# Supporting Information

to the manuscript

# Hydrosilylation of olefins catalyzed by well-defined cationic aluminum complexes: Lewis acid versus insertion mechanisms.

by

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## Materials and Methods

Unless stated otherwise, all manipulations were performed using standard inert atmosphere ($N_2$ gas) glove-box and Schlenk techniques. The solvents hexanes, diethyl ether, and dichloromethane were dried using a Grubbs-type solvent purification system. Chlorobenzene was dried over $CaH_2$ and then degassed. $C_6D_5Br$ was predried and distilled from $CaH_2$ and stored in a glass vessel in the glovebox. NMR spectra were obtained with a Bruker DPX-300 ($^1$H, 300 MHz; $^{13}$C, 75.5 MHz; $^{29}$Si, 59.6 MHz; $^{11}$B, 96.3 MHz; $^{19}$F, 282.4 MHz; $^{31}$P 121.5 MHz), Bruker DPX-400 ($^1$H, 400 MHz; $^{13}$C, 100.6 MHz; $^{29}$Si, 79.5 MHz; $^{11}$B, 128.4 MHz; $^{19}$F, 376.5 MHz; $^{31}$P, 162.0 MHz), and Bruker DPX-600 ($^1$H, 600 MHz; $^{13}$C, 150.9 MHz; $^{29}$Si, 119.2 MHz; $^{11}$B, 192.5 MHz; $^{19}$F, 564.7MHz; $^{31}$P, 242.9 MHz) instruments at room temperature, unless otherwise specified. For NMR spectra recorded in protonated solvents, either a $D_2O$ insert was used to lock and shim the sample or it was left unlocked and shimming was performed using the automation program "shim1h", courtesy of Robin Stein (McGill University NMR Facility). The program runs a one-scan proton spectrum to find the largest peak and then selectively shims that signal using the Bruker TopShim routine. All catalytic NMR scale reactions and kinetic experiments were done under nitrogen atmosphere using NMR tubes equipped with Teflon valves. The yields of all hydrosilylated products were determined by NMR analysis with a ferrocene insert used as an internal standard. All alkenes and alkynes used were obtained from Sigma Aldrich and dried and distilled over $CaH_2$ then degassed before use. $H_2SiMePh$, $HSiMe_2Ph$, and $HSiEt_3$ were obtained from Gelest and dried and distilled over $CaH_2$ then degassed before use. $[CPh_3][B(C_6F_5)_4]$ was purchased from Strem Chemicals and used as received. NacNacAl$H_2$[1] and NacNacAl$Me_2$[2] were prepared according to literature procedures.

## Experimental Procedures and Characterization Data

[NacNacAlH][B($C_6F_5$)$_4$] (**2**)

NacNacAl$H_2$ (24.7 mg, 0.0553 mmol) was dissolved in $C_6D_5Br$ (~0.6mL) making a clear colourless solution. The solution was transferred to a vial containing $[CPh_3][B(C_6F_5)_4]$ (51.6 mg, 0.0559 mmol). Solution became yellow and then yellow-orange. **2** was unstable outside of solution but could be characterized by NMR spectroscopy. **$^1$H NMR** (400 MHz; $C_6D_5Br$; δ, ppm): δ 7.09–7.13 (m, 6H, aryl), 5.29 (s, 1H, *H*C($C_6H_5$)$_3$), 5.14 (s, 1H, backbone), 4.20 (br s, 1H, Al*H*), 2.55 (sept, 4H, C*H*($CH_3$)$_2$, $^3J_{H–H}$ = 6.8 Hz), 1.52 (s, 6H, C$H_3$), 0.88 (d, 12H, CH(C$H_3$)$_2$, $^3J_{H–H}$ = 2.9 Hz), 0.87 (d, 12H, CH(C$H_3$)$_2$, $^3J_{H–H}$ = 3.2 Hz). **$^{13}$C{$^1$H} NMR** (100.6 MHz; $C_6D_5Br$; δ, ppm): δ 175.6 (N*C*$CH_3$), 144.2 ($C_{ipso}$ from $HCPh_3$ byproduct), 143.7 ($C_{ipso}$), 134.8, 129.8, 128.6, 126.4, 125.9 (Ar C), 101.0 (*C*H), 57.2 (H*C*$Ph_3$), 29.0 (*C*H($CH_3$)$_2$), 24.8, 24.5 (CH(*C*$H_3$)$_2$), 23.3 (NC*C*$H_3$). **$^{11}$B{$^1$H} NMR** (128.4 MHz; $C_6D_5Br$; δ, ppm): δ −15.9 (s, *B*($C_6F_5$)$_4$). **$^{19}$F{$^1$H} NMR** (376.5 MHz; $C_6D_5Br$; δ, ppm): δ −131.3 (d, *o*-F), −161.9 (t, *p*-F), −165.7 (t, *m*-F).

[NacNacAl(hexyl)][B($C_6F_5$)$_4$] (**3**)

NacNacAl$H_2$ (15.9 mg, 0.0356 mmol) was dissolved in chlorobenzene (~0.6 mL) making a clear colourless solution. The solution was transferred to a vial containing $[CPh_3][B(C_6F_5)_4]$ (33.2 mg, 0.0360 mmol) and swirled. Solution became yellow and then yellow-orange. Solution was transferred to an NMR tube then 1-hexene (4.4 μL, 0.0354 mmol) was added and tube was inverted multiple times. **$^1$H NMR** (300 MHz; $C_6H_5Cl$; δ, ppm): δ 5.56 (s, 1H, backbone C*H*), 2.56 (sept, 4H, C*H*($CH_3$)$_2$, $^3J_{H–H}$ = 7.0 Hz), 1.69 (s, 6H, C$H_3$), 0.52–1.48 (m, 8H, C$H_2$), 1.06 (d, 6H, CH(C$H_3$)$_2$, $^3J_{H–H}$ = 7.3 Hz), 1.04 (d, 6H, CH(C$H_3$)$_2$, $^3J_{H–H}$ =7.3 Hz), 0.68 (t, 3H, $CH_2$C$H_3$, $^3J_{H–H}$ = 7.7 Hz), 0.11 (m, 2H, Al–C$H_2$). **$^{13}$C{$^1$H} NMR** (75.5 MHz; $C_6H_5Cl$; δ, ppm): δ 176.4

(N*C*$CH_3$), 143.9 ($C_{ipso}$), 142.4 ($C_{ipso}$), 129.3, 128.1, 126.1 (Ar C), 103.3 (*C*H), 33.8. 30.6, 22.2, 21.9 (*C*$H_2$), 29.2 (*C*H($CH_3$)$_2$), 24.0, 23.0 (CH(*C*$H_3$)$_2$), 13.6 ($CH_2$*C*$H_3$), 4.6 (Al–*C*$H_2$). Due to the protonated solvent, aromatic $^1$H signals could not be observed. **$^{11}$B{$^1$H} NMR** (96.3 MHz; $C_6H_5Cl$; δ, ppm): δ −16.4 (s, *B*($C_6F_5$)$_4$). **$^{19}$F{$^1$H} NMR** (282.4 MHz; $C_6H_5Cl$; δ, ppm): δ −131.9 (d, *o*-F), −162.6 (t, *p*-F), −165.5 (t, *m*-F).

[NacNacAl(neohexyl)][B($C_6F_5$)$_4$] (**4**)

NacNacAl$H_2$ (23.2 mg, 0.0519 mmol) was dissolved in chlorobenzene (~0.6 mL) making a clear colourless solution. The solution was transferred to a vial containing [C$Ph_3$][B($C_6F_5$)$_4$] (48.0 mg, 0.0520 mmol) and swirled. Solution became yellow and then yellow-orange. Solution was transferred to an NMR tube, then 3,3-dimethyl-1-butene (6.7 μL, 0.052 mmol) was added and tube was inverted multiple times. **$^1$H NMR** (400 MHz; $C_6H_5Cl$; δ, ppm): δ 5.57 (s, 1H, backbone C*H*), 2.58 (sept, 4H, C*H*($CH_3$)$_2$, $^3J_{H–H}$ = 7.1 Hz), 1.71 (s, 6H, C*H*$_3$), 1.07 (d, 6H, CH(C*H*$_3$)$_2$, $^3J_{H–H}$ = 6.9 Hz), 1.03 (d, 6H, CH(C*H*$_3$)$_2$, $^3J_{H–H}$ = 7.1 Hz), 0.38 (s, 9H, C(C*H*$_3$)$_3$), 0.28 (m, 2H, Al–C*H*$_2$), 0.07 (m, 2H, Al–$CH_2$C*H*$_2$). **$^{13}$C{$^1$H} NMR** (100.6 MHz; $C_6H_5Cl$; δ, ppm): δ 176.4 (N*C*$CH_3$), 143.9 ($C_{ipso}$), 142.5 ($C_{ipso}$), 129.3, 128.1, 126.1 (Ar C), 103.1 (*C*H), 35.8 (Al–$CH_2$*C*$H_2$), 30.7 (*C*($CH_3$)$_3$), 29.2 (*C*H($CH_3$)$_2$), 27.1 (C(*C*$H_3$)$_3$), 24.0, 23.0 (CH(*C*$H_3$)$_2$), 12.1 (Al–*C*$H_2$). Due to the protonated solvent, aromatic $^1$H signals could not be observed. **$^{11}$B{$^1$H} NMR** (128.4 MHz; $C_6H_5Cl$; δ, ppm): δ −16.2 (s, *B*($C_6F_5$)$_4$). **$^{19}$F{$^1$H} NMR** (376.5 MHz; $C_6H_5Cl$; δ, ppm): δ −131.5 (d, *o*-F), −162.3 (t, *p*-F), −165.6 (t, *m*-F).

[κ$_3$-*N*,*N*,*C*-{HC(C(Me)N(2,6-$Pr^i_2C_6H_3$))$_2$($^n$butyl–CH–$CH_2$)}AlH][B($C_6F_5$)$_4$] (**5**)

NacNacAl$H_2$ (15.9 mg, 0.0356 mmol) was dissolved in chlorobenzene (~0.6 mL) making a clear colourless solution. The solution was transferred to a vial containing [C$Ph_3$][B($C_6F_5$)$_4$] (33.2 mg, 0.0360 mmol) and swirled. Solution became yellow and then yellow-orange. Solution was transferred to an NMR tube then 1-hexene (9.0 μL, 0.0725 mmol) was added and tube was inverted multiple times. **$^1$H NMR** (600 MHz; $C_6H_5Cl$; −21 °C; δ, ppm): δ 3.85 (s, 1H, backbone C*H*), 2.01 (sept, 1H, C*H*($CH_3$)$_2$, $^3J_{H–H}$ = 6.9 Hz), 1.87 (m, 2H, C*H*($CH_3$)$_2$), 1.73 (m, 2H, C*H*($CH_3$)$_2$ and Al–$CH_2$C*H*$CH_2$), 1.41 (s, 3H, C*H*$_3$), 1.38 (s, 3H, C*H*$_3$), 0.71 (d, 6H, CH(C*H*$_3$)$_2$, $^3J_{H–H}$ = 6.9 Hz), 0.64 (d, 3H, CH(C*H*$_3$)$_2$, $^3J_{H–H}$ = 6.9 Hz), 0.61 (d, 3H, CH(C*H*$_3$)$_2$, $^3J_{H–H}$ = 6.9 Hz), 0.52 (t, 6H, CH(C*H*$_3$)$_2$, $^3J_{H–H}$ = 7.0 Hz), 0.41 (m, 6H, CH(C*H*$_3$)$_2$), 0.35 (m, 3H, $CH_2$C*H*$_3$), 0.29 (br s, 4H, Al–$CH_2$C*H*$_2$C*H*$_2$), 0.23 (t, 3H, $CH_2$C*H*$_3$, $^3J_{H–H}$ = 7.3 Hz), 0.11 (m, 1H, Al–C*H*$_2$CH$CH_2$), −0.64 (m, 1H, Al–C*H*$_2$CH$CH_2$), −0.68 (m, 2H, Al–C*H*$_2$$CH_2$$CH_2$). **$^{13}$C{$^1$H} NMR** (150.9 MHz; $C_6H_5Cl$; −21 °C; δ, ppm): δ 188.5, 187.8 (N*C*$CH_3$), 60.3 (*C*H), 56.2 (H*C*$Ph_3$), 42.9 (Al–$CH_2$C*H*$CH_2$), 38.0, 34.4, 33.3, 30.8, 30.6, 30.2 (*C*$H_2$), 29.1, 28.9, 27.7, 27.4 (*C*H($CH_3$)$_2$), 26.1, 23.4 (NC*C*$H_3$), 24.1, 23.9, 23.4, 23.3, 23.2, 23.1 (CH(*C*$H_3$)$_2$), 22.1, 21.9 (Al–$CH_2$*C*$H_2$*C*$H_2$), 13.6, 13.4 ($CH_2$*C*$H_3$), 6.0 (Al–*C*$H_2$CH$CH_2$), 2.7 (Al–*C*$H_2$$CH_2$$CH_2$). Due to the protonated solvent, aromatic $^1$H signals could not be observed. **$^{11}$B{$^1$H} NMR** (192.5 MHz; $C_6H_5Cl$; −21 °C; δ, ppm): δ −16.0 (s, *B*($C_6F_5$)$_4$). **$^{19}$F{$^1$H} NMR** (564.7 MHz; $C_6H_5Cl$; −21 °C; δ, ppm): δ −131.3 (d, *o*-F), −162.9 (t, *p*-F), −165.2 (t, *m*-F).

[κ$_3$-*N*,*N*,*C*-{HC(C(Me)N(2,6-$Pr^i_2C_6H_3$))$_2$(PhC=CH)}AlH][B($C_6F_5$)$_4$] (**6**)

NacNacAl$H_2$ (18.8 mg, 0.0421 mmol) was dissolved in $C_6D_5Br$ (~0.6 mL) making a clear colourless solution. The solution was transferred to a vial containing [C$Ph_3$][B($C_6F_5$)$_4$] (38.5 mg, 0.0417 mmol) and swirled. Solution became yellow and then yellow-orange. Solution was transferred to an NMR tube then phenylacetylene (4.6 μL, 0.042 mmol) was added and tube was

inverted multiple times. **5** was unstable outside of solution but could be characterized by NMR spectroscopy. **$^{1}$H NMR** (400 MHz; $C_6D_5Br$; δ, ppm): δ 7.09–7.18 (m, 5H, alkenyl phenyl H), 7.09–7.18 (m, 6H, diisopropylaryl), 5.66 (d, 1H, backbone, $^{4}J_{H–H}$ = 1.5 Hz), 5.30 (s, 1H, *H*C($C_6H_5$)$_3$), 3.86 (br s, 1H, Al*H*), 2.26 (sept, 2H, C*H*($CH_3$)$_2$, $^{3}J_{H–H}$ = 6.5 Hz), 2.11 (sept, 2H, C*H*($CH_3$)$_2$, $^{3}J_{H–H}$ = 6.5 Hz), 1.88 (s, 6H, C*H*$_3$), 1.00 (d, 6H, CH(C*H*$_3$)$_2$, $^{3}J_{H–H}$ = 6.8 Hz), 0.81 (d, 6H, CH(C*H*$_3$)$_2$, $^{3}J_{H–H}$ = 6.9 Hz), 0.79 (d, 6H, CH(C*H*$_3$)$_2$, $^{3}J_{H–H}$ = 7.0 Hz), 0.69 (d, 6H, CH(C*H*$_3$)$_2$, $^{3}J_{H–H}$ = 6.8 Hz). **$^{13}$C{$^{1}$H} NMR** (150.9 MHz; $C_6D_5Br$; δ, ppm): δ 189.8 (N*C*CH$_3$), 147.7 (H*C*=CPh), 143.8 ($C_{ipso}$ from $HCPh_3$ byproduct), 140.8 (Dipp $C_{ipso}$), 140.2 (Dipp $C_{ipso}$), 135.1 (HC=*C*Ph), 130.2 (Dipp *C*$_6$H$_3$), 129.6 (alkenyl phenyl *C*$_6$H$_5$), 129.5 (Dipp *C*$_6$H$_3$), 129.4 (Dipp *C*$_6$H$_3$), 128.2 (alkenyl phenyl *C*$_6$H$_5$), 128.2 (Dipp *C*$_6$H$_3$), 125.6 (alkenyl phenyl *C*$_6$H$_5$), 122.2 (Dipp *C*$_6$H$_3$), 63.6 (*C*H), 56.8 (H*C*Ph$_3$), 29.6, 28.4 (*C*H($CH_3$)$_2$), 25.0, 24.5 (CH(*C*H$_3$)$_2$), 23.9 (NC*C*H$_3$). **$^{11}$B{$^{1}$H} NMR** (128.4 MHz; $C_6D_5Br$; δ, ppm): δ −15.8 (s, *B*($C_6F_5$)$_4$). **$^{19}$F{$^{1}$H} NMR** (376.5 MHz; $C_6D_5Br$; δ, ppm): δ −131.4 (d, *o*-F), −162.2 (t, *p*-F), −165.7 (t, *m*-F).

[κ$_3$-*N*,*N*,*C*-{HC(C(Me)N(2,6-Pr$^{i}_2$C$_6$H$_3$))$_2$(PhC=CMe)}AlH][B($C_6F_5$)$_4$] (**7**)

$NacNacAlH_2$ (16.7 mg, 0.0374 mmol) was dissolved in $C_6D_5Br$ (~0.6 mL) making a clear colourless solution. The solution was transferred to a vial containing [$CPh_3$][B($C_6F_5$)$_4$] (34.8 mg, 0.0377 mmol) and swirled. Solution became yellow and then yellow-orange. Solution was transferred to an NMR tube then 1-phenyl-1-propyne (4.7 μL, 0.038 mmol) was added and tube was inverted multiple times. **6** was unstable outside of solution but could be characterized by NMR spectroscopy. **$^{1}$H NMR** (400 MHz; $C_6D_5Br$; δ, ppm): δ 6.77–7.13 (m, 5H, alkenyl phenyl H), 6.77–7.13 (m, 6H, diisopropylaryl), 5.28 (s, 1H, *H*C($C_6H_5$)$_3$), 5.21 (s, 1H, backbone), 3.86 (br s, 1H, Al*H*), 2.21 (sept, 2H, C*H*($CH_3$)$_2$, $^{3}J_{H–H}$ = 6.6 Hz), 2.20 (sept, 2H, C*H*($CH_3$)$_2$, $^{3}J_{H–H}$ = 6.6 Hz), 1.83 (s, 6H, C*H*$_3$), 1.72 (s, 3H, alkenyl C*H*$_3$), 0.98 (d, 6H, CH(C*H*$_3$)$_2$, $^{3}J_{H–H}$ = 6.7 Hz), 0.85 (d, 6H, CH(C*H*$_3$)$_2$, $^{3}J_{H–H}$ = 6.7 Hz), 0.82 (d, 6H, CH(C*H*$_3$)$_2$, $^{3}J_{H–H}$ = 6.8 Hz), 0.80 (d, 6H, CH(C*H*$_3$)$_2$, $^{3}J_{H–H}$ = 6.8 Hz). **$^{13}$C{$^{1}$H} NMR** (100.6 MHz; $C_6D_5Br$; δ, ppm): δ 189.8 (N*C*CH$_3$), 144.2 ($C_{ipso}$ from $HCPh_3$ byproduct), 140.8 (Dipp $C_{ipso}$), 140.2 (Dipp $C_{ipso}$), 138.4 ((CH$_3$)*C*=CPh),135.3 ((CH$_3$)C=*C*Ph), 130.6, 130.3, 127.1, 125.8, 125.7, 122.5 (Ar C), 66.5 (*C*H), 57.2 (H*C*Ph$_3$), 29.8, 29.1 (*C*H($CH_3$)$_2$), 25.5 (NC*C*H$_3$), 25.2, 24.4, 24.0, 23.2 (CH(*C*H$_3$)$_2$), 18.7 (alkenyl *C*H$_3$). **$^{11}$B{$^{1}$H} NMR** (128.4 MHz; $C_6D_5Br$; δ, ppm): δ −15.8 (s, *B*($C_6F_5$)$_4$). **$^{19}$F{$^{1}$H} NMR** (376.5 MHz; $C_6D_5Br$; δ, ppm): δ −131.1 (d, *o*-F), −161.8 (t, *p*-F), −165.5 (t, *m*-F).

