Carbonyl and Ester C-O Bond Hydrosilylation Using κ^4-Diimine Nickel Catalysts

Electronic Supplementary Information

*Christopher L. Rock, Thomas L. Groy, and Ryan J. Trovitch**

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

ryan.trovitch@asu.edu

Table S1. Crystallographic Data for **(^{iPr2PPr}DI)Ni** (**2**) and **(^{tBu2PPr}DI)Ni** (**3**).

	(^{iPr2PPr}DI)Ni	**(^{tBu2PPr}DI)Ni**
chemical formula	$C_{22}H_{44}N_2NiP_2$	$C_{26}H_{54}N_2NiP_2$
formula weight	459.26	515.36
crystal dimensions	0.253 x 0.182 x 0.104	0.228 x 0.193 x 0.137
crystal system	triclinic	monoclinic
space group	P -1	C 1 2/c 1
a (Å)	9.0477(5)	13.1585(5)
b (Å)	10.1518(6)	17.2832(7)
c (Å)	15.4698(9)	12.2496(5)
α (deg)	94.4200(10)	90
β (deg)	100.1970(10)	91.5308(6)
γ (deg)	115.7230(10)	90
V ($Å^3$)	1240.76(12)	2784.82(19)
Z	2	4
T (°C)	123.(2)	123.(2)
ρcalcd (g cm^{-3})	1.229	1.229
μ (mm^{-1})	0.921	0.828
reflections collected	10079	11141
data/restraints/parameters	4368/0/254	2458/0/148
R_1 [$I > 2\sigma(I)$]	0.0416	0.0370
wR_2 (all data)	0.1071	0.0957
Goodness-of-fit	1.070	1.095
Largest peak, hole ($eÅ^{-3}$)	0.859, -0.246	1.027, -0.193

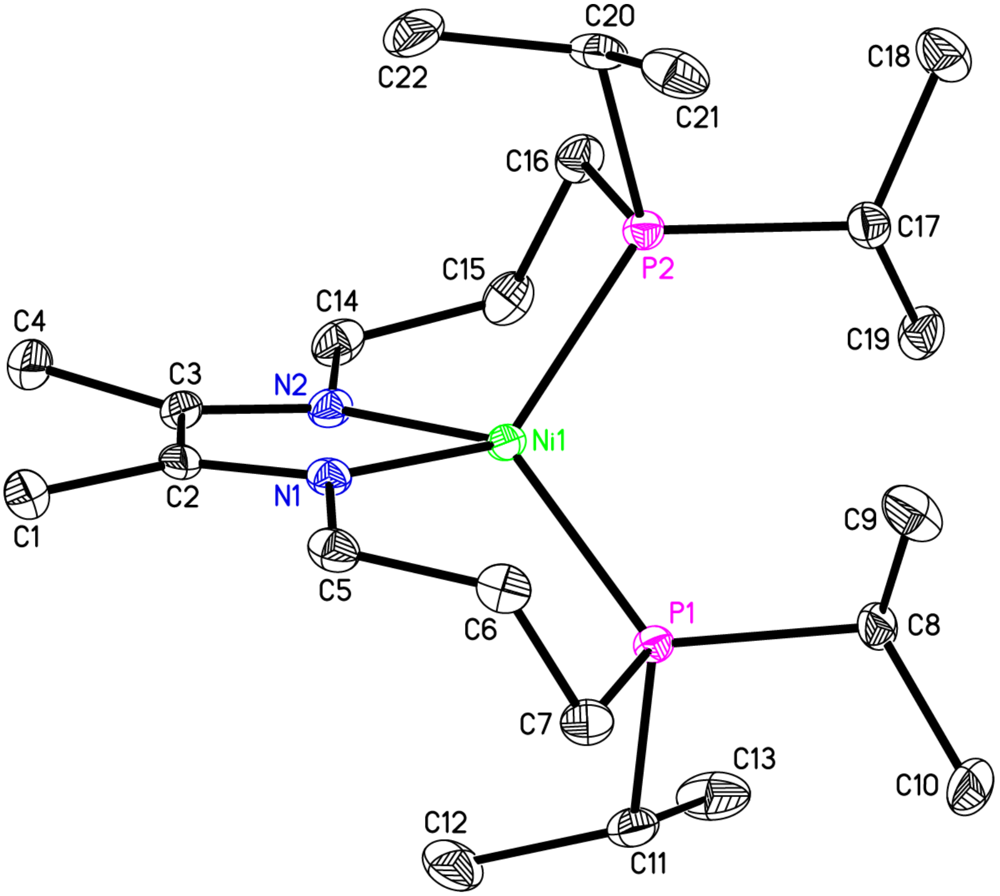

Figure S1. The molecular structure of **(^{iPr2PPr}DI)Ni** (**2**) shown at 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

Table S2. Metrical parameters for **(^{iPr2PPr}DI)Ni** (**2**).

Ni1-N2	1.931(2)	N1-C2	1.350(3)	C8-C10	1.537(4)
Ni1-N1	1.933(2)	N1-C5	1.467(3)	C11-C13	1.521(4)
Ni1-P1	2.1455(7)	N2-C3	1.350(3)	C11-C12	1.529(4)
Ni1-P2	2.1544(7)	N2-C14	1.468(3)	C14-C15	1.512(4)
P1-C7	1.848(3)	C1-C2	1.508(4)	C15-C16	1.528(4)
P1-C11	1.861(3)	C2-C3	1.420(4)	C17-C19	1.531(4)
P1-C8	1.863(3)	C3-C4	1.506(4)	C17-C18	1.536(4)
P2-C16	1.850(3)	C5-C6	1.515(4)	C20-C21	1.523(4)
P2-C20	1.859(3)	C6-C7	1.530(4)	C20-C22	1.527(4)
P2-C17	1.861(3)	C8-C9	1.534(4)		

N2-Ni1-N1	82.46(9)	C20-P2-Ni1	112.30(9)	C6-C7-P1	111.04(18)
N2-Ni1-P1	136.15(6)	C17-P2-Ni1	124.45(9)	C9-C8-C10	109.3(2)
N1-Ni1-P1	97.54(7)	C2-N1-C5	116.1(2)	C9-C8-P1	109.6(2)
N2-Ni1-P2	96.12(6)	C2-N1-Ni1	113.92(17)	C10-C8-P1	116.0(2)
N1-Ni1-P2	133.06(6)	C5-N1-Ni1	128.48(17)	C13-C11-C12	109.7(3)
P1-Ni1-P2	113.80(3)	C3-N2-C14	116.0(2)	C13-C11-P1	109.86(19)
C7-P1-C11	102.27(12)	C3-N2-Ni1	113.90(17)	C12-C11-P1	109.44(19)
C7-P1-C8	101.69(13)	C14-N2-Ni1	128.30(17)	N2-C14-C15	113.8(2)
C11-P1-C8	103.44(13)	N1-C2-C3	114.6(2)	C14-C15-C16	112.2(2)
C7-P1-Ni1	110.71(9)	N1-C2-C1	121.9(2)	C15-C16-P2	110.89(18)
C11-P1-Ni1	114.01(9)	C3-C2-C1	123.5(2)	C19-C17-C18	109.8(2)
C8-P1-Ni1	122.31(9)	N2-C3-C2	114.4(2)	C19-C17-P2	109.83(18)
C16-P2-C20	102.47(13)	N2-C3-C4	122.3(2)	C18-C17-P2	115.35(19)
C16-P2-C17	101.08(12)	C2-C3-C4	123.3(2)	C21-C20-C22	110.6(2)
C20-P2-C17	103.87(12)	N1-C5-C6	114.2(2)	C21-C20-P2	110.15(19)
C16-P2-Ni1	110.10(9)	C5-C6-C7	113.0(2)	C22-C20-P2	109.2(2)

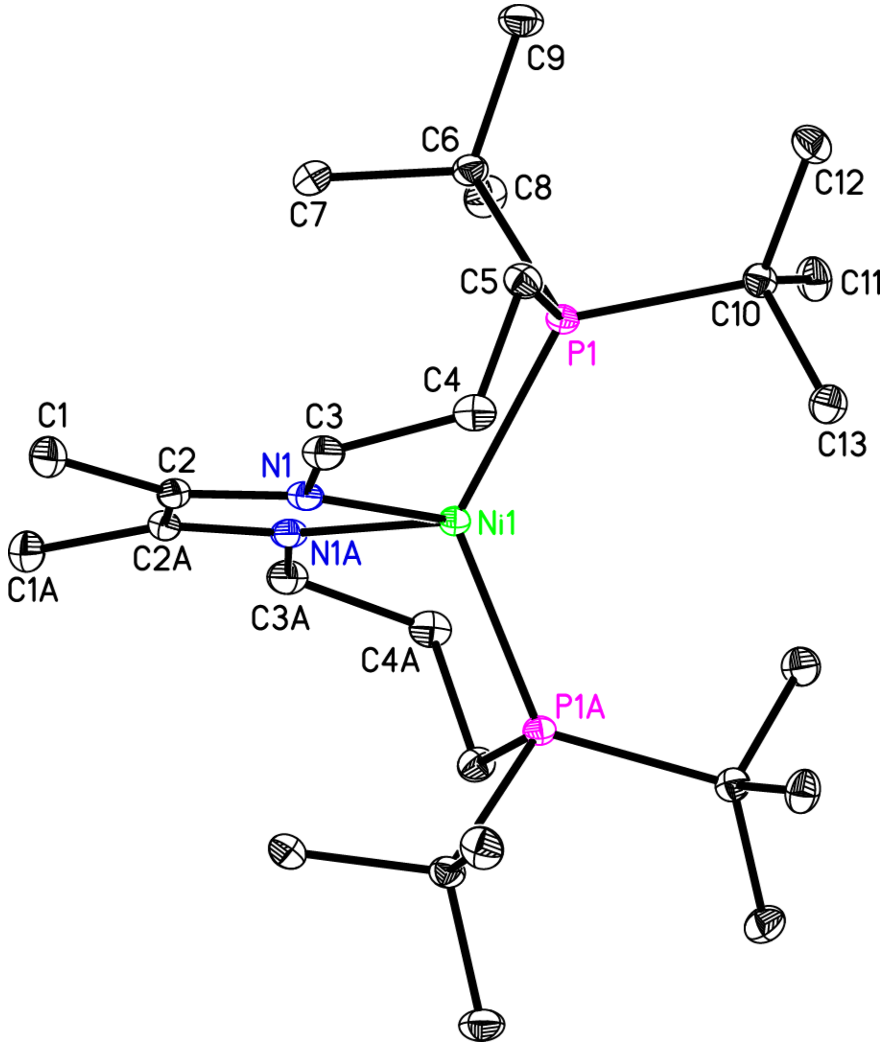

Figure S2. The molecular structure of **(^{tBu2PPr}DI)Ni** (**3**) shown at 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

Table S3. Metrical parameters for **(^{tBu2PPr}DI)Ni** (**3**).

Ni1-N1	1.9582(17)	N1-C2	1.339(3)	C6-C8	1.534(3)
Ni1-N1A	1.9582(17)	N1-C3	1.468(3)	C6-C7	1.534(3)
Ni1-P1A	2.2261(5)	C1-C2	1.509(3)	C10-C11	1.531(3)
Ni1-P1	2.2262(5)	C2-C2A	1.423(4)	C10-C13	1.538(3)
P1-C5	1.868(2)	C3-C4	1.515(3)	C10-C12	1.540(3)
P1-C10	1.908(2)	C4-C5	1.529(3)		
P1-C6	1.910(2)	C6-C9	1.532(3)		

N1-Ni1-N1A	80.53(10)	C6-P1-Ni1	108.40(7)	C9-C6-C7	107.86(17)
N1-Ni1-P1A	123.57(5)	C2-N1-C3	116.97(16)	C8-C6-C7	107.16(17)
N1A-Ni1-P1A	94.34(5)	C2-N1-Ni1	115.16(14)	C9-C6-P1	115.97(14)
N1-Ni1-P1	94.34(5)	C3-N1-Ni1	126.71(13)	C8-C6-P1	108.68(14)
N1A-Ni1-P1	123.57(5)	N1-C2-C2A	114.28(11)	C7-C6-P1	107.75(14)
P1A-Ni1-P1	131.35(3)	N1-C2-C1	122.00(19)	C11-C10-C13	109.44(17)
C5-P1-C10	99.91(9)	C2A-C2-C1	123.71(12)	C11-C10-C12	107.69(17)
C5-P1-C6	103.72(9)	N1-C3-C4	112.28(16)	C13-C10-C12	106.78(16)
C10-P1-C6	107.53(9)	C3-C4-C5	112.66(18)	C11-C10-P1	109.93(14)
C5-P1-Ni1	106.77(7)	C4-C5-P1	112.15(14)	C13-C10-P1	104.94(13)
C10-P1-Ni1	127.84(6)	C9-C6-C8	109.08(18)	C12-C10-P1	117.80(14)

Characterization of Newly Prepared Complexes:

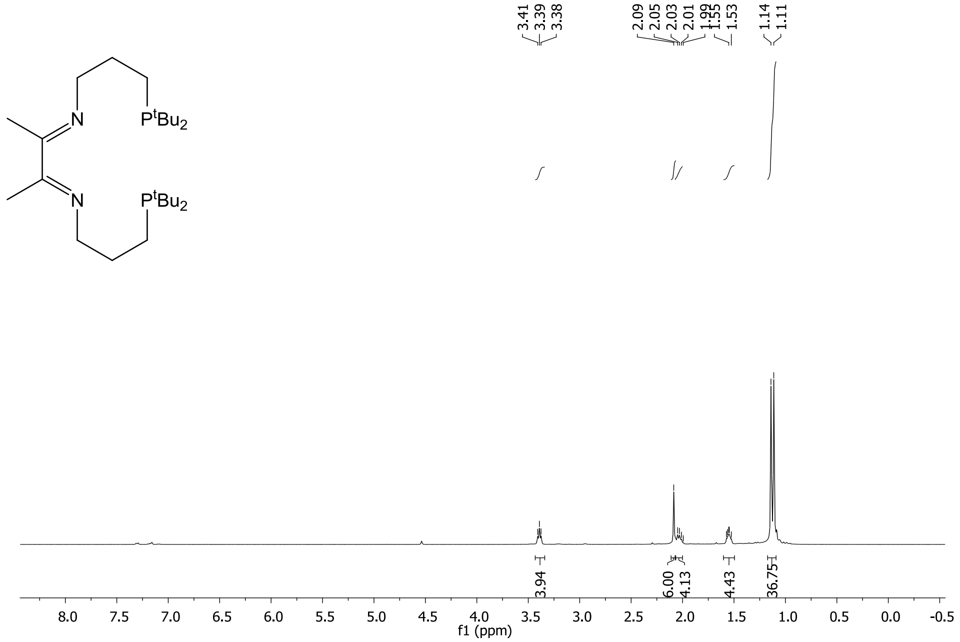

Figure S3. ^{1}H NMR spectrum of $^{\mathbf{tBu2PPr}}$**DI** in benzene-*d*$_6$.

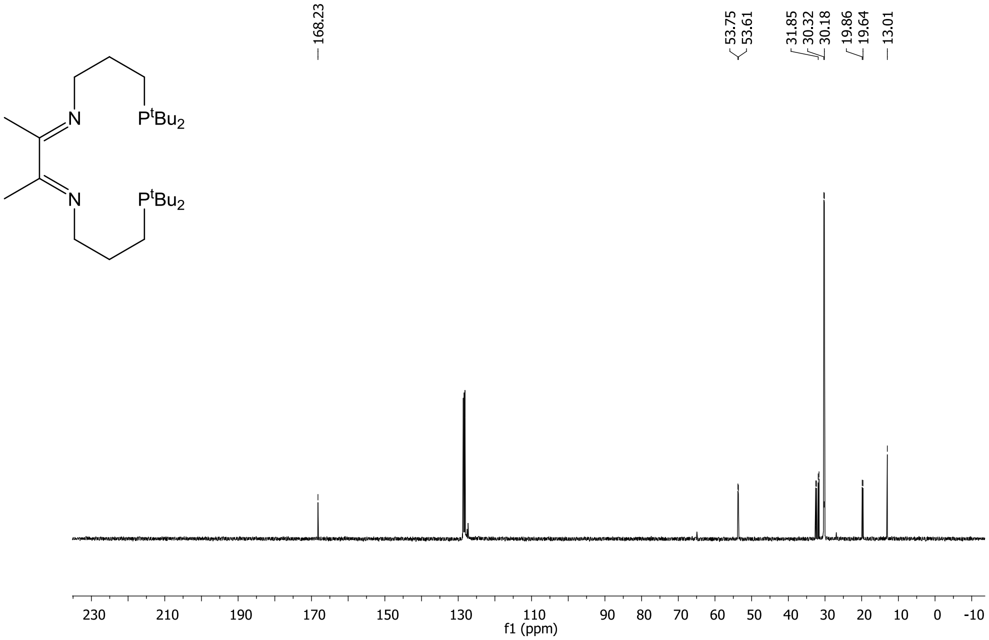

Figure S4. ^{13}C NMR spectrum of $^{\mathbf{tBu2PPr}}$**DI** in benzene-*d*$_6$.

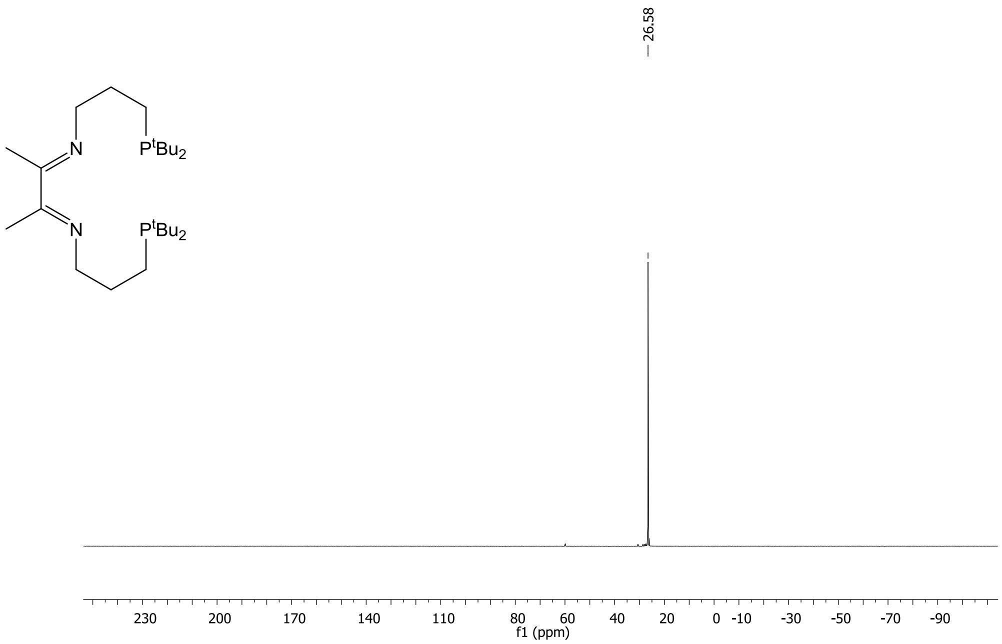

Figure S5. ^{31}P NMR spectrum of **^{tBu2PPr}DI** in benzene-d_6.

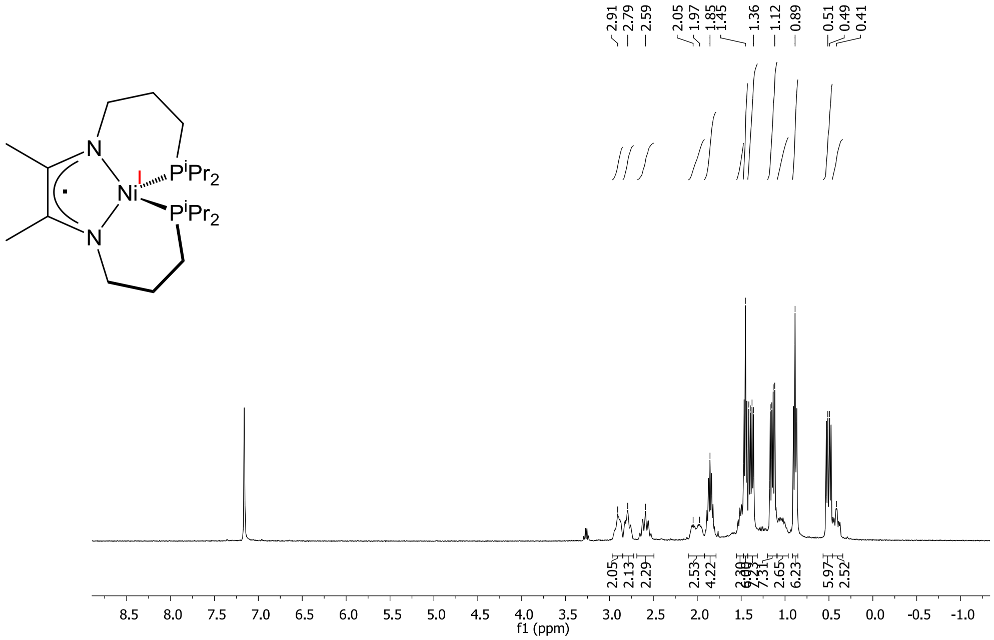

Figure S6. ^{1}H NMR spectrum of **(^{iPr2PPr}DI)Ni** (**2**) in benzene-d_6.

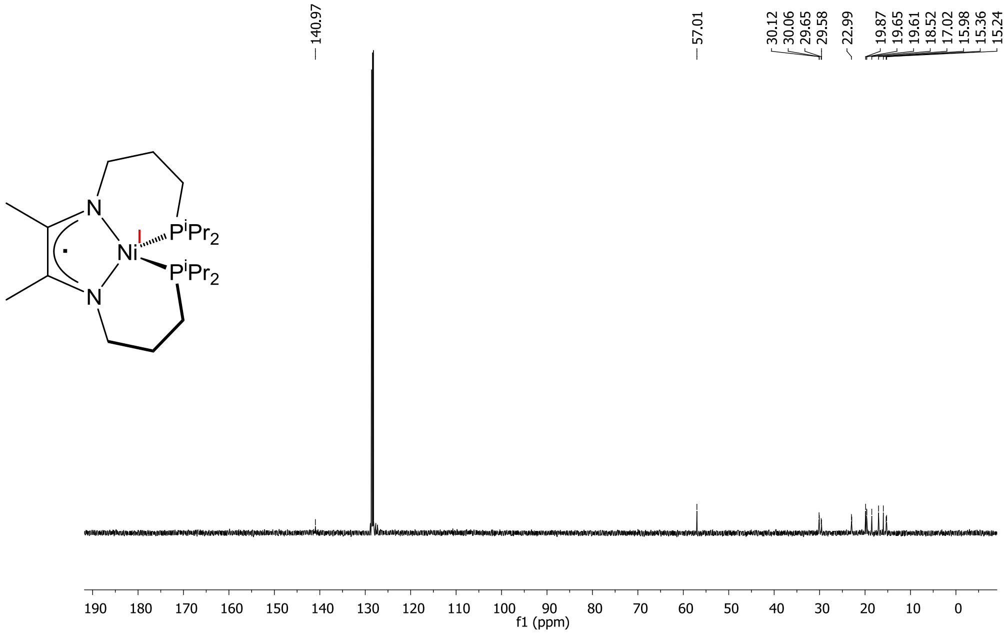

Figure S7. ^{13}C NMR spectrum of **($^{\mathbf{iPr2PPr}}$DI)Ni** (**2**) in benzene-*d*$_6$.

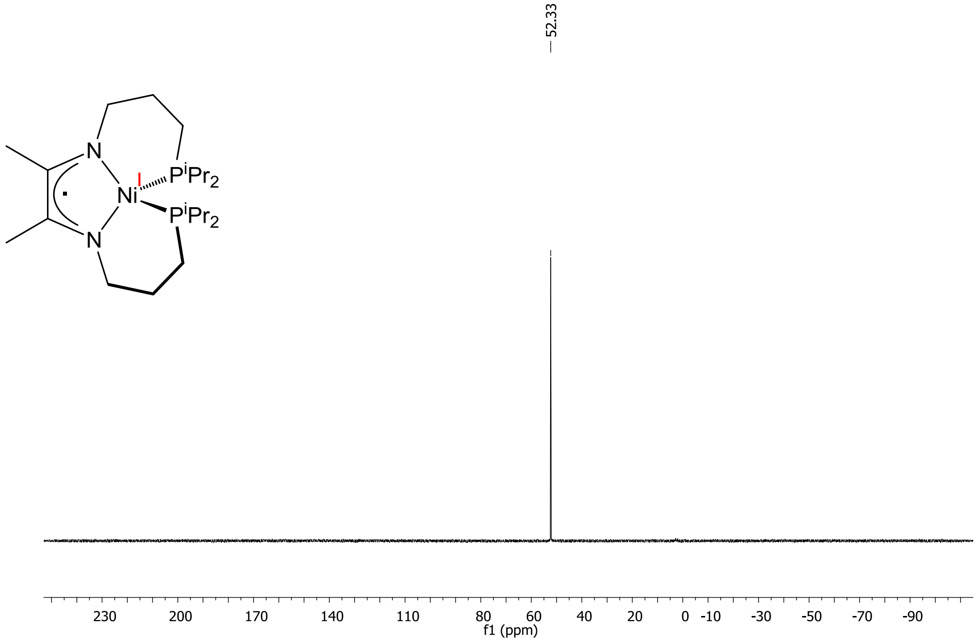

Figure S8. ^{31}P NMR spectrum of **($^{\mathbf{iPr2PPr}}$DI)Ni** (**2**) in benzene-*d*$_6$.

