Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information: Experimental and Computational Studies of Borohydride catalyzed Hydrosilylation of a variety of C=O and C=N Functionalities including Esters, Amides and Heteroarenes.

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Experimental:

General. All reagents were purchased from Sigma-Aldrich, Alfa-Aesar and Fisher Chemicals and used as received unless otherwise indicated. All air-free reactions were run under 1 atm of dry nitrogen using standard Schlenk techniques and dried and sparged solvents. All reusable glassware and stir bars were extensively soaked concentrated base bath to ensure a minimal risk of reaction contamination by reactive transition metals. NMR spectra were recorded at room temperature on a Bruker Avance 400 MHz NMR spectrometer running Topspin version 1.3 with a 5 mm gradient BBI probe and a BACS-60 automatic sample changer and referenced to the residual solvent peak (δ in ppm and J in Hz). GC-MS spectra recorded on Agilent 6890N GC with a 5973N MSD and a 7683 series injector using a 15 meter, 0.25mm ID Restek Rtx-1 column.

Additional catalytic screens

Table S1: Silane screen with 5 mol% $NaBH_4$

Entry	Silane	Time (hr)	Silane equiv.	Temp. (°C)	Substrate	Yield
1	Ph_2SiH_2	1	0.5	RT	Benzaldehyde	57%
2	Ph_3SiH	1	1.0	RT	Benzaldehyde	28%

Experiments run with $NaBH_4$ (0.13 mmol), Silane and substrate (2.64 mmol) in THF (4 ml) under 1 atm N_2. Yield determined by ^{1}H NMR spectroscopy using 1,3,5 trimethoxybenzene as an internal standard.

Table S2: Hydrosilylation using $SiPhH_3$

Entry	Catalyst	Time (hr)	Silane equiv.	Temp. (°C)	Substrate	Yield
1	$NaBH_4$ (5 mol%)	0.25	0.35	RT	Benzaldehyde	>95
2	$LiBH_4$ (5 mol%)	0.25	0.35	RT	Benzaldehyde	80
3	KBH_4 (5 mol%)	2/24	0.35	RT	Benzaldehyde	9/38
4[a]	$NaBH_4$ (5 mol%)	1	0.35	RT	Benzaldehyde	>95
5[b]	$NaBH_4$ (5 mol%)	1	0.35	RT	Benzaldehyde	>95
4	$LiHBEt_3$ (5 mol%)	4	1.05	60	Stilbene	-
5	$LiHBEt_3$ (5 mol%)	1	0.35	RT	Styrene	-
6	$LiHBEt_3$ (5 mol%)	1	0.35	RT	Phenylacetylene	-
7	$LiHBEt_3$ (5 mol%)	24	1.05	60	Benzonitrile	-
8	KBH_4[c] (5 mol%)	2	0.35	RT	Benzaldehyde	11
9	KBH_4[d] (5 mol%)	2	0.35	RT	Benzaldehyde	9
10	$NaBH_4$[e] (5 mol%)	1	0.35	RT	Benzaldehyde	>95

Experiments run with $LiHBEt_3$ / $NaBH_4$ / $LiBH_4$ / KBH_4 (0.13 mmol), $SiPhH_3$ (0.92-2.77 mmol) and substrate (2.64 mmol) in THF (4 ml) under 1 atm N_2. Yield determined by ^{1}H NMR spectroscopy using 1,3,5 trimethoxybenzene as an internal standard. [a]Pyrene (2.64 mmol) added as a radical trap. [b]Reaction run with exclusion of light. [c]20mol% $NaBF_4$ added to the reaction. [d]20mol% $LiBF_4$ added to the reaction. [e]50mol% 15-crown-5 ether added to the reaction.

Table S3: Negative controls

Entry	Catalyst	Time (hr)	Silane equiv.	Temp. (°C)	Substrate	Yield
1	None	1	0.35	RT	Benzaldehyde	-
2	None	2	0.35	60	N-benzylideneaniline	-
3	None	2	1.05	60	N,N-dimethylbenzamide	-
4	None	4	1.05	60	Methylbenzoate	-

Experiments run with $SiPhH_3$ and substrate (1.32 mmol) in THF (4 ml) under 1 atm N_2. Yield determined by ^{1}H NMR spectroscopy using 1,3,5 trimethoxybenzene as an internal standard.

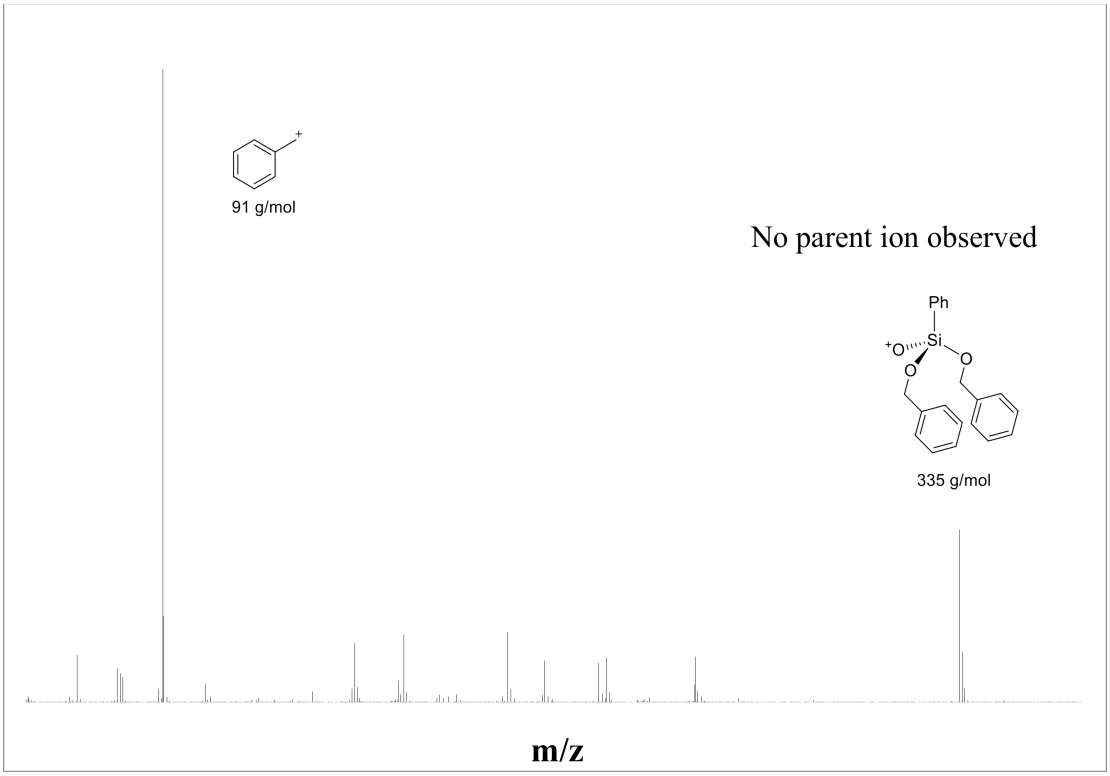
Mechanistic experiments:

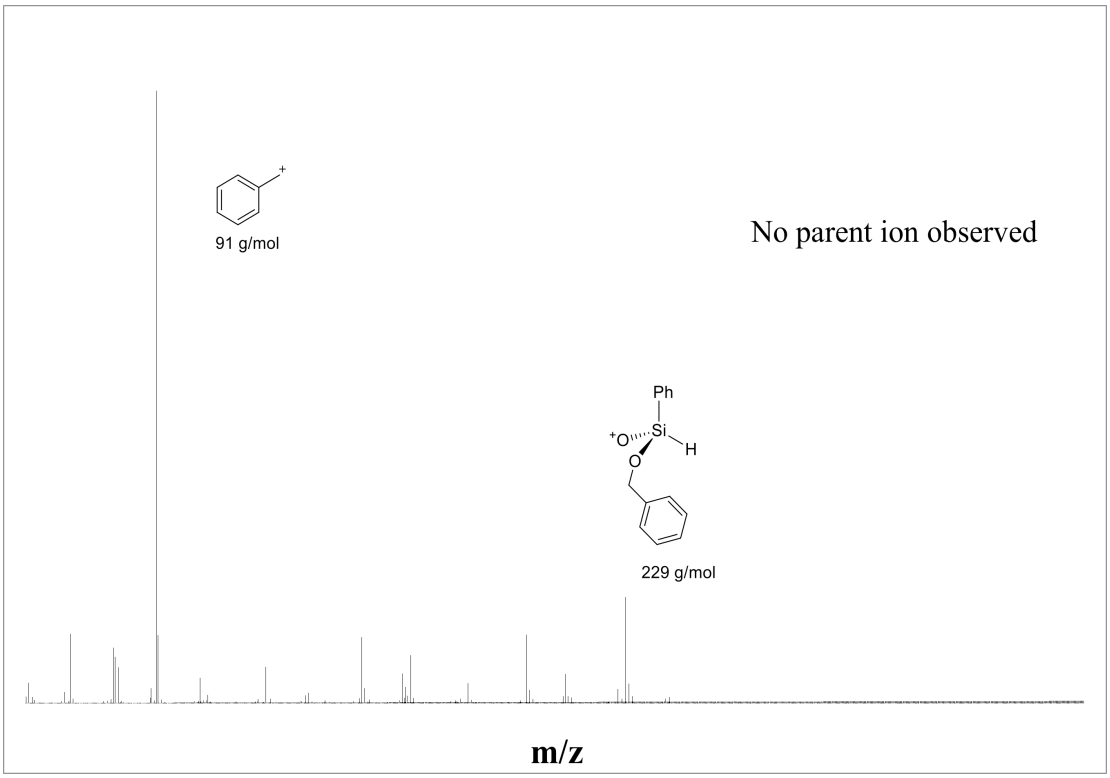
Lithium benzyloxide synthesis. To a 100 ml schlenk flask containing a stir bar under a nitrogen atmosphere was added dry THF (20 ml) and dry benzaldehyde (1.35 ml, 0.013 mmol) via syringe. $LiBH_4$ in THF (3.25 ml of a 2 M solution) was added drop wise via syringe to this stirring solution. The exothermic reaction proceeded nearly instantaneously producing a white precipitate. The solution was allowed to stir at room temperature for 10 minutes. The precipitate was then filtered in air and washed thoroughly with dry THF and dry pentane. The colorless white powder was dried under reduced pressure and stored in a sealed vial in a desiccator until it was used. ^{1}H NMR (400 MHz, dmso) δ 7.35 (d, *J*=7.3 Hz, 2H), 7.22 (t, *J*=7.5 Hz, 2H), 7.09 (t, *J*=7.3 Hz, 1H), 4.53 (s, 1H).

*The lithium benzyloxide salt yielded benzyl alcohol after addition of a small amount of water. The benzyl alcohol ^{1}H NMR spectrum matched that of a commercially available sample. No evidence for any residual borane was found in the ^{1}H NMR. Small quantities of residual THF were found in the NMR even after exposing the sample to vacuum over long periods of time allowing for the possibility that THF is incorporated into the solid state structure of the salt.

Lithium benzyloxide initiated hydrosilylation. To a flame dried 15 ml Schlenk tube under nitrogen was added a stir bar 1,3,5-trimethoxybenzene (26.5 mg, internal ^{1}H NMR standard) and lithium benzyloxide (15.1 mg, .132 mmol). Dried and N_2 sparged THF (4 ml) was added to the sealed Schlenk tube via syringe. Benzaldehyde (134 μl, 1.32 mmol), $LiHBEt_3$, 1 M in THF (66 μl, 0.066 mmol) and $SiPhH_3$ (54.0 μl, 0.44 mmol) were then added by syringe in the order listed. The reaction was allowed to stir at RT 1 hour. After the allotted time, the reaction was stopped by the addition of base and methanol (4 ml of 1:1 2 M aqueous KOH + MeOH). The reaction was allowed to stir in air for 2 additional hours at RT. Additional water was added to the solution (4 ml) and then the mixture was extracted with diethyl ether. The organic layers were collected and dried over sodium sulfate. The solvent was removed in vacuo and the resulting liquid was taken up in $CDCl_3$. The yield was determined by comparative integration of the product and starting material peaks to the internal standard in the ^{1}H NMR spectrum and account was taken for benzyl alcohol formed from the protonation of the alkoxide.

GC/MS spectra of silyl ethers formed from the reaction of $SiPhH_3$, benzaldehyde, and $NaBH_4$ catalyst.





Characterization of products.

All reduction products are either commercially available or previously reported in the literature. NMR spectra of all reduced compounds matched published spectra. The identity of most products was also verified by comparing with purchased authentic compound. ^{1}H NMR spectra of representative reactions are given below.

Heterocycles.

1,2,3,4-tetrahydro- and 1,2,3,4,7,8,9,10-octahydro-1,10 phenanthroline[1]

9,10-dihydroacridine[2]

1,2,3,4 tetrahydroquinoxaline[3]

1,2,3,4 tetrahydroquinoline, 2-methyl-1,2,3,4-tetrahydroquinoline, 2-phenyl-1,2,3,4 tetrahydroquinoline, 1,2,3,4 tetrahydroisoquinoline[4]

Amines.

N-Benzylaniline[5]

Diphenylmethanamine[6]

1-Benzylpiperidine[7]

N,N-Dimethylbenzylamine[8]

