

Hydrosilylation of Aldehydes and Formates Using a Dimeric Manganese Precatalyst

Supporting Information

*Tufan K. Mukhopadhyay, Chandrani Ghosh, Marco Flores, Thomas L. Groy, Ryan J. Trovitch**

School of Molecular Sciences, Arizona State University, Tempe, Arizona 85287

ryan.trovitch@asu.edu

PRECATALYST CHARACTERIZATION

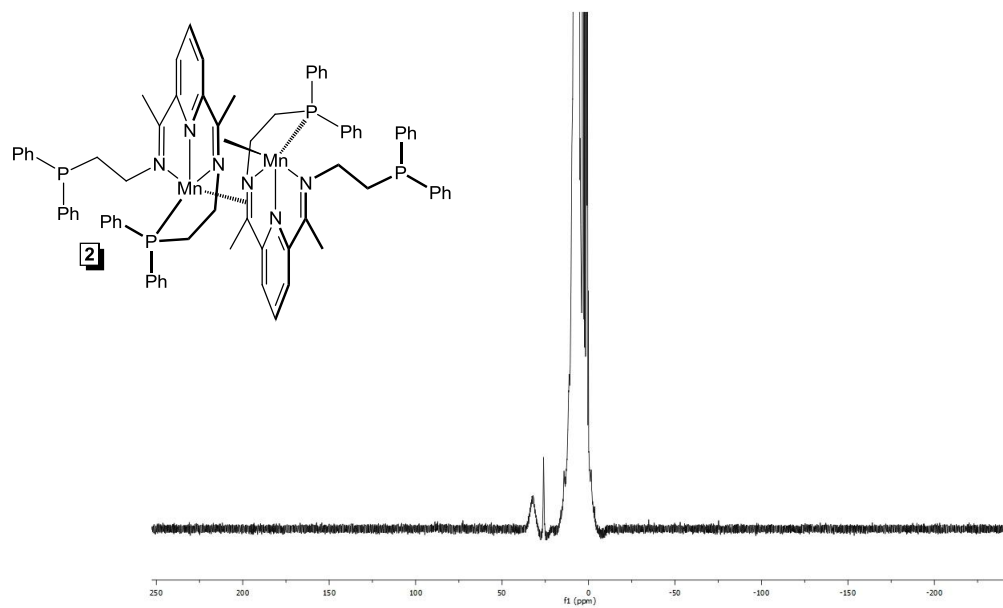


Figure S1. ^1H NMR spectrum of **2** in benzene- d_6 at 23 °C.

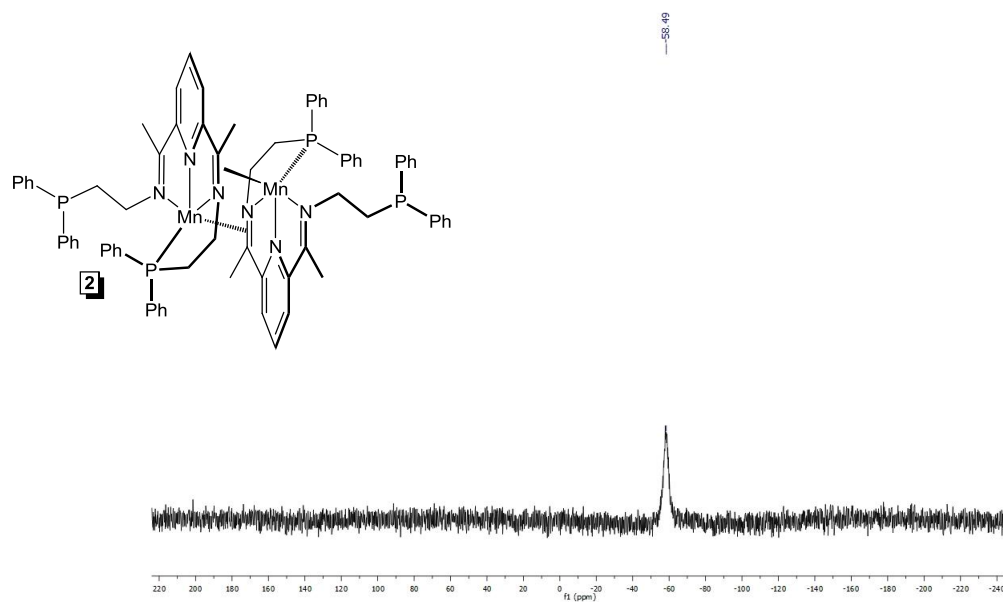


Figure S2: ^{31}P NMR spectrum of **2** in benzene- d_6 at 23 °C.

X-RAY CRYSTALLOGRAPHIC DATA

Table S1. Crystallographic Data for [(^{Ph}2PEtPDI)Mn]₂ (**2**).

	2
chemical formula	C ₇₄ H ₇₄ Mn ₂ N ₆ P ₄ , 4(C ₇ H ₈)
formula weight	1649.68
crystal dimensions	0.386 x 0.086 x 0.038
crystal system	monoclinic
space group	P 1 21/c 1
<i>a</i> (Å)	14.488(3)
<i>b</i> (Å)	20.146(5)
<i>c</i> (Å)	14.872(4)
α (deg)	90
β (deg)	95.390(3)
γ (deg)	90
<i>V</i> (Å ³)	4321.6(18)
<i>Z</i>	2
<i>T</i> (°C)	123.(2)
ρ _{calcd} (g cm ⁻³)	1.268
μ (mm ⁻¹)	0.418
reflections collected	33859
data/restraints/parameters	7610/0/518
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0696
w <i>R</i> ₂ (all data)	0.1890
Goodness-of-fit	1.037
Largest peak, hole (eÅ ⁻³)	1.123, -0.416

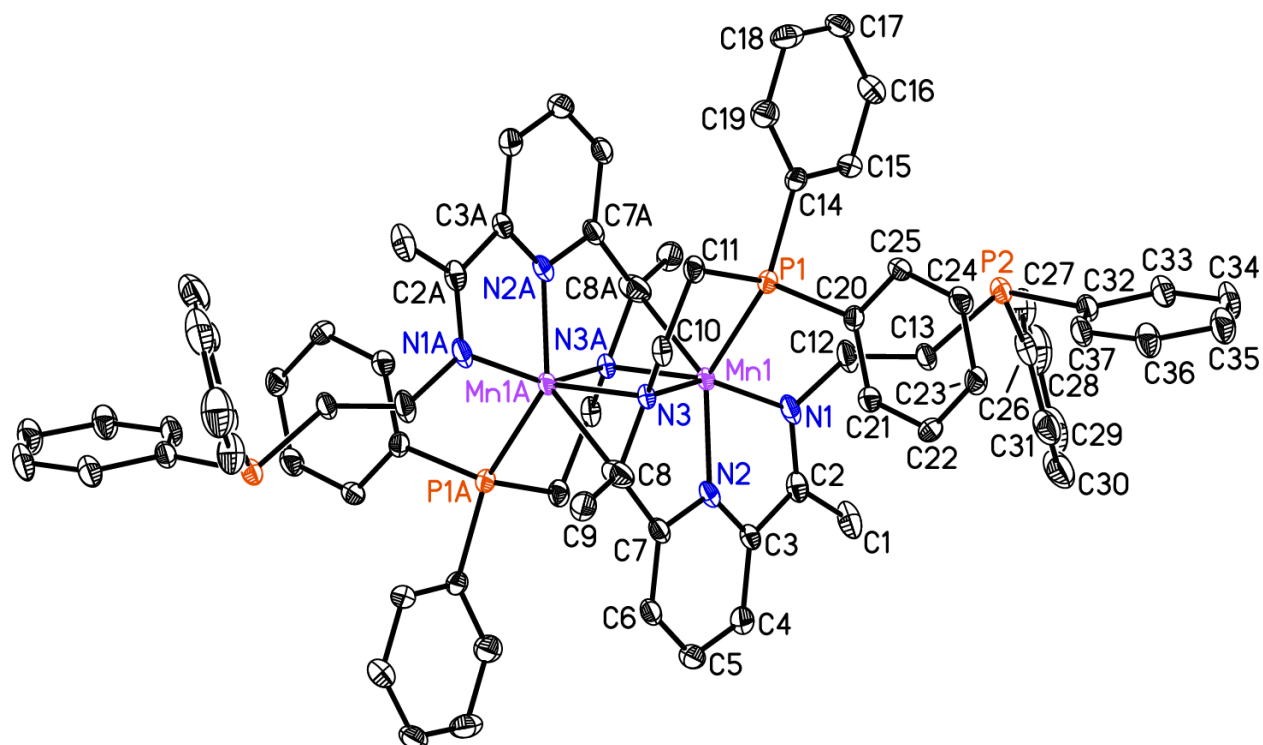


Figure S3. The molecular structure of **2** shown at 30% probability ellipsoids. Hydrogen atoms and co-crystallized toluene molecules (4 per dimer) are omitted for clarity.

Table S2. Bond distances (Å) and angles (°) determined for **2**.

Mn1-N2	1.947(4)	N3-Mn1A	1.977(4)	C20-C21	1.393(7)
Mn1-N3A	1.977(4)	C1-C2	1.495(7)	C21-C22	1.384(6)
Mn1-N1	2.022(4)	C2-C3	1.425(7)	C22-C23	1.372(7)
Mn1-N3	2.092(4)	C3-C4	1.412(7)	C23-C24	1.369(7)
Mn1-C8A	2.233(6)	C4-C5	1.382(7)	C24-C25	1.387(7)
Mn1-P1	2.3525(15)	C5-C6	1.390(7)	C26-C31	1.380(8)
Mn1-Mn1A	2.7889(14)	C6-C7	1.378(7)	C26-C27	1.404(8)
P1-C14	1.835(5)	C7-C8	1.462(7)	C27-C28	1.373(9)
P1-C20	1.842(5)	C8-C9	1.508(7)	C28-C29	1.388(11)
P1-C11	1.844(5)	C8-Mn1A	2.233(6)	C29-C30	1.354(11)
P2-C26	1.806(6)	C10-C11	1.517(7)	C30-C31	1.397(9)
P2-C32	1.834(5)	C12-C13	1.528(6)	C32-C37	1.377(7)
P2-C13	1.849(5)	C14-C19	1.375(7)	C32-C33	1.403(7)
N1-C2	1.338(6)	C14-C15	1.383(7)	C33-C34	1.380(8)
N1-C12	1.463(6)	C15-C16	1.391(7)	C34-C35	1.371(8)
N2-C7	1.367(6)	C16-C17	1.362(8)	C35-C36	1.393(8)
N2-C3	1.368(6)	C17-C18	1.361(8)	C36-C37	1.391(7)
N3-C8	1.395(6)	C18-C19	1.406(7)		
N3-C10	1.456(6)	C20-C25	1.386(7)		
N2-Mn1-N3A	100.30(15)	C26-P2-C32	102.0(2)	N3-C8-C7	113.9(4)
N2-Mn1-N1	77.00(16)	C26-P2-C13	100.2(2)	N3-C8-C9	121.6(5)
N3A-Mn1-N1	106.59(16)	C32-P2-C13	101.5(2)	C7-C8-C9	117.1(5)
N2-Mn1-N3	78.82(16)	C2-N1-C12	116.6(5)	N3-C8-Mn1A	60.9(3)
N3A-Mn1-N3	93.50(15)	C2-N1-Mn1	116.7(3)	C7-C8-Mn1A	113.7(4)
N1-Mn1-N3	150.85(16)	C12-N1-Mn1	126.7(4)	C9-C8-Mn1A	117.4(4)
N2-Mn1-C8A	137.46(18)	C7-N2-C3	121.3(4)	N3-C10-C11	110.6(4)
N3A-Mn1-C8A	38.09(17)	C7-N2-Mn1	118.4(3)	C10-C11-P1	107.6(3)
N1-Mn1-C8A	102.86(18)	C3-N2-Mn1	119.1(3)	N1-C12-C13	110.5(4)
N3-Mn1-C8A	105.93(18)	C8-N3-C10	120.0(4)	C12-C13-P2	112.4(3)
N2-Mn1-P1	129.25(12)	C8-N3-Mn1A	81.0(3)	C19-C14-C15	117.3(5)
N3A-Mn1-P1	126.39(12)	C10-N3-Mn1A	121.8(3)	C19-C14-P1	123.3(4)
N1-Mn1-P1	103.71(12)	C8-N3-Mn1	110.7(3)	C15-C14-P1	119.4(4)
N3-Mn1-P1	79.55(11)	C10-N3-Mn1	124.2(3)	C14-C15-C16	121.8(5)
C8A-Mn1-P1	92.61(15)	Mn1A-N3-Mn1	86.50(15)	C17-C16-C15	119.8(5)
N2-Mn1-Mn1A	88.93(12)	N1-C2-C3	113.8(4)	C18-C17-C16	119.9(5)
N3A-Mn1-Mn1A	48.47(11)	N1-C2-C1	124.4(5)	C17-C18-C19	120.2(5)
N1-Mn1-Mn1A	149.02(12)	C3-C2-C1	121.9(5)	C14-C19-C18	121.0(5)
N3-Mn1-Mn1A	45.03(10)	N2-C3-C4	119.7(4)	C25-C20-C21	118.5(4)
C8A-Mn1-Mn1A	69.39(14)	N2-C3-C2	111.7(4)	C25-C20-P1	122.8(4)
P1-Mn1-Mn1A	106.53(5)	C4-C3-C2	128.6(5)	C21-C20-P1	118.4(4)
C14-P1-C20	102.8(2)	C5-C4-C3	118.5(5)	C22-C21-C20	120.3(5)
C14-P1-C11	103.5(2)	C4-C5-C6	120.9(5)	C23-C22-C21	120.4(5)
C20-P1-C11	101.0(2)	C7-C6-C5	119.5(5)	C24-C23-C22	120.0(5)
C14-P1-Mn1	129.95(16)	N2-C7-C6	120.1(5)	C23-C24-C25	120.2(5)
C20-P1-Mn1	114.22(16)	N2-C7-C8	112.8(4)	C20-C25-C24	120.6(5)
C11-P1-Mn1	101.29(15)	C6-C7-C8	127.1(4)	C31-C26-C27	118.4(6)

