Electronic Supplementary Information

An Aryl Diimine Cobalt(I) Catalyst for Carbonyl Hydrosilylation

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GENERAL CONSIDERATIONS

Unless otherwise stated, all synthetic manipulations were performed in an MBraun glovebox under an atmosphere of purified nitrogen. Toluene, tetrahydrofuran, diethyl ether and pentane were purchased from Oakwood Chemicals and degassed using a Pure Process Technology solvent system and were dried over 4 Å molecular sieves and potassium before use. Benzene-d_6 was purchased from Oakwood Chemicals and dried over 4 Å molecular sieves and potassium before use. Chloroform-*d* was obtained from Oakwood Chemicals and dried over 4 Å molecular sieves before use. Anhydrous $CoCl_2$ was used as received from Strem Chemicals. Cobalt powder (-22 mesh) was used as received from Puratronic (Alfa Aesar). Benzaldehyde, acetophenone, diacetyl benzene, *p*-toluenesulfonic acid and sodium triethylborohydride were obtained from Sigma Aldrich. Phenylsilane, 4-anisaldehyde, 4-methylbenzaldehye, 4-cyanobenzaldehyde, furan-2-carbaldehyde, 4-fluorobenzaldehyde, 4-chlorobenzaldehyde, 4-bromobenzaldehyde, pyridine-2-carbaldehyde, thiophene-2-carbaldehyde, 3-cyclohexene-1-carbaldehyde, 2-hexenal, cinnamaldehyde, heptanal, 1-naphthaldehyde, 4-methoxyacetophenone, 4-methylacetophenone, benzophenone, 4-cyanoacetophenone, 4-fluoroacetophenone, 4-chloroacetophenone, 2’-(trifluoromethyl)acetophenone, 3-acetylpyridine, hexanone, cyclohexanone and diisopropylketone were acquired from Oakwood Chemicals and distilled and dried over 4 Å molecular sieves before use. 3-(Diphenylphosphino)-1-propylamine was prepared according to literature procedure.[1] All NMR spectra were recorded at room temperature on a Varian 400 MHz spectrometer. All ^{1}H NMR and ^{13}C NMR chemical shifts are reported relative to $Si(CH_3)_4$ using ^{1}H (residual) and ^{13}C chemical shifts of the solvent as secondary standards. ^{19}F NMR chemical shifts are reported relative to trifluoroacetic acid using the absolute ^{1}H NMR frequency of an internal $Si(CH_3)_4$ standard. ^{31}P NMR chemical shifts are reported relative to H_3PO_4 using the absolute ^{1}H NMR frequency of an internal $Si(CH_3)_4$ standard.

X-ray Crystallography: Low-temperature X-ray diffraction data for **1** and **2** were collected on a Rigaku XtaLAB Synergy diffractometer coupled to a Rigaku Hypix detector with Cu Kα radiation ($\lambda = 1.54184$ Å), from a PhotonJet micro-focus X-ray source at 103 and 123 K, respectively. The diffraction images were processed and scaled using the CrysAlisPro software.[2] The structures were solved through intrinsic phasing using SHELXT[3] and refined against F^2 on all data by full-matrix least squares with SHELXL[4] following established refinement strategies.[5] All hydrogen atoms bound to carbon were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the Ueq value of the atoms they are linked to (1.5 times for methyl groups). Details of the data quality and a summary of the residual values of the refinements are listed in Tables S1-S11.

COMPOUND CHARACTERIZATION

Preparation of ^{Ph_2PPr}ADI-H. In a glovebox, a 100 mL thick-walled glass bomb was charged with 1,3-diacetylbenzene (0.104 g, 0.64 mmol), *p*-toluenesulfonic acid (0.004 g, 0.023 mmol) and 5 mL of toluene. After stirring the mixture for 10 min, 3-(diphenylphosphino)-1-propylamine (0.312 g, 1.28 mmol) and 4 Å molecular sieves were added. The bomb was sealed and stirred in an oil bath outside the glovebox at 120 °C for 3 days. The reaction was subsequently cooled to room temperature, brought inside the glovebox, filtered through Celite, and the solvent was removed *in vacuo*. The resulting product was obtained as an orange oil in 79% yield (0.310 g, 0.506 mmol). Anal. calcd. for $C_{40}H_{42}N_2P_2$: C, 78.41%; H, 6.91%; N, 4.57%. Found: C, 78.55%; H, 6.75%; N, 3.79%. ^{1}H NMR (400 MHz, benzene-d_6): 8.62 (s, 1H, *phenyl*), 7.93 (d, J = 7.7 Hz, 2H, *phenyl*), 7.52 (t, J = 7.0 Hz, 8H, *phenyl*), 7.23 (t, J = 7.7 Hz, 1H, *phenyl*), 7.08 (t, J = 7.0 Hz, 12H, *phenyl*), 3.33 (t, J = 6.3 Hz, 4H, -CH_2), 2.26 (t, J = 8.0 Hz, 4H, -CH_2), 2.03 (m, J = 8.0 Hz, 4H, -CH_2), 1.80 (s, 6H, -CH_3). ^{13}C NMR (126 MHz, benzene-d_6): 164.10 (s, -*C*=N), 141.28 (s, *phenyl*), 139.89 (s, *phenyl*), 137.59 (s, *phenyl*), 133.30 (s, *phenyl*), 133.13 (s, *phenyl*), 128.76 (s, *phenyl*), 128.70 (s, *phenyl*), 126.76 (s, *phenyl*), 53.02 (s, -*C*H_2), 28.02 (s, -*C*H_2), 26.53 (s, -*C*H_2), 14.93 (s, -*C*H_3). ^{31}P NMR (162 MHz, benzene-d_6): -17.19 (s, Pr*P*Ph_2).

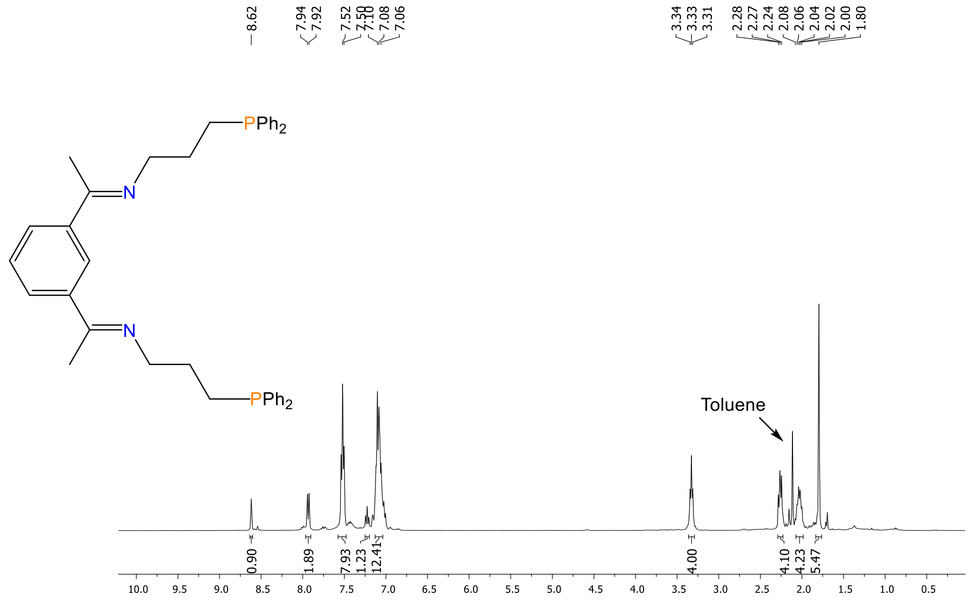


Figure S1. ^{1}H NMR spectrum of ^{Ph_2PPr}ADI-H in benzene-d_6 at 25 °C.

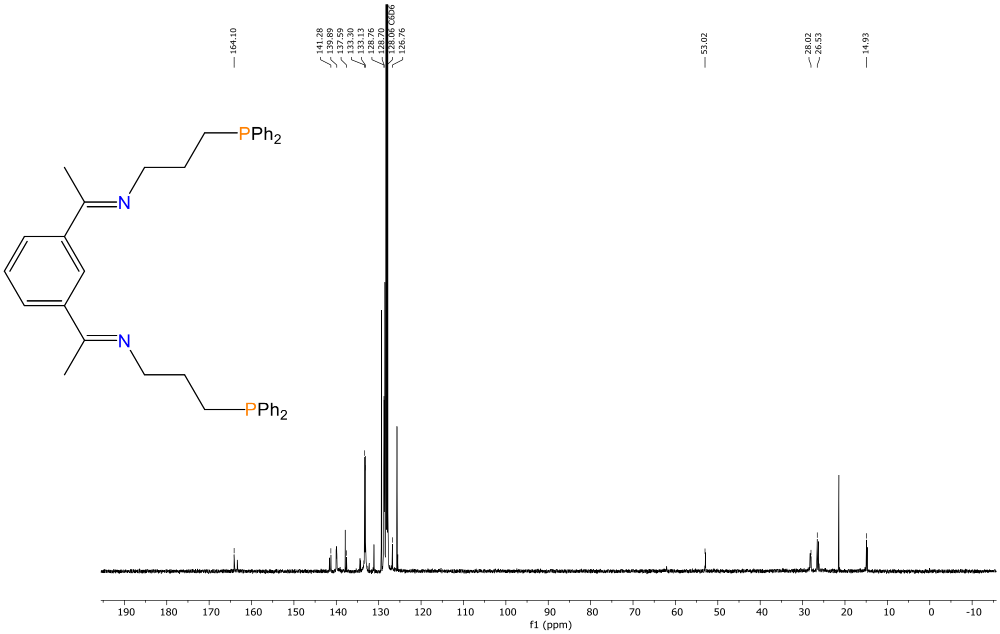


Figure S2. ^{13}C NMR spectrum of $^{\mathrm{Ph_2PPr}}$ADI-H in benzene-d_6 at 25 °C.

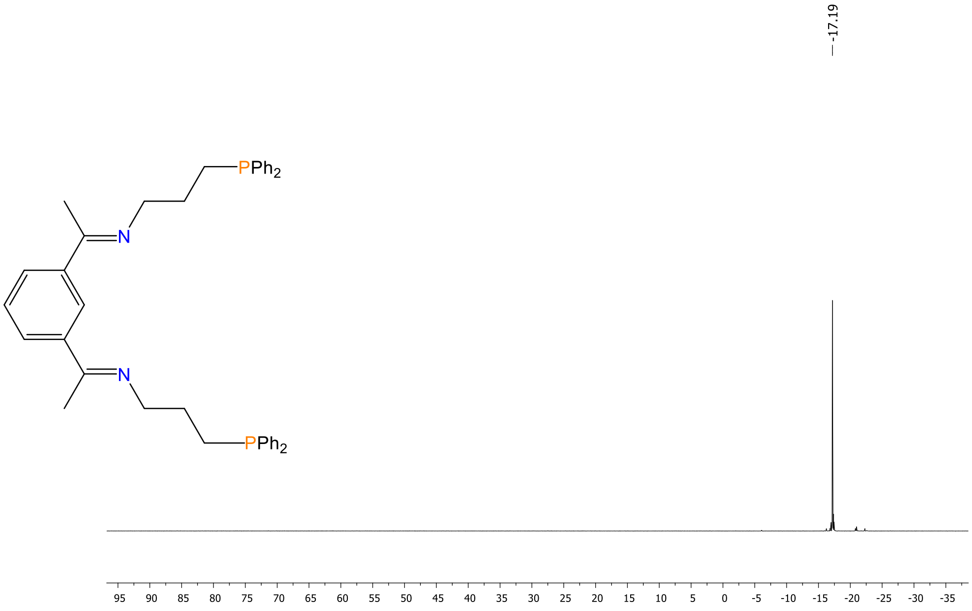


Figure S3. ^{31}P NMR spectrum of $^{\mathrm{Ph_2PPr}}$ADI-H in benzene-d_6 at 25 °C.

Preparation of [(^{Ph_2PPr}ADI)CoCl][Co_2Cl_6]$_{0.5}$ (1). In a nitrogen-filled glovebox, a 100 mL thick-walled glass bomb was charged with $CoCl_2$ (0.570 g, 4.39 mmol) and ^{Ph_2PPr}ADI-H (1.042 g, 2.19 mmol) in approximately 20 mL of toluene. The mixture turned green over the next 10 min. The bomb was sealed, taken outside the glovebox, and heated in an oil bath at 80 °C. After stirring for 12 h, a green solid precipitated from the solution. The mixture was filtered and the residual solid collected on the top of the frit was washed with 10 mL of toluene to remove any unreacted ligand. The product was allowed to dry under vacuum to yield a dark green solid identified as **1** (0.890 g, 1.024 mmol, 47%). Single crystals were obtained from a concentrated solution of acetone at room temperature. Anal. calcd. for $C_{40}H_{41}Cl_4Co_2N_2P_2$: C, 55.13%; H, 4.74%; N, 3.21%. Found: C, 55.52%; H, 5.59%; N, 3.40%. Magnetic susceptibility (Evans NMR method, 25 °C): $\mu_{eff} = 4.1\ \mu_B$. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): 13.45 (2388 Hz), 12.75 (3971 Hz), 7.38 (6881 Hz), 7.11 (38 Hz), 6.77 (375 Hz), 6.18 (64 Hz), 5.45 (5118 Hz), 5.07 (1360 Hz), 3.40 (134 Hz), 3.11 (134 Hz), 1.47 (1199 Hz), 1.18 (262 Hz), 0.40 (3393 Hz), -0.91 (4187 Hz), -1.69 (88 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 20.13 (s, Pr*P*Ph_2).

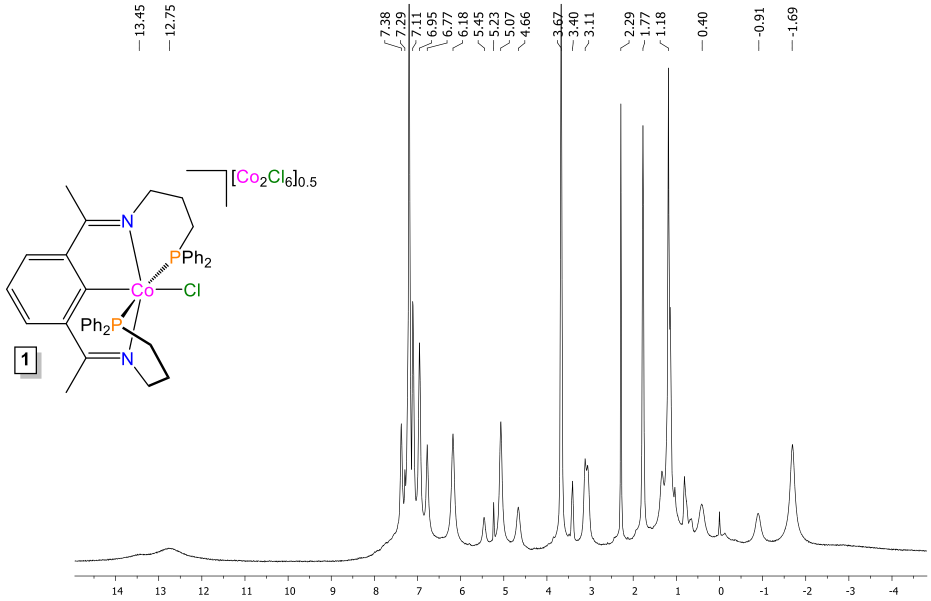


Figure S4. ^1H NMR spectrum of **1** in chloroform-*d* at 25 °C.

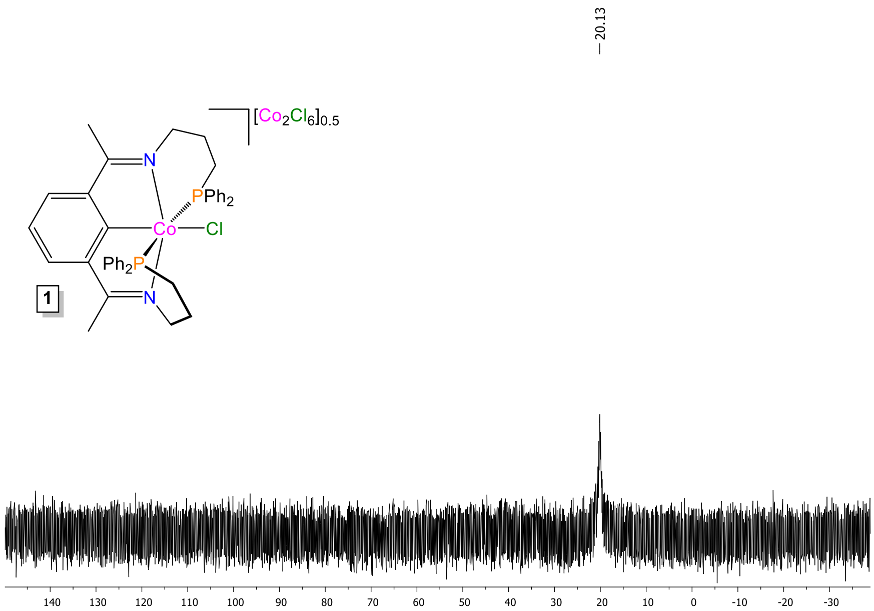


Figure S5. ^{31}P NMR spectrum of **1** in chloroform-*d* at 25 °C.

Preparation of ($^{\mathrm{Ph_2PPr}}$ADI)Co (2). In a nitrogen-filled glovebox, a 20 mL scintillation vial was filled with **1** (0.183 g, 0.210 mmol) in approximately 5 mL of toluene and cooled in a liquid nitrogen-cooled cold well for 20 min. Another 20 mL scintillation vial containing a 1.0 M solution of $NaEt_3BH$ (0.9 mL, 0.882 mmol) in toluene was also cooled in the cold well for 20 min. The cold solution of $NaEt_3BH$ was then added dropwise to the vial containing the suspension of **1** in toluene. The color changed from green to orange within 10 min. After stirring for 4 h, the reaction mixture was filtered through Celite to remove the NaCl byproduct and the solvent was removed from the filtrate under vacuum. The solid residue left was washed with pentane (2 x 3 mL) and then dried to obtain (0.063 g, 0.0934 mmol, 45%) of a dark orange solid identified as **2**. Single crystals were obtained from a concentrated toluene solution layered with diethyl ether at room temperature. Anal. calcd. for $C_{40}H_{41}CoN_2P_2$: C, 71.64%; H, 6.16%; N, 4.18%. Found: C, 71.64% H, 6.25% N, 3.45%. ^{1}H NMR (500 MHz, benzene-d_6): 8.20 (d, *J* = 7.4 Hz, 2H, *phenyl*), 7.50 (q, *J* = 7.3 Hz, 5H, *phenyl*), 7.07 (d, *J* = 5.9 Hz, 1H, *phenyl*), 7.04 (d, *J* = 8.1 Hz, 5H, *phenyl*), 6.81 (d, *J* = 3.6 Hz, 5H, *phenyl*), 6.78 (s, 5H, *phenyl*), 3.70 (d, *J* = 17.5 Hz, 2H, -CH_2), 3.02 (t, *J* = 11.2 Hz, 2H, -CH_2), 2.27 (m, 4H, -CH_2), 1.81 (s, 6H, -CH_3), 1.12 (s, 4H, -CH_2). ^{13}C NMR (126 MHz, benzene-d_6): 159.42 (s, -*C*=N), 144.00 (s, *phenyl*), 143.21 (s, *phenyl*), 138.06 (s, *phenyl*), 134.08 (s, *phenyl*), 131.40 (s, *phenyl*), 127.58 (s, *phenyl*), 121.10 (s, *phenyl*), 115.66 (s, *phenyl*), 54.48 (s, -*C*H_2), 29.14 (s, -*C*H_2), 27.62 (s, -*C*H_2), 14.68 (s, -*C*H_3). ^{31}P NMR (162 MHz, benzene-d_6): 33.87 (s, Co-*P*).

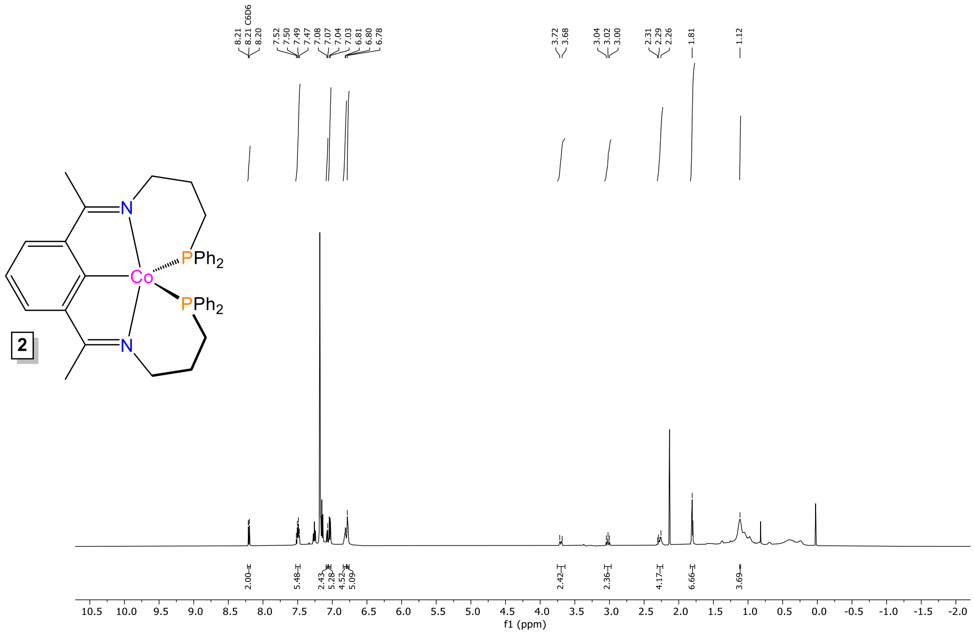


Figure S6. ^{1}H NMR spectrum of **2** in benzene-d_6 at 25 °C.

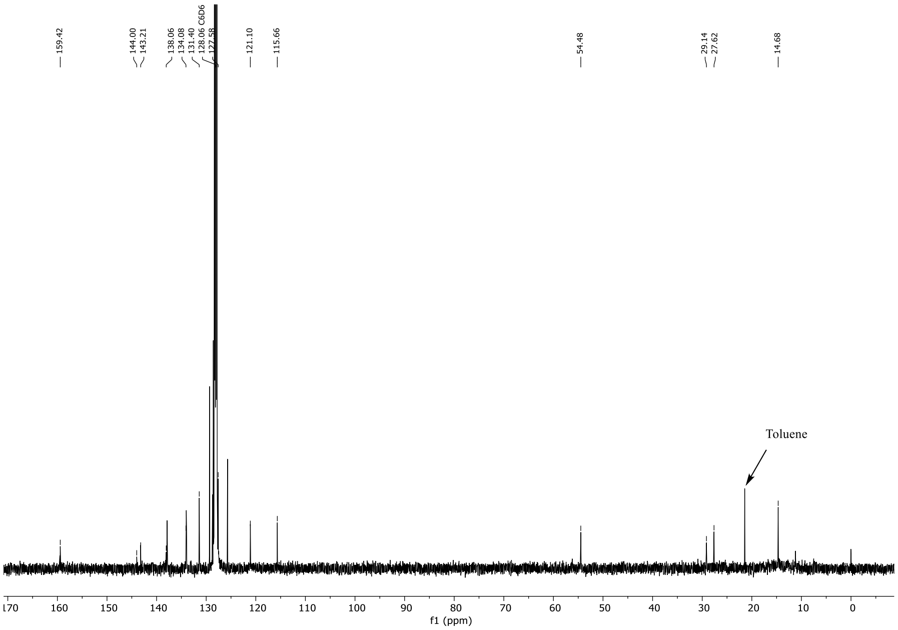


Figure S7. ^{13}C NMR spectrum of **2** in benzene-d_6 at 25 °C.

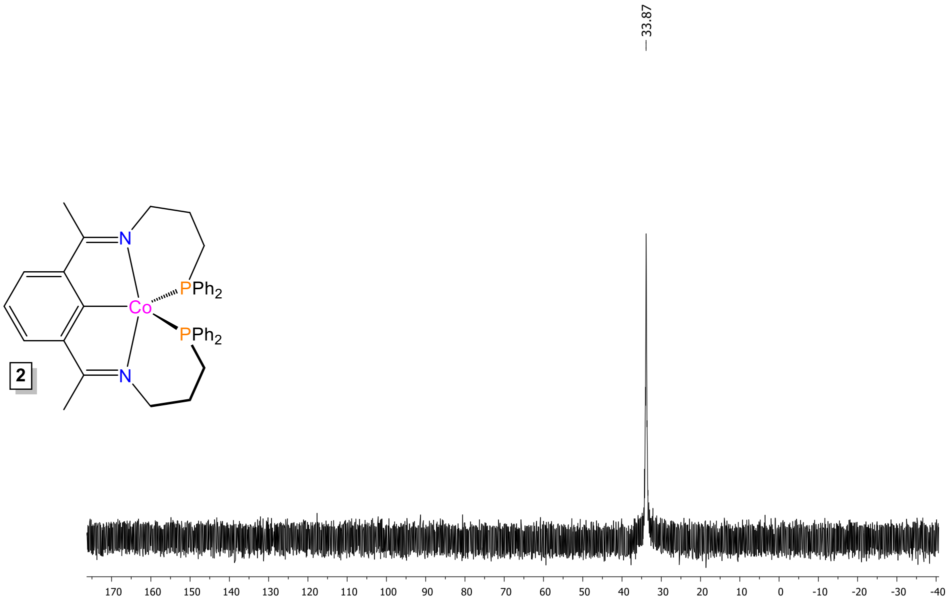


Figure S8. ^{31}P NMR spectrum of **2** in benzene-d_6 at 25 °C.

CRYSTALLOGRAPHIC DATA

Table S1. Crystallographic Data for [(^{Ph_2PPr}ADI)CoCl][Co_2Cl_6]$_{0.5}$ (**1**) and (^{Ph_2PPr}ADI)Co (**2**).

	1	**2**
chemical formula	$C_{40}H_{41}Cl_4Co_2N_2P_2$	$C_{40}H_{41}CoN_2P_2$
formula weight	871.35	670.62
crystal dimensions	0.138 × 0.068 × 0.06	0.323 × 0.135 × 0.082
crystal system	monoclinic	monoclinic
space group	P 1 21/n 1	P 1 21/n 1
a (Å)	14.21000(10)	17.46782(6)
b (Å)	15.25040(10)	20.13749(9)
c (Å)	17.82880(10)	19.21388(7)
α (deg)	90	90
β (deg)	100.2250(10)	92.7683(3)
γ (deg)	90	90
V (Å^3)	3802.28(4)	6750.75(4)
Z	4	8
T (°C)	103(6)	123.00(10)
ρ_{calcd} (Mg m^{-3})	1.522	1.320
μ (mm^{-1})	10.466	5.111
reflections collected	50524	108237
data/restraints/parameters	7755/0/453	14138/0/815
R_1 [$I > 2\sigma(I)$]	0.0413	0.0309
wR_2 (all data)	0.1173	0.0827
Goodness-of-fit	1.058	1.025
Largest peak, hole (eÅ^{-3})	0.665, -0.405	0.287, –0.476

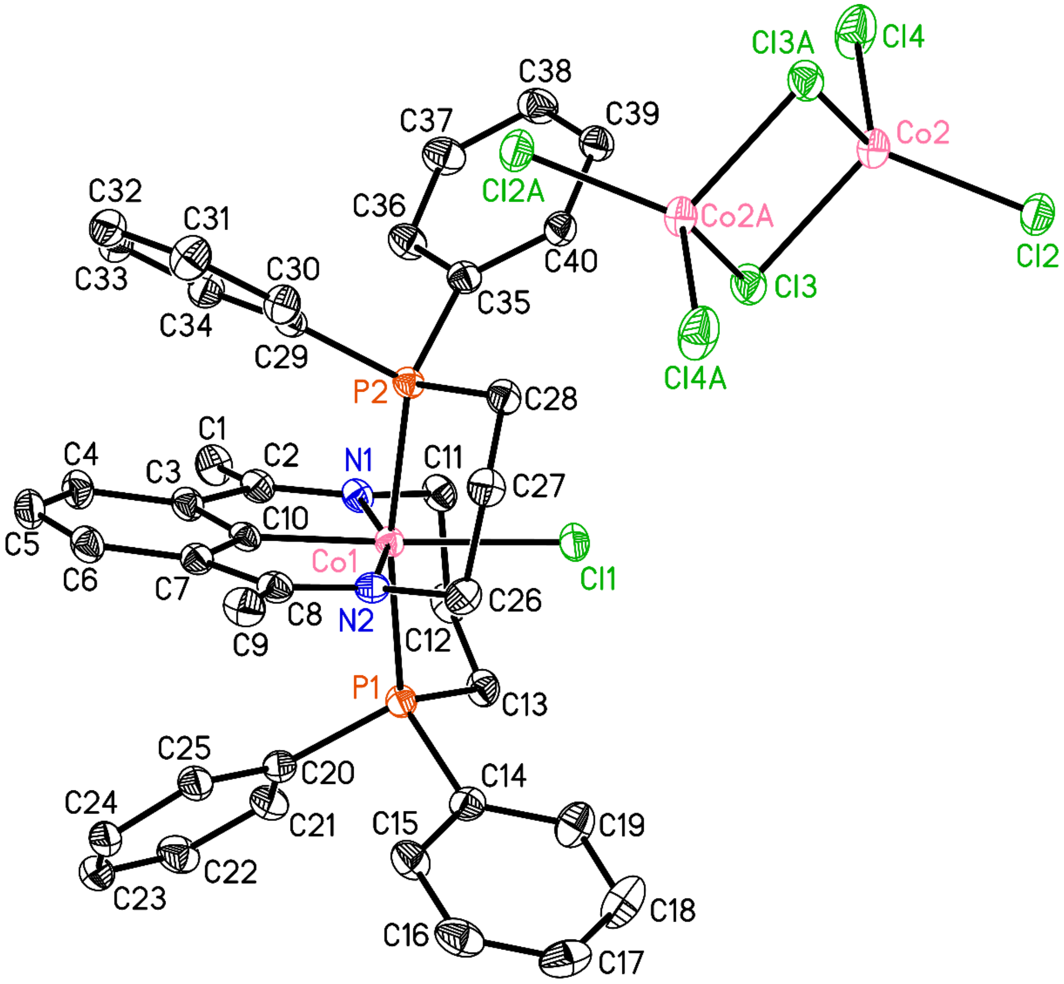


Figure S9. The molecular structure of **1** displayed at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Atoms with labels ending in "A" were generated by symmetry to show the entire Co_2Cl_6 dianion and highlight the tetrahedral geometry about Co(2).

Table S2. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	5128(1)	4468(1)	2946(1)	24(1)
Cl(1)	5677(1)	4167(1)	4231(1)	33(1)
P(1)	6006(1)	5701(1)	3167(1)	27(1)
P(2)	4343(1)	3182(1)	2937(1)	26(1)
N(1)	4084(2)	5285(1)	3045(1)	28(1)
N(2)	6023(2)	3723(1)	2499(1)	28(1)
C(1)	2862(2)	6302(2)	2346(2)	38(1)
C(2)	3599(2)	5597(2)	2412(2)	30(1)
C(3)	3883(2)	5214(2)	1735(1)	30(1)
C(4)	3468(2)	5301(2)	966(2)	36(1)
C(5)	3862(2)	4837(2)	424(2)	39(1)
C(6)	4666(2)	4304(2)	626(2)	35(1)
C(7)	5082(2)	4216(2)	1393(1)	29(1)
C(8)	5866(2)	3664(2)	1756(2)	31(1)
C(9)	6383(2)	3062(2)	1299(2)	41(1)
C(10)	4669(2)	4666(2)	1936(1)	26(1)
C(11)	3980(2)	5667(2)	3784(2)	32(1)
C(12)	4613(2)	6485(2)	3931(2)	34(1)
C(13)	5671(2)	6278(2)	3987(1)	34(1)
C(14)	7293(2)	5520(2)	3438(2)	33(1)
C(15)	7842(2)	5382(2)	2874(2)	42(1)
C(16)	8813(2)	5244(2)	3069(2)	51(1)
C(17)	9244(2)	5226(2)	3820(2)	52(1)
C(18)	8712(3)	5337(3)	4380(2)	60(1)
C(19)	7735(2)	5487(2)	4195(2)	47(1)
C(20)	5915(2)	6533(2)	2417(1)	31(1)
C(21)	5720(2)	7409(2)	2562(2)	36(1)
C(22)	5679(2)	8037(2)	1997(2)	44(1)
C(23)	5852(2)	7811(2)	1284(2)	45(1)
C(24)	6054(2)	6952(2)	1129(2)	43(1)
C(25)	6063(2)	6309(2)	1687(2)	38(1)
C(26)	6669(2)	3114(2)	2972(2)	34(1)
C(27)	6139(2)	2254(2)	3047(2)	36(1)
C(28)	5197(2)	2341(2)	3355(2)	32(1)
C(29)	3762(2)	2743(2)	2010(1)	29(1)
C(30)	4058(2)	1960(2)	1725(2)	37(1)
C(31)	3599(2)	1650(2)	1015(2)	46(1)
C(32)	2852(2)	2099(2)	590(2)	43(1)
C(33)	2552(2)	2874(2)	874(2)	41(1)
C(34)	2998(2)	3195(2)	1577(2)	36(1)
C(35)	3398(2)	3149(2)	3515(2)	30(1)
C(36)	2593(2)	3681(2)	3319(2)	37(1)
C(37)	1836(2)	3607(2)	3709(2)	42(1)
C(38)	1876(2)	3020(2)	4306(2)	40(1)
C(39)	2683(2)	2516(2)	4521(2)	36(1)
C(40)	3445(2)	2576(2)	4128(1)	33(1)
Co(2)	4724(1)	187(1)	5837(1)	36(1)
Cl(2)	5772(1)	95(1)	6927(1)	43(1)
Cl(3)	5332(1)	1044(1)	4954(1)	43(1)
Cl(4)	3267(1)	563(1)	6016(1)	62(1)

Table S3. Bond lengths (Å) determined for **1**.

Co(1)-Cl(1)	2.3320(7)
Co(1)-P(1)	2.2521(7)
Co(1)-P(2)	2.2545(7)
Co(1)-N(1)	1.969(2)
Co(1)-N(2)	1.975(2)
Co(1)-C(10)	1.828(2)
P(1)-C(13)	1.839(3)
P(1)-C(14)	1.828(3)
P(1)-C(20)	1.832(3)
P(2)-C(28)	1.832(3)
P(2)-C(29)	1.837(3)
P(2)-C(35)	1.833(3)
N(1)-C(2)	1.303(3)
N(1)-C(11)	1.473(3)
N(2)-C(8)	1.307(3)
N(2)-C(26)	1.463(3)
C(1)-C(2)	1.490(4)
C(2)-C(3)	1.461(4)
C(3)-C(4)	1.400(4)
C(3)-C(10)	1.389(4)
C(4)-C(5)	1.393(4)
C(5)-C(6)	1.395(4)
C(6)-C(7)	1.397(4)
C(7)-C(8)	1.453(4)
C(7)-C(10)	1.397(3)
C(8)-C(9)	1.503(4)
C(11)-C(12)	1.532(4)
C(12)-C(13)	1.523(4)
C(14)-C(15)	1.394(4)
C(14)-C(19)	1.384(4)
C(15)-C(16)	1.378(5)
C(16)-C(17)	1.370(6)
C(17)-C(18)	1.366(6)
C(18)-C(19)	1.388(5)
C(20)-C(21)	1.398(4)
C(20)-C(25)	1.397(4)
C(21)-C(22)	1.382(4)
C(22)-C(23)	1.381(5)
C(23)-C(24)	1.378(5)
C(24)-C(25)	1.396(4)
C(26)-C(27)	1.530(4)
C(27)-C(28)	1.540(4)
C(29)-C(30)	1.393(4)
C(29)-C(34)	1.396(4)
C(30)-C(31)	1.398(4)
C(31)-C(32)	1.373(5)
C(32)-C(33)	1.382(5)
C(33)-C(34)	1.390(4)
C(35)-C(36)	1.396(4)
C(35)-C(40)	1.392(4)
C(36)-C(37)	1.386(4)
C(37)-C(38)	1.383(4)
C(38)-C(39)	1.377(4)
C(39)-C(40)	1.393(4)
Co(2)-Cl(2)	2.2333(8)
Co(2)-Cl(3)	2.3269(8)
Co(2)-Cl(3A)	2.3423(8)
Co(2)-Cl(4)	2.2252(9)

Symmetry transformations used to generate equivalent “A” atoms: -x+1,-y,-z+1

Table S4. Angles (°) determined for **1**.

