Mechanistic Investigation of Bis(imino)pyridine Manganese Catalyzed Carbonyl and Carboxylate Hydrosilylation

Supporting Information

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CRYSTALLOGRAPHIC DATA

Table S1. Crystallographic data for **(^{Ph_2PPr}PDI)MnH** (**2**) and **[(μ-*O*,*N*$_{py}$-4-OC(CF_3)(Ph)-4-H-^{Ph_2PPr}PDI)Mn]$_2$** (**4**).

	2	**4** · 6(THF)
chemical formula	$C_{39}H_{42}N_3MnP_2$	$C_{94}H_{92}F_6Mn_2N_6O_2P_4$, 6($C_4H_8O$)
formula weight	669.63	2118.11
crystal dimensions	0.200 x 0.090 x 0.075	0.335 x 0.230 x 0.085
crystal system	triclinic	triclinic
space group	P -1	P -1
a (Å)	10.6382(4)	14.5008(8)
b (Å)	17.4039(7)	14.7881(9)
c (Å)	18.8993(7)	15.1141(9)
α (deg)	79.8920(10)	92.0219(9)
β (deg)	87.5530(10)	115.4329(8)
γ (deg)	77.8400(10)	109.4571(9)
V (Å^3)	3367.5(2)	2698.6(3)
Z	4	1
T (°C)	123.00(10)	123.00(10)
ρcalcd (g cm^{-3})	1.321	1.303
μ (mm^{-1})	0.520	0.364
reflections collected	12336	22407
data/restraints/parameters	12336/0/823	9794/21/667
R_1 [$I > 2\sigma(I)$]	0.0416	0.0529
wR_2 (all data)	0.0967	0.1417
Goodness-of-fit	1.029	1.027
Largest peak, hole (eÅ^{-3})	0.376, -0.447	0.906, -0.507

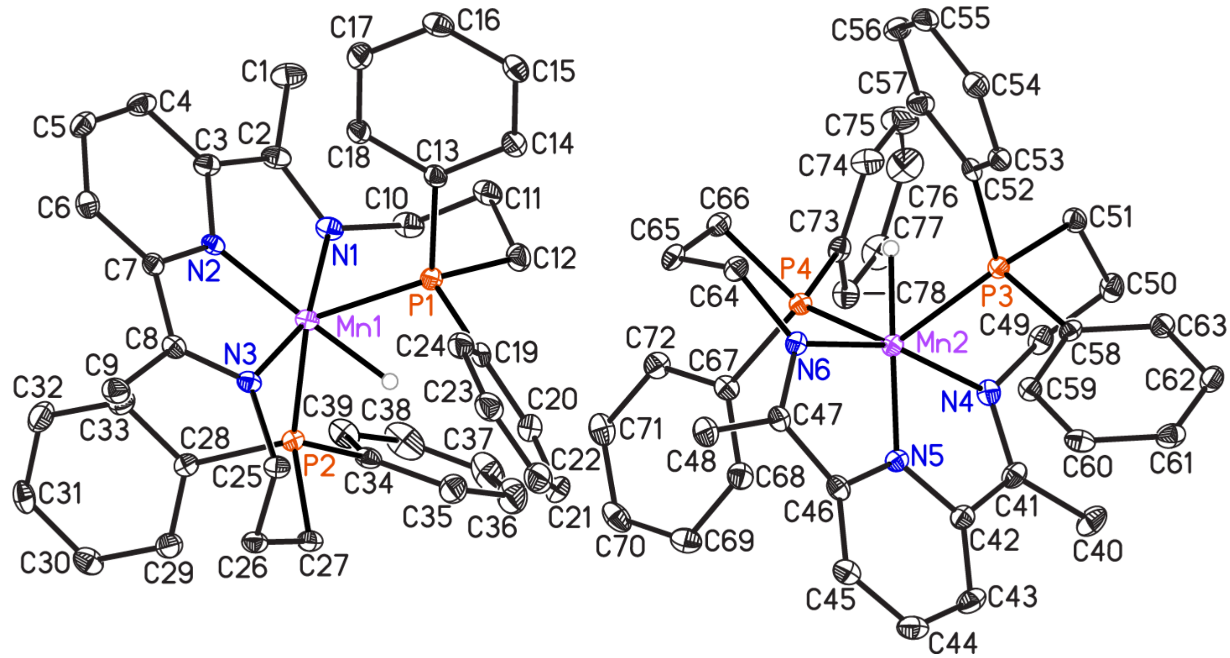


Figure S1. The molecular structure of **2** shown at 30% probability ellipsoids. Hydrogen atoms except those attached to Mn are omitted for clarity.

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

Mn1-N2	1.860(2)	C20-C21	1.394(4)	C40-C41	1.506(3)
Mn1-N1	1.945(2)	C21-C22	1.381(4)	C41-C42	1.418(4)
Mn1-N3	1.947(2)	C22-C23	1.373(4)	C42-C43	1.390(4)
Mn1-P1	2.2067(8)	C23-C24	1.379(4)	C43-C44	1.398(4)
Mn1-P2	2.2158(7)	C25-C26	1.528(3)	C44-C45	1.380(4)
Mn1-H1M	1.57(3)	C26-C27	1.528(3)	C45-C46	1.399(4)
P1-C19	1.827(3)	C28-C33	1.377(4)	C46-C47	1.419(4)
P1-C12	1.838(3)	C28-C29	1.399(4)	C47-C48	1.507(3)
P1-C13	1.845(3)	C29-C30	1.380(4)	C49-C50	1.528(4)
P2-C34	1.832(3)	C30-C31	1.378(4)	C50-C51	1.537(4)
P2-C27	1.841(3)	C31-C32	1.377(4)	C52-C53	1.390(3)
P2-C28	1.845(3)	C32-C33	1.390(4)	C52-C57	1.394(3)
N1-C2	1.351(3)	C34-C35	1.390(4)	C53-C54	1.390(4)
N1-C10	1.469(3)	C34-C39	1.391(4)	C54-C55	1.382(4)
N2-C3	1.387(3)	C35-C36	1.382(4)	C55-C56	1.381(4)
N2-C7	1.393(3)	C36-C37	1.365(5)	C56-C57	1.383(4)
N3-C8	1.342(3)	C37-C38	1.373(5)	C58-C59	1.395(3)
N3-C25	1.462(3)	C38-C39	1.396(4)	C58-C63	1.396(3)
C1-C2	1.504(4)	Mn2-N5	1.862(2)	C59-C60	1.386(4)
C2-C3	1.424(4)	Mn2-N6	1.948(2)	C60-C61	1.380(4)
C3-C4	1.398(4)	Mn2-N4	1.951(2)	C61-C62	1.374(4)
C4-C5	1.385(4)	Mn2-P4	2.2064(7)	C62-C63	1.390(4)
C5-C6	1.387(4)	Mn2-P3	2.2117(8)	C64-C65	1.526(3)
C6-C7	1.391(3)	Mn2-H2M	1.51(3)	C65-C66	1.533(4)
C7-C8	1.418(3)	P3-C52	1.837(3)	C67-C68	1.391(4)
C8-C9	1.505(3)	P3-C58	1.837(3)	C67-C72	1.394(4)
C10-C11	1.526(4)	P3-C51	1.841(3)	C68-C69	1.386(4)
C11-C12	1.531(4)	P4-C73	1.835(3)	C69-C70	1.382(4)
C13-C18	1.379(3)	P4-C66	1.840(3)	C70-C71	1.381(4)
C13-C14	1.392(4)	P4-C67	1.843(3)	C71-C72	1.382(4)
C14-C15	1.381(4)	N4-C41	1.343(3)	C73-C78	1.394(4)
C15-C16	1.378(4)	N4-C49	1.467(3)	C73-C74	1.395(4)
C16-C17	1.376(4)	N5-C42	1.388(3)	C74-C75	1.381(4)
C17-C18	1.387(4)	N5-C46	1.398(3)	C75-C76	1.380(4)
C19-C20	1.392(4)	N6-C47	1.346(3)	C76-C77	1.380(4)
C19-C24	1.398(4)	N6-C64	1.473(3)	C77-C78	1.385(4)

N2-Mn1-N1	79.32(9)	N3-Mn1-H1M	98.5(10)	C34-P2-Mn1	119.12(8)
N2-Mn1-N3	79.49(9)	P1-Mn1-H1M	61.7(10)	C27-P2-Mn1	111.67(8)
N1-Mn1-N3	158.81(9)	P2-Mn1-H1M	62.2(10)	C28-P2-Mn1	119.53(8)
N2-Mn1-P1	114.01(6)	C19-P1-C12	104.92(12)	C2-N1-C10	117.9(2)
N1-Mn1-P1	86.64(7)	C19-P1-C13	99.66(12)	C2-N1-Mn1	117.21(17)
N3-Mn1-P1	101.59(6)	C12-P1-C13	100.69(12)	C10-N1-Mn1	124.07(17)
N2-Mn1-P2	122.13(6)	C19-P1-Mn1	117.26(8)	C3-N2-C7	119.9(2)
N1-Mn1-P2	103.15(6)	C12-P1-Mn1	112.03(9)	C3-N2-Mn1	120.09(17)
N3-Mn1-P2	88.56(6)	C13-P1-Mn1	119.93(8)	C7-N2-Mn1	119.78(16)
P1-Mn1-P2	123.85(3)	C34-P2-C27	102.12(12)	C8-N3-C25	117.9(2)
N2-Mn1-H1M	175.0(10)	C34-P2-C28	100.74(11)	C8-N3-Mn1	116.96(17)
N1-Mn1-H1M	102.5(10)	C27-P2-C28	100.83(11)	C25-N3-Mn1	124.92(16)

N1-C2-C3	112.7(2)
N1-C2-C1	125.0(2)
C3-C2-C1	122.2(2)
N2-C3-C4	119.8(2)
N2-C3-C2	110.4(2)
C4-C3-C2	129.7(2)
C5-C4-C3	119.7(2)
C4-C5-C6	120.8(2)
C5-C6-C7	119.2(2)
C6-C7-N2	120.5(2)
C6-C7-C8	129.3(2)
N2-C7-C8	110.1(2)
N3-C8-C7	113.4(2)
N3-C8-C9	124.0(2)
C7-C8-C9	122.7(2)
N1-C10-C11	110.7(2)
C10-C11-C12	114.0(2)
C11-C12-P1	111.62(19)
C18-C13-C14	118.6(2)
C18-C13-P1	119.69(19)
C14-C13-P1	121.71(19)
C15-C14-C13	121.0(3)
C16-C15-C14	119.7(3)
C17-C16-C15	120.0(3)
C16-C17-C18	120.1(3)
C13-C18-C17	120.7(2)
C20-C19-C24	118.0(3)
C20-C19-P1	122.4(2)
C24-C19-P1	119.1(2)
C19-C20-C21	120.5(3)
C22-C21-C20	120.0(3)
C23-C22-C21	120.1(3)
C22-C23-C24	120.1(3)
C23-C24-C19	121.2(3)
N3-C25-C26	111.5(2)
C27-C26-C25	113.1(2)
C26-C27-P2	112.81(17)
C33-C28-C29	118.7(2)
C33-C28-P2	118.9(2)
C29-C28-P2	122.4(2)
C30-C29-C28	120.4(3)
C31-C30-C29	120.4(3)
C32-C31-C30	119.6(3)
C31-C32-C33	120.2(3)
C28-C33-C32	120.7(3)
C35-C34-C39	118.1(3)
C35-C34-P2	120.9(2)
C39-C34-P2	120.8(2)

C36-C35-C34	121.2(3)
C37-C36-C35	120.2(3)
C36-C37-C38	120.0(3)
C37-C38-C39	120.4(3)
C34-C39-C38	120.1(3)
N5-Mn2-N6	79.42(9)
N5-Mn2-N4	79.26(9)
N6-Mn2-N4	158.64(9)
N5-Mn2-P4	122.08(7)
N6-Mn2-P4	89.74(6)
N4-Mn2-P4	100.48(6)
N5-Mn2-P3	109.40(6)
N6-Mn2-P3	104.73(6)
N4-Mn2-P3	83.67(6)
P4-Mn2-P3	128.30(3)
N5-Mn2-H2M	172.9(10)
N6-Mn2-H2M	96.9(10)
N4-Mn2-H2M	104.5(10)
P4-Mn2-H2M	63.5(10)
P3-Mn2-H2M	65.6(10)
C52-P3-C58	102.58(11)
C52-P3-C51	101.07(12)
C58-P3-C51	103.80(12)
C52-P3-Mn2	120.46(8)
C58-P3-Mn2	114.78(8)
C51-P3-Mn2	112.05(9)
C73-P4-C66	101.67(12)
C73-P4-C67	100.56(11)
C66-P4-C67	100.05(12)
C73-P4-Mn2	121.48(8)
C66-P4-Mn2	111.75(9)
C67-P4-Mn2	118.12(9)
C41-N4-C49	118.9(2)
C41 -N4-Mn2	116.65(17)
C49-N4-Mn2	123.90(17)
C42-N5-C46	119.9(2)
C42-N5-Mn2	120.09(17)
C46-N5-Mn2	119.76(17)
C47-N6-C64	117.8(2)
C47-N6-Mn2	117.29(16)
C64-N6-Mn2	124.65(16)
N4-C41-C42	113.7(2)
N4-C41-C40	125.0(2)
C42-C41-C40	121.3(2)
N5-C42-C43	120.4(2)
N5-C42-C41	110.0(2)
C43-C42-C41	129.6(2)
C42-C43-C44	119.5(3)

C45-C44-C43	120.5(3)
C44-C45-C46	120.0(3)
N5-C46-C45	119.7(2)
N5-C46-C47	110.3(2)
C45-C46-C47	130.0(2)
N6-C47-C46	113.1(2)
N6-C47-C48	125.4(2)
C46-C47-C48	121.5(2)
N4-C49-C50	110.6(2)
C49-C50-C51	113.6(2)
C50-C51-P3	114.11(18)
C53-C52-C57	117.6(2)
C53-C52-P3	123.01(19)
C57-C52-P3	119.33(19)
C52-C53-C54	121.0(2)
C55-C54-C53	120.3(3)
C56-C55-C54	119.5(3)
C55-C56-C57	120.0(3)
C56-C57-C52	121.5(2)
C59-C58-C63	118.7(2)
C59-C58-P3	116.90(19)
C63-C58-P3	124.3(2)
C60-C59-C58	120.5(2)
C61-C60-C59	120.1(3)
C62-C61-C60	120.2(3)
C61-C62-C63	120.3(3)
C62-C63-C58	120.2(3)
N6-C64-C65	111.9(2)
C64-C65-C66	113.4(2)
C65-C66-P4	111.92(17)
C68-C67-C72	118.8(2)
C68-C67-P4	119.13(19)
C72-C67-P4	122.0(2)
C69-C68-C67	120.4(3)
C70-C69-C68	120.0(3)
C71-C70-C69	120.2(3)
C70-C71-C72	119.8(3)
C71-C72-C67	120.7(3)
C78-C73-C74	117.7(2)
C78-C73-P4	121.8(2)
C74-C73-P4	120.4(2)
C75-C74-C73	121.3(3)
C76-C75-C74	120.2(3)
C75-C76-C77	119.4(3)
C76-C77-C78	120.5(3)
C77-C78-C73	120.8(3)

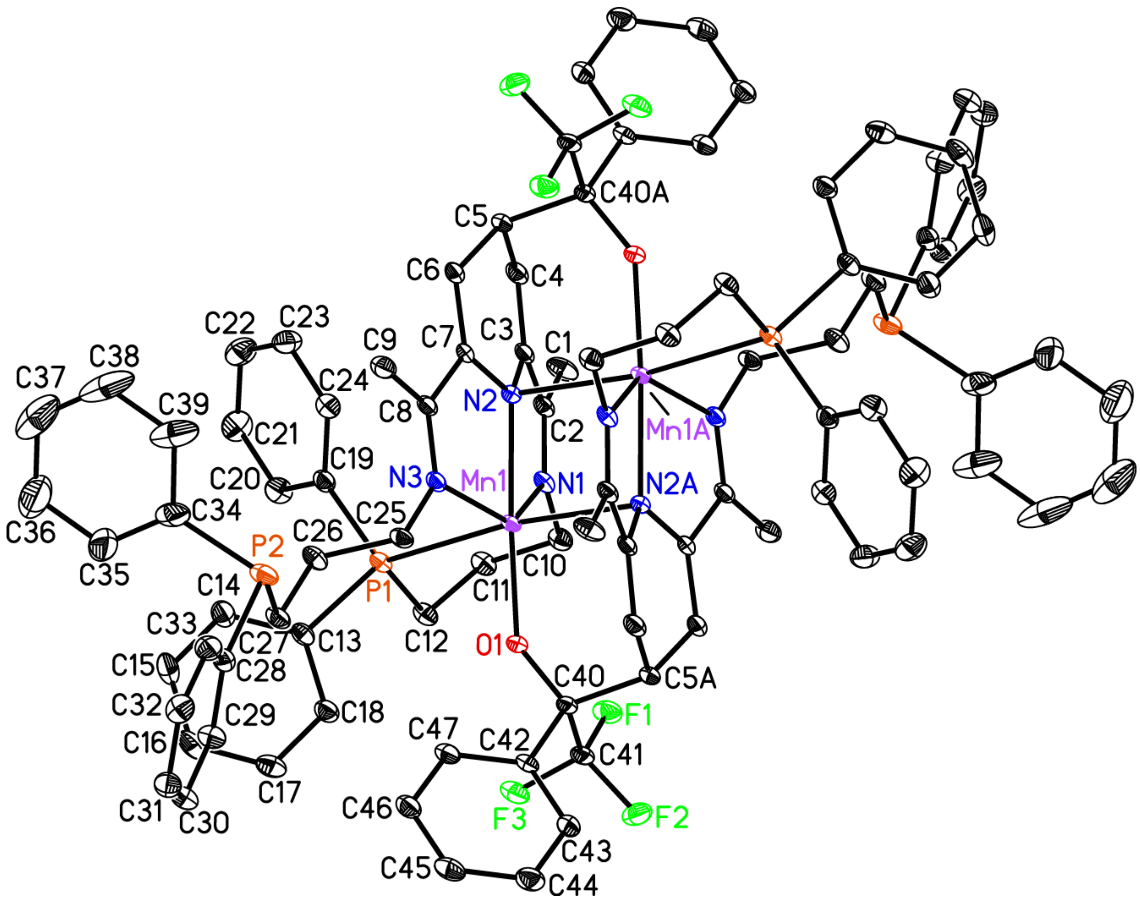


Figure S2. The molecular structure of **4** shown at 30% probability ellipsoids. Hydrogen atoms and co-crystallized THF molecules are omitted for clarity.

Table S3. Bond distances (Å) and angles (°) for **4**.

Mn1-O1	2.025(2)	C2-C3	1.486(4)	C26-C27	1.521(4)
Mn1-N2	2.159(2)	C3-C4	1.350(4)	C28-C33	1.382(5)
Mn1-N3	2.270(3)	C4-C5	1.504(5)	C28-C29	1.399(4)
Mn1-N1	2.303(2)	C5-C6	1.503(4)	C29-C30	1.384(5)
Mn1-N2A	2.429(2)	C5-C40A	1.581(4)	C30-C31	1.370(5)
Mn1-P1	2.8055(9)	C6-C7	1.353(4)	C31-C32	1.389(5)
P1-C19	1.827(3)	C7-C8	1.485(4)	C32-C33	1.380(5)
P1-C13	1.838(3)	C8-C9	1.507(4)	C34-C35	1.367(7)
P1-C12	1.844(3)	C10-C11	1.530(4)	C34-C39	1.400(6)
P2-C28	1.830(3)	C11-C12	1.537(4)	C35-C36	1.397(7)
P2-C34	1.836(4)	C13-C14	1.383(5)	C36-C37	1.386(10)
P2-C27	1.843(3)	C13-C18	1.391(4)	C37-C38	1.359(9)
F1-C41	1.349(4)	C14-C15	1.386(5)	C38-C39	1.391(8)
F2-C41	1.348(4)	C15-C16	1.374(5)	C40-C41	1.534(5)
F3-C41	1.361(4)	C16-C17	1.376(5)	C40-C42	1.565(4)
O1-C40	1.365(4)	C17-C18	1.388(4)	C42-C47	1.373(4)
N1-C2	1.288(4)	C19-C20	1.391(4)	C42-C43	1.385(4)
N1-C10	1.468(4)	C19-C24	1.393(5)	C43-C44	1.394(4)
N2-C3	1.388(4)	C20-C21	1.387(5)	C44-C45	1.382(5)
N2-C7	1.389(4)	C21-C22	1.382(5)	C45-C46	1.379(5)
N3-C8	1.291(4)	C22-C23	1.376(5)	C46-C47	1.398(4)
N3-C25	1.470(4)	C23-C24	1.387(5)		
C1-C2	1.505(4)	C25-C26	1.528(4)		

O1-Mn1-N2	174.27(9)	C2-N1-C10	120.3(3)	N2-C7-C8	113.8(3)
O1-Mn1-N3	105.08(9)	C2-N1-Mn1	117.4(2)	N3-C8-C7	116.5(3)
N2-Mn1-N3	72.71(9)	C10-N1-Mn1	122.21(19)	N3-C8-C9	124.8(3)
O1-Mn1-N1	111.83(9)	C3-N2-C7	114.7(2)	C7-C8-C9	118.7(3)
N2-Mn1-N1	71.99(9)	C3-N2-Mn1	120.09(19)	N1-C10-C11	112.0(3)
N3-Mn1-N1	139.32(9)	C7-N2-Mn1	119.03(19)	C10-C11-C12	114.5(3)
O1-Mn1-N2A	92.54(8)	C3-N2-Mn1A	99.69(17)	C11-C12-P1	115.2(2)
N2-Mn1-N2A	82.54(9)	C7-N2-Mn1A	97.81(17)	C14-C13-C18	118.3(3)
N3-Mn1-N2A	96.34(9)	Mn1-N2-Mn1A	97.46(9)	C14-C13-P1	123.4(2)
N1-Mn1-N2A	98.48(8)	C8-N3-C25	120.2(3)	C18-C13-P1	118.0(2)
O1-Mn1-P1	82.23(6)	C8-N3-Mn1	117.6(2)	C13-C14-C15	120.9(3)
N2-Mn1-P1	103.17(7)	C25-N3-Mn1	122.13(19)	C16-C15-C14	120.3(3)
N3-Mn1-P1	95.93(7)	N1-C2-C3	116.7(3)	C15-C16-C17	119.6(3)
N1-Mn1-P1	73.30(6)	N1-C2-C1	124.5(3)	C16-C17-C18	120.3(3)
N2A-Mn1-P1	167.55(6)	C3-C2-C1	118.9(3)	C17-C18-C13	120.6(3)
C19-P1-C13	103.26(14)	C4-C3-N2	122.7(3)	C20-C19-C24	119.1(3)
C19-P1-C12	102.99(15)	C4-C3-C2	123.6(3)	C20-C19-P1	123.5(3)
C13-P1-C12	100.69(14)	N2-C3-C2	113.7(2)	C24-C19-P1	117.4(2)
C19-P1-Mn1	118.66(10)	C3-C4-C5	120.4(3)	C21-C20-C19	120.2(3)
C13-P1-Mn1	123.00(10)	C6-C5-C4	107.7(2)	C22-C21-C20	120.4(3)
C12-P1-Mn1	105.08(11)	C6-C5-C40A	113.2(3)	C23-C22-C21	119.5(3)
C28-P2-C34	100.93(15)	C4-C5-C40A	109.2(3)	C22-C23-C24	120.8(3)
C28-P2-C27	102.01(15)	C7-C6-C5	119.7(3)	C23-C24-C19	120.0(3)
C34-P2-C27	101.56(19)	C6-C7-N2	123.2(3)	N3-C25-C26	110.9(3)
C40-O1-Mn1	143.11(18)	C6-C7-C8	123.0(3)	C27-C26-C25	112.2(3)

C26-C27-P2	112.3(2)	C37-C36-C35	119.7(7)	F2-C41-C40	114.6(3)
C33-C28-C29	117.8(3)	C38-C37-C36	119.4(6)	F1-C41-C40	113.6(2)
C33-C28-P2	116.8(3)	C37-C38-C39	120.9(6)	F3-C41-C40	112.1(3)
C29-C28-P2	125.3(3)	C38-C39-C34	120.4(6)	C47-C42-C43	118.5(3)
C30-C29-C28	120.3(3)	O1-C40-C41	107.5(3)	C47-C42-C40	118.9(3)
C31-C30-C29	121.3(3)	O1-C40-C42	112.1(2)	C43-C42-C40	122.5(3)
C30-C31-C32	118.9(3)	C41-C40-C42	105.9(2)	C42-C43-C44	121.0(3)
C33-C32-C31	120.0(3)	O1-C40-C5A	113.3(2)	C45-C44-C43	120.0(3)
C32-C33-C28	121.7(3)	C41-C40-C5A	109.2(2)	C46-C45-C44	119.3(3)
C35-C34-C39	118.0(5)	C42-C40-C5A	108.7(2)	C45-C46-C47	120.3(3)
C35-C34-P2	123.6(3)	F2-C41-F1	105.7(2)	C42-C47-C46	120.9(3)
C39-C34-P2	118.4(4)	F2-C41-F3	105.6(2)		
C34-C35-C36	121.5(6)	F1-C41-F3	104.3(3)		

PROCEDURES AND SPECTROSCOPIC DATA FOR CATALYTIC TRIALS

Hydrosilylation of benzaldehyde catalyzed by 0.1 mol% 1: In the glove box, a mixture of $PhSiH_3$ (0.461 mL, 3.74 mmol) and benzaldehyde (0.380 mL, 3.74 mmol) was added to 0.0025 g (0.0037 mmol) of **1** pre-weighed in a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was allowed to stir for 2 min and then exposed to air to deactivate the catalyst. The resulting colorless solution was filtered through Celite and a ^{1}H NMR spectrum was recorded to determine the percent conversion. The mixture was then stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (4 x 3 mL) and dried over anhydrous Na_2SO_4. Removal of the diethyl ether on a rotavap at 35-38 °C afforded a colorless oil identified as benzyl alcohol (0.38 g, yield = 94%). ^{1}H NMR (benzene-d_6): δ (ppm) = 7.24 – 7.12 (m, 4H), 7.08 (m, 1H), 4.32 (s, 2H). ^{13}C NMR (benzene-d_6): δ (ppm) = 128.90, 127.80, 127.29, 110.79, 65.24.

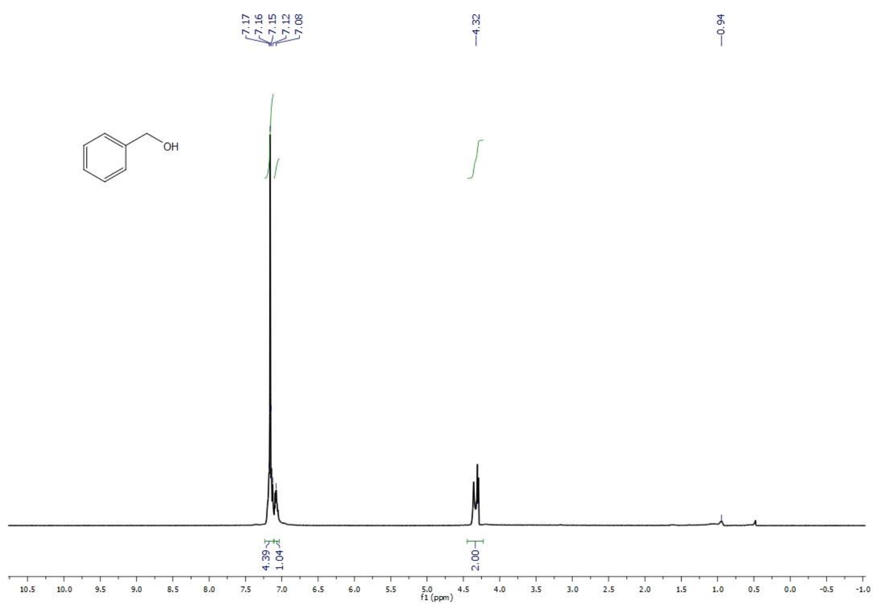


Figure S3. ^{1}H NMR spectrum of benzyl alcohol in benzene-d_6.

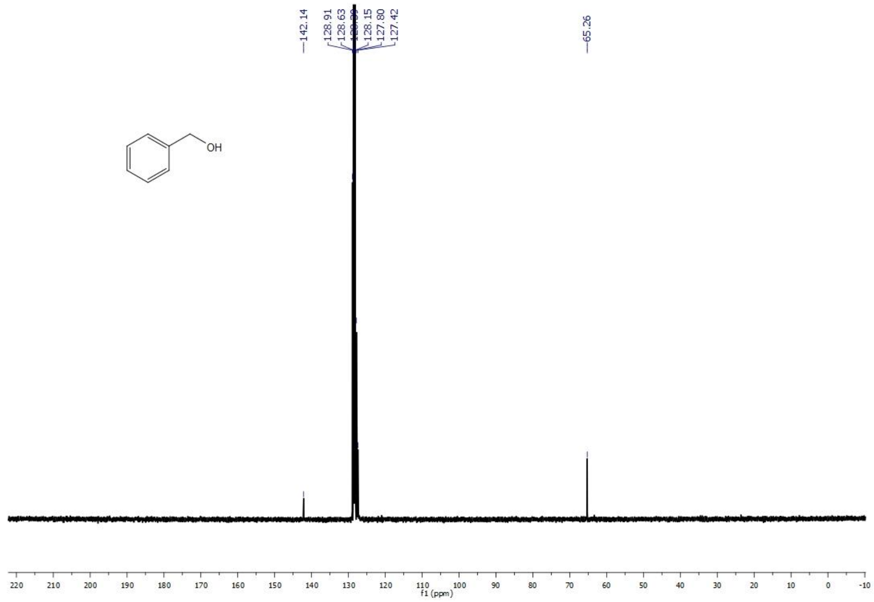


Figure S4. ^{13}C NMR spectrum of benzyl alcohol in benzene-d_6.

Hydrosilylation of 4-fluorobenzaldehyde catalyzed by 0.1 mol% 1: In the glove box, a mixture of $PhSiH_3$ (0.277 mL, 2.24 mmol) and 4-fluorobenzaldehyde (0.242 mL, 2.24 mmol) was added to 0.0015 g (0.0022 mmol) of **1** pre-weighed in a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^{1}H NMR spectrum was recorded to determine percent conversion. The mixture was then stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (4 x 3 mL) and dried over anhydrous Na_2SO_4. Removal of the diethyl ether on a rotavap at 35-38 °C afforded a colorless oil identified as 4-fluorobenzyl alcohol (0.25 g, yield = 89%). ^{1}H NMR (benzene-d_6): δ (ppm) = 6.94 (d, J = 2.1 Hz, 2H), 6.79 (t, J = 8.7 Hz, 2H), 4.21 (s, 2H). ^{13}C NMR (benzene-d_6): δ (ppm) = 164.16, 161.69, 137.52, 115.78, 64.25.

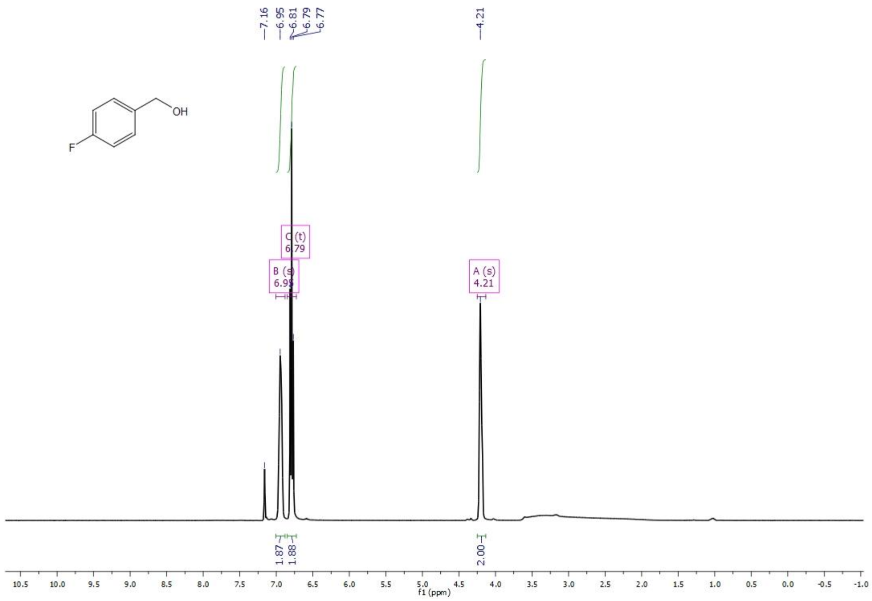


Figure S5. ^{1}H NMR spectrum of 4-fluorobenzyl alcohol in benzene-d_6.

