

## **Supporting Information**

### **Quantitative determination of Pt- catalyzed D-glucose oxidation products using 2D NMR**

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## Directory of Contents

### Experimental Procedures

**Scheme S1.** The pulse sequence used for  $^{13}\text{C}$ - $^1\text{H}$  HMBC NMR experiments.

**Figure S1.** HPLC elution peaks showing standards of  $\text{C}_6$  glucose oxidation products and a mixture thereof – illustrating overlap and co-elution of major reaction products.

**Figure S2.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  spectra of the product stream of 5% Pt/ $\text{TiO}_2^{\text{IMP Red 400}}$  catalysed glucose oxidation at 80 °C showing extensive overlap of resonances.

**Figure S3.** HMBC NMR  $^{13}\text{C}$  - $^1\text{H}$  spectrum of the product stream of 5% Pt/ $\text{TiO}_2^{\text{IMP Red 400}}$  catalysed glucose oxidation at 80 °C with false colouring of correlations assigned through analysis of standard solutions.

**Table S1.** The chemical structures and CAS numbers of  $\text{C}_6$  reaction products formed in Pt-catalysed glucose oxidation reactions.

**Table S2.** Structural assignment of  $^{13}\text{C}$ - $^1\text{H}$  correlations as observed in Fig. 1.

**Table S3.**  $\text{C}_6$  oxidation products of uronic and aldaric acid derivatives of D-glucose showing false coloured HMBC NMR spectra of product streams.

**Table S4.** Initial rates for catalytic conversion of D-gluconic acid and D-glucono 1,4 lactone as a function of reaction temperature

**Figure S4.** Annotated  $^{13}\text{C}$ - $^1\text{H}$  HMBC NMR spectrum of D-glucaric acid.

**Table S5.** Assignment of peaks from Fig. S4 with experimentally calibrated rF values and corresponding  $R^2$  values.

**Table S6.** Sensitivity analysis of calibrated rF values from Table S2, with Correlation 8 identified as most suitable for use in quantitative analyses.

**Figure S5.** Regions of the HMBC spectrum of a D-glucaro 1,4 lactone solution following 65 h equilibration- with peaks false coloured to identify D-glucaric acid, D-glucaro 1,4 lactone and D-glucaro 6,3 lactone.

**Table S7.** Calibrated  $^1\text{H}$  NMR response factors for proton resonances in D-glucaric acid, D-glucaro 1,4 lactone and D-glucaro 1,4 6,3 dilactone.

**Table S8.**  $^1\text{H}$  NMR assignments for D-glucaro 6,3 lactone.

**Table S9.** Quantified HMBC NMR rFs for  $^{13}\text{C}$ - $^1\text{H}$  correlations in the HMBC spectrum of D-glucaro 6,3 lactone.

**Figure S6.** Peak area vs mol calibration plots for  $^{13}\text{C}$ - $^1\text{H}$  correlation peaks as determined through glucarate equilibrium studies.

**Figure S7.** Calibration of  $\alpha$ -D-glucopyranose and  $\beta$ - D-glucopyranose in aqueous solutions of D-glucose via equilibrium studies.

**Figure S8.** A test of rF values determined in Figure S7 via analysis of a series of D-glucose solutions of differing concentration, following equilibration at room temperature.

**Table S10.** A summary of  $^{13}\text{C}$ - $^1\text{H}$  HMBC NMR correlations used for quantification of  $\text{C}_6$  products and unreacted glucose.

**Figure S9.** The  $^{13}\text{C}$ - $^1\text{H}$  HMBC NMR (a) and  $^{13}\text{C}$ - $^1\text{H}$  HSQC spectra (b) of Pt- catalysed D-glucose oxidation product streams.

**Figure S10.** Temporal evolution of D-gluconic acid and D-glucono 1,4 lactone in 5% Au/ $\text{TiO}_2$  – catalyzed D-glucose oxidation, as quantified by either  $^{13}\text{C}$ - $^1\text{H}$  HMBC NMR or HPLC; a comparative study.

**Figure S11.** Expanded region of a HMBC NMR  $^{13}\text{C}$  –  $^1\text{H}$  spectrum of 5% Pt/ $\text{TiO}_2^{\text{IMP Red 400}}$  catalysed glucose oxidation at 80 °C in either  $\text{D}_2\text{O}$  or  $\text{H}_2\text{O}$  false coloured to assign correlations to key  $\text{C}_6$  products – highlighting quenching of product correlations due to a strong solvent contribution when  $\text{H}_2\text{O}$  is used as reaction solvent.

**Figure S12.** Glucose conversion (measured at 24 h on line) as a function of Pt- metal surface area and specific activity as a function of time on line in 5 % Pt/ $\text{TiO}_2^{\text{IMP Red 400}}$  catalysed glucose oxidation.

**Figure S13.**  $^2\text{H}$  NMR spectra for 5% Pt/ $\text{TiO}_2^{\text{IMP Red 400}}$  catalysed glucose oxidation at 80 °C in either  $\text{D}_2\text{O}$  or  $\text{H}_2\text{O}$  showing no apparent  $^2\text{H}$ -  $^1\text{H}$  exchange.

**Table S11.** A systematic study of the source of Pt-leaching from 5% Pt/ $\text{TiO}_2^{\text{IMP Red 400}}$

**Figure S14.** Adsorption of leached Pt from aqueous solution onto a series of unmodified catalyst supports.

**Figure S15.** Observed Pt- leaching under continuous flow trickle bed operation- showing Pt-sequestration by carbon.

**Figure S16.** Thermogravimetric analyses (TGAs) of as-synthesised 5% Pt/ $\text{TiO}_2^{\text{IMP Red 400}}$  and solid residues following catalytic assessments at reaction temperatures of 60 and 100 °C.

**Figure S17.** Expanded region of an HMBC-NMR spectrum of the oxidation of glucose using 5 wt. % Pt/ $\text{TiO}_2^{\text{IMP Red 400}}$  with NaOH (1 eq. 5.54 mmol) added at  $t = 0$ .

## Experimental Procedures

### Materials and Methods

D-glucaric acid (99.9 %) was prepared from K-glucarate as previously reported.<sup>[1]</sup> An aqueous solution of K-glucarate (0.05 M, 100 ml) was ion exchanged twice with Amberlyst-15 ( $\text{H}^+$ )(5.0 g). Following filtration the solution was azeotroped with acetonitrile (1.9 l, 5 min) and the solvent was then removed *in vacuo* (50 mbar, 22 °C) to yield pure crystalline D-glucaric acid as an off- white dry solid.

D-Glucaro 1,4: 6,3 dilactone was prepared from K-glucarate as previously reported.<sup>[2]</sup> Following ion exchange steps (as for D-glucaric acid synthesis) the water solvent was removed *in vacuo* (50 mbar, 50 °C) to yield an orange syrup. This was then dried under vacuum (12 h, 90 °C) to form an orange "glass." This was dissolved in 1,4- dioxane (50 ml) and glucaro 1,4: 6,3 dilactone was precipitated through addition of dichloromethane (50 ml). Recrystallization of this crude

product from 1,4 dioxane : dichloromethane (3:1) yielded D-glucaro 1,4: 6,3 dilactone (NMR pure).

D-Glucaro 1,4 lactone, D-glucono 1,5 lactone, D-glucuronic acid, D-glucurono 6,3 lactone, D-glucose, oxalic acid, tartronic acid, tartaric acid, glyceric acid, formic acid, acetic acid, glycolic acid and fructose (all > 99.6 %) were purchased from Sigma Aldrich and used as received. L-gulurono 6,3 lactone and D-glucono 1,4 lactone was purchased from Carbosynth and used as received.

5- Keto D- gluconic acid potassium salt (> 98 %) and D- gluconic acid Na salt (> 99 %) were purchased from Sigma Aldrich. Aqueous solutions of the desired free acids (of varying concentration) were prepared through ion exchange with Amberlyst- 15 (H<sup>+</sup>) at ambient temperature followed by filtration. L-Guluronic acid Na salt was purchased from Carbosynth and ion exchanged as above prior to analysis.

### Catalyst Preparation

Catalysts were prepared via dry chemical vapour impregnation (CVI) from Pt(acac)<sub>3</sub>, incipient wetness impregnation from Pt(NO<sub>3</sub>)<sub>4</sub> (IWI) and wet impregnation from H<sub>2</sub>PtCl<sub>6</sub>.4H<sub>2</sub>O (IMP).

The procedure for preparation of a 5 wt% Pt/TiO<sub>2</sub> catalyst via CVI is as follows. TiO<sub>2</sub> (P25, 0.95 g) was physically mixed with Pt (acac)<sub>3</sub> (0.1008 g, 0.256 mmol). The resulting dry mixture was transferred to a Schlenk flask and heated under continuous vacuum (1 h, 140 °C). Following this, the sample was heat treated (3 h, 400 °C, 20 °C min<sup>-1</sup>) in 5% H<sub>2</sub>/Ar (30 ml min<sup>-1</sup>) leading to the descriptor 5% Pt/TiO<sub>2</sub><sup>CVI Red 400</sup>.

The procedure for preparation of 5% wt. % Pt/TiO<sub>2</sub> via wet impregnation (IMP) is as follows. To an aqueous solution of H<sub>2</sub>PtCl<sub>6</sub>.4H<sub>2</sub>O (0.256 mmol, 0.052 M) was added TiO<sub>2</sub> (P25, 0.95 g), with vigorous stirring. The resulting mixture was stirred at 80 °C to form a paste, which was dried (110 °C, 16 h). The sample was then ground in a pestle and mortar and heat treated as described above to yield 5 wt. % Pt/TiO<sub>2</sub><sup>IMP Red 400</sup>. 5% Au/TiO<sub>2</sub><sup>IMP Red 400</sup> was prepared from HAuCl<sub>4</sub> aq following the same procedure.

The procedure for preparing 5 wt. % Pt/TiO<sub>2</sub> via incipient wetness impregnation (IWI) is as follows. To an aqueous solution of Pt(NO<sub>3</sub>)<sub>4</sub> (2.2 ml, 0.256 mmol, 0.116 M) was added TiO<sub>2</sub> (P25, 0.95 g) to form a dry mix. Impregnation was carried out at 110 °C for 16 h. The sample was then ground in a pestle and mortar and heat treated as described previously to yield 5 wt. % Pt/TiO<sub>2</sub><sup>IWI Red 400</sup>.

### Catalyst Assessment

Catalytic assessments were carried out in a Teflon lined 50 ml Parr Autoclave reactor according to the following procedure. D-Glucose (0.996 g, 5.53 mmol) were added to a Teflon liner followed by solvent, 10 ml (typically D<sub>2</sub>O). The resulting solution was determined to have a total volume of 10.5 ml. Catalyst (typically 40 mg) was then added. The reactor was then sealed, purged 3 times with N<sub>2</sub> and charged with a premixed feed comprising of 20% O<sub>2</sub> in N<sub>2</sub> (total pressure typically 25 bar). The system was then heated to a predefined set point (typically 80 °C) and held for the desired time (typically 24 h). Following this the reactor was cooled to ca. 10 °C and gas phase vented into a gas sampling bag. The liquid phase was then filtered prior to analysis.

### Product Analysis

C<sub>6</sub>/C<sub>5</sub> molecules; D-glucose ( $\alpha$  &  $\beta$  glucopyranose), D-gluconic acid, D-glucono 1,4 lactone, D-glucaric acid, D-glucaro 1,4 lactone, D-glucaro 6,3 lactone, D-glucaro 1,4: 6,3 dilactone, D-glucuronic acid, D-glucurono 6,3 lactone, L-guluronic acid, L-gulurono 6,3 lactone, tartronic acid and tartaric acid were quantified using a Bruker Avance 500 MHz (11.7 Tesla; multinuclear) NMR spectrometer. Spectral peaks/ correlations were normalised to TMS (1 % v/v in CDCl<sub>3</sub>) within a sealed ampoule. Standards and reaction solutions were analysed at a constant 0.7 ml volume. TMS ( $\delta$  <sup>1</sup>H = 0 ppm,  $\delta$  <sup>13</sup>C = 0 ppm). The pulse sequence used, a modified version of Bruker hmbcetgpl2nd is shown in Scheme S1.

Short chain liquid phase carboxylic acid products; oxalic, glyceric, glycolic and acetic acids were analysed using an Agilent 2000 series HPLC fitted with a MetaCarb 67H column (0.1 M H<sub>3</sub>PO<sub>4</sub> aq mobile phase, 0.5 ml min<sup>-1</sup>, 30 °C column) and both RID and DAD detectors.

Gas phase CO<sub>2</sub> was analysed using a Varian 450-GC fitted with an FID, TCD and methaniser (CP-Sil 5CB capillary column, 50 m length, 0.32 mm diameter, carrier gas He). CO<sub>2</sub> was quantified by GC-FID, calibrated versus commercial standards (BOC).

### Quantification of leached metals

Microwave Plasma Atomic Emission Spectroscopy (MP-AES) was performed using an Agilent 4100 MP-AES. The Pt content of reaction solutions was analysed using emission lines at 265.95 and 299.79 nm, calibrated versus a commercially available standard. The samples were introduced to the nitrogen plasma using a single pass spray chamber at a pressure of 120 kPa with air injection. Samples were read thrice, with the mean value reported.

