Electronic Supplementary Material (ESI) for Green Chemistry.

SUPPLEMENTARY DATA FOR:

Valorization of monosaccharides towards fructopyrazines in a new sustainable and efficient eutectic medium

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Materials

Saccharides arabinose (Alfa Aesar, 99%), xylose (Roth, 99%), glucose (Roth, 99%), fructose (Sigma-Aldrich, 99%), mannose (Alfa Aesar, 99%), galactose (Roth, 97%), sucrose (Sigma-Aldrich, 99%), maltose (Roth, 99%) were used without further purification. Due to the high hydrophobicity, ammonium formate (Alfa Aesar, 98%) was dried in the vacuum oven at room temperature for 24 hours prior the use in reaction.

Table S1. Composition of the eutectic mixtures

Entry	Sample	Type of saccharide	Saccharides used as HBD component	Ratio saccharide /ammonium formate
1	EM-A	pentoses	arabinose	1:1
2	EM-X		xylose	1:1
3	EM-G	hexoses	glucose	1:0.5, 1:0.75, 1:1, 1:1.2, 1:1.5
4	EM-F		fructose	1:1
5	EM-Man		mannose	1:1
6	EM-Gal		galactose	1:1
7	EM-S	disaccharides	sucrose	1:2
8	EM-Mal		maltose	1:2

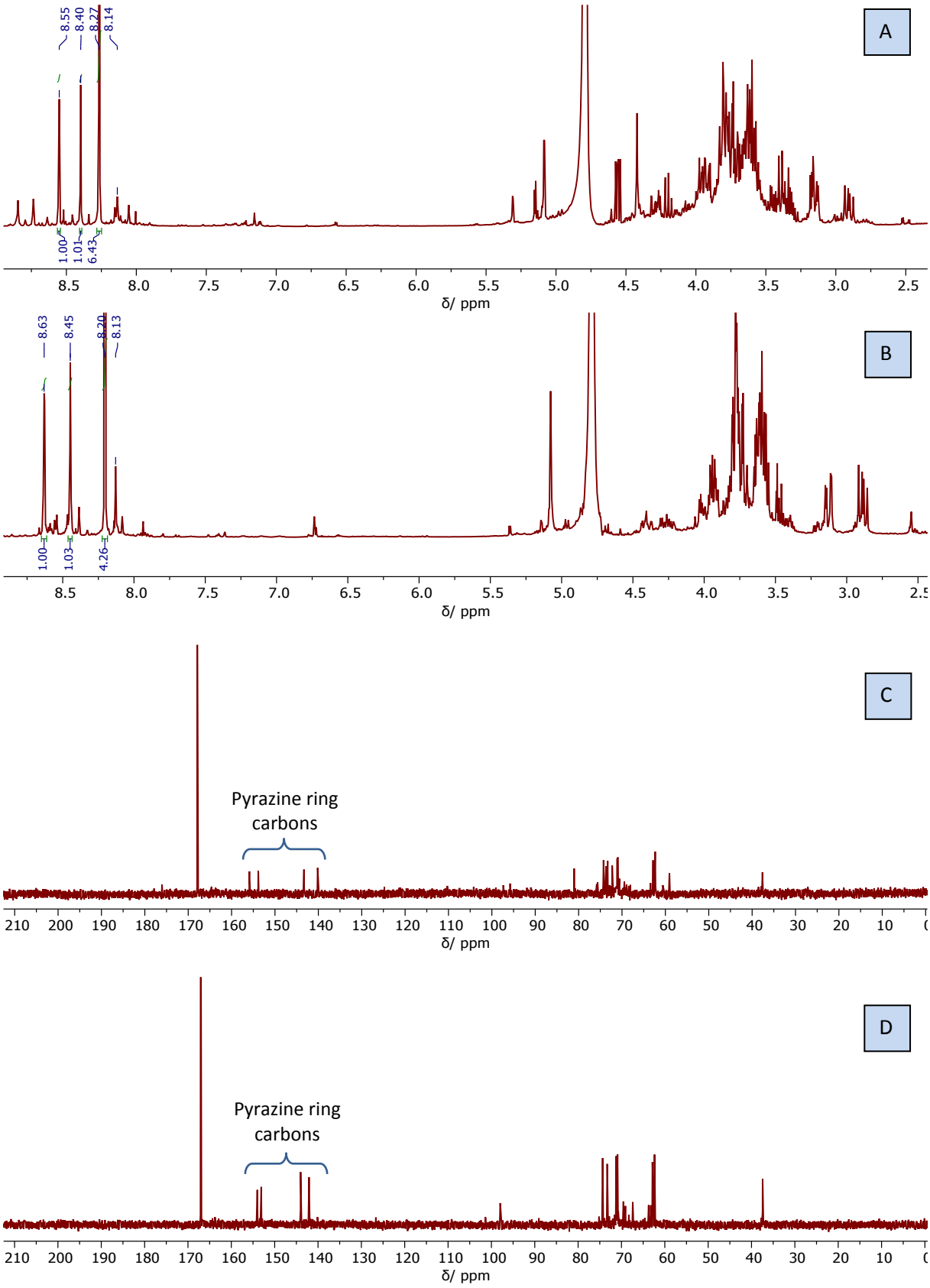

Fig. S1. ^{1}H and ^{13}C NMR spectra (D_2O) of reaction mixture of ammonium formate with glucose, representing formation of 2,6-DOF (A and C, respectively), and ammonium formate with fructose, representing 2,5-DOF formation (B and D, respectively). The signals in ^{1}H are not allowing distinguishing between the formation of 2,5-DOF and 2,6-DOF, while ^{13}C NMR spectra give a different signals.