C31-C26-P2	124.4(5)	C29-C30-C31	119.5(7)	C34-C33-C32	120.6(5)
C27-C26-P2	117.2(5)	C26-C31-C30	120.8(7)	C35-C34-C33	121.1(5)
C28-C27-C26	120.5(7)	C37-C32-C33	117.7(5)	C34-C35-C36	119.3(5)
C27-C28-C29	119.6(8)	C37-C32-P2	123.5(4)	C37-C36-C35	119.3(6)
C30-C29-C28	121.1(7)	C33-C32-P2	118.7(4)	C32-C37-C36	121.9(5)

CATALYTIC TRIALS

Hydrosilylation of benzaldehyde catalyzed by 0.05 mol% **2 (0.1 mol% relative to Mn):** In the glove box, a neat mixture of PhSiH₃ (0.347 mL, 2.81 mmol) and benzaldehyde (0.286 mL, 2.81 mmol) was added to 0.0018 g (0.0014 mmol) of **2** pre-weighed into a 20 mL vial. The resulting red solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ¹H NMR spectrum was recorded to determine the percent conversion. The products were hydrolyzed with 2 mL aqueous 10% NaOH at room temperature for 2 h. The organic fraction was extracted with diethyl ether (3 x 4 mL) and the organic layer was dried over anhydrous Na₂SO₄. Removal of the solvent on a rotavap afforded a colorless oil identified as benzyl alcohol (0.281 g, 2.61 mmol, yield = 93%). ¹H NMR (benzene-*d*₆): 7.08-7.15 (5H, m, *phenyl*), 4.32 (2H, s, -CH₂OH). {¹H} ¹³C NMR (benzene-*d*₆): 142.14, 128.91, 127.80, 127.42, 65.26.¹

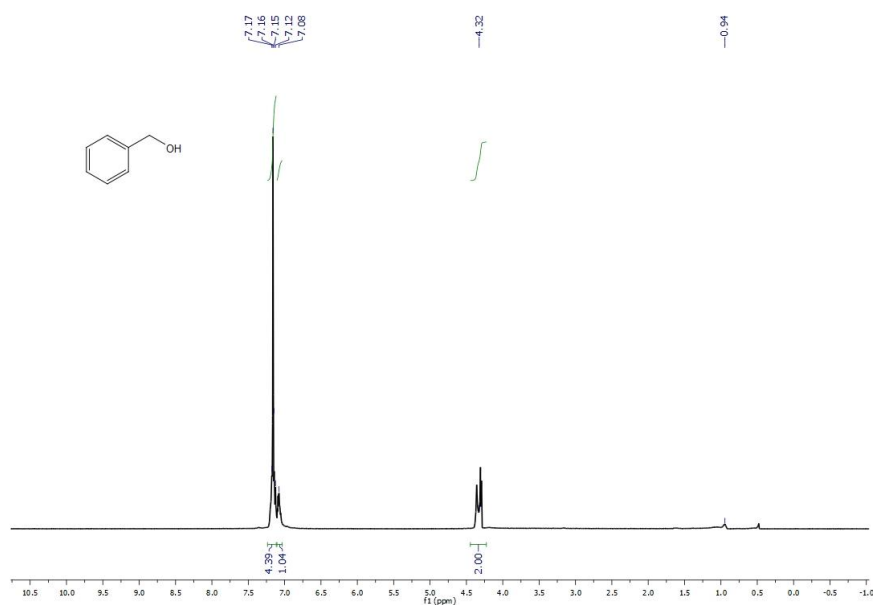


Figure S4: ¹H NMR spectrum of benzyl alcohol in benzene-*d*₆.

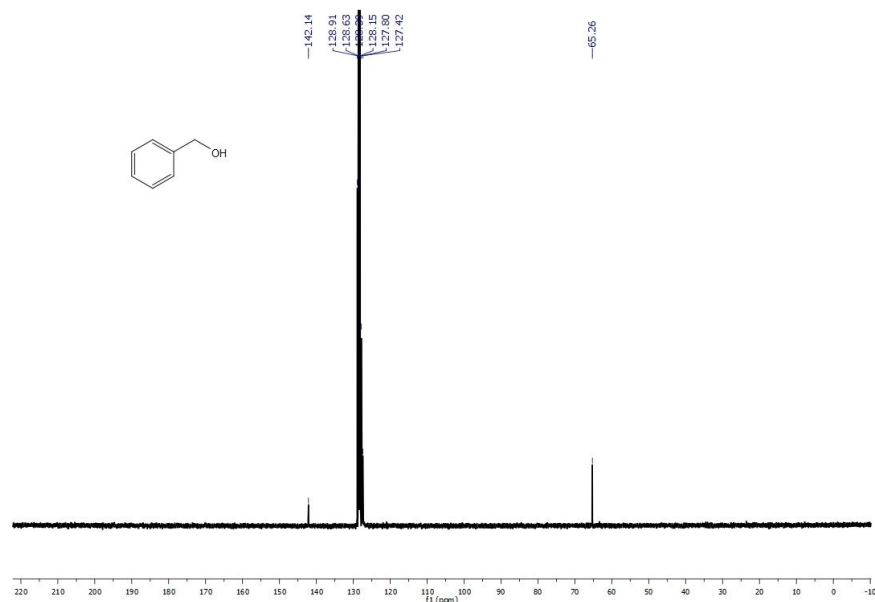


Figure S5: $\{^1\text{H}\}^{13}\text{C}$ NMR spectrum of benzyl alcohol in benzene- d_6 .

Hydrosilylation of 4-fluorobenzaldehyde catalyzed by 0.05 mol% **2 (0.1 mol% relative to **Mn**):** In the glove box, a neat mixture of PhSiH_3 (0.365 mL, 2.96 mmol) and 4-fluorobenzaldehyde (0.319 mL, 2.96 mmol) was added to 0.0019 g (0.0015 mmol) of **2** pre-weighed in a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^1H NMR spectrum was recorded to determine the percent conversion. The products were hydrolyzed with 2 mL aqueous 10% NaOH at room temperature for 2 h. The organic fraction was extracted with diethyl ether (3 x 4 mL) and the organic layer was dried over anhydrous Na_2SO_4 . Removal of the solvent on a rotavap afforded a colorless oil identified as 4-fluorobenzyl alcohol (0.334 g, 2.64 mmol, yield = 90%). ^1H NMR (benzene- d_6): 6.95 (2H, d, *phenyl*), 6.79 (2H, d, *phenyl*), 4.21 (2H, s, $-\text{CH}_2\text{OH}$). $\{^1\text{H}\}^{13}\text{C}$ NMR (benzene- d_6): 162.91 (d, $^1J_{\text{CF}} = 244$ Hz), 137.57, 129.16 (d, $^3J_{\text{CF}} = 8$ Hz), 115.68 (d, $^2J_{\text{CF}} = 21$ Hz), 64.34.¹

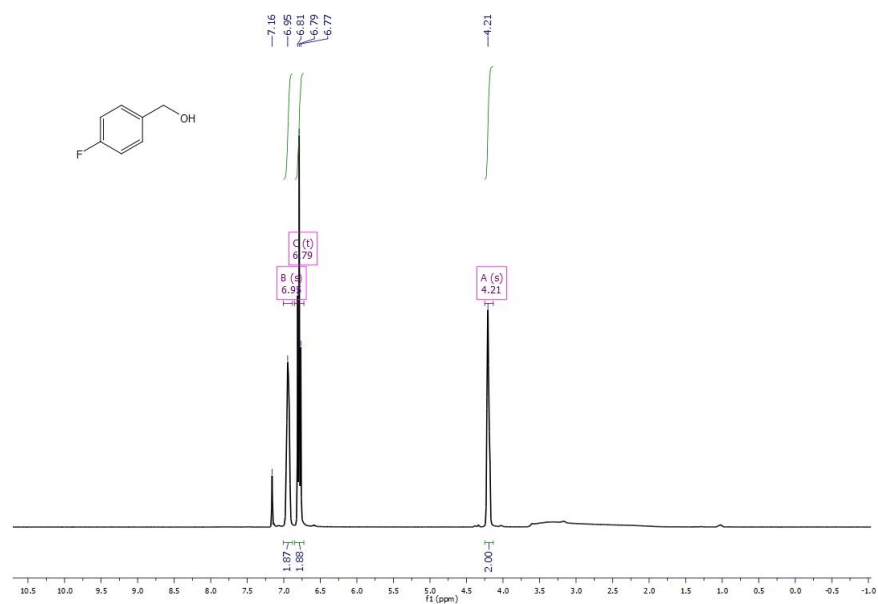


Figure S6: ¹H NMR spectrum of 4-fluorobenzyl alcohol in benzene-*d*₆.

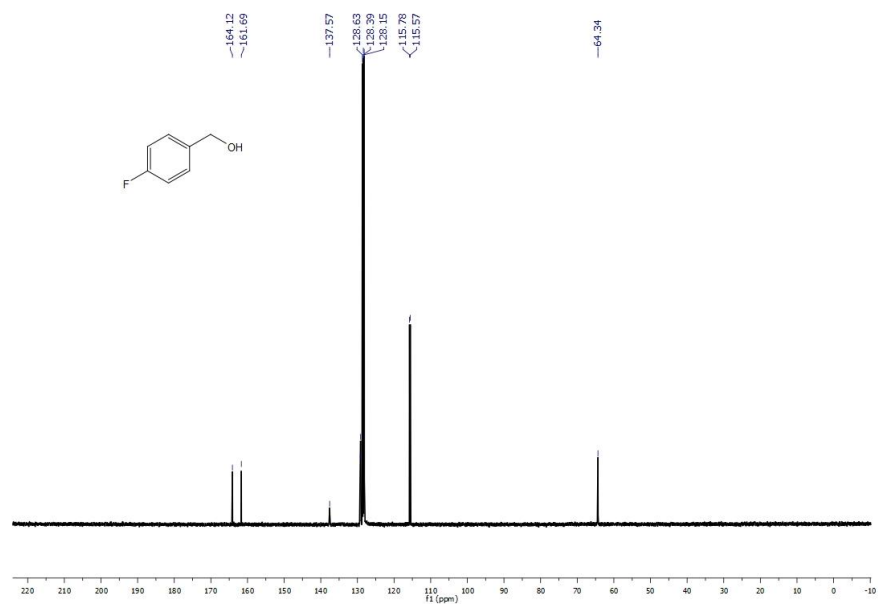


Figure S7: {¹H}¹³C NMR spectrum of 4-fluorobenzyl alcohol in benzene-*d*₆.

Hydrosilylation of 4-chlorobenzaldehyde catalyzed by 0.05 mol% **2 (0.1 mol% relative to **Mn**):** In the glove box, a mixture of PhSiH₃ (0.424 mL, 3.43 mmol) and 4-chlorobenzaldehyde (0.483 g, 3.43 mmol) in 0.5 mL of diethyl ether was added to 0.0022 g (0.0017 mmol) of **2** pre-weighed into a 20 mL vial. The resulting red solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ¹H NMR spectrum was recorded to determine the percent conversion. It was followed by a hydrolytic work up whereby the mixture was stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (3 x 4 mL) and the organic layer was dried over anhydrous Na₂SO₄. Removal of the solvent on a rotavap afforded a white solid identified as 4-chlorobenzyl alcohol (0.405 g, 2.83 mmol, yield = 83%). ¹H NMR (benzene-*d*₆): 7.08 (2H, d, *phenyl*), 6.83 (2H, d, *phenyl*), 4.10 (2H, s, -CH₂OH). {¹H}¹³C NMR (benzene-*d*₆): 140.50, 133.60, 129.02, 128.63, 64.41. Melting Point: 71.1-72.3 °C (colorless crystalline solid).¹

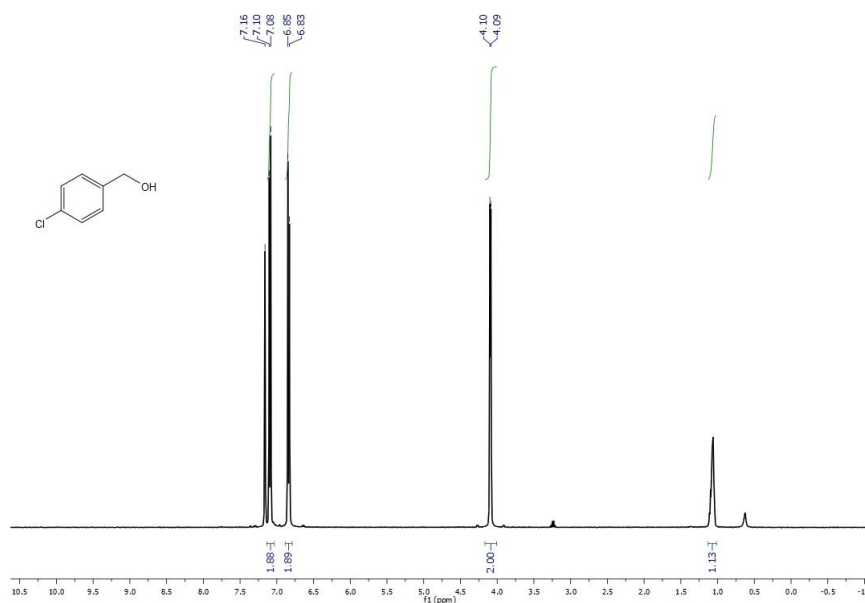


Figure S8: ¹H NMR spectrum of 4-chlorobenzyl alcohol in benzene-*d*₆.

