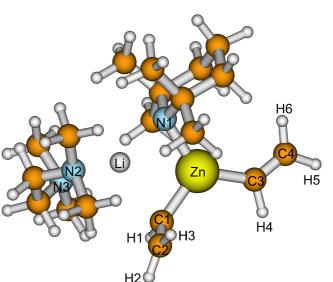
Supplementary Information for calculated compounds

Cartesian coordinates (in Å) of compound 1-calc

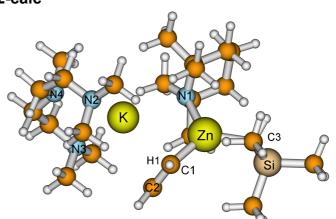
		nates (in A) t	•
С	1.435837	-0.967510	1.443997
Li	-1.043912	0.135284	0.007770
Zn	1.272060	1.422616	-0.249663
С	-0.486627	2.450939	-0.461190
H	-0.775910	3.109434	0.367207
C	-1.121271	2.750633	-1.605070
Н	-0.918532	2.221968	-2.536996
Н	-1.850560	3.559282	-1.701656
С	2.958678	2.453371	-0.423209
Н	2.800702	3.517661	-0.630309
С	4.247147	2.102392	-0.353679
H	4.571561	1.081475	-0.156785
H	5.063490	2.813967	-0.490334
N	0.901164	-0.569141	0.108022
С	1.127499	0.178425	2.428453
Н	1.658674	1.097702	2.158479
Η	1.440967	-0.080305	3.443746
Н	0.056596	0.395475	2.452605
С	0.764144	-2.240146	2.024861
Н	1.077687	-3.153245	1.521800
Н			1.937494
	-0.322856	-2.172827	
Η	1.014044	-2.355719	3.085030
С	2.974092	-1.162181	1.425898
Η	3.438455	-0.177958	1.309401
Η	3.307042	-1.556679	2.393364
С	3.451581	-2.065496	0.286177
H	3.136543	-3.101030	0.458015
H	4.546273	-2.086088	0.263585
С	2.913090	-1.555297	-1.053268
Н	3.209873	-2.227707	-1.867111
Н	3.362844	-0.580252	-1.266038
С	1.372251	-1.388936	-1.048044
С	0.971347	-0.642785	-2.337384
Н	-0.108374	-0.464729	-2.372499
Н	1.243038	-1.221004	-3.224860
H	1.481768	0.322768	-2.424395
C	0.714771	-2.792641	-1.128509
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Н	-0.355836	-2.723150	-0.934769
Η	1.134355	-3.499602	-0.414571
Н	0.856512	-3.225471	-2.124612
Ν	-2.965401	-0.750480	-1.253885
С	-2.887915	-2.112354	-1.801849
H	-2.646831	-2.823321	-1.010097
Н	-2.102707	-2.163204	-2.556601
H	-3.837563	-2.103204	-2.270022
С	-3.251338	0.185299	-2.352657
Η	-3.299026	1.208706	-1.985208
Н	-4.201854	-0.062411	-2.853888
Н	-2.449446	0.139416	-3.090644
С	-4.028787	-0.689254	-0.233872
H	-5.022682	-0.648665	-0.710488



Н	-4.004025	-1.619567	0.336972
С	-3.897756	0.499012	0.712259
Η	-4.805943	0.547569	1.337656
Η	-3.858746	1.428073	0.138958
Ν	-2.691783	0.454103	1.563044
С	-2.771658	-0.645862	2.537922
Η	-1.907516	-0.607741	3.200885
Н	-2.761021	-1.614599	2.038505
Н	-3.684002	-0.578153	3.152902
С	-2.581869	1.728503	2.293567
Н	-1.673736	1.734448	2.897605
Н	-3.444168	1.887534	2.960851
Н	-2.526317	2.555336	1.586705

Cartesian coordinates (in Å) of compound 2-calc

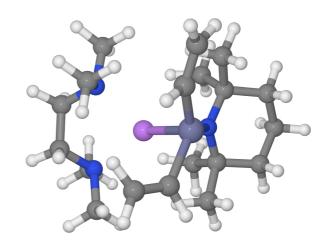
Car	tesian coordi	nates (in Å) ເ	of compound
K	1.504282	-0.187517	0.170252
Zn	-1.949245	-0.026943	0.417732
С	-0.932888	-1.576168	1.266945
Η	-1.084339	-2.572476	0.826753
С	-0.254802	-1.631356	2.425777
Η	-0.056976	-0.737604	3.023249
Η	0.096153	-2.559169	2.884254
С	-3.959936	0.161353	0.471017
Η	-4.198452	0.742582	1.374991
Н	-4.301186	0.779515	-0.369081
Si	-4.960001	-1.404473	0.548095
С	-4.659909	-2.306115	2.190060
Η	-3.597291	-2.516218	2.340518
Н	-5.204088	-3.255549	2.234351
Н	-4.996012	-1.695115	3.034724
С	-6.833604	-1.097916	0.411969
Н	-7.179548	-0.441451	1.217075
Η	-7.406150	-2.030174	0.472575
Η	-7.086998	-0.613120	-0.536695
С	-4.501999	-2.588774	-0.870371
Η	-3.455134	-2.903561	-0.807697
Η	-4.646158	-2.111870	-1.845975
Н	-5.119995	-3.492641	-0.852464
Ν	-0.748344	1.373806	-0.496215
С	-0.957820	1.445255	-1.962923
С	-1.325789	0.031928	-2.457867
Н	-2.279818	-0.304174	-2.041081
Н	-0.555687	-0.694722	-2.180156
Н	-1.427384	0.007711	-3.547065
С	0.319108	1.847607	-2.758652
Н	1.157721	1.197019	-2.486723
Н	0.629747	2.875708	-2.580291
Н	0.155499	1.740725	-3.836971
С	-2.115930	2.399786	-2.360613
Н	-2.160125	2.503826	-3.451774
Н	-3.058743	1.940666	-2.044933
С	-2.001316	3.772389	-1.694458
Н	-1.135374	4.319459	-2.085661
Н	-2.877498	4.381738	-1.940914