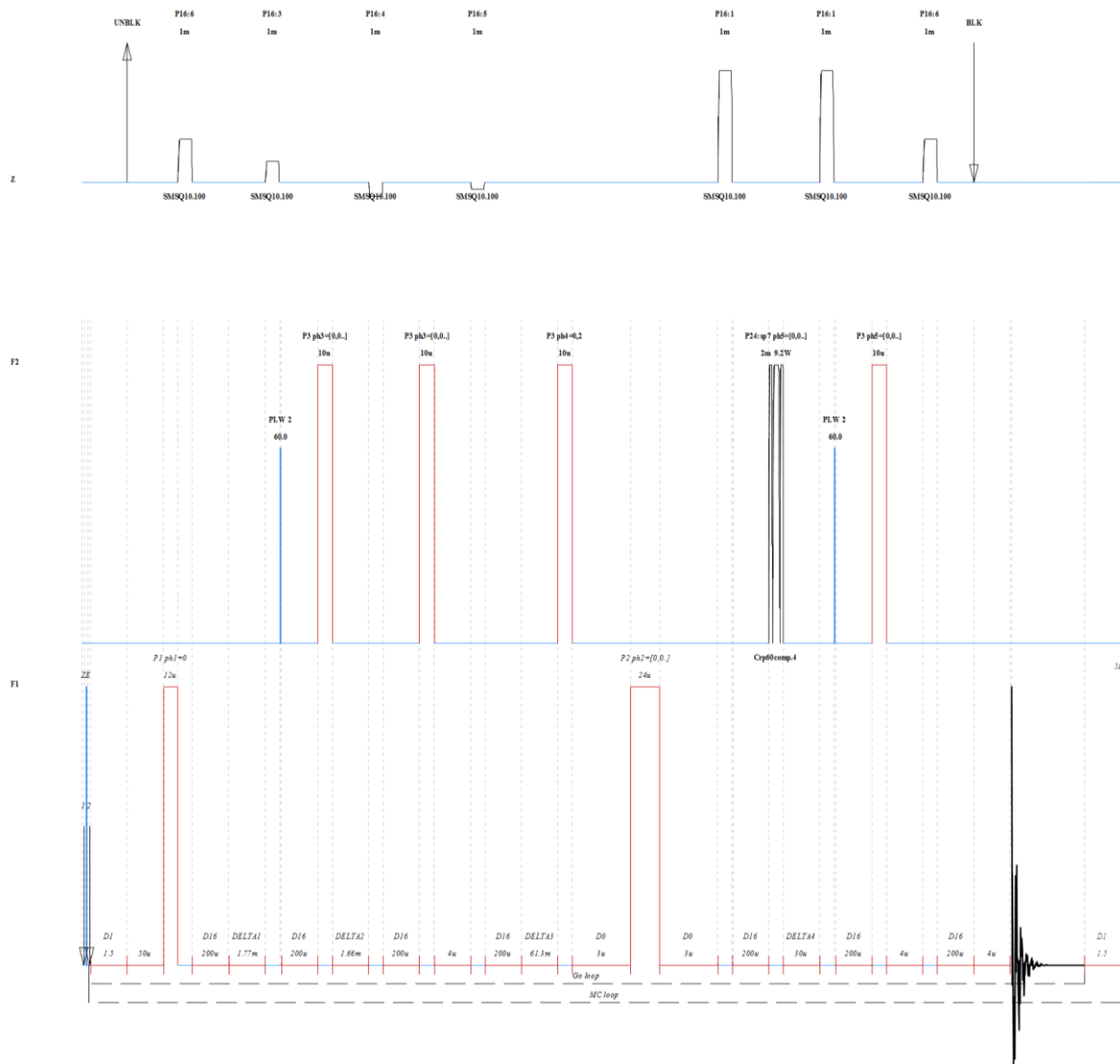
Select samples were analysed using an Agilent 7900 ICP-MS instrument, calibrated versus commercial standards.

### Catalyst Characterization

CO chemisorption was carried out on a ChemBet TPR/TPD chemisorption analyzer, Quantachrome Industries, fitted with a TCD. Prior to analysis the sample (50 mg) was pretreated in helium (80 ml min<sup>-1</sup>) at 130 °C (1 h). Pulse chemisorption of CO (70  $\mu$ l pulse volume) was then carried out at 30 °C.

### References

- [1] Armstrong, R. D.; Kariuki, B. M.; Knight, D. W.; Hutchings, G. J. How to Synthesise High Purity, Crystalline d-Glucaric Acid Selectively. *European J Org Chem.* 2017, 6811-6814.
- [2] Brown, J. M.; Manley-Harris, M.; Field, R. J.; Kiely, D. E. An NMR study of the equilibration of D-glucaric acid with lactone forms in aqueous acid solutions. *J. Carbohydr. Chem.* 2007, 26, 455-467.



Scheme S1. The pulse sequence used for  $^{13}\text{C}$ - $^1\text{H}$  HMBC NMR experiments.

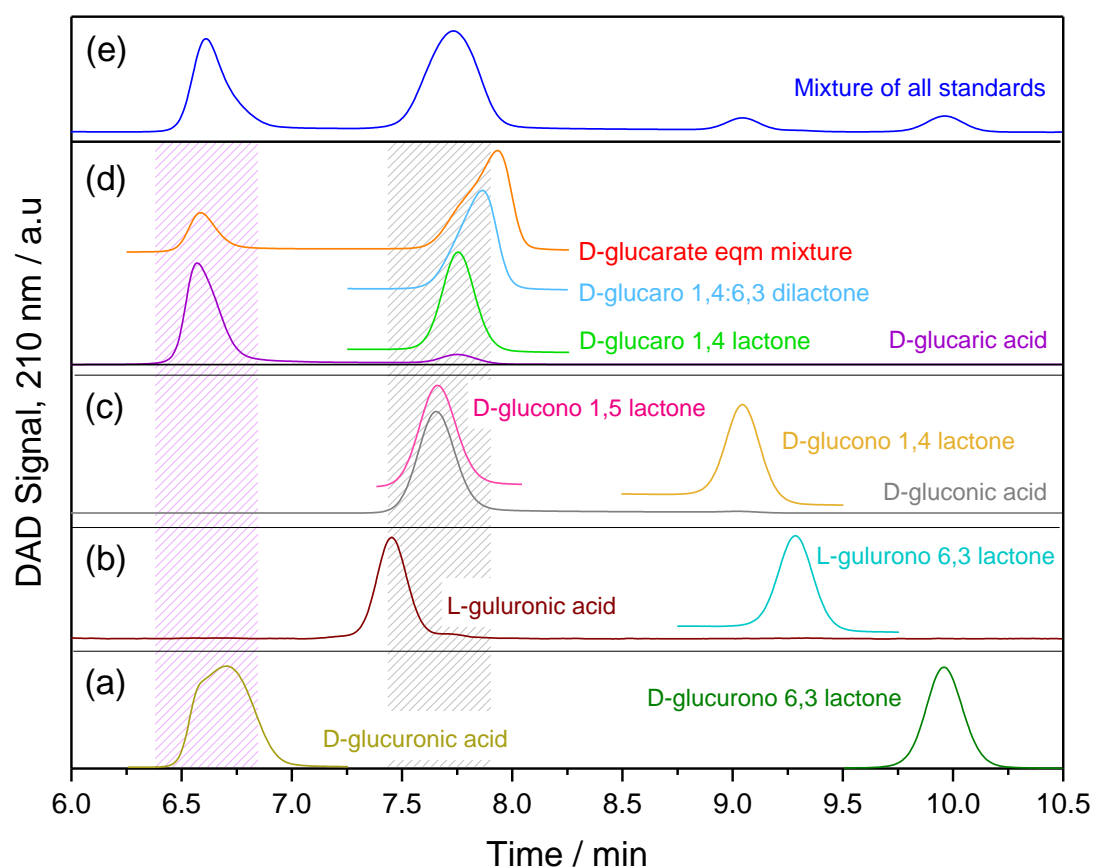


Figure S1. An overlay of DAD signals (measured at  $\lambda = 210$  nm) for potential  $C_6$  glucose oxidation products showing (a) D-glucuronates, (b) L-guluronates, (c) D-gluconates, (d) D-glucarates and (e) a mixture comprising all standards. Single component mixtures (0.1 M), with the exception of L-guluronates (0.01 M).

Analysis conditions; 10  $\mu$ L injection, Metacarb 67H column, 0.5 ml min<sup>-1</sup>, 30 °C, 0.1 M H<sub>3</sub>PO<sub>4</sub> aq mobile phase.

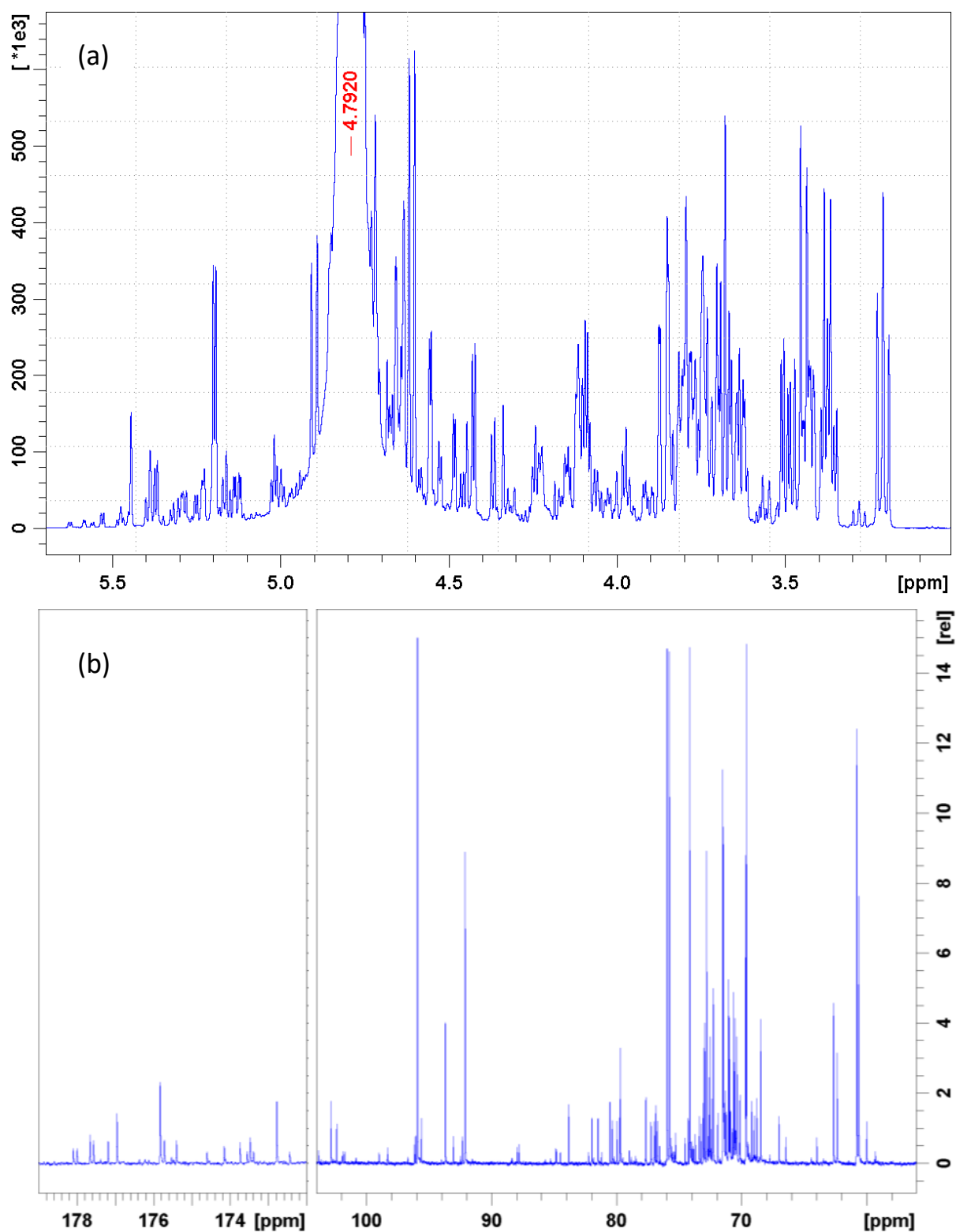


Figure S2.  $^1\text{H}$  NMR (a), and  $^{13}\text{C}$  spectra (b) normalised to TMS at  $\delta = 0$  ppm,  $\text{D}_2\text{O}$  lock. Reaction conditions; 40 mg 5% Pt/ $\text{TiO}_2^{\text{IMP Red 400}}$ , 1000 rpm,  $P(\text{O}_2) = 20$  bar, 80  $^\circ\text{C}$ , 24 h,  $[\text{D-glucose}] = 0.554$  M (D-glucose/ Pt = 540 : 1 mol : mol)



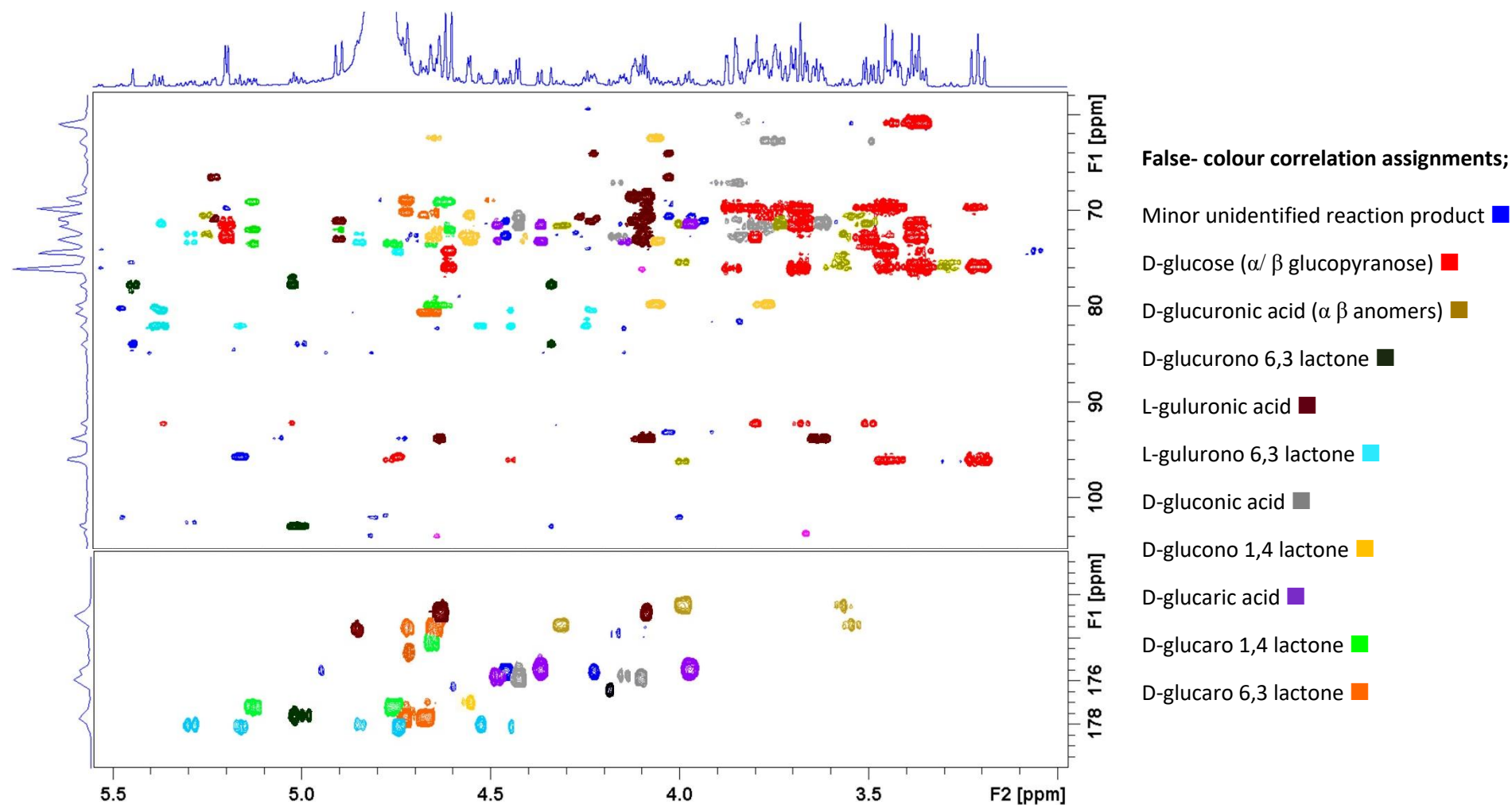
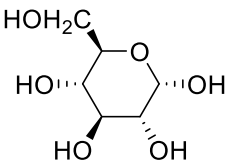
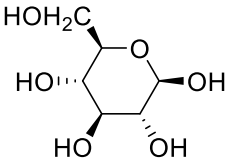
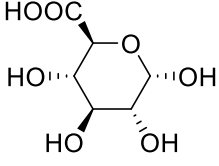
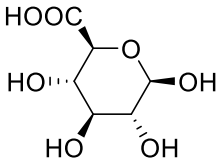
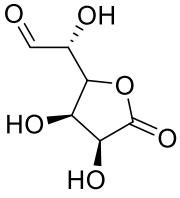
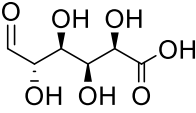
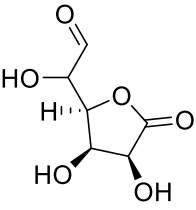
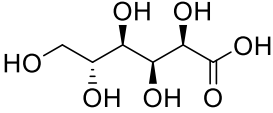


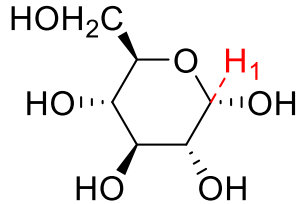
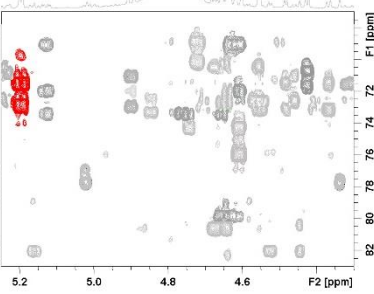
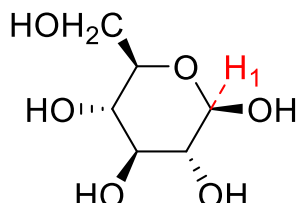
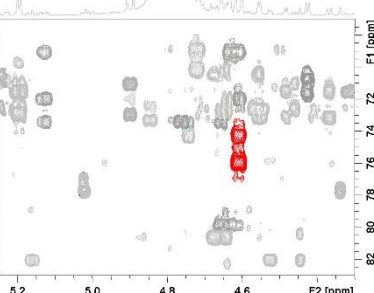
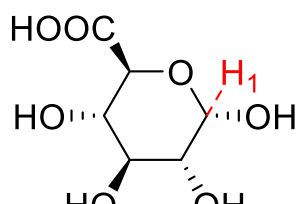
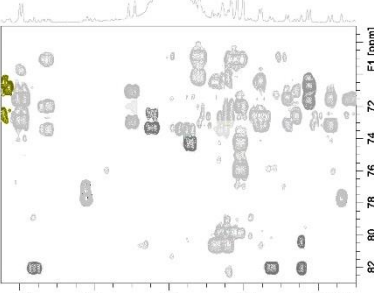
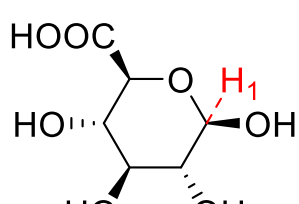
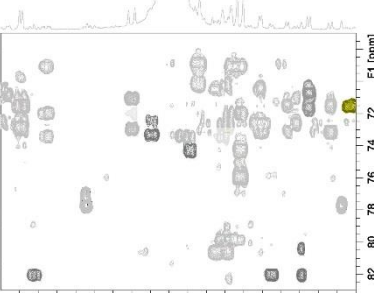
Figure S3. HMBC NMR spectra false coloured to show correlations corresponding to glucose and C<sub>6</sub> oxidation products thereof. Assignments based on analysis of standards and spectra calibrated to TMS at  $\delta^1\text{H} = 0$  ppm  $\delta^{13}\text{C} = 0$  ppm, D<sub>2</sub>O lock. Reaction conditions; 40 mg 5% Pt/TiO<sub>2</sub><sup>IMP Red 400</sup>, 1000 rpm, P(O<sub>2</sub>) = 20 bar, 80 °C, 24 h, [D-glucose] = 0.554 M (D-glucose/ Pt = 540 : 1 mol : mol)

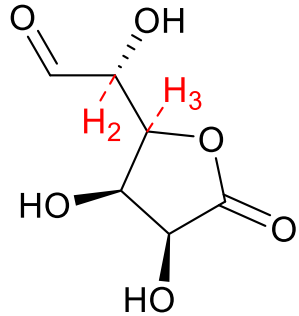
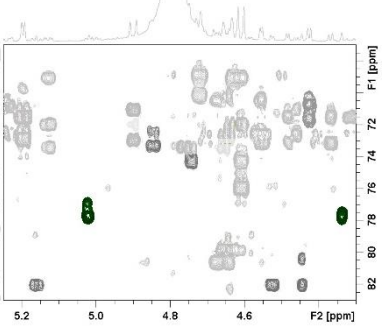
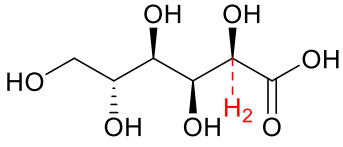
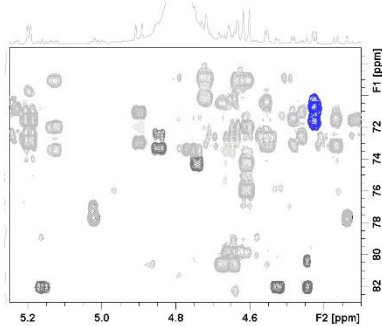
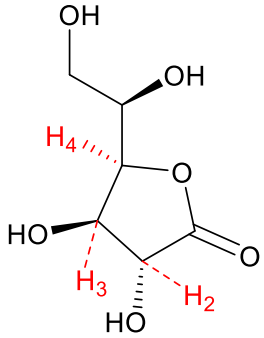
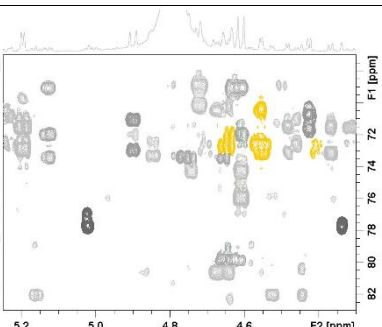
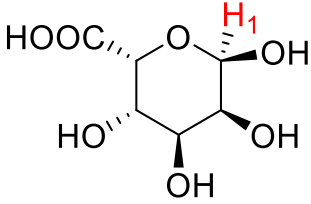
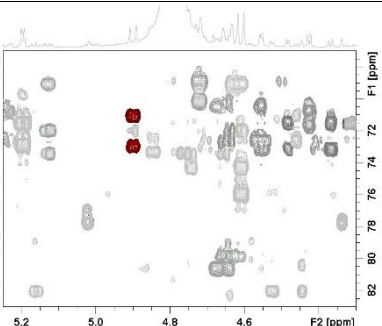
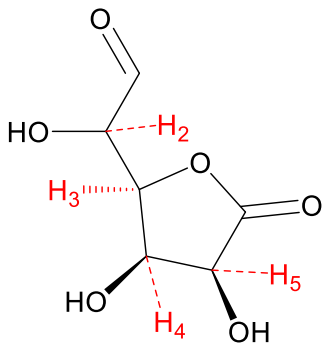
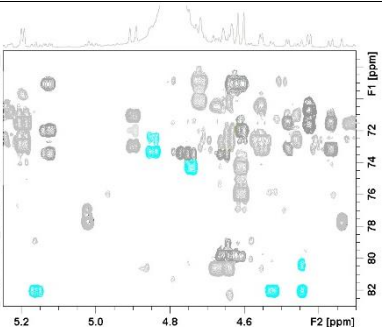
Table S1. The chemical structures of C<sub>6</sub> Glucose oxidation reaction products identified in Figure S3.

Product	CAS number	Structure
$\alpha$ -D- glucopyranose	492-62-6	
$\beta$ -D- glucopyranose	492-61-5	
$\alpha$ -D- glucuronic acid	70021-34-0	
$\beta$ -D- glucuronic acid	23018-83-9	
D-glucurono 6,3 lactone	32449-92-6	
L-guluronic acid	1986-15-8	
L-Gulurono-6,3-lactone	14474-04-5	
D-gluconic acid	526-95-4	

D-glucono 1,5- lactone	90-80-2	
D-gluconic acid 1,4- lactone	1198-69-2	
D-glucaric acid	87-73-0	
D-glucaro 1,4 lactone	5027-63-4	
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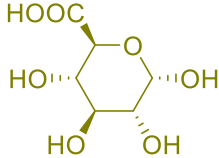
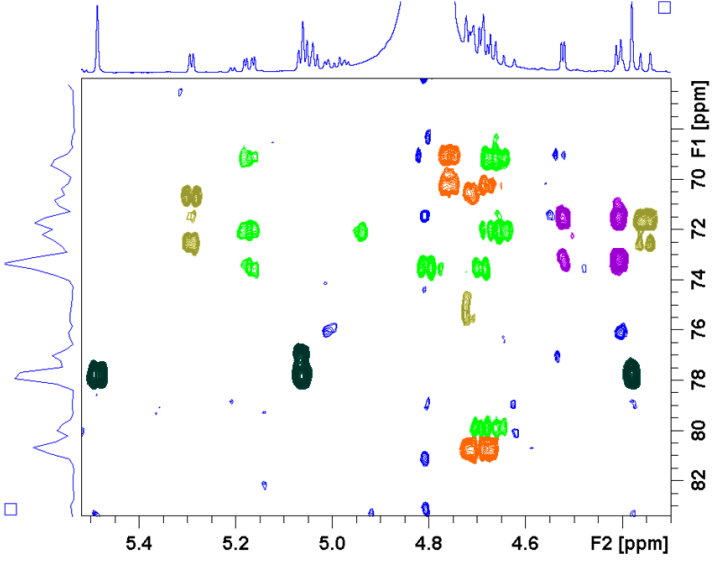
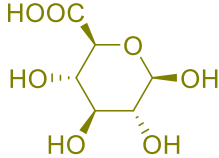
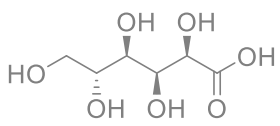
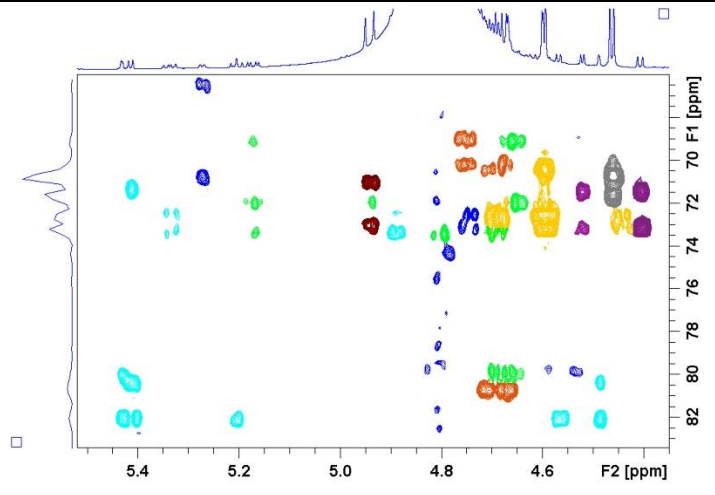
Table S2. Structural assignment of  $^{13}\text{C}$ - $^1\text{H}$  correlations as observed in Fig. 1.

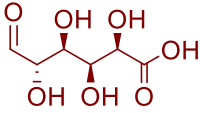
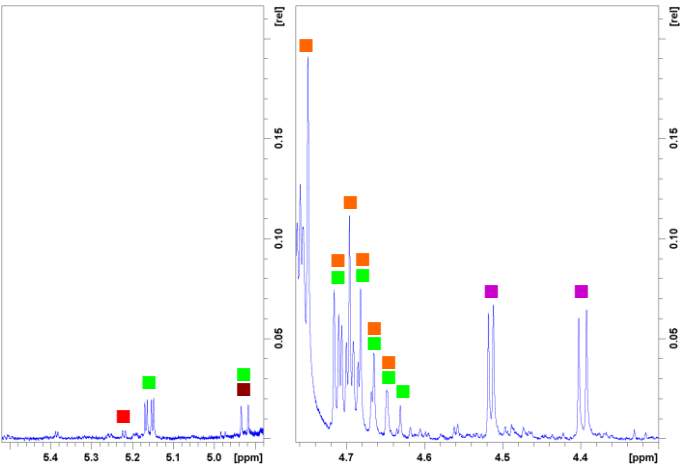
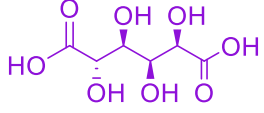
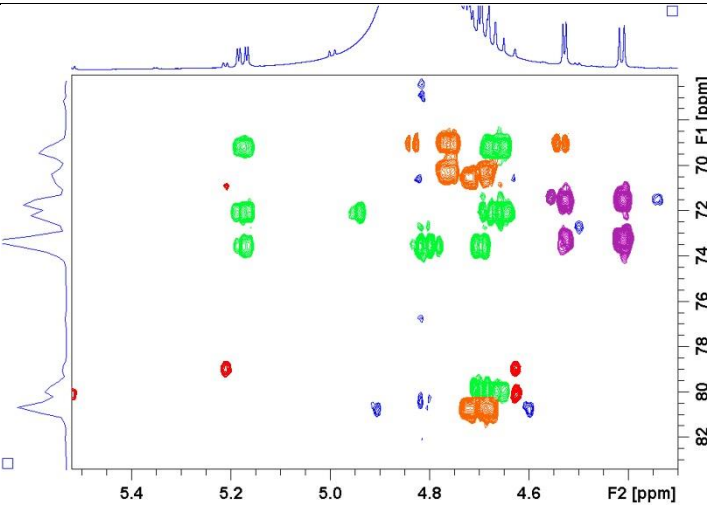
Species	Structure	$^{13}\text{C}$ - $^1\text{H}$ correlation(s)	Assignment
$\alpha$ -D-glucopyranoside			$\delta^1\text{H}$ , 5.20 ppm ( <b>H<sub>1</sub></b> ) $\delta^{13}\text{C}$ , 71.6 ppm (C <sub>3</sub> ) $\delta^{13}\text{C}$ , 72.9 ppm (C <sub>2</sub> )
$\beta$ -D-glucopyranoside			$\delta^1\text{H}$ , 4.60 ppm ( <b>H<sub>1</sub></b> ) $\delta^{13}\text{C}$ , 74.3 ppm (C <sub>3</sub> ) $\delta^{13}\text{C}$ , 75.9 ppm (C <sub>2</sub> )
$\alpha$ -D-glucuronic acid			$\delta^1\text{H}$ , 5.25 ppm ( <b>H<sub>1</sub></b> ) $\delta^{13}\text{C}$ , 70.6 ppm (C <sub>3</sub> ) $\delta^{13}\text{C}$ , 72.4 ppm (C <sub>2</sub> )
$\beta$ -D-glucuronic acid			$\delta^1\text{H}$ , 4.31 ppm ( <b>H<sub>1</sub></b> ) $\delta^{13}\text{C}$ , 71.5 ppm (C <sub>3</sub> , C <sub>2</sub> )

