Electronic Supplementary Information

# A strategy of ketalization for catalytic selective dehydration of biomass-based polyols over H-beta zeolite

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## Contents

## 1. Materials and methods

Materials

All chemicals here were commercially available with analytical grade purity or better and were used without further purification unless otherwise stated. Sorbitol (≥99.5%) was available from Sigma-Aldrich Co., LLC. Mannitol (≥99%) and (±)-1,2,4-butanetriol (98%) were obtained from Aladdin Reagent Inc. (China). Xylitol and *meso*-erythritol (99%) were supplied from (≥99%) Acros Organics and J&K Scientific Ltd. Isosorbide (≥98%) and isomannide were purchased from Wuhan DKY Technology Co., Ltd. (China) and HWRK Chemical Engineering Co., Ltd. (China), respectively. 1,4-Sorbitan (97%) and 2,5-sorbitan (98%) standards were obtained from Toronto Research Chemicals, while 1,5-sorbitan was purchased from J&K Scientific Ltd. 1,4-Erythritan (>98%) and 3-hydroxytetrahydrofuran (98%) were obtained from TCI and Aladdin Reagent Inc. (China), separately. Diethyl ketone (DEK, >98%) and methyl isobutyl ketone (MIBK, >99.5%) were supplied by TCI. Methyl *n*-butyl ketone (MNBK, 99%), sulfolane (>99%), γ-valerolcatone (98%) and *n*-butanol (≥99.7%) were purchased from Aladdin Reagent Inc. (China). Naphthalene (≥99%) was supplied by Alfa-Aesar Chemical Co., Ltd., separately. Methyl *sec*-butyl ketone (MSBK, 99%) and deuterated dimethyl sulfoxide (DMSO-$d_6$, 99.8% D) were also available from J&K Scientific Ltd. Besides, methanol, 1,4-dioxane and dimethyl carbonate were provided from local suppliers.

The following catalysts were employed in the present study. H-forms of two beta zeolites with Si/Al ratios of 12.5 and 20, purchased from Nankai University Catalyst Co., Ltd., were calcined at 550 $^{o}$C for 6 h in air to remove strongly adsorbed water prior to use. These zeolites are designated as H-beta(12.5) and H-beta(20). Amberlyst 70 resin, kindly given by Rohm and Haas Company, was dried at 105 $^{o}$C for 10 h under air flow to remove large amounts of water prior to use. 12-Tungstophosphoric acid ($H_3PW_{12}O_{40}$, Sigma-Aldrich Co., LLC.) was dried at 130 $^{o}$C for 2 h under air for removal of physisorbed water before being used. *p*-Toluene sulfonic acid (*p*-TSA, Sinopharm Chemical Reagent Co., Ltd.) was used as received without further treatment.

Methods

Nuclear magnetic resonance spectra were recorded on a Bruker Avance III 400 spectrometer ($^{1}$H at 400 MHz, $^{13}$C at 101 MHz) at room temperature. Chemical shifts are given with reference to the solvent resonance (DMSO-$d_6$: 2.50 ppm for proton and 39.52 ppm for carbon). High-resolution (HR) electrospray ionization (ESI) mass spectrum was recorded on a LCMS Q-TOF instrument. Mass spectra were run on gas chromatograph-mass spectrometry (Agilent 7890A GC/5975C MS) with a HP-5 MS capillary column (30 m × 0.25 mm× 0.25 μm) and electron impact ionization mode (EI). GC analyses were performed on an Agilent 7890 GC apparatus equipped with a flame ionization detector and HP-5 capillary column (30 m × 0.53 mm × 1.5 μm). HPLC analyses were conducted on a waters 2695 apparatus fitted with a 2414 refractive index detector (at 40 $^{o}$C) and Prevail Carbohydrate ES column (250 × 4.6 mm, 5 μm), using acetonitrile/water (75/25) mixture as eluent (0.80 mL/min at 30 $^{o}$C) with 20 μL of injection volume. Experiments were conducted in a 15 mL stainless steel Teflon-lined autoclave provided with a manometer, automatic temperature controller and a magnetic stirring bar.

## 2. Experimental procedure and quantification

### Experimental procedure

*General procedure for transformation of sorbitol into isosorbide:* sorbitol (2 mmol), acid catalyst (0.037 g), and solvent (4.5 mL) were charged into a stainless steel autoclave (15 mL) followed by flushing with $N_2$ for four times. The reaction was performed at 170 $^{o}$C for specific time with magnetically stirring at around 900 rpm under autogeneous pressure. Zero time was taken as soon as the target temperature was reached. After the reaction, the reactor was cooled down to room temperature. The reaction mixture was diluted by water and ethanol, followed by centrifugation to separate the solid catalyst. Finally, the sample was filtered with a 0.2 μm syringe filter prior to GC and HPLC analysis.

*General procedure for the conversion of sugar-derived polyols into the corresponding five-membered cyclic ethers:* The catalytic conversion of sugar-derived polyols, including mannitol, 1,4-sorbitan, xylitol, *meso*-erythritol and (±)-1,2,4-butanetriol, was performed in a 15 mL stainless steel autoclave. In a typical procedure, sugar-derived polyol (2 mmol), H-beta(20) catalyst (0.037 g), and MIBK (4.50 mL) were charged into the reactor followed by flushing with $N_2$ for four times to remove air. The reaction was performed at 170 $^{o}$C with magnetically stirring at around 900 rpm under autogeneous pressure. Zero time was taken as soon as the target temperature was reached. After specific reaction time, the reaction was quenched by cooling down the autoclave reactor in an ice-water bath. Subsequently, the reaction mixture was diluted by water and ethanol, followed by centrifugation to separate the solid catalyst. Finally, the sample was filtered with a 0.2 μm syringe filter prior to GC and HPLC analysis.

Different to other polyol conversion in MIBK, *meso*-erythritol conversion in MIBK with H-beta(20) as catalyst mainly leads to five-membered 1,4-erythritan ketal. Therefore, 1,4-erythritan was obtained by further conventional acidic deprotection of erythritan ketal. According to the previous deprotection method,[1] the reaction mixture of *meso*-erythritol conversion was concentrated by rotary evaporation. Then, a solution of the residual in THF:4M HCl (1:1 *v*/*v*, 4 mL) was heated at 60 °C for 3 h, followed by neutralization with $NaHCO_3$.

*Time-course experiments for polyol conversion in 3-pentanone (DEK) using H-beta(20) catalyst*: To elucidate reaction pathway of sorbitol dehydration, 1,4-sorbitan and sorbitol were used as reactants for different reaction times, separately. 1,4-Sorbitan (2 mmol) and sorbitol (2 mmol) were separately mixed with 0.037 g H-beta(20) catalyst in 4.50 mL DEK in the autoclave reactor followed by flushing with $N_2$ for four times. The reaction was conducted at 170 °C for specified time with magnetically stirring (ca. 900 rpm). Zero time was taken as soon as the target temperature was reached. Each catalytic result at the different time was obtained based on a separate experiment.

*$^{13}$C NMR monitoring of polyol conversion to isosorbide in DEK*: To follow the changing trend of five-membered cyclic ketal intermediate, the reaction courses of 1,4-sorbitan and sorbitol in DEK were also monitored by $^{13}$C NMR, respectively. The detailed reaction procedure is the same as above. When a portion of the reactant like sorbitol and 1,4-sorbitan remained unreacted, a separation of layer was observed at room temperature wherein the bottom layer mainly consisted of water and H-beta(20) catalyst. This phenomenon is due to the poor solubility of sorbitol and sorbitan in DEK at ambient temperature. After the transparent upper layer (DEK as solvent) was thoroughly withdrawn, the bottom layer including H-beta(20) catalyst was added with 4.50 mL of deionized water followed by centrifugation to obtain a clear solution. Aliquot samples of 0.60 mL from the upper solution (DEK as solvent) and bottom solution (water as solvent) were separately transferred into a 5 mm NMR tube with a DMSO-$d_6$ capillary insert as the NMR lock and reference. The $^{13}$C NMR spectra (101 MHz) were recorded at ambient temperature.

Also, conversion of C4 sugar-derived polyol (2 mmol), including (±)-1,2,4-butanetriol and *meso*-erythritol, was conducted in DEK (4.5 mL) with H-beta(20) catalyst (0.012 g) at 170 °C for 1 min. After the reaction, a separation of layer was also found when using meso-erythritol as reactant, whereas the phenomena was not observed with (±)-1,2,4-butanetriol as reactant. The sampling procedure for $^{13}$C NMR analysis was the same as above.

As shown in the $^{13}$C NMR spectra (Figures 2 and S5−S7), all the ketal intermediates and most of isosorbide appeared in DEK layer at ambient temperature, whereas unreacted sorbitol and most of 1,4-sorbitan were present in bottom layer. This is because sorbitol and 1,4-sorbitan can be further hydrophobized by the production of five-membered cyclic ketals, which are readily soluble in DEK at ambient temperature. Therefore, the time temporal evolution of ketal intermediates was fully recorded by $^{13}$C NMR spectra of DEK layer.

*Procedure for recycling the catalyst*: In the typical recycling experiment, a mixture of sorbitol (0.364 g, 2 mmol), H-beta(20) catalyst (0.037 g) and methyl isobutyl ketone (4.5 mL) was added in a 15 mL stainless steel autoclave followed by flushing with $N_2$ for four times to remove air. The reaction was performed at 170 $^{o}$C with magnetically stirring at around 900 rpm under autogeneous pressure. After the reaction, H-beta(20) catalyst was separated from reaction mixture by centrifugation, and then washed by ethanol for three times. After being dried at 110 $^{o}$C for 2 h, the used catalyst was calcined at 550 $^{o}$C for 8 h in a flow of air. The regenerated catalyst was accumulated by repeating the same reaction because of the partial loss of catalyst in the recovery process. Afterwards, the recycled catalyst of 0.037 g was used in the next cycle under identical conditions.

*Preparation of 1,4-sorbitan*: 1,4-Sorbitan was prepared according to the previous reports[2] with slight modifications. Sorbitol (11 mmol) and 3 M sulfuric acid (10 mL) were charged into a 100-mL flask equipped with a reflux condenser under nitrogen atmosphere. This reactor was placed into a preheated oil bath kept at 105 $^{o}$C with magnetically stirring. After 18 h, the reaction mixture was cooled to room temperature, and subsequently slowly neutralized by $Na_2CO_3$ with stirring for 30 min. Thereafter, isopropanol was added into the mixture followed by adding anhydrous $Na_2SO_4$. The mixture was centrifuged to collect transparent liquid, which was then concentrated by rotary evaporation. Toluene was added to the residue followed by evaporation by rotary evaporation to remove water to give a yellow viscous liquid. Afterwards, it was extracted by MIBK and AcOEt under reflux, respectively. This clear solution was quickly transferred while hot. The collected solution was evaporated by rotary evaporation to obtain a crude solid, which was finally recrystallized from ethanol to achieve pure 1,4-sorbitan as a white solid with HPLC purity of above 99%. It was ascertained by $^{1}$H and $^{13}$C NMR spectroscopy.

1,4-Sorbitan: $^{1}$H NMR (400 MHz; DMSO-$d_6$): $\delta$ 4.98 (d, *J*=3.1, 1H, OH), 4.80 (d, *J*=4.2, 1H, OH), 4.47 (d, *J*=4.7, 1H, OH), 4.33 (t, *J*=5.8, 1H, OH), 3.98–3.85 (m, 3H), 3.69–3.60 (m, 2H), 3.60–3.51 (m, 1H), 3.43 (d, *J*=8.9, 1H), 3.39–3.28 ppm (m, 1H); $^{13}$C NMR (101 MHz; DMSO-$d_6$): $\delta$ 80.35 (4-C), 76.39 (2-C), 75.80 (3-C), 73.30 (1-C), 69.19 (5-C), 64.12 ppm (6-C).

