

Supporting Information

For

Synthesis and Structural Characterization of Novel Cyclam-based Zirconium Complexes and Their Use in the Controlled ROP of *rac*-lactide: Access to Cyclam- functionalized Polylactide Material

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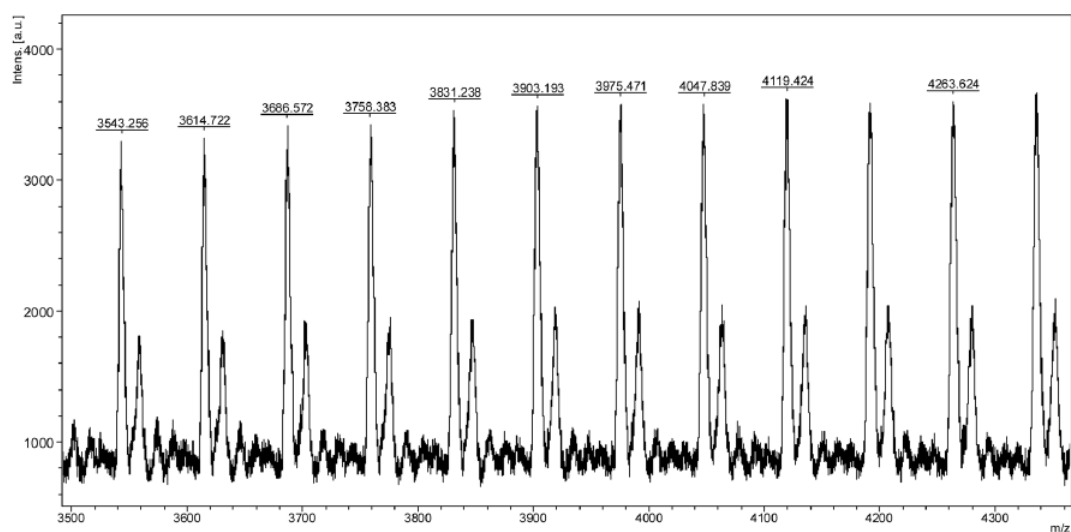


Figure S1. Zoom-in of the MALDI-TOF spectrum of the O'Pr-end PLA prepared by ROP of *rac*-lactide initiated by complex **2**. Conditions: 100 equiv. *rac*-lactide, $[\text{monomer}]_0 = 1 \text{ M}$, CH_2Cl_2 , room temperature, polymer isolated at 95% conversion to PLA.

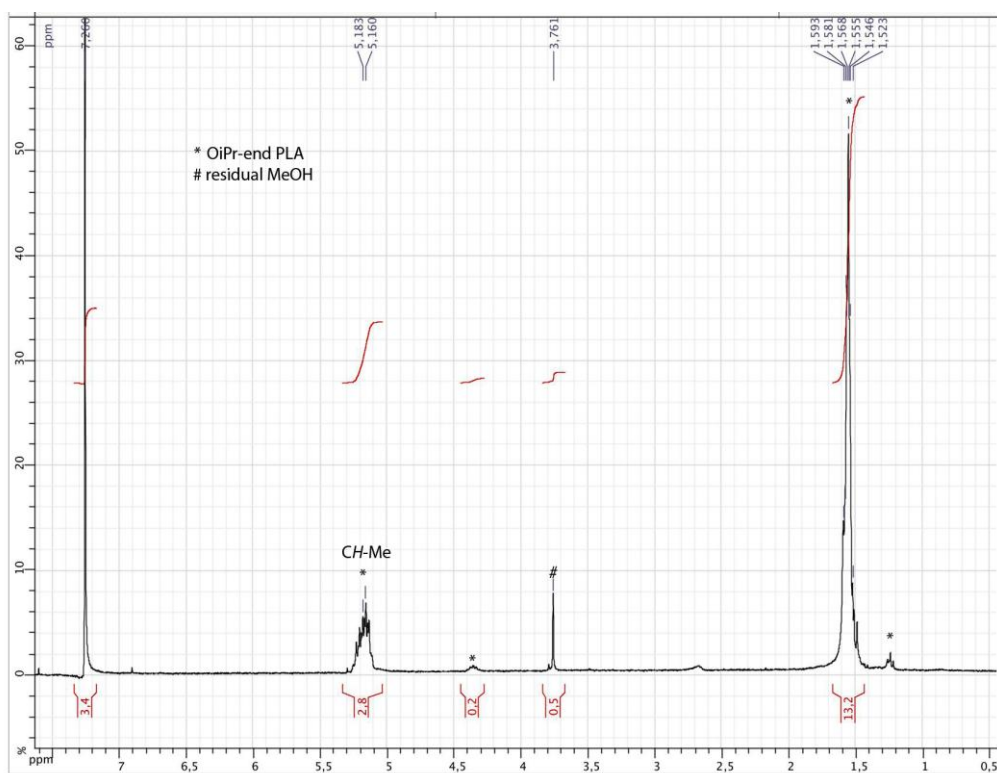
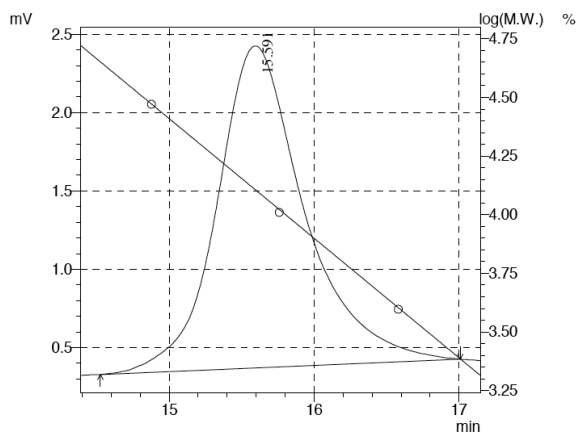


Figure S2. ^1H NMR spectrum of O'Pr-end PLA prepared by ROP of *rac*-lactide initiated by complex **2**. Conditions: 100 equiv. *rac*-lactide, $[\text{monomer}]_0 = 1 \text{ M}$, CH_2Cl_2 , room temperature, polymer isolated at 95% conversion to PLA.