D-glucurono 6,3 lactone			$\delta^1\text{H}$ , 5.02 ppm ( <b>H<sub>2</sub></b> ) $\delta^1\text{H}$ , 4.34 ppm ( <b>H<sub>3</sub></b> ) $\delta^{13}\text{C}$ , 77.7 ppm (C <sub>4</sub> )
D-gluconic acid			$\delta^1\text{H}$ , 4.42 ppm ( <b>H<sub>2</sub></b> ) $\delta^{13}\text{C}$ , 70.7 ppm (C <sub>3</sub> ) $\delta^{13}\text{C}$ , 71.5 ppm (C <sub>4</sub> )
D-glucono 1,4 lactone			$\delta^1\text{H}$ , 4.65 ppm ( <b>H<sub>2</sub></b> ) $\delta^1\text{H}$ , 4.55 ppm ( <b>H<sub>3,4</sub></b> ) $\delta^{13}\text{C}$ , 70.4 ppm (C <sub>5</sub> ) $\delta^{13}\text{C}$ , 72.65 ppm (C <sub>2</sub> ) $\delta^{13}\text{C}$ , 73.2 ppm (C <sub>3</sub> )
L-guluronic acid			$\delta^1\text{H}$ , 4.89 ppm ( <b>H<sub>1</sub></b> ) $\delta^{13}\text{C}$ , 71.1 ppm (C <sub>2</sub> ) $\delta^{13}\text{C}$ , 72.9 ppm (C <sub>3</sub> )
L-gulurono 6,3 lactone			$\delta^1\text{H}$ , 5.37 ppm ( <b>H<sub>5</sub></b> ) $\delta^1\text{H}$ , 5.16 ppm ( <b>H<sub>3</sub></b> ) $\delta^{13}\text{C}$ , 72.9 ppm (C <sub>4</sub> ) $\delta^{13}\text{C}$ , 80.4 ppm (C <sub>3</sub> ) $\delta^{13}\text{C}$ , 82.0 ppm (C <sub>5</sub> )

D-glucaric acid			$\delta^1\text{H}$ , 4.48 ppm ( <b>H<sub>2</sub></b> ) $\delta^1\text{H}$ , 4.37 ppm ( <b>H<sub>5</sub></b> )  $\delta^{13}\text{C}$ , 71.5 ppm ( <b>C<sub>3</sub></b> ) $\delta^{13}\text{C}$ , 73.2 ppm ( <b>C<sub>4</sub></b> )
D-glucaro 1,4 lactone			$\delta^1\text{H}$ , 5.13 ppm ( <b>H<sub>4</sub></b> ) $\delta^1\text{H}$ , 4.76 ppm ( <b>H<sub>2</sub></b> ) $\delta^1\text{H}$ , 4.65 ppm ( <b>H<sub>5</sub></b> ) $\delta^1\text{H}$ , 4.62 ppm ( <b>H<sub>3</sub></b> )  $\delta^{13}\text{C}$ , 69.1 ppm ( <b>C<sub>5</sub></b> ) $\delta^{13}\text{C}$ , 72.1 ppm ( <b>C<sub>2</sub></b> ) $\delta^{13}\text{C}$ , 73.4 ppm ( <b>C<sub>3</sub></b> ) $\delta^{13}\text{C}$ , 79.8 ppm ( <b>C<sub>4</sub></b> )
D-glucaro 6,3 lactone			$\delta^1\text{H}$ , 4.72ppm ( <b>H<sub>3</sub></b> ) $\delta^1\text{H}$ , 4.67 ppm ( <b>H<sub>2</sub></b> ) $\delta^1\text{H}$ , 4.64 ppm ( <b>H<sub>4</sub></b> ) $\delta^1\text{H}$ , 4.63 ppm ( <b>H<sub>5</sub></b> )  $\delta^{13}\text{C}$ , 68.9 ppm ( <b>C<sub>2</sub></b> ) $\delta^{13}\text{C}$ , 70.2 ppm ( <b>C<sub>4</sub></b> ) $\delta^{13}\text{C}$ , 70.4 ppm ( <b>C<sub>5</sub></b> ) $\delta^{13}\text{C}$ , 80.5 ppm ( <b>C<sub>3</sub></b> )

Table S3. C<sub>6</sub> oxidation products of uronic and aldaric acid derivatives of D-glucose showing false coloured HMBC NMR spectra of product streams.

Entry	Substrate	Structure & assignment	HMBC NMR spectrum of product stream
1	$\alpha$ -D-glucuronic acid		 <p> <span style="color: black;">■</span> D-glucurono 6,3 lactone,            <span style="color: purple;">■</span> D-glucaric acid,            <span style="color: green;">■</span> D-glucaro 1,4 lactone,            <span style="color: orange;">■</span> D-glucaro 6,3 lactone         </p>
	$\beta$ -D-glucuronic acid		
2	D-gluconic acid		 <p> <span style="color: yellow;">■</span> Glucono 1,4- lactone            <span style="color: purple;">■</span> D-glucaric acid,            <span style="color: green;">■</span> D-glucaro 1,4 lactone,            <span style="color: orange;">■</span> D-glucaro 6,3 lactone,            <span style="color: darkred;">■</span> L-Guluronic acid,            <span style="color: cyan;">■</span> L-gulurono-6,3-lactone,         </p>

3*	L-guluronic acid		 <p> <span style="color: purple;">■</span> D-glucaric acid, <span style="color: green;">■</span> D-glucaro 1,4 lactone, <span style="color: orange;">■</span> D-glucaro 6,3 lactone, <span style="color: red;">■</span> D-glucaro 1,4: 6,3 dilactone         </p>
4	D-glucaric acid		 <p> <span style="color: green;">■</span> D-glucaro 1,4 lactone, <span style="color: orange;">■</span> D-glucaro 6,3 lactone, <span style="color: red;">■</span> D-glucaro 1,4: 6,3 dilactone         </p>

Conditions; 5 % Pt/TiO<sub>2</sub> IMP Red 400 (40 mg), [Substrate] = 0.1 M (D<sub>2</sub>O), 80 °C, 1000 rpm, P(20 % O<sub>2</sub>/N<sub>2</sub>)=25 bar, 24 h. \*[L-guluronic acid] = 0.01 M, 2 h, 0.1 M DCl added prior to solvent suppressed <sup>1</sup>H NMR analysis (Entry 3).



Table S4 Initial rates for catalytic conversion of D-gluconic acid and D-glucono 1,4 lactone as a function of reaction temperature

Entry	Substrate	Temp / °C	$\chi$ / %	$\frac{\text{mol } \chi}{\text{h}^{-1}} \text{ kg}_{\text{cat}}^{-1}$	Major Products (% Yield)
1	D-gluconic Acid	75	29.5	2.1	D-glucono 1,4 lactone (15.3 %) L-guluronic acid (3.6 %)
2		90	61.5	4.3	D-glucono 1,4 lactone (25.7 %) L-guluronic acid (8.3 %)
3*		90	35.2	2.5	D-glucono 1,4 lactone (29.6 %) L-guluronic acid (3.7 %)
4	D-glucono 1,4 lactone	75	28.2	2.0	D-gluconic acid (22.9%) L-guluronic acid (1.0 %)
5		90	50.3	3.5	D-gluconic acid (43.4 %) L-guluronic acid (3.0 %)

Reaction conditions; 40 mg 5% Pt/TiO<sub>2</sub><sup>IMP Red 400</sup>, 1000 rpm, P(20 % O<sub>2</sub> / N<sub>2</sub>) = 25 bar, 1 h, [substrate] = 0.028 M (0.28 mmol in D<sub>2</sub>O). \*Entry 3; P(N<sub>2</sub>) = 25 bar.

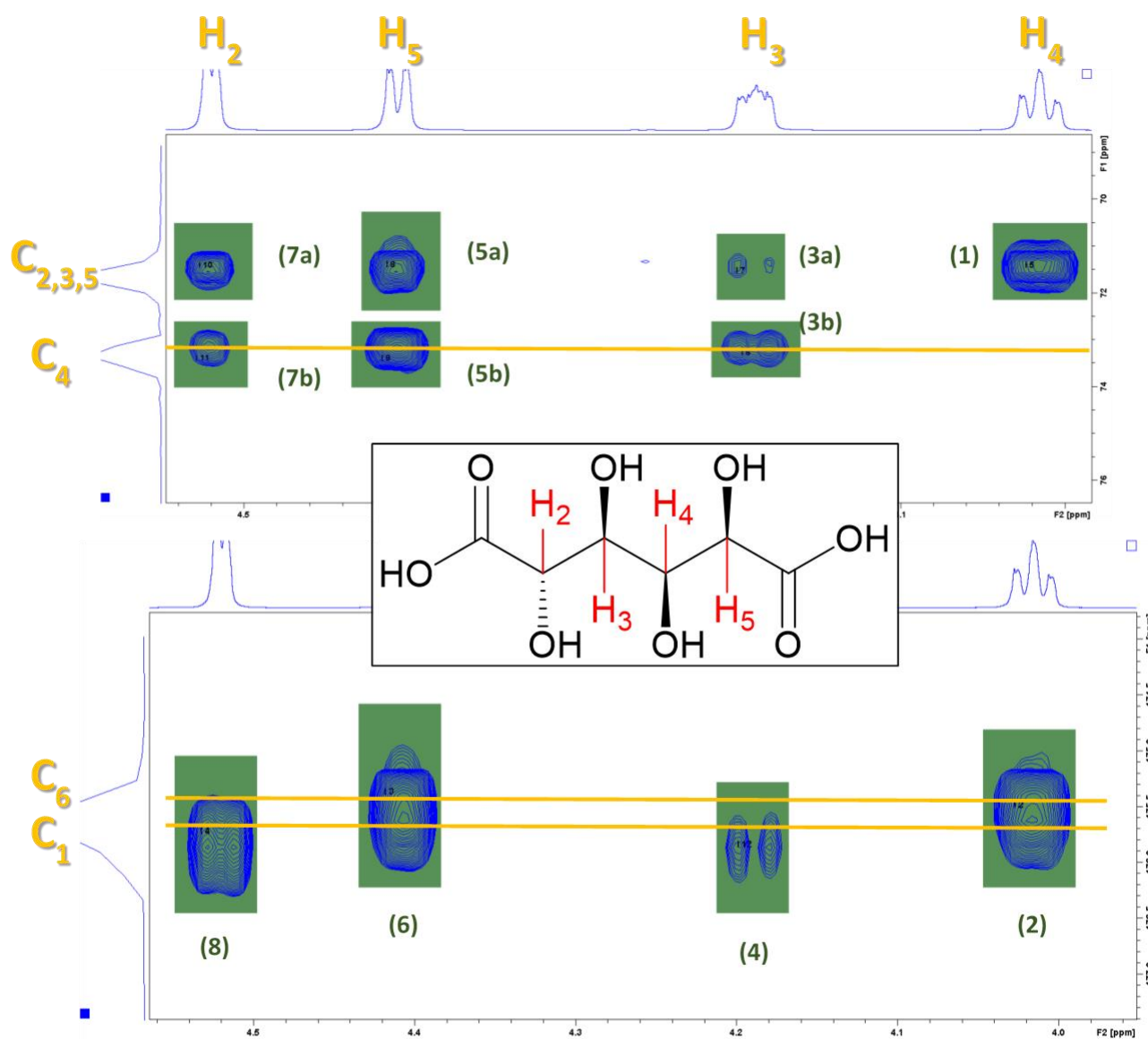


Figure S4. The HMBC NMR assignment of D-glucaric acid, synthesised in 99.9 % purity as previously reported in *European. J. Org. Chem.* **2018**, 45, 6811.

Table S5. Calibration of HMBC correlations from Fig. S4, with areas normalised to TMS internal standard.

Assignment	1	2	3 a	3 b	4	5 a	5 b	6	7 a	7 b	8
$\delta^1\text{H}$	4	4	3	3	3	5	5	5	2	2	2
$\delta^{13}\text{C}$	3 + 5	6	2	4	1	3	4	6	3	4	1
$^{[a]}\text{rF}$	88348	67250	-	9747	-	33681	59134	82291	10447	-	29491
$R^2$	0.994	0.996	-	0.964	-	0.990	0.992	0.995	0.947	-	0.998

<sup>[a]</sup> Spectra integrated using TopSpin 3.5 nmr processing software. rF as relative counts per mol, normalised to TMS internal standard peak at  $\delta^1\text{H} = 0$  ppm,  $\delta^{13}\text{C} = 0$  ppm. Only the most intense peaks were calibrated for as, at the lowest [D-glucaric acid] (0.0065 M, 1% yield) correlations 7a, 7b, 3a, 3b and 4 were too low in intensity for objective integration.

Table S6. Sensitivity analysis of rFs derived via HMBC NMR calibrations shown in Table 2, showing selection of correlation 8 for quantitative analyses.

Simulated $\chi$ Glucose / %	% Deviation from theoretical peak volume (as calculated using calibrated rF values)					
	1	2	5a	5b	6	8
9.0 @ 100% <i>S</i> (D-glucaric Acid)	27.4	19.2	17.7	15.0	13.8	2.1
25	10.1	12.7	12.1	9.4	7.6	3.8
50	-4.4*	9.0	10.2	6.9	9.8	1.1
75	26.0	29.1	6.2	17.9	24.7	5.2
100	19.0	26.0	11.8	22.5	26.2	3.8

Fixed [D-glucaric acid] = 0.05 M. Variable D-glucose / Gluconic acid- $\gamma$ -lactone such that the total concentration of organics = 0.554 M. \* (-) indicates a peak with lower integrated area than expected based on [glucaric acid] and rF.

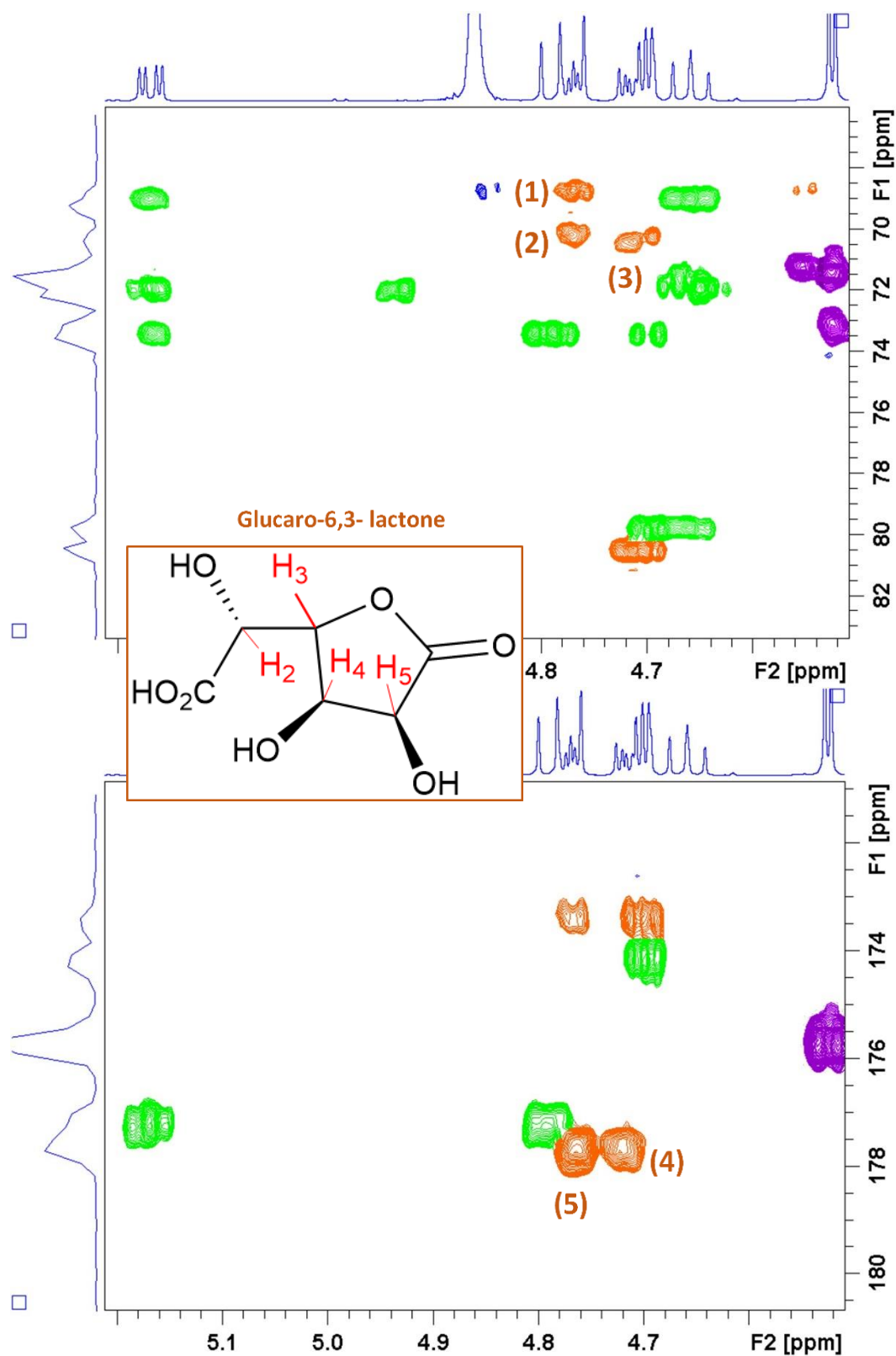


Figure S5. The assigned HMBC NMR spectrum of an equilibrium mixture of ■ D-glucaric acid, ■ D-glucaro 1,4 lactone, ■ D- glucaro 6,3 lactone and ■ D- glucaro 1,4 : 6,3 lactone. Equilibrated at STP, 65 h. [D-glucaro 1,4 lactone = 0.1 M], D-glucaro 1,4 lactone : DCl = 1 : 1 mol/mol.

## Cross calibration of D-glucaro 6,3 lactone through equilibration studies.

Single component  $^1\text{H}$  NMR standards comprising; D-glucaric acid, D-glucaro 1,4 lactone or D-glucaro 1,4:6,3 lactone of varying concentrations were collected.  $^1\text{H}$  NMR resonances were normalised to TMS at  $\delta\ ^1\text{H} = 0.0$  ppm and linear rFs determined.

Table S7. Quantified  $^1\text{H}$  NMR rFs for protons in glucarate derivative products

Product	$^1\text{H}$ resonance / ppm	rF / counts mol $^{-1}$	R $^2$
Glucaric Acid	4.02	38273	0.997
	4.18	38736	0.997
	4.40	38582	0.997
	4.52	39212	0.997
Glucaro-1,4-lactone	4.66	20840	0.998
	4.70	23379	0.995
	5.16	28590	0.995
Glucaro- 1,4 6,3- lactone	4.63	34967	0.998
	5.00	36330	0.999
	5.22	35726	0.999
	5.53	35633	0.999

Solutions of known [D-glucaro 1,4 lactone] were then prepared.  $^1\text{H}$  NMR spectra were collected at  $t = 0$  to determine accurate concentrations.  $^{13}\text{C}$  and  $^1\text{H}$  chemical shifts for D-glucaro 6,3 lactone are assigned in Table S7.

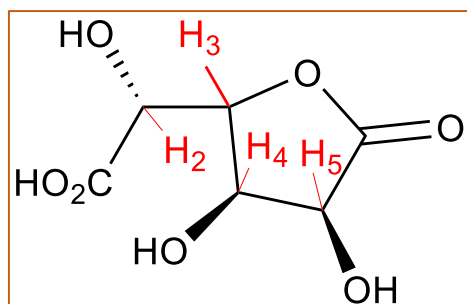


Table S8.  $^1\text{H}$  NMR assignments for D- glucaro 6,3 lactone

Carbon no.	$\delta\ ^1\text{H}$ / ppm	$\delta\ ^{13}\text{C}$ / ppm
1	-	177.7
2	4.72	68.8
3	4.77	80.5
4	4.71	70.2
5	4.69	70.4
6	-	173.4

To the NMR tube was then added DCl (D-glucaro 1,4 lactone : DCl = 1 : 1 mol/mol). Solutions were equilibrated under ambient conditions for 96 h, with  $^1\text{H}$  NMR and HMBC NMR spectra collected at 24 h intervals. Through quantification of molecules in Table S4 via  $^1\text{H}$  NMR, the [D-glucaro 6,3 lactone] was calculated for each NMR analysis. In this way, the [D-glucaro 6,3 lactone] was calculated. Plotting of HMBC correlation areas for D-glucaro 6,3 lactone vs mol afforded a rF for each correlation as shown in Table S8 and Fig. S6. Note, correlation assignment is as in Figure S5.

Table S9. Quantified HMBC NMR rFs for  $^{13}\text{C}$ - $^1\text{H}$  peaks in D-glucaro 6,3 lactone

Assignment	Correlation no. (as assigned in Fig S5)				
	1	2	3	4	5
$\delta^1\text{H}$ / ppm	4.77	4.77	4.71 / 4.69	4.72	4.77
H no.*	3	3	4 / 5	2	3
$\delta^{13}\text{C}$ / ppm	68.8	70.4	70.4 / 70.2	177.7	177.7
C no.*	2	4	5 / 4	1	1
$^{[a]}\text{rF}$	14272	11695	18591	22773	50322
$\text{R}^2$	0.999	0.988	0.995	0.996	0.999

[a]

Spectra integrated using TopSpin 3.5 nmr processing software. rF as relative counts per mol. \* Carbon and hydrogen assignment as in inset of Fig. S5.

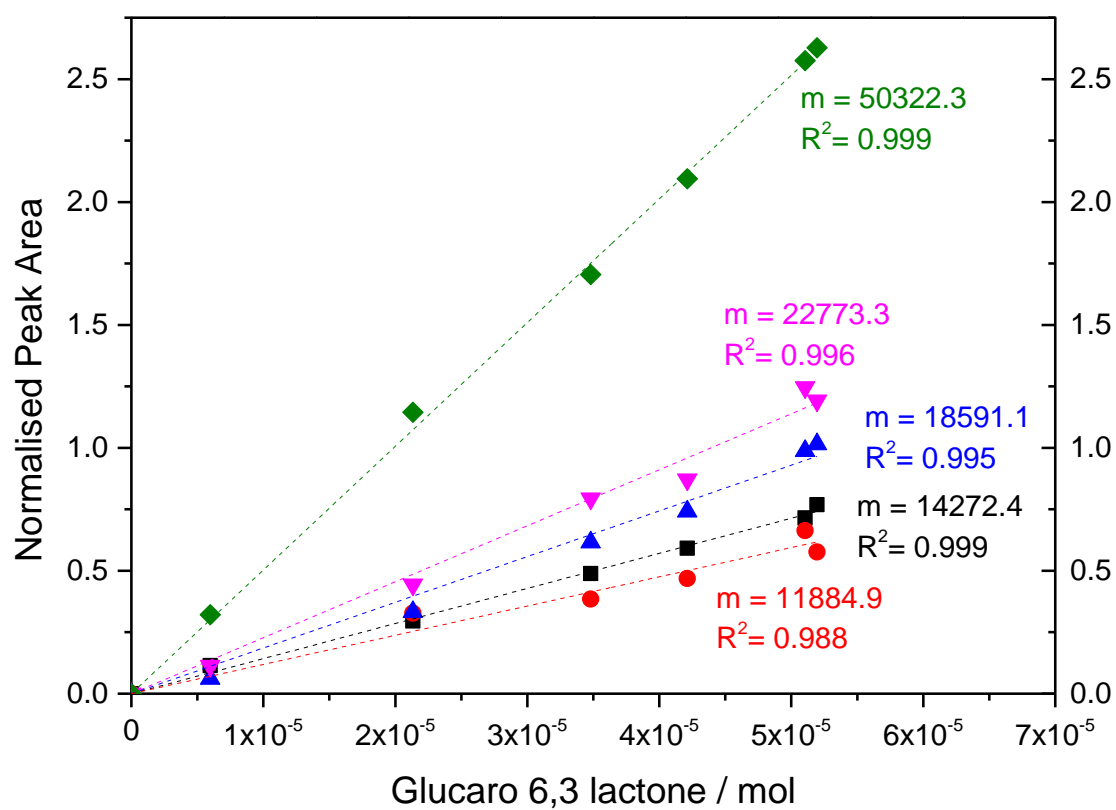


Figure S6. Calibration plots for correlation features within the HMBC spectrum of D-glucaro 6,3 lactone showing linear regressions.



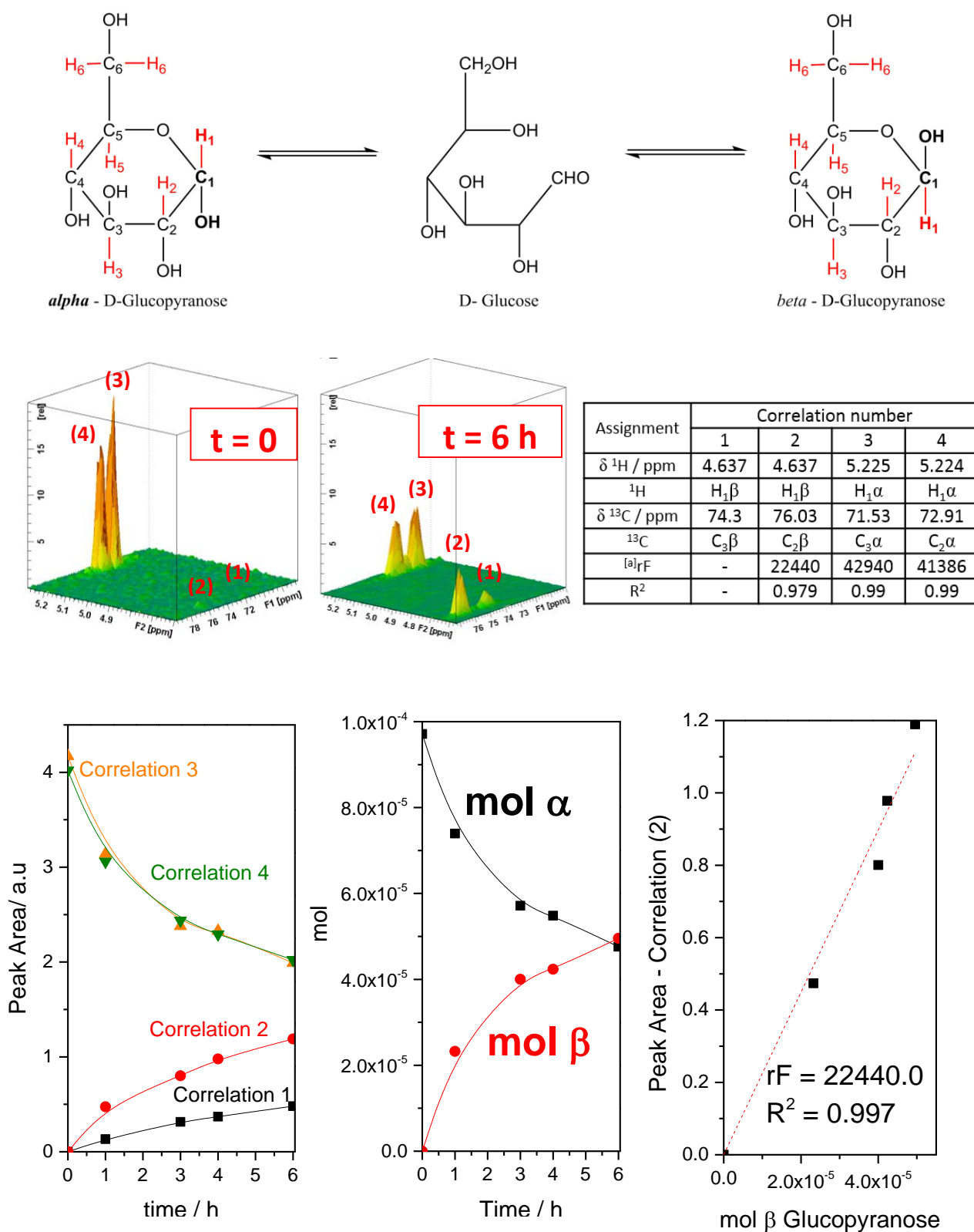


Figure S7 Cross calibration of  $\beta$ -D-glucopyranose using HMBC NMR through equilibration studies, showing data from calibration at  $[\text{D-glucose}] = 0.2 \text{ M}$ .

For HMBC NMR correlations for  $\alpha$ -D-glucopyranose were calibrated using Route (i) as, upon addition to  $\text{D}_2\text{O}$ , the  $t=0$  D-glucose solution contains 100 %  $\alpha$ -D-glucopyranose.

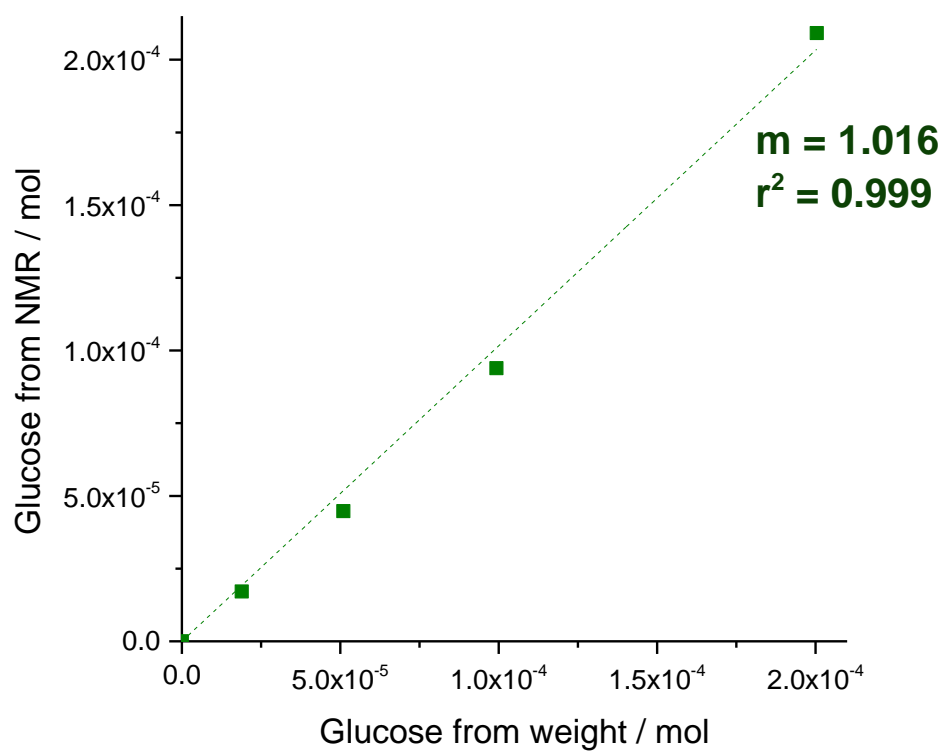
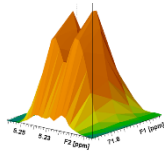
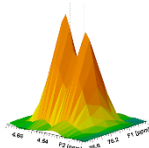
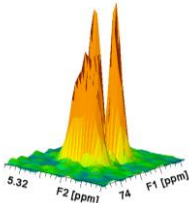
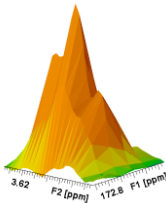
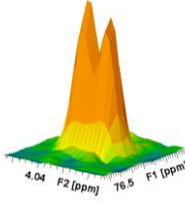
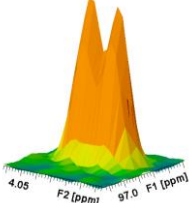
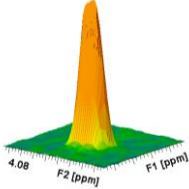


Figure S8. Testing of  $\alpha$ -D-glucopyranose and  $\beta$ -D-glucopyranose HMBC NMR calibrations through analysis of equilibrated solutions of varying [D-glucose].

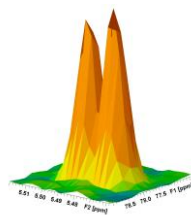
Solutions equilibrated at room temperature for 72 h. [D-glucose] = 0.05 M – 0.4 M at t=0.

**Table S10.** A summary of  $^{13}\text{C}$ - $^1\text{H}$  HMBC NMR correlations used for quantification of  $\text{C}_6$  products and unreacted glucose.

Compound	$\delta^1\text{H}$	$\delta^{13}\text{C}$	Peak Shape	$\text{R}^2$
D- $\alpha$ - glucopyranose	5.23	71.5		-
D- $\beta$ glucopyranose	4.64	76.0		0.979
D- $\alpha$ -glucuronic acid	5.29	71.6		1.000
	3.60	172.6		0.995
	4.03	75.4		0.996
D- $\beta$ - glucuronic Acid	4.03	96.2		0.998
	4.03	172.6		0.996

5.49

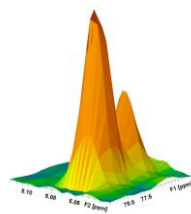
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0.993

5.07

77.4

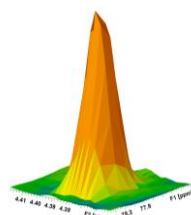


0.992

D-glucurono 6,3 lactone

4.38

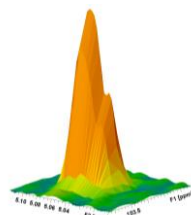
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0.997

5.07

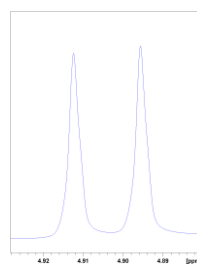
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0.995

4.90

-

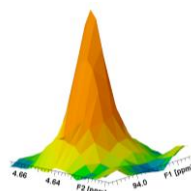


0.997

L-guluronic acid

4.64

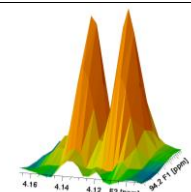
93.8



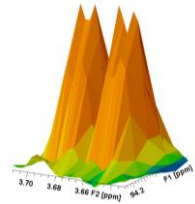
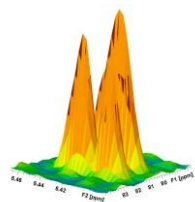
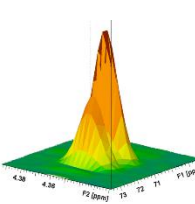
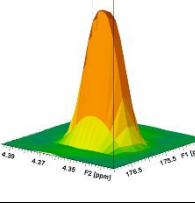
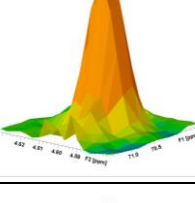
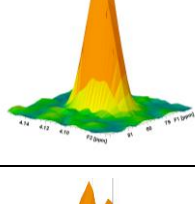
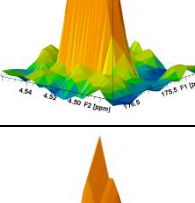
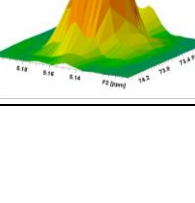
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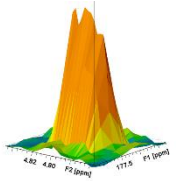
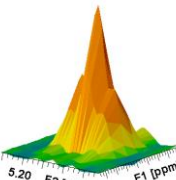
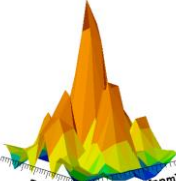
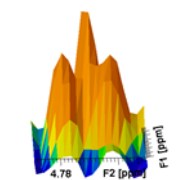
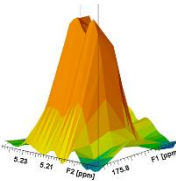
4.13

93.8



0.982

	3.67	93.8		0.988
L-gulurono 6,3 lactone	5.42	81.3		0.998
D-gluconic acid	4.36	71.1		0.986
D-gluconic acid	4.36	175.8		0.971
D-glucono 1,4 lactone	4.60	70.5		0.999
	4.11	79.8		0.998
D-gluucaric Acid	4.52	175.8		0.998
D-glucaro-1,4 lactone	5.16	73.5		0.987

	4.80	177.3		0.986
	5.17	177.3		0.990
D-glucaro- 6,3 lactone	4.77	68.6		0.996
	4.77	70.1		0.976
D-glucaro 1,4 6,3 dilactone	5.21	175.6		0.988

<sup>[a]</sup> As determined through sensitivity analyses. Note, where multiplet peaks (split in the F<sub>1</sub> or F<sub>2</sub> axis) were used (see Peak Shape), stated chemical shifts (<sup>13</sup>C and <sup>1</sup>H) correspond to the centre of the integrated region.

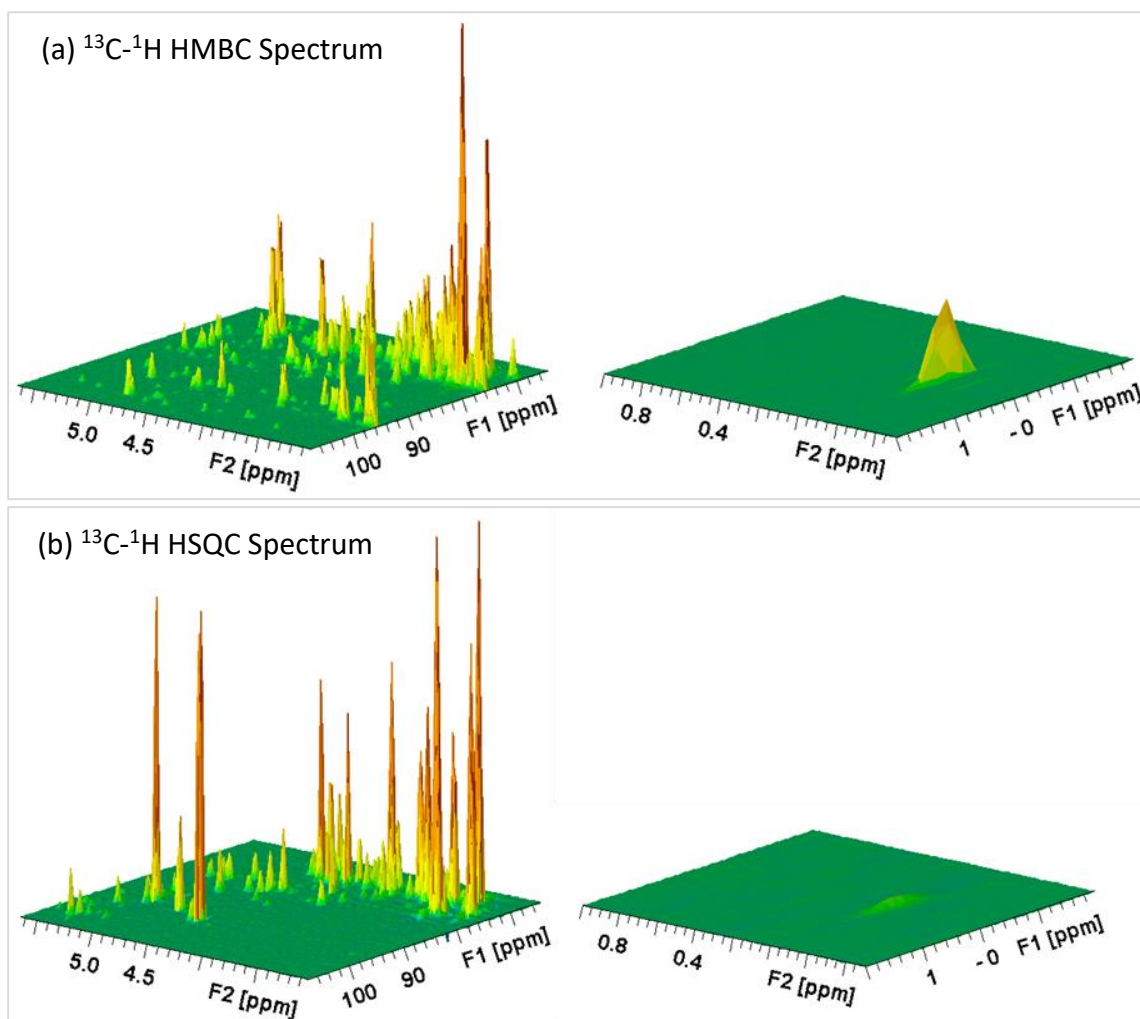


Figure S9. The  $^{13}\text{C}$ - $^1\text{H}$  HMBC NMR (a) and  $^{13}\text{C}$ - $^1\text{H}$  HSQC spectra (b) of Pt- catalysed D-glucose oxidation product streams showing relative intensity of TMS peaks at  $\delta\ ^1\text{H} = 0\text{ ppm}$   $\delta\ ^{13}\text{C} = 0\text{ ppm}$ ,  $\text{D}_2\text{O}$  lock. Note, spectral regions in either (a) or (b) are shown at the same signal to noise zoom. Spectra are presented in this way to highlight the greater suitability of  $^{13}\text{C}$ - $^1\text{H}$  HMBC for TMS- normalised quantitative analyses.

Reaction conditions; 40 mg 5% Pt/ $\text{TiO}_2^{\text{IMP Red 400}}$ , 1000 rpm,  $\text{P}(\text{O}_2) = 20\text{ bar}$ ,  $80\text{ }^\circ\text{C}$ , 24 h,  $[\text{D-glucose}] = 0.554\text{ M}$  (D-glucose/ Pt = 540 : 1 mol : mol). 2D NMR Bruker NMR programs used were (a) hmbcetgp12nd.2 and (b) hsqcedetgsp.3.

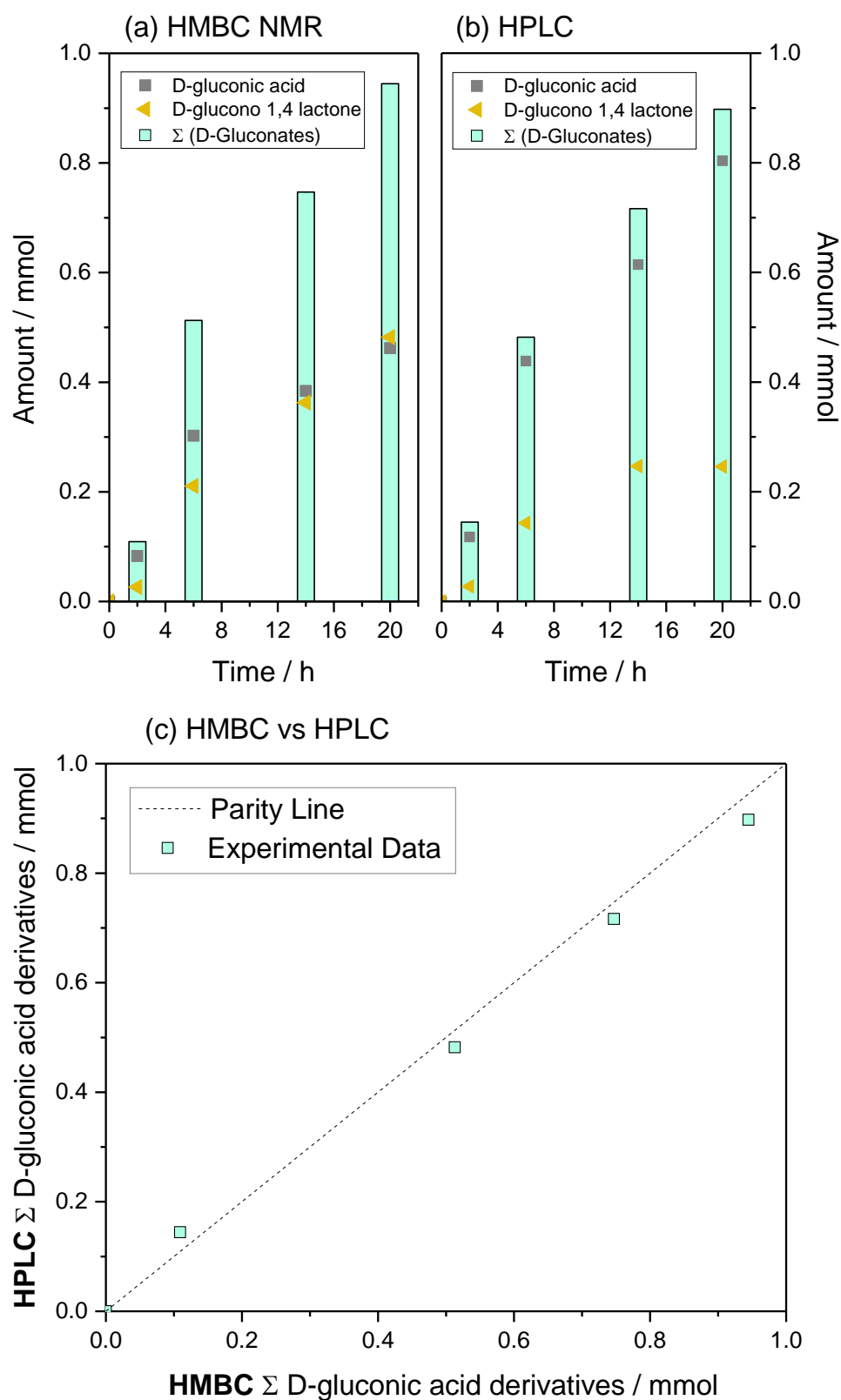


Figure S10. Temporal evolution of D-gluconic acid and D-glucono 1,4 lactone in 5% Au/TiO<sub>2</sub> - catalyzed D-glucose oxidation, as quantified by <sup>13</sup>C-<sup>1</sup>H HMBC NMR (a) and HPLC (b).

Reaction conditions; 80 mg 5% Au/TiO<sub>2</sub><sup>IMP Red 400</sup>, 1000 rpm, P(20% O<sub>2</sub>/N<sub>2</sub>) = 25 bar, 80 °C, [D-glucose] = 0.554 M (D-glucose/ Au = 272 : 1 mol : mol).



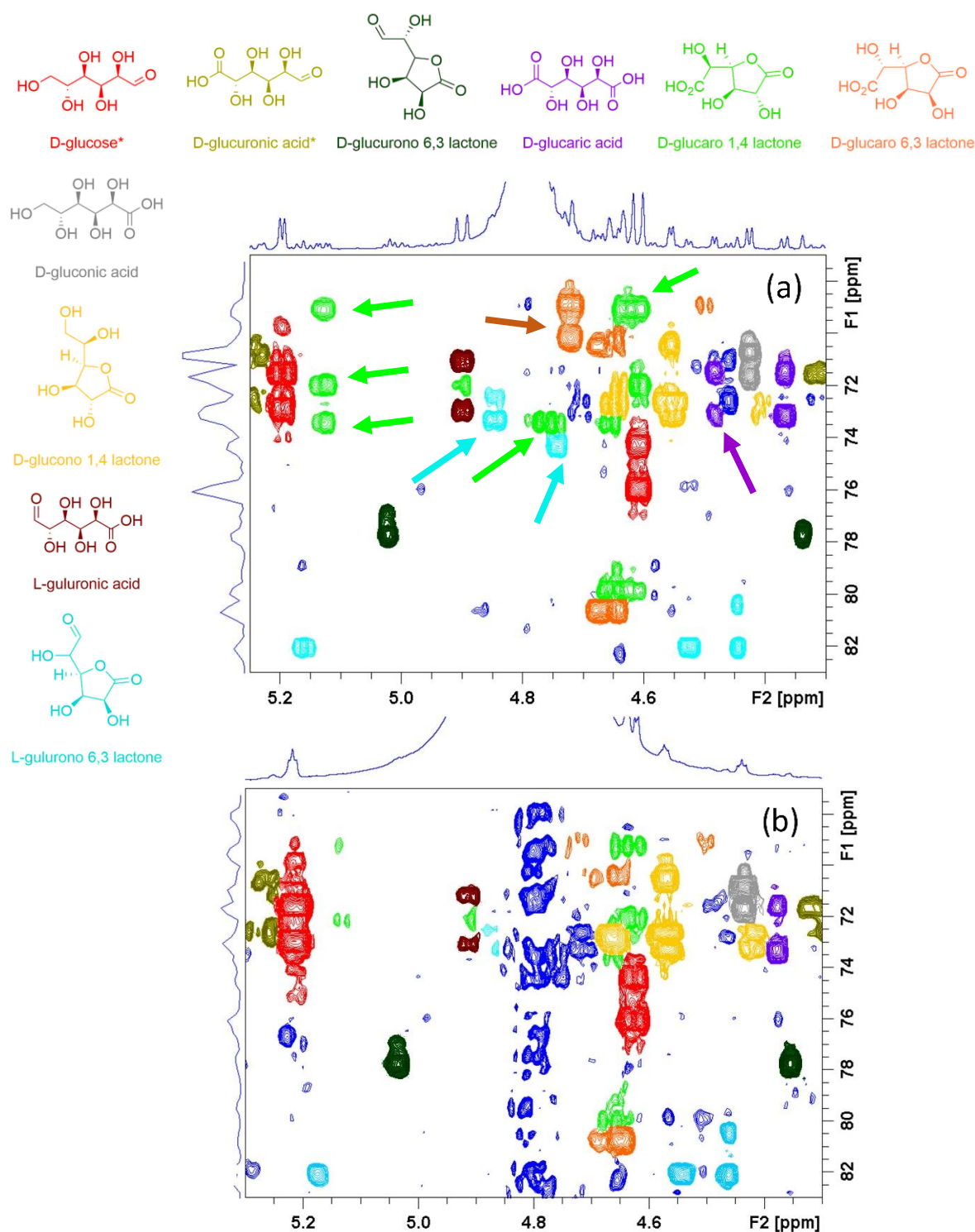


Figure S11. Expanded region of an HMBC-NMR spectrum of the oxidation of glucose using 5 wt. %  $\text{Pt}/\text{TiO}_2^{\text{IMP Red 400}}$  and  $\text{O}_2$  in either (a)  $\text{D}_2\text{O}$  or (b)  $\text{H}_2\text{O}$ . The structures of key gluconate, glucuronate, guluronate and glucarate products are shown. F1 axis is the  $^{13}\text{C}$  spectrum, F2 is the  $^1\text{H}$  spectrum.

Conditions; 5 %  $\text{Pt}/\text{TiO}_2^{\text{IMP Red 400}}$  (40 mg),  $[\text{D-glucose}] = 0.554 \text{ M}$ ,  $80^\circ\text{C}$ , 1000 rpm,  $P(\text{O}_2) = 20 \text{ bar}$ , 24 h.

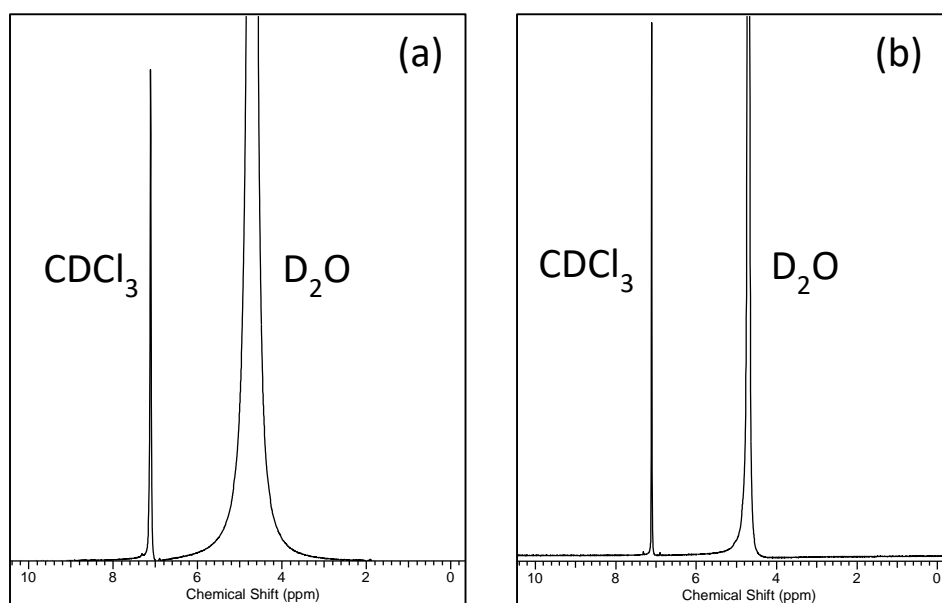


Figure S12.  $^2\text{H}$  NMR spectra for D-glucose oxidation reactions carried out in (a)  $\text{D}_2\text{O}$  or (b)  $\text{H}_2\text{O}$ .

Conditions; 5 % Pt/ $\text{TiO}_2^{\text{IMP Red 400}}$  (40 mg), [D-glucose] = 0.554 M, 80  $^\circ\text{C}$ , 1000 rpm,  $\text{P}(\text{O}_2)$  = 20 bar, 24 h. 10 ml solvent.

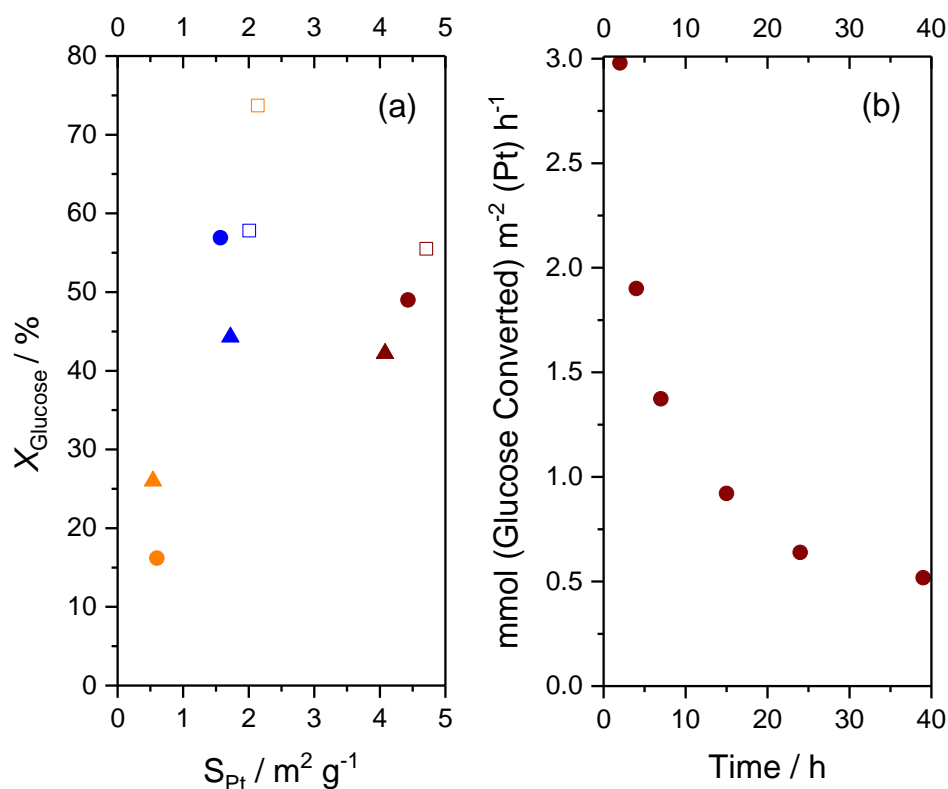


Figure S13. Glucose conversion (measured at 24 h on line) as a function of Pt- metal surface area (a) and specific activity as a function of time on line in 5 % Pt/TiO<sub>2</sub><sup>IMP Red 400</sup> catalysed glucose oxidation (b)

Test conditions; Catalyst (40 mg), 80 °C, 1000 rpm, [D-Glucose] = 0.554 M (5.54 mmol), 10 ml D<sub>2</sub>O, P(20 % O<sub>2</sub>/ N<sub>2</sub>) = 25 bar.

Showing; ▲ 5% Pt/TiO<sub>2</sub><sup>IWI</sup>, ● 5% Pt/TiO<sub>2</sub><sup>IMP</sup>, □ 5% Pt/TiO<sub>2</sub><sup>CVI</sup>, ▲ 5% Pt/SiO<sub>2</sub><sup>IWI</sup>, ● 5% Pt/SiO<sub>2</sub><sup>IMP</sup>, □ 5% Pt/SiO<sub>2</sub><sup>CVI</sup>, ▲ 5% Pt/C<sup>IWI</sup>, ● 5% Pt/C<sup>IMP</sup>, □ 5% Pt/C<sup>CVI</sup>

Table S11. A systematic study of the source of Pt-leaching from 5% Pt/TiO<sub>2</sub><sup>IMP Red 400</sup>

Entry	Mass Cat / mg	<i>P</i> (N <sub>2</sub> ) / bar	<i>P</i> (O <sub>2</sub> ) / bar	[D-glucose] / M	$\chi_{\text{glucose}}$ / % <sup>[a]</sup>	[Pt] / ppm <sup>[b]</sup>
1	40 <sup>[c]</sup>	0	20	0.554	0	0
2	40	0	20	0	-	0
3	40	20	0	0.554	0	0
4	40	0	10	0.554	59.5	11.3

<sup>[a]</sup> Determined by HMBC NMR, <sup>[b]</sup> Determined by MPAES. <sup>[c]</sup> 40 mg TiO<sub>2</sub> (P25).  
 Conditions; 80 °C, 1000 rpm, 10 ml D<sub>2</sub>O, 24 h.

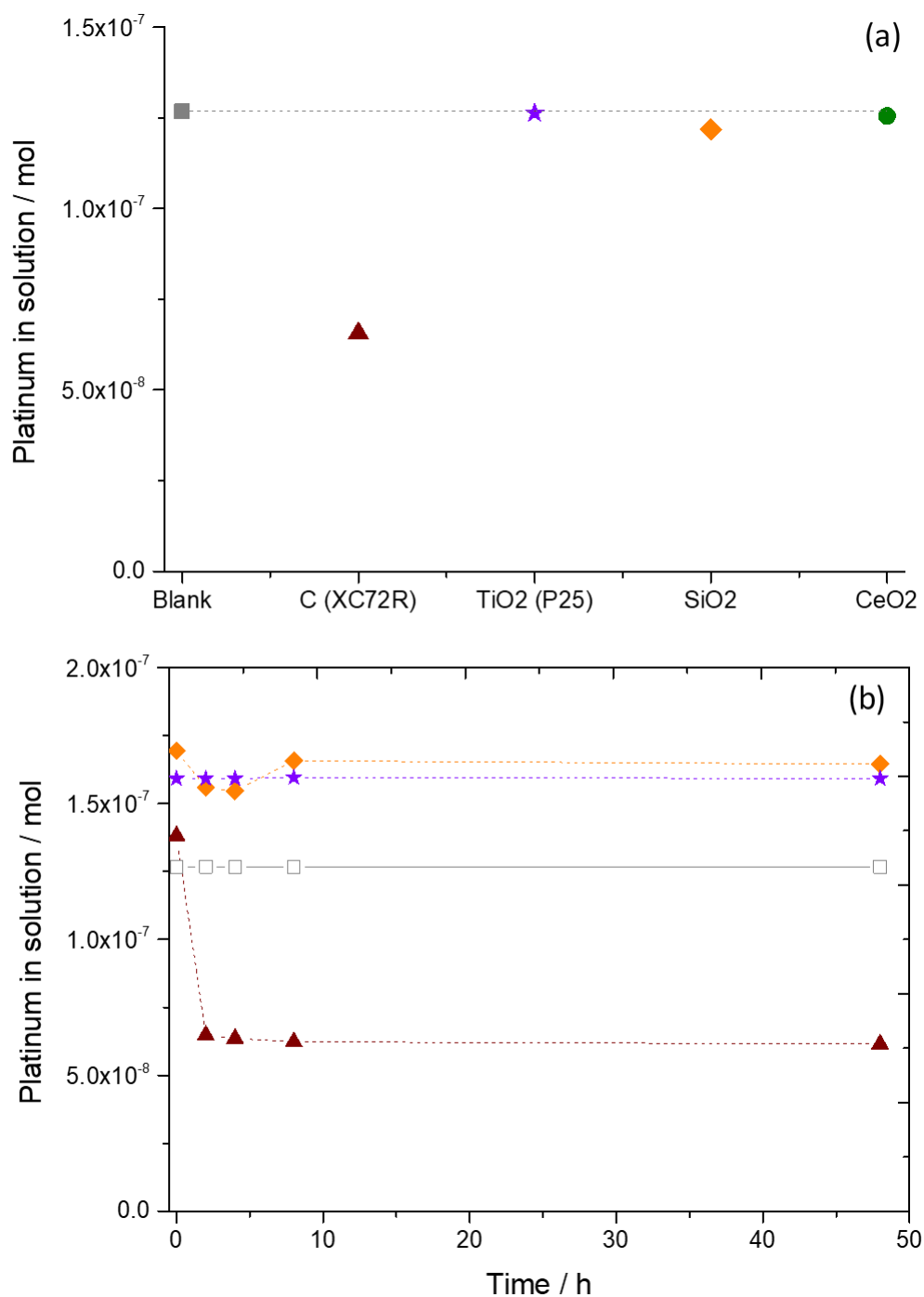


Figure S14. Adsorption of leached Pt from aqueous solution onto a series of unmodified catalyst supports at (a) 24 h and (b) as a function of time.

Step 1. Test conditions; 5% Pt/C<sup>IMP Red 400</sup> (40 mg), 72 h, 80 °C, 1000 rpm, [D-Glucose] = 0.554 M, 10 ml, P(O<sub>2</sub>) = 4 bar to yield Solution 1. Step 2. 8 ml reaction aqueous Pt solution (Solution 1), 40 mg “bare” support, 48 h, 80 °C, 1000 rpm, P(O<sub>2</sub>) = 4 bar. □ Control, ▲ carbon (Vulcan, XC72R), ★ TiO<sub>2</sub> (Degussa, P25), ◆ SiO<sub>2</sub> (Divasil 635)

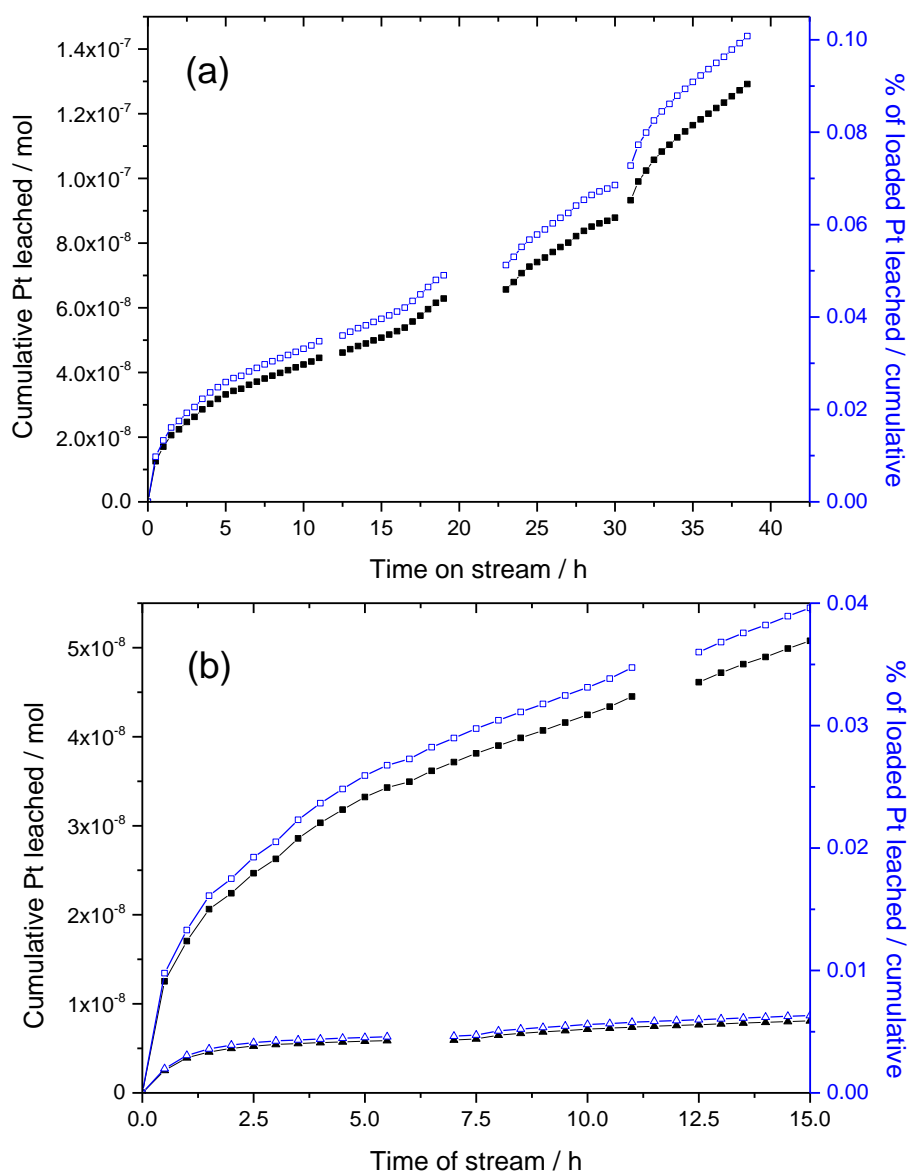


Figure S15. Observed Pt- leaching under continuous flow operation as determined by ICP-MS for 5% Pt/TiO<sub>2</sub> IMP Red 400 (■□) and a dual bed comprising (i) 5% Pt/TiO<sub>2</sub> IMP Red 400 + (ii) carbon extrudates (▲△).

Reaction conditions: P(synthetic air) = 20 bar, gas flow rate = 20 ml min<sup>-1</sup>, [Glucose] = 0.554 M, liquid flow rate 0.166 ml min<sup>-1</sup> (10 ml h<sup>-1</sup>), 80 °C, 0.5 g 5% Pt/TiO<sub>2</sub> IMP Red 400 and where applicable carbon extrudates (0.5 g). For ON/OFF experiments shown in Fig S13 ab, the catalyst bed was purged with H<sub>2</sub>O and N<sub>2</sub> prior to OFF periods.

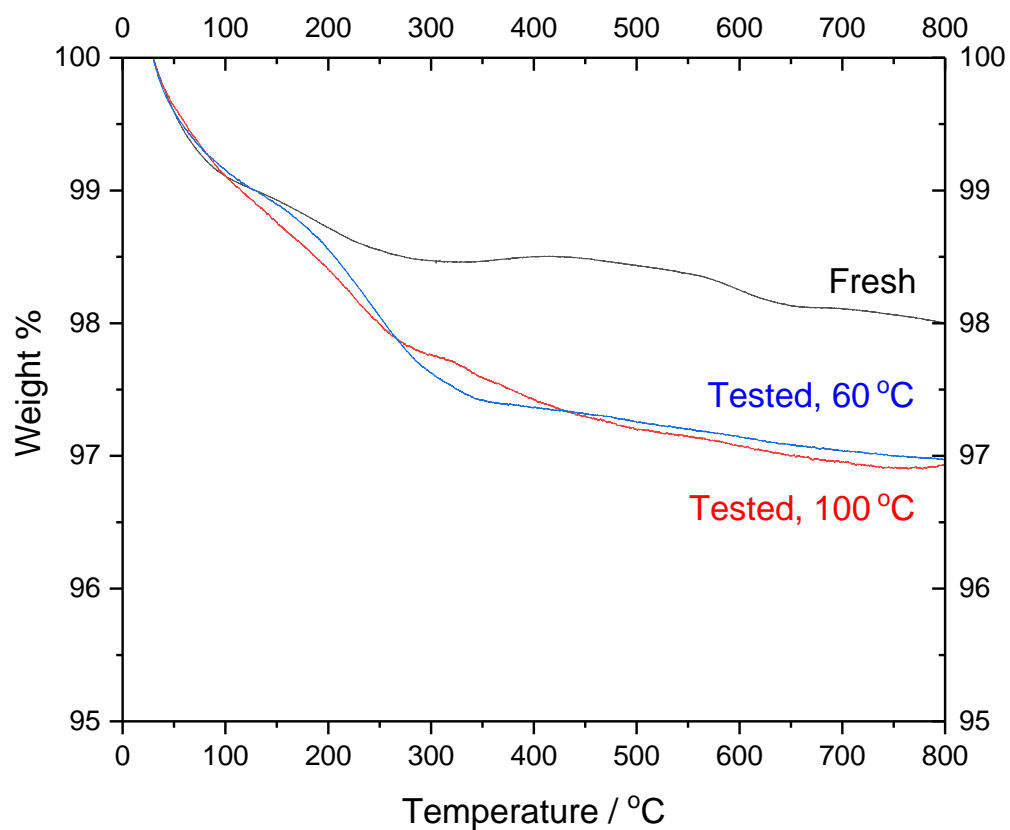


Figure S16. Thermogravimetric analyses (TGAs) of as-synthesised 5% Pt/TiO<sub>2</sub> IMP Red 400 and solid residues following catalytic assessments at reaction temperatures of 60 and 100 °C.

Catalyst assessment conditions; 5 % Pt/TiO<sub>2</sub> IMP Red 400 (40 mg), [D-glucose] = 0.554 M (5.54 mmol in D<sub>2</sub>O), 24 h, 1000 rpm, P(20% O<sub>2</sub>/ N<sub>2</sub>) = 25 bar.

TGA conditions; 30 – 800 °C, 5 °C min<sup>-1</sup>, 20 ml min<sup>-1</sup> air.

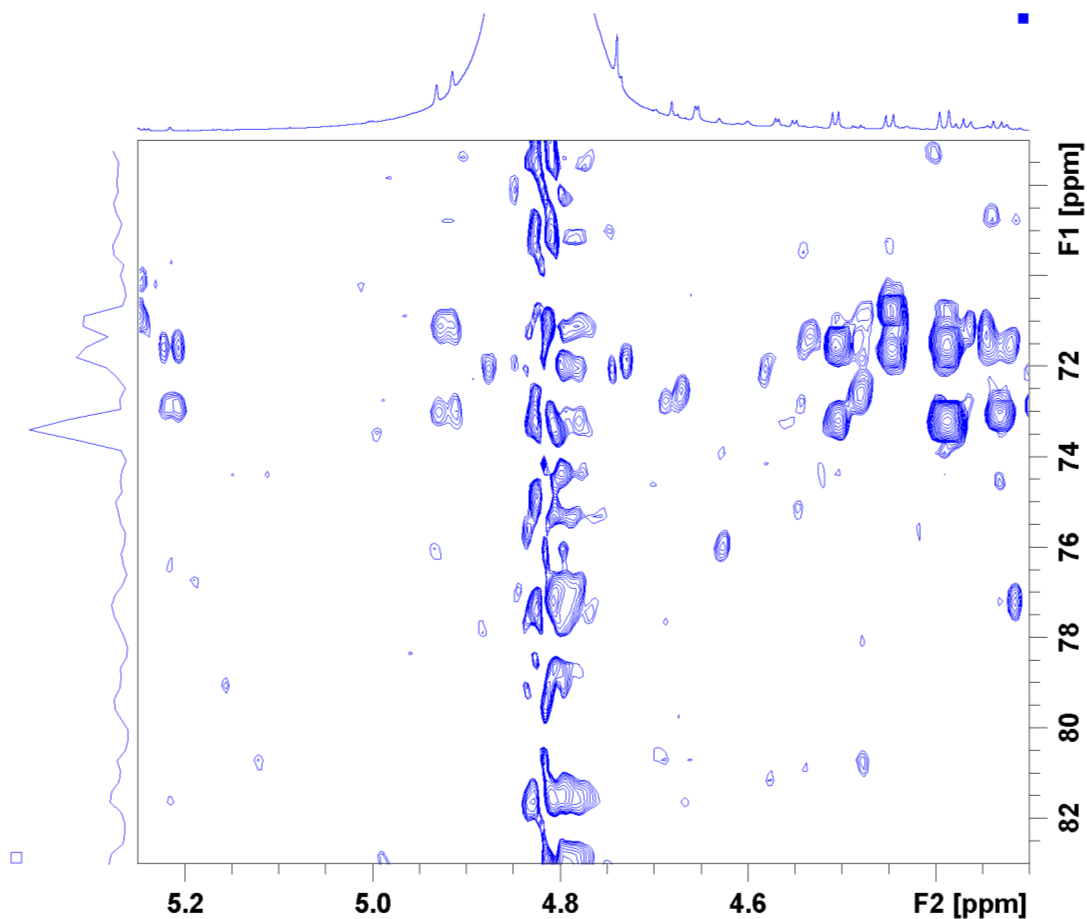


Figure S17. Expanded region of an HMBC-NMR spectrum of the oxidation of glucose using 5 wt. % Pt/TiO<sub>2</sub> <sup>IMP Red 400</sup> with NaOH (1 eq. 5.54 mmol) added at t = 0. F1 axis is the  $^{13}\text{C}$  spectrum, F2 is the  $^1\text{H}$  spectrum.

Conditions; 5 % Pt/TiO<sub>2</sub> <sup>IMP Red 400</sup> (40 mg), [D-glucose] = 0.554 M (D<sub>2</sub>O), 80 °C, 1000 rpm, P(O<sub>2</sub>) = 20 bar, 24 h.