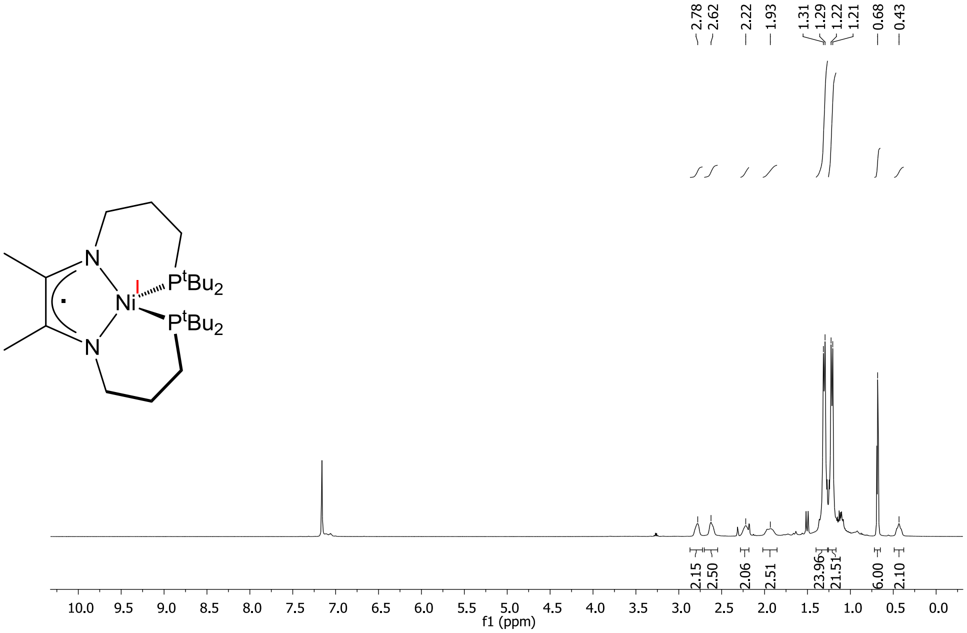

Figure S9. ^{1}H NMR spectrum of **(^{tBu2PPr}DI)Ni** (**3**) in benzene-*d*$_6$.

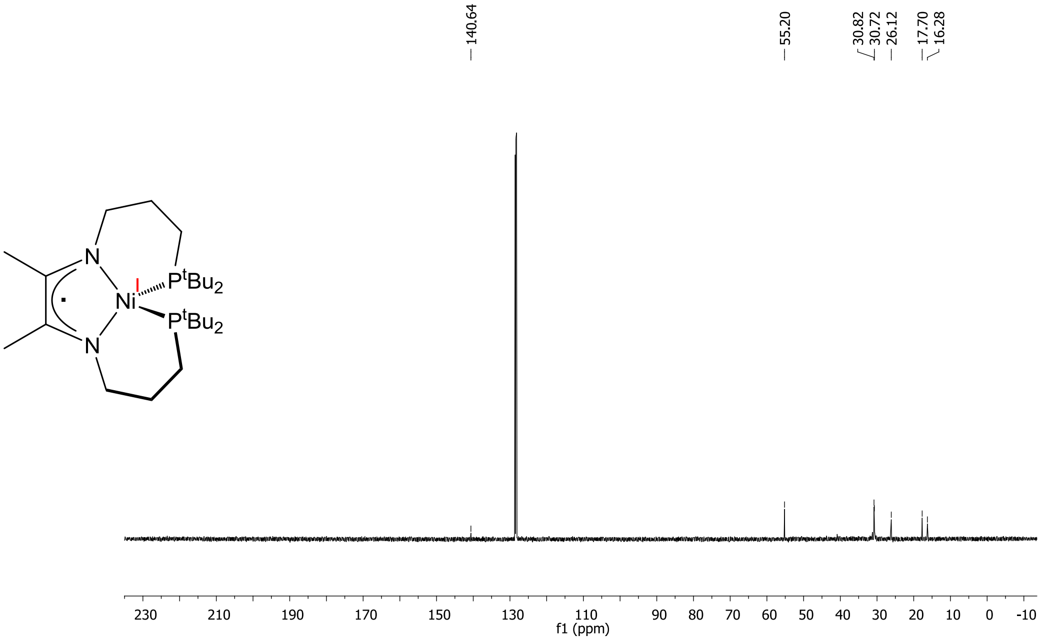

Figure S10. ^{13}C NMR spectrum of **(^{tBu2PPr}DI)Ni** (**3**) in benzene-*d*$_6$.

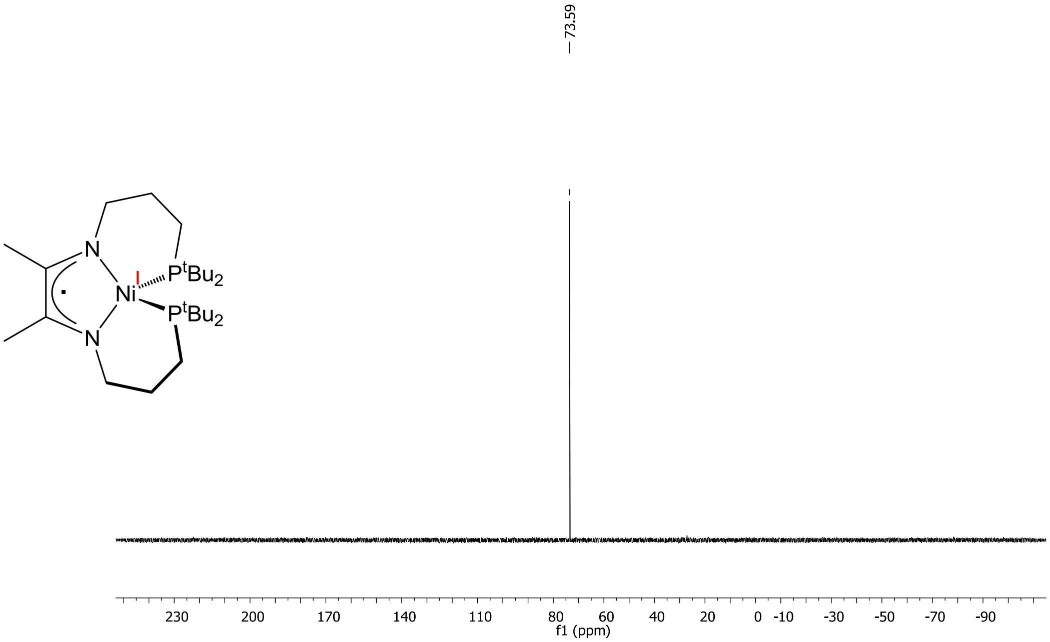

Figure S11. ^{31}P NMR spectrum of **(^{tBu2PPr}DI)Ni** (**3**) in benzene-*d*$_6$**.**

Aldehyde Hydrosilylation:

Hydrosilylation of Benzaldehyde Using 0.1 mol% 1: In a glove box, benzaldehyde (478 μL, 3.88 mmol) and $PhSiH_3$ (395 μL, 3.88 mmol) were added sequentially to a 20 mL scintillation vial containing **1** (2.3 mg, 0.00388 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed *via* ^{1}H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% $NaOH_{(aq)}$ and the organic product was extracted using Et_2O and dried over Na_2SO_4. The solvent was removed *in vacuo* and the product was identified as benzyl alcohol (337.8 mg, 3.12 mmol, 80.5%). ^{1}H NMR (benzene-*d*$_6$): δ 7.10 (m, 2H), 7.06 (m, 2H), 7.03 (m, 1H), 5.12 (s, 1H), 4.34 (s, 2H). ^{13}C NMR (benzene-*d*$_6$): δ 141.83, 128.95, 127.85, 127.81, 64.88.

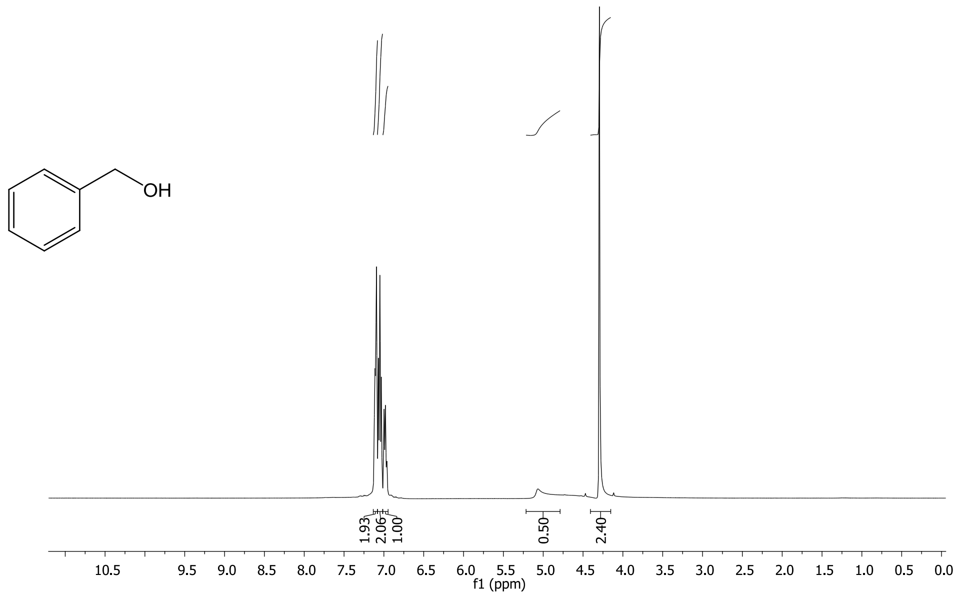

Figure S12. ^{1}H NMR spectrum of benzyl alcohol in benzene-d_6.

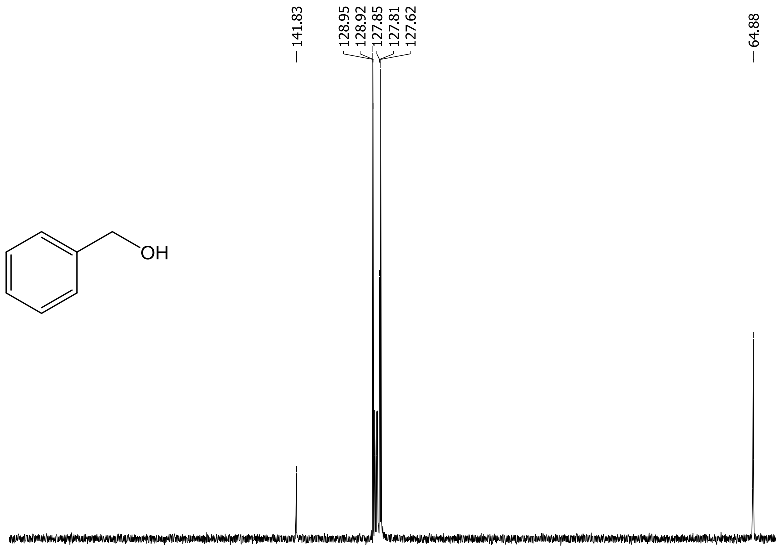

Figure S13. ^{13}C NMR spectrum of benzyl alcohol in benzene-d_6.

Hydrosilylation of 4-Fluorobenzaldehyde Using 0.1 mol% 1: In a glove box, 4-fluorobenzaldehyde (378 μL, 3.53 mmol) and PhSiH$_3$ (435 μL, 3.53 mmol) were added sequentially to a 20 mL scintillation vial containing **1** (2.1 mg, 0.00353 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed *via* ^{1}H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% NaOH$_{(aq)}$ and the organic product was extracted using Et$_2$O (2x3 mL) and dried over Na$_2$SO$_4$. The solvent was removed *in vacuo* and the product was identified as 4-fluorobenzyl alcohol (408.8 mg, 3.24 mmol, 91.9%). ^{1}H NMR (benzene-d_6): δ 6.93 (m, 2H), 6.79 (m, 2H), 4.18 (s, 2H), 2.37 (bs, 1H). ^{13}C NMR (benzene-d_6): δ 162.88 (d, J = 244.7 Hz), 137.47 (d, J = 3.1 Hz), 129.23 (d, J = 8.0 Hz), 115.67 (d, J = 21.3 Hz), 64.24.

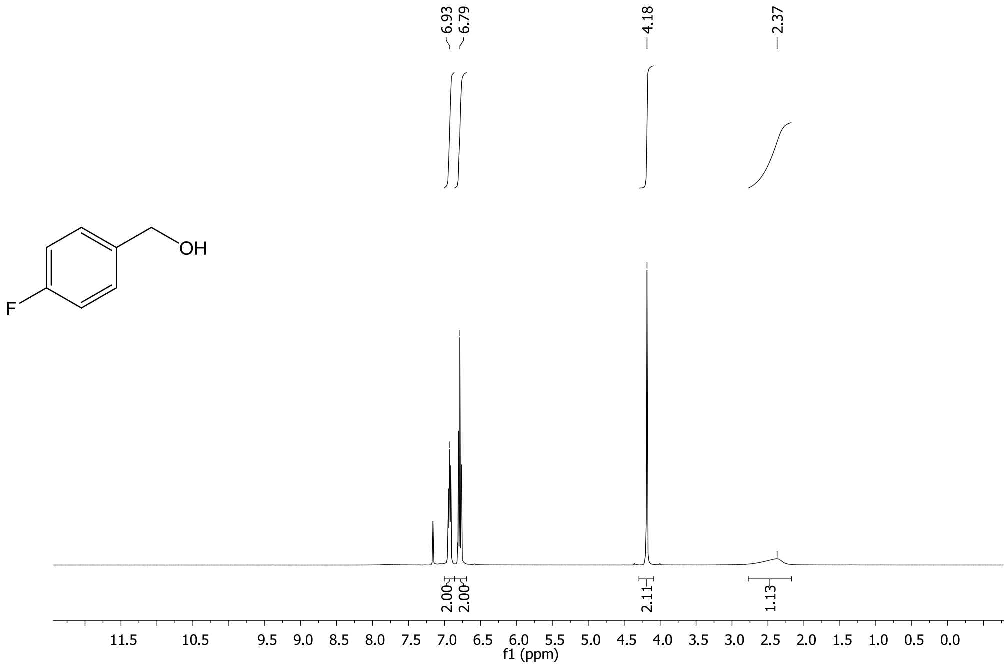

Figure S14. ^{1}H NMR spectrum of 4-fluorobenzyl alcohol in benzene-d_6.

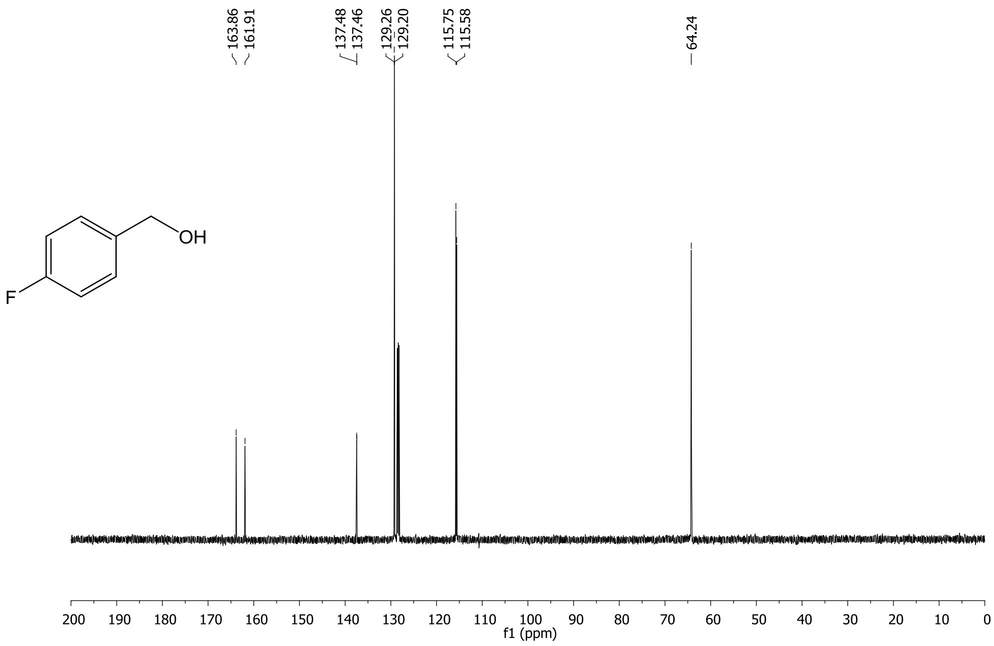

Figure S15. ^{13}C NMR spectrum of 4-fluorobenzyl alcohol in benzene-*d*$_6$.

Hydrosilylation of 4-Chlorobenzaldehyde Using 0.1 mol% 1: In a glove box, 4-chlorobenzaldehyde (371 μL, 2.64 mmol) and $PhSiH_3$ (326 μL, 2.64 mmol) were added sequentially to a 20 mL scintillation vial containing **1** (1.5 mg, 0.00264 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed *via* ^{1}H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% $NaOH_{(aq)}$ and the organic product was extracted using Et_2O and dried over Na_2SO_4. The solvent was removed *in vacuo* and the product was identified as 4-chlorobenzyl alcohol (273.0 mg, 1.91 mmol, 72.5%). ^{1}H NMR (benzene-*d*$_6$): δ 7.09 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 4.11 (s, 2H), 1.83 (s, 1H). ^{13}C NMR (benzene-*d*$_6$): δ 140.41, 133.58, 129.03, 128.62, 64.38.

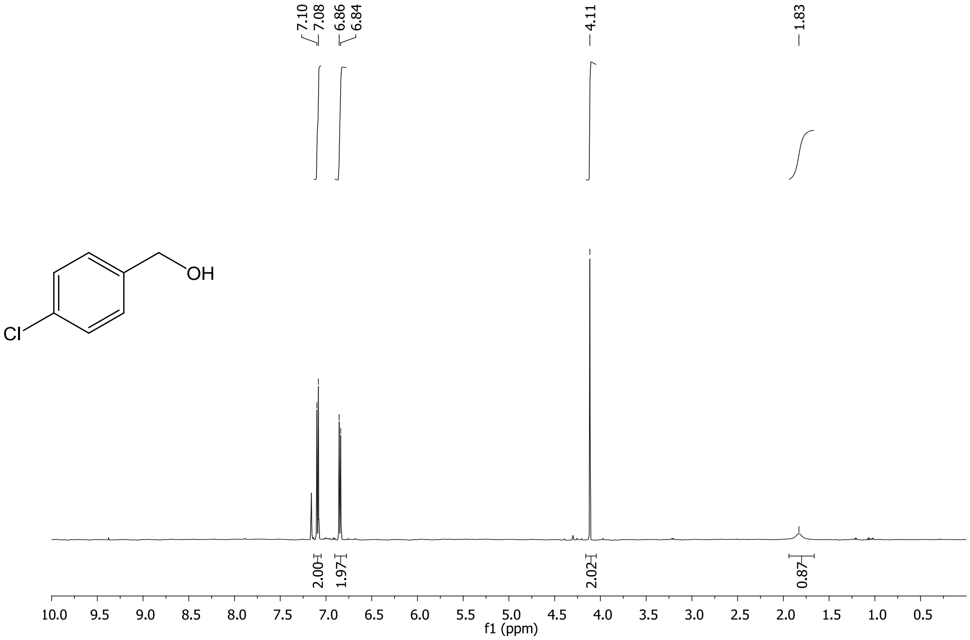

Figure S16. ^{1}H NMR spectrum of 4-chlorobenzyl alcohol in benzene-d_6.

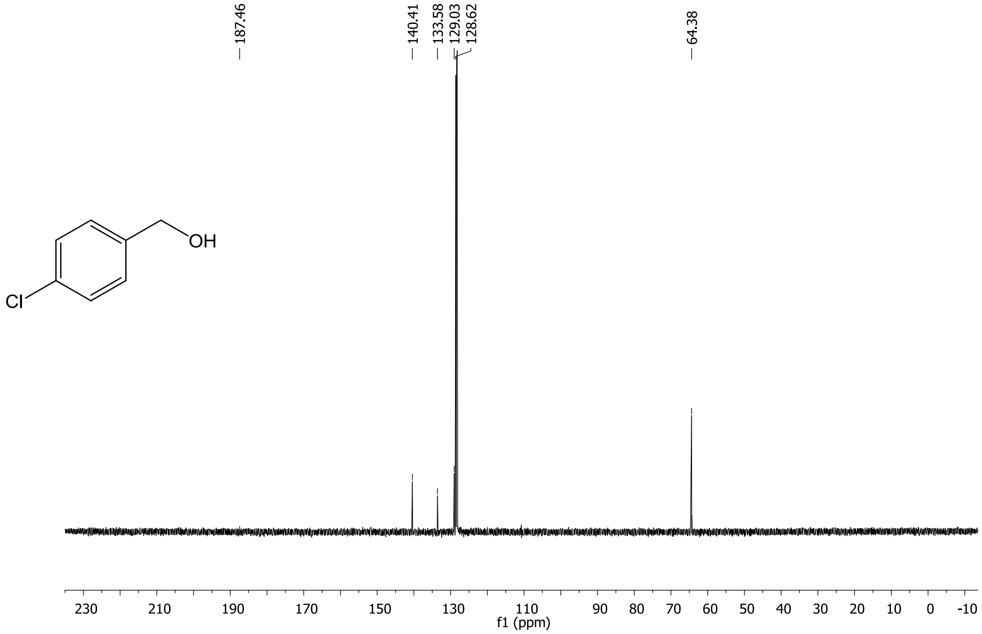

Figure S17. ^{13}C NMR spectrum of 4-chlorobenzyl alcohol in benzene-d_6.

Hydrosilylation of 4-Methylbenzaldehyde Using 0.1 mol% 1: In a glove box, 4-methylbenzaldehyde (911 µL, 7.73 mmol) and $PhSiH_3$ (952 µL, 7.73 mmol) were added sequentially to a 20 mL scintillation vial containing **1** (4.6 mg, 0.00773 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed *via* ^1H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% $NaOH_{(aq)}$ and the organic product was extracted using Et_2O and dried over Na_2SO_4. The solvent was removed *in vacuo* and the product was identified as 4-methylbenzyl alcohol (762.5 mg, 6.24 mmol, 85.3%). ^1H NMR (benzene-d_6): δ 7.14 (d, *J* = 7.8 Hz, 2H), 6.98 (d, *J* = 7.8 Hz, 2H), 4.38 (s, 2H), 2.58 (bs, 1H), 2.09 (s, 3H). ^{13}C NMR (benzene-d_6): δ 139.29, 137.17, 129.62, 127.61, 65.17, 21.45.

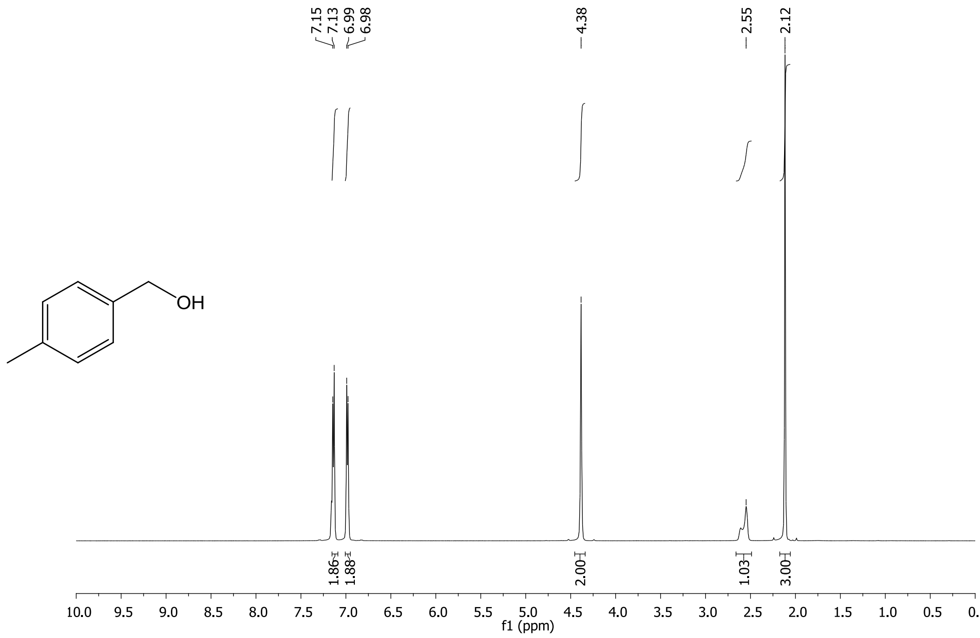

Figure S18. ^1H NMR spectrum of 4-methylbenzyl alcohol in benzene-d_6.

