Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Mechanism and Malleability of Glucose Dehydration to HMF: Entry Points and Water-Induced Diversions

Sebastian Meier[1]

[1]Department of Chemistry, Technical University of Denmark, Kemitorvet, Bulding 207, 2800 Kgs Lyngby (Denmark),
E-mail: semei@kemi.dtu.dk

Supplementary Figures:

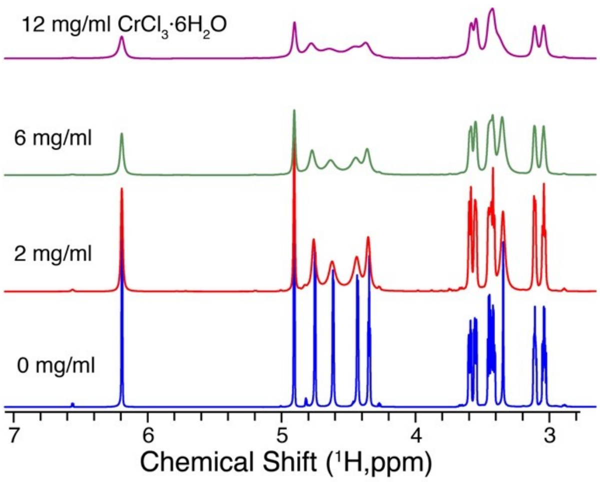

Figure S1. Effect of CrCl$_3$·6H$_2$O at the indicated concentrations on the spectral properties of 20 mg glucose in 600 μl d_6-DMSO, 25 ºC.

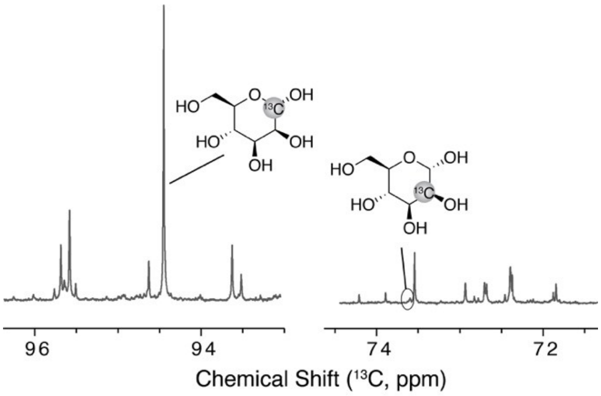

Figure S2. Mannose isotopomers formed from [1-^{13}C] glucose indicate that mannose is predominantly formed from a reversible 1,2 H-shift ([1-^{13}C] mannose at 94.5 ppm), and to a lesser degree by 1,2 C-shift ([2-^{13}C] mannose at 73.6 ppm). Reaction conditions: 50 mg [1-^{13}C] glucose, 2.5 mg $CrCl_3 \cdot 6H_2O$, 550 μl d_6-DMSO, after 20 hours at 110 ºC.

