Supplementary Information

Reduction of Carbon Dioxide and Organic Carbonyls by Hydrosilanes Catalyzed by the Perrhenate Anion

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1. General Procedures

NMR spectra were recorded on a Bruker AVA400 spectrometer for ^{1}H (399.90 MHz); a Bruker AVA500 spectrometer ^{1}H (500.12 MHz), ^{13}C (125.76 MHz); a Bruker PRO500 spectrometer ^{1}H (500.23 MHz) or a Bruker AVA600 spectrometer ^{1}H (599.81 MHz). Mass spectrometry data was collected on a Bruker 12 T SolariX ESI spectrometer. All FT-IR spectra were recorded using JASCO 410 or JASCO 460 plus spectrometers.

All chemicals were purchased from Sigma-Aldrich and used as supplied without further purification. Deuterated solvents were purchased from Cambridge Isotopes. CO_2 was supplied by BOC gases UK, labelled $^{13}CO_2$ from Cambridge Isotopes. Elemental analysis was performed by Mr. Stephen Boyer at the London Metropolitan University, measured in duplicate.

2. Synthesis of $[N(hexyl)_4][ReO_4]$

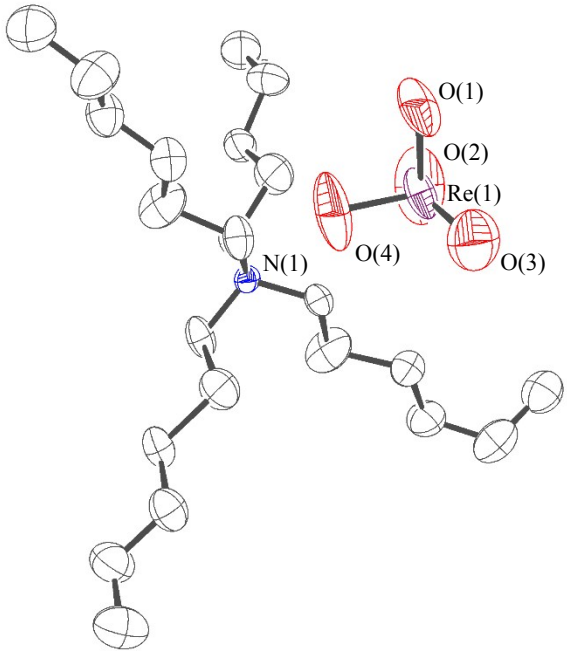


Figure S1. ORTEP representation of $[N(Hexyl)_4][ReO_4]$ with displacement ellipsoids drawn at 50%, disordered atoms and hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (◦): Re-O(1)/(4) 1.741(10), Re-O(2) 1.450 (19), Re-O(3) 1.854 (17), O(1)-Re(1)-O(2) 78.0(9), O(2)-Re(1)-O(3) 102.0(9), O(3)-Re(1)-O(4) 153.5(12). Symmetry transformations used to generate equivalent atoms: [1]+X,1-Y,+Z; [2]-X,+Y,1-Z; [3]-X,1-Y,1-Z; [4]1-X,1-Y,1-Z; [5]1-X,+Y,1-Z.

An aqueous solution of ammonium perrhenate (1.26 g, 4.7 mmol) was added to a chloroform solution of tetrahexylammonium bromide (2.00 g, 4.6 mmol) and stirred together for 6 hours at room temperature at which point the two layers were separated, the aqueous layer was extracted with chloroform (2 x 10 mL). The combined chloroform extracts were dried over magnesium sulphate and the solvent removed under reduced pressure to provide a colourless solid of tetrahexylammonium perrhenate (2.10 g, 75 % yield).

^{1}H NMR (500 MHz; d_3-MeCN, 300 K): δ_H (ppm) 3.07 (m, 8H, NCH_2), 1.60 (m, 8H, CH_2), 1.33 (m, 24H, CH_2), 0.91 (t, 12H, CH_3).

$^{13}C\{^{1}H\}$ NMR (500 MHz; d_3-MeCN, 300 K): δ_C (ppm) 59.48 (NCH_2), 31.84 (CH_2), 26.57 (CH_2), 26.57 (CH_2), 23.10 (CH_2), 22.34 (CH_2), 14.21 (CH_3).

FTIR (ATR): υ_{max}/cm^{-1} 902 (Re-O).

ESI mass spectrometry: M^+ m/z found (calculated): 354.41068 (354.40943 $C_{24}H_{52}N_2$), 959.77918 (959.75512 $(C_{24}H_{54}N)_2ReO_4$), 1565.16124 (1565.10132 $(C_{24}H_{54}N)_3(ReO_4)_2$). M^- m/z found (calculated): 250.93270 (250.93597 ReO_4), 854.26749 (854.27860 $(C_{24}H_{52}N)(ReO_4)_2$), 1459.59185 (1459.62427 $(C_{24}H_{52}N)_2(ReO_4)_3$) 2064.90770 (2064.97026 $(C_{24}H_{52}N)_3(ReO_4)_4$).

Elemental analysis for $C_{24}H_{52}NO_4Re$ found (calc.); C: 47.55 % (47.65), H: 8.72 % (8.67), N: 2.38 % (2.32).

3. General Procedure for catalytic reactions of silanes with CO_2

$[N(hexyl)_4][ReO_4]$ (3 mg, 2.5 mol %) in 0.6 mL d-solvent, silane (0.2 mmol) and trimethylphenylsilane (2 μL) as an internal standard (unless otherwise stated) were added to a Teflon tapped NMR tube. The solution was freeze-pump-thaw degassed three times before being refilled with 1 bar of CO_2. The ^1H NMR spectrum was recorded and then the tube was placed in a preheated oil bath (80 °C). The reactions were monitored by ^1H NMR spectroscopy regularly until the silane was consumed. At this point the reaction was quenched with water (10 μL, 0.56 mmol), heated for 2 h and the ^1H NMR spectrum recorded.

4. General Procedure for catalytic *N*-methylation of amines with CO_2

$[N(hexyl)_4][ReO_4]$ (3 mg, 2.5 mol %) in 0.6 mL d-solvent, amine (0.2 mmol), silane (0.8 mmol) and trimethylphenylsilane (2 μL) as an internal standard (unless otherwise stated) were added to a Teflon tapped NMR tube. The solution was freeze-pump-thaw degassed three times before being refilled with 2 bar of CO_2. The ^1H NMR spectrum was recorded and then the tube was placed in a preheated oil bath (80 °C) for 2 hours.

5. General Procedure for catalytic reactions of aldehydes and ketones

$[N(hexyl)_4][ReO_4]$ (3 mg, 2.5 mol %) in 0.5 mL CD_3CN, phenylsilane (0.24 mmol), carbonyl (0.2 mmol) and trimethylphenylsilane (2 μL) as an internal standard were added to a NMR tube. The ^1H NMR spectrum was recorded and then the tube was placed in a preheated oil bath (80 °C). The reactions were monitored by ^1H NMR spectroscopy regularly until the silane or carbonyl was consumed. At this point the reaction was quenched with water (10 μL, 0.56 mmol), heated for 15 minutes and the ^1H NMR spectrum recorded.

6. Mechanistic Reactions

NMR reaction to rule out carbonate formation

$[N(hexyl)_4][ReO_4]$ (20 mg, 0.033 mmol) in 0.5 mL C_6D_6 was added to a Youngs tap NMR tube in a nitrogen filled glove box. The solution was freeze-pump-thaw degassed three times before being refilled with 1 bar of $^{13}CO_2$. The ^1H and ^{13}C NMR spectrum was recorded and monitored over time and with subsequent heating, no observed signs of reactivity by ^1H and ^{13}C NMR spectroscopy (Figure S20).

Stoichiometric reactions with varying equivalents of diphenylsilane

1 eq Ph_2SiH_2: $[N(hexyl)_4][ReO_4]$ (32 mg, 0.054 mmol) in 0.5 mL of C_6D_6, diphenylsilane (10 μL, 0.054 mmol) were added to a NMR tube. ^1H and ^{29}Si NMR spectra was recorded after addition and then the reaction mixture was heated for 16 hr 80 ^oC (Figure S22 & Figure S23).

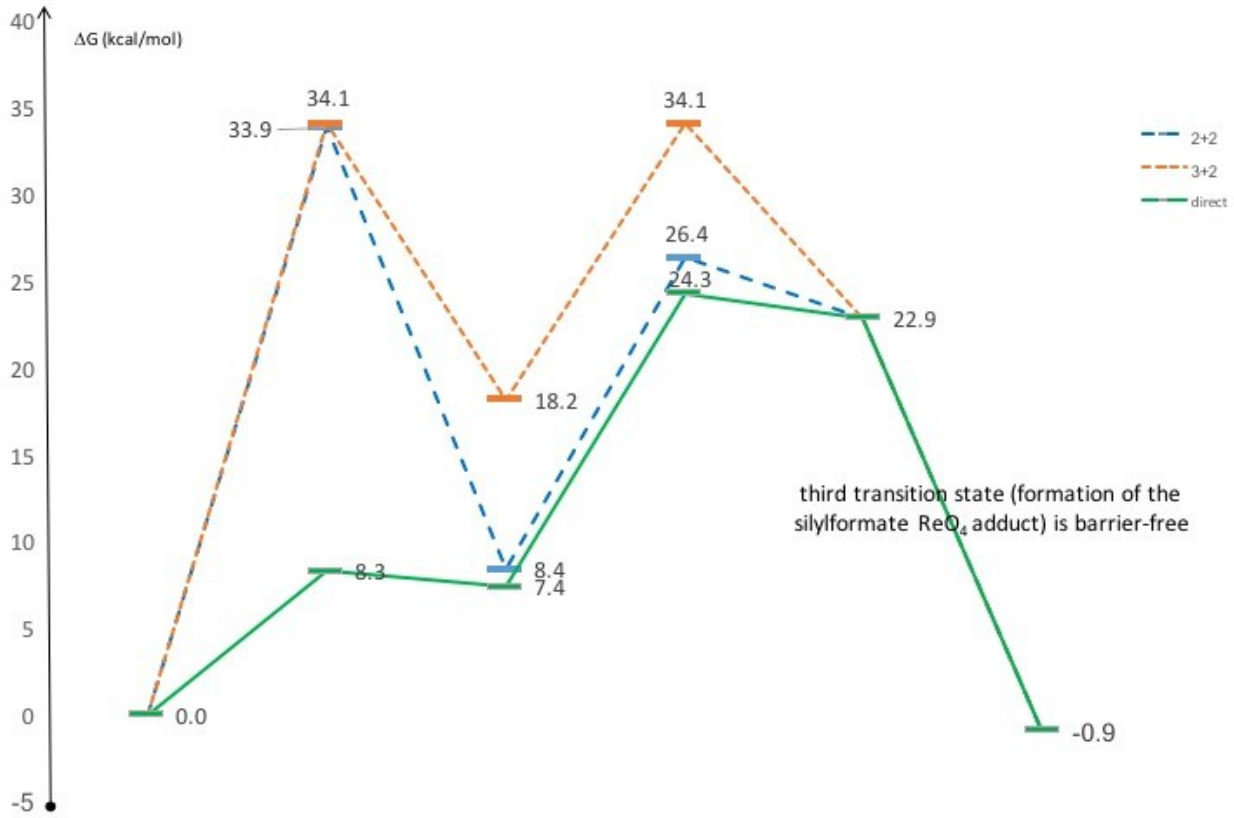
10 eq Ph_2SiH_2: [N(hexyl)$_4$][ReO_4] (16 mg, 0.026 mmol) in 0.5 mL of C_6D_6, diphenylsilane (50 µL, 0.26 mmol) were added to a NMR tube. ^{1}H NMR spectra was recorded after addition and then the reaction mixture was heated for 18 hr 80 ^{o}C (Figure S25).

7. DFT calculations

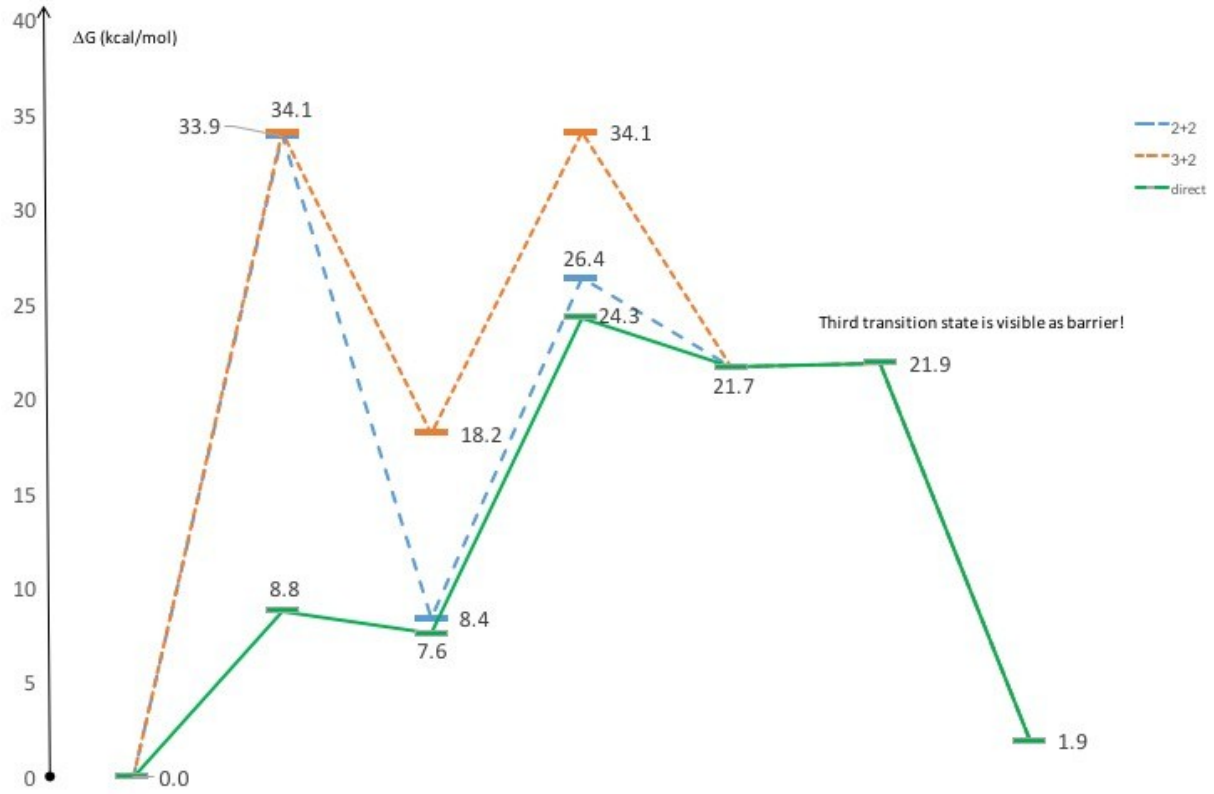
a. Solvent calculations

In addition to the gas-phase, SMD optimisations and frequency calculations for benzene and DMF have been performed.

Here are the free energy profiles for both solvents similar to Scheme 2 in the manuscript.



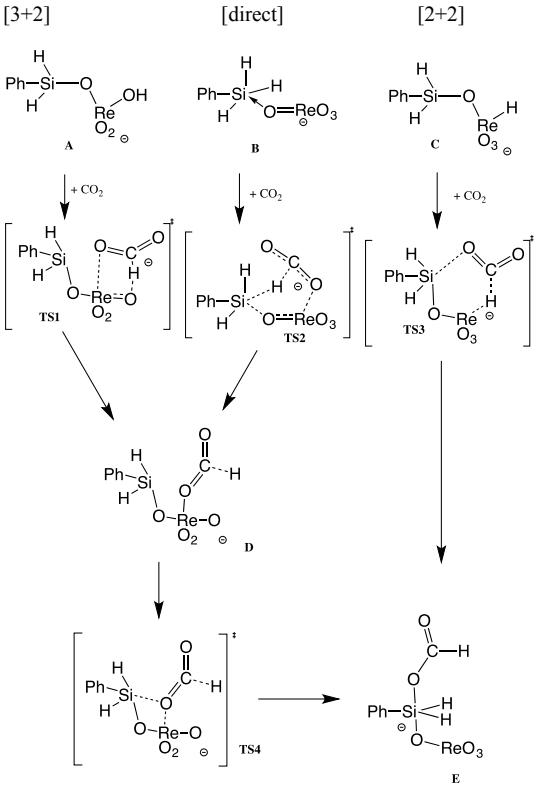
Scheme S1. Free energy profile in benzene



Scheme S2. Free energy profile in DMF

b. CO_2 cycloaddition as alternative pathway

The following scheme shows additional modes of CO_2 activation with higher barriers than that presented in the manuscript Scheme 2 / Figure 1.



Scheme S3. Cycloaddition modes of CO_2 to the catalyst/substrate complex

The calculated free energies are summarized in Table S1.

Table S1. Free Energies of the alternative CO_2 cycloadditions (gas-phase, benzene, DMF)

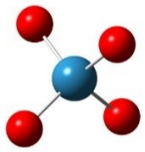
3+2	ΔG gas-phase	ΔG benzene	ΔG DMF	direct	ΔG gas-phase	ΔG benzene	ΔG DMF	2+2	ΔG gas-phase	ΔG benzene	ΔG DMF
A	13.9	18.2	18.2	**B**	1.8	7.4	7.6	**C**	2.9	8.4	10.6
TS1	36.1	42.7	---	**TS2**	30.0	37.4	40.1	**TS3**	20.1	27.8	31.2
D	-1.3	6.1	9.0	**D**	-1.3	6.1	9.0	**E**	-8.2	-0.9	1.9
TS4	6.3	13.9	19.1	**TS4**	6.3	13.9	19.1				
E	-8.2	-0.9	1.9	**E**	-8.2	-0.9	1.9				

c. Optimised structures (gas-phase) from Scheme 2

Note: Structures of the solvent calculations can be requested

a) Starting material

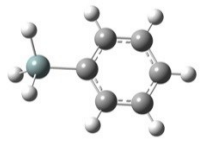
ReO_4^-



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	75	0	0.000038	0.000040	-0.000089
2	8	0	-0.714491	-0.151889	1.598142
3	8	0	-1.268813	-0.050472	-1.214756
4	8	0	0.860831	1.527858	-0.114161
5	8	0	1.122122	-1.325872	-0.268390

HF = -379.5150788
Sum of electronic and thermal Enthalpies= -379.497219
Sum of electronic and thermal Free Energies= -379.533196

$PhSiH_3$



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	-2.343937	0.000017	0.005621
2	1	0	-2.851264	-1.210737	-0.690236
3	1	0	-2.850528	1.219605	-0.675142
4	1	0	-2.870794	-0.008773	1.396627
5	6	0	-0.466162	0.000065	-0.012467
6	6	0	0.255226	-1.203197	-0.009676
7	6	0	0.255277	1.203218	-0.009700
8	6	0	1.648206	-1.205540	0.003254
9	1	0	-0.273189	-2.151097	-0.022068
10	6	0	1.648328	1.205462	0.003270
11	1	0	-0.273089	2.151129	-0.022061
12	6	0	2.347057	-0.000036	0.010245
13	1	0	2.187624	-2.145893	0.003684
14	1	0	2.187762	2.145804	0.003697
15	1	0	3.430997	-0.000108	0.017240

HF = -523.0569036
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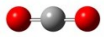
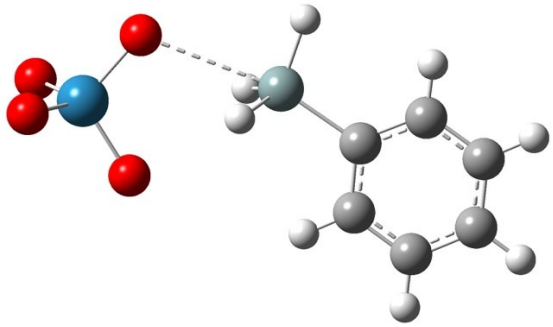
CO_2



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	8	0	0.000000	0.000000	1.160730
3	8	0	0.000000	0.000000	-1.160730

b) Pathway "Direct Addition of CO_2 to SiH"

TS "Forming of a $PhSiH_3$-ReO_4^- complex"



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.843811	-0.592053	0.000886
2	6	0	6.001970	0.791926	0.000574
3	6	0	4.874210	1.613386	-0.000255
4	6	0	3.599975	1.050591	-0.000765
5	6	0	3.416768	-0.342118	-0.000453
6	6	0	4.563590	-1.147849	0.000365
7	14	0	1.656612	-1.060433	-0.000769
8	8	0	-1.263964	-1.482441	-0.000475
9	75	0	-2.084478	0.077142	0.000093
10	8	0	-3.085202	0.221391	-1.433453
11	8	0	-0.861841	1.339172	-0.000242
12	8	0	-3.083975	0.220986	1.434535
13	1	0	1.816724	-2.539716	-0.001869
14	1	0	0.998337	-0.595109	-1.235950
15	1	0	0.998720	-0.597039	1.235359
16	1	0	2.731053	1.702293	-0.001371
17	1	0	4.456434	-2.228401	0.000598
18	1	0	4.988846	2.692428	-0.000493
19	1	0	6.715768	-1.238408	0.001525
20	1	0	6.995318	1.228240	0.000977

HF = -902.5834017 / NImag=1 (-28.5655 cm-1)
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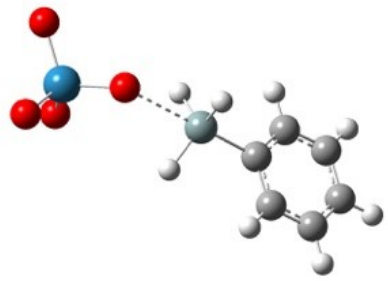
Sum of electronic and thermal Free Energies= -902.499892

$PhSiH_3$-ReO_4^- complex



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.704687	-1.214996	-0.196790
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3	6	0	-5.724618	1.192572	-0.211244
4	6	0	-4.349574	1.199020	0.022293
5	6	0	-3.620079	0.008294	0.157601
6	6	0	-4.330226	-1.196073	0.036391
7	14	0	-1.743753	0.023148	0.533167
8	8	0	0.823078	0.043843	1.035207
9	75	0	2.216800	-0.001683	-0.050325
10	8	0	3.179195	1.447630	0.165425
11	8	0	1.641942	-0.085440	-1.703757
12	8	0	3.194071	-1.413115	0.305058
13	1	0	-1.648246	-0.060965	2.009711
14	1	0	-1.270940	1.317213	-0.003540
15	1	0	-1.216629	-1.178366	-0.147662
16	1	0	-3.832345	2.151385	0.095539
17	1	0	-3.798050	-2.139401	0.120612
18	1	0	-6.261886	2.130119	-0.313451
19	1	0	-6.226613	-2.162326	-0.287671
20	1	0	-7.476846	-0.027379	-0.505432

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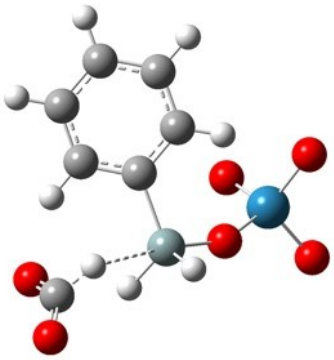
TS CO_2 attack on Si-H



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.932794	1.213564	-0.546320
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4	6	0	-1.331319	3.145301	0.692192
5	6	0	-2.439322	3.533837	-0.059742
6	6	0	-3.236795	2.568533	-0.671710
7	14	0	-1.355406	-0.990987	0.351885
8	8	0	0.391250	-0.964038	0.313554
9	75	0	2.036613	-0.251193	-0.067598
10	8	0	2.025202	0.564312	-1.590668
11	8	0	-4.393264	-1.439793	-1.014692
12	6	0	-4.527511	-1.896038	0.148122
13	8	0	-5.152009	-2.878853	0.573690
14	8	0	3.210581	-1.521411	-0.121531
15	8	0	2.487318	0.878480	1.165306

16	1	0	-1.591095	-1.591362	1.679096
17	1	0	-1.720005	-1.846793	-0.782138
18	1	0	-3.566415	0.447176	-0.993386
19	1	0	-0.158112	1.514171	1.415144
20	1	0	-4.104660	2.868206	-1.249353
21	1	0	-0.707557	3.890179	1.174124
22	1	0	-2.680215	4.586658	-0.164917
23	1	0	-3.970010	-1.300381	0.952843

HF = -1091.2252186
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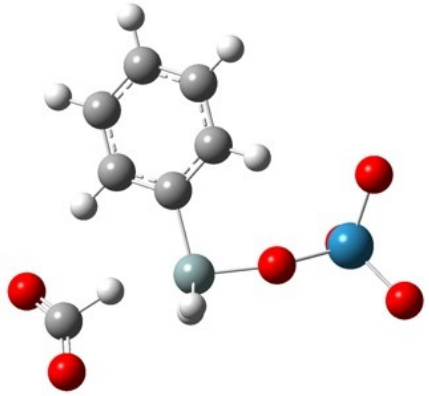
Sum of electronic and thermal Free Energies= -1091.133960

$PhSiH_3$-O-ReO_3 complex plus HCO_2^-



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.125570	1.128334	-0.447256
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3	6	0	-1.152425	1.835982	0.745932
4	6	0	-1.546702	3.166268	0.618933
5	6	0	-2.727580	3.481774	-0.049874
6	6	0	-3.513472	2.460409	-0.580603
7	14	0	-1.378647	-0.999117	0.372109
8	8	0	0.406569	-0.696670	0.524773
9	75	0	2.043478	-0.181435	-0.077039
10	8	0	3.245761	-1.305914	0.469486
11	8	0	-4.918968	-1.573802	-0.729703
12	6	0	-4.141774	-2.178846	0.005220
13	8	0	-4.059075	-3.280457	0.529055
14	8	0	2.416297	1.395706	0.543734
15	8	0	2.064052	-0.127642	-1.808085
16	1	0	-1.493070	-1.693966	1.669283
17	1	0	-1.300223	-1.802841	-0.864373
18	1	0	-3.767636	0.345984	-0.840235
19	1	0	-0.226273	1.615188	1.261989
20	1	0	-4.438170	2.696820	-1.096127
21	1	0	-0.927069	3.952436	1.036624
22	1	0	-3.033732	4.517471	-0.155144
23	1	0	-3.181562	-1.468438	0.294911

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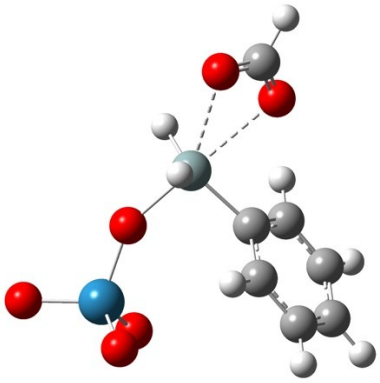
TS HCO_2 addition to Si



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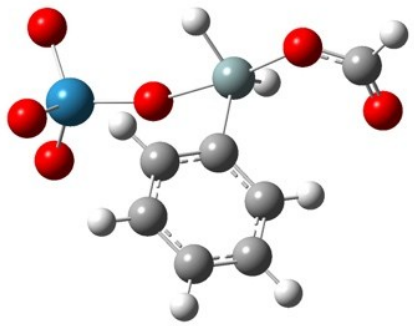
4	6	0	1.799802	0.695578	-0.116877
5	6	0	1.208750	1.399249	-1.175308
6	6	0	1.166194	2.792645	-1.180522
7	14	0	1.647878	-1.181218	-0.117661
8	8	0	3.663942	-2.599028	-0.707471
9	6	0	4.417366	-1.924468	0.030668
10	8	0	4.072460	-0.886608	0.643501
11	8	0	-0.221633	-1.135715	0.118091
12	75	0	-1.796961	-0.248821	0.066098
13	8	0	-2.082713	0.366759	-1.534399
14	8	0	-1.793847	1.073699	1.189819
15	8	0	-3.078904	-1.344724	0.489066
16	1	0	1.507916	-1.683323	-1.492496
17	1	0	1.793806	-1.995129	1.090265
18	1	0	2.851903	0.901361	1.741883
19	1	0	0.759887	0.858182	-2.002134
20	1	0	2.729777	3.372388	1.774714
21	1	0	0.697897	3.314839	-2.007884
22	1	0	1.667677	4.590922	-0.108631
23	1	0	5.466404	-2.272083	0.158017

HF= -1091.241079 / NImag = 1 (-232.1622 cm^{-1})
Sum of electronic and thermal Enthalpies= -1091.080118
Sum of electronic and thermal Free Energies= -1091.146416

Complex HCO_2-$PhSiH_3$-O-ReO_3



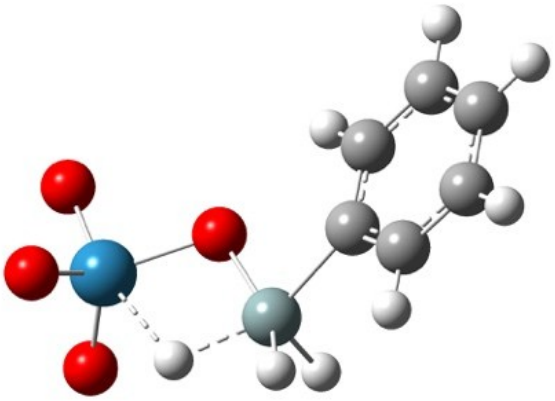
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.460297	2.309552	0.786414
2	6	0	3.111797	0.962535	0.691917
3	6	0	2.064392	0.547251	-0.143236
4	6	0	1.379981	1.524055	-0.881892
5	6	0	1.732007	2.869008	-0.795134
6	6	0	2.774324	3.266450	0.040716
7	14	0	1.568186	-1.264700	-0.280333
8	8	0	-0.344724	-0.693777	0.325509
9	75	0	-2.013180	-0.108656	0.077643
10	8	0	-2.688928	0.414465	1.597871

11	8	0	3.151498	-1.947316	-0.909923
12	6	0	4.221014	-2.234719	-0.220136
13	8	0	4.434831	-1.998757	0.954577
14	8	0	-2.995953	-1.389624	-0.582811
15	8	0	-1.993395	1.227645	-1.045041
16	1	0	0.880122	-1.661987	-1.522114
17	1	0	1.510317	-2.100628	0.931102
18	1	0	3.658223	0.225967	1.269188
19	1	0	0.546442	1.244647	-1.514990
20	1	0	4.269008	2.610808	1.444656
21	1	0	1.180761	3.605334	-1.370072
22	1	0	3.044824	4.314795	0.115498
23	1	0	4.974678	-2.749786	-0.845177

HF= -1091.2736863
Sum of electronic and thermal Enthalpies= -1091.110950
Sum of electronic and thermal Free Energies= -1091.177976

c) Pathway “2+2 addition”

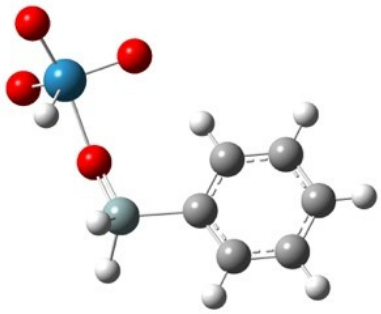
TS 2+2 addition of silane to perrhenate



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	0.954088	-1.236667	-0.427345
2	1	0	1.400849	-2.510208	0.287672
3	6	0	2.657043	-0.359176	-0.121156
4	6	0	2.887458	1.009771	-0.337555
5	6	0	3.754133	-1.138715	0.268542
6	6	0	4.156418	1.566971	-0.183406
7	1	0	2.050850	1.636139	-0.621173
8	6	0	5.029360	-0.593126	0.422687
9	1	0	3.599260	-2.197130	0.460754
10	6	0	5.234684	0.766483	0.195213
11	1	0	4.305580	2.628814	-0.355729
12	1	0	5.859051	-1.224627	0.726804
13	1	0	6.222485	1.199615	0.318064
14	8	0	0.120400	0.384827	-0.431514
15	75	0	-1.672406	0.086390	0.055604
16	8	0	-2.255012	1.723697	-0.036649
17	8	0	-1.952712	-0.413961	1.700694
18	8	0	-2.667066	-0.808348	-1.060577
19	1	0	-0.547765	-1.679222	0.022090
20	1	0	0.903473	-1.622234	-1.867529