P(1)-Co(1)-Cl(1)	85.03(3)
P(1)-Co(1)-P(2)	170.14(3)
P(2)-Co(1)-Cl(1)	85.10(2)
N(1)-Co(1)-Cl(1)	99.31(6)
N(1)-Co(1)-P(1)	81.85(6)
N(1)-Co(1)-P(2)	99.87(6)
N(1)-Co(1)-N(2)	161.70(9)
N(2)-Co(1)-Cl(1)	98.98(7)
N(2)-Co(1)-P(1)	100.09(6)
N(2)-Co(1)-P(2)	81.36(6)
C(10)-Co(1)-Cl(1)	177.77(8)
C(10)-Co(1)-P(1)	97.19(8)
C(10)-Co(1)-P(2)	92.68(8)
C(10)-Co(1)-N(1)	80.87(10)
C(10)-Co(1)-N(2)	80.84(10)
C(13)-P(1)-Co(1)	109.02(9)
C(14)-P(1)-Co(1)	114.64(8)
C(14)-P(1)-C(13)	104.48(13)
C(14)-P(1)-C(20)	103.59(12)
C(20)-P(1)-Co(1)	119.01(8)
C(20)-P(1)-C(13)	104.75(12)
C(28)-P(2)-Co(1)	108.37(9)
C(28)-P(2)-C(29)	105.68(12)
C(28)-P(2)-C(35)	104.49(12)
C(29)-P(2)-Co(1)	117.79(8)
C(35)-P(2)-Co(1)	115.54(8)
C(35)-P(2)-C(29)	103.79(12)
C(2)-N(1)-Co(1)	116.41(17)
C(2)-N(1)-C(11)	120.6(2)
C(11)-N(1)-Co(1)	121.86(17)
C(8)-N(2)-Co(1)	116.22(18)
C(8)-N(2)-C(26)	121.1(2)
C(26)-N(2)-Co(1)	121.07(17)
N(1)-C(2)-C(1)	126.0(2)
N(1)-C(2)-C(3)	112.8(2)
C(3)-C(2)-C(1)	121.1(2)
C(4)-C(3)-C(2)	129.9(3)
C(10)-C(3)-C(2)	110.9(2)
C(10)-C(3)-C(4)	119.2(2)
C(5)-C(4)-C(3)	118.7(3)
C(4)-C(5)-C(6)	121.8(3)
C(5)-C(6)-C(7)	119.6(3)
C(6)-C(7)-C(8)	130.5(2)
C(6)-C(7)-C(10)	118.2(2)
C(10)-C(7)-C(8)	111.1(2)
N(2)-C(8)-C(7)	113.0(2)
N(2)-C(8)-C(9)	125.4(3)
C(7)-C(8)-C(9)	121.5(2)
C(3)-C(10)-Co(1)	118.85(18)
C(3)-C(10)-C(7)	122.3(2)
C(7)-C(10)-Co(1)	118.70(19)
N(1)-C(11)-C(12)	109.0(2)
C(13)-C(12)-C(11)	112.7(2)
C(12)-C(13)-P(1)	116.02(18)
C(15)-C(14)-P(1)	119.6(2)
C(19)-C(14)-P(1)	121.5(2)
C(19)-C(14)-C(15)	118.8(3)
C(16)-C(15)-C(14)	120.3(3)
C(17)-C(16)-C(15)	120.3(3)
C(18)-C(17)-C(16)	120.1(3)
C(17)-C(18)-C(19)	120.4(3)
C(14)-C(19)-C(18)	120.0(3)
C(21)-C(20)-P(1)	121.2(2)
C(25)-C(20)-P(1)	120.5(2)
C(25)-C(20)-C(21)	118.3(2)
C(22)-C(21)-C(20)	120.7(3)
C(23)-C(22)-C(21)	120.4(3)
C(24)-C(23)-C(22)	119.9(3)
C(23)-C(24)-C(25)	120.0(3)
C(24)-C(25)-C(20)	120.5(3)
N(2)-C(26)-C(27)	109.1(2)
C(26)-C(27)-C(28)	115.4(2)
C(27)-C(28)-P(2)	118.08(18)
C(30)-C(29)-P(2)	121.6(2)
C(30)-C(29)-C(34)	118.5(2)
C(34)-C(29)-P(2)	119.9(2)
C(29)-C(30)-C(31)	119.8(3)
C(32)-C(31)-C(30)	121.5(3)
C(31)-C(32)-C(33)	118.9(3)
C(32)-C(33)-C(34)	120.7(3)
C(33)-C(34)-C(29)	120.7(3)
C(36)-C(35)-P(2)	119.5(2)
C(40)-C(35)-P(2)	121.4(2)
C(40)-C(35)-C(36)	119.0(2)
C(37)-C(36)-C(35)	120.2(3)
C(38)-C(37)-C(36)	120.6(3)
C(39)-C(38)-C(37)	119.6(3)
C(38)-C(39)-C(40)	120.5(3)
C(35)-C(40)-C(39)	120.2(3)
Cl(2)-Co(2)-Cl(3A)	114.82(3)
Cl(2)-Co(2)-Cl(3)	110.68(3)
Cl(3)-Co(2)-Cl(3A)	91.14(3)
Cl(4)-Co(2)-Cl(2)	112.68(4)
Cl(4)-Co(2)-Cl(3A)	111.12(4)
Cl(4)-Co(2)-Cl(3)	114.76(4)
Co(2)-Cl(3)-Co(2A)	88.86(3)

Symmetry transformations used to generate equivalent “A” atoms: -x+1,-y,-z+1

Table S5. Anisotropic displacement parameters ($Å^2$ x 10^3) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	29(1)	21(1)	23(1)	0(1)	5(1)	-1(1)
Cl(1)	43(1)	30(1)	24(1)	2(1)	2(1)	-1(1)
P(1)	34(1)	23(1)	24(1)	-2(1)	4(1)	-3(1)
P(2)	29(1)	22(1)	27(1)	2(1)	5(1)	0(1)
N(1)	34(1)	22(1)	27(1)	1(1)	8(1)	1(1)
N(2)	28(1)	24(1)	32(1)	-2(1)	6(1)	-2(1)
C(1)	43(2)	32(1)	40(1)	4(1)	8(1)	8(1)
C(2)	35(1)	22(1)	33(1)	2(1)	8(1)	0(1)
C(3)	38(1)	24(1)	29(1)	2(1)	6(1)	-2(1)
C(4)	43(2)	32(1)	31(1)	6(1)	2(1)	2(1)
C(5)	51(2)	40(2)	25(1)	3(1)	2(1)	-5(1)
C(6)	46(2)	34(1)	27(1)	-3(1)	10(1)	-5(1)
C(7)	35(1)	25(1)	27(1)	-4(1)	7(1)	-6(1)
C(8)	35(1)	26(1)	33(1)	-4(1)	10(1)	-5(1)
C(9)	44(2)	40(2)	42(2)	-7(1)	17(1)	0(1)
C(10)	32(1)	20(1)	26(1)	0(1)	8(1)	-5(1)
C(11)	41(1)	30(1)	29(1)	-2(1)	12(1)	1(1)
C(12)	49(2)	26(1)	30(1)	-3(1)	13(1)	2(1)
C(13)	46(2)	28(1)	25(1)	-4(1)	6(1)	-4(1)
C(14)	37(1)	23(1)	37(1)	-2(1)	3(1)	-3(1)
C(15)	44(2)	39(2)	44(2)	9(1)	13(1)	4(1)
C(16)	46(2)	37(2)	74(2)	15(2)	21(2)	4(1)
C(17)	36(2)	36(2)	83(3)	-2(2)	2(2)	0(1)
C(18)	53(2)	60(2)	58(2)	-15(2)	-16(2)	11(2)
C(19)	46(2)	52(2)	40(2)	-9(1)	1(1)	5(1)
C(20)	34(1)	28(1)	31(1)	0(1)	3(1)	-6(1)
C(21)	39(1)	30(1)	41(1)	3(1)	10(1)	-2(1)
C(22)	42(2)	34(2)	56(2)	11(1)	11(1)	3(1)
C(23)	41(2)	44(2)	45(2)	18(1)	-2(1)	-9(1)
C(24)	51(2)	49(2)	28(1)	4(1)	2(1)	-19(1)
C(25)	49(2)	31(1)	32(1)	-1(1)	5(1)	-12(1)
C(26)	28(1)	35(1)	39(1)	-1(1)	4(1)	6(1)
C(27)	37(1)	28(1)	42(1)	2(1)	7(1)	7(1)
C(28)	38(1)	23(1)	34(1)	3(1)	4(1)	1(1)
C(29)	32(1)	26(1)	30(1)	3(1)	8(1)	-4(1)
C(30)	39(1)	37(1)	35(1)	-3(1)	6(1)	3(1)
C(31)	50(2)	47(2)	40(2)	-14(1)	9(1)	4(1)
C(32)	42(2)	51(2)	34(1)	-4(1)	5(1)	-10(1)
C(33)	39(2)	41(2)	38(1)	6(1)	-3(1)	-5(1)
C(34)	40(1)	26(1)	38(1)	1(1)	1(1)	-3(1)
C(35)	35(1)	23(1)	31(1)	-2(1)	6(1)	-4(1)
C(36)	39(1)	32(1)	42(1)	5(1)	12(1)	1(1)
C(37)	37(2)	41(2)	50(2)	1(1)	15(1)	3(1)
C(38)	41(2)	43(2)	39(1)	-5(1)	15(1)	-6(1)
C(39)	44(2)	38(1)	28(1)	-4(1)	9(1)	-9(1)
C(40)	37(1)	32(1)	28(1)	-1(1)	3(1)	-4(1)
Co(2)	38(1)	39(1)	31(1)	3(1)	2(1)	5(1)
Cl(2)	42(1)	50(1)	34(1)	2(1)	-2(1)	2(1)
Cl(3)	53(1)	34(1)	38(1)	5(1)	2(1)	-3(1)
Cl(4)	44(1)	97(1)	46(1)	-1(1)	5(1)	20(1)

Table S6. Hydrogen coordinates (x10^4) and isotropic displacement parameters (Å^2 x 10^3) for **1**.

	x	y	z	U(eq)
H(1A)	2763	6468	2845	57
H(1B)	2272	6090	2054	57
H(1C)	3076	6802	2095	57
H(4)	2940	5661	820	43
H(5)	3582	4884	-87	47
H(6)	4922	4010	252	42
H(9A)	7007	2934	1583	61
H(9B)	6444	3340	827	61
H(9C)	6028	2527	1195	61
H(11A)	4170	5242	4188	39
H(11B)	3317	5824	3779	39
H(12A)	4421	6901	3521	41
H(12B)	4513	6758	4402	41
H(13A)	5874	5924	4439	40
H(13B)	6025	6824	4058	40
H(15)	7551	5383	2364	50
H(16)	9177	5162	2690	61
H(17)	9901	5139	3949	63
H(18)	9006	5311	4889	72
H(19)	7378	5566	4579	57
H(21)	5616	7572	3043	43
H(22)	5534	8614	2098	52
H(23)	5833	8237	909	54
H(24)	6184	6802	652	52
H(25)	6168	5726	1572	45
H(26A)	6883	3367	3472	41
H(26B)	7225	3004	2740	41
H(27A)	6563	1866	3382	43
H(27B)	6002	1976	2550	43
H(28A)	5358	2452	3898	38
H(28B)	4874	1778	3291	38
H(30)	4560	1644	2005	44
H(31)	3804	1128	828	55
H(32)	2553	1886	119	51
H(33)	2046	3183	592	49
H(34)	2786	3716	1761	43
H(36)	2564	4086	2926	44
H(37)	1296	3956	3569	50
H(38)	1361	2966	4560	48
H(39)	2720	2133	4931	44
H(40)	3987	2233	4277	39

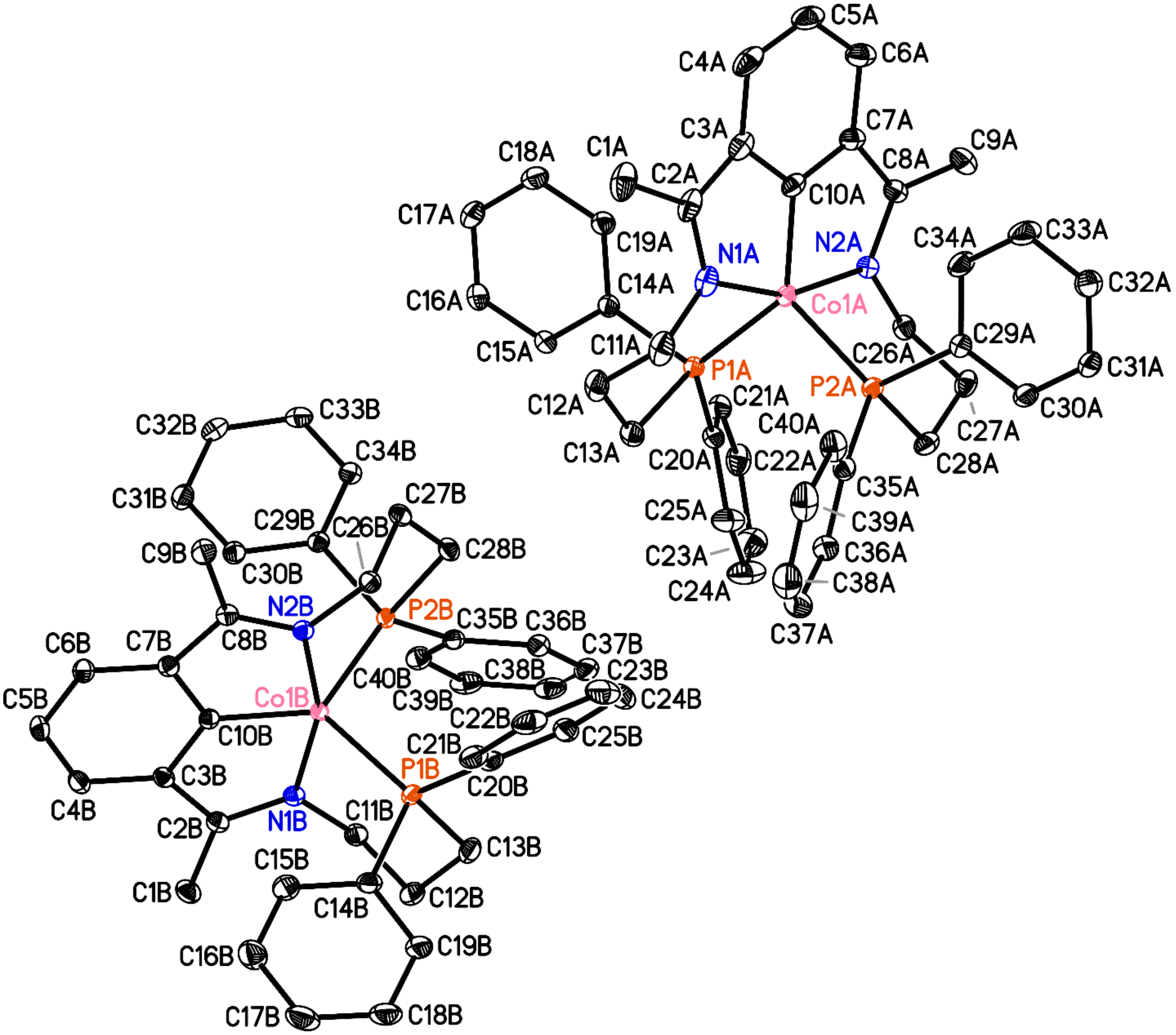


Figure S10. The molecular structure of **2** displayed at 30% probability ellipsoids. Two unique molecules (A and B) were located in the asymmetric unit. Hydrogen atoms are omitted for clarity.

Table S7. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1A)	4228(1)	3312(1)	2525(1)	18(1)
P(1A)	4870(1)	4258(1)	2557(1)	20(1)
P(2A)	3572(1)	3327(1)	1516(1)	20(1)
N(1A)	3526(1)	3687(1)	3185(1)	28(1)
N(2A)	4924(1)	2681(1)	2121(1)	20(1)
C(1A)	2992(1)	3604(1)	4372(1)	47(1)
C(2A)	3432(1)	3354(1)	3770(1)	32(1)
C(3A)	3808(1)	2724(1)	3780(1)	31(1)
C(4A)	3798(1)	2203(1)	4266(1)	41(1)
C(5A)	4165(1)	1612(1)	4128(1)	43(1)
C(6A)	4567(1)	1520(1)	3527(1)	36(1)
C(7A)	4606(1)	2043(1)	3051(1)	26(1)
C(8A)	5005(1)	2090(1)	2416(1)	24(1)
C(9A)	5466(1)	1529(1)	2134(1)	33(1)
C(10A)	4219(1)	2643(1)	3169(1)	24(1)
C(11A)	3138(1)	4328(1)	3088(1)	36(1)
C(12A)	3675(1)	4919(1)	3181(1)	37(1)
C(13A)	4231(1)	4989(1)	2596(1)	32(1)
C(14A)	5441(1)	4410(1)	3377(1)	23(1)
C(15A)	5878(1)	4986(1)	3478(1)	28(1)
C(16A)	6243(1)	5125(1)	4119(1)	35(1)
C(17A)	6166(1)	4691(1)	4671(1)	38(1)
C(18A)	5731(1)	4118(1)	4579(1)	33(1)
C(19A)	5373(1)	3975(1)	3933(1)	26(1)
C(20A)	5542(1)	4545(1)	1917(1)	25(1)
C(21A)	6307(1)	4348(1)	1963(1)	28(1)
C(22A)	6809(1)	4537(1)	1461(1)	35(1)
C(23A)	6551(1)	4930(1)	905(1)	43(1)
C(24A)	5794(1)	5122(1)	846(1)	48(1)
C(25A)	5291(1)	4931(1)	1345(1)	37(1)
C(26A)	5317(1)	2814(1)	1477(1)	24(1)
C(27A)	4783(1)	2768(1)	824(1)	28(1)
C(28A)	4191(1)	3332(1)	765(1)	27(1)
C(29A)	3008(1)	2572(1)	1319(1)	22(1)
C(30A)	2642(1)	2471(1)	666(1)	29(1)
C(31A)	2192(1)	1919(1)	530(1)	31(1)
C(32A)	2083(1)	1469(1)	1054(1)	42(1)
C(33A)	2453(1)	1557(1)	1705(1)	55(1)
C(34A)	2918(1)	2105(1)	1834(1)	37(1)
C(35A)	2828(1)	3941(1)	1283(1)	28(1)
C(36A)	2956(1)	4501(1)	883(1)	37(1)
C(37A)	2375(1)	4975(1)	776(1)	50(1)
C(38A)	1684(1)	4902(1)	1074(1)	54(1)
C(39A)	1551(1)	4352(1)	1480(1)	48(1)
C(40A)	2115(1)	3872(1)	1578(1)	36(1)
Co(1B)	5832(1)	8392(1)	2553(1)	16(1)
P(1B)	5135(1)	8322(1)	1569(1)	21(1)
P(2B)	6537(1)	7482(1)	2642(1)	17(1)
N(1B)	6497(1)	9022(1)	2096(1)	20(1)
N(2B)	5162(1)	8023(1)	3241(1)	18(1)
C(1B)	7018(1)	10183(1)	2074(1)	28(1)

C(2B)	6585(1)	9616(1)	2382(1)	21(1)
C(3B)	6218(1)	9672(1)	3033(1)	19(1)
C(4B)	6222(1)	10193(1)	3513(1)	24(1)
C(5B)	5848(1)	10114(1)	4133(1)	26(1)
C(6B)	5450(1)	9531(1)	4276(1)	24(1)
C(7B)	5430(1)	9011(1)	3796(1)	20(1)
C(8B)	5054(1)	8375(1)	3809(1)	20(1)
C(9B)	4583(1)	8151(1)	4402(1)	28(1)
C(10B)	5826(1)	9076(1)	3173(1)	18(1)
C(11B)	6854(1)	8884(1)	1434(1)	24(1)
C(12B)	6284(1)	8887(1)	802(1)	29(1)
C(13B)	5722(1)	8303(1)	796(1)	30(1)
C(14B)	4546(1)	9063(1)	1353(1)	27(1)
C(15B)	4500(1)	9574(1)	1831(1)	32(1)
C(16B)	4075(1)	10145(1)	1670(1)	41(1)
C(17B)	3696(1)	10210(1)	1024(1)	46(1)
C(18B)	3739(1)	9705(1)	542(1)	48(1)
C(19B)	4157(1)	9135(1)	703(1)	39(1)
C(20B)	4430(1)	7663(1)	1389(1)	26(1)
C(21B)	3687(1)	7737(1)	1616(1)	32(1)
C(22B)	3167(1)	7213(1)	1562(1)	41(1)
C(23B)	3381(1)	6616(1)	1280(1)	48(1)
C(24B)	4110(1)	6538(1)	1047(1)	44(1)
C(25B)	4636(1)	7055(1)	1104(1)	33(1)
C(26B)	4817(1)	7357(1)	3182(1)	21(1)
C(27B)	5403(1)	6807(1)	3340(1)	23(1)
C(28B)	5969(1)	6723(1)	2761(1)	23(1)
C(29B)	7169(1)	7448(1)	3441(1)	19(1)
C(30B)	7243(1)	7999(1)	3872(1)	23(1)
C(31B)	7737(1)	7987(1)	4464(1)	27(1)
C(32B)	8149(1)	7421(1)	4637(1)	26(1)
C(33B)	8071(1)	6862(1)	4216(1)	27(1)
C(34B)	7588(1)	6876(1)	3620(1)	24(1)
C(35B)	7230(1)	7214(1)	2010(1)	21(1)
C(36B)	7051(1)	6753(1)	1484(1)	26(1)
C(37B)	7575(1)	6614(1)	980(1)	33(1)
C(38B)	8277(1)	6936(1)	989(1)	34(1)
C(39B)	8462(1)	7394(1)	1506(1)	32(1)
C(40B)	7944(1)	7528(1)	2014(1)	26(1)

Table S8. Bond lengths (Å) determined for **2**.

Co(1A)-P(1A)	2.2107(4)	Co(1B)-P(1B)	2.2028(4)
Co(1A)-P(2A)	2.2043(4)	Co(1B)-P(2B)	2.2098(4)
Co(1A)-N(1A)	1.9573(13)	Co(1B)-N(1B)	1.9560(12)
Co(1A)-N(2A)	1.9446(12)	Co(1B)-N(2B)	1.9540(11)
Co(1A)-C(10A)	1.8293(15)	Co(1B)-C(10B)	1.8225(14)
P(1A)-C(13A)	1.8517(16)	P(1B)-C(13B)	1.8447(16)
P(1A)-C(14A)	1.8493(15)	P(1B)-C(14B)	1.8479(16)
P(1A)-C(20A)	1.8339(16)	P(1B)-C(20B)	1.8327(15)
P(2A)-C(28A)	1.8446(15)	P(2B)-C(28B)	1.8440(14)
P(2A)-C(29A)	1.8418(15)	P(2B)-C(29B)	1.8480(14)
P(2A)-C(35A)	1.8341(16)	P(2B)-C(35B)	1.8362(14)
N(1A)-C(2A)	1.326(2)	N(1B)-C(2B)	1.3220(19)
N(1A)-C(11A)	1.465(2)	N(1B)-C(11B)	1.4713(17)
N(2A)-C(8A)	1.3237(19)	N(2B)-C(8B)	1.3241(18)
N(2A)-C(26A)	1.4688(18)	N(2B)-C(26B)	1.4715(17)
C(1A)-C(2A)	1.507(2)	C(1B)-C(2B)	1.5059(19)
C(2A)-C(3A)	1.428(3)	C(2B)-C(3B)	1.4364(19)
C(3A)-C(4A)	1.405(2)	C(3B)-C(4B)	1.397(2)
C(3A)-C(10A)	1.415(2)	C(3B)-C(10B)	1.4138(19)
C(4A)-C(5A)	1.382(3)	C(4B)-C(5B)	1.395(2)
C(5A)-C(6A)	1.394(3)	C(5B)-C(6B)	1.399(2)
C(6A)-C(7A)	1.399(2)	C(6B)-C(7B)	1.395(2)
C(7A)-C(8A)	1.438(2)	C(7B)-C(8B)	1.4398(19)
C(7A)-C(10A)	1.408(2)	C(7B)-C(10B)	1.4168(18)
C(8A)-C(9A)	1.502(2)	C(8B)-C(9B)	1.5057(19)
C(11A)-C(12A)	1.521(3)	C(11B)-C(12B)	1.532(2)
C(12A)-C(13A)	1.528(2)	C(12B)-C(13B)	1.532(2)
C(14A)-C(15A)	1.396(2)	C(14B)-C(15B)	1.384(2)
C(14A)-C(19A)	1.391(2)	C(14B)-C(19B)	1.401(2)
C(15A)-C(16A)	1.388(2)	C(15B)-C(16B)	1.397(2)
C(16A)-C(17A)	1.386(2)	C(16B)-C(17B)	1.383(3)
C(17A)-C(18A)	1.387(2)	C(17B)-C(18B)	1.380(3)
C(18A)-C(19A)	1.394(2)	C(18B)-C(19B)	1.386(3)
C(20A)-C(21A)	1.393(2)	C(20B)-C(21B)	1.396(2)
C(20A)-C(25A)	1.398(2)	C(20B)-C(25B)	1.396(2)
C(21A)-C(22A)	1.387(2)	C(21B)-C(22B)	1.392(2)
C(22A)-C(23A)	1.387(3)	C(22B)-C(23B)	1.377(3)
C(23A)-C(24A)	1.378(3)	C(23B)-C(24B)	1.380(3)
C(24A)-C(25A)	1.385(3)	C(24B)-C(25B)	1.389(2)
C(26A)-C(27A)	1.529(2)	C(26B)-C(27B)	1.528(2)
C(27A)-C(28A)	1.535(2)	C(27B)-C(28B)	1.533(2)
C(29A)-C(30A)	1.397(2)	C(29B)-C(30B)	1.388(2)
C(29A)-C(34A)	1.379(2)	C(29B)-C(34B)	1.398(2)
C(30A)-C(31A)	1.379(2)	C(30B)-C(31B)	1.395(2)
C(31A)-C(32A)	1.374(2)	C(31B)-C(32B)	1.381(2)
C(32A)-C(33A)	1.392(3)	C(32B)-C(33B)	1.389(2)
C(33A)-C(34A)	1.385(2)	C(33B)-C(34B)	1.389(2)
C(35A)-C(36A)	1.390(2)	C(35B)-C(36B)	1.397(2)
C(35A)-C(40A)	1.400(2)	C(35B)-C(40B)	1.398(2)
C(36A)-C(37A)	1.401(3)	C(36B)-C(37B)	1.391(2)
C(37A)-C(38A)	1.369(3)	C(37B)-C(38B)	1.386(3)
C(38A)-C(39A)	1.381(3)	C(38B)-C(39B)	1.383(3)
C(39A)-C(40A)	1.385(3)	C(39B)-C(40B)	1.390(2)

Table S9. Angles (°) determined for **2**.

P(2A)-Co(1A)-P(1A)	104.688(16)
N(1A)-Co(1A)-P(1A)	88.97(4)
N(1A)-Co(1A)-P(2A)	104.45(4)
N(2A)-Co(1A)-P(1A)	104.31(4)
N(2A)-Co(1A)-P(2A)	88.07(4)
N(2A)-Co(1A)-N(1A)	159.00(6)
C(10A)-Co(1A)-P(1A)	129.56(5)
C(10A)-Co(1A)-P(2A)	125.75(5)
C(10A)-Co(1A)-N(1A)	79.66(6)
C(10A)-Co(1A)-N(2A)	79.35(6)
C(13A)-P(1A)-Co(1A)	112.34(6)
C(14A)-P(1A)-Co(1A)	114.77(5)
C(14A)-P(1A)-C(13A)	97.76(7)
C(20A)-P(1A)-Co(1A)	126.44(5)
C(20A)-P(1A)-C(13A)	100.50(7)
C(20A)-P(1A)-C(14A)	100.55(7)
C(28A)-P(2A)-Co(1A)	112.91(5)
C(29A)-P(2A)-Co(1A)	114.74(5)
C(29A)-P(2A)-C(28A)	99.88(7)
C(35A)-P(2A)-Co(1A)	123.78(5)
C(35A)-P(2A)-C(28A)	103.98(7)
C(35A)-P(2A)-C(29A)	98.11(7)
C(2A)-N(1A)-Co(1A)	117.38(12)
C(2A)-N(1A)-C(11A)	118.53(14)
C(11A)-N(1A)-Co(1A)	123.99(11)
C(8A)-N(2A)-Co(1A)	118.26(10)
C(8A)-N(2A)-C(26A)	118.58(12)
C(26A)-N(2A)-Co(1A)	122.99(9)
N(1A)-C(2A)-C(1A)	124.76(18)
N(1A)-C(2A)-C(3A)	112.71(14)
C(3A)-C(2A)-C(1A)	122.53(17)
C(4A)-C(3A)-C(2A)	130.72(16)
C(4A)-C(3A)-C(10A)	119.20(17)
C(10A)-C(3A)-C(2A)	110.03(14)
C(5A)-C(4A)-C(3A)	119.69(16)
C(4A)-C(5A)-C(6A)	122.02(16)
C(5A)-C(6A)-C(7A)	118.92(18)
C(6A)-C(7A)-C(8A)	130.16(16)
C(6A)-C(7A)-C(10A)	120.15(15)
C(10A)-C(7A)-C(8A)	109.70(13)
N(2A)-C(8A)-C(7A)	112.02(13)
N(2A)-C(8A)-C(9A)	124.84(14)
C(7A)-C(8A)-C(9A)	123.14(14)
C(3A)-C(10A)-Co(1A)	119.84(13)
C(7A)-C(10A)-Co(1A)	120.20(11)
C(7A)-C(10A)-C(3A)	119.95(14)
N(1A)-C(11A)-C(12A)	113.21(13)
C(11A)-C(12A)-C(13A)	113.39(14)
C(12A)-C(13A)-P(1A)	111.21(12)
C(15A)-C(14A)-P(1A)	121.66(11)
C(19A)-C(14A)-P(1A)	119.09(11)
C(19A)-C(14A)-C(15A)	118.91(14)
C(16A)-C(15A)-C(14A)	121.02(15)
C(17A)-C(16A)-C(15A)	119.64(15)
C(16A)-C(17A)-C(18A)	119.93(15)
C(17A)-C(18A)-C(19A)	120.38(15)
C(14A)-C(19A)-C(18A)	120.10(15)
C(21A)-C(20A)-P(1A)	120.65(12)
C(21A)-C(20A)-C(25A)	118.12(15)
C(25A)-C(20A)-P(1A)	121.10(12)
C(22A)-C(21A)-C(20A)	120.93(16)
C(23A)-C(22A)-C(21A)	119.94(17)
C(24A)-C(23A)-C(22A)	119.94(17)
C(23A)-C(24A)-C(25A)	120.15(18)
C(24A)-C(25A)-C(20A)	120.90(17)
N(2A)-C(26A)-C(27A)	112.88(12)
C(26A)-C(27A)-C(28A)	113.52(12)
C(27A)-C(28A)-P(2A)	110.83(10)
C(30A)-C(29A)-P(2A)	121.43(12)
C(34A)-C(29A)-P(2A)	119.68(11)
C(34A)-C(29A)-C(30A)	118.84(14)
C(31A)-C(30A)-C(29A)	121.28(15)
C(32A)-C(31A)-C(30A)	119.41(15)
C(31A)-C(32A)-C(33A)	119.97(16)
C(34A)-C(33A)-C(32A)	120.35(17)
C(29A)-C(34A)-C(33A)	120.08(15)
C(36A)-C(35A)-P(2A)	123.41(13)
C(36A)-C(35A)-C(40A)	118.33(16)
C(40A)-C(35A)-P(2A)	117.99(13)
C(35A)-C(36A)-C(37A)	119.92(19)
C(38A)-C(37A)-C(36A)	120.8(2)
C(37A)-C(38A)-C(39A)	119.88(18)
C(38A)-C(39A)-C(40A)	119.9(2)
C(39A)-C(40A)-C(35A)	121.15(19)
P(1B)-Co(1B)-P(2B)	107.249(16)
N(1B)-Co(1B)-P(1B)	88.41(4)
N(1B)-Co(1B)-P(2B)	103.39(4)
N(2B)-Co(1B)-P(1B)	103.42(4)
N(2B)-Co(1B)-P(2B)	88.99(4)
N(2B)-Co(1B)-N(1B)	159.68(5)
C(10B)-Co(1B)-P(1B)	126.09(4)
C(10B)-Co(1B)-P(2B)	126.67(4)
C(10B)-Co(1B)-N(1B)	79.89(5)
C(10B)-Co(1B)-N(2B)	79.79(5)
C(13B)-P(1B)-Co(1B)	112.73(6)
C(13B)-P(1B)-C(14B)	99.30(8)
C(14B)-P(1B)-Co(1B)	114.80(5)
C(20B)-P(1B)-Co(1B)	123.14(5)
C(20B)-P(1B)-C(13B)	103.17(7)
C(20B)-P(1B)-C(14B)	100.38(7)
C(28B)-P(2B)-Co(1B)	113.29(5)
C(28B)-P(2B)-C(29B)	99.72(7)
C(29B)-P(2B)-Co(1B)	113.81(5)
C(35B)-P(2B)-Co(1B)	125.10(5)
C(35B)-P(2B)-C(28B)	102.42(7)
C(35B)-P(2B)-C(29B)	98.78(6)
C(2B)-N(1B)-Co(1B)	117.48(9)
C(2B)-N(1B)-C(11B)	118.96(12)

C(11B)-N(1B)-Co(1B)	123.43(9)
C(8B)-N(2B)-Co(1B)	117.95(9)
C(8B)-N(2B)-C(26B)	118.46(11)
C(26B)-N(2B)-Co(1B)	123.45(9)
N(1B)-C(2B)-C(1B)	124.98(13)
N(1B)-C(2B)-C(3B)	112.56(12)
C(3B)-C(2B)-C(1B)	122.46(13)
C(4B)-C(3B)-C(2B)	130.23(13)
C(4B)-C(3B)-C(10B)	119.83(13)
C(10B)-C(3B)-C(2B)	109.91(12)
C(5B)-C(4B)-C(3B)	119.48(14)
C(4B)-C(5B)-C(6B)	121.37(13)
C(7B)-C(6B)-C(5B)	119.80(13)
C(6B)-C(7B)-C(8B)	130.70(13)
C(6B)-C(7B)-C(10B)	119.41(13)
C(10B)-C(7B)-C(8B)	109.89(12)
N(2B)-C(8B)-C(7B)	112.19(12)
N(2B)-C(8B)-C(9B)	124.69(13)
C(7B)-C(8B)-C(9B)	123.11(13)
C(3B)-C(10B)-Co(1B)	119.92(10)
C(3B)-C(10B)-C(7B)	120.06(12)
C(7B)-C(10B)-Co(1B)	120.02(10)
N(1B)-C(11B)-C(12B)	113.44(12)
C(11B)-C(12B)-C(13B)	113.24(13)
C(12B)-C(13B)-P(1B)	111.02(11)
C(15B)-C(14B)-P(1B)	120.03(12)
C(15B)-C(14B)-C(19B)	118.27(15)
C(19B)-C(14B)-P(1B)	121.67(13)
C(14B)-C(15B)-C(16B)	120.76(16)
C(17B)-C(16B)-C(15B)	120.26(18)
C(18B)-C(17B)-C(16B)	119.52(18)
C(17B)-C(18B)-C(19B)	120.37(17)
C(18B)-C(19B)-C(14B)	120.81(17)
C(21B)-C(20B)-P(1B)	119.38(13)
C(25B)-C(20B)-P(1B)	121.67(13)
C(25B)-C(20B)-C(21B)	118.51(15)
C(22B)-C(21B)-C(20B)	120.58(18)
C(23B)-C(22B)-C(21B)	120.16(19)
C(22B)-C(23B)-C(24B)	119.95(17)
C(23B)-C(24B)-C(25B)	120.43(19)
C(24B)-C(25B)-C(20B)	120.36(18)
N(2B)-C(26B)-C(27B)	112.17(11)
C(26B)-C(27B)-C(28B)	112.68(12)
C(27B)-C(28B)-P(2B)	111.61(10)
C(30B)-C(29B)-P(2B)	120.04(11)
C(30B)-C(29B)-C(34B)	118.63(13)
C(34B)-C(29B)-P(2B)	121.33(11)
C(29B)-C(30B)-C(31B)	120.59(14)
C(32B)-C(31B)-C(30B)	120.41(14)
C(31B)-C(32B)-C(33B)	119.54(14)
C(34B)-C(33B)-C(32B)	120.15(14)
C(33B)-C(34B)-C(29B)	120.66(14)
C(36B)-C(35B)-P(2B)	122.86(11)
C(36B)-C(35B)-C(40B)	118.22(13)
C(40B)-C(35B)-P(2B)	118.67(11)
C(37B)-C(36B)-C(35B)	120.34(15)
C(38B)-C(37B)-C(36B)	120.59(16)
C(39B)-C(38B)-C(37B)	119.76(14)
C(38B)-C(39B)-C(40B)	119.78(16)
C(39B)-C(40B)-C(35B)	121.30(15)

Table S10. Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1A)	17(1)	22(1)	16(1)	-1(1)	2(1)	1(1)
P(1A)	22(1)	18(1)	20(1)	-1(1)	-2(1)	3(1)
P(2A)	21(1)	22(1)	19(1)	1(1)	-1(1)	0(1)
N(1A)	19(1)	38(1)	28(1)	-9(1)	3(1)	0(1)
N(2A)	18(1)	22(1)	22(1)	0(1)	1(1)	0(1)
C(1A)	45(1)	60(1)	36(1)	-17(1)	21(1)	-16(1)
C(2A)	24(1)	50(1)	24(1)	-10(1)	9(1)	-13(1)
C(3A)	27(1)	43(1)	22(1)	-2(1)	3(1)	-15(1)
C(4A)	43(1)	60(1)	21(1)	5(1)	4(1)	-25(1)
C(5A)	52(1)	44(1)	32(1)	16(1)	-6(1)	-21(1)
C(6A)	38(1)	34(1)	36(1)	11(1)	-10(1)	-11(1)
C(7A)	23(1)	27(1)	26(1)	5(1)	-6(1)	-6(1)
C(8A)	21(1)	22(1)	29(1)	2(1)	-3(1)	-2(1)
C(9A)	32(1)	23(1)	44(1)	0(1)	0(1)	4(1)
C(10A)	21(1)	32(1)	19(1)	2(1)	-1(1)	-9(1)
C(11A)	25(1)	49(1)	36(1)	-14(1)	2(1)	13(1)
C(12A)	37(1)	36(1)	37(1)	-13(1)	-4(1)	18(1)
C(13A)	36(1)	26(1)	32(1)	-3(1)	-7(1)	12(1)
C(14A)	25(1)	21(1)	23(1)	-2(1)	-3(1)	3(1)
C(15A)	39(1)	19(1)	25(1)	0(1)	-3(1)	-1(1)
C(16A)	47(1)	25(1)	32(1)	-4(1)	-7(1)	-7(1)
C(17A)	50(1)	38(1)	24(1)	-2(1)	-11(1)	-5(1)
C(18A)	41(1)	32(1)	26(1)	6(1)	-7(1)	-3(1)
C(19A)	27(1)	24(1)	27(1)	1(1)	-3(1)	0(1)
C(20A)	30(1)	19(1)	25(1)	0(1)	-2(1)	-4(1)
C(21A)	30(1)	26(1)	28(1)	-3(1)	-2(1)	-2(1)
C(22A)	30(1)	38(1)	37(1)	-8(1)	2(1)	-8(1)
C(23A)	47(1)	45(1)	38(1)	7(1)	9(1)	-16(1)
C(24A)	51(1)	51(1)	42(1)	23(1)	1(1)	-7(1)
C(25A)	36(1)	38(1)	38(1)	14(1)	-3(1)	-2(1)
C(26A)	23(1)	24(1)	25(1)	-3(1)	7(1)	1(1)
C(27A)	29(1)	34(1)	21(1)	-5(1)	7(1)	-4(1)
C(28A)	28(1)	33(1)	19(1)	3(1)	1(1)	-5(1)
C(29A)	21(1)	24(1)	22(1)	-1(1)	1(1)	0(1)
C(30A)	34(1)	30(1)	23(1)	3(1)	-4(1)	-5(1)
C(31A)	34(1)	33(1)	24(1)	-2(1)	-6(1)	-4(1)
C(32A)	52(1)	34(1)	36(1)	4(1)	-14(1)	-19(1)
C(33A)	82(2)	46(1)	35(1)	17(1)	-22(1)	-36(1)
C(34A)	46(1)	40(1)	24(1)	4(1)	-9(1)	-17(1)
C(35A)	30(1)	26(1)	27(1)	-3(1)	-8(1)	4(1)
C(36A)	49(1)	28(1)	32(1)	0(1)	-10(1)	3(1)
C(37A)	75(2)	30(1)	44(1)	-1(1)	-18(1)	13(1)
C(38A)	55(1)	48(1)	58(1)	-14(1)	-25(1)	26(1)
C(39A)	32(1)	54(1)	56(1)	-21(1)	-14(1)	13(1)
C(40A)	27(1)	38(1)	42(1)	-7(1)	-7(1)	4(1)
Co(1B)	18(1)	15(1)	14(1)	0(1)	1(1)	-3(1)
P(1B)	26(1)	21(1)	16(1)	1(1)	-3(1)	-4(1)
P(2B)	20(1)	15(1)	16(1)	-1(1)	2(1)	-2(1)
N(1B)	21(1)	20(1)	19(1)	2(1)	2(1)	-1(1)
N(2B)	17(1)	18(1)	19(1)	1(1)	1(1)	-1(1)
C(1B)	31(1)	21(1)	31(1)	3(1)	5(1)	-5(1)

