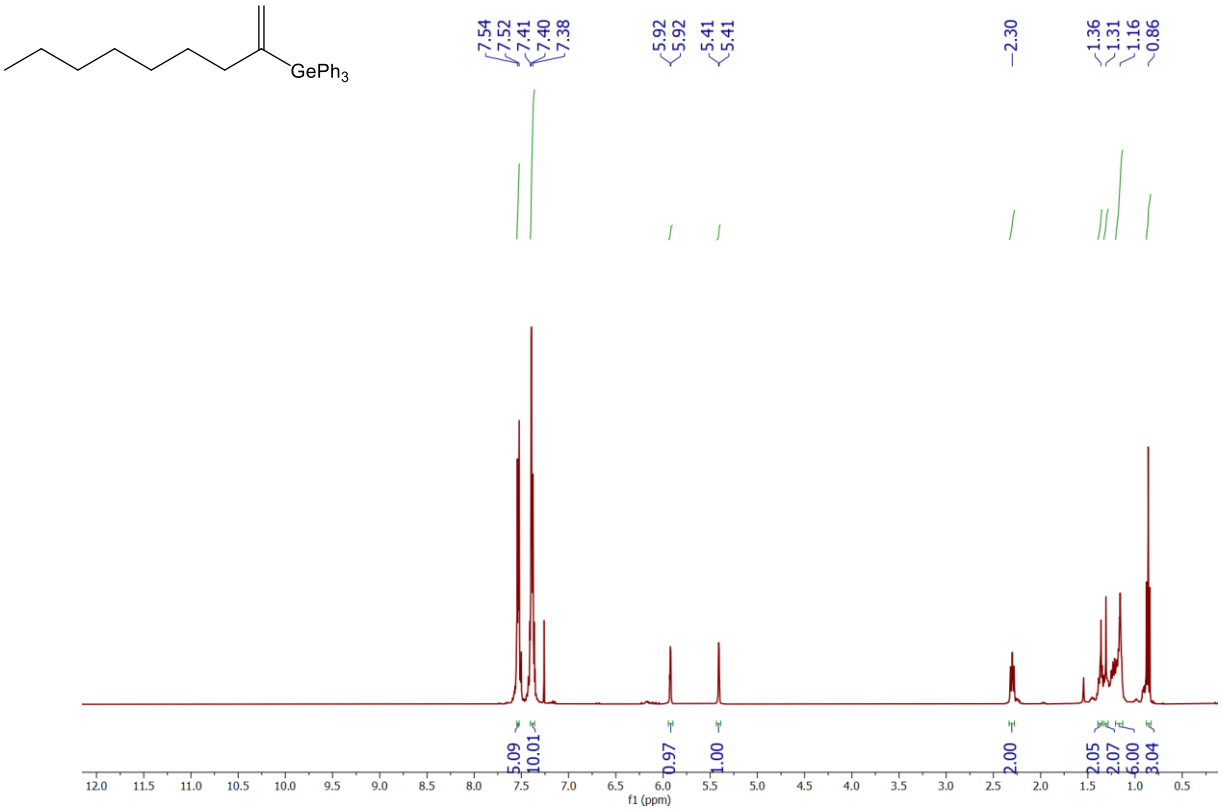


Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P18**

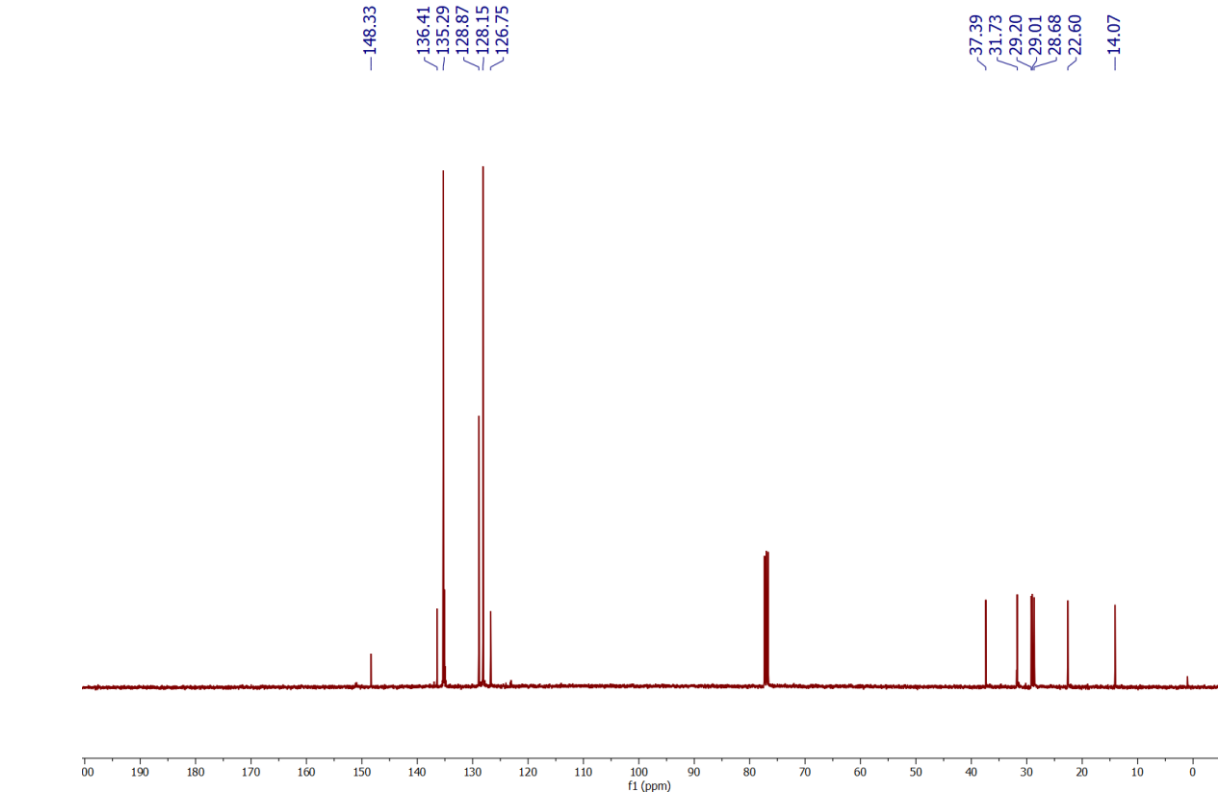


Figure S36. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P18**

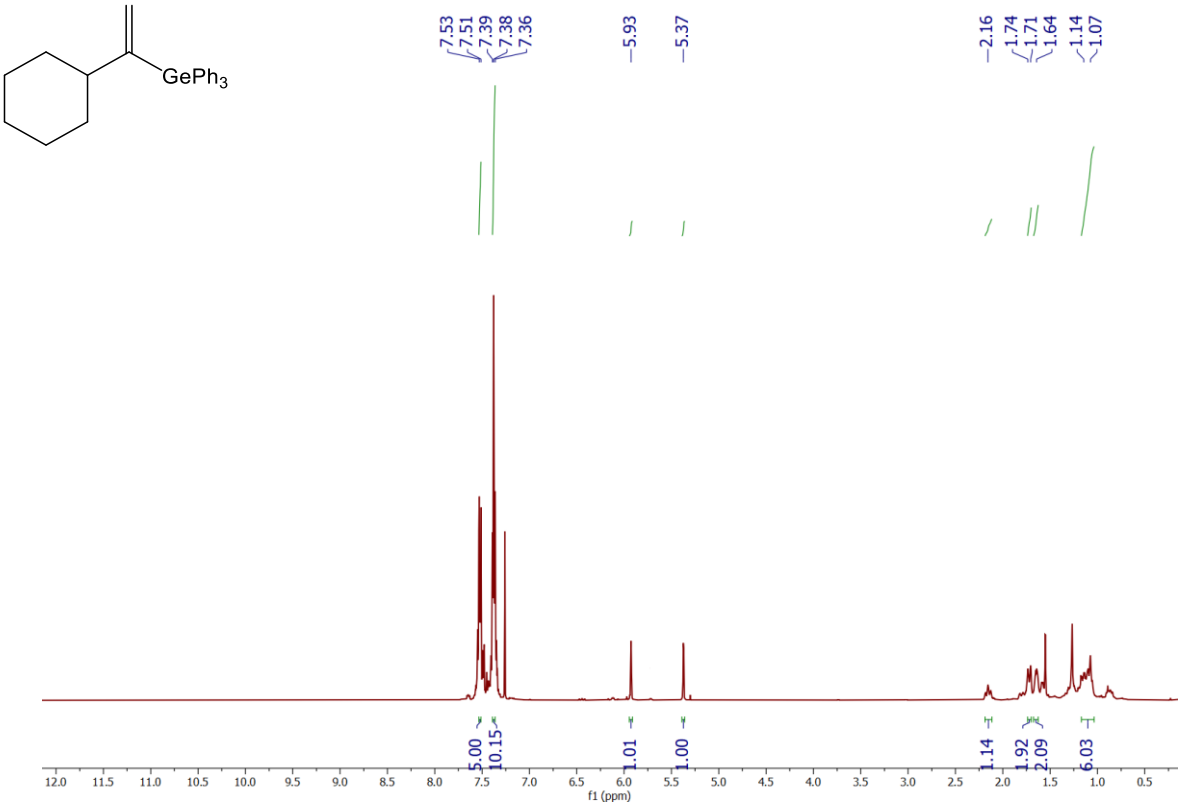


Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P19**

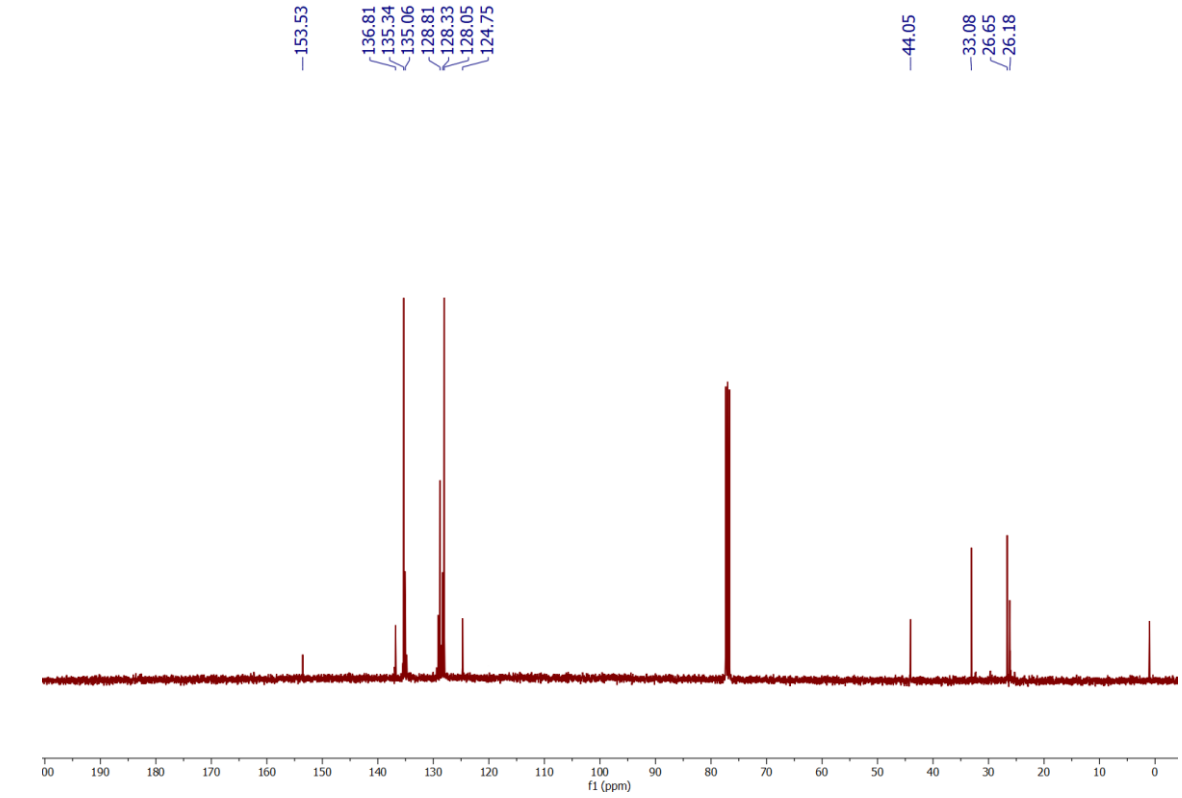


Figure S38. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P19**

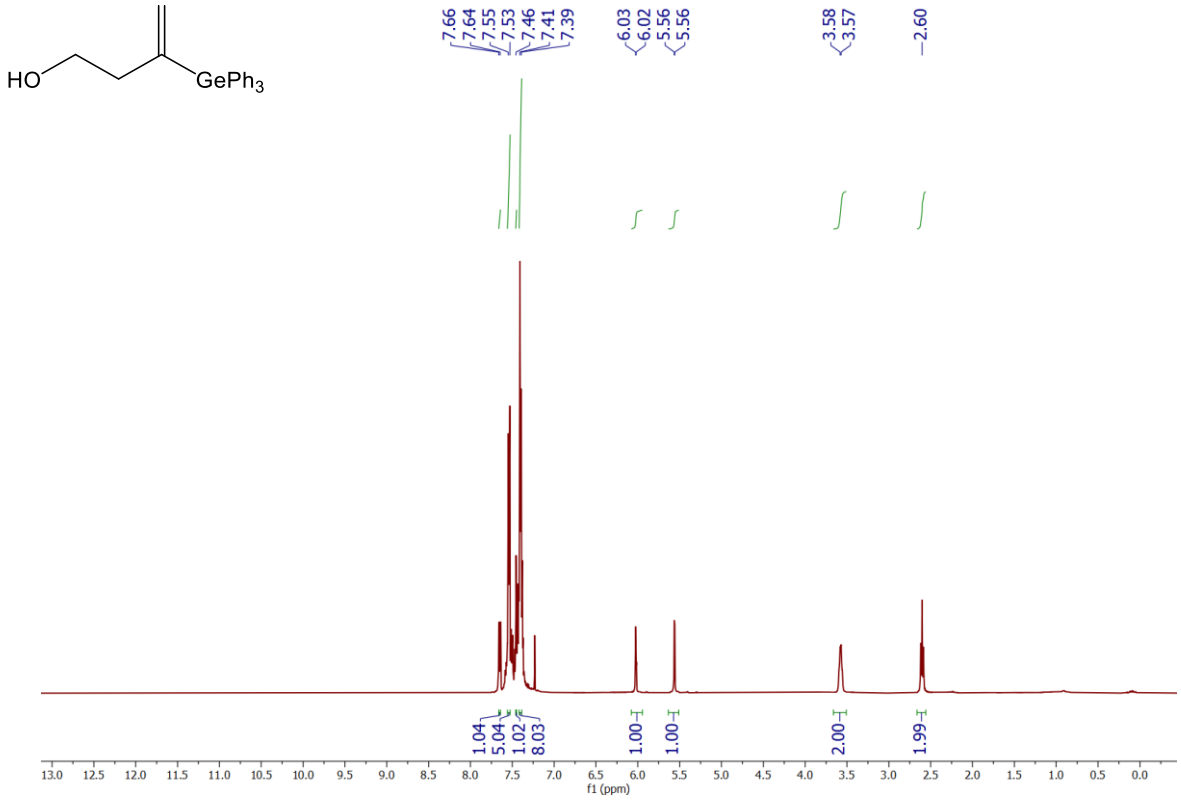


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P20**