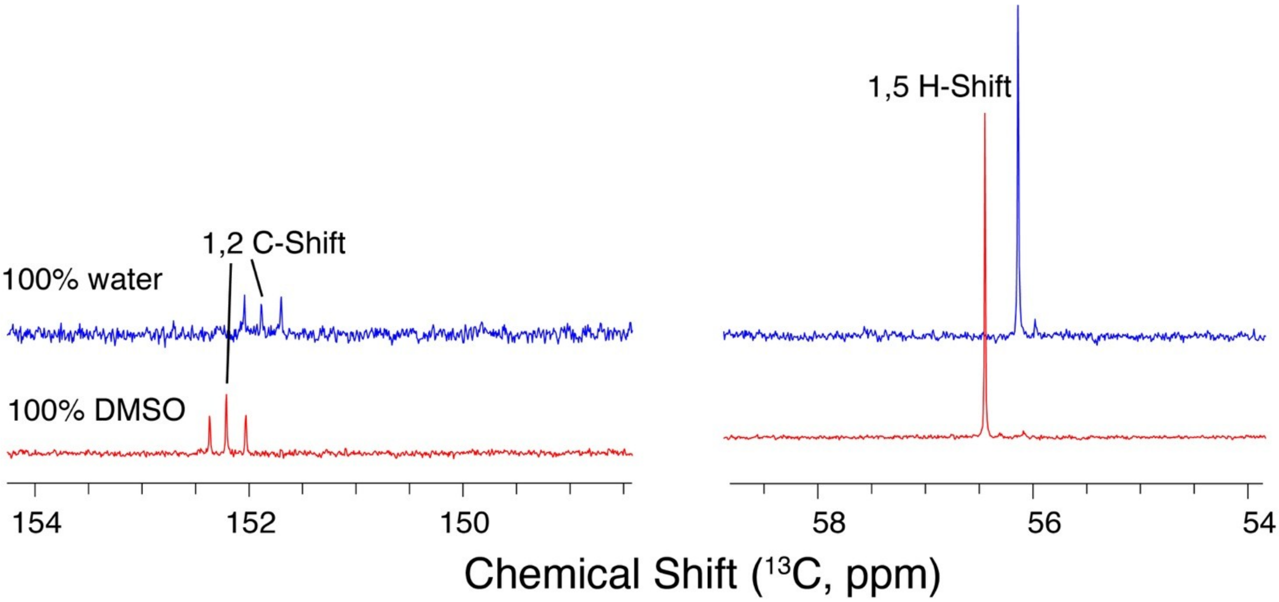

Figure S3. HMF isotopomer distributions in ^{13}C NMR spectra upon Cr^{III} catalysis in DMSO and water. Cr^{III} catalysis showed approximately twofold lower propensity for 1,2 C-shift in water than in DMSO. Reaction conditions: 30 mg [1-^{13}C] glucose, 2.5 mg $CrCl_3 \cdot 6H_2O$, 550 µl d_6-DMSO or D_2O, 100 °C for 20 hours.

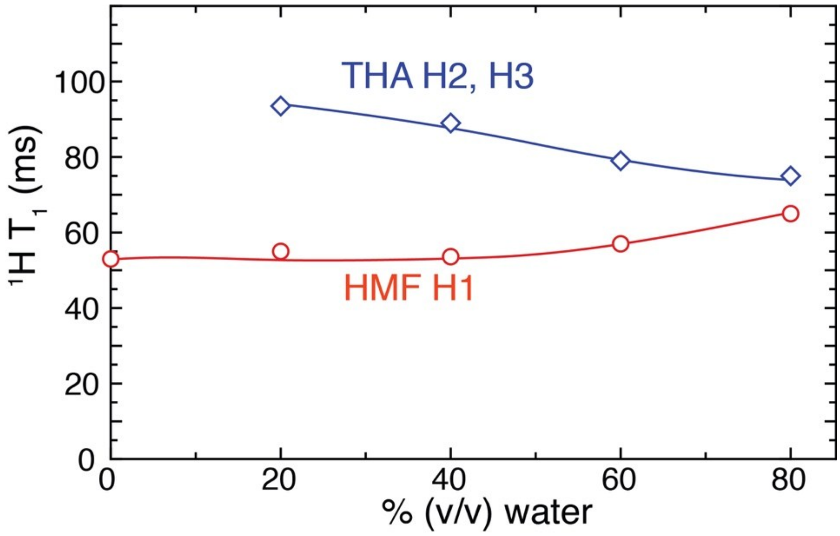

Figure S4. Spin-lattice relaxation time T_1 for protons (measured by inversion-recovery method on a 800 MHz instrument at 303 K) in THA and HMF in the presence of 2.5 mg $CrCl_3 \cdot 6H_2O$ **in** 550 μl *d*$_6$-DMSO or D_2O with the indicated compositions. Different trends in relaxation time T_1 indicate different binding behavior of the two molecules to the paramagnetic Cr^{III} center in response to altered solvent composition.