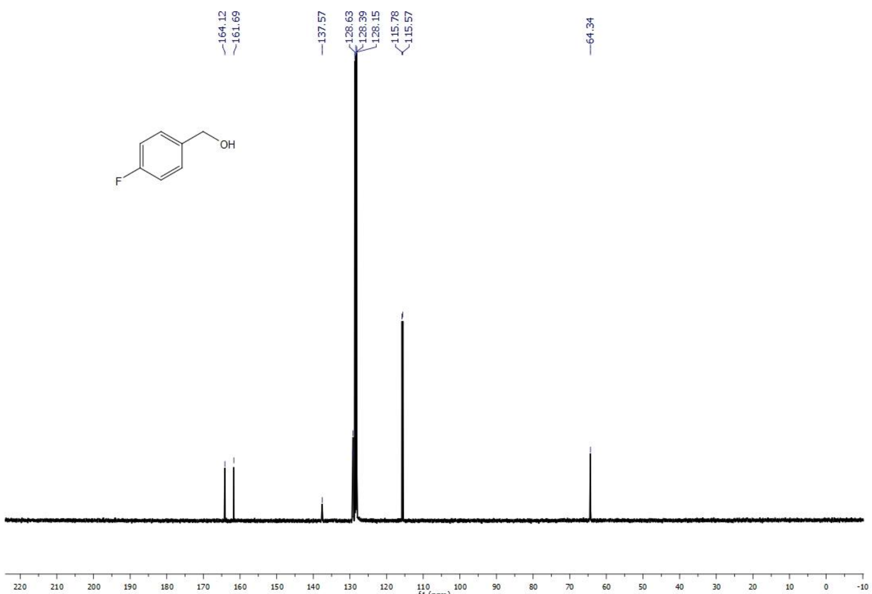


Figure S6. ^{13}C NMR spectrum of 4-fluorobenzyl alcohol in benzene-d_6.

Hydrosilylation of 4-chlorobenzaldehyde catalyzed by 0.1 mol% 1: In the glove box, a mixture of $PhSiH_3$ (0.369 mL, 2.99 mmol) and 4-chlorobenzaldehyde (0.420 g, 2.99 mmol) in 0.5 mL of toluene was added to 0.0020 g (0.0030 mmol) of **1** pre-weighed in a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^{1}H NMR spectrum was recorded to determine the percent conversion. The mixture was then stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (4 x 3 mL) and dried over anhydrous Na_2SO_4. Removal of the diethyl ether on a rotavap at 35-38 °C afforded a white solid identified as 4-chlorobenzyl alcohol (0.38 g, 88%). ^{1}H NMR (benzene-d_6): δ (ppm) = 7.09 (d, J = 8.3 Hz, 2H), 6.84 (d, J = 8.1 Hz, 2H), 4.09 (d, J = 5.3 Hz, 2H), 1.06 (s, 1H). ^{13}C NMR (benzene-d_6): δ (ppm) = 140.58, 133.44, 129.02, 128.56, 64.27.

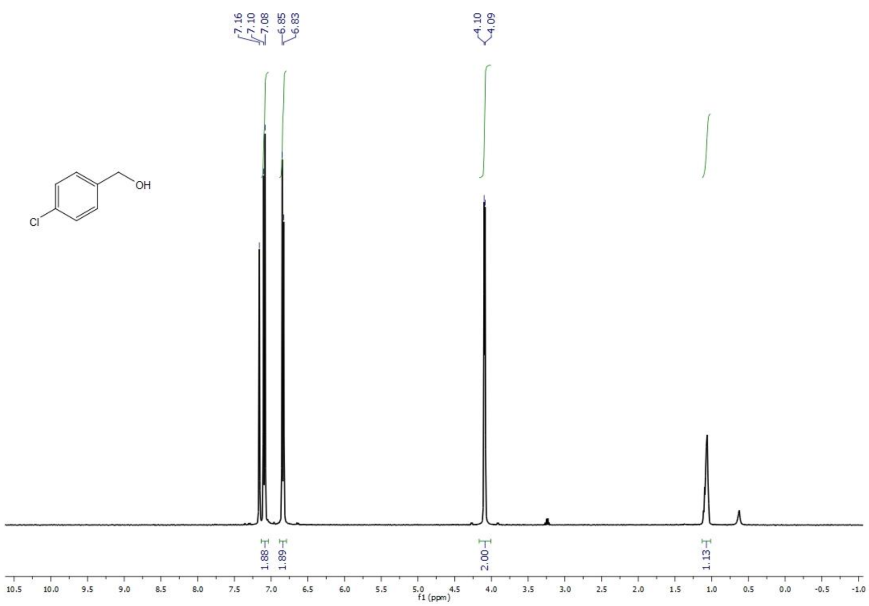


Figure S7. ^{1}H NMR spectrum of 4-chlorobenzyl alcohol in benzene-d_6.

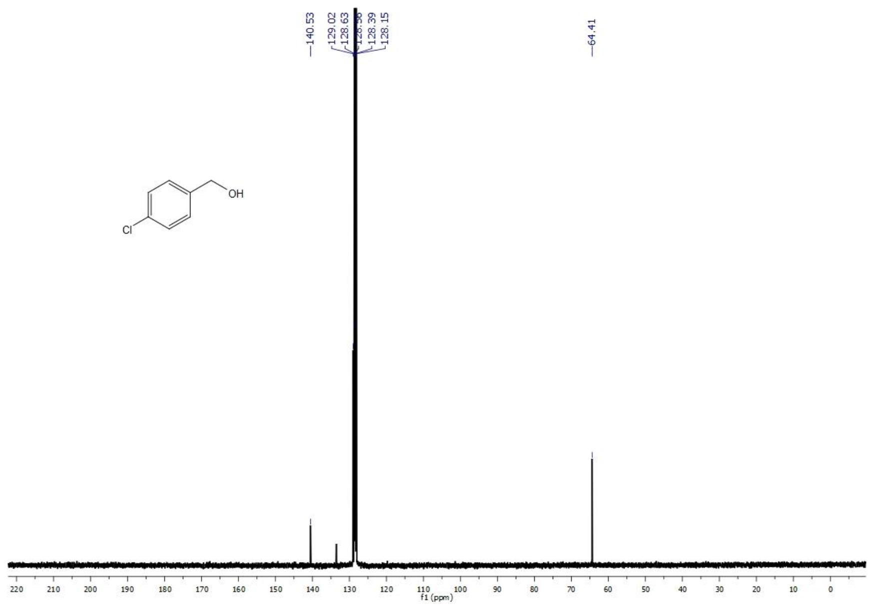


Figure S8. ^{13}C NMR spectrum of 4-chlorobenzyl alcohol in benzene-d_6.

Hydrosilylation of 4-bromobenzaldehyde catalyzed by 0.1 mol% 1: In the glove box, a mixture of $PhSiH_3$ (0.369 mL, 2.99 mmol) and 4-bromobenzaldehyde (0.553 g, 2.99 mmol) in 0.5 mL toluene was added to 0.0020 g (0.0030 mmol) of **1** pre-weighed in a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^{1}H NMR spectrum was recorded to determine the percent conversion. The mixture was then stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (4 x 3 mL) and dried over anhydrous Na_2SO_4. Removal of the diethyl ether on a rotavap at 35-38 °C afforded white a solid identified as 4-bromobenzyl alcohol (0.46 g, 92%). ^{1}H NMR (benzene-d_6): δ (ppm) = 7.24 (d, J = 8.3 Hz, 2H), 6.77 (d, J = 8.2 Hz, 2H), 4.07 (s, 2H), 1.36 (s, 1H). ^{13}C NMR (benzene-d_6): δ (ppm) = 140.94, 131.98, 128.90, 121.66, 64.41.

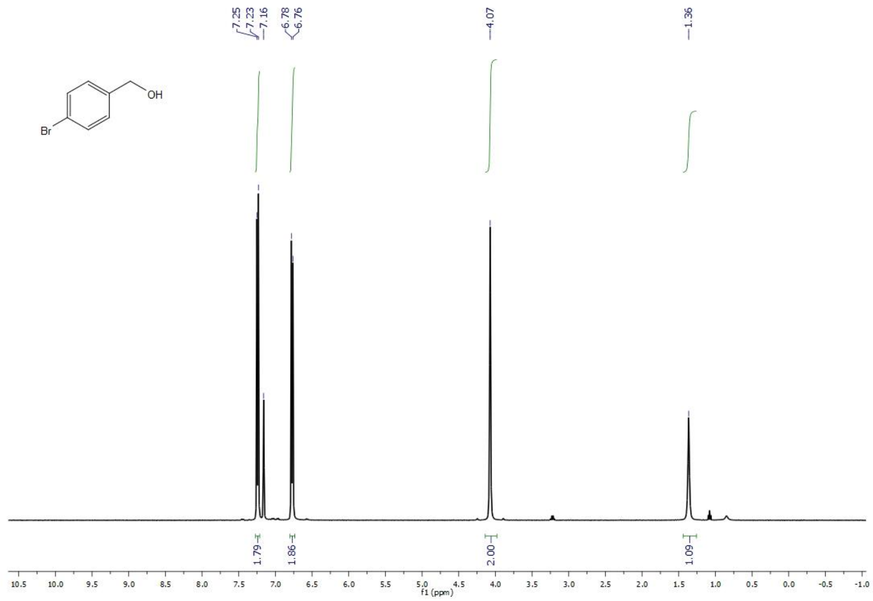


Figure S9. ^{1}H NMR spectrum of 4-bromobenzyl alcohol in benzene-d_6.

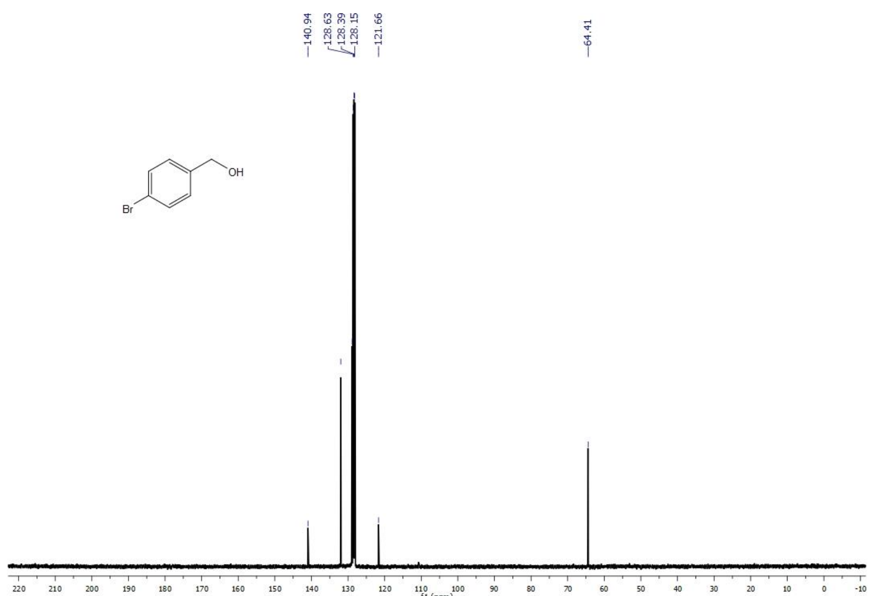


Figure S10. ^{13}C NMR spectrum of 4-bromobenzyl alcohol in benzene-d_6.

Hydrosilylation of 4-iodobenzaldehyde catalyzed by 0.1 mol% 1: In the glove box, a mixture of $PhSiH_3$ (0.369 mL, 2.99 mmol) and 4-iodobenzaldehyde (0.694 g, 2.99 mmol) in 0.5 mL toluene was added to 0.0020 g (0.00299 mmol) of **1** pre-weighed in a 20 mL vial. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^{1}H NMR spectrum was recorded, which showed only 32% conversion. Several trials did not afford silyl ether products, even at reaction times up to 1 h.

Hydrosilylation of 2-nitrobenzaldehyde catalyzed by 0.1 mol% 1: In the glove box, a mixture of $PhSiH_3$ (0.369 mL, 2.99 mmol) and 2-nitrobenzaldehyde (0.452 g, 2.99 mmol) in 0.5 mL of toluene was added to 0.0020 g (0.0030 mmol) of **1** pre-weighed in a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^{1}H NMR spectrum was recorded to determine percent conversion. The mixture was then stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (4 x 3 mL) and dried over anhydrous Na_2SO_4. Removal of the diethyl ether on a rotavap at 35-38 °C afforded a pale yellow solid identified as 2-nitrobenzyl alcohol (0.33 g, 72%). ^{1}H NMR (benzene-d_6): δ (ppm) = 7.63 (d, J = 8.2 Hz, 1H), 7.36 (d, J = 7.8, 1H), 6.93 (t, J = 7.6 Hz, 1H), 6.66 (t, J = 7.8 Hz, 1H), 4.54 (s, 2H), 1.51 (s, 1H). ^{13}C NMR (benzene-d_6): δ (ppm) = 137.98, 133.68, 129.20, 127.99, 124.95, 62.27.

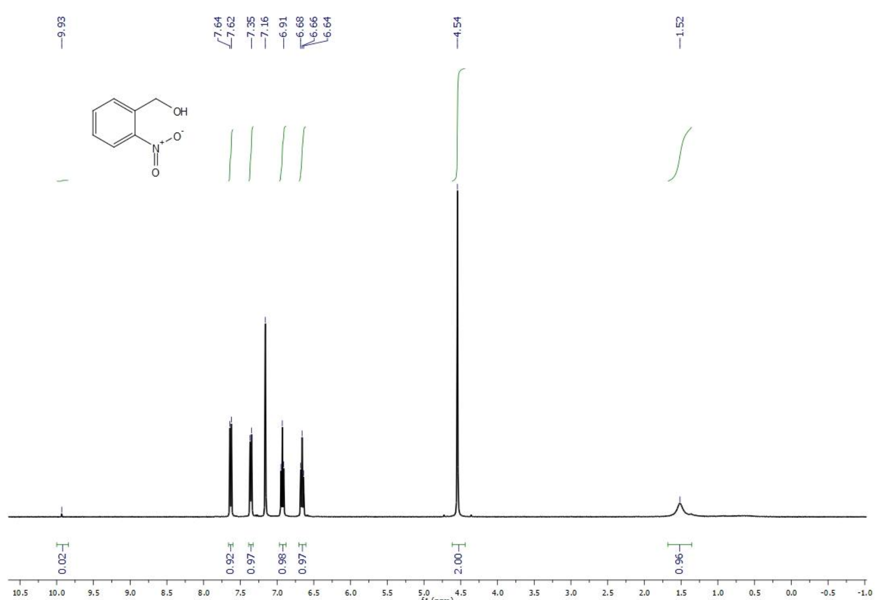


Figure S11. ^{1}H NMR spectrum of 2-nitrobenzyl alcohol in benzene-d_6.

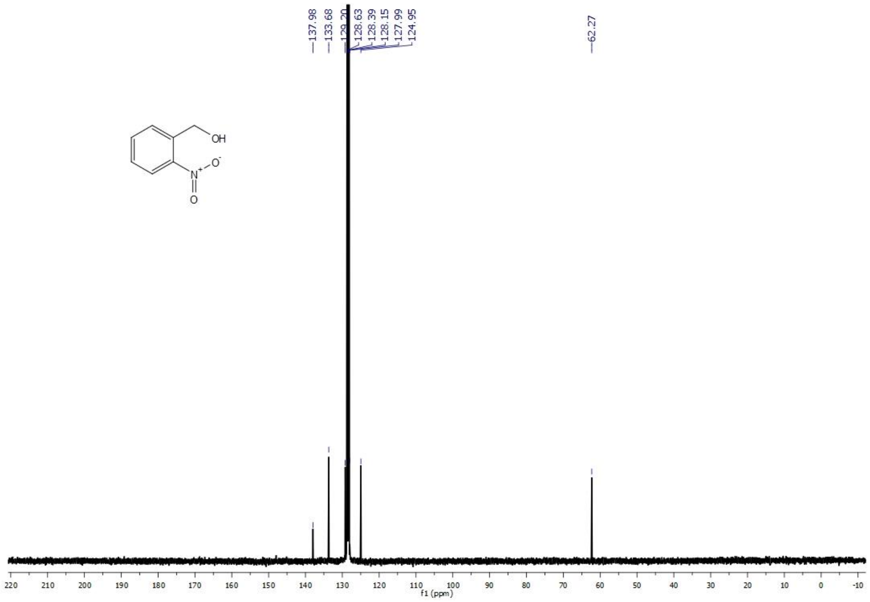


Figure S12. ^{13}C NMR spectrum of 2-nitrobenzyl alcohol in benzene-d_6.

Hydrosilylation of 4-cyanobenzaldehyde catalyzed by 0.1 mol% 1: In the glove box, a mixture of $PhSiH_3$ (0.369 mL, 2.99 mmol) and 4-cyanobenzaldehyde (0.392 g, 2.99 mmol) in 0.5 mL of diethyl ether was added to 0.0020 g (0.0030 mmol) of **1** pre-weighed in a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^1H NMR spectrum was recorded to determine the percent conversion. It was followed by a hydrolytic work up while the mixture was stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (4 x 3 mL) and dried over anhydrous Na_2SO_4. Removal of the diethyl ether on a rotavap at 35-38 °C afforded a white solid identified as 4-cyanobenzyl alcohol (0.37 g, 79%). ^1H NMR (benzene-d_6): δ (ppm) = 7.00 (d, J = 8.2 Hz, 2H), 6.77 (d, J = 7.9 Hz, 2H), 4.05 (d, J = 16.6 Hz, 2H), 1.23 (s, 1H). ^{13}C NMR (benzene-d_6): δ (ppm) = 146.84, 132.37, 127.02, 119.32, 111.65, 63.96.

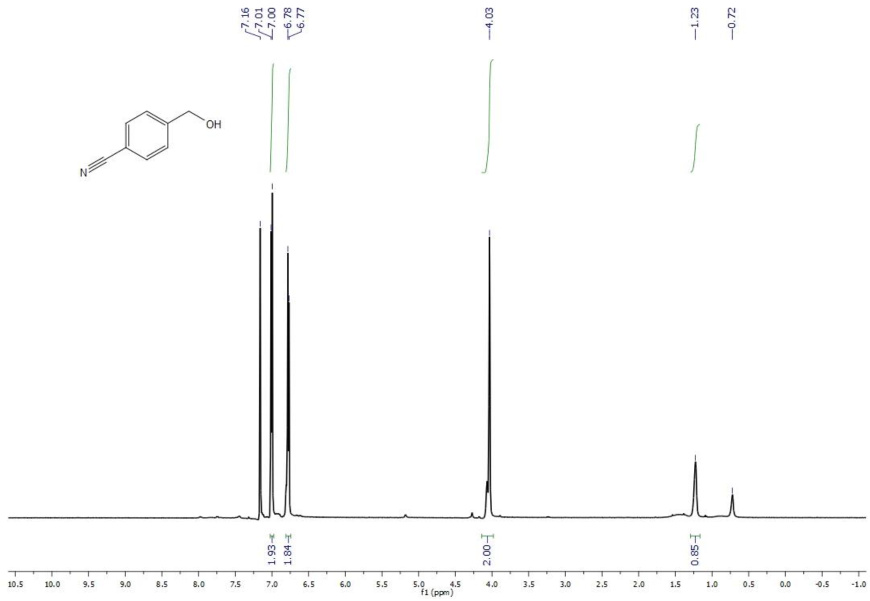


Figure S13. ^{1}H NMR spectrum of 4-cyanobenzyl alcohol in benzene-d_6.

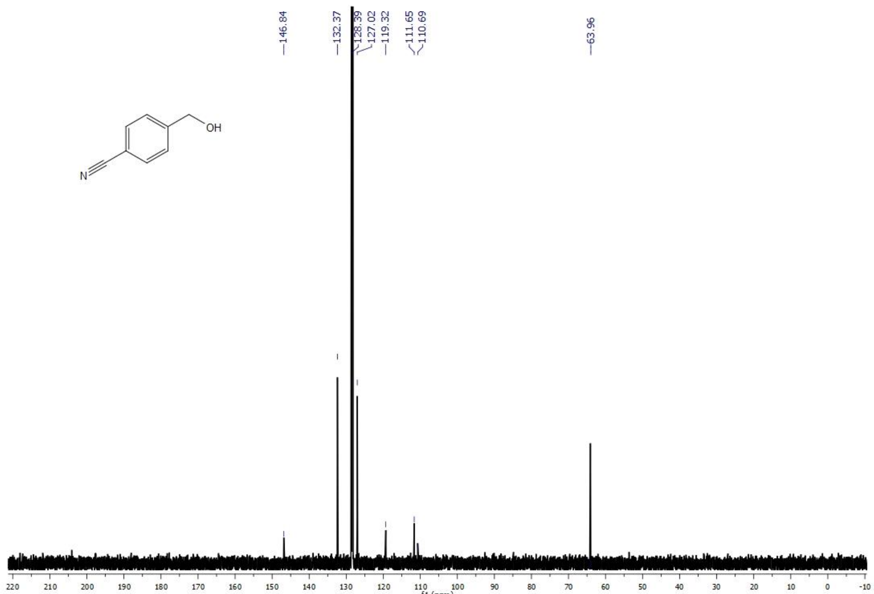


Figure S14. ^{13}C NMR spectrum of 4-cyanobenzyl alcohol in benzene-d_6.

Hydrosilylation of *p*-anisaldehyde catalyzed by 0.1 mol% 1: In the glove box, a mixture of $PhSiH_3$ (0.369 mL, 2.99 mmol) and *p*-anisaldehyde (0.342 mL, 2.99 mmol) was added to 0.0020 g (0.0030 mmol) of **1** pre-weighed in a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and ^{1}H NMR was recorded to determine the percent conversion. It was then stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (4 x 3 mL) and dried over anhydrous Na_2SO_4. Removal of the diethyl ether on a rotavap at 35-38 °C afforded a colorless oil identified as 4-methoxybenzyl alcohol (0.34 g, 81%). ^{1}H NMR (benzene-d_6): δ (ppm) = 7.16 – 7.13 (m, 2H), 6.78 – 6.76 (m, 2H), 4.38 (s, 2H), 3.32 (s, 3H), 2.56 (s, 1H). ^{13}C NMR (benzene-d_6): δ (ppm) = 159.85, 134.35, 129.05, 114.44, 65.01, 55.15.

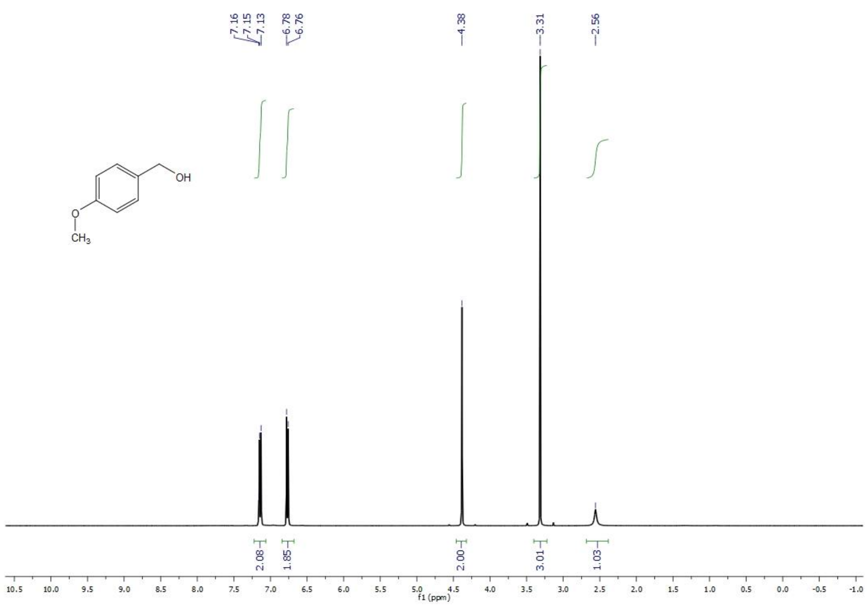


Figure S15. ^{1}H NMR spectrum of 4-methoxybenzyl alcohol in benzene-d_6.

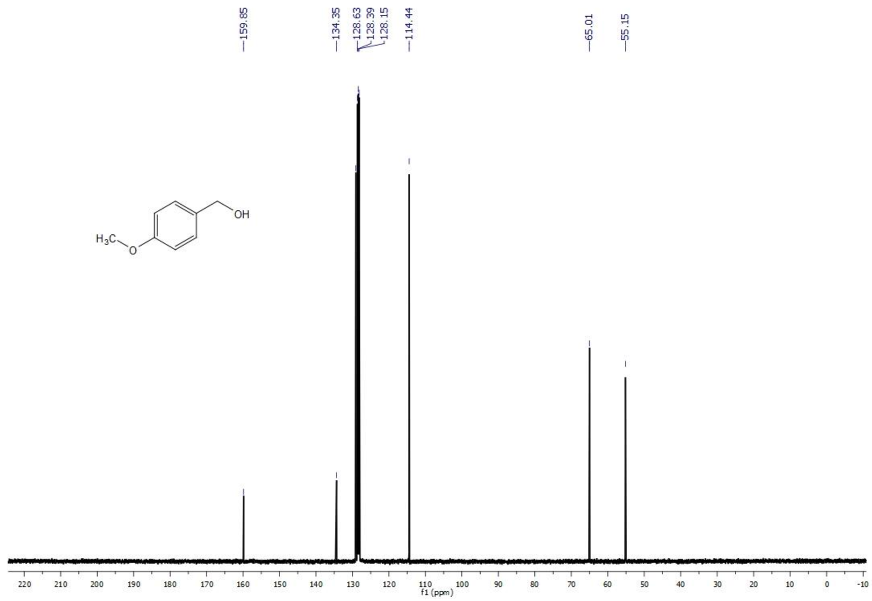


Figure S16. ^{13}C NMR spectrum of 4-methoxybenzyl alcohol in benzene-d_6.

Hydrosilylation of *p*-tolualdehyde catalyzed by 0.1 mol% 1: In the glove box, a mixture of $PhSiH_3$ (0.369 mL, 2.99 mmol) and *p*-tolualdehyde (0.353 mL, 2.99 mmol) was added to 0.002 g (0.0030 mmol) of **1** pre-weighed in a 20 mL vial. The resulting brown solution was vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^1H NMR spectrum was recorded to determine the percent conversion. It was then stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (4 x 3 mL) and dried over anhydrous Na_2SO_4. Removal of the diethyl ether on a rotavap at 35-38 °C afforded a white solid identified as 4-methylbenzyl alcohol (0.34 g, 90%). ^1H NMR (benzene-d_6): δ (ppm) = 7.12 (d, J = 7.8 Hz, 2H), 6.99 (d, J = 7.8 Hz, 2H), 4.35 (d, J = 4.9 Hz, 2H), 2.12 (s, 3H), 1.49 (s, 1H). ^{13}C NMR (benzene-d_6): δ (ppm) = 139.35, 137.20, 129.62, 127.52, 65.29, 21.46.

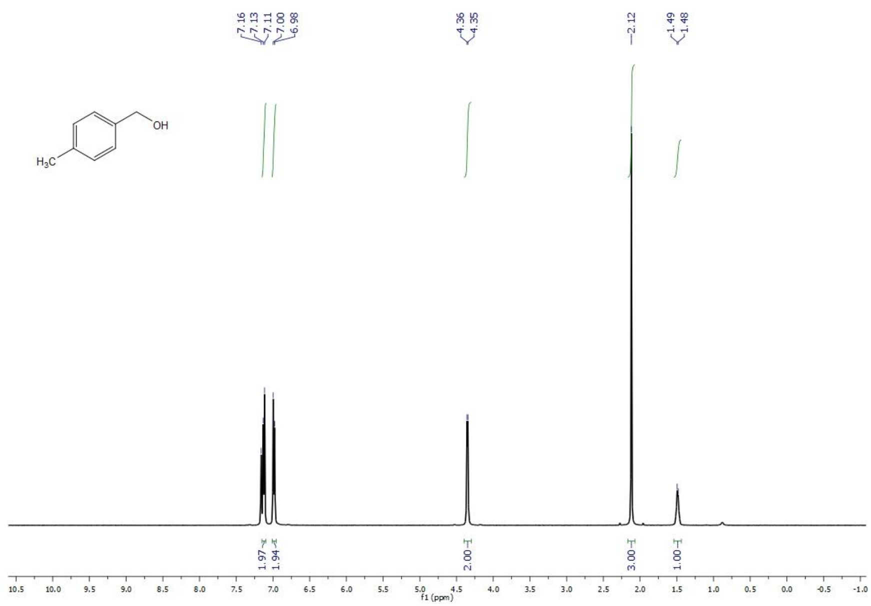


Figure S17. ^{1}H NMR spectrum of 4-methylbenzyl alcohol in benzene-d_6.

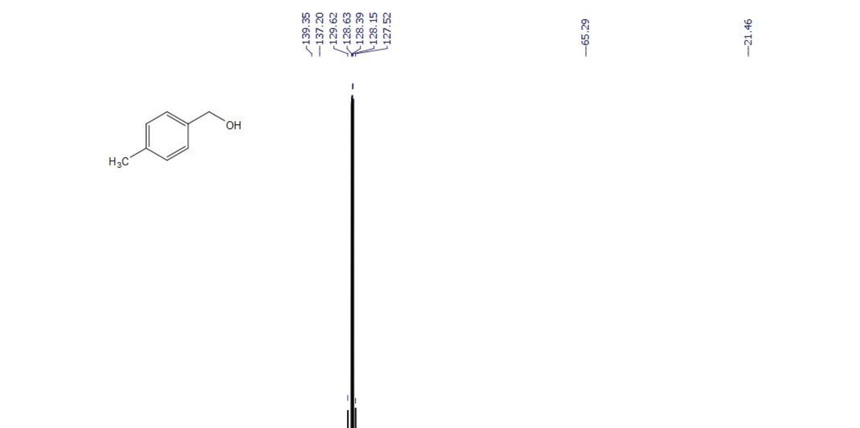


Figure S18. ^{13}C NMR spectrum of 4-methylbenzyl alcohol in benzene-d_6.

Hydrosilylation of 2-naphthaldehyde catalyzed by 0.1 mol% 1: In the glove box, a mixture of $PhSiH_3$ (0.369 mL, 2.99 mmol) and 2-naphthaldehyde (0.467 g, 2.99 mmol) in 0.5 mL of diethyl ether was added to 0.0020 g (0.0030 mmol) of **1** pre-weighed in a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^{1}H NMR spectrum was recorded to determine the percent conversion. It was then stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (4 x 3 mL) and dried over anhydrous Na_2SO_4. Removal of the diethyl ether on a rotavap at 35-38 °C afforded a white solid identified as 2-naphthalenemethanol (0.36 g, 77%). ^{1}H NMR (benzene-d_6): δ (ppm) = 7.99 – 7.95 (m, 1H), 7.68 (s, 1H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.53 (dd, *J* = 5.8 and 3.6 Hz, 1H), 7.40 (dd, *J* = 8.4 and 1.5 Hz, 1H), 7.25 – 7.21 (m, 3H), 5.06 (d, *J* = 9.7 Hz, 2H). ^{13}C NMR (benzene-d_6): δ (ppm) = 138.37, 135.86, 134.27, 133.78, 131.46, 131.10, 128.80, 128.15, 126.61, 126.31, 126.08, 125.75, 66.03.