С	-1.891059	3.605348	-0.177342
_			
Η	-2.825622	3.169693	0.192580
Н	-1.777437	4.581506	0.310353
С	-0.724979	2.665768	0.231416
С	-0.873448	2.363775	1.737132
H	-1.846371	1.916347	1.962748
Η	-0.798411	3.278208	2.333091
Н	-0.093911	1.677070	2.083505
C	0.615680	3.446135	0.085600
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Η	1.466114	2.790679	0.301169
Н	0.656712	4.285078	0.789555
Н	0.763589	3.858606	-0.911469
Ν	2.409350	-2.512212	-1.505693
С	1.444268	-2.897778	-2.539503
H	0.462914	-3.055590	-2.088722
Η	1.736178	-3.825868	-3.061208
Н	1.353342	-2.102391	-3.282060
C	3.716939		
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Η	3.555221	-1.564532	-2.955572
Н	4.142954	-3.170227	-2.552207
С	4.776792	-1.671533	-1.172304
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Ν	4.420538	-0.398038	-0.531113
С	4.423507	0.705107	-1.494296
H	4.101179	1.631732	-1.016821
	-		
Н	3.728105	0.505489	-2.310470
Н	5.423738	0.874763	-1.930764
С	5.314940	-0.118139	0.601147
_			
Н	6.314076	0.197569	0.248891
Н	5.468274	-1.053216	1.143804
С	4.819467	0.953467	1.576149
N	3.542865	0.659176	2.238691
С	3.102592	1.824141	3.011767
Н	2.133652	1.619307	3.470845
Н	2.989066	2.688493	2.354658
Η	3.813544	2.089050	3.813644
С	3.624768	-0.514981	3.110095
Н	2.659593	-0.675996	3.593366
H			
	4.391577	-0.402357	3.896775
Η	3.855739	-1.411930	2.533423
Н	5.622709	1.105201	2.321984
H	4.707310	1.908094	1.055356
С	2.475341	-3.549986	-0.474360
Н	1.477244	-3.719785	-0.066721
Н	3.117916	-3.236828	0.350173
Η	2.858504	-4.508560	-0.866424
Η	4.982134	-2.395896	-0.381256
Н	5.713775	-1.577574	-1.751589
	0.1 10110	1.011017	1.751508

Cartesian coordinates (in $\mbox{\normalfont\AA}$) of compound **TS1** at the B3LYP/6-31G(d) level of theory

С	1.692247	-1.577580	0.647313
Li	-0.753115	-0.507270	-0.322142
Zn	0.486304	1.288198	1.052209
С	-0.529113	0.889382	2.749984
Н	-0.099028	0.278826	3.552469
С	-1.717989	1.429218	3.079470
Н	-2.265748	2.085169	2.397780
Η	-2.203739	1.292769	4.051253
С	0.213341	3.239448	0.656460
Η	-0.508358	3.624797	1.392005
С	0.689982	4.211424	-0.138267
Н	1.422959	4.035106	-0.926298
Η	0.384360	5.258327	-0.046800
Ν	1.390092	-0.234636	0.038886
С	1.107774	-1.673920	2.063902
Н	1.531150	-0.906499	2.715209
Н	1.348711	-2.653841	2.494001
Н	0.021868	-1.555408	2.083762
С	1.118690	-2.789875	-0.143856
Н	1.657369	-3.005446	-1.067030
Н	0.067394	-2.634119	-0.410108
Н	1.162744	-3.698094	0.470634
С	3.222372	-1.795353	0.821968
Н	3.573930	-1.091155	1.588510
H	3.400811 4.025377	-2.806540 -1.563222	1.213609
Н	4.025377 3.798777	-1.503222	-0.454330 -1.204548
Н	5.099861	-1.652581	-0.247039
C	3.703892	-0.171834	-0.247039
Н	4.230743	0.011740	-1.937784
Н	4.073367	0.573247	-0.273198
C	2.185694	0.078576	-1.195547
Č	2.044782	1.568704	-1.521519
H	1.002868	1.855825	-1.689040
Н	2.617312	1.814193	-2.424271
Н	2.422726	2.181380	-0.700275
С	1.714262	-0.685279	-2.468185
Н	0.625134	-0.614442	-2.580293
Η	1.980627	-1.743371	-2.473049
Η	2.162110	-0.241199	-3.366110
Ν	-2.201502	0.638860	-1.566203
С	-1.757347	0.955567	-2.935646
Η	-1.459576	0.040207	-3.456026
Η	-0.897146	1.626967	-2.893277
Η	-2.555157	1.445655	-3.518796
С	-2.576870	1.901957	-0.892738
Н	-2.894633	1.708941	0.134203
Н	-3.400847	2.403040	-1.429102
Н	-1.713246	2.568925	-0.846771
С	-3.361269	-0.276529	-1.618311
Н	-4.272650 3.166695	0.263888	-1.927655
Н	-3.166685	-1.026875	-2.392092
С	-3.615661	-0.964422	-0.280025



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Η
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Ν
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               -1.863898
                           0.116192
C
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Н
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Η
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               -2.922777
                           -1.725699
Η
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                           -0.529661
C
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Н
   -1.848283
               -2.887891
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Н
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               -2.641019
                           1.782487
   -2.512305
               -1.270810
                           2.143551
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Cartesian coordinates (in Å) of compound TS2 from clockwise-rotation

