Supporting information

Detecting Elusive Intermediates in Carbohydrate Conversion:

A Dynamic Ensemble of Acyclic Glucose-Catalyst Complexes

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SI Contents (4 pages, 3 figures, 1 table)

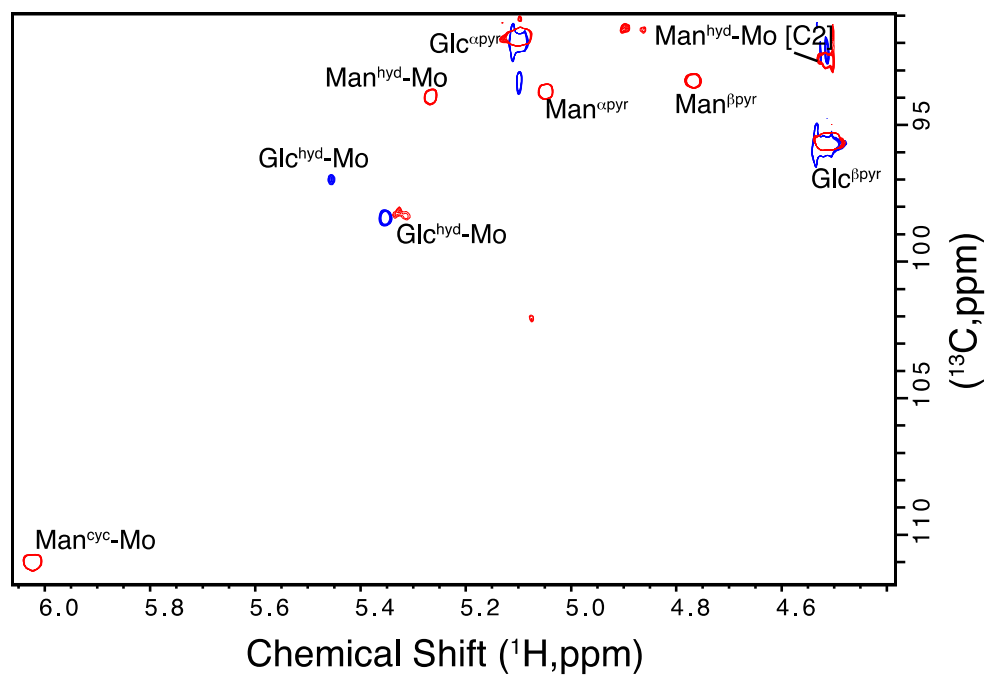**Assignment of molybdate-glucose and molybdate-mannose complexes.**

Figure S1. Assignments of 40 mg carbohydrate forms in the presence of 40 mg/ml molybdate by ^{1}H-^{13}C HSQC spectroscopy of the anomeric spectral region. Reaction progress at 323 K and pH 5.5 is followed 8 hours (red) after acquisition of the spectrum displayed in blue.

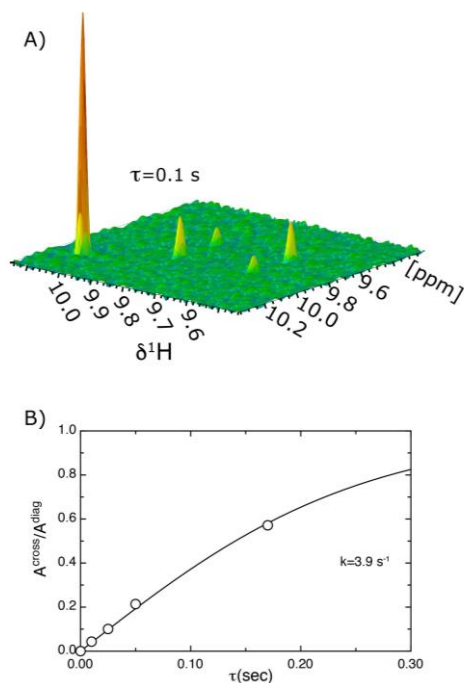**Exchange NMR spectroscopy of molybdate-glucose complexes.**

Figure S2. A) The exchange spectrum for a sample of 40 mg/ml glucose and 40 mg/ml molybdate with a mixing time of 100 ms at 313 K and pH 5.5 shows that two species of non-hydrated aldehyde complexes are in exchange with each other on the NMR timescale under these conditions. A third aldehyde species is in slower exchange on this time scale under these conditions. B). The exchange rate between the two species is determined to 3.9 s^{-1}.
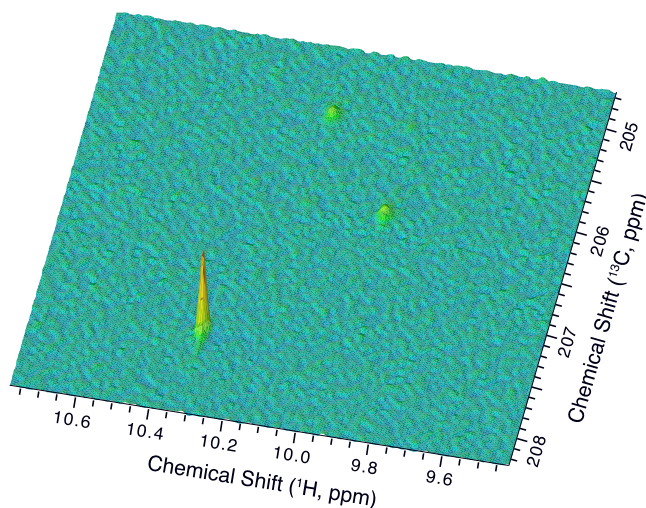
HSQC NMR spectroscopy of acylic glucose species.

Figure S3. The aldehyde region of a HSQC spectrum of a stabilized sample of [1-^{13}C] glucose (40 mg, pH 5.5, 313 K) in the presence of 40 mg/ml molybdate, showing the presence of three different major acyclic aldehyde forms.

Kinetic fit: Coefficients of determination

Table S1. Individual coefficients of determination (R^2) for the kinetic fits of the obtained data to coupled differential equations described in the data analysis section.

R^2	Substrate	Intermediates (I)	Products (P)
pH=3.3	0.99	0.91	0.98
pH=5.5	0.99	0.90	0.97