C(2B)	20(1)	19(1)	23(1)	2(1)	1(1)	-1(1)
C(3B)	18(1)	17(1)	22(1)	1(1)	-1(1)	1(1)
C(4B)	26(1)	17(1)	28(1)	-1(1)	-1(1)	0(1)
C(5B)	33(1)	20(1)	26(1)	-6(1)	1(1)	3(1)
C(6B)	28(1)	23(1)	22(1)	-2(1)	5(1)	4(1)
C(7B)	19(1)	20(1)	20(1)	1(1)	1(1)	2(1)
C(8B)	18(1)	22(1)	20(1)	1(1)	3(1)	1(1)
C(9B)	29(1)	29(1)	25(1)	-1(1)	10(1)	-3(1)
C(10B)	16(1)	19(1)	18(1)	0(1)	-2(1)	1(1)
C(11B)	29(1)	22(1)	22(1)	2(1)	8(1)	-4(1)
C(12B)	39(1)	30(1)	19(1)	2(1)	7(1)	-4(1)
C(13B)	41(1)	32(1)	18(1)	-3(1)	2(1)	-8(1)
C(14B)	30(1)	24(1)	26(1)	6(1)	-5(1)	-6(1)
C(15B)	29(1)	33(1)	31(1)	1(1)	-6(1)	2(1)
C(16B)	41(1)	34(1)	48(1)	-2(1)	-10(1)	6(1)
C(17B)	50(1)	30(1)	57(1)	14(1)	-17(1)	2(1)
C(18B)	64(1)	36(1)	42(1)	15(1)	-24(1)	-6(1)
C(19B)	55(1)	29(1)	30(1)	6(1)	-16(1)	-6(1)
C(20B)	33(1)	25(1)	20(1)	5(1)	-9(1)	-6(1)
C(21B)	33(1)	36(1)	26(1)	8(1)	-6(1)	-8(1)
C(22B)	33(1)	50(1)	38(1)	18(1)	-14(1)	-15(1)
C(23B)	51(1)	36(1)	53(1)	18(1)	-28(1)	-22(1)
C(24B)	57(1)	23(1)	50(1)	5(1)	-26(1)	-6(1)
C(25B)	39(1)	25(1)	32(1)	3(1)	-15(1)	-2(1)
C(26B)	22(1)	21(1)	22(1)	1(1)	1(1)	-6(1)
C(27B)	26(1)	18(1)	25(1)	2(1)	3(1)	-6(1)
C(28B)	25(1)	18(1)	26(1)	-1(1)	2(1)	-4(1)
C(29B)	20(1)	21(1)	18(1)	2(1)	4(1)	-2(1)
C(30B)	24(1)	23(1)	23(1)	-1(1)	-2(1)	2(1)
C(31B)	29(1)	29(1)	22(1)	-3(1)	-2(1)	-1(1)
C(32B)	22(1)	37(1)	18(1)	4(1)	0(1)	-1(1)
C(33B)	28(1)	28(1)	24(1)	7(1)	2(1)	5(1)
C(34B)	27(1)	22(1)	22(1)	1(1)	2(1)	2(1)
C(35B)	25(1)	20(1)	18(1)	2(1)	2(1)	3(1)
C(36B)	34(1)	22(1)	21(1)	0(1)	1(1)	4(1)
C(37B)	52(1)	28(1)	20(1)	1(1)	4(1)	13(1)
C(38B)	40(1)	38(1)	25(1)	11(1)	14(1)	20(1)
C(39B)	27(1)	40(1)	30(1)	12(1)	8(1)	8(1)
C(40B)	25(1)	29(1)	24(1)	2(1)	3(1)	1(1)

Table S11. Hydrogen coordinates (x10^4) and isotropic displacement parameters (Å^2 x 10^3) for **2**.

	x	y	z	U(eq)
H(1AA)	2455	3611	4242	70
H(1AB)	3160	4044	4493	70
H(1AC)	3081	3315	4765	70
H(4A)	3547	2255	4678	49
H(5A)	4142	1266	4447	51
H(6A)	4806	1117	3443	44
H(9AA)	5998	1650	2149	50
H(9AB)	5294	1439	1661	50
H(9AC)	5400	1139	2413	50
H(11A)	2739	4363	3421	44
H(11B)	2894	4343	2624	44
H(12A)	3967	4873	3621	44
H(12B)	3372	5321	3204	44
H(13A)	4538	5386	2671	38
H(13B)	3943	5037	2154	38
H(15A)	5924	5281	3110	33
H(16A)	6538	5507	4178	42
H(17A)	6406	4783	5103	45
H(18A)	5678	3828	4951	40
H(19A)	5087	3588	3873	31
H(21A)	6484	4085	2335	34
H(22A)	7318	4401	1498	42
H(23A)	6889	5063	573	52
H(24A)	5619	5380	469	58
H(25A)	4780	5060	1298	45
H(26A)	5731	2497	1438	28
H(26B)	5541	3254	1503	28
H(27A)	4514	2347	828	33
H(27B)	5089	2776	417	33
H(28A)	3878	3279	337	32
H(28B)	4455	3755	744	32
H(30A)	2703	2782	315	35
H(31A)	1963	1852	88	37
H(32A)	1762	1106	973	50
H(33A)	2387	1247	2055	66
H(34A)	3169	2158	2268	44
H(36A)	3428	4562	686	44
H(37A)	2460	5344	498	60
H(38A)	1305	5223	1004	65
H(39A)	1084	4303	1687	58
H(40A)	2018	3499	1843	43
H(1BA)	7545	10059	2037	42
H(1BB)	6988	10566	2369	42
H(1BC)	6798	10285	1619	42
H(4B)	6472	10588	3420	29
H(5B)	5862	10457	4457	31
H(6B)	5200	9490	4690	29
H(9BA)	4065	8071	4233	42
H(9BB)	4588	8490	4754	42
H(9BC)	4797	7750	4598	42
H(11C)	7103	8453	1465	29
H(11D)	7247	9214	1364	29

H(12C)	6567	8874	380	35
H(12D)	5996	9299	800	35
H(13C)	6006	7889	789	36
H(13D)	5390	8323	378	36
H(15B)	4756	9536	2265	38
H(16B)	4045	10483	1997	49
H(17B)	3414	10591	916	55
H(18B)	3487	9748	107	58
H(19B)	4178	8797	375	47
H(21B)	3539	8139	1805	38
H(22B)	2674	7267	1716	49
H(23B)	3033	6266	1248	57
H(24B)	4250	6137	850	53
H(25B)	5129	6995	953	39
H(26C)	4595	7297	2714	26
H(26D)	4408	7323	3504	26
H(27C)	5134	6392	3403	28
H(27D)	5686	6909	3774	28
H(28C)	5688	6616	2328	28
H(28D)	6311	6356	2877	28
H(30B)	6960	8380	3765	28
H(31B)	7790	8363	4744	32
H(32B)	8477	7413	5033	31
H(33B)	8342	6477	4333	32
H(34B)	7544	6502	3337	28
H(36B)	6580	6537	1470	31
H(37B)	7453	6303	635	40
H(38B)	8622	6844	648	41
H(39B)	8932	7611	1514	38
H(40B)	8075	7832	2364	31

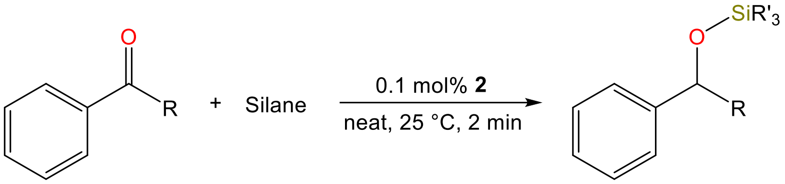
HYDROSILYLATION TRIALS

Hydrosilylation of benzaldehyde using 0.1 mol% Co(0) powder: In a glove box, a mixture of benzaldehyde (5.19 mL, 50.90 mmol) and $PhSiH_3$ (6.27 mL, 50.90 mmol) was added to a 20 mL scintillation vial containing Co(0) powder (3.0 mg, 0.051 mmol). The resulting mixture was allowed to stir at room temperature for 2 min and then exposed to air. The resulting solution was filtered through Celite and a ^1H NMR spectrum was collected in $CDCl_3$, which revealed no conversion.

Hydrosilylation of benzaldehyde using 0.1 mol% $CoCl_2$: In a glove box, a mixture of benzaldehyde (2.67 mL, 26.18 mmol) and $PhSiH_3$ (3.22 mL, 26.18 mmol) was added to a 20 mL scintillation vial containing $CoCl_2$ (3.4 mg, 0.00262 mmol). The resulting mixture was allowed to stir at room temperature for 2 min and then exposed to air. The resulting solution was filtered through Celite and a ^1H NMR spectrum was collected in $CDCl_3$, which revealed no conversion.

Hydrosilylation of benzaldehyde using 0.1 mol% $[(^{Ph_2PPr}ADI)CoCl][Co_2Cl_6]_{0.5}$: In a glove box, a mixture of benzaldehyde (1.22 mL, 11.96 mmol) and $PhSiH_3$ (1.47 mL, 11.96 mmol) was added to a 20 mL scintillation vial containing $[(^{Ph_2PPr}ADI)CoCl][Co_2Cl_6]_{0.5}$ (10.4 mg, 0.0119 mmol). The resulting mixture was allowed to stir at room temperature for 2 min and then exposed to air. The resulting solution was filtered through Celite and a ^1H NMR spectrum was collected in $CDCl_3$, which revealed no conversion.

General procedure for silane screening: In the glovebox, a neat equimolar solution of silane and benzaldehyde was added to a 20 mL scintillation vial containing 0.1 mol% of **2**. The resulting brown solution was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was then filtered through Celite directly into an NMR tube. The progress of the reaction was determined following analysis by ^1H NMR spectroscopy.



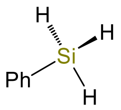
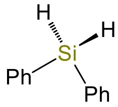
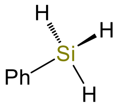
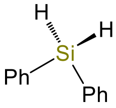
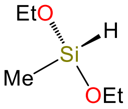
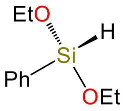
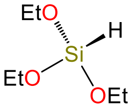
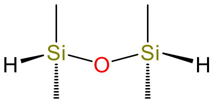
Entry	R	Silane	% Conversion
1	H		99%
2	H		99%
3	CH_3		99%
4	CH_3		45%
5	H		-
6	H		-
7	H		-
8	H		10%

Table S12. Percent conversion based on ^{1}H NMR integration of substrate against silyl ether intermediates.

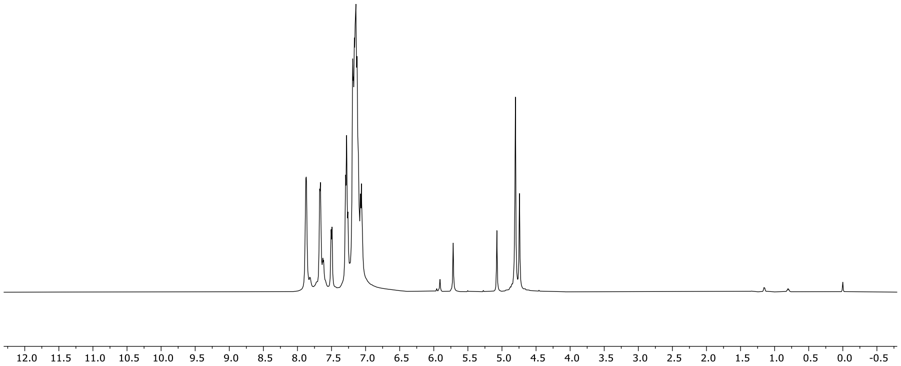


Figure S11. ^{1}H NMR spectrum of silyl ethers generated via **2**-catalyzed benzaldehyde hydrosilylation using diphenylsilane in benzene-d_6.

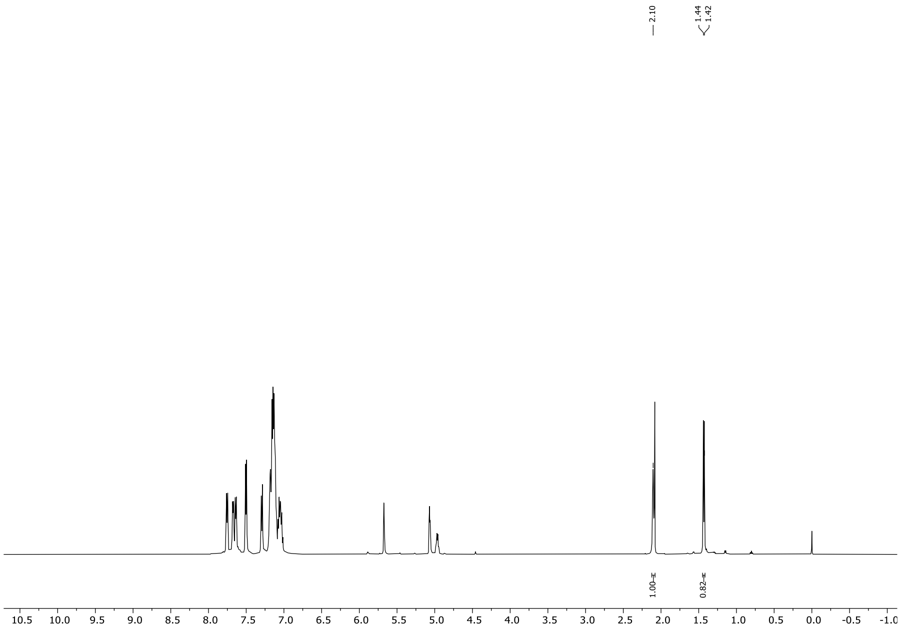


Figure S12. ^{1}H NMR spectrum of silyl ethers generated via **2**-catalyzed acetophenone hydrosilylation using diphenylsilane in benzene-d_6.

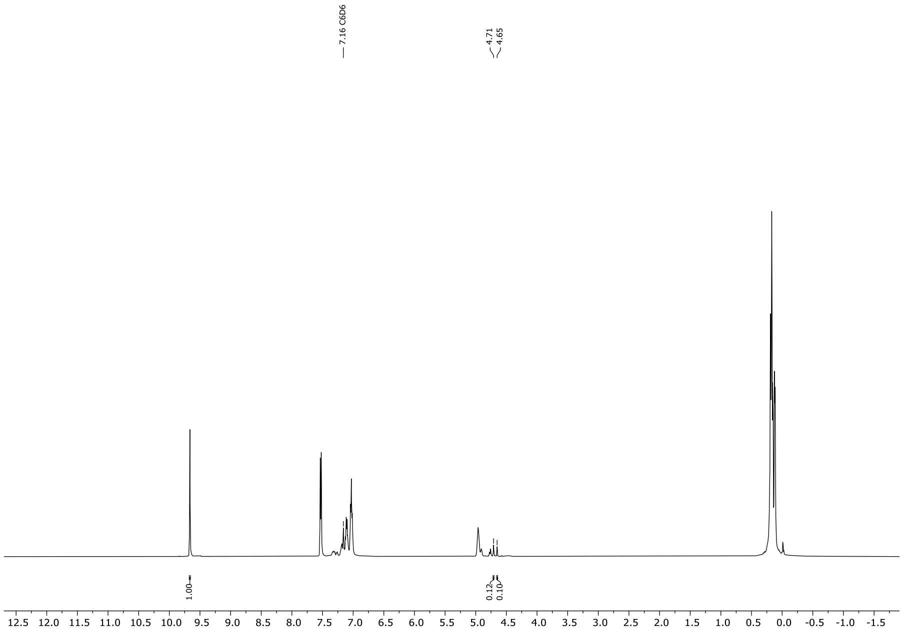


Figure S13. ^{1}H NMR spectrum of silyl ethers generated via **2**-catalyzed benzaldehyde hydrosilylation using 1,1,3,3-tetramethyldisiloxane in benzene-d_6.

Hydrosilylation of benzaldehyde using 0.1 mol% 2: In a glove box, a mixture of benzaldehyde (470 μL, 4.62 mmol) and $PhSiH_3$ (570 μL, 4.62 mmol) was added to a 20 mL scintillation vial containing **2** (3.1 mg, 0.00462 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 2 min and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was collected in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 3 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Evaporation of the solvent by rotary evaporation at 25 °C yielded a colorless liquid identified as benzyl alcohol[6] (430.12 mg, 4.01 mmol, 87%). ^{1}H NMR (400 MHz, benzene-d_6): 7.21 (d, 2H, *phenyl*), 7.14 (d, 2H, *phenyl*), 7.07 (d, 1H, *phenyl*), 4.38 (s, 2H, -CH_2), 3.76 (s, 1H, -OH). ^{13}C NMR (101 MHz, benzene-d_6): 141.60 (s, *phenyl*), 128.52 (s, *phenyl*), 127.41 (s, *phenyl*), 127.13 (s, *phenyl*), 64.56 (s, CH$_2$).

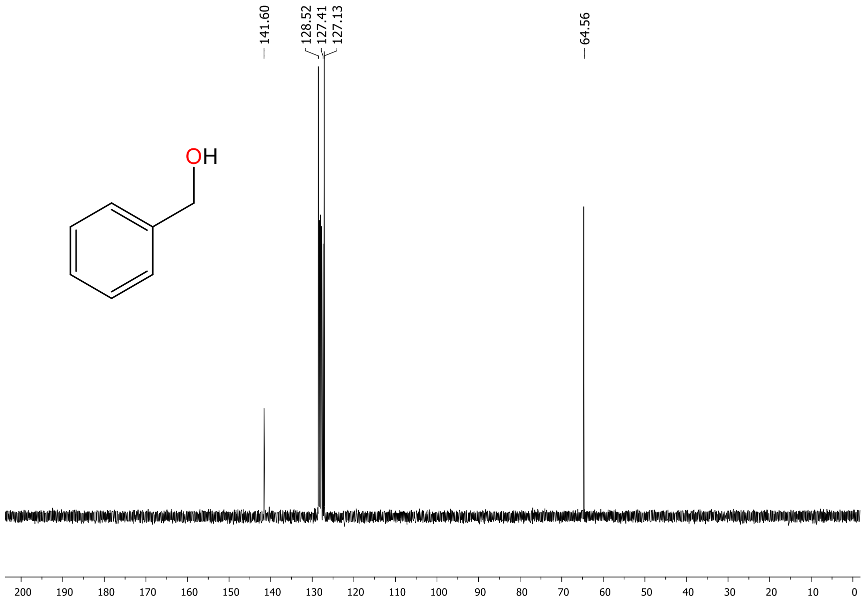


Figure S14. ^{1}H NMR spectrum of benzyl alcohol in benzene-d_6.

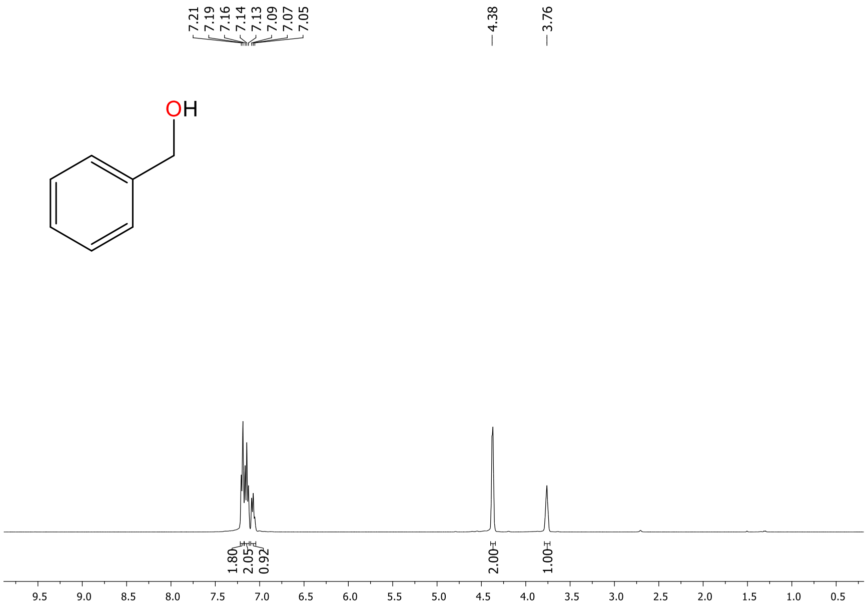


Figure S15. ^{13}C NMR spectrum of benzyl alcohol in benzene-d_6.

Atom-efficient hydrosilylation of benzaldehyde using 0.1 mol% 2: In a glove box, a mixture of benzaldehyde (0.47 mL, 4.62 mmol) and $PhSiH_3$ (0.19 mL, 1.52 mmol) was added to a scintillation vial containing **2** (0.0031 g, 0.0046 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 2 min and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^1H NMR spectrum was collected in benzene-d_6, which revealed greater than 99% conversion.

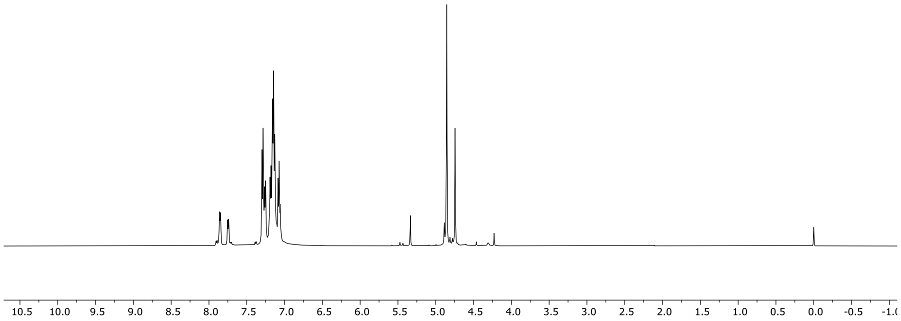


Figure S16. ^1H NMR spectrum of silyl ethers generated via **2**-catalyzed atom-efficient benzaldehyde hydrosilylation in benzene-d_6.

Hydrosilylation of 4-anisaldehyde using 0.1 mol% 2: In a glove box, a mixture of 4-anisaldehyde (0.39 mL, 3.28 mmol) and $PhSiH_3$ (0.4 mL, 3.28 mmol) was added to a 20 mL scintillation vial containing **2** (2.2 mg, 0.00328 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 2 min and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^1H NMR spectrum was collected in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 2 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Evaporation of the solvent by rotary evaporation at 25 °C yielded a colorless liquid identified as 4-methoxybenzyl alcohol[6] (389 mg, 2.81 mmol, 85%). ^1H NMR (400 MHz, benzene-d_6): 7.15 (d, J = 7.6 Hz, 2H, *phenyl*), 6.79 (d, J = 7.3 Hz, 2H, *phenyl*), 4.39 (s, 2H, -CH_2), 3.33 (s, 3H, -OCH_3), 2.11 (s, 1H, -OH). ^{13}C NMR (101 MHz, benzene-d_6): 159.49 (s, *phenyl*), 133.99 (s, *phenyl*), 128.62 (s, *phenyl*), 114.06 (s, *phenyl*), 64.67 (s, -CH_2), 54.74 (s, -OCH_3).

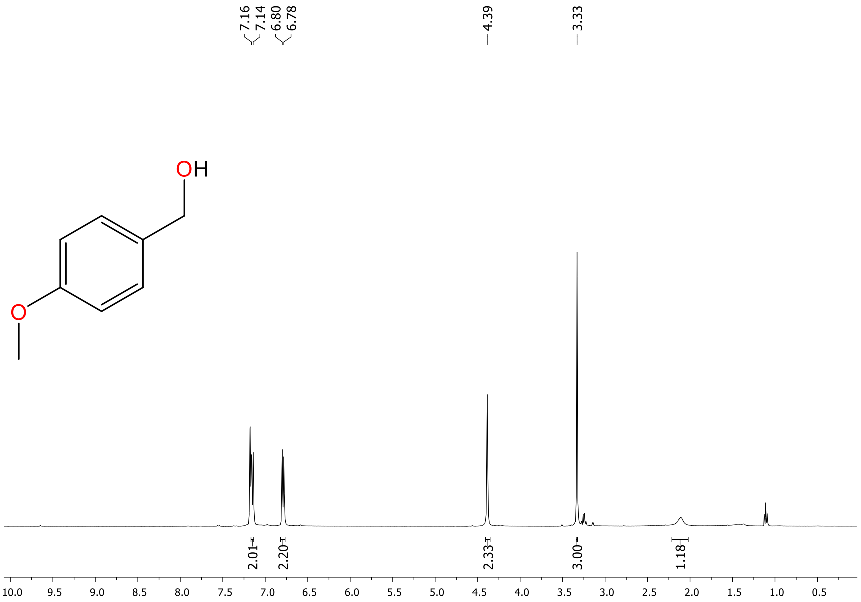


Figure S17. ^{1}H NMR spectrum of 4-methoxybenzyl alcohol in benzene-d_6.

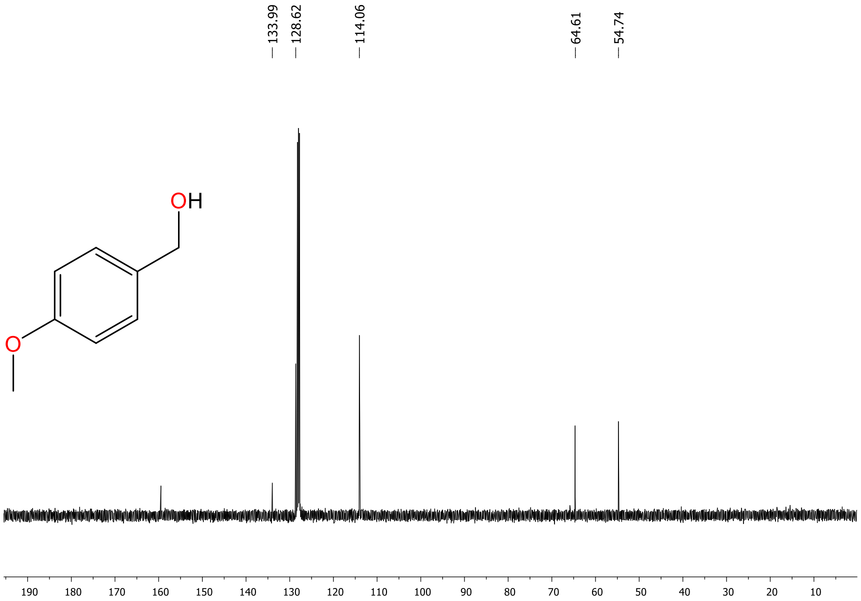


Figure S18. ^{13}C NMR spectrum of 4-methoxybenzyl alcohol in benzene-d_6.

Hydrosilylation of 4-methylbenzaldehyde using 0.1 mol% 2: In a glove box, a mixture of 4-methylbenzaldehyde (232 mg, 1.93 mmol) and $PhSiH_3$ (0.24 mL, 1.93 mmol) was added to a 20 mL scintillation vial containing **2** (1.3 mg, 0.00193 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 2 min and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was collected in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 2 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Evaporation of the solvent by rotary evaporation at 25 °C yielded a colorless liquid identified as 4-methylbenzyl alcohol[6] (221 mg, 1.81 mmol, 93%). ^{1}H NMR (400 MHz, benzene-d_6): 7.13 (d, J = 7.7 Hz, 2H, *phenyl*), 6.98 (d, J = 7.7 Hz, 2H, *phenyl*), 4.36 (s, 2H, -CH_2), 2.12 (s, 3H, -CH_3), 1.79 (s, 1H, -OH). ^{13}C NMR (101 MHz, benzene-d_6): 139.07 (s, *phenyl*), 136.93 (s, *phenyl*), 129.36 (s, *phenyl*), 127.28 (s, *phenyl*), 64.79 (s, -CH$_2$), 21.19 (s, -CH$_3$).

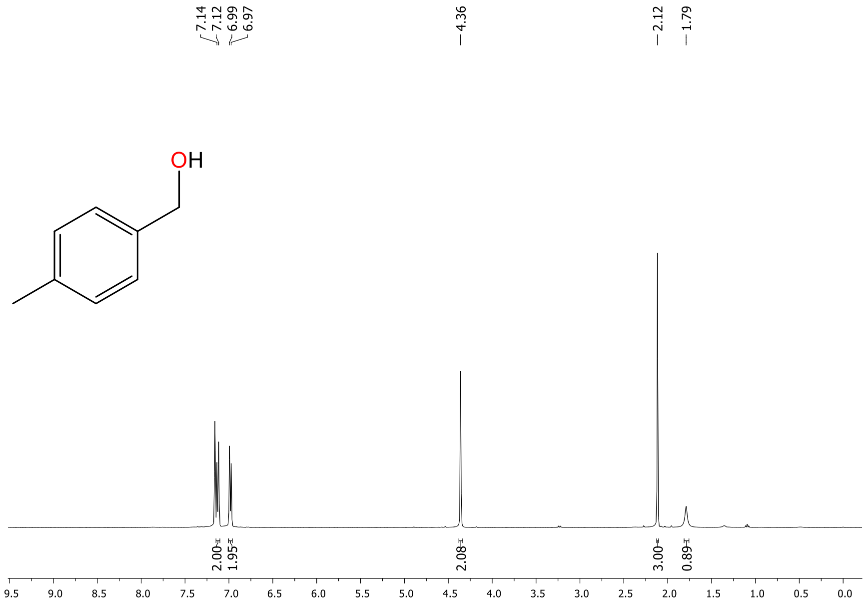


Figure S19. ^{1}H NMR spectrum of 4-methylbenzyl alcohol in benzene-d_6.

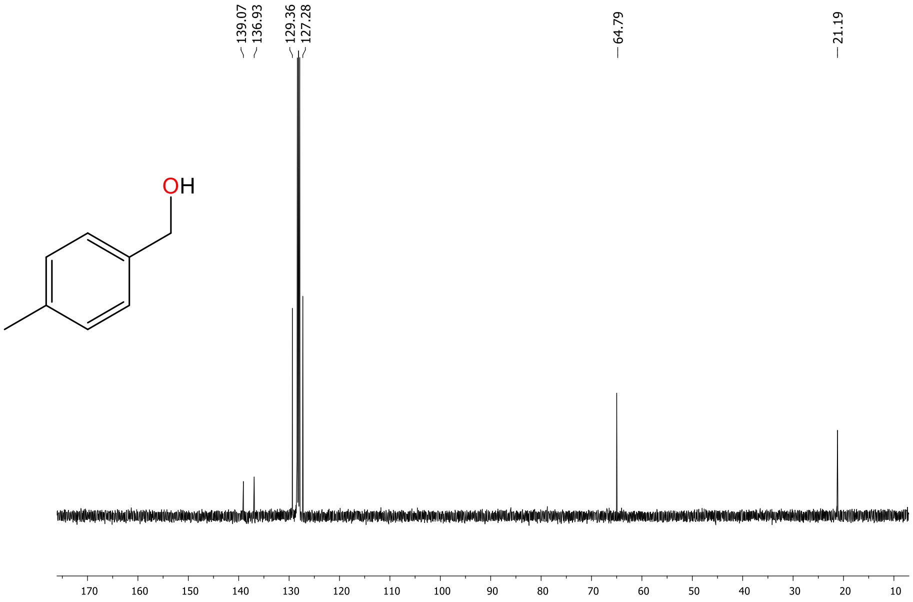


Figure S20. ${}^{13}C$ NMR spectrum of 4-methylbenzyl alcohol in benzene-d_6.

Hydrosilylation of 4-fluorobenzaldehyde using 0.1 mol% 2: In a glove box, a mixture of 4-fluorobenzaldehyde (0.27 mL, 2.68 mmol) and $PhSiH_3$ (0.33 mL, 2.68 mmol) was added to a 20 mL scintillation vial containing **2** (1.8 mg, 0.00268 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 2 min and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ${}^{1}H$ NMR spectrum was collected in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 2 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Evaporation of the solvent by rotary evaporation at 25 °C yielded a colorless liquid identified as 4-fluorobenzyl alcohol[6] (318 mg, 2.52 mmol, 94%). ${}^{1}H$ NMR (400 MHz, benzene-d_6): 6.91 (m, J = 16 Hz, 2H, *phenyl*), 6.78 (t, J = 8.1 Hz, 2H, *phenyl*), 4.15 (s, 2H, -CH_2), 1.36 (s, 1H, OH). ${}^{13}C$ NMR (101 MHz, benzene-d_6): 162.52 (d, J = 255.5 Hz, *phenyl*), 137.38 (s, *phenyl*), 128.75 (d, J = 8.0 Hz, *phenyl*), 115.33 (d, J = 21.2 Hz, *phenyl*), 64.12 (s, CH_2). ${}^{19}F$ NMR (376 MHz, benzene-d_6): -116.23 (s, Ph-F).

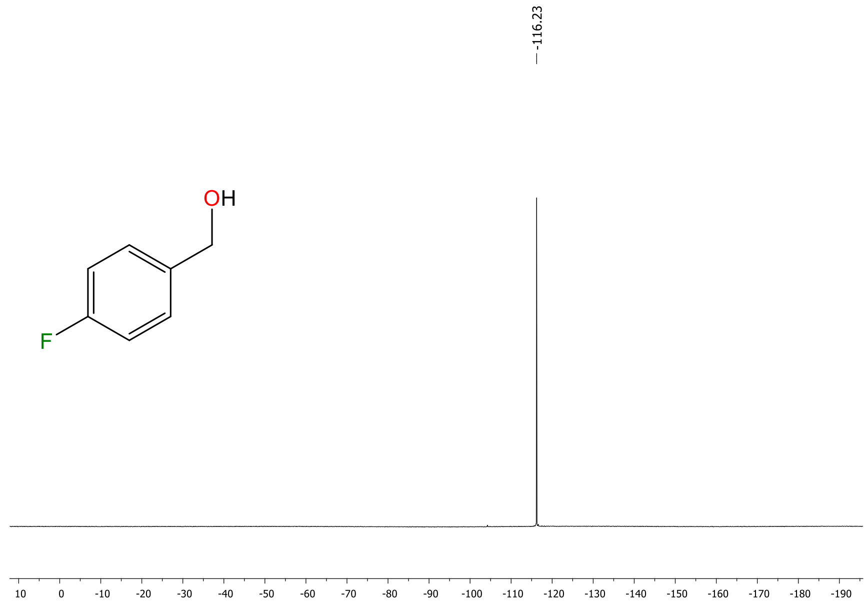


Figure S21. ^{1}H NMR spectrum of 4-fluorobenzyl alcohol in benzene-d_6.

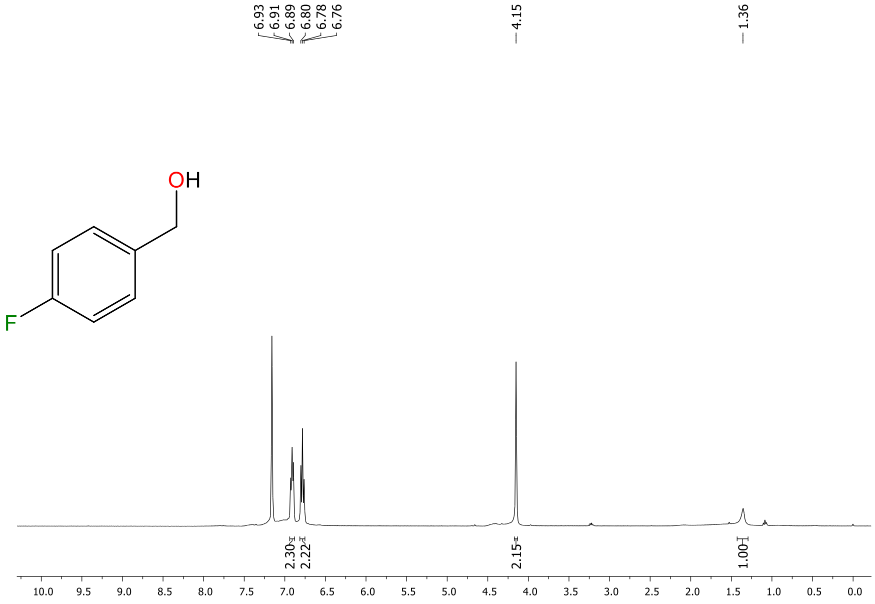


Figure S22. ^{13}C NMR spectrum of 4-fluorobenzyl alcohol in benzene-d_6.

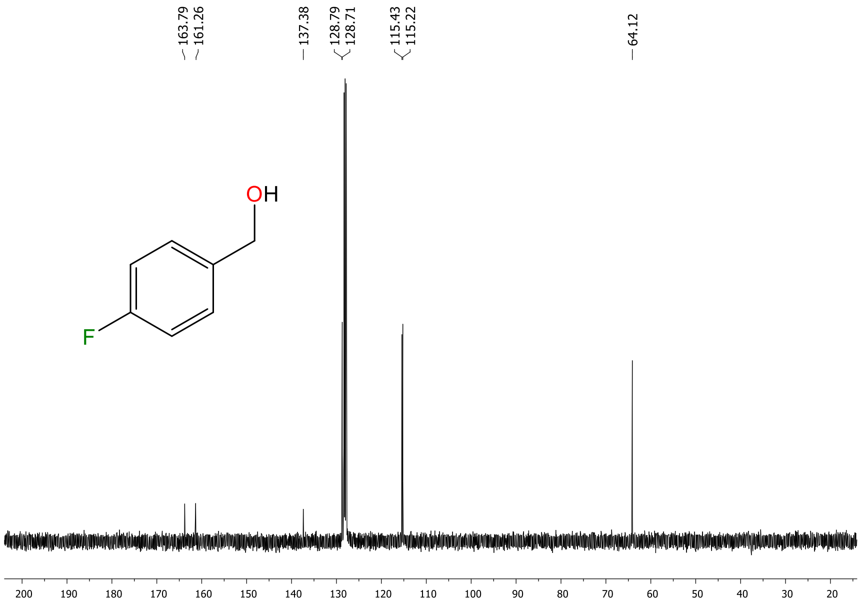


Figure S23. ^{19}F NMR spectrum of 4-fluorobenzyl alcohol in benzene-*d*$_6$.