*Typical procedure for isolation of 5,6-O-(3-pentylidene)-1,4-sorbitan intermediate*: 1,4-Sorbitan (2 mmol) was mixed with 0.037 g H-beta(20) in 4.50 mL DEK in the autoclave reactor followed by flushing with $N_2$ for four time. The reaction was performed at 170 °C for 1 min. After the reaction, the mixture was centrifuged to obtain a clear solution, which was subsequently kept in refrigerator overnight to crystallize out the unreacted 1,4-sorbitan. The upper clear liquid was collected and concentrated by rotary evaporation. Subsequently, the residue was subjected to silica-gel column chromatography eluted with a gradient mixture of cyclohexane/ethyl acetate (2/1 to 1/1, *v/v*) to give 5,6-*O*-(3-pentylidene)-1,4-sorbitan as a colorless oil. The five-membered 5,6-*O*-ketal was confirmed by 1D ($^{1}$H, $^{13}$C) and 2D (H-H COSY and HSQC) NMR and HRMS spectroscopies.

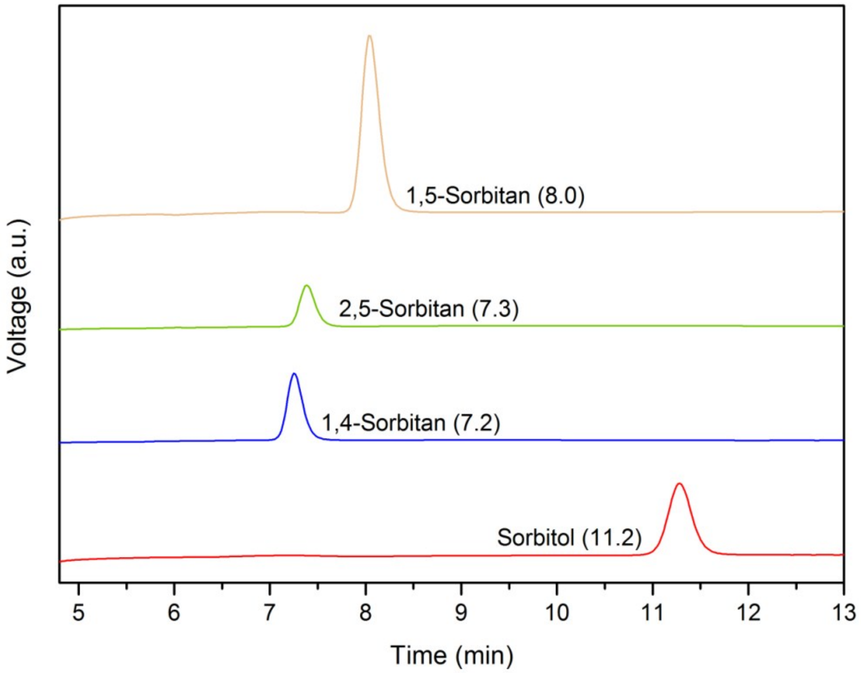
5,6-*O*-(3-Pentylidene)-1,4-sorbitan (ketalization of 1,4-sorbitan with DEK): $^{1}$H NMR (400 MHz; DMSO-$d_6$): $\delta$ 5.05 (d, *J*=3.6, 2H, 2H, 2-COH, 3-COH), 4.19 (q, *J*=6.7, 1H, 5-CH), 4.01–3.92 (m, 2H, 6-CH, 2-CH), 3.90–3.85 (m, 2H, 1-CH, 3-CH), 3.83 (dd, *J*=6.7, 3.0, 1H, 4-CH), 3.78–3.71 (m, 1H, 6-CH), 3.48 (d, *J*=9.0, 1H, 1-CH), 1.54 (dq, *J*=10.6, 7.5, 4H, 8-$CH_2$, 10-$CH_2$), 0.82 ppm (td, *J*=7.4, 2.9, 6H, 9-$CH_3$, 11-$CH_3$); $^{13}$C NMR (101 MHz; DMSO-$d_6$): $\delta$ 111.35 (7-C), 81.14 (4-C), 76.63 (2-C), 75.53 (3-C), 73.39 (1-C), 73.25 (5-C), 66.93 (6-C), 29.20, 28.84 (8-C, 10-C), 8.14, 7.94 ppm (9-C, 11-C); HRMS (*m/z*): $[M + H]^+$ calcd. for $C_{11}H_{21}O_5$, 233.1384; found, 233.1383.

*Isolation of the final product isosorbide*: After the completion of reaction, solid catalyst was separated from the reaction mixture by centrifugation. The clear organic layer was collected followed by rotary evaporation. Then, the orange viscous liquid residue was completely dissolved by ethyl acetate (AcOEt) through elevated temperature, followed by being placed in refrigerator (5 °C) over night. Thereafter, the solution was separated into two layers. The upper layer (AcOEt layer) was removed, and subsequently the residue was treated by vacuum freeze-pump-thaw technique with liquid nitrogen for several hours to remove residual AcOEt, trace of water and other low-boiling point organic impurities. Finally, isosorbide as a yellow solid was obtained, which was confirmed by $^{1}$H and $^{13}$C NMR spectroscopy with GC purity above 96.5%.

Purified isosorbide :$^1$H NMR (400 MHz; DMSO-$d_6$): $\delta$ 5.10 (d, $J$=3.8, 1H, 2-C-OH), 4.70 (d, $J$=6.7, 1H, 5-C-OH), 4.35 (t, $J$=4.4, 1H, 4-CH), 4.23 (d, $J$=4.1, 1H, 3-CH), 4.08 (ddd, $J$=8.3, 6.7, 3.4, 1H, 5-CH), 4.03 (t, $J$=3.4, 1H, 2-CH), 3.76–3.65 (m, 3H, 1-CH$_2$, 6-CH), 3.25 ppm (t, $J$=8.2, 1H, 6-CH); $^{13}$C NMR (101 MHz, DMSO-$d_6$): $\delta$ 87.73, 81.22, 75.67, 75.22, 72.21, 70.81 ppm.

Quantification

HPLC chromatograms of authentic samples: sorbitol, 1,4-sorbitan, 2,5-sorbitan, and 1,5-sorbitan



Quantitative analyses of the main components of the reaction mixture were performed by GC and HPLC. Specifically, quantification of isosorbide was determined by GC internal standard method using naphthalene as internal standard, while sorbitol and sorbitan were quantitatively determined by HPLC external standard method based on peak areas of authentic samples of sorbitol and 1,4-sorbitan, respectively. In the present work, 1,4-sorbitan and 2,5-sorbitan signals overlap in the HPLC chromatogram due to their similar structures. Therefore, the sorbitan quantity is the combined amounts of 1,4-sorbitan and 2,5-sorbitan. Despite of this, we simultaneously used $^{13}$C NMR spectroscopy to determine whether 1,4-sorbitan or 2,5-sorbitan was present in the reaction mixture. Additionally, other sugar-derived polyols including mannitol, xylitol, *meso*-erythritol, (±)-1,2,4-butanetriol and 1,4-xylitan were quantified by HPLC, using external standardization. However, it was difficult to purchase a standard of 1,4-xylitan, so here identification was performed by $^{13}$C NMR and it was assumed that 1,4-xylitan has the same response as 1,4-sorbitan, due to their similar structures. The desired five-membered cyclic ethers including isomannide, 1,4-erythritan and 3-hydroxytetrahydrofuran were quantified by GC, using internal standardization with naphthalene as internal standard.

Reaction results shown as conversion and yield in mol% were defined as follows:

$$\text{Conversion (mol\%)} = \left(1 - \frac{\text{moles of unreacted substrate}}{\text{moles of initial substrate}}\right) \times 100\%$$

$$\text{Yield of product (mol\%)} = \left(\frac{\text{moles of formed product}}{\text{moles of initial substrate}}\right) \times 100\%$$

$$\text{Selectivity to product (mol\%)} = \left(\frac{\text{moles of formed product}}{\text{moles of converted substrate}}\right) \times 100\%$$

Selectivity for non-identified products or others = 100% − total selectivity for all identified products

### 3. $^{13}$C NMR traces for reaction mixture from the reaction of sorbitol in different solvents

After the reaction, the reaction mixture was diluted with methanol and then centrifuged to collect a clear solution. The solution was concentrated by rotary evaporation. Finally, the residual was added with 2.0 mL of deionized water, and an aliquot of the solution (0.15 mL) was taken into a 5 mm NMR tube, and was added with 0.40 mL of DMSO-$d_6$. It was then analyzed by $^{13}$C NMR.

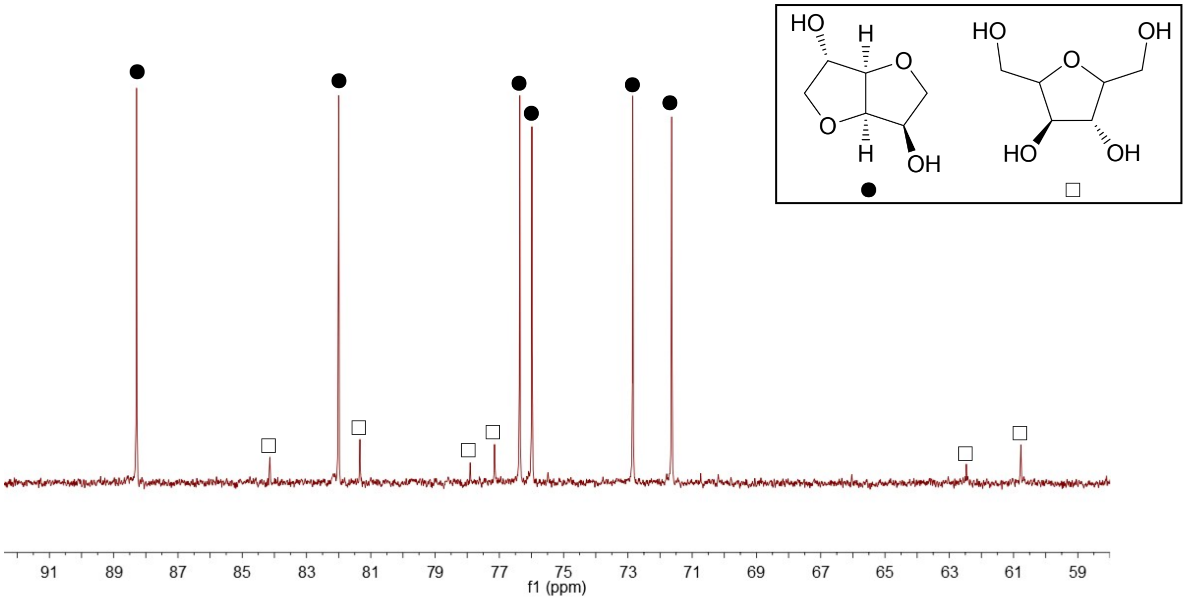


**Figure S1.** $^{13}$C NMR spectrum in DMSO-$d_6$ of a crude reaction mixture for the conversion of sorbitol in solvent-free medium. Reaction condition: sorbitol (2 mmol), H-beta(20) (0.037 g), 170 °C, 2 h.

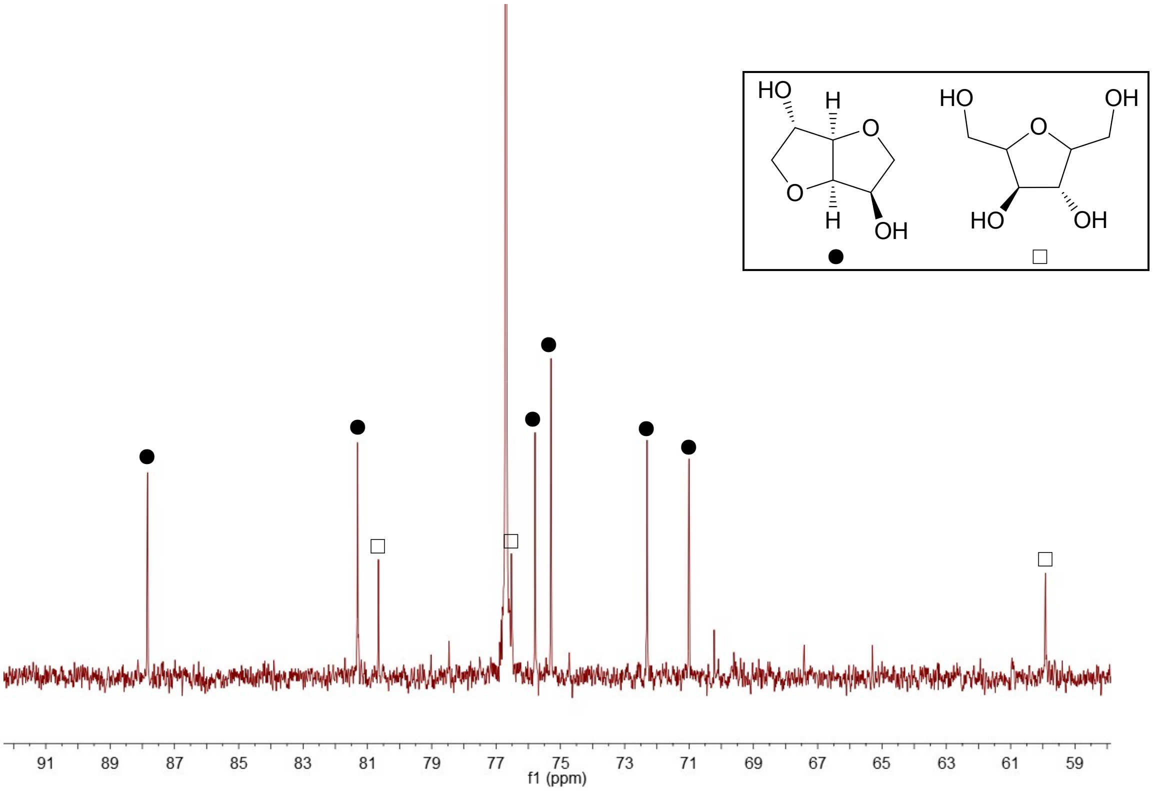


**Figure S2.** $^{13}$C NMR spectrum in DMSO-$d_6$ of a crude reaction mixture for the conversion of sorbitol in γ-valerolactone medium. Reaction condition: sorbitol (2 mmol), γ-valerolactone (4.5 mL), H-beta(20) (0.037 g), 170 °C, 2 h.

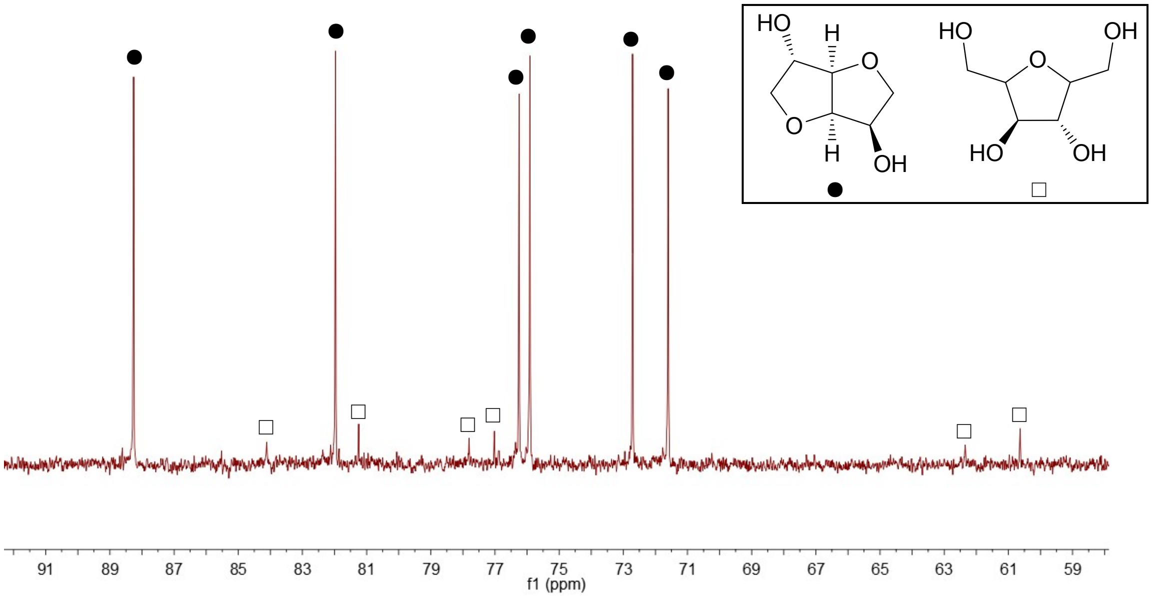


**Figure S3.** $^{13}$C NMR spectrum in DMSO-$d_6$ of a crude reaction mixture for the conversion of sorbitol in dimethyl carbonate medium. Reaction condition: sorbitol (2 mmol), dimethyl carbonate (4.5 mL), H-beta(20) (0.037 g), 170 °C, 2 h.

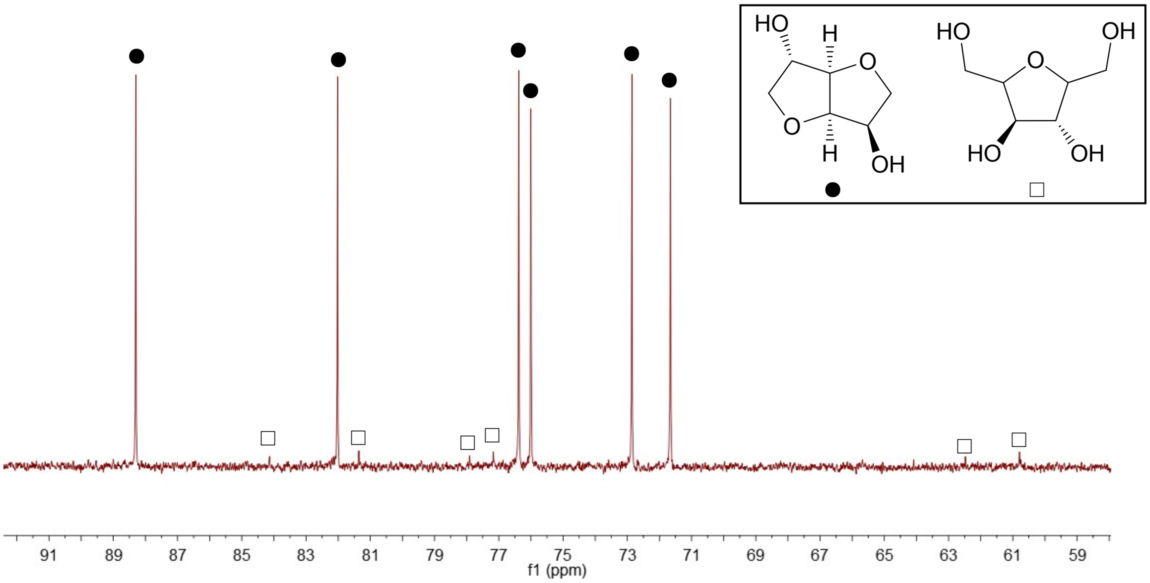


**Figure S4.** $^{13}C$ NMR spectrum in DMSO-$d_6$ of a crude reaction mixture for the conversion of sorbitol in methyl isobutyl ketone (MIBK) medium. Reaction condition: sorbitol (2 mmol), MIBK (4.5 mL), H-beta(20) (0.037 g), 170 °C, 2 h.

## 4. Screening of catalysts

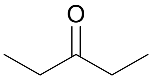
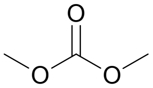
**Table S1.** Conversion of sorbitol catalyzed by various catalysts[a]

| Entry | Catalyst | Conversion (%) | Selectivity (%) | | |
|---|---|---|---|---|---|
| | | | Isosorbide | Sorbitan[b] | Others |
| 1 | None | 10.3 | 11.7 | 0 | 88.3[c] |
| 2 | *p*-TSA | 100 | 52.1 | 31.8 | 16.1 |
| 3 | Amberlyst 70 | 100 | 75.2 | 3.9 | 20.9 |
| 4 | $H_3PW_{12}O_{40}$ | 100 | 76.9 | 1.2 | 21.9 |
| 5 | H-beta(12.5) | 100 | 90.1 | 3.2 | 6.7 |
| 6 | H-beta(20) | 100 | 93.0 | 2.3 | 4.7 |

[a] Reaction conditions: sorbitol (2 mmol), acid catalyst (0.037 g), MIBK (4.5 mL), 170 $^{o}$C, 2 h. [b] 1,4-Sorbitan and 2,5-sorbitan. [c] Mainly including sorbitol ketals.

## 5. Comparison of different solvents for 1,4-sorbitan conversion over H-beta(20)

**Table S2.** Comparison of different solvents for 1,4-sorbitan conversion to isosorbide over H-beta(20)[a]

| Entry | Solvent | Conversion (%) | Isosorbide yield (%) |
|---|---|---|---|
| 1 |  | 100 | 95.1 |
| 2 |  | 95.7 | 80.0 |
| 3 | Neat | 87.7 | 74.9 |

[a] Reaction conditions: 1,4-sorbitan (2 mmol), H-beta(20) (0.037 g), solvent (4.5 mL), 170 $^{o}$C, 1 h.

## 6. $^{13}$C NMR monitoring of the formation of isosorbide in DEK

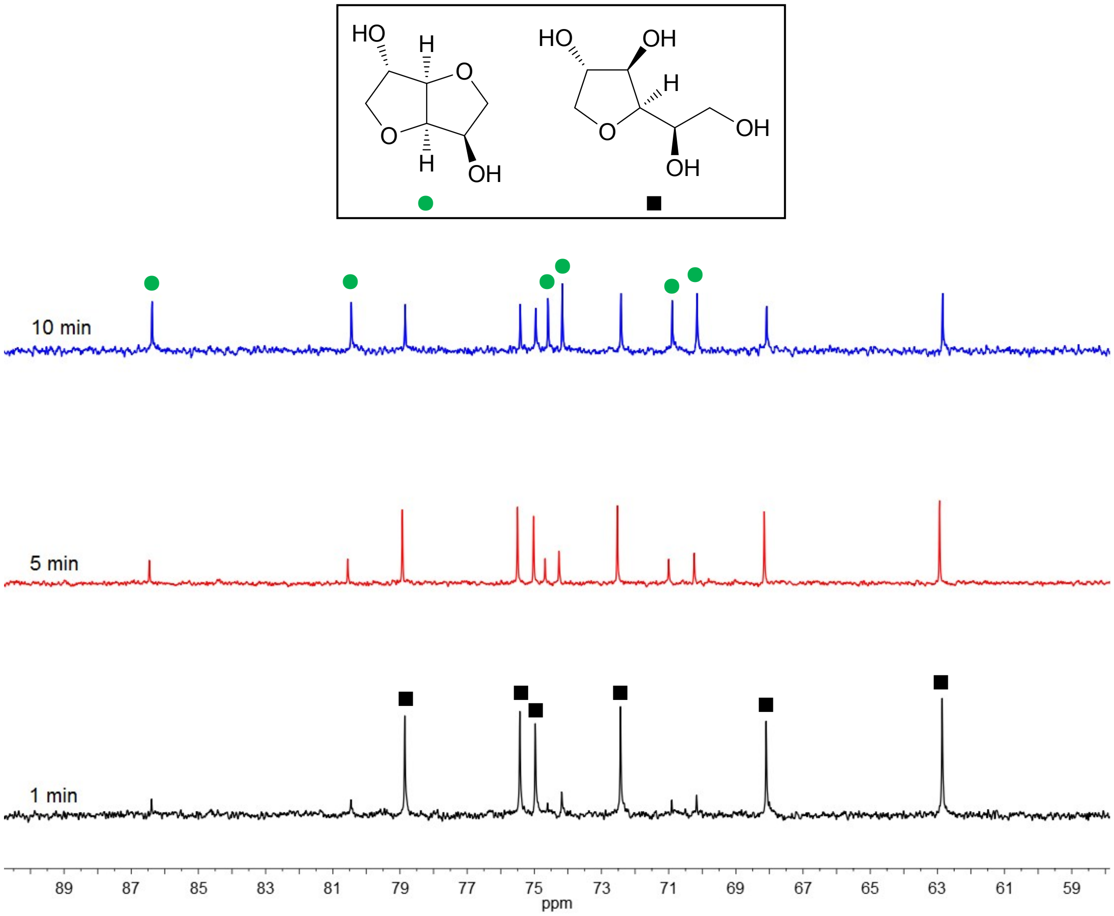


**Figure S5.** Stack of $^{13}$C NMR spectra for the conversion of 1,4-sorbitan to isosorbide in DEK medium over H-beta(20) with reaction times (bottom layer), under conditions in Figure 2b.

