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Supplementary Information

Fischer-Helferich Glycosidation Mechanism of Glucose to Methyl Glycosides over Al-Based Catalysts in Alcoholic Media

Mengting Yu[a], Yao Li[b], Cheng Zhang[c], Huaying Luo[c], Chengsheng Ge[a], Xiaobin Chen[a], Lanlan Fu[a], Zhaoyang Ju[a,c] and Xiaoqian Yao*[b]*

[a]College of Chemical & Material Engineering, Quzhou University, Quzhou 324000, P. R. China

[b]CAS Key Laboratory of Green Process and Engineering, Beijing Key Laboratory of Ionic Liquids Clean Process, State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, P. R. China

[c]Xianhe Co., Ltd, Quzhou 324000, P. R. China

**Corresponding author: Zhaoyang Ju, Email: jzy@qzc.edu.cn; Xiaoqian Yao, Email: xqyao@ipe.ac.cn;*

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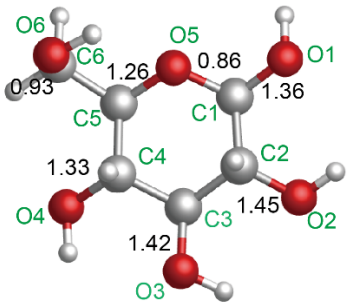

Figure S 1 The Mayer bond analysis of C-O bond of glucose calculated at M06-2X-D3/6-311+G** level.

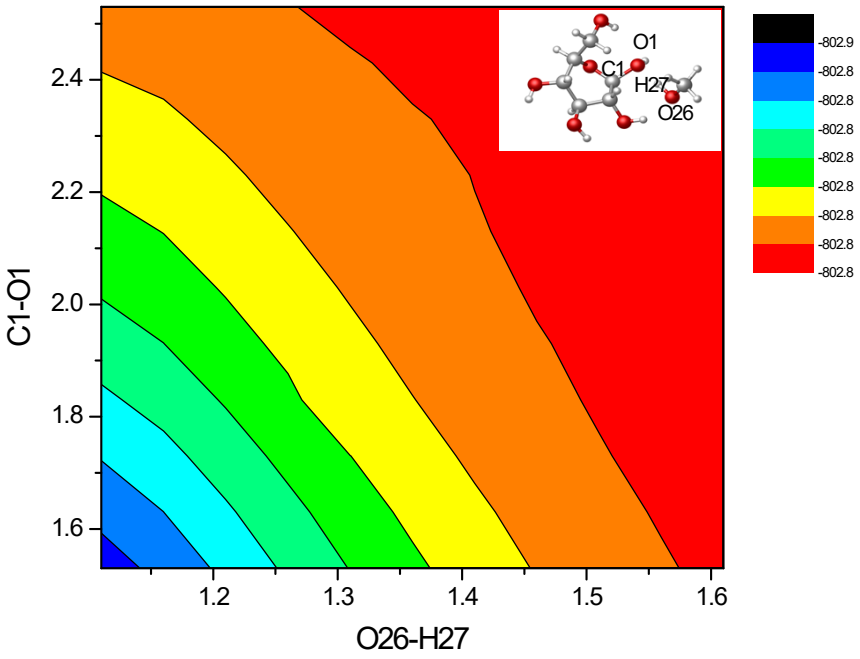

Figure S 2 Potential energy 3D surface scan for the direct etherification reaction along with the increasing both C1-O1 (the steps and step size are 10 and 0.10 Å) and O26-H27 bond (the steps and step size are 10 and 0.05 Å).

Table S 1 The NPA charge of IM1 and IM2 calculated in M06-2X-D3/6-311+G** level. (unit a.u.)

		Methoxyl	**1**	**2**	**3**	**4**	**5**	**6**
IM1	O(OH)	-	-0.552	-0.767	-0.773	-0.760	-0.773	-0.773
	H(OH)	-	-	0.496	0.502	0.490	0.491	0.478
	C	-	0.427	-0.001	0.094	0.091	0.087	-0.055
	H	-	0.164	0.212	0.172	0.187	0.191	0.169
	H	-	-	-	-	-	-	0.201
IM2	O(OH)	-0.601	-0.777	-0.763	-0.778	-0.776	-0.781	-0.763
	H(OH)	-	0.477	0.499	0.499	0.495	0.493	0.473
	C	-0.208	0.430	0.073	0.078	0.098	0.074	-0.054
	H	0.189	0.166	0.173	0.185	0.197	0.212	0.173
	H	0.171	-	-	-	-	-	0.176
	H	0.170	-	-	-	-	-	-

The three-membered ring closure reaction

The presence of hydroxyls provides possible ways to dehydrate three-membered ring products with the neighboring hydrogen with hydroxyls. As mentioned before, since there are six hydroxyls in IM2, it provides the possibility to undergo the three-membered ring closure reaction through two adjacent C, O atoms (O1-C2, O2-C3, O3-C4, O4-C5, and O5-C6), and oppositely close loop (O2-C1, O3-C2, O4-C3, O5-C4, and O6-C5). For the three-membered ring closure reaction, the computed energy profile of the ring-closure reaction is shown in Figure S3. The energy barrier of the three-membered ring closure reaction is ranging from 53.6 to 80.3 kcal/mol. They are endothermic by about 12.3~22.7 kcal/mol. The energy barrier of various ways to render the same product, taking O1-C2 and O2-C1 for example, is also different. O3-C4 is not preferable with an 80.3 kcal/mol energy barrier. While the energy barrier of O1-C2 (72.3 kcal/mol) is relatively higher than that of O2-C1 (53.6 kcal/mol). So, the lowest energy barrier for the three-membered ring closure reaction is the O2-C1 way.

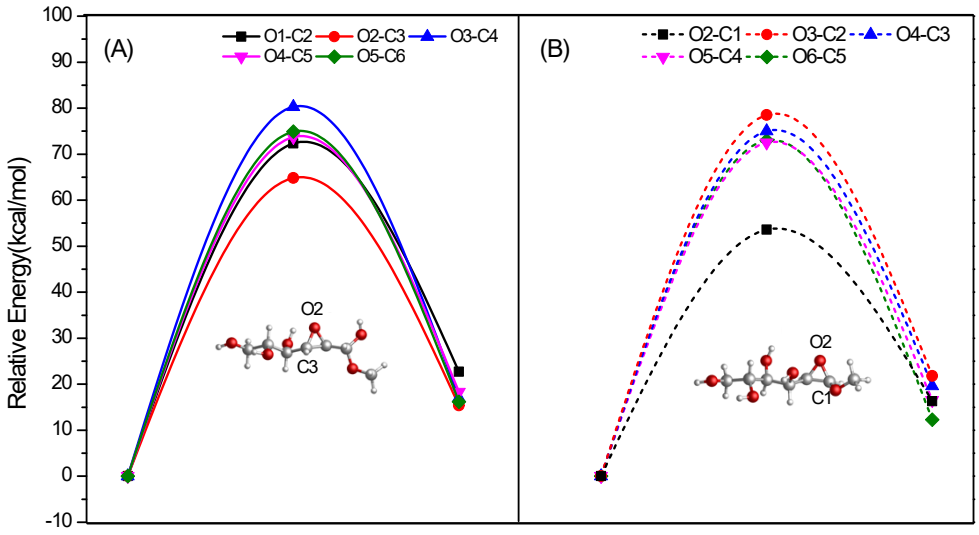

Figure S3 The potential energy (kcal/mol) profile of ring-closure reaction for the three-membered ring with different ways (A)O1-C2, O2-C3, O3-C4, O4-C5 and O5-C6 (B) O6-C5, O5-C4, O4-C3, O3-C2, and O2-C1.

The four-membered ring closure reaction

To compare the ability to generate differently membered ring products, the possible routes in four-membered ring closure reactions were also probed. There are eight kinds of ways for the four-membered ring closure reaction, whose computed energy profiles are displayed in Figure S4. The energy barriers for the four-membered ring closure reactions (O1-C3, O2-C4, O3-C5, O4-C6, O6-C4, O5-C3, O4-C2, and O3-C1) are 77.1, 79.9, 92.3, 81.3, 82.7, 88.2, 82.2 and 57.7 kcal/mol, respectively. The energy barrier of the four-membered ring closure reaction is in the range of 57.7~92.3 kcal/mol. These processes are endothermic with about 13.0~19.1 kcal/mol. Compared with the different ways for the four-membered ring closure reaction, it is hard to achieve the O3-C5 ring closure reaction due to the relatively high energy barrier (92.3 kcal/mol), and the O3-C1 is easier to undergo with 57.7 kcal/mol energy barrier.

