Supporting Information

Hydroxyapatite: Catalyst for a one-pot pentose formation

Kaho Usami, Akimitsu Okamoto*

okamoto@chembio.t.u-tokyo.ac.jp

Figs. S1 to S10. Mass and ^{1}H-NMR charts of the reaction products and control compounds.

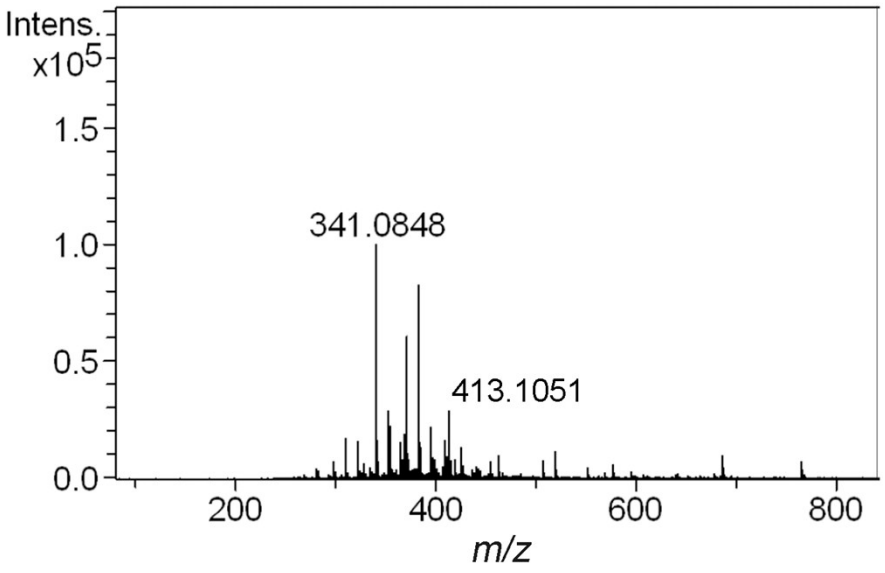
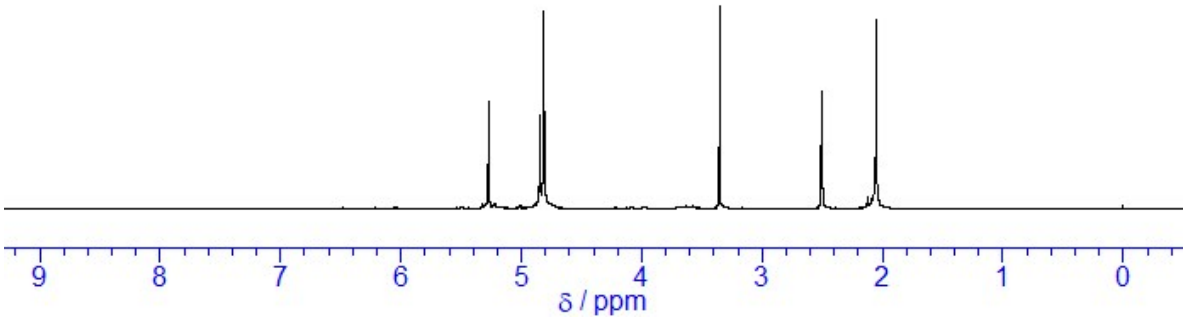
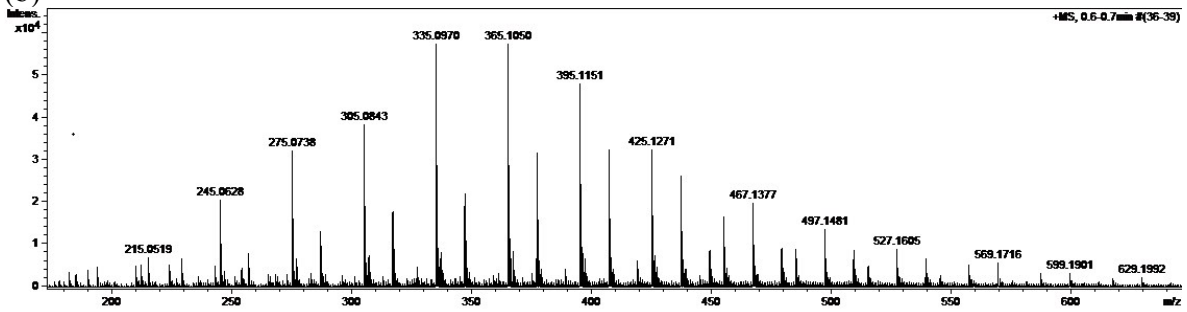


Figure S1. ESI mass spectrometry for the one-pot reaction products after acetylation treatment.

