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## 1. Materials and methods

### 1.1. General

Ethylene (99.9 %, «Mostehgaz» LLC), ethylene glycol (99.5%, «Component-Reactive» LLC), technical mixture of 1,2-propanediol and 1,3-propanediol (99.0%, appr. 1:1 mol., «Component-Reactive» LLC), glycerol (99,3%, «Component-Reactive» LLC) and  $\text{RhCl}_3 \cdot 4\text{H}_2\text{O}$  «Aurat» LLC) were used without any pretreatment. The solvents were pretreated by standard procedures. Liquid products were analyzed by gas-liquid chromatography on a Khromos chromatograph equipped with a flame ionization detector and a 50-m-long capillary column coated with the SE-30 phase using temperature programming of 60-230°C, helium as a carrier gas.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectra were registered on a spectrometer Bruker Avance 400. Gaseous mixtures were analyzed by gas chromatography on Crystallux-4000M chromatograph with a thermal conductivity detector, Porapak-Q column of 5m length, the detector temperature of 70°C, evaporator temperature of 70°C, and column constant temperature 70°C, gas-carrier helium, flow rate 15 ml/min.

### 1.2. TPPTS synthesis

TPPTS (triphenylphosphine-3,3',3''-trisulfonic acid trisodium salt) ligand was synthesized according to the described procedure [1].

### 1.3. Catalytic Testing Procedure

The reactions were carried out in a steel reactor connected to thermostat and equipped with a manometer and magnetic stir bar. TPPTS ligand, polyol, catalytic precursor  $\text{RhCl}_3$  (previously dissolved in water, with concentration 3 mg/ml), sulfonic acid (5% vol.), and solvent were introduced into the reactor. The reactor was closed, then sealed with Ar and with  $\text{CO}/\text{H}_2$  for 3 times, after this pressurized with ethylene and  $\text{CO}/\text{H}_2$  at the demanded pressures. The mixture was stirred at demanded temperature, and after the reaction was finished, the reactor was cooled down and depressurized. The organic phase was carefully separated from the aqueous phase. Then 2 ml of fresh solvent was added to aqueous phase for extraction of residual products. Joint organic phases were analyzed by GLC using heptane as an internal standard. In recycles, water phase from the previous cycle was put into the autoclave, fresh portions of EG and toluene were added, then the procedure was made as described above.

**2. Table S1. Comparison of Rh/TPPTS activities in ethylene hydroformylation without and with ethylene glycol**

Run No	Solvent	Total amount of oxygenates, mol		Total yield of oxygenates, % n (ald+ac)/n(ethylene)	Selectivity, %		System after the reaction
		In organic phase	In water phase <sup>c</sup>		Propanal	2-ethyl-1,3-dioxolane	
1 <sup>a</sup>	-	-	0.023	99	99	-	Homogeneous Fig S1, a
		Total 0.023					
2 <sup>a</sup>	Toluene <sup>b</sup>	0.017	0.006	99	99	-	Biphasic Fig S1, b
		Total 0.023					
		Total 0.023					
3	Toluene <sup>b</sup>	0.019	1 <sup>st</sup> extraction 0.003	99	10	90	Biphasic Fig S1, c
			2 <sup>nd</sup> extraction 0.001				
		Total 0.023					
		Total 0.023					

Conditions: RhCl<sub>3</sub> (3 mg, 0.011 mol), TPPTS (35 mg, 0.06 mol), EG (4.0 mL, 0.71 mol), water (1.0 mL), H<sub>2</sub>SO<sub>4</sub> (5% vol., 90 μL), pH = 4.0, ethylene 0.65 g (0.023 mol), CO/H<sub>2</sub> (1:1) (total pressure 6.0 MPa, 0.75 g), 90 °C, 2 h

<sup>a</sup> reaction without EG

<sup>b</sup> toluene 2 ml

<sup>c</sup> determined by extraction with toluene (2.0 mL) followed by the GLC analysis

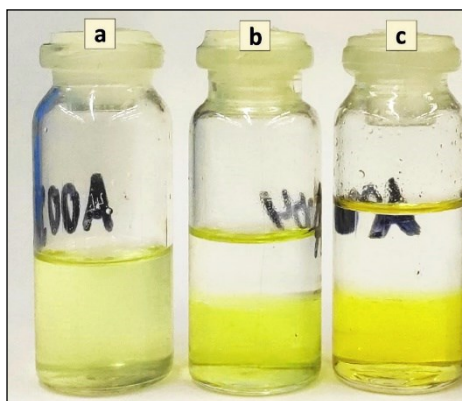


Fig. S1. Photographs of the samples obtained in reactions presented in tab. S1

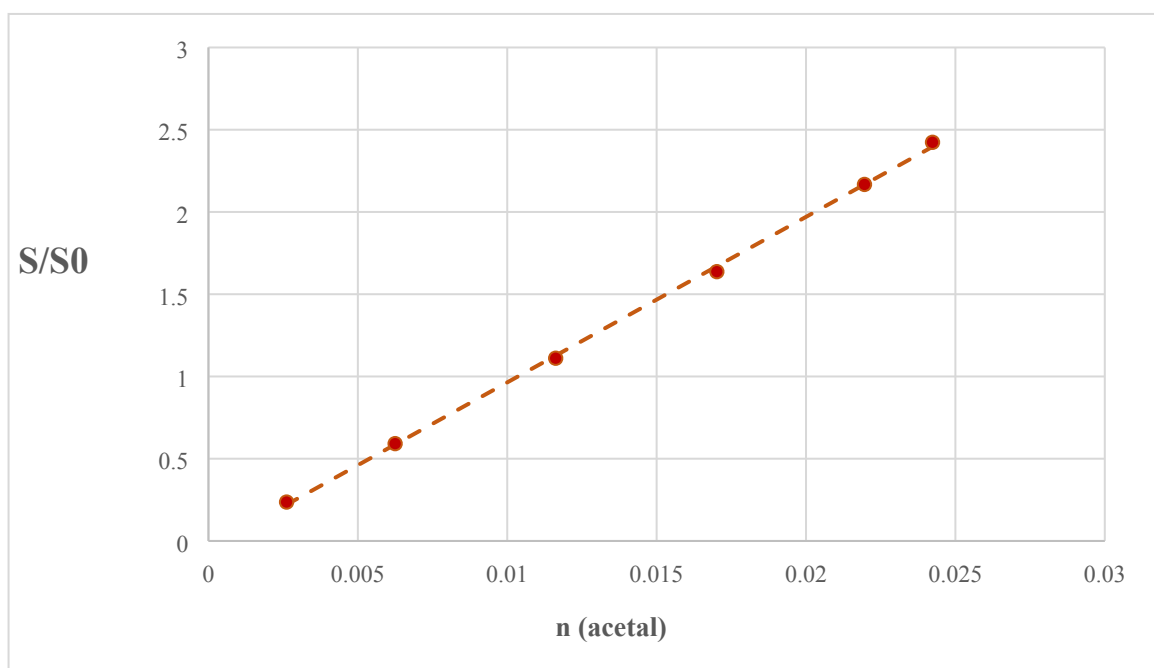
### 3. Calibration graph and equation for estimation propanal and 2-ethyl-1,3-dioxolane yield by GCL

Calibration graphs were obtained for 2-ethyl-1,3-dioxolane and propanal quantitative determination by GLC with heptane as an internal standard. For 2-ethyl-1,3-dioxolane, the ratio of peak areas  $S_{\text{acetal}}/S_{\text{heptane}}$  was calculated at a number of 2-ethyl-1,3-dioxolane concentration values. The data used for the graph are given below:

	m (2-ethyl-1,3-dioxolane), g	n (2-ethyl-1,3-dioxolane), mol	S/S <sub>0</sub>
1	0.1519	0.002614	0.2365
2	0.363	0.006248	0.5917
3	0.6752	0.011621	1.1109
4	0.9886	0.017015	1.6371
5	1.2757	0.021957	2.1674
6	1.408	0.024234	2.4235

**m** is a mass of the acetal added to the initial mixture of the solvent (diphenyl ether, 2.0 mL) and the internal standard (heptane, 0.5 mL), **n** is a molar quantity of the acetal, **S** is a peak area of the acetal, and **S<sub>0</sub>** is a peak area of the internal standard.

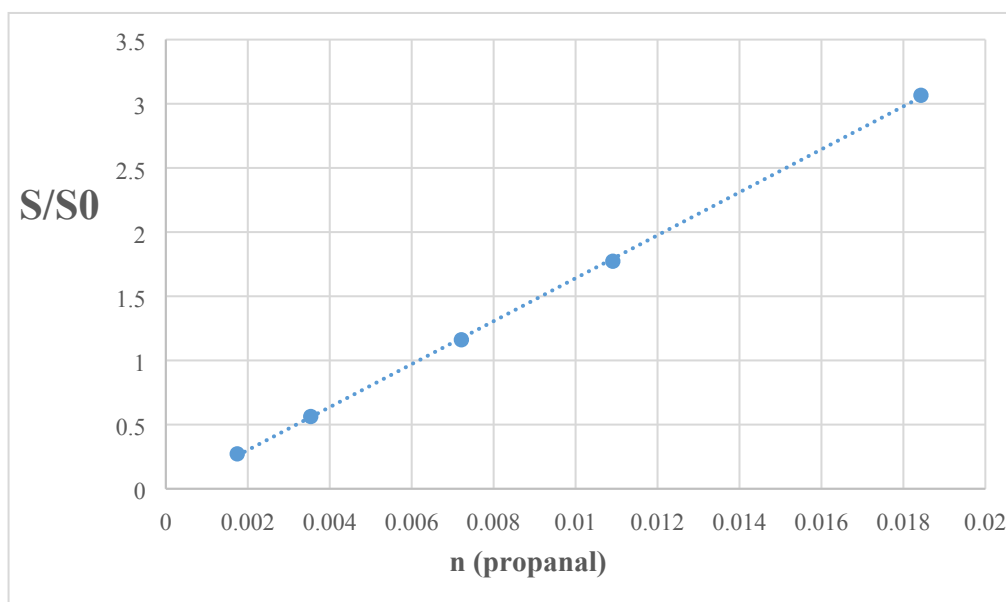
The equation was derived by Microsoft Excel LINEST function.



The analogous graph was obtained for several propanal quantities.

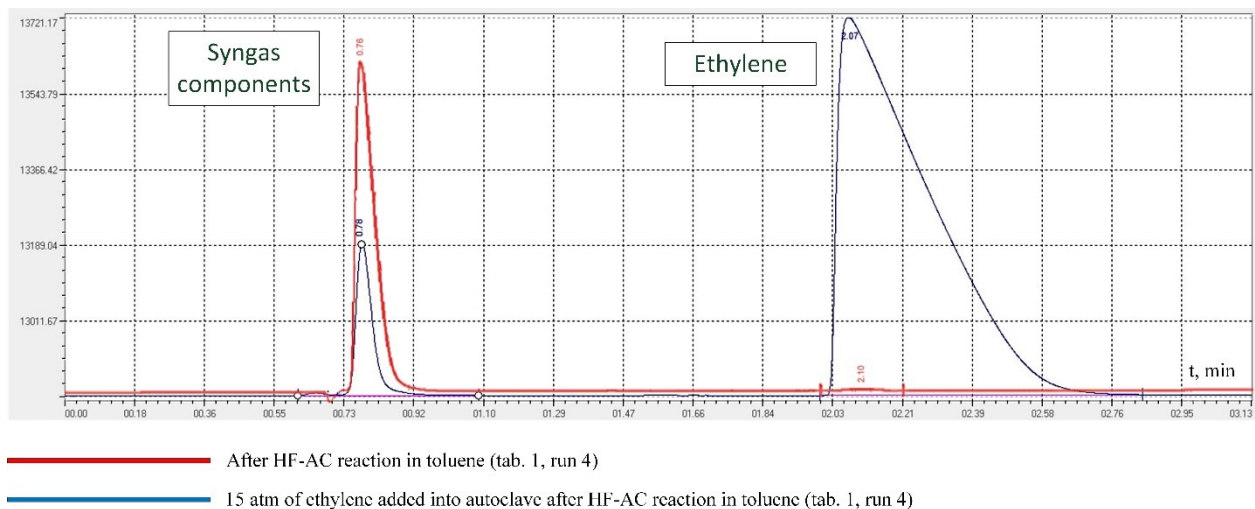
	<b>m (propanal), g</b>	<b>n (propanal), mol</b>	<b>S/S<sub>0</sub></b>
<b>1</b>	0.1777	0.001742	0.272
<b>2</b>	0.3607	0.003536	0.563
<b>3</b>	0.7357	0.007213	1.161
<b>4</b>	1.1127	0.010909	1.773
<b>5</b>	1.8797	0.018428	3.066

**m** is a mass of the propanal added to the initial mixture of the solvent (toluene, 2.0 mL) and the internal standard (heptane, 0.5 mL), **n** is a molar quantity of propanal, **S** is a peak area of propanal, and **S<sub>0</sub>** is a peak area of the internal standard.



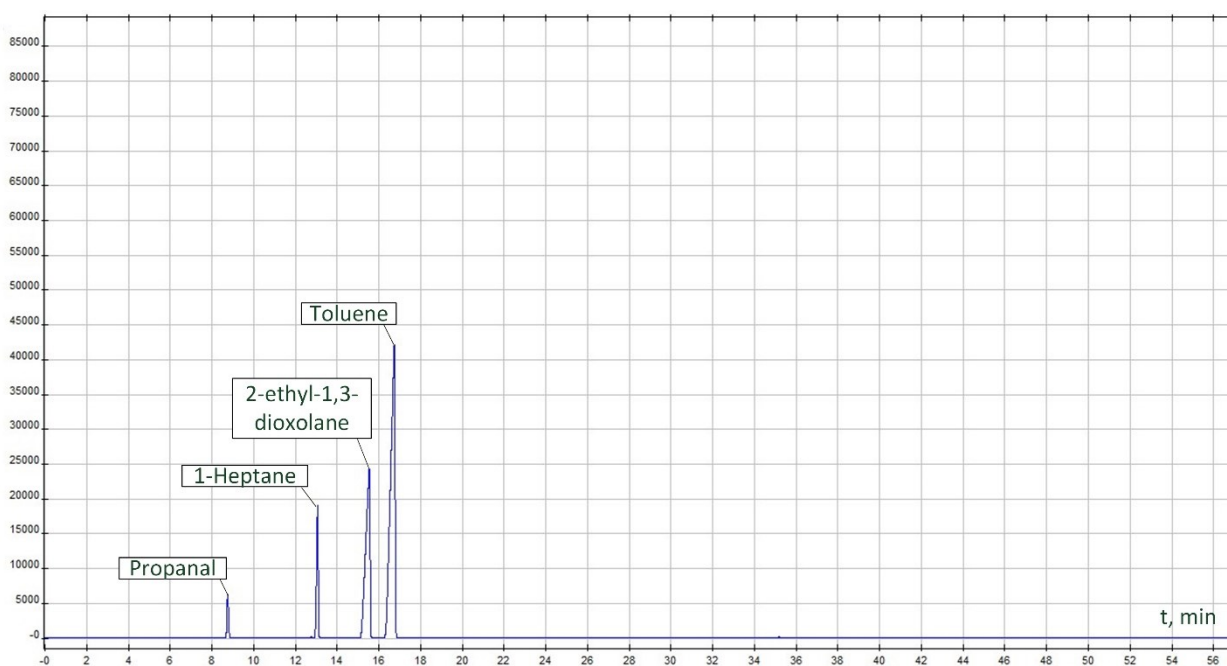
For the estimation of the yield of propanal and acetal by GLC, after the reaction, heptane (0.5 mL) was added as an internal standard, the **S/S<sub>0</sub>** ratio was determined, then the molar quantities of the products was calculated by the equations presented on the graphs. The yields were calculated by dividing these quantities by the quantity of ethylene determined from its mass. Analogously, the yield of propanal was calculated.