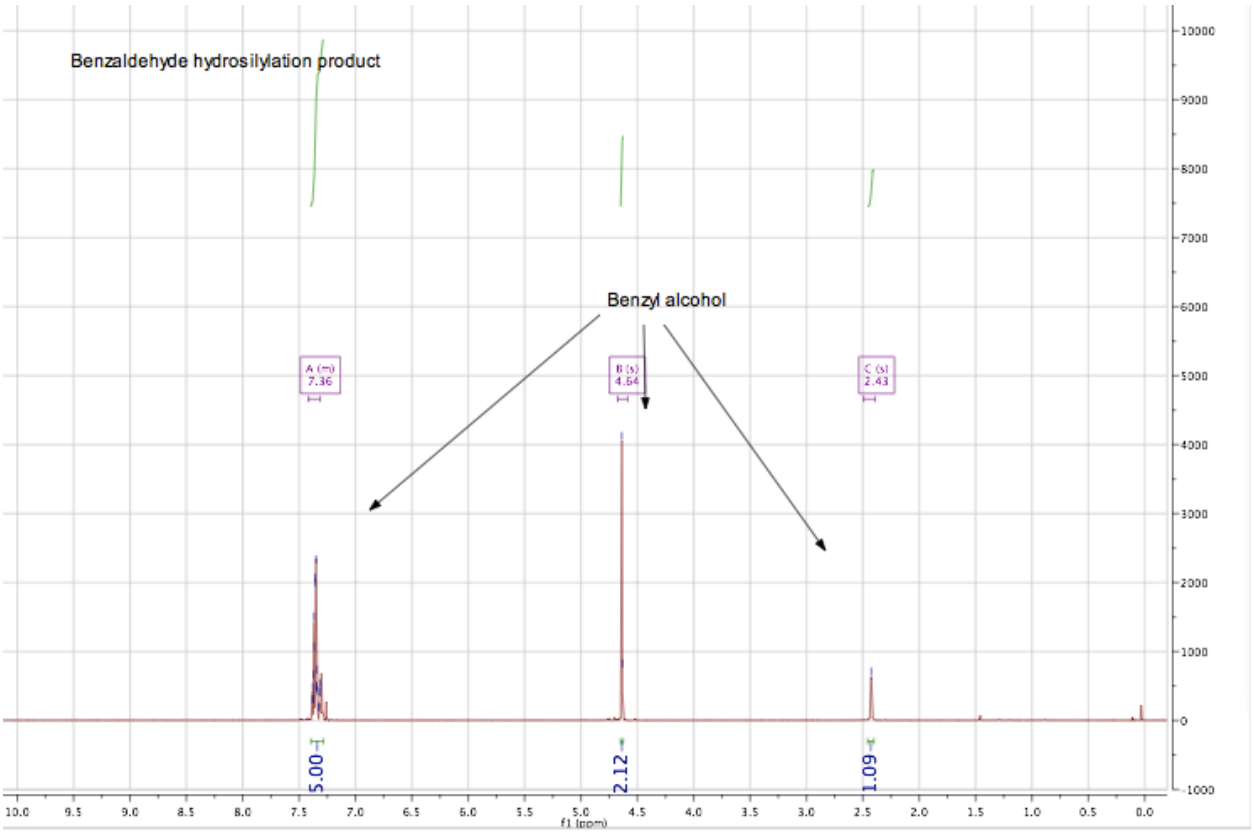
Alcohols.

Benzyl alcohol, 4-Nitrophenylmethanol, 4-Chlorophenylmethanol, 4-Methoxyphenylmethanol, 1-Phenylethanol, 1-(4'-Nitrophenyl)ethanol, 1-(4'-Chlorophenyl)ethanol, 1-(4'-Methoxyphenyl)ethanol and Cinnamyl alcohol[9]

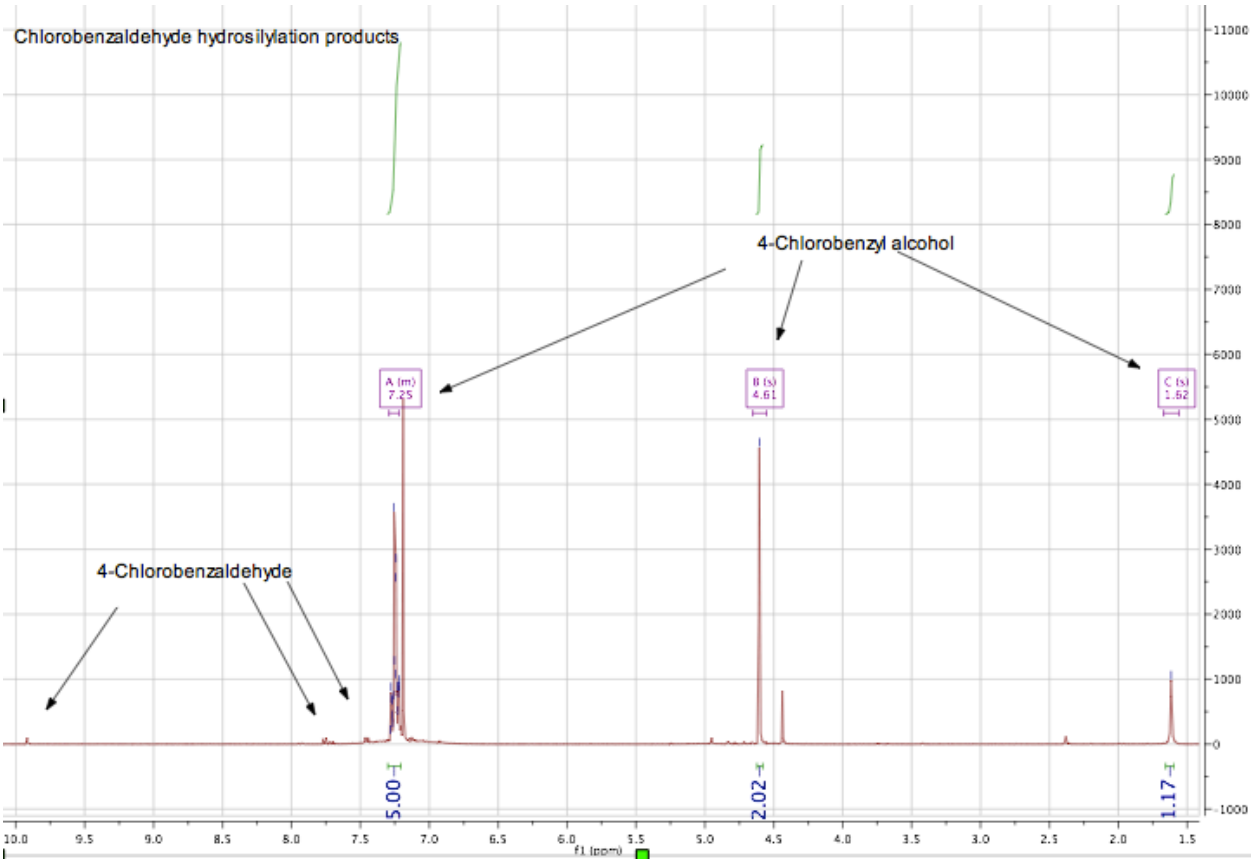
Cyclopentanol[10]

