Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

Sensitive NMR Method for Detecting Carbohydrate Influx into Competing Chemocatalytic Pathways

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Materials and Methods

The general reaction procedure for Sn-Beta catalysed carbohydrate conversion followed previously described methodology.[1] Reactions were conducted using isotope-labelled [1-^{13}C] xylose substrate with a Biotage Initiator + microwave reactor in 500 μL glass reaction vials. Reactions employed 18 mg Sn-Beta (Si/Sn=200, hydrothermally synthesized as described[2]), 36 mg D-[1-^{13}C]xylose, 500 μL methanol (containing 0 mM or 0.5 mM K_2CO_3) and 5 mg dimethyl sulfoxide as internal standard. All reactions were conducted at 160 °C for 5 min.

Reaction conditions for the reduction of methyl lactate followed the described procedure, and the procedure was followed by NMR and LCMS analysis.[3] Sodium borohydride (0.6 mmol) was mixed with sodium methoxide (0.015 mmol) in deuterated methanol (0.5 ml) in a Schlenk tube with magnetic stirring. Post reaction material from the Sn-Beta catalysed conversion of D-[1-^{13}C]-xylose was added to an estimated methyl lactate amount of 0.3 mmol for 90 minutes. To the resultant reaction mixture, 4N HCl (aq) was added to a final concentration of 50 mM HCl to liberate 1,2 diols from cyclic borate esters in the borate containing postreaction mixture.

NMR spectra were recorded on an 800 MHz Bruker Avance III NMR spectrometer equipped with a TCI CryoProbe and a Sample-Jet sample changer. Quantitative proton-decoupled 1D ^{13}C spectra were acquired with recycle delays of 60 s using a pulse sequence that employs inverse gated decoupling. ^{1}H-^{1}H TOCSY spectra were acquired by acquiring 2048 and 400 complex data points to sample the FID for 233 and 45 milliseconds in the direct and indirect dimensions, respectively. For comparison, ^{1}H-^{1}H TOCSY spectra were acquired on a Bruker Avance II 400 MHz NMR instrument equipped with a room temperature probe. On this standard instrument, 1024 and 256 complex data points were acquired to sample the FID for 256 and 64 milliseconds in the direct and indirect dimensions, respectively, and non-uniform sampling (30%) was applied in the indirect dimension to result in an experiment time of 10 minutes. ^{1}H-^{1}H TOCSY spectra were processed with ample zero filling in all spectral dimensions in Bruker Topspin 3.5 pl7 software, prior to manual phasing, automatic baseline correction and integration in the same software. These integrals derived from intensity counting in integration intervals were used without any line fitting.

Supplementary Figures

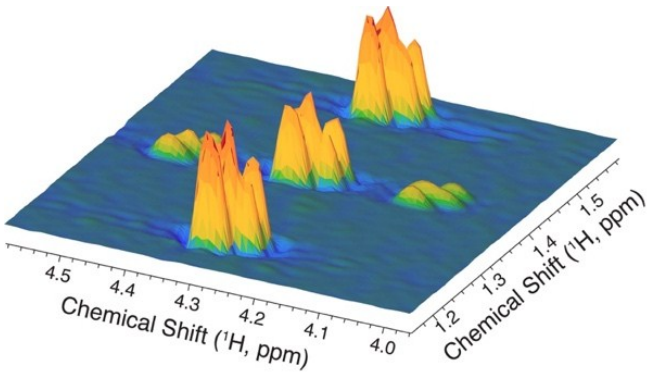

Figure S1. Multiplet of the H1-H2 cross signal in the ^{1}H-^{1}H TOCSY spectrum of the sample of main text Figure 1. The experiment was acquired in 10 minutes on a 400 MHz routine instrument.

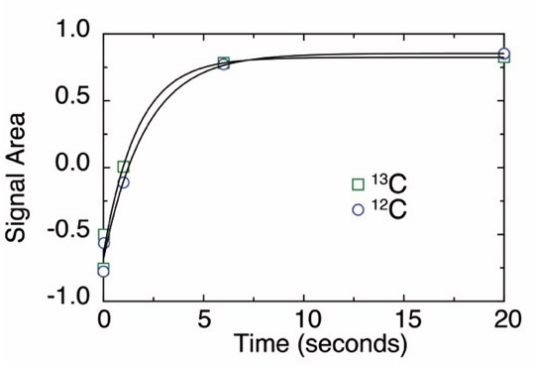

Figure S2. Similar relaxation behaviour of ^{1}H attached to ^{12}C or ^{13}C in the C3 methyl group (of the lactate part) of methyl lactate. If similar relaxation is not given, correction factors or the addition of small amounts of paramagnetic additives may be warranted.

