Supplementary Information (SI) for Dalton Transactions.

Supplementary Information for

Well-defined Pt(0) heterogeneous hydrosilylation catalysts supported by a surface bound phosphenium ligand

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General considerations

All manipulations were performed in a nitrogen or argon filled inert atmosphere glovebox or on a Schlenk line using standard techniques. Grafting reactions were performed under high vacuum in double Schlenk flasks using standard techniques.[1] Benzene-*d₆*, toluene-*d₈*, and chloroform-*d₁* were purchased from Cambridge Isotope Laboratories. Benzene-*d₆* and toluene-*d₈*, were dried over sodium and benzophenone, degassed using three freeze, pump, and thaw cycles, then distilled under high vacuum and stored over activated 3 or 4 Å molecular sieves in an inert atmosphere glovebox. Chloroform-*d₁* was dried over CaH_2, degassed using three freeze, pump, thaw cycles, then distilled under high vacuum and stored over activated 3 or 4 Å molecular sieves in an inert atmosphere glovebox. Anhydrous solvents were purchased from Sigma Aldrich and stored over 3 or 4 Å molecular sieves and degassed prior to use. Toluene for grafting reactions was stored over sodium and benzophenone, and degassed using three freeze, pump, and thaw cycles prior to use. 1-octyne was dried over calcium hydride, distilled under vacuum and stored over 3 Å molecular sieves in a nitrogen filled glovebox prior to use. Ethylenebis(triphenylphosphine)platinum(0) and Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (2 % Pt in xylene) (Karstedt's catalyst) were purchased from Sigma Aldrich and used without further purification. DippNHPCl (**2b**) was synthesized using a reported procedure[2] then sublimed under vacuum at 150 °C prior to use. DippNHPOTf[2] and $[^iPr_3Si][ASO]$[3] were synthesized using reported procedures.

Solution NMR spectroscopy was performed at the Iowa State University Chemical Instrumentation Facility on a Varian MR-400, a Bruker Avance NEO 400 MHz system with LN2-cooled broadband Prodigy Probe, or a Bruker Avance III Spectrometer. Solution ^1H NMR spectra were referenced to solvent residual signal. Solution ^{31}P NMR spectra were referenced to an external standard of 85 % H_3PO_4 (0.0 ppm). Solution ^{19}F NMR spectra were referenced to an internal standard of hexafluorobenzene (-163.9 ppm).

Solid-state NMR (SSNMR) experiments were performed using a Bruker Avance NEO 600 MHz NMR spectrometer equipped with a 4 mm triple-resonance magic-angle spinning (MAS) probe using standard Bruker 4 mm zirconia MAS rotors and Kel-F caps. Chemical shifts were indirectly referenced using an adamantane (^1H chemical shift = 1.82 ppm) and the universal shielding scale.[4] ^{31}P SSNMR spectra were acquired using a Bloch decay sequence with a 1.7 μs excitation pulse and a relaxation delay of 2 s; 20k, 32k, and 35k scans were acquired for **1**, **2**, and **3**, respectively. Solid state $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ cross-polarization (CP)MAS NMR spectra were recorded with 2 and 5 ms contact times, respectively, with 2 s relaxation delays. Fast MAS ^1H SSNMR experiments were performed using a Bruker AVANCE III 600 MHz NMR spectrometer equipped with a 1.6 mm triple-resonance Varian probe. The experiments used a 40 kHz spinning frequency, a rotor-synchronized Hahn echo sequence with a ^1H radiofrequency power of 100 kHz, and a 1 s relaxation delay. A ^{31}P NMR spectrum was also acquired under fast MAS conditions using the same system and spinning frequency. The spectrum was acquired using a Bloch decay sequence with a 4 μs excitation pulse, a 0.5 s recycle delay and 163840 scans.

Scanning electron microscopy energy-dispersive X-ray spectroscopy (SEM-EDS) was performed at the Ames National Laboratory Sensitive Instrument Facility (SIF) on a FEI Teneo LoVac Field-Emission Scanning Electron Microscope (FE-SEM) with an Everhart–Thornley detector (ETD).

Fourier transform infrared spectroscopy was performed on Bruker Alpha II spectrometer with a transmission module in an argon filled glovebox. Samples were pressed into self-supported 7 mm pellets and analyzed directly. Elemental analyses were performed on an Agilent 5800 ICP-OES spectrometer. No singular digestion method was effective for all the materials in this study, therefore the method(s) that provided the highest and precise data are reported in the synthetic sections.

Characterization data summary tables

Table S1. Summary of the ^{31}P SSNMR data and chemical shift anisotropy simulation parameters.[a]

Material	**Assign.**	**δ_{iso} (ppm)**	**δ_{11} (ppm)**	**δ_{22} (ppm)**	**δ_{33} (ppm)**	**Ω (ppm)**	**κ**
1	DippNH**P**	273	554	196	68	486	-0.47
2	(DippNH**P)**Pt	294	517	254	110	408	-0.29
	Pt(**P**Ph$_3$)$_2$	45	ND	ND	ND	<100	ND
3	(DippNH**P)**Pt	277	566	174	91	474	-0.65
4	Pt(**P**Ph$_3$)$_2$	14	ND	ND	ND	ND	ND
	Pt(**P**Ph$_3$)$_2$	21	ND	ND	ND	ND	ND

a. SSNMR spectra shown in the main text (**Figure 2**) or ESI (Figure S12) for **4**. ND = not determined.

Table S2. Summary of the SSNMR chemical shifts (ppm) and assignments.[a]

Material	^{1}H	Assign.	^{13}C	Assign.	^{29}Si	Assign.
1	7.2	*m*-Ar**H**	133 – 115	Ar + $\mathrm{C(}\mathbf{C}\mathrm{F_3)_3}$	ND	ND
	7.0	*p*-Ar**H**	59	$\mathrm{N}\mathbf{C}\mathrm{H_2}$		
	4.5	$\mathrm{NC}\mathbf{H_2}$	29	$\mathbf{C}\mathrm{H(CH_3)_2}$		
	2.9	$\mathrm{C}\mathbf{H}\mathrm{(CH_3)_2}$	24	$\mathrm{CH(}\mathbf{C}\mathrm{H_3)_2}$		
	2.0	$^{i}\mathrm{Pr_3Si}$	22	$\mathrm{CH(}\mathbf{C}\mathrm{H_3)_2}$		
	1.3	$\mathrm{CH(C}\mathbf{H_3}\mathrm{)_2}$				
	1.1	$\mathrm{CH(C}\mathbf{H_3}\mathrm{)_2}$				
	0.9	$^{i}\mathrm{Pr_3Si}$				
2	6.8	Ar**H**	135 – 117	Ar	ND	ND
	3.9	$\mathrm{NC}\mathbf{H_2}$	54	$\mathrm{N}\mathbf{C}\mathrm{H_2}$		
	3.2	$\mathrm{C}\mathbf{H}\mathrm{(CH_3)_2}$	29	$\mathbf{C}\mathrm{H(CH_3)_2}$		
	2.0	$^{i}\mathrm{Pr_3Si}$	24	$\mathrm{CH(}\mathbf{C}\mathrm{H_3)_2}$		
	0.9	$\mathrm{CH(C}\mathbf{H_3}\mathrm{)_2}$				
	0.8	$^{i}\mathrm{Pr_3Si}$				
3	7.1	Ar	146	Ar	3	dvtms
	4.0	$\mathrm{SiC}\mathbf{H}\mathrm{=C}\mathbf{H_2}$	132 – 117	Ar + $\mathrm{C(}\mathbf{C}\mathrm{F_3)_3}$		
	3.0	$\mathrm{NC}\mathbf{H_2}$ + $\mathrm{C}\mathbf{H}\mathrm{(CH_3)_2}$	79	$\mathrm{C(}\mathbf{C}\mathrm{F_3)_3}$		
	1.3	$\mathrm{CH(C}\mathbf{H_3}\mathrm{)_2}$	75 – 52	$\mathrm{N}\mathbf{C}\mathrm{H_2}$ + $\mathrm{Si}\mathbf{C}\mathrm{H=}\mathbf{C}\mathrm{H_2}$		
	0.9	$^{i}\mathrm{Pr_3Si}$	29	$\mathbf{C}\mathrm{H(CH_3)_2}$		
	0.0	$\mathrm{Si(C}\mathbf{H}\mathrm{_3)_2}$	23	$\mathrm{CH(}\mathbf{C}\mathrm{H_3)_2}$		
	-0.7	$\mathrm{Si(C}\mathbf{H}\mathrm{_3)_2}$	-2	$\mathrm{Si(}\mathbf{C}\mathrm{H_3)_2}$		
			-5	$\mathrm{Si(}\mathbf{C}\mathrm{H_3)_2}$		
4	6.9	Ph	143 – 116	Ph	ND	ND
	1.0	$^{i}\mathrm{Pr_3Si}$				
5	6.1	$\mathrm{SiC}\mathbf{H}\mathrm{=C}\mathbf{H_2}$	3	$\mathrm{Si(}\mathbf{C}\mathrm{H_3)_2}$	6	dvtms
	1.0	$^{i}\mathrm{Pr_3Si}$				
	-0.3	$\mathrm{Si(C}\mathbf{H}\mathrm{_3)_2}$				

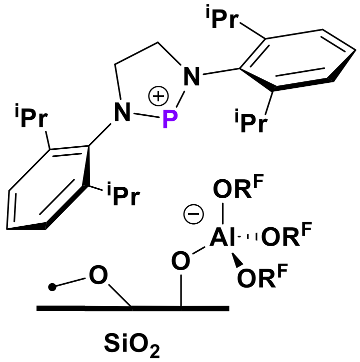
a. Signals for unreacted $^{i}\mathrm{Pr_3Si}$- and bulk SiO2 signals are not included in the ^{13}C (15 and 12 ppm) or ^{29}Si (70, 14 and -105 ppm) (CP)MAS SSNMR data table. ND = not determined.

Table S3. Summary of the elemental analyses in this study.^{a}

Material	% mass			mmol/g			P:Pt mol ratio	L:Pt^b
	Pt	P	Al	Pt	P	Al		
1	0.00	0.330 (5)	0.588 (3)	0.000	0.107 (2)	0.218 (1)	NA	NA
2	1.09 (9)	0.52 (1)	0.58 (2)	0.056 (5)	0.168 (4)	0.216 (7)	3.0 (3)	1.9 (2) (PPh$_3$)
3	1.45 (5)	0.27 (1)	0.58 (2)	0.075 (2)	0.089 (5)	0.214 (8)	1.2 (1)	1.07 (7) (dvtms)
4	0.31 (2)	0.105 (9)	0.56 (2)	0.016 (1)	0.034 (3)	0.209 (6)	2.2 (3)	ND
5	0.28 (3)	0.00	0.55 (3)	0.014 (2)	0.00	0.21 (1)	NA	ND

a. Determined by ICP-OES, see general considerations and synthetic details for more information. Average of 2-4 runs. Absolute errors are indicated in parentheses. b. Determined by desorption of the ligand (noted in parentheses) followed by ^{1}H NMR spectroscopic analyses of the washings in the presence of an internal standard, see the synthetic details for more information. NA = not applicable. ND = not determined.

Syntheses, SSNMR and FTIR spectra



[DippNHP][ASO] (**1**): In a double Schlenk flask, [^{i}Pr$_3$Si][ASO] (1.00 g, 0.2 mmol of iPr3Si$^+$) and DippNHPCl (100. mg, 0.22 mmol) were combined on one side of the flask, along with small stir bar in an argon filled glovebox. The flask was sealed, removed from the glovebox, and connected to a high vacuum line. Under high vacuum, toluene (20 mL) was condensed over the solids at 77 K. The flask was sealed under static vacuum and the solution was allowed to warm up to 0 °C while stirring (100 – 200 rpm). The reaction was stirred at 0 °C for one hour. The solution was filtered to the opposite side of the double

Schlenk. The toluene was vacuum distilled back over the solid at 77 K, warmed to room temperature, and stirred for 2 minutes followed by filtration to wash the solid. The solid was washed two more times using this technique. After the final wash, the solid was dried under high vacuum for 1 hour at 0 °C resulting in cream-colored solid **1**. Table S1 – S3 contain summaries of the characterization data for **1**. Figure S1 – S3, Figure S16, and Figure 2 in the main text contain FTIR and SSNMR spectra of **1**.

The formation of $^{i}Pr_3SiCl$ was confirmed by performing the reaction on a 30 mg scale of $[^{i}Pr_3Si][ASO]$ in a PTFE – valved NMR tube and monitoring the reaction by ^1H NMR spectroscopy in the presence of hexamethylbenzene as an internal standard. The reaction revealed that 0.062 (±0.001) mmol/g of $^{i}Pr_3SiCl$ is released during the reaction for **1** (average of 2 grafting reactions) which is less than the 0.107 (±0.002) mmol/g of P found on **1** via ICP-OES, suggesting that some $^{i}Pr_3SiCl$ may physisorb to the surface. The physisorbed $^{i}Pr_3SiCl$ was confirmed by reacting the support with pyridine (1 – 2 drops), resulting in a total of 0.108 (±0.001) mmol/g of $^{i}Pr_3SiCl$ forms in the synthesis of **1** which is in good agreement with the ICP-OES results. Representative NMR spectra of the NMR tube reactions are provided in Figure S21. ICP samples of **1** were prepared by digesting ~20 mg in nitric acid (20 %, 2 mL) for 1 month followed by decantation followed by dilution or in hydrofluoric acid (48 %, 0.5 mL) for 24 hours followed by addition of aqua regia (2 mL) which was allowed to react for another 24 hours then dilution to 14 mL prior to analyses (Table S3).