Hexyl alcohol - compared with purchased sample

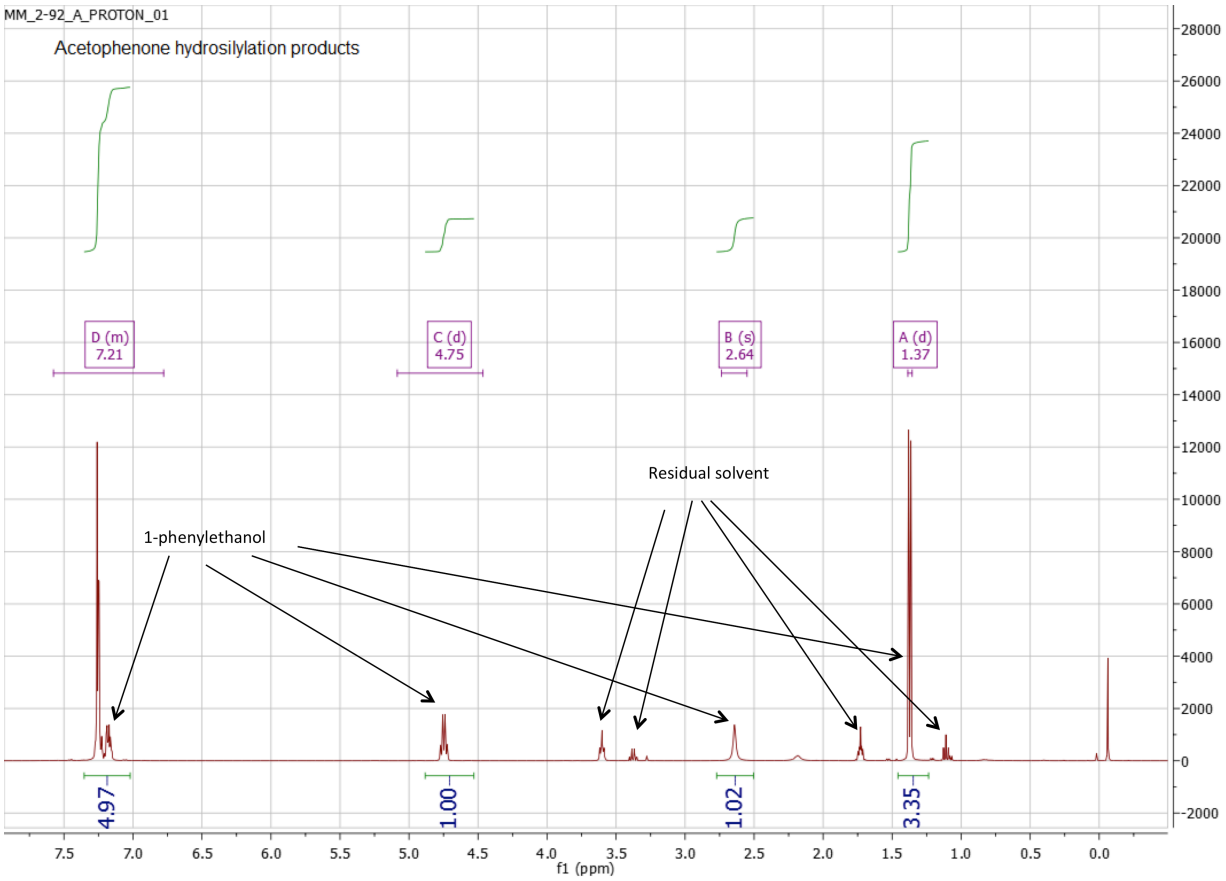
^{1}H NMR spectrum of hydrosilylation products of benzaldehyde under optimized conditions with $NaBH_4$ and $SiPhH_3$ after basic workup.



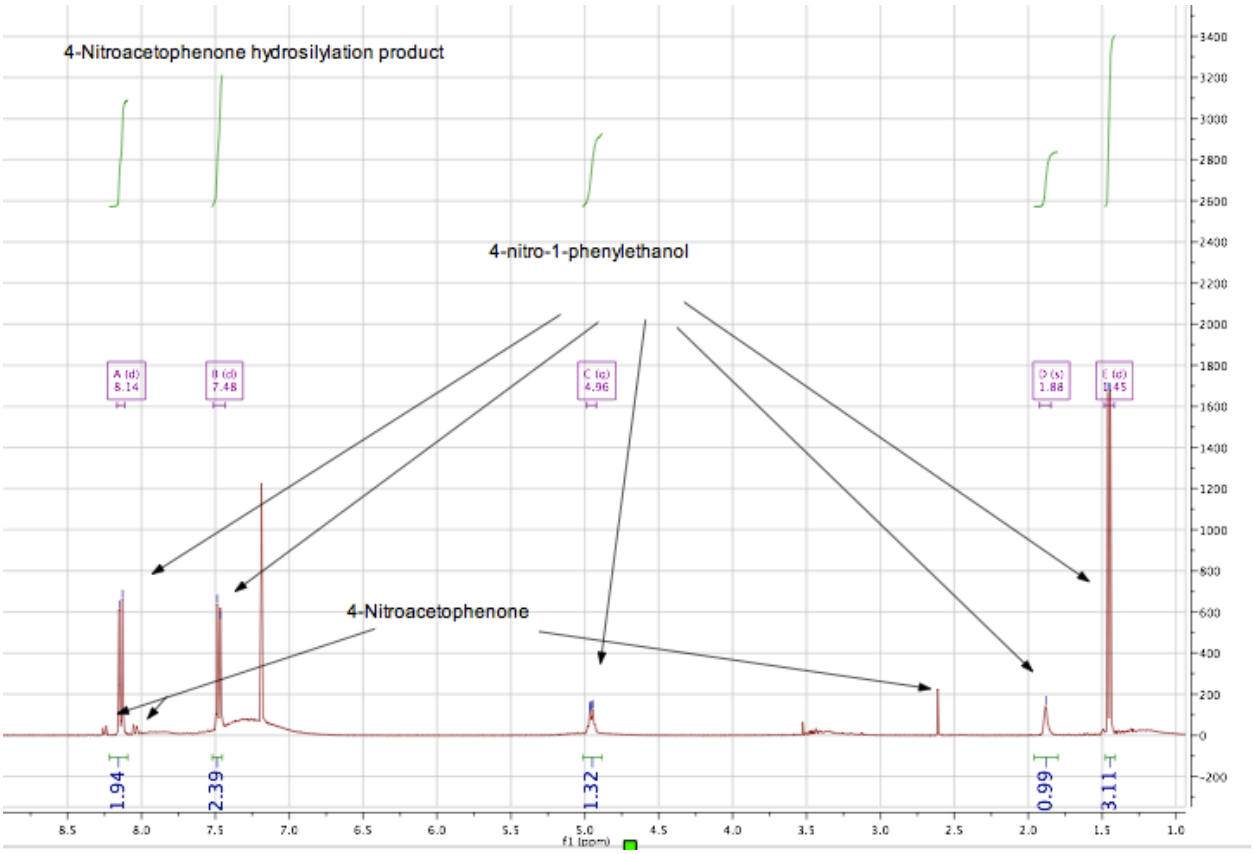
^{1}H NMR spectrum of hydrosilylation products of 4-chlorobenzaldehyde under optimized conditions with $LiHBEt_3$ and $SiPhH_3$ after basic workup.