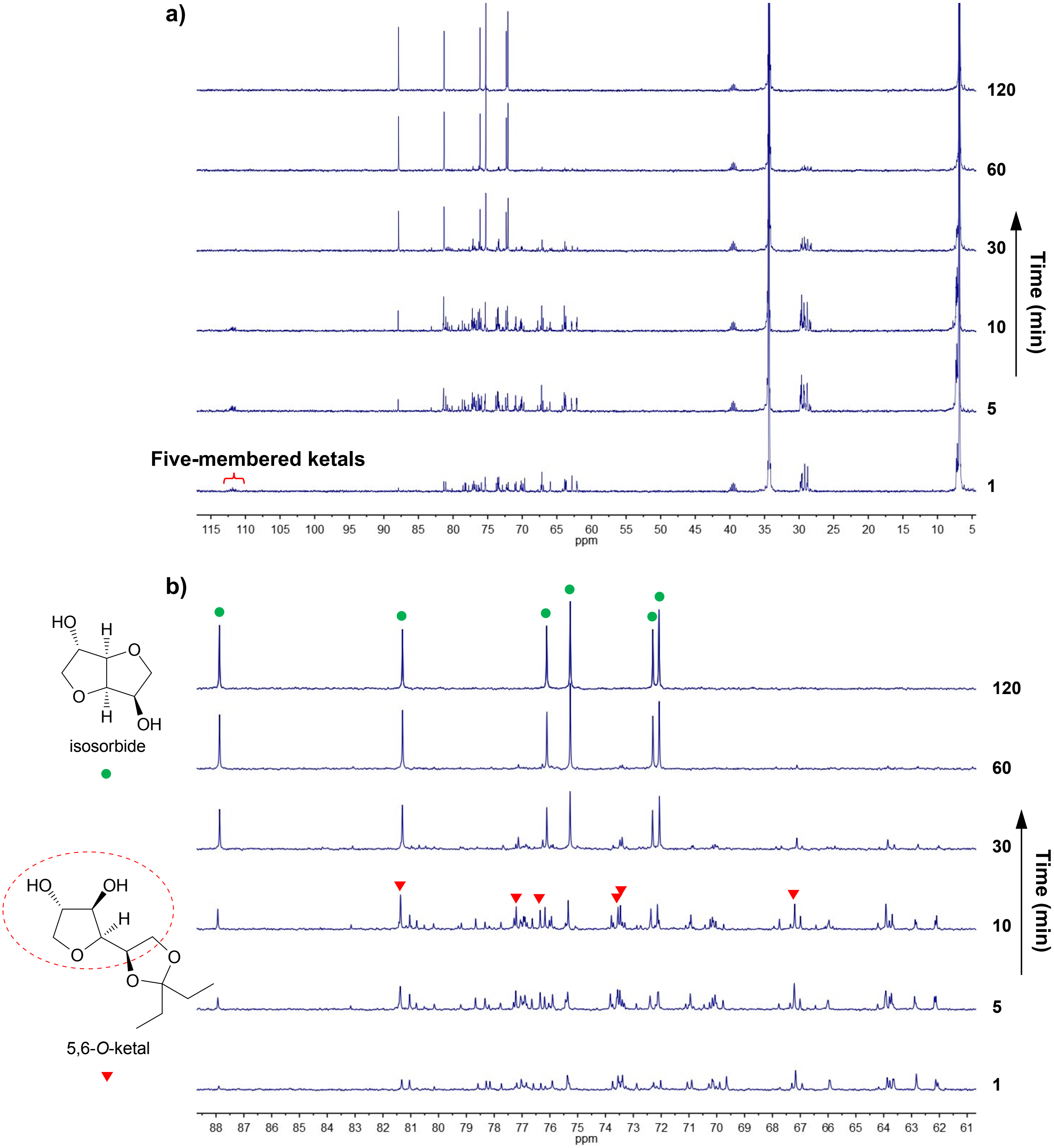


**Figure S6.** Stack of $^{13}C$ NMR spectra for the conversion of sorbitol in DEK over H-beta(20) with reaction times (DEK layer), under conditions in Figure 2a: (a) $^{13}C$ NMR spectra and (b) enlarged $^{13}C$ NMR spectra between 60 and 89 ppm.

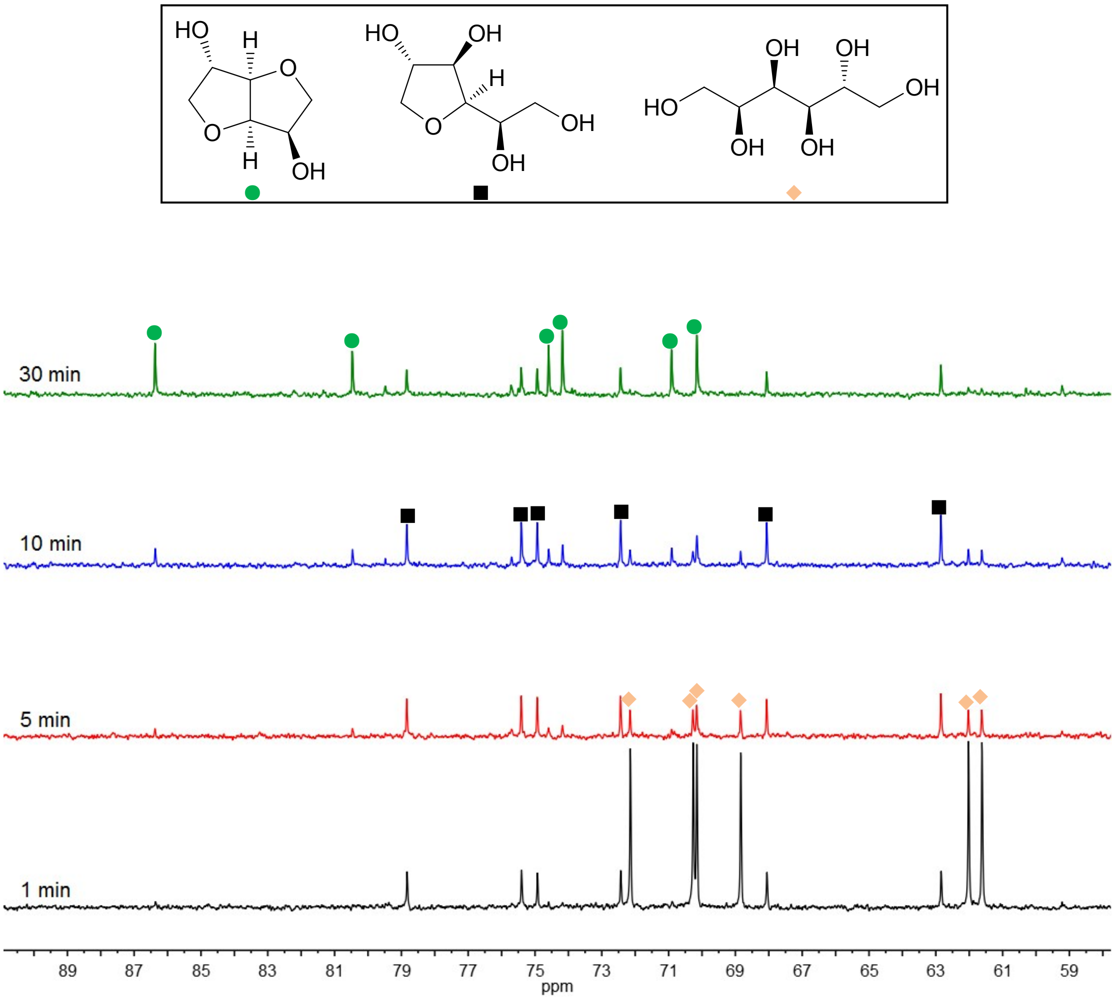


**Figure S7.** Stack of $^{13}$C NMR spectra for the conversion of sorbitol to isosorbide in DEK medium over H-beta(20) with reaction times (bottom layer), under conditions in Figure 2a.

## 7. $^{13}$C NMR spectra for the reaction of C4 sugar-derived polyol in DEK at the initial stage

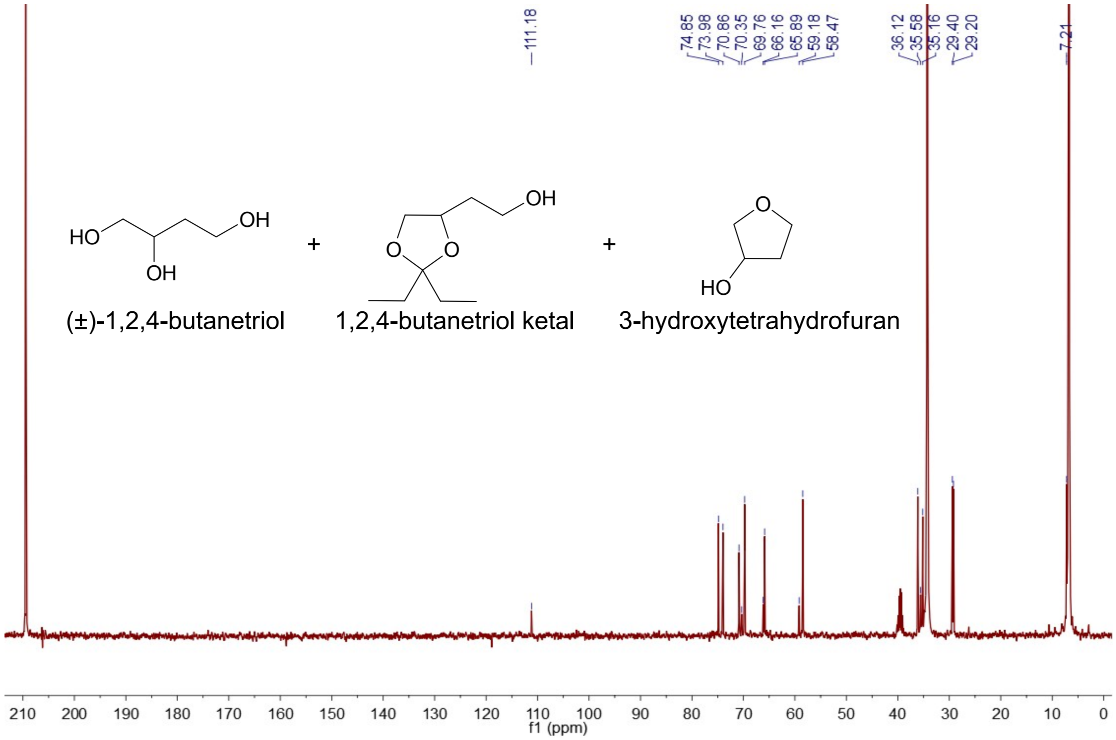


**Figure S8.** $^{13}$C NMR spectrum of the conversion of (±)-1,2,4-butanetriol via DEK over H-beta(20) (DEK layer). Reaction condition: (±)-1,2,4-butanetriol (2 mmol), DEK (4.5 mL), H-beta(20) (0.012 g), 170 $^{o}$C, 1 min.

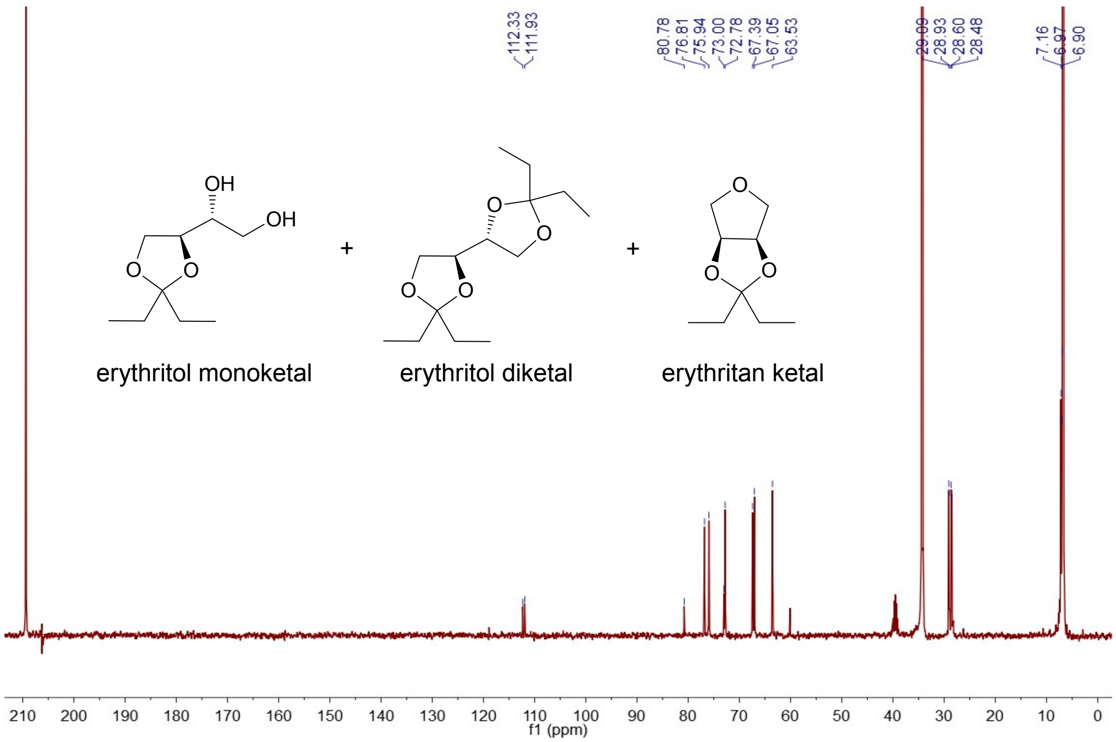


**Figure S9.** $^{13}$C NMR spectrum of the conversion of *meso*-erythritol via DEK over H-beta(20) (DEK layer). Reaction condition: *meso*-erythritol (2 mmol), DEK (4.5 mL), H-beta(20) (0.012 g), 170 $^{o}$C, 1 min.

## 8. Recyclability of catalyst

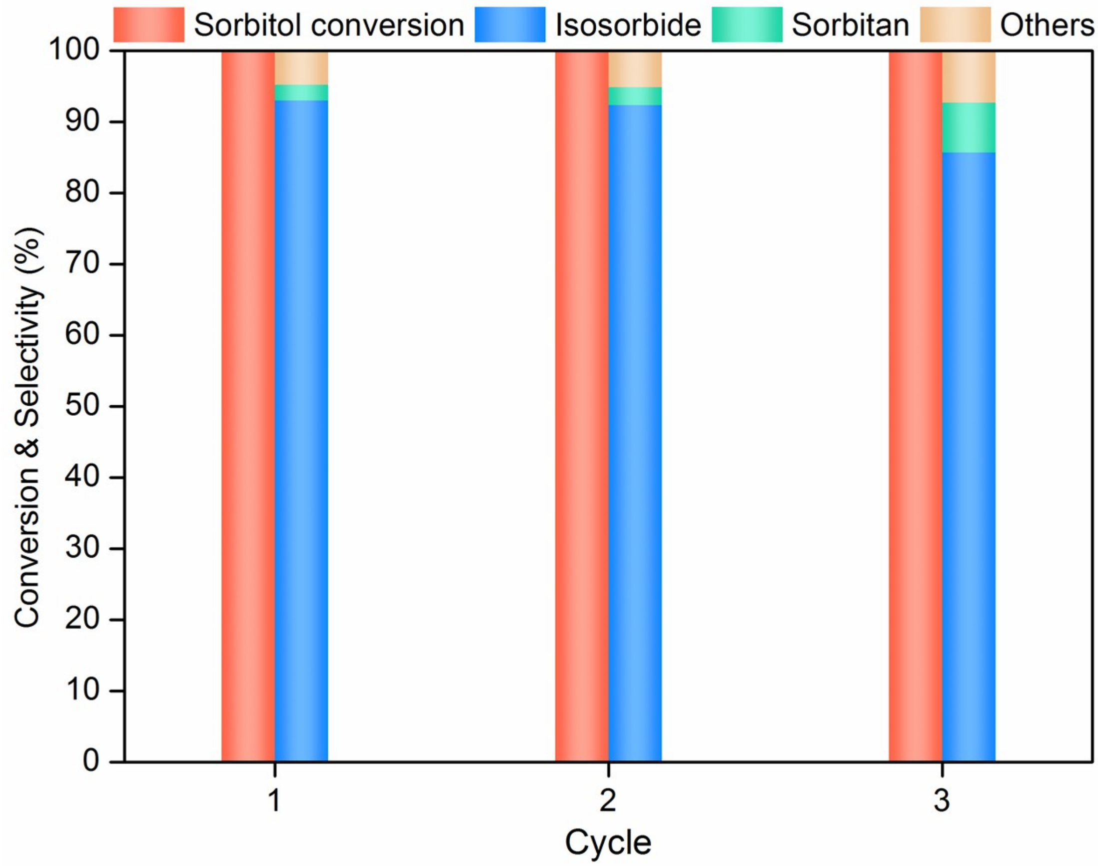
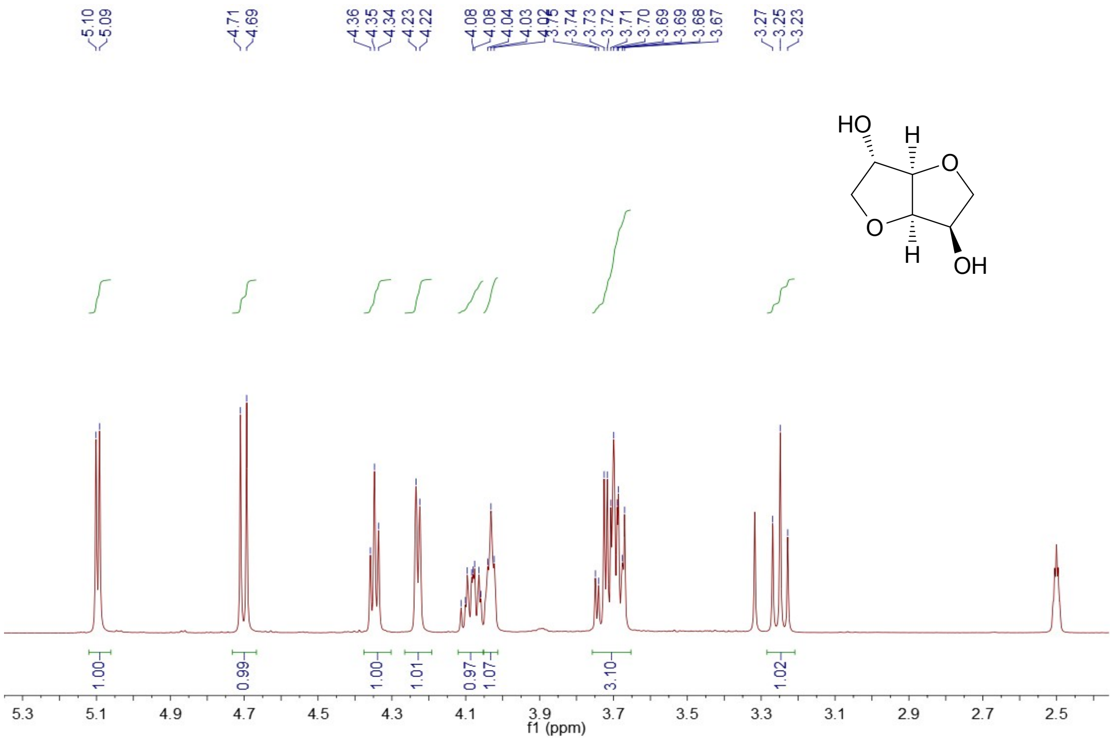
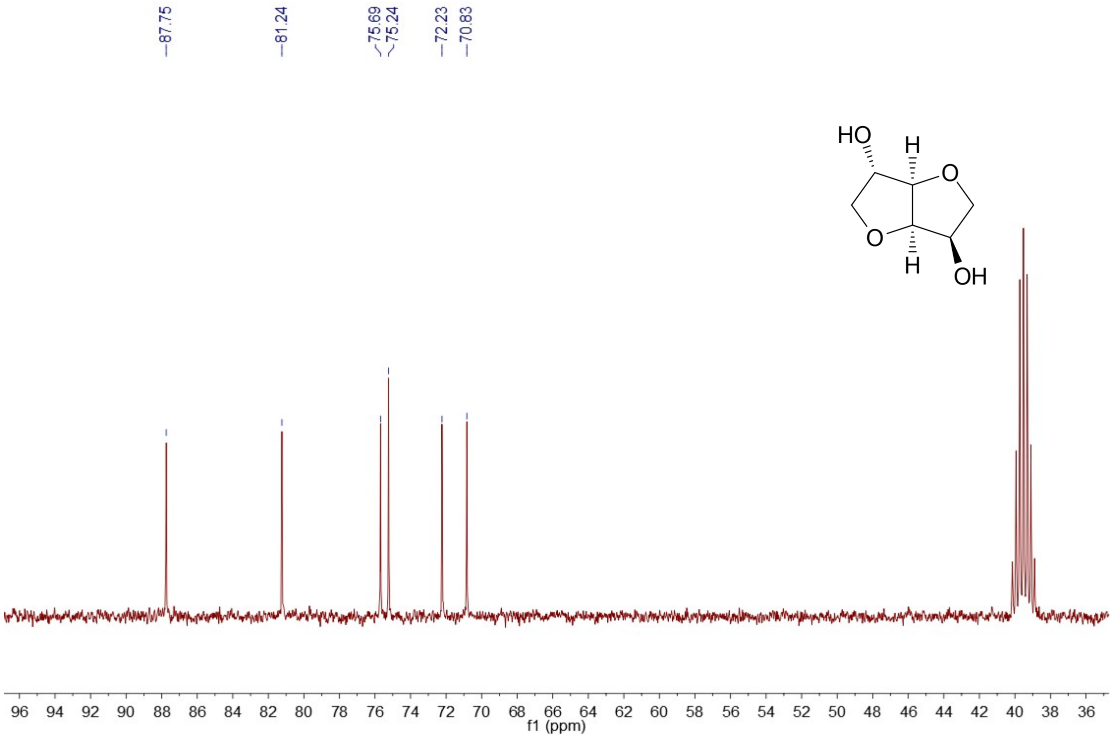


**Figure S10.** Recycling use of H-beta(20) for the conversion of sorbitol in MIBK. Reaction conditions: sorbitol (2 mmol), H-beta(20) catalyst (0.037 g), MIBK (4.5 mL), 170 $^{o}$C, 2 h.