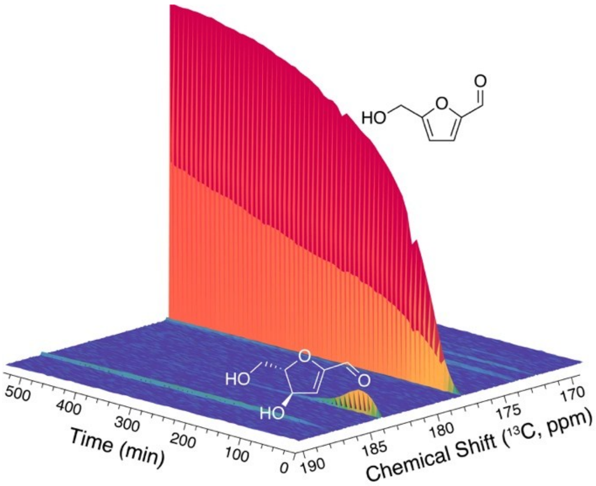

Figure S5. Time series of ^{13}C NMR spectra displaying reaction progress from [1-13C] to HMF via (4R,5R)-4-hydroxy-5-hydroxymethyl-4,5-dihydrofuran-2-carbaldehyde. Reaction conditions: 30 mg [1-^{13}C] glucose, 2.5 mg $CrCl_3 \cdot 6H_2O$ at 110 ºC in 550 μl d_6-DMSO.

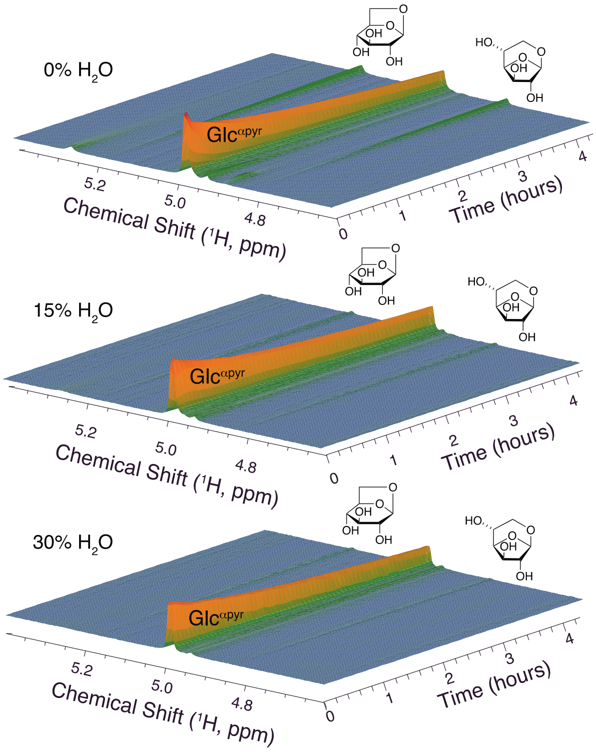

Figure S6. Time series of ^{1}H NMR spectra displaying the reduced formation of anhydrosugars (anhydroglucofuranose, AGF and anhydroglucopyranose, AGP) in the presence of water at 15% (middle) and 30% (bottom) volume ratios. Reaction conditions: 50 mg glucose, 2.5 mg $CrCl_3 \cdot 6H_2O$ in 570 µl d_6-DMSO, 130 ºC.