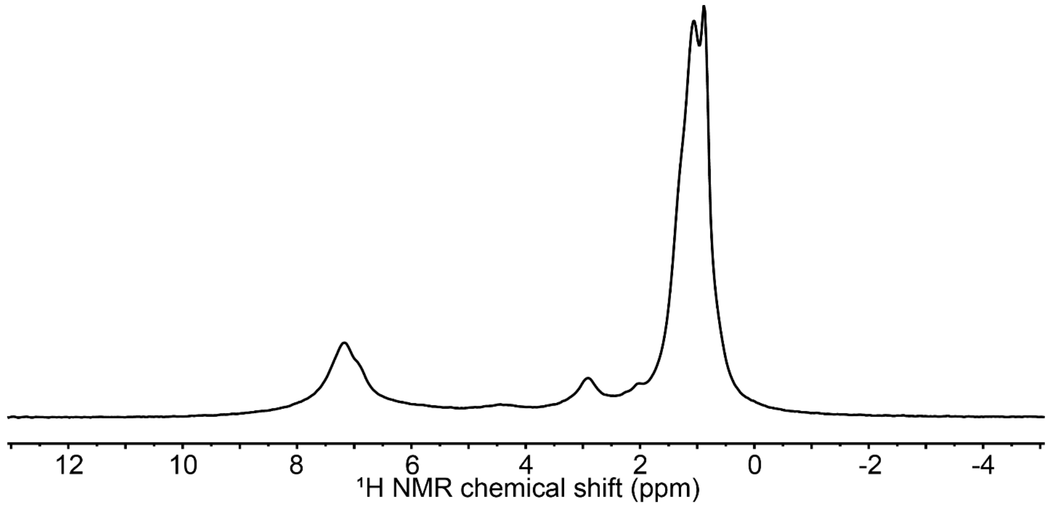


Figure S1. ^1H Hahn-echo SSNMR spectrum of **1** spinning at 40 kHz (64 scans).

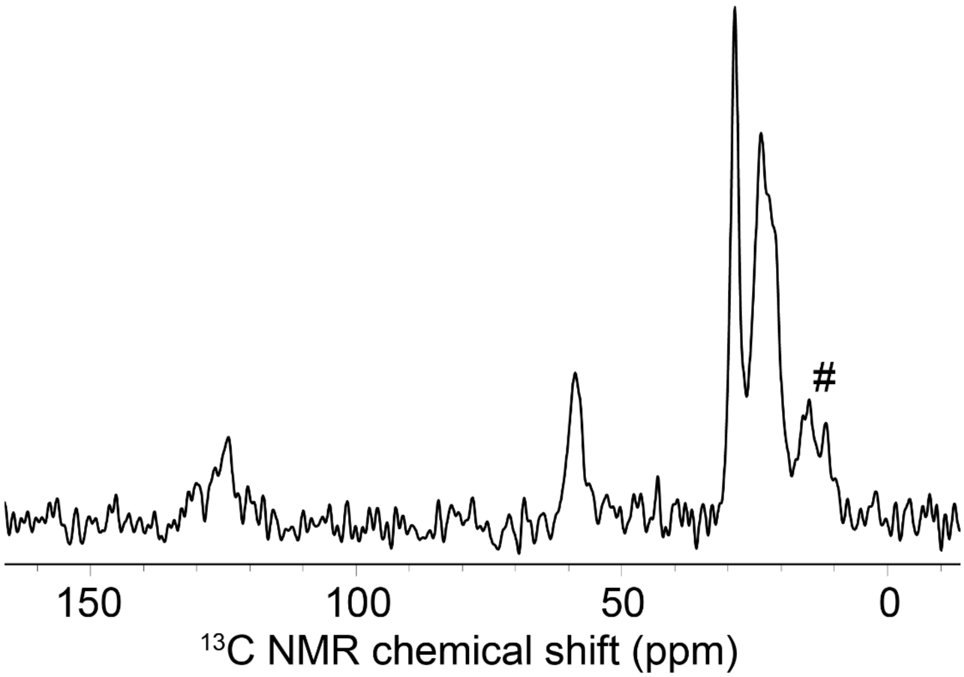


Figure S2. ^{13}C (CP)MAS SSNMR spectrum of **1** spinning at 10 kHz (40k scans). # denotes unreacted $^{i}Pr_3Si$- signals.

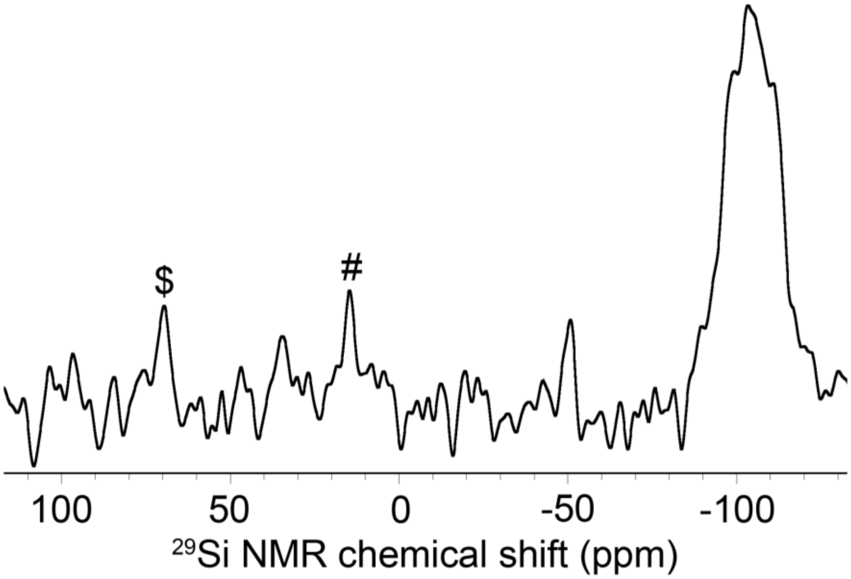
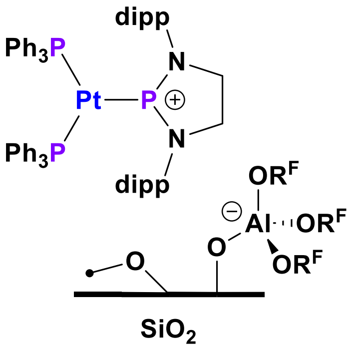


Figure S3. ^{29}Si (CP)MAS SSNMR spectrum of **1** spinning at 8 kHz (80k scans). The $ and # denote unreacted [$^{i}Pr_3Si$] and $^{i}Pr_3Si$-O signals, respectively. The broad signal at ~-105 ppm is bulk SiO_2.



[DippNHPPt(PPh_3)$_2$][ASO] (**2**): **1** (400 mg, 43 µmol P) and (PPh_3)$_2$Pt(C_2H_4) (43 mg, 58 µmol) were combined in a double Schlenk flask along with a small stir bar. The flask was sealed, removed from the glovebox, and connected to a high vacuum line. Under high vacuum, toluene (10 mL) was condensed over the solids at 77 K. The flask was sealed under static vacuum and the solution was allowed to warm up to room temperature while stirring (100 – 200 rpm). Effervescence was observed during the reaction indicating that ethylene was released. The reaction was stirred at room temperature for 30 minutes. The solution was filtered to the opposite side of the double Schlenk. The toluene was vacuum distilled back over the solid at 77 K, warmed to room temperature, and stirred for 2 minutes followed by filtration to wash the solid. The solid was washed two more times using this technique. After the final wash, the solid was dried under high vacuum for 1 hour resulting in bright yellow **2**. Tables S1 – S3 contain summaries of the characterization data for **2**. Figure S4 – S5, Figure S16, and Figure 2 in the main text contain FTIR and SSNMR spectra of **2**. ICP samples were prepared by digesting ~20 mg of **2** in hydrofluoric acid (48 %, 0.5 mL) for 1 week followed by decantation, addition of nitric acid (70 %, 0.5 mL) and dilution to 14 mL. The resulting residues were further digested using Aqua Regia (2 mL) for 3 days followed by dilution to 14 mL. The process was repeated and the results of all 4 digestions were added together (Table S3).

Surface PPh_3 quantification: In an NMR tube, **2** (30 mg, 2.25 µmol Pt) was combined with hexamethylbenzene (internal standard) and suspended in C_6D_6 (0.5 mL). At room temperature, PMe_3 (20 µL, 0.2 mmol) was added and allowed to react overnight. The PPh_3 released was quantified by solution ^{1}H NMR against the internal standard (see Figure S22 for a representative spectrum). The average of two experiments was 0.106 (±0.003) mmol/g of PPh_3.

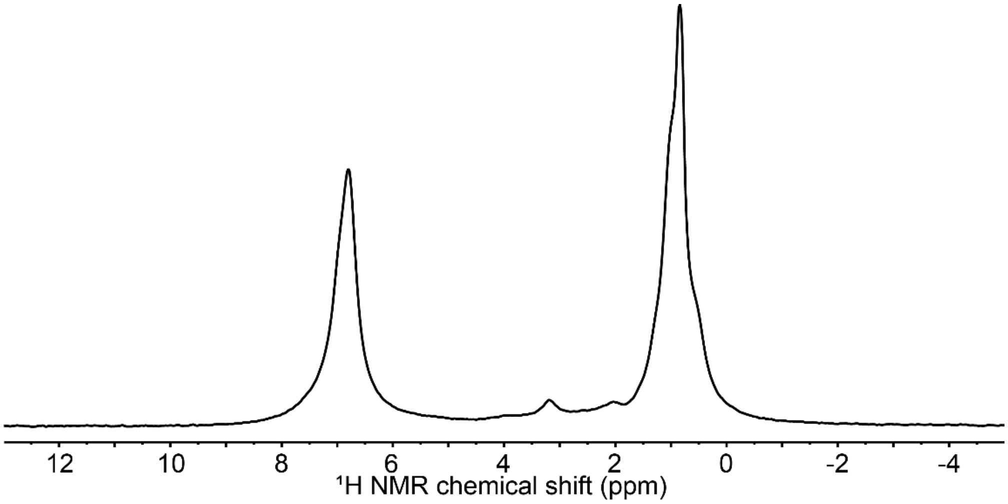


Figure S4. ^{1}H Hahn-echo SSNMR spectrum of **2** spinning at 10 kHz (16 scans).

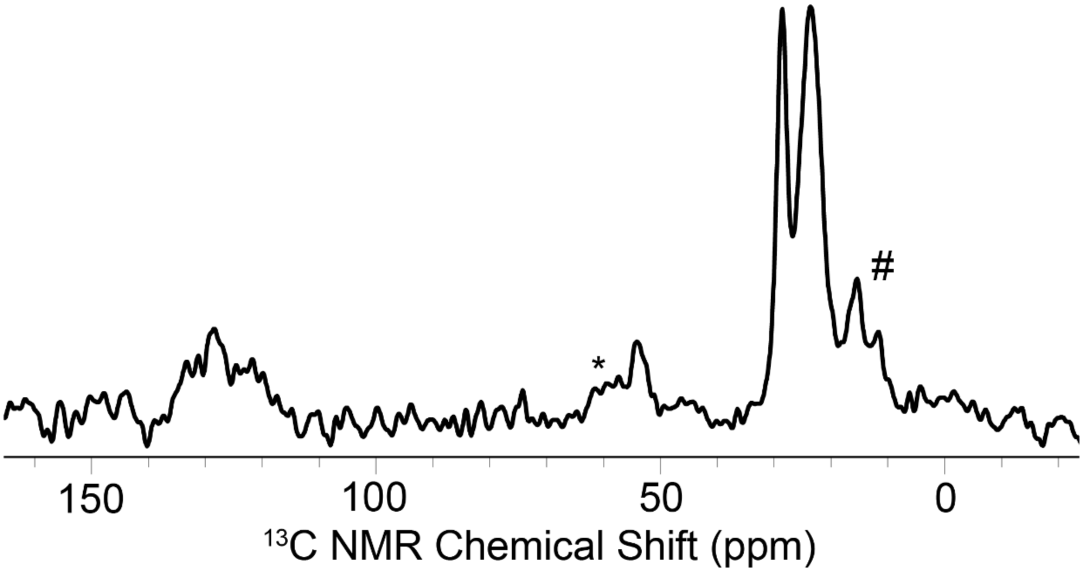
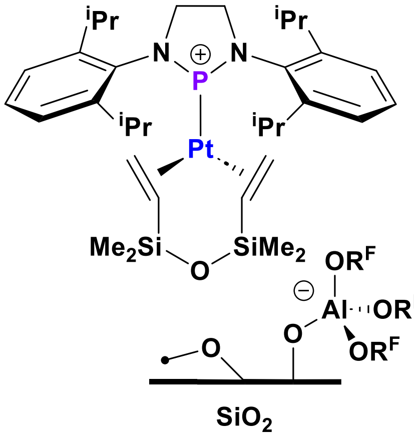


Figure S5. ^{13}C (CP)MAS SSNMR spectrum of **2** spinning at 10 kHz (40k scans). # denotes unreacted ^{i}Pr$_3$Si- signals. * denotes spinning sideband.



[DippNHPPt(dvtms)][ASO] (**3**): **1** (400 mg, 43 μmol P) was added to a Schlenk bomb along with a small stir bar. The flask was sealed, removed from the glovebox, and connected to a high vacuum line. Under high vacuum, toluene (2 mL) was condensed over solid **1** at 77 K. In a Schlenk flask, Karstedt's catalyst solution (2 % Pt in xylene, 640 mg, ~66 μmol) was diluted to 8 mL with toluene. The slurry of **1** in toluene was cooled to -40 °C and the diluted Karstedt's catalyst solution was added dropwise under argon flow while stirring (200 rpm) via syringe or cannula. The flask was sealed under argon and the reaction was allowed to warm up to 0 °C and stirred for 2 hours. After the reaction, the solution was removed via decantation with a cannula under argon flow. Then, fresh toluene (5 mL) was vacuum distilled over the solid at 77 K, warmed to room temperature, and stirred for 2 minutes followed by decantation to wash the solid. The solid was washed two more times using this technique. After the final wash, the solid was dried under high vacuum for 1 hour at 0 °C resulting in pale yellow solid **3**. Table S1 – S3 contain summaries of the characterization data for **3**. Figure S6 – S8, Figure S16, and Figure 2 of the main text contain FTIR and SSNMR spectra of **3**. ICP samples of **3** were prepared by digesting ~20 mg in nitric acid (20 %, 2 mL) for 1 month followed by decantation followed by dilution or in aqua regia (2 mL) for 3 days followed by dilution prior to analyses (Table S3). Both methods produced consistent Pt and Al concentrations, however the aqua regia failed to dissolve the P under the above conditions. Attempts to dissolute the Pt and P in the presence of hydrofluoric acid as described in the digestion methods for the other materials resulted in significantly lower values for both elements.

