A Highly Active Manganese Precatalyst for the Hydrosilylation of Ketones and Esters

Supporting Information

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Experimental Procedures:

General Considerations. All synthetic reactions were performed in an MBraun glovebox under an atmosphere of purified nitrogen. Aldrich or Acros anhydrous solvents were purified using a Pure Process Technology solvent system and stored in the glovebox over activated 4Å molecular sieves and sodium before use. Benzene-d_6 and $CDCl_3$ were purchased from Cambridge Isotope Laboratories and dried over 4Å molecular sieves before use. $(THF)_2MnCl_2$ was purchased from Acros and 3-(diphenylphosphino)-1-propylamine was used as received from Strem. 1,3,5,7-Cyclooctatetraene and mercury were used as received from Sigma-Aldrich. Acetophenone, dicyclohexyl ketone, 4'-methoxyacetophenone, 4'-dimethylaminoacetophenone, 2,2,2-trifluoroacetophenone, 2',4',6'-trimethylacetophenone, isopropyl acetate, *tert*-butyl acetate, phenyl acetate, and triethoxysilane were purchased from TCI America. Cyclohexanone, 2-hexanone, 2,4-dimethyl-3-pentanone, methyl acetate, triethylsilane, diethoxymethylsilane, and dimethoxyethylsilane were bought from Sigma-Aldrich. Phenylsilane, diphenylsilane, triphenylsilane, 4'-fluoroacetophenone, and 2',3',4',5',6'-pentafluoroacetophenone were obtained from Oakwood Products Inc. Ethyl acetate was purchased from VWR. All the ketones, silanes, and esters were dried over sieves before use and the solid substrates were recrystallized from ether. ^{Ph_2PPr}PDI[1] and phenylsilane-d_3[2] were prepared according to literature procedure.

Solution ^{1}H nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a Varian 400-MR 400 MHz NMR spectrometer. All ^{1}H and ^{13}C NMR chemical shifts (ppm) are reported relative to $Si(CH_3)_4$ using ^{1}H (residual) and ^{13}C chemical shifts of the solvent as secondary standards. ^{31}P NMR data is reported relative to H_3PO_4. Elemental analyses were performed at Robertson Microlit Laboratories Inc. (Ledgewood, NJ) and the Arizona State University CLAS Goldwater Environmental Laboratory (Tempe, AZ). Solid state magnetic

susceptibilities were determined at 23 °C using a Johnson Matthey magnetic susceptibility balance calibrated with $HgCo(SCN)_4$ and $K_3Fe(CN)_6$. Solution state magnetic susceptibility was determined from Evans method using Varian 400 MHz NMR spectrometer.

X-ray Crystallography. Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in the glovebox and transferred to glass fiber with Apiezon N grease, which was then mounted on the goniometer head of a Bruker APEX Diffractometer (Arizona State University) equipped with Mo K_α radiation. A hemisphere routine was used for data collection and determination of the lattice constants. The space group was identified and the data was processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix, least-squares procedures on [F^2] (SHELXL). The solid-state structure of (^{Ph_2PPr}PDI)$MnCl_2$ was found to possess a disordered THF molecule near an inversion center that was successfully modeled in three orientations.

Electron Paramagnetic Resonance Spectroscopy.

Instrumentation. Studies were performed at the EPR Facility of Arizona State University. Continuous wave EPR spectra were recorded at 77 K using a Bruker ELEXSYS E580 continuous wave X-band spectrometer (Bruker, Rheinstetten, Germany) equipped with an Oxford Model ESR900 liquid helium cryostat (Oxford Instruments, Oxfordshire, UK). The magnetic field modulation frequency was 100 kHz with a field modulation of 1 mT peak-to-peak. The microwave power was 0.25 mW, the microwave frequency was 9.44 GHz and the sweep time was 84 seconds.

Spin Hamiltonian. The EPR spectrum of (^{Ph_2PPr}PDI)Mn was interpreted using a spin Hamiltonian, $\mathcal{H}$, containing the electron Zeeman interaction with the applied magnetic field B_o and the hyperfine coupling (hfc) term:[3]

$$\mathcal{H} = \beta_e \, \mathbf{S}\cdot\boldsymbol{g}\cdot\mathbf{B_o} + h \, \mathbf{S}\cdot\boldsymbol{A}\cdot\mathbf{I} \qquad (1)$$

where **S** is the electron spin operator, **I** is the nuclear spin operator of ^{55}Mn, $\boldsymbol{A}$ is the hfc tensor in frequency units, $\boldsymbol{g}$ is the electronic *g*-tensor, β_e is the electron magneton, and *h* is Planck's constant. The best fit of the spectrum was obtained considering a single low-spin Mn(II) ion (S = ½, I = 5/2).

Fitting of EPR spectra. To quantitatively compare experimental and simulated spectra, we divided the spectra into N intervals, i.e. we treated the spectrum as an N-dimensional vector **R**. Each component R_j has the amplitude of the EPR signal at a magnetic field B_j, with j varying from 1 to N. The amplitudes of the experimental and simulated spectra were normalized so that the span between the maximum and minimum values of R_j is 1. We compared the calculated amplitudes R_j^{calc} of the signal with the observed values R_j defining a root-mean-square deviation σ by:

$$\sigma(p_1, p_2, \ldots, p_n) = [\sum_j (R_j^{calc}(p_1, p_2, \ldots, p_n) - R_j^{exp})^2/N]^{1/2} \qquad (2)$$

where the sums are over the N values of j, and p's are the fitting parameters that produced the calculated spectrum. For our simulations, N was set equal to 1024. The EPR spectra were simulated using EasySpin (v 4.5.0), a computational package developed by Stoll and Schweiger[4] and based on Matlab (The MathWorks, Natick, MA, USA). EasySpin calculates EPR resonance fields using the energies of the states of the spin system obtained by direct diagonalization of the spin Hamiltonian (see Eq. 1). The EPR fitting procedure used a Monte Carlo type iteration to minimize the root-mean-square deviation, σ (see Eq. 2) between measured

and simulated spectra. We searched for the optimum values of the following parameters: the principal components of $\boldsymbol{g}$ (i.e. g_x, g_y, g_z), the principal components of the hfc tensor $\boldsymbol{A}$ (i.e. A_x, A_y, A_z) and the peak-to-peak line-widths (ΔB_x, ΔB_y, and ΔB_z).

Table S1. Crystallographic Data for **(^{Ph_2PPr}PDI)MnCl$_2$**·0.5THF and **(^{Ph_2PPr}PDI)Mn**.

	(^{Ph_2PPr}PDI)MnCl$_2$·0.5THF	**(^{Ph_2PPr}PDI)Mn**
chemical formula	$C_{41}H_{45}N_3Cl_2MnO_{0.5}P_2$	$C_{39}H_{41}N_3MnP_2$
formula weight	775.58	668.63
crystal dimensions	0.200 x 0.180 x 0.050	0.270 x 0.160 x 0.120
crystal system	monoclinic	triclinic
space group	C12/c1	P-1
a (Å)	16.9540(7)	10.773(2)
b (Å)	12.1473(5)	12.341(2)
c (Å)	37.0711(15)	14.004(3)
α (deg)	90	95.103(3)
β (deg)	100.2760(10)	90.505(3)
γ (deg)	90	115.432(2)
V (Å^3)	7512.2(5)	1672.5(5)
Z	8	2
T (°C)	123.(2)	123.(2)
ρcalcd (g cm^{-3})	1.372	1.328
μ (mm^{-1})	0.615	0.523
reflections collected	30382	14656
data/restraints/parameters	6888/1/453	6766/0/408
R_1 [I > 2σ(I)]	0.0443	0.0462
wR_2 (all data)	0.1000	0.1286
Goodness-of-fit	1.088	1.014
Largest peak, hole (eÅ^{-3})	0.511, -1.137	0.955, -0.528

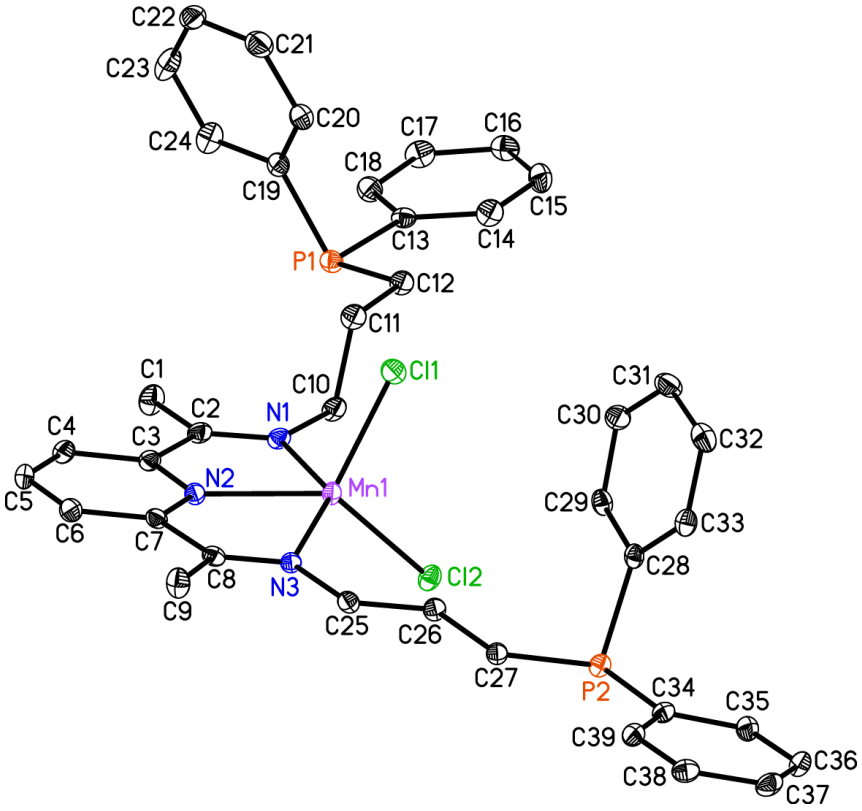


Figure S1. The molecular structure of **(^{Ph_2PPr}PDI)MnCl$_2$** shown at 30% probability ellipsoids. Hydrogen atoms and a co-crystallized THF molecule are omitted for clarity.

Table S2. Metrical parameters for **(^{Ph_2PPr}PDI)$MnCl_2$**.

Mn(1)-N(2)	2.196(2)	C(2)-C(3)	1.493(4)	C(21)-C(22)	1.386(5)
Mn(1)-N(1)	2.300(2)	C(3)-C(4)	1.385(4)	C(22)-C(23)	1.371(5)
Mn(1)-N(3)	2.338(2)	C(4)-C(5)	1.371(4)	C(23)-C(24)	1.393(4)
Mn(1)-Cl(1)	2.3514(8)	C(5)-C(6)	1.387(4)	C(25)-C(26)	1.510(4)
Mn(1)-Cl(2)	2.3748(8)	C(6)-C(7)	1.387(4)	C(26)-C(27)	1.526(4)
P(1)-C(12)	1.841(3)	C(7)-C(8)	1.502(4)	C(28)-C(33)	1.393(4)
P(1)-C(13)	1.843(3)	C(8)-C(9)	1.501(4)	C(28)-C(29)	1.402(4)
P(1)-C(19)	1.850(3)	C(10)-C(11)	1.518(4)	C(29)-C(30)	1.383(4)
P(2)-C(34)	1.831(3)	C(11)-C(12)	1.538(4)	C(30)-C(31)	1.377(4)
P(2)-C(28)	1.837(3)	C(13)-C(18)	1.390(4)	C(31)-C(32)	1.381(4)
P(2)-C(27)	1.856(3)	C(13)-C(14)	1.390(4)	C(32)-C(33)	1.390(4)
N(1)-C(2)	1.278(4)	C(14)-C(15)	1.389(4)	C(34)-C(39)	1.393(4)
N(1)-C(10)	1.465(3)	C(15)-C(16)	1.382(4)	C(34)-C(35)	1.398(4)
N(2)-C(7)	1.344(3)	C(16)-C(17)	1.377(4)	C(35)-C(36)	1.385(4)
N(2)-C(3)	1.344(3)	C(17)-C(18)	1.386(4)	C(36)-C(37)	1.387(4)
N(3)-C(8)	1.282(3)	C(19)-C(20)	1.387(4)	C(37)-C(38)	1.387(4)
N(3)-C(25)	1.477(3)	C(19)-C(24)	1.393(4)	C(38)-C(39)	1.385(4)
C(1)-C(2)	1.506(4)	C(20)-C(21)	1.384(4)		

