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Supplementary Materials

$CaCl_2$ Molten Salt Hydrate-promoted Conversion of Carbohydrates to 5-Hydroxymethylfurfural: An Experimental and Theoretical Study

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Content

Table S 1 the results of isomerization of glucose in literature

Entry	Catalysts	Glucose	Temperature (℃)	Conversion (%)	Yield of fructose (%)	Selectivity of fructose (%)	Liteature
1	$CrCl_3$	4.5wt%	120	52.00	25.00	49.00	[1]
2	$AlCl_3$	4.5wt%	120	32.00	26.00	83.00	[1]
3	$SnCl_4$	4.5wt%	120	18.00	5.00	26.00	[1]
4	$CrCl_3$	10wt%	140	41.00	20.00	48.78	[2]
5	$ZrCl_4$	na	140	69.00	7.00	10.14	[3]
6	Al-Ni-C	2wt%	170	59.00	19.00	32.20	[4]
7	GIO-Al200	5wt%	140	53.23	34.60	65.00	[5]
8	Sn-silicate	10wt%	110	23.40	16.70	71.37	[6]
9	H-USY	9.1wt%	120	53.00	38.00	71.70	[7]
10	Sn-Beta	10wt%	140	46.00	30.00	65.22	[8]
11	Sn-Beta	1wt%	110	48.00	21.00	43.75	[9]
12	Sn/deAl-β	10wt%	110	45.00	30.00	66.67	[10]
13	$CaCl_2$	10wt%	80	42.00	33.60	80.00	This work

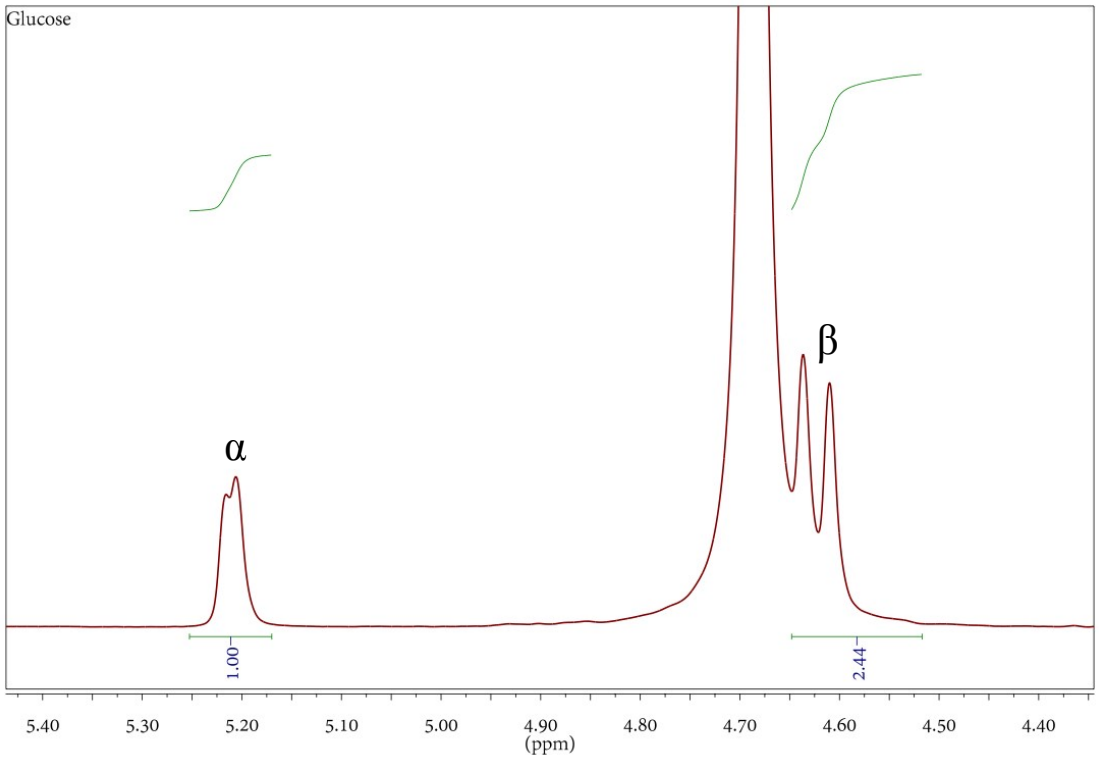


Figure S 1 ^{1}H NMR spectrum of glucose in D_2O

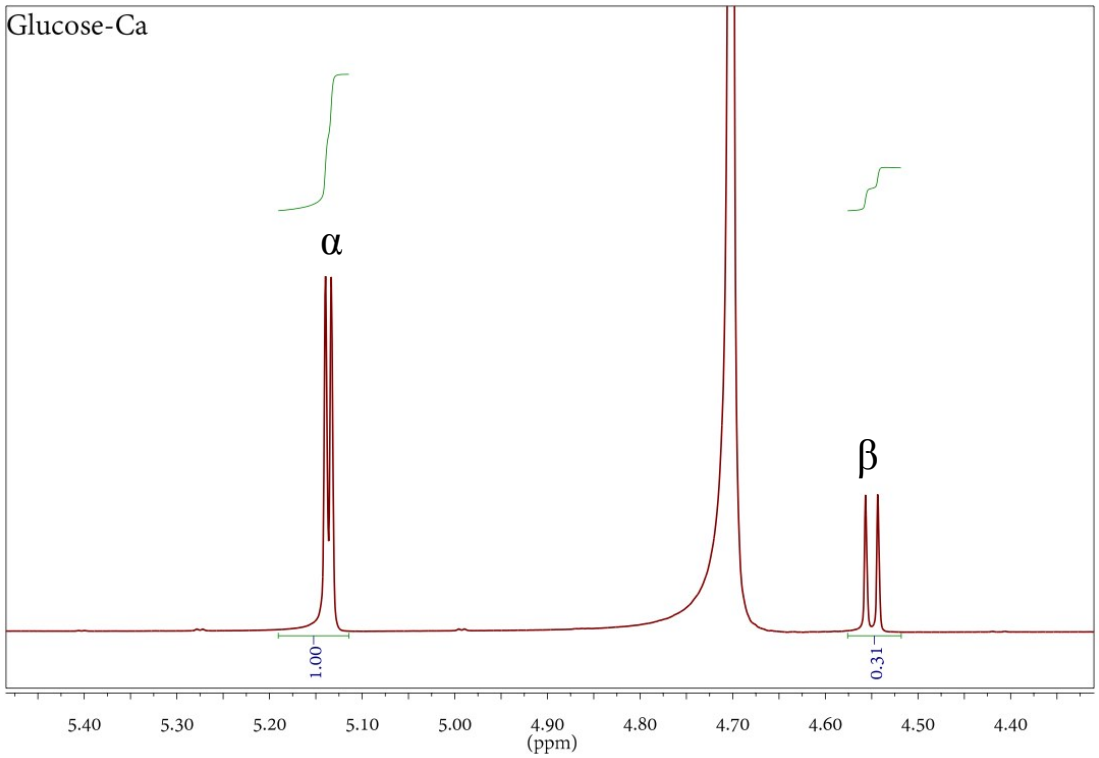
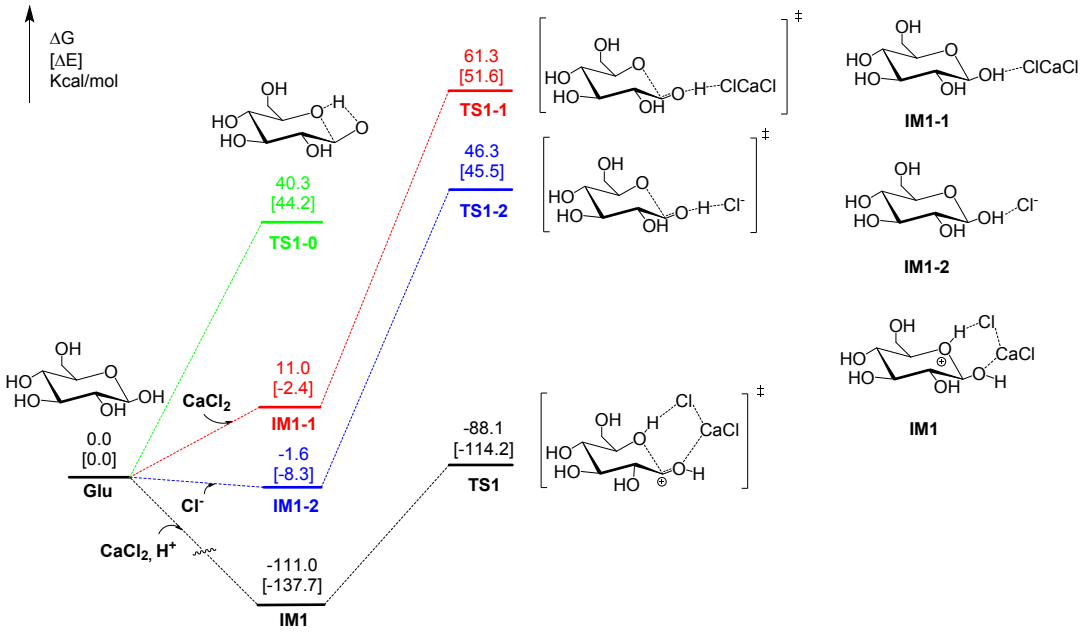


Figure S 2 ^{1}H NMR spectrum of glucose with $CaCl_2$ in D_2O



Scheme S 1 Computed free energy profiles (in kcal/mol) for the different paths for the ring-opening step of cyclic pyranose. The electronic energies (in kcal/mol) are given in brackets for reference.

