# A β-Diketiminate Manganese Catalyst for Alkene Hydrosilylation: Substrate Scope, Silicone Preparation, and Mechanistic Insight *Electronic Supplementary Information*

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#### EXPERIMENTAL SECTION

General Considerations: Unless otherwise stated, all synthetic reactions were performed in an MBraun glovebox under an atmosphere of purified nitrogen. Aldrich anhydrous solvents were purified using a Pure Process Technology solvent system and stored in the glovebox over activated 4Å molecular sieves and sodium (from Alfa Aesar) before use. Benzene- $d_6$  was purchased from Oakwood Chemicals and dried over metallic potassium and 4Å molecular sieves before use. o-Xylene-d<sub>10</sub> was obtained from Santa Cruz Biotechnology. (THF)<sub>2</sub>MnCl<sub>2</sub> was prepared by refluxing MnCl<sub>2</sub> in THF followed by filtration and drying in vacuo at 40 °C. 2,6-Diisopropyl aniline, 4-methyl-1-pentene, and styrene were purchased from TCI America. 2,4-Pentanedione, 1-hexene, vinyltrimethylsilane, allyltrimethylsilane, vinylcyclohexane, allylbenzene, 4-methyl-1-pentene, 4-methylstyrene, 4-fluorostyrene, 4-tert-butylstyrene, cis-βmethylstyrene, α-methylstyrene, D-limonene, and anhydrous Na<sub>2</sub>SO<sub>4</sub> were obtained from Oakwood Chemicals. Et<sub>2</sub>SiH<sub>2</sub>, (EtO)<sub>3</sub>SiH, Ph<sub>2</sub>SiH<sub>2</sub>, and PhSiH<sub>3</sub> were also obtained from Oakwood Chemicals. Trans-\beta-methylstyrene, myrcene, isoprene, cyclohexene, 1,3cyclohexadiene, 1,4-cyclohexadiene, allyldiphenylphosphine, trans-2-hexene, 2-vinylpyridine, 4-bromopyridine, indene, 4-diphenylphosphinostyrene, 9-vinylcarbazole, and 1,2,4trivinylcyclohexane (mixture of isomers) were purchased from Sigma-Aldrich. Na<sub>2</sub>CO<sub>3</sub> was sourced from Strem Chemicals. All the liquid substrates were scrupulously dried over 4Å molecular sieves or distilled if necessary before use. The solid substrates were recrystallized from diethyl ether or tetrahydrofuran before use. The ligand <sup>2,6-iPr2Ph</sup>BDIH<sup>1</sup> and benzyl potassium<sup>2</sup> were prepared according to literature procedure.

Solution <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded in benzene-*d*<sub>6</sub> at room temperature on a Varian 400 MHz or 500 MHz NMR spectrometer. All <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts (ppm) are reported relative to Si(CH<sub>3</sub>)<sub>4</sub> using <sup>1</sup>H (residual) and <sup>13</sup>C chemical shifts of the solvent as secondary standards. <sup>29</sup>Si NMR shifts are referenced relative to Si(CH<sub>3</sub>)<sub>4</sub> as an external standard. <sup>31</sup>P NMR shifts are referenced relative to H<sub>3</sub>PO<sub>4</sub> as an external standard. Elemental analysis was conducted at Robertson Microlit Laboratories Inc. (Ledgewood, NJ). Solution state magnetic susceptibility was determined via Evans method on the Varian 500 MHz NMR spectrometer.

**X-ray Crystallography:** Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in the glovebox and transferred to a glass fiber with Apiezon N grease, which was then mounted on the goniometer head of a Bruker APEX Diffractometer equipped with Mo Ka 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 structure was solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix, least-squares procedures on [F2]. Crystallographic parameters for [ $(^{2,6-iPr2Ph}BDI)Mn(\mu-H)$ ]<sub>2</sub> (1) (CCDC - 1851177) and  $(^{2,6-iPr2Ph}BDI)Mn(CH(CH_3)(4-Ph^{t}Bu))$  (2) (CCDC - 1851178) are provided in Table S1.

### **EPR Spectroscopy:**

*Instrumentation*. Studies were performed at the EPR Facility of Arizona State University. Continuous wave (CW) EPR spectra were recorded at 106 K using a Bruker ELEXSYS E580 CW X-band spectrometer (Bruker, Rheinstetten, Germany) equipped with a liquid nitrogen temperature control system (ER 4131VT). The magnetic field modulation frequency was 100 kHz with a field modulation amplitude of 1 mT peak-to-peak. The microwave power was 4 mW, the microwave frequency was 9.40 GHz and the sweep time was 168 seconds. *Spin Hamiltonian*. The EPR spectra of a coupled dimer system can be described with the spin Hamiltonian:<sup>2</sup>

$$\mathcal{H} = hJ_0 \mathbf{S}_1 \cdot \mathbf{S}_2 + h\mathbf{S}_1 \cdot \mathbf{J} \cdot \mathbf{S}_2 + \mathcal{H}_1 + \mathcal{H}_2 \tag{1}$$

where  $J_0$  is the isotropic exchange coupling constant between the two Mn(II) ions of the dimer, J is the tensor describing the dipole-dipole interaction between the two Mn(II) spin centers, and  $\mathcal{H}_i$  (i = 1, 2) are the spin Hamiltonians corresponding to each individual Mn(II) ion. The spin Hamiltonian of each Mn(II) spin center contains the electron Zeeman interaction with the applied magnetic field **B**<sub>0</sub>, the zero-field interaction, and the hyperfine coupling (hfc) interaction with the nucleus of <sup>55</sup>Mn:

$$\mathcal{H}_{i} = \beta_{e} \mathbf{S}_{i} \cdot \mathbf{g}_{i} \cdot \mathbf{B}_{o} + h \mathbf{S}_{i} \cdot \mathbf{d}_{i} \cdot \mathbf{S}_{i} + h \mathbf{S}_{i} \cdot \mathbf{a}_{i} \cdot \mathbf{I}_{i}$$
(2)

where  $S_i$  and  $I_i$  are the electron and nuclear spin operators, respectively,  $d_i$ , and  $a_i$  are the zerofield splitting and hfc tensors, respectively, all in frequency units,  $g_i$  is the electronic *g*-tensor,  $\beta_e$  is the electron magneton, and *h* is Planck's constant. For Mn(II) dimers, the electron and nuclear spins of each Mn(II) ion are  $S_i = 5/2$  and  $I_i = 5/2$ , respectively. Mn(II) ions have a singlet orbital ground state (<sup>6</sup>A), with the first excited orbital state (<sup>4</sup>T) more than 10,000 cm<sup>-1</sup> above the ground state. Consequently, the zero-field energies of Mn(II) ions are generally small,  $|D_i| < 0.1$  cm<sup>-1</sup>.<sup>3</sup> For dimeric manganese complexes, the bridging atoms typically give a Mn–Mn exchange interaction that is significantly larger than 0.1 cm<sup>-1</sup>. In this strong exchange regimen, the isotropic exchange coupling energy is much larger than the electronic Zeeman energy ( $|J_0| >> g_i\beta_eB_0$ ) and the zero-field splitting ( $|J_0| >> |D_i|$ ). The dimer system may then be regarded as a ladder of isolated spin manifolds. These spin manifolds have total spin quantum numbers of S = 0, 1, 2, 3, 4, and 5, each with a degeneracy of (2S+1). The separation between the spin manifolds is much larger than the microwave energy (*h*v) at the X-band (9.40 GHz) frequency and no transitions are observable between spin manifolds. The individual spin manifolds can be considered independently and their corresponding spectra can be simulated using a spin Hamiltonian for each individual spin manifold given by:<sup>4</sup>

$$\mathcal{H}_{\mathbf{S}} = \beta_{\mathbf{e}} \mathbf{S} \cdot \mathbf{G}_{\mathbf{S}} \cdot \mathbf{B}_{\mathbf{0}} + h \mathbf{S} \cdot \mathbf{D}_{\mathbf{S}} \cdot \mathbf{S} + h \mathbf{S} \cdot \mathbf{A}_{1} \cdot \mathbf{I}_{1} + h \mathbf{S} \cdot \mathbf{A}_{2} \cdot \mathbf{I}_{2}$$
(3)

where  $G_S$ ,  $D_S$ , and  $A_i$  (i = 1, 2) are the electronic Zeeman, zero-field splitting, and hfc tensors, respectively, of the spin manifolds of the coupled system, and **S** is the spin operator of the coupled spin manifolds. The parameters of the coupled spin system can be expressed as linear combinations of the parameters of the individual spin centers:

$$G_{S} = c_{1}g_{1} + c_{2}g_{2} \qquad (4)$$
$$D_{S} = d_{1}d_{1} + d_{2}d_{2} + d_{12}J \qquad (5)$$
$$A_{i} = c_{i}a_{i} \qquad (6)$$

where the coefficients  $c_1$ ,  $c_2$ ,  $d_1$ ,  $d_2$ , and  $d_{12}$  are specific to the particular spin manifold and have been tabulated elsewhere.<sup>5</sup> For Mn(II) ions, the contributions from spin–orbit coupling to the  $g_i$ tensor and hfc tensor are small, thus we will assume that both tensors  $g_i$  and  $A_i$  are isotropic. In the complex studied here, the two manganese centers of the dimer have identical ligation. The coordination geometry of one manganese ion is related to the other by a mirror plane, thus, we assume  $g_1 = g_2 = g_{iso}$ ,  $a_1 = a_2 = a$ , and  $d_1 = d_2$ . In this study, hfc's due to Mn(II) were not explicitly included in the spin Hamiltonian (Eq. 3) since they are not resolved in the observed spectrum. However, they significantly contribute to its EPR linewidth,  $\Delta B$ .

*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  $\sigma$  by:

$$\sigma(p_1, p_2, \dots, p_n) = \left[\sum_{j} (R_j^{\text{calc}}(p_1, p_2, \dots, p_n) - R_j^{\text{exp}})^2 / N\right]^{\frac{1}{2}}$$
(7)

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 2048. The EPR spectra were simulated using EasySpin (v 5.2.11), a computational package developed by Stoll and Schweiger<sup>6</sup> 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. 3). The EPR fitting procedure used a Monte Carlo type iteration to minimize the root-mean-square deviation,  $\sigma$  (see Eq. 7) between measured and simulated spectra. We searched for the optimum values of the following parameters: the isotropic *g*-value (*g*<sub>iso</sub>), the zero-field splitting parameters (*D* and *E*), the principal components of the *J* tensor ( $J_{x'}$ ,  $J_{y'}$  and  $J_{z'}$ ) and the isotropic peak-to-peak linewidth ( $\Delta B$ ).