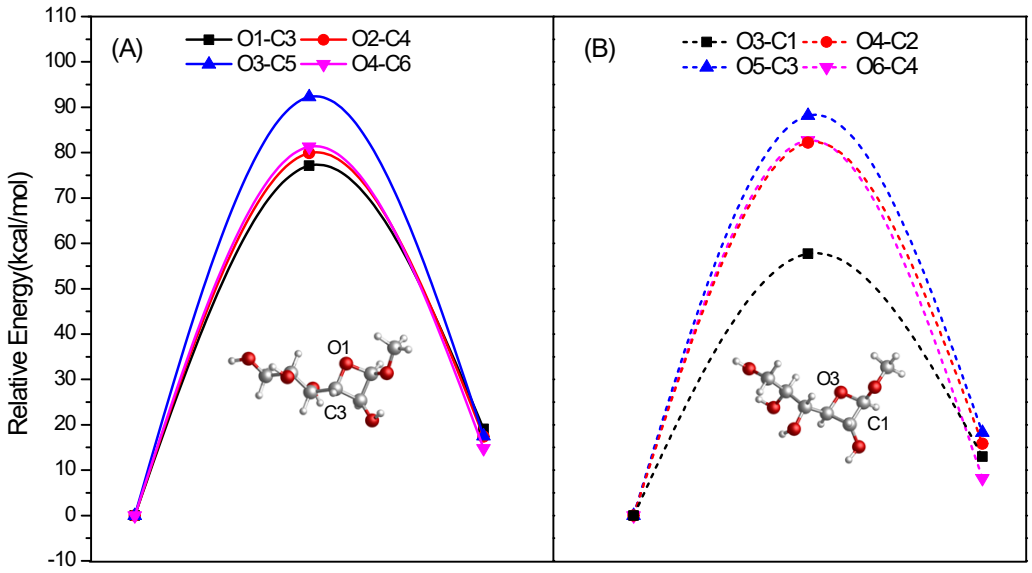

Figure S4 The potential energy (kcal/mol) profile of ring-closure reaction for the four-membered ring with different ways (A) O1-C3, O2-C4, O3-C5, and O4-C6 (B) O6-C4, O5-C3, O4-C2, and O3-C1.

The five-membered ring closure reaction

In the conversion of glucose in methanol media, there are some important intermediates, such as methyl fructoside, 5-methoxymethylfurfural (5-MMF) which have five-membered ring structures.[1] Some studies reported that the formation of methyl fructoside is the etherification reaction of fructose.[2] The methyl fructoside and the product of O5-C2/O2-C5 ring closure are isomers where the hydroxyl is located in C2 and C1, respectively. Hydroxyl isomerization is very common in the conversion of glucose to valuable biofuels.[3, 4] Actually, it also makes a possible route to generate methyl fructoside from glucose in the methanol solvent. Furthermore, it provides potential reaction pathways to generate 5-MMF which is another important intermediate found in the experiments.[5] The dehydration of the product of O5-C2 and O2-C5 rendering the 5-MMF was described in Figure S5. Besides, methyl furanose can come from the product of O4-C1 and C1-O4 which is also detected by the GC-MS experiments.[5]

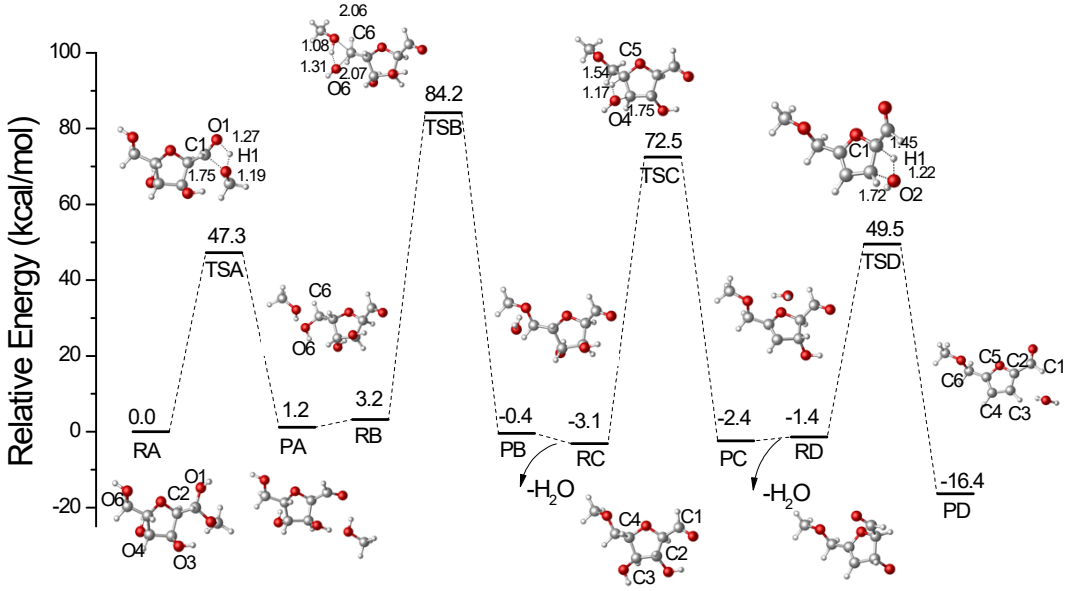

Figure S5 The computed energy (kcal/mol) profile with the structures of reactants, transition states, and products for the dehydration of the product of O5-C2 and O2-C5 to make 5-MMF.

Considering all the possible ways for the five-membered ring, the energy profile of five-membered ring closure reactions was calculated and listed in Figure S6. The energy barrier of the five-membered ring closure reaction ranges between 65.1 and 76.3 kcal/mol. And O1-C4, O2-C5, O3-C6, O4-C1, and O5-C2 are exothermic with -1.3, -4.6, -0.8, -3.5, and -5.5 kcal/mol, only O6-C3 is endothermic with 1.8 kcal/mol. The energy barriers for the O5-C2 and O2-C5 are 74.7 and 70.9 kcal/mol, respectively. Compared with the different ways of the five-membered ring closure reaction, O4-C1 has the lowest energy barrier with 65.1 kcal/mol.

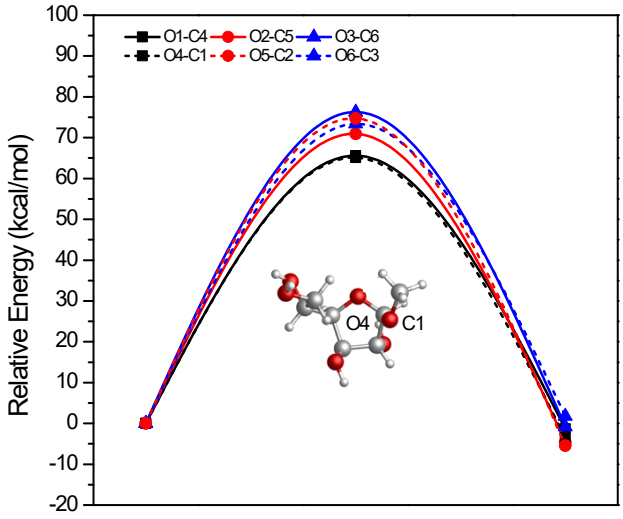

Figure S6 The potential energy (kcal/mol) profile of ring-closure reaction five-membered ring.

The six-membered ring closure reaction

As one of the important intermediates, MDGP has a six-membered ring structure.[2, 5] There are four kinds of ways to make the six-membered ring closure reaction which are O1-C5, O2-C6, O6-C2, and O5-C1. As shown in Figure S7, the energy barriers of six-membered ring closure reactions are ranging from 52.8 to 71.1 kcal/mol. All the routes are exothermic with about -5.4~12.0 kcal/mol. As the number of formed rings increases, it gradually changes from endothermic to exothermic in thermodynamics. To obtain MDGP, there are two kinds of ways which are O5-C1 and O1-C5. It is easier to proceed through O5-C1 (52.8 kcal/mol) which is lower than O1-C5 (70.3 kcal/mol). The H5 of O5 transfers to O1H1 and the O5-C1 bond will be formed to produce MDGP based on the pathway with the lowest energy barrier.