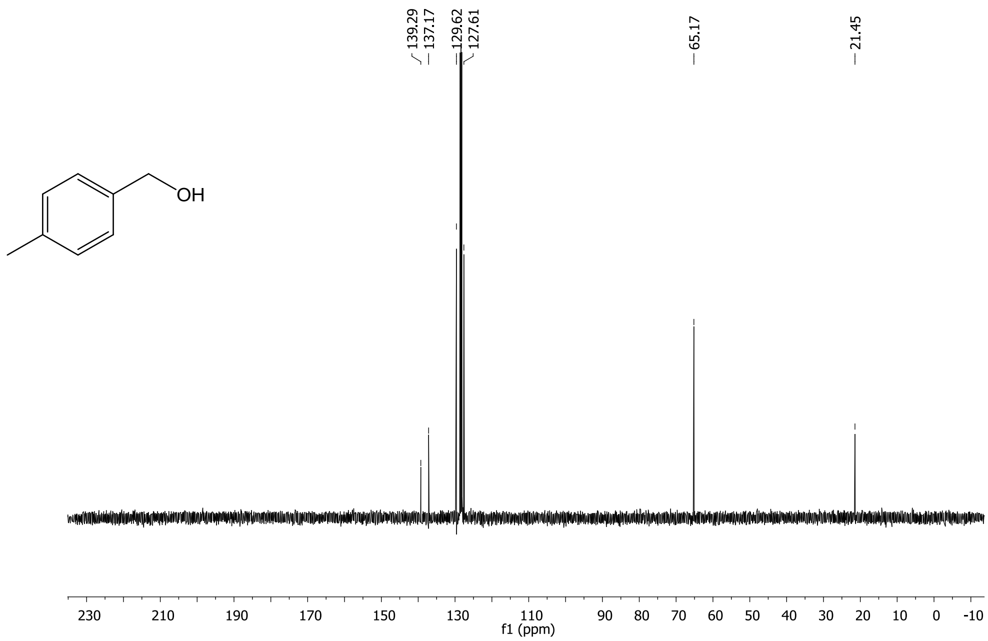

Figure S19. ^{13}C NMR spectrum of 4-methylbenzyl alcohol in benzene-*d_6*.

Hydrosilylation of 4-Methoxybenzaldehyde Using 0.1 mol% 1: In a glove box, 4-methoxybenzaldehyde (515 µL, 4.23 mmol) and $PhSiH_3$ (521 µL, 4.23 mmol) were added sequentially to a 20 mL scintillation vial containing **1** (2.4 mg, 0.00423 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed *via* ^{1}H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% $NaOH_{(aq)}$ and the organic product was extracted using Et_2O and dried over Na_2SO_4. The solvent was removed *in vacuo* and the product was identified as 4-methoxybenzyl alcohol (437.5 mg, 3.17 mmol, 74.9%). ^{1}H NMR (benzene-*d_6*): δ 7.17 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 4.44 (s, 2H), 4.39 (s, 1H), 3.35 (s, 3H). ^{13}C NMR (benzene-*d_6*): δ 159.71, 134.23, 129.18, 114.41, 64.74, 55.21.

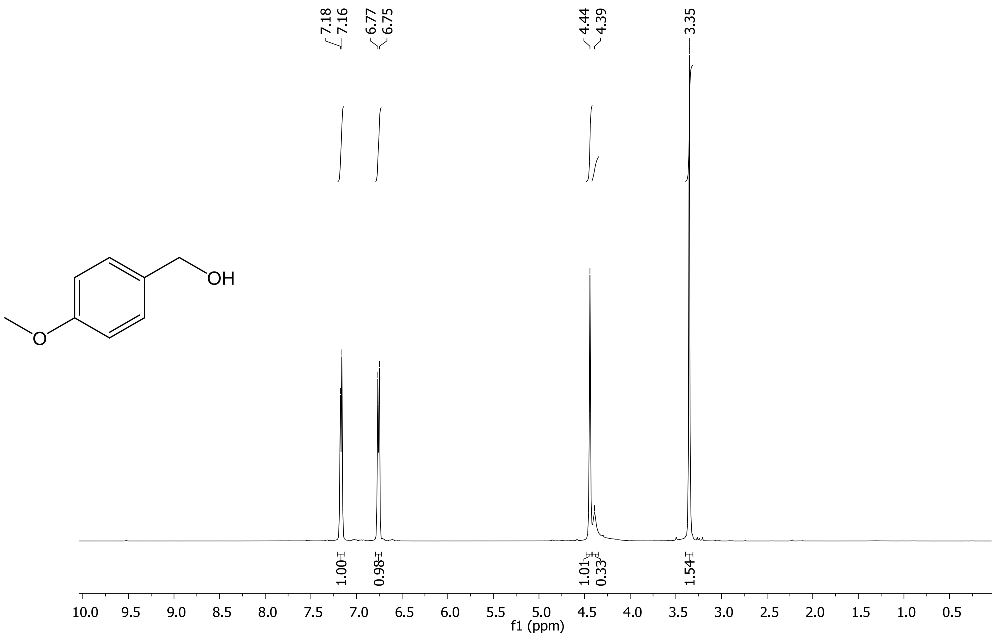

Figure S20. ^{1}H NMR spectrum of 4-methoxybenzyl alcohol in benzene-d_6.

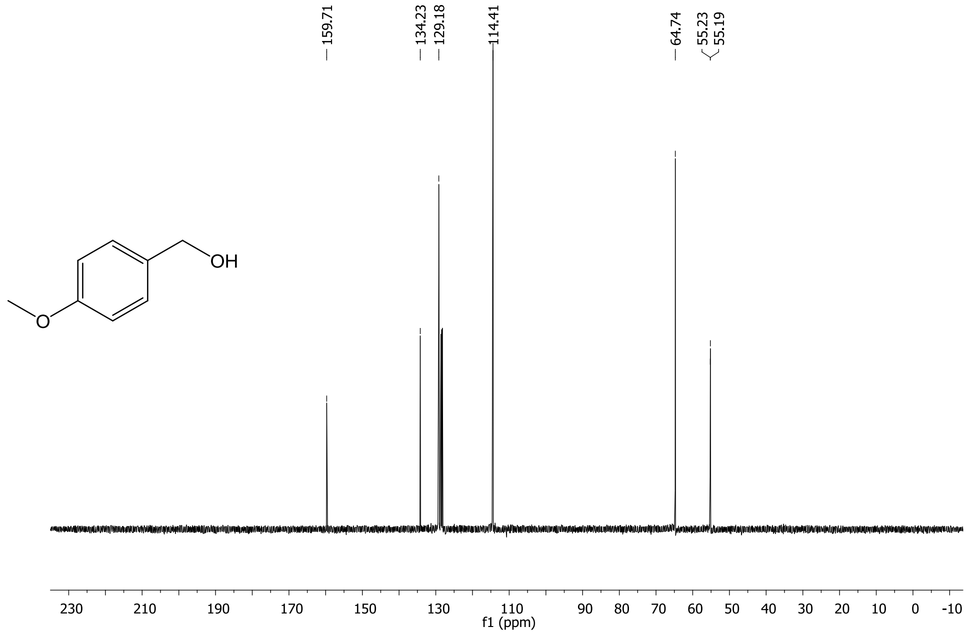

Figure S21. ^{13}C NMR spectrum of 4-methoxybenzyl alcohol in benzene-d_6.

Hydrosilylation of 4-Cyanobenzaldehyde Using 0.1 mol% 1: In a glove box, 4-cyanobenzaldehyde (859 mg, 6.55 mmol) and $PhSiH_3$ (807 µL, 6.55 mmol) were added sequentially to a 20 mL scintillation vial containing **1** (3.9 mg, 0.00655 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed *via* ^1H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% $NaOH_{(aq)}$ and the organic product was extracted using Et_2O and dried over Na_2SO_4. The solvent was removed *in vacuo* and the product was identified as 4-cyanobenzyl alcohol (413.4 mg, 3.10 mmol, 47.4%). ^1H NMR (benzene-d_6): δ 7.12 (d, J = 8.2 Hz, 2H), 7.03 (d, J = 8.2 Hz, 2H), 4.38 (s, 2H), 4.20 (s, 1H). ^{13}C NMR (benzene-d_6): δ 147.62, 132.57, 127.40, 119.63, 110.80, 63.91.

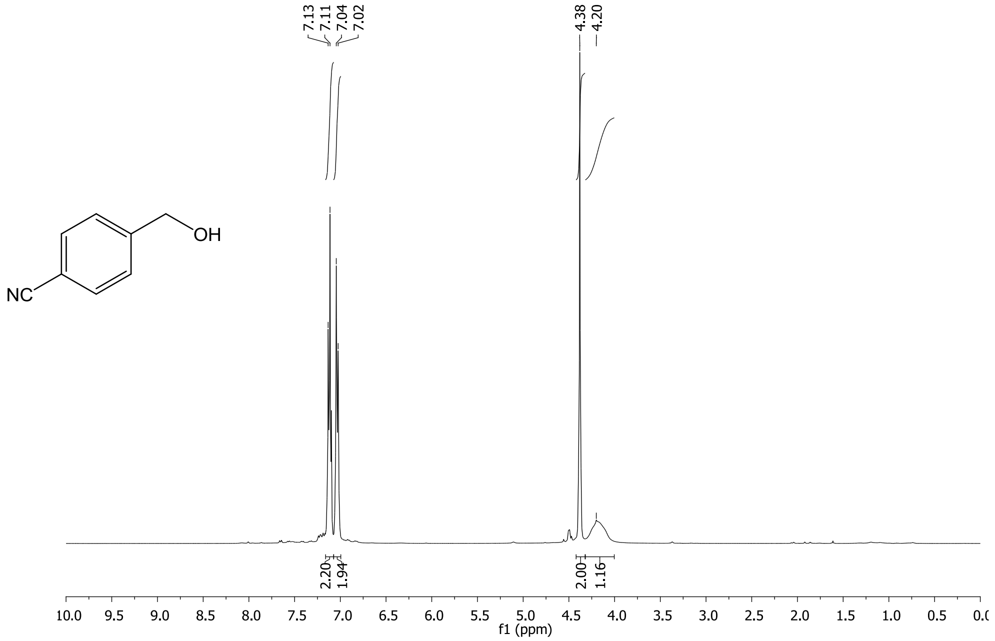

Figure S22. ^1H NMR spectrum of 4-cyanobenzyl alcohol in benzene-d_6.

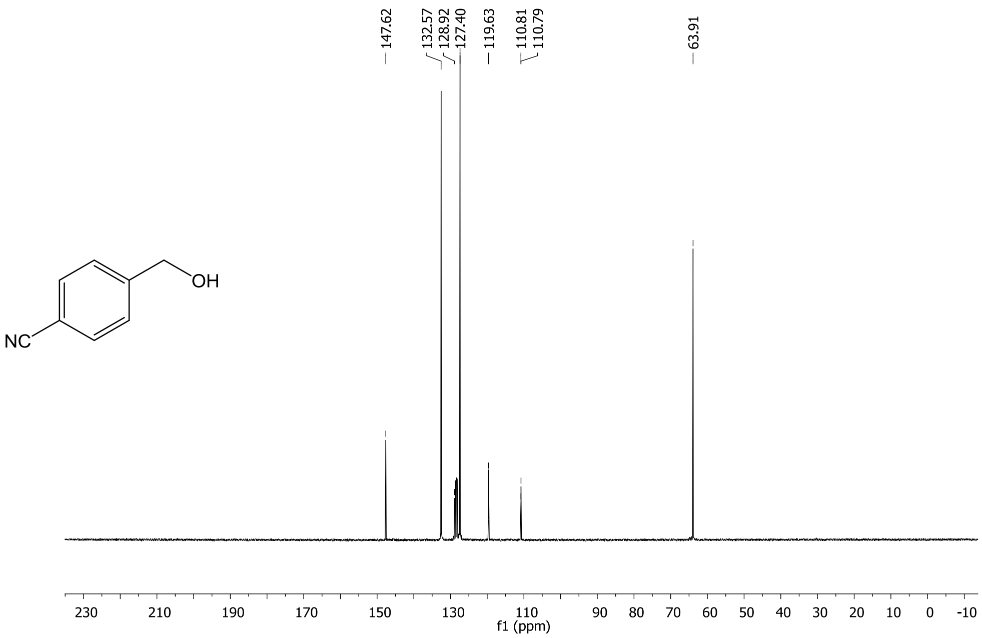

Figure S23. ^{13}C NMR spectrum of 4-cyanobenzyl alcohol in benzene-d_6.

Hydrosilylation of Furfural Using 0.1 mol% 1: In a glove box, furfural (292 µL, 3.52 mmol) and $PhSiH_3$ (435 µL, 3.52 mmol) were added sequentially to a 20 mL scintillation vial containing **1** (2.1 mg, 0.00352 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed *via* ^{1}H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% $NaOH_{(aq)}$ and the organic product was extracted using Et_2O and dried over Na_2SO_4. The solvent was removed *in vacuo* and the product was identified as furfuryl alcohol (178.2 mg, 1.81 mmol, 51.6%). ^{1}H NMR (benzene-d_6): δ 7.10 (m, 1H), 6.06 (m, 2H), 4.36 (s, 2H), 3.92 (s, 1H). ^{13}C NMR (benzene-d_6): δ 155.35, 142.72, 110.89, 108.02, 57.38.

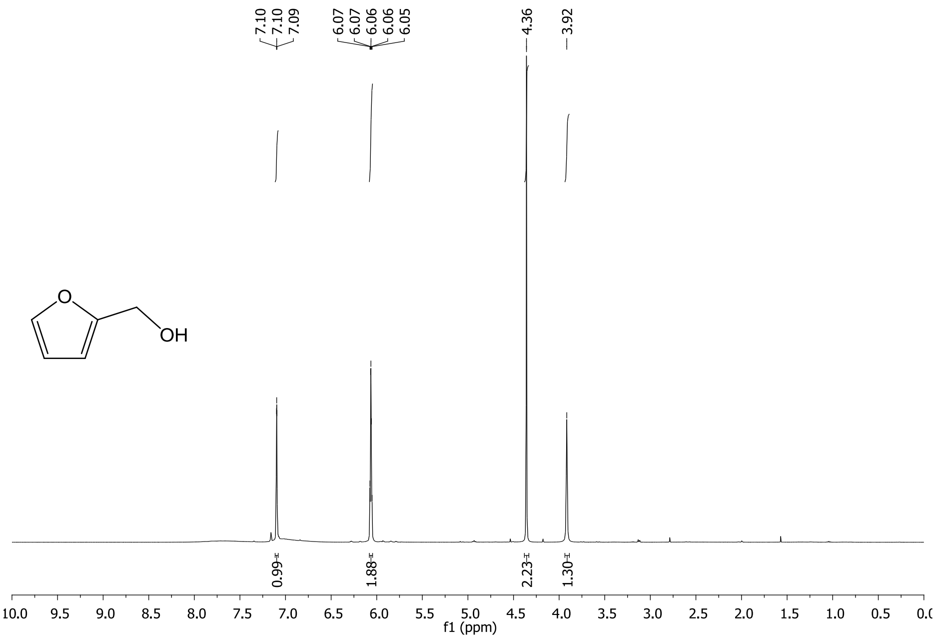

Figure S24. ^{1}H NMR spectrum of furfuryl alcohol in benzene-d_6.

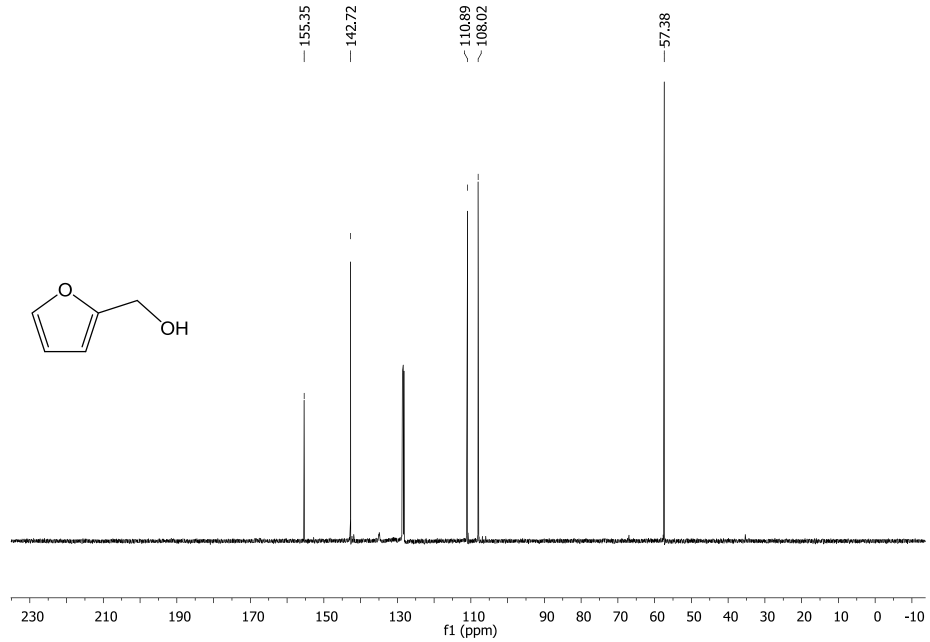

Figure S25. ^{13}C NMR spectrum of furfuryl alcohol in benzene-d_6.

Hydrosilylation of Cyclohexanecarboxaldehyde Using 0.1 mol% 1: In a glove box, cyclohexanecarboxaldehyde (726 μL, 5.99 mmol) and $PhSiH_3$ (739 μL, 5.99 mmol) were added sequentially to a 20 mL scintillation vial containing **1** (3.6 mg, 0.00599 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed *via* ^1H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% $NaOH_{(aq)}$ and the organic product was extracted using Et_2O and dried over Na_2SO_4. The solvent was removed *in vacuo* and the product was identified as cyclohexanemethanol (499.3 mg, 4.37 mmol, 73.0%). ^1H NMR (benzene-d_6): δ 3.18 (s, 2H), 1.64 (s, 5H), 1.25 (m, 1H), 1.11 (m, 3H), 0.80 (s, 2H), 0.69 (m, 1H). ^{13}C NMR (benzene-d_6): δ 68.70, 41.26, 30.54, 27.50, 26.77.

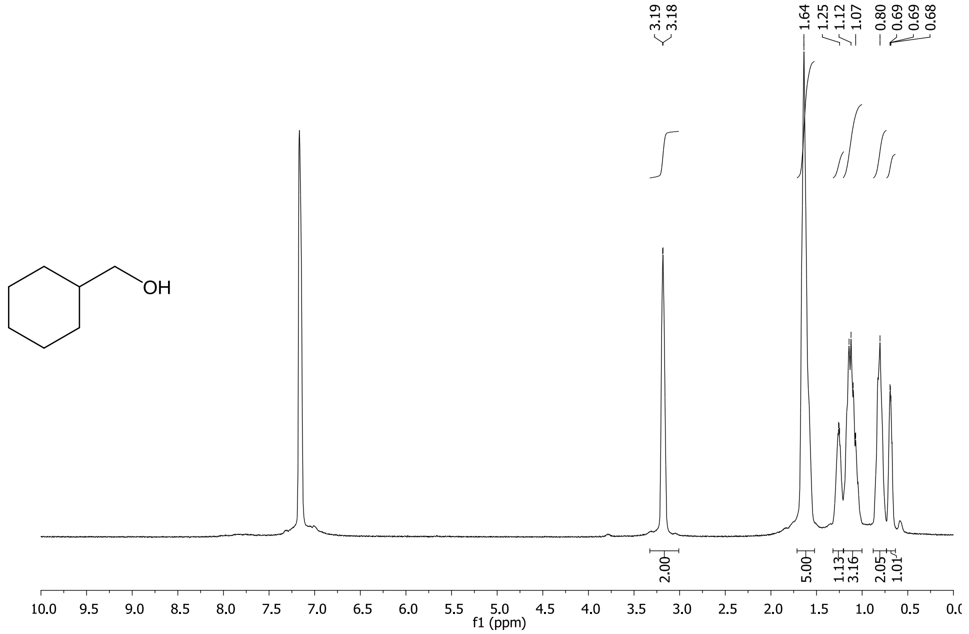

Figure S26. ^1H NMR spectrum of cyclohexanemethanol in benzene-d_6.

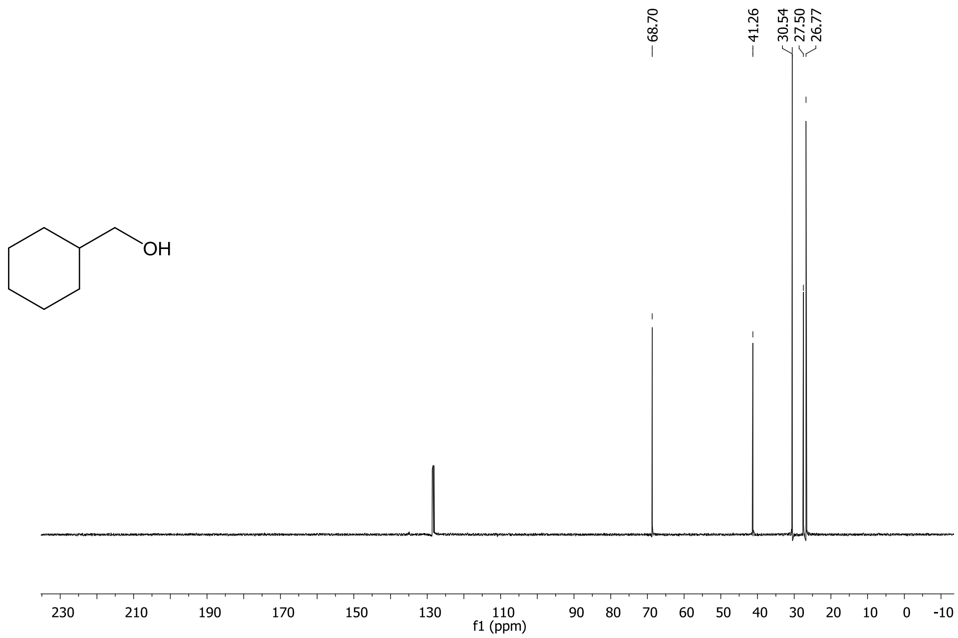

Figure S27. ^{13}C NMR spectrum of cyclohexanemethanol in benzene-d_6.

Hydrosilylation of 3-Cyclohexenecarboxaldehyde Using 0.1 mol% 1: In a glove box, 3-cyclohexenecarboxaldehyde (541 μL, 4.76 mmol) and $PhSiH_3$ (586 μL, 4.76 mmol) were added sequentially to a 20 mL scintillation vial containing **1** (2.8 mg, 0.00476 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed *via* ^{1}H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% $NaOH_{(aq)}$ and the organic product was extracted using Et_2O and dried over Na_2SO_4. The solvent was removed *in vacuo* and the product was identified as 3-cyclohexene-1-methanol (431.4 mg, 3.84 mmol, 80.1%). ^{1}H NMR (benzene-d_6): δ 5.65 (s, 2H), 3.21 (s, 2H), 1.94 (m, 3H), 1.62 (m, 3H), 1.14 (m, 1H), 0.75 (s, 1H). ^{13}C NMR (benzene-d_6): δ 127.64, 126.76, 67.84, 37.05, 28.98, 26.07, 25.44.

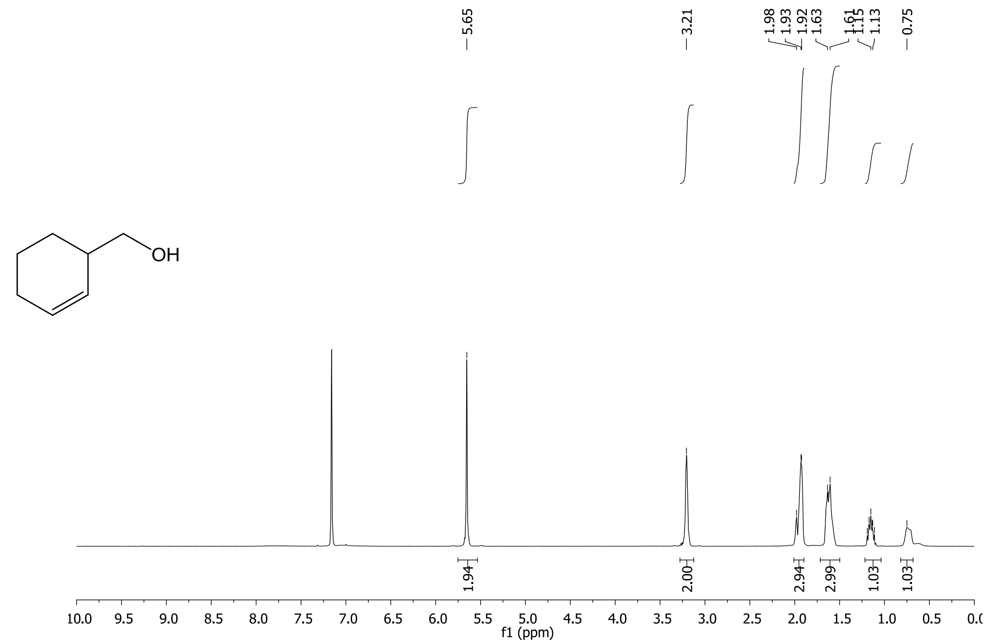

Figure S28. ^{1}H NMR spectrum of 3-cyclohexene-1-methanol in benzene-d_6.

