Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Pharmaceutical Formulation Affects Titanocene Transferrin Interactions

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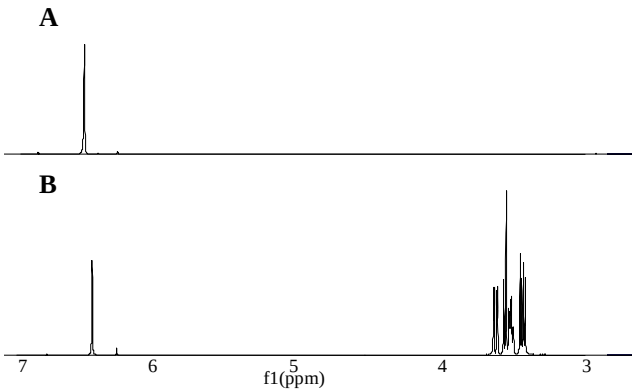

Fig S1: ^{1}H NMR spectra of A. TDC and B. MKT4 in D_2O at room temperature.

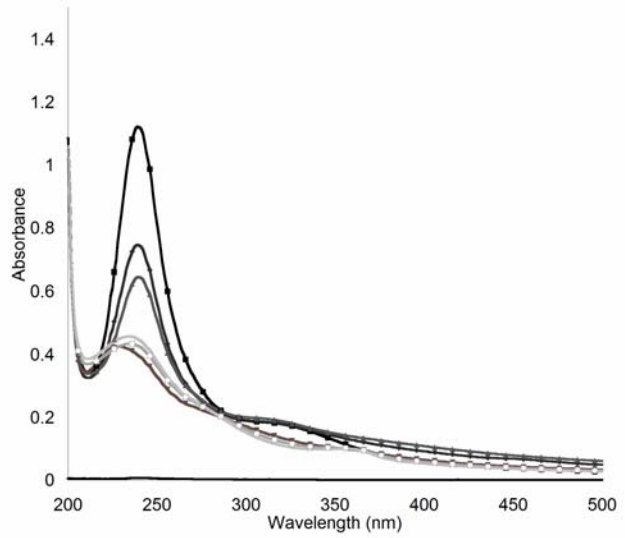

Fig S2: TDC batch titration, pH values were : 4.18 (■), 5.00 (◆), 6.04(▲), 6.90 (▼), 8.08 (◘) and 9.06 (x). Samples were 60 µM in Ti, and had 0.1 M NaCl. The pH was adjusted using 0.10 M KOH.

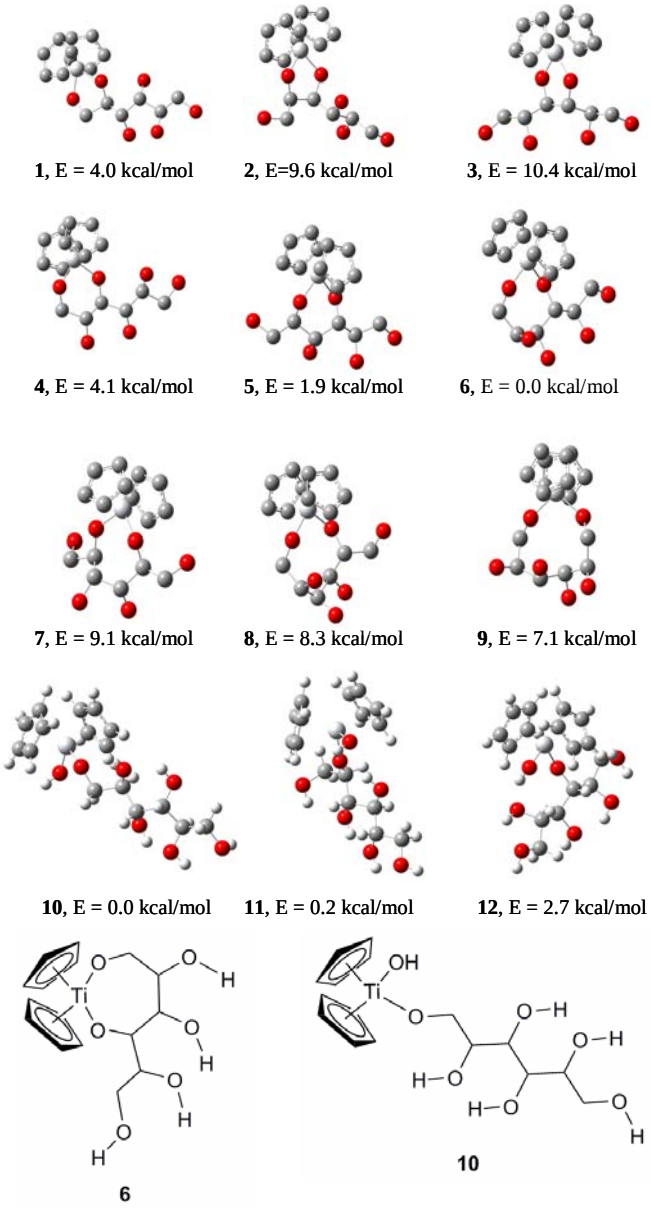

Fig S3: Modeled structures of MKT4 isomers, structures **1** – **9** have mannitol bound through two hydroxides. Structures **10** – **12** have one bond to mannitol and one hydroxide bound. Energies listed are relative to the lowest energy conformer in the set. The low energy conformers, **6** and **10** are shown for clarity.

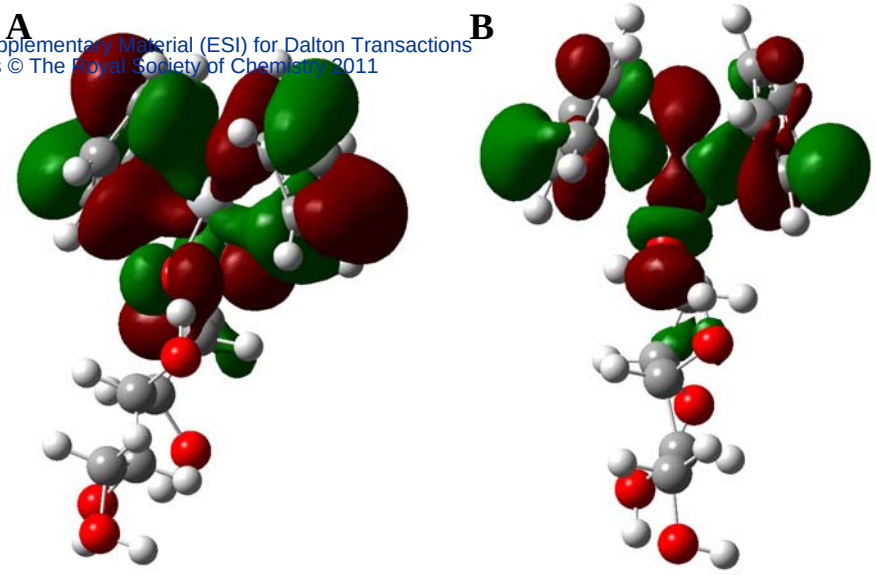

Fig S4 : Representative simulated ground (A) and excited (B) state energy surfaces for **1**. The molecular orbitals show a decreased electron density on the Cp rings and an increase in electron density on the Ti in going from the ground state to the excited state. This change is consistent with the Cp – to – Ti charge transfer character for the electronic excitation.

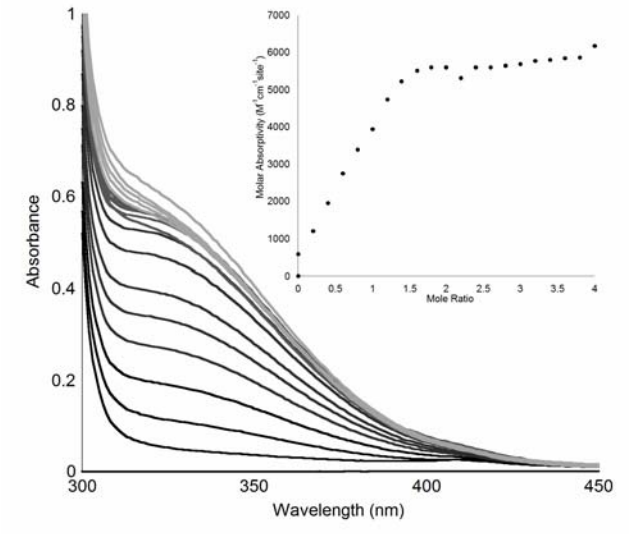

Fig S5 : TDC_{DMSO} Tf binding, Tf was held at 50 µM and the TDC ratio was varied from 0.0 to 4.0 molar equivalents. Inset is the A_{321} for binding. Binding saturation is seen slightly below two equivalents of titanium.

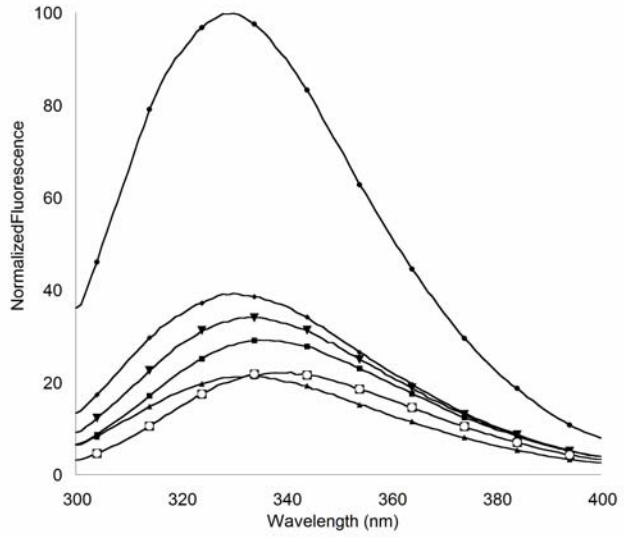

Fig S6: Fluorescence comparison of different titanium sources. Quenching increases when malate is the synergistic anion. Transferrin (●), $MKT4_{HEPES}$ (■), $MKT4_{mal}$ (◆), TDC_{mal} (▲), TDC_{water} (▼), $Fe(NTA)_2$ (◘). Spectra are of 50 µM Tf in HEPES buffer with a 5 fold excess of Ti. All fluorescence values are shown in reference to apo-Tf fluorescence.

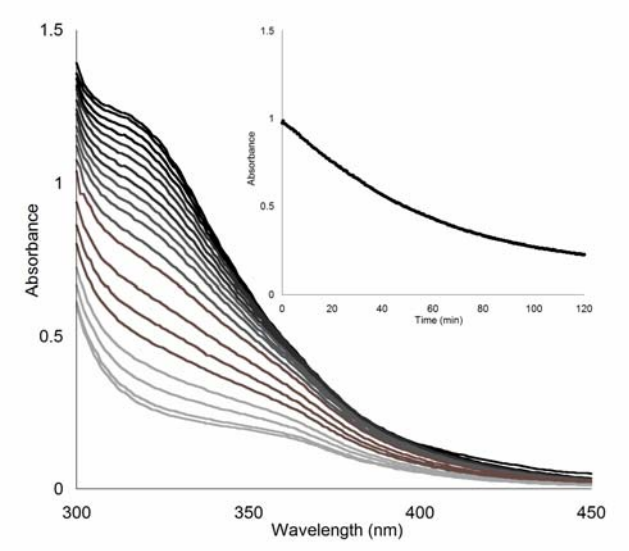

Fig S7 : $MKT4_{mal}$ Tf binding over two hours. A 20 fold molar excess of $MKT4_{mal}$ was added to 12.5 µM Tf in HEPES buffer. Inset is the A_{333} for binding.