N(2)-Mn(1)-N(1)	71.47(8)	N(1)-C(2)-C(1)	126.7(3)	C(20)-C(19)-P(1)	124.6(2)
N(2)-Mn(1)-N(3)	70.84(8)	C(3)-C(2)-C(1)	116.9(2)	C(24)-C(19)-P(1)	117.6(2)
N(1)-Mn(1)-N(3)	141.81(8)	N(2)-C(3)-C(4)	121.4(3)	C(21)-C(20)-C(19)	121.0(3)
N(2)-Mn(1)-Cl(1)	113.63(6)	N(2)-C(3)-C(2)	114.8(2)	C(20)-C(21)-C(22)	120.3(3)
N(1)-Mn(1)-Cl(1)	98.64(6)	C(4)-C(3)-C(2)	123.8(3)	C(23)-C(22)-C(21)	119.7(3)
N(3)-Mn(1)-Cl(1)	101.75(6)	C(5)-C(4)-C(3)	119.0(3)	C(22)-C(23)-C(24)	119.9(3)
N(2)-Mn(1)-Cl(2)	133.16(7)	C(4)-C(5)-C(6)	119.8(3)	C(23)-C(24)-C(19)	121.2(3)
N(1)-Mn(1)-Cl(2)	92.47(6)	C(7)-C(6)-C(5)	118.7(3)	N(3)-C(25)-C(26)	109.9(2)
N(3)-Mn(1)-Cl(2)	108.91(6)	N(2)-C(7)-C(6)	121.3(2)	C(25)-C(26)-C(27)	113.2(2)
Cl(1)-Mn(1)-Cl(2)	112.13(3)	N(2)-C(7)-C(8)	114.4(2)	C(26)-C(27)-P(2)	111.16(18)
C(12)-P(1)-C(13)	102.19(13)	C(6)-C(7)-C(8)	124.3(2)	C(33)-C(28)-C(29)	118.4(3)
C(12)-P(1)-C(19)	102.32(13)	N(3)-C(8)-C(9)	124.6(3)	C(33)-C(28)-P(2)	124.5(2)
C(13)-P(1)-C(19)	99.76(12)	N(3)-C(8)-C(7)	116.5(2)	C(29)-C(28)-P(2)	117.0(2)
C(34)-P(2)-C(28)	101.65(13)	C(9)-C(8)-C(7)	119.0(2)	C(30)-C(29)-C(28)	120.5(3)
C(34)-P(2)-C(27)	102.29(12)	N(1)-C(10)-C(11)	110.9(2)	C(31)-C(30)-C(29)	120.3(3)
C(28)-P(2)-C(27)	98.73(12)	C(10)-C(11)-C(12)	111.2(2)	C(30)-C(31)-C(32)	120.2(3)
C(2)-N(1)-C(10)	120.8(2)	C(11)-C(12)-P(1)	111.5(2)	C(31)-C(32)-C(33)	119.9(3)
C(2)-N(1)-Mn(1)	117.61(18)	C(18)-C(13)-C(14)	118.2(3)	C(32)-C(33)-C(28)	120.6(3)
C(10)-N(1)-Mn(1)	121.53(17)	C(18)-C(13)-P(1)	117.7(2)	C(39)-C(34)-C(35)	118.2(3)
C(7)-N(2)-C(3)	119.8(2)	C(14)-C(13)-P(1)	124.1(2)	C(39)-C(34)-P(2)	124.5(2)
C(7)-N(2)-Mn(1)	120.26(17)	C(15)-C(14)-C(13)	120.8(3)	C(35)-C(34)-P(2)	117.2(2)
C(3)-N(2)-Mn(1)	119.54(18)	C(16)-C(15)-C(14)	120.1(3)	C(36)-C(35)-C(34)	121.1(3)
C(8)-N(3)-C(25)	117.8(2)	C(17)-C(16)-C(15)	119.8(3)	C(35)-C(36)-C(37)	119.8(3)
C(8)-N(3)-Mn(1)	116.39(18)	C(16)-C(17)-C(18)	120.1(3)	C(38)-C(37)-C(36)	119.8(3)
C(25)-N(3)-Mn(1)	125.12(16)	C(17)-C(18)-C(13)	121.1(3)	C(39)-C(38)-C(37)	120.1(3)
N(1)-C(2)-C(3)	116.4(2)	C(20)-C(19)-C(24)	117.8(3)	C(38)-C(39)-C(34)	120.9(3)

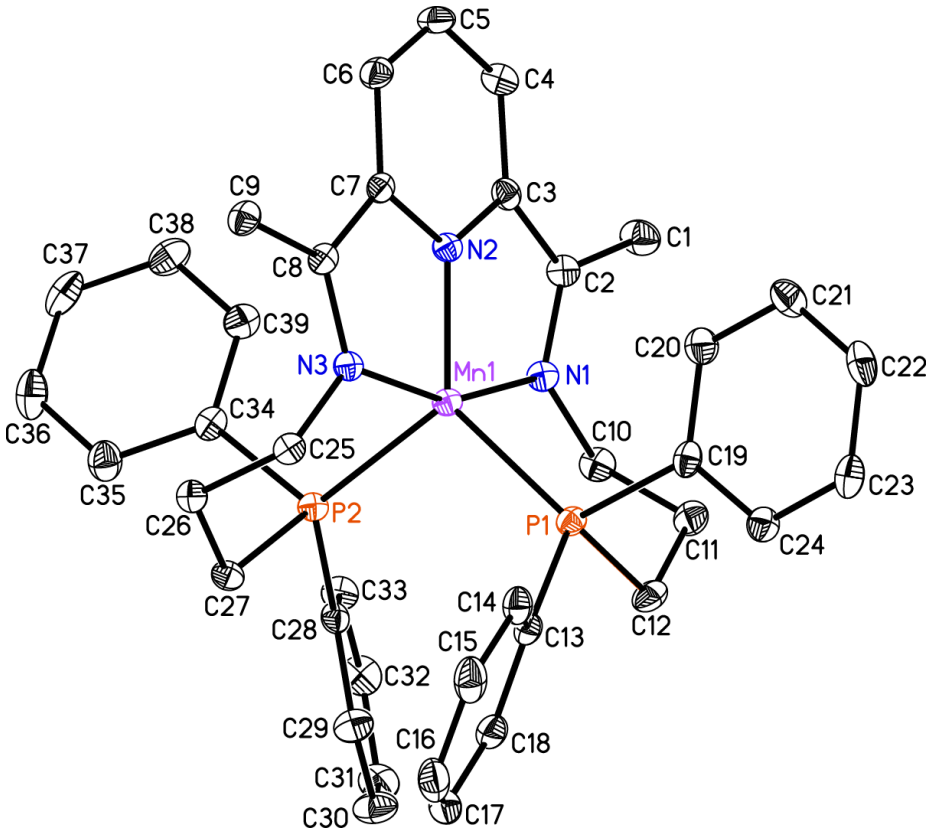


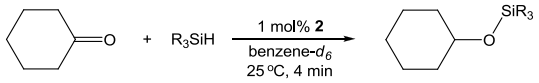
Figure S2. The molecular structure of **(^{Ph_2PPr}PDI)Mn** displayed with non-H atom labels at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table S3. Metrical parameters for **(^{Ph_2PPr}PDI)Mn**.

Mn(1)-N(2)	1.887(2)	C(2)-C(3)	1.416(4)	C(21)-C(22)	1.385(4)
Mn(1)-N(1)	1.944(2)	C(3)-C(4)	1.403(4)	C(22)-C(23)	1.381(4)
Mn(1)-N(3)	1.949(2)	C(4)-C(5)	1.388(4)	C(23)-C(24)	1.387(4)
Mn(1)-P(2)	2.2634(8)	C(5)-C(6)	1.390(4)	C(25)-C(26)	1.531(3)
Mn(1)-P(1)	2.2697(8)	C(6)-C(7)	1.402(4)	C(26)-C(27)	1.528(3)
P(1)-C(13)	1.830(3)	C(7)-C(8)	1.414(3)	C(28)-C(29)	1.391(4)
P(1)-C(12)	1.851(3)	C(8)-C(9)	1.498(3)	C(28)-C(33)	1.399(4)
P(1)-C(19)	1.854(3)	C(10)-C(11)	1.525(4)	C(29)-C(30)	1.389(4)
P(2)-C(28)	1.840(2)	C(11)-C(12)	1.532(4)	C(30)-C(31)	1.380(4)
P(2)-C(27)	1.850(3)	C(13)-C(14)	1.397(4)	C(31)-C(32)	1.382(4)
P(2)-C(34)	1.851(3)	C(13)-C(18)	1.398(4)	C(32)-C(33)	1.395(4)
N(1)-C(2)	1.354(3)	C(14)-C(15)	1.383(4)	C(34)-C(39)	1.382(4)
N(1)-C(10)	1.476(3)	C(15)-C(16)	1.378(5)	C(34)-C(35)	1.394(4)
N(2)-C(3)	1.385(3)	C(16)-C(17)	1.383(5)	C(35)-C(36)	1.400(4)
N(2)-C(7)	1.398(3)	C(17)-C(18)	1.393(4)	C(36)-C(37)	1.369(5)
N(3)-C(8)	1.355(3)	C(19)-C(20)	1.387(4)	C(37)-C(38)	1.377(4)
N(3)-C(25)	1.469(3)	C(19)-C(24)	1.403(4)	C(38)-C(39)	1.389(4)
C(1)-C(2)	1.506(4)	C(20)-C(21)	1.390(4)		

N(2)-Mn(1)-N(1)	78.69(9)	C(8)-N(3)-C(25)	118.1(2)	C(17)-C(18)-C(13)	120.8(3)
N(2)-Mn(1)-N(3)	78.91(9)	C(8)-N(3)-Mn(1)	117.85(17)	C(20)-C(19)-C(24)	118.7(2)
N(1)-Mn(1)-N(3)	157.54(9)	C(25)-N(3)-Mn(1)	123.64(15)	C(20)-C(19)-P(1)	119.9(2)
N(2)-Mn(1)-P(2)	123.14(6)	N(1)-C(2)-C(3)	112.8(2)	C(24)-C(19)-P(1)	121.4(2)
N(1)-Mn(1)-P(2)	102.14(6)	N(1)-C(2)-C(1)	124.1(2)	C(19)-C(20)-C(21)	120.8(3)
N(3)-Mn(1)-P(2)	88.82(6)	C(3)-C(2)-C(1)	123.1(2)	C(22)-C(21)-C(20)	119.8(3)
N(2)-Mn(1)-P(1)	130.90(6)	N(2)-C(3)-C(4)	119.6(2)	C(23)-C(22)-C(21)	120.3(3)
N(1)-Mn(1)-P(1)	90.60(6)	N(2)-C(3)-C(2)	110.5(2)	C(22)-C(23)-C(24)	119.9(3)
N(3)-Mn(1)-P(1)	105.32(6)	C(4)-C(3)-C(2)	129.8(2)	C(23)-C(24)-C(19)	120.5(3)
P(2)-Mn(1)-P(1)	105.93(3)	C(5)-C(4)-C(3)	120.0(3)	N(3)-C(25)-C(26)	111.53(19)
C(13)-P(1)-C(12)	103.74(12)	C(4)-C(5)-C(6)	120.6(2)	C(27)-C(26)-C(25)	112.5(2)
C(13)-P(1)-C(19)	101.18(12)	C(5)-C(6)-C(7)	119.5(2)	C(26)-C(27)-P(2)	112.10(17)
C(12)-P(1)-C(19)	99.13(12)	N(2)-C(7)-C(6)	119.8(2)	C(29)-C(28)-C(33)	118.1(2)
C(13)-P(1)-Mn(1)	120.81(8)	N(2)-C(7)-C(8)	110.9(2)	C(29)-C(28)-P(2)	121.97(19)
C(12)-P(1)-Mn(1)	112.79(9)	C(6)-C(7)-C(8)	129.3(2)	C(33)-C(28)-P(2)	119.84(19)
C(19)-P(1)-Mn(1)	116.23(9)	N(3)-C(8)-C(7)	112.8(2)	C(30)-C(29)-C(28)	121.2(3)
C(28)-P(2)-C(27)	102.23(11)	N(3)-C(8)-C(9)	124.5(2)	C(31)-C(30)-C(29)	120.0(3)
C(28)-P(2)-C(34)	99.89(11)	C(7)-C(8)-C(9)	122.7(2)	C(30)-C(31)-C(32)	119.9(3)
C(27)-P(2)-C(34)	102.38(12)	N(1)-C(10)-C(11)	112.8(2)	C(31)-C(32)-C(33)	120.2(3)
C(28)-P(2)-Mn(1)	124.93(8)	C(10)-C(11)-C(12)	112.7(2)	C(32)-C(33)-C(28)	120.6(3)
C(27)-P(2)-Mn(1)	112.60(8)	C(11)-C(12)-P(1)	111.26(17)	C(39)-C(34)-C(35)	118.7(2)
C(34)-P(2)-Mn(1)	111.96(8)	C(14)-C(13)-C(18)	117.7(3)	C(39)-C(34)-P(2)	118.61(19)
C(2)-N(1)-C(10)	118.2(2)	C(14)-C(13)-P(1)	119.7(2)	C(35)-C(34)-P(2)	122.7(2)
C(2)-N(1)-Mn(1)	117.88(17)	C(18)-C(13)-P(1)	122.1(2)	C(34)-C(35)-C(36)	119.9(3)
C(10)-N(1)-Mn(1)	123.84(16)	C(15)-C(14)-C(13)	121.4(3)	C(37)-C(36)-C(35)	120.4(3)
C(3)-N(2)-C(7)	120.4(2)	C(16)-C(15)-C(14)	120.2(3)	C(36)-C(37)-C(38)	120.0(3)
C(3)-N(2)-Mn(1)	119.99(17)	C(15)-C(16)-C(17)	119.8(3)	C(37)-C(38)-C(39)	120.0(3)
C(7)-N(2)-Mn(1)	119.41(16)	C(16)-C(17)-C(18)	120.2(3)	C(34)-C(39)-C(38)	120.9(3)

Table S4. Cyclohexanone hydrosilylation catalyzed by **2**.[a]



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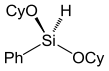
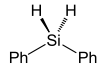
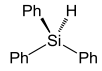
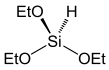
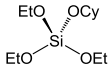
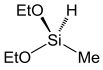
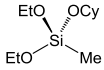
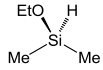
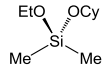
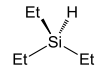
1			>99
2			26
3		-	-
4			28
5			5
6			3
7		-	-

[a]Reactions conducted in 0.7 mL of benzene-d_6 with approximately 0.003 mmol of **2**, 0.3 mmol of silane, and 0.3 mmol of substrate. [b]Conversion determined by ^{1}H NMR spectroscopy.

Preparation of ^{Ph_2PPr}PDIMnCl$_2$ (1): Under an inert atmosphere, a thick-walled glass bomb was charged with 0.199 g (0.737 mmol) of $(THF)_2MnCl_2$, 0.452 g (0.737 mmol) of ^{Ph_2PPr}PDI, and approximately 30 mL of toluene. The bomb was then sealed and brought out of the glove box. The mixture was heated at 90 °C in an oil bath for 48 h. The resulting light orange suspension was vacuum filtered, the solvent was removed, and the residue was washed several times with toluene and dried to obtain 0.509 g (0.689 mmol, 93% yield) of **1** as a light orange solid. Analysis for $C_{39}H_{41}N_3Cl_2MnP_2$: Calcd. C, 63.34%; H, 5.59%; N, 5.68%. Found: C, 62.97%; H, 5.66%; N, 5.41%. Magnetic susceptibility (Gouy balance, 23 °C) μ_{eff} = 6.0 μ_B. ^{1}H NMR ($CDCl_3$, 23 °C): 70.31 (9210 Hz), 7.34 (265 Hz), –37.59 (2872 Hz).