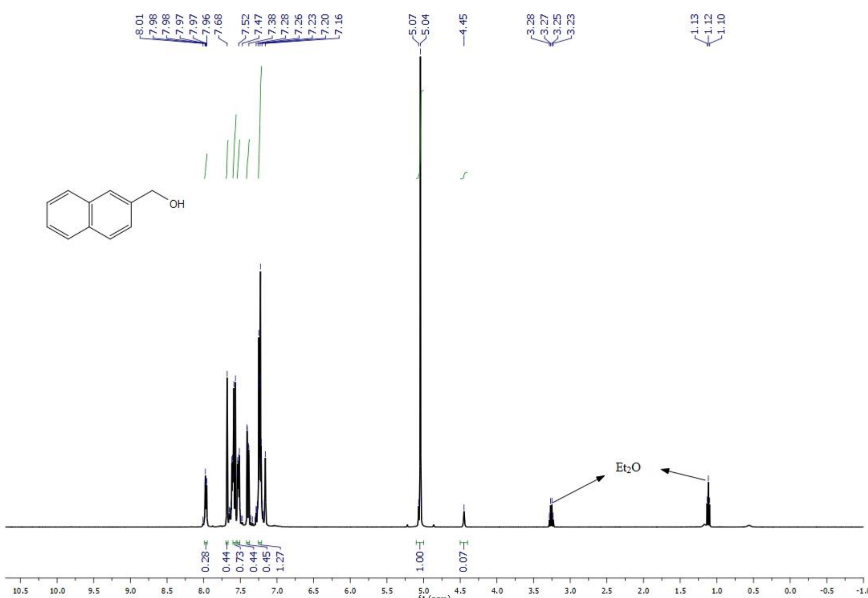


Figure S19. ^{1}H NMR spectrum of 2-naphthalenemethanol in benzene-d_6.

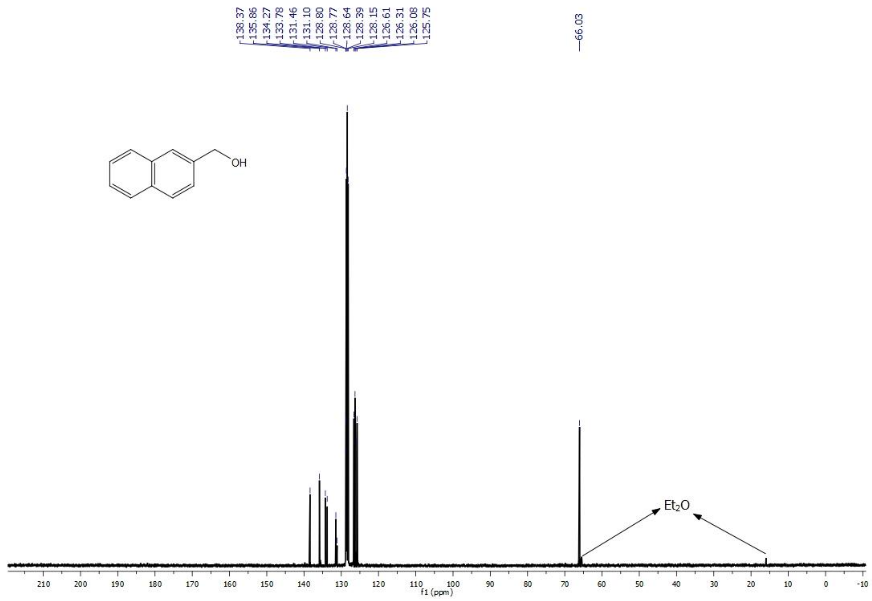


Figure S20. ^{13}C NMR spectrum of 2-naphthalenemethanol in benzene-d_6.

Hydrosilylation of pyridine-3-carbaldehyde catalyzed by 0.1 mol% 1: In the glove box, a mixture of $PhSiH_3$ (0.369 mL, 2.99 mmol) and pyridine-3-carbaldehyde (0.281 mL, 2.99 mmol) was added to 0.0020 g (0.0030 mmol) of **1** pre-weighed in a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and ^{1}H NMR was recorded to determine the percent conversion. It was then stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (4 x 3 mL) and dried over anhydrous Na_2SO_4. Removal of the diethyl ether on a rotavap at 35-38 °C afforded yellow oil identified as pyridine-3-carbinol (0.065 g, 27%). ^{1}H NMR (benzene-d_6): δ (ppm) = 8.47 (d, J = 1.4 Hz, 1H), 8.22 (d, J = 4.8 Hz, 1H), 7.36 (d, J = 7.8 Hz, 1H), 6.72 (dd, J = 7.7 and 4.9 Hz, 1H), 5.27 (s, 1H), 4.41 (s, 2H). ^{13}C NMR (benzene-d_6): δ (ppm) = 148.70, 148.52, 138.35, 135.29, 123.94, 62.29.

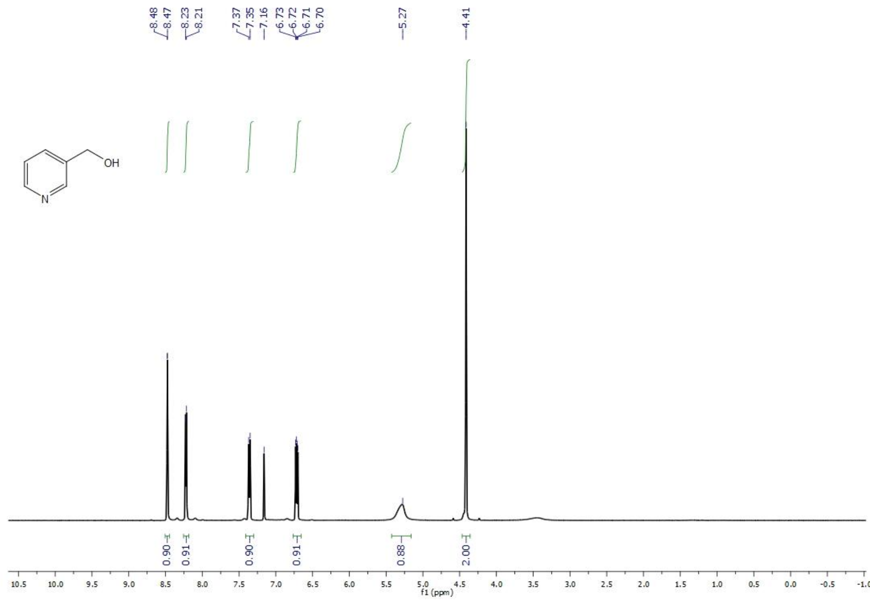


Figure S21. ^{1}H NMR spectrum of pyridine-3-carbinol in benzene-d_6.

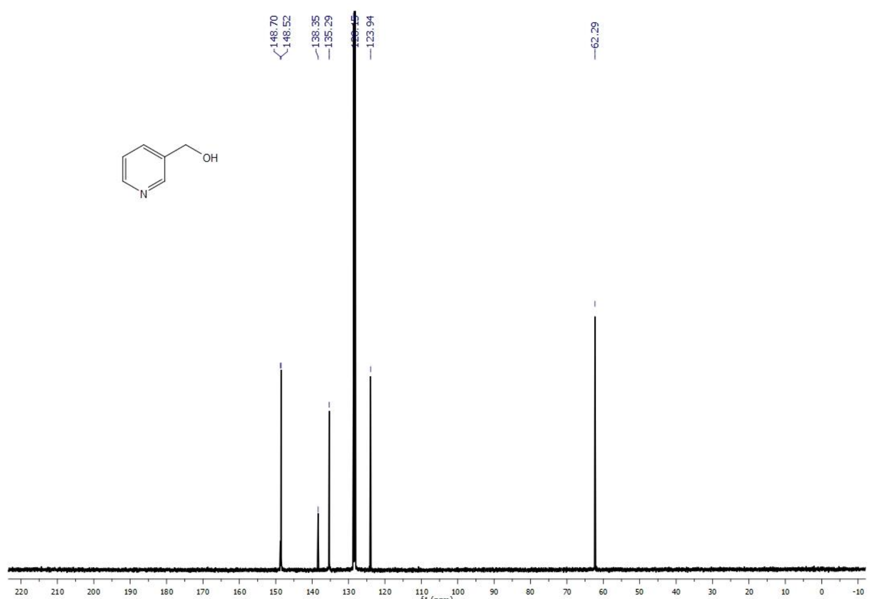


Figure S22. ^{13}C NMR spectrum of pyridine-3-carbinol in benzene-d_6.

Hydrosilylation of furfural catalyzed by 0.1 mol% 1: In the glove box, a mixture of $PhSiH_3$ (0.369 mL, 2.99 mmol) and furfural (0.248 mL, 2.99 mmol) was added to 0.0020 g (0.0030 mmol) of **1** pre-weighed in a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^{1}H NMR spectrum was recorded to determine the percent conversion. It was then stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (4 x 3 mL) and dried over anhydrous Na_2SO_4. Removal of the diethyl ether on a rotavap at 35-38 °C afforded yellow oil identified as furfuryl alcohol (0.23 g, 89%). ^{1}H NMR (benzene-d_6): δ (ppm) = 7.08 – 7.02 (m, 1H), 6.05 – 6.01 (m, 1H), 5.96 (t, J = 3.6 Hz, 1H), 4.22 (d, J = 5.2 Hz, 2H), 1.28 (s, 1H). ^{13}C NMR (benzene-d_6): δ (ppm) = 155.39, 142.64, 110.84, 107.71, 57.73.

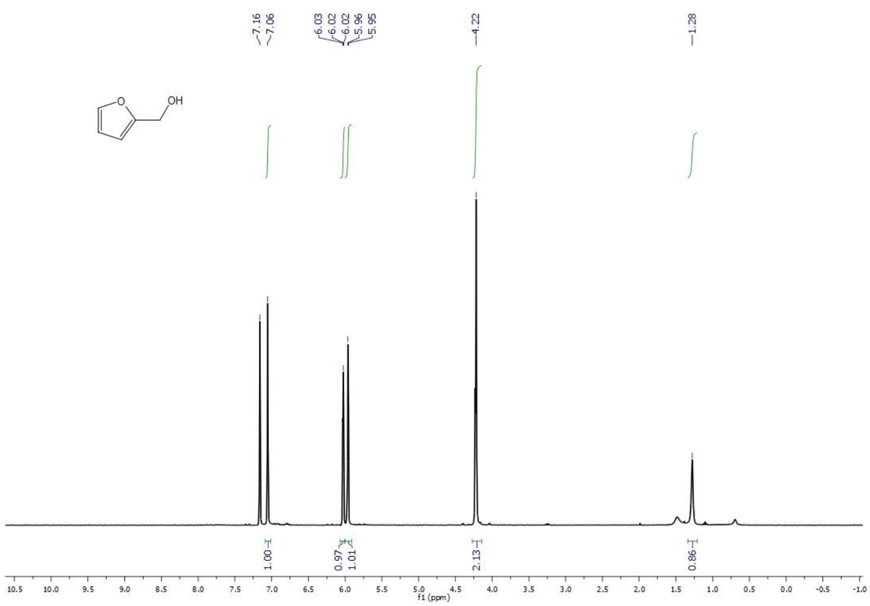


Figure S23. ^{1}H NMR spectrum of furfuryl alcohol in benzene-d_6.

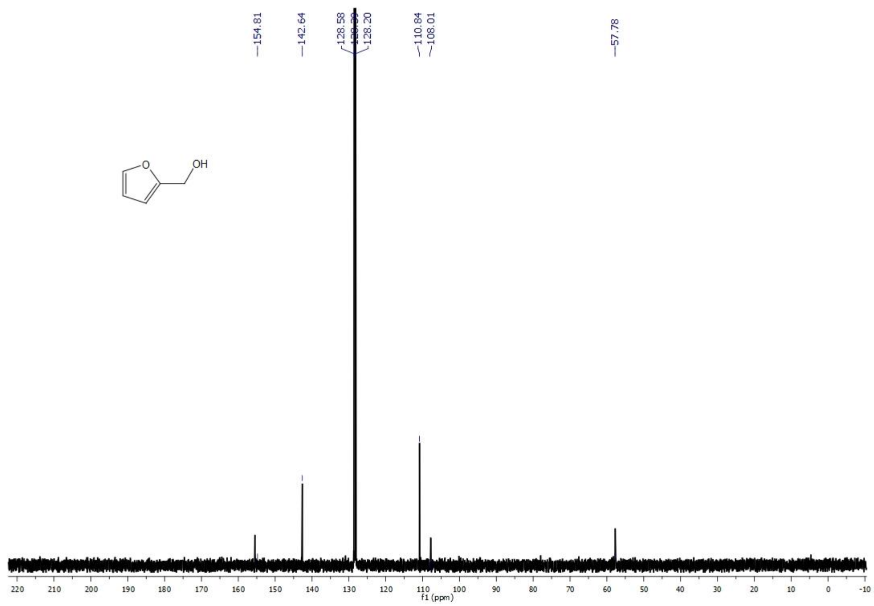


Figure S24. ^{13}C NMR spectrum of furfuryl alcohol in benzene-d_6.

Hydrosilylation of 3-cyclohexene-1-carboxaldehyde catalyzed by 0.1 mol% of 1: In the glove box, a mixture of $PhSiH_3$ (0.369 mL, 2.99 mmol) and 3-cyclohexene-1-carboxaldehyde (0.339 mL, 2.99 mmol) was added to 0.002 g (0.0030 mmol) of **1** pre-weighed in a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^{1}H NMR spectrum was recorded to determine the percent conversion. It was then stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (4 x 3 mL) and dried over anhydrous Na_2SO_4. Removal of the diethyl ether on a rotavap at 35-38 °C afforded a pale yellow oil identified as 3-cyclohexene-1-carbinol (0.29 g, 87%). ^{1}H NMR (benzene-d_6): δ (ppm) = 5.74 – 5.57 (m, 2H), 3.26 (s, 2H), 2.12 – 1.82 (m, 4H), 1.78 – 1.54 (m, 3H), 1.36 (s, 1H), 1.18 (dq, J = 11.9 and 8.0 Hz, 1H). ^{13}C NMR (benzene-d_6): δ (ppm) = 127.60, 126.74, 67.92, 37.03, 28.81, 25.91, 25.39.

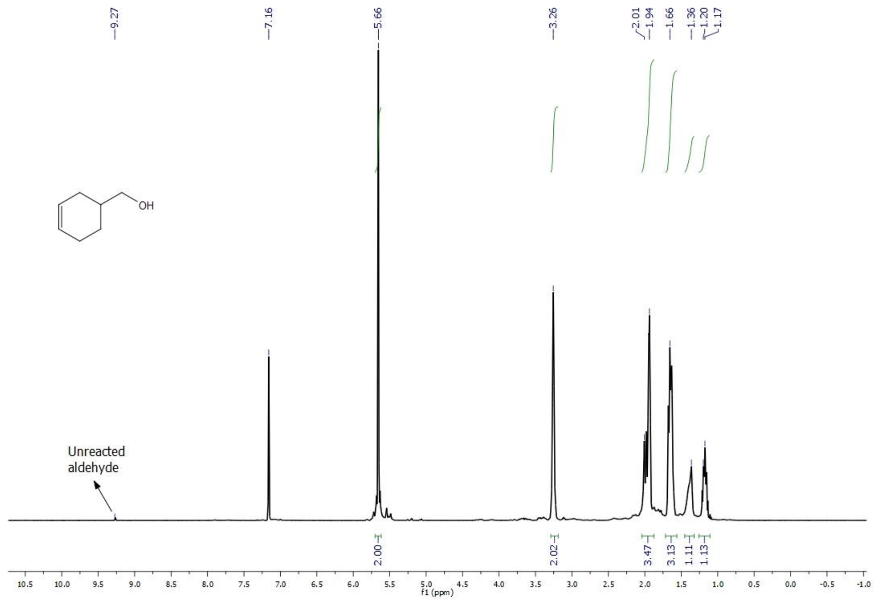


Figure S25. ^{1}H NMR spectrum of 3-cyclohexene-1-methanol in benzene-d_6.

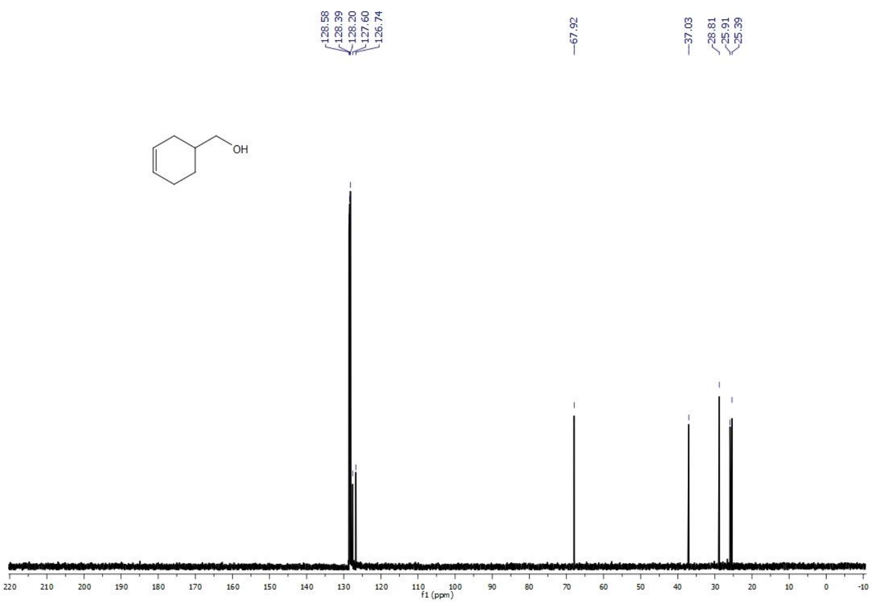


Figure S26. ^{13}C NMR spectrum of 3-cyclohexene-1-methanol in benzene-d_6.

Hydrosilylation of citral catalyzed by 0.1 mol% 1: In the glove box, a mixture of $PhSiH_3$ (0.369 mL, 2.99 mmol) and citral (0.0.509 mL, 2.99 mmol) was added to 0.0020 g (0.0030 mmol) of **1** pre-weighed in a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^{1}H NMR spectrum was recorded to determine the percent conversion. It was then stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (4 x 3 mL) and dried over anhydrous Na_2SO_4. Removal of the diethyl ether on a rotavap at 35-38 °C afforded a pale yellow oil identified as geraniol (0.38 g, 82%). ^{1}H NMR (benzene-d_6): δ (ppm) = 5.52 – 5.33 (m, 1H), 5.25 – 5.06 (m, 1H), 4.05 (dd, J = 3.8 and 2.8 Hz, 2H), 2.11 (dd, J = 15.0 and 7.1 Hz, 1H), 2.00 (dd, J = 14.2 and 4.9 Hz, 3H), 1.68 – 1.60 (m, 4H), 1.53 (s, 2H), 1.51 (d, J = 3.8 Hz, 3H). ^{13}C NMR (benzene-d_6): δ (ppm) = 138.45, 131.97, 126.38, 125.42, 59.66, 40.40, 32.67, 27.39, 26.18, 24.01, 17.70.

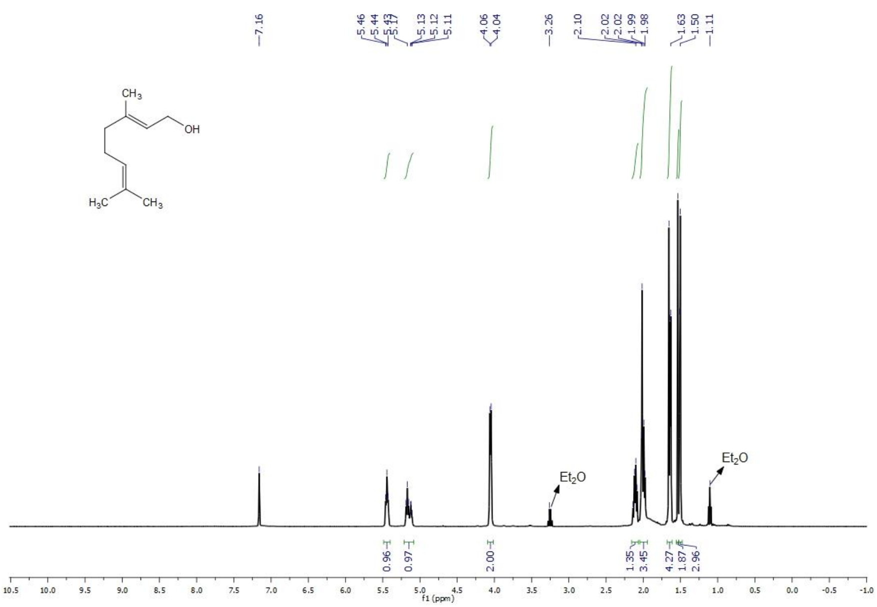


Figure S27. ^{1}H NMR spectrum of geraniol in benzene-d_6.

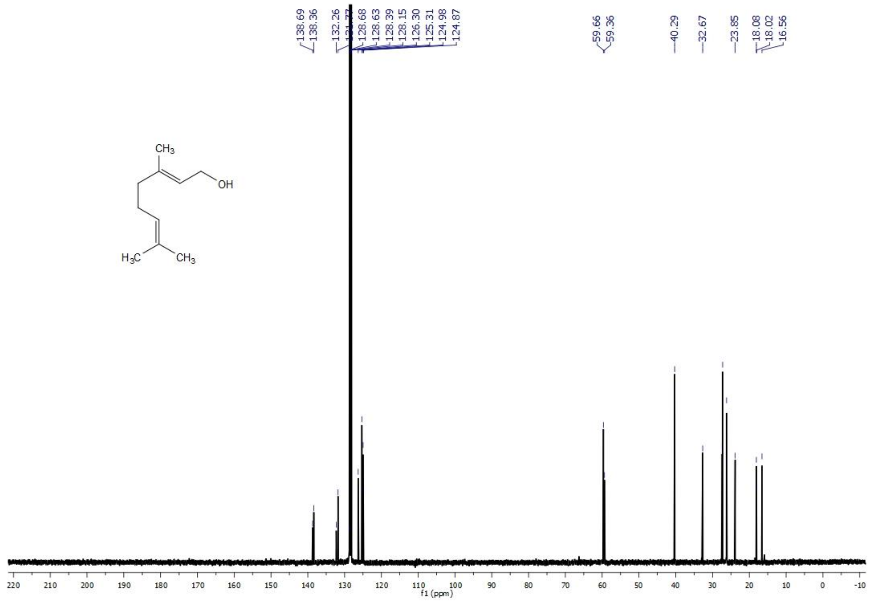


Figure S28. ^{13}C NMR spectrum of geraniol in benzene-d_6.

Procedure for the hydrosilylation of benzaldehyde in the presence of mercury: Under an inert atmosphere, a 20 mL scintillation vial was charged with 16.4 g (82.0 mmol) mercury and 0.17 mL (1.6 mmol) benzaldehyde. A solution of **1** (0.0021 g, 0.0016 mmol) and $PhSiH_3$ (0.20 mL, 1.6 mmol) was added. The resulting solution vigorously bubbled and became hot. The reaction was stirred for 2 min before exposure to air to deactivate the catalyst and then filtered through Celite. ^{1}H NMR spectroscopy revealed >99% conversion.

Procedure for the hydrosilylation of benzaldehyde in the absence of light: In the glove box, a mixture of $PhSiH_3$ (0.332 mL, 2.69 mmol) and benzaldehyde (0.273 mL, 2.69 mmol) was prepared in a wrapped 20 mL scintillation vial under dark conditions. Another wrapped vial was charged with 0.0018 g (0.0027 mmol) of **4**. The mixture was added to the catalyst in absence of light. The solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^{1}H NMR spectrum was recorded, which revealed >99% conversion to a mixture of silyl ethers.

Hydrosilylation of benzaldehyde catalyzed by 0.01 mol% 1: Under an inert atmosphere, a 50 mL round bottom flask was charged with 0.0018 g (0.0027 mmol) **1**. A mixture of 3.32 mL $PhSiH_3$ (26.9 mmol) and 2.74 mL benzaldehyde (26.9 mmol) was added. The resulting brown solution vigorously bubbled and became hot. The solution was stirred for 2 min before exposure to air to deactivate the catalyst and then filtered through Celite. ^{1}H NMR spectroscopy revealed >99% conversion. A 2 mL solution of 10% aqueous NaOH was added and stirred for 2 hours. The solution was extracted with diethyl ether (3 x 2 mL), organic layers were combined, and dried over Na_2SO_4. Solvent was removed using a rotovap, isolating benzyl alcohol (2.7 g, 24.8 mmol, yield = 92%). Complete conversion was also noted after 2 min upon adding 0.370 mL of a 0.1 mol% stock solution of **1** in $PhSiH_3$ [0.0110 g of **1** in 2.03 mL $PhSiH_3$ (0.00810 M)] to a flask containing 3.05 mL (29.9 mmol) benzaldehyde and 3.32 mL $PhSiH_3$ (total 29.9 mmol, overall loading of 0.01 mol% **1**).

Hydrosilylation of 4-fluorobenzaldehyde catalyzed by 0.01 mol% 1: Under an inert atmosphere, a 50 mL round bottom flask was charged with 0.0012 g (0.0018 mmol) **1**. A mixture of 2.21 mL $PhSiH_3$ (18.0 mmol) and 1.94 mL 4-fluorobenzaldehyde (18.0 mmol) was added. The resulting brown solution vigorously bubbled and became hot. The solution was stirred for 2 min before exposure to air to deactivate the catalyst. ^{1}H NMR spectroscopy revealed >99% conversion. A 2 mL solution of 10% aqueous NaOH was added and stirred for 2 hours. The solution was extracted with diethyl ether (3 x 2 mL), organic layers were combined, and dried over Na_2SO_4. Solvent was removed using a rotovap, isolating 4-fluorobenzyl alcohol (2.0 g, 15.6 mmol, yield = 87%).

Hydrosilylation of 2-naphthaldehyde catalyzed by 0.01 mol% 1: In the glove box, a mixture of $PhSiH_3$ (4.24 mL, 34.4 mmol) and 2-naphthaldehyde (5.37 g, 34.4 mmol) in 0.5 mL of diethyl ether was added to 0.0020 g (0.0034 mmol) of **1** pre-weighed in a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^{1}H NMR spectrum was recorded to determine the percent conversion. It was followed by a hydrolytic work up while the mixture was stirred with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (4 x 3 mL) and was dried over anhydrous Na_2SO_4. Removal of the diethyl ether on a rotavap at 35-38 °C afforded a white solid identified as 2-naphthalenemethanol (4.7 g, 87%)

Hydrosilylation of furfural catalyzed by 0.01 mol% 1: In the glove box, a mixture of $PhSiH_3$ (2.58 mL, 20.9 mmol) and furfural (1.73 mL, 20.9 mmol) was added to 0.0014 g (0.0021 mmol) of **1** pre-weighed in a 20 mL vial. The resulting brown solution vigorously bubbled and became hot. It was stirred for 2 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^1H NMR spectrum was recorded to determine the percent conversion. The mixture was then hydrolyzed with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (4 x 3 mL) and dried over anhydrous Na_2SO_4. Removal of the diethyl ether on a rotavap at 35-38 °C afforded a yellow oil identified as furfuryl alcohol (1.2 g, 12.2 mmol, 57%).

Procedure for the determination of maximum aldehyde hydrosilylation TON: Under an inert atmosphere, a round bottom flask was charged with 0.0015 g (0.0022 mmol) of **1**. A mixture of 2.768 mL (22.43 mmol) of $PhSiH_3$ and 2.280 mL (22.43 mmol) of benzaldehyde was added to the flask and stirred for 2 min. The resulting brown solution became hot and the solution was 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 brown mixture was exposed to air to deactivate the catalyst. Collecting a ^1H NMR spectrum of the mixture revealed an overall 63% conversion of the substrate into silyl ethers, resulting in a TON of 31,000.

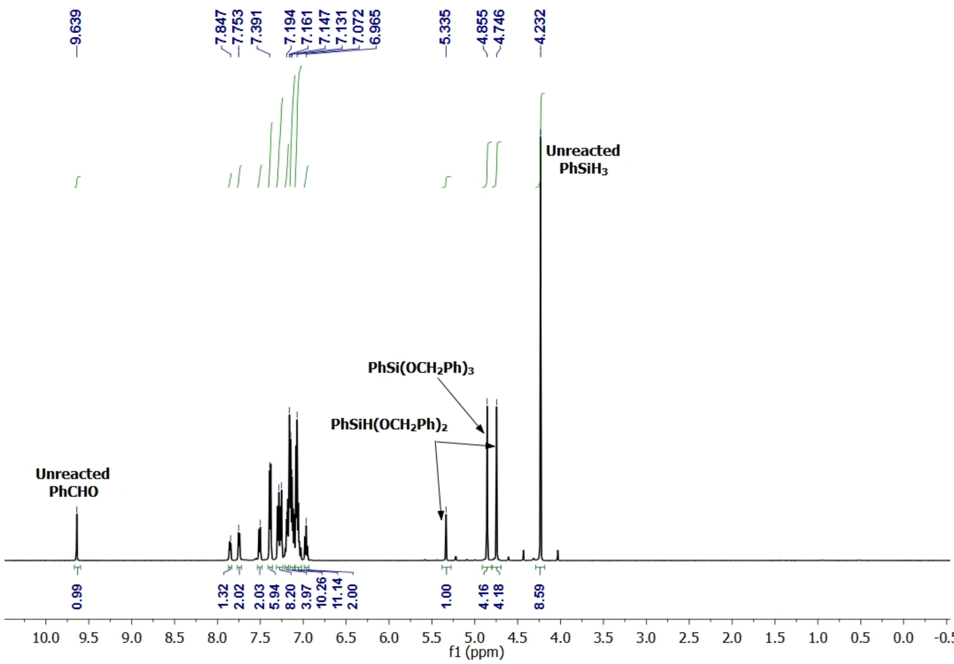


Figure S29. ^{1}H NMR spectrum of silyl ethers and unreacted benzaldehyde in benzene-d_6.

Dihydrosilylation of benzyl formate using 0.02 mol% 1 or 2: Under an inert atmosphere, a 100 mL round bottom flask was charged with 0.0021 g (0.0031 mmol) of **1**. A neat mixture of $PhSiH_3$ (1.94 mL, 15.7 mmol) and benzyl formate (1.96 mL, 15.7 mmol) was added to the flask and stirred at ambient temperature for 15 min during which time vigorous bubbling and heat generation was noticed. The reaction mixture was then exposed to air to deactivate the catalyst. After filtration through Celite, ^{1}H NMR spectroscopy revealed complete consumption of starting material to a mixture of silyl ethers. Then 2 mL of 10% aq. NaOH was added to the colorless solution and was allowed to react over the course of 2 h. The organic fraction was then extracted with Et_2O (3 x 2 mL) and the combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed using a rotavap to isolate pure benzyl alcohol (1.5 g, 13.8 mmol, yield = 88%). Complete conversion was also noted after 15 min upon adding 0.370 mL of a 0.1 mol% stock solution of **1** in $PhSiH_3$ [0.0110 g of **1** in 2.03 mL $PhSiH_3$ (0.00810 M)] to a mixture of 1.87 mL (15.0 mmol) benzyl formate and 1.47 mL $PhSiH_3$, (total 15.0 mmol, overall loading of 0.02 mol% **1**). An analogous procedure was performed using 0.0010 g (0.0015 mmol) **2**, 0.92 mL g (7.5 mmol) $PhSiH_3$, and 0.94 mL (7.5 mmol) benzyl formate to yield 0.65 g (6.0 mmol, yield = 81%) benzyl alcohol.