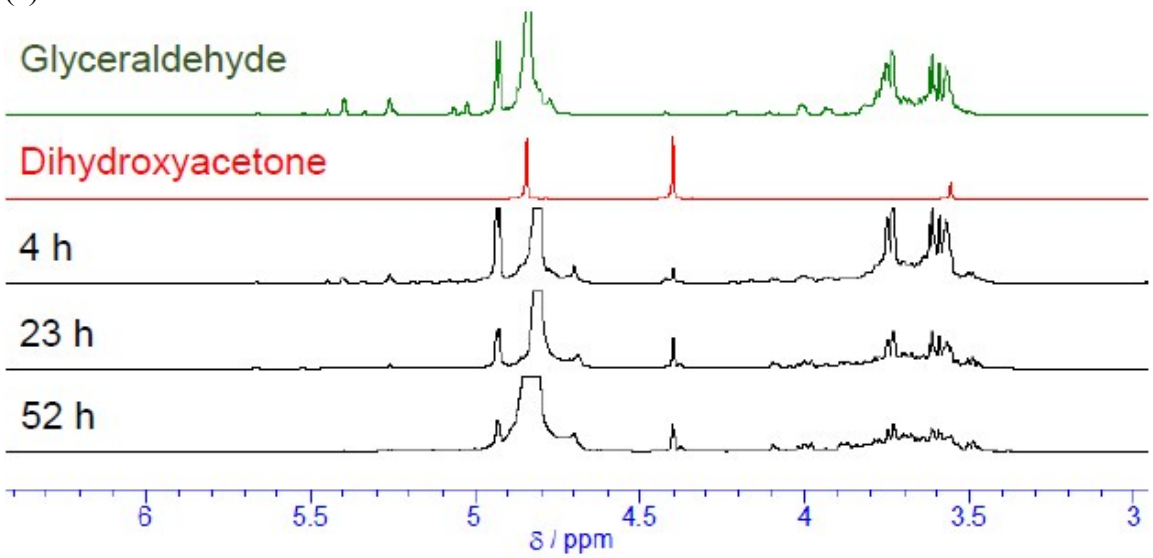
(a)


9
8
7
6
5
4
3
2
1
0
δ / ppm

(b)


Intens.
x10^4
+MS, 0.6-0.7min #(36-39)
335.0970
365.1050
395.1151
305.0843
275.0738
425.1271
245.0628
467.1377
497.1481
215.0519
527.1605
569.1716
599.1901
629.1992
200
250
300
350
400
450
500
550
600
m/z

(c)


Glyceraldehyde
Dihydroxyacetone
4 h
23 h
52 h
6
5.5
5
4.5
4
3.5
3
δ / ppm

(d)