[κ$_3$-*N*,*N*,*C*-{HC(C(Me)N(2,6-Pr$^{i}_2$C$_6$H$_3$))$_2$(PhC=CPh)}AlH][B($C_6F_5$)$_4$] (**8**)

$NacNacAlH_2$ (18.8 mg, 0.0421 mmol) was dissolved in $C_6D_5Br$ (~0.6 mL) making a clear colourless solution. The solution was transferred to a vial containing [$CPh_3$][B($C_6F_5$)$_4$] (38.4 mg, 0.0416 mmol) and swirled. Solution became yellow and then yellow-orange. The solution was transferred to a vial containing diphenylacetylene (7.4 mg, 0.042 mmol) was added and solution was transferred to an NMR tube. After 30 mins at RT, solution became a darker orange. **7** was unstable outside of solution but could be characterized by NMR spectroscopy. **$^{1}$H NMR** (400 MHz; $C_6D_5Br$; δ, ppm): δ 6.78–7.18 (m, 10H, alkenyl phenyl H), 6.78–7.18 (m, 6H, diisopropylaryl), 5.42 (s, 1H, backbone), 5.28 (s, 1H, *H*C($C_6H_5$)$_3$), 4.11 (br s, 1H, Al*H*), 2.38 (sept, 2H, C*H*($CH_3$)$_2$, $^{3}J_{H–H}$ = 6.7 Hz), 2.25 (sept, 2H, C*H*($CH_3$)$_2$, $^{3}J_{H–H}$ = 6.9 Hz), 1.91 (s, 6H, C*H*$_3$), 1.02 (d, 6H, CH(C*H*$_3$)$_2$, $^{3}J_{H–H}$ = 6.7 Hz), 0.85 (d, 6H, CH(C*H*$_3$)$_2$, $^{3}J_{H–H}$ = 6.7 Hz), 0.71 (d, 6H, CH(C*H*$_3$)$_2$, $^{3}J_{H–H}$ = 6.4 Hz), 0.61 (d, 6H, CH(C*H*$_3$)$_2$, $^{3}J_{H–H}$ = 6.4 Hz). **$^{13}$C{$^{1}$H} NMR** (100.6 MHz; $C_6D_5Br$; δ, ppm): 190.1 (N*C*CH$_3$), 144.2 ($C_{ipso}$ from $HCPh_3$ byproduct), 141.3 (Dipp $C_{ipso}$), 140.7 (Dipp $C_{ipso}$), 139.8(PhC=*C*Ph), 138.0 (Ph $C_{ipso}$), 135.2 (PhC=*C*Ph), 130.6, 130.4, 130.3,

127.7, 125.9, 125.7, 122.5 (Ar C), 67.6 (*C*H), 57.2 (H*C*Ph$_3$), 29.9, 29.4 (*C*H(CH$_3$)$_2$), 25.7 (NC*C*H$_3$), 24.8, 24.6, 24.0, 23.6 (CH(*C*H$_3$)$_2$). **$^{11}$B{$^1$H} NMR** (128.4 MHz; $C_6D_5Br$; δ, ppm): δ −16.5 (s, *B*($C_6F_5$)$_4$). **$^{19}$F{$^1$H} NMR** (376.5 MHz; $C_6D_5Br$; δ, ppm): δ −131.7 (d, *o*-F), −161.3 (t, *p*-F), −165.8 (t, *m*-F).

**Catalytic Reactions Mediated by 2**

Optimizing choice of silane

Three NMR samples with catalyst loading of 5 mol% each were prepared with three different silanes: $H_2SiMePh$ (50.0 µL, 0.364 mmol), $HSiMe_2Ph$ (62.5 µL, 0.408 mmol), and $HSiEt_3$ (61.0 µL, 0.382 mmol), respectively. To an NMR tube equipped with a $D_2O$ insert, 3,3-dimethyl-1-butene (46.7–60.0 µL, 0.362–0.466 mmol) and silane were added followed by a solution of **2** in chlorobenzene. For each sample the catalyst was prepared fresh. Reactions were monitored by $^1$H NMR spectroscopy and conversions were determined by normalizing integrals for the newly formed $CH_2$ on the hydrosilylation product and the combination of CH signal and half the $CH_2$ signal of the starting alkene reagent (the $CH_2$ doublet of doublets could not be accurately integrated due to overlap with the $D_2O$ insert peak). For $H_2SiMePh$ and $HSiMe_2Ph$ there were mixtures of products.

A blank reaction was also completed with a 5 mol% loading of **2**. To an NMR tube equipped with a $D_2O$ insert, 3,3-dimethyl-1-butene (60.0 µL, 0.466 mmol) was added. Then a solution of **2** in chlorobenzene was freshly prepared and added to the NMR tube. Reaction was monitored with $^1$H NMR spectroscopy. No reaction was observed in the first 20 min but after 18 h oligomerization had occurred.

Optimizing catalyst loading

Four NMR samples with catalyst loadings of 0.1–1 mol% were prepared. For the samples with 0.1 mol%, 0.3 mol%, and 0.5 mol %, a stock solution of **2** in chlorobenzene was used in preparation but for the 1 mol% sample the catalyst was prepared fresh. To an NMR tube equipped with a $D_2O$ insert, 3,3-dimethyl-1-butene (32.0–130.0µL, 0.248–1.008 mmol) and $HSiEt_3$ (39.0–132.0 µL, 0.244–0.826 mmol) were added followed by the solution of **2** in chlorobenzene. Additional solvent was added if necessary to make the volume ~0.6mL. Reactions were monitored by $^1$H NMR spectroscopy and conversions were determined by normalizing integrals for the newly formed $CH_2$ on the hydrosilylation product and the combination of CH signal and half the $CH_2$ signal of the starting alkene reagent (the $CH_2$ doublet of doublets could not be accurately integrated due to overlap with the $D_2O$ insert peak).

Hydrosilylation of 3,3-dimethyl-1-butene

To an NMR tube equipped with a ferrocene insert, 3,3-dimethyl-1-butene (54.0 µL, 0.419 mmol) and $HSiEt_3$ (67.0 µL, 0.419 mmol) were added. Chlorobenzene was added to bring up to volume then a reference $^1$H NMR spectrum was recorded. A stock solution prepared the same day of **2** in chlorobenzene (0.5 mL, 1 mol%) was added. The solution became colourless. After 10 min at room temperature, full conversion to was achieved, with (2,3-dimethylbutyl)triethylsilane being the major product. Other unidentified silane redistribution products were also observed. **$^1$H NMR** (400 MHz; $C_6H_5Cl$; δ, ppm): δ 1.47 (m, 1H, C*H*(CH$_3$)$_2$), 1.47 (m, 1H, C*H*(CH$_3$)), 0.93 (t, 9H, Si(CH$_2$C*H*$_3$)$_3$, $^3J_{H–H}$ = 8.0 Hz), 0.83 (d, 3H, CH(C*H*$_3$), $^3J_{H–H}$ = 6.6 Hz), 0.82 (d, 3H, CH(C*H*$_3$)$_2$, $^3J_{H–H}$ = 7.0 Hz), 0.80 (d, 3H, CH(C*H*$_3$)$_2$, $^3J_{H–H}$ = 6.9 Hz), 0.59 (dd, 1H, C*H*$_2$Si(CH$_2$CH$_3$)$_3$, $^3J_{H–H}$ = 15.0 Hz, $^2J_{H–H}$ = 3.2 Hz), 0.50 (q, 6H, Si(C*H*$_2$CH$_3$)$_3$, $^3J_{H–H}$ =

7.6Hz) 0.31 (dd, 1H, C$H_2$Si($CH_2$C$H_3$)$_3$, $^3J_{H–H}$ = 14.7Hz, $^2J_{H–H}$ = 9.8Hz). **$^{13}$C{$^1$H} NMR** (100.6 MHz; $C_6H_5Cl$; δ, ppm): δ 34.9 (*C*H($CH_3$)), 34.5 (*C*H($CH_3$)$_2$), 19.1 (CH(*C*$H_3$)$_2$), 18.6 (CH(*C*$H_3$)), 18.1 (CH(*C*$H_3$)$_2$), 15.5 (*C*$H_2$Si($CH_2$C$H_3$)$_3$), 7.4 (Si($CH_2$*C*$H_3$)$_3$), 3.9 (Si(*C*$H_2$$CH_3$)$_3$).

Hydrosilylation of styrene

To an NMR tube equipped with a ferrocene insert, styrene (48.0 µL, 0.418 mmol) and $HSiEt_3$ (67.0 µL, 0.419 mmol) were added. Chlorobenzene was added to bring up to volume then a reference $^1$H NMR spectrum was recorded. A stock solution prepared the same day of **2** in chlorobenzene (0.5 mL, 1 mol%) was added. The solution became colourless. After 10 min at room temperature, full conversion was achieved. The main products are triethyl(phenylethyl)silane and diethyl(diphenylethyl)silane. **$^1$H NMR** (400 MHz; $C_6H_5Cl$; δ, ppm): δ 2.53–2.64 (m, 2H, PhC$H_2$), 0.93 (t, 9H, Si($CH_2$C$H_3$)$_3$, $^3J_{H–H}$ = 7.6Hz), 0.80–0.86 (m, 2H, C$H_2$Si($CH_2$$CH_3$)$_3$), 0.50 (q, 6H, Si(C$H_2$$CH_3$)$_3$, $^3J_{H–H}$ = 8.3Hz). **$^{13}$C{$^1$H} NMR** (100.6 MHz; $C_6H_5Cl$; δ, ppm): δ 30.0 (Ph*C*$H_2$), 13.5 (*C*$H_2$Si($CH_2$C$H_3$)$_3$), 7.3 (Si($CH_2$*C*$H_3$)$_3$), 2.9 (Si(*C*$H_2$$CH_3$)$_3$). Due to the protonated solvent, aromatic $^1$H signals could not be observed. The aromatic $^{13}$C signals could also not be differentiated from the aromatic signals of other compounds due to signal interference in the 2D heteronuclear spectra.

Hydrosilylation of 1-hexene

To an NMR tube equipped with a ferrocene insert, 1-hexene (52.0 µL, 0.419 mmol) and $HSiEt_3$ (67.0 µL, 0.419 mmol) were added. Chlorobenzene was added to bring up to volume then a reference $^1$H NMR spectrum was recorded. A stock solution prepared the same day of **2** in chlorobenzene (0.5 mL, 1 mol%) was added. The solution became colourless. After 10 min at room temperature, full conversion was achieved, with triethyl(hexyl)silane being the major product. Trace amounts of another silane products were observed.

Reaction was also repeated at 0.75 mol% catalyst loading. To an NMR tube, 1-hexene (47.0µL, 0.379 mmol) and $HSiEt_3$ (83.0 µL, 0.52 mmol) were added. A freshly prepared solution of **2** in chlorobenzene (0.75mol%) was added to the NMR tube. Solution immediately became peach. After 15 min at room temperature, full conversion to the hydrosilylated products was observed. **$^1$H NMR** (400 MHz; $C_6H_5Cl$; δ, ppm): δ 1.20–1.33 (m, 8H, C$H_2$), 0.93 (t, 9H, Si($CH_2$C$H_3$)$_3$, $^3J_{H–H}$ = 8.1 Hz), 0.87 (t, 3H, C$H_3$, $^3J_{H–H}$ = 6.8 Hz), 0.50 (m, 2H, C$H_2$Si($CH_2$$CH_3$)$_3$), 0.49 (q, 6H, Si(C$H_2$$CH_3$)$_3$, $^3J_{H–H}$ = 8.1 Hz). **$^{13}$C{$^1$H} NMR** (100.6 MHz; $C_6H_5Cl$; δ, ppm): δ 33.6, 31.6, 23.8, 22.7 (*C*$H_2$), 14.0 (*C*$H_3$), 11.3 (*C*$H_2$Si($CH_2$$CH_3$)$_3$), 7.3 (Si($CH_2$*C*$H_3$)$_3$), 3.3 (Si(*C*$H_2$$CH_3$)$_3$).

Hydrosilylation of cyclohexene

To an NMR tube equipped with a ferrocene insert, cyclohexene (43.0 µL, 0.425 mmol) and $HSiEt_3$ (67.0 µL, 0.419 mmol) were added. Chlorobenzene was added to bring up to volume then a reference $^1$H NMR spectrum was recorded. A stock solution prepared the same day of **2** in chlorobenzene (0.5 mL, 1 mol%) was added. The solution became colourless. After 10 min at room temperature, full conversion was achieved, with cyclohexyltriethylsilane being the major product. Trace amounts of other unidentified silane products were also observed. **$^1$H NMR** (400 MHz; $C_6H_5Cl$; δ, ppm): δ 1.04–1.74 (m, 10H, C$H_2$), 1.04–1.26 (m, 1H, C*H*), 0.93 (t, 9H, Si($CH_2$C$H_3$)$_3$, $^3J_{H–H}$ = 7.9Hz), 0.48 (q, 6H, Si(C$H_2$$CH_3$)$_3$, $^3J_{H–H}$ = 8.1Hz). **$^{13}$C{$^1$H} NMR** (100.6 MHz; $C_6H_5Cl$; δ, ppm): δ 28.3, 27.8, 27.0 (*C*$H_2$), 23.5 (*C*H), 7.6 (Si($CH_2$*C*$H_3$)$_3$), 2.9 (Si(*C*$H_2$$CH_3$)$_3$).

Hydrosilylation of 1-methyl-1-cyclohexene

To an NMR tube equipped with a ferrocene insert, 1-methyl-1-cyclohexene (63.0 µL, 0.531 mmol) and $HSiEt_3$ (85.0 µL, 0.532 mmol) were added. Chlorobenzene was added to bring up to volume then a reference $^1$H NMR spectrum was recorded. A freshly prepared solution of **2** in chlorobenzene (5 mol%) was added. The solution became colourless. After 10 min at room temperature, full conversion to the triethyl(*cis*-2-methylcyclohexyl)silane was achieved. Trace amounts of other unidentified silane products were also observed. **$^1$H NMR** (400 MHz; $C_6H_5Cl$; δ, ppm): δ 1.94 (m, 1H, C*H*$CH_3$), 1.67 (m, 1H, C$H_2$, $^2J_{H–H}$ = 12.0 Hz), 1.43 (m, 6H, C$H_2$), 1.18 (m, 1H, C$H_2$), 0.94 (d, 3H, C$H_3$, $^3J_{H–H}$ = 7.3Hz), 0.94 (t, 10H, Si($CH_2CH_3$)$_3$, $^3J_{H–H}$ = 8.0 Hz and C*H*Si($CH_2CH_3$)$_3$), 0.52 (q, 6H, Si(C$H_2CH_3$)$_3$, $^3J_{H–H}$ = 8.0 Hz). **$^{13}$C{$^1$H} NMR** (100.6 MHz; $C_6H_5Cl$; δ, ppm): δ 35.1, 28.6, 22.3, 21.1 (*C*$H_2$), 29.2 (*C*H$CH_3$), 28.0 (*C*$H_3$), 16.3 (*C*HSi($CH_2CH_3$)$_3$), 7.7 (Si($CH_2$*C*$H_3$)$_3$), 3.1 (Si(*C*$H_2CH_3$)$_3$).

Hydrosilylation of 2-methyl-1-phenyl-1-propene

To an NMR tube equipped with a ferrocene insert, 2-methyl-1-phenyl-1-propene (100.0 µL, 0.682 mmol) and $HSiEt_3$ (120.0 µL, 0.751 mmol) were added. Chlorobenzene was added to bring up to volume then a reference $^1$H NMR spectrum was recorded. A freshly prepared solution of **2** in chlorobenzene (5 mol%) was added. The solution became colourless. After 10 min at room temperature, full conversion was achieved, with to triethyl(2-methyl-1-phenylpropyl)silane being the major product. Other unidentified silane redistribution products were also observed. **$^1$H NMR** (400 MHz; $C_6H_5Cl$; δ, ppm): δ 2.06–2.16 (m, 1H, C*H*($CH_3$)$_2$), 1.82 (d, 1H, C*H*Si($CH_2CH_3$)$_3$, $^3J_{H–H}$ = 9.8 Hz), 1.03 (d, 3H, CH(C$H_3$)$_2$, $^3J_{H–H}$ = 6.7 Hz), 0.85 (t, 9H, Si($CH_2$C$H_3$)$_3$, $^3J_{H–H}$ = 8.0 Hz), 0.77 (d, 3H, CH(C$H_3$)$_2$, $^3J_{H–H}$ = 6.5 Hz), 0.50 (q, 6H, Si(C$H_2CH_3$)$_3$, $^3J_{H–H}$ = 7.8 Hz). **$^{13}$C{$^1$H} NMR** (100.6 MHz; $C_6H_5Cl$; δ, ppm): δ 144.1 ($C_{ipso}$), 128.6, 127.7, 124.2 (Ar C), 50.3 (*C*HSi($CH_2CH_3$)$_3$), 42.5 (*C*H($CH_3$)$_2$), 23.3, 23.2 (*C*$H_3$), 7.4 (Si($CH_2$*C*$H_3$)$_3$), 3.8 (Si(*C*$H_2CH_3$)$_3$). Due to the use of protonated solvent, aromatic $^1$H signals could not be observed.

Hydrosilylation of 2,3-dimethyl-2-butene

To an NMR tube equipped with a ferrocene insert, 2,3-dimethyl-2-butene (98.0 µL, 0.824 mmol) and $HSiEt_3$ (132 µL, 0.826 mmol) were added. Chlorobenzene was added to bring up to volume then a reference $^1$H NMR spectrum was recorded. A freshly prepared solution of **2** in chlorobenzene (5 mol%) was added. The solution became colourless. After 10 min at room temperature, about 60% conversion to (2,3-dimethylbutan-2-yl)triethylsilane was observed. Other unidentified silane redistribution products were also observed. **$^1$H NMR** (400 MHz; $C_6H_5Cl$; δ, ppm): δ 1.58 (sept, 1H, C*H*($CH_3$)$_2$, $^3J_{H–H}$ = 6.9 Hz), 0.96 (t, 9H, Si($CH_2$C$H_3$)$_3$, $^3J_{H–H}$ = 8.0 Hz), 0.81 (d, 6H, CH(C$H_3$)$_2$, $^3J_{H–H}$ = 6.7 Hz), 0.81 (s, 6H, SiC(C$H_3$)$_2$), 0.57 (t, 9H, Si($CH_2$C$H_3$)$_3$, $^3J_{H–H}$ = 8.0 Hz), 0.57 (q, 6H, Si(C$H_2CH_3$)$_3$, $^3J_{H–H}$ = 8.0 Hz). **$^{13}$C{$^1$H} NMR** (100.6 MHz; $C_6H_5Cl$; δ, ppm): δ 34.5 (*C*H($CH_3$)$_2$), 24.3 (Si*C*($CH_3$)$_2$), 21.3 (CH(*C*$H_3$)$_2$), 18.2 (SiC(*C*$H_3$)$_2$), 8.2 (Si($CH_2$*C*$H_3$)$_3$), 3.3 (Si(*C*$H_2CH_3$)$_3$).