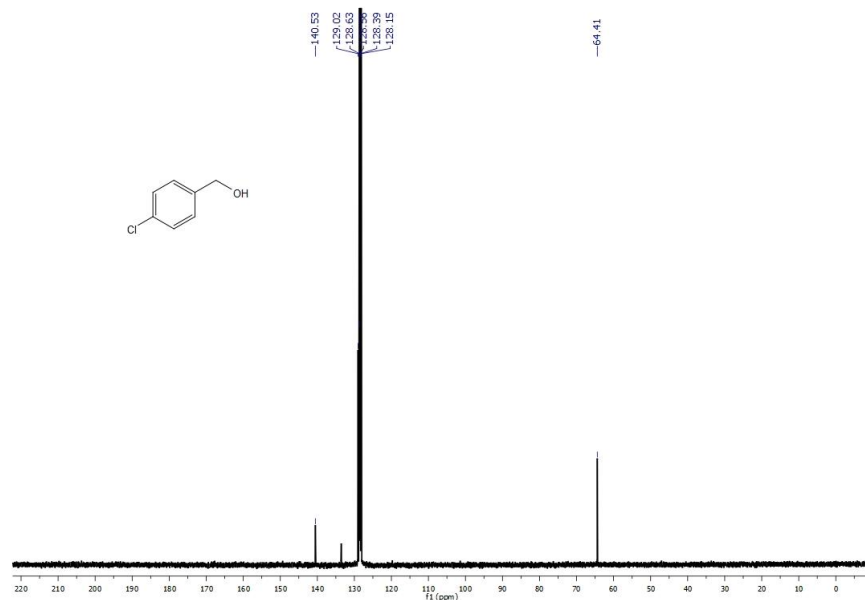


Figure S9: $\{^1\text{H}\}^{13}\text{C}$ NMR spectrum of 4-chlorobenzyl alcohol in benzene- d_6 .

Hydrosilylation of 4-bromobenzaldehyde catalyzed by 0.05 mol% **2 (0.1 mol% relative to **Mn**):** In the glove box, a mixture of PhSiH_3 (0.424 mL, 3.43 mmol) and 4-bromobenzaldehyde (0.635 g, 3.43 mmol) in 0.5 mL diethyl ether was added to 0.0022 g (0.0017 mmol) of **2** pre-weighed into a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^1H NMR spectrum was recorded to determine the percent conversion. It was followed by a hydrolytic work up whereby the mixture was stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (3 x 4 mL) and the organic layer was dried over anhydrous Na_2SO_4 . Removal of the solvent on a rotavap afforded a white solid identified as 4-bromobenzyl alcohol (0.536 g, 2.87 mmol, yield = 83%). ^1H NMR (benzene- d_6): 7.23 (2H, d, *phenyl*), 6.76 (2H, d, *phenyl*), 4.07 (2H, s, $-\text{CH}_2\text{OH}$), 1.36 (1H, s, $-\text{CH}_2\text{OH}$). $\{^1\text{H}\}^{13}\text{C}$ NMR (benzene- d_6): 140.94, 131.50, 121.66, 64.41, one resonance not located. Melting Point: 77.1-78.4 °C (colorless crystalline solid).¹

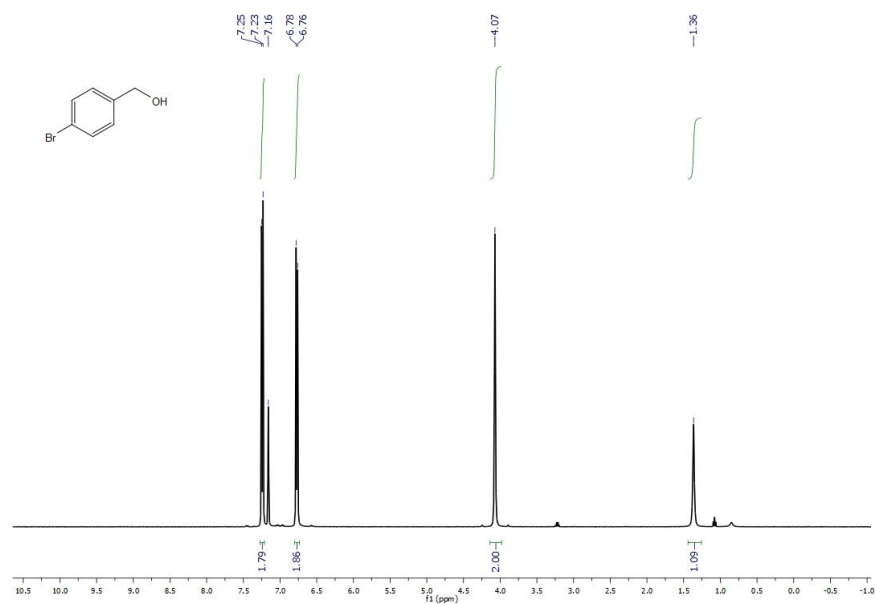


Figure S10: ^1H NMR spectrum of 4-bromobenzyl alcohol in benzene- d_6 .

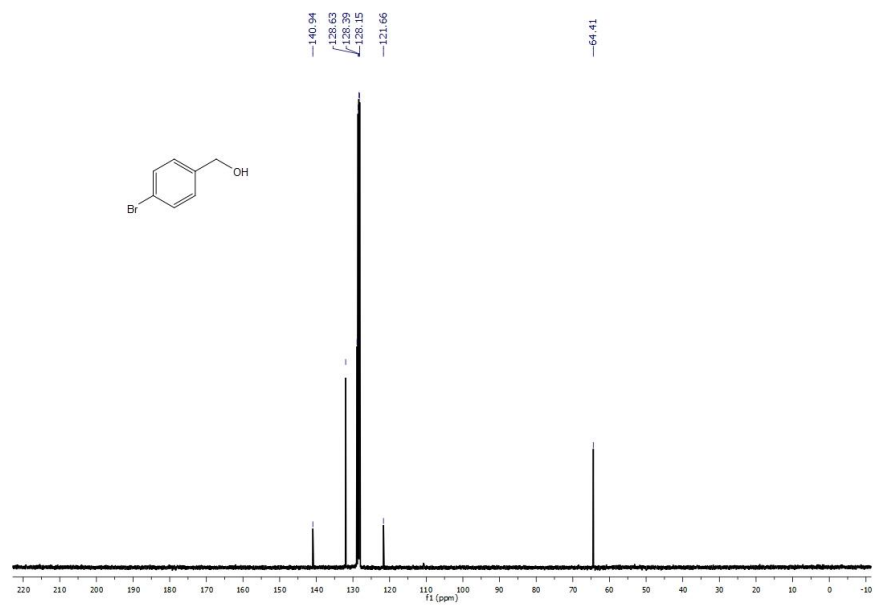


Figure S11: $\{^1\text{H}\}^{13}\text{C}$ NMR spectrum of 4-bromobenzyl alcohol in benzene- d_6 .

Attempt to hydrosilylate 4-iodobenzaldehyde using 0.05 mol% **2 (0.1 mol% relative to Mn):**

In the glove box, a mixture of PhSiH₃ (0.385 mL, 3.12 mmol) and 4-iodobenzaldehyde (0.724 g, 3.12 mmol) in 0.5 mL toluene was added to 0.002 g (0.0016 mmol) of **2** pre-weighed into a 20 mL vial. The resulting solution was stirred for 2 min and then exposed to air to deactivate the catalyst. The solution was then filtered through Celite and ¹H NMR spectroscopy revealed no conversion.

Hydrosilylation of 2-nitrobenzaldehyde catalyzed by 0.05 mol% **2 (0.1 mol% relative to Mn):**

In the glove box, a neat mixture of PhSiH₃ (0.327 mL, 2.65 mmol) and 2-nitrobenzaldehyde (0.400 g, 2.65 mmol) was added to 0.0017 g (0.0013 mmol) of **2** pre-weighed into a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ¹H NMR spectrum was recorded to determine the percent conversion. It was followed by a hydrolytic work up whereby the mixture was stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (3 x 4 mL) and the organic layer was dried over anhydrous Na₂SO₄. Removal of the diethyl ether on a rotavap afforded a pale yellow solid identified as 2-nitrobenzyl alcohol (0.322 g, 2.17 mmol, yield = 79%). ¹H NMR (benzene-*d*₆): 7.62 (1H, d, *phenyl*), 7.35 (1H, d, *phenyl*), 6.91 (1H, d, *phenyl*), 6.64 (1H, d, *phenyl*), 4.54 (2H, s, -CH₂OH), 1.52 (1H, s, -CH₂OH). {¹H}¹³C NMR (benzene-*d*₆): 137.98, 133.68, 129.20, 127.99, 124.95, 62.27. Melting Point: 70.3-72.1 °C (orange crystalline solid).¹

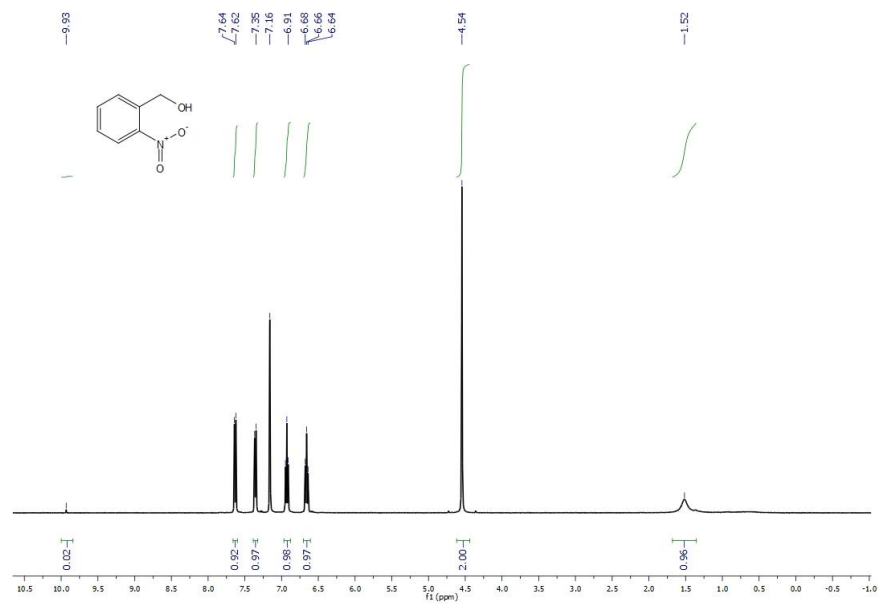


Figure S12: ¹H NMR spectrum of 2-nitrobenzyl alcohol in benzene-*d*₆.

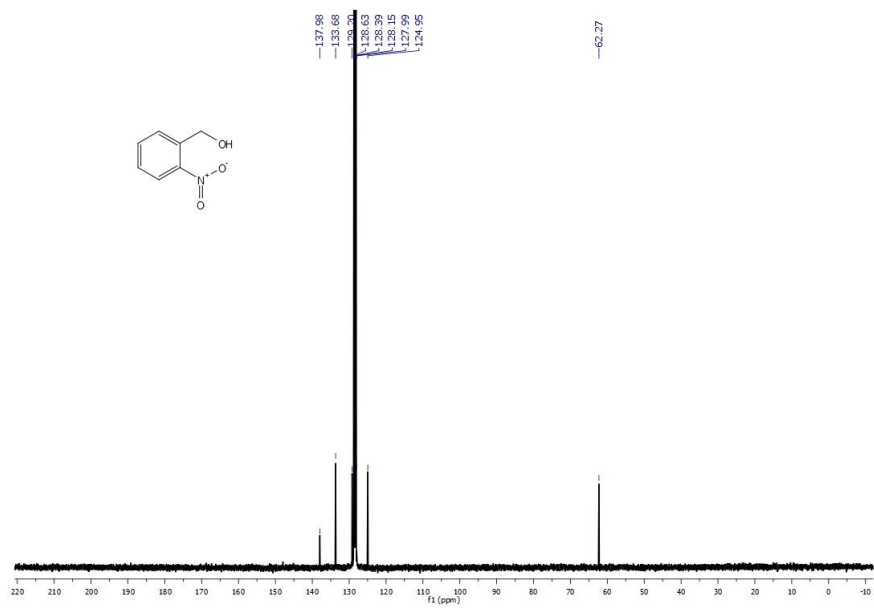


Figure S13: {¹H} ¹³C NMR spectrum of 2-nitrobenzyl alcohol in benzene-*d*₆.

Hydrosilylation of 4-cyanobenzaldehyde catalyzed by 0.05 mol% **2 (0.1 mol% relative to **Mn**):** In the glove box, a mixture of PhSiH₃ (0.347 mL, 2.81 mmol) and 4-cyanobenzaldehyde (0.368 g, 2.81 mmol) was added to 0.0018 g (0.0014 mmol) of **2** pre-weighed into a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ¹H NMR spectrum was recorded to determine the percent conversion. It was followed by a hydrolytic work up whereby the mixture was stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (3 x 4 mL) and the organic layer was dried over anhydrous Na₂SO₄. Removal of the diethyl ether on a rotavap afforded a white solid identified as 4-cyanobenzyl alcohol (0.266 g, 1.997 mmol, yield = 71%). ¹H NMR (benzene-*d*₆): 7.00 (2H, d, *phenyl*), 6.77 (2H, d, *phenyl*), 4.03 (2H, s, -CH₂OH), 1.23 (1H, s, -CH₂OH). {¹H}¹³C NMR (benzene-*d*₆): 146.84, 132.37, 127.02, 119.32, 111.65, 110.69, 63.96. Melting Point: 34.1-37.4 °C (yellow crystalline solid).¹

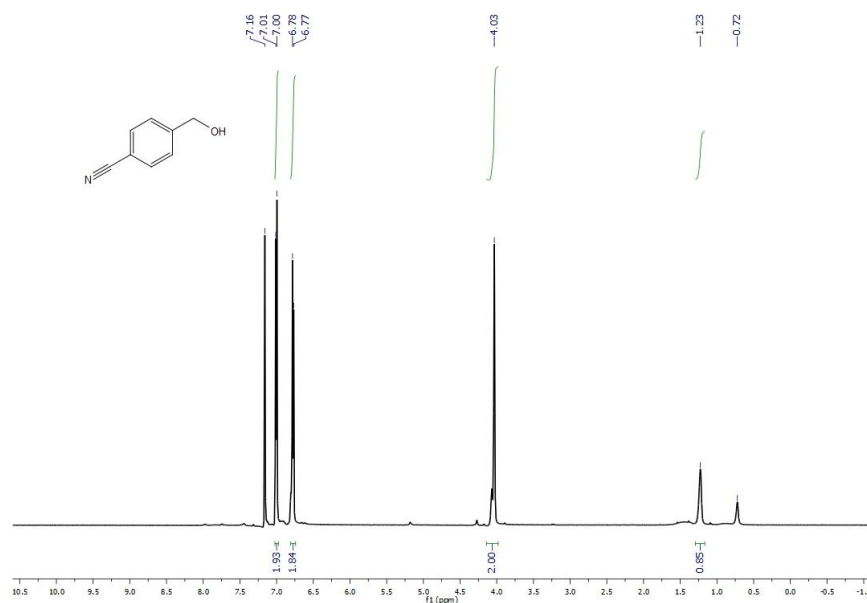


Figure S14: ¹H NMR spectrum of 4-cyanobenzyl alcohol in benzene-*d*₆.