Hydrosilylation of 4-chlorobenzaldehyde using 0.1 mol% 2: In a glove box, a mixture of 4-chlorobenzaldehyde (335 mg, 2.38 mmol) and $PhSiH_3$ (0.29 mL, 2.38 mmol) was added to a 20 mL scintillation vial containing **2** (1.6 mg, 0.00238 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 2 min and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was collected in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 2 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Evaporation of the solvent by rotary evaporation at 25 °C yielded a colorless liquid identified as 4-chlorobenzyl alcohol[6] (313 mg, 2.19 mmol, 91%). ^{1}H NMR (400 MHz, benzene-*d*$_6$): 7.10 (d, *J* = 7.8 Hz, 2H, *phenyl*), 6.86 (d, *J* = 7.8 Hz, 2H, *phenyl*), 4.14 (s, 2H, -C*H*$_2$), 1.77 (s, 1H, -O*H*). ^{13}C NMR (101 MHz, benzene-*d*$_6$): 140.21 (s, *phenyl*), 133.20 (s, *phenyl*), 128.69 (s, *phenyl*), 128.28 (s, *phenyl*), 64.03 (s, -*C*H$_2$).

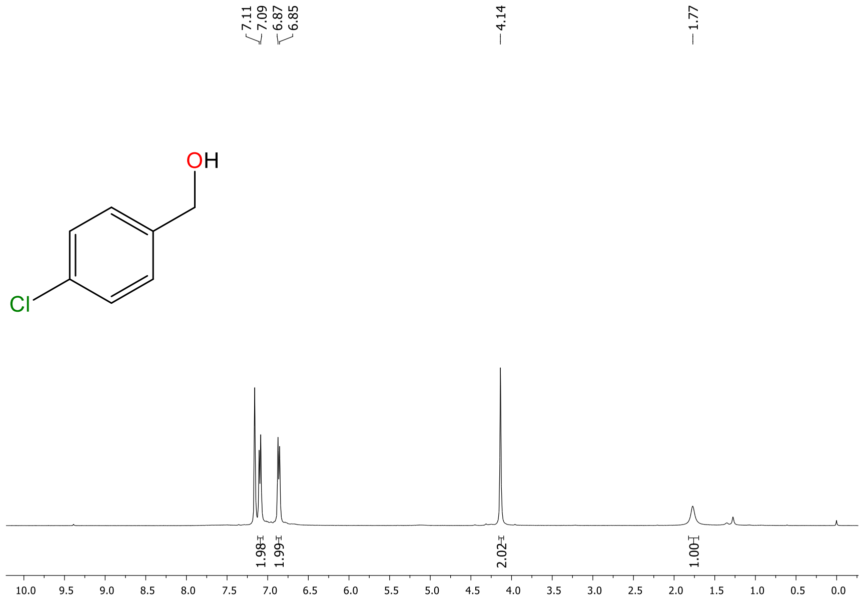


Figure S24. ^{1}H NMR spectrum of 4-chlorobenzyl alcohol in benzene-d_6.

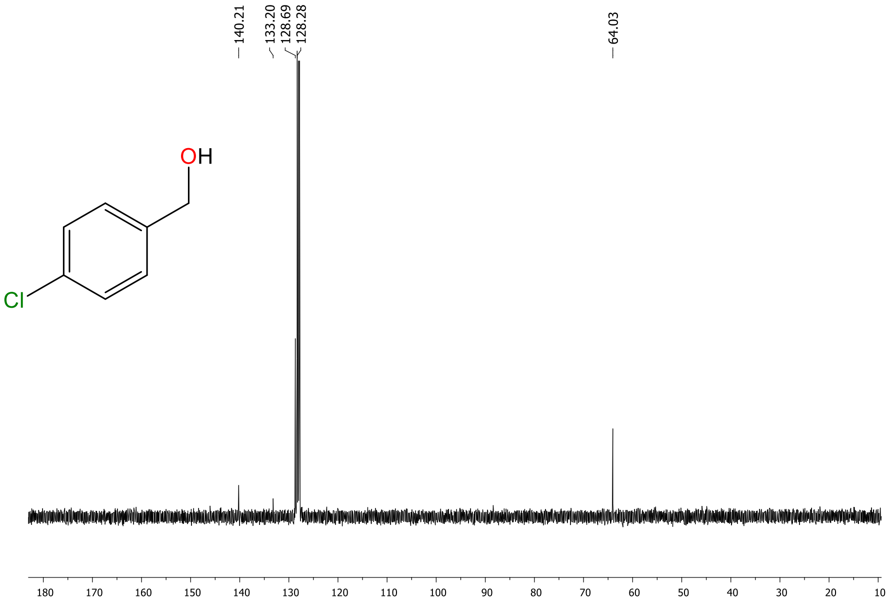


Figure S25. ^{13}C NMR spectrum of 4-chlorobenzyl alcohol in benzene-d_6.

Hydrosilylation of 4-bromobenzaldehyde using 0.1 mol% 2: In a glove box, a mixture of 4-bromobenzaldehyde (331 mg, 1.78 mmol) and $PhSiH_3$ (0.22 mL, 1.78 mmol) was added to a 20 mL scintillation vial containing **2** (1.2 mg, 0.00178 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 2 min and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was collected in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 2 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Evaporation of the solvent by rotary evaporation at 25 °C yielded a colorless liquid identified as 4-bromobenzyl alcohol[6] (298 mg, 1.59 mmol, 89%). ^{1}H NMR (400 MHz, benzene-d_6): 7.24 (d, J = 7.4 Hz, 2H, *phenyl*), 6.77 (d, J = 7.8 Hz, 2H, *phenyl*), 4.07 (s, 2H, -CH_2), 1.26 (s, 1H, -O*H*). ^{13}C NMR (101 MHz, benzene-d_6): 140.58 (s, *phenyl*), 131.59 (s, *phenyl*), 128.52 (s, *phenyl*), 121.26 (s, *phenyl*), 63.88 (s, *C*H_2).

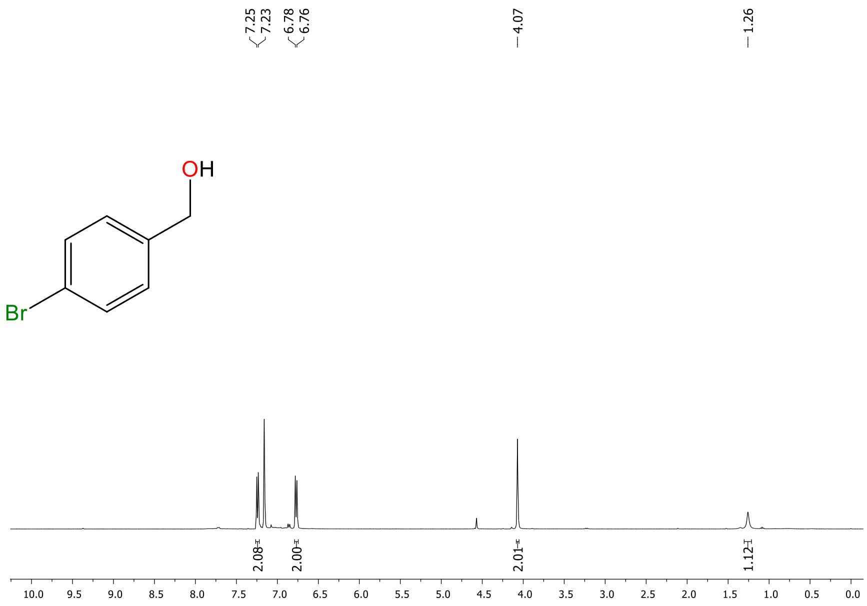


Figure S26. ^{1}H NMR spectrum of 4-bromobenzyl alcohol in benzene-d_6.

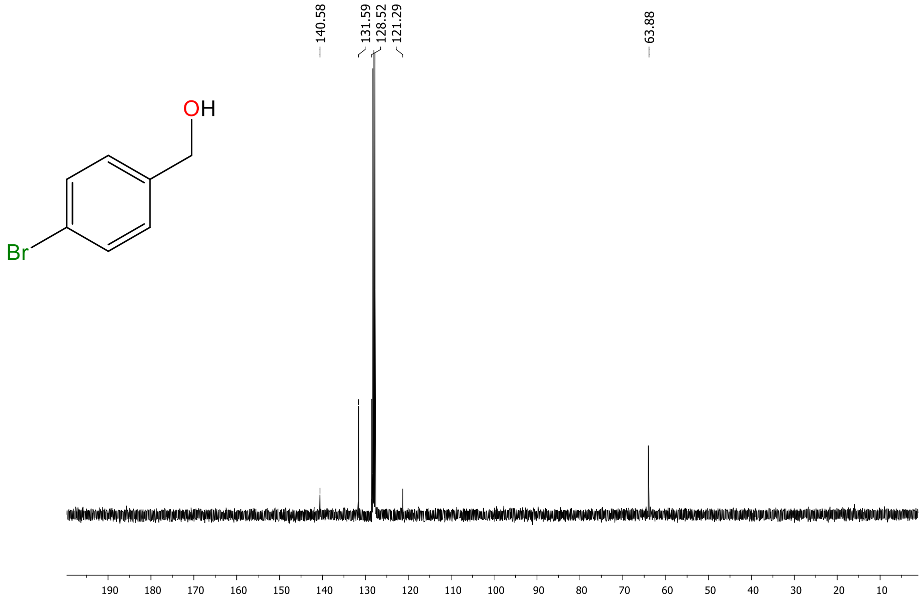


Figure S27. ^{13}C NMR spectrum of 4-bromobenzyl alcohol in benzene-d_6.

Hydrosilylation of 4-cyanobenzaldehyde using 0.1 mol% 2: In a glove box, a 20 mL scintillation vial was charged with 4-cyanobenzaldehyde (215 mg, 1.64 mmol) and $PhSiH_3$ (0.20 mL, 1.64 mmol) and the mixture was added to another scintillation vial containing **2** (1.1 mg, 0.00164 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 2 min and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was taken in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 2 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Evaporation of the solvent by rotary evaporation at 25 °C yielded a colorless liquid identified as 4-cyanobenzyl alcohol[6] (192 mg, 1.43 mmol, 87%). ^{1}H NMR (400 MHz, benzene-d_6): 7.08 (d, J = 7.6 Hz, 2H, *phenyl*), 6.95 (d, J = 8.1 Hz, 2H, *phenyl*), 4.28 (s, 2H, -CH_2), 2.98 (s, 1H, -O*H*). ^{13}C NMR (101 MHz, benzene-d_6): 147.01 (s, -*C*N), 132.02 (s, *phenyl*), 126.83 (s, *phenyl*), 119.14 (s, *phenyl*), 110.74 (s, *phenyl*), 63.63 (s, -CH_2).

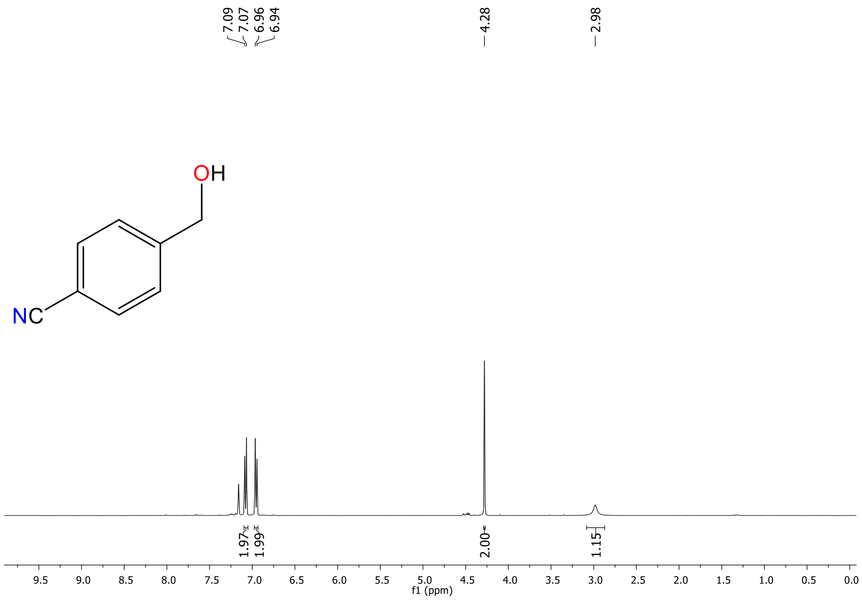


Figure S28. ^{1}H NMR spectrum of 4-cyanobenzyl alcohol in benzene-d_6.

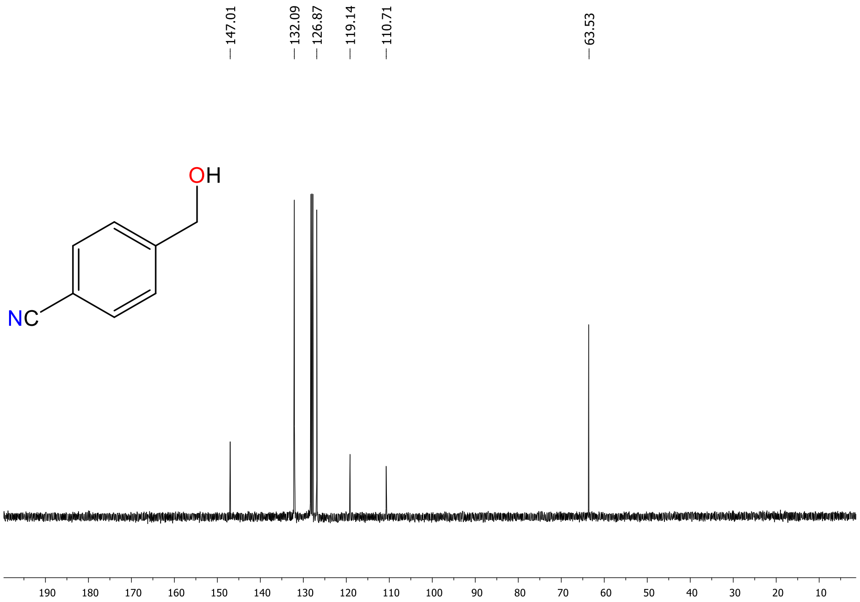


Figure S29. ^{13}C NMR spectrum of 4-cyanobenzyl alcohol in benzene-d_6.

Hydrosilylation of 1-naphthaldehyde using 0.1 mol% 2: In a glove box, a mixture of 1-naphthaldehyde (0.22 mL, 1.64 mmol) and $PhSiH_3$ (0.20 mL, 1.64 mmol) was added to a scintillation vial containing **2** (0.0011 g, 0.00164 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 2 min and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was collected in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 2 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Evaporation of the solvent by rotary evaporation at 25 °C yielded a white solid identified as 1-naphthalenemethanol[6] (221 mg, 1.39 mmol, 85%). ^{1}H NMR (400 MHz, benzene-d_6): 7.91 (d, *J* = 8.5 Hz, 1H, *aryl*), 7.62 (d, *J* = 9.2 Hz, 1H, *aryl*), 7.54 (d, *J* = 8.2 Hz, 1H, *aryl*), 7.29 (d, *J* = 6.8 Hz, 1H, *aryl*), 7.25 (d, *J* = 4.7 Hz, 1H, *aryl*), 7.19 (d, *J* = 7.5 Hz, 1H, *aryl*), 7.16 (s, 1H, *aryl*), 4.73 (s, 2H, -CH_2), 2.40 (s, 1H, -O*H*). ^{13}C NMR (101 MHz, benzene-d_6): 137.12 (s, *aryl*), 134.18 (s, *aryl*), 131.72 (s, *aryl*), 128.84 (s, *aryl*), 128.36 (s, *aryl*), 126.27 (s, *aryl*), 125.91 (s, *aryl*), 125.62 (s, *aryl*), 125.14 (s, *aryl*), 124.16 (s, *aryl*), 63.07 (s, -*C*H_2).

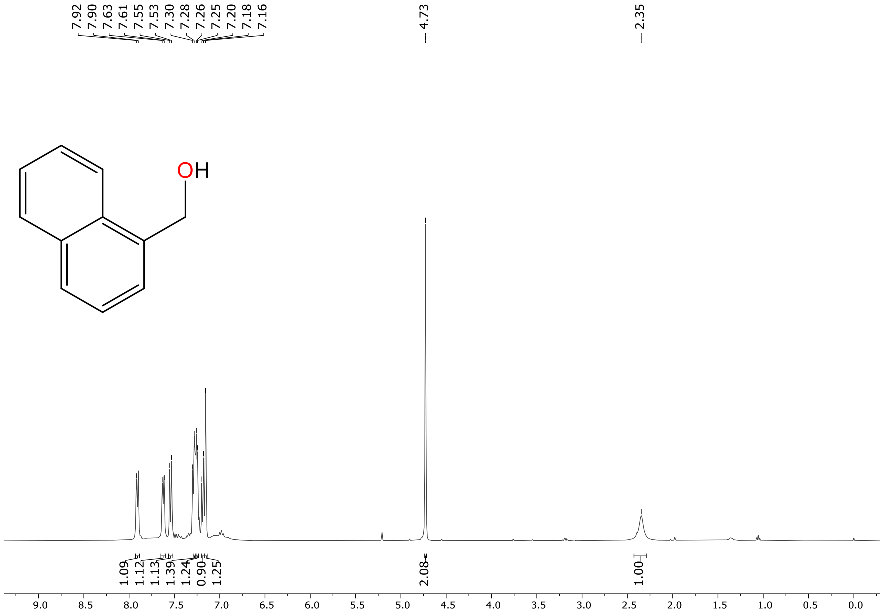


Figure S30. ^{1}H NMR spectrum of 1-naphthalenemethanol in benzene-d_6.

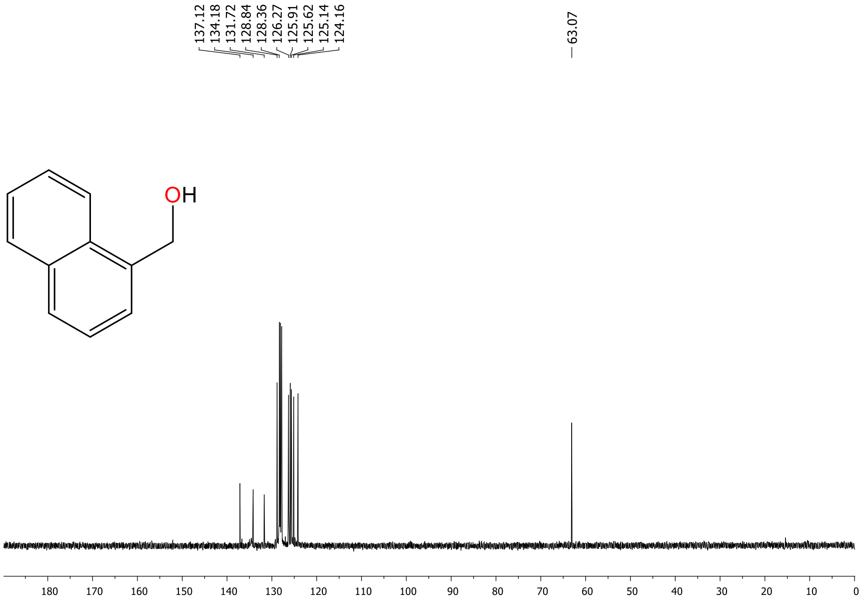


Figure S31. ^{13}C NMR spectrum of 1-naphthalenemethanol in benzene-d_6.

Hydrosilylation of 3,5-dimethylbenzaldehyde using 0.1 mol% 2: In a glove box, a mixture of 3,5-dimethylbenzaldehyde (0.72 mL, 5.37 mmol) and $PhSiH_3$ (0.66 mL, 5.37 mmol) was added to a scintillation vial containing **2** (0.0036 g, 0.0054 mmol). The resulting light orange solution was allowed to stir at room temperature for 4 h and then exposed to air to deactivate the catalyst. The solution was then filtered through Celite and a ^{1}H NMR spectrum was taken in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 3 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Rotary evaporation of the solvent at 25 °C yielded a colorless liquid identified as 3,5-dimethylbenzyl alcohol[7] (707 mg, 5.19 mmol, 97%). ^{1}H NMR (500 MHz, benzene-d_6): 6.87 (s, 2H, *phenyl*), 6.74 (s, 1H, *phenyl*), 4.42 (s, 2H, -CH_2), 2.86 (s, 1H, -O*H*), 2.14 (s, 6H, -CH_3). ^{13}C NMR (126 MHz, benzene-d_6): 141.74 (s, *phenyl*), 137.80 (s, *phenyl*), 129.14 (s, *phenyl*), 125.12 (s, *phenyl*), 65.02 (s, -*C*H_2), 21.31 (s, -*C*H_3).

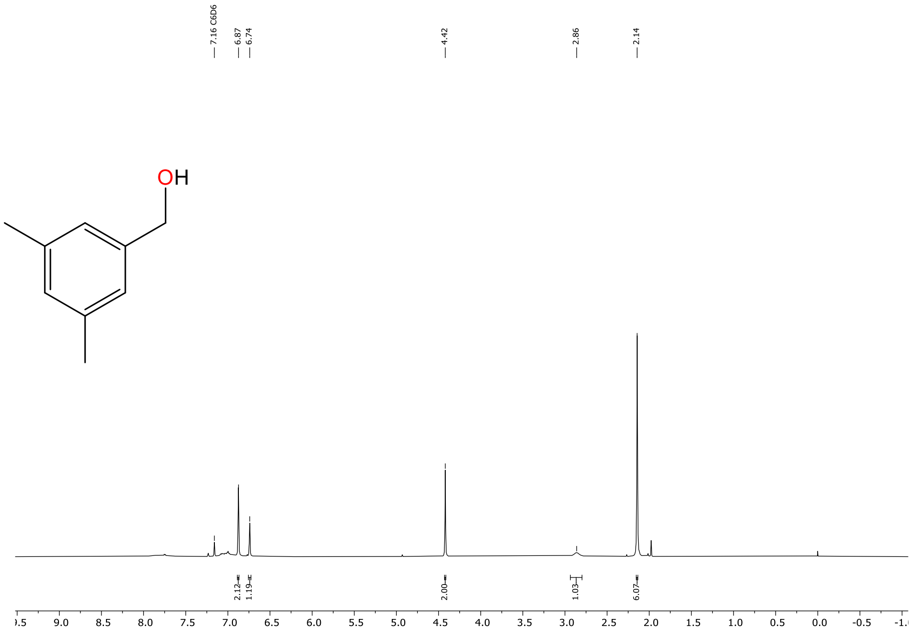


Figure S32. ^{1}H NMR spectrum of 3,5-dimethylbenzyl alcohol in benzene-*d*$_6$.

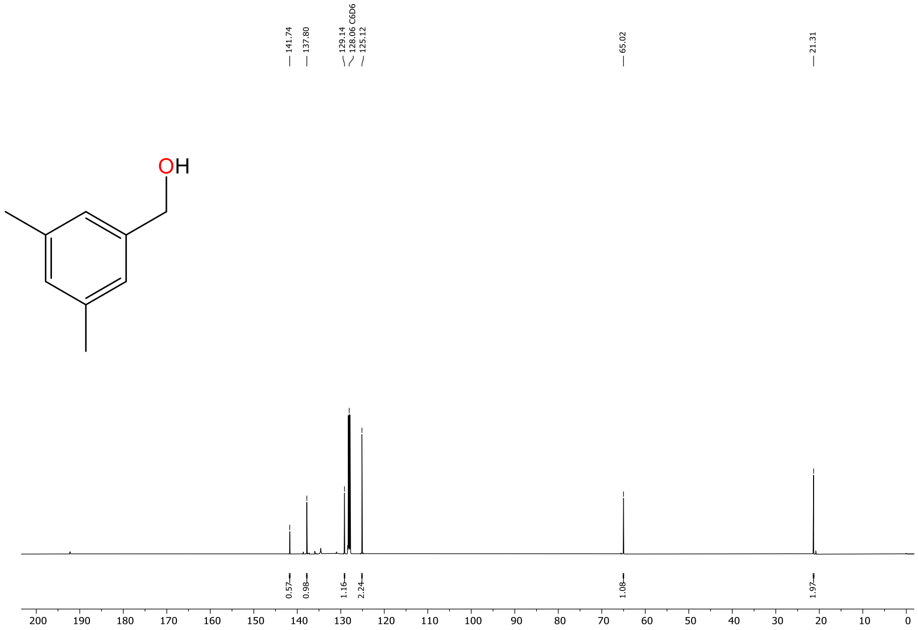


Figure S33. ^{13}C NMR spectrum of 3,5-dimethylbenzyl alcohol in benzene-*d*$_6$.

Hydrosilylation of 2,4,6-trimethylbenzaldehyde using 0.1 mol% 2: In a glove box, a mixture of 2,4,6-trimethylbenzaldehyde (0.68 mL, 4.62 mmol) and $PhSiH_3$ (0.57 mL, 4.62 mmol) was added to a scintillation vial containing **2** (0.0031 g, 0.0046 mmol). The resulting light orange solution was allowed to stir at room temperature for 4 h and then exposed to air to deactivate the catalyst. The solution was then filtered through Celite and a ^{1}H NMR spectrum was taken in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 3 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Rotary evaporation of the solvent at 25 °C yielded a colorless liquid identified as 2,4,6-trimethylbenzyl alcohol[8] (666 mg, 4.43 mmol, 96%). ^{1}H NMR (500 MHz, benzene-d_6): 6.71 (s, 2H, *phenyl*), 4.42 (s, 2H, -CH_2), 2.22 (s, 6H, -CH_3), 2.12 (s, 3H, -CH_3). ^{13}C NMR (126 MHz, benzene-d_6): 137.36 (s, *phenyl*), 137.18 (s, *phenyl*), 134.54 (s, *phenyl*), 129.34, (s, *phenyl*) 58.94 (s, -*C*H_2), 21.04 (s, -*C*H_3), 19.40 (s, -*C*H_3).

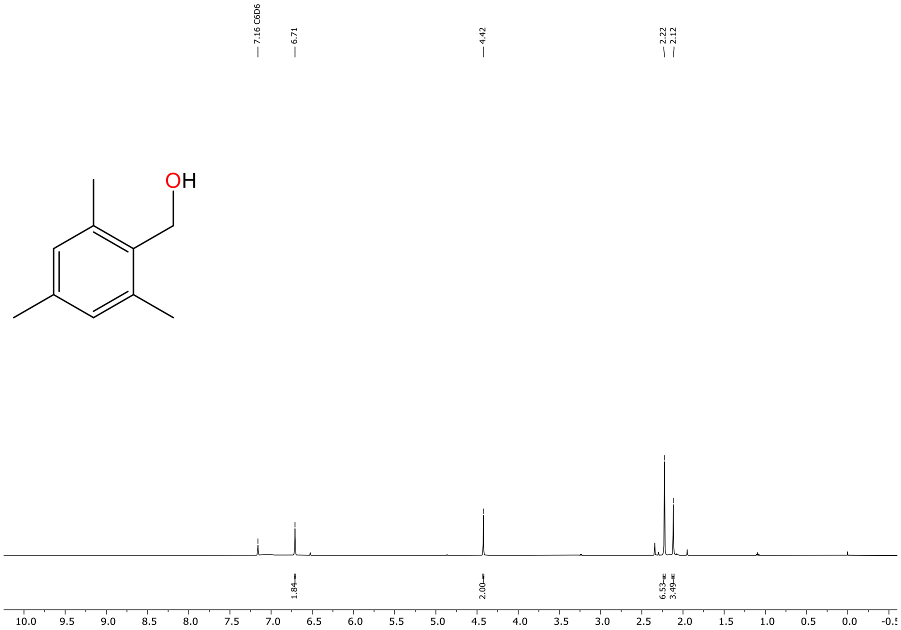


Figure S34. ^{1}H NMR spectrum of 2,4,6-trimethylbenzyl alcohol in benzene-d_6.

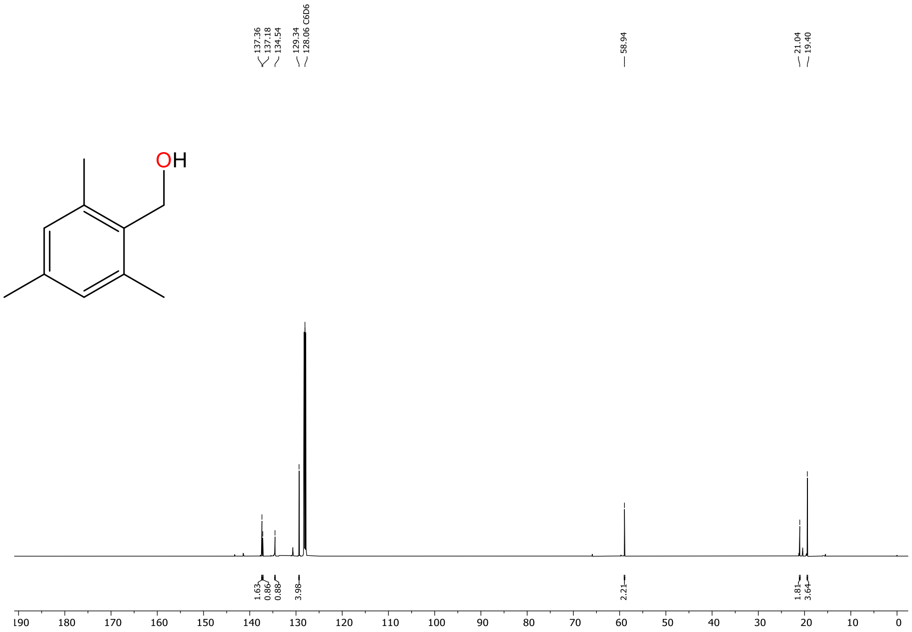


Figure S35. ^{13}C NMR spectrum of 2,4,6-trimethylbenzyl alcohol in benzene-d_6.

Hydrosilylation of pyridine-3-carbaldehyde using 0.1 mol% 2: In a glove box, a mixture of pyridine-3-carbaldehyde (0.20 mL, 2.23 mmol) and $PhSiH_3$ (0.28 mL, 2.23 mmol) was added to another scintillation vial containing **2** (0.0015 g, 0.00223 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 2 min and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was collected in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 2 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Evaporation of the solvent by rotary evaporation at 25 °C yielded a yellow liquid identified as pyridine-3-carbinol[6] (99.7 mg, 0.91 mmol, 41%). ^{1}H NMR (400 MHz, benzene-d_6): 8.50 (s, 1H, *pyridyl*), 8.23 (d, J = 3.5 Hz, 1H, *pyridyl*), 7.40 (d, J = 7.7 Hz, 1H, *pyridyl*), 6.73 (t, J = 6 Hz, 1H, *pyridyl*), 5.45 (s, 1H, -CH_2), 4.47 (s, 2H, -OH). ^{13}C NMR (101 MHz, benzene-d_6): 148.30 (s, *pyridyl*), 148.09 (s, *pyridyl*), 138.17 (s, *pyridyl*), 135.03 (s, *pyridyl*), 123.68 (s, *pyridyl*), 61.90 (s, -CH_2).

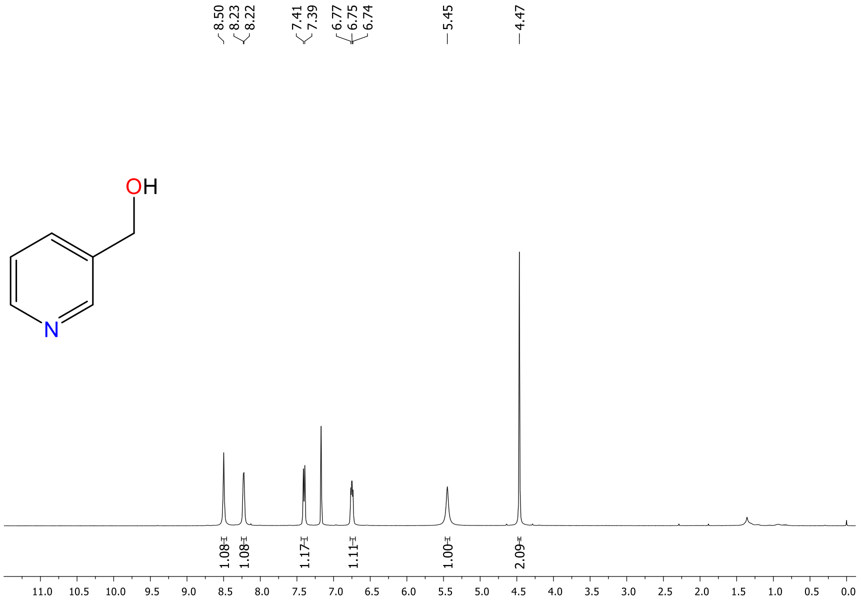


Figure S36. ^{1}H NMR spectrum of pyridine-3-carbinol in benzene-d_6.

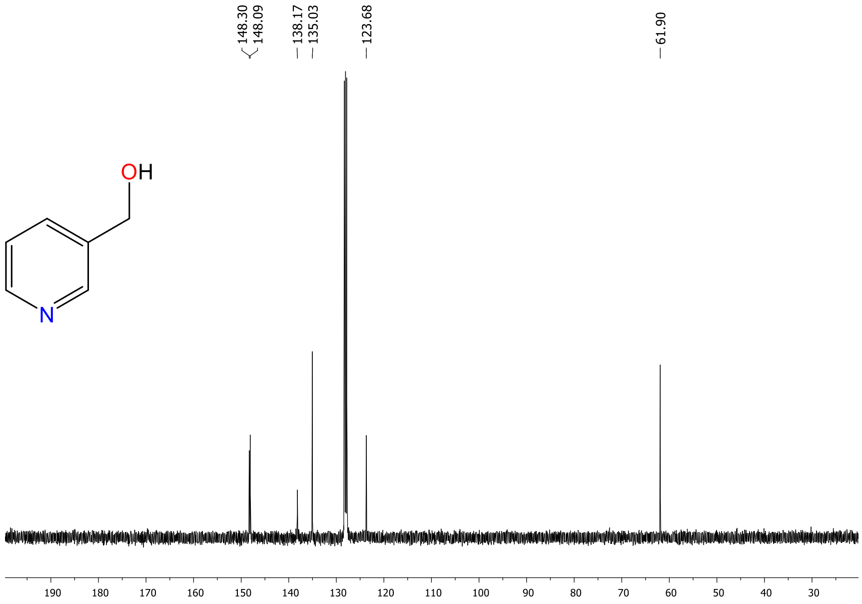


Figure S37. ^{13}C NMR spectrum of pyridine-3-carbinol in benzene-d_6.

Hydrosilylation of furfural using 0.1 mol% 2: In a glove box, a mixture of furfural (0.24 mL, 2.98 mmol) and $PhSiH_3$ (0.37 mL, 2.98 mmol) was added to a scintillation vial containing **2** (0.002 g, 0.00298 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 2 min and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was taken in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 2 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Evaporation of the solvent by rotary evaporation at 25 °C yielded a yellow liquid identified as furfuryl alcohol[6] (191 mg, 1.94 mmol, 65%). ^{1}H NMR (400 MHz, benzene-d_6): 7.07 (s, 1H, *furyl*), 6.03 (s, 1H, *furyl*), 6.00 (s, 1H, *furyl*), 4.27 (s, 2H, -C*H*$_2$), 2.22 (s, 1H, -O*H*). ^{13}C NMR (101 MHz, benzene-d_6): 155.16 (s, *furyl*), 142.33 (s, *furyl*), 110.52 (s, *furyl*), 107.59 (s, *furyl*), 57.25 (s, -*C*H$_2$).

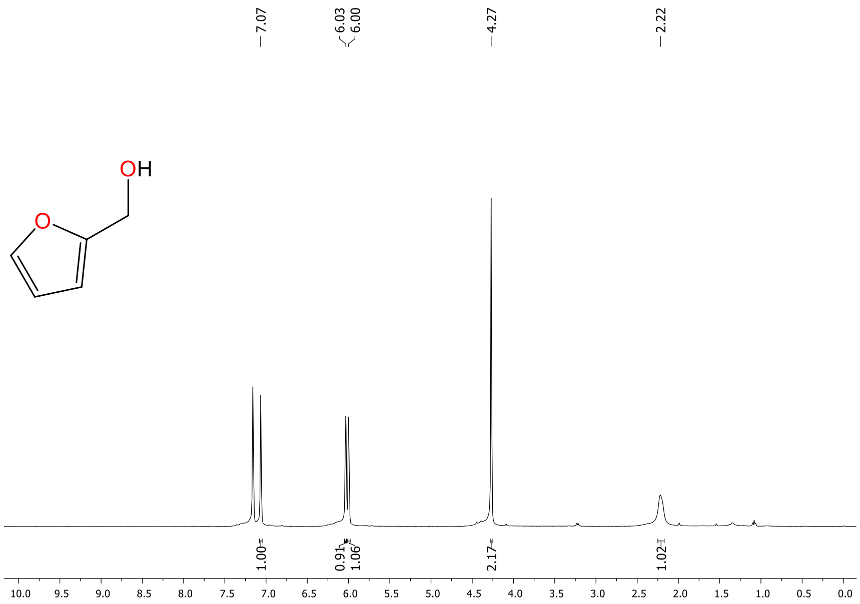


Figure S38. ^{1}H NMR spectrum of furfuryl alcohol in benzene-d_6.

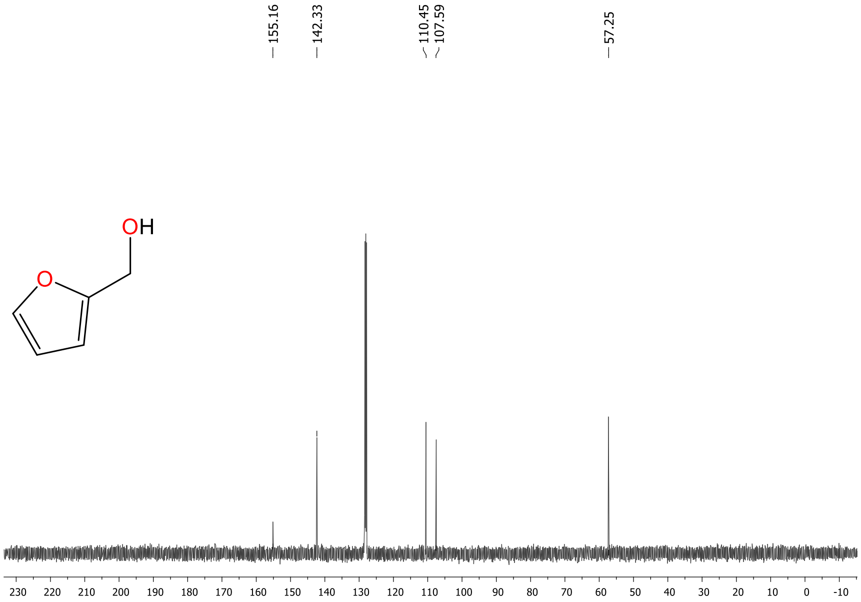


Figure S39. ^{13}C NMR spectrum of furfuryl alcohol in benzene-d_6.