Hydrosilylation of phenylacetylene

To an NMR tube equipped with a ferrocene insert, phenylacetylene (58.0 µL, 0.528 mmol) and $HSiEt_3$ (84.0 µL, 0.526 mmol) were added. Chlorobenzene was added to bring up to volume then a reference $^1$H NMR spectrum was recorded. A freshly prepared solution of **2** in chlorobenzene (5 mol%) was added. After 5 days at 70 °C, the substrate was fully polymerized.

Hydrosilylation of cyclohexylacetylene

To an NMR tube equipped with a ferrocene insert, cyclohexylacetylene (63.0 µL, 0.482 mmol) and $HSiEt_3$ (77.0 µL, 0.482 mmol) were added. Chlorobenzene was added to bring up to volume then a reference $^1$H NMR spectrum was recorded. A freshly prepared solution of **2** in chlorobenzene (5 mol%) was added. The solution became a pale yellow. After 26 h at room temperature, good conversion to (*E*)-(2-cyclohexylvinyl)triethylsilane was observed. Other silane products were also observed. **$^1$H NMR** (400 MHz; $C_6H_5Cl$; δ, ppm): δ 6.19 (dd, 1H, C*H*=CHSi, $^3J_{H–H}$ = 10.1 Hz, $^3J_{H–H}$ = 14.0 Hz), 5.31 (d, 1H, CH=C*H*Si, $^3J_{H–H}$ = 13.9 Hz), 1.06–2.15 (m, 10H, cyclohexyl C$H_2$), 2.09 (m, 1H, cyclohexyl CH), 1.03 (t, 9H, Si($CH_2CH_3$)$_3$, $^3J_{H–H}$ = 7.9 Hz), 0.62 (q, 6H, Si($CH_2CH_3$)$_3$, $^3J_{H–H}$ = 8.0 Hz). **$^{13}$C{$^1$H} NMR** (100.6 MHz; $C_6H_5Cl$; δ, ppm): δ 155.8 (*C*H=CHSi), 143.9 (CH=*C*HSi), 43.4 (cyclohexyl *C*H), 33.1, 26.0, 25.8 (cyclohexyl *C*$H_2$), 4.9 (Si($CH_2CH_3$)$_3$), 1.0 (Si($CH_2CH_3$)$_3$).

Hydrosilylation of 3-cyclohexyl-1-propyne

To an NMR tube equipped with a ferrocene insert, 3-cyclohexyl-1-propyne (74.0 µL, 0.512 mmol) and $HSiEt_3$ (82.0 µL, 0.513 mmol) were added. Chlorobenzene was added to bring up to volume then a reference $^1$H NMR spectrum was recorded. A freshly prepared solution of **2** in chlorobenzene (5 mol%) was added. The solution became a pale yellow. After 24 h at room temperature, moderate conversion to (*E*)-(3-cyclohexylprop-1-en-1-yl)triethylsilane was observed. Other silane redistribution products were also observed. **$^1$H NMR** (400 MHz; $C_6H_5Cl$; δ, ppm): δ 6.37 (dt, 1H, $CH_2$C*H*=CHSi, $^3J_{H–H}$ = 14.4 Hz, $^3J_{H–H}$ = 7.0 Hz), 5.96 (d, 1H, CH=C*H*Si($CH_2CH_3$)$_3$, $^3J_{H–H}$ = 14.2Hz), 1.00–2.50 (m, 11H, $C_6H_{11}$), 1.99 (m, 2H, C$H_2$CH=CHSi), 0.96 (t, 9H, Si($CH_2CH_3$)$_3$, $^3J_{H–H}$ = 7.7 Hz), 0.62 (q, 6H, Si($CH_2CH_3$)$_3$, $^3J_{H–H}$ = 8.1 Hz). **$^{13}$C{$^1$H} NMR** (100.6 MHz; $C_6H_5Cl$; δ, ppm): δ 148.8 ($CH_2$*C*H=CHSi), 125.3 (CH=*C*HSi), 43.2, 33.0, 26.2, (cyclohexyl *C*$H_2$), 41.4 (*C*$H_2$CH=CHSi), 38.1 (cyclohexyl CH), 7.2 (Si($CH_2CH_3$)$_3$), 4.6 (Si($CH_2CH_3$)$_3$).

Hydrosilylation of 3-hexyne

To an NMR tube equipped with a ferrocene insert, 3-hexyne (69.0 µL, 0.607 mmol) and $HSiEt_3$ (95.0 µL, 0.595 mmol) were added. Chlorobenzene was added to bring up to volume then a reference $^1$H NMR spectrum was recorded. A freshly prepared solution of **2** in chlorobenzene (5 mol%) was added. The solution became a pale yellow. After 25 h at room temperature, poor conversion to (*E*)-triethyl(hex-3-en-3-yl)silane was observed. Other silane redistribution products were also observed. **$^1$H NMR** (400 MHz; $C_6H_5Cl$; δ, ppm): δ 5.98 (tt, 1H, C*H*=CSi, $^3J_{H–H}$ = 7.5 Hz, $^4J_{H–H}$ = 1.4 Hz), 2.07 (m, 2H, C$H_2$CH=CSi), 0.96 (t, 3H, C$H_3$CH$_2$C=CSi, $^3J_{H–H}$ = 6.5 Hz), 0.95 (t, 9H, Si($CH_2CH_3$)$_3$, $^3J_{H–H}$ = 7.6 Hz), 0.93 (t, 3H, C$H_3$CH$_2$CSi, $^3J_{H–H}$ = 7.1 Hz), 0.82 (q, 2H, C$H_2$CSi, $^3J_{H–H}$ = 7.1 Hz), 0.47 (q, 6H, Si($CH_2CH_3$)$_3$, $^3J_{H–H}$ = 7.7 Hz). **$^{13}$C{$^1$H} NMR** (100.6 MHz; $C_6H_5Cl$; δ, ppm): δ 144.2 (*C*H=CSi), 136.9 (CH=*C*Si), 25.2 (SiC=CH*C*$H_2$), 22.1 (CH=CSi*C*$H_2$), 15.4, 14.3 (*C*$H_3$), 7.3 (Si($CH_2CH_3$)$_3$), 2.9 (Si($CH_2CH_3$)$_3$).

**Mechanistic Studies**

Redistribution of $HSiEt_3$ by **2**

NacNacAl$H_2$ (24.7 mg, 0.0553 mmol) was dissolved in $C_6D_5Br$ (~0.6 mL) making a clear colourless solution. The solution was transferred to a vial containing [$CPh_3$][B($C_6F_5$)$_4$] (51.6 mg, 0.0559 mmol) and swirled. Solution became yellow and then yellow-orange. Solution was

transferred to an NMR tube then $HSiEt_3$ (7.2 μL, 0.045 mmol) was added and upon inversion solution became a pale orange-peach. Interaction was monitored by $^1H$ NMR spectroscopy with variable temperature in an attempt to freeze fluxionality. Fluxional species could not be separated. Instead, more equivalents of $HSiEt_3$, (7.2 μL, 0.045 mmol) and (74.0 μL, 0.463 mmol), were added to show redistribution of the silane.

Redistribution of $H_2SiEt_2$ by **2**

NacNacAl$H_2$ (24.8 mg, 0.0555 mmol) was dissolved in $C_6D_5Br$ (~0.6 mL) making a clear colourless solution. The solution was transferred to a vial containing $[CPh_3][B(C_6F_5)_4]$ (50.9 mg, 0.0552 mmol) and swirled. Solution became yellow and then yellow-orange. Solution was transferred to an NMR tube then $H_2SiEt_2$ (7.1 μL, 0.055 mmol) was added and upon inversion solution became a pale orange-peach. Interaction was monitored by $^1H$ NMR spectroscopy with variable temperature in an attempt to freeze fluxionality. Full redistribution was observed to $HSiEt_3$, $H_2SiEt_2$, and $H_3SiEt$ with $HSiEt_3$ and $H_2SiEt_2$ in exchange. $SiEt_4$ was suspected to be formed as well but the signal could not be detected by $^1H$–$^{29}Si$ HSQC. Silicon species were identified by the INEPT+ experiment at −25 °C. Another unidentified Si–H species was also present. **$^{29}$Si INEPT+ NMR** (109.2 MHz; $C_6D_5Br$; −25°C; δ, ppm): δ 5.1 ($HSiEt_3$), −22.9 ($H_2SiEt_2$), −55.0 ($H_3SiEt$).

Redistribution of hexyltriethylsilane by **2**

To an NMR tube equipped with a ferrocene insert, 1-hexene (52.0 μL, 0.419 mmol) and $HSiEt_3$ (67.0 μL, 0.419 mmol) were added. Chlorobenzene was added to bring up to volume then a reference $^1H$ NMR spectrum was recorded. A stock solution prepared the same day of **2** in chlorobenzene (0.5 mL, 1 mol%) was added. The solution became colourless. After 10 min at room temperature, full conversion to hexyltriethylsilane was observed. After another 2 weeks at room temperature, $^1H$ NMR signals had changed. Solution was transferred to a clean NMR tube with a $D_2O$ insert then the silicon species were identified by $^1H$–$^{29}Si$ HSQC. **$^{29}$Si NMR 2D Projection** (109.2 MHz; $C_6H_5Cl$; δ, ppm): δ 7.3 ($SiEt(hexyl)_3$), 6.2 ($SiEt_2(hexyl)_2$), 5.0 ($SiEt_3(hexyl)$), 3.8 ($SiEt_4$).

Hydrosilylation of 1-hexene by **3**

NacNacAl$H_2$ (23.2 mg, 0.519 mmol) was dissolved in chlorobenzene (~0.6 mL) making a clear colourless solution. The solution was transferred to a vial containing $[CPh_3][B(C_6F_5)_4]$ (48.0 mg, 0.520 mmol) and swirled. Solution became yellow and then yellow-orange. Solution was transferred to an NMR tube, then 1-hexene (4.4 μL, 0.0354 mmol) was added and tube was inverted multiple times. $^1H$ NMR spectroscopy was used to confirm formation of **3**.

In a separate NMR tube with a ferrocene insert, 1-hexene (88.0 μL, 0.709 mmol) and $HSiEt_3$ (113 μL, 0.707 mmol) were added with chlorobenzene to bring solution up to volume. A reference $^1H$ NMR spectrum was recorded then **3** (5 mol%, prepared in previous NMR tube) was added. Solution became colourless. After 10 min at room temperature, full conversion was observed. NMR spectroscopic data matched that of hexyltriethylsilane previously reported.

Hydrosilylation of cyclohexene by **3** (5 mol%)

NacNacAl$H_2$ (9.8 mg, 0.022 mmol) was dissolved in chlorobenzene (~0.6 mL) making a clear colourless solution. The solution was transferred to a vial containing $[CPh_3][B(C_6F_5)_4]$ (20.5 mg, 0.0222 mmol) and swirled. Solution became yellow and then yellow-orange. Solution

was transferred to an NMR tube, then 1-hexene (2.7 μL, 0.022 mmol) was added and tube was inverted multiple times. $^1$H NMR spectroscopy was used to confirm formation of **3**.

In a separate NMR tube with a ferrocene insert, cyclohexene (36.0 μL, 0.355 mmol) and $HSiEt_3$ (57.0 μL, 0.357 mmol) were added with chlorobenzene to bring solution up to volume. A reference $^1$H NMR spectrum was recorded then **3** (5 mol%, prepared in previous NMR tube) was added. Solution became colourless. After 10 min at room temperature, full conversion was observed. NMR spectroscopic data matched that of triethyl(cyclohexyl)silane previously reported with no evidence for the formation of hexyltriethylsilane.

Hydrosilylation of cyclohexene by **3** (stoichiometric)

$NacNacAlH_2$ (17.9 mg, 0.0401 mmol) was dissolved in chlorobenzene (~0.6 mL) making a clear colourless solution. The solution was transferred to a vial containing $[CPh_3][B(C_6F_5)_4]$ (37.0 mg, 0.0401 mmol) and swirled. Solution became yellow and then yellow-orange. Solution was transferred to an NMR tube, then 1-hexene (5.2 μL, 0.041 mmol) was added and tube was inverted multiple times. $^1$H NMR spectroscopy was used to confirm formation of **3**. Then cyclohexene (4.0 μL, 0.039 mmol) and $HSiEt_3$ (6.5 μL, 0.041 mmol) were added. Solution became colourless. After 10 min at room temperature, full conversion was observed. NMR spectroscopic data matched that of triethyl(cyclohexyl)silane previously reported with no evidence for the formation of hexyltriethylsialne. Signals for **3** also remain unchanged.

Hydrosilylation of 1-hexene by $[NacNacAlMe][B(C_6F_5)_4]$

$[NacNacAlMe][B(C_6F_5)_4]$ was prepared as reported with the exception that it was formed in chlorobenzene.[3] $NacNacAlMe_2$ (12.0 mg, 0.0253 mmol) was dissolved in chlorobenzene (~0.6 mL) making a cloudy colourless solution. The solution was transferred to a vial containing $[CPh_3][B(C_6F_5)_4]$ (23.4 mg, 0.0254 mmol) and swirled. Solution became yellow and then orange. Solution was transferred to an NMR tube and $^1$H NMR spectroscopy was used to confirm formation of the cationic $[NacNacAlMe][B(C_6F_5)_4]$ complex.

In a separate NMR tube with a ferrocene insert, 1-hexene (63.0 μL, 0.508 mmol) and $HSiEt_3$ (81.0 μL, 0.507 mmol) were added with chlorobenzene to bring solution up to volume. A reference $^1$H NMR spectrum was recorded then $[NacNacAlMe][B(C_6F_5)_4]$ (5 mol%, prepared in previous NMR tube) was added. Solution became colourless. After 10 min at room temperature, full conversion was observed. NMR spectroscopic data matched that of hexyltriethylsilane previously reported.

Attempted redistribution of silanes by **3**

$NacNacAlH_2$ (23.2 mg, 0.519 mmol) was dissolved in chlorobenzene (~0.6 mL) making a clear colourless solution. The solution was transferred to a vial containing $[CPh_3][B(C_6F_5)_4]$ (48.0 mg, 0.520 mmol) and swirled. Solution became yellow and then yellow-orange. Solution was transferred to an NMR tube, then 1-hexene (4.4 μL, 0.0354 mmol) was added and tube was inverted multiple times. $^1$H NMR spectroscopy was used to confirm formation of **3**.

In a separate NMR tube with a ferrocene insert, 1-hexene (88.0 μL, 0.709 mmol) and $HSiEt_3$ (113 μL, 0.707 mmol) were added with chlorobenzene to bring solution up to volume. A reference $^1$H NMR spectrum was recorded then **3** (5 mol%, prepared in previous NMR tube) was added. Solution became colourless. After 10 min at room temperature, full conversion was observed. NMR spectroscopic data matched that of hexyltriethylsilane previously reported. After 2 weeks at room temperature, no change in the spectrum was observed.

Hydrosilylation of 3-hexyne by **6**

NacNacAlH$_2$ (10.5 mg, 0.0235 mmol) was dissolved in chlorobenzene (~0.6 mL) making a clear colourless solution. The solution was transferred to a vial containing [CPh$_3$][B(C$_6$F$_5$)$_4$] (21.9 mg, 0.0237 mmol) and swirled. Solution became yellow and then yellow-orange. Solution was transferred to an NMR tube, then phenylacetylene (2.1 μL, 0.0234 mmol) was added and tube was inverted multiple times. Solution became a deep red. After 10 min at room temperature $^1$H NMR spectroscopy was used to confirm formation of **6**.

In a separate NMR tube with a ferrocene insert, 3-hexyne (53.0 μL, 0.467 mmol) and HSiEt$_3$ (75.0 μL, 0.470 mmol) were added with chlorobenzene to bring solution up to volume. A reference $^1$H NMR spectrum was recorded then **6** (5 mol%, prepared in previous NMR tube) was added. Solution became a paler yellow. After 10 min at room temperature, 44% conversion was observed. NMR spectroscopic data matched that of (*E*)-3-triethylsilyl-3-hexene previously reported. After 1 week at room temperature, full conversion was observed.

Stoichiometric reaction between **6** and HSiEt$_3$

NacNacAlH$_2$ (14.7 mg, 0.0329 mmol) was dissolved in chlorobenzene (~0.6 mL) making a clear colourless solution. The solution was transferred to a vial containing [CPh$_3$][B(C$_6$F$_5$)$_4$] (30.3 mg, 0.0329 mmol) and swirled. Solution became yellow and then yellow-orange. Solution was transferred to an NMR tube, then phenylacetylene (3.6 μL, 0.0328 mmol) was added and tube was inverted multiple times. Solution became a deep red. After 30 min at room temperature $^1$H NMR spectroscopy was used to confirm formation of **6**. Then HSiEt$_3$ (5.3 μL, 0.0332 mmol) was added to the solution which became a deep violet. After 30 min at room temperature, solution had become a light purple, then grey. After sitting overnight at room temperature, solution had become a pale yellow. Mixture appeared to have redistribution and slow hydrosilylation of **5** to form a polymer and the original cation **2**.

Stoichiometric reaction of **2** with 2-methyl-1-phenylpropene and DSiEt$_3$

DSiEt$_3$ (7.9 μL, 0.0496 mmol) and 2-methyl-1-phenylpropene (7.2 μL, 0.0491 mmol) was added to an NMR tube. In a vial, NacNacAlH$_2$ (22.1 mg, 0.0495 mmol) was dissolved in chlorobenzene (~0.6 mL) making a clear colourless solution. The solution was transferred to a vial containing [CPh$_3$][B(C$_6$F$_5$)$_4$] (45.4 mg, 0.0492 mmol) and swirled. Solution became yellow and then yellow-orange. Solution was transferred to the NMR tube and turned yellow, gradually lightening to a pale peach. The reaction was monitored by $^1$H and $^2$H NMR spectroscopy. There appeared to be some minor deuterium labelling of the ligand backbone proton of **2** but otherwise deuterium strictly found on the hydrosilylation product. As well, Al–H signal remains in the $^1$H NMR spectrum.