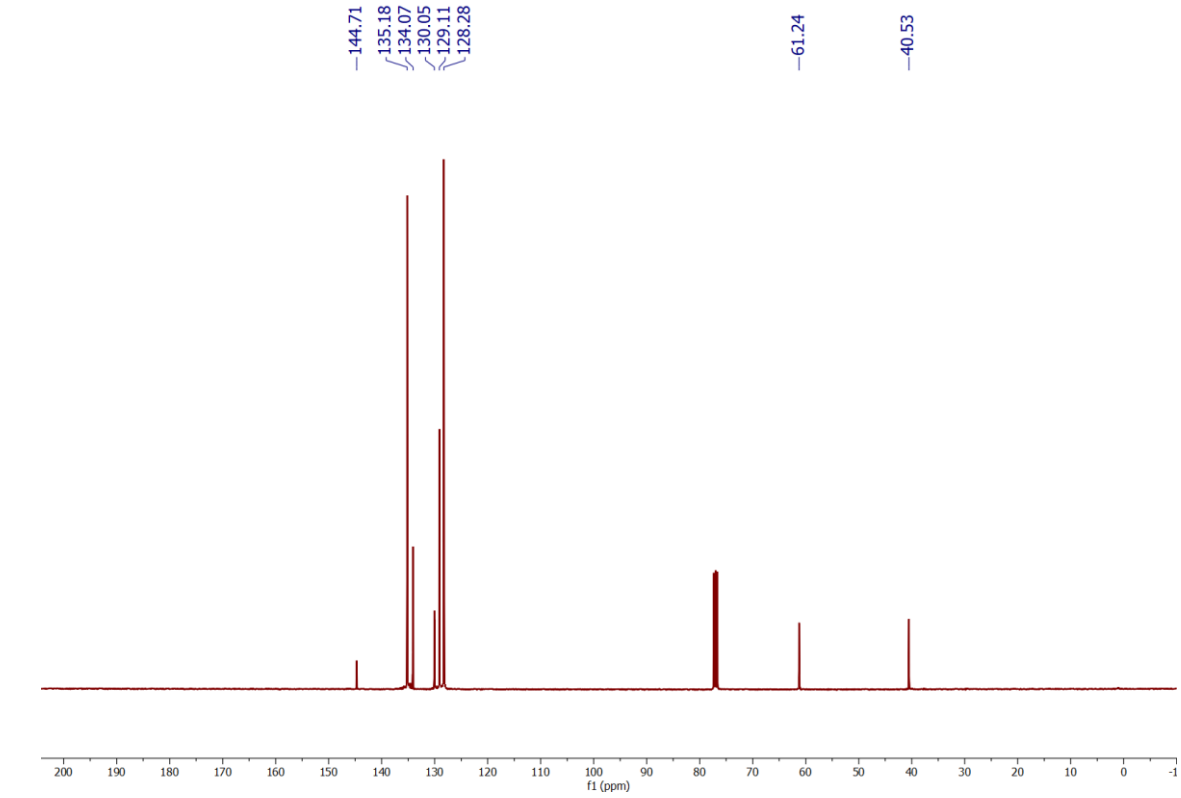


Figure S40. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P20**

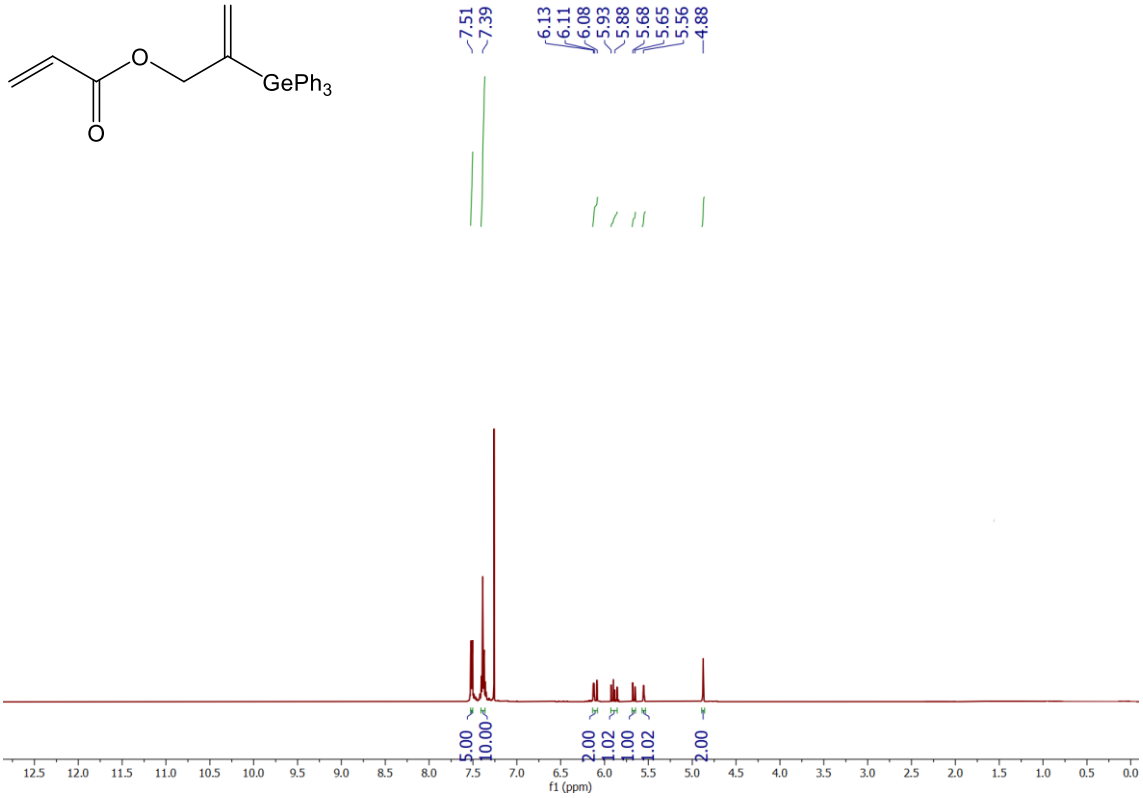


Figure S41. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P21**

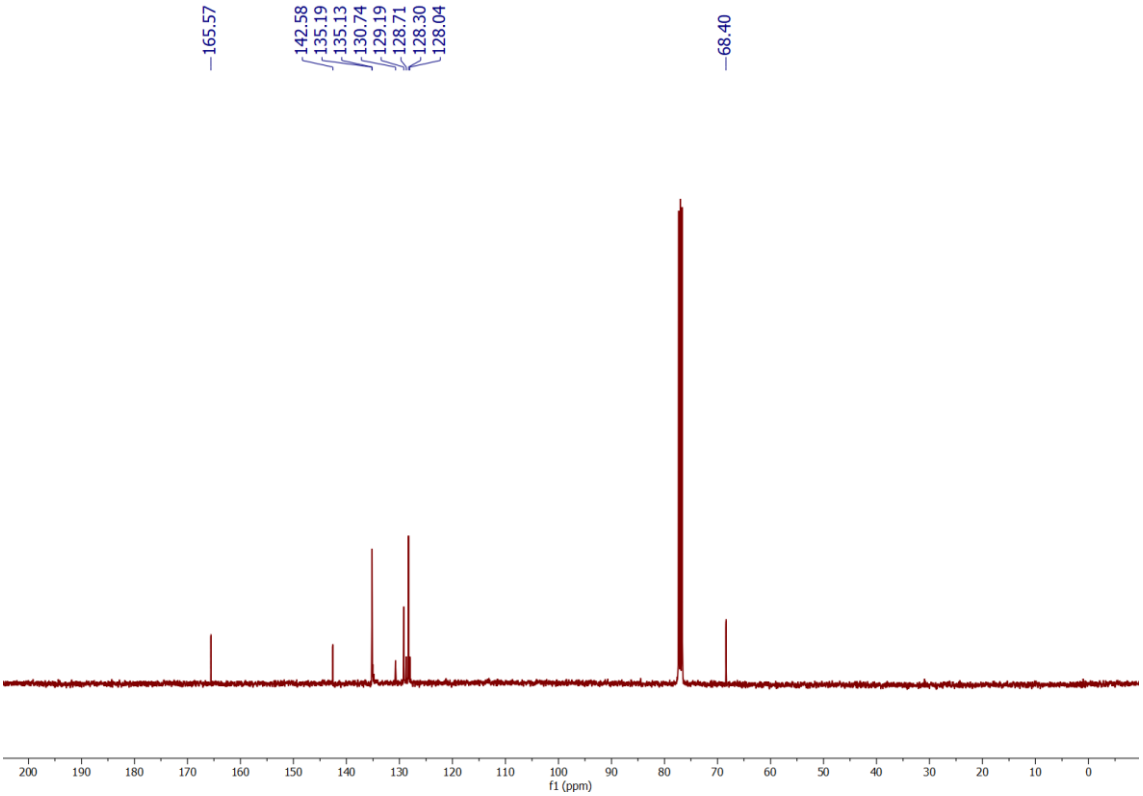


Figure S42. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P21**

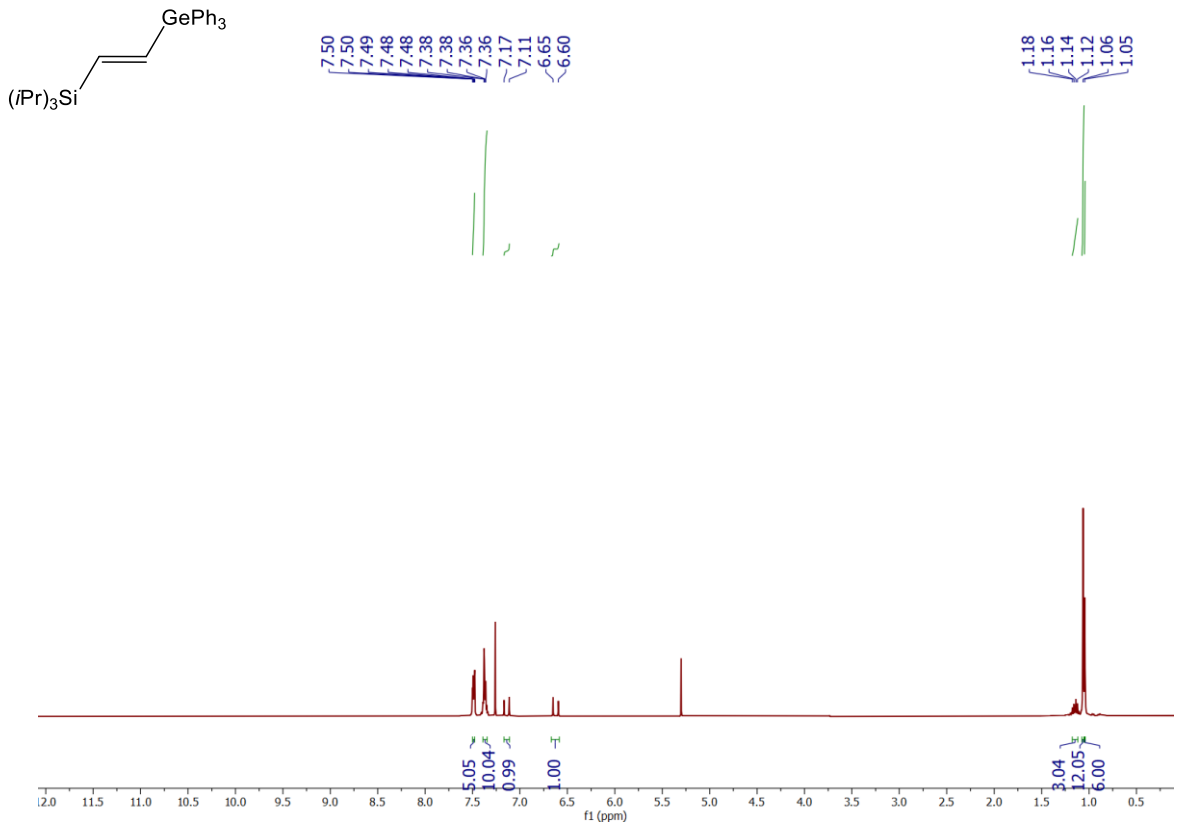


Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P22**

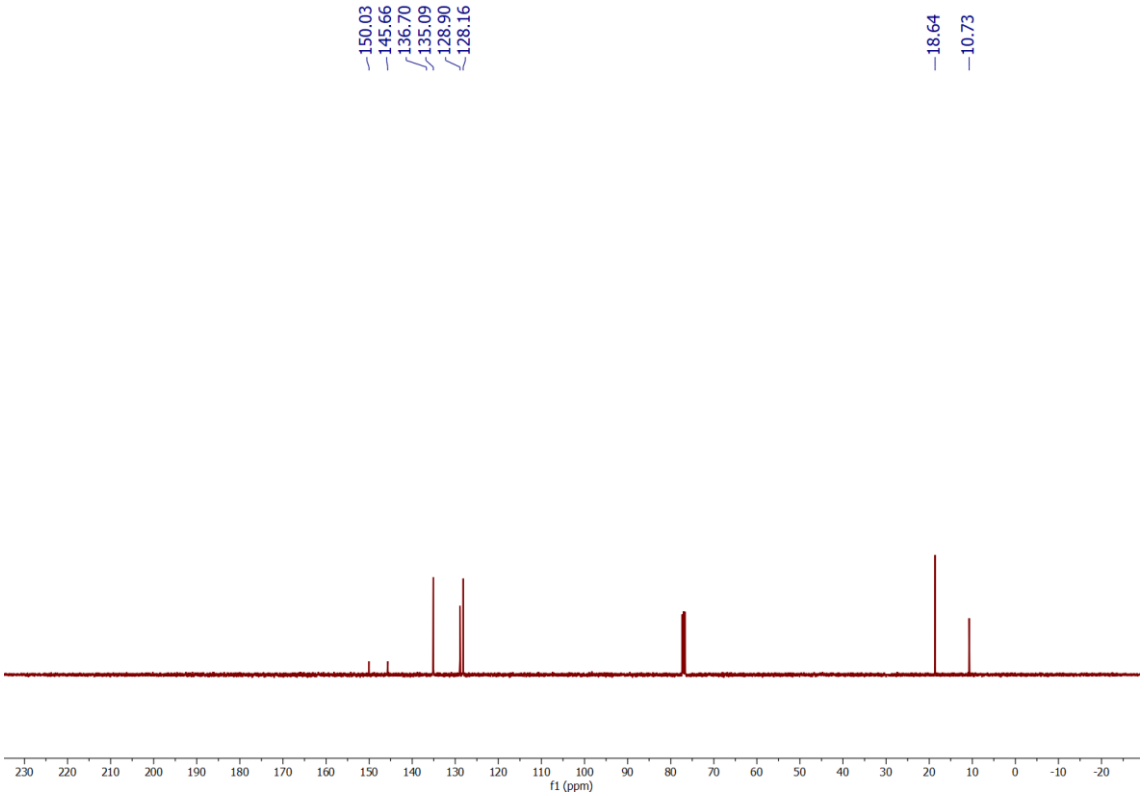


Figure S44. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P22**