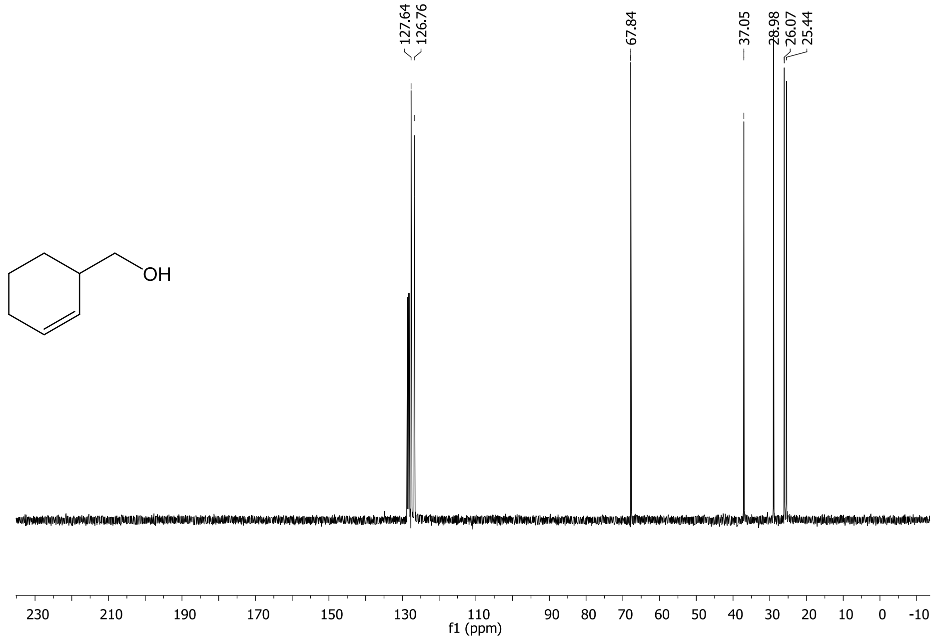

Figure S29. ^{13}C NMR spectrum of 3-cyclohexene-1-methanol in benzene-d_6.

Hydrosilylation of Hexanal Using 0.1 mol% 1: In a glove box, hexanal (682 μL, 5.54 mmol) and PhSiH$_3$ (683 μL, 5.54 mmol) were added sequentially to a 20 mL scintillation vial containing **1** (3.3 mg, 0.00554 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed *via* ^{1}H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% NaOH$_{(aq)}$ and the organic product was extracted using Et$_2$O and dried over Na$_2$SO$_4$. The solvent was removed *in vacuo* and the product was identified as hexanol (459.6 mg, 4.50 mmol, 81.2%). ^{1}H NMR (benzene-d_6): δ 4.04 (s, 1H), 3.55 (t, J = 6.7 Hz, 2H), 1.52 (pseudo p, J = 7.0 Hz, 2H), 1.25 (m, 6H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C NMR (benzene-d_6): δ 63.04, 33.49, 32.43, 26.26, 23.41, 14.64.

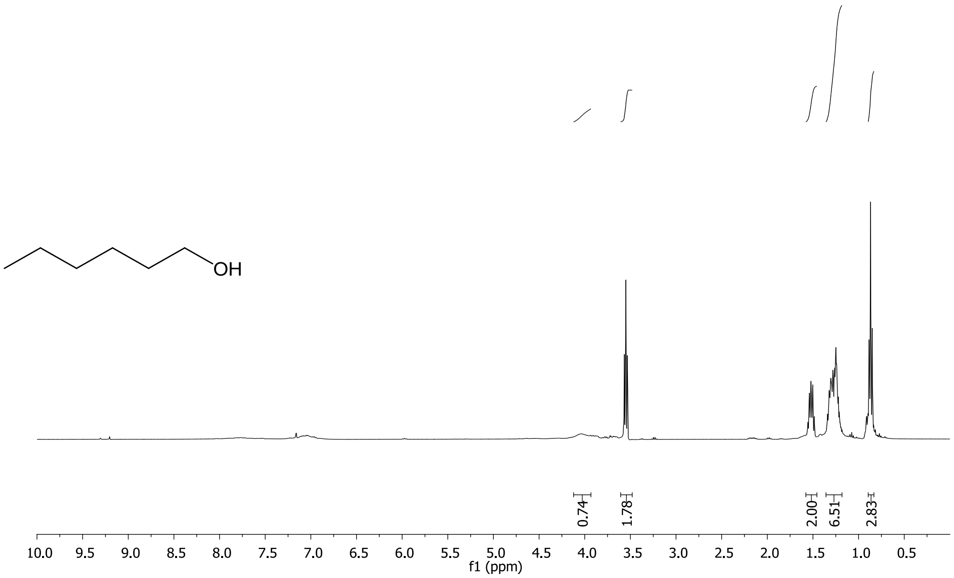

Figure S30. ^{1}H NMR spectrum of hexanol in benzene-d_6.

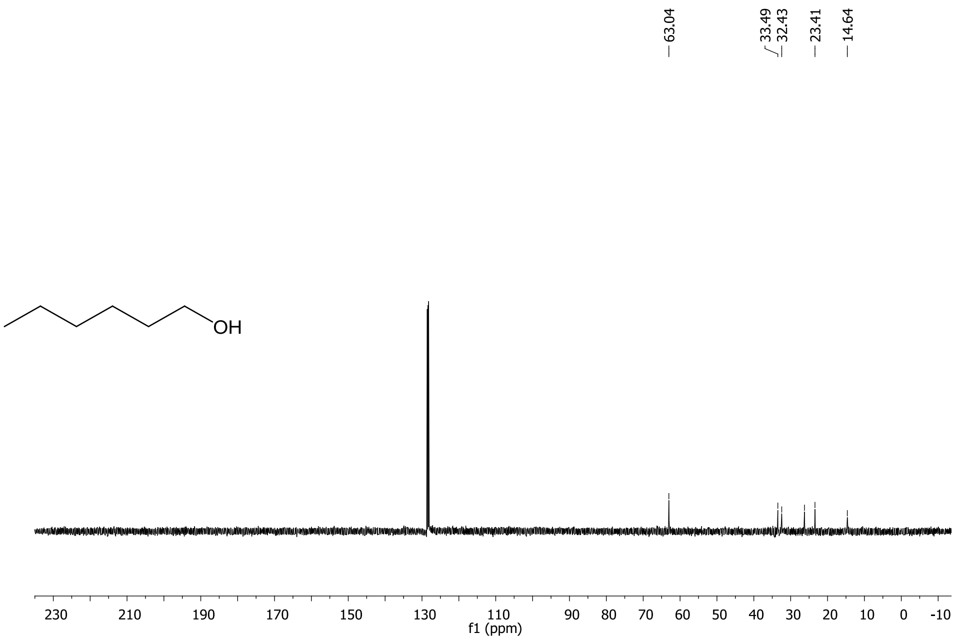

Figure S31. ^{13}C NMR spectrum of hexanol in benzene-d_6.

Hydrosilylation of Decanal Using 0.1 mol% 1: In a glove box, decanal (948 μL, 5.04 mmol) and $PhSiH_3$ (621 μL, 5.04 mmol) were added sequentially to a 20 mL scintillation vial containing **1** (3.0 mg, 0.00504 mmol). The resulting red solution was stirred at room temperature for 24 h. Greater than 99% conversion was observed *via* ^{1}H NMR spectroscopy. The solution was hydrolyzed with 2 mL of 10% $NaOH_{(aq)}$ and the organic product was extracted using Et_2O and dried over Na_2SO_4. The solvent was removed *in vacuo* and the product was identified as decanol (716 mg, 4.52 mmol, 89.8%). ^{1}H NMR (benzene-d_6): δ 4.29 (s, 1H), 3.46 (s, 2H), 1.49 (d, 2H), 1.24 (s, 16H), 0.87 (s, 3H). ^{13}C NMR (benzene-d_6): δ 62.93, 33.66, 32.86, 30.70, 30.65, 30.54, 30.34, 26.86, 23.58, 14.80.

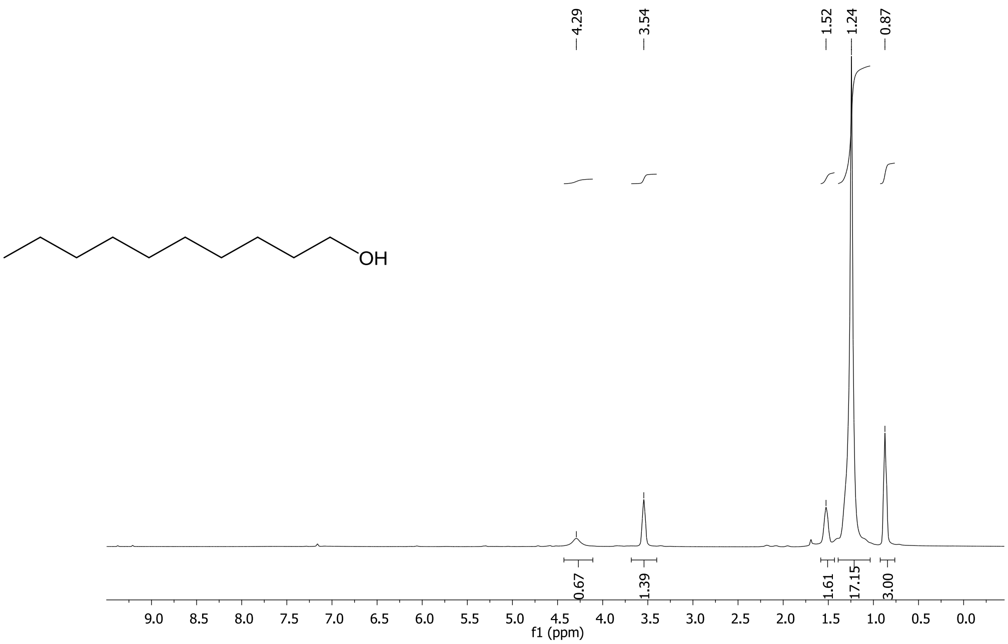

Figure S32. ^{1}H NMR spectrum of decanol in benzene-d_6.

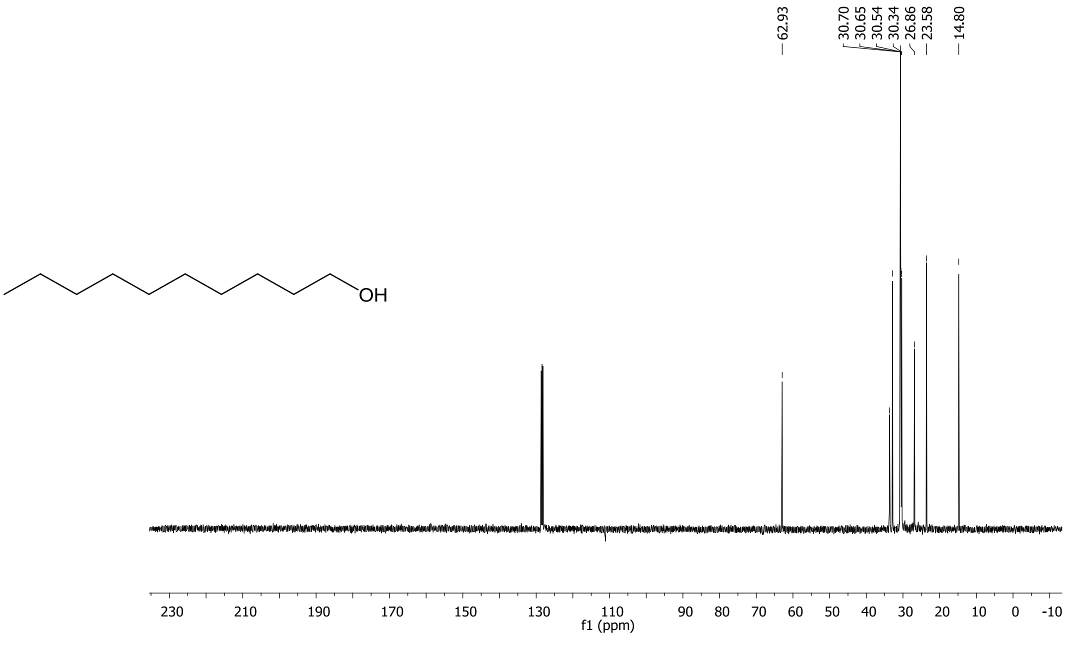

Figure S33. ^{13}C NMR spectrum of decanol in benzene-d_6.

Ketone Hydrosilylation:

Hydrosilylation of Acetophenone with 1.0 mol% 1: In a glove box, acetophenone (80.3 µL, 0.689 mmol) and $PhSiH_3$ (84.8 µL, 0.689 mmol) were added sequentially to a 20 mL scintillation vial containing **1** (4.1 mg, 0.00689 mmol). The resulting red solution was dissolved in benzene-d_6 and transferred into a J. Young NMR tube and heated at 60 °C for 24 h. Greater than 99% conversion was observed *via* ^{1}H NMR spectroscopy. The solution was hydrolyzed with 1 mL of 10% $NaOH_{(aq)}$ and the organic product was extracted using Et_2O and dried over Na_2SO_4. The solvent was removed *in vacuo* and the product was identified as 1-phenylethanol (56.8 mg, 0.465 mmol, 67.5%). ^{1}H NMR (benzene-d_6): δ 7.23 (d, *J* = 7.5 Hz, 2H), 7.14 (t, *J* = 7.5 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 4.57 (q, *J* = 6.5 Hz, 1H), 2.52 (s, 1H), 1.29 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (benzene-d_6): δ 147.17, 128.88, 127.66, 126.08, 70.50, 25.97.

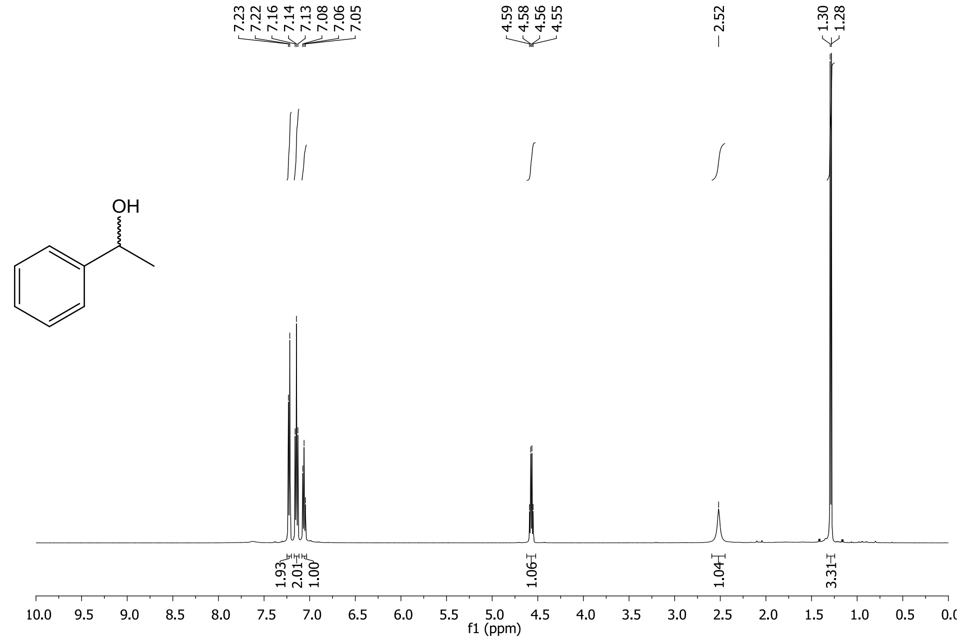

Figure S34. ^{1}H NMR spectrum of 1-phenylethanol in benzene-d_6.

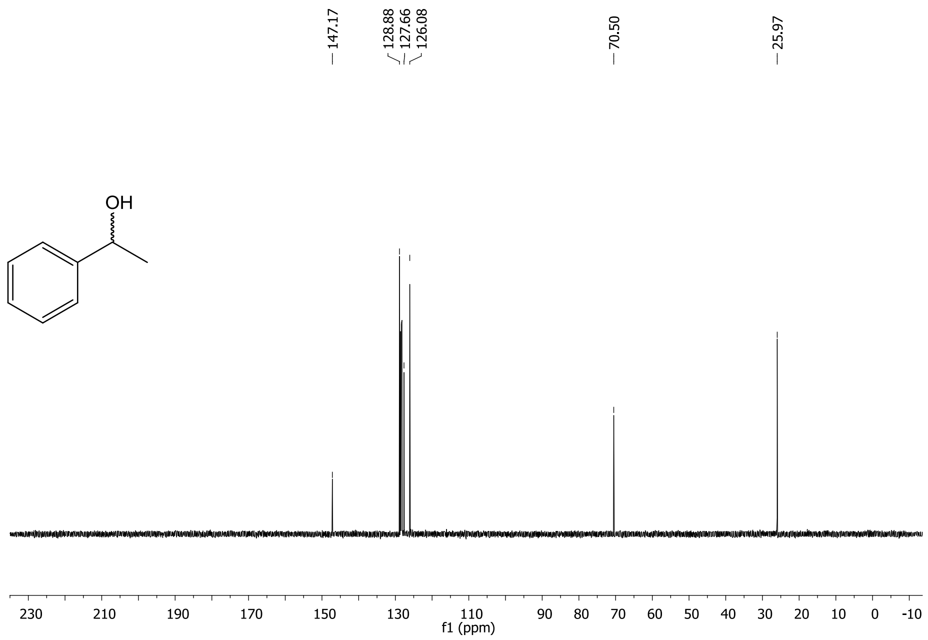

Figure S35. ^{13}C NMR spectrum of 1-phenylethanol in benzene-d_6.

Hydrosilylation of 4-Fluoroacetophenone with 1.0 mol% 1: In a glove box, 4-fluoroacetophenone (116 µL, 0.957 mmol) and $PhSiH_3$ (117 µL, 0.957 mmol) were added sequentially to a 20 mL scintillation vial containing **1** (5.7 mg, 0.00957 mmol). The resulting red solution was dissolved in benzene-d_6 and transferred into a J. Young NMR tube and heated at 60 °C for 24 h. Greater than 99% conversion was observed *via* ^{1}H NMR spectroscopy. The solution was hydrolyzed with 1 mL of 10% $NaOH_{(aq)}$ and the organic product was extracted using Et_2O and dried over Na_2SO_4. The solvent was removed *in vacuo* and the product was identified as 1-(4-fluorophenyl)ethanol (120.9 mg, 0.863 mmol, 90.1%). ^{1}H NMR (benzene-d_6): δ 7.00 (m, 2H), 6.81 (m, 2H), 4.44 (q, *J* = 6.5 Hz, 1H), 2.15 (s, 1H), 1.20 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (benzene-d_6): δ 162.02 (d, *J* = 244.2 Hz), 142.02 (d, *J* = 3.3 Hz), 126.92 (d, *J* = 7.9 Hz), 114.83 (d, *J* = 21.4 Hz), 69.06, 25.15.

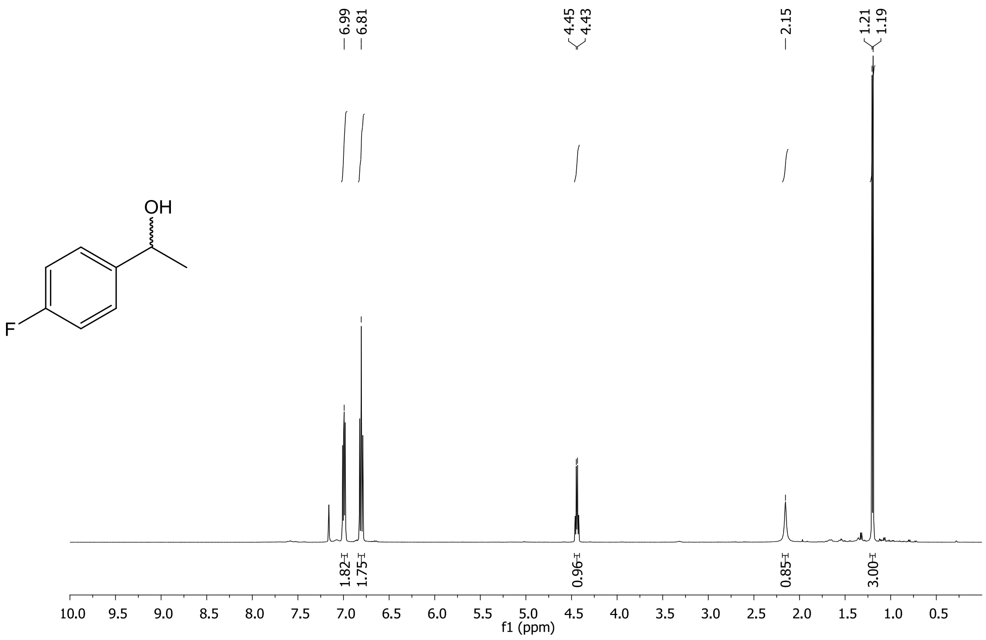

Figure S36. ^{1}H NMR spectrum of 1-(4-fluorophenyl)ethanol in benzene-d_6.

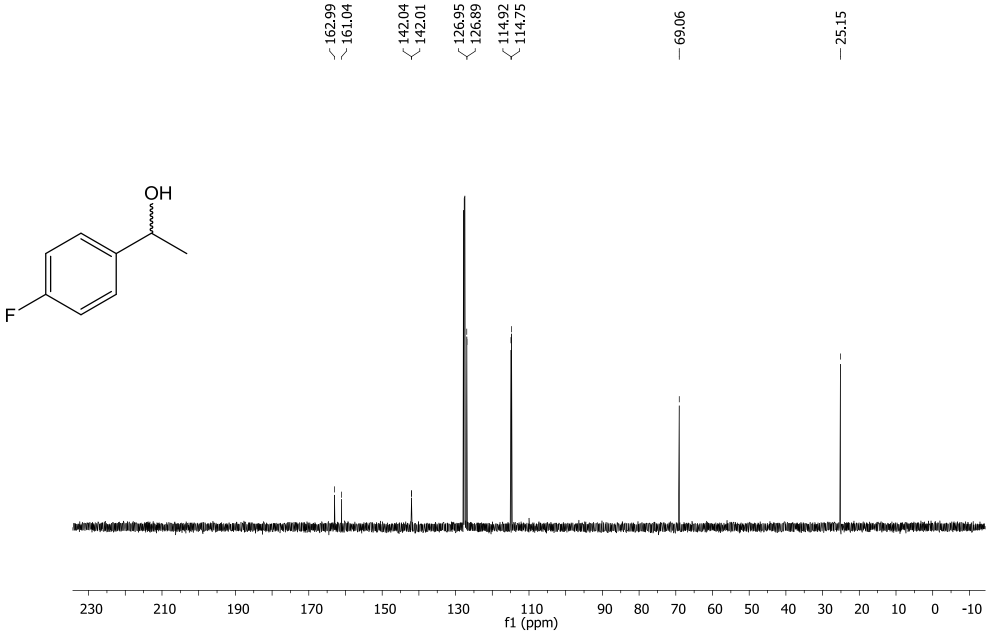

Figure S37. ^{13}C NMR spectrum of 1-(4-fluorophenyl)ethanol in benzene-d_6.

Hydrosilylation of 4-Chloroacetophenone with 1.0 mol% 1: In a glove box, 4-chloroacetophenone (94.0 µL, 0.723 mmol) and $PhSiH_3$ (89.0 µL, 0.723 mmol) were added sequentially to a 20 mL scintillation vial containing **1** (4.3 mg, 0.00723 mmol). The resulting red solution was dissolved in benzene-*d*$_6$ and transferred into a J. Young NMR tube and heated at 60 °C for 24 h. Greater than 99% conversion was observed *via* ^{1}H NMR spectroscopy. The solution was hydrolyzed with 1 mL of 10% $NaOH_{(aq)}$ and the organic product was extracted using Et_2O and dried over Na_2SO_4. The solvent was removed *in vacuo* and the product was identified as 1-(4-chlorophenyl)ethanol (97.8 mg, 0.624 mmol, 86.5%). ^{1}H NMR (benzene-*d*$_6$): δ 7.11 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 4.39 (q, *J* = 6.5 Hz, 1H), 2.48 (s, 1H), 1.16 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (benzene-*d*$_6$): δ 145.34, 133.39, 129.01, 127.44, 69.77, 25.74.

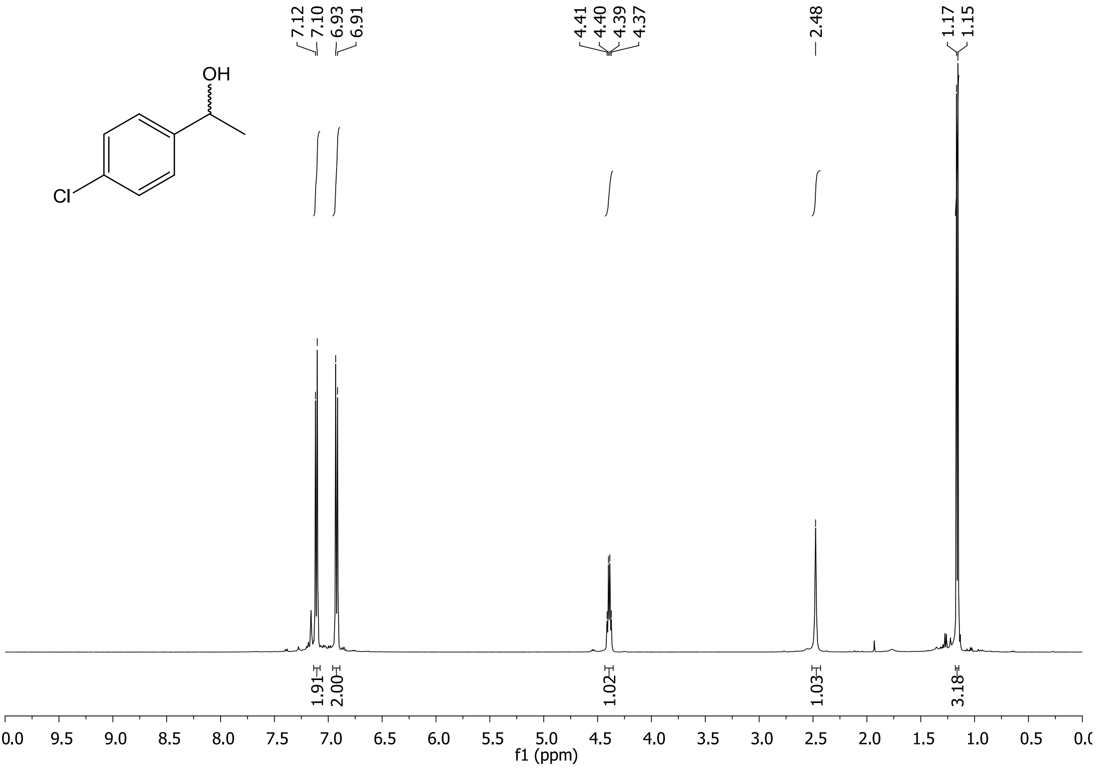

Figure S38. ^{1}H NMR spectrum of 1-(4-chlorophenyl)ethanol in benzene-*d*$_6$.