Stoichiometric reaction of **6** with 3-hexyne and DSiEt$_3$

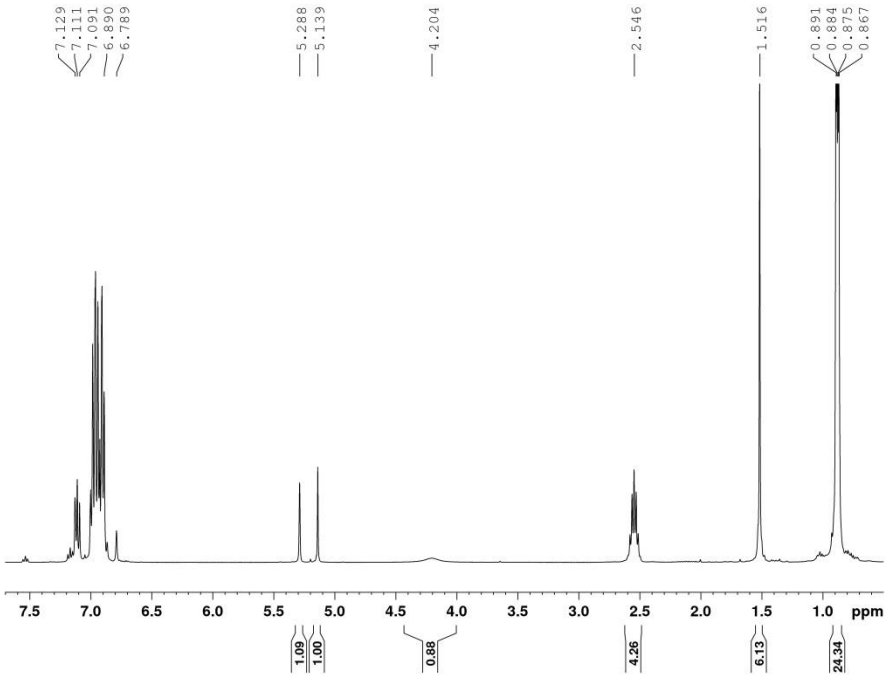
NacNacAlH$_2$ (16.6 mg, 0.0372 mmol) was dissolved in chlorobenzene (~0.6 mL) making a clear colourless solution. The solution was transferred to a vial containing [CPh$_3$][B(C$_6$F$_5$)$_4$] (34.6 mg, 0.0375 mmol) and swirled. Solution became yellow and then yellow-orange. Solution was transferred to an NMR tube, then phenylacetylene (4.1 μL, 0.0373 mmol) was added and tube was inverted multiple times, becoming deep red in color. After 3.5 h at room temperature $^1$H NMR spectroscopy was used to confirm formation of **6**. Then 3-hexyne (4.2 μL, 0.0370 mmol) and DSiEt$_3$ (5.9 μL, 0.0371 mmol) was added to solution which became a deep purple. The reaction was monitored by $^1$H and $^2$H NMR spectroscopy. After 1 h complete consumption

of silane was observed. There appeared to be some deuterium labelling of the backbone methyl groups from **5** but otherwise deuterium predominantly found on the hydrosilylation product. As well, Al–H signal remains in the $^{1}$H NMR spectrum. Some other deuterium signals were observed as well, likely from other side products.

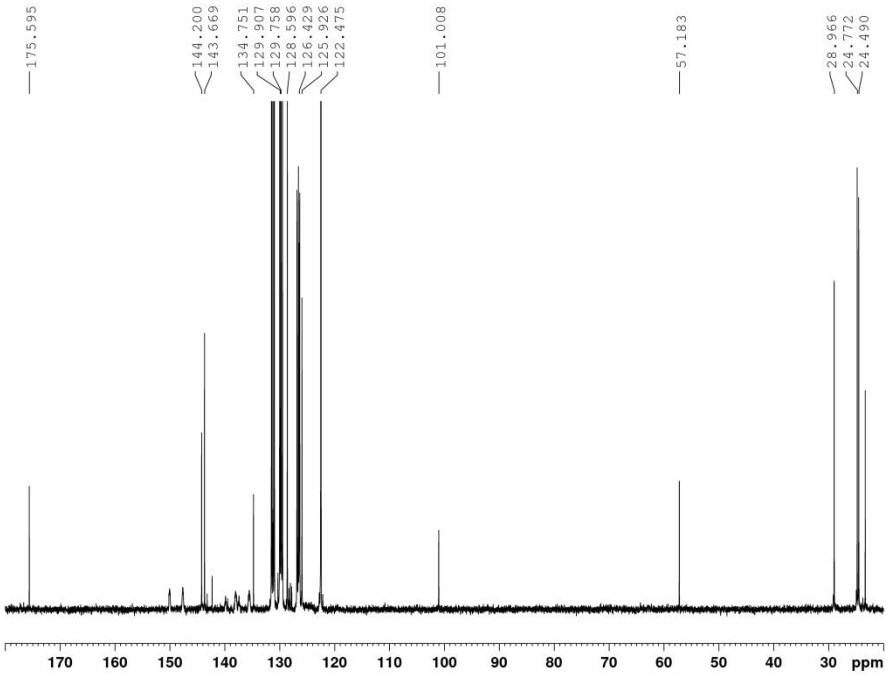
**NMR Spectra**

*[NacNacAlH][B($C_6F_5$)$_4$]* ***(2)***

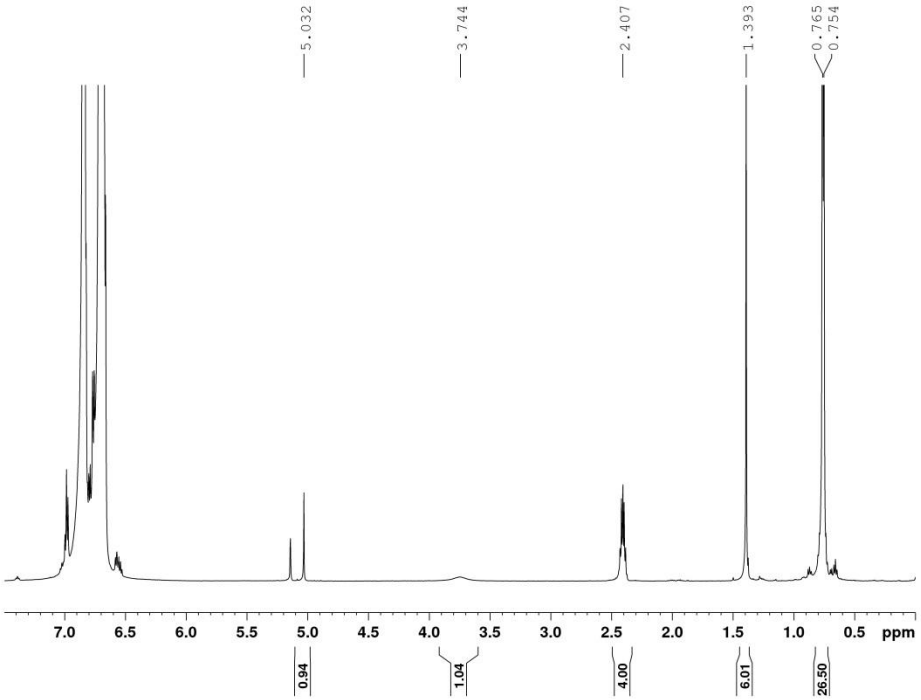
$^1$H NMR Spectrum



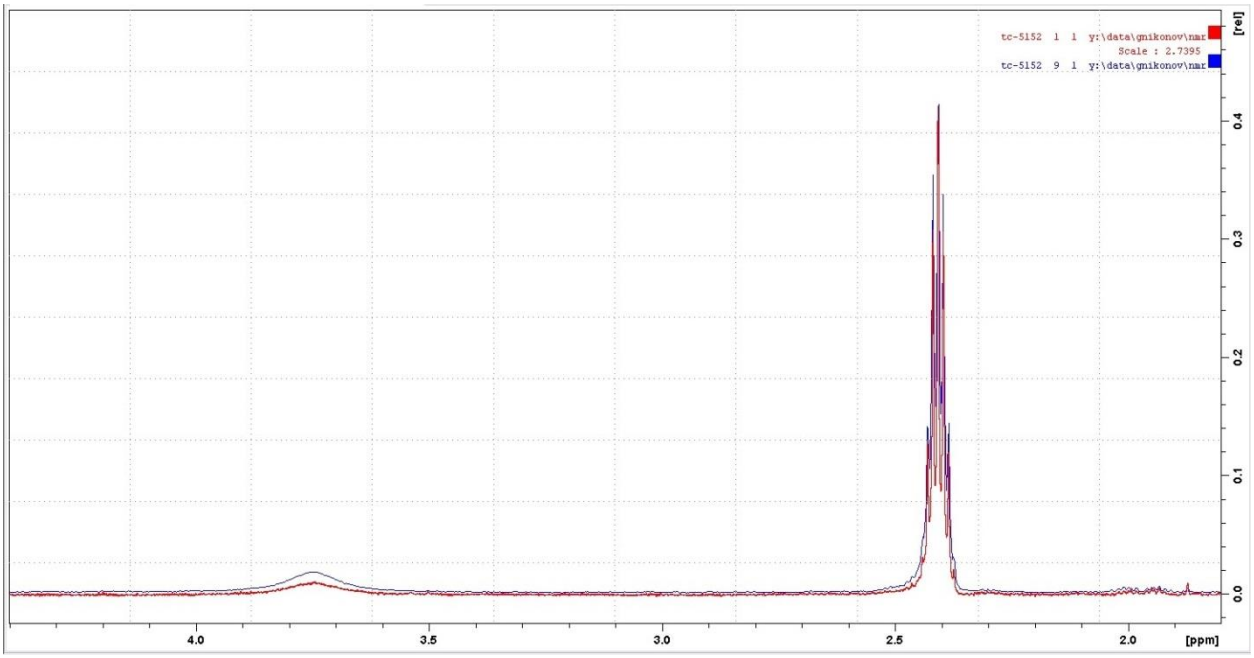

$^{13}$C{$^1$H}NMR Spectrum



$^1$H NMR Spectrum with the acquisition time reduced from 2.75 to 0.6 seconds in order to match the $T_2$ relaxation time of the hydride signal. As a result the hydride signal now integrates to a value of one relative to the other signals (chlorobenzene, 600 MHz).

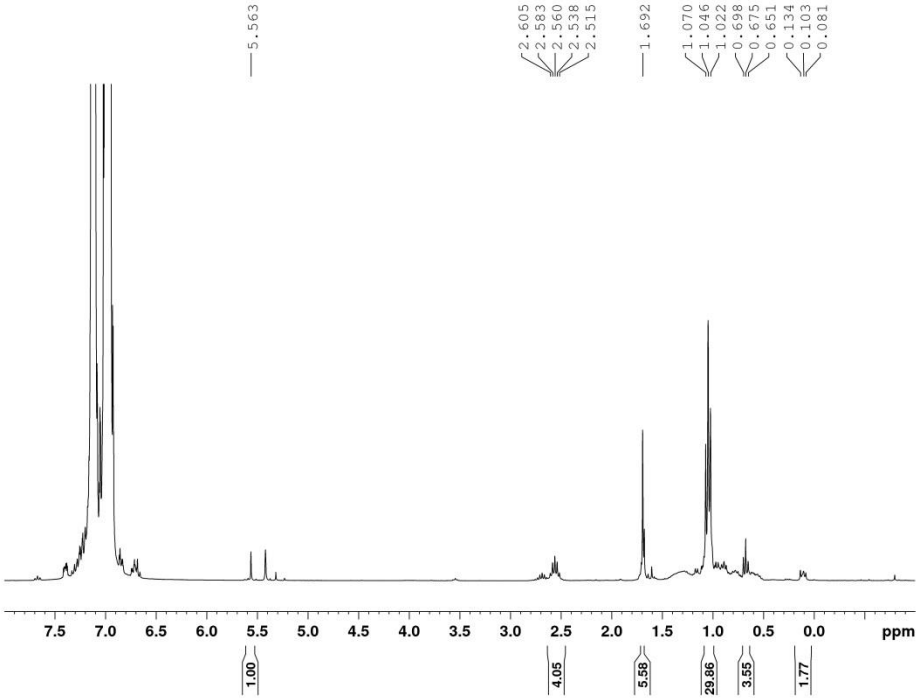



Overlap of $^1$H NMR Spectra recorded with an acquisition time of 2.75 (red) and 0.6 (blue) seconds.