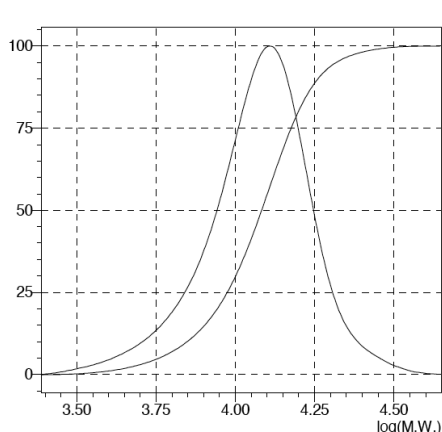
==== Shimadzu LCsolution GPC Analysis Report ====

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 Sample ID :
 Vail# :
 Injection Volume : 100 uL
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 Method Filename : gpc_30_juin2011.lcm
 Batch Filename :
 Report Filename : Report_template.lcr
 Date Acquired : 05/10/2011 11:36:50
 Data Processed : 05/10/2011 11:58:33

Chromatogram & Calibration Curve



Molecular Weight Distribution Curve



GPC Calculation Results

Peak#:1 (Detector A Ch1)

[Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	14.525	14.525	44824	328
Top	15.591	15.591	12828	2055
End	17.008	17.008	2430	427

Area : 86325

Area% : 100.0000

[Average Molecular Weight]

Number Average Molecular Weight(Mn)	10827
Weight Average Molecular Weight(Mw)	12605
Z Average Molecular Weight(Mz)	14391
Z+1 Average Molecular Weight(Mz1)	16337
Mw/Mn	1.16420
Mv/Mn	1.14234
Mz/Mw	1.14169

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Number Average Molecular Weight(Mn)	10827
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Z+1 Average Molecular Weight(Mz1)	16337
Mw/Mn	1.16420
Mv/Mn	1.14234
Mz/Mw	1.14169

Figure S3. SEC traces of isolated cyclam-functionalized PLA prepared via ROP of *rac*-lactide by complex **4**. Conditions: 100 equiv. of *rac*-lactide, 80 °C, toluene, quantitative conversion, 17h.

D:\data\Melanie\Service de spectrometrie de masse\20111007\B6433ML HF268\0_K81

Comment 1
Comment 2

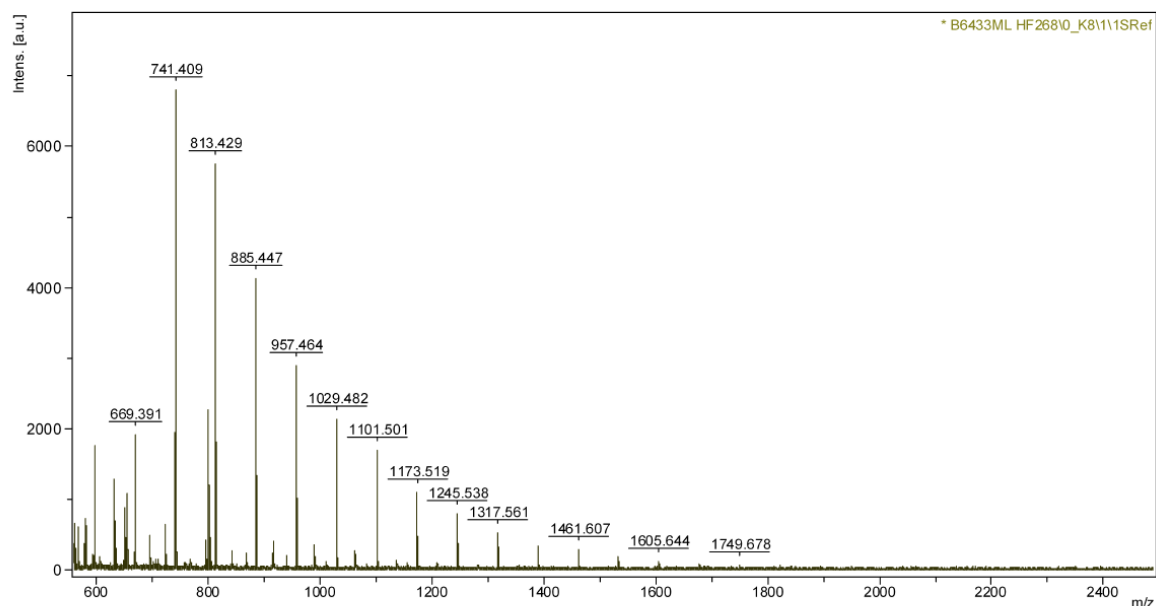
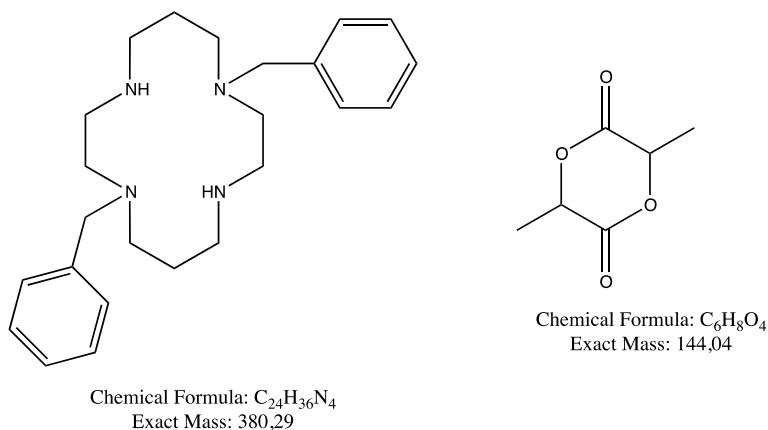


Figure S4. MALDI-TOF spectrum of the cyclam-functionalized PLA prepared by ROP of *rac*-lactide initiated by complex **3**. Conditions: 20 equiv. *rac*-lactide, $[\text{monomer}]_0 = 1 \text{ M}$, toluene, 80 °C, polymer isolated after quantitative conversion of LA to PLA.