Surface 1,3-Divinyltetramethyldisiloxane (dvtms) quantification: In a PTFE – valved NMR tube, **3** (30 mg, 2.25 μmol Pt) was combined with PPh_3 (5 mg, 19 μmol) and hexamethylbenzene (internal standard). The solids were dissolved or suspended in C_6D_6 (0.5 mL) at room temperature and allowed to react overnight. The dvtms released was quantified by solution ^{1}H NMR against the internal standard (see Figure S24 for a representative spectrum). The average of two experiments was 0.080 (±0.003) mmol/g of dvtms.

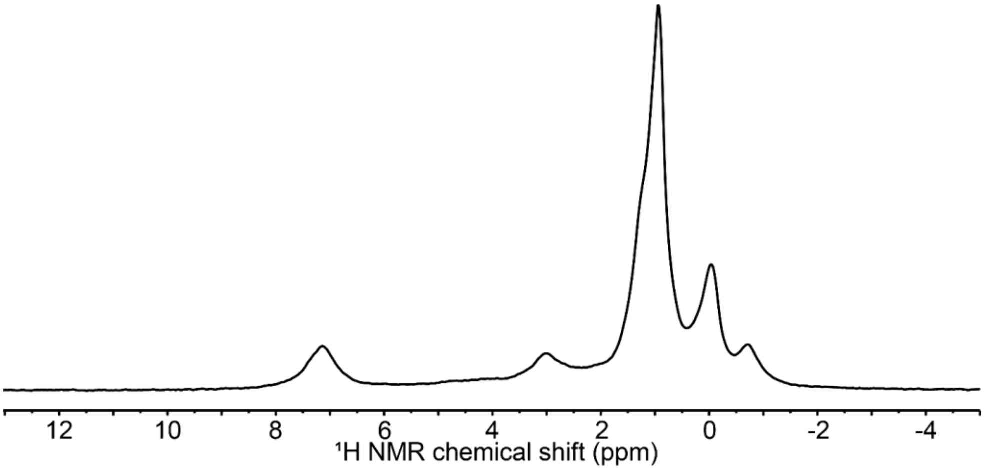


Figure S6. ^{1}H Hahn-echo SSNMR spectrum of **3** spinning at 10 kHz (16 scans).

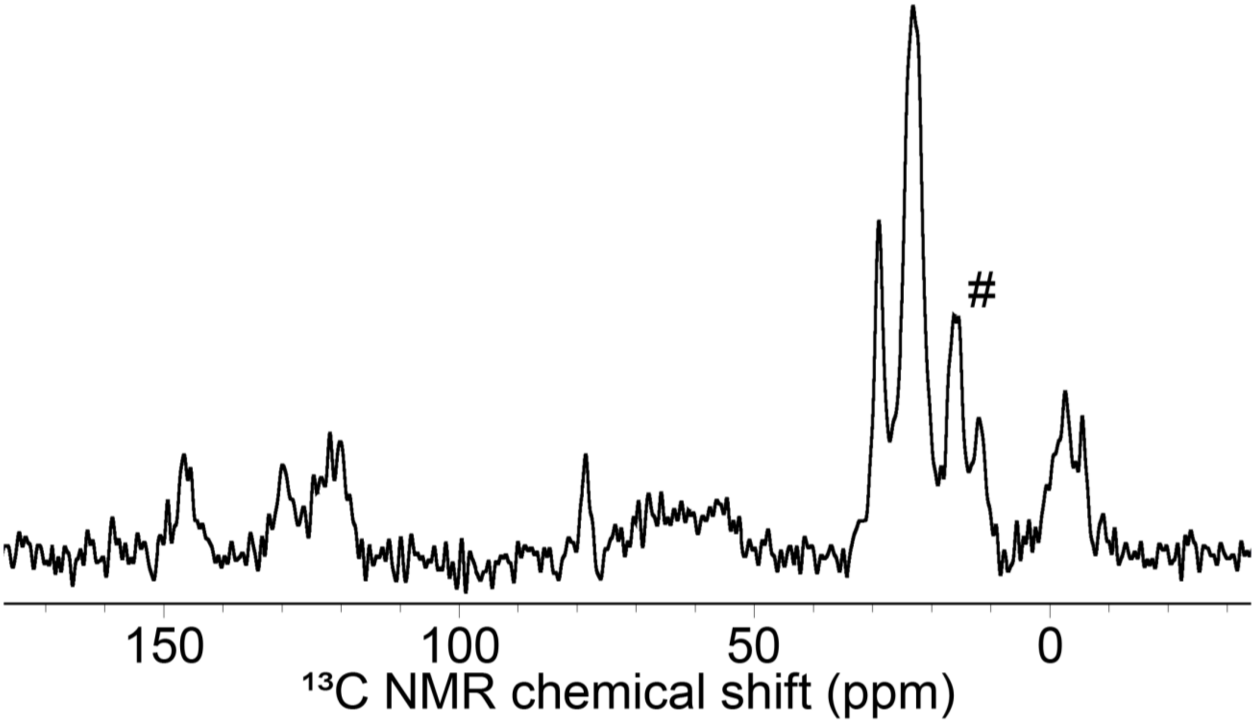


Figure S7. ^{13}C (CP)MAS SSNMR spectrum of **3** spinning at 10 kHz (77k scans). # denotes unreacted $^{i}Pr_3Si$- signals.

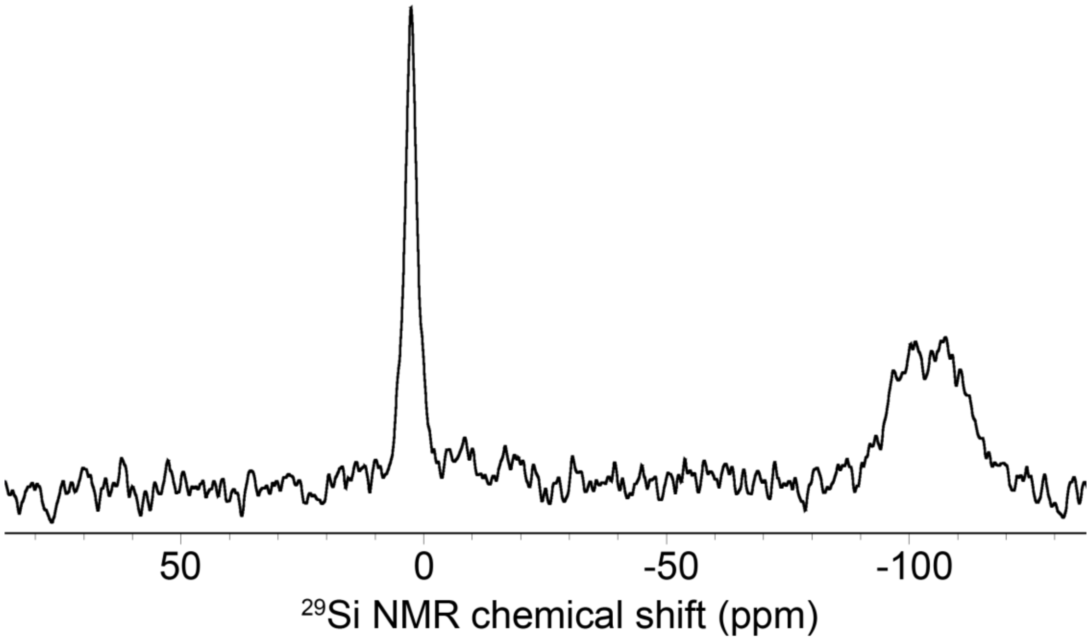


Figure S8. ^{29}Si (CP)MAS SSNMR spectrum of **3** spinning at 8 kHz (80k scans). The broad signal at ~-105 ppm is bulk SiO_2.

[$^{i}Pr_3Si$][ASO] + $(PPh_3)_2Pt(C_2H_4)$ (**4**): [$^{i}Pr_3Si$][ASO] (200 mg, ~40 μmol [$^{i}Pr_3Si$]) and $(PPh_3)_2Pt(C_2H_4)$ (22.5 mg, 30 μmol) were combined in a swivel frit along with a small stir bar. The flask was sealed, removed from the glovebox, and connected to a high vacuum line. Under high vacuum, toluene (4 mL) was condensed over the solids at 77 K. The flask was sealed under static vacuum and the solution was allowed to warm up to room temperature while stirring (100 – 200 rpm). The reaction was stirred at room temperature for 30 minutes. The solution was filtered to the opposite side of the swivel frit. The toluene was vacuum distilled back over the solid at 77 K, warmed to room temperature, and stirred for 2 minutes followed by filtration to wash the solid. The solid was washed two more times using this technique. After the final wash, the solid was dried under high vacuum for 1 hour resulting in pale yellow **4**. Table S1 – S3 contain summaries of the characterization data for **4**. Figure S9 – S12 contain SSNMR spectra of **4**. ICP samples of **4** were prepared by digesting ~20 mg in a mixture of hydrofluoric acid (48 %, 0.5 mL) and aqua regia (2 mL) overnight followed by dilution or in hydrofluoric acid (48 %, 0.5 mL) for 24 hours followed by addition of aqua regia (2 mL) which was allowed to react for another 24 hours then dilution to 14 mL prior to analyses (Table S3).

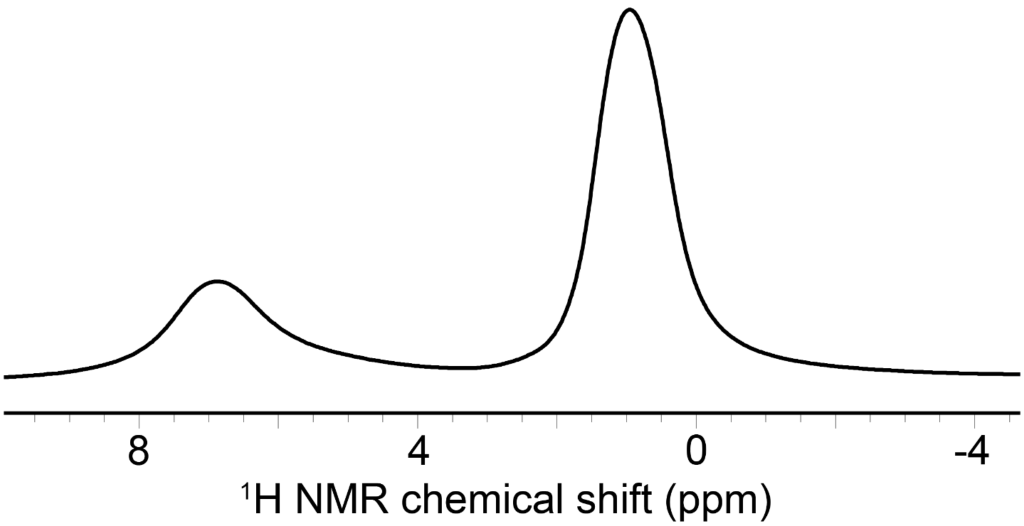


Figure S9. ^{1}H SSNMR spectrum of **4** spinning at 10 kHz (16 scans).

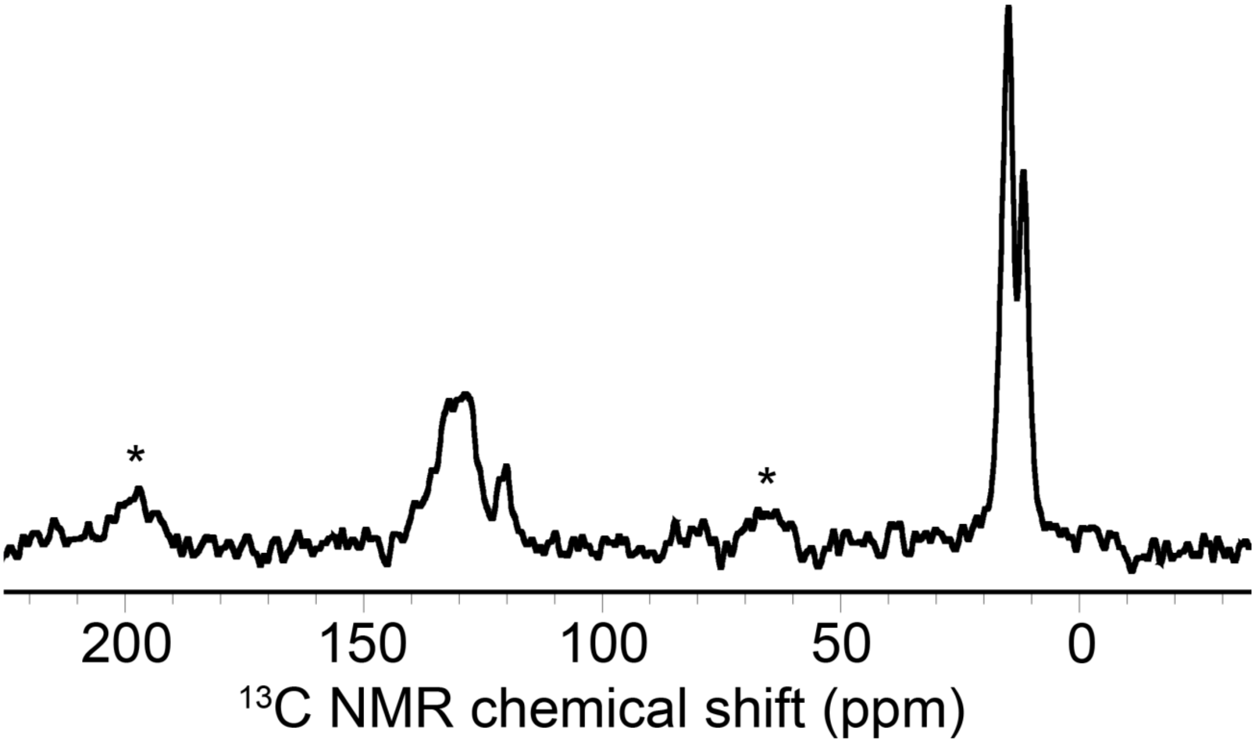


Figure S10. ^{13}C (CP)MAS SSNMR spectrum of **4** spinning at 10 kHz (40k scans).