**Synthesis of**  $[(^{2,6-iPr2Ph}BDI)Mn(\mu-Cl)]_2$ : This compound was prepared using a modified literature procedure.<sup>1b</sup> In this manuscript, the base used to prepare  $[K][^{2,6-iPr2Ph}BDI]$  was benzyl potassium. A 20 mL vial was charged with benzyl potassium (0.645 g, 4.95 mmol) and a 5 mL THF solution of <sup>2,6-iPr2Ph</sup>BDIH (2.071 g, 4.95 mmol) was added to it, while an immediate color change from deep orange to pale yellow was observed due to the formation of  $[K][^{2,6-iPr2Ph}BDI]$ . The pale-yellow solution was added to a vial containing (THF)<sub>2</sub>MnCl<sub>2</sub> (1.305 g, 4.84 mmol) and stirred at ambient temperature. After 6 h, the bright yellow suspension was transferred into a 250 mL round bottom flask and 60 mL pentane was added to it. The precipitate was collected by filtration after cooling the mixture, washed with 30 mL of pentane, and dried thoroughly to isolate a bright yellow powder identified as  $[(^{2,6-iPr2Ph}BDI)Mn(\mu-Cl)]_2$  (2.30 g, 2.26 mmol, 93%).

Elemental analysis for C<sub>29</sub>H<sub>41</sub>N<sub>2</sub>Cl<sub>2</sub>Mn: Calcd. C, 68.56; H, 8.13; N, 5.51. Found: C, 68.82; H, 7.85; N, 5.25.

**Synthesis of**  $[(^{2,6-iPr2Ph}BDI)Mn(\mu-H)]_2$  (1): A 20 mL vial was charged with  $[(^{2,6-iPr2Ph}BDI)Mn(\mu-Cl)]_2$  (0.501 g, 0.986 mmol) in 10 mL toluene and cooled at -35 °C. A solution of NaEt<sub>3</sub>BH (1.23 mL, 1.232 mmol) in 5 mL toluene was also cooled at -35 °C. After 30 min, the NaEt<sub>3</sub>BH solution was slowly added to the toluene slurry of  $[(^{2,6-iPr2Ph}BDI)Mn(\mu-Cl)]_2$  while stirring. A color change from yellow to dark brown was noticed along with a disappearance of yellow solid. After stirring at room temperature for 1 h, the dark brown solution was filtered through Celite. The filtrate was concentrated, layered with pentane and upon cooling at -35 °C overnight, yellowish-green crystals of  $[(^{2,6-iPr2Ph}BDI)Mn(\mu-H)]_2$  (1) (0.308 g, 0.650 mmol, 66%) were obtained. Elemental analysis for C<sub>58</sub>H<sub>84</sub>N<sub>4</sub>Mn<sub>2</sub>: Calcd. C, 73.55; H, 8.94; N, 5.92. Found: C, 73.69; H, 8.82; N, 5.78. Magnetic susceptibility (Evans method, 25 °C)  $\mu_{eff} = 5.2 \ \mu_B$  (considering a dimeric structure in solution). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 25 °C):  $\delta = 20.10$  (peak width at half-height = 1854 Hz), 11.56 (557 Hz), 5.45 (728 Hz), -4.18 (715 Hz).



**Figure S1:** <sup>1</sup>H NMR spectrum of **1** in benzene- $d_6$  at 25 °C.

Synthesis of (<sup>2,6-iPr2Ph</sup>BDI)Mn(CH(CH<sub>3</sub>)(4-<sup>t</sup>BuPh)) (2): A J. Young tube was charged with  $[(^{iPr2Ph}BDI)Mn(\mu-H)]_2$  (0.030 g, 0.0317 mmol) dissolved in 0.7 mL benzene- $d_6$ . Two equivalents of 4-tert-butylstyrene (11.6 µL, 0.0633 mmol) were added. The tube was capped under N2 atmosphere and heated at 130 °C for 16 h, during which time a greenish-brown solution formed. The <sup>1</sup>H NMR spectrum showed paramagnetically broadened resonances for a new complex and the starting material was completely consumed. The tube was cooled to room temperature and brought under N<sub>2</sub>. The solution was then filtered through Celite and dried under vacuum. The residue was dissolved in pentane (2 mL) and filtered through Celite. The filtrate yielded dark green crystals upon cooling at -35 °C. The mother liquor was decanted off and the crystals were recrystallized from 1 mL pentane. After 12 h, the supernatant was removed and the yellowishgreen crystals were dried thoroughly under vacuum to isolate (<sup>2,6-iPr2Ph</sup>BDI)Mn(CH(CH<sub>3</sub>)(4-<sup>t</sup>BuPh)) (2) (0.022 g, 55%). Elemental analysis for C<sub>41</sub>H<sub>58</sub>N<sub>2</sub>Mn: Calcd. C, 77.69; H, 9.22; N, 4.42. Found: C, 77.09; H, 9.02; N, 4.36. Elemental analysis data for this compound has consistently indicated low carbon content; the values provided here are the closest obtained to date. Magnetic susceptibility (Evans method, 25 °C)  $\mu_{eff} = 6.0 \ \mu_B$ . <sup>1</sup>H NMR (benzene- $d_6$ , 25 °C, ppm): 24.61 (16700 Hz), 18.33 (13343 Hz), 11.43 (2430 Hz), 3.56 (1872 Hz), 2.62 (161 Hz), 2.12 (495 Hz), -1.76 (7088 Hz).



Figure S2. <sup>1</sup>H NMR spectrum of 2 in benzene- $d_6$  at 25 °C.

## X-RAY DIFFRACTION DATA

	1	2		
chemical formula	$C_{58}H_{84}Mn_2N_4$	$C_{41}H_{58}MnN_2$		
formula weight	947.17 g/mol	633.83 g/mol		
crystal dimensions	0.171 x 0.214 x 0.235 mm	0.092 x 0.502 x 0.759 mm		
crystal system	Monoclinic	Monoclinic		
space group	P 1 21/n 1	P 1 21/c 1		
<i>a</i> (Å)	14.1097 (13)	12.443 (6)		
<i>b</i> (Å)	14.3190 (13)	13.455 (6)		
<i>c</i> (Å)	14.2262 (13)	22.132 (10)		
$\alpha$ (deg)	90	90		
$\beta$ (deg)	111.8865 (14)	102.382 (5)		
γ (deg)	90	90		
$V(Å^3)$	2667.1 (4)	3619. (3)		
Ζ	2	4		
T (°C)	123.(10)	123.(10)		
$\rho$ calcd (g cm <sup>-3</sup> )	1.179	1.163		
$\mu$ (mm <sup>-1</sup> )	0.513	0.394		
reflections collected	21914	28947		
data/restraints/parameters	4892/0/303	6784/0/411		
$R_1 [I > 2\sigma(I)]$	0.0536	0.0678		
wR <sub>2</sub> (all data)	0.1452	0.2102		
Goodness-of-fit	1.066	1.032		
Largest peak, hole (eÅ <sup>-3</sup> )	1.045, -0.266	1.243, -0.576		

## Table S1. Crystallographic data for 1 and 2.



**Figure S3.** Solid-state structure of **1** shown at 30% probability ellipsoids. Hydrogen atoms except for H1 are omitted for clarity.

Table S2. Metrical p	parameters for 1	
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Mn1-N1	2.086(2)	C6-C7	1.405(4)	C18-C19 1.40	03(4)
Mn1-N2	2.098(2)	C6-C11	1.408(4)	C18-C23 1.40	06(4)
Mn1-Mn1A	2.8138(7)	C7-C8	1.391(4)	C19-C20 1.38	87(4)
Mn1-H1	1.79(2)	C7-C15	1.524(4)	C19-C27 1.53	32(4)
N1-C2	1.329(3)	C8-C9	1.381(4)	C20-C21 1.37	74(4)
N1-C6	1.444(3)	C9-C10	1.381(4)	C21-C22 1.38	81(4)
N2-C4	1.326(3)	C10-C11	1.400(4)	C22-C23 1.38	87(4)
N2-C18	1.452(3)	C11-C12	1.517(4)	C23-C24 1.52	27(4)
C1-C2	1.515(4)	C12-C14	1.521(4)	C24-C25 1.50	08(4)
C2-C3	1.395(4)	C12-C13	1.531(4)	C24-C26 1.53	39(4)
C3-C4	1.406(4)	C15-C17	1.507(5)	C27-C28 1.50	07(5)
C4-C5	1.518(3)	C15-C16	1.523(6)	C27-C29 1.5	12(4)
N1-Mn1-N2	91.48(8)	C7-C6-C11	121.1(2)	C19-C18-N2	118.7(2)
N1-Mn1-Mn1A	132.19(6)	C7-C6-N1	118.9(2)	C23-C18-N2	120.5(2)
N2-Mn1-Mn1A	136.24(6)	C11-C6-N1	119.9(2)	C20-C19-C18	118.7(2)
N1-Mn1-H1	122.8(8)	C8-C7-C6	118.2(3)	C20-C19-C27	120.2(2)
N2-Mn1-H1	121.1(8)	C8-C7-C15	119.7(3)	C18-C19-C27	121.1(2)
Mn1A-Mn1-H1	43.0(8)	C6-C7-C15	122.1(2)	C21-C20-C19	121.0(3)
C2-N1-C6	116.9(2)	C9-C8-C7	121.7(3)	C20-C21-C22	120.0(3)
C2-N1-Mn1	121.52(17)	C10-C9-C8	119.6(3)	C21-C22-C23	121.3(3)
C6-N1-Mn1	121.57(16)	C9-C10-C11	121.4(3)	C22-C23-C18	118.2(2)
C4-N2-C18	115.4(2)	C10-C11-C6	118.0(3)	C22-C23-C24	120.9(2)
C4-N2-Mn1	121.69(16)	C10-C11-C12	2 119.9(2)	C18-C23-C24	120.9(2)
C18-N2-Mn1	122.77(15)	C6-C11-C12	122.0(2)	C25-C24-C23	111.5(2)
N1-C2-C3	124.9(2)	C11-C12-C14	110.5(2)	C25-C24-C26	109.1(3)
N1-C2-C1	119.7(2)	C11-C12-C13	3 112.6(2)	C23-C24-C26	113.7(2)
C3-C2-C1	115.4(2)	C14-C12-C13	3 109.7(2)	C28-C27-C29	109.6(3)
C2-C3-C4	129.4(2)	C17-C15-C16	5 109.6(3)	C28-C27-C19	111.6(3)
N2-C4-C3	124.4(2)	C17-C15-C7	113.0(3)	C29-C27-C19	112.5(3)
N2-C4-C5	121.0(2)	C16-C15-C7	111.2(3)		
C3-C4-C5	114.4(2)	C19-C18-C23	3 120.8(2)		



**Figure S4.** Solid-state structure of **2** shown at 30% probability ellipsoids. The hydrogen atoms are omitted for clarity.