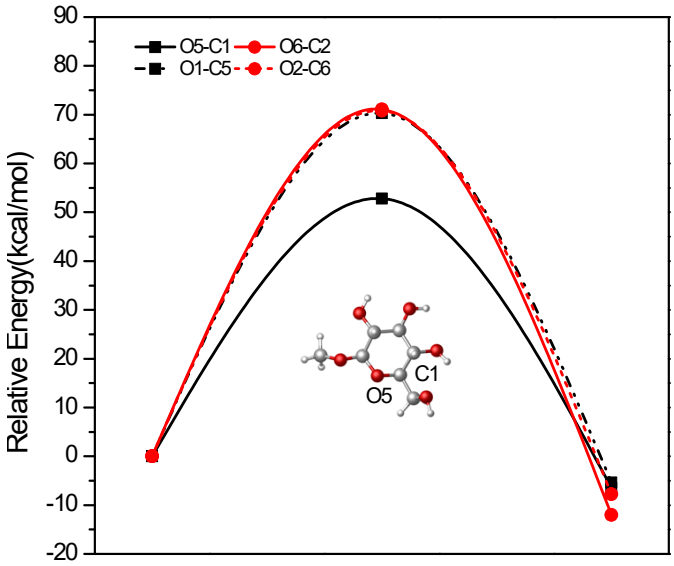

Figure S7 The potential energy (kcal/mol) profile of ring-closure reaction for the six-membered ring.

Table S 2 The XYZ coordinates of all TSs which includes ring-opening, addition and ring-closure reaction without catalysts.

TS1				TS2			
C	-1.029023	0.960982	-0.223289	C	-0.064377	-0.158583	0.930064
C	-1.528735	-0.373979	0.298188	C	0.958040	-0.325737	-0.208774
C	-0.917906	-1.557246	-0.446686	C	2.327464	-0.154673	0.443906
C	1.293176	0.133835	-0.714641	C	-2.066960	-0.060872	-0.712139
C	0.451716	1.120560	0.087814	C	-1.483666	-0.627127	0.587246
H	-1.266511	-0.471039	1.358540	H	0.868218	-1.347090	-0.603670
H	-1.189750	1.020645	-1.310877	H	0.270751	-0.810469	1.755350
H	1.377592	0.518350	-1.735524	H	-1.564301	-0.551019	-1.551618
H	0.601634	0.949326	1.162277	H	-2.124835	-0.313444	1.419616
H	-1.358278	-1.703033	-1.441870	H	2.648863	-1.059614	0.987931
O	0.657035	-1.150997	-0.792611	O	-1.818369	1.326833	-0.854653
O	0.910139	2.402293	-0.278096	O	-1.511264	-2.038943	0.429319
H	0.305393	3.043437	0.112099	H	-1.529546	-2.451166	1.295766
O	-1.688230	2.027833	0.424921	O	-0.143794	1.178002	1.367268
H	-2.634315	1.846566	0.400641	H	0.770683	1.507215	1.435537
O	-2.936103	-0.381023	0.125069	O	0.817288	0.605537	-1.244625
H	-3.311660	-1.112882	0.622847	H	0.054048	1.177859	-1.070552
C	2.682686	-0.047566	-0.122882	C	-3.557435	-0.337278	-0.800650
H	3.287746	-0.674837	-0.784489	H	-3.925210	0.075280	-1.745082
H	3.144752	0.938987	-0.054398	H	-3.734483	-1.417163	-0.774659

O	2.625494	-0.577708	1.185753	O	-4.168047	0.309692	0.308717
H	2.593843	-1.536324	1.148490	H	-5.108842	0.397581	0.149331
O	-0.554001	-2.599106	0.245360	O	2.575949	1.017731	1.013706
H	0.623394	-2.009048	-0.031936	H	-2.031833	1.763943	-0.021881
				C	4.588619	-0.752663	-0.571457
				H	4.358800	-1.785714	-0.827240
				H	4.965018	-0.685796	0.452832
				H	5.321263	-0.356198	-1.271588
				O	3.393834	0.023807	-0.710070
				H	3.386524	0.976123	-0.116535
Ring-closure reaction							
Three numbered-ring closure reaction							
TS(O1-C2)				TS(O2-C3)			
C	0.264019	0.782374	0.279446	C	-0.118740	0.227271	-0.260943
C	1.372549	0.580319	-0.690727	C	-1.285979	-0.673296	-0.332852
C	2.425058	-0.432997	-0.395971	C	-2.586679	-0.032476	0.131809
C	-2.191985	0.155256	-0.071463	C	2.365519	0.244362	0.085534
C	-0.769181	-0.372728	-0.000950	C	1.170944	-0.270078	-0.728558
H	1.295679	1.070262	-1.651701	H	-1.437245	-0.995768	-1.380340
H	0.661380	0.650448	1.289615	H	-0.155418	1.253187	0.095394
H	-2.287634	0.832977	-0.928475	H	2.323105	-0.222043	1.077490
H	-0.693788	-1.074454	0.834369	H	1.202616	0.304406	-1.691251
O	-2.434220	0.862839	1.138499	O	2.232757	1.642334	0.177633
O	-0.518406	-1.043706	-1.223258	O	1.237511	-1.626969	-0.974672
H	0.201527	-1.666754	-1.044685	H	0.532285	-2.029751	-0.398774
O	-0.257863	2.084497	0.105006	O	-0.119852	0.131881	2.189578
H	-1.045153	2.152750	0.662895	H	0.575957	0.057836	2.845532
C	-3.194712	-0.973526	-0.222790	C	3.672414	-0.133445	-0.585934
H	-3.068978	-1.446921	-1.198698	H	3.780704	-1.220151	-0.601490
H	-3.036563	-1.713945	0.570918	H	3.678732	0.252029	-1.613402
O	-4.471698	-0.360439	-0.090786	O	4.681583	0.494372	0.193536
H	-5.157720	-1.030218	-0.105475	H	5.543950	0.316824	-0.186737
O	1.778180	-1.628191	0.087270	O	-2.931438	0.920867	-0.814367
C	2.708006	-2.498620	0.711597	C	-4.098311	1.650742	-0.475119
H	3.217845	-1.986295	1.529058	H	-3.979066	2.132880	0.502197
H	2.144021	-3.348265	1.093571	H	-4.229748	2.411787	-1.241982
H	3.451309	-2.851256	-0.013188	H	-4.970066	0.993859	-0.450972
O	3.089842	0.263024	0.518602	H	3.082342	1.990874	0.471557
H	2.924840	2.013397	0.205344	O	-0.862155	-1.687584	0.510899
H	-3.390066	0.971294	1.215344	H	-0.382743	-0.775152	1.901782
H	3.009727	-0.720466	-1.288162	H	-2.449467	0.441737	1.117348
O	2.365619	2.538008	-0.402635	O	-3.574841	-1.023514	0.212952
H	1.679420	2.978732	0.112824	H	-3.139453	-1.802126	0.585561
TS(O3-C4)				TS(O4-C5)			

C	0.179743	-0.272083	0.042667	C	-0.155592	0.068369	-0.051817
C	1.332404	0.329114	-0.754340	C	-1.395166	-0.747958	-0.402067
C	2.632145	0.115483	0.005850	C	-2.653383	-0.078876	0.135282
C	-2.338024	-0.633628	-0.013991	C	2.301113	0.200992	-0.757112
C	-1.153320	0.217825	-0.349207	C	1.137577	-0.676809	-0.506250
H	1.422148	-0.180622	-1.724194	H	-1.493314	-0.792064	-1.497502
H	0.223067	-1.369185	-0.035984	H	-0.256087	1.032437	-0.561210
H	-2.096906	-1.303440	0.816988	H	2.859335	0.176621	-1.686128
H	-1.293808	1.014224	-1.070938	H	0.913518	-1.308086	-1.375942
O	-2.474786	-1.357756	-1.226644	O	4.059966	-1.044268	-0.323467
O	-1.389496	2.019338	0.887513	O	1.740319	-1.346857	0.540318
H	-2.075743	2.043335	1.560143	H	3.344871	-1.462560	0.229401
O	0.094307	0.166556	1.357595	O	-0.064745	0.307206	1.329698
H	-0.622274	1.443128	1.286720	H	0.465476	-0.445624	1.655119
C	-3.613262	0.145730	0.280178	C	2.579829	1.342805	0.137777
H	-3.587955	0.528342	1.303534	H	1.915247	2.138399	-0.248689
H	-3.706815	0.979180	-0.424673	H	2.267519	1.119544	1.158440
O	-4.669507	-0.788589	0.115969	O	3.937399	1.722363	0.040175
H	-5.515035	-0.338261	0.162026	H	4.070404	2.533167	0.536708
O	2.888496	-1.251927	-0.009690	O	-2.802384	1.128366	-0.544596
C	3.954840	-1.642563	0.827116	C	-3.867053	1.921428	-0.067347
H	3.787188	-1.301124	1.855875	H	-3.760520	2.109927	1.008372
H	3.992876	-2.730207	0.813538	H	-3.827476	2.869309	-0.601111
H	4.910167	-1.252598	0.459955	H	-4.833273	1.445715	-0.262679
H	-3.397041	-1.642475	-1.275028	H	4.586514	-0.470917	0.243790
O	1.078713	1.704237	-0.925818	O	-1.254948	-2.033359	0.149097
H	1.900010	2.110774	-1.221119	H	-2.094731	-2.487328	0.024860
H	2.521888	0.475787	1.036574	H	-2.553487	0.097308	1.214364
O	3.632058	0.858853	-0.665791	O	-3.730403	-0.961822	-0.112391
H	4.292804	1.158166	-0.038122	H	-4.369578	-0.908594	0.600743
TS(O5-C6)				TS(O2-C1)			
C	0.168309	-0.195082	-0.209640	C	0.080572	-0.207908	-0.372677
C	1.285024	0.827464	-0.402197	C	1.211845	0.731888	-0.813166
C	2.667128	0.273607	-0.041521	C	2.558493	0.076986	-0.740157
C	-2.204905	0.273975	0.532893	C	-2.365675	-0.237364	0.196275
C	-1.219779	0.379140	-0.636136	C	-1.271728	0.498344	-0.571465
H	1.300248	1.138392	-1.448086	H	1.062530	0.926218	-1.901975
H	0.400404	-1.066897	-0.827551	H	0.080366	-1.102130	-1.009947
H	-1.877433	0.966578	1.329446	H	-2.239560	-0.000676	1.259767
H	-1.608416	-0.235377	-1.454128	H	-1.497874	0.440829	-1.649987
O	-2.426959	-1.017512	0.970069	O	-2.210456	-1.636688	-0.014895
O	-1.220112	1.701677	-1.126833	O	-1.300760	1.838404	-0.149952
H	-0.679020	2.241891	-0.532986	H	-0.371796	2.125642	0.006317
O	0.194806	-0.571600	1.163065	O	0.324428	-0.567741	0.970116

