Electronic Supplementary Information

Hydrogen Bonds Distinction and Activation on Catalytic Etherification of Hydroxyl Compounds

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Materials and Methods

Materials

All chemicals employed here were commercially available with analytical grade purity or better, except isosorbide ethyl ethers and isoidide. Isosorbide (98%) and naphthalene (99%) were available from Alfa Aesar Chemical Co., Ltd. Isomannide (99%) was obtained from HWRK Chemical Engineering Co. Ltd. (China). 5-Hydroxymethylfurfural (99%) was purchased from Sigma-Aldrich Co., Llc. Furfuryl alcohol (98%), tetrahydrofurfuryl alcohol (99%), (*S*)-3-hydroxytetrahydrofuran (98%), and carbon tetrachloride (CCl_4, 99%) were purchased from Aladdin Reagent Inc. (China). Deuterated chloroform ($CDCl_3$, 99.8% D) containing tetramethylsilane (TMS, 0.03% v/v) was available from Cambridge Isotope Laboratories Inc. 12-Tungstosilicic acid ($H_4SiW_{12}O_{40}$) was also supplied by Aladdin Reagent Inc., which was dried at 403 K for 2 h prior to use. Because the authentic samples for isosorbide ethyl ethers and isoidide are not commercial available, pure isoidide was obtained according to the reported procedure,[1] and pure isosorbide ethyl ethers were achieved in our lab (see Purification of isosorbide ethyl ethers section).

Methods

NMR spectra (^1H, ^{13}C and 2D ^1H-^{13}C HMQC) for characterization were recorded on a Bruker Ultrashield 400 Plus NMR spectrometer (^1H at 400 MHz, ^{13}C at 101 MHz) in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Variable-temperature ^1H NMR experiments were performed on a Bruker Ultrashield 400 Plus NMR spectrometer (400 MHz) equipped with a Bruker BVT-3200 temperature controller with an accuracy of ±0.2 K over the temperature range of 263 to 328 K in $CDCl_3$. All measured samples were purified by vacuum distillation or dried over 3 Å molecular sieves followed by vacuum freeze-pump-thaw technique with liquid nitrogen overnight. Ethanol, toluene, $CDCl_3$ and

CCl_4 were stored over activated 3 Å molecular sieves until used. 5 mm NMR tubes, dried on a vacuum line at room temperature overnight, contained the specific amounts of sample in 0.60 mL $CDCl_3$. Temperature was measured with a thermocouple close to the sample. Samples were kept for at least 15 min at a given temperature to stabilize temperature before acquiring ^{1}H NMR data. All chemical shifts were measured with reference to TMS at 0 ppm. An 8-scan ^{1}H NMR spectrum was recorded with typical parameters (the acquisition time of 5.1118 s, the spectral width 6410.3 Hz, a 30^o pulse length, the relaxation delay of 1 s and 65 K data points). The error in ^{1}H chemical shifts was ±0.001 ppm at a given temperature.

FT-IR spectral data was recorded on Bruker Tensor 27 Fourier transform infrared spectrophotometer with a scan number of 8 from 400 to 4000 cm^{-1} having a resolution of 4 cm^{-1} at room temperature. A Bruker KBr window with a 1.0 mm path length was used. All samples were dissolved in dry CCl_4 with concentration of 2.5 mmol L^{-1}.

Column chromatography was performed on silica gel (200-300 mesh) using a gradient mixture of petroleum ether–ethyl acetate as eluent.

Specific optical rotations were measured with an Anion Parr MCP 200 polarimeter. $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}.

Column chromatography was performed on silica gel (200-300 mesh).

All etherification experiments were conducted in a 15 mL stainless steel Teflon-lined autoclave provided with a manometer, automatic temperature controller and a magnetic stirring bar.

General Procedure for the Etherification of Isohexides with Ethanol

Experimental procedure

Competitive etherification of isomannide and isoidide with ethanol: Competitive etherification of isomannide and isoidide with ethanol were conducted in the same reactor, a 15 mL stainless steel Teflon-lined autoclave reactor provided with a manometer, automatic temperature controller and a magnetic stirring bar. Specifically, isomannide (2.40 mmol), isoidide (2.40 mmol), ethanol (2.80 mL), tungstosilicic acid (0.05 mmol) and toluene (2.70 mL) were charged into the autoclave reactor followed by flushing with nitrogen for four times in order to remove air. The etherification reaction was performed at 453 K with a stirring speed of ca. 900 rpm for a chosen reaction time under autogeneous pressure. After the reaction, the reactor was cooled to ambient temperature. Subsequently, the reaction mixture had been neutralized by triethylamine prior to gas chromatography analysis. Each catalytic result at the different time corresponds to a separate experiment.

Etherification of isosorbide with ethanol: The etherification of isosorbide with ethanol was carried out in the autoclave reactor. In a typical procedure, isosorbide (4.80 mmol), ethanol (2.80 mL), tungstosilicic acid (0.05 mmol) and toluene (2.70 mL) were charged into the autoclave reactor followed by flushing with nitrogen for four times in order to remove air. The etherification reaction was performed at 453 K with a stirring speed of ca. 900 rpm for a chosen reaction time under autogeneous pressure. After the reaction, the reactor was cooled to ambient temperature. Subsequently, the reaction mixture had been neutralized by triethylamine prior to gas chromatography analysis. Each catalytic result at the different time corresponds to a separate experiment.

Procedure for product isolation: After the reaction mixture was neutralized by triethylamine, it was then filtrated and condensed under reduced pressure. The residue was extracted by ethyl ether, and the organic phase was dried over anhydrous Na_2SO_4 followed by rotary evaporation. The obtained viscous brown liquid was partially separated by distillation under reduced pressure. Then, the enriched distillation fractions were subjected to column chromatography eluted with a gradient mixture of petroleum ether - ethyl acetate (2/1 to 1/2, *v/v*) on silica gel. Finally, pure monoethers (2- and 5-*O*-monoethyl isosorbide) and diether (diethyl isosorbide) were obtained as colorless liquids.

Analysis of reaction products

The testing liquid reaction mixture neutralized by triethylamine was analyzed offline by a gas chromatography, Agilent 7890, equipped with a flame ionization detector and a HP-INNOWAX capillary column (30.0 m × 320 μm × 0.5 μm) under the following oven temperature program with splitless injection:

$$50\ ^{\circ}\mathrm{C} \xrightarrow{40\ ^{\circ}\mathrm{C/min}} 120\ ^{\circ}\mathrm{C} \xrightarrow{15\ ^{\circ}\mathrm{C/min}} 250\ ^{\circ}\mathrm{C} \xrightarrow{5\ \mathrm{min}} 250\ ^{\circ}\mathrm{C}$$

The identification of reaction products was performed on a gas chromatograph-mass spectrometry (Agilent 7890A GC/5975C MS) with a HP-5MS capillary column (30.0 m × 250 μm × 0.25 μm) and electrospray ionization mode by comparison with retention time and mass spectra of authentic samples. The isosorbide ethyl ether products were also ascertained by ^1H, ^{13}C and HMQC NMR.

2-*O*-Monoethyl Isosorbide (2-MEI): $[\alpha]_D^{20}$ +55.6 (*c* 1 in MeOH); ^1H NMR (400 MHz; $CDCl_3$; Me_4Si): δ 4.61 (t, J = 5.0 Hz, 1H, H-4), 4.46 (d, J = 4.5 Hz, 1H, H-3), 4.32–4.22 (m, 1H, H-5), 4.02 (t, J = 7.7 Hz, 2H, H-1, H-2), 3.92–3.81 (m, 2H, H-1, H-6), 3.61–3.51 (m, 3H, H-6 isosorbide, CH_2O-C-2), 2.69 (d, J = 7.1 Hz, 1H, OH), 1.21 ppm (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$; Me_4Si): δ 86.12 (C-3), 84.09 (C-2), 81.83 (C-4), 73.75

(C-1), 73.63 (C-6), 72.35 (C-5), 65.29 (CH_2), 15.43 ppm (CH_3); MS (70 eV): *m/z* 174 (M^+, 24%), 114 (48), 86 (27), 69 (100), 58 (22), 44 (62).

5-*O*-Monoethyl Isosorbide (5-MEI): $[\alpha]_D^{20}$ +103.5 (*c* 1, in MeOH); ^1H NMR (400 MHz; $CDCl_3$; Me_4Si): δ 4.69 (t, *J* = 4.3 Hz, 1H, H-4), 4.45 (d, *J* = 4.1 Hz, 1H, H-3), 4.32 (s, 1H, H-2), 4.06–3.97 (m, 2H, H-5, H-1), 3.97–3.87 (m, 2H, H-1, H-6), 3.74 (dq, *J* = 9.1, 7.0 Hz, 1H, CH_2O-C-5), 3.61–3.48 (m, 2H, H-6, CH_2O-C-5), 2.20 (d, *J* = 3.2 Hz, 1H, OH), 1.25 ppm (t, *J* = 7.0 Hz, 3H, CH_3); ^{13}C NMR (101 MHz; $CDCl_3$; Me_4Si): δ 88.42 (C-3), 80.38 (C-5), 80.21 (C-4), 77.01 (C-2), 76.09 (C-1), 70.21 (C-6), 66.36 (CH_2), 15.50 ppm (CH_3); MS (70 eV): *m/z* 174 (M^+, 15%), 114 (8), 88 (31), 72 (100), 58 (19), 44 (66).

Diethyl Isosorbide (DEI): $[\alpha]_D^{20}$ +95.9 (*c* 1, in MeOH); ^1H NMR (400 MHz; $CDCl_3$; Me_4Si): δ 4.63 (t, *J* = 4.2 Hz, 1H, H-4), 4.51 (d, *J* = 4.1 Hz, 1H, H-3), 4.06–3.90 (m, 5H, H-1, H-2, H-5, H-6), 3.80–3.69 (m, 1H, CH_2-OC-5), 3.63–3.49 (m, 4H, H-6, CH_2-OC-5, CH_2-OC-2), 1.23 ppm (dt, *J* = 17.8, 7.0 Hz, 6H, CH_3CH_2O-C-2, CH_3CH_2O-C-5); ^{13}C NMR (101 MHz; $CDCl_3$; Me_4Si): δ 86.57 (C-3), 84.45 (C-2), 80.36 (C-5), 80.27 (C-4), 73.64 (C-1), 69.81 (C-6), 66.28 (CH_2-O-C-5), 65.24 (CH_2-O-C-2), 15.49 ppm (CH_3-CH_2OC-5), 15.44 (CH_3-CH_2OC-2); MS (70 eV): *m/z* 202 (M^+, 6%), 157 (1), 113 (17), 89 (33), 69 (100), 57 (11), 44 (39).

The quantitative results were based on GC internal standard method using naphthalene as internal standard. The results reported here as conversion and yields were expressed in mol%, based on the total isohexides intake. Yields of monoethyl isomannide and monoethyl isoidide were determined assuming the same FID response factor as the pure 2-*O*-monoethyl isosorbide due to their isomeric relationships. Likewise, yields of diethyl isomannide and diethyl isoidide were estimated with assumption of the same FID response factor as the pure diethyl isosorbide.

The isohexides conversion, yields of 2-*O*-monoethyl isosorbide (2-MEI), 5-*O*-monoethyl isosorbide (5-MEI) and diethyl isosorbide (DEI) were calculated as follows:

$$\text{Isohexides conversion (mol\%)} = \left(1 - \frac{\text{moles of unreacted isohexides}}{\text{moles of starting isohexides}}\right) \times 100\%$$

$$\text{2-MEI yield (mol\%)} = \frac{\text{moles of formed 2-MEI}}{\text{moles of starting isosorbide}} \times 100\%$$

$$\text{5-MEI yield (mol\%)} = \frac{\text{moles of formed 5-MEI}}{\text{moles of starting isosorbide}} \times 100\%$$

$$\text{DEI yield (mol\%)} = \frac{\text{moles of formed DEI}}{\text{moles of starting isosorbide}} \times 100\%$$

In this work, the turnover frequency (TOF) for isohexides conversion is calculated as moles of isohexides converted per mole of catalyst ($H_4SiW_{12}O_{40}$: six moles of hydrate water were confirmed to each mole of $H_4SiW_{12}O_{40}$ by thermogravimetric analysis.) per hour in the initial 10 min.

Variable-temperature ^{1}H NMR Spectra of Sugar-derived Alcohols

Isosorbide bears two nonequivalent hydroxyl groups on the C2 and C5 positions in an *exo*-*endo* configuration. Especially, the *endo*-configured C5-OH is involved in an intramolecular hydrogen bond with the oxygen atom of the neighboring tetrahydrofuran ring,[2] whereas the *exo*-configured C2-OH can only form intermolecular hydrogen bond in $CDCl_3$. The proton resonances of C5-OH and C2-OH of isosorbide were attributed by comparison of the coupling constant ^3J (CH, OH) of OH groups of isosorbide with the OH groups of isomannide due to the dependence of ^3J (CH, OH) on the dihedral H-O-C-H angle.[2] The vicinal coupling constants ^3J (CH,OH) of C5-OH proton is 7.0 Hz (Figure S1) in accordance with that of OH protons (7.2 Hz) in isomannide (Figure S4), which has hydroxyl groups in exclusive *endo*-configuration, whereas ^3J (CH, OH) is 4.8 Hz for C2-OH proton in accordance with that of OH protons (4.3 Hz) in isoidide (Figure S6), which has hydroxyl groups in exclusive *exo*-configuration.

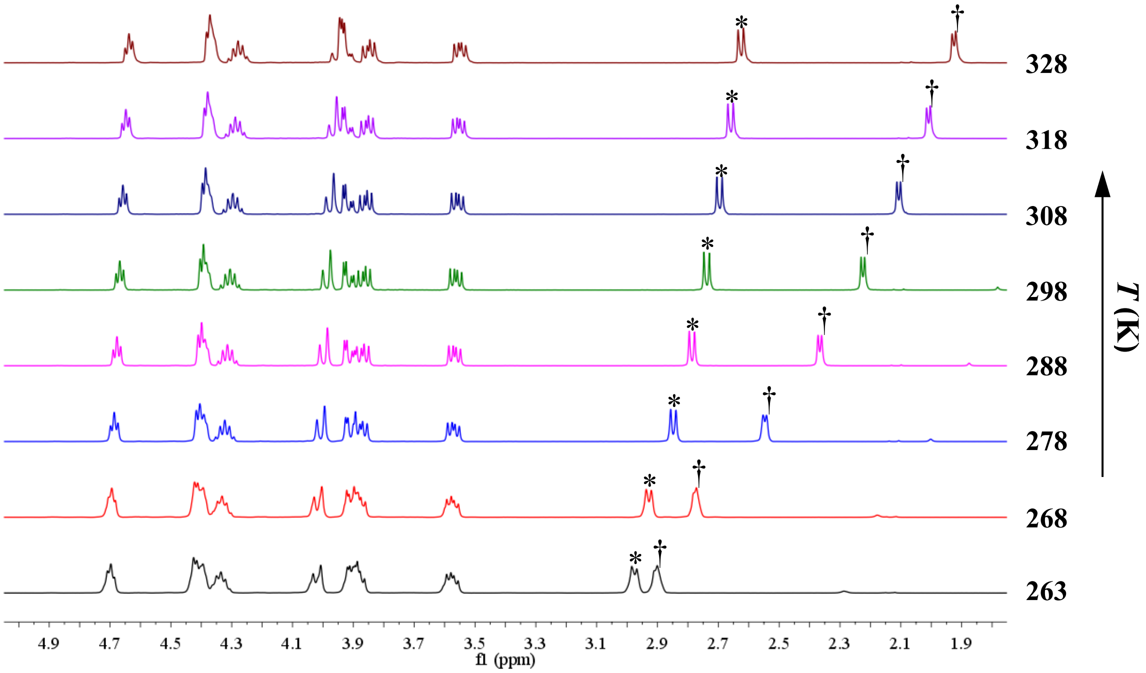


Figure S1. Variable-temperature 1H NMR spectra of 0.13 mol L^{-1} CDCl3 solution of isosorbide (400 MHz). The C5-OH signal is labeled with *, and C2-OH signal is labeled with †.

