Electronic Supplementary Information

Methyl isobutyl ketone-enabled selective dehydration-esterification of sorbitol to isosorbide esters over H-beta catalyst

Penghua Che,[a] Hong Ma,[a] Xin Nie,[a] Weiqiang Yu[a] and Jie Xu*[a]

[a]State Key Laboratory of Catalysis, Dalian National Laboratory for Clean Energy,
Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China.
E-mail: xujie@dicp.ac.cn

Contents

1. Materials and methods

Materials

Unless otherwise specified, all chemical regents here were commercially available and employed as received without further purification. Sorbitol (≥99.5%) and erythritol (99%) were provided by Sigma-Aldrich and J&K Scientific Ltd, respectively. Acetic acid (≥99.5%), methyl isobutyl ketone (MIBK, >99.5%), methyl isopropyl ketone (>99%) and diethyl ketone (>98%) were supplied by TCI. 1,4-Sorbitan (97%) was purchased from Toronto Research Chemicals. Isosorbide (≥98%) was obtained from Wuhan DKY Technology Co., Ltd. (China). Butyric acid (99.5%), octanoic acid (99%), sulfolane (>99%) and γ-valerolactone (98%) were available from Aladdin Reagent Inc. (China). Hexanoic acid (99%) and naphthalene (≥99%) were supplied by Sigma-Aldrich and Alfa-Aesar, respectively. Deuterated reagents with tetramethylsilane (TMS) like DMSO-d_6 and $CDCl_3$ were purchased by Qingdao Tenglong Weibo technology Co., Ltd. Other reagents like dimethyl carbonate, *n*-butyl acetate, 1,4-dioxane, and toluene were supplied from local suppliers. Besides, 1,4-sorbitan was also self-made according to our previously reported methods[1].

Beta zeolites in H-forms with Si/Al ratios of 12.5 and 20 (Nankai University Catalyst Co., Ltd.), 50 (Nanjing JCNANO Technology Co., Ltd.), and 75 (Zeolyst) were designated as H-beta(12.5), H-beta(20), H-beta(50) and H-beta(75), respectively. All the zeolites were calcined at 550 ^{o}C for 6 h in air prior to use. Amberlyst-70 resin, kindly supplied by Rohm & Haas Company, was dried before use at 105 ^{o}C for 10 h under air. 12-Tungstophosphoric acid ($H_3PW_{12}O_{40}$, Sigma-Aldrich) was dried at 130 ^{o}C for 2 h under air to remove physisorbed water before use. Nafion-H (NR-50, Alfa-Aesar) and *p*-toluene sulfonic acid (*p*-TSA, 3A Chemicals) were used as received without pretreatment.

Methods

^{1}H, ^{13}C and HSQC NMR were run on a Bruker Avance III 400 spectrometer (^{1}H at 400 MHz, ^{13}C at 101 MHz) at room temperature in DMSO-d_6 and $CDCl_3$ with tetramethylsilane (TMS) as internal standard. ^{13}C NMR spectra of the initial reaction mixture were also recorded on a Bruker Avance III 400 spectrometer (^{13}C at 101 MHz) at room temperature with DMSO-d_6 as external standard. High resolution mass spectra (HMRS) were obtained on a HRMS ESI-Q-TOF spectrometer operating in positive and negative ion modes. Gas chromatography-mass spectrometry (GC-MS) analysis was performed using an Agilent 7890A GC/5975C MS coupled

with a HP-5 MS capillary column (30 m × 0.25 mm × 0.25 μm) and electron impact ionization mode (EI). GC analyses were carried out 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 25 μL of injection volume. FT-IR spectra were acquired using a Bruker Tensor II Fourier transform infrared spectrophotometer ranging from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. Column chromatograph was performed on silica gel (200-300 mesh).

2. Experimental procedure and quantification

Experimental procedure

Procedure for direct conversion of sorbitol to isosorbide acetates. In a typical procedure, sorbitol (0.75 mmol), acetic acid (3.0 mL), co-solvent (2.5 mL) and acid catalyst (27 mg) were loaded into a 15 mL heavy-wall glass pressure vessel sealed with a Teflon lid (Synthware). Then, the sealed reactor was placed into an oil bath preheated at 190 ^{o}C and then stirred magnetically at 700 rpm for specific time. Zero time was taken as soon as the reaction vessel was put into the oil bath. After the reaction, the reaction mixture was rapidly cooled down to room temperature and then diluted with water and acetone, followed by centrifugation to separate the solid catalyst. Finally, after being filtered through a 0.2 μm syringe filter, the sample was quantified by using GC and HPLC analysis.

Time-course experiment for the conversion of polyol in acetic acid/MIBK solvent system over H-beta(20) zeolite. To clarify the reaction pathway of the synthesis of isosorbide acetates directly from sorbitol, polyol like sorbitol, 1,4-sorbitanel or isosorbide was employed as starting material for different reaction times. Sorbitol, 1,4-sorbian or isosorbide (0.75 mmol) was mixed with H-beta(20) zeolite (27 mg) in the solvent system composed of acetic acid (3.0 mL) and MIBK (2.5 mL) in a 15 mL heavy-wall glass pressure vessel. The reactor was dipped into an oil bath preheated at 190 ^{o}C for given time with magnetically stirring (700 rpm). Zero time was taken as soon as the reaction vessel was put into the oil bath. Each reaction result at the different time was obtained based on a separate experiment.

^{13}C NMR analysis confirming the formation of the five-membered 1,3-dioxolane ketals as the initial intermediates. To confirm the presence of five-membered cyclic ketal intermediates,

the initial reaction of 1,4-sorbitan or sorbitol in the acetic acid/MIBK solvent system over H-beta(20) zeolite at 190 ^{o}C for 1 min was detected by ^{13}C NMR technique, respectively. The reaction procedure was the same as above. After the reaction, the reaction mixture was centrifuged to obtain a clear solution. A sample of 0.40 mL from the clear solution was then transferred to a 5 mm NMR tube equipped with a NI5CCI-B co-axial insert (Norell) which contains DMSO-d_6 as external standard and as deuterium lock. The ^{13}C NMR spectra (101 MHz) were recorded at room temperature.

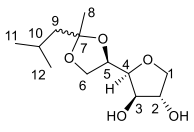
Besides, the initial reaction of erythritol (0.75 mmol) was conducted in MIBK (2.5 mL) with H-beta(20) catalyst (4 mg) at 190 ^{o}C for 1 min. The sampling procedure for ^{13}C NMR analysis was the same as above.

Procedure for recycling the catalyst. Sorbitol (0.75 mmol), acetic acid (3.0 mL), MIBK (2.5 mL) and H-beta(20) zeolite (27 mg) were charged into a 15 mL heavy-wall glass pressure vessel sealed with a Teflon lid. The reactor was transferred into an oil bath preheated at 190 ^{o}C and then stirred magnetically at 700 rpm for 4 h. After the reaction, H-beta(20) catalyst was separated from reaction mixture by centrifugation, and then washed by acetone and ethanol, respectively. After being dried at 110 ^{o}C for 2 h, the spent catalyst was calcined at 550 ^{o}C for 8 h in a flow of air for complete removal of deposited humins. The regenerated catalyst was accumulated by repeating the same reaction due to unavoidable loss of the catalyst during the process of recovery. After that, the regenerated catalyst of 27 mg was employed in the next cycle under the identical conditions.

Procedure for direct conversion of sorbitol in different fatty acid/MIBK solvent systems. The direct dehydrative esterification of sorbitol with fatty acid was conducted in a 15 mL heavy-wall glass pressure vessel. In a typical procedure, sorbitol (0.75 mmol), fatty acid (52.14 mmol, 3.0 mL of acetic acid, 4.8 mL of butyric acid, 6.6 mL of hexanoic acid and 8.3 mL of octanoic acid), MIBK (2.5 mL) and H-beta(20) zeolite (27 mg) were charged into the reactor. Then, the reactor sealed by a Teflon lid was dipped into a preheated 190 ^{o}C oil bath and then stirred magnetically at 700 rpm for 4 h. Zero time was taken as soon as the reaction vessel was put into the oil bath. After the reaction, the reaction mixture was quickly cooled down to room temperature and then diluted with water and acetone, 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.

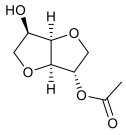
Procedure for isolation of 5,6-*O*-(1-methylisopentylidene)-1,4-sorbitan intermediates. 1,4-Sorbitan (0.75 mmol), acetic acid (3.0 mL), MIBK (2.5 mL) and H-beta(20) zeolite (27 mg) were charged into a 15 mL heavy-wall glass pressure vessel sealed with a Teflon lid. The reactor was immersed into an oil bath preheated at 190 ^{o}C and then stirred magnetically at 700 rpm for 1 min. After the reaction, the mixture was centrifuged to obtain a clear solution, and was then 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*-(1-methylisopentylidene)-1,4-sorbitan (5,6-*O*-ketal) as a colorless oil. The five-membered cyclic 5,6-*O*-ketal was ascertained by ^{1}H, ^{13}C and HSQC NMR as well as GC-MS and HRMS.

5,6-*O*-(1-methylisopentylidene)-1,4-sorbitan. ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.11–4.97 (m, 2H, 2-COH, 3-COH), 4.28–4.11 (m, 1H, 5-CH), 3.99–3.91 (m, 2H, 6-CH, 2-CH), 3.90–3.72 (m, 4H, 1-CH, 3-CH, 4-CH, 6-CH), 3.49 (d, *J*=9.0 Hz, 1H, 1-CH), 1.81–1.68 (m, 1H, 10-CH), 1.54–1.42 (m, 2H, 9-CH_2), 1.28–1.19 (2s, 3H, 8-CH_3), 0.90 (d, *J*=6.6 Hz, 6H, 11-CH_3, 12-CH_3); ^{13}C NMR (101 MHz, DMSO-d_6): δ 109.53 and 109.46 (7-C), 81.14 and 81.04 (4-C), 76.64 and 76.62 (2-C), 75.53 and 75.50 (3-C), 73.41 (1-C), 73.21 and 72.40 (5-C), 66.26 (6-C), 47.69 and 46.73 (9-C), 25.03 and 23.92 (8-C), 23.99, 23.96, 23.76 and 23.72 (11-C, 12-C), 23.93 and 23.68 (10-C); HRMS (ESI) *m/z* Calculated for $C_{12}H_{23}O_5$ $[M+H]^+$ 247.1540, found 247.1545.

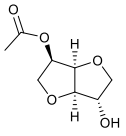


Procedure for isolation of isosorbide fatty esters. After the completion of reaction, the catalyst was separated from the reaction mixture by centrifugation, and washed with dichloromethane and toluene. The filtrate was neutralized by triethylamine, and was concentrated by reduced pressure to remove the solvent. Next, the viscous residue was subjected to silica-gel column chromatography eluted with a gradient mixture of cyclohexane/ethyl acetate (7/1 to 1/1, *v/v*) to sequentially obtain isosorbide diester, isosorbide-2-ester and isosorbide-5-ester as pure compounds, which were finally ascertained by ^{1}H and ^{13}C NMR as well as HRMS.

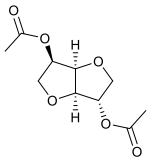
Isosorbide-2-acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.26–5.18 (m, 1H), 4.63 (t, *J*=4.9 Hz, 1H), 4.48 (d, *J*=4.4 Hz, 1H), 4.31 (dq, *J*=7.1, 5.9 Hz, 1H), 4.07–3.98 (m, 2H), 3.90 (dd, *J*=9.5, 6.0 Hz, 1H), 3.58 (dd, *J*=9.5, 6.0 Hz, 1H), 2.60 (d, *J*=7.3 Hz, 1H), 2.09 ppm (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.10, 85.74, 82.10, 78.52, 73.76, 73.70, 72.42, 21.05 ppm; HRMS (ESI) *m/z* Calculated for $C_8H_{13}O_5$ $[M+H]^+$ 189.0757, found 189.0772.



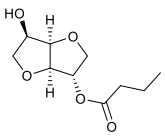
Isosorbide-5-acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.15 (q, J=5.6 Hz, 1H), 4.85 (t, J=4.9 Hz, 1H), 4.41 (d, J=4.5 Hz, 1H), 4.34 (br s, 1H), 3.97–3.87 (m, 3H), 3.76 (dd, J=9.7, 5.4 Hz, 1H), 2.12 (s, 3H), 1.96 ppm (d, J=5.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.64, 88.33, 80.47, 76.39, 75.71, 74.24, 70.30, 20.83 ppm; HRMS (ESI) *m/z* Calculated for $C_8H_{13}O_5$ $[M+H]^+$ 189.0757, found 189.0765.



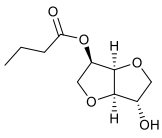
Isosorbide-2,5-diacetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.21–5.18 (m, 1H), 5.15 (dd, J=11.4, 5.6 Hz, 1H), 4.83 (t, J=5.0 Hz, 1H), 4.49 (d, J=4.6 Hz, 1H), 4.03–3.92 (m, 3H), 3.79 (dd, J=9.8, 5.6 Hz, 1H), 2.13 (s, 3H), 2.08 ppm (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.47, 170.18, 86.02, 80.86, 78.21, 74.07, 73.63, 70.34, 21.05, 20.81 ppm; HRMS (ESI) *m/z* Calculated for $C_{10}H_{15}O_6$ $[M+H]^+$ 231.0863, found 231.0886.



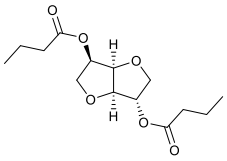
Isosorbide-2-butyrate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.27–5.20 (m, 1H), 4.63 (t, J=4.9 Hz, 1H), 4.47 (d, J=4.4Hz, 1H), 4.37–4.24 (m, 1H), 4.06–3.97 (m, 2H), 3.90 (dd, J=9.5, 6.0 Hz, 1H), 3.57 (dd, J=9.5, 6.0 Hz, 1H), 2.61 (d, J=7.0 Hz, 1H), 2.31 (t, J=7.4 Hz, 2H), 1.72–1.60 (m, 2H), 0.95 ppm (t, J=7.4 Hz, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.75, 85.81, 82.10, 78.27, 73.85, 73.70, 72.44, 36.12, 18.47, 13.72 ppm; HRMS (ESI) *m/z* Calculated for $C_{10}H_{17}O_5$ $[M+H]^+$ 217.1071, found 217.1076.



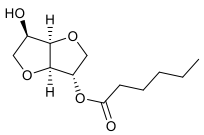
Isosorbide-5-butyrate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.16 (dd, J=11.1, 5.5 Hz, 1H), 4.85 (t, J=5.0 Hz, 1H), 4.40 (d, J=4.6 Hz, 1H), 4.33 (br s, 1H), 3.96–3.84 (m, 3H), 3.77 (dd, J=9.8, 5.2 Hz, 1H), 2.41–2.30 (m, 2H), 2.17 (br s, 1H), 1.68 (h, J=7.4 Hz, 2H), 0.97 ppm (t, J=7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.28, 88.36, 80.47, 76.38, 75.60, 73.98, 70.48, 35.98, 18.49, 13.74 ppm; HRMS (ESI) *m/z* Calculated for $C_{10}H_{17}O_5$ $[M+H]^+$ 217.1071, found 217.1067.



Isosorbide-2,5-dibutyrate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.20 (d, J=3.2 Hz, 1H), 5.16 (dd, J=11.3, 5.6 Hz, 1H), 4.83 (t, J=5.0 Hz, 1H), 4.48 (d, J=4.6 Hz, 1H), 4.04–3.89 (m, 3H), 3.80 (dd, J=9.8, 5.4 Hz, 1H), 2.39–2.33 (m, 2H), 2.30 (t, J=7.4 Hz, 2H), 1.66 (dh, J=12.5, 7.4 Hz, 4H), 0.96 ppm (dt, J=8.8, 7.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.14, 172.83, 86.10, 80.87, 77.97, 73.85, 73.63, 70.49, 36.14, 35.97, 18.50, 18.48, 13.74, 13.72 ppm; HRMS (ESI) *m/z* Calculated for $C_{14}H_{23}O_6$ $[M+H]^+$ 287.1489, found 287.1480.

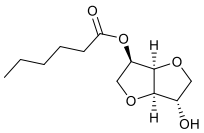


Isosorbide-2-hexanoate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.25–5.21 (m, 1H), 4.63 (t, J=4.9 Hz, 1H), 4.47 (d, J=4.4 Hz, 1H), 4.31 (d, J=4.5 Hz, 1H), 4.06–3.97 (m, 2H), 3.90 (dd, J=9.5, 6.0 Hz,



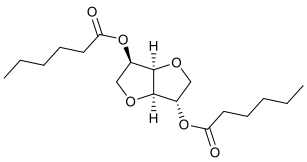
1H), 3.57 (dd, *J*=9.5, 6.0 Hz, 1H), 2.59 (s, 1H), 2.32 (t, *J*=7.5 Hz, 2H), 1.68–1.56 (m, 2H), 1.37–1.24 (m, 4H), 0.90 ppm (t, *J*=6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.94, 85.81, 82.10, 78.28, 73.85, 73.71, 72.45, 34.24, 31.35, 24.65, 22.40, 14.02 ppm; HRMS (ESI) *m/z* Calculated for $C_{12}H_{21}O_5$ $[M+H]^+$ 245.1384, found 245.1407.

Isosorbide-5-hexanoate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.15 (dd, *J*=11.1, 5.5 Hz, 1H), 4.85 (t, *J*=5.0 Hz, 1H), 4.40 (d, *J*=4.6 Hz, 1H), 4.33 (br s, 1H), 3.96–3.84 (m, 3H), 3.77 (dd, *J*=9.8, 5.2



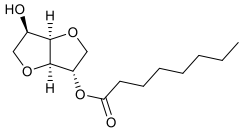
Hz, 1H), 2.44–2.27 (m, 2H), 2.08 (s, 1H), 1.73–1.56 (m, 2H), 1.39–1.24 (m, 4H), 0.90 ppm (dd, *J*=9.1, 4.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.45, 88.36, 80.49, 76.40, 75.61, 73.98, 70.50, 34.07, 31.34, 24.68, 22.43, 14.03 ppm; HRMS (ESI) *m/z* Calculated for $C_{12}H_{21}O_5$ $[M+H]^+$ 245.1384, found 245.1381.

Isosorbide-2,5-dihexanoate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.19 (d, *J*=3.1 Hz, 1H), 5.15 (q, *J*=5.6 Hz, 1H), 4.83 (t, *J*=5.0 Hz, 1H), 4.47 (d, *J*=4.6 Hz, 1H), 4.03–3.90 (m, 3H), 3.80 (dd,



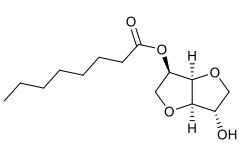
J=9.8, 5.4 Hz, 1H), 2.37 (dd, *J*=7.9, 7.2 Hz, 2H), 2.31 (t, *J*=7.5 Hz, 2H), 1.69–1.56 (m, 4H), 1.39–1.23 (m, 8H), 0.89 ppm (td, *J*=6.9, 1.5 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.34, 173.03, 86.11, 80.88, 77.98, 73.86, 73.63, 70.50, 34.26, 34.06, 31.35, 24.69, 24.65, 22.43, 22.40, 14.02, 14.01 ppm; HRMS (ESI) *m/z* Calculated for $C_{18}H_{31}O_6$ $[M+H]^+$ 343.2115, found 343.2127.

Isosorbide-2-octanoate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.27–5.16 (m, 1H), 4.63 (t, *J*=4.9 Hz, 1H), 4.47 (d, *J*=4.4 Hz, 1H), 4.31 (p, *J*=5.9 Hz, 1H), 4.06–3.96 (m, 2H), 3.90 (dd, *J*=9.5, 6.0 Hz,



1H), 3.57 (dd, *J*=9.5, 6.0 Hz, 1H), 2.59 (d, *J*=6.8 Hz, 1H), 2.32 (t, *J*=7.5 Hz, 2H), 1.62 (p, *J*=7.4 Hz, 2H), 1.38–1.17 (m, 8H), 0.88 ppm (t, *J*=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.95, 85.82, 82.10, 78.28, 73.85, 73.72, 72.45, 34.29, 31.76, 29.16, 29.01, 24.98, 22.72, 14.19 ppm; HRMS (ESI) *m/z* Calculated for $C_{14}H_{25}O_5$ $[M+H]^+$ 273.1697, found 273.1701.