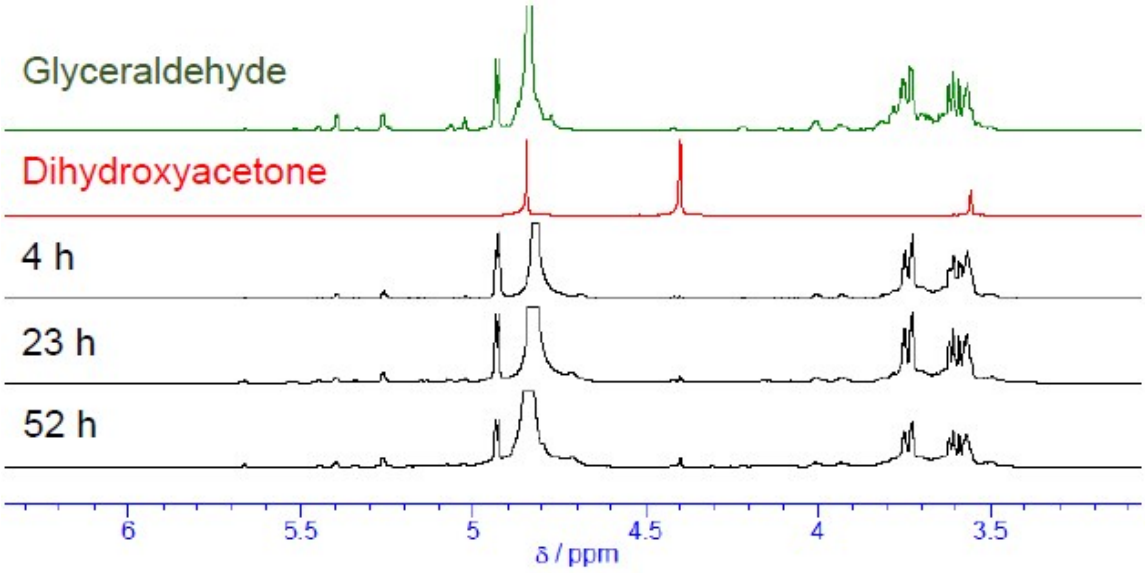
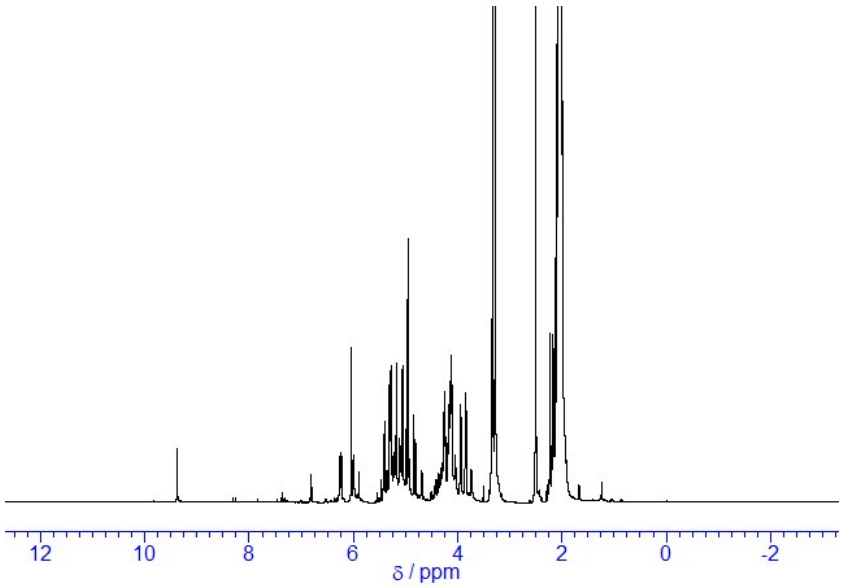


Figure S2. ^{1}H NMR and ESI mass spectrometry after the reactions in the absence of HAp. (a) ^{1}H NMR chart of the products after the reactions of glycolaldehyde (1 mmol) and formaldehyde (10 mmol) in water (2 mL) at 80 °C for 40 h followed by acetylation. (b) ESI mass spectrometry for the products in (a). The main product in (a) and (b) is acetylated paraformaldehyde (polymerized formaldehyde; $AcO(CH_2O)_nAc$). $[M+Na]^+$ calcd. n=3, 215.05; n=4, 245.06; n=5, 275.07; n=6, 305.08; n=7, 335.09; n=8, 365.11; n=9, 395.12; n=10, 425.13. (c) ^{1}H NMR charts of the products after the reactions of glyceraldehyde (1 mmol) and HAp (60 mg) in D_2O (2 mL) at 80 °C. (d) ^{1}H NMR charts of the products after the reactions of glyceraldehyde (1 mmol) in D_2O (2 mL) at 80 °C. Isomerization to dihydroxyacetone was observed in (c), whereas the reaction was negligible in (d).

(a)



(b)

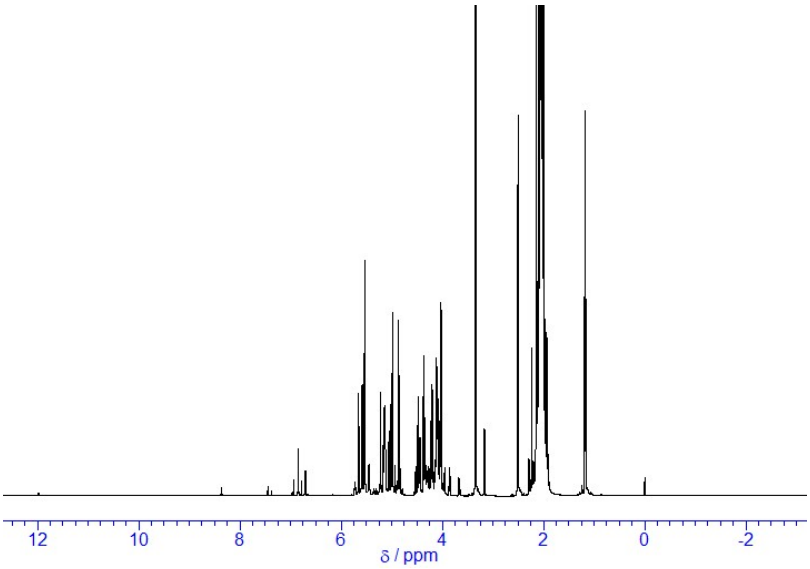


Figure S3. Full range ^{1}H NMR charts of acetylated monosaccharides. (a) acetylated erythrose; (b) acetylated fructose.

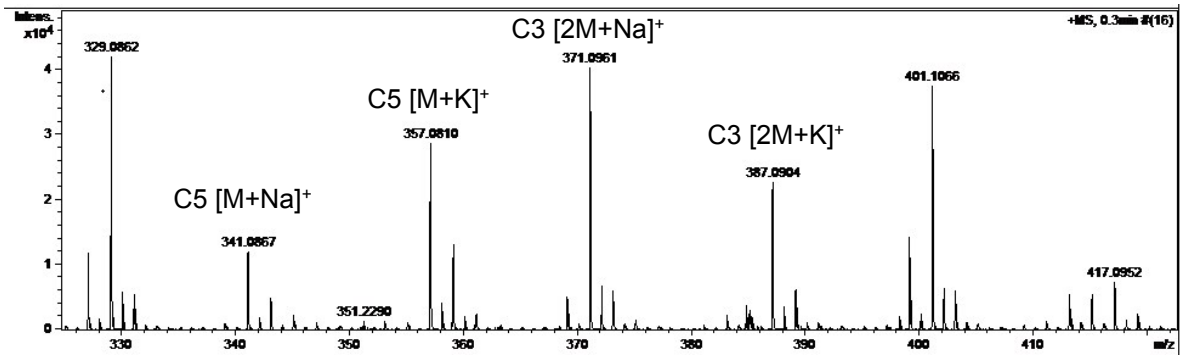


Figure S4. ESI mass chart of the mixture of the reaction products from glycolaldehyde and dihydroxyacetone. C5: $[M+Na]^+$ calcd 341.0843, found 341.0867. C3: $[2M+Na]^+$ calcd 371.0949, found 371.0961.

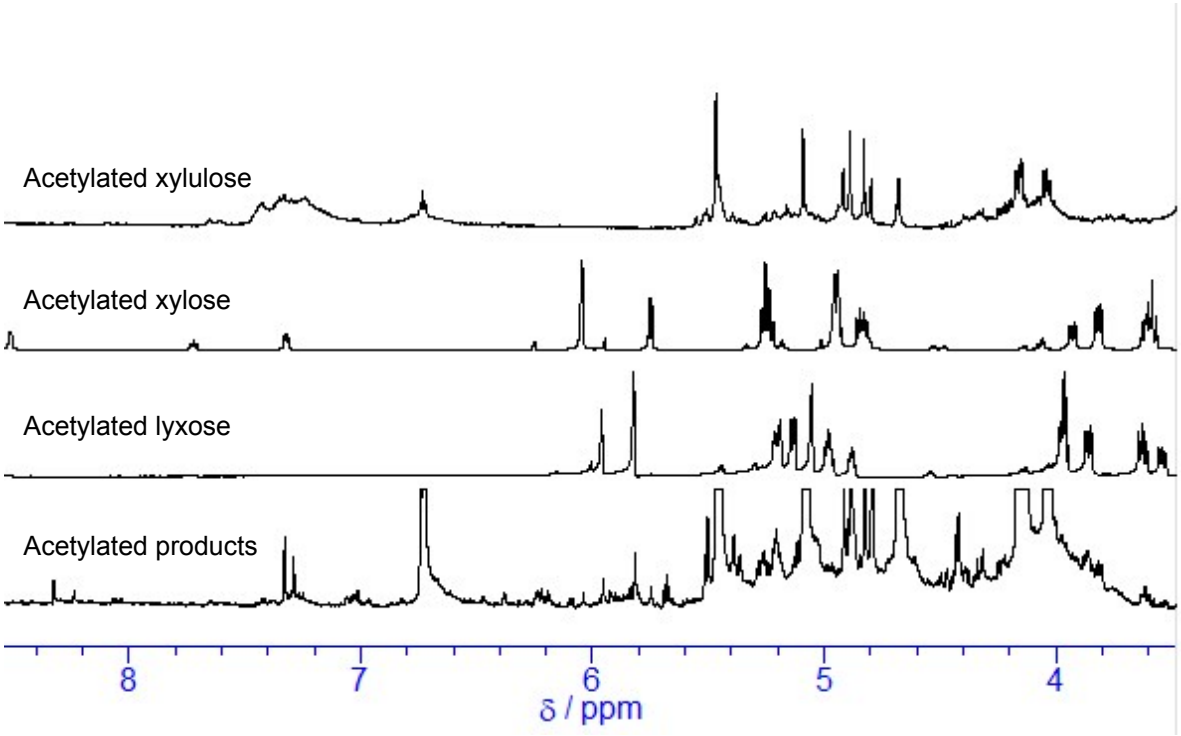


Figure S5. ^{1}H NMR charts of acetylated xylulose, acetylated xylose, acetylated lyxose, and the mixture of the isomerization products (acetylated) from xylulose.

