Supplementary Information

Modified Boehmite: A choice of catalyst for the selective conversion of glycerol to five-membered dioxolane

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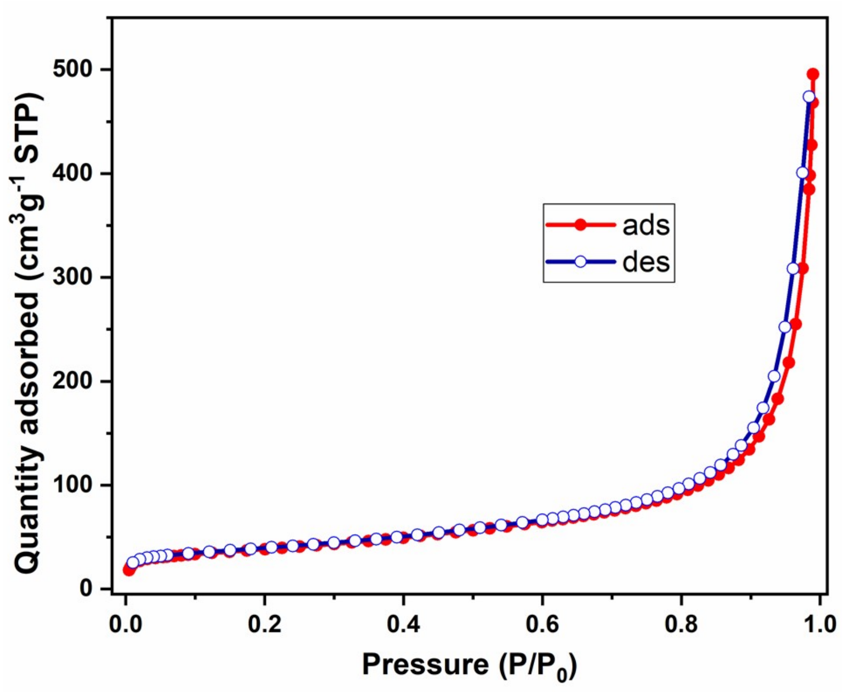
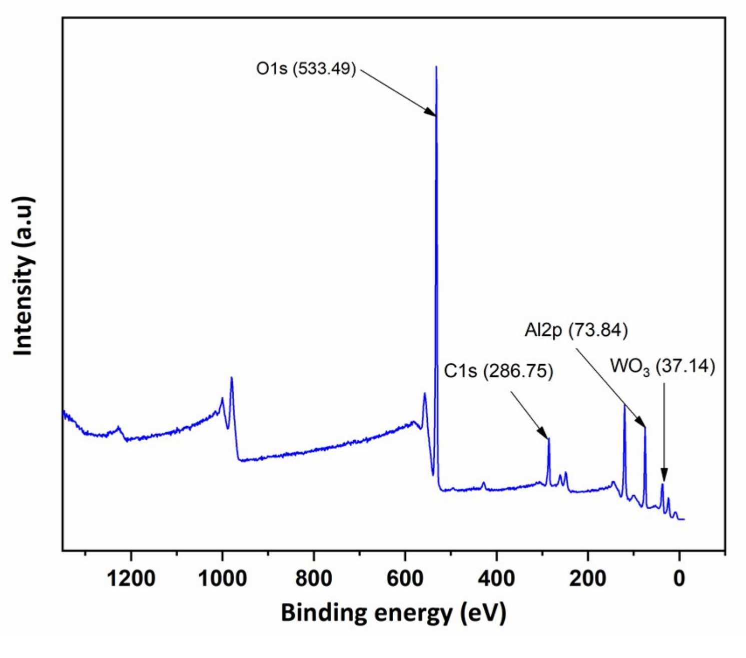
S1. General Methods

Glycerol was purchased from Laboratory Rasayan, 4-bromo benzaldehyde from Sigma Aldrich, ammonium(para)tungstate (APT) from Otto chemicals, Aluminium nitrate from Sigma Aldrich, urea from local vendor and used without further purification. Gas chromatography-mass spectroscopy (GC-MS) analysis were performed on a Shimadzu TQ8040 GC-MS system instrument equipped with a SH-Rxi-5ms column (30mL, ID 0.25mm, DF 0.25micrometer). ^{1}H, ^{13}C NMR spectra were recorded on a Bruker 500 MHz. Chemical shifts for proton resonances are reported in ppm (δ) relative to tetramethylsilane (TMS) while ^{13}C is related to the deuterated standard solvent. BET surface area values were obtained *via* micromeritics (ASAP 2020) instrument. Powder X-ray diffraction patterns of the catalyst were recorded with Phillips XRD Rigaku Miniflex II Desktop X-ray Diffractometer equpped with (λ = 1.54050 Å) over a 2θ range of 1-10 °C at a step time of 0.05° s^{-1} Field Emission-Scanning Electron Microscopy (FE-SEM) micrographs were recorded using a JEOL JSM-7100F instrument employing an 18-kV accelerating voltage. High resolution-transmission electron microscope (HR-TEM) images were obtained using a JEOL JEM-2100 microscope with an acceleration voltage of 200 kV using carbon coated 200 mesh copper grids. XPS measurements for the catalyst were done on Thermo Kalpha+ spectrometer using Al - Kα radiation with energy of 1486.6 eV. All the spectra were charge corrected with reference to C1s at 284.6 eV. The peak fitting were carried out using CasaXPS software with Shirley type background. Fourier-transform infrared spectroscopy (FT-IR) data were obtained using IR spectra were recorded using KBr pellet method on a Perkin–Elmer GX FTIR spectrometer. TGA analysis was carried out using Mettler Toledo Star SW 8.10. TG analysis was performed in nitrogen environment while the heating rate was ramped from room temperature to 600 °C at 10 °C/min.

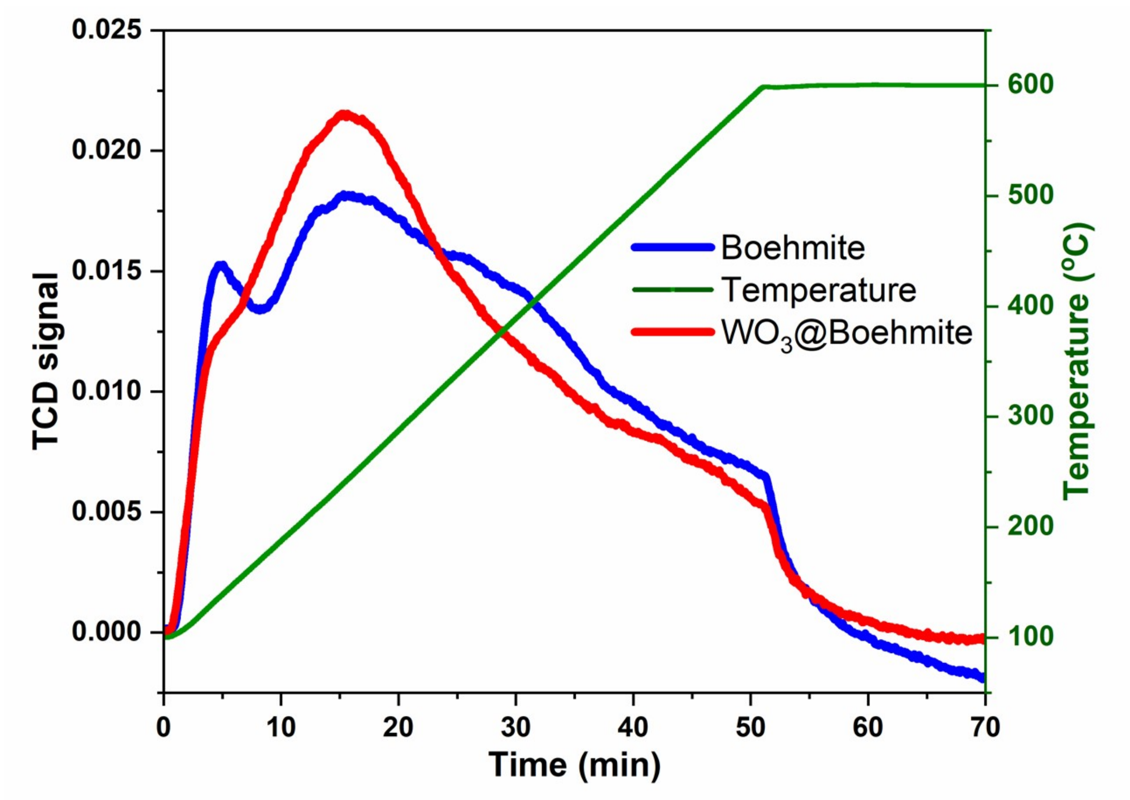
S2. BET surface area Analysis for synthesized Boehmite



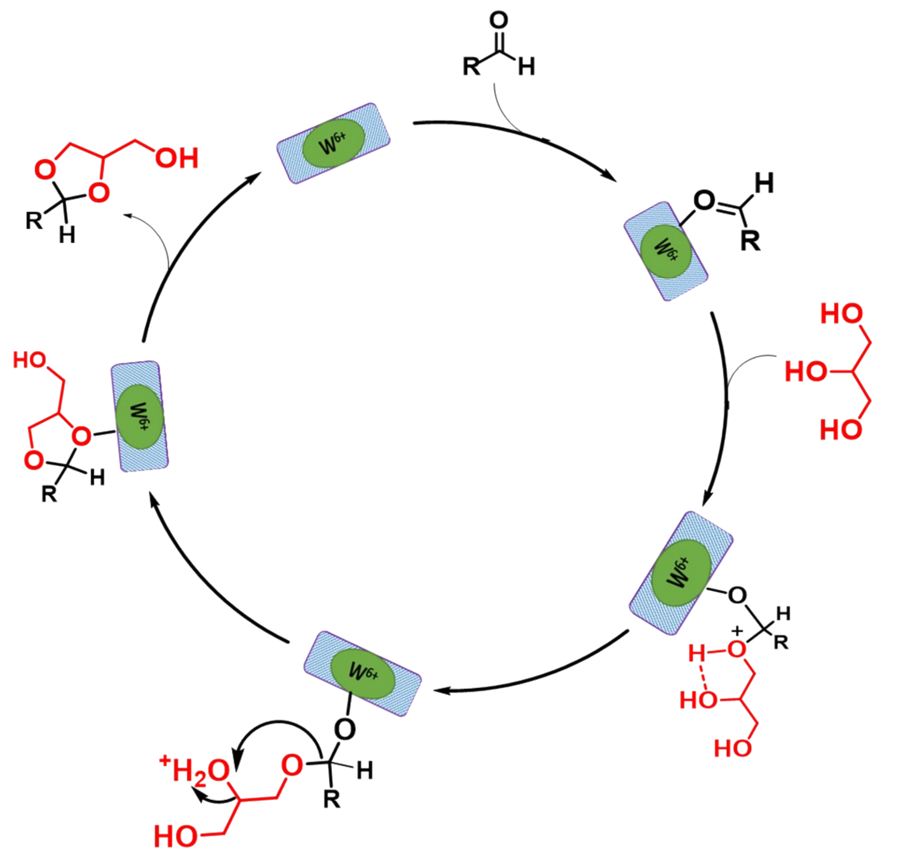
S3. XPS recorded for WO_3@Boehmite



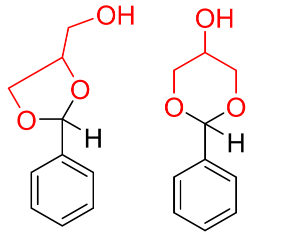
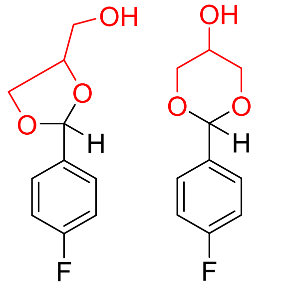
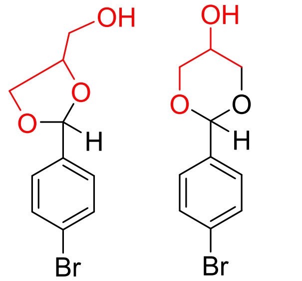
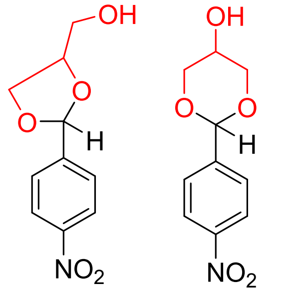
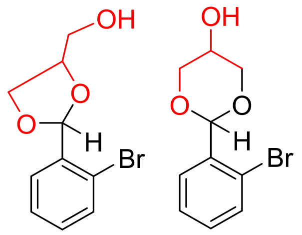
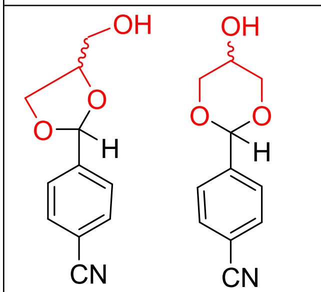
S4. NH_3-TPD recorded for Boehmite and WO_3@Boehmite

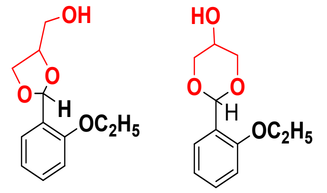
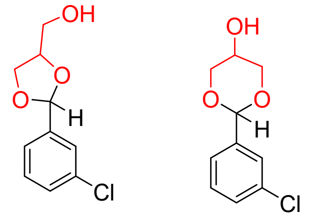
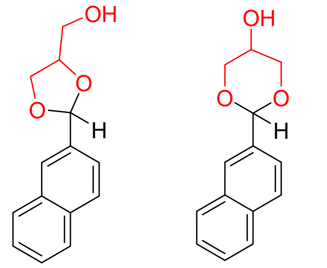
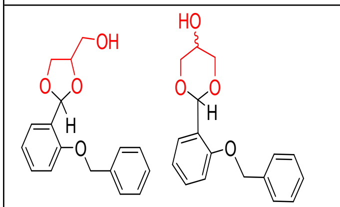
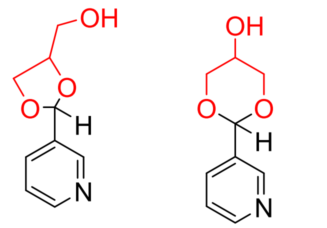
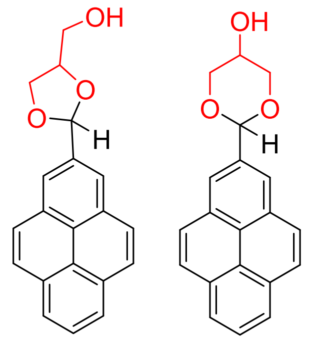


S5. Plausible mechanism of WO_3@Boehmite catalyzed acetalization of glycerol

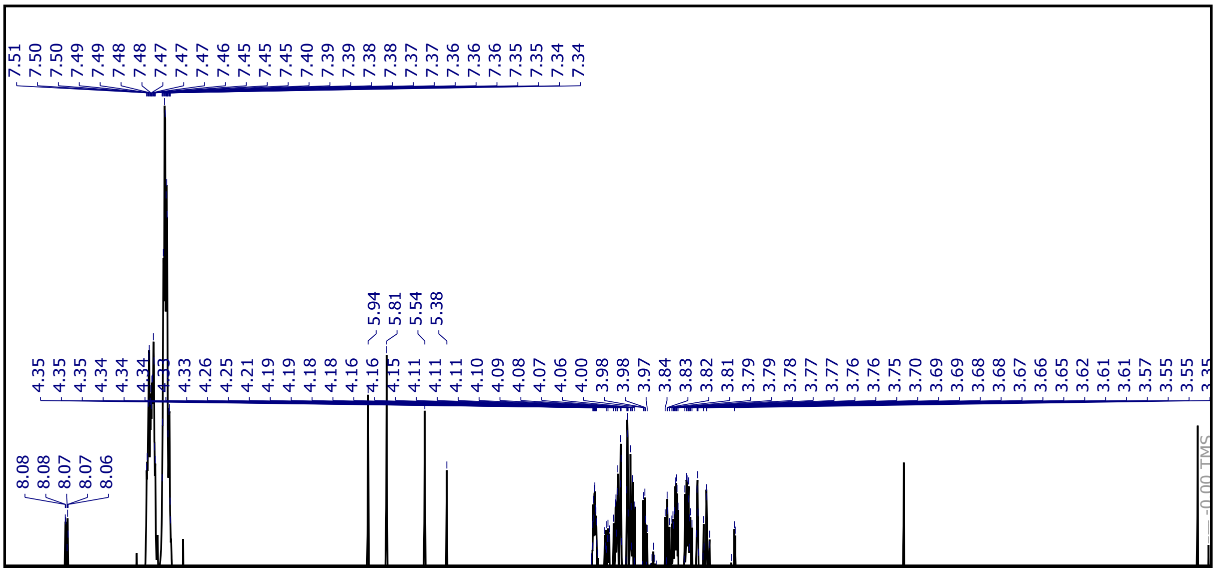


S6. Characterization data of glycerol products obtained from acetylization (NMR, MS & GC)

	**1b:** Colourless liquid, Conv: 97%, selectivity: 57%, ^{1}H NMR (500 MHz, $CDCl_3$–d) δ (TMS, ppm) = 8.08 – 7.34 (m, 10H), 5.94,5.81 & 5.54,5.38(2s & 2s, 2H), 4.34 - 3.55 (m, 12H). ^{13}C NMR (126 MHz) δ= 137.81, 133.52, 130.16, 129.66, 129.40, 129.20, 129.08, 128.55, 128.50, 128.40, 126.79, 126.68, 126.48, 126.19, 125.97, 104.40, 103.87, 101.70, 101.02, 72.29, 71.71, 66.99, 66.82, 64.03, 63.29, 62.71, 61.28.
	**2b:** colourless liquid, Conv: 100%, selectivity: 58%, ^{1}H NMR (500 MHz, $CDCl_3$-d) δ (TMS, ppm) = 7.48-7.46(m, 4H), 7.26-7.03 (m, 4H), 5.92,5.79 & 5.52,5.38 (2s & 2s 2H), 4.38- 3.58 (m 12H). ^{13}C NMR (126 MHz) δ= 133.83, 132.97, 132.90, 128.82, 128.75, 128.60, 128.54, 128.28, 128.21, 128.09, 128.02, 115.93, 115.76, 115.72, 115.65, 115.55, 115.48, 115.32, 103.91, 103.41, 101.18, 100.51, 72.41, 71.83, 67.09, 66.95, 64.08, 63.40, 62.82, 61.38.
	**3b:** colourless liquid, Conv: 88%, selectivity 84%, ^{1}H NMR (500 MHz, $CDCl_3$-d) δ (TMS, ppm)=7.53–7.33 (m, 8H), 5.92–5.78 & 5.51–5.37 (2s & 2s, 2H), 4.37–3.63 (m, 10H). ^{13}C NMR (126 MHz) δ= 137.02, 136.24, 131.75, 131.69, 131.55, 128.41, 128.24, 127.79, 123.73, 103.72, 103.26, 72.35, 67.01, 66.80, 64.00, 63.28, 62.75, 1.14.
	**4b:** Brownish liquid, Conv: 57%, selectivity: 87%, ^{1}H NMR (500 MHz, $CDCl_3$-d) δ (TMS, ppm) = 8.26–8.24 (m, 4H), 7.69–7.65 (m, 4H), 6.06,5.91 & 5.63, 5.49 (2s & 2s, 2H), 4.43–3.69 (m, 10H). ^{13}C NMR (126 MHz) δ= 127.68, 127.50, 123.80, 102.88, 102.57, 67.15, 66.90, 63.12, 62.70, 22.79.
	5b: : Colourless liquid, Conv: 84%%, selectivity: 90%, ^{1}H NMR (500 MHz, $CDCl_3$-d) δ (TMS, ppm) = 7.57–7.13 (m, 8H), 6.12, 6.02 & 5.69, 5.54 (2s & 2s, 2H), 4.29–3.59 (m, 10H). ^{13}C NMR (126 MHz) δ = 135.85, 134.68, 133.13, 133.04, 132.08, 131.03, 130.84, 128.13, 127.95, 127.73, 127.55, 127.29, 123.12, 122.88, 103.08, 102.85, 72.50, 66.99, 63.09, 62.58.
	**6b:** Colourless liquid, Conv: 97%, selectivity: 96%, ^{1}H NMR (500 MHz,$CDCl_3$–d) δ (TMS, ppm) = 7.68 – 7.59 (m, 8H), 5.99, 5.84 & 5.59, 5.43 (2s & 2s, 2H), 4.41 – 3.66 (m, 10H). ^{13}C NMR (126 MHz) δ = 143.11, 142.27, 132.28, 132.12, 127.38, 127.15, 118.58, 118.53, 113.03, 112.81, 102.93, 102.54, 72.24, 67.07, 66.81, 62.91, 62.46.

	**9b:** Colourless liquid, Conv: 98%, selectivity: 50%, ^{1}H NMR (500 MHz, $CDCl_3$–d) δ (TMS,ppm) = 7.32 –6.88 (m,8H), 6.32, 6.16 & 5.88, 5.78 (2s & 2s, 2H), 4.33–3.03 (m, 10H), 3.87–3.57 (m, 4H), 1.44–1.41 (m, 6H). ^{13}C NMR (126 MHz) δ = 130.80, 130.51, 130.29, 127.72, 127.12, 126.91, 120.70, 120.49, 112.24, 112.11, 112.02, 100.51, 99.77, 98.09, 96.71, 77.41, 77.16, 76.91, 72.53, 72.30, 66.91, 66.83, 64.25, 64.14, 63.34, 62.83, 14.96, 1.14.
	**10b:** Brownish liquid, Conv: 60%, selectivity: 82%, ^{1}H NMR (500 MHz, $CDCl_3$-d) δ (TMS, ppm) = 7.42–7.23 (m, 8H), 5.85, 5.70 & 5.44, 5.29 (2s & 2s, 2H), 4.29–3.56 (m, 10H). ^{13}C NMR (126 MHz) δ = 140.08, 139.21, 134.49, 133.57, 129.88, 129.85, 129.71, 129.45, 126.83, 126.64, 124.93, 124.70, 103.46, 103.01, 72.31, 66.98, 66.76, 63.97, 63.18, 62.66.
	**13b:** Brownish liquid, Conv: 78%, selectivity: 52%, ^{1}H NMR (500 MHz, $CDCl_3$-d) δ (TMS, ppm) = 8.12–8.10 (m, 3H), 7.77–7.64 (m, 5H), 7.40–7.39 (m, 6H) 6.51, 6.37 & 6.02, 5.78 (2s & 2s, 2H), 4.33–3.59 (m, 10H). ^{13}C NMR (126 MHz) δ = 133.93, 132.97, 129.85, 128.78, 128.72, 126.46, 125.91, 125.79, 125.18, 125.09, 124.06, 123.97, 123.77, 123.67, 102.60, 100.31, 72.53, 72.20, 66.82, 64.16, 62.83.
	**14b:** Colourless liquid, Conv: 63%, selectivity: 66%, ^{1}H NMR (500 MHz, $CDCl_3$-d) δ (TMS, ppm) = 7.37–7.18 (m, 13H), 6.94–6.86 (m, 5H), 6.28, 6.16 & 5.85, 5.75 (2s & 2s, 2H), 5.08–5.04 (m, 4H), 4.30–3.61 (m, 10H). ^{13}C NMR (126 MHz) δ = 137.08, 130.78, 130.56, 129.31, 128.69, 128.05, 127.62, 127.36, 127.17, 125.39, 121.16, 120.97, 112.69, 112.59, 100.27, 99.84, 98.07, 72.57, 72.26, 70.44, 66.86, 64.23, 63.39, 62.79, 61.50.
	**15b:** Colourless liquid, Conv: 79%, selectivity: 95%, ^{1}H NMR (500 MHz, $CDCl_3$-d) δ (TMS, ppm)=8.72–8.60 (m, 4H), 7.85–7.81 (m, 2H),), 7.35–7.29 (m, 2H), 5.98, 5.86 & 5.61 (2s & 1s, 2H), 4.39–3.71 (m, 10H). ^{13}C NMR (126 MHz) δ= 152.69, 151.09, 150.27, 150.08, 148.12, 147.96, 134.89, 134.70, 133.96, 133.32, 123.63, 123.45, 102.42, 101.96, 72.35, 67.18, 67.00, 62.97, 62.49.
	**16b:** Brownish liquid, Conv: , selectivity: 52%, ^{1}H NMR (500 MHz, $CDCl_3$d) δ (TMS,ppm) = 8.40–7.98 (m,18H), 6.86, 6.73 & 6.36, 6.14 (2s & 2s, 2H), 4.51–3.70 (m, 10H). ^{13}C NMR (126 MHz) δ = 132.02, 131.26, 130.67, 128.20, 128.12, 128.06, 127.99, 127.47, 126.10, 125.65, 125.54, 124.95, 124.85, 124.80, 124.75, 124.70, 124.60, 123.56, 123.37, 123.11, 122.93, 102.63, 102.56, 100.56, 72.71, 72.38, 67.05, 64.22, 63.34, 62.94, 61.45.