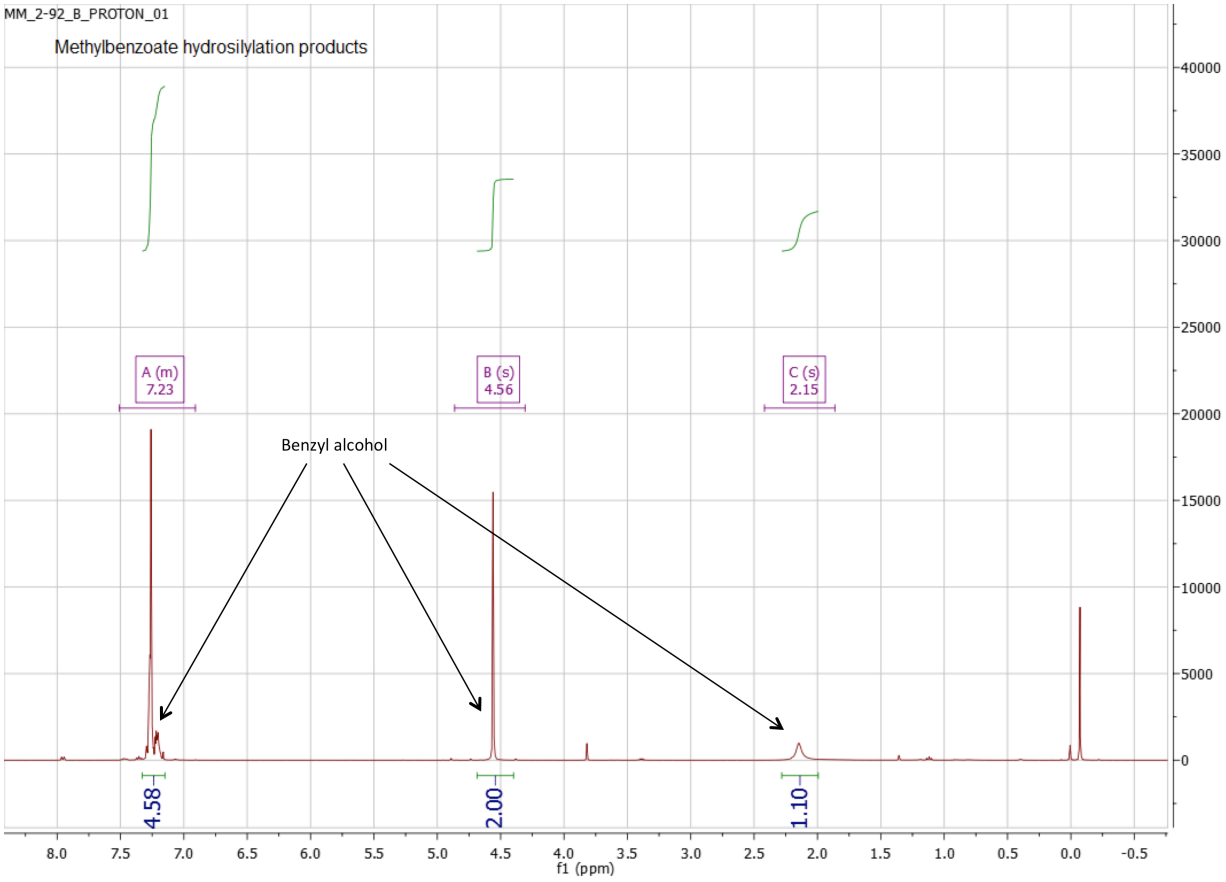
^{1}H NMR spectrum of hydrosilylation products of acetophenone under optimized conditions with $LiHBEt_3$ and $SiPhH_3$ after basic workup.



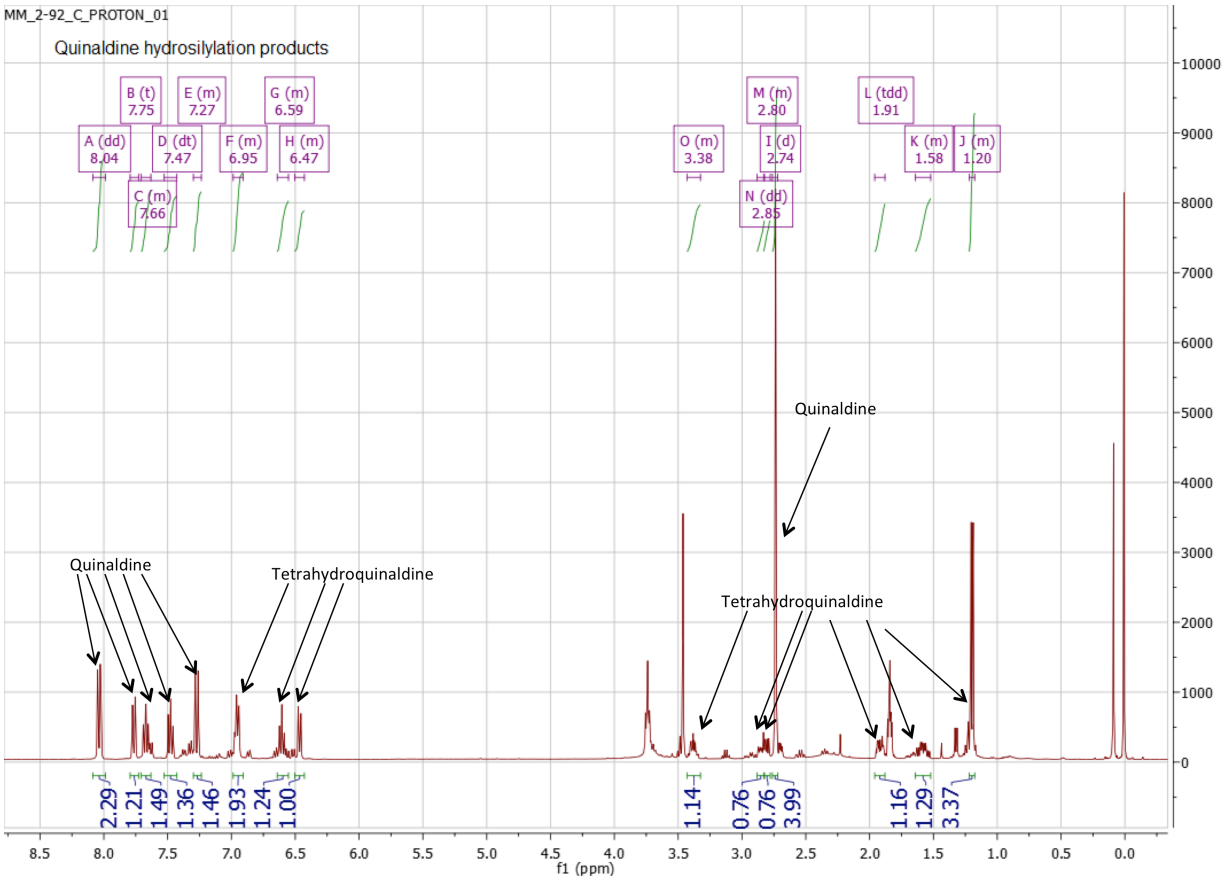
^{1}H NMR spectrum of hydrosilylation products of 4-Nitroacetophenone under optimized conditions with $NaBH_4$ and $SiPhH_3$ after basic workup.