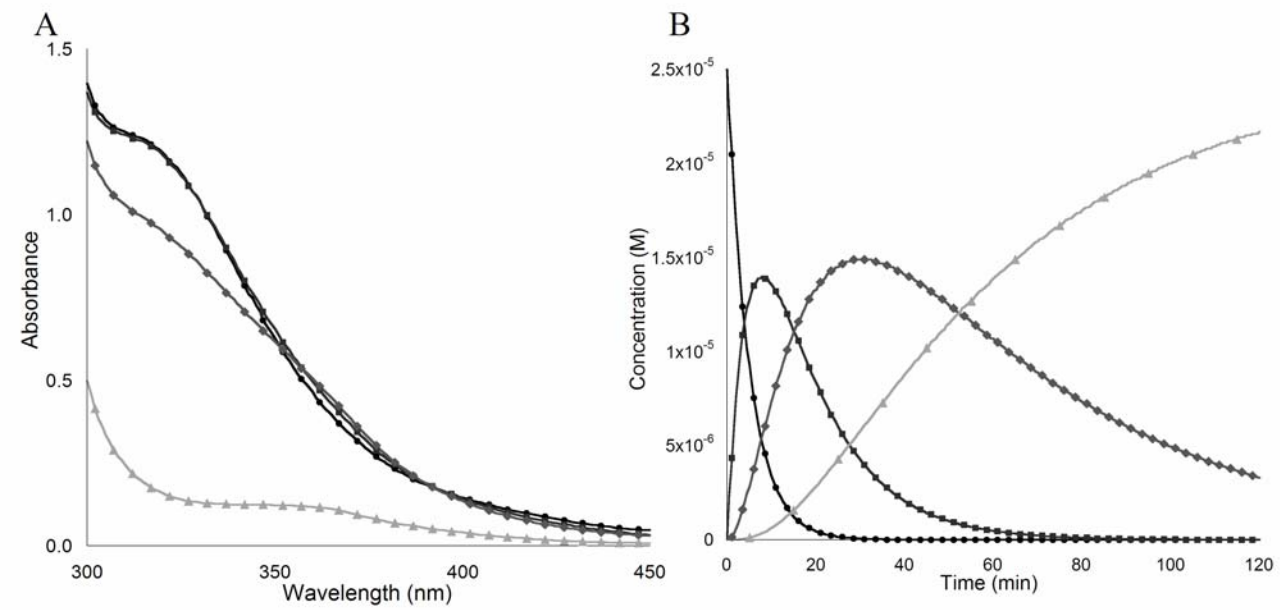

Fig S8 : Kinetics fitting of two hour $MKT4_{mal}$ Tf binding. A shows the 4 species that the absorbance is comprised of. B shows the concentrations of these species over time. The absorbances are dominated by the low pH MKT4 spectra.

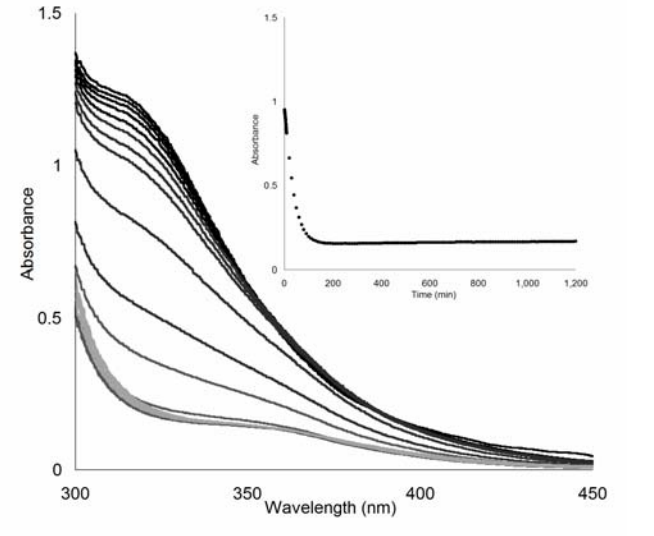

Fig S9 : $MKT4_{mal}$ Tf binding over 20 hours. A 20 fold molar excess of $MKT4_{mal}$ was added to 12.5 µM Tf in HEPES buffer. Inset is the A333 for binding, the major absorbance changes are complete within 200 min.

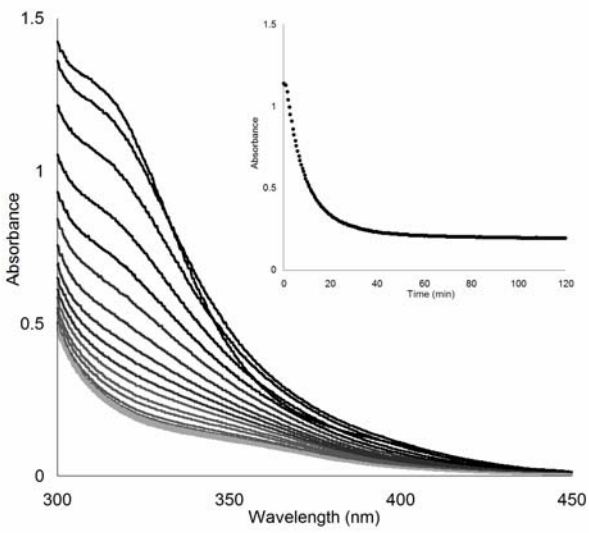

Fig S10 : TDC_{DMSO} Tf binding over two hours. A 20 fold molar excess of TDC_{DMSO} was added to 12.5µM Tf in HEPES buffer. Inset is the A_{321} for binding, most absorbance changes are complete within 2 h.

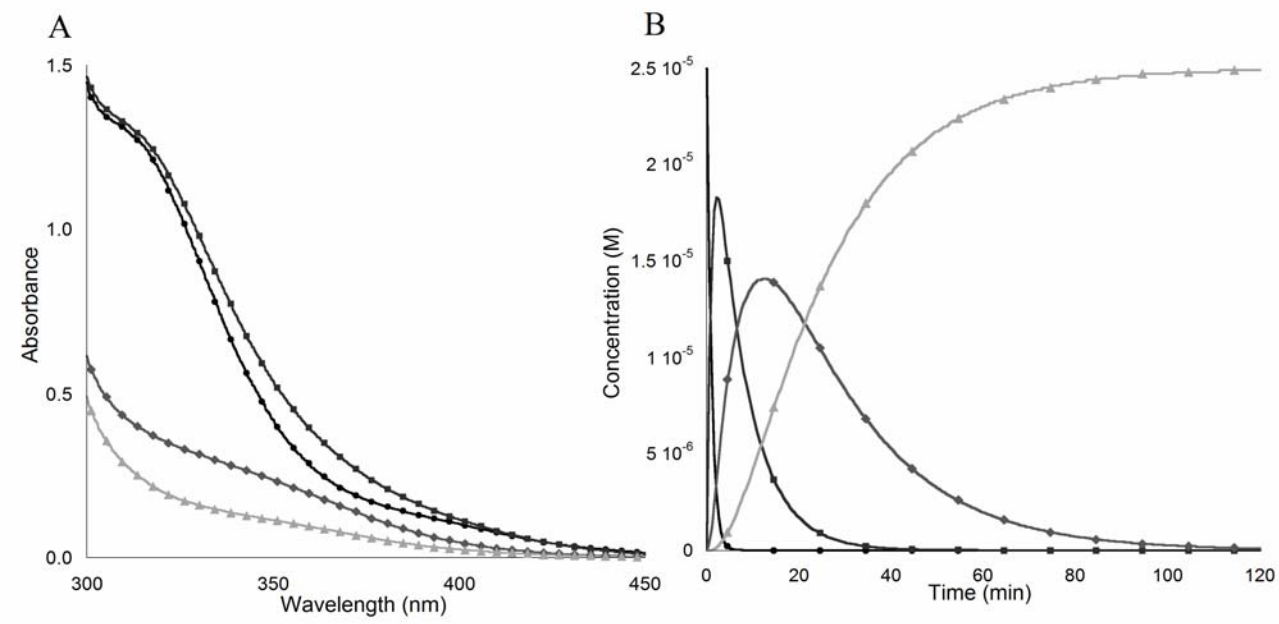

Fig S11 : Kinetics fitting of two hour TDC Tf binding in 10% DMSO. A shows the 4 species that the absorbance is comprised of. B shows the concentrations of these species over time.

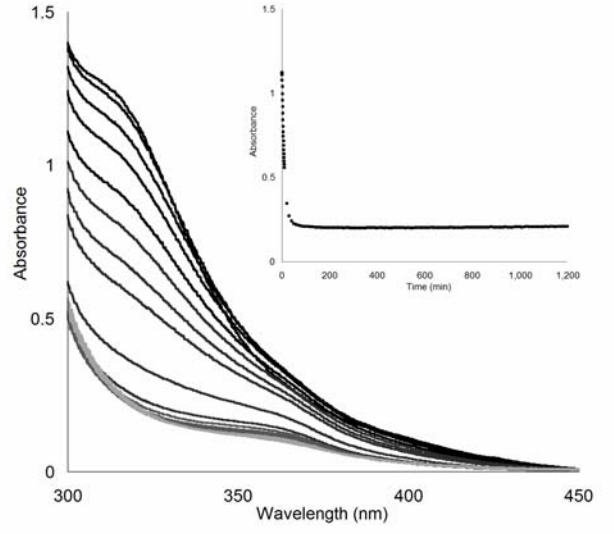

Fig S12 : TDC_{DMSO} Tf binding over twenty hours. A 20 fold molar excess of TDC_{DMSO} was added to 12.5µM Tf in HEPES buffer. Inset is the A_{321} for binding, most absorbance changes are complete within 2 h.

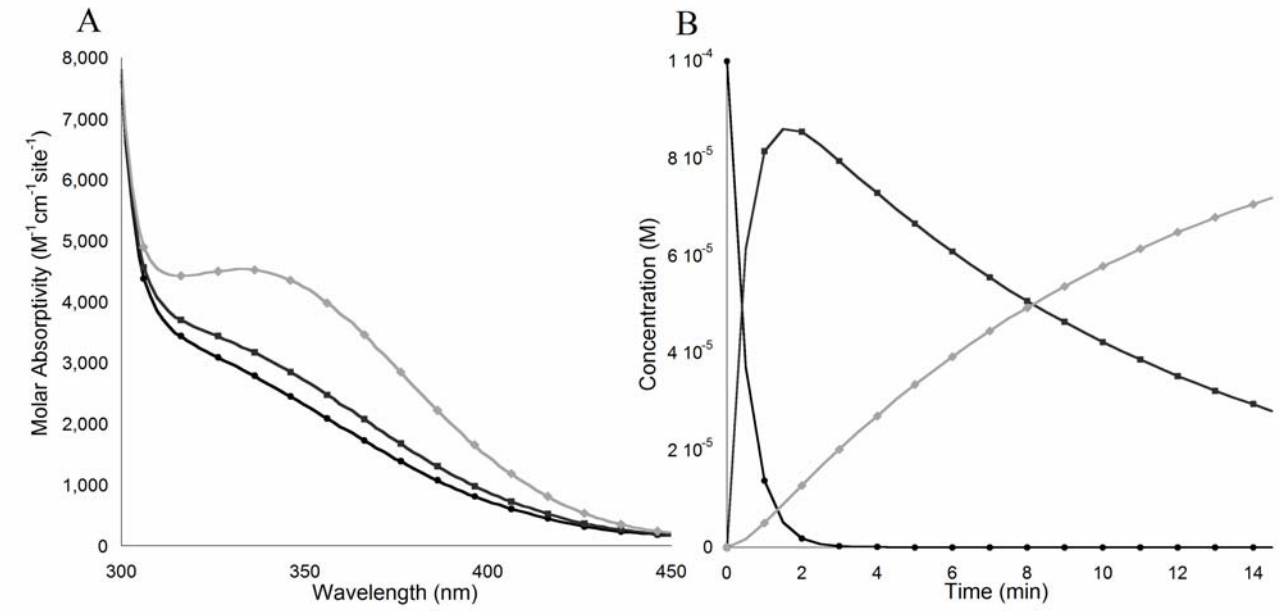

Fig S13 : Kinetics fitting of $MKT4_{mal}$, pH 7.5 Tf binding. A shows the 3 species that the absorbance is comprised of. B shows the concentrations of these species over time.

Reaction	ΔU (kcal/mol)
1 + H_2O ⇌ **10**	-10.3
1 + H_2O ⇌ **11**	-10.1
2 + H_2O ⇌ **11**	-15.7
2 + H_2O ⇌ **12**	-13.2
3 + H_2O ⇌ **12**	-14.0
4 + H_2O ⇌ **10**	-10.4
4 + H_2O ⇌ **12**	-7.7
5 + H_2O ⇌ **11**	-8.0
5 + H_2O ⇌ **12**	-5.5
6 + H_2O ⇌ **10**	-6.3
6 + H_2O ⇌ **12**	-3.6
7 + H_2O ⇌ **11**	-15.2
8 + H_2O ⇌ **10**	-14.6
8 + H_2O ⇌ **11**	-14.4
9 + H_2O ⇌ **10**	-13.4
10 + H_2O ⇌ $Cp_2Ti(OH)_2$ + $C_6H_{14}O_6$	-0.7
11 + H_2O ⇌ $Cp_2Ti(OH)_2$ + $C_6H_{14}O_6$	-0.9
12 + H_2O ⇌ $Cp_2Ti(OH)_2$ + $C_6H_{14}O_6$	-3.4

Table S1 : Calculated reaction energies for hydrolysis of MKT4 isomers and titanocene dichloride

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XYZ coordinates of structure **1**