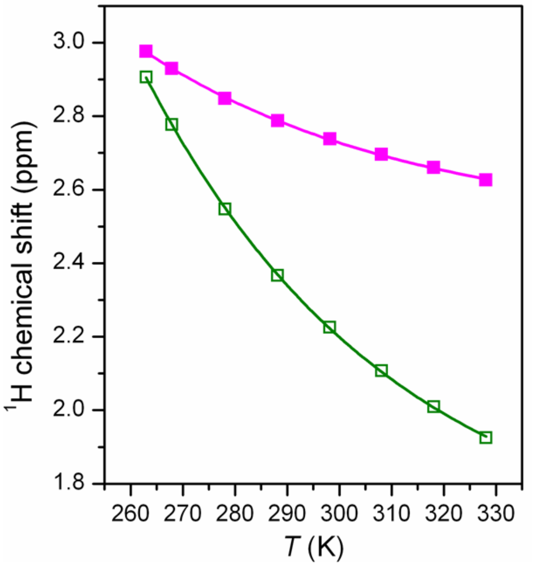


Figure S2. Temperature dependences for the proton chemical shifts of the C5-OH (solid square) and C2-OH (open square) of isosorbide in CDCl$_3$. The solid lines represent non-linear curve fits.

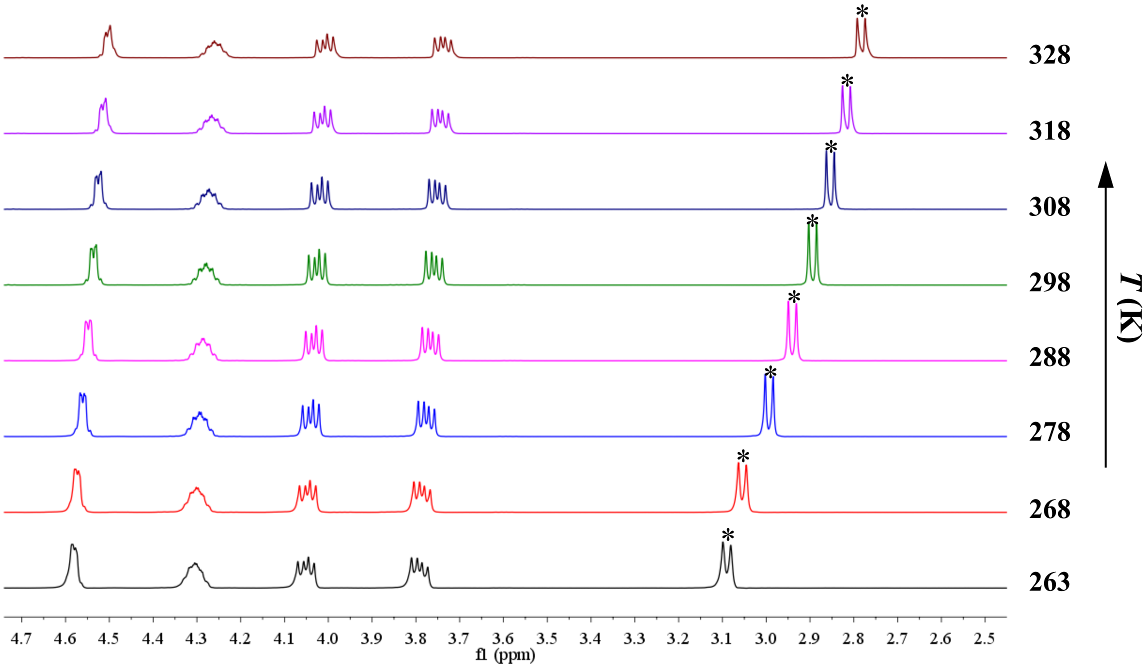


Figure S3. Variable-temperature ^{1}H NMR spectra of 0.13 mol L^{-1} CDCl$_3$ solution of isomannide (400 MHz). The OH signal is labeled with *.

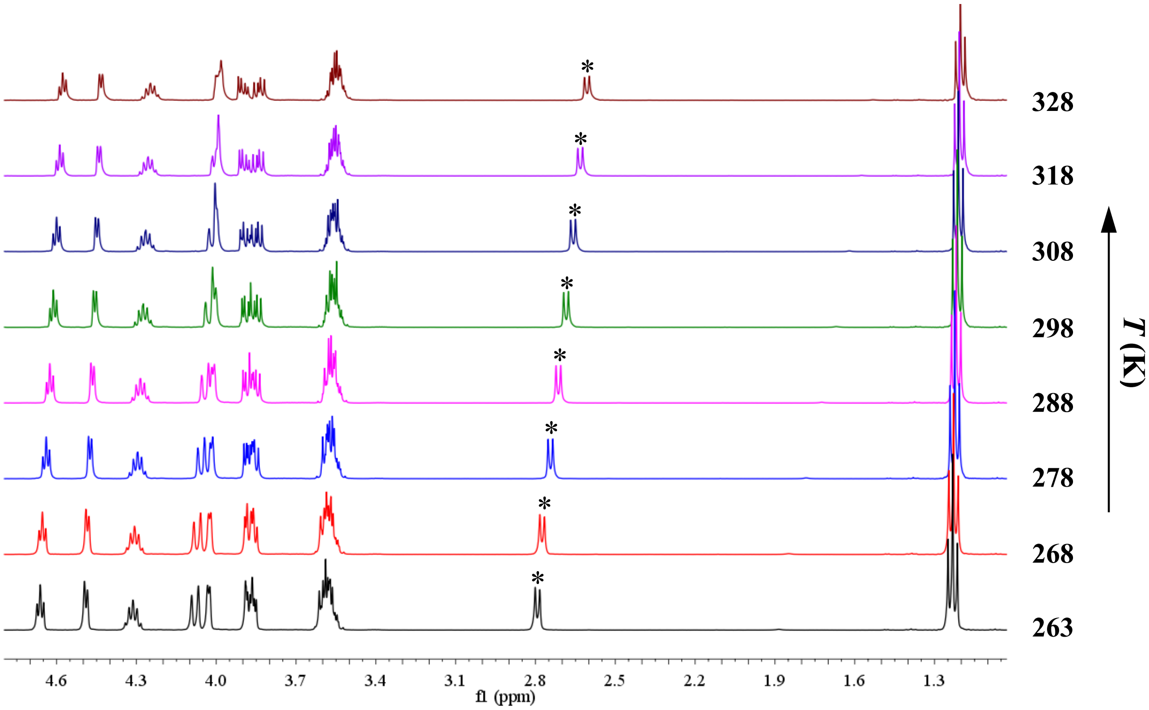


Figure S4. Variable-temperature ^{1}H NMR spectra of 0.13 mol L^{-1} CDCl$_3$ solution of 2-*O*-monoethyl isosorbide (400 MHz). The C5-OH signal is labeled with *.

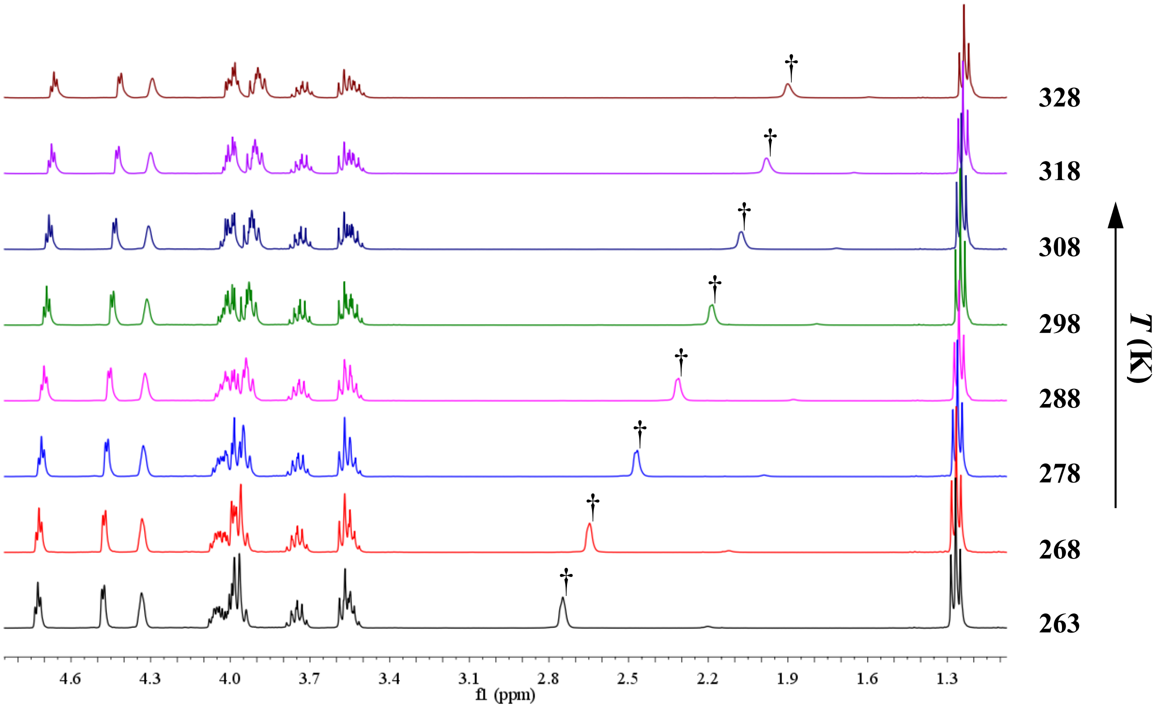


Figure S5. Variable-temperature ^{1}H NMR spectra of 0.13 mol L^{-1} CDCl$_3$ solution of 5-*O*-monoethyl isosorbide (400 MHz). The OH signal is labeled with †.

The variable-temperature ^{1}H NMR experiment for isoidide can be performed by decreasing the concentration to 0.02 mol L^{-1}, due to its poor solubility in $CDCl_3$. Within the investigated concentration, it can be ensured that the OH protons of isoidide are involved in the intermolecular hydrogen bonds among solute molecules.

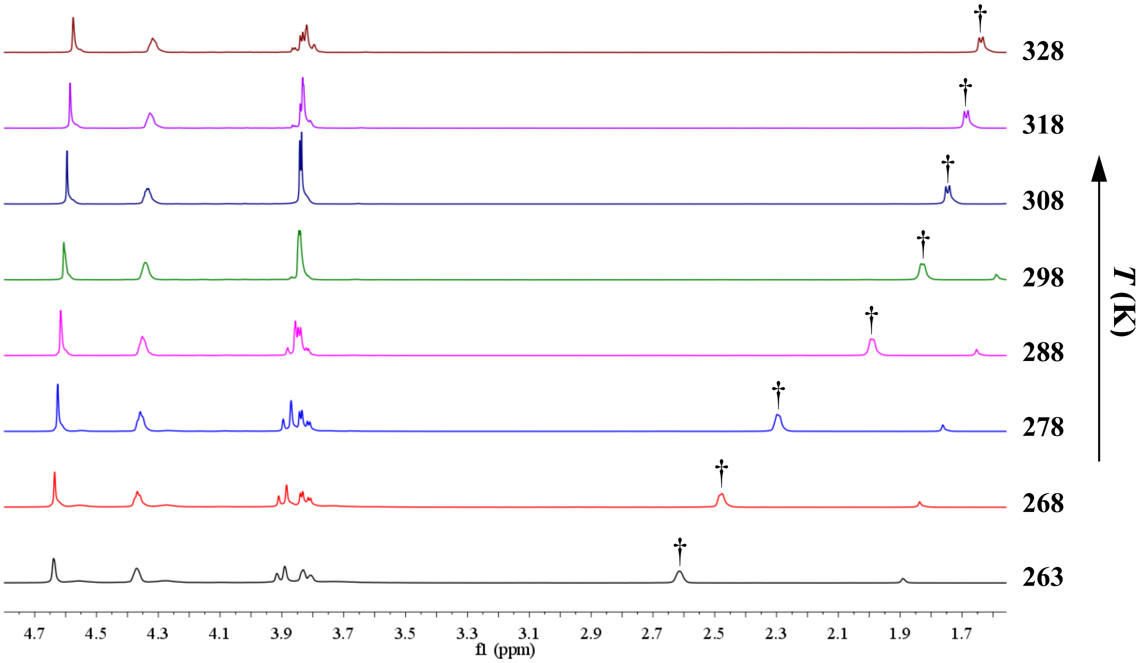


Figure S6. Variable-temperature ^{1}H NMR spectra of 0.02 mol L^{-1} $CDCl_3$ solution of isoidide (400 MHz). The OH signal is labeled with †.

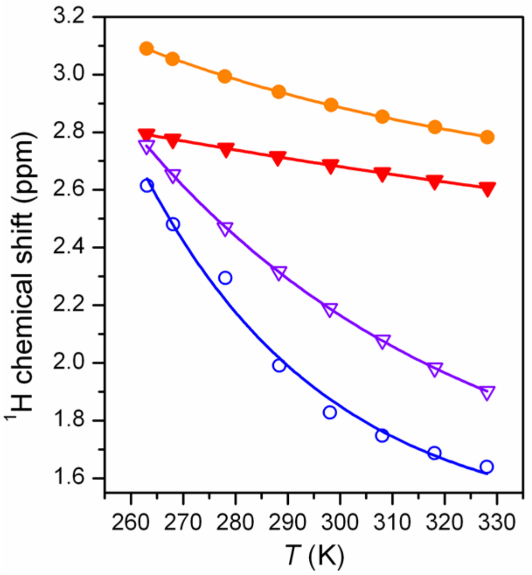


Figure S7. Temperature dependences for the chemical shifts of the OH protons in isomannide (solid circle), 2-*O*-monoethyl isosorbide (solid down-triangle), 5-*O*-monoethyl isosorbide (open down-triangle) and isoidide (open circle) in $CDCl_3$. The solid lines represent non-linear curve fits.

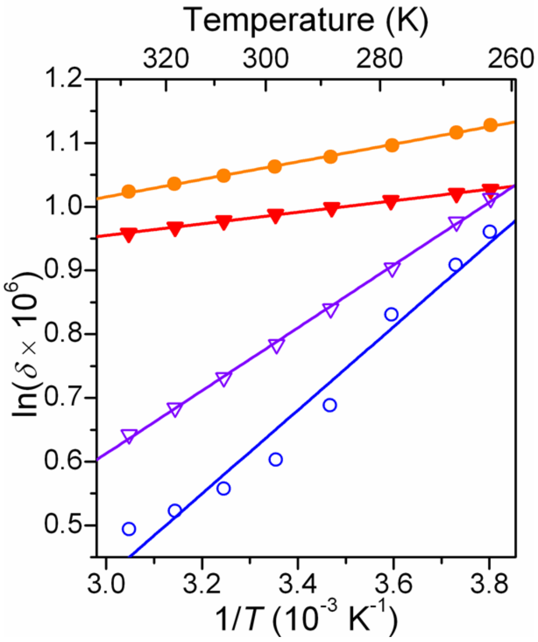


Figure S8. Plots of lnδ of OH protons versus $1/T$ for isomannide (solid circle), 2-*O*-monoethyl isosorbide (solid down-triangle), 5-*O*-monoethyl isosorbide (open down-triangle) and isoidide (open circle) in $CDCl_3$. The solid symbols correspond to OH with intramolecular H-bonds, while the open ones are OH with intermolecular H-bonds. The solid lines represent linear fits ($R^2 > 0.9$) (Table S2).