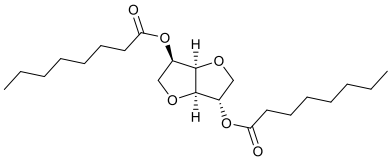
Isosorbide-5-octanoate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.15 (dd, *J*=11.2, 5.5 Hz, 1H), 4.85 (t, *J*=5.0 Hz, 1H), 4.40 (d, *J*=4.6 Hz, 1H), 4.36–4.30 (m, 1H), 3.95–3.86 (m, 3H), 3.76 (dd, *J*=9.8,



5.2 Hz, 1H), 2.40–2.33 (m, 2H), 2.02 (br s, 1H), 1.73–1.55 (m, 2H), 1.38–1.20 (m, 8H), 0.88 ppm (dd, *J*=9.1, 4.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.45, 88.36, 80.49, 76.42, 75.61, 73.98, 70.49, 34.11, 31.78, 29.15, 29.04, 25.00, 22.72, 14.19 ppm; HRMS (ESI) *m/z* Calculated for $C_{14}H_{25}O_5$ $[M+H]^+$

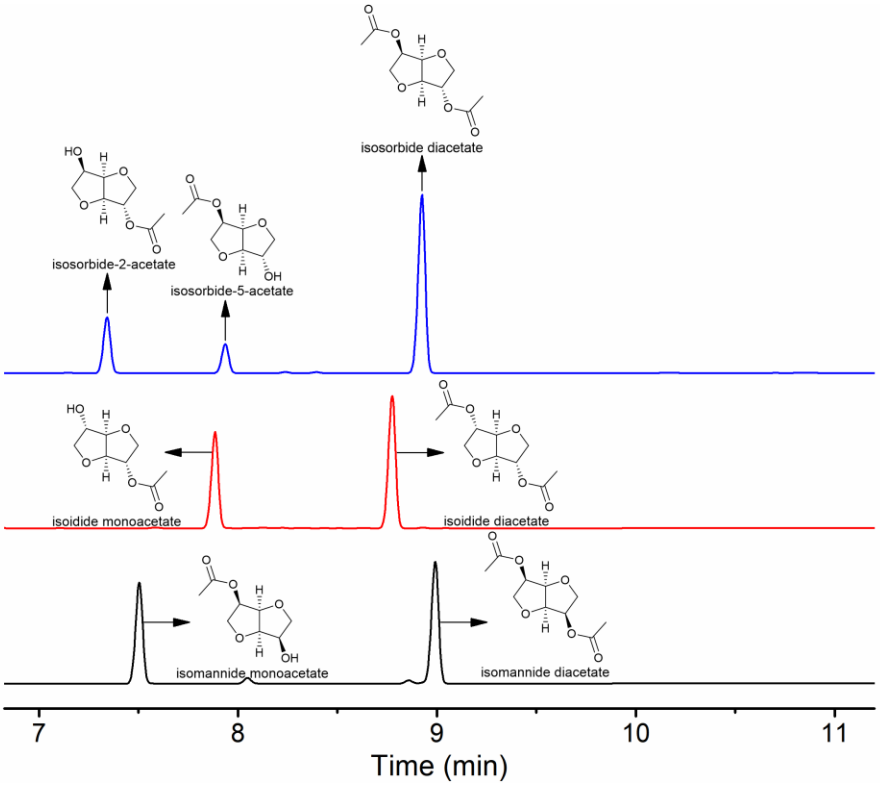
273.1697, found 273.1689.

Isosorbide-2,5-dioctanoate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.19 (d, J=3.2 Hz, 1H), 5.15 (dd, J=11.3, 5.6 Hz, 1H), 4.83 (t, J=5.0 Hz, 1H), 4.47 (d, J=4.6 Hz, 1H), 4.05–3.89 (m, 3H), 3.79 (dd, J=9.8, 5.5 Hz, 1H), 2.37 (dd, J=8.0, 7.2 Hz, 2H), 2.31 (t, J =7.5 Hz, 2H), 1.71–1.55 (m, 4H), 1.30 (m, 16H), 0.88 ppm (t, J=6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.34, 173.03, 86.11, 80.88, 77.98, 73.86, 73.64, 70.48, 34.30, 34.10, 31.77, 31.75, 29.15, 29.04, 29.00, 25.01, 24.97, 22.72, 22.71, 14.19, 14.18 ppm; HRMS (ESI) *m/z* Calculated for $C_{22}H_{39}O_6$ $[M+H]^+$ 399.2741, found 399.2752.



Quantification

GC chromatograms of acetylated isohexides: isosorbide acetates (isosorbide-2-monoacetate, isosorbide-5-monoacetate and isosorbide-2,5-diacetate), isomannide acetates (isomannide monoacetate and isomannide diacetate) and isoidide acetates (isoidide monoacetate and isoidide diacetate)



Quantitative analysis of the reaction mixture was conducted on a GC and HPLC. Specifically, quantification of isosorbide and its esterified derivatives was determined by GC

internal standard method using naphthalene as an internal standard, while sorbitol and 1,4-sorbitan were quantitatively determined by HPLC external standard method based on peak areas of authentic samples of sorbitol and 1,4-sorbitan, respectively. Additionally, the quantification of acetylated isosorbide isomers, including isoidide acetates (mono- and di-acetate) and isomannide acetates (mono- and di-acetate), was determined by assuming the same FID response factors as isosorbide-2-monoacetate and isosorbide-2,5-diacetate, respectively, due to their corresponding isomeric relationships.

All the reaction results were calculated based on the initial amount of polyol (sorbitol, 1,4-sorbitan and isosorbide). Reaction results shown as conversion, selectivity and yield in mol% were as follows:

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

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

$$\text{Selectivity of others (mol\%)} = 100\% - \text{total selectivity of identified products}$$

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

$$\text{Yield of non-/un-identified products (mol\%)} = \text{Conversion} - \text{total yield of identified products}$$

Besides, the primary goal of this work is to obtain mono- and di-esters of isosorbide, so the total selectivity or yield for IS-esters is defined as the sum of the selectivities or yields for mono- and di-esters of isosorbide.

3. ^{13}C NMR spectrum for the reaction of sorbitol in acetic acid/MIBK at the initial stage

After the reaction, the reaction mixture was centrifuged to collect a clear solution. Then, an aliquot of the solution (1.0 mL) was concentrated by rotary evaporation. Finally, the viscous residual was mixed with 0.60 mL of DMSO-d_6. Subsequently, the solution was filled into a 5 mm NMR tube, and was analyzed by ^{13}C NMR.

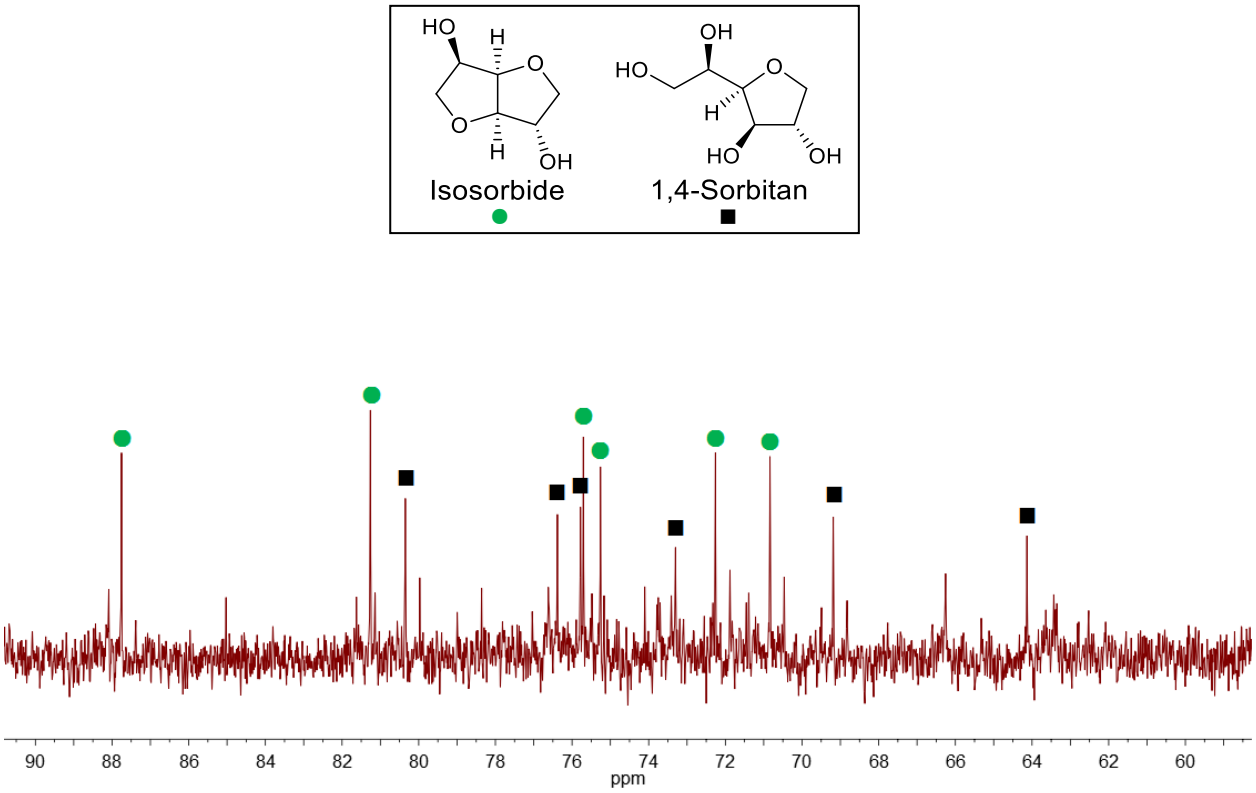


Figure S1. ^{13}C NMR spectrum in DMSO-d_6 of an initial reaction mixture for the direct conversion of sorbitol in acetic acid/MIBK solvent system over H-beta(20) zeolite. Reaction conditions: Sorbitol (0.75 mmol), H-beta(20) (27 mg), acetic acid (3.0 mL), MIBK (2.5 mL), 190 ^{o}C, 2 min.

4. Time-course study for the esterification of isosorbide in acetic acid/MIBK

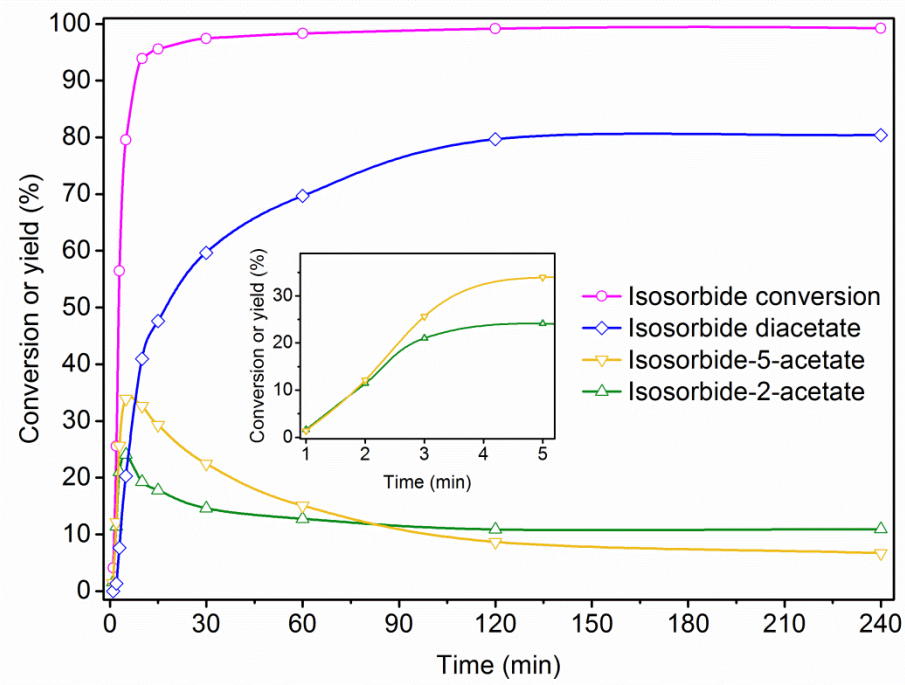


Figure S2. Time course for the esterification of isosorbide in acetic acid/MIBK solvent system catalyzed by H-beta(20). Reaction conditions: isosorbide (0.75 mmol), H-beta(20) (27 mg), acetic acid (3.0 mL), MIBK (2.5 mL), 190 ^{o}C.

5. Monitoring the temporal evolution of five-membered cyclic ketals during the initial conversion of sorbitol in acetic acid/MIBK

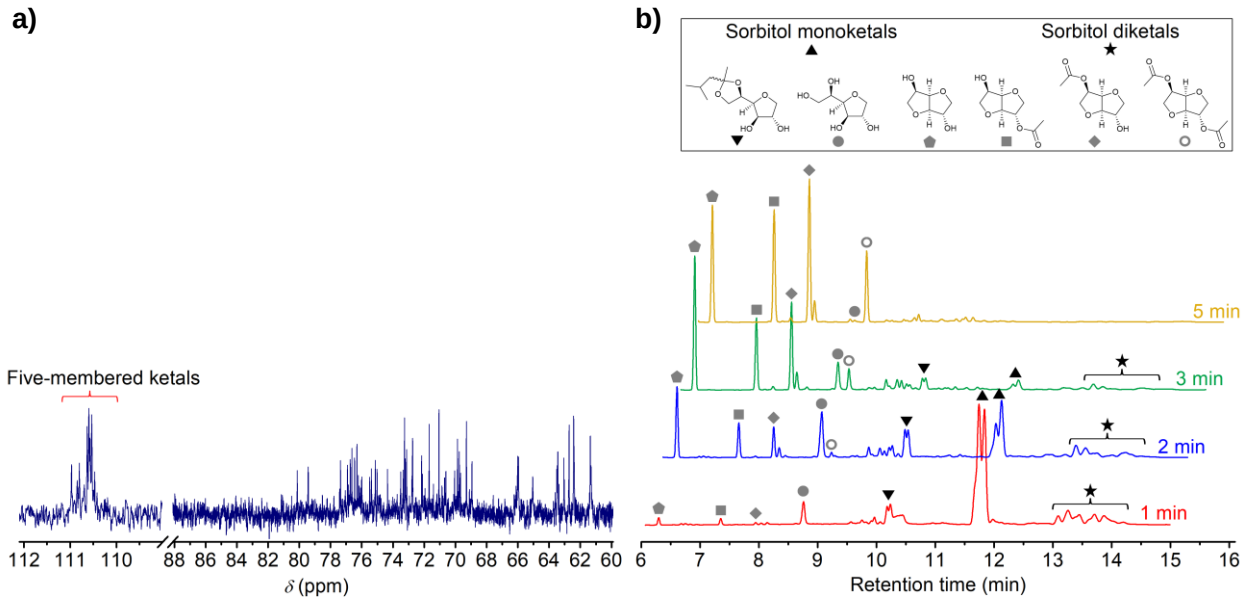


Figure S3. Confirming the formation of five-membered sorbitol ketals and 5,6-*O*-ketals of 1,4-sorbitan as the initial intermediates during the direct transformation of sorbitol in acetic acid/MIBK solvent system over H-beta(20). (a) Partial ^{13}C NMR spectrum of the reaction mixture obtained after 1 min. (b) GC traces showing the evolution of five-membered sorbitol ketals and 5,6-*O*-ketals of 1,4-sorbitan over time. Reaction conditions: sorbitol (0.75 mmol), H-beta(20) (27 mg), acetic acid (3.0 mL), MIBK (2.5 mL), 190 ^{o}C.

6. HRMS analysis for the initial conversion of sorbitol in acetic acid/MIBK

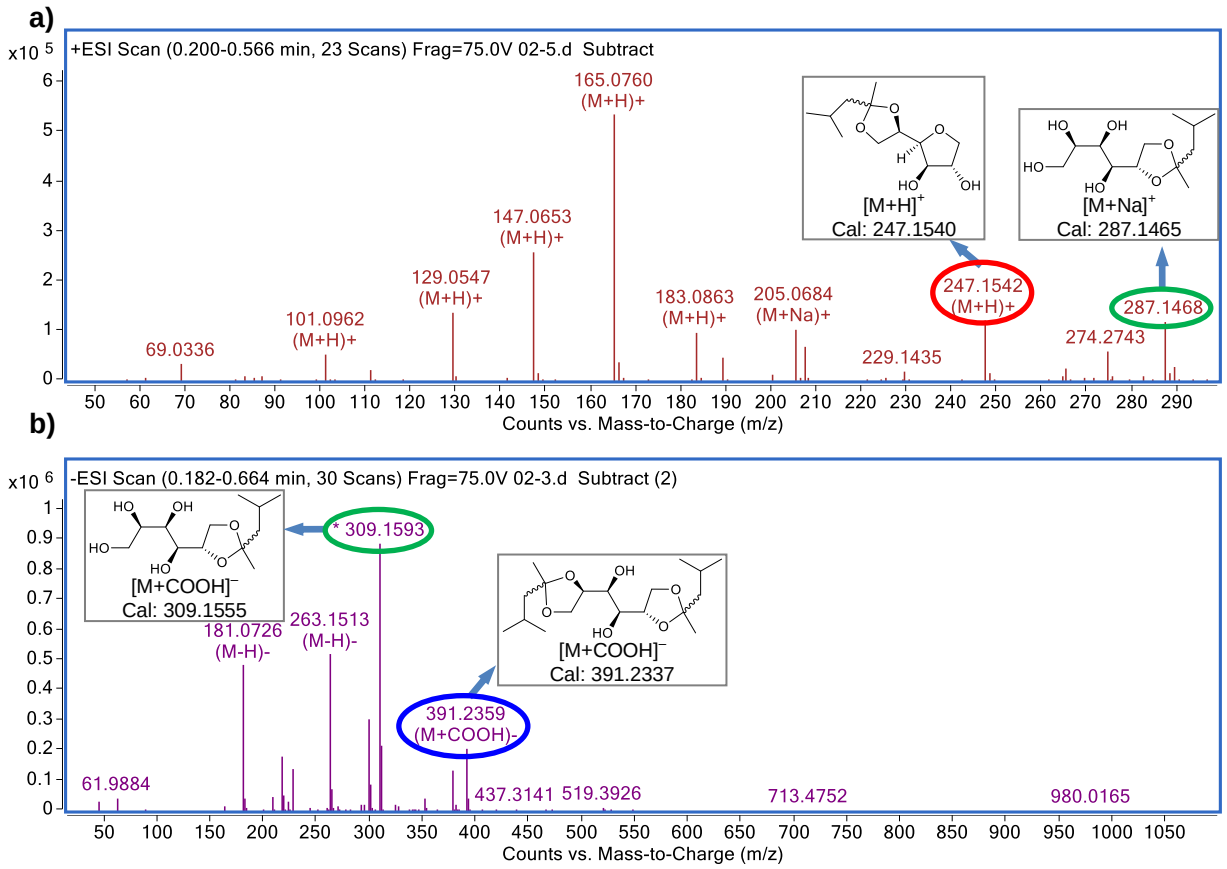


Figure S4. HRMS spectra in positive mode (a) and negative mode (b) for the initial conversion of sorbitol in acetic acid/MIBK solvent system on H-beta(20) showing formation of three types of the five-membered ketal intermediates, corresponding to 5,6-*O*-ketal of 1,4-sorbitan (HRMS data for $C_{12}H_{23}O_5$ $[M+H]^+$ cal: 247.1540, found: 247.1542), sorbitol monoketals (HRMS data for $C_{12}H_{24}O_6Na$ $[M+Na]^+$ cal: 287.1465, found: 287.1468; $C_{13}H_{25}O_8$ $[M+COOH]^-$ cal: 309.1555, found: 309.1593) and sorbitol diketals (HRMS data for $C_{19}H_{35}O_8$ $[M+COOH]^-$ cal: 391.2337, found: 391.2359). Reaction conditions: sorbitol (0.75 mmol), acetic acid (3.0 mL), MIBK (2.5 mL), H-beta(20) (27 mg), 190 ^oC, 1 min.