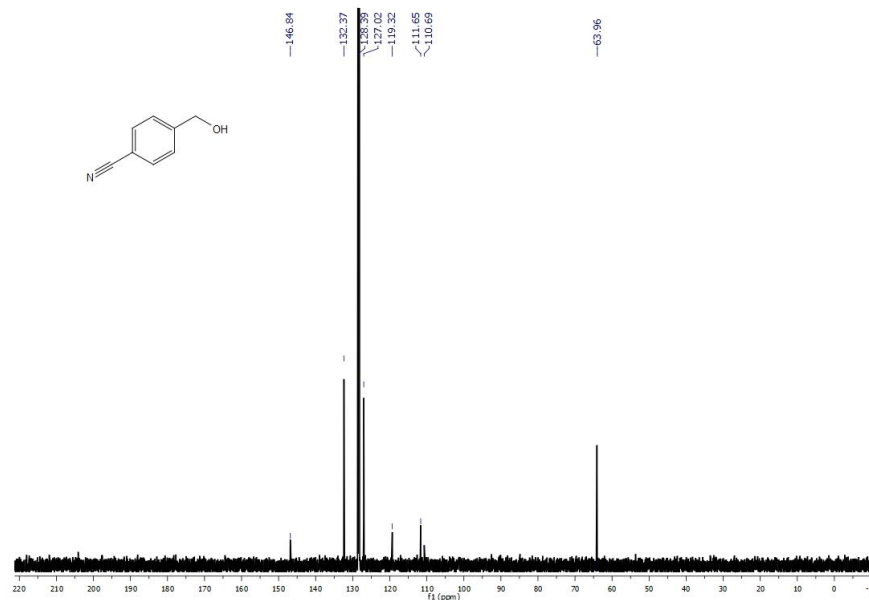


Figure S15: $\{^1\text{H}\}^{13}\text{C}$ NMR spectrum of 4-cyanobenzyl alcohol in benzene- d_6 .

Hydrosilylation of *p*-anisaldehyde catalyzed by 0.05 mol% **2 (0.1 mol% relative to Mn):** In the glove box, a neat mixture of PhSiH_3 (0.424 mL, 3.43 mmol) and *p*-anisaldehyde (0.393 mL, 3.43 mmol) was added to 0.0022 g (0.0017 mmol) of **2** pre-weighed in a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^1H NMR spectrum was recorded to determine the percent conversion. It was followed by a hydrolytic work up whereby the mixture was stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (3 x 4 mL) and the organic layer was dried over anhydrous Na_2SO_4 . Removal of the diethyl ether on a rotavap afforded a colorless oil identified as 4-methoxybenzyl alcohol (0.406 g, 2.94 mmol, yield = 86%). ^1H NMR (benzene- d_6): 7.13 (2H, d, *phenyl*), 6.76 (2H, d, *phenyl*), 4.38 (2H, s, $-\text{CH}_2\text{OH}$), 3.31 (3H, s, $-\text{OCH}_3$), 2.56 (1H, s, $-\text{CH}_2\text{OH}$). $\{^1\text{H}\}^{13}\text{C}$ NMR (benzene- d_6): 159.85, 134.35, 114.44, 65.01, 55.15.¹

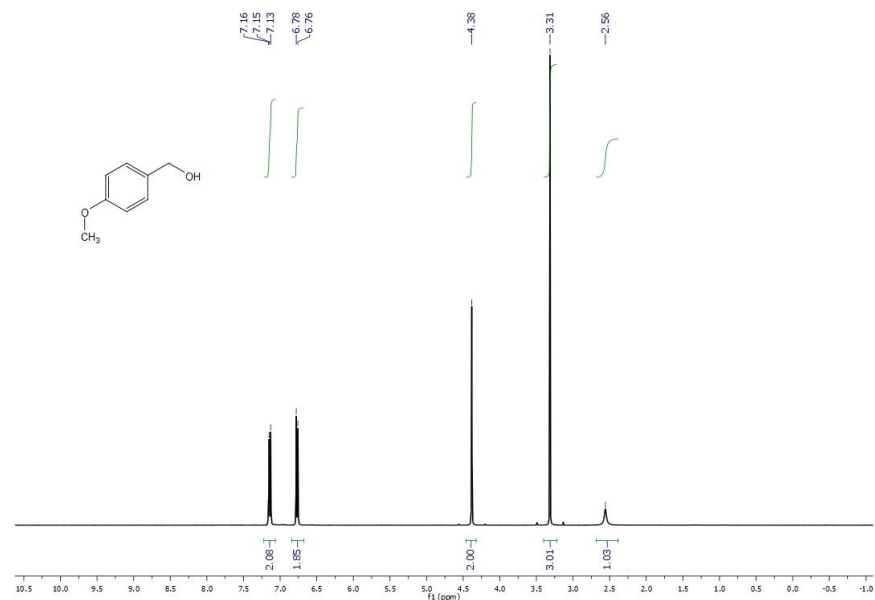


Figure S16: ¹H NMR spectrum of 4-methoxybenzyl alcohol in benzene-*d*₆.

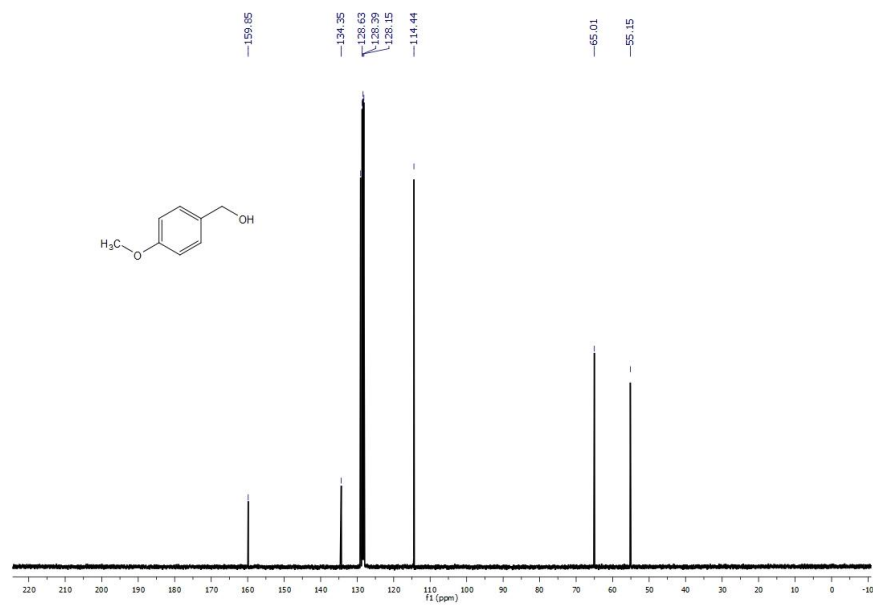


Figure S17: {¹H}¹³C NMR spectrum of 4-methoxybenzyl alcohol in benzene-*d*₆.

Hydrosilylation of *p*-tolualdehyde catalyzed by 0.05 mol% **2 (0.1 mol% relative to Mn):** In the glove box, a neat mixture of PhSiH₃ (0.347 mL, 2.81 mmol) and *p*-tolualdehyde (0.331 mL, 2.81 mmol) was added to 0.0018 g (0.0014 mmol) of **2** pre-weighed into a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ¹H NMR spectrum was recorded to determine the percent conversion. It was followed by a hydrolytic work up whereby the mixture was stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (3 x 4 mL) and the organic layer was dried over anhydrous Na₂SO₄. Removal of the diethyl ether on a rotavap afforded a white solid identified as 4-methylbenzyl alcohol (0.303 g, 2.48 mmol, yield = 88%). ¹H NMR (benzene-*d*₆): 7.11 (2H, d, *phenyl*), 6.98 (2H, d, *phenyl*), 4.35 (2H, s, -CH₂OH), 2.12 (3H, s, -CH₃), 1.48 (1H, s, -CH₂OH). {¹H}¹³C NMR (benzene-*d*₆): 139.35, 137.20, 129.62, 127.52, 65.29, 21.46. Melting Point: 59.9-61.2 °C (colorless crystalline solid).¹

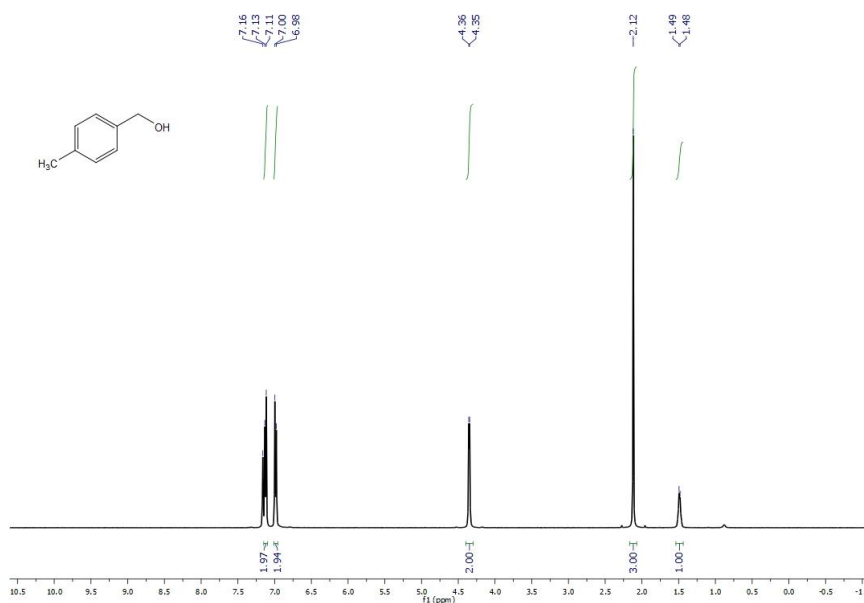


Figure S18: ¹H NMR spectrum of 4-methylbenzyl alcohol in benzene-*d*₆.

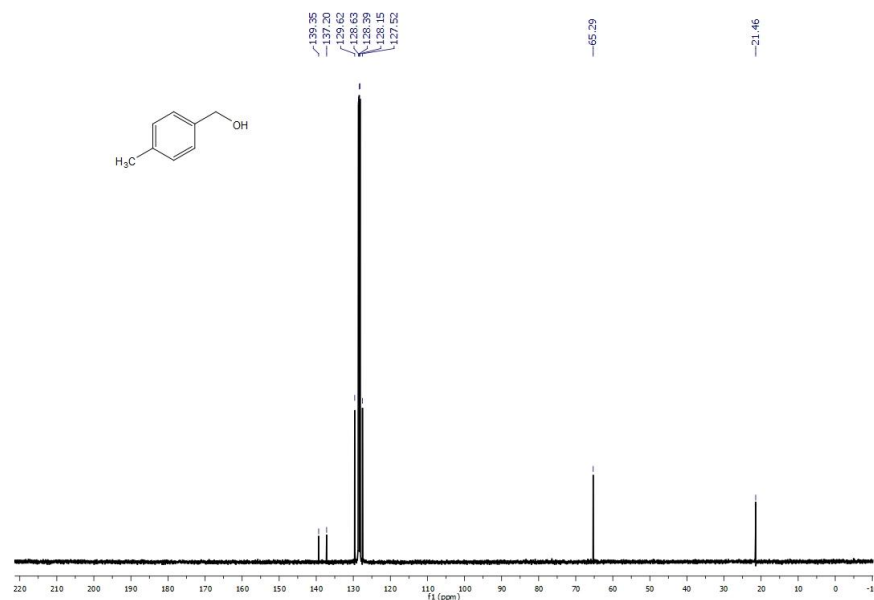


Figure S19: $\{^1\text{H}\}^{13}\text{C}$ NMR spectrum of 4-methylbenzyl alcohol in benzene- d_6 .