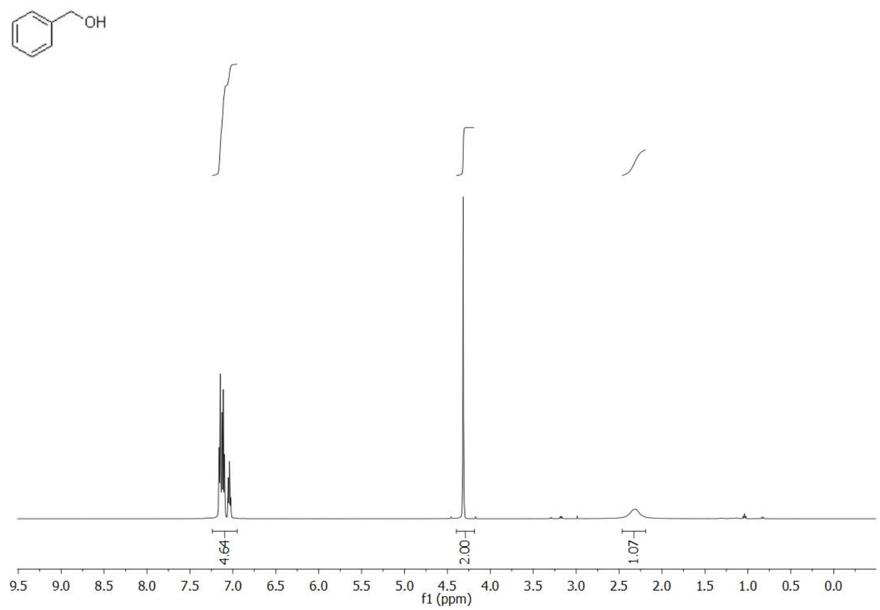


Figure S30. ^{1}H NMR spectrum of benzyl alcohol in benzene-d_6.

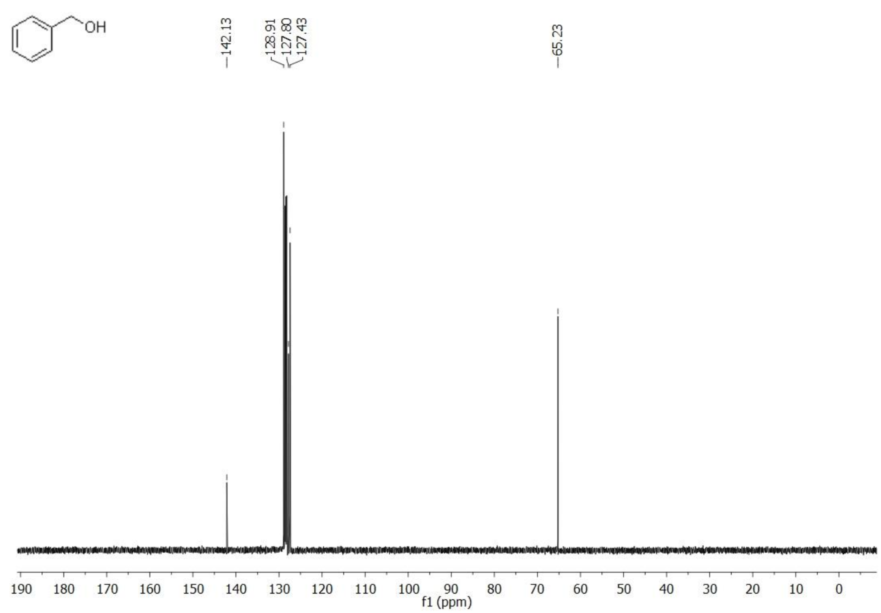


Figure S31. ^{13}C NMR spectrum of benzyl alcohol in benzene-d_6.

Dihydrosilylation of *p*-anisyl formate using 0.02 mol% 1 or 2: Under an inert atmosphere, a 50 mL round bottom flask was charged with 0.0024 g (0.0036 mmol) of **1**. A neat mixture of $PhSiH_3$ (2.21 mL, 18.0 mmol) and *p*-anisyl formate (2.88 mL, 18.0 mmol) was added to the flask and stirred at ambient temperature for 15 min, during which time bubbling and heat generation was observed. The reaction mixture was then exposed to air to deactivate the catalyst. After filtration through Celite, ^{1}H NMR spectroscopy showed complete consumption of the starting material. Then 2 mL of 50% aq. NaOH was added to the colorless solution and allowed to react over the course of 2 h. The organic fraction was then extracted with Et_2O (3 x 2 mL) and the combined organic layer was dried over anhydrous Na_2SO_4. Solvent was then removed using a rotovap to isolate pure 4-methoxybenzyl alcohol (2.1 g, 15.3 mmol, yield = 85%). An analogous procedure was performed using 0.0013 g (0.0019 mmol) **2**, 1.56 mL (9.72 mmol) *p*-anisyl formate, and 1.20 mL (9.72 mmol) $PhSiH_3$ to yield 0.68 g 4-methoxybenzyl alcohol (4.94 mmol, yield = 51%).

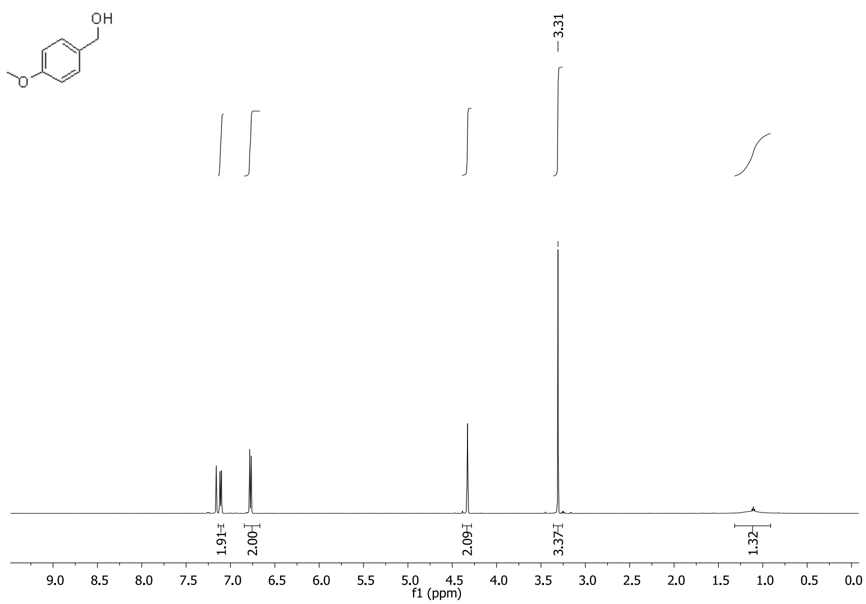


Figure S32. ^{1}H NMR spectrum of 4-methoxybenzyl alcohol in benzene-d_6.

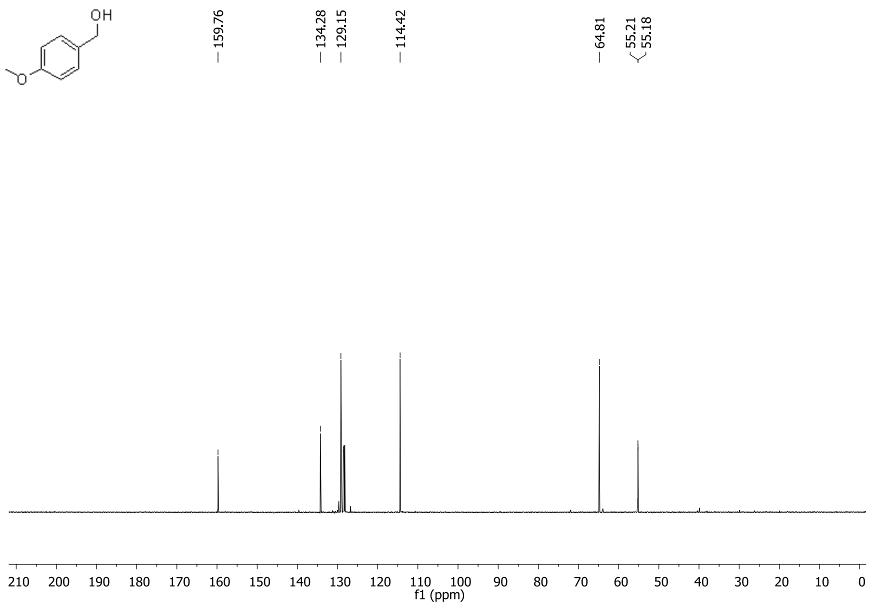


Figure S33. ^{13}C NMR spectrum of 4-methoxybenzyl alcohol in benzene-d_6.

Dihydrosilylation of 2-phenylethyl formate using 0.02 mol% 1 or 2: Under an inert atmosphere, a 100 mL round bottom flask was charged with 0.0014 g (0.0021 mmol) of **1**. A neat mixture of $PhSiH_3$ (1.3 mL, 10.47 mmol) and 2-phenylethyl formate (149 mL, 10.5 mmol) was added to the flask and stirred at ambient temperature for 15 min during which time vigorous bubbling and heat generation was noticed. The reaction mixture was then exposed to air to deactivate the catalyst. After filtration through Celite, ^1H NMR spectroscopy showed complete consumption of starting material. Then 2 mL of 10% aq. NaOH was added to the colorless solution and allowed to react over the course of 2 h. The organic fraction was then extracted with Et_2O (3 x 2 mL) and the combined organic layer was dried over anhydrous Na_2SO_4. Solvent was removed using a rotavap to isolate pure 2-phenylethanol (1.1 g, 9.0 mmol, yield = 86%). An analogous procedure was performed using 0.0012 g (0.0018 mmol) **2**, 1.10 mL (8.96 mmol) $PhSiH_3$, and 1.28 mL (8.96 mmol) 2-phenylethyl formate to yield 0.79 g (6.5 mmol, yield = 72%) of 2-phenylethanol. ^1H NMR (benzene-d_6): δ (ppm) = 7.26 (m, 2H), 7.17 (m, 3H), 3.64 (s, 2H), 2.70 (t, J = 6.6 Hz, 2H), 1.49 (s, 1H). ^{13}C NMR (benzene-d_6): δ (ppm) = 139.66, 129.68, 129.02, 126.84, 64.02, 40.00.

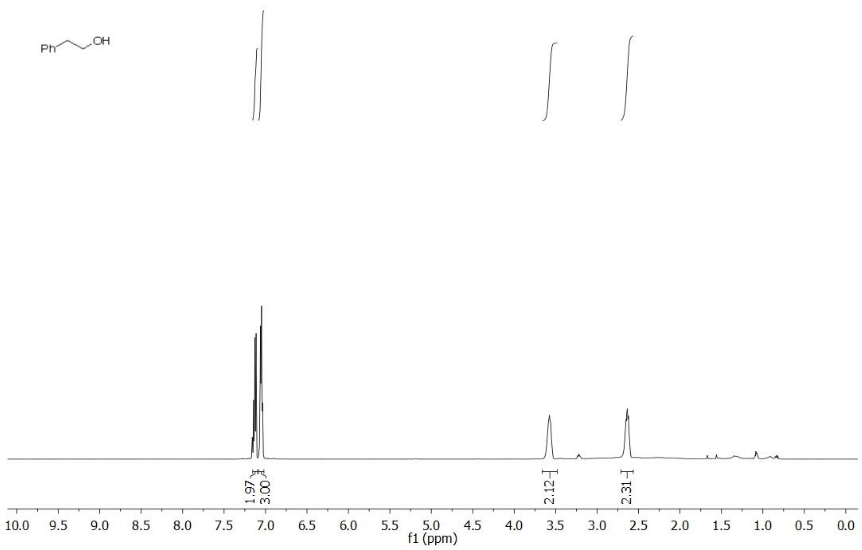


Figure S34. ^{1}H NMR spectrum of 2-phenylethanol in benzene-d_6.

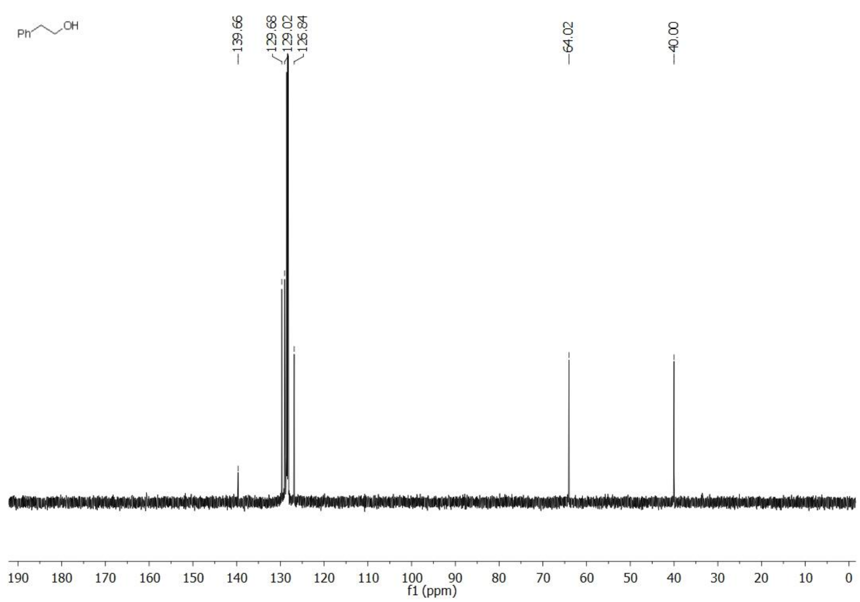


Figure S35. ^{13}C NMR spectrum of 2-phenylethanol in benzene-d_6.

Dihydrosilylation of hexyl formate using 0.02 mol% 1 or 2: Under an inert atmosphere, a 100 mL round bottom flask was charged with 0.0026 g (0.0039 mmol) of **1**. A neat mixture of $PhSiH_3$ (2.4 mL, 19 mmol) and hexyl formate (2.8 mL, 19 mmol) was added to the flask and stirred at ambient temperature for 15 min during which time vigorous bubbling and heat generation was noticed. The reaction mixture was then exposed to air to deactivate the catalyst. After filtration through Celite, ^1H NMR spectroscopy showed complete consumption of starting material. Then 2 mL of 10% aq. NaOH was added to the colorless solution and allowed to react over the course of 2 h. The organic fraction was then extracted with Et_2O (3 x 2 mL) and the combined organic layer was dried over anhydrous Na_2SO_4. Solvent was removed using a rotavap to isolate pure 1-hexanol (1.2 g, 12 mmol, yield = 62%). An analogous procedure was performed using 0.0013 g (0.0019 mmol) **2**, 1.20 mL (9.71 mmol) $PhSiH_3$, and 1.44 mL (9.71 mmol) hexyl formate to yield 0.65 g (6.3 mmol, yield = 65%) 1-hexanol. ^1H NMR (benzene-d_6): δ (ppm) = 3.46 (t, J = 6.6 Hz, 2H, CH_2OH), 2.21 (br s, 1H, CH_2OH), 1.51-1.37 (m, 2H, CH_2), 1.35-1.11 (m, 4H, CH_2), 0.87 (t, J = 6.9 Hz, 3H, CH_3). ^{13}C NMR (benzene-d_6): δ (ppm) = 63.03 ($C$$H_2$OH), 33.50 ($CH_2$), 32.42 ($CH_2$), 26.25 ($CH_2$), 23.41 ($CH_2$), 14.61 ($CH_3$).

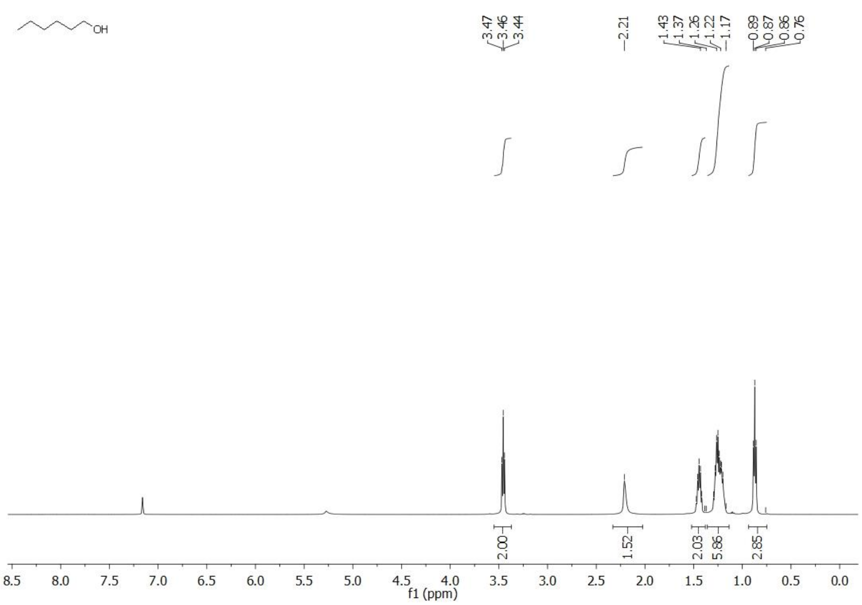


Figure S36. ^1H NMR spectrum of 1-hexanol in benzene-d_6.

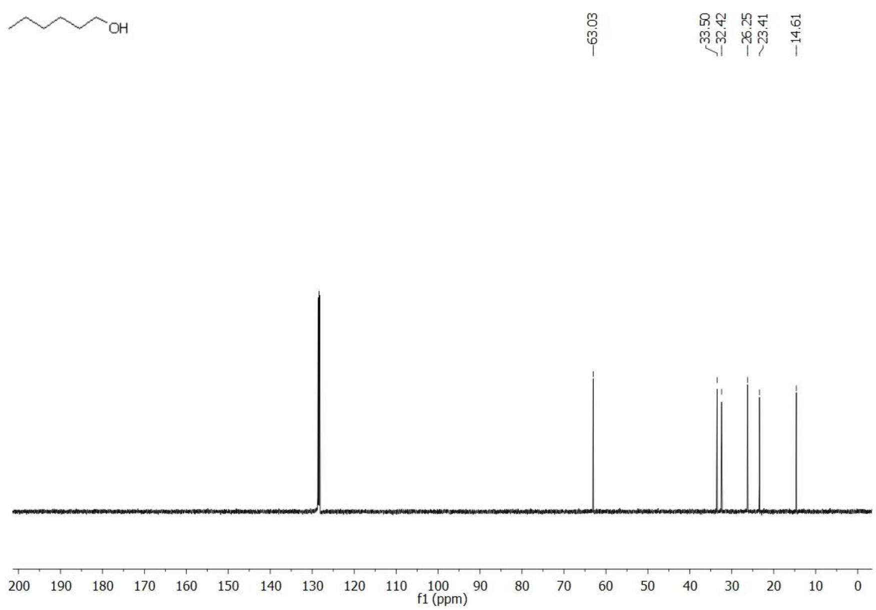


Figure S37. ^{13}C NMR spectrum of 1-hexanol in benzene-d_6.

Dihydrosilylation of isoamyl formate using 0.02 mol% 1 or 2: Under an inert atmosphere, a 100 mL round bottom flask was charged with 0.0021 g (0.0031 mmol) of **2**. A neat mixture of $PhSiH_3$ (1.94 mL, 15.7 mmol) and isoamyl formate (2.07 mL, 15.7 mmol) was added to the flask and stirred at ambient temperature for 15 min during which time vigorous bubbling and heat generation was noticed. The reaction mixture was then exposed to air to deactivate the catalyst. After filtration through Celite, ^{1}H NMR spectroscopy showed complete consumption of starting material. Then 2 mL of 10% aq. NaOH was added to the colorless solution and allowed to react over the course of 2 h. The organic fraction was then extracted with Et_2O (3 x 2 mL) and the combined organic layer was dried over anhydrous Na_2SO_4. Solvent was removed using a rotavap to isolate pure isoamyl alcohol (0.79 g, 8.9 mmol, yield = 57%). An analogous procedure was performed using 0.0010 g (0.0015 mmol) **2**, 0.92 mL (7.5 mmol) $PhSiH_3$, and 1.01 mL (7.5 mmol) isoamyl formate to yield 0.45 g (5.1 mmol, yield = 68%) isoamyl alcohol. ^{1}H NMR (benzene-d_6): δ (ppm) = 3.44 (dt, J = 31.1, 6.6 Hz, 2H, CH_2OH), 2.72 (br s, 1H, CH_2OH), 1.62 (sept, J = 7.0 Hz, 1H, CH), 1.36-1.27 (m, 2H, CH_2), 0.8 (dd, J = 8.8, 6.7 Hz, 6H, CH_3). ^{13}C NMR (benzene-d_6): δ (ppm) = 61.25 (CH$_2$OH), 42.40, 25.33, 23.13.

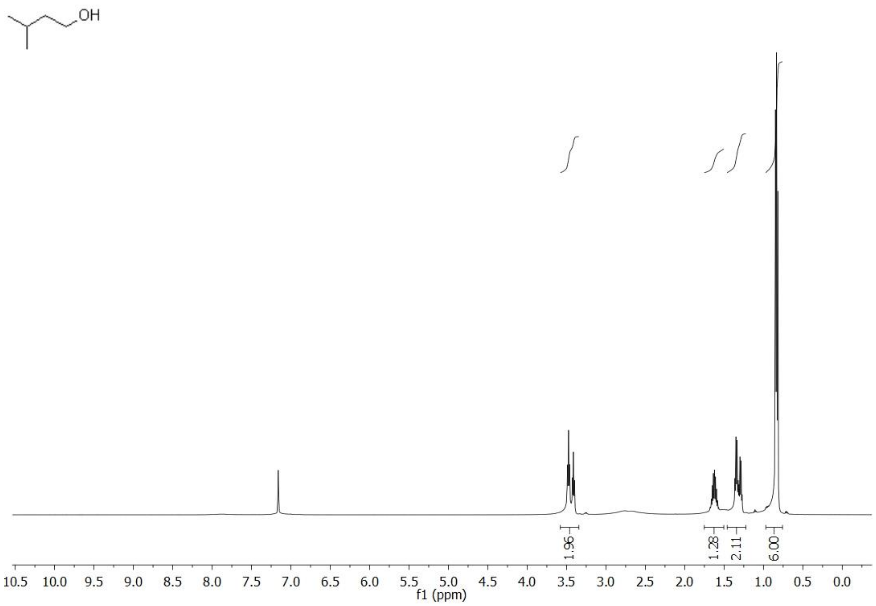


Figure S38. ^{1}H NMR spectrum of isoamyl alcohol in benzene-d_6.

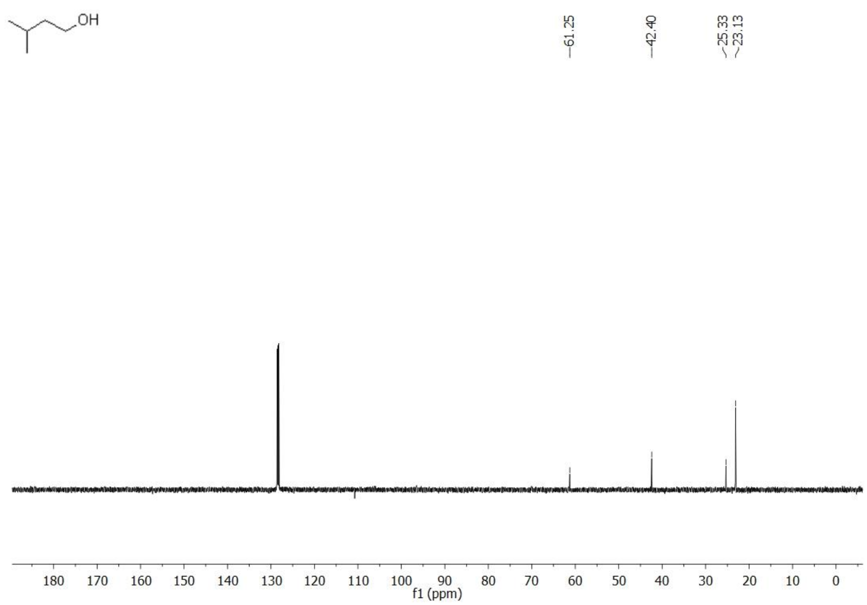


Figure S39. ^{13}C NMR spectrum of isoamyl alcohol in benzene-d_6.

Dihydrosilylation of citronellyl formate using 0.1 mol% 1 or 2: Under an inert atmosphere, a 20 mL scintillation vial was charged with 0.0010 (0.0015 mmol) of **1**. A neat mixture of $PhSiH_3$ (0.18 mL, 1.5 mmol) and citronellyl formate (0.31 mL, 1.5 mmol) was added to the vial and stirred at ambient temperature for 15 min, during which time bubbling and heat generation was observed. The reaction mixture was then exposed to air to deactivate the catalyst. After filtration through Celite, ^1H NMR spectroscopy showed complete consumption of the starting material. Then 2 mL of 50% aq. NaOH was added to the colorless solution and allowed to react over the course of 2 h. The organic fraction was then extracted with Et_2O (3 x 2 mL) and the combined organic layer was dried over anhydrous Na_2SO_4. Solvent was then removed using a rotovap to isolate pure citronellol (0.15 g, 0.95 mmol, yield = 64%). An analogous procedure was performed using 0.0017 g (0.0025 mmol) **2**, 0.52 mL (2.54 mmol) citronellyl formate, and 0.31 mL (2.5 mmol) $PhSiH_3$ to yield 0.28 g (1.8 mmol, yield = 70%) citronellol. ^1H NMR (benzene-d_6): δ (ppm) = 5.20 (m, 1H), 3.41 (m, 2H), 2.03 (m, 2H), 1.68 (s, 3H), 1.56 (s, 3H), 1.48 (m, 2H), 1.34 (m, 2H), 1.16 (m, 2H), 0.83 (dd, J = 6.6 and 0.8 Hz, 3H). ^{13}C NMR (benzene-d_6): δ (ppm) = 130.47, 125.03, 124.93, 60.29, 39.83, 37.32, 29.20, 25.55, 25.45, 19.31, 17.30.

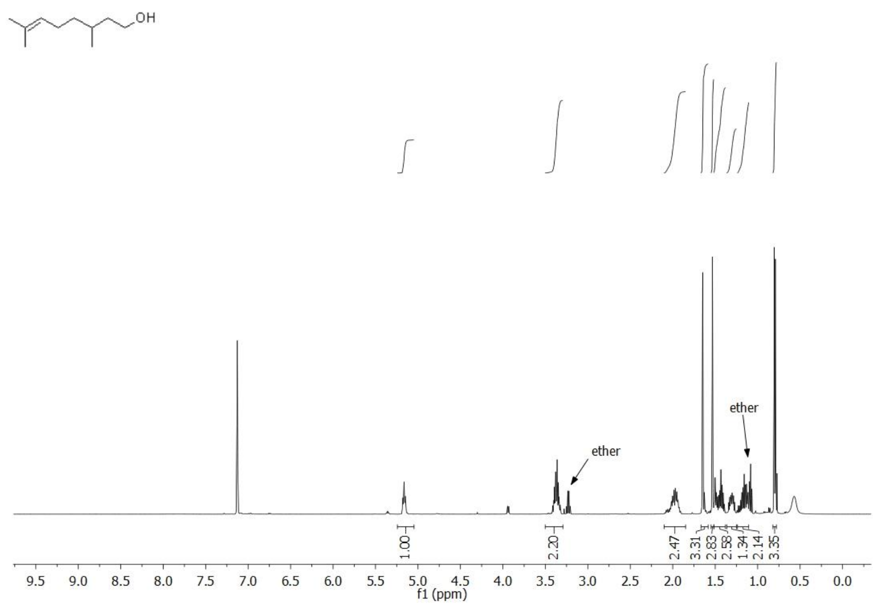


Figure S40. ^1H NMR spectrum of citronellol in benzene-d_6.

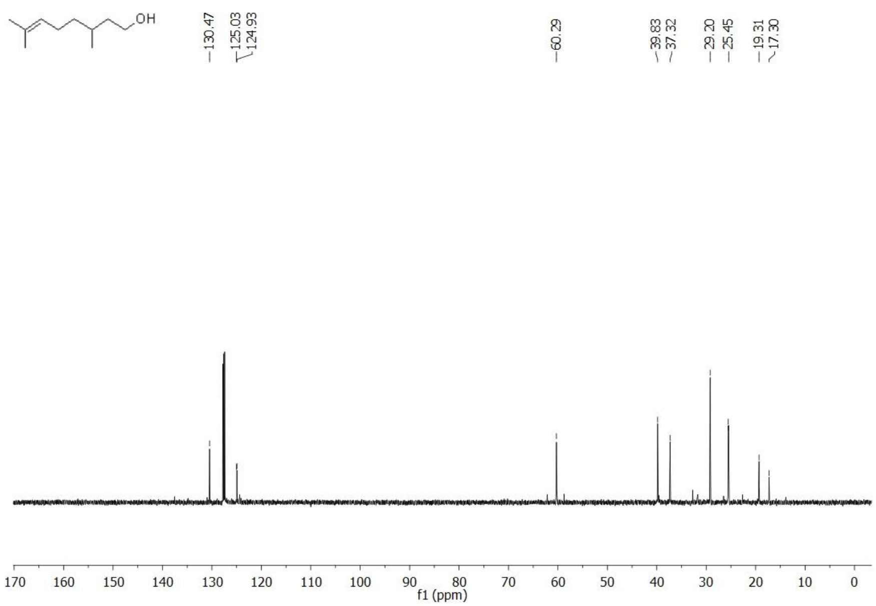


Figure S41. ^{13}C NMR spectrum of citronellol in benzene-d_6.

Dihydrosilylation of geranyl formate using 0.1 mol% 1 or 2: Under an inert atmosphere, a 20 mL scintillation vial was charged with 0.0010 g (0.0015 mmol) of **1**. A neat mixture of $PhSiH_3$ (0.18 mL, 1.5 mmol) and geranyl/neranyl formate (0.30 mL, 1.5 mmol) was added to the vial and stirred at ambient temperature for 15 min, during which time bubbling and heat generation was observed. The reaction mixture was then exposed to air to deactivate the catalyst. After filtration through Celite, ^{1}H NMR spectroscopy showed complete consumption of the starting material. Then 2 mL of 50% aq. NaOH was added to the colorless solution and allowed to react over the course of 2 h. The organic fraction was then extracted with Et_2O (3 x 2 mL) and the combined organic layer was dried over anhydrous Na_2SO_4. Solvent was then removed using a rotovap to isolate a mixture of geraniol and nerol (0.15 g, 0.95 mmol, yield = 64%). An analogous procedure was performed using 0.0010 g (0.0015 mmol) **2**, 0.30 mL (1.5 mmol) geranyl/neranyl formate, and 0.18 mL (1.5 mmol) $PhSiH_3$ to yield 0.21 g geraniol and nerol (1.3 mmol, yield = 90%). ^{1}H NMR (benzene-d_6): δ (ppm) = 5.38 (m, 1H), 5.15 (m, 1H), 3.98 (s, 1H), 3.44 (t, J = 19.0 Hz, 1H), 2.06 (m, 1H), 1.96 (m, 1H), 1.64 (d, J = 4.9 Hz, 1H), 1.62 (s, 1H), 1.53 (s, 1H), 1.50 (s, 1H), 1.45 (d, J = 5.3 Hz, 1H), 1.32 (m, 1H), 1.14 (m, 1H), 0.81 (dd, J = 6.6 and 3.8 Hz, 1H). ^{13}C NMR (benzene-d_6): δ (ppm) = 138.22, 131.72, 131.23, 125.85, 125.76, 125.29, 125.25, 125.06, 124.97, 61.04, 59.52, 40.63, 40.36, 38.12, 30.01, 27.29, 26.34, 26.23, 26.17, 20.11, 18.08, 16.63, 16.61.

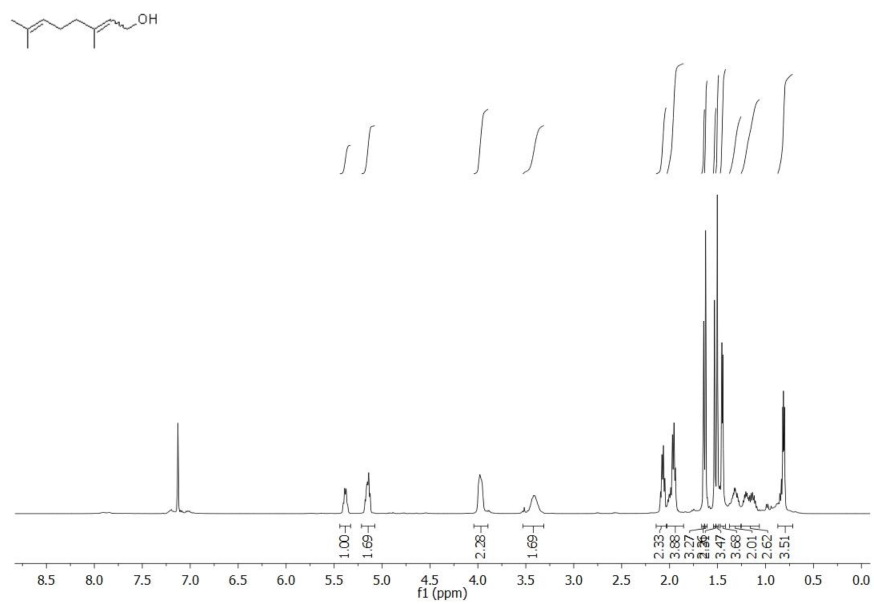


Figure S42. ^{1}H NMR spectrum of geraniol and nerol in benzene-d_6.