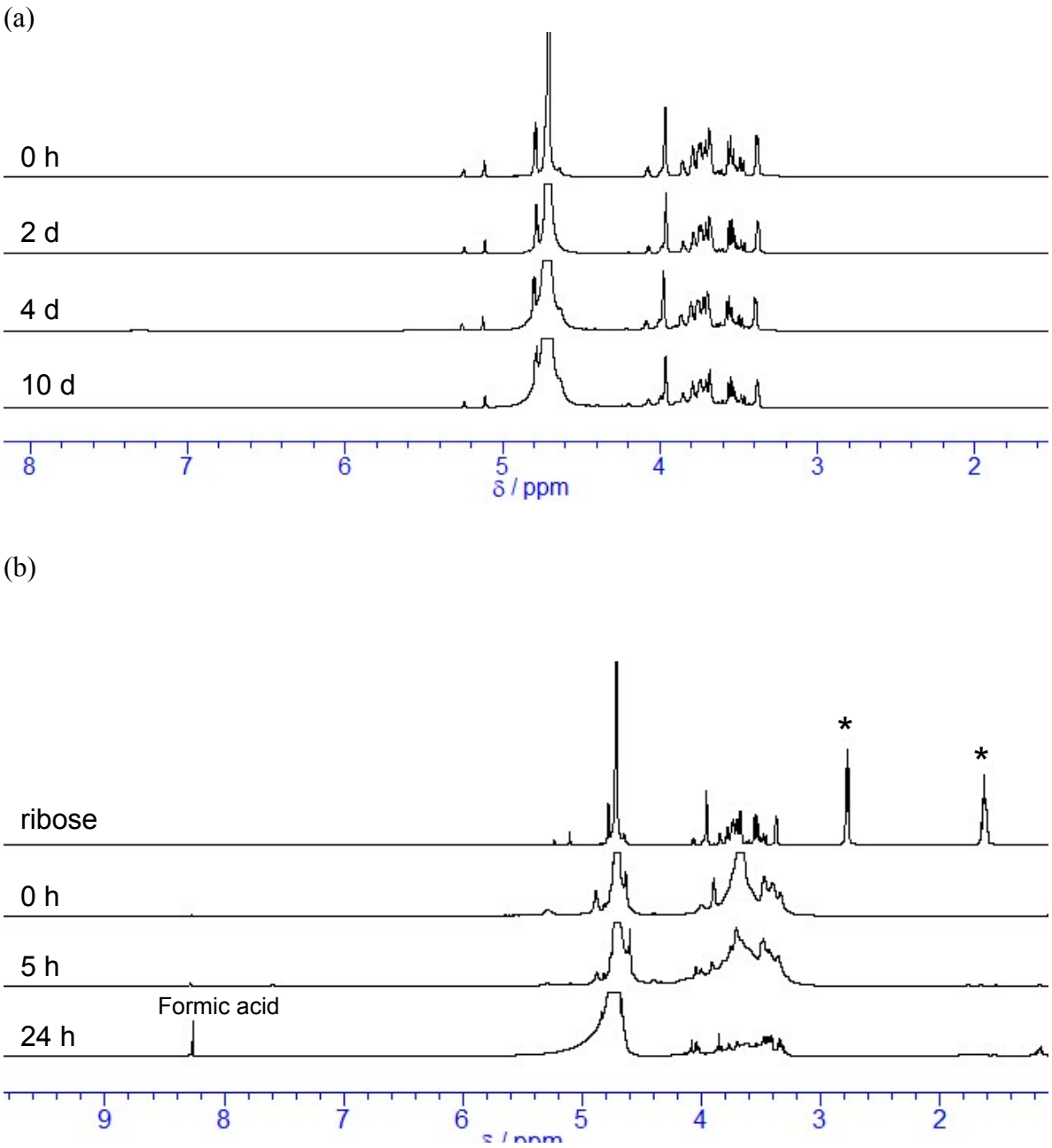


Figure S6. Stability of ribose. (a) ^{1}H NMR charts of ribose in the presence of HAp (ribose 1 mmol and HAp 0.12 mmol in D_2O at 80 °C); (b) ^{1}H NMR charts of ribose in the presence of calcium hydroxide (ribose 1 mmol and calcium hydroxide 0.10 mmol in D_2O at 80 °C). * in (b) denotes an internal standard (sodium 3-(trimethylsilyl)-1-propanesulfonate).