HF=-902.5508573 / NImag = 1 (-262.7878 cm^{-1})
Sum of electronic and thermal Enthalpies= -902.409858
Sum of electronic and thermal Free Energies= -902.464345

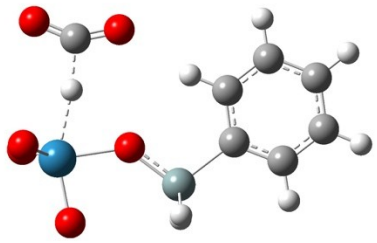
GS 2+2



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.886130	-1.292170	-0.050962
2	6	0	-5.130473	0.059020	0.196802
3	6	0	-4.066967	0.958798	0.236952
4	6	0	-2.745514	0.534758	0.035668
5	6	0	-2.516050	-0.827292	-0.213135
6	6	0	-3.578943	-1.730543	-0.255943
7	14	0	-1.289858	1.739104	0.104550
8	8	0	0.058540	1.053733	-0.455368
9	75	0	1.697788	-0.106932	0.050985
10	8	0	0.729164	-1.540035	-0.239246
11	8	0	2.967412	-0.724207	1.090872
12	8	0	2.590238	0.582210	-1.280399
13	1	0	1.368455	0.864725	1.389985
14	1	0	-1.168343	2.211733	1.523279
15	1	0	-1.681195	2.942364	-0.695699
16	1	0	-4.273239	2.009797	0.425254
17	1	0	-1.500817	-1.176140	-0.374537
18	1	0	-6.146299	0.408178	0.354423
19	1	0	-3.382205	-2.780232	-0.448498
20	1	0	-5.710827	-1.996995	-0.084944

HF=-902.5887063
Sum of electronic and thermal Enthalpies= -902.445832
Sum of electronic and thermal Free Energies= -902.502785

TS CO_2 activation of the Re-H bond



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.064964	0.792309	-0.000008
2	6	0	3.044431	-0.610061	-0.000008
3	6	0	4.266300	-1.298755	0.000005
4	6	0	5.478509	-0.612337	0.000018
5	6	0	5.485010	0.783047	0.000018
6	6	0	4.278785	1.480719	0.000005
7	14	0	1.403724	-1.526592	-0.000026
8	8	0	0.238092	-0.353354	-0.000017
9	75	0	-1.727782	-0.367075	0.000004
10	8	0	-1.637304	-2.127518	-0.000002
11	8	0	-2.611040	0.065181	-1.425731
12	8	0	-2.611001	0.065175	1.425765
13	8	0	0.417275	2.829107	-0.000028
14	6	0	-0.785276	2.762300	-0.000009
15	8	0	-1.816729	3.375571	0.000007
16	1	0	1.331103	-2.398982	-1.204080

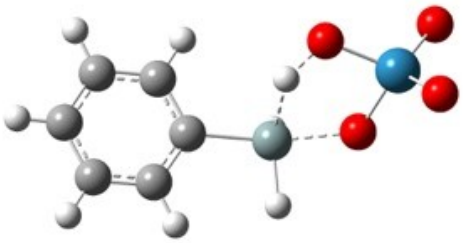
17	1	0	2.129820	1.341929	-0.000017
18	1	0	4.277138	-2.386039	0.000006
19	1	0	4.276180	2.565439	0.000005
20	1	0	6.414752	-1.161266	0.000029
21	1	0	6.427246	1.321440	0.000028
22	1	0	-1.086535	1.402788	-0.000005
23	1	0	1.331097	-2.399010	1.204007

HF=-1091.2240315 / NImag = 1 (-164.9744 cm^{-1})
Sum of electronic and thermal Enthalpies= -1091.067079
Sum of electronic and thermal Free Energies= -1091.135110

(final structures already shown under b)

d) Pathway “3+2 addition”

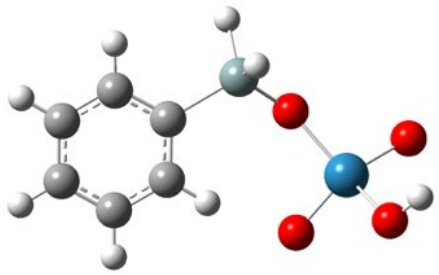
TS 3+2 addition of silane to perrhenate



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.414059	-1.080945	0.356490
2	6	0	-4.700787	-1.492101	0.017119
3	6	0	-5.634126	-0.561382	-0.443639
4	6	0	-5.263632	0.776944	-0.557806
5	6	0	-3.973137	1.177686	-0.205500
6	6	0	-3.020050	0.263862	0.266013
7	14	0	-1.225460	0.826087	0.765848
8	8	0	0.712368	1.059361	0.689186
9	75	0	1.930395	-0.068021	-0.086048
10	8	0	2.817120	0.689275	-1.386148
11	8	0	2.906405	-0.925517	1.080618
12	8	0	0.514084	-1.054860	-0.664836
13	1	0	-0.560675	-0.427000	-0.217431
14	1	0	-1.241848	0.530674	2.229550
15	1	0	-3.700711	2.225552	-0.295600
16	1	0	-2.694105	-1.822388	0.692781
17	1	0	-5.979544	1.508881	-0.920388
18	1	0	-4.976836	-2.538803	0.102982
19	1	0	-6.635553	-0.878534	-0.716062
20	1	0	-1.399005	2.287495	0.509240

HF=-902.5456326 / NImag = 1 (-983.3065 cm^{-1})
Sum of electronic and thermal Enthalpies= -902.406759
Sum of electronic and thermal Free Energies= -902.462836

GS 3+2 addition



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.834409	-1.225954	-0.050694

2	6	0	-5.050272	0.137275	0.151711
3	6	0	-3.963454	1.007277	0.214325
4	6	0	-2.647200	0.539304	0.086115
5	6	0	-2.445064	-0.835114	-0.118468
6	6	0	-3.533052	-1.706036	-0.187418
7	14	0	-1.191213	1.730491	0.208008
8	8	0	0.156677	1.128022	-0.484770
9	75	0	1.604627	-0.119103	-0.069743
10	8	0	0.697957	-1.595470	-0.440975
11	8	0	2.613615	-0.971467	1.383335
12	8	0	2.937549	0.911724	-0.603430
13	1	0	-0.973232	2.078019	1.643103
14	1	0	-1.601883	2.985369	-0.492101
15	1	0	-4.146947	2.069181	0.359660
16	1	0	-1.436261	-1.223192	-0.227254
17	1	0	-6.061128	0.519791	0.252944
18	1	0	-3.358300	-2.764684	-0.348596
19	1	0	-5.677074	-1.907947	-0.104598
20	1	0	3.179138	-0.333646	1.828739

HF=-902.5715894
Sum of electronic and thermal Enthalpies= -902.425969
Sum of electronic and thermal Free Energies= -902.485180

TS CO_2 attack on Re-OH

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.400378	-0.871749	1.034412
2	6	0	4.440211	-1.251420	0.187205
3	6	0	4.568900	-0.648575	-1.062413
4	6	0	3.659123	0.331502	-1.458082
5	6	0	2.623692	0.716540	-0.609706
6	6	0	2.482372	0.117154	0.653331
7	14	0	1.078956	0.603156	1.792037
8	8	0	-0.381104	0.407724	1.027457
9	75	0	-1.401591	-0.726113	-0.129474
10	8	0	-2.746200	-1.465363	0.685061
11	8	0	0.393403	3.000579	-0.771181
12	6	0	-0.766194	2.977761	-0.353023
13	8	0	-1.511331	3.708865	0.285618
14	8	0	-1.907622	0.694998	-1.098007
15	8	0	-0.456432	-1.820551	-1.086585
16	1	0	1.159083	2.006384	2.248801
17	1	0	1.150052	-0.303945	2.976183
18	1	0	1.918550	1.481964	-0.920021
19	1	0	3.298383	-1.358172	1.999942
20	1	0	3.753125	0.797372	-2.433087
21	1	0	5.139873	-2.021134	0.495963
22	1	0	5.372024	-0.946396	-1.728629
23	1	0	-1.353757	1.920914	-0.706336

HF= -1091.2103056 / NImag = 1 (-558.7799 cm^{-1})
Sum of electronic and thermal Enthalpies= -1091.053225
Sum of electronic and thermal Free Energies= -1091.119759

(final structures already shown under b)

8. NMR spectra

8.1 Hydrosilylation of CO_2 NMRs

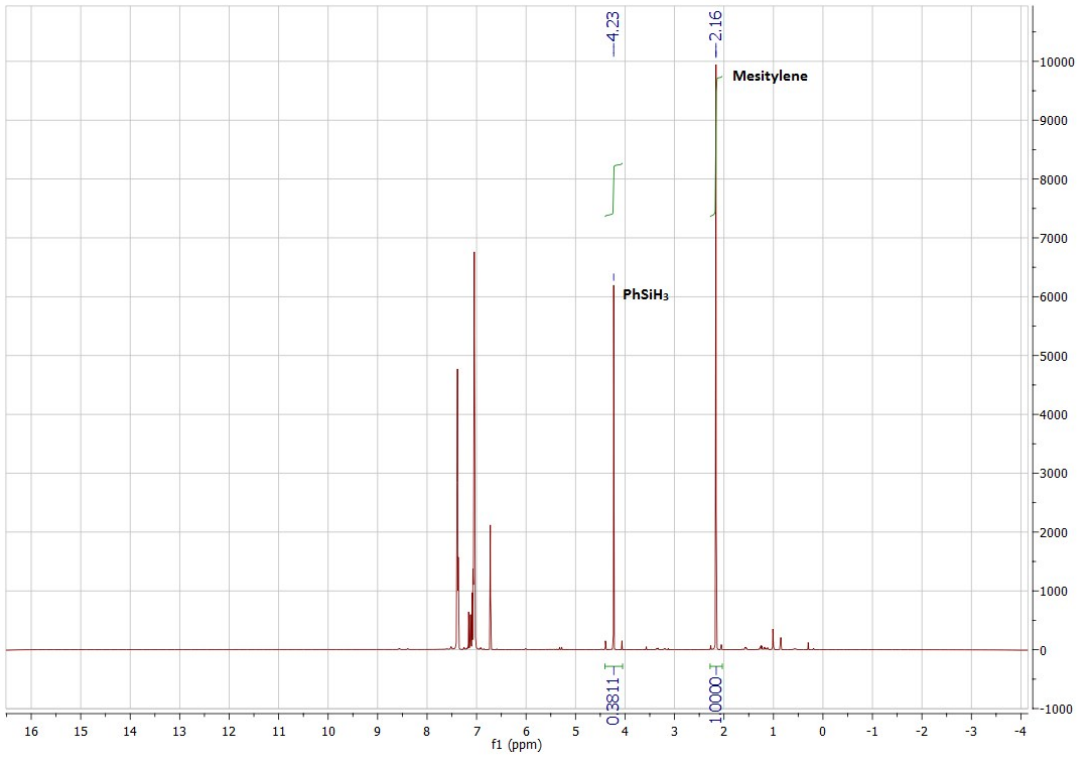


Figure S2. [Pyridinium][ReO_4] (2 mol%) in C_6D_6 (0.5 mL), with phenylsilane (0.2 mmol) and CO_2 (2.5 bar). Start point.

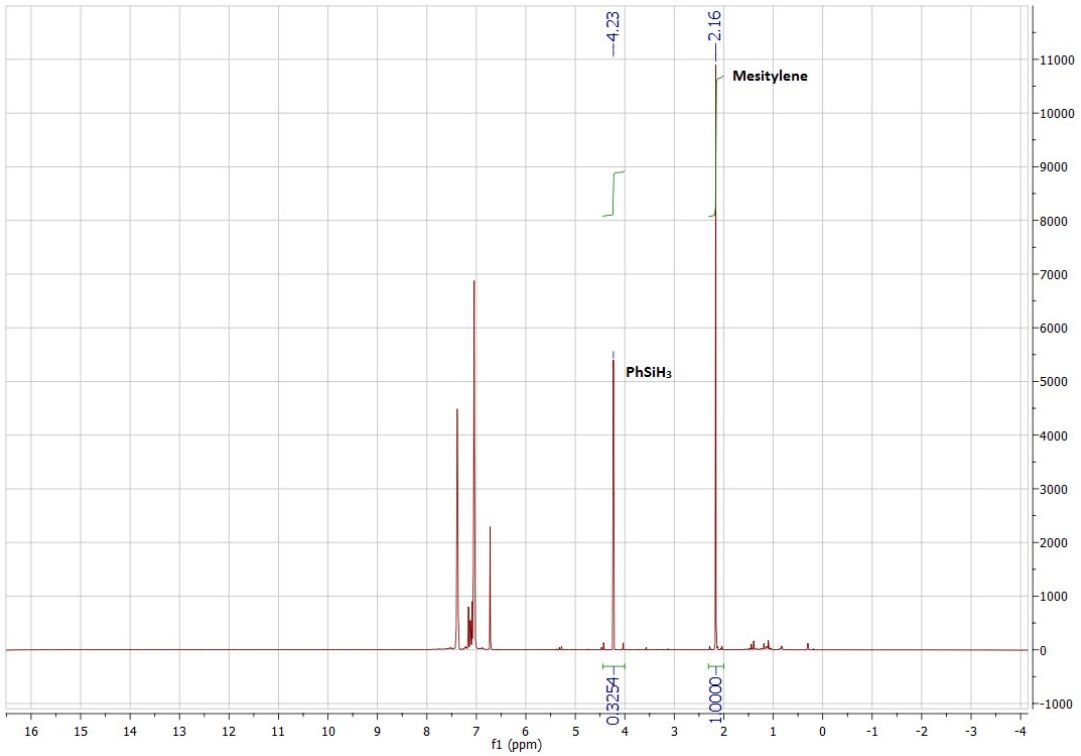


Figure S3. [Pyridinium][ReO_4] (2 mol%) in C_6D_6 (0.5 mL), with phenylsilane (0.2 mmol) and CO_2 (2.5 bar). End point after heating for 16 hr at 80 ^oC.

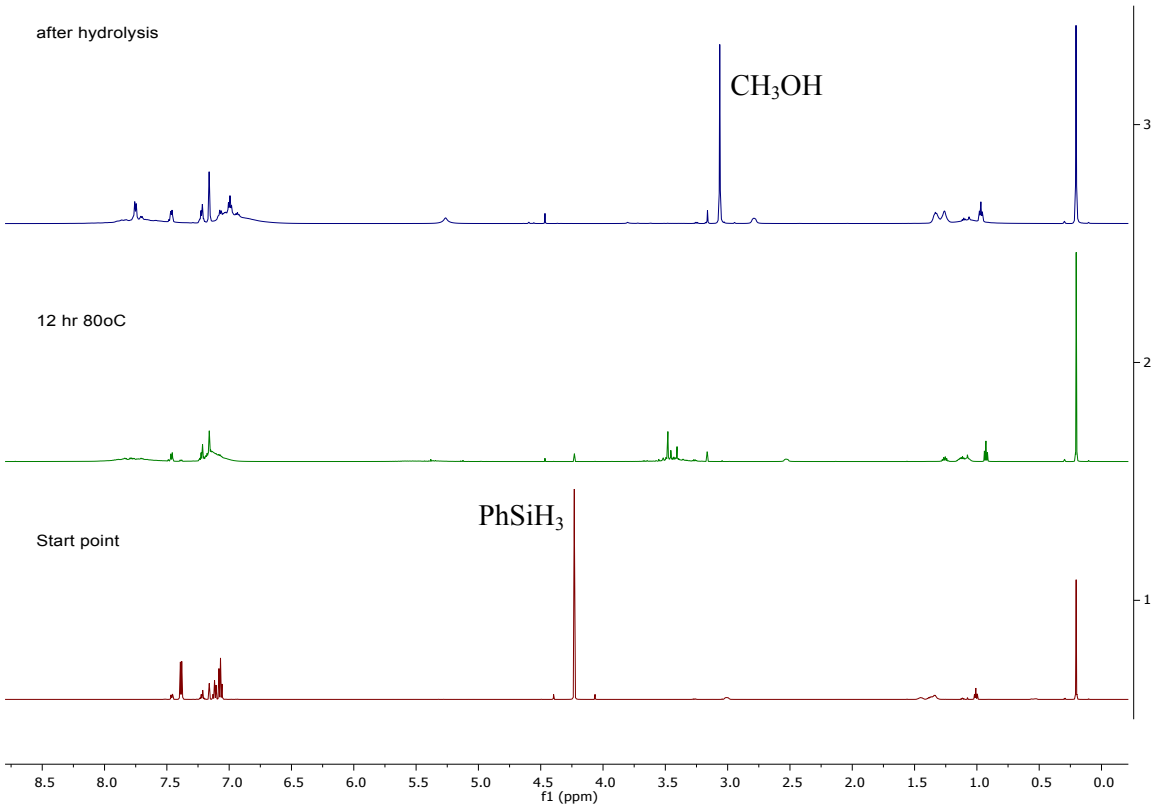


Figure S4. [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in C_6D_6 (0.5 mL), with phenylsilane (0.2 mmol) and CO_2 (1 bar).

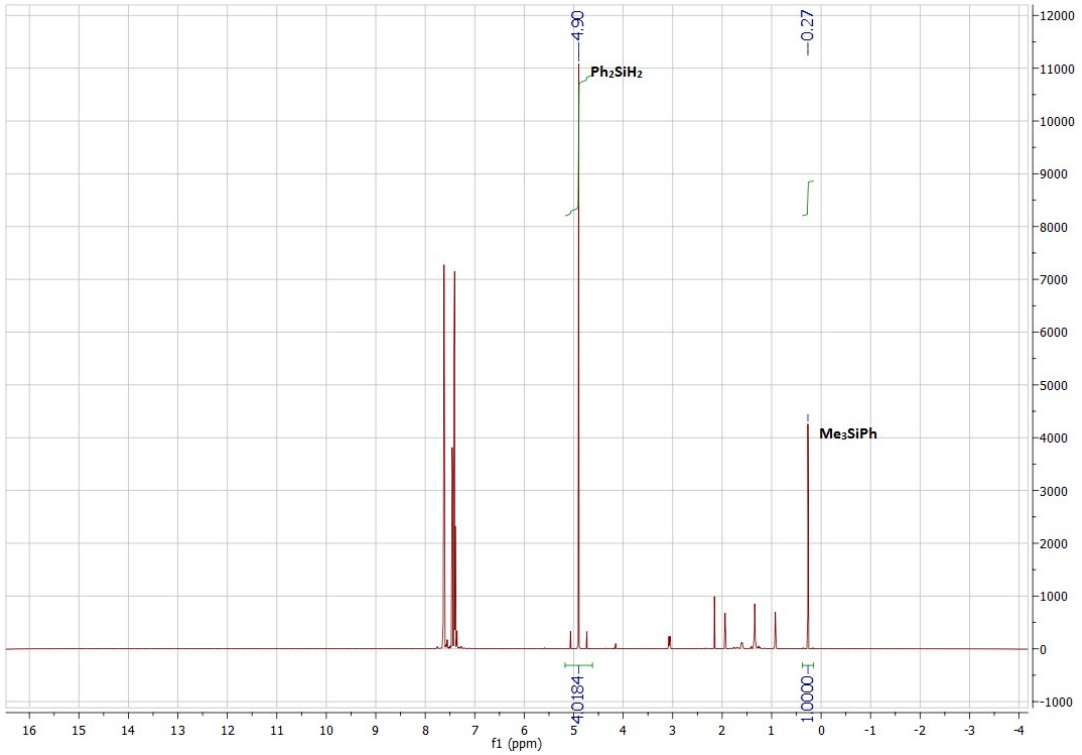


Figure S5. [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in d_3-MeCN (0.5 mL), with diphenylsilane (0.2 mmol) and air (1 bar). Start point.

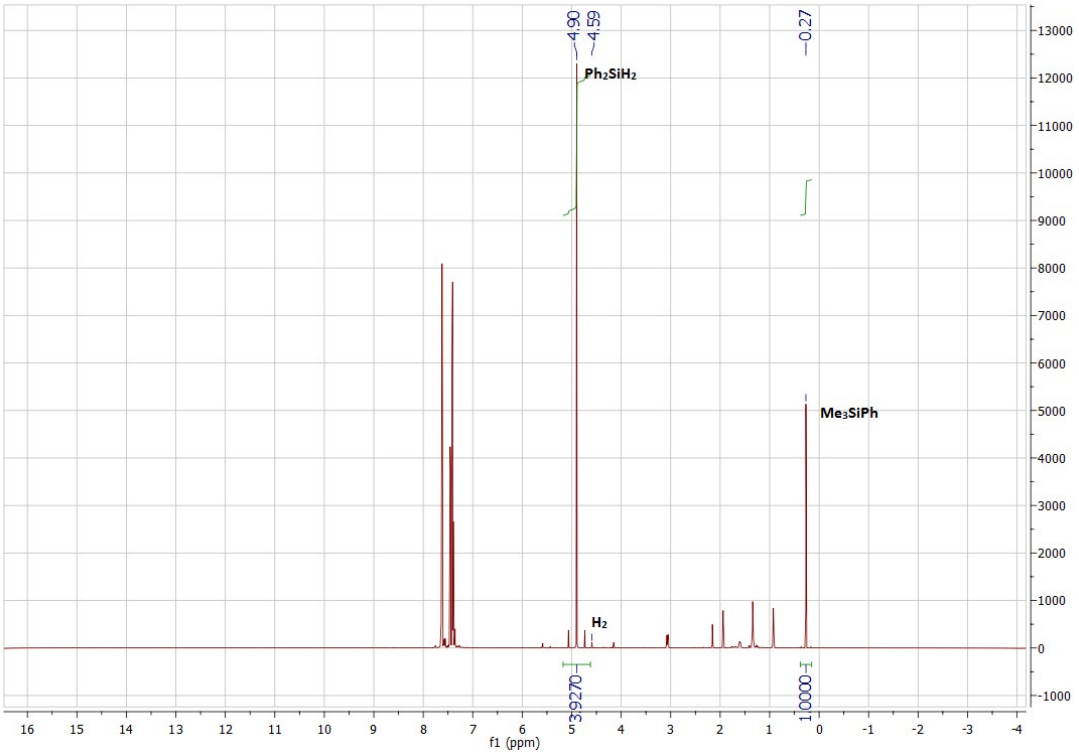


Figure S6. [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in d$_3$-MeCN (0.5 mL), with diphenylsilane (0.2 mmol) and air (1 bar). End point after heating for 1 hr at 80 ^{o}C.

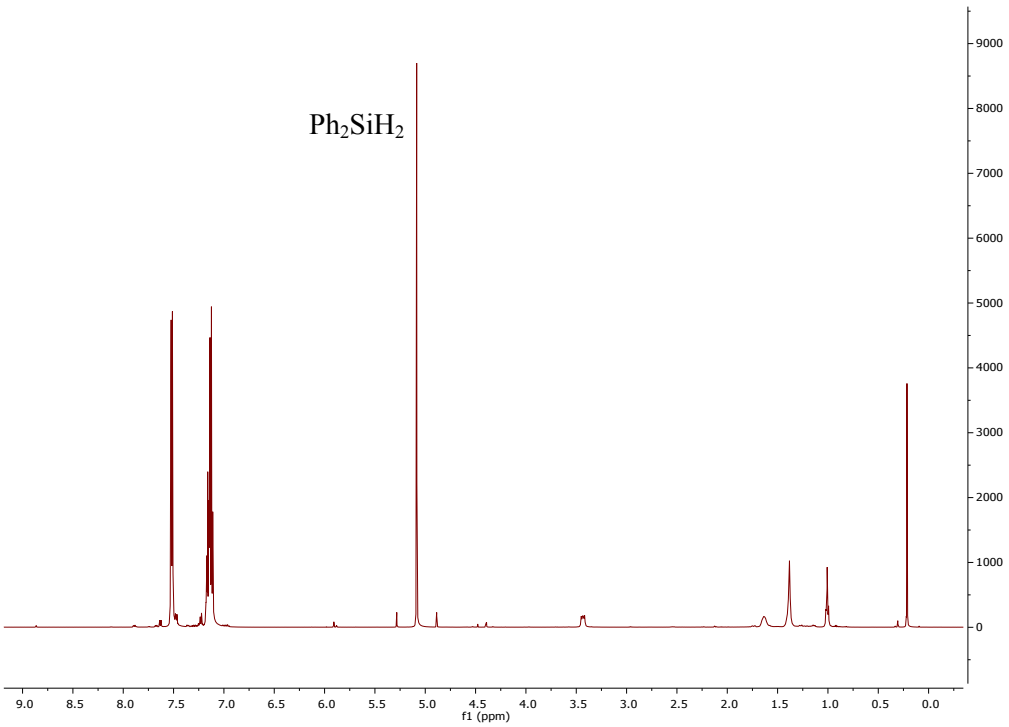


Figure S7. ^{1}H NMR spectra after heating 80 ^{o}C for 16 h for the reaction of [N(hexyl)$_4$][Br] (5 mol%), Ph_2SiH_2 (0.2 mmol), and CO_2 in C_6D_6 (0.5 mL). No observed consumption of hydrosilane or formation of products.

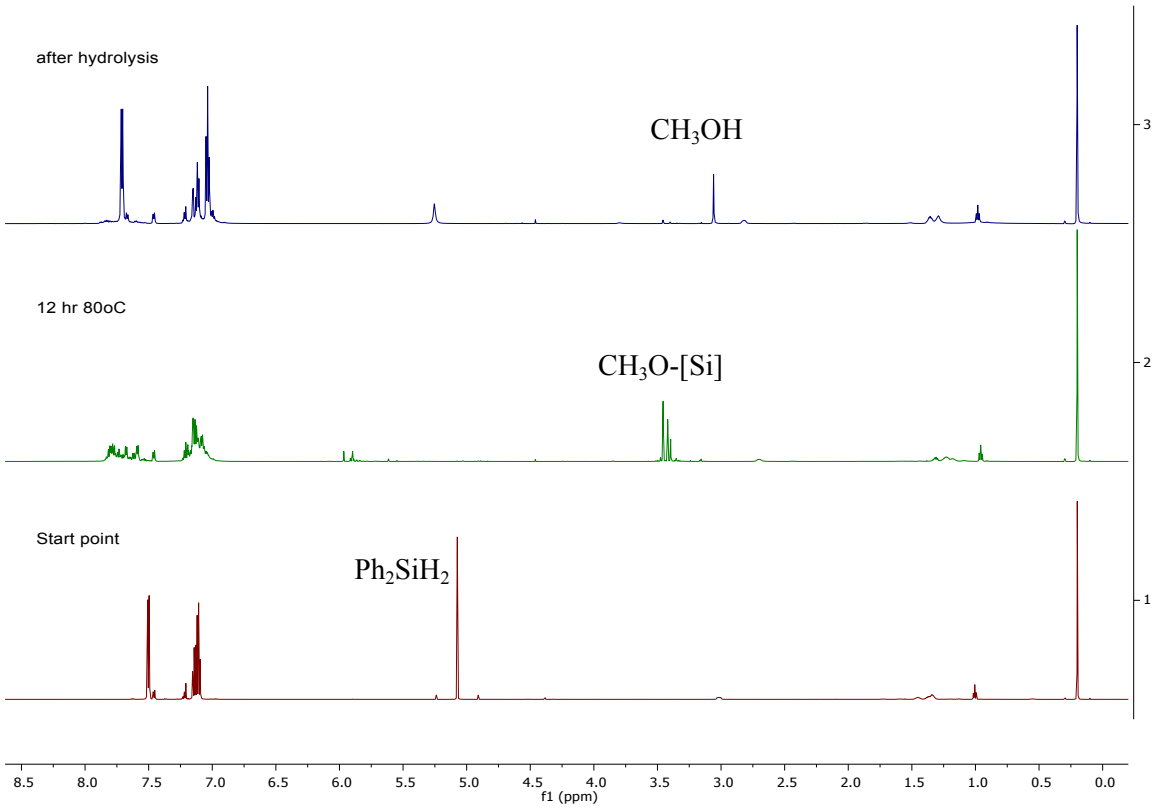


Figure S8. $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%) in C_6D_6 (0.5 mL), with diphenylsilane (0.2 mmol) and CO_2 (1 bar).

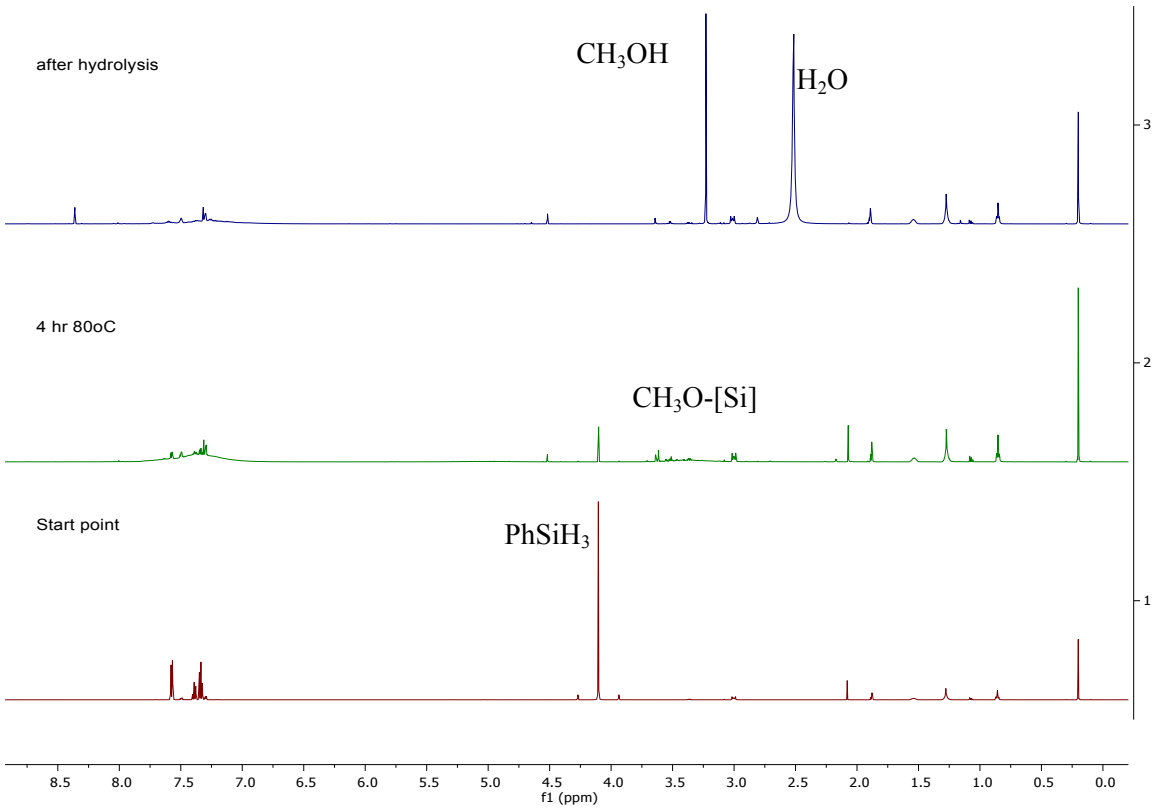


Figure S9. $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%) in d_3-MeCN (0.5 mL), with phenylsilane (0.2 mmol) and CO_2 (1 bar).