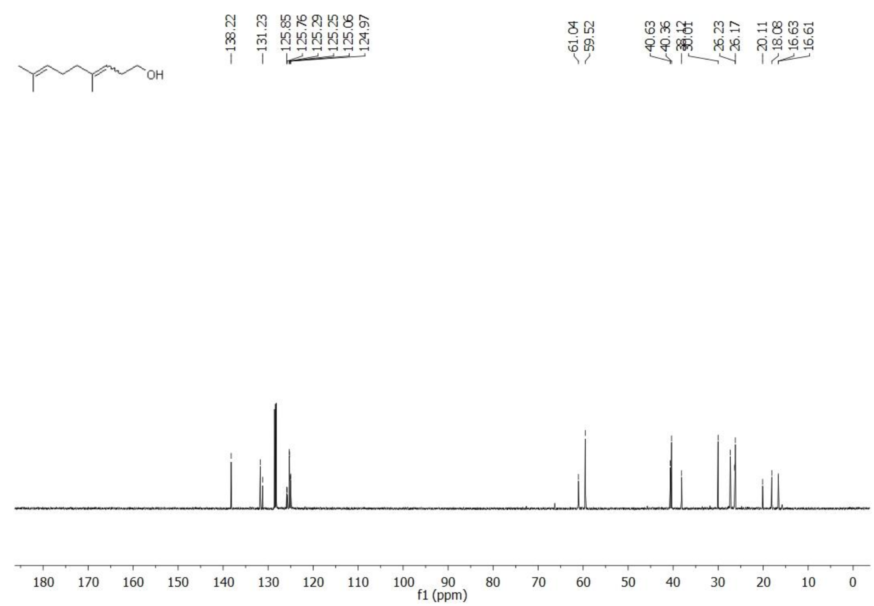


Figure S43. ^{13}C NMR spectrum of geraniol and nerol in benzene-d_6.

Hydrosilylation of benzaldehyde catalyzed by 1.0 mol% ($^{2,6\text{-iPr}_2\text{Ph}}$PDI)Mn(THF)$_2$: In the glove box, a mixture of $PhSiH_3$ (0.106 mL, 0.86 mmol) and benzaldehyde (0.087 mL, 0.86 mmol) was added to 0.0065 g (0.0086 mmol) of **($^{2,6\text{-iPr}_2\text{Ph}}$PDI)Mn(THF)$_2$** preweighed in a 20 mL scintillation vial. The resulting red solution bubbled and became hot. It was stirred for 10 min and then exposed to air to deactivate the catalyst. The colorless solution was filtered through Celite and a ^{1}H NMR spectrum was recorded to determine the percent conversion. The mixture was then hydrolyzed with 2 mL aqueous 10% NaOH solution at room temperature for 2 h. The organic fraction was extracted with diethyl ether (3 x 2 mL) and dried over anhydrous Na_2SO_4. Removal of the solvent on a rotovap afforded a clear liquid identified as benzyl alcohol (0.082 g, 0.76 mmol, 88%).

COMPOUND CHARACTERIZATION

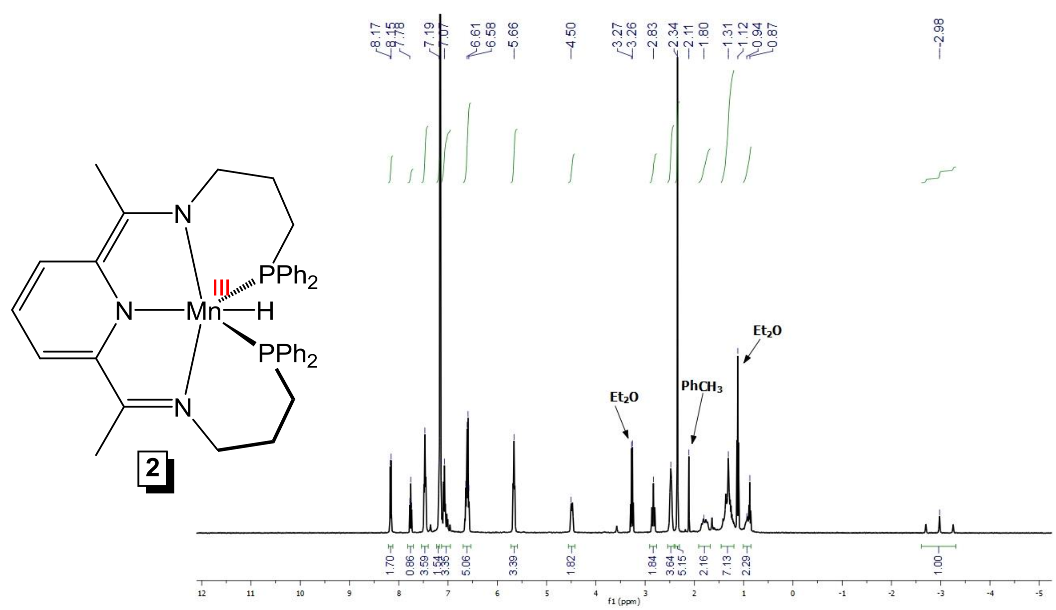


Figure S44. ^{1}H NMR spectrum of **2** in benzene-d_6.

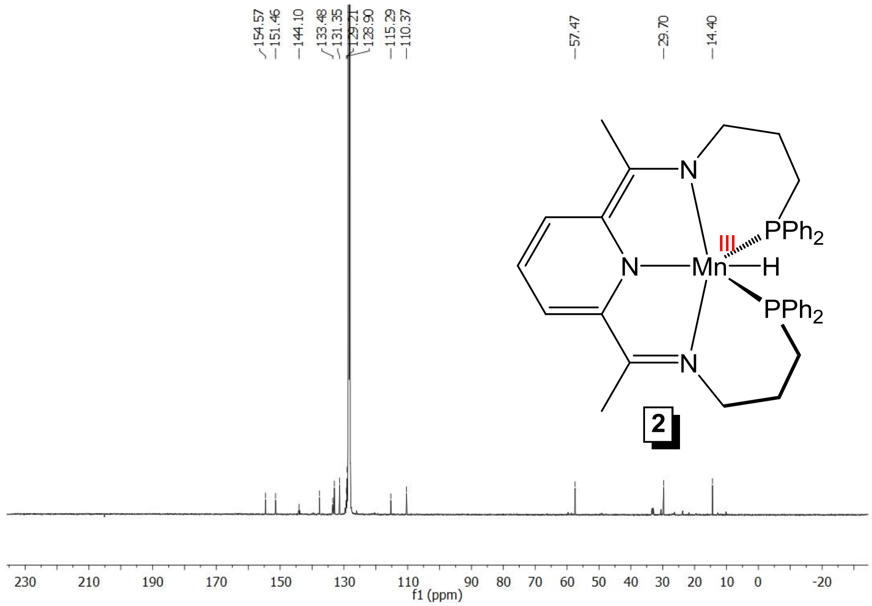


Figure S45. ^{13}C NMR spectrum of **2** in benzene-d_6.

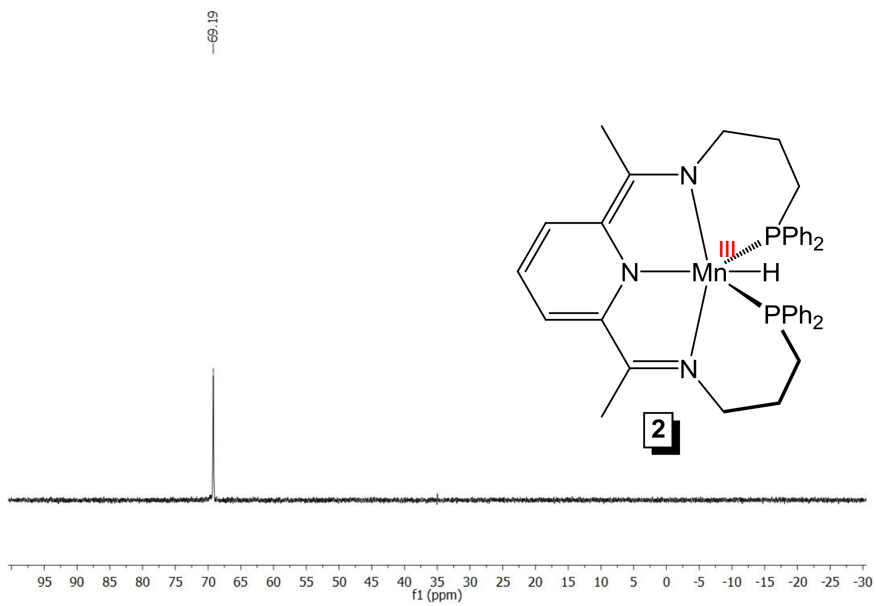


Figure S46. ^{31}P NMR spectrum of **2** in benzene-d_6.

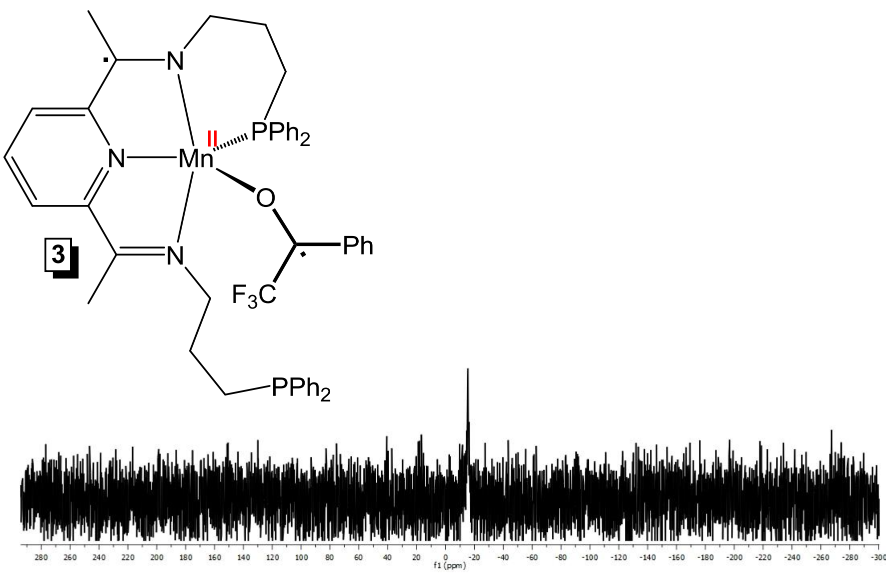


Figure S47. ^{31}P NMR spectrum of **3** in benzene-d_6.

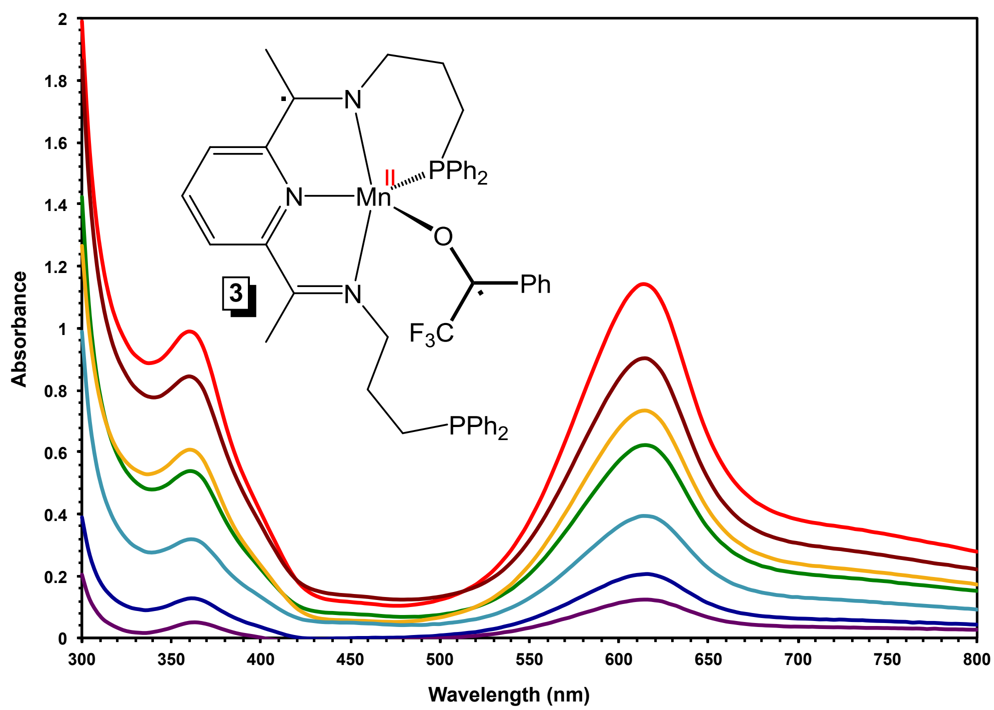


Figure S48. UV-visible spectrum of **3** (7 different concentrations in toluene).

KINETIC TRIALS

Use of AIBN for diisopropyl ketone hydrosilylation: In the glove box, a mixture of $PhSiH_3$ (0.183 mL, 1.48 mmol) and benzaldehyde (0.151 mL, 1.48 mmol) was prepared in a 20 mL scintillation vial in the dark. A second vial was charged with 0.0019 g (0.0015 mmol) of 2,2'-azobis(2-methylpropionitrile) (AIBN) and the reagent mixture was added. The solution was transferred into a J. Young tube and the progress of the reaction was monitored by ^1H NMR spectroscopy. After 24 h at 25 °C or 2 h at 90 °C, 0% conversion was noted.

Procedure for 1-catalyzed diisopropyl ketone hydrosilylation using $PhSiD_3$: In the glove box, a J. Young tube was charged with a 0.7 mL benzene-d_6 solution containing 0.0020 g (0.0030 mmol) **1** and placed into a liquid N_2 jacketed cold well. While the catalyst solution was frozen, 0.0372 mL (0.299 mmol) of $PhSiD_3$ and 0.0424 mL (0.299 mmol) of diisopropyl ketone was injected. Then 0.010 mL (0.092 mmol) of anisole was added as an internal standard. The tube was sealed under N_2 and quickly transferred into a dewar filled with liquid N_2. The mixture was warmed to room temperature and ^1H NMR data was collected every 30 s. Percent conversion was determined by integrating the reactant and product peaks with respect to anisole. This experiment was repeated two more times to obtain a standard deviation.

Procedure for 2-catalyzed diisopropyl ketone hydrosilylation using $PhSiD_3$: In the glove box, a J. Young tube was charged with a 0.7 mL benzene-d_6 containing 0.0020 g (0.0030 mmol) of **2** and placed into a liquid N_2 jacketed cold well. While the catalyst solution was frozen, 0.0371 mL (0.299 mmol) of $PhSiD_3$ and 0.0423 mL (0.299 mmol) of diisopropyl ketone was injected. Then 0.010 mL (0.092 mmol) of anisole was added as an internal standard. The tube was sealed under N_2 and quickly transferred into a dewar filled with liquid N_2. The mixture was warmed to room temperature and ^1H NMR data was collected every 30 s. Percent conversion was determined by integrating the reactant and product peaks with respect to unchanged anisole. This experiment was repeated two more times to obtain a standard deviation.

Hydrosilylation of diisopropyl ketone in the presence of 20 equiv. PPh_3: In glove box a J. Young tube was charged with a benzene-d_6 solution (0.7 mL) containing 0.0020 g of **1** and 0.016

g (0.060 mmol) of triphenylphosphine. The tube was then placed into a liquid N_2 jacketed cold well to freeze the catalyst solution. While the solution was frozen, 0.0369 mL (0.299 mmol) of $PhSiH_3$ was added followed by 0.0424 mL (0.299 mmol) of diisopropyl ketone. Finally, 10 μL of anisole was added as an internal standard. The tube was sealed under N_2 atmosphere and promptly transferred into a dewar filled with liquid N_2. After warming the reaction mixture in the tube to room temperature, a ^{1}H NMR experiment was started quickly and data was collected at 1 min intervals. The substrate consumption rate was calculated by integrating the starting material and product with respect to the known concentration of anisole.

Hydrosilylation of diisopropyl ketone in the presence of 40 equiv. PPh_3: In glove box, a J. Young tube was charged with a benzene-d_6 solution (0.7 mL) containing 0.0020 g of **1** and 0.0314 g (0.120 mmol) of triphenylphosphine. The tube was then placed into a liquid N_2 jacketed cold well to freeze the catalyst solution. While the solution was frozen, 0.0369 mL (0.299 mmol) of $PhSiH_3$ was added followed by 0.0424 mL (0.299 mmol) of diisopropyl ketone. Finally, 10 μL of anisole was added as an internal standard. The tube was sealed under N_2 atmosphere and promptly transferred into a dewar filled with liquid N_2. After warming the reaction mixture in the tube to room temperature, a ^{1}H NMR experiment was started quickly and data was collected at 1 min intervals. The substrate consumption rate was calculated by integrating the starting material and product with respect to the known concentration of anisole.

Hydrosilylation of diisopropyl ketone in the presence of 80 equiv. PPh_3: In glove box, a J. Young tube was charged with a benzene-d_6 solution (0.7 mL) containing 0.0020 g of **1** and 0.0628 g (0.239 mmol) of triphenylphosphine. The tube was then placed into a liquid N_2 jacketed cold well to freeze the catalyst solution. While the solution was frozen, 0.0369 mL (0.299 mmol) of $PhSiH_3$ was injected followed by 0.0424 mL (0.299 mmol) of diisopropyl ketone. Finally, 10 μL of anisole was added as an internal standard. The tube was sealed under N_2 atmosphere and promptly transferred into a dewar filled with liquid N_2. After warming the reaction mixture in the tube to room temperature, a ^{1}H NMR experiment was started quickly and NMR data was collected at 1 min intervals. The substrate consumption rate was calculated by integrating the starting material and product with respect to the known concentration of anisole.

Kinetic profiles for 1-catalyzed diisopropyl ketone hydrosilylation with varying concentrations of ketone (average of three runs):

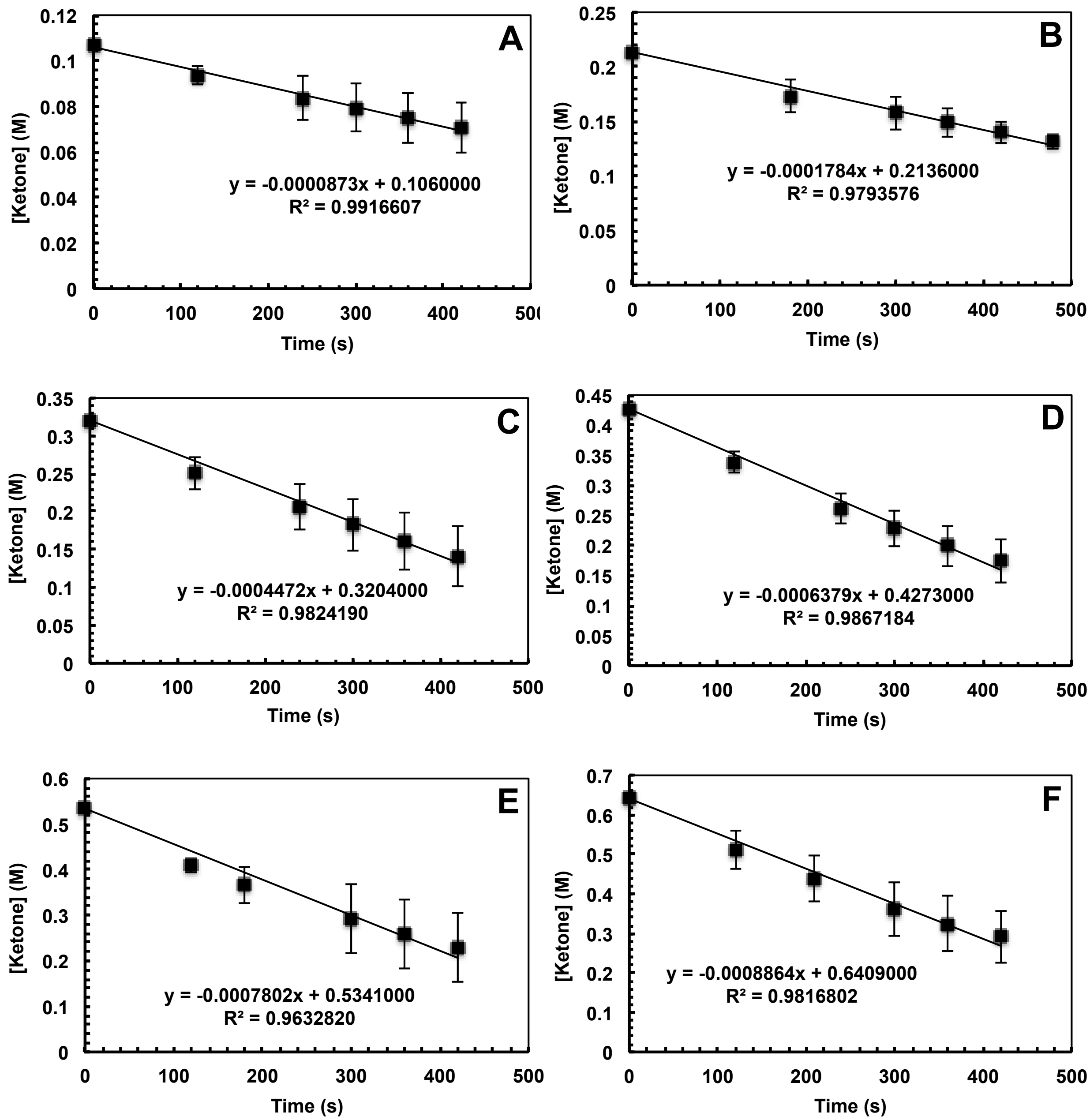


Figure S49. Concentration profiles for 1 mol% **1**-catalyzed diisopropyl ketone hydrosilylation with 0.1069 M (**A**), 0.2136 M (**B**), 0.3204 M (**C**), 0.4273 M (**D**), 0.5341 M (**E**), and 0.6409 M (**F**) ketone.

Kinetic profiles for 1-catalyzed diisopropyl ketone hydrosilylation with varying concentrations of silane (average of three runs):

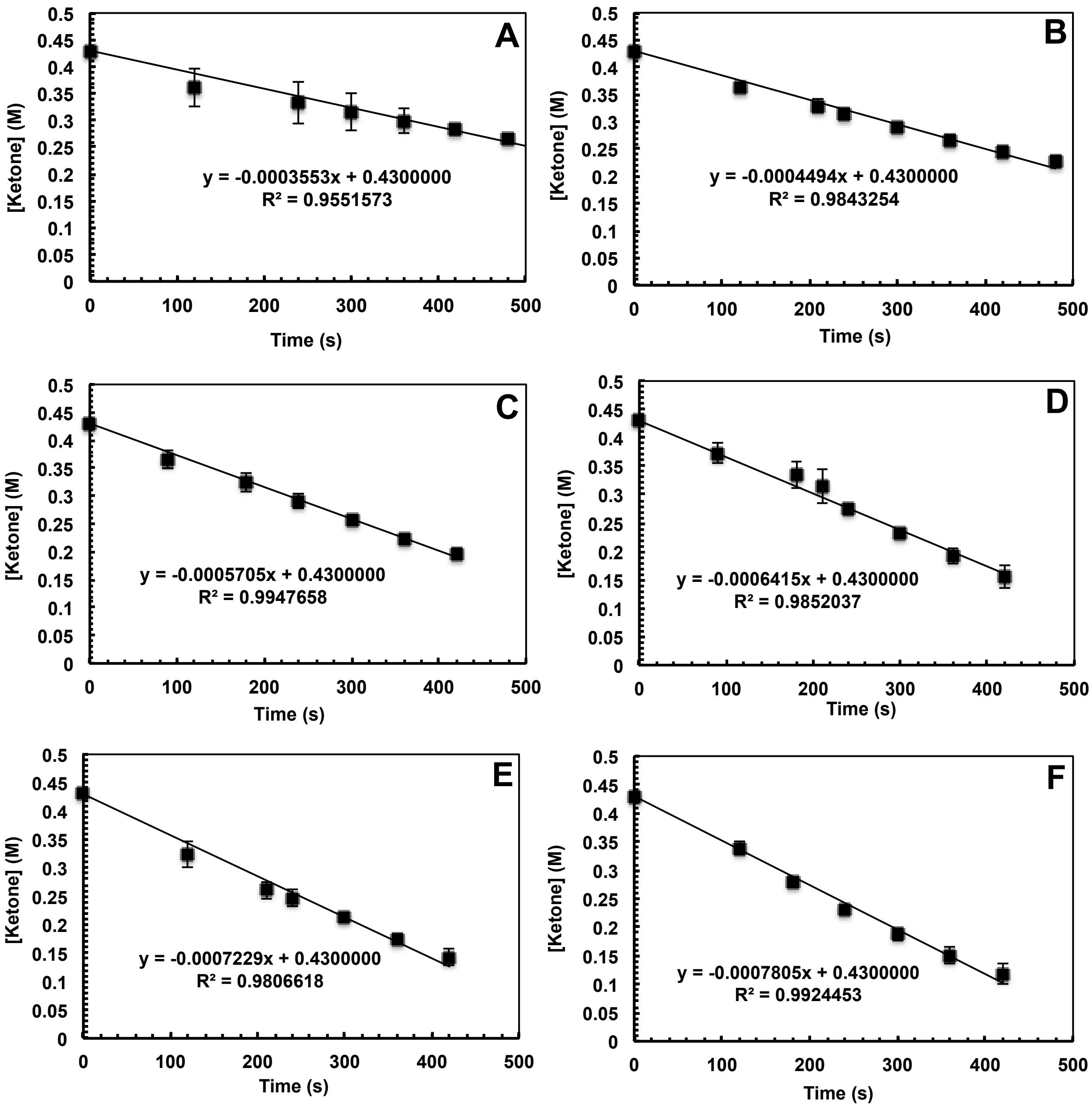


Figure S50. Concentration profiles for 1 mol% **1-**catalyzed diisopropyl ketone hydrosilylation with 0.2136 M (**A**), 0.3204 M (**B**), 0.4273 M (**C**), 0.5341 M (**D**), 0.641 M (**E**), and 0.8546 M (**F**) $PhSiH_3$.

Kinetic profiles for 1-catalyzed diisopropyl ketone hydrosilylation with varying concentrations of 1 (average of three runs):

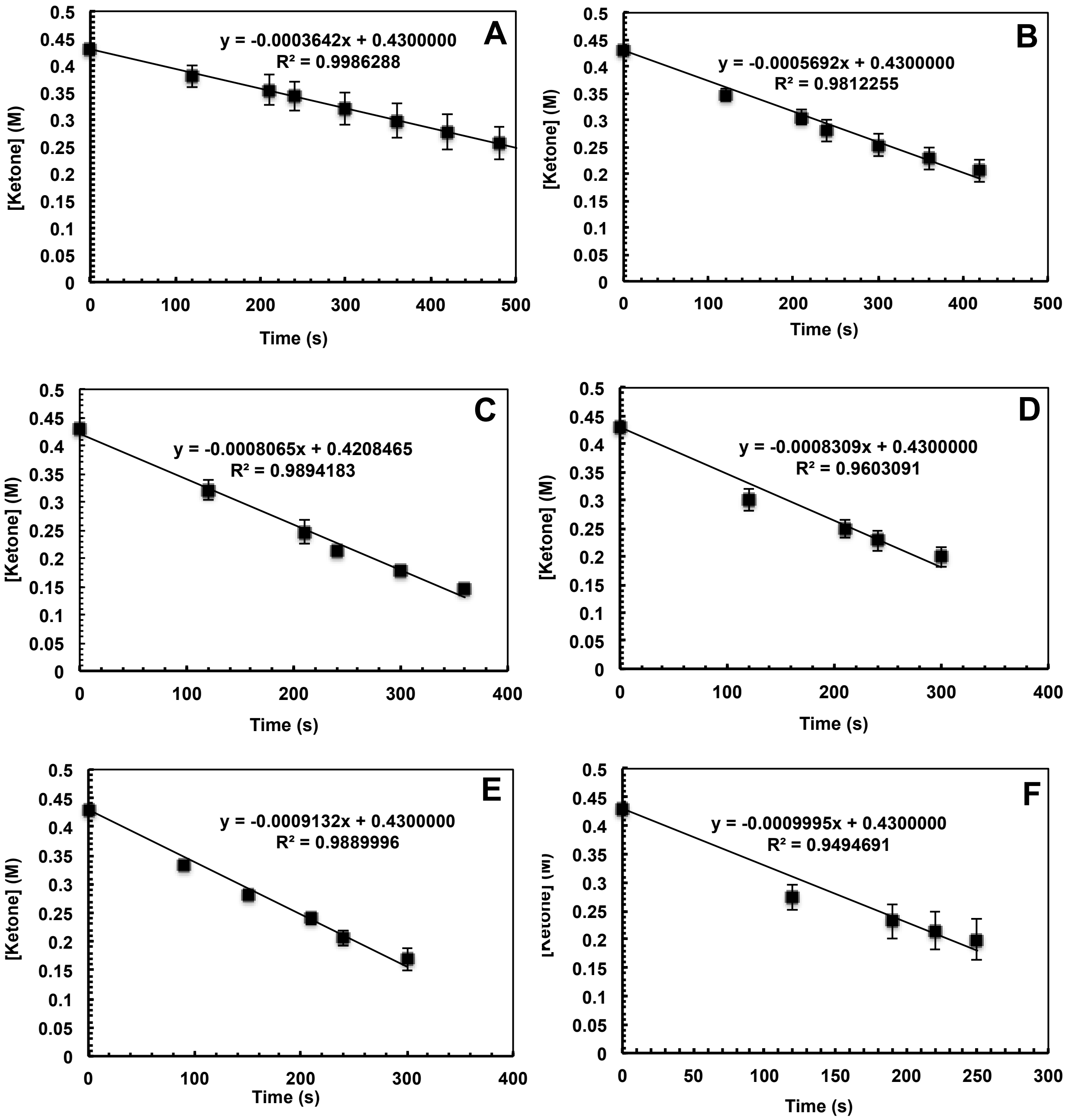


Figure S51. Concentration profiles for diisopropyl ketone hydrosilylation using 0.002136 M (**A**), 0.004273 M (**B**), 0.006409 M (**C**), 0.008546 M (**D**), 0.01068 M (**E**), and 0.01282 M (**F**) **1**.