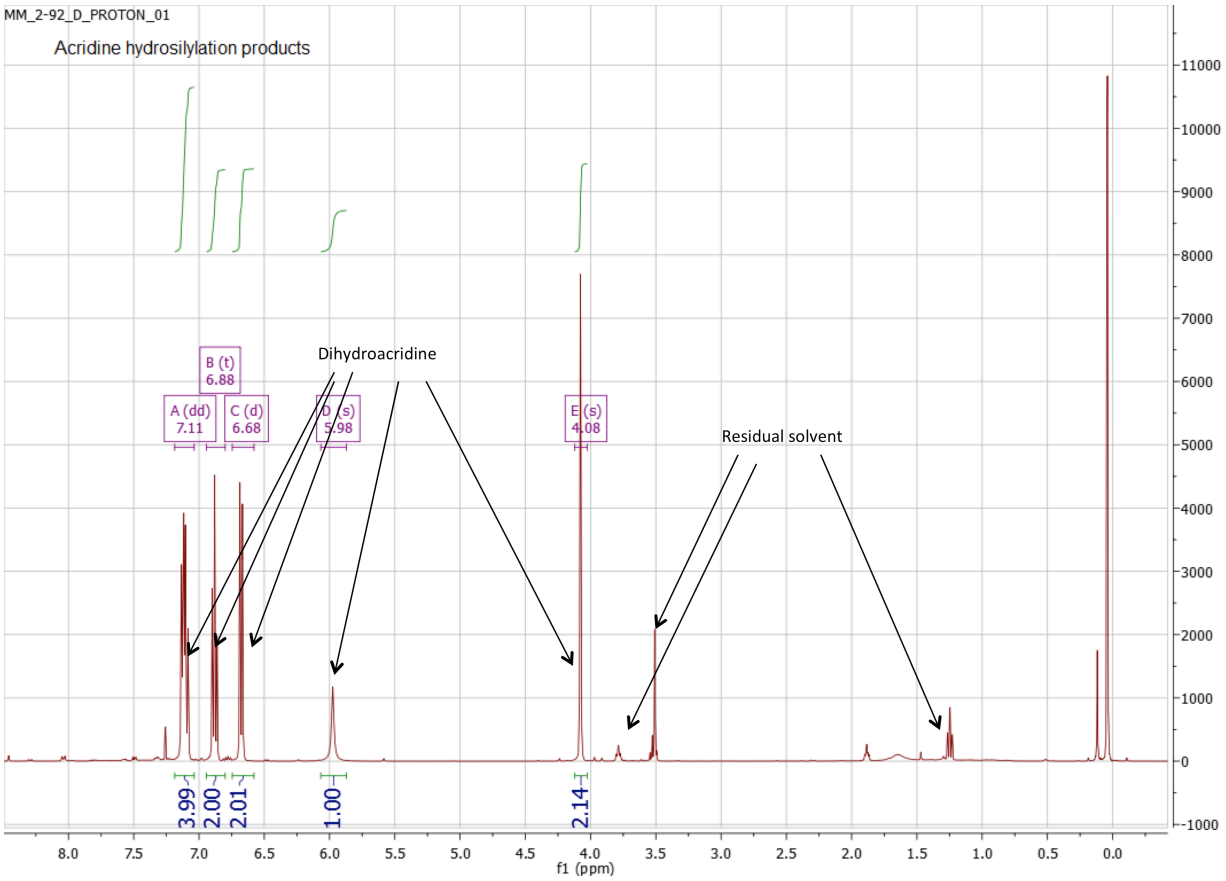
^{1}H NMR spectrum of hydrosilylation products of methylbenzoate under optimized conditions with $LiHBEt_3$ and $SiPhH_3$ after basic workup.



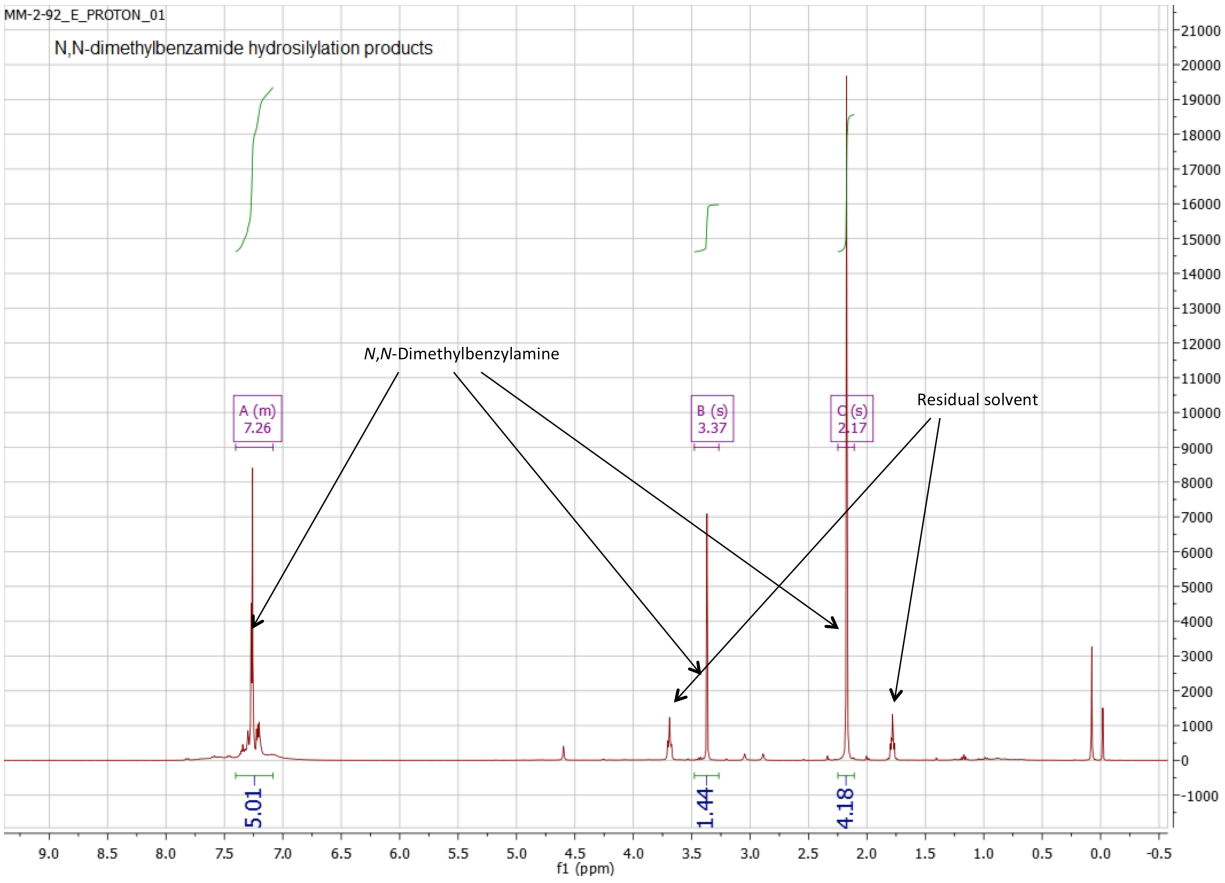
^{1}H NMR spectrum of hydrosilylation products of quinaldine under optimized conditions with $LiHBEt_3$ and PMHS after basic workup.