7. GC-MS analysis for the initial conversion of sorbitol in acetic acid/MIBK

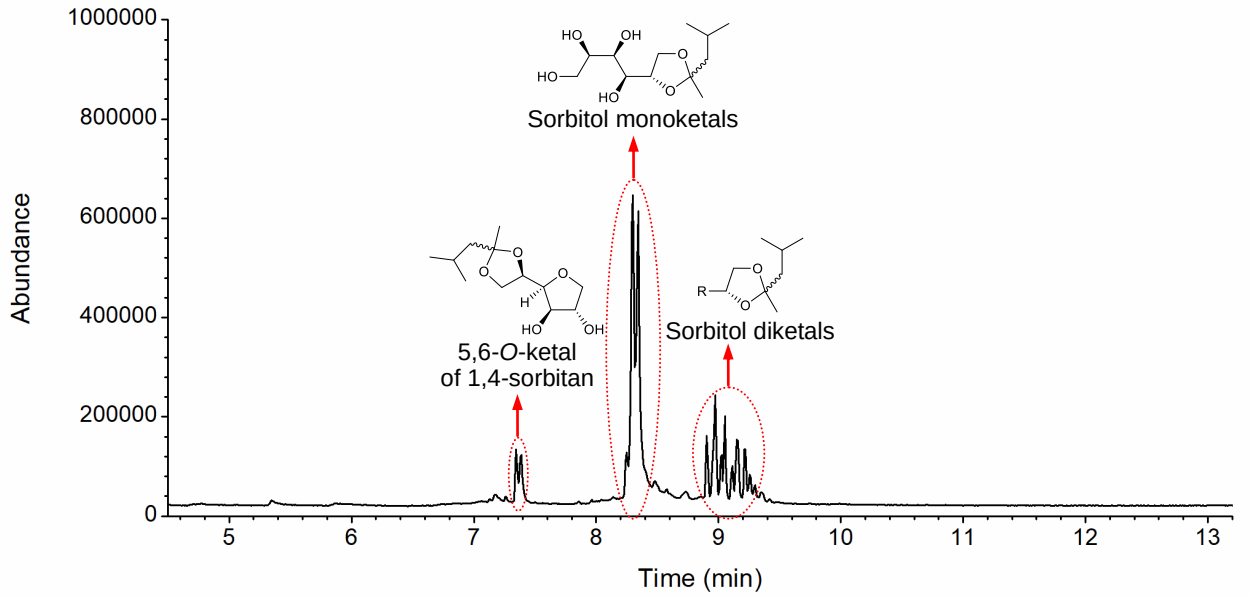


Figure S5. Typical total ion chromatogram (TIC) spectrum for the reaction mixture from the direct conversion of sorbitol in acetic acid/MIBK solvent system over H-beta(20) zeolite showing the formation of three types of the five-membered ketal intermediates, corresponding to 5,6-*O*-ketal of 1,4-sorbitan (7.32–7.45 min), mono- (8.22–8.45 min) and di-ketals (8.88–9.32 min) of sorbitol. Reaction conditions: sorbitol (0.75 mmol), acetic acid (3.0 mL), MIBK (2.5 mL), H-beta(20) (27 mg), 190 ^{o}C, 1 min.

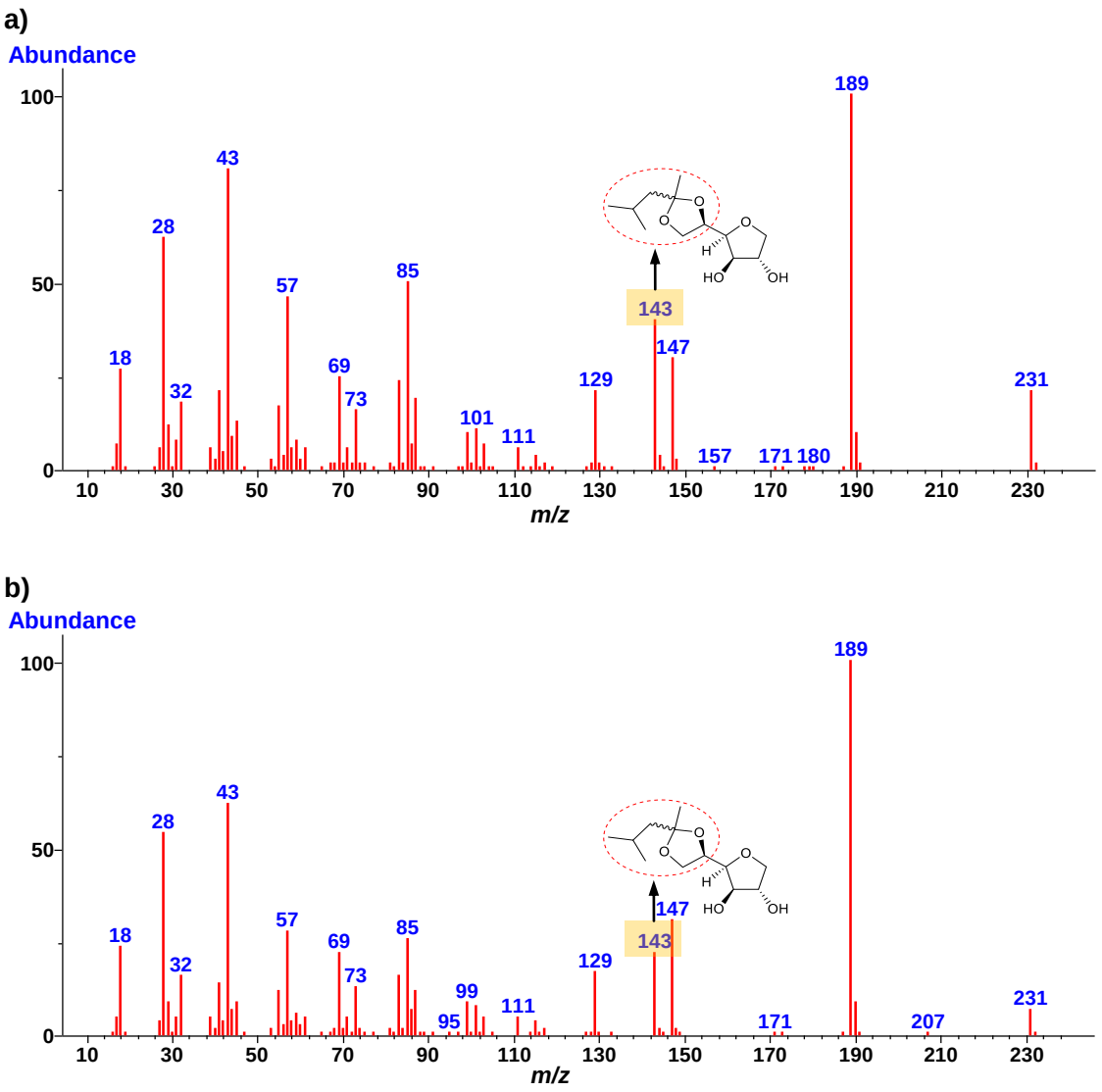


Figure S6. Mass spectra at 7.34 min (a) and 7.39 min (b) for 5,6-*O*-ketal of 1,4-sorbitan showing the typical peak at *m/z* 143 due to a terminal 1,3-dioxolane ring. EI-MS (70 eV): *m/z* 231 (M^+–CH_3), 189 (M^+–C_4H_9), 143 ($C_8H_{15}O_2^+$, terminal 1,3-dioxolane ring).

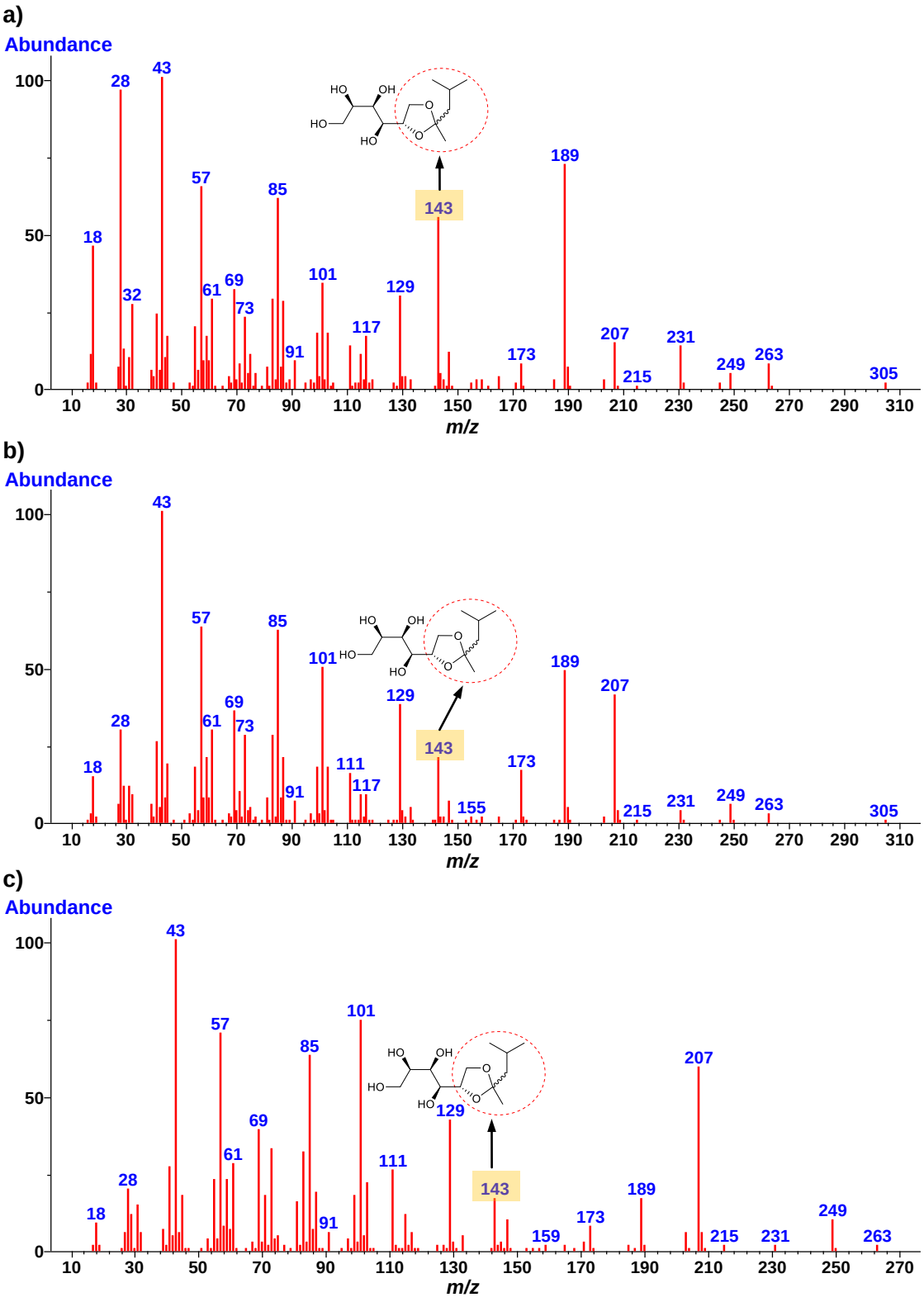
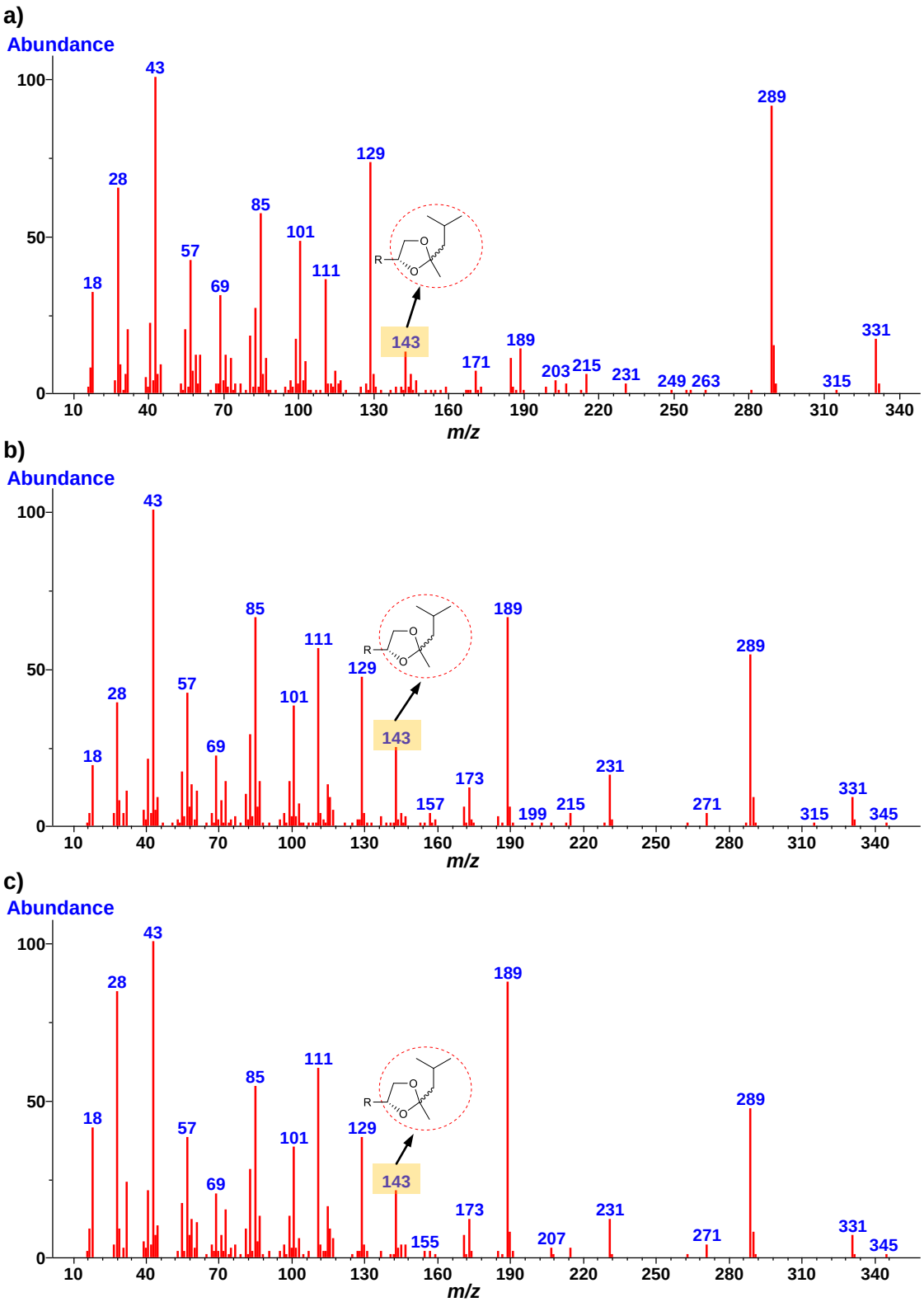
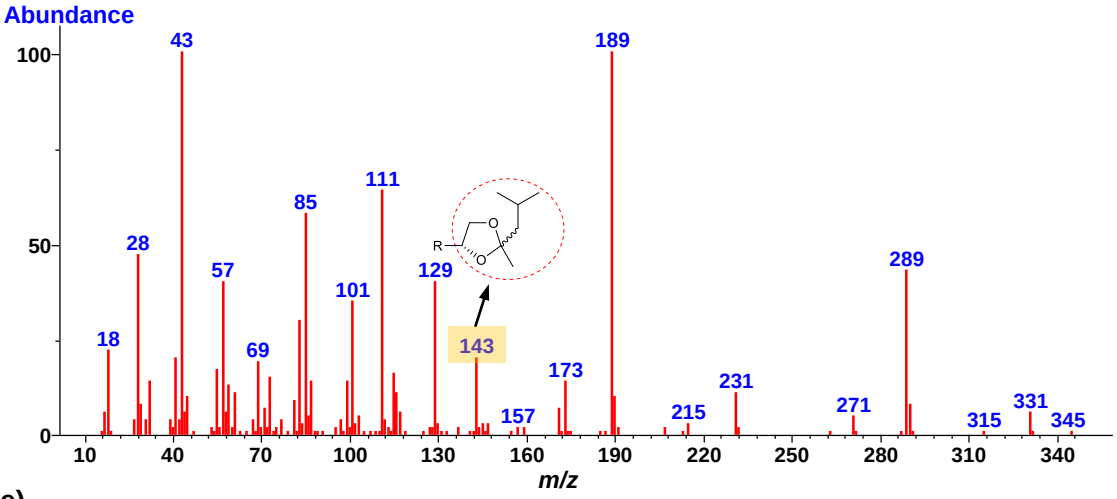


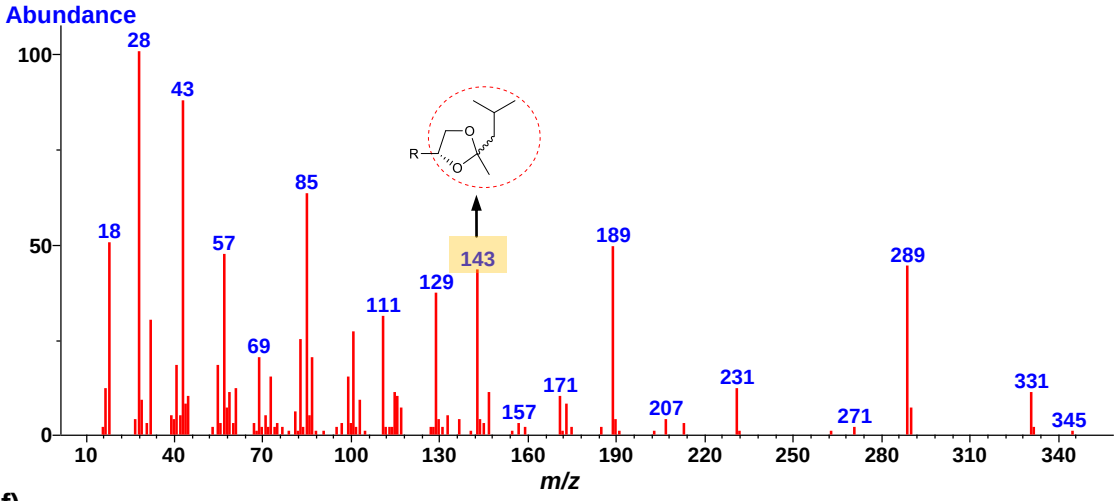
Figure S7. Mass spectra at 8.25 min (a), 8.28 min (b), and 8.33 min (c) for sorbitol monoketals showing the typical peak at *m/z* 143 due to a terminal 1,3-dioxolane ring. EI-MS (70 eV): *m/z* 263 (M^+–H), 249 (M^+–CH_3), 207 (M^+–C_4H_9), 143 ($C_8H_{15}O_2^+$, terminal 1,3-dioxolane ring).


a)
Abundance
100
50
0
43
289
129
28
85
101
57
111
18
69
143
189
171
203
215
231
249
263
315
331
10
40
70
100
130
160
190
220
250
280
310
340
m/z
b)
Abundance
100
50
0
43
85
189
111
129
57
28
101
289
69
143
18
173
231
157
199
215
271
315
331
345
10
40
70
100
130
160
190
220
250
280
310
340
m/z
c)
Abundance
100
50
0
43
189
28
111
85
289
18
57
129
101
69
143
173
231
155
207
271
331
345
10
40
70
100
130
160
190
220
250
280
310
340
m/z

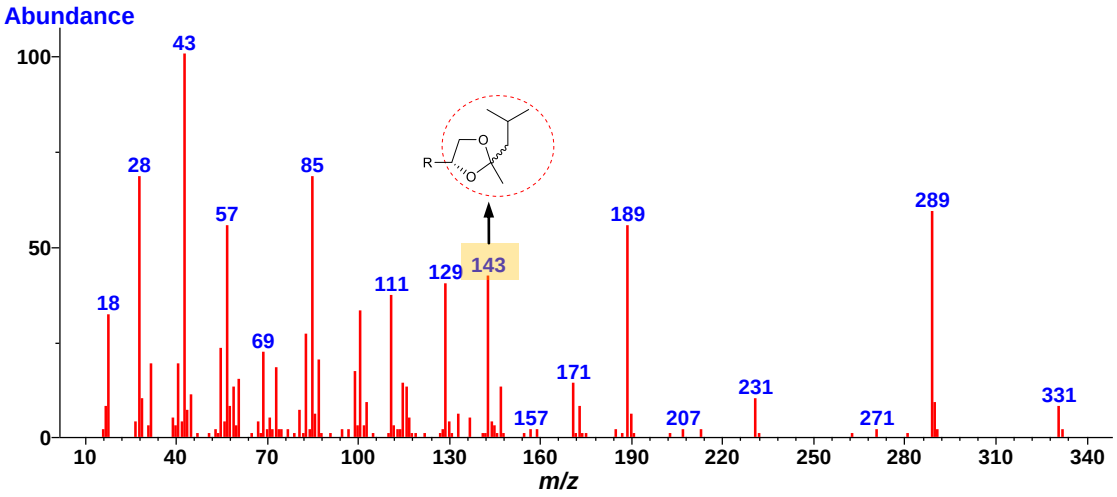
d)


Abundance
100
50
0
43
189
111
85
28
57
129
101
143
289
18
69
173
231
271
157
215
315
331
345
10
40
70
100
130
160
190
220
250
280
310
340
m/z

e)


Abundance
100
50
0
28
43
85
18
57
143
189
289
129
111
69
171
231
331
157
207
271
345
10
40
70
100
130
160
190
220
250
280
310
340
m/z

f)


Abundance
100
50
0
43
28
85
57
189
289
143
129
111
18
69
171
231
331
157
207
271
10
40
70
100
130
160
190
220
250
280
310
340
m/z

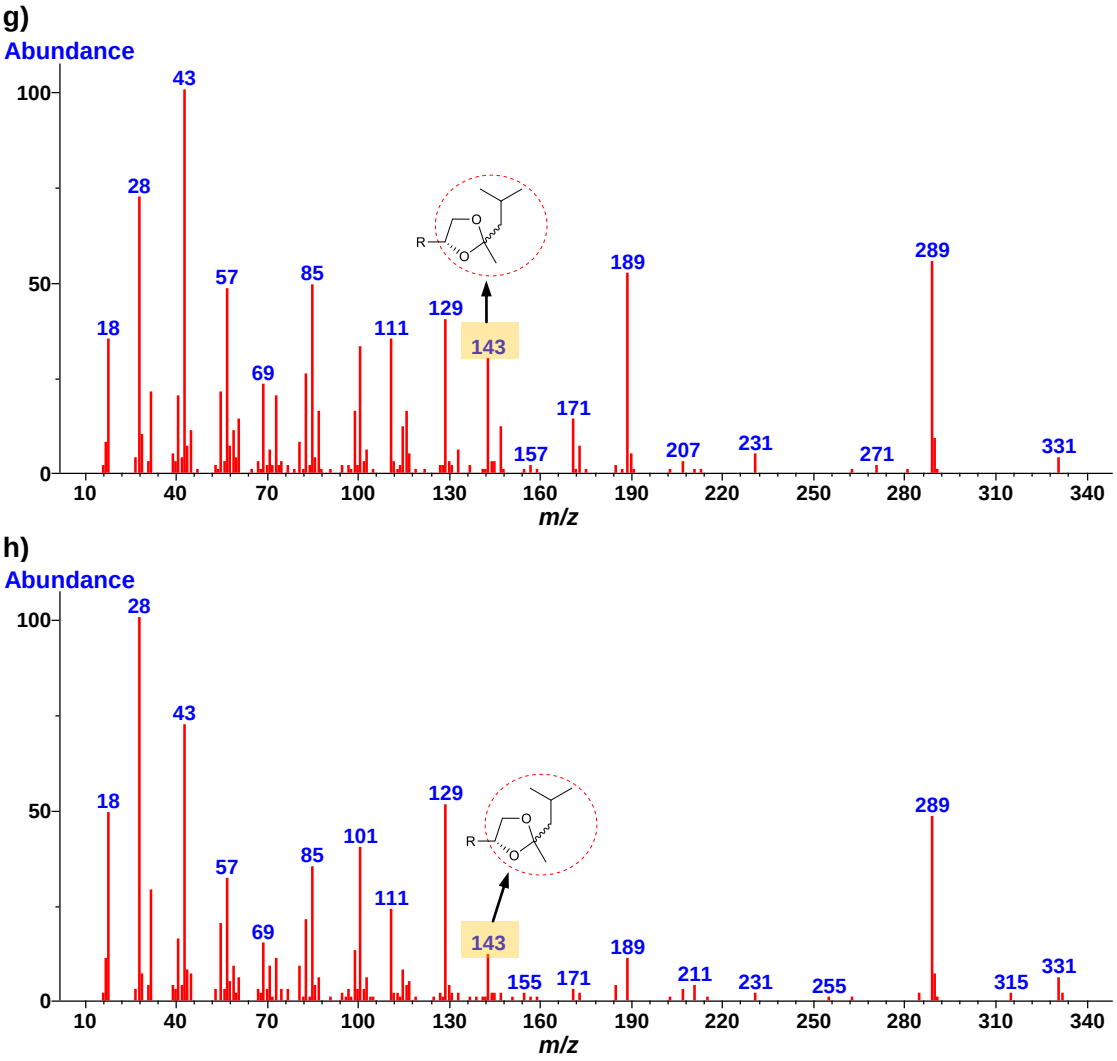


Figure S8. Mass spectra at 8.90 min (a), 8.97 min (b), 9.02 min (c), 9.05 min (d), 9.11 min (e), 9.15 min (f), 9.21 min (g),and 9.25 min (h) for sorbitol diketals showing the typical peak at *m/z* 143 due to a terminal 1,3-dioxolane ring. EI-MS (70 eV): *m/z* 331 (M^+–CH_3), 289 (M^+–C_4H_9), 143 ($C_8H_{15}O_2^+$, terminal 1,3-dioxolane ring).

8. GC-MS analysis for the reaction of erythritol in MIBK at the initial stage

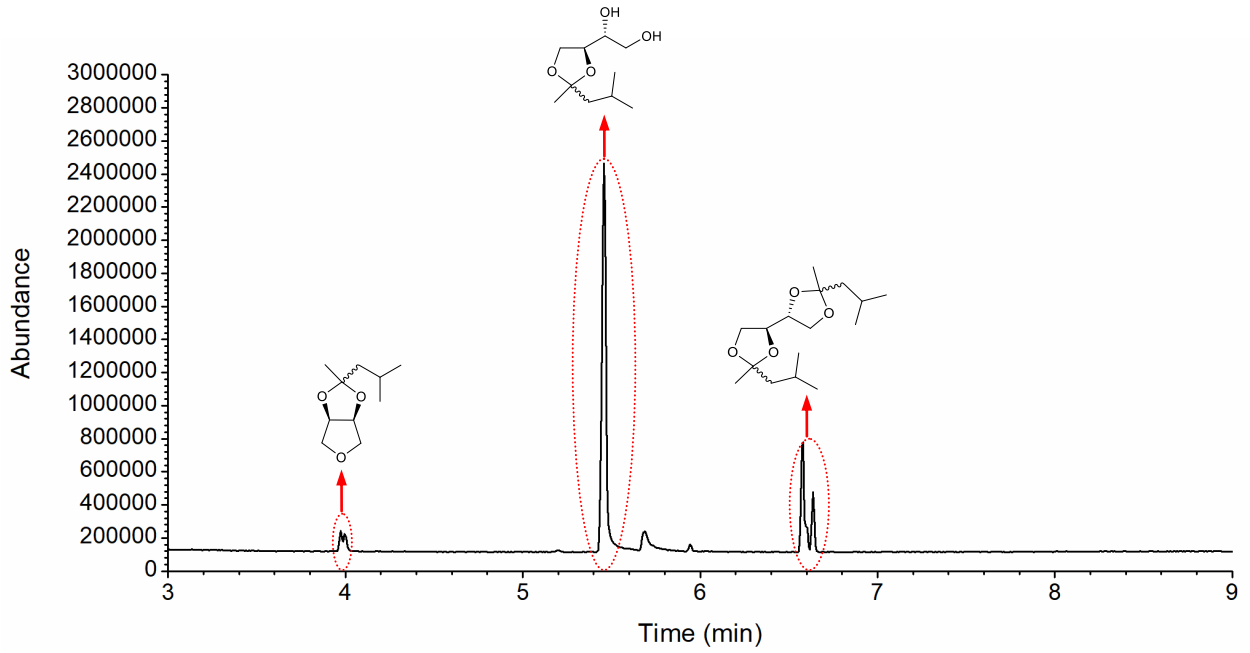


Figure S9. Typical total ion chromatogram (TIC) spectrum for the reaction mixture from the conversion of erythritol in MIBK solvent over H-beta zeolite showing the presence of five-membered cyclic ketal products including 1,2-*O*-(1-methylisopentylidene)-erythritol (erythritol monoketal), 1,2:3,4-*O*-di(1-methylisopentylidene)-erythritol (erythritol diketal) and trace amount of 2,3-*O*-(1-methylisopentylidene)-1,4-erythritan (1,4-erythritan ketal). Reaction conditions: erythritol (0.75 mmol), MIBK (2.5 mL), H-beta(20) (5 mg), 190 ^{o}C, 1 min.

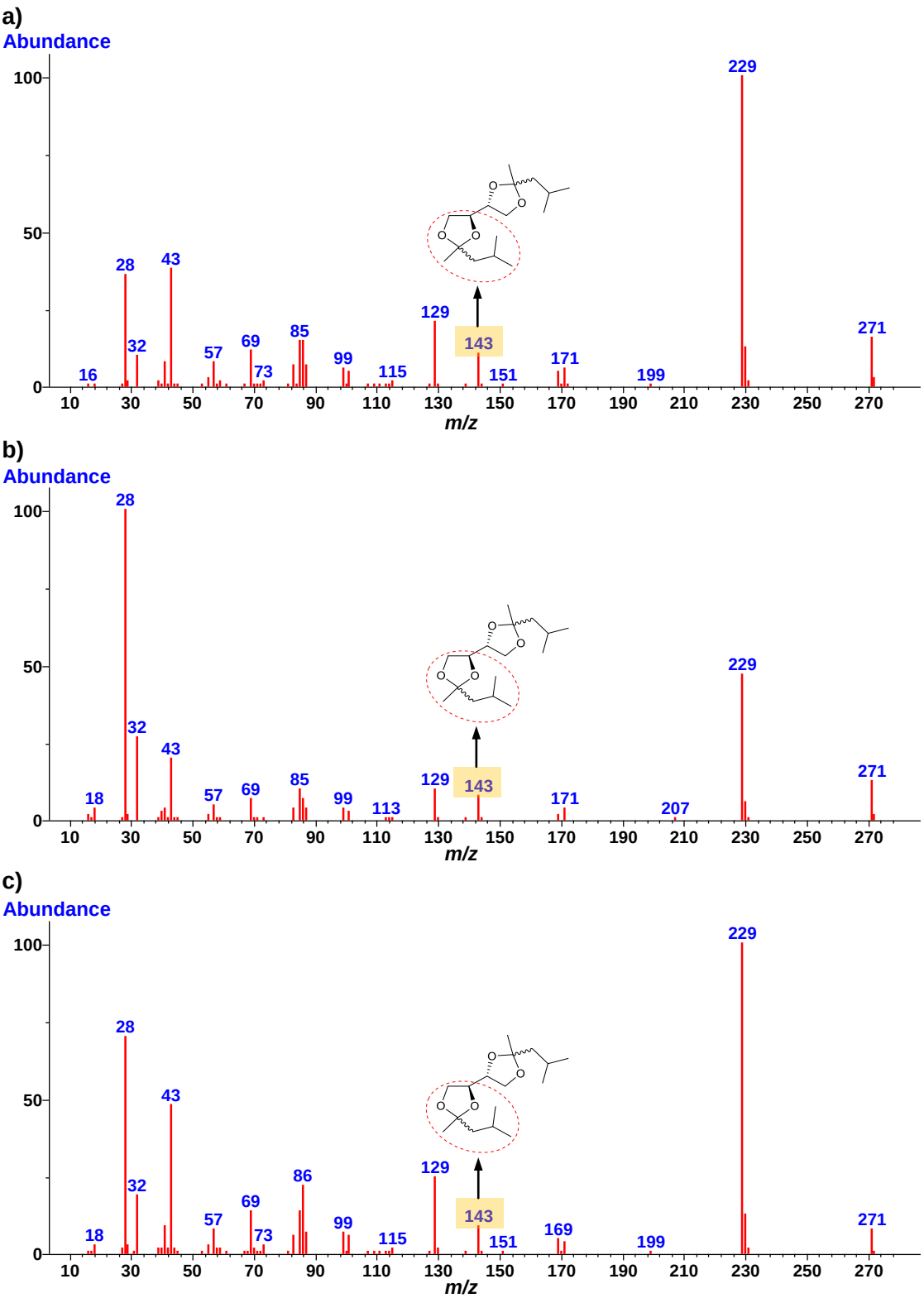


Figure S10. Mass spectra at 6.58 min (a), 6.60 min (b), and 6.63 min (c) for erythritol diketals showing the typical peak at *m/z* 143 due to a terminal 1,3-dioxolane ring. EI-MS (70 eV): *m/z* 271 (M^+–CH_3), 229 (M^+–C_4H_9), 143 ($C_8H_{15}O_2^+$, terminal 1,3-dioxolane ring).

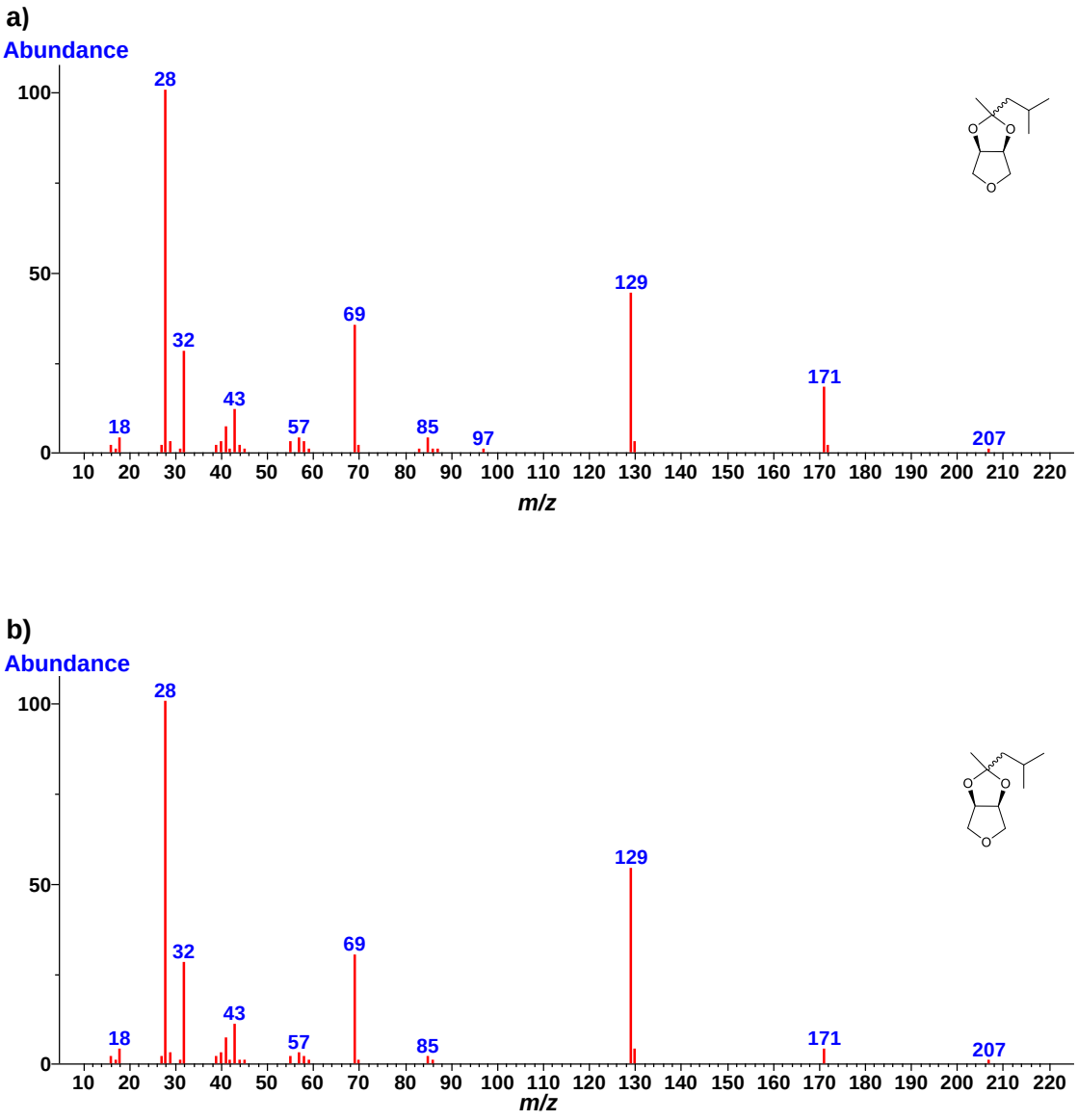


Figure S11. Mass spectra at 3.97 min (a) and 3.99 (b) min for 1,4-erythritan ketal showing no peak at *m/z* 143 due to a terminal 1,3-dioxolane ring. EI-MS (70 eV): *m/z* 171 (M^+–CH_3), 129 (M^+–C_4H_9).

9. Comparison of sorbitol reactivity for ketalization and esterification

Table S1 Comparison of sorbitol reactivity in pure MIBK and pure acetic acid on H-beta(20)[a]

Entry	Solvent	Sorbitol conversion (%)	Specific activity[b] (mmol·g^{-1}·h^{-1})
1	Acetic acid	1.2	4.0
2	MIBK	8.9	29.7

[a] Reaction condition: sorbitol (0.75 mmol), H-beta(20) zeolite (27 mg), solvent (2.5 mL), 70 °C for 5 min. [b] Specific activity, defined as mmol of sorbitol converted per gram of catalyst per hour.

10. FT-IR characterization of H-beta(20) catalyst

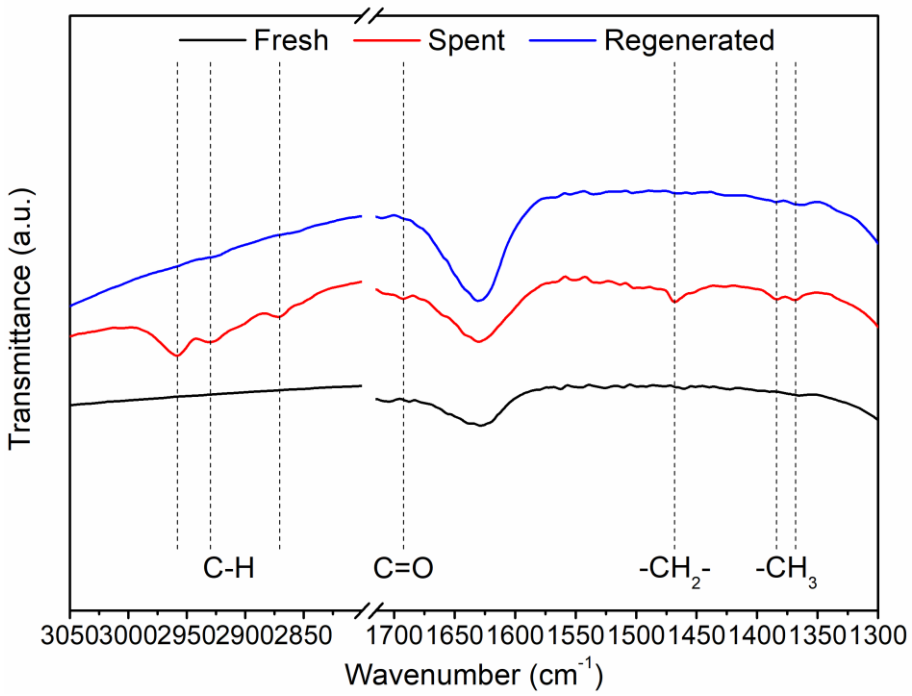
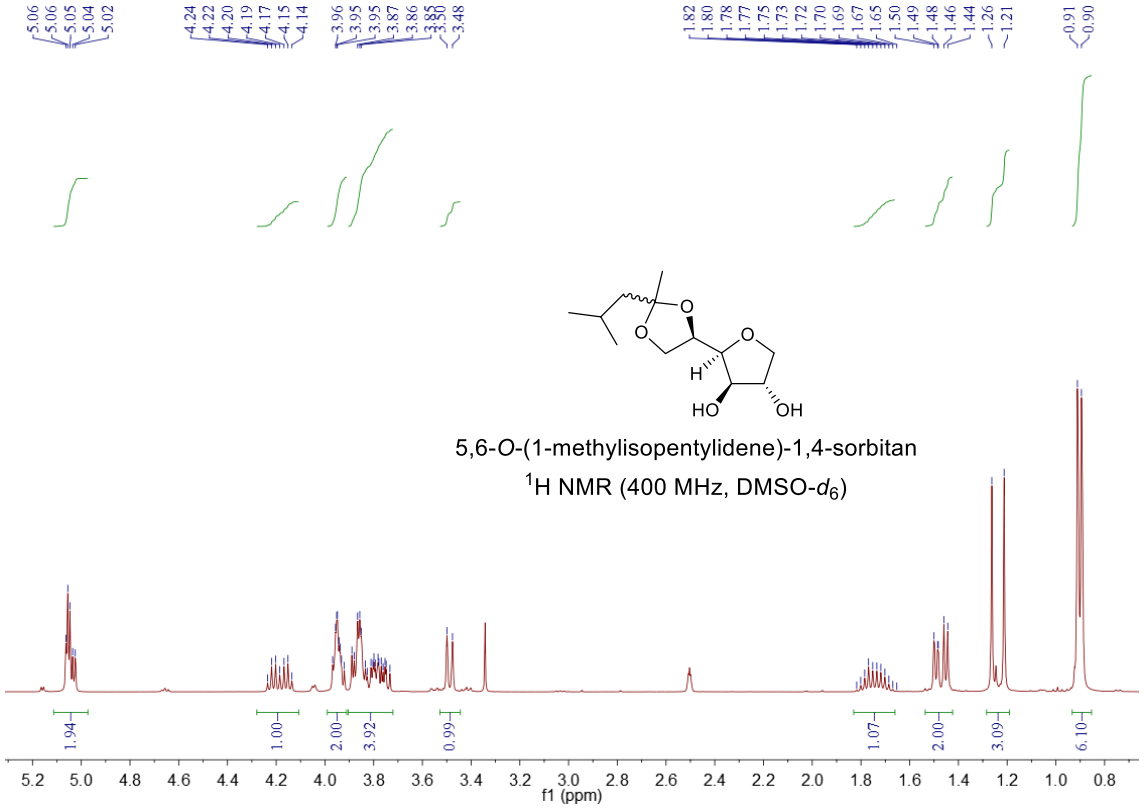


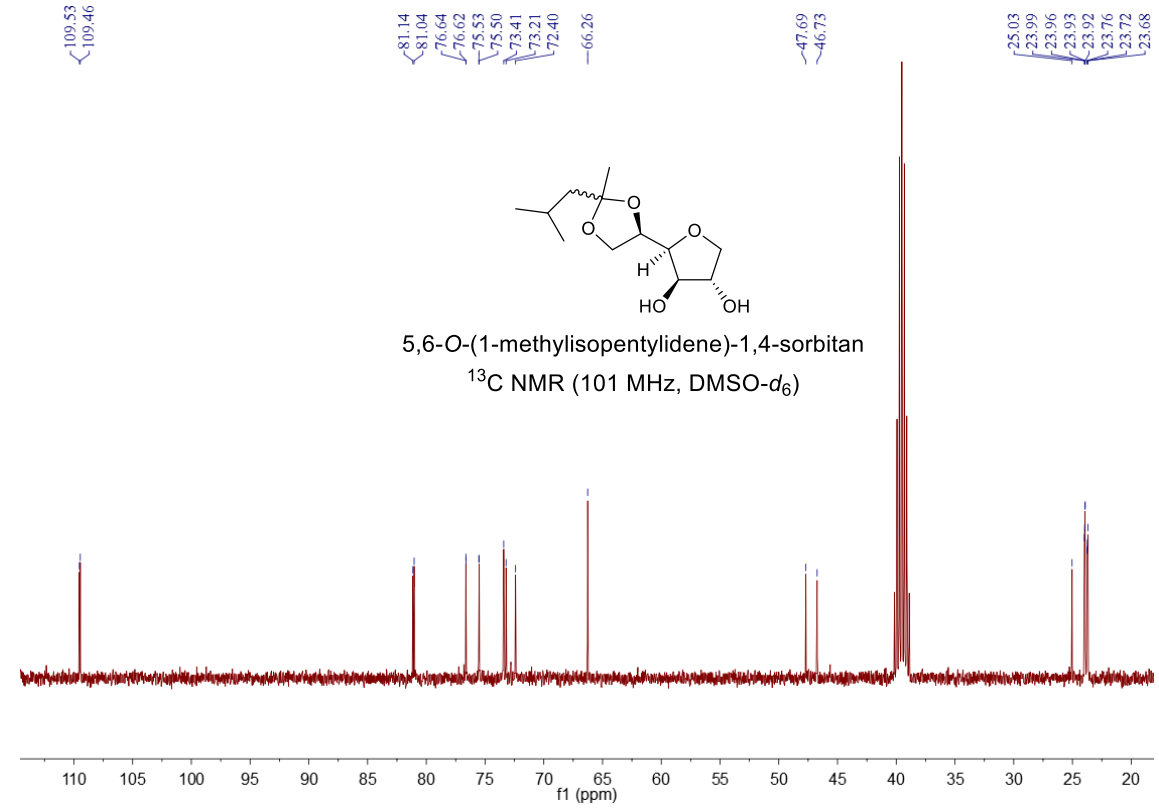
Figure S12. FT-IR spectra of the fresh, used and regenerated H-beta(20) catalysts. Spent catalyst refers to the catalyst recovered after undergoing one reaction run without calcination. Regenerated catalyst refers to the catalyst recovered after one reaction run followed by calcination at 550 °C for 8 h in air flow.

The spent catalyst exhibited three distinct bands at 2958, 2929 and 2870 cm^{-1}, which are assigned to the stretching vibrations of the alkyl C-H[2]. Correspondingly, three characteristic peaks were clearly observed at 1468, 1384 and 1368 cm^{-1} belonging to the deformation

vibrations of the C-H in -CH_2- and -CH_3 group[3]. Besides, a weak band located at 1692 cm^{-1} can be due to the stretching vibration of C=O functional group. These characteristic absorptions indicate the presence of humins on the spent H-beta(20) zeolite. After calcination at 550 ^oC for 8 h, the regenerated H-beta(20) catalyst displayed the quite similar spectrum to the fresh catalyst without these identification bands for humins. This result suggests that humins deposited on the spent catalyst can be completely removed by calcination in air flow.

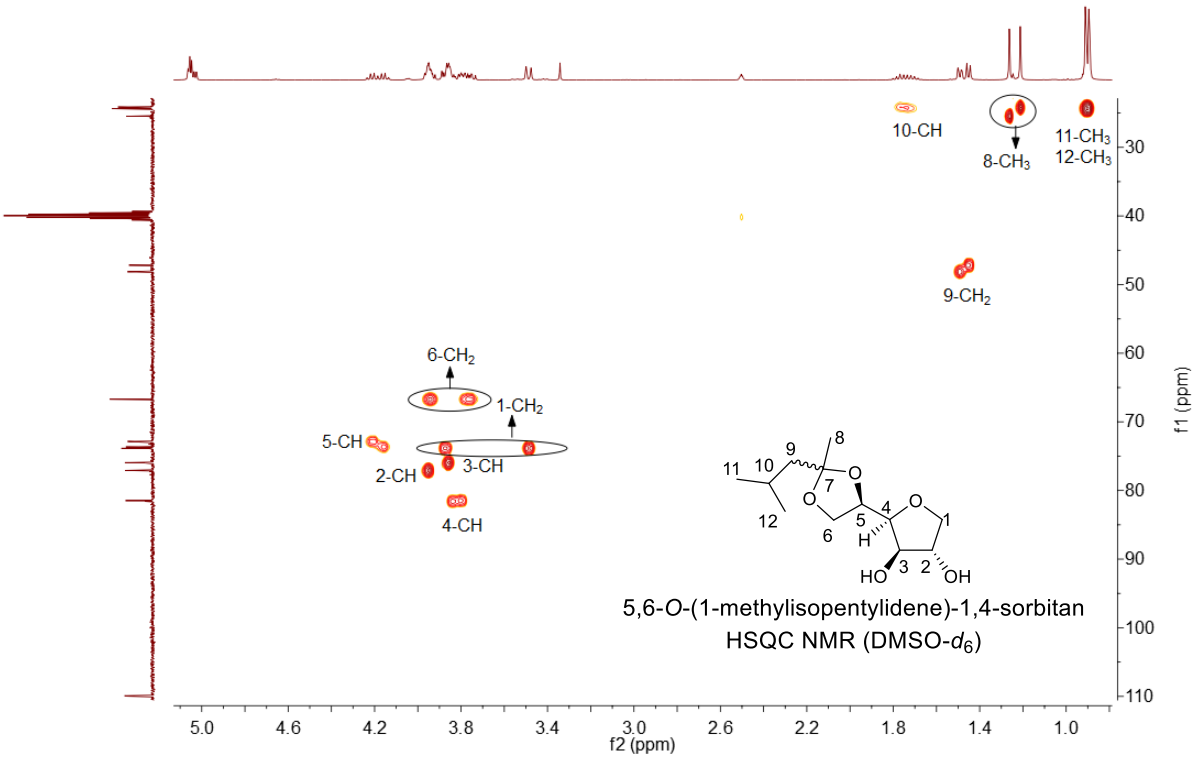
11. NMR spectra of purified compounds





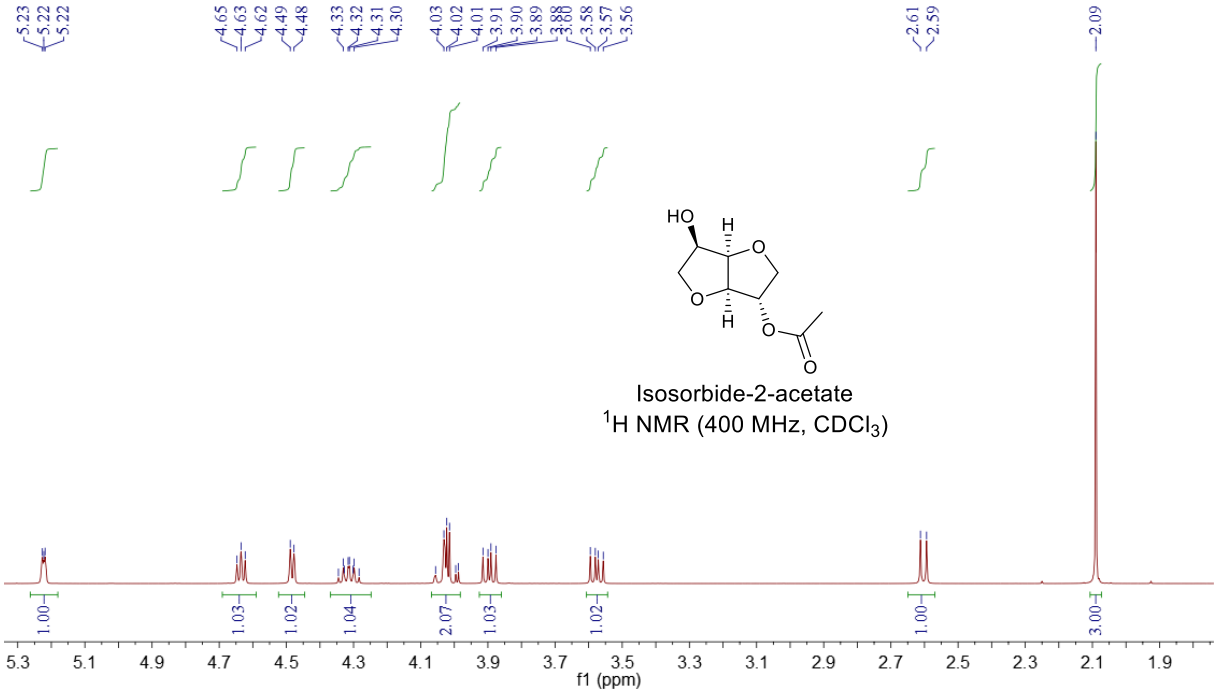
5,6-*O*-(1-methylisopentylidene)-1,4-sorbitan

^{13}C NMR (101 MHz, DMSO-d_6)



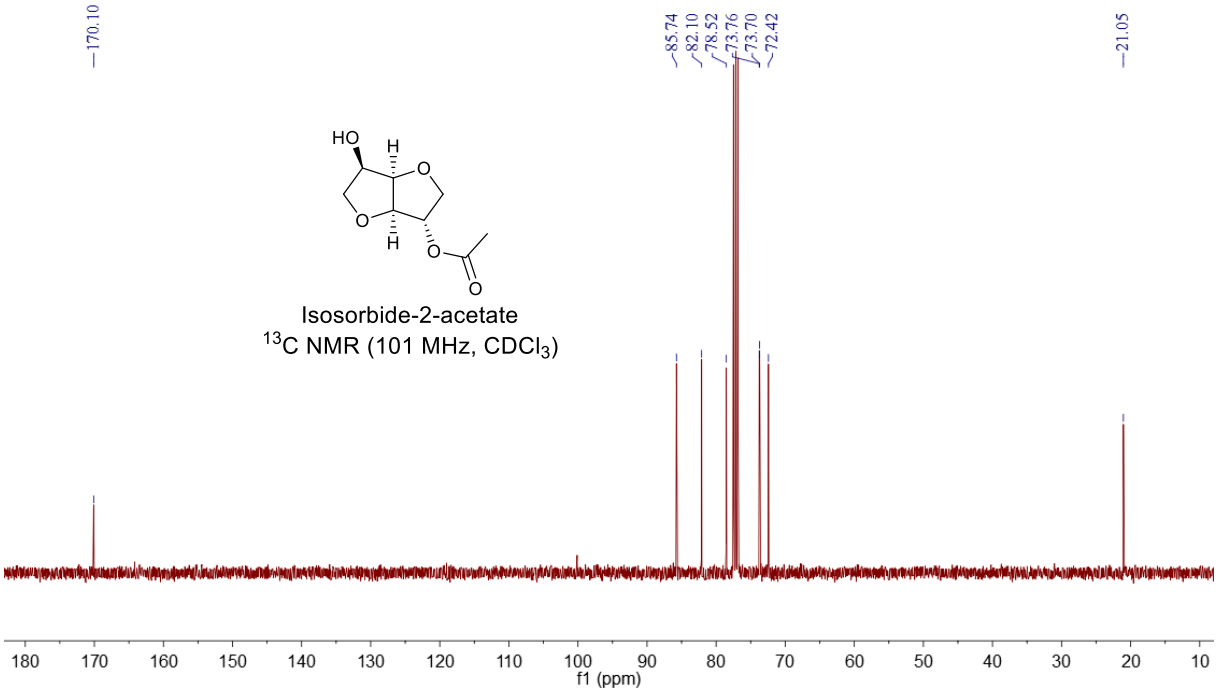
5,6-*O*-(1-methylisopentylidene)-1,4-sorbitan

HSQC NMR (DMSO-d_6)



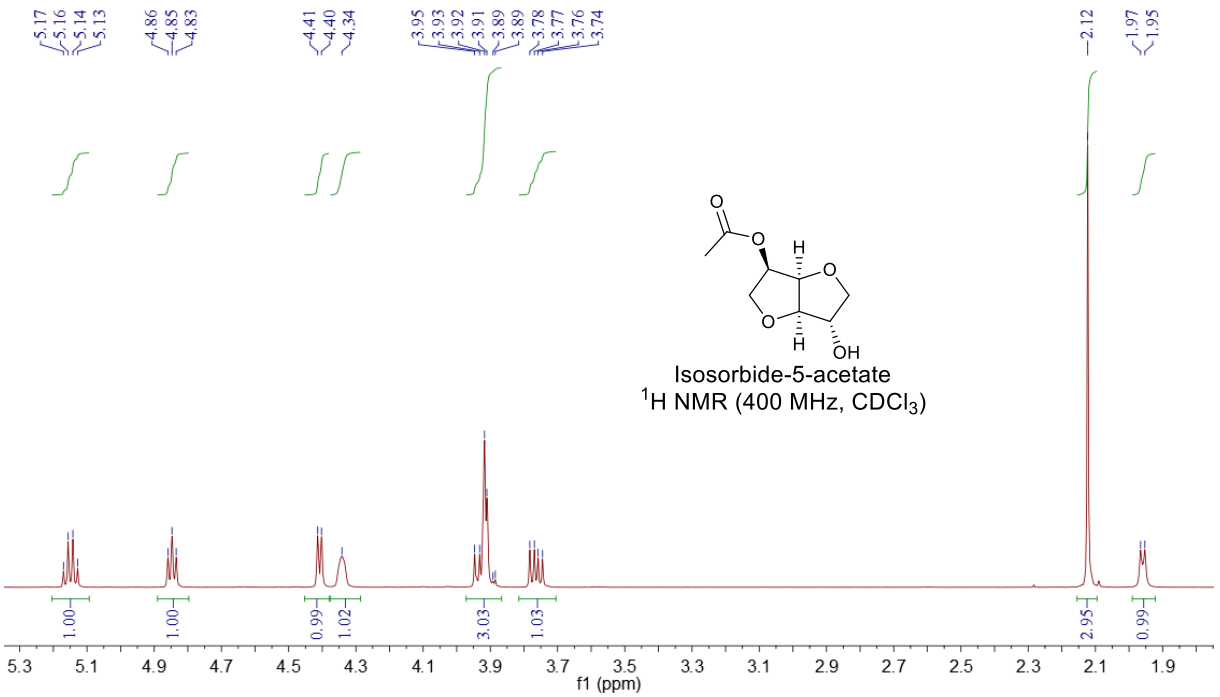
Isosorbide-2-acetate

^{1}H NMR (400 MHz, $CDCl_3$)