S7. Selected ^{1}H NMR spectra of glycerol products obtained through acetalization.



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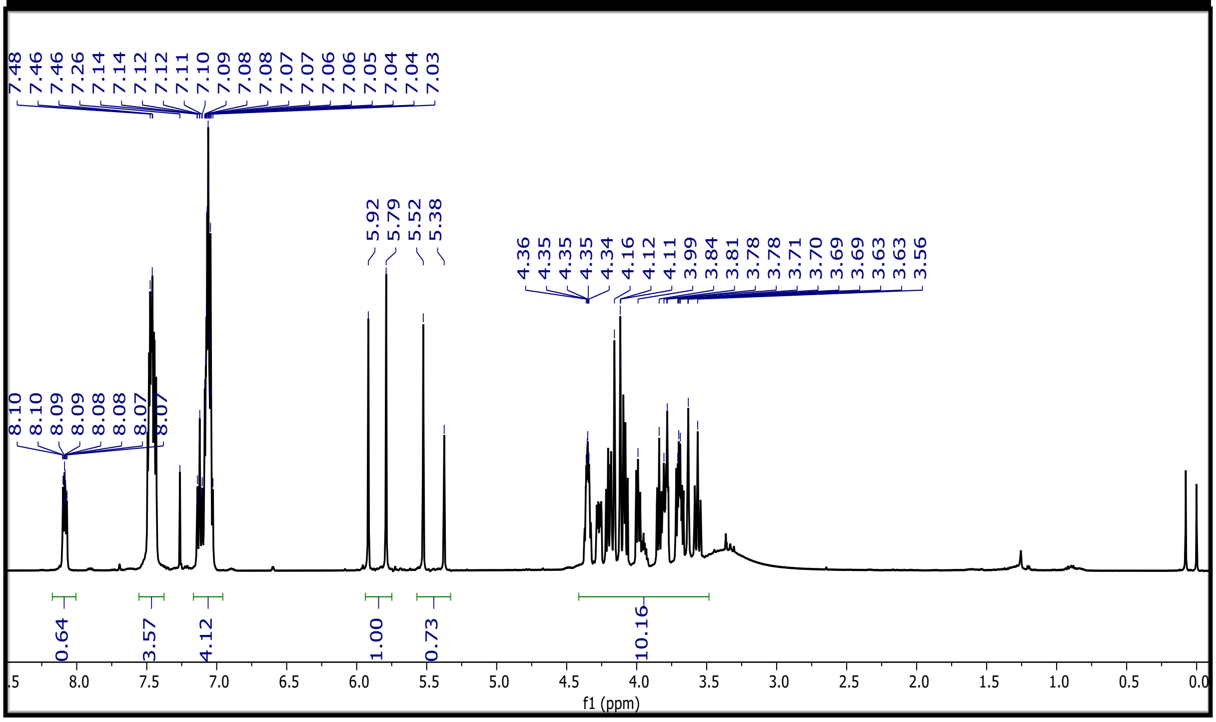
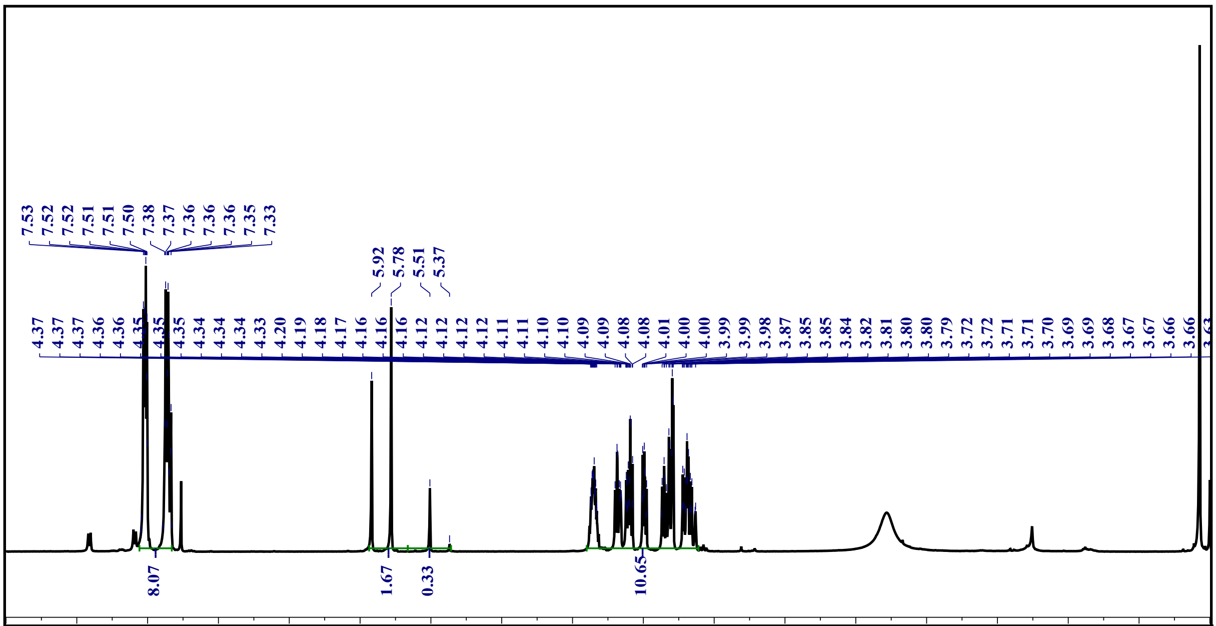


(ii). ^{1}H-NMR spectra of **2b**



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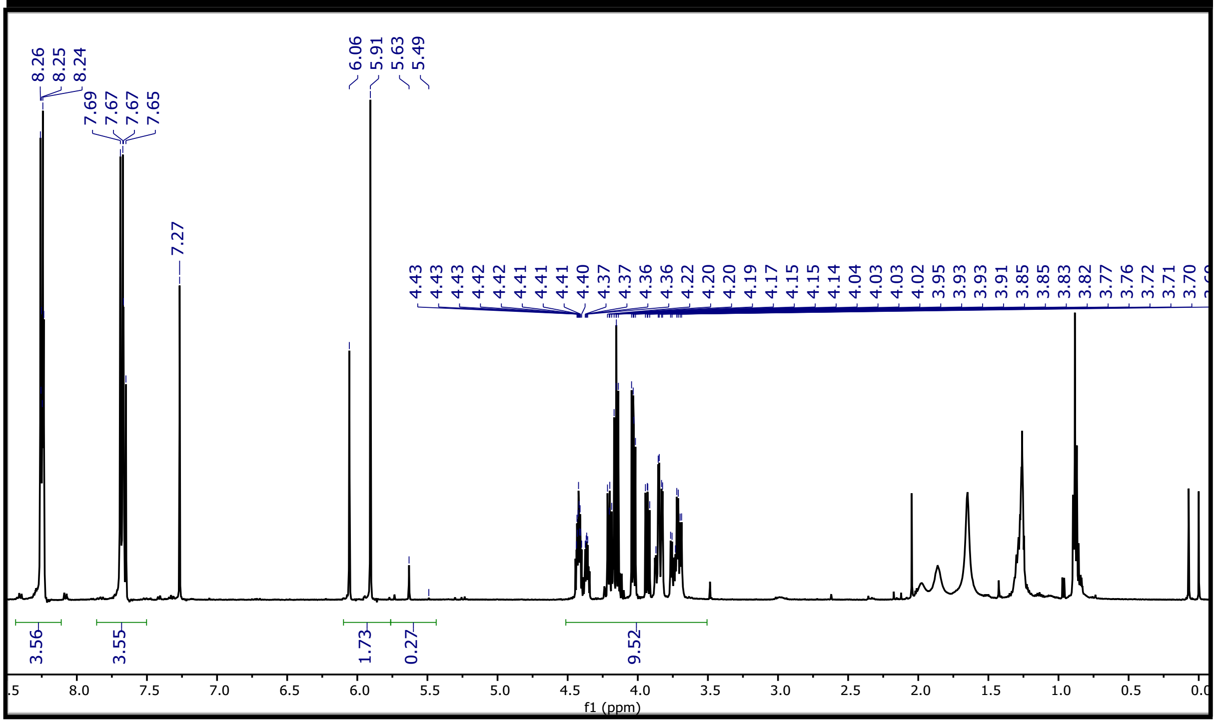
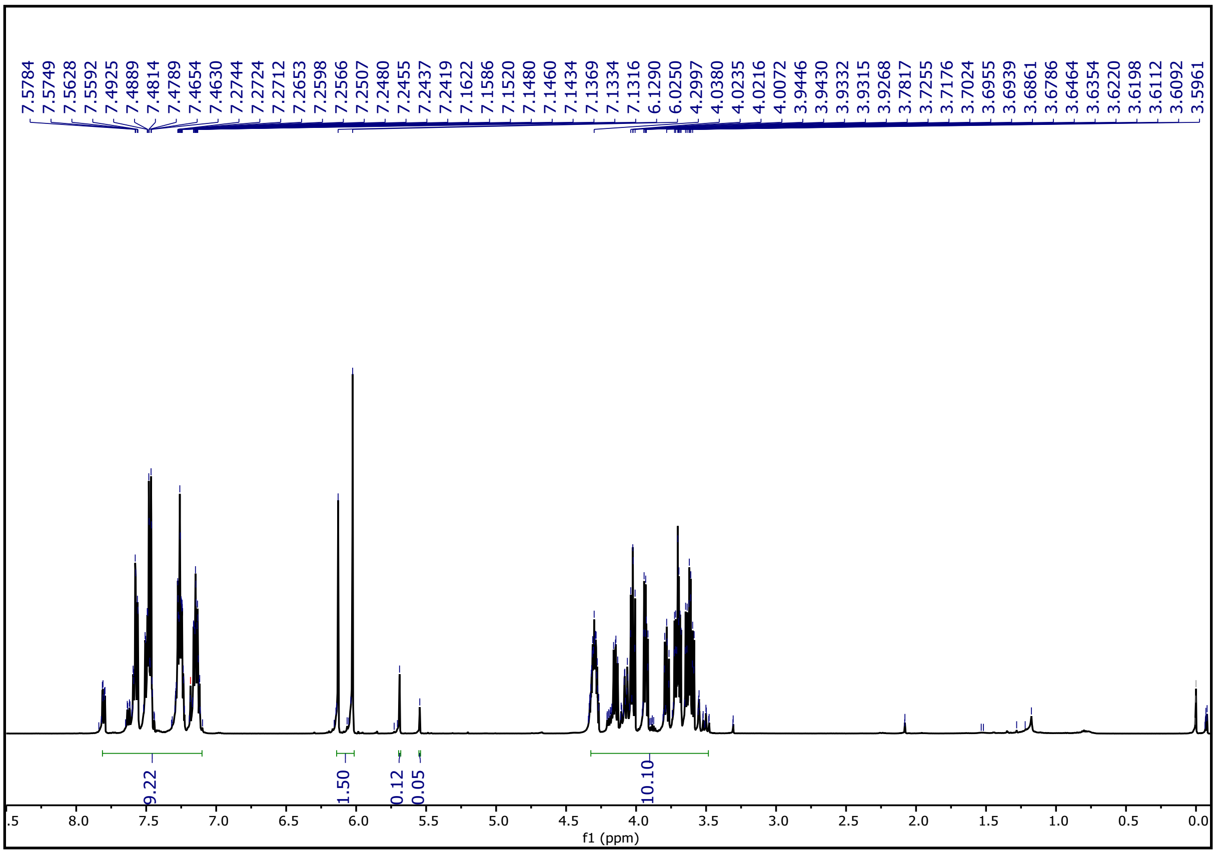