#### 4. Chromatogram of the gaseous mixtures

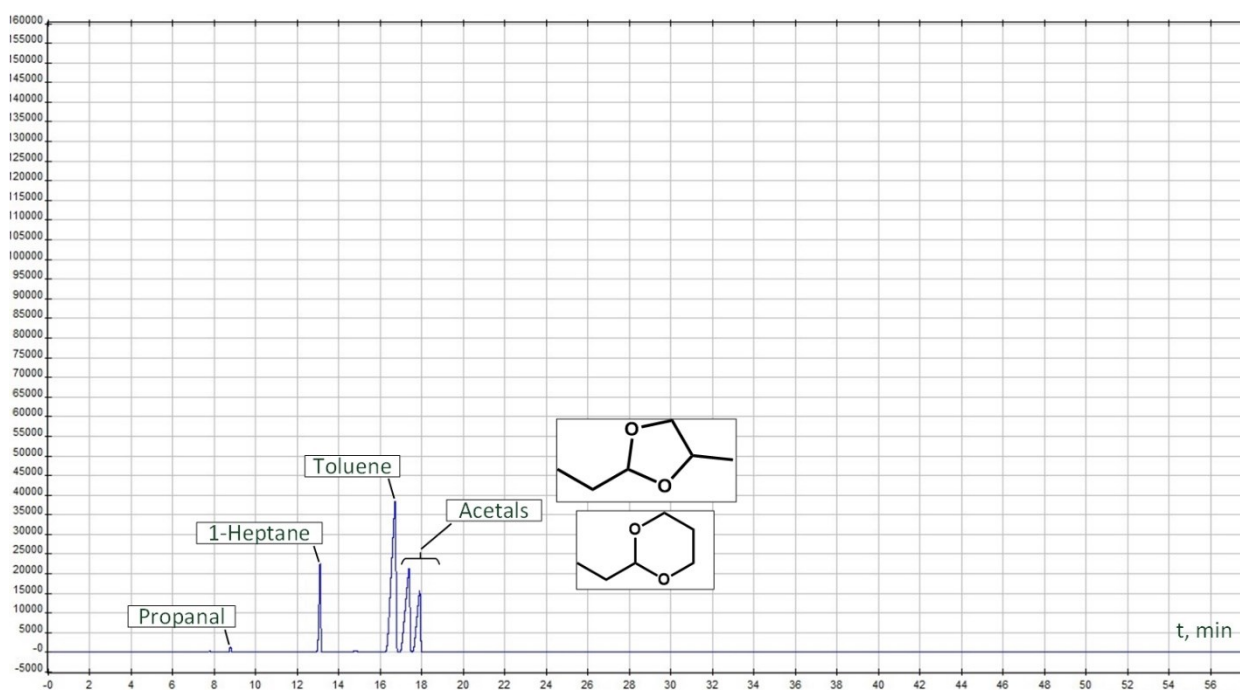


**Fig S2.** The chromatogram of the gaseous mixtures

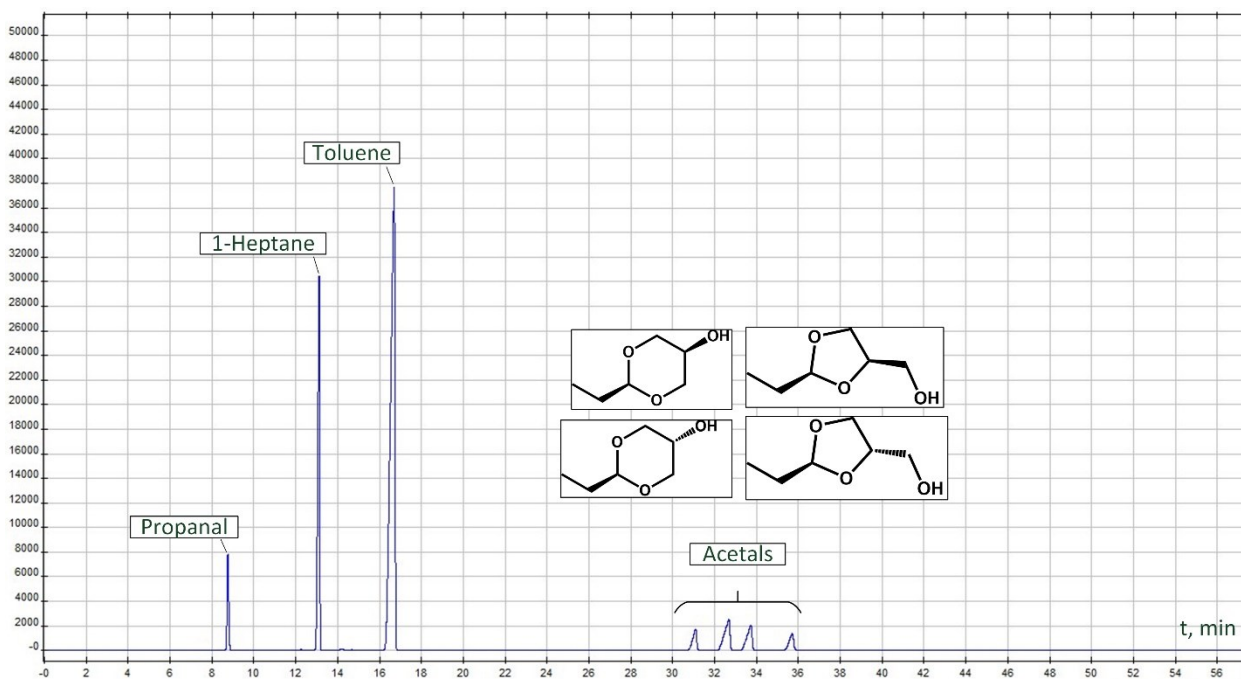
## 5. Chromatograms of product mixtures



**Fig S3.** The chromatogram of the final mixture of ethylene HF-AC reaction in the presence of EG (tab. 2, run 1)



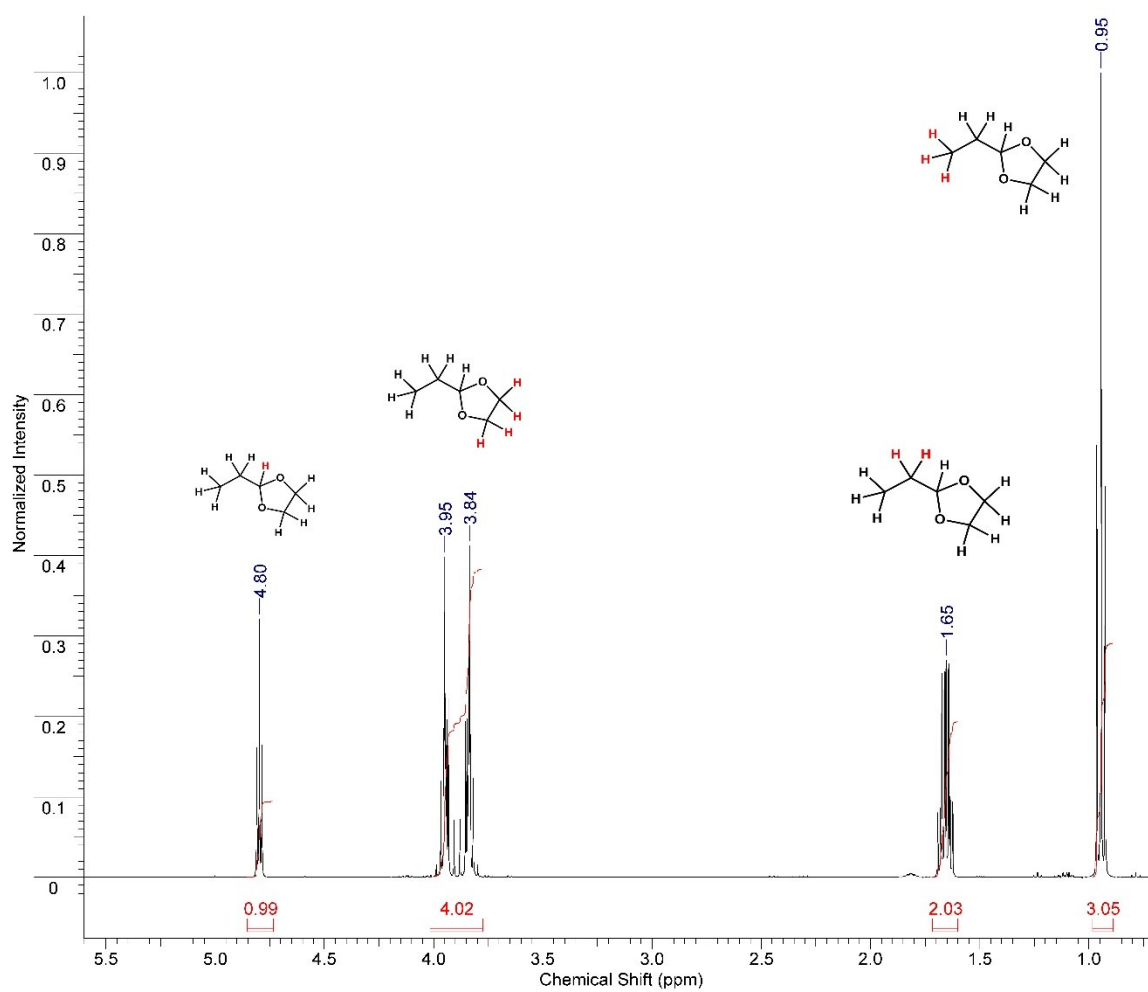