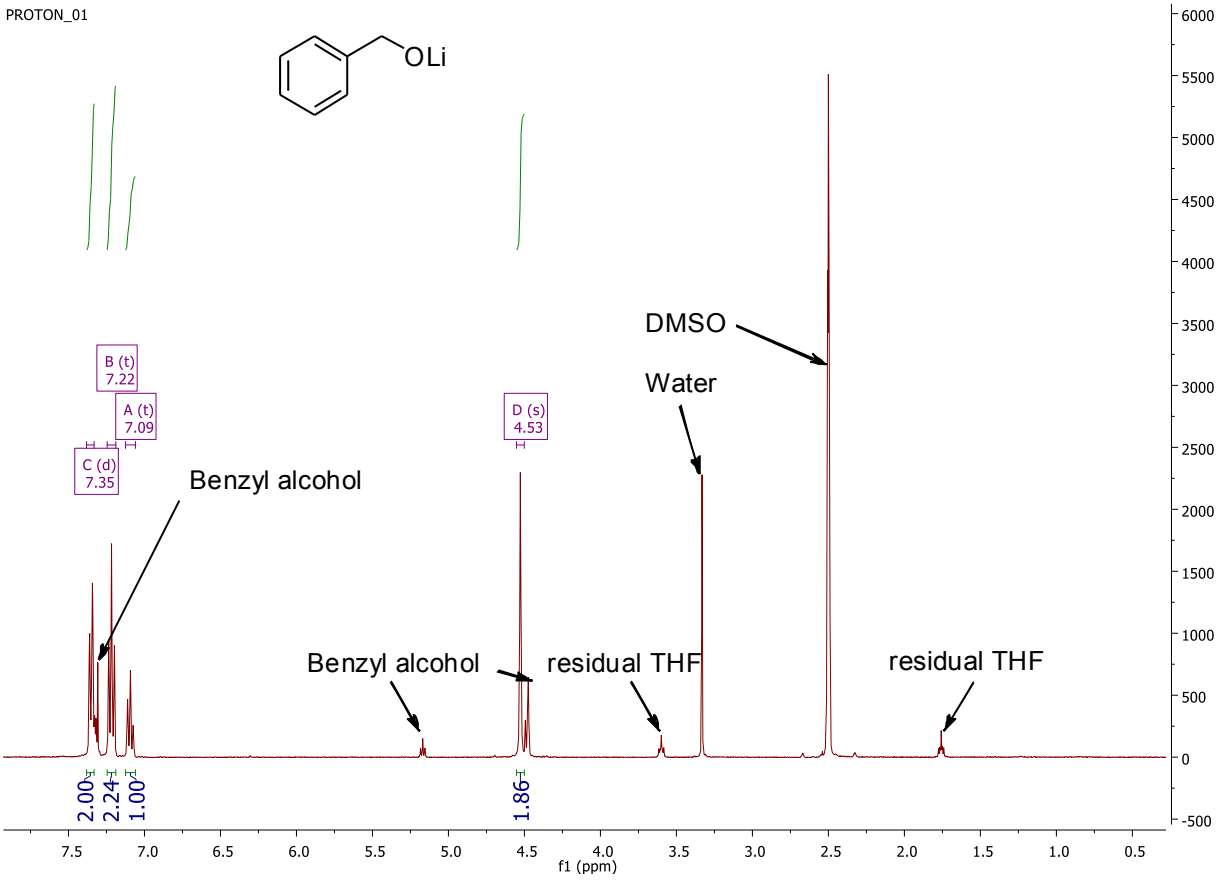
^{1}H NMR spectrum of hydrosilylation products of acridine under optimized conditions with $LiHBEt_3$ and $SiPhH_3$ after basic workup.



^{1}H NMR spectrum of hydrosilylation products of N,N-dimethylbenzamide under optimized conditions with $LiHBEt_3$ and $SiPhH_3$ after basic workup.



^{1}H NMR spectrum of lithium benzylalkoxide mechanistic intermediate



Computational Section

Optimized Cartesian coordinates (in Å) and energies (E, in hartrees) of all geometries reported in the text.

$NaBH_4$ E = -189.546376558

B	1.34616200	-0.00087800	0.00046800
H	0.91102400	1.13750900	-0.18250700
H	0.94270300	-0.72681100	-0.90915700
H	0.89973900	-0.42484400	1.06753900
H	2.55708900	0.01569700	0.02287200
Na	-1.09467000	0.00025800	-0.00009900

PhCHO E = -345.423845470

C	1.97853800	0.46018600	0.00023400
H	2.24696500	1.54072200	0.00052000
C	0.53154100	0.20098400	0.00014500
C	0.03607300	-1.10429100	0.00014300
C	-0.34815200	1.28209800	0.00003400
C	-1.32986400	-1.32106200	0.00004100
H	0.73498600	-1.93575600	0.00030100
C	-1.71773200	1.06321100	-0.00010800
H	0.05145000	2.29391800	0.00001700
C	-2.20543400	-0.23732900	-0.00011000
H	-1.72185600	-2.33349200	0.00010300
H	-2.40550900	1.90306600	-0.00024200
H	-3.27762100	-0.41093300	-0.00020100
O	2.83772100	-0.39003800	-0.00034800

$SiPhH_3$ E = -522.808067715

Si	2.33854800	0.00014900	0.00383800
H	2.86718200	-0.23865400	1.36914400
H	2.83072700	1.31567900	-0.46805400
H	2.83655400	-1.07840400	-0.88210000
C	0.46288800	0.00255200	-0.00792700
C	-0.25306200	-1.19449100	-0.10857100
C	-0.25609700	1.19695700	0.09505900
C	-1.64143400	-1.19962000	-0.09911200
H	0.27872800	-2.14011400	-0.20134600
C	-1.64508500	1.19618500	0.10415900
H	0.27283000	2.14569300	0.16761200
C	-2.33922900	-0.00294100	0.00779200

H	-2.18083000	-2.13911900	-0.18098200
H	-2.18719400	2.13426000	0.18442600
H	-3.42547500	-0.00501800	0.01204400

$PhCH_2OSiPhH_2$ E = -868.278754324

Si	-1.13272500	1.63844100	-0.11765700
H	-1.12371000	2.39022200	-1.39795100
H	-1.19155000	2.58494400	1.02347100
C	-2.55560800	0.44242800	-0.04234400
C	-3.28946100	0.26394800	1.13374400
C	-2.89675200	-0.31953500	-1.16466200
C	-4.33174900	-0.65263000	1.18963800
H	-3.04573600	0.84758400	2.01951600
C	-3.93669500	-1.23695500	-1.11208800
H	-2.34426900	-0.19438800	-2.09469000
C	-4.65367000	-1.40402600	0.06695900
H	-4.89300500	-0.78189500	2.11062400
H	-4.19070800	-1.82276400	-1.99083400
H	-5.46833100	-2.12145600	0.10946200
O	0.26692100	0.74387000	-0.03006900
C	1.52964200	1.35477700	-0.13056300
H	1.65561100	2.11421200	0.65993000
H	1.62110200	1.89103400	-1.09081100
C	2.63739600	0.34752200	-0.02330900
C	3.95686800	0.79807900	-0.03209200
C	2.38780200	-1.01540800	0.07707900
C	5.00950900	-0.09948600	0.05605300
H	4.15556500	1.86585800	-0.10829000
C	3.44397400	-1.91657200	0.16632400
H	1.36124000	-1.36641100	0.08538000
C	4.75515200	-1.46390300	0.15579400
H	6.03310000	0.26425700	0.04872200
H	3.23698700	-2.98039700	0.24428500
H	5.57804300	-2.16937300	0.22573800

$SiPhH_4Na$ E = -685.666581296

Si	-0.71382000	2.52945100	-0.17773000
H	-1.71875300	1.67573200	0.59550900
H	-0.65024200	2.57691700	-1.68201600
H	0.36059800	3.14152800	0.67320800
C	-1.91318800	4.10106200	-0.08734800
C	-2.43608900	4.53735300	1.13444200
C	-2.26216000	4.83735300	-1.22015600