H	-0.617185	-1.077883	1.357075	H	-0.291724	-1.277230	1.181626
C	-3.580988	0.541350	0.132605	C	-3.743552	0.211873	-0.237072
H	-4.347467	0.513226	0.897602	H	-3.858232	1.277383	-0.021569
H	-3.877707	0.795305	-0.877985	H	-3.860941	0.035966	-1.313707
O	-4.344206	-1.473426	-0.602946	O	-4.668988	-0.584270	0.498964
H	-4.134738	-1.835953	-1.468295	H	-5.563241	-0.370161	0.227664
O	2.845970	-0.891748	-0.789714	O	2.713843	-1.145842	-0.481215
C	4.162513	-1.408386	-0.714016	C	4.035184	-1.620215	-0.145033
H	4.427058	-1.652522	0.317185	H	4.177348	-1.381884	0.907975
H	4.184791	-2.309549	-1.323847	H	4.029570	-2.690625	-0.324314
H	4.883428	-0.683661	-1.109989	H	4.776559	-1.117266	-0.766626
O	2.806661	0.064815	1.335441	O	3.072270	0.838289	1.431313
H	2.057266	-0.483801	1.616753	H	3.730018	1.501908	1.653128
H	-3.591269	-1.694718	0.007270	H	-3.028472	-2.052353	0.280672
H	3.431757	1.017541	-0.299526	H	3.434484	0.689353	-0.952294
O	1.036410	1.992938	0.370569	O	1.333915	1.870610	-0.074234
H	1.243916	1.773875	1.287928	H	2.276110	1.371307	1.082279
TS(O3-C2)				TS(O4-C3)			
C	-0.039571	-0.390856	-0.171716	C	0.064215	0.179385	-0.307707
C	1.217148	0.236137	-0.614690	C	1.222584	0.912403	0.227933
C	2.472231	-0.563326	-0.422533	C	2.359415	-0.123241	0.432223
C	-2.506671	-0.297989	0.104997	C	-1.245269	0.160158	0.374354
C	-1.314597	0.300400	-0.635299	H	1.575119	1.607836	-0.546432
H	1.272788	1.090504	-1.277460	O	2.654411	-0.667840	-0.807220
H	-0.096428	-1.453911	-0.452395	C	3.663429	-1.660184	-0.772236
H	-2.294651	-0.271412	1.180764	H	3.393156	-2.462670	-0.074877
H	-1.444908	0.111420	-1.711082	H	3.739583	-2.069096	-1.777176
O	-2.622352	-1.630989	-0.354367	H	4.625510	-1.227777	-0.485683
O	-1.169437	1.685776	-0.375357	O	0.925593	1.533477	1.439360
H	-1.781299	2.182921	-0.921567	H	1.712217	2.014221	1.714372
O	0.268336	-0.188957	1.170675	H	2.040666	-0.904894	1.138444
H	0.937122	1.457467	1.257970	O	3.435174	0.598425	0.974053
C	-3.795052	0.457984	-0.167296	H	3.859742	0.090806	1.669062
H	-3.735060	1.465709	0.256601	H	0.275303	-0.434427	-1.175271
H	-3.961394	0.517087	-1.252332	O	-0.370342	1.632109	-2.051072
O	-4.826654	-0.294439	0.454675	H	-0.819729	1.385993	-2.863769
H	-5.680379	0.087684	0.244207	O	-1.716240	1.406469	0.004593
O	3.543729	0.322828	-0.215454	H	-1.083334	1.759511	-1.331087
C	4.801257	-0.335137	-0.211748	C	-2.115936	-1.003341	-0.082099
H	4.979141	-0.823340	-1.176960	H	-2.208351	-0.969641	-1.177364
H	5.555741	0.432355	-0.051841	C	-3.509067	-0.886678	0.528556
H	4.846776	-1.079267	0.585343	H	-4.085691	-1.791574	0.310033
H	-3.428985	-1.992977	0.027478	H	-3.406996	-0.810080	1.620921
O	1.568752	1.942011	0.683998	H	-1.078655	0.069851	1.462182

H	2.454885	1.685226	0.968796	O	-1.426435	-2.173285	0.337490
H	2.619540	-1.065698	-1.401198	H	-1.898191	-2.949924	0.026547
O	2.373860	-1.532297	0.545529	O	-4.212092	0.203661	-0.011798
H	1.658765	-1.218504	1.155789	H	-3.597121	0.956717	0.000698
TS(O5-C4)				TS(O6-C5)			
C	0.163269	-0.098932	-0.156727	C	0.009494	0.875512	-0.045865
C	1.243934	-0.000023	0.921152	C	1.416902	0.931418	-0.646244
C	2.647155	-0.163233	0.338424	C	2.436837	0.031998	0.045249
C	-2.395498	0.080969	-0.477351	C	-2.130117	-0.496004	-0.500832
C	-1.223163	0.090851	0.388373	C	-0.662165	-0.497022	-0.215778
H	1.188141	0.992817	1.365834	H	1.367503	0.675048	-1.710182
H	0.352867	0.628020	-0.950328	H	0.087179	1.075581	1.026744
H	-2.128247	0.048435	-1.542589	H	-2.470103	0.201559	-1.260821
O	-2.887649	1.314551	-0.058454	H	-0.432677	-1.122882	0.649647
O	0.052586	-1.426472	-0.663621	O	-2.502501	1.145161	1.180834
H	0.916333	-1.689256	-1.007407	O	-0.307429	-1.165636	-1.425662
C	-3.434058	-1.009971	-0.165404	H	0.529092	-1.618424	-1.241535
H	-3.170119	-1.956678	-0.638416	O	-0.701379	1.917950	-0.681039
O	2.813409	0.816756	-0.628081	H	-1.479704	2.078375	-0.120791
C	4.121337	0.896197	-1.158163	C	-3.134937	-1.441779	-0.004518
H	4.361433	0.010890	-1.754786	H	-3.509688	-2.066671	-0.830114
H	4.152014	1.773506	-1.800296	H	-2.728247	-2.102980	0.775318
H	4.859359	1.011966	-0.355128	O	-4.057267	-0.511499	0.435052
O	2.744135	-1.469393	-0.209598	H	-3.348679	0.489282	0.994875
H	3.645023	-1.796604	-0.163379	O	2.051860	-1.304074	-0.082420
H	-1.706122	2.177961	0.266223	C	3.000382	-2.218393	0.456294
H	3.392418	-0.055237	1.138625	H	3.097394	-2.077386	1.533188
O	1.026803	-0.941595	1.943659	H	2.631176	-3.219376	0.241378
H	0.993199	-1.812690	1.529472	H	3.974395	-2.076297	-0.023114
H	-1.392163	0.019446	1.458078	O	2.534223	0.335064	1.413000
O	-0.738307	2.284465	0.593847	H	2.684175	1.286494	1.475728
H	-0.802985	2.626484	1.490451	H	-2.280556	1.112396	2.114899
H	-3.491187	-1.147134	0.923231	H	3.414982	0.179423	-0.437437
O	-4.661780	-0.575348	-0.682180	O	1.935497	2.236198	-0.468074
H	-4.701388	0.369218	-0.465986	H	1.221348	2.846164	-0.691145
Four numbered-ring closure reaction							
TS(O1-C3)				TS(O2-C4)			
C	0.335467	0.105012	-0.029288	C	-0.252641	-0.598789	-0.044209
C	1.446970	0.914561	0.571701	C	-1.250444	-0.118410	-1.097491
C	2.610873	-0.065597	0.459411	C	-2.670239	-0.063035	-0.529772
C	-2.209455	-0.210593	-0.016903	C	2.315024	-0.456374	0.084354
C	-1.006951	0.723857	-0.089174	C	1.068707	-0.268076	-0.673069
H	1.231547	1.062871	1.632192	H	-1.281857	-0.823384	-1.946091
H	0.554155	-0.646221	-0.776529	H	-0.403121	0.047659	0.824589

H	-2.366232	-0.447918	1.039397	H	2.477624	-1.547488	-0.030508
H	-0.952293	1.089636	-1.143000	O	2.164843	-0.199183	1.455106
O	-1.897382	-1.372429	-0.757863	O	-0.273631	-1.965675	0.324578
O	-1.225231	1.787259	0.788903	H	0.003295	-2.045890	1.243988
H	-0.547881	2.457096	0.632494	C	3.556837	0.231726	-0.481358
O	-0.417088	-1.489055	1.780063	H	3.690406	-0.026138	-1.533976
H	-0.755957	-2.157635	1.174969	H	3.421484	1.315692	-0.395809
C	-3.453041	0.457599	-0.576980	O	4.701609	-0.204759	0.204316
H	-3.723216	1.313576	0.046540	H	4.538739	-0.081072	1.145788
H	-3.261542	0.793229	-1.604492	O	-2.607400	0.574759	0.713616
O	-4.454495	-0.549506	-0.560741	C	-3.877805	0.919163	1.231340
H	-5.271420	-0.204737	-0.926257	H	-4.507473	0.032583	1.343114
O	3.034104	0.047072	-0.907683	H	-3.713700	1.379078	2.204512
C	4.033435	-0.896714	-1.235748	H	-4.377438	1.638439	0.572489
H	3.673951	-1.912748	-1.054297	O	-3.222586	-1.350280	-0.425243
H	4.271376	-0.768103	-2.290897	H	-2.564118	-1.926379	-0.017287
H	4.937570	-0.724016	-0.638571	H	1.774419	0.691926	1.497164
O	2.001297	-1.214265	0.765820	H	-3.321250	0.496450	-1.209675
H	0.553782	-1.565235	1.700510	O	-0.691193	1.087564	-1.440354
H	-2.734747	-1.811021	-0.950855	O	0.962810	1.905606	0.141950
H	3.471572	0.187360	1.100334	H	1.407856	2.695711	-0.176638
O	1.500438	2.179777	-0.057365	H	1.122109	-0.230685	-1.757509
H	2.042403	2.054279	-0.848730	H	0.120765	1.722008	-0.494667
TS(O3-C5)				TS(O4-C6)			
C	-0.196735	0.013809	-0.703730	C	0.249179	-0.483745	-0.251313
C	-0.978532	-0.872720	0.274031	C	1.052600	0.615023	0.467724
C	-2.359636	-0.313840	0.601979	C	2.533253	0.276583	0.533749
C	1.890873	0.437114	0.255860	C	-2.209873	-0.920109	-0.785771
C	1.266371	-0.424425	-0.827077	C	-1.087891	0.101130	-0.734298
H	-0.441346	-0.948304	1.229524	H	0.680940	0.655708	1.498951
H	-0.724804	-0.014810	-1.662622	H	0.808049	-0.848130	-1.120564
H	1.387376	0.444947	1.217022	H	-1.946811	-1.964792	-1.009846
H	1.655883	-0.073865	-1.792408	H	-0.912397	0.524985	-1.734249
O	2.077731	2.406804	-0.448215	O	-3.230764	-0.548156	-1.685573
O	1.538858	-1.805783	-0.664876	O	-1.630466	1.044283	0.144740
H	2.443078	-1.929588	-0.350123	H	-3.084783	1.328635	0.762135
O	0.008247	1.300550	-0.220311	O	-0.005628	-1.569199	0.641596
H	1.061761	2.157362	-0.544572	H	0.840649	-1.830273	1.024543
C	3.400800	0.444350	0.358184	C	-2.707196	-0.870210	0.628247
H	3.866196	0.547621	-0.621748	H	-3.713366	-1.214908	0.827248
O	-2.899344	0.247833	-0.557604	H	-1.993379	-0.873737	1.439166
C	-4.238600	0.653335	-0.420600	O	-3.897038	0.957524	1.195849
H	-4.327045	1.536832	0.221728	H	-4.662125	1.216520	0.674352
H	-4.603225	0.910125	-1.413864	O	3.021483	0.124033	-0.758563

H	-4.856797	-0.159054	-0.013876	C	4.426227	0.065018	-0.844825
O	-2.240919	0.608372	1.655232	H	4.820156	-0.867994	-0.423921
H	-3.101548	0.730550	2.061986	H	4.685756	0.101801	-1.901253
H	2.456572	2.521761	-1.326338	H	4.887112	0.919806	-0.334564
H	-2.993159	-1.158631	0.914754	O	2.643189	-0.925817	1.282899
O	-1.192057	-2.155126	-0.283422	H	3.548923	-1.060662	1.569276
H	-0.325322	-2.525607	-0.484093	H	-3.269370	0.415385	-1.673412
H	3.757970	1.236684	1.014033	H	3.075126	1.085724	1.042819
O	3.756543	-0.853701	0.835343	O	0.936177	1.867502	-0.156057
H	3.644687	-0.893343	1.789532	H	0.002107	2.108423	-0.040885
TS(O6-C4)				TS(O5-C3)			
C	-2.350046	1.079273	-0.438450	C	2.559429	0.229135	0.209679
C	-1.397983	0.214629	0.374574	C	3.025004	-0.983789	-0.594835
C	-3.281307	0.018874	-1.008024	C	0.314513	0.668309	-0.349201
H	-4.206732	0.040214	-0.415116	C	1.138423	0.055130	0.768914
O	-2.548099	-1.167590	-0.827273	H	2.244139	-1.290055	-1.311732
H	-2.643810	-1.524099	0.607696	H	3.286927	0.389786	1.019112
O	-2.349117	-1.333857	1.573195	H	0.544700	0.344546	-1.356049
H	-1.637960	-1.957915	1.758439	H	1.017663	0.653285	1.673089
H	-1.722588	1.554444	-1.209594	O	0.416650	2.811991	-0.419741
O	-3.024727	2.046894	0.316206	O	0.657371	-1.244230	1.084924
H	-2.435964	2.786114	0.490905	H	0.650088	-1.759606	0.268910
C	-0.149275	-0.351334	-0.284034	O	2.346759	1.336500	-0.577744
H	-0.164692	-0.043011	-1.336043	H	1.384739	2.580622	-0.389735
H	-1.298690	0.506464	1.414418	C	-1.161243	0.877674	-0.132484
O	-0.068223	-1.751884	-0.191842	H	0.140127	3.108581	0.454353
H	-0.857349	-2.058786	-0.673477	O	3.409359	-2.070734	0.230722
H	-3.544055	0.189184	-2.057423	H	2.777924	-2.144613	0.952370
C	1.062665	0.269862	0.393301	H	-1.564789	1.439171	-0.979821
H	1.112659	-0.058757	1.440806	C	-1.901395	-0.469142	-0.105672
C	2.372349	-0.138767	-0.276491	H	-1.694202	-1.000462	0.830329
H	2.313590	0.034725	-1.365936	O	-1.393425	1.543123	1.088432
O	3.344445	0.694388	0.269778	H	-2.347371	1.610523	1.202606
C	4.633649	0.504885	-0.292121	O	-1.470860	-1.221249	-1.211431
H	5.285818	1.250579	0.157947	H	-1.878517	-2.091618	-1.193250
H	5.004887	-0.497099	-0.071834	O	-3.256466	-0.125701	-0.159668
H	4.601716	0.653285	-1.377621	C	-4.138405	-1.204085	0.084365
O	0.851488	1.664441	0.297916	H	-5.136974	-0.784701	0.188869
H	1.679745	2.093883	0.542469	H	-4.146236	-1.909353	-0.753728
O	2.701918	-1.470408	-0.008800	H	-3.868117	-1.730344	1.007275
H	1.911639	-2.009636	-0.151603	H	3.896828	-0.692760	-1.181151
TS(O4-C2)				TS(O3-C1)			
C	0.121429	0.647146	1.222850	C	1.215067	0.762701	-0.373870
C	-1.176082	0.718141	0.445926	C	0.054064	0.000614	0.296620