Preparation of (^{Ph_2PPr}PDI)Mn (2): Under an inert atmosphere, a 20 mL scintillation vial was charged with 4.33 g (21.66 mmol) of mercury, 0.025 g (1.083 mmol) of sodium, and approximately 4 mL of tetrahydrofuran. The mixture was stirred at ambient temperature for 20 minutes, after which time 0.011 g (0.108 mmol) of cyclooctatetraene was added. A slurry of **1** (0.160 g, 0.216 mmol) and approximately 10 mL of tetrahydrofuran was then added to the vial. After stirring at ambient temperature for 15 h, the resulting deep brown solution was filtered through a Celite pad and the solvent was evacuated to obtain a brown solid. This solid was scraped off the sides of the flask in the presence of pentane (2 x 10 mL) and dried again to remove any residual solvent. The solid was dissolved in 15 mL toluene and filtered through a Celite column to ensure NaCl removal. After evacuating the toluene, the resulting solid was crystallized from a toluene solution layered with diethyl ether to yield 0.068 g (47%) of dark brown crystals identified as **2**. Analysis for $C_{39}H_{41}N_3MnP_2$: Calcd. C, 70.05%; H, 6.18%; N, 6.28%. Found: C, 69.75%; H, 5.96%; N, 5.99%. Magnetic susceptibility (Evans method, 23 °C)

μ_{eff} = 2.2 μ_B. ^{1}H NMR (benzene-d_6, 23 °C): 96.28 (2265 Hz), 68.38 (2176 Hz), 28.59 (2176 Hz), 18.77 (55.3 Hz), 8.15 (30.7 Hz), 6.90 (16.6 Hz), 6.68 (16.6 Hz), 4.56 (45.4 Hz), –7.79 (1014 Hz), –95.61 (3502 Hz).

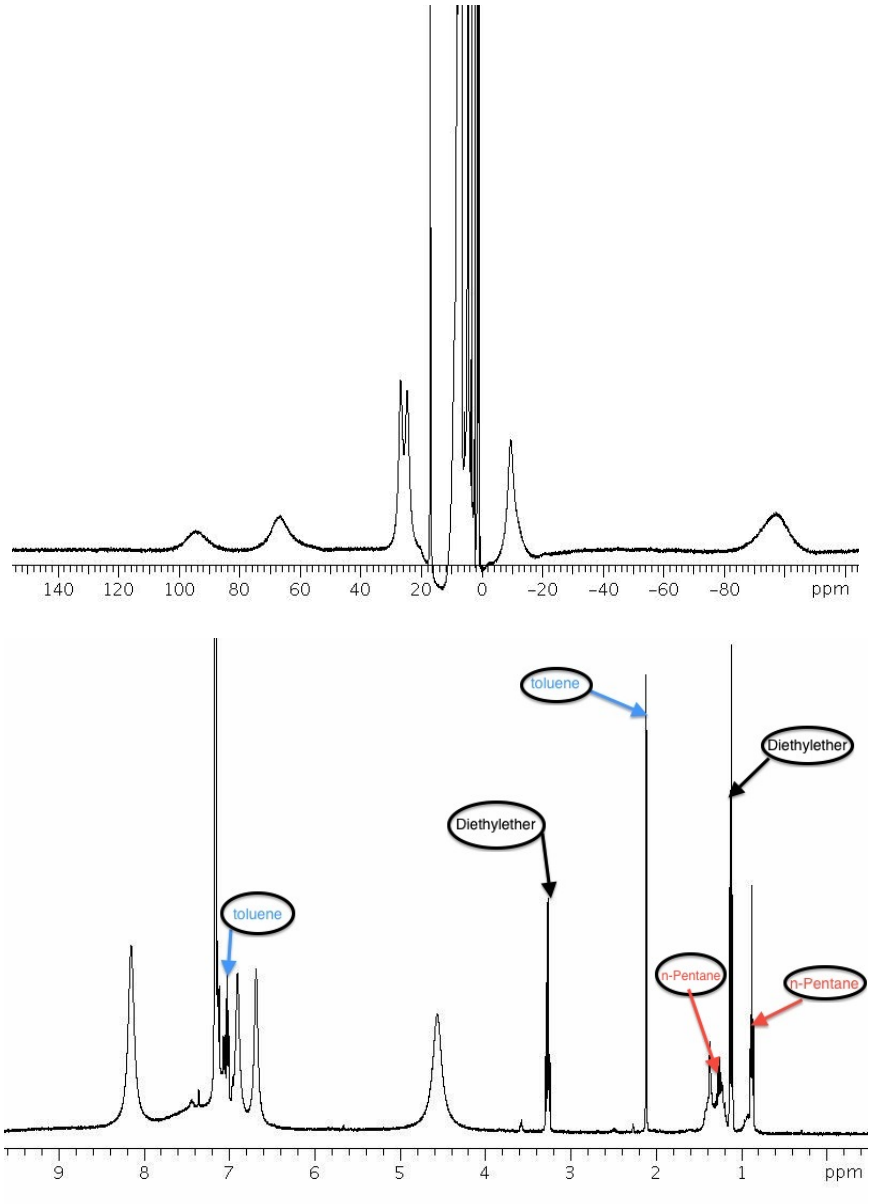


Figure S3. ^{1}H NMR spectrum of **2** in benzene-d_6 at 23 °C.

General procedure for silane screening: In the glovebox, an ambient temperature benzene-d_6 (approximately 0.7 mL) solution of silane (0.3 mmol) and cyclohexanone (0.030 mL, 0.3 mmol) was added to a 20 mL scintillation vial containing 2 mg (0.003 mmol) of complex **2**. The resulting brown solution was stirred for 4 min and then exposed to air to deactivate the catalyst. The colorless solution was then filtered through Celite directly into an NMR tube. The progress of the reaction was determined following analysis by ^{1}H NMR spectroscopy.

General procedure for hydrosilylation of ketones: An ambient temperature benzene-d_6 (0.7 mL) solution of $PhSiH_3$ (0.33 mmol) and ketone (0.33 mmol) was added to a vial containing 0.0033 mmol of **2**. The resulting brown solution was then transferred into a J. Young tube and the progress of the reaction was monitored by NMR spectroscopy at ambient temperature. In the case of acetophenone and substituted acetophenones, enantiomeric product mixtures were observed. A control experiment was performed in a similar fashion by adding 0.3 mmol of $PhSiH_3$ and 0.3 mmol of acetophenone to 0.7 mL of benzene-d_6 in the absence of complex **2**. The solution was monitored by ^{1}H NMR spectroscopy over time and no reaction was observed after 24 h at room temperature.

NMR scale hydrosilylation of acetophenone: In the glovebox, a benzene-d_6 (0.7 mL) solution of $PhSiH_3$ (27.6 μL, 0.224 mmol) and acetophenone (26.2 μL, 0.224 mmol) was added to a 20 mL scintillation vial containing 1.5 mg (0.00224 mmol) of complex **2**. The resulting brown solution was stirred for 4 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and analyzed by NMR spectroscopy. Complete disappearance of the acetophenone resonances was observed along with the formation of

$PhSiH(OCH(Me)(Ph))_2$[5] (75%) and $PhSi(OCH(Me)(Ph))_3$[6] (25%). The product ratio was determined upon integrating the peaks at 5.02 ppm [$PhSiH(OCH(Me)(Ph))_2$] and 5.19 ppm [$PhSi(OCH(Me)(Ph))_3$]. Unreacted $PhSiH_3$ was observed at 7.38, 7.07 and 4.23 ppm.

$PhSiH(OCH(Me)(Ph))_2$: ^{1}H NMR (benzene-d_6): 7.72 (m, 2H, *phenyl*), 7.25 (m, 4H *phenyl*), 7.15 (m, 9H, phenyl), 5.28 (s, 1H, Si*H*), 5.02 (m, 2H, C*H*), 1.40 (m, 6H, CH_3).

$PhSi(OCH(Me)(Ph))_3$: ^{1}H NMR (benzene-d_6): 7.80 (m, *phenyl*), 7.23 (m, *phenyl*), 7.20-7.10 (m, *phenyl*), 5.19 (m, C*H*MePh), 1.36 (m, CH_3).

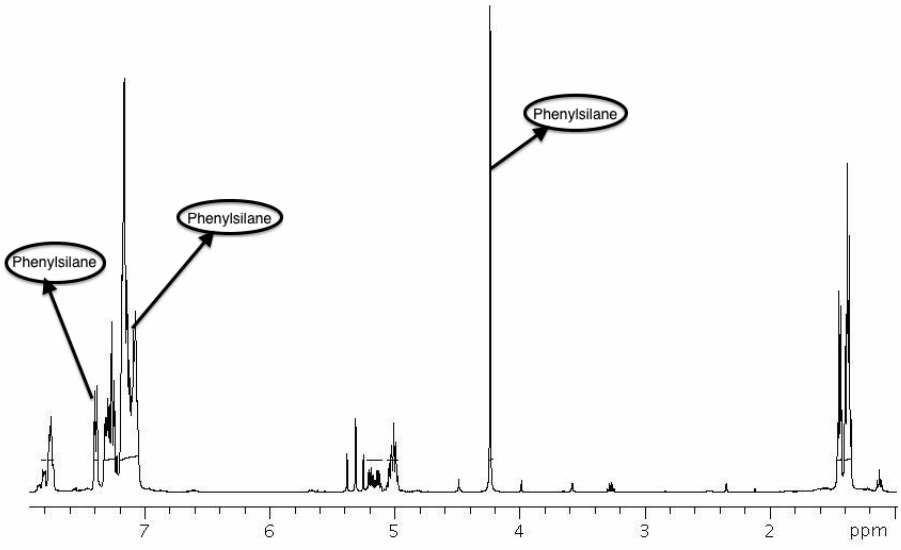


Figure S4. ^{1}H NMR spectrum of **2**-catalyzed (1 mol%) acetophenone hydrosilylation with $PhSiH_3$ in benzene-d_6 solution.

Neat hydrosilylation of acetophenone (0.1 mol% catalyst loading): In the glovebox, a mixture of $PhSiH_3$ (922 μL, 7.48 mmol), and acetophenone (874 μL, 7.48 mmol) was added to a 20 mL scintillation vial containing 5 mg (0.00748 mmol) of complex **2**. The mixture was then stirred vigorously and significant heat generation was noticed. After 4 min the mixture was exposed to air to deactivate the catalyst. The resulting colorless solution was filtered through Celite and analysis by ^{1}H NMR spectroscopy revealed the complete conversion of acetophenone into a

mixture of $PhSiH(OCH(Me)(Ph))_2$ (83%) and $PhSi(OCH(Me)(Ph))_3$ (17%). The product ratio was determined upon integrating the peaks at 5.02 ppm [$PhSiH(OCH(Me)(Ph))_2$] and 5.19 ppm [$PhSi(OCH(Me)(Ph))_3$].

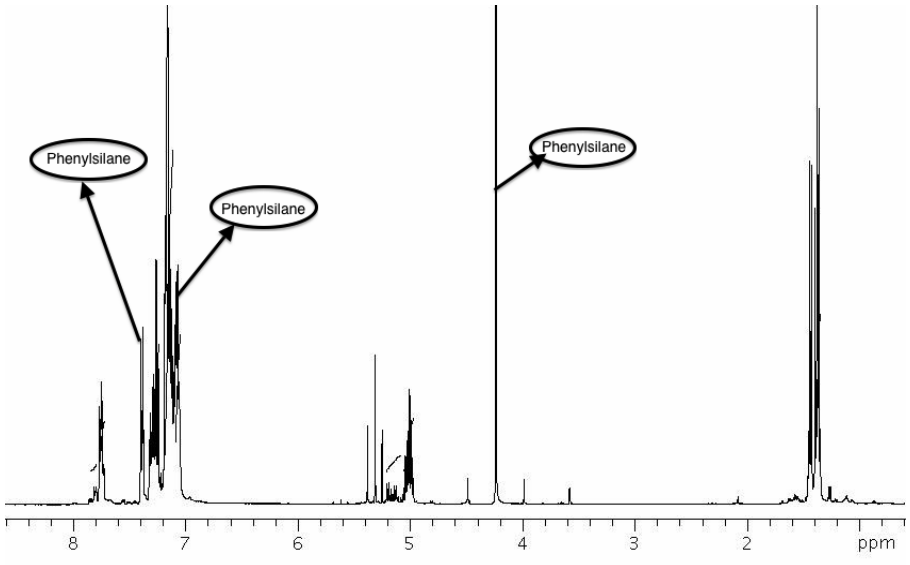


Figure S5. ^{1}H NMR spectrum of **2**-catalyzed (0.1 mol%) acetophenone hydrosilylation with $PhSiH_3$ in the absence of solvent.

Atom-efficient hydrosilylation of acetophenone: In the glovebox, a benzene-d_6 (0.7 mL) solution of $PhSiH_3$ (33.2 μL, 0.269 mmol) and acetophenone (94.4 μL, 0.808 mmol) was added to a vial containing 1.8 mg (0.00269 mmol) of complex **2**. The resulting brown solution was transferred into a J. Young tube and the progress of the reaction was monitored by ^{1}H NMR spectroscopy. Complete conversion to $PhSi(OCH(Me)(Ph))_3$ was observed after 6.5 h at room temperature.