Symbol	X	Y	Z
C	4.9348	0.067424	-1.51639
H	4.750308	1.079173	-1.89143
H	4.575508	-0.65655	-2.25468
O	6.356649	-0.02005	-1.33152
H	6.614126	-0.95069	-1.29843
C	4.216597	-0.13026	-0.18347
H	4.380764	-1.16129	0.165989
C	2.704968	0.08514	-0.29061
H	2.521304	1.035914	-0.8154
C	2.02428	0.210389	1.105747
H	2.037234	1.279607	1.365188
C	0.571402	-0.2916	1.094479
H	0.606676	-1.38703	1.200705
C	-0.30969	0.285571	2.222935
H	-0.07286	-0.14867	3.201811
H	-0.16862	1.37817	2.279076
O	-1.63676	-0.03506	1.857112
O	4.73506	0.79234	0.784932
H	5.693487	0.834933	0.642385
O	2.213268	-0.99505	-1.07982
H	1.256729	-0.82848	-1.16011
O	2.669362	-0.53318	2.139406
H	3.545794	-0.13654	2.262673
O	-0.09727	0.068174	-0.10946
Ti	-2.01405	0.034658	0.026487
C	-2.74121	-1.59726	-1.62517
C	-3.52676	-1.83352	0.518737
C	-1.73163	-2.23646	-0.84932
H	-2.67224	-1.34737	-2.67555
C	-2.2172	-2.38463	0.465604
H	-4.14738	-1.76127	1.402138
H	-0.74908	-2.52281	-1.19885
H	-1.66206	-2.77001	1.308363
C	-1.85603	1.93961	-1.53477
C	-3.74191	1.700508	-0.25205
C	-1.5752	2.447799	-0.23375
H	-1.1539	1.881124	-2.35602
C	-2.73269	2.303588	0.554119
H	-4.74868	1.463248	0.064968
H	-0.61642	2.811842	0.104823
H	-2.8238	2.543889	1.604344
C	-3.20272	1.515104	-1.55503
H	-3.71982	1.084607	-2.40114
C	-3.86117	-1.37863	-0.77944
H	-4.79559	-0.91825	-1.06846

XYZ coordinates of structure **2**

Symbol	X	Y	Z
C	4.653384	-0.96104	-0.35607
H	5.165539	-0.03141	-0.62492
H	4.411016	-1.50674	-1.27317
O	5.586085	-1.68675	0.462246
H	5.316366	-2.61371	0.500336
C	3.38647	-0.64213	0.439085
H	2.84991	-1.58136	0.658619
C	2.438498	0.291491	-0.33417
H	2.984782	1.222033	-0.52389
C	1.149564	0.580392	0.46822
H	1.450946	0.739959	1.511923
C	0.275843	1.829396	0.018495
H	-0.0266	2.357712	0.936571
C	0.978047	2.862827	-0.85489
H	1.946087	3.121487	-0.39977
H	1.154332	2.442185	-1.85315
O	0.142456	4.020423	-0.91557
H	0.503041	4.63156	-1.56926
O	3.738892	0.010401	1.658766
H	4.546561	-0.41854	1.98119
O	2.113429	-0.27953	-1.59816
O	0.323673	-0.56626	0.36078
O	-0.87024	1.33218	-0.636
Ti	-1.5315	-0.27444	0.04497
C	-2.61571	-0.40539	-2.14116
C	-1.30193	-0.91751	-2.3111
C	-1.19496	-2.10713	-1.5541
H	-0.50753	-0.43228	-2.86027
C	-2.4416	-2.33726	-0.91382
H	-0.30768	-2.7148	-1.43595
H	-2.67518	-3.16921	-0.26314
C	-3.48262	0.400298	1.333193
C	-2.41763	1.233555	1.771253
C	-1.46194	0.421041	2.414167
H	-2.33263	2.295065	1.582789
C	-1.93301	-0.92306	2.388273
H	-0.51762	0.747255	2.826309
H	-1.40672	-1.78544	2.776023
C	-3.32523	-1.29256	-1.29638
C	-3.1943	-0.92888	1.753746
H	-4.35276	-1.18119	-0.97989
H	-3.81588	-1.79711	1.585272
H	-4.3695	0.729653	0.808676
H	-2.9903	0.520169	-2.55752
H	1.315157	-0.80571	-1.42098

XYZ coordinates of structure **3**

Symbol	X	Y	Z
C	-2.10068	-2.91506	1.126307
H	-2.71689	-2.53374	1.946547
H	-1.10054	-3.1388	1.513481
O	-2.76823	-4.10172	0.669077
H	-2.16284	-4.61301	0.116081
C	-2.02898	-1.86956	0.012054
H	-1.36836	-2.24563	-0.7872
C	-1.46266	-0.53595	0.533075
H	-2.09627	-0.21528	1.372458
C	-1.43029	0.592746	-0.55466
H	-2.0808	0.311145	-1.39504
C	-1.91991	1.952788	-0.02627
H	-1.26266	2.2816	0.79199
C	-1.89114	3.014228	-1.1205
H	-0.86734	3.155104	-1.4858
H	-2.53146	2.69171	-1.95337
O	-2.40079	4.220626	-0.52958
H	-2.59139	4.864629	-1.22172
O	-3.32855	-1.63273	-0.51604
H	-3.79289	-2.48364	-0.51673
O	-0.13447	-0.71854	0.983539
O	-0.09391	0.694893	-1.00651
O	-3.24702	1.787008	0.461819
H	-3.60421	2.675626	0.606194
Ti	1.306386	-0.03248	0.003184
C	1.658682	2.27544	0.759832
C	2.247736	0.601713	2.21132
C	2.928515	1.769406	0.358477
H	1.097397	3.04505	0.249624
C	3.302915	0.759939	1.284255
H	2.202974	-0.1234	3.013424
H	3.513688	2.118494	-0.48196
H	4.216485	0.18286	1.26026
C	1.614481	-2.35475	-0.72951
C	2.233835	-0.71424	-2.20484
C	2.894274	-1.86898	-0.33656
H	1.037934	-3.10038	-0.20097
C	3.285684	-0.87789	-1.2753
H	2.201043	0.002683	-3.01475
H	3.473233	-2.21817	0.507961
H	4.209085	-0.31638	-1.25905
C	1.242458	1.558502	1.899034
H	0.294866	1.659377	2.40748
C	1.210659	-1.64669	-1.87924
H	0.258622	-1.73145	-2.38247