The above MALDI-TOF spectrum features peaks consistent with $[\text{M}+\text{H}]^+$ cations exactly corresponding to a cyclam-PLA polymer.

For instance:

- The peak at 813.429 matches that expected for a cyclam-PLA oligomer with three lactide units: $380.29 + (3 \times 144.04) + 1.008 = 813.418$
- The peak at 1245.538 matches exactly that expected for a cyclam-PLA oligomer with six lactide units: $380.29 + (6 \times 144.04) + 1.008 = 1245.538$

D:\data\Melanie\Service de spectrometrie de masse\20111007\B6434ML HF270\0_K9\1

Comment 1
Comment 2

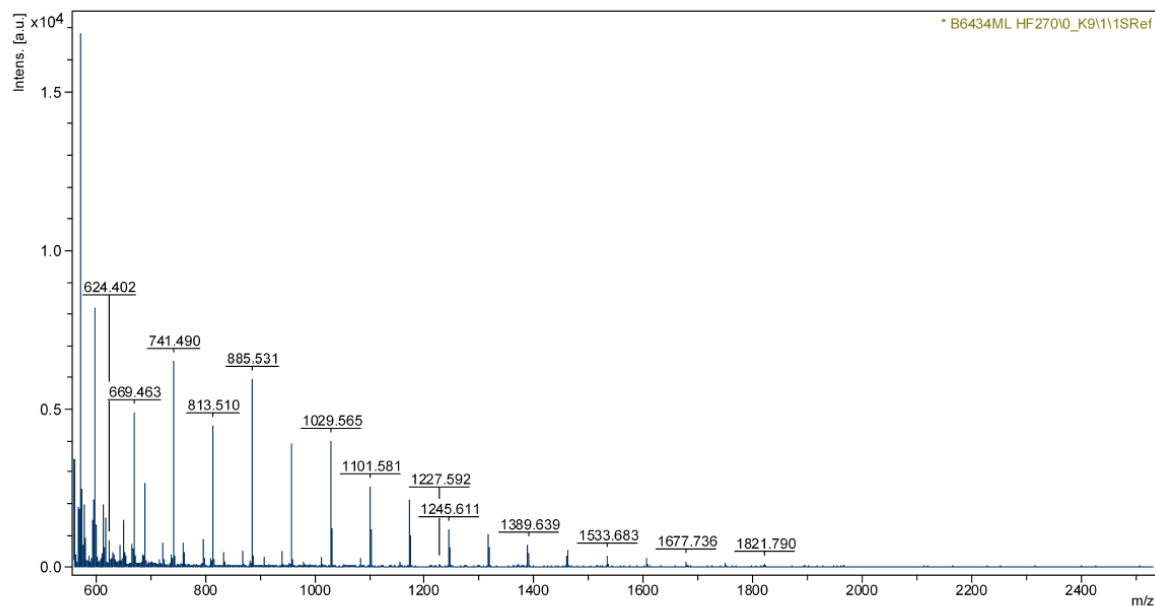


Figure S5. MALDI-TOF spectrum of the cyclam-functionalized PLA prepared by ROP of *rac*-lactide initiated by complex **4**. Conditions: 20 equiv. *rac*-lactide, [monomer]₀ = 1 M, toluene, 80 °C, polymer isolated after quantitative conversion of LA to PLA.

The above MALDI-TOF spectrum is nearly identical to that in figure S3 and is thus consistent with a cyclam-functionalized PLA.

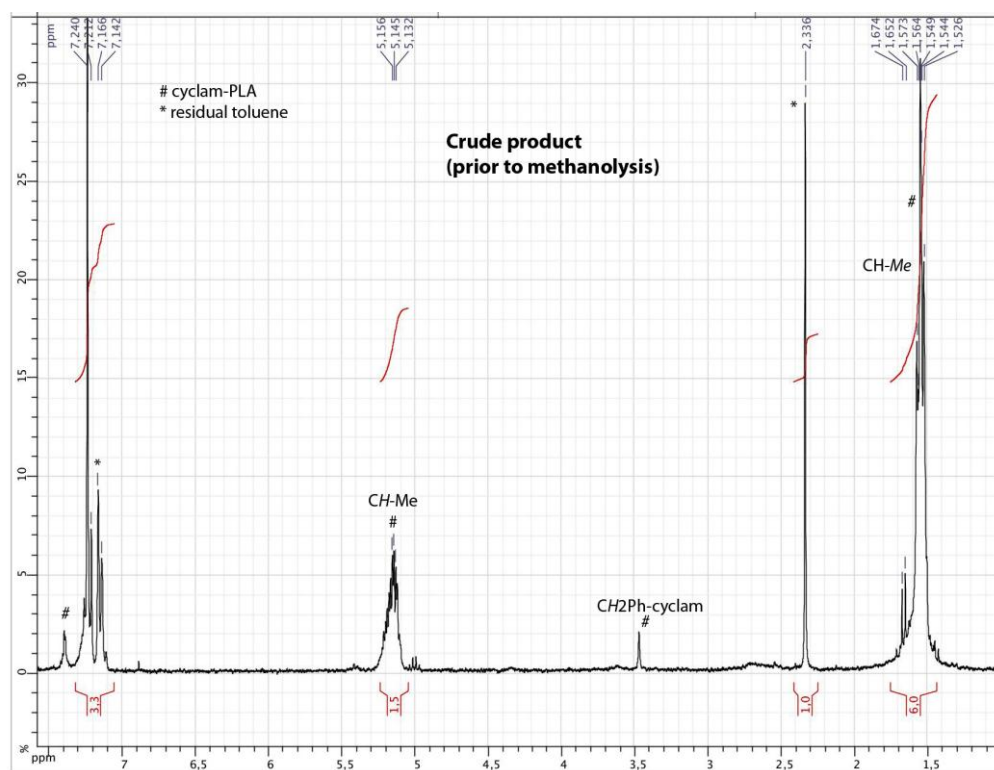


Figure S6. ¹H NMR spectrum of the cyclam-functionalized PLA prepared by ROP of *rac*-lactide initiated by complex **4**. Conditions: 20 equiv. *rac*-lactide, [monomer]₀ = 1 M, toluene, 80 °C, crude polymerization product.