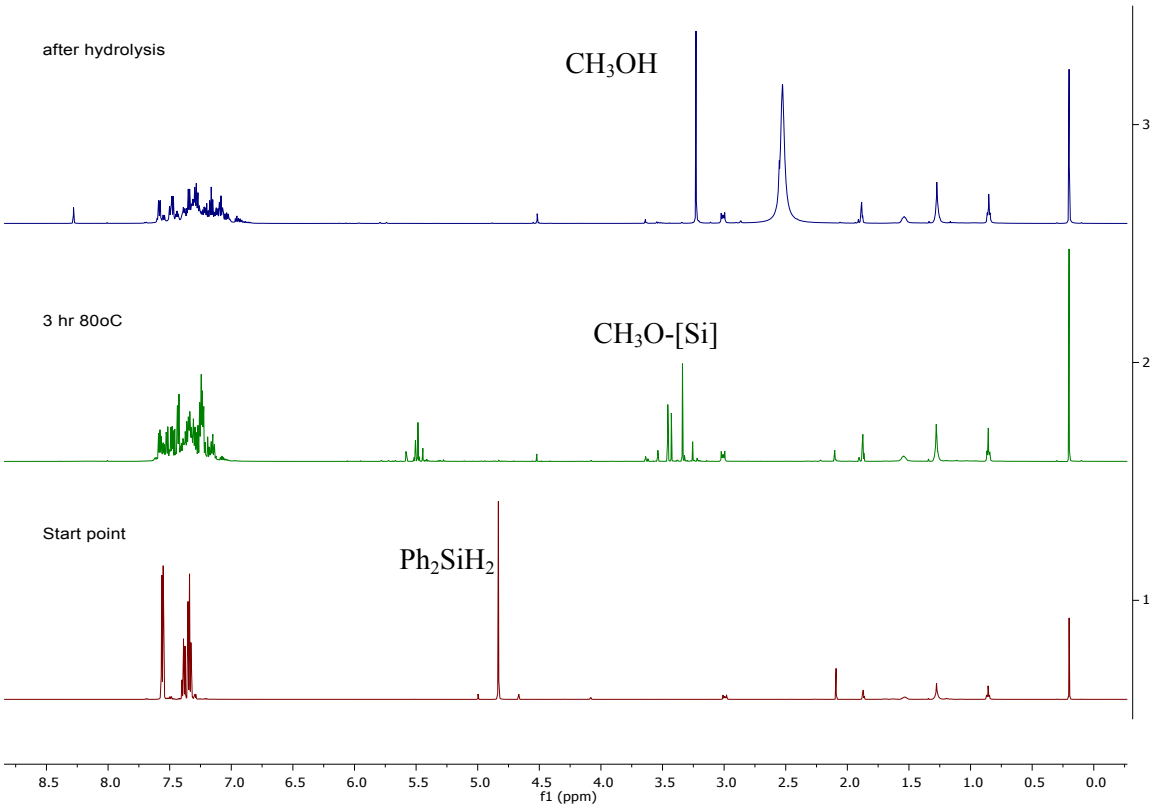


Figure S10. [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in d$_3$-MeCN (0.5 mL), with diphenylsilane (0.2 mmol) and CO_2 (1 bar).

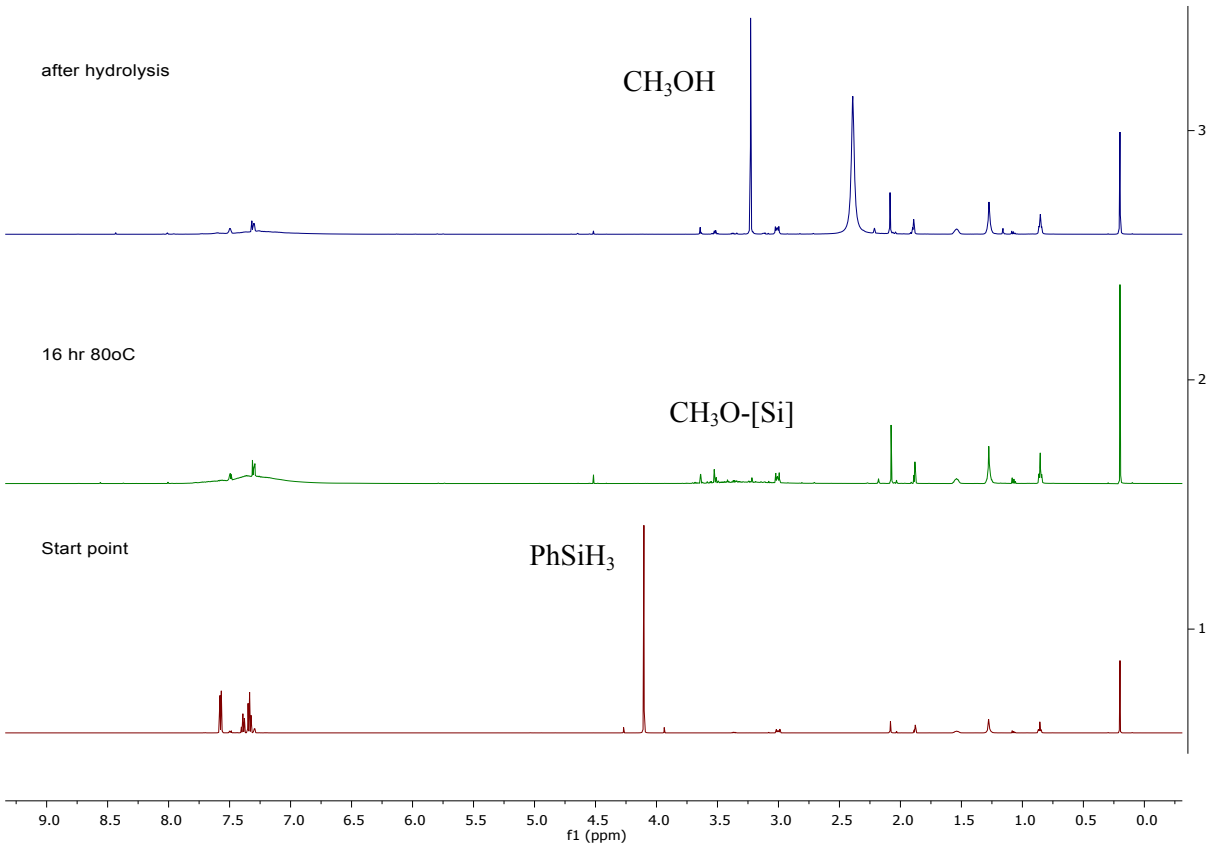


Figure S11. [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in d$_3$-MeCN (0.5 mL), with phenylsilane (0.2 mmol) and CO_2 (1 bar).

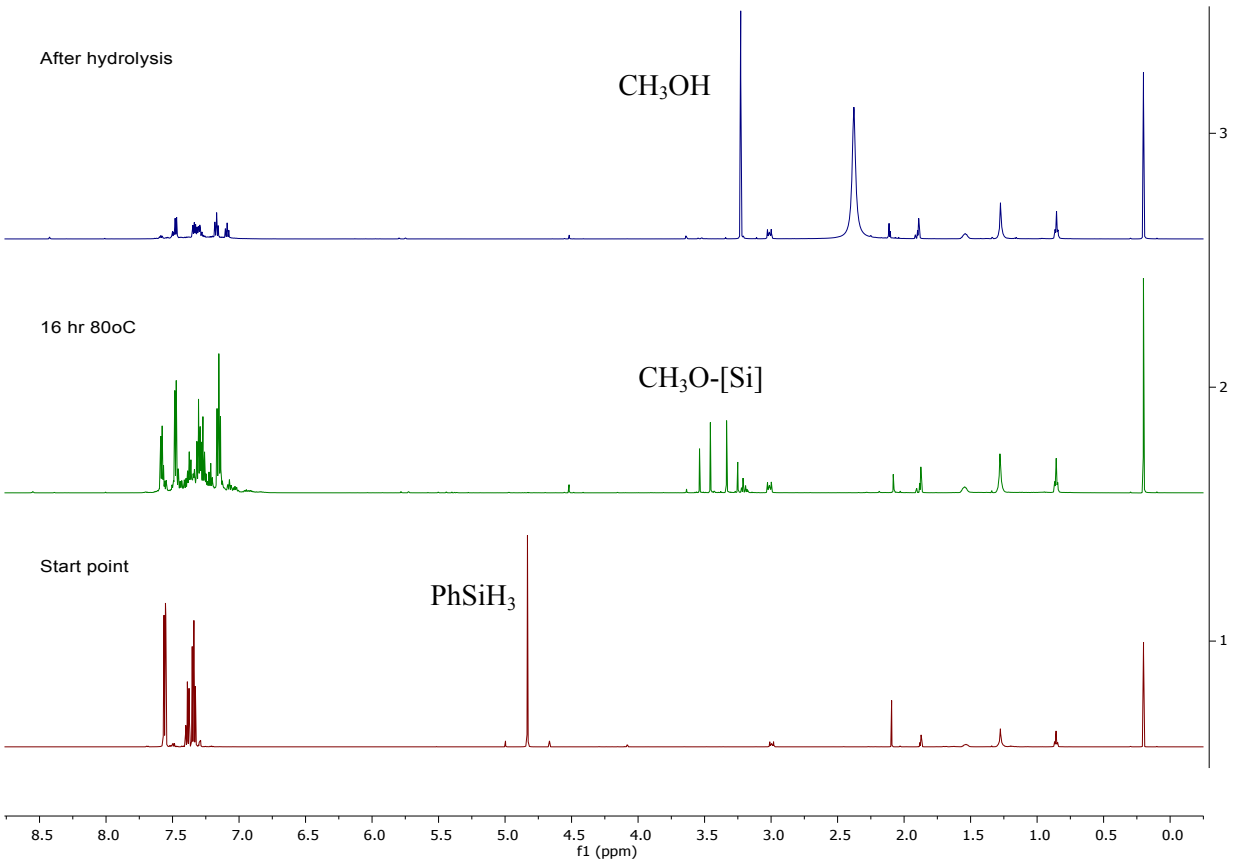


Figure S12. [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in d$_3$-MeCN (0.5 mL), with diphenylsilane (0.2 mmol) and CO_2 (1 bar).

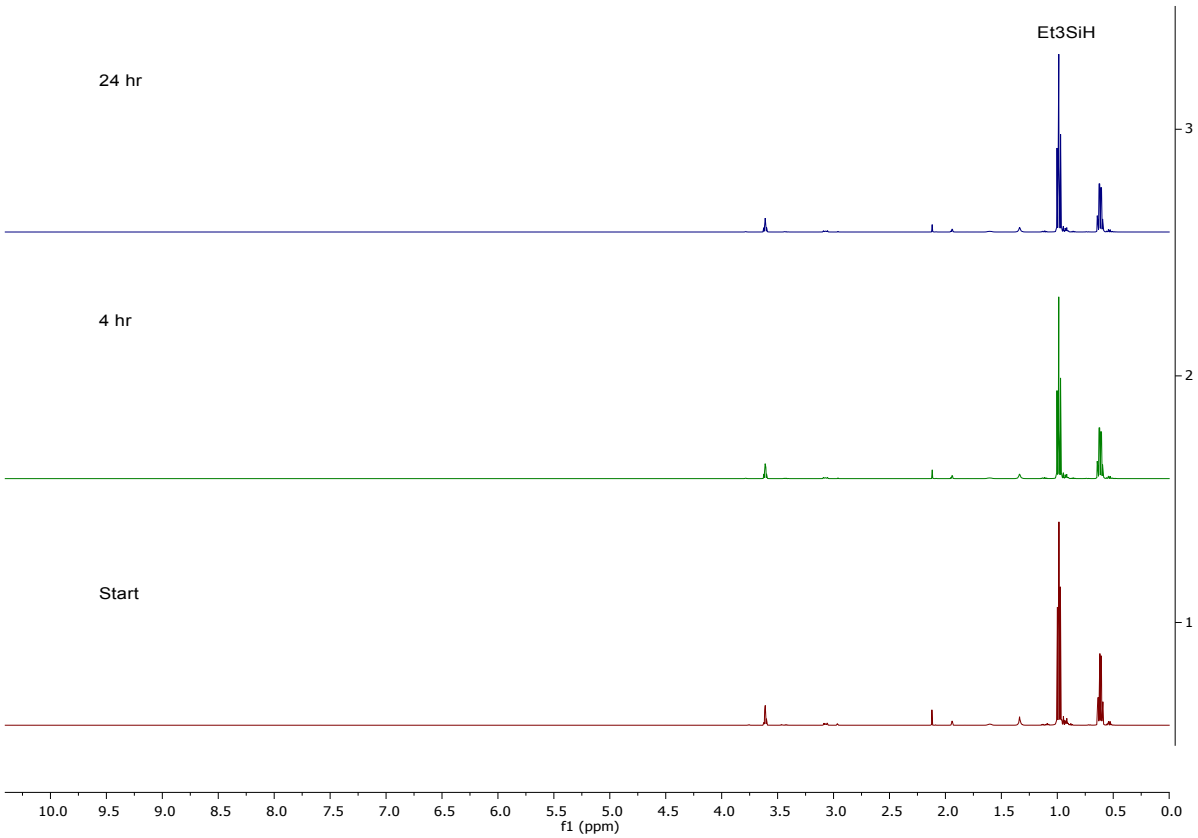


Figure S13 ^{1}H NMR stack plot for the reaction of triethylsilane (0.2 mmol), CO_2 (1 bar), cat (2.5 mol%) in d$_3$-MeCN heated at 80 ◦C for a total of 24 hr. No reaction.

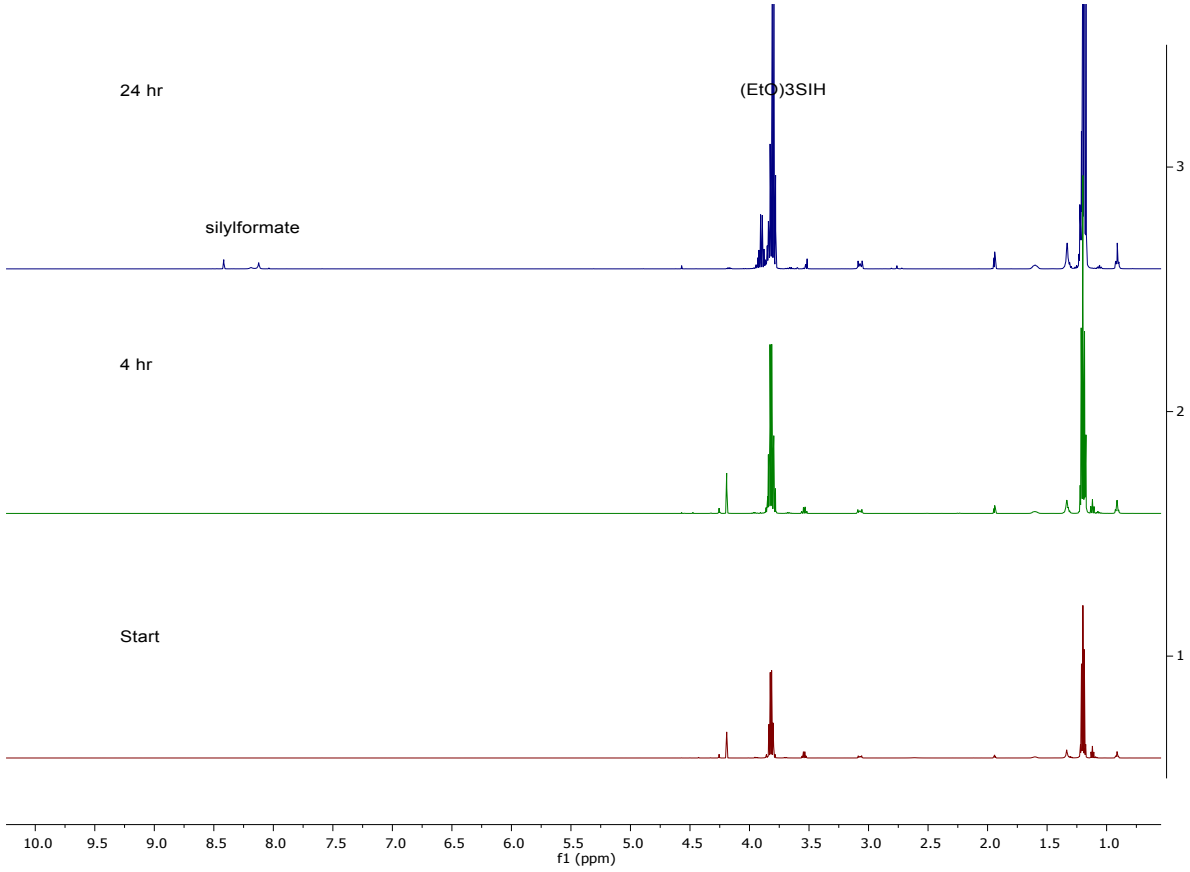


Figure S14 ^{1}H NMR stack plot for the reaction of triethoxysilane (0.2 mmol), CO_2 (1 bar), cat (2.5 mol%) in d_3-MeCN heated at 80 ◦C for a total of 24 hr. No reaction.

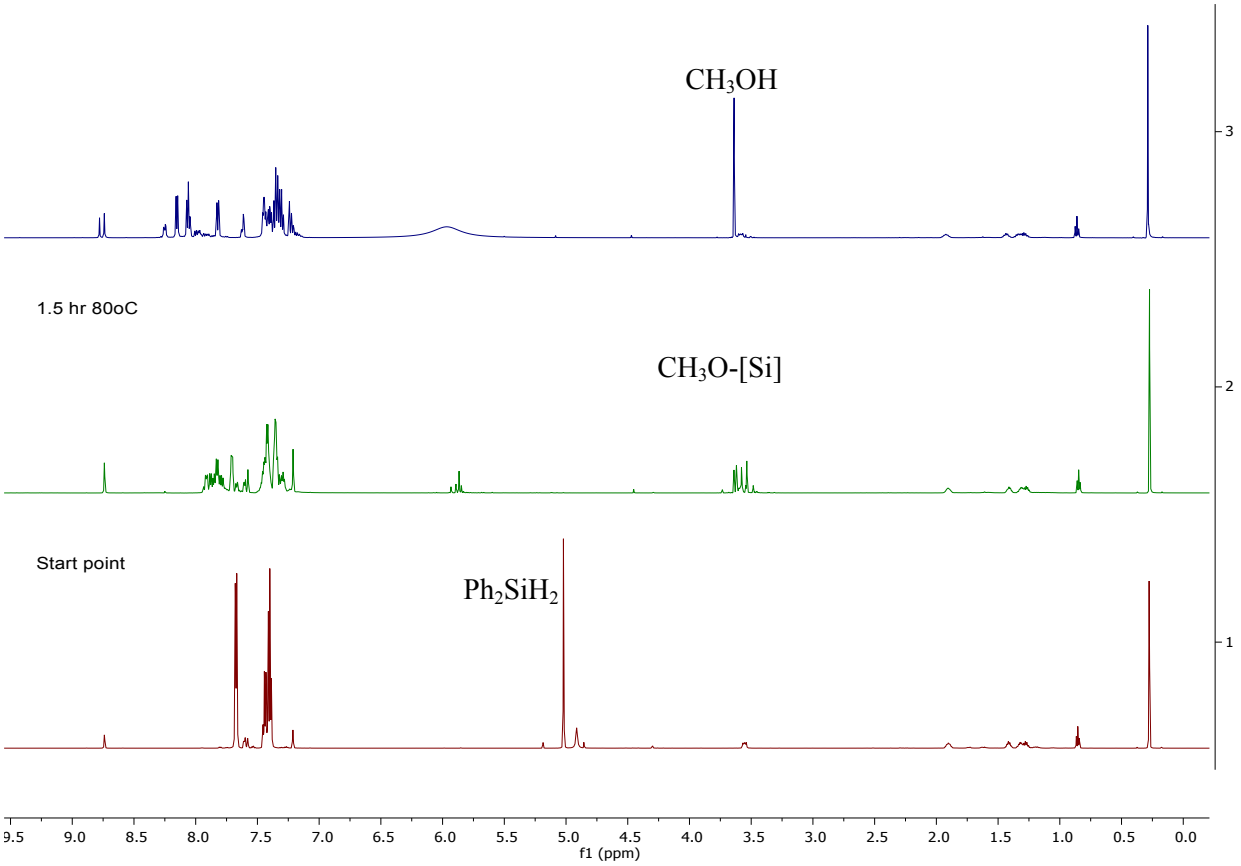


Figure S15. [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in d_5-Py (0.5 mL), with diphenylsilane (0.2 mmol) and CO_2 (1 bar).

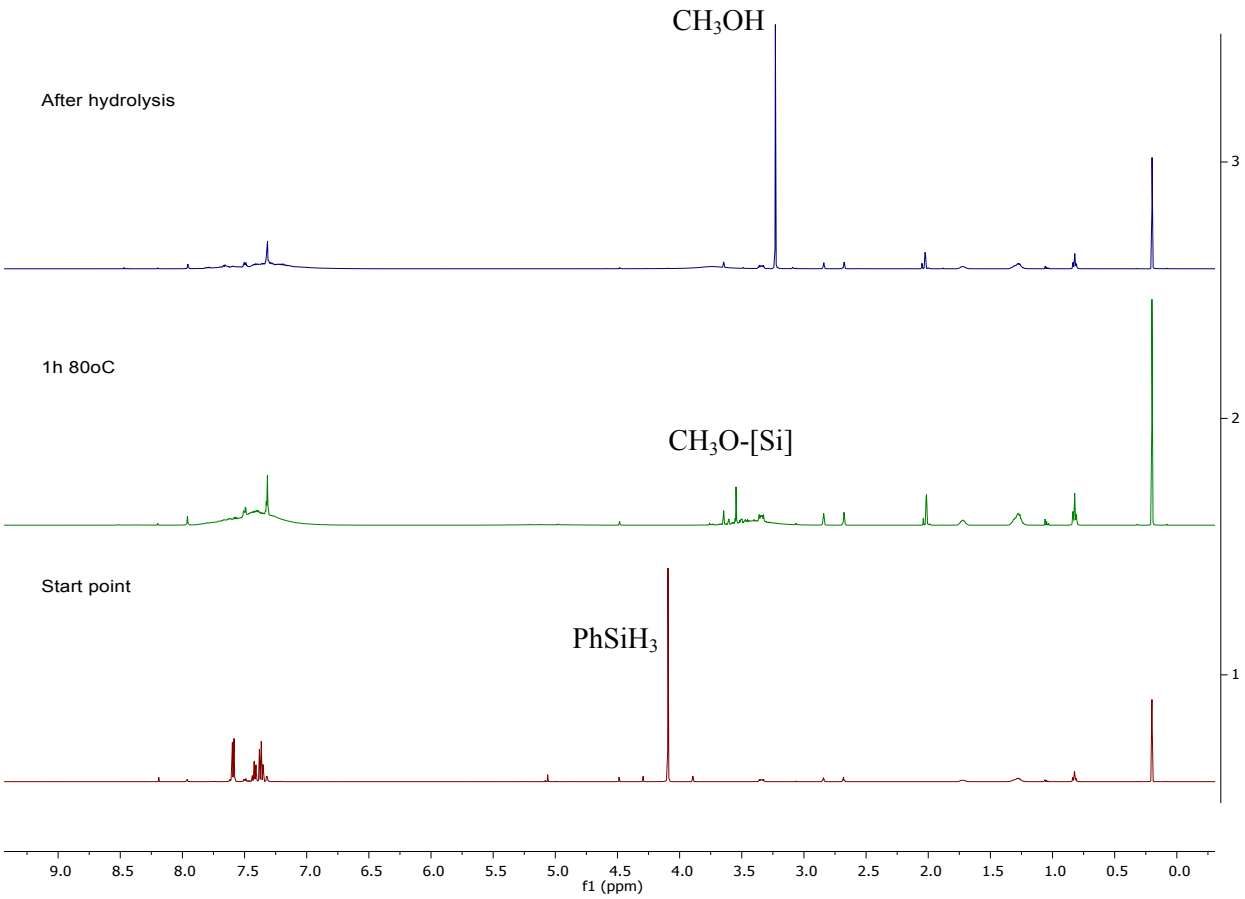


Figure S16. $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%) in d_7-DMF (0.5 mL), with phenylsilane (0.2 mmol) and CO_2 (1 bar).

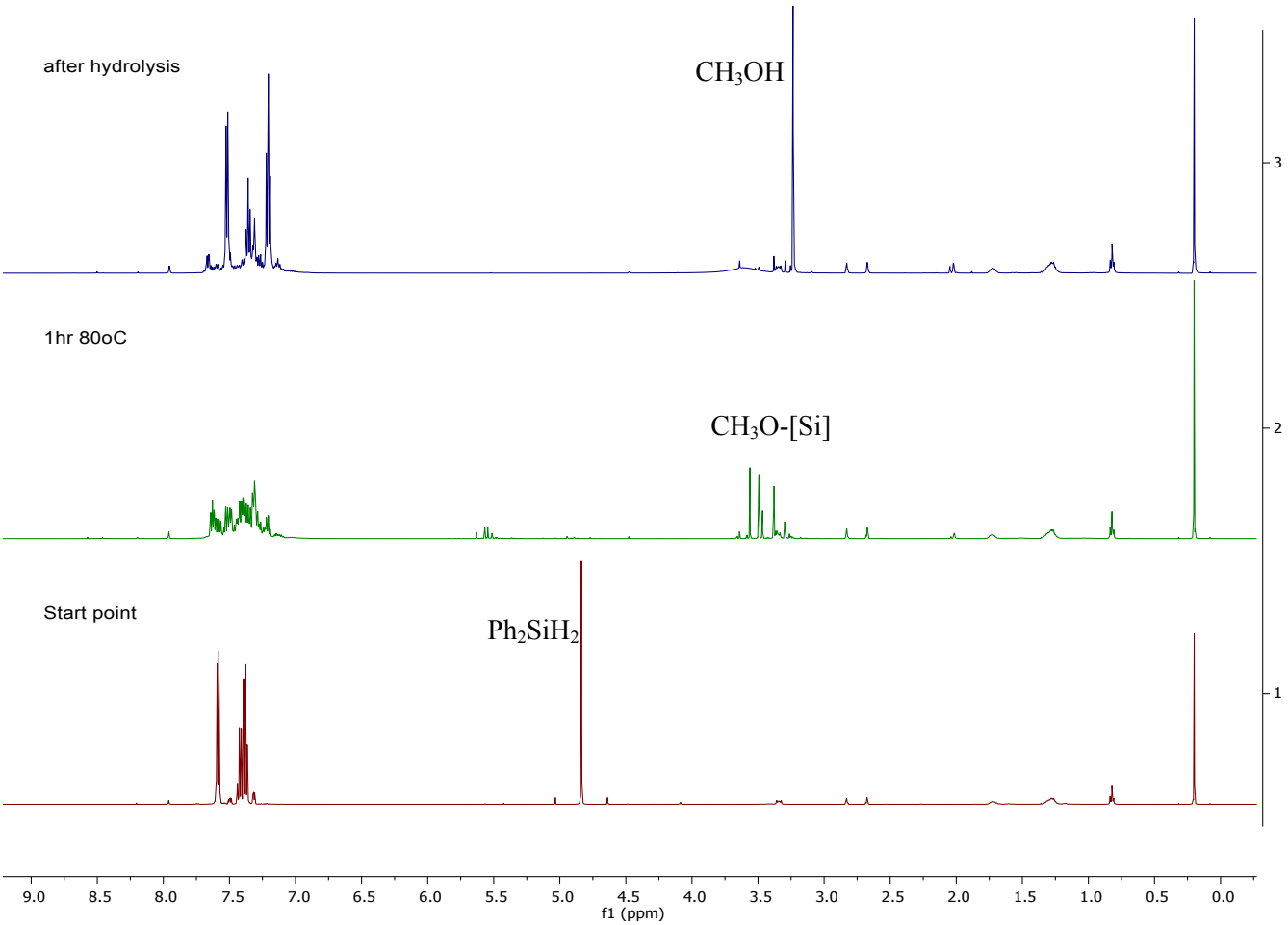


Figure S17. $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%) in d_7-DMF (0.5 mL), with diphenylsilane (0.2 mmol) and CO_2 (1 bar).

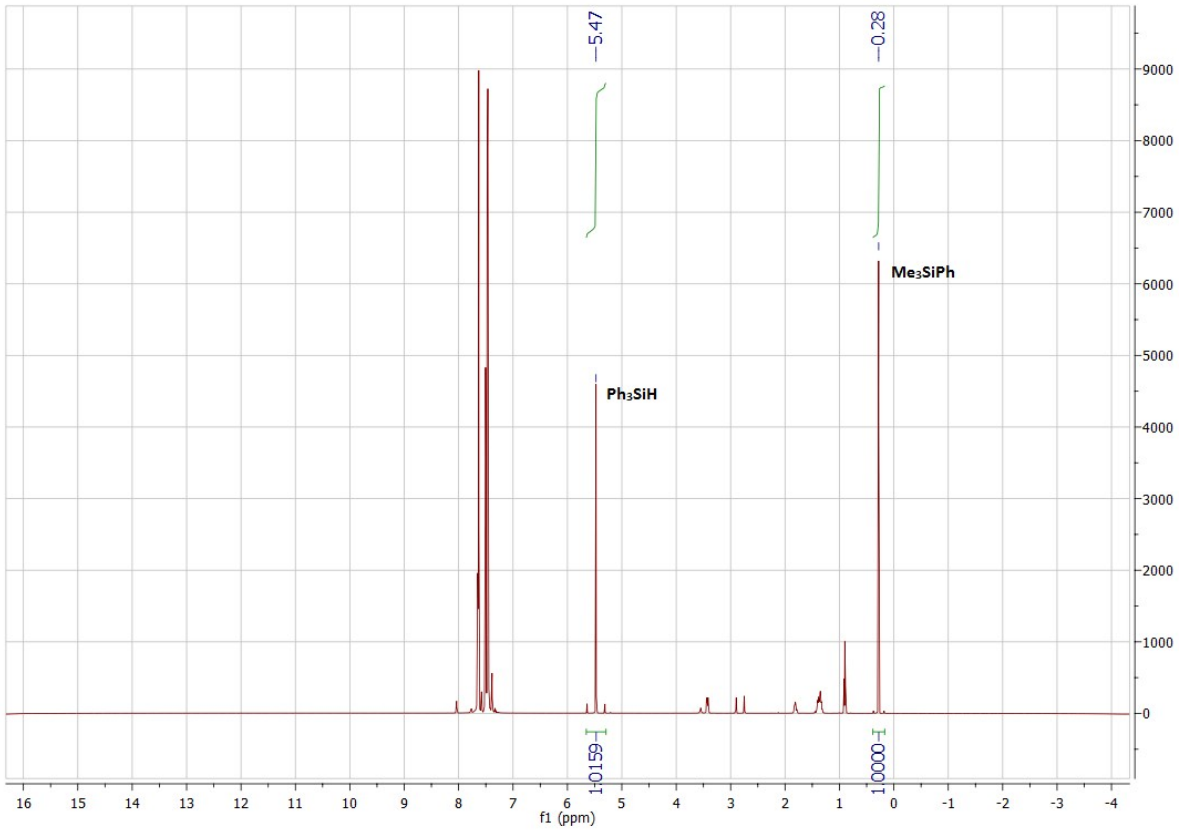


Figure S18 Triphenylsilane reaction (0.2 mmol), CO_2 (1 bar), cat. (2.5 mol %) in d_7-DMF heated at 150 °C 8 h. Start point.