Car	tesian coord	inates (in Å) (of compound
С	2.913565	-1.798735	-0.954380
С	1.369689	-1.648179	-0.931537
Ν	0.910274	-0.689439	0.118838
С	1.494256	-0.897047	1.478187
С	3.035524	-1.072445	1.440138
С	3.495172	-2.119211	0.423747
С	0.935898	-1.089085	-2.301829
С	0.735026	-3.060840	-0.814146
Zn	1.212933	1.267580	-0.525757
С	-0.563016	2.070034	-1.094569
С	-0.702300	3.379009	-1.350597
С	1.198660	0.361752	2.316868
С	0.859679	-2.088908	2.244947
С	2.988474	2.141530	-0.552250
С	3.252966	3.423173	-0.270323
Li	-1.025802	-0.053879	0.030342
Ν	-2.576765	0.650545	1.503379
С	-2.711320	-0.244701	2.665265
С	-2.343034	2.027212	1.980477
С	-3.802909	0.632378	0.679997
С	-4.009073	-0.676078	-0.076491
Ν	-2.967049	-0.931245	-1.090829
С	-2.922298	-2.366911	-1.408045
С	-3.258331	-0.185943	-2.327526
Н	-1.456143	1.507292	-1.400535
Н	0.096452	4.092077	-1.155354
Н	-1.603221	3.816017	-1.787859
Н	3.874915	1.549198	-0.804218
Н	2.472533	4.132911	0.002340
Н	4.259983	3.843915	-0.289091
Н	1.705430	1.243367	1.913749
Н	1.545973	0.236672	3.346377
Н	0.125210	0.564116	2.351027
Н	1.151088	-3.058540	1.845212
Н	-0.231748	-2.030852	2.204000
Н	1.160381	-2.071976	3.298110
Н	3.482081	-0.108589	1.174790
Н	3.400698	-1.325494	2.442690
Н	3.197540	-3.124715	0.742761
Н	4.589021	-2.132932	0.372568
Н	3.196225	-2.570849	-1.680066

3.349993	-0.858016	-1.307649
-0.146244	-0.932377	-2.344706
1.205146	-1.779110	-3.106398
1.422409	-0.134964	-2.530808
-0.333009	-2.982387	-0.608149
1.179559	-3.661995	-0.022519
0.865163	-3.618803	-1.747647
-2.670824	-2.941095	-0.515008
-2.156529	-2.555021	-2.160983
-3.887003	-2.730018	-1.798131
-3.346573	0.881268	-2.126527
-4.196325	-0.531933	-2.790684
-2.445853	-0.322455	-3.042694
-5.009425	-0.664958	-0.539257
-4.007758	-1.511635	0.626130
-4.690416	0.819987	1.307949
-3.736867	1.463922	-0.025419
-1.816686	-0.176628	3.283926
-2.816083	-1.283598	2.351003
-3.583165	0.022708	3.283823
-1.454586	2.052465	2.612103
-3.196896	2.399150	2.568625
-2.170040	2.687054	1.130890
	-0.146244 1.205146 1.422409 -0.333009 1.179559 0.865163 -2.670824 -2.156529 -3.887003 -3.346573 -4.196325 -2.445853 -5.009425 -4.007758 -4.690416 -3.736867 -1.816686 -2.816083 -3.583165 -1.454586 -3.196896	-0.146244 -0.932377 1.205146 -1.779110 1.422409 -0.134964 -0.333009 -2.982387 1.179559 -3.661995 0.865163 -3.618803 -2.670824 -2.941095 -2.156529 -2.555021 -3.887003 -2.730018 -3.346573 0.881268 -4.196325 -0.531933 -2.445853 -0.322455 -5.009425 -0.664958 -4.007758 -1.511635 -4.690416 0.819987 -3.736867 1.463922 -1.816686 -0.176628 -2.816083 -1.283598 -3.583165 0.022708 -1.454586 2.052465 -3.196896 2.399150

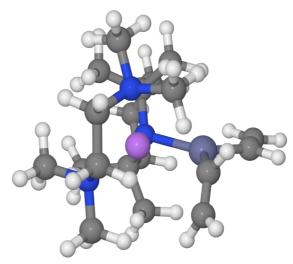
Cartesian coordinates (in Å) of compound **TS3** from *anticlockwise*-rotation C =1 206703 0.818289 1.504523

С	-1.206703	0.818289	1.504523
Li	1.138696	0.100638	-0.010816
Zn	-1.457923	-1.352333	-0.528132
С	-0.201633	-2.391674	-1.730336
Η	-0.756116	-3.100226	-2.359084
С	1.110208	-2.402520	-1.989786
Н	1.815689	-1.760716	-1.460092
Η	1.585086	-3.041089	-2.738418
С	-3.213695	-2.198332	-0.082733
Η	-3.162272	-3.286533	0.054004
С	-4.464105	-1.724277	-0.032978
Η	-4.698665	-0.668260	-0.165691
Η	-5.337525	-2.357340	0.135618
Ν	-0.840005	0.540564	0.075721
С	-0.988010	-0.479600	2.307239
Н	-1.696770	-1.255346	2.008057
Η	-1.127107	-0.306461	3.378500
Η	0.025175	-0.862856	2.161728
С	-0.305948	1.900897	2.162725
Η	-0.505517	2.905889	1.794806
Η	0.754526	1.691854	1.982991
Η	-0.457608	1.919194	3.247068
С	-2.693050	1.218763	1.685685
Н	-3.306834	0.330686	1.511625
Н	-2.861646	1.524296	2.725251
С	-3.144849	2.315234	0.721285
Н	-2.659124	3.269558	0.955109
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С	-2.834302	1.890261	-0.713677

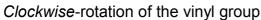
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Н	-3.432691	1.004587	-0.952699
С	-1.340080	1.541706	-0.926634
Č	-1.202525	0.932944	-2.335745
H	-0.185931	0.581143	-2.529950
H	-1.459773	1.673947	-3.098205
Н	-1.874714	0.082142	-2.485721
C	-0.520578	2.857021	-0.948585
H	0.541831	2.631901	-1.048047
H	-0.649984	3.461353	-0.052750
Н	-0.814117	3.477614	-1.801775
N	3.097403	1.084343	-0.805077
C	3.222953	2.549531	-0.700788
H	3.005268	2.875607	0.318015
Н	2.514861	3.032740	-1.372637
Н	4.235317	2.888871	-0.970531
С	3.248356	0.697145	-2.220899
Н	3.207026	-0.384998	-2.333474
Н	4.203549	1.056958	-2.634605
Н	2.432451	1.123111	-2.806805
С	4.150067	0.455791	0.023606
Н	5.115900	0.467256	-0.505849
Н	4.285378	1.071408	0.914728
С	3.834190	-0.977414	0.437411
Н	4.703596	-1.380855	0.983515
Н	3.703066	-1.606141	-0.445637
Ν	2.610726	-1.091446	1.258705
С	2.822640	-0.489358	2.588129
Н	1.935351	-0.638163	3.202174
Н	2.995233	0.584351	2.512624
Н	3.682709	-0.945875	3.103021
С	2.276023	-2.519787	1.433053
Η	1.386359	-2.614148	2.056457
Η	3.098725	-3.067337	1.918579
Η	2.060288	-2.974453	0.466878