C	2.435245	0.140519	0.107745	C	-1.250785	0.313912	-0.442033
C	1.121056	0.922543	0.104703	C	2.420832	0.183967	0.287779
H	1.357131	1.996560	0.158224	H	-0.058687	0.395528	1.330477
O	3.023703	0.309759	-1.173121	H	1.248634	0.416484	-1.419645
O	0.378173	0.612833	-1.052040	O	1.292392	2.164202	-0.280410
H	-0.529414	1.884353	-1.321801	H	0.381099	2.467747	-0.410425
H	2.275779	0.343991	-1.789640	O	-1.484686	1.723097	-0.491690
O	-1.322476	2.391218	-0.978455	H	-1.968352	1.934920	0.319131
H	-2.065537	2.097407	-1.519148	O	0.406813	-1.308893	0.237586
H	0.183388	-0.386412	1.600397	O	2.687034	-2.229284	-0.487334
O	0.229511	1.573807	2.266138	H	2.683172	-2.860450	-1.208426
H	-0.213939	1.245384	3.051969	H	2.316106	-0.466746	1.156024
C	2.265014	-1.356055	0.365056	H	1.725397	-2.009302	-0.274378
H	1.434786	-1.731485	-0.252912	O	3.566945	0.505394	-0.112854
H	2.038128	-1.549874	1.416916	C	4.711248	-0.145232	0.494285
O	3.458062	-2.044657	0.074940	H	4.732856	-1.157713	0.093396
H	3.815290	-1.632915	-0.721379	H	5.575513	0.441434	0.201193
H	3.136775	0.556346	0.836128	H	4.587090	-0.153577	1.576348
C	-1.749081	-0.531782	-0.198514	H	-1.140601	-0.035838	-1.474747
H	-1.019875	-1.350009	-0.115806	C	-2.430622	-0.395204	0.208961
O	-2.877962	-0.796426	0.559010	H	-2.110239	-1.406628	0.480982
C	-3.466006	-2.059863	0.272663	C	-3.635107	-0.453495	-0.712835
H	-4.292223	-2.182151	0.969067	H	-3.849734	0.550363	-1.097600
H	-3.833444	-2.084893	-0.754266	H	-3.421744	-1.127269	-1.549605
H	-2.736884	-2.863419	0.423140	O	-2.754833	0.357434	1.372066
H	-1.921642	1.410391	0.819660	H	-3.620045	0.055733	1.669938
O	-2.099274	-0.340843	-1.535920	O	-4.719814	-0.937740	0.071437
H	-1.255665	-0.282688	-2.007530	H	-5.539458	-0.841950	-0.416517
Five numbered-ring closure reaction							
TS(O1-C4)				TS(O2-C5)			
C	-0.009824	1.066461	-1.024597	C	0.107232	-0.910303	0.392016
C	-1.146894	0.733948	0.032987	C	0.932849	-0.146323	-0.685860
C	-2.060344	-0.397462	-0.532098	C	2.045788	0.672254	-0.017840
C	2.230078	-0.064064	-0.404344	C	-1.988025	0.172417	-0.418486
C	0.939239	-0.042046	-1.087653	C	-1.264446	-1.121146	-0.272008
H	-0.671262	0.403653	0.960494	H	1.424372	-0.899248	-1.323431
H	-0.510751	1.151076	-2.000785	H	0.536850	-1.890343	0.625180
H	2.791791	0.710174	-0.970270	H	-2.272443	0.454067	-1.427455
H	0.754653	-0.806939	-1.832102	H	-1.882424	-1.753868	0.375390
O	2.888847	-1.287119	-0.554685	O	-1.067837	2.199193	0.078808
O	0.411805	-2.047456	0.165656	O	-1.120934	-1.772857	-1.503426
H	0.087071	-2.317180	1.028975	H	-0.681429	-1.127755	-2.081345
O	0.639945	2.249912	-0.653218	O	-0.085970	-0.161289	1.581939
H	-0.023567	2.807079	-0.222836	H	0.770177	-0.133226	2.028475

O	-1.795584	1.947305	0.319879	O	0.080510	0.649306	-1.418861
H	-2.527366	2.060140	-0.298814	H	-0.443001	1.754125	-0.609701
C	2.275493	0.380099	1.075414	C	-2.937559	0.575506	0.685269
H	1.873272	1.382455	1.197054	H	-3.303796	1.588786	0.546360
O	-2.661484	-1.071223	0.573499	O	2.657299	-0.011031	1.070463
C	-3.637826	-0.336358	1.275440	C	3.423478	-1.154534	0.714861
H	-4.378808	0.092017	0.586373	H	2.785585	-1.984285	0.392849
H	-4.146097	-1.034422	1.939645	H	4.129006	-0.916596	-0.082605
H	-3.203899	0.472720	1.873272	H	3.968504	-1.451326	1.609397
O	-1.361384	-1.247770	-1.274438	O	2.972733	1.015722	-0.998689
H	-0.453501	-1.857475	-0.453905	H	3.479049	1.775336	-0.699010
H	2.229580	-1.957992	-0.291343	H	-0.673384	1.983010	0.931507
H	-2.877251	0.104879	-1.105971	H	1.611860	1.565834	0.440815
H	1.674573	-0.341069	1.642260	H	-2.467731	0.468261	1.661065
O	3.608504	0.398820	1.506118	O	-3.973297	-0.396324	0.603108
H	3.996824	-0.452332	1.274585	H	-4.597131	-0.141756	-0.081960
TS(O3-C6)				TS(O6-C3)			
C	0.528895	-0.196144	-0.992504	C	0.248550	0.207916	-0.415447
C	-0.611854	0.593044	-0.346093	C	-1.055437	0.583217	0.226972
C	-1.781190	-0.291599	0.077703	C	-2.143336	-0.347809	-0.348217
C	1.759701	-0.773677	1.074871	C	2.474651	-0.889780	-0.593376
C	1.066647	-1.373172	-0.151121	C	1.128645	-0.827725	0.155940
H	-0.260725	1.078912	0.572988	H	-1.015335	0.422705	1.306882
H	0.130263	-0.622913	-1.923706	H	0.230072	0.279018	-1.499733
H	2.460168	-1.554691	1.428967	H	2.293108	-1.259863	-1.607559
O	1.649094	0.566436	-1.244746	H	0.589164	-1.764729	-0.076651
H	1.779201	1.775836	-0.575039	O	3.340694	-1.794871	0.030019
O	-1.016959	1.562745	-1.286058	O	1.299156	-0.739109	1.534707
H	-1.887241	1.873223	-1.013500	H	1.292032	0.235359	1.723222
C	2.692553	0.335077	0.741746	O	1.122361	1.772296	1.083842
H	2.998652	0.941515	1.584912	H	0.469035	2.458557	1.238015
O	-2.818918	0.593261	0.422457	O	-1.385192	1.905084	-0.115618
C	-3.990319	-0.042946	0.882704	H	-2.310800	2.028286	0.125404
H	-3.759676	-0.738254	1.700559	C	3.047885	0.535808	-0.663420
H	-4.654752	0.733964	1.256388	H	3.429767	0.802206	0.331217
H	-4.494990	-0.580937	0.074485	H	3.874536	0.554093	-1.378614
O	-2.140372	-1.140917	-0.979539	O	2.038248	1.422255	-1.059631
H	-2.608566	-1.906373	-0.639195	H	1.679721	1.840021	-0.132862
H	-1.505978	-0.877758	0.965637	O	-3.334001	0.113283	0.220763
H	3.476166	0.129905	0.025705	C	-4.497228	-0.520189	-0.275911
O	2.111611	2.327185	0.261081	H	-5.351713	0.010694	0.138232
H	1.328494	2.654262	0.716289	H	-4.533528	-0.464800	-1.370739
H	0.314014	-2.098686	0.163343	H	-4.544823	-1.565037	0.045987
O	2.043262	-2.041518	-0.915036	O	-1.835395	-1.662023	0.008173