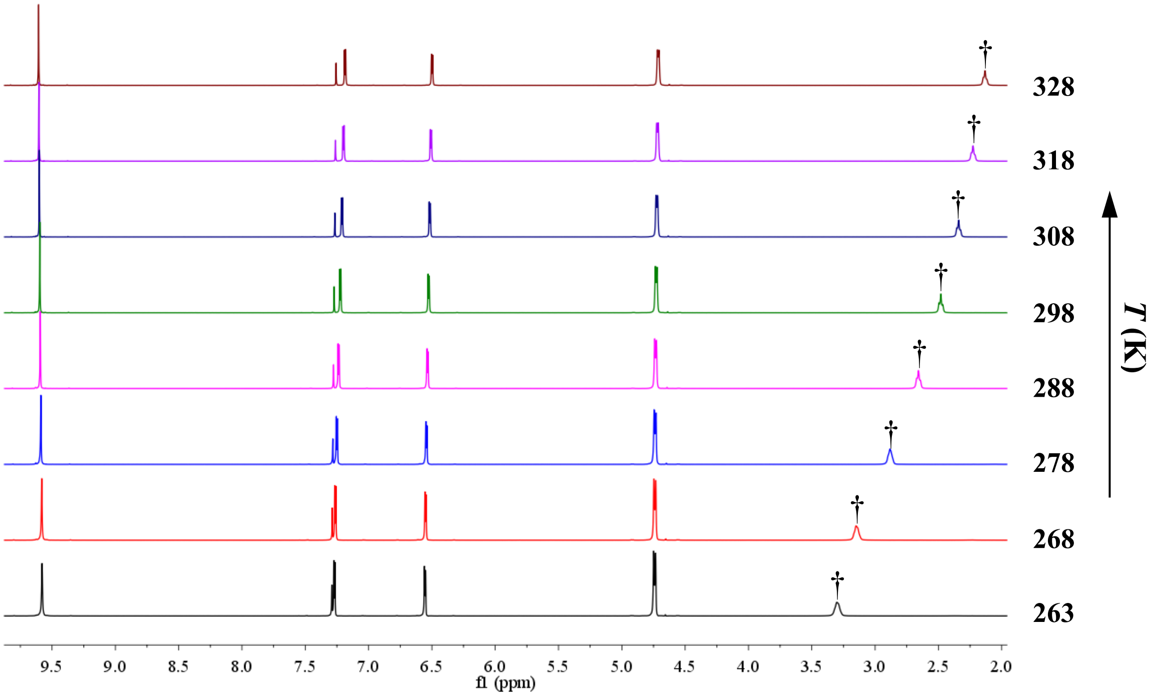


Figure S9. Variable-temperature ^{1}H NMR spectra of 0.13 mol L^{-1} CDCl$_3$ solution of 5-hydroxymethylfurfural (400 MHz). The OH signal is labeled with †.

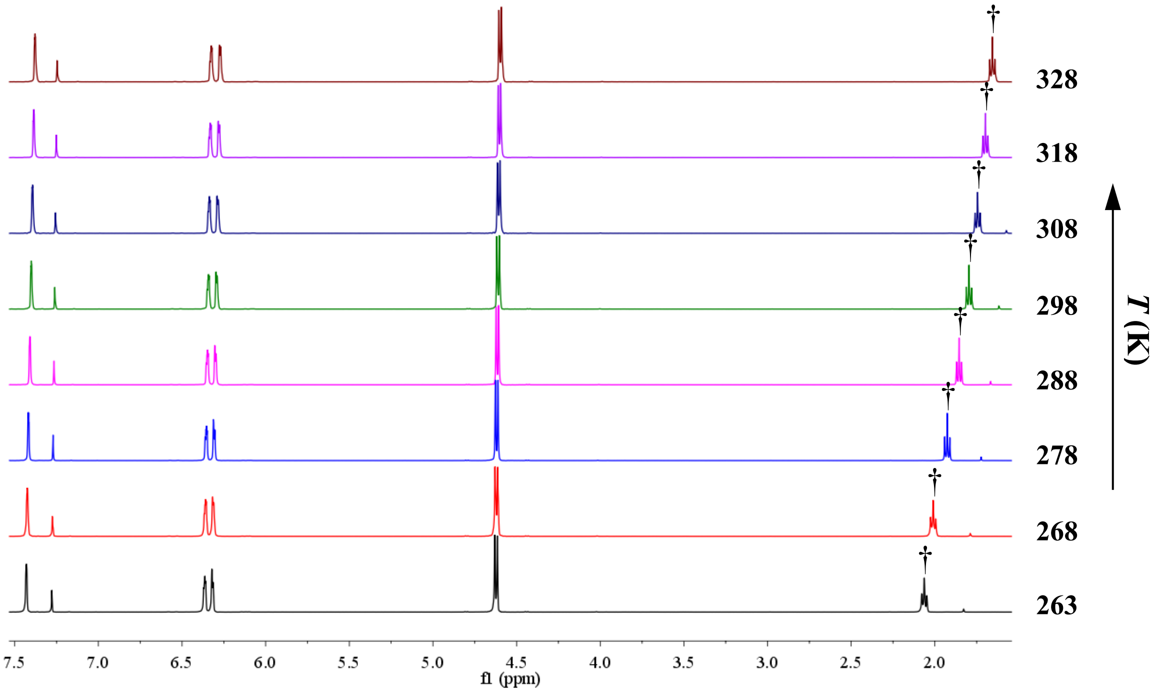


Figure S10. Variable-temperature ^{1}H NMR spectra of 0.13 mol L^{-1} CDCl$_3$ solution of furfuryl alcohol (400 MHz). The OH signal is labeled with †.

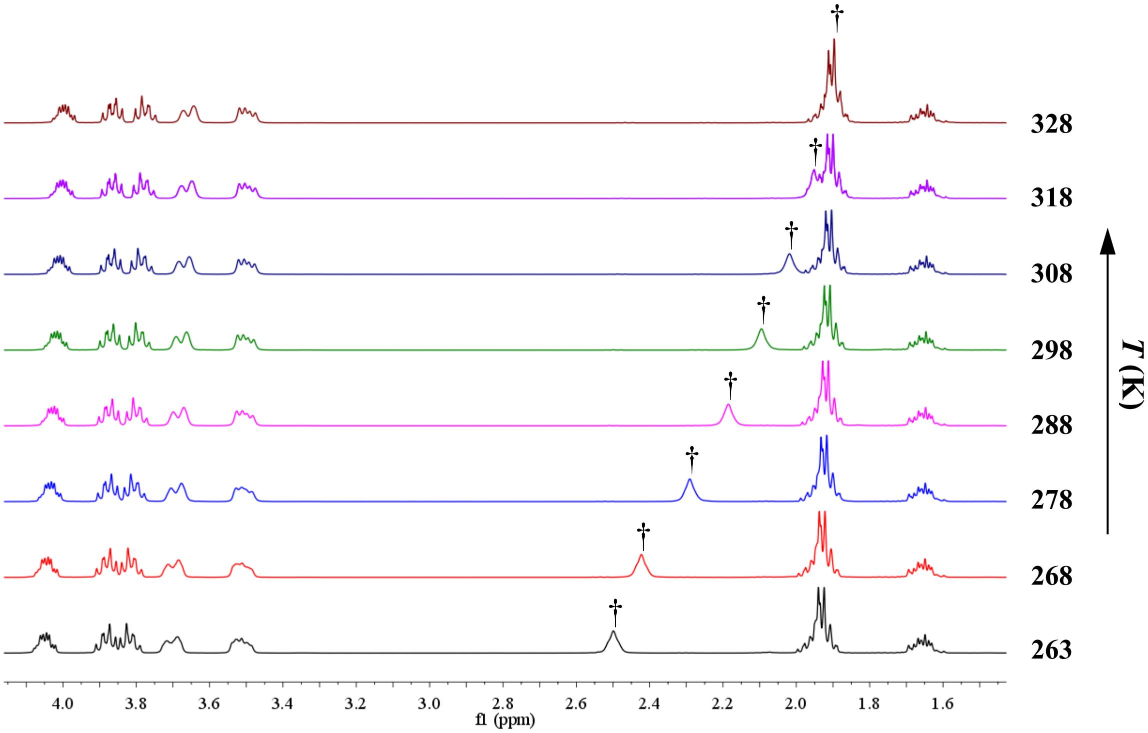


Figure S11. Variable-temperature ^1H NMR spectra of 0.13 mol L^{-1} $CDCl_3$ solution of tetrahydrofurfuryl alcohol (400 MHz). The OH signal is labeled with †.

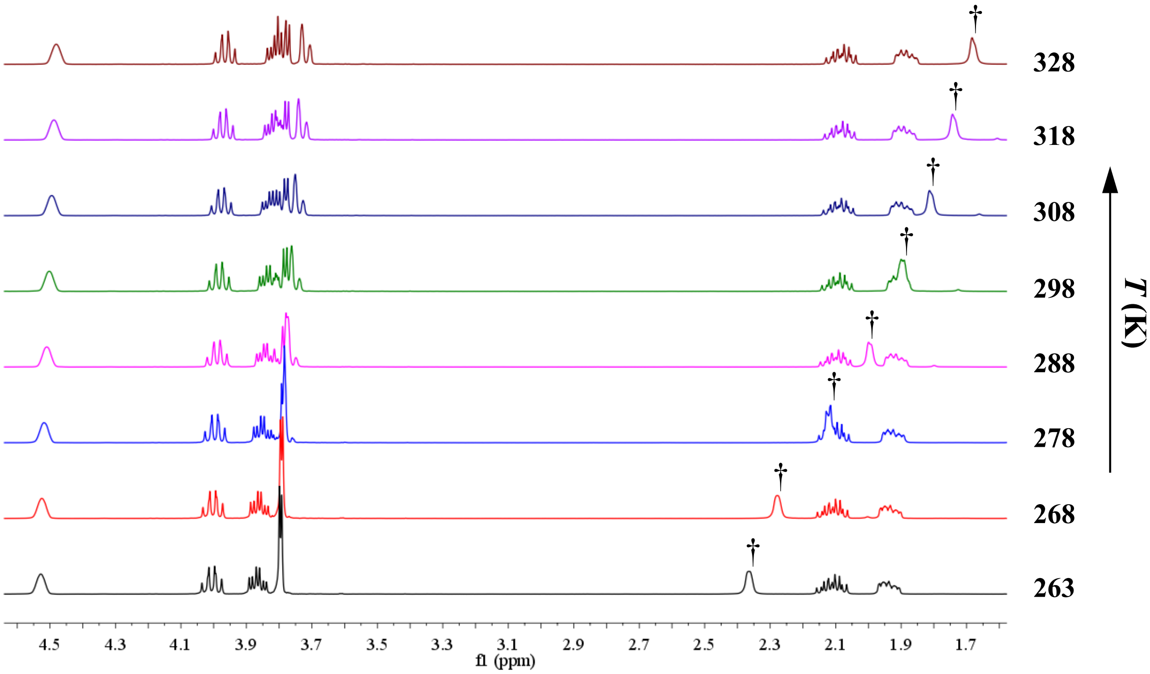


Figure S12. Variable-temperature ^1H NMR spectra of 0.13 mol L^{-1} $CDCl_3$ solution of (*S*)-3-hydroxytetrahydrofuran (400 MHz). The OH signal is labeled with †.

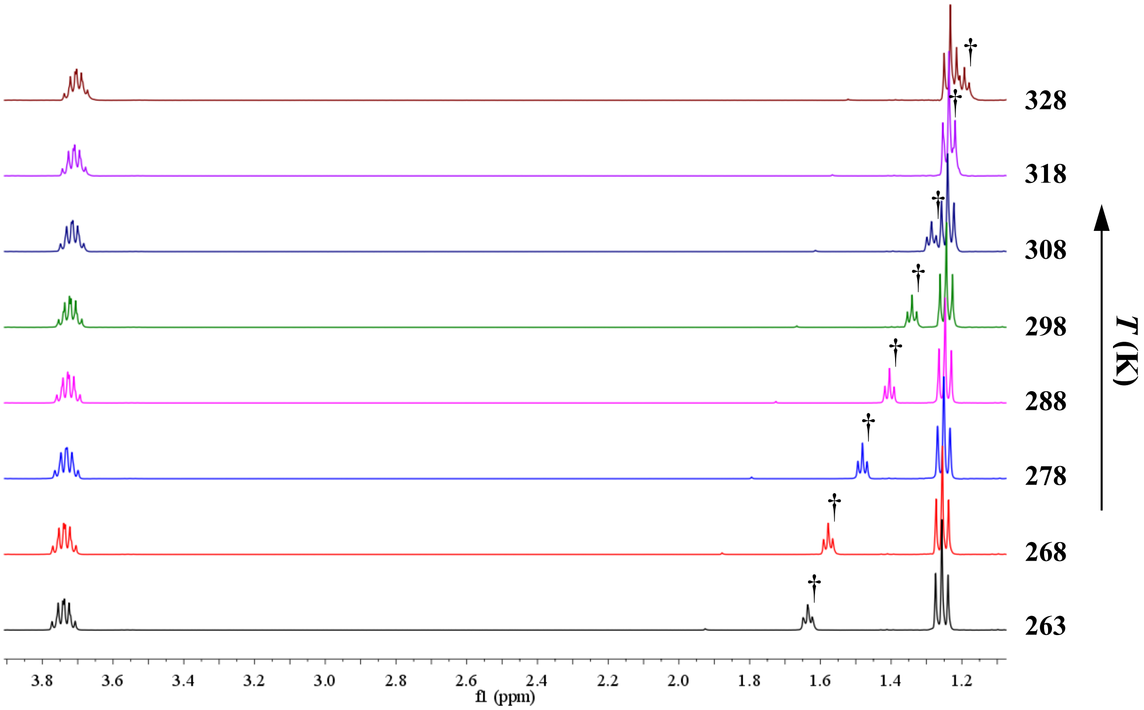


Figure S13. Variable-temperature ^{1}H NMR spectra of 0.13 mol L^{-1} $CDCl_3$ solution of ethanol (400 MHz). The OH signal is labeled with †.

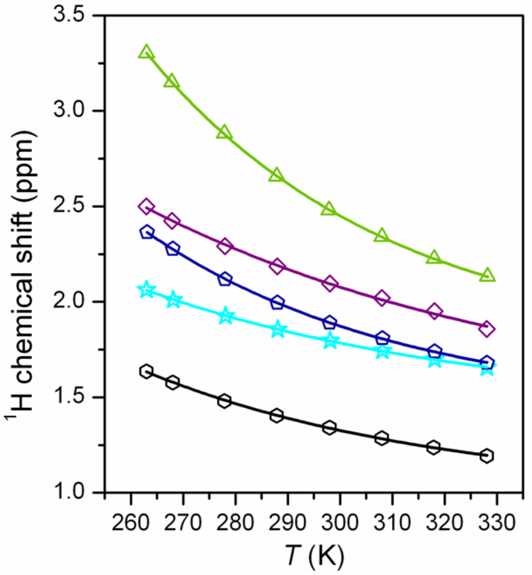


Figure S14. Temperature dependences for the chemical shifts of the OH protons in 5-hydroxymethylfurfural (open up-triangle), furfuryl alcohol (open star), tetrahydrofurfuryl alcohol (open diamond), (*S*)-3-hydroxytetrahydrofuran (open pentagon) and ethanol (open hexagon). The solid lines represent non-linear curve fits.