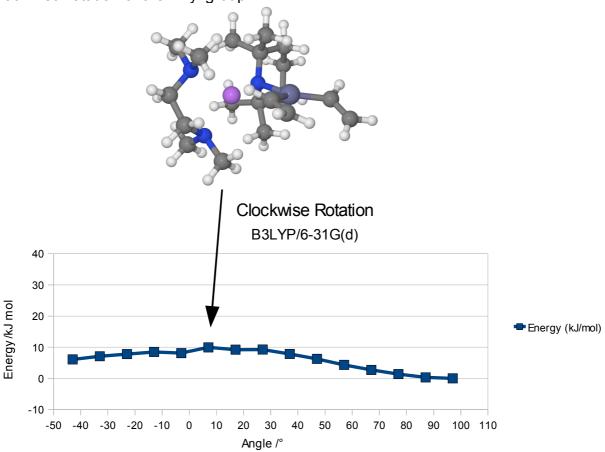
Cartesian coordinates (in Å) of compound 5 from vinyl-rotation

С	-1.575517	-1.371234	-1.021232
Li	1.005628	0.052667	-0.194814
Zn	-1.261062	1.450753	-0.286665
С	0.496860	2.350557	-0.824262
Н	0.912366	3.090832	-0.130680
С	1.016761	2.448695	-2.058243
Н	0.679496	1.817022	-2.880728
Н	1.771028	3.186846	-2.343070
С	-2.913562	2.539204	-0.159676
Н	-2.767369	3.608764	-0.347150
С	-4.183661	2.203365	0.091004
Н	-4.492985	1.178587	0.292184
Н	-4.997653	2.930366	0.109495
Ν	-0.941664	-0.553185	0.056501
С	-1.418017	-0.605283	-2.351031
Н	-1.961882	0.345756	-2.340414
Н	-1.822027	-1.186296	-3.184905

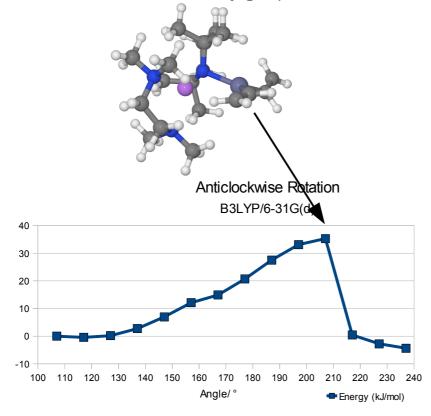


	0.266276	0.200440	2 571045
Н	-0.366276	-0.398149	-2.571045
С	-0.899977	-2.750216	-1.237243
Н	-1.083730	-3.450601	-0.423880
Н	0.180227	-2.627511	-1.330459
Η	-1.270155	-3.218449	-2.155452
С	-3.090495	-1.585270	-0.779432
H	-3.596652	-0.621422	-0.900512
Н	-3.495091	-2.255697	-1.546776
С	-3.391639	-2.124230	0.619881
Н	-3.003220	-3.142600	0.733232
H	-4.474273	-2.197594	0.767608
С	-2.785947	-1.194617	1.672120
Н	-2.955197	-1.589559	2.680842
Н	-3.301564	-0.230325	1.619657
С	-1.271929	-0.938820	1.460774
С	-0.876525	0.242295	2.370757
Н	0.168073	0.524185	2.213815
Н	-0.997401	-0.015956	3.426875
Н	-1.505052	1.118531	2.182943
С	-0.464527	-2.168780	1.955637
Н	0.601065	-2.028605	1.750316
Н	-0.771270	-3.098463	1.478502
Н	-0.586217	-2.303888	3.035838
Ν	2.874447	0.502614	1.526377
С	2.820641	-0.039010	2.891571
H	2.669060	-1.119632	2.862306
Н	1.985600	0.404456	3.434258
Н	3.745400	0.171135	3.454058
С	2.979790	1.967591	1.592664
H	3.037479	2.393707	0.592174
Н	3.868740	2.283013	2.164400
Н	2.092161	2.378815	2.075500
С	4.030318	-0.067917	0.812701
H	4.961095	0.448640	1.101632
Н	4.149220	-1.104599	1.132658
С	3.904115	-0.013719	-0.706051
Н	4.860982	-0.350622	-1.141468
Н	3.749506	1.016681	-1.034929
Ν	2.789509	-0.821255	-1.244107
С	2.991192	-2.253268	-0.965883
Н	2.235626	-2.834631	-1.492764
H	2.887958	-2.467419	0.097740
Н	3.983877	-2.596076	-1.300287
С	2.725177	-0.625155	-2.702614
Н	1.881928	-1.182345	-3.113623
H	3.645547	-0.971740	-3.199246
Н	2.582173	0.431900	-2.924298