XYZ coordinates of structure **4**

Symbol	X	Y	Z
Ti	-1.54676	-0.13161	-0.01956
C	-0.9143	-1.90016	-1.59647
C	-1.85123	-2.45489	-0.6869
C	-1.57481	-0.898	-2.34007
H	0.145417	-2.1163	-1.62012
C	-3.10708	-1.81749	-0.90425
H	-1.6465	-3.23541	0.033875
C	-2.93115	-0.84219	-1.91127
H	-1.11495	-0.23424	-3.05788
H	-4.02696	-2.02779	-0.37684
H	-3.68021	-0.14718	-2.26666
C	-1.38447	0.913161	2.241231
C	-2.66082	1.234853	1.727858
C	-1.32501	-0.49609	2.422575
H	-0.58619	1.611675	2.449849
C	-3.3903	0.032337	1.567982
H	-3.00375	2.220039	1.443305
C	-2.56397	-1.03959	2.021842
H	-0.46547	-1.05623	2.765498
H	-4.40271	-0.05108	1.197214
H	-2.8351	-2.08573	2.045341
O	-1.63595	1.535767	-0.90187
C	-0.74147	2.577068	-0.61905
C	0.721817	2.160561	-0.86059
H	-0.97221	3.422988	-1.28773
H	-0.83529	2.946981	0.415681
C	1.205394	1.025109	0.06768
H	0.818721	1.814697	-1.89963
O	1.594601	3.285751	-0.63339
C	2.638207	0.562555	-0.31632
O	0.311661	-0.0443	0.004853
H	1.27002	1.426779	1.095831
H	1.433447	3.959062	-1.30713
C	3.008784	-0.81419	0.261228
H	2.706048	0.468284	-1.41165
O	3.591974	1.514272	0.159011
C	4.517407	-0.96997	0.455512
O	2.546373	-1.81276	-0.65053
H	2.520604	-0.95502	1.237816
H	3.262053	2.394041	-0.08715
O	4.715052	-2.33817	0.858545
H	4.879487	-0.27844	1.221323
H	5.038747	-0.76848	-0.48935
H	2.994695	-2.63317	-0.3933
H	5.657045	-2.54314	0.843141

XYZ coordinates of structure **5**

Symbol	X	Y	Z
C	3.299799	-1.85782	0.151451
H	3.280409	-2.13369	-0.9081
H	2.540031	-2.43721	0.686334
O	4.625232	-2.17801	0.60204
H	4.629067	-2.21895	1.56751
C	3.03106	-0.36368	0.304479
H	3.024524	-0.10593	1.374505
C	1.672458	0.05342	-0.28153
H	1.615493	-0.32986	-1.31347
C	1.542535	1.610206	-0.37631
H	1.915448	1.898582	-1.37042
C	0.083142	2.095832	-0.21781
H	-0.08988	2.209814	0.860481
C	-0.11632	3.466384	-0.85174
H	0.718022	4.115665	-0.55446
H	-0.12392	3.358364	-1.94621
O	-1.36218	3.992565	-0.38361
H	-1.50177	4.863818	-0.77351
O	4.061994	0.380126	-0.36214
H	4.897409	-0.08187	-0.19053
O	0.673758	-0.5366	0.520549
O	2.288192	2.303997	0.624615
H	3.225879	2.136641	0.441592
O	-0.81497	1.169785	-0.78981
Ti	-1.15235	-0.48318	0.017653
C	-2.71353	-1.88234	-1.28333
C	-2.21481	-0.90144	-2.16965
C	-0.82459	-1.13984	-2.35016
H	-2.77913	-0.09096	-2.6106
C	-0.46189	-2.24455	-1.55328
H	-0.15546	-0.52865	-2.93838
H	0.533023	-2.65173	-1.43866
C	-3.21969	-0.14178	1.242841
C	-2.3369	0.900773	1.640996
C	-1.25956	0.314163	2.336666
H	-2.44272	1.947067	1.386742
C	-1.46855	-1.09352	2.375865
H	-0.38516	0.827607	2.70964
H	-0.79512	-1.82152	2.808036
C	-1.62463	-2.69824	-0.87095
C	-2.69567	-1.36936	1.732479
H	-1.67307	-3.53469	-0.18676
H	-3.13791	-2.34705	1.600819
H	-4.13846	-0.01323	0.686369
H	-3.73825	-1.97645	-0.95257

XYZ coordinates of structure **6**

Symbol	X	Y	Z
C	0.314011	2.6149	-0.74646
C	-1.15355	2.648968	-0.30775
C	-2.05772	1.444047	-0.64924
H	-2.02759	1.294985	-1.74156
C	-1.70064	0.083264	0.009708
C	-2.72861	-1.00929	-0.37237
H	-2.78812	-1.05859	-1.47061
C	-2.35739	-2.39497	0.141231
H	-2.28033	-2.37518	1.237249
H	-1.40441	-2.7143	-0.291
O	1.121102	1.779998	0.033565
O	-3.35401	1.904937	-0.2494
O	-0.45718	-0.36286	-0.46454
O	-4.01366	-0.65082	0.159358
H	-4.6079	-1.40006	0.000379
O	-3.43059	-3.2587	-0.26599
H	-3.33471	-4.12042	0.156401
O	-1.21392	2.940475	1.084578
H	-2.15841	2.967696	1.302896
H	0.704545	3.638063	-0.64999
H	0.343734	2.343821	-1.81542
H	-1.60475	3.482434	-0.87493
H	-1.71222	0.21346	1.10278
H	-3.94544	1.139457	-0.13755
Ti	1.339292	-0.05757	0.02185
C	1.52321	-0.28808	-2.44251
C	2.613204	0.496822	-2.01752
C	1.677735	-1.59302	-1.8943
H	0.680389	0.053204	-3.02631
C	3.438764	-0.30617	-1.18563
H	2.76474	1.546629	-2.2267
C	2.870779	-1.61182	-1.14161
H	0.983813	-2.41414	-2.01125
H	4.354071	0.012356	-0.70558
H	3.271108	-2.46046	-0.60469
C	0.939714	0.359124	2.403657
C	0.594549	-0.98922	2.163889
C	2.338572	0.491891	2.193118
H	0.25534	1.171248	2.607001
C	1.769618	-1.69455	1.790866
H	-0.3993	-1.40914	2.219368
C	2.853347	-0.77489	1.833146
H	2.896838	1.416432	2.245003
H	1.829954	-2.74571	1.542987
H	3.886755	-1.00156	1.610852