Hydrosilylation of 2-naphthaldehyde catalyzed by 0.05 mol% **2 (0.1 mol% relative to Mn):**

In the glove box, a mixture of PhSiH_3 (0.289 mL, 2.34 mmol) and 2-naphthaldehyde (0.365 g, 2.34 mmol) in 0.5 mL toluene was added to 0.0015 g (0.0012 mmol) of **2** pre-weighed into a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^1H NMR spectrum was recorded to determine the percent conversion. It was followed by a hydrolytic work up whereby the mixture was stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (3 x 4 mL) and the organic layer was dried over anhydrous Na_2SO_4 . Removal of the diethyl ether on a rotavap afforded a white solid identified as 2-naphthalenemethanol (0.344 g, 2.18 mmol, yield = 93%). ^1H NMR (benzene- d_6): 8.01-7.96 (1H, m, *phenyl*), 7.68 (1H, s, *phenyl*), 7.52-7.47 (1H, m, *phenyl*), 7.38 (1H, m, *phenyl*), 7.26 (1H, d, *phenyl*), 7.20 (2H, m, *phenyl*), 5.04 (2H, s, $-\text{CH}_2\text{OH}$), 4.45 (1H, s, $-\text{CH}_2\text{OH}$). $\{^1\text{H}\}^{13}\text{C}$ NMR (benzene- d_6): 138.37, 135.86, 134.27, 133.78, 131.46, 131.10, 126.61, 126.31, 126.08, 125.75, 66.03. Melting Point: 79.5-80.6 $^\circ\text{C}$ (colorless crystalline solid).¹

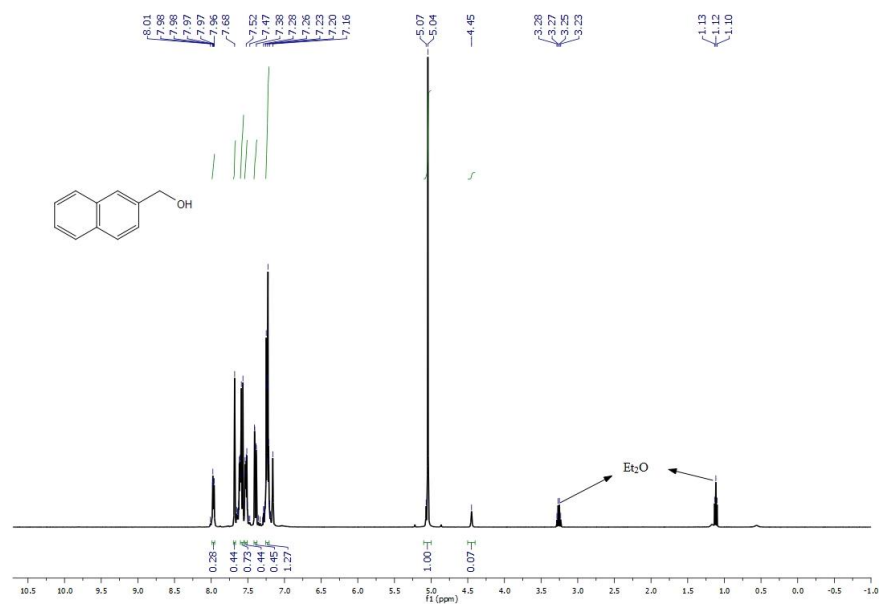


Figure S20: ¹H NMR spectrum of 2-naphthalenemethanol in benzene-*d*₆.

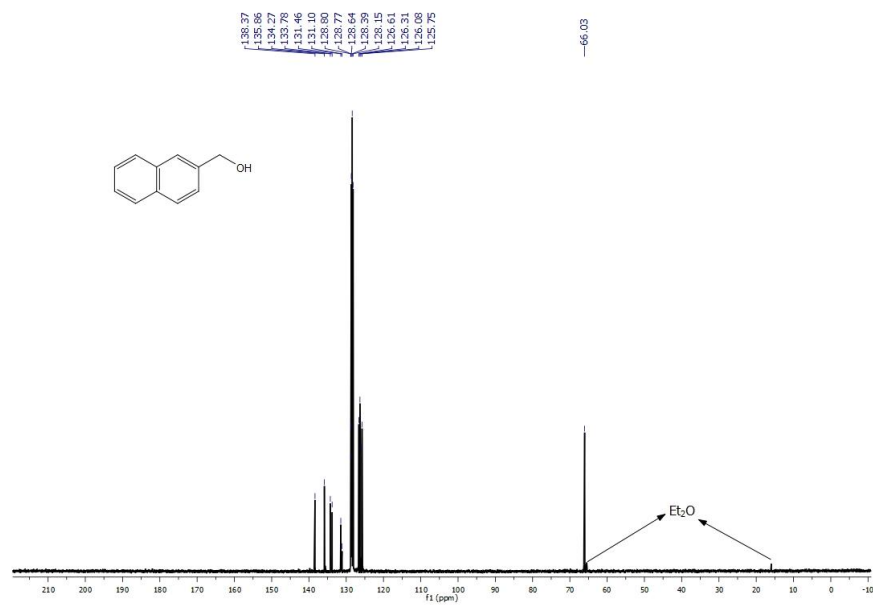


Figure S21: {¹H}¹³C NMR spectrum of 2-naphthalenemethanol in benzene-*d*₆.

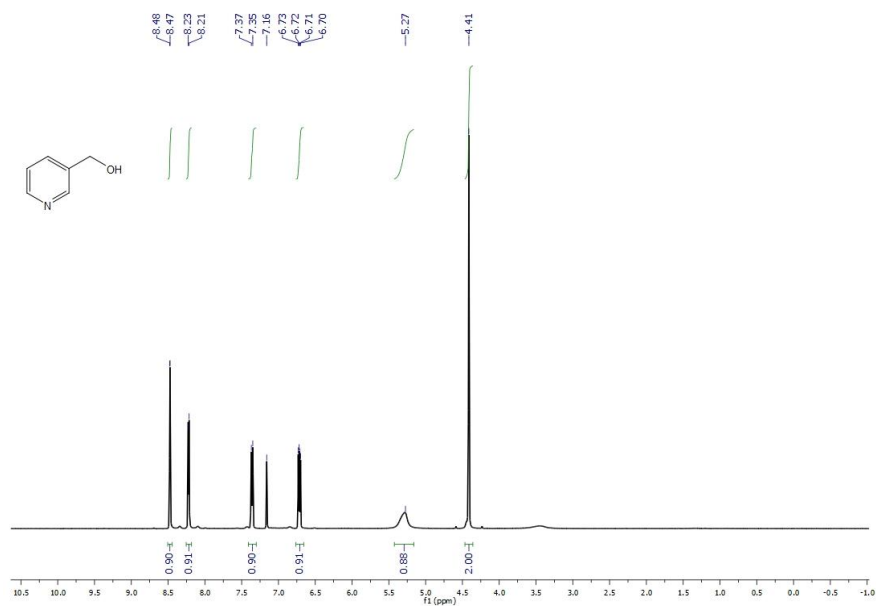


Figure S23: ^1H NMR spectrum of isolated pyridine-3-carbinol in benzene- d_6 .

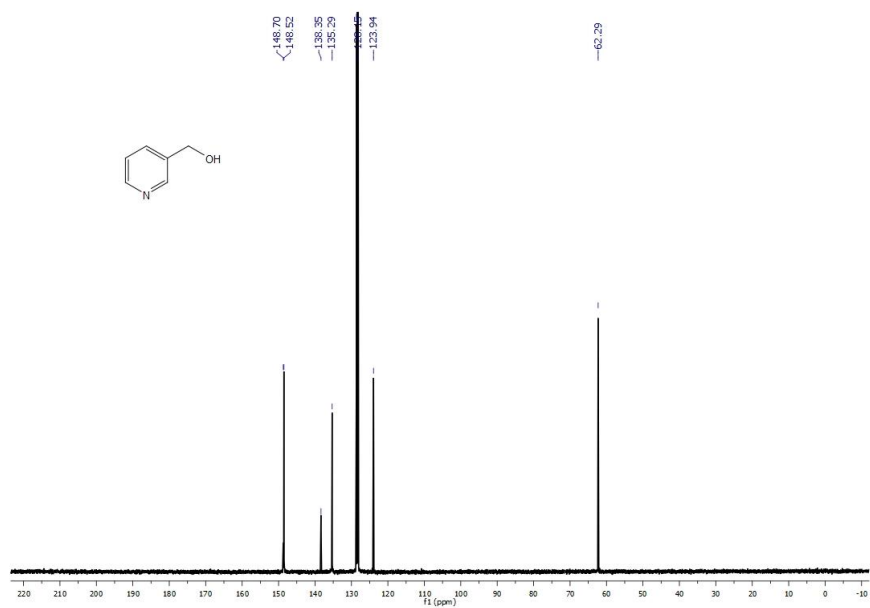


Figure S24: $\{^1\text{H}\}^{13}\text{C}$ NMR spectrum of isolated pyridine-3-carbinol in benzene- d_6 .

Hydrosilylation of furfural catalyzed by 0.05 mol% **2 (0.1 mol% relative to Mn):** In the glove box, a neat mixture of PhSiH₃ (0.327 mL, 2.65 mmol) and furfural (0.219 mL, 2.65 mmol) was added to 0.0017 g (0.0013 mmol) of **2** pre-weighed into a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ¹H NMR spectrum was recorded to determine the percent conversion. It was followed by a hydrolytic work up whereby the mixture was stirred with 2 mL aqueous 10% NaOH at room temperature for 2 h. The organic fraction was extracted with diethyl ether (3 x 4 mL) and the organic layer was dried over anhydrous Na₂SO₄. Removal of the diethyl ether on a rotavap afforded a yellow oil identified as furfuryl alcohol (0.1998 g, 2.04 mmol, yield = 77%). ¹H NMR (benzene-*d*₆): 7.06 (1H, d, *furfuryl*), 6.02 (1H, m, *furfuryl*), 5.95 (1H, d, *furfuryl*), 4.22 (2H, s, -CH₂OH), 1.28 (1H, br, -CH₂OH). ¹³C NMR (benzene-*d*₆): 154.81, 142.64, 110.84, 108.01, 57.78.¹

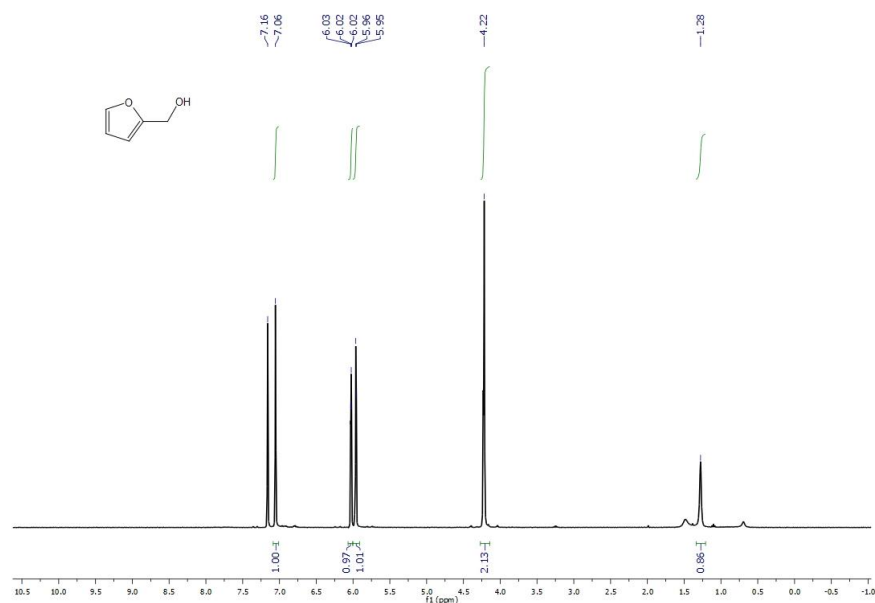


Figure S25: ¹H NMR spectrum of furfuryl alcohol in benzene-*d*₆.

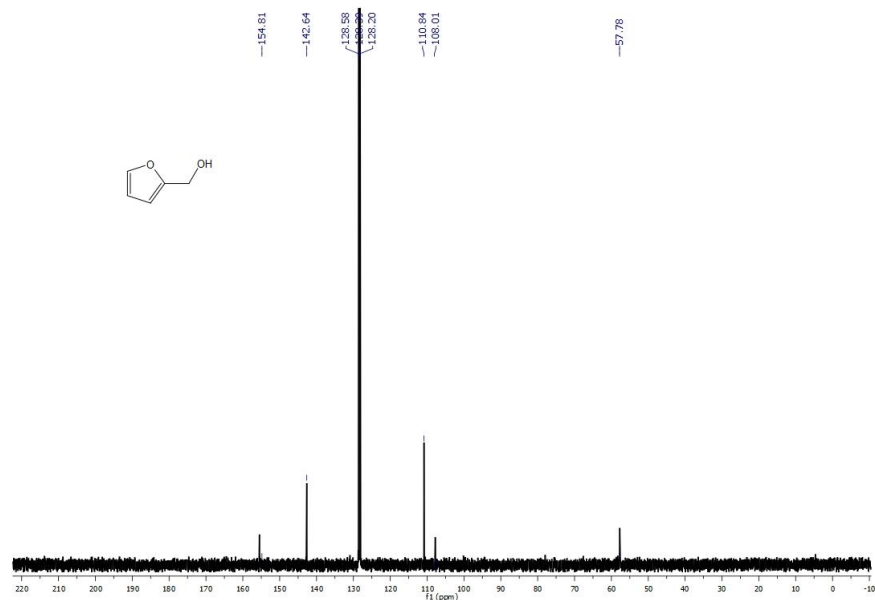


Figure S26: $\{^1\text{H}\}^{13}\text{C}$ NMR spectrum of furfuryl alcohol in benzene- d_6 .

Hydrosilylation of 3-cyclohexene-1-carboxaldehyde using 0.05 mol% **2 (0.1 mol% relative to Mn):** In the glove box, a neat mixture of PhSiH_3 (0.424 mL, 3.43 mmol) and 3-cyclohexene-1-carboxaldehyde (0.389 mL, 3.43 mmol) was added to 0.0022 g (0.0017 mmol) of **2** pre-weighed in a 20 mL vial. The resulting brown solution became warm. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^1H NMR spectrum was recorded, which revealed 32% conversion to the quaternary silane product.

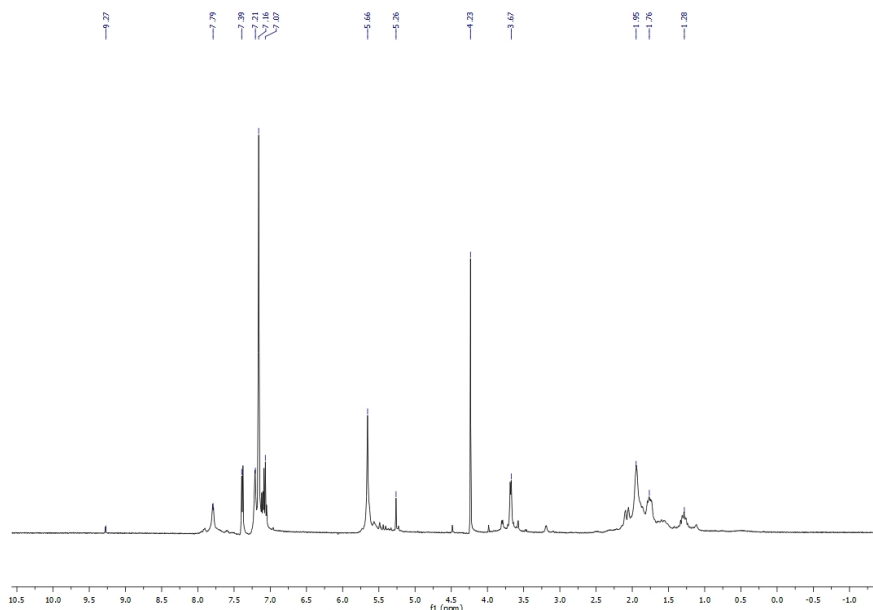


Figure S27: ^1H NMR spectrum showing partial 3-cyclohexene-1-carboxaldehyde hydrosilylation in benzene- d_6 .

Hydrosilylation of citral using 0.05 mol% **2 (0.1 mol% relative to Mn):** In the glove box, a mixture of PhSiH_3 (0.347 mL, 2.81 mmol) and citral (0.480 mL, 2.81 mmol) was added to 0.0018 g (0.0014 mmol) of **2** pre-weighed into a 20 mL vial. The resulting brown solution became warm. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^1H NMR spectrum was recorded, which showed only 18% conversion made up of 84% quaternary silane and 16% tertiary silane.

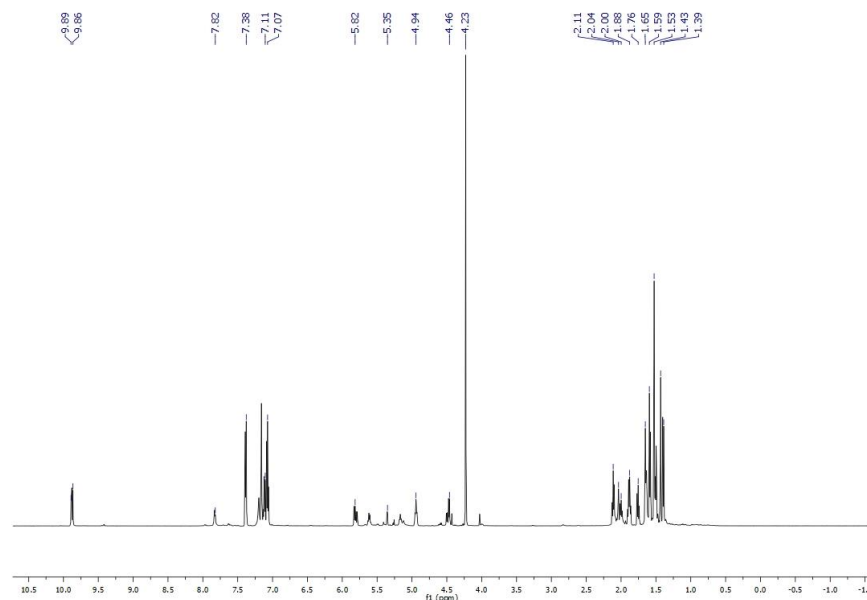


Figure S28: ^1H NMR spectrum showing partial citral hydrosilylation in benzene- d_6 .

Hydrosilylation of acetophenone using 0.05 mol% of **2 (0.1 mol% relative to Mn):** In the glove box, a neat mixture of PhSiH_3 (0.233 mL, 1.873 mmol) and acetophenone (0.218 mL, 1.873 mmol) was added to **2** (0.0012 g, 0.00094 mmol) pre-weighed into a 20 mL vial. The resulting red solution became hot and started to bubble. It was stirred for 4 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered and a ^1H NMR spectrum was recorded. Greater than 99% conversion to $\text{PhSiH}\{\text{OCH}(\text{Me})(\text{Ph})\}_2$ (55%) and $\text{PhSi}\{\text{OCH}(\text{Me})(\text{Ph})\}_3$ (45%) was detected. Excess PhSiH_3 was also observed. These percentages were obtained by integrating the peaks at 4.99 ppm ($\text{PhSiH}\{\text{OCH}(\text{Me})(\text{Ph})\}_2$) and 5.10-5.17 ppm ($\text{PhSi}\{\text{OCH}(\text{Me})(\text{Ph})\}_3$).²

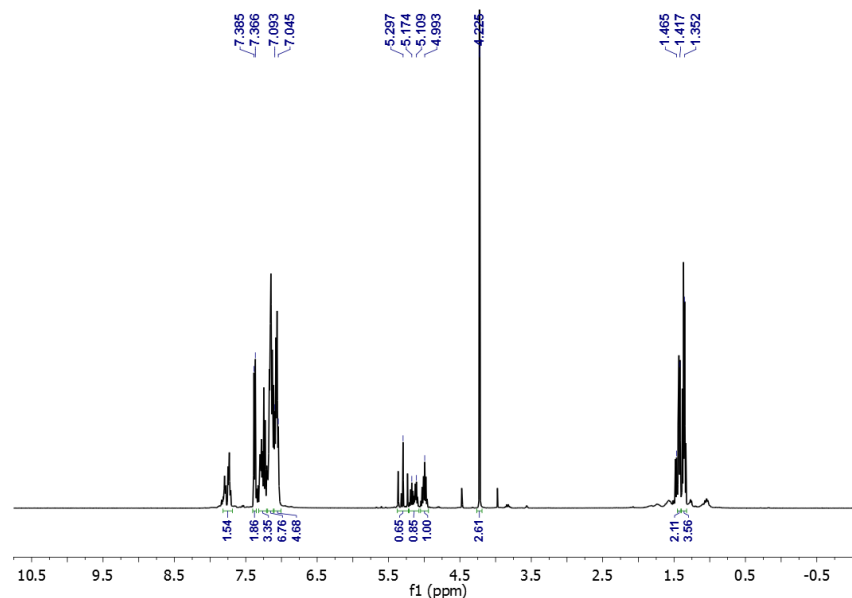


Figure S29: ^1H NMR spectrum showing the silyl ethers prepared from acetophenone using PhSiH_3 and 0.05 mol% of **2** in benzene- d_6 .

Hydrosilylation of cyclohexanone using 0.05 mol% of **2 (0.1 mol% relative to Mn):** In the glove box, a neat mixture of PhSiH_3 (0.233 mL, 1.873 mmol) and cyclohexanone (0.193 mL, 1.873 mmol) was added to **2** (0.0012 g, 0.00094 mmol) pre-weighed in a 20 mL vial. The resulting red solution became hot and started to bubble. It was stirred for 4 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered and a ^1H NMR spectrum was recorded, revealing 99% conversion to $\text{PhSiH}(\text{OCy})_2$ and the presence of excess PhSiH_3 . ^1H NMR (400 MHz, benzene- d_6): 7.84 (m, 2H), 7.38 (m, 2H, excess PhSiH_3), 7.22 (s, 3H), 7.13-7.06 (m, 3H, excess PhSiH_3), 5.34 (s, 1H, SiH), 4.22 (s, 3H, excess PhSiH_3), 3.97 (s, 2H, OCH), 1.87 (s, 4H, Cy), 1.65 (s, 4H, Cy), 1.53 (s, 4H, Cy), 1.33 (s, 2H, Cy), 1.15 (s, 6H, Cy).³

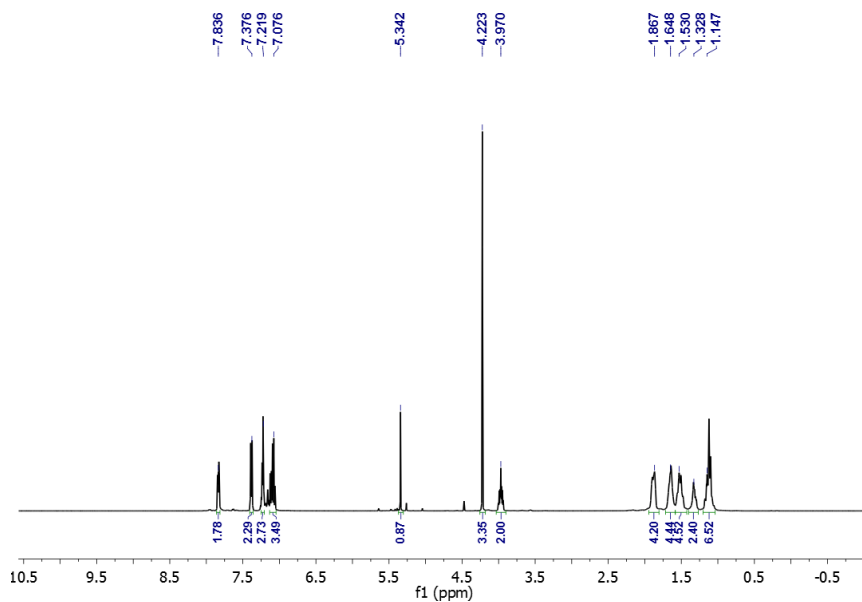


Figure S30: ^1H NMR spectrum of $\text{PhSiH}(\text{OCy})_2$ and PhSiH_3 in benzene- d_6 .

Hydrosilylation of benzaldehyde catalyzed by 0.005 mol% of **2 (0.01 mol% relative to Mn):**

In the glove box, a mixture of PhSiH_3 (3.08 mL, 24.98 mmol) and benzaldehyde (2.54 mL, 24.98 mmol) was added to 0.0016 g (0.0013 mmol) of **2** pre-weighed in a 20 mL vial. The resulting red solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^1H NMR spectrum was recorded to determine the percent conversion. It was followed by a hydrolytic work up whereby the mixture was stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (3 x 4 mL) and the organic layer was dried over anhydrous Na_2SO_4 . Removal of the solvent on a rotavap afforded a colorless oil identified as benzyl alcohol (2.477 g, 22.89 mmol, yield = 92%).¹

Hydrosilylation of 4-fluorobenzaldehyde catalyzed by 0.005 mol% of **2 (0.01 mol% relative to Mn):** In the glove box, a mixture of PhSiH₃ (2.50 mL, 20.29 mmol) and 4-fluorobenzaldehyde (2.19 mL, 20.29 mmol) was added to 0.0013 g (0.0010 mmol) of **2** pre-weighed into a 100 mL round bottom flask. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The resulting colorless solution was filtered through Celite and a ¹H NMR spectrum was recorded, which showed only 18% conversion (equating to a TOF of 900 min⁻¹ per Mn).

Attempt at benzaldehyde hydrosilylation using 0.2 mol% of Mn⁰: In the glove box, a mixture of PhSiH₃ (2.2 mL, 18.2 mmol) and benzaldehyde (1.85 mL, 18.2 mmol) was added to 0.002 g (0.036 mmol) of Mn⁰ powder pre-weighed into a 20 mL vial. The resulting solution was stirred for 2 min (no heat or bubbling was noticed) and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ¹H NMR spectrum was recorded, which revealed no conversion.

Attempt at benzaldehyde hydrosilylation using 0.1 mol% of (THF)₂MnCl₂: In the glove box, a mixture of PhSiH₃ (0.900 mL, 7.41 mmol) and benzaldehyde (0.750 mL, 7.41 mmol) was added to 0.002 g (0.0074 mmol) of (THF)₂MnCl₂ pre-weighed into a 20 mL vial. The resulting solution was stirred for 2 min (no heat or bubbling was noticed) and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ¹H NMR spectrum was recorded, which revealed no conversion.

Attempt at benzaldehyde hydrosilylation using 0.1 mol% **1:** In the glove box, a mixture of PhSiH₃ (0.350 mL, 2.81 mmol) and benzaldehyde (0.285 mL, 2.81 mmol) was added to 0.002 g (0.0028 mmol) of **1** pre-weighed in a 20 mL vial. The resulting solution was stirred for 2 min (no heat or bubbling was noticed) and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ¹H NMR spectrum was recorded, which revealed no conversion.

Test for catalyst homogeneity: A 20 mL scintillation vial was charged with 15.61 g of Hg^0 (78.05 mmol) and 0.31 mL benzaldehyde (3.12 mmol) was added to it. A solution of **2** (0.002 g, 0.0016 mmol) in 0.38 mL PhSiH_3 (3.12 mmol) was added to the vial and stirred for 2 min, while heat and bubble formation was noticed. Then it was exposed to air to deactivate the catalyst. The mixture was filtered through Celite and a ^1H NMR spectrum was collected, which showed >99% conversion.

Hydrosilylation of benzaldehyde catalyzed by 0.05 mol% of **2 in absence of light:** In the glove box, a mixture of PhSiH_3 (0.40 mL, 3.28 mmol) and benzaldehyde (0.33 mL, 3.28 mmol) was prepared in an electrical tape-wrapped 20 mL scintillation vial under dark conditions. Another wrapped vial was charged with 0.0021 g (0.0016 mmol) of **2**. The mixture was added to the catalyst in absence of light. The solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^1H NMR spectrum was recorded, which revealed >99% conversion.