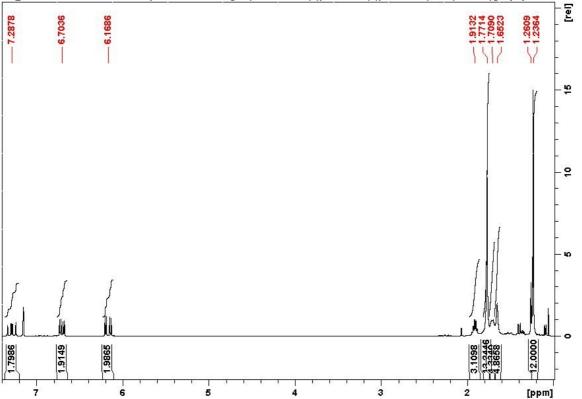


Anticlockwise-rotation of the vinyl group



Supporting Information for prepared compounds

Figure S1: ¹H NMR spectrum of [Li(TMEDA)(μ -TMP)(μ -C₂H₃)Zn(C₂H₃)], **(1)** in C6D6:



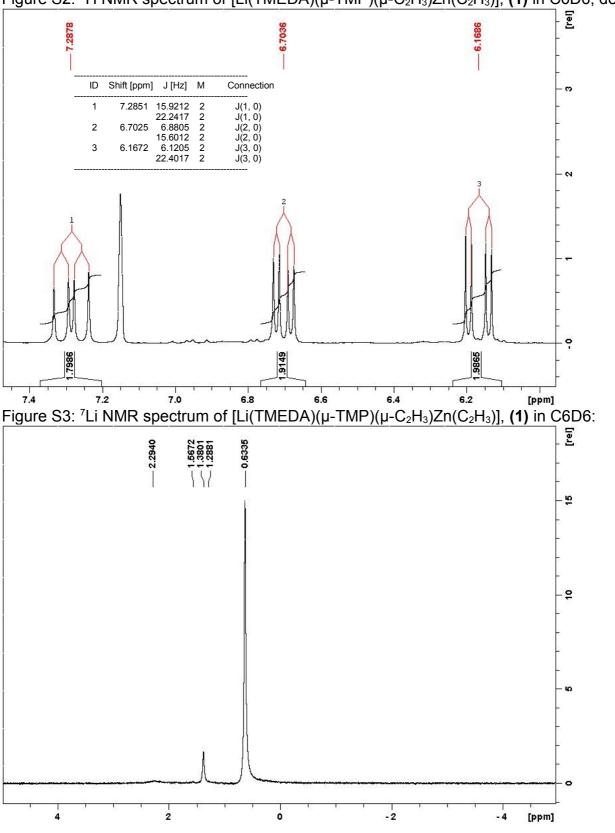


Figure S2: 1H NMR spectrum of [Li(TMEDA)(μ -TMP)(μ -C $_2H_3$)Zn(C $_2H_3$)], **(1)** in C6D6, detail:

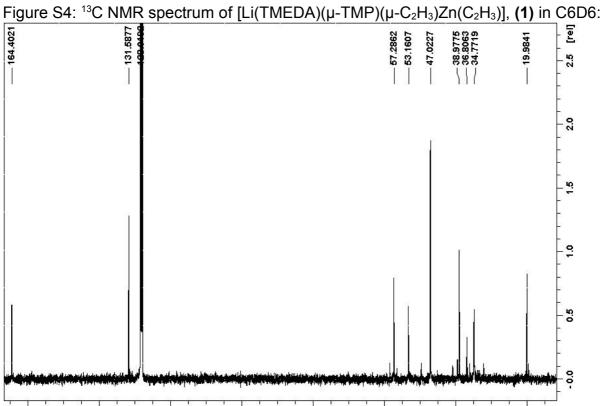
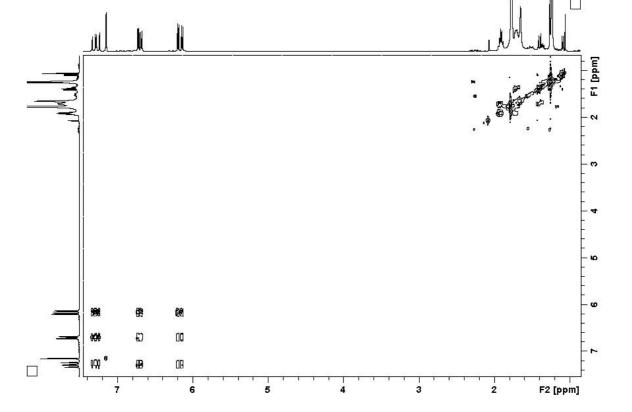
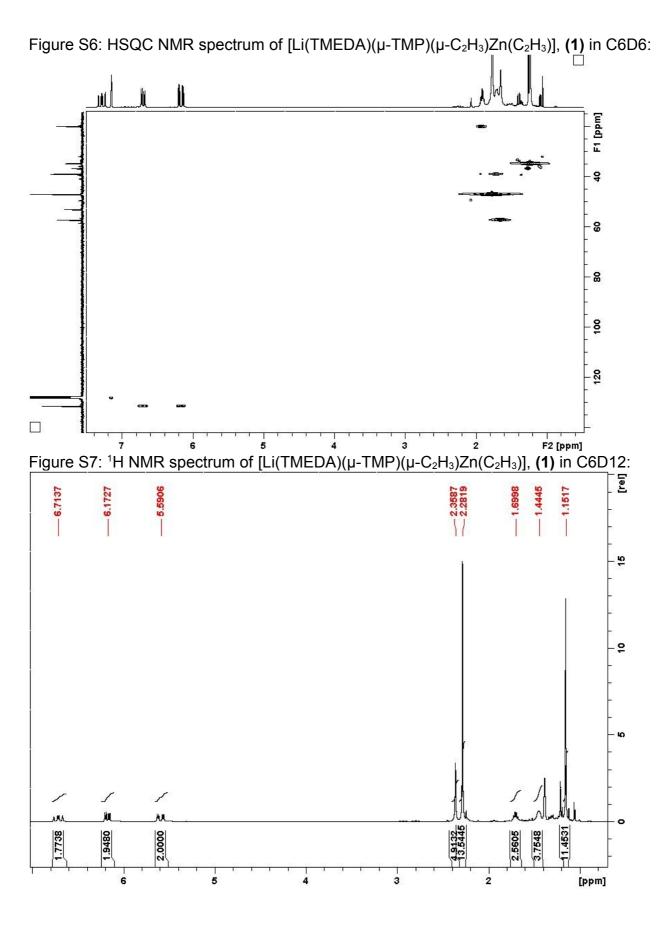
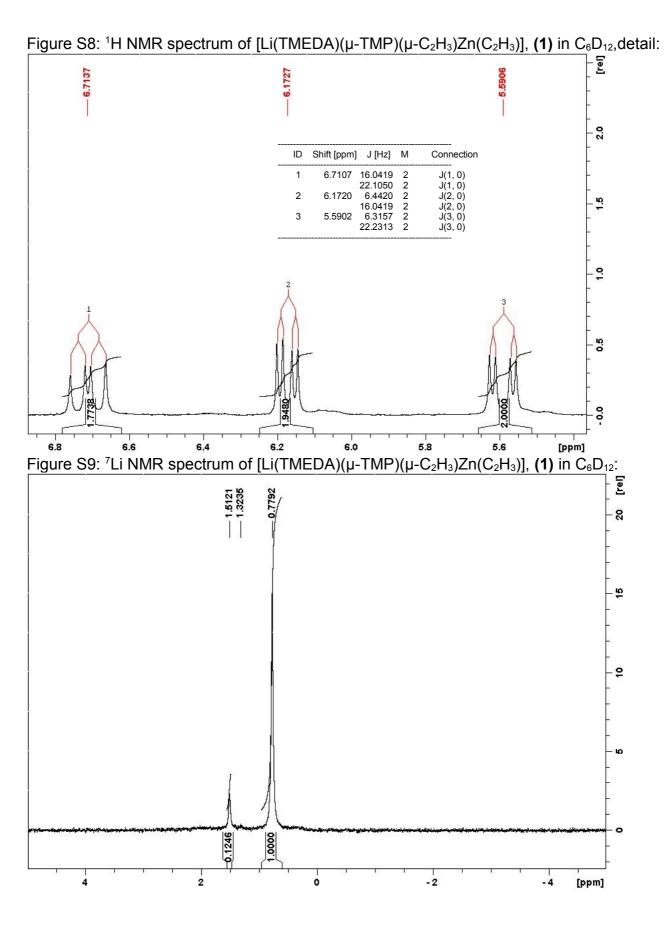
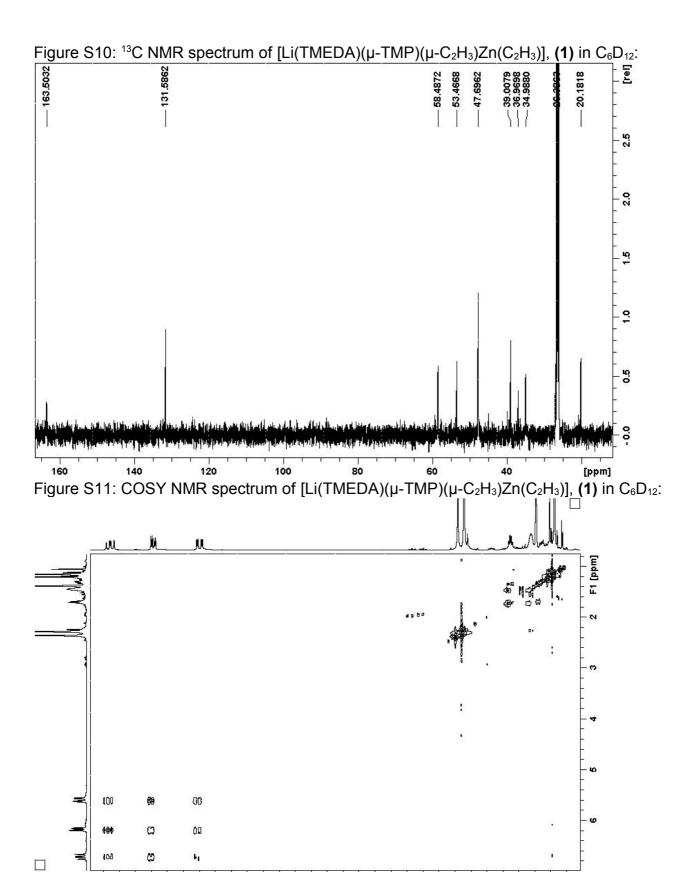


Figure S5: COSY NMR spectrum of [Li(TMEDA)(μ -TMP)(μ -C₂H₃)Zn(C₂H₃)], **(1)** in C6D6:









F2 [ppm]

Figure S12: HSQC NMR spectrum of [Li(TMEDA)(μ -TMP)(μ -C₂H₃)Zn(C₂H₃)], (1) in C₆D₁₂:

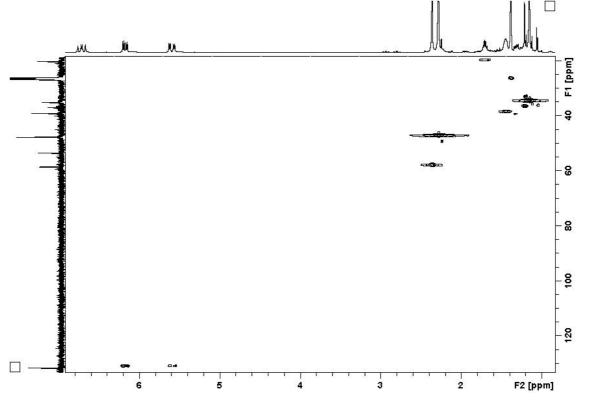


Figure S13: EXSY NMR spectrum of [Li(TMEDA)(μ -TMP)(μ -C₂H₃)Zn(C₂H₃)], **(1)** in C₆D₁₂:

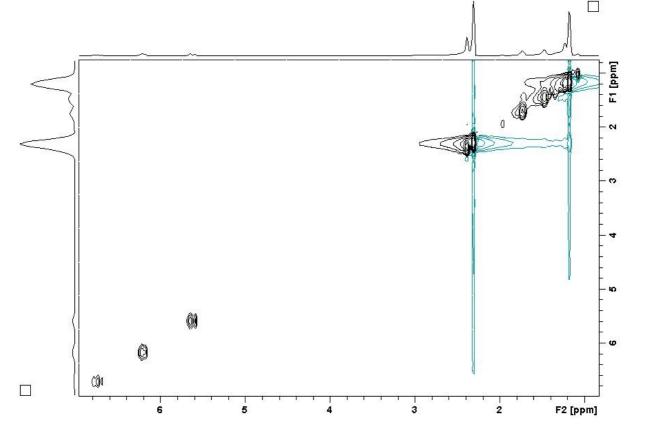


Figure S14: 1H NMR spectrum of [Li(TMEDA)(μ -TMP)(μ -C $_2H_3$)Zn(C $_2H_3$)], **(1)** in [D8] toluene:

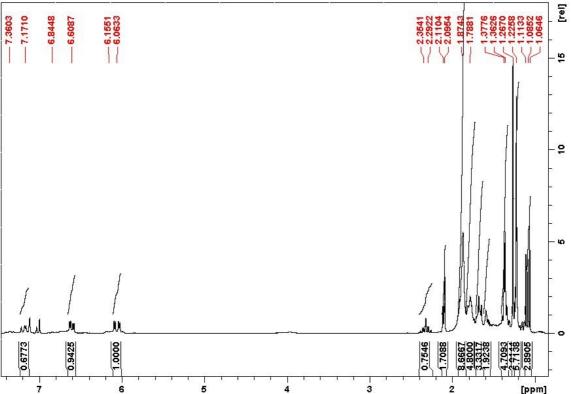


Figure S15: ^{1}H NMR spectrum of [Li(TMEDA)(μ -TMP)(μ -C₂H₃)Zn(C₂H₃)], **(1)** in [D8] toluene, detail:

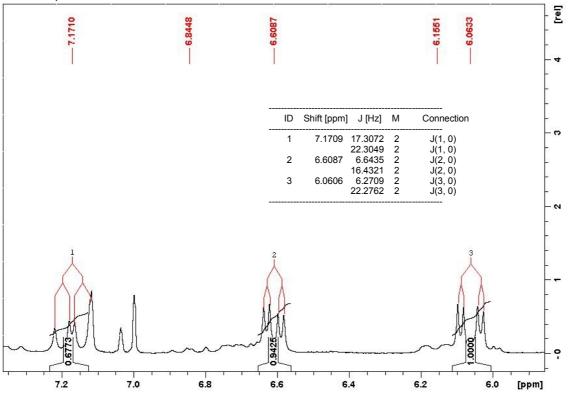
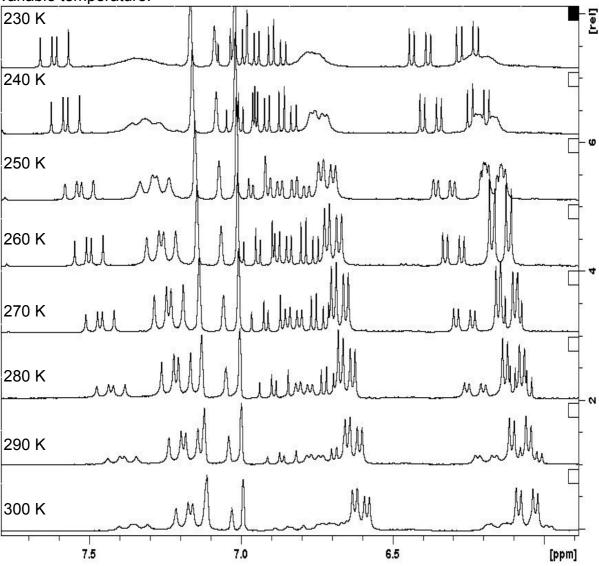
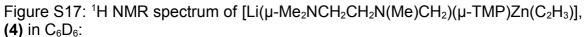


Figure S16: 1H NMR spectra of [Li(TMEDA)(μ -TMP)(μ -C $_2H_3$)Zn(C $_2H_3$)], **(1)** in [D8]toluene, variable temperature:





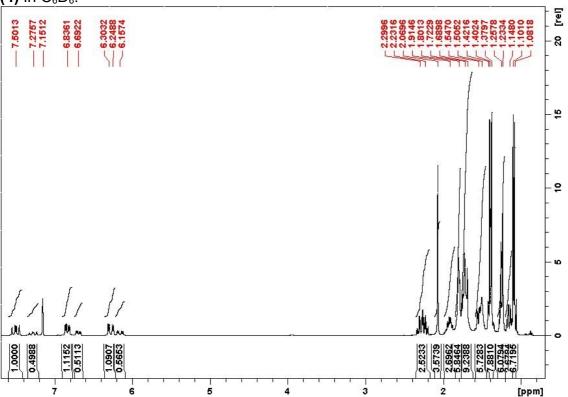
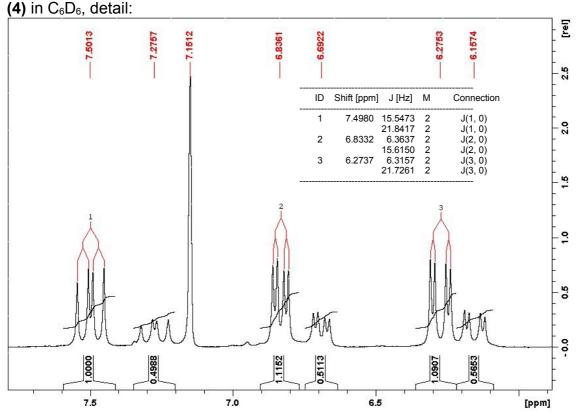
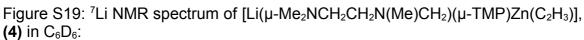