**Table S3**. Metrical parameters for 2.

Mn1-N1	2.048	(3)	C9-C10	1.364	(6)	C24-C25	1.528	8(5)
Mn1-N2	2.053	(3)	C10-C11	1.387	(5)	C27-C29	1.51	7(6)
Mn1-C30	2.111	(4)	C11-C15	1.521	(5)	C27-C28	1.522	2(6)
N1-C2	1.322(4)		C12-C14	1.513	(6)	C30-C32	1.492	2(6)
N1-C6	1.429(4)		C12-C13	1.522	(6)	C30-C31	1.507	7(6)
N2-C4	1.328(4)		C15-C17	1.515	(5)	C32-C33	1.380	0(5)
N2-C18	1.434(4)		C15-C16 1.516(6)		(6)	C32-C37 1.382(6)		
C1-C2	1.504(5)		C18-C19 1.390(5)		(5)	C33-C34 1.382(6)		2(6)
C2-C3	1.393	(5)	C18-C23 1.395(5)		(5)	C34-C35 1.390(5)		0(5)
C3-C4	1.394	(5)	C19-C20 1.393(5)		(5)	C35-C36 1.390(6)		
C4-C5	1.486	(5)	C19-C24 1.508(5)		(5)	C35-C38 1.511(6)		
C6-C7	1.394	(5)	C20-C21 1.367(5)		(5)	C36-C37 1.392(6)		
C6-C11	1.412	(5)	C21-C22 1.373(5)		(5)	C38-C40 1.521(6)		
C7-C8	1.380	(5)	C22-C23	1.385	(5)	C38-C41 1.526(6)		
C7-C12	1.513	(5)	C23-C27	1.523	(5)	C38-C39	1.54	1(6)
C8-C9	1.382	(6)	C24-C26	1.521	(5)			
N1-Mn1-N2	2	90.74(11)	C9-C10-C1	11	121.5(4)	C26-C24-	C25	110.2(3)
N1-Mn1-C3	80	135.27(14)	C10-C11-C	26	117.5(3)	C29-C27-	C28	111.4(3)
N2-Mn1-C3	80	133.74(14)	C10-C11-C	C15	122.1(3)	C29-C27-	C23	111.2(3)
C2-N1-C6		119.8(3)	C6-C11-C1	15	120.5(3)	C28-C27-	C23	111.1(3)
C2-N1-Mn1	_	125.4(2)	C14-C12-C	27	112.4(3)	C32-C30-	C31	114.9(4)
C6-N1-Mn1	_	114.8(2)	C14-C12-C	C13	109.4(3)	C32-C30-	Mn1	107.1(3)
C4-N2-C18		120.2(3)	C7-C12-C1	13	111.0(3)	C31-C30-	Mn1	113.7(3)
C4-N2-Mn1		126.4(2)	C17-C15-C	C16	108.2(3)	C33-C32-	C37	115.7(4)
C18-N2-Mr	n1	113.4(2)	C17-C15-C	C11	114.3(3)	C33-C32-	C30	121.6(4)
N1-C2-C3		124.5(3)	C16-C15-C	C11	111.2(3)	C37-C32-	C30	122.7(4)
N1-C2-C1		119.0(3)	C19-C18-C	223	121.3(3)	C32-C33-	C34	122.4(4)
C3-C2-C1		116.5(3)	C19-C18-N	<b>N</b> 2	119.7(3)	C33-C34-	C35	122.5(4)
C2-C3-C4		129.7(3)	C23-C18-N	N2	118.8(3)	C34-C35-	C36	115.0(4)
N2-C4-C3		122.9(3)	C18-C19-C	220	118.6(3)	C34-C35-	C38	124.0(4)
N2-C4-C5		119.4(3)	C18-C19-C	224	121.0(3)	C36-C35-	C38	121.1(4)
C3-C4-C5		117.7(3)	C20-C19-C	224	120.4(3)	C35-C36-	C37	122.3(4)
C7-C6-C11		121.4(3)	C21-C20-C	C19	120.6(3)	C32-C37-	C36	122.1(4)
C7-C6-N1		119.7(3)	C20-C21-C	222	120.1(3)	C35-C38-	C40	112.5(4)
C11-C6-N1		118.9(3)	C21-C22-C	223	121.4(3)	C35-C38-	C41	110.0(4)
C8-C7-C6		118.6(3)	C22-C23-C	C18	117.9(3)	C40-C38-	C41	108.1(4)
C8-C7-C12		119.9(3)	C22-C23-C	227	119.9(3)	C35-C38-	C39	109.1(4)
C6-C7-C12		121.5(3)	C18-C23-C	227	122.2(3)	C40-C38-	C39	109.0(4)
C7-C8-C9		120.6(4)	C19-C24-C	226	111.4(3)	C41-C38-	C39	108.0(4)
C10-C9-C8		120.5(4)	C19-C24-C	225	112.3(3)			

## PROCEDURES AND SPECTROSCOPIC DATA FOR CATALYTIC TRIALS

**Hydrosilylation of 1-hexene catalyzed by 0.5 mol% of 1 (1 mol% based on Mn):** In the glove box, PhSiH<sub>3</sub> (78.2 μL, 0.633 mmol) and 1-hexene (79.1 μL, 0.633 mmol) were added to a J. Young tube containing a benzene- $d_6$  solution of **1** (0.003 g, 0.00317 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 38 h of heating, >99% conversion was observed. The tube was then brought back into the glove box and the solution was dried under vacuum. The residue was filtered with pentane (3 mL) through Celite to separate the insoluble catalyst from the generated silane. The pentane solution was then dried under vacuum to isolate an oil identified as PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub> (0.0898 g, 74%). <sup>1</sup>H NMR (benzene- $d_6$ , 25 °C)  $\delta$  7.56 – 7.47 (m, 2H, *phenyl*), 7.20 – 7.12 (m, 3H, *phenyl*), 4.51 (m, 2H, SiH<sub>2</sub>Ph), 1.39 (m, 2H, CH<sub>2</sub>), 1.24 (m, 6H, CH<sub>2</sub>), 0.86 (m, 3H, CH<sub>3</sub>), 0.81 (m, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (benzene- $d_6$ , 25 °C)  $\delta$  135.58 (*phenyl*), 132.91 (*phenyl*), 129.84 (*phenyl*), 128.35 (*phenyl*), 32.93 (CH<sub>2</sub>), 31.84 (CH<sub>2</sub>), 25.45 (CH<sub>2</sub>), 22.96 (CH<sub>2</sub>), 14.35 (CH<sub>2</sub>), 10.40 (CH<sub>3</sub>). <sup>29</sup>Si NMR (benzene- $d_6$ , 25 °C)  $\delta$  -31.05 (SiH<sub>2</sub>Ph).



Figure S5. <sup>1</sup>H NMR spectrum of 1-hexene hydrosilylation catalyzed by **1** after 38 h.



Figure S6. <sup>1</sup>H NMR spectrum of isolated PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub> in benzene-*d*<sub>6</sub>.



**Figure S7.** <sup>13</sup>C NMR spectrum of isolated PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub> in benzene-*d*<sub>6</sub>.



Figure S8. <sup>29</sup>Si NMR spectrum of isolated PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub> in benzene-d<sub>6</sub>.

Hydrosilylation of 4-methyl-1-pentene catalyzed by 0.5 mol% of 1 (1 mol% based on Mn): In the glove box, PhSiH<sub>3</sub> (78.2 μL, 0.633 mmol) and 4-methyl-1-pentene (80.7 μL, 0.633 mmol) were added to a J. Young tube containing a benzene- $d_6$  solution of 1 (0.003 g, 0.00317 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 38 h of heating, >99% conversion was observed. The tube was then brought back into the glove box and the solution was dried under vacuum. The residue was filtered with pentane (3 mL) through Celite to separate the insoluble catalyst from the generated silane. The pentane solution was then dried under vacuum to isolate an oil identified as PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH(CH<sub>3</sub>)<sub>2</sub> (0.071 g, 58%). <sup>1</sup>H NMR (benzene- $d_6$ , 25 °C) δ 7.52 (m, 2H, *phenyl*), 7.17 (m, 3H, *phenyl*), 4.51 (m, 2H, SiH<sub>2</sub>Ph), 1.41 (m, 3H, CH<sub>2</sub> and CH), 1.18 (m, 2H, CH<sub>2</sub>), 0.82 (d, *J* = 6.6 Hz, 6H, CH<sub>3</sub>), 0.79 (m, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (benzene- $d_6$ , 25 °C) δ 135.58 (*phenyl*), 132.89 (*phenyl*), 129.85 (*phenyl*), 128.35 (*phenyl*), 42.54 (CH<sub>2</sub>), 27.97 (CH), 23.26 (CH<sub>2</sub>), 22.73 (CH<sub>3</sub>), 10.53 (CH<sub>2</sub>). <sup>29</sup>Si NMR (benzene- $d_6$ , 25 °C) δ -30.99 (*Si*H<sub>2</sub>Ph).



Figure S9. <sup>1</sup>H NMR spectrum of 4-methyl-1-pentene hydrosilylation catalyzed by 1 after 38 h.



Figure S10. <sup>1</sup>H NMR spectrum of isolated PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH(CH<sub>3</sub>)<sub>2</sub> in benzene-*d*<sub>6</sub>.



Figure S11. <sup>13</sup>C NMR spectrum of isolated PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH(CH<sub>3</sub>)<sub>2</sub> in benzene-*d*<sub>6</sub>.



Figure S12. <sup>29</sup>Si NMR spectrum of PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH(CH<sub>3</sub>)<sub>2</sub> in benzene-*d*<sub>6</sub>.

Hydrosilylation of allyltrimethylsilane catalyzed by 0.5 mol% of 1 (1 mol% based on Mn): In the glove box, PhSiH<sub>3</sub> (78.2 μL, 0.633 mmol) and allyltrimethylsilane (100.6 μL, 0.633 mmol) were added to a J. Young tube containing a benzene- $d_6$  solution of 1 (0.003 g, 0.00317 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting <sup>1</sup>H NMR alkene resonances. After 38 h of heating, >99% conversion was observed. The tube was then brought back into the glove box and the solution was dried under vacuum. The residue was filtered with pentane (3 mL) through Celite to separate the insoluble catalyst from the generated silane. The pentane solution was then dried under vacuum to isolate an oil identified as PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>Si(CH<sub>3</sub>)<sub>3</sub> (0.110 g, 78%). <sup>1</sup>H NMR (benzene- $d_6$ , 25 °C) δ 7.52 (m, 2H, *phenyl*), 7.17 (m, 3H, *phenyl*), 4.53 (m, 2H, SiH<sub>2</sub>Ph), 1.49 (m, 2H, CH<sub>2</sub>), 0.93 (m, 2H, CH<sub>2</sub>), 0.56 (m, 2H, CH<sub>2</sub>), -0.05 (m, 9H, CH<sub>3</sub>). <sup>13</sup>C NMR (benzene- $d_6$ , 25 °C) δ 135.59 (*phenyl*), 132.85 (*phenyl*), 129.85 (*phenyl*), 20.65 (CH<sub>2</sub>), 20.14 (CH<sub>2</sub>), 14.69 (CH<sub>2</sub>), -1.56 (CH<sub>3</sub>). <sup>29</sup>Si NMR (benzene- $d_6$ , 25 °C) δ 0.37 (*Si*Me<sub>3</sub>), -32.10 (*Si*H<sub>2</sub>Ph).



Figure S13. <sup>1</sup>H NMR spectrum of allyltrimethylsilane hydrosilylation catalyzed by 1 after 38 h.



Figure S14. <sup>1</sup>H NMR spectrum of isolated PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>Si(CH<sub>3</sub>)<sub>3</sub> in benzene-*d*<sub>6</sub>.



**Figure S15.** <sup>13</sup>C NMR spectrum of isolated PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>Si(CH<sub>3</sub>)<sub>3</sub> in benzene-*d*<sub>6</sub>.



Figure S16. <sup>29</sup>Si NMR spectrum of isolated PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>Si(CH<sub>3</sub>)<sub>3</sub> in benzene-*d*<sub>6</sub>.

Hydrosilylation of vinyltrimethylsilane catalyzed by 0.5 mol% of 1 (1 mol% based on Mn): In the glove box, PhSiH<sub>3</sub> (78.2 µL, 0.633 mmol) and vinyltrimethylsilane (92.8 µL, 0.633 mmol) were added to a J. Young tube containing a benzene- $d_6$  solution of 1 (0.003 g, 0.00317 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 5 d of heating, >99% conversion was observed, which showed the formation of the anti-Markovnikov product PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>SiMe<sub>3</sub> (74%) along with 26% of the Markovnikov product PhSiH<sub>2</sub>CH(CH<sub>3</sub>)(SiMe<sub>3</sub>). The tube was then brought back into the glove box and the solution was dried under vacuum. The residue was filtered with pentane (3 mL) through Celite to separate the insoluble catalyst from the generated silane. The pentane solution was then dried under vacuum to isolate an oil identified as a mixture of 74% PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>SiMe<sub>3</sub> and 26% PhSiH<sub>2</sub>CH(CH<sub>3</sub>)(SiMe<sub>3</sub>) (0.104 g, 78%). *PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>SiMe<sub>3</sub>*: <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 25 °C) δ 7.52 (broad m, 2H, phenyl), 7.17 (broad m, 3H, phenyl), 4.52 (broad, SiH<sub>2</sub>Ph), 0.74 (broad m, 2H, CH<sub>2</sub>), 0.53 (broad m, 2H, CH<sub>2</sub>), -0.07 (s, 9H, SiMe<sub>3</sub>). <sup>13</sup>C NMR (benzene- $d_6$ , 25 °C)  $\delta$  135.60 (phenvl), 133.00 (phenvl), 129.88 (phenvl), 128.37 (phenvl), 10.84 (CH<sub>2</sub>), 3.10 (CH<sub>2</sub>), 2.09 (SiMe<sub>3</sub>). <sup>29</sup>Si NMR (benzene-d<sub>6</sub>, 25 °C) δ -26.90 (SiH<sub>2</sub>Ph), 2.56 (SiMe<sub>3</sub>). *PhSiH*<sub>2</sub>*CH*(*CH*<sub>3</sub>)(*SiMe*<sub>3</sub>): <sup>1</sup>H NMR (benzene- $d_6$ , 25 °C)  $\delta$  aromatic and SiH<sub>2</sub>Ph resonances are overlapped with the major product, 1.05 (d,  $CH_3$ ), 0.11 (broad m, CH), 0.01 (s,  $SiMe_3$ ). <sup>13</sup>C NMR (benzene-d<sub>6</sub>, 25 °C) δ 135.80 (phenyl), 133.22 (phenyl), 129.79 (phenyl), 10.72 (CH<sub>3</sub>), 2.45 (*C*H), 1.78 (Si*Me*<sub>3</sub>). <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>, 25 °C) δ -27.61 (*Si*H<sub>2</sub>Ph), 3.94 (*Si*Me<sub>3</sub>).



Figure S17. <sup>1</sup>H NMR spectrum of vinyltrimethylsilane hydrosilylation catalyzed by 1 after 5 d.



**Figure S18.** <sup>1</sup>H NMR spectrum of isolated PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>SiMe<sub>3</sub> and PhSiH<sub>2</sub>CH(CH<sub>3</sub>)(SiMe<sub>3</sub>) in benzene-*d*<sub>6</sub>.



**Figure S19.** <sup>13</sup>C NMR spectrum of isolated PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>SiMe<sub>3</sub> and PhSiH<sub>2</sub>CH(CH<sub>3</sub>)(SiMe<sub>3</sub>) in benzene-*d*<sub>6</sub>.



**Figure S20.** <sup>29</sup>Si NMR spectrum of isolated  $PhSiH_2(CH_2)_2SiMe_3$  and  $PhSiH_2CH(CH_3)(SiMe_3)$  in benzene- $d_6$ .

**Hydrosilylation of allylbenzene catalyzed by 0.5 mol% of 1 (1 mol% based on Mn):** In the glove box, PhSiH<sub>3</sub> (78.2 μL, 0.633 mmol) and allylbenzene (83.9 μL, 0.633 mmol) were added to a J. Young tube containing a benzene- $d_6$  solution of **1** (0.003 g, 0.00317 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 72 h of heating, >99% conversion was observed. The tube was then brought back into the glove box and the solution was dried under vacuum. The residue was filtered with pentane (3 mL) through Celite to separate the insoluble catalyst from the generated silane. The pentane solution was then dried under vacuum to isolate an oil identified as PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>Ph (0.132 g, 92%). <sup>1</sup>H NMR (benzene- $d_6$ , 25 °C)  $\delta$  7.47 (m, 2H, *phenyl*), 7.17 (m, 5H, *phenyl*), 7.09 (m, 1H, *phenyl*), 7.04 (m, 2H, *phenyl*), 4.48 (t, *J* = 3.2 Hz, 2H, SiH<sub>2</sub>Ph), 2.49 (t, *J* = 7.5 Hz, 2H, CH<sub>2</sub>), 1.68 (m, 2H, CH<sub>2</sub>), 0.80 (m, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (benzene- $d_6$ , 25 °C)  $\delta$  142.26 (*phenyl*), 125.57 (*phenyl*), 132.60 (*phenyl*), 129.88 (*phenyl*), 128.84 (*phenyl*), 128.63 (*phenyl*), 126.14 (*phenyl*), 39.27 (CH<sub>2</sub>), 27.35 (CH<sub>2</sub>), 9.98 (CH<sub>2</sub>). <sup>29</sup>Si NMR (benzene- $d_6$ , 25 °C)  $\delta$  -31.02 (*Si*H<sub>2</sub>Ph).



**Figure S21.** <sup>1</sup>H NMR spectrum of allylbenzene hydrosilylation catalyzed by **1** after 72 h.



**Figure S22.** <sup>1</sup>H NMR spectrum of isolated PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>Ph in benzene-*d*<sub>6</sub>.



**Figure S23.** <sup>13</sup>C NMR spectrum of isolated  $PhSiH_2(CH_2)_3Ph$  in benzene- $d_6$ .



Figure S24. <sup>29</sup>Si NMR spectrum of isolated PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>Ph in benzene-d<sub>6</sub>.

Hydrosilylation of vinylcyclohexane catalyzed by 0.5 mol% of 1 (1 mol% based on Mn): In the glove box, PhSiH<sub>3</sub> (78.2 μL, 0.633 mmol) and vinylcyclohexane (86.6 μL, 0.633 mmol) were added to a J. Young tube containing a benzene- $d_6$  solution of 1 (0.003 g, 0.00317 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 48 h of heating, >99% conversion was observed. The tube was then brought back into the glove box and the solution was dried under vacuum. The residue was filtered with pentane (3 mL) through Celite to separate the insoluble catalyst from the generated silane. The pentane solution was then dried under vacuum to isolate an oil identified as PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Cy (0.110 g, 80%). <sup>1</sup>H NMR (benzene- $d_6$ , 25 °C) δ 7.52 (m, 2H, *phenyl*), 7.17 (m, 3H, *phenyl*), 4.51 (t, *J* = 3.4 Hz, 2H, SiH<sub>2</sub>Ph), 1.64 (m, 5H, *Cy*), 1.30 (m, 2H, *CH*<sub>2</sub>), 1.12 (m, 4H, *CH*<sub>2</sub>), 0.81 (m, 2H, *CH*<sub>2</sub>), 0.76 (m, 2H, *CH*<sub>2</sub>). <sup>13</sup>C NMR (benzene- $d_6$ , 25 °C) δ 135.58 (*phenyl*), 132.94 (*phenyl*), 129.85 (*phenyl*), 128.35 (*phenyl*), 40.52 (*C*H, *Cy*), 33.15 (*C*H<sub>2</sub>), 32.96 (*C*H<sub>2</sub>), 27.09 (*C*H<sub>2</sub>), 26.75 (*C*H<sub>2</sub>), 7.51 (*C*H<sub>2</sub>). <sup>29</sup>Si NMR (benzene- $d_6$ , 25 °C) δ -30.24 (*Si*H<sub>2</sub>Ph).



**Figure S25.** <sup>1</sup>H NMR spectrum of vinylcyclohexane hydrosilylation catalyzed by **1** after 48 h.



Figure S26. <sup>1</sup>H NMR spectrum of isolated PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Cy in benzene-*d*<sub>6</sub>.



**Figure S27.** <sup>13</sup>C NMR spectrum of isolated PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Cy in benzene- $d_6$ .



Figure S28. <sup>29</sup>Si NMR spectrum of isolated  $PhSiH_2(CH_2)_2Cy$  in benzene- $d_6$ .