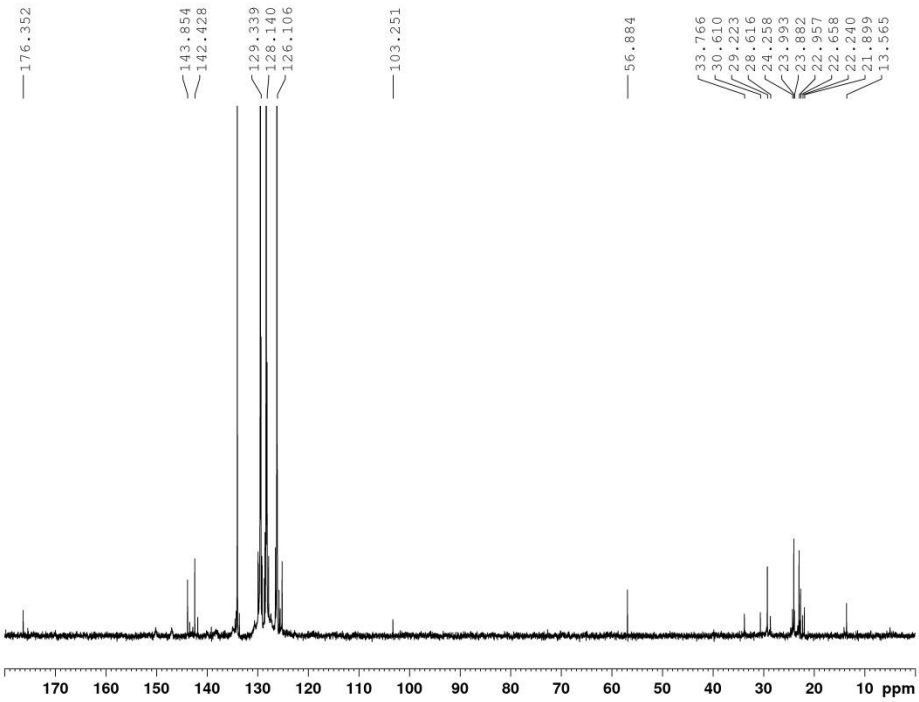


*[NacNacAl(hexyl)][B($C_6F_5$)$_4$] (**3**)*

$^1$H NMR Spectrum

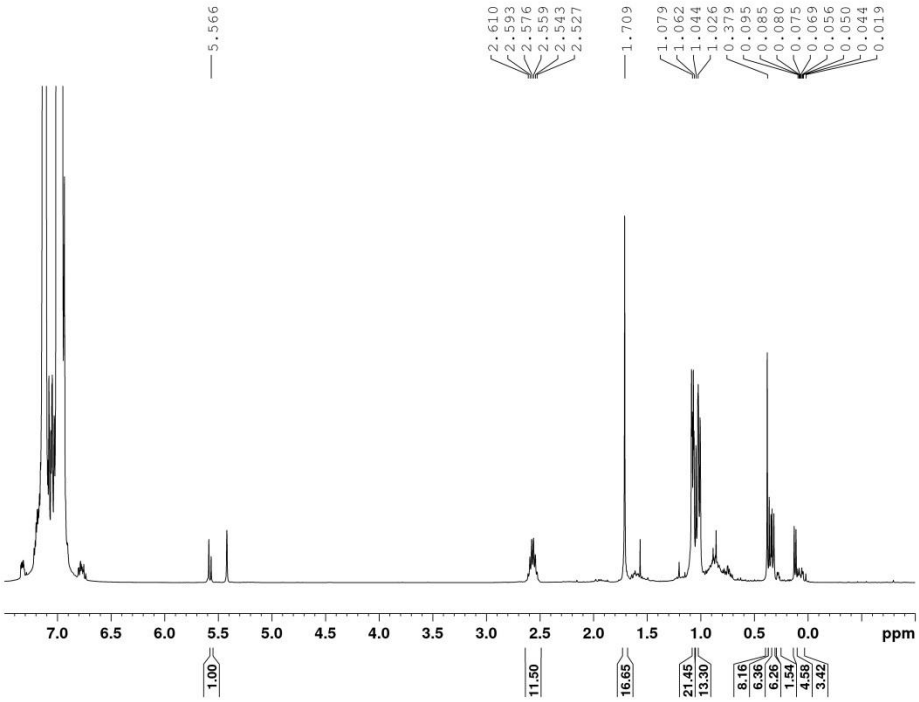



$^{13}$C{$^1$H }NMR Spectrum

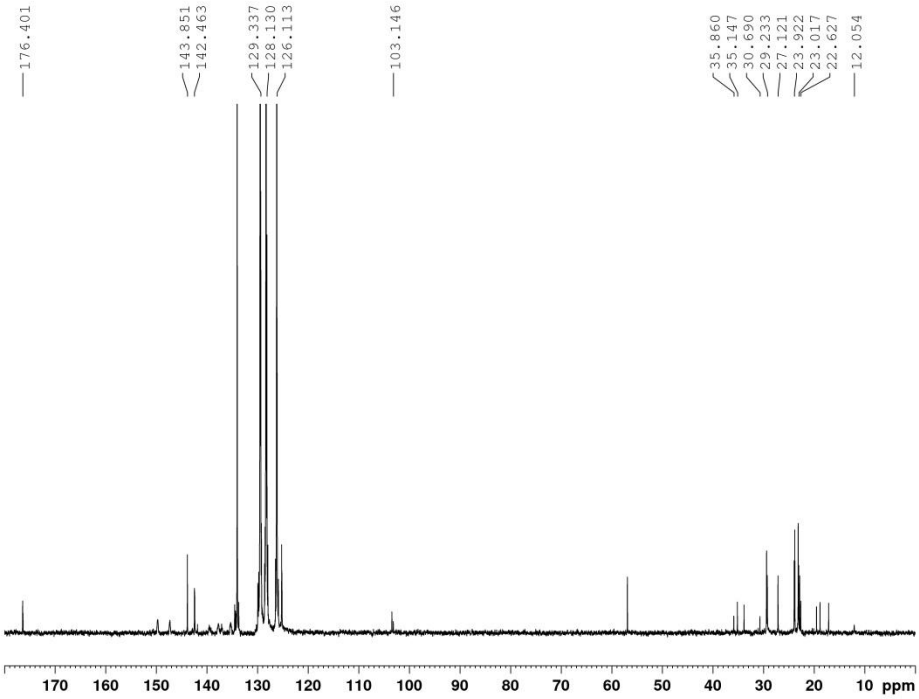


*[NacNacAl(neohexyl)][B($C_6F_5$)$_4$] (**4**)*

$^1$H NMR Spectrum

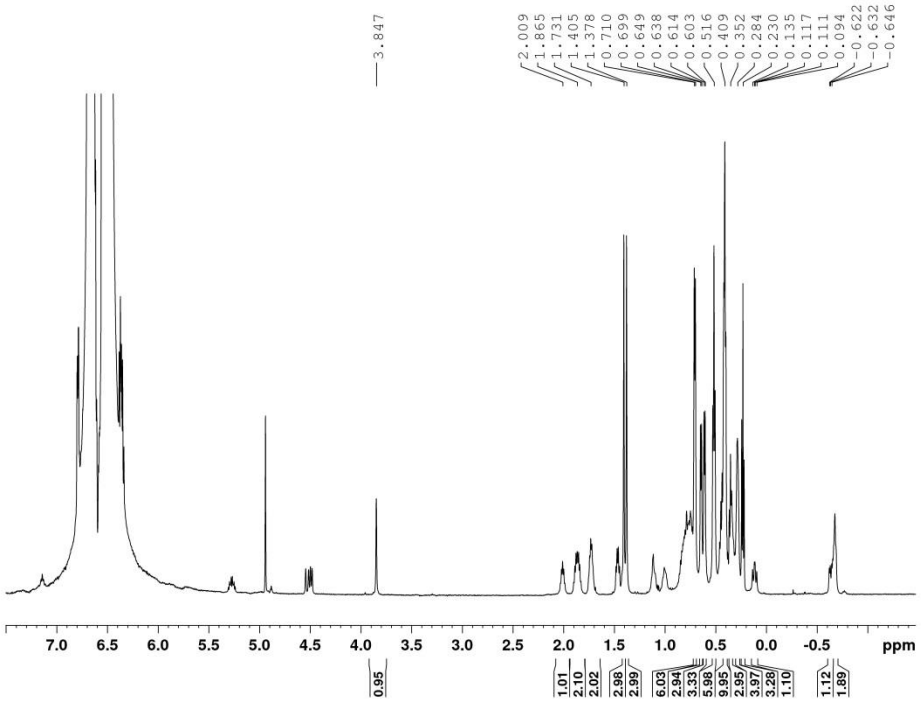



$^{13}$C{$^1$H }NMR Spectrum

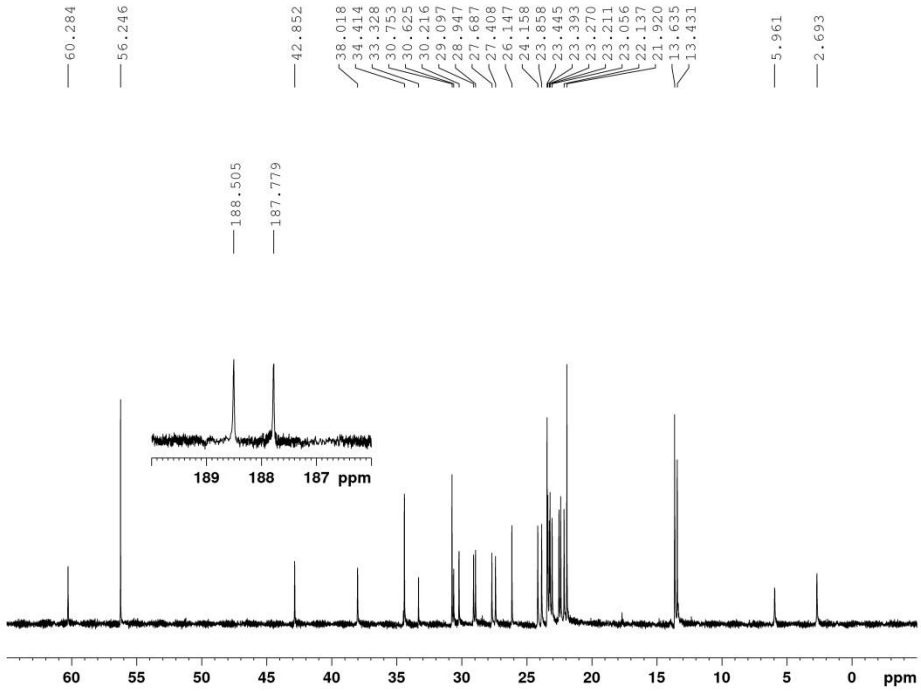


*[κ3-N,N,C-{HC(C(Me)N(2,6-Pr$^{i}_{2}$C$_6$H$_3$))$_2$($^{n}$butyl–CH–CH$_2$)}AlH][B(C$_6$F$_5$)$_4$]* ***(5)***

$^{1}$H NMR Spectrum

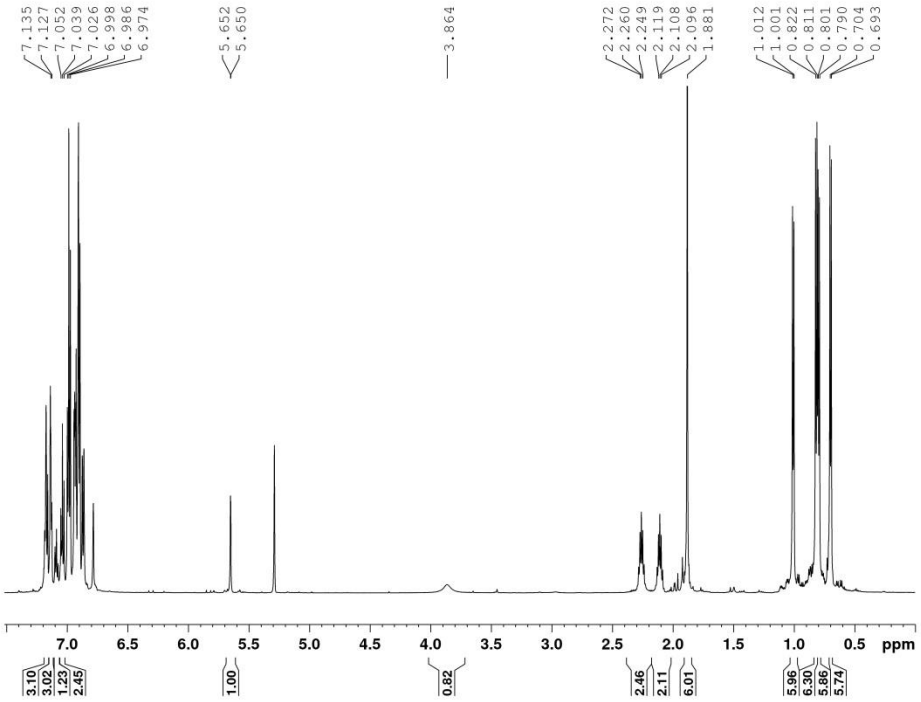



$^{13}$C{$^{1}$H }NMR Spectrum

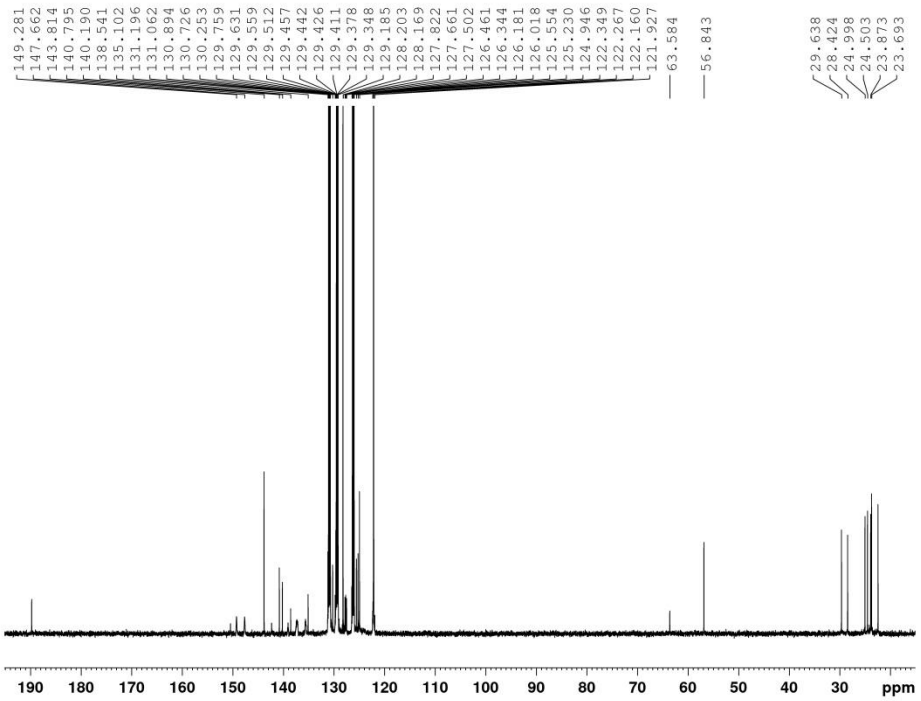


*[κ3-N,N,C-{HC(C(Me)N(2,6-Pr$^{i}_{2}$C6H3))2(PhC=CH)}AlH][B(C6F5)4]* ***(6)***

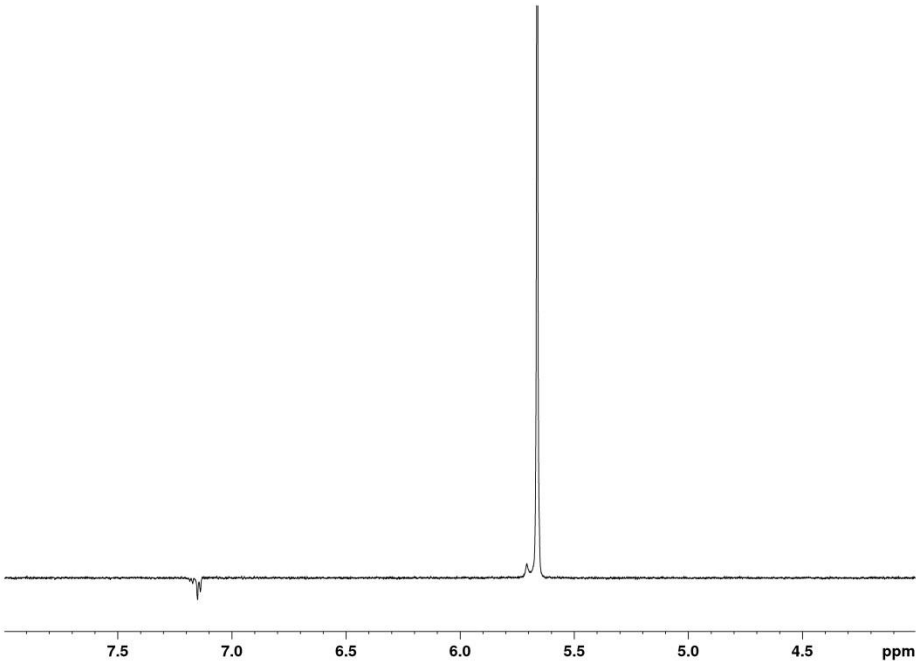
$^{1}$H NMR Spectrum




$^{13}$C{$^{1}$H }NMR Spectrum

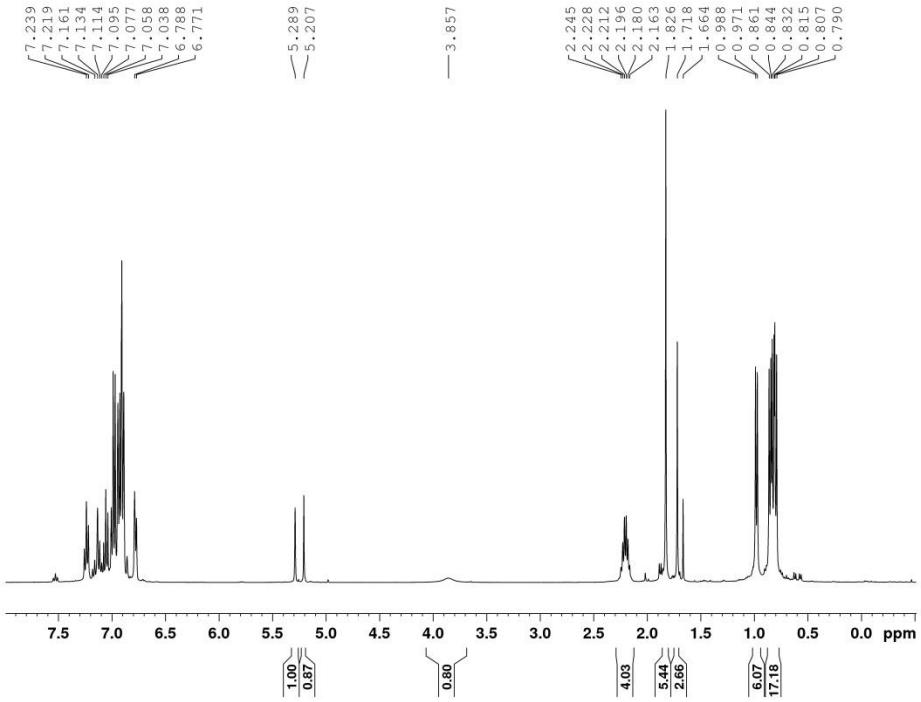


1D NOESY NMR Spectrum

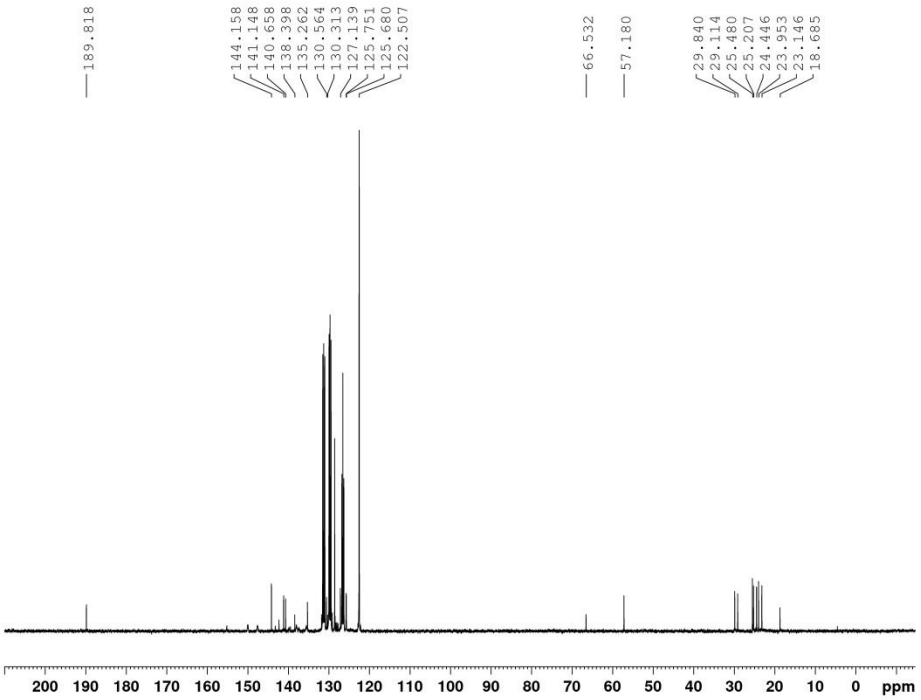


*[κ3-N,N,C-{HC(C(Me)N(2,6-Pr$^{i}_{2}$C$_6$H$_3$))$_2$(PhC=CMe)}AlH][B(C$_6$F$_5$)$_4$]* ***(7)***

$^{1}$H NMR Spectrum

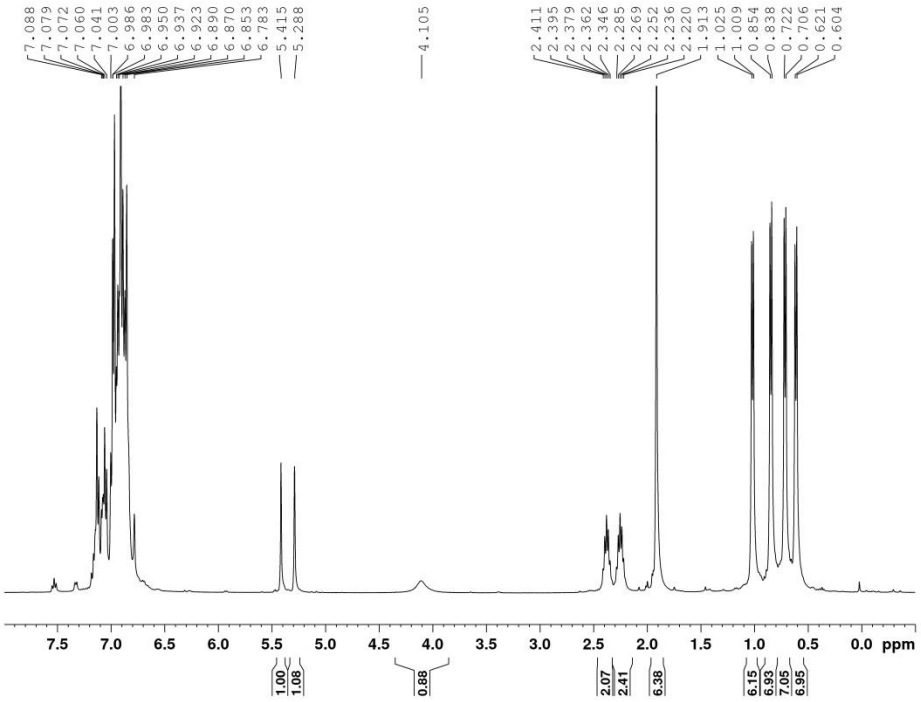



$^{13}$C{$^{1}$H }NMR Spectrum

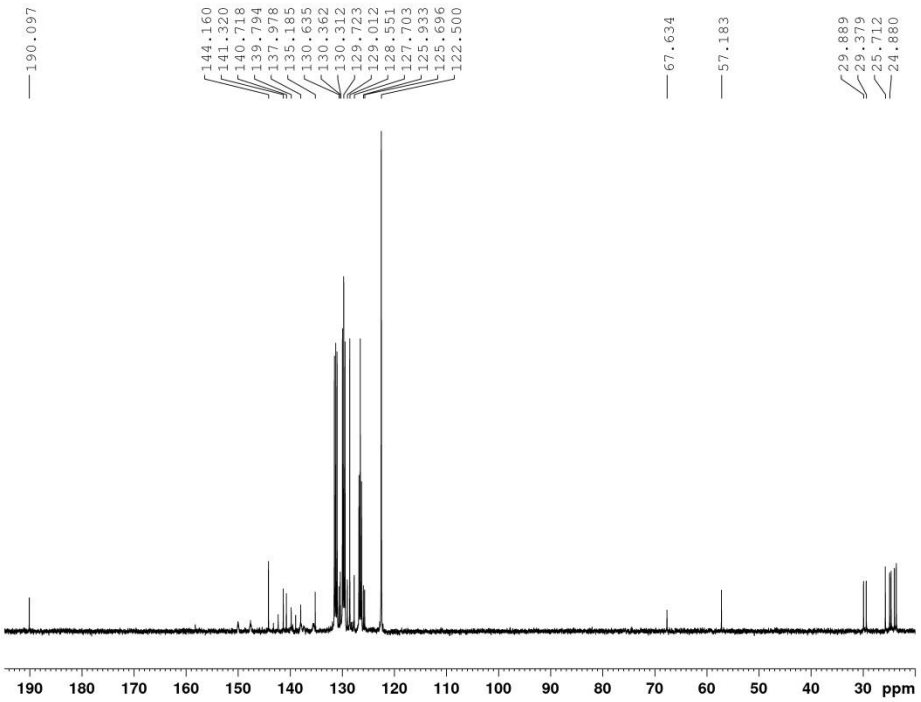


*[κ3-N,N,C-{HC(C(Me)N(2,6-Pr$^{i}_{2}$C$_6$H$_3$))$_2$(PhC=CPh)}AlH][B(C$_6$F$_5$)$_4$]* ***(8)***

