

Supplementary data

Clay catalysed rapid valorization of glycerol towards cyclic acetals and ketals

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Table S1: Characteristic tests and properties of bentonite “BBnR” and bentonite “BBnU”.

Properties	Swelling ¹ ml/g	LOI ² % w/w	CEC ³ meq/g	pH ⁴	WI ⁵	Bulk Density ⁶ cc/g	
						Loose	Packed
BBnR	18	16.9	66	7.53	42	0.81	1.11
BBnU	21	12.0	75	7.16	44	0.76	1.12

¹Specification for bentonite, published by Bureau of Indian standard publications, BIS IS 6186:1986 (R2003). ²Loss of ignition was determined gravimetrically at 1000 °C (2 h). ³The cation exchange capacity (CEC) was measured with the standard ammonium acetate method. ⁴pH of the aqueous clay suspensions (1 wt %), measured with Toshniwal digital pH meter at 30 °C. ⁵Whiteness index with respect to standard MgO. ⁶Weight of clay of known volume before and after packing by 200 strokes.

S1. Purification of raw bentonite

The raw bentonite lumps, was purify by the sedimentation techniques, with dispersing 4% bentonite in deionized water and allowed to swell overnight. After swelling, the suspension stirred vigorously by a top stirrer for 30 min and then allowed to stand for ca 4 h for sedimentation of the non-clay and heavy matter. Subsequently, the supernatant, decanted and the sediment was re-suspended in deionized water and allowed to stand for further sedimentation. This sedimentation process repeated thrice, and the supernatant thus obtained consider as purified clay suspension. Solid content in the suspension was analyzed gravimetrically. Clay from the suspension was separated by centrifuge then dried, ground and passed through 100

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meshes BSS sieve and designated as “BBnU” (Where, BBnU = Banaskantha Bentonite Upgraded). The properties of samples were comparable with those of natural bulk bentonite (Table S1).

S2. Methodologies for surface acidity

S2.1. Volumetric titration method

In details experiment exactly; 1 g of the acid activated clay (previously dried at 110 °C for 6 h) was slightly warmed and stirred for 15 min with 10 ml distilled water, then clay water suspension was titrated with 0.01 N potassium hydroxide (KOH) solution using phenolphthalein as indicator. Acidity was then determined as mg of KOH used per gram of clay by equation (iii) [1]

$$\text{Acidity} = [(V \times N \times 56.10) / \text{Wt}] \times 100 \quad (\text{iii})$$

Where V is the volume of used KOH in titration (ml), N is normality of potassium hydroxide solutions and Wt. is weight of clay (g).