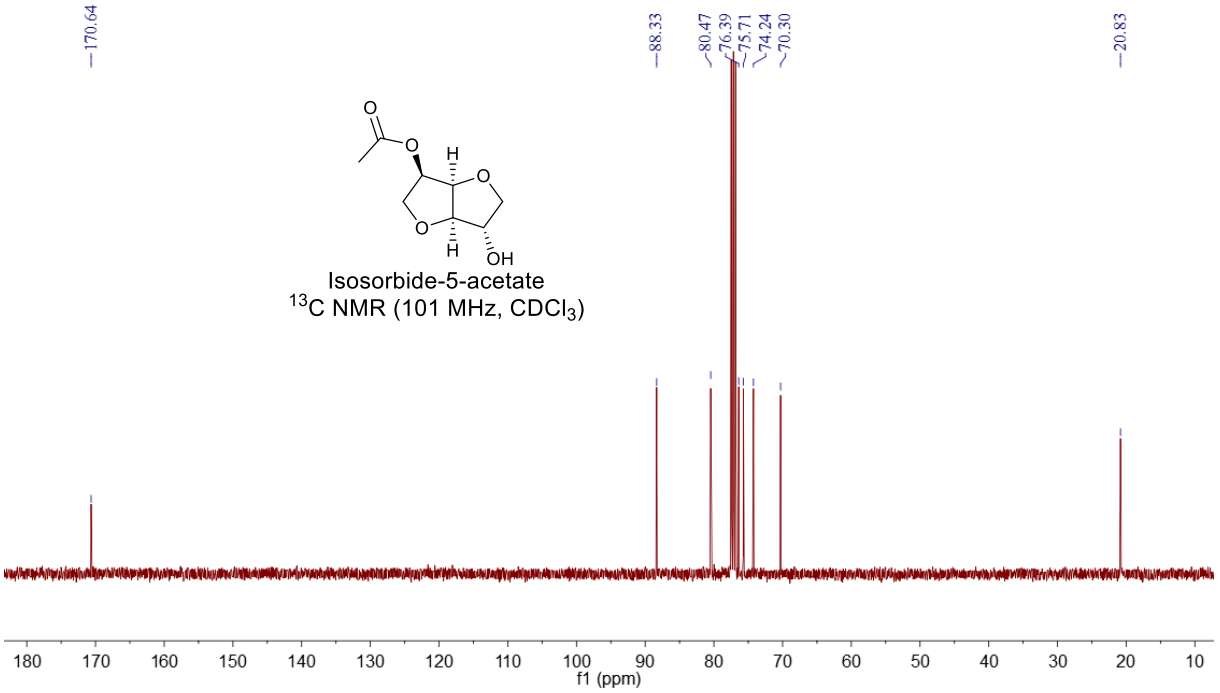


Isosorbide-2-acetate

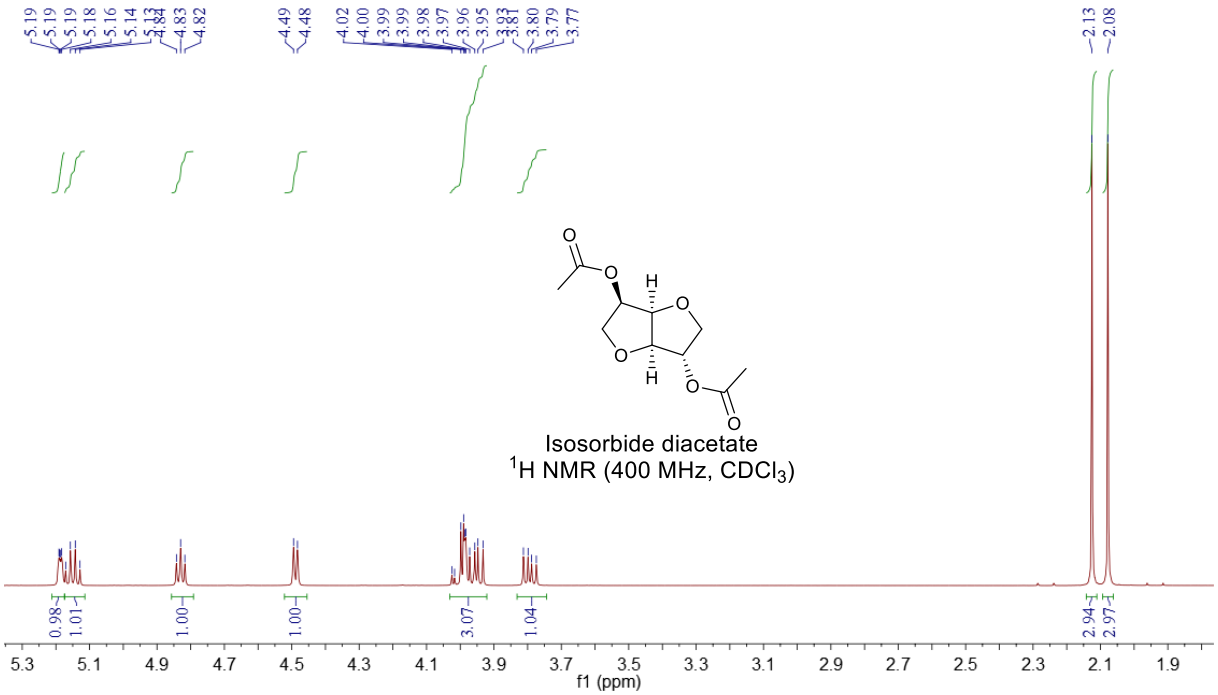
^{13}C NMR (101 MHz, $CDCl_3$)



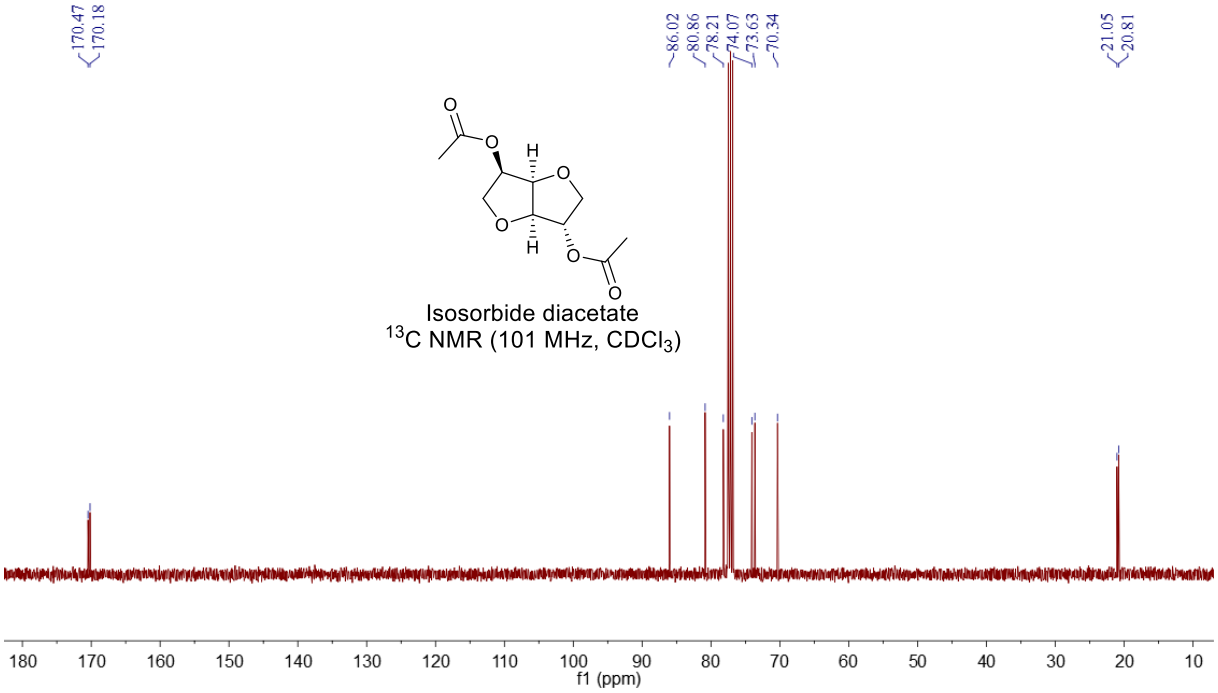
Isosorbide-5-acetate
^{1}H NMR (400 MHz, $CDCl_3$)



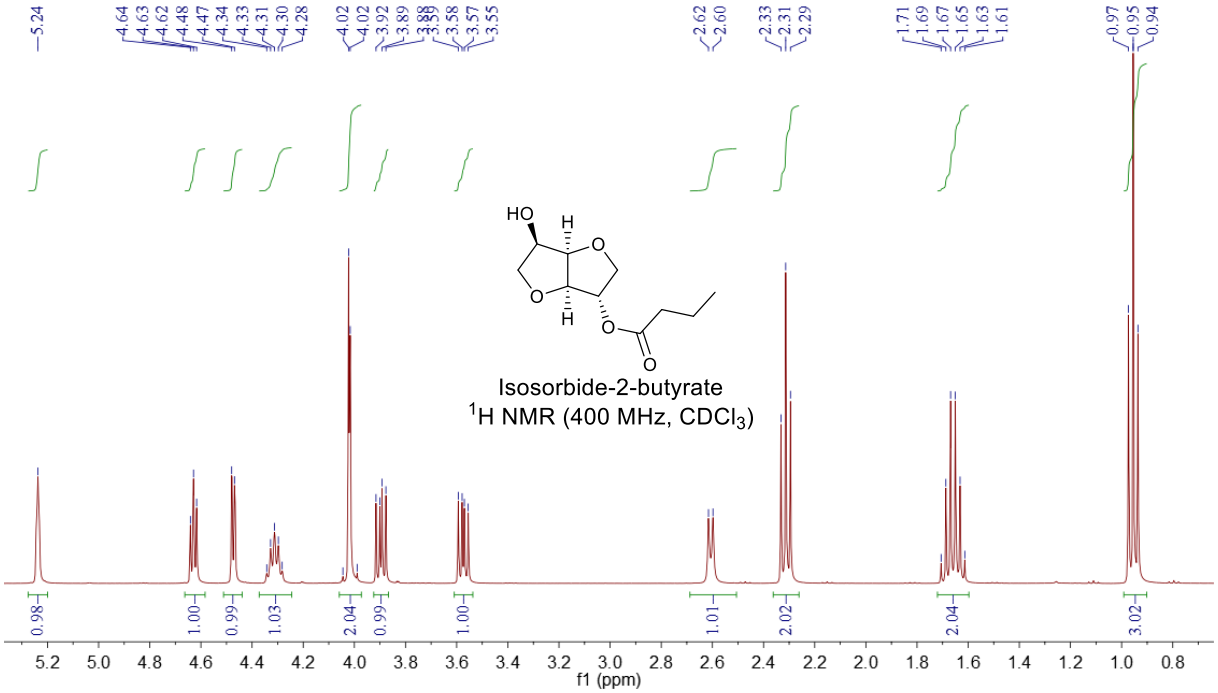
Isosorbide-5-acetate
^{13}C NMR (101 MHz, $CDCl_3$)



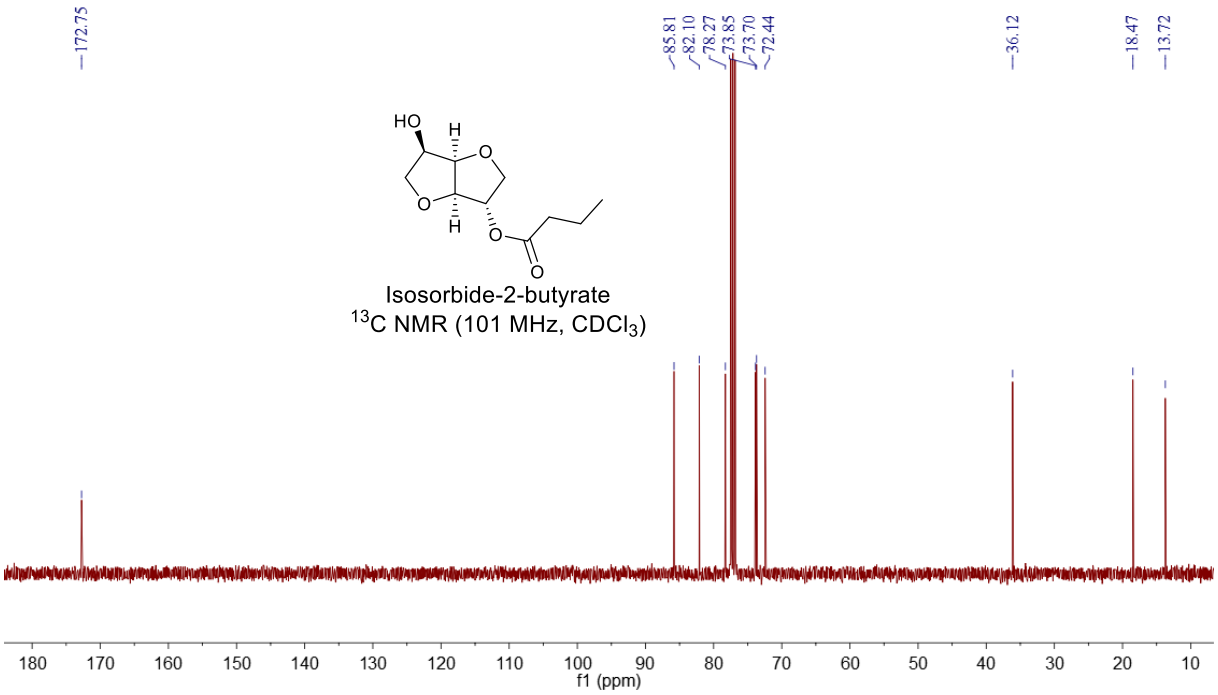
Isosorbide diacetate
^{1}H NMR (400 MHz, $CDCl_3$)



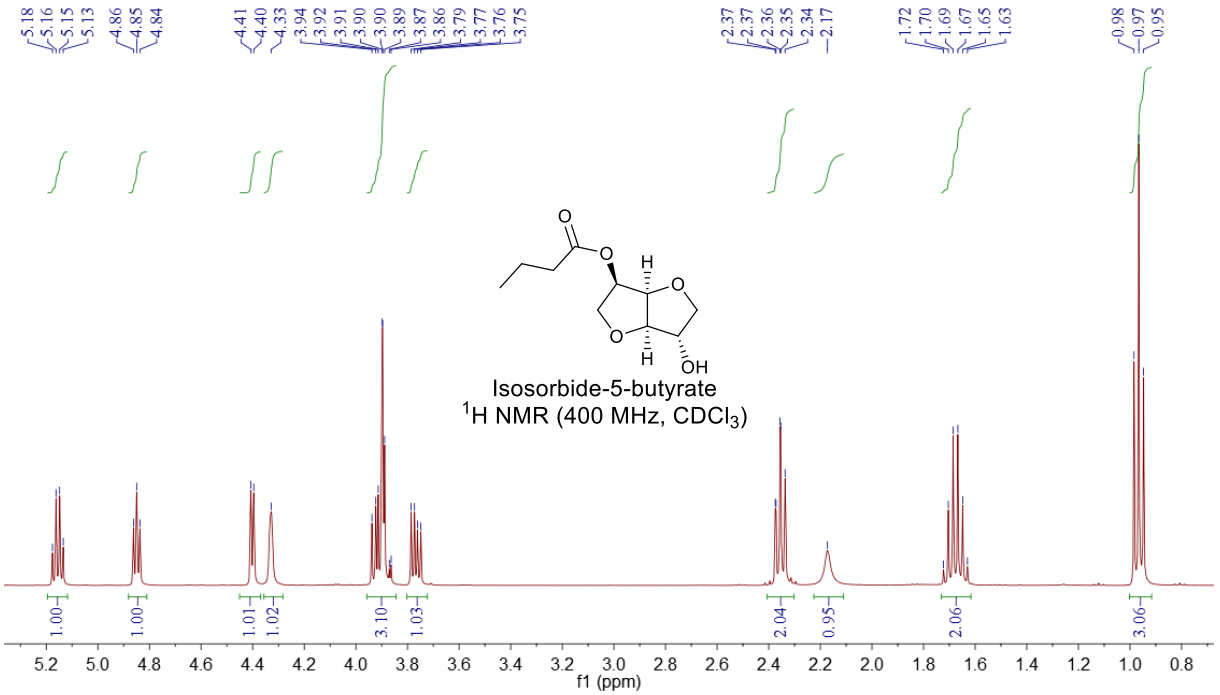
Isosorbide diacetate
^{13}C NMR (101 MHz, $CDCl_3$)

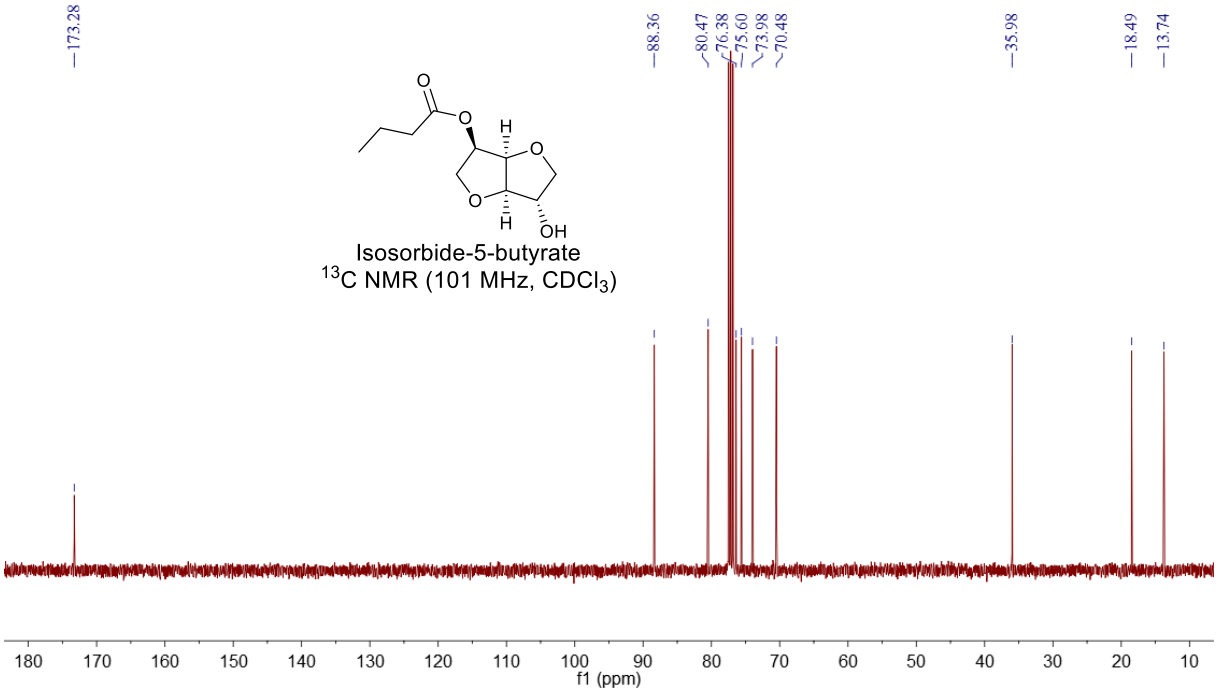


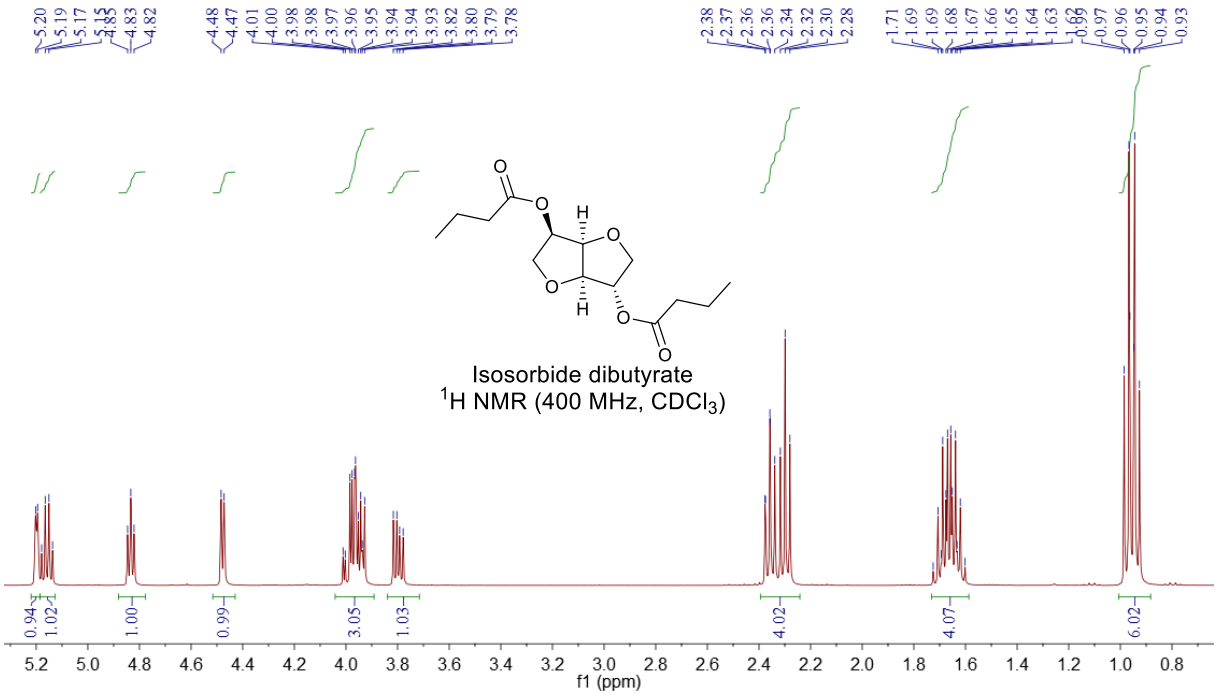
Isosorbide-2-butyrate
^{1}H NMR (400 MHz, $CDCl_3$)