$^{1}$H NMR Spectrum

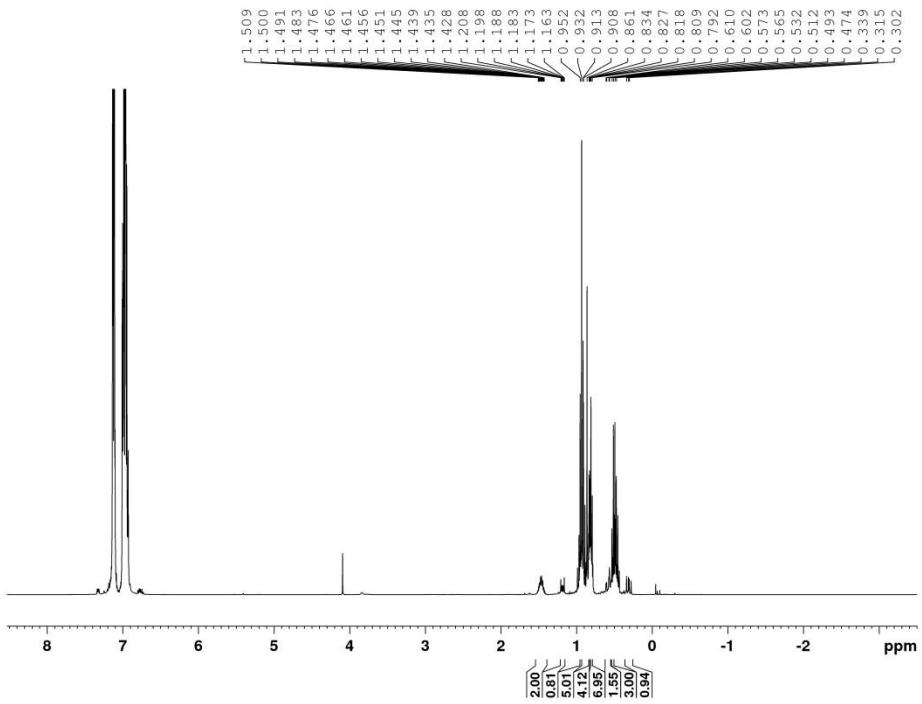



$^{13}$C{$^{1}$H }NMR Spectrum

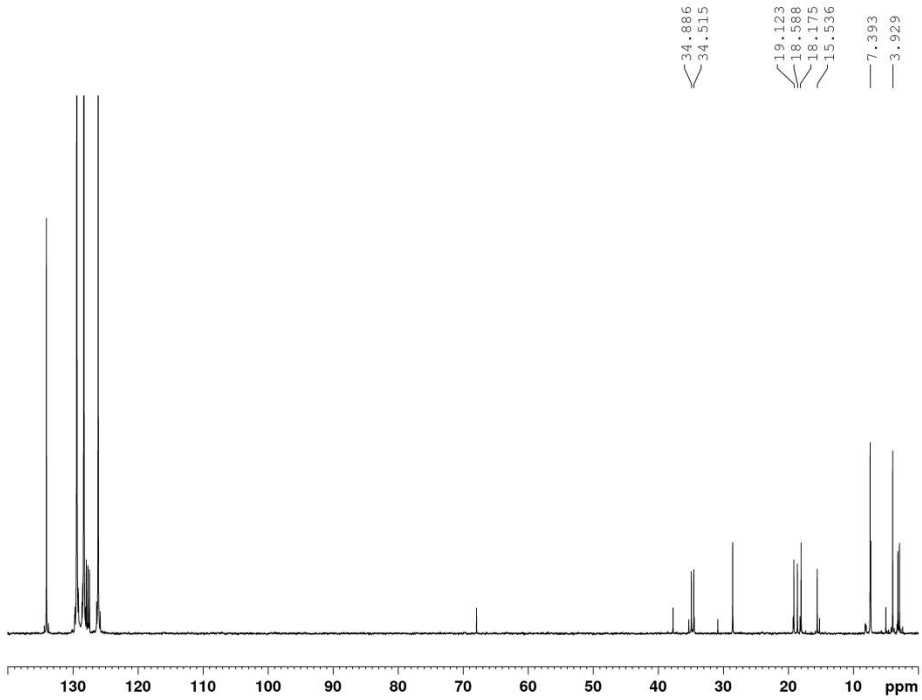


*(2,3-dimethylbutyl)triethylsilane*

$^{1}$H NMR Spectrum

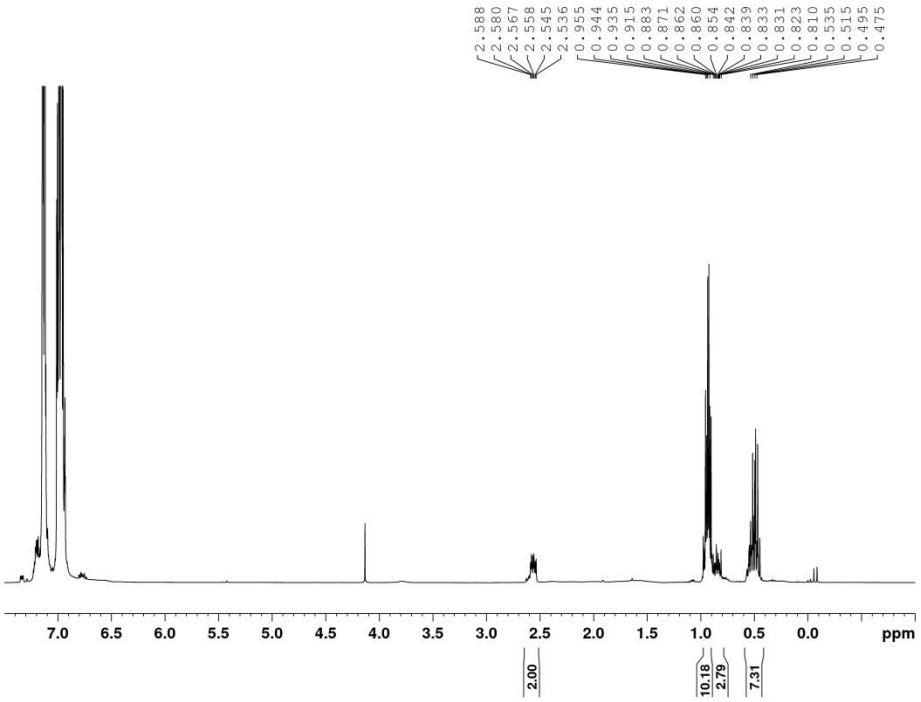



$^{13}$C{$^{1}$H}NMR Spectrum

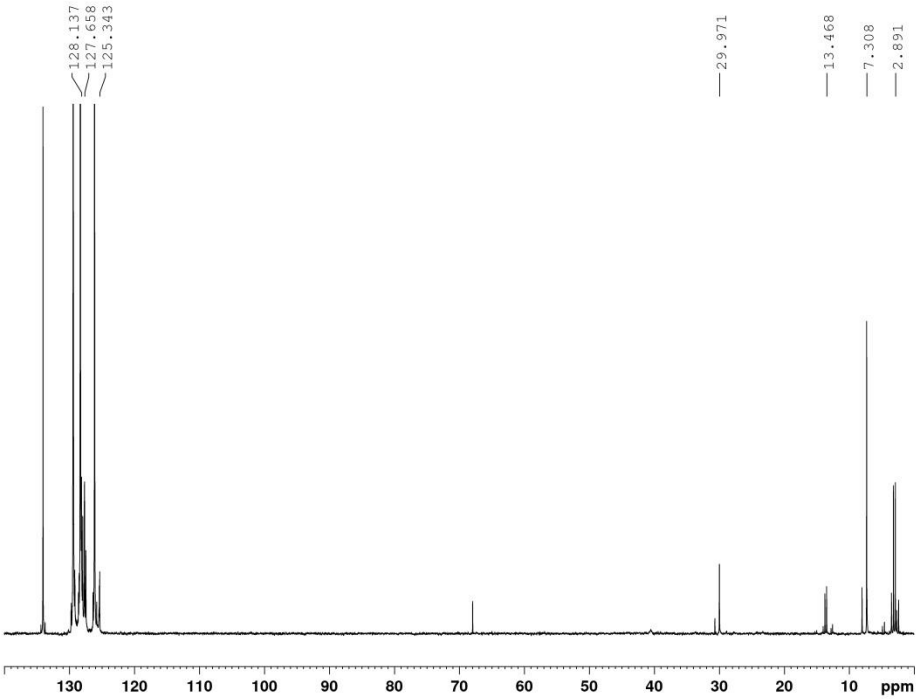


*triethyl(phenylethyl)silane*

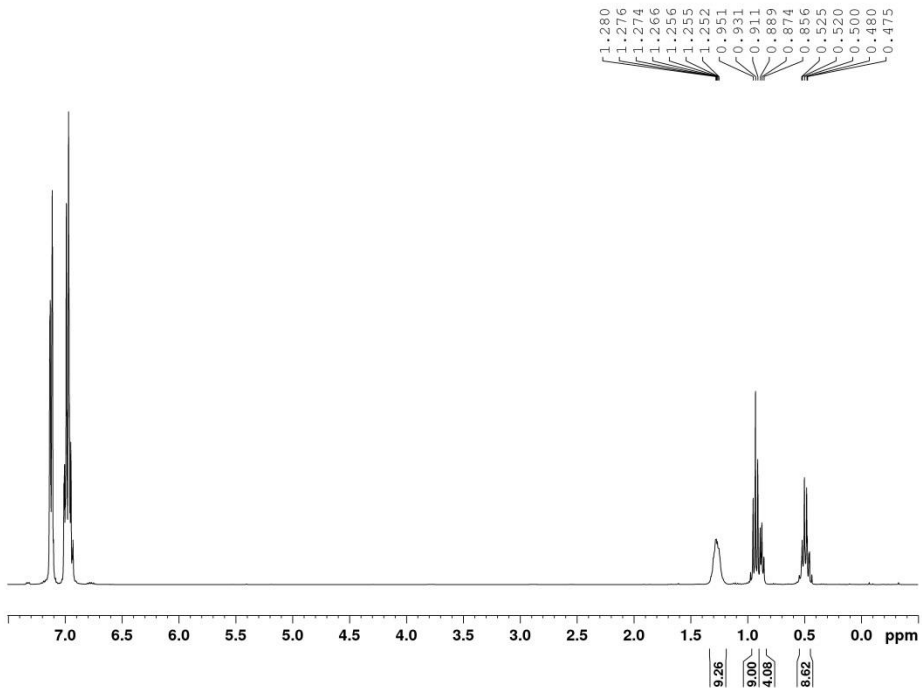
$^{1}$H NMR Spectrum



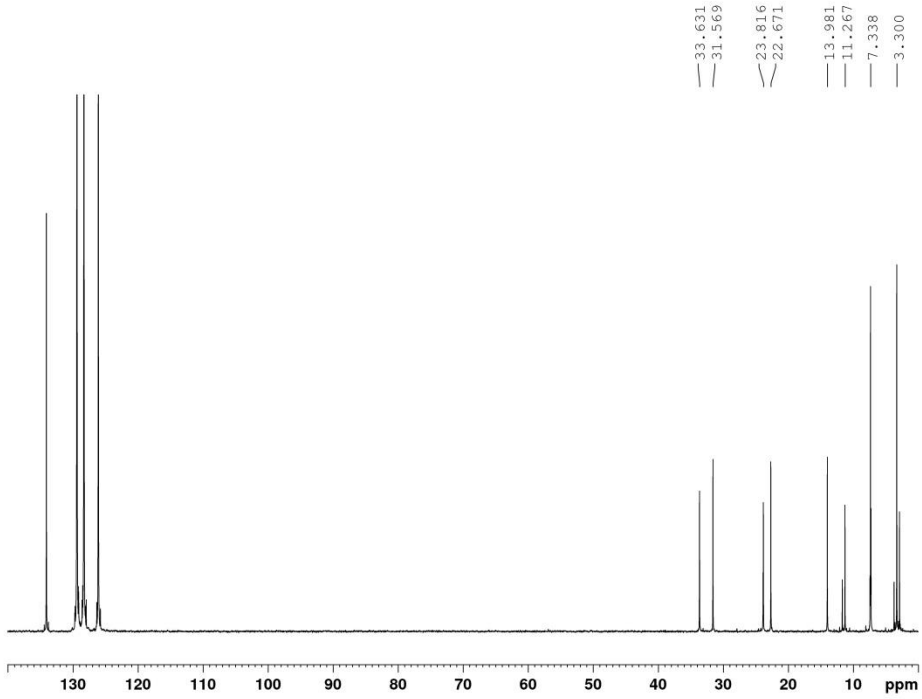

$^{13}$C{$^{1}$H}NMR Spectrum



*triethyl(hexyl)silane*
$^{1}$H NMR Spectrum

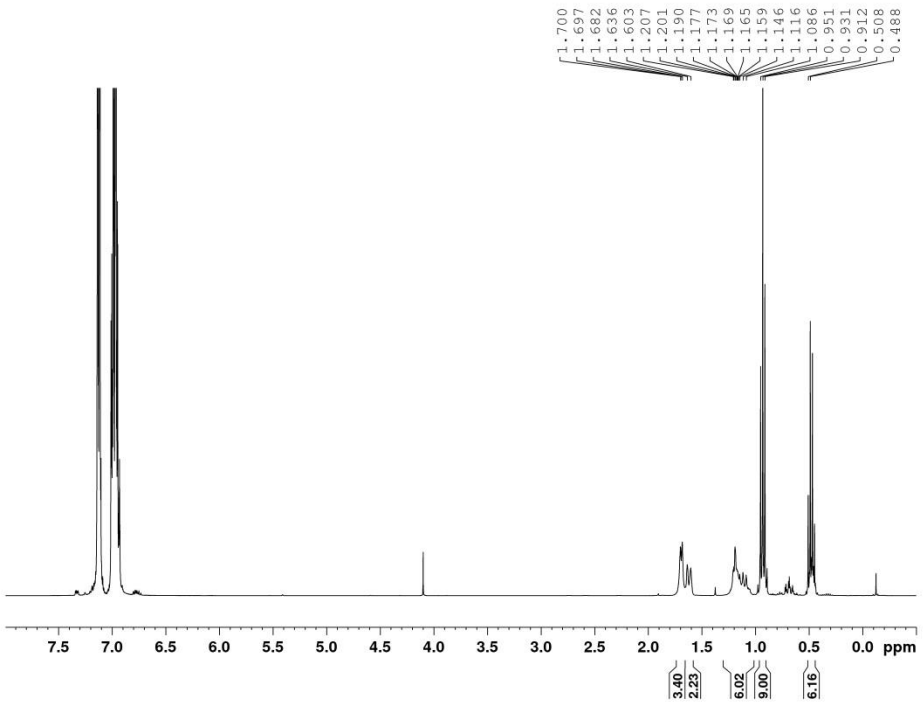



$^{13}$C{$^{1}$H}NMR Spectrum

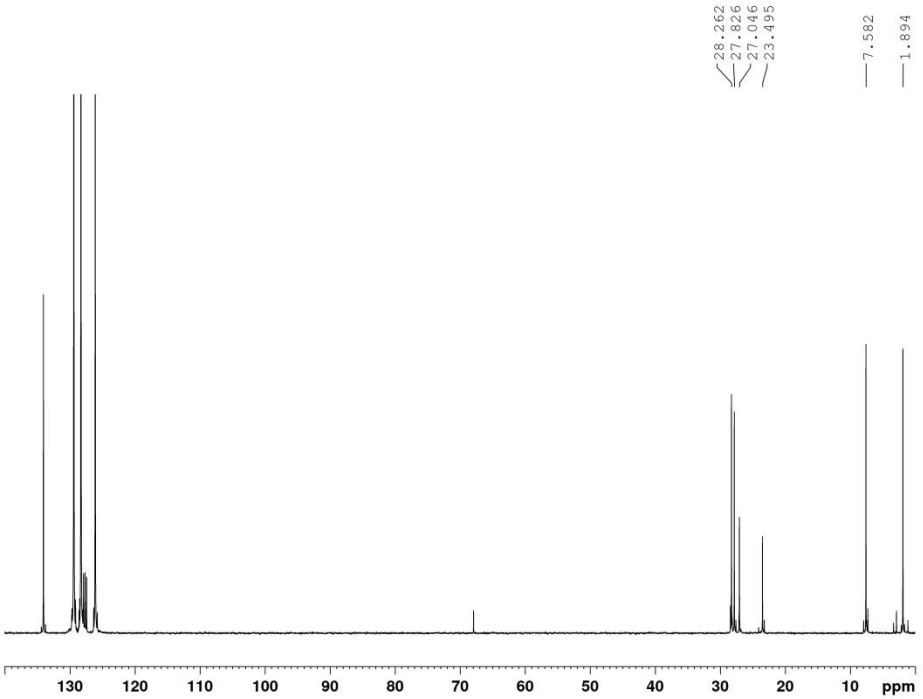


*cyclohexyltriethylsilane*

$^{1}$H NMR Spectrum

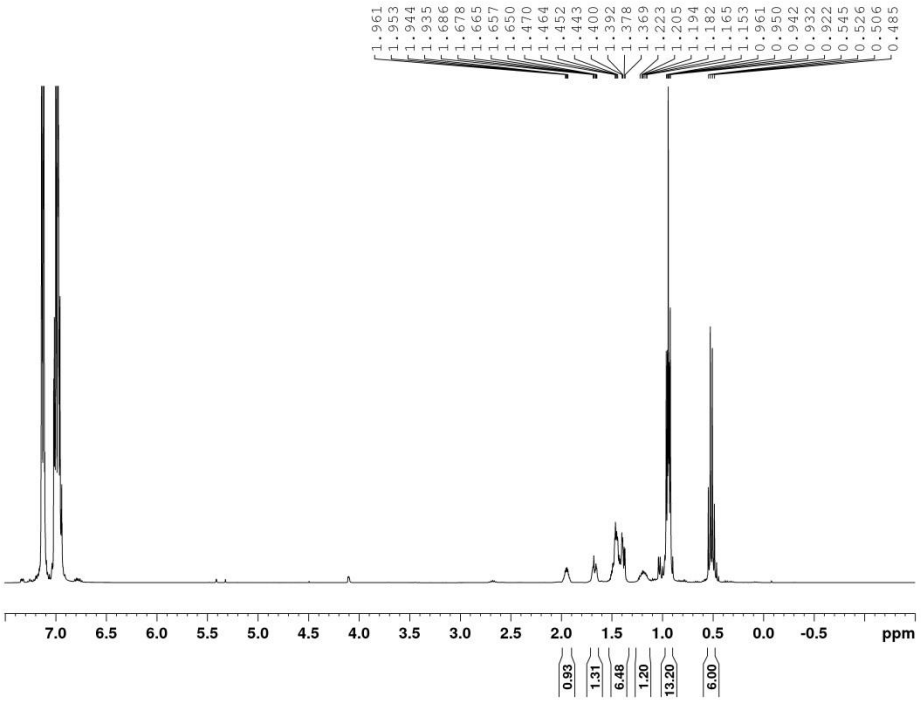



$^{13}$C{$^{1}$H}NMR Spectrum

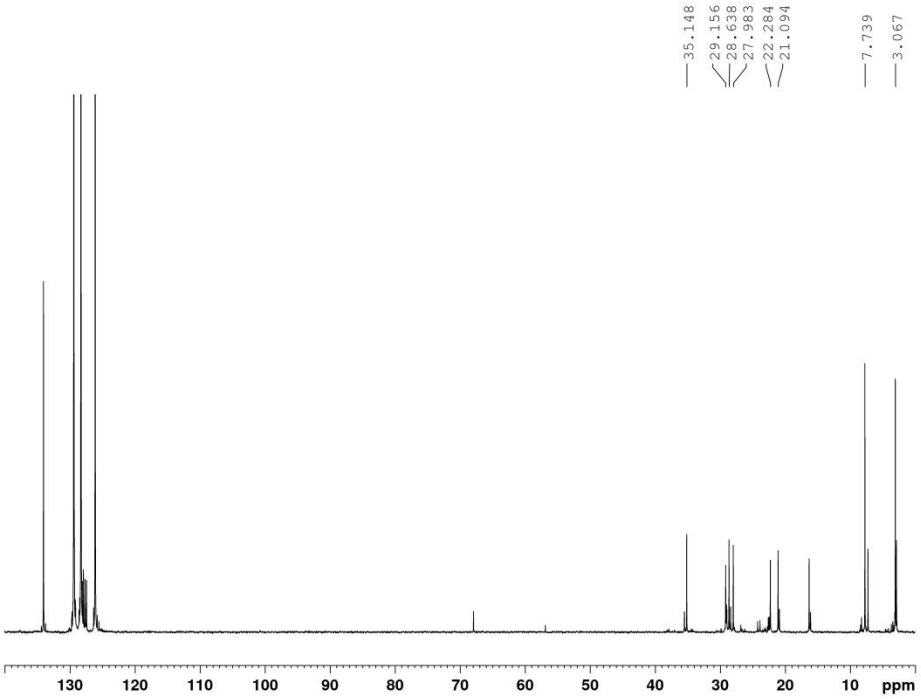


*triethyl(cis-2-methylcyclohexyl)silane*

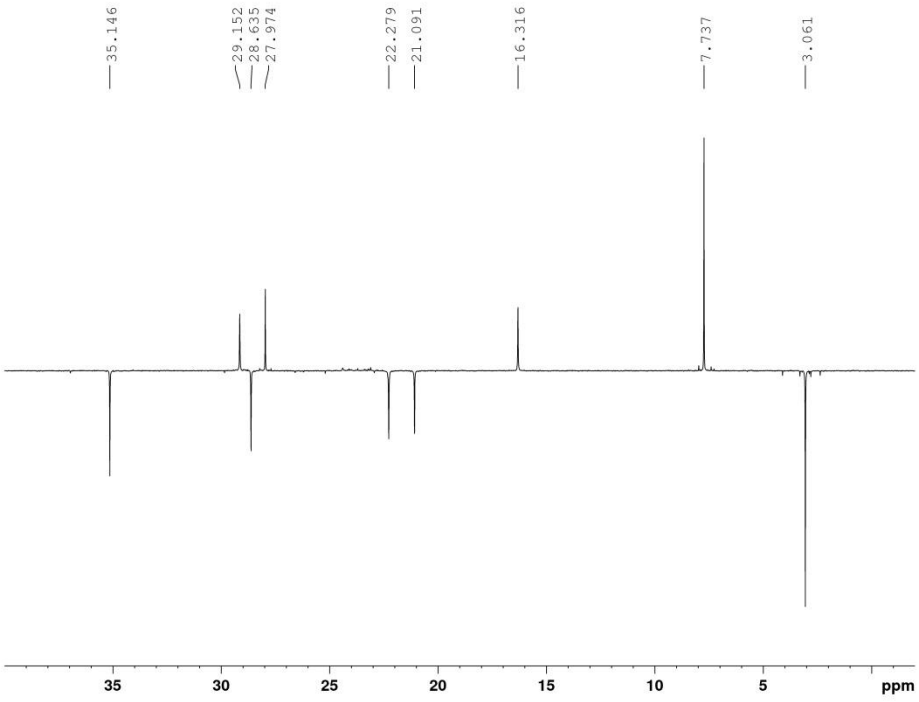