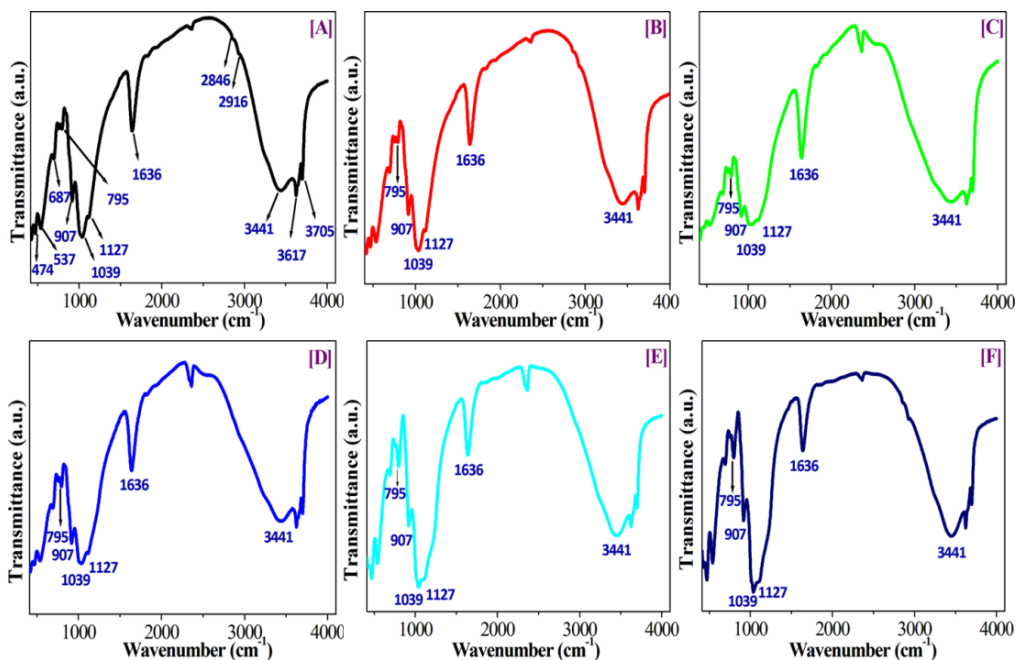


Fig. S1. FT-IR spectra of natural and acid activated bentonite sample. Where, [A]: BBnR, [B]: BBnU, [C]: 6/BBnU/6, [D]: 8/BBnU/6, [E]: 12/BBnU/6, [F]: 15/BBnU/6.

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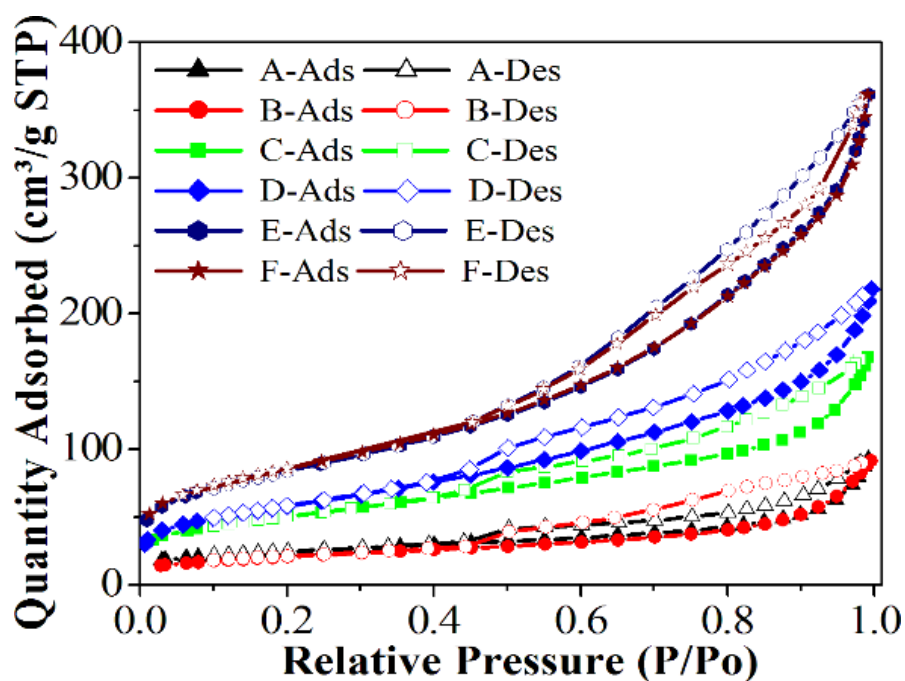


Fig. S2. N₂ adsorption desorption isotherm of raw, purified and acid activated bentonite samples. [A]: BBnR, [B]: BBnU, [C]:6/BBnU/6, [D]:8/BBnU/6, [E]:12/BBnU/6, [F]:15/BBnU/6.

Table S2: The total peak area concentration due to ammonia in ammonia TPD plot for amount of acidic sites in acid activated samples.

Sample	Temperature at Maximum (°C)	Quantity (cm ³ /g STP)	Peak Concentration (%)
6/BBnU/6	479.3	50	3.15
8/BBnU/6	461.0	48	2.57
12/BBnU/6	459.2	44	1.44
15/BBnU/6	464.4	41	1.33

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Table: S3 Cyclohexanone glycerol acetalization data for finest catalyst screening

Sample	SA (m ² /g)	Amount of catalyst used (g)	%Conversion	% Selectivity 5-M ketal	Conversion mol/g catalyst	Conversion mol/m ²
6/BBnU/6	180	0.05	90	98	0.184	0.00100
8/BBnU/6	209	0.05	92	98	0.187	0.00091
12/BBnU/6	302	0.05	80	97	0.163	0.00053
15/BBnU/6	308	0.05	73	97	0.148	0.00048