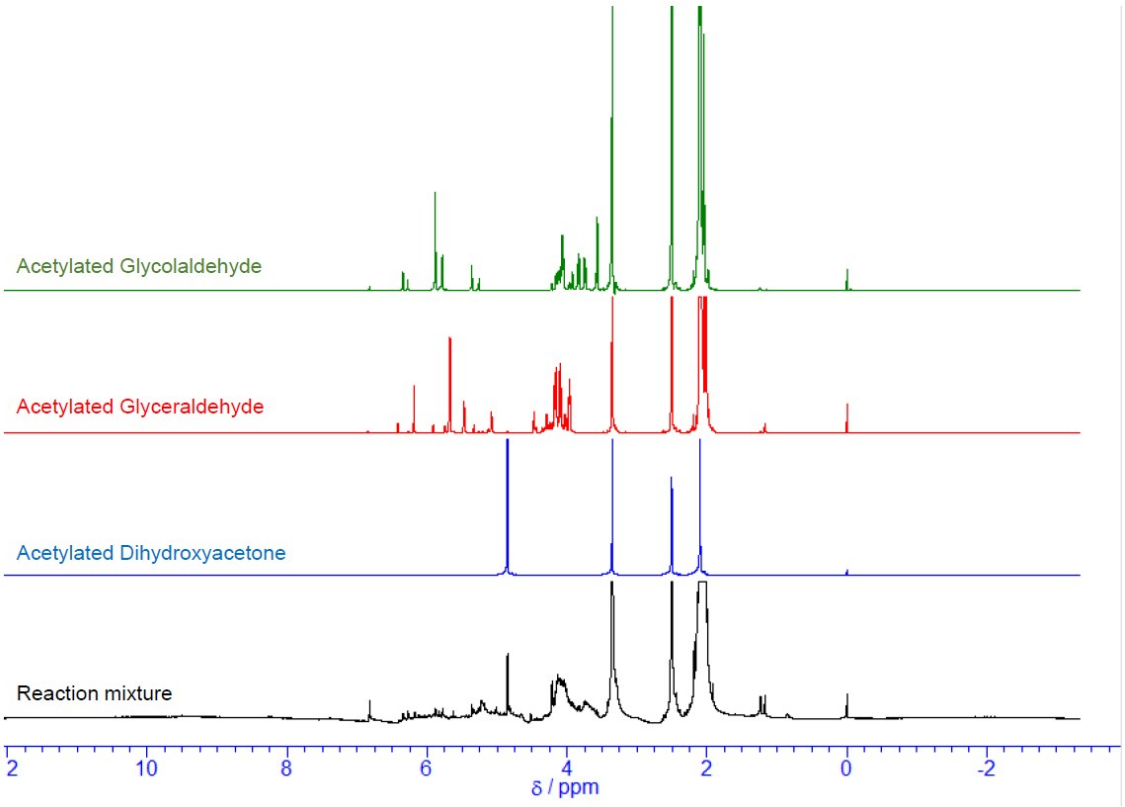


Figure S7. Full range ^{1}H NMR charts of acetylated glycolaldehyde, acetylated glyceraldehyde, acetylated dihydroxyacetone, and the mixture of the reaction products (acetylated) from glycolaldehyde and excess formaldehyde (Corresponding to Figure 2(a)).