Hydrosilylation of thiophene-2-carbaldehyde using 0.1 mol% 2: In a glove box, a mixture of thiophene-2-carbaldehyde (0.26 mL, 2.83 mmol) and $PhSiH_3$ (0.35 mL, 2.83 mmol) was added to a scintillation vial containing **2** (2 mg, 0.00298 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 2 min and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was taken in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 2 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Evaporation of the solvent by rotary evaporation at 25 °C yielded an yellow liquid identified as thiophene-2-carbinol[8] (323 mg, 2.83 mmol, 95%). ^{1}H NMR (400 MHz, benzene-d_6): 6.88 (d, J = 5.0 Hz, 1H, =C*H*), 6.73 (d, J = 3.9 Hz, 1H, =C*H*), 6.70 (t, J = 4.0 Hz, 1H, =C*H*), 4.46 (s, 2H, -CH_2), 3.44 (s, 1H, -O*H*). ^{13}C NMR (101 MHz, benzene-d_6): 144.92 (s, =*C*H), 134.56 (s, =*C*H), 126.88 (s, =*C*H), 125.31 (s, =*C*H), 59.60 (s, -*C*H_2).

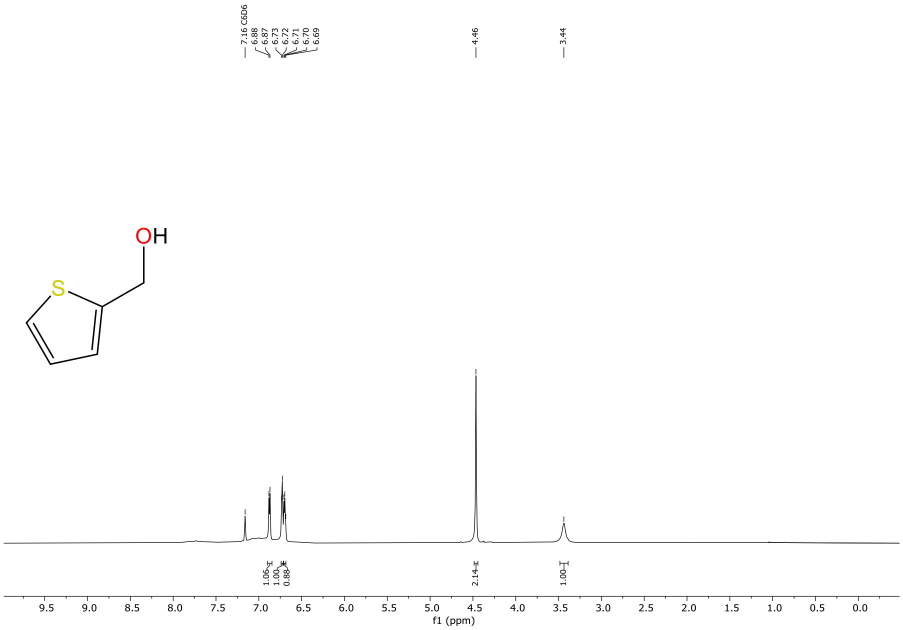


Figure S40. ^{1}H NMR spectrum of thiophene-2-carbinol in benzene-d_6.

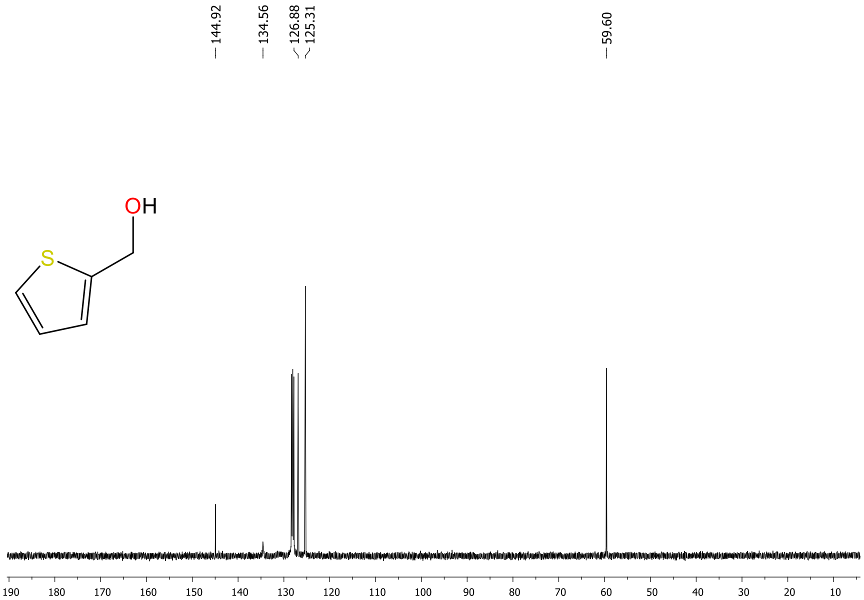


Figure S41. ^{13}C NMR spectrum of thiophene-2-carbinol in benzene-d_6.

Hydrosilylation of 3-cyclohexene-1-carbaldehyde using 0.1 mol% 2: In a glove box, a mixture of 3-cyclohexene-1-carbaldehyde (0.21 mL, 1.78 mmol) and $PhSiH_3$ (0.22 mL, 1.78 mmol) was added to a scintillation vial containing **2** (1.2 mg, 0.00178 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 2 min and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^1H NMR spectrum was collected in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 2 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Evaporation of the solvent at 25 °C under vacuum yielded a colorless liquid identified as 3-cyclohexene-1-carbinol[6] (208 mg, 2.13 mmol, 84%). ^1H NMR (400 MHz, benzene-d_6): 5.65 (s, 2H, =C*H*), 3.76 (m, *J* = 7.8 Hz, 1H, -C*H*), 3.40 (d, *J* = 6.1 Hz, 2H, -CH_2), 2.07 (d, *J* = 15.3 Hz, 1H, -CH_2), 1.97 (d, *J* = 4.8 Hz, 2H, -CH_2), 1.74 (d, *J* = 12.7 Hz, 2H, -CH_2), 1.22 (dd, *J* = 20.1, 7.9 Hz, 1H, -CH_2). ^{13}C NMR (101 MHz, benzene-d_6): 127.31 (s, =*C*H), 126.43 (s, =*C*H), 67.53 (s, -*C*H_2), 36.69 (s, -*C*H), 28.62 (s, -*C*H_2), 25.71 (s, -*C*H_2), 25.10 (s, -*C*H_2).

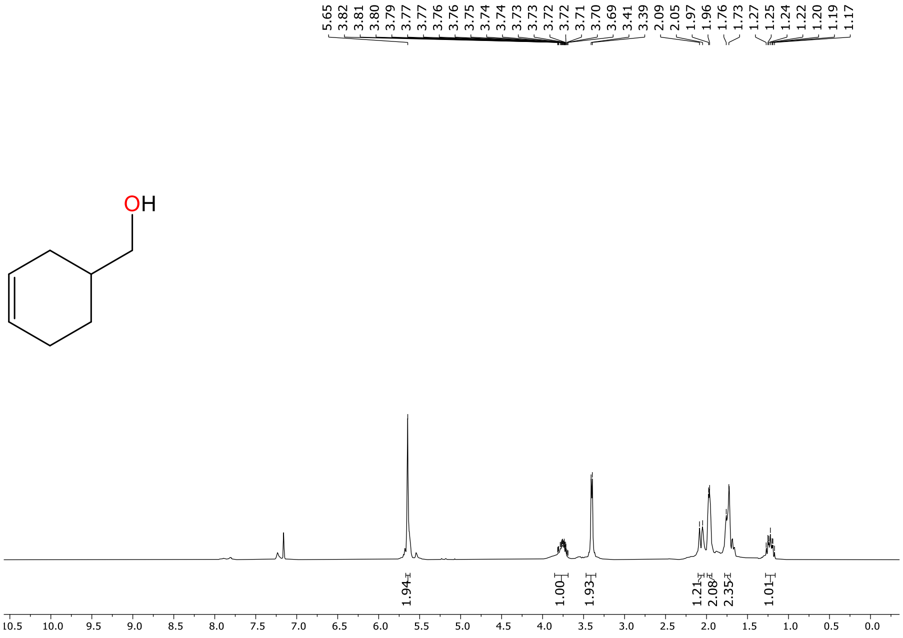


Figure S42. ^1H NMR spectrum of 3-cyclohexene-1-carbinol in benzene-d_6.

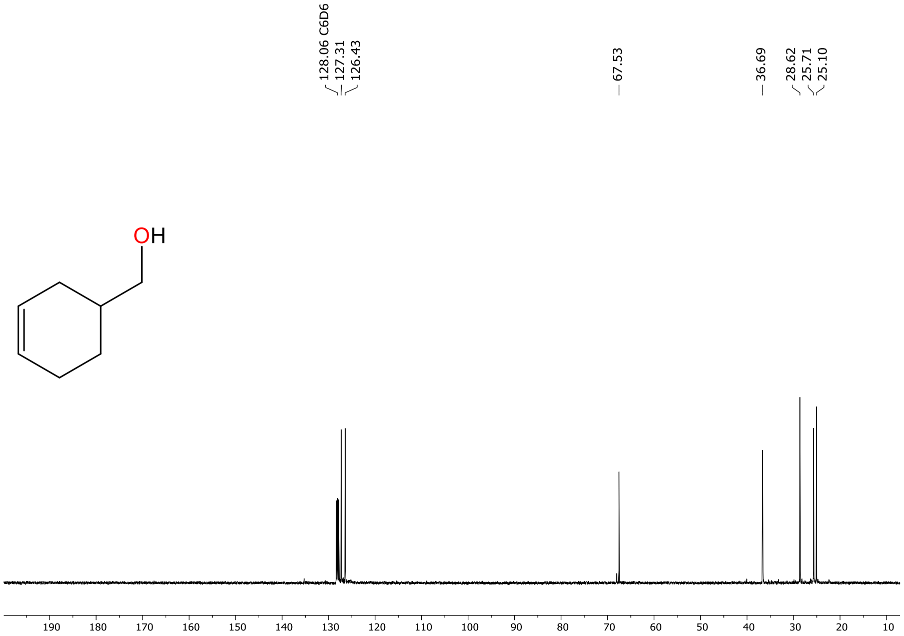


Figure S43. ^{13}C NMR spectrum of 3-cyclohexene-1-carbinol in benzene-*d*$_6$.

Hydrosilylation of heptanal using 0.1 mol% 2: In a glove box, a mixture of heptanal (0.22 mL, 1.56 mmol) and PhSiH$_3$ (0.22 mL, 1.56 mmol) was added to a scintillation vial containing **2** (1.1 mg, 0.0016 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 2 min and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was collected in CDCl$_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 2 h. The organic product was extracted using Et$_2$O (3 x 3 mL), filtered through Celite, and dried over Na$_2$SO$_4$. Evaporation of the solvent under vacuum at 25 °C yielded a colorless liquid identified as heptan-1-ol[9] (121 mg, 1.04 mmol, 67%). ^{1}H NMR (400 MHz, benzene-*d*$_6$): 3.56 (t, J = 6.7 Hz, 3H, -CH_2), 1.54 (p, J = 6.6 Hz, 2H, -CH_2), 1.26 (m, J = 6 Hz, 8H, -CH_2), 0.88 (t, J = 6 Hz, 3H, -CH_3). ^{13}C NMR (101 MHz, benzene-*d*$_6$): 62.64 (s, -CH$_2$), 33.21 (s, -CH$_2$), 32.34 (s, -CH$_2$), 29.68 (s, -CH$_2$), 26.30 (s, -CH$_2$), 23.09 (s, -CH$_2$), 14.33 (s, -CH$_3$).

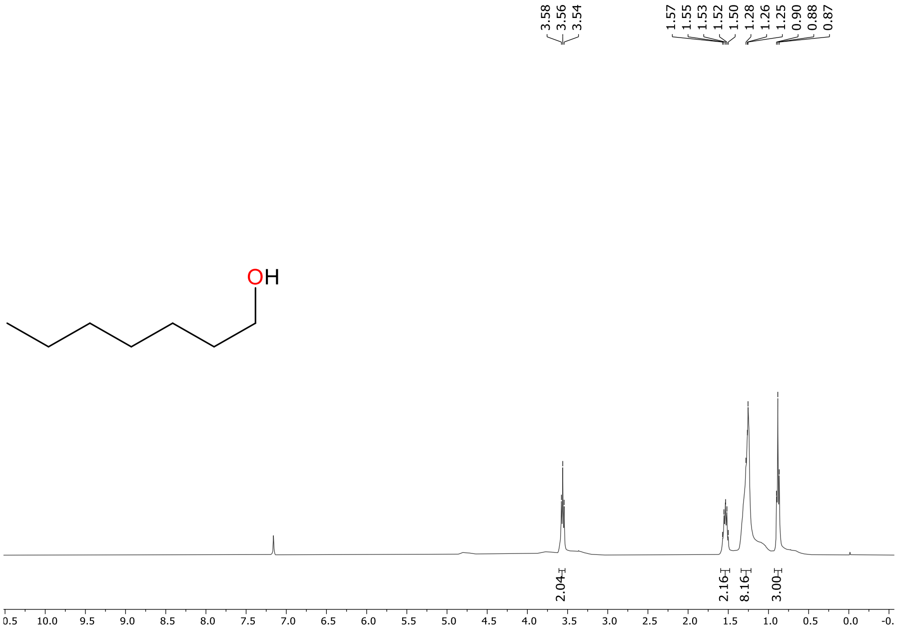


Figure S44. ^{1}H NMR spectrum of heptan-1-ol in benzene-d_6.

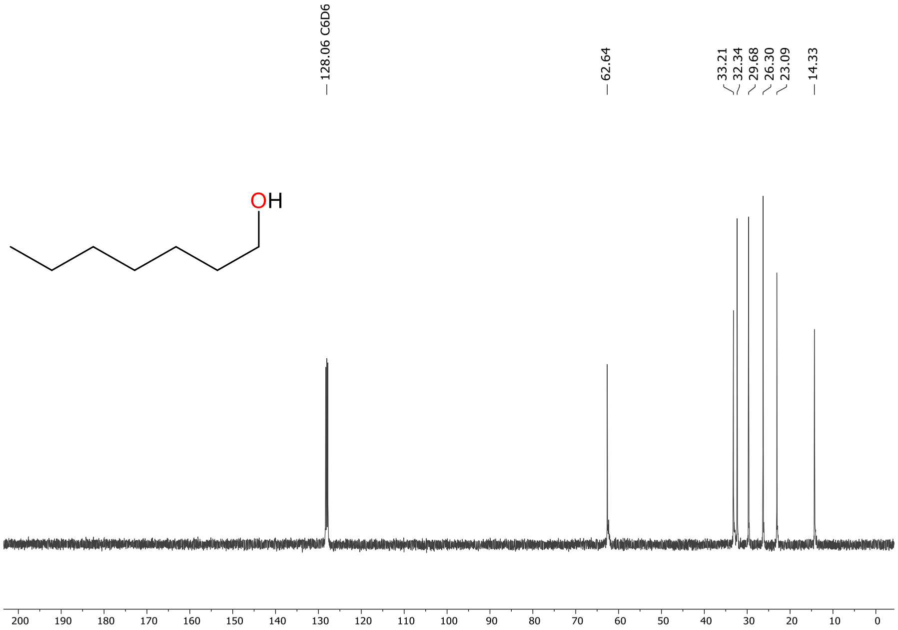


Figure S45. ^{13}C NMR spectrum of heptan-1-ol in benzene-d_6.

Hydrosilylation of 2-hexenal using 0.1 mol% 2: In a glove box, a mixture of 2-hexenal (0.33 mL, 2.83 mmol) and $PhSiH_3$ (0.35 mL, 2.83 mmol) was added to a scintillation vial containing **2** (1.9 mg, 0.00283 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 2 min and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was collected in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 2 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Evaporation of the solvent under vacuum at 25 °C yielded a colorless liquid identified as 2-hexen-1-ol[10] (208 mg, 2.07 mmol, 73%). ^{1}H NMR (400 MHz, benzene-d_6): 5.70–5.59 (m, 1H, -C*H*), 5.39 (m, 1H, -C*H*), 4.08 (d, J = 6.6 Hz, 2H, -CH_2), 1.89 (q, J = 7.4 Hz, 2H, -CH_2), 1.25 (q, J = 7.4 Hz, 2H, -CH_2), 0.80 (t, J = 7.4 Hz, 3H, -CH_3). ^{13}C NMR (101 MHz, benzene-d_6): 131.92 (s, -*C*H), 130.17 (s, -*C*H), 63.54 (s, -*C*H_2), 34.64 (s, -*C*H_2), 22.70 (s, -*C*H_2), 13.83 (s, -*C*H_3).

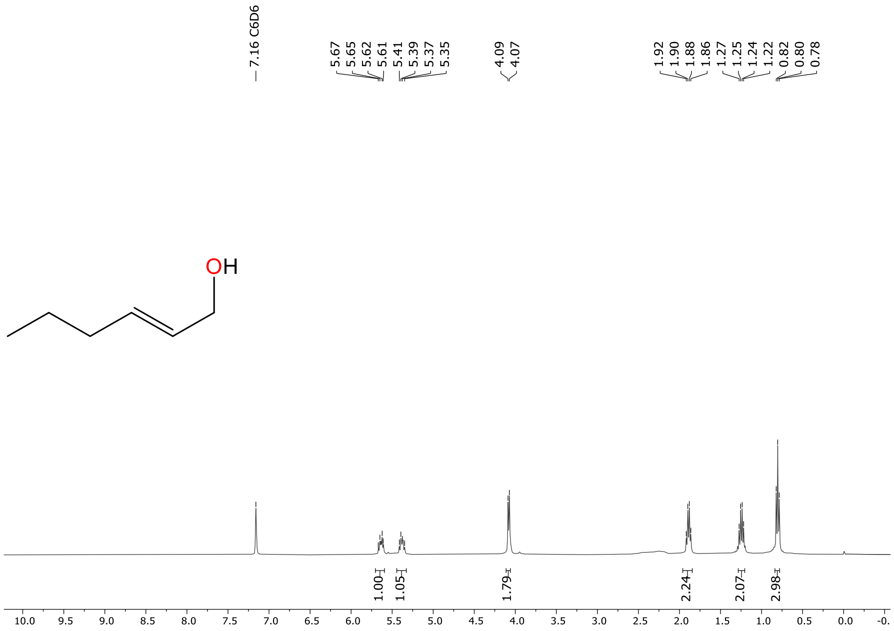


Figure S46. ^{1}H NMR spectrum of 2-hexen-1-ol in benzene-d_6.

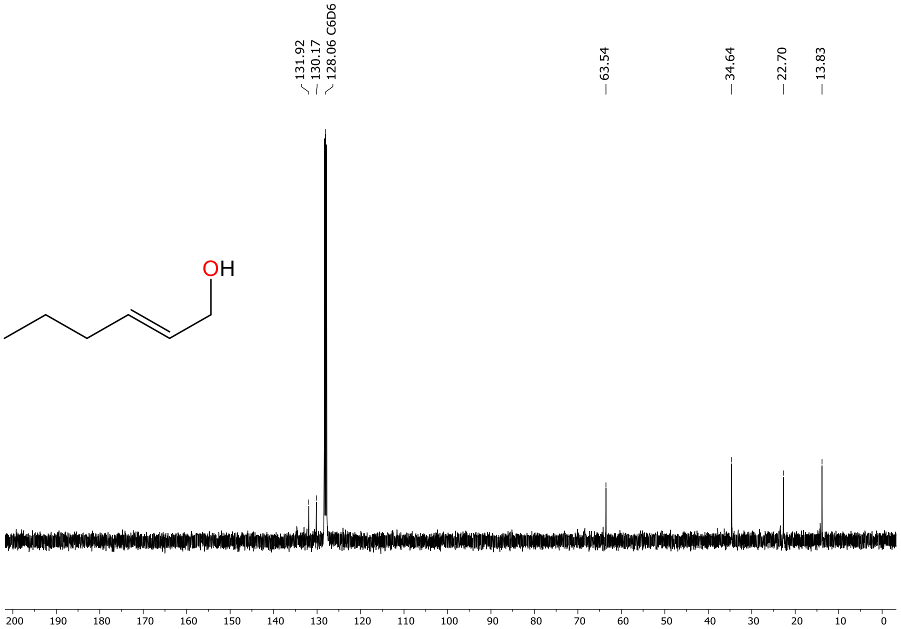


Figure S47. ^{13}C NMR spectrum of 2-hexen-1-ol in benzene-*d*$_6$.

Hydrosilylation of cinnamaldehyde using 0.1 mol% 2: In a glove box, a mixture of cinnamaldehyde (0.39 mL, 3.13 mmol) and $PhSiH_3$ (0.38 mL, 2.53 mmol) was added to a scintillation vial containing **2** (0.0021 g, 0.00313 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 2 min and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was collected in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 2 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. The solvent was removed by rotary evaporation at 25 °C to yield a colorless liquid identified as cinnamyl alcohol[11] (400 mg, 2.98 mmol, 95%). ^{1}H NMR (400 MHz, benzene-*d*$_6$): 7.24 (d, *J* = 7.4 Hz, 2H, *phenyl*), 7.12 (t, *J* = 7.5 Hz, 2H, *phenyl*), 7.05 (t, *J* = 7.2 Hz, 1H, *phenyl*), 6.50 (d, *J* = 15.9 Hz, 1H, -C*H*), 6.19 (dt, *J* = 15.9, 5.6 Hz, 1H, -C*H*), 4.11 (d, *J* = 3.9 Hz, 2H, -C*H*$_2$), 3.29 (s, 1H, -O*H*). ^{13}C NMR (101 MHz, benzene-*d*$_6$): 137.42 (s, *phenyl*), 130.67 (s, *phenyl*), 129.37 (s, *phenyl*), 128.85 (s, *phenyl*), 127.71 (s, -*C*H), 126.84 (s, -*C*H), 63.36 (s, -*CH*$_2$).

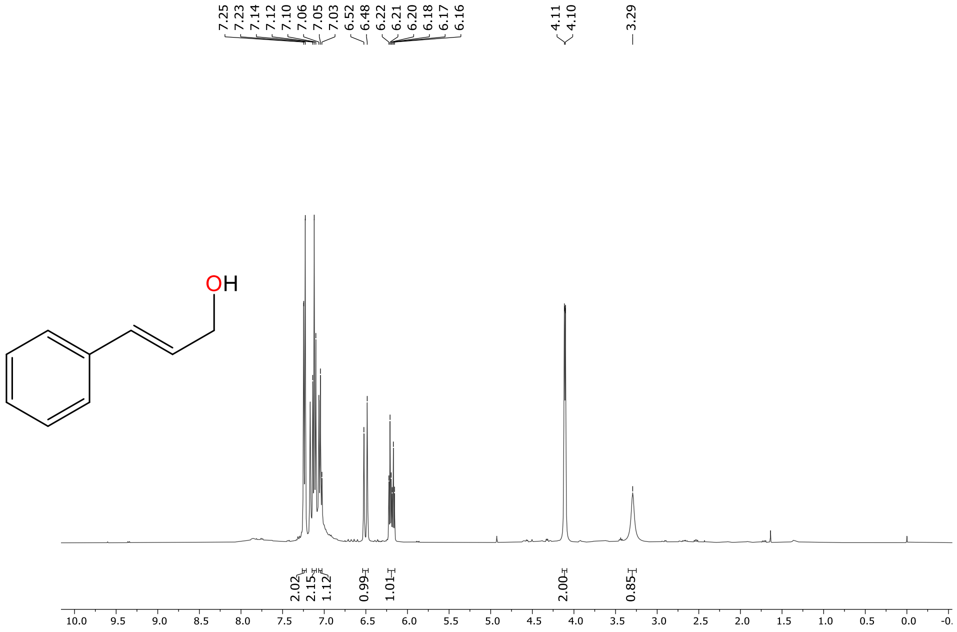


Figure S48. ^{1}H NMR spectrum of cinnamyl alcohol in benzene-*d*$_{6}$.

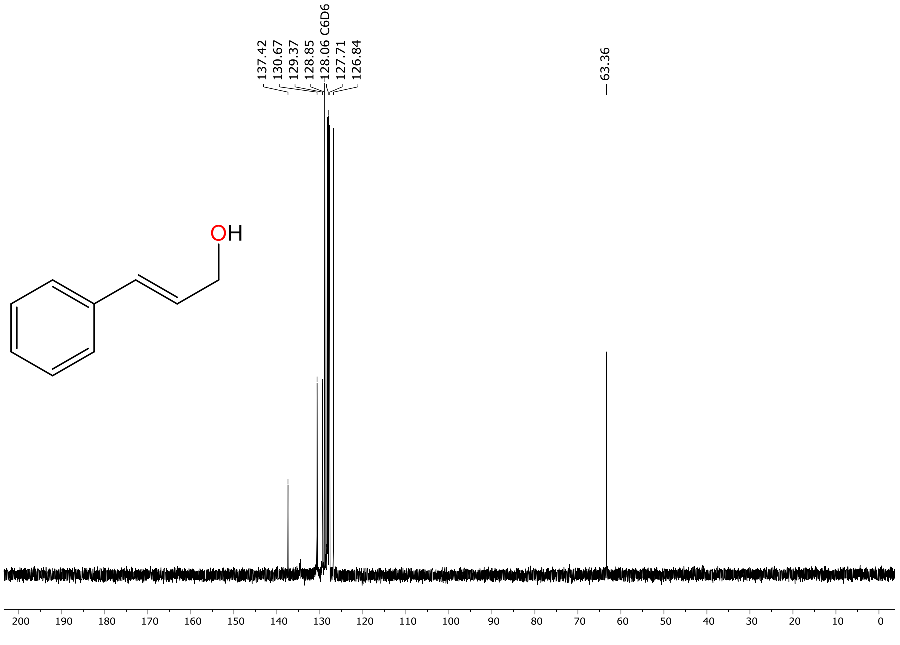


Figure S49. ^{13}C NMR spectrum of cinnamyl alcohol in benzene-*d*$_{6}$.

Hydrosilylation of acetophenone using 0.1 mol% 2: In a glove box, a mixture of acetophenone (0.66 mL, 5.66 mmol) and $PhSiH_3$ (0.70 mL, 5.66 mmol) were added to a scintillation vial containing **2** (0.0038 g, 0.0057 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 2 min and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^1H NMR spectrum was collected in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 3 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Evaporation of the solvent under vacuum at 25 °C yielded a colorless liquid identified as 1-phenylethanol[9] (686 mg, 5.65 mmol, 91%). ^1H NMR (400 MHz, benzene-d_6): 7.18 (d, J = 6.7 Hz, 2H, *phenyl*), 7.09 (t, J = 7.2 Hz, 2H, *phenyl*), 7.01 (t, J = 7.9 Hz, 1H, *phenyl*), 4.56 (q, J = 6.5 Hz, 1H, -C*H*), 3.55 (s, 1H, -O*H*), 1.25 (dd, J = 6.5, 1.1 Hz, 3H, -C*H₃*). ^{13}C NMR (101 MHz, benzene-d_6): 146.65 (s, *phenyl*), 128.49 (s, *phenyl*), 127.26 (s, *phenyl*), 125.75 (s, *phenyl*), 69.75 (s, -*C*H), 25.29 (s, -*C*H_3).

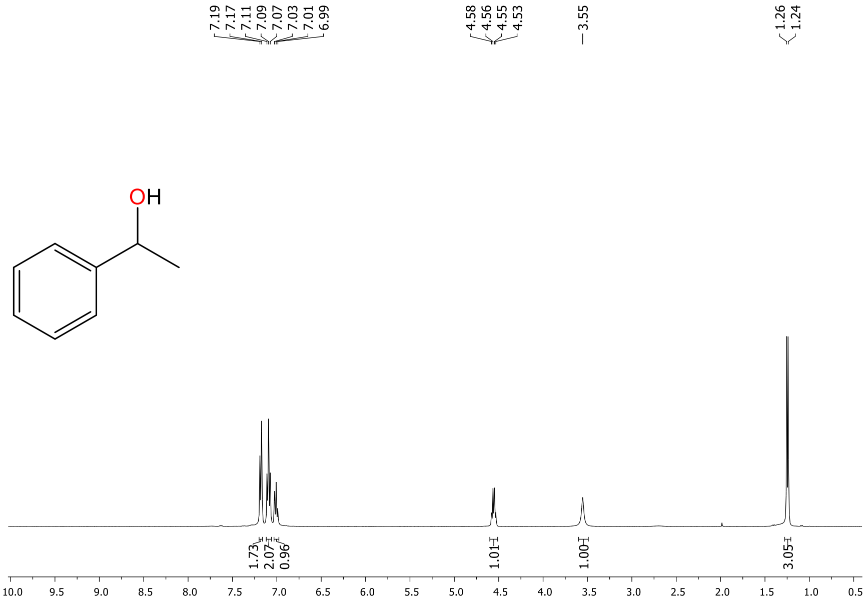


Figure S50. ^1H NMR spectrum of 1-phenylethanol in benzene-d_6.

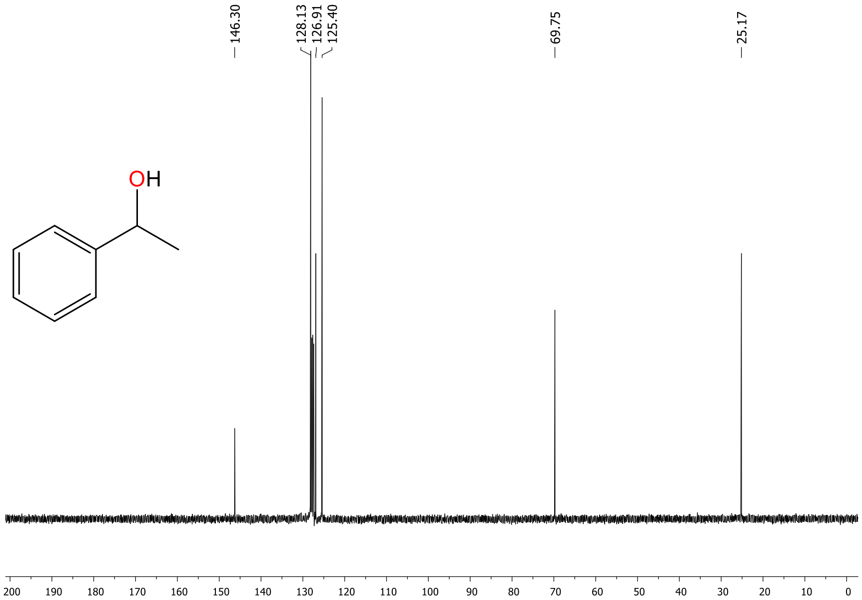


Figure S51. ^{13}C NMR spectrum of 1-phenylethanol in benzene-d_6.

Hydrosilylation of 4-methoxyacetophenone using 0.1 mol% 2: In a glove box, a mixture of 4-methoxyacetophenone (291 mg, 1.938 mmol) and $PhSiH_3$ (0.24 mL, 1.938 mmol) was added to another scintillation vial containing **2** (0.0013 g, 0.0019 mmol). The resulting light orange solution was allowed to stir at room temperature for 5 h and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was taken in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 3 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Rotary evaporation of the solvent at 25 °C yielded a colorless liquid identified as 1-(4-methoxy)phenylethanol[9] (208 mg, 1.369 mmol, 71%). ^{1}H NMR (400 MHz, benzene-d_6): 7.17 (d, J = 7.8 Hz, 2H, *phenyl*), 6.79 (d, J = 7.6 Hz, 2H, *phenyl*), 4.60 (m, J = 5.8 Hz, 1H, -C*H*), 3.34 (s, 3H, -OCH_3), 1.95 (s, 1H, -O*H*), 1.34 (d, J = 7.6 Hz, 3H, -CH_3). ^{13}C NMR (101 MHz, benzene-d_6): 159.39 (s, *phenyl*), 138.98 (s, *phenyl*), 126.94 (s, *phenyl*), 114.05 (s, *phenyl*), 69.84 (s, -O*C*H$_3$), 54.85 (s, -*C*H), 25.64 (s, -*C*H$_3$).

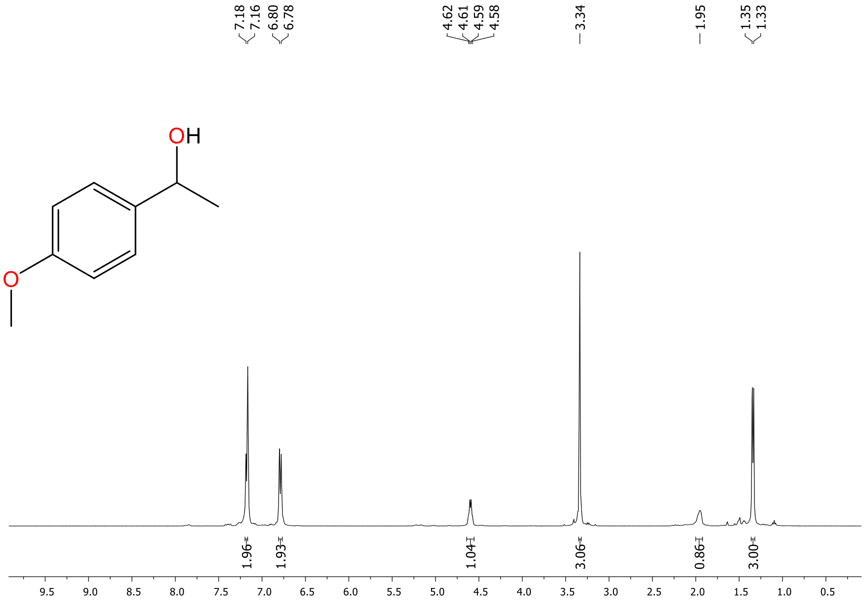


Figure S52. ^{1}H NMR spectrum of 1-(4-methoxy)phenylethanol in benzene-d_6.

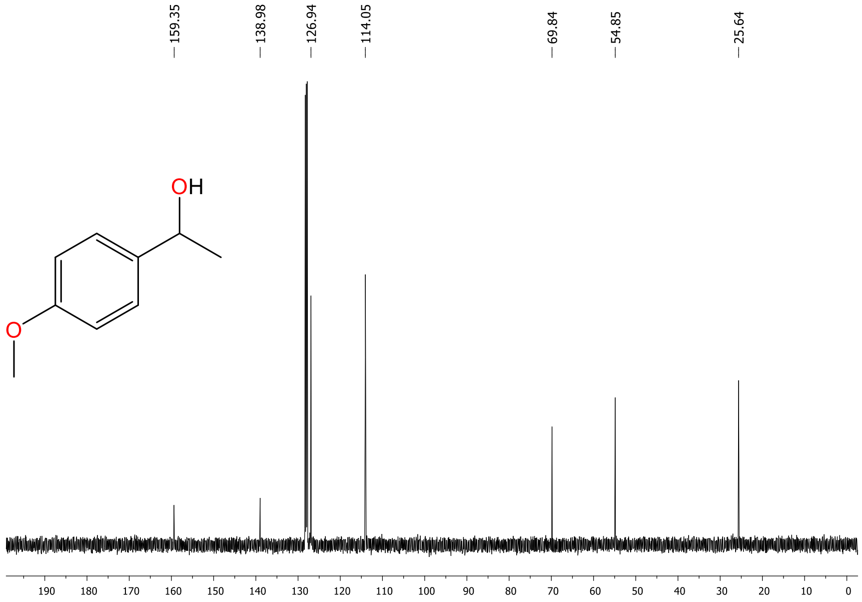


Figure S53. ^{13}C NMR spectrum of 1-(4-methoxy)phenylethanol in benzene-d_6.

Hydrosilylation of 4-methylacetophenone using 0.1 mol% 2: In a glove box, a mixture of 4-methylacetophenone (0.35 mL, 2.684 mmol) and PhSiH$_3$ (0.33 mL, 2.684 mmol) was added to a scintillation vial containing **2** (0.0018 g, 0.00268 mmol). The resulting light orange solution was allowed to stir at room temperature for 14 h and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was collected in CDCl$_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 3 h. The organic product was extracted using Et$_2$O (3 x 3 mL), filtered through Celite, and dried over Na$_2$SO$_4$. Rotary evaporation of the solvent at 25 °C yielded a colorless liquid identified as 1-(4-methyl)phenylethanol[9] (297 mg, 2.18 mmol, 81%). ^{1}H NMR (400 MHz, benzene-d_6): 7.24 (d, *J* = 5.6 Hz, 2H, *phenyl*), 7.06 (d, *J* = 6.4 Hz, 2H, *phenyl*), 4.67 (q, *J* = 6.9 Hz, 1H, -C*H*), 2.46 (s, 1H, -O*H*), 2.20 (s, 3H, -C*H*$_3$), 1.40 (d, *J* = 7.6 Hz, 3H -C*H*$_3$). ^{13}C NMR (101 MHz, benzene-d_6): 143.93 (s, *phenyl*), 136.65 (s, *phenyl*), 129.23 (s, *phenyl*), 125.76 (s, *phenyl*), 70.09 (s, -*C*H), 25.63 (s, -*C*H$_3$), 21.11 (s, -*C*H$_3$).

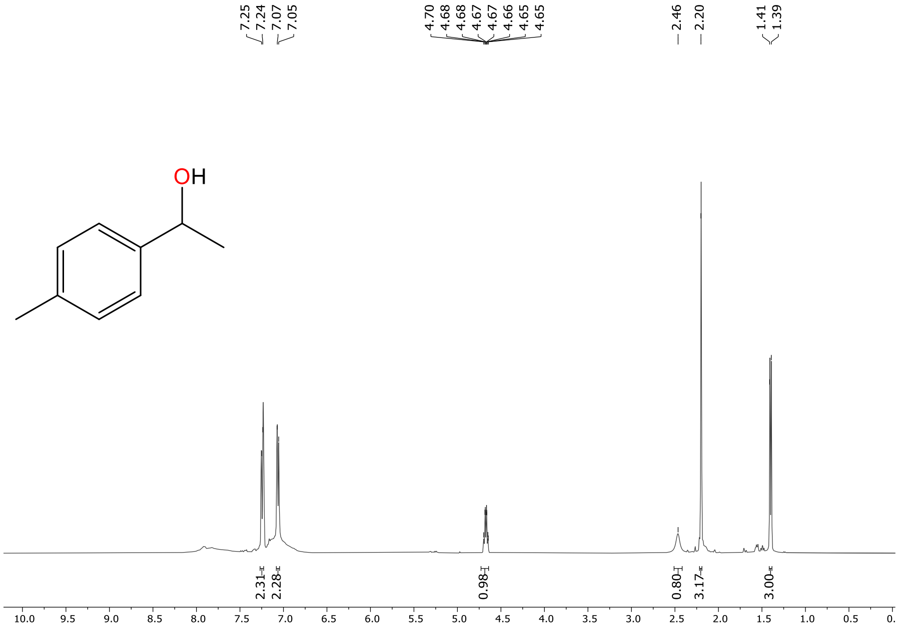


Figure S54. ^{1}H NMR spectrum of 1-(4-methyl)phenylethanol in benzene-d_6.