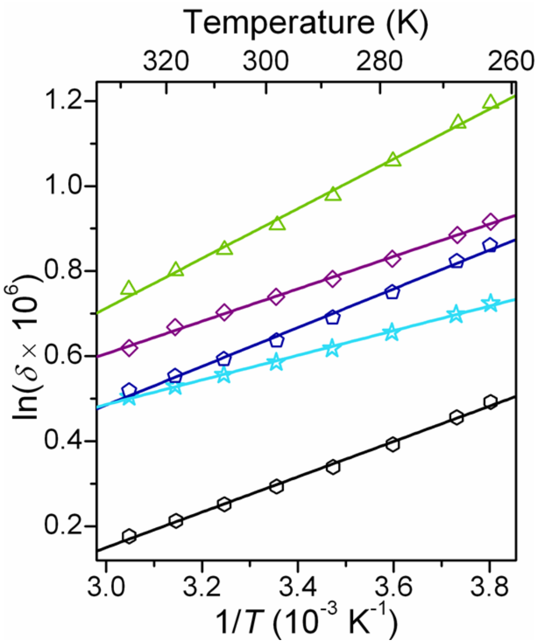


Figure S15. Plots of lnδ of OH protons versus 1/T for 5-hydroxymethylfurfural (open up-triangle), furfuryl alcohol (open star), tetrahydrofurfuryl alcohol (open diamond), (*S*)-3-hydroxytetrahydrofuran (open pentagon) and ethanol (open hexagon). The open ones are OH with intermolecular H-bonds. The solid lines represent linear fits ($R^2 > 0.99$) (Table S2).

Correlation of the Apparent Energy Difference with the Proton Nuclei Resonance Absorption Energy Difference

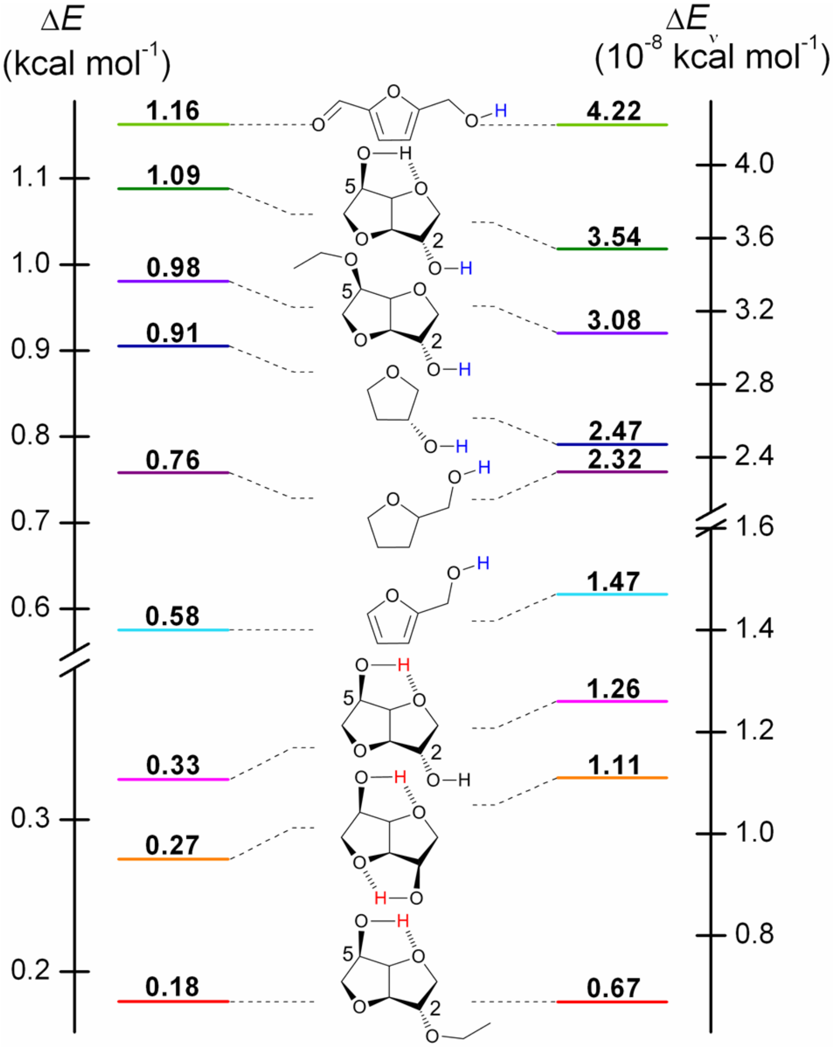


Figure S16. The correlation of apparent energy difference Δ*E* for H-bond with nuclei resonance absorption energy difference ΔE_{ν} for hydroxyl proton.

Catalytic Results for the Etherification of Isohexides with Ethanol over $H_4SiW_{12}O_{40}$

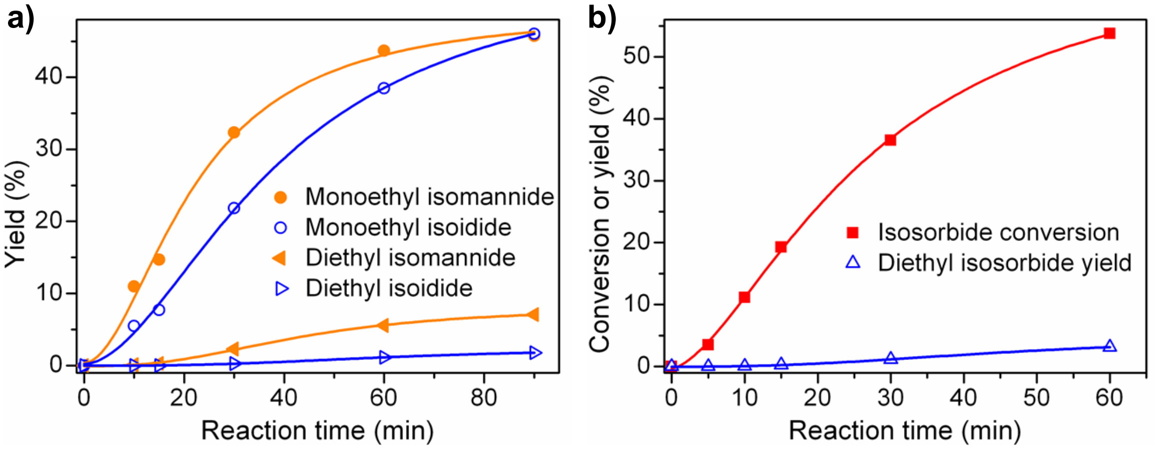


Figure S17. Reaction time course of $H_4SiW_{12}O_{40}$-catalyzed etherification of OH groups in isohexides with ethanol. a) Competition etherification of isomannide and isoidide with ethanol. b) Etherification of isosorbide with ethanol. Reaction conditions: a) isomannide (2.40 mmol) and isoidide (2.40 mmol) or b) isosorbide (4.80 mmol), tungstosilicic acid (0.05 mmol), ethanol (2.80 mL) and toluene (2.70 mL) were stirred in an autoclave at 453 K.

Table S1. Fourier transform infrared spectral data for certain sugar-derived alcohols in carbon tetrachloride of concentration 2.5 mmol L^{-1}.

Alcohol	FT-IR absorptions (cm^{-1})
	Free OH
(S)-3-Hydroxytetrahydrofuran	3625
Furfuryl alcohol	3622
Tetrahydrofurfuryl alcohol	3600
5-Hydroxymethylfurfural	3618

A low concentration in CCl_4 (2.5 mmol L^{-1}) was used to eliminate the intermolecular H-bonding interaction of solute molecules. To clearly obtain OH stretching vibration wavenumber, the spectrum of the pure solvent (CCl_4), had been subtracted from the alcohol spectrum. The sharp and high frequency band is assigned to the free OH, whereas the broad and low frequency band is due to the intramolecularly hydrogen bonded OH. Furthermore, the absorptions at ca. 3620 cm^{-1} may be associated with free hydroxyl groups.[3]

Table S2. The coefficients of determination (R^2) of the linear fits for the plots of the natural logarithm hydroxyl proton chemical shifts versus the inverse temperature.

Entry	Compound	Proton type	R^2
1	Isosorbide	C5-OH*	0.9915
		C2-OH†	0.9959
2	Isomannide	OH*	09985
3	Isoidide	OH†	0.9697
4	2-*O*-Monoethyl isosorbide	C5-OH*	0.9990
5	5-*O*-Monoethyl isosorbide	C2-OH†	0.9990
6	(*S*)-3-hydroxytetrahydrofuran	OH†	0.9949
7	Tetrahydrofurfuryl alcohol	OH†	0.9980
8	Furfuryl alcohol	OH†	0.9977
9	Ethanol	OH†	0.9973
10	5-Hydroxymethylfurfural	OH†	0.9951

*OH proton involved in intramolecular hydrogen bond.
†OH proton involved in intermolecular hydrogen bond.

Equations

$$\Delta E = A \times R \tag{S1}$$

$$\delta_{\mathrm{H,sample}} = \frac{(\nu_{\mathrm{H,sample}} - \nu_{\mathrm{H,reference}})}{\nu_{\mathrm{H,reference}}} \tag{S2}$$

$$\Delta \nu = (\delta_{\mathrm{H,263\,K}} - \delta_{\mathrm{H,328\,K}}) \times \nu_{\mathrm{spectrometer}} \tag{S3}$$

$$\Delta E_{\nu} = N_A \times h \times \Delta \nu \tag{S4}$$

$$\nu = \frac{\gamma}{2\pi} B_0 (1 - \sigma) \tag{S5}$$

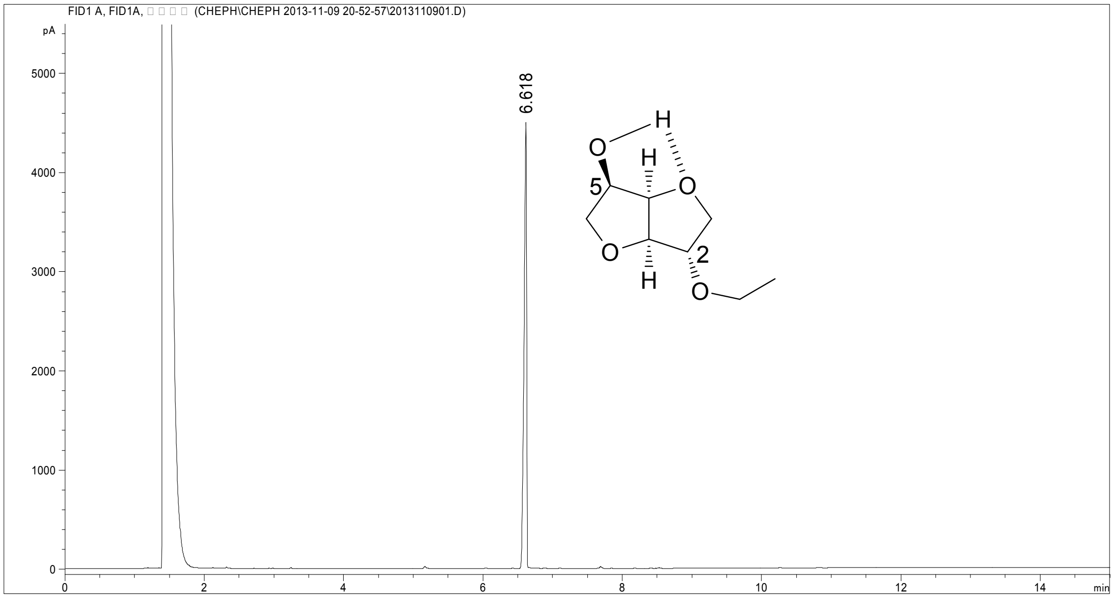
In eq. S1, A is the slope of the plot of $\ln\delta$ versus $1/T$, and R is the universal gas constant. In eq. S2,[4] OH chemical shift δ is defined by the frequency of the resonance expressed with reference to a standard compound which is defined to be at 0 ppm, and is independent of the spectrometer frequency. Here, spectrometer frequency is 400 MHz.

In eq. S3, $\Delta\nu$ is resonance frequency difference of OH protons from 263 to 328 K, deduced from eq. S2; $\delta_{\mathrm{H,263\,K}}$ and $\delta_{\mathrm{H,328\,K}}$ are the OH chemical shifts at 263 and 328 K, respectively.

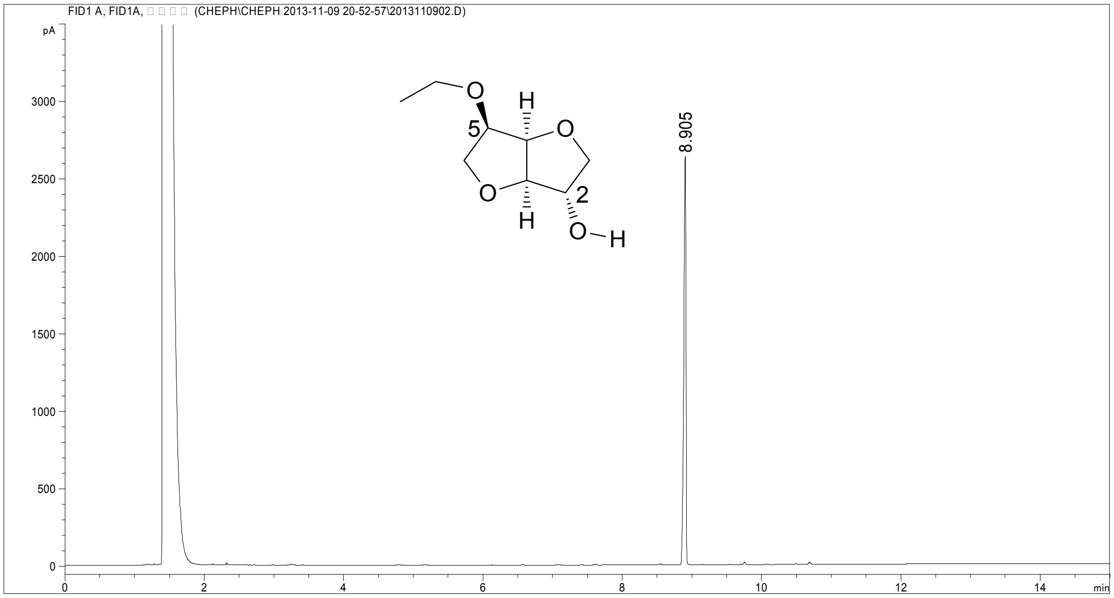
In eq. S4, ΔE_{ν} is the proton nuclei absorption energy difference; N_A is Avogadro's constant; h is Planck's constant.

In eq. S5,[4] the resonance frequency ν is related to the applied magnetic flux density B_0 by the magnetogyric ratio of the nucleus and the shielding constant σ. Hence, shielding constant change $\Delta\sigma$ is proportional to the resonance absorption frequency difference $\Delta\nu$, which is proportional to the chemical shift difference $\Delta\delta$ according to eq. S3.