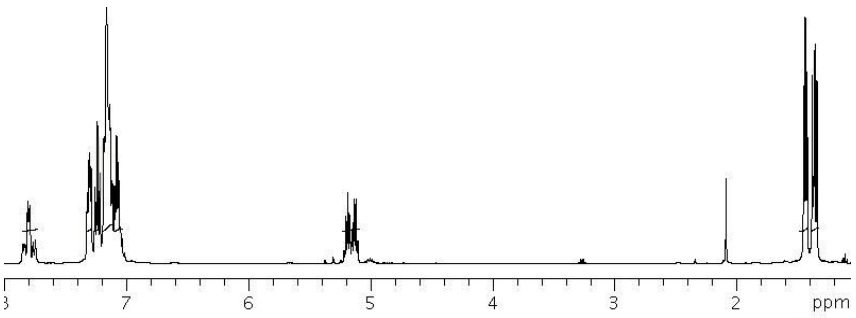


Figure S6. ^{1}H NMR spectrum of **2**-catalyzed (0.33 mol%) acetophenone hydrosilylation with 0.33 eq. of $PhSiH_3$ in benzene-d_6 solution.

NMR scale hydrosilylation of 4'-dimethylaminoacetophenone: In the glovebox, a benzene-d_6 (0.7 mL) solution of $PhSiH_3$ (33.2 μL, 0.269 mmol) and 4'-dimethylaminoacetophenone (43.9 mg, 0.269 mmol) was added to a vial containing 1.8 mg (0.00269 mmol) of complex **2**. The brown solution was then transferred into a J. Young tube and the progress of reaction was monitored by NMR spectroscopy. The resonance observed at 5.15 ppm revealed the complete conversion of 4'-dimethylaminoacetophenone to $PhSiH(OCH(Me)(p\text{-}NMe_2C_6H_4))_2$ after 6 h at room temperature. Unreacted $PhSiH_3$ was also observed at 7.38, 7.07, and 4.23 ppm.

$PhSiH(OCH(Me)(p\text{-}NMe_2C_6H_4))_2$: ^{1}H NMR (benzene-$d_6$): 7.85 (m, 2H, *phenyl*), 7.33 (m, 4H, *phenyl*), 7.19 (m, 3H, *phenyl*), 6.60 (m, 4H, *phenyl*), 5.41 (s, 1H Si*H*), 5.15 (m, 2H, C*H*), 2.53 (12H, *NMe_2*), 1.55 (d, $J_{H\text{-}H}$ = 6.2 Hz, 6H, C*H_3*).

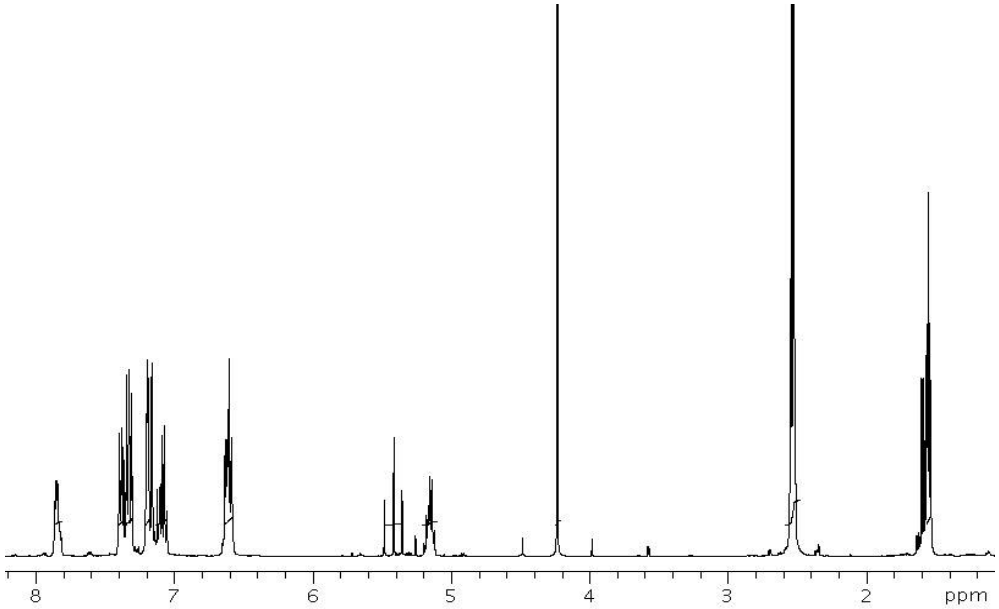


Figure S7. ^{1}H NMR spectrum of **2**-catalyzed (1 mol%) 4'-dimethylaminoacetophenone hydrosilylation with $PhSiH_3$ in benzene-d_6 solution.

NMR scale hydrosilylation of *p*-methoxyacetophenone: In the glovebox, a benzene-d_6 (0.7 mL) solution of $PhSiH_3$ (46.1 μL, 0.374 mmol) and *p*-methoxyacetophenone (56.1 μL, 0.374 mmol) was added to a vial containing 2.5 mg (0.00374 mmol) of complex **2**. The brown solution was then transferred into a J. Young tube and the progress of reaction was monitored by NMR spectroscopy. Complete conversion to a mixture of $PhSiH(OCH(Me)(p\text{-}OMeC_6H_4))_2$ (80%) and $PhSi(OCH(Me)(p\text{-}OMeC_6H_4))_3$ (20%) was observed after 25 min by ^{1}H NMR spectroscopy. The product ratio was determined from the integration of the resonances at 5.04 ppm [$PhSiH(OCH(Me)(p\text{-}OMeC_6H_4))_2$] and 5.20 ppm [$PhSi(OCH(Me)(p\text{-}OMeC_6H_4))_3$].

$PhSiH(OCH(Me)(p\text{-}OMeC_6H_4))_2$: ^{1}H NMR (benzene-$d_6$): 7.78 (m, 2H, *phenyl*), 7.20-7.10 (m, 6H, *phenyl*), 6.77 (m, 5H, *phenyl*), 5.33 (s, 1H Si*H*), 5.04 (m, 2H, C*H*), 3.33 (s, 6H, OCH_3), 1.44 (m, 6H, CH_3).

$PhSi(OCH(Me)(p\text{-}OMeC_6H_4))_3$: ^{1}H NMR (benzene-$d_6$, selected resonances): 5.20 (m, 3H, C*H*), 1.51 (m, 9H, CH_3).

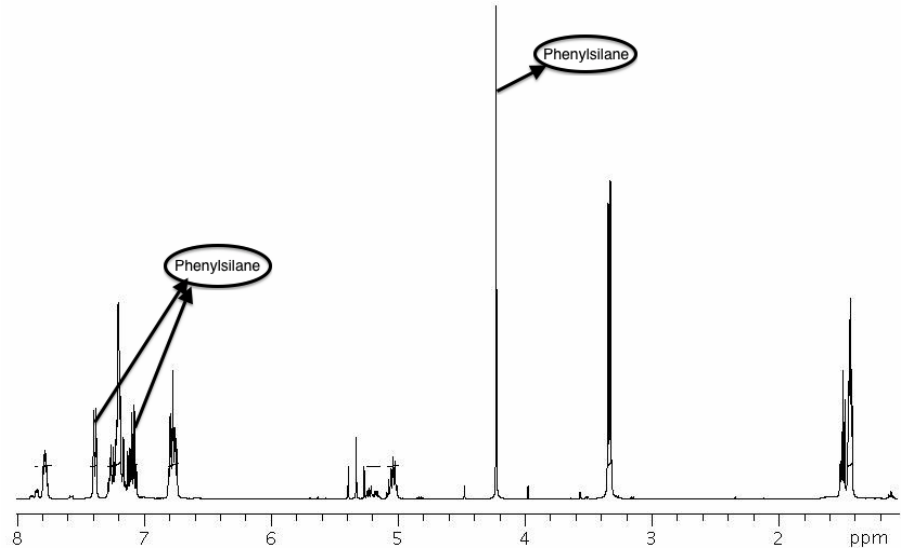


Figure S8. ^{1}H NMR spectrum of **2**-catalyzed (1 mol%) *p*-methoxyacetophenone hydrosilylation with $PhSiH_3$ in benzene-d_6 solution.

NMR scale hydrosilylation of *p*-fluoroacetophenone: In the glovebox, a benzene-d_6 (0.7 mL) solution of $PhSiH_3$ (20.3 μL, 0.165 mmol) and *p*-fluoroacetophenone (19.9 μL, 0.165 mmol) was added to a vial containing 1.1 mg (0.00165 mmol) of complex **2**. The brown solution was then transferred to a J. Young tube and the progress of reaction was monitored via ^{1}H NMR spectroscopy. Complete conversion to a mixture of $PhSiH(OCH(Me)(p\text{-}F\text{-}C_6H_4))_2$ (87%) and $PhSi(OCH(Me)(p\text{-}F\text{-}C_6H_4))_3$ (13%) was identified after 4 h by ^{1}H NMR spectroscopy. The product ratio was determined upon integrating the resonances at 4.85 ppm [$PhSiH(OCH(Me)(p\text{-}F\text{-}C_6H_4))_2$] and 5.01 ppm [$PhSi(OCH(Me)(p\text{-}F\text{-}C_6H_4))_3$]. Unreacted $PhSiH_3$ was also observed at 7.38, 7.07 and 4.23 ppm.

$PhSiH(OCH(Me)(p\text{-}F\text{-}C_6H_4))_2$: ^{1}H NMR (benzene-$d_6$): 7.69 (m, 2H, *phenyl*), 7.19 (m, 3H, *phenyl*), 6.98 (m, 4H, *phenyl*), 6.77 (m, 4H, *phenyl*), 5.22 (s, 1H, Si*H*), 4.85 (m, 2H C*H*), 1.28 (d, $J_{H\text{-}H}$ = 6.5 Hz, 6H, CH_3).

$PhSi(OCH(Me)(p\text{-}F\text{-}C_6H_4))_3$: ^{1}H NMR (benzene-$d_6$, selected resonance): 5.01 (m, 3H, C*H*).

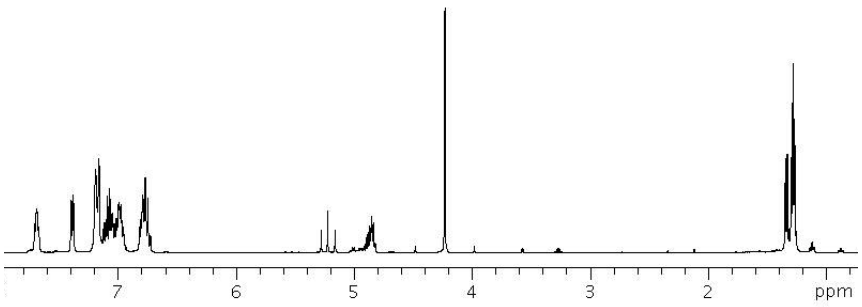


Figure S9. ^{1}H NMR spectrum of **2**-catalyzed (1 mol%) *p*-fluoroacetophenone hydrosilylation with $PhSiH_3$ in benzene-d_6 solution.

NMR scale hydrosilylation of 2',3',4',5',6'-pentafluoroacetophenone: In the glovebox, a benzene-d_6 (0.7 mL) solution of $PhSiH_3$ (22.1 μL, 0.179 mmol) and 2',3',4',5',6'-

pentafluoroacetophenone (25.5 μL, 0.179 mmol) was added to a vial containing 1.2 mg (0.00179 mmol) of complex **2**. The brown solution was then transferred into a J. Young tube and the progress of the reaction was monitored by ^{1}H NMR spectroscopy. Complete conversion to a mixture of PhSiH(OCH(Me)(C_6F_5))$_2$ (75%) and PhSi(OCH(Me)(C_6F_5))$_3$ (25%) was observed after 3.5 h. The product ratio was determined upon integrating the proton resonances at 5.26 ppm [PhSiH(OCH(Me)(C_6F_5))$_2$] and 5.42 ppm [PhSi(OCH(Me)(C_6F_5))$_3$].

PhSiH(OCH(Me)(C_6F_5))$_2$: ^{1}H NMR (benzene-d_6): 7.54 (m, 2H, *phenyl*), 7.12-7.09 (m, 3H, *phenyl*), 5.26 (m, 2H, C*H*), 5.09 (s, 1H, Si*H*), 1.38 (d, $J_{H\text{-}H}$ = 6.4 Hz, 6H, CH_3). *PhSi(OCH(Me)(C_6F_5))$_3$*: ^{1}H NMR (benzene-d_6): 7.59 (m, 2H, *phenyl*), 7.15-7.12 (m, 3H *phenyl*), 5.42 (m, 3H, C*H*), 1.33 (d, $J_{H\text{-}H}$ = 6.4 Hz, 9H, CH_3).

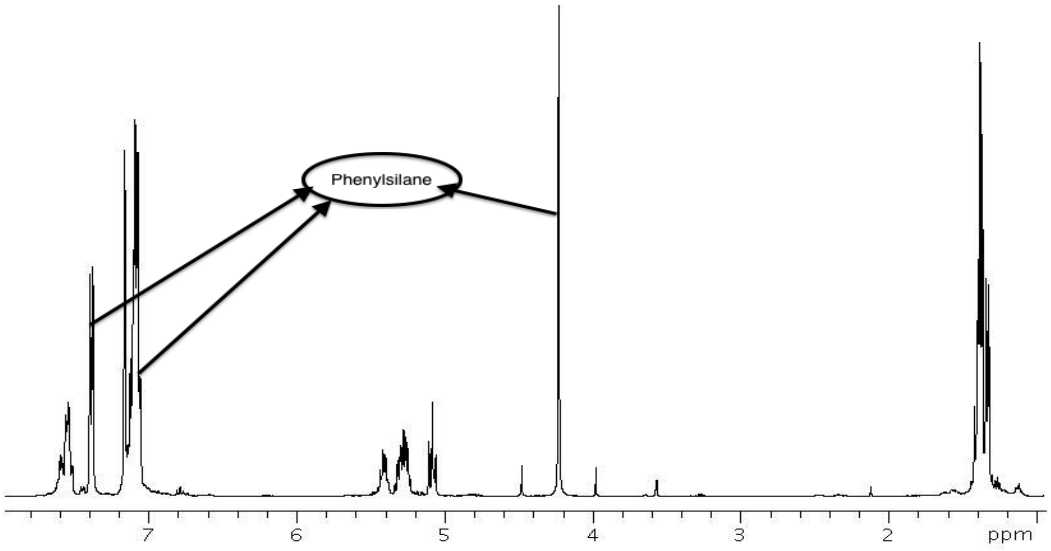


Figure S10. ^{1}H NMR spectrum of **2**-catalyzed (1 mol%) 2',3',4',5',6'-pentafluoroacetophenone hydrosilylation with $PhSiH_3$ in benzene-d_6 solution.