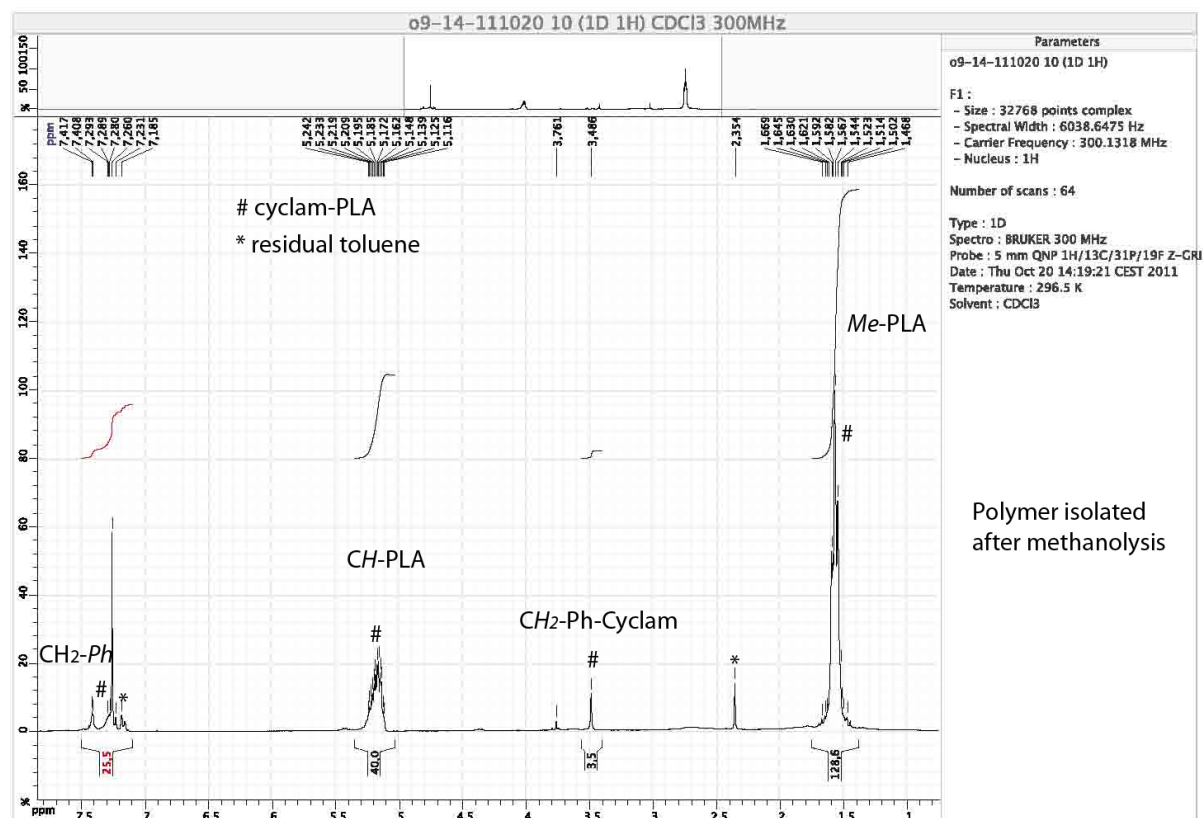


Figure S7. ^1H NMR spectrum of the cyclam-functionalized PLA prepared by ROP of *rac*-lactide initiated by complex **4**. Conditions: 20 equiv. *rac*-lactide, $[\text{monomer}]_0 = 1 \text{ M}$, toluene, 80°C , polymer after methanolysis.

