Supplementary Materials

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1. Experimental Section

General. All the substrates and reagents were obtained commercially and were degasified and dried over molecular sieves prior to the reaction. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 500 or AVANCE NEO 400 NMR spectrometer and referenced to the residue peaks in $CDCl_3$ (7.26), CD_3CN (1.94), or C_6D_6 (7.16). High resolution mass spectrometry (HRMS) was performed using high- resolution time of flight G1969A instrumentation (Agilent, Santa Clara, CA, USA). UV-vis measurement was performed on a PerkinElmer Lamda 35 spectrophotometer.

1.1 Synthesis and Characterization of 2a[77]

Ethylenediamine (55.1 mg, 0.917 mmol) in 30 mL of methanol was added dropwise to a stirred solution of salicylaldehyde (224 mg, 1.83 mmol) in 10 mL of methanol at RT. The reaction mixture was stirred for 5 min and sodium borohydride (693 mg, 1.83 mmol) was added portionwise within 10 min. After it became colorless, the mixture was washed with distilled H_2O and extracted with dichloromethane. The organic phase was collected and dried over anhydrous Na_2SO_4, and the solvent was removed in a rotavapor. Compound **2a** was obtained as a white solid, and the yield was 244 mg (98%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.77 (s, 4H), 3.93 (s, 4H), 6.72 (td, 2H), 6.77 (d, 2H), 6.91 (d, 2H), 7.11 (td, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 47.8 (*C*H_2), 52.6 (*C*H_2), 116.4, 119.2, 122.1, 128.4, 128.9, 157.9.

1.2 Synthesis and Characterization of 2b[88]

To a stirred solution of 3,5-di-t-butyl salicylaldehyde (424 mg, 1.81 mmol) in 10 mL of methanol was slowly added a solution of ethylenediamine (54.3 mg, 0.904 mmol) in 30 mL of methanol. The mixture was refluxed for two hours and then filtered. A yellow solid was obtained as the product. The yield was 440 mg (99%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.28 (s, 18H), 1.43 (s, 18H), 3.92 (m, 4H), 7.06 (d, 2H), 7.36 (d, 2H), 8.38 (s, 2H), 13.65 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 24.4 (C(*C*H_3)$_3$), 29.5 (C(*C*H_3)$_3$), 33.3 (*C*(CH_3)$_3$), 34.1 (*C*(CH_3)$_3$), 35.0 (*C*H_2), 117.9 (Ar-*C*), 126.1 (Ar-*C*), 126.8 (Ar-*C*), 136.4 (Ar-*C*), 139.9 (Ar-*C*), 158.1 (Ar-*C*), 165.9 (*C*H=N). In the second step, the compound obtained in the first step (541 mg, 1.09 mmol) was dissolved in 12 ml of THF. Then, sodium borohydride (247 mg, 60 mmol) was added, and the reaction mixture was refluxed for three hours. When the mixture was colorless, it was washed with 100 mL of water and extracted with dichloromethane. The organic phases were dried over anhydrous Na_2SO_4, and the solvents were removed under the vacuum to obtain **2b** as a white solid. The yield was 528 mg (97%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.28 (s, 18H), 1.41 (s, 18H), 2.87 (s, 4H), 3.96 (s, 4H), 6.85 (d, 2H),7.22 (d, 2H) 10.79 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 29.6 (*C*H_3), 31.7 (*C*H_3), 34.1 (*C*Me_3), 34.9 (*C*Me_3), 48.0 (*C*H_2), 53.5 (*C*H_2), 121.7, 123.1, 123.2, 136.0, 140.6, 154.4.