(iv).[1]H-NMR spectra of **4b**



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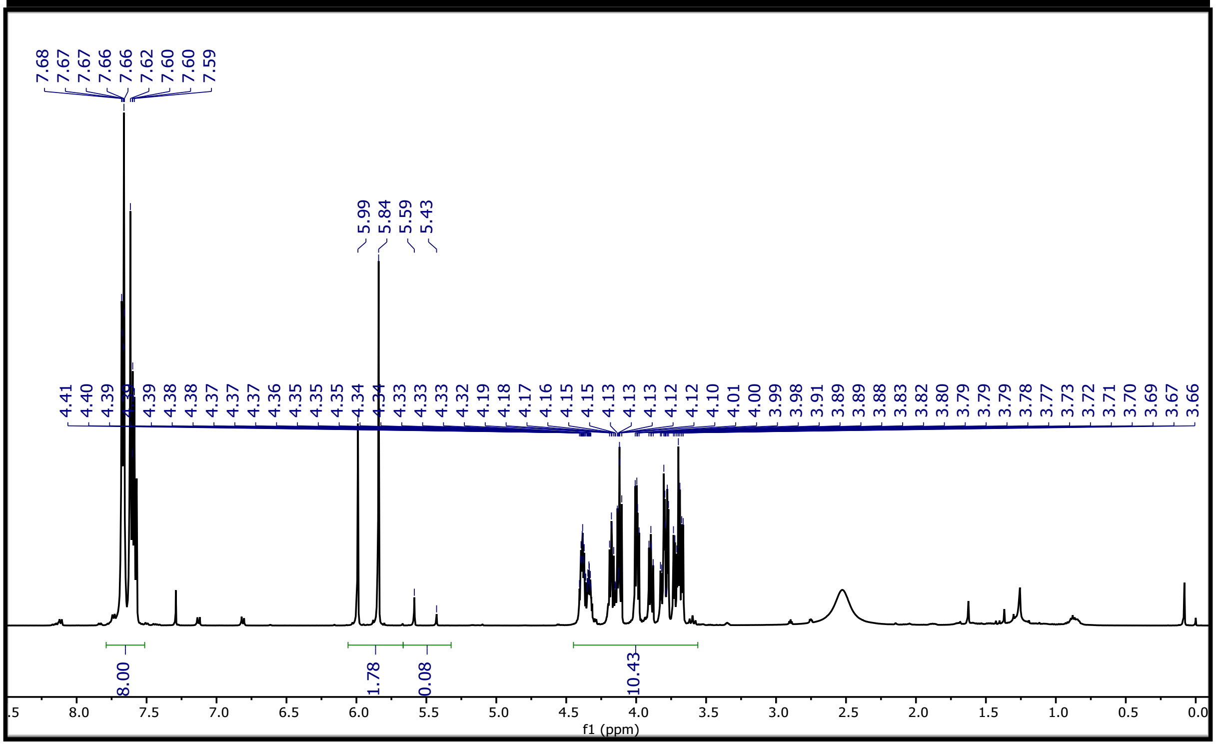
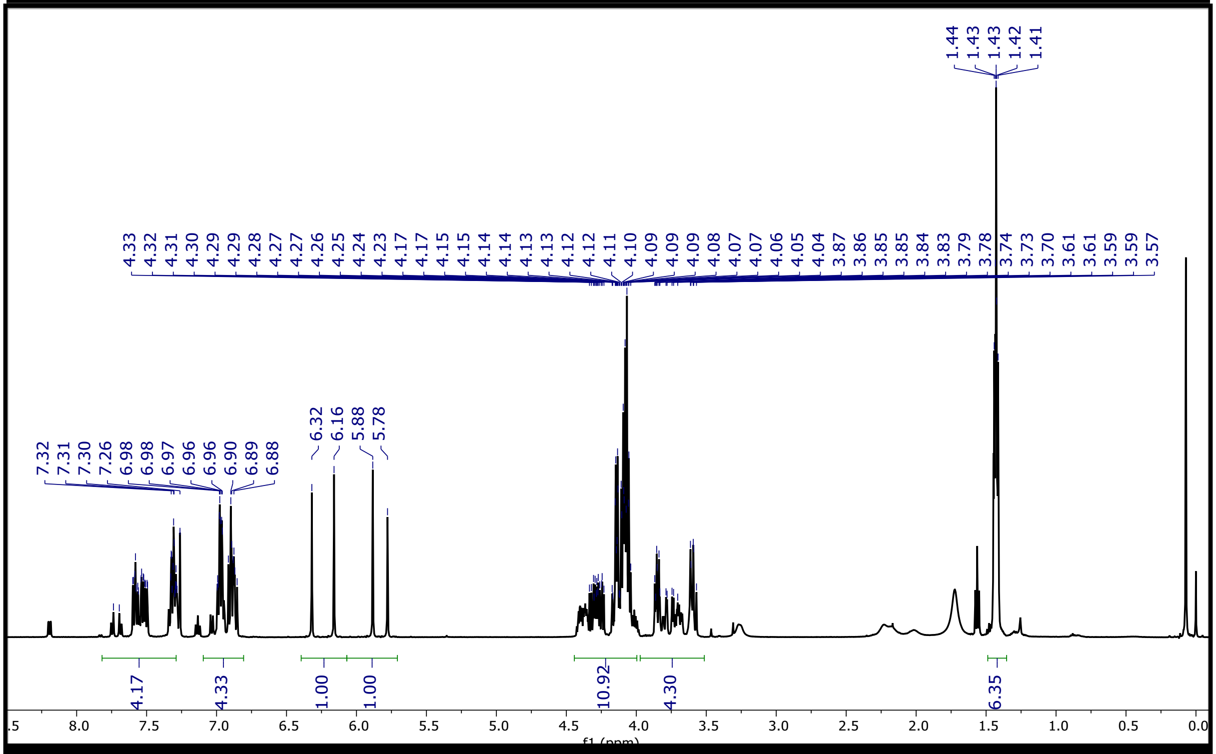


(vi).[1]H-NMR spectra of **6b**

[redacted]



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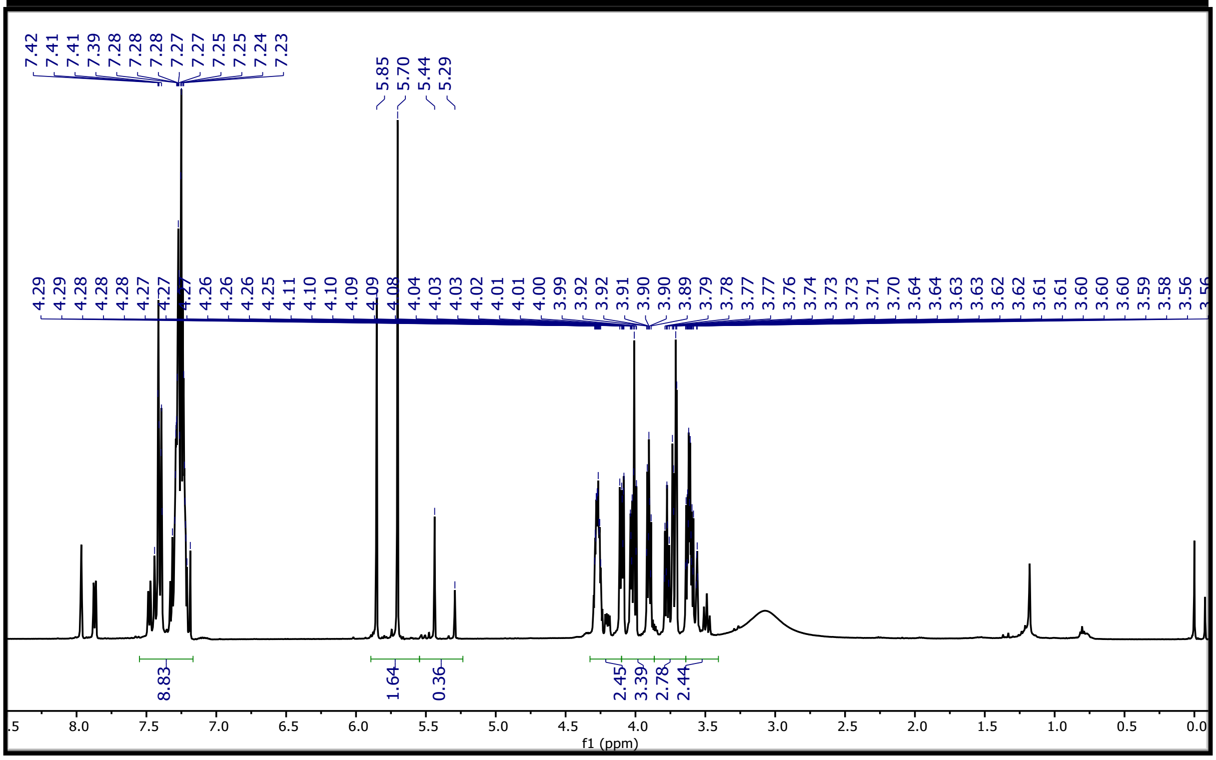

(viii).[1]H-NMR spectra of **10b**

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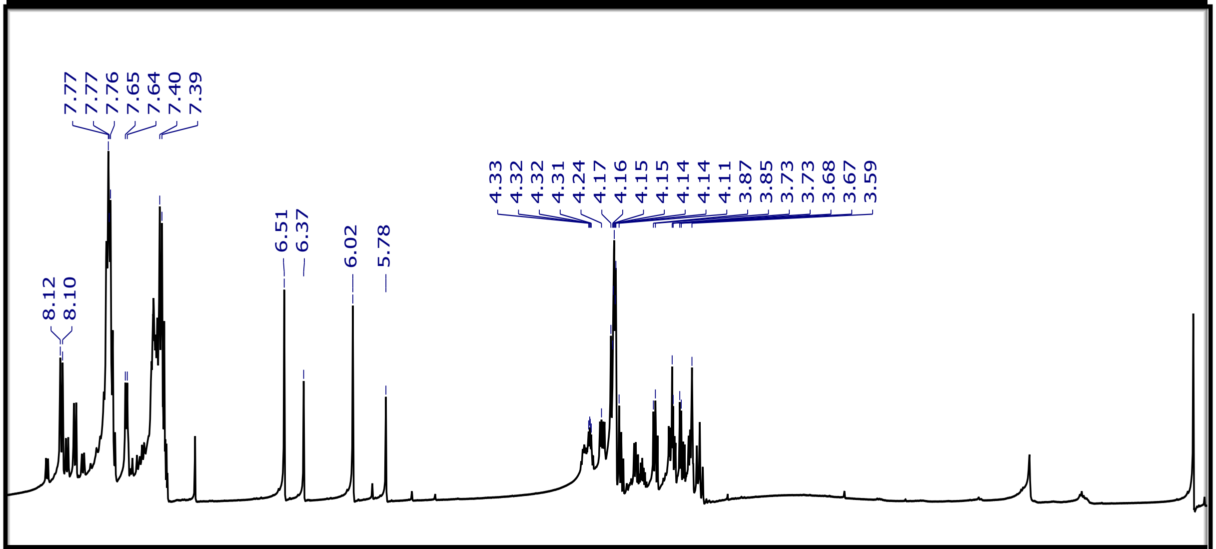

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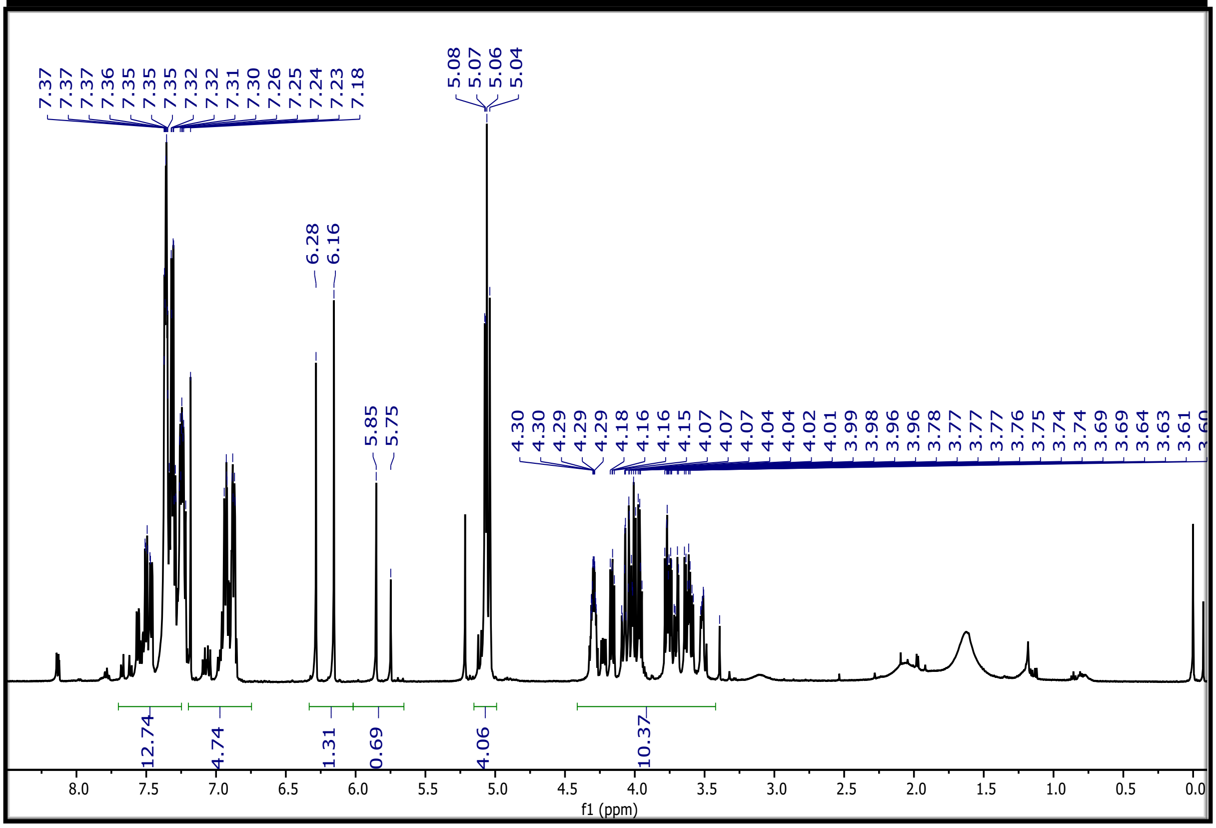
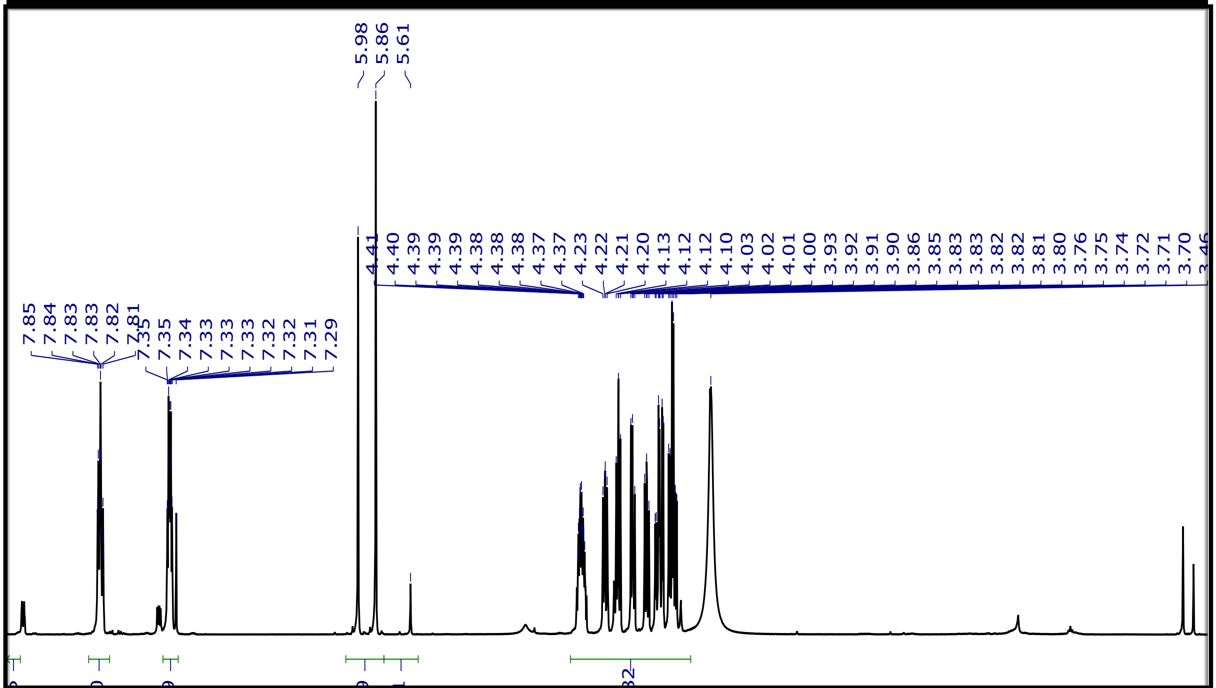


(x).¹H-NMR spectra of **14b**

[redacted]



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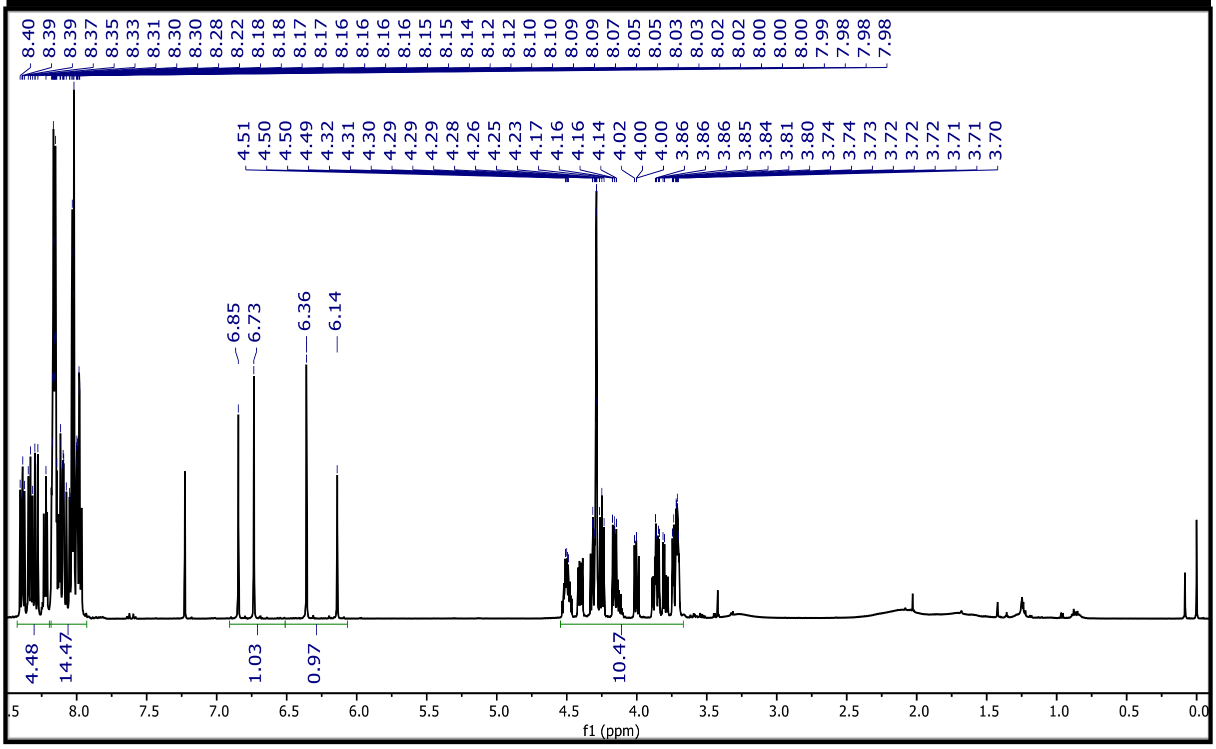

(xii).[1]H-NMR spectra of **16b**

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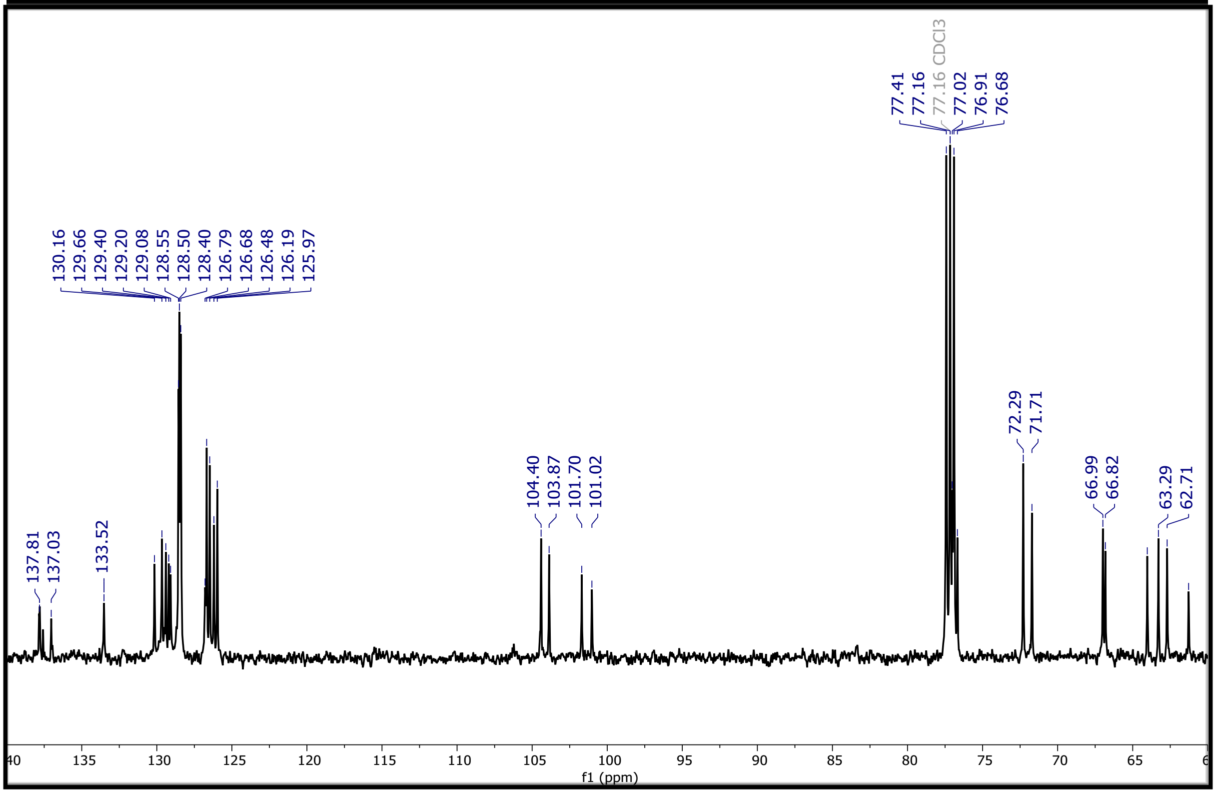

