Supporting Information for

Reactions of Heteroallenes with Cyclam-Based Zr(IV) Complexes

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Atomic coordinates of all optimized species (M06/b1)

CS_2

C	-1.253733	0.000000	-0.467077
S	-1.077561	0.343392	-1.981791
S	-1.429905	-0.343392	1.047637

^{i}PrNCO

C	-0.675367	-0.439576	-0.017298
N	-0.104340	0.892018	-0.089648
O	1.895288	2.112814	0.315170
H	-1.713820	-0.343835	-0.361857
H	-0.407493	-2.372812	-0.946443
C	0.066627	-1.384828	-0.947487
H	1.105710	-1.503855	-0.614665
H	0.075407	-1.004072	-1.973235
H	-1.169454	-1.914479	1.483867
C	-0.676415	-0.937994	1.418130
H	-1.198524	-0.239464	2.078941
H	0.353669	-1.050568	1.780033
C	0.938112	1.451151	0.136193

MesNCO

O	-0.031811	1.154937	0.053872
C	-0.324395	0.155210	-0.492661
N	-0.740387	-0.850928	-1.003032
C	0.171550	-4.144369	-3.421852
C	-1.104541	-3.963845	-2.889521
C	1.150353	-3.198208	-3.122851
H	-1.882259	-4.697691	-3.105062
H	2.156840	-3.325236	-3.523640
C	-1.421159	-2.872653	-2.086622
C	0.885862	-2.089279	-2.323509
C	-0.412032	-1.939614	-1.812191
C	-2.794123	-2.686730	-1.522291
H	-3.446360	-3.522793	-1.792195
H	-2.768149	-2.606461	-0.429109
H	-3.253645	-1.761098	-1.890077
C	0.475288	-5.311628	-4.312110
H	1.535173	-5.584842	-4.270170
H	-0.113090	-6.193107	-4.034449
H	0.240678	-5.084682	-5.360271
C	1.951516	-1.087050	-2.011874
H	1.679599	-0.080547	-2.357091
H	2.139902	-1.012427	-0.932423
H	2.895818	-1.357217	-2.493500

2

Zr	-0.489804	-0.258022	-0.006197
N	-1.009447	-1.561954	2.095748
N	0.397365	-1.122928	-2.204789
O	-1.034015	1.128290	-1.355752
O	-0.416755	1.101610	1.470198
C	-2.769459	-1.566561	3.939875
C	1.497721	0.023803	-5.240461
H	0.557500	0.576096	-5.246831
C	-3.696501	-2.610498	3.873624
H	-4.042769	-2.955299	2.899109
C	-0.644261	-1.414022	-3.215189
H	-0.167196	-1.858347	-4.105771
H	-1.052038	-0.438457	-3.516679
C	-2.375485	-1.112462	5.201988
H	-1.674683	-0.280099	5.270551
N	-2.018354	-1.665487	-0.387151
C	1.319285	-0.072389	-2.728114
H	2.042902	0.140403	-1.931580
H	0.701409	0.825490	-2.844192
C	1.464380	-1.996266	2.601566
H	2.105899	-2.024259	3.495270
H	1.459263	-3.024537	2.210300
C	0.083040	-1.583624	3.093575
H	-0.207451	-2.240833	3.931436
H	0.150309	-0.560634	3.491240
N	1.422418	-1.110376	0.276156
C	-2.219867	-0.923229	2.692607
H	-1.932786	0.116257	2.892100
H	-2.984721	-0.896779	1.906297
C	2.034377	-0.386723	-4.016635
C	3.258230	-1.062095	-4.024852
H	3.709674	-1.359877	-3.078205
C	-2.288834	-2.826461	0.421595
H	-2.204904	-3.769910	-0.154294
H	-3.333831	-2.819330	0.801505
C	-2.871019	-1.696704	6.361928
H	-2.551198	-1.326768	7.333609
C	-1.860975	2.251867	-1.424896
H	-1.280771	3.144530	-1.111521
C	-3.780809	-2.746284	6.278729
H	-4.172954	-3.202927	7.184655
C	-1.804475	-2.302222	-2.784179
H	-1.454653	-3.303131	-2.490529
H	-2.414979	-2.456994	-3.686537
C	2.049256	-2.037938	-0.629591
H	2.291699	-3.003837	-0.142575
H	3.026084	-1.651671	-0.993890
C	-2.679605	-1.713822	-1.678884
H	-2.986332	-0.699380	-1.983495
H	-3.611409	-2.303436	-1.607394
C	2.150009	-0.248228	-6.437420
H	1.716897	0.084078	-7.378333
C	-0.011979	2.422895	1.671859
H	-0.860096	3.098076	1.435826
C	1.119291	-2.336772	-1.793617
H	1.661017	-2.789059	-2.643033
H	0.363503	-3.059300	-1.462320
C	2.078226	-1.051863	1.570118
H	2.031461	-0.026144	1.971948
H	3.152668	-1.286350	1.462150
C	-1.297877	-2.905231	1.570606
H	-1.653011	-3.581137	2.368502
H	-0.351435	-3.311790	1.193974
C	3.361073	-0.933973	-6.429608
H	3.876048	-1.144508	-7.364221
C	-3.057593	2.115020	-0.493116
H	-3.648284	1.230955	-0.774192
H	-3.710873	2.995252	-0.542150
H	-2.726126	1.987223	0.545974
C	-4.196479	-3.198752	5.030757
H	-4.919679	-4.007969	4.956750
C	3.915556	-1.337354	-5.219352
H	4.868925	-1.860995	-5.203918
C	-2.302448	2.458271	-2.865288
H	-1.429259	2.527158	-3.525933
H	-2.897817	3.372491	-2.980380
H	-2.913635	1.606433	-3.194854
C	0.348733	2.616320	3.136340
H	-0.492730	2.325885	3.777663
H	0.608074	3.659364	3.356363
H	1.210416	1.985671	3.396128
C	1.150704	2.790185	0.760288
H	2.011845	2.140014	0.971751
H	1.463473	3.831786	0.905935
H	0.871428	2.656070	-0.293176

3

Zr	0.624263	-0.747361	0.045292
S	-0.005908	1.723781	0.394098
S	2.938497	-0.317114	1.078289
N	-1.859826	-0.848250	0.483215
N	2.104323	-2.355602	-1.202592
C	1.411700	2.531545	-0.318945
N	0.196627	-2.466250	1.160149
C	1.907761	2.185091	-1.581663
H	1.402056	1.414456	-2.164042
C	2.785489	-3.389447	-0.378273
H	3.559389	-2.866575	0.199835
H	3.295710	-4.094306	-1.054504