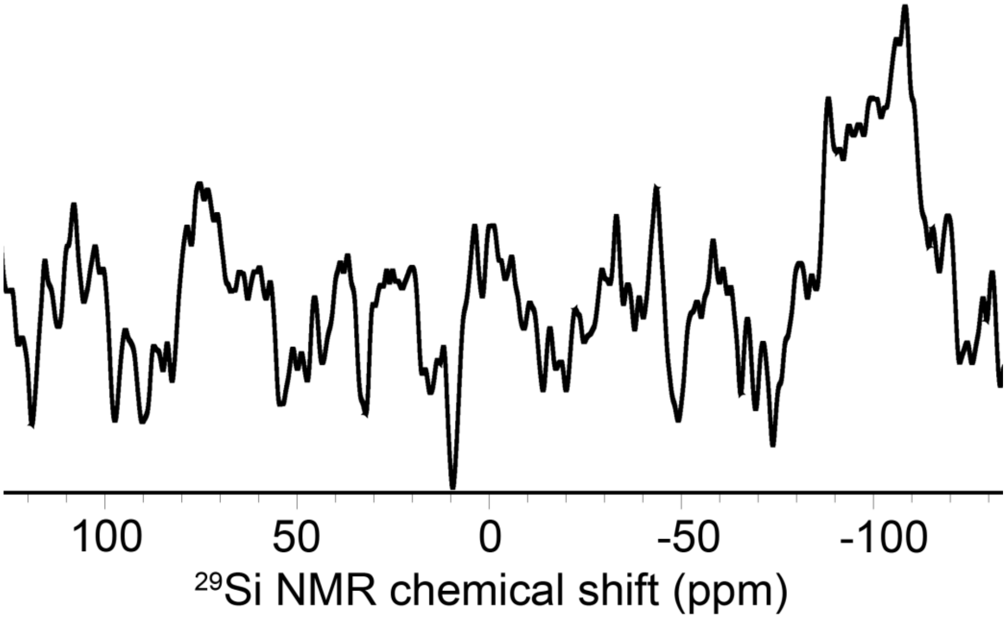


Figure S11. ^{29}Si (CP)MAS SSNMR spectrum of **4** spinning at 8 kHz (72k scans). The broad signal at ~-105 ppm is bulk SiO_2.

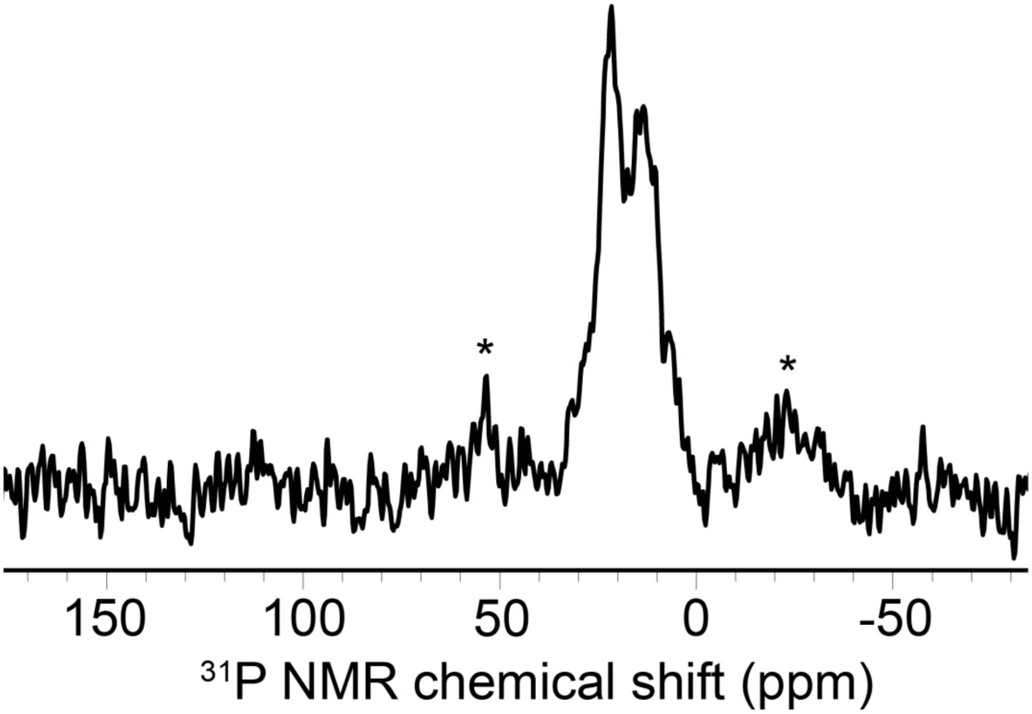


Figure S12. ^{31}P SSNMR spectrum of **4** spinning at 10 kHz (2200 scans).

[^{i}Pr$_3$Si][ASO] + Karstedt's catalyst (**5**): [^{i}Pr$_3$Si][ASO] (400 mg, ~80 μmol [^{i}Pr$_3$Si]) was added to a Schlenk bomb along with a small stir bar. The flask was sealed, removed from the glovebox, and connected to a high vacuum line. Under high vacuum, toluene (2 mL) was condensed over solid **1** at 77 K. In a Schlenk flask, Karstedt's catalyst solution (2 % Pt in xylene, 640 mg, ~66 μmol) was diluted to 8 mL with toluene. The slurry of 1 in toluene was cooled to -40 °C and the diluted Karstedt's catalyst solution was added dropwise under argon flow while stirring (200 rpm) via syringe or cannula. The flask was sealed under argon and the reaction was allowed to warm up to 0 °C and stirred for 2 hours. After the reaction, the solution was removed via decantation with a cannula under argon flow. Then, fresh toluene (5 mL) was vacuum distilled over the solid at 77 K, warmed to room temperature, and stirred for 2 minutes followed by decantation to wash the solid. The solid was washed two more times using this technique. After the final wash, the solid was dried under high vacuum for 1 hour at 0 °C resulting in pale yellow solid **5**. Table S1 – S3 contain summaries of the characterization data for **5**. Figure S13 – S15 contain FTIR and SSNMR spectra of **5**. ICP samples of **5** were prepared by digesting ~20 mg in a mixture of hydrofluoric acid (48 %, 0.5 mL) and aqua regia (2 mL) overnight followed by dilution or in hydrofluoric acid (48 %, 0.5 mL) for 24 hours followed by addition of aqua regia (2 mL) which was allowed to react for another 24 hours then dilution to 14 mL prior to analyses (Table S3).

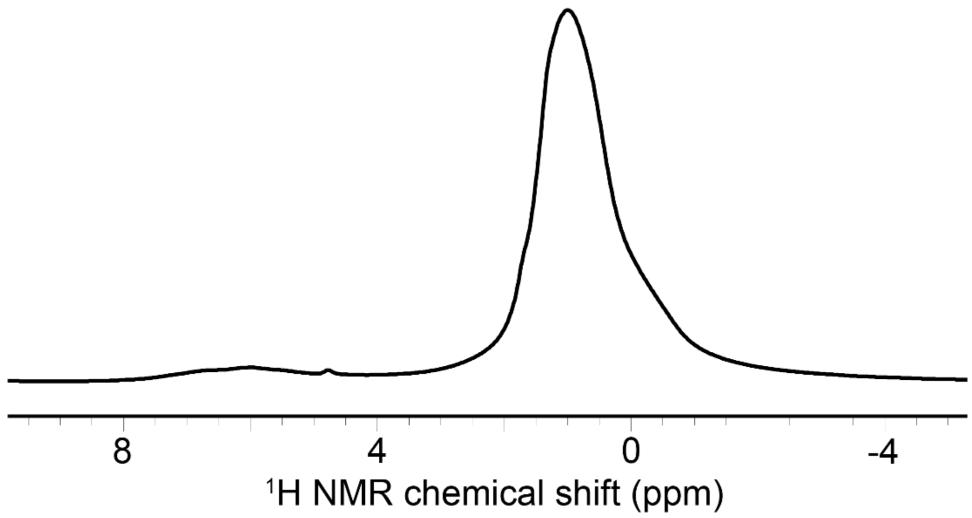


Figure S13. ^{1}H SSNMR spectrum of **5** spinning at 10 kHz (16 scans).

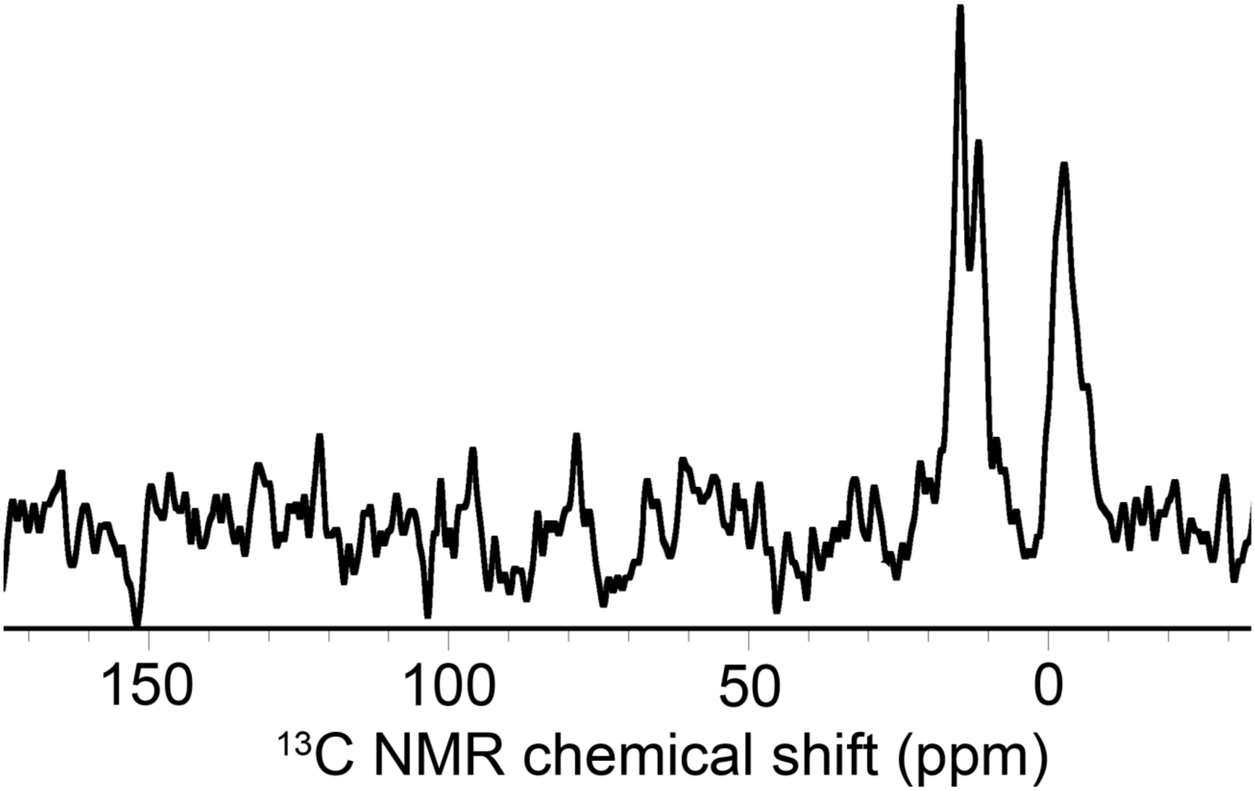


Figure S14. ^{13}C (CP)MAS SSNMR spectrum of **5** spinning at 10 kHz (40k scans).

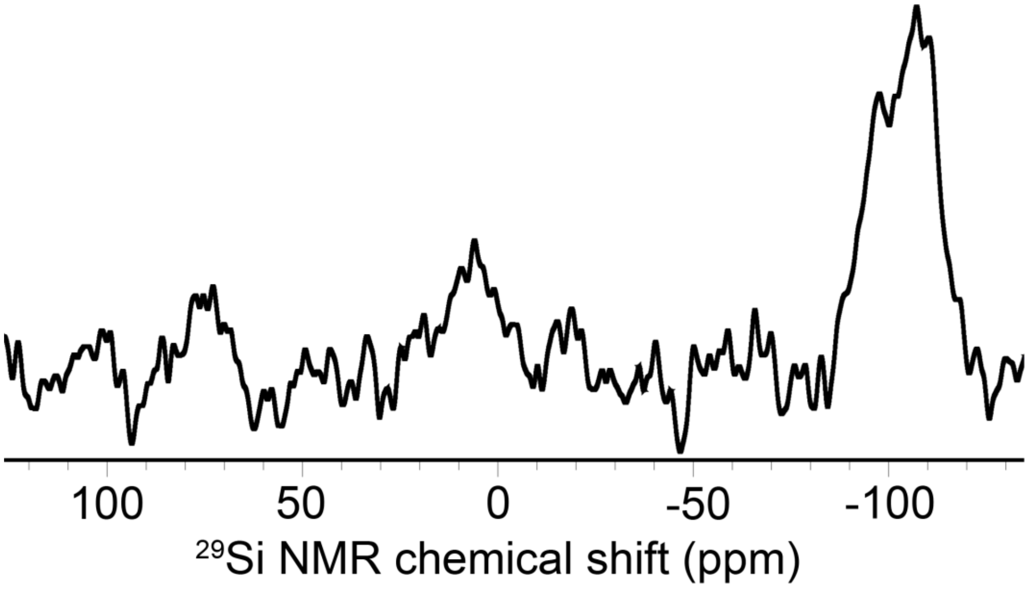


Figure S15. ^{29}Si (CP)MAS SSNMR spectrum of **5** spinning at 8 kHz (120k scans). The broad signal at ~-105 ppm is bulk SiO_2.