XYZ coordinates of structure **7**

Symbol	X	Y	Z
C	-1.33118	3.233361	-0.20928
C	-1.2002	1.723723	-0.01202
C	-2.44695	1.011895	-0.58826
H	-2.7103	1.480325	-1.55546
C	-2.30368	-0.50641	-0.86807
C	-1.60782	-1.32791	0.252136
H	-1.75536	-0.82774	1.221449
C	-2.16819	-2.74089	0.404594
H	-1.96275	-3.31812	-0.50824
H	-3.25223	-2.69067	0.555091
O	-0.35841	3.884717	0.614744
O	-3.4992	1.238309	0.346617
O	-3.64153	-1.01189	-1.09959
H	-3.88329	-0.84512	-2.01968
O	-0.24176	-1.40761	-0.0729
O	-1.52248	-3.33064	1.538356
H	-1.88683	-4.21317	1.675405
O	-0.01754	1.258874	-0.60865
H	-0.45733	4.839834	0.522923
H	-2.34636	3.540961	0.073848
H	-1.16	3.467175	-1.27033
H	-1.21557	1.537308	1.069638
H	-1.70156	-0.64955	-1.77024
H	-4.20931	0.6181	0.11743
Ti	1.13173	-0.13861	-0.07538
C	1.427589	-0.97155	2.219828
C	2.695508	-0.56902	1.749604
C	0.608629	0.184746	2.304993
H	1.101964	-1.98617	2.405584
C	2.661189	0.846239	1.543768
H	3.542006	-1.21802	1.571926
C	1.375292	1.307222	1.902202
H	-0.42221	0.198818	2.629617
H	3.476174	1.462962	1.191224
H	1.019217	2.32459	1.807561
C	1.41348	-0.17445	-2.54107
C	2.44249	0.648364	-2.00303
C	1.634444	-1.49674	-2.10526
H	0.570562	0.173224	-3.12074
C	3.299946	-0.17553	-1.24016
H	2.526649	1.71971	-2.12574
C	2.782739	-1.50237	-1.27461
H	0.984946	-2.3416	-2.28175
H	4.187683	0.144847	-0.71429
H	3.203333	-2.36652	-0.77777

XYZ coordinates of structure **8**

Symbol	X	Y	Z
C	-0.77239	2.226368	-1.09047
C	-2.20535	1.955853	-0.59421
C	-2.86625	0.642168	-1.06539
H	-3.07795	0.751157	-2.14034
C	-2.08554	-0.67706	-0.9175
C	-1.39123	-0.96656	0.456459
H	-1.46914	-0.07361	1.084194
C	-2.04301	-2.1	1.24573
H	-1.8269	-3.06471	0.764749
H	-3.13033	-1.95356	1.272585
O	0.125535	1.165013	-0.99423
O	-4.10797	0.582161	-0.34941
O	-3.05601	-1.68194	-1.29751
H	-2.59835	-2.50196	-1.51818
O	-0.0353	-1.28547	0.203276
O	-1.49886	-2.07068	2.570451
H	-1.85878	-2.81102	3.073307
O	-2.24825	2.076777	0.827051
H	-3.12874	1.776264	1.102452
H	-0.41247	3.10251	-0.52807
H	-0.84254	2.524798	-2.1495
H	-2.81887	2.765083	-1.02453
H	-1.28396	-0.65547	-1.65808
H	-4.5074	-0.27876	-0.54328
Ti	1.284234	0.045821	-0.07681
C	3.443749	-0.9986	-0.69952
C	2.442035	-1.93872	-1.01834
C	3.257787	0.14301	-1.53252
H	4.204243	-1.11411	0.059532
C	1.661923	-1.40308	-2.08225
H	2.26843	-2.88125	-0.51752
C	2.175099	-0.13309	-2.40773
H	3.85932	1.042246	-1.53056
H	0.787928	-1.86639	-2.51696
H	1.758274	0.553854	-3.13051
C	2.922639	1.133954	1.397547
C	1.841634	2.027028	1.256498
C	2.437786	-0.04218	2.043063
H	3.93208	1.297719	1.04711
C	0.691857	1.426702	1.850796
H	1.873518	2.991992	0.76697
C	1.067121	0.16114	2.348559
H	3.017585	-0.92136	2.290017
H	-0.30365	1.846817	1.86835
H	0.404197	-0.56671	2.796812

XYZ coordinates of structure **9**

Symbol	X	Y	Z
C	-0.77429	2.157264	0.096595
C	-2.2258	1.968583	0.582574
C	-2.83327	0.554655	0.416773
H	-3.92303	0.67215	0.480689
C	-2.55192	-0.09795	-0.96332
C	-2.279	-1.60922	-0.94571
H	-2.31176	-1.93709	-1.9972
C	-0.91738	-2.03165	-0.35889
H	-0.74364	-3.08029	-0.6466
H	-0.99045	-1.98945	0.730867
O	0.118555	1.205429	0.599477
O	-2.39286	-0.22742	1.53057
O	-3.74894	0.153627	-1.73542
H	-3.53555	0.097181	-2.67604
O	-3.28764	-2.31048	-0.20165
H	-4.13977	-2.13193	-0.62513
O	0.119277	-1.23019	-0.86096
O	-2.38902	2.392336	1.9291
H	-2.1987	1.621251	2.485307
H	-0.46923	3.159529	0.435499
H	-0.77711	2.174751	-1.00569
H	-2.83032	2.654836	-0.02607
H	-1.69657	0.368956	-1.45588
H	-2.90939	-1.048	1.520473
Ti	1.350997	-0.04351	-0.04189
C	2.920313	-1.56959	1.087711
C	3.14708	-0.27427	1.637123
C	1.616985	-1.97298	1.461484
H	3.622278	-2.15409	0.509459
C	1.977022	0.120433	2.321664
H	4.055629	0.30385	1.543711
C	1.023224	-0.92535	2.206174
H	1.14723	-2.90505	1.181518
H	1.806476	1.078785	2.791356
H	0.002436	-0.88562	2.558745
C	3.339041	0.046192	-1.49701
C	2.240841	-0.25028	-2.33133
C	3.145529	1.353554	-0.96216
H	4.17888	-0.60368	-1.29671
C	1.369746	0.871773	-2.32706
H	2.058457	-1.18966	-2.8335
C	1.940137	1.865295	-1.4977
H	3.812773	1.879406	-0.29375
H	0.420139	0.933509	-2.83937
H	1.514818	2.832526	-1.27066