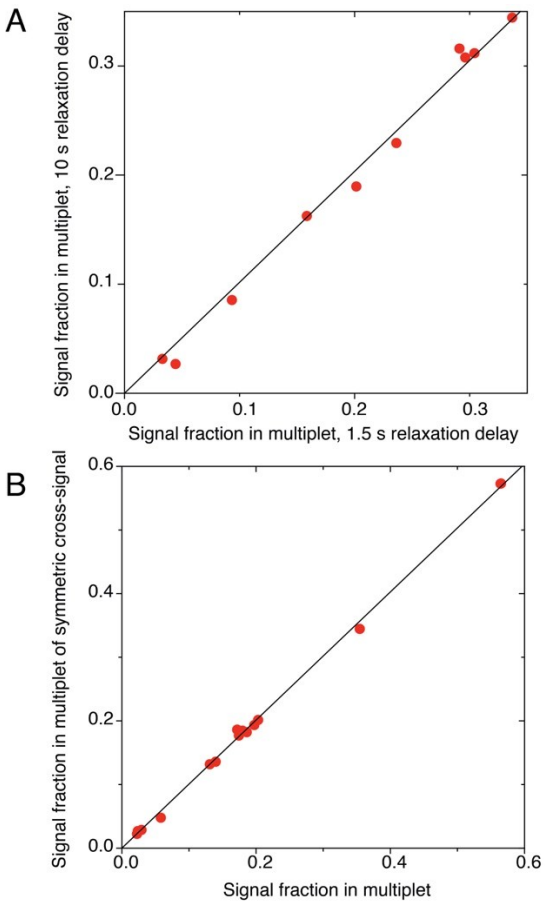

Figure S3. Correlation of signal fractions from different isotopomers in cross signals of 2D ^{1}H-^{1}H TOCSY experiments acquired with different inter-scan relaxation delays (A), and on either side of the diagonal in a 2D ^{1}H-^{1}H TOCSY experiment acquired with 1.5 seconds inter-scan relaxation delay at 800 MHz (B). Sufficiently high correlations were found to allow reliable conclusions about the extent of mechanistic changes in Sn-Beta catalysed carbohydrate influx into competing pathways even from single cross signals in fast 2D ^{1}H-^{1}H TOCSY experiments with moderately fast inter-scan repetition (1.5 seconds).

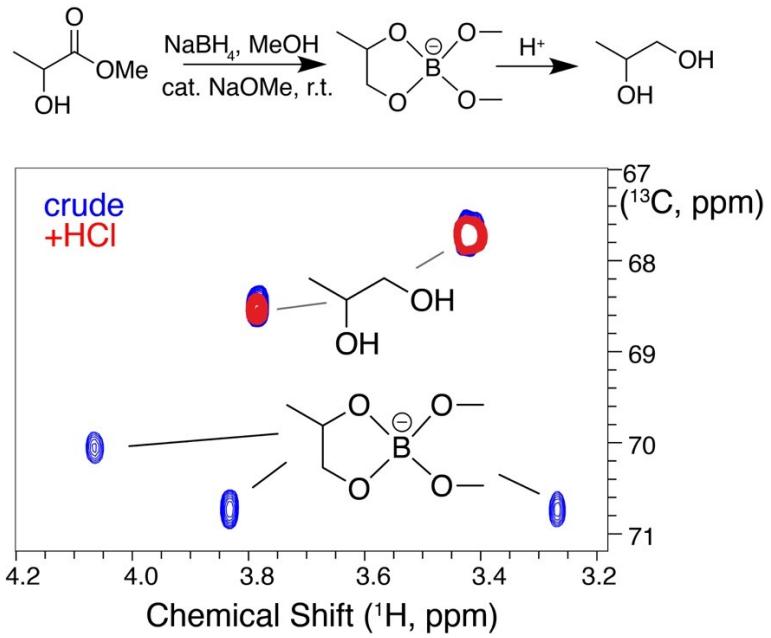

Figure S4. Reaction scheme for the conversion of methyl lactate to the borate ester of propylenglycol and its subsequent dissociation by the addition of acid (top). An overlay of ^{1}H-^{13}C HSQC spectra of postreaction material upon reduction is shown (bottom), displaying the hydrolysis of the borate ester upon acidification with HCl(aq). Formation of a borate ester was validated by ^{1}H-^{11}C HMBC spectroscopy and by LC-MS.

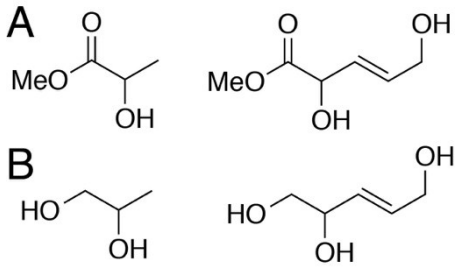

Figure S5. Main products after conversion of xylose with Sn-Beta (top; methyl lactate left, DPM right) and resultant alcohols observed after treating post-reaction material with $NaBH_4$ and aqueous acid, leaving olefinic bonds intact under the conditions employed.

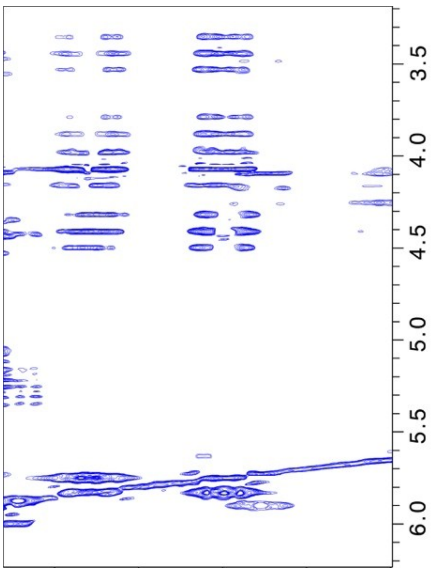

Figure S6. Region of the ^{1}H-^{1}H TOCSY showing the olefinic alcohol of Figure S3B, with the olefinic bond intact and little ^{13}C enrichment at the olefinic positions, opposite to more significant enrichment at the alcoholic C1, C2 and C5 positions due to direct conversion, 1,2-CS and 1,5-HS, respectively.

References

1. S. G. Elliot, E. Taarning, R. Madsen and S. Meier, *ChemCatChem*, 2018, **10**, 1414-1419.
2. S. Tolborg, A. Katerinopoulou, D. D. Falcone, I. Sádaba, C. M. Osmundsen, R. J. Davis, E. Taarning, P. Fristrup and M. S. Holm, *Journal of Materials Chemistry A*, 2014, **2**, 20252-20262.
3. P. C. P, E. Joseph, A. A, N. D. S, I. Ibnusaud, J. Raskatov and B. Singaram, *The Journal of Organic Chemistry*, 2018, **83**, 1431-1440.