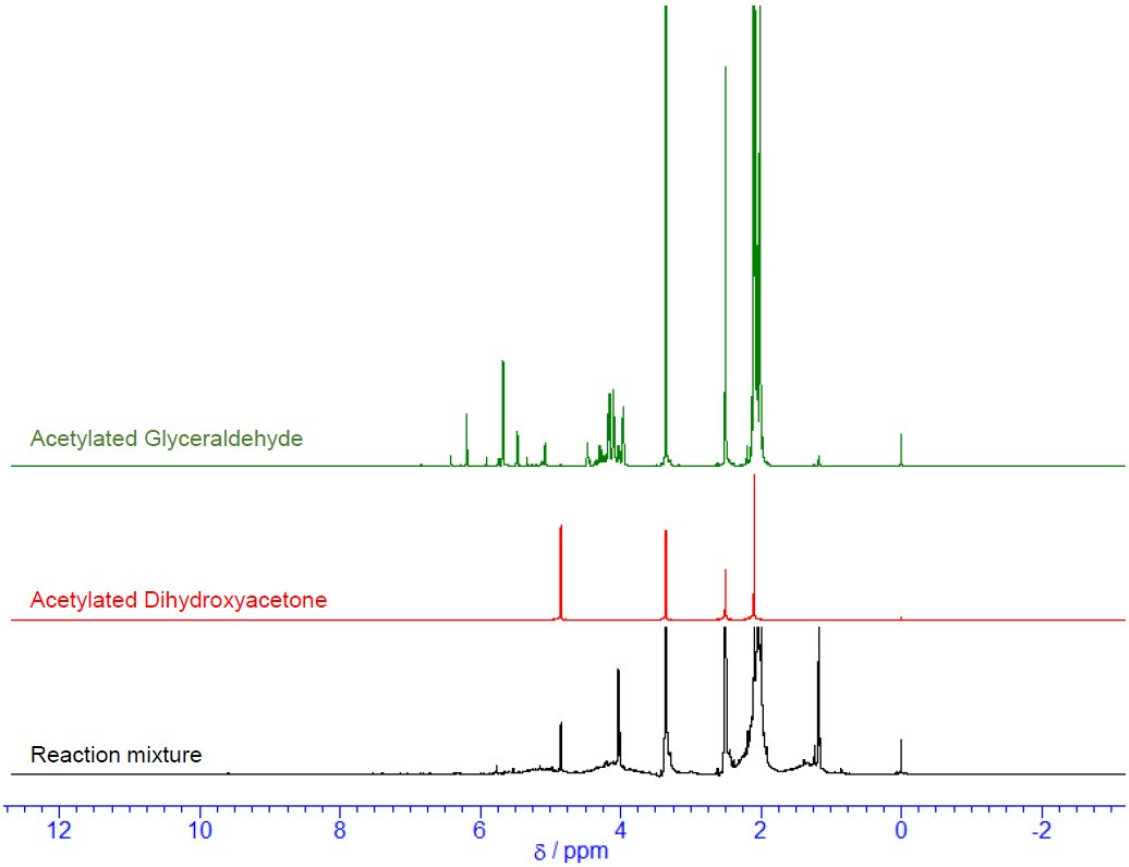


Figure S8. Full range ^{1}H NMR charts of acetylated glyceraldehyde, acetylated dihydroxyacetone, and the mixture of the isomerization products (acetylated) from glyceraldehyde (Corresponding to Figure 2(b)).