N	-0.011744	-0.858119	-1.944142
C	2.446578	0.487712	2.590661
C	-2.723648	-0.137477	-0.496614
H	-2.576080	0.936832	-0.322256
H	-3.776412	-0.368709	-0.265218
C	3.126002	-1.577266	-1.978274
H	3.719190	-1.017265	-1.245000
H	2.576837	-0.835332	-2.569284
C	-2.131406	-0.330606	1.864348
H	-1.819313	0.720220	1.871592
H	-1.454398	-0.863992	2.541720
C	3.041345	1.704785	2.939088
H	3.803200	2.123259	2.284506
C	3.711243	-2.697663	-4.178662
H	2.761771	-2.352658	-4.588174
C	2.053793	3.541166	0.405650
H	1.662701	3.819443	1.382213
C	4.050331	-2.375487	-2.861800
C	-1.085552	-0.019528	-2.467437
H	-1.076458	-0.060213	-3.570428
H	-0.910671	1.029960	-2.191328
C	-3.552456	-0.437099	2.356997
C	1.474338	-0.056706	3.438652
H	1.015854	-1.013655	3.189625
C	1.121469	-2.989571	-2.104312
H	0.441185	-3.573310	-1.473926
H	1.618392	-3.688169	-2.798416
C	-1.112590	-3.063338	1.265935
H	-1.448132	-3.101819	2.323116
H	-1.117390	-4.117544	0.926119
C	-2.094531	-2.303242	0.401768
H	-1.929075	-2.593401	-0.642228
H	-3.139990	-2.547353	0.656110
C	-4.002740	-1.572744	3.035644
H	-3.310155	-2.393450	3.222051
C	5.296045	-2.786325	-2.378240
H	5.585263	-2.515113	-1.362932
C	5.807156	-3.849593	-4.478621
H	6.487474	-4.421365	-5.105485
C	1.914436	-4.182758	0.585553
H	2.585598	-4.911505	1.062864
H	1.165069	-4.783141	0.048722
C	0.308932	-1.944759	-2.838709
H	0.842241	-1.574482	-3.738886
H	-0.599932	-2.442982	-3.228963
C	3.048051	2.802710	-2.083967
H	3.428839	2.511628	-3.061534
C	6.166729	-3.519672	-3.175427
H	7.131892	-3.828611	-2.780612
C	-2.469179	-0.424189	-1.969994
H	-3.227348	0.151132	-2.521079
H	-2.667498	-1.477975	-2.215215
C	1.073671	0.627383	4.581402
H	0.306409	0.196480	5.222561
C	3.184661	4.164642	-0.108420
H	3.675395	4.946138	0.468942
C	-4.444823	0.623125	2.173047
H	-4.097630	1.529375	1.677099
C	1.242288	-3.347366	1.669709
H	0.813405	-4.024975	2.428273
H	2.018100	-2.757994	2.179849
C	2.645521	2.376875	4.089620
H	3.114169	3.326123	4.343210
C	4.578896	-3.432298	-4.980532
H	4.298195	-3.670839	-6.003969
C	3.694236	3.792147	-1.349433
H	4.584453	4.275889	-1.744881
C	-5.313192	-1.659642	3.493929
H	-5.643201	-2.550552	4.023509
C	1.652989	1.848435	4.910977
H	1.339808	2.381581	5.805663
C	-5.755908	0.540967	2.627764
H	-6.434665	1.377157	2.476635
C	-6.194756	-0.604390	3.285065
H	-7.218864	-0.668894	3.645352

6

Zr	0.084992	0.990622	0.114600
N	-1.531404	2.275711	-1.155749
S	-1.436303	-0.802765	1.121613
N	-0.668932	0.279231	-1.845512
S	2.159114	-0.507862	0.251667
N	1.713384	2.448812	-1.479258
C	-1.111932	-1.156477	2.840834
N	1.248065	2.299574	1.157029
O	-2.364839	1.273457	-3.123788
C	0.185122	-1.248894	3.359498
C	-0.609193	-0.989346	-2.597556
H	1.038908	-1.103565	2.697682
N	-1.786127	2.682713	1.792157
C	-1.575855	1.188168	-2.198561
C	1.174267	3.746859	-1.926495
H	1.941876	4.259910	-2.532162
C	1.958012	-2.057606	-0.614192
H	1.025801	4.367548	-1.031798
C	-2.823259	2.251424	-0.423519
H	-3.025298	1.210213	-0.135746
H	-3.630681	2.566216	-1.103329
C	-1.374234	3.581035	-1.828254
H	-1.346870	4.366467	-1.061524
H	-2.267261	3.748153	-2.450025
C	2.849184	2.713528	-0.572826
H	3.535255	3.461478	-1.005172
H	3.399434	1.773461	-0.458629
C	4.613944	1.739922	-3.123928
C	1.084592	-3.051422	-0.162290
H	4.774816	1.053494	-2.291681
H	0.506265	-2.885116	0.743809
C	3.309261	2.130406	-3.439407
C	-0.136020	3.700499	-2.692312
H	-0.227217	4.648751	-3.239108
C	-2.199098	-1.385119	3.694720
H	-0.139711	2.921318	-3.465847
H	-3.209645	-1.331267	3.291944
C	2.147396	1.614327	-2.632701
H	2.387896	0.627544	-2.218358
H	1.271629	1.473692	-3.273275
C	2.353935	3.143811	0.795236
H	3.182726	3.036174	1.518041
C	2.689448	-2.277875	-1.787080
H	2.079474	4.217123	0.815003
H	3.388037	-1.515676	-2.131970
C	-2.422285	1.945659	2.910170
H	-1.627858	1.570058	3.567564
H	-2.881410	1.053700	2.465318
C	3.114833	2.978405	-4.533664
H	2.101016	3.261555	-4.818437
C	-3.449930	2.697112	3.718656
C	-0.951002	3.809100	2.231709
H	-1.554972	4.591600	2.726116
H	-0.536969	4.258304	1.318153
C	-4.811754	2.471444	3.497131
H	-5.109767	1.736762	2.748074
C	0.955053	2.188374	2.567789
H	1.877619	1.993558	3.142532
H	0.336117	1.285943	2.738332
C	-3.085753	3.610023	4.713681
H	-2.031215	3.775394	4.932440
H	0.179951	-1.571268	-2.111341
C	0.382109	-1.533529	4.707762
H	1.397329	-1.602680	5.093856
C	0.211867	3.400308	3.121904
H	0.894394	4.258999	3.193954
H	-0.113084	3.184652	4.149584
C	-1.911746	-1.766387	-2.457790
H	-2.162837	-1.914715	-1.400181
H	-1.804389	-2.754612	-2.922138
C	2.513547	-3.446383	-2.520417
H	-2.735766	-1.238115	-2.950794
H	3.077305	-3.595337	-3.439176
C	-1.993335	-1.669675	5.039162
C	-2.790849	3.126367	0.809430

H	-2.850148	-1.839337	5.688076
H	-2.588027	4.169101	0.534031
H	-3.796257	3.144662	1.253425
C	5.695989	2.199179	-3.865977
H	6.703704	1.880932	-3.608637
C	0.916276	-4.219982	-0.897079
H	0.220623	-4.977493	-0.541797
C	-0.701675	-1.738900	5.555128
H	-0.542297	-1.960225	6.607896
C	-4.051102	4.293093	5.444700
H	-3.746799	4.996375	6.216706
C	1.617793	-4.418043	-2.083633
C	5.488215	3.056186	-4.942829
H	1.473745	-5.329289	-2.659646
H	6.333094	3.412749	-5.527515
C	4.194323	3.440927	-5.279139
H	4.023635	4.096262	-6.130306
C	-0.224274	-0.805141	-4.059550
H	-0.953742	-0.177109	-4.582732
H	-0.194092	-1.785337	-4.551241
H	0.772236	-0.360522	-4.165964
C	-5.782061	3.150525	4.226376
H	-6.835689	2.956419	4.038794
C	-5.402640	4.068666	5.199536
H	-6.157707	4.600235	5.773915