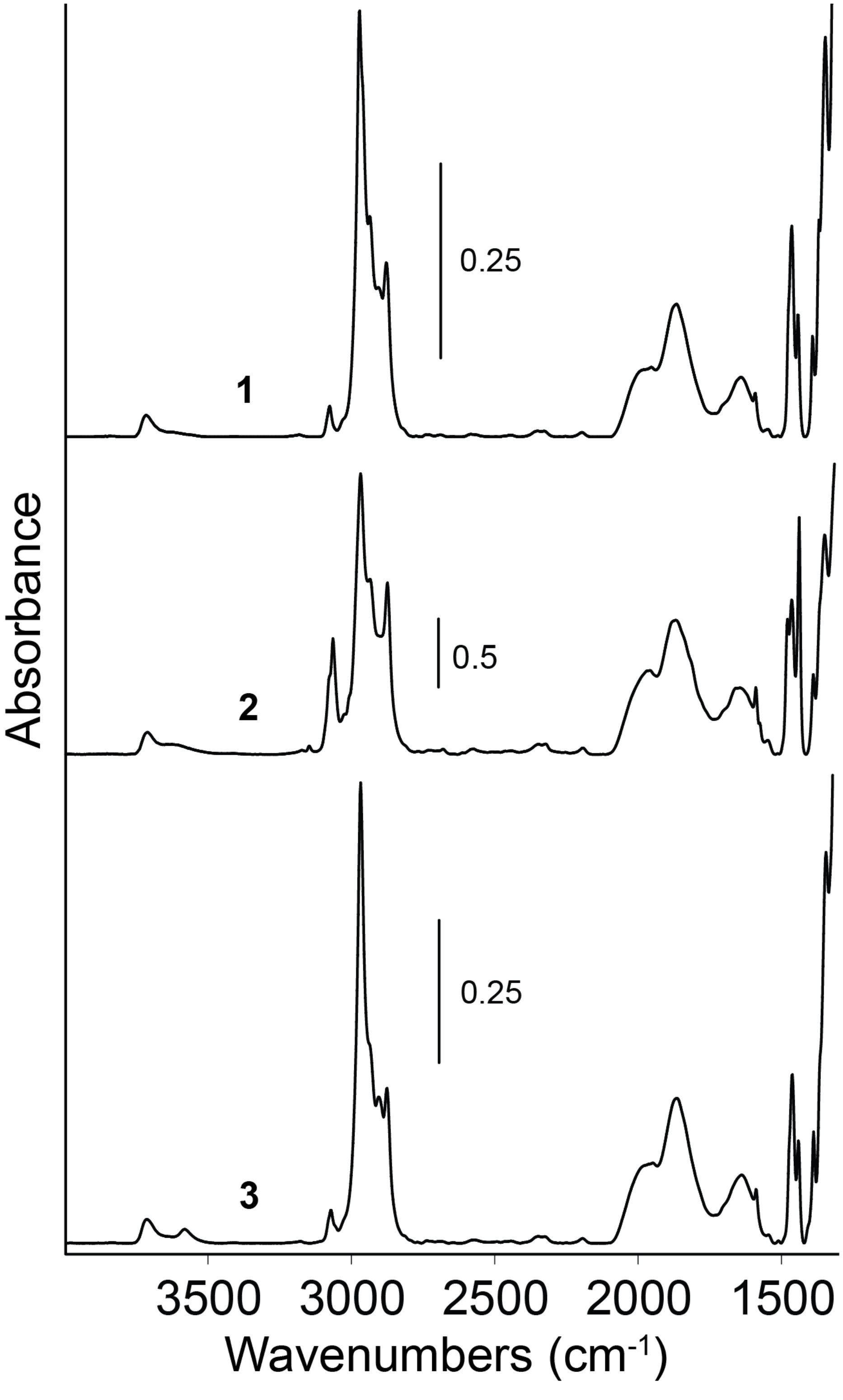
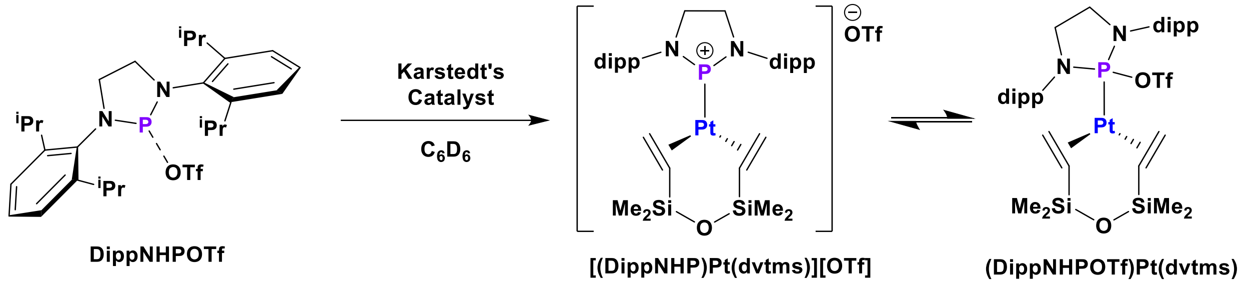


Figure S16. FTIR spectra of **1** (top), **2** (middle) and **3** (bottom).



Reaction of DippNHPOTf with Karstedt's Catalyst: In a teflon-valved NMR tube, DippNHPOTf (12.5 mg, 22.4 μmol) was dissolved in benzene-*d*₆ (0.5 mL) then Karstedt's catalyst (174 mg, 18 umol) was added slowly dropwise. The reaction was shaken then analyzed by solution NMR spectroscopy. The proposed structures of the two major species are shown in the scheme above. $^{31}P\{^{1}H\}$ NMR (benzene-*d*₆, 161.9 MHz): 272.2 (s/d, $^{1}J_{PtP}$ = 5850 Hz, (DippNH**P**$^{+}$)Pt), and 121.5 ppm (s/d, $^{1}J_{PtP}$ = 5350 Hz, (DippNH**P**OTf)Pt)) ppm.

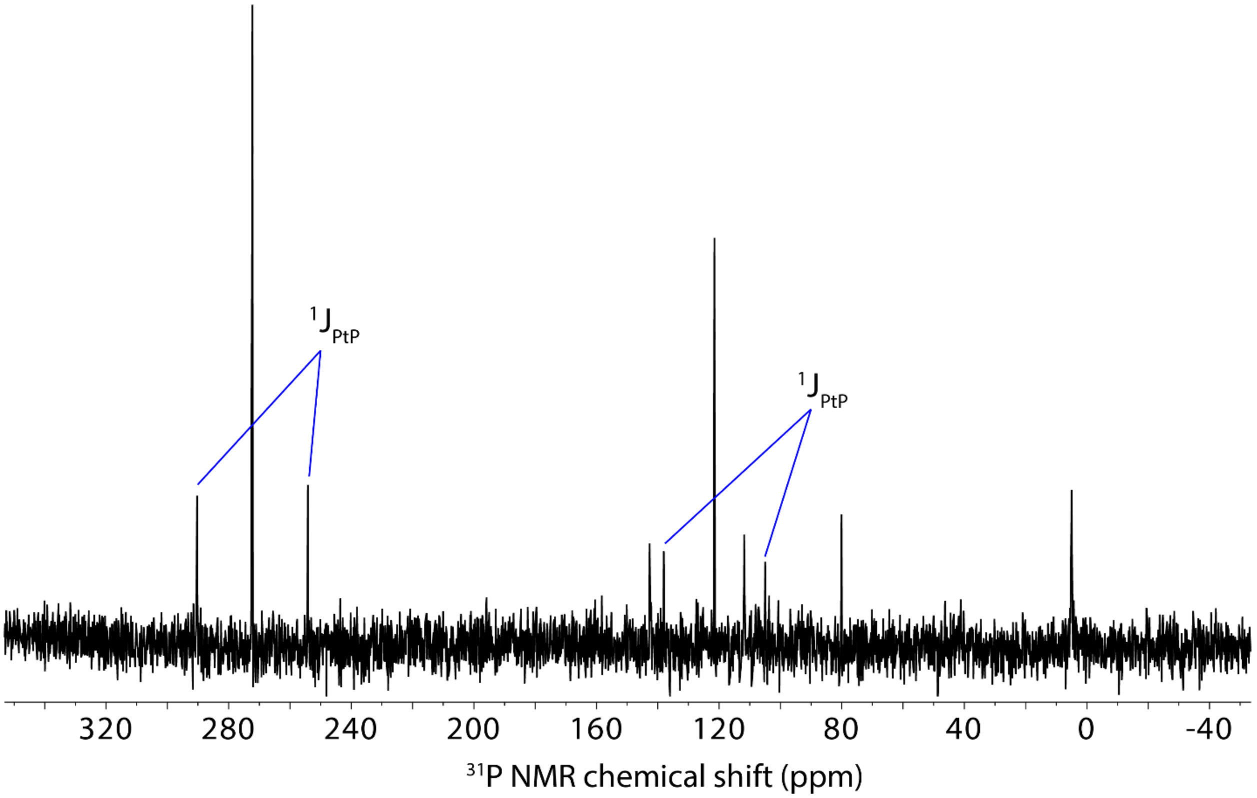
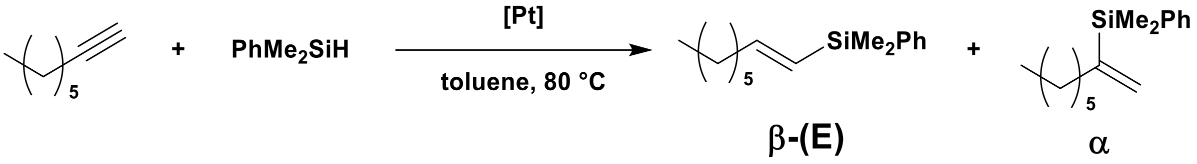


Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum of DippNHPCl + Karstedt's catalyst in benzene-*d*₆ at 25 °C.

Catalysis



General hydrosilylation reaction setup: In an argon filled glovebox, catalyst (4.8 – 20 mg) was weighed out in a 20 mL glass vial and a small stir bar was added to the vial. The vial was transferred to a nitrogen filled glovebox, then a solution containing 1-octyne (0.5 M), $PhMe_2SiH$ (0.5 M), and internal standard of cyclooctane in toluene was added to the vial via syringe. The vial was sealed and placed in a heating block preheated to 80 °C. The reactions were stirred at 500 rpm and monitored by taking small aliquots (<10 µL) of the reactions and analyzing the aliquot in chloroform-d_1 or analyzing reactions in toluene-d_8 at room temperature directly by ^1H NMR spectroscopy. The reaction times in Table 1 and Table S4 are the times determined when greater than 95 % consumption of silane and/or alkyne. The reactions were checked every 30 minutes for **3** and every 2+ hours for **2** to obtain the reaction times to the nearest 0.5 or 2 hours for each catalyst. Reactions were filtered through 0.45 µM syringe filters after the reaction and stored in a freezer prior to analyses. The substrate consumption, product turnover number, and product ratio were determined using GC-FID (see General considerations for further details). A summary of the results is provided in **Table 1** of the main text and Table S4.

Table S4. Summary of the 1-octyne hydrosilylation catalysis results for the precursors and starting materials.[a]

Material	Pt loading (mol %)	Time (h)[b]	OY conv. (%)	$PhMe_2SiH$ conv. (%)	Combined yield (%)[c]	Product TON[c]	Product TOF[c]	β-(E):α[c,d]
Karstedt's Catalyst	0.006	0.17	94.1 (3)	99.8 (1)	85.5 (2)	14250 (30)	83820	5.14 (1)
$(PPh_3)_2Pt(C_2H_4)$	0.6	0.17	97.2 (1)	>99.9	96.3 (3)	161 (1)	950	4.79 (1)
$[{}^iPr_3Si][ASO]$	0[d]	24	NR	NR	NA	NA	NA	NA
1	0[d]	24	NR	NR	NA	NA	NA	NA

a. Average of 2 runs. Errors are provided in parentheses. b. Time to indicated conversions of 1-octyne (OY) or $PhMe_2SiH$. c. Combined yield, TON (mol products X mol Pt^{-1}), and TOF (mol products X mol Pt^{-1} X h^{-1}) of the β-(E) and α hydrosilylation products as determined by GC-FID with an internal standard of cyclooctane. The TOF was determined at the time indicated in the table and should be considered a minimum. d. Ratio of the β-(E):α product isomers. NR = no reaction, and NA = not applicable.

Hot filtration studies

In an argon filled glovebox, catalyst (16 mg for **2** and **4**, or 5.0 mg for **3** and **5**) was weighed out in a standard NMR tube. The reaction vessel was transferred to a nitrogen filled glovebox, then a solution (0.40 mL, 0.2 mmol substrate for **2** and **4**, or 1.3 mL, 0.65 mmol for **3** and **5**) containing 1-octyne (0.5 M), PhMe$_2$SiH (0.5 M), and an internal standard of cyclooctane in toluene was added to the tube via syringe. The tube was sealed and placed in a heating block preheated to 80 °C for the time indicated in Table S4. After the reaction period, the solution was decanted into a syringe then filtered through a 45 μm syringe filter into two clean NMR tubes. One tube was placed in freezer for later analysis and the other was placed in the heating block preheated to 80 °C for the time indicated in the table. Both solutions were returned to room temperature and analyzed via GC-FID. The reaction results for all catalysts in this study are summarized below in Table S5.

Table S5. Summary of the hot filtration studies for the hydrosilylation of 1-octyne with PhMe$_2$SiH with the catalysts in this study.[a]

Catalyst	**Pt (%)**[a]	**Prior to hot filtration**				**Post hot filtration**				**% yield increase**
		Time (h)	**Silane cons. (%)**	**β-(E) + α yield (%)**	**β-(E):α**	**Time (h)**	**Silane cons. (%)**	**β-(E) + α yield (%)**	**β-(E):α**	
2	0.43 (4)	4	73 (2)	58 (5)	21 (4)	20	>99	86 (1)	19 (1)	47 (5)
3	0.058 (2)	0.17	50 (6)	46 (5)	8.2 (5)	0.35	81 (5)	75 (4)	8.5 (8)	64 (10)
4	0.12 (1)	4	65 (2)	50 (1)	4.8 (0)	20	>99	77 (3)	5.4 (2)	55 (3)
5	0.011 (2)	0.17	64 (2)	59 (1)	5.30 (4)	0.35	79 (3)	73 (2)	5.27 (4)	24 (1)

a. Absolute errors are provided in parantheses.