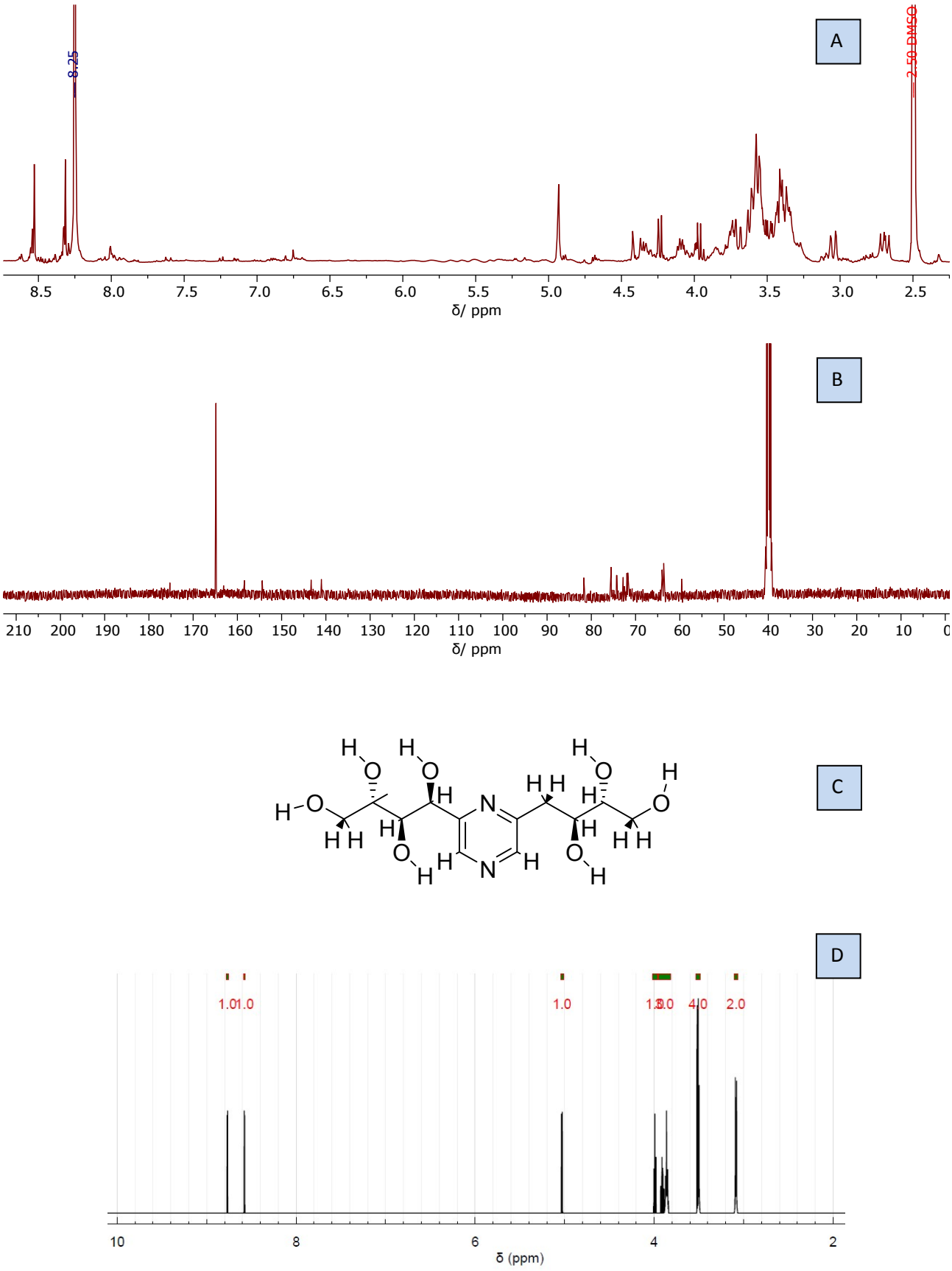

Fig. S2. ^{1}H and ^{13}C NMR spectra (d6-DMSO) of crude reaction mixture of ammonium formate with glucose after freeze drying, representing formation of 2,6-DOF (A and B, respectively); the signal at 8.25 ppm corresponds to protons of formate anions ionically bonded to 2,6-DOF; ^{1}H spectrum (D) predicted for the structure of 2,6-DOF (C). [1-3]

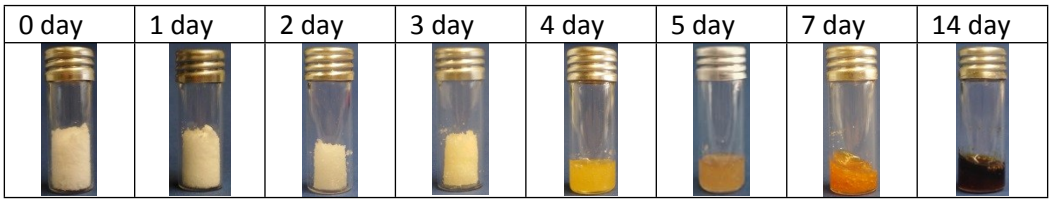

Fig. S3. Physical occurrence of the ammonium formate / glucose mixture kept at room temperature over time

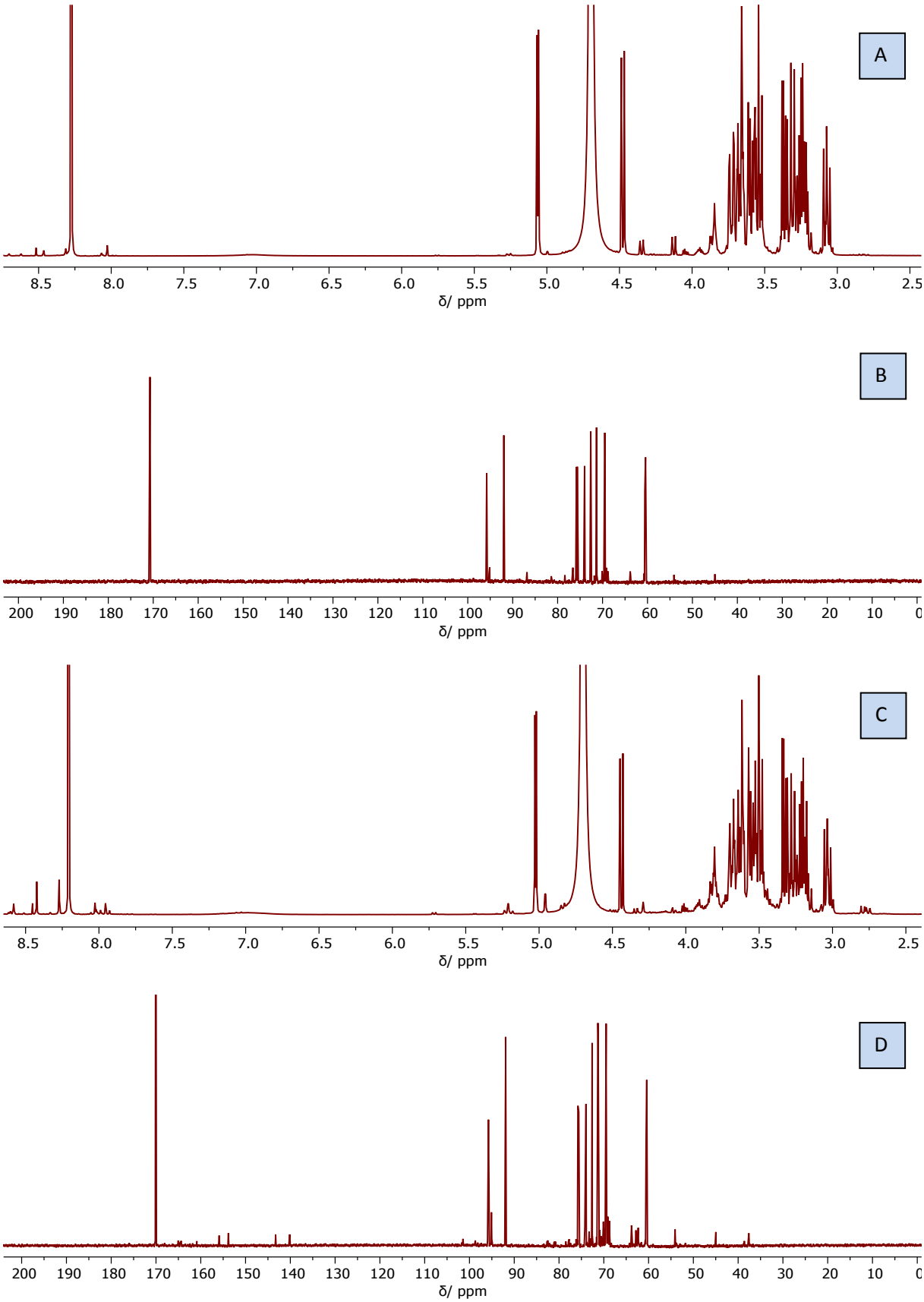

Fig. S4. ^{1}H and ^{13}C NMR spectra of the mixture of ammonium formate with glucose kept at room temperature for five days (A and B, respectively) and two weeks (C and D, respectively) representing different degree of 2,6-DOF formation.

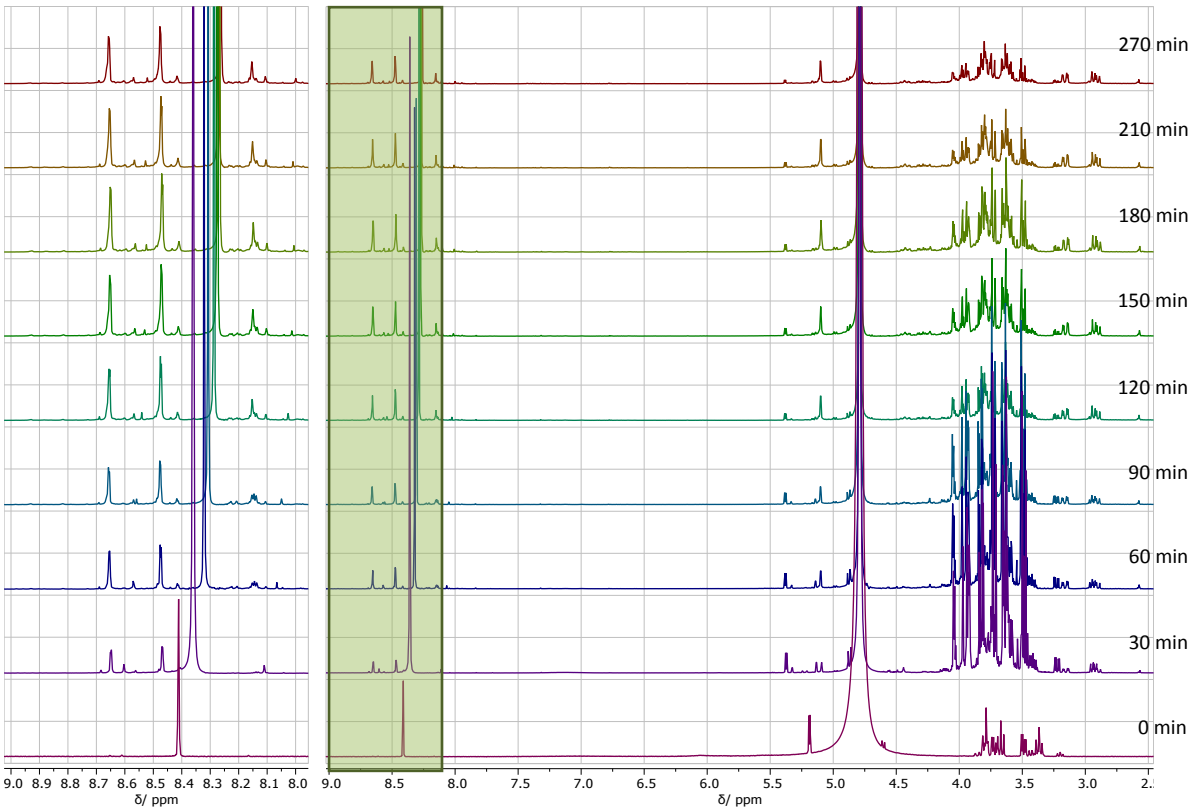

Fig. S5. In situ ^{1}H NMR spectra as a function of reaction time for the fructose transformation in eutectic medium in isochoric process at 80 °C.