6a

Zr	0.227092	1.087112	0.974536
N	-1.565551	1.908311	-0.519669
S	-1.256308	0.066751	2.740756
O	-0.416962	-0.046030	-0.713992
S	2.243792	-0.371851	1.380666
N	1.702904	2.088320	-0.995376
C	-1.191505	-1.698108	2.457834
N	1.306949	2.692167	1.617542
N	-2.267884	0.281043	-2.103933
C	-0.224736	-2.487483	3.083155
C	-2.020557	-0.977864	-2.806855
H	0.544554	-2.010208	3.687389
N	-1.854840	3.266837	2.144647
C	-1.451895	0.592567	-1.186413
C	1.083570	3.203145	-1.738701
H	1.808258	3.579755	-2.480968
C	2.127403	-2.097891	0.934556
H	0.917211	4.021998	-1.025752
C	-2.852482	2.039514	0.202913
H	-2.984987	1.135222	0.809748
H	-3.674564	2.078643	-0.529445
C	-1.461862	2.974466	-1.541633
H	-1.463626	3.943239	-1.025342
H	-2.364708	2.924654	-2.169679
C	2.847017	2.626213	-0.229433
H	3.505427	3.233930	-0.873286
H	3.421956	1.768333	0.139174
C	4.526296	1.254143	-2.709314
C	2.950461	-2.984970	1.638698
H	4.857023	0.853450	-1.751278
H	3.596054	-2.596053	2.424413
C	3.156905	1.380427	-2.958196
C	-0.235538	2.900260	-2.428533
H	-0.374778	3.660018	-3.209620
C	-2.169836	-2.305802	1.667208
H	-0.212691	1.940327	-2.961070
H	-2.926949	-1.688654	1.184298
C	2.151289	0.992697	-1.906317
H	2.566026	0.214648	-1.253946
H	1.255786	0.552899	-2.361151
C	2.362644	3.425842	0.965261
H	3.212361	3.575965	1.654833
C	1.304278	-2.593716	-0.081679
H	2.039144	4.442700	0.668825
H	0.665363	-1.920903	-0.648074
C	-2.443515	3.048690	3.485067
H	-1.624551	2.979242	4.211779
H	-2.906135	2.052998	3.465960
C	2.751812	1.854164	-4.209481
H	1.687434	1.926261	-4.434636
C	-3.454710	4.071459	3.944034
C	-0.999392	4.454206	2.055251
H	-1.578201	5.386243	2.199545
H	-0.611122	4.484049	1.026742
C	-4.822072	3.791462	3.866411
H	-5.142748	2.814824	3.502483
C	0.984679	3.135424	2.963290
H	1.909444	3.241375	3.555675
H	0.409894	2.342663	3.469340
C	-3.064318	5.311283	4.459931
H	-2.004412	5.539377	4.567425
H	-0.934507	-1.080437	-2.997590
C	-0.241293	-3.867439	2.917138
H	0.527598	-4.472593	3.393093
C	0.191063	4.440119	3.002832
H	0.837166	5.286595	2.729583
H	-0.117472	4.629530	4.041047
C	-2.456607	-2.173003	-1.972134
H	-1.851894	-2.258095	-1.062386
H	-2.354159	-3.104548	-2.542773
C	1.292482	-3.956300	-0.361461
H	-3.510878	-2.065382	-1.681723
H	0.630473	-4.328994	-1.141860
C	-2.175299	-3.686349	1.497878
C	-2.890826	3.263322	1.097288
H	-2.936343	-4.145568	0.868957
H	-2.813718	4.183227	0.500881
H	-3.892609	3.312789	1.545047
C	5.463911	1.609920	-3.672835
H	6.525145	1.498514	-3.461957
C	2.939909	-4.342788	1.343085
H	3.586686	-5.017902	1.900546
C	-1.211590	-4.471309	2.122822
H	-1.209453	-5.550444	1.985808
C	-4.009160	6.249286	4.861061
H	-3.683455	7.206295	5.262694
C	2.105356	-4.837364	0.344731
C	5.045093	2.095293	-4.907659
H	2.091784	-5.900921	0.116693
H	5.777082	2.370194	-5.663568
C	3.685120	2.212835	-5.176244
H	3.348932	2.576170	-6.144857
C	-2.753691	-0.930022	-4.135733
H	-3.834788	-0.850754	-3.964559
H	-2.561663	-1.833721	-4.726392
H	-2.444593	-0.057866	-4.723025
C	-5.771987	4.725717	4.266495
H	-6.830372	4.483883	4.200703
C	-5.366790	5.961032	4.759802
H	-6.106042	6.692997	5.076648

6b

Zr	-0.191793	-0.009124	0.356952
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N	2.109835	-0.748796	-0.453318
N	-0.932423	-1.923234	-0.703633
C	3.482965	-1.094432	-2.587423
C	-1.077487	3.069449	1.651438
H	-1.248929	3.698510	2.540500
H	-1.986068	3.105383	1.036752
O	-1.745013	-1.429516	1.306388
N	0.854154	1.662033	-0.381959
C	2.139514	-0.851923	-1.943482
C	-0.971468	-2.544682	-2.035110
H	1.692191	0.066609	-2.341522
H	1.471064	-1.677906	-2.206571
C	-1.772661	-2.174189	0.287359
C	-2.496836	1.569975	5.149444
H	-1.849688	0.709373	5.319288
C	-2.798100	1.947784	3.837623
S	-2.454435	1.010328	-0.643600
S	-2.969110	-3.531287	0.278730
C	2.606820	-2.020424	0.125845
H	3.629141	-2.208223	-0.241864
H	1.965360	-2.817685	-0.279861

C	2.911685	0.399781	0.018354
H	2.884575	0.371322	1.110364
H	3.961357	0.305976	-0.306530
C	-2.242769	1.182909	2.664241
H	-2.130386	0.125512	2.920562
H	-2.957956	1.219431	1.834172
C	2.299565	1.709496	-0.436490
H	2.712744	2.505757	0.214332
H	2.632892	1.978900	-1.461379
C	2.597990	-2.122942	1.641372
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H	2.940296	-3.140521	1.879149
N	0.790049	-0.506877	2.135227
C	4.315935	-0.034540	-2.955634
H	3.989922	0.989219	-2.773564
C	-4.205957	3.715211	4.721507
H	-4.886137	4.546082	4.547858
C	-3.672134	3.021188	3.641651
H	-3.945247	3.304511	2.625363
C	-3.027771	2.260862	6.233463
H	-2.782817	1.949853	7.246642
C	-4.582585	-1.833837	1.754231
C	-1.104438	0.942630	-3.094525
H	-0.183006	1.062996	-2.524570
H	-4.427476	-1.114753	0.951216
C	5.543054	-0.268364	-3.566975
H	6.174987	0.571139	-3.847608
C	-2.327467	0.936748	-2.409656
C	-3.956368	-3.080945	1.695252
C	5.128713	-2.636309	-3.485410
H	5.434841	-3.657265	-3.701694
C	-3.879868	3.339890	6.021325
H	-4.299720	3.879275	6.867358
C	5.954298	-1.570995	-3.830168
H	6.911743	-1.754703	-4.312124
C	3.903669	-2.396449	-2.873388
H	3.252437	-3.233416	-2.621065
C	0.301913	3.003618	-0.512700
H	-0.647214	2.972151	-1.064935
H	-0.351134	-1.884305	-2.658564
H	0.988377	3.634434	-1.104693
C	-3.508215	0.857497	-3.163586
C	-4.141515	-4.011566	2.714463
H	-4.463620	0.863006	-2.641672
C	-0.336820	-3.930563	-2.027705
H	-3.642351	-4.976785	2.659604
C	1.235985	-1.886538	2.273630
H	0.677685	-3.910109	-1.610117
H	-0.282304	-4.332914	-3.046604
H	0.506288	-2.601398	1.844275
H	-0.927627	-4.631226	-1.424155
H	1.291452	-2.149796	3.341865
C	0.511040	0.135073	3.393134
H	1.394092	0.124986	4.061181
H	-0.292806	-0.386311	3.954697
C	0.065786	3.665617	0.840933
H	1.003289	3.681326	1.417487
H	-0.199382	4.721787	0.684334
C	0.141901	1.572404	3.122338
H	-0.152085	2.106907	4.040197
H	1.025564	2.074232	2.710186
C	-3.463653	0.750400	-4.547277
C	-4.957585	-3.695077	3.797486
H	-4.393702	0.684586	-5.108962
H	-5.106223	-4.424303	4.590733
C	-1.065351	0.818582	-4.480609
C	-5.371906	-1.516611	2.851265
H	-0.101528	0.814249	-4.988683
H	-5.844851	-0.538380	2.907432
C	-2.333598	-2.563712	-2.724546
C	-2.241459	0.716410	-5.216506
H	-2.981206	-3.369208	-2.365356
C	-5.565287	-2.446950	3.871237
H	-2.178118	-2.714403	-3.799909
H	-6.191924	-2.196070	4.724054
H	-2.208070	0.621852	-6.299305
H	-2.855637	-1.610113	-2.592792