Kinetic profiles for 1-catalyzed isopropyl formate dihydrosilylation with varying concentrations of isopropyl formate (average of two runs):

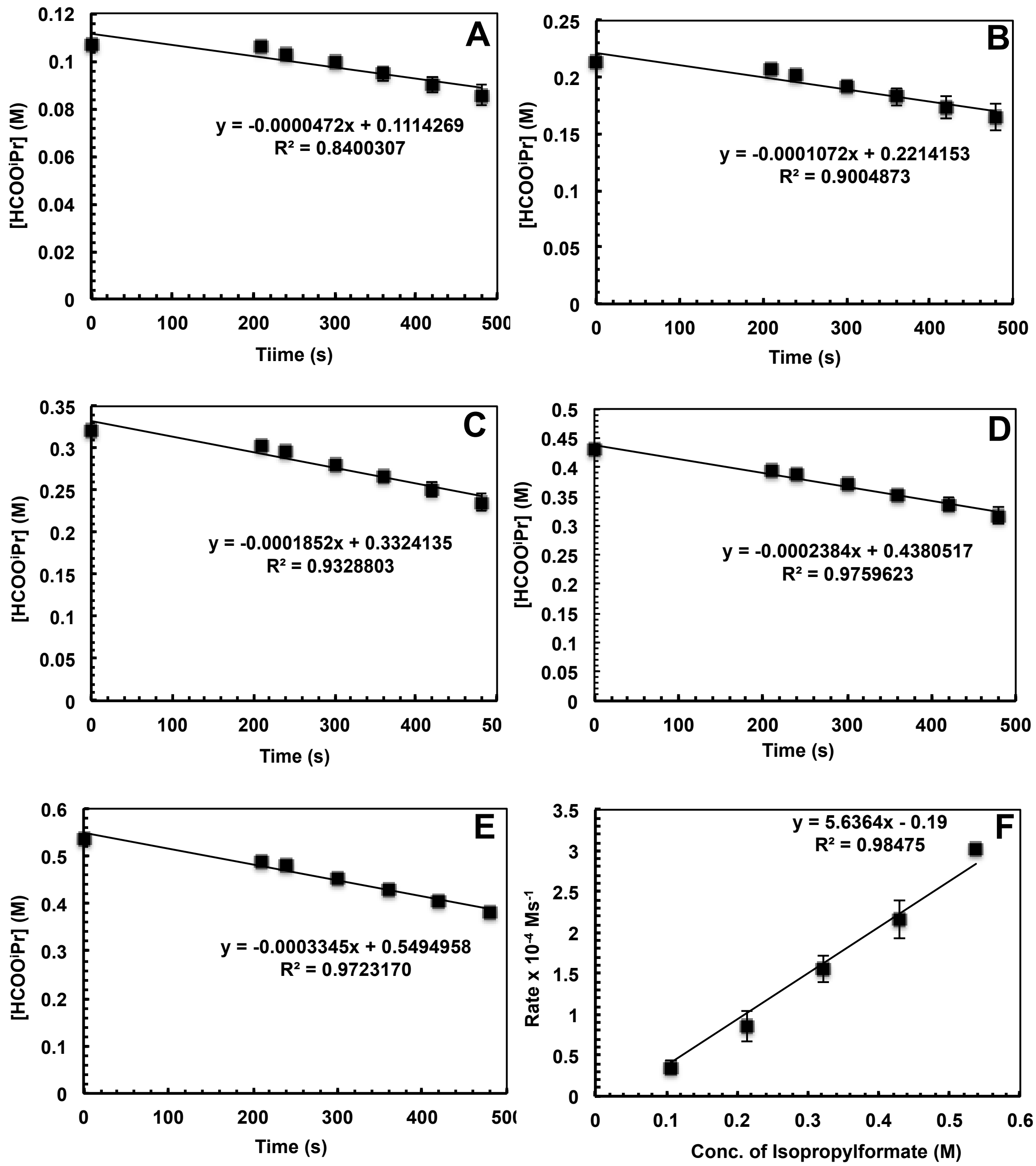


Figure S52. Concentration profiles for 1 mol% **1-**catalyzed isopropyl formate dihydrosilylation with 0.107 M (**A**), 0.2137 M (**B**), 0.3217 M (**C**), 0.43 M (**D**), and 0.5374 M (**E**) isopropyl formate. Rate dependence on [HCOO^{i}Pr] (**F**).

Kinetic profiles for 1-catalyzed isopropyl formate dihydrosilylation with varying concentrations of $PhSiH_3$ (average of two runs):

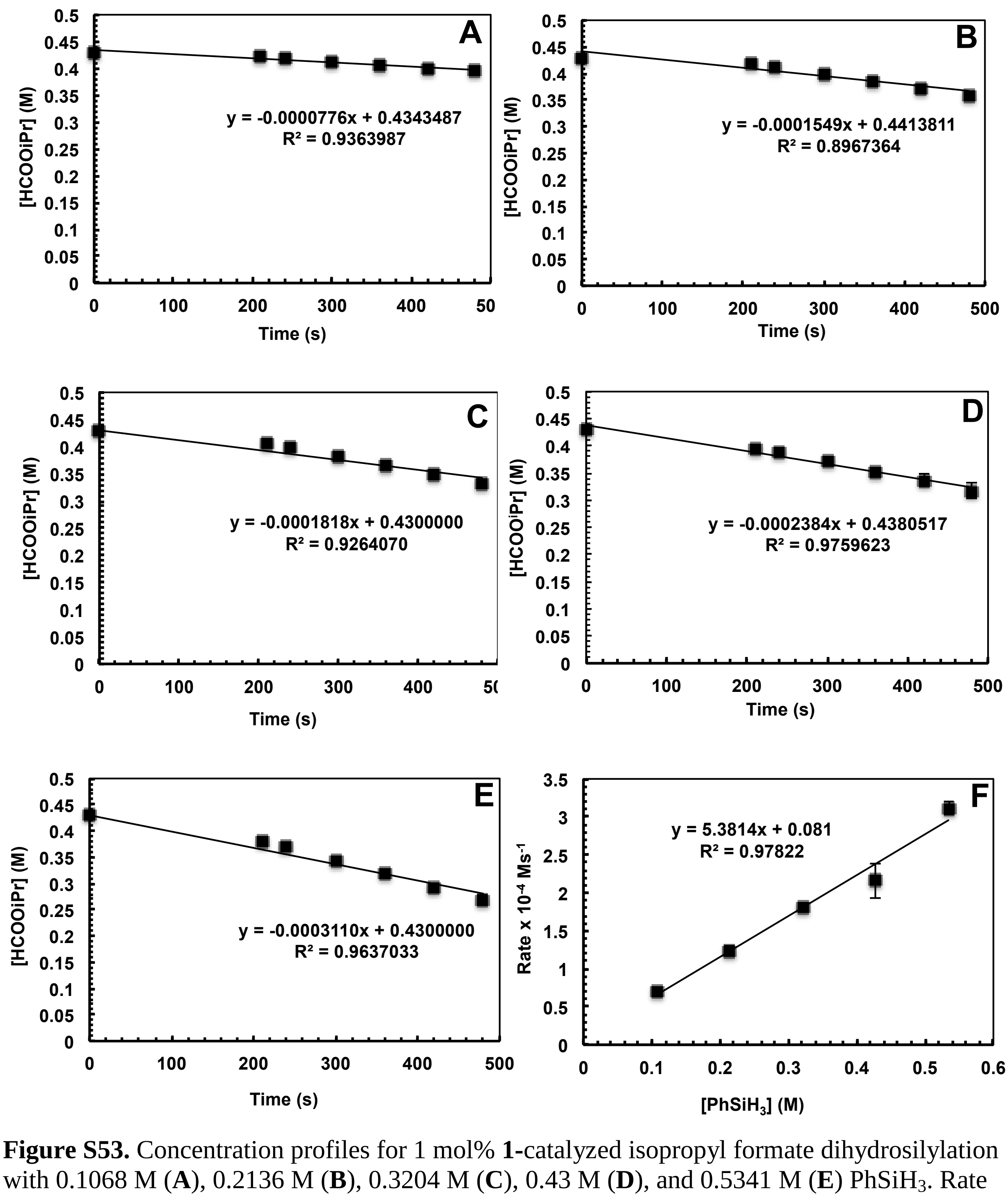


Figure S53. Concentration profiles for 1 mol% **1**-catalyzed isopropyl formate dihydrosilylation with 0.1068 M (**A**), 0.2136 M (**B**), 0.3204 M (**C**), 0.43 M (**D**), and 0.5341 M (**E**) $PhSiH_3$. Rate dependence on [$PhSiH_3$] (**F**).

Kinetic profiles for isopropyl formate dihydrosilylation with varying concentrations of 1 (average of two runs):

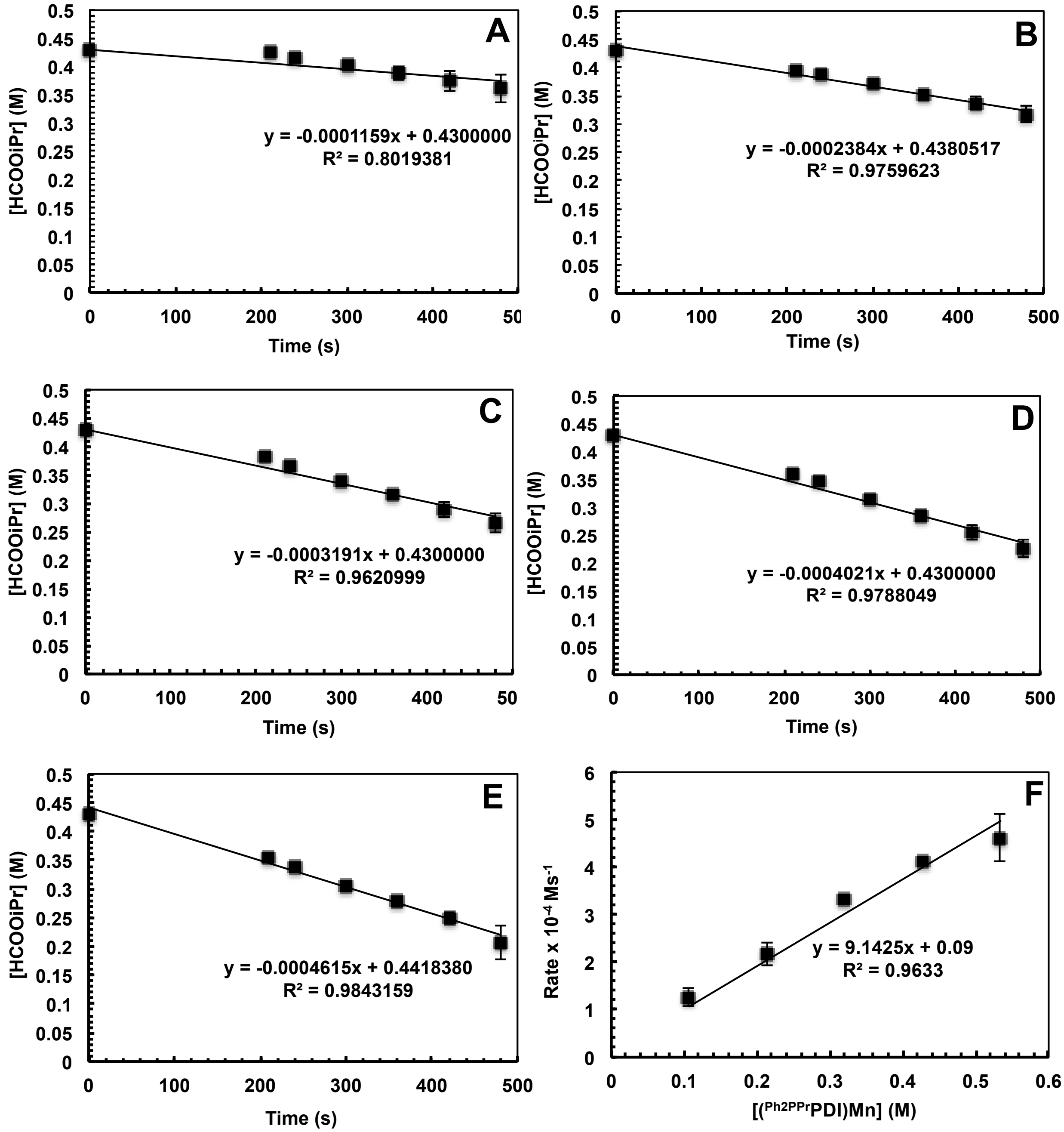
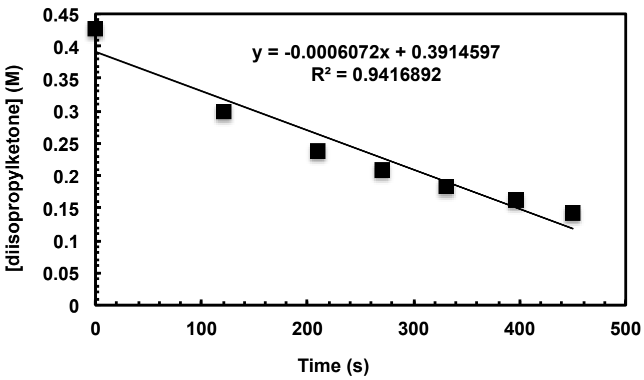
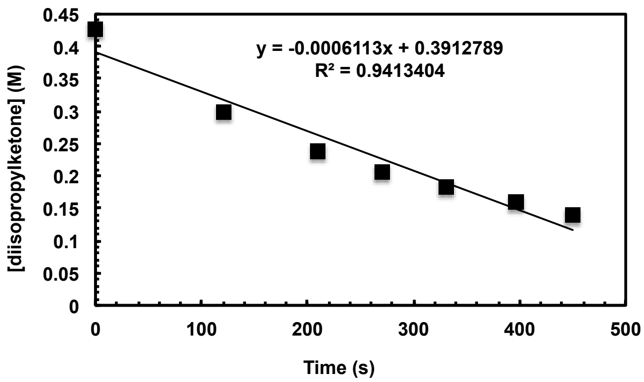


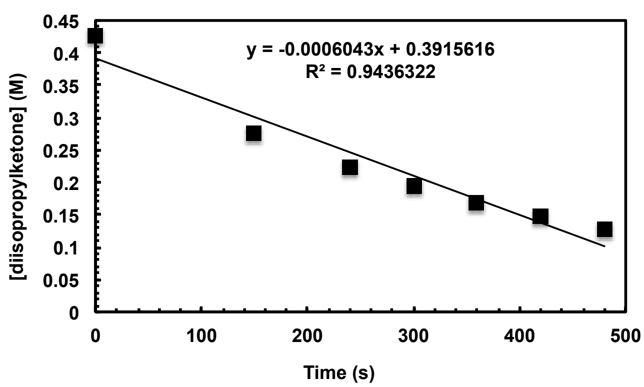
Figure S54. Concentration profiles for **1** catalyzed isopropyl formate dihydrosilylation with 0.002136 M (**A**), 0.004273 M (**B**), 0.006409 M (**C**), 0.008546 M (**D**), and 0.01068 M (**E**) **1**. Rate dependence on [**1**] (**F**).



Rate for 20 equiv. $PPh_3 = 6.07 \times 10^{-4}$ Ms^{-1}.



Rate for 40 equiv. $PPh_3 = 6.11 \times 10^{-4}$ Ms^{-1}.



Rate for 80 equiv. $PPh_3 = 6.04 \times 10^{-4}$ Ms^{-1}.

Figure S55. Influence of exogenous PPh_3 on the rate of diisopropyl ketone hydrosilylation using 1 mol% **1**.

Kinetic profiles for 2-catalyzed diisopropyl ketone hydrosilylation with varying concentrations of ketone (average of three runs):

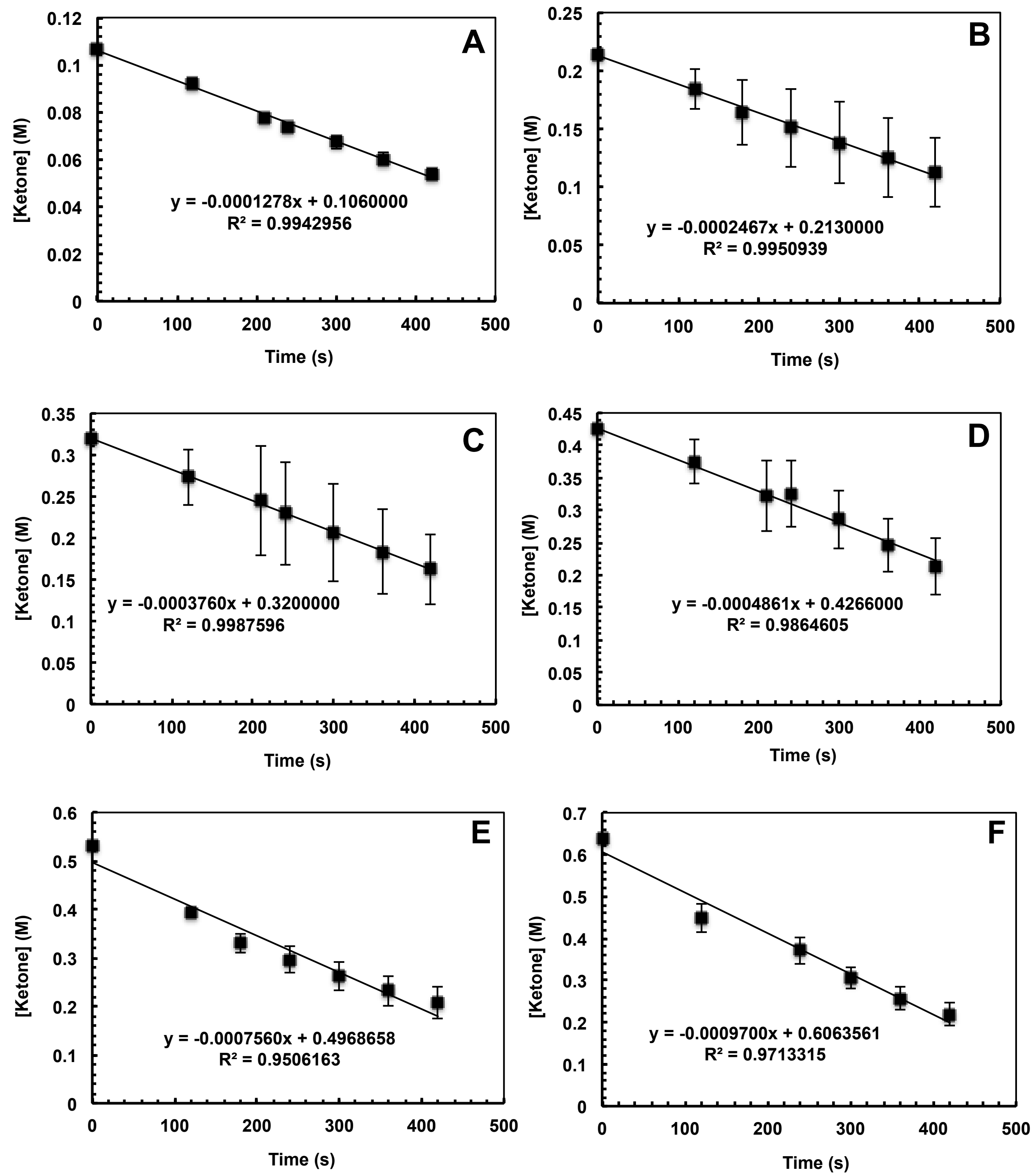


Figure S56. Concentration profiles for 1 mol% **2**-catalyzed diisopropyl ketone hydrosilylation with 0.1066 M (**A**), 0.2133 M (**B**), 0.3200 M (**C**), 0.4266 M (**D**), 0.5333 M (**E**), and 0.6399 M (**F**) diisopropyl ketone.

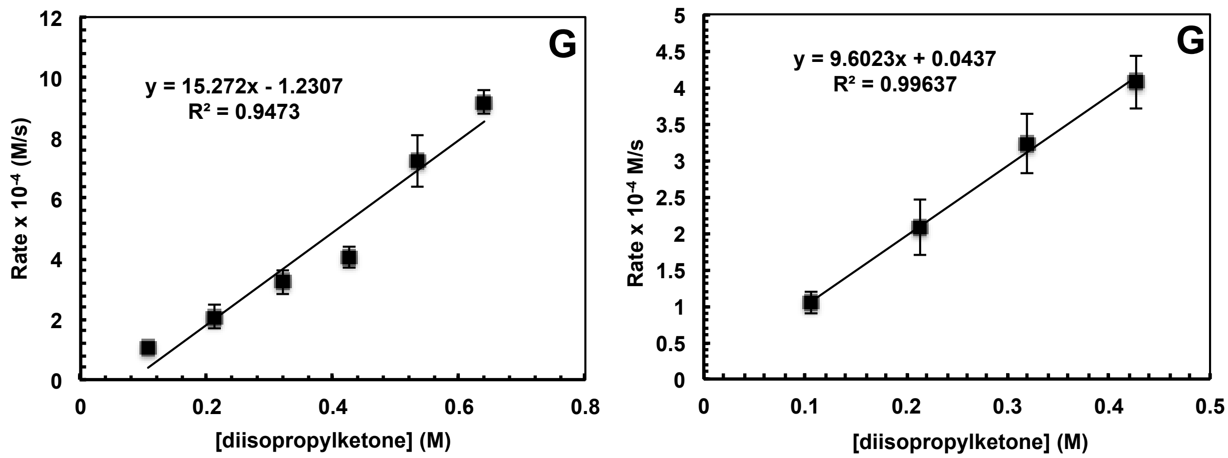


Figure S57. Rate dependence of **2-**catalyzed diisopropyl ketone hydrosilylation against varying concentrations of ketone (left: 6 concentrations; right: first 4 concentrations).

Kinetic profiles for 2-catalyzed diisopropyl ketone hydrosilylation with varying concentrations of silane (average of three runs):

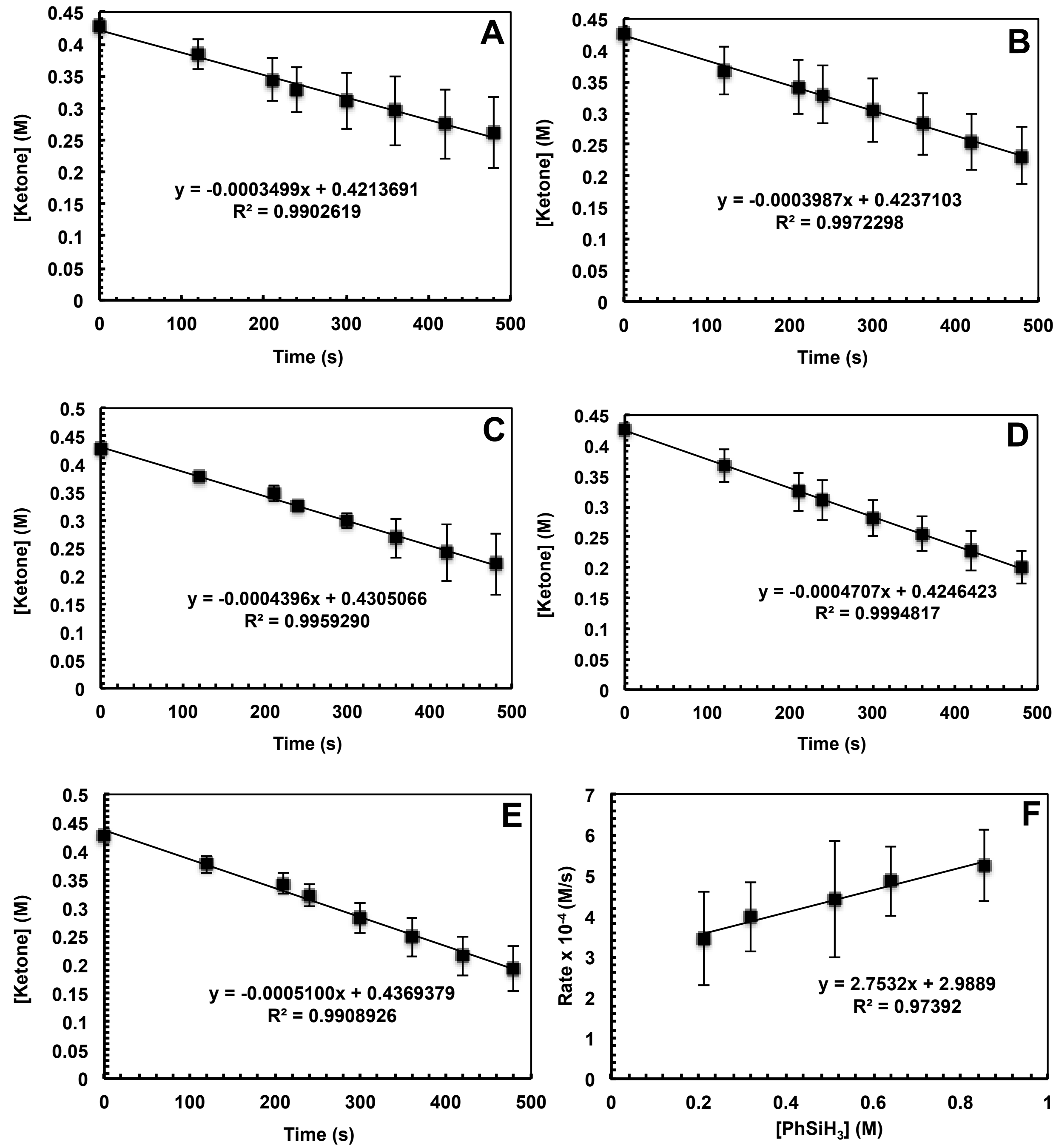


Figure S58. Concentration profiles for 1 mol% **2-**catalyzed diisopropyl ketone hydrosilylation with 0.2133 M (**A**), 0.3199 M (**B**), 0.5119 M (**C**), 0.6399 M (**D**), and 0.8532 M (**E**) $PhSiH_3$. Rate dependence on the varying concentration of $PhSiH_3$ (**F**).

Kinetic profiles for diisopropyl ketone hydrosilylation with varying concentrations of 2 (average of three runs):

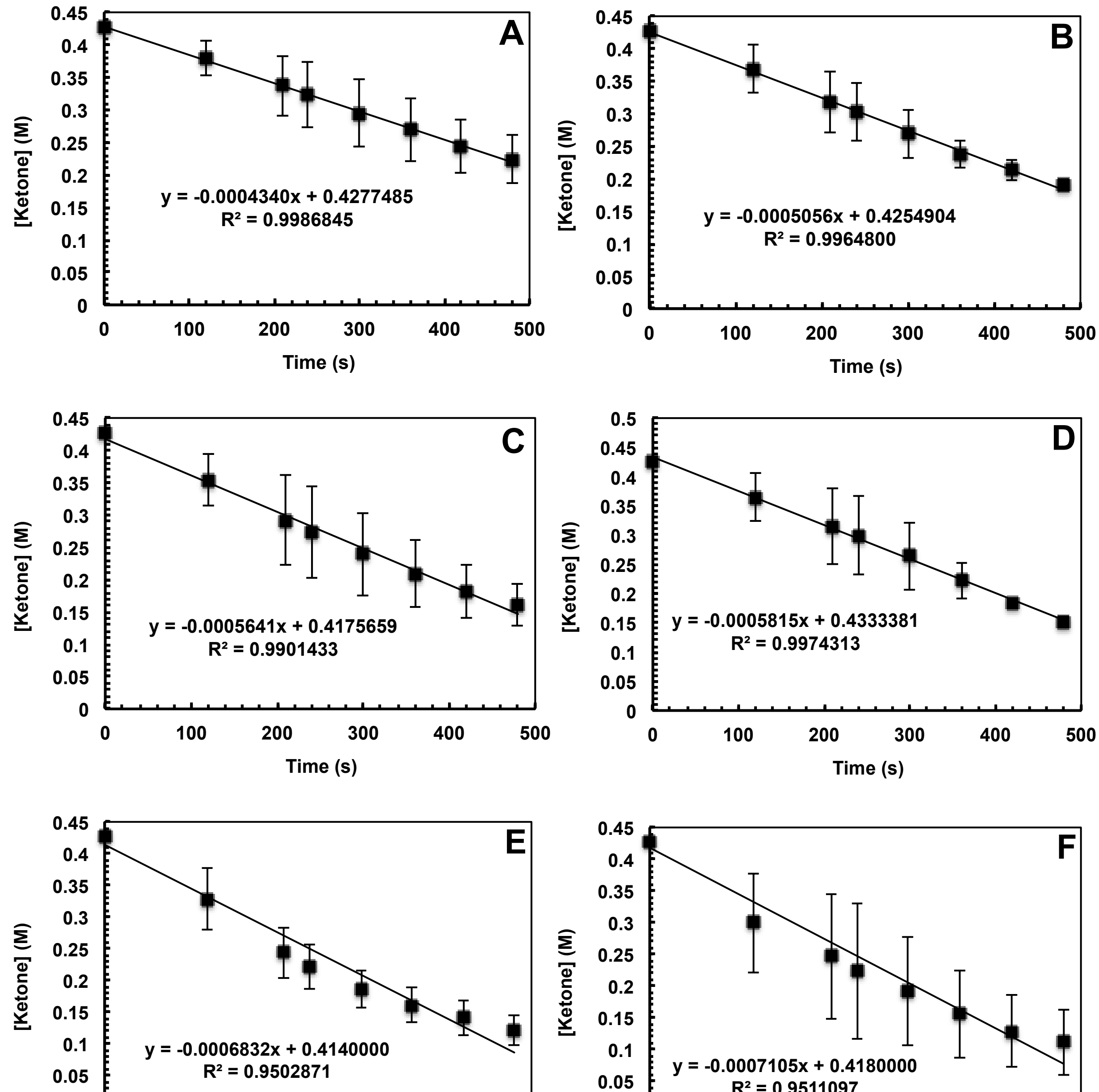


Figure S59. Concentration profiles for **2-**catalyzed diisopropyl ketone hydrosilylation with 0.002133 M (**A**), 0.004266 M (**B**), 0.006399 M (**C**), 0.008533 M (**D**), and 0.01067 M (**E**) and 0.01279 M (**F**) **2**.

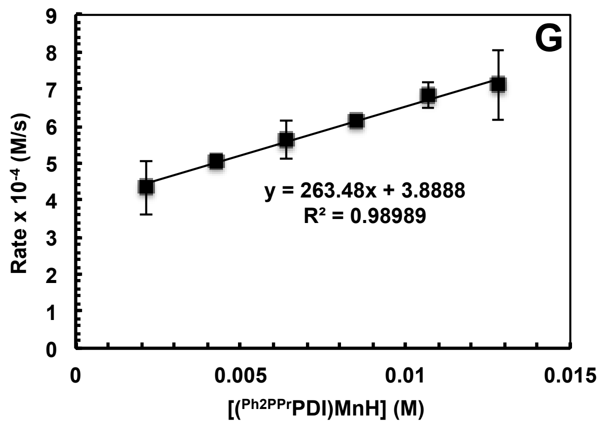


Figure S60. Rate dependence on diisopropyl ketone hydrosilylation with varying concentrations of **2** (**G**).

COMPUTATIONAL DATA

Table S4. Bond distances (Å) and angles (°) for **1** in both experimental and computational structures.