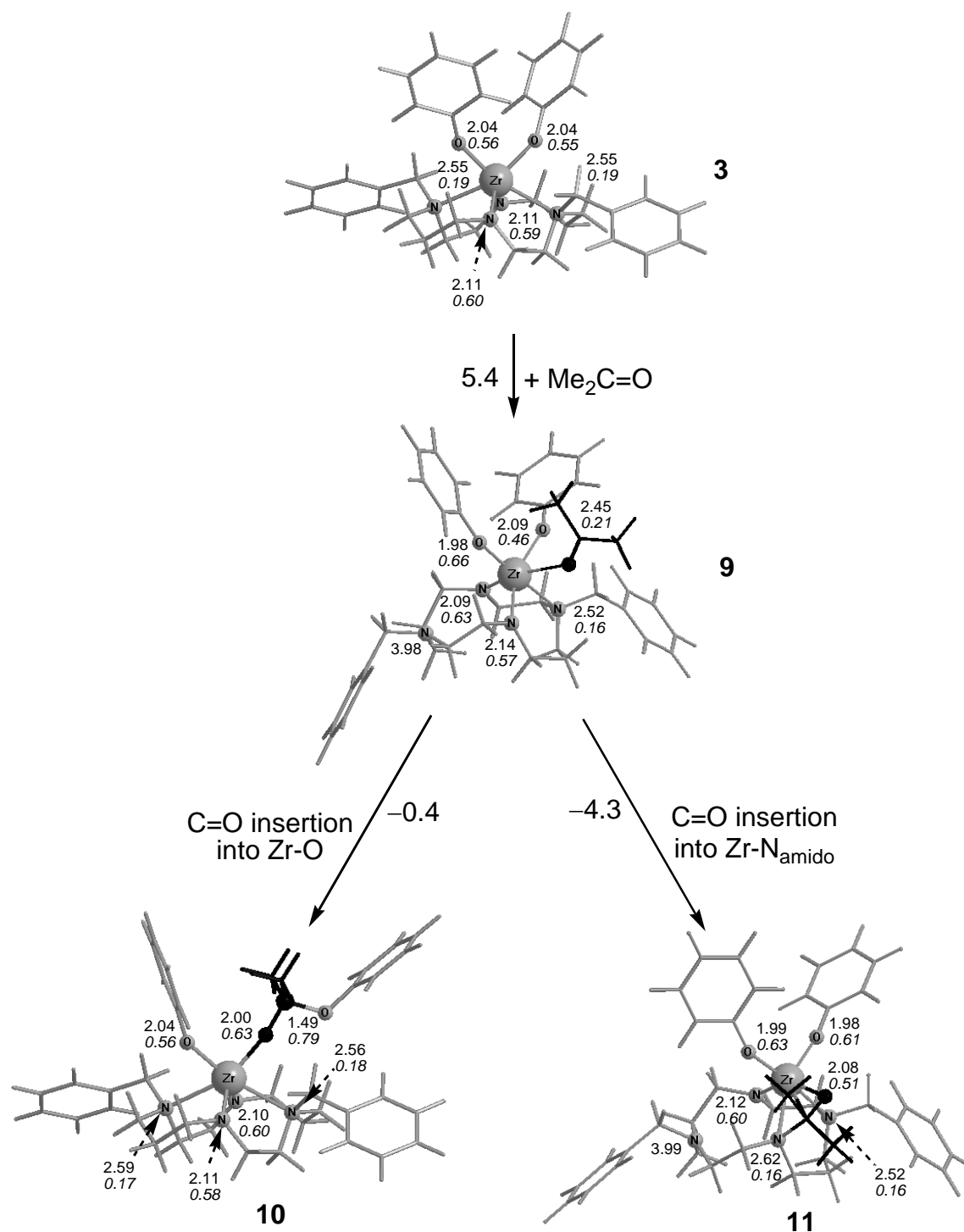


Figure S8. Energy balance (kcal/mol) for the addition of acetone to **3**, and for C=O insertion into a Zr-O bond (bottom left) and into a Zr-N_{amido} bond (bottom right) of that complex. The geometry optimised for the various species is represented with the more relevant distances (Å) and Wiberg indices (italics). The acetone moiety is darkened.

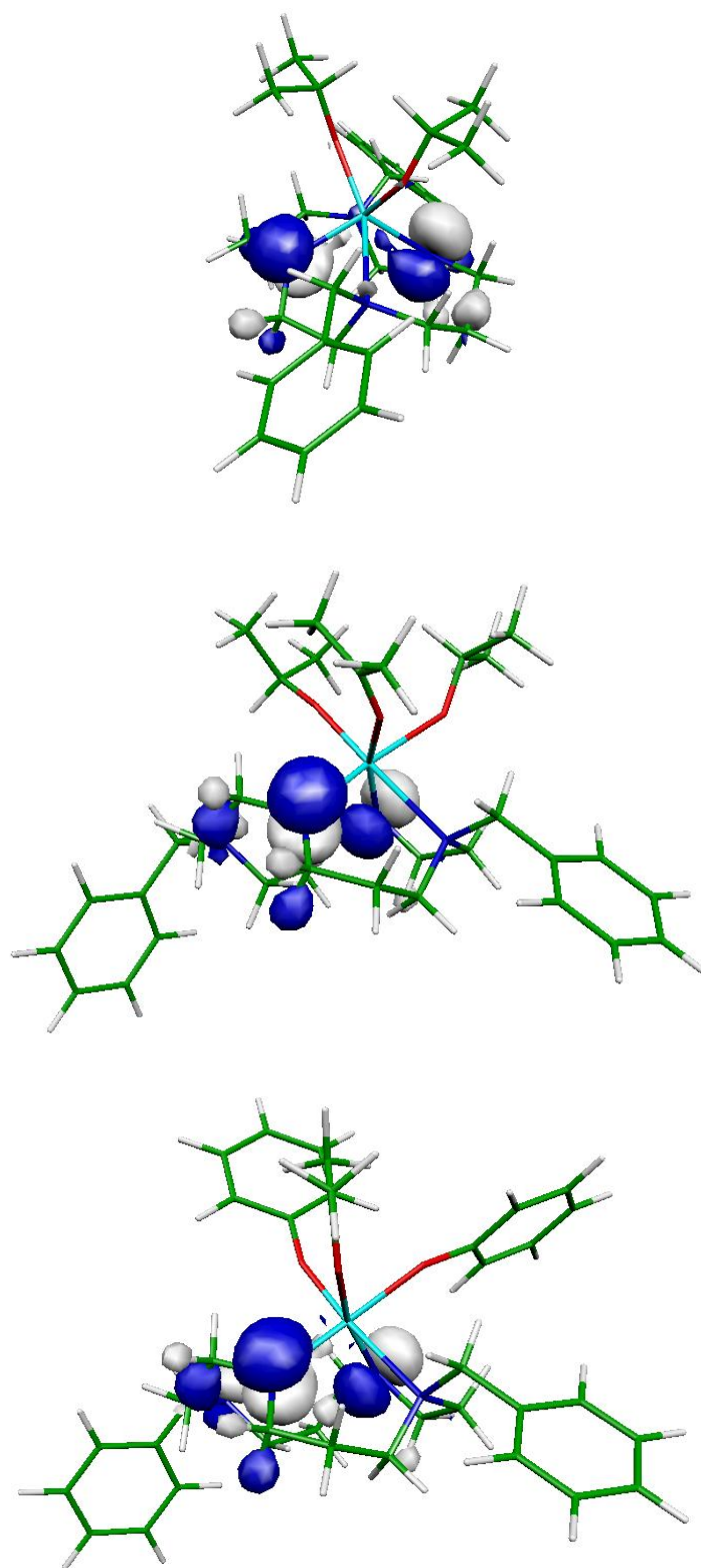


Figure S9. Representation of the HOMO of complexes **2** (top), **6** (centre) and **9** (bottom).