6c

Zr	0.138458	0.762993	0.028810
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N	2.055523	-0.800593	-0.170431
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N	-2.767169	-1.987212	0.517659
C	3.107448	-2.339779	-1.914496
C	0.214927	4.179625	0.372752
H	0.201017	5.064911	1.029301
H	-0.636035	4.268954	-0.317055
N	1.729692	1.757013	-0.913366
C	2.016805	-1.363244	-1.559958
H	2.027527	-0.510646	-2.248840
C	-3.046127	-0.931500	1.477065
H	1.038046	-1.844323	-1.670454
C	-1.347913	4.265282	4.062044
H	-0.937124	3.359684	4.508510
C	-1.652594	4.280184	2.698185
S	-1.792394	1.873288	-1.254111
S	-1.360702	-3.235542	-1.415417
C	2.046230	-1.910097	0.816004
H	2.971649	-2.496604	0.695903
H	1.207703	-2.562587	0.534937
C	3.216376	0.086618	0.024597
H	3.206188	0.407965	1.073080
H	4.162842	-0.454162	-0.144501
C	-1.407679	3.078243	1.821663
H	-1.577072	2.149321	2.380255
H	-2.126611	3.082895	0.993718
C	3.102160	1.312814	-0.861922
H	3.775101	2.089355	-0.447225
H	3.496689	1.106814	-1.879393
C	1.887494	-1.528064	2.281734
H	2.725719	-0.907187	2.630035
H	1.963691	-2.468507	2.846397
N	0.440808	0.487096	2.065603
C	4.345853	-1.907737	-2.397122
H	4.522084	-0.841753	-2.543658
C	-2.455812	6.555764	2.950766
H	-2.901215	7.445772	2.512122
C	-2.221808	5.437534	2.158989
H	-2.493315	5.452320	1.103575
C	-1.579221	5.381676	4.858817
H	-1.336783	5.349278	5.918569
C	-4.093111	-3.725963	-1.591448
C	-0.635601	0.489693	-3.375080
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H	-4.218167	-2.646716	-1.646580
C	5.346397	-2.820607	-2.714742
H	6.303171	-2.465461	-3.091150
C	-1.780132	0.692279	-2.594505
C	-2.814739	-4.261401	-1.414430
C	3.882693	-4.629612	-2.102622
H	3.691381	-5.695227	-1.998067
C	-2.129020	6.532178	4.303147
H	-2.314259	7.404778	4.925107
C	5.118556	-4.184306	-2.561880
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H	5.898587	-4.899801	-2.811824
C	2.885746	-3.714098	-1.785513
H	1.911426	-4.063462	-1.443096
C	1.597774	3.089771	-1.490031
H	0.702476	3.141321	-2.128961
H	2.459339	3.297633	-2.147844
C	-2.930267	-0.054187	-2.877402
H	-2.176856	-0.255445	1.602362
C	-2.645437	-5.642322	-1.326757
H	-3.825019	0.101668	-2.276467
H	-1.647442	-6.049990	-1.177436
C	0.559318	-0.856018	2.614953
H	-0.254050	-1.490721	2.231976
C	-4.226181	-0.112138	0.977072
H	0.430709	-0.819257	3.710246
C	0.835837	1.520291	2.988867
H	-3.964076	0.411892	0.050340
H	1.798859	1.294447	3.487120

H	-4.526862	0.637767	1.720840
H	0.098890	1.616039	3.812943
C	1.502115	4.190027	-0.439199
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H	2.387534	4.164545	0.213201
H	1.533387	5.168926	-0.939559
C	0.999503	2.827257	2.238399
H	0.999543	3.695004	2.918732
H	1.963329	2.810114	1.718194
C	-2.932581	-0.977115	-3.915612
C	-3.746344	-6.488061	-1.426049
H	-3.834956	-1.549606	-4.123393
H	-3.607228	-7.564916	-1.359505
C	-0.637670	-0.454344	-4.398908
C	-5.188823	-4.575255	-1.671381
H	0.265280	-0.607863	-4.987486
H	-6.184105	-4.155381	-1.801458
C	-1.784755	-1.188645	-4.675871
C	-5.019354	-5.956479	-1.594759
H	-5.881733	-6.615718	-1.664139
H	-1.786661	-1.923031	-5.477517
C	-3.356867	-1.569683	2.823111
H	-4.223815	-2.235227	2.729028
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H	-2.513317	-2.169995	3.183268

6d

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C	3.221037	-1.766638	-2.428981
C	-0.054569	3.880737	1.314722
H	0.123816	4.672198	2.061405
H	-1.063077	4.031606	0.910459
O	-2.861064	-2.793063	0.922673
N	1.086646	1.714865	-0.668399
C	1.966678	-1.253134	-1.762269
C	-1.298248	-2.171524	-1.312002
H	1.564828	-0.394506	-2.315282
H	1.213021	-2.043372	-1.799994
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C	-0.710528	3.501845	5.237204
H	-0.184429	2.575016	5.467688
C	-1.321429	3.650876	3.988546
S	-2.235884	1.830497	-0.179773
S	-2.022654	-0.727116	2.428651
C	2.524076	-2.006578	0.469471
H	3.505638	-2.345861	0.096448
H	1.811941	-2.821044	0.271383
C	3.014359	0.274774	-0.177115
H	3.087083	0.485844	0.893906
H	4.021104	-0.001393	-0.536025
C	-1.251790	2.553475	2.957600
H	-1.247286	1.581210	3.459443
H	-2.151713	2.577928	2.330564
C	2.508005	1.515641	-0.874485
H	3.102653	2.365541	-0.486990
H	2.731125	1.489186	-1.960716
C	2.601730	-1.803463	1.974025
H	3.409440	-1.110469	2.249752
H	2.880723	-2.776562	2.402790
N	0.976292	0.047243	2.241501
C	4.115949	-0.908567	-3.073971
H	3.908386	0.160798	-3.101167
C	-2.111577	5.834290	4.689479
H	-2.673886	6.740068	4.474083
C	-2.035284	4.825688	3.735733
H	-2.546928	4.940401	2.780521
C	-0.782601	4.508420	6.194438
H	-0.302211	4.372470	7.160835
C	-4.149437	0.365526	3.700123
C	-1.555177	1.108657	-2.800874
H	-0.509814	1.141942	-2.490987
H	-3.485502	0.352536	4.563712
C	5.256537	-1.402456	-3.698154
H	5.938757	-0.717727	-4.196784
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C	-3.713358	-0.165466	2.484256
C	4.628443	-3.637995	-3.071040
H	4.816557	-4.709151	-3.076633
C	-1.479047	5.680627	5.919527
H	-1.540851	6.467689	6.667534
C	5.518502	-2.768508	-3.693679
H	6.408599	-3.156059	-4.183764
C	3.489757	-3.138604	-2.449437
H	2.783896	-3.824898	-1.980579
C	0.747513	3.097832	-0.996725
H	-0.295196	3.162642	-1.328459
H	-0.645795	-1.614853	-1.999154
H	1.372985	3.438840	-1.841091
C	-3.897714	1.382565	-2.304657
C	-4.567444	-0.171799	1.380137
H	-4.683461	1.613452	-1.586465
C	-0.787679	-3.601568	-1.182775
H	-4.241165	-0.591337	0.432015
C	1.284130	-1.336552	2.571564
H	0.203322	-3.643304	-0.713864
H	-0.718384	-4.072148	-2.171799
H	0.492123	-2.016607	2.212663
H	-1.472483	-4.192099	-0.566435
H	1.293182	-1.462429	3.667572
C	1.308728	0.970699	3.291694
H	2.349436	0.828812	3.645704
H	0.671215	0.813643	4.188473
C	0.946202	4.046209	0.181155
H	1.980727	3.983996	0.550298
H	0.828291	5.081445	-0.171168
C	1.188969	2.381998	2.764350
H	1.285650	3.129661	3.568782
H	2.006840	2.553213	2.055722
C	-4.212125	1.062103	-3.619453
C	-5.846984	0.356201	1.503294
H	-5.254186	1.050253	-3.933086
H	-6.509626	0.345698	0.640313
C	-1.879684	0.775854	-4.112868
C	-5.427056	0.902865	3.808152
H	-1.082328	0.542719	-4.816838
H	-5.757510	1.316414	4.758300
C	-2.688202	-2.151514	-1.938606
C	-3.205966	0.749891	-4.531143
H	-3.386112	-2.778189	-1.376748
C	-6.279977	0.899278	2.709331
H	-2.626254	-2.532350	-2.965714
H	-7.281703	1.314045	2.793715
H	-3.454504	0.493235	-5.558224
H	-3.082533	-1.131419	-1.985172