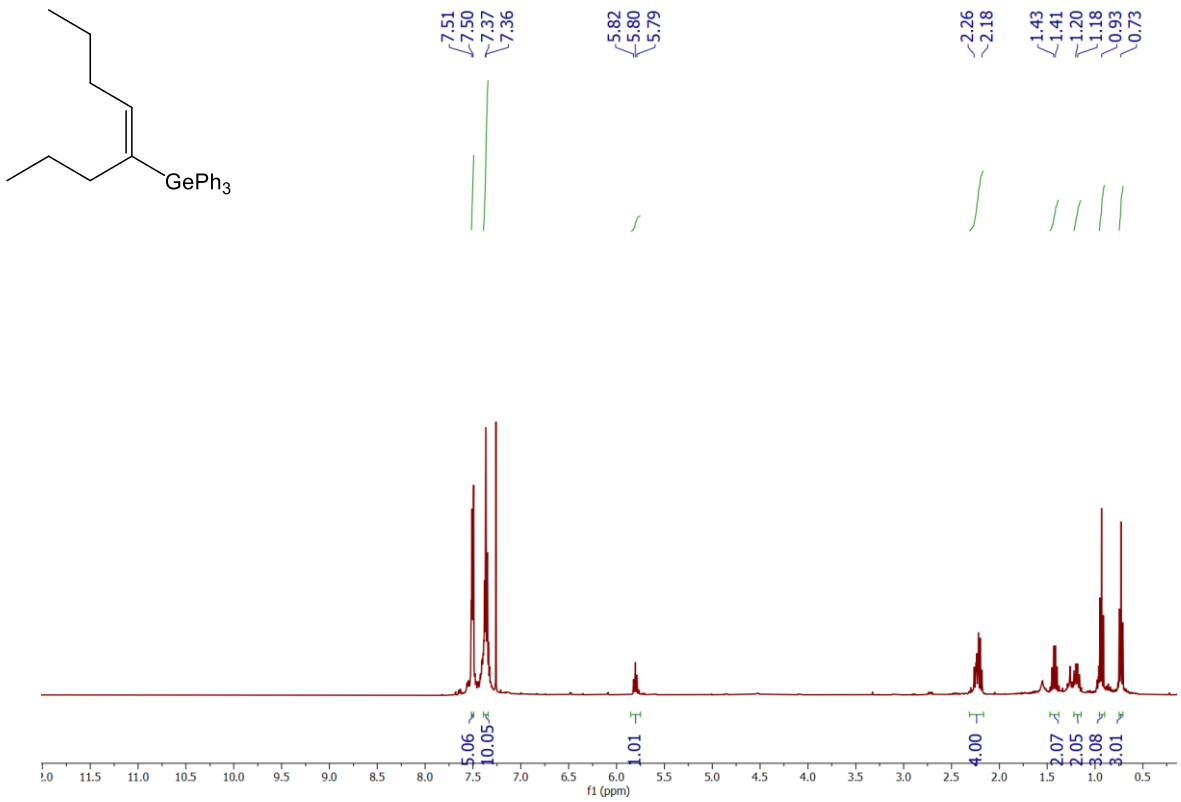


Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P23**

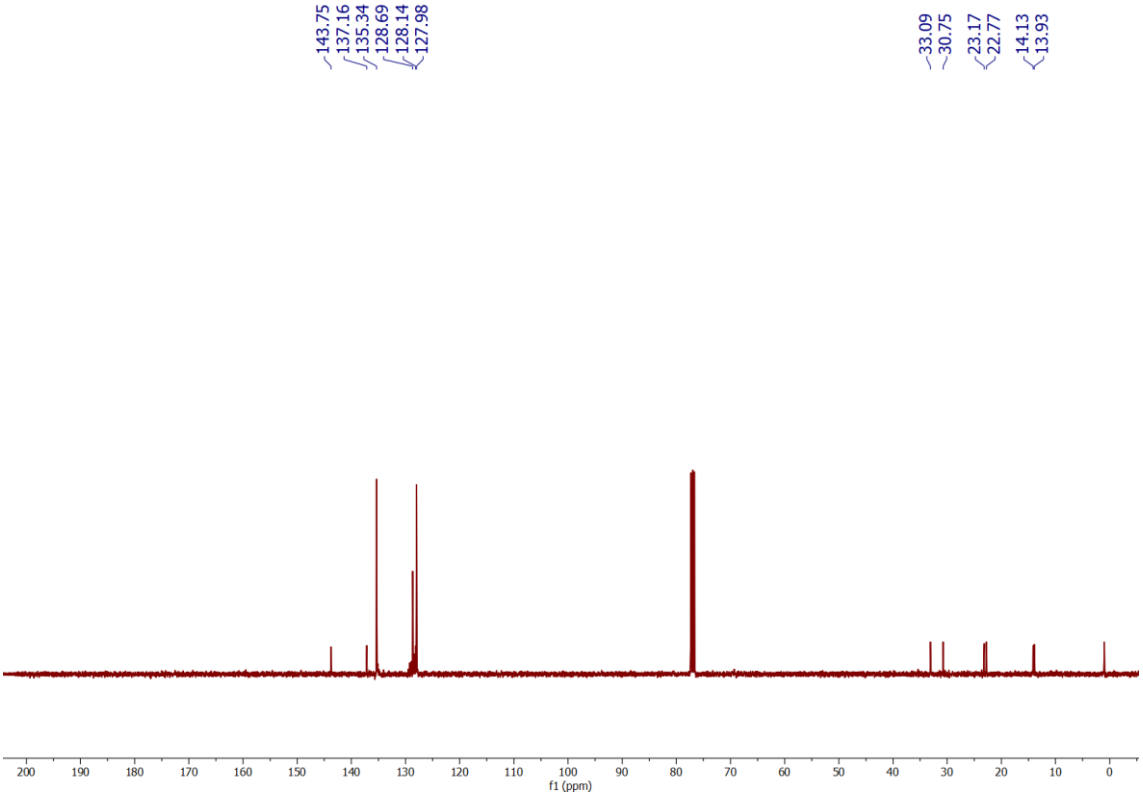


Figure S46. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P23**

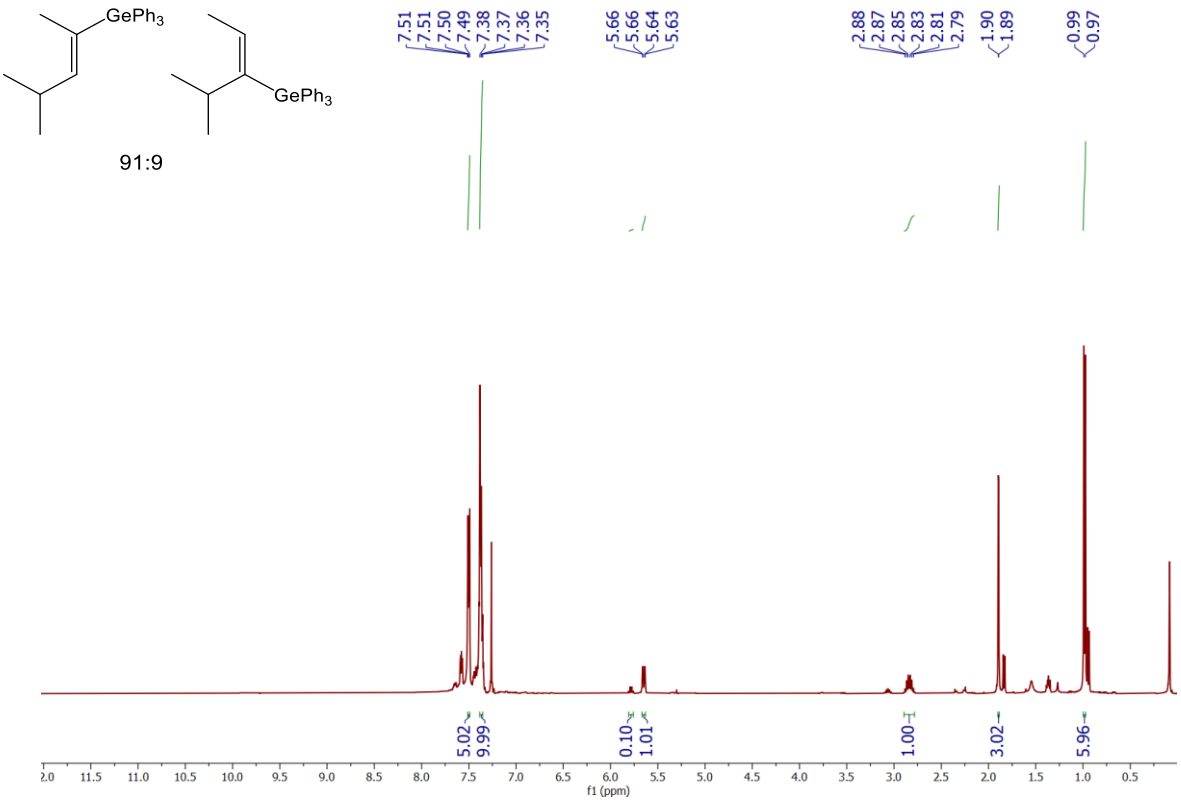


Figure S47. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P24**

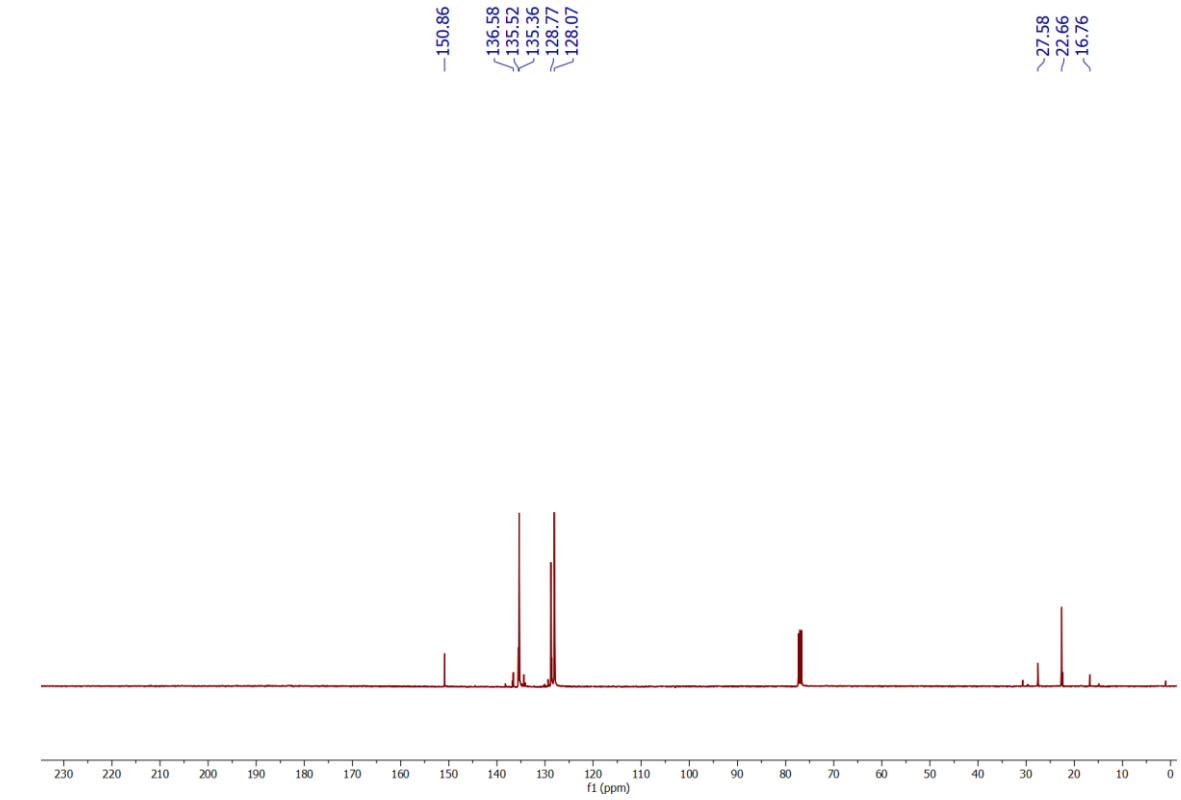


Figure S48 ^{13}C NMR (101 MHz, $CDCl_3$) of product **P24**

6. X-ray analysis