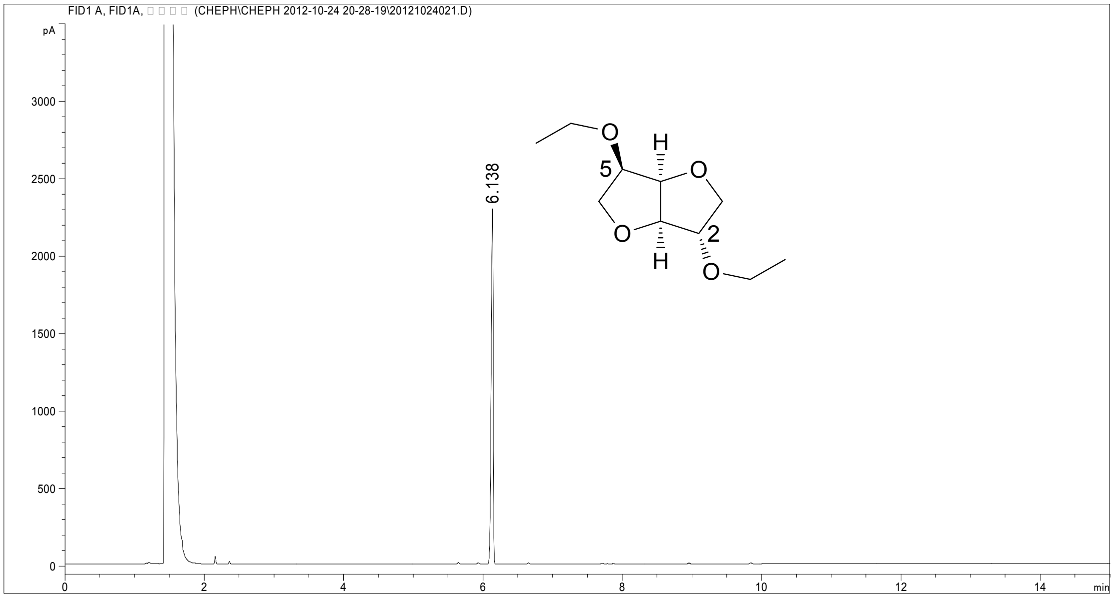
GC Purity



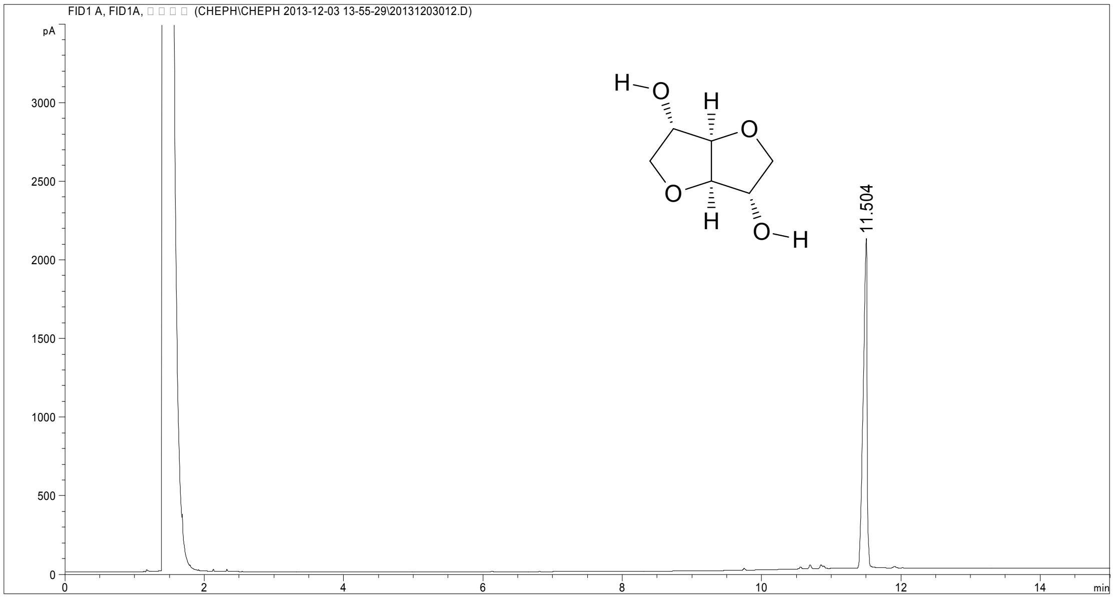
2-*O*-Monoethyl isosorbide (GC purity: > 98%)



5-*O*-Monoethyl isosorbide (GC purity: > 97%)

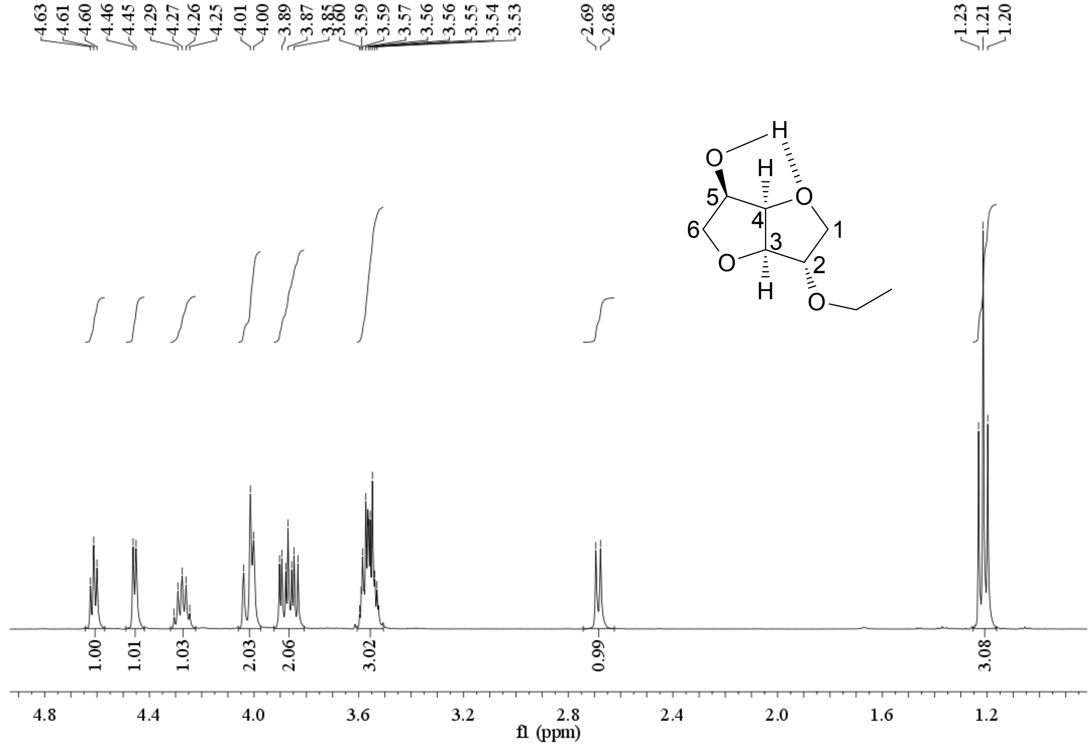


Diethyl isosorbide (GC purity: > 98%)

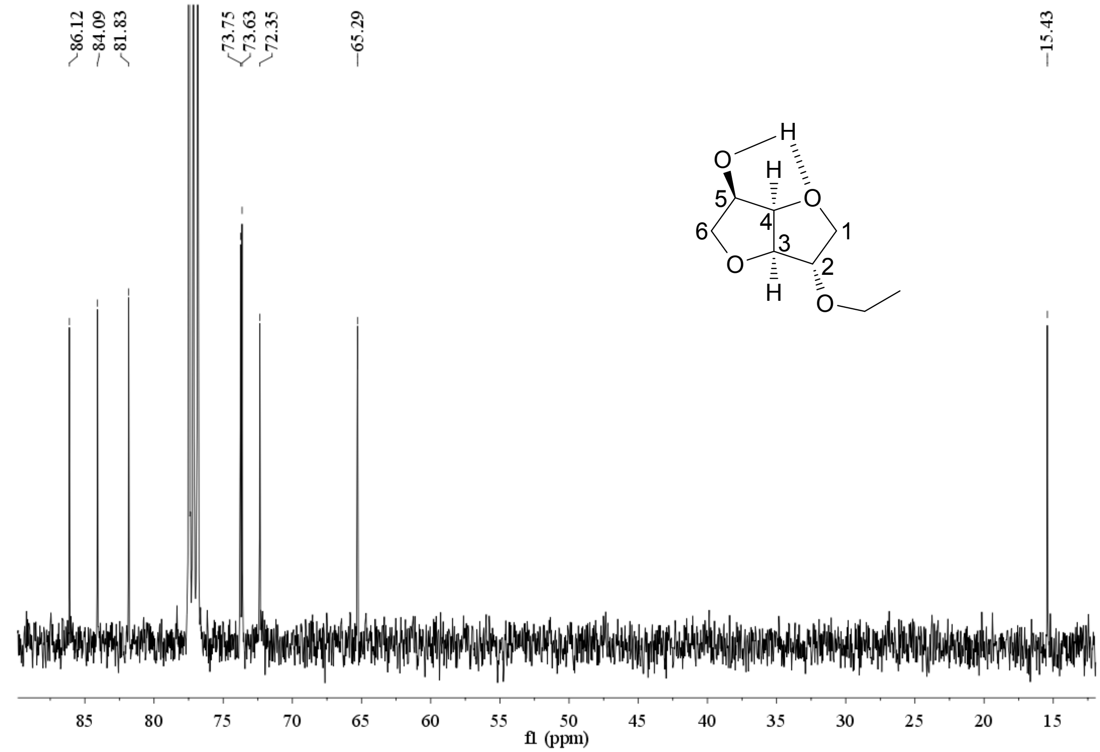


Isoidide (GC purity: > 97%)

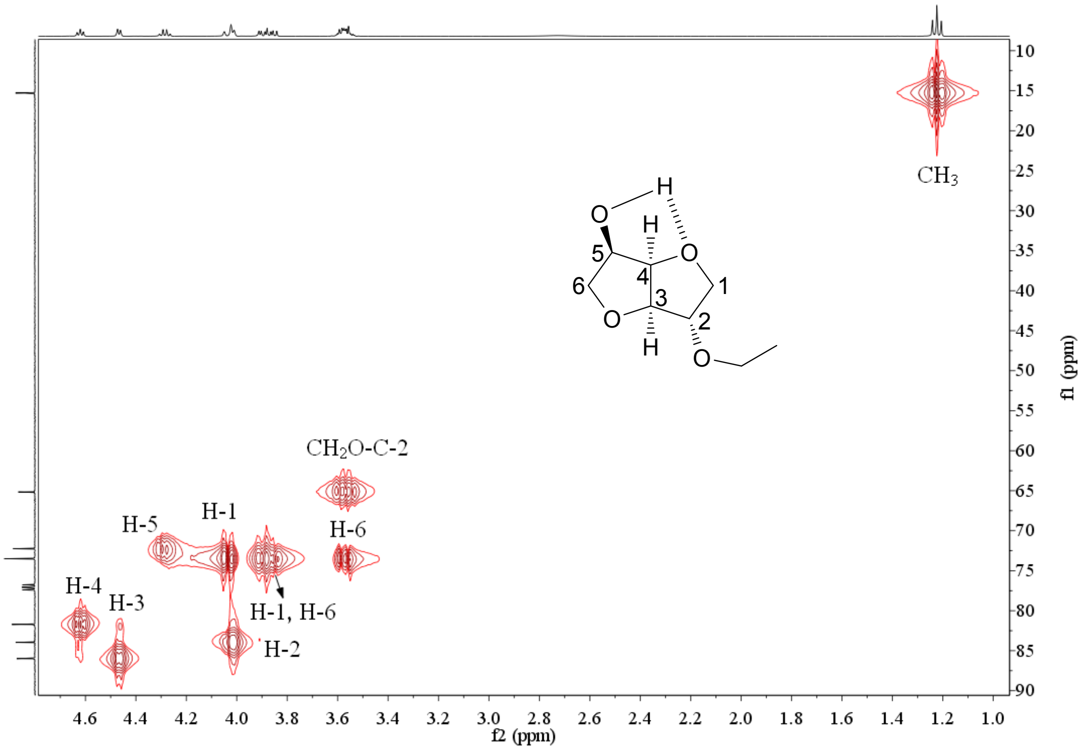
NMR Traces



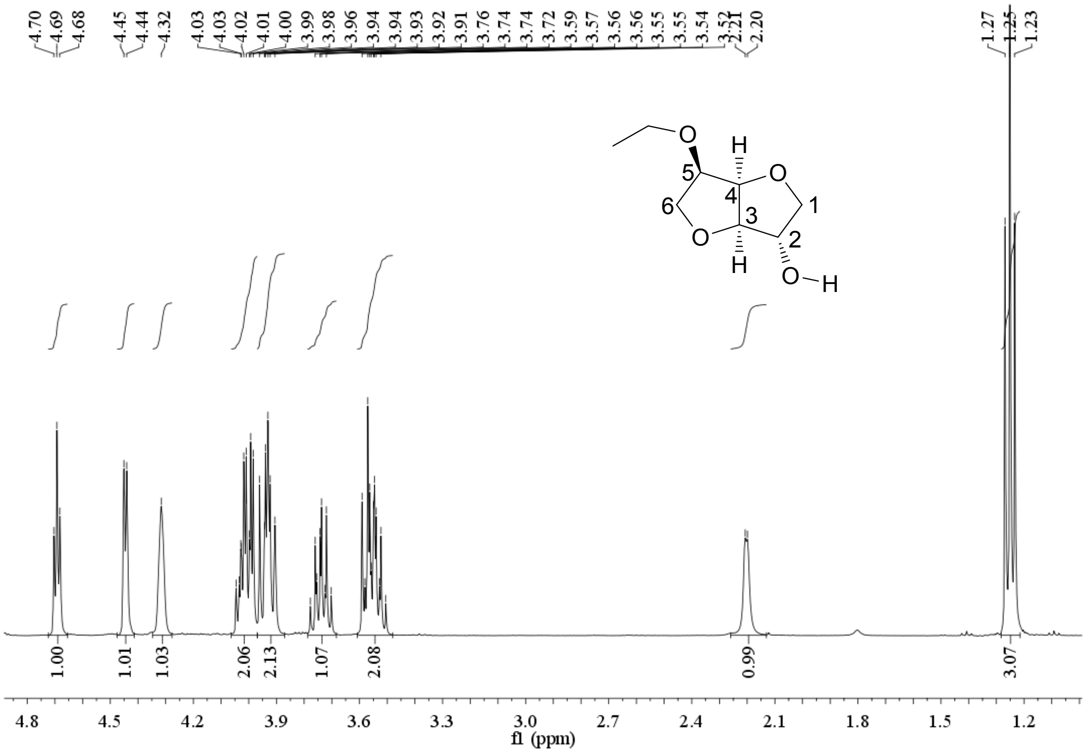
^{1}H NMR spectrum of 2-*O*-monoethyl isosorbide (400 MHz, $CDCl_3$, rt).