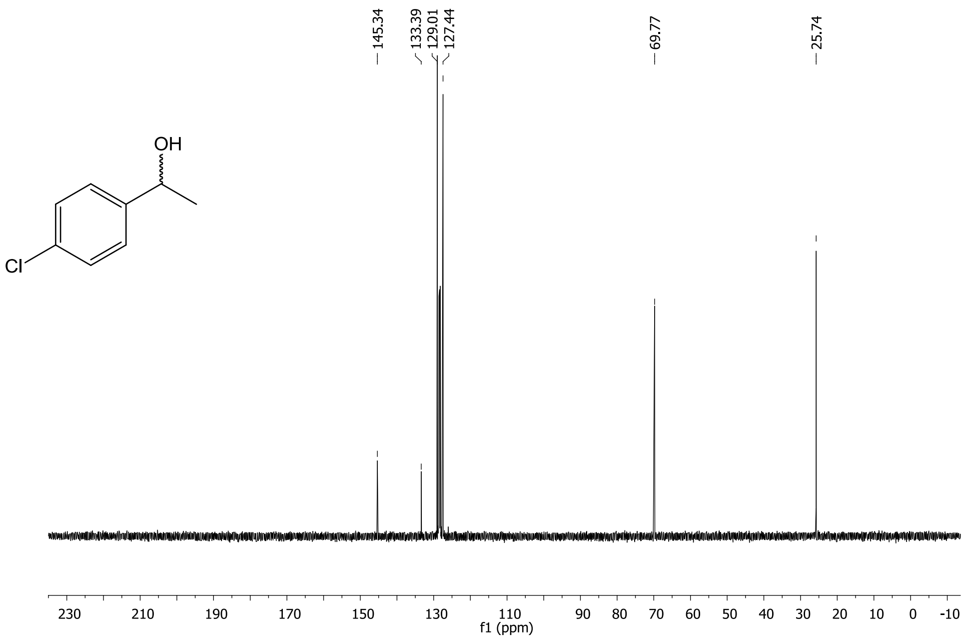

Figure S39. ^{13}C NMR spectrum of 1-(4-chlorophenyl)ethanol in benzene-*d*$_6$.

Hydrosilylation of 2,4,6-Trimethylacetophenone with 1.0 mol% 1: In a glove box, 2,4,6-trimethylacetophenone (109.0 μL, 0.655 mmol) and $PhSiH_3$ (80.7 μL, 0.655 mmol) were added sequentially to a 20 mL scintillation vial containing **1** (3.9 mg, 0.00655 mmol). The resulting red solution was dissolved in benzene-*d*$_6$ and transferred into a J. Young NMR tube and heated at 60 °C for 24 h. Greater than 99% conversion was observed *via* ^{1}H NMR spectroscopy. The solution was hydrolyzed with 1 mL of 10% $NaOH_{(aq)}$ and the organic product was extracted using Et_2O and dried over Na_2SO_4. The solvent was removed *in vacuo* and the product was identified as 1-mesitylethanol (89.7 mg, 0.546 mmol, 83.3%). ^{1}H NMR (benzene-*d*$_6$): δ 6.70 (s, 2H), 5.10 (q, *J* = 6.7 Hz, 1H), 2.45 (s, 1H), 2.32 (s, 6H), 2.12 (s, 3H), 1.37 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (benzene-*d*$_6$): δ 138.86, 136.20, 135.95, 130.75, 130.68, 67.69, 67.56, 22.22, 22.17, 21.18, 21.13, 21.08, 21.00.

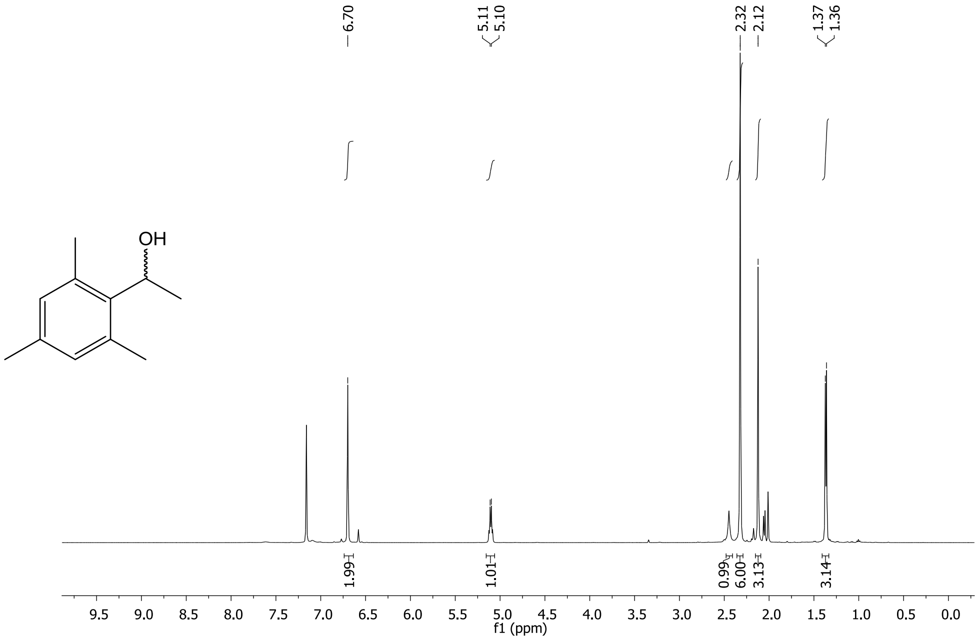

Figure S40. ^{1}H NMR spectrum of 1-mesitylethanol in benzene-d_6.

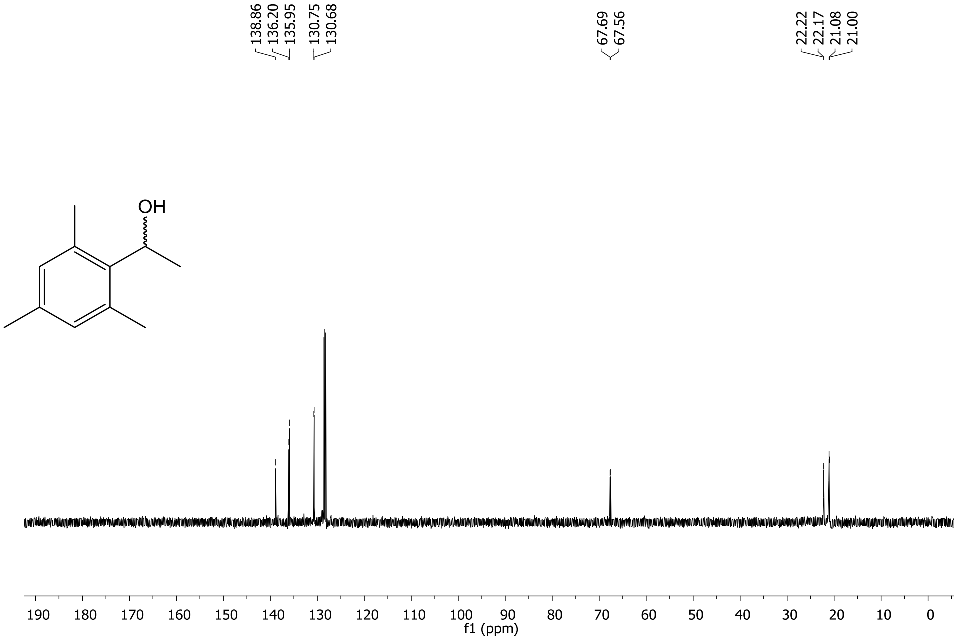

Figure S41. ^{13}C NMR spectrum of 1-mesitylethanol in benzene-d_6.

Hydrosilylation of 4-Methoxyacetophenone with 1.0 mol% 1: In a glove box, 4-methoxyacetophenone (75.7 mg, 0.504 mmol) and $PhSiH_3$ (62.1 µL, 0.504 mmol) were added sequentially to a 20 mL scintillation vial containing **1** (3.0 mg, 0.00504 mmol). The resulting red solution was dissolved in benzene-*d*$_6$ and transferred into a J. Young NMR tube and heated at 60 °C for 24 h. Greater than 99% conversion was observed *via* ^{1}H NMR spectroscopy. The solution was hydrolyzed with 1 mL of 10% $NaOH_{(aq)}$ and the organic product was extracted using Et_2O and dried over Na_2SO_4. The solvent was removed *in vacuo* and the product was identified as 1-(4-methoxyphenyl)ethanol (64.1 mg, 0.421 mmol, 83.6%). ^{1}H NMR (benzene-*d*$_6$): δ 7.19 (d, *J* = 8.3 Hz, 2H), 6.78 (d, *J* = 8.3 Hz, 2H), 4.65 (q, *J* = 6.1 Hz, 1H), 3.34 (s, 3H), 2.78 (s, 1H), 1.36 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (benzene-*d*$_6$): δ 159.66, 139.36, 127.36, 114.36, 70.17, 70.09, 55.21, 55.17, 26.02, 25.97.

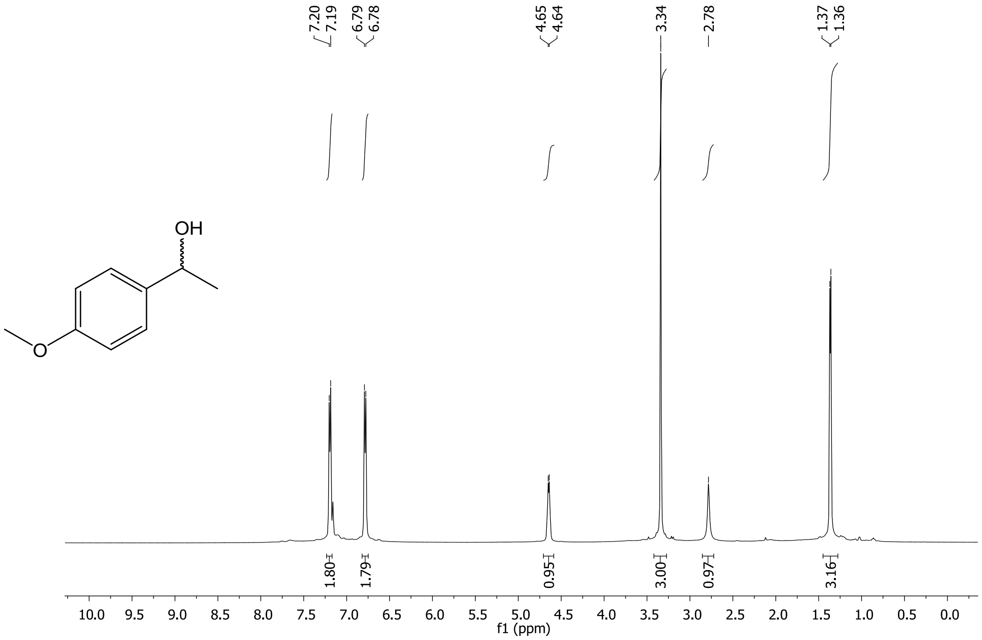

Figure S42. ^{1}H NMR spectrum of 1-(4-methoxyphenyl)ethanol in benzene-*d*$_6$.

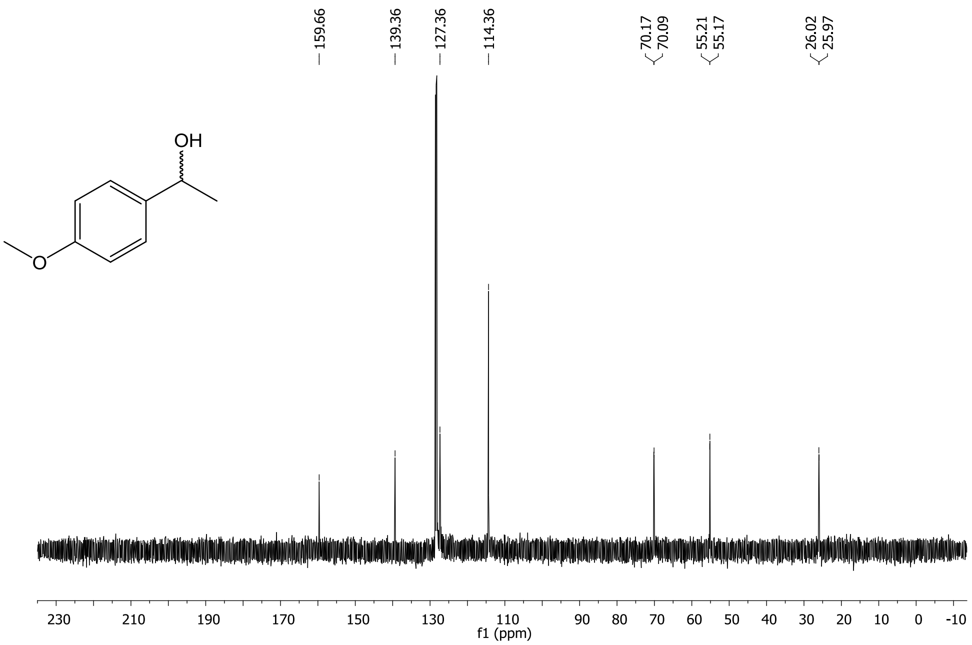

Figure S43. ^{13}C NMR spectrum of 1-(4-methoxyphenyl)ethanol in benzene-*d*$_6$.

Hydrosilylation of Dicyclohexyl Ketone with 1.0 mol% 1: In a glove box, dicyclohexylketone (125.8 μL, 0.638 mmol) and $PhSiH_3$ (78.7 μL, 0.638 mmol) were added sequentially to a 20 mL scintillation vial containing **1** (3.8 mg, 0.00638 mmol). The resulting red solution was dissolved in benzene-*d*$_6$ and transferred into a J. Young NMR tube and heated at 60 °C for 24 h. Greater than 99% conversion was observed *via* ^{1}H NMR spectroscopy. The solution was hydrolyzed with 1 mL of 10% $NaOH_{(aq)}$ and the organic product was extracted using Et_2O and dried over Na_2SO_4. The solvent was removed *in vacuo* and the product was identified as dicyclohexylmethanol (111.5 mg, 0.568 mmol, 89.0%). ^{1}H NMR (benzene-*d*$_6$): δ 2.91 (t, *J* = 5.5 Hz, 1H), 1.84 (d, *J* = 12.6 Hz, 2H), 1.74 (dd, *J* = 16.7, 7.1 Hz, 4H), 1.64 (dd, *J* = 6.8, 3.5 Hz, 2H), 1.49 (d, *J* = 12.5 Hz, 2H), 1.36 (m, 3H), 1.10 (m, 9H). ^{13}C NMR (benzene-*d*$_6$): δ 80.51, 40.67, 30.72, 28.11, 27.40, 27.31, 27.03.

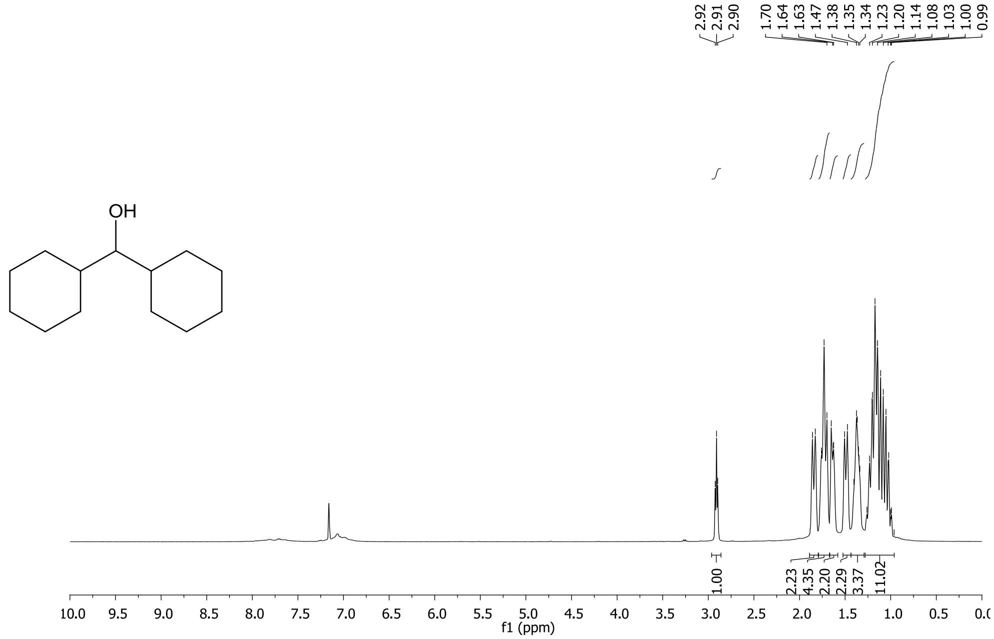

Figure S44. ^{1}H NMR spectrum of dicyclohexylmethanol in benzene-d_6.

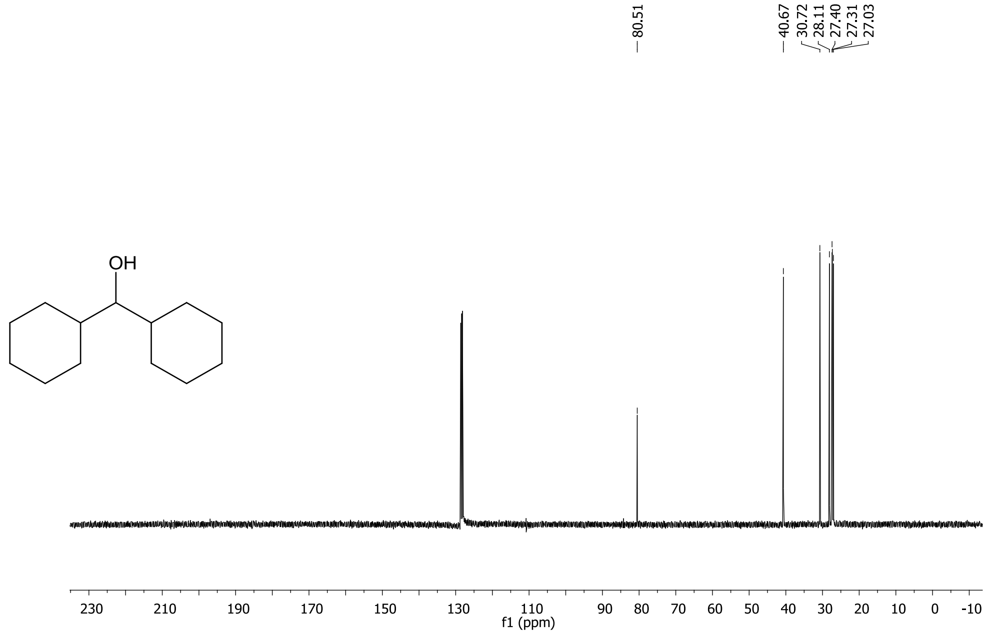

Figure S45. ^{13}C NMR spectrum of dicyclohexylmethanol in benzene-d_6.

Hydrosilylation of Cyclohexanone with 1.0 mol% 1: In a glove box, cyclohexanone (78.3 μL, 0.756 mmol) and $PhSiH_3$ (93.2 μL, 0.756 mmol) were added sequentially to a 20 mL scintillation vial containing **1** (4.5 mg, 0.00756 mmol). The resulting red solution was dissolved in benzene-d_6 and transferred into a J. Young NMR tube and heated at 60 °C for 24 h. Greater than 99% conversion was observed *via* ^{1}H NMR spectroscopy. The solution was hydrolyzed with 1 mL of 10% $NaOH_{(aq)}$ and the organic product was extracted using Et_2O and dried over Na_2SO_4. The solvent was removed *in vacuo* and the product was identified as cyclohexanol (42.6 mg, 0.425 mmol, 56.3%). ^{1}H NMR (benzene-d_6): δ 3.43 (m, 1H), 1.84 (bs, 1H), 1.75 (m, 2H), 1.59 (m, 2H), 1.35 (m, 1H), 1.21 (m, 2H), 1.09 (m, 3H). ^{13}C NMR (benzene-d_6): 30.37, 36.18, 26.33, 24.89.

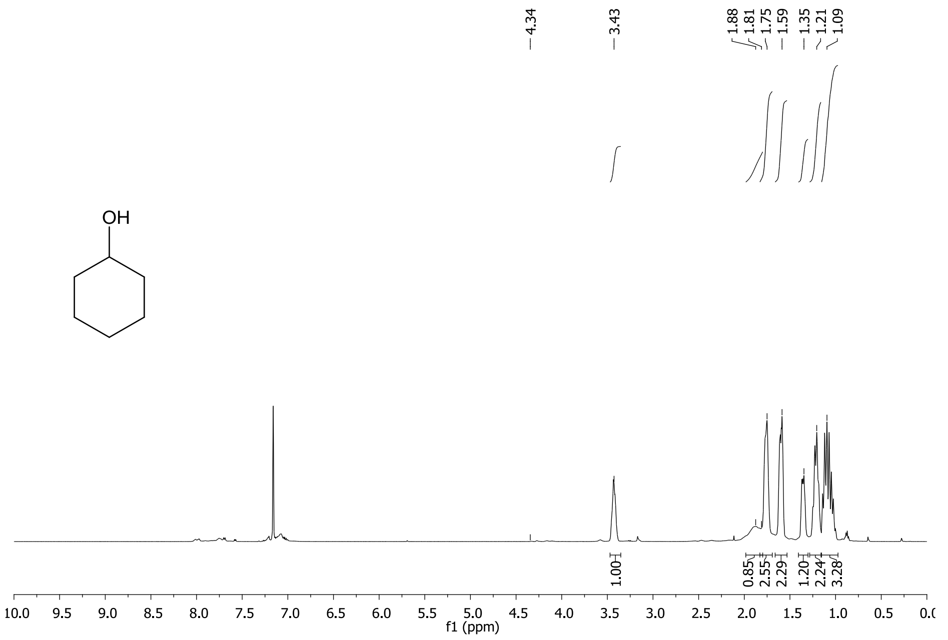

Figure S46. ^{1}H NMR spectrum of cyclohexanol in benzene-d_6.

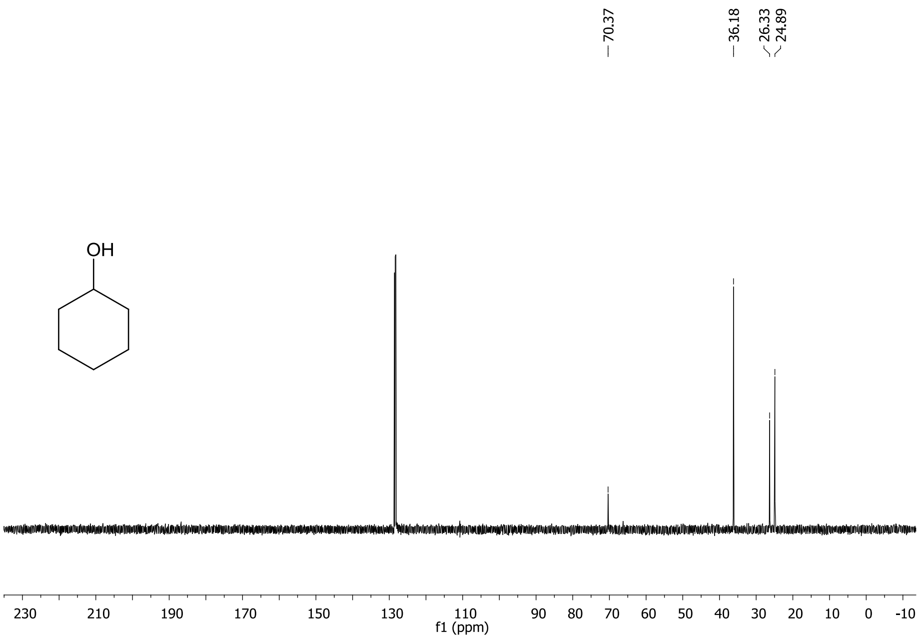

Figure S47. ^{13}C NMR spectrum of cyclohexanol in benzene-d_6.