Recycling studies

General recycling study setup: In an argon filled glovebox, catalyst **2** (16 mg, 1.2 μmol Pt), **3** (5 mg, 1.2 μmol Pt), **4** (16 mg, 0.3 μmol Pt), or 5 (5 mg, 0.1 μmol Pt) were weighed out into a standard NMR tube. The NMR tube was transferred to a nitrogen filled glovebox, then a solution (0.40 mL, 0.20 mmol substrate for **2** and **4**, or 1.3 mL, 0.65 mmol for **3** and **5**) containing 1-octyne (0.5 M), $PhMe_2SiH$ (0.5 M), and an internal standard of cyclooctane in toluene was added to the tube via syringe. The tube was sealed and placed in a heating block preheated to 80 °C for 4 hours for **2** and **4** or, 10 minutes for **3** and **5**. After the reaction period, the solution was decanted into a syringe then filtered through a 45 μm syringe filter into a GC vial. The solution was then stored in freezer (-20 °C) prior to analysis by GC-FID. The remaining catalyst in the NMR tube was then washed with toluene (1 X 1 mL). The process was repeated with the remaining solid in the NMR tube. Visually, the solid loss during decantation was negligible. The final starting material consumption, product turnover number, and product ratio were determined using GC-FID (see General considerations for further details). A summary of the results is provided in Figure S18, Figure 3 of the main text and with the full results are provided in Table S6. SEM of **3** before (Figure S19) and after recycling (Figure S20) shows a decrease in the Pt surface density, supporting the leaching of Pt off the surface.

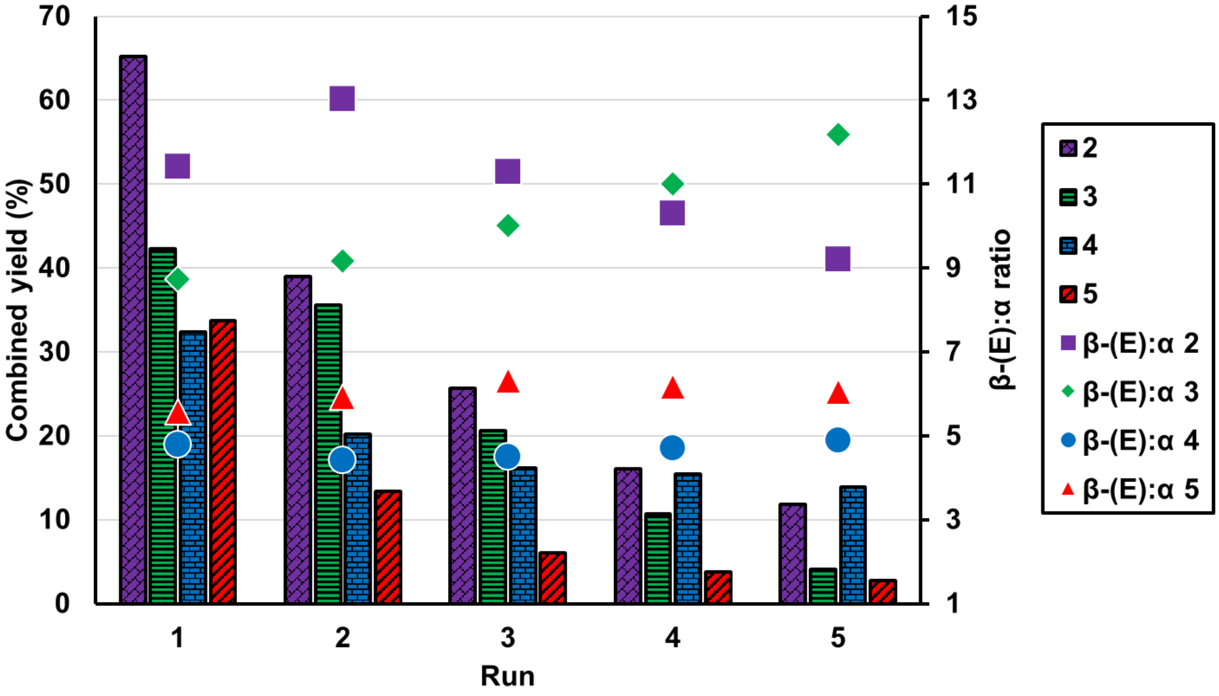


Figure S18. Summary of the recycling study results for the hydrosilylation of 1-octyne with $PhMe_2SiH$ with **2**, **3, 4,** and **5** (left). The bar graph represents the combined product yield and the scatter represents the ratio of the β-(E):α isomers after each run.

Table S6. Summary of the recycling study results for the hydrosilylation of 1-octyne with $PhMe_2SiH$ using **2**, **3**, **4**, and **5**.[a]

Catalyst	Pt (%)	Run	OY cons. (%)	Silane cons. (%)	β-(E) isomer yield (%)	α isomer yield (%)	β-(Z) isomer yield (%)	β-(E) + α yield (%)	β-(E):α	Relative β-(E) + α yield (%)
2	0.6	1	71.3	73.8	60.0	5.3	0.3	65.2	11.4	100
		2	61.7	43.8	36.2	2.8	0.8	39.0	13.0	60
		3	31.1	31.8	23.5	2.1	0.3	25.6	11.3	39
		4	21.6	22.0	14.7	1.4	0.1	16.1	10.3	25
		5	14.1	16.5	10.7	1.2	0.0	11.8	9.2	18
3	0.06	1	59.9	49.5	38.0	4.3	0.0	42.3	8.7	100
		2	56.7	40.4	32.1	3.5	2.0	35.6	9.2	84
		3	43.1	23.9	18.8	1.9	1.4	20.6	10.0	49
		4	30.4	12.5	9.8	0.9	0.7	10.7	11.0	25
		5	19.7	5.3	3.8	0.3	0.3	4.1	12.2	10
4	0.12	1	56.4	43.2	26.8	5.6	4.5	32.4	4.8	100
		2	49.3	26.6	16.4	3.7	3.4	20.2	4.4	62
		3	36.6	21.2	13.3	2.9	0.9	16.2	4.5	50
		4	40.1	19.4	12.7	2.7	0.1	15.4	4.7	48
		5	34.3	17.6	11.6	2.4	0.0	13.9	4.9	43
5	0.01	1	45.8	39.2	28.6	5.1	0.0	33.7	5.6	100
		2	24.2	15.7	11.5	1.9	2.2	13.4	5.9	40
		3	14.8	7.5	5.3	0.8	0.7	6.1	6.3	18
		4	10.5	4.6	3.2	0.5	0.3	3.8	6.2	11
		5	7.9	3.5	2.4	0.4	0.2	2.8	6.1	8

a. See full details above.

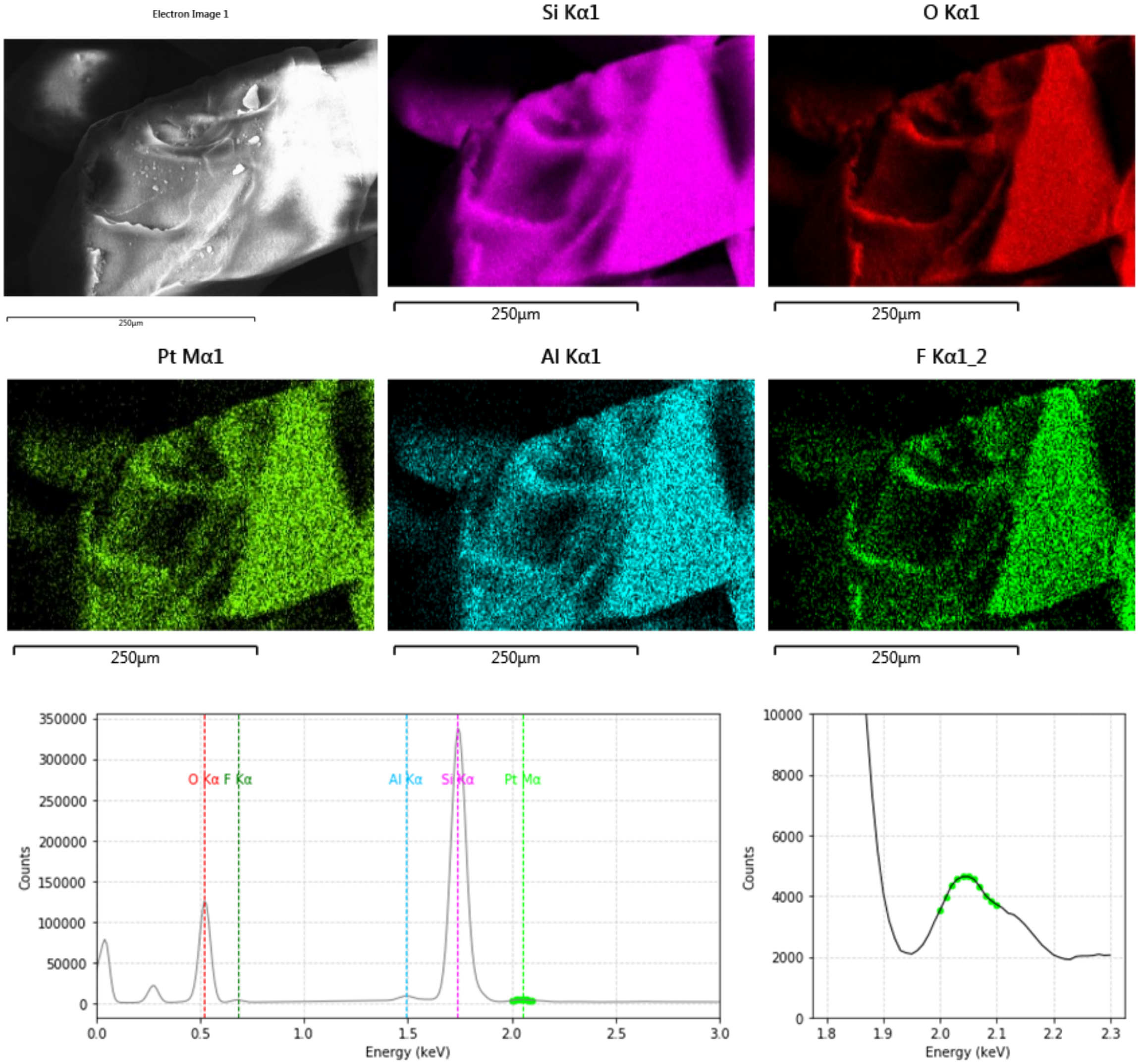


Figure S19. SEM-EDS images and spectrum of **3**.

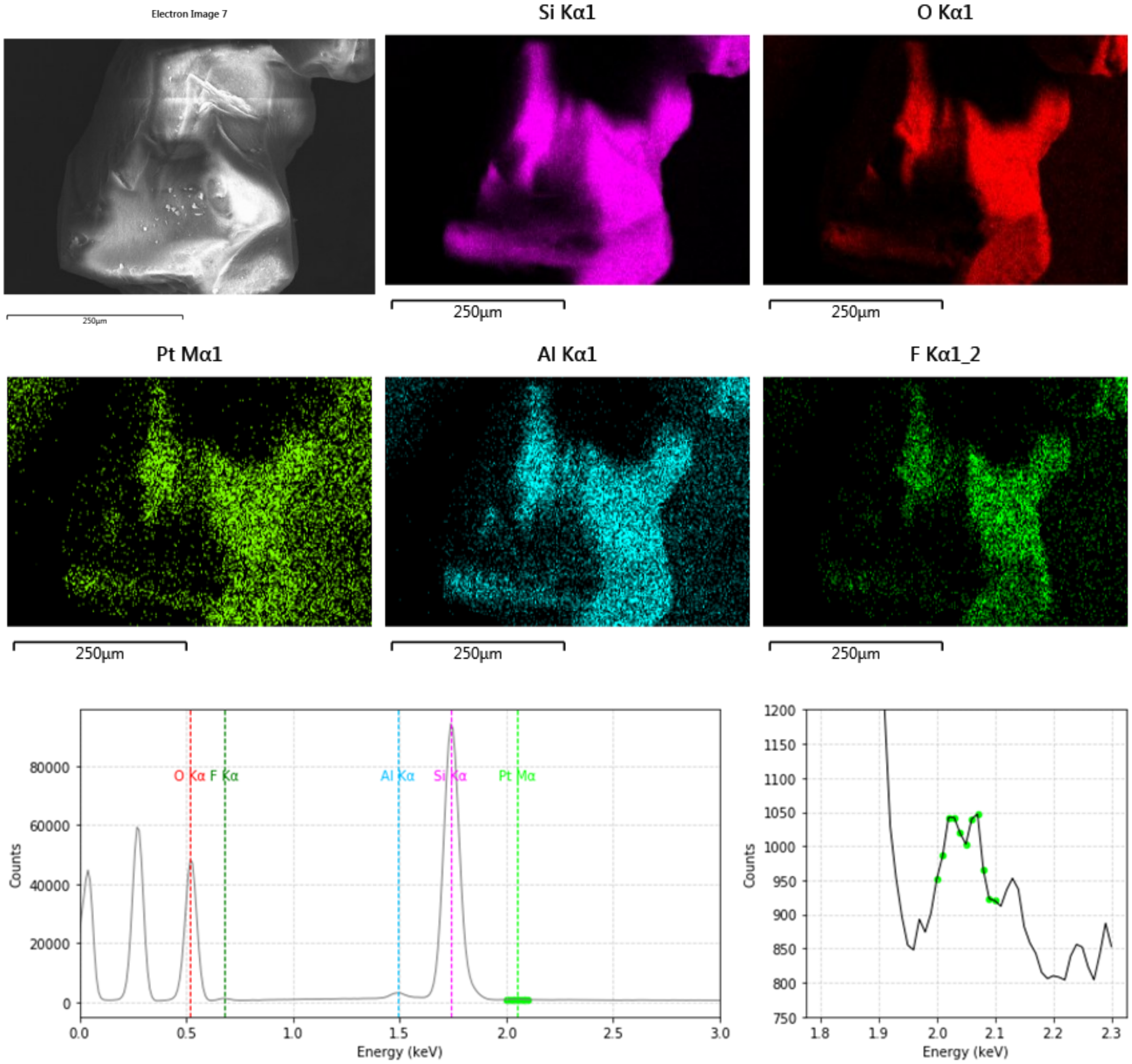


Figure S20. SEM-EDS images and spectrum of **3** after 4 catalysis cycles.