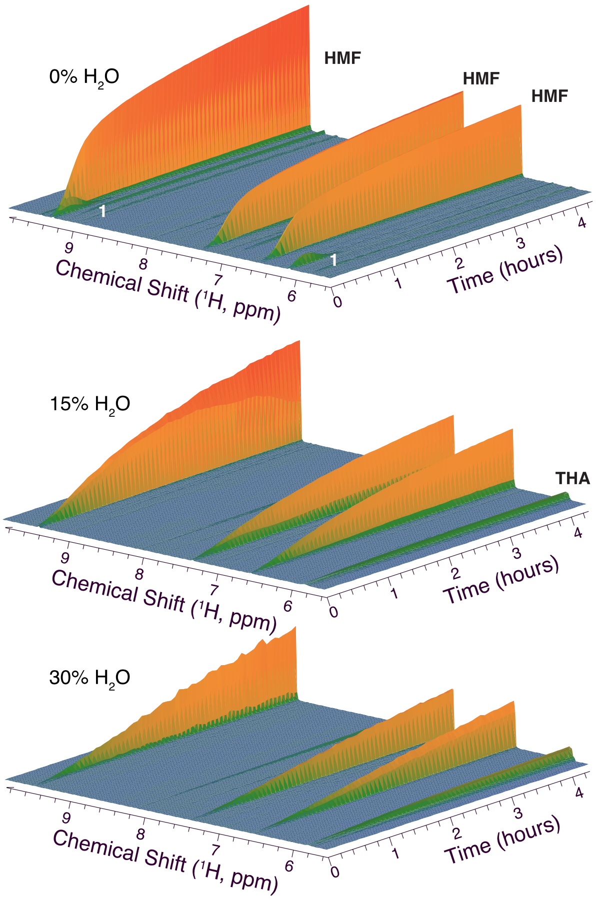

Figure S7. Time series of ^{1}H NMR spectra displaying the slower formation of HMF and emergence of THA in the presence of water at 15% (middle) and 30% (bottom) volume ratios. Reaction conditions: 50 mg glucose, 2.5 mg $CrCl_3 \cdot 6H_2O$ in 570 μl d_6-DMSO, 130 °C.