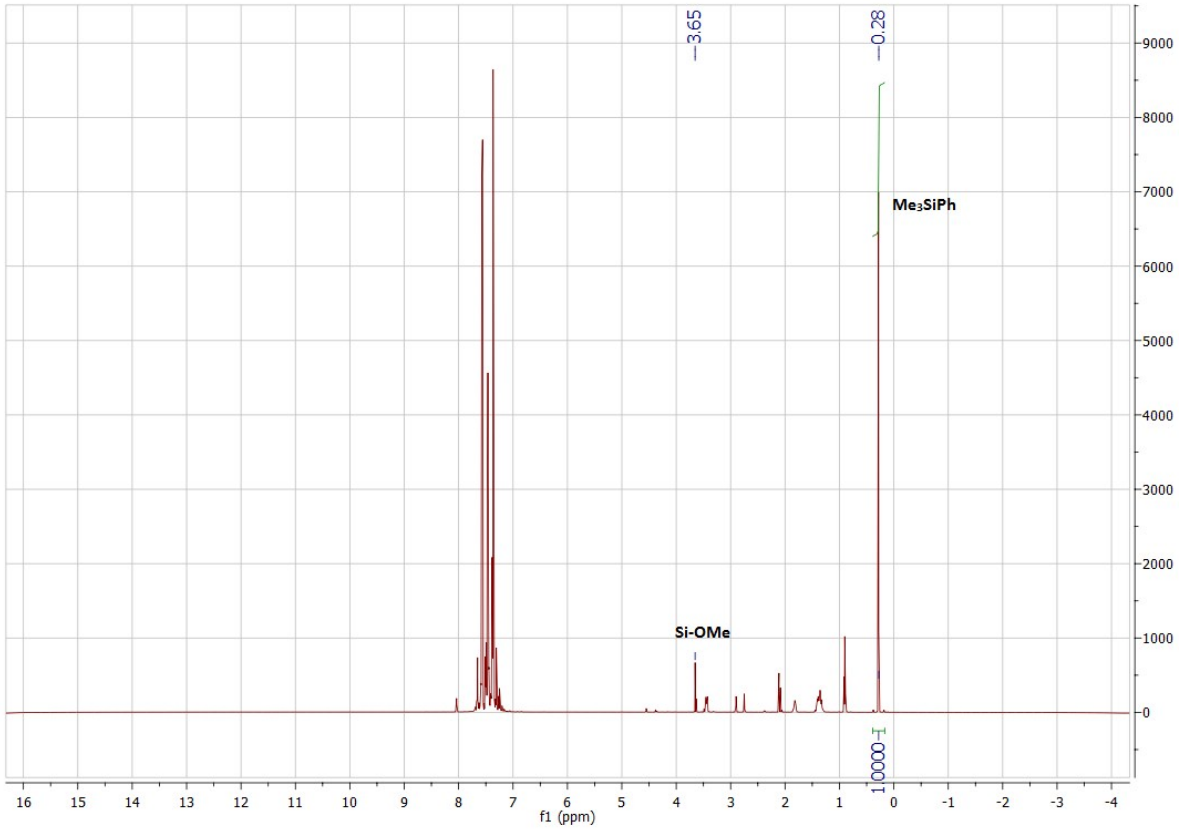


Figure S19 Triphenylsilane reaction (0.2 mmol), CO_2 (1 bar), cat. (2.5 mol %) in d_7-DMF heated at 150 °C 8 h. End point.

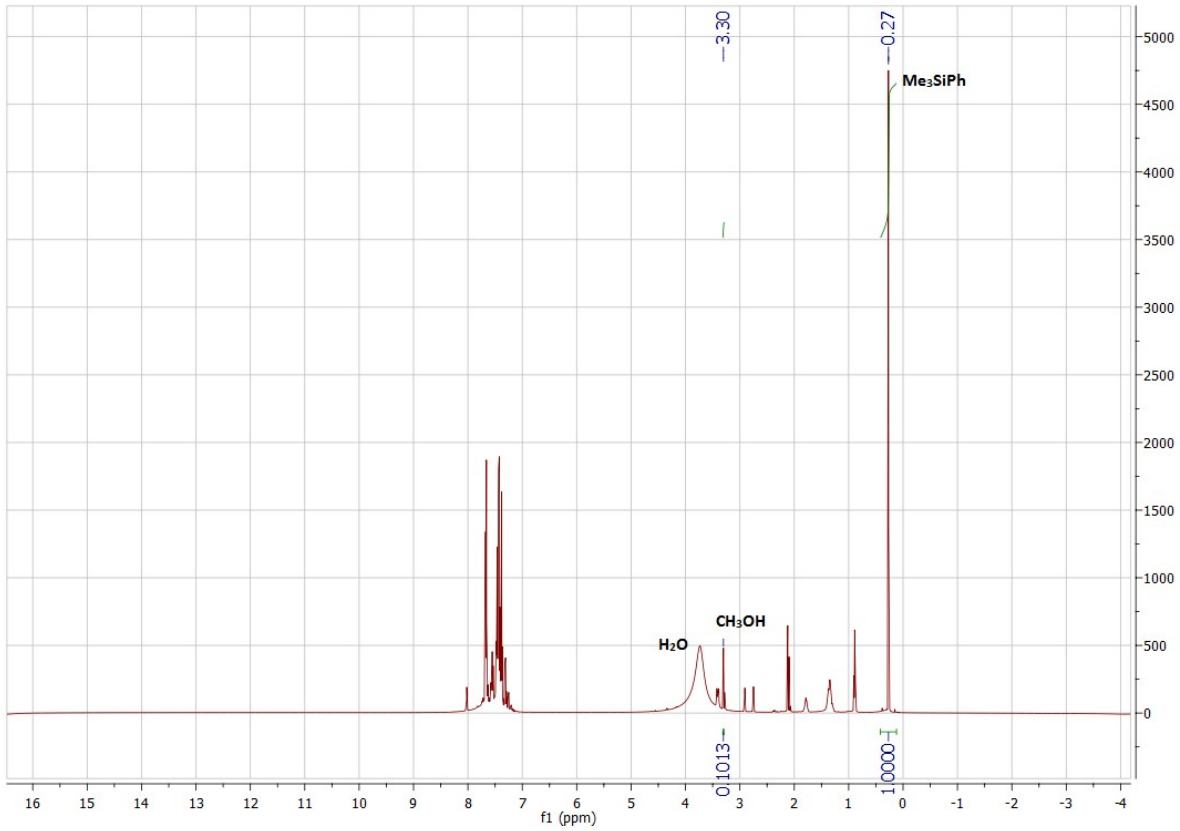


Figure S20 Triphenylsilane reaction (0.2 mmol), CO_2 (1 bar), cat. (2.5 mol %) in d_7-DMF heated at 150 °C 8 h. After hydrolysis.

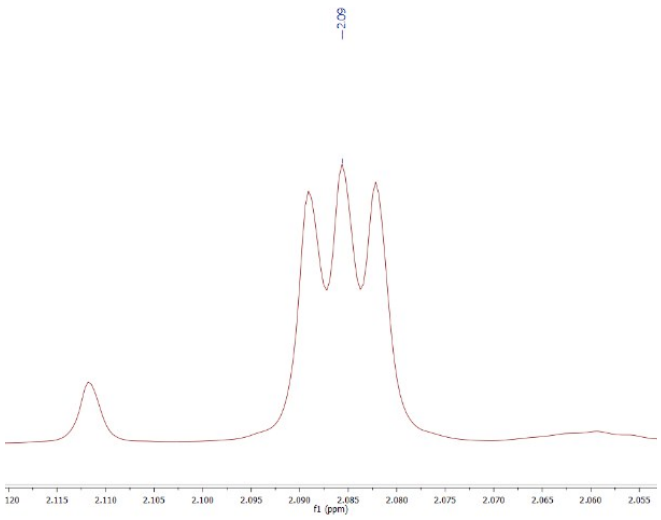


Figure S21. Multiplet at 2.09 ppm for $CDH_2N(CD_3)_2$ in d_7-DMF

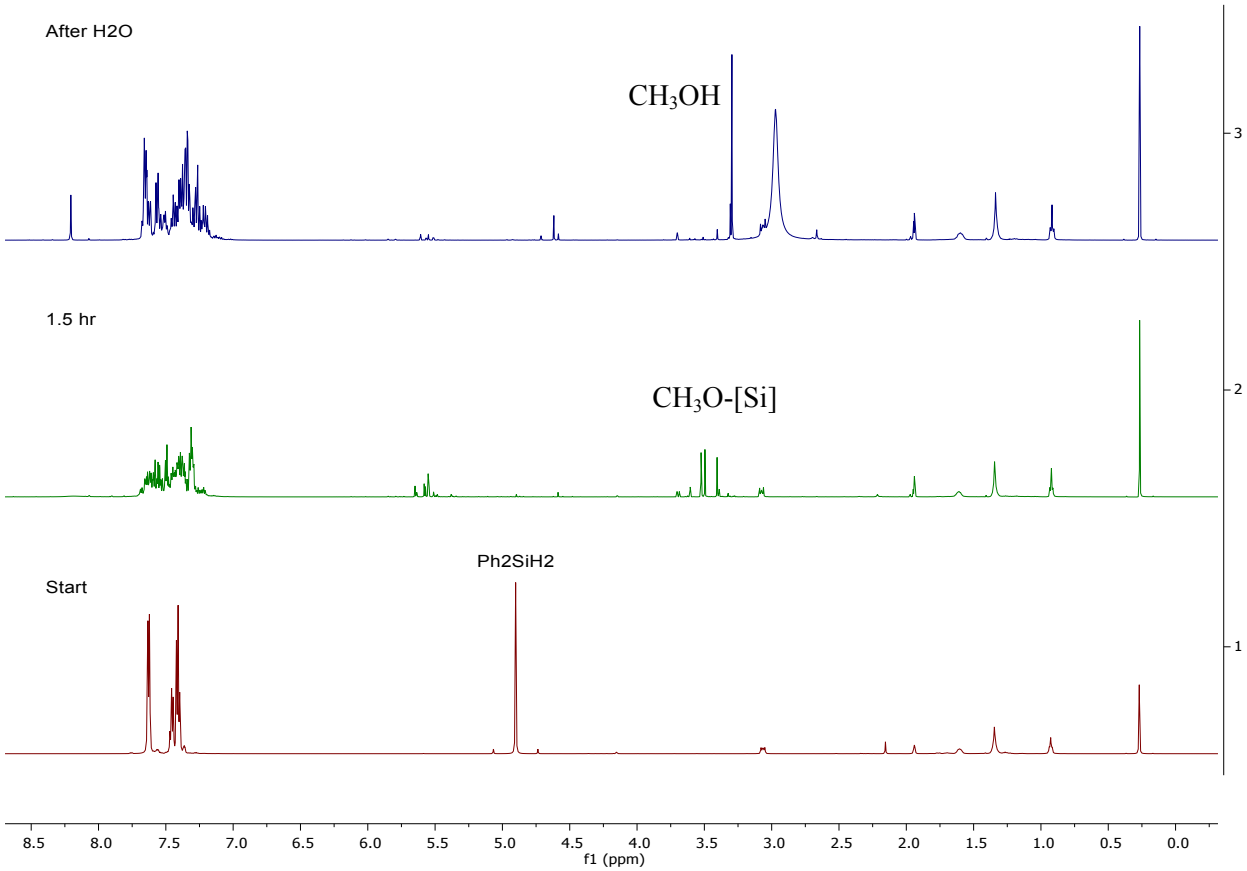


Figure S22. [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in d$_3$-MeCN (0.5 mL), with diphenylsilane (0.2 mmol) and CO_2 (2 bar).

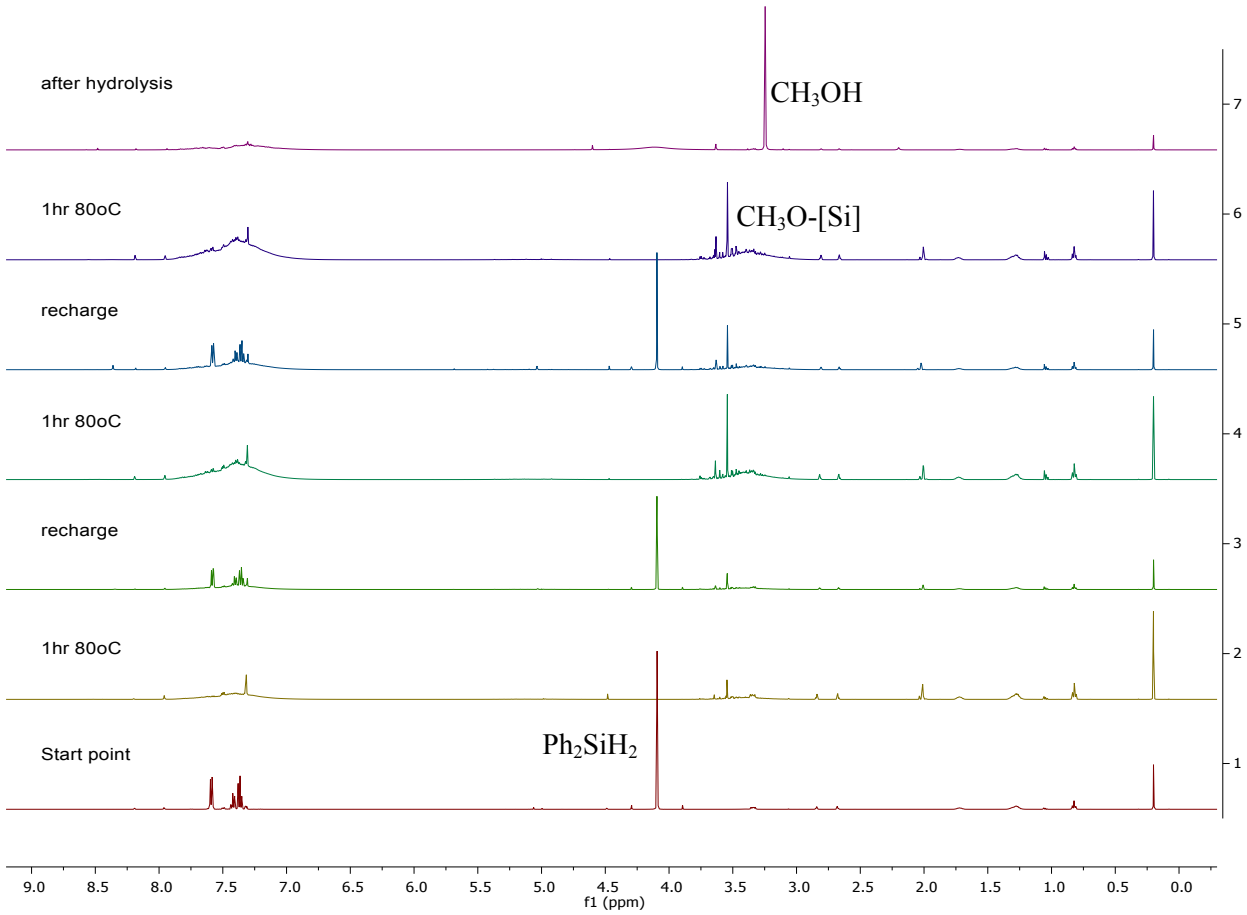


Figure S23. [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in d$_7$-DMF (0.5 mL), with diphenylsilane (0.2 mmol) and CO_2 (1 bar).

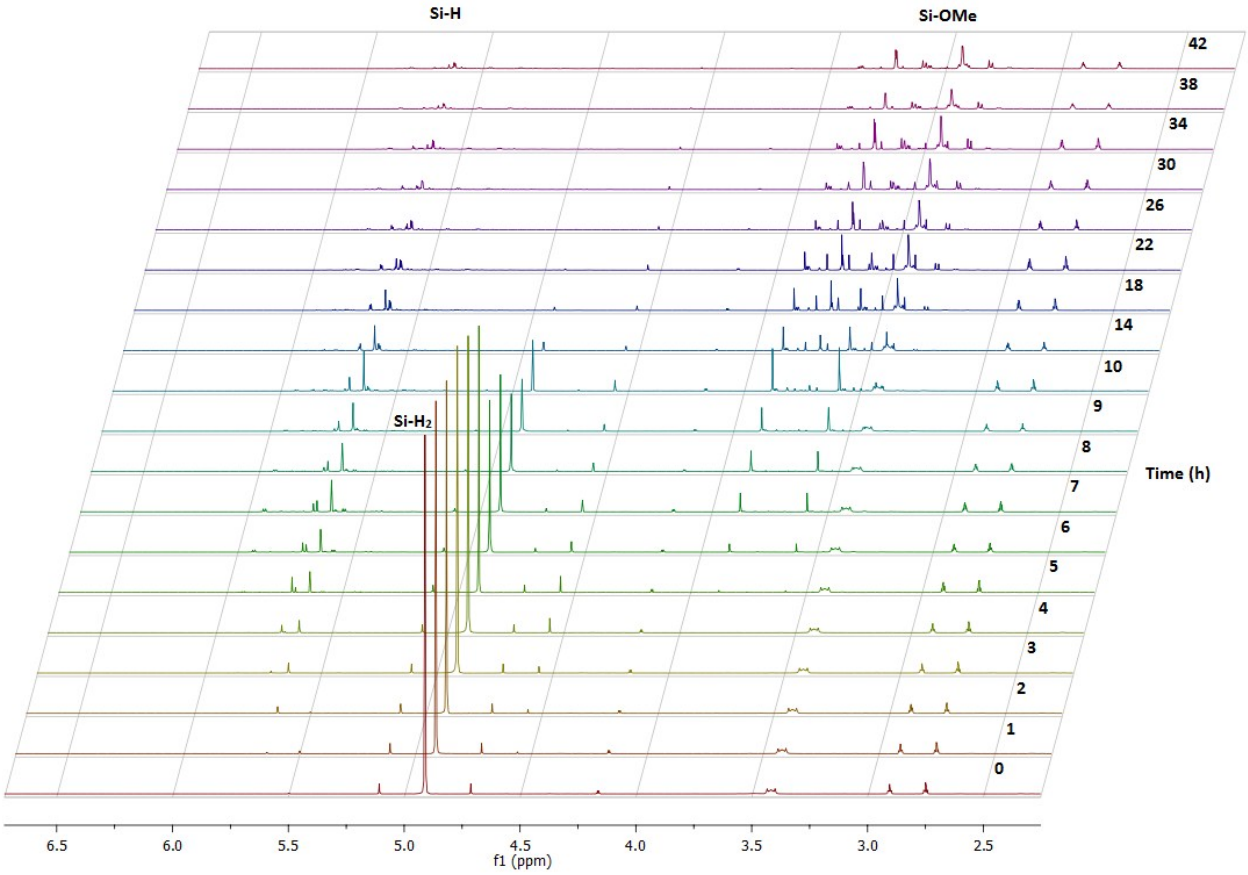


Figure S24. ^{1}H NMR spectra for reaction of Ph_2SiH_2 with $^{13}CO_2$ (1 bar) in d_7-DMF at room temperature with 2.5 mol% $[N(hexyl)_4][ReO_4]$ **2**, showing consumption of diphenylsilane and growth of Si-OMe products/ Si-H byproducts.

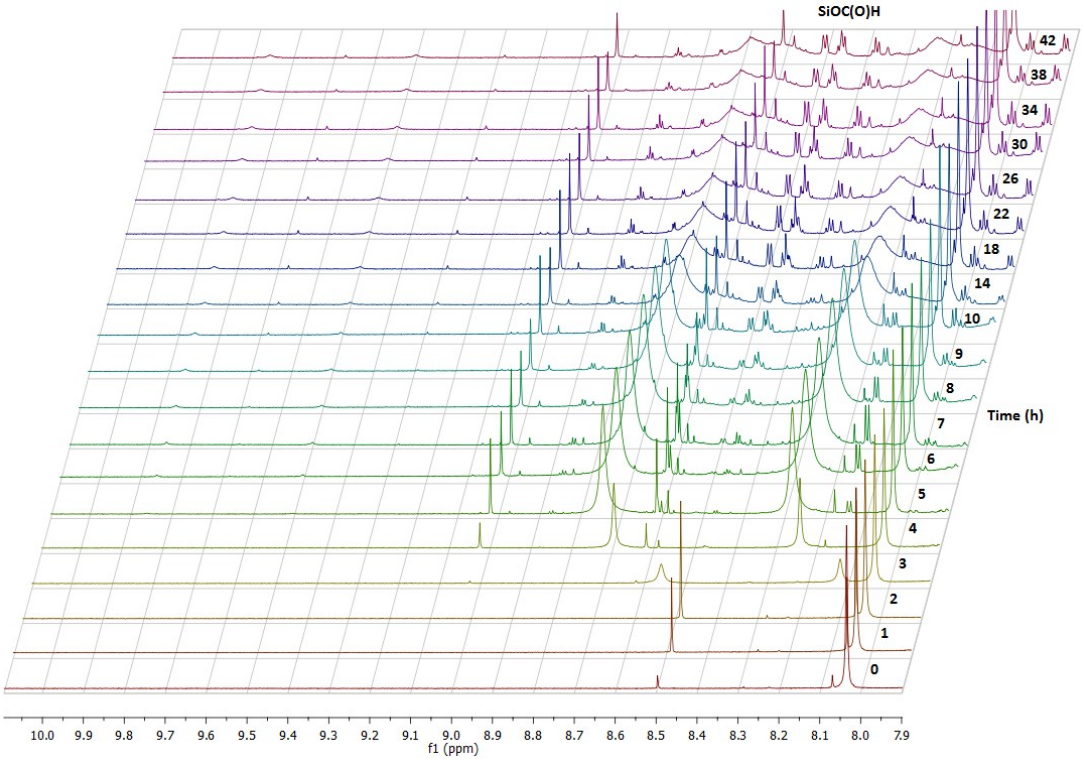


Figure S25. ^{1}H NMR spectra for reaction of Ph_2SiH_2 with $^{13}CO_2$ (1 bar) in d_7-DMF at room temperature with 2.5 mol% $[N(hexyl)_4][ReO_4]$ **2**, showing growth of formate products/intermediates.

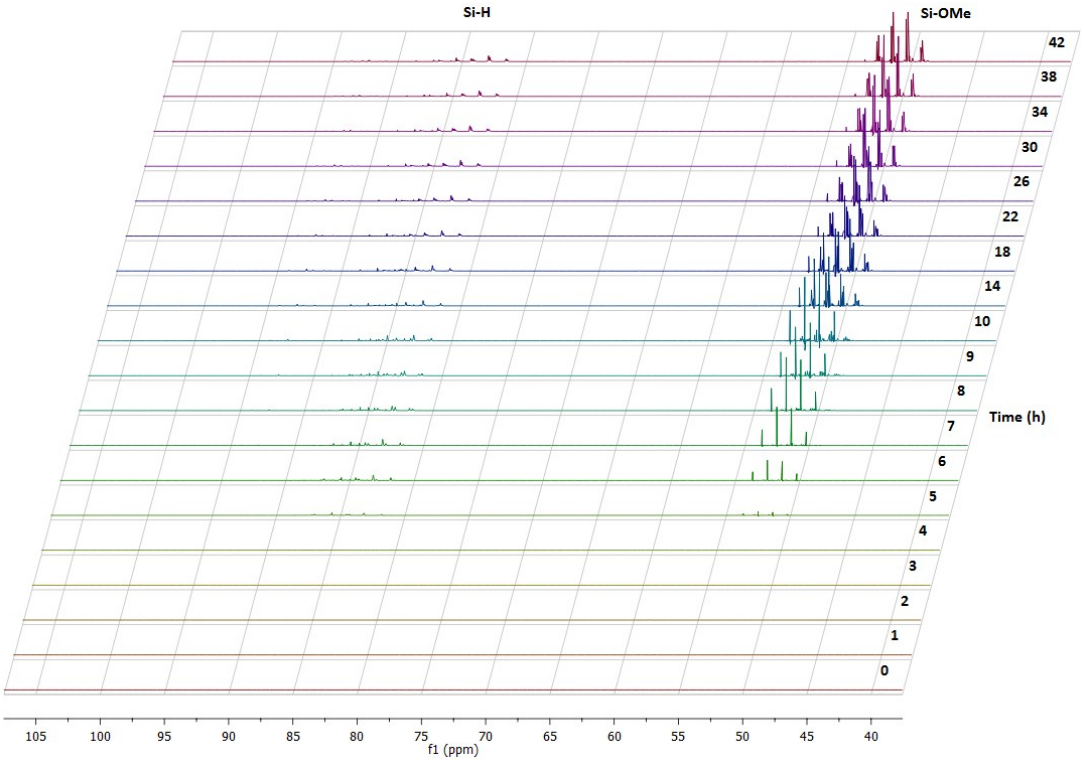


Figure S26. ^{13}C NMR spectra for reaction of Ph_2SiH_2 with $^{13}CO_2$ (1 bar) in d_7-DMF at room temperature with 2.5 mol% $[N(hexyl)_4][ReO_4]$ **2**, showing growth of Si-OMe products.

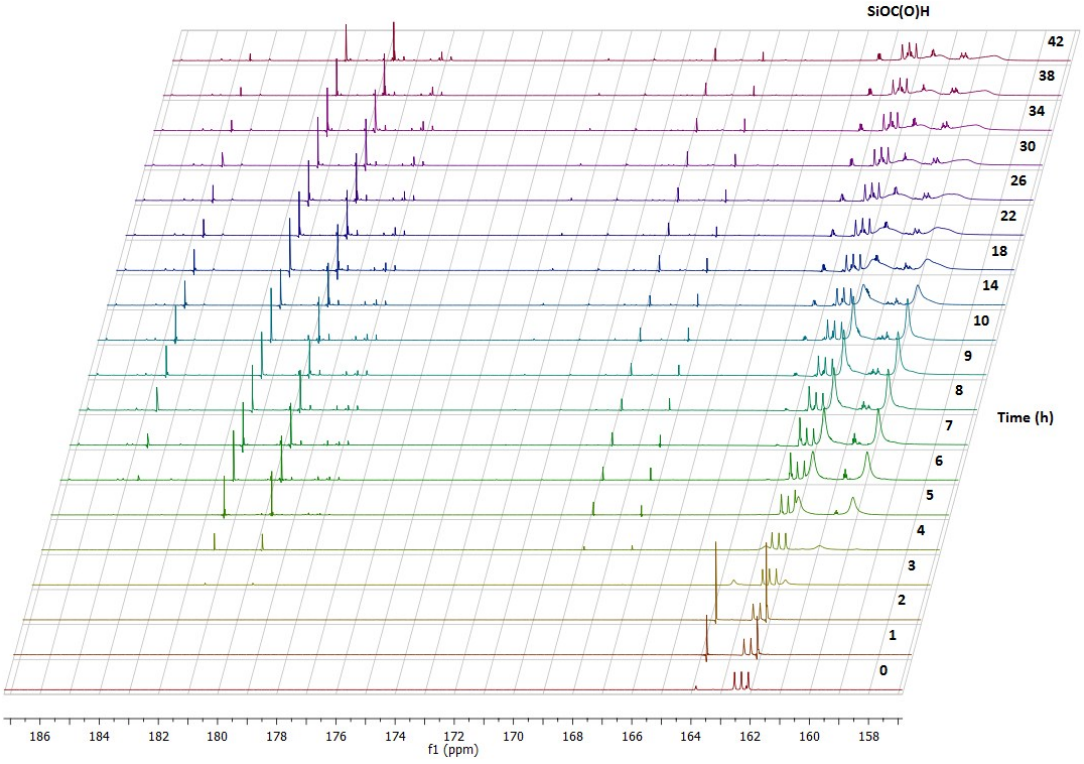


Figure S27. ^{13}C NMR spectra for reaction of Ph_2SiH_2 with $^{13}CO_2$ (1 bar) in d_7-DMF at room temperature with 2.5 mol% $[N(hexyl)_4][ReO_4]$ **2**, showing growth of formate products.

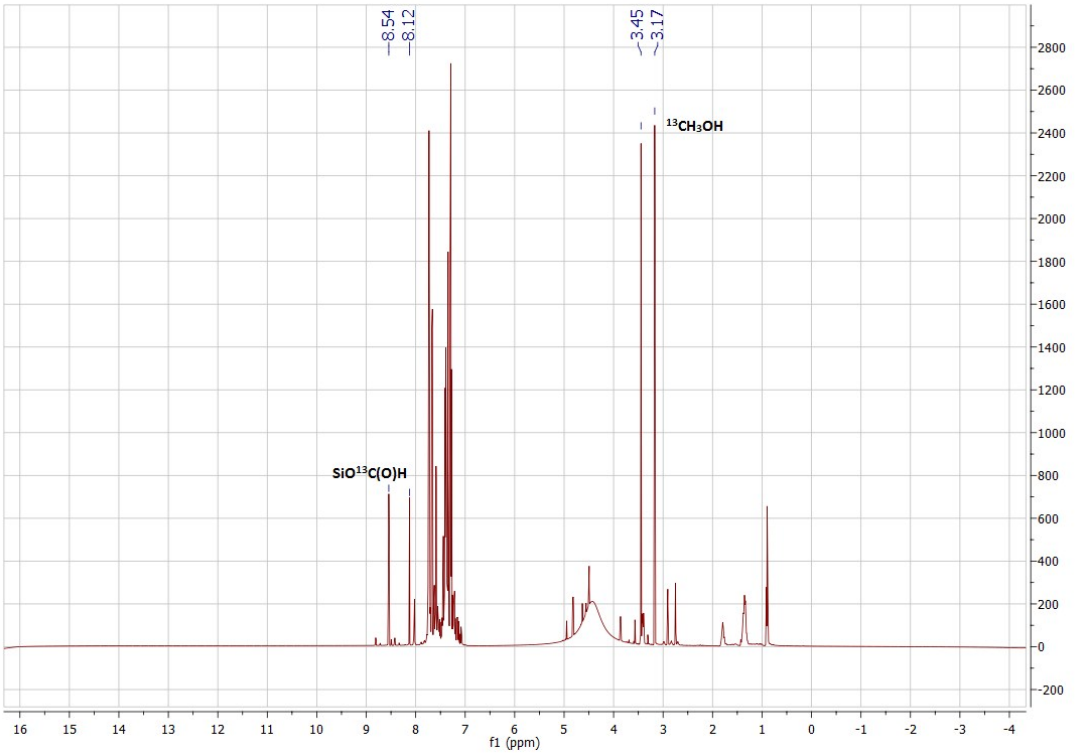


Figure S28. ^{1}H NMR spectrum of reaction of Ph_2SiH_2 with $^{13}CO_2$ (1 bar) with 2.5 mol% $[N(hexyl)_4][ReO_4]$ **2** in d_7-DMF at room temperature after hydrolysis, showing formate and methanol products.