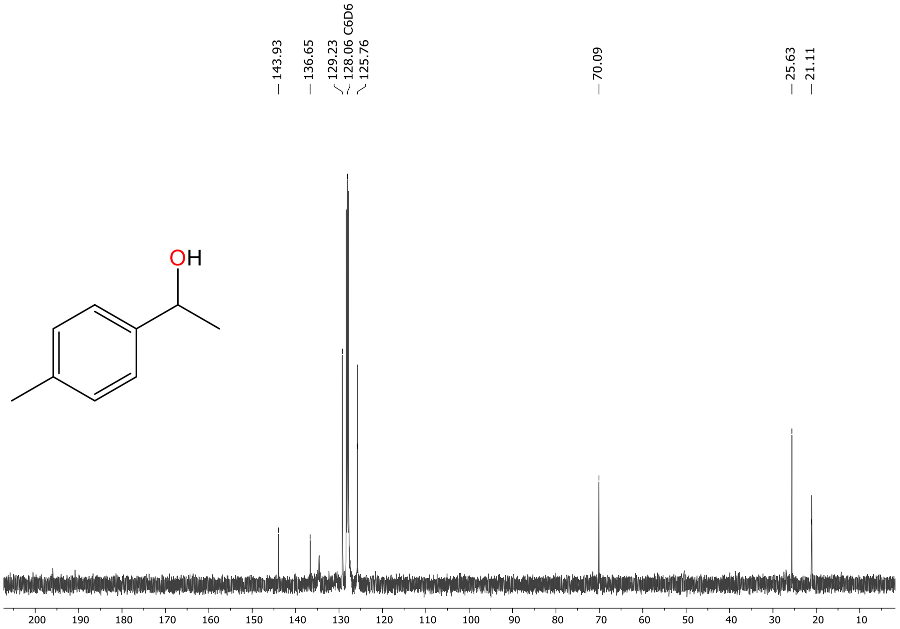


Figure S55. ^{13}C NMR spectrum of 1-(4-methyl)phenylethanol in benzene-*d*$_6$.

Hydrosilylation of 4-fluoroacetophenone using 0.1 mol% 2: In a glove box, a mixture of 4-fluoroacetophenone (0.54 mL, 4.47 mmol) and $PhSiH_3$ (0.55 mL, 4.47 mmol) was added to a scintillation vial containing **2** (0.003 g, 0.00447 mmol). The resulting light orange solution was allowed to stir at room temperature for 2 h and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was taken in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 3 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Rotary evaporation of the solvent at 25 °C yielded a colorless liquid identified as 1-(4-fluoro)phenylethanol[9] (429 mg, 3.06 mmol, 69%). ^{1}H NMR (400 MHz, benzene-*d*$_6$): 7.01 (pseudo t, 2H, *phenyl*), 6.83 (pseudo t, *J* = 8.7 Hz, 2H, *phenyl*), 4.47 (q, *J* = 6.3 Hz, 1H, -C*H*), 2.48 (s, 1H, -O*H*), 1.22 (d, *J* = 6.5 Hz, 3H, -C*H*$_3$). ^{13}C NMR (101 MHz, benzene-*d*$_6$): 162.37 (d, *J* = 245 Hz, *phenyl*), 142.27 (s, *phenyl*), 127.28 (d, *J* = 7.9 Hz, *phenyl*), 115.19 (d, *J* = 21.2 Hz, *phenyl*), 69.42 (s, -*C*H), 25.40 (s, -*C*H$_3$). ^{19}F NMR (376 MHz, benzene-*d*$_6$): -115.68 (s, Ph-*F*).

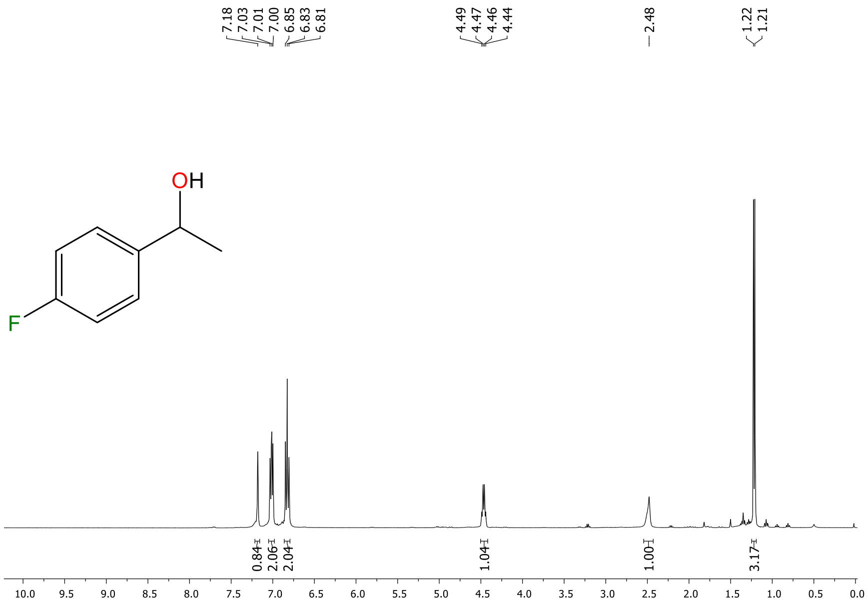


Figure S56. ^{1}H NMR spectrum of 1-(4-fluoro)phenylethanol in benzene-d_6.

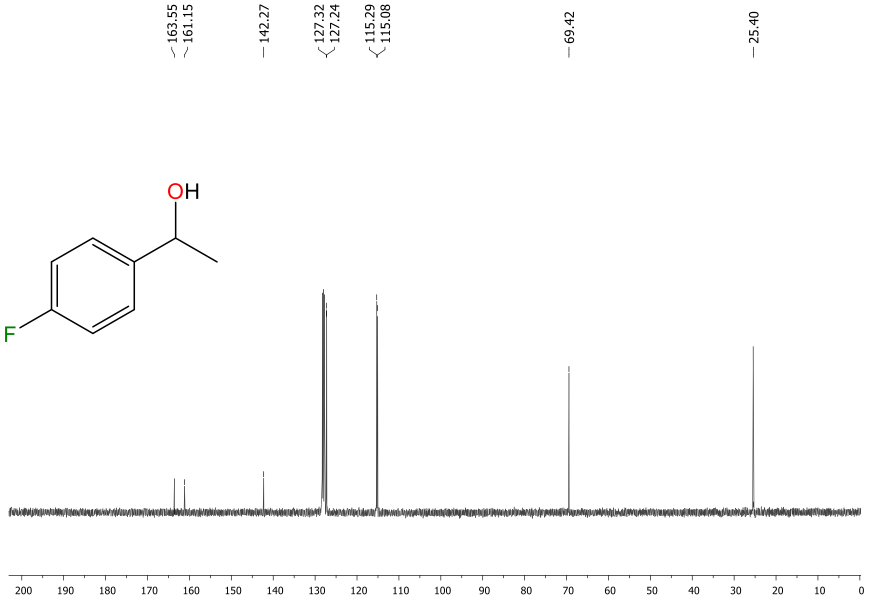


Figure S57. ^{13}C NMR spectrum of 1-(4-fluoro)phenylethanol in benzene-d_6.

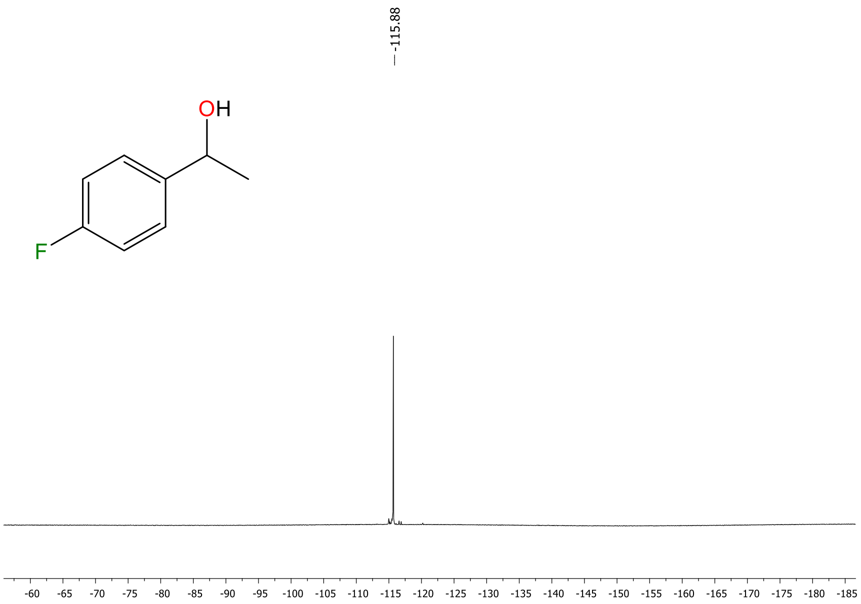


Figure S58. ^{19}F NMR spectrum of 1-(4-fluoro)phenylethanol in benzene-d_6.

Hydrosilylation of 4-chloroacetophenone using 0.1 mol% 2: In a glove box, a 20 mL scintillation vial containing a mixture of 4-chloroacetophenone (0.38 mL, 2.98 mmol) and $PhSiH_3$ (3.67 mL, 2.98 mmol) was added to another scintillation vial containing **2** (0.002 g, 0.00298 mmol). The resulting light orange solution was allowed to stir at room temperature for 11 h and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was collected in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 11 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite and dried over Na_2SO_4. Rotary evaporation of the solvent at 25 °C yielded a colorless liquid identified as 1-(4-chloro)phenylethanol[9] (356 mg, 2.289 mmol, 77%). ^{1}H NMR (400 MHz, benzene-d_6): 7.11 (d, J = 8.4 Hz, 2H, *phenyl*), 6.90 (d, J = 8.2 Hz, 2H, *phenyl*), 4.34 (m, J = 5.7 Hz, 1H, -C*H*), 1.14 (d, J = 6.5 Hz, 3H, -C*H*$_3$). ^{13}C NMR (101 MHz, benzene-d_6): 144.98 (s, *phenyl*), 132.98 (s, *phenyl*), 128.61 (s, *phenyl*), 126.94 (s, *phenyl*), 69.35 (s, -*C*H), 25.41 (s, -*C*H$_3$).

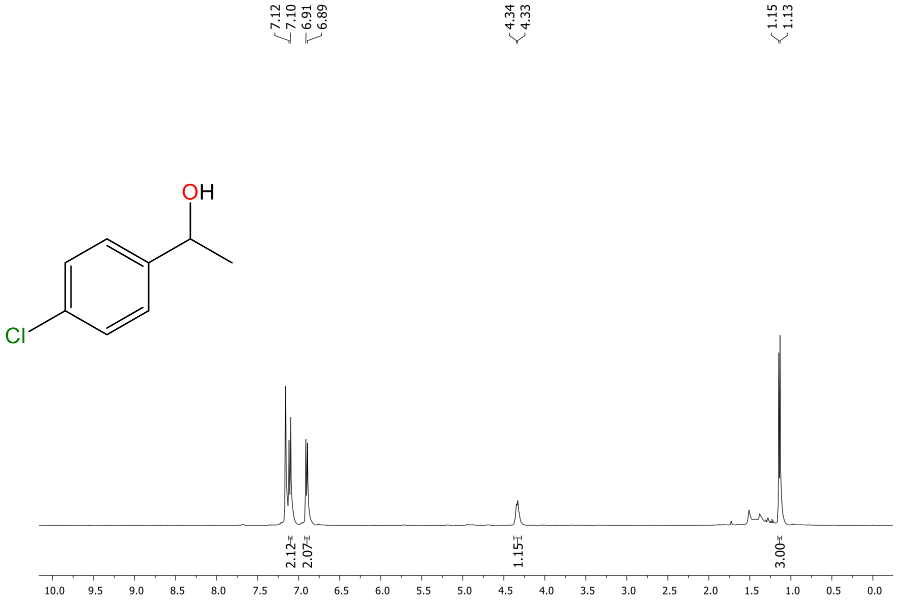


Figure S59. ^{1}H NMR spectrum of 1-(4-chloro)phenylethanol in benzene-d_6.

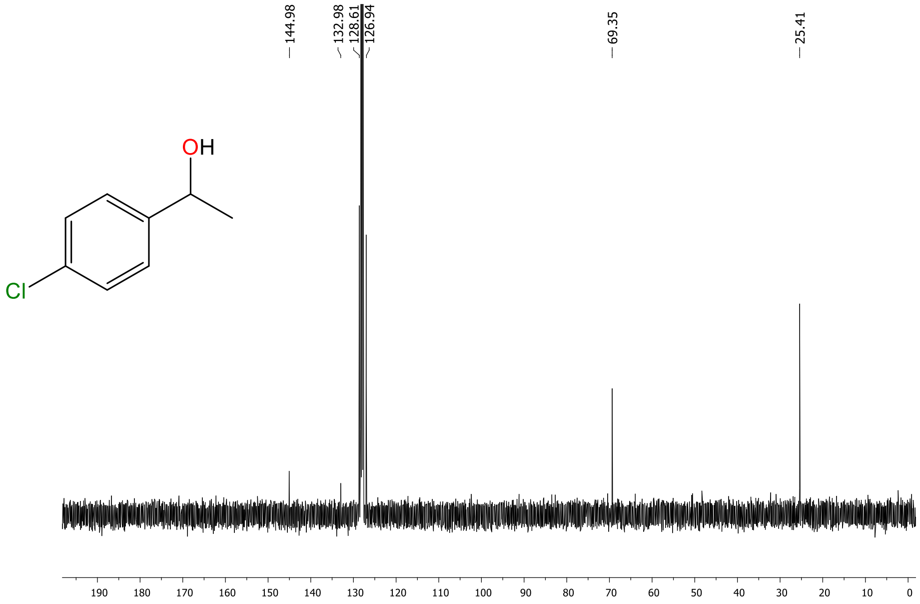


Figure S60. ^{13}C NMR spectrum of 1-(4-chloro)phenylethanol in benzene-d_6.

Hydrosilylation of 4-cyanoacetophenone using 0.1 mol% 2: In a glove box, a mixture of 4-cyanoacetophenone (346 mg, 2.385 mmol) and $PhSiH_3$ (0.29 mL, 2.385 mmol) was added to another scintillation vial containing **2** (0.0016 g, 0.00238 mmol). The resulting light orange solution was allowed to stir at room temperature for 6 h and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was collected in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 3 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Rotary evaporation of the solvent at 25 °C yielded a colorless liquid identified as 1-(4-cyano)phenylethanol[8] (330 mg, 2.24 mmol, 94%). ^{1}H NMR (400 MHz, benzene-d_6): 7.06 (d, J = 8.1 Hz, 2H, *phenyl*), 6.93 (d, J = 8.1 Hz, 2H, *phenyl*), 4.38 (q, J = 6.6 Hz, 1H, -CH), 2.09 (s, 1H, -OH), 1.12 (d, J = 6.5 Hz, 3H, -CH_3). ^{13}C NMR (101 MHz, benzene-d_6): 151.59 (s, -CN), 132.16 (s, *phenyl*), 126.07 (s, *phenyl*), 119.09 (s, *phenyl*), 111.05 (s, *phenyl*), 69.27 (s, -CH), 25.35 (s, -CH$_3$).

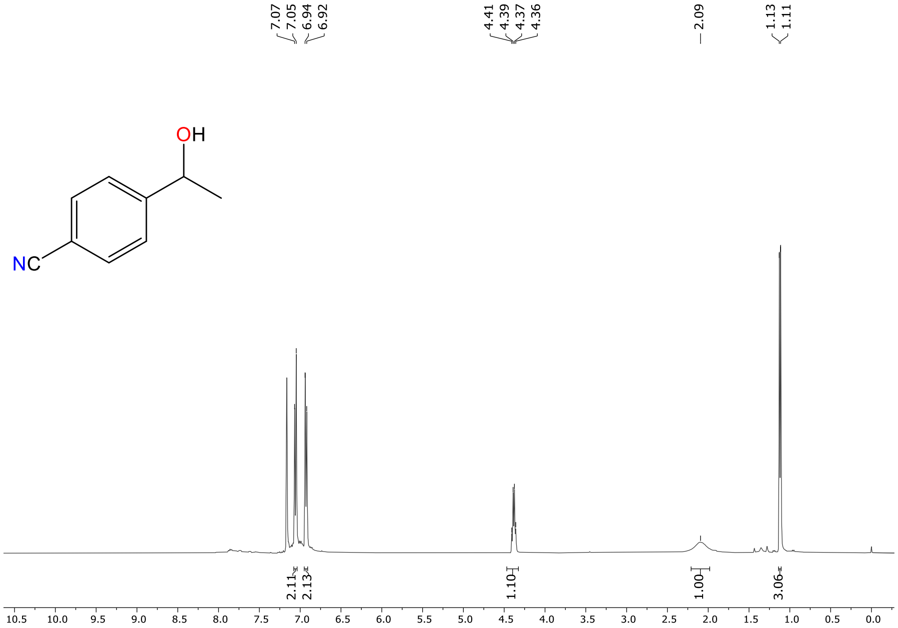


Figure S61. ^{1}H NMR spectrum of 1-(4-cyano)phenylethanol in benzene-d_6.

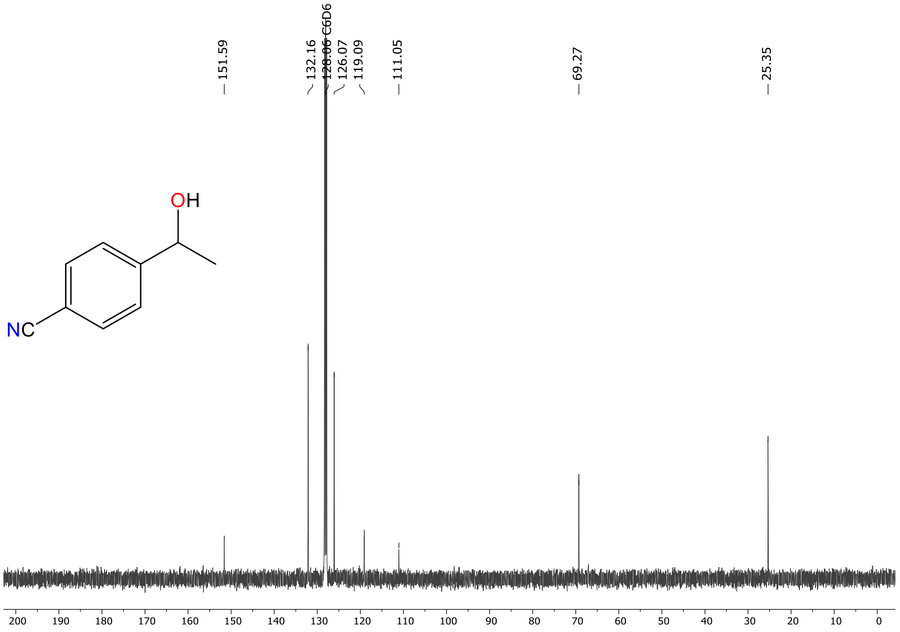


Figure S62. ^{13}C NMR spectrum of 1-(4-cyano)phenylethanol in benzene-*d*$_6$.

Hydrosilylation of 2-acetylpyridine using 0.1 mol% 2: In a glove box, a mixture of 2-acetylpyridine (0.35 mL, 2.684 mmol) and $PhSiH_3$ (0.33 mL, 2.684 mmol) were added to a scintillation vial containing **2** (0.0018 g, 0.00268 mmol). The resulting light orange solution turned slightly warm. The mixture was allowed to stir at room temperature for 5 min and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was collected in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 3 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite and dried over Na_2SO_4. Rotary evaporation of the solvent at 25 °C yielded a colorless liquid identified as 1-(2-pyridine)ethanol[12] (161 mg, 1.31 mmol, 80%). ^{1}H NMR (400 MHz, benzene-*d*$_6$): 8.29 (d, *J* = 4.8 Hz, 1H, *aromatic*), 7.06 (t, *J* = 7.6 Hz, 1H, *aromatic*), 6.97 (d, *J* = 7.9 Hz, 1H, *aromatic*), 6.59 (m, 1H, *aromatic*), 4.89 (m, *J* = 6.5 Hz, 1H, -C*H*), 1.46 (d, *J* = 6.5 Hz, 3H, -C*H*$_3$). ^{13}C NMR (101 MHz, benzene-*d*$_6$): 164.56 (s, *aromatic*), 148.30 (s, *aromatic*), 136.53 (s, *aromatic*), 121.96 (s, *aromatic*), 119.84 (s, *aromatic*), 69.42 (s, -*C*H), 24.65 (s, -*C*H$_3$).

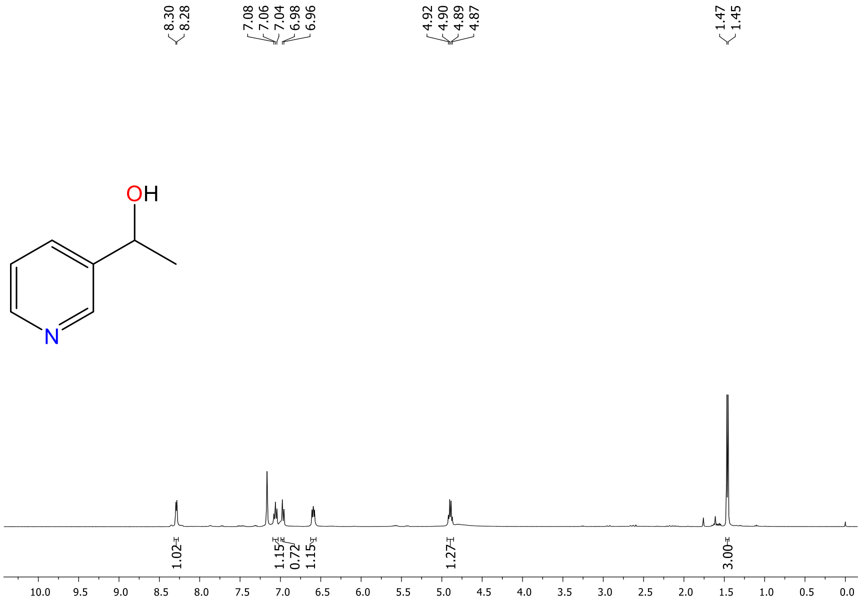


Figure S63. ^{1}H NMR spectrum of 1-(2-pyridine)ethanol in benzene-d_6.

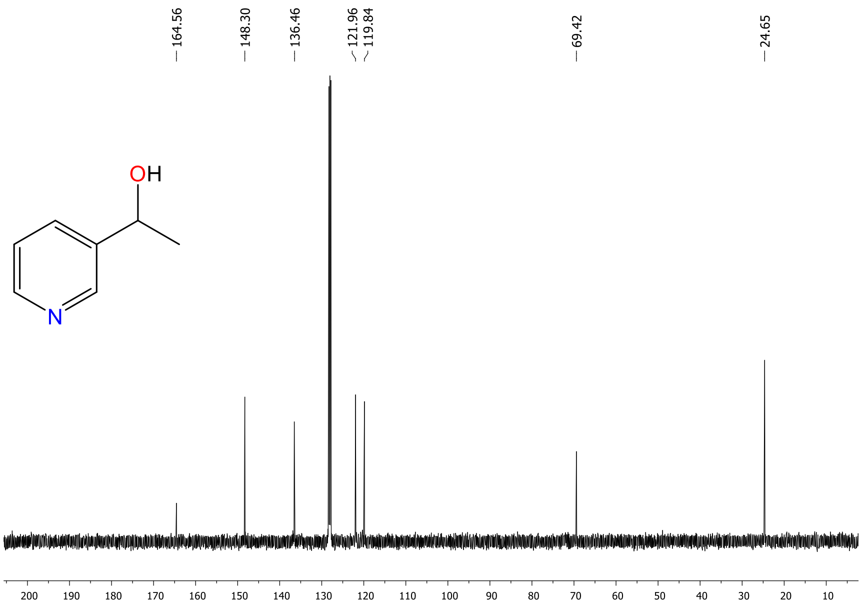


Figure S64. ^{13}C NMR spectrum of 1-(2-pyridine)ethanol in benzene-d_6.

Hydrosilylation of 2-acetylfuran using 0.1 mol% 2: In a glove box, a mixture of 2-acetylfuran (0.49 mL, 4.92 mmol) and $PhSiH_3$ (0.61 mL, 4.92 mmol) was added to a scintillation vial containing **2** (0.0033 g, 0.0049 mmol). The resulting light orange solution was allowed to stir at room temperature for 1 h and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was taken in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 3 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Rotary evaporation of the solvent at 25 °C yielded a colorless liquid identified as 1-(furan-2-yl)ethanol[13] (470 mg, 4.19 mmol, 85%). ^{1}H NMR (500 MHz, benzene-*d*$_6$): 7.27 (d, *J* = 10.2 Hz, 1H, *aromatic*), 6.15 (pseudo t, *J* = 4.0 Hz, 1H, *aromatic*), 6.10 (d, *J* = 3.1 Hz, 1H, *aromatic*), 4.71 (q, *J* = 6.5 Hz, 1H, -C*H*), 1.62 (s, 1H, -O*H*), 1.42 (d, *J* = 6.6 Hz, 3H, C*H*$_3$). ^{13}C NMR (126 MHz, benzene-*d*$_6$): 158.75 (s, *aromatic*), 141.70 (s, *aromatic*), 110.31 (s, *aromatic*), 105.07 (s, *aromatic*), 63.72 (s, -*C*H), 21.68 (s, -*C*H_3).

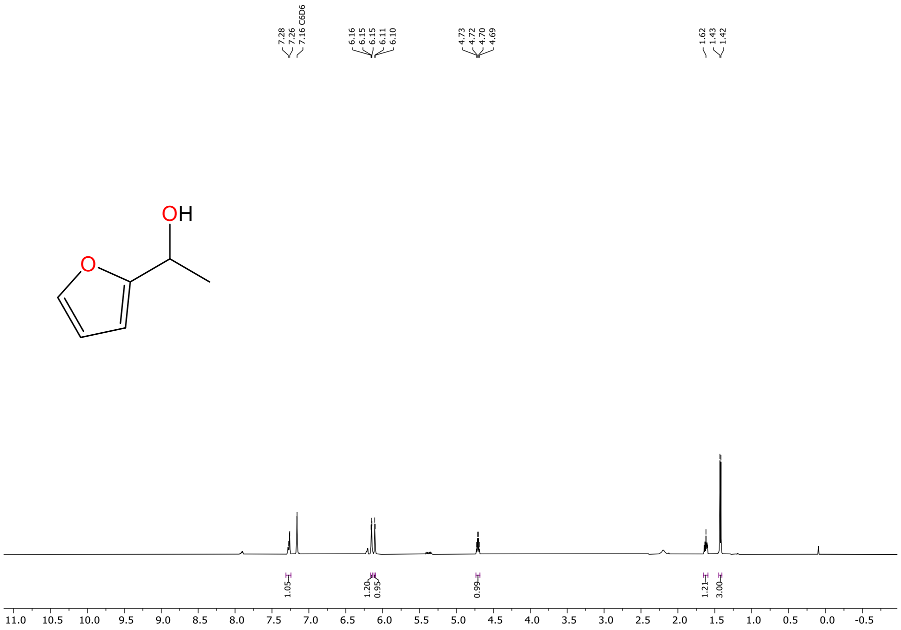


Figure S65. ^{1}H NMR spectrum of 1-(furan-2-yl)ethanol in benzene-*d*$_6$.

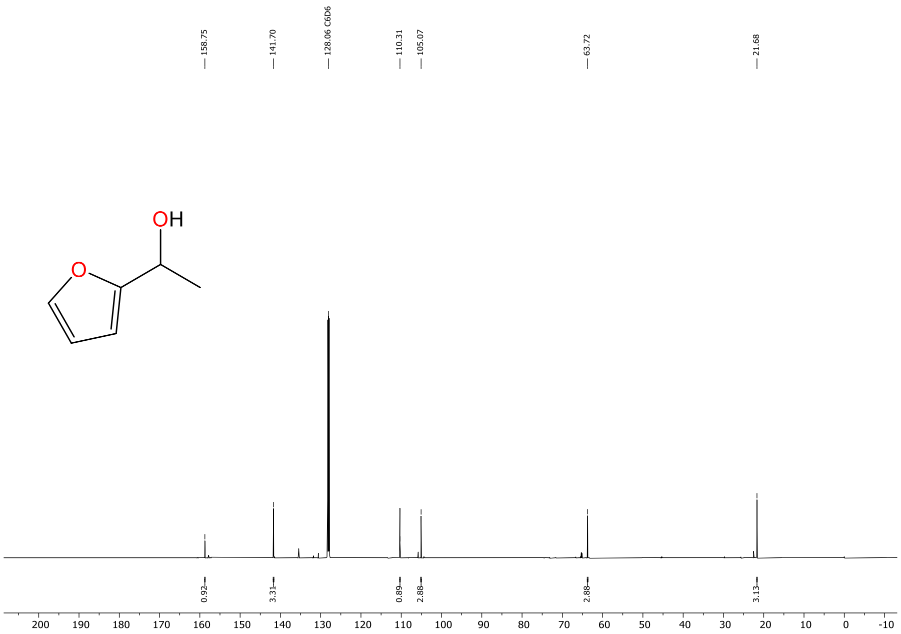


Figure S66. ^{13}C NMR spectrum of 1-(furan-2-yl)ethanol in benzene-d_6.

Hydrosilylation of 2-acetylthiophene using 0.1 mol% 2: In a glove box, a mixture of 2-acetylthiophene (0.56 mL, 5.22 mmol) and $PhSiH_3$ (0.64 mL, 5.22 mmol) was added to a scintillation vial containing **2** (0.0035 g, 0.0052 mmol). The resulting light orange solution was allowed to stir at room temperature for 2 h and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was taken in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 3 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Rotary evaporation of the solvent at 25 °C yielded a colorless liquid identified as 1-(Thiophen-2-yl)ethanol[12] (641 mg, 5.00 mmol, 96%). ^{1}H NMR (500 MHz, benzene-d_6): 6.86 (t, J = 4.1 Hz, 1H, *aromatic*), 6.70 (d, J = 4.6 Hz, 2H, *aromatic*), 4.76 (q, J = 6.4 Hz, 1H, -C*H*), 2.00 (s, 1H, -O*H*), 1.34 (d, J = 6.4 Hz, 3H, -C*H*$_3$). ^{13}C NMR (126 MHz, benzene-d_6): 150.94 (s, *aromatic*), 126.68 (s, *aromatic*), 124.22 (s, *aromatic*), 123.07 (s, *aromatic*), 66.20 (s, -*C*H), 25.61 (s, -*C*H$_3$).

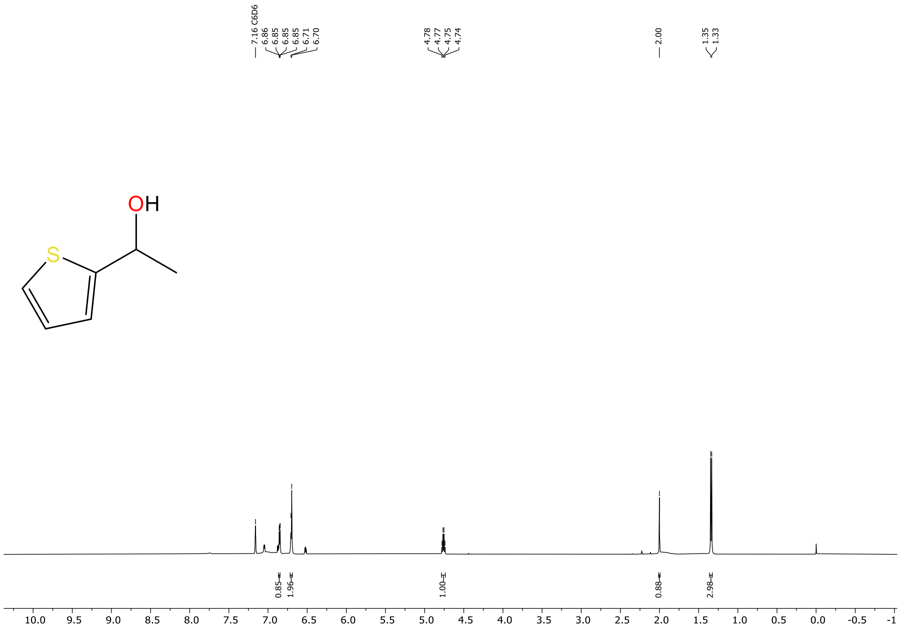


Figure S67. ^{1}H NMR spectrum of 1-(thiophen-2-yl)ethanol in benzene-d_6.

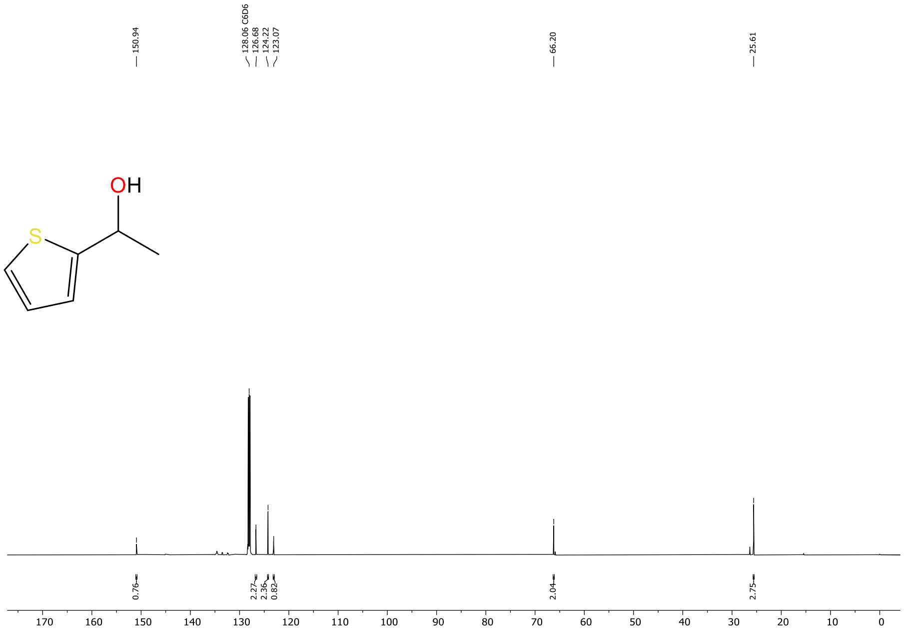


Figure S68. ^{13}C NMR spectrum of 1-(thiophen-2-yl)ethanol in benzene-d_6.

Hydrosilylation of 2,2,2-trifluoroacetophenone using 0.1 mol% 2: In a glove box, a mixture of 2,2,2-trifluoroacetophenone (0.41 mL, 2.982 mmol) and $PhSiH_3$ (0.37 mL, 2.982 mmol) was added to another scintillation vial containing **2** (0.002 g, 0.00298 mmol). The resulting light orange solution was allowed to stir at room temperature for 5 min and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was taken in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 3 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite and dried over Na_2SO_4. Rotary evaporation of the solvent at 25 °C yielded a colorless liquid identified as 2,2,2-trifluoro-1-phenylethanol[12] (381 mg, 2.16 mmol, 73%).^{1}H NMR (400 MHz, benzene-*d*$_6$): 7.23 (d, *J* = 5.1 Hz, 2H, *phenyl*), 7.06 (m, 3H, *phenyl*), 4.47 (m, *J* = 6.9 Hz, 1H, -C*H*). ^{13}C NMR (101 MHz, benzene-*d*$_6$): 134.56 (s, *phenyl*), 129.54 (s, *phenyl*), 128.70 (s, *phenyl*), 126.38 (s, *phenyl*), 123.57 (s, -*C*H), 75.63 (q, *J* = 32.3 Hz, -*C*F$_3$). ^{19}F NMR (376 MHz, benzene-*d*$_6$): -76.00 (d, *J* = 7.5 Hz, -C*F*$_3$).

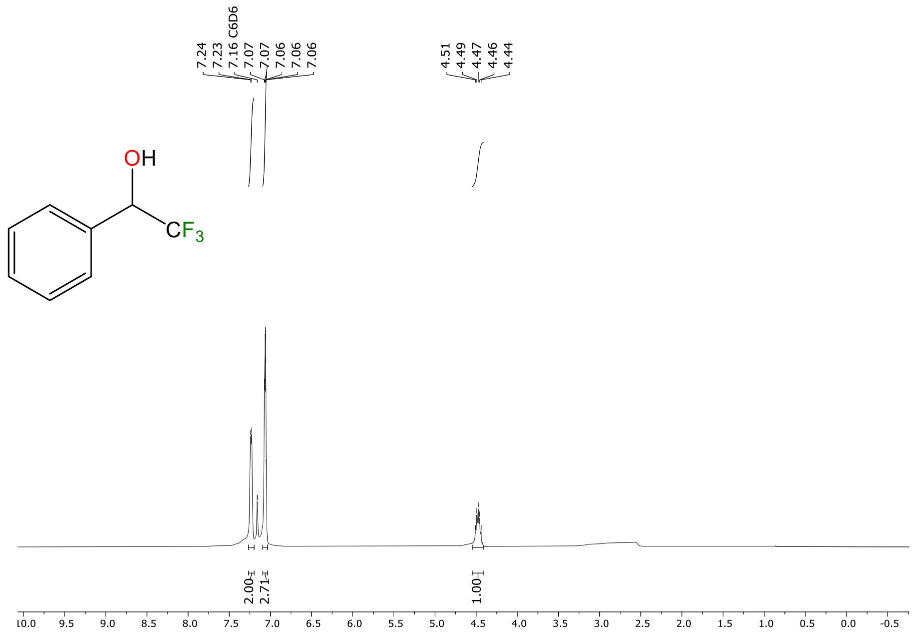


Figure S69. ^{1}H NMR spectrum of 2,2,2-trifluoro-1-phenylethanol in benzene-*d*$_6$.