12

Zr	4.407057	0.892010	-0.209870
N	3.116752	-0.718123	-1.872215
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N	1.920567	1.261367	0.436509
N	3.342515	3.752317	-0.541118
C	1.845882	-0.129471	-2.325220
H	1.511074	-0.614182	-3.261031
H	2.064055	0.914080	-2.583091
C	6.454823	2.625233	1.708824
C	4.452312	0.762721	-3.357872
H	5.330706	0.716775	-4.030416
H	3.647111	1.218056	-3.973062
C	5.347588	2.811619	-2.446014
H	6.102476	2.715011	-3.248377
H	5.904561	3.127675	-1.553129
C	1.025088	0.105041	0.131280
H	0.084345	0.258538	0.686324
H	1.507443	-0.771208	0.570079
C	4.093503	-0.660248	-2.984929
H	3.709684	-1.201807	-3.865551
H	4.995999	-1.173643	-2.633212
C	2.994994	-2.126569	-1.399458
H	2.224312	-2.160315	-0.622766

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C	3.101779	3.938813	-1.975408
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C	2.085412	3.746969	0.204750
H	1.458693	4.621935	-0.051999
H	2.321943	3.841168	1.271306
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C	0.697589	-0.153038	-1.327977
H	0.193800	-1.130044	-1.341151
H	-0.058577	0.555236	-1.692795
C	4.252116	4.765305	0.034746
H	5.164300	4.791165	-0.572628
H	4.546534	4.387328	1.021638
C	4.355264	3.909478	-2.839095
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H	4.028841	3.777004	-3.880611
C	1.248523	2.504839	0.010660
H	0.312552	2.625143	0.578073
H	0.980885	2.377809	-1.044938
C	6.654954	-1.343074	0.310595
C	1.395829	-3.397598	-2.901824
H	0.566394	-2.852066	-2.452276
C	3.736527	-3.905913	-3.023643
H	4.756821	-3.742586	-2.675779
C	2.181753	-5.066346	-4.452301
H	1.981362	-5.806073	-5.223828
C	3.178747	6.589604	1.401917
H	3.218525	5.916733	2.259559
C	3.483913	-4.850334	-4.011772
H	4.305699	-5.422581	-4.436193
C	6.378128	-1.828440	1.722050
H	6.111024	-0.991046	2.379311
H	7.252142	-2.338911	2.144933
H	5.532714	-2.530466	1.713660
C	1.136626	-4.339831	-3.891378
H	0.114080	-4.512888	-4.219357
C	7.758909	1.852597	1.782743
H	7.575397	0.835060	2.153223
H	8.464367	2.342856	2.464206
H	8.221334	1.782293	0.791601
C	7.056591	-2.489570	-0.601879
H	6.257404	-3.244146	-0.627980
H	7.972054	-2.977890	-0.247176
H	7.229529	-2.130627	-1.623214
C	3.653146	7.044570	-0.906251
H	4.077317	6.742127	-1.863594
C	3.102617	8.314453	-0.770548
H	3.084837	8.989993	-1.622985
C	5.754646	2.687701	3.054778
H	4.786682	3.200799	2.975573
H	6.372880	3.216057	3.790093
H	5.550923	1.675368	3.426038
C	2.586351	8.723834	0.454794
H	2.158396	9.717862	0.563049
C	2.630599	7.859165	1.544093
H	2.240674	8.175705	2.508834
S	3.408311	0.003356	2.201044
C	2.180457	1.159614	1.897249
S	1.310556	2.015163	3.014444
H	7.482842	-0.610019	0.341113
H	6.681520	3.655812	1.374185
O	5.519874	-0.713896	-0.216720
O	5.602913	2.052819	0.753135

12a

Zr	3.829244	1.163078	-0.529742
N	2.566155	-0.454732	-2.251481
N	4.247214	1.793935	-2.471154
N	1.799357	1.415531	0.034419
N	3.169867	3.880212	-0.530669
C	1.218250	0.109569	-2.480113
H	0.773663	-0.339742	-3.386622
H	1.360696	1.173549	-2.700707
C	5.894187	2.251928	1.798607
C	3.736650	1.209110	-3.683235
H	4.492076	1.249209	-4.491365
H	2.858896	1.759219	-4.083661
C	4.941390	3.046078	-2.673498
H	5.621865	2.975427	-3.541787
H	5.592706	3.231639	-1.807083
C	0.893270	0.286209	0.045869
H	0.089847	0.442051	0.789782
H	1.433162	-0.607352	0.383908
C	3.389925	-0.247994	-3.462168
H	2.885058	-0.660437	-4.352291
H	4.321707	-0.807107	-3.313978
C	2.519503	-1.907247	-1.924485
H	1.863475	-2.034282	-1.056782
H	3.530851	-2.177404	-1.598452
C	2.822412	4.247650	-1.911065
H	2.315952	5.230673	-1.938534
H	2.088275	3.511995	-2.261352
C	2.092620	-2.832573	-3.036788
C	1.977873	3.830157	0.325345
H	1.411144	4.778091	0.278246
H	2.331334	3.705840	1.359036
C	3.718095	6.201850	0.334414
C	0.251373	-0.017732	-1.311975
H	-0.202153	-1.019107	-1.272678
H	-0.580005	0.673159	-1.512221
C	4.172975	4.786701	0.070728
H	5.062585	4.789869	-0.569526
H	4.477580	4.320630	1.013774
C	4.005192	4.241937	-2.872316
H	4.590779	5.169679	-2.792605
H	3.594981	4.239596	-3.892179
C	1.076071	2.663731	0.004472
H	0.266314	2.661877	0.760211
H	0.557751	2.842188	-0.962185
C	5.880750	-2.952168	2.371095
C	0.745363	-3.072406	-3.320960
H	-0.024809	-2.590735	-2.718953
C	3.057860	-3.499114	-3.796557
H	4.112180	-3.339706	-3.568514
C	1.346676	-4.582101	-5.101507
H	1.057088	-5.260429	-5.900827
C	3.280769	6.570737	1.609157
H	3.288108	5.827107	2.406811
C	2.692211	-4.364673	-4.821115
H	3.460079	-4.875930	-5.397440
C	5.098590	-4.223882	2.136277
H	4.129984	-4.010338	1.672977
H	4.919554	-4.735769	3.088289
H	5.664461	-4.897384	1.481962
C	0.373555	-3.935789	-4.346210
H	-0.680568	-4.111437	-4.549636
C	7.001549	1.218073	1.924552
H	6.582597	0.232060	2.167043
H	7.697324	1.498670	2.724842
H	7.557477	1.127528	0.985649
C	7.242153	-3.189539	2.979466
H	7.838320	-3.848714	2.337952
H	7.136200	-3.664687	3.960671
H	7.784391	-2.246939	3.104655
C	3.731678	7.177443	-0.666355
H	4.101528	6.922552	-1.659324
C	3.302008	8.474833	-0.407408
H	3.323613	9.219628	-1.199939
C	5.018274	2.284411	3.040674
H	4.250163	3.064656	2.960185
H	5.612644	2.476559	3.942229
H	4.508203	1.318184	3.151771
C	2.857233	8.822205	0.864075
H	2.524895	9.837304	1.068927
C	2.852480	7.866532	1.875140
H	2.520184	8.132166	2.876279
H	5.297802	-2.246737	2.979616
H	6.368203	3.245666	1.672585
O	6.136313	-2.318781	1.090217
O	5.103306	2.017291	0.669544
S	3.816902	-1.002400	1.293360