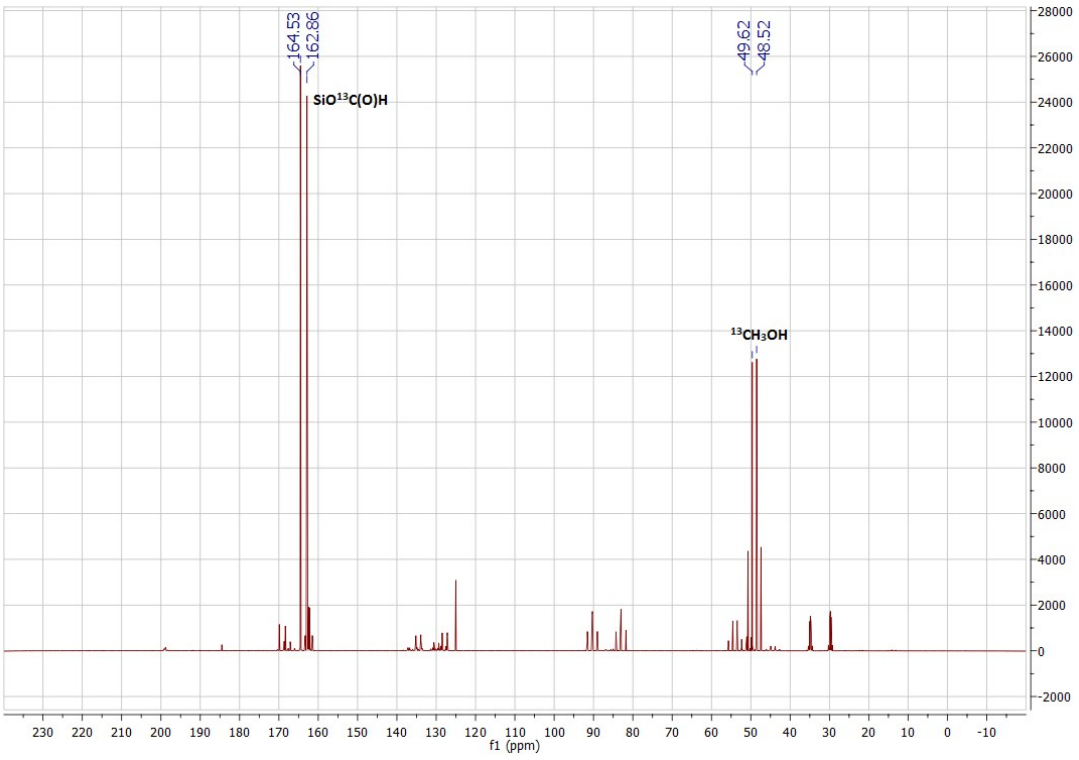


Figure S29. ^{13}C NMR spectrum of reaction of Ph_2SiH_2 with $^{13}CO_2$ (1 bar) with 2.5 mol% $[N(hexyl)_4][ReO_4]$ **2** in d_7-DMF at room temperature after hydrolysis, showing formate and methanol products.

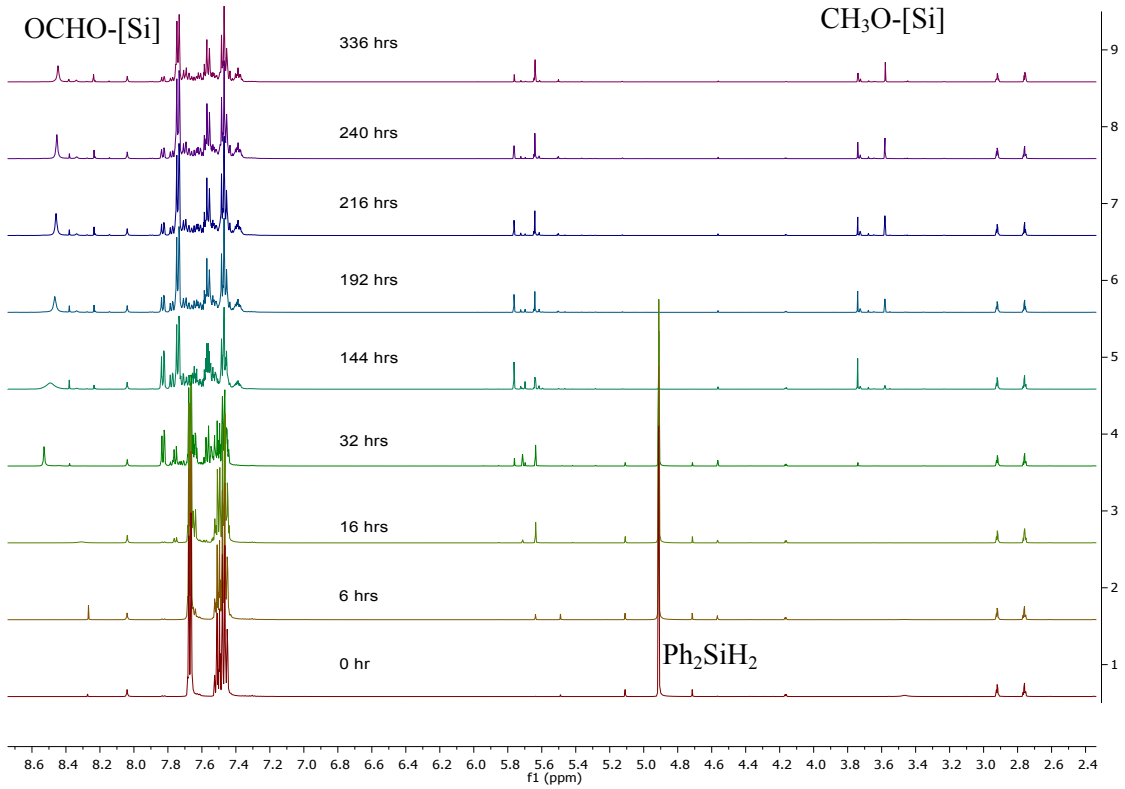


Figure S30. Stacked ^{1}H NMR spectra for the uncatalysed hydrosilylation of CO_2 (1 bar) with Ph_2SiH_2 (0.2 mmol) in d_7-DMF (0.5 mL) at room temperature. Diphenylsilane is consumed after 144 h.

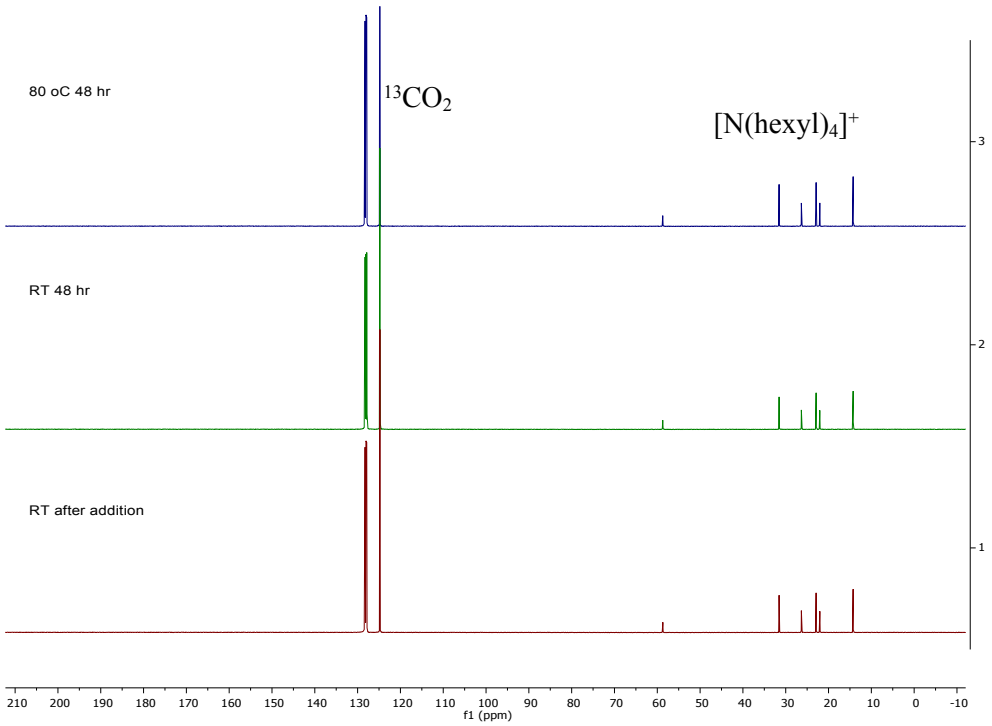


Figure 31. $^{13}C\{^{1}H\}$ NMR spectrum of a stoichiometric reaction between $[ReO_4][N(Hexyl)_4]$ (20 mg) in C_6D_6 (0.5 mL) with 1 bar of $^{13}CO_2$. No observed reactivity, even after heating.

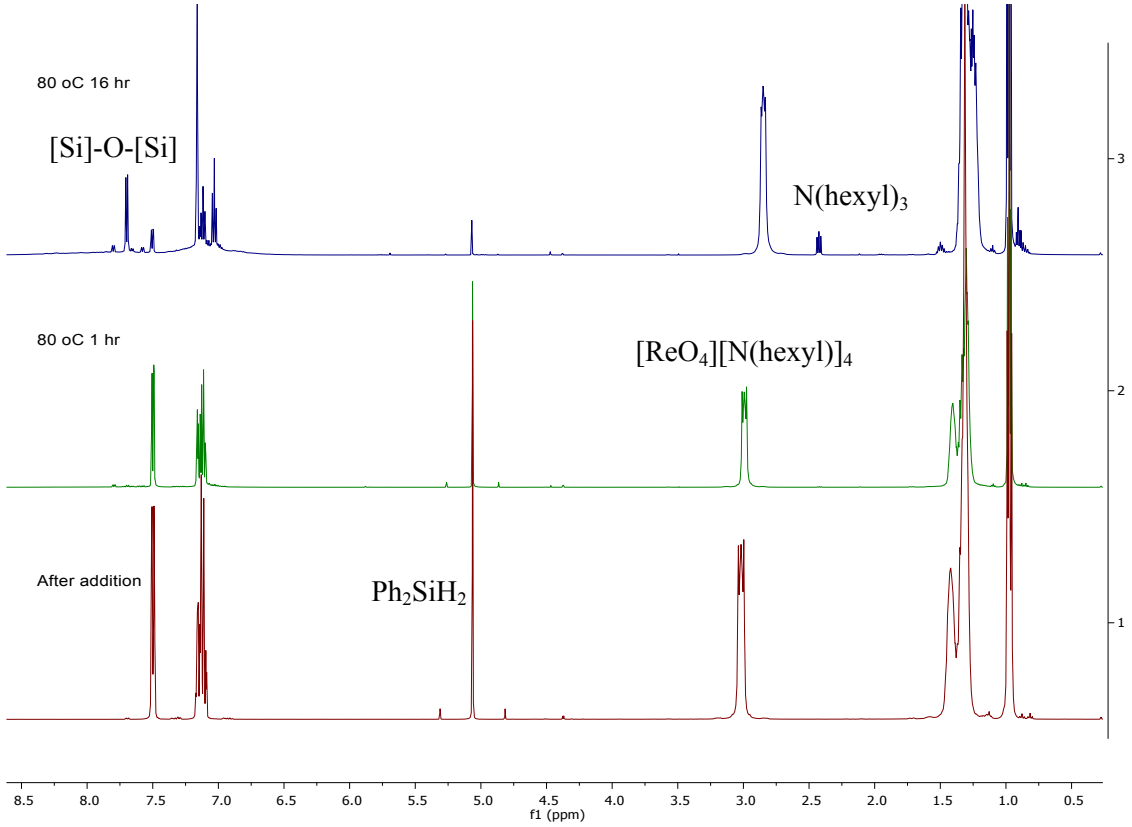


Figure S32. ^{1}H NMR spectra for the reaction of $[ReO_4][N(Hexyl)_4]$ (32 mg, 0.054 mmol) with 1 eq. of diphenylsilane (10 µL, 0.054 mmol) in C_6D_6 (0.5 mL).

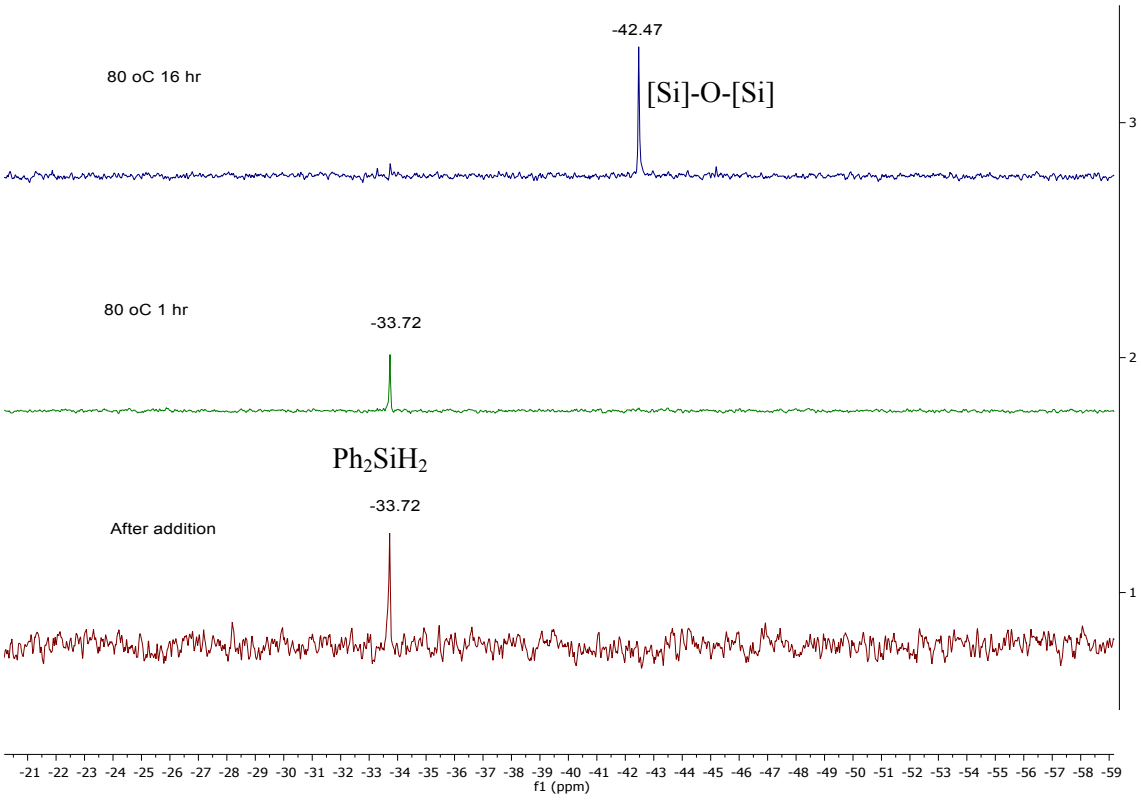


Figure S33. ^{29}Si NMR spectra for the reaction of $[ReO_4][N(Hexyl)_4]$ (32 mg, 0.054 mmol) with 1 eq. of diphenylsilane (10 µL, 0.054 mmol) in C_6D_6 (0.5 mL).

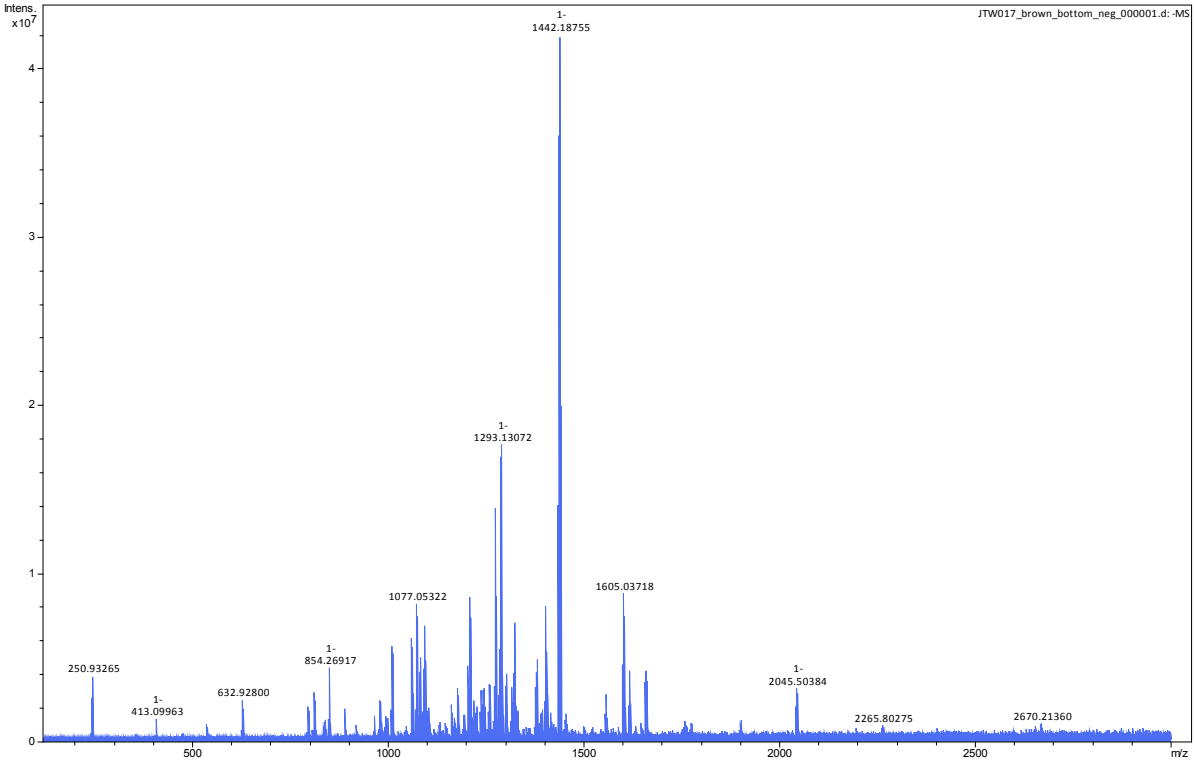


Figure S34. ESI mass spectrometry collected in negative mode for brown precipitate for the reaction of $[ReO_4][N(Hexyl)_4]$ (32 mg, 0.054 mmol) with 1 eq. of diphenylsilane (10 µL, 0.054 mmol) in C_6D_6 (0.5 mL).at 80 °C showing a variety of products due to siloxane and rhenium-oxo cluster formation.

8.2 N-Methylation NMRs

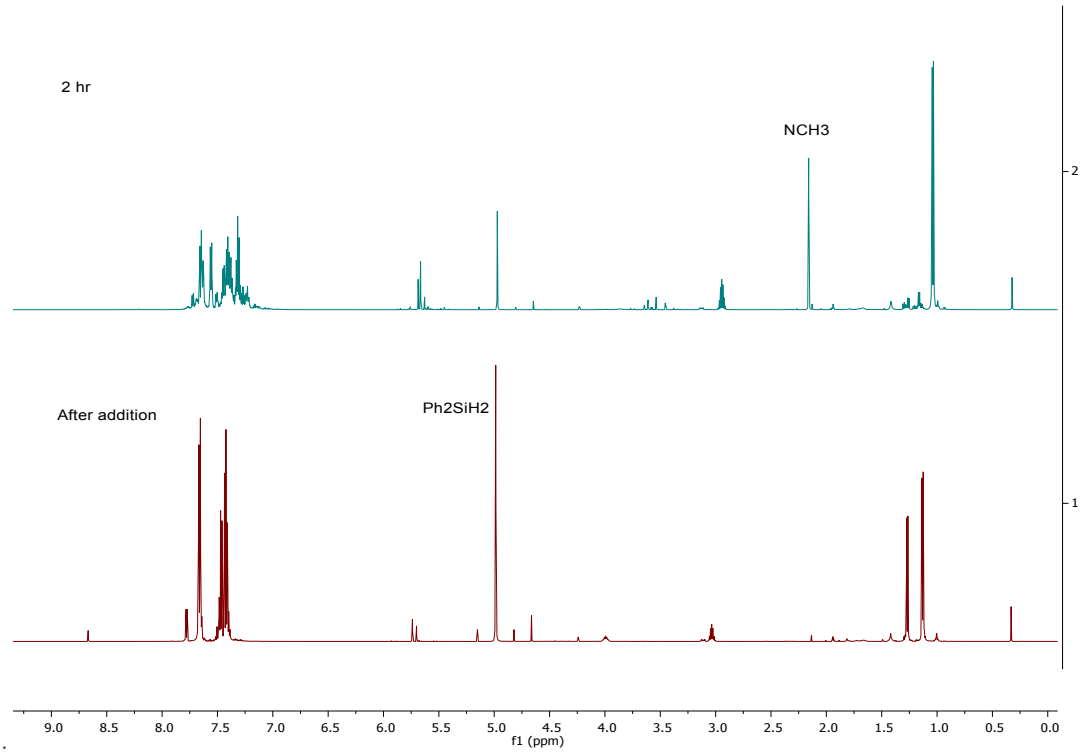


Figure S35 Methylation of HN^iPr_2 in d_3-MeCN with $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%), diphenylsilane (4 eq.), CO_2 (2 bar) heated at 80 °C for 2 h.

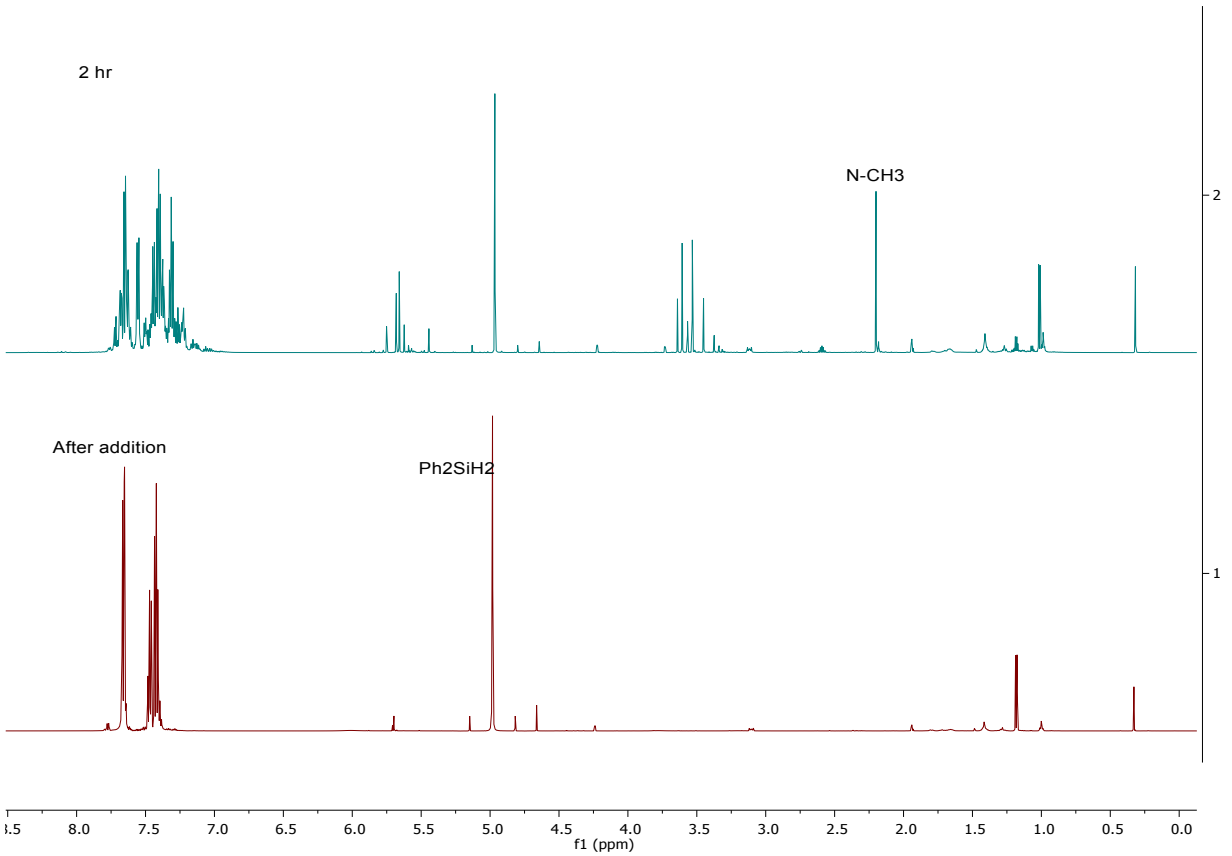


Figure S36 Methylation of H_2N^iPr in d_3-MeCN with $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%), diphenylsilane (8 eq.), CO_2 (2 bar) heated at 80 °C for 2 h.

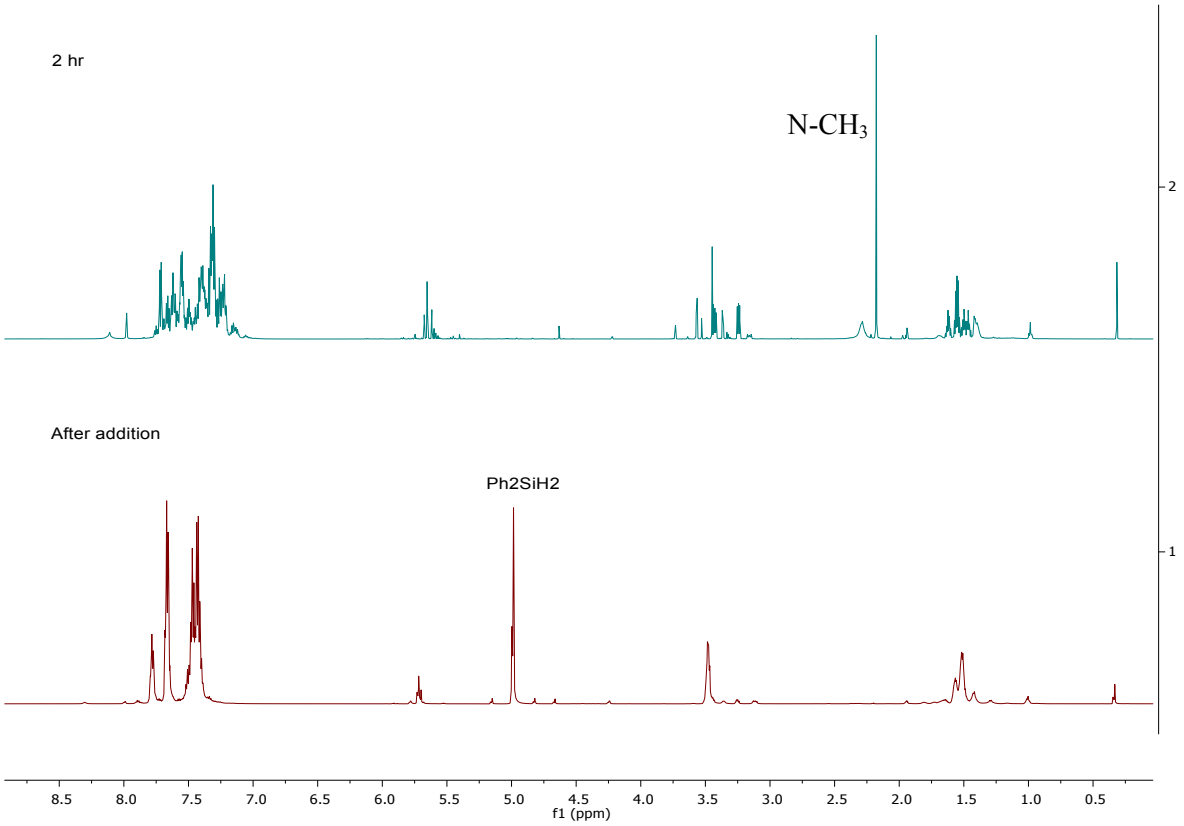


Figure S37 Methylation of Piperidine in d_3-MeCN with $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%), diphenylsilane (8 eq.), CO_2 (2 bar) heated at 80 °C for 2 h.

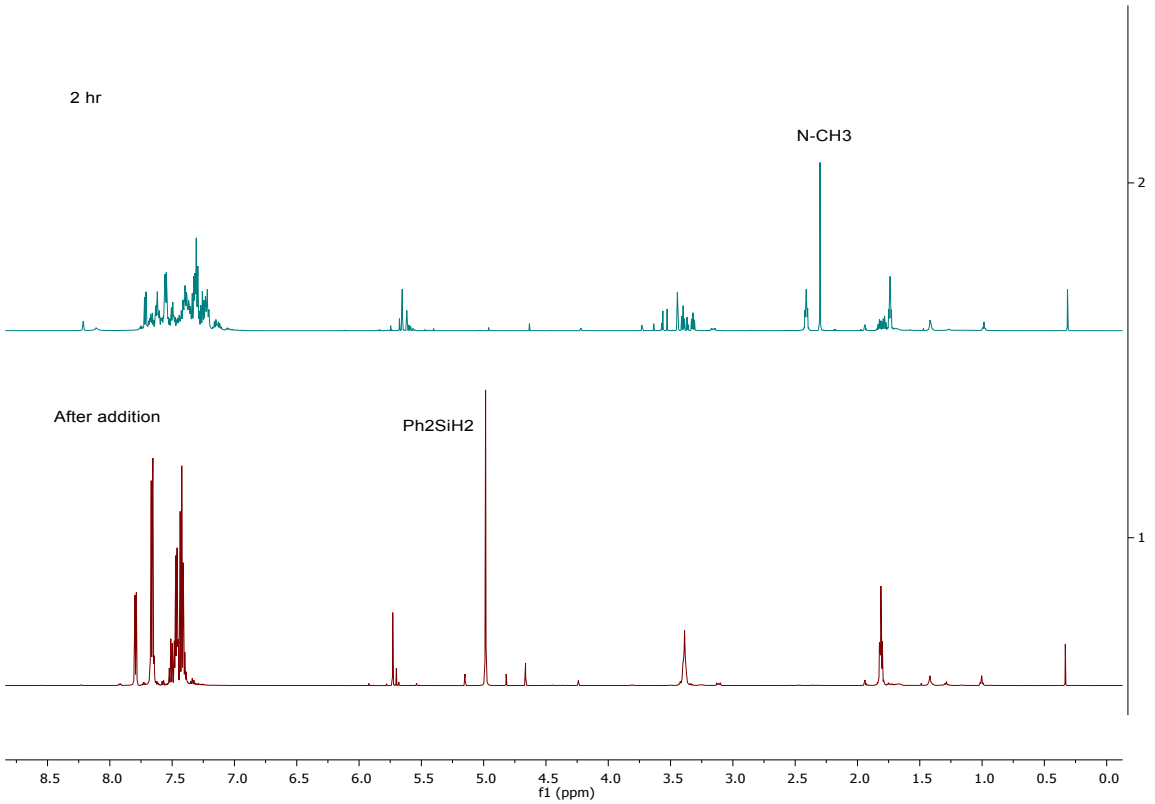


Figure S38 Methylation of Pyrollidine in d_3-MeCN with $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%), diphenylsilane (4 eq.), CO_2 (2 bar) heated at 80 °C for 2 h.

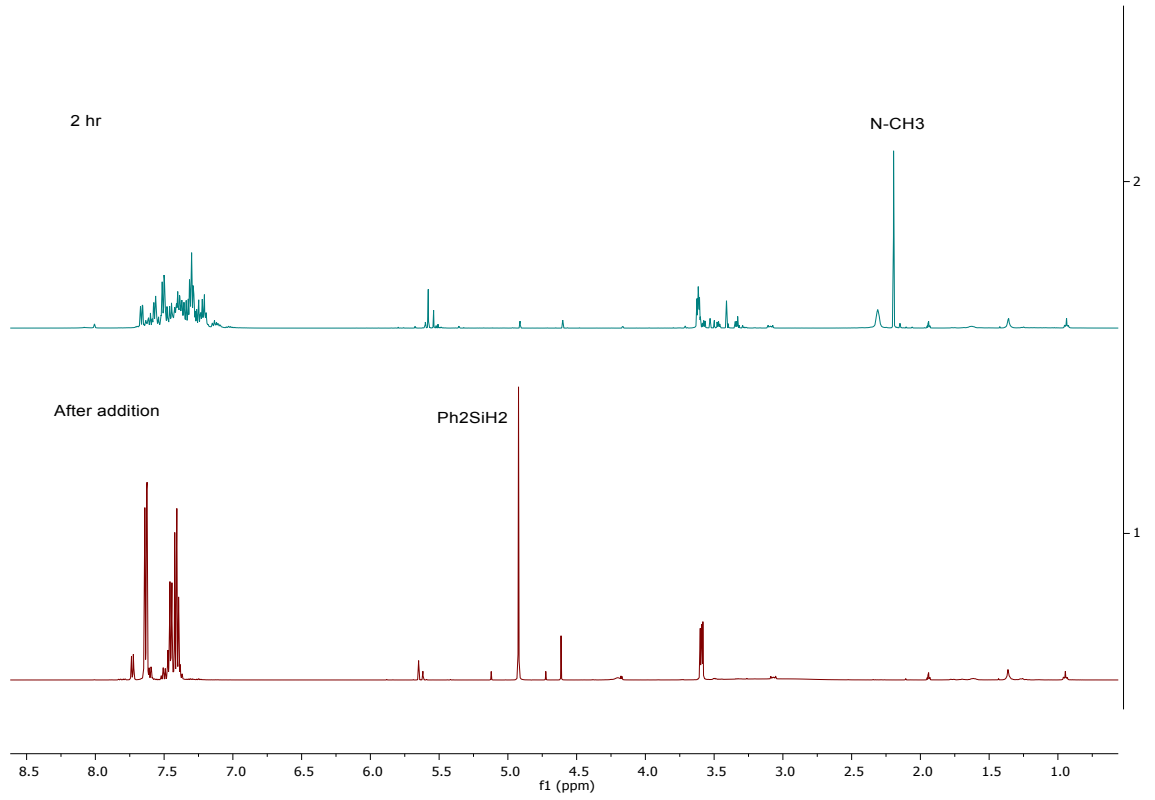


Figure S39 Methylation of Morpholine in d_3-MeCN with $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%), diphenylsilane (4 eq.), CO_2 (2 bar) heated at 80 °C for 2 h.