	Crystal 1	**Doublet 1**	**Quartet 1**	**Sextet 1**	**Octet 1**
Mn(1)-N(1)	1.944(2)	1.993	1.957	2.162	2.153
Mn(1)-N(2)	1.887(2)	1.876	1.901	2.014	2.070
Mn(1)-N(3)	1.949(2)	1.923	1.955	2.205	2.146
Mn(1)-P(1)	2.2697(8)	2.242	2.399	2.558	2.602
Mn(1)-P(2)	2.2634(8)	2.260	2.405	2.577	2.599
Mn(1)-H(1M)	-	-	-	-	-
Mn(1)-O(1)	-	-	-	-	-
Mn(1)-N(2A)	-	-	-	-	-
N(1)-C(2)	1.354(3)	1.352	1.368	1.349	1.365
N(3)-C(8)	1.355(3)	1.362	1.367	1.351	1.365
C(2)-C(3)	1.416(4)	1.430	1.421	1.441	1.444
C(7)-C(8)	1.414(3)	1.423	1.420	1.442	1.443
N(1)-Mn(1)-N(3)	157.54(9)	158.7	158.5	152.0	153.7
P(1)-Mn(1)-P(2)	105.93(3)	110.7	124.6	125.1	118.2
P(1)-Mn(1)-N(2A)	-	-	-	-	-
N(2)-Mn(1)-H(1M)	-	-	-	-	-
N(2)-Mn(1)-O(1)	-	-	-	-	-

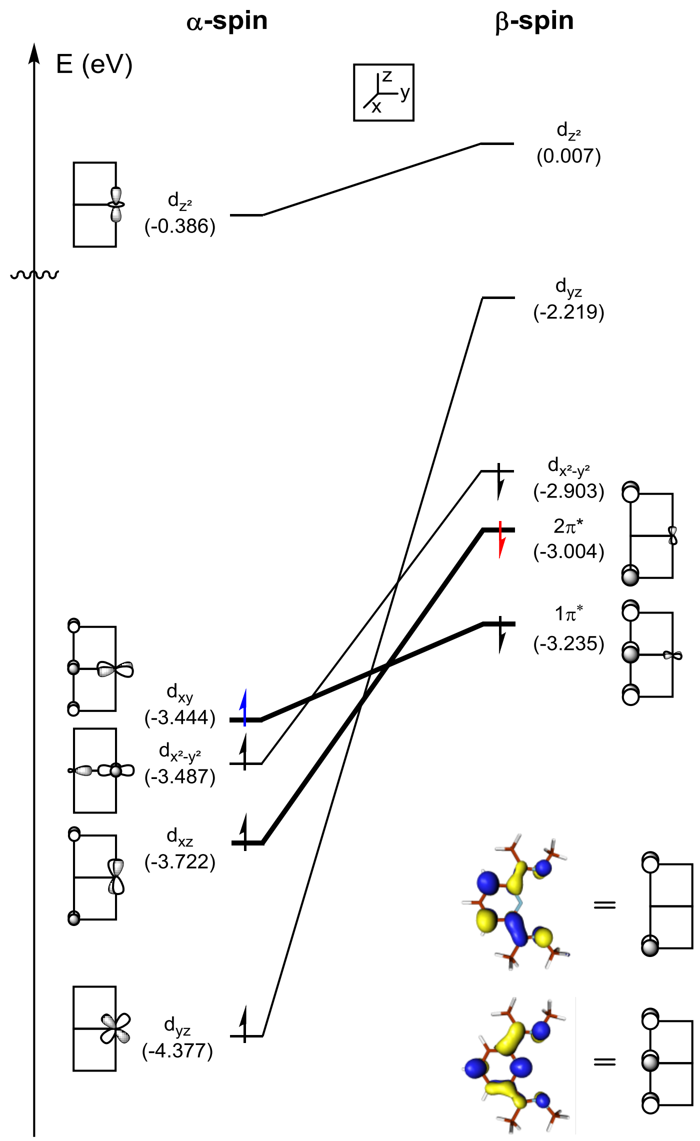


Figure S61. Calculated frontier MOs for the antiferromagnetic coupling of **1**.

Table S5. Bond distances (Å) and angles (°) for **2** in both experimental and computational structures.

	Crystal 2	**Singlet 2**	**Triplet 2**	**Quintet 2**	**Septet 2**
Mn(1)-N(1)	1.945(2) [1.951(2)]	1.953	1.967	1.982	2.267
Mn(1)-N(2)	1.860(2) [1.862(2)]	1.852	1.924	1.926	2.193
Mn(1)-N(3)	1.947(2) [1.948(2)]	1.948	1.968	1.982	2.270
Mn(1)-P(1)	2.2067(8) [2.2117(8)]	2.202	2.272	2.308	2.792
Mn(1)-P(2)	2.2158(7) [2.2064(7)]	2.202	2.268	2.315	2.774
Mn(1)-H(1M)	1.57(3) [1.51(3)]	1.615	1.625	1.6190	1.754
Mn(1)-O(1)	-	-	-	-	-
Mn(1)-N(2A)	-	-	-	-	-
N(1)-C(2)	1.351(3) [1.343(3)]	1.351	1.357	1.387	1.325
N(3)-C(8)	1.342(3) [1.346(3)]	1.352	1.357	1.387	1.325
C(2)-C(3)	1.424(4) [1.418(4)]	1.433	1.430	1.414	1.466
C(7)-C(8)	1.418(3) [1.419(4)]	1.433	1.429	1.415	1.466
N(1)-Mn(1)-N(3)	158.81(9) [158.64(9)]	160.1	157.2	160.2	143.1
P(1)-Mn(1)-P(2)	123.85(3) [128.30(3)]	128.3	148.5	153.1	167.9
P(1)-Mn(1)-N(2A)	-	-	-	-	-
N(2)-Mn(1)-H(1M)	175.0(10) [172.9(10)]	178.3	179.5	179.7	179.5
N(2)-Mn(1)-O(1)	-	-	-	-	-

Table S6. Computed energy components of the optimized geometry **1**.

	E(SCF) **eV** cc-pVTZ(-f)/LACVP**	**ZPE** **kcal/mol** 6-31G**/LACVP**	**S(gas)** **cal/mol** 6-31**/LACVP**	**G(solv)** **kcal/mol** 6-31G**/LACVP**	**∆G** **kcal/mol**
Doublet 1	-66938.810	433.24	251.461	-4.83	0.00
Quartet 1	-66938.111	431.10	262.322	-5.07	10.50
Sextet 1	-66937.516	430.02	270.320	-5.18	20.65
Octet 1	-66937.072	429.78	271.762	-5.42	31.62

Table S7. Computed energy components of the optimized geometry **2**.

	E(SCF) eV cc-pVTZ(-f)/LACVP**	ZPE kcal/mol 6-31G**/LACVP**	S(gas) cal/mol 6-31**/LACVP**	G(solv) kcal/mol 6-31G**/LACVP**	ΔG kcal/mol
Singlet 2	-66955.008	438.40	248.980	-4.74	0.00
Triplet 2	-66954.402	436.55	256.239	-4.72	9.98
Quintet 2	-66953.536	435.53	261.543	-4.90	27.17
Septet 2	-66952.903	433.70	275.903	-6.10	34.46

Table S8. Cartesian coordinates of the optimized structures of each spin state for **1** and **2**.

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Doublet 1

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Mn	0.035561603	-0.057160721	-0.089553751
P	-0.320596474	1.681199811	-1.459572190
P	0.239540199	-1.975225817	-1.266756212
N	-1.933860770	-0.066028092	0.216851716
N	-0.059782427	0.075440601	1.779744015
N	1.912847538	-0.029911030	0.326047833
C	-3.809113509	0.137286841	1.902174660
H	-4.349114909	0.952794888	1.388726242
H	-3.894313184	0.322509650	2.982747948
H	-4.356296351	-0.799500051	1.687833107
C	-2.360150673	0.064769752	1.492983019
C	-1.288358167	0.131897572	2.437545641
C	-1.339096708	0.237248291	3.837978073
H	-2.302722123	0.285480100	4.352424865
C	-0.140084592	0.275525899	4.571573298
H	-0.170954561	0.354941598	5.662282467
C	1.094934727	0.211374987	3.911388071
H	2.025864923	0.240478825	4.484624376
C	1.139848058	0.111391950	2.506512159
C	2.265784495	0.031951609	1.639789082
C	3.688065021	0.012405738	2.134458530
H	4.237014942	-0.890790490	1.810092965
H	3.709471405	0.021901501	3.234211038
H	4.272554201	0.887520574	1.792905209
C	-2.943134979	-0.085154011	-0.846590266
H	-3.917135512	-0.432884849	-0.458829206
H	-2.624211222	-0.809133150	-1.613674897
C	-3.128786418	1.298848899	-1.504582009
H	-3.288456243	2.060544477	-0.718778457
H	-4.049266738	1.274430309	-2.117385631
C	-1.946976198	1.699436319	-2.398511093
H	-2.108085410	2.695866625	-2.845859734
H	-1.853127454	0.969456532	-3.221378802
C	0.903413277	2.033757069	-2.807031387
C	2.015127197	2.869347365	-2.563770392
H	2.094397411	3.397643753	-1.608294386
C	3.014412979	3.033985327	-3.533421521
H	3.867997098	3.687275825	-3.323787839
C	2.923070544	2.369510582	-4.764387978
H	3.703403473	2.499537410	-5.520769057
C	1.824556591	1.534309604	-5.018182442
H	1.741610637	1.012982464	-5.977706532
C	0.829130467	1.362289074	-4.046770734
H	-0.012047087	0.693960725	-4.257311108
C	-0.412565321	3.337550306	-0.604899565
C	-0.279854997	3.380818050	0.794713221
H	-0.102785221	2.443404602	1.333796573
C	-0.366449807	4.601294702	1.480869959
H	-0.261008032	4.618762468	2.570824896

C	-0.583301215	5.791308011	0.774191195
H	-0.646975418	6.744894854	1.308604185
C	-0.714496966	5.759469304	-0.623218740
H	-0.877397524	6.688273081	-1.180245124
C	-0.631863902	4.540835313	-1.308576508
H	-0.716881650	4.528952148	-2.401104851
C	2.963208714	-0.182128286	-0.686953466
H	3.944220925	0.117520672	-0.278880470
H	2.744093964	0.504932266	-1.523207975
C	3.062894580	-1.623022427	-1.230135265
H	4.004404305	-1.709798785	-1.804528603
H	3.138032559	-2.329378508	-0.382963549
C	1.897007557	-2.019515235	-2.149398109
H	2.050900745	-3.031039676	-2.564884926
H	1.843960487	-1.309242070	-2.993577900
C	-0.912974130	-2.639453006	-2.563476090
C	-0.754784045	-2.346376367	-3.934810042
H	0.125193388	-1.794407160	-4.279947963
C	-1.707671642	-2.764231743	-4.874104330
H	-1.557419867	-2.537980216	-5.935070472
C	-2.844181037	-3.475025877	-4.461446489
H	-3.588811208	-3.798845327	-5.195212563
C	-3.016404234	-3.770194082	-3.101182615
H	-3.897177104	-4.329016290	-2.767557427
C	-2.061590883	-3.358731374	-2.162611282
H	-2.199329209	-3.607313058	-1.104786135
C	0.387740059	-3.481554805	-0.173352762
C	0.624106105	-4.766886588	-0.704923168
H	0.679857749	-4.907892587	-1.790258446
C	0.764088037	-5.871922035	0.144291772
H	0.946895893	-6.865323847	-0.278958332
C	0.662626351	-5.708031890	1.535036114
H	0.767643752	-6.573506301	2.197683462
C	0.422437681	-4.435904632	2.070835721
H	0.337151212	-4.301613456	3.154357650
C	0.288997593	-3.327005233	1.221219350
H	0.105194897	-2.325645337	1.627094049

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Quartet 1

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Mn	-0.025401756	-0.108496252	-0.316664294
P	-0.172641503	1.935111139	-1.564595410
P	0.160956046	-2.296196336	-1.298225754
N	-1.945528230	0.065972687	0.016292831
N	-0.040055430	0.080815293	1.574695644
N	1.885600344	-0.230037381	0.077200000
C	-3.793123243	0.397301047	1.714680520
H	-4.263835220	1.274199380	1.231420503
H	-3.870803319	0.548923169	2.801700070
H	-4.419219204	-0.481060299	1.464633558
C	-2.354429150	0.220411485	1.312267963
C	-1.273674311	0.197340588	2.234185463
C	-1.283415853	0.287638784	3.637875287
H	-2.232841383	0.382578452	4.173608536
C	-0.070854942	0.243401310	4.351252353
H	-0.082488647	0.312915561	5.442962579
C	1.155729242	0.098657345	3.676173690
H	2.091758911	0.056522730	4.241022583
C	1.175169732	0.007375248	2.272981024
C	2.271196316	-0.170595689	1.387608066
C	3.702915460	-0.270091370	1.837654254
H	4.195556512	-1.194675576	1.482948915
H	3.758709231	-0.276942040	2.936442705
H	4.322488750	0.578392279	1.487909541
C	-2.913436986	0.121438590	-1.076622692
H	-3.923714159	-0.150110373	-0.719029243
H	-2.631885849	-0.639732321	-1.829675123
C	-2.985086732	1.504586920	-1.759497102
H	-3.160118383	2.280558835	-0.991822069
H	-3.863439089	1.515524663	-2.432183302
C	-1.740472126	1.862120024	-2.590494684
H	-1.875803152	2.831549966	-3.103162887
H	-1.587720464	1.091034556	-3.367621168
C	1.094253248	2.542449939	-2.760314372

C	2.244681013	3.182669038	-2.240391479
H	2.302927601	3.400114067	-1.168289839
C	3.298040266	3.555123211	-3.080982670
H	4.174509086	4.057999261	-2.658844789
C	3.232733524	3.289178261	-4.458871104
H	4.058145982	3.579239925	-5.116067687
C	2.101132813	2.649566837	-4.985137332
H	2.037671865	2.443825659	-6.058840248
C	1.042207793	2.275534639	-4.146191188
H	0.167895056	1.782245267	-4.582127820
C	-0.444520966	3.441508424	-0.526749998
C	-0.455984387	3.327907485	0.875894534
H	-0.290635300	2.345629511	1.329312877
C	-0.665912014	4.463343436	1.672386762
H	-0.669923579	4.362492534	2.762691007
C	-0.867688519	5.715664411	1.077279347
H	-1.031587039	6.600896113	1.700749667
C	-0.854801918	5.835927907	-0.322018546
H	-1.004718208	6.814419318	-0.790219822
C	-0.643117992	4.706532481	-1.121242824
H	-0.610627754	4.810651816	-2.211324617
C	2.879059624	-0.423903911	-0.975968242
H	3.877168552	-0.090324883	-0.638471402
H	2.606410088	0.220866611	-1.834021676
C	2.979320727	-1.888200324	-1.454870490
H	3.878828050	-1.985546021	-2.091673563
H	3.133059389	-2.546768299	-0.580571558
C	1.764399109	-2.370017979	-2.266335767
H	1.916167310	-3.404485963	-2.623148456
H	1.640719041	-1.723594781	-3.154561618
C	-1.054568180	-3.100745638	-2.430525579
C	-0.929261633	-3.084144966	-3.837296461
H	-0.031129970	-2.671594061	-4.307402932
C	-1.944810524	-3.605357969	-4.651170989
H	-1.822756499	-3.591702052	-5.739471403
C	-3.105817532	-4.148037354	-4.081191713
H	-3.896039589	-4.555168337	-4.719166504
C	-3.243602471	-4.166230804	-2.682860062
H	-4.142554492	-4.591748947	-2.224449042
C	-2.234038612	-3.645385965	-1.866891306
H	-2.349375031	-3.670639602	-0.777699254
C	0.400384557	-3.609445598	-0.018517330
C	0.650722264	-4.948704967	-0.388063654
H	0.670029587	-5.229878704	-1.446664766
C	0.850559024	-5.925915755	0.594377125
H	1.041196252	-6.963208733	0.299868674
C	0.800403054	-5.578625221	1.954191472
H	0.956700486	-6.344867066	2.720672098
C	0.546309128	-4.252143728	2.326613210
H	0.501366379	-3.973189940	3.384386379
C	0.347301739	-3.269061107	1.345976940
H	0.144352419	-2.231547615	1.628201218

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Sextet 1

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Mn	-0.052423717	-0.088061859	-0.303250757
P	-0.356280424	2.088288888	-1.611757459
P	0.341932718	-2.406422991	-1.356752240
N	-2.131464610	0.253431408	0.180361936
N	-0.063691299	0.082511919	1.702978600
N	2.061732765	-0.344035632	0.267178646
C	-3.792912327	0.733777266	2.003773568
H	-4.225460806	1.628043568	1.518766433
H	-3.792838295	0.921790111	3.086056888
H	-4.496419191	-0.100201353	1.816367380
C	-2.405835581	0.434235092	1.488561771
C	-1.271026968	0.301011435	2.366998418
C	-1.296576506	0.379913545	3.769914182
H	-2.238678843	0.556351947	4.296542631
C	-0.107317108	0.215312135	4.502097722
H	-0.120172550	0.271947557	5.594107501
C	1.101771357	-0.031064285	3.822951816
H	2.023976561	-0.158203075	4.397278871
C	1.125578619	-0.098753129	2.422799138

C	2.283581372	-0.346746515	1.599388819
C	3.648344638	-0.585242834	2.200833625
H	4.098631532	-1.525249908	1.832388072
H	3.606473997	-0.655148309	3.296177307
H	4.360771328	0.225310309	1.952881216
C	-3.189800760	0.381486649	-0.817082870
H	-4.191434512	0.178390193	-0.391000592
H	-3.019599265	-0.388689599	-1.596035371
C	-3.216986134	1.769733260	-1.494874772
H	-3.264988600	2.553353648	-0.717025343
H	-4.148315514	1.852118164	-2.087246238
C	-2.038728107	2.052758360	-2.445472704
H	-2.185958939	3.017525736	-2.962554453
H	-1.997722136	1.267443817	-3.221968320
C	0.758557841	2.650659883	-2.969382787
C	1.834738215	3.526462993	-2.706313976
H	1.936136006	3.976959296	-1.713737821
C	2.771102283	3.826351175	-3.703065964
H	3.596954060	4.509546716	-3.478595000
C	2.655111216	3.259838006	-4.981152511
H	3.388949492	3.495457125	-5.757941212
C	1.592342045	2.385320020	-5.253684191
H	1.489171492	1.938912889	-6.248398705
C	0.657095489	2.077717983	-4.257918184
H	-0.156840821	1.382727235	-4.490357860
C	-0.472305637	3.568064183	-0.512091852
C	-0.292419591	3.393837232	0.874172411
H	-0.078797197	2.389381267	1.261814424
C	-0.388298990	4.493681790	1.740521155
H	-0.243655189	4.344896427	2.815570875
C	-0.669311111	5.770758698	1.235389423
H	-0.746907700	6.626783925	1.913350333
C	-0.850675555	5.949813713	-0.146111377
H	-1.066863405	6.945874777	-0.546825647
C	-0.752482857	4.856997156	-1.016360276
H	-0.876662400	5.008181941	-2.094500625
C	3.156372553	-0.580113773	-0.664321975
H	4.144093132	-0.352349732	-0.219598464
H	3.032131862	0.111093909	-1.523037972
C	3.194705782	-2.027417007	-1.203793922
H	4.139357938	-2.165205259	-1.765085391
H	3.226102640	-2.732488746	-0.353214473
C	2.040407289	-2.409002977	-2.149955496
H	2.217691185	-3.413529520	-2.575341158
H	2.005869622	-1.693528402	-2.992617659
C	-0.715738818	-3.235873422	-2.625106134
C	-0.409828705	-3.232206816	-4.002692783
H	0.538477453	-2.814596330	-4.355956806
C	-1.306694761	-3.773933712	-4.935760537
H	-1.044784332	-3.771977211	-5.999063191
C	-2.525209575	-4.323377020	-4.513292967
H	-3.223133634	-4.746160347	-5.242302125
C	-2.842144186	-4.326416813	-3.144314320
H	-3.789580419	-4.755060759	-2.801327144
C	-1.952001400	-3.785056049	-2.211210952
H	-2.208153941	-3.796151524	-1.146017143
C	0.478182415	-3.710392703	-0.057701548
C	0.757059210	-5.054554972	-0.385811448
H	0.871860715	-5.349871820	-1.434594868
C	0.866945464	-6.017108956	0.624522874
H	1.081468874	-7.058790245	0.363645479
C	0.696174191	-5.649773535	1.969369514
H	0.780674005	-6.405560519	2.757116397
C	0.413668501	-4.317625933	2.300248429
H	0.273415561	-4.025892562	3.346220501
C	0.306760933	-3.347489466	1.292684712
H	0.082314362	-2.303321153	1.543023055

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Octet 1

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Mn	0.021121197	-0.087373235	-0.174403862
P	-0.342120079	2.008962396	-1.672508104
P	0.366447919	-2.385348909	-1.338553025
N	-2.069593969	0.193998306	0.257693810

N	-0.019095142	0.063998535	1.889848753
N	2.081950354	-0.334654930	0.369928854
C	-3.728790553	0.721459660	2.078039057
H	-4.190552148	1.553468597	1.515749876
H	-3.717538110	1.013606943	3.137679215
H	-4.413756883	-0.144053929	1.984705273
C	-2.339877680	0.411749007	1.577758971
C	-1.230171064	0.303640324	2.495015168
C	-1.268093829	0.412729223	3.919209206
H	-2.206629139	0.588529690	4.449443898
C	-0.066802403	0.275405378	4.632796061
H	-0.085526162	0.360472192	5.725102754
C	1.157672512	0.030952574	3.990963076
H	2.075764536	-0.060901516	4.575135073
C	1.169009535	-0.082249172	2.566429040
C	2.306848147	-0.339647086	1.716536435
C	3.675533437	-0.573795339	2.305150975
H	4.140291770	-1.495160602	1.908999426
H	3.629585924	-0.678552944	3.398200515
H	4.376017373	0.255349255	2.084832647
C	-3.127655629	0.264997698	-0.737011857
H	-4.126705222	0.076884965	-0.297691568
H	-2.962880680	-0.543585327	-1.479913547
C	-3.186514640	1.608119566	-1.504309527
H	-3.243546715	2.442282871	-0.781427024
H	-4.123311736	1.631270584	-2.093696876
C	-2.023716508	1.845849664	-2.485569802
H	-2.200656589	2.759247453	-3.081440069
H	-1.960644903	0.994673665	-3.189584811
C	0.746563157	2.564743462	-3.054101919
C	1.929938826	3.273778120	-2.745831757
H	2.123852054	3.578694120	-1.711757366
C	2.847104944	3.603678108	-3.749096499
H	3.752029206	4.162556356	-3.489346569
C	2.610146136	3.224525191	-5.080599195
H	3.329321981	3.481181045	-5.864101411
C	1.443973099	2.513286391	-5.395485049

H	1.245776124	2.215125393	-6.430199568
C	0.519871964	2.184019127	-4.393756449
H	-0.385417145	1.632236472	-4.665968891
C	-0.507447956	3.517378368	-0.632050090
C	-0.398247048	3.399551559	0.769216127
H	-0.198707921	2.422135470	1.221955069
C	-0.544689330	4.530615548	1.584142080
H	-0.458225219	4.424711038	2.670281183
C	-0.797506085	5.785651974	1.011972053
H	-0.909853697	6.668091379	1.650237879
C	-0.903302162	5.910670380	-0.382835554
H	-1.096904779	6.889991092	-0.832916494
C	-0.759639623	4.785127183	-1.202137551
H	-0.828973931	4.890867763	-2.290266833
C	3.166743424	-0.584895890	-0.564950894
H	4.156815122	-0.353968431	-0.126046862
H	3.048293849	0.100268252	-1.430610187
C	3.211418130	-2.034318078	-1.108009723
H	4.170629928	-2.175527111	-1.642256496
H	3.211755754	-2.743205457	-0.260008451
C	2.082978422	-2.397453541	-2.092353114
H	2.256499062	-3.399351846	-2.524873466
H	2.077590584	-1.669185100	-2.925225188
C	-0.702775280	-3.107992676	-2.657215669
C	-0.385233290	-3.035480815	-4.029874521
H	0.579978812	-2.633370596	-4.353560248
C	-1.296257214	-3.485616762	-4.997829854
H	-1.027688010	-3.427558459	-6.057847961
C	-2.537611876	-4.012603753	-4.616192708
H	-3.244892532	-4.363692019	-5.373523907
C	-2.864610608	-4.085976390	-3.251740709
H	-3.829466986	-4.498686983	-2.939326749
C	-1.961713355	-3.633669623	-2.282941808
H	-2.226945120	-3.696793440	-1.221848237
C	0.439045018	-3.725443394	-0.077830908
C	0.604108172	-5.078797316	-0.445386082
H	0.663513931	-5.353947453	-1.503989691

C	0.673204658	-6.072228480	0.538183690
H	0.797881153	-7.119842172	0.245108564
C	0.579366238	-5.728065607	1.896419148
H	0.631742932	-6.507732785	2.663205084
C	0.414973901	-4.386373287	2.268169282
H	0.336933900	-4.110362423	3.324628213
C	0.343694475	-3.386752032	1.288114501
H	0.210930936	-2.340035590	1.583014030

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Singlet 2

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Mn	-0.088403160	-0.053401133	0.015145476
P	-0.922117822	-2.081536005	-0.190208941
P	-1.171687829	1.850491701	0.244077208
N	1.760209916	0.043350094	-0.025951877
N	0.209830616	-0.082343427	-1.914705482
N	0.285860184	0.007706322	1.926340046
C	2.478297732	0.100077621	1.172120379
C	3.884751315	0.146552154	1.148184676
H	4.449286854	0.183887430	2.084627055
C	4.559347798	0.135424753	-0.083290691
H	5.653079051	0.168749905	-0.105733158
C	3.836908013	0.075878003	-1.286171625
H	4.364139743	0.061279770	-2.244607655
C	2.431057644	0.030067240	-1.251694387
C	1.494262569	-0.056872255	-2.332673625
C	-0.845921690	-0.275873669	-2.913664017
H	-0.517606940	0.040884698	-3.920748819
H	-1.700703581	0.361078997	-2.631689207
C	-1.304843053	-1.748592515	-2.980109092
H	-0.432040834	-2.393587417	-3.195786219
H	-1.997539190	-1.856596186	-3.836088995
C	-2.011340259	-2.240514731	-1.705761747
H	-2.342002646	-3.287280727	-1.823889225
H	-2.907776079	-1.623251339	-1.519568456
C	0.234188227	-3.530129542	-0.450566928
C	-0.238542092	-4.826273950	-0.749561836
H	-1.315809327	-5.016156282	-0.815457831
C	0.656650694	-5.886980638	-0.937565912
H	0.275063918	-6.888330211	-1.165348172
C	2.038983829	-5.670037964	-0.824681209
H	2.738006597	-6.500937032	-0.968844243
C	2.518700276	-4.389909188	-0.520509663
H	3.595352127	-4.212137211	-0.425171790
C	1.621276727	-3.326913627	-0.334730908
H	1.991332338	-2.326395843	-0.093817163
C	-1.992242187	-2.753445475	1.169590338
C	-3.332838620	-2.336580135	1.304984423
H	-3.773936282	-1.666843089	0.558240183
C	-4.111363252	-2.761978757	2.390078167
H	-5.154232147	-2.436572716	2.471259529
C	-3.557918538	-3.598846174	3.369936612
H	-4.163353041	-3.925781086	4.221664338
C	-2.222261075	-4.009770164	3.253432379
H	-1.779446000	-4.660887415	4.015000322
C	-1.447010295	-3.593449579	2.162924864
H	-0.407381053	-3.926292573	2.078698882
C	1.924535525	-0.133941190	-3.775284649
H	1.568915120	-1.055070795	-4.272199181
H	3.022004393	-0.129054015	-3.852582270
H	1.553433713	0.719864955	-4.372193289
C	1.584366337	0.097122270	2.291811266
C	-0.740481722	0.090420946	2.970789107
H	-0.336235783	-0.184393796	3.962189586
H	-1.532446524	-0.637684676	2.727100100
C	-1.351922966	1.505498621	3.056786629
H	-2.002144999	1.547969298	3.951105636
H	-0.542158093	2.242046895	3.218872893
C	-2.179515072	1.905086535	1.823726909
H	-2.612674982	2.912039592	1.955505882
H	-3.014521387	1.194114474	1.694840080
C	-0.187326999	3.430902763	0.424614182
C	1.211809877	3.380343429	0.287749210
H	1.685706096	2.419148058	0.065936604

C	1.987301550	4.540683289	0.435191861
H	3.075786597	4.482224286	0.326804928
C	1.371730555	5.766017809	0.720872380
H	1.975930848	6.672452448	0.835995778
C	-0.024214641	5.830238293	0.854531282
H	-0.511473538	6.787507061	1.069797440
C	-0.797855456	4.672224549	0.705566554
H	-1.888341826	4.740718815	0.790366935
C	-2.409497609	2.362458741	-1.044794290
C	-2.059022217	3.270327319	-2.065936148
H	-1.073903339	3.747973209	-2.049569416
C	-2.957780905	3.571574409	-3.098885190
H	-2.662678379	4.279113317	-3.881468080
C	-4.226781486	2.975051761	-3.132201612
H	-4.929298013	3.213615769	-3.937120961
C	-4.586379726	2.068115753	-2.123838844
H	-5.574666090	1.595682637	-2.137150624
C	-3.683772147	1.759172748	-1.096623178
H	-3.974527759	1.033035561	-0.329108073
C	2.066692191	0.200440726	3.716435773
H	1.634194550	1.068967148	4.245705588
H	3.160341341	0.318048100	3.746243940
H	1.820034133	-0.698136714	4.312491829
H	-1.697371699	-0.166330807	0.087617741

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Triplet 2

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Mn	-0.386425763	-0.080632854	0.019942205
P	-0.871667374	-2.294864865	-0.137702361
P	-1.132366036	2.052670775	0.209101926
N	1.533978223	0.031247525	-0.028091731
N	-0.042363863	-0.135698197	-1.916367705
N	0.044684881	0.015536654	1.937379299
C	2.238879361	0.075257586	1.174799161
C	3.642459171	0.143732006	1.143168495
H	4.213316143	0.177970938	2.075071574
C	4.308710869	0.176387559	-0.096927737
H	5.400599000	0.234366429	-0.124109014
C	3.582214911	0.133996209	-1.302793096
H	4.106801677	0.155477478	-2.261817949
C	2.179483771	0.053473327	-1.264160553
C	1.244155189	-0.056236584	-2.340011032
C	-1.111435331	-0.434224882	-2.864658939
H	-0.857270413	-0.076341871	-3.879359037
H	-2.017209181	0.109772313	-2.545222459
C	-1.409824031	-1.949637231	-2.927040500
H	-0.484224946	-2.490008071	-3.199059184
H	-2.132578024	-2.128745631	-3.744894966
C	-1.989749229	-2.532216383	-1.626838142
H	-2.208947770	-3.606722788	-1.751123857
H	-2.936559160	-2.021382993	-1.384665272
C	0.387052159	-3.636850723	-0.423034651
C	0.007401533	-4.974744618	-0.667547609
H	-1.051754064	-5.252914751	-0.663198257
C	0.975410916	-5.961115273	-0.890260153
H	0.667311485	-6.995231313	-1.075656847
C	2.338403612	-5.626282438	-0.870464032
H	3.094093284	-6.398673359	-1.045378810
C	2.726186964	-4.303893172	-0.621225454
H	3.786903795	-4.034934481	-0.597629461
C	1.756801601	-3.313847974	-0.398158719
H	2.055580581	-2.282846671	-0.198739094
C	-1.865634165	-3.017512408	1.243450090
C	-3.237985402	-2.720179803	1.381671514
H	-3.740778604	-2.106347261	0.627852239
C	-3.964633073	-3.192254298	2.482529868
H	-5.031711197	-2.962037567	2.566052052
C	-3.329306940	-3.951716104	3.476118375
H	-3.896659085	-4.316062039	4.337954912
C	-1.961366200	-4.236949469	3.358144897
H	-1.454629518	-4.825285401	4.129776979
C	-1.235572106	-3.776635429	2.251816141
H	-0.171396377	-4.016321312	2.164700662
C	1.647963864	-0.104246316	-3.789261627

H	1.344775594	-1.045872366	-4.283150677
H	2.740034274	-0.024230242	-3.889476472
H	1.205620255	0.722458812	-4.375514017
C	1.352091610	0.081308112	2.295748729
C	-1.002028771	0.192822252	2.939958142
H	-0.657445003	-0.131117800	3.939209437
H	-1.854523779	-0.452244762	2.665490822
C	-1.469455697	1.664186788	3.023164962
H	-2.161097175	1.762374462	3.880744445
H	-0.598159468	2.308207195	3.244093350
C	-2.184854879	2.170809297	1.759088977
H	-2.515786906	3.214756145	1.896189040
H	-3.080083217	1.555111817	1.570644139
C	-0.034611085	3.541277186	0.413816266
C	1.361852755	3.383262326	0.338477864
H	1.773796862	2.391022828	0.144144603
C	2.212661889	4.486850277	0.503959615
H	3.296372940	4.346476326	0.441326347
C	1.677798397	5.758417087	0.746212791
H	2.341193391	6.619468685	0.876077362
C	0.286119200	5.928279911	0.816859384
H	-0.136998337	6.921712481	0.997795684
C	-0.563714291	4.828564107	0.651297074
H	-1.648308853	4.976596903	0.686876110
C	-2.286323877	2.633969453	-1.114575751
C	-1.823209950	3.481394031	-2.143079444
H	-0.800783530	3.869680082	-2.105834373
C	-2.662356455	3.839652815	-3.206133878
H	-2.284469361	4.498153781	-3.994760344
C	-3.979878255	3.362104280	-3.259649733
H	-4.636256827	3.646352743	-4.087748527
C	-4.449633693	2.514586909	-2.245597228
H	-5.476048007	2.135200414	-2.278777597
C	-3.607893628	2.144755101	-1.188524520
H	-3.979513374	1.460144296	-0.419840186
C	1.819293416	0.174730371	3.723213597
H	1.436360622	1.075693297	4.237033794
H	2.917091853	0.219338816	3.768108286
H	1.503570008	-0.697273632	4.325506751
H	-2.007103872	-0.182350965	0.072879124