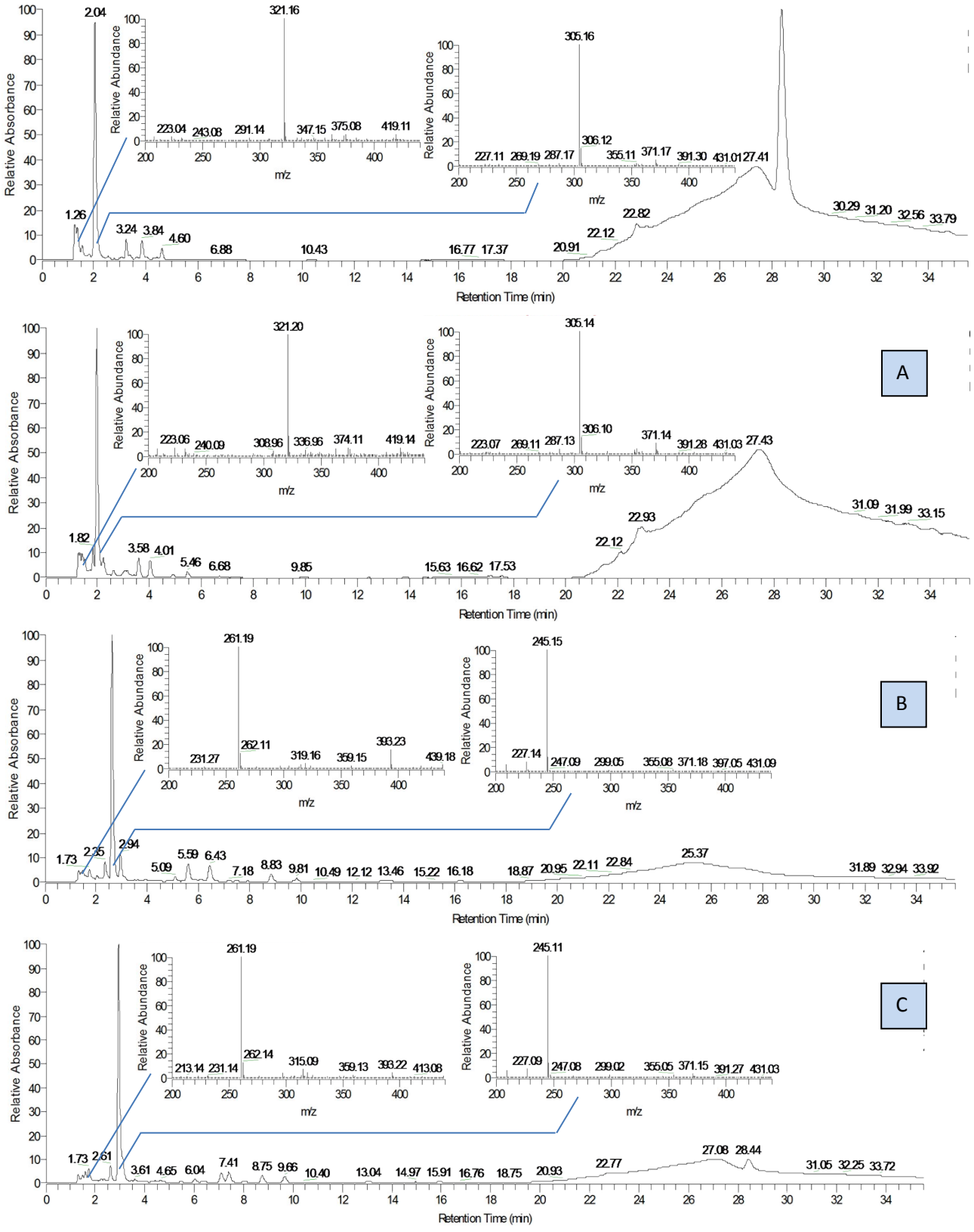

Fig. S6. Identification of reaction products by UHPLC-MS method: representative UHPLC chromatogram of reaction mixture of ammonium formate with mannose (A), galactose (B), arabinose (C), xylose (D) incubated at 90 °C for 4 hours, and product ion scans (MS/MS spectra) corresponding to respective pyrazine derivatives formed.

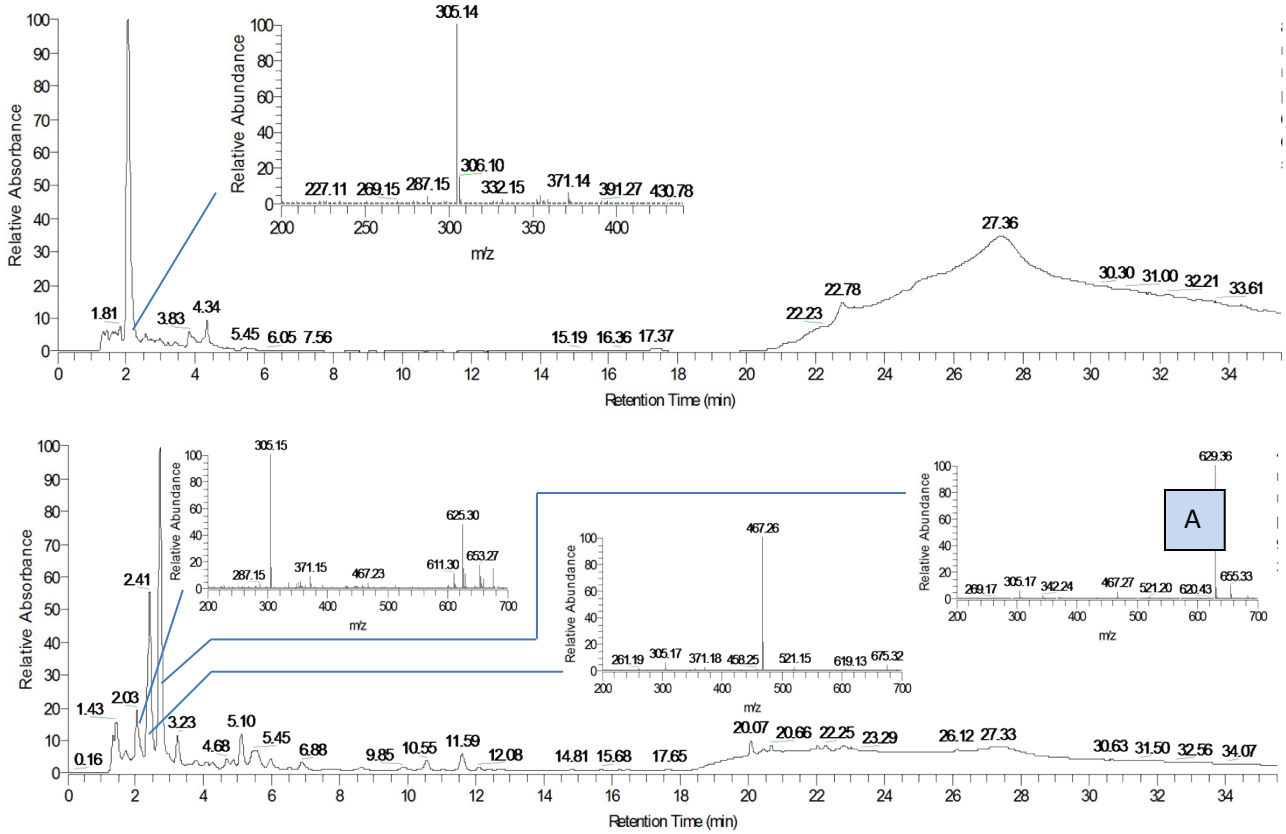

Fig. S7. Identification of reaction products by UHPLC-MS method: representative UHPLC chromatogram of reaction mixture of ammonium formate with sucrose (A), maltose (B), incubated at 90 °C for 4 hours, and product ion scans (MS/MS spectra) corresponding to respective pyrazine derivatives formed