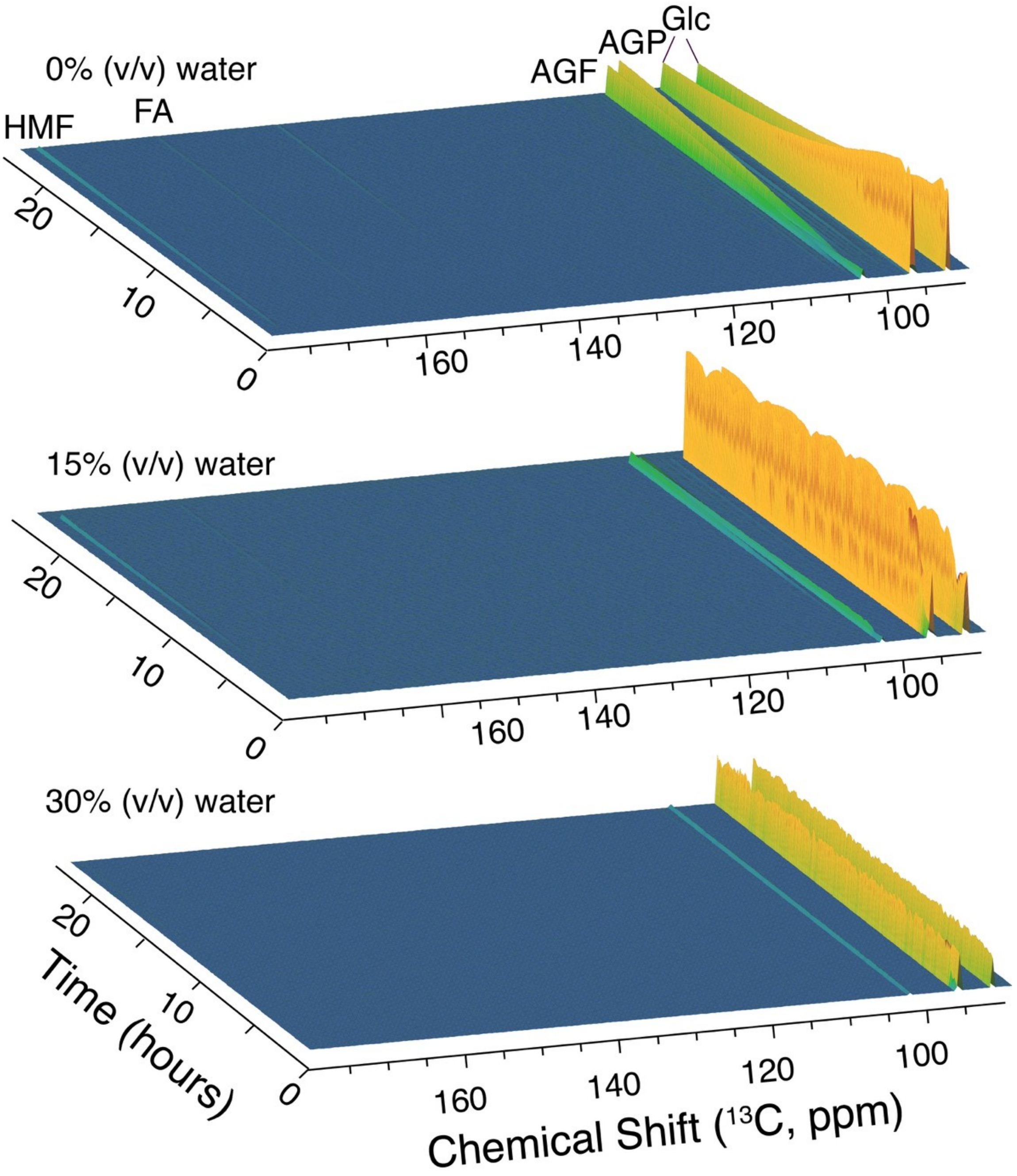

Figure S8. Series of ^{13}C spectra for the hydrothermal dehydration of [1-^{13}C] glucose at varying water content. Reaction conditions: 30 mg [1-^{13}C] glucose, 3.5 mg $CrCl_3 \cdot 6H_2O$, 550 μl total volume of *d*$_6$-DMSO and D_2O, 110 °C. AGF and AGP are anhydrosugars as shown in Figure S6.

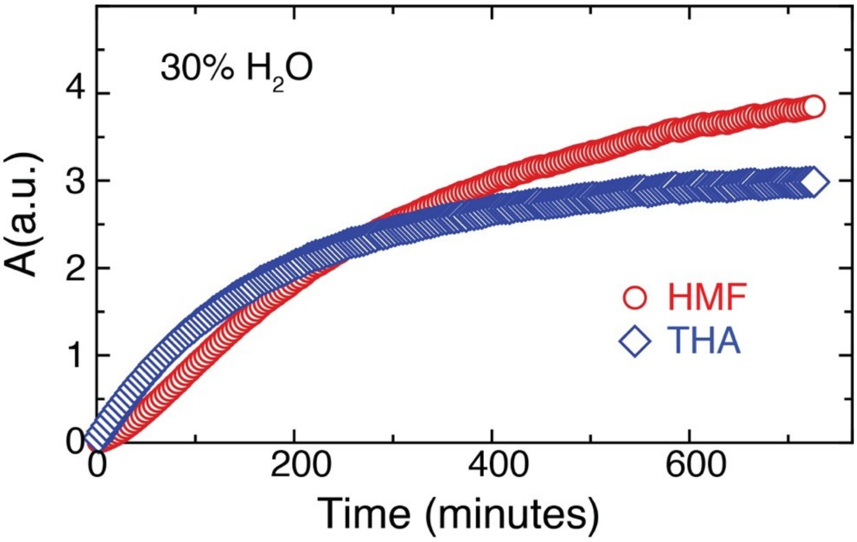

Figure S9. Integrals for the time series of the ^{1}H NMR spectra in the presence of 30% (v/v) water. Reaction conditions: 50 mg glucose, 2.5 mg $CrCl_3 \cdot 6H_2O$ in 570 μl d_6-DMSO, 130 ºC.