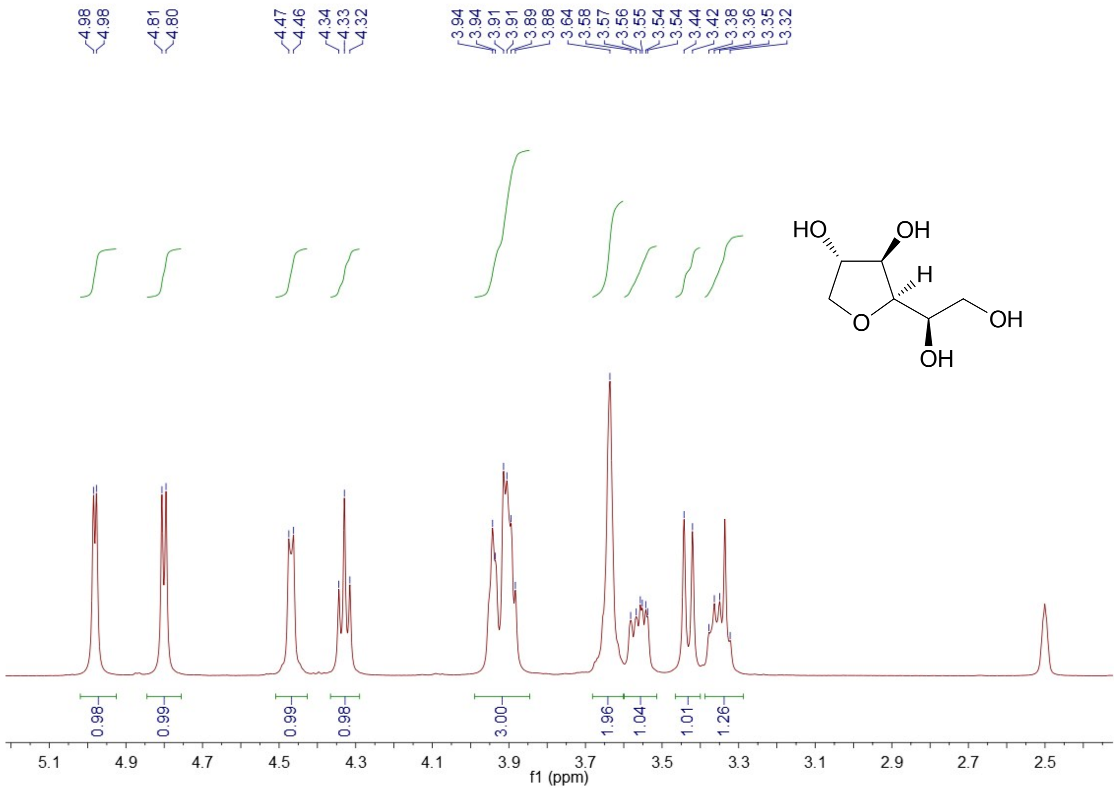
## 9. NMR analysis of purified compounds



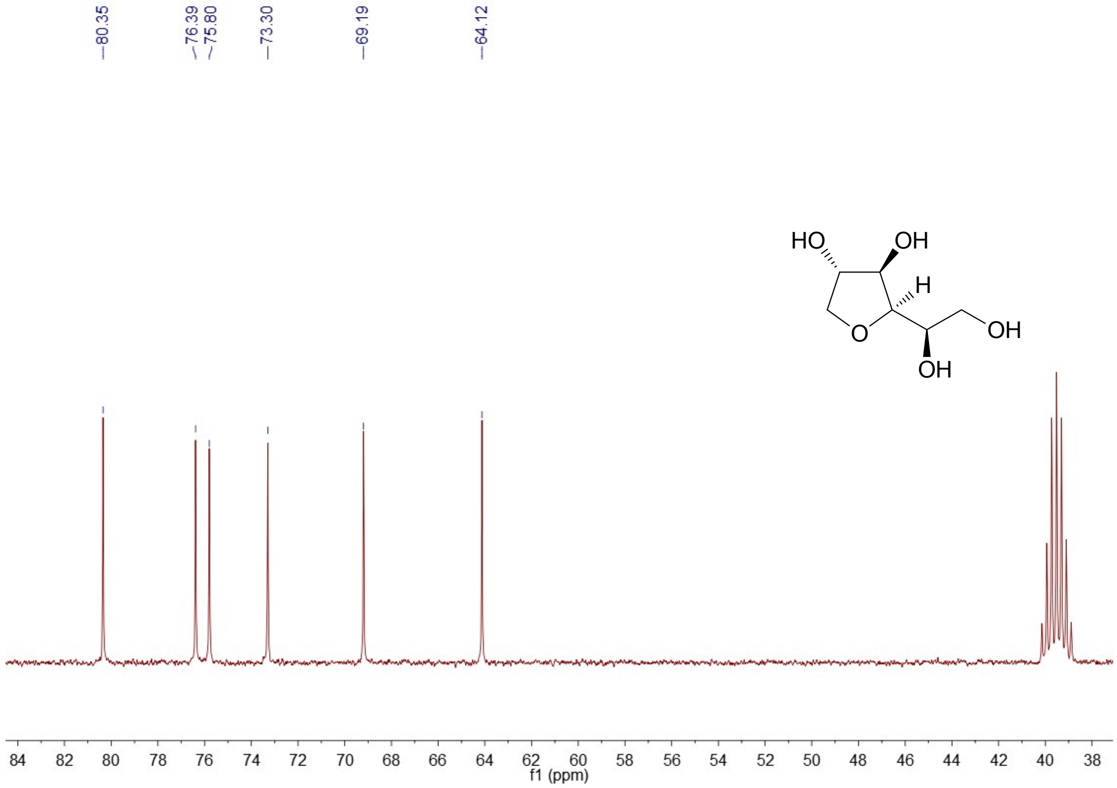
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of **isosorbide** at rt.



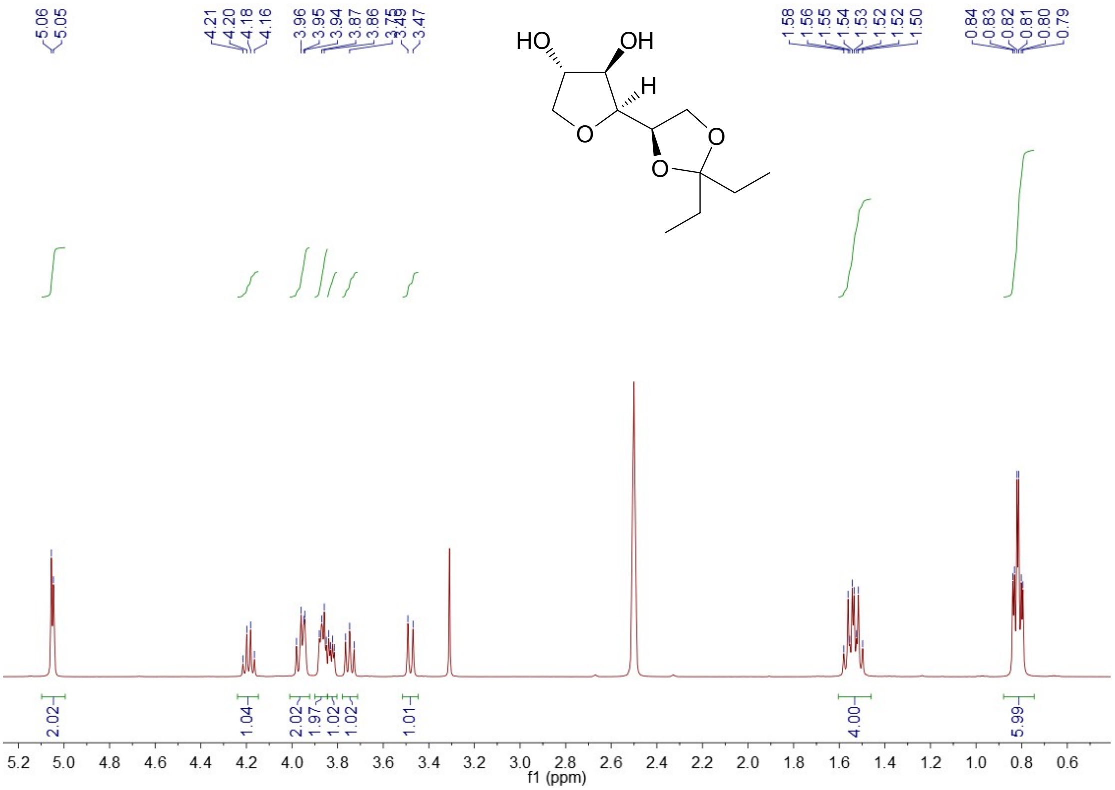
$^{13}$C NMR (101 MHz, DMSO-$d_6$) spectrum of **isosorbide** at rt.



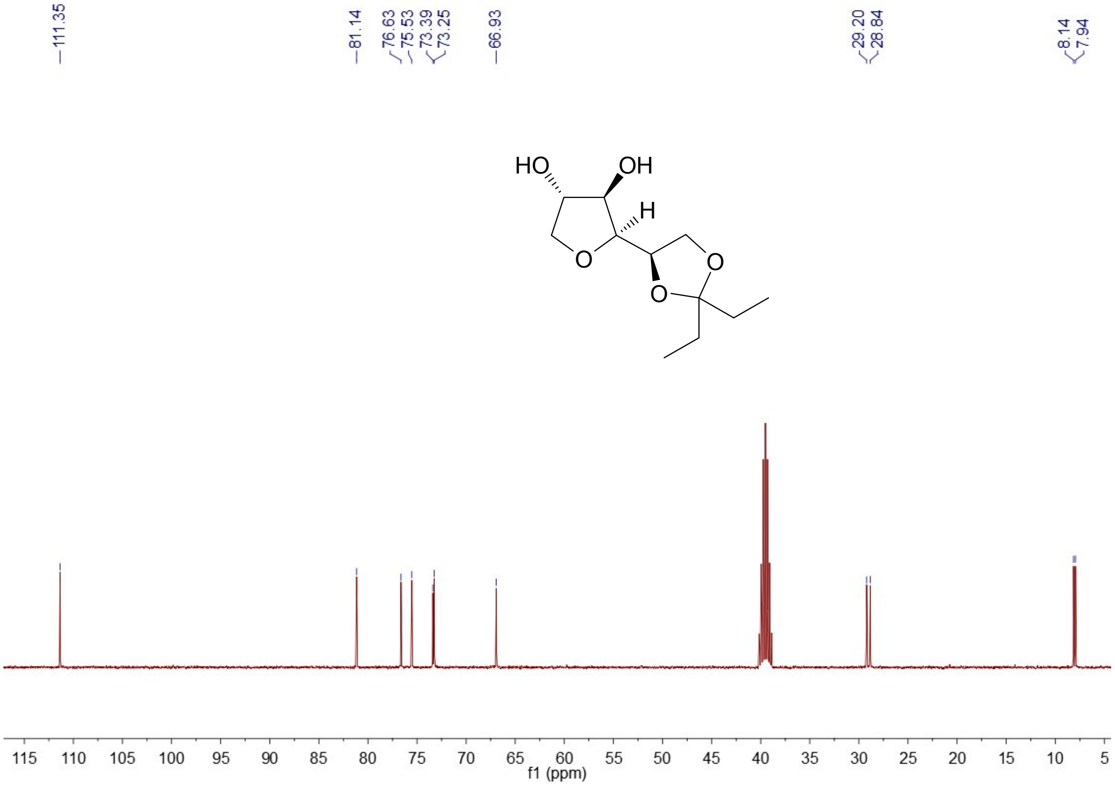
$^{1}$H NMR (400 MHz, DMSO-$d_6$) spectrum of **1,4-sorbitan** at rt.