C	5.286562	-1.460165	0.556368
S	5.761332	-0.777026	-0.931240

12b

Zr	0.145907	-1.075373	0.560793
N	-1.028042	-2.775900	-1.170742
N	0.717884	-0.580429	-1.391979
N	-1.884966	-0.772470	1.009423
N	-0.404832	1.579453	0.442628
C	-2.357818	-2.198041	-1.468984
H	-2.776265	-2.670880	-2.375578
H	-2.191433	-1.143905	-1.720957
C	2.138440	-0.359729	2.988537
C	0.237130	-1.184489	-2.605628
H	1.027965	-1.192784	-3.382765
H	-0.606819	-0.626713	-3.063061
C	1.451676	0.647447	-1.601804
H	2.162674	0.533487	-2.442936
H	2.080000	0.840932	-0.717221
C	-2.793767	-1.902206	1.032415
H	-3.627502	-1.708677	1.731313
H	-2.270707	-2.777329	1.438655
C	-0.157032	-2.623614	-2.353100
H	-0.633414	-3.054314	-3.250282
H	0.753073	-3.203958	-2.152921
C	-1.109991	-4.219735	-0.809934
H	-1.765311	-4.313589	0.062258
H	-0.110176	-4.513801	-0.468847
C	-0.668446	1.923064	-0.965821
H	-1.137089	2.921604	-1.035036
H	-1.411245	1.204916	-1.333018
C	-1.552337	-5.161007	-1.904469
C	-1.645546	1.625949	1.235031
H	-2.154924	2.598297	1.115740
H	-1.351334	1.526794	2.289503
C	0.197218	3.916530	1.248314
C	-3.373054	-2.268811	-0.337198
H	-3.830357	-3.266449	-0.268466
H	-4.192906	-1.587808	-0.607242
C	0.602654	2.474320	1.065386
H	1.525208	2.415478	0.476589
H	0.837998	2.027061	2.036667
C	0.557400	1.861641	-1.869594
H	1.162331	2.775984	-1.788401
H	0.192872	1.841122	-2.906392
C	-2.580391	0.486917	0.910987
H	-3.418704	0.531213	1.632171
H	-3.050235	0.645429	-0.083229
C	3.075828	-2.660483	-0.533344
C	-2.902796	-5.378523	-2.192670
H	-3.667418	-4.869023	-1.607620
C	-0.599800	-5.869932	-2.641248
H	0.456827	-5.737615	-2.407891
C	-2.325473	-6.943657	-3.933197
H	-2.625655	-7.634951	-4.717208
C	-0.297377	4.353447	2.480173
H	-0.382090	3.639395	3.299904
C	-0.977523	-6.751393	-3.647545
H	-0.217498	-7.295843	-4.203281
C	4.195007	-1.990412	0.228288
H	3.838770	-1.051087	0.667395
H	5.008581	-1.759690	-0.469535
H	4.589106	-2.632829	1.020827
C	-3.287590	-6.257346	-3.199841
H	-4.344272	-6.414417	-3.404610
C	1.187605	-0.138262	4.151382
H	0.765378	0.876426	4.106825
H	1.703351	-0.251622	5.112360
H	0.364290	-0.860333	4.110309
C	3.456586	-3.951583	-1.226063
H	3.973180	-4.644538	-0.558737
H	4.114405	-3.709322	-2.069616
H	2.570098	-4.458731	-1.626836
C	0.331158	4.855436	0.221249
H	0.747750	4.549080	-0.737929
C	-0.035815	6.183232	0.412341
H	0.081229	6.898599	-0.398686
C	3.290074	0.630820	3.008754
H	3.937295	0.501236	2.133388
H	3.900086	0.498198	3.909886
H	2.914730	1.662593	3.000897
C	-0.538617	6.598558	1.640906
H	-0.821061	7.637668	1.793155
C	-0.664854	5.679624	2.677966
H	-1.043145	5.998391	3.646639
H	2.691586	-1.953280	-1.282430
H	2.547272	-1.386341	3.064174
O	1.872696	-2.796824	0.304155
O	1.438012	-0.245617	1.774688
S	2.878114	-4.683940	1.938925
C	1.758137	-3.589720	1.429074
S	0.240248	-3.231219	2.178421

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Zr	-0.686856	1.270799	-0.542864
N	1.176417	2.653017	1.223245
N	1.168094	1.627590	-1.477600
N	-0.577254	-0.028678	1.113618
N	0.192721	-1.415736	-1.302883
C	1.782616	1.539152	1.965923
H	2.712700	1.862051	2.471478
H	2.082635	0.787110	1.228022
C	-2.574729	1.298636	-3.254076
C	2.366100	2.194541	-0.911147
H	2.943302	2.735893	-1.687059
H	3.067214	1.422381	-0.531076
N	-1.959553	0.679323	-2.077319
C	1.469429	0.857078	-2.670170
H	2.060688	1.464688	-3.382938
H	0.526427	0.618246	-3.179464
N	-1.704984	2.952969	0.132933
C	-0.556973	0.584763	2.428804
H	-1.082118	-0.057345	3.162639
H	-1.125746	1.523175	2.384207
C	2.072583	3.184519	0.191850
H	3.026344	3.541476	0.623214
H	1.567295	4.058392	-0.249018
C	0.739846	3.741388	2.121636
H	0.045157	3.319118	2.856311
H	0.154510	4.447467	1.517122
C	1.656553	-1.293805	-1.278701
H	2.136223	-2.291462	-1.275792
H	1.922686	-0.826411	-0.324242
C	1.833246	4.510234	2.826684
C	-0.324550	-2.127804	-0.130412
H	0.099169	-3.146477	-0.049510
H	-1.410822	-2.236339	-0.276967
C	0.080109	-3.510715	-2.729647
C	0.847275	0.880498	2.973116
H	0.743837	1.491775	3.881589
H	1.334305	-0.047465	3.304671
C	-0.289595	-2.058226	-2.541476
H	0.066416	-1.467108	-3.393247
H	-1.384767	-1.972078	-2.547897
C	2.232153	-0.447827	-2.409427
H	2.275987	-1.016443	-3.350475
H	3.279681	-0.235706	-2.151084
C	-0.094616	-1.386013	1.165397
H	-0.617803	-1.953513	1.960614
H	0.979553	-1.449670	1.439155
C	-3.053984	3.291919	0.592912
C	2.377523	4.072166	4.037250
H	1.991904	3.166090	4.503772
C	2.319681	5.699254	2.277160
H	1.890003	6.068098	1.345471
C	3.873086	5.962646	4.098712
H	4.662886	6.524178	4.592325
C	-0.793587	-4.521326	-2.320048
H	-1.752760	-4.248113	-1.879756
C	3.330665	6.420261	2.901950
H	3.691459	7.344946	2.456979
C	-3.885232	2.016469	0.692819