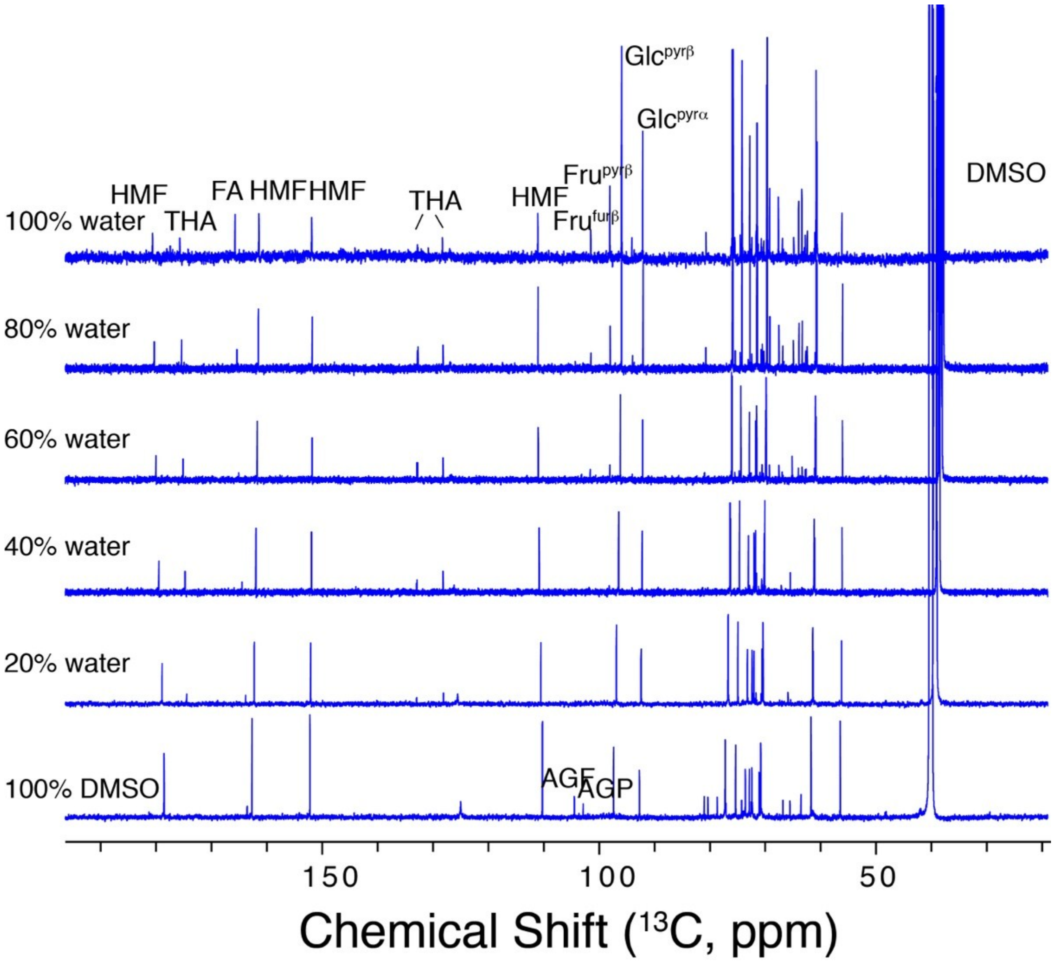

Figure S10. Quantitative ^{13}C NMR spectra displaying the product composition from glucose at varying solvent composition. AGF and AGP are anhydrosugars. FA denotes formic acid. Samples are identical to main text Figure 8.

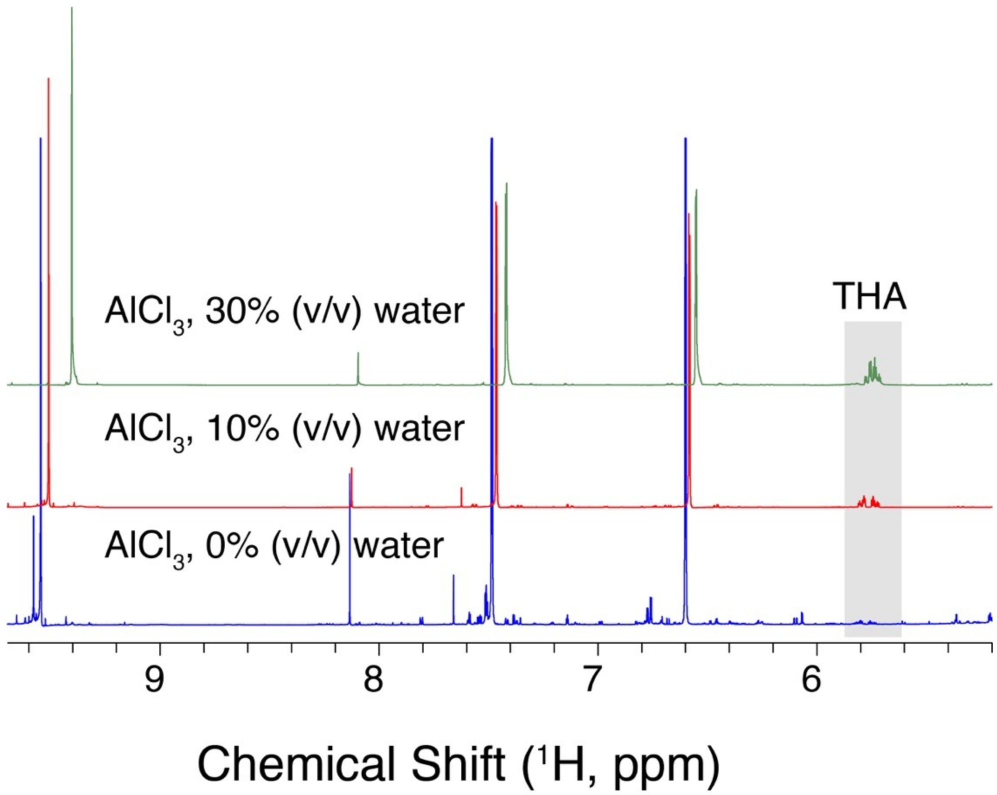

Figure S11. ^{1}H NMR spectra identifying THA formation at increasing water content from glucose by $AlCl_3$. Reaction conditions: 30 mg glucose, 3 mg $AlCl_3{\cdot}6H_2O$ at 100 ºC in 550 μl d_6-DMSO/D_2O with the indicated composition (v/v).