Representative solution NMR spectra and gas chromatographs

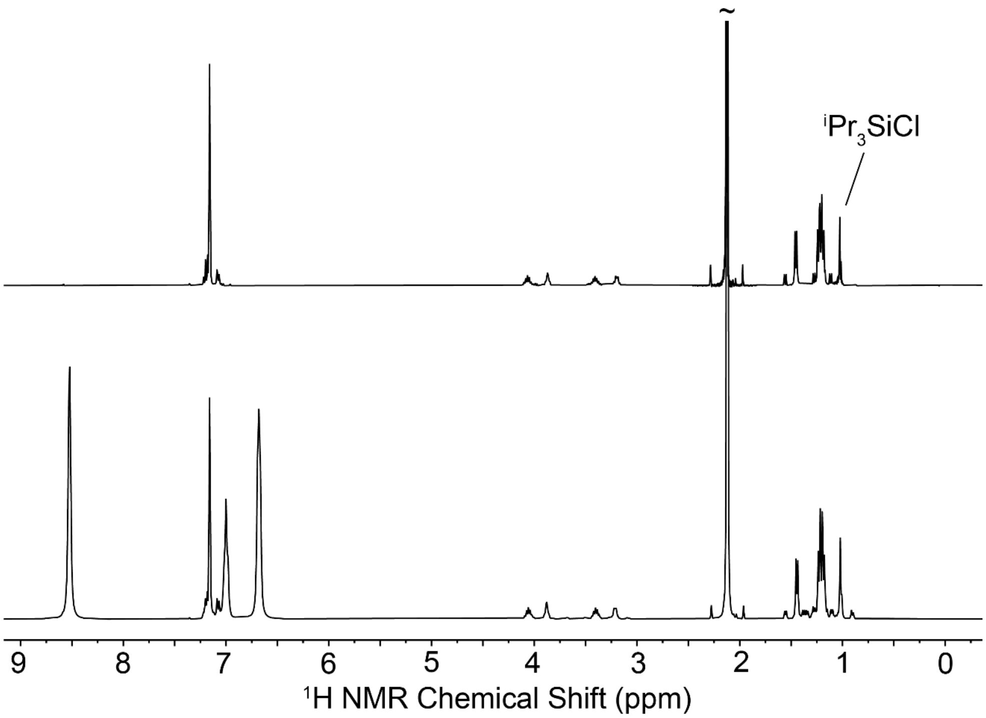


Figure S21. ^{1}H NMR spectra of the reaction of [$^{i}Pr_3Si$][ASO] and DippNHPCl before (top) and after adding pyridine (bottom) in benzene-d_6. ~ denotes hexamethylbenzene signal cutoff.

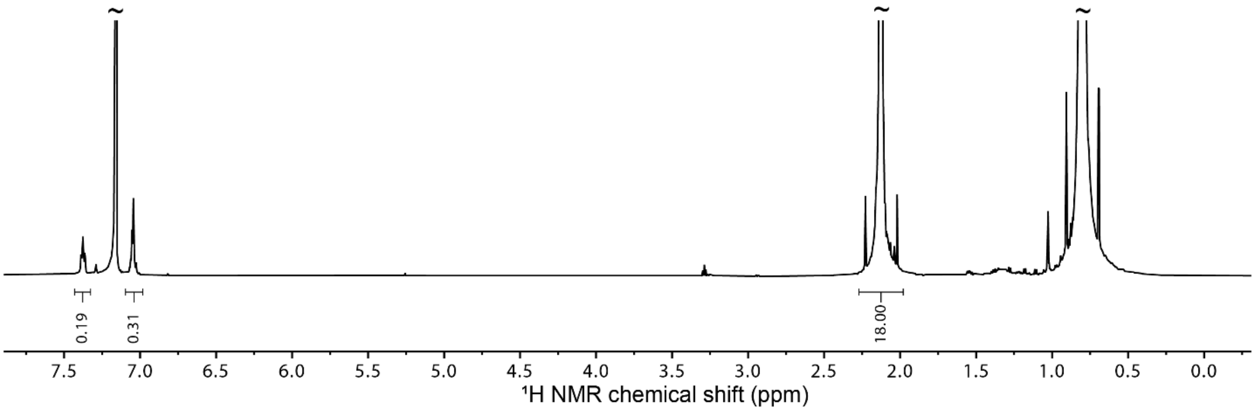


Figure S22. Representative ^{1}H NMR spectrum of the reaction of **2** with excess PMe_3 in C_6D_6 with hexamethylbenzene as an internal standard. ~ denote benzene-d6 residual (7.16 ppm), hexamethylbenzene (~2.2 ppm), and PMe_3 (~0.8 ppm) signal cutoffs.

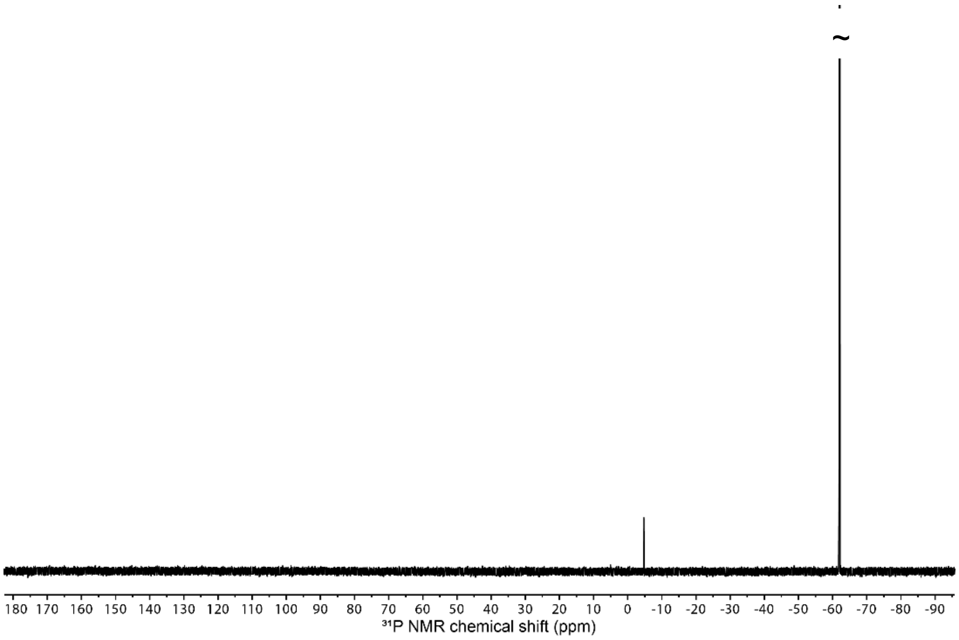


Figure S23. Representative $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **2** with excess PMe_3 in C_6D_6 with hexamethylbenzene as an internal standard. The signal at 5 ppm is PPh_3. ~ denotes PMe_3 signal cutoff.

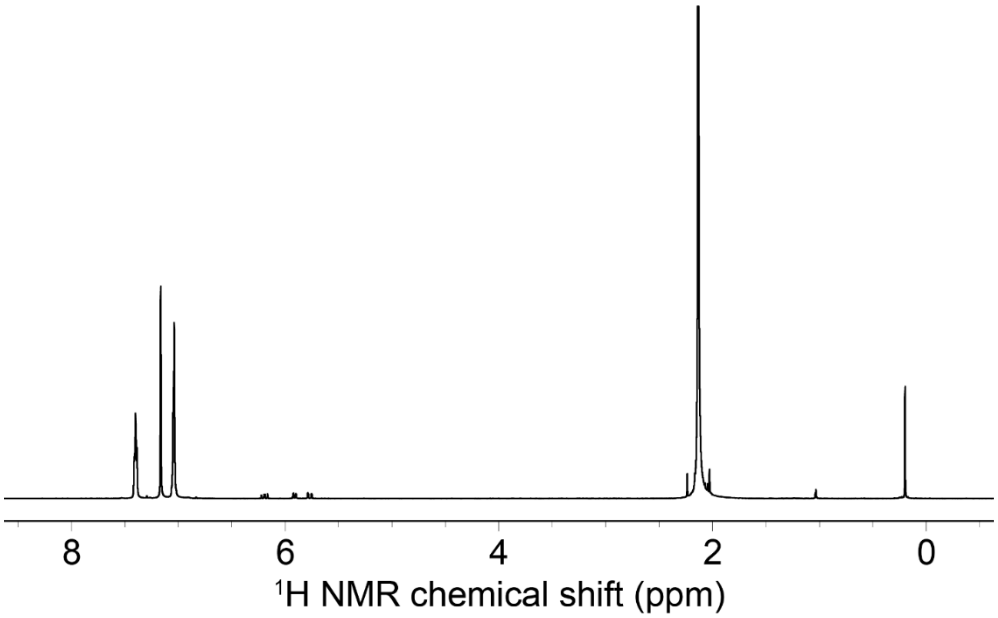


Figure S24. Representative ^{1}H NMR spectrum of the reaction of **3** with excess PPh_3 in C_6D_6 with hexamethylbenzene as an internal standard.

Table S7. Summary of GC-FID signal identities.[a]

Retention time (min)	**Assignment**
13.9	Toluene (solvent)
14.4	*n*-octane
15.5	1-octyne
15.9-16.8	octenes
18.8	Cyclooctane (internal standard)
19.5	Dimethylphenylsilane
30.3	α product
30.55	β-(Z) product
30.75	β-(E) product

a. For more details, see General considerations. Other trace signals in the GC-FID chromatographs were not identified.

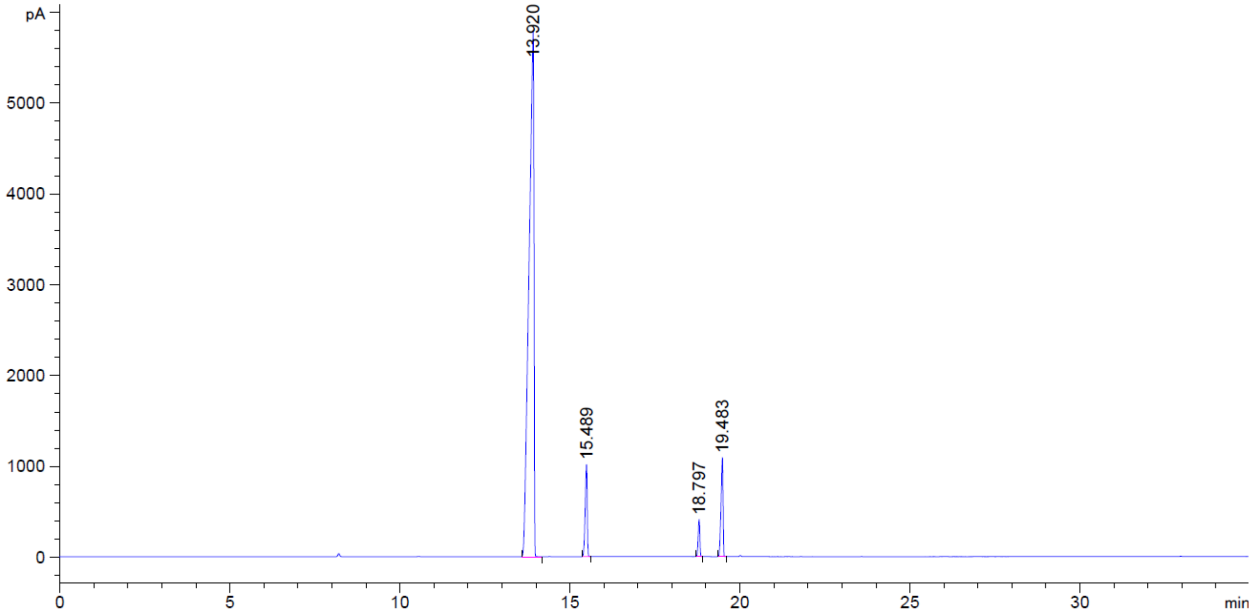


Figure S25. GC-FID of 1-octyne (15.5 min), cyclooctane (internal standard, 18.8 min), and $PhMe_2SiH$ (19.5 min) in toluene (13.9 min).

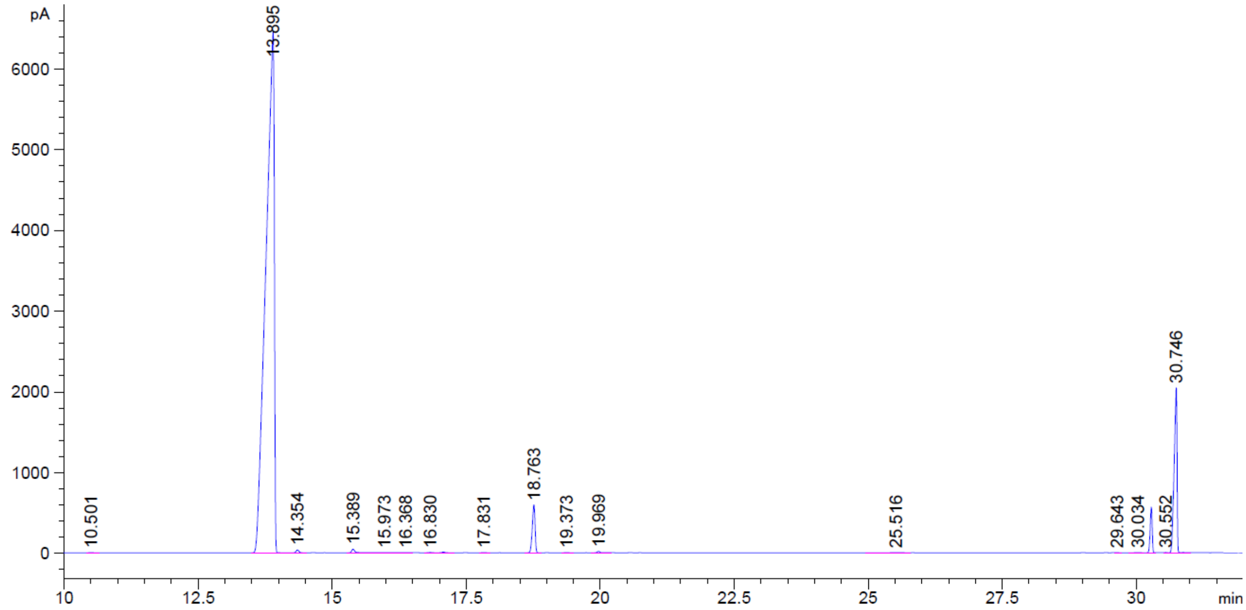


Figure S26. Representative GC-FID of the hydrosilylation catalysis results utilizing Karstedt's catalyst (0.006 % Pt).