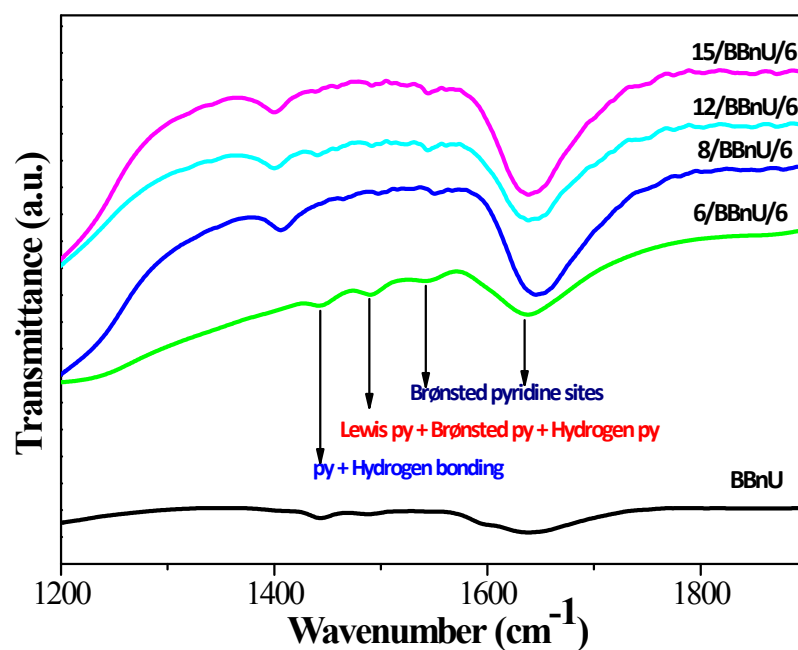


Fig. S3. Pyridine FT-IR spectra of the acid-activated and pure bentonite samples.

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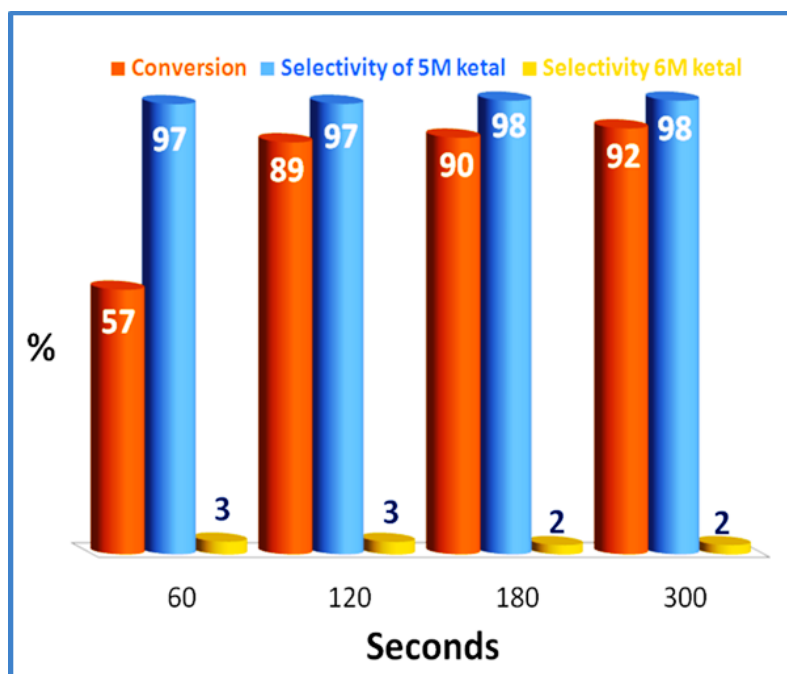


Fig. S4. Influence of reaction time over cyclohexanone acetalization under ultra-sonication conditions.

S.3 Gas Chromatograph for acetalization glycerol with respective carbonyl compounds

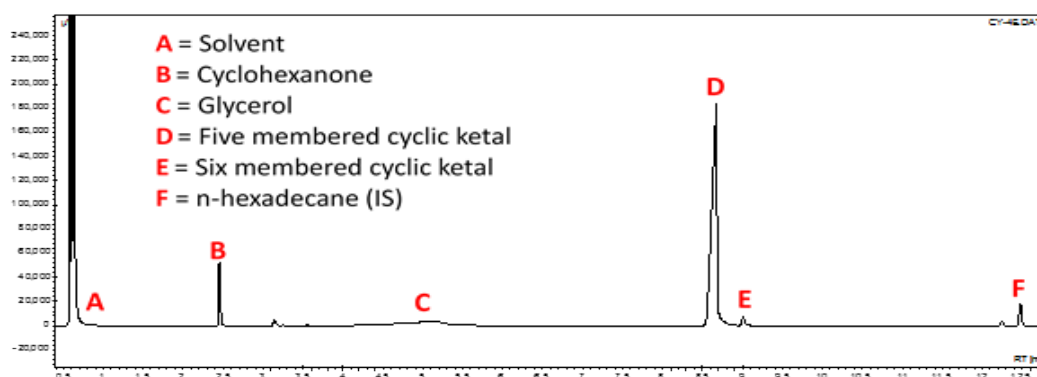


Fig. S5. GC analysis chromatograph for cyclohexanone glycerol acetalization reaction.