Diffraction data were collected at 100K by the ω-scan technique on Rigaku Xcalibur four-circle diffractometer with Eos CCD detector and graphite-monochromated MoK_α radiation (λ=0.71069 Å). The data were corrected for Lorentz-polarization as well as for absorption effects[S4]. Precise unit-cell parameters were determined by a least-squares fit of 4038 (**P17**) reflections of the highest intensity, chosen from the whole experiment. The structures were solved with SHELXT[S5] and refined with the full-matrix least-squares procedure on F^2 by SHELXL[S6]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms H2A and H2B (bonded with C2 atom) were found in subsequent difference Fourier maps and refined isotropically. Rest of hydrogen atoms were placed in idealized positions and refined as 'riding model' with isotropic displacement parameters set at 1.2 times U_{eq} of appropriate carrier atoms.

Table S2 lists the relevant experimental data and refinement details. Crystallographic data (excluding structure factors) for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC-2277547 (**P17**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, e-mail:deposit@ccdc.cam.ac.uk, or www: www.ccdc.cam.ac.uk.

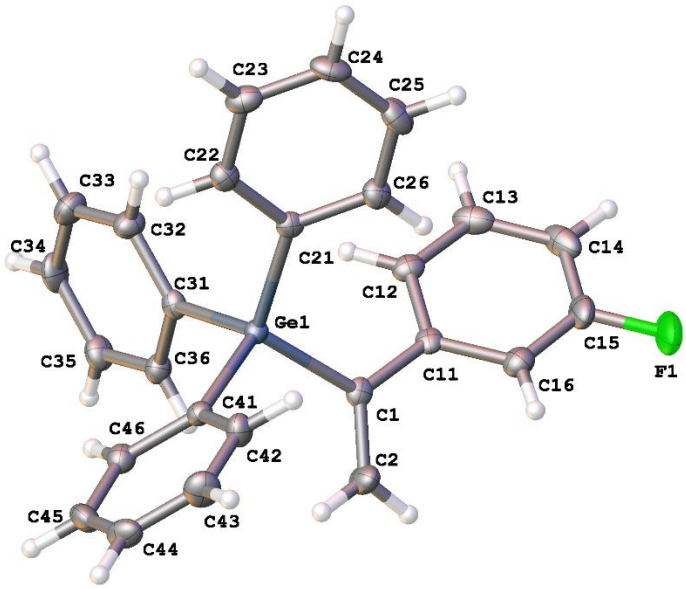


Figure S49. A perspective view of the molecule **P17**. Displacement ellipsoids are drawn at the 50% probability level.

Table S2. Crystal data, data collection and structure refinement

Compound	P17
Empirical formula	$C_{26}H_{21}FGe$
Formula weight	425.02
Temperature/K	100(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.1158(3)
b/Å	10.3844(3)
c/Å	19.5215(5)
α/°	90
β/°	94.317(2)
γ/°	90
Volume/Å^3	2044.87(10)