B

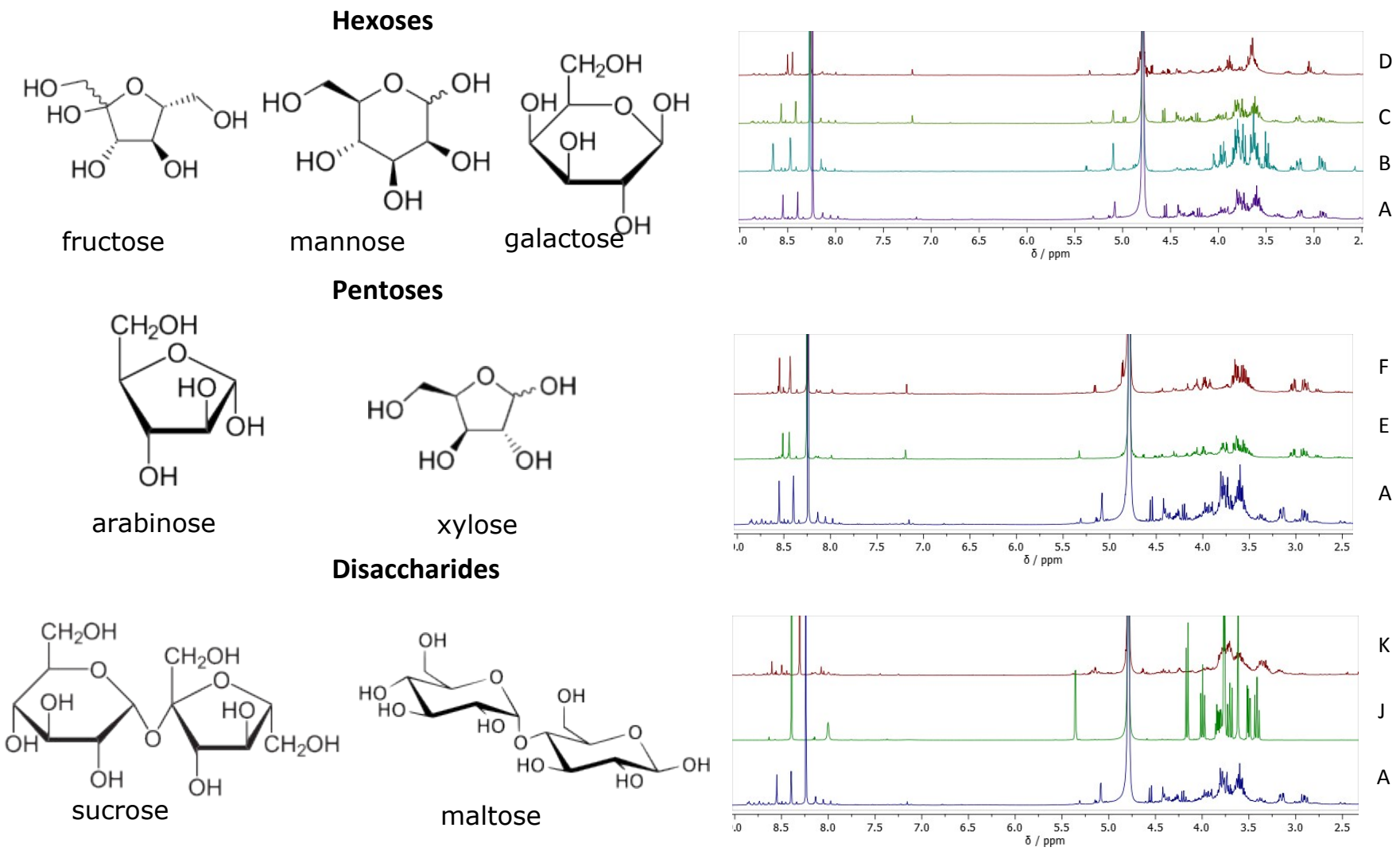

Fig. S8. Formulas of corresponding saccharides and the ^{1}H NMR spectrum of bare mixture after reaction with ammonium formate for 4h at 90 °C: glucose (A), fructose (B), mannose (C), galactose (D), arabinose (E), xylose (F), sucrose (J), maltose (K).

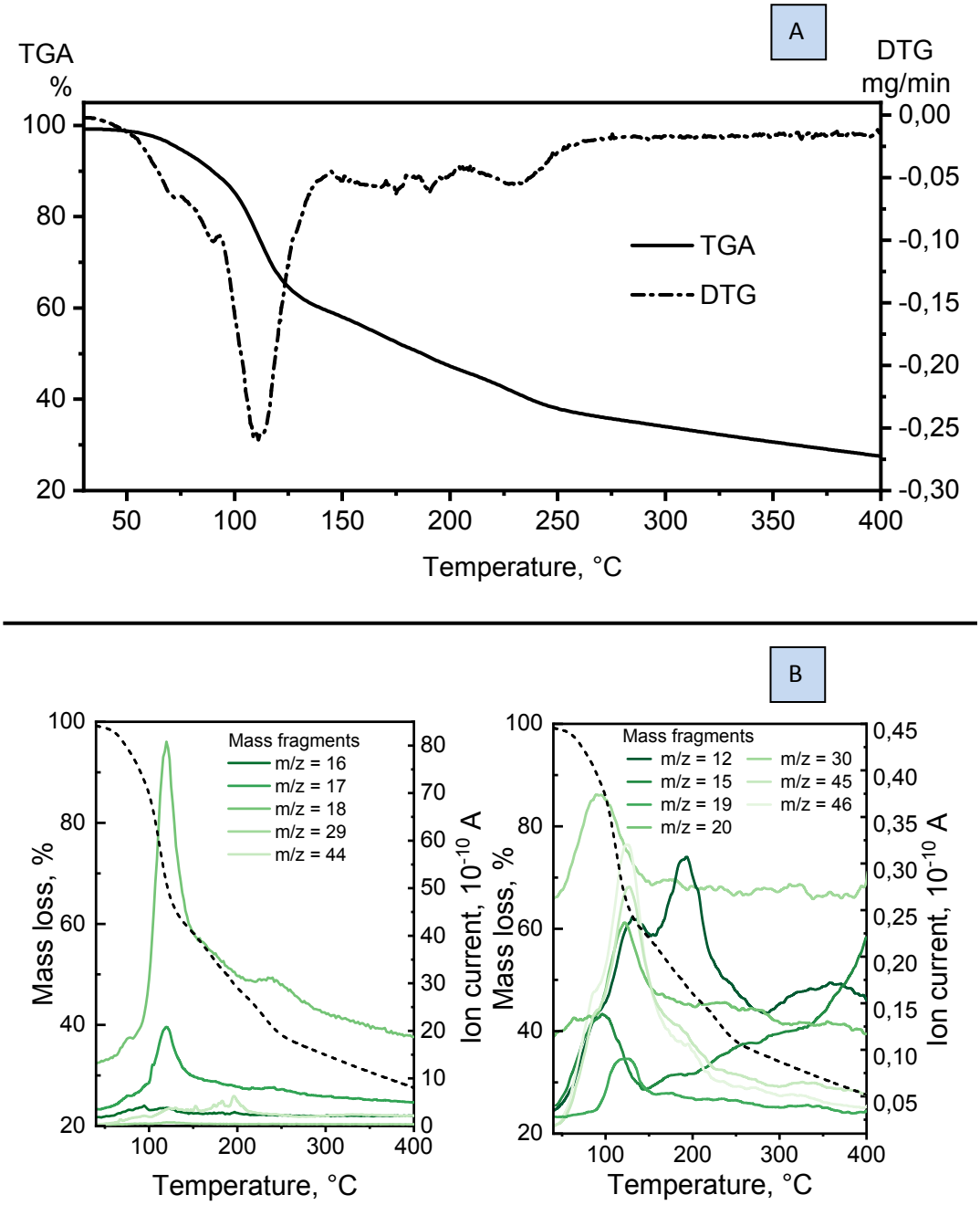

Fig. S9. TGA–MS weight loss and derivative of weight loss curves for ammonium formate / glucose mixture (A); mass spectra from thermal dermal decomposition of ammonium formate / glucose mixture (B)

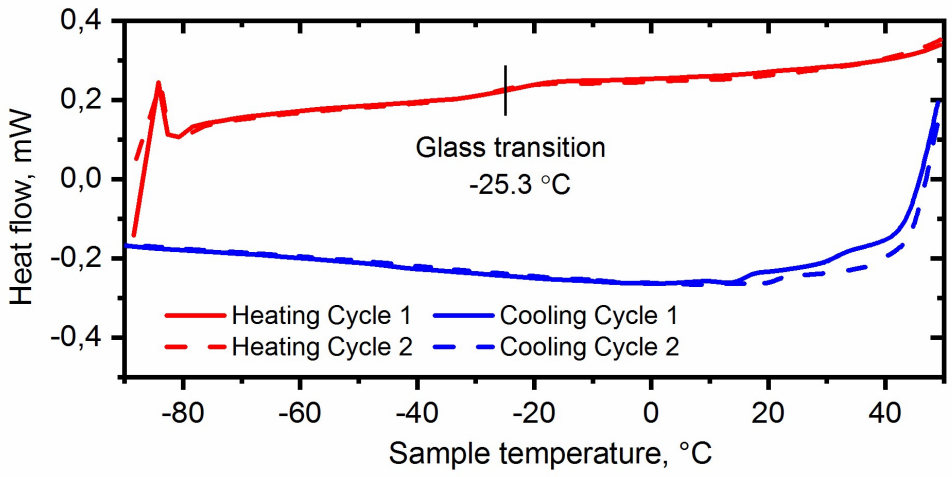

Fig. S10. DSC measurement of fructose / ammonium formate mixture in temperature range from -90 to 60 °C, heating/cooling rate is 10.0 °C/min; sample was heated from room temperature to 60 °C in order to form the eutectic mixture and cooled down immediately to avoid the reaction between the components