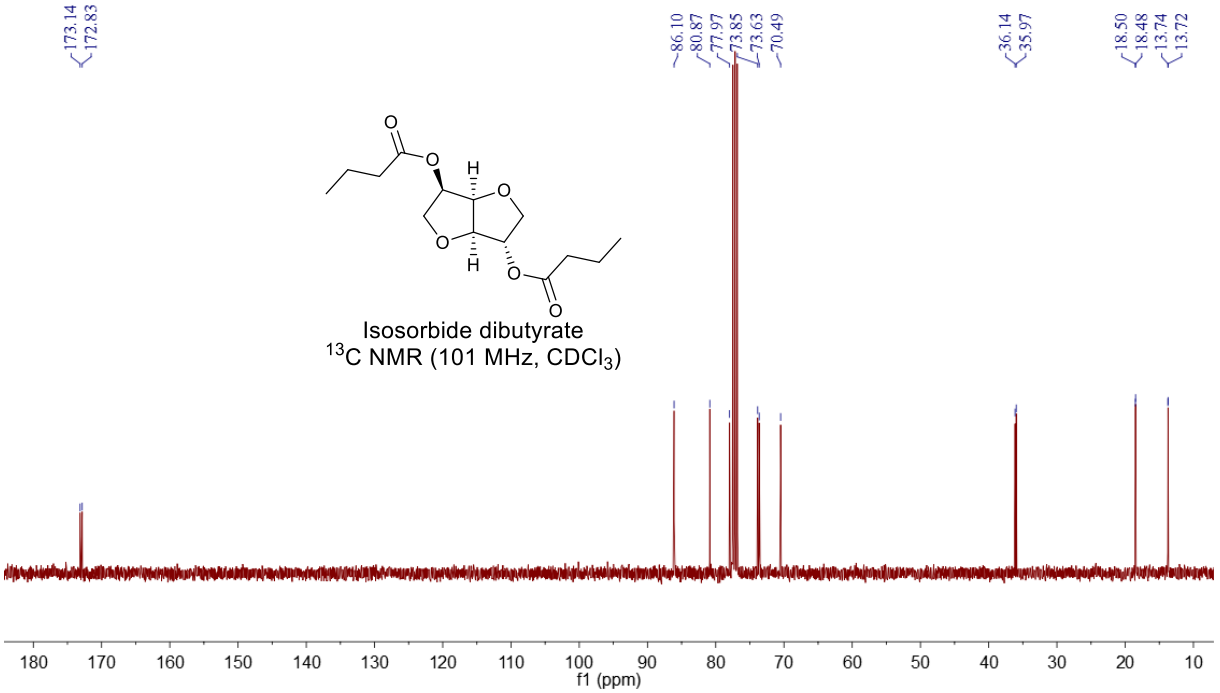
Isosorbide-2-butyrate
^{13}C NMR (101 MHz, $CDCl_3$)


5.18
5.16
5.15
5.13
4.86
4.85
4.84
4.41
4.40
4.33
3.94
3.92
3.91
3.90
3.90
3.89
3.87
3.86
3.79
3.77
3.77
3.76
3.75
2.37
2.37
2.36
2.35
2.34
2.17
1.72
1.70
1.69
1.67
1.65
1.63
0.98
0.97
0.95
O
O
H
O
O
H
OH
Isosorbide-5-butyrate
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.01
1.02
3.10
1.03
2.04
0.95
2.06
3.06
5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
f1 (ppm)

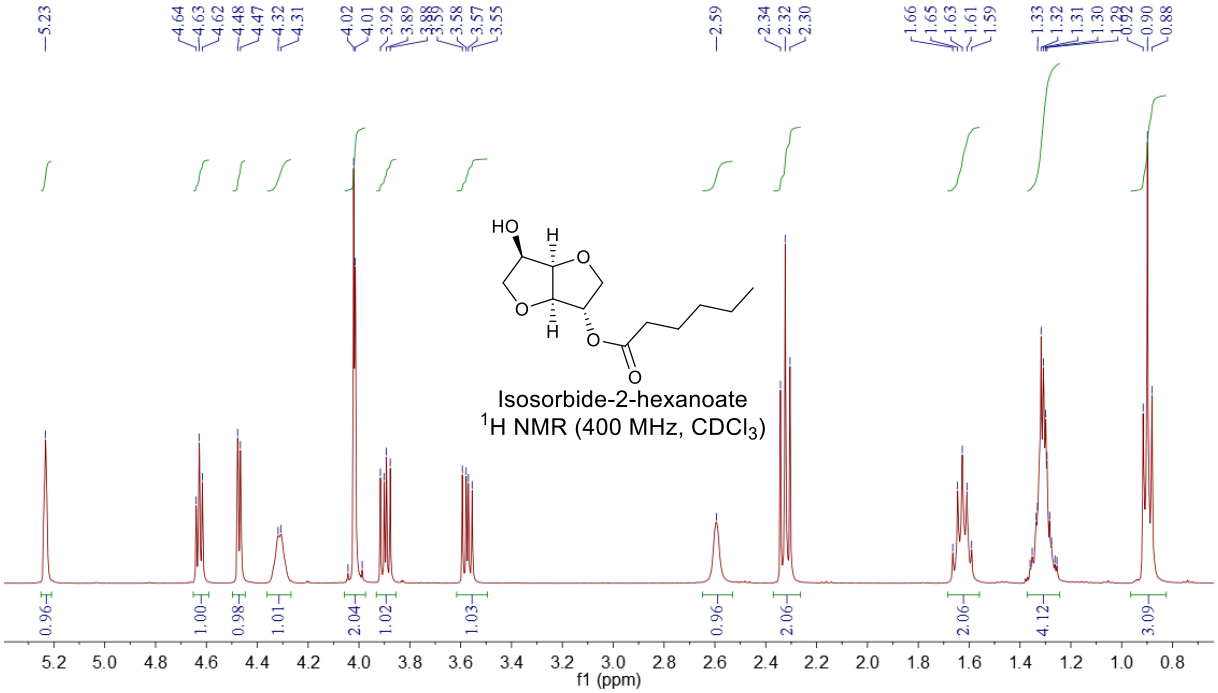

173.28
88.36
80.47
76.38
75.60
73.98
70.48
35.98
18.49
13.74
O
O
H
O
O
H
OH
Isosorbide-5-butyrate
13C NMR (101 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



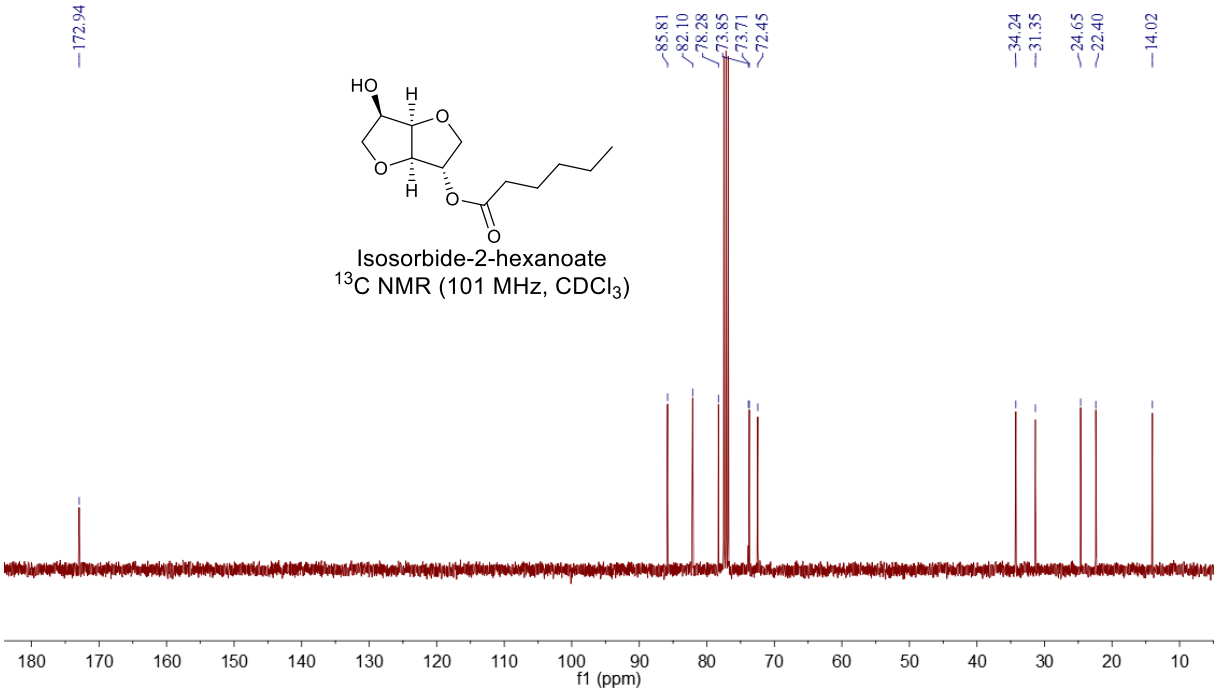
Isosorbide dibutyrate
^{1}H NMR (400 MHz, $CDCl_3$)



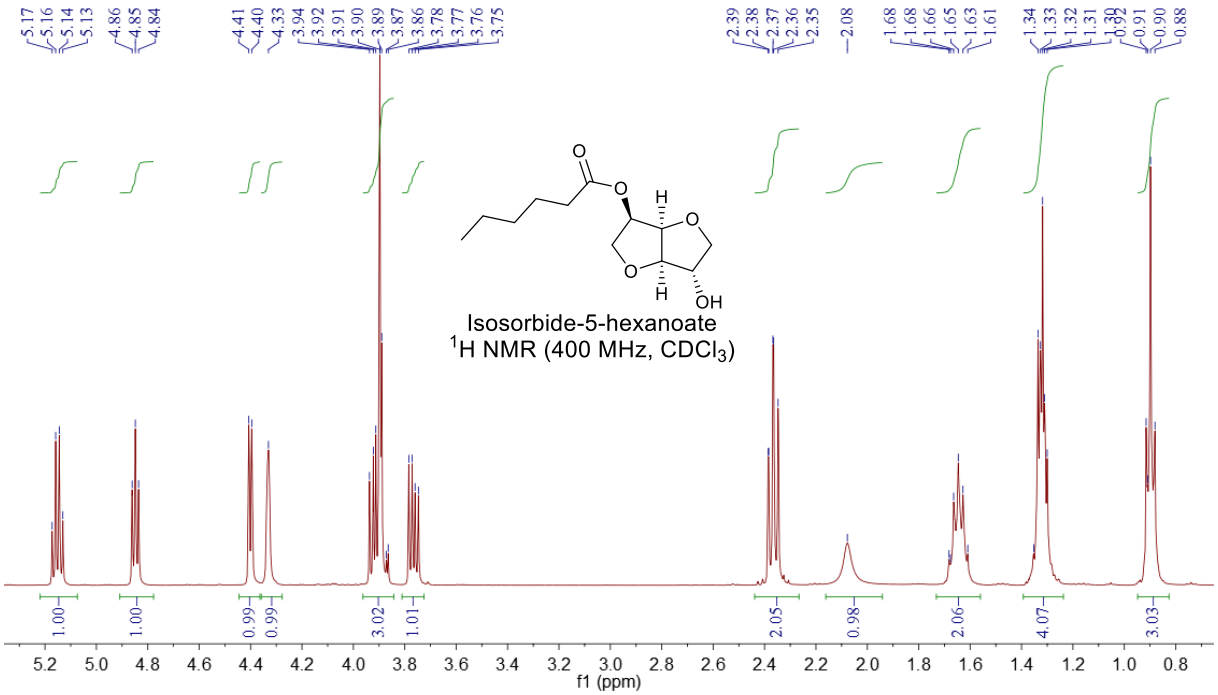
Isosorbide dibutyrate
^{13}C NMR (101 MHz, $CDCl_3$)

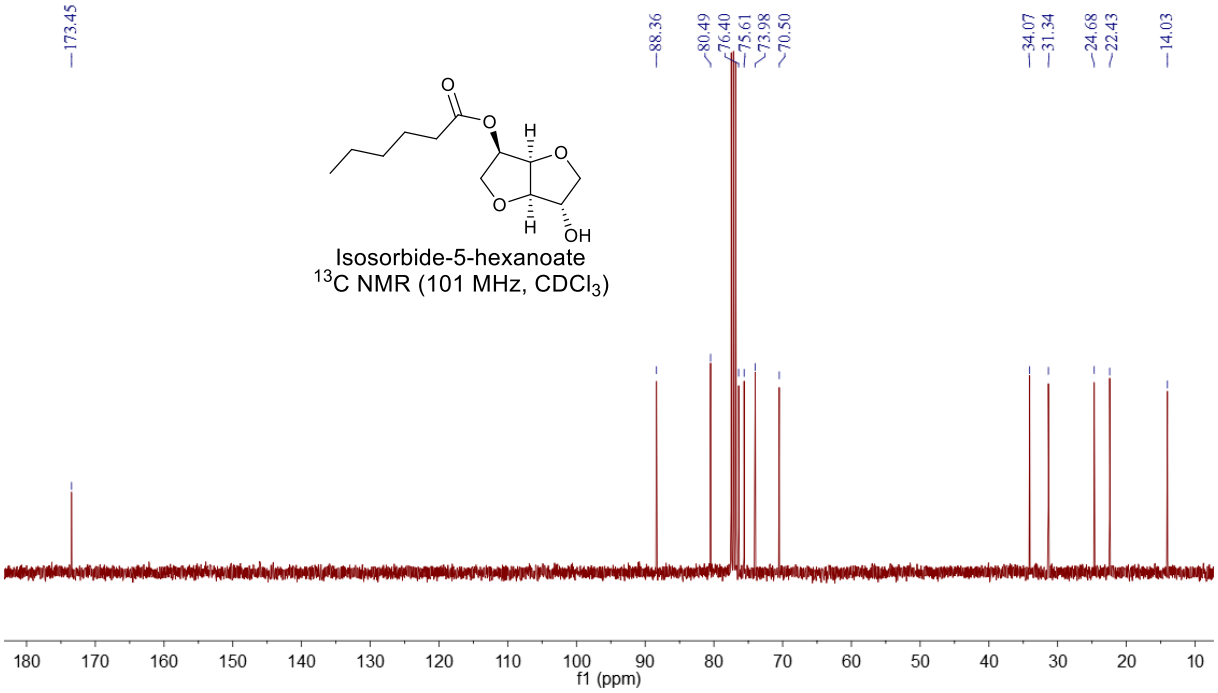


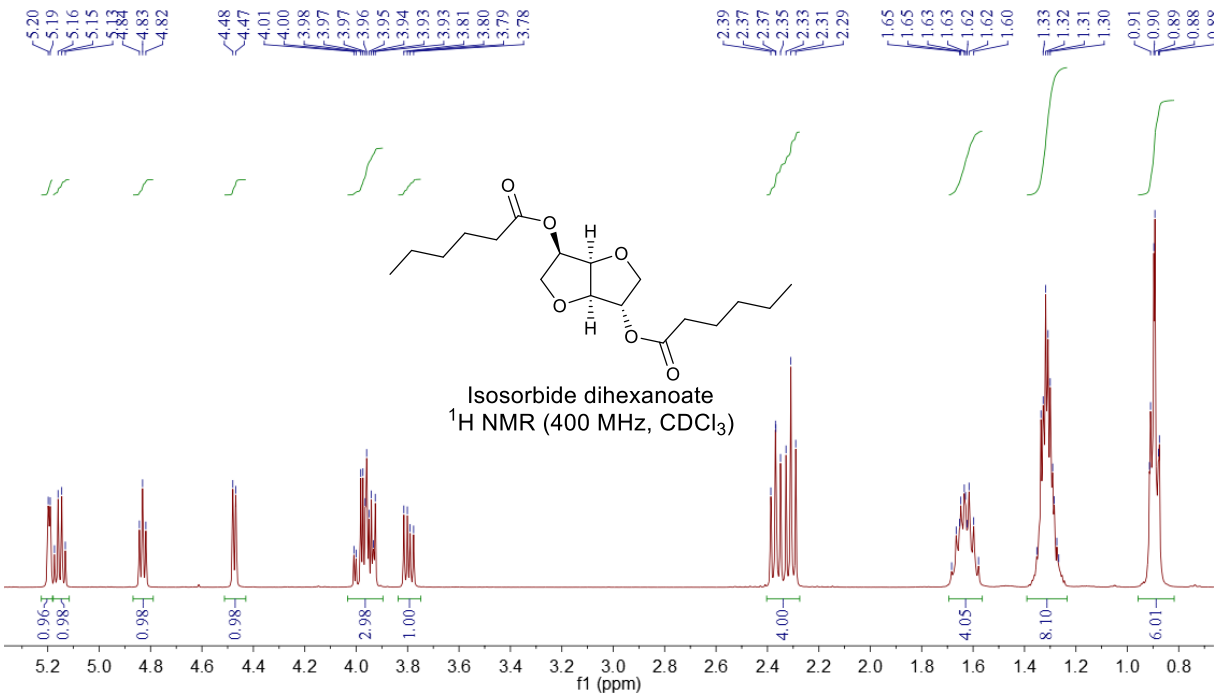
Isosorbide-2-hexanoate
^{1}H NMR (400 MHz, $CDCl_3$)