1.3 Preparation of Ligand 3a [77]

Compound **2a** (325 mg, 1.19 mmol) was dissolved in acetonitrile (27 mL) and acetic acid (4 mL) in a round bottom flask. Then, formaldehyde (0.886 mL, 11.9 mmol, 37% in water) was added. After 20 min of stirring at room temperature, sodium borohydride (225 mg, 5.95 mmol) was added to the mixture and stirred for an additional 24 h at RT. Acetonitrile was evaporated in a rotavapor, and the remaining residue was hydrolyzed with 2 N NaOH. The product was extracted using dichloromethane. The solvent was removed to obtain **3a** as a white powder. The yield was 510 mg (89%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.24(s, 6H), 2.67 (s, 4H), 3.70 (s, 4H), 6.78 (td, 2H), 6.84 (dd, 2H), 6.96 (dd, 2H), 7.18, 10.75 (s, 2H) (td, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 41.7 (CH_3), 54.1 (CH_2), 61.8 (CH_2), 116.2, 119.1, 121.6, 128.5, 128.9, 157.8.

1.4 Preparation of Ligand 3b [76]

Ligand **3b** was prepared by a similar procedure as ligand **3a**. Ligand **2b** (541 mg, 1.09 mmol) was added to a flask that contained acetonitrile (27 mL) and acetic acid (4 mL). After 5 min, formaldehyde (0.812 mL,10.9 mmol) was added. The reaction was stirred at RT for 10 min, and sodium borohydride (206 mg, 5.45 mmol) was added. Then, the reaction was stirred at RT for 24 h. Acetonitrile was removed under vacuum, the mixture was hydrolyzed with 2N NaOH, and the product was extracted with dichloromethane. The yield was 542 mg (95%). M. p. 142-147 ºC;^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.27 (s, 18H), 1.39 (s, 18H), 2.26 (s, 6H), 2.63 (s, 4H), 3.66 (s, 4H), 6.80 (d, 2H), 7.20 (d, 2H), 10.68 (b, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 29.6 (CH_3), 31.7 (CH_3), 34.1 ($C(CH_3)_3$), 34.8 ($C(CH_3)_3$), 41.6 (NCH_3), 53.8 (NCH_2), 62.7 (NCH_2), 121.0, 123.0, 123.3, 135.6, 140.5, 154.2.

1.5 Preparation of Manganese Complex 4a

Ligand **3a** (121mg, 10 mmol) was dissolved in ethanol (70 mL), and then $Mn(Oac)_2{\cdot}4H_2O$ (182 mg, 20 mmol) was added to the reaction mixture. The resulting mixture was refluxed for 3 hours, and LiCl (47.4 mg, 30 mmol) was added. This solution was refluxed for an additional two hours. The solvent was removed under a vacuum, and dichloromethane was added. The mixture was washed with brine and H_2O solutions, then dried with an anhydrous Na_2SO_4. The solvent was removed under a vacuum to obtain **4a** as a brown solid. The yield was 115 mg (80 %); m. p. 178 -185 ºC (decomp.); FT-IR 3362, 1554, 1353, 1263, 1184, 1034, 943, 756, 671, 756 cm^{-1}. UV-vis in CH_3CN [nm, ε (M^{-1} cm^{-1})]: 325 (1.70 x 10^4), 275 (7.84 x 10^4), 220 (1.70 x 10^5).

1.6 Preparation of Manganese Complex 4b

The manganese complex **4b** was prepared by a similar procedure to manganese complex **4a**. Ligand **3b** (231 mg, 0.440 mmol) was dissolved in ethanol (100 mL) with constant stirring at RT, then $Mn(Oac)_2{\cdot}4H_2O$ (215 mg, 0.880 mmol) was added to the mixture. The reaction mixture was refluxed for

three hours, and LiCl (55.9 mg, 1.32 mmol) was added. The mixture was then refluxed for an additional two hours. Ethanol was removed, and dichloromethane was added. The mixture was washed with brine and H_2O. The organic phase was isolated, and the solvent was removed. The yield was 231 mg (86 %); mp 184-185 ºC (decomp.); IR 2953, 2904, 2867, 1605, 1463, 1443, 1390, 1304, 1236, 1203, 1166, 1172, 1104, 1019, 979 cm^{-1}. UV-vis in CH_3CN [nm, ε (M^{-1} cm^{-1})]: 325 (5.83 x 10^4), 285 (1.16 x 10^5), 225 (2.04 x 10^5).