XYZ coordinates of structure **10**

Symbol	X	Y	Z
C	-6.479	-0.71656	0.108354
H	-6.42357	-1.21649	1.080628
H	-6.50751	-1.47494	-0.68071
O	-7.6861	0.060973	0.144827
H	-7.94914	0.27791	-0.75918
C	-5.26844	0.19541	-0.07523
H	-5.3229	0.670803	-1.06684
C	-3.94072	-0.5662	-0.00771
H	-3.95798	-1.24463	0.858357
C	-2.72812	0.387121	0.20076
H	-2.63259	0.538223	1.285967
C	-1.42688	-0.21084	-0.34207
H	-1.44089	-0.10406	-1.43588
C	-0.17582	0.479685	0.205813
H	-0.14881	1.513246	-0.16156
H	-0.21011	0.513391	1.306622
O	0.94848	-0.27066	-0.20221
O	-5.26721	1.207359	0.941193
H	-6.18954	1.482933	1.059367
O	-3.88386	-1.32867	-1.21174
H	-3.10619	-1.90398	-1.13413
O	-2.86677	1.6507	-0.44716
H	-3.59714	2.10882	-0.00347
O	-1.38695	-1.60654	-0.00323
Ti	2.77029	0.037293	0.219659
O	2.489908	0.377801	2.052816
H	2.254154	-0.38119	2.601301
H	-0.45502	-1.85672	-0.11137
C	3.847822	-1.96375	1.166954
C	2.699623	-2.40356	0.469921
C	4.746438	-1.39985	0.22765
H	4.006234	-2.00628	2.236013
C	2.894678	-2.13346	-0.91215
H	1.811521	-2.83014	0.915768
C	4.159855	-1.52533	-1.06401
H	5.714463	-0.9755	0.454679
H	2.178307	-2.3107	-1.70221
H	4.601546	-1.20125	-1.99566
C	2.536519	2.466205	0.199823
C	3.886506	2.191878	0.552639
C	2.336245	2.034175	-1.13107
H	1.786565	2.877309	0.860356
C	4.512615	1.580722	-0.55404
H	4.328919	2.360351	1.524147
C	3.544648	1.459526	-1.59502
H	1.40835	2.073927	-1.6842
H	5.541571	1.253227	-0.60353
H	3.707471	1.036381	-2.57664

XYZ coordinates of structure **11**

Symbol	X	Y	Z
Ti	1.91059	-0.47323	0.121079
C	1.675892	0.230615	2.447912
C	2.766995	-0.67875	2.425087
C	2.048245	1.386252	1.71515
H	0.716001	0.066533	2.919629
C	3.796974	-0.10862	1.649224
H	2.794962	-1.66129	2.876742
C	3.345439	1.171287	1.198498
H	1.412108	2.238772	1.516489
H	4.756329	-0.56177	1.443905
H	3.908266	1.863626	0.586958
C	1.848871	-0.42726	-2.36134
C	2.978872	0.314647	-1.92772
C	2.023399	-1.76952	-1.96982
H	0.977124	-0.02042	-2.85394
C	3.882029	-0.59714	-1.31437
H	3.140751	1.375181	-2.06851
C	3.28263	-1.87788	-1.31683
H	1.294854	-2.56132	-2.06701
H	4.853761	-0.34784	-0.91393
H	3.687088	-2.77615	-0.87125
O	-0.26576	3.374389	0.303474
C	-0.15077	2.649556	-0.91784
C	-0.63736	1.190916	-0.83484
H	-0.69846	3.159414	-1.71909
H	0.912661	2.642048	-1.17585
C	-2.01316	1.085595	-0.1319
H	-0.76026	0.847352	-1.8797
O	0.259389	0.352959	-0.16198
C	-2.68614	-0.28432	-0.38048
O	-2.79914	2.174808	-0.61671
H	-1.83795	1.189168	0.950021
C	-4.03946	-0.42246	0.334925
H	-2.85979	-0.38275	-1.46625
O	-1.897	-1.36336	0.102987
C	-4.66674	-1.79655	0.128485
O	-4.92683	0.585359	-0.17196
H	-3.88579	-0.2677	1.413525
H	-0.95102	-1.14046	0.018711
O	-5.96067	-1.72738	0.750602
H	-4.04091	-2.56643	0.58908
H	-4.76718	-1.9986	-0.94704
H	-5.81511	0.37372	0.153426
H	-6.45747	-2.53096	0.557199
O	1.208551	-2.16889	0.58922
H	0.852735	-2.26675	1.480999
H	-3.73924	1.965158	-0.47085
H	-1.20917	3.551327	0.433147

XYZ coordinates of structure **12**

Symbol	X	Y	Z
Ti	-1.5311	-0.43591	-0.07905
C	-1.91178	0.090046	-2.45509
C	-2.89594	-0.86905	-2.10186
C	-2.18367	1.278775	-1.73252
H	-1.08373	-0.06108	-3.13439
C	-3.74784	-0.29246	-1.13627
H	-2.96494	-1.88461	-2.46777
C	-3.30017	1.044192	-0.90162
H	-1.59113	2.181524	-1.75884
H	-4.59581	-0.77731	-0.67409
H	-3.75021	1.757282	-0.22447
C	-0.89771	-0.07258	2.27545
C	-2.16255	0.532078	2.058952
C	-1.03476	-1.46424	2.092805
H	0.018517	0.454643	2.497743
C	-3.09789	-0.50924	1.800118
H	-2.3794	1.590254	2.117153
C	-2.39917	-1.73672	1.796965
H	-0.23899	-2.19497	2.099786
H	-4.15586	-0.37749	1.625755
H	-2.81067	-2.70849	1.563373
O	0.842182	4.533692	0.476738
C	0.566913	3.145661	0.605894
C	1.637748	2.307219	-0.0884
H	0.521787	2.85841	1.669087
H	-0.41098	2.969162	0.157046
C	1.386461	0.783782	0.049989
H	1.655997	2.572899	-1.15727
O	2.86471	2.691809	0.534255
C	2.340451	-0.03873	-0.85211
O	0.077979	0.480346	-0.344
H	1.563261	0.527751	1.10689
C	2.386471	-1.54032	-0.54162
H	1.965085	0.067827	-1.87942
O	3.670089	0.501572	-0.78659
C	2.918745	-1.8802	0.85119
O	3.269127	-2.08946	-1.53369
H	1.3812	-1.96427	-0.64945
H	4.234677	-0.09852	-1.2982
O	3.106765	-3.30385	0.866614
H	2.194201	-1.58302	1.619192
H	3.867826	-1.36161	1.033143
H	3.502148	-2.98235	-1.23663
H	3.625199	-3.55343	1.640727
O	-0.95662	-2.1873	-0.53437
H	-0.84421	-2.35773	-1.47765
H	1.779708	4.649234	0.693348
H	3.574686	2.181989	0.111004