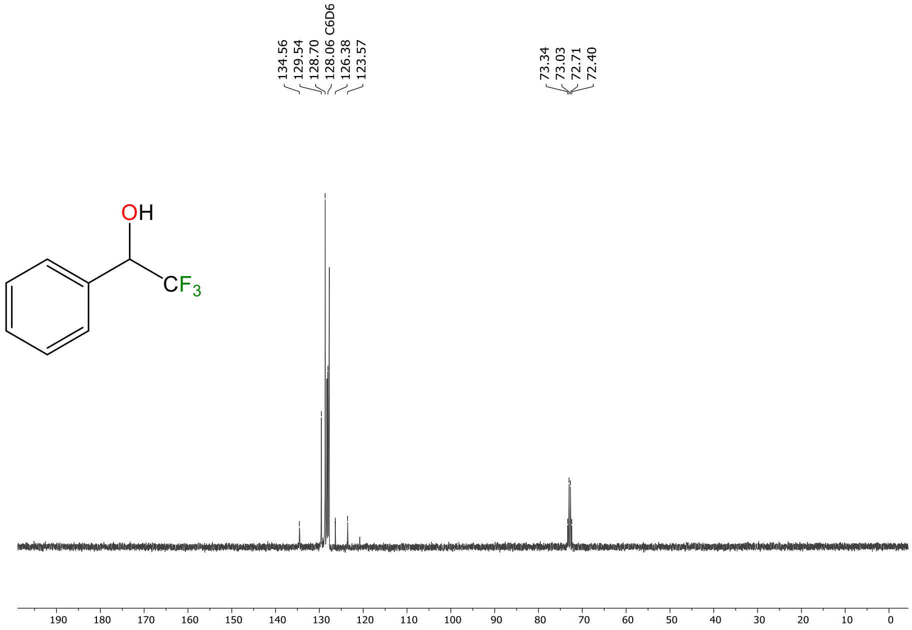


Figure S70. ^{13}C NMR spectrum of 2,2,2-trifluoro-1-phenylethanol in benzene-*d*$_6$.

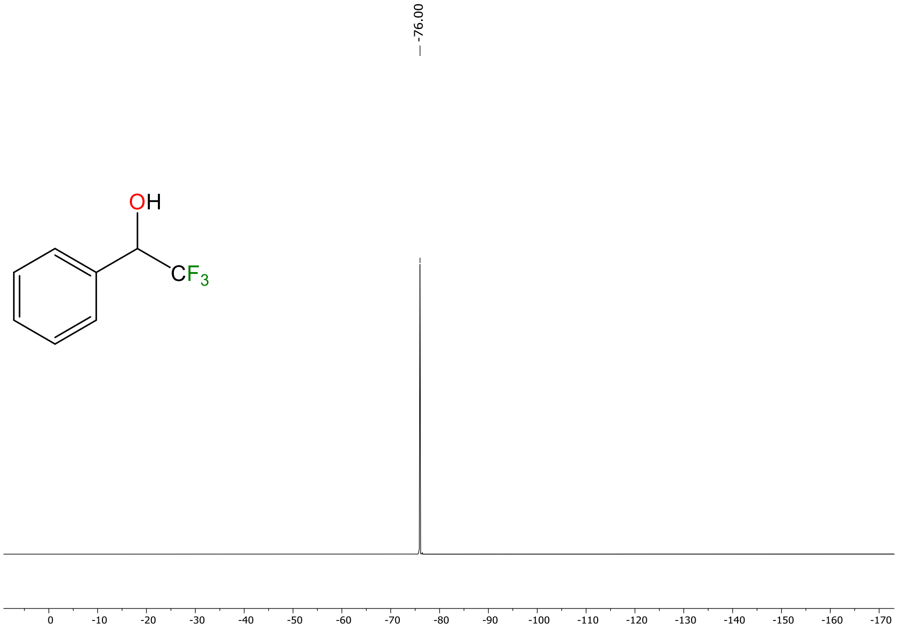


Figure S71. ^{19}F NMR spectrum of 2,2,2-trifluoro-1-phenylethanol in benzene-*d*$_6$.

Hydrosilylation of benzophenone using 0.1 mol% 2: In a glove box, a mixture of benzophenone (0.35 mL, 2.684 mmol) and $PhSiH_3$ (0.33 mL, 2.684 mmol) were added to a scintillation vial containing **2** (0.0018 g, 0.00268 mmol). The resulting light orange solution was allowed to stir at room temperature for 18 h and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^1H NMR spectrum was collected in $CDCl_3$, which revealed >99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 3 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Rotary evaporation of the solvent at 25 °C yielded a colorless liquid identified as diphenylmethanol[13] (411 mg, 2.23 mmol, 83%). ^1H NMR (400 MHz, benzene-d_6): 7.27 (d, J = 7.6 Hz, 4H, *phenyl*), 7.11 (t, J = 7.8 Hz, 4H, *phenyl*), 7.04 (d, J = 7.7 Hz, 2H, *phenyl*), 5.48 (s, 1H, -C*H*), 2.24 (s, 1H, -O*H*). ^{13}C NMR (101 MHz, benzene-d_6): 144.74 (s, *phenyl*), 128.57 (s, *phenyl*), 127.51 (s, *phenyl*), 127.02 (s, *phenyl*), 76.19 (s, -*C*H).

Figure S72. ^1H NMR spectrum of diphenylmethanol in benzene-d_6.

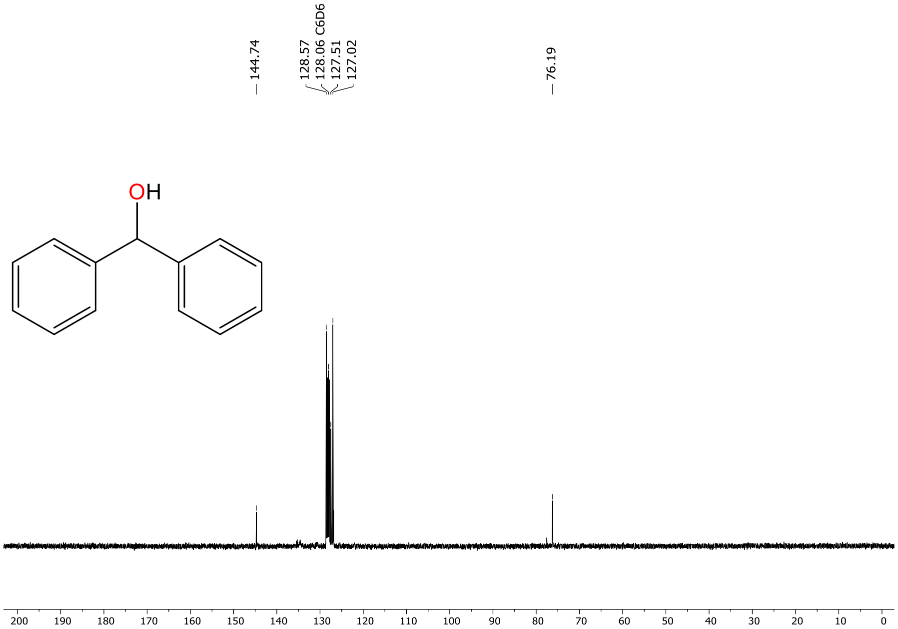


Figure S73. ^{13}C NMR spectrum of diphenylmethanol in benzene-d_6.

Hydrosilylation of 2-hexanone using 0.1 mol% 2: In a glove box, a mixture of hexanone (0.26 mL, 2.09 mmol) and $PhSiH_3$ (0.26 mL, 2.09 mmol) were added to another scintillation vial containing **2** (0.0014 g, 0.0021mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 2 min and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was collected in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 3 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. Rotary evaporation of the solvent at 25 °C yielded a colorless liquid identified as 2-hexanol[9] (187 mg, 1.83 mmol, 88%). ^{1}H NMR (400 MHz, benzene-d_6): 3.68 (m, J = 6.0 Hz, 1H, -CH), 3.47 (s, 1H, -OH), 1.45 (m, 1H, -CH_2), 1.34 (m, J = 4.7 Hz, 2H, -CH_2), 1.25 (m, 3H, -CH_2), 1.13 (d, J = 6.3 Hz, 3H, -CH_3), 0.89 (t, J = 7.1 Hz, 3H, -CH_3). ^{13}C NMR (101 MHz, benzene-d_6): 67.84 (s, -CH), 39.43 (s, -CH$_2$), 28.46 (s, -CH$_2$), 23.61 (s, -CH$_2$), 23.21 (s, -CH$_3$), 14.36 (s, -CH$_3$).

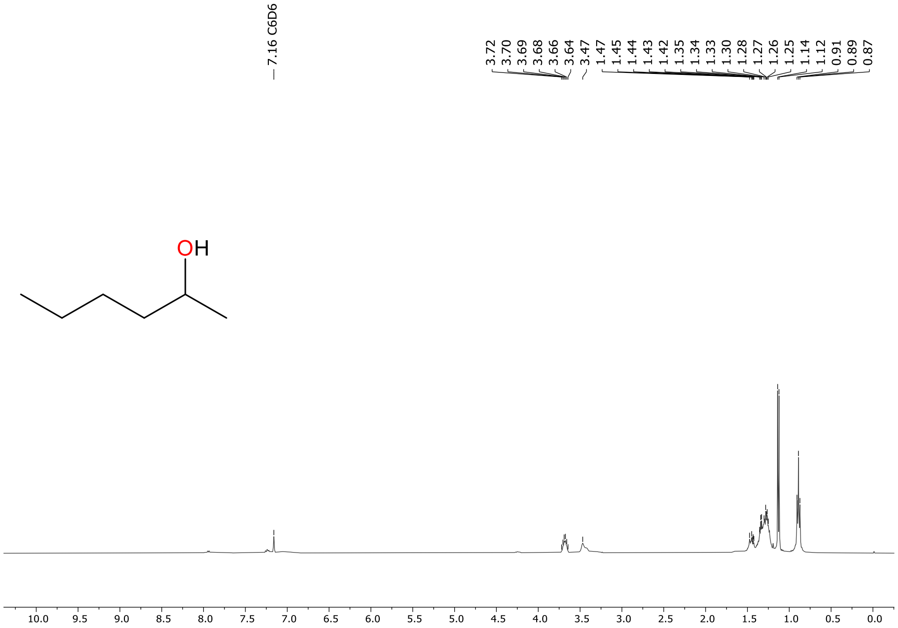


Figure S74. ^{1}H NMR spectrum of 2-hexanol in benzene-*d*$_{6}$.

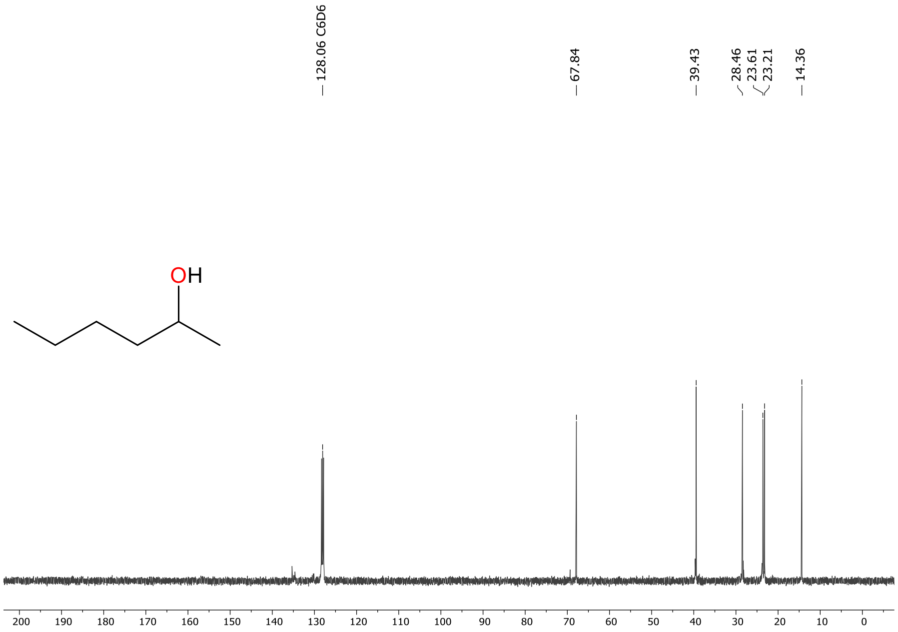


Figure S75. ^{13}C NMR spectrum of 2-hexanol in benzene-*d*$_{6}$.

Hydrosilylation of cyclohexanone using 0.1 mol% 2: In a glove box, a mixture of cyclohexanone (0.26 mL, 2.53 mmol) and PhSiH$_3$ (0.31 mL, 2.53 mmol) was added to a scintillation vial containing **2** (0.0017 g, 0.00253 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 2 min and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was collected in CDCl$_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 2 h. The organic product was extracted using Et$_2$O (3 x 3 mL), filtered through Celite and dried over Na$_2$SO$_4$. Rotary evaporation at 25 °C yielded a colorless liquid identified as cyclohexanol[9] (197.6 mg, 1.97 mmol, 78%). ^{1}H NMR (400 MHz, benzene-d_6): 3.95 (s, 1H, -O*H*), 3.58 (dt, *J* = 9.7, 5.4 Hz, 1H, -C*H*), 1.91 (d, *J* = 12.8 Hz, 2H, -CH_2), 1.67 (dd, *J* = 8.9, 4.4 Hz, 2H, -CH_2), 1.37 (m, 3H, -CH_2), 1.13 (dt, *J* = 22.3, 11.9 Hz, 3H, -CH_2). ^{13}C NMR (101 MHz, benzene-d_6): 69.82 (s, -*C*H), 35.82 (s, -*C*H$_2$), 25.91 (s, -*C*H$_2$), 24.38 (s, -*C*H$_2$).

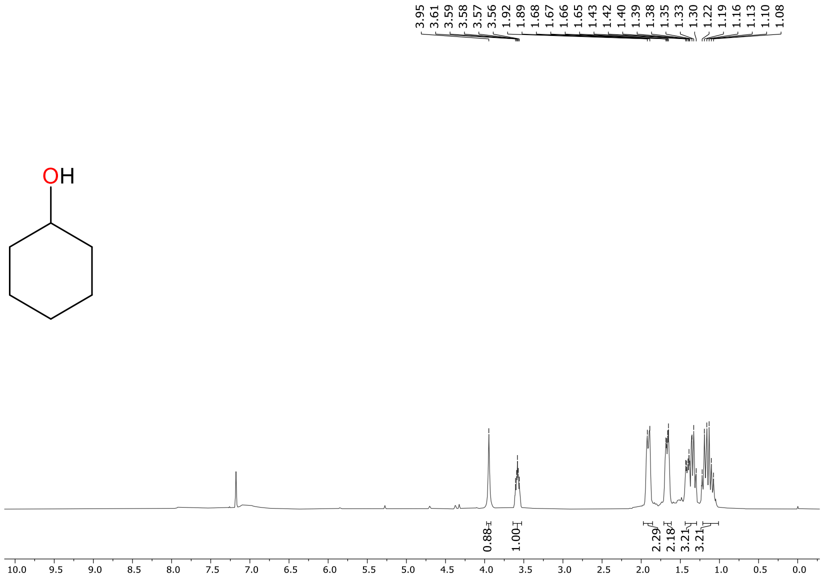


Figure S76. ^{1}H NMR spectrum of cyclohexanol in benzene-d_6.

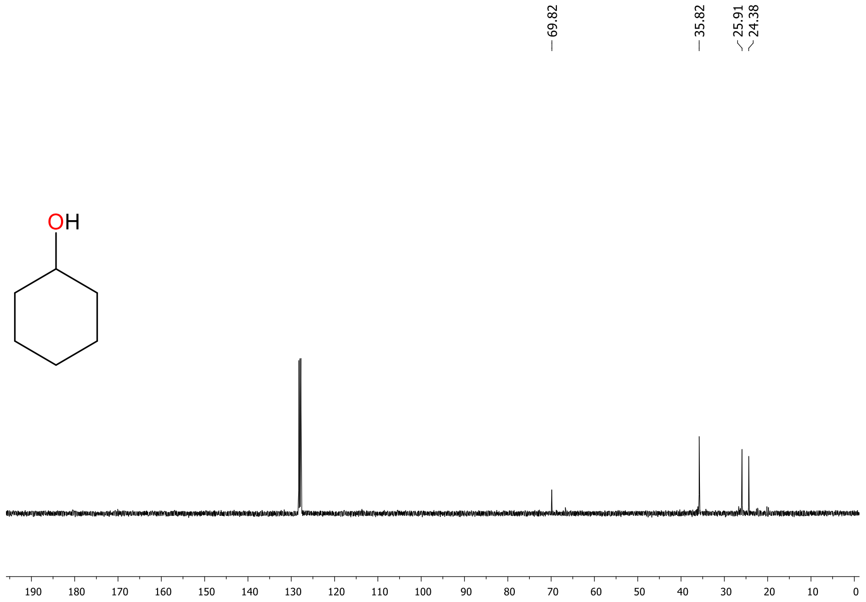


Figure S77. ^{13}C NMR spectrum of cyclohexanol in benzene-d_6.

Hydrosilylation of 2,4-dimethylpentan-3-one using 0.1 mol% 2: In a glove box, a mixture of Diisopropyl ketone (0.35 mL, 2.53 mmol) and PhSiH$_3$ (0.31 mL, 2.53 mmol) was added to a scintillation vial containing **2** (0.0017 g, 0.00253 mmol). The resulting light orange solution was allowed to stir at room temperature for 24 h and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was taken in CDCl$_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 2 mL of 10% NaOH(aq) and allowed to stir for 3 h. The organic product was extracted using Et$_2$O (3 x 3 mL), filtered through Celite, and dried over Na$_2$SO$_4$. Rotary evaporation of the solvent at 25 °C yielded a colorless liquid identified as 2,4-dimethyl-3-pentanol[9] (291 mg, 1.69 mmol, 68%). ^{1}H NMR (400 MHz, benzene-d_6): 3.37 (t, J = 5.5 Hz, 1H, -C*H*), 1.77 (ddt, J = 25.8, 12.4, 6.3 Hz, 2H, -C*H*), 1.08 (d, J = 6.7 Hz, 3H, -C*H*$_3$), 0.94 (d, J = 6.7 Hz, 6H, -C*H*$_3$), 0.80 (d, J = 6.8 Hz, 3H, -C*H*$_3$). ^{13}C NMR (101 MHz, benzene-d_6): 83.93 (s, -*C*H), 30.71 (s, -*C*H), 19.46 (s, -*C*H$_3$), 17.09 (s, -*C*H$_3$).

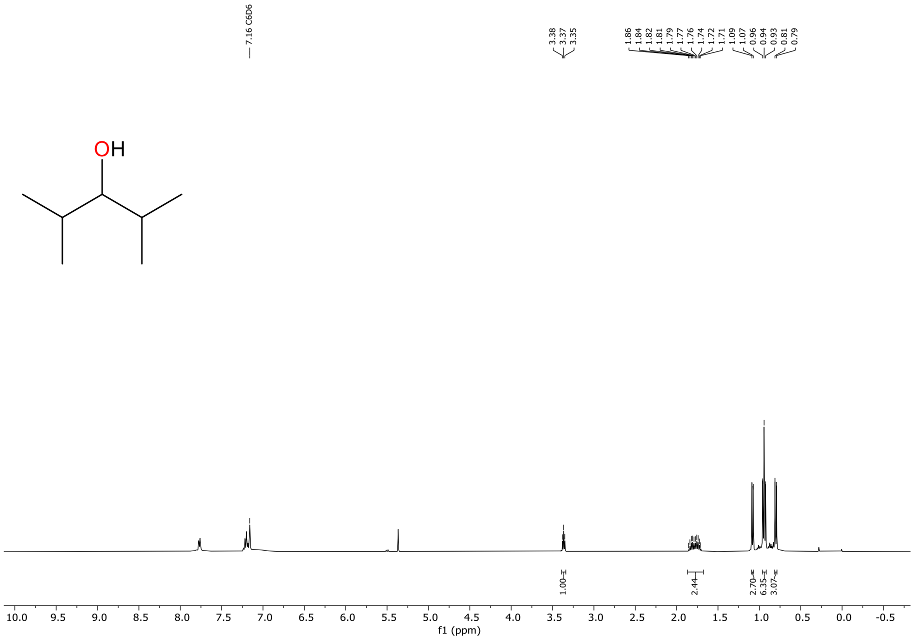


Figure S78. ^{1}H NMR spectrum of 2,4-dimethyl-3-pentanol in benzene-d_6.

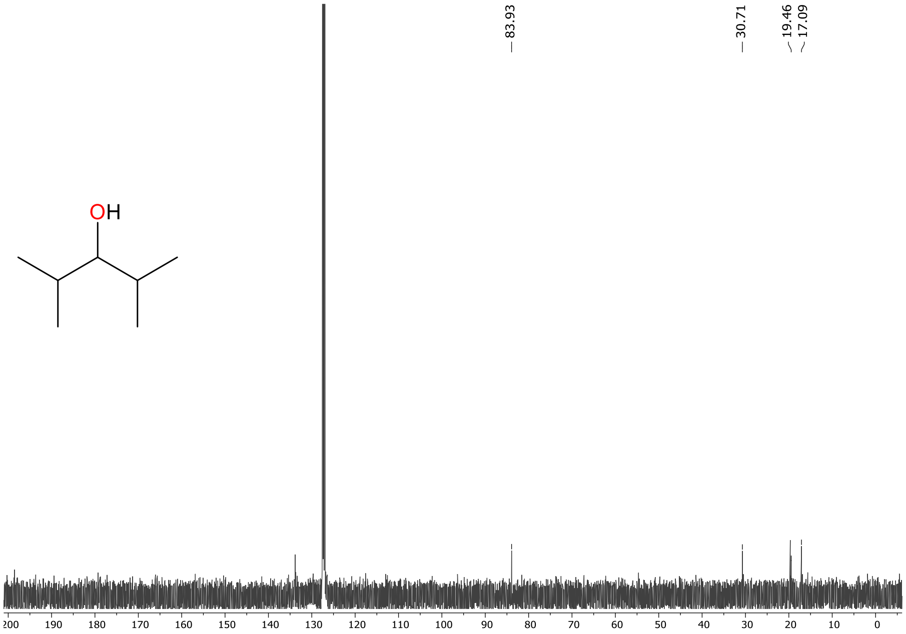


Figure S79. ^{13}C NMR spectrum of 2,4-dimethyl-3-pentanol in benzene-d_6.

Hydrosilylation of benzaldehyde using 0.01 mol% 2: In a glove box, a mixture of benzaldehyde (1.67 mL, 16.40 mmol) and $PhSiH_3$ (2.02 mL, 16.40 mmol) was added to a scintillation vial containing **2** (0.0011 g, 0.0016 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 30 s and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was collected in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 5 mL of 10% NaOH(aq) and allowed to stir for 2 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. The solvent was evaporated using a rotovap at 25 °C to yield a colorless liquid identified as benzyl alcohol[6] (0.896, 8.28 mmol, 51%). ^{1}H NMR (400 MHz, benzene-d_6): 7.21 (d, *J* = 7.2 Hz, 2H, *phenyl*), 7.16 (d, *J* = 6.3 Hz, 2H, *phenyl*), 7.10 (t, *J* = 7.8 Hz, 1H, *phenyl*), 4.37 (s, 2H, -C*H*$_2$), 2.70 (s, 1H, -O*H*). ^{13}C NMR (101 MHz, benzene-d_6): 141.77 (s, *phenyl*), 128.58 (s, *phenyl*), 127.47 (s, *phenyl*), 127.11 (s, *phenyl*), 64.88 (s, -*C*H$_2$).

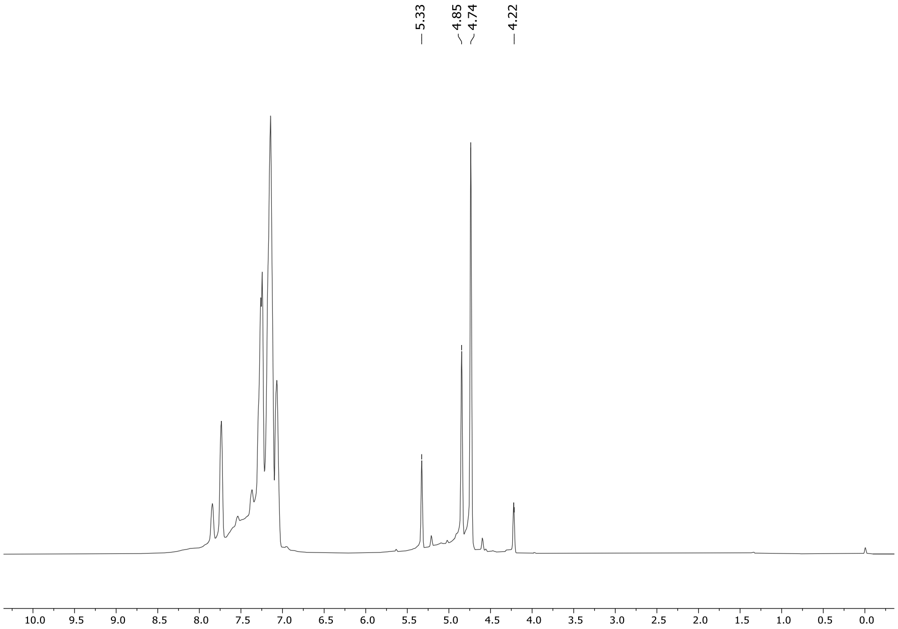


Figure S80. ^{1}H NMR spectrum of silyl ethers generated via **2**-catalyzed benzaldehyde hydrosilylation prior to hydrolysis in chloroform-*d*.

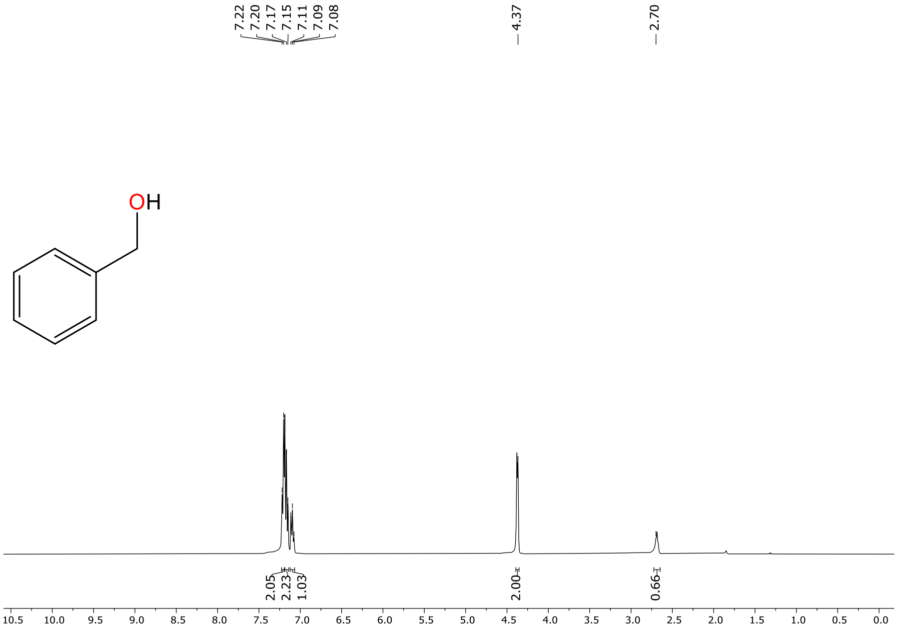


Figure S81. ^{1}H NMR spectrum of benzyl alcohol in benzene-d_6.

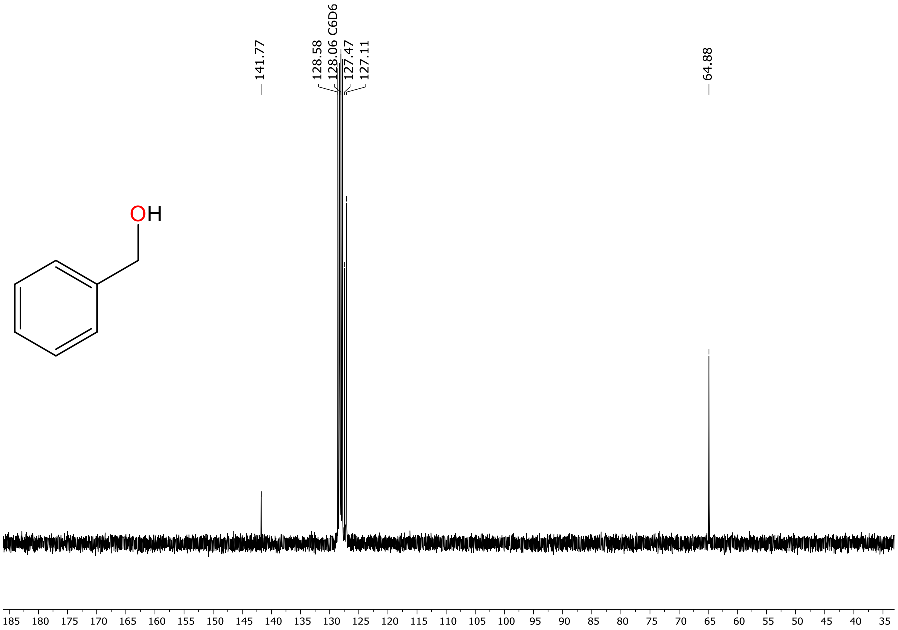


Figure S82. ^{13}C NMR spectrum of benzyl alcohol in benzene-d_6.

Hydrosilylation of acetophenone using 0.01 mol% 2: In a glove box, a mixture of acetophenone (2.08 mL, 17.89 mmol) and $PhSiH_3$ (2.2 mL, 17.89 mmol) was added to a scintillation vial containing **2** (0.0012 g, 0.0018 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 30 s and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was collected in $CDCl_3$, which revealed 98% conversion. The solution was hydrolyzed with 5 mL of 10% NaOH(aq) and allowed to stir for 2 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite, and dried over Na_2SO_4. The solvent was evaporated under vacuum at 25 °C to yield a colorless liquid identified as 1-phenylethanol[9] (0.947, 8.28 mmol, 43%). ^{1}H NMR (400 MHz, benzene-*d*$_6$): 7.24 (d, *J* = 7.0 Hz, 2H, *phenyl*), 7.18 (t, *J* = 7.6 Hz, 2H, *phenyl*), 7.09 (d, *J* = 6.6 Hz, 1H, *phenyl*), 4.59 (m, *J* = 8.9 Hz, 1H, -C*H*), 1.30 (d, *J* = 6.5 Hz, 3H, -C*H*$_3$). ^{13}C NMR (101 MHz, benzene-*d*$_6$): 146.62 (s, *phenyl*), 128.56 (s, *phenyl*), 127.36 (s, *phenyl*), 125.79 (s, *phenyl*), 70.22 (s, -*C*H), 25.56 (s, -*C*H$_3$).

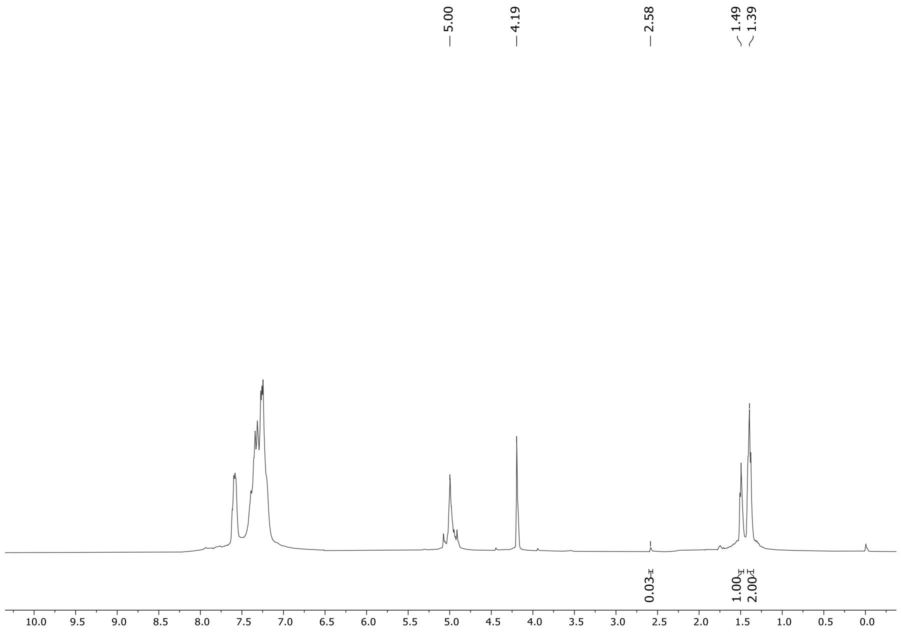


Figure S83. ^{1}H NMR spectrum of silyl ethers generated via **2**-catalyzed acetophenone hydrosilylation prior to hydrolysis in chloroform-*d*.

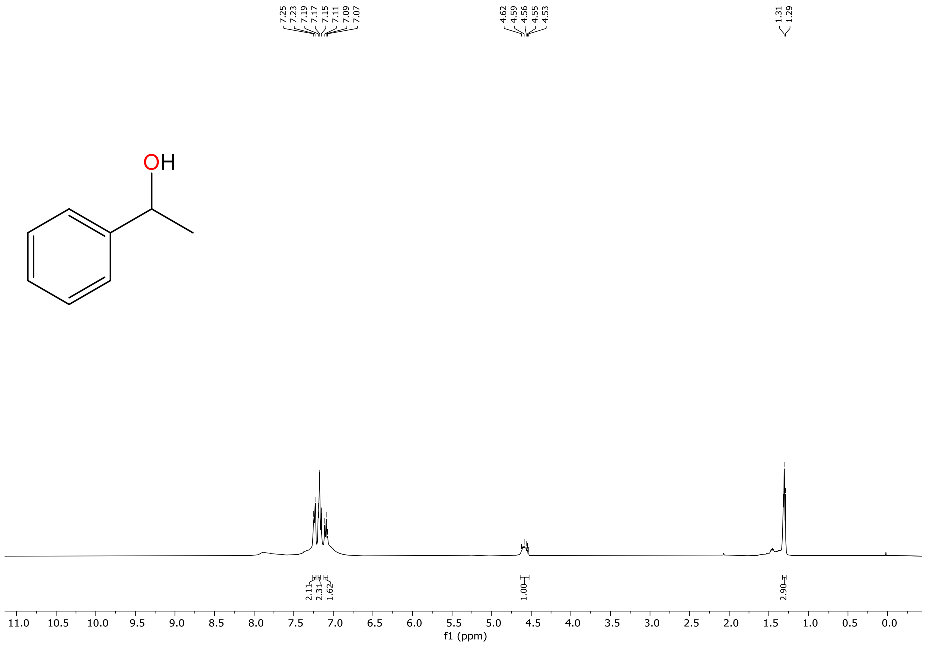


Figure S84. ^{1}H NMR spectrum of 1-phenylethanol in benzene-*d₆*.

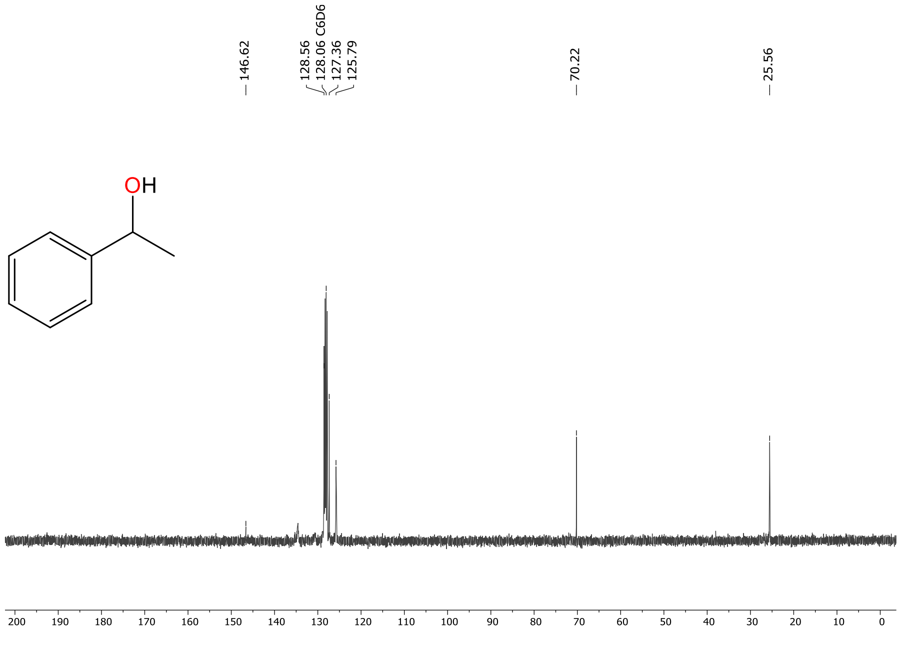


Figure S85. ^{13}C NMR spectrum of 1-phenylethanol in benzene-*d₆*.

Hydrosilylation of cyclohexanone using 0.01 mol% 2: In a glove box, a mixture of cyclohexanone (1.54 mL, 14.91 mmol) and $PhSiH_3$ (1.84 mL, 14.91 mmol) was added to a scintillation vial containing **2** (0.001 g, 0.0015 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was allowed to stir at room temperature for 30 s and then exposed to air to deactivate the catalyst. The resulting solution was filtered through Celite and a ^{1}H NMR spectrum was collected in $CDCl_3$, which revealed greater than 99% conversion. The solution was hydrolyzed with 5 mL of 10% NaOH(aq) and allowed to stir for 2 h. The organic product was extracted using Et_2O (3 x 3 mL), filtered through Celite and dried over Na_2SO_4. Rotary evaporation of the solvent at 25 °C yielded a colorless liquid identified as cyclohexanol[9] (1.49 g, 10.28 mmol, 69%). ^{1}H NMR (400 MHz, benzene-d_6): 3.68 (s, 1H, -O*H*), 3.55 (m, J = 4.1 Hz, 1H, -C*H*), 1.89 (d, J = 16.9 Hz, 2H, -CH_2), 1.65 (dt, J = 8.8, 4.1 Hz, 2H, -CH_2), 1.38 (m, 1H, J = 6.0 Hz, -CH_2), 1.30 (m, 2H, -CH_2), 1.12 (dq, J = 21.8, 11.1 Hz, 3H, -CH_2). ^{13}C NMR (101 MHz, benzene-d_6): 70.01 (s, -*C*H), 35.88 (s, -*C*H_2), 26.02 (s, -*C*H_2), 24.59 (s, -*C*H_2).