1.7 Preparation of Manganese Complex 5a

In flask 1, compound **4a** (221 mg, 0.568 mmol) was dissolved in in 10 mL of CH_3CN. In flask 2, $AgClO_4$ (117 mg, 0.568 mmol) was dissolved in 2 mL of CH_3CN. The mixture of flask 1 was added to flask 2 over a 5 min period. The precipitation of AgCl was observed immediately, and the mixture was stirred at RT for 16 hours. The mixture was then washed with CH_3CN through a silica pad, and NaN_3 (111 mg, 1.71 mmol) was added to the filtrate. The filtrate was stirred at RT for 24 hours. Then, ethyl ether was added, and the solution mixture was washed with H_2O three times. The organic phase was isolated and dried, and the solvent was evaporated under the vacuum to obtain **5a** as a brown solid. The yield was 135 mg (60%); m.p. 169- 173 ºC (decomp.); IR 2855, 2037 (ν_{N3}), 1629, 1594, 1566, 1531, 1477, 1448, 1370, 1267, 1242, 1145, 1107, 1037, 1009, 966. UV-vis in CH_3CN [nm, ε (M^{-1} cm^{-1})]: 460 (2.27 x 10^4), 375 (5.45 x 10^4), 340 (5.91 x 10^4), 310 (9.09 x 10^4), 260 (1.09 x 10^5), 240 (1.45 x 10^5).

1.8 Preparation of Manganese Complex 5b

It was prepared by a procedure similar to complex **5a**. Compound **4b** (343 mg, 0.561 mmol) in acetonitrile was added to the solution of $AgClO_4$ (116 mg, 0.561 mmol) in acetonitrile over 5 min. The mixture was stirred for 16 hours and filtered through silica with 20 mL of CN_3CN. After that, NaN_3 (109 mg, 1.63 mmol) was added to the filtrate, and the mixture was stirred at RT for 24 h. The mixture was then diluted with ethyl ether (15 mL) and washed with H_2O. The organic phase was isolated and dried, and the solvent was removed under a vacuum. The yield was 242 mg (70%); m.p. 183-184 ºC (decomp.); IR 2956, 2904, 2866, 2050 (ν_{N3}), 1612, 1534, 1474, 1467, 1443, 1390, 1360, 1303, 1234, 1202, 1165, 1103, 1018, 979 cm^{-1}. UV-vis in CH_3CN [nm, ε (M^{-1} cm^{-1})]: 475 (3.09 x 10^4), 285 (7.32 x 10^4), 240 (8.53 x 10^4), 215(3.41 x 10^5), 225 (2.43 x 10^4).

1.9 General Procedure for Catalytic hydrosilylation

In a typical procedure, manganese catalyst **5b** (2-3 mg, 0.5 mol%), the carbonyl substrate (~1 mmol, 1.0 equivalent), $PhSiH_3$ (1 equivalent), and a deuterated solvent (i.e. C_6D_6, 0.2-0.4 ml) were added to a J Young NMR tube. This was then heated in an oil bath set at ~120 °C and the reaction progress was monitored by ^1H NMR spectroscopy at preset time intervals. After the consumption of the carbonyl substrates was complete or nearly complete, the reaction mixture was transferred to a round bottom flask while being washed with diethylether (3-5 mL). After the addition of aqueous HCl (1 M) to the flask, the mixture was stirred for 1-2 h. After hydrolysis, the organic layer was extracted with diethylether and subjected to column chromatography using silica with hexane-EtOAc as an eluent. The

resultant products were characterized by ^{1}H NMR in $CDCl_3$ and confirmed by comparison with the literature data or authentic samples.

The gram scale hydrosilylation was carried out as follows: manganese catalyst **5b** (30.4 mg, 0.5 mol%), PhCHO (992 µL, 9.82 mmol, 1.0 equivalent), and $PhSiH_3$ (1.21 mL, 9.81 mmol, 1 equivalent) were added to a vial and sealed, then it was heated in an oil bath set at ~120 °C and the reaction progress was monitored by ^{1}H NMR spectroscopy at preset time intervals. After completion of the reaction, the mixture was hydrolyzed and purified as described above. Yield: 80%.