NMR scale hydrosilylation of 2,2,2-trifluoroacetophenone: In the glovebox, a benzene-d_6 (0.7 mL) solution of $PhSiH_3$ (64.6 μL, 0.523 mmol) and 2,2,2-trifluoroacetophenone (71.2 μL, 0.523

mmol) was added to a vial containing 3.5 mg (0.00523 mmol) of complex **2**. The solution, which had turned blue in color, was transferred into a J. Young tube. No reaction was observed within 6 h, after which time the solution became brown in color. A ^{1}H NMR spectrum collected after 12 h revealed complete conversion to an enantiomeric mixture of $PhSi(OCH(CF_3)(Ph))_3$. Unreacted $PhSiH_3$ was found at 7.38, 7.07, and 4.23 ppm. Complete conversion was detected by comparing the aromatic peaks of $PhSi(OCH(CF_3)(Ph))_3$ with those of the starting material.

$PhSi(OCH(CF_3)(Ph))_3$: ^{1}H NMR (benzene-d_6): 7.62 (m, 2H, *phenyl*), 7.24 (m, 4H, *phenyl*), 7.03 (m, 8H, *phenyl*), 6.96 (m, 6H, *phenyl*), 5.20 (m, 3H, OC*H*, enantiomeric mixture).

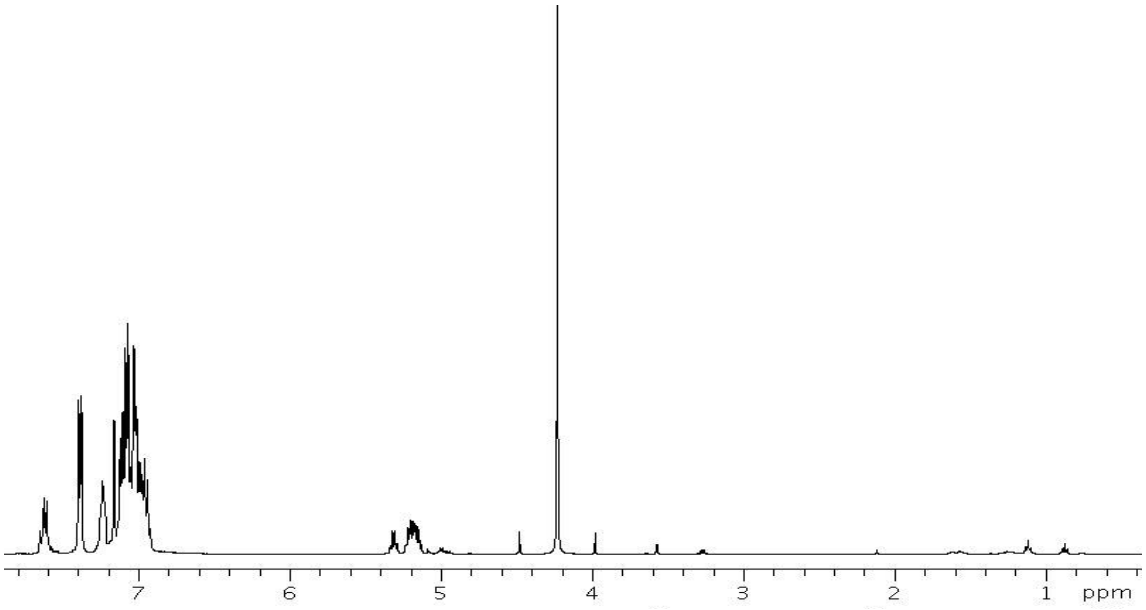


Figure S11. ^{1}H NMR spectrum of **2**-catalyzed (1 mol%) 2,2,2-trifluoroacetophenone hydrosilylation with $PhSiH_3$ in benzene-d_6 solution.

NMR scale hydrosilylation of benzophenone: In the glovebox, a benzene-d_6 (0.7 mL) solution of $PhSiH_3$ (36.9 μL, 0.299 mmol) and benzophenone (54.5 mg, 0.299 mmol) was added to a vial containing 2 mg (0.00299 mmol) of complex **2**. The brown solution was then transferred into a J. Young tube and the progress of the reaction was monitored. ^{1}H NMR spectroscopy revealed

complete conversion after 20 min at room temperature to a mixture of $PhSiH(OCH(Ph)_2)_2$ (87%) and $PhSi(OCH(Ph)_2)_3$ (13%). The product ratio was determined upon integrating the resonances at 5.94 ppm [$PhSi(OCH(Ph)_2)_3$] and 6.05 ppm [$PhSi(OCH(Ph)_2)_3$]. Unreacted $PhSiH_3$ was found at 7.38, 7.07, and 4.23 ppm.

$PhSiH(OCH(Ph)_2)_2$: ^{1}H NMR (benzene-d_6): 7.68 (d, $J_{H\text{-}H}$ = 7.1 Hz, 2H, *phenyl*), 7.30 (d, $J_{H\text{-}H}$ = 7.1 Hz, 8H, *phenyl*), 7.11-7.08 (m, 8H, *phenyl*), 7.05-7.08 (m, 3H, *phenyl*), 7.03 (m, 4H, *phenyl*) 5.94 (s, 2H, C*H*), 5.36 (s, 1H, Si*H*).

$PhSi(OCH(Ph)_2)_3$: ^{1}H NMR (benzene-d_6, selected resonance): 6.05 (s, 3H, C*H*).

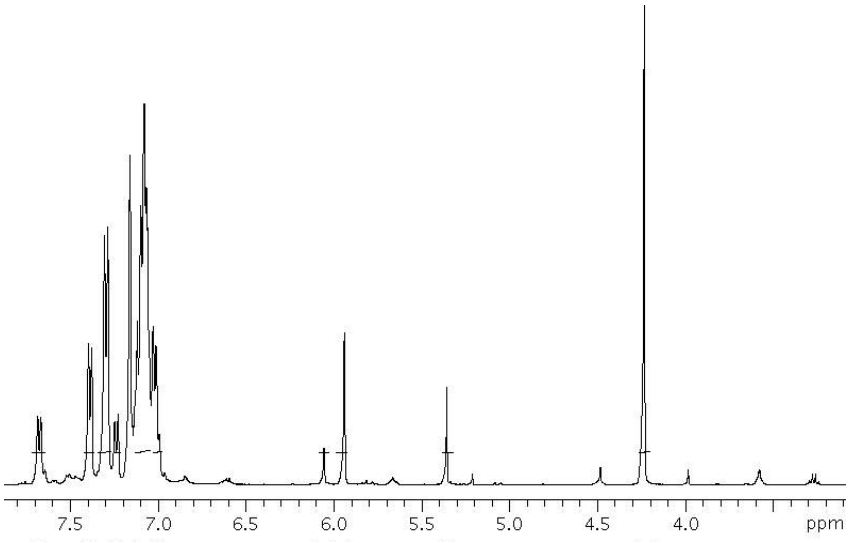


Figure S12. ^{1}H NMR spectrum of **2**-catalyzed (1 mol%) benzophenone hydrosilylation with $PhSiH_3$ in benzene-d_6 solution.

NMR scale hydrosilylation of 2',4',6'-trimethylacetophenone: In the glovebox, a benzene-d_6 (0.7 mL) solution of $PhSiH_3$ (40.6 μL, 0.329 mmol) and 2',4',6'-trimethylacetophenone (54.7 μL, 0.329 mmol) was added to a vial containing 2.2 mg (0.00329 mmol) of complex **2**. The brown solution was then transferred into a J. Young tube and the progress of reaction was monitored over time. After 5 d at room temperature, analysis by ^{1}H NMR spectroscopy revealed 80%

conversion along with the formation of $PhSiH(OCH(Me)(Mes))_2$ as the only product. Unreacted $PhSiH_3$ was observed at 4.23 ppm.

$PhSiH(OCH(Me)(Mes))_2$: ^{1}H NMR (benzene-d_6): 7.69 (m, 2H, *phenyl*), 7.14-7.09 (m, 3H, *phenyl*), 6.68 (s, 4H, *Mes*), 5.51 (m, 2H, C*H*), 5.21 (s, 1H, Si*H*), 2.30 (m, 12H, *o*-CH_3), 2.11 (m, 6H, *p*-CH_3), 1.45 (d, $J_{H\text{-}H}$ = 6.6 Hz, 6H, CH_3).

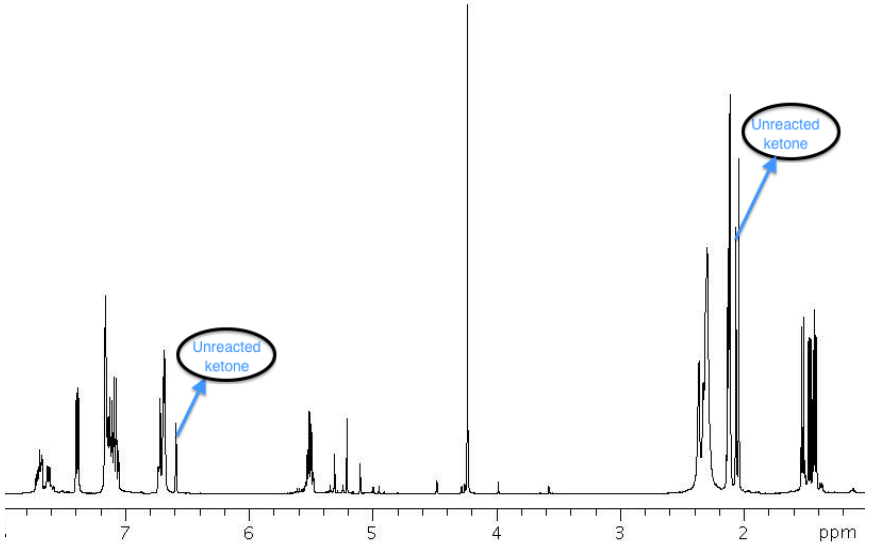


Figure S13. ^{1}H NMR spectrum of **2**-catalyzed (1 mol%) 2',4',6'-trimethylacetophenone hydrosilylation with $PhSiH_3$ in benzene-d_6 solution.

NMR scale hydrosilylation of 2,4-dimethyl-3-pentanone (1 mol% catalyst): In the glovebox a benzene-d_6 (0.7 mL) solution of $PhSiH_3$ (47.9 μL, 0.389 mmol) and 2,4-dimethyl-3-pentanone (33.9 μL, 0.389 mmol) was added to a vial containing 2.6 mg (0.00389 mmol) of complex **2**. The brown solution was transferred to a J. Young tube and sealed. ^{1}H NMR spectroscopy revealed complete conversion to form $PhSiH_2(OCH(^iPr)_2)$ (82%) and $PhSiH(OCH(^iPr)_2)_2$ (18%) after 36 min at room temperature. The product ratio was determined upon integrating the resonances at 3.14 ppm [$PhSiH_2(OCH(^iPr)_2$] and 3.36 ppm [$PhSiH(OCH(^iPr)_2)_2$]. Unreacted $PhSiH_3$ was identified at 7.38, 7.07, and 4.23 ppm.

^{1}H NMR (benzene-d_6): 7.76 (m, 2H, *phenyl*), 7.66 (m, 2H, *phenyl*), 7.20 (m, 3H, *phenyl*), 7.18 (m, 3H, *phenyl*), 5.37 (s, 1H, PhSi*H*(OCH(^{i}Pr)$_2$)$_2$), 5.33 (s, 2H, PhSi*H*$_2$(OCH(^{i}Pr)$_2$)), 3.36 (t, J_{H-H} = 5.4 Hz, 2H, PhSiH(OC*H*(^{i}Pr)$_2$)$_2$), 3.14 (t, J_{H-H} = 5.4 Hz, 1H, PhSiH$_2$(OC*H*(^{i}Pr)$_2$), 1.80 (m, 2H, C*H*), 1.74 (m, 4H, C*H*), 1.09 (d, J_{H-H} = 6.5 Hz, 6H, C*H*$_3$), 0.94 (m, 18H, C*H*$_3$), 0.81 (m, 12H, C*H*$_3$).

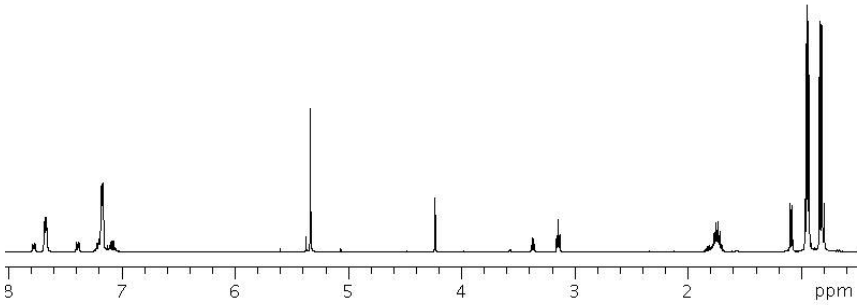


Figure S14. ^{1}H NMR spectrum of **2**-catalyzed (1 mol%) diisopropyl ketone hydrosilylation with $PhSiH_3$ in benzene-d_6 solution.

Atom-efficient hydrosilylation of 2,4-dimethyl-3-pentanone: In the glovebox, a benzene-d_6 (0.7 mL) solution of $PhSiH_3$ (44.3 μL, 0.359 mmol) and 2,4-dimethyl-3-pentanone (101.7 μL, 0.718 mmol) was added to a vial containing 2.4 mg (0.00359 mmol) of complex **2**. The resulting brown solution was transferred to a J. Young tube and the progress of the reaction was monitored over time by NMR spectroscopy. Complete conversion to a mixture of PhSiH(OCH(^{i}Pr)$_2$)$_2$ (90%) and PhSiH$_2$(OCH(^{i}Pr)$_2$) (10%) was observed after 42 min at room temperature. The product ratio was determined upon integrating the silane proton resonances at 5.36 ppm [PhSiH(OCH(^{i}Pr)$_2$)$_2$] and 5.33 ppm [PhSiH$_2$(OCH(^{i}Pr)$_2$)].