Z	4
ρ_{calc}g/cm^3	1.381
μ/mm^{-1}	1.515
F(000)	872.0
Crystal size/mm^3	0.4 × 0.4 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.594 to 56.85
Index ranges	-12 ≤ h ≤ 13, -13 ≤ k ≤ 12, -25 ≤ l ≤ 23
Reflections collected	15432
Independent reflections	4436 [R_{int} = 0.0498, R_{sigma} = 0.0622]
Data/restraints/parameters	4436/0/261
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0436, wR_2 = 0.0839
Final R indexes [all data]	R_1 = 0.0633, wR_2 = 0.0926
Largest diff. peak/hole / e Å^{-3}	0.74/-0.44

7. References

[S1] M. Hans, J. Lorkowski, A. Demonceau, L. Delaude, *Beilstein J. Org. Chem*., **2015**, *11*, 2318–2325.

[S2] K. de la Vega-Hernández, F. Chemla, F. Ferreira, O. Jackowski, A. Perez-Luna, *Org. Lett.* **2021**, *23*, 4426−4430.

[S3] S. Dérien, H. Klein, C. Bruneau, *Angew. Chem. Int. Ed.* **2015**, *54*, 12112–12115.

[S4] CrysAlisPro 1.171.42.56a (Rigaku Oxford Diffraction, 2022).

[S5] G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.* **2015**, *71*, 3–8.

[S6] G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8.