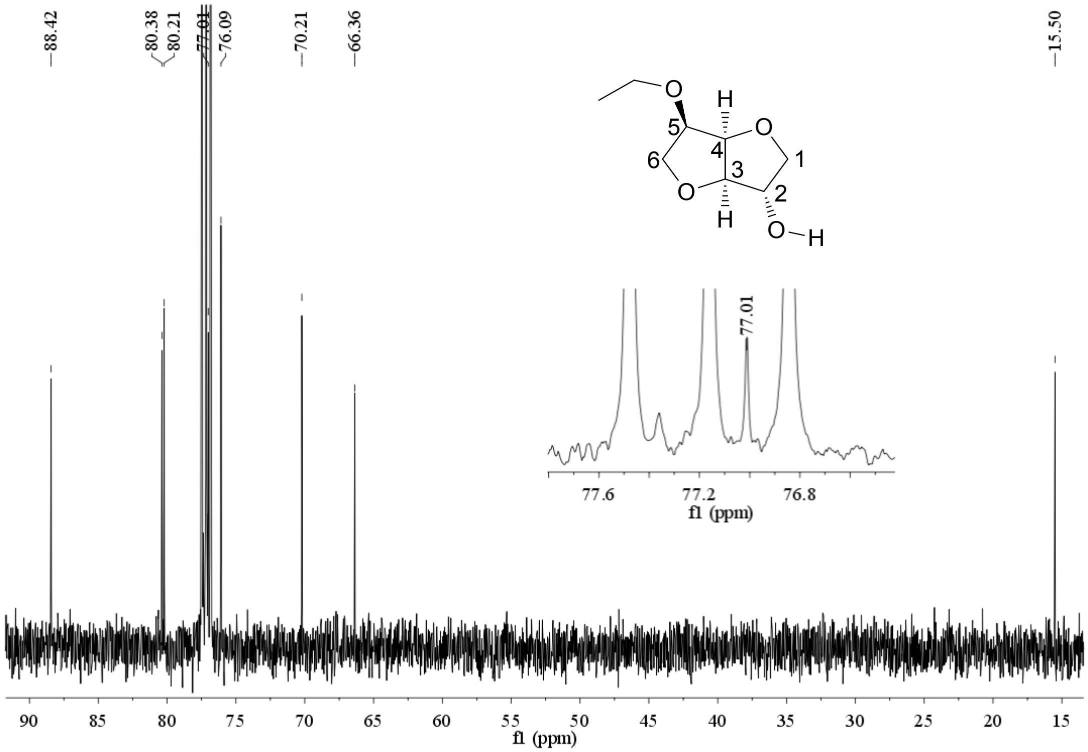
^{13}C NMR spectrum of 2-*O*-monoethyl isosorbide (101 MHz, $CDCl_3$).



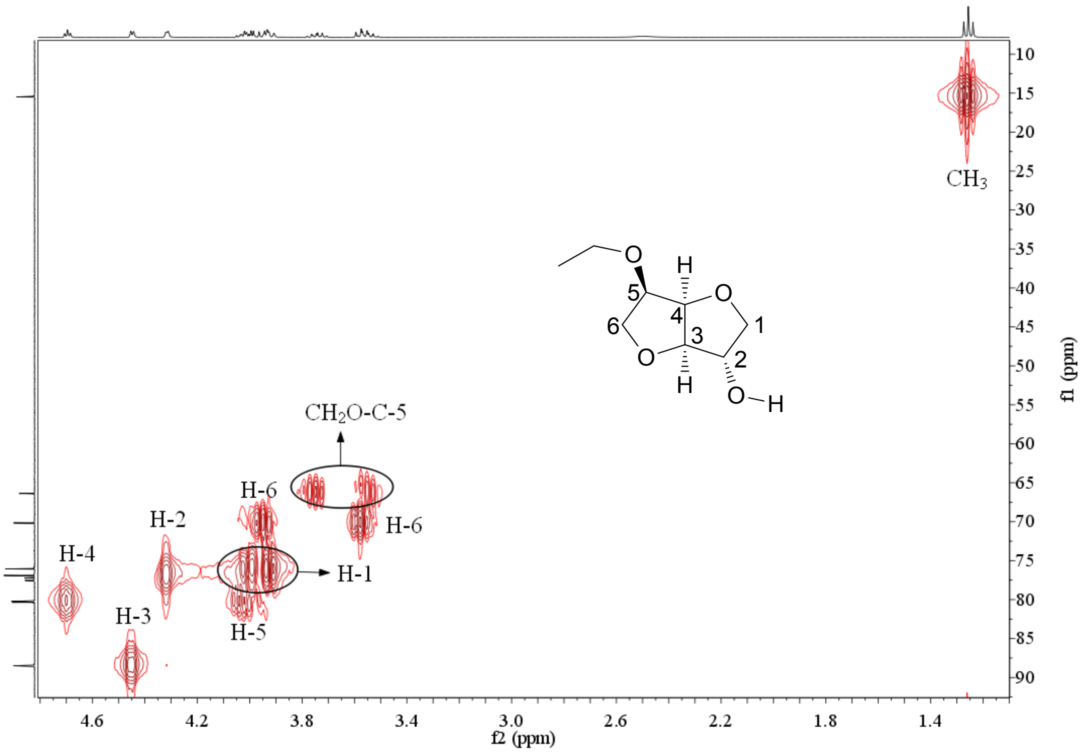
HMQC spectrum of 2-*O*-monoethyl isosorbide in CDCl$_3$.



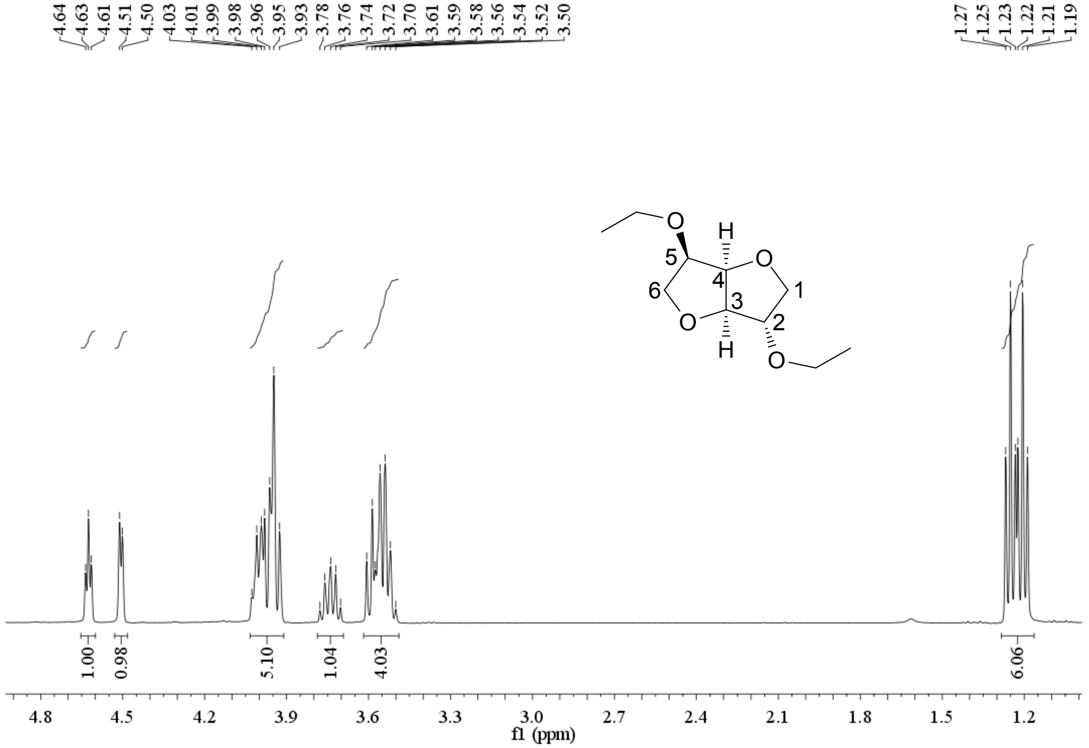
^{1}H NMR spectrum of 5-*O*-monoethyl isosorbide (400 MHz, CDCl$_3$).



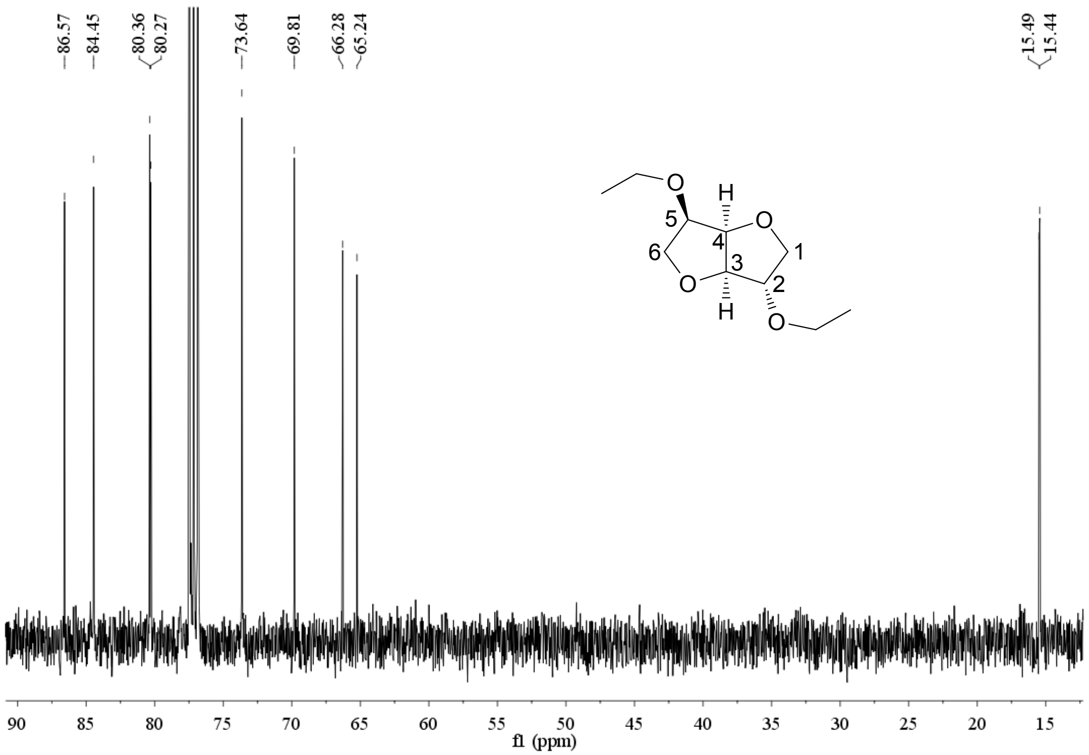
^{13}C NMR spectrum of 5-*O*-monoethyl isosorbide (101 MHz, CDCl$_3$).



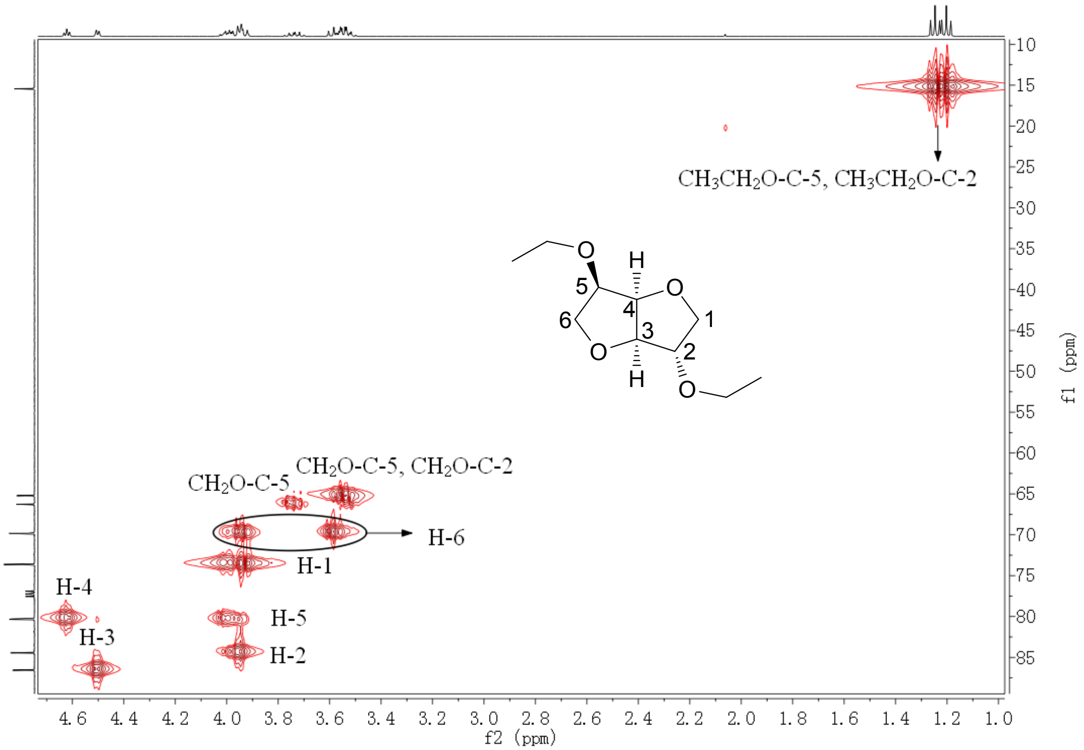
HMQC spectrum of 5-*O*-monoethyl isosorbide in CDCl$_3$.



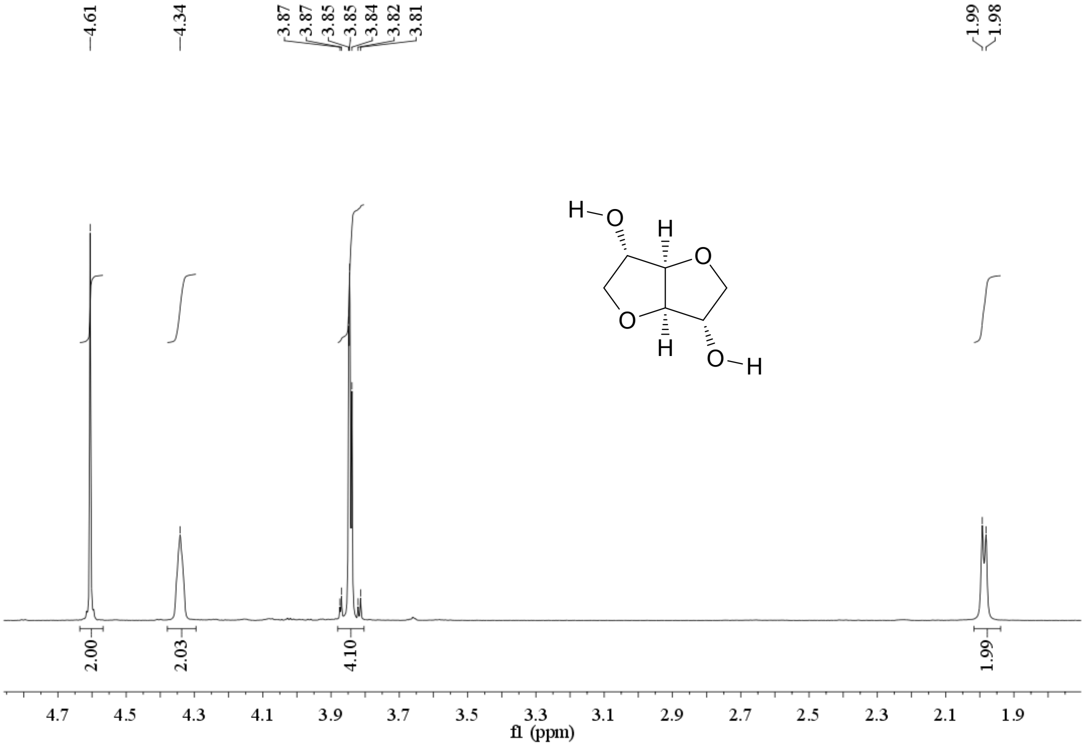
^{1}H NMR spectrum of diethyl isosorbide (400 MHz, $CDCl_3$).