Atomic Coordinates for all the optimized molecules (B3LYP/b1)

2

Zr	-0.499679	-0.241283	-0.005560
N	-0.965834	-1.608977	2.153376
N	0.365732	-1.173033	-2.263618
O	-1.051907	1.142550	-1.356374
O	-0.417942	1.120711	1.469641
C	-2.697812	-1.649924	4.064718
C	1.425860	-0.112375	-5.372029
H	0.468914	0.402845	-5.391447
C	-3.656944	-2.672211	3.999933
H	-4.032915	-2.990991	3.031437
C	-0.703623	-1.494880	-3.248158
H	-0.253784	-1.975277	-4.129322
H	-1.109575	-0.531872	-3.574184
C	-2.265634	-1.231685	5.332727
H	-1.543584	-0.422633	5.408053
N	-2.033255	-1.667020	-0.352724
C	1.281138	-0.128138	-2.835115
H	2.013660	0.103299	-2.058476
H	0.659928	0.759902	-2.962272
C	1.549464	-2.020372	2.568819
H	2.220082	-2.048771	3.439594
H	1.554836	-3.036871	2.156380
C	0.165875	-1.648763	3.120276
H	-0.081955	-2.335953	3.942589
H	0.230951	-0.642706	3.547003
N	1.425887	-1.100045	0.240565
C	-2.165006	-0.983025	2.806300
H	-1.871970	0.046094	3.020217
H	-2.948701	-0.940682	2.046435
C	1.991915	-0.463517	-4.136639
C	3.244705	-1.095547	-4.142444
H	3.719862	-1.347585	-3.198166
C	-2.290971	-2.839672	0.461918
H	-2.225823	-3.776039	-0.121086
H	-3.322026	-2.826312	0.866191
C	-2.755873	-1.827177	6.495437
H	-2.407722	-1.484444	7.465920
C	-1.718738	2.373622	-1.528698
H	-1.108372	3.172564	-1.075224
C	-3.698045	-2.854035	6.411966
H	-4.083710	-3.317330	7.315665
C	-1.873035	-2.360130	-2.758804
H	-1.530904	-3.353768	-2.444169
H	-2.508293	-2.529367	-3.640015
C	2.048447	-2.041773	-0.669972
H	2.307999	-2.994395	-0.173861
H	3.009465	-1.649774	-1.056295
C	-2.719198	-1.720821	-1.642486
H	-2.996022	-0.707394	-1.958069
H	-3.663521	-2.281932	-1.547497
C	2.075931	-0.401164	-6.572376
H	1.618668	-0.116948	-7.516109
C	-0.184160	2.477517	1.775609
H	-1.031793	3.075257	1.400399
C	1.101853	-2.377574	-1.824210
H	1.645952	-2.847253	-2.658030
H	0.356630	-3.092424	-1.469415
C	2.109619	-1.032297	1.530272
H	2.027437	-0.018554	1.940661
H	3.187332	-1.225639	1.400096
C	-1.270195	-2.944369	1.596951
H	-1.618983	-3.638533	2.376958
H	-0.336107	-3.342481	1.194924
C	3.314989	-1.044418	-6.560062
H	3.824886	-1.267323	-7.492999
C	-3.084858	2.371075	-0.830896
H	-3.734725	1.603484	-1.266124
H	-3.583850	3.341553	-0.935364
H	-2.970814	2.157267	0.236249
C	-4.150598	-3.272241	5.159642
H	-4.894691	-4.060427	5.084624
C	3.899845	-1.387207	-5.340116

H	4.870817	-1.874358	-5.319271
C	-1.856731	2.685508	-3.023552
H	-0.874158	2.704525	-3.505585
H	-2.332486	3.659852	-3.182707
H	-2.467695	1.921247	-3.517461
C	-0.120828	2.664612	3.296236
H	-1.043977	2.311240	3.766513
H	0.012835	3.719834	3.560237
H	0.718226	2.097769	3.715837
C	1.091989	2.991152	1.096593
H	1.965759	2.436167	1.456244
H	1.251121	4.055026	1.307607
H	1.028912	2.862534	0.011667

3

Zr	0.037984	0.198871	0.908799
N	1.774321	1.894110	1.698822
O	-1.506278	-1.035537	1.390892
N	0.363399	-1.821656	-0.614553
C	-0.903976	-3.020304	-2.517806
C	1.854945	3.131778	0.868902
H	2.695197	3.745989	1.221711
H	0.935566	3.690038	1.071985
N	0.681864	0.835827	-0.998129
C	-0.881379	-1.932603	-1.456011
H	-1.032771	-0.955121	-1.919684
H	-1.698674	-2.081497	-0.748069
C	3.433888	2.724770	4.592498
H	3.606778	1.653671	4.653404
C	2.347656	3.207501	3.847111
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C	0.596058	-3.111016	0.099385
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H	-0.359878	-3.375538	0.561872
C	1.540662	-1.415192	-1.416275
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C	1.409713	2.263123	3.113003
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C	1.350901	-0.003532	-1.974653
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C	1.670652	-3.124131	1.195013
H	2.663587	-2.902491	0.784614
H	1.719619	-4.162236	1.552359
N	1.514593	-0.776068	2.048392
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H	-0.051627	-1.796218	-4.075306
C	2.969316	5.469313	4.508734
H	2.774627	6.537752	4.481254
C	2.123865	4.592883	3.827723
H	1.270892	4.986915	3.281256
C	4.283505	3.597103	5.274904
H	5.116935	3.200480	5.847963
C	-2.868535	-0.416256	3.276136
H	-2.398974	0.561331	3.305957
C	-2.904072	2.389236	-0.073095
H	-2.532451	1.688683	-0.815977
C	-0.467183	-3.779227	-4.792417
H	-0.099469	-3.569306	-5.792928
C	-2.189553	2.545999	1.129911
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H	-1.012787	-5.816997	-5.243845
C	-1.434260	-4.287922	-2.232196