H	-3.901348	1.487169	-0.267087
H	-4.918630	2.249121	0.980895
H	-3.468251	1.333747	1.445071
C	3.390857	4.788032	4.666454
H	3.798691	4.430282	5.609361
C	-4.097610	1.369440	-3.107477
H	-4.512462	0.365531	-2.940434
H	-4.569045	1.782351	-4.010061
H	-4.385183	1.995328	-2.255093
C	-2.982463	3.946756	1.976487
H	-2.518048	3.271368	2.706451
H	-3.983712	4.209589	2.344047
H	-2.387661	4.870823	1.941265
C	1.290754	-3.884016	-3.319485
H	1.974149	-3.112629	-3.673866
C	1.626707	-5.224391	-3.478484
H	2.572848	-5.492955	-3.943176
C	-2.255826	0.466696	-4.500367
H	-1.172236	0.407245	-4.663244
H	-2.712018	0.903286	-5.399281
H	-2.641761	-0.557463	-4.394255
C	-2.005409	2.702408	-3.438869
H	-2.159305	3.307886	-2.537602
H	-2.487204	3.206920	-4.286510
H	-0.925580	2.663368	-3.635867
C	-3.730824	4.278044	-0.363720
H	-3.122158	5.186824	-0.470245
H	-4.721653	4.578276	0.004251
H	-3.854561	3.839654	-1.360314
C	0.751196	-6.218235	-3.053365
H	1.010844	-7.266727	-3.179936
C	-0.464074	-5.862896	-2.476669
H	-1.160930	-6.632766	-2.152800
H	-2.231845	-0.303548	-2.051673
H	-1.121299	3.786943	0.206315

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Zr	0.485883	1.847622	-0.472426
N	1.447753	4.265234	0.497990
N	1.414426	2.911006	-2.024305
N	1.773660	1.201374	1.049542
N	2.519220	0.009997	-1.451366
C	2.766295	3.977824	1.089434
H	3.307851	4.920755	1.288570
H	3.346203	3.445134	0.326104
C	-1.797605	0.210635	-2.093858
C	2.168192	4.133341	-1.876803
H	2.127603	4.729483	-2.809050
H	3.249935	3.948226	-1.707895
N	-0.483821	0.336283	-1.447767
C	1.755952	2.224676	-3.255507
H	1.663885	2.910564	-4.118988
H	1.025004	1.422242	-3.421772
N	-1.690874	2.974893	2.510464
C	1.736059	1.967317	2.281898
H	1.901534	1.303858	3.151276
H	0.730021	2.381836	2.418275
C	1.615065	4.998329	-0.768613
H	2.251036	5.890554	-0.627575
H	0.620774	5.349968	-1.073498
C	0.575975	5.041577	1.415729
H	0.412131	4.447167	2.319764
H	-0.403785	5.111503	0.931102
C	3.551516	0.922897	-1.967301
H	4.511432	0.389099	-2.101318
H	3.725141	1.681944	-1.194790
C	1.043215	6.427547	1.786210
C	2.908005	-0.587941	-0.169131
H	3.869380	-1.128129	-0.245970
H	2.133607	-1.327875	0.085042
C	3.307085	-2.043518	-2.723546
C	2.730056	3.128353	2.352113
H	2.485092	3.734946	3.236264
H	3.749122	2.755164	2.525433
C	2.199557	-1.060190	-2.422851
H	1.846453	-0.587388	-3.346566
H	1.346066	-1.623181	-2.020760
C	3.171120	1.634596	-3.260248
H	3.270579	0.970441	-4.130897
H	3.916867	2.427020	-3.416558
C	2.981148	0.418116	0.953498
H	3.150536	-0.147260	1.890096
H	3.887204	1.047268	0.834971
C	-2.406818	3.423562	3.711304
C	1.841137	6.649500	2.911796
H	2.127027	5.804632	3.539126
C	0.647946	7.533184	1.027491
H	-0.006692	7.380810	0.169164
C	1.870086	9.019439	2.478261
H	2.189358	10.023814	2.746774
C	3.391395	-3.244636	-2.014134
H	2.641956	-3.465564	-1.253902
C	1.059551	8.817366	1.365216
H	0.738434	9.664762	0.763596
C	-3.691580	2.631306	3.947129
H	-4.389458	2.783600	3.118740
H	-4.172950	2.949625	4.880970
H	-3.471086	1.558392	4.026143
C	2.255362	7.932108	3.255425
H	2.873290	8.083485	4.137703
C	-2.856905	-0.157128	-1.054791
H	-2.616490	-1.121690	-0.587097
H	-3.857290	-0.229339	-1.505216
H	-2.885697	0.609465	-0.271508
C	-1.435368	3.186675	4.865425
H	-1.181578	2.120794	4.958699
H	-1.880710	3.506666	5.814323
H	-0.504005	3.750917	4.713886
C	4.259462	-1.795933	-3.715727
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C	-5.520552	1.843656	0.396525
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H	-5.897782	2.387782	1.272805
C	-2.299750	5.464347	-0.955294
H	-2.360772	5.855140	0.070336
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H	-2.251505	6.311867	-1.648807
C	-5.876795	3.961699	-4.148140
H	-5.219280	4.394732	-4.910478
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H	-6.761205	4.609265	-4.078072

15a

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N	-2.105053	-1.177960	-0.021208
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C	-2.689022	5.042577	-3.813443
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C	0.518861	-7.395783	-2.774758
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H	-3.318605	-4.059105	7.736351
H	-2.019909	-3.001187	8.287756
H	-3.724725	0.530217	3.307505

Crystallographic Structures

Crystals of **5** and **11** suitable for single crystal X-ray diffraction were grown in concentrated toluene solutions at -20 ºC. Compounds **5** and **11** crystallized in the triclinic space group P -1 with one molecule in the asymmetric unit. The solid state molecular structures of complexes **5** and **11** are displayed in Figures S1 and S2, respectively. Both compounds show distorted octahedral geometry around zirconium defined by atoms N(1), N(2) and N(4), belonging to the cyclam, N(5), which is the new amido function resulting from incorporation of the *tert*-butyl isocyanate (in **5**) or *N,N'*-dicyclohexylcarbodiimide (in **11**) and two oxygen atoms (O(1) and O(2)) of the isopropoxido ligands. In both complexes the N(3) atom of the macrocycle is not bonded to zirconium. The equatorial planes, defined by N(2), N(4), N(5) and O(1), are slightly twisted, displaying combined equatorial angles of 354.7º and 356.2º in **5** and **11**, respectively. The axial positions are occupied by one nitrogen atom of the macrocycle (N(1)) and the other O^{i}Pr ligand with N(1)-Zr(1)-O(2) angles of 171.3(1)º and 170.80(6)º in **5** and in **11**, respectively.

The Zr-O distances are 1.938(3) and 1.925(3) Å in **5** and 1.942(2) and 1.941(2) Å in **11** and compare with the same bonds observed in the parent complex **2**.[1] The bond distances between the nitrogen atoms of the urea

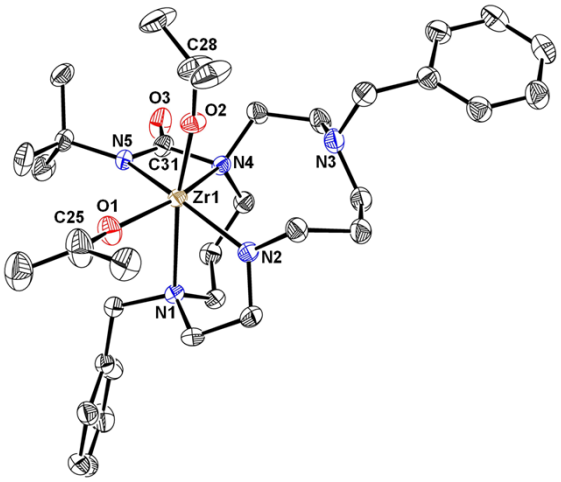

Figure S1. ORTEP diagram of **5** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (º): Zr(1)-O(1) 1.938(3), Zr(1)-O(2) 1.925(3), Zr(1)-N(1) 2.511(3), Zr(1)-N(2) 2.094(3), Zr(1)-N(4) 2.459(3), Zr(1)-N(5) 2.276(3); N(1)-Zr(1)-O(2) 171.3(1), N(4)-C(31)-N(5) 109.2(7).

fragment and the metal in complex **5** (2.459(3) and 2.276(3) Å) and between the two nitrogen atoms of the guanidine fragment and the metal in **11** (2.439(2) and 2.245(2) Å) are within the normal ranges.[2] The four-member metallacycles defined by Zr(1)-N(4)-C(31)-N(5) are planar, with an internal sum of angles of 359.7(3)º and 358.0(2)º in **5** and **11**, respectively.