Hydrosilylation of 2,4-dimethyl-3-pentanone with 1.0 mol% 1: In a glove box, 2,4-dimethyl-3-pentanone (85.6 µL, 0.605 mmol) and $PhSiH_3$ (74.5 µL, 0.605 mmol) were added sequentially to a 20 mL scintillation vial containing **1** (3.6 mg, 0.00605 mmol). The resulting red solution was dissolved in benzene-d_6 and transferred into a J. Young NMR tube and heated at 60 °C for 24 h. Greater than 99% conversion was observed *via* ^{1}H NMR spectroscopy. The solution was hydrolyzed with 1 mL of 10% $NaOH_{(aq)}$ and the organic product was extracted using Et_2O and dried over Na_2SO_4. The solvent was removed *in vacuo* and the product was identified as 2,4-dimethyl-3-pentanol (0.01458 mg, 0.125 mmol, 20.7%). ^{1}H NMR (benzene-d_6): δ 2.78 (t, J = 5.8 Hz, 1H), 1.60 (dh, J = 13.2, 6.7 Hz, 2H), 0.89 (d, J = 6.7 Hz, 6H), 0.81 (d, J = 6.8 Hz, 6H). ^{13}C NMR (benzene-d_6): δ 31.21, 20.37, 17.51.

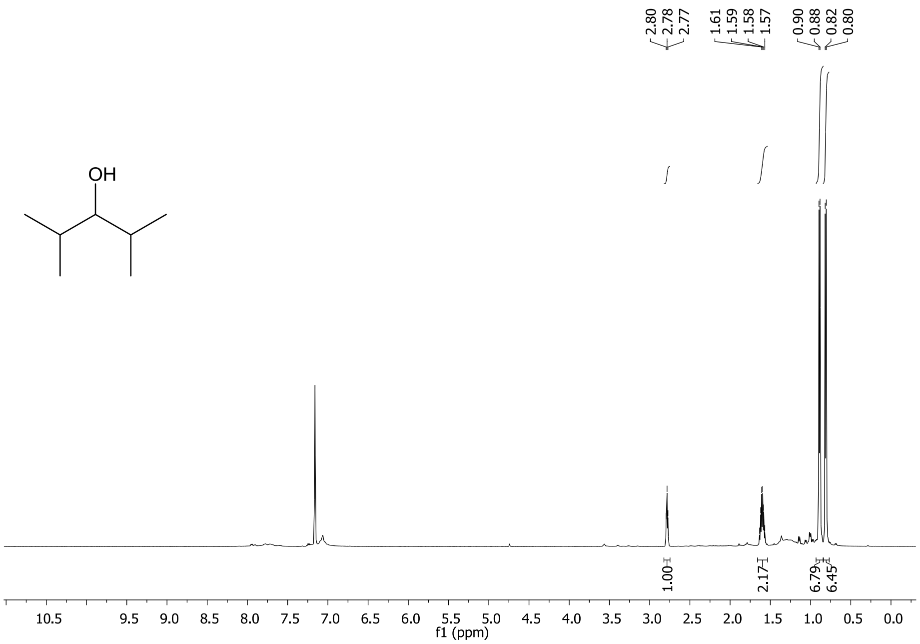

Figure S48. ^{1}H NMR spectrum of 2,4-dimethyl-3-pentanol in benzene-d_6.

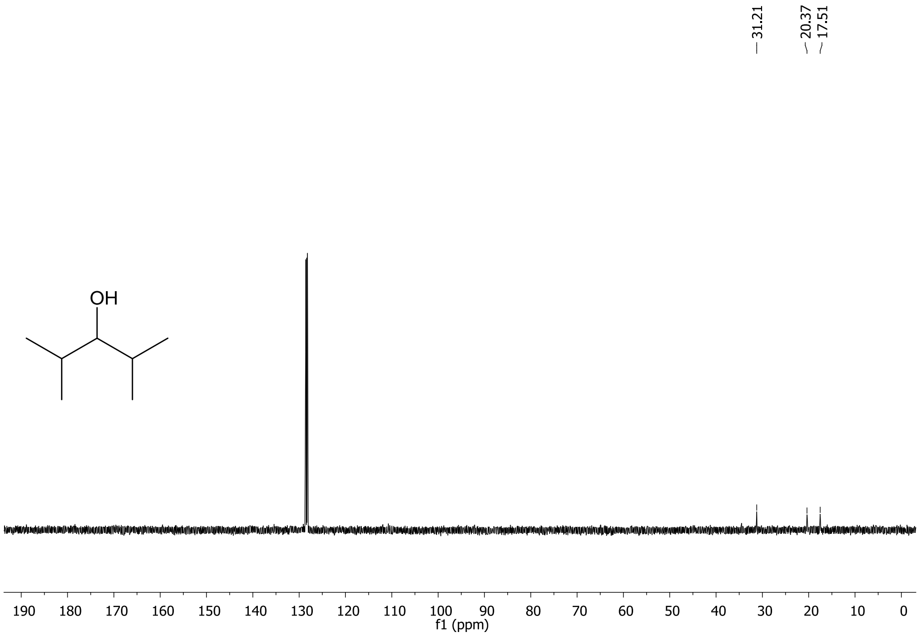

Figure S49. ^{13}C NMR spectrum of 2,4-dimethyl-3-pentanol in benzene-d_6.

Hydrosilylation of 2-Hexanone with 1.0 mol% 1: In a glove box, 2-hexanone (89.1 µL, 0.722 mmol) and $PhSiH_3$ (89.0 µL, 0.722 mmol) were added sequentially to a 20 mL scintillation vial containing **1** (4.3 mg, 0.00722 mmol). The resulting red solution was dissolved in benzene-d_6 and transferred into a J. Young NMR tube and heated at 60 °C for 24 h. Greater than 99% conversion was observed *via* ^1H NMR spectroscopy. The solution was hydrolyzed with 1 mL of 10% $NaOH_{(aq)}$ and the organic product was extracted using Et_2O and dried over Na_2SO_4. The solvent was removed *in vacuo* and the product was identified as 2-hexanol (35.7 mg, 0.349 mmol, 63.1%). ^1H NMR (benzene-d_6): δ 3.54 (h, *J* = 5.7 Hz, 1H), 1.23 (m, 7H), 1.02 (d, *J* = 6.2 Hz, 3H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C NMR (benzene-d_6): δ 68.12, 68.03, 39.83, 28.75, 24.12, 24.07, 23.51, 14.70.

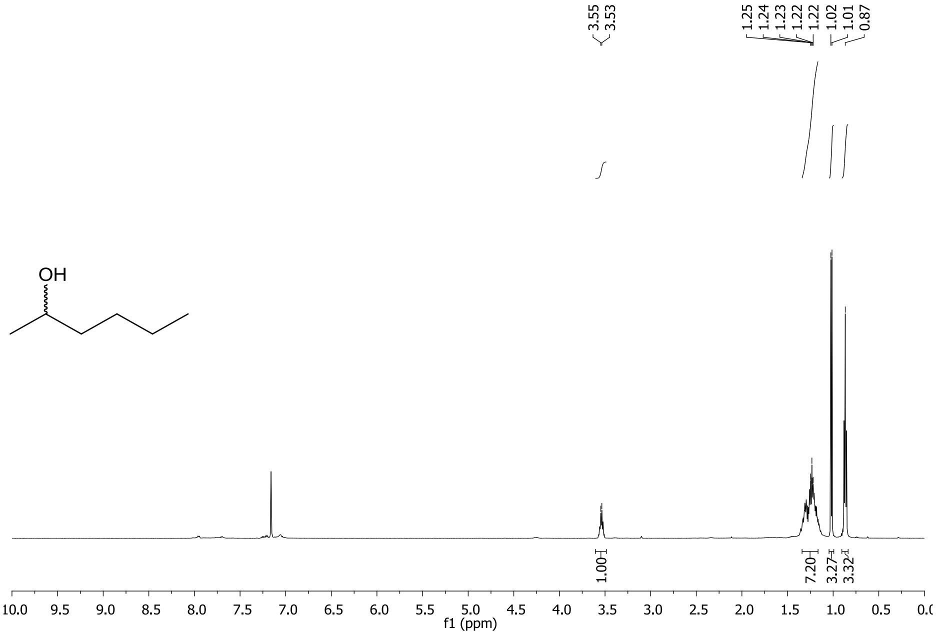

Figure S50. ^1H NMR spectrum of 2-hexanol in benzene-d_6.

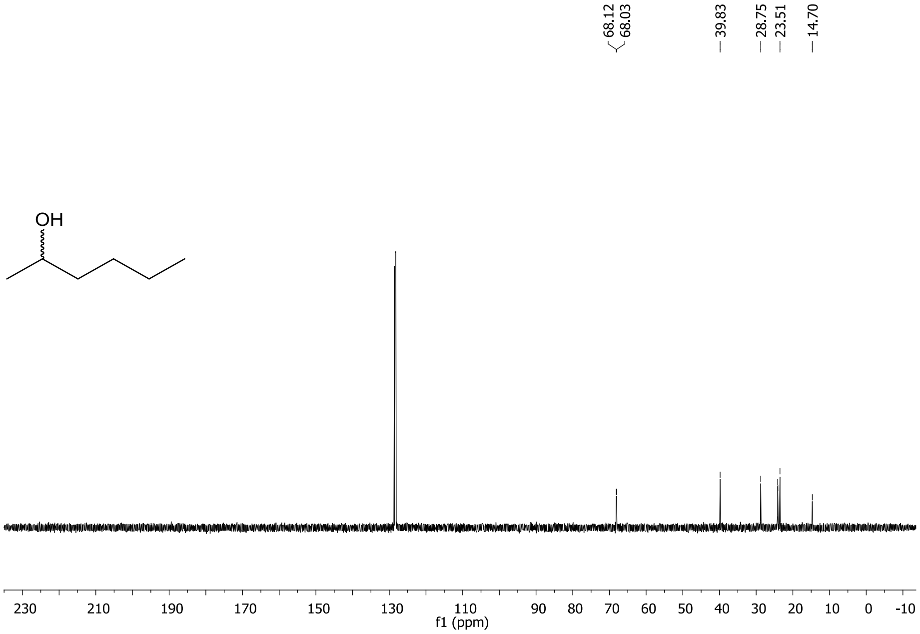

Figure S51. ^{13}C NMR spectrum of 2-hexanol in benzene-d_6.

Ester Hydrosilylation:

Dihydrosilylation of Ethyl Acetate with 1.0 mol% 1: In a glove box, 90.7 µL of ethyl acetate (0.924 mmol) and 342.0 µL $PhSiH_3$ (2.77 mmol) were combined in a 20 mL scintillation vial and then added to a vial containing 5.5 mg **1** (0.00924 mmol) in 0.5 mL benzene-*d*$_6$. The red solution was then transferred into a J. Young NMR tube, sealed, and heated to 60 °C for 24 h. Analysis by ^{1}H NMR spectroscopy revealed 80% conversion of ethyl acetate to a mixture of silyl ethers.

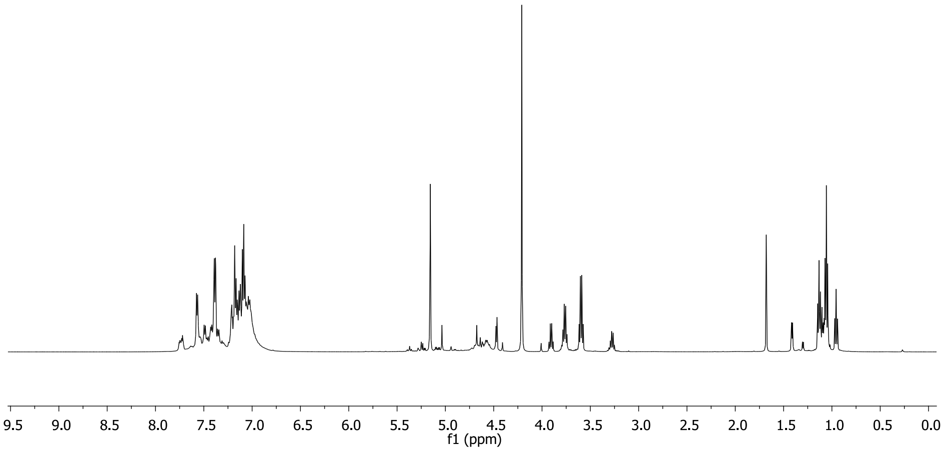

Figure S52. ^{1}H NMR spectrum of silyl ether mixture collected at 24 h in benzene-*d*$_6$.

Cleavage of Allyl Acetate Using 1.0 mol% 1: Under an inert atmosphere, allyl acetate (83.4 µL, 0.773 mmol) and $PhSiH_3$ (95.2 µL, 0.773 mmol) were combined in a 20 mL scintillation vial and then transferred to a vial containing **1** (4.6 mg, 0.00773 mmol) in 0.5 mL benzene-d_6. The red solution was transferred into a J. Young NMR tube and sealed. A color change to pale yellow was quickly observed. After 30 min, the solution returned to red and greater than 99% conversion was observed by ^{1}H NMR spectroscopy. The solution was diluted with benzene and a benzene solution containing 1 equivalent of I_2 (relative to Ni, 31.2 µL of a 0.248 M solution) was added. The mixture was allowed to sit for 1 h, after which it was filtered and volatile compounds were removed under reduced pressure, yielding phenylsilanetriyl triacetate (55.9 mg, 0.198 mmol, 76.8%) as a dark yellow oil. ^{1}H NMR (benzene-d_6): δ 8.02 – 7.99 (m, *J* = 3.5 Hz, 2H), 7.19 – 7.08 (m, 3H), 1.67 (s, 9H). ^{13}C NMR (benzene-d_6): δ 169.11, 135.62, 132.70, 128.78, 127.19, 22.22.

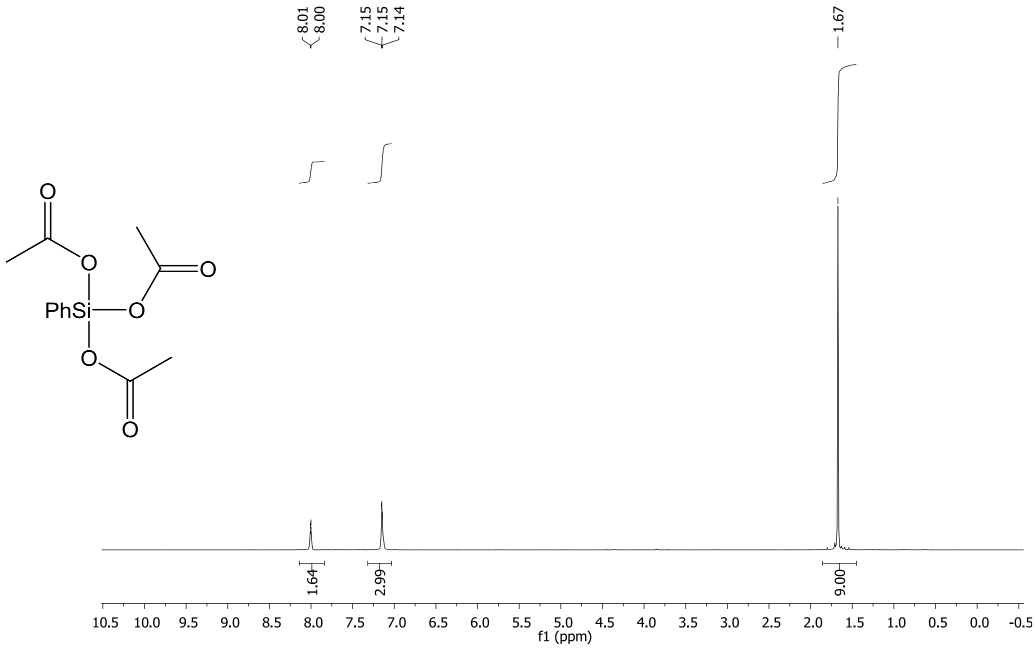

Figure S53. ^{1}H NMR spectrum of phenylsilanetriyl triacetate in benzene-d_6.

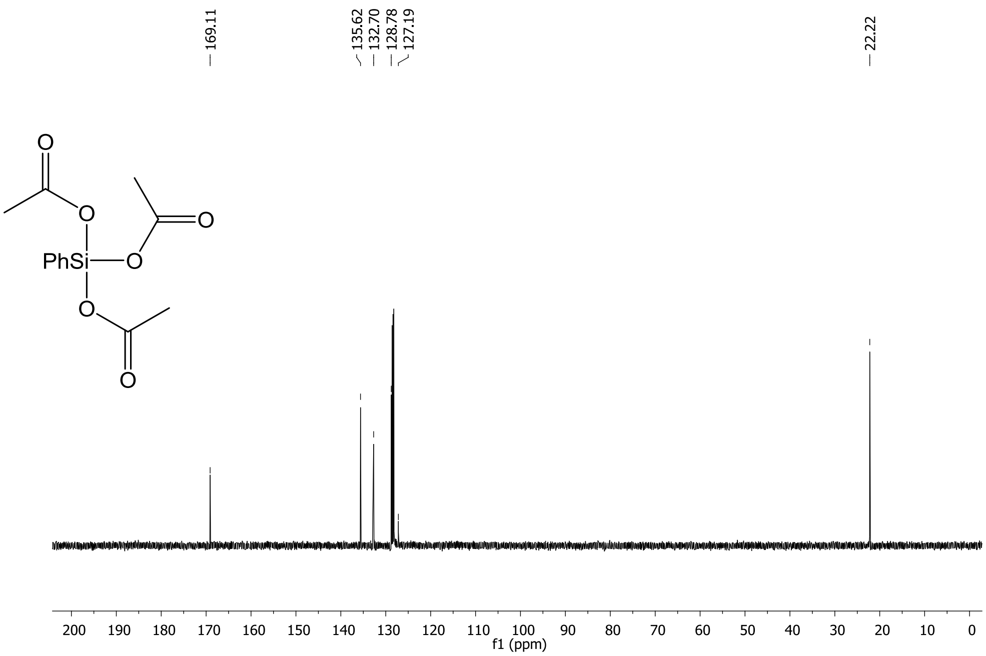

Figure S54. ^{13}C NMR spectrum of phenylsilanetriyl triacetate in benzene-d_6.

Atom Efficient Cleavage of Allyl Acetate Using 1.0 mol% 1: Under an inert atmosphere, allyl acetate (90.6 µL, 0.840 mmol) and $PhSiH_3$ (34.5 µL, 0.280 mmol) were combined in a 20 mL scintillation vial and then transferred to a vial containing **1** (5.0 mg, 0.00840 mmol) in 0.5 mL benzene-d_6. The red solution was transferred into a J. Young NMR tube and sealed. A color change to pale yellow was quickly observed. After 3 h, the solution returned to red and greater than 99% conversion was observed via ^{1}H NMR spectroscopy.

Cleavage of Allyl Acetate Using 0.1 mol% 1: Under an inert atmosphere, allyl acetate (0.94 mL, 8.73 mmol) and $PhSiH_3$ (1.08 mL, 8.73 mmol) were combined in a 20 mL scintillation vial and then transferred to a vial containing **1** (5.2 mg, 0.00521 mmol). A color change to pale yellow and vigorous bubbling was quickly observed. The vial was left loosely capped and after 1 h, the solution returned to red. Greater than 99% conversion was observed via ^{1}H NMR spectroscopy.

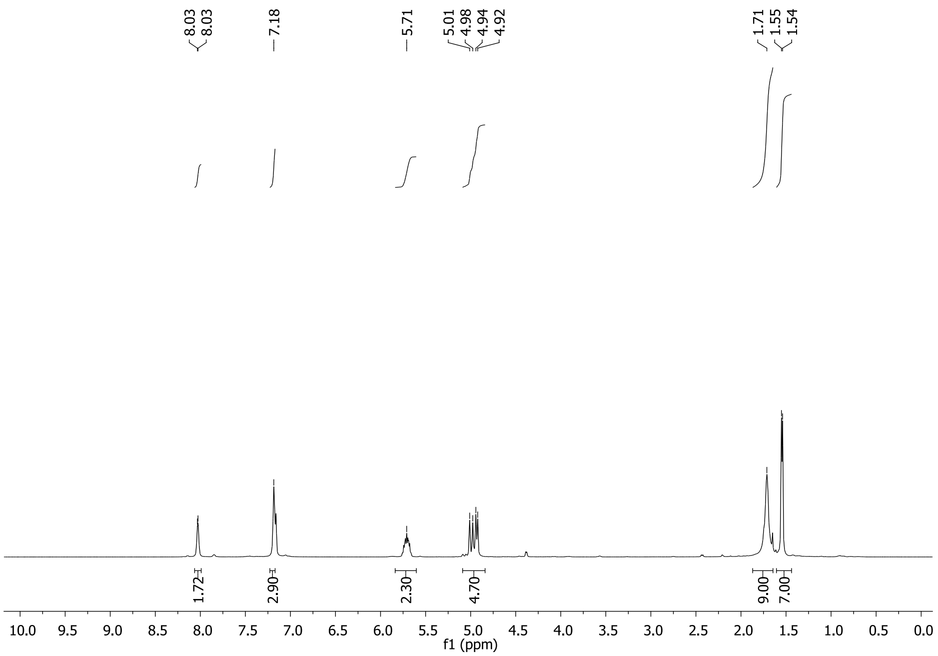

Figure S55. ^{1}H NMR spectrum of phenylsilanetriyl triacetate and propylene obtained following allyl acetate cleavage using 0.33 equivalents of $PhSiH_3$ in benzene-d_6.

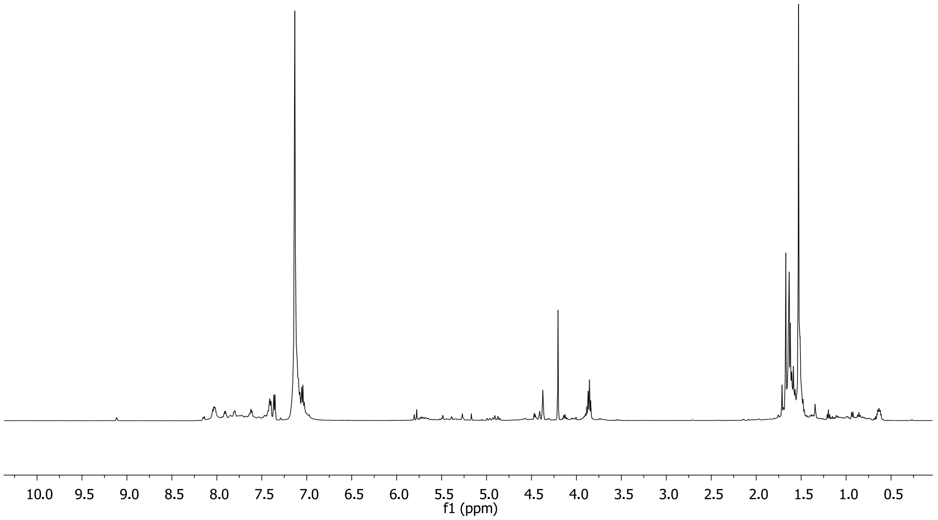

Figure S56. ^{1}H NMR spectrum of the silyl esters obtained following allyl acetate cleavage using 0.1 mol% **1** in benzene-d_6.

Cleavage of Allyl Benzoate Using 1.0 mol% 1: Under an inert atmosphere, allyl benzoate (93.1 µL, 0.605 mmol) and $PhSiH_3$ (75.6 µL, 0.605 mmol) were combined in a 20 mL scintillation vial and then transferred to a vial containing **1** (3.6 mg, 0.00605 mmol) in 0.5 mL benzene-d_6. The red solution was transferred into a J. Young NMR tube and sealed. A color change to pale yellow was quickly observed. After 30 min, the solution returned to red and greater than 99% conversion was observed via ^{1}H NMR spectroscopy. The solution was diluted with benzene and 1 equivalent of I_2 in benzene (relative to Ni, 24.4 µL of a 0.248 M solution) was added. The mixture was allowed to sit for 1 h, after which it was filtered and volatile compounds were removed under reduced pressure, yielding phenylsilanetriyl triabenzoate (80.4 mg, 0.172 mmol, 85.1%) as a dark yellow oil. ^{1}H NMR (benzene-d_6): 8.27 (dd, *J* = 4.8, 2.3 Hz, 2H), 8.21 (d, *J* = 7.3 Hz, 6H), 7.14 (d, *J* = 6.6 Hz, 4H), 7.04 (t, *J* = 7.4 Hz, 3H), 6.93 (t, *J* = 7.7 Hz, 6H). ^{13}C NMR (benzene-d_6): δ 164.95, 135.89, 134.16, 132.83, 131.51, 131.42, 130.47, 129.06, 128.99.