**Fig S4.** The chromatogram of the final mixture of ethylene HF-AC reaction in the presence of propanediols (tab. 2, run 2)



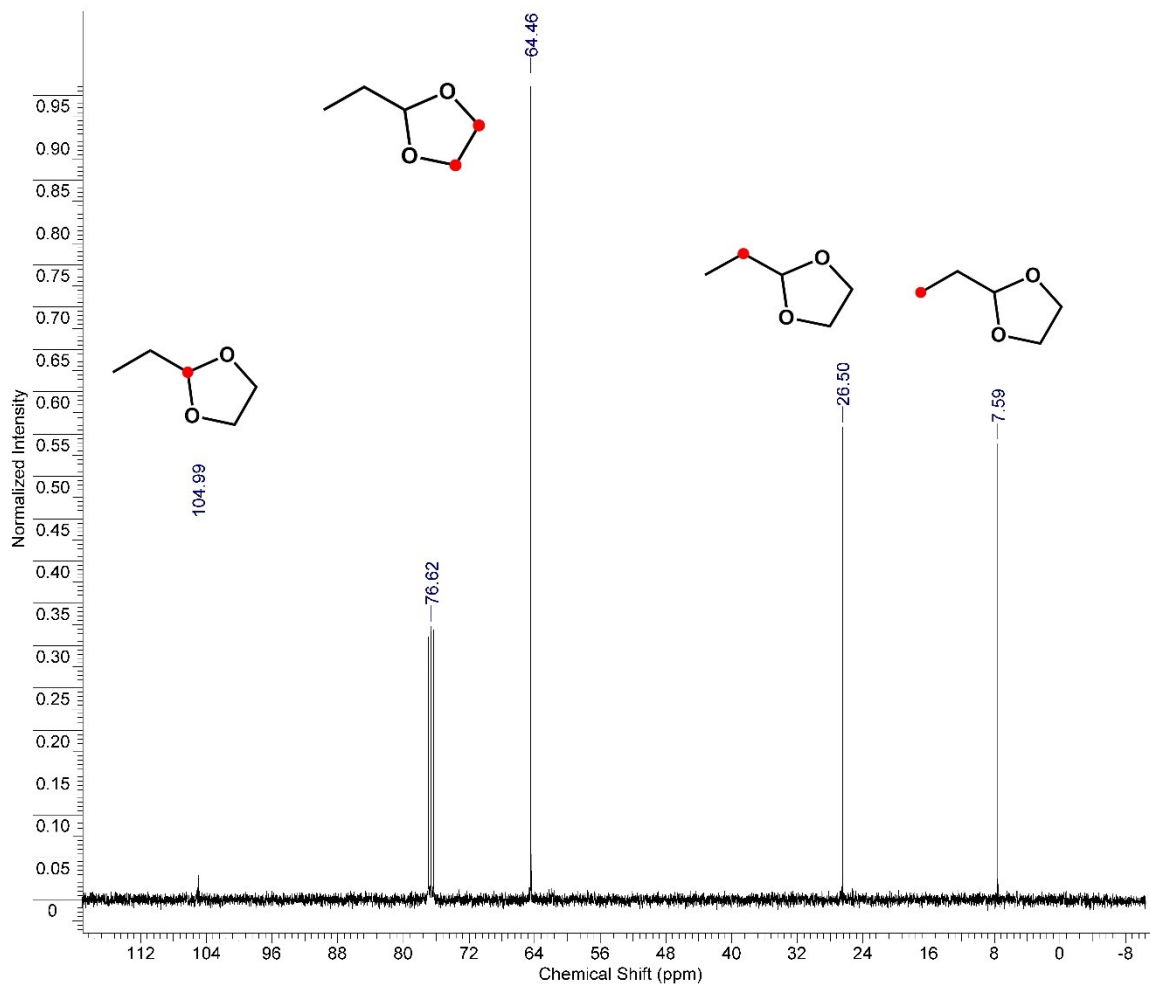
**Fig S5.** The chromatogram of the final mixture of ethylene HF-AC reaction in the presence of glycerol (tab. 2, run 4)