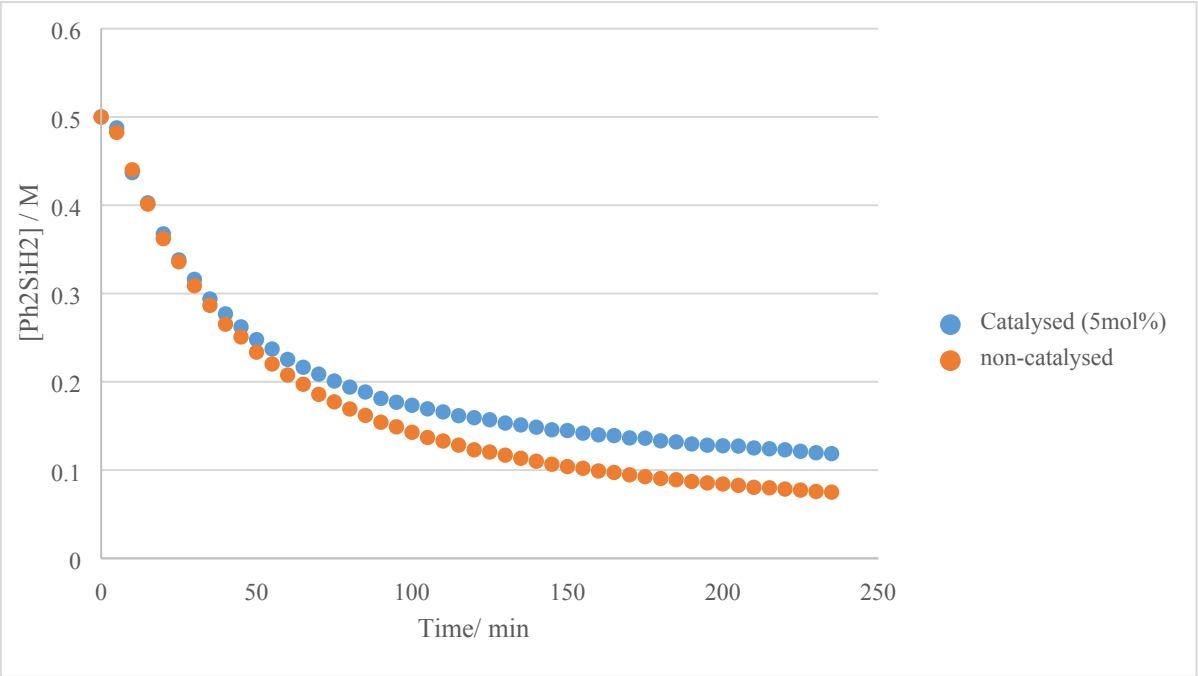


Figure S40. Comparison of rate of consumption of diphenylsilane (0.2 mmol) for the catalysed (5 mol%) and non-catalysed N-methylation of $^{i}Pr_2NH$ (0.05 mmol) in d_7-DMF (0.5 mL).

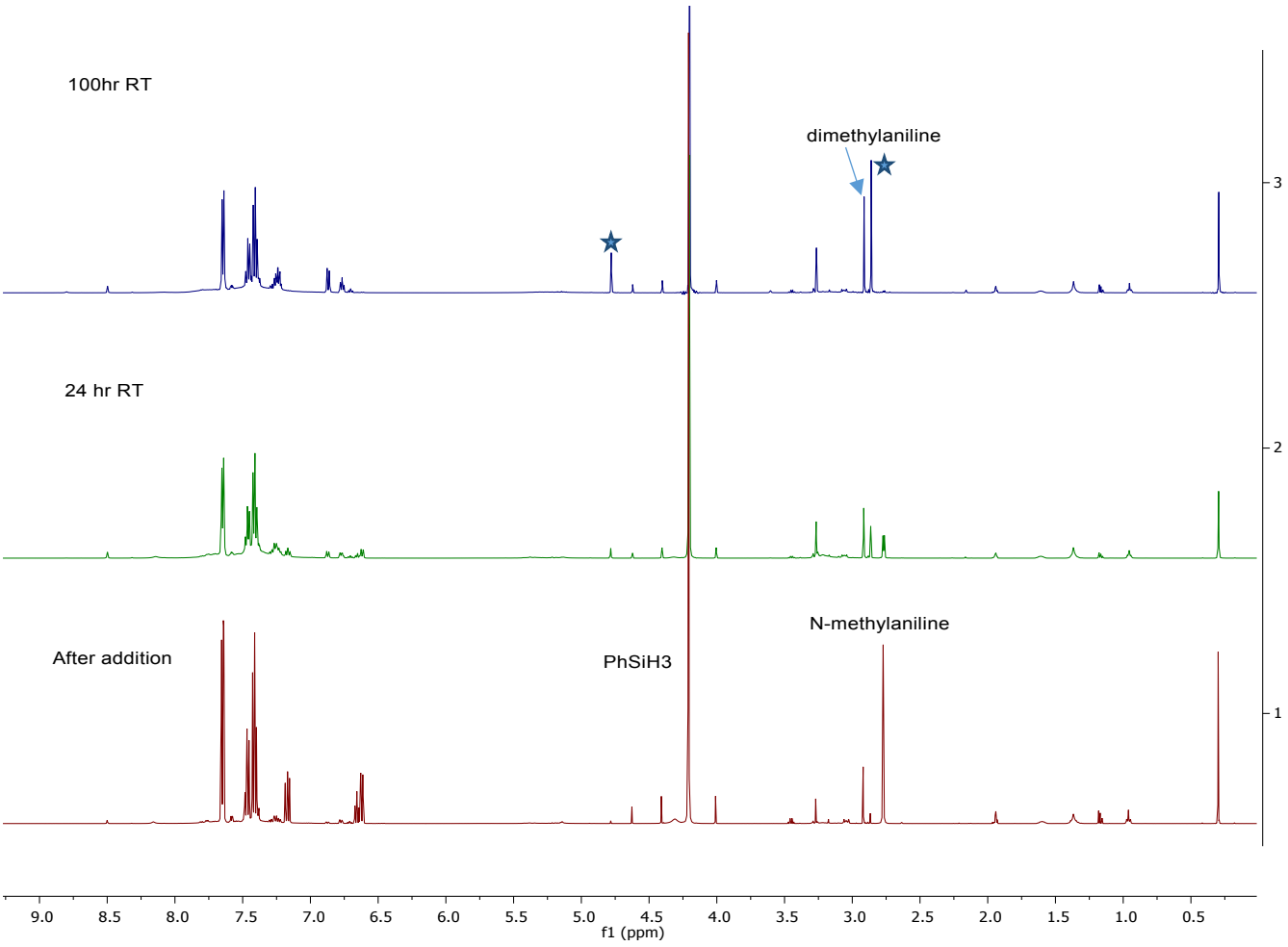


Figure S41 Methylation of N-methylaniline in d_3-MeCN with $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%), phenylsilane (4 eq.), CO_2 (2 bar) at room temperature. Star signifies resonances due to $CH_2(NMePh)_2$.

8.3 Hydrosilylation of Aldehydes NMRs

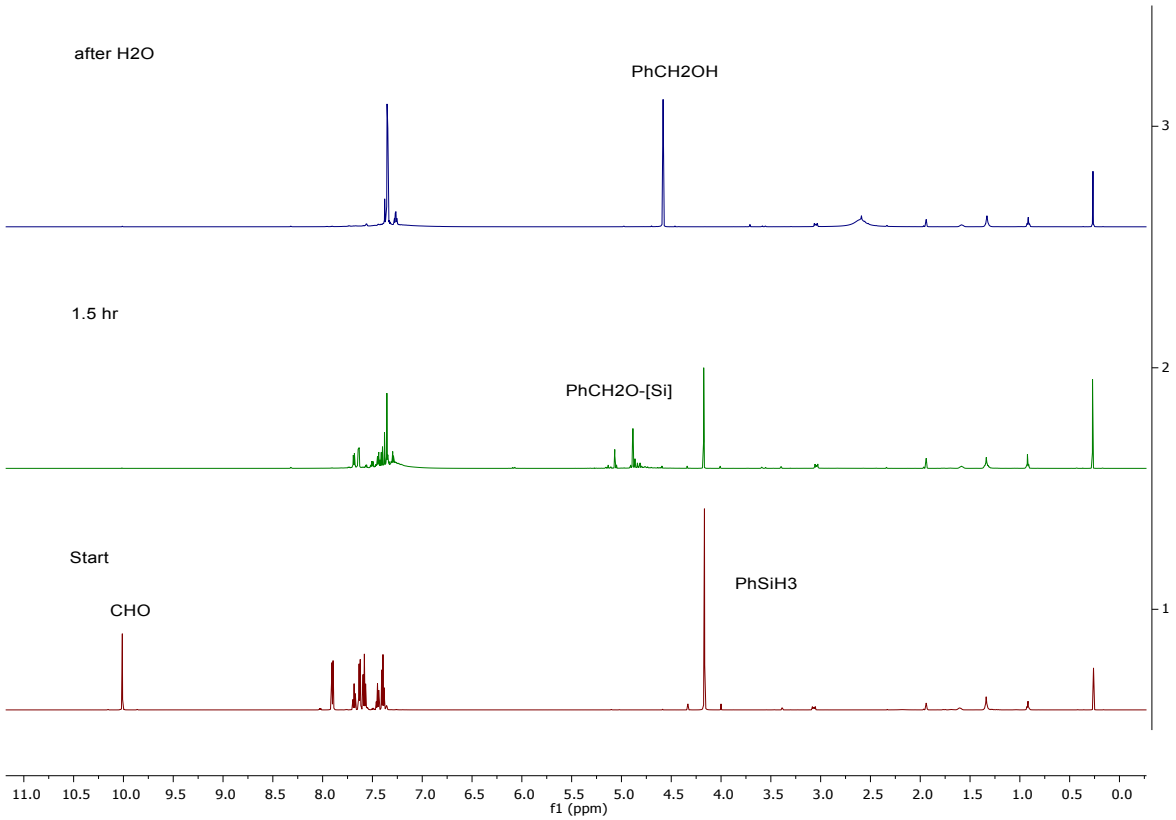


Figure S42 $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%) in d_3-MeCN (0.5 mL), with phenylsilane (1.2 eq) and benzaldehyde (0.2mmol), 80 °C.

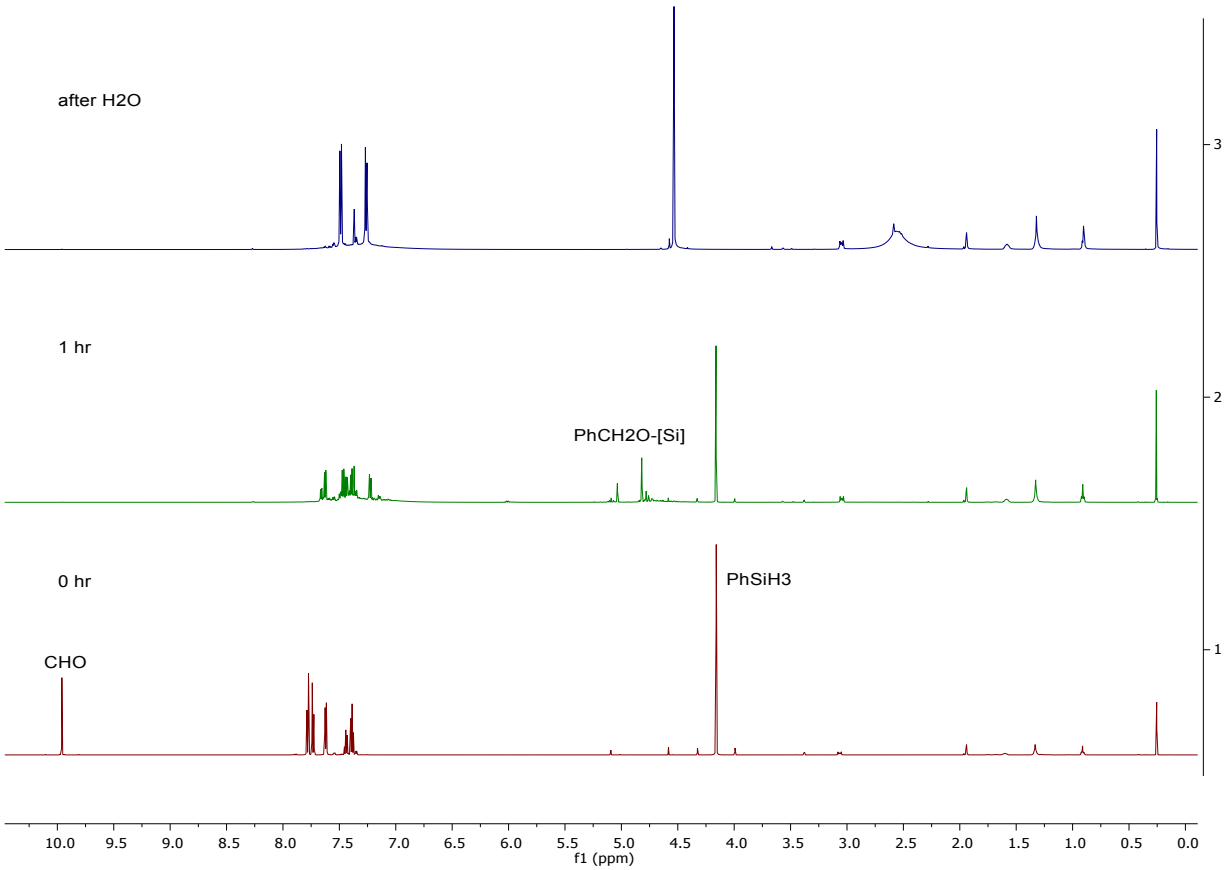


Figure S43 [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in d$_3$-MeCN (0.5 mL), with phenylsilane (1.2 eq) and 4-bromobenzaldehyde (0.2mmol),80 °C.

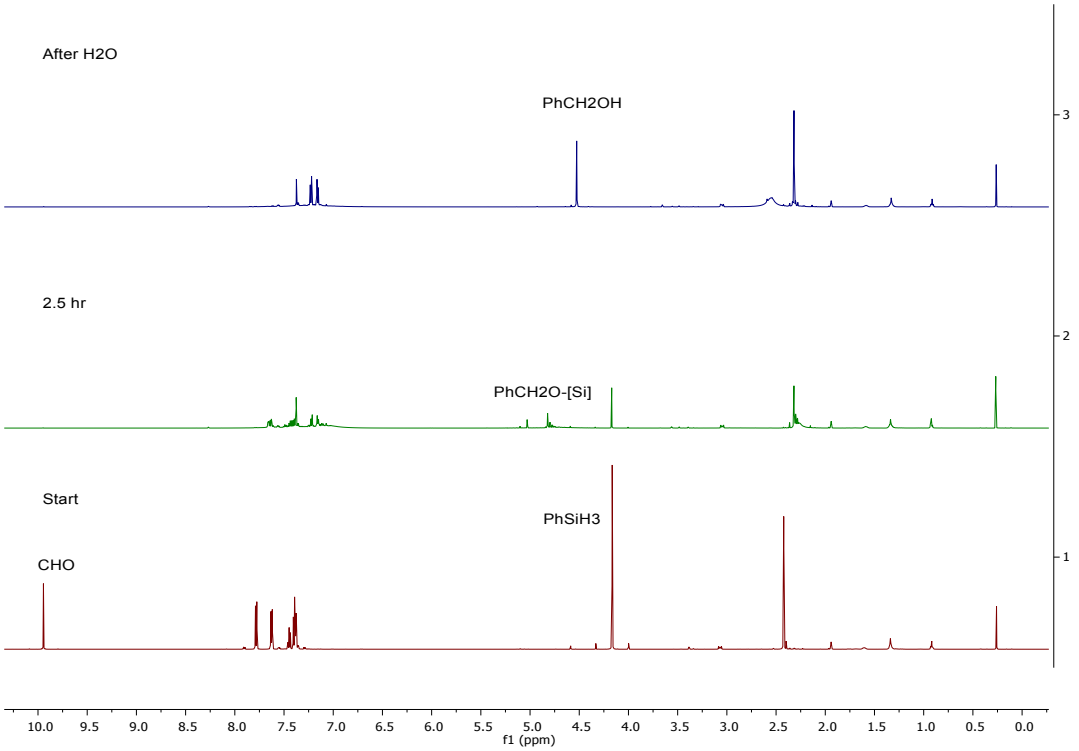


Figure S44 [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in d$_3$-MeCN (0.5 mL), with phenylsilane (1.2 eq) and 4-methylbenzaldehyde (0.2mmol), 80 °C.

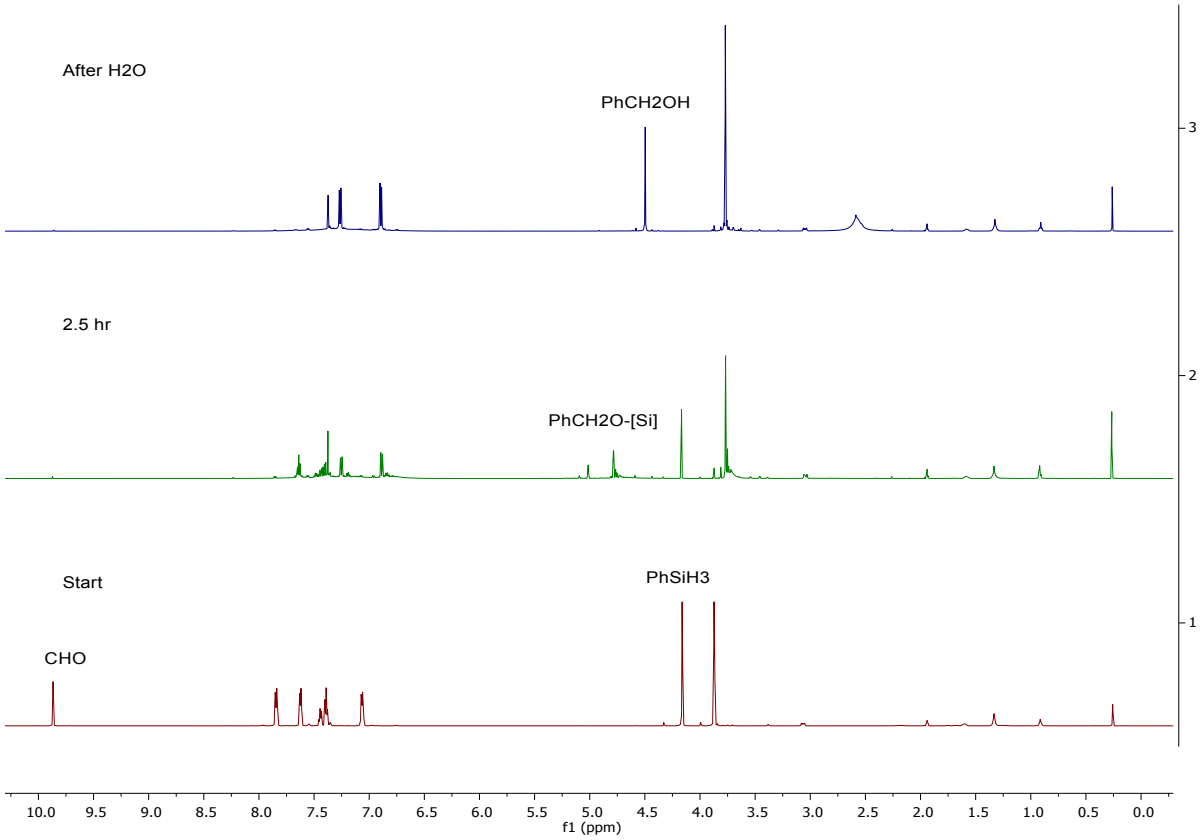


Figure S45 [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in d_3-MeCN (0.5 mL), with phenylsilane (1.2 eq) and 4-methoxybenzaldehyde (0.2mmol), 80 °C.

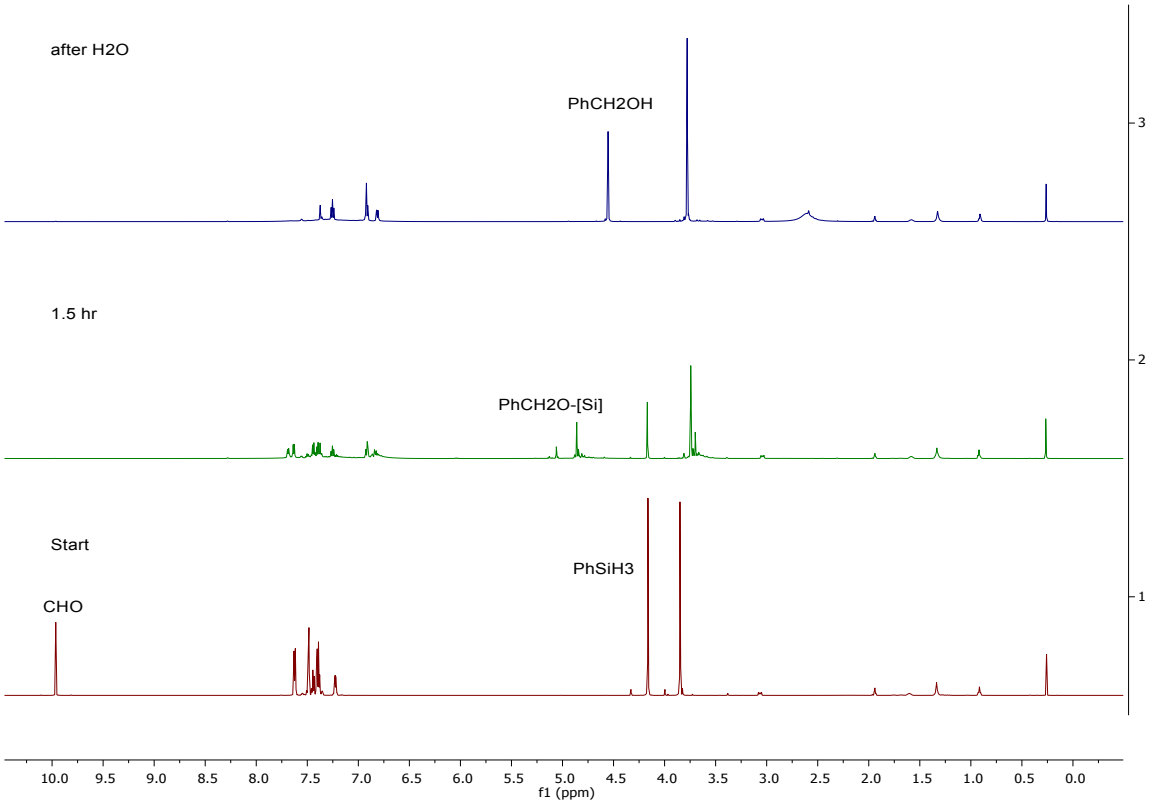


Figure S46 [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in d_3-MeCN (0.5 mL), with phenylsilane (1.2 eq) and 3-methoxybenzaldehyde (0.2mmol), 80 °C.

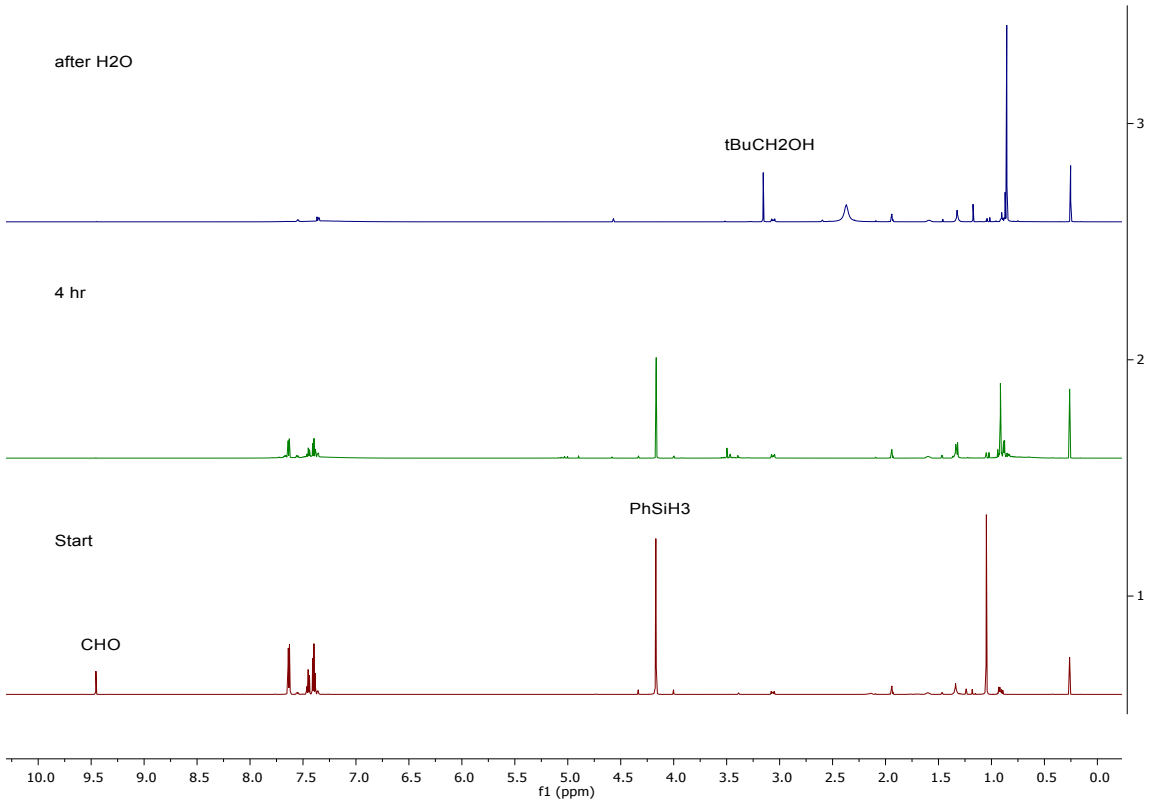


Figure S47 [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in d$_3$-MeCN (0.5 mL), with phenylsilane (1.2 eq) and trimethylacetaldehyde (0.2mmol), 80 °C.

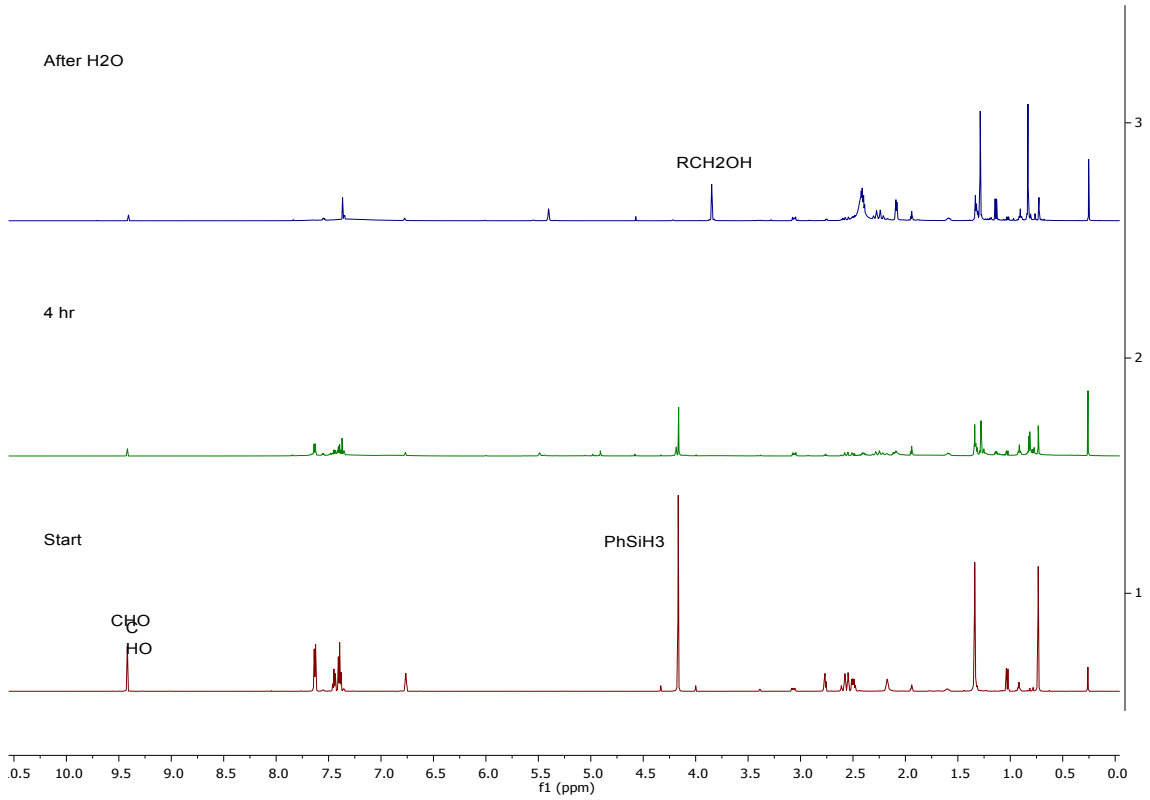


Figure S48 [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in d$_3$-MeCN (0.5 mL), with phenylsilane (1.2 eq) and myrtenal (0.2mmol), 80 °C.