PhSiH(OCH(^{i}Pr)$_2$)$_2$: ^{1}H NMR (benzene-d_6): 7.76 (m, 2H, *phenyl*), 7.20 (m, 3H, *phenyl*), 5.36 (s, 1H, Si*H*), 3.36 (t, J_{H-H} = 5.6 Hz, 2H, O*CH*), 1.80 (m, 4H, C*H*), 1.08 (d, J_{H-H} = 7.0 Hz, 6H, C*H*$_3$), 0.94 (m, 12H, C*H*$_3$), 0.80 (d, J_{H-H} = 7.0 Hz, 6H, C*H*$_3$).

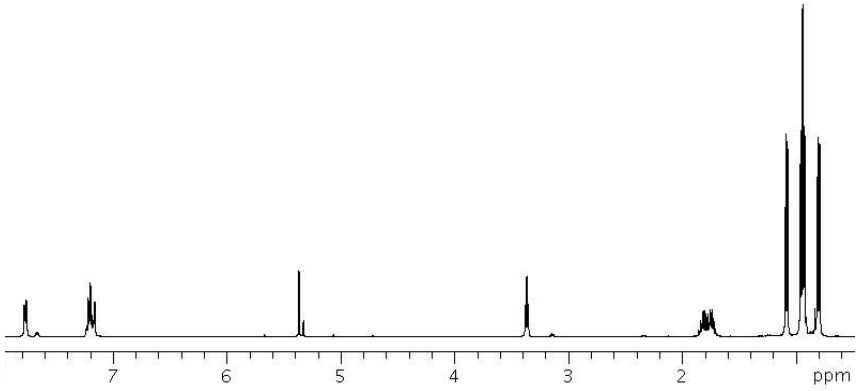


Figure S15. ^{1}H NMR spectrum of **2**-catalyzed (0.5 mol%) diisopropyl ketone hydrosilylation with 0.5 eq. of $PhSiH_3$ in benzene-d_6 solution.

NMR scale hydrosilylation of dicyclohexyl ketone: In the glovebox, a benzene-d_6 (0.7 mL) solution of $PhSiH_3$ (18.5 μL, 0.149 mmol) and dicyclohexyl ketone (30.3 μL, 0.149 mmol) was added to a vial containing 1 mg (0.00149 mmol) of complex **2**. The brown solution was transferred into a J. Young tube, which was sealed under N_2. ^{1}H NMR spectroscopy revealed complete conversion to a mixture of $PhSiH(OCH(Cy)_2)_2$ (75%) and $PhSiH_2(OCH(Cy)_2)$ (25%) after 24 h at room temperature. The product ratio was determined upon integrating the resonances at 3.47 ppm [$PhSiH(OCH(Cy)_2)_2$] and 3.25 ppm [$PhSiH_2(OC\mathit{H}(Cy)_2)$]. Unreacted $PhSiH_3$ was observed at 7.38, 7.07, and 4.23 ppm.

^{1}H NMR (benzene-d_6): 7.83 (m, 2H, *phenyl*), 7.71 (m, 2H, *phenyl*), 7.24 (m, 3H, *phenyl*), 7.19 (m, 3H, *phenyl*), 5.42 (s, 1H, $PhSi\mathit{H}(OCH(Cy)_2)_2$), 5.36 (s, 2H, $PhSi\mathit{H}_2(OCH(Cy)_2)$), 3.47 (t, $J_{H\text{-}H}$ = 5.0 Hz, 2H, $PhSiH(OC\mathit{H}(Cy)_2)_2$), 3.25 (t, $J_{H\text{-}H}$ = 5.0 Hz, 1H, $PhSiH_2(OC\mathit{H}(Cy)_2)$), 2.12 (m), 1.96 (m), 1.84 (m), 1.76-1.68 (broad m), 1.61 (m), 1.52 (m), 1.28-1.18 (m).

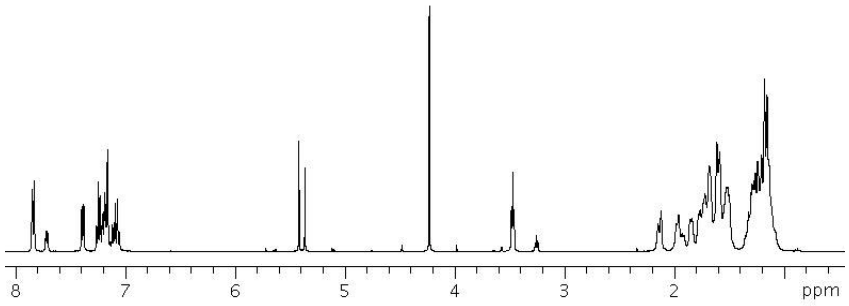


Figure S16. ^{1}H NMR spectrum of **2**-catalyzed (1 mol%) dicyclohexyl ketone hydrosilylation with $PhSiH_3$ in benzene-d_6 solution.

NMR scale hydrosilylation of cyclohexanone: In the glovebox, a benzene-d_6 (0.7 mL) solution of $PhSiH_3$ (18.5 μL, 0.149 mmol) and cyclohexanone (15 μL, 0.149 mmol) was added to a vial containing 1 mg (0.00149 mmol) of complex **2**. The brown solution was stirred for 4 min and then exposed to air to deactivate the catalyst. The resulting colorless solution was then filtered through a Celite column directly into an NMR tube. After 4 min at room temperature, analysis by ^{1}H NMR spectroscopy revealed complete conversion along with the formation of $PhSiH(OCy)_2$.[7] Unreacted $PhSiH_3$ was observed at 7.38, 7.07, and 4.23 ppm.

$PhSiH(OCy)_2$: ^{1}H NMR (benzene-d_6): 7.86 (m, 2H, *phenyl*), 7.22 (m, 3H, *phenyl*), 5.38 (s, 1H, Si*H*), 3.99 (m, 2H, C*H*), 1.88 (m, 4H, CH_2), 1.65 (m, 4H, CH_2), 1.53 (m, 4H, CH_2), 1.32 (m, 2H, CH_2), 1.12 (m, 6H, CH_2).

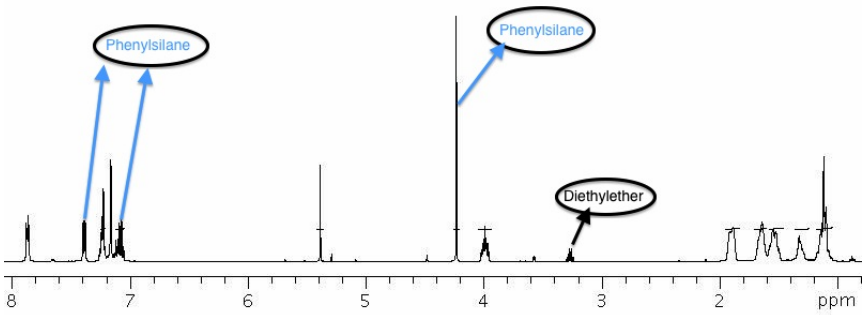


Figure S17. ^{1}H NMR spectrum of **2**-catalyzed (1 mol%) cyclohexanone hydrosilylation with $PhSiH_3$ in benzene-d_6 solution.

Neat hydrosilylation of cyclohexanone (0.01 mol% catalyst loading): In the glovebox, a mixture of $PhSiH_3$ (6.46 mL, 52.34 mmol) and cyclohexanone (5.42 mL, 52.34 mmol) was added to a 250 mL round-bottom flask containing 3.5 mg (0.00523 mmol) of complex **2**. Heat generation was noticed during the addition. The mixture was stirred vigorously for 5 minutes, after which time the solution was exposed to air to deactivate the catalyst. The resulting colorless organic solution was filtered through Celite and the excess silane was removed from the product by rotary evaporation. $PhSiH(O(Cy))_2$[7] (64%) was isolated as the only hydrosilylated product as confirmed by ^{1}H and ^{13}C NMR spectroscopy.

PhSiH(OCy)$_2$: ^{1}H NMR (benzene-d_6): 7.86 (m, 2H, *phenyl*), 7.22 (m, 3H, *phenyl*), 5.38 (s, 1H, Si*H*), 3.99 (m, 2H, C*H*), 1.88 (m, 4H, C*H$_2$*), 1.65 (m, 4H, C*H$_2$*), 1.53 (m, 4H, C*H$_2$*), 1.32 (m, 2H, C*H$_2$*), 1.12 (m, 6H, C*H$_2$*). ^{13}C NMR: δ: 135.48 (*C*, *phenyl*), 134.93 (*C*H, *phenyl*), 130.99 (*C*H, *phenyl*), 128.59 (*C*H, *phenyl*), 72.44 (O*C*H, *Cy*), 36.24 (CH_2, *Cy*), 26.22 (CH_2, *Cy*), 24.49 (CH_2, *Cy*).

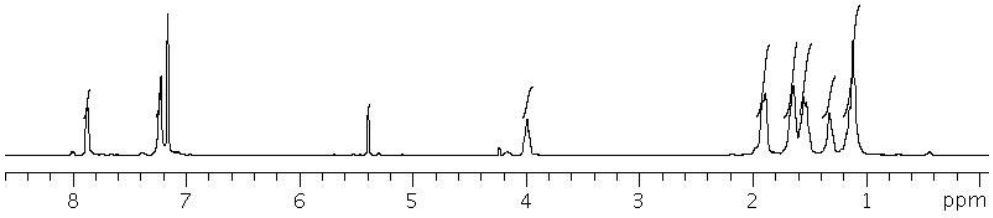


Figure S18. ^{1}H NMR spectrum of **2**-catalyzed (0.01 mol%) cyclohexanone hydrosilylation with $PhSiH_3$ in the absence of solvent.

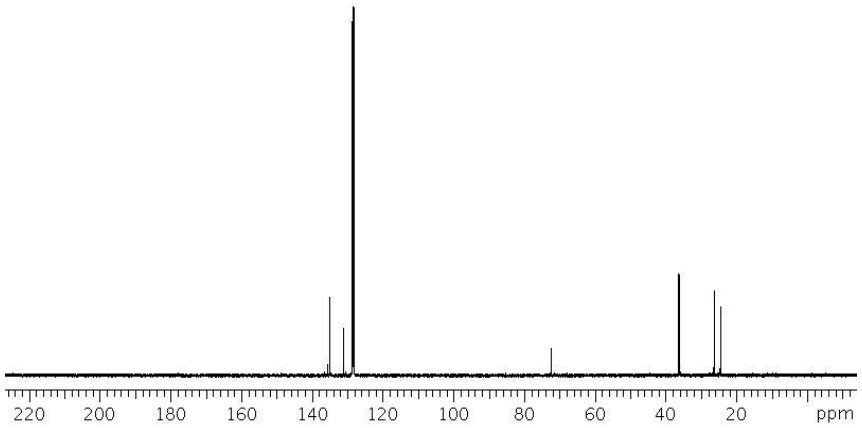


Figure S19. ^{13}C NMR spectrum of **2**-catalyzed (0.01 mol%) cyclohexanone hydrosilylation with $PhSiH_3$ in the absence of solvent.

Atom-efficient hydrosilylation of cyclohexanone: In the glovebox, a benzene-d_6 (0.7 mL) solution of $PhSiH_3$ (35.1 μL, 0.284 mmol) and cyclohexanone (85.9 μL, 0.852 mmol) was added to a vial containing 1.9 mg (0.00284 mmol) of complex **2**. The resulting brown solution was transferred into a J. Young tube and the progress of the reaction was monitored by NMR spectroscopy. Complete conversion to $PhSi(OCy)_3$[7] was observed after 4 h at room temperature.

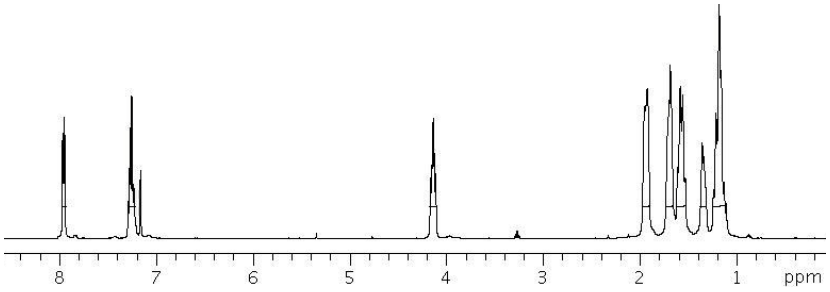


Figure S20. ^{1}H NMR spectrum of **2**-catalyzed (0.33 mol%) cyclohexanone hydrosilylation with 0.33 eq. of $PhSiH_3$ in benzene-d_6 solution.

NMR scale hydrosilylation of 2-hexanone (1 mol% catalyst): In the glovebox, a benzene-d_6 (0.7 mL) solution of $PhSiH_3$ (60.9 μL, 0.494 mmol) and 2-hexanone (60.9 μL, 0.494 mmol) was added to a vial containing 3.3 mg (0.00494 mmol) of complex **2**. The brown solution was stirred

for 4 min and then exposed to air to deactivate the catalyst. The resulting colorless solution was then filtered through Celite directly into an NMR tube. ^{1}H NMR spectroscopy revealed complete conversion after 4 min along with the formation of PhSiH(OCH(Me)(^{n}Bu))$_2$ as the only product. Unreacted $PhSiH_3$ was found at 7.38, 7.07, and 4.23 ppm.

PhSiH(OCH(Me)(^{n}Bu))$_2$: ^{1}H NMR (benzene-d_6): 7.81 (m, 2H, *phenyl*), 7.21 (m, 3H, *phenyl*), 5.32 (s, 1H, Si*H*), 4.08 (m, 2H, C*H*), 1.60 (m, 2H, CH_2), 1.40 (m, 4H, CH_2), 1.22 (m, 12H, CH_3), 0.87 (m, 6H, CH_2).