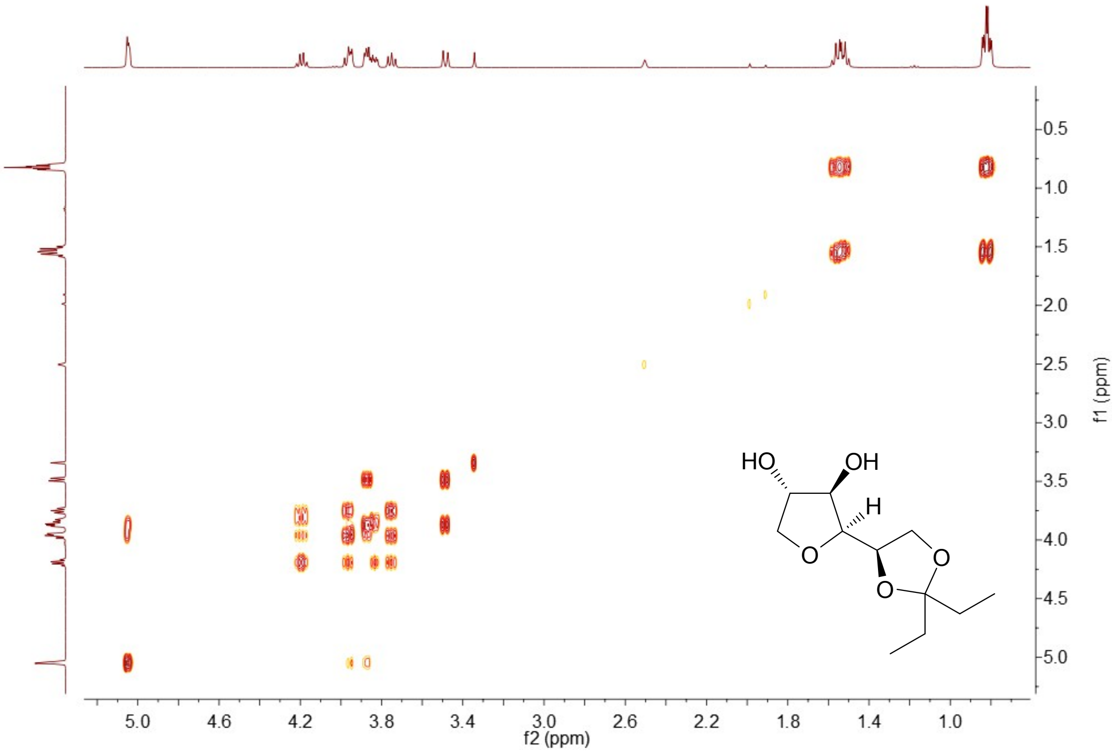
$^{13}$C NMR (101 MHz, DMSO-$d_6$) spectrum of **1,4-sorbitan** at rt.



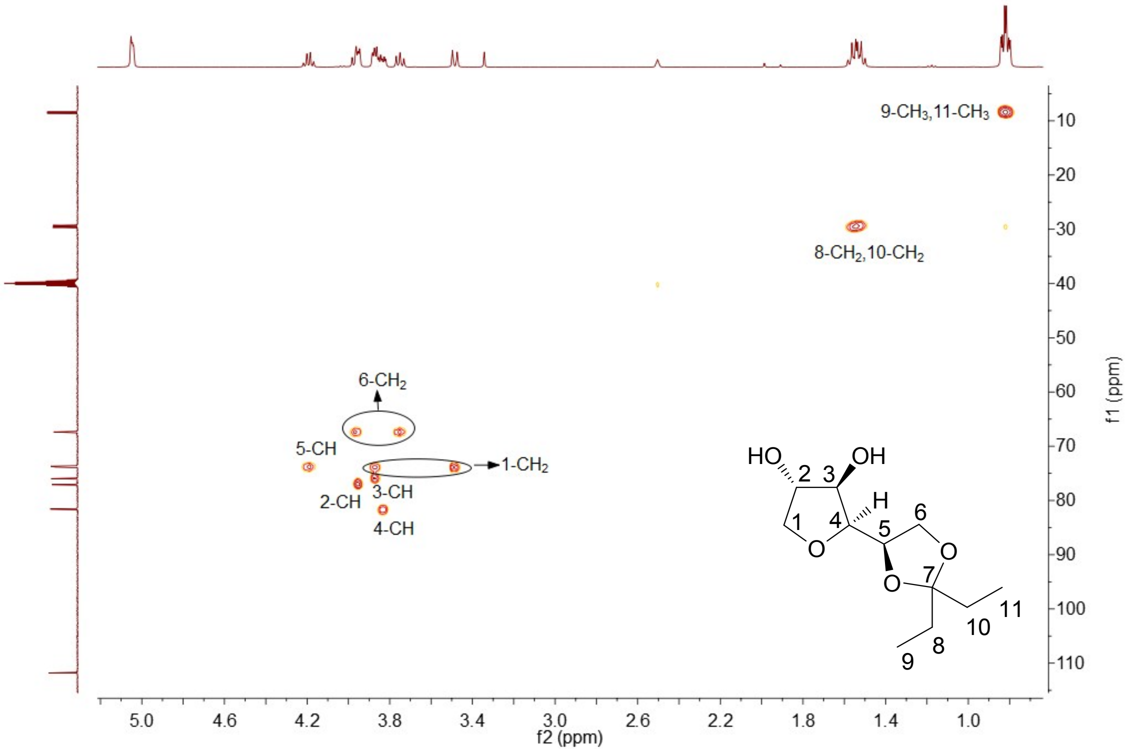
$^{1}$H NMR (400 MHz, DMSO-$d_6$) spectrum of **5,6-*O*-(3-pentylidene)-1,4-sorbitan** at rt.



$^{13}$C NMR (101 MHz, DMSO-$d_6$) spectrum of **5,6-*O*-(3-pentylidene)-1,4-sorbitan** at rt.



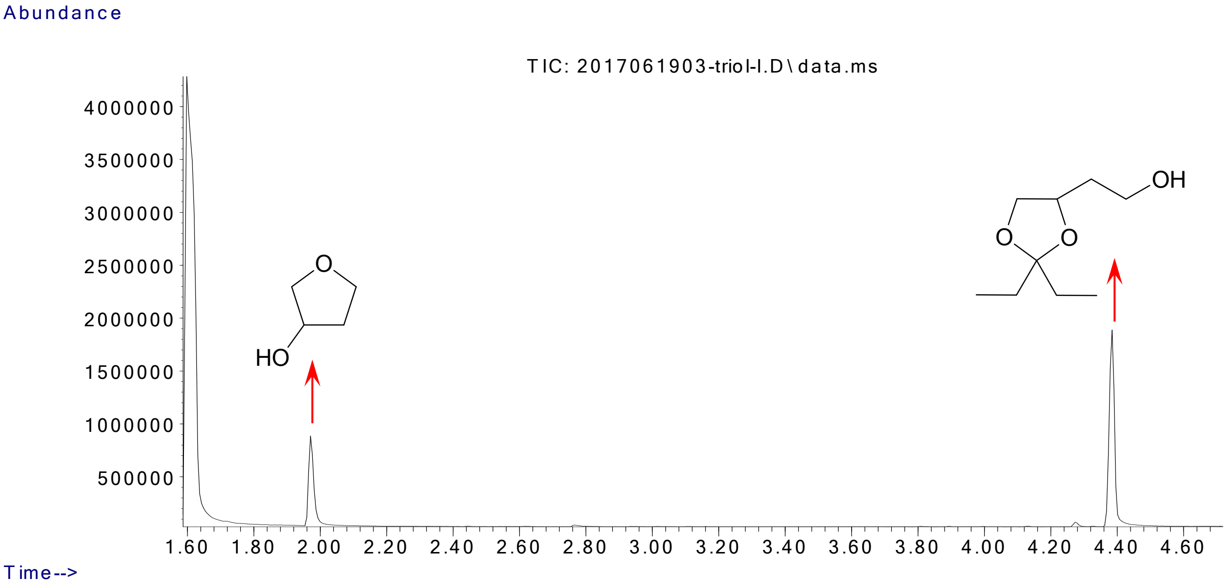
$^1$H-$^1$H COSY NMR spectrum of **5,6-*O*-(3-pentylidene)-1,4-sorbitan** in DMSO-$d_6$ at rt.



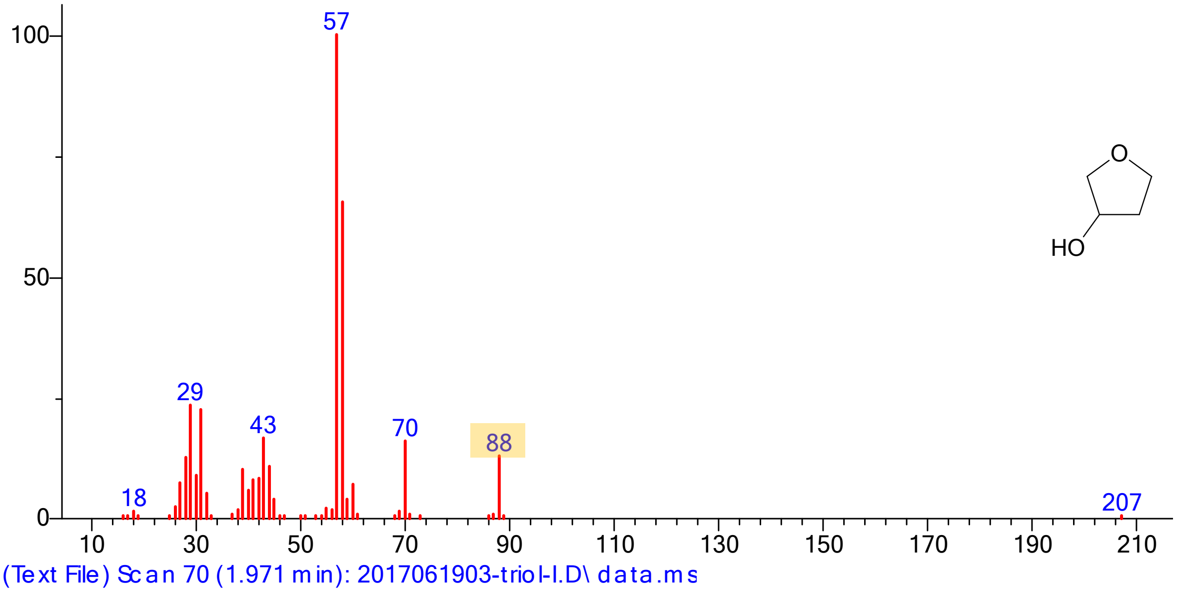
$^1$H-$^{13}$C HSQC NMR spectrum of **5,6-*O*-(3-pentylidene)-1,4-sorbitan** in DMSO-$d_6$ at rt.

## 10. GC-MS analysis of reaction mixture

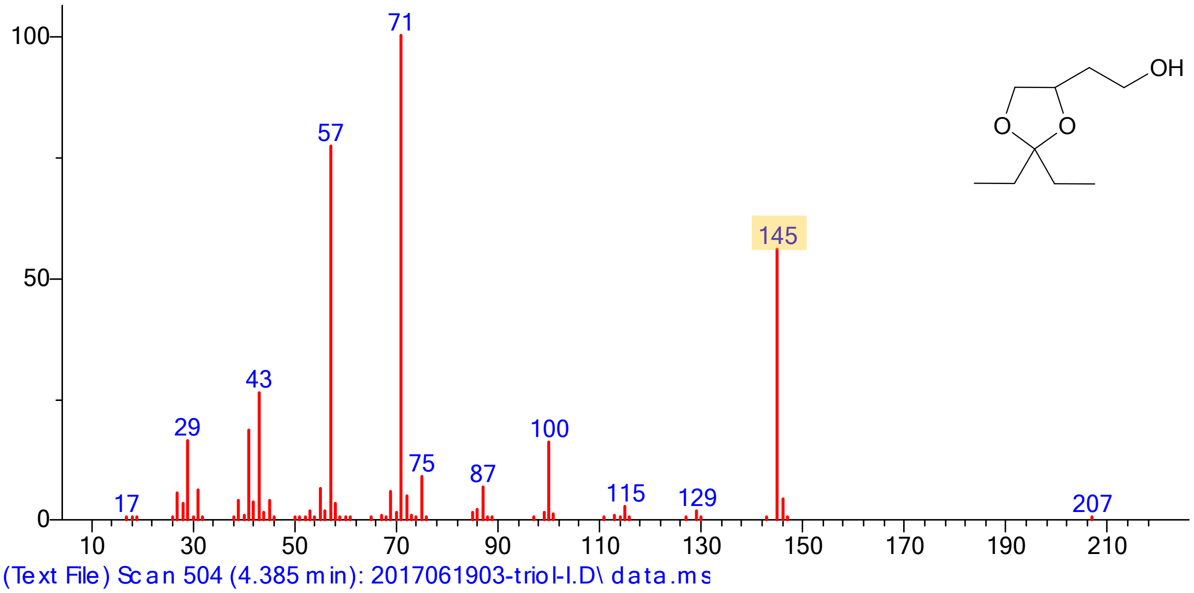
*Reaction of (±)-1,2,4-butanetriol via DEK over H-beta(20)*



Typical total ion chromatogram (TIC) for the conversion of (±)-1,2,4-butanetriol via DEK over H-beta(20).