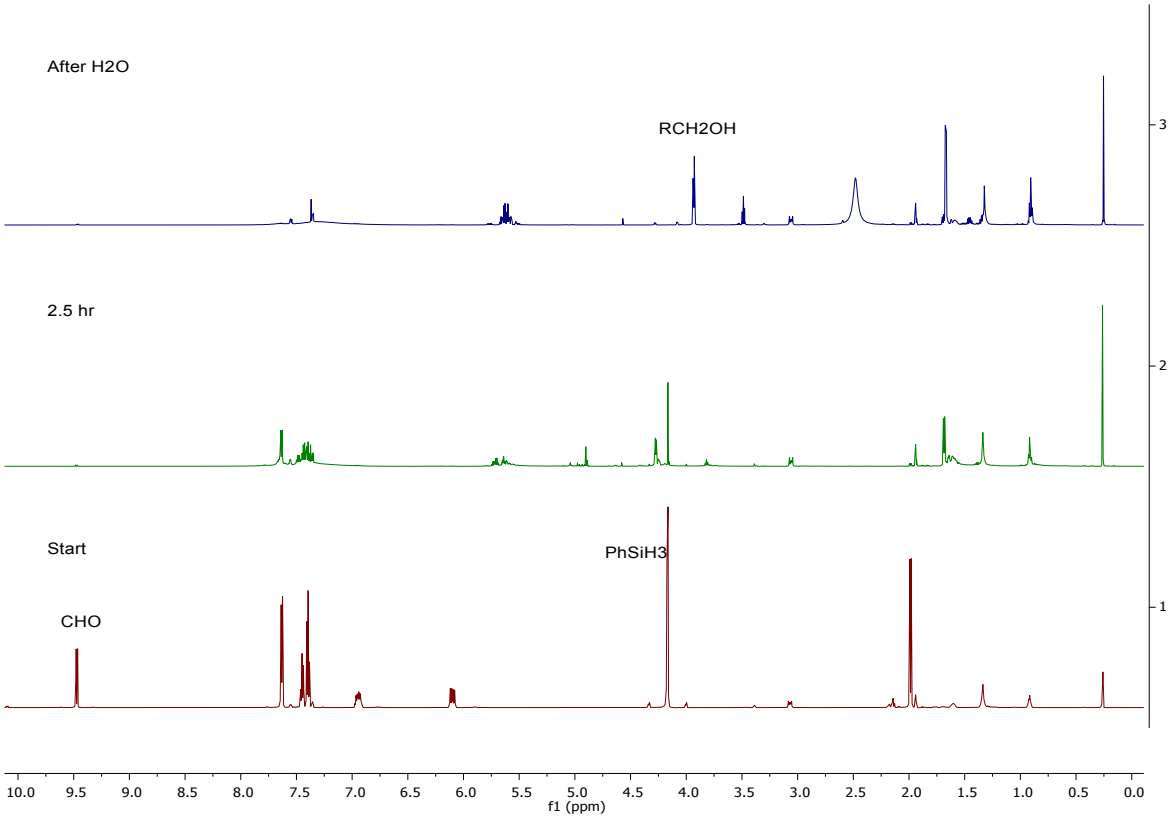


Figure S49 $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%) in d_3-MeCN (0.5 mL), with phenylsilane (1.2 eq) and crotonaldehyde (0.2mmol), 80 °C.

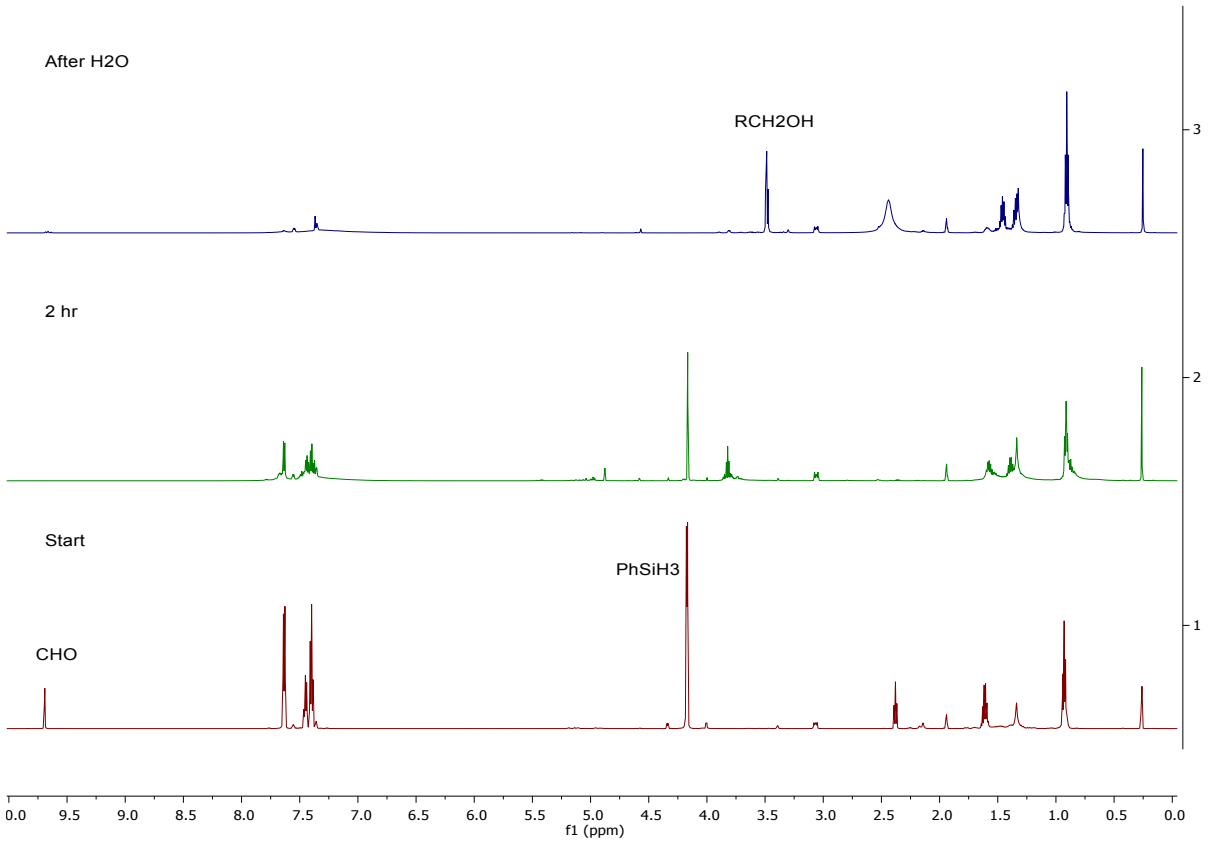


Figure S50 $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%) in d_3-MeCN (0.5 mL), with phenylsilane (1.2 eq) and Butyraldehyde (0.2mmol), 80 °C.

8.4 Hydrosilylation of Ketones NMRs

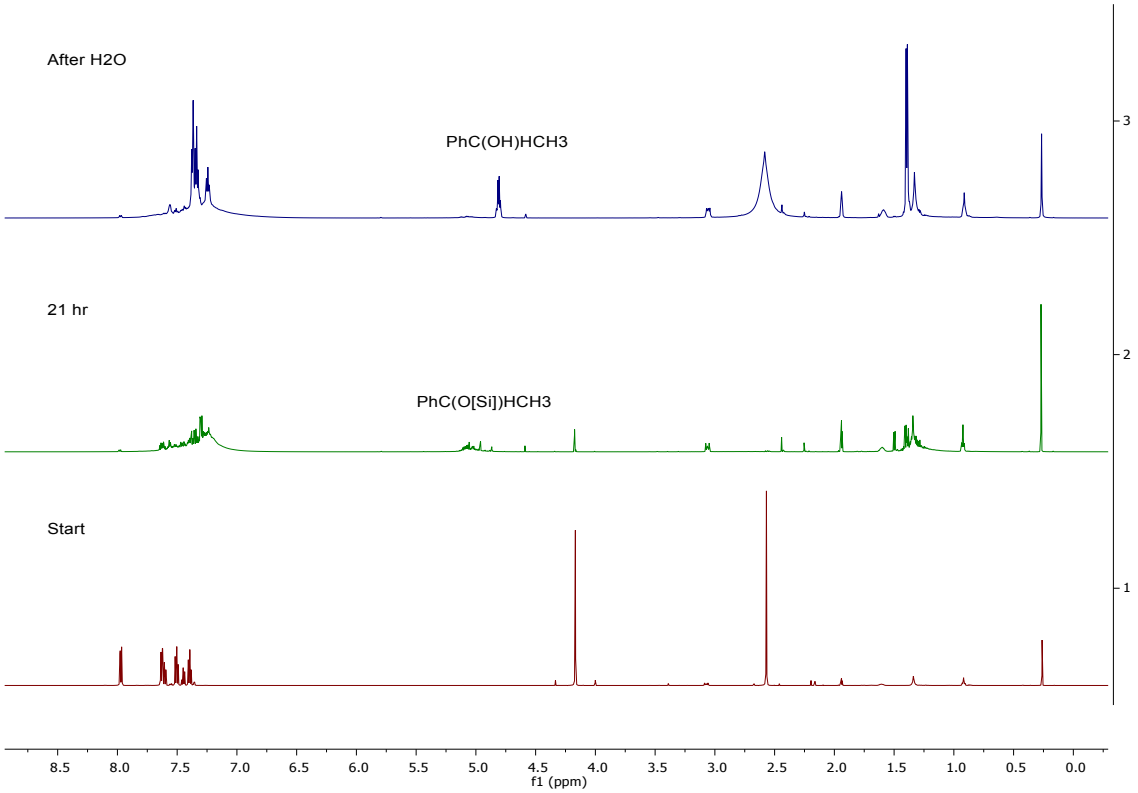


Figure S51 [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in d$_3$-MeCN (0.5 mL), with phenylsilane (1.2 eq) and acetophenone (0.2mmol), 80 °C.

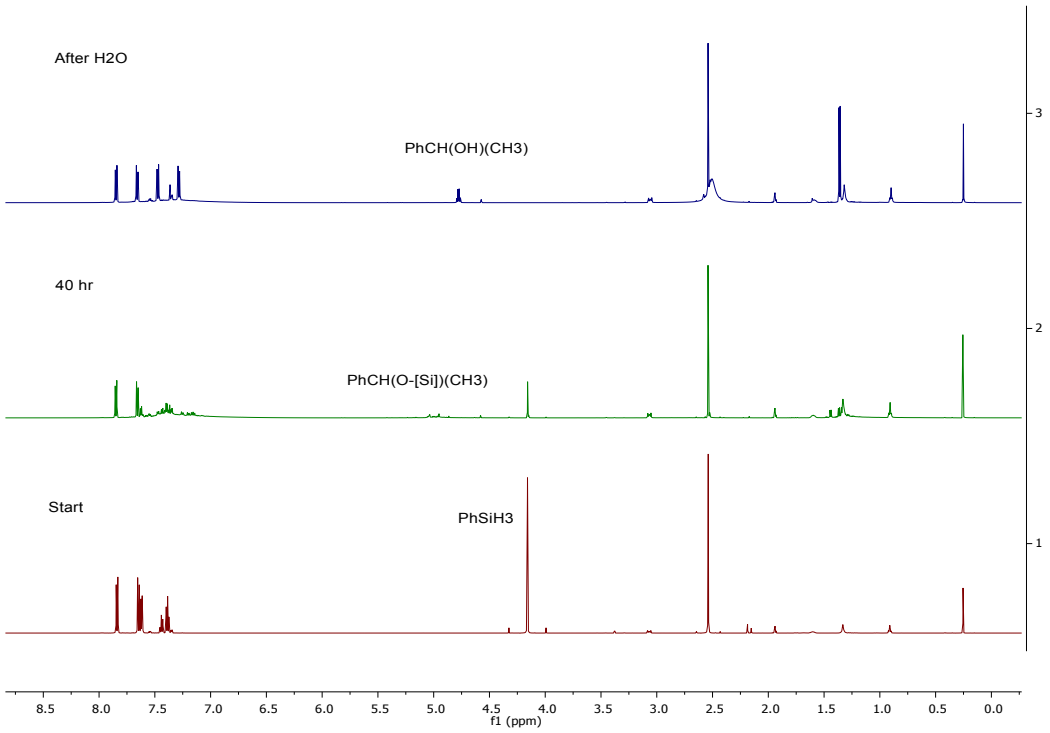


Figure S52 [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in d$_3$-MeCN (0.5 mL), with phenylsilane (1.2 eq) and 4-bromoacetophenone (0.2mmol), 80 °C.

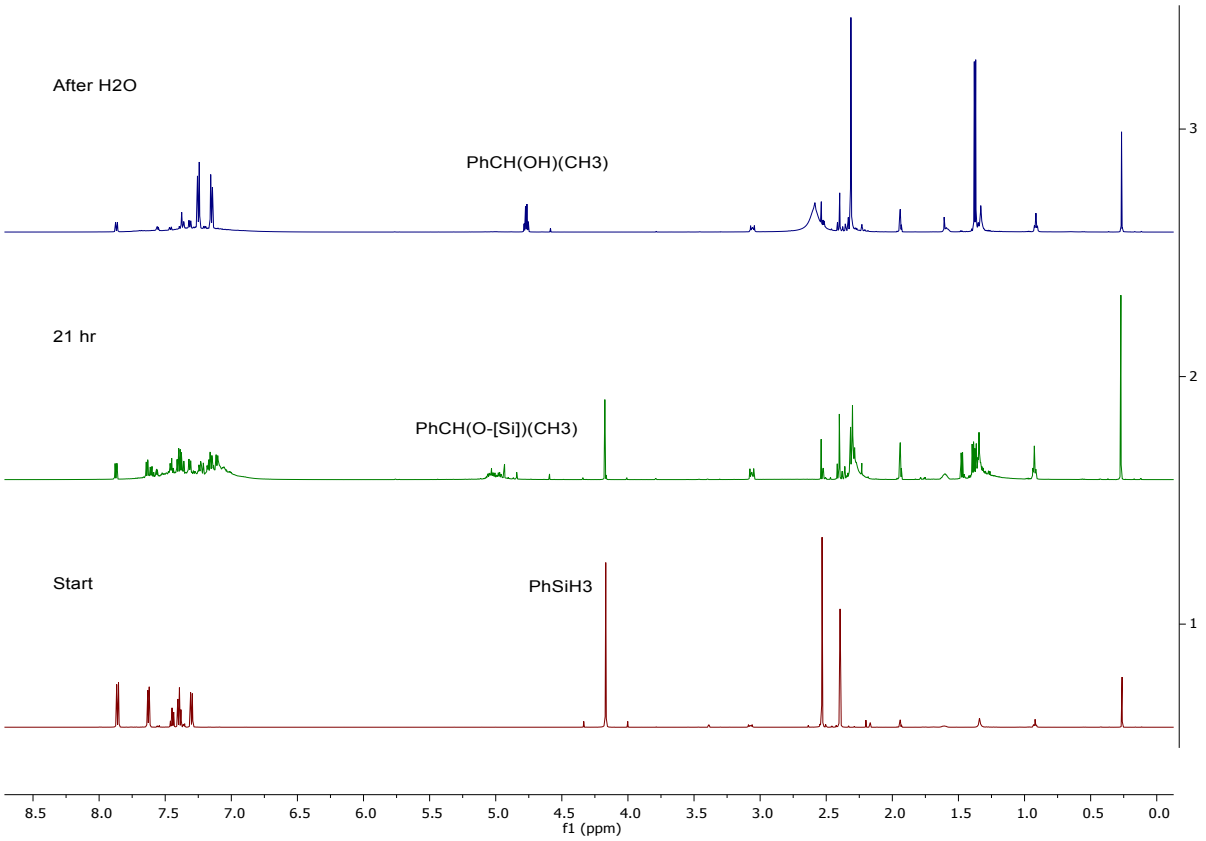


Figure S53 $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%) in d_3-MeCN (0.5 mL), with phenylsilane (1.2 eq) and 4-methylacetophenone (0.2mmol), 80 °C.

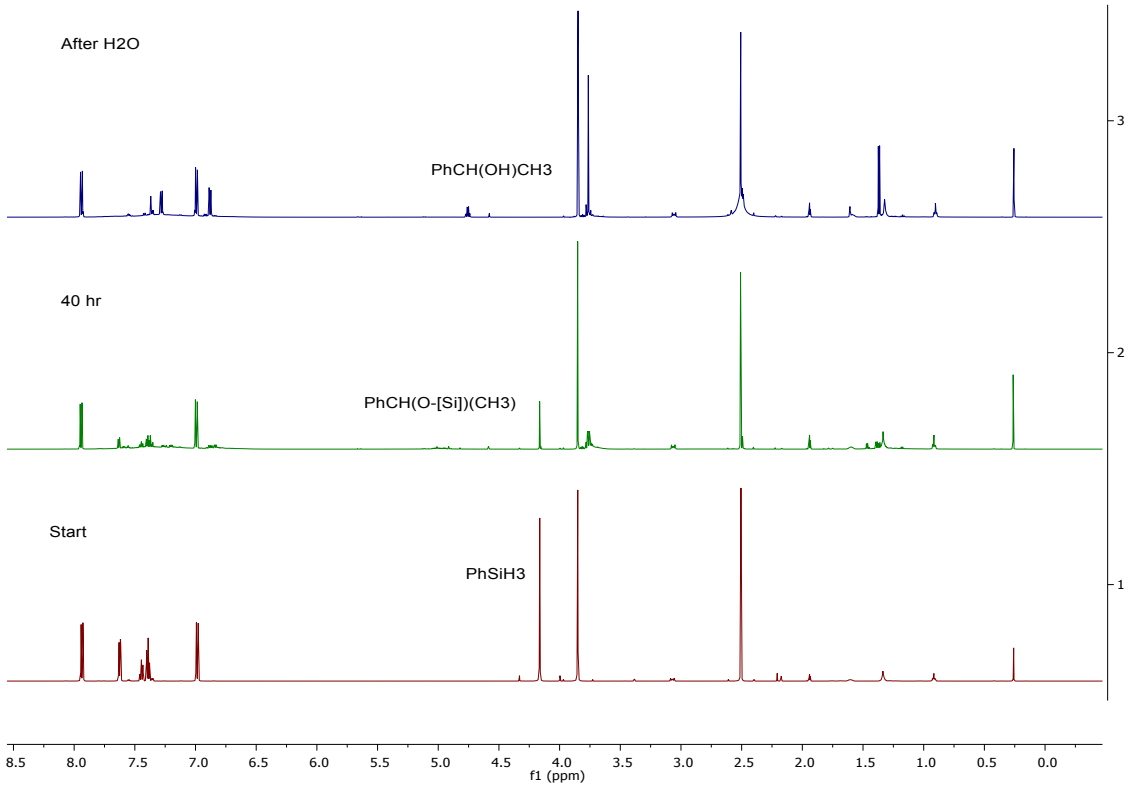


Figure S54 $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%) in d_3-MeCN (0.5 mL), with phenylsilane (1.2 eq) and 4-methoxyacetophenone (0.2mmol), 80 °C.

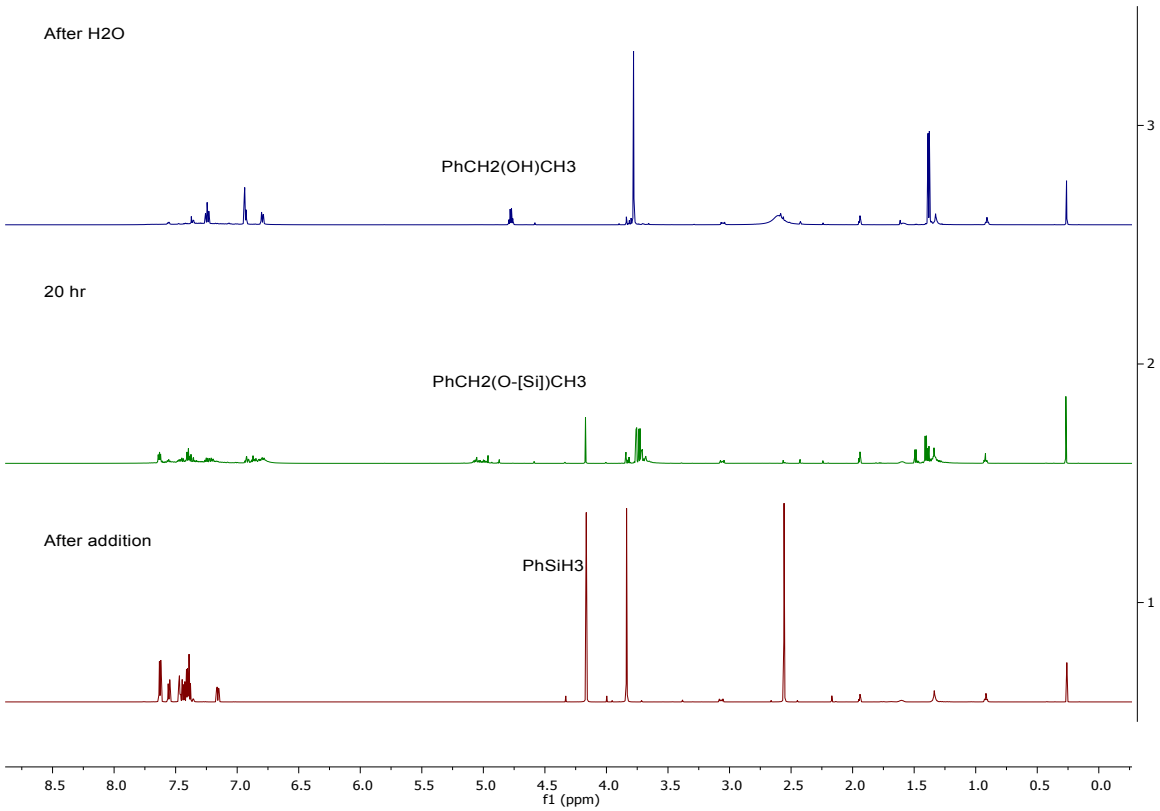


Figure S55 [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in d$_3$-MeCN (0.5 mL), with phenylsilane (1.2 eq) and 3-methoxyacetophenone (0.2mmol), 80 °C.

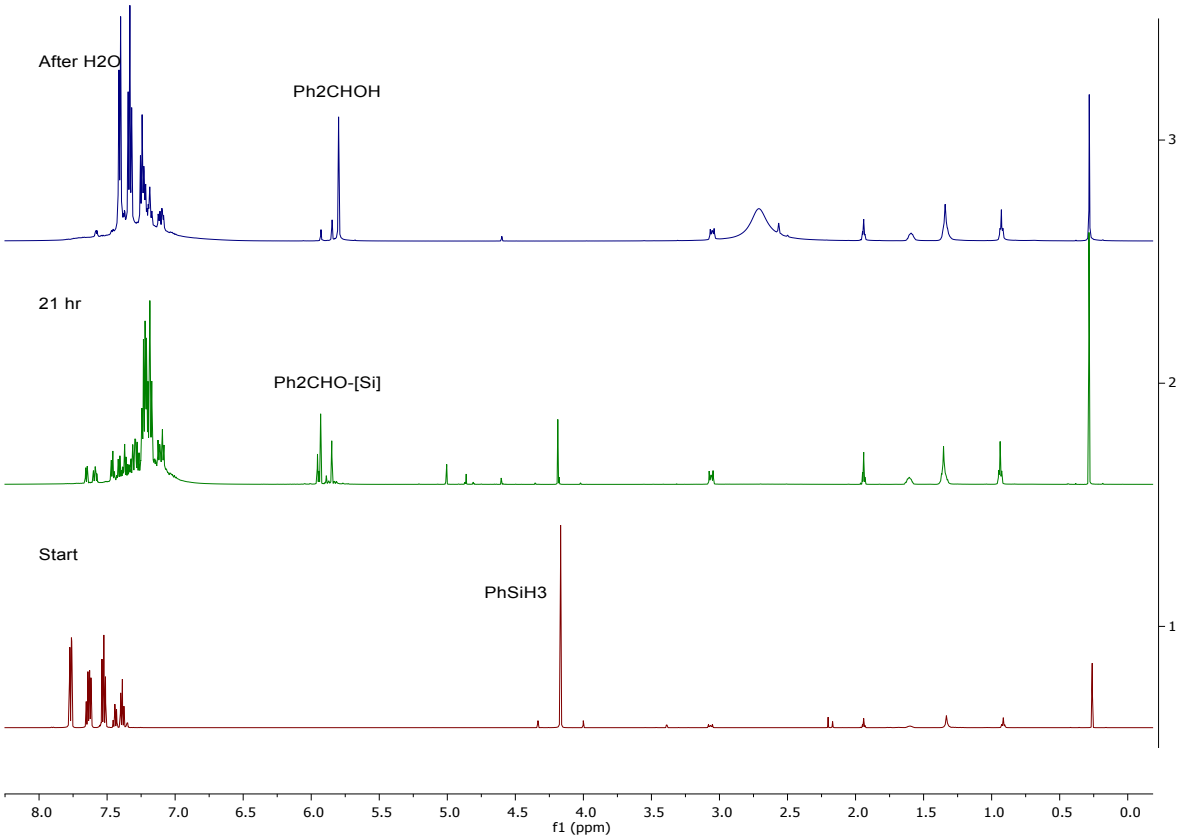


Figure S56 [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in d$_3$-MeCN (0.5 mL), with phenylsilane (1.2 eq) and benzophenone (0.2mmol), 80 °C.

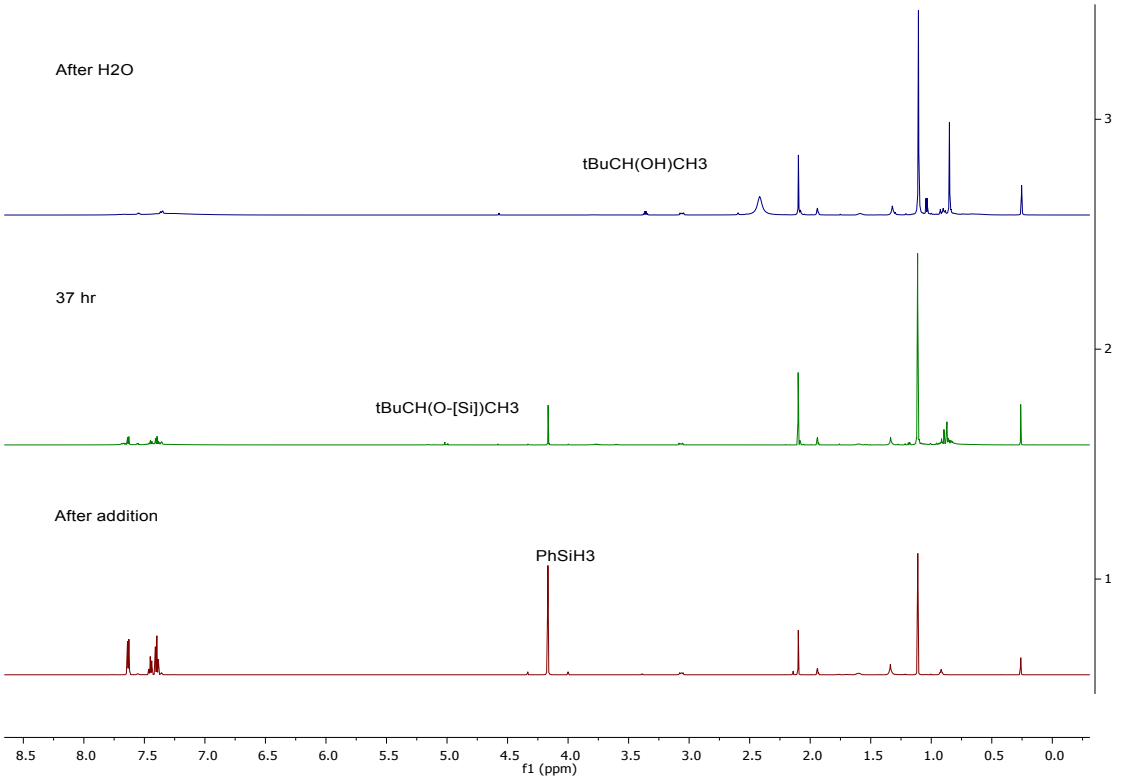


Figure S57 [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in d$_3$-MeCN (0.5 mL), with phenylsilane (1.2 eq) and pinacolone (0.2mmol), 80 °C.

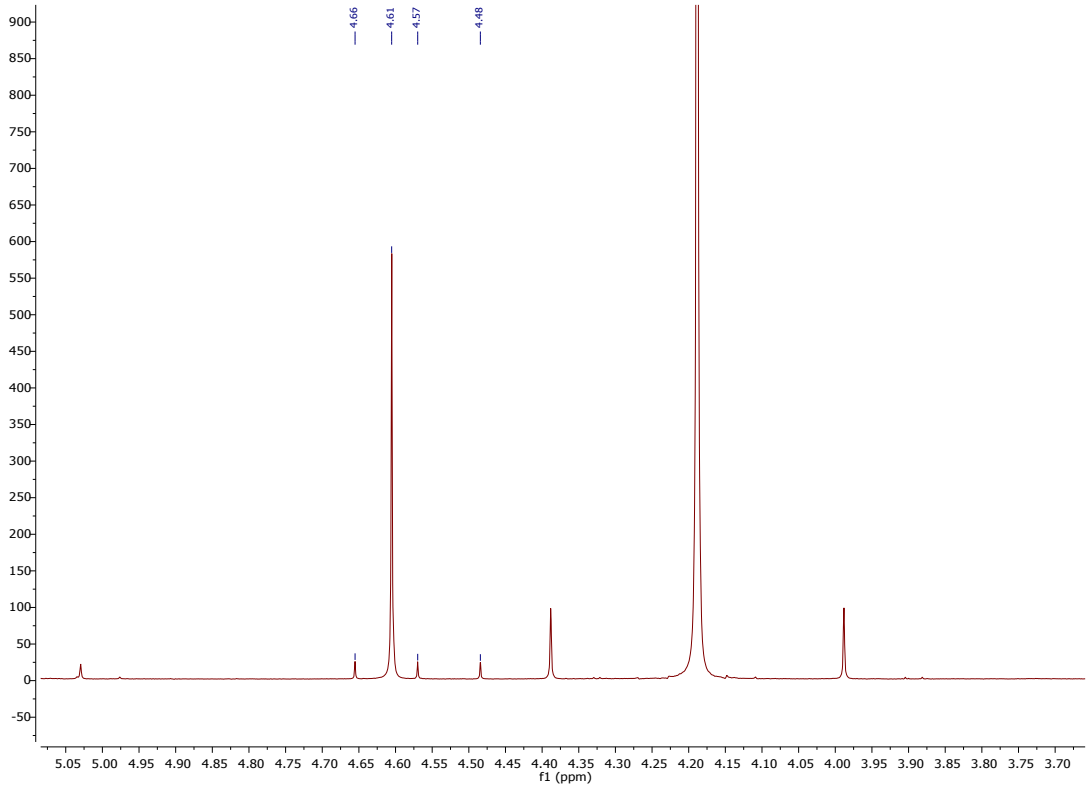


Figure S58 1:1:1 triplet for HD formation from the reaction of $PhSiH_3$ and H_2O