Hydrosilylation of D-limonene catalyzed by 0.5 mol% of 1 (1 mol% based on Mn): In the glove box, PhSiH<sub>3</sub> (78.2 µL, 0.633 mmol) and D-limonene (102.5 µL, 0.633 mmol) were added to a J. Young tube containing a benzene- $d_6$  solution of 1 (0.003 g, 0.00317 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 6 d of heating, only 71% conversion was observed, which showed the formation of *anti*-Markovnikov product. <sup>1</sup>H NMR (benzene- $d_6$ , 25 °C, ppm):  $\delta$  7.51 (*phenyl*), 7.15 (*phenyl*), 5.40 (=CH, ring olefin), 4.53 (SiH<sub>2</sub>Ph), 2.05 (br m, 3H, CH<sub>2</sub> and CH), 1.63 (s, 3H, CH<sub>3</sub>), 1.57 (br m, 3H, CH<sub>2</sub>), 1.35 (br m, 1H, CH<sub>2</sub>), 1.15 (br m, 1H, CH<sub>2</sub>), 1.00 (br m, 1H, CH<sub>2</sub>), 0.90 (br d, 3H, CH<sub>3</sub>), 0.71 (br m, 1H, CH<sub>2</sub>).



**Figure S29.** <sup>1</sup>H NMR spectrum of D-limonene hydrosilylation catalyzed by **1** after 6 d.

Hydrosilylation of myrcene catalyzed by 0.5 mol% of 1 (1 mol% based on Mn): In the glove box, PhSiH<sub>3</sub> (78.2 µL, 0.633 mmol) and isoprene (108.6 µL, 0.633 mmol) were added to a J. Young tube containing a benzene- $d_6$  solution of **1** (0.003 g, 0.00317 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 48 h of heating, >99% hydrosilylation of the terminal olefin was observed. The tube was then brought back into the glove box and the solution was dried under vacuum. The residue was filtered with pentane (3 mL) through Celite to separate the insoluble catalyst from the generated silane. The pentane solution was then dried under vacuum to isolate an oil identified as PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>C(=CH<sub>2</sub>)(CH<sub>2</sub>)<sub>2</sub>CH=C(CH<sub>3</sub>)<sub>2</sub> (0.149 g, 96%). <sup>1</sup>H NMR (benzene- $d_6$ , 25 °C)  $\delta$  7.52 (broad m, 2H, *phenyl*), 7.15 (broad m, 3H, *phenyl*), 5.23 (m, alkene CH<sub>2</sub>), 5.20 (m, 1H, alkene CH), 4.54 (broad, 2H, SiH<sub>2</sub>Ph), 2.16 (CH<sub>2</sub>), 2.09 (CH<sub>2</sub>), 1.83 (broad m, 2H, CH<sub>2</sub>), 1.66 (s, 3H, CH<sub>3</sub>), 1.54 (s, 3H, CH<sub>3</sub>), 1.47 (broad m, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (benzene-d<sub>6</sub>, 25 °C) δ 136.33 (C, phenyl), 135.59 (CH, phenyl), 132.87 (C, alkene), 131.30 (C, alkene), 129.97 (CH, phenyl), 124.88 (CH, phenvl), 117.59 (=CH<sub>2</sub>), 39.09 (CH<sub>2</sub>), 27.26 (CH<sub>2</sub>), 25.88 (CH<sub>3</sub>), 17.80 (CH<sub>3</sub>), 15.18 (CH<sub>2</sub>), 13.83 (CH<sub>2</sub>). <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>, 25 °C) δ -35.07 (*Si*H<sub>2</sub>Ph).



Figure S30. <sup>1</sup>H NMR spectrum of myrcene hydrosilylation catalyzed by 1 after 48 h.



**Figure S31.** <sup>1</sup>H NMR spectrum of isolated PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>C(=CH<sub>2</sub>)(CH<sub>2</sub>)<sub>2</sub>CH=C(CH<sub>3</sub>)<sub>2</sub> in benzene-*d*<sub>6</sub>.



**Figure S32.** <sup>13</sup>C NMR spectrum of isolated  $PhSiH_2(CH_2)_2C(=CH_2)(CH_2)_2CH=C(CH_3)_2$  in benzene-*d*<sub>6</sub>.



**Figure S33.** <sup>29</sup>Si NMR spectrum of isolated PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>C(=CH<sub>2</sub>)(CH<sub>2</sub>)<sub>2</sub>CH=C(CH<sub>3</sub>)<sub>2</sub> in benzene- $d_6$ .

Hydrosilylation of 1,4-cyclohexadiene catalyzed by 0.5 mol% of 1 (1 mol% based on Mn): In the glove box, PhSiH<sub>3</sub> (78.2 μL, 0.633 mmol) and 1,4-cyclohexadiene (59.8 μL, 0.633 mmol) were added to a J. Young tube containing a benzene- $d_6$  solution of 1 (0.003 g, 0.00317 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 4 d of heating, >99% hydrosilylation of one olefin bond was observed, while the other olefin was untouched. The mixture was then brought into glove box and benzene- $d_6$  was removed under vacuum. The residue was dissolved in 2 mL of pentane and filtered through Celite to exclude the solid catalyst. The filtrate was dried under vacuum to isolate an oil (0.101 g, 85%) identified as monosilylated cyclohexene. <sup>1</sup>H NMR (benzene- $d_6$ , 25 °C) δ 7.51 (br m, 2H), 7.15 (br m, 3H), 5.71 (m, 2H, *H*C=C*H*), 4.46 (br, 2H, Si*H*<sub>2</sub>Ph), 1.89 (br m, 3H, *Cy*), 1.76 (br m, 1H, *Cy*), 1.63 (br m, 2H, *Cy*), 1.44 (br m, 1H, *Cy*). <sup>13</sup>C NMR (benzene- $d_6$ , 25 °C) δ 135.92 (*phenyl*), 131.95 (*phenyl*), 129.98 (*phenyl*), 127.55 (*phenyl*), 126.64 (H*C*=CH), 25.23 (*Cy*), 25.04 (*Cy*), 22.45 (*Cy*), 22.11 (*Cy*). <sup>29</sup>Si NMR (benzene- $d_6$ , 25 °C) δ -27.43 (s, *Si*H<sub>2</sub>Ph).



Figure S34. <sup>1</sup>H NMR spectrum of 1,4-cyclohexadiene hydrosilylation catalyzed by 1 after 4 d.



Figure S35. <sup>1</sup>H NMR spectrum of isolated cyclohexene product in benzene- $d_6$ .



Figure S36. <sup>13</sup>C NMR spectrum of isolated cyclohexene product in benzene- $d_6$ .



Figure S37. <sup>29</sup>Si NMR spectrum of isolated cyclohexene product in benzene- $d_6$ .

Hydrosilylation of 1,3-cyclohexadiene catalyzed by 0.5 mol% of 1 (1 mol% based on Mn): In the glove box, PhSiH<sub>3</sub> (78.2 μL, 0.633 mmol) and 1,3-cyclohexadiene (60.3 μL, 0.633 mmol) were added to a J. Young tube containing a benzene- $d_6$  solution of 1 (0.003 g, 0.00317 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 24 h of heating, >99% hydrosilylation of one olefin bond was observed, while the other olefin was untouched. The mixture was then brought into glove box and benzene- $d_6$  was removed under vacuum. The residue was dissolved in 2 mL of pentane and filtered through Celite to exclude the solid catalyst. The filtrate was dried under vacuum to isolate an oil (0.095 g, 80%) identified as monosilylated cyclohexene. <sup>1</sup>H NMR (benzene- $d_6$ , 25 °C) δ 7.52 (br m, 2H), 7.15 (br m, 3H), 5.72 (m, 2H, *H*C=*CH*), 4.46 (br, 2H, Si*H*<sub>2</sub>Ph), 1.89 (br m, 3H, *Cy*), 1.78 (br m, 1H, *Cy*), 1.64 (br m, 2H, *Cy*), 1.45 (br m, 1H, *Cy*). <sup>13</sup>C NMR (benzene- $d_6$ , 25 °C) δ 135.92 (*phenyl*), 131.95 (*phenyl*), 129.98 (*phenyl*), 127.55 (*phenyl*), 126.64 (H*C*=*C*H), 25.23 (*Cy*), 25.04 (*Cy*), 22.46 (*Cy*), 22.12 (*Cy*). <sup>29</sup>Si NMR (benzene- $d_6$ , 25 °C) δ -27.50 (s, *Si*H<sub>2</sub>Ph).



**Figure S38.** <sup>1</sup>H NMR spectrum of 1,3-cyclohexadiene hydrosilylation catalyzed by **1** after 24 h.



Figure S39. <sup>1</sup>H NMR spectrum of isolated cyclohexene product in benzene- $d_6$ .



Figure S40. <sup>13</sup>C NMR spectrum of isolated cyclohexene product in benzene- $d_6$ .


Figure S41. <sup>29</sup>Si NMR spectrum of isolated cyclohexene product in benzene-*d*<sub>6</sub>.

**Deuterosilylation of 1,4-cyclohexadiene using PhSiD**<sub>3</sub> and 0.5 mol% of 1 (1 mol% based on Mn): In the glove box, PhSiD<sub>3</sub> (80.2  $\mu$ L, 0.633 mmol) and 1,4-cyclohexadiene (59.8  $\mu$ L, 0.633 mmol) were added to a J. Young tube containing a benzene-*d*<sub>6</sub> solution of 1 (0.003 g, 0.00317 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 4 d of heating, >99% hydrosilylation of one olefin bond was observed, while the other olefin was untouched. The mixture was then brought into glove box and benzene-*d*<sub>6</sub> was removed under vacuum. The residue was dissolved in 2 mL of pentane and filtered through Celite to exclude the solid catalyst. The filtrate was dried under vacuum to isolate an oil (0.106 g, 88%) containing a mixture of regioisomeric deuterated silane products. The <sup>2</sup>H NMR spectrum of the isolated product is shown below.



**Figure S42.** <sup>2</sup>H NMR spectrum of 1,4-cyclohexadiene deuterosilylation catalyzed by **1** after 4 d at 130 °C.

Hydrosilylation of cyclohexene catalyzed by 0.5 mol% of 1 (1 mol% based on Mn): In the glove box, PhSiH<sub>3</sub> (78.2  $\mu$ L, 0.633 mmol) and cyclohexene (64.1  $\mu$ L, 0.633 mmol) were added to a J. Young tube containing a benzene- $d_6$  solution of 1 (0.003 g, 0.00317 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 5 d of heating, 37% conversion was observed. It is believed that the resulting mixture consists of the hydrosilylated product (new SiH<sub>2</sub>Ph at 4.37 ppm and cyclohexane peaks at 1.61, 1.52, and 1.12 ppm) and another product caused by dehydrogenative silylation (new Si-H peak at 5.06 ppm).

## $\begin{array}{c} 7.51\\ 7.49\\ 7.136\\ 7.136\\ 7.136\\ 7.136\\ 7.136\\ -5.68\\ -5.6$



Figure S43. <sup>1</sup>H NMR spectrum of cyclohexene hydrosilylation catalyzed by 1 after 5 d.