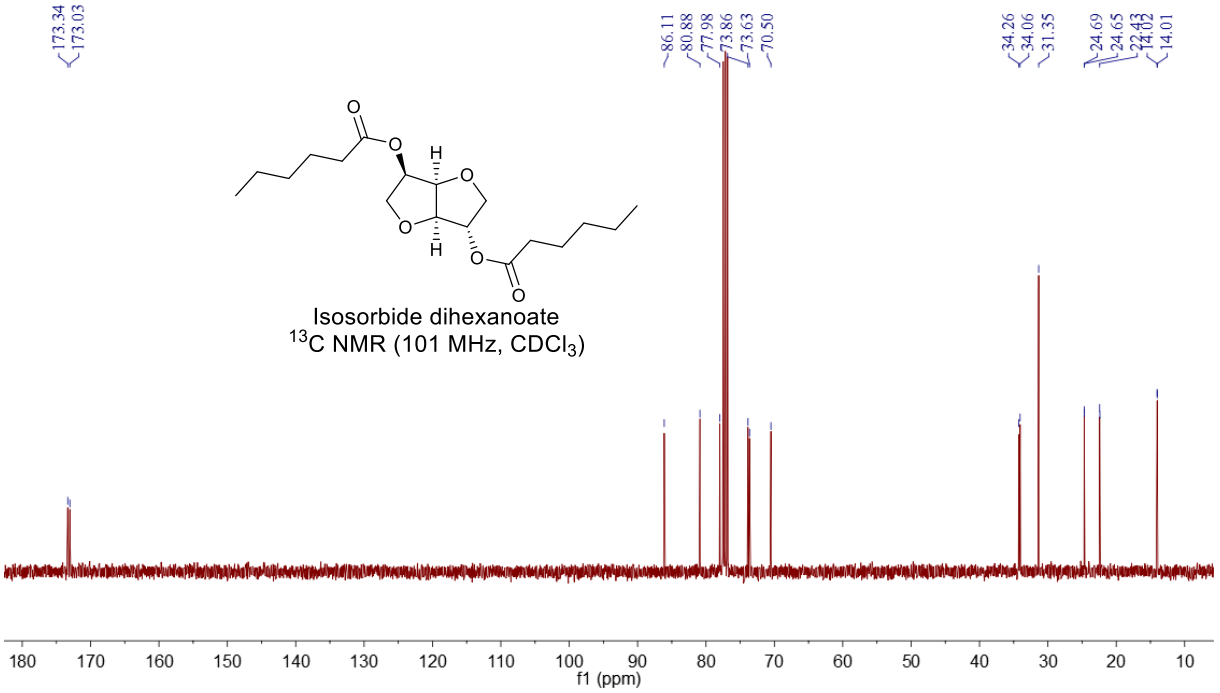


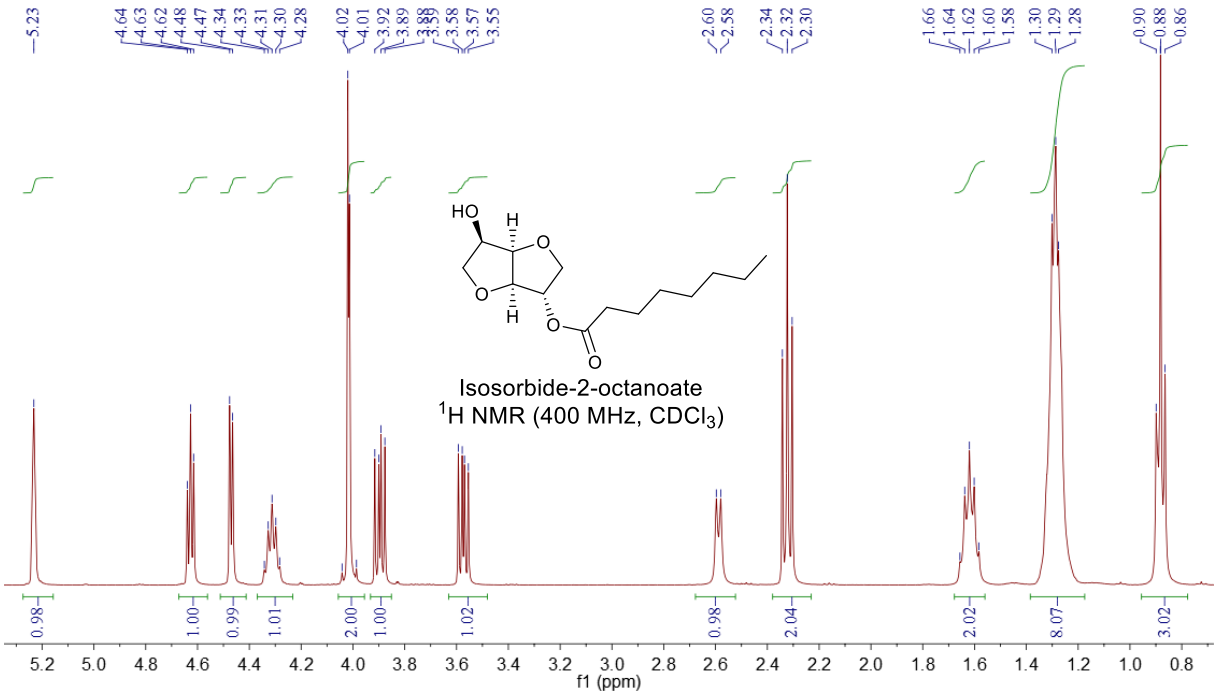
Isosorbide-2-hexanoate
^{13}C NMR (101 MHz, $CDCl_3$)

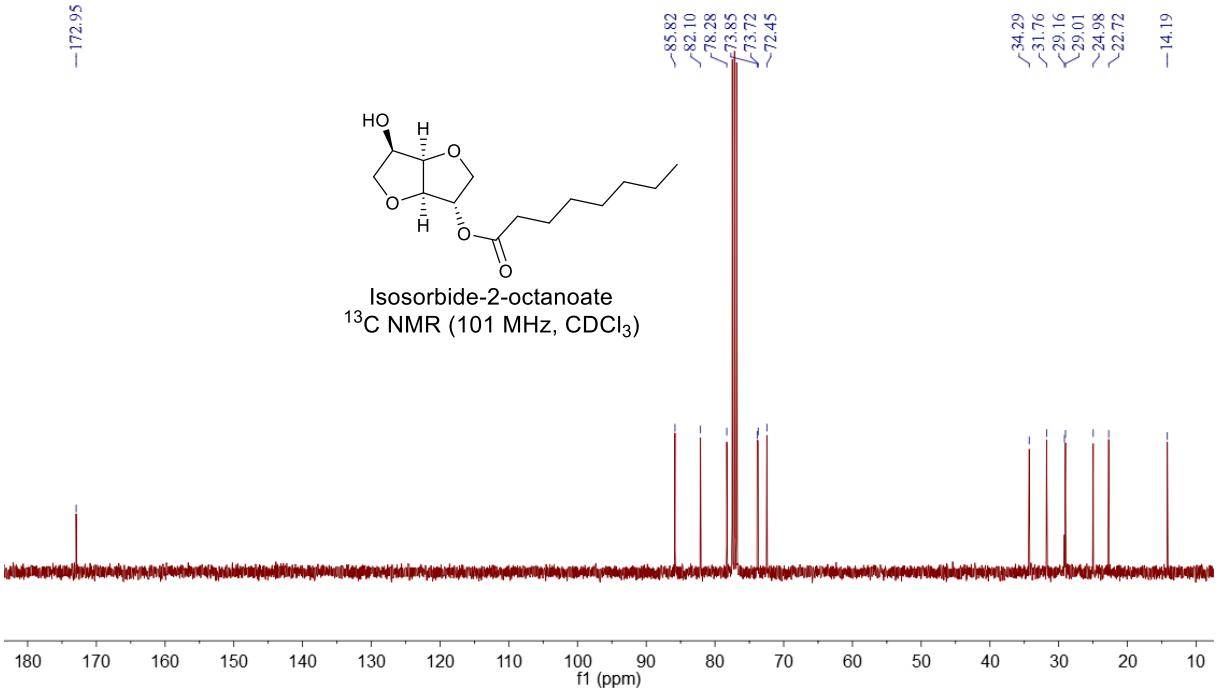

Isosorbide-5-hexanoate
1H NMR (400 MHz, CDCl3)
f1 (ppm)

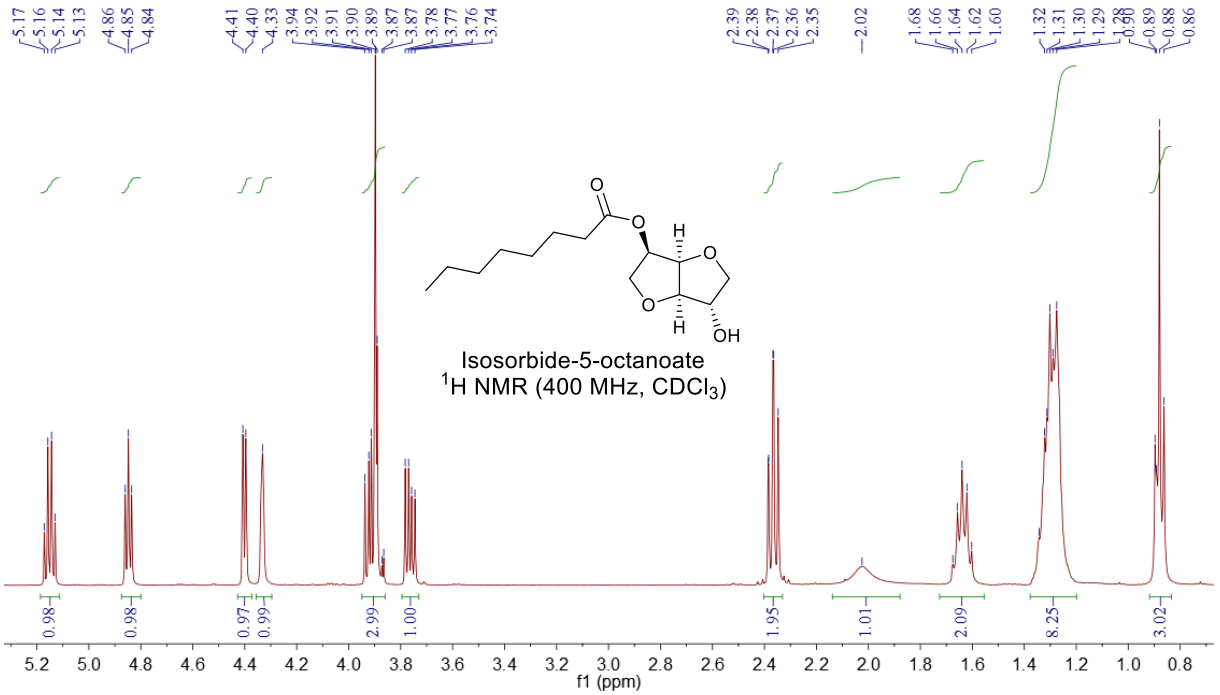

Isosorbide-5-hexanoate
13C NMR (101 MHz, CDCl3)
f1 (ppm)


Isosorbide dihexanoate
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

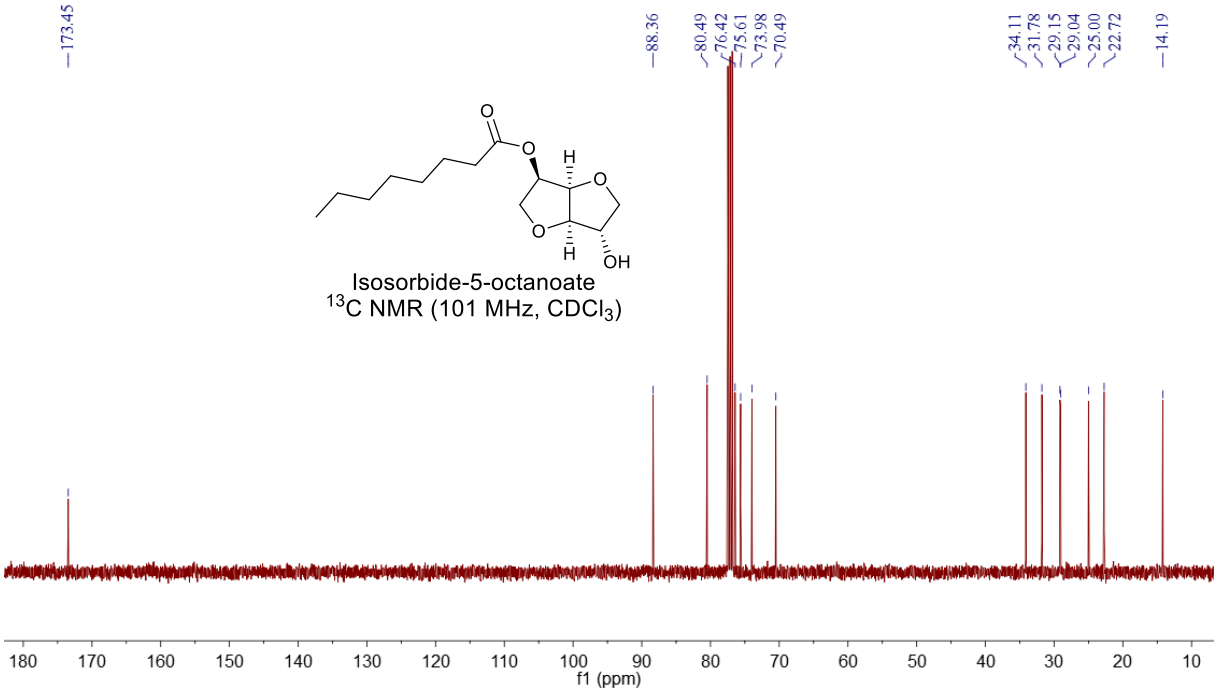

Isosorbide dihexanoate
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)


5.23
4.64
4.63
4.62
4.48
4.47
4.34
4.33
4.31
4.30
4.28
4.02
4.01
3.92
3.89
3.88
3.58
3.57
3.55
2.60
2.58
2.34
2.32
2.30
1.66
1.64
1.62
1.60
1.58
1.30
1.29
1.28
0.90
0.88
0.86
HO
H
O
O
H
O
O
Isosorbide-2-octanoate
^{1}H NMR (400 MHz, CDCl$_3$)
0.98
1.00
0.99
1.01
2.00
1.00
1.02
0.98
2.04
2.02
8.07
3.02
5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
f1 (ppm)

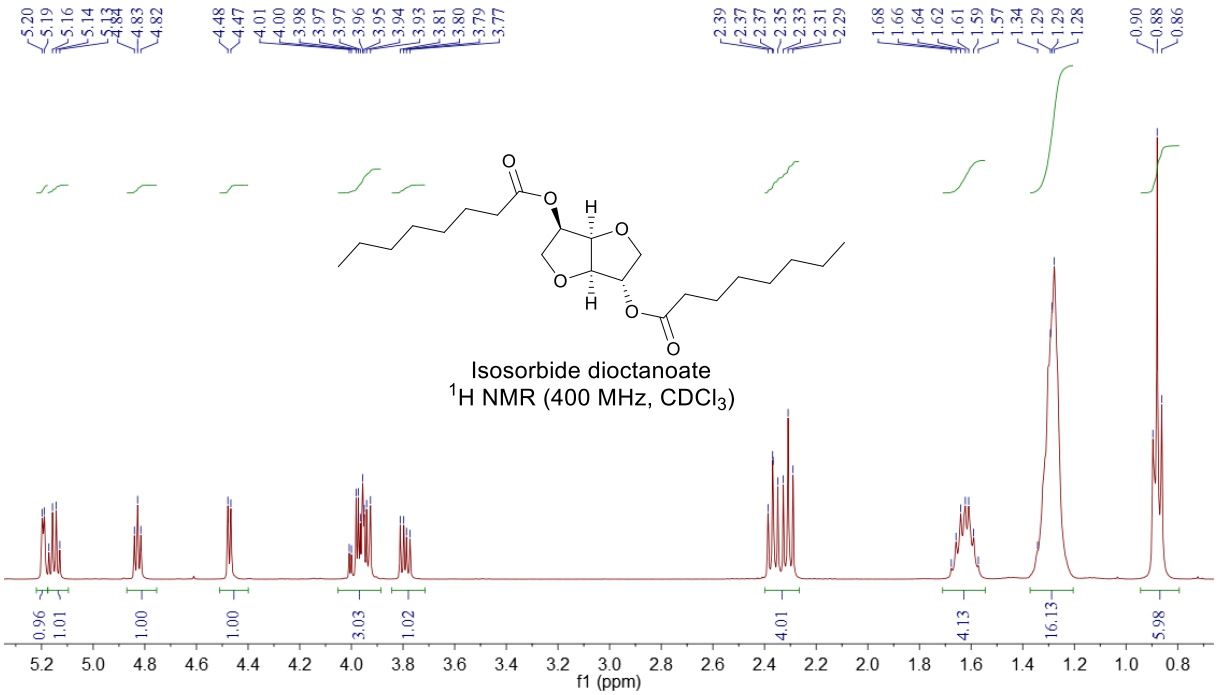

172.95
85.82
82.10
78.28
73.85
73.72
72.45
34.29
31.76
29.16
29.01
24.98
22.72
14.19
HO
H
O
O
H
O
O
Isosorbide-2-octanoate
^{13}C NMR (101 MHz, CDCl$_3$)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

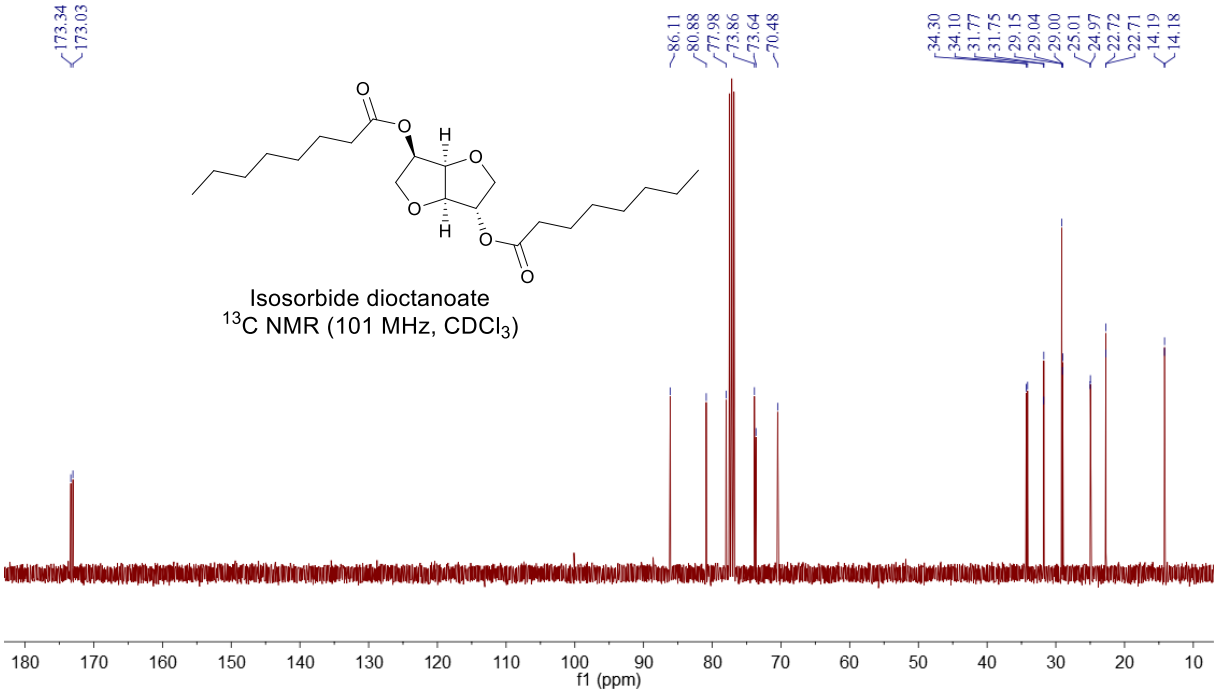


Isosorbide-5-octanoate
^{1}H NMR (400 MHz, $CDCl_3$)



Isosorbide-5-octanoate
^{13}C NMR (101 MHz, $CDCl_3$)


Isosorbide dioctanoate
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Isosorbide dioctanoate
13C NMR (101 MHz, CDCl3)
f1 (ppm)

12. References

1. P. Che, F. Lu, X. Si, H. Ma, X. Nie and J. Xu, *Green Chem.*, 2018, **20**, 634-640.
2. B. Op de Beeck, J. Geboers, S. Van de Vyver, J. Van Lishout, J. Snelders, W. J. Huijgen, C. M. Courtin, P. A. Jacobs and B. F. Sels, *ChemSusChem*, 2013, **6**, 199-208.
3. L. Yang, X. Yang, E. Tian and H. Lin, *ChemSusChem*, 2016, **9**, 36-41.