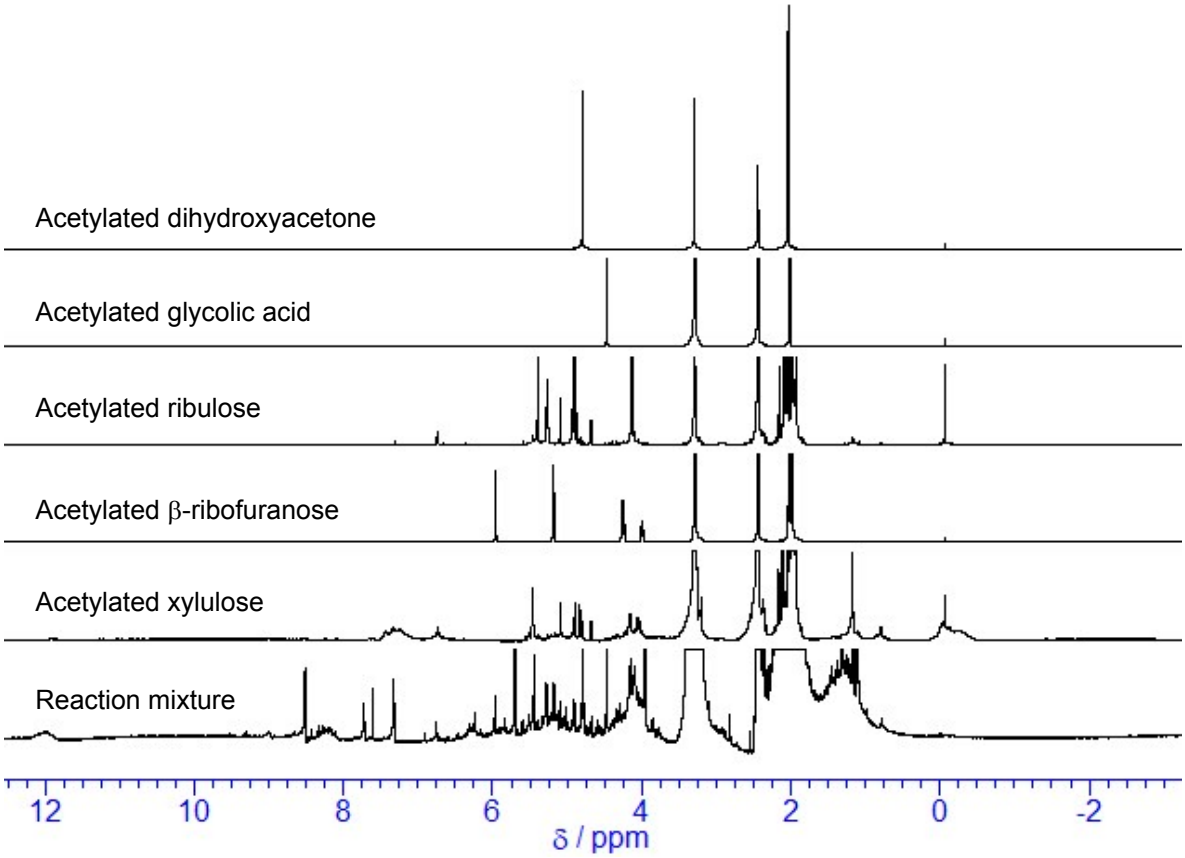


Figure S9. Full range ^{1}H NMR charts of acetylated dihydroxyacetone, acetylated glycolic acid, acetylated ribulose, acetylated β-ribofuranose, acetylated xylulose, and the mixture of the reaction products (acetylated) from dihydroxyacetone and glycolaldehyde (Corresponding to Figure 3).

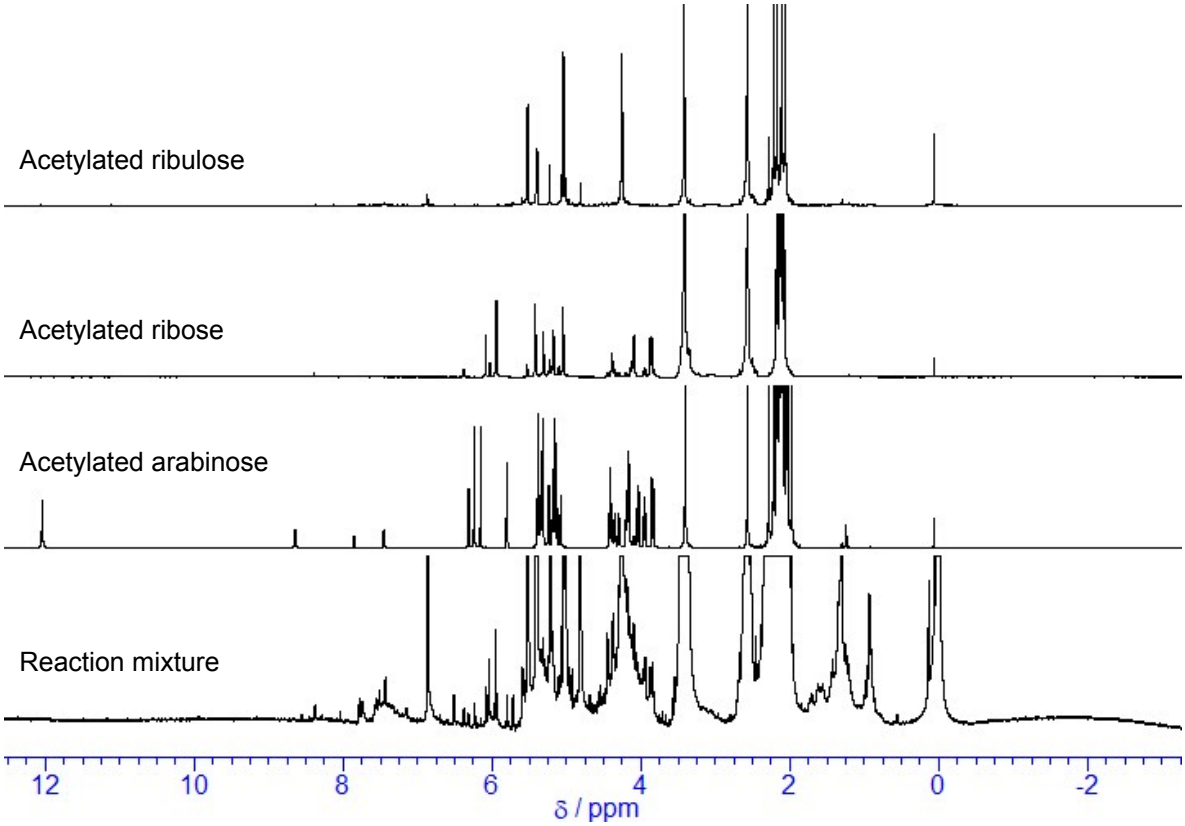


Figure S10. Full range ^{1}H NMR charts of acetylated ribulose, acetylated ribose, acetylated arabinose, and the mixture of the isomerization products (acetylated) from ribulose (Corresponding to Figure 5(b)).