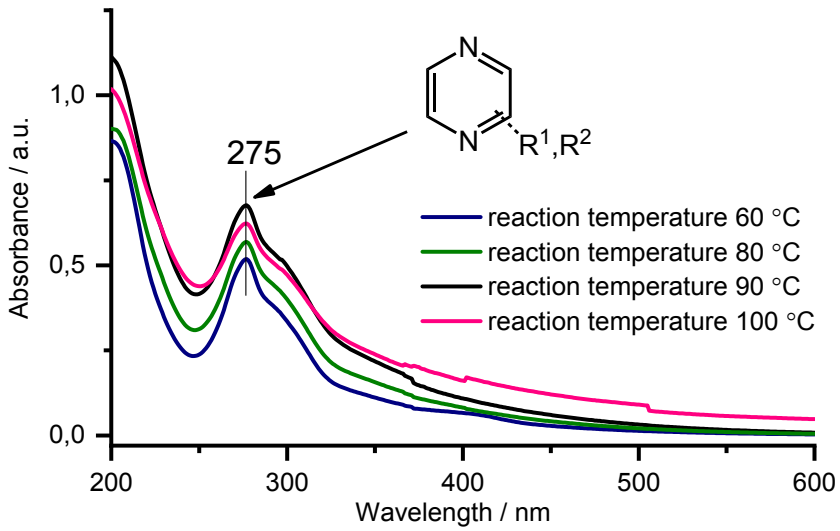

Fig. S11. UV-vis spectra of eutectic mixture solutions after reaction showing formation of (polyhydroxyalkyl)pyrazines formation.

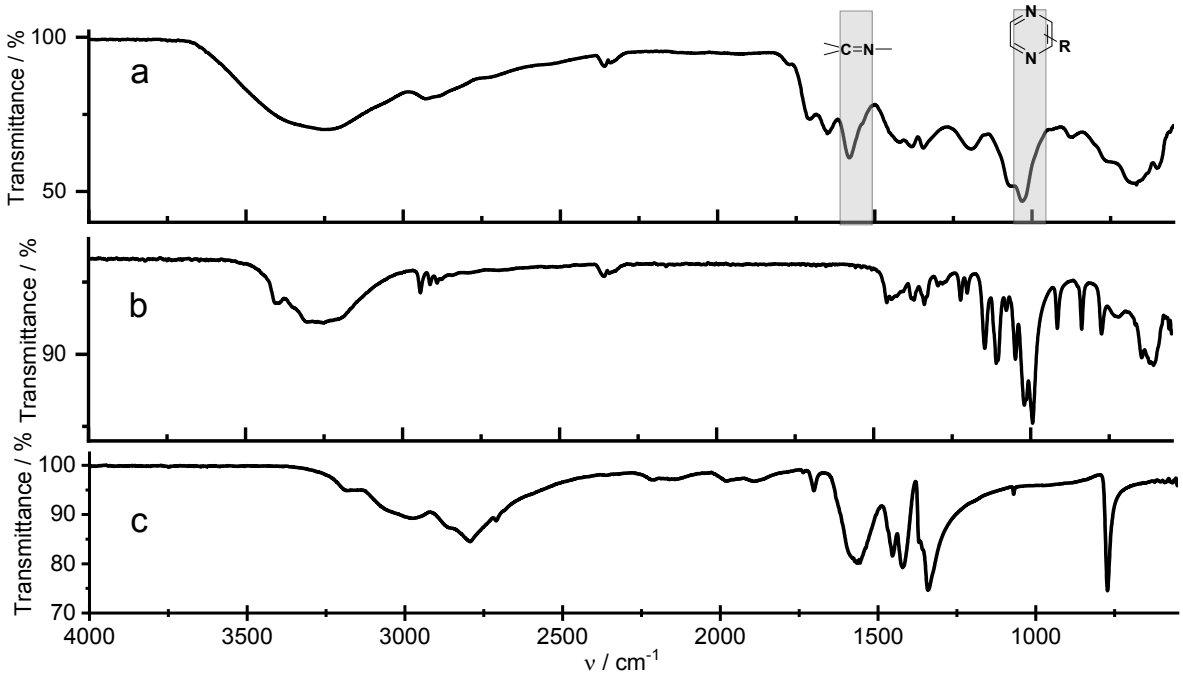

Fig. S12. FTIR spectra of eutectic mixture of glucose with ammonium formate after reaction (a), pristine glucose (b) and ammonium formate (c).

References

1. Banfi, D.; Patiny, L. www.nmrdb.org: Resurrecting and processing NMR spectra on-line *Chimia*, **2008**, *62*(4), 280-281.
2. Andrés M. Castillo, Luc Patiny and Julien Wist. Fast and Accurate Algorithm for the Simulation of NMR spectra of Large Spin Systems. *Journal of Magnetic Resonance* **2011.**
3. Aires-de-Sousa, M. Hemmer, J. Gasteiger, " Prediction of 1H NMR Chemical Shifts Using Neural Networks", *Analytical Chemistry*, **2002**, *74*(1), 80-90.