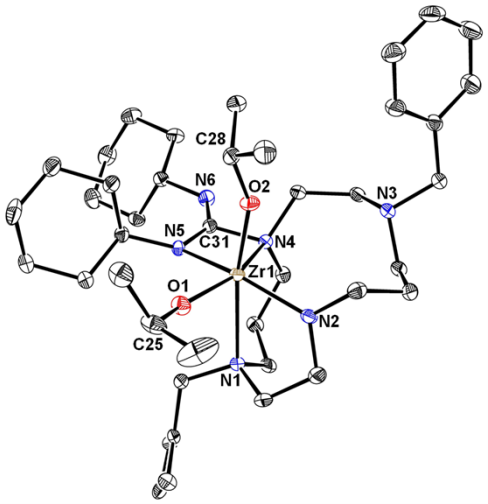

Figure S2. ORTEP diagram of **11** with thermal ellipsoids at 40% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (º): Zr(1)-O(1) 1.942(2), Zr(1)-O(2) 1.941(2), Zr(1)-N(1) 2.505(2), Zr(1)-N(2) 2.089(2), Zr(1)-N(4) 2.439(2), Zr(1)-N(5) 2.245(2); N(1)-Zr(1)-O(2) 170.80(6), N(4)-C(31)-N(5) 106.4(2).

The N-C-N angles within the metallacycle are 108.7(3)º and 106.4(2)º in **5** and **11**, respectively. Although these angles are slightly narrow than 120º, they are comparable with values reported for compounds presenting this type of frame[3,4] and, in combination with the values registered for N(4)-C(31) and N(5)-C(31) distances (1.516(5) and 1.312(5) Å for **5** and 1.521(3) and 1.350(3) Å for **11**, respectively), indicate sp_2 carbon hybridization.

Crystals of **16** and **18** suitable for single crystal X-ray diffraction were grown in C_6D_6 solutions at room temperature in the NMR tubes. Compounds **16** and **18** crystallized in the orthorhombic space group Pbca and in the monoclinic space group $P2_1$, respectively, with one molecule in the asymmetric unit in both cases.

The molecular structure of **16**, displayed in Figure S3, shows a capped trigonal prismatic zirconium coordination geometry with the four nitrogen atoms of the cyclam ring defining the rectangular face of the prism and the Zr(1)-C(24) and Zr(1)-N(5) bonds occupying the vertices of the two trigonal

faces that define a dihedral angle of 7.74º. The Zr(1)-O(1) bond of the ureate moiety caps the face defined by C(24), N(5), N(2) and N(1). The zirconium sits above the plane defined by the four nitrogen atoms of the macrocycle at a distance of 1.222(3) Å that is slightly longer than in other trigonal prismatic complexes with the same ancillary ligand, usually ranging from 1.0-1.2 Å.[1, 5-7] The κ^2-*O*,*N*-ureate fragment defines a planar four-member metallacycle Zr(1)-O(1)-C(29)-N(2) in agreement with sp_2 hybridization of the carbon atom. The Zr-NH^{t}Bu distance of 2.040(6) Å and the Zr-$N_{macrocycle}$ bond lengths of 2.090(6) Å for the Zr-N_{amido} and 2.661(7), 2.418(7) and 2.526(6) Å for the Zr-N_{amine} bonds are within the usual values.[2] The Zr(1)-N(2) distance of 2.418(7) Å is slightly short and, in conjunction with the bond distances of 1.290(9) and 1.28(1) Å observed for the C(29)-O(1) and C(29)-N(6) respectively, suggests charge delocalization along the ureate fragment.[8]
The orthometallation reaction leads to the formation of a 5-member metallacycle with a dihedral angle between the plane containing the N(3), C(20) and C(24) atoms and the aromatic ring of 24.47º. The orthometallation did not affect the Zr-N and Zr-C bonds within the metallacycle.

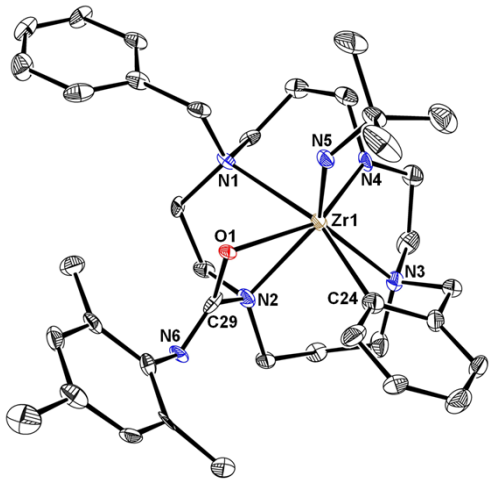

Figure S3. ORTEP diagram of **16** with thermal ellipsoids at 40% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (º): Zr(1)-O(1) 2.245(5), Zr(1)-C(24) 2.305(9), Zr(1)-N(1) 2.661(7), Zr(1)-N(2) 2.418(7), Zr(1)-N(3) 2.527(6), Zr(1)-N(4) 2.090(6), Zr(1)-N(5) 2.040(6); N(24)-Zr(1)-N(5) 89.9(3), O(1)-C(29)-N(2) 109.2(2).

The solid-state molecular structure of **18** is presented in Figure S4. The metal coordination geometry is capped octahedral with two nitrogen atoms (N(3) and N(4)) and two *ortho*-carbon atoms of the macrocycle pendant arms (C(17) and C(24)) defining a slightly twisted square plane having a combined equatorial angle of 352.76º. The axial positions are occupied by one nitrogen atom of the

cyclam ring (N(2)) and one nitrogen atom of the ureate fragment (N(5)) that define a N(2)-Zr(1)-N(5) angle of 155.58(5)º. The N(1) atom caps the face defined by N(2), N(4), C(17).

The bond distances between the zirconium and the two nitrogen atoms of the κ^2-*N*,*N'* ureate fragment (2.466(1) and 2.279(1) Å) are within the expected values[2] and show that there is no charge delocalization along the NC(N)O core. The angle N(4)-C(25)-N(5) inside the four-member metallacycle is 108.3(1)º revealing sp_2 hybridization of the carbon atom.

The orthometallation reactions give rise to two 5-member metallacycles for which the diehral angle between the plane C(17)-Zr(1)-N(1) and the plane containing the aromatic ring containing is 25.71º while the similar angle involving the N(3)-Zr(1)-C(24) plane and the corresponding phenyl ring is 15.71º. The Zr-N and Zr-C bond lenghts are similar in both metallacycles.

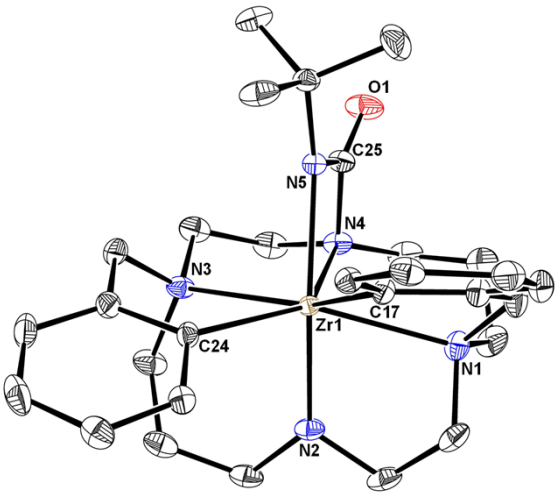

Figure S4. ORTEP diagram of **18** with thermal ellipsoids at 40% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (º): Zr(1)-C(17) 2.379(2), Zr(1)-C(24) 2.338(1), Zr(1)-N(1) 2.470(1), Zr(1)-N(2) 2.090(1), Zr(1)-N(3) 2.498(2), Zr(1)-N(4) 2.466(1), Zr(1)-N(5) 2.279(1); N(2)-Zr(1)-N(5) 155.58(5), N(4)-C(25)-N(5) 108.3(1).

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