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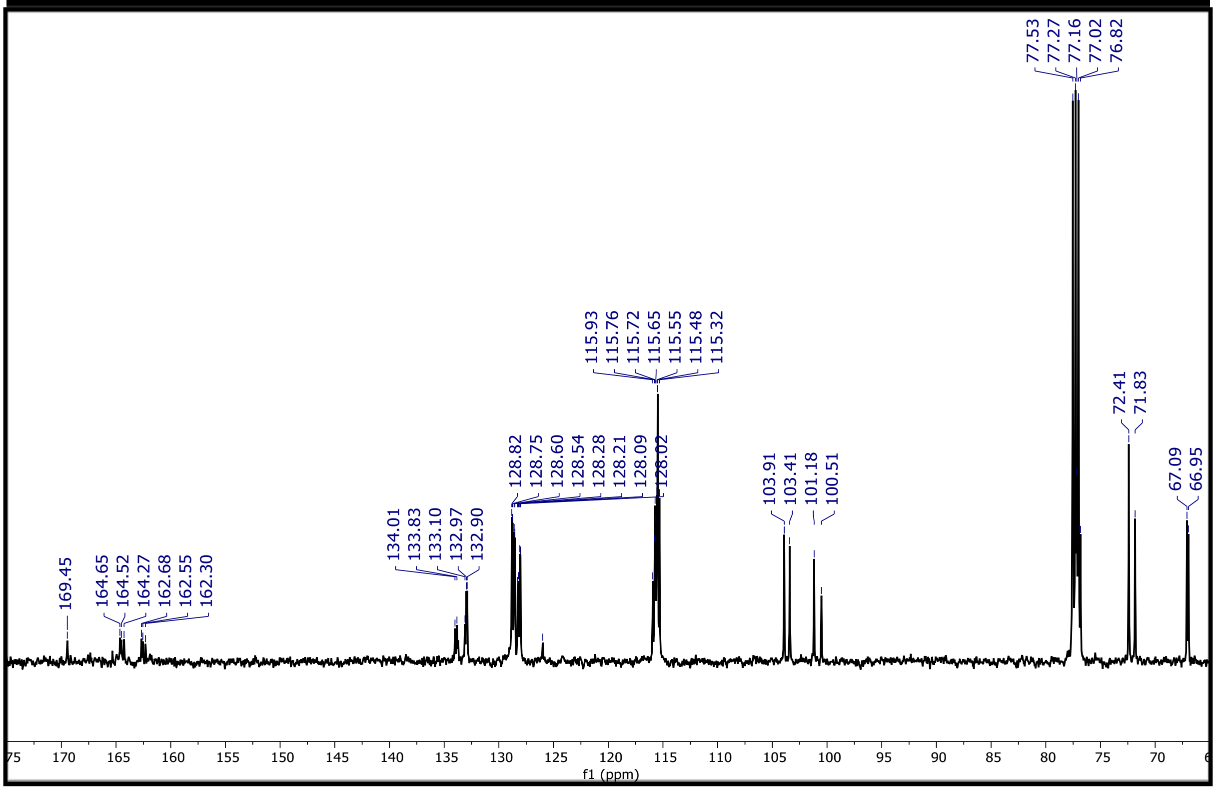
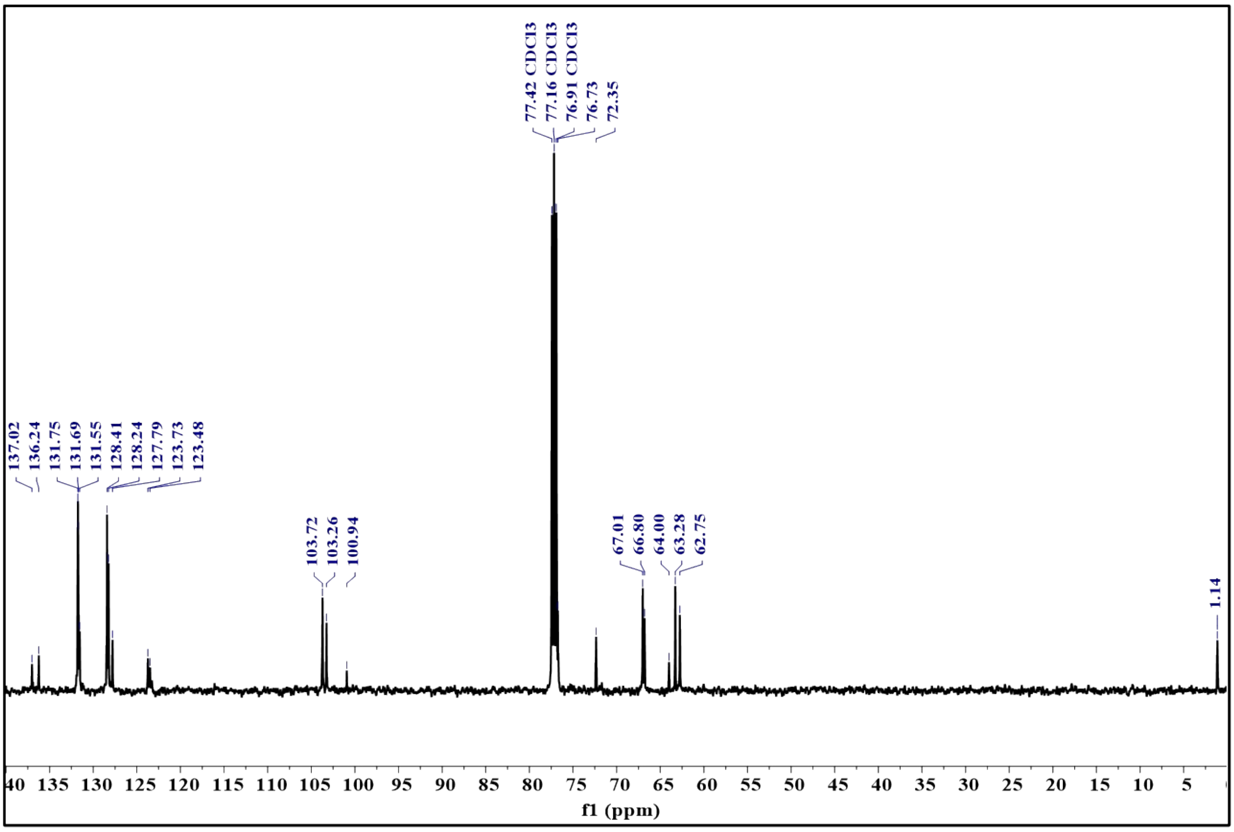
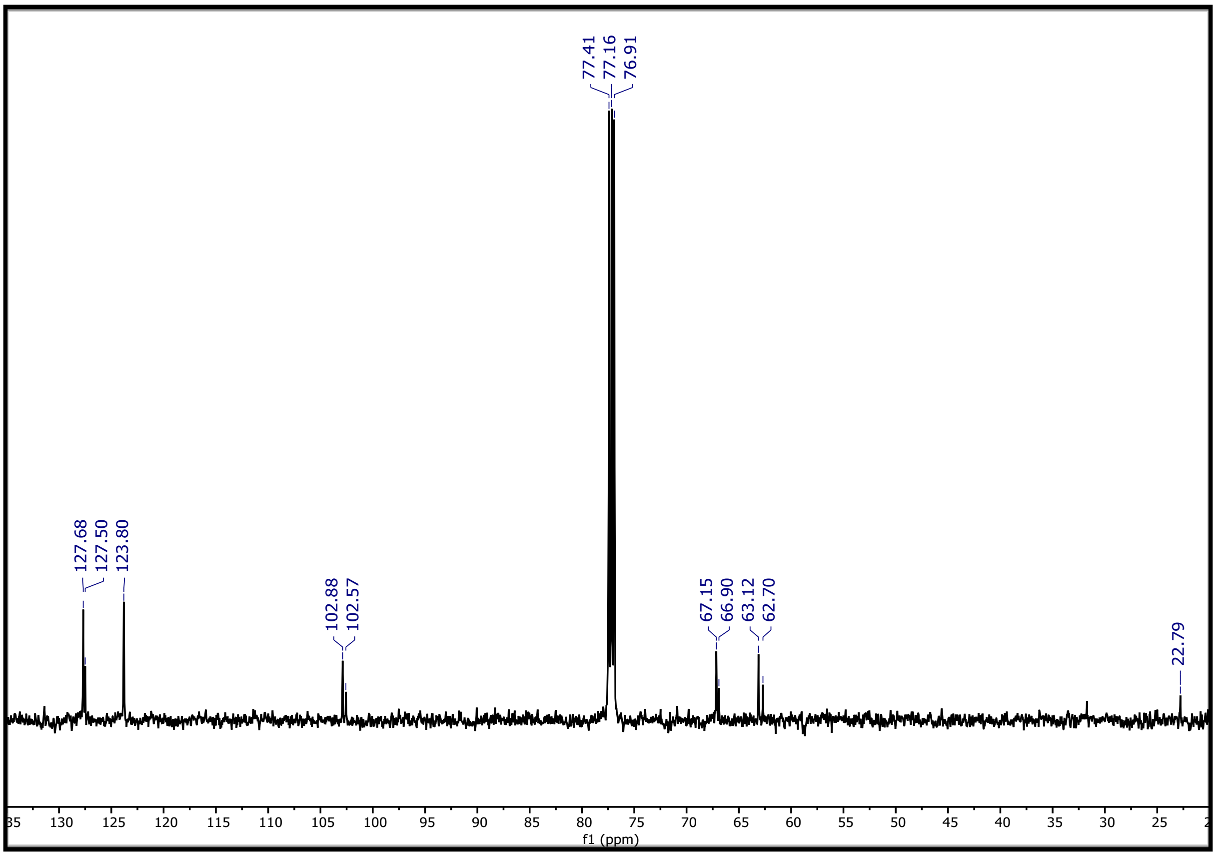