Benzyl alcohol (Table 2, entry 1).[89] ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, δ): 4.68 (s, 2H, OC*H*$_2$), 7.19 (m, 2H, *Ph*), 7.35-7.40 (m, 3H, *Ph*).

***p*-Bromobenzyl alcohol (Table 2, entry 2).**[89] ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, δ): 4.55 (s, 2H, OC*H*$_2$), 7.22 (m, 2H, *Ph*), 7.37 (m, 2H, *Ph*).

***p*-Nitrobenzyl alcohol (Table 2, entry 3).**[89] ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, δ): 4.81 (s, 2H, OC*H*$_2$), 7.45 (m, 2H, *Ph*), 8.09 (m, 2H, *Ph*).

***p*-Methoxybenzyl alcohol (Table 2, entry 4).**[89] ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, δ): 3.52 (s, 3H, OC*H*$_3$), 4.61 (s, 2H, OC*H*$_2$), 6.82 (m, 2H, *Ph*), 7.11 (m, 2H, *Ph*).

1-Phenylethanol (Table 2, entry 5).[90] ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, δ): 1.42 (d, 3H, C*H*$_3$), 4.84 (q, 1H, OC*H*), 7.18 (d, 2H, *Ph*), 7.20 (m, 3H, *Ph*).

1-(4-Nitrophenyl)ethanol (Table 2, entry 6).[90] ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, δ): 1.49 (d, 3H, C*H*$_3$), 4.97 (q, 1H, OC*H*), 7.51 (d, 2H, *Ph*), 8.04 (d, 2H, *Ph*).

1-(4-Methoxyphenyl)ethanol) (Table 2, entry 7).[89] ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, δ): 1.50 (d, 3H, C*H*$_3$), 3.60 (s, 3H, OC*H*$_3$), 4.87 (q, 1H, OC*H*), 6.88 (d, 2H, *Ph*), 7.27 (d, 2H, *Ph*).

***α*-Cyclopropylbenzylalcohol (Table 2, entry 8).**[89] ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, δ): 0.35-0.46 (m, 4H, cyclopropyl 2C*H*$_2$), 0.56 (m, 1H, cyclopropyl C*H*), 4.02 (m, 1H, OC*H*), 7.20 (m, 1H, *Ph*), 7.31 (m, 2H, *Ph*), 7.48 (m, 2H, *Ph*).

Cinnamyl alcohol (Table 2, entry 9).[91] ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, δ): 4.12 (s, 2H, OC*H*$_2$), 6.20 (m, 1H, -C*H*=CHPh), 6.34 (m, 1H, -CH=C*H*Ph), 7.01 (m, 2H, *Ph*), 7.08-7.17 (m, 3H, *Ph*).

2-Pentanol (Table 2, entry 10).[91] ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, δ): 0.91 (t, 3H, C*H*$_3$), 1.17(d, 3H, OCHC*H*$_3$), 1.39 (m, 4H, C*H*$_2$), 3.80 (m, 1H, OC*H*).

Cyclohexanol (Table 2, entry 11).[92] ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, δ): 1.21 (m, 2H, C*H*$_2$), 1.40 (m, 2H, C*H*$_2$), 1.49 (m, 2H, C*H*$_2$), 1.71 (m, 2H, C*H*$_2$), 1.83 (m, 2H, C*H*$_2$), 3.60 (m, 1H, OC*H*).