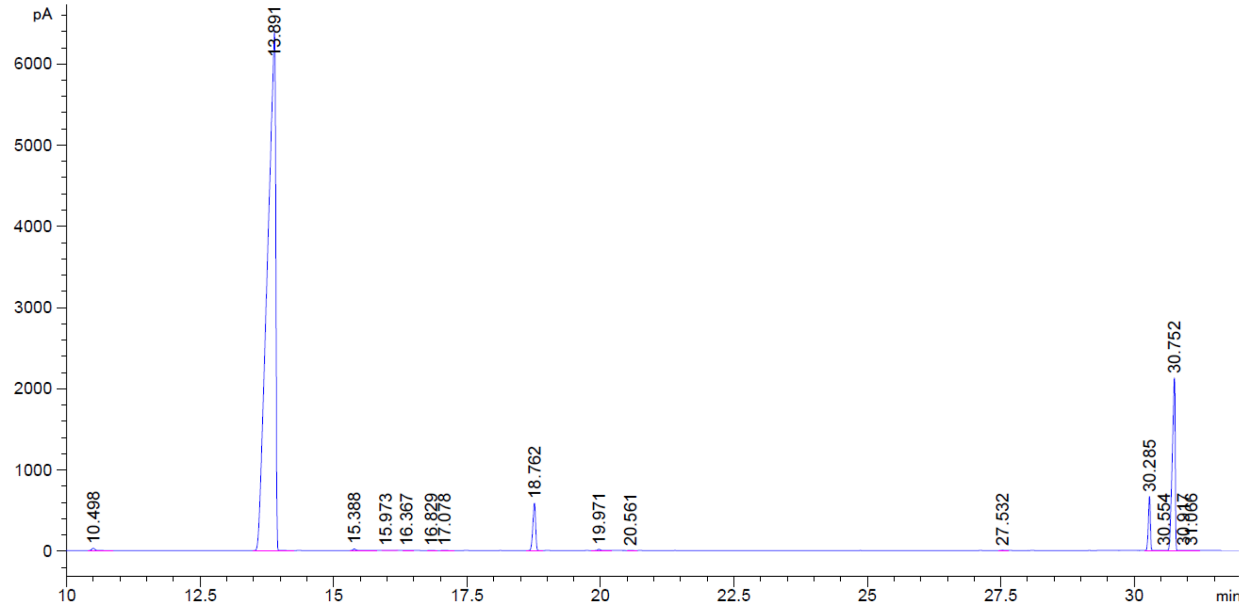


Figure S27. Representative GC-FID of the hydrosilylation catalysis results utilizing $(PPh_3)_2Pt(C_2H_4)$ (0.6 % Pt).

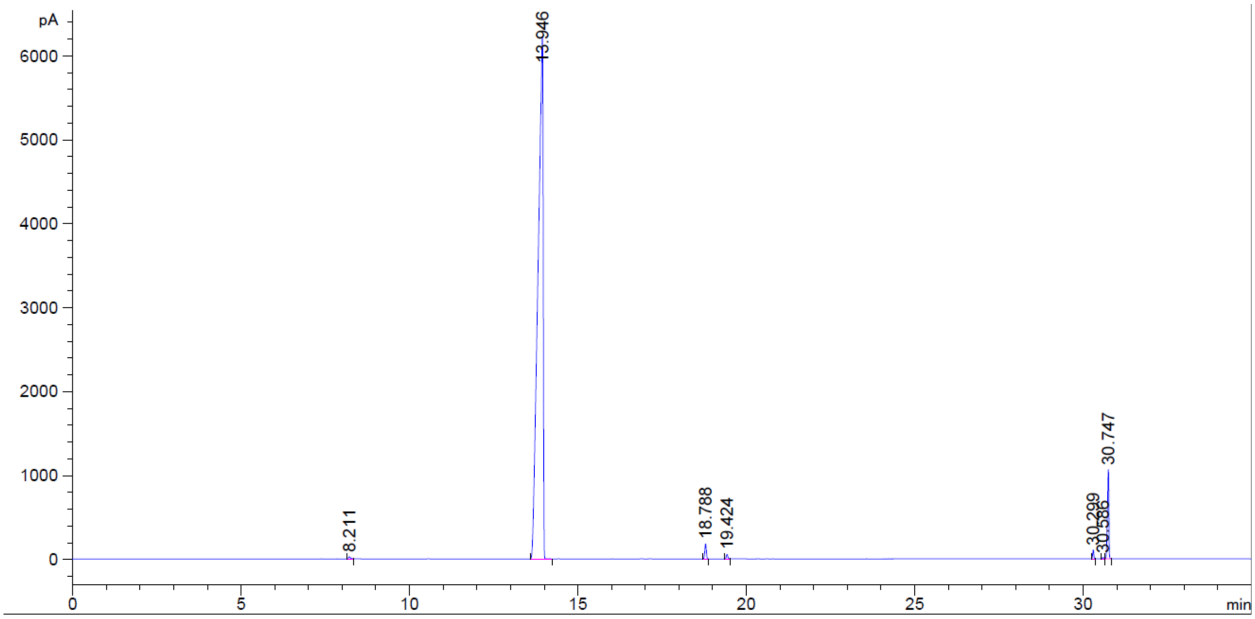


Figure S28. Representative GC-FID of the hydrosilylation catalysis results utilizing **2** (0.58 % Pt).

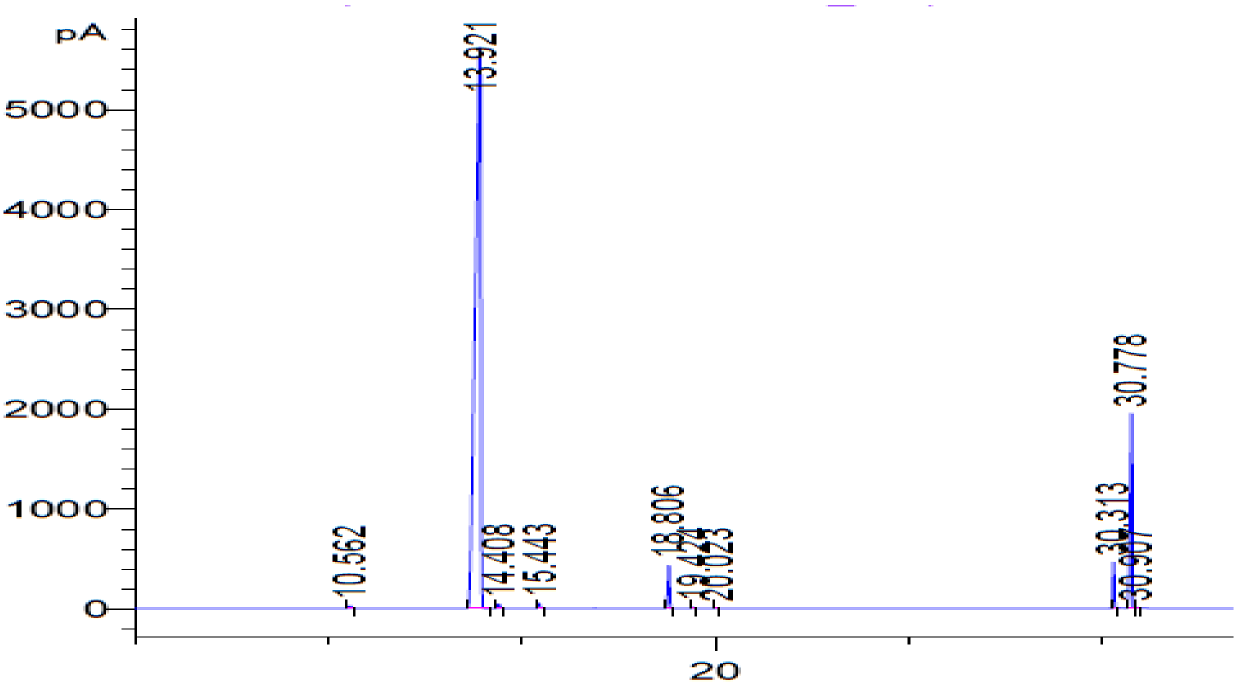


Figure S29. Representative GC-FID of the hydrosilylation catalysis results utilizing **3** (0.0058 % Pt) (X-axis = min).

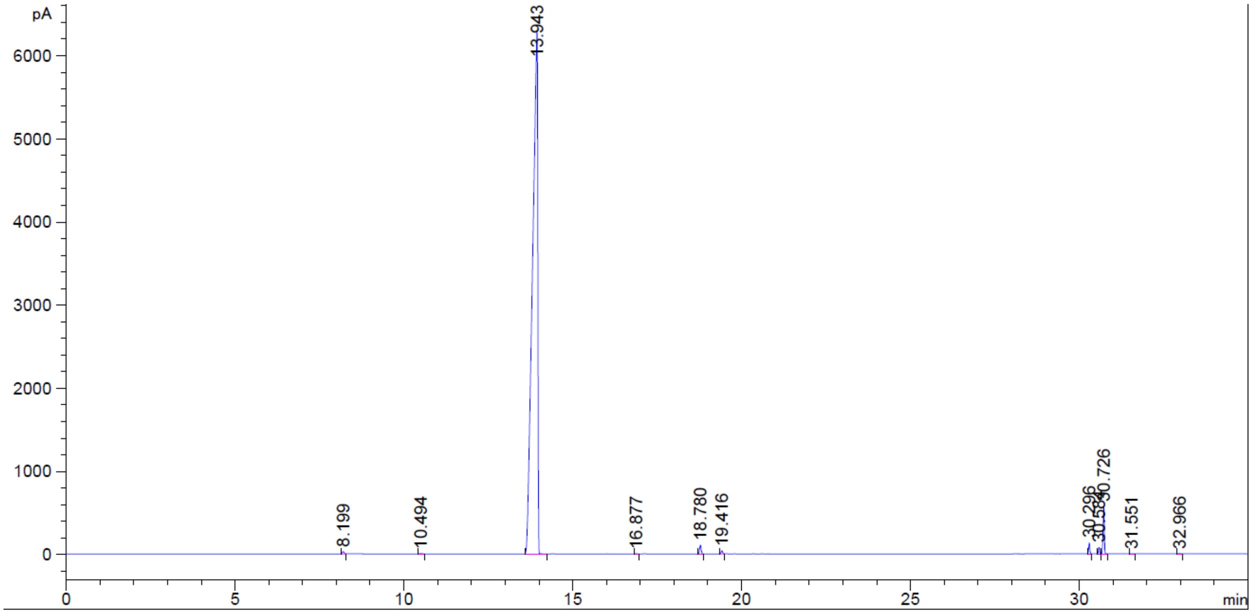


Figure S30. Representative GC-FID of the hydrosilylation catalysis results utilizing **4** (0.12 % Pt).

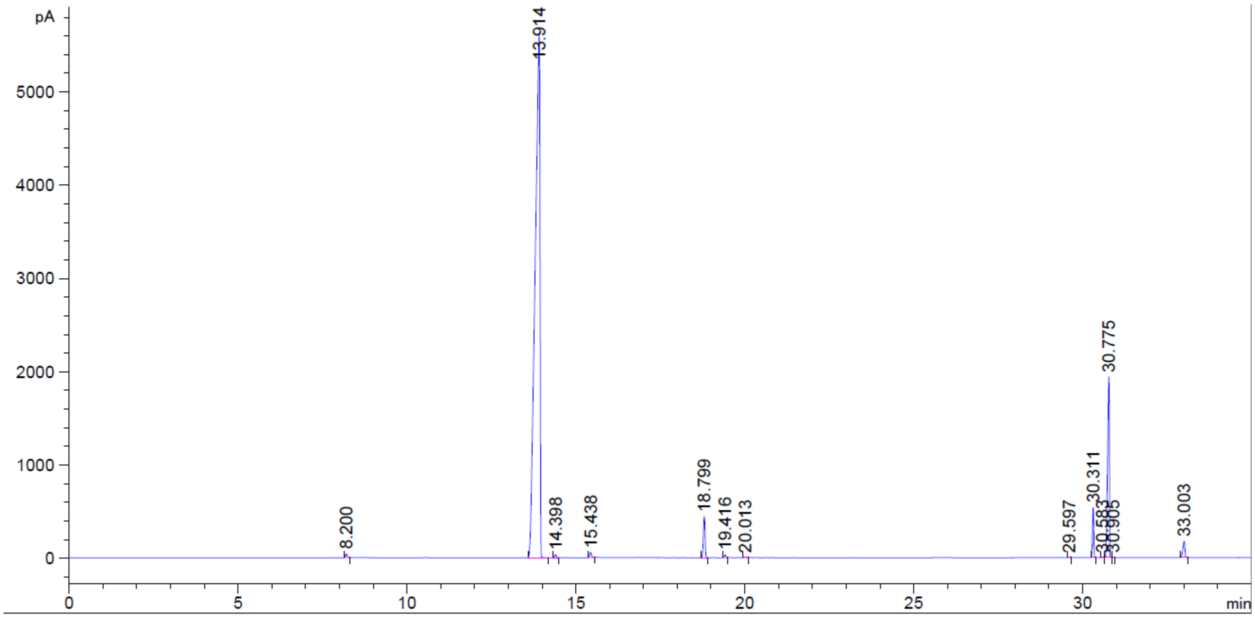


Figure S31. Representative GC-FID of the hydrosilylation catalysis results utilizing **5** (0.011 % Pt).

References

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