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H	0.835061	2.404249	-2.402118
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H	-2.124975	3.576636	3.018216
C	1.376187	-2.193829	2.383777
H	0.358573	-2.393775	2.740908
H	2.050016	-2.451301	3.216013
C	2.838142	-0.251086	2.327514
H	3.638063	-0.919978	1.963547
H	3.009364	-0.162878	3.416902
C	1.977538	2.952689	-0.650129
H	2.902843	2.427554	-0.917211
H	2.080908	3.966489	-1.061684
C	3.024672	1.102093	1.638298
H	3.871885	1.654163	2.070812
H	3.242675	0.933390	0.581498
C	-3.838854	4.181639	1.847634
H	-4.198586	4.876923	2.601927
C	-4.487328	-2.007975	4.135803
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C	-4.067458	3.122309	-0.303452
H	-4.606020	2.986237	-1.237861
C	-4.544258	4.022582	0.652258
H	-5.451820	4.589868	0.469347
C	-3.866574	-0.757181	4.187521
H	-4.163868	-0.034927	4.943570
C	-4.097896	-2.919074	3.151725
H	-4.573009	-3.895302	3.095489

5

Zr	-0.569578	-0.228998	-0.189753
Cl	-2.544649	0.301404	-1.681578
N	-2.450121	-0.078392	1.545505
O	0.205917	-1.169115	-1.751895
N	1.933141	0.102485	0.159837
C	3.914791	1.214394	-1.065600
C	2.699524	-1.160762	0.364780
H	3.745064	-0.913672	0.595893
H	2.690978	-1.674869	-0.601630
N	-0.286893	-1.710028	1.262636
N	-0.196048	1.730642	0.502572
C	-3.122850	1.252406	1.649359
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H	-3.717494	1.359539	0.737238
C	-4.507361	-2.228661	3.289720
H	-3.597265	-2.809886	3.411340
C	1.013502	2.160538	1.176847
H	0.808129	2.571934	2.181289
H	1.508597	2.982217	0.625791
C	-3.477633	-1.136805	1.227655
H	-2.931235	-2.074946	1.102559
H	-3.884404	-0.869324	0.251020
C	-6.876548	-0.804769	2.958050
H	-7.802570	-0.255126	2.814534
C	5.667628	2.842058	-0.596905
H	5.959062	3.818521	-0.220223
C	2.450248	0.806208	-1.067710
H	1.815563	1.682524	-1.216113
H	2.252469	0.124928	-1.896033
C	-0.853096	-1.664291	2.599598
H	-0.075636	-1.655470	3.383929
H	-1.453475	-2.571001	2.797352
C	-2.217992	2.485806	1.779044
H	-2.898077	3.344123	1.871245
H	-1.641582	2.461987	2.712321
C	2.174192	-2.136688	1.425815
H	2.190358	-1.687048	2.426072
H	2.898154	-2.962793	1.459322
C	6.632616	1.970254	-1.103235
H	7.678957	2.261511	-1.118303
C	-4.611983	-1.324584	2.222020
C	4.323126	2.466974	-0.582842
H	3.578860	3.163627	-0.206706
C	-1.697111	-0.401406	2.781579

H	-2.371279	-0.501115	3.644717
H	-1.032007	0.441798	2.976319
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H	-5.935126	0.055297	1.226438
C	6.241897	0.727020	-1.603889
H	6.983172	0.047706	-2.015402
C	4.896479	0.357631	-1.587229
H	4.600374	-0.604905	-1.996162
C	1.967776	0.977507	1.353724
H	2.989825	1.321014	1.570549
H	1.632587	0.375535	2.201159
C	-6.749092	-1.695896	4.025189
H	-7.572565	-1.839702	4.718826
C	0.776599	-2.704767	1.126151
H	0.773547	-3.103829	0.105487
H	0.583109	-3.556806	1.796959
C	-5.561863	-2.411586	4.186013
H	-5.458628	-3.119706	5.003503
C	-1.276338	-1.717217	0.584858
H	-1.868195	2.695506	-0.337133
H	-0.852159	3.731238	0.656316
C	-0.085855	-1.764954	-3.004658
H	-1.082427	-1.419093	-3.317114
C	0.934401	-1.311410	-4.051726
H	0.939779	-0.220309	-4.133530
H	0.691974	-1.725463	-5.036752
H	1.943428	-1.645732	-3.781757
C	-0.120854	-3.289350	-2.864170
H	0.859231	-3.672967	-2.556955
H	-0.389267	-3.761903	-3.815609
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6

Zr	0.879260	-0.428835	-0.038491
C	-0.534068	-2.328885	-2.735382
N	-1.011437	0.580342	-0.394043
O	0.099065	-1.404567	-2.237441
C	-0.818554	-2.351276	-4.219894
N	1.968759	1.419560	-1.389021
H	-0.458295	-1.435663	-4.689961
O	2.524277	-1.387674	-0.753531
H	-0.324794	-3.215805	-4.679266
O	0.243172	-1.832220	1.165594
H	-1.892923	-2.466042	-4.402032
N	1.721583	0.882630	1.375360
C	-1.055563	-3.473809	-1.904107
H	-0.718508	-3.376307	-0.872514
H	-2.151890	-3.477820	-1.931655
H	-0.725015	-4.431044	-2.322906
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C	1.028936	2.555664	-1.591394
H	1.526264	3.332054	-2.188820
H	0.820724	2.992600	-0.611921
C	-2.173153	0.121764	0.365263
H	-1.943543	-0.847252	0.816850
H	-3.035148	-0.036829	-0.317784
C	-1.379627	1.687504	-1.254656
H	-1.668390	2.581100	-0.664776
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C	3.078803	1.784686	-0.461959
H	3.595219	2.691551	-0.807927
H	3.784267	0.950794	-0.492770
C	4.718354	2.039865	-3.342924
H	5.222589	1.428642	-2.599183
C	3.332884	1.904577	-3.519704
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H	-0.693422	2.999441	-2.795277
H	-0.128932	1.349484	-2.982055
C	2.531656	0.916605	-2.689708
H	3.138281	0.051093	-2.422102
H	1.695680	0.537300	-3.279970
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H	3.498735	2.018233	1.616463
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C	-2.417870	1.173411	3.955545
H	-1.630135	1.119759	4.714823