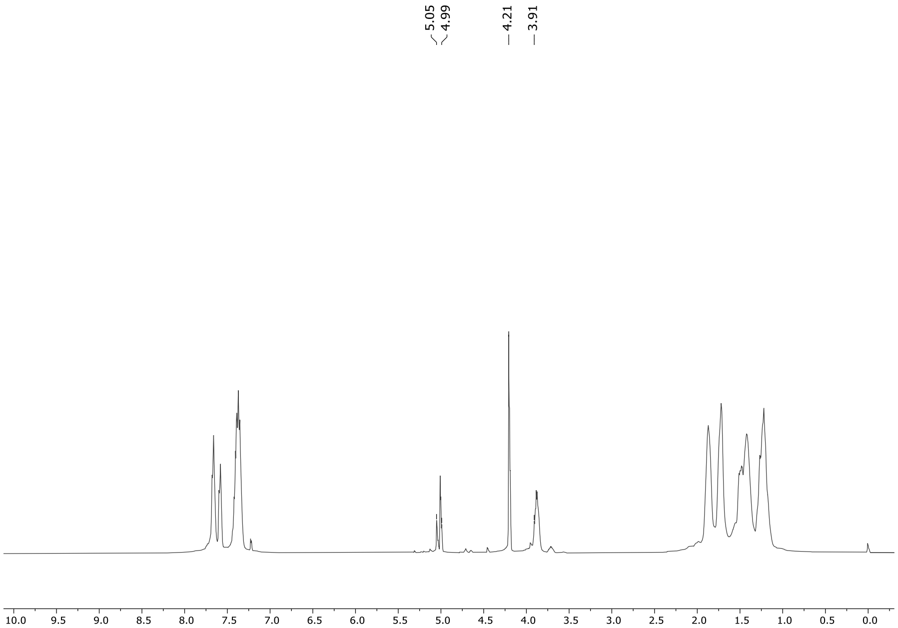


Figure S86. ^{1}H NMR spectrum of silyl ethers generated via **2**-catalyzed cyclohexanone hydrosilylation prior to hydrolysis in chloroform-*d*.

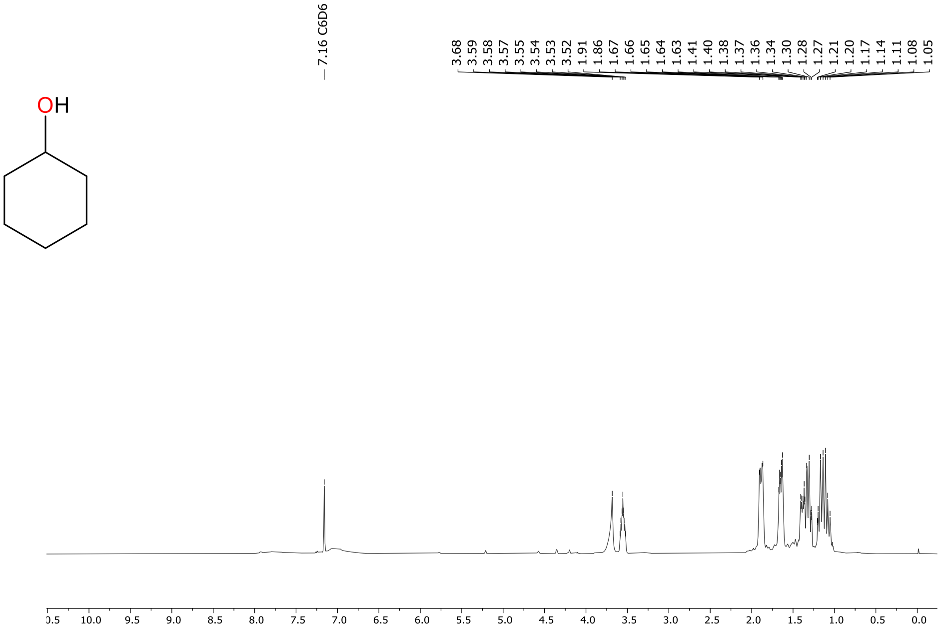


Figure S87. ^{1}H NMR spectrum of cyclohexanol in benzene-d_6.

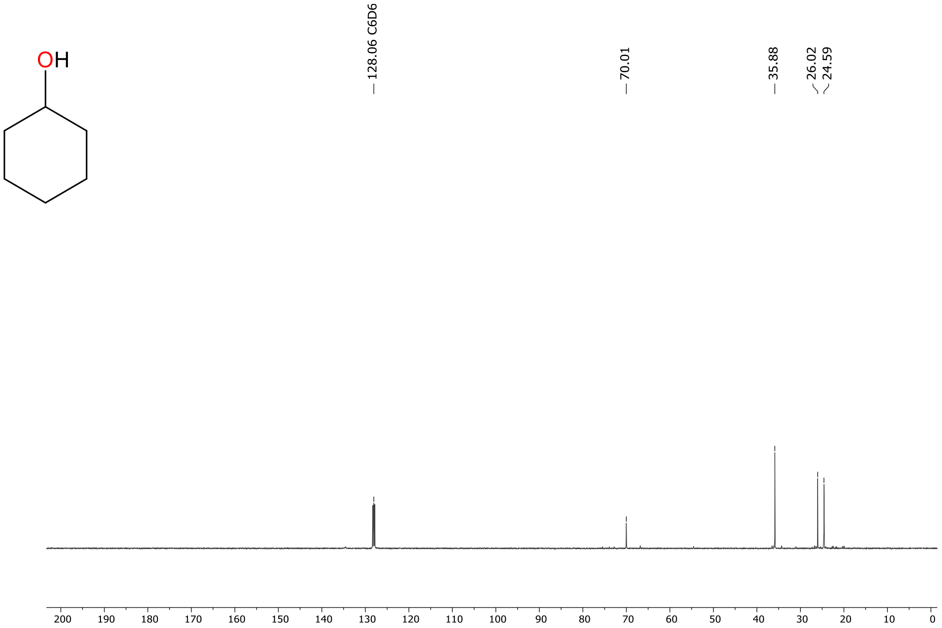


Figure S88. ^{13}C NMR spectrum of cyclohexanol in benzene-d_6.

Determination of maximum aldehyde hydrosilylation TON: Under an inert atmosphere, a round bottom flask was charged with 0.0013 g (0.0019 mmol) of **2**. A mixture of 2.38 mL (19.38 mmol) of $PhSiH_3$ and 1.97 mL (19.38 mmol) of benzaldehyde was added to the flask and stirred for 2 min. The resulting light orange solution became hot and was then allowed to cool to room temperature over the next 15 min. At that time, an additional 10,000 equivalents of $PhSiH_3$ and benzaldehyde were added. This process was repeated three additional times until a total of 50,000 equivalents of $PhSiH_3$ and benzaldehyde were added. Finally, the pale orange mixture was exposed to air to deactivate the catalyst. Collecting a ^{1}H NMR spectrum of the mixture revealed 38% overall conversion of the substrate into silyl ethers, equating to a TON of 19,000.

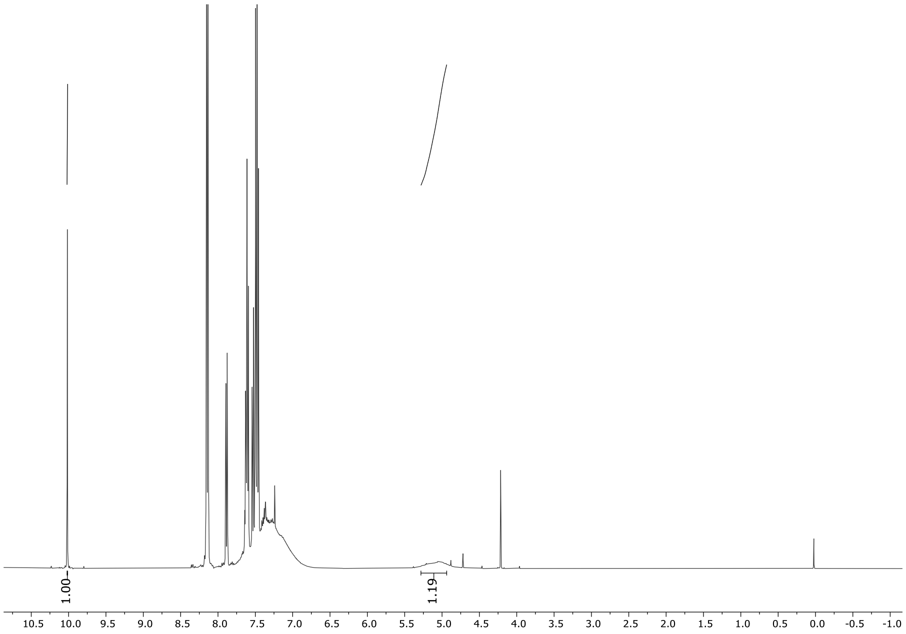


Figure 89. ^{1}H NMR spectrum of silyl ethers and unreacted benzaldehyde in benzene-d_6.

Procedure for the determination of maximum ketone hydrosilylation TON: Under an inert atmosphere, a round bottom flask was charged with 0.0011 g (0.0016 mmol) of **2**. A mixture of 2.02 mL (16.40 mmol) of $PhSiH_3$ and 1.70 mL (16.40 mmol) of cyclohexanone was added to the flask and stirred for 2 min. The resulting brown solution became hot and was then allowed to cool to room temperature over the next 15 min. At that time, an additional 10,000 equivalents of $PhSiH_3$ and cyclohexanone were added. This process was repeated two additional times until a total of 40,000 equivalents of $PhSiH_3$ and cyclohexanone were added. Finally, the pale brown mixture was exposed to air to deactivate the catalyst. Collecting a ^1H NMR spectrum of the mixture revealed an overall 44% conversion of the substrate into silyl ethers, resulting in a TON of 17,600.

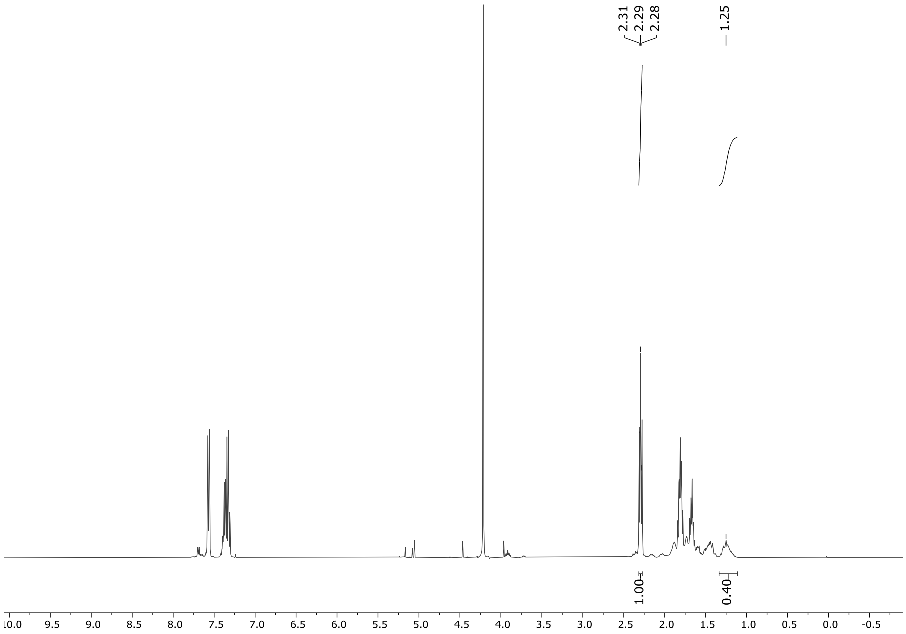


Figure 90. ^1H NMR spectrum of silyl ethers and unreacted cyclohexanone in benzene-d_6.

MECHANISTIC EXPERIMENTS

Given the activity observed for **2**, there was interest in elucidating the mechanism through which it operates. Unfortunately, its efficiency precluded our ability to observe catalytically-relevant intermediates. The independent addition of benzaldehyde to 5 mol% **2** in benzene-*d*$_6$ did not result in a reaction at 25 °C or upon heating to 80 °C for 24 h, as judged by multinuclear NMR spectroscopy. Similarly, the addition of excess phenylsilane to **2** did not result in conversion to a new Co complex. Benzaldehyde hydrosilylation was then conducted using a 5 mol% loading of **2** to allow for post-catalysis Co complex identification. After 2 min, complete substrate hydrosilylation was noted and ^{31}P NMR analysis confirmed the presence of **2**, which also appears to be the catalyst resting state (no color change was noted during catalysis).

It was recently proposed that the ability of (^{Ph_2PPr}PDI)Mn to catalyze efficient carbonyl hydrosilylation through a Si–H activation, carbonyl insertion, and Si–O reductive elimination pathway[6] is enabled by a particularly small thermodynamic penalty associated with phosphine arm dissociation (2.6 kcal/mol).[14,15] To provide additional insight into the activity of **2**, DFT calculations were performed to elucidate the relative energy of its 4-coordinate analog, which was found to be 20.5 kcal/mol uphill. This energy penalty is sufficiently large to suggest that the superior hydrosilylation activity of **2** is not due to facile phosphine dissociation and subsequent Si–H oxidative addition. Computational models considering several reaction pathways failed to produce a convincing mechanism, implying that an unconventional hydrosilylation cycle may be operative.

Reaction between benzaldehyde and 5 mol% of 2: Under an inert atmosphere, a J. Young tube was charged with a mixture of 0.020 g (0.0298 mmol) of **2** and 0.06 mL (0.596 mmol) of benzaldehyde in benzene-*d*$_6$ and sealed. The collection of ^{1}H and ^{31}P NMR spectra at room temperature revealed no reaction. After heating the J. Young tube at 80 °C for 24 h, no change was noted by ^{1}H and ^{31}P NMR spectroscopy.

Reaction between PhSiH$_3$ and 5 mol% of 2: Under an inert atmosphere, a J. Young tube was charged with a mixture of 0.015 g (0.0224 mmol) of **2** and 0.05 mL (0.447 mmol) of PhSiH$_3$ in benzene-*d*$_6$ and sealed. The collection of ^{1}H, ^{29}Si, and ^{31}P NMR spectra at room temperature revealed no reaction. After heating the J. Young tube at 80 °C for 12 h, no change was noted by ^{1}H and ^{31}P NMR spectroscopy.

Hydrosilylation of benzaldehyde using 5 mol% of 2: In the glove box, a mixture of benzaldehyde (0.076 mL, 0.745 mmol) and $PhSiH_3$ (0.092 mL, 0.745 mmol) was added to a scintillation vial containing **2** (0.025 g, 0.0373 mmol). The resulting light orange solution became hot and the reaction vigorously bubbled. The mixture was then allowed to stir at room temperature for 2 min. This resulting solution was transferred to a J. Young tube and sealed. A ^1H NMR spectrum was collected in benzene-d_6, which revealed greater than 99% conversion. The ^{31}P NMR spectrum revealed **2**.

COMPUTATIONAL DETAILS

All calculations were carried out using DFT[16] as implemented in the Jaguar 9.1 suite[17] of *ab initio* quantum chemistry programs. Geometry optimizations were performed with B3LYP-D3[18-23] functional and the 6-31G** basis set[24] for main group atoms. Co was represented using the Los Alamos LACVP basis.[25-27] The energies of the optimized structures were reevaluated by additional single-point calculations on each optimized geometry with Dunning's correlation consistent triple-ζ basis set cc-pVTZ(-f),[28] which includes a double set of polarization functions. For Co, we used a modified version of LACVP, designated as LACV3P, in which the exponents were decontracted to match the effective core potential with triple-ζ quality. Solvation energies were evaluated by a self-consistent reaction field (SCRF) approach based on accurate numerical solutions of the Poisson-Boltzmann equation. In the results reported, solvation calculations were carried out with the 6-31G**/LACVP basis at the optimized gas-phase geometry employing the dielectric constants of $\varepsilon = 2.379$ for toluene. As is the case for all continuum models, the solvation energies are subject to empirical parametrization of the atomic radii that are used to generate the solute surface. We employed the standard set of optimized radii in Jaguar for H (1.150 Å), C (1.900 Å), N (1.600 Å), P (2.074 Å), and Co (1.436 Å). Analytical vibrational frequencies within the harmonic approximation were computed with the 6-31G**/LACVP basis to confirm proper convergence to well-defined minima or saddle points on the potential energy surface. The energy components have been computed with the following protocol. The free energy in solution-phase, $G(\mathrm{sol})$, has been calculated as follows:

$$G(\mathrm{sol}) = G(\mathrm{gas}) + G_{\mathrm{solv}}$$

$$G(\mathrm{gas}) = H(\mathrm{gas}) - TS(\mathrm{gas})$$

$$H(\mathrm{gas}) = E(\mathrm{SCF}) + \mathrm{ZPE}$$

$$\Delta E(\mathrm{SCF}) = \sum E(\mathrm{SCF}) \text{ for products} - \sum E(\mathrm{SCF}) \text{ for reactants}$$

$$\Delta G(\mathrm{sol}) = \sum G(\mathrm{sol}) \text{ for products} - \sum G(\mathrm{sol}) \text{ for reactants}$$

Table S13. Computed energy components for DFT-optimized structures.

	E(SCF)/(eV) cc-pVTZ(-f)/LACV3P	**ZPE/(kcal/mol)** 6-31G**/LACVP	**S(gas)/(cal/mol·K)** 6-31G**/LACVP	**G(solv)/(kcal/mol)** 6-31G**/LACVP
^{1}**2**	-67674.453	446.28	244.73	-9.62
^{3}**2**	-67674.094	444.65	258.12	-10.28
^{5}**2**	-67672.961	443.83	249.74	-12.90

Table S14. Cartesian coordinates of the optimized geometries.

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^{1}**2**

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Co	12.901490211	-0.344653994	1.470313430
P	13.101685524	-2.033988953	2.938718081
P	12.899350166	1.534884691	2.711048841
N	14.838886261	-0.543676198	0.999368489
N	10.914701462	-0.202355593	1.264177799
C	15.106206894	-0.729627669	-0.281731784
C	11.974620819	-2.306014776	4.373012543
C	10.458076477	-0.216774419	0.023855284
C	13.930342674	-0.673584700	-1.122490883
C	14.210640907	2.023911715	3.918224812
C	14.141819000	1.695695519	5.282721519
C	10.801686287	-3.066740036	4.223432541
C	11.498385429	-0.404393494	-0.963177025
C	12.789234161	3.078372478	1.691197753
C	15.914418221	-0.605542839	1.988044739
C	14.777140617	-2.069148064	3.768084288
C	12.767742157	-0.477593243	-0.333745927
C	10.075902939	-2.480704069	6.460179329
C	9.994302750	0.008442366	2.380813122
C	11.354489326	1.707674623	3.747301340
C	12.751323700	4.357904911	2.269483328
C	15.387534142	2.635026455	3.447499990
C	13.151228905	-6.208437443	0.869836390
C	16.454666138	2.899371624	4.305702209
C	12.176611900	-1.638851404	5.593586922
C	12.555033684	5.364768982	0.079364702
C	11.398231506	-0.515042067	-2.357773781
C	13.090521812	-3.711417437	2.153238535
C	10.073084831	1.440341830	2.944958448

C	13.257776260	-4.892223358	2.896288633
C	15.930256844	-1.937429905	2.762761354
C	13.819295883	-0.795461774	-2.515185833
C	12.557695389	-0.711416423	-3.122866869
C	11.240569115	-1.726764083	6.625023365
C	16.488945007	-0.991100609	-0.828513086
C	9.864090919	-3.151529551	5.253716946
C	15.210107803	1.960793376	6.142469883
C	13.288390160	-6.131990910	2.259397984
C	12.634414673	5.493179321	1.469492912
C	9.004718781	-0.044724390	-0.347130001
C	12.946736336	-3.799284935	0.762890399
C	12.979771614	-5.042221069	0.124658361
C	16.374403000	2.559915543	5.658574581
C	12.711398125	2.959457397	0.298014909
C	12.593845367	4.097919941	-0.503589511
H	12.477763176	-0.802167058	-4.202522278
H	10.436047554	-0.456284255	-2.863101006
H	14.696279526	-0.953291655	-3.140777588
H	8.886215210	-0.009238696	-1.431433082
H	8.388006210	-0.870834351	0.027129725
H	8.591731071	0.883862972	0.062530331
H	16.957424164	-1.854169250	-0.342210799
H	16.447374344	-1.196915865	-1.899536014
H	17.154094696	-0.131432354	-0.681420267
H	12.816191673	-2.880546808	0.197130471
H	12.869126320	-5.095254421	-0.955418110
H	13.175646782	-7.175448418	0.373866558
H	13.416264534	-7.039345741	2.844496727
H	13.349480629	-4.842657566	3.978626251
H	10.623197556	-3.598219156	3.292665005
H	8.965630531	-3.746906519	5.111963749
H	9.345547676	-2.546116829	7.261596680
H	11.423389435	-1.204718232	7.561040401
H	13.070286751	-1.042159319	5.745202541
H	13.245986938	1.238238692	5.689207077
H	15.127318382	1.701783180	7.195086479
H	17.205583572	2.764575481	6.327377796
H	17.351320267	3.374227762	3.915439606
H	15.463043213	2.910911560	2.399008036
H	12.744160652	1.964483023	-0.139107987
H	12.536926270	3.991243362	-1.583943248
H	12.466424942	6.251133442	-0.543782175
H	12.609603882	6.478863716	1.927415252
H	12.832143784	4.467162132	3.348293543
H	8.959197044	-0.206875056	2.097192287
H	10.258646965	-0.697818816	3.171273708
H	9.981495857	2.161042452	2.122320652
H	9.210027695	1.597110868	3.605163813
H	11.325958252	2.704487085	4.201675415
H	11.420982361	0.970355153	4.554724693

H	16.895376205	-0.447999537	1.527798772
H	15.764769554	0.210972518	2.697892904
H	16.879419327	-2.003566027	3.310574532
H	15.912620544	-2.773522615	2.051970720
H	14.815618515	-1.221882463	4.461734295
H	14.878729820	-2.988904476	4.354783535

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Co	12.950459480	-0.210257143	1.377243400
P	13.319458961	-1.920967340	2.832038164
P	12.722759247	1.504578710	2.830333948
N	15.173606873	-0.631740689	0.630687237
N	10.627135277	-0.126506165	0.995399535
C	15.180751801	-0.995123804	-0.612362385
C	12.305869102	-2.044893026	4.368191719
C	10.352075577	-0.233682364	-0.264873534
C	13.893212318	-0.875676811	-1.357388973
C	13.913664818	1.857084990	4.195426464
C	13.610134125	1.768624425	5.562012672
C	11.008333206	-2.581061602	4.270228386
C	11.496386528	-0.524153948	-1.179281473
C	12.647330284	3.137817621	1.972549558
C	16.332286835	-0.804690301	1.491497278
C	15.062526703	-1.861422420	3.507017612
C	12.761925697	-0.604906440	-0.561169505
C	10.541963577	-1.996075630	6.573150158
C	9.618434906	0.126873329	2.007705212
C	11.071876526	1.489572287	3.702203989
C	12.714746475	4.362569332	2.652939320
C	15.240583420	2.145553112	3.825214148
C	13.170776367	-6.246015072	1.141344786
C	16.230047226	2.336766481	4.787374973
C	12.703937531	-1.493974686	5.596047878
C	12.463529587	5.555706978	0.563699126
C	11.364689827	-0.725105941	-2.566025972
C	13.240878105	-3.654984713	2.208839417
C	9.857587814	1.455639243	2.755247593
C	13.375569344	-4.772274017	3.048069000
C	16.164350510	-2.010578871	2.441841125
C	13.764163971	-1.053839564	-2.746296644
C	12.500579834	-0.980149329	-3.340038538
C	11.828303337	-1.467586994	6.685685158
C	16.408775330	-1.572507143	-1.297480822
C	10.137786865	-2.559620142	5.358617783
C	14.605711937	1.952326536	6.527783871
C	13.339562416	-6.060715675	2.517243624
C	12.624955177	5.564644814	1.951975346
C	8.946425438	-0.093178898	-0.825377643
C	13.066708565	-3.848607779	0.832465887

C	13.034608841	-5.140361309	0.301290393
C	15.917598724	2.234376431	6.147432804
C	12.488061905	3.137111425	0.578730762
C	12.393245697	4.341637135	-0.121266060
H	12.400403976	-1.123668194	-4.412666321
H	10.398225784	-0.697270811	-3.063395023
H	14.625469208	-1.237769604	-3.384598017
H	8.950180054	0.054079298	-1.904974461
H	8.350030899	-0.988572657	-0.612816632
H	8.426266670	0.759863079	-0.380134225
H	16.804281235	-2.419107914	-0.726737440
H	16.188806534	-1.930592299	-2.302520752
H	17.208747864	-0.826776087	-1.372087836
H	12.950619698	-2.975898743	0.194226623
H	12.897343636	-5.280001163	-0.767989755
H	13.141037941	-7.251512527	0.729324996
H	13.439327240	-6.921180248	3.174091578
H	13.491528511	-4.632149696	4.120320320
H	10.684279442	-3.023169994	3.331204891
H	9.141522408	-2.983024836	5.258978367
H	9.862742424	-1.974585176	7.420732021
H	12.158917427	-1.031629801	7.625268459
H	13.691862106	-1.063205719	5.711966038
H	12.601894379	1.537577033	5.887696743
H	14.349492073	1.874159336	7.581465244
H	16.688884735	2.374854088	6.899449825
H	17.247190475	2.561565399	4.477240562
H	15.490614891	2.224591017	2.769756079
H	12.447559357	2.186561823	0.048877444
H	12.273420334	4.329856873	-1.201505780
H	12.397369385	6.493695259	0.018589962
H	12.685040474	6.509143353	2.486810446
H	12.851241112	4.374181271	3.731525183
H	8.590948105	0.132357448	1.618152976
H	9.679524422	-0.692383230	2.736690283
H	9.926491737	2.271846056	2.024964809
H	8.962065697	1.652446508	3.359015465
H	11.008301735	2.382402658	4.336363316
H	11.057365417	0.609629393	4.355787754
H	17.277286530	-0.924324095	0.943373442
H	16.428634644	0.102143377	2.101011992
H	17.120004654	-2.154221535	2.963020086
H	15.992400169	-2.917232752	1.847578168
H	15.176716805	-0.894661188	4.010863304
H	15.170874596	-2.648867607	4.262606621

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Co	12.897266388	-0.327631503	1.294604778
P	13.329332352	-1.994486332	3.011707306

P	12.667760849	1.555609703	2.818942547
N	15.004285812	-0.700259030	0.721161902
N	10.706372261	-0.103190191	1.013104200
C	15.094392776	-0.960210621	-0.588999033
C	12.294640541	-2.127281189	4.521808147
C	10.409185410	-0.070679769	-0.287575126
C	13.892145157	-0.818604648	-1.394483685
C	13.899601936	1.881485343	4.137464046
C	13.646750450	1.681493640	5.502504349
C	10.992106438	-2.642646551	4.394400597
C	11.476758003	-0.347796500	-1.240238428
C	12.631837845	3.122829437	1.865508080
C	16.161954880	-0.763380170	1.594159365
C	15.064755440	-1.864049315	3.668040991
C	12.738623619	-0.519372284	-0.657095313
C	10.525969505	-2.138757467	6.716163635
C	9.697237968	0.092803247	2.036970377
C	11.037393570	1.549159765	3.709837675
C	12.756092072	4.379052162	2.480161428
C	15.198721886	2.245663166	3.737968683
C	13.288246155	-6.238476753	1.151596546
C	16.216421127	2.397815943	4.676443577
C	12.697895050	-1.625094414	5.768592358
C	12.534462929	5.466749668	0.329215407
C	11.359791756	-0.475845873	-2.665081978
C	13.277615547	-3.688409805	2.310966969
C	9.819710732	1.443593740	2.774867773
C	13.332439423	-4.834439754	3.120683908
C	16.141332626	-1.957692862	2.571814299
C	13.769371033	-0.949042320	-2.819165230
C	12.511327744	-0.771896660	-3.404190063
C	11.817652702	-1.629001379	6.854788780
C	16.394386292	-1.389158010	-1.233102560
C	10.118504524	-2.650880098	5.480188847
C	14.671229362	1.829297900	6.442060471
C	13.334706306	-6.102700233	2.542114019
C	12.708795547	5.543689728	1.714574575
C	9.011566162	0.228865832	-0.784837127
C	13.227682114	-3.831026793	0.915685058
C	13.236017227	-5.103437901	0.341432452
C	15.956593513	2.184130192	6.033741474
C	12.457285881	3.050683498	0.474184394
C	12.406451225	4.220356464	-0.286889762
H	12.423642159	-0.870407999	-4.484943867
H	10.409256935	-0.368222654	-3.180181980
H	14.624179840	-1.164321899	-3.454588413
H	9.015214920	0.457583815	-1.851404428
H	8.334383965	-0.622141838	-0.630536854
H	8.575734138	1.088315487	-0.263122350
H	16.881219864	-2.187415123	-0.660749674
H	16.227468491	-1.764210701	-2.243627310

H	17.110738754	-0.559238195	-1.302300811
H	13.181647301	-2.948251247	0.284430683
H	13.195539474	-5.202546120	-0.739732802
H	13.289825439	-7.228467941	0.703120708
H	13.371285439	-6.985691071	3.174839020
H	13.359720230	-4.733366966	4.202660561
H	10.667321205	-3.044754744	3.437887192
H	9.117691040	-3.057105303	5.361317635
H	9.843493462	-2.140855074	7.561320782
H	12.148764610	-1.235400200	7.812554359
H	13.694482803	-1.218643188	5.902171612
H	12.657891273	1.395871401	5.844242096
H	14.459740639	1.666762471	7.495834827
H	16.751451492	2.296009302	6.765855789
H	17.213787079	2.678478956	4.349246025
H	15.406660080	2.413956642	2.684338331
H	12.368791580	2.081413746	-0.011871830
H	12.277418137	4.152283192	-1.363492608
H	12.502462387	6.375396729	-0.265860736
H	12.813948631	6.511639595	2.197717667
H	12.904033661	4.444332123	3.555213690
H	8.674265862	0.007511840	1.648273826
H	9.808238029	-0.705392241	2.784962177
H	9.834673882	2.259633780	2.041476965
H	8.920439720	1.583571792	3.389804840
H	10.978977203	2.462537527	4.314225674
H	11.048280716	0.690873146	4.393077374
H	17.110231400	-0.794698119	1.042495370
H	16.190521240	0.155764669	2.197950840
H	17.118021011	-2.008047342	3.072200775
H	16.024990082	-2.890275240	2.006299496
H	15.148790359	-0.897064149	4.178852558
H	15.206179619	-2.654106379	4.414858341

Table S15. Vibrational frequencies (in cm^{-1}) of the optimized structures.

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     19.31     23.35     28.19     32.43     34.94     44.49
     46.03     48.56     51.15     56.73     70.72     76.30
     77.00     84.55     95.25     97.62    122.83    142.37
    151.93    154.01    158.65    161.82    165.83    177.79
    179.41    189.76    211.12    211.99    220.34    225.25
    228.01    245.88    262.31    267.26    277.41    283.30
    287.10    326.55    334.01    336.50    338.92    341.90
    358.80    370.17    397.41    406.31    408.05    412.19
    414.68    416.06    420.69    432.31    436.26    448.56
    450.14    469.63    476.19    491.29    493.57    497.96
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 525.71    531.63    542.18    565.24    567.28    607.13
 628.47    631.04    631.70    632.95    633.41    650.11
 652.24    663.60    667.83    698.03    699.92    707.86
 708.90    710.43    715.12    715.49    717.29    723.70
 745.17    756.88    758.23    766.47    766.84    795.18
 815.24    842.31    844.05    859.51    868.37    871.47
 873.50    875.47    881.78    904.77    909.18    918.95
 928.49    929.24    945.38    946.37    946.63    975.22
 983.64    989.22    989.40    989.53    997.44    999.85
1009.67   1012.75   1013.51   1015.01   1015.28   1016.68
1017.43   1037.99   1039.06   1043.99   1045.41   1045.90
1051.86   1052.45   1053.37   1054.43   1055.83   1062.96
1084.13   1093.91   1107.91   1108.83   1110.78   1110.92
1112.56   1113.37   1115.42   1117.25   1118.53   1131.73
1180.72   1190.68   1192.51   1194.61   1194.82   1196.15
1196.68   1214.99   1217.21   1219.61   1224.53   1225.98
1227.07   1233.04   1302.28   1304.28   1318.42   1318.87
1325.89   1327.12   1330.52   1330.98   1355.75   1360.91
1361.73   1365.95   1367.19   1375.49   1376.83   1383.21
1388.05   1393.33   1394.65   1402.60   1418.09   1422.49
1470.57   1471.48   1473.31   1475.12   1477.01   1477.43
1480.45   1496.03   1497.16   1497.98   1498.50   1501.02
1508.94   1523.22   1523.43   1524.91   1525.97   1526.79
1527.09   1536.61   1565.18   1594.62   1621.04   1621.36
1627.76   1628.02   1628.55   1642.03   1643.31   1644.25
1644.88   3027.38   3027.63   3035.96   3036.99   3045.13
3045.24   3061.25   3063.17   3073.81   3074.53   3090.80
3091.91   3100.69   3101.48   3124.19   3124.83   3142.74
3143.77   3152.35   3158.23   3165.48   3165.85   3170.46
3170.75   3172.83   3174.11   3176.83   3177.34   3179.44
3182.02   3186.69   3188.34   3188.79   3190.36   3190.58
3196.75   3197.35   3198.30   3200.31   3204.68   3208.67
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  16.58     24.15     29.86     32.02     34.49     37.96
  41.08     43.92     47.20     50.29     53.45     61.14
  65.99     67.31     83.11     85.13     92.22     95.98
 104.44    109.84    117.88    128.86    146.39    153.83
 154.59    165.00    181.23    197.94    203.55    211.73
 218.28    222.61    227.31    253.81    260.09    271.90
 276.96    285.97    290.84    327.13    331.58    337.18
 343.07    353.41    373.95    380.11    408.43    410.67
 412.60    414.39    417.14    421.35    428.21    443.66
 447.66    467.26    470.38    476.03    492.03    495.25
 516.16    526.38    529.25    548.39    552.51    594.27
 622.40    630.90    631.32    632.05    632.75    634.22
 659.48    661.98    666.07    701.27    703.55    710.70
 711.84    712.71    714.08    715.64    716.81    716.99
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 728.29   757.88   759.23   764.91   767.20   791.00
 807.91   831.90   837.93   863.46   866.00   870.24
 871.02   874.61   877.77   903.58   912.84   916.83
 925.57   926.09   941.08   946.15   960.84   976.52
 978.76   980.98   984.76   989.10   998.09   998.99
1002.88  1006.36  1013.31  1013.83  1013.96  1014.45
1016.75  1032.42  1034.97  1035.99  1046.31  1047.75
1052.10  1052.59  1052.99  1053.92  1060.53  1063.50
1084.32  1095.89  1108.12  1108.92  1111.08  1111.36
1113.83  1117.87  1118.32  1121.18  1122.24  1139.34
1172.49  1192.41  1194.74  1195.16  1195.76  1196.58
1197.43  1216.58  1219.25  1223.31  1223.38  1225.59
1232.09  1239.13  1279.99  1294.15  1305.95  1318.30
1321.04  1322.25  1326.31  1331.42  1331.84  1332.51
1351.37  1361.94  1366.18  1366.74  1368.10  1382.27
1385.56  1387.28  1393.01  1395.97  1410.94  1417.44
1471.82  1472.35  1475.09  1475.65  1476.80  1478.33
1478.75  1492.28  1495.49  1498.55  1499.78  1500.49
1505.18  1523.93  1526.94  1527.31  1527.46  1530.89
1532.45  1579.41  1612.43  1622.72  1623.15  1628.56
1629.00  1643.05  1643.83  1645.53  1645.74  1653.18
1658.93  3009.93  3011.43  3028.68  3028.76  3038.28
3038.48  3048.60  3049.02  3056.52  3061.78  3075.56
3076.08  3095.49  3097.81  3105.59  3111.42  3153.96
3157.57  3158.03  3166.06  3167.12  3169.12  3169.27
3169.44  3172.28  3173.16  3175.29  3175.61  3178.87
3180.28  3186.43  3186.67  3187.63  3188.17  3190.11
3197.95  3199.31  3200.57  3201.31  3213.99  3218.93
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^{5}2

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 -67.29   26.79   27.81   33.53   36.47   40.94
  45.13   51.99   53.40   54.79   61.19   68.35
  70.72   76.72   79.11   84.85   86.94  106.59
 114.64  124.89  129.89  132.60  136.53  145.11
 152.54  155.73  185.82  190.22  205.04  208.25
 213.61  217.52  248.86  258.88  271.60  276.55
 283.75  286.14  292.31  319.18  323.34  331.01
 343.63  367.16  370.66  380.90  408.18  410.96
 411.24  413.08  418.81  423.32  424.39  430.06
 454.18  461.33  477.98  483.36  493.63  496.70
 515.99  523.63  527.83  534.61  539.53  558.17
 624.06  630.47  630.79  631.43  631.89  633.04
 639.99  668.97  669.33  694.56  705.67  709.02
 709.86  711.84  715.01  716.37  718.31  720.97
 732.54  755.44  759.34  762.56  764.92  765.62
 769.92  831.83  832.32  835.97  864.39  866.11
 870.90  871.06  871.51  892.38  900.78  928.57
 929.99  936.51  941.41  943.42  949.75  977.71
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981.36	981.97	987.16	987.67	989.51	1002.29
1003.20	1011.98	1012.56	1013.54	1014.03	1014.68
1015.10	1025.25	1031.84	1034.17	1037.44	1039.58
1051.65	1052.38	1053.27	1054.46	1055.86	1062.36
1080.02	1092.59	1112.09	1112.56	1113.46	1113.58
1121.43	1121.64	1122.13	1124.69	1125.92	1134.75
1173.23	1185.67	1187.13	1197.10	1197.12	1197.84
1198.44	1201.26	1223.66	1225.09	1225.38	1226.75
1229.91	1233.39	1286.19	1294.55	1301.39	1322.89
1323.40	1325.61	1326.41	1332.99	1333.76	1345.31
1352.30	1368.82	1369.18	1369.68	1369.97	1379.05
1379.51	1391.13	1393.73	1403.97	1415.31	1424.43
1460.67	1472.07	1472.99	1473.60	1475.26	1477.57
1478.17	1487.80	1493.43	1493.95	1495.88	1497.79
1498.48	1507.45	1522.09	1524.79	1527.92	1528.46
1528.54	1528.80	1539.84	1560.63	1586.13	1622.75
1623.96	1626.74	1627.54	1641.73	1642.65	1644.17
1645.74	3004.31	3008.14	3021.02	3023.19	3023.72
3025.00	3034.82	3037.77	3050.64	3051.34	3074.62
3075.65	3077.83	3081.65	3091.30	3094.29	3144.80
3146.43	3150.42	3171.05	3171.25	3172.00	3173.25
3174.07	3176.01	3178.40	3179.60	3180.95	3182.31
3183.74	3189.63	3190.21	3190.84	3192.85	3196.71
3203.20	3203.42	3203.74	3204.13	3213.28	3215.10

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