Hydrosilylation of 9-vinylcarbazole catalyzed by 0.5 mol% of 1 (1 mol% based on Mn): In the glove box, a benzene- $d_6$  solution of PhSiH<sub>3</sub> (75.6 µL, 0.612 mmol) and 9-vinylcarbazole (118.3 mg, 0.612 mmol) was added to a J. Young tube containing a benzene- $d_6$  solution of 1 (0.0029 g, 0.00306 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 4 d of heating, only 39% conversion was observed, which showed a mixture of Markovnikov and *anti*-Markovnikov products. Prolonged heating did not afford complete conversion and resulted other unidentified products caused by dehydrogenative silylation.

## 



**Figure S44.** <sup>1</sup>H NMR spectrum of 9-vinylcarbazole hydrosilylation catalyzed by **2** after 4 d.

Hydrosilylation of 5-hexen-2-one catalyzed by 0.5 mol% of 1 (1 mol% based on Mn): In the glove box, PhSiH<sub>3</sub> (172  $\mu$ L, 1.395 mmol) and 5-hexene-2-one (73.5  $\mu$ L, 0.634 mmol) were added to a J. Young tube containing a benzene-*d*<sub>6</sub> solution of 1 (0.003 g, 0.00634 mmol). Bubbling was noticed and the tube became hot due to exothermic ketone hydrosilylation. The tube was sealed under N<sub>2</sub> atmosphere and allowed to sit at room temperature for 1.5 h. The <sup>1</sup>H NMR showed complete conversion to the respective tertiary silyl ether while the olefin functionality remained untouched. The tube was then heated at 130 °C for 24 h during which time greater than 99% olefin hydrosilylation was observed with the formation of a mixture of products.



**Figure S45.** Stacked <sup>1</sup>H NMR spectra of 5-hexene-2-one (red, bottom), **1**-catalyzed hydrosilylation of 5-hexene-2-one after 1.5 h at ambient temperature (green, middle), and 1-catalyzed hydrosilylation of 5-hexene-2-one after 24 h at 130 °C (blue, top, note disappearance of olefin resonances).

Hydrosilylation of styrene catalyzed by 0.5 mol% of 1 (1 mol% based on Mn): In the glove box, PhSiH<sub>3</sub> (78.2 µL, 0.633 mmol) and styrene (72.5 µL, 0.633 mmol) were added to a J. Young tube containing a benzene- $d_6$  solution of 1 (0.003 g, 0.00317 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 38 h of heating, >99% conversion was observed, which showed Markovnikov's product, PhSiH<sub>2</sub>CH(CH<sub>3</sub>)Ph (81%) along with the anti-Markovnikov product PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Ph (19%). The tube was then brought back into the glove box and the solution was dried under vacuum. The residue was filtered with pentane (3 mL) through Celite to separate the insoluble catalyst from the generated silane. The pentane solution was then dried under vacuum to isolate an oil (0.125 g, 93%) containing PhSiH<sub>2</sub>CH(CH<sub>3</sub>)Ph (89% of the isolated product) and PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Ph (11% of the isolated product). *PhSiH*<sub>2</sub>*CH*(*CH*<sub>3</sub>)*Ph*: <sup>1</sup>H NMR (benzene-d<sub>6</sub>, 25 °C) δ 7.37 (m, 2H, *phenyl*), 7.18-7.11 (m, 5H, *phenyl*), 7.04 (m, 3H, *phenyl*), 4.51 (t, *J* = 3.2 Hz, 2H, Si*H*<sub>2</sub>Ph), 2.44 (m, 1H, CH), 1.37 (d, J = 7.5 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (benzene- $d_6$ , 25 °C)  $\delta$  144.70 (*phenyl*), 136.02 (*phenyl*), 131.61 (phenyl), 130.05 (phenyl), 128.74 (phenyl), 128.18 (phenyl), 127.49 (phenyl), 125.44 (*phenyl*), 25.68 (CH), 16.54 (CH<sub>3</sub>). <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>, 25 °C) δ -21.17 (SiH<sub>2</sub>Ph). *PhSiH*<sub>2</sub>(*CH*<sub>2</sub>)<sub>2</sub>*Ph*: <sup>1</sup>H NMR (benzene- $d_6$ , 25 °C)  $\delta$  7.47 (m, *phenyl*), 4.48 (t, SiH<sub>2</sub>Ph), 2.65 (m, CH<sub>2</sub>), 1.14 (CH<sub>2</sub>). <sup>13</sup>C NMR (benzene- $d_6$ , 25 °C)  $\delta$  144.09 (*phenyl*), 135.59 (*phenyl*), 132.33 (phenyl), 129.93 (phenyl), 126.14 (phenyl), 31.41 (CH<sub>2</sub>), 12.34 (CH<sub>2</sub>). <sup>29</sup>Si NMR (benzene-d<sub>6</sub>, 25 °C) δ -31.30 (*Si*H<sub>2</sub>Ph).



\_4.52 4.57 4.27 4.27 -2.66 -2.66 -2.45 -1.15

**Figure S46.** <sup>1</sup>H NMR spectrum of styrene hydrosilylation catalyzed by **1** after 36 h.

7.49



**Figure S47.** <sup>1</sup>H NMR spectrum of isolated products in benzene-*d*<sub>6</sub>.



Figure S48. <sup>13</sup>C NMR spectrum of isolated products in benzene- $d_6$ .



Figure S49. <sup>29</sup>Si NMR spectrum of isolated products in benzene- $d_6$ .

Hydrosilylation of 4-tert-butylstyrene catalyzed by 0.5 mol% of 1 (1 mol% based on Mn): In the glove box, PhSiH<sub>3</sub> (104.2 µL, 0.845 mmol) and 4-tert-butylstyrene (154.6 µL, 0.845 mmol) were added to a J. Young tube containing a benzene- $d_0$  solution of 1 (0.004 g, 0.00422 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 24 h of heating, >99% conversion was observed, which showed the formation of Markovnikov's product, PhSiH<sub>2</sub>CH(CH<sub>3</sub>)(4-<sup>t</sup>BuC<sub>6</sub>H<sub>4</sub>) (95%) along with the *anti*-Markovnikov product  $PhSiH_2(CH_2)_2(4^{-t}BuC_6H_4)$  (5%). The tube was then brought back into the glove box and the solution was dried under vacuum. The residue was filtered with pentane (3 mL) through Celite to separate the insoluble catalyst from the generated silane. The pentane solution was then dried under vacuum to isolate an oil (0.166 g, 73%) containing  $PhSiH_2CH(CH_3)(4-^{t}BuC_6H_4)$ (95% of the isolated product) and PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>( $4^{-t}BuC_6H_4$ ) (5% of the isolated product). *PhSiH*<sub>2</sub>*CH*(*CH*<sub>3</sub>)(4-<sup>*t*</sup>*BuC*<sub>6</sub>*H*<sub>4</sub>): <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 25 °C) δ 7.37 (m, 2H, *phenyl*), 7.24 (m, 2H, phenyl), 7.14-7.04 (m, 5H, phenyl), 4.52 (dq, J = 8.4 and 3.2 Hz, 2H, SiH<sub>2</sub>Ph), 2.46 (m, 1H, CH), 1.39 (d, J = 7.6 Hz, 3H, CH<sub>3</sub>), 1.24 (s, 9H, CMe<sub>3</sub>). <sup>13</sup>C NMR (benzene- $d_6$ , 25 °C)  $\delta$  147.89 (phenvl), 141.63 (phenvl), 136.02 (phenvl), 131.85 (phenvl), 130.01 (phenvl), 128.18 (phenvl), 127.24 (phenyl), 125.64 (phenyl), 34.38 (CMe<sub>3</sub>), 31.64 (CMe<sub>3</sub>), 25.11 (CH), 16.81 (CH<sub>3</sub>). <sup>29</sup>Si NMR (benzene- $d_6$ , 25 °C)  $\delta$  -21.50 (SiH<sub>2</sub>Ph). PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>(4-<sup>t</sup>BuC<sub>6</sub>H<sub>4</sub>): <sup>1</sup>H NMR (benzene- $d_6$ , 25 °C) δ7.45 (phenyl), 7.36 (phenyl), 3.96 (SiH<sub>2</sub>Ph), 2.68 (CH<sub>2</sub>), 1.25 (CMe<sub>3</sub>), 0.86 (CH<sub>2</sub>). <sup>13</sup>C NMR (benzene- $d_6$ , 25 °C)  $\delta$  No significant resonances observed. <sup>29</sup>Si NMR (benzene- $d_6$ , 25 °C)  $\delta$ No significant resonances observed.



Figure S50. <sup>1</sup>H NMR spectrum of 4-*tert*-butylstyrene hydrosilylation catalyzed by **1** after 38 h.



Figure S51. <sup>1</sup>H NMR spectrum of isolated Markovnikov product in benzene-*d*<sub>6</sub>.



Figure S52. <sup>13</sup>C NMR spectrum of isolated Markovnikov product in benzene- $d_6$ .



Figure S53. <sup>29</sup>Si NMR spectrum of isolated Markovnikov product in benzene-*d*<sub>6</sub>.

Hydrosilylation of 4-methylstyrene catalyzed by 0.5 mol% of 1 (1 mol% based on Mn): In the glove box, PhSiH<sub>3</sub> (104.2 µL, 0.845 mmol) and 4-methylstyrene (111.5 µL, 0.845 mmol) were added to a J. Young tube containing a benzene- $d_6$  solution of 1 (0.004 g, 0.00422 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 48 h of heating, >99% conversion was observed, which showed the formation of only Markovnikov product, PhSiH<sub>2</sub>CH(CH<sub>3</sub>)(4-MeC<sub>6</sub>H<sub>4</sub>). The tube was then brought back into the glove box and the solution was dried under vacuum. The residue was filtered with pentane (3 mL) through Celite to separate the insoluble catalyst from the generated silane. The pentane solution was then dried under vacuum to isolate an oil (0.151 g, 79%).  $PhSiH_2CH(CH_3)(4-$ *MeC*<sub>6</sub>*H*<sub>4</sub>: <sup>1</sup>H NMR (benzene-d<sub>6</sub>, 25 °C) δ 7.37 (m, 2H, phenyl), 7.11-7.09 (m, 3H, phenyl), 6.97  $(m, 4H, phenyl), 4.51 (dq, J = 6.7 and 3.1 Hz, SiH_2Ph), 2.42 (m, 1H, CH), 2.12 (s, 3H, CH_3),$ 1.36 (d, J = 7.5 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (benzene- $d_6$ , 25 °C)  $\delta$  141.63 (*phenyl*), 136.04 (*phenyl*), 134.55 (phenyl), 131.83 (phenyl), 130.01 (phenyl), 129.49 (phenyl), 128.18 (phenyl), 127.44 (phenyl), 25.20 (CH), 21.01 (CH<sub>2</sub>), 16.61 (CH<sub>3</sub>). <sup>29</sup>Si NMR (benzene-d<sub>6</sub>, 25 °C) δ -21.43 (SiH<sub>2</sub>Ph).



