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Supporting Information

Choosing the best molecular precursor to prepare $Li_4Ti_5O_{12}$ by the sol-gel method using ^1H NMR. Evidences of $[Ti_3(OEt)_{13}]^-$ in solution.

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TABLE OF CONTENTS

S0. Gravimetric determination of alcohol exchange between $Ti(OPr^i)_4$ and EtOH to give $Ti(OEt)_4$ and Pr^iOH.

Experimental values found during gravimetric determination. Units: grams.

Three weighted samples of $5LiOEt/5Ti(OPr^i)_4$ were independently evaporated in tared Schlenk flasks under vacuum for 7 h at room temperature. Volatile product could be ethanol with no alcohol exchange. With alcohol exchange both ethanol and isopropanol are the volatile products. The found percent mean value of solid residues was 28.2% (calculated solid residues for alcohol exchange 28.6%). With no alcohol exchange the calculated solid residue is 34.5%.

Before formation LiOEt					After formation LiOEt (-1/2H_2) without exchange				With exchange		
Sample	Li	$Ti(OPri)_4$	EtOH	Weight	Li(OEt)	$Ti(OPr)_4$	EtOH	Weight	Li(OEt)	$Ti(OEt)_4$	EtOH+ iPrOH
5Ti/5Li	0.223	9.66*	23.76	33.64	1.671	9.66	22.28	33.611	1.671	7.753	24.187
%	0.66%	28.72%	70.63%		4.97%	28.74%	66.29%		4.97%	23.07%	71.96%
					Calculated solid residues		Calculated volatile loss		Calculated solid residues		Calculated volatile loss
					33.7%		66.3%		28.0%		72.0%

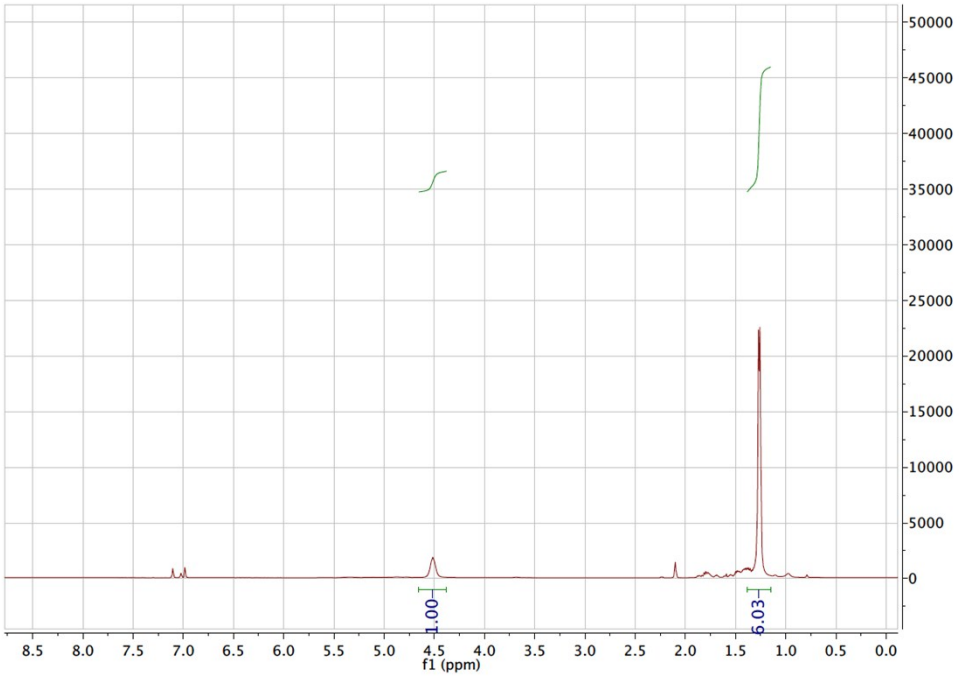
Evaporated samples

Samples	Weight before evaporation	Weight after evaporation (solid residues)	Weight loss (volatiles)	Found % of solid
1	1.051	0.297	0.754	28.26%
2	1.147	0.325	0.822	28.33%
3	1.149	0.321	0.828	27.94%
			Found mean value	28.2%

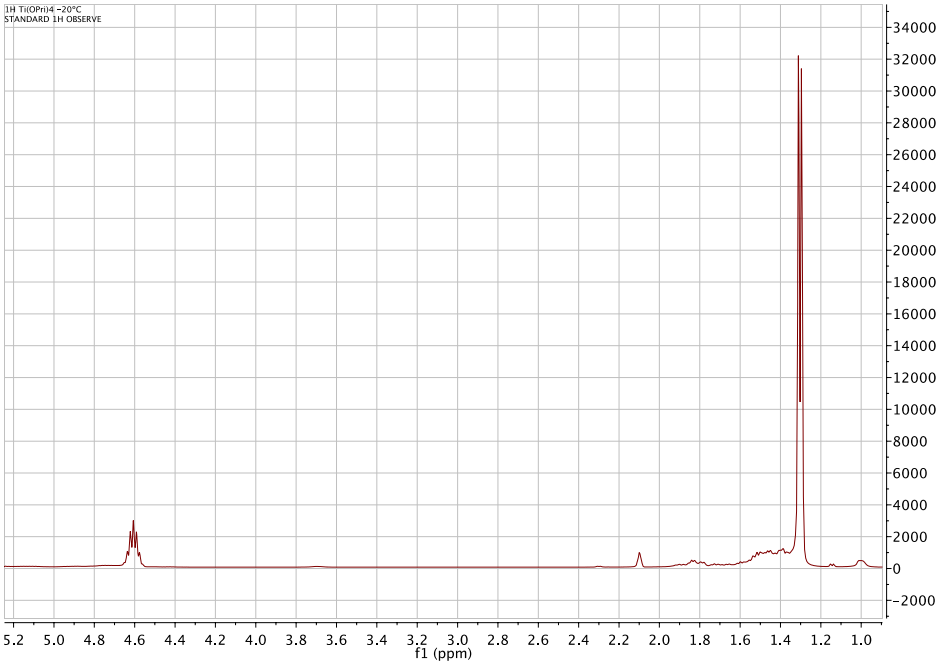
The gravimetric results indicate that alcohol exchange occurs according to the reaction:

$$LiOEt + Ti(O\,Pr^i)_4 \xrightarrow{EtOH} "LiOEt + Ti(OEt)_4" + 4\,Pr^i\,OH$$

S1. ^{1}H NMR spectra of commercial Ti(OPr^i)$_4$.

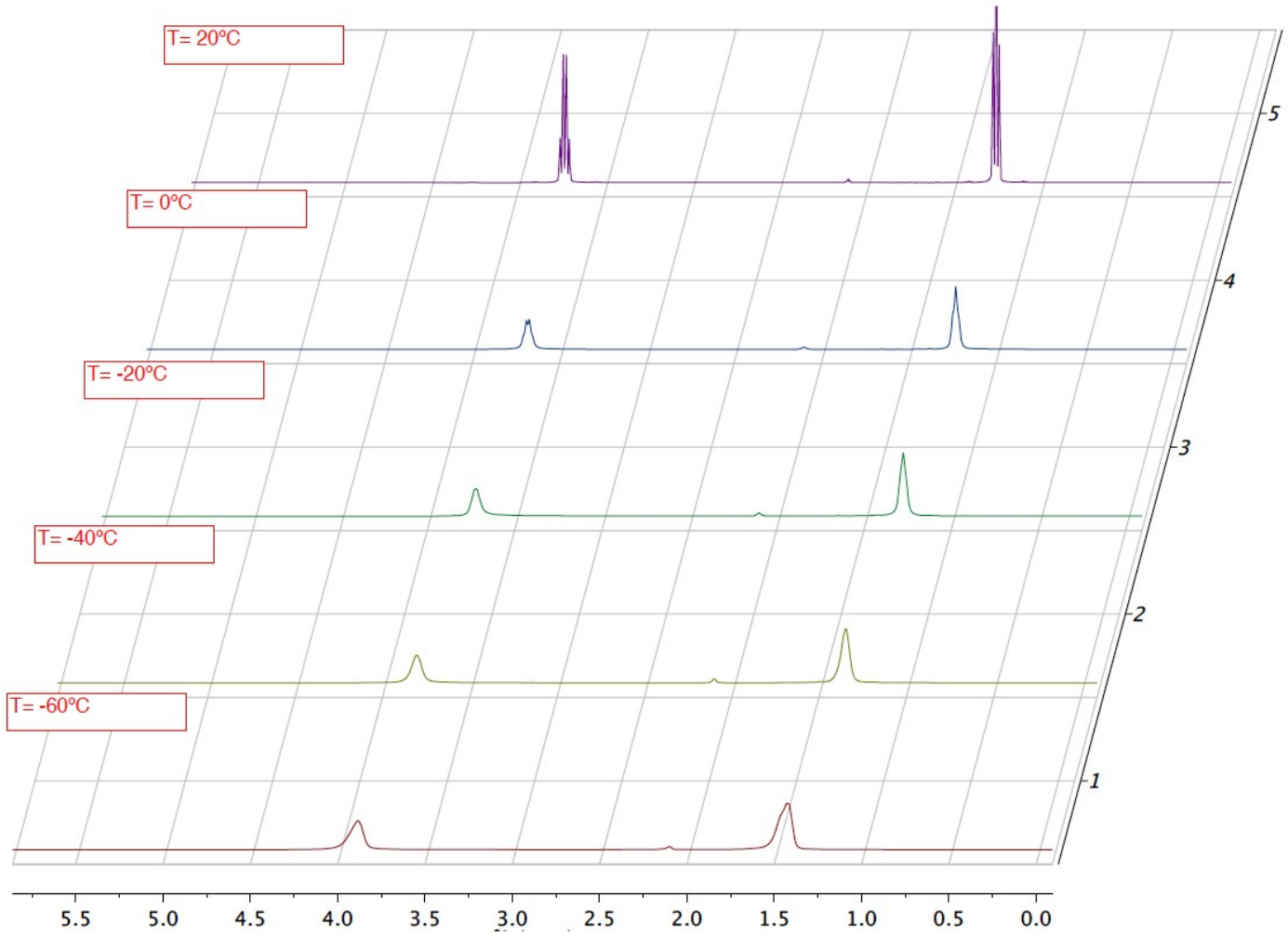


Top +20ºC. Bottom -20ºC. Shifts referred to signal of residual non-deuterated toluene at 2.10 ppm. In addition to residual signals of non-deuterated toluene the commercial sample shows impurities in the range 1-2 ppm. Septuplet is well resolved at -20°C below.



Procedure to prepare the sample: Commercial Ti(OPr^i)$_4$ (0.5 ml) was dissolved in 1 ml of toluene-d$_8$. The calculated concentration is 1.1M.

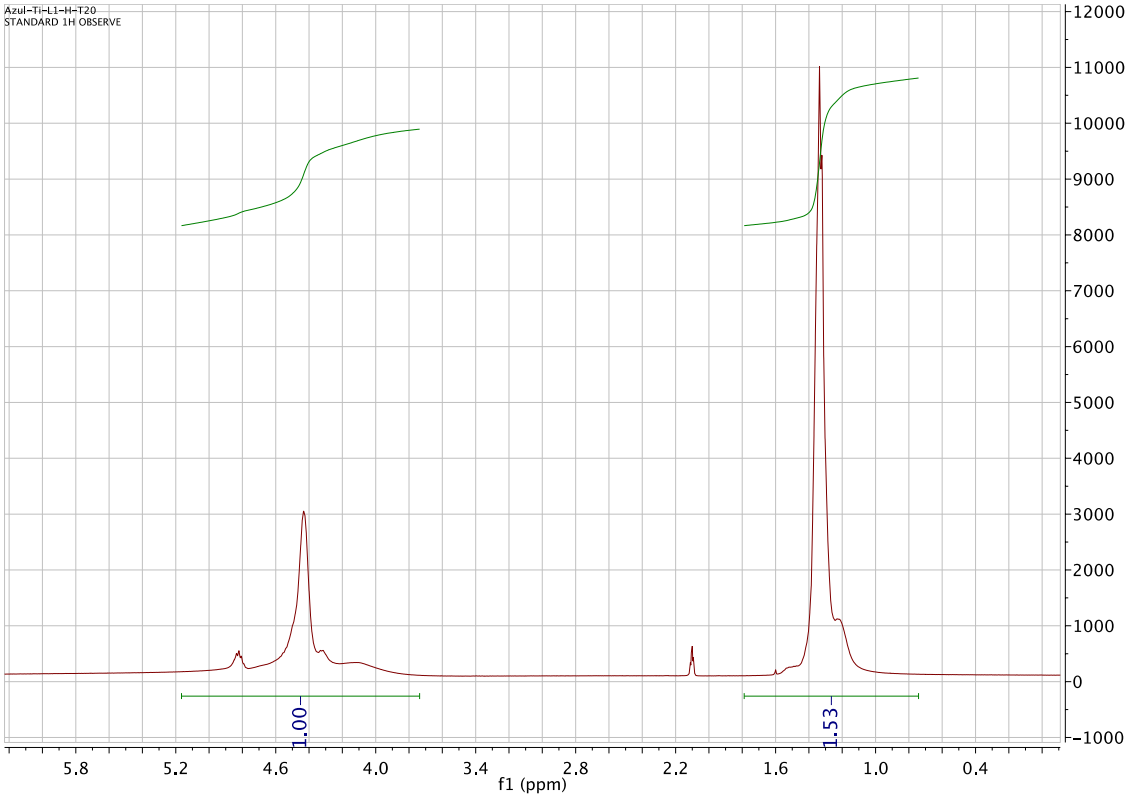
S2. VT ^{1}H NMR spectra of lithium ethoxide (LiOEt).



Variable temperature ^{1}H NMR spectra of lithium ethoxide in d_8-toluene. Shifts referred to signal of residual non-deuterated toluene at 2.10 ppm. Chemical shifts drift slightly with temperature between 3.72 ppm(20°) and 3.88 ppm(-60°) for the methylene group and between 1.25 ppm(20°) and 1.43 ppm(-60°) for the methyl group. Coupling values ^{2}J= 7 Hz. only observed at 20°C.

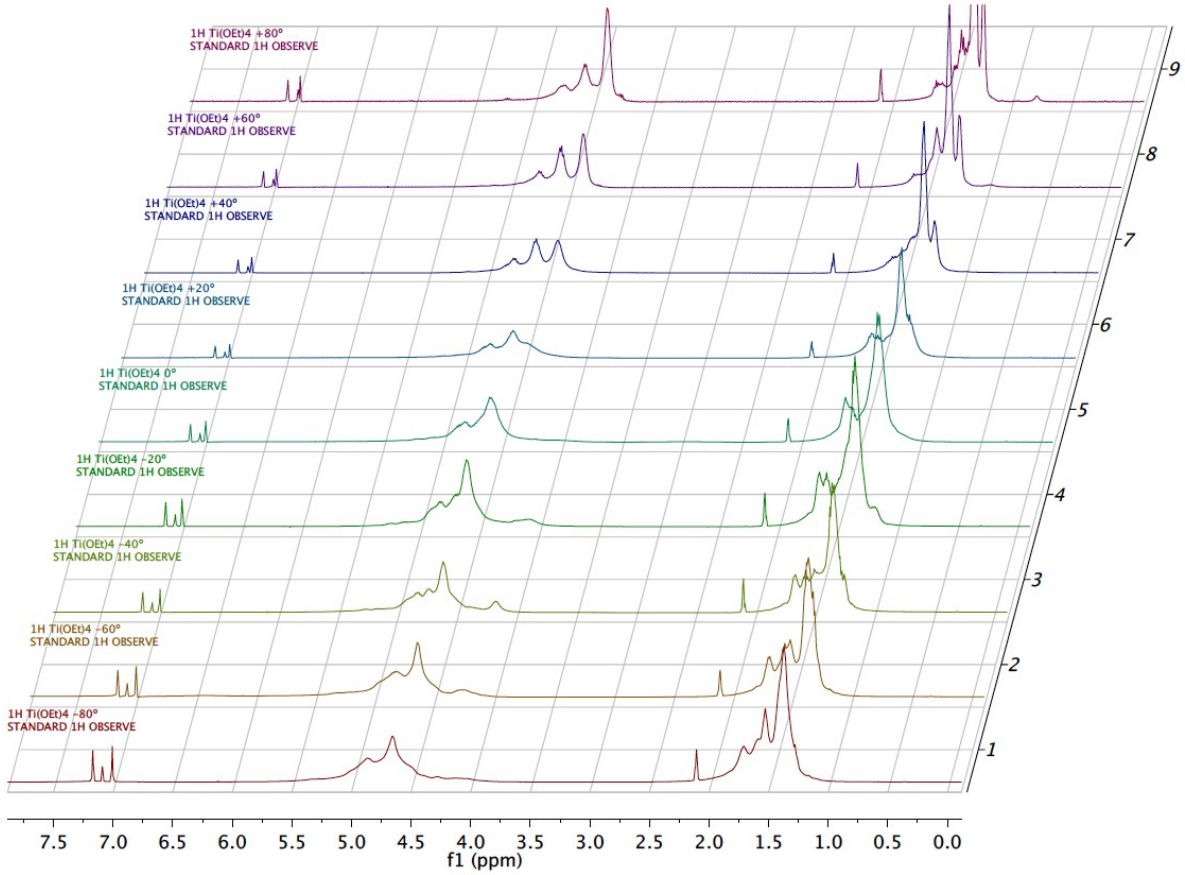
Procedure to prepare the sample: Lithium ethoxide was prepared by solving metallic lithium (0.298g, 43 mmol) in 40 ml of ethanol. An aliquot of 1.5 ml was evaporated to dryness. The residue was dissolved in 1.5 ml of deuterated toluene. The calculated concentration is 1,07M.

S3. ^{1}H NMR spectra of 5LiOEt:5Ti(OPr^{i})$_4$.



^{1}H NMR spectrum, at 20°C in $C_6D_5CD_3$ (1 ml), of an evaporated aliquot (1.5 ml) of the precursor 5LiOEt/5Ti(OPr^{i})$_4$. See the integer ratio 1:1.5 between methylene:methyl protons as expected for a mixture containing only ethoxide groups.(Signal at 2.1 ppm of residual toluene).

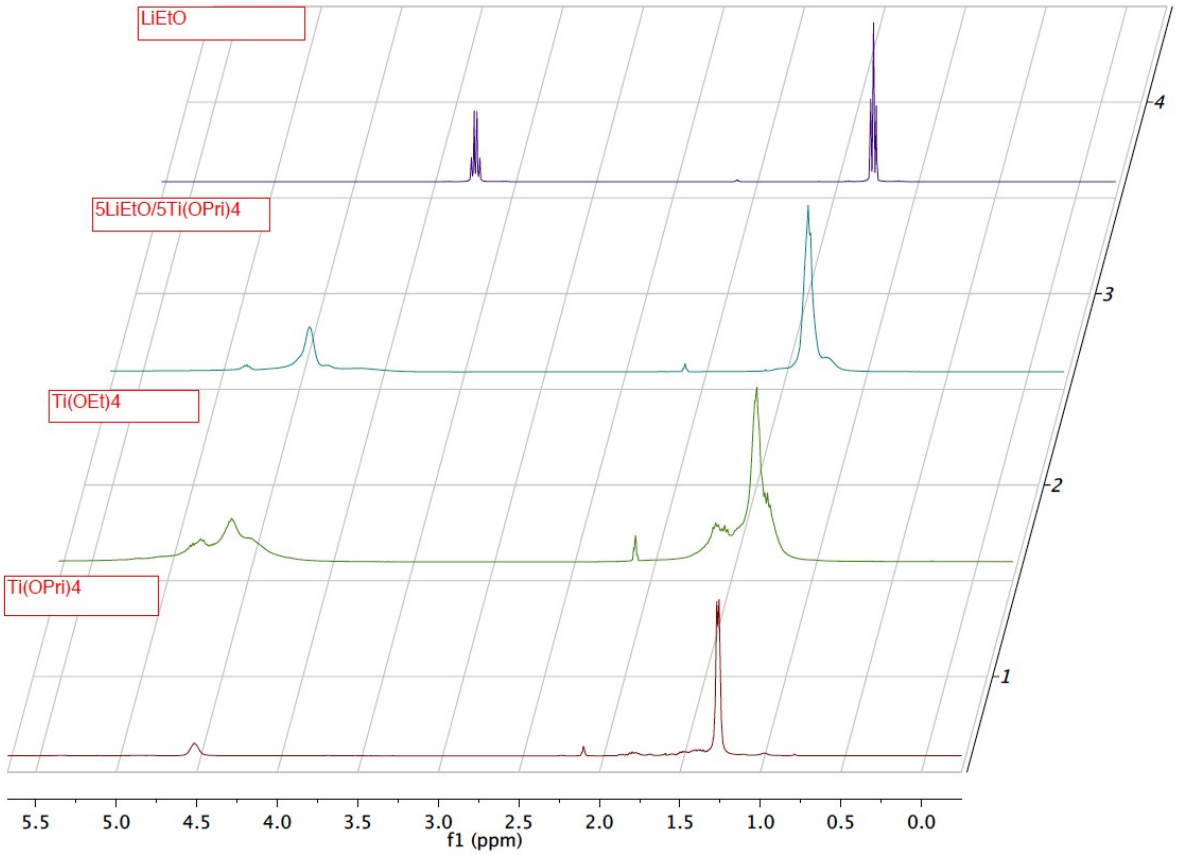
S4. VT ^{1}H NMR spectra of commercial $Ti(OEt)_4$.



Variable temperarture ^{1}H NMR spectra of commercial $Ti(OEt)_4$ in d_8-toluene. From -80ºC (bottom) to +80ºC (top) in 20ºC steps.

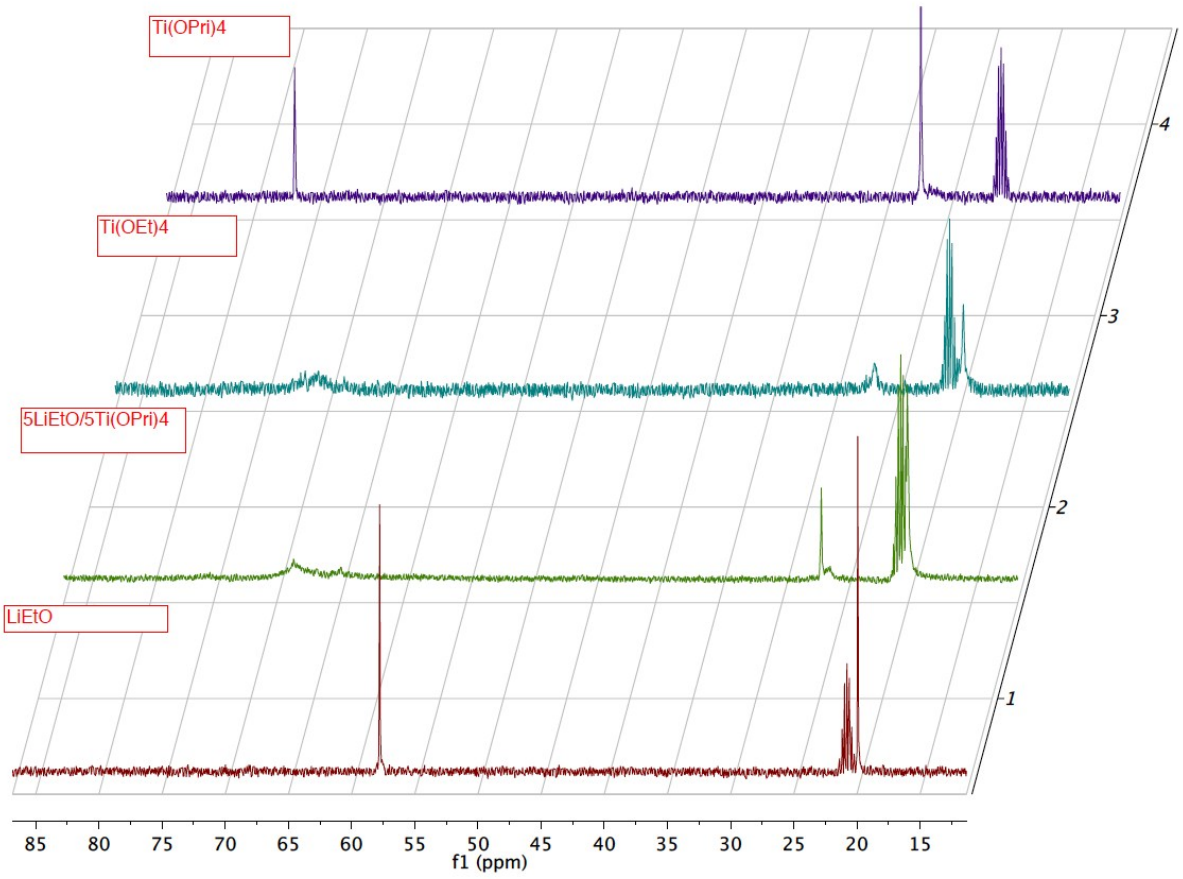
Procedure to prepare the sample: Commercial $Ti(OEt)_4$ (0.3 ml) was dissolved in 1.5 ml of deuterated toluene. The calculated concentration is 0.9M.

S5. ^{1}H NMR spectra overlay of LiOEt, 5LiOEt/5Ti(OPr^i)$_4$, Ti(OEt)$_4$ and Ti(OPr^i)$_4$.



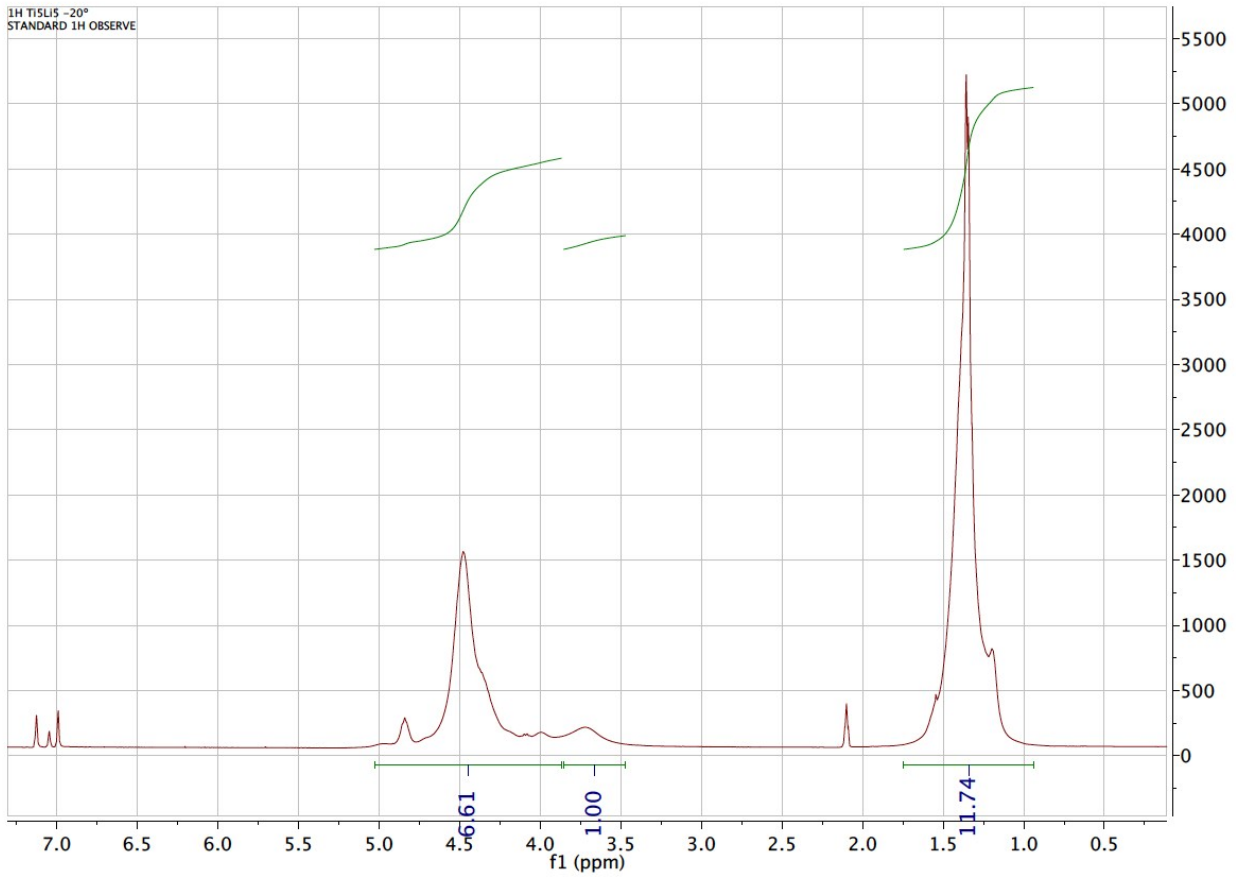
^{1}H NMR spectra of LiOEt, *5LiOEt/5Ti(OPr^i)$_4$*, Ti(OEt)$_4$ and Ti(OPr^i)$_4$ in d$_8$-toluene at 20°C. See that *5LiOEt/5Ti(OPr^i)$_4$* is not the simple addition of LiOEt and Ti(OPr^i)$_4$ or LiOEt and Ti(OEt)$_4$. No free LiOEt appears in *5LiOEt/5Ti(OPr^i)$_4$*. New double lithium-titanium ethoxides have formed.

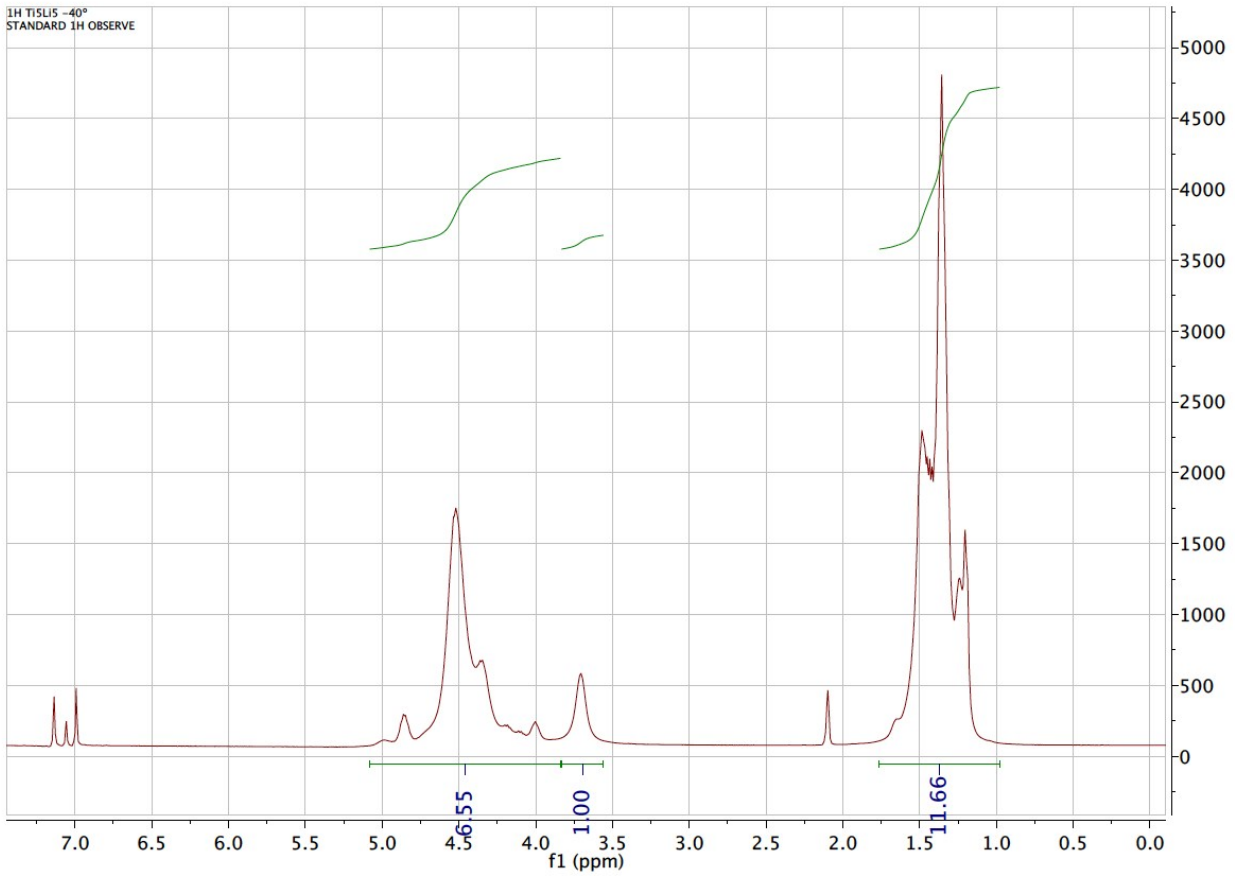
S6. ^{13}C NMR spectra overlay of LiOEt, 5LiOEt/5Ti(OPr^i)$_4$, Ti(OEt)$_4$ and Ti(OPr^i)$_4$.

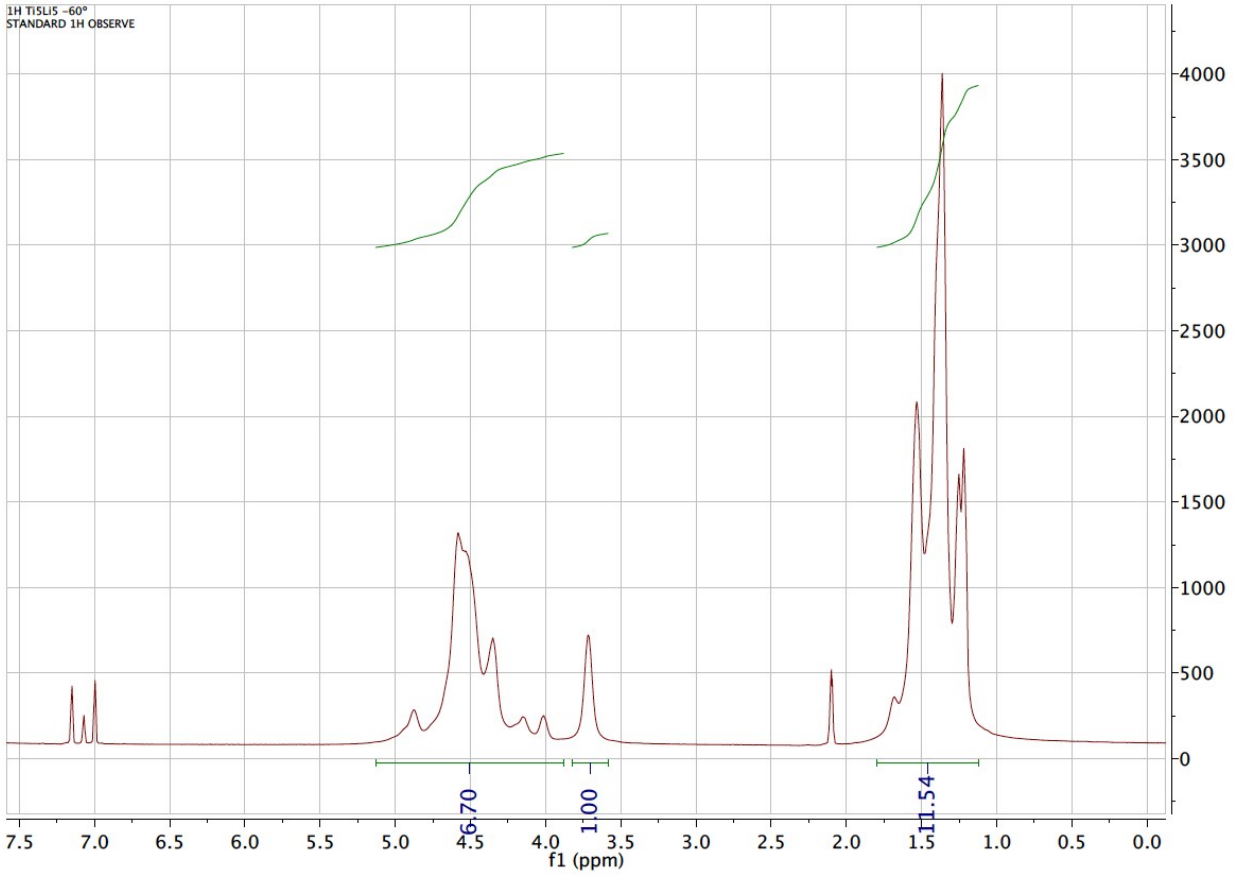


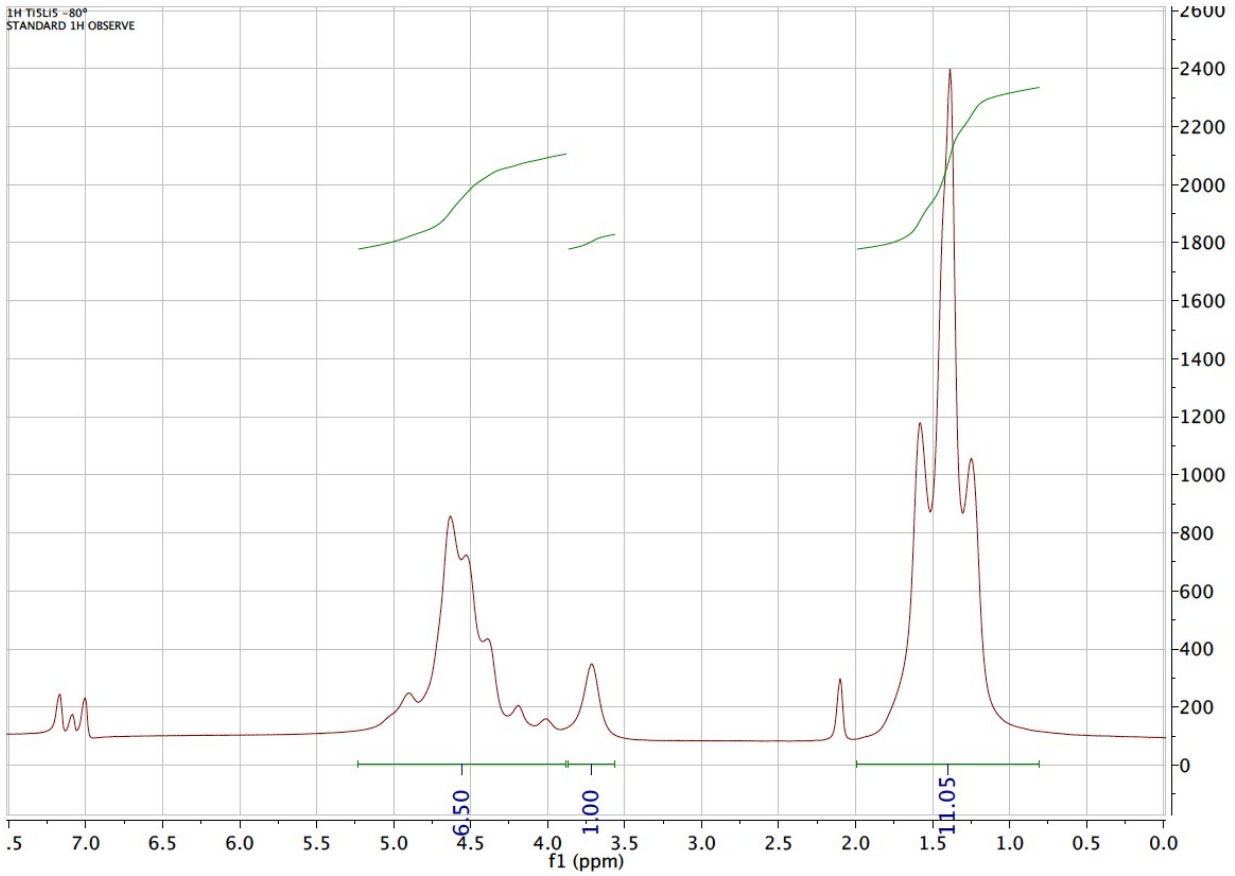
^{13}C NMR spectra of LiOEt, *5LiOEt/5Ti(OPr^i)$_4$*, Ti(OEt)$_4$ and Ti(OPri)$_4$ in d_8-toluene at 20°C. See that *5LiOEt/5Ti(OPr^i)$_4$* is not the simple addition of LiOEt and Ti(OPri)$_4$ or LiOEt and Ti(OEt)$_4$. No free LiOEt neither Ti(OPr^i)$_4$ appear in *5LiOEt/5Ti(OPr^i)$_4$*. New double lithium-titanium ethoxides have formed. Shifts referred to signal of toluene at 20.6ppm.

S7. Integer values of 5LiOEt/5Ti(OPr^{i})$_4$ between -80ºC(bottom) and -20º(top).

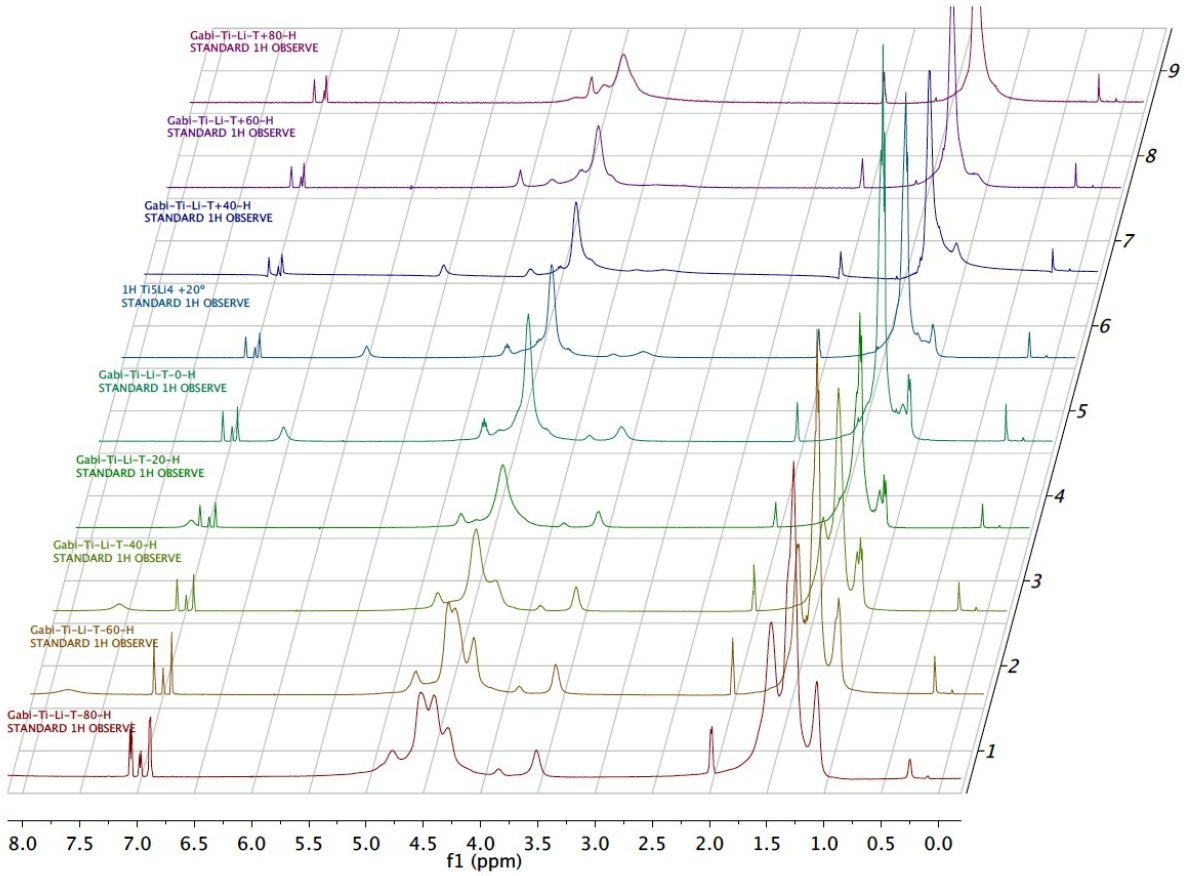



1H Ti5Li5 -40°
STANDARD 1H OBSERVE
6.55
1.00
11.66
f1 (ppm)


1H Ti5Li5 -60°
STANDARD 1H OBSERVE
6.70
1.00
11.54
f1 (ppm)

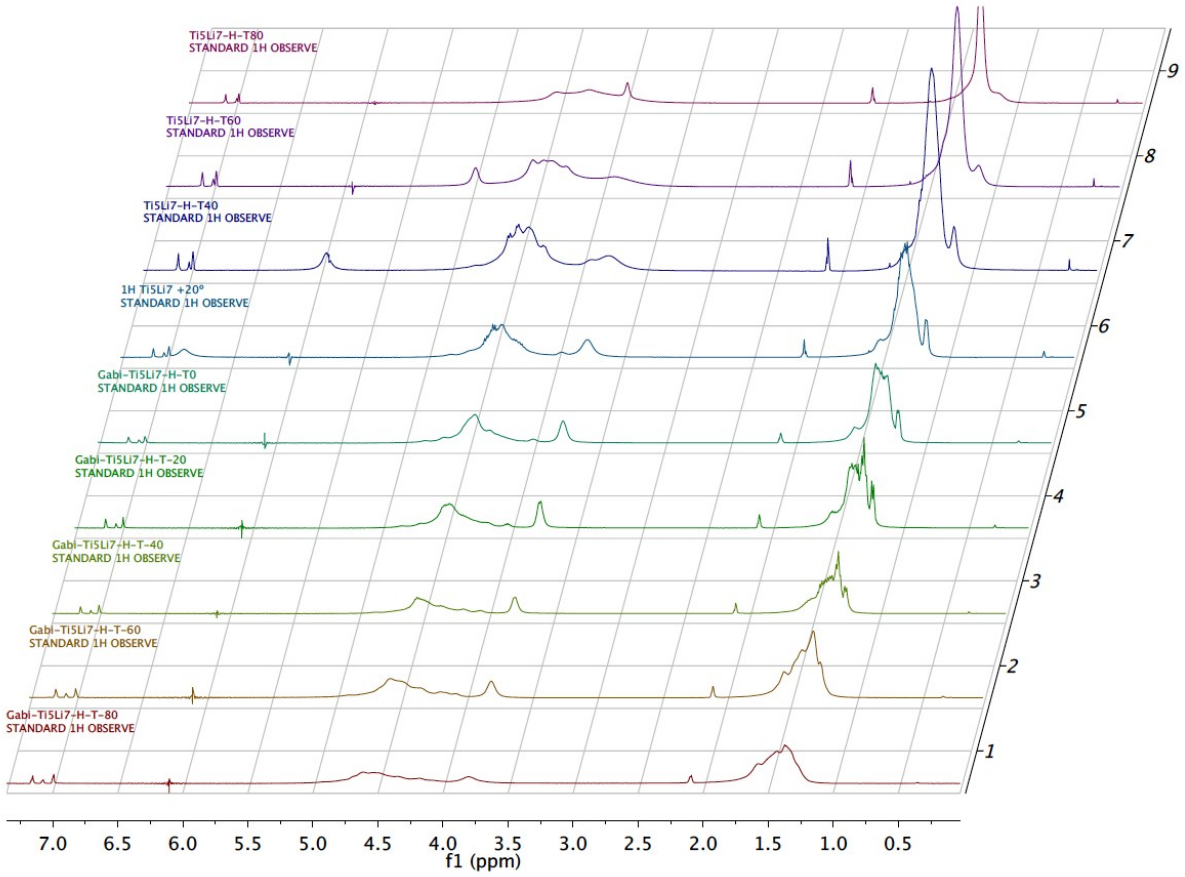

1H Ti5Li5 -80°
STANDARD 1H OBSERVE
6.50
1.00
11.05
f1 (ppm)

S8. VT ^{1}H NMR spectra of 4LiOEt/5Ti(OPr^i)$_4$ from -80ºC to +80ºC

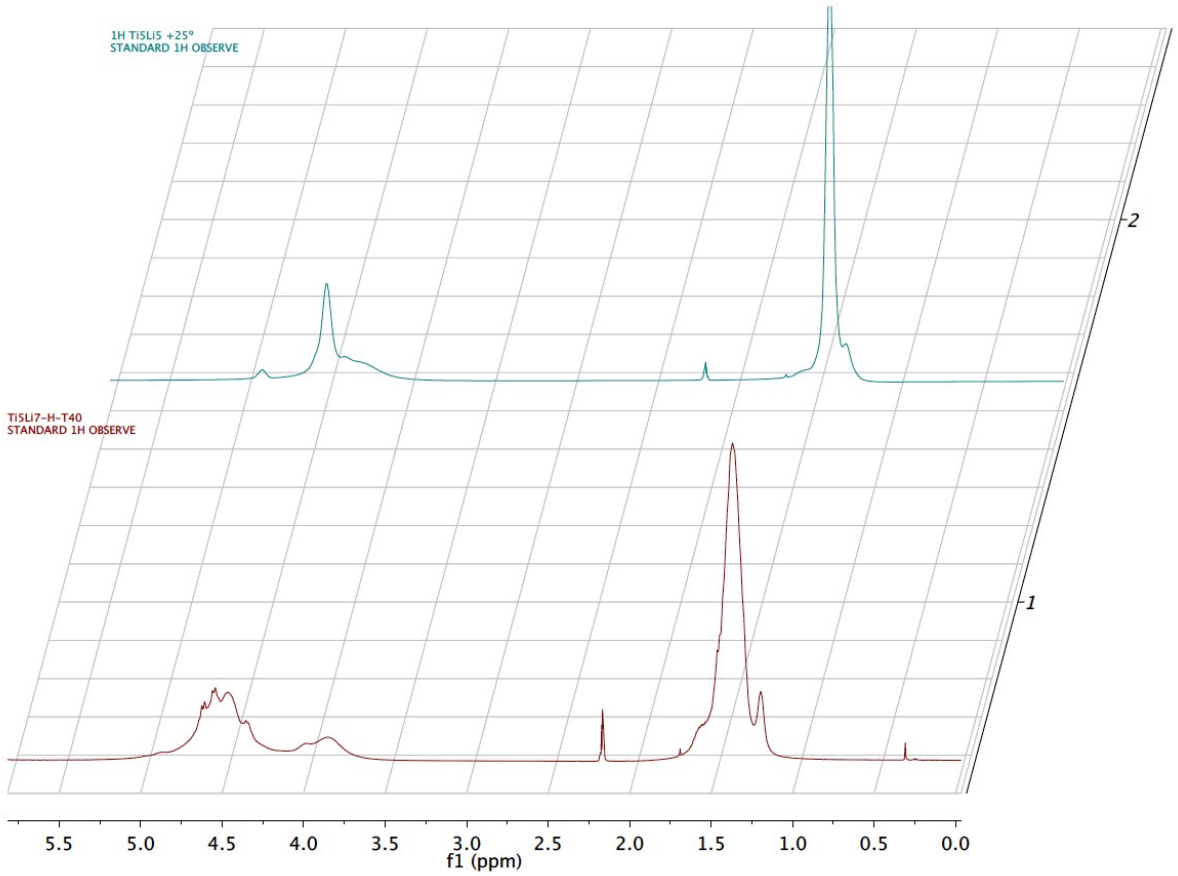


Variable temperature (VT) ^{1}H NMR spectra in $C_6D_5CD_3$ of the precursor 4LiOEt/5Ti(OPr^i)$_4$ (4Li/5Ti). The calculated concentration for Ti is 0.82M and for Li is 0.64M. Top +80°C. Bottom -80°C. Steps 20°C.

S9. VT ^{1}H NMR spectra of 7LiOEt/5Ti(OPr^{i})$_4$ from -80ºC to +80ºC

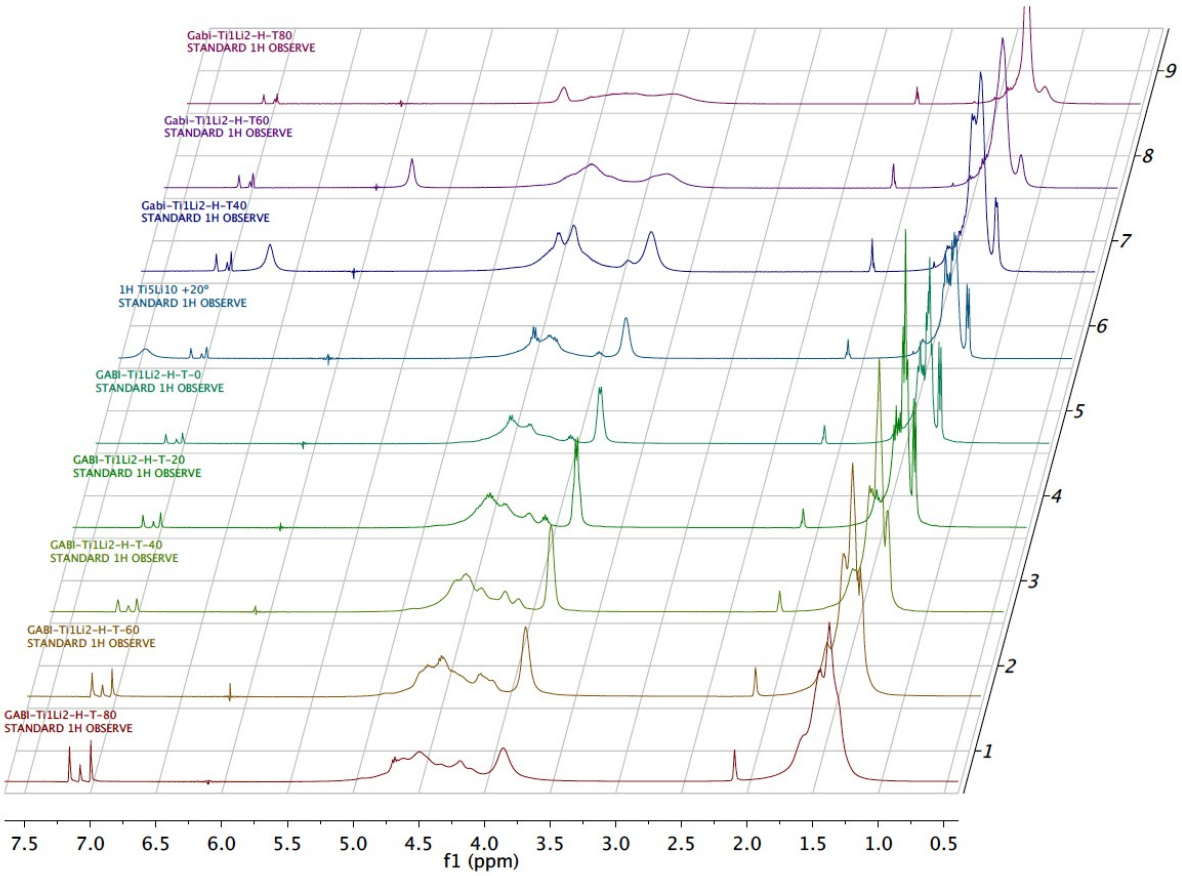


S10. Comparing ^{1}H NMR spectra of 5LiOEt/5Ti(OPr^{i})$_4$ with 7LiOEt/5Ti(OPr^{i})$_4$



Top ^{1}H NMR spectra of 5LiOEt/5Ti(OPr^{i})$_4$ at 20°C. Bottom 7LiOEt/5Ti(OPr^{i})$_4$ at 40°C. Chemical exchange is hampered down.

S11. VT ^{1}H NMR spectra of 10LiOEt/5Ti(OPr^{i})$_4$ from -80ºC to +80ºC



S12. Cartesian coordinates and figures for optimized model structures B-$[Ti_3(OMe)_{13}]^-$ and B'-$[Ti_3(OMe)_{13}]^-$.

Cartesian coordinates for optimized structure of B-$[Ti_3(OMe)_{13}]^-$.

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	22	-0.133536	0.157714	-0.466692
2	8	1.032.267	-0.427668	0.953438
3	8	1.596.960	0.339569	-1.392689
4	8	-1.673.669	0.068587	1.066277
5	8	-2.132.143	0.346925	-1.305632
6	22	-3.431.497	-0.031223	0.174183
7	22	3.116.197	0.020978	0.226739
8	8	-0.379656	-1.499.445	-1.308901
9	8	3.205.582	-1.828.557	-0.205581
10	8	3.856.294	-0.243490	1.930179
11	8	4.562.905	0.372564	-0.893485
12	8	2.854.666	1.828.872	0.656901
13	8	-0.240351	2.002.322	-0.435260
14	8	-4.418.462	1.486.731	-0.129138
15	8	-4.268.907	-0.421074	1.797091
16	8	-4.100.720	-1.517.046	-0.661347
17	6	4.073.000	-2.632.876	-0.934132
18	1	4.634.005	-3.321.042	-0.273757
19	1	3.514.798	-3.258.537	-1.655427
20	1	4.805.470	-2.029.069	-1.495782
21	6	4.484.950	-1.355.327	2.493044
22	1	4.341.978	-1.355.352	3.587991
23	1	4.087.347	-2.299.481	2.088703
24	1	5.572.379	-1.336.358	2.299643
25	6	5.399.125	1.491.232	-0.961616
26	1	6.252.529	1.386.487	-0.269484
27	1	5.804.103	1.596.122	-1.982821
28	1	4.857.262	2.412.098	-0.696053
29	6	2.642.941	2.573.453	1.810817
30	1	3.124.320	2.097.705	2.682519
31	1	3.056.940	3.591.912	1.698444
32	1	1.564.145	2.673.405	2.019634
33	6	-0.978867	3.118.168	-0.819602
34	1	-0.910565	3.896.315	-0.041797
35	1	-0.583149	3.550.138	-1.755340
36	1	-2.038.564	2.865.024	-0.970102
37	6	0.498824	-2.447.541	-1.856928
38	1	0.831376	-3.167.333	-1.095498

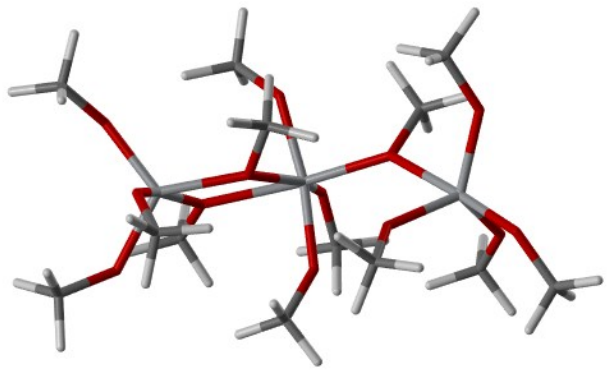
39	1	-0.015314	-3.002.654	-2.660916
40	1	1.393.499	-1.960.950	-2.265075
41	6	-5.685.953	1.889.498	0.319734
42	1	-5.896.794	1.480.860	1.319066
43	1	-5.724.880	2.988.574	0.365710
44	1	-6.471.530	1.546.243	-0.372195
45	6	-4.572.362	-1.606.177	2.470449
46	1	-3.690.853	-2.002.624	3.002565
47	1	-5.363.384	-1.427.019	3.216881
48	1	-4.923.519	-2.378.121	1.766053
49	6	-3.636.156	-2.563.906	-1.480663
50	1	-2.553.714	-2.492.007	-1.642644
51	1	-3.862.788	-3.531.192	-1.006104
52	1	-4.151.907	-2.534.138	-2.453093
53	6	-2.369.560	0.298420	-2.691969
54	1	-1.795.550	-0.518513	-3.150855
55	1	-3.437.637	0.141396	-2.898839
56	1	-2.069.334	1.249.358	-3.160651
57	6	1.857.285	1.361.992	-2.334508
58	1	1.905.325	2.338.981	-1.836663
59	1	2.818.135	1.158.256	-2.824295
60	1	1.070.557	1.391.502	-3.104920
61	6	-1.491.767	0.741587	2.307130
62	1	-0.512067	0.485596	2.721259
63	1	-1.525.762	1.829.621	2.158496
64	1	-2.285.155	0.448356	3.004061
65	6	0.853397	-1.572.053	1.774230
66	1	1.303.333	-1.379.114	2.757364
67	1	-0.213603	-1.790.108	1.899402
68	1	1.355.677	-2.433.786	1.320725

Optimized structure of B-$[Ti_3(OMe)_{13}]^-$.

Cartesian coordinates for optimized structure of B'-$[Ti_3(OMe)_{13}]^-$.

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	22	3.190.206	-0.517074	0.095098
2	8	-1.051.870	-0.709603	0.439267
3	8	1.636.100	0.913509	0.701304
4	22	-2.968.348	-0.607780	0.046918
5	22	-0.238658	1.328.494	0.107218
6	8	-2.327.905	1.238.358	-0.376131
7	8	-0.776344	1.638.390	1.881425
8	8	-0.097774	3.151.615	-0.208387
9	8	0.085838	0.876419	-1.663859
10	8	-3.133.918	-2.460.076	0.248357
11	8	-4.135.490	-0.217838	1.391996
12	8	-3.775.813	-0.630921	-1.635257
13	8	1.984.128	-1.537.190	-0.833725
14	8	4.665.977	-1.612.428	-0.279566
15	8	3.996.067	0.908614	-0.777594
16	8	3.378.527	-0.894673	1.894617
17	6	4.347.295	-1.493.512	2.703089
18	1	3.875.393	-2.224.696	3.379662
19	1	5.101.198	-2.011.635	2.090244
20	1	4.856.566	-0.737977	3.325106
21	6	3.505.766	2.017.114	-1.490155
22	1	3.418.612	2.893.775	-0.829560
23	1	4.209.034	2.268.711	-2.300905
24	1	2.517.123	1.820.398	-1.923195
25	6	1.889.839	-2.899.580	-1.136903
26	1	1.199.309	-3.405.680	-0.443761
27	1	1.498.072	-3.029.557	-2.158225
28	1	2.873.271	-3.390.806	-1.068807
29	6	5.532.582	-1.608.409	-1.376266
30	1	5.797.698	-0.578199	-1.662261
31	1	6.456.504	-2.157.533	-1.128208
32	1	5.075.613	-2.098.451	-2.254199
33	6	-1.728.749	2.468.775	2.466310
34	1	-1.593.301	3.516.322	2.141963
35	1	-2.750.466	2.154.187	2.199731
36	1	-1.637.500	2.436.332	3.566118
37	6	0.170358	3.910.475	-1.351265
38	1	0.313718	3.271.286	-2.235566
39	1	-0.659453	4.609.379	-1.550664
40	1	1.083.799	4.509.444	-1.200855

41	6	-0.284474	0.048641	-2.720897
42	1	-1.373.023	-0.115078	-2.742061
43	1	0.013549	0.499832	-3.683675
44	1	0.215228	-0.926632	-2.631058
45	6	-4.955.873	-0.948593	2.262813
46	1	-6.014.909	-0.715469	2.070735
47	1	-4.800.778	-2.029.985	2.133094
48	1	-4.728.114	-0.678016	3.304879
49	6	-4.845.642	-1.385.051	-2.132487
50	1	-4.977.937	-2.328.309	-1.579184
51	1	-5.788.321	-0.816174	-2.064515
52	1	-4.673.714	-1.624.940	-3.194445
53	6	-2.581.750	-3.556.712	-0.422902
54	1	-3.011.199	-4.493.603	-0.032873
55	1	-2.784.633	-3.509.702	-1.505399
56	1	-1.489.382	-3.597.880	-0.290840
57	6	-0.526157	-1.453.417	1.535335
58	1	-1.115.550	-2.365.464	1.690014
59	1	0.514341	-1.717.609	1.324638
60	1	-0.556704	-0.843802	2.447054
61	6	-2.939.565	2.199.306	-1.207358
62	1	-2.383.804	2.308.039	-2.149809
63	1	-3.967.486	1.899.333	-1.445719
64	1	-2.952.409	3.172.848	-0.697281
65	6	2.125.352	1.754.546	1.750836
66	1	1.890.020	1.316.420	2.727316
67	1	3.214.988	1.857.567	1.663038
68	1	1.670.145	2.748.351	1.685844



Optimized structure of B'-$[Ti_3(OMe)_{13}]^-$.