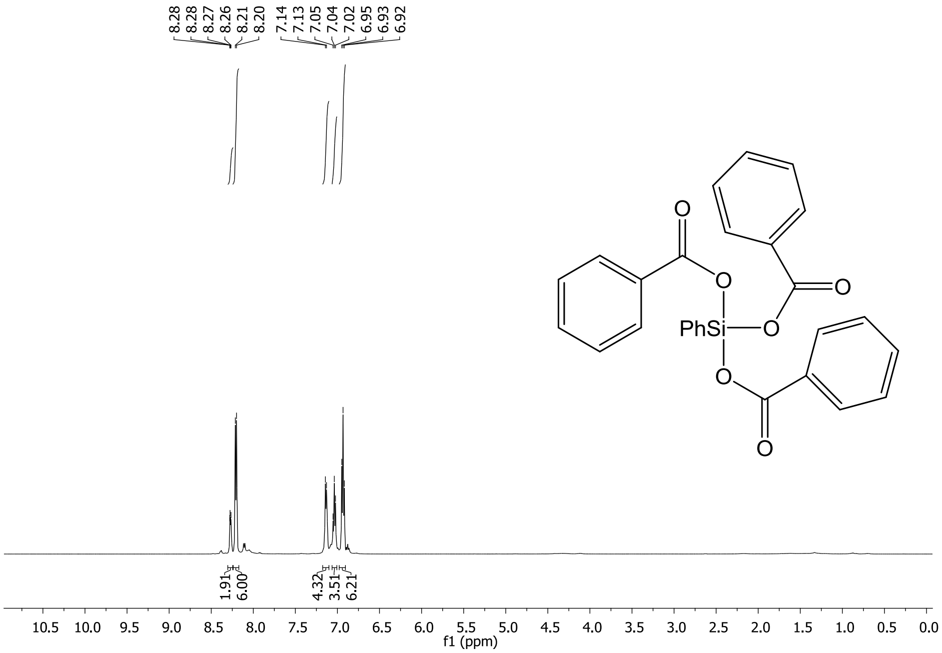

Figure S57. ^{1}H NMR spectrum of phenylsilanetriyl tribenzoate in benzene-d_6.

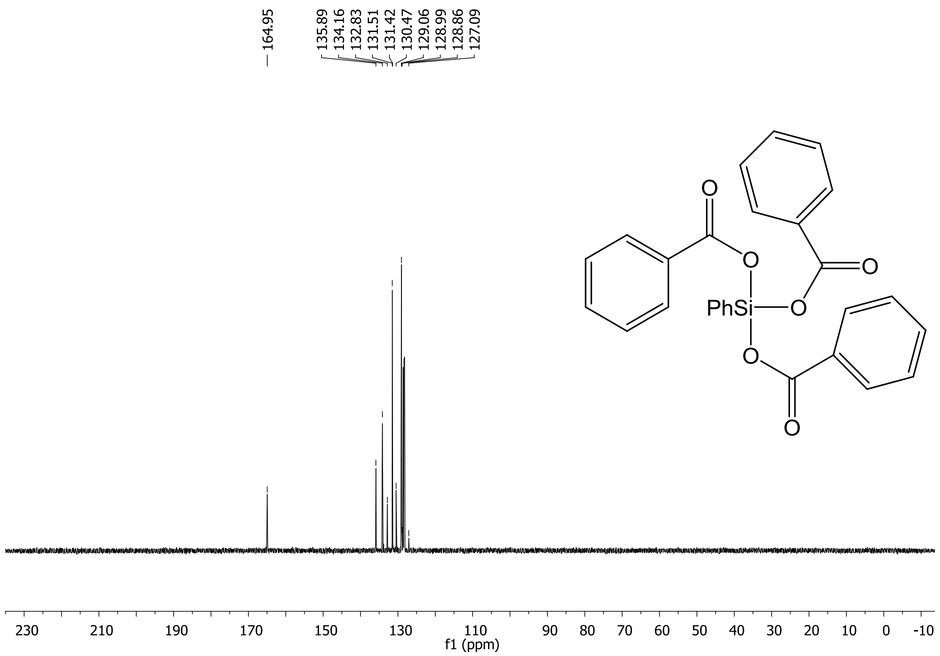

Figure S58. ^{13}C NMR spectrum of phenylsilanetriyl tribenzoate in benzene-d_6.

Cleavage of Allyl Phenylacetate Using 1.0 mol% 1: Under an inert atmosphere, allyl phenylacetate (111.3 µL, 0.655 mmol) and $PhSiH_3$ (80.7 µL, 0.655 mmol) were combined in a 20 mL scintillation vial and then transferred to a vial containing **1** (3.9 mg, 0.00655 mmol) in 0.5 mL benzene-d_6. The red solution was transferred into a J. Young NMR tube and sealed. A color change to pale yellow was quickly observed. After 30 min, the solution returned to red and greater than 99% conversion was observed via ^{1}H NMR spectroscopy. The solution was diluted with benzene and 1 equivalent of I_2 in benzene (relative to Ni, 24.4 µL of a 0.248 M solution) was added. The mixture was allowed to sit for 1 h, after which it was filtered and volatile compounds were removed under reduced pressure, yielding phenylsilanetriyl tris(2-phenylacetate) (94.1 mg, 0.184 mmol, 84.4%) as an off white solid. ^{1}H NMR (benzene-d_6): δ 7.80 (d, J = 6.7 Hz, 2H), 7.16 – 6.99 (m, 18H), 3.41 (s, 6H). ^{13}C NMR (benzene-d_6): δ 169.66, 135.55, 134.06, 132.71, 130.18, 129.04, 128.72, 127.64, 126.58, 42.69.

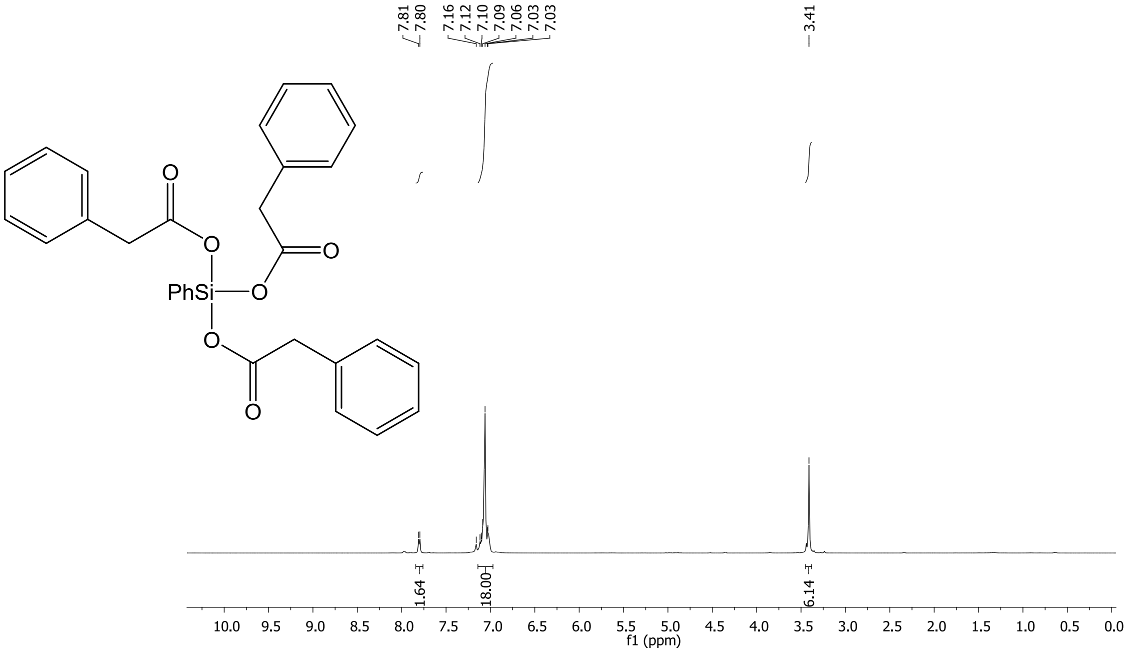

Figure S59. ^{1}H NMR spectrum of phenylsilanetriyl tris(2-phenylacetate) in benzene-d_6.

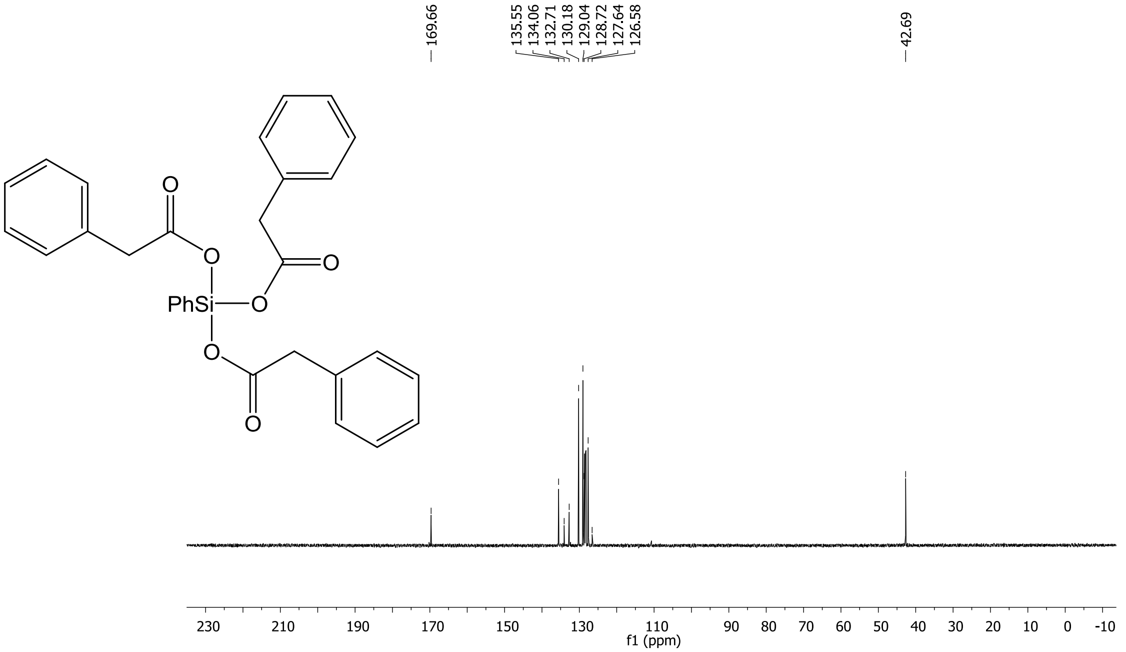

Figure S60. ^{13}C NMR spectrum of phenylsilanetriyl tris(2-phenylacetate) in benzene-d_6.

Cleavage of Allyl Phenoxyacetate Using 1.0 mol% 1: Under an inert atmosphere, allyl phenoxyacetate (101.8 μL, 0.588 mmol) and PhSiH$_3$ (72.5 μL, 0.588 mmol) were combined in a 20 mL scintillation vial and then transferred to a vial containing **1** (3.5 mg, 0.00588 mmol) in 0.5 mL benzene-d_6. The red solution was transferred into a J. Young NMR tube and sealed. A color change to pale yellow was quickly observed. After 30 min, the solution returned to red and greater than 99% conversion was observed via ^{1}H NMR spectroscopy. The solution was diluted with benzene and 1 equivalent of I$_2$ in benzene (relative to Ni, 23.7 μL of a 0.248 M solution) was added. The mixture was allowed to sit for 1 h, after which it was filtered and volatile compounds were removed under reduced pressure, yielding phenylsilanetriyl tris(2-phenoxyacetate) (98.1 mg, 0.176 mmol, 90%) as an off white solid. ^{1}H NMR (benzene-d_6): δ 7.81 (d, J = 6.8 Hz, 2H), 7.17 – 7.04 (m, 4H), 7.00 (t, J = 7.9 Hz, 6H), 6.75 (dd, J = 10.3, 4.5 Hz, 8H), 4.20 (s, 6H). ^{13}C NMR (benzene-d_6): δ 167.15, 158.38, 135.54, 133.35, 130.16, 129.01, 125.11, 122.27, 115.33, 65.59.

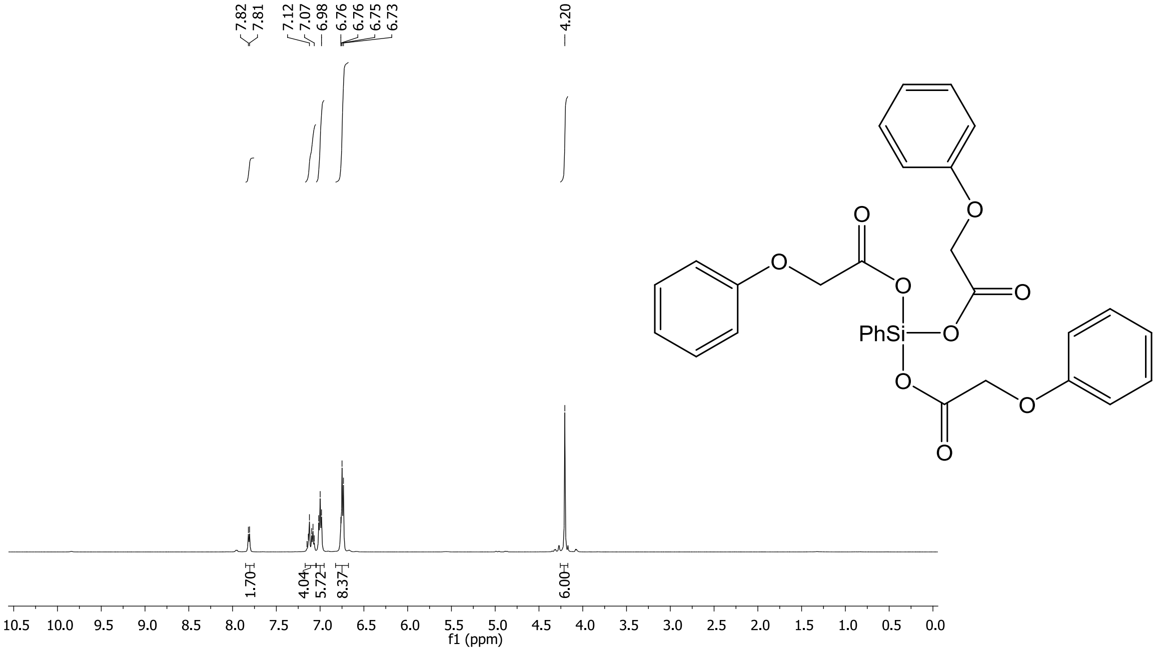

Figure S61. ^{1}H NMR spectrum of phenylsilanetriyl tris(2-phenoxyacetate) in benzene-d_6.

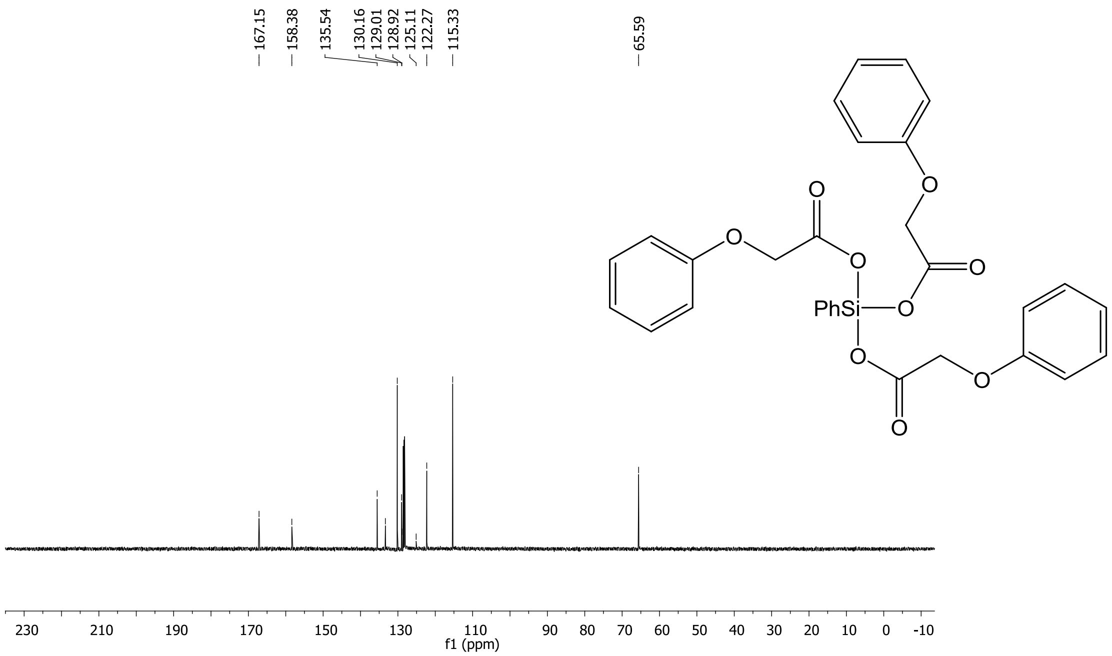

Figure S62. ^{13}C NMR spectrum of phenylsilanetriyl tris(2-phenoxyacetate) in benzene-*d*$_6$.

Cleavage of Allyl Hexanoate Using 1.0 mol% 1: Under an inert atmosphere, allyl hexanoate (118.0 µL, 0.672 mmol) and $PhSiH_3$ (83.0 µL, 0.672 mmol) were combined in a 20 mL scintillation vial and then transferred to a vial containing **1** (4.0 mg, 0.672 mmol) in 0.5 mL benzene-*d*$_6$. The red solution was transferred into a J. Young NMR tube and sealed. A color change to pale yellow was quickly observed. After 3 h, the solution returned to red and greater than 99% conversion was observed via ^{1}H NMR spectroscopy. The solution was diluted with benzene and 1 equivalent of I_2 in benzene (relative to Ni, 27.1 µL of a 0.248 M solution) was added. The mixture was allowed to sit for 1 h, after which it was filtered and volatile compounds were removed under reduced pressure, yielding phenylsilanetriyl trihexanoate (94.8 mg, 0.210 mmol, 93.9%) as a dark yellow oil. ^{1}H NMR (benzene-*d*$_6$): δ 8.33 – 8.00 (m, 2H), 7.18 (m, 3H), 2.28 – 2.08 (m, 6H), 1.58 – 1.43 (m, 6H), 1.10 (m, 12H), 0.76 (m, 9H). ^{13}C NMR (benzene-*d*$_6$): δ 171.94, 135.68, 132.65, 128.80, 127.69, 35.98, 31.61, 24.95, 22.92, 14.37.

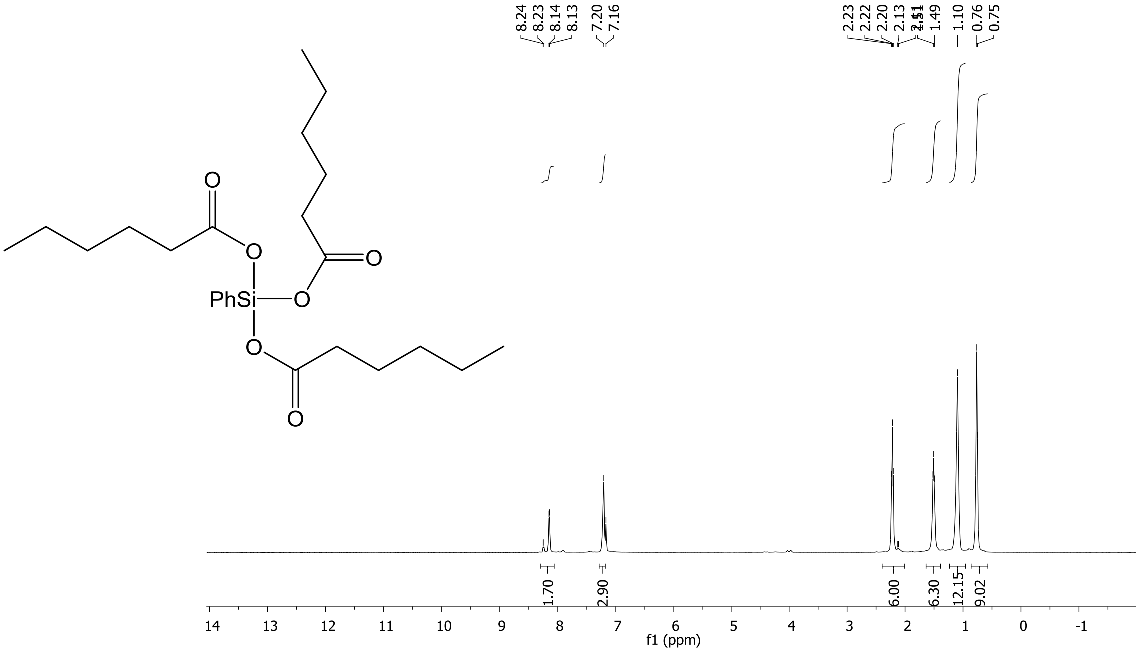

Figure S63. ^{1}H NMR spectrum of phenylsilanetriyl trihexanoate in benzene-d_6.

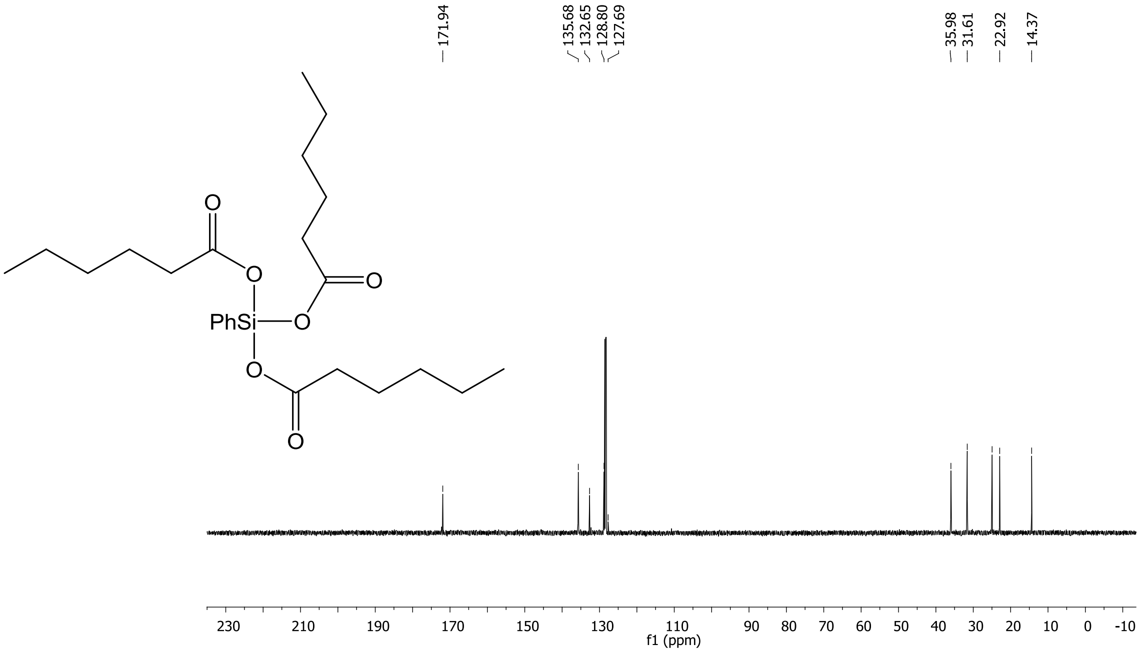

Figure S64. ^{13}C NMR spectrum of phenylsilanetriyl trihexanoate in benzene-d_6.

Cleavage of Allyl Cyclohexylpropanoate using 1.0 mol% 1: Under an inert atmosphere, allyl cyclohexylpropanoate (100.1 µL, 0.487 mmol) and $PhSiH_3$ (60.0 µL, 0.487 mmol) were combined in a 20 mL scintillation vial and then transferred to a vial containing **1** (2.9 mg, 0.00621 mmol) in 0.5 mL benzene-*d*$_6$. The red solution was transferred into a J. Young NMR tube and sealed. A color change to pale yellow was quickly observed. After 3 h, the solution returned to red and greater than 99% conversion was observed via ^{1}H NMR spectroscopy. The solution was diluted with benzene and 1 equivalent of I_2 in benzene (relative to Ni, 19.6 µL of a 0.248 M solution) was added. The mixture was allowed to sit for 1 h, after which it was filtered and volatile compounds were removed under reduced pressure, yielding phenylsilanetriyl tris(3-cyclohexylpropanoate) (86.3 mg, 0.151, 93.0%) as a dark yellow oil. ^{1}H NMR (benzene-*d*$_6$): δ 8.37 – 8.10 (m, 2H), 7.33 – 7.16 (m, 3H), 2.33 – 2.26 (m, 6H), 1.63 – 1.41 (m, 21H), 1.16 – 0.96 (m, 12H), 0.69 (m, 6H). ^{13}C NMR (benzene-*d*$_6$): δ 172.25, 135.71, 132.65, 128.80, 127.72, 37.50, 33.70, 33.43, 32.60, 27.17, 26.88.

Figure S65. ^{1}H NMR spectrum of phenylsilanetriyl tris(3-cyclohexylpropanoate) in benzene-*d*$_6$.