**Figure S54.** <sup>1</sup>H NMR spectrum of 4-methylstyrene hydrosilylation catalyzed by **1** after 4 d.



Figure S55. <sup>1</sup>H NMR spectrum of isolated Markovnikov product in benzene-*d*<sub>6</sub>.



Figure S56. <sup>13</sup>C NMR spectrum of isolated Markovnikov product in benzene- $d_6$ .



Figure S57. <sup>29</sup>Si NMR spectrum of isolated Markovnikov product in benzene-*d*<sub>6</sub>.

Hydrosilylation of *trans*-β-methylstyrene catalyzed by 0.5 mol% of 1 (1 mol% based on **Mn**): In the glove box, PhSiH<sub>3</sub> (78.2  $\mu$ L, 0.633 mmol) and *trans*- $\beta$ -methylstyrene (82.2  $\mu$ L, 0.633 mmol) were added to a J. Young tube containing a benzene- $d_0$  solution of 1 (0.003 g. 0.00317 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 36 h of heating, >99% conversion was observed, which showed the formation of the Markovnikov product, PhSiH<sub>2</sub>CH(Et)Ph, along with traces of anti-Markovnikov product PhSiH<sub>2</sub>CH(CH<sub>3</sub>)(CH<sub>2</sub>Ph). The tube was then brought back into the glove box and the solution was dried under vacuum. The residue was filtered with pentane (3 mL) through Celite to separate the insoluble catalyst from the generated silane. The pentane solution was then dried under vacuum to isolate an oil (0.109 g, 76%) containing PhSiH<sub>2</sub>CH(Et)Ph (94% of the isolated product) and PhSiH<sub>2</sub>CH(CH<sub>3</sub>)(CH<sub>2</sub>Ph) (6% of the isolated product). *PhSiH<sub>2</sub>CH(Et)Ph*: <sup>1</sup>H NMR (benzene-d<sub>6</sub>, 25 °C) δ 7.34 (m, 2H, phenyl), 7.16 – 7.05 (m, 5H, phenyl), 6.99 (m, 3H, phenyl), 4.52 (d, J = 3.1 Hz, 2H, Si $H_2$ Ph), 2.21 (m, 1H, CH), 1.80 (m, 2H, CH<sub>2</sub>), 0.83 (t, J = 7.3 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (benzene-d<sub>6</sub>, 25 °C) δ 142.93 (phenyl), 136.09 (phenyl), 131.68 (phenyl), 130.01 (phenyl), 128.79 (phenyl), 128.29 (phenyl), 128.16 (phenyl), 125.50 (phenyl), 34.72 (CH), 24.90 (CH<sub>2</sub>), 14.10 (CH<sub>3</sub>). <sup>29</sup>Si NMR (benzene-d<sub>6</sub>, 25 °C) δ -23.96 (SiH<sub>2</sub>Ph). The anti-Markovnikov product, PhSiH<sub>2</sub>CH(CH<sub>3</sub>)(CH<sub>2</sub>Ph), was observed at 7.61 (phenyl), 7.52 (phenyl), 1.20, 1.17, and 0.88 ppm in the <sup>1</sup>H NMR spectrum and a small peak at -33.73 ppm was observed in the <sup>29</sup>Si NMR spectrum.



**Figure S58.** <sup>1</sup>H NMR spectrum of *trans*- $\beta$ -methylstyrene hydrosilylation catalyzed by **1** after 36 h.



Figure S59. <sup>1</sup>H NMR spectrum of isolated PhSiH<sub>2</sub>CH(Et)Ph in benzene-*d*<sub>6</sub>.



**Figure S60.** <sup>13</sup>C NMR spectrum of isolated PhSiH<sub>2</sub>CH(Et)Ph in benzene-*d*<sub>6</sub>.



Figure S61. <sup>29</sup>Si NMR spectrum of isolated PhSiH<sub>2</sub>CH(Et)Ph in benzene-*d*<sub>6</sub>.

Hydrosilylation of *cis*-β-methylstyrene catalyzed by 0.5 mol% of 1 (1 mol% of Mn): In the glove box, PhSiH<sub>3</sub> (78.2 μL, 0.633 mmol) and *cis*-β-methylstyrene (82.2 μL, 0.633 mmol) were added to a J. Young tube containing a benzene- $d_6$  solution of 1 (0.003 g, 0.00317 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 36 h of heating, >99% conversion was observed, which showed the Markovnikov product, PhSiH<sub>2</sub>CH(Et)Ph. The tube was then brought back into the glove box and the solution was dried under vacuum. The residue was filtered with pentane (3 mL) through Celite to separate the insoluble catalyst from the generated silane. The pentane solution was then dried under vacuum to isolate an oil (0.128 g, 89%). PhSiH<sub>2</sub>CH(Et)Ph: <sup>1</sup>H NMR (benzene- $d_6$ , 25 °C)  $\delta$  7.34 (d, J = 7.3 Hz, 2H, phenyl), 7.10 (m, 5H, phenyl), 6.99 (m, 3H, phenyl), 4.52 (d, J = 2.9 Hz, 2H, Si*H*<sub>2</sub>Ph), 2.21 (m, 1H, C*H*), 1.81 (m, 2H, C*H*<sub>2</sub>), 0.83 (t, *J* = 7.2 Hz, 3H, C*H*<sub>3</sub>). <sup>13</sup>C NMR (benzene-d<sub>6</sub>, 25 °C) δ 142.93 (phenyl), 136.08 (phenyl), 131.68 (phenyl), 130.01 (phenyl), 128.78 (phenyl), 128.30 (phenyl), 128.16 (phenyl), 125.50 (phenyl), 34.72 (CH), 24.90 (CH<sub>2</sub>), 14.10 (CH<sub>3</sub>).<sup>29</sup>Si NMR (benzene-d<sub>6</sub>, 25 °C) δ -23.88 (SiH<sub>2</sub>Ph). Less than 5% of the anti-Markovnikov product, PhSiH<sub>2</sub>CH(CH<sub>3</sub>)(CH<sub>2</sub>Ph), was observed at 7.52 (phenyl), 1.65 (CH), 1.28 (CH<sub>2</sub>), and 0.88 (CH<sub>3</sub>) ppm in the <sup>1</sup>H NMR spectrum and a small peak at -33.66 ppm was observed in the <sup>29</sup>Si NMR spectrum.



**Figure S62.** <sup>1</sup>H NMR spectrum of *cis*- $\beta$ -methylstyrene hydrosilylation catalyzed by **1** after 36 h.





Figure S63. <sup>1</sup>H NMR spectrum of isolated PhSiH<sub>2</sub>CH(Et)Ph in benzene-*d*<sub>6</sub>.



Figure S64. <sup>13</sup>C NMR spectrum of isolated PhSiH<sub>2</sub>CH(Et)Ph in benzene-*d*<sub>6</sub>.



Figure S65. <sup>29</sup>Si NMR spectrum of isolated PhSiH<sub>2</sub>CH(Et)Ph in benzene-*d*<sub>6</sub>.

Hydrosilylation of α-methylstyrene catalyzed by 0.5 mol% of 1 (1 mol% of Mn): In the glove box, PhSiH<sub>3</sub> (78.2 µL, 0.633 mmol) and α-methylstyrene (82.2 µL, 0.633 mmol) were added to a J. Young tube containing a benzene- $d_6$  solution of 1 (0.003 g, 0.00317 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 4 d of heating, only 56% conversion was observed and prolonged heating did not afford further conversion. Anti-Markovnikov's product, PhSiH<sub>2</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)(Ph) was observed by NMR spectroscopy. Prolonged heating resulted in additional resonances, which are believed to originate from dehydrogenative silylation.



**Figure S66.** <sup>1</sup>H NMR spectrum of  $\alpha$ -methylstyrene hydrosilylation catalyzed by **1** after 4 d.

Hydrosilylation of 4-diphenylphosphinostyrene catalyzed by 0.5 mol% of 1 (1 mol% of Mn): In the glove box, PhSiH<sub>3</sub> (75.6 µL, 0.612 mmol) and 4-diphenylphosphinostyrene (0.176 g, 0.612 mmol) were added to a J. Young tube containing a benzene- $d_6$  solution of 1 (0.0029 g. 0.00306 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 3 d of heating, >99% conversion was observed, which showed only the Markovnikov product,  $PhSiH_2CH(CH_3)(C_6H_4PPh_2)$ . The tube was then brought back into the glove box and the solution was dried under vacuum. The residue was filtered with pentane (3 mL) through Celite to separate the insoluble catalyst from the generated silane. The pentane solution was then dried under vacuum to isolate an oil identified as  $PhSiH_2CH(CH_3)(C_6H_4PPh_2)$ (0.190 g, 78%). *PhSiH*<sub>2</sub>*CH*(*CH*<sub>3</sub>)(*C*<sub>6</sub>*H*<sub>4</sub>*PPh*<sub>2</sub>): <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 25 °C)  $\delta$  7.44-7.40 (m, 4H, phenyl), 7.36-7.32 (m, 2H, phenyl), 7.29 (m, 2H, phenyl), 7.13-7.06 (m, 9H, phenyl), 6.90 (m, 2H, phenyl), 4.43 (d, J = 3.2 Hz, 2H, SiH<sub>2</sub>Ph), 2.34 (m, 1H, CH), 1.27 (d, J = 7.4 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (benzene-d<sub>6</sub>, 25 °C) δ 145.68 (phenyl), 138.45 (phenyl), 136.00 (phenyl), 134.64 (phenvl), 134.44 (phenvl), 134.22 (phenvl), 134.03 (phenvl), 131.38 (phenvl), 130.11 (phenvl), 128.82 (phenvl), 128.76 (phenvl), 128.17 (phenvl), 25.64 (CH), 16.21 (CH<sub>3</sub>). <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>, 25 °C) δ -21.25 (*Si*H<sub>2</sub>Ph). <sup>31</sup>P NMR (benzene-*d*<sub>6</sub>, 25 °C) δ -6.29 (*P*Ph<sub>2</sub>).



**Figure S67.** <sup>1</sup>H NMR spectrum of 4-diphenylphosphinostyrene hydrosilylation catalyzed by **1** after 3 d.



Figure S68. <sup>1</sup>H NMR spectrum of isolated PhSiH<sub>2</sub>CH(CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>) in benzene-*d*<sub>6</sub>.