H	2.385789	-1.376440	-1.529995	H	-2.348881	-2.280785	-0.517657
O	0.805751	-0.455734	2.064430	H	3.260593	-1.639785	0.980443
H	1.244827	-0.226727	2.887620	H	-2.202287	-0.239897	-1.442879
TS(O5-C2)				TS(O4-C1)			
C	-0.019479	0.994889	0.421442	C	-0.072788	1.148188	0.866549
C	0.689681	-0.165332	-0.214713	C	0.885928	1.203464	-0.336057
C	2.147048	-0.407700	0.162875	C	2.033375	0.253008	-0.227596
C	-2.059802	-0.403031	0.421696	C	-2.192784	-0.243988	0.402603
C	-1.513472	0.985445	0.128213	C	-0.770183	-0.233173	0.965404
H	0.499358	-0.349107	-1.267288	H	0.358304	1.035388	-1.274085
H	0.149461	0.994805	1.506010	H	0.547145	1.289604	1.768344
H	-2.061632	-0.560482	1.511004	H	-2.737847	0.625522	0.786539
H	-1.636691	1.190270	-0.943469	H	-0.879557	-0.474562	2.031456
O	-1.199653	-1.308440	-0.227857	O	-2.796150	-1.435702	0.866968
O	-2.185791	1.939223	0.911238	O	0.027139	-1.173792	0.318023
H	-1.934172	2.815102	0.603544	H	0.863454	-1.422696	0.948665
O	0.494921	2.175180	-0.176669	O	-1.008330	2.194760	0.751689
H	1.458599	2.118371	-0.228857	H	-0.542843	3.016289	0.564073
O	0.515402	-1.946829	1.206094	O	1.485863	2.495486	-0.422346
H	0.396210	-1.764004	2.141886	H	1.876575	2.720311	0.431077
C	-3.472484	-0.590033	-0.120163	C	-2.222614	-0.204870	-1.115545
H	-3.868486	-1.545028	0.244211	H	-1.853902	0.764074	-1.471570
H	-4.113619	0.218905	0.234416	H	-1.598827	-1.016647	-1.500168
O	-3.471986	-0.547635	-1.529935	O	-3.586457	-0.377938	-1.497114
H	-2.807923	-1.184691	-1.817261	H	-3.625663	-0.670822	-2.408734
O	2.784182	0.631351	-0.534418	O	2.313242	-0.503811	-1.186814
C	4.205971	0.597640	-0.421629	C	3.479620	-1.375042	-1.056879
H	4.603093	-0.293068	-0.907009	H	3.452690	-1.782061	-0.043784
H	4.573599	1.494558	-0.915331	H	3.344076	-2.137718	-1.816496
H	4.501956	0.605939	0.632782	H	4.364882	-0.774503	-1.262404
O	2.624785	-1.624724	-0.279979	O	2.104559	-1.397533	1.524748
H	2.114802	-2.277942	0.229086	H	2.149320	-1.653512	2.447060
H	-0.533492	-1.803838	0.519931	H	-3.607430	-1.544805	0.360290
H	2.299267	-0.276062	1.242232	H	2.727369	0.328848	0.607624
Six numbered-ring closure reaction							
TS(O1-C5)				TS(O2-C6)			
C	0.145989	1.513263	-0.245028	C	-0.043046	-1.187041	-0.492807
C	-1.084298	0.892273	0.412164	C	0.404637	0.278459	-0.464891
C	-1.687087	-0.219108	-0.451423	C	1.940720	0.440885	-0.551397
C	1.581987	-0.519180	-0.725577	C	-2.309273	-0.488212	0.480925
C	1.462410	0.777648	0.005773	C	-1.569043	-1.305268	-0.591189
H	-0.827737	0.493457	1.400649	H	0.009892	0.751172	-1.383749
H	-0.017528	1.565118	-1.333416	H	0.378141	-1.676576	-1.388006
H	1.116813	-0.560970	-1.705877	H	-1.826041	-2.355551	-0.416844

H	1.657881	0.659564	1.072025	O	-2.070096	-0.842413	-1.830491
O	0.586736	-1.739473	1.107751	H	-1.722503	-1.388418	-2.540073
O	2.516891	1.484204	-0.636631	O	0.310802	-1.894876	0.674266
H	2.309481	2.424462	-0.543256	H	1.243724	-1.694090	0.838649
O	0.394499	2.811192	0.254510	O	-0.083587	0.912047	0.669894
H	-0.459934	3.222621	0.435807	H	-0.613385	2.100240	0.239522
O	-2.025029	1.944783	0.542197	C	-2.522810	0.927056	0.218010
H	-2.859591	1.544549	0.810711	H	-2.784569	1.237403	-0.784676
C	2.627909	-1.501308	-0.472448	H	-2.856450	1.521402	1.057955
H	2.304030	-2.471288	-0.880319	O	-1.295331	2.788270	-0.198504
H	3.408723	-1.130115	-1.172490	H	-1.383349	3.546702	0.384050
O	3.124668	-1.556934	0.806126	O	2.563004	-0.594331	0.195153
H	2.308333	-1.767336	1.319162	C	3.977090	-0.540718	0.159162
O	-2.799696	-0.666040	0.298202	H	4.345102	-1.390986	0.731198
C	-3.593304	-1.610117	-0.397149	H	4.335717	-0.615589	-0.874500
H	-3.012967	-2.504073	-0.633455	H	4.340728	0.389903	0.598311
H	-4.425039	-1.870434	0.255130	O	2.301696	1.690291	-0.076270
H	-3.981653	-1.176691	-1.326957	H	1.673166	1.863642	0.644169
O	-0.807508	-1.225459	-0.767227	H	2.293903	0.368315	-1.588446
H	-0.297947	-1.576367	0.143680	H	-3.401868	-0.725103	0.323292
H	0.187097	-1.503717	1.948981	O	-2.008398	-0.808552	1.783861
H	-2.056086	0.232202	-1.387673	H	-1.046580	-0.686915	1.868994
TS(O6-C2)				TS(O5-C1) (TS3)			
C	-0.302775	-1.210661	-0.383218	C	0.301853	1.376287	-0.430681
C	0.410272	0.048306	-0.711040	C	-0.955965	1.189132	0.438938
C	1.900360	0.230808	-0.679072	C	-1.930705	0.172127	-0.072236
C	-2.496599	0.066167	0.366831	C	1.285837	-0.937518	-0.317707
C	-1.847095	-1.032378	-0.492189	C	1.482715	0.530955	0.036911
H	0.003015	0.533405	-1.590209	H	-0.691163	0.954915	1.472318
H	-0.042109	-1.826914	-1.269598	H	0.072689	1.145895	-1.481364
H	-2.260233	-1.989405	-0.160392	H	1.115714	-1.004516	-1.405885
O	-2.188149	-0.746630	-1.842330	H	1.565836	0.618098	1.125779
H	-2.275827	-1.567358	-2.331879	O	0.165858	-1.390946	0.373091
O	0.093567	-1.891125	0.748200	O	2.635491	1.093562	-0.580527
H	0.345594	-1.183133	1.379411	H	3.398111	0.738509	-0.109573
O	0.349497	0.566092	1.505777	O	0.621681	2.750513	-0.307016
H	1.208098	0.823299	1.850246	H	1.561877	2.834953	-0.511856
C	-2.190895	1.486148	-0.117906	O	-1.791197	2.334369	0.368045
H	-2.598876	1.617708	-1.121907	H	-1.216779	3.081327	0.144651
H	-2.699973	2.179259	0.562005	C	2.554625	-1.741351	-0.017651
O	-0.813994	1.808260	-0.172474	H	2.249219	-2.765721	0.209080
H	-0.352459	1.562507	0.708689	H	3.215137	-1.744937	-0.892429
O	2.523644	-0.482422	0.326268	O	3.242982	-1.152066	1.088954
C	3.926899	-0.561569	0.175810	H	3.841227	-1.796088	1.471191

H	4.285921	-1.251278	0.936235	O	-2.596745	-0.462540	0.774941
H	4.195316	-0.951269	-0.814602	C	-3.710880	-1.292965	0.325201
H	4.400701	0.413452	0.328455	H	-3.333949	-1.895006	-0.502844
O	2.180288	1.599818	-0.654205	H	-3.980225	-1.888895	1.190843
H	3.002044	1.772762	-1.119746	H	-4.523650	-0.624202	0.045430
H	2.207611	-0.194499	-1.659041	O	-1.467865	-1.871013	-1.326512
H	-3.574551	-0.065989	0.223444	H	-1.168251	-2.249442	-2.153860
O	-2.258702	-0.122064	1.736800	H	-0.530915	-1.755028	-0.387874
H	-1.334488	0.111097	1.939299	H	-2.221394	0.155108	-1.118066

Table S3 The XYZ coordinates of all TSs from glucose to MDGP catalyzed by $[Al(CH_3O)_2(CH_3OH)_2]^+$