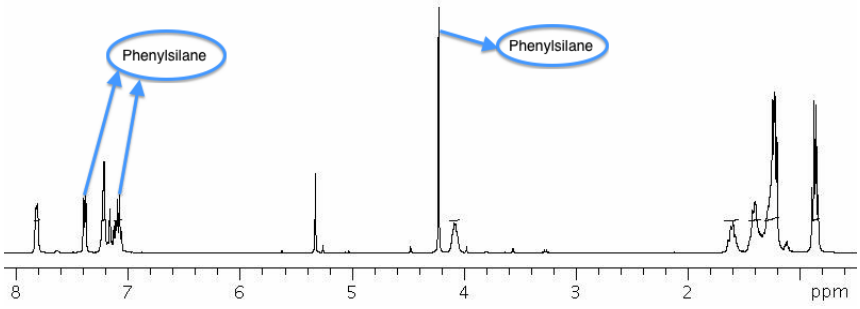


Figure S21. ^{1}H NMR spectrum of **2**-catalyzed (1 mol%) 2-hexanone hydrosilylation with $PhSiH_3$ in benzene-d_6 solution.

Neat hydrosilylation of 2-hexanone (0.01 mol% catalyst loading): In the glovebox, a mixture of $PhSiH_3$ (6.64 mL, 53.84 mmol), and cyclohexanone (6.65 mL, 53.84 mmol) was added to a 250 mL round-bottom flask containing 3.6 mg (0.00538 mmol) of complex **2**. The mixture was stirred vigorously for 5 minutes. During this time significant heat generation was noticed. After 5 minutes, the mixture was exposed to air to deactivate the catalyst. The resulting colorless organic solution was filtered through Celite and the excess silane was removed from the product by rotary evaporation. PhSiH(OCHMe(^{n}Bu))$_2$ (62%) was isolated as the only hydrosilylated product, as confirmed by ^{1}H and ^{13}C NMR spectroscopy.

^{1}H NMR (benzene-d_6): δ: *PhSiH(OCHMe(^{n}Bu))$_2$*: 7.81 (m, 2H, *phenyl*), 7.21 (m, 3H, *phenyl*), 5.32 (s, 1H, Si*H*), 4.08 (m, 2H, C*H*), 1.60 (m, 2H, CH_2), 1.40 (m, 4H, CH_2), 1.22 (m, 12H, CH_3), 0.87 (m, 6H, CH_2). ^{13}C NMR: δ: 135.40 (*C*, *phenyl*), 134.85 (*C*H, *phenyl*), 130.98 (*C*H, *phenyl*), 128.56 (*C*H, *phenyl*), 70.76 (O*C*H), 39.90 (*C*H_2), 28.53 (*C*H_2), 24.14 (*C*H_2), 23.43 (*C*H_3), 14.63 (*C*H_3).

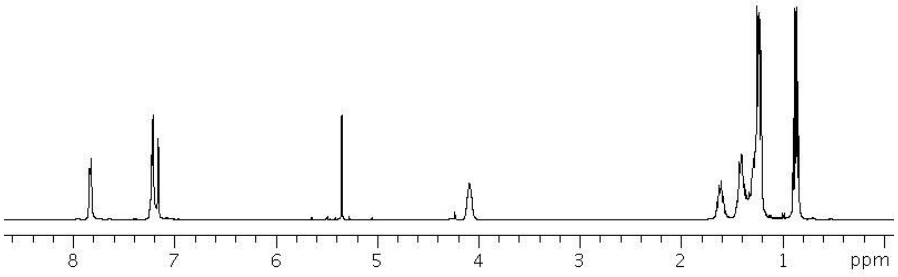


Figure S22. ^{1}H NMR spectrum of **2**-catalyzed (0.01 mol%) 2-hexanone hydrosilylation with $PhSiH_3$ in the absence of solvent.

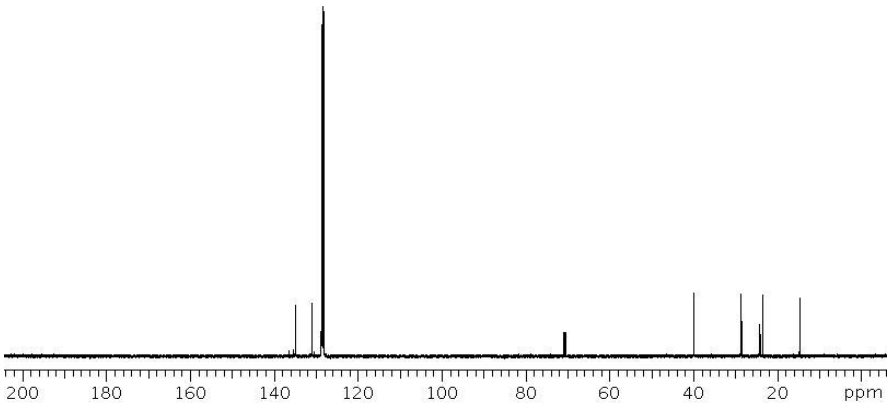


Figure S23. ^{13}C NMR spectrum of **2**-catalyzed (0.01 mol%) 2-hexanone hydrosilylation with $PhSiH_3$ in the absence of solvent.

Atom-efficient hydrosilylation of 2-hexanone: In the glovebox, a benzene-d_6 (0.7 mL) solution of $PhSiH_3$ (31.4 μL, 0.254 mmol) and 2-hexanone (94.1 μL, 0.762 mmol) was added to a vial containing 1.7 mg (0.00254 mmol) of complex **2**. The resulting brown solution was transferred

into a J. Young tube and the progress of the reaction was monitored over time. ^{1}H NMR spectroscopy revealed 74% conversion of 2-hexanone to a mixture of PhSiH(OCH(Me)(^{n}Bu))$_2$ (75%) and PhSi(OCH(Me)(^{n}Bu))$_3$ (25%) after 24 h at room temperature. The conversion of PhSiH(OCH(Me)(^{n}Bu))$_2$ to PhSi(OCH(Me)(^{n}Bu))$_3$ appeared to be slow under these conditions.

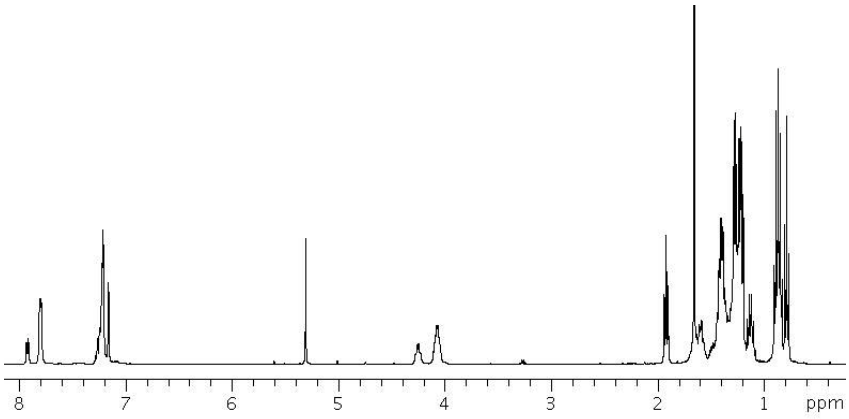


Figure S24. ^{1}H NMR spectrum of **2**-catalyzed (0.33 mol%) 2-hexanone hydrosilylation with 0.33 eq. of $PhSiH_3$ in benzene-d_6 solution.

NMR scale hydrosilylation of methyl acetate: In the glovebox, a benzene-d_6 solution (0.7 mL) of $PhSiH_3$ (73.8 μL, 0.598 mmol) and methyl acetate (47.5 μL, 0.598 mmol) was added to a 20 mL scintillation vial containing 4 mg (0.00598 mmol) of complex **2**. The resulting brown solution was then transferred into a J. Young tube and sealed under N_2. The progress of the reaction was monitored by ^{1}H NMR spectroscopy over time at room temperature. Complete conversion was observed after 24 h, as judged by the disappearance of starting material resonances. A mixture of products containing PhSi(OEt)$_2$(OMe) (35%), PhSi(OMe)$_3$ (26%), PhSi(OEt)$_3$ (21%), and PhSi(OEt)(OMe)$_2$ (18%) was identified by ^{1}H NMR spectroscopy. The product ratios were determined from the integration of ethyl CH_2 resonances at 3.87 ppm [PhSi(OEt)$_3$], 3.86 ppm [PhSi(OEt)$_2$(OMe)], and 3.77 ppm [PhSi(OEt)(OMe)$_2$]. The methyl proton resonances at 3.53 ppm, 3.51 ppm, and 3.50 ppm were also used.

^{1}H NMR (benzene-d_6): 7.81 (m), 7.24 (m), 7.19-7.13 (m), 3.87 (q, J_{H-H} = 6.8 Hz, 6H, CH_2 for PhSi(OEt)$_3$), 3.86 (q, J_{H-H} = 6.8 Hz, 4H, CH_2 for PhSi(OEt)$_2$(OMe)), 3.77 (q, J_{H-H} = 6.8 Hz, 2H, CH_2 for PhSi(OEt)(OMe)$_2$), 3.53 (s, CH_3), 3.51 (s, CH_3), 3.50 (s, CH_3), 1.20-1.15 (m), 1.13 (m). Unreacted phenylsilane was found at 7.38, 7.09 and 4.23 ppm. A trace of dihydrosilylated products PhSiH(OMe)$_2$ and PhSiH(OEt)$_2$ were also noticed.

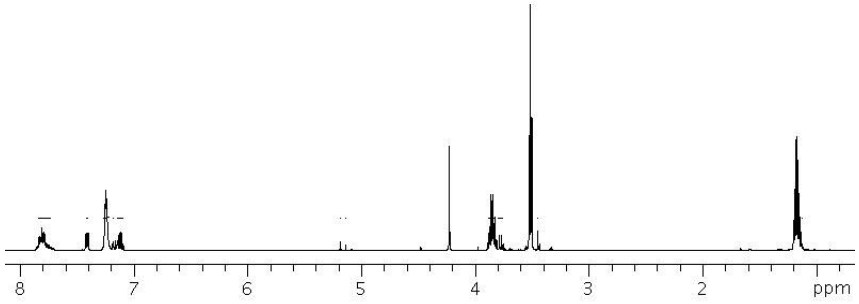


Figure S25. ^{1}H NMR spectrum of **2**-catalyzed (1 mol%) methyl acetate dihydrosilylation with PhSiH$_3$ in benzene-d_6 solution.

NMR scale hydrosilylation of ethyl acetate: In the glovebox, a benzene-d_6 solution (1 mL) of PhSiH$_3$ (44.3 μL, 0.359 mmol) and ethyl acetate (35.2 μL, 0.359 mmol) was injected into a 20 mL scintillation vial containing 2.4 mg (0.00359 mmol) of complex **2**. The resulting brown solution was then transferred into a J. Young tube and the progress of the reaction was monitored by ^{1}H NMR spectroscopy at room temperature. Complete conversion was observed after 5.5 h, as judged by the disappearance of ethyl acetate resonances and the identification of PhSi(OCH$_2$CH$_3$)$_3$ as the lone product.

PhSi(OCH$_2$CH$_3$)$_3$: ^{1}H NMR 400 MHz (benzene-d_6): 7.87 (m, 2H, *phenyl*), 7.23 (m, 3H, *phenyl*), 3.85 (q, J_{H-H} = 7.1 Hz, 6H, CH_2), 1.17 (t, J_{H-H} = 7.0 Hz, 9H, CH_3). A small amount of PhSiH$_3$ was found at 7.38, 7.07 and 4.23 ppm.

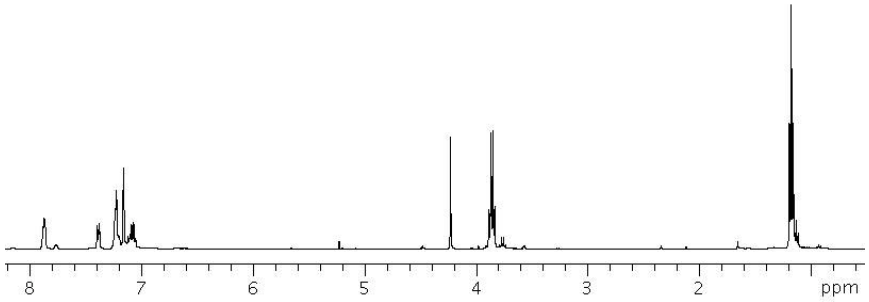


Figure S26. ^{1}H NMR spectrum of **2**-catalyzed (1 mol%) ethyl acetate dihydrosilylation with $PhSiH_3$ in benzene-d_6 solution.

NMR scale hydrosilylation of isopropyl acetate: In the glovebox, a benzene-d_6 solution (1 mL) of $PhSiH_3$ (55.3 μL, 0.449 mmol) and isopropyl acetate (52.6 μL, 0.449 mmol) was added to a 20 mL scintillation vial containing 3 mg (0.00449 mmol) of complex **2**. The resulting brown solution was then transferred to a J. Young tube and sealed under N_2. The progress of the reaction was monitored by NMR spectroscopy over time while the tube was heated at 80 ^{o}C. Complete conversion was observed after 3 days, as judged by the disappearance of isopropyl acetate ^{1}H NMR resonances. A mixture of products including $PhSi(OEt)_3$ (36%), $PhSiH(O^{i}Pr)_2$ (28%), $PhSiH(OEt)_2$ (18%), and $PhSi(O^{i}Pr)_3$ (18%) was observed by ^{1}H NMR spectroscopy. ^{1}H NMR (benzene-d_6): δ: 7.86 (m), 7.77 (m), 7.21 (m), 5.26 (s, Si*H*), 5.23 (s, Si*H*), 4.32 (m, C*H*, $O^{i}Pr$), 4.19 (m, C*H*, $O^{i}Pr$), 3.84 (q, CH_2, OEt), 3.75 (m, CH_2, OEt), 1.22-1.115 (m), 1.12 (m). Integration of the silane proton resonances at 5.26 ppm and 5.23 ppm along with ethyl peaks at 3.84 ppm and 3.75 ppm and the isopropyl CH peaks at 4.32 ppm and 4.19 ppm was used to determine the product ratios.