$^{1}$H NMR Spectrum



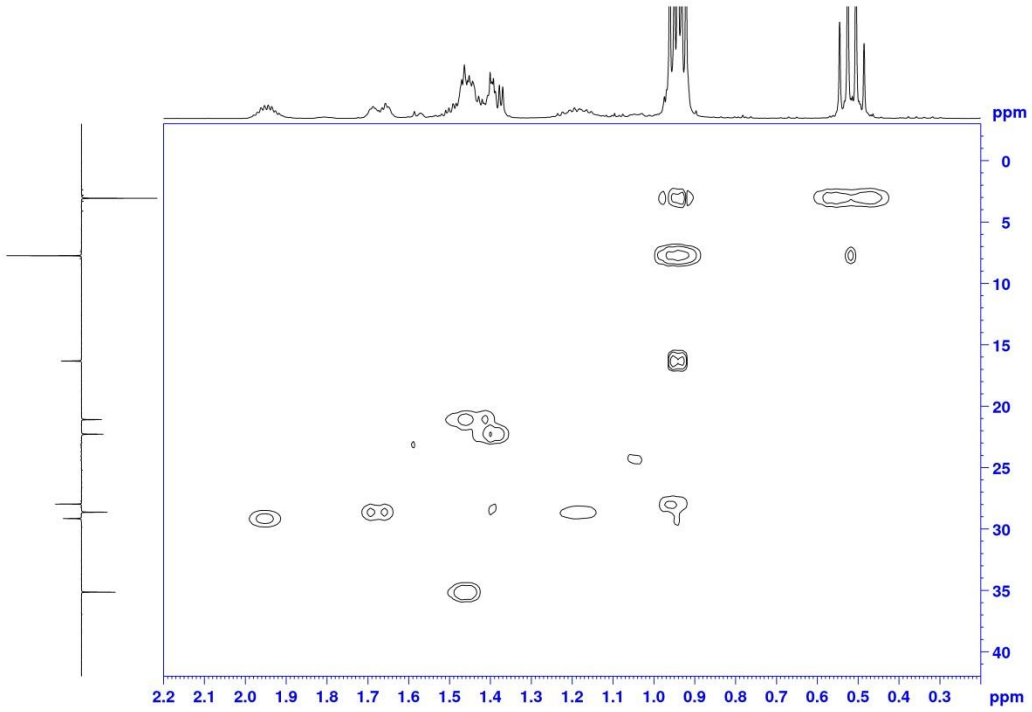

$^{13}$C{$^{1}$H}NMR Spectrum



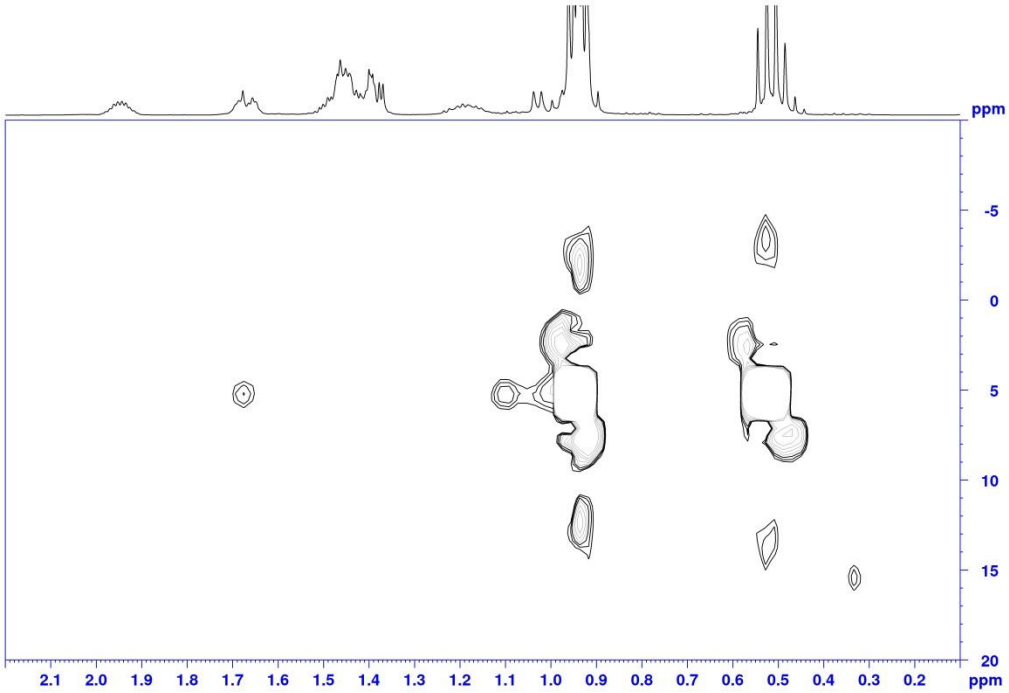
DEPT135 NMR Spectrum



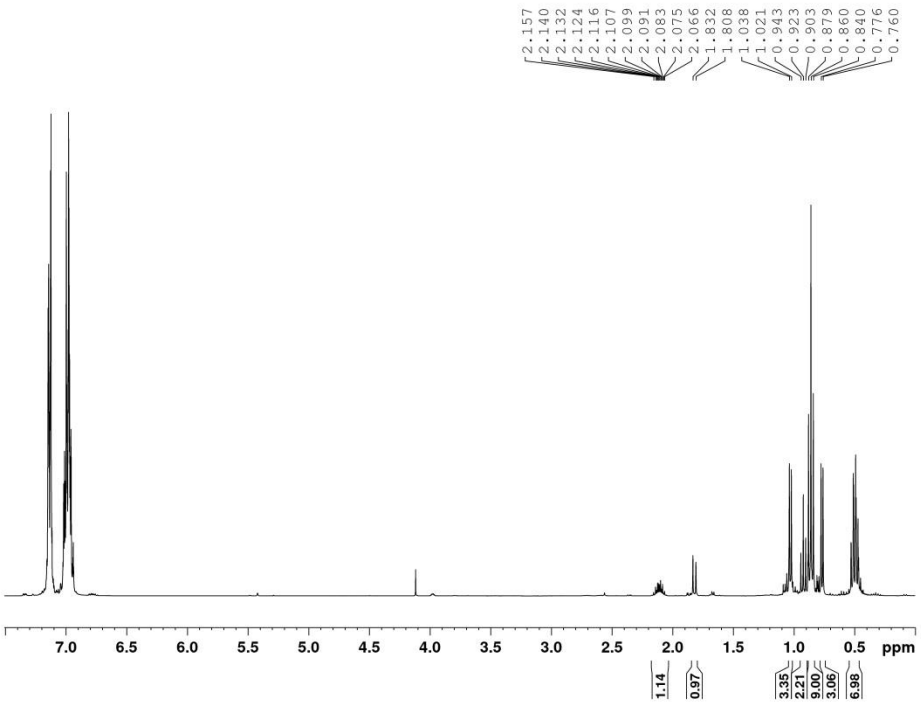

$^{1}H$-$^{13}C$ HSQC NMR Spectrum



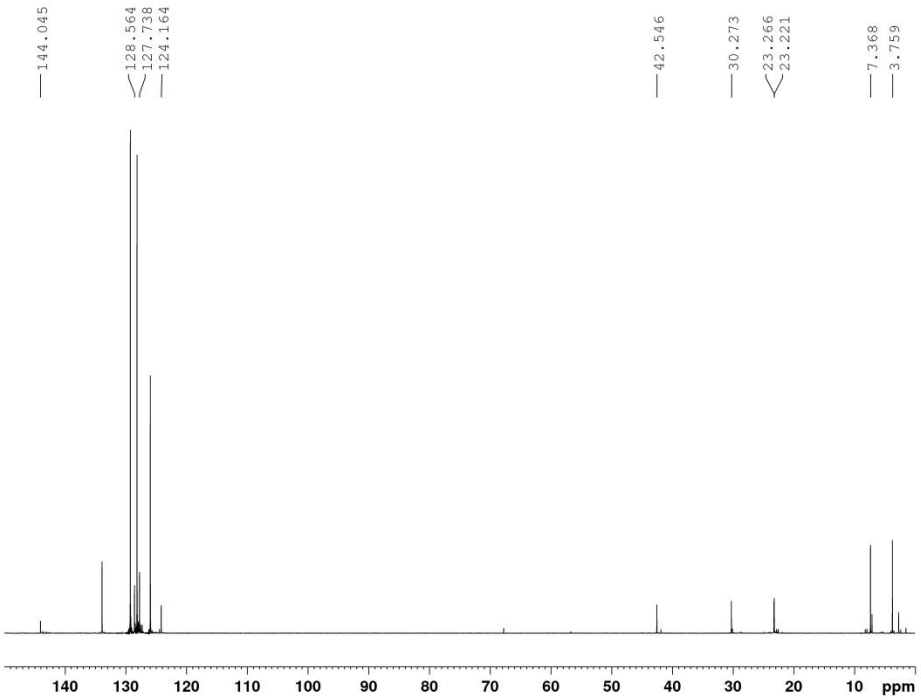
$^{1}H$-$^{29}Si$ HSQC NMR Spectrum



*triethyl(2-methyl-1-phenylpropyl)silane*
$^{1}$H NMR Spectrum

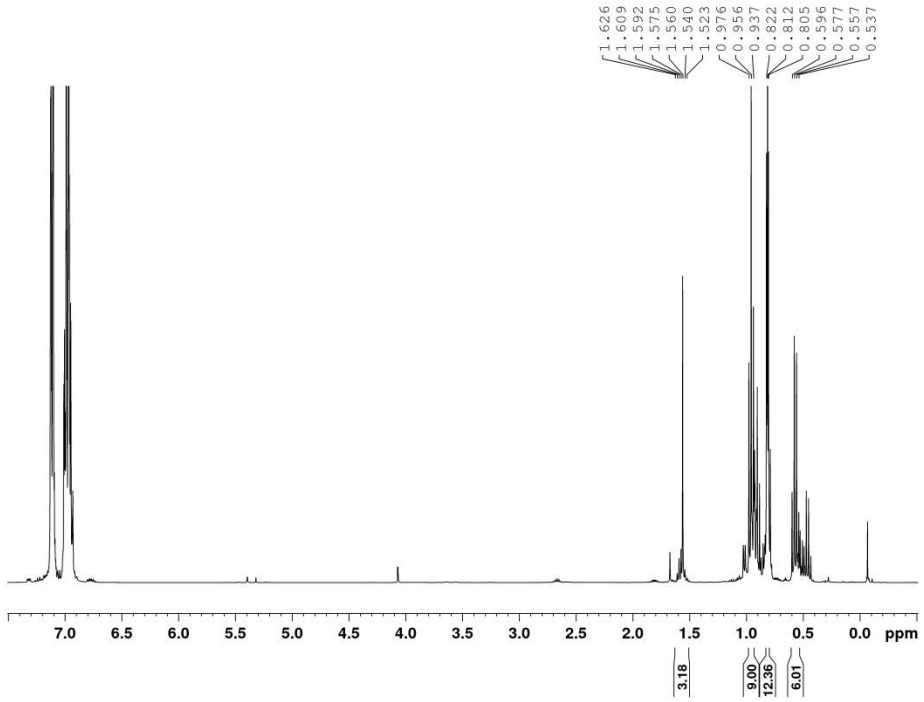



$^{13}$C{$^{1}$H}NMR Spectrum

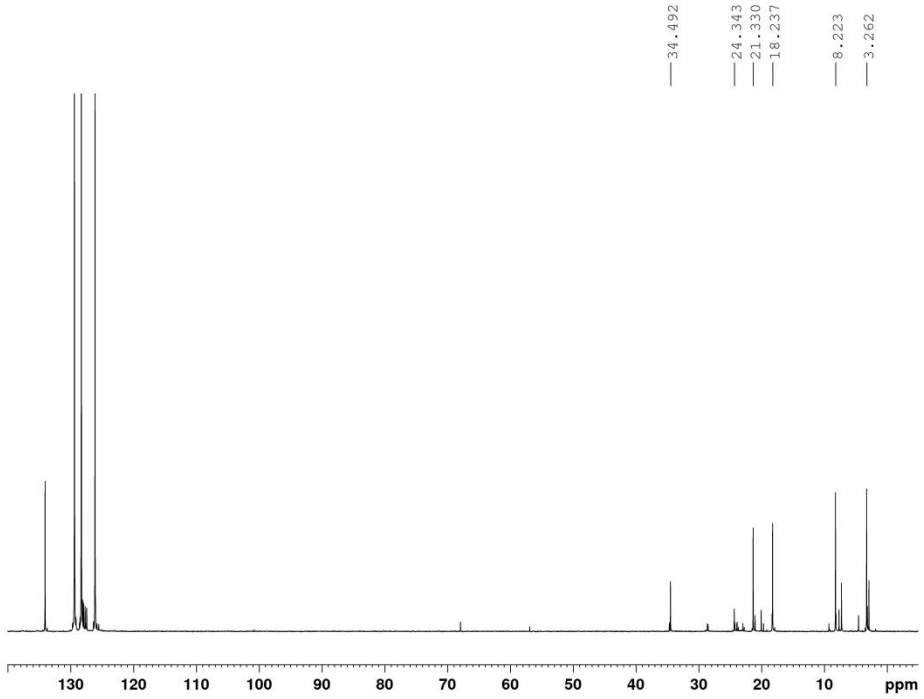


*(2,3-dimethylbutan-2-yl)triethylsilane*

$^{1}$H NMR Spectrum

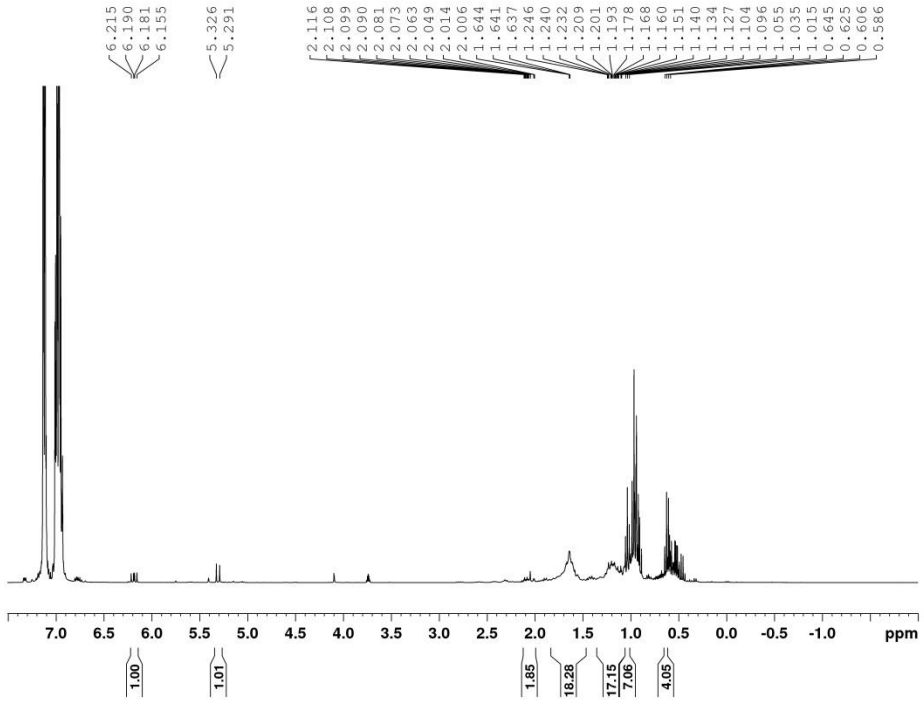



$^{13}$C{$^{1}$H}NMR Spectrum

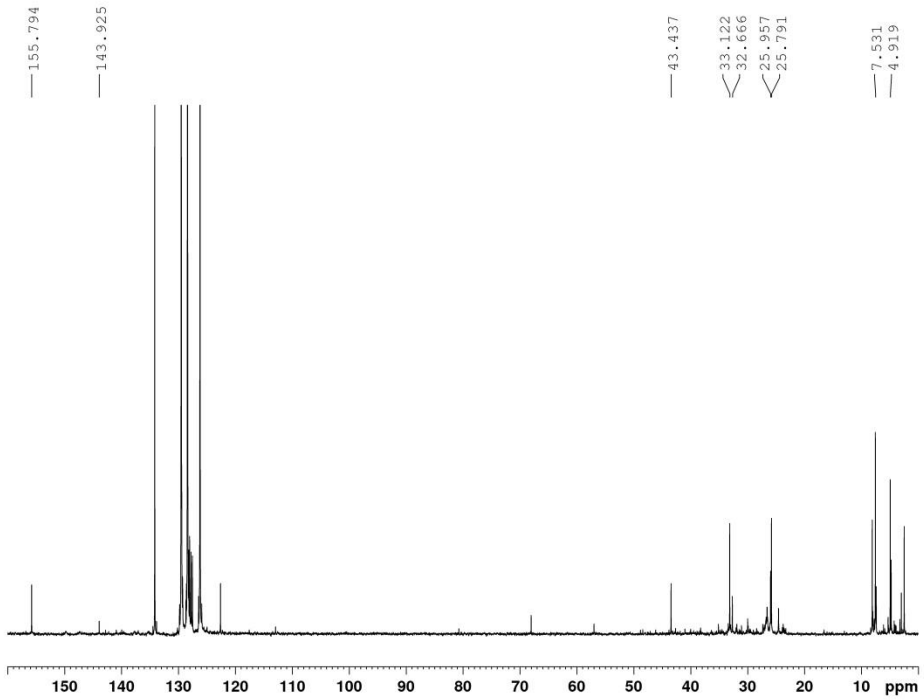


*(E)-(2-cyclohexylvinyl)triethylsilane*

$^{1}$H NMR Spectrum

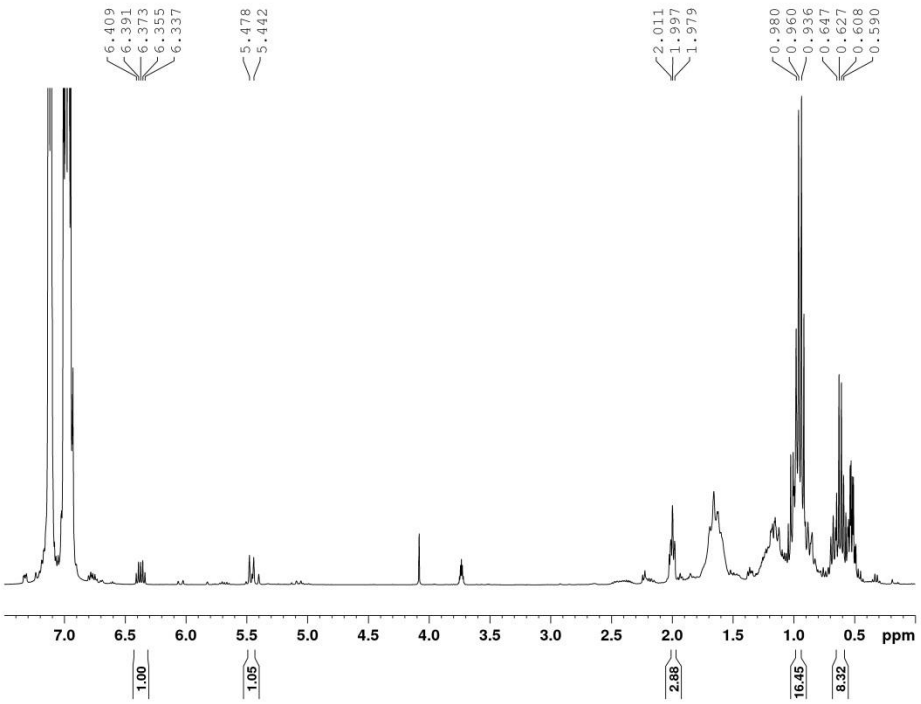



$^{13}$C{$^{1}$H}NMR Spectrum

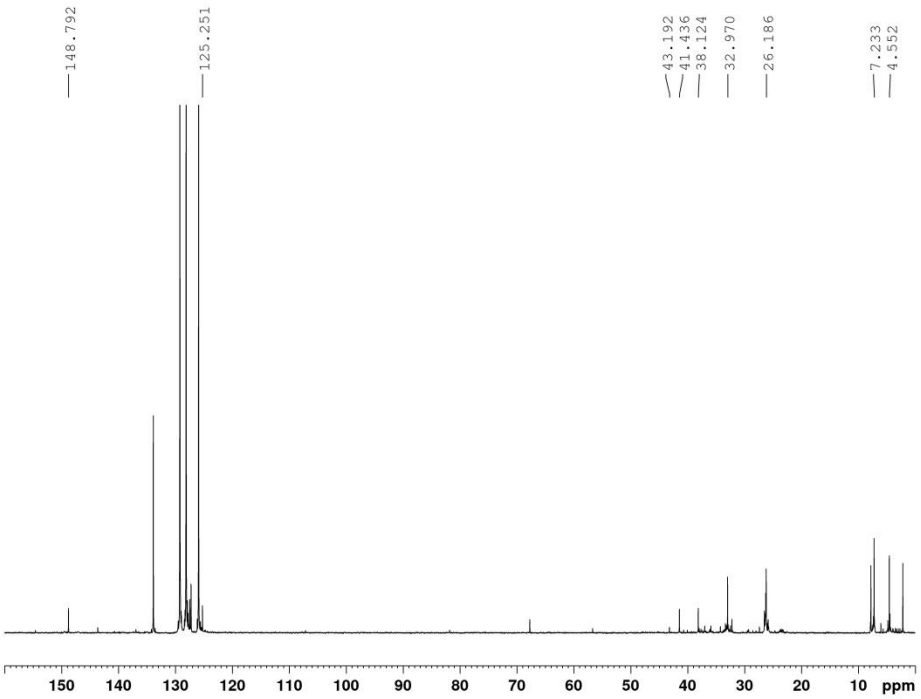


*(E)-(3-cyclohexylprop-1-en-1-yl)triethylsilane*