(ii). ^{13}C NMR spectra of **2b**



(iii). ^{13}C NMR spectra of **3b**



(iv). ^{13}C NMR spectra of **4b**

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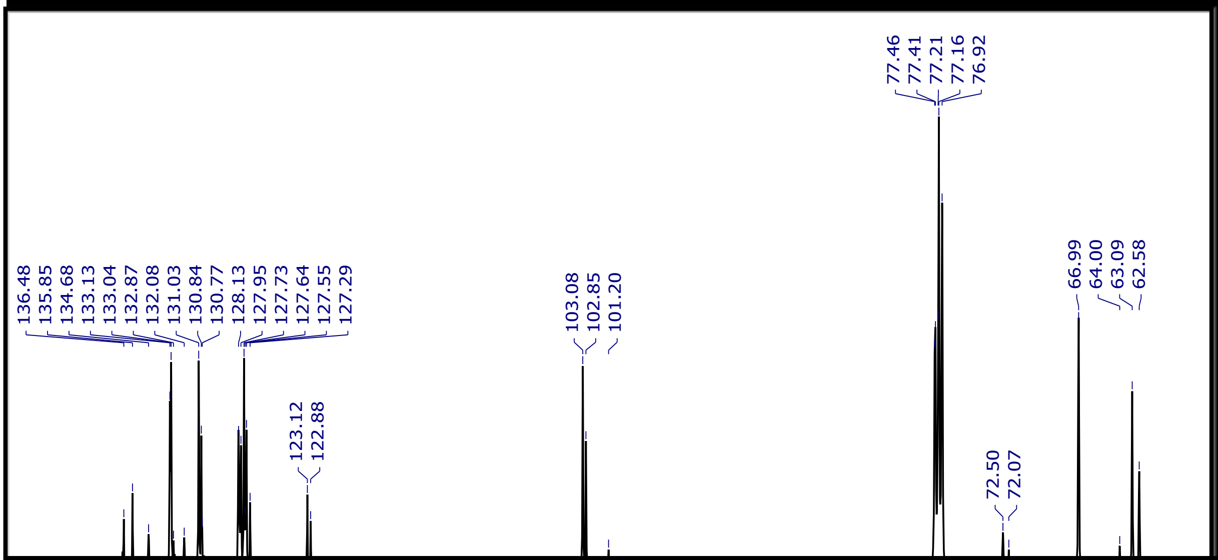

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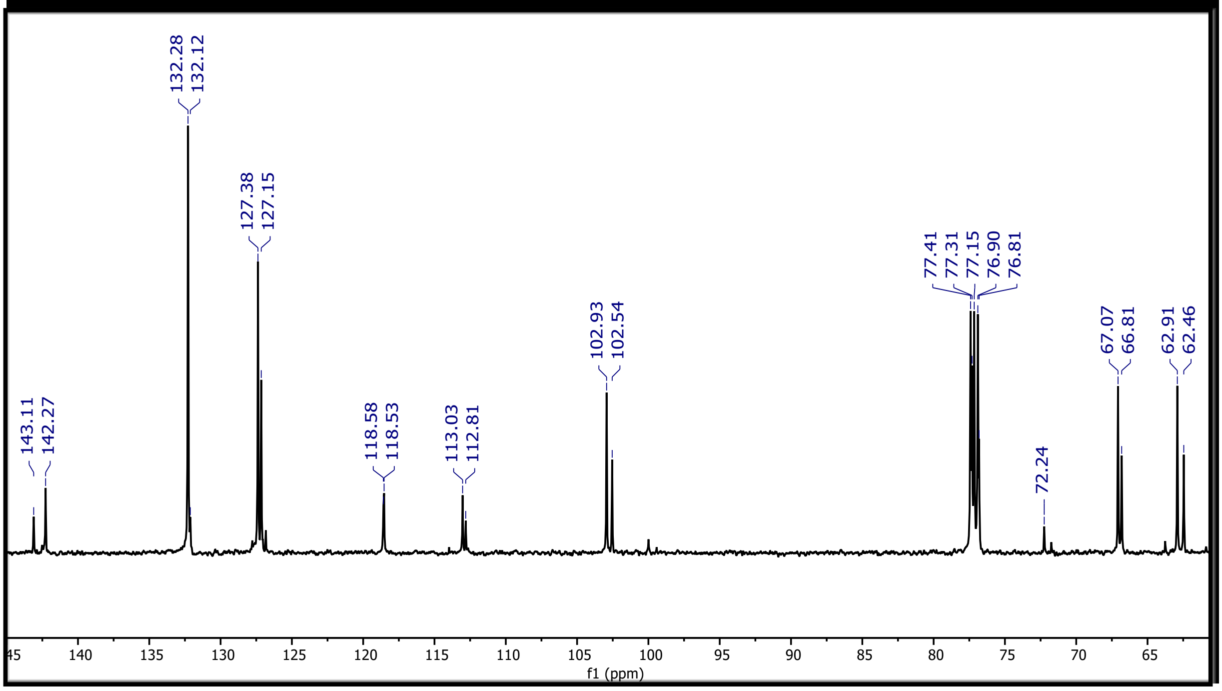
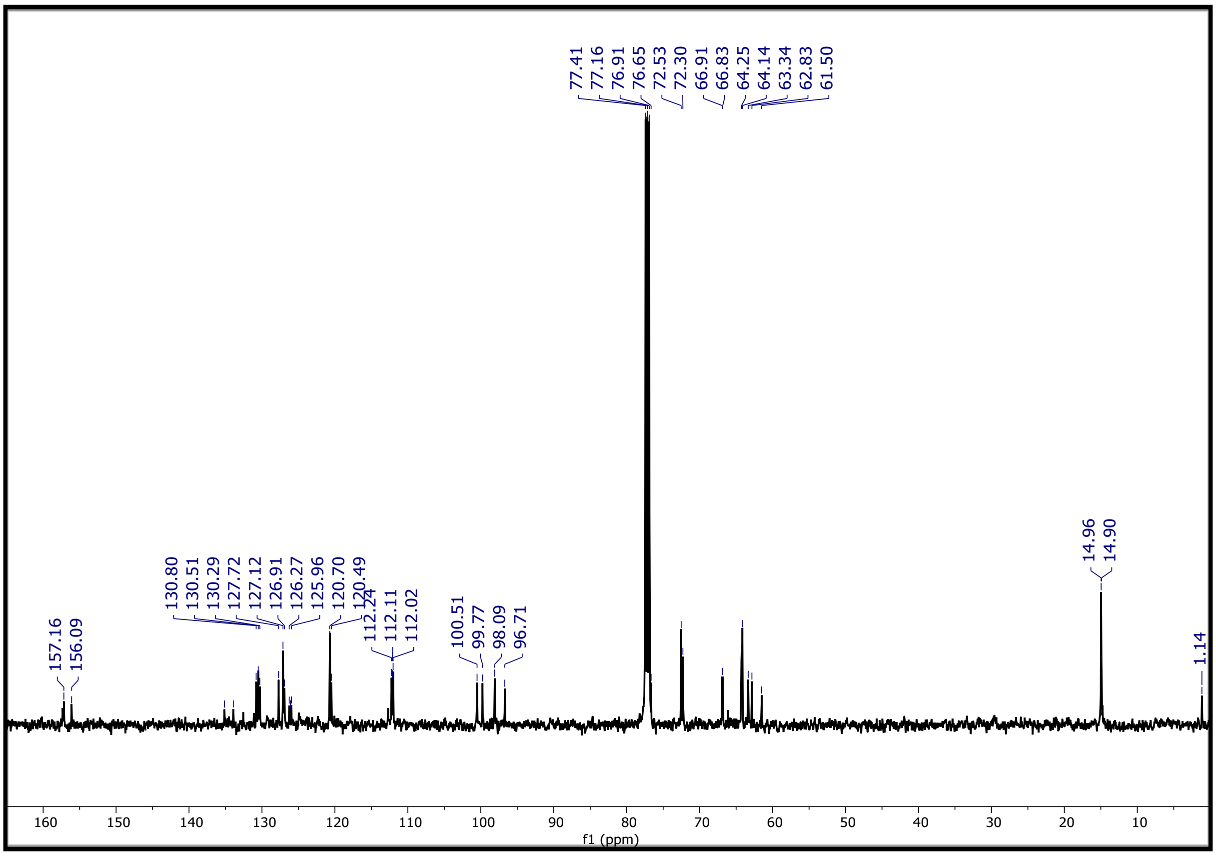


(vi). ^{13}C NMR spectra of **6b**



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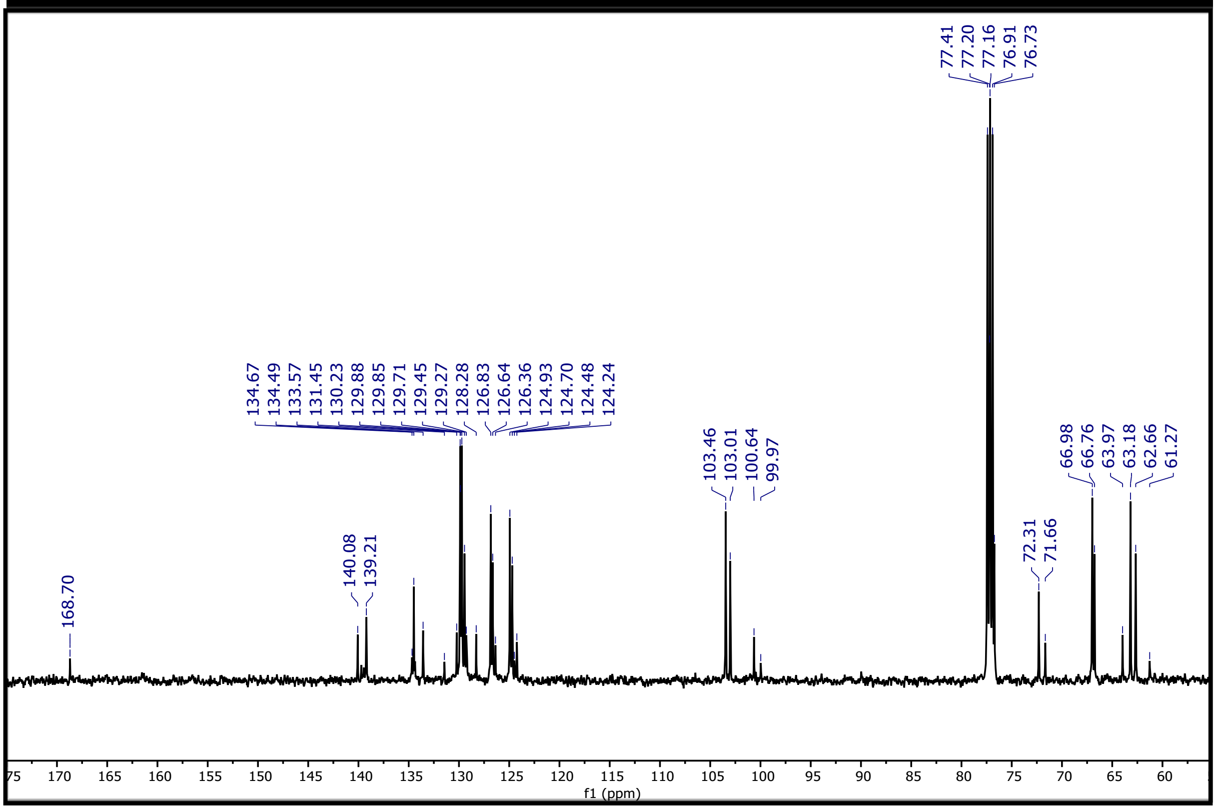
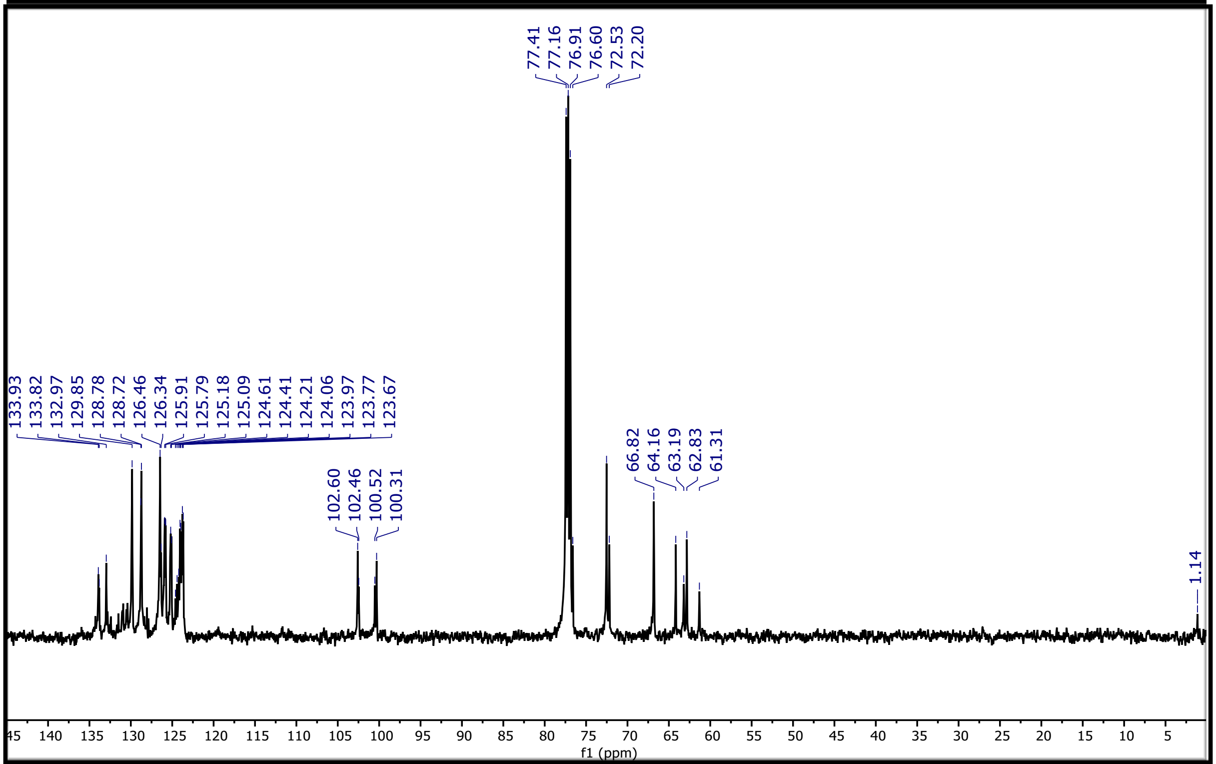