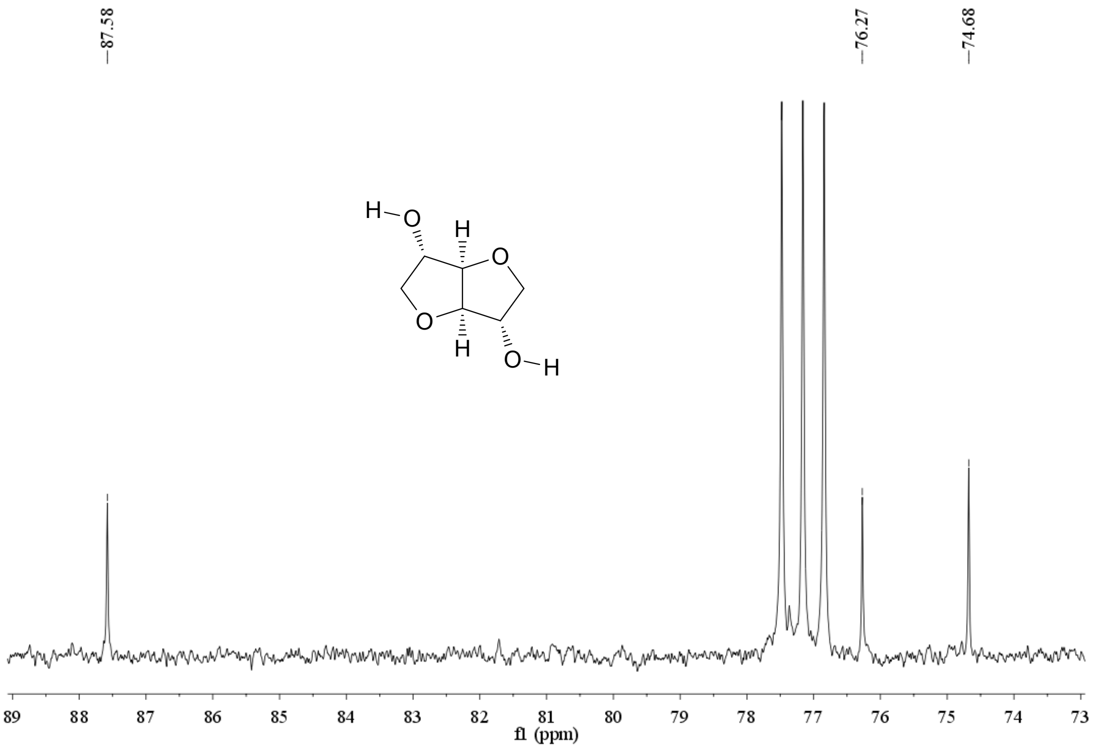
^{13}C NMR spectrum of diethyl isosorbide (101 MHz, $CDCl_3$).



HMQC spectrum of diethyl isosorbide in $CDCl_3$.

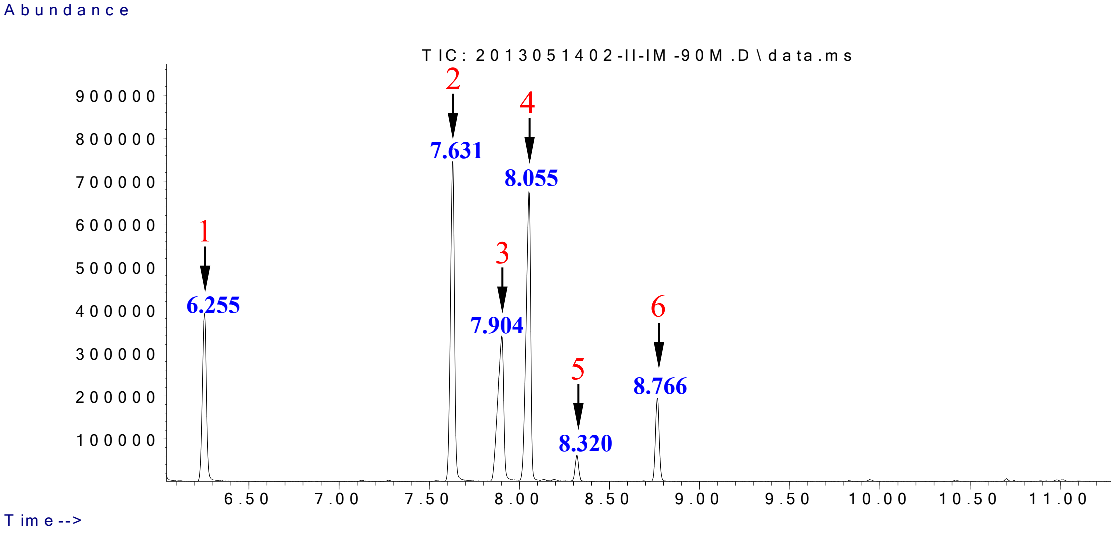


^1H NMR spectrum of isoidide (400 MHz, $CDCl_3$).

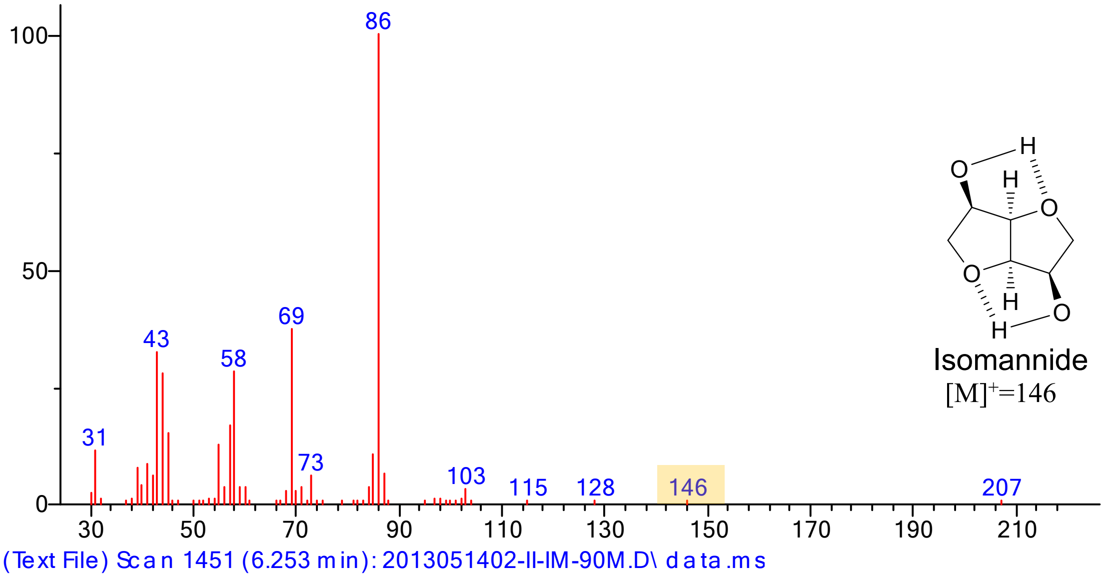


^{13}C NMR spectrum of isoidide (101 MHz, $CDCl_3$).

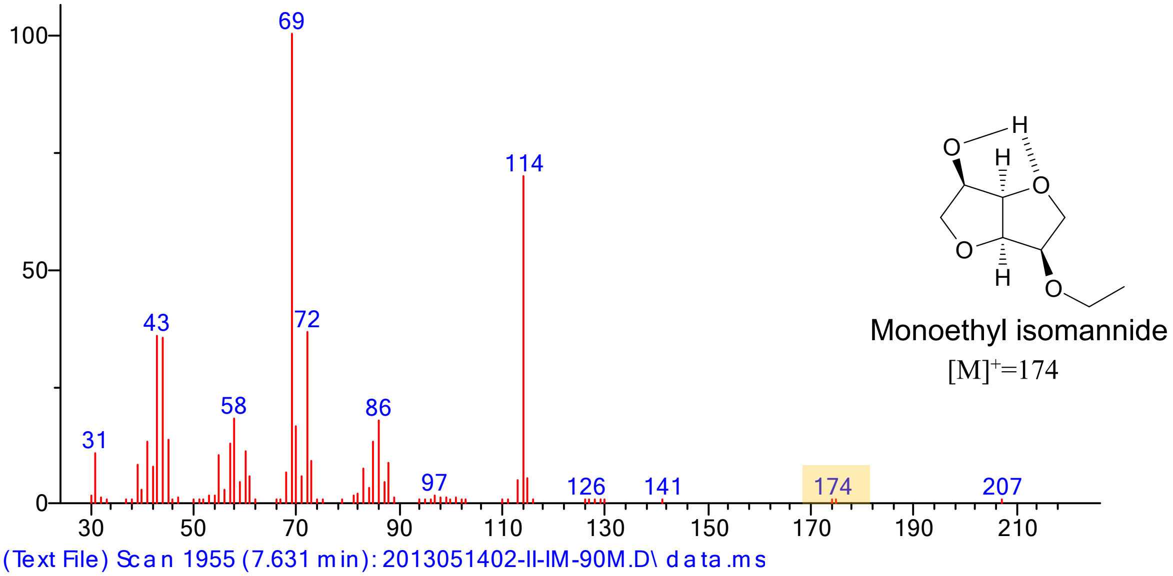
GC-MS Traces



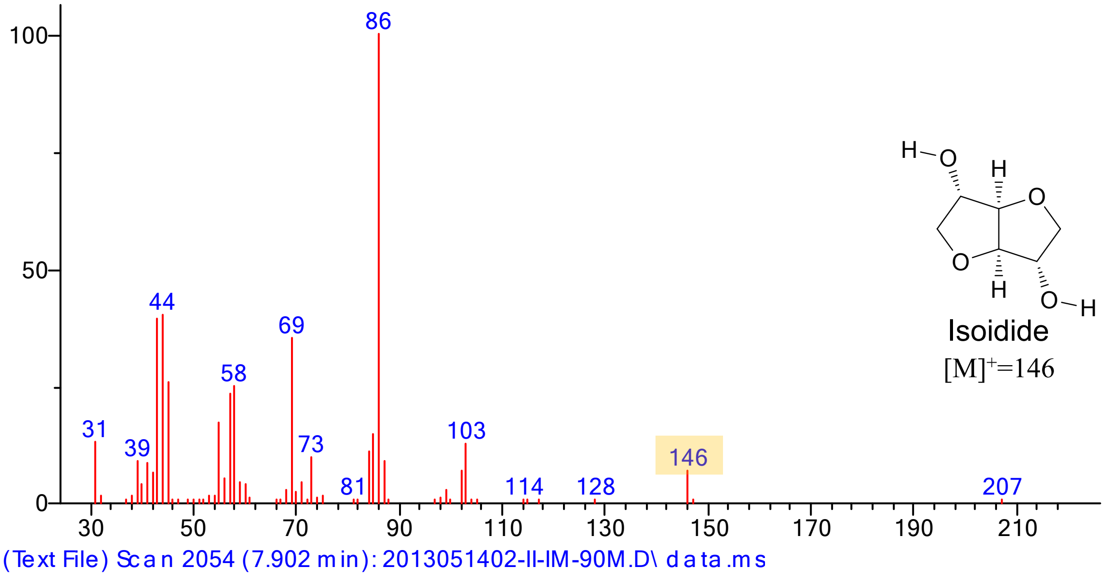
Typical total ion chromatogram (TIC) spectrum of the etherification of isomannide and isoidide with ethanol in the presence of $H_4SiW_{12}O_{40}$. Peaks assignment of the etherification reaction mixture: 1, isomannide; 2, monoethyl isomannide; 3, isoidide; 4, monoethyl isoidide; 5, diethyl isoidide; 6, diethyl isomannide.



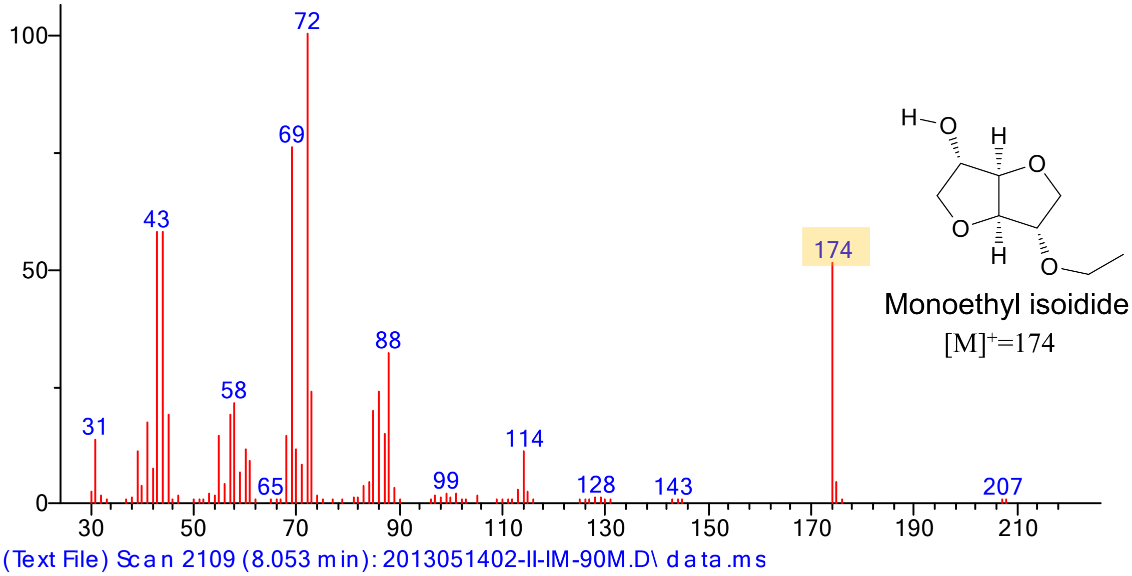
Mass spectrum of isomannide. MS (70 eV): *m/z* (%): 146 (1) [M^+], 103 (3), 86 (100), 69 (37), 58 (28), 44 (32).



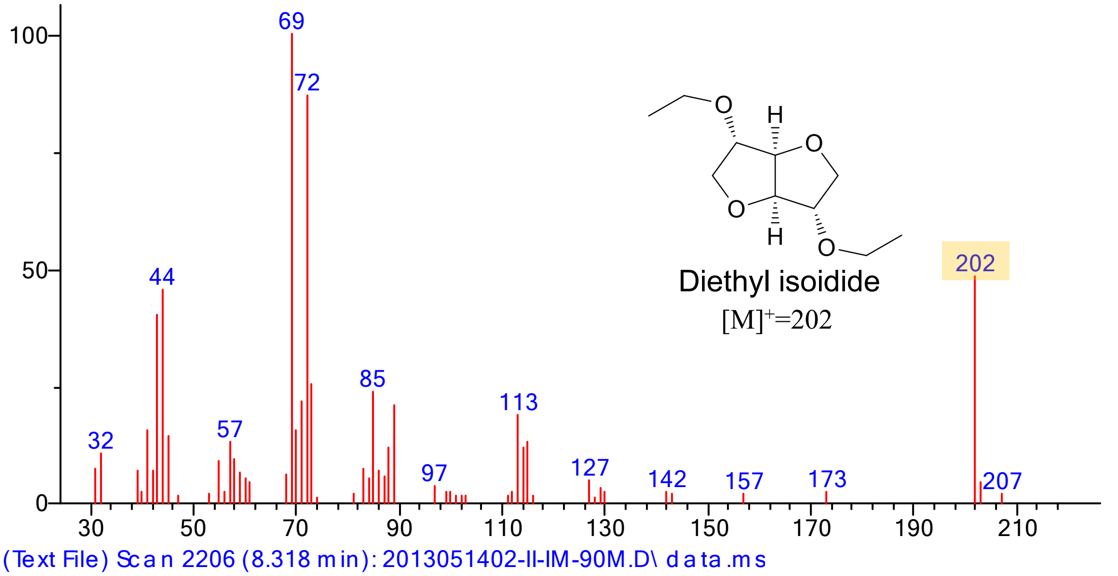
Mass spectrum of monoethyl isomannide. MS (70 eV): *m/z* (%): 174 (1) [M^{+}], 114 (70), 86 (18), 69 (100), 58 (18), 43 (35).