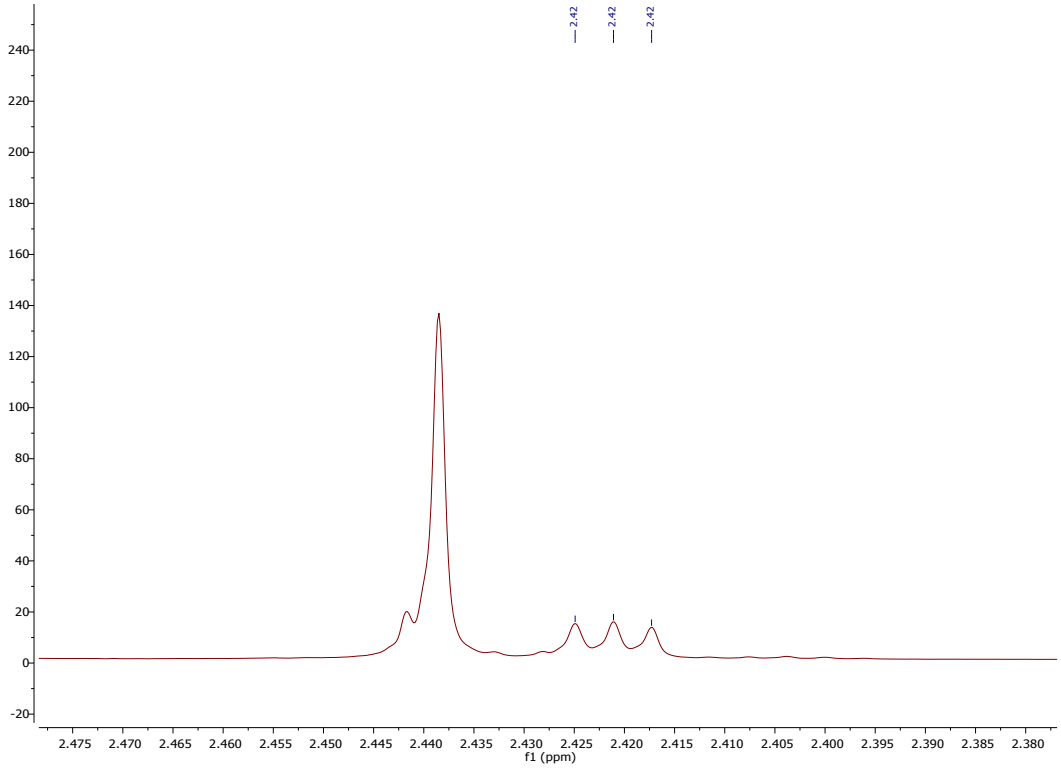
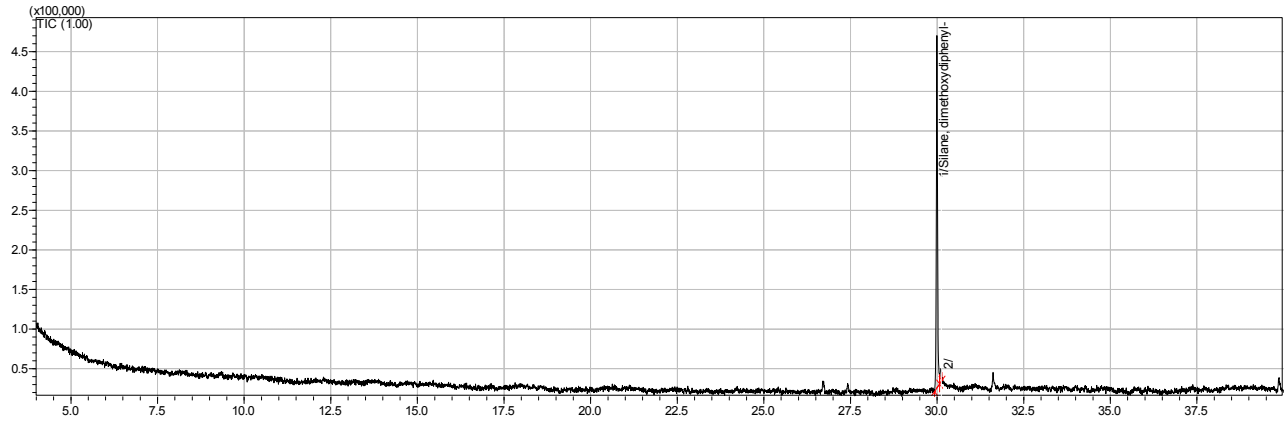


Figure S59 1:1:1 triplet for CH_2D formation from the reaction of $PhSiH_3$ and Acetophenone

9. GC-MS data

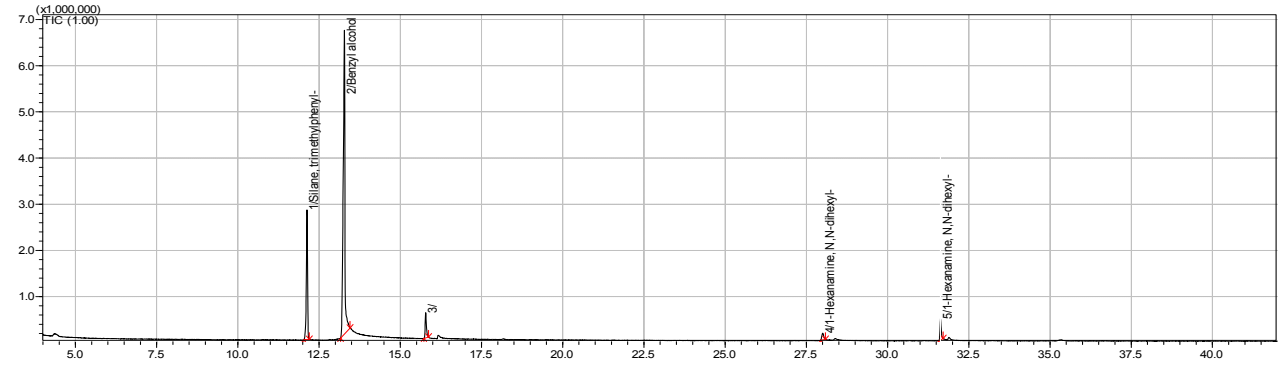
9.1 Hydrosilylation of CO_2



PEAK	R. TIME	I. TIME	F. TIME	M/Z	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	29.995	29.925	30.070	TIC	1133967	95.79	444522	96.52	2.55	Silane, dimethoxydiphenyl-
2	30.125	30.070	30.140	TIC	49890	4.21	16004	3.48	3.12	Silane, dimethoxydiphenyl

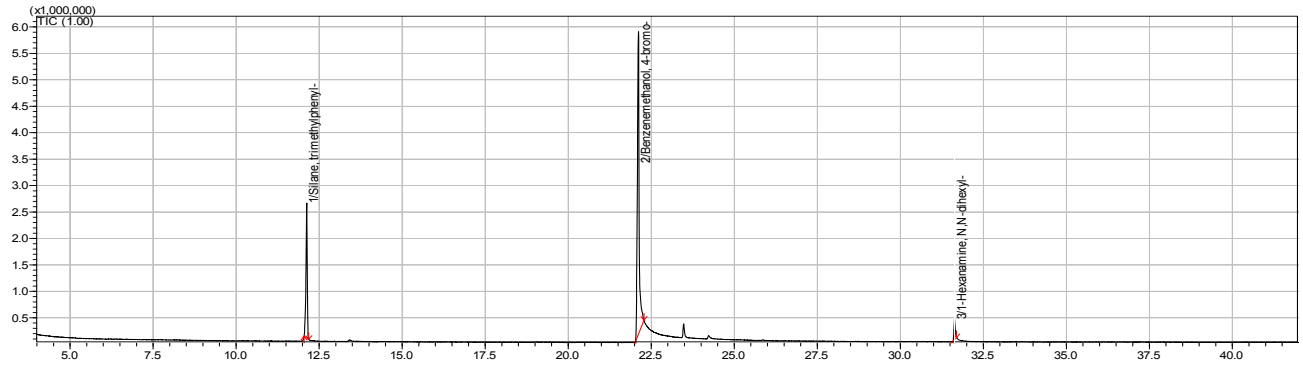
Figure S60 $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%) in d_3-MeCN (0.5 mL), with diphenylsilane (0.2 mmol) and CO_2 (1 bar), 80 °C.

9.2 Hydrosilylation of aldehydes



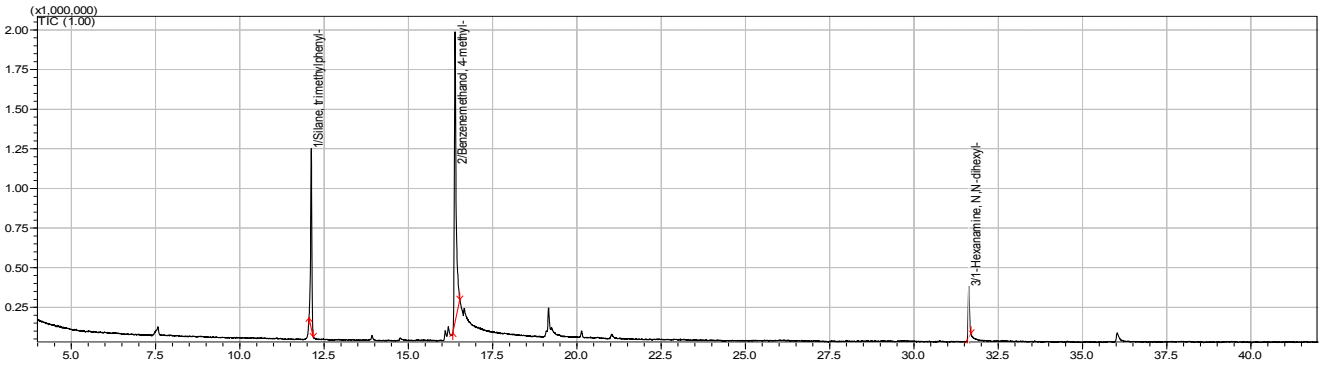
PEAK	R. TIME	I. TIME	F. TIME	M/Z	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	12.130	12.035	12.200	TIC	7332756	21.18	2807960	26.65	2.61	Silane, trimethylphenyl-
2	13.280	13.160	13.450	TIC	23986415	69.29	6580767	62.46	3.64	Benzyl alcohol
3	15.782	15.730	15.870	TIC	1471163	4.25	545611	5.18	2.70	
4	28.001	27.940	28.085	TIC	597945	1.73	147760	1.40	4.05	1-Hexanamine, N,N-dihexyl-
5	31.630	31.575	31.710	TIC	1228922	3.55	453944	4.31	2.71	1-Hexanamine, N,N-dihexyl-

Figure S61 $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%) in d_3-MeCN (0.5 mL), with phenylsilane (1.2 eq.) and benzaldehyde (0.2 mmol), 80 °C.



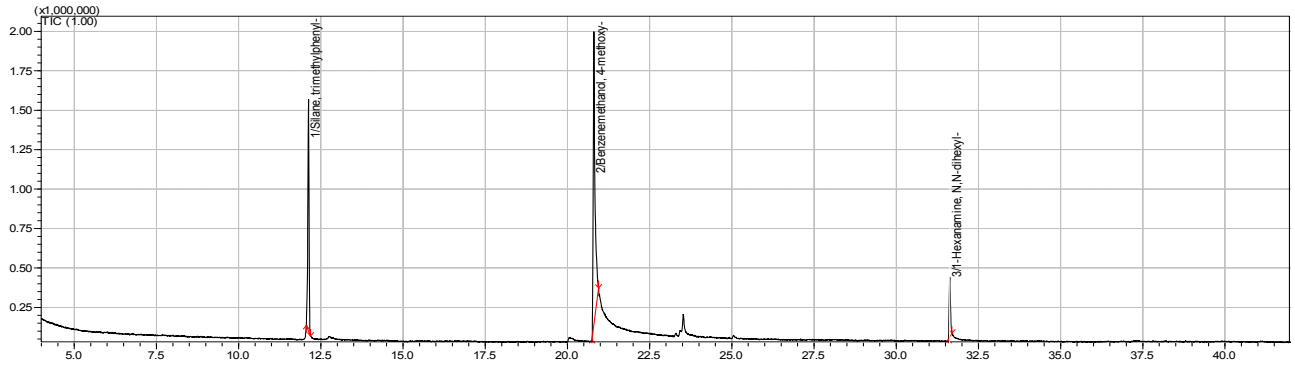
PEAK	R. TIME	I. TIME	F. TIME	M/Z	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	12.125	12.045	12.185	TIC	6884324	23.14	2553713	29.49	2.70	Silane, trimethylphenyl-
2	22.115	22.025	22.280	TIC	21834339	73.38	5721603	66.06	3.82	Benzenemethanol, 4-bromo-
3	31.634	31.590	31.695	TIC	1036928	3.48	385234	4.45	2.69	1-Hexanamine, N,N-dihexyl-

Figure S62 $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%) in d_3-MeCN (0.5 mL), with phenylsilane (1.2 eq.) and 4-bromobenzaldehyde (0.2 mmol), 80 °C.



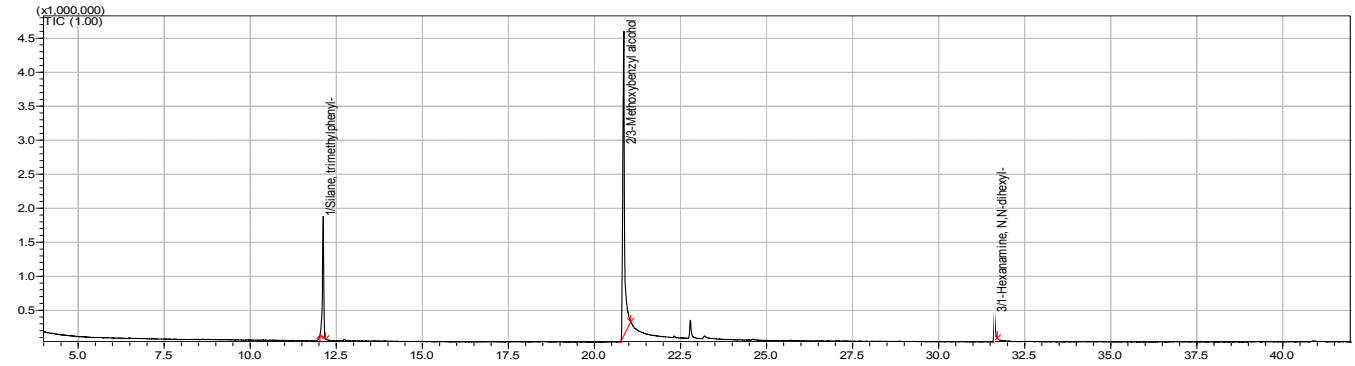
PEAK	R. TIME	I. TIME	F. TIME	M/Z	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	12.118	12.050	12.175	TIC	2963728	28.28	1134749	34.52	2.61	Silane, trimethylphenyl-
2	16.387	16.320	16.525	TIC	6632878	63.28	1831464	55.71	3.62	Benzenemethanol, 4-methyl-
3	31.628	31.580	31.690	TIC	884424	8.44	321182	9.77	2.75	1-Hexanamine, N,N-dihexyl-

Figure S63 $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%) in d_3-MeCN (0.5 mL), with phenylsilane (1.2 eq.) and 4-methylbenzaldehyde (0.2 mmol), 80 °C.



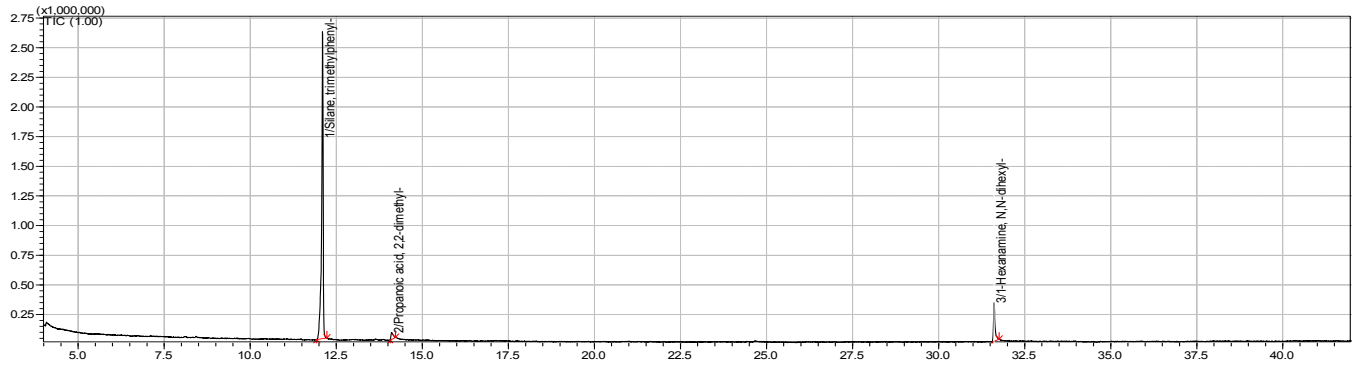
PEAK	R. TIME	I. TIME	F. TIME	M/Z	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	12.124	12.055	12.185	TIC	3840649	31.98	1468530	39.65	2.62	Silane, trimethylphenyl-
2	20.805	20.745	20.945	TIC	7112940	59.21	1854842	50.08	3.83	Benzenemethanol, 4-methoxy-
3	31.626	31.585	31.695	TIC	1057587	8.81	380547	10.27	2.78	1-Hexanamine, N,N-dihexyl-

Figure S64 $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%) in d_3-MeCN (0.5 mL), with phenylsilane (1.2 eq.) and 4-methoxybenzaldehyde (0.2 mmol), 80 °C.



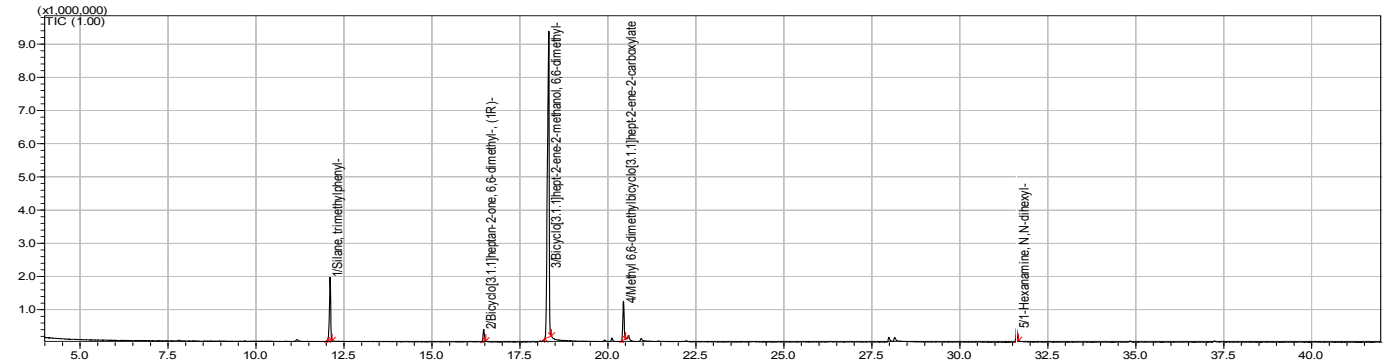
PEAK	R. TIME	I. TIME	F. TIME	M/Z	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	12.120	12.025	12.190	TIC	4734221	21.19	1781282	26.68	2.66	Silane, trimethylphenyl-
2	20.853	20.765	21.055	TIC	16455558	73.65	4476692	67.05	3.68	3-Methoxybenzyl alcohol
3	31.622	31.575	31.705	TIC	1152758	5.16	418494	6.27	2.75	1-Hexanamine, N,N-dihexyl-

Figure S65 $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%) in d_3-MeCN (0.5 mL), with phenylsilane (1.2 eq.) and 3-methoxybenzaldehyde (0.2 mmol), 80 °C.



PEAK	R. TIME	I. TIME	F. TIME	M/Z	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	12.102	11.935	12.225	TIC	8040853	86.32	2588445	87.20	3.11	Silane, trimethylphenyl-
2	14.111	14.065	14.220	TIC	246209	2.64	56015	1.89	4.40	Propanoic acid, 2,2-dimethyl-
3	31.611	31.555	31.755	TIC	1028442	11.04	323869	10.91	3.18	1-Hexanamine, N,N-dihexyl-

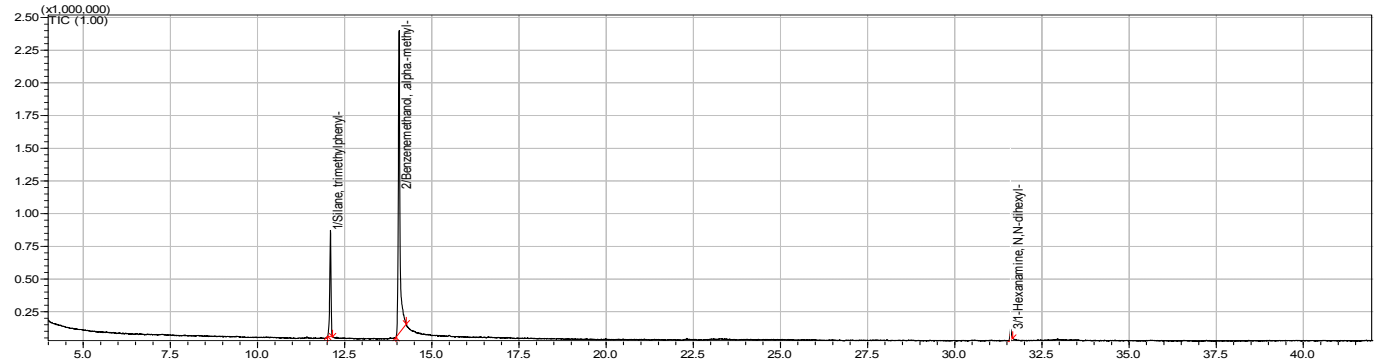
Figure S66 $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%) in d_3-MeCN (0.5 mL), with phenylsilane (1.2 eq.) and trimethylacetaldehyde (0.2 mmol), 80 °C.



PEAK	R. TIME	I. TIME	F. TIME	M/Z	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	12.105	12.040	12.165	TIC	4780483	11.26	1894434	14.54	2.52	Silane, trimethylphenyl-
2	16.470	16.430	16.530	TIC	880203	2.07	355415	2.73	2.48	Bicyclo[3.1.1]heptan-2-one, 6,6-dimethyl-, (1R)-
3	18.319	18.205	18.395	TIC	32799156	77.23	9213222	70.72	3.56	Bicyclo[3.1.1]hept-2-ene-2-methanol, 6,6-dimethyl-
4	20.443	20.390	20.505	TIC	3020297	7.11	1163379	8.93	2.60	Methyl 6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-carboxylate
5	31.609	31.565	31.670	TIC	990025	2.33	400831	3.08	2.47	1-Hexanamine, N,N-dihexyl-

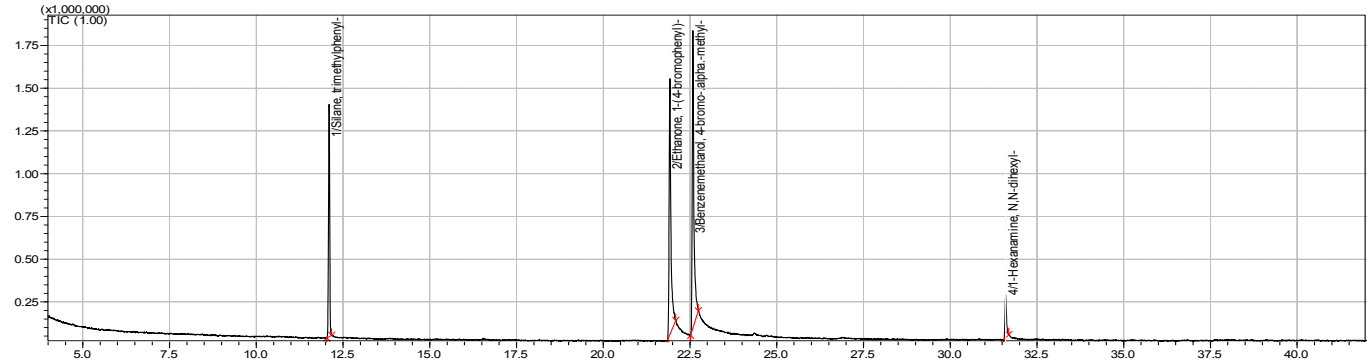
Figure S67 $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%) in d_3-MeCN (0.5 mL), with phenylsilane (1.2 eq.) and myrtenal (0.2 mmol), 80 °C.

9.3 Hydrosilylation of ketones



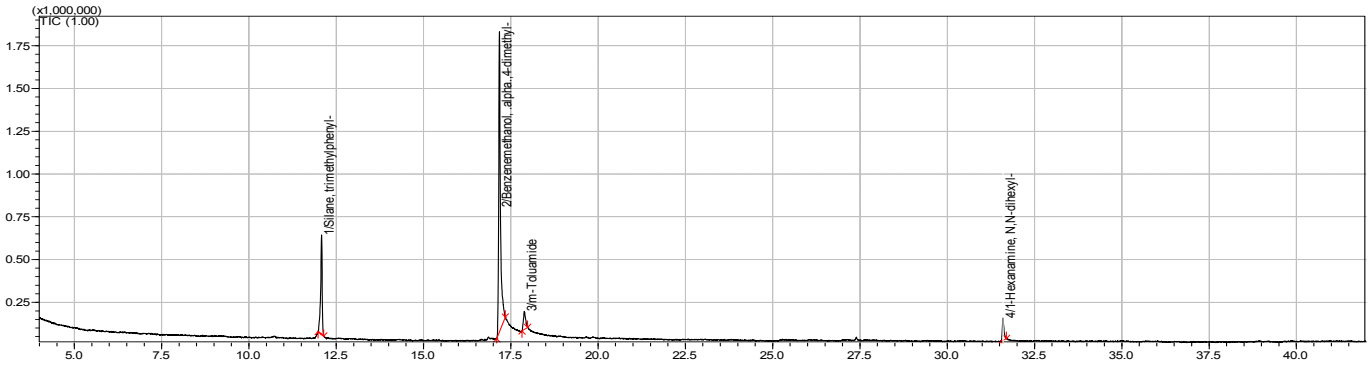
PEAK	R. TIME	I. TIME	F. TIME	M/Z	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	12.092	12.010	12.150	TIC	2073273	20.22	813009	25.32	2.55	Silane, trimethylphenyl-
2	14.063	13.970	14.270	TIC	7946823	77.50	2316391	72.15	3.43	Benzenemethanol, .alpha.-methyl-
3	31.602	31.560	31.665	TIC	234178	2.28	81138	2.53	2.89	1-Hexanamine, N,N-dihexyl-

Figure S68 $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%) in d_3-MeCN (0.5 mL), with phenylsilane (1.2 eq.) and acetophenone (0.2 mmol), 80 °C.



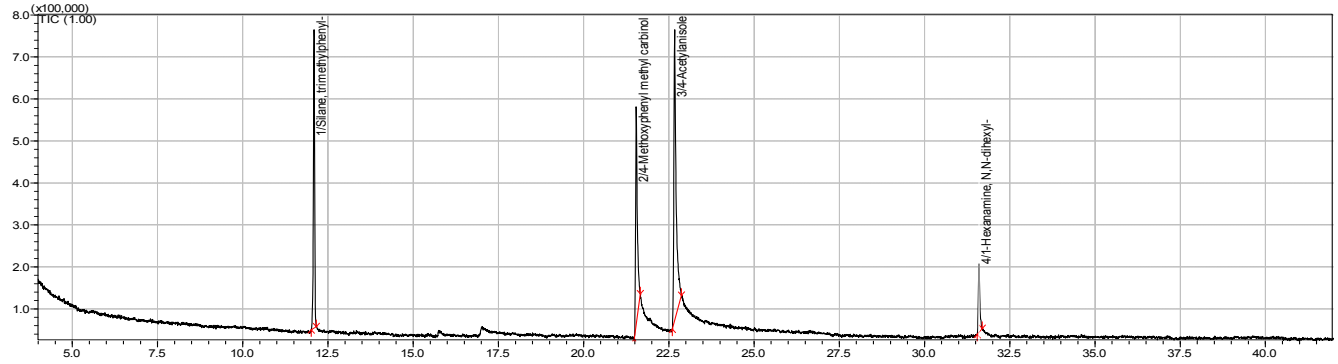
PEAK	R. TIME	I. TIME	F. TIME	M/Z	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	12.099	12.035	12.170	TIC	3266537	21.57	1358868	28.05	2.40	Silane, trimethylphenyl-
2	21.920	21.850	22.085	TIC	5317532	35.12	1495244	30.86	3.56	Ethanone, 1-(4-bromophenyl)-
3	22.584	22.520	22.740	TIC	5810937	38.39	1739949	35.92	3.34	Benzenemethanol, 4-bromo-.alpha.-methyl-
4	31.597	31.540	31.685	TIC	745645	4.92	250517	5.17	2.98	1-Hexanamine, N,N-dihexyl-

Figure S69 $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%) in d_3-MeCN (0.5 mL), with phenylsilane (1.2 eq.) and 4-bromoacetophenone (0.2 mmol), 80 °C.



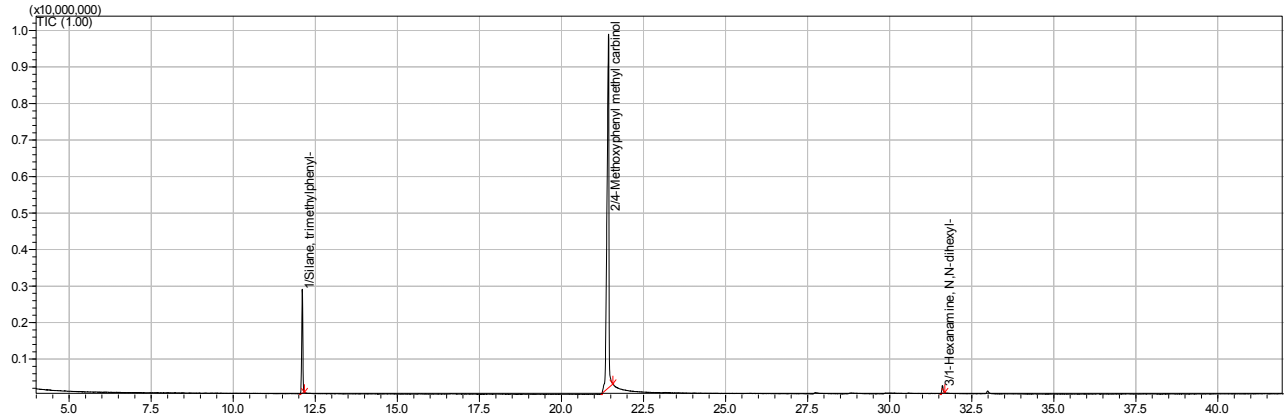
PEAK	R. TIME	I. TIME	F. TIME	M/Z	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	12.080	11.980	12.140	TIC	1760499	19.96	581703	22.61	3.03	Silane, trimethylphenyl-
2	17.174	17.100	17.340	TIC	6185547	70.12	1755192	68.23	3.52	Benzenemethanol, .alpha.,4-dimethyl-
3	17.887	17.820	17.980	TIC	458495	5.20	105836	4.11	4.33	m-Toluamide
4	31.595	31.545	31.690	TIC	416497	4.72	129998	5.05	3.20	1-Hexanamine, N,N-dihexyl-

Figure S70 [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in d$_3$-MeCN (0.5 mL), with phenylsilane (1.2 eq.) and 4-methylacetophenone (0.2 mmol), 80 °C.



PEAK	R. TIME	I. TIME	F. TIME	M/Z	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	12.091	12.010	12.155	TIC	1816899	24.77	710591	34.09	2.56	Silane, trimethylphenyl-
2	21.542	21.485	21.660	TIC	1832681	24.98	518227	24.87	3.54	4-Methoxyphenyl methyl carbinol
3	22.670	22.600	22.865	TIC	3181315	43.36	691857	33.20	4.60	4-Acetylanisole
4	31.596	31.545	31.690	TIC	505482	6.89	163408	7.84	3.09	1-Hexanamine, N,N-dihexyl-

Figure S71 [N(hexyl)$_4$][ReO$_4$] **2** (2.5 mol%) in d$_3$-MeCN (0.5 mL), with phenylsilane (1.2 eq.) and 4-methoxyacetophenone (0.2 mmol), 80 °C.



PEAK	R. TIME	I. TIME	F. TIME	M/Z	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	12.104	12.040	12.170	TIC	6908126	14.25	2844526	22.32	2.43	Silane, trimethylphenyl-
2	21.434	21.225	21.570	TIC	40994993	84.53	9692031	76.05	4.23	3-Methoxyphenyl methyl carbinol
3	31.608	31.555	31.680	TIC	591836	1.22	208074	1.63	2.84	1-Hexanamine, N,N-dihexyl-

Figure S72 $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%) in d_3-MeCN (0.5 mL), with phenylsilane (1.2 eq.) and 3-methoxyacetophenone (0.2 mmol), 80 °C.

PEAK	R. TIME	I. TIME	F. TIME	M/Z	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	12.096	12.035	12.155	TIC	3003239	9.34	1249184	12.35	2.40	Silane, trimethylphenyl-
2	29.672	29.570	29.795	TIC	28513559	88.68	8612211	85.11	3.31	Benzenemethanol, .alpha.-phenyl-
3	31.597	31.555	31.650	TIC	635971	1.98	256499	2.54	2.48	1-Hexanamine, N,N-dihexyl-

Figure S73 $[N(hexyl)_4][ReO_4]$ **2** (2.5 mol%) in d_3-MeCN (0.5 mL), with phenylsilane (1.2 eq.) and benzophenone (0.2 mmol), 80 °C.