Hydrosilylation of methyl formate catalyzed by 0.01 mol% of **2 (0.02 mol% relative to Mn):** In the glove box, a neat mixture of PhSiH_3 (1.5 mL, 12.49 mmol) and methyl formate (0.76 mL, 12.49 mmol) was added to 0.0016 g (0.0013 mmol) of **2** pre-weighed into a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 30 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^1H NMR spectrum was recorded to determine the percent conversion (>99 %).



In the glove box, a neat mixture of PhSiH₃ (1.9 mL, 15.6 mmol) and ethyl formate (1.3 mL, 15.6 mmol) was added to 0.002 g (0.0016 mmol) of **2** pre-weighed into a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 30 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ¹H NMR spectrum was recorded to determine the percent conversion (>99 %).

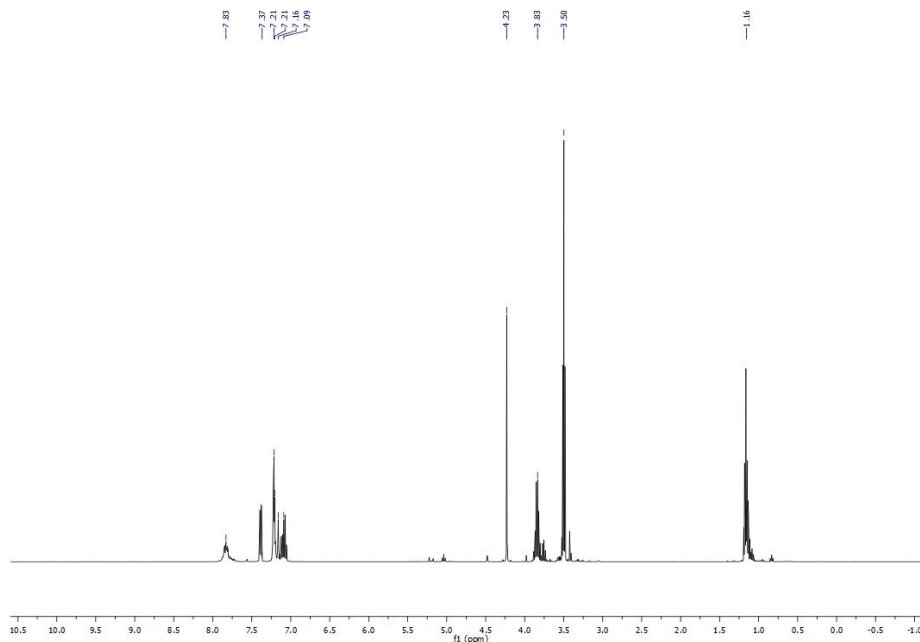


Figure S32: ^1H NMR spectrum showing complete ethyl formate hydrosilylation in benzene- d_6 .

Hydrosilylation of octyl formate catalyzed by 0.01 mol% of **2 (0.02 mol% relative to Mn):**

In the glove box, a neat mixture of PhSiH_3 (1.6 mL, 13.2 mmol) and octyl formate (2.4 mL, 13.2 mmol) was added to 0.0021 g (0.0016 mmol) of **2** pre-weighed into a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 30 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^1H NMR spectrum was recorded to determine the percent conversion (>99 %). Then the reaction mixture was hydrolyzed with 2 mL 10% aqueous NaOH solution upon stirring for 2 h at room temperature. The organic fraction was extracted with diethyl ether (3 x 4 mL) and the organic layer was dried over anhydrous Na_2SO_4 . Removal of the solvent on a rotavap afforded a colorless oil identified as 1-octanol (1.64 g, yield = 95 %). ^1H NMR (benzene- d_6): 3.40 (2H, t, - CH_2), 1.40 (2H, m, - CH_2), 1.23 (10H, m, - CH_2), 0.90 (3H, t, - CH_3). $\{^1\text{H}\}^{13}\text{C}$ NMR (benzene- d_6): 63.09, 33.57, 32.58, 30.20, 30.09, 26.54, 23.42 14.68.⁴

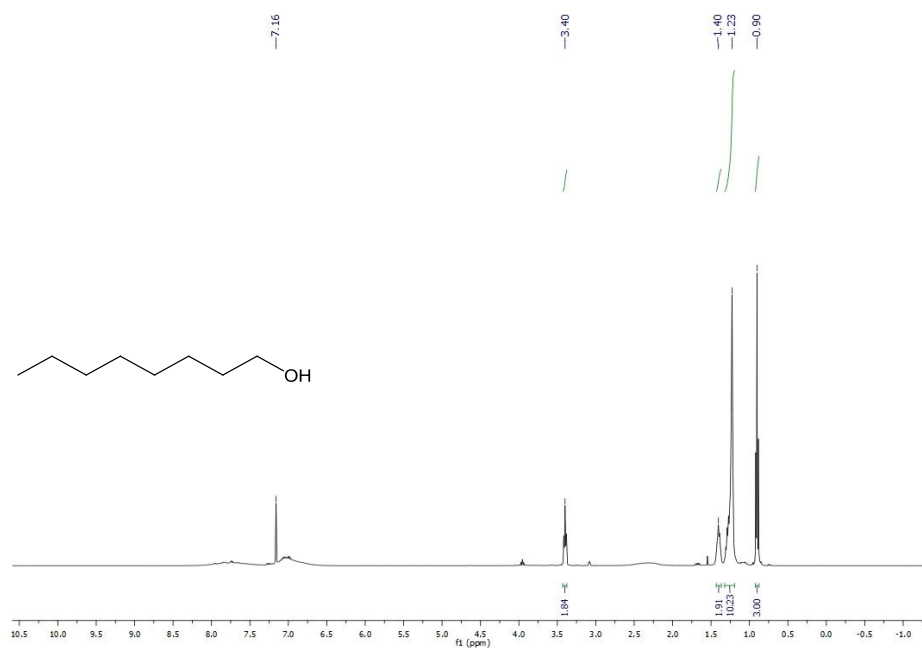


Figure S33: ^1H NMR spectrum of 1-octanol in benzene- d_6 .

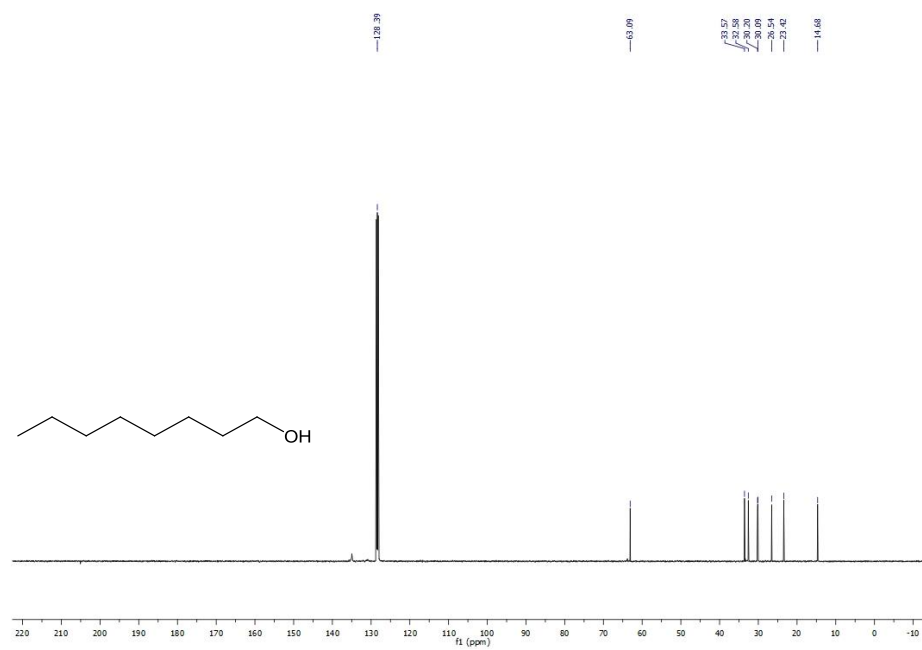


Figure S34: $\{^1\text{H}\}^{13}\text{C}$ NMR spectrum of 1-octanol in benzene- d_6 .

Hydrosilylation of isoamyl formate catalyzed by 0.01 mol% of **2 (0.02 mol% relative to **Mn**):** In the glove box, a neat mixture of PhSiH₃ (2.4 mL, 19.5 mmol) and isoamyl formate (2.6 mL, 19.5 mmol) was added to 0.0026 g (0.0019 mmol) of **2** pre-weighed in a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 30 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ¹H NMR spectrum was recorded to determine the percent conversion. Then the reaction mixture was hydrolyzed with 2 mL 10% aqueous NaOH solution upon stirring for 2 h at room temperature. The organic fraction was extracted with diethyl ether (3 x 4 mL) and the organic layer was dried over anhydrous Na₂SO₄. Removal of the solvent on a rotavap afforded a pale yellow oil identified as isoamyl alcohol (1.4 g, 15.88 mmol, yield = 83 %). ¹H NMR (benzene-*d*₆): 3.34 (2H, t, -CH₂), 1.57 (1H, m, -CH), 1.25 (2H, m, -CH₂), 0.81 (6H, d, CH₃). {¹H}¹³C NMR (benzene-*d*₆): 61.33, 42.30, 25.28, 23.09.¹

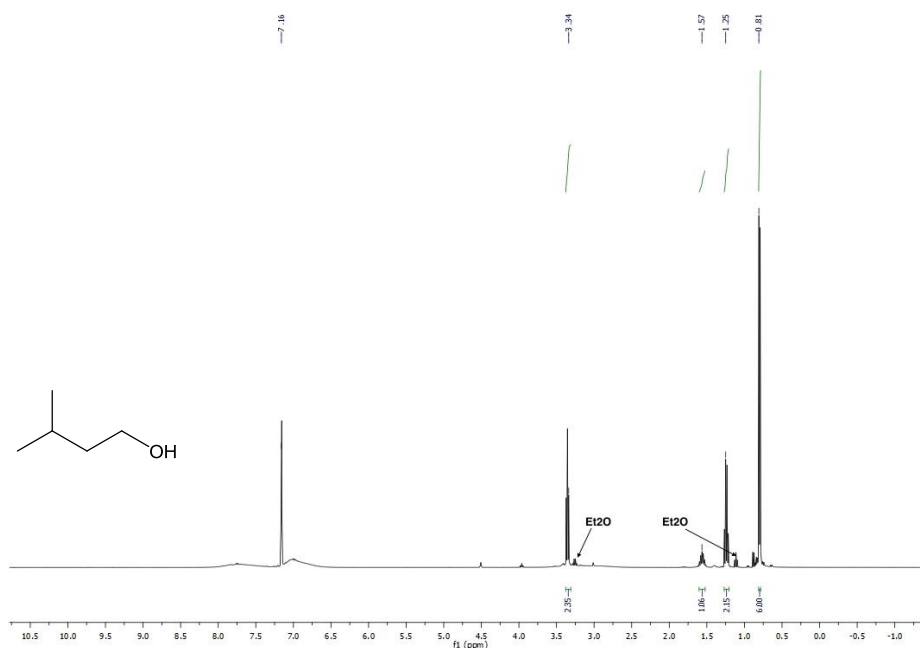


Figure S35: ¹H NMR spectrum of isoamyl alcohol in benzene-*d*₆.

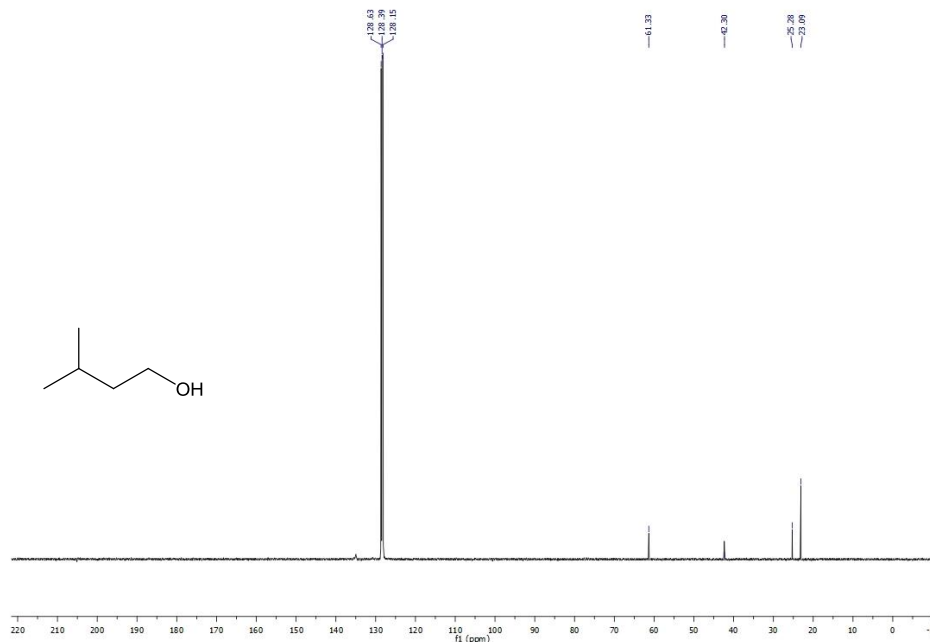


Figure S36: $\{^1\text{H}\}^{13}\text{C}$ NMR spectrum of isoamyl alcohol in benzene- d_6 .

Hydrosilylation of benzyl formate catalyzed by 0.01 mol% of **2 (0.02 mol% relative to Mn):**

In the glove box, a neat mixture of PhSiH_3 (2.4 mL, 19.51 mmol) and benzyl formate (2.4 mL, 19.51 mmol) was added to 0.0025 g (0.0019 mmol) of **2** pre-weighed into a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 30 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^1H NMR spectrum was recorded to determine the percent conversion. Then the reaction mixture was hydrolyzed with 2 mL 10% aqueous NaOH solution upon stirring for 2 h at room temperature. The organic fraction was extracted with diethyl ether (3 x 4 mL) and the organic layer was dried over anhydrous Na_2SO_4 . Removal of the solvent on a rotavap afforded a pale yellow oil identified as benzyl alcohol (2.06 g, 19.05 mmol, yield = 99%). ^1H NMR (benzene- d_6): 7.09-7.14 (5H, m, *phenyl*), 4.30 (2H, s, $-\text{CH}_2\text{OH}$), 1.42 (1H, br, $-\text{OH}$). $\{^1\text{H}\}^{13}\text{C}$ NMR (benzene- d_6): 142.11, 128.91, 127.80, 127.32, 65.20.¹

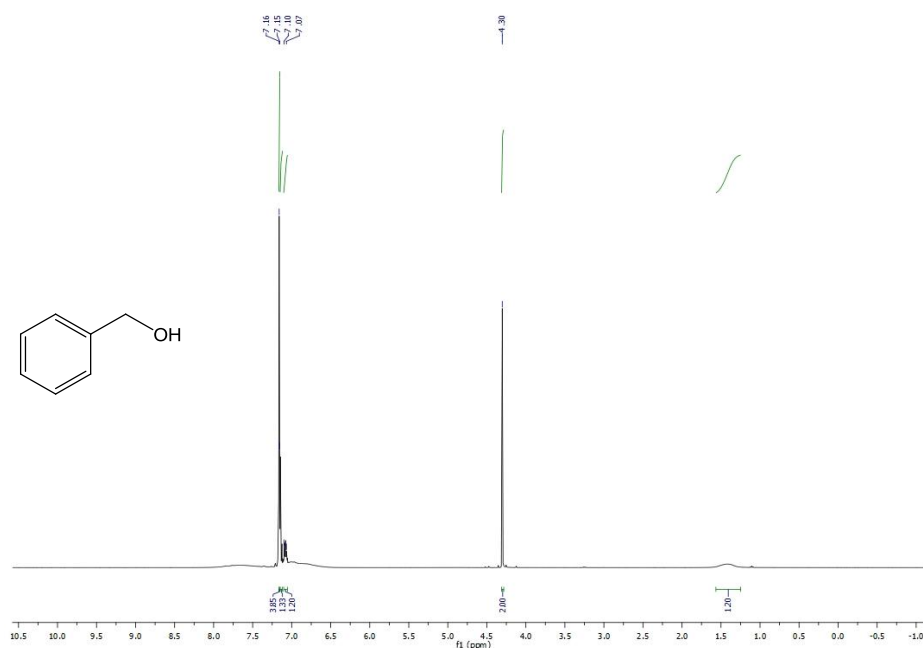


Figure S37: ¹H NMR spectrum of benzyl alcohol in benzene-*d*₆.

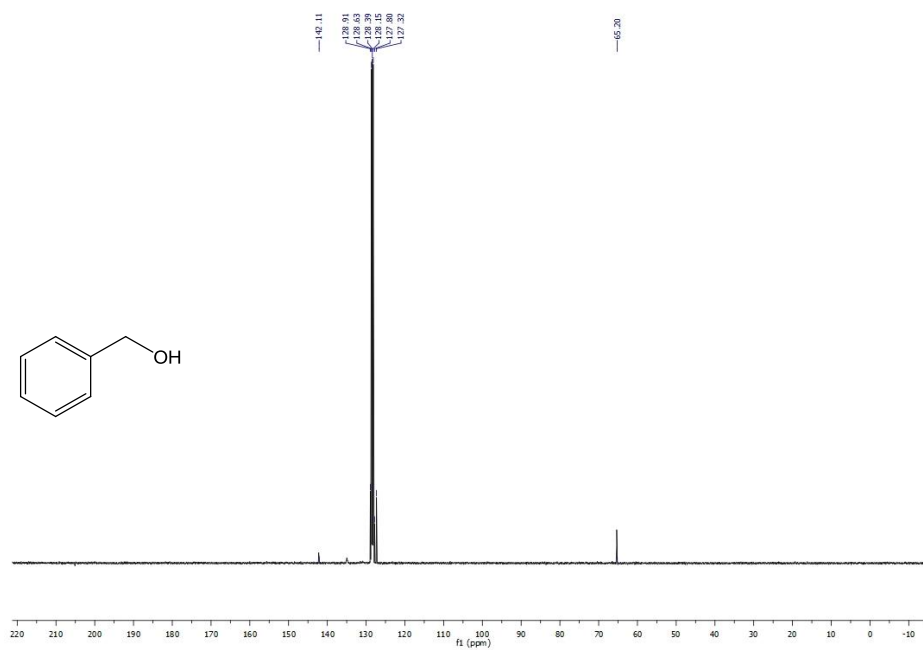


Figure S38: {¹H} ¹³C NMR of benzyl alcohol in benzene-*d*₆.

Hydrosilylation of *p*-anisyl formate catalyzed by 0.01 mol% of **2 (0.02 mol% relative to **Mn**):** In the glove box, a neat mixture of PhSiH₃ (2.7 mL, 21.8 mmol) and *p*-anisyl formate (3.5 mL, 21.8 mmol) was added to 0.0028 g (0.0022 mmol) of **2** pre-weighed into a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 30 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ¹H NMR spectrum was recorded to determine the percent conversion. Then the reaction mixture was hydrolyzed with 2 mL 10% aqueous NaOH solution upon stirring for 2 h at room temperature. The organic fraction was extracted with diethyl ether (3 x 4 mL) and the organic layer was dried over anhydrous Na₂SO₄. Removal of the solvent on a rotavap afforded a pale yellow oil identified as 4-methoxybenzyl alcohol (2.9 g, 20.99 mmol, yield = 86%). ¹H NMR (benzene-*d*₆): 7.09 (2H, d, *phenyl*), 6.75 (2H, d, *phenyl*), 4.34 (2H, s, -CH₂OH), 3.31 (3H, s, -OCH₃). {¹H} ¹³C NMR (benzene-*d*₆): 159.76, 134.37, 114.46, 65.06, 55.14.¹

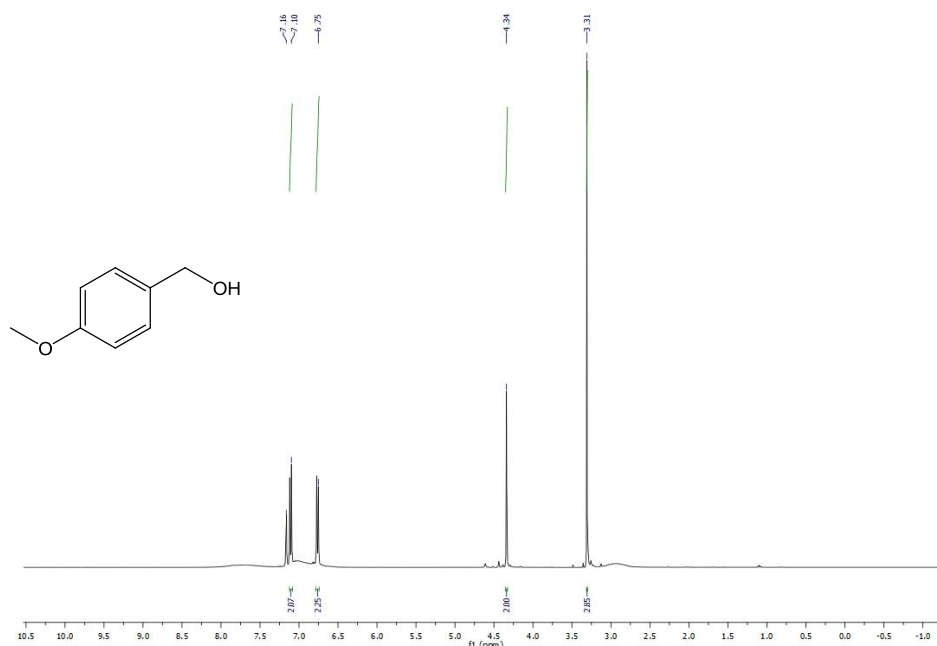


Figure S39: ¹H NMR spectrum of 4-methoxybenzyl alcohol in benzene-*d*₆.

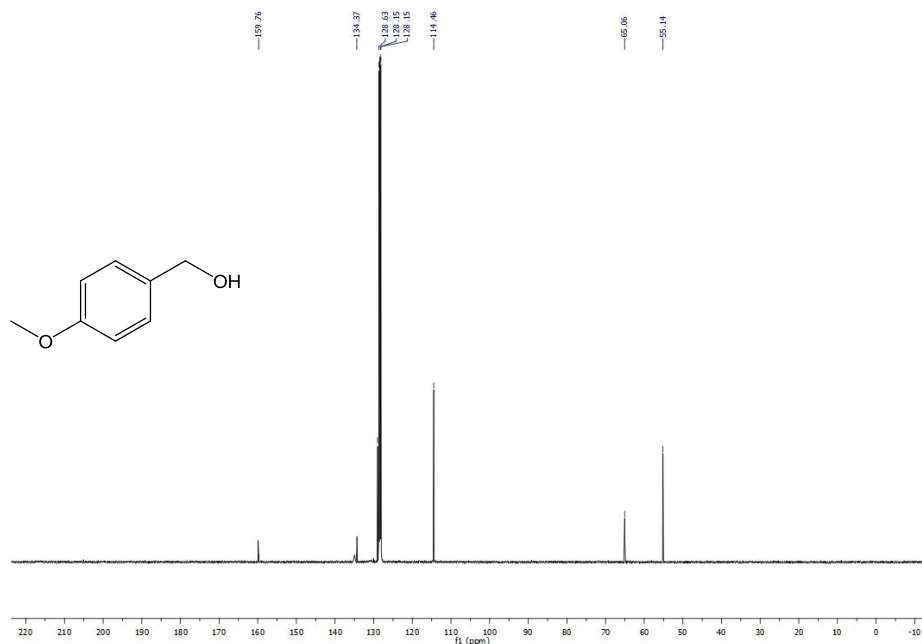


Figure S40: $\{^1\text{H}\}^{13}\text{C}$ NMR spectrum of 4-methoxybenzyl alcohol in benzene- d_6 .

Hydrosilylation of ethyl acetate using 0.5 mol% of **2 (1 mol% relative to Mn):** In the glove box, a solution of PhSiH_3 (53.9 μL , 0.437 mmol) and ethyl acetate (42.9 μL , 0.437 mmol) in 0.7 mL of benzene- d_6 was added to **2** (0.0028 g, 0.00219 mmol) pre-weighed in a 20 mL vial. The resulting red solution was transferred into a J. Young tube and sealed under N_2 atmosphere. The progress of the reaction was monitored by ^1H NMR spectroscopy, which revealed >99% conversion after 7.2 h to $\text{PhSi}(\text{OEt})_3$. Excess PhSiH_3 was also observed. ^1H NMR (400 MHz, benzene- d_6): 7.85 (m, 2H), 7.38 (excess PhSiH_3), 7.22 (m, 3H), 7.13-7.06 (m, 2H, excess PhSiH_3), 4.22 (s, excess PhSiH_3), 3.85 (qd, $J = 7.0, 0.9$ Hz, 6H), 1.17 (td, $J = 7.0, 0.9$ Hz, 9H).²

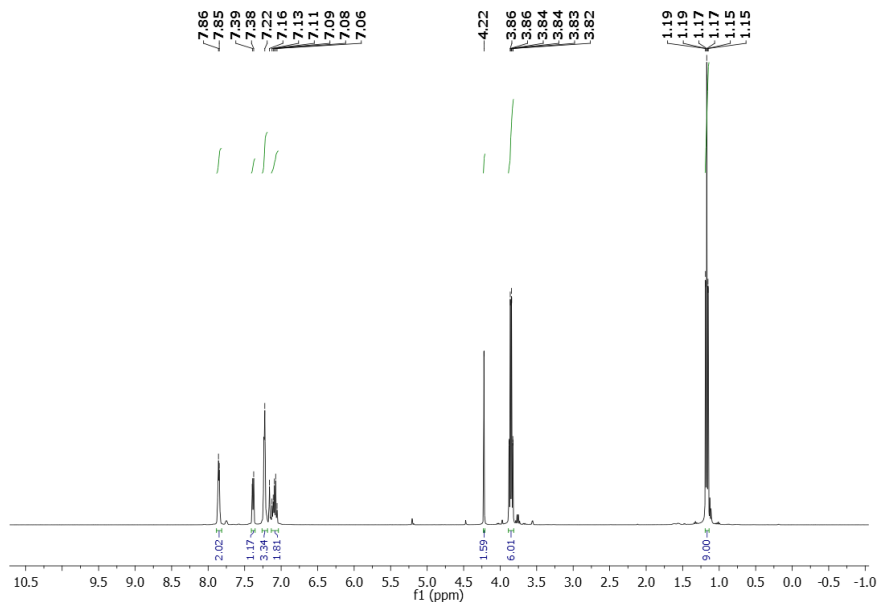


Figure S41: ^1H NMR spectrum of $\text{PhSi}(\text{OEt})_3$ and PhSiH_3 in benzene- d_6 .

REFERENCES

- ¹ Mukhopadhyay, T. K.; Rock, C. L.; Ashley, D. C.; Hong, M.; Groy, T. L.; Baik, M.-H.; Trovitch, R. J. *J. Am. Chem. Soc.* **2017**, *139*, 4901-4915.
- ² Mukhopadhyay, T. K.; Flores, M.; Groy, T. L.; Trovitch, R. J. *J. Am. Chem. Soc.* **2014**, *136*, 882-885.
- ³ Ghosh, C.; Mukhopadhyay, T. K.; Flores, M.; Groy, T. L.; Trovitch, R. J. *Inorg. Chem.* **2015**, *54*, 10398-10406.
- ⁴ Zhang, G.; Scott, B. L.; Hanson, S. K. *Angew. Chem., Int. Ed.* **2012**, *51*, 12102-12106.