(viii). ^{13}C NMR spectra of **10b**

[redacted]



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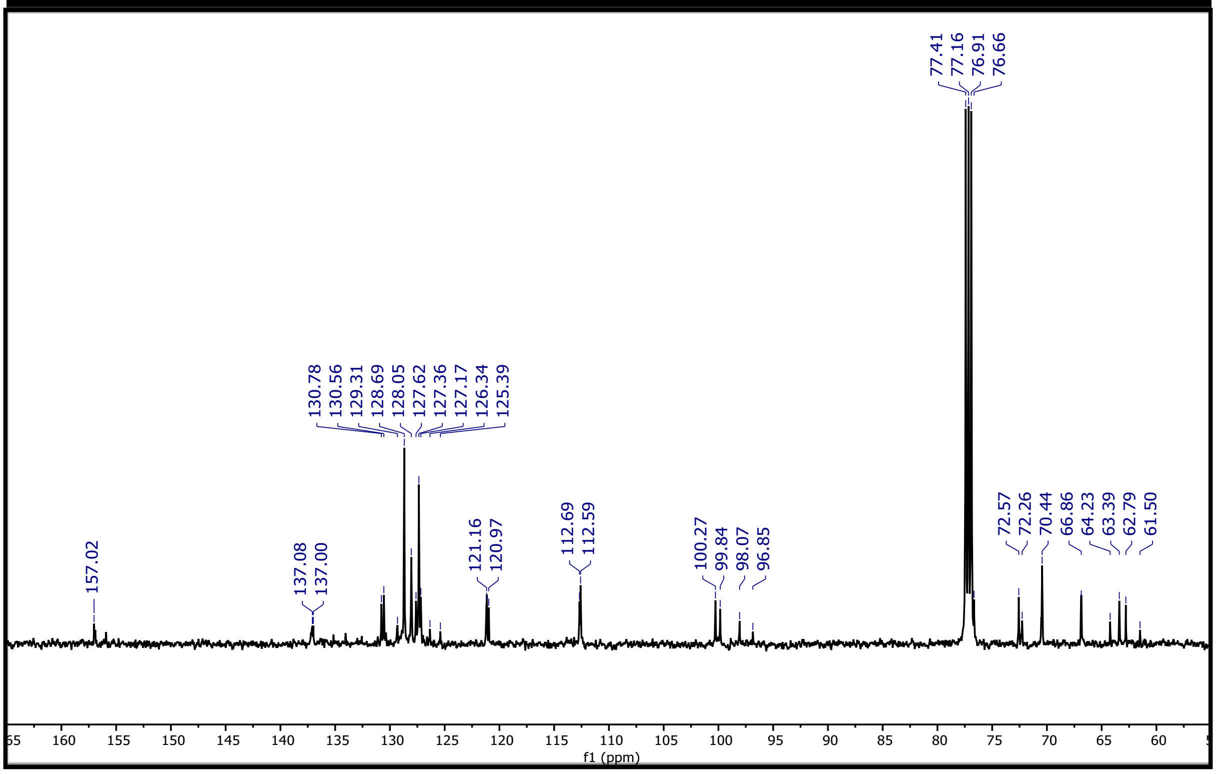
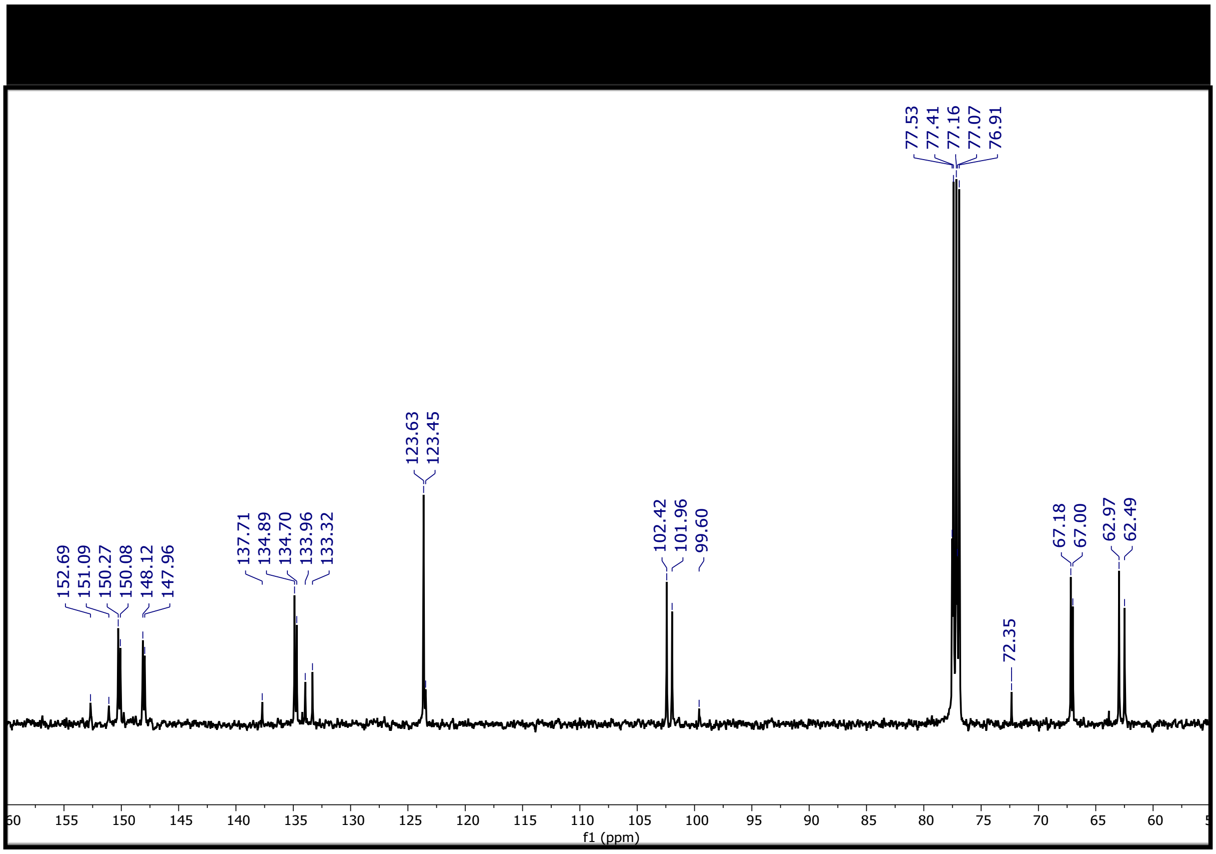
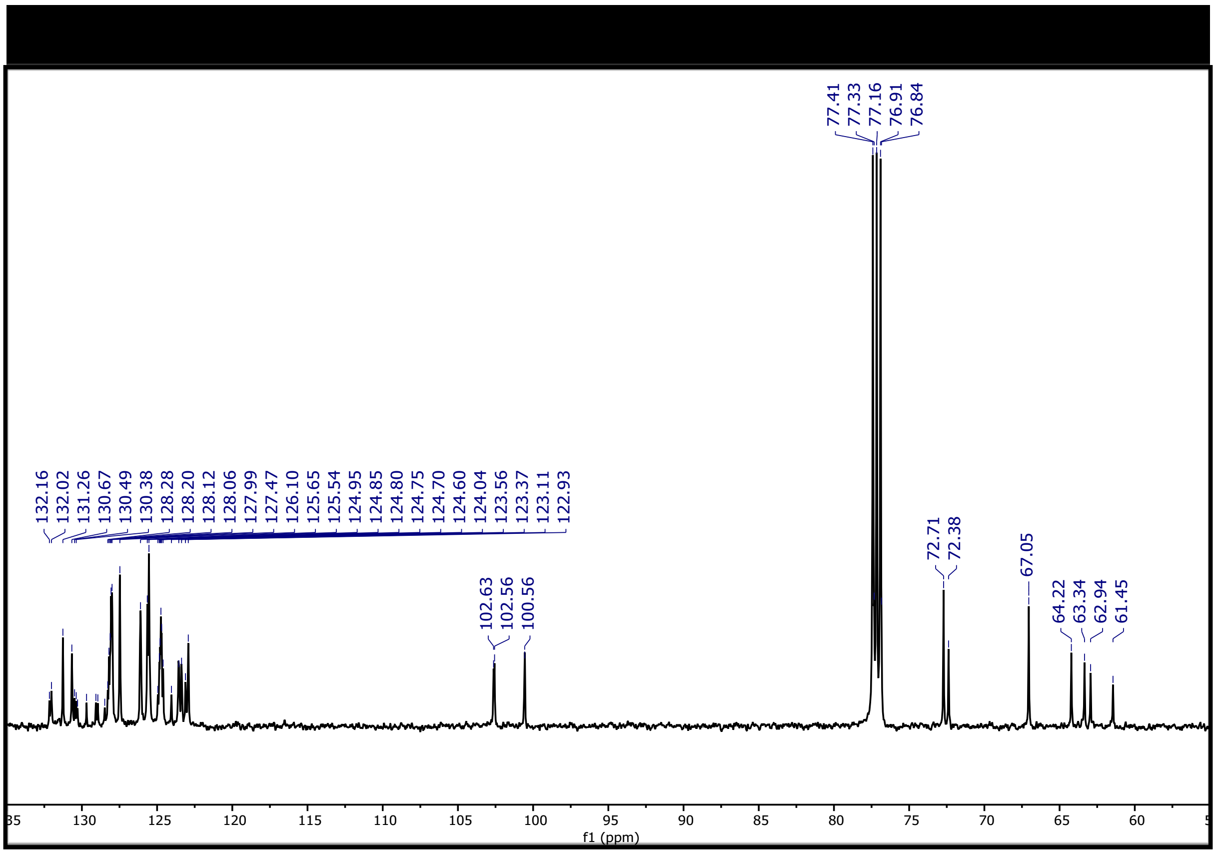


(**x**). ^{13}C NMR spectra of **14b**



(xi). ^{13}C NMR spectra of **15b**