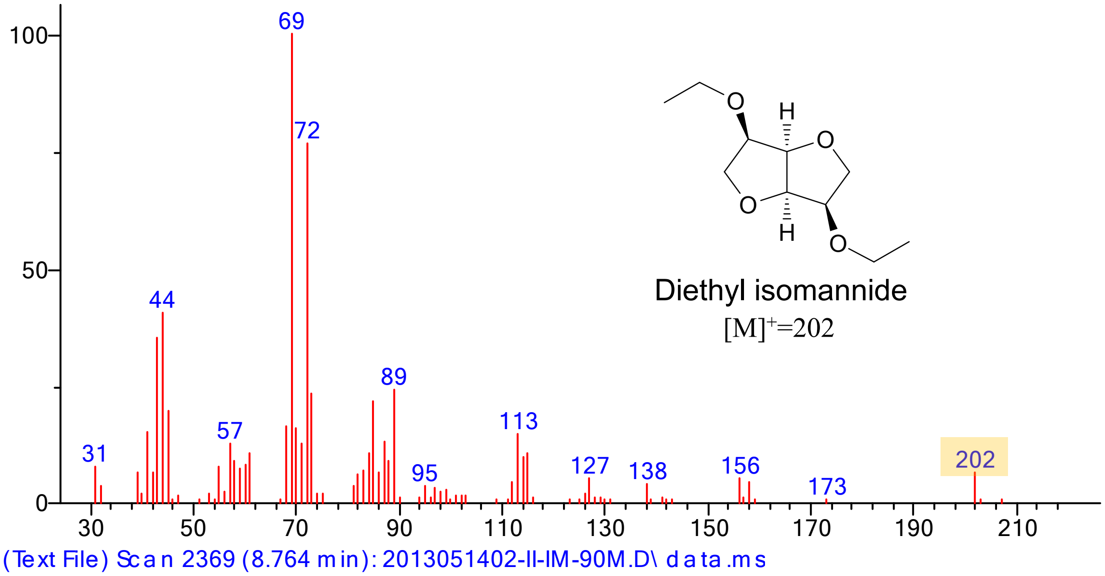
Mass spectrum of isoidide. MS (70 eV): *m/z* (%): 146 (7) [M^{+}], 103 (12), 86 (100), 69 (35), 58 (25), 44 (40).



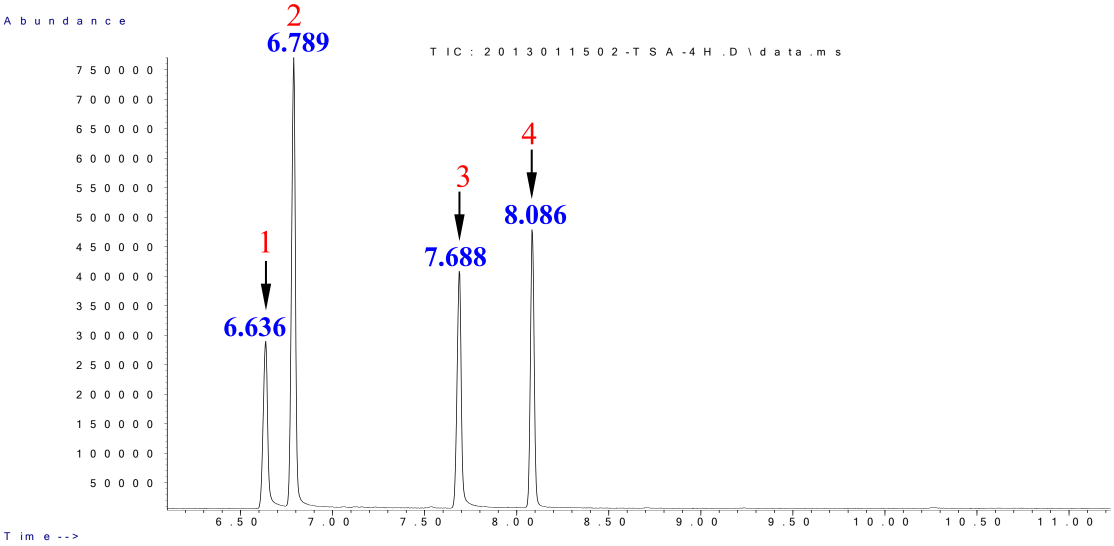
Mass spectrum of monoethyl isoidide. MS (70 eV): *m/z* (%): 174 (50) [M^+], 114 (10), 88 (30), 72 (100), 58 (2), 43 (60).



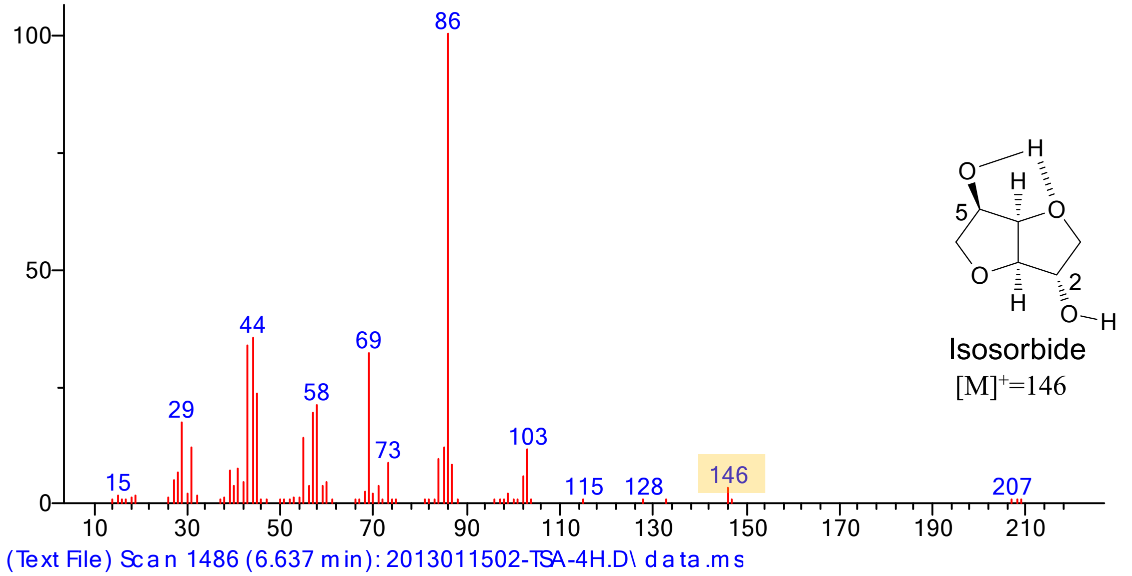
Mass spectrum of diethyl isoidide. MS (70 eV): *m/z* (%): 202 (48) [M^+], 157 (2), 113 (19), 85 (24), 69 (100), 57 (13), 44 (45).



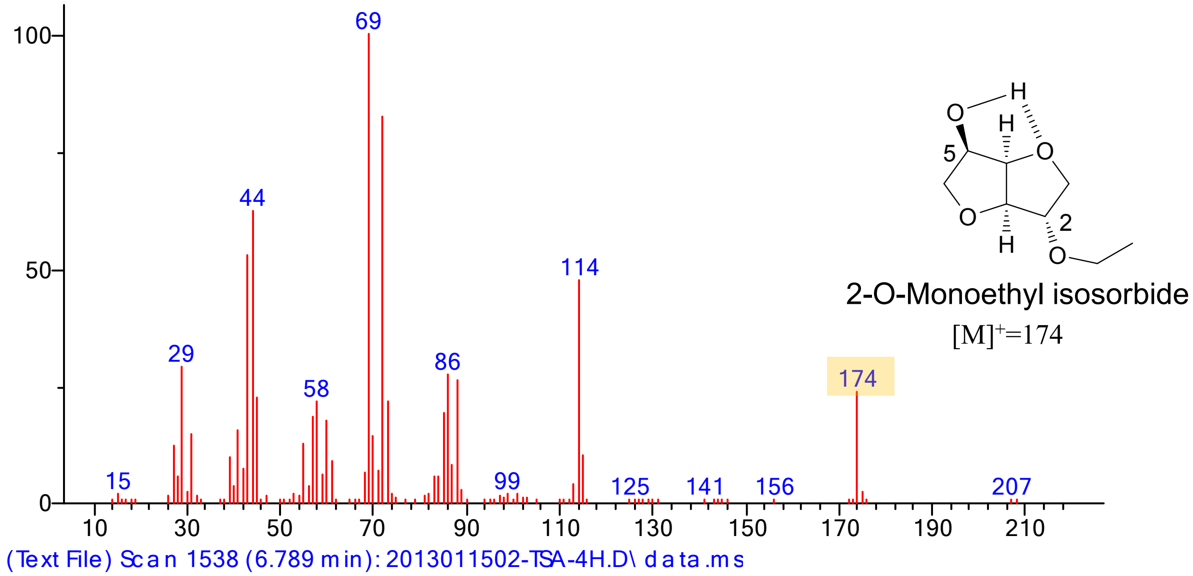
Mass spectrum of diethyl isomannide. MS (70 eV): *m/z* (%): 202 (6) [M^+], 156 (5), 113 (15), 89 (24), 69 (100), 57 (13), 44 (40).



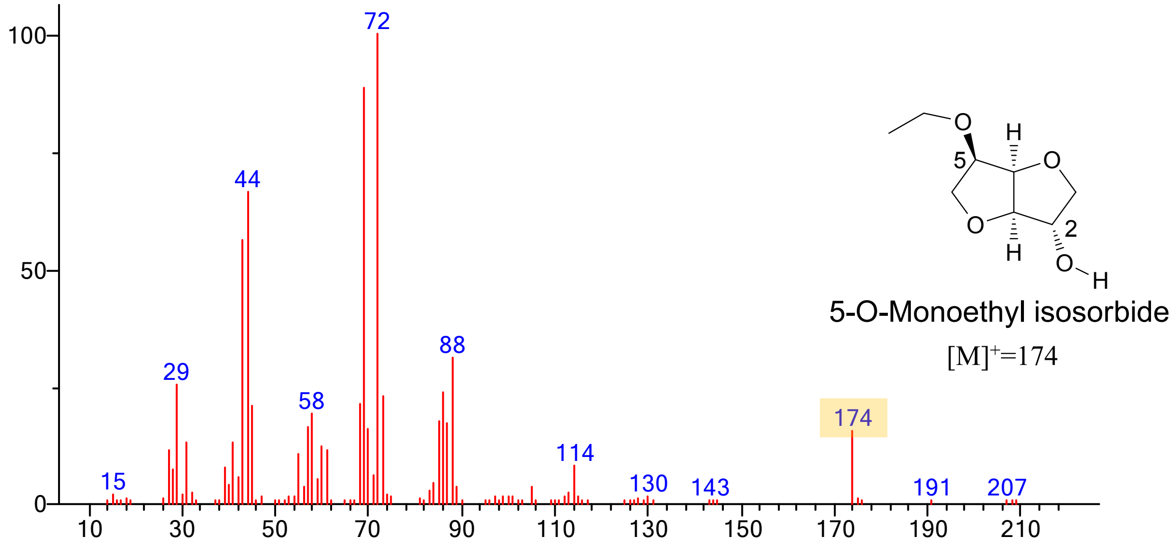
Typical total ion chromatogram (TIC) spectrum of the etherification of isosorbide with ethanol in the presence of $H_4SiW_{12}O_{40}$. Peaks assignment of the etherification reaction mixture: 1, isosorbide; 2, 2-*O*-monoethyl isosorbide; 3, 5-*O*-monoethyl isosorbide ; 4, diethyl isosorbide.



Mass spectrum of isosorbide. MS (70 eV): *m/z* (%): 146 (3) [M^+], 103 (11), 86 (100), 69 (32), 58 (21), 44 (35).

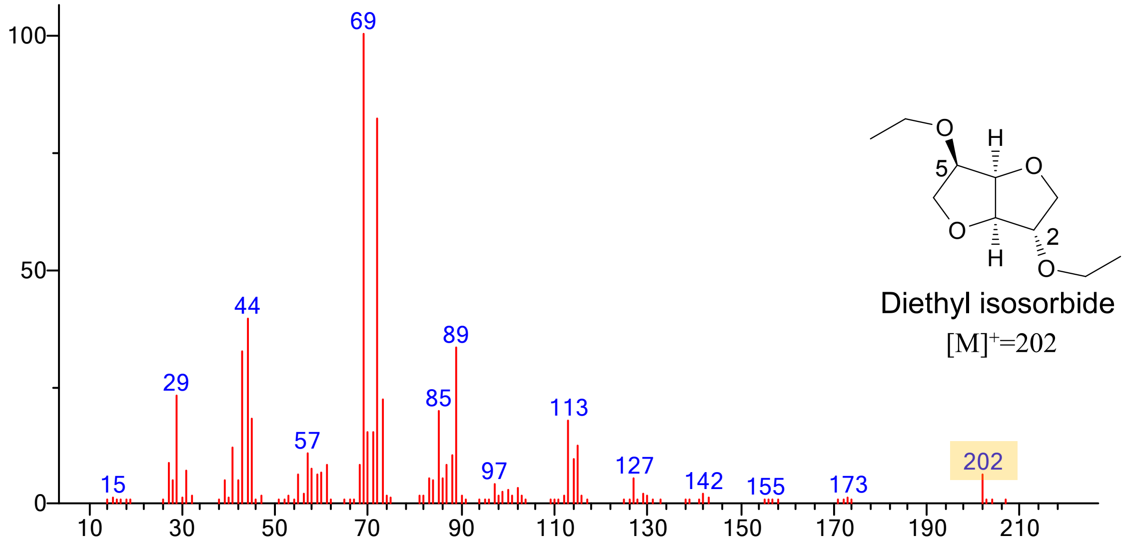


Mass spectrum of 2-*O*-monoethyl isosorbide. MS (70 eV): *m/z* (%): 174 (24) [M^+], 114 (48), 86 (27), 69 (100), 58 (22), 44 (62).



(Text File) Scan 1845 (7.688 min): 2013011502-TSA-4H.D\ data.ms

Mass spectrum of 5-*O*-monoethyl isosorbide. MS (70 eV): *m/z* (%): 174 (15) [M^+], 114 (8), 88 (31), 72 (100), 58 (19), 44 (66).



(Text File) Scan 1980 (8.083 min): 2013011502-TSA-4H.D\ data.ms

Mass spectrum of diethyl isosorbide. MS (70 eV): *m/z* (%): 202 (6) [M^+], 157 (1), 113 (17), 89 (33), 69 (100), 57 (11), 44 (39).

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