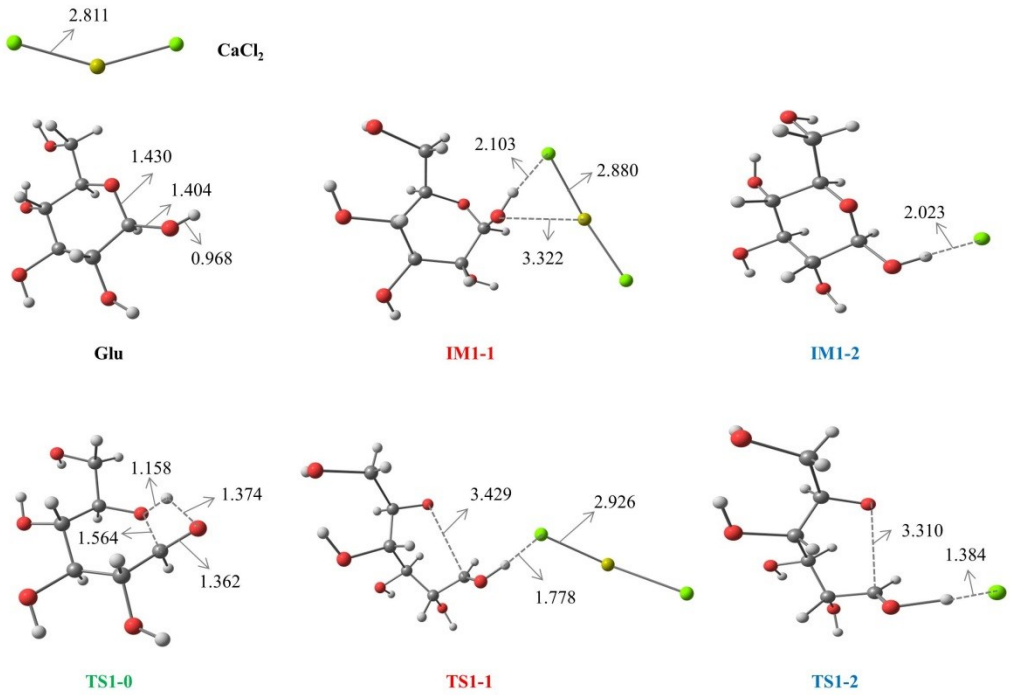


Figure S 3 Optimized structures of the transition states **TS1-0~TS1-2** and the key intermediates along the pathway shown in Scheme S1. The key bond distances and the average bond length are in Å (color code, C: gray, H: white, O: red, Cl: green, Ca: yellow).

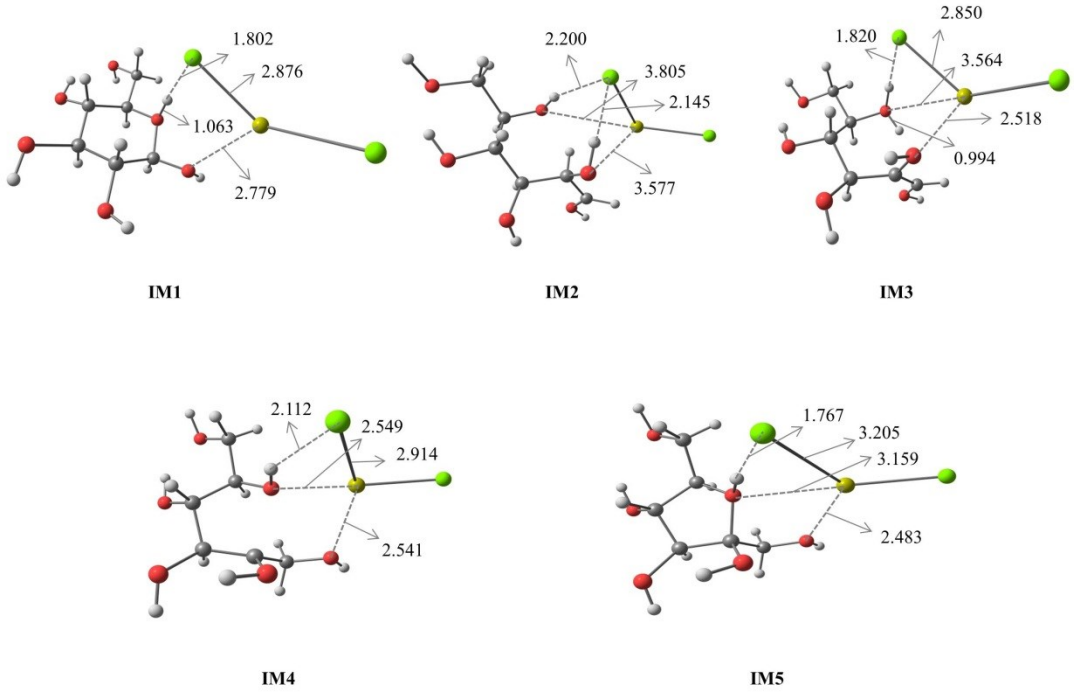
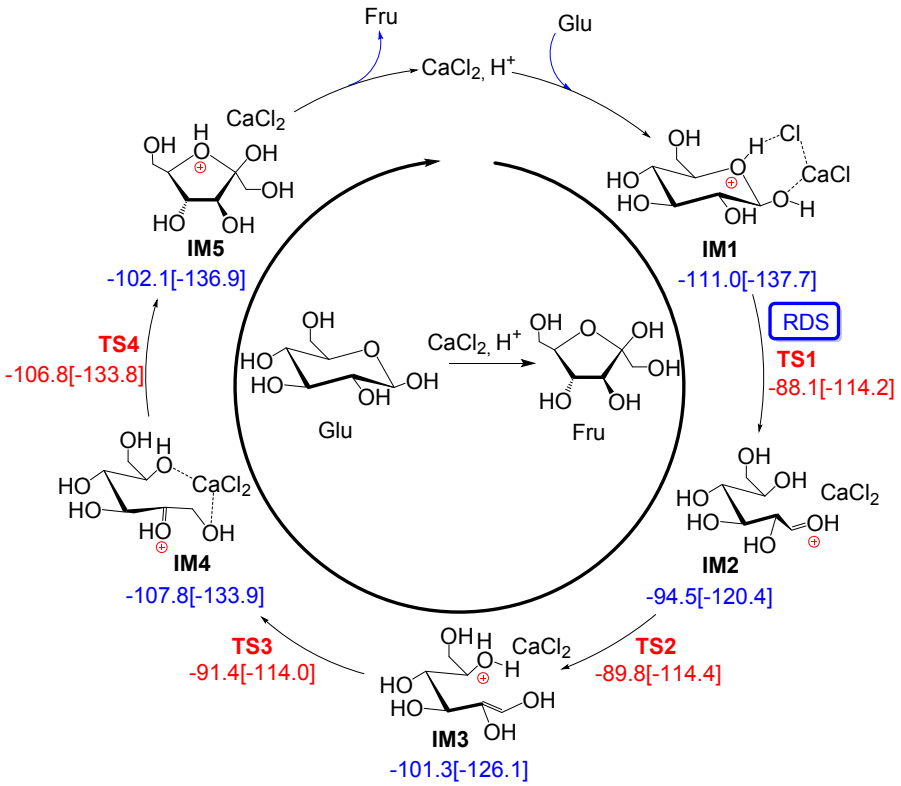
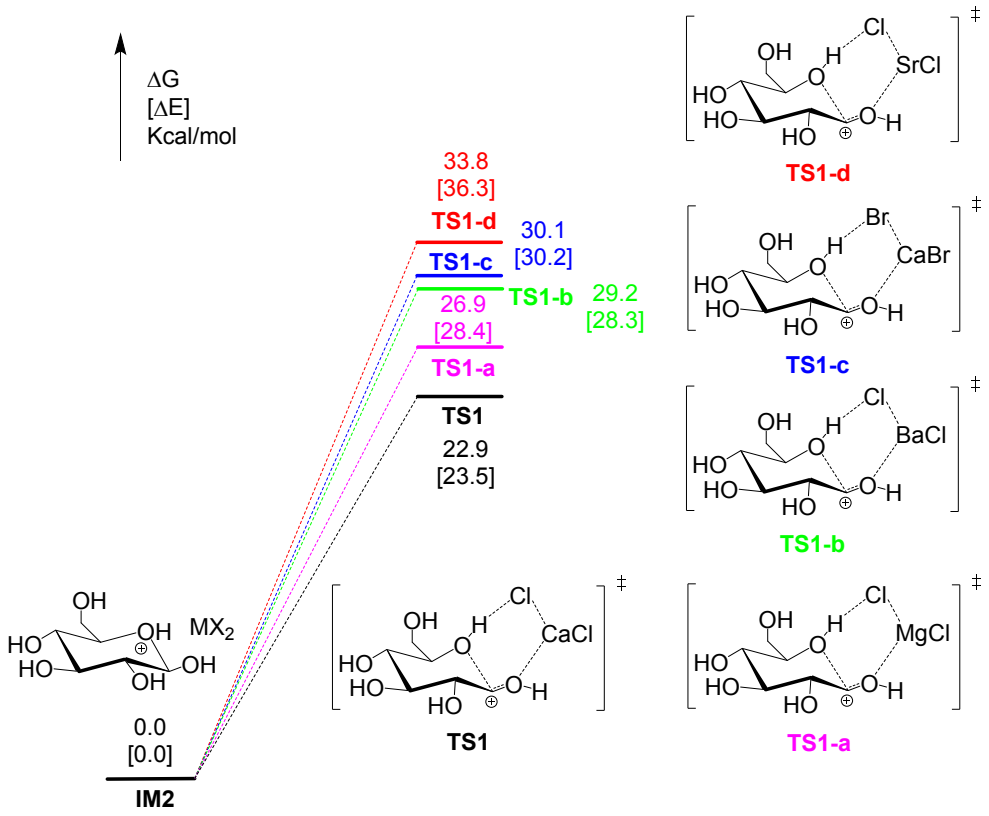


Figure S 4 Optimized structures of the key intermediates along the pathway shown in Scheme 1. The key bond distances and the average bond length are in Å (color code, C: gray, H: white, O: red, Cl: green, Ca: yellow).



Scheme S 2 Complete catalytic cycle for the $CaCl_2$-catalyzed isomerization of glucose to fructose.



Scheme S 3 Computed free energy profiles (in kcal/mol) for the different molten salt hydrates for the ring-opening step of cyclic pyranose. The electronic energies (in kcal/mol) are given in brackets for reference.

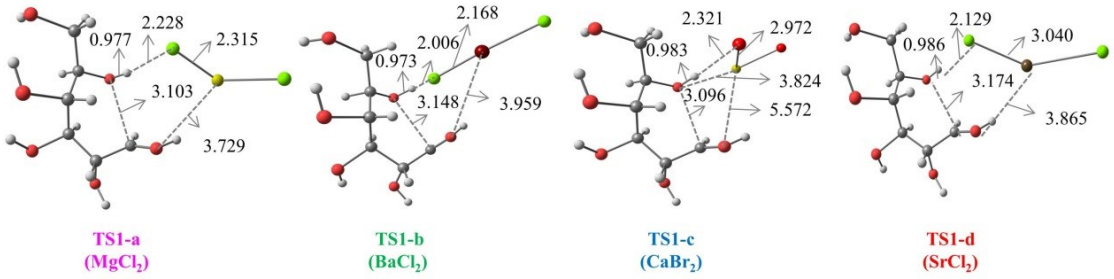


Figure S 5 Optimized structures of the transition states **TS1-a~TS1-d** along the pathway shown in Scheme S3. The key bond distances and the average bond length are in Å (color code, C: gray, H: white, O, Br: red, Cl: green, Ca, Mg: yellow, Sr: brown, Ba: dark red).

Table S 2 Effect of temperature and time on dehydration of fructose

Temp.(℃)	Time(min)	Yield(%)	Con.(%)	Selectivity(%)
140	60	25.21	40.37	62.46
140	120	45.62	76.22	59.85
140	180	59.53	100.00	59.53
140	240	54.23	100.00	54.23
150	30	32.49	75.00	43.32
150	60	47.87	84.70	56.51
150	90	51.39	90.75	56.62
150	120	61.63	100.00	61.63
150	150	56.97	100.00	56.97
150	180	53.85	100.00	53.85
160	30	39.44	76.47	51.58
160	60	47.73	86.00	55.50
160	90	65.57	100.00	65.57
160	120	57.02	100.00	57.02
170	120	49.27	100.00	49.27
180	120	47.08	100.00	47.08

Reaction condition: 100 $g \cdot L^{-1}$ fructose, 17.9wt% $CaCl_2$, water/MeTHF=1/4.

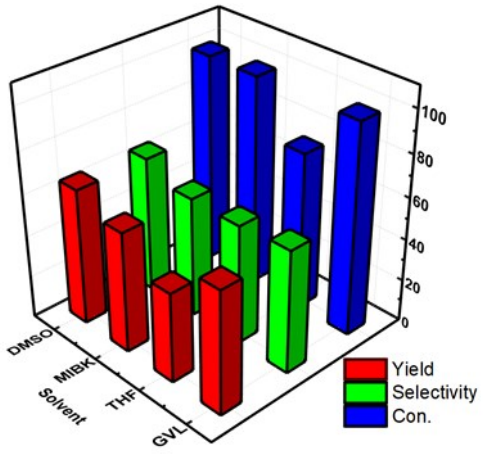


Figure S 6 Effect of solution on the dehydration of fructose to HMF

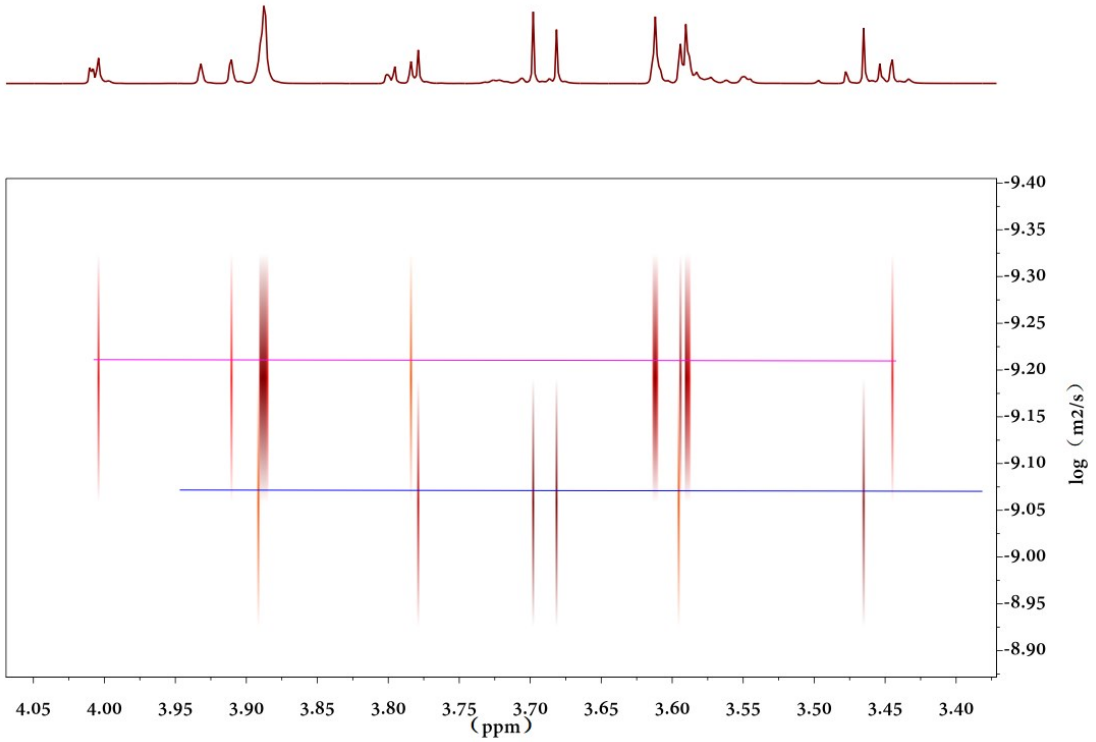


Figure S 7 2D DOSY NMR spectra of the fructose with $CaCl_2$ in D_2O

Table S 3 The optimized structures, energy differences (ΔG in hartree) for $C_6H_{12}O_6$, α-D-Fructofuranose, β-D-Fructofuranose and β-D-Fructopyranose at the B3LYP/AUG-cc-pVDZ level.

	$C_6H_{12}O_6$	α-D-Fructofuranose	β-D-Fructofuranose	β-D-Fructopyranose
ΔG	-687.2045314	-687.2039814	-687.206687	-687.207196

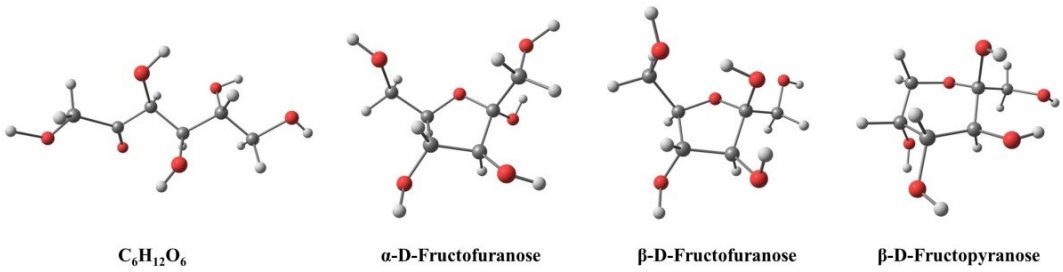


Table S 4 The optimal structures, energy differences (ΔE, ΔH, ΔG in kcal/mol) for Ca^{2+}+ α -D-Fructofuranose, Ca^{2+}+ β -D-Fructofuranose and Ca^{2+}+ β -D-Fructopyranose at the B3LYP/AUG-cc-pVDZ/cc-pVDZ level.

	Ca^{2+}+β-D-Fructofuranose	Ca^{2+}+β-D-Fructopyranose	Ca^{2+}+α-D-Fructofuranose
ΔG	0	0.6	2.3

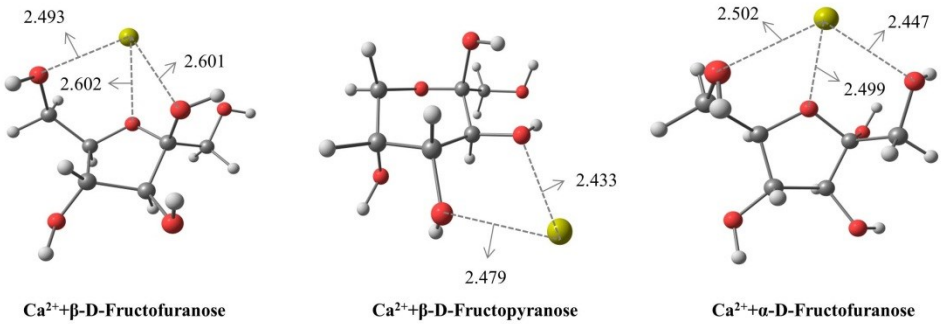


Figure S 8 Optimized structures of the complexes in Table S4. The key bond distances and the average bond length are in Å (color code, C: gray, H: white, O: red, Cl: green, Ca: yellow).

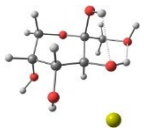
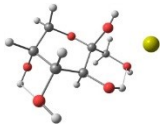
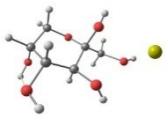
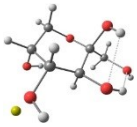
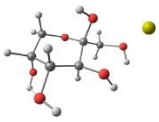
Table S 5 The isomers, energy differences (ΔG in hartree) for Ca^{2+}+β-D-Fructofuranose at the B3LYP/BSI level.

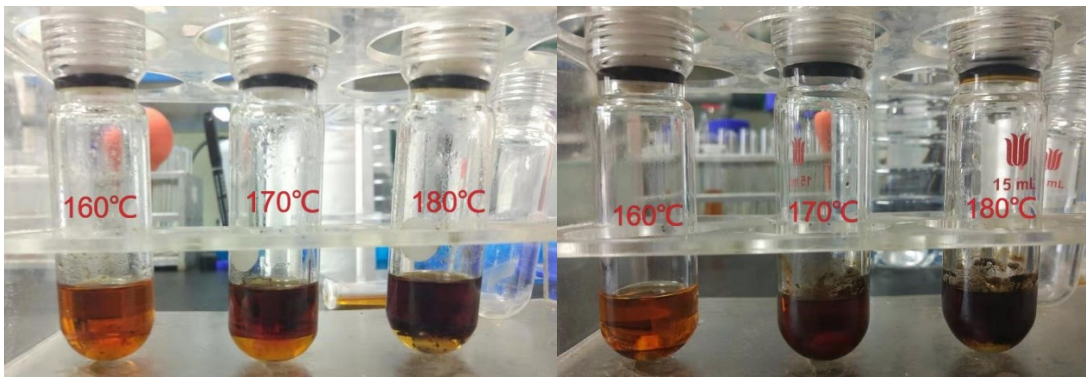
Ca^{2+}+β-D-Fructofuranose	Iso-1	Iso-2	Iso-3	Iso-4	Iso-5
ΔG	-1364.751674	-1364.748888	-1364.746115	-1364.747458	-1364.748522

Table S 6 The isomers, energy differences (ΔG in hartree) for Ca^{2+}+α-D-Fructofuranose at the B3LYP/BSI level.

Ca^{2+}+α-D-Fructofuranose	Iso-1	Iso-2	Iso-3	Iso-4	Iso-5
ΔG	-1364.748074	-1364.744576	-1364.745985	-1364.744735	-1364.747669

Table S7 The isomers, energy differences (ΔG in hartree) for Ca^{2+}+β-D-Fructopyranose at the B3LYP/BSI level.

					
Ca^{2+}+β-D-Fructopyranose	Iso-1	Iso-2	Iso-3	Iso-4	Iso-5
ΔG	-1364.750756	-1364.750434	-1364.750433	-1364.749652	-1364.74802



17.9wt% $CaCl_2$ 25.6wt% $CaCl_2$

Figure S 9 The dehydration of glucose into HMF in 17.9 or 25.6wt% $CaCl_2$ solution

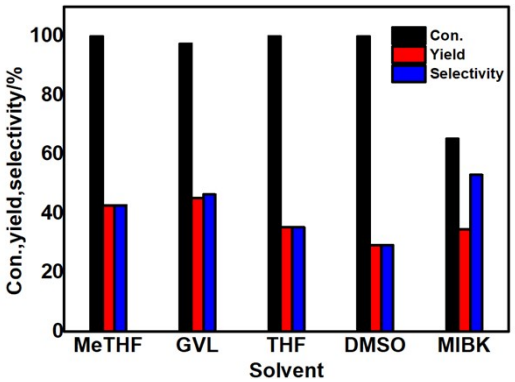


Figure S 10 Effect of solution on the dehydration of glucose to HMF at 180℃ for 120 min

Table S8 Effect of reaction temperature and time on the dehydration of glucose to HMF

Temp.(℃)	$CaCl_2$（wt%）	Time(min)	Con. (%)	Yield (%)	Selectivity(%)
160	17.9	120	62.40	28.30	45.35
170	17.9	120	72.28	39.74	54.99
180	17.9	120	100.00	42.75	42.75
180	17.9	10	46.59	13.12	28.16
180	17.9	20	79.62	34.35	43.14
180	17.9	40	84.24	42.49	50.43
180	17.9	60	93.59	52.06	55.62
180	17.9	90	100.00	45.09	45.09
180	17.9	120	100.00	42.75	42.75
200	17.9	50	92.70	34.97	37.72
200	17.9	60	100.00	44.11	44.11
200	17.9	90	100.00	37.48	37.48
160	25.6	120	100	32.25	32.25
170	25.6	120	100	39.67	39.67
180	25.6	120	100	38.24	38.24
200	25.6	30	100.00	38.21	38.21
200	25.6	45	100.00	46.73	46.73
200	25.6	60	100.00	32.59	32.59
200	37.8	15	100.00	34.49	34.49
200	37.8	30	100.00	30.72	30.72
200	37.8	45	100.00	29.65	29.65
200	37.8	60	100.00	25.14	25.14

Reaction condition: 100 $g \cdot L^{-1}$ glucose, water/MeTHF=1/4.

Table S9 the conversion (C)、selectivity (S) and yield (Y) of dehydration of glucose into HMF

Entry	Catalyst	Glucose (wt %)	Solvent	T (℃)	Time/ min	C (%)	S (%)	Y (%)	Literature
1	$AlCl_3$/HCl	5	water/MIBK	130	300	na	na	43	[11]
2	Al $(NO_3)_3$/H_2SO_4	2.5	water/DMSO	na	10	na	na	29	[12]
3	MIL-101(Cr)-SO_3H	3	water/GVL	150	120	98	46	45	[13]
4	Al-KCC-1	12.5	DMSO	170	120	98	40	39	[14]
5	$AlCl_3$/HCl/ NaCl	1.8	water/MIBK	160	na	83	80	66	[15]
6	0.4-Cr/β zeolite/NaCl	10	water/THF	150	90	87	83	72	[16]
7	AlSiO-20/NaCl	10	water/THF	160	90	92	69	63	[17]
8	SnP-1/NaCl	5	water/THF	175	60	98	62	61	[18]
9	Cr-Beta	10	[BMIM]Cl	130	60	na	na	58.8	[19]
10	$CaCl_2$	10	water/MeTHF	180	90	94	53	50.00	This work

Purification of HMF

In the fructose or glucose dehydration, organic extractor 2-MeTHF was put into ACE pressure tube. After reaction, the organic phase is concentrated and dried though BUCHI Rotary Steamer, dissolved in 2-3 volumes of diethyl ether, and the upper layer is separated and recrystallized at -40 ℃ for 24 h in low constant temperature bath to obtain HMF crystals.

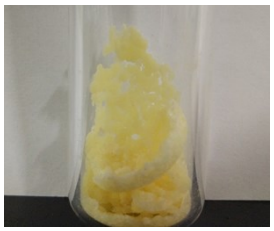


Figure S 11. HMF crystal

Table S10 Coordinates and energies (in hatree) of the calculated structures at the B3LYP/BSI level.

Glu

E= -687.3646726

G= -687.2071386

C	-0.755142000	0.821993000	-0.244033000
C	-1.068605000	-0.602575000	0.244319000
C	1.231215000	-1.203737000	0.293051000
C	1.669844000	0.165743000	-0.219935000
C	0.649249000	1.229137000	0.174064000
H	-1.089096000	-0.606169000	1.346701000
H	-0.818960000	0.835634000	-1.344514000
H	1.192553000	-1.217106000	1.394123000
H	1.746517000	0.114079000	-1.316400000
H	0.669660000	1.341796000	1.269955000
O	0.950772000	2.487381000	-0.440065000
H	1.826887000	2.759681000	-0.133595000
O	-1.674649000	1.769822000	0.310128000
H	-2.557170000	1.360306000	0.250487000
O	2.923063000	0.555137000	0.347924000
H	3.611738000	-0.009045000	-0.029291000
O	2.128053000	-2.169363000	-0.190162000
H	2.039208000	-2.968730000	0.347931000
O	-0.065622000	-1.512740000	-0.224526000
C	-2.387719000	-1.137940000	-0.296649000
H	-2.516734000	-2.180550000	0.026295000
H	-2.376746000	-1.098360000	-1.394727000
O	-3.452005000	-0.318109000	0.221613000
H	-4.237814000	-0.464288000	-0.321164000

$CaCl_2$

E= -1598.348157

G= -1598.376824

Ca	-0.000000000	0.000000000	0.481105000
Cl	-0.000000000	2.705070000	-0.283003000
Cl	-0.000000000	-2.705070000	-0.283003000

IM1

E= -2285.72782

G= -2285.575881

C	2.393201000	0.000186000	0.437292000
C	1.980751000	-1.158763000	-0.482976000
C	0.381388000	0.197011000	-1.631097000

C	0.729018000	1.417977000	-0.783749000
C	2.158410000	1.329027000	-0.262760000
H	2.632031000	-1.161728000	-1.372732000
H	1.775624000	-0.040204000	1.349273000
H	0.960185000	0.173923000	-2.566371000
H	0.036751000	1.453674000	0.069959000
H	2.853881000	1.406229000	-1.114296000
O	2.423870000	2.383581000	0.668610000
H	2.241943000	3.220449000	0.217941000
O	3.780602000	-0.082125000	0.780168000
H	3.948164000	-1.010380000	1.021983000
O	0.629745000	2.620584000	-1.551473000
H	-0.307050000	2.834978000	-1.656915000
O	-1.002958000	0.240720000	-1.900364000
H	-1.200861000	-0.338427000	-2.651034000
O	0.612791000	-0.998314000	-0.886625000
C	2.034138000	-2.520843000	0.205091000
H	1.676604000	-3.292553000	-0.489792000
H	1.385403000	-2.508785000	1.089157000
O	3.353384000	-2.836231000	0.677295000
H	3.911888000	-3.024018000	-0.090844000
Ca	-2.264907000	-0.490164000	0.190685000
Cl	-4.973029000	-0.871378000	-0.198857000
Cl	-1.559755000	1.217074000	2.268757000

IM2

E= -2286.147398

G= -2285.986063

C	-2.701713000	0.059821000	-0.421788000
C	-2.092787000	-0.818666000	0.679397000
C	-0.348170000	0.923280000	1.135049000
C	-0.869061000	1.764714000	-0.022361000
C	-2.369572000	1.533547000	-0.218150000
H	-2.517202000	-0.566201000	1.656834000
H	-2.299747000	-0.262230000	-1.395828000
H	-0.892753000	1.093722000	2.067781000
H	-0.322888000	1.494518000	-0.937631000
H	-2.893304000	1.890796000	0.682561000
O	-2.837277000	2.239314000	-1.365571000
H	-2.691509000	3.183102000	-1.210175000
O	-4.121053000	-0.076401000	-0.403221000
H	-4.314084000	-1.030157000	-0.364172000
O	-0.694102000	3.142903000	0.283007000
H	0.238293000	3.368404000	0.158805000

O	1.015703000	1.046151000	1.280272000
H	1.253337000	0.891826000	2.208305000
O	-0.643007000	-0.525759000	0.810858000
C	-2.199520000	-2.321184000	0.412221000
H	-1.658657000	-2.869931000	1.193743000
H	-1.766538000	-2.562031000	-0.564918000
O	-3.572837000	-2.716919000	0.355252000
H	-3.932600000	-2.700756000	1.254486000
Ca	3.053403000	-0.618514000	0.387244000
Cl	5.591265000	0.178611000	-0.322736000
Cl	0.945086000	-1.381039000	-1.414339000
H	-0.082839000	-0.842887000	-0.035372000

TS1

E= -2286.109989

G= -2285.949604

C	-2.536064000	-0.171709000	-0.406931000
C	-2.408752000	-1.229646000	0.701856000
C	-0.256399000	1.831942000	0.233241000
C	-1.616737000	2.193448000	-0.252878000
C	-2.719028000	1.240416000	0.217987000
H	-3.294681000	-1.178227000	1.350970000
H	-1.585283000	-0.190214000	-0.969149000
H	-0.079748000	1.611756000	1.290007000
H	-1.631589000	2.314769000	-1.341648000
H	-2.648231000	1.165371000	1.311450000
O	-3.979980000	1.788349000	-0.138030000
H	-4.105147000	2.589045000	0.390575000
O	-3.607104000	-0.448556000	-1.305881000
H	-3.698560000	-1.420340000	-1.341382000
O	-1.769834000	3.447325000	0.429765000
H	-1.362574000	4.144928000	-0.107328000
O	0.724528000	1.922409000	-0.559609000
H	1.591932000	1.796059000	-0.117621000
O	-1.282115000	-0.907481000	1.523648000
C	-2.262068000	-2.654743000	0.161077000
H	-2.063484000	-3.337619000	0.998020000
H	-1.424800000	-2.706969000	-0.544861000
O	-3.425902000	-3.082226000	-0.573925000
H	-4.159464000	-3.176153000	0.051248000
Ca	3.675671000	-0.164177000	0.402607000
Cl	6.254786000	0.110570000	-0.477332000
Cl	1.329092000	-1.654405000	-0.050620000
H	-0.460175000	-1.100487000	1.018912000

IM3

E= -2286.11983

G= -2285.959774

C	2.469349000	0.246145000	0.346325000
C	2.348185000	-0.759074000	-0.823907000
C	-0.693531000	2.377567000	-0.299555000
C	0.150602000	1.295151000	0.206277000
C	1.677137000	1.545228000	0.146290000
H	2.753231000	-0.281057000	-1.725549000
H	2.128742000	-0.242067000	1.273860000
H	-1.714293000	2.504752000	0.077061000
H	-0.040117000	0.515212000	-0.572335000
H	1.922224000	1.959013000	-0.841605000
O	2.058486000	2.452993000	1.176972000
H	1.827985000	3.349774000	0.898190000
O	3.842763000	0.635636000	0.481302000
H	4.377888000	-0.165992000	0.321420000
O	-0.317861000	0.883242000	1.471391000
H	-0.471779000	-0.088246000	1.448481000
O	-0.273436000	3.137413000	-1.223514000
H	-0.954339000	3.768608000	-1.535188000
O	0.997623000	-1.112169000	-1.140536000
C	3.113033000	-2.055947000	-0.545663000
H	2.907045000	-2.763553000	-1.360481000
H	2.765115000	-2.489142000	0.403452000
O	4.527346000	-1.782240000	-0.476156000
H	4.956732000	-2.516451000	-0.017105000
Ca	-2.743258000	-0.543659000	-0.737237000
Cl	-5.318613000	-0.263644000	0.140069000
Cl	-0.989954000	-2.131160000	1.051867000
H	0.584343000	-1.579421000	-0.382648000

TS2

E= -2286.110229

G= -2285.952292

C	2.466512000	0.170617000	0.533631000
C	2.272118000	-0.626703000	-0.771610000
C	-0.380186000	2.194270000	-0.735170000
C	0.255136000	1.382981000	0.194408000
C	1.758292000	1.524574000	0.477091000
H	2.674817000	-0.052621000	-1.613548000
H	2.059652000	-0.418217000	1.372371000

H	-1.471496000	2.232877000	-0.771778000
H	0.335232000	0.354876000	-0.676480000
H	2.203303000	2.102579000	-0.344406000
O	1.977686000	2.181235000	1.722834000
H	1.681167000	3.098257000	1.636485000
O	3.855376000	0.429201000	0.737721000
H	4.337343000	-0.377693000	0.475196000
O	-0.559546000	0.973586000	1.261859000
H	-0.520678000	-0.001714000	1.355452000
O	0.291875000	2.859303000	-1.648350000
H	-0.312161000	3.269772000	-2.289673000
O	0.848345000	-0.781220000	-1.064773000
C	2.893359000	-2.017441000	-0.736415000
H	2.611933000	-2.560321000	-1.649291000
H	2.523033000	-2.566079000	0.141070000
O	4.320478000	-1.858903000	-0.663488000
H	4.704970000	-2.698699000	-0.377761000
Ca	-2.765414000	-0.409406000	-0.654237000
Cl	-5.334947000	-0.132905000	0.220752000
Cl	-0.982716000	-2.159234000	0.939349000
H	0.416340000	-1.423940000	-0.432647000

IM4

E= -2286.128911

G= -2285.97058

C	-2.016469000	0.202243000	-0.783194000
C	-2.239260000	-0.474868000	0.579674000
C	0.123559000	2.217366000	1.258257000
C	-0.092693000	1.686049000	0.041855000
C	-1.413145000	1.613154000	-0.681518000
H	-2.768208000	0.187917000	1.271075000
H	-1.343375000	-0.432661000	-1.381582000
H	1.125226000	2.270007000	1.683560000
H	-0.429497000	0.095719000	1.308268000
H	-2.137896000	2.257830000	-0.169072000
O	-1.217563000	2.046114000	-2.038245000
H	-1.065721000	3.001960000	-2.027491000
O	-3.272042000	0.349296000	-1.446328000
H	-3.855998000	-0.381830000	-1.166419000
O	1.004300000	1.163234000	-0.639950000
H	0.796700000	1.157038000	-1.588665000
O	-0.910156000	2.714810000	2.016196000
H	-0.545567000	3.082520000	2.832745000
O	-0.941999000	-0.753217000	1.244087000

C	-2.927727000	-1.834730000	0.500841000
H	-2.857442000	-2.324029000	1.481445000
H	-2.436906000	-2.462555000	-0.255163000
O	-4.296337000	-1.596894000	0.145859000
H	-4.680630000	-2.434549000	-0.147138000
Ca	2.536463000	-0.460904000	0.523077000
Cl	5.020984000	-0.087096000	-0.560912000
Cl	0.760148000	-2.571942000	-0.189600000
H	-0.344397000	-1.437689000	0.707153000

TS3

E= -2286.109554

G= -2285.954826

C	2.140072000	0.161214000	0.692009000
C	2.153505000	-0.574756000	-0.665723000
C	0.057650000	1.711756000	-1.362988000
C	0.243083000	1.744670000	0.009130000
C	1.603175000	1.613808000	0.674193000
H	2.626895000	0.043253000	-1.434843000
H	1.497787000	-0.411610000	1.380829000
H	-0.947578000	1.870572000	-1.761729000
H	0.237593000	0.351959000	-1.209794000
H	2.323567000	2.250231000	0.148004000
O	1.470590000	1.993112000	2.041652000
H	1.524248000	2.958039000	2.103683000
O	3.459431000	0.257981000	1.222981000
H	3.992964000	-0.470999000	0.846893000
O	-0.807634000	1.734012000	0.801858000
H	-0.486059000	1.655719000	1.725970000
O	1.131307000	2.110210000	-2.169305000
H	1.108789000	1.593160000	-2.987451000
O	0.797164000	-0.820015000	-1.138063000
C	2.842579000	-1.936660000	-0.602217000
H	2.653505000	-2.464949000	-1.546064000
H	2.435500000	-2.526656000	0.230817000
O	4.252400000	-1.718170000	-0.420108000
H	4.654705000	-2.552190000	-0.141052000
Ca	-2.666225000	-0.378383000	-0.609980000
Cl	-5.241209000	-0.093548000	0.262062000
Cl	-0.949152000	-2.151927000	0.921072000
H	0.272263000	-1.333027000	-0.447487000

IM5

E= -2286.141263
G= -2285.980909

C	-2.680430000	0.194322000	-0.043416000
C	-1.487288000	0.959230000	-0.611440000
C	-0.174809000	-1.990500000	-1.222916000
C	-0.976426000	-1.693343000	-0.009080000
C	-2.449323000	-1.328749000	-0.106858000
H	-1.402284000	0.788012000	-1.690720000
H	-2.762463000	0.442187000	1.028304000
H	-0.429239000	-1.291933000	-2.028954000
H	-2.820020000	-1.709226000	-1.067649000
O	-3.134673000	-1.908991000	0.992784000
H	-3.312938000	-2.841745000	0.796726000
O	-3.893815000	0.484780000	-0.720286000
H	-3.923391000	1.454405000	-0.818155000
O	-0.537529000	-2.141722000	1.108931000
H	-1.254446000	-2.089789000	1.784897000
O	1.207928000	-1.989145000	-0.907691000
H	1.686755000	-2.405376000	-1.638630000
O	-0.318569000	0.381068000	-0.012966000
C	-1.538097000	2.453714000	-0.319707000
H	-0.627358000	2.933168000	-0.704652000
H	-1.600605000	2.613001000	0.766427000
O	-2.705627000	2.978162000	-0.972295000
H	-2.897468000	3.848283000	-0.597600000
Ca	2.210581000	0.266432000	-0.304725000
Cl	4.968679000	0.261182000	-0.674253000
Cl	1.310598000	0.990338000	2.370195000
H	-0.203122000	0.649112000	0.937007000
H	-0.516220000	-2.995840000	-1.530840000

TS4

E= -2286.141114
G= -2285.979342

C	-2.700096000	0.186548000	-0.032261000
C	-1.508715000	0.936908000	-0.621522000
C	-0.195019000	-1.996594000	-1.230922000
C	-0.952970000	-1.653401000	0.002814000
C	-2.442873000	-1.330692000	-0.064110000
H	-1.441926000	0.759596000	-1.701014000
H	-2.782244000	0.460332000	1.032850000
H	-0.481484000	-1.328568000	-2.051820000
H	-2.829580000	-1.744683000	-1.004436000
O	-3.085675000	-1.901598000	1.065539000

H	-3.247381000	-2.841813000	0.893537000
O	-3.915366000	0.453589000	-0.715024000
H	-3.966290000	1.421766000	-0.808719000
O	-0.484184000	-2.103867000	1.114960000
H	-1.181640000	-2.045660000	1.808552000
O	1.200246000	-1.973639000	-0.966995000
H	1.656671000	-2.392077000	-1.710871000
O	-0.342992000	0.334625000	-0.035872000
C	-1.530043000	2.432078000	-0.335350000
H	-0.620417000	2.897913000	-0.739407000
H	-1.572375000	2.599295000	0.750277000
O	-2.702737000	2.962983000	-0.972369000
H	-2.875190000	3.841050000	-0.607036000
Ca	2.228613000	0.265870000	-0.364339000
Cl	5.000607000	0.263312000	-0.568344000
Cl	1.241554000	1.020325000	2.319421000
H	-0.186581000	0.623442000	0.909187000
H	-0.536586000	-3.015643000	-1.486435000

IM6

E= -2286.146035

G= -2285.987831

C	-2.907782000	-0.067276000	-0.059607000
C	-1.792640000	0.735621000	-0.724535000
C	-0.092791000	-2.033174000	-0.984533000
C	-0.786878000	-1.327869000	0.157485000
C	-2.340123000	-1.473367000	0.118219000
H	-1.725729000	0.494950000	-1.791145000
H	-3.104046000	0.352980000	0.938731000
H	-0.468988000	-1.634339000	-1.935649000
H	-2.617855000	-2.096158000	-0.740370000
O	-2.827173000	-2.027390000	1.329197000
H	-2.745517000	-2.991498000	1.287328000
O	-4.096006000	-0.112135000	-0.833634000
H	-4.392818000	0.803168000	-0.955611000
O	-0.219339000	-1.623448000	1.358651000
H	-0.916922000	-1.592536000	2.039822000
O	1.322007000	-1.861792000	-0.875554000
H	1.743501000	-2.358888000	-1.590258000
O	-0.575692000	0.192965000	-0.109054000
C	-1.857065000	2.236556000	-0.512089000
H	-0.963673000	2.720520000	-0.930607000
H	-1.926050000	2.463698000	0.559705000
O	-3.043447000	2.657898000	-1.197433000

H	-3.219114000	3.575453000	-0.949760000
Ca	2.579287000	0.188800000	-0.261053000
Cl	5.347949000	0.181543000	-0.439240000
Cl	0.738946000	1.736719000	1.858219000
H	-0.188312000	0.741704000	0.730195000
H	-0.356554000	-3.097236000	-0.910988000

TS1-0

E= -687.2942247

G= -687.1428777

C	-0.637714000	0.833044000	-0.212613000
C	-1.161383000	-0.451114000	0.441775000
C	1.379481000	-1.341244000	0.335659000
C	1.723277000	0.040111000	-0.225660000
C	0.779423000	1.140508000	0.248792000
H	-1.364629000	-0.246984000	1.500339000
H	-0.637968000	0.718025000	-1.308205000
H	1.752043000	-1.475878000	1.361277000
H	1.675522000	-0.015544000	-1.321785000
H	0.803741000	1.206926000	1.349000000
O	1.167560000	2.394382000	-0.318156000
H	2.113684000	2.502382000	-0.142259000
O	-1.482412000	1.923184000	0.162795000
H	-2.391893000	1.645017000	-0.040059000
O	3.045382000	0.397738000	0.190655000
H	3.678708000	-0.066991000	-0.373197000
O	1.526992000	-2.395185000	-0.514814000
H	0.166023000	-2.226496000	-0.433685000
O	-0.172080000	-1.522141000	0.421340000
C	-2.405837000	-1.013188000	-0.243926000
H	-2.706805000	-1.949564000	0.243759000
H	-2.180916000	-1.211734000	-1.298618000
O	-3.475818000	-0.059137000	-0.225426000
H	-3.847997000	-0.038595000	0.668120000

IM1-1

E= -2285.71673

G= -2285.566487

C	-2.769673000	0.460905000	-0.430644000
C	-2.400318000	-0.666513000	0.551031000
C	-0.199146000	0.362615000	0.537758000
C	-0.745630000	1.767782000	0.217021000
C	-2.273398000	1.784075000	0.124033000

H	-3.160869000	-0.663735000	1.343948000
H	-2.309040000	0.278439000	-1.412594000
H	0.641016000	0.443074000	1.241231000
H	-0.331947000	2.078535000	-0.750938000
H	-2.681907000	1.916760000	1.137671000
O	-2.736620000	2.845311000	-0.718337000
H	-2.475669000	3.681671000	-0.308589000
O	-4.193033000	0.520438000	-0.586065000
H	-4.469235000	-0.372329000	-0.849676000
O	-0.382146000	2.714800000	1.229346000
H	0.570565000	2.869990000	1.167086000
O	0.207448000	-0.232369000	-0.676308000
H	0.560892000	-1.127575000	-0.462916000
O	-1.147352000	-0.437569000	1.231900000
C	-2.390898000	-2.042801000	-0.114996000
H	-2.068726000	-2.801677000	0.610810000
H	-1.705571000	-2.052101000	-0.968334000
O	-3.693376000	-2.360546000	-0.641034000
H	-4.283781000	-2.532323000	0.106672000
Ca	3.404284000	-0.611813000	0.141529000
Cl	5.098375000	1.451690000	-0.587066000
Cl	1.599484000	-2.856358000	0.133761000

TS1-1

E= -2285.630624

G= -2285.486333

C	-3.248835000	-0.047486000	-0.363843000
C	-3.608957000	-1.110254000	0.698163000
C	-0.512574000	1.079150000	0.104909000
C	-1.675733000	1.958467000	-0.216109000
C	-2.973092000	1.315798000	0.311955000
H	-4.539696000	-0.763372000	1.208406000
H	-2.314033000	-0.408991000	-0.825395000
H	-0.254932000	0.900425000	1.156120000
H	-1.739903000	2.134581000	-1.297175000
H	-2.830528000	1.141265000	1.386280000
O	-4.059579000	2.211892000	0.110327000
H	-3.924233000	2.964727000	0.702330000
O	-4.226461000	0.119263000	-1.400646000
H	-4.662648000	-0.749174000	-1.497071000
O	-1.453577000	3.168722000	0.509363000
H	-0.809582000	3.707463000	0.026771000
O	0.210086000	0.597141000	-0.798089000
H	0.997629000	-0.003550000	-0.405966000

O	-2.536685000	-1.262762000	1.581083000
C	-3.931770000	-2.458448000	0.035288000
H	-4.091958000	-3.212193000	0.819391000
H	-3.086216000	-2.774724000	-0.590357000
O	-5.081589000	-2.424560000	-0.852523000
H	-5.863897000	-2.241094000	-0.312684000
Ca	4.999675000	-0.283381000	0.328284000
Cl	7.577352000	-0.006359000	-0.547074000
Cl	2.188218000	-1.095327000	0.337978000

IM1-2

E= -1147.778758

G= -1147.625507

C	-1.902549000	0.088840000	-0.102464000
C	-0.888566000	-1.058403000	0.041264000
C	0.969838000	0.417090000	-0.162994000
C	0.059638000	1.629463000	-0.349001000
C	-1.280778000	1.403842000	0.340724000
H	-0.653619000	-1.195209000	1.110761000
H	-2.190120000	0.169254000	-1.163704000
H	1.185973000	0.253594000	0.905935000
H	-0.099619000	1.777022000	-1.428112000
H	-1.111365000	1.362974000	1.428746000
O	-2.203628000	2.459280000	0.041543000
H	-1.809617000	3.287893000	0.347995000
O	-3.065958000	-0.146487000	0.700608000
H	-3.303117000	-1.082367000	0.570507000
O	0.639606000	2.802477000	0.230284000
H	1.453293000	3.000326000	-0.254292000
O	2.146780000	0.607845000	-0.888255000
H	2.867726000	0.070068000	-0.460586000
O	0.308382000	-0.748031000	-0.680926000
C	-1.396436000	-2.374409000	-0.544010000
H	-0.603465000	-3.131463000	-0.479110000
H	-1.667462000	-2.230409000	-1.596778000
O	-2.587641000	-2.832265000	0.119033000
H	-2.340946000	-3.133966000	1.005350000
Cl	4.294419000	-0.995813000	0.499640000

TS1-2

E= -1147.693085

G=-1147.549181

C	-1.333936000	0.078020000	-0.297779000

C	-1.614392000	-1.004802000	0.767665000
C	1.601183000	0.824273000	-0.038342000
C	0.509749000	1.840699000	-0.266355000
C	-0.809036000	1.373841000	0.368653000
H	-2.423728000	-0.606817000	1.427633000
H	-0.539823000	-0.333203000	-0.942906000
H	1.948812000	0.706553000	1.002885000
H	0.373920000	2.010746000	-1.342845000
H	-0.607111000	1.161282000	1.427136000
O	-1.776825000	2.419542000	0.273202000
H	-1.413288000	3.177733000	0.751941000
O	-2.468263000	0.388507000	-1.125331000
H	-2.979116000	-0.440368000	-1.195865000
O	0.911387000	3.041700000	0.402270000
H	1.587274000	3.478933000	-0.134658000
O	2.134479000	0.193152000	-0.949242000
H	3.225663000	-0.731824000	-0.480854000
O	-0.442793000	-1.297690000	1.469598000
C	-2.155180000	-2.287369000	0.115806000
H	-2.255415000	-3.063460000	0.888075000
H	-1.449087000	-2.639484000	-0.648311000
O	-3.423505000	-2.120789000	-0.574518000
H	-4.092970000	-1.907179000	0.091092000
Cl	4.232864000	-1.573897000	-0.041709000

TS1-a

E= -1808.506652

G= -1808.343000

C	-2.099110000	-0.295727000	-0.410212000
C	-1.846366000	-1.308501000	0.712372000
C	-0.262042000	2.010694000	0.350759000
C	-1.628373000	2.199864000	-0.214475000
C	-2.580675000	1.065403000	0.186392000
H	-2.731921000	-1.360383000	1.361217000
H	-1.144354000	-0.151984000	-0.940255000
H	-0.113433000	1.929592000	1.431360000
H	-1.585859000	2.305976000	-1.304995000
H	-2.587384000	1.011054000	1.282830000
O	-3.888983000	1.393103000	-0.246596000
H	-4.119716000	0.708696000	-0.904010000
O	-3.068242000	-0.738459000	-1.364140000
H	-3.200077000	-1.699318000	-1.233297000
O	-2.040062000	3.408692000	0.427824000
H	-1.650231000	4.158579000	-0.047085000

O	0.742283000	2.058782000	-0.414858000
H	1.600185000	2.013546000	0.061803000
O	-0.780845000	-0.812270000	1.530124000
C	-1.535766000	-2.713403000	0.192850000
H	-1.204782000	-3.347653000	1.025616000
H	-0.745879000	-2.681175000	-0.567105000
O	-2.688523000	-3.286955000	-0.456073000
H	-3.348990000	-3.483706000	0.224500000
Cl	5.671704000	0.275075000	-0.567738000
Cl	1.974507000	-1.471704000	0.045956000
H	0.062161000	-0.922684000	1.047846000
Mg	3.691139000	-0.005913000	0.559626000

TS1-b

E= -9185.473494

G= -9185.294466

C	2.326781000	0.675127000	-0.574404000
C	1.926055000	1.390950000	0.726030000
C	1.945313000	-2.309226000	0.447706000
C	3.108503000	-1.879075000	-0.337940000
C	3.385438000	-0.349339000	-0.102542000
H	2.882942000	1.860549000	1.002416000
H	1.553736000	0.268288000	-1.228465000
H	2.076929000	-2.666340000	1.475243000
H	2.953160000	-2.061296000	-1.409809000
H	3.504906000	-0.263602000	0.982558000
O	4.641162000	-0.129174000	-0.737078000
H	5.255883000	-0.762424000	-0.338372000
O	3.037234000	1.634318000	-1.388559000
H	2.485266000	2.434428000	-1.378724000
O	4.273734000	-2.535433000	0.150135000
H	4.274780000	-3.444436000	-0.183828000
O	0.784730000	-2.211869000	-0.034516000
H	0.078712000	-2.435102000	0.613628000
O	1.639643000	0.503451000	1.827776000
C	0.934842000	2.565221000	0.690487000
H	0.920825000	2.961219000	1.717816000
H	-0.050021000	2.221161000	0.403210000
O	1.300394000	3.589878000	-0.246515000
H	2.061697000	4.077196000	0.100277000
Cl	-5.084410000	-0.591579000	-0.335685000
Cl	-0.407089000	0.238877000	0.149407000
H	0.687321000	0.304079000	1.829580000
Ba	-2.544775000	-0.069091000	-0.037228000

TS1-c

E= -6513.964365

G= -6513.80533

C	3.254258000	-0.540209000	0.128143000
C	2.195168000	-1.200550000	-0.761397000
C	2.166584000	2.239724000	0.564491000
C	3.610872000	1.998571000	0.298837000
C	3.804796000	0.741769000	-0.576314000
H	2.605451000	-1.332334000	-1.773096000
H	2.762275000	-0.273856000	1.075469000
H	1.490926000	2.531871000	-0.244870000
H	4.156427000	1.885147000	1.244291000
H	3.261560000	0.916333000	-1.513834000
O	5.180009000	0.614462000	-0.884089000
H	5.463164000	-0.212264000	-0.446608000
O	4.359110000	-1.395849000	0.432975000
H	4.098124000	-2.310290000	0.200396000
O	4.042251000	3.135625000	-0.442174000
H	4.171623000	3.874254000	0.171451000
O	1.734804000	2.180803000	1.749788000
H	0.779297000	2.390338000	1.827469000
O	1.099110000	-0.283538000	-0.876337000
C	1.736508000	-2.562948000	-0.242288000
H	0.879684000	-2.915861000	-0.830362000
H	1.440102000	-2.500205000	0.811142000
O	2.817250000	-3.516877000	-0.299135000
H	2.990751000	-3.719032000	-1.230385000
H	0.452845000	-0.459374000	-0.156625000
Br	-5.301128000	0.472534000	-0.151830000
Br	-1.453132000	-0.961508000	1.068656000
Ca	-2.631127000	0.465209000	-1.257020000

TS1-d

E= -4713.596122

G= -4713.437386

C	-2.996958000	-0.145715000	-0.449577000
C	-2.888059000	-1.215252000	0.650139000
C	-0.724067000	1.823396000	0.248645000
C	-2.074656000	2.215180000	-0.240209000
C	-3.191444000	1.259214000	0.188474000
H	-3.786034000	-1.170616000	1.283361000
H	-2.036573000	-0.158793000	-0.995514000
H	-0.556189000	1.583881000	1.302523000

H	-2.074644000	2.364989000	-1.325660000
H	-3.148588000	1.169763000	1.282292000
O	-4.440732000	1.817301000	-0.191977000
H	-4.574206000	2.613372000	0.341615000
O	-4.052465000	-0.413166000	-1.369661000
H	-4.148572000	-1.384286000	-1.411241000
O	-2.229417000	3.450993000	0.473265000
H	-1.802861000	4.159372000	-0.033851000
O	0.261305000	1.908867000	-0.539119000
H	1.123533000	1.756793000	-0.096342000
O	-1.775906000	-0.900750000	1.493521000
C	-2.733652000	-2.634056000	0.095241000
H	-2.543384000	-3.326345000	0.926411000
H	-1.889271000	-2.677897000	-0.602282000
O	-3.890818000	-3.053766000	-0.655283000
H	-4.629825000	-3.154507000	-0.037640000
Cl	6.113973000	0.230401000	-0.787943000
Cl	0.842541000	-1.736566000	0.030973000
H	-0.943462000	-1.119352000	1.012450000
Sr	3.405964000	-0.140632000	0.383688000

Ca^{2+}+β-D-Fructofuranose

E= -1364.90604

G= -1364.751674

C	-1.859671000	-0.082297000	0.136905000
C	-1.145152000	-1.433398000	0.137229000
C	0.323657000	-1.045329000	-0.109203000
C	-1.099414000	0.683509000	-0.941059000
H	-1.503160000	-2.019788000	-0.718078000
H	-1.533456000	0.439848000	-1.921347000
O	0.260664000	0.157707000	-0.892001000
O	-3.236753000	-0.142189000	-0.213471000
H	-3.718721000	-0.523036000	0.533464000
O	0.955945000	-0.708885000	1.121311000
C	1.109779000	-2.122623000	-0.837272000
H	0.935042000	-3.081441000	-0.330652000
H	0.744357000	-2.184036000	-1.870729000
O	2.497804000	-1.774687000	-0.792313000
H	3.015442000	-2.575563000	-0.945878000
O	-1.343929000	-2.229770000	1.289155000
H	-0.905530000	-1.788642000	2.033085000
H	-1.738571000	0.386833000	1.124625000
C	-1.057605000	2.192794000	-0.797629000
H	-0.509364000	2.628066000	-1.640347000

H	-2.082667000	2.584689000	-0.801320000
O	-0.354673000	2.617218000	0.385553000
Ca	1.926603000	1.615679000	0.475075000
H	-0.911743000	2.473095000	1.163346000
H	1.814288000	-1.164696000	1.152637000

Ca^{2+}+β-D-Fructopyranose

E= -1364.907474

G= -1364.750756

C	-0.432563000	1.060397000	0.425219000
C	0.584544000	2.178562000	0.200825000
C	1.958952000	1.674803000	0.608205000
C	1.443540000	-0.622687000	0.116750000
C	0.003395000	-0.220700000	-0.269232000
H	2.728396000	2.404921000	0.341232000
H	0.325810000	3.035835000	0.836085000
H	-0.520245000	0.877827000	1.502431000
H	1.979700000	1.505702000	1.692271000
O	2.320072000	0.464563000	-0.087073000
O	0.614548000	2.583024000	-1.176880000
H	-0.048737000	3.273904000	-1.304146000
O	-1.757890000	1.418396000	-0.006089000
C	1.977886000	-1.742200000	-0.781620000
H	3.011951000	-1.966310000	-0.487568000
H	1.956020000	-1.414265000	-1.825929000
O	1.154365000	-2.913502000	-0.699572000
H	1.299631000	-3.319505000	0.167748000
O	1.509383000	-1.025027000	1.481382000
H	0.629870000	-1.322248000	1.760411000
H	-0.022636000	-0.077678000	-1.357125000
O	-0.940220000	-1.240461000	0.106373000
Ca	-3.271274000	-0.544407000	0.056640000
H	-1.709195000	1.705879000	-0.932344000
H	-0.621668000	-2.080911000	-0.271871000

Ca^{2+}+α-D-Fructofuranose

E= -1364.906715

G= -1364.748074

C	1.597141000	0.916545000	-0.273088000
C	1.901829000	-0.536553000	0.072559000
C	0.512024000	-1.120536000	0.402799000
C	0.490398000	1.242920000	0.722408000

H	2.509199000	-0.565983000	0.987152000
H	0.946883000	1.423924000	1.707495000
O	-0.302454000	0.028392000	0.768254000
O	2.688170000	1.806939000	-0.085558000
H	3.317216000	1.666246000	-0.806344000
O	0.635912000	-1.974566000	1.516700000
H	-0.221531000	-2.383264000	1.710659000
C	-0.137274000	-1.802572000	-0.803450000
H	0.359108000	-2.757588000	-1.003931000
H	-0.040559000	-1.150933000	-1.677187000
O	-1.547284000	-1.998336000	-0.612082000
H	1.226037000	0.974566000	-1.307470000
O	2.578094000	-1.179438000	-0.997765000
H	2.943720000	-2.013792000	-0.672632000
C	-0.411496000	2.420481000	0.397063000
H	-1.038551000	2.654664000	1.264218000
H	0.209775000	3.295407000	0.165050000
O	-1.331294000	2.143104000	-0.674811000
Ca	-2.657586000	0.111327000	-0.062506000
H	-0.842785000	2.061270000	-1.506702000
H	-1.701683000	-2.761526000	-0.037839000

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