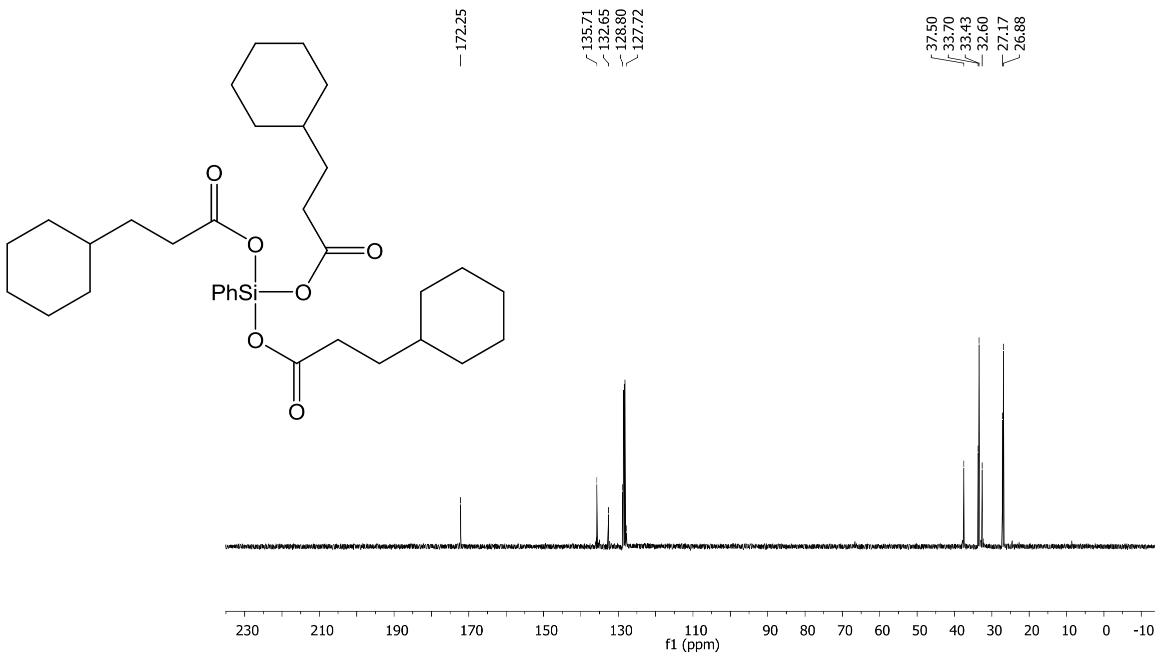

Figure S66. ^{13}C NMR spectrum of phenylsilanetriyl tris(3-cyclohexylpropanoate) in benzene-*d*$_6$.

Cleavage of Allyl Cinnamate Using 1.0 mol% 1: Under an inert atmosphere, allyl cinnamate (75.9 mg, 0.403 mmol) and $PhSiH_3$ (49.7 µL, 0.403 mmol) were combined in a 20 mL scintillation vial and then transferred to a vial containing **1** (2.4 mg, 0.00403 mmol) in 0.5 mL benzene-*d*$_6$. The red solution was transferred into a J. Young NMR tube and sealed. After 3 h, greater than 99% conversion was observed via ^{1}H NMR spectroscopy. Since I_2 addition was found to result in product alteration, this tricarboxyphenylsilane could not be isolated.

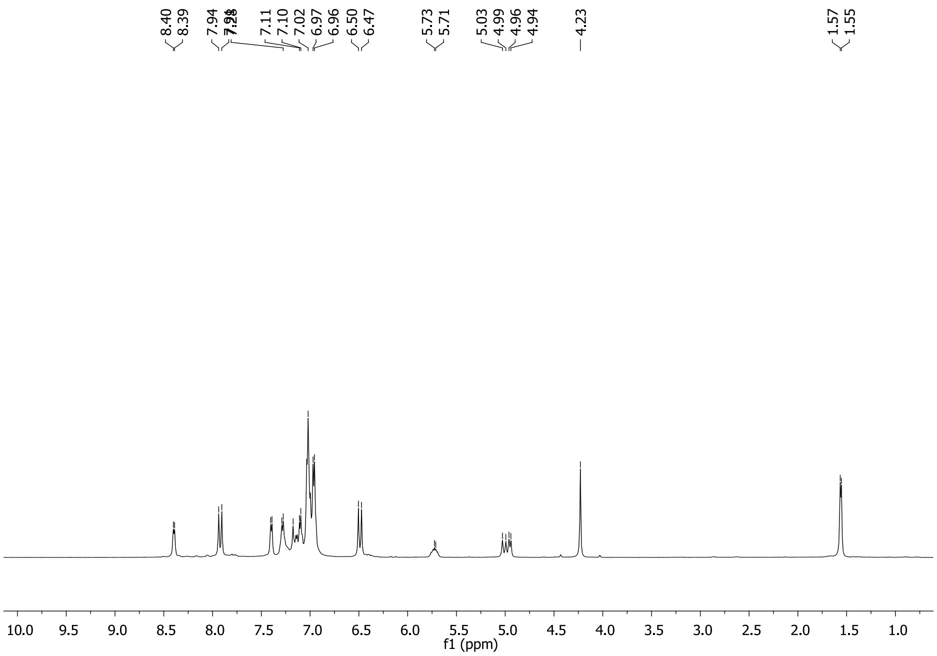

Figure S67. ^{1}H NMR spectrum showing the conversion of allyl cinnamate to phenylsilanetriyl tris(3-phenylacrylate) and propylene in benzene-*d*$_6$.

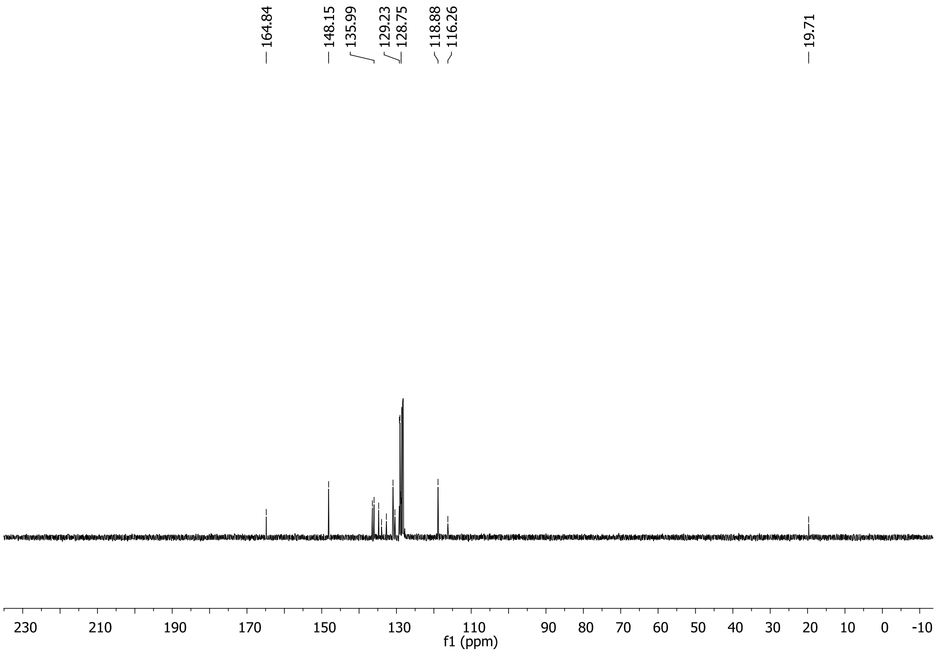

Figure S68. ^{13}C NMR spectrum showing the conversion of allyl cinnamate to phenylsilanetriyl tris(3-phenylacrylate) and propylene in benzene-*d*$_6$.

Hydrosilylation of 5-(acetoxymethyl)furfural with 1.0 mol% 1: Under inert atmosphere, 5-(acetoxymethyl)furfural (107.3 mg, 0.638 mmol) and $PhSiH_3$ (157.3 µL, 1.28 mmol) were added to a 20 mL scintillation vial containing **1** (3.8 mg, 0.00639 mmol) dissolved in benzene-*d*$_6$. After 3 h, greater than 99% conversion of the aldehyde to a mixture of silyl ethers was observed by ^{1}H NMR. Additional time and heating did not result in ester C-O bond hydrosilylation.

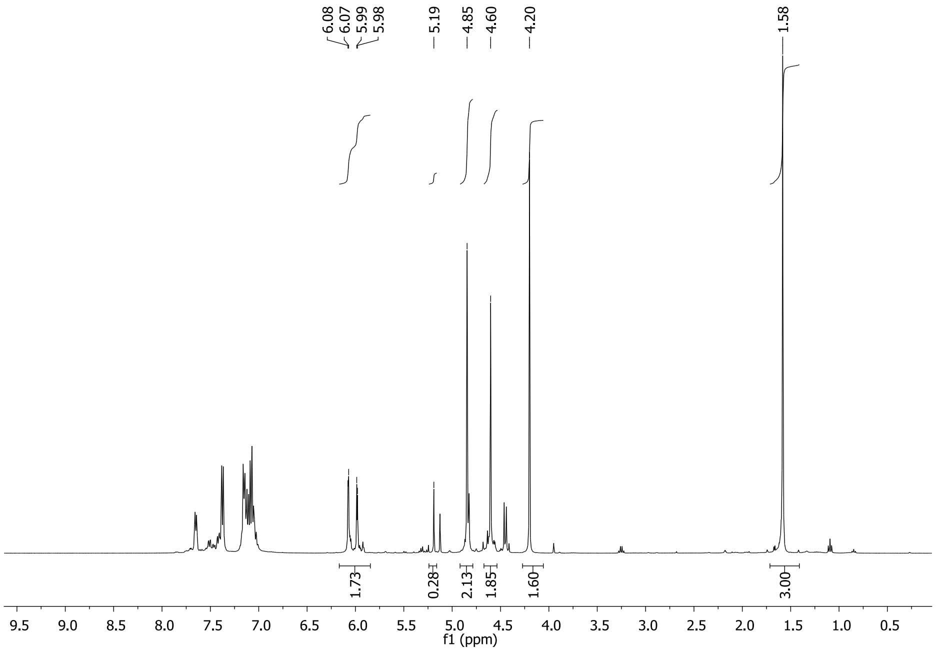

Figure S69. ^{1}H NMR spectrum collected following the hydrosilylation of 5-(acetoxymethyl)furfural with $PhSiH_3$ using 1.0 mol% **1** in benzene-*d*$_6$.

Dehydrogenative coupling of $PhSiH_3$ using 1.0 mol% 1: Under inert atmosphere, $PhSiH_3$ (72.5 µL, 0.588 mmol) was added to a 20 mL scintillation vial containing **1** (3.5 mg, 0.00588 mmol) dissolved in benzene-*d*$_6$. After 24 h, several coupled silane products were observed by ^{1}H NMR, indicating approximately 35% conversion of $PhSiH_3$. ^{29}Si NMR revealed the presence of two coupled silanes in appreciable quantity [$(PhSiH_2)_2$ (-61.50 ppm), $(PhSiH_2)_2SiHPh$ (-58.85 ppm)] and a small amount of $(PhSiH_2)_3SiPh$ (-56.12 ppm). Quaternary silane resonances not located.

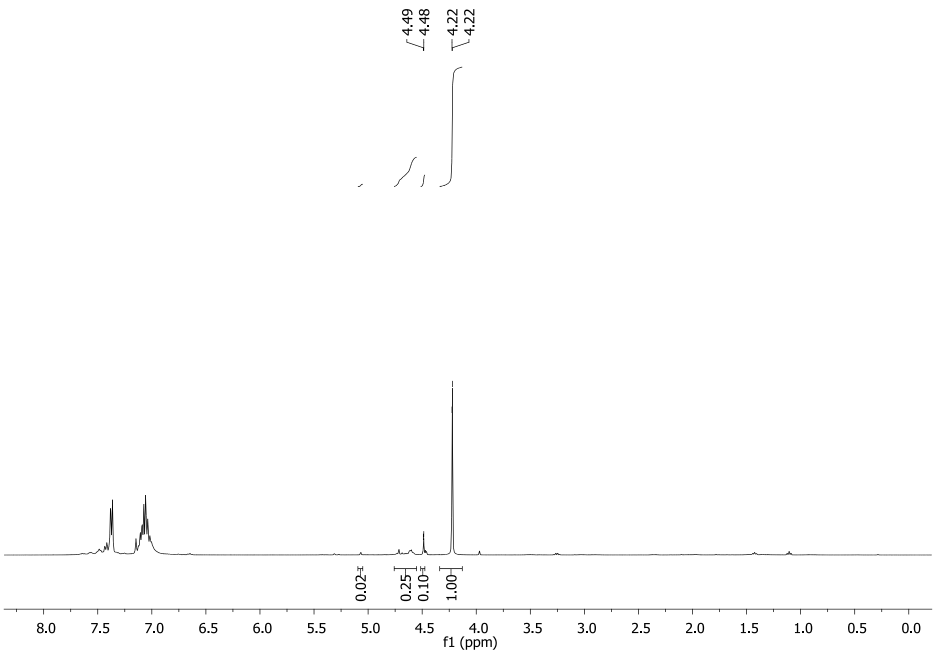

Figure S70. ^{1}H NMR spectrum of $PhSiH_3$ coupling using 1.0 mol% **1** in benzene-d_6.

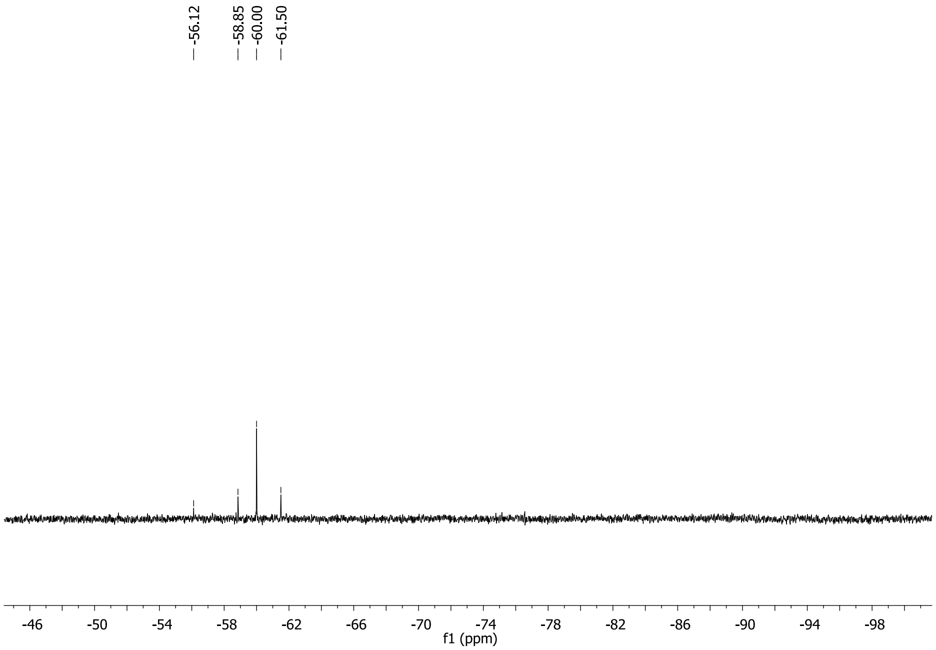

Figure S71. ^{29}Si NMR spectrum of $PhSiH_3$ coupling using 1.0 mol% **1** in benzene-d_6.

Hydrosilylation of Benzaldehyde with 1.0 mol% 1 and 20 mol% PMe_3: Under an inert atmosphere, benzaldehyde (66.8 µL, 0.655 mmol) and $PhSiH_3$ (80.7 µL, 0.655 mmol) were combined in a 20 mL scintillation vial before transferring to another vial containing PMe_3 (13.6 µL, 0.13 mmol) and **1** (3.9 mg, 0.00655 mmol) dissolved in benzene-d_6. The resulting yellow solution was transferred to a J. Young NMR tube and allowed to stand for 3 h at 25 °C. Only 3% conversion was observed by ^1H NMR spectroscopy. ^{31}P NMR spectroscopy indicates the displacement of the pendant phosphine arms by PMe_3.

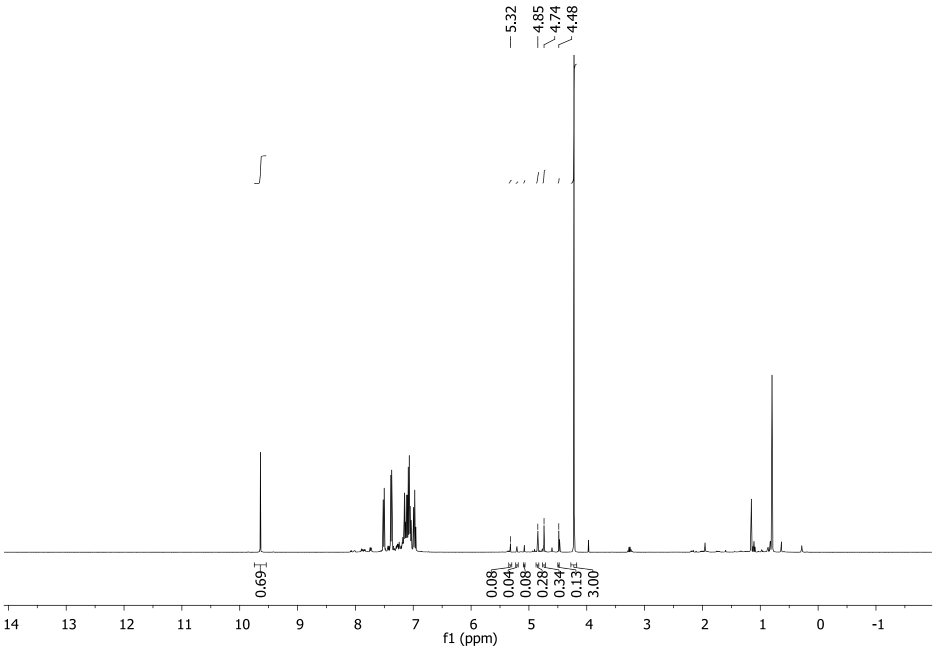

Figure S72. ^1H NMR spectrum of attempted benzaldehyde hydrosilylation using $PhSiH_3$ and 1.0 mol% **1** in the presence of 20 mol% PMe_3 in benzene-d_6.

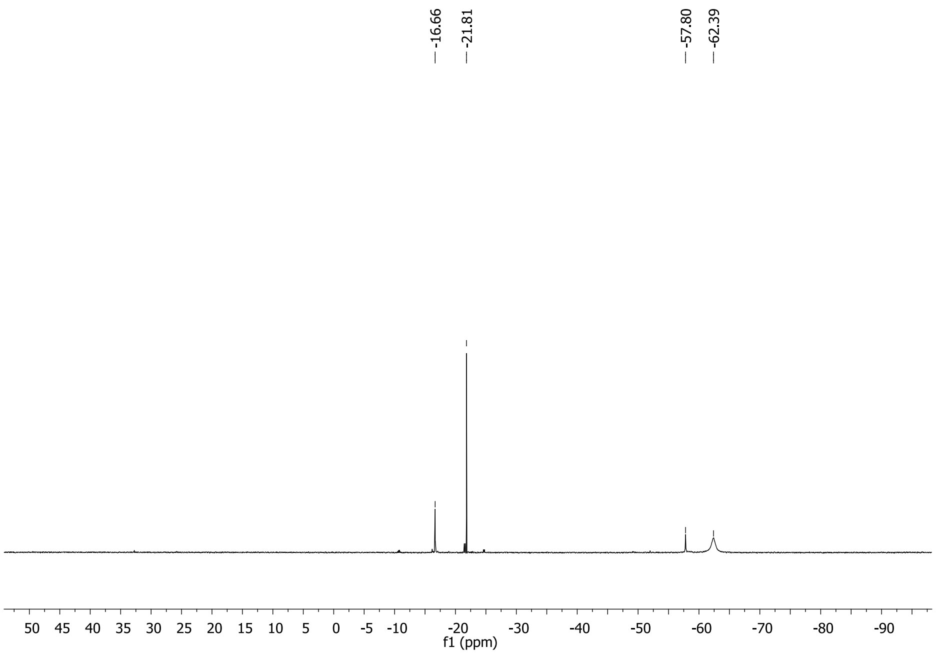

Figure S73. ^{31}P NMR spectrum collected during the catalytic hydrosilylation of benzaldehyde using $PhSiH_3$ and 1.0 mol% **1** in the presence of 20 mol% PMe_3 in benzene-d_6.

Addition of PMe_3 to 1: Under inert atmosphere, PMe_3 (7.5 µL, 0.0729 mmol) was added to a vial containing **1** (21.7 mg, 0.0364 mmol) dissolved in benzene-*d*$_6$. After 1 h, ^{31}P NMR spectroscopy revealed partial displacement of the diphenylphosphine arms by PMe_3.

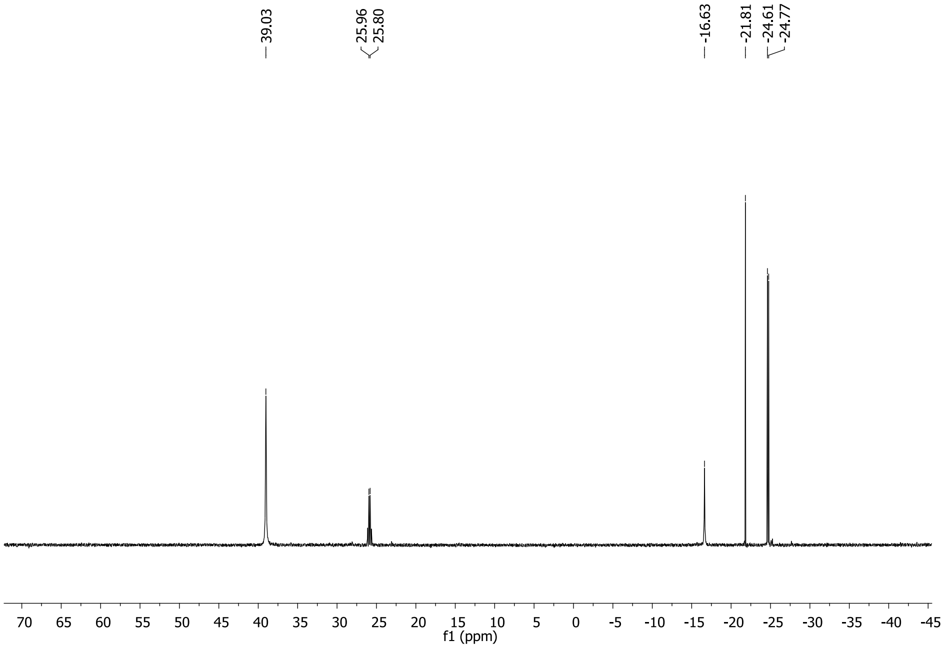

Figure S74. ^{31}P NMR spectrum collected upon adding two equivalents of PMe_3 to **1** in benzene-*d*$_6$. The resonance at 39.03 ppm is unreacted **1**. Partial conversion to two new compounds is observed: one that exhibits a singlet at -21.81 ppm [$Ni(PMe_3)_4$][1] and a second possessing resonances at 25.88 (q) and -24.69 (d) ppm [proposed to be (κ^1-*P*-^{Ph2PPr}DI)$Ni(PMe_3)_3$].

Hydrosilylation of Allyl Acetate with 1.0 mol% 1 and 20 mol% PMe_3: Under an inert atmosphere, allyl acetate (49.0 µL, 0.454 mmol) and $PhSiH_3$ (56.0 µL, 0.454 mmol) were combined in a 20 mL scintillation vial before transferring to another vial containing PMe_3 (9.4 µL, 0.09 mmol) and **1** (2.7 mg, 0.00454 mmol) dissolved in benzene-*d*$_6$. The resulting yellow solution was transferred to a J. Young NMR tube and allowed to stand for 30 min. Only 12% conversion was observed by ^1H NMR spectroscopy. ^{31}P NMR spectroscopy reveals the formation of (κ^2-*N*,*N*-^{Ph2PPr}DI)$Ni(PMe_3)_2$.

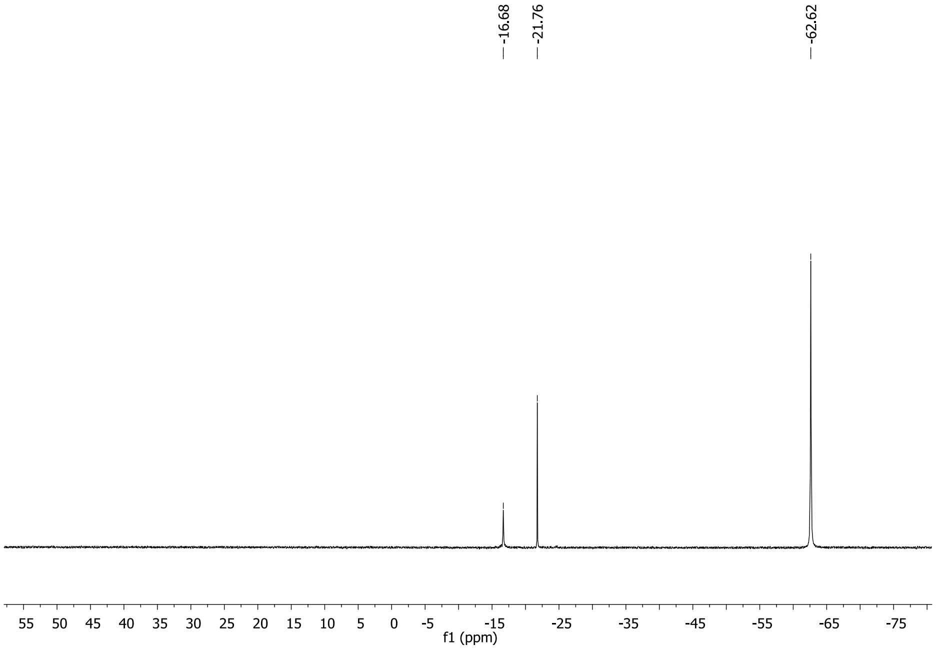

Figure S75. ^{31}P NMR spectrum collected during the catalytic hydrosilylation of allyl acetate using $PhSiH_3$ and 1.0 mol% **1** in the presence of 20 mol% PMe_3 in benzene-d_6.

References:

1. Despagnet-Ayoub, E.; Takase, M. K.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2015**, *127*, 10500-10503.