$^{1}$H NMR Spectrum

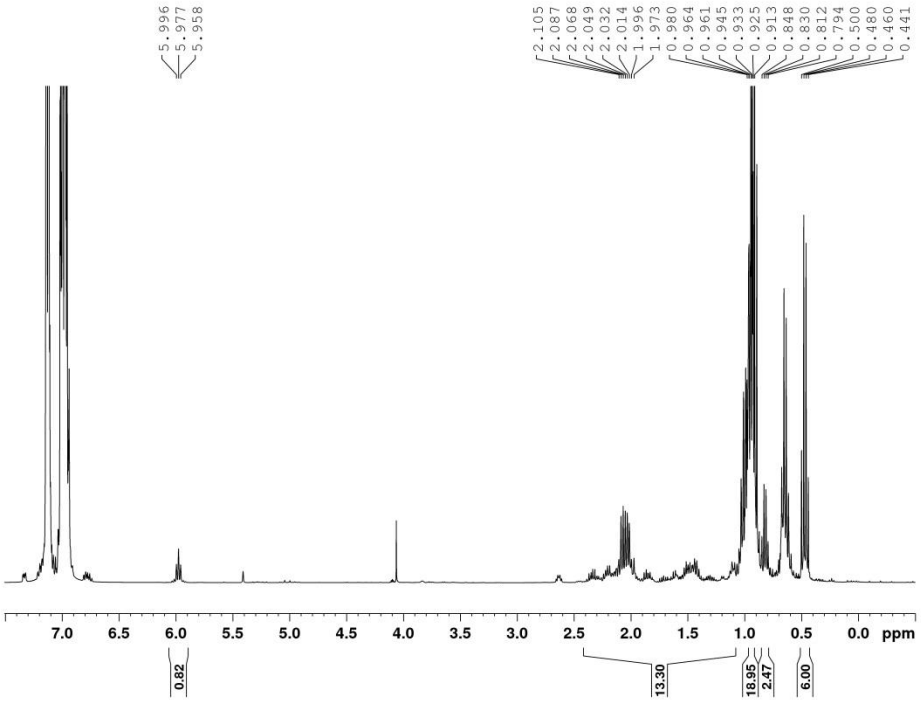



$^{13}$C{$^{1}$H}NMR Spectrum

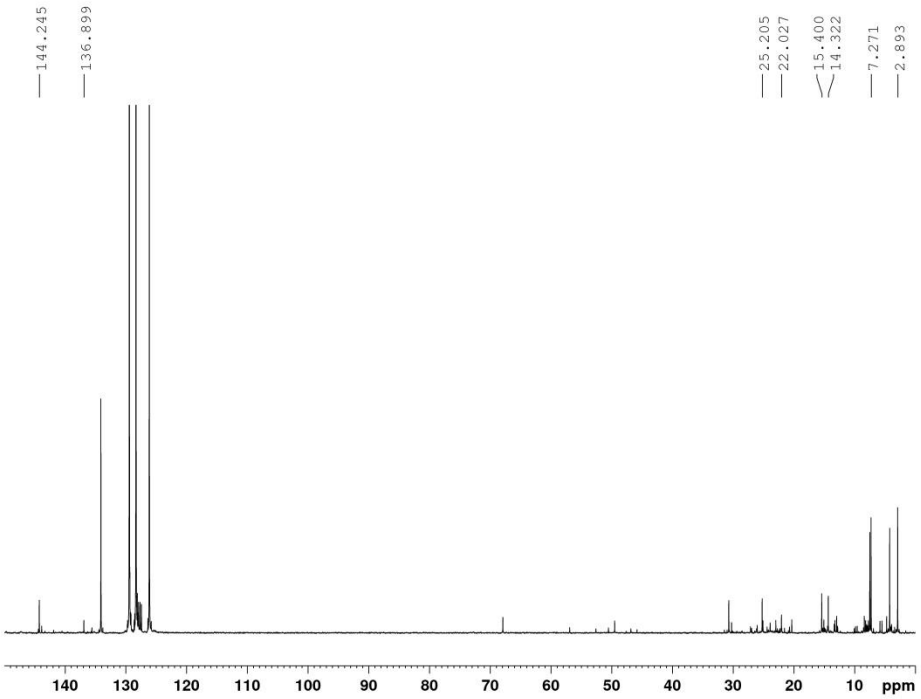


*(E)-triethyl(hex-3-en-3-yl)silane*

$^{1}$H NMR Spectrum

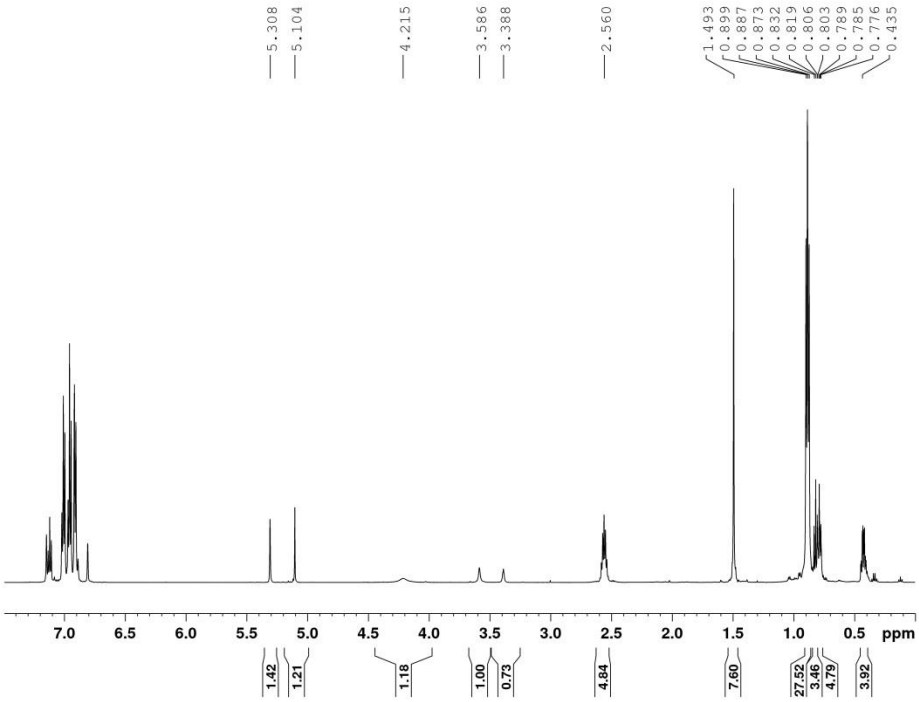



$^{13}$C{$^{1}$H }NMR Spectrum

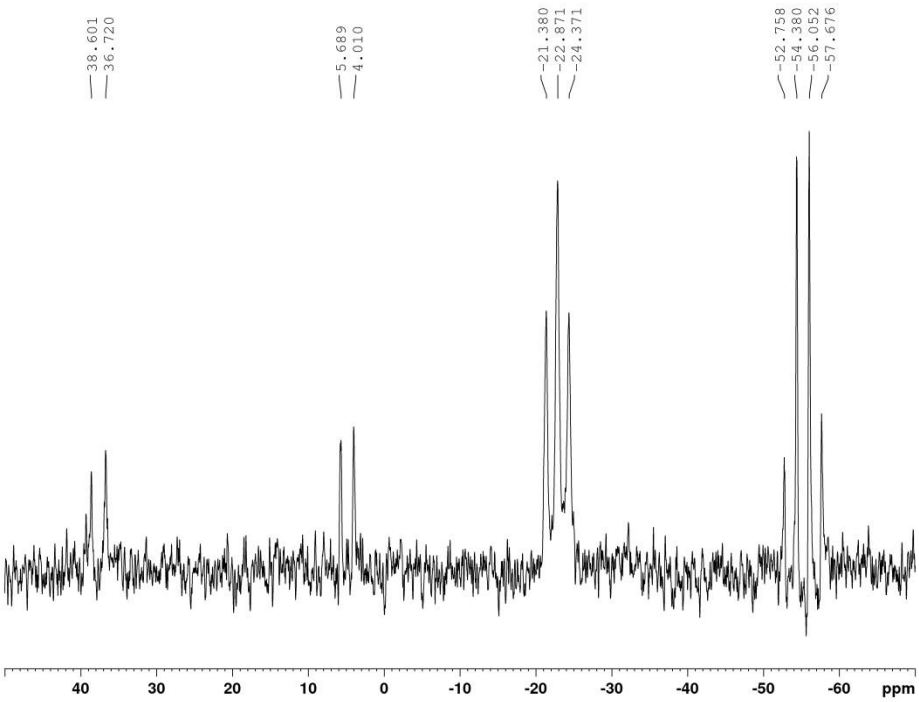


*Redistribution of $H_2SiEt_2$ by **2***

$^{1}$H NMR Spectrum

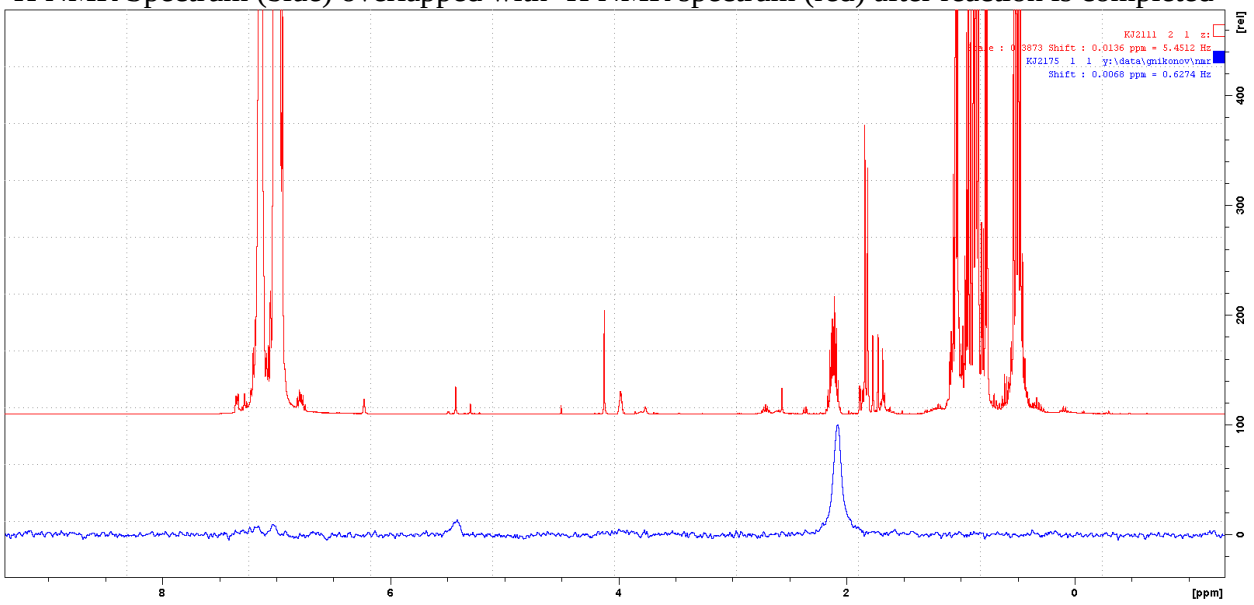



$^{29}$Si INEPT+ NMR Spectrum



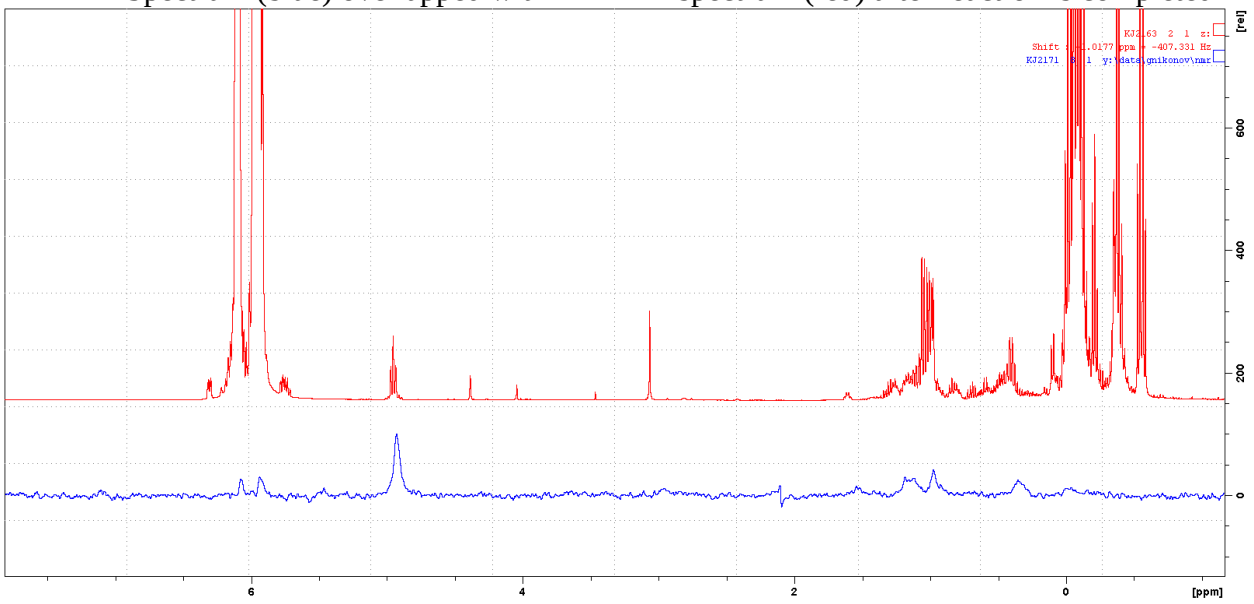
*Stoichiometric reaction of **2** with 2-methyl-1-phenylpropene and $DSiEt_3$*

$^2H$ NMR Spectrum (blue) overlapped with $^1H$ NMR spectrum (red) after reaction is completed




*Stoichiometric reaction of **6** with 3-hexyne and $DSiEt_3$*

$^2H$ NMR Spectrum (blue) overlapped with $^1H$ NMR spectrum (red) after reaction is completed



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