Supporting information

Boosting utilization efficiency of glucose via favored C-C coupling reaction

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Experimental section

Chemicals

Microcrystalline cellulose powder (PH-101) was purchased from Fluka Analytical Co. Ltd. D-Glucose (>99.5%), NaCl and KCl were obtained from Sigma-Aldrich and used without further purification. 5-(Hydroxymethyl)furfural (HMF, > 98%) was purchased from Alfa Aesar Chemical Reagent Co. $CoCl_2$ and $CrCl_3$ were purchased from Aladdin Reagent Co., 2,4-pentanedione were purchased from shanghai Titan Technology Co., Ltd.

Catalytic reaction

Catalytic test for glucose, starch and fructose conversion in 2,4-pentandione/H_2O-NaCl biphasic system.

Catalytic experiments were conducted in a Teflon-lined stainless steel autoclave (50 ml, Anhui Kemi Machinery Technology Co. Ltd.; with Teflon liner), equipped with a temperature-controlled heating jacket and magnetic stirring. The mixture of glucose or starch or fructose (0.1 g), H_2O (1 g), 2,4-pentanedione (6 g) and NaCl (0.3 g) were put in the sealed autoclave and 0.5 MPa N_2 was used for purging air out of the reactor and retaining all solvent in liquid phase. Then the mixture was stirred at 700 rpm to guarantee that it is properly stirred. When the reactor was raised to the desired temperature, zero time was recorded. Then, the reactor was held at this temperature for a given period of time. After reaction, the mixtures were cooled down quickly. The 2,4-pentanedione phase was used to analyze the products yield and the aqueous phase was used to analyze the glucose conversion. The products were directly obtained by removing 2,4-pentanedione with rotary evaporation at 75 °C and 2,4-pentanedione can be reused without further purification.

Conversion of glucose into HMF in THF/H_2O-NaCl biphasic system.

The glucose dehydration into HMF reaction experiments were conducted in a Teflon-lined stainless steel autoclave (50 ml, Anhui Kemi Machinery Technology Co. Ltd.; with Teflon liner), equipped with a temperature-controlled heating jacket and magnetic stirring. The mixture of glucose (0.1 g), H_2O (1 g), THF (6 g) and NaCl (0.3 g) were put in the sealed autoclave and 0.5 MPa N_2 was used for purging air out of the reactor and retaining all solvent in liquid phase. Then the mixture was stirred at 700 rpm to guarantee that it is properly stirred. When the reactor was raised to the desired temperature, zero time was recorded. Then, the reactor was held at this temperature for a given period of time. After reaction, the mixtures were cooled down quickly, and the reaction liquid was taken for analysis.

Hydrodeoxygenation of C_{11}-glu into liquid fuel.

The HDO of the C_{11}-glu was conducted in a 50 mL Teflon-lined stainless-steel autoclave. 5% Pd/$NbOPO_4$ (0.1 g), C_{11}-glu (0.2 g), and cyclohexane (5 g) were transferred into the autoclave. The reactor was then sealed, purged with H_2 three times, and charged to 4 MPa H_2 pressure. The reaction was then performed at 190 °C and 4 MPa under magnetic stirring for 20 h. After the reaction, the autoclave was quenched in an ice-water bath to room temperature. The liquid solution was separated from the solid catalyst by centrifugation was taken for analysis.

Product analysis.

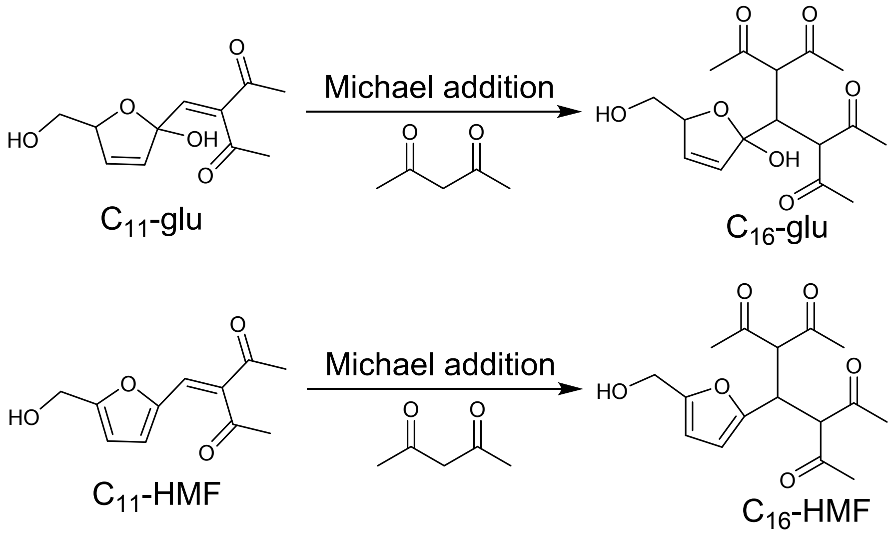
The analysis of HMF was carried out by means of an HPLC apparatus (Agilent 1200 Series) equipped with an XDB-C18 column (Eclipse USA) and quantified with an ultraviolet detector (Agilent G1314B) at 254 nm. The eluent with a flow rate of 0.6 mL min^{-1} was a mixture of methanol and water with volumetric ratio of 20:80. An auto-sampler (Agilent G1329A) was used to enhance the reproducibility. The quantification of HMF was performed using an external standard method. The yield of HMF was calculated by using the equation: HMF yield [%] = (moles of HMF produced) / (moles of starting glucose) × 100%.

Glucose and fructose were analyzed on the same HPLC apparatus (Agilent 1200 Series), but with a refractive index detector (Agilent G1362A) and using a Biorad Aminex HPX-87H sugar column at 55 °C. The mobile phase was 0.004 M H_2SO_4 with a flow rate of 0.45 mL min^{-1}. The quantification of glucose was performed using an external standard method. The conversion of glucose was calculated by using the equation: glucose conversion [%] = (moles of glucose reacted) / (moles of starting glucose) × 100%. The conversion of fructose was calculated by using the equation: fructose conversion [%] = (moles of fructose reacted) / (moles of starting fructose) × 100%.

The products (C11-glu, C_{16}-glu, C_{11}-HMF and C_{16}-HMF) were analyzed qualitatively by GC-MS (Agilent 7890A-5975C) and quantitatively by GC equipped with a flame ionization detector (FID, Agilent 7890) using isophorone as the internal standard. The relatively pure products were purified by silica-gel column chromatography and used as standard. The structures were confirmed by^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, mass spectrometry and FT-IR spectrum. The yield of C11-glu and C_{16}-Glu was calculated by using the equation: C_{11}-glu (C_{16}-glu) yield [%] = (moles of C_{11}-glu (C_{16}-glu) produced) / (moles of starting glucose) × 100%. The yield of C_{11}-HMF and C_{16}-HMF was calculated by using the equation: C_{11}-HMF (C_{16}-HMF) yield [%] = (moles of C_{11}-HMF (C_{16}-HMF) produced) / (moles of starting fructose) × 100%.

Computational details

The density functional theory (DFT) method based on quantum mechanics was employed in the present study. To stimulate the experimental condition, the Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM) was adopted together with conducting an IEFPCM calculation with radii and non-electrostatic terms for Truhlar and coworkers' SMD solvation model, which can have a good description on ΔG of solvation.[1] Under the hot water condition (413 K and 0.5 MPa), the equilibrium geometries of all reactants, intermediates, transition states and products involved in every chemical reaction were performed at B3LYP method with AUG-cc-pVDZ basis set,[2] which can offer accurate computational results with tolerable computing time. The transition states were located by the synchronous transit-guided quasi-Newton method according to the structures of reactants and products and were further confirmed by frequency analysis and intrinsic reaction coordinate (IRC) calculations with the same basis set. All energies of structures were obtained after zero-point energy (ZPE) correction. The correctness of all the optimized structures were confirmed through frequency analysis in which reactants, intermediates and products had no imaginary frequencies while transition states have exactly one imaginary frequencies. The coordinates of optimised geometries including all reported intermediates and transition states from the density functional theory calculations are listed in Figure S24. All calculations were performed by employing Gaussian 09W suite of programs.[3] The Gibbs free energy change of a chemical reaction is calculated as the difference of product and reactant: $\Delta G_a = G_{\mathrm{reactant}} - G_{\mathrm{Product}}$. The free energy barrier of a reaction is defined as $\Delta G_b = G_{\mathrm{Transition\ state}} - G_{\mathrm{Reactant}}$, where $G_{\mathrm{Transition\ state}}$ is the free energy of the transition state in a reaction step.



Scheme S1 The deep condensation of C_{11}-glu and C_{11}-HMF with 2,4-pentanedione into C_{16}-glu and C_{16}-HMF, respectively.

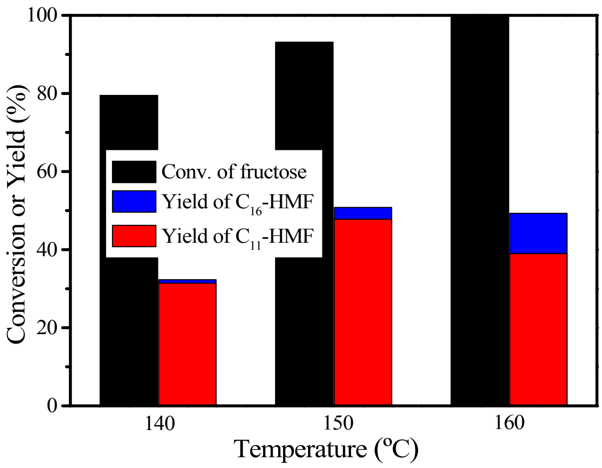


Figure S1 Influence of the reaction temperature on fructose conversion and $C_{11\text{-}16}$-HMF yield. Reaction conditions: 0.1 g fructose, 1 g H_2O saturated with NaCl (0.3 g), 6 g 2,4-pentanedione, 0.5 MPa N_2, 3 h.

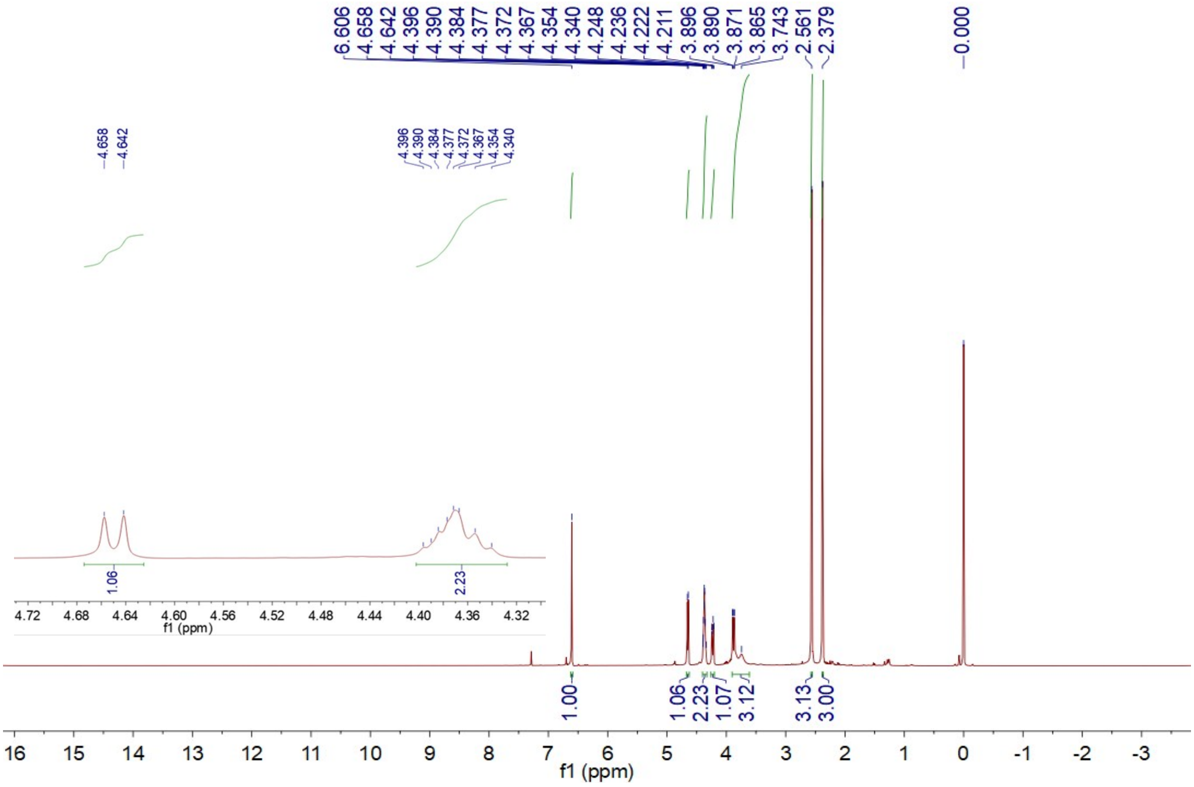


Figure S2 ^{1}H NMR spectrum of C_{11}-glu.

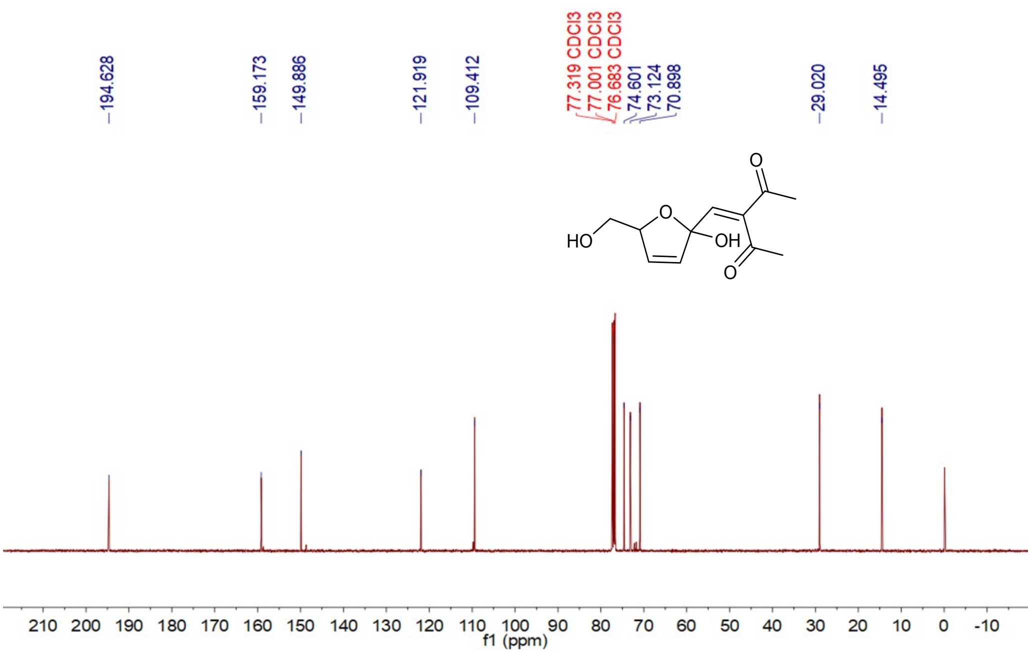


Figure S3 ^{13}C NMR spectrum of C_{11}-glu.

Although ^{13}C NMR of C_{11}-glu shows 10 signals, we can confirm that C_{11}-glu contains 11 carbons based on high-resolution mass spectrum, molecular mass and reaction mechanism. In addition, the carbon numbers of C_{11} alkane after HDO also confirm the carbon numbers of

C_{11}-glu. We guessed that the signals of two C=O groups overlap at 194 ppm as chemical shift of C=O groups are generally above 180 ppm.

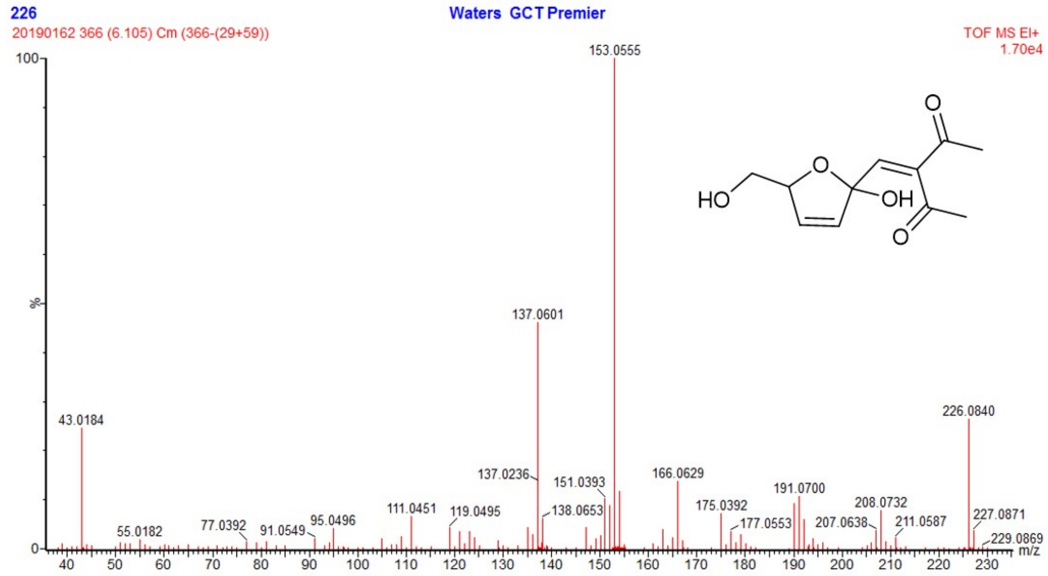


Figure S4 High-resolution Mass spectrum of C_{11}-glu.

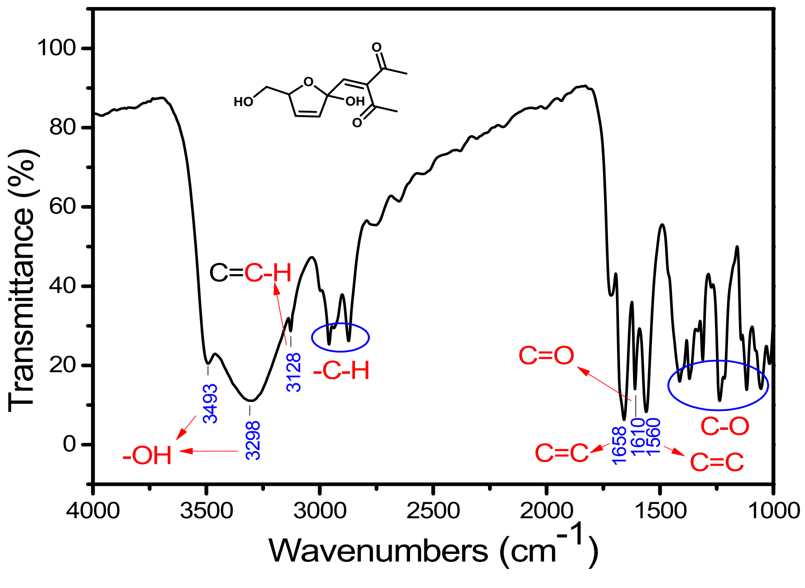


Figure S5 FTIR spectrum of C_{11}-glu

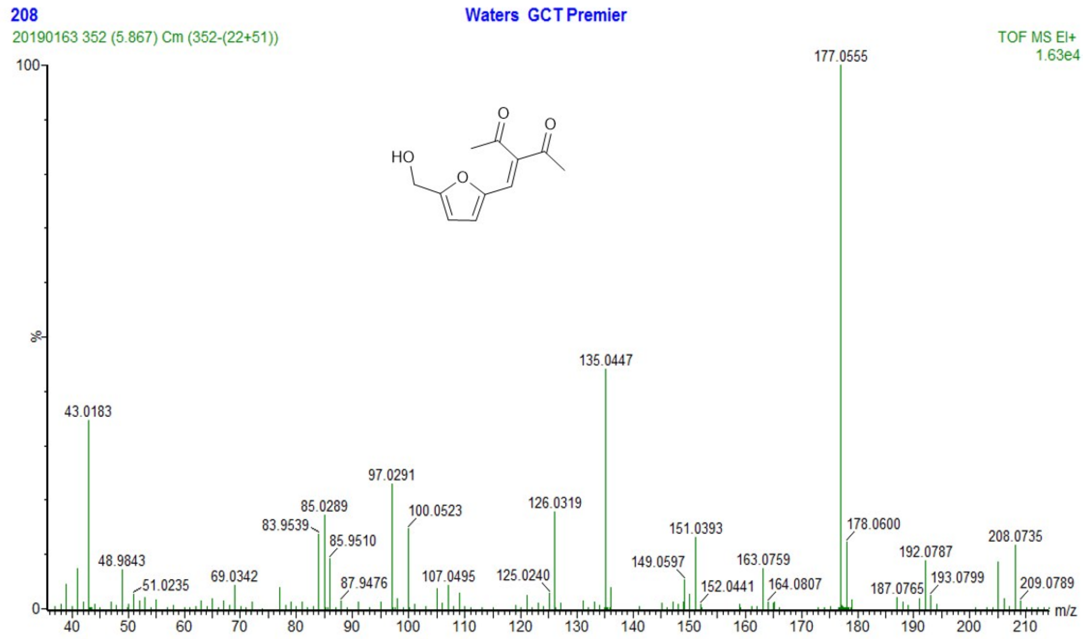


Figure S6 High-resolution mass spectrum of C_{11}-HMF.

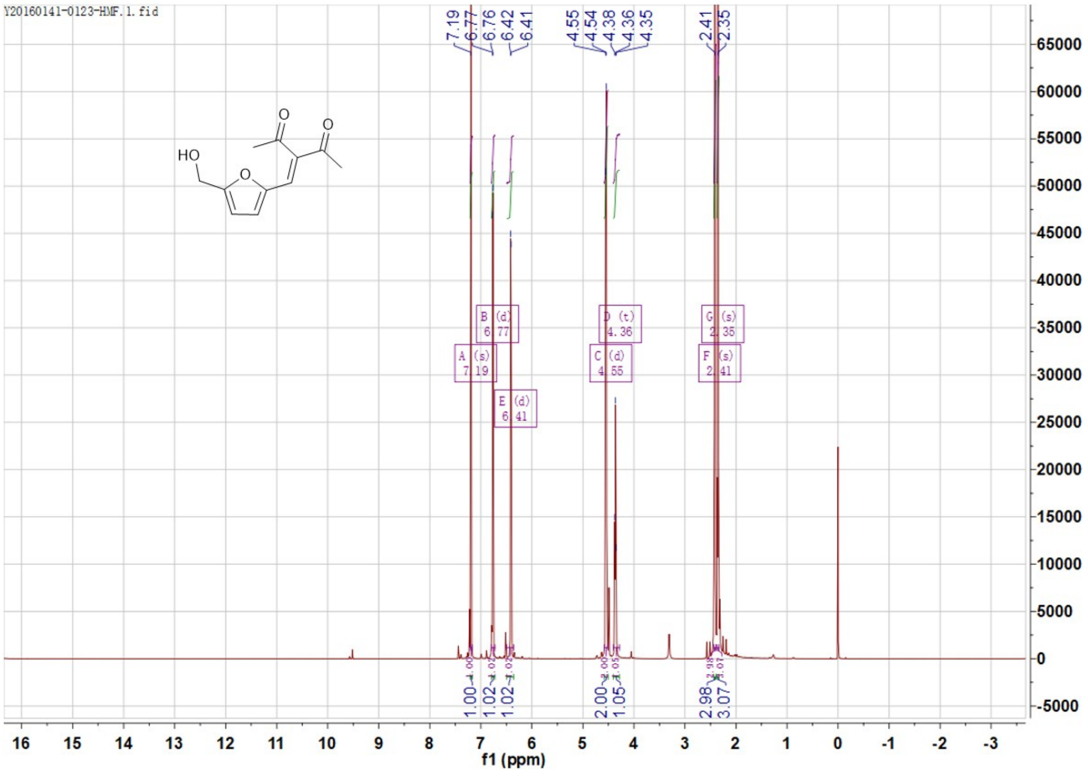


Figure S7 ^{1}H NMR spectrum of C_{11}-HMF.

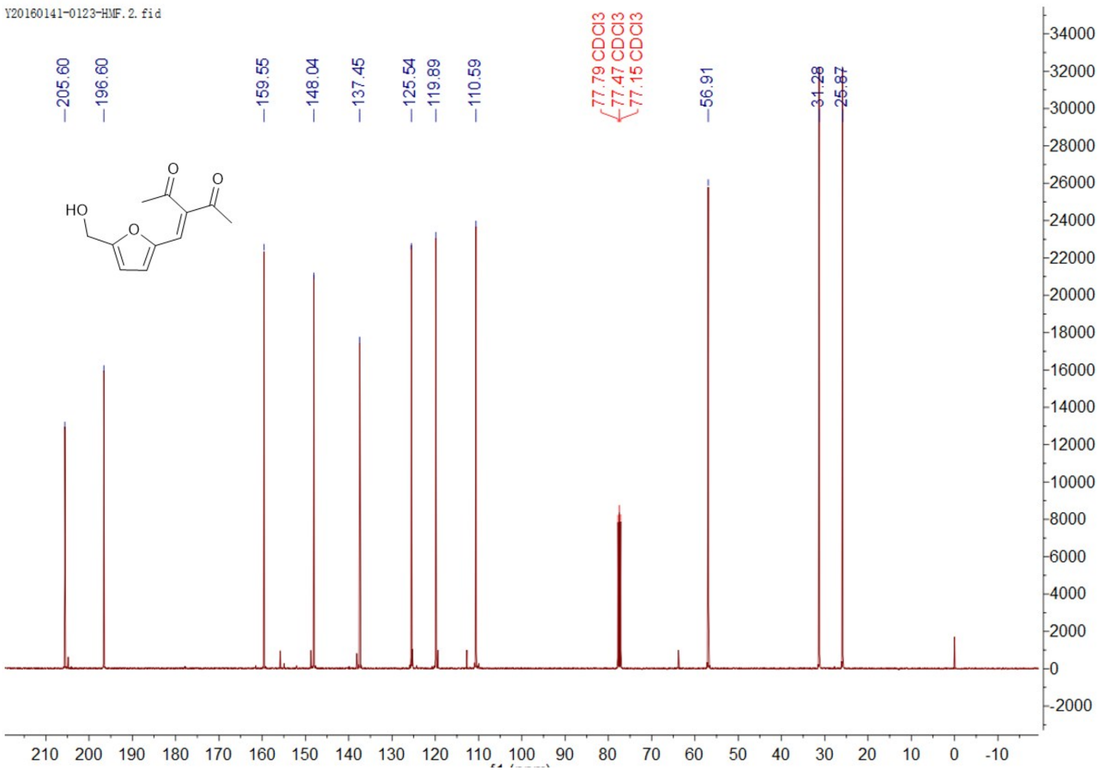


Figure S8 ^{13}C NMR spectrum of C_{11}-HMF.

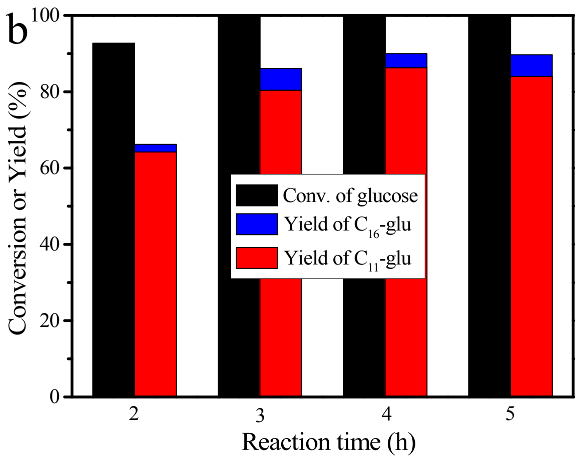


Figure S9 Reaction time for the conversion of glucose into C_{11}-glu and C_{16}-glu. Reaction conditions: 0.1 g glucose, 1 g H_2O saturated with NaCl (0.3 g), 6 g 2,4-pentanedione, 0.5 MPa N_2, 140 °C.

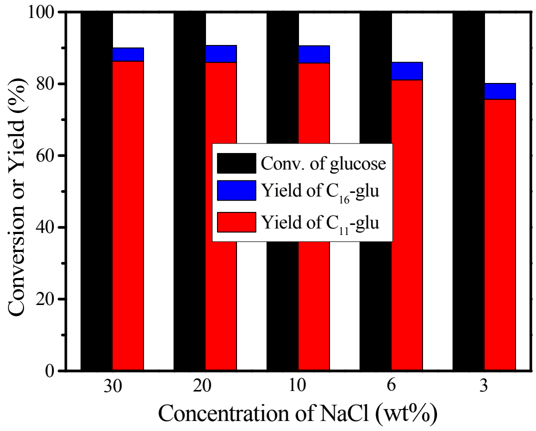


Figure S10 Influence of the concentration of NaCl on the conversion of glucose into C_{11}-glu and C_{16}-glu. Reaction conditions: 0.1 g glucose, 1 g H_2O, 6 g 2,4-Pentanedione, 0.5 MPa N_2, 140 °C, 4 h.

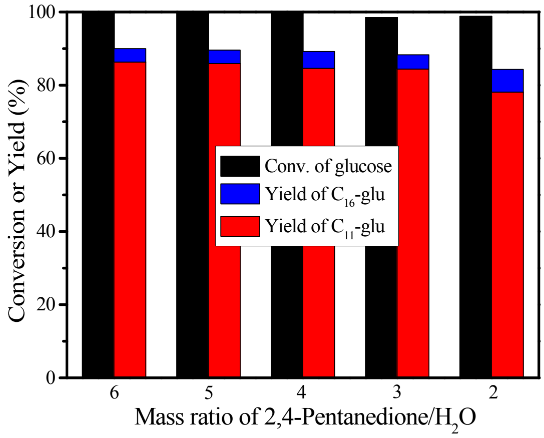


Figure S11 Influence of mass ratio of 2,4-Pentancedione/H_2O on the conversion of glucose into C_{11}-glu and C_{16}-glu. Reaction conditions: 0.1 g glucose, 1 g H_2O, 0.1 g NaCl, 0.5 MPa N_2, 140 °C, 4 h.

The obtained C_{11} branched alkanes through the total hydrodeoxygenation of C_{11}-glu contains a branch, leading to a lower freezing point than that of straight alkanes and can be directly used as transportation fuels or additives for conventional fuels.[4] When the engine operates under very low temperature, highly branched alkanes are intensively desired to decrease the freezing point. According to our previous study, the $CoCl_2$-catalyzed Michael addition of 2,4-pentanedione with α, β-unsaturated carbonyl compounds can be employed to produce highly branched alkanes precursors.[5] We therefore attempted the $CoCl_2$-catalyzed Michael addition of 2,4-pentanedione with C_{11}-glu to synthesize higher branched C_{16}-glu and the result indicates that C_{16}-glu is the main product (Figure S9). Because the branched structure of C_{16}-glu alkane is highly similar with that of reported branched alkanes, the branched C_{16} alkanes should have low freezing point.[5] In short, this new system not only enables the direct conversion of glucose into branched C_{11}-glu fuel precursor, but can further upgrade C_{11}-glu to highly branched fuel precursor through tandem Michael addition.

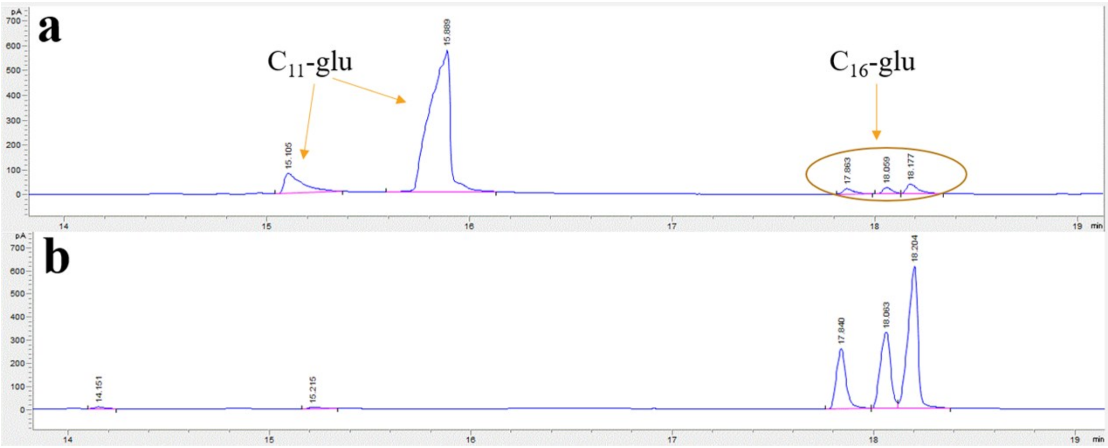


Figure S12 GC trace of products from glucose in a 2,4-pentanedione/H_2O-NaCl biphasic system and the following Michael addition products. Reaction conditions: (a) 0.1 g glucose, 1 g H_2O, 0.3 g NaCl, 0.5 MPa N_2, 6 g 2,4-pentanedione, 140 °C, 4 h. (b) the obtained 2,4-pentanedione phase, 0.1 g $CoCl_2$, 0.1 g $CaCl_2$, 120 °C, 10 h.

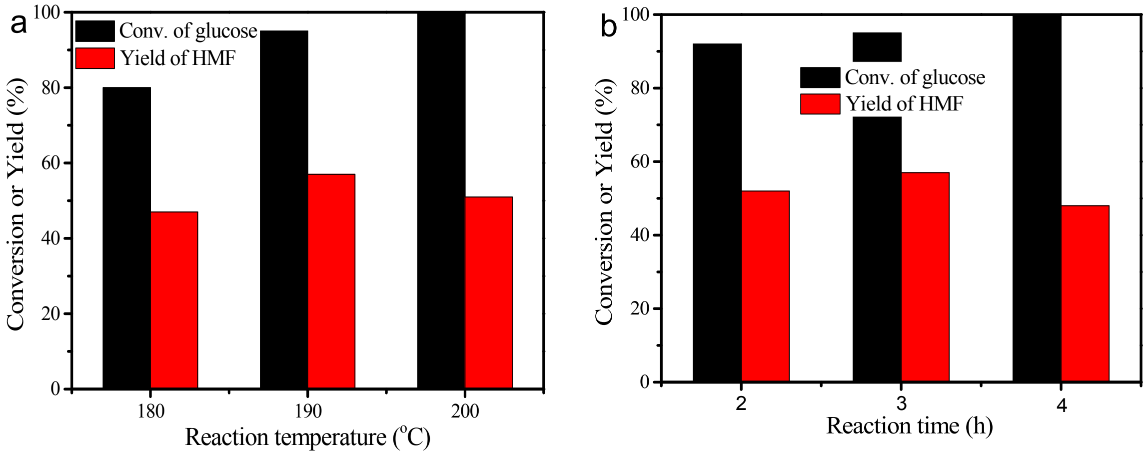


Figure S13 Reaction conditions optimization for the conversion of glucose into HMF. Reaction conditions: a) 0.1 g glucose, 1 g H_2O saturated with NaCl (0.3 g), 6 g THF, 0.5 MPa N_2, 3 h; b) 0.1 g glucose, 1 g H_2O saturated with NaCl (0.3 g), 6 g THF, 0.5 MPa N_2, 190 °C.

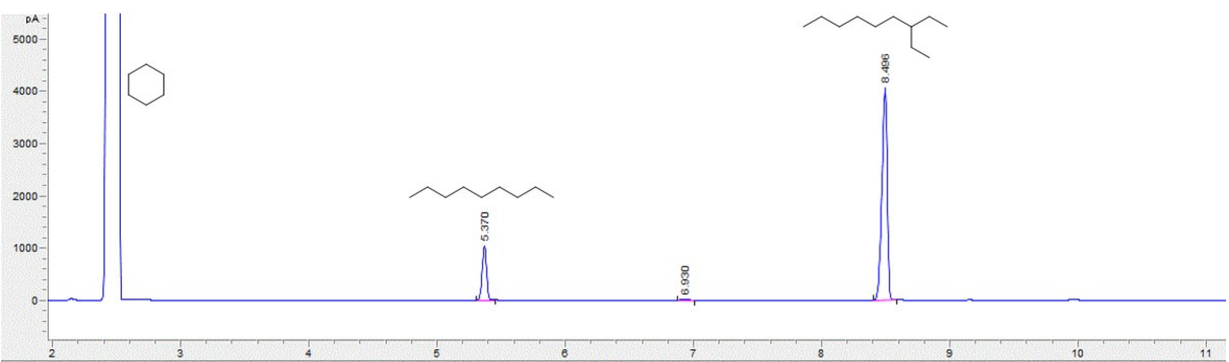


Figure S14 The hydrodeoxygenation of C_{11}-glu over Pd/$NbOPO_4$. Reaction conditions: 0.1 g 5% Pd/$NbOPO_4$, 0.2 g C_{11}-glu, 5 g cyclohexane, 4MPa H_2, 190 °C, 20 h.

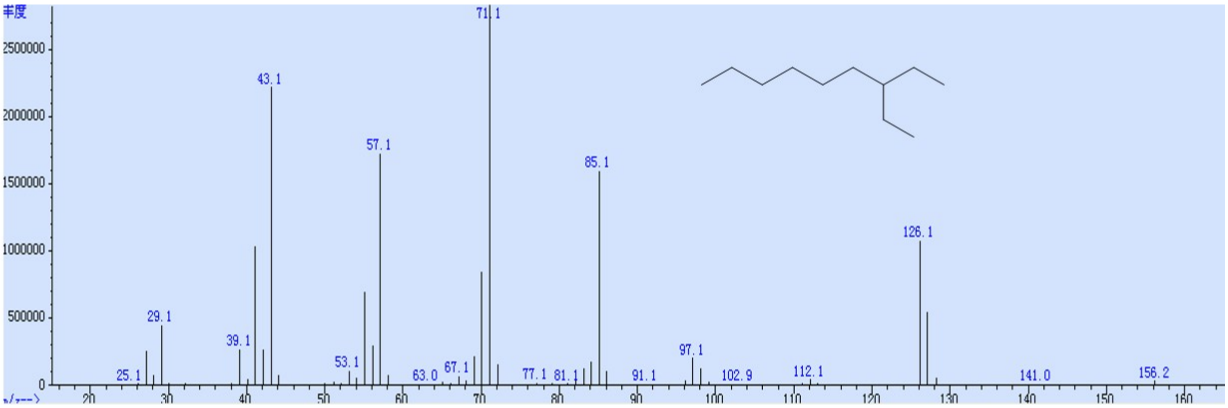


Figure S15 Mass spectrum of C_{11} branched alkanes.

Table S1 Reaction results of the glucose conversion in the 2,4-pentanedione/H_2O-NaCl and THF/H_2O-NaCl biphasic systems.

Organic phase	Product	Optimal conditions	Conv. of glucose	Yield
THF	HMF	190 °C, 3 h	95.0	57.2
2,4-pentanedione	C_{11-16}-glu	140 °C, 4 h	> 99	90.0

Reaction conditions: 0.1 g glucose, 1 g H_2O saturated with NaCl (0.3 g), 6 g organic phase, 0.5 MPa N_2. (a) the THF/H_2O-NaCl biphasic system image under optimal reaction conditions. (b) the 2,4-pentanedione/H_2O-NaCl biphasic system image under optimal reaction conditions.

Table S2 Direct conversion of glucose into fuel precursors over various catalysts.

Catalyst	Conversion (%)	Yield (%)			Selectivity (%)	
	glucose	C_{11}-glu	C_{16}-glu	C_{11-16}-glu	2,4-Pentanedione	Acetone + acetic acid
NaCl	99.7	80.4	5.7	86.1	99.5	0.5
Blank	22.3	0.2	0	0.2	99.5	0.5
$CoCl_2$	>99.9	0	0	0	89.1	10.9
KCl	99.9	77.7	6.3	84	99.4	0.6
$CrCl_3$	>99.9	0	0	0	22.7	77.3
Na_2SO_4	83.4	1.8	0	1.8	99.5	0.5

Reaction conditions: 0.1 g glucose, 1 g H_2O saturated with metal chloride (0.3 g), 6 g 2,4-pentanedione, 0.5 MPa N_2, 140 °C, 3h

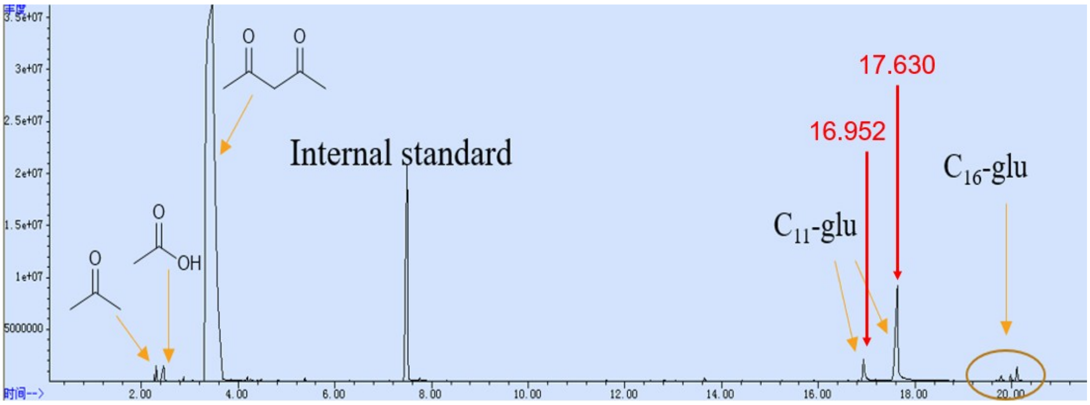


Figure S16 GC-MS trace of products in a 2,4-pentanedione/H_2O-NaCl biphasic system. Reaction conditions: 0.1 g glucose, 1 g H_2O, 0.3 g NaCl, 0.5 MPa N_2, 6 g 2,4-pentanedione, 140 °C, 3 h.

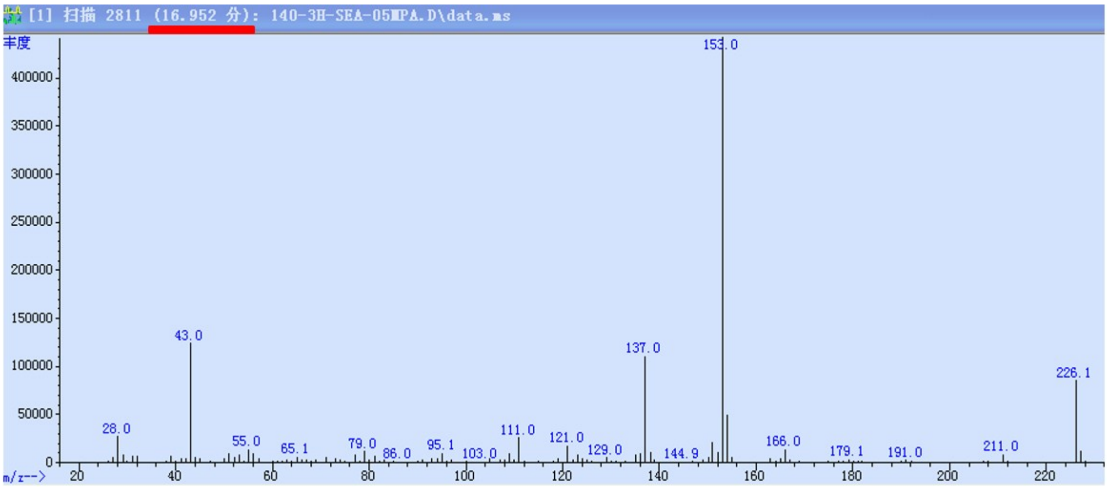


Figure S17 Mass spectrum of C_{11}-glu on 16.952 minute.

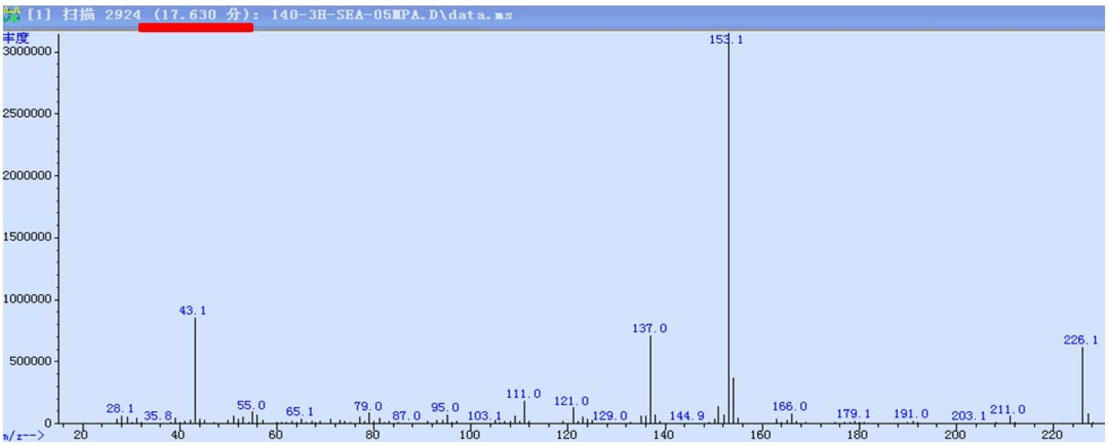


Figure S18 Mass spectrum of C_{11}-glu on 17.630 minute.

The two peaks of C_{11}-glu are assigned to the completely the same structure owing to their completely same mass spectrum fragments, see Figure S16-18, therefore, the two peaks are attributed to different configuration, rather than isomers. In our system, we focus on the chain structure of fuel precursor, whereas pay less attention to their configuration. This is because the chain structure of target alkanes after HDO contributes directly to the properties of fuel and the configuration has not obvious influence.

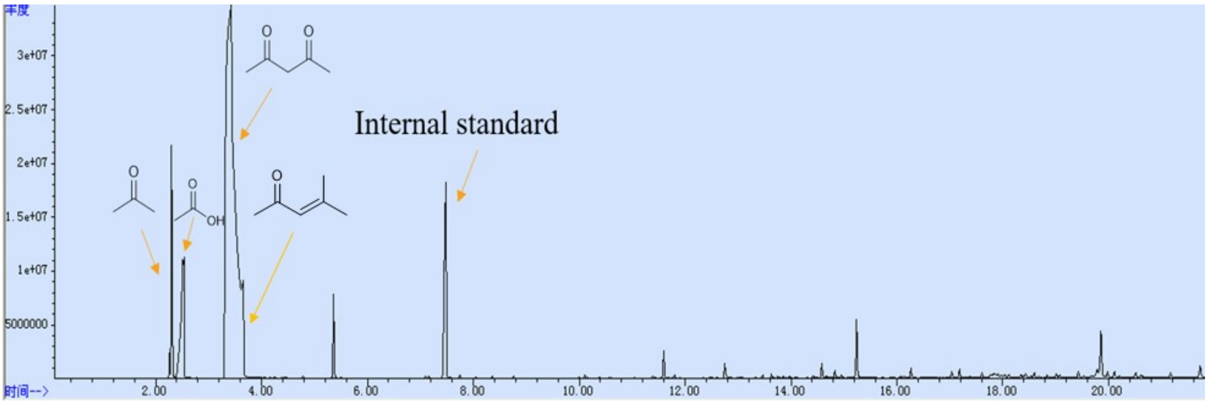


Figure S19 GC-MS trace of products in a 2,4-pentanedione/H_2O-$CoCl_2$ biphasic system. Reaction conditions: 0.1 g glucose, 1 g H_2O, 0.3 g $CoCl_2$, 0.5 MPa N_2, 6 g 2,4-pentanedione, 140 °C, 3 h.

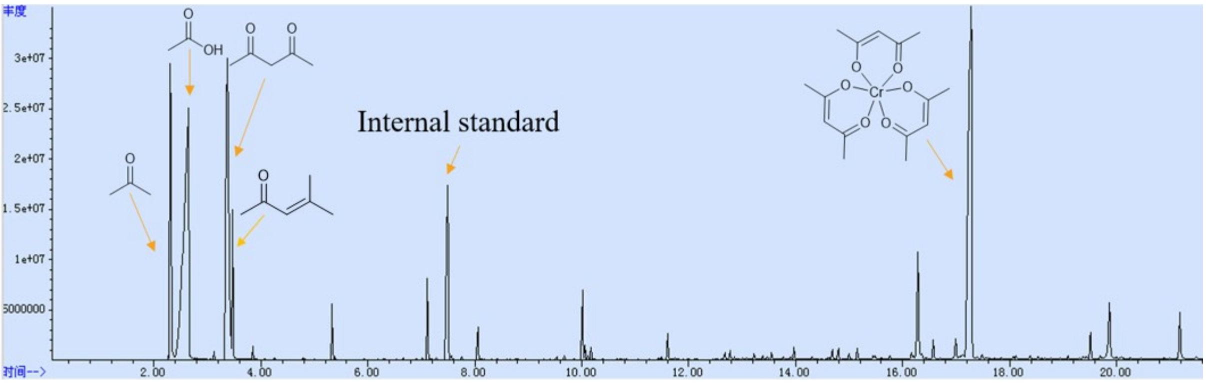


Figure S20 GC-MS trace of products in a 2,4-pentanedione/H_2O-$CrCl_3$ biphasic system. Reaction conditions: 0.1 g glucose, 1 g H_2O, 0.3 g $CrCl_3$, 0.5 MPa N_2, 6 g 2,4-pentanedione, 140 °C, 3 h.

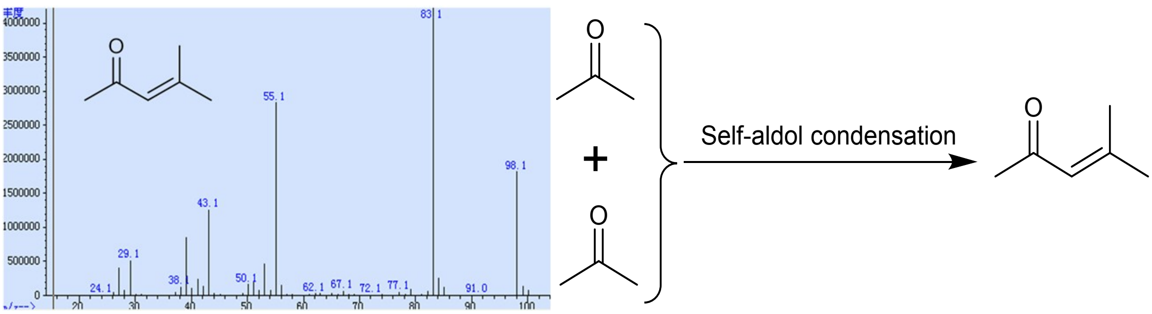


Figure S21 Self-aldol condensation product of acetone.

Compared with the result without NaCl (Table S2), the existence of NaCl had a notable improvement on the yield of C_{11-16}-glu, from 0.2 to 86.1%, indicating that NaCl plays a key role in the reaction. Then Na_2SO_4 was tested and a much lower C_{11-16}-glu yield of 1.8% at 99.5% glucose conversion was obtained, confirming the promotion effect of chlorides. Several cheap and commercially available metal chlorides, such as NaCl, KCl, $CoCl_2$ and $CrCl_3$ were therefore employed to conduct the reaction and found that an exceptionally high C_{11-16}-glu yield of 86.1% was realized over NaCl (Table S2). However, C_{11}-glu and C_{16}-glu were not detected when using $CoCl_2$ as catalyst, meanwhile glucose was completely converted. As we know, 2,4-pentanedione can easily hydrolyze to acetic acid and acetone in the presence of water. On the basis of the results for selectivity of 2,4-pentanedione and its hydrolysis products, it is clear that $CoCl_2$ can markedly promote the hydrolysis of 2,4-pentanedione, which can be explained by the catalytic performance of its Lewis acid, resulting in some undesired side reactions. In contrast, acidity-free NaCl was inert for the hydrolysis of 2,4-pentanedione (Figure S11). The GC-MS trace (Figure S12) reveals that many by-products were generated over $CoCl_2$, indicating that some undesired side reactions indeed happen in the presence of Lewis acid. To further confirm this, acidity-free KCl and stronger Lewis acid $CrCl_3$ were employed to conduct the reaction under the same conditions. The results were similar with that of NaCl and $CoCl_2$, respectively and stronger Lewis acid $CrCl_3$ is easier to promote the hydrolysis of 2,4-pentanedione than $CoCl_2$ (Figure S13). The above results indicate that Cl^- plays a key role in the reaction.

The molecule peak on 3.5-3.6 minute is ascribed to 4-methylpent-3-en-2-one, which was produced by self-aldol condensation of acetone formed the hydrolysis of 2,4-pentanedione (Figure S20-S21). It is clear that 4-methylpent-3-en-2-one was not formed in our NaCl system, but was obviously generated over $CrCl_3$ and $CoCl_2$ (Figure S16, S19-S21), suggesting that Lewis acid $CrCl_3$ and $CoCl_2$ significantly promote the hydrolysis of 2,4-pentanedione to generate plenty of acetone, then the acetone undergoes the self-aldol condensation to 4-methylpent-3-en-2-one. In short, the production of undesirable 4-methylpent-3-en-2-one over $CrCl_3$ and $CoCl_2$ also confirm our conclusion, this is, acidity-free NaCl is highly responsible for our proposed system.

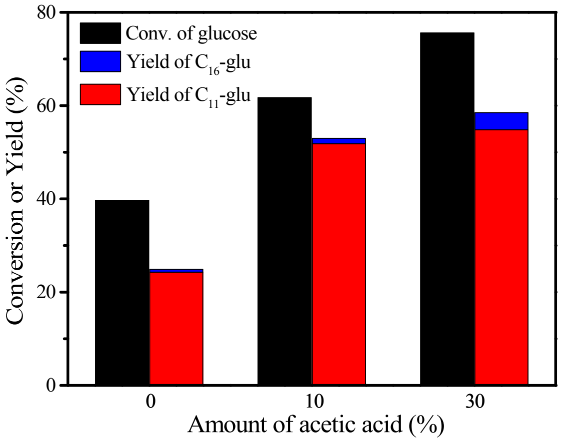


Figure S22 Influence of the amount of acetic acid on the conversion of glucose into C_{11}-glu and C_{16}-glu. Reaction conditions: 0.1 g glucose, 1 g H_2O, 0.3 g NaCl, 6 g 2,4-Pentanedione, 0.5 MPa N_2, 120 °C, 3 h.

Table S3 Influence of NaCl on the hydrolysis of 2,4-pentanedione.

Catalyst	Selectivity (%)		pH
	2,4-pentanedione	Acetone + acetic acid	
NaCl (0.1 g)	99.6	0.4	2.98
Without NaCl	99.6	0.4	3.02

Reaction conditions: 1 g H_2O, 6 g 2,4-Pentanedione, 0.5 MPa N_2, 140 °C, 4 h.

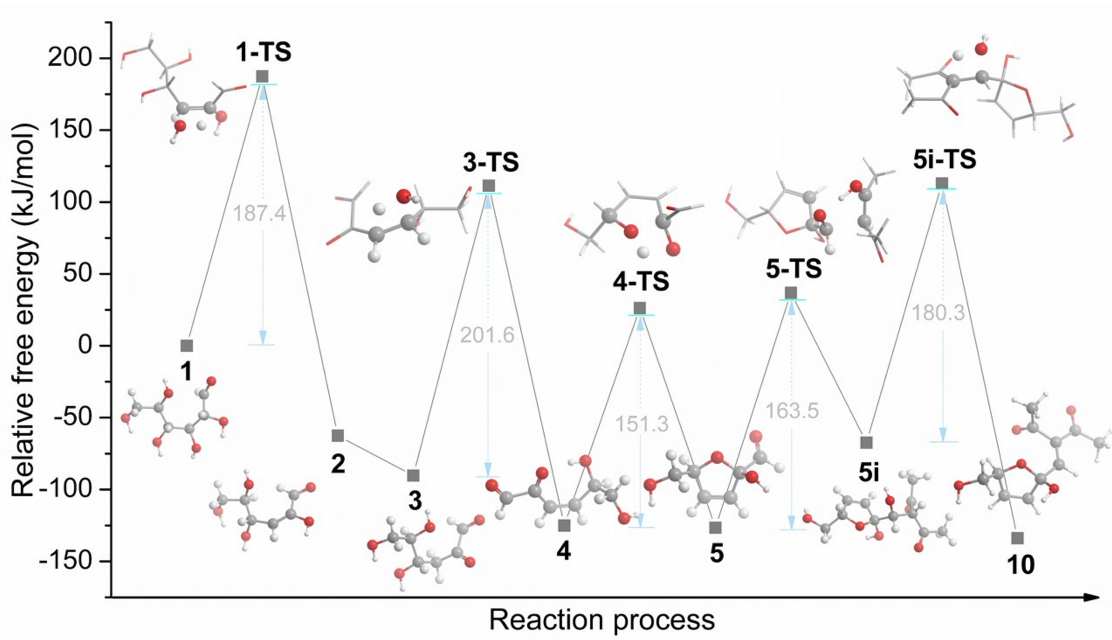
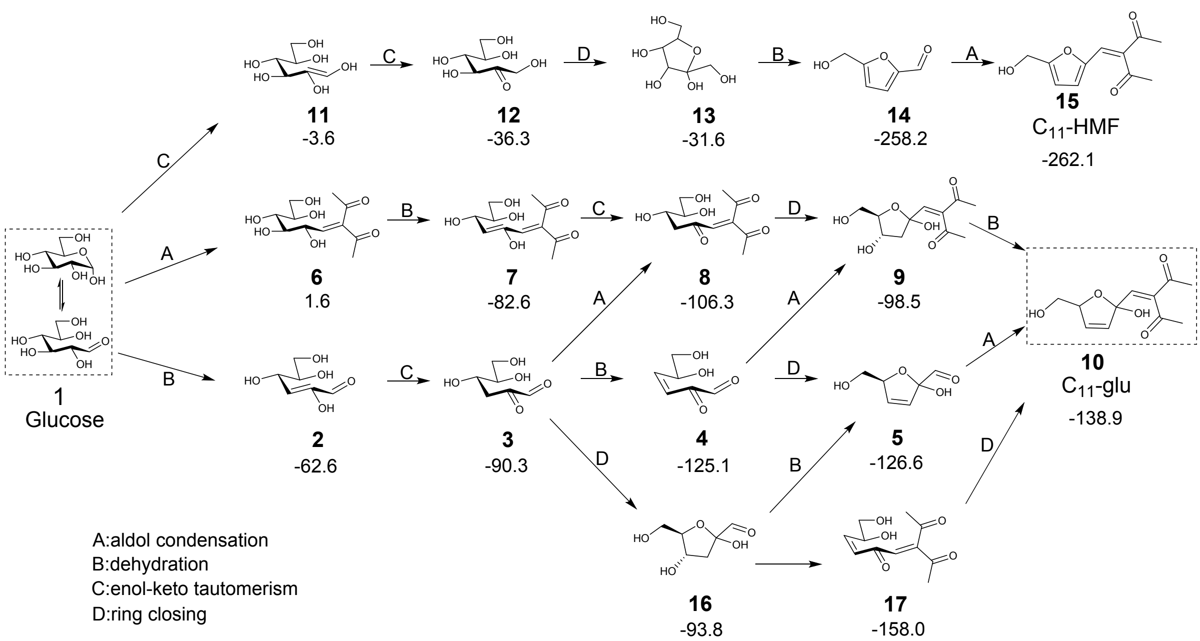
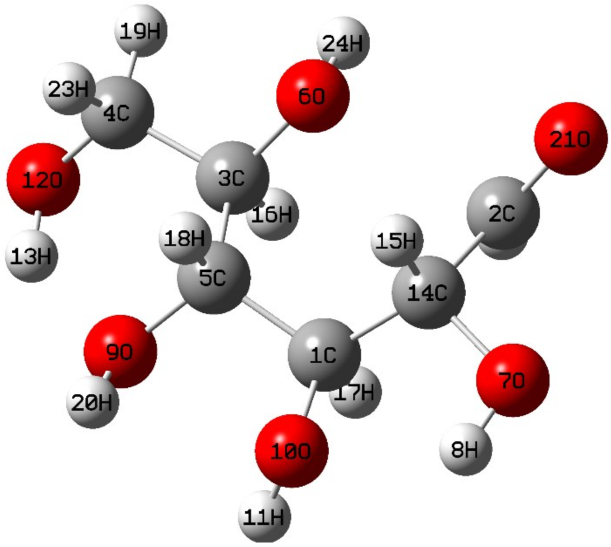


Figure S23 The relative free energy along with the glucose conversion to C_{11}-glu under water condition without H^+ and Cl^-.



Scheme S2. The proposed reaction pathways of glucose conversion to C_{11}-glu in the 2,4-pentanedione/H_2O-NaCl biphasic system, which contain six routes: 1-2-3-4-5-10; 1-6-7-8-9-10; 1-2-3-8-9-10; 1-2-3-4-9-10; 1-2-3-16-5-10; 1-2-3-16-17-10. The traditional mechanism of glucose conversion to HMF is also depicted for comparation as well as the subsequent formation of C_{11}-HMF. A~D represents aldol condensation, dehydration, enol-keto tautomerism, and ring closing reaction steps, respectively. The relative Gibbs free energy of each intermediates and product to the reactant are also listed for the reference, and the unit is kJ/mol.



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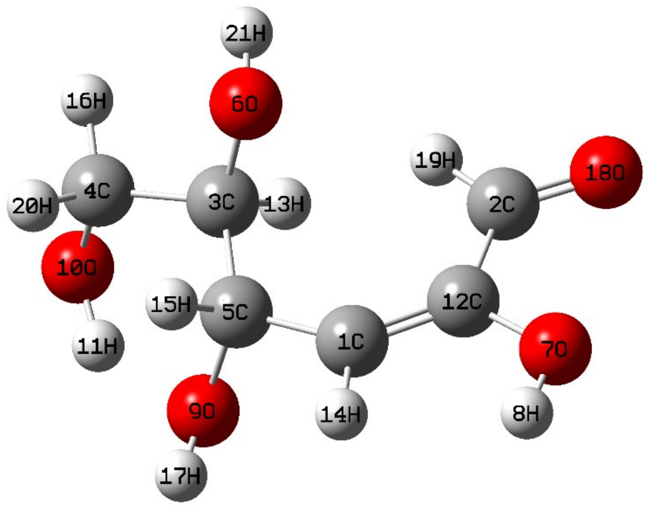
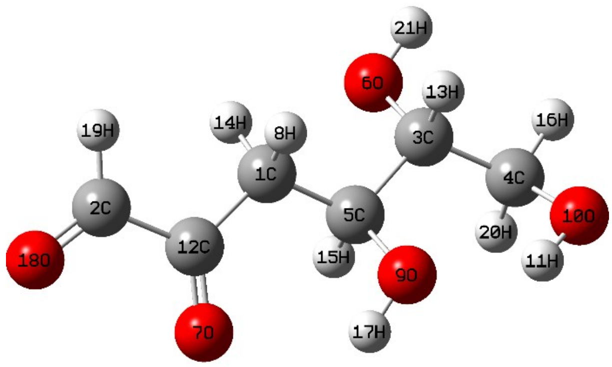
C	-0.66816700	0.99350300	-0.22804700
C	-1.92110200	-1.25045100	-0.45556800
C	1.27263600	-0.70576400	-0.14338500
C	2.72428800	-0.95177700	0.28809900
C	0.71857500	0.63765400	0.33913000
O	0.42632300	-1.70547500	0.44539000
O	-3.07985700	0.72764200	-0.10942200
H	-2.92187900	1.68437200	-0.03085100
O	1.66060700	1.64473300	-0.07095500
O	-1.01421200	2.32364500	0.20926900
H	-0.67931100	2.95764000	-0.43852300
O	3.66955600	-0.19397600	-0.47645000
H	3.38156300	0.73172100	-0.41109700
C	-1.83151700	0.10372500	0.24392600
H	-1.78490200	-0.05006500	1.33249700
H	1.21311600	-0.75771000	-1.24139900
H	-0.62363600	0.97879700	-1.32699600
H	0.66071200	0.61908600	1.43855900
H	2.96091400	-2.01003200	0.11832100
H	1.46563700	2.45697600	0.41626300
O	-2.58636500	-2.16653300	0.00031500
H	-1.46697900	-1.32695900	-1.46272000
H	2.83265100	-0.74021600	1.36436300
H	0.58542200	-2.54523700	-0.00852000



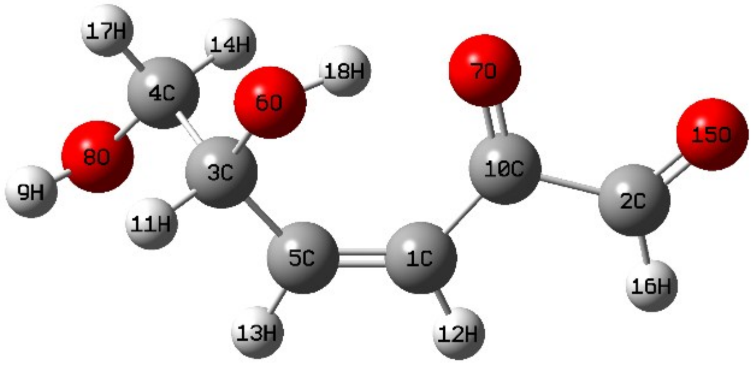
2

C	-0.82472900	1.09639300	0.47291400
C	-1.95674200	-0.94673800	-0.48810500
C	1.19567100	-0.58831100	0.16494000
C	2.73141300	-0.63428600	0.19208000
C	0.66082800	0.81538400	0.46242700
O	0.67477200	-1.43614300	1.19671200
O	-3.19093100	0.95905000	0.15611300
H	-3.13873100	1.85706800	0.51709300
O	1.27486600	1.70295800	-0.50682600
O	3.33100000	-0.08797500	-0.98868300
H	2.95558000	0.80245800	-1.09079400
C	-1.92319600	0.41796100	0.07094600
H	0.86449700	-0.92474200	-0.82923900
H	-1.02243900	2.10097200	0.86315500
H	1.03273500	1.08565800	1.46346600
H	3.04215800	-1.68577200	0.24006200
H	1.25090800	2.60400100	-0.15486400
O	-3.00250600	-1.49596200	-0.82501200
H	-0.99607800	-1.46750600	-0.59715200
H	3.10283700	-0.11985400	1.09351500
H	0.91146200	-2.35012800	0.98510700



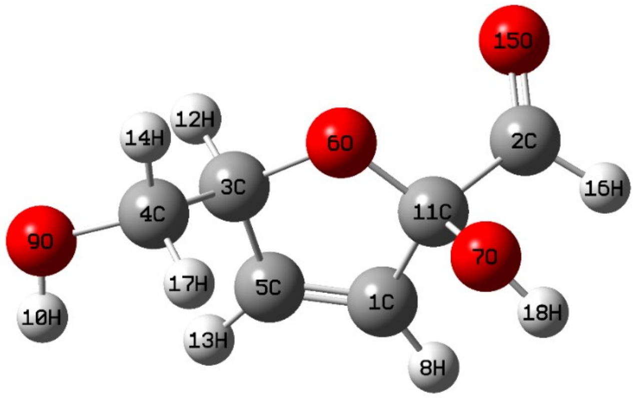
3

C	0.74573700	0.53227300	-0.36016700
C	3.32788000	0.49565000	-0.40919200
C	-1.78416500	0.69986700	-0.19326300
C	-3.07912400	0.05377000	0.31663500
C	-0.52989300	-0.08823100	0.20167600
O	-1.63901100	2.00180800	0.39403200
O	2.05890500	-1.15348200	0.76524000
H	0.73363300	0.53658800	-1.46392500
O	-0.70730400	-1.43212700	-0.28735600
O	-3.45005200	-1.11846600	-0.42012500
H	-2.66812300	-1.69548300	-0.41463100
C	2.00553000	-0.14992700	0.07249200
H	-1.83233600	0.78171200	-1.29102800
H	0.83112900	1.59064300	-0.06482600
H	-0.47296300	-0.10863500	1.30057500
H	-3.90016300	0.77206300	0.19346300
H	-0.02773500	-1.98514100	0.12436400
O	4.40033300	0.09265000	-0.01087100
H	3.24491100	1.33716400	-1.12463600
H	-2.97780100	-0.17575100	1.39024400
H	-2.34931000	2.56337300	0.05394800



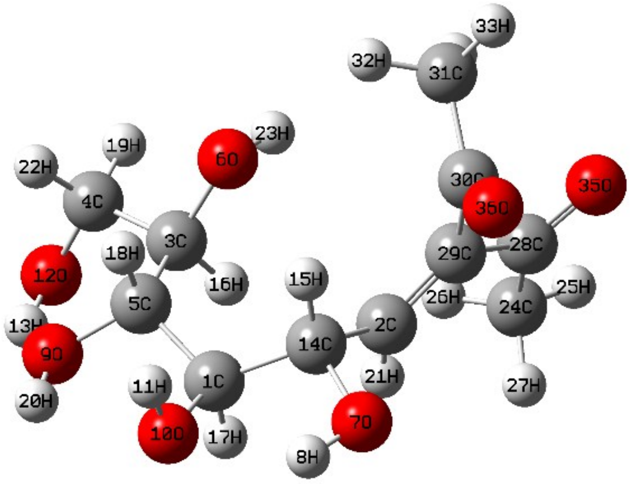
4

C	-0.56625400	-1.03557500	-0.53143000
C	-2.98741300	-0.60148200	0.07236200
C	1.65436700	0.33474300	-0.61704900
C	2.45041600	0.26468400	0.71332100
C	0.76116900	-0.86235000	-0.76143200
O	1.02392200	1.60351100	-0.73818200
O	-1.30966700	1.04359500	0.44890300
O	3.26876400	-0.90192500	0.81738500
H	3.96965100	-0.83954400	0.15270300
C	-1.53156800	-0.09028300	0.01372100
H	2.38756000	0.28348500	-1.43657700
H	-0.97697200	-2.02338800	-0.74529600
H	1.29559600	-1.75306000	-1.10009400
H	1.75421600	0.23924700	1.56058400
O	-3.88491000	0.11739400	0.45886200
H	-3.17156100	-1.64227400	-0.25772600
H	3.05731800	1.17967600	0.77650800
H	0.21503100	1.59683000	-0.18281100



5

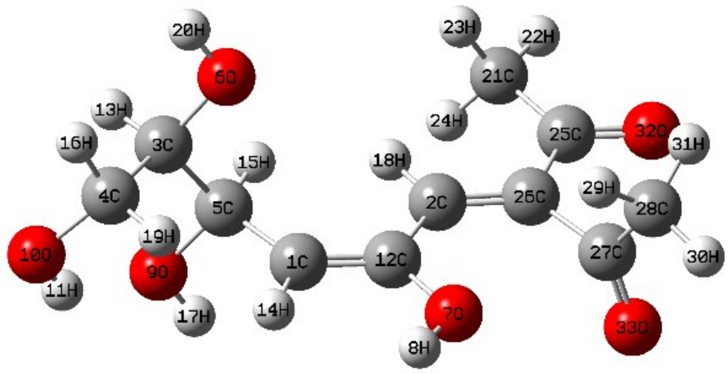
C	-0.46838700	1.07760000	-1.00899200
C	-2.43112400	-0.30900300	-0.21964400
C	1.06317700	-0.49893000	-0.23571900
C	2.24839500	-0.22663200	0.70099500
C	0.75845600	0.59340000	-1.21551900
O	-0.15170400	-0.60859600	0.55822100
O	-1.36527100	1.19347700	1.28816000
H	-0.97454600	1.87677100	-1.54579100
O	3.49644100	-0.30579500	0.00509300
H	3.60180200	0.49213900	-0.53151800
C	-1.09743400	0.35185900	0.15469000
H	1.22426900	-1.46542600	-0.73698100
H	1.47066000	0.92822100	-1.96735700
H	2.27123400	-1.00506400	1.47313500
O	-2.60189800	-1.51037400	-0.29113700
H	-3.25640500	0.40573200	-0.42069100
H	2.12694300	0.75256400	1.18626800
H	-1.92301000	1.93559800	1.00537200



6

C	1.48495100	1.38655400	-0.48634500
C	-0.87951900	0.47815700	-0.79923700
C	1.74094100	-1.07422700	0.32214100
C	2.81679000	-2.13409100	0.59770000
C	2.26571500	0.37057800	0.36383600
O	0.74079700	-1.14976100	1.35024100
O	-0.47161800	2.77777800	-0.81538200
H	0.28970500	3.38313400	-0.78613400
O	3.63130700	0.36570500	-0.09105200
O	2.12701000	2.67070500	-0.34508800
H	2.13382100	2.91067500	0.59583100
O	3.69916200	-2.33802700	-0.51283200
H	4.11644300	-1.47855900	-0.68319300
C	-0.02520600	1.55775200	-0.18639200
H	-0.17826600	1.63297800	0.89915200
H	1.29331300	-1.29042100	-0.65928300
H	1.60607700	1.13133400	-1.54738700
H	2.24176100	0.70145900	1.41574000
H	2.31007100	-3.09150500	0.77121200
H	3.90723100	1.28876200	-0.19209500
H	-0.56307300	0.14482200	-1.78858400
H	3.38342100	-1.87315100	1.50526600
H	0.14751900	-1.88493600	1.14431000
C	-2.36194600	-1.62501100	-2.29175800
H	-3.09121100	-2.36174300	-2.64272100
H	-1.38196000	-2.10202000	-2.15752800
H	-2.24720900	-0.83869200	-3.05120800
C	-2.84435600	-1.02902000	-0.99770500
C	-2.00589900	-0.03488300	-0.26911500
C	-2.53646800	0.38918900	1.08265900

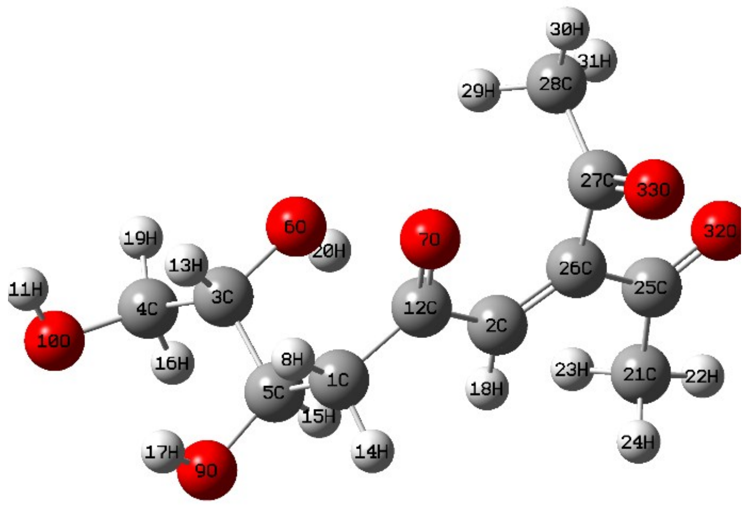
C	-2.55313600	-0.62381900	2.19210800
H	-1.61184200	-0.50210900	2.75113100
H	-3.38652700	-0.42002900	2.87407100
H	-2.59620000	-1.65188300	1.81968600
O	-3.94550700	-1.33151100	-0.52596900
O	-2.90418600	1.54696100	1.26062900



7

C	-1.35751600	-0.74044300	-0.36935300
C	0.91571400	0.25864500	-0.20269000
C	-3.21423800	0.69253400	0.63772200
C	-4.27584500	-0.41254300	0.69879700
C	-2.14838900	0.52894600	-0.46625900
O	-2.49448800	0.74683600	1.87698200
O	0.59878700	-2.09226900	-0.19067900
H	-0.07271400	-2.79141100	-0.18924200
O	-2.87627300	0.56829800	-1.72050700
O	-5.16074600	-0.39466600	-0.43082100
H	-4.60424300	-0.30103000	-1.22190200
C	-0.01162100	-0.85997600	-0.25767800
H	-3.72168600	1.65240600	0.45481900
H	-1.93236700	-1.66791000	-0.42648400
H	-1.49601400	1.40831200	-0.40788200
H	-4.89882400	-0.24026600	1.58660500
H	-2.24885700	0.39442700	-2.43641300
H	0.45462400	1.23977100	-0.26957300
H	-3.80159700	-1.40020300	0.80630000
H	-3.11533400	1.00925500	2.57082800

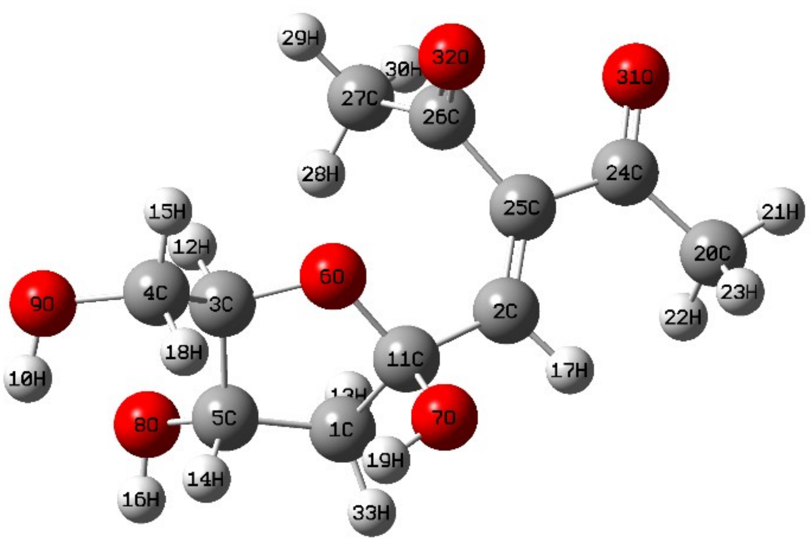
C	2.41953600	2.80047300	-0.13396800
H	3.19078500	3.57648700	-0.10435500
H	1.72171100	2.94558200	0.70241600
H	1.84496000	2.88926100	-1.06590900
C	3.08112500	1.44968700	-0.04377200
C	2.26600900	0.20709500	-0.08872100
C	3.09102100	-1.06394900	-0.02023200
C	3.38141000	-1.63058600	1.33647700
H	2.44911100	-1.76842700	1.89885000
H	3.92937300	-2.57508300	1.25291800
H	3.98588100	-0.89711900	1.89203000
O	4.30972600	1.35392700	0.07010800
O	3.55198800	-1.53879500	-1.05320100



8

C	1.30242500	-0.49443100	1.60124100
C	-0.91750400	0.37947300	0.65603700
C	2.64009800	-0.24750400	-0.56796400
C	3.74429300	0.49912200	-1.33438000
C	2.27222200	0.38605400	0.78638300
O	1.45119500	-0.33482500	-1.37014200
O	-0.43987700	-1.93409100	0.79878300
H	1.78590600	-1.45088800	1.83701600
O	3.42814500	0.67900800	1.57815400
O	5.06845600	0.14531500	-0.91136500
H	5.22600900	-0.77513700	-1.16521200
C	-0.03895100	-0.78292500	0.97407000
H	2.96479300	-1.28678800	-0.41378500

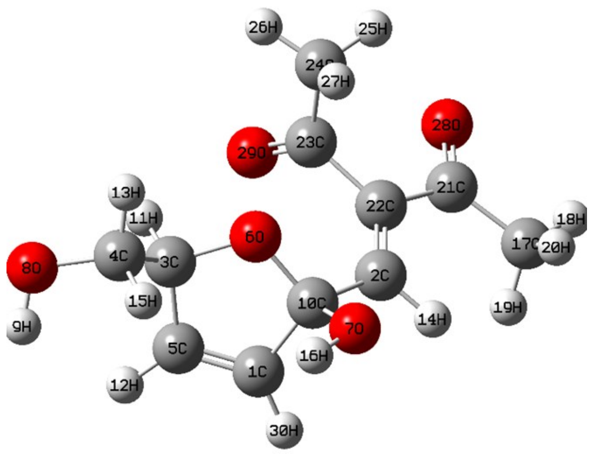
H	1.09752800	0.03866100	2.54324800
H	1.81550200	1.36484700	0.58401600
H	3.65358900	1.58350900	-1.18953700
H	3.90605600	-0.14711900	1.74485700
H	-0.52324800	1.37027100	0.87319900
H	3.61782300	0.27995400	-2.40469800
H	1.14282000	0.56448400	-1.55892900
C	-2.52006400	2.81982100	0.11835700
H	-3.28779600	3.54481300	-0.16852900
H	-1.59626300	3.01668500	-0.44317900
H	-2.28774700	2.92807000	1.18693100
C	-3.02113300	1.43253000	-0.16824100
C	-2.15576100	0.24554000	0.14198700
C	-2.80284000	-1.09410700	-0.15445300
C	-2.56864500	-1.69292800	-1.50733900
H	-1.50429200	-1.66198800	-1.76978800
H	-2.95177000	-2.71825300	-1.54355800
H	-3.10607200	-1.07423400	-2.24356700
O	-4.13259100	1.23574800	-0.66056200
O	-3.57003700	-1.57624900	0.67229700



9

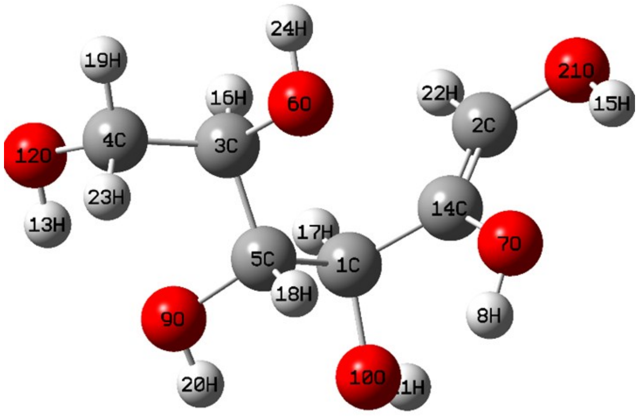
C	1.03162500	-1.66606200	0.69455000
C	-1.21799100	-1.06486300	-0.30930800

C	2.04114800	0.41663900	0.02009100
C	3.06281800	0.95748500	-0.97881500
C	2.38442300	-0.94225100	0.65157000
O	0.79081900	0.22812400	-0.68778300
O	0.46092700	-1.85114300	-1.71067000
O	2.96924100	-0.72989100	1.94011600
O	4.28362400	1.34984400	-0.33932700
H	4.75158800	0.55381600	-0.05125900
C	0.27443000	-1.09167300	-0.51769900
H	1.87813600	1.15513800	0.81813400
H	0.51148200	-1.38890200	1.61969800
H	3.09672400	-1.48842400	0.01617700
H	2.66143900	1.86018600	-1.45427300
H	3.31879000	-1.57538000	2.25377100
H	-1.67171400	-2.05456200	-0.34434000
H	3.25413100	0.20496700	-1.75908100
H	1.40515100	-2.03296600	-1.83247300
C	-4.10810100	-1.48690700	0.15692800
H	-5.18014100	-1.37081000	0.34441800
H	-3.66589800	-2.12517000	0.93435600
H	-3.95374100	-1.98611900	-0.80933800
C	-3.46058400	-0.12799700	0.16323900
C	-1.99156800	0.00914500	-0.07830300
C	-1.49613500	1.44317200	-0.03379700
C	-1.00519900	1.95994000	1.28461800
H	-0.29030400	1.26213700	1.73675000
H	-0.56539100	2.95633800	1.17172600
H	-1.87106400	2.01518500	1.96297300
O	-4.12551000	0.88965400	0.37821600
O	-1.61370400	2.15476900	-1.02614500
H	1.10842100	-2.75605900	0.63905500



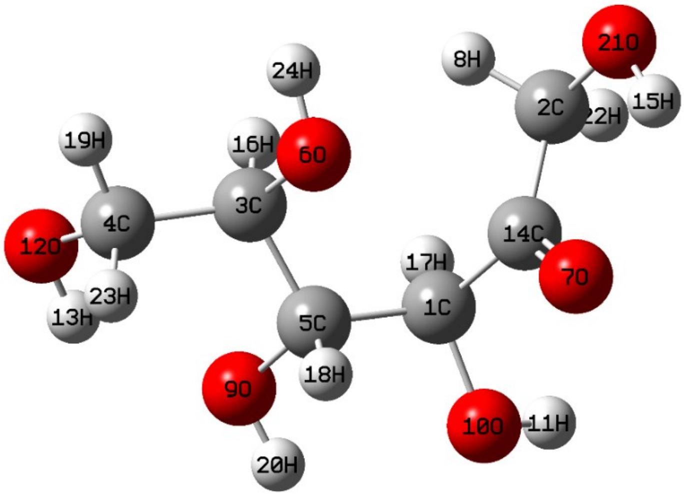
10

C	1.20038800	1.64152300	-0.99183000
C	-1.00295900	1.13409700	0.11790100
C	2.15596100	-0.35400200	-0.26339200
C	3.45913600	-0.48922400	0.53734000
C	2.14399700	0.74464700	-1.28393900
O	1.08173000	-0.00502900	0.64519400
O	0.67763800	2.20027200	1.33178800
O	4.52169600	-1.02032800	-0.26083400
H	4.81752200	-0.33506100	-0.87610600
C	0.49279400	1.24835700	0.28760500
H	1.91220100	-1.32855000	-0.71371600
H	2.83191300	0.77692000	-2.12655700
H	3.29824600	-1.20192600	1.35497100
H	-1.51097800	2.09656500	0.06982300
H	3.73598100	0.48540800	0.96595600
H	1.62234900	2.41649300	1.37368700
C	-3.93196800	1.34363200	-0.19435400
H	-4.99871600	1.15536500	-0.35078300
H	-3.55704700	2.00686000	-0.98612500
H	-3.78268100	1.85614800	0.76578300
C	-3.19345900	0.03244500	-0.21450500
C	-1.71373300	0.00105700	-0.01041900
C	-1.11606500	-1.39383000	-0.01774600
C	-1.15328900	-2.17194800	1.26342700
H	-2.20638400	-2.37781200	1.50833600
H	-0.61171200	-3.11756800	1.15515900
H	-0.74106500	-1.57703300	2.08733600
O	-3.79063200	-1.03199100	-0.40059100
O	-0.71562500	-1.87123400	-1.07504000
H	0.94710700	2.55013400	-1.53241600



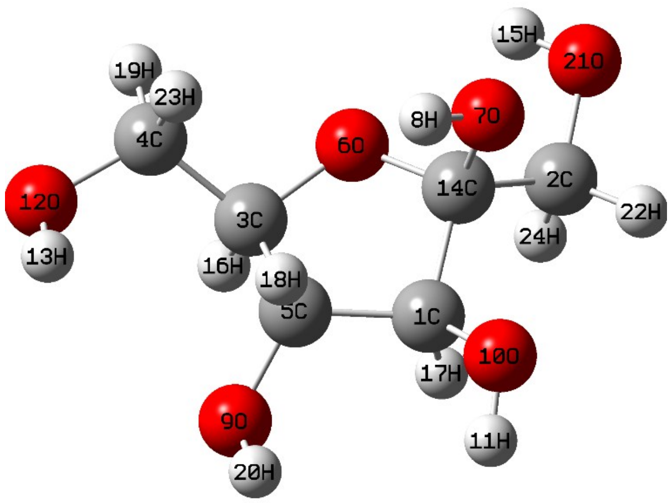
11

C	0.52980500	1.00354200	0.36175600
C	2.35790300	-0.58595400	0.96156300
C	-1.23779700	-0.82730100	-0.02406600
C	-2.74799400	-1.03530600	-0.20965600
C	-0.77035200	0.59730400	-0.35805200
O	-0.53252300	-1.70121800	-0.92053200
O	2.20778800	0.16762700	-1.26144000
H	1.87395600	0.95608200	-1.71526600
O	-1.80816400	1.51434300	0.02950400
O	0.75232000	2.37856600	-0.03986500
H	1.41483700	2.76203300	0.55219800
O	-3.52765900	-0.45724000	0.84475600
H	-3.30673800	0.48780600	0.85410000
C	1.73227600	0.16769500	0.04600900
H	3.71183200	-1.27098100	-0.22983100
H	-0.97812100	-1.07003600	1.01819000
H	0.34695100	0.95709200	1.44433600
H	-0.62061800	0.66400200	-1.44759200
H	-2.94735000	-2.11435500	-0.18705600
H	-1.42269600	2.40306500	0.01030200
O	3.46269600	-1.37654600	0.70202600
H	2.02126400	-0.64437900	1.99245100
H	-3.06598400	-0.64679200	-1.19023500
H	-0.64604000	-2.60767300	-0.60251400



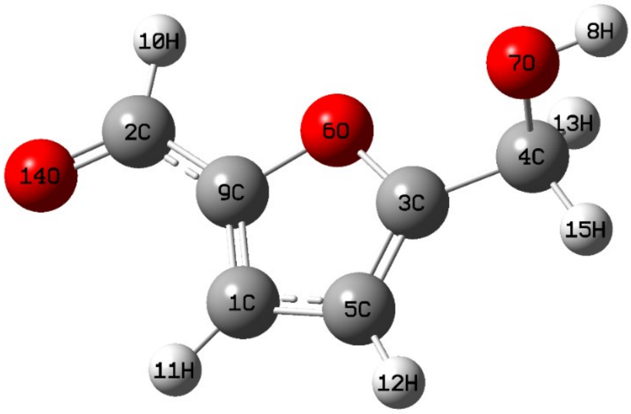
12

C	-0.52183300	1.13159200	-0.34263100
C	-2.28761700	-0.67067200	-0.94592900
C	1.18098200	-0.79086200	-0.04683600
C	2.61953300	-1.14585800	0.35478900
C	0.81166000	0.65976200	0.27386100
O	0.26674700	-1.60020300	0.70793000
O	-2.24009900	0.38685700	1.18211500
H	-1.48472000	-1.25743000	-1.41291900
O	1.86493900	1.49476400	-0.21916300
O	-0.69637000	2.47817900	0.10708100
H	-1.35489300	2.90763700	-0.45664700
O	3.60236400	-0.62960400	-0.55083500
H	3.47026700	0.33126500	-0.57688500
C	-1.71267300	0.26885300	0.08308400
H	-3.54122800	-1.15295800	0.44711800
H	1.05546800	-0.97862500	-1.12409700
H	-0.42931100	1.10397000	-1.43802300
H	0.73519200	0.76612100	1.36785600
H	2.72031600	-2.23817800	0.33199800
H	1.65140300	2.41021400	0.01126800
O	-3.26288200	-1.54122700	-0.39990500
H	-2.72275900	-0.02917600	-1.73570100
H	2.81433300	-0.80063600	1.38292300
H	0.26802300	-2.48920900	0.32730400



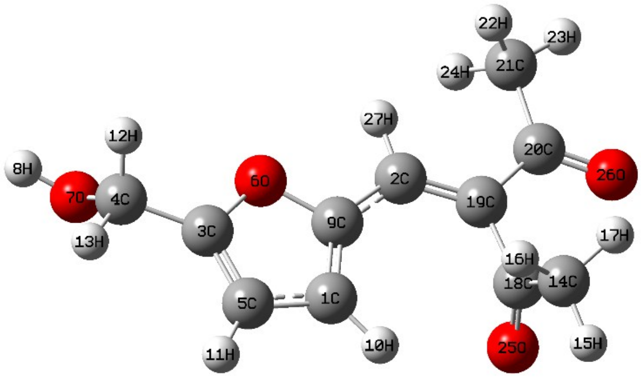
13

C	0.42016100	1.23996500	0.23186000
C	2.46682600	-0.23451700	0.66178500
C	-1.10038700	-0.59515700	0.43185200
C	-2.03860300	-1.49447600	-0.37003800
C	-1.05046800	0.87367400	0.00096100
O	0.25137300	-1.09904000	0.25527700
O	1.49295500	-0.16862100	-1.49752300
H	0.69423300	-0.04826200	-2.03169500
O	-1.96973800	1.64690300	0.77332400
O	0.89736900	2.33424800	-0.54096800
H	0.54937800	3.14832400	-0.15084200
O	-3.41787600	-1.20514600	-0.11147000
H	-3.62553700	-0.33380600	-0.47701400
C	1.16696000	-0.06141700	-0.12360000
H	2.57077700	-2.18709400	0.74726300
H	-1.35671100	-0.65000800	1.50000700
H	0.56051000	1.44077500	1.30463900
H	-1.28833400	0.97598000	-1.06930200
H	-1.88327600	-2.53720300	-0.06816400
H	-2.02419100	2.52784900	0.37658600
O	3.12414800	-1.47438600	0.39763100
H	3.16541900	0.55948900	0.37322300
H	-1.81344800	-1.40144100	-1.44365700
H	2.23840200	-0.13471000	1.73187500



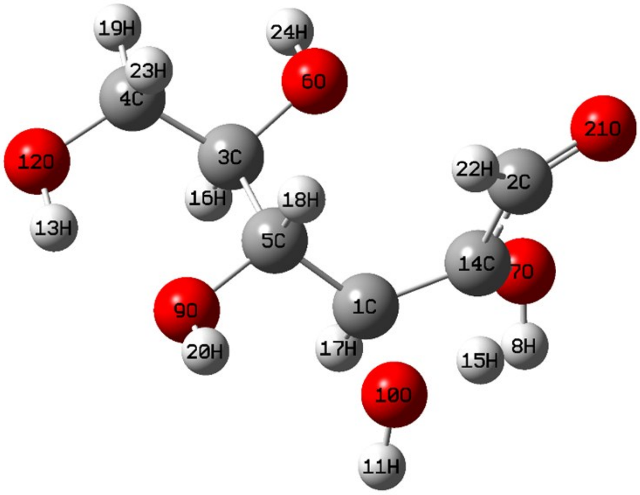
HMF

C	-0.93228300	1.34391500	-0.17981000
C	-2.30664600	-0.84600000	0.05360700
C	1.03823100	0.34276100	0.20998000
C	2.44621300	-0.07248600	0.44516700
C	0.46592300	1.56324900	-0.06889900
O	0.07769500	-0.62136700	0.27836400
O	2.87970400	-0.89855400	-0.65280600
H	3.77646000	-1.20107800	-0.45109800
C	-1.13742100	-0.00304400	0.03405400
H	-2.11409000	-1.91765300	0.25705100
H	-1.70385000	2.07695100	-0.39291300
H	0.99862600	2.50213400	-0.17938900
H	2.51836500	-0.63255200	1.38995500
O	-3.45521200	-0.43399700	-0.13916600
H	3.06289800	0.83317400	0.52067300



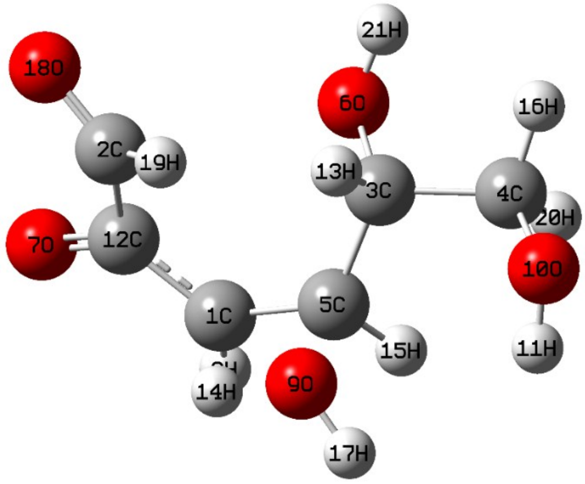
C_{11}- HMF

C	1.06670800	-1.42944400	0.05570000
C	-0.47219600	0.68014900	-0.08377100
C	2.94637000	-0.23529400	-0.22795000
C	4.31070800	0.32414100	-0.40620000
C	2.48288600	-1.51368300	-0.03582800
O	1.89652600	0.63870400	-0.26270300
O	4.64488500	1.13048700	0.74171000
H	5.47342500	1.58942800	0.54367500
C	0.73119000	-0.09604400	-0.08437200
H	0.38271600	-2.25510000	0.21520700
H	3.09474100	-2.40716200	0.03399400
H	4.34975500	0.93829000	-1.31865000
H	5.01341600	-0.51343100	-0.51228400
C	-2.44742300	-1.98790000	-1.01347500
H	-2.70640200	-3.02278600	-0.76689900
H	-1.57824800	-1.96017600	-1.68744000
H	-3.27723900	-1.50216800	-1.54747500
C	-2.13698400	-1.20400700	0.22483500
C	-1.75771100	0.24960100	0.04453300
C	-2.89704400	1.18345800	0.02546000
C	-2.67377300	2.66008800	-0.18347100
H	-2.20592900	2.84508500	-1.16045900
H	-3.63834100	3.17569600	-0.13913300
H	-2.00712600	3.06946000	0.58780100
O	-2.18586000	-1.68987900	1.35068700
O	-4.04510300	0.73394800	0.17791700
H	-0.30074800	1.75038800	-0.20200000



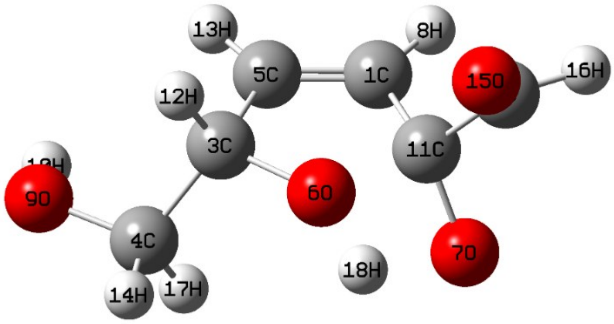
1-TS

C	-0.58917300	0.93408600	-0.36921000
C	-2.18341700	-0.63500300	0.87713400
C	1.36820500	-0.69080300	-0.38930700
C	2.73300800	-1.04091900	0.22384400
C	0.70152700	0.50000300	0.32070800
O	0.48528600	-1.81112200	-0.25729800
O	-2.51766000	-0.19643200	-1.45792200
H	-2.71496700	0.60486300	-1.96173000
O	1.65142900	1.57845500	0.27150600
O	-1.07502000	2.22551100	0.35270900
H	-1.09364800	2.98900300	-0.25582300
O	3.77188200	-0.12932300	-0.15106000
H	3.44537600	0.75580300	0.08111800
C	-1.88482700	0.16718000	-0.24975500
H	-2.07605700	1.58546100	0.33324200
H	1.51029500	-0.43961000	-1.45272700
H	-0.39565800	1.21374800	-1.40865900
H	0.50635900	0.23043200	1.36707300
H	3.03462200	-2.02726200	-0.15248200
H	1.37499200	2.25622900	0.90362800
O	-3.11629100	-1.47912500	0.95911300
H	-1.56440300	-0.43336600	1.77236300
H	2.64196300	-1.10181200	1.32058500
H	0.86219000	-2.54445200	-0.76345000



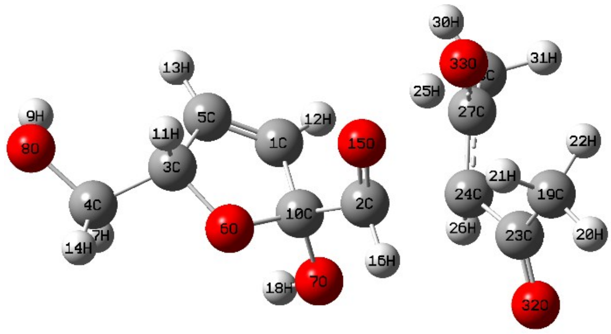
3-TS

C	-0.79651600	1.18947700	0.61127300
C	-1.88993500	-0.64383000	-0.80953100
C	1.12892500	-0.59938100	0.07906700
C	2.62529200	-0.78508000	0.36977200
C	0.64686900	0.82521800	0.37535800
O	0.36655500	-1.46916800	0.92582300
O	-3.11215700	0.72314400	0.69498400
H	-0.94768000	1.87463700	1.44822600
O	0.84171300	1.67260600	-0.90965500
O	3.46786800	-0.06988900	-0.54103100
H	3.44399400	0.87099900	-0.31803400
C	-1.96791500	0.46220700	0.25075700
H	0.94678900	-0.83549000	-0.97887300
H	-0.28847700	1.95097300	-0.58359600
H	1.27305300	1.29660900	1.13749800
H	2.87130800	-1.84720700	0.24130200
H	1.49014100	2.38879800	-0.76957000
O	-2.78208400	-1.46458300	-0.93482500
H	-1.02184900	-0.65045800	-1.49397600
H	2.83839300	-0.49914800	1.41107200
H	0.65884200	-2.37825400	0.76340900



4-TS

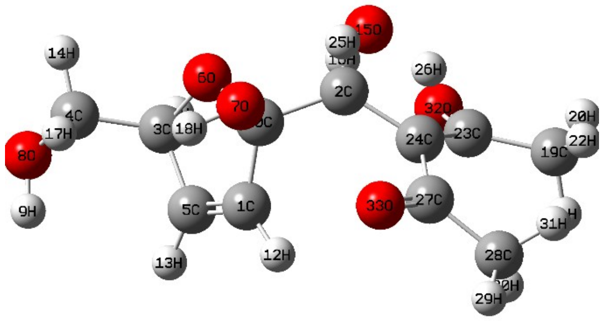
C	-0.48368700	1.51358700	-0.20826300
C	-2.52432000	-0.03832900	-0.32284800
C	1.06798900	-0.25351800	-0.47235100
C	2.27317300	-0.58652700	0.41714900
C	0.74609400	1.20480100	-0.62771600
O	-0.15779000	-0.80584500	0.14617600
O	-1.29402300	0.16696000	1.71268000
H	-0.94801000	2.49721100	-0.21590900
O	3.49376600	-0.26835500	-0.24917700
H	3.61847200	0.69089300	-0.22864700
C	-1.20577300	0.31879800	0.34649000
H	1.17744100	-0.76037100	-1.43948900
H	1.47301700	1.90327000	-1.03927900
H	2.28644000	-1.66656800	0.60514300
O	-2.71718200	-1.03688300	-0.98950400
H	-3.33496800	0.68881100	-0.11111700
H	2.19107300	-0.05582200	1.37649600
H	-0.30249200	-0.69731200	1.29664200



5-TS

C	1.19322200	0.99353700	0.65707400
C	-0.45046800	-0.71971000	-0.42152000
C	2.87410000	-0.12631300	-0.50306200
C	4.23737300	-0.61739600	-0.00003800
C	2.38999900	1.16227000	0.09296100
O	1.86546900	-1.09261600	-0.11992900
O	0.46299500	-1.08676600	1.74131000
O	5.31000700	0.16843400	-0.53078300
H	5.30574300	1.03142100	-0.09406100
C	0.74697600	-0.43810500	0.52170300
H	2.90676800	-0.06862600	-1.60306900
H	0.59864600	1.74212600	1.17338900
H	2.96462400	2.08578200	0.04938300
H	4.39744800	-1.64210100	-0.35632700
O	-0.44705400	-0.18826300	-1.59014900
H	-0.80150100	-1.75942900	-0.31431700
H	4.25519700	-0.61622200	1.09984200
H	1.18822400	-0.89948300	2.35609200
C	-3.70907000	-0.92462500	-1.25864800
H	-4.42936600	-1.74090100	-1.36959100
H	-2.94194900	-1.00275400	-2.04163900
H	-4.21475100	0.04069300	-1.39488300
C	-3.07651200	-1.00332500	0.10360700
C	-2.11893100	0.03229800	0.58025800
H	-1.50946500	0.83931100	-1.60837800
H	-1.95351400	-0.05265600	1.65270900
C	-2.13074700	1.36766200	0.10125800
C	-2.17527200	2.55050000	1.00005500
H	-1.89958400	2.28048600	2.02421900
H	-1.54272100	3.35978600	0.61649700

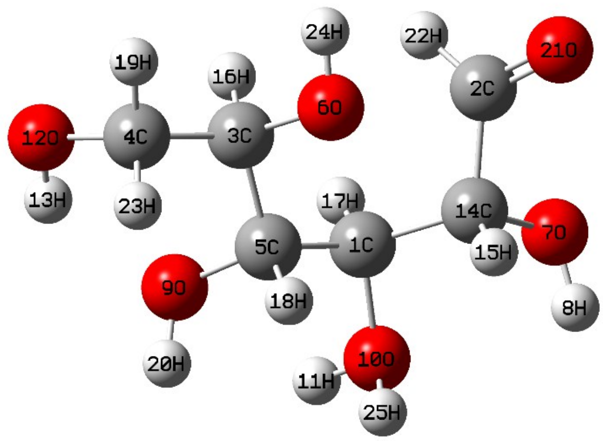
H	-3.21515900	2.91621400	1.01554100
O	-3.35297300	-1.93225100	0.87289100
O	-2.06252800	1.60966200	-1.17925200



5i-TS

C	0.99288000	-0.44273400	1.10481900
C	-0.51212800	0.00903900	-0.92938900
C	2.74357100	0.69878200	0.07596000
C	4.17748500	0.18630700	-0.11778200
C	2.08725700	0.27739200	1.35506600
O	1.90003000	0.13423900	-0.95573000
O	0.87049700	-1.94574300	-0.84036900
O	5.10436100	0.86249000	0.73883400
H	4.97948700	0.54456900	1.64392400
C	0.80066800	-0.60799000	-0.38406400
H	2.74345500	1.79414400	-0.03816200
H	0.32022400	-0.89296700	1.82755300
H	2.48395300	0.53233300	2.33597200
H	4.49320800	0.40023200	-1.14592400
O	-1.04123100	-0.75217100	-2.14176500
H	-0.25660200	0.99109600	-1.32292200
H	4.20999700	-0.90126100	0.04487400
H	1.65259100	-2.36186700	-0.44739600
C	-3.85891300	1.75698100	0.09953700
H	-4.11935500	2.69411000	-0.40581700
H	-4.04218600	1.89402500	1.17433500
H	-4.50460700	0.95132200	-0.26244300
C	-2.39042200	1.48956300	-0.14716600
C	-1.84385500	0.11941400	-0.19410300
H	-0.79720100	-1.69493400	-2.03953300
H	-2.06987100	-0.50851800	-1.50467400

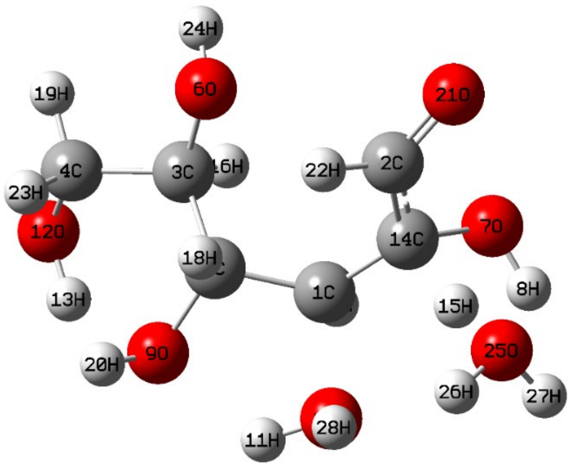
C	-2.29226300	-0.99342200	0.65565100
C	-3.52116900	-0.89255400	1.53194500
H	-3.57076000	-1.79408700	2.15149300
H	-3.48812900	-0.00702500	2.17775300
H	-4.43410900	-0.83418000	0.92556200
O	-1.65751400	2.46903900	-0.38619700
O	-1.66349000	-2.06931300	0.65804800



1H-p

C	-0.66308800	0.94273200	-0.25101200
C	-1.82692900	-1.32184900	-0.46662500
C	1.27053300	-0.73015400	-0.08642900
C	2.73731700	-0.92682500	0.31730900
C	0.73364600	0.65006000	0.31337700
O	0.44356300	-1.67358200	0.60812600
O	-3.08080800	0.63396800	-0.23362300
H	-3.34201800	1.32138500	0.39516400
O	1.63529000	1.64815800	-0.18516000
O	-1.02944300	2.34625600	0.18422700
H	-0.48315800	3.01989700	-0.27146800
O	3.64862500	-0.25854000	-0.56050900
H	3.37538000	0.67318200	-0.57282300
C	-1.84119100	0.06644500	0.19666000
H	-1.83103300	-0.06480600	1.28646100
H	1.17810200	-0.86720800	-1.17445300
H	-0.63709100	1.04216900	-1.34030500
H	0.69140600	0.69927200	1.41106700
H	2.96812300	-1.99770400	0.25342400
H	1.74760200	2.33326900	0.48792300
O	-2.54938600	-2.21262000	-0.05902700
H	-1.23929700	-1.44078500	-1.39574600

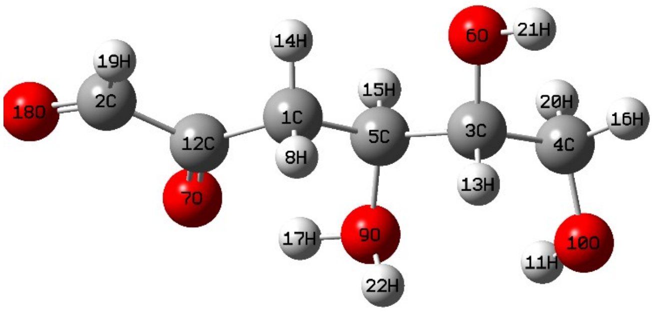
H	2.88398500	-0.60099700	1.35968100
H	0.60747900	-2.55417200	0.23998700
H	-0.92393500	2.48492700	1.14914800



1H-TS

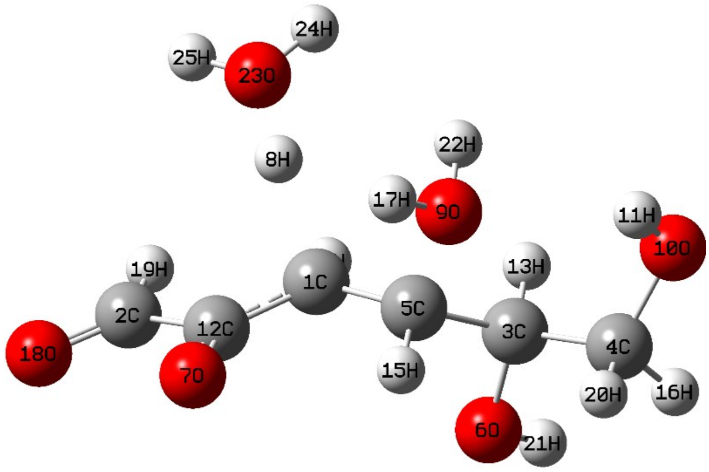
C	0.32731500	-0.63602000	-0.45597900
C	1.62187300	1.31658400	0.47172300
C	-1.76313000	0.73534600	-0.11819100
C	-3.25143000	0.58071600	0.23105200
C	-0.89390900	-0.42425200	0.43729100
O	-1.26035100	1.94441600	0.46097200
O	2.10489000	0.42087200	-1.71494100
H	2.62210500	-0.36538400	-1.93864000
O	-1.63456800	-1.66450100	0.41024300
O	0.78690300	-2.26183000	-0.07899000
H	-0.09997200	-2.65332900	0.11279000
O	-3.92767500	-0.36448500	-0.60487500
H	-3.47500400	-1.21345000	-0.48368200
C	1.49314400	0.22962300	-0.44756900
H	2.69895500	-0.48252900	0.34740800
H	-1.67227500	0.77524600	-1.21448200
H	0.01743700	-0.88815400	-1.47268600
H	-0.61267300	-0.19761600	1.47117100
H	-3.73715400	1.54878400	0.05705200
H	-2.00698200	-1.82105300	1.28966700
O	2.35039400	2.32017800	0.30939800
H	1.07257700	1.19361600	1.42087200
H	-3.37065500	0.32280200	1.29546500
H	-1.65495600	2.68736600	-0.01717800
O	3.62676900	-0.94474300	0.73045600

H	3.39581800	-1.49390500	1.50350600
H	3.98473100	-1.54415200	0.04883400
H	1.26398300	-2.27949000	0.77185200



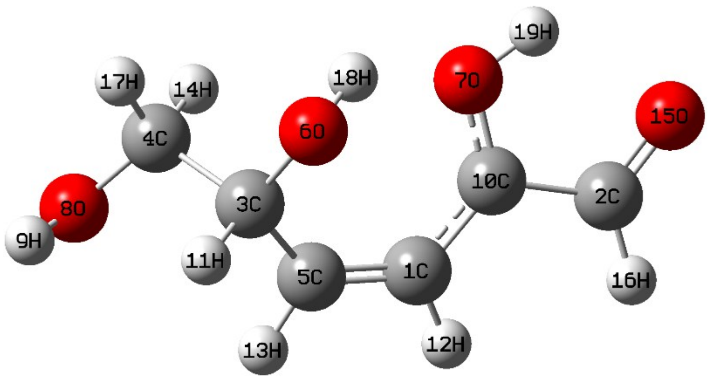
3H-p

C	0.81758800	0.08746000	0.63778400
C	3.41862900	0.07941200	0.57939200
C	-1.74700300	-0.09729700	0.65852800
C	-2.98440400	-0.92024000	0.26533800
C	-0.41611900	-0.68453800	0.18760500
O	-1.62385600	-0.07206400	2.08338600
O	2.08891000	-0.94390000	-1.12498200
H	0.70461500	1.17424500	0.47372100
O	-0.42834800	-0.75700400	-1.31372000
O	-3.39327900	-0.73483300	-1.09391900
H	-2.84575800	-1.29059600	-1.66434100
C	2.07530900	-0.32849100	-0.06228300
H	-1.84920100	0.92535100	0.25956500
H	0.95273700	-0.04462000	1.71957100
H	-0.33838900	-1.73848400	0.47084900
H	-3.81790500	-0.56812900	0.88638400
H	0.54111300	-0.95673900	-1.56437800
O	4.46409700	-0.33928500	0.13564300
H	3.36547300	0.75799700	1.45148900
H	-2.81272100	-1.98446300	0.48324400
H	-2.39660300	0.38628200	2.44280900
H	-0.67399100	0.10003100	-1.71943700



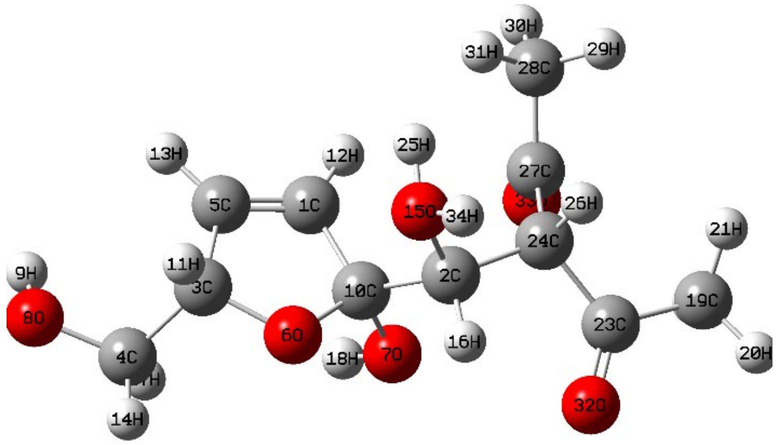
3H-TS

C	-0.67317600	-0.01238400	-0.33394300
C	-3.07589000	-0.56316800	-0.53952100
C	1.77347500	-0.69708500	-0.48663200
C	3.16676800	-0.63939800	0.16013100
C	0.63454800	-0.09225200	0.33810900
O	1.37420600	-2.06672900	-0.63339700
O	-1.99361400	-0.54282100	1.59890600
H	-1.11374200	1.54330700	-0.50930100
O	1.17875600	1.35234100	0.76177400
O	3.85717500	0.59495000	-0.06306200
H	3.51105900	1.25878100	0.54774800
C	-1.85010000	-0.38744400	0.36221600
H	1.81350100	-0.20074100	-1.46905300
H	-0.67609000	-0.14862500	-1.41733100
H	0.58269700	-0.54062200	1.33397400
H	3.77605200	-1.41520200	-0.32060900
H	0.56775700	1.75532500	1.41043400
O	-4.15549400	-0.92326600	-0.10464800
H	-2.93631700	-0.35567500	-1.62004500
H	3.10170700	-0.86725800	1.23421800
H	1.95738700	-2.47799700	-1.28731600
H	1.21951700	1.96451700	-0.00157000
O	-1.35176200	2.60577800	-0.63412100
H	-0.70319600	3.00111900	-1.24741400
H	-2.22821900	2.67143100	-1.05952100



4-p

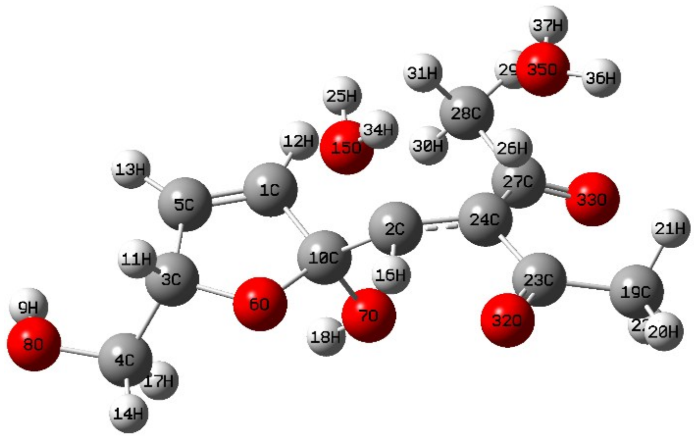
C	0.57451100	1.13183100	-0.43589000
C	3.00774400	0.59902400	0.01624600
C	-1.64138800	-0.24507300	-0.65601100
C	-2.49346100	-0.34736800	0.66405800
C	-0.78438300	0.95989700	-0.60907800
O	-1.01861600	-1.47934100	-0.95285900
O	1.27741700	-0.95764900	0.48896100
O	-3.38249600	0.73964700	0.84915000
H	-4.09249700	0.67038200	0.19438900
C	1.53651200	0.21471100	0.00692800
H	-2.36474100	-0.07452300	-1.46894600
H	0.97067800	2.13353100	-0.60692300
H	-1.34605000	1.88588200	-0.75565800
H	-1.82498900	-0.37645400	1.53189300
O	3.80805600	-0.21560900	0.42349700
H	3.27563300	1.59977800	-0.36064700
H	-3.02859700	-1.30377700	0.58226700
H	-0.38103300	-1.71154700	-0.26024200
H	2.11950600	-1.39778600	0.75634900



5iH-p

C	-1.11924300	1.13038100	-0.45356500
C	0.54243100	-0.40767200	0.88801300
C	-2.92387500	-0.05752700	0.41830800
C	-4.02052900	-0.75917300	-0.39693100
C	-2.41911800	1.22491200	-0.16804200
O	-1.75316700	-0.90978700	0.45847400
O	-0.16086200	-0.97195900	-1.25672200
O	-5.26379000	-0.05385600	-0.32997600
H	-5.20846500	0.72871300	-0.89584600
C	-0.61949300	-0.25881800	-0.12592200
H	-3.28158900	0.07994000	1.44997100
H	-0.49438500	1.89116400	-0.91218200
H	-3.05822700	2.08775400	-0.34397700
H	-4.20025000	-1.75029800	0.03645800
O	0.08020400	0.28834300	2.13857100
H	0.56371400	-1.45358100	1.20209100
H	-3.68903700	-0.88124600	-1.43848800
H	-0.76791000	-0.79276000	-1.99166000
C	4.22282500	-0.91031300	-0.39824600
H	4.84574300	-1.79246800	-0.21636900
H	4.63580300	-0.03211300	0.11305200
H	4.21839200	-0.70090300	-1.47778500
C	2.81291900	-1.19438700	0.03754600
C	1.98031700	0.00931100	0.52582500
H	0.13221100	1.26593500	2.11330300
H	2.46252300	0.28070000	1.47900200
C	2.12604500	1.23322500	-0.40462000

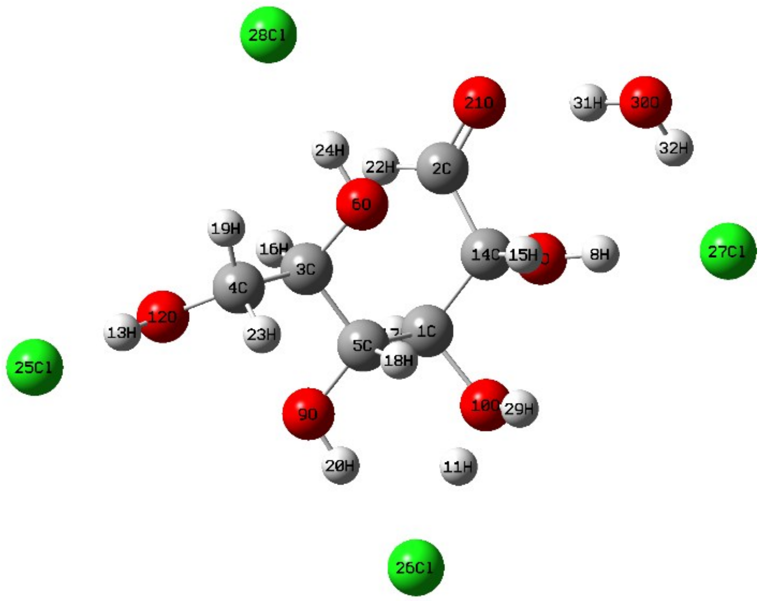
C	2.24176600	2.57747100	0.24602500
H	3.18214100	2.60490500	0.81783800
H	2.23736800	3.37120300	-0.50703400
H	1.43005800	2.73194000	0.97050600
O	2.36070100	-2.32905500	0.06364200
O	2.17292200	1.08372300	-1.61692700
H	0.55957300	-0.02261400	2.93428100



5iH-TS

C	-1.59359800	1.37519000	-0.09200100
C	0.39296700	-0.30834100	0.49118000
C	-3.16125800	-0.23600100	0.52544700
C	-4.23534100	-0.83377500	-0.40065600
C	-2.85838200	1.21351500	0.30582400
O	-1.90117500	-0.89775000	0.26016500
O	-0.64045500	-0.27168300	-1.61941100
O	-5.54869900	-0.35962300	-0.07956700
H	-5.62922000	0.55456400	-0.39259300
C	-0.92540600	0.02029800	-0.26005800
H	-3.43866100	-0.44386500	1.56879900
H	-1.10804500	2.31250700	-0.34386100
H	-3.59903500	2.00253400	0.44581400
H	-4.25595600	-1.92220800	-0.25640200
O	0.10147100	0.37681500	1.91616300
H	0.30225500	-1.35010800	0.81278000
H	-3.98027500	-0.62081500	-1.45015900
H	-1.45138500	-0.10614100	-2.12736000
C	3.71780500	-1.61637600	-0.82632400
H	4.11116800	-2.61454400	-0.60464500

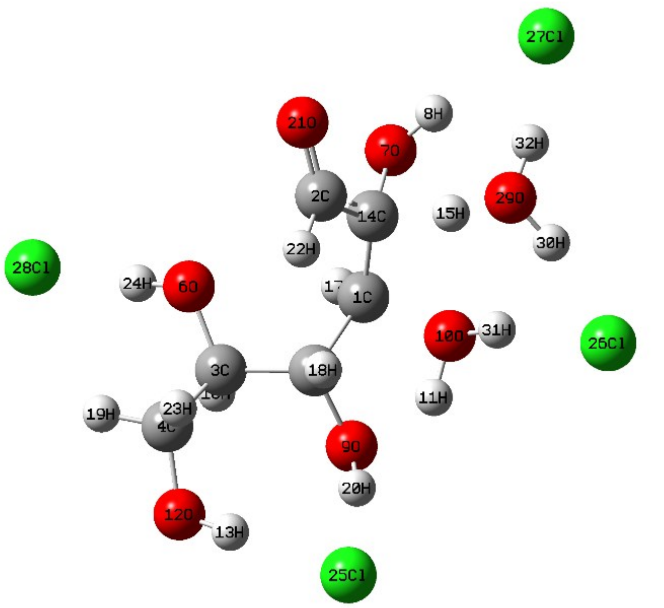
H	4.43975400	-0.84635000	-0.50748800
H	3.58790900	-1.49879500	-1.90749800
C	2.38938600	-1.45739600	-0.11545400
C	1.68249100	-0.16058400	-0.05837400
H	0.11337200	1.37673400	1.86104000
H	2.47124200	0.26884500	0.98861900
C	2.09420700	0.96881500	-0.89517600
C	1.45368600	2.33763800	-0.74785500
H	2.21833700	3.08653000	-1.00131800
H	0.64175300	2.43936300	-1.48396200
H	1.06813400	2.55864500	0.25380000
O	1.94413200	-2.46497100	0.47492100
O	3.02351000	0.89439700	-1.72803800
H	0.77475200	0.08701600	2.58562600
O	3.31584300	0.81497900	2.04514600
H	4.20131000	0.40168900	2.03643700
H	3.43624500	1.75918400	1.80800900



1Cl-p

C	-0.80772000	1.02116400	-0.52995100
C	-1.42638800	-1.44247700	-1.00522900
C	1.33308900	-0.37758500	-0.16490100
C	2.75108000	-0.40296800	0.42755600
C	0.57217300	0.91819500	0.14799900
O	0.54754600	-1.43049700	0.39734700
O	-3.02496200	0.27436000	-1.05160000
H	-3.79684900	0.19067600	-0.43647900
O	1.40508500	1.99616000	-0.28076100

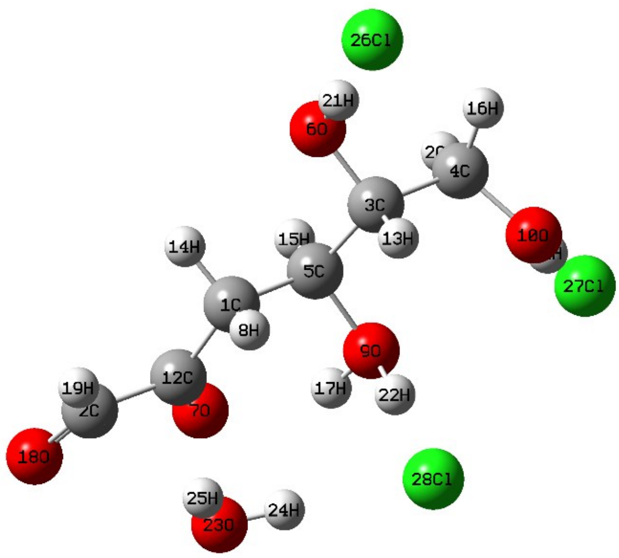
O	-1.50809300	2.22170900	0.02813900
H	-1.03566600	3.18243300	-0.12006900
O	3.68924800	0.12062900	-0.51543600
H	4.57330700	0.15740500	-0.07522900
C	-1.83121900	-0.11209200	-0.36551900
H	-2.03501700	-0.28373900	0.69963700
H	1.41464800	-0.50188600	-1.25660600
H	-0.68974100	1.27039200	-1.58954600
H	0.41887000	0.96464600	1.23889900
H	2.99250600	-1.45253700	0.65520100
H	0.99226600	2.85643500	-0.07803100
O	-2.01289000	-2.48193700	-0.72941500
H	-0.71780100	-1.40952800	-1.85259000
H	2.78181200	0.16714500	1.36987800
H	0.90799100	-2.30364700	0.08619600
Cl	6.46807400	0.26777800	0.82498000
Cl	-0.26691800	4.74622700	-0.27957800
Cl	-5.47778300	0.14805800	0.79511800
Cl	1.59453300	-4.16176600	-0.52296800
H	-1.68876900	2.11623000	0.98320800
O	-4.00374600	-2.60705500	1.34412800
H	-3.30863800	-2.56397200	0.65880600
H	-4.49690100	-1.76746300	1.21939700



1Cl-TS

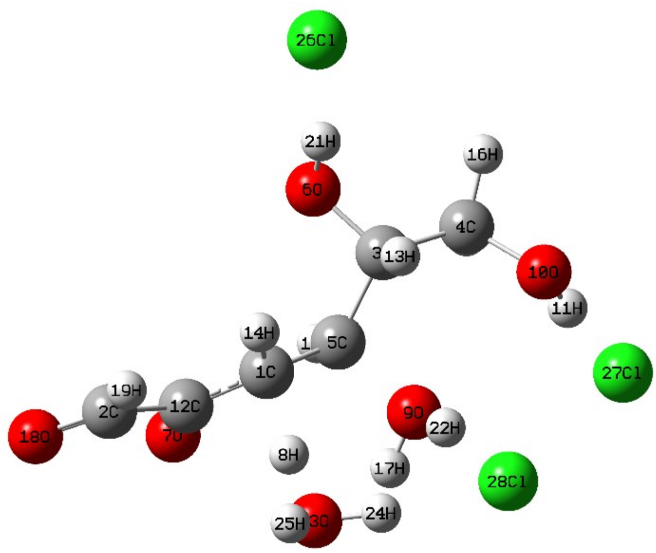
C	-0.19353800	-0.18885100	-0.78567300
C	-0.73387300	-1.33275200	1.40629800
C	2.29897400	-0.30758100	-0.15753400
C	3.39694900	0.25141900	0.76728000

C	1.02104900	0.55914200	-0.17692400
O	1.97636200	-1.62931900	0.27910200
O	-1.82415500	-1.93506100	-0.67536900
H	-2.76200700	-1.96529600	-0.39619300
O	1.25938200	1.69719500	-1.03354800
O	-0.95193000	0.90872000	-1.59759800
H	-0.20338700	1.58841100	-1.67850600
O	4.03349100	1.44417900	0.29715100
H	3.46410300	2.21880100	0.49076300
C	-1.10973900	-0.96516800	0.08787000
H	-2.28188800	-0.09368000	0.71866100
H	2.67704900	-0.33596300	-1.19190200
H	0.14204200	-0.81008500	-1.62361400
H	0.77869700	0.92805500	0.82615900
H	4.18350800	-0.51073100	0.83679500
H	1.47149800	2.49075900	-0.47548400
O	-1.17612600	-2.33102700	2.03709900
H	-0.08116000	-0.61834900	1.93911100
H	2.97809700	0.40438400	1.77466400
H	2.68577500	-2.24207600	-0.03967500
Cl	2.17911500	3.98427900	0.75084900
Cl	-3.16378100	2.73892800	-0.70427700
Cl	-5.00332000	-1.86469300	0.04901700
Cl	4.07706600	-3.64301100	-0.73784100
O	-3.26699600	0.33825500	1.04265100
H	-3.37768200	1.17520200	0.49249500
H	-1.70569100	1.39855300	-1.13040500
H	-3.96249100	-0.33231500	0.73161500



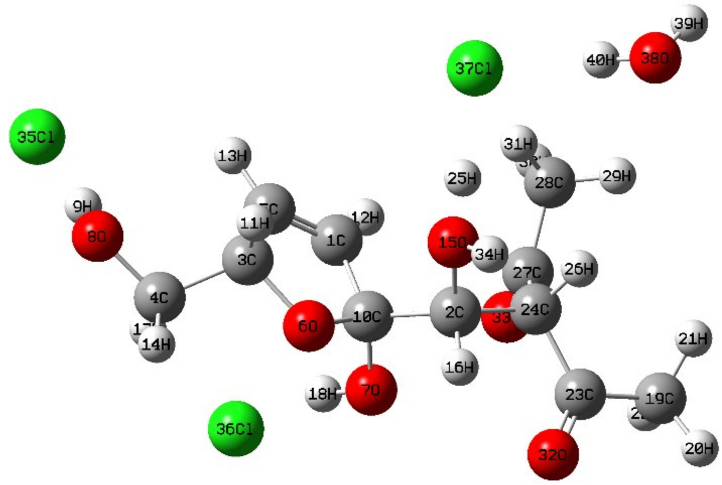
3Cl-p

C	-1.32371100	0.81384200	-0.66220700
C	-3.89390800	0.70434300	-0.94281300
C	1.21691700	0.85275200	-0.31935600
C	2.55807600	0.11907800	-0.48347800
C	-0.00099000	0.07785200	-0.83298600
O	1.23649400	2.04746000	-1.10020700
O	-2.48086000	-1.17899400	-1.36567800
H	-1.45414000	1.19648900	0.36124400
O	-0.06365200	-1.24207700	-0.13982600
O	2.78427000	-0.85946000	0.53208100
H	2.86183900	-1.74871400	0.10936300
C	-2.52694800	-0.00737400	-1.01553600
H	1.07045500	1.09150800	0.74575200
H	-1.32973100	1.70178900	-1.31261600
H	0.15552500	-0.19698500	-1.88100200
H	3.34193800	0.88813400	-0.41589100
H	-0.80510400	-1.73698100	-0.56158900
O	-4.88319000	0.20152100	-1.43330300
H	-3.91110900	1.69949400	-0.46082000
H	2.61566800	-0.33701100	-1.48302900
H	1.65473100	2.77099200	-0.56501800
H	-0.28014300	-1.20399400	0.90887100
O	-3.61178600	-0.17198200	1.70084400
H	-2.73545000	-0.49308400	1.99978800
H	-3.63225400	0.75341800	1.98215600
Cl	2.41799000	4.36630900	0.50069400
Cl	3.17204500	-3.63769500	-0.75004100
Cl	-0.74174300	-1.32389300	2.63521600



3Cl-TS

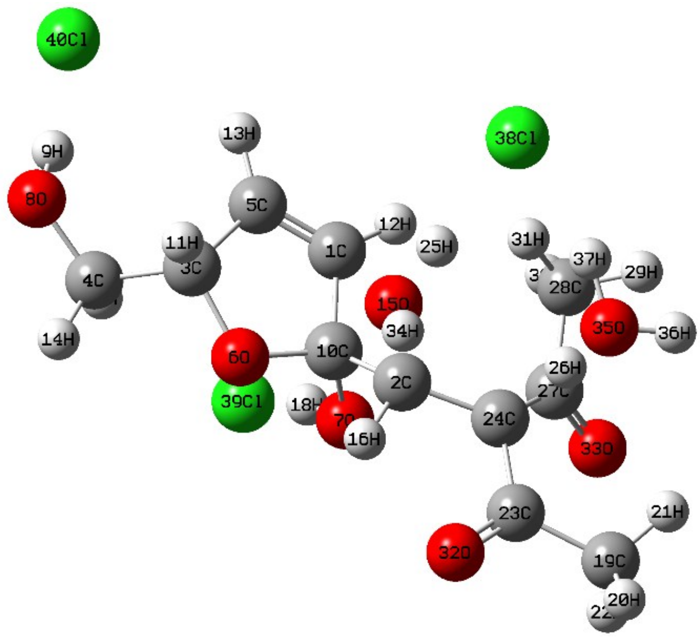
C	-1.55108600	-0.47988200	-0.11892800
C	-3.95508700	-1.03670700	-0.42452300
C	0.35006400	1.25349500	-0.23156200
C	1.81952100	1.57535300	-0.60547200
C	-0.21388900	-0.11678800	-0.67060700
O	-0.56499300	2.19652500	-0.78627500
O	-2.34340000	-1.56552400	-2.11105700
H	-1.50891300	-1.66975200	0.76308400
O	0.86034500	-1.17769700	-0.27887400
O	2.74859000	0.92821300	0.26246400
H	3.31478300	0.32753900	-0.27568500
C	-2.52959400	-1.03865000	-0.99821100
H	0.23998900	1.28542400	0.86475900
H	-1.93737800	0.18069600	0.66266500
H	-0.16677400	-0.21499400	-1.75961600
H	2.05252400	2.67155600	-0.50853600
H	0.60779300	-2.04084800	-0.66097200
O	-4.91200700	-1.43586300	-1.06151700
H	-4.04229600	-0.63442700	0.60673700
H	2.18775400	1.33997500	-1.65743200
H	-0.65773400	2.96886600	-0.16927500
H	1.00654200	-1.33593800	0.72769200
O	-1.34796100	-2.62138500	1.46707500
H	-0.44257200	-2.49705700	1.91060500
H	-1.99735400	-2.58744300	2.20428700
Cl	-1.14399400	4.60508800	1.03899200
Cl	4.62360100	-0.77820500	-1.48736400
Cl	1.36153800	-2.02268800	2.54560600



5iCl-p

C	0.75805300	0.06071300	0.62227600
C	-1.30112300	-0.26099400	-0.97012900
C	1.99273000	0.76675900	-1.22271300
C	3.37893000	0.28352500	-1.67540900
C	1.78713700	0.82733700	0.25986100
O	0.98831100	-0.17175900	-1.67754300
O	0.14553800	-2.02475500	-0.53370100
O	4.36984500	1.29412700	-1.50164000
H	4.69533600	1.28651800	-0.56819100
C	0.15811900	-0.62174800	-0.58668200
H	1.79681000	1.74230700	-1.69655300
H	0.39996100	-0.10699900	1.63365100
H	2.42615800	1.41173400	0.91814000
H	3.32814100	0.05554600	-2.74836700
O	-1.33364000	1.19986800	-1.23070000
H	-1.46188700	-0.69261700	-1.96130300
H	3.65022100	-0.63645900	-1.13637800
H	0.97323100	-2.37847600	-0.10946600
C	-4.44313000	-2.40139400	0.07019400
H	-5.13348500	-2.89820500	-0.61933500
H	-4.94692900	-1.58290900	0.59933200
H	-4.11082900	-3.13270700	0.82128200
C	-3.23913100	-1.91040300	-0.68545400
C	-2.49412600	-0.69897600	-0.08696300
H	-1.42853300	1.93293900	-0.44299700
H	-3.23084100	0.11662100	-0.14747000
C	-2.21322200	-0.92477000	1.41597300
C	-2.50735300	0.20896400	2.34758300

H	-3.59894000	0.35570100	2.36554300
H	-2.14742500	-0.01696200	3.35597200
H	-2.07274300	1.14541100	1.97236300
O	-2.89526300	-2.41546000	-1.74412700
O	-1.81028400	-2.01078700	1.81045100
H	-1.99807400	1.40929200	-1.91157400
Cl	5.61992300	1.41829400	1.32427600
Cl	2.49101900	-3.56143600	0.68363700
Cl	-1.56781300	3.40127700	0.53740100
O	-4.57909100	4.17227900	-0.26176000
H	-5.04759400	4.33937200	0.56750600
H	-3.67040800	3.93942200	0.01844800



5iCl-TS

C	-0.93186900	0.23761100	-0.67762100
C	1.23385800	-0.03887300	0.83501200
C	-2.14601200	0.47977400	1.29504100
C	-3.44322100	-0.22317000	1.71567100
C	-2.03271400	0.79066300	-0.16482400
O	-1.01926400	-0.38818700	1.55598300
O	0.02283100	-1.88992500	0.08428200
O	-4.55203500	0.67527000	1.73090800
H	-4.90348700	0.78925200	0.81523800
C	-0.17463800	-0.53081900	0.38504800
H	-2.03195000	1.39034900	1.90803000
H	-0.61951800	0.26332900	-1.71275500
H	-2.78450200	1.36410800	-0.70441800
H	-3.31727800	-0.59989600	2.74346000

O	1.04399000	1.46819500	1.09444100
H	1.32969800	-0.39342400	1.86333500
H	-3.63311300	-1.08000700	1.05454500
H	-0.80976100	-2.29689900	-0.27962200
C	4.84540200	-1.49747100	0.55691100
H	5.58368900	-1.30981900	1.34439500
H	5.14284500	-0.99188400	-0.36588100
H	4.82051300	-2.57732900	0.36178200
C	3.48935500	-1.05116700	1.06653000
C	2.51946200	-0.41817800	0.14943200
H	1.17627600	2.12733000	0.31715500
H	3.35769600	0.91216400	0.00966700
C	2.55054800	-0.77595800	-1.28192800
C	1.93289800	0.15228600	-2.31045700
H	2.75555900	0.49975500	-2.94947400
H	1.24033200	-0.40847200	-2.94907800
H	1.43753600	1.03088200	-1.88786300
O	3.28500000	-1.13097100	2.29787400
O	3.15163800	-1.77799500	-1.70968500
H	1.64046600	1.75316900	1.81140600
O	3.90006800	1.89284800	-0.09177000
H	4.60471200	1.77612200	-0.75993800
H	3.23383000	2.56800100	-0.45097700
Cl	1.59181200	3.67204900	-0.79825900
Cl	-2.26748300	-3.55615000	-1.08684700
Cl	-5.90902200	1.15711200	-1.01361000

Figure S24. The Cartesian coordinates of optimised geometries including all reported intermediates and transition states from the density functional theory calculations (unit: Å).

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