TS1’				TS2’			
C	3.163013	1.221906	-0.089442	C	2.990464	-1.240172	0.264110
C	1.750976	1.734562	0.158504	C	1.636576	-1.885766	-0.018556
C	0.729923	0.757484	-0.415017	C	0.465587	-1.118120	0.554069
C	2.253086	-1.094279	-0.199118	C	2.190653	1.155020	0.136258
C	3.296892	-0.191894	0.446248	C	3.158868	0.118229	-0.409076
H	1.586401	1.813786	1.242591	H	1.495275	-2.003323	-1.099064
H	3.350646	1.213772	-1.173315	H	3.112534	-1.122993	1.351253
H	2.394530	-1.108745	-1.288194	H	2.303816	1.237039	1.224493
H	3.120062	-0.173211	1.531878	H	2.971436	-0.004138	-1.487404
H	0.810530	0.726560	-1.510107	H	0.567380	-0.749588	1.581591
O	0.953664	-0.558150	0.108782	O	0.877774	0.655305	-0.176960
O	4.560321	-0.741539	0.159972	O	4.455294	0.617402	-0.191234
H	5.237083	-0.116665	0.446684	H	5.087459	-0.083685	-0.392423
O	4.124718	2.002861	0.574525	O	4.015464	-2.047286	-0.262708
H	4.113828	2.894527	0.210999	H	3.990502	-2.910077	0.165161
O	1.652473	2.985336	-0.475522	O	1.658206	-3.135105	0.644764
H	0.847370	3.433404	-0.200841	H	0.990043	-3.720995	0.275784
C	2.312162	-2.528885	0.317031	C	2.394974	2.541419	-0.477250
H	2.409860	-2.522017	1.410576	H	2.527496	2.442070	-1.563444
H	1.374627	-3.035474	0.066582	H	1.495277	3.137340	-0.299357
O	3.336077	-3.252523	-0.304233	O	3.456615	3.220531	0.129116
H	4.173410	-2.806093	-0.128441	H	4.259531	2.701459	0.001196
O	-0.562045	1.126804	-0.069383	O	-0.682024	-1.320575	0.086849
H	-0.989941	1.199867	1.052550	H	-0.795317	0.485226	-1.694200
Al	-2.265570	0.211715	-0.161468	Al	-2.192413	-0.151671	0.230134
C	-2.856291	1.362837	2.576427	C	-2.309185	-0.425922	-2.663088
H	-3.860128	0.937874	2.521112	H	-3.378288	-0.488597	-2.474349
H	-2.413741	1.117569	3.541340	H	-2.117064	0.084288	-3.604100
H	-2.925380	2.446001	2.467901	H	-1.871518	-1.423867	-2.652639
O	-2.053449	0.810137	1.539505	O	-1.751199	0.362895	-1.578629
C	-1.736811	-2.521980	-1.164256	C	-1.641883	2.004624	2.097571
H	-1.092261	-2.467942	-2.040731	H	-1.231086	1.743272	3.074519
H	-2.772815	-2.387252	-1.467296	H	-2.729942	2.060625	2.185078
H	-1.611080	-3.472885	-0.650039	H	-1.262849	2.988923	1.810979
C	-2.583997	1.667478	-2.605680	C	-3.370275	-2.753652	0.576122
H	-1.594161	2.086555	-2.394683	H	-3.891755	-3.278624	-0.228023
H	-3.299132	2.489665	-2.675140	H	-3.875935	-2.979791	1.517575
H	-2.549473	1.158710	-3.571600	H	-2.345720	-3.135165	0.632110
C	-4.321054	-1.601052	1.235624	C	-3.847582	2.387357	-0.391176
H	-5.231448	-1.265694	1.729626	H	-4.172674	2.389303	-1.431329

H	-4.465272	-2.582850	0.785993	H	-4.545908	2.941896	0.233855
H	-3.498505	-1.632074	1.947529	H	-2.854432	2.824836	-0.313049
O	-1.410647	-1.449246	-0.251599	O	-1.250658	1.037088	1.132879
O	-2.993072	0.760684	-1.602574	O	-3.400750	-1.365109	0.333877
O	-3.941639	-0.648949	0.222588	O	-3.733873	1.038887	0.090630
H	-0.426777	-1.354495	-0.086851	H	0.167082	1.084912	0.393260
H	-4.614440	-0.465564	-0.447446	H	-4.561945	0.540993	0.118203
TS3’				TS4’			
C	-1.619740	-1.302812	-0.782266	C	2.593919	-0.821138	0.990821
C	-0.816684	-1.248373	0.526876	C	2.350543	-2.005410	0.020789
C	0.342012	-2.226072	0.500117	C	1.557608	-1.683105	-1.175832
C	-3.226216	0.476689	0.145111	C	2.115335	1.471169	-0.000360
C	-2.380982	0.007515	-1.036776	C	3.198269	0.438607	0.332921
H	-0.436184	-0.235692	0.697440	H	3.349060	-2.252414	-0.394482
H	-0.897059	-1.396205	-1.598400	H	1.627642	-0.586012	1.443856
H	-2.595204	0.568141	1.039131	H	1.484806	1.618215	0.885359
H	-3.054967	-0.158922	-1.885166	H	3.717478	0.175964	-0.598103
H	0.251232	-3.109995	-0.137249	H	1.868481	-0.877437	-1.837136
O	-4.189082	-0.549591	0.309751	O	1.337667	0.950182	-1.059063
O	-1.436729	1.039389	-1.335492	O	4.126254	0.971271	1.257668
H	-1.039961	0.854682	-2.192284	H	4.718724	1.557210	0.772079
O	-2.419905	-2.443332	-0.838024	O	3.456884	-1.392862	1.946126
H	-3.160918	-2.317659	-0.228448	H	4.085206	-0.711409	2.222472
O	-1.665337	-1.662324	1.576514	O	1.782748	-3.084650	0.687565
H	-1.207855	-1.615713	2.422190	H	2.298213	-3.214735	1.494686
C	-3.879979	1.838047	-0.093527	C	2.744676	2.813386	-0.361064
H	-4.381063	1.849711	-1.068694	H	2.020258	3.385538	-0.947512
H	-4.641016	2.000248	0.672906	H	2.981175	3.366634	0.553878
O	-2.944067	2.889850	0.031599	O	3.932768	2.562960	-1.104173
H	-2.348270	2.815705	-0.719548	H	4.238308	3.375268	-1.514192
O	1.187793	-2.268989	1.424077	O	-0.494951	-0.870429	0.618130
H	1.489726	-1.222127	1.717101	H	0.380160	1.090479	-0.846003
Al	2.239015	0.327767	-0.126585	C	-0.255867	-2.053826	-2.622652
C	2.472282	0.680723	2.721229	H	-0.263005	-2.935370	-3.258117
H	3.121934	1.489402	2.380110	H	0.166386	-1.186889	-3.130218
H	1.663654	1.092039	3.325940	H	-1.242428	-1.847105	-2.204592
H	3.062595	-0.012354	3.320059	O	0.574467	-2.389092	-1.473413
O	1.920616	-0.011381	1.591858	H	-0.504805	-1.828690	0.693924
C	1.844551	-1.677361	-2.068072	Al	-1.998128	-0.039364	0.113045
H	2.386047	-2.587747	-1.800275	C	-4.114882	-1.467467	-1.289993
H	2.506302	-1.031343	-2.650489	H	-4.866165	-1.470350	-0.487707
H	0.985345	-1.944624	-2.686790	H	-4.395629	-0.704546	-2.032979
C	5.010026	0.423460	-1.080896	H	-4.185082	-2.435766	-1.791771
H	5.440956	1.112405	-1.807878	O	-2.820183	-1.276128	-0.798089

H	4.974372	-0.574665	-1.526783	C	-3.472967	-0.297454	2.826293
H	5.660510	0.390770	-0.204291	H	-3.559839	-1.383971	2.811532
C	0.445906	2.702752	0.474696	H	-3.357078	0.066041	3.845582
H	0.914657	2.997635	1.412080	H	-4.350988	0.148850	2.369656
H	0.088239	3.571288	-0.073117	C	-1.645875	2.381385	-1.446023
H	-0.382054	2.019203	0.631833	H	-1.784573	3.332164	-0.920974
O	1.393502	-1.010699	-0.887867	H	-2.589706	2.114283	-1.935875
O	3.721148	0.878393	-0.722122	H	-0.897856	2.537785	-2.229277
O	1.422426	2.008264	-0.354927	C	-3.978937	2.343961	0.669418
H	-4.657888	-0.428964	1.140417	H	-3.059356	2.595176	1.194310
H	2.079697	2.609765	-0.736055	H	-4.146240	3.057572	-0.136474
				H	-4.820176	2.351659	1.363394
				O	-2.335969	0.120243	2.044966
				O	-1.201680	1.379183	-0.563153
				O	-3.791956	1.022363	0.136817
				H	-1.508895	-0.256119	2.385512
				H	-4.507742	0.764747	-0.453372

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