C	-3.26409700	5.64958100	1.22715800
H	-2.19081900	3.98926900	2.04794400
C	-3.09120100	5.95439900	-1.14843900
H	-1.87560100	4.52888600	-2.19400800
C	-3.59432000	6.36472000	0.07952500
H	-3.65472600	5.96488800	2.19235800
H	-3.34496600	6.50730900	-2.05038100
H	-4.24144900	7.23548400	0.14410100
Na	-0.69073500	-0.39550700	0.74236100
H	0.25640000	1.14492700	-0.28229500

$PhCH_2ONa$ E = -508.339809221

O	0.23738900	1.24936700	-0.21019800
C	1.36417300	1.95861400	0.06960600
H	1.34891900	2.43003200	1.08286800
H	1.54039600	2.80579500	-0.63780700
C	2.58907800	1.06616400	0.01032800
C	2.98145900	0.32321300	1.12512000
C	3.24394500	0.83649100	-1.20109200
C	4.00586900	-0.61299500	1.03719200
H	2.47555600	0.49218800	2.07501000
C	4.26904200	-0.09821900	-1.29590200
H	2.94303200	1.40892500	-2.07772000
C	4.65147400	-0.82774500	-0.17559400
H	4.30616000	-1.17428900	1.91830000
H	4.77492900	-0.25572400	-2.24504600
H	5.45458400	-1.55594300	-0.24559400
Na	0.41188300	-0.82026600	-0.64386200

$PhCH_2O(Na)SiPhH_3$ E = -1031.17128639

Si	-1.48752000	2.20499200	-0.00027200
H	-2.79579400	3.04477300	-0.00085400
H	-0.98891300	2.78091600	-1.29444900
H	-0.98958000	2.78158000	1.29385800
C	-2.39764900	0.52524200	-0.00007100
C	-2.70092500	-0.13647300	1.19635000
C	-2.70099700	-0.13663500	-1.19638300
C	-3.26752000	-1.40859800	1.20086600
H	-2.48187900	0.34469400	2.14920100
C	-3.26757000	-1.40877100	-1.20069700
H	-2.48203400	0.34441700	-2.14931400

C	-3.54444600	-2.05300500	0.00013700
H	-3.48907900	-1.90053500	2.14455100
H	-3.48916400	-1.90084500	-2.14430200
H	-3.97993400	-3.04800800	0.00021700
O	0.09464000	1.09196900	0.00037300
C	1.33329700	1.72084300	0.00047700
H	1.45301900	2.37328100	0.88771600
H	1.45294700	2.37367100	-0.88648900
C	2.41108900	0.67228800	0.00020100
C	2.87781500	0.13518600	1.19986200
C	2.87745200	0.13547600	-1.19973500
C	3.80052200	-0.90410600	1.20177900
H	2.51593100	0.54700600	2.14019200
C	3.80015600	-0.90381500	-1.20218300
H	2.51528500	0.54752300	-2.13985600
C	4.26509000	-1.42463200	-0.00033400
H	4.16396100	-1.30461800	2.14410400
H	4.16331600	-1.30409800	-2.14471300
H	4.99125700	-2.23244600	-0.00054200
Na	-0.12809700	-1.08463200	-0.00000900

BH_3 E = -26.5920800099

B	0.00010600	0.00000700	0.00000100
H	-0.67546200	0.97438600	-0.00000100
H	-0.50675200	-1.07177200	-0.00000100
H	1.18168400	0.09735100	-0.00000100

$PhCH_2O(Na)SiPhH_3 \cdot BH_3$ E = -1057.77970853

Si	-1.41795000	2.09038000	-0.12275700
H	-2.82521800	2.74360700	-0.24768600
H	-0.98763900	2.57513700	-1.48250000
H	-1.02190700	2.91188300	1.07151300
C	-2.21931700	0.35685000	0.11503800
C	-1.82365600	-0.54306700	1.10219500
C	-3.30525200	-0.02499300	-0.68051100
C	-2.44528400	-1.79742000	1.26495500
H	-0.98856100	-0.29648700	1.75574500
C	-3.94273300	-1.25618200	-0.54700100

H	-3.67328100	0.67103400	-1.43439100
C	-3.53413500	-2.13297200	0.43946200
H	-2.26047400	-2.37475500	2.16937900
H	-4.77026600	-1.51584800	-1.20011100
H	-4.02974000	-3.09056800	0.57094200
O	0.24694600	1.19982800	-0.00700400
C	1.39207300	1.99047600	0.08637200
H	1.40653800	2.55969900	1.03447300
H	1.43913500	2.73562200	-0.73131700
C	2.59114800	1.08632100	0.01196400
C	2.95754300	0.32686600	1.12521600
C	3.24854200	0.86516500	-1.19742000
C	3.96062200	-0.62908900	1.03153900
H	2.44285900	0.49084300	2.07033500
C	4.25500100	-0.09136500	-1.29401800
H	2.96387100	1.45000200	-2.07010500
C	4.60980300	-0.84167600	-0.18062400
H	4.23858700	-1.21078300	1.90579700
H	4.76150400	-0.25067500	-2.24176000
H	5.39342700	-1.58990000	-0.25469100
Na	0.69028800	-0.86572700	-0.70314800
B	-1.04780300	-2.85393100	0.27790500
H	-0.06289600	-2.57708900	0.91350700
H	-1.46072000	-3.96050300	0.44596900
H	-1.09790100	-2.44088800	-0.85111400

$PhCH_2O(Na)SiPhH_2 \cdot BH_4$ E = -1057.82736195

Si	1.22511600	-1.68280300	0.10186200
H	3.38388000	-2.63461300	0.23261500
H	1.29679600	-2.49653500	-1.12474700
H	1.31492000	-2.44720700	1.36088900
C	2.16479000	-0.06818800	0.09132400
C	2.48421100	0.57070200	1.29379200
C	2.42469300	0.59919100	-1.11067900
C	3.04827000	1.84148900	1.29568300
H	2.30194000	0.06574000	2.24111400
C	2.98804400	1.87010600	-1.11061900
H	2.20132300	0.11343500	-2.05924400
C	3.29696400	2.49230300	0.09342900
H	3.29999200	2.32222000	2.23660500
H	3.19456500	2.37226900	-2.05133500

H	3.74057800	3.48356800	0.09410600
O	-0.34040800	-0.99043300	0.09417300
C	-1.53252400	-1.76861400	0.06105700
H	-1.60122500	-2.39225100	0.96330800
H	-1.51574800	-2.43639700	-0.81320800
C	-2.68863200	-0.81897700	-0.01448200
C	-3.42879700	-0.49910000	1.12022300
C	-2.96630100	-0.16255100	-1.21548300
C	-4.43924900	0.45353200	1.05618700
H	-3.21378000	-1.00737500	2.05754800
C	-3.96847100	0.79609500	-1.27835700
H	-2.39574900	-0.41824600	-2.10701700
C	-4.70706200	1.10430000	-0.14068500
H	-5.01759000	0.68934300	1.94466700
H	-4.18238900	1.29632900	-2.21840800
H	-5.49608800	1.84881900	-0.19045600
B	4.41208600	-2.44136900	-0.42445100
H	5.08172600	-3.46716200	-0.39815900
H	5.02603100	-1.51026900	0.08415100
H	4.10590300	-2.15993700	-1.57667700
Na	-0.36995500	1.27328200	0.03806500

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