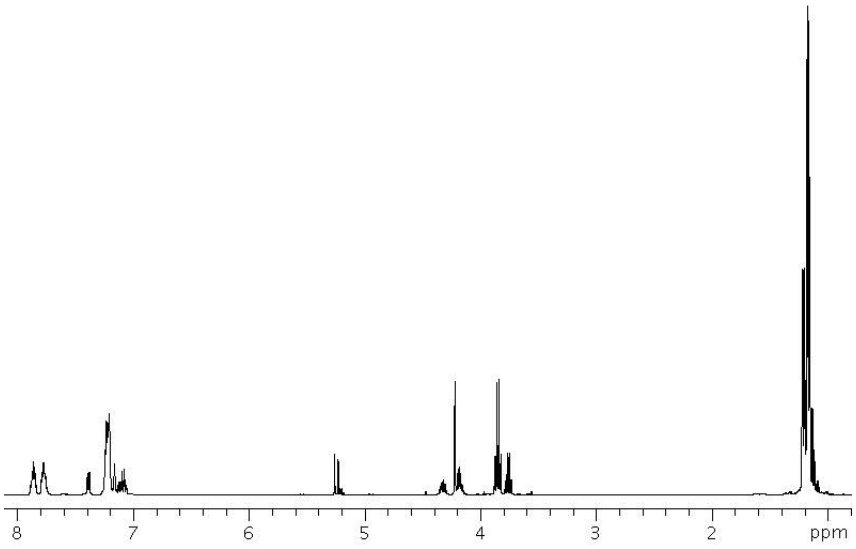


Figure S27. ^{1}H NMR spectrum of **2**-catalyzed (1 mol%) isopropyl acetate dihydrosilylation with $PhSiH_3$ in benzene-d_6 solution.

NMR scale hydrosilylation of phenyl acetate: In the glovebox, a benzene-d_6 solution (1 mL) of $PhSiH_3$ (44.3 μL, 0.359 mmol) and phenyl acetate (45.7 μL, 0.359 mmol) was added to a 20 mL scintillation vial containing 2.4 mg (0.00359 mmol) of complex **2**. The resulting brown solution was then transferred into a J. Young tube and the progress of the reaction was monitored by NMR spectroscopy over time at room temperature. After 10 d, 95% of the phenyl acetate had been hydrosilylated to form a mixture of products including $PhSi(OPh)_3$ (36%), $PhSi(OEt)_3$ (36%), and $PhSi(OEt)_2(OPh)$ (28%). Integration of the methyl resonances at 1.12 ppm [$PhSi(OEt)_3$] and 1.06 ppm [$PhSi(OEt)_2(OPh)$] along with the aromatic peaks at 7.15 ppm, 7.13 ppm and 7.03 ppm was used to determine the product ratio.

^{1}H NMR (benzene-d_6): 7.88 (m, *phenyl*), 7.15 (m, *phenyl*), 7.13 (m, *phenyl*), 7.03 (m, *phenyl*), 6.80 (m, *phenyl*), 3.87 (q, $J_{H\text{-}H}$ = 7.1 Hz, 6H, CH_2 for $PhSi(OEt)_3$), 3.86 (q, $J_{H\text{-}H}$ = 7.1 Hz, 4H, CH_2 for $PhSi(OEt)_2(OPh)$), 1.12 (t, $J_{H\text{-}H}$ = 6.8 Hz, 9H, CH_3 for $PhSi(OEt)_3$), 1.06 (t, $J_{H\text{-}H}$ = 6.8 Hz, 6H, CH_3 for $PhSi(OEt)_2(OPh)$).

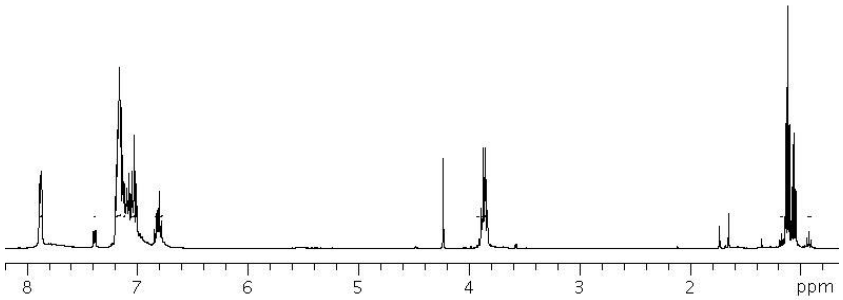


Figure S28. ^{1}H NMR spectrum of **2**-catalyzed (1 mol%) phenyl acetate dihydrosilylation with $PhSiH_3$ in benzene-d_6 solution.

NMR scale hydrosilylation of *tert*-butyl acetate: In the glovebox, a benzene-d_6 solution (1 mL) of $PhSiH_3$ (36.9 μL, 0.299 mmol) and *tert*-butylacetate (40.4 μL, 0.299 mmol) was added to a 20 mL scintillation vial containing 2 mg (0.00299 mmol) of complex **2**. The resulting brown solution was then transferred to a J. Young tube. The progress of the reaction was monitored by NMR spectroscopy over time while it was heated at 80 ^{o}C. After heating for 10 d, 85% of the *tert*-butylacetate had been transformed into mixture of products including $PhSiH(O^tBu)_2$ (36%), $PhSiH(OEt)(O^tBu)$ (36%), and $PhSi(OEt)_3$ (28%). Integration of the silane proton resonances at 5.46 ppm [$PhSiH(O^tBu)_2$] and 5.35 ppm [$PhSiH(OEt)(O^tBu)$] along with the ethyl CH_2 resonances at 3.85 ppm [$PhSi(OEt)_3$] and 3.73 ppm [$PhSiH(OEt)(O^tBu)$] was used to determine the product ratio.

^{1}H NMR (benzene-d_6): 7.88 (m, 2H, *phenyl*), 7.82 (m, 2H, *phenyl*), 7.79 (m, 2H, *phenyl*), 7.25-7.20 (m, 9H, *phenyl*), 5.46 (s, 1H, Si*H* for $PhSiH(O^tBu)_2$), 5.35 (s, 1H, Si*H* for $PhSiH(OEt)(O^tBu)$), 3.85 (q, $J_{H\text{-}H}$ = 6.8 Hz, 6H, C*H*$_2$ for $PhSi(OEt)_3$), 3.73 (q, $J_{H\text{-}H}$ = 6.8 Hz, 2H, C*H*$_2$ for $PhSiH(OEt)(O^tBu)$), 1.37 (s, 9H, C*H*$_3$), 1.31 (s, 18H, C*H*$_3$), 1.17 (t, $J_{H\text{-}H}$ = 7.1 Hz, 9H, C*H*$_3$), 1.13 (t, $J_{H\text{-}H}$ = 7.1 Hz, 3H, C*H*$_3$). Unreacted phenylsilane was found at 7.39, 7.09 and 4.23 ppm.

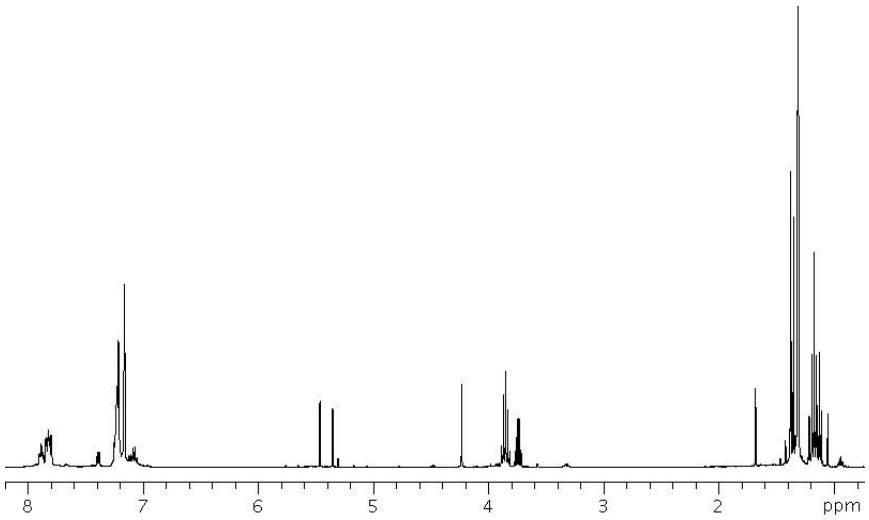


Figure S29. ^{1}H NMR spectrum of **2**-catalyzed (1 mol%) *t*-butyl acetate dihydrosilylation with $PhSiH_3$ in benzene-d_6 solution.

NMR scale deuterosilylation of methyl acetate using $PhSiD_3$ in benzene-d_6: In the glovebox, a benzene-d_6 solution (1 mL) of $PhSiD_3$ (16.63 mg, 0.149 mmol) and methyl acetate (11.8 μL, 0.149 mmol) was added to a 20 mL scintillation vial containing 5 mg (0.00748 mmol) of complex **2**. The resulting brown solution was then transferred to a sealed J. Young tube. The progress of the reaction was monitored by ^{1}H NMR spectroscopy over time at room temperature and complete conversion was detected after 24 h. A mixture of products including $PhSi(OCD_2CH_3)_3$, $PhSi(OMe)_3$, $PhSi(OCD_2CH_3)_2(OMe)$, and $PhSi(OCD_2CH_3)(OMe)_2$ were identified by ^{1}H NMR spectroscopy. ^{1}H NMR (benzene-d_6): δ: 7.83 (m), 7.23 (m), 7.19-7.13 (m), 3.87 (q, $J_{H\text{-}H}$ = 6.8 Hz, 6H, CH_2 for *PhSi(OEt)$_3$*), 3.86 (q, $J_{H\text{-}H}$ = 6.8 Hz, 4H, CH_2 for $PhSi(OEt)_2(OMe)$), 3.77 (q, $J_{H\text{-}H}$ = 6.8 Hz, 2H, CH_2 for $PhSi(OEt)(OMe)_2$), 3.51 (s, CH_3), 3.50 (s, CH_3), 3.48 (s, CH_3), 1.15 (broad m), 1.13 (m). Unreacted phenylsilane-d_3 was observed at 7.38, and 7.08 ppm.

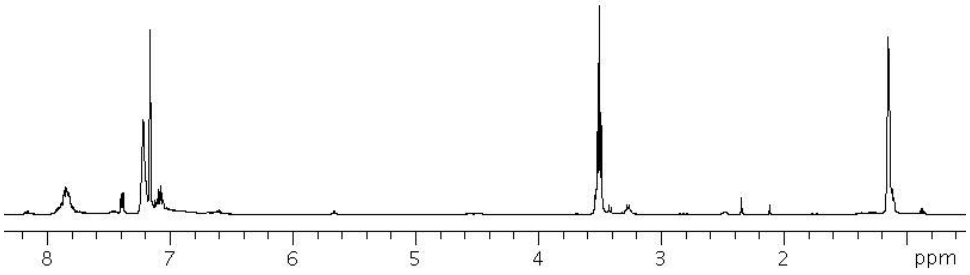


Figure S30. ^{1}H NMR spectrum of **2**-catalyzed (5 mol%) methyl acetate deuterosilylation with $PhSiD_3$ in benzene-d_6 solution.

NMR scale deuterosilylation of methyl acetate using $PhSiD_3$ in benzene: In the glovebox, a benzene solution (1 mL) of $PhSiD_3$ (16.63 mg, 0.149 mmol) and methyl acetate (11.8 μL, 0.149 mmol) was added to a 20 mL scintillation vial containing 5 mg (0.00748 mmol) of complex **2**. The resulting brown solution was then transferred into a J. Young tube and a drop of benzene-d_6 wad added. The progress of the reaction was monitored by ^{2}H NMR spectroscopy over time at room temperature and complete conversion was detected after 24 h. ^{2}H NMR (benzene): δ: 3.78 (broad m). Unreacted phenylsilane-d_3 was found at 4.22 ppm.

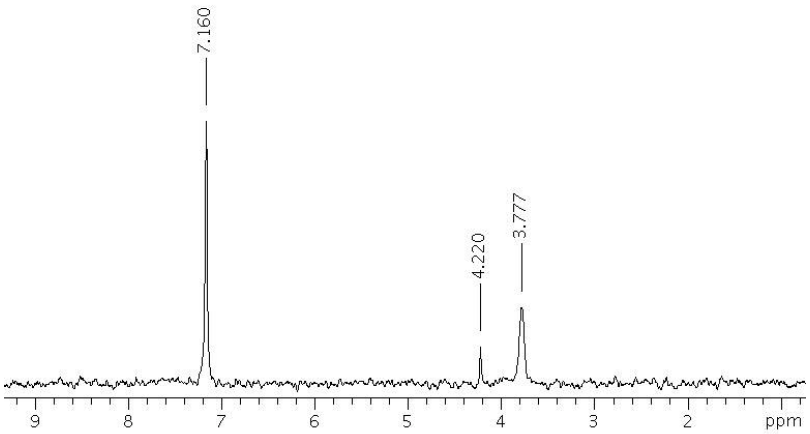


Figure S31. ^{2}H NMR spectrum of **2**-catalyzed (5 mol%) methyl acetate deutrosilylation with $PhSiD_3$ in benzene solution with one drop of benzene-d_6.

Test for Catalyst Homogeneity: In the glovebox, a mixture of $PhSiH_3$ (0.369 mL, 2.991 mmol) and acetophenone (0.349 mL, 2.991 mmol) was transferred to a 100 mL round bottom flask containing Hg (29.99 g, 149.55 mmol). To this mixture, complex **2** (2 mg, 0.002991 mmol) was added and the resulting brown mixture was stirred vigorously for 4 min. After 4 min, the reaction was exposed to air to deactivate the catalyst. The resulting colorless organic solution was pipetted out carefully and filtered through a Celite column. ^{1}H NMR spectroscopy in benzene-d_6 revealed the complete conversion of acetophenone to a mixture of $PhSiH(OCH(Me)(Ph))_2$ (82%) and $PhSi(OCH(Me)(Ph))_3$ (18%).

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