Figure S69. <sup>13</sup>C NMR spectrum of isolated PhSiH<sub>2</sub>CH(CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>) in benzene-d<sub>6</sub>.



Figure S70. <sup>29</sup>Si NMR spectrum of isolated PhSiH<sub>2</sub>CH(CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>) in benzene-*d*<sub>6</sub>.



Figure S71. <sup>31</sup>P NMR spectrum of isolated PhSiH<sub>2</sub>CH(CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>) in benzene-d<sub>6</sub>.

Hydrosilylation of indene catalyzed by 0.5 mol% of 1 (1 mol% based on Mn): In the glove box, a benzene- $d_6$  solution of PhSiH<sub>3</sub> (75.6 µL, 0.612 mmol) and indene (71.3 µL, 0.612 mmol) was added to a J. Young tube containing a benzene- $d_6$  solution of 1 (0.0029 g, 0.00306 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 4 d of heating, only 19% conversion was observed. Prolonged heating did not afford complete conversion and resulted other unidentified products caused by dehydrogenative silylation. The observed mixture shows resonances for the product resulting from hydrosilylation at the benzylic position.

## 7,150 7,120,



**Figure S72.** <sup>1</sup>H NMR spectrum of indene hydrosilylation catalyzed by **1** after 4 d.

Attempt to hydrosilylate 4-bromostyrene using 0.5 mol% of 1 (1 mol% based on Mn): In the glove box, PhSiH<sub>3</sub> (78.2  $\mu$ L, 0.633 mmol) and 4-bromostyrene (82.8  $\mu$ L, 0.633 mmol) were added to a J. Young tube containing a benzene- $d_6$  solution of 1 (0.003 g, 0.00317 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 5 d of heating, no conversion was observed. It is believed that dehalogenation of the substrate is inhibiting the reaction. Hydrosilylation of 4-fluorostyrene catalyzed by 0.5 mol% of 1 (1 mol% of Mn): In the glove box, PhSiH<sub>3</sub> (78.2  $\mu$ L, 0.633 mmol) and 4-fluorostyrene (75.5  $\mu$ L, 0.633 mmol) were added to a J. Young tube containing a benzene-*d*<sub>6</sub> solution of 1 (0.003 g, 0.00317 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 5 d of heating, >99% consumption of the starting alkene was observed. Analysis of the reaction mixture using <sup>1</sup>H and <sup>29</sup>Si NMR revealed formation of a mixture of Markovnikov and *anti*-Markovnikov products along with products formed by benzene-*d*<sub>6</sub> dehydrogenative silylation. In addition, multiple resonances were observed in the <sup>19</sup>F NMR spectrum, which suggest that 4-fluorostyrene defluorination may be occurring.



Figure S73. <sup>1</sup>H NMR spectrum of 4-fluorostyrene hydrosilylation catalyzed by 1.



Figure S74. <sup>1</sup>H NMR spectrum of isolated products from 4-fluorostyrene hydrosilylation.



Figure S75. <sup>13</sup>C NMR spectrum of isolated products from 4-fluorostyrene hydrosilylation.



**Figure S76.** <sup>19</sup>F NMR spectrum of isolated products from 4-fluorostyrene hydrosilylation.



Figure S77. <sup>29</sup>Si NMR spectrum of isolated products from 4-fluorostyrene hydrosilylation.

Neat catalytic polymerization of vinyl-terminated poly(dimethylsiloxane) using 10 mol% 1 (5 mol% relative to olefin; 20 mol% based on Mn, 10 mol% based on Mn and olefin): In the glove box, a scintillation vial was charged with 1 (0.004 g, 0.004222 mmol). Then, vinyl-terminated poly(dimethylsiloxane) (1.094 mL, 0.0422 mmol) and polymethylhydrosiloxane (65  $\mu$ L, 0.0277 mmol, 1.05 mmol of Si-H) were added to it. The vial was capped under N<sub>2</sub> and heated at 130 °C for 4 d. The yellow mixture upon cooling afforded a high viscosity gel, which upon exposure to air turned brown as a result of catalyst deactivation. The gel was vigorously stirred with isopropanol (15 mL) and then the yellow isopropanol wash was decanted off. This was repeated once more and finally the material was dried to isolate a 0.620 g of a gummy silicone gel. The product of this reaction is shown below:





**Figure S78.** Silicone obtained following the **1**-catalyzed hydrosilylation of vinyl-terminated poly(dimethylsiloxane) using PMHS.

Neat catalytic polymerization of 1,2,4-trivinylcyclohexane using 0.05 mol% of 1 (relative to substrate, 0.0167 mol% relative to olefin; 0.1 mol% based on Mn, 0.033 mol% based on Mn and olefin): In the glove box, a vial was charged with 1 (0.0025 g, 0.00264 mmol). Polymethylhydrosiloxane (1.00 mL, 0.4264 mmol, 16.20 mmol of Si-H) was then added to the vial in portions to transfer the catalyst slurry into a Schlenk flask. To the slurry was then added 1,2,4-trivinylcyclohexane (1.023 mL, 5.279 mmol) and the flask was sealed under N<sub>2</sub> atmosphere. The neat mixture was heated at 130 °C for 5 d, during which time a yellow oil formed. The flask was cooled to room temperature and the mixture was exposed to air to deactivate the catalyst. The resulting brown oil was transferred into a vial and stirred vigorously with isopropanol (15 mL). From the two layers, the top brown layer was decanted off and the gluey residue was allowed to sit at room temperature. After 2 days a clear colorless gummy solid was obtained (0.805 g).





**Figure S79.** Silicone obtained following the **1**-catalyzed hydrosilylation of 1,2,4-trivinylcyclohexane using PMHS.

Addition of PhSiH<sub>3</sub> to 2: In the glove box, PhSiH<sub>3</sub> (5.6  $\mu$ L, 0.0459 mmol) was added to a J. Young tube containing a solution of 2 (0.0194 g, 0.0306 mmol) in 0.7 mL benzene-*d*<sub>6</sub>. The tube was sealed under N<sub>2</sub> and heated at 130 °C. After 24 h, complete conversion of 2 to [(<sup>iPr2Ph</sup>BDI)Mn( $\mu$ -H)]<sub>2</sub> (1) was observed along with the formation of the hydrosilylated product PhSiH<sub>2</sub>CH(CH<sub>3</sub>)(4-<sup>t</sup>BuC<sub>6</sub>H<sub>4</sub>).



**Figure S80:** Stacked <sup>1</sup>H NMR spectra of **1** (purple), **2** after heating with 1.5 eq. of PhSiH<sub>3</sub> for 24 h at 130 °C (**1** is formed, blue), **2** after treating with 1.5 eq. of PhSiH<sub>3</sub> for 24 h at 25 °C (no reaction, green), and **2** (red).



**Figure S81:** Stacked <sup>1</sup>H NMR spectra showing the product of **1** catalyzed 4-*tert*-butylstyrene hydrosilylation (top, red) and **2** after heating with 1.5 eq. of PhSiH<sub>3</sub> for 24 h at 130 °C (at bottom).

Hydrosilylation of 1-hexene catalyzed by 1.0 mol% of 2: In the glove box, PhSiH<sub>3</sub> (62.2  $\mu$ L, 0.505 mmol) and 1-hexene (63.1  $\mu$ L, 0.505 mmol) were added to a J. Young tube containing a benzene-*d*<sub>6</sub> solution of 2 (0.0032 g, 0.00505 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 22 h of heating, greater than 99% conversion was observed. The tube was then brought back into the glove box and the solution was dried under vacuum. The residue was filtered with pentane (3 mL) through Celite to separate the insoluble catalyst from the silane product. The pentane was then removed under vacuum to isolate an oil identified as PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub> (0.074 g, 77%). The multinuclear NMR spectra match those of the product obtained from 1-catalyzed 1-hexene hydrosilylation.



--4.49 --4.22

1.26 1.26 1.23 1.16 0.85 0.81

~7.50 -7.38 -7.16 ~7.07

**Figure S82.** <sup>1</sup>H NMR spectrum of 1-hexene hydrosilylation catalyzed by 1 mol% of **2** after 22 h at 130 °C.



**Figure S83.** <sup>1</sup>H NMR spectrum of isolated anti-Markovnikov product from 1-hexene hydrosilylation catalyzed by **2**.



**Figure S84.** <sup>13</sup>C NMR spectrum of isolated anti-Markovnikov product from 1-hexene hydrosilylation catalyzed by **2**.



**Figure S85.**<sup>29</sup>Si NMR spectrum of isolated anti-Markovnikov product from 1-hexene hydrosilylation catalyzed by **2**.

**Hydrosilylation of styrene catalyzed by 1.0 mol% of 2:** In the glove box, PhSiH<sub>3</sub> (77.8 μL, 0.631 mmol) and styrene (72.2 μL, 0.631 mmol) were added to a J. Young tube containing a benzene- $d_6$  solution of **2** (0.004 g, 0.00631 mmol). The tube was sealed under N<sub>2</sub> atmosphere and heated at 130 °C. The progress of the reaction was monitored closely by examining the consumption of starting alkene <sup>1</sup>H NMR resonances. After 16 h of heating, greater than 99% conversion was observed, which showed Markovnikov's product, PhSiH<sub>2</sub>CH(CH<sub>3</sub>)Ph (91%) along with the anti-Markovnikov product PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Ph (9%). The tube was then brought back into the glove box and the solvent was removed under vacuum. The residue was filtered with pentane (3 mL) through Celite to separate the insoluble catalyst from the silane product. The pentane solution was then dried under vacuum to isolate an oil (0.116 g, 87%) containing PhSiH<sub>2</sub>CH(CH<sub>3</sub>)Ph (91% of the isolated product) and PhSiH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Ph (9% of the isolated product). The multinuclear NMR spectra matched those of the product obtained from **1**-catalyzed styrene hydrosilylation.



-4.52

-2.66

-1.37

-7.36 -7.16 -7.04

**Figure S86.** <sup>1</sup>H NMR spectrum of styrene hydrosilylation catalyzed by 1 mol% of **2** after 16 h at 130 °C.
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Figure S87. <sup>1</sup>H NMR spectrum of isolated products from styrene hydrosilylation catalyzed by 2.



Figure S88. <sup>13</sup>C NMR spectrum of isolated products from styrene hydrosilylation catalyzed by 2.



**Figure S89.** <sup>29</sup>Si NMR spectrum of isolated products from styrene hydrosilylation catalyzed by **2**.



**Figure S90**. Variable temperature <sup>1</sup>H NMR spectra of **1** in *o*-xylene- $d_{10}$ . The probe temperature (400 MHz NMR) was calibrated using neat ethylene glycol.

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