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Quintet 2

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Mn	-0.476445398	-0.092545114	0.019758533
P	-0.876723192	-2.356939135	-0.174567441
P	-1.147688792	2.111531306	0.240657289
N	1.445317587	0.027589685	-0.031763265
N	-0.186493827	-0.101638826	-1.941335170
N	-0.085831542	-0.037473910	1.962087135
C	2.133551318	0.079399993	1.171683725
C	3.561351122	0.141301682	1.138533261
H	4.135658743	0.153158742	2.067973987
C	4.212926963	0.191141446	-0.105722801
H	5.305601347	0.256907458	-0.135310785
C	3.495532223	0.158955211	-1.312443132
H	4.017864507	0.211994120	-2.270606047
C	2.069552401	0.050689131	-1.270097900
C	1.143941303	-0.067636716	-2.332938064
C	-1.222412647	-0.493846944	-2.884008065
H	-0.982091619	-0.130190224	-3.901289938
H	-2.165039098	0.000141692	-2.585332635
C	-1.447958116	-2.024367036	-2.946593867
H	-0.497220671	-2.523074263	-3.212900333
H	-2.162146933	-2.246664690	-3.762540382
C	-2.001906567	-2.625245165	-1.643014796
H	-2.185932928	-3.707302075	-1.759244289
H	-2.961842036	-2.144000755	-1.388136075
C	0.429576689	-3.645476251	-0.455456586
C	0.090914005	-4.986252782	-0.741082860
H	-0.960691915	-5.290703775	-0.780458686
C	1.090976585	-5.943310452	-0.949371715
H	0.815430701	-6.980603247	-1.166653988
C	2.443815324	-5.575314165	-0.873279340
H	3.225004614	-6.325283497	-1.035514737

C	2.789202471	-4.249810021	-0.583778872
H	3.841026991	-3.953708386	-0.517229945
C	1.788673268	-3.288304898	-0.375070135
H	2.058655140	-2.256883453	-0.143147976
C	-1.810042822	-3.062995959	1.253736500
C	-3.171571005	-2.752249781	1.448988704
H	-3.696997136	-2.125536722	0.721196929
C	-3.855001559	-3.221421616	2.578460073
H	-4.915299804	-2.981001468	2.708653067
C	-3.183593706	-3.986927251	3.543244906
H	-3.716399845	-4.346558514	4.429258988
C	-1.825161590	-4.284098301	3.367508971
H	-1.290465986	-4.876218910	4.117443428
C	-1.143186576	-3.829141933	2.231248737
H	-0.085051713	-4.075005278	2.099811599
C	1.549003870	-0.125949745	-3.779030022
H	1.210643025	-1.054531885	-4.276560901
H	2.643219170	-0.086014525	-3.876985927
H	1.132040079	0.717394040	-4.363331514
C	1.258004293	0.086872690	2.282738962
C	-1.109743138	0.229293073	2.959545472
H	-0.771264539	-0.095128318	3.962187445
H	-1.998875271	-0.379383900	2.712494414
C	-1.518756530	1.720187215	3.037140700
H	-2.206690058	1.855792340	3.893671839
H	-0.623557149	2.334296427	3.249286342
C	-2.217459250	2.241029501	1.769081345
H	-2.531811899	3.290879423	1.900065816
H	-3.119642308	1.638472649	1.566560693
C	0.002245466	3.552692369	0.455218478
C	1.388929426	3.364199789	0.302009066
H	1.771012403	2.374231747	0.045778255
C	2.273903570	4.440267409	0.470045693
H	3.349265125	4.275869493	0.347393882
C	1.784589417	5.712059374	0.791306367
H	2.475800558	6.551162871	0.922343714
C	0.402683412	5.911802417	0.939759957
H	0.014556648	6.906544725	1.182507511
C	-0.482481630	4.840498002	0.772543663
H	-1.559951803	5.012789687	0.869846630
C	-2.237203809	2.689183287	-1.132197864
C	-1.712018975	3.499915966	-2.159518567
H	-0.678627103	3.854242268	-2.096575803
C	-2.503892538	3.860637922	-3.257559883
H	-2.079231443	4.489670282	-4.046819492
C	-3.832438033	3.422014775	-3.345671290
H	-4.451510115	3.707596816	-4.202027873
C	-4.362565999	2.611700579	-2.331031678
H	-5.398324501	2.261760925	-2.392677364
C	-3.568916400	2.238480661	-1.238477479
H	-3.984410928	1.578578150	-0.470145511
C	1.728053105	0.190324926	3.705928975
H	1.310931072	1.073515041	4.225836490
H	2.823245594	0.276704403	3.746799865
H	1.441577801	-0.695939988	4.304909090
H	-2.091984085	-0.192316431	0.054707730

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Septet 1

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Mn	-0.762442460	-0.110435713	0.098572178
P	-0.883719645	-2.896984839	-0.016902408
P	-1.215916408	2.626679564	0.105840326
N	1.425332663	0.040027495	0.050963992
N	-0.056390048	-0.630994333	-1.991395990
N	-0.041287477	0.567357462	2.141370387
C	2.112384222	0.391009590	1.191201773
C	3.512750581	0.487220031	1.181064541
H	4.065441756	0.766582532	2.080951334
C	4.212317958	0.231308271	-0.012585279
H	5.303150956	0.303820757	-0.038515674
C	3.498364954	-0.114473657	-1.173986924
H	4.042042125	-0.312207802	-2.101002741
C	2.098638406	-0.206747241	-1.124648637
C	1.241563362	-0.578966164	-2.253897117

C	-1.012351410	-1.084916786	-2.990464762
H	-0.683959922	-0.867612320	-4.026169790
H	-1.954105149	-0.531469424	-2.819950241
C	-1.303750940	-2.599604509	-2.876740084
H	-0.370442454	-3.167712855	-3.048193972
H	-1.987742825	-2.867228140	-3.704252017
C	-1.955838912	-3.051655120	-1.557430926
H	-2.304768505	-4.095199456	-1.648917127
H	-2.839795635	-2.425987868	-1.338021428
C	0.537421285	-4.018625066	-0.393145805
C	0.411898097	-5.246235619	-1.078864373
H	-0.576697445	-5.601281316	-1.388721291
C	1.541425485	-6.025346677	-1.362807470
H	1.428285266	-6.974532306	-1.896946550
C	2.814496970	-5.591048229	-0.963294721
H	3.696463801	-6.199148464	-1.188951239
C	2.952783519	-4.375931903	-0.279372496
H	3.943405394	-4.027027810	0.029612015
C	1.822939185	-3.593514353	0.000078086
H	1.932570750	-2.633426654	0.514914760
C	-1.897084517	-3.845302730	1.203735737
C	-3.103086549	-3.246021107	1.633721779
H	-3.390079851	-2.269062778	1.224571127
C	-3.907522583	-3.878575432	2.589714175
H	-4.841793196	-3.404289605	2.907998632
C	-3.516427386	-5.106064774	3.146947098
H	-4.143702707	-5.596415046	3.897819514
C	-2.310375997	-5.694694560	2.741291634
H	-1.991544528	-6.648142916	3.175633165
C	-1.504698737	-5.071769589	1.776906037
H	-0.566853868	-5.543622398	1.468171858
C	1.820104361	-0.891872003	-3.615162468
H	1.588422888	-1.927241865	-3.921679066
H	2.910945212	-0.775664467	-3.647792849
H	1.395376381	-0.226877678	-4.388407840
C	1.262057873	0.680380894	2.349772304

C	-1.003283237	0.962573103	3.158649102
H	-0.620054675	0.819278323	4.188477181
H	-1.891580410	0.315227873	3.041908309
C	-1.442708680	2.437905455	2.998974168
H	-2.102947599	2.680075341	3.853083629
H	-0.558830123	3.096187970	3.092554276
C	-2.204990123	2.766886826	1.701651721
H	-2.642848848	3.778439229	1.767090716
H	-3.040874788	2.057686855	1.563897288
C	0.101909345	3.910804912	0.299264444
C	1.358498666	3.632211069	-0.276977888
H	1.506905830	2.681036421	-0.798526627
C	2.414587650	4.547781935	-0.170188753
H	3.383702145	4.312911886	-0.622013322
C	2.232940589	5.751456775	0.523980614
H	3.058560948	6.464789221	0.614006230
C	0.990028974	6.039041672	1.107889297
H	0.843861580	6.978677537	1.650867889
C	-0.068349413	5.127076156	0.994817246
H	-1.036350831	5.370570087	1.445263824
C	-2.400302931	3.386097501	-1.093974107
C	-2.214183525	4.641552510	-1.706335475
H	-1.342113576	5.250708970	-1.448862597
C	-3.141606738	5.117666527	-2.644946800
H	-2.982384786	6.095491492	-3.111781673
C	-4.266177988	4.352020622	-2.983988181
H	-4.988956670	4.728211225	-3.714669111
C	-4.452312987	3.095983487	-2.385385721
H	-5.321853566	2.485420227	-2.650529005
C	-3.524639885	2.609247815	-1.455669244
H	-3.649849342	1.612756115	-1.012827094
C	1.853090030	1.102639526	3.675820198
H	1.529072906	2.120899775	3.955003589
H	2.950548361	1.096761912	3.669750408
H	1.524857129	0.428558610	4.487071325
H	-2.511437402	-0.227715233	0.152767247

Table S9. Vibrational frequencies (in cm^{-1}) of the optimized geometries of each spin state for **1** and **2**.

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Doublet 1

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19.17	24.19	31.61	33.54	38.68	42.43
45.71	47.23	50.43	51.20	63.87	65.96
72.65	78.74	86.99	97.56	114.04	135.55
146.77	150.51	159.15	164.80	165.65	171.19
176.98	183.95	200.77	203.10	210.97	217.55
227.66	239.20	250.74	256.25	263.57	282.08
290.07	312.20	318.24	323.71	328.08	331.64
349.82	371.22	380.03	388.22	391.50	396.44
396.90	404.73	410.58	412.12	420.75	423.06
440.62	446.93	449.08	469.96	472.85	483.26
499.04	508.27	511.80	547.27	553.49	574.17
608.75	609.12	610.41	610.71	615.78	624.84
637.51	640.38	646.79	675.28	676.29	680.39
682.08	684.55	685.32	688.94	690.08	691.06
713.06	726.84	728.88	734.30	735.52	735.71
795.67	804.63	807.95	810.40	825.45	831.43
838.08	839.10	849.31	858.28	879.14	881.19
885.36	888.49	901.50	903.20	904.03	931.82
937.05	945.22	945.88	951.62	956.02	957.91
968.67	970.28	972.51	981.61	981.90	982.05
982.46	989.36	1000.99	1002.73	1005.00	1006.76
1021.89	1022.62	1025.83	1026.36	1027.76	1028.52
1054.39	1064.77	1071.55	1072.66	1073.41	1075.85
1077.52	1078.57	1079.70	1081.28	1082.80	1114.30
1140.95	1144.62	1146.03	1153.02	1153.17	1154.29
1154.65	1162.02	1168.63	1172.07	1174.64	1178.38
1180.61	1181.94	1250.84	1251.93	1268.03	1268.73
1289.35	1289.37	1297.61	1298.08	1319.79	1323.28
1323.63	1329.35	1330.62	1336.49	1353.78	1354.38
1358.85	1359.06	1360.79	1371.85	1376.99	1398.03
1404.65	1410.94	1411.99	1426.99	1428.61	1429.16
1432.28	1432.47	1437.74	1440.09	1440.73	1442.66
1445.66	1451.56	1464.73	1471.10	1471.39	1473.62
1474.10	1474.35	1480.91	1519.00	1579.99	1580.14
1585.38	1586.33	1586.63	1595.59	1596.83	1597.95
1599.25	2954.94	2963.25	2966.31	2967.36	2980.93
2983.56	2984.29	2984.73	3004.35	3014.07	3016.87
3017.17	3031.44	3042.15	3043.82	3048.10	3077.11
3081.83	3101.92	3102.27	3107.02	3107.73	3107.80
3109.33	3112.51	3114.58	3114.59	3116.15	3117.54
3122.59	3123.09	3123.34	3124.47	3127.97	3130.06
3130.08	3134.08	3134.21	3138.56	3138.80	3141.43

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Quartet 1

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15.75	24.51	27.30	27.92	30.39	33.26
37.44	40.18	48.06	49.10	54.42	54.85
67.15	70.06	78.79	82.00	99.75	117.38
127.27	128.68	136.19	147.67	156.51	165.32
168.55	181.87	182.88	189.58	195.85	206.10
210.30	213.41	228.95	246.41	256.23	265.34
269.31	282.73	303.38	311.91	315.10	322.12
330.84	354.96	360.68	382.36	388.74	389.13
390.74	395.87	396.74	402.65	406.47	409.88
422.53	433.04	437.60	457.96	461.06	475.45
491.24	501.27	503.86	520.00	531.12	553.80
608.40	608.70	609.62	609.73	616.89	622.06
626.18	640.41	642.96	648.33	676.28	678.44
683.74	684.32	686.13	686.79	690.01	690.47
711.59	721.38	722.75	723.59	734.70	735.06
793.53	804.61	809.30	810.77	821.67	822.76
835.57	837.31	846.13	854.56	871.41	872.20
872.96	874.61	893.06	901.43	903.54	928.97
930.42	944.37	945.79	946.62	952.43	953.21
957.53	969.42	971.70	978.57	978.99	981.89
982.11	995.35	1000.38	1000.62	1004.66	1006.86
1022.40	1022.88	1024.13	1025.17	1025.80	1026.29
1052.55	1063.74	1063.88	1072.06	1073.56	1075.53
1076.44	1080.59	1081.22	1081.79	1083.03	1095.83
1115.86	1145.22	1146.37	1153.02	1153.54	1153.69
1153.87	1160.86	1171.63	1172.93	1175.00	1178.22
1179.91	1183.95	1214.68	1247.97	1258.10	1269.03
1272.23	1292.05	1292.31	1297.62	1298.05	1318.48
1321.76	1325.73	1327.14	1333.07	1339.59	1353.98

1354.75	1360.29	1360.52	1367.43	1370.99	1392.43
1397.80	1411.90	1412.34	1417.69	1428.96	1429.80
1432.84	1433.63	1436.21	1436.63	1437.99	1438.35
1442.60	1446.00	1458.18	1461.08	1471.18	1471.69
1471.91	1472.26	1474.05	1514.63	1567.88	1570.00
1583.25	1583.46	1584.63	1589.00	1592.70	1596.30
1597.42	2943.98	2945.34	2954.93	2955.76	2966.40
2966.60	2974.17	2974.61	2989.56	2992.64	3003.84
3005.49	3019.10	3019.95	3033.05	3034.00	3074.25
3074.78	3105.62	3106.49	3107.22	3107.92	3112.09
3112.85	3114.14	3114.73	3115.24	3122.94	3122.97
3123.70	3124.03	3124.43	3129.08	3129.46	3130.26
3131.42	3136.30	3137.49	3139.14	3140.22	3140.36

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Sextet 1

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10.78	18.58	19.64	24.10	26.30	33.73
35.89	37.28	46.53	51.58	53.10	57.08
60.92	62.72	74.03	82.92	89.89	103.66
111.77	122.33	128.29	134.24	150.72	151.78
164.17	168.11	170.84	186.16	187.88	189.35
200.55	201.91	205.29	234.08	240.24	248.55
257.98	260.99	268.91	297.20	308.17	315.74
320.29	342.65	352.58	359.00	374.67	388.60
388.93	395.06	397.52	398.35	401.33	405.83
409.09	426.24	432.72	449.28	461.75	466.68
487.95	501.05	503.72	510.32	521.84	536.77
590.24	600.27	608.41	608.44	609.51	610.25
628.99	636.76	640.63	658.11	676.29	678.01
684.46	685.41	686.93	689.12	690.35	691.92
696.97	723.42	725.08	726.76	733.51	735.63
782.79	799.89	804.70	823.72	824.96	835.28
836.59	838.17	840.24	846.26	871.52	874.08
877.23	879.18	891.93	900.69	905.94	930.87
932.85	935.25	943.42	947.59	949.28	954.35
955.71	969.28	975.60	977.78	979.53	980.00
980.83	981.24	995.92	999.63	1002.37	1003.49
1022.43	1023.94	1025.10	1025.39	1025.97	1027.35
1055.17	1063.90	1071.72	1073.29	1076.07	1078.86
1079.32	1080.46	1081.58	1083.33	1084.22	1087.49
1110.32	1146.69	1148.16	1153.39	1153.59	1153.88
1154.39	1154.86	1174.43	1175.52	1176.48	1177.99
1181.52	1181.61	1225.71	1247.06	1251.62	1269.90
1271.34	1295.42	1295.67	1300.15	1300.62	1310.68
1319.41	1324.76	1325.65	1330.54	1333.13	1353.15
1354.06	1357.05	1359.74	1366.59	1367.20	1379.82
1384.55	1409.85	1413.31	1427.52	1429.10	1429.22
1433.26	1433.72	1435.67	1435.93	1438.64	1440.11
1444.27	1448.18	1464.42	1466.70	1472.96	1473.09
1473.53	1473.68	1476.82	1507.36	1565.56	1572.92
1574.68	1581.28	1581.51	1591.88	1594.02	1594.76
1596.65	2927.99	2934.40	2950.60	2951.89	2956.74
2962.25	2968.47	2977.13	2978.66	2980.99	3000.57
3001.59	3015.27	3018.99	3027.69	3036.00	3082.98
3089.84	3090.21	3091.86	3105.47	3106.45	3106.53
3107.73	3112.36	3113.61	3115.90	3116.34	3116.86
3122.63	3122.93	3124.88	3125.78	3127.66	3128.55
3129.55	3136.39	3136.89	3139.89	3140.70	3141.99

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Octet 1

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13.45	20.13	21.89	23.44	25.30	32.87
34.08	37.03	44.70	50.94	52.51	55.09
57.98	62.83	68.91	81.39	86.61	103.50
114.51	117.36	129.18	129.45	142.66	144.09
152.61	164.93	168.02	178.49	186.09	186.94
197.18	199.35	216.17	234.95	241.87	244.13
257.61	264.78	272.26	302.19	304.09	311.70
317.87	348.54	348.60	371.23	375.65	389.31
389.35	390.49	394.34	396.40	399.81	402.95
408.22	424.67	432.77	450.37	459.31	467.28
477.32	494.44	498.76	502.75	503.76	531.36
603.36	607.25	608.02	609.27	609.59	610.20
615.73	637.79	638.77	652.69	676.93	678.22
684.15	684.22	686.18	686.57	690.14	691.00
693.81	695.76	719.34	724.51	725.29	731.22
731.52	780.39	800.05	805.47	824.78	825.87
830.32	830.44	837.17	843.63	872.98	879.84
881.01	889.39	892.79	893.36	894.20	932.14
933.06	938.36	938.78	939.45	956.31	956.40
961.32	963.20	963.36	979.54	979.75	979.94
980.58	981.10	992.68	992.98	998.20	1000.58

1023.81	1024.32	1024.81	1025.66	1026.57	1027.12
1053.46	1064.43	1074.81	1075.47	1078.21	1079.75
1081.28	1081.49	1082.00	1084.80	1085.29	1117.15
1142.14	1144.42	1147.01	1153.92	1154.04	1154.23
1154.39	1159.49	1176.62	1177.44	1177.81	1179.04
1181.67	1184.19	1247.70	1249.25	1269.25	1269.71
1295.90	1296.04	1301.08	1301.22	1315.74	1318.83
1321.26	1322.58	1328.24	1329.09	1352.94	1354.53
1358.59	1358.78	1361.57	1362.46	1367.78	1388.15
1391.23	1410.94	1412.32	1414.12	1428.17	1429.06
1431.09	1432.66	1433.39	1434.69	1435.29	1441.04
1442.09	1447.12	1451.20	1468.86	1472.80	1473.41
1473.74	1474.10	1484.22	1511.36	1521.56	1574.74
1574.77	1578.06	1578.78	1591.57	1591.98	1594.23
1596.37	2916.52	2916.98	2946.45	2947.35	2957.87
2957.97	2966.09	2966.77	2973.77	2974.42	2999.86
3000.54	3017.09	3017.16	3027.91	3028.66	3083.24
3085.32	3105.18	3106.40	3107.00	3108.82	3109.97
3110.89	3111.62	3113.44	3114.40	3118.29	3118.75
3124.04	3124.94	3127.68	3128.08	3129.62	3130.18
3137.62	3137.97	3141.29	3141.67	3142.13	3147.37

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Singlet 2

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20.69	22.21	25.57	29.59	37.34	40.18
46.02	46.83	50.10	53.95	57.21	63.36
80.57	82.33	92.69	101.00	116.97	143.10
156.05	159.50	162.33	166.84	170.24	172.75
181.91	192.04	203.88	209.06	216.24	230.86
240.61	252.48	252.85	255.66	269.74	287.99
312.33	314.55	329.02	340.00	341.79	347.30
367.54	385.67	388.59	390.55	393.72	395.39
396.06	412.33	415.37	424.26	425.94	437.70
450.71	460.52	469.33	474.80	479.97	492.94
509.34	514.27	519.70	552.66	564.41	581.07
607.98	609.55	609.75	610.77	611.12	621.69
633.80	646.58	650.49	659.46	676.76	678.99
682.97	683.83	686.06	686.83	690.25	690.71
701.52	718.20	729.76	730.47	735.70	735.74
749.10	797.39	806.91	812.04	816.39	824.41
828.46	829.18	836.21	837.22	848.64	858.16
878.03	884.64	887.10	891.08	898.81	900.65
901.91	933.71	935.50	942.45	943.60	950.53
958.36	958.81	965.89	966.77	971.03	982.04
982.40	982.63	982.93	996.47	1003.17	1003.47
1007.09	1007.48	1020.30	1023.39	1026.49	1026.62
1027.78	1028.76	1054.63	1064.65	1073.38	1073.64
1074.16	1078.77	1079.06	1079.56	1080.64	1082.93
1084.77	1119.34	1142.85	1148.20	1149.70	1153.42
1153.53	1153.95	1154.89	1162.55	1168.14	1173.83
1176.04	1178.35	1179.76	1181.25	1247.44	1247.98
1269.16	1269.78	1289.24	1289.59	1296.55	1296.70
1322.51	1324.11	1326.58	1327.30	1328.54	1335.39
1353.34	1354.40	1356.53	1357.25	1357.76	1372.31
1375.72	1401.11	1401.68	1404.82	1406.50	1428.45
1429.17	1431.62	1432.01	1439.28	1439.59	1440.13
1442.51	1443.35	1446.49	1450.78	1465.23	1472.30
1472.58	1474.55	1475.01	1475.36	1483.46	1518.95
1581.09	1583.02	1586.45	1586.64	1586.98	1597.11
1598.60	1598.75	1599.09	1692.54	2959.27	2960.19
2961.43	2962.03	2974.45	2975.70	2984.24	2984.30
3008.06	3008.70	3012.14	3012.51	3036.74	3039.61
3044.00	3044.16	3074.27	3075.83	3100.57	3100.84
3100.95	3101.22	3108.89	3108.96	3109.14	3109.80
3113.48	3117.78	3117.85	3118.58	3119.03	3125.24
3126.26	3126.40	3129.63	3130.38	3134.58	3135.62
3137.15	3139.39	3147.71			

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Triplet 2

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19.65	24.12	25.27	26.05	34.59	37.26
44.37	44.87	48.65	55.45	57.56	61.59
78.53	83.17	90.70	96.34	110.63	135.49
146.36	148.97	151.86	157.51	163.72	167.33
178.29	179.10	197.37	201.67	212.34	215.42
227.59	236.19	250.89	251.85	257.55	263.66
280.79	295.12	305.20	318.36	325.32	336.36
344.79	357.71	365.55	388.49	389.46	389.75
393.34	395.25	403.07	406.50	410.93	416.64
430.83	438.10	439.56	463.30	469.20	478.26
492.61	507.02	508.23	528.51	537.37	549.52
555.24	608.89	609.10	610.48	610.60	617.37

621.63 635.46 643.36 646.69 662.60 677.60
679.74 683.32 683.91 685.93 686.44 689.06
689.74 709.85 721.51 726.19 727.18 729.71
734.16 734.61 792.38 799.82 807.19 818.75
822.69 823.19 833.65 834.53 847.43 855.65
871.22 874.78 878.02 882.04 884.31 900.00
900.78 930.75 932.32 940.55 941.98 946.99
949.58 955.08 955.47 964.81 965.31 981.80
981.97 982.77 983.24 997.02 998.17 1001.64
1002.79 1004.96 1017.88 1024.20 1026.56 1026.94
1027.47 1028.57 1045.89 1050.05 1063.34 1072.89
1074.51 1075.07 1079.94 1080.24 1081.43 1081.81
1083.17 1084.70 1115.05 1150.53 1151.39 1152.86
1152.93 1154.27 1154.85 1158.97 1169.67 1172.73
1176.84 1178.99 1179.77 1182.90 1198.99 1250.22
1254.59 1267.77 1268.60 1289.74 1290.17 1297.17
1297.37 1319.46 1321.59 1326.87 1327.30 1334.94
1335.52 1355.51 1355.70 1359.45 1359.58 1368.12
1370.69 1388.05 1402.02 1402.54 1404.12 1419.53
1429.18 1429.54 1432.59 1432.99 1435.88 1436.06
1438.68 1439.21 1443.40 1446.89 1460.81 1464.38
1472.40 1472.74 1474.00 1474.40 1475.06 1510.93
1580.97 1581.04 1582.11 1586.41 1586.62 1596.01
1598.08 1599.24 1599.64 1649.83 2956.01 2956.99
2966.19 2966.45 2973.61 2974.56 2994.14 2994.35
3003.65 3004.41 3013.25 3013.38 3029.82 3030.18
3055.25 3055.87 3081.47 3082.05 3108.00 3108.55
3110.76 3111.24 3117.44 3117.85 3118.18 3118.21
3120.42 3126.81 3127.33 3127.72 3128.29 3132.97
3133.06 3133.56 3137.92 3138.50 3141.87 3142.28
3143.94 3166.84 3167.80

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Quintet 2

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15.50 18.00 23.90 26.00 34.23 35.82
41.11 45.22 48.77 54.42 55.94 58.56
70.58 76.33 90.11 90.38 98.74 129.05
142.45 144.62 147.67 148.64 158.04 168.91
171.57 176.66 193.08 195.45 198.11 202.76
227.72 228.32 245.24 248.42 254.54 262.42
280.12 287.08 298.64 317.14 319.77 331.39
338.87 353.25 353.99 370.75 385.96 389.25
389.51 392.83 392.96 401.06 407.79 414.14
424.07 429.84 430.28 458.72 465.28 472.90
477.74 484.88 504.51 508.40 512.55 540.20
548.38 602.38 608.87 609.11 610.03 610.42
616.53 630.65 640.47 649.47 651.19 679.69
681.81 682.92 683.68 684.42 687.32 687.87
689.79 689.95 700.81 719.82 722.31 728.41
729.36 735.46 735.57 782.90 798.57 803.39
823.81 824.69 832.63 833.35 846.87 849.35
866.34 875.99 884.33 886.11 889.05 900.08
900.73 933.03 933.19 936.71 940.68 941.21
958.20 958.57 959.54 965.57 966.04 981.91
982.30 982.57 982.85 989.82 998.14 998.35
999.63 1000.54 1021.69 1021.86 1027.10 1027.31
1028.53 1029.21 1050.06 1059.24 1067.86 1076.69
1077.57 1080.98 1081.31 1082.32 1082.69 1085.35
1086.77 1114.52 1133.71 1147.04 1149.23 1153.88
1154.06 1154.89 1155.45 1157.14 1168.29 1174.28
1177.26 1179.20 1180.59 1182.26 1248.38 1249.20
1265.08 1265.52 1290.66 1291.66 1298.14 1298.44
1307.40 1315.68 1320.52 1324.47 1330.38 1341.39
1347.01 1351.23 1355.72 1356.10 1358.72 1359.80
1360.23 1371.99 1377.71 1401.57 1401.84 1418.82
1425.61 1429.63 1430.12 1432.89 1433.11 1433.36
1433.57 1436.74 1437.80 1441.39 1443.37 1465.90
1467.29 1473.17 1473.57 1475.66 1476.12 1503.48
1551.55 1583.68 1584.08 1586.68 1587.16 1597.74
1599.04 1599.25 1599.80 1650.14 2944.01 2944.43
2954.81 2955.97 2961.87 2962.62 2988.84 2989.71
2990.12 2990.25 3001.45 3002.58 3015.36 3016.04
3050.20 3050.60 3083.36 3083.75 3105.97 3105.99
3109.34 3109.49 3111.61 3115.61 3115.64 3116.71
3116.82 3125.81 3125.98 3126.08 3126.25 3132.76
3132.91 3136.28 3136.55 3138.78 3140.19 3140.38
3145.43 3170.65 3175.91

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Septet 2

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12.00 17.32 22.28 25.17 31.52 33.84
36.45 38.11 43.77 45.45 46.79 52.11

60.60	63.51	68.12	69.86	82.05	84.47
99.93	102.38	113.84	118.59	129.05	145.17
147.61	158.75	160.79	174.73	177.22	195.72
196.22	203.65	205.17	219.39	226.86	242.74
242.98	244.53	263.97	296.71	303.08	324.47
326.70	343.98	344.22	356.45	376.51	377.14
391.11	391.62	395.83	396.47	397.22	401.08
405.51	412.05	431.37	432.73	447.85	467.27
468.31	475.67	494.20	498.47	503.76	516.78
519.88	549.82	599.35	606.74	607.98	609.09
609.91	610.24	631.17	632.64	639.30	676.40
677.59	677.95	686.72	686.95	690.40	690.99
691.58	692.24	694.34	729.61	730.93	734.89
735.51	741.26	782.37	791.35	800.35	833.37
834.42	837.08	838.08	843.79	846.88	847.77
872.94	878.19	887.57	894.90	896.65	899.22
901.52	939.17	940.74	941.14	942.37	943.94
944.27	961.38	962.59	963.46	964.15	980.19
980.71	980.87	983.06	983.67	994.37	995.54
1004.33	1006.30	1024.80	1026.75	1027.69	1027.98
1028.31	1031.51	1056.73	1067.64	1070.76	1076.42
1076.75	1078.50	1079.19	1079.57	1081.63	1082.89
1086.92	1087.00	1115.42	1153.58	1153.67	1153.69
1154.50	1154.79	1158.31	1159.28	1173.81	1174.98
1177.28	1177.54	1181.66	1181.86	1217.22	1250.12
1252.59	1264.99	1265.79	1294.26	1294.47	1298.31
1300.55	1307.59	1313.07	1322.37	1324.70	1330.07
1331.76	1335.42	1354.04	1354.26	1355.27	1355.84
1361.73	1364.11	1379.15	1381.06	1408.94	1409.51
1429.26	1429.74	1431.98	1432.31	1435.10	1435.91
1440.24	1441.21	1442.66	1448.28	1458.74	1463.29
1474.41	1474.62	1474.81	1475.11	1480.33	1527.70
1531.03	1576.29	1580.52	1580.73	1585.63	1585.87
1597.32	1598.07	1599.84	1600.10	2941.21	2941.78
2964.98	2965.30	2975.14	2976.20	2980.79	2981.90
2997.63	2999.38	3015.11	3015.52	3028.43	3029.25
3038.77	3039.17	3087.60	3089.73	3101.57	3101.98
3108.09	3108.42	3109.80	3110.08	3116.09	3116.24
3119.26	3119.77	3123.69	3123.85	3127.10	3129.80
3130.30	3130.76	3131.05	3138.46	3138.83	3139.28
3139.60	3142.36	3150.81			