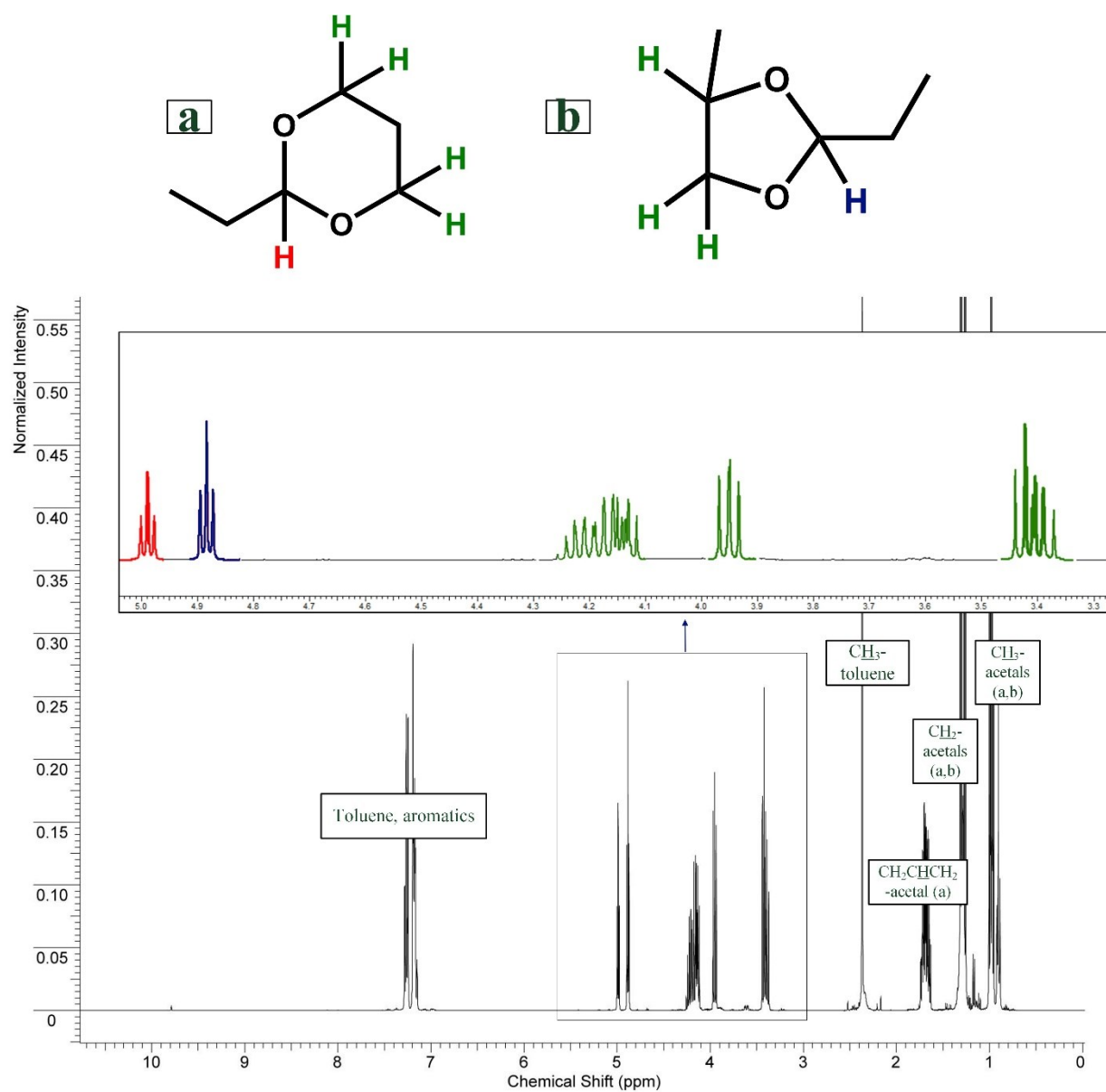
## 6. NMR spectra of obtained acetals



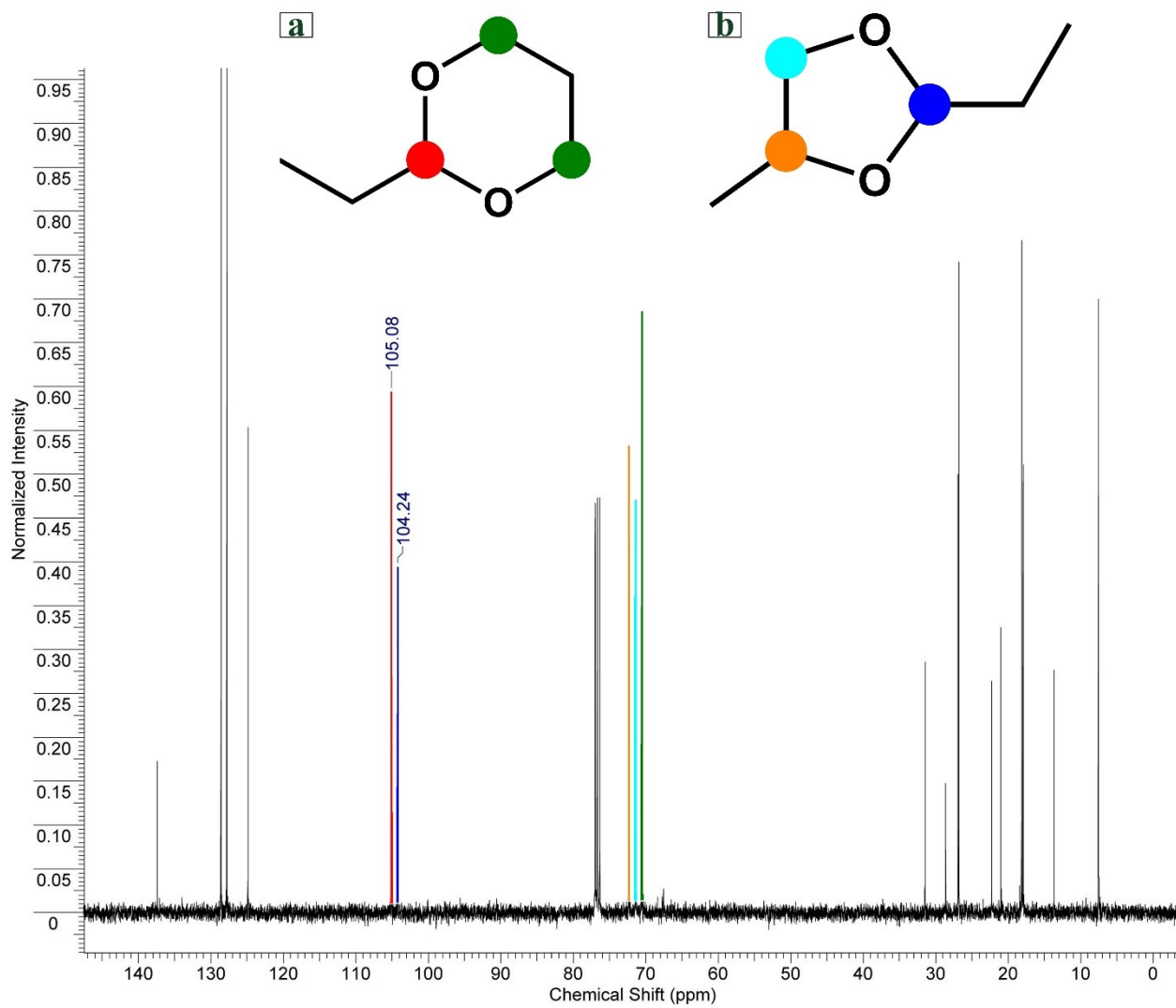
**Fig S6.**  $^1\text{H}$  NMR spectra of 2-ethyl-1,3-dioxolane ( $\text{CDCl}_3$ , 400 MHz)



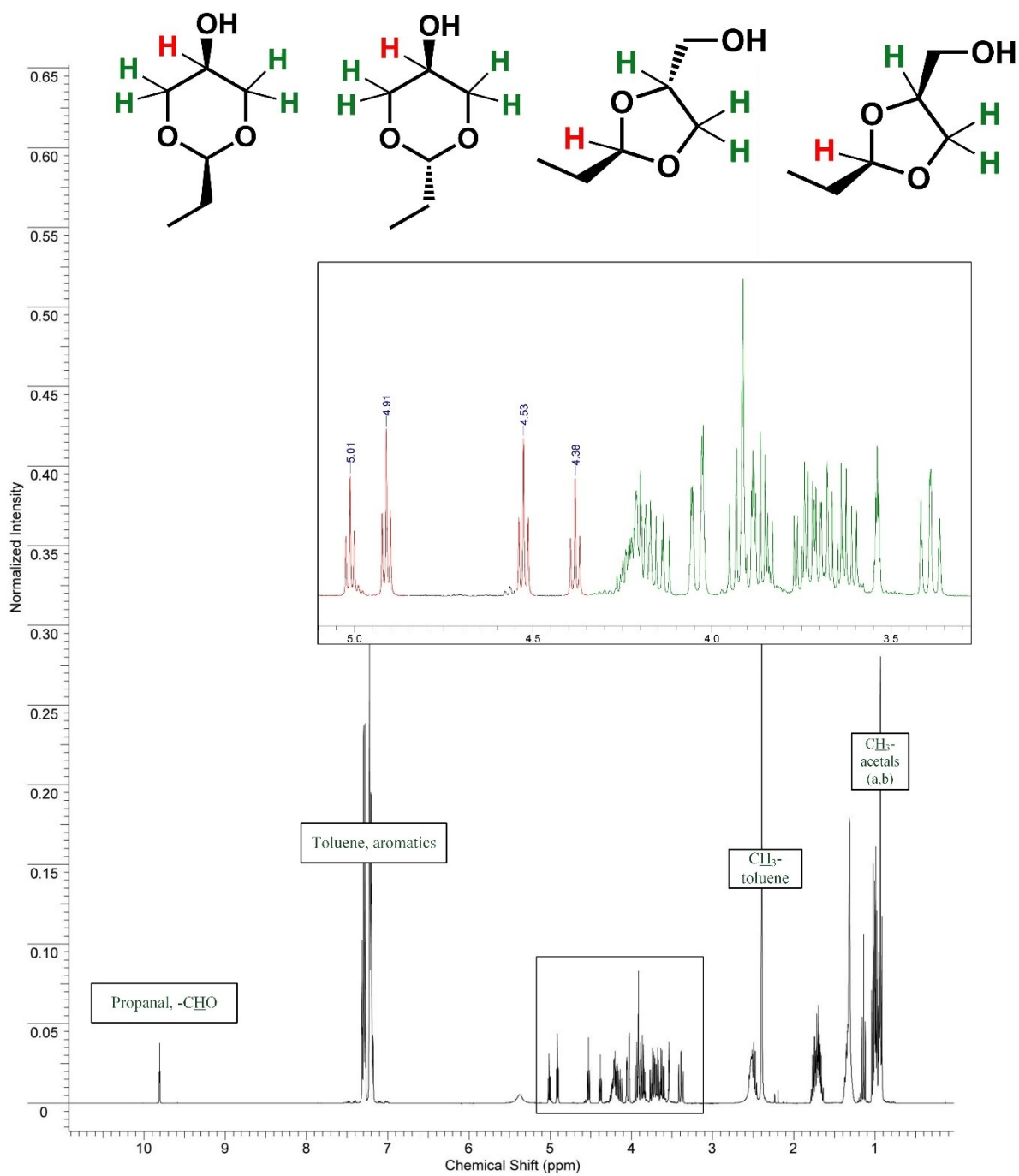
**Fig S7.**  $^{13}\text{C}$  NMR spectra of 2-ethyl-1,3-dioxolane ( $\text{CDCl}_3$ , 100 MHz)