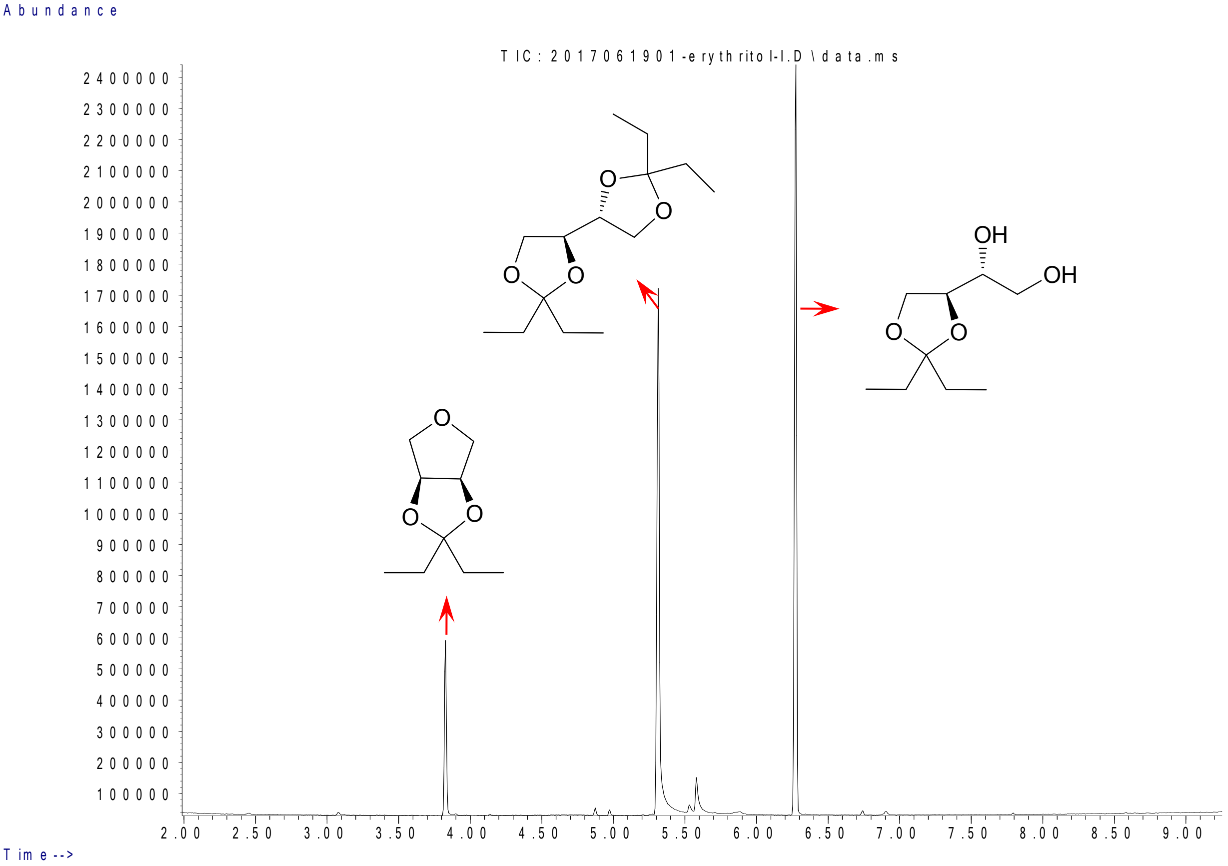


Mass spectrum of 3-hydroxytetrahydrofuran.

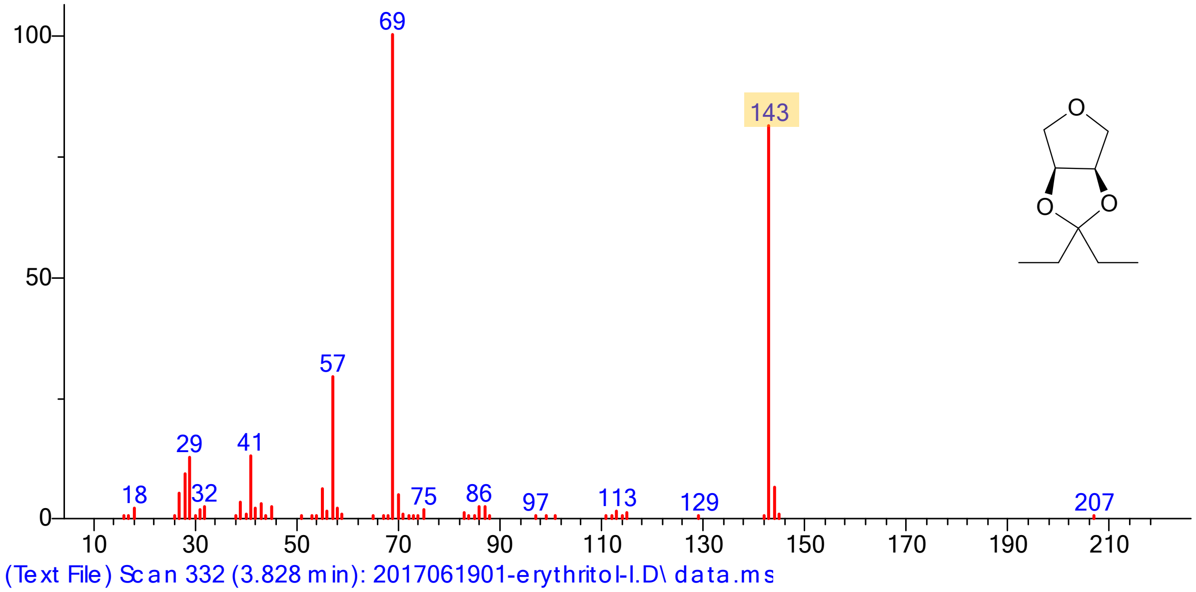


Mass spectrum of five-membered 1,2,4-butanetriol ketal.

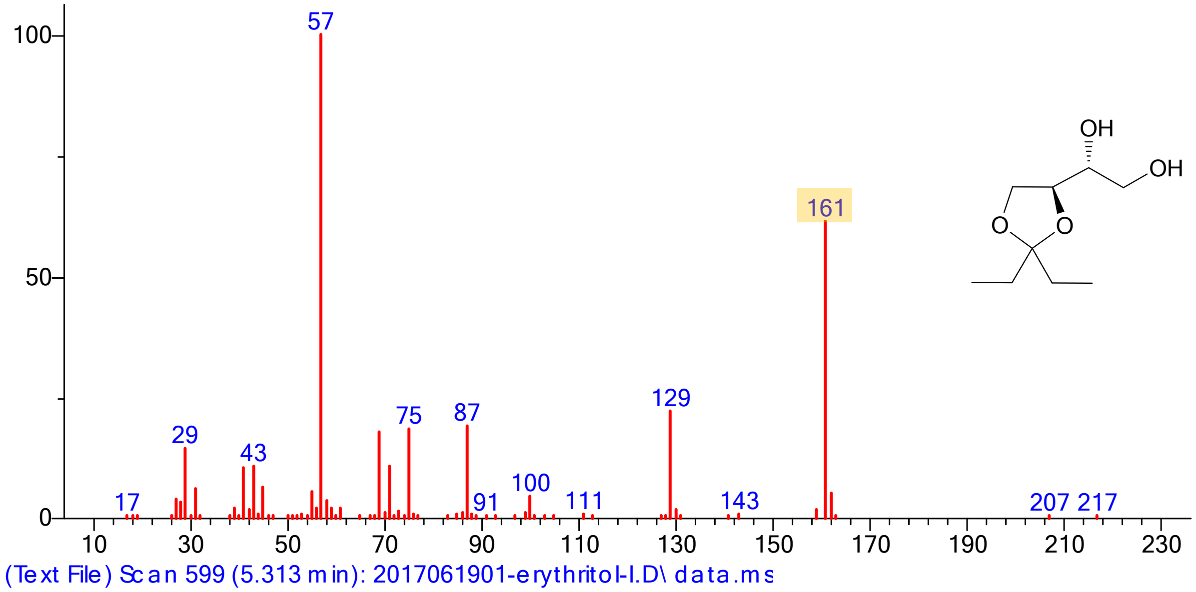
*Reaction of meso-erythritol via DEK over H-beta(20)*



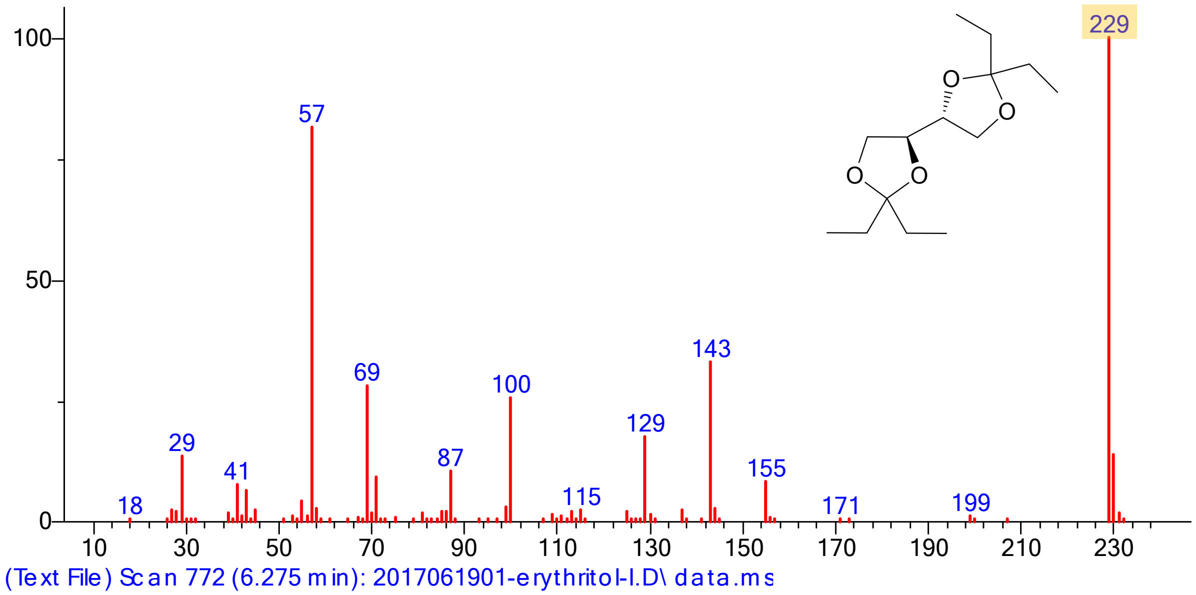
Typical total ion chromatogram (TIC) for the conversion of *meso*-erythritol via DEK over H-beta(20)



Mass spectrum of five-membered 1,4-erythritan ketal.



Mass spectrum of five-membered erythritol monoketal.



Mass spectrum of five-membered erythritol diketal.

## 11. Additional References

1 J. L. Carr, D. A. Offermann, M. D. Holdom, P. Dusart, A. J. P. White, A. J. Beavil, R. J. Leatherbarrow, S. D. Lindell, B. J. Sutton and A. C. Spivey, *Chem. Commun.*, 2010, **46**, 1824-1826.

2 K. Bock, C. Pedersen and H. Thogersen, *Acta Chem. Scand. Ser. B*, 1981, **35**, 441-449.