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C	2.716029	2.679371	-4.513980	C	0.273109	-1.410389	3.084271
H	1.648381	2.570284	-4.688448	H	0.070657	-2.066983	3.943429
C	-3.332449	2.350673	4.279546	H	0.293724	-0.379297	3.446814
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H	-1.284664	3.253857	2.640836	C	-2.086633	-0.867723	2.760758
H	-0.563863	2.264352	1.364341	H	-1.821939	0.176974	2.927031
C	-4.701827	2.308235	3.978758	H	-2.878546	-0.888246	2.007647
H	-5.124330	1.407804	3.539869	C	1.955055	-0.756614	-4.279030
C	1.351347	0.930189	2.785622	C	3.230772	-1.340196	-4.245724
H	2.261191	0.923975	3.415252	H	3.723709	-1.491667	-3.289155
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C	3.118054	-2.658732	-0.792473	H	-2.057916	-3.886027	0.054588
H	2.394588	-3.416172	-0.436324	H	-3.184138	-2.907523	0.977000
C	-2.825426	3.514616	4.876884	C	-2.616133	-1.531769	6.494581
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C	-0.058274	-2.557669	2.338578	C	0.785756	3.031508	4.021111
H	-0.582791	-1.873876	3.024646	C	-1.820831	2.141534	-1.855378
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H	2.952635	4.164527	-6.055488	H	3.226531	-0.892856	1.285968
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H	-5.656829	5.398729	5.041365	C	3.277392	-1.495801	-6.659593
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C	-0.998081	-3.723171	2.016701	H	2.551501	1.904199	4.573902
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				H	0.221220	1.845531	5.743937
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N	1.485215	1.061055	1.193721	C	-5.534967	2.723089	4.845757
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C	-2.815196	0.722409	0.100414	C	-0.343020	-4.060350	1.483582
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C	3.020204	1.698969	-0.598485	9			
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C	-3.267658	2.045233	4.256367	H	0.555893	1.964947	1.320322
C	-0.834237	2.753074	2.301520	C	-1.024462	-1.681458	2.961619
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C	3.168016	-2.716563	-0.335952	H	-0.112830	1.475357	-2.176904
H	2.753422	-3.273547	0.520736	C	-1.525520	4.209401	-2.498495
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C	-0.361151	-2.688482	2.167397	C	-1.396191	2.021290	2.221881
H	-1.397214	-2.472808	2.479259	H	-1.324154	2.835000	2.954388
H	-1.792049	0.315906	-3.697103	H	-2.434829	2.014081	1.874474
H	-3.348302	-0.099736	-2.955127	C	-2.053409	2.385065	-0.815666
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C	0.527820	-2.673230	3.414697	H	2.917686	-0.890698	2.982875
H	1.568938	-2.871627	3.138015	C	-0.527288	-0.821079	-3.795773
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C	3.041623	-3.593067	-1.585256	H	0.273372	-1.144739	-3.137431
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C	-3.653432	3.941220	5.736966	C	1.878390	-1.558822	-0.315183
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C	4.362309	-2.915797	4.154945
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C	0.339968	-2.015444	3.611364
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H	-1.253572	-5.763172	-3.433119
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C	5.155159	-2.797135	5.297763
H	6.159174	-2.388911	5.218671
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H	1.121374	-2.493474	-0.842088
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H	3.208052	0.468081	-0.677831
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H	-1.302403	2.549591	1.070964
H	-1.892618	3.447009	-0.319300
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H	3.207465	1.003704	-3.678608
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H	2.810733	-0.755327	1.044782
H	2.047860	-2.291241	1.400143
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H	4.028426	-0.940175	-4.476659

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H	-1.568237	2.140754	-4.817888
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C	1.405108	3.092802	-3.185188
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H	2.128398	3.225856	-4.005812
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C	1.100342	1.711630	1.467498
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C	-2.074087	-6.171027	-3.401628
H	-3.627742	2.307446	-6.195506
H	-1.983439	-6.647360	-4.374013
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C	-2.681813	-6.850104	-2.343565
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C	-1.406521	0.694328	2.752029	H	2.480412	-4.887349	7.190040
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C	-1.542563	4.121987	-2.715711				
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C	-2.137387	2.134874	-1.247280				
H	-2.240350	1.582133	-2.182441				
H	-3.005959	1.875861	-0.638989				
C	1.395632	0.754349	-0.866758				
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C	-2.675970	4.543444	-0.633886				
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C	2.595885	-3.706684	3.984238				
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H	2.973397	-0.935861	3.020013				
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H	1.660743	-0.109704	2.181810				
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C	2.081897	-4.248508	5.171733				
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H	1.030780	-4.524329	5.220347				
C	1.868113	-1.552971	-0.269610				
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H	2.463587	-1.657922	-1.195142				
H	1.363630	-2.509146	-0.111062				
C	3.966128	-3.405841	3.934959				
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H	-4.119293	-0.357185	3.666719				
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C	2.856393	-1.316539	0.891536				
H	3.498726	-0.452101	0.679459				
C	-2.881004	-0.482104	-4.329309				
C	-2.186792	-4.447593	-1.724089				
H	3.535414	-2.178446	0.937146				
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H	-2.691831	-3.614560	-2.202713				
H	-3.731395	-2.701323	2.865772				
C	0.269362	-1.634729	3.673635				
H	0.564804	-0.649421	4.048095				
H	0.343763	-2.289899	4.551935				
C	-1.523222	5.491101	-2.984578				
H	-1.083729	5.853050	-3.909787				
C	-2.820851	-0.412028	-5.720618				
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H	-3.065869	-5.948039	-2.981681				
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H	5.847571	-3.380823	4.980490				
C	-0.856913	-6.561277	-0.473337				
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H	0.463009	-1.161206	-6.172985				
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C	-2.659949	5.913921	-0.898410				
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