2. NMR Spectra of Selected Hydrosilylation Reactions

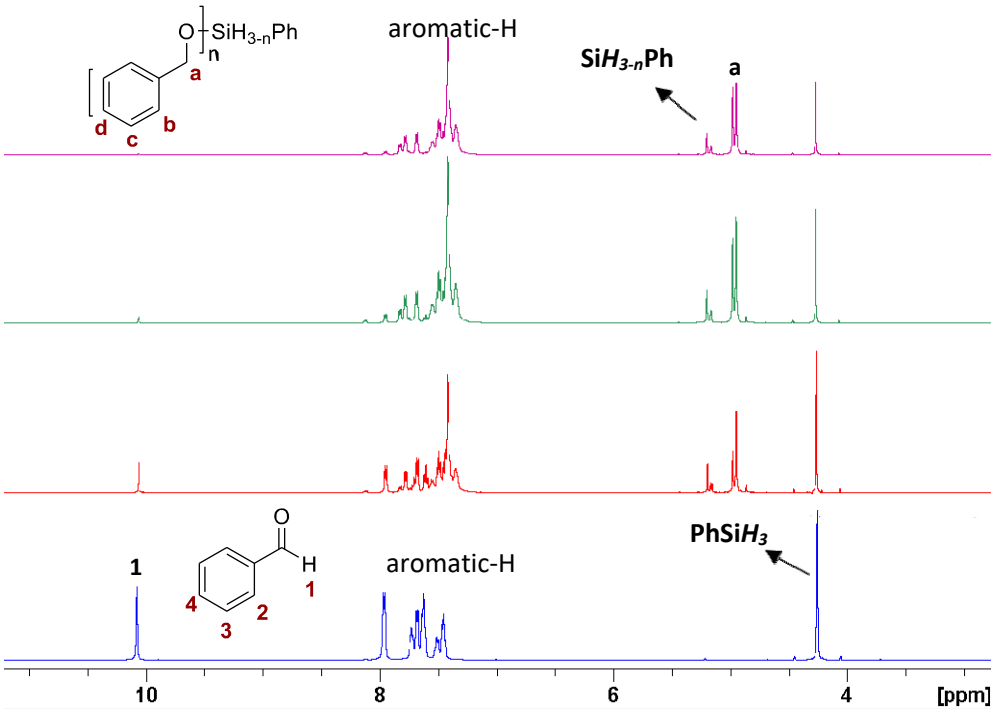


Figure S1. ^{1}H NMR of the reaction of benzaldehyde with $PhSiH_3$ (Table 1, entry 1)

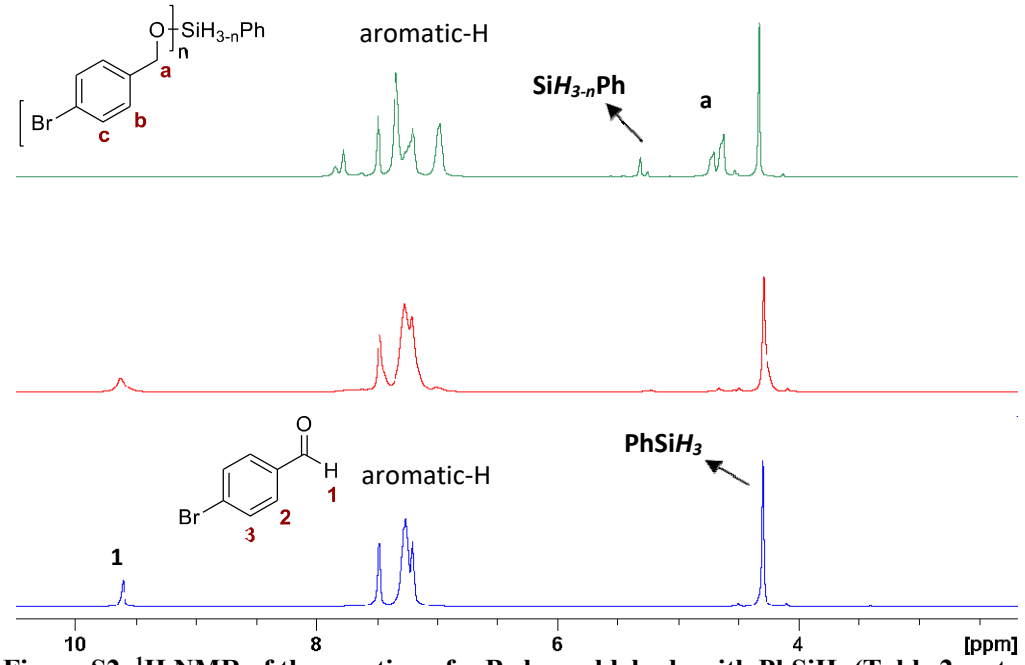


Figure S2. ^{1}H NMR of the reaction of *p*-Br benzaldehyde with $PhSiH_3$ (Table 2, entry 2)

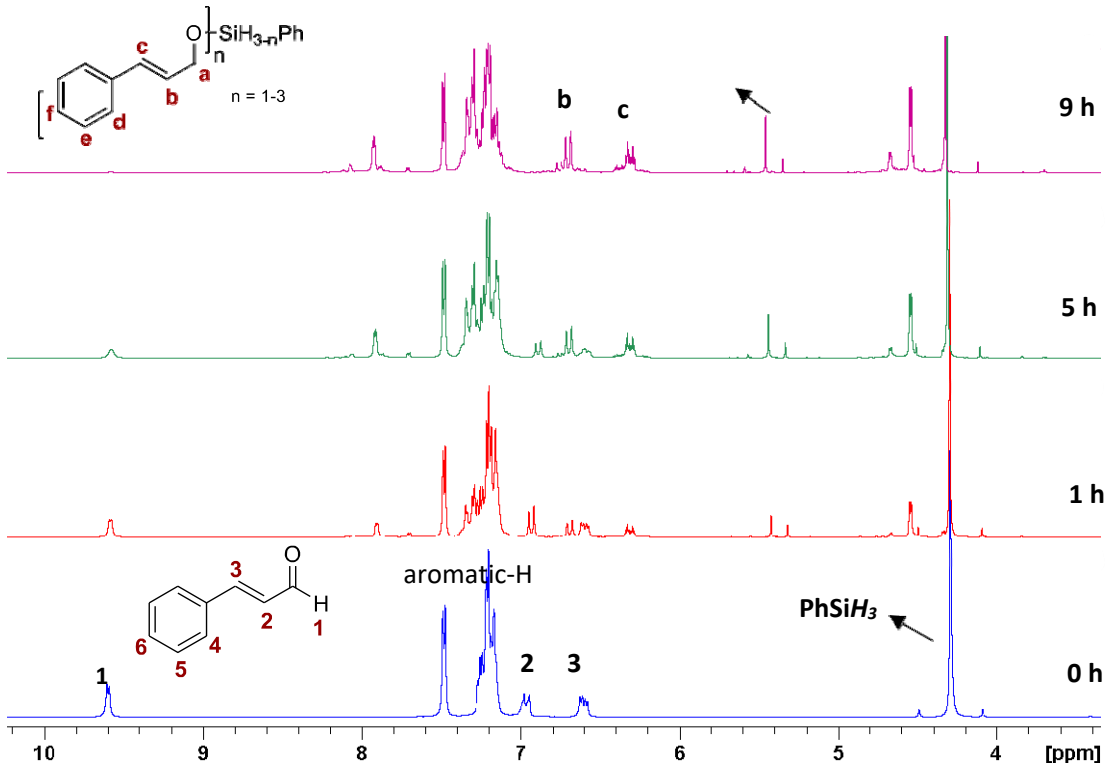


Figure S3. ^{1}H NMR of the reaction of cinnamaldehyde with $PhSiH_3$ (Table 2, entry 10)

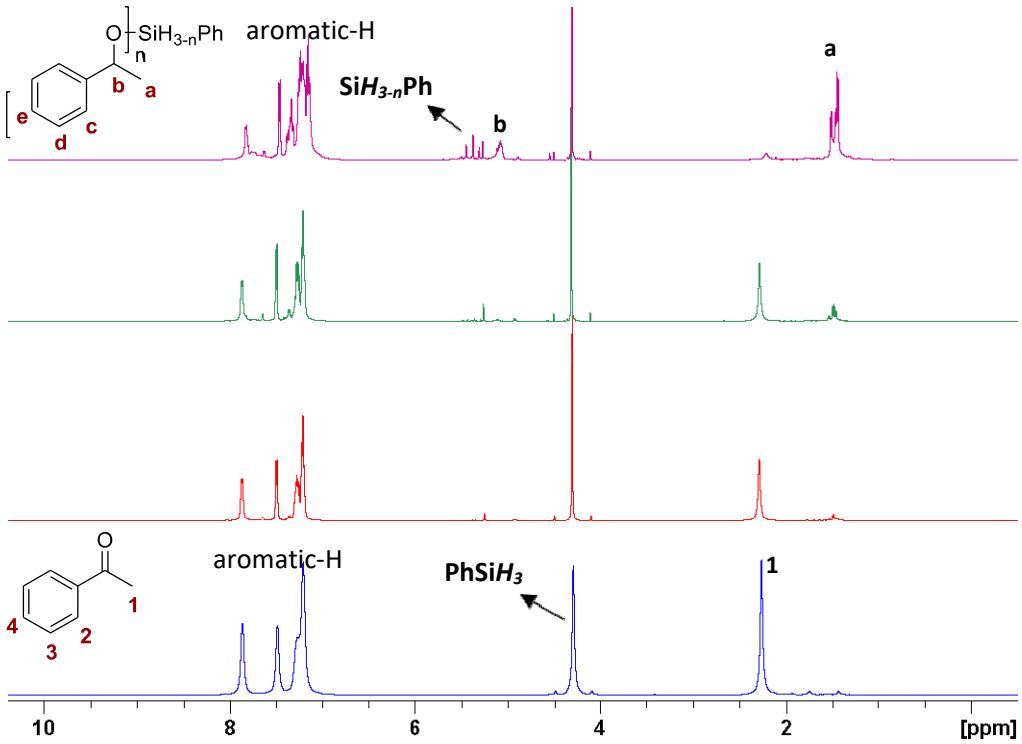


Figure S4. ^{1}H NMR of the reaction of acetophenone with $PhSiH_3$ (Table 2, entry 5)

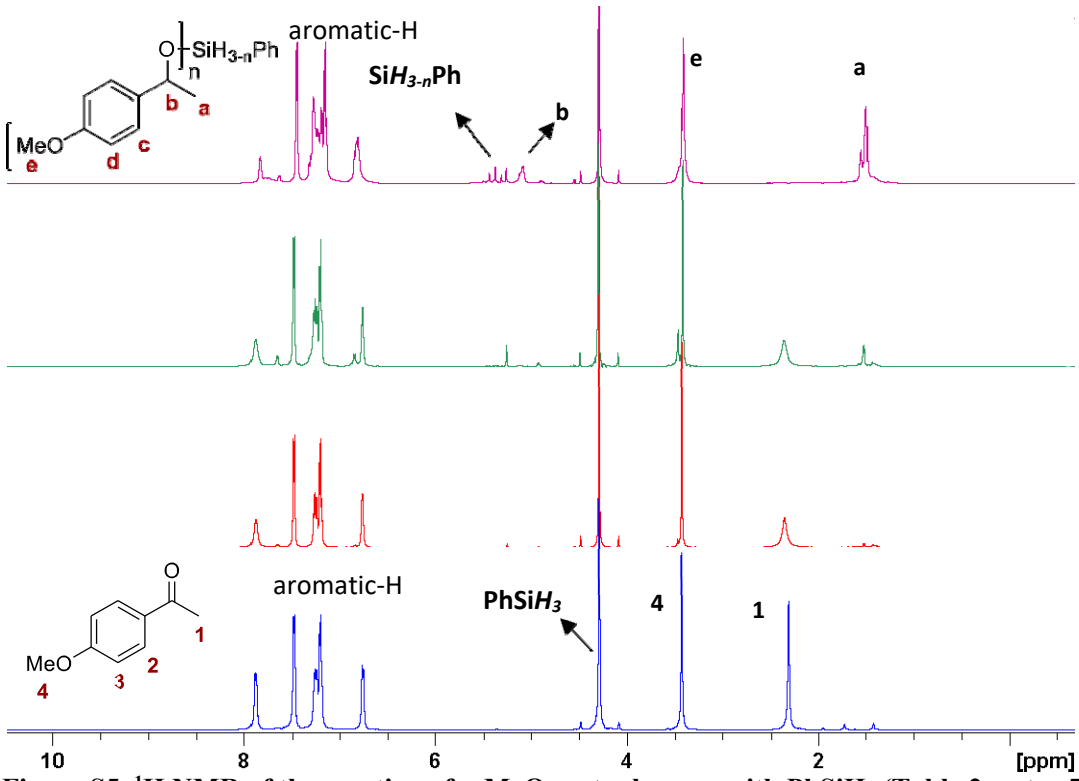
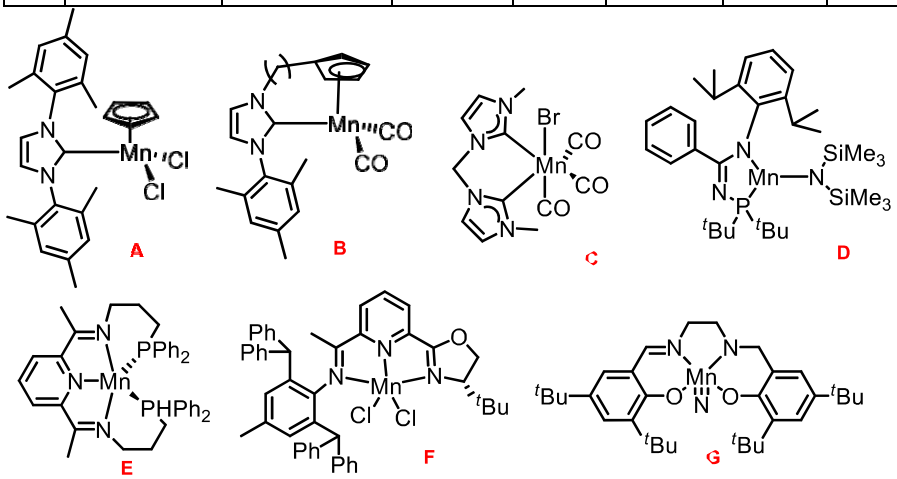


Figure S5. ^{1}H NMR of the reaction of *p*-MeO acetophenone with $PhSiH_3$ (Table 2, entry 7)

3. Table S1: Comparison of Catalytic Activity of Selective Mn Complexes in Scheme 1

	Substrate	Silane (equiv)	Cat (mol%)	Temp °C	Solvent	Time	Convn	activation	Ref
1	PhCHO	Ph_2SiH_2 (1.5)	**A** (1)	25	Toluene	1 h	97%	hυ(350nm)	65
2	NaphCOMe	Ph_2SiH_2 (1.0)	**B** (0.5)	25	Toluene	24 h	98%	hυ(350nm)	70
3	PhCHO	PhSiH3 (1.2)	**C** (1)	80	Benzene	16 h	98%		57
4	PhCOMe	$PhSiH_3$ (1.2)	**C** (1)	80	CH_3CN	5 h	97%		57
5	PhCHO	$PhSiH_3$ (1.0)	**D** (1)	25	Benzene	4 h	90%		62
6	PhCOMe	$PhSiH_3$ (1.0)	**D** (1)	25	Benzene	4 h	90%		62
7	PhCOMe	$PhSiH_3$ (1.0)	**E** (1)	25	Benzene	4 min	>99%		66
8	PhCOMe	$PhSiH_3$ (1.0)	**F** (1)	25	Toluene	12 h	68%	$NaBEt_3H$	63
9	PhCHO	$PhSiH_3$ (0.5)	**G** (0.5)	80	CH_3CN	20 min	98%		68
10	PhCOMe	$PhSiH_3$ (0.5)	**G** (0.5)	80	CH_3CN	2 h	98%		68
11	PhCHO	$PhSiH_3$ (1.0)	**5b** (0.5)	120	Benzene	40 min	>99%		this work
12	PhCOMe	$PhSiH_3$ (1.0)	**5b** (0.5)	120	Benzene	41 h	93%		this work



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