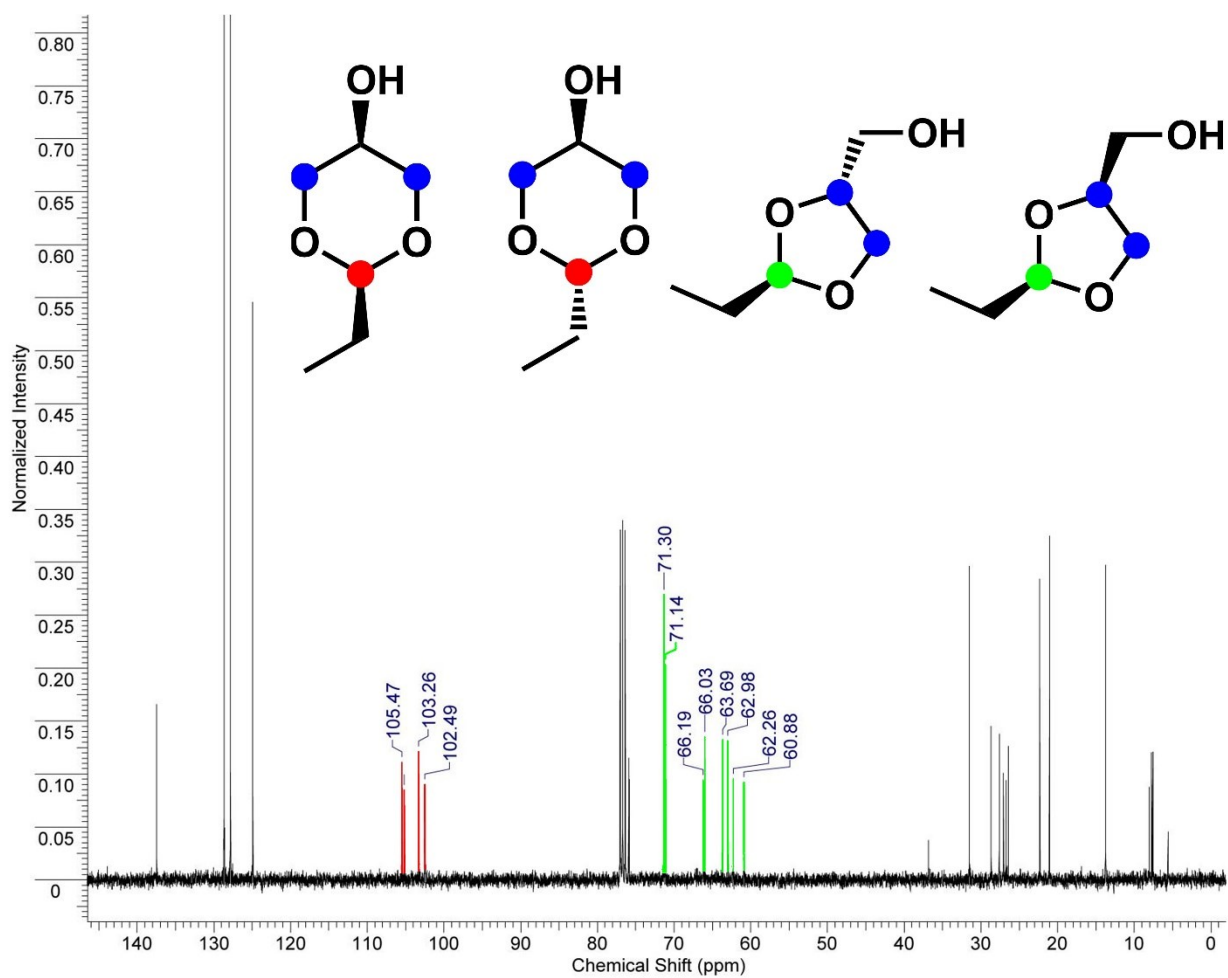
**Fig S8.**  $^1\text{H}$  NMR spectra of 1,2- and 1,3- propanediol acetals ( $\text{CDCl}_3$ , 400 MHz)



**Fig S9.**  $^{13}\text{C}$  NMR spectra of 1,2- and 1,3- propanediol acetals ( $\text{CDCl}_3$ , 100 MHz)



**Fig S10.**  $^1\text{H}$  NMR spectra of glycerol acetals ( $\text{CDCl}_3$ , 400 MHz)



## 7. References

1. H. Chen, Y. Li, J. Chen, P. Cheng and X. Li, *Catal. Today*, 2002, **74**, 131.