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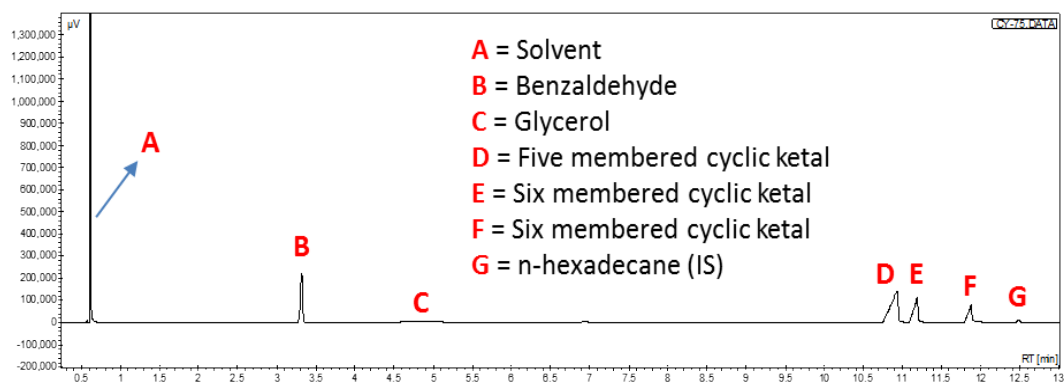


Fig. S6. GC analysis chromatograph for Benzaldehyde glycerol acetalization reaction.

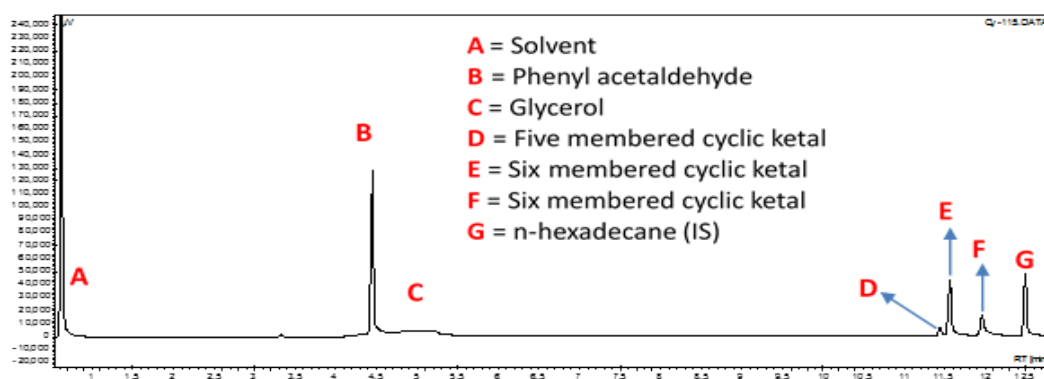


Fig. S7. GC analysis chromatograph for phenyl acetaldehyde glycerol acetalization reaction.

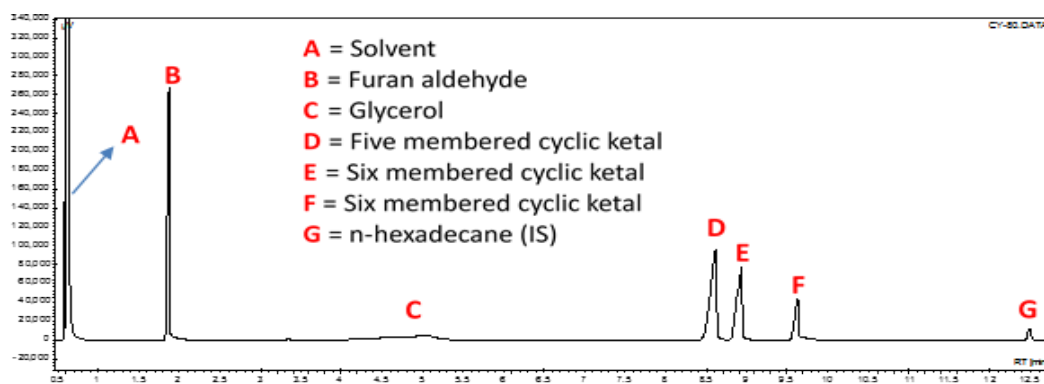


Fig. S8. GC analysis chromatograph for furan aldehyde glycerol acetalization reaction.

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S4. NMR Study

S4.1 Product of acetalization with cyclohexanone

NMR data of the major product 1, 3 dioxalane were assigned as follows the trace amount of six member product was only identified on the basis of GC characterization data.

1, 4 Dioxalane [4, 5] decane-2 methanol

$^1\text{H NMR}$ (CDCl_3) δ – 4.217 (m, 1H, CH), 4.03(dd, 1h, CH_2) 3.77 (dd, 1H, CH_2) 3.66 (dd, 1H, CH_2OH), 3.60 (dd, 1H, CH_2OH), 2.33 (1H, OH) 1.85-1.40 (m, 10H, CH_2)

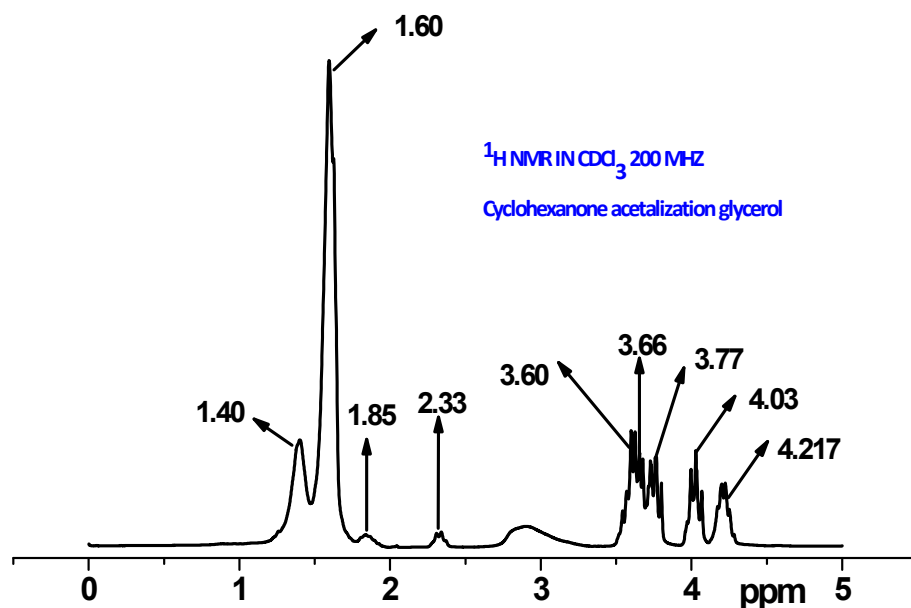


Fig. S9 $^1\text{H NMR}$ Product of glycerol acetalization with cyclohexanone

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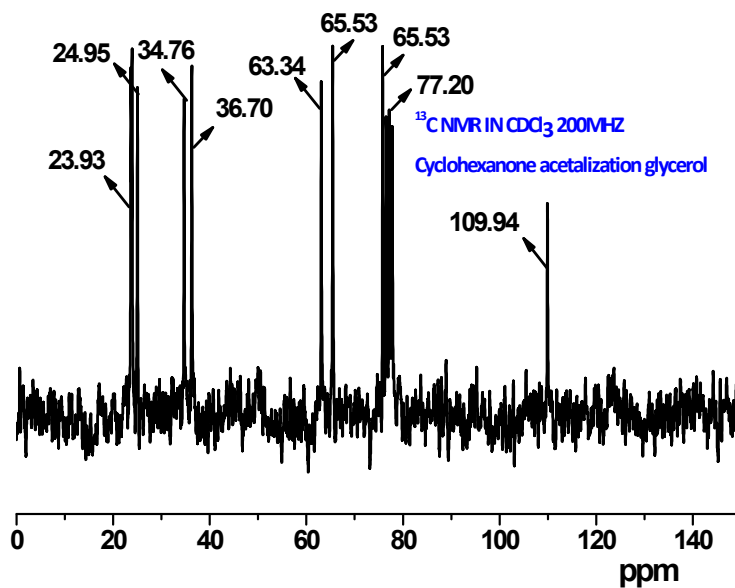


Fig. S10 ¹³CNMR Product of glycerol acetalization with cyclohexanone

S4.2 Product of acetalization with Benzaldehyde

The four isomeric products (*Cis*- and *trans*-1, 3 dioxalane and *Cis*- and *trans*-1, 3 dioxane) were identified by both NMR and GC-MS.

Cis- and *trans*-(2-phenyl-[1-3]-dioxalan-4-yl) methanol

¹H NMR (CDCl₃) δ – 5.90 and δ 5.70 (s, PhCH) ¹³CNMR (CDCl₃) 104.17 and 103.63ppm (t₁) (PhCH)

Cis- and *trans*-2-phenyl-[1-3]-dioxan-5-ol

¹H NMR (CDCl₃) δ – 5.50 and δ 5.34 (s, PhCH) ¹³CNMR (CDCl₃) 104.17 and 103.63ppm (t₁) (PhCH)

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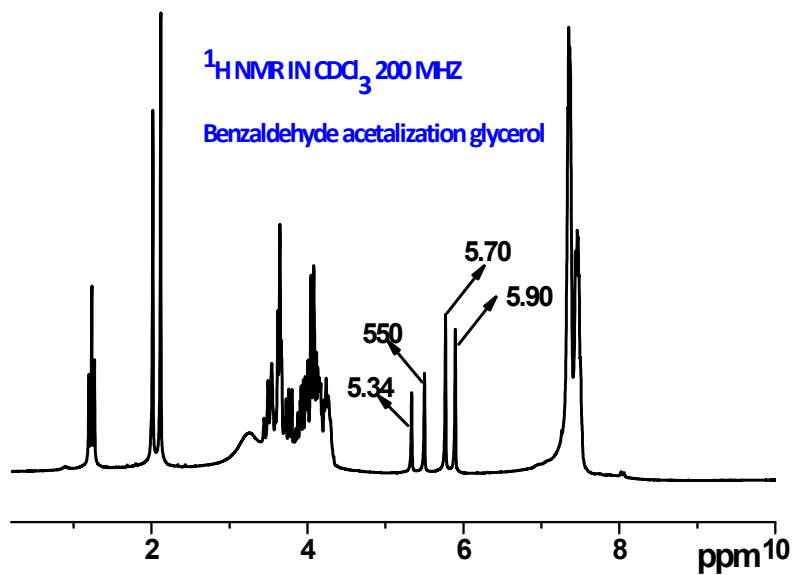


Fig. S11 $^1\text{H NMR}$ Product of glycerol acetalization with benzaldehyde.

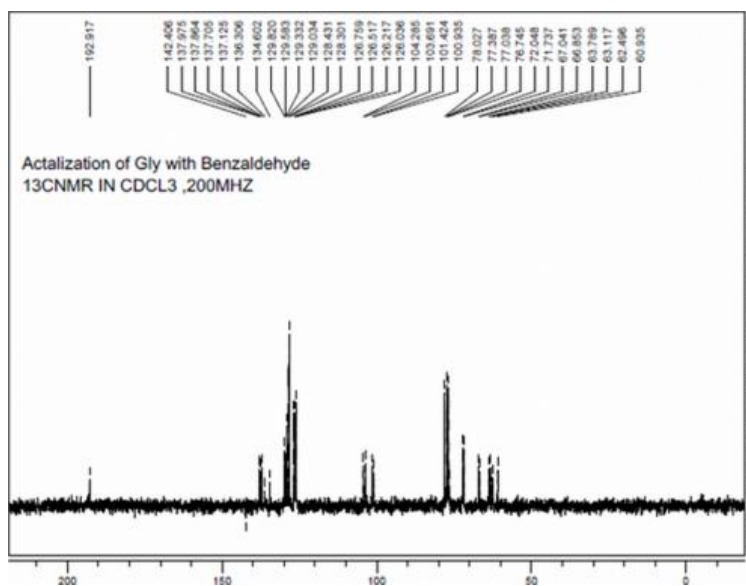


Fig. S12 $^{13}\text{C NMR}$ Product glycerol of acetalization with benzaldehyde