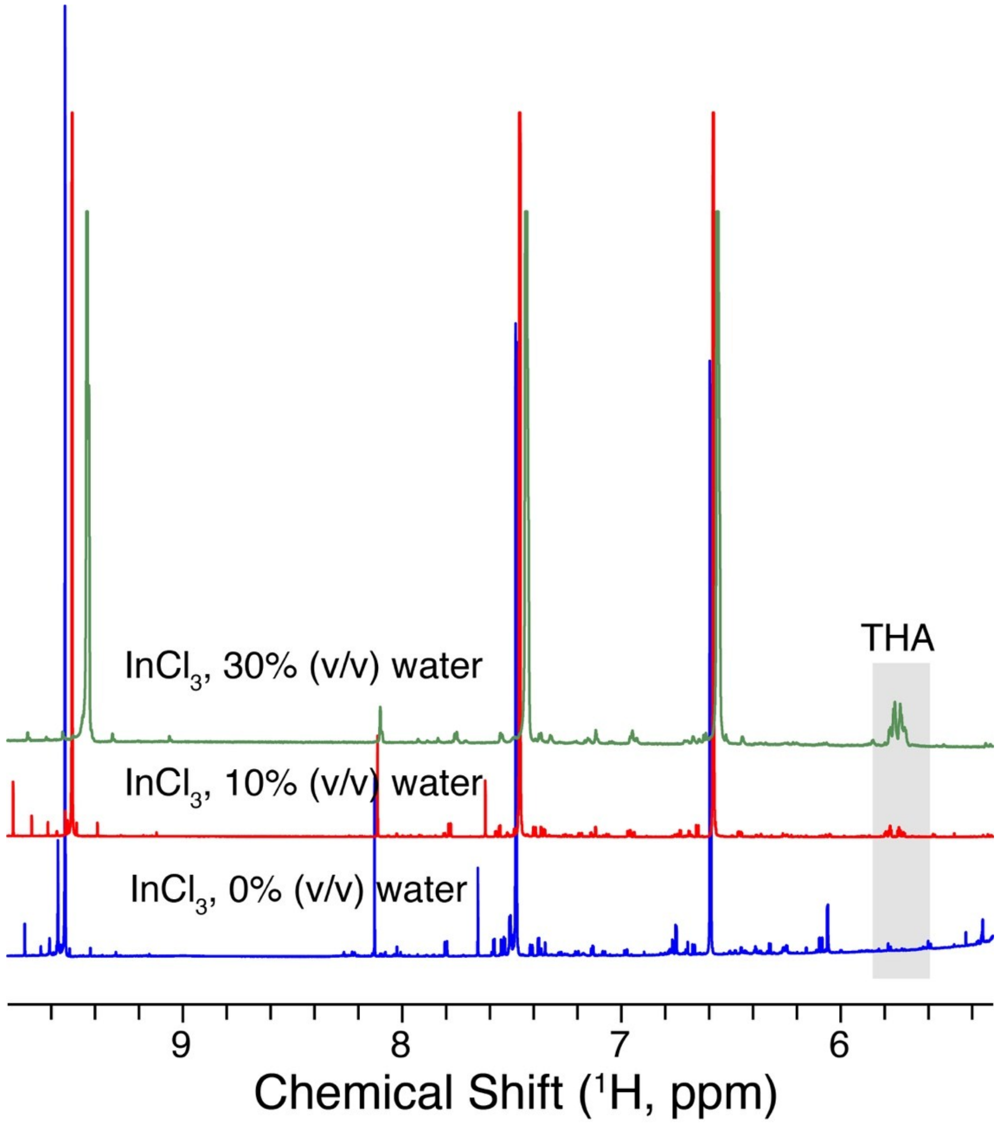

Figure S12. ^{1}H NMR spectra identifying THA formation at increasing water content from glucose by $InCl_3$. Reaction conditions: 30 mg glucose, 3 mg $InCl_3$ at 100 ºC in 550 μl d_6-DMSO/D_2O with the indicated composition (v/v).

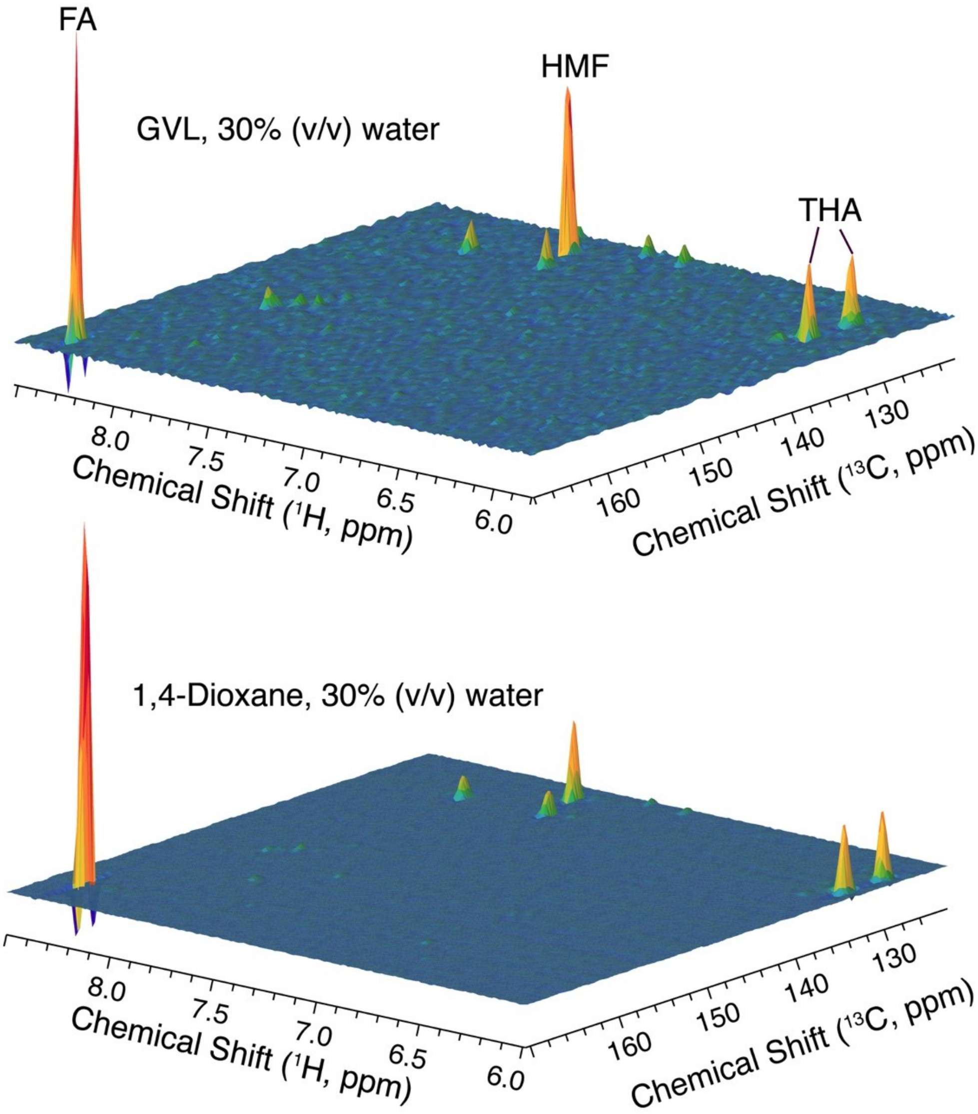

Figure S13. ^1H NMR spectra identifying THA formation at from glucose catalyzed by $CrCl_3$ in different solvent systems. FA denotes formic acid. Reaction conditions: 30 mg glucose, 3 mg $CrCl_3{\cdot}6H_2O$ at 100 ºC in 400 μl d_6-DMSO/170 μl D_2O.