Figure S18: ^{1}H NMR spectrum of [Li(μ -Me₂NCH₂CH₂N(Me)CH₂)(μ -TMP)Zn(C₂H₃)],





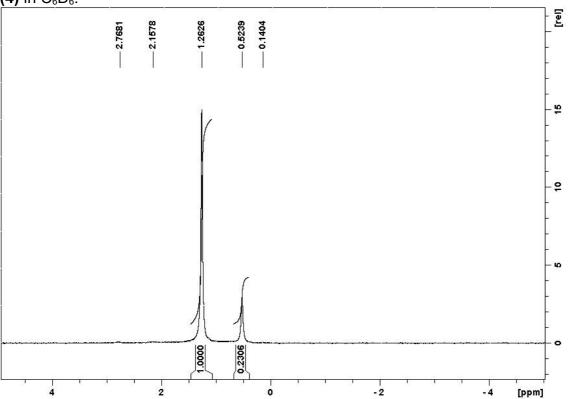
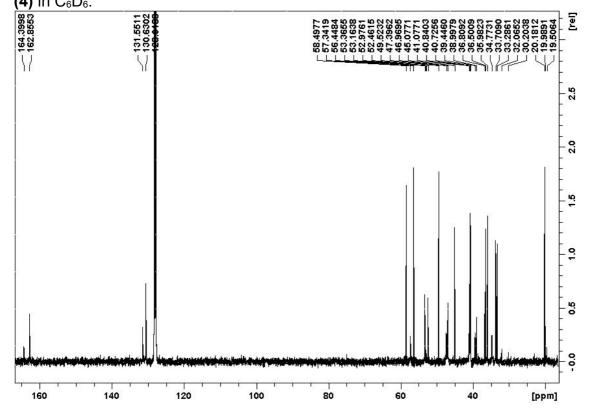
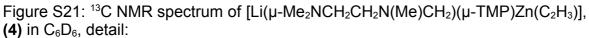


Figure S20: 13 C NMR spectrum of [Li(μ -Me $_2$ NCH $_2$ CH $_2$ N(Me)CH $_2$)(μ -TMP)Zn(C $_2$ H $_3$)], **(4)** in C $_6$ D $_6$:





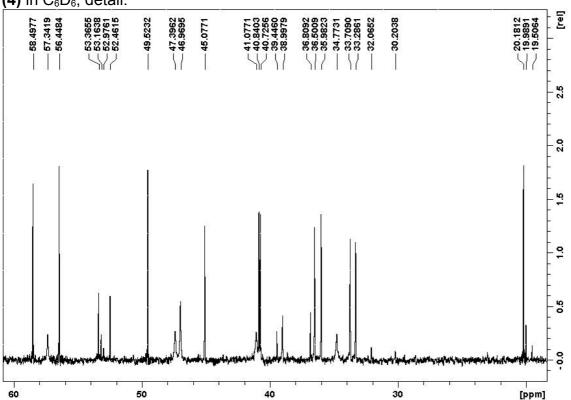


Figure S22: COSY NMR spectrum of [Li(μ -Me₂NCH₂CH₂N(Me)CH₂)(μ -TMP)Zn(C₂H₃)], **(4)** in C₆D₆:

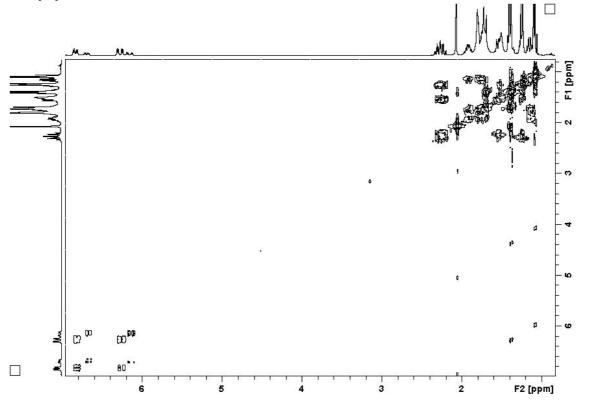


Figure S23: COSY NMR spectrum of [Li(μ -Me₂NCH₂CH₂N(Me)CH₂)(μ -TMP)Zn(C₂H₃)], **(4)** in C₆D₆, detail:

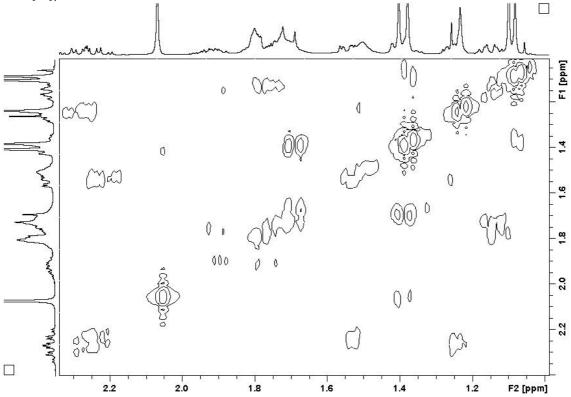


Figure S24: HSQC NMR spectrum of [Li(μ -Me₂NCH₂CH₂N(Me)CH₂)(μ -TMP)Zn(C₂H₃)], **(4)** in C₆D₆:

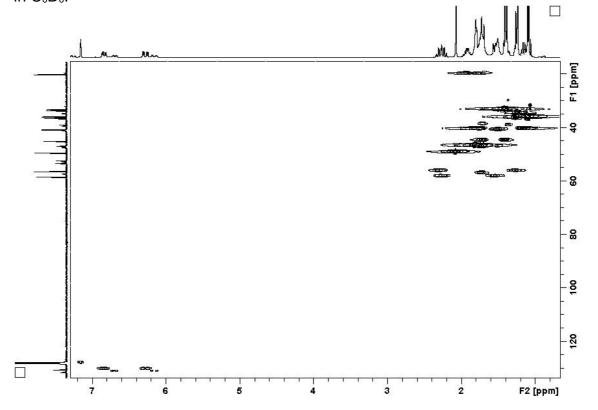


Figure S25: HSQC NMR spectrum of [Li(μ -Me₂NCH₂CH₂N(Me)CH₂)(μ -TMP)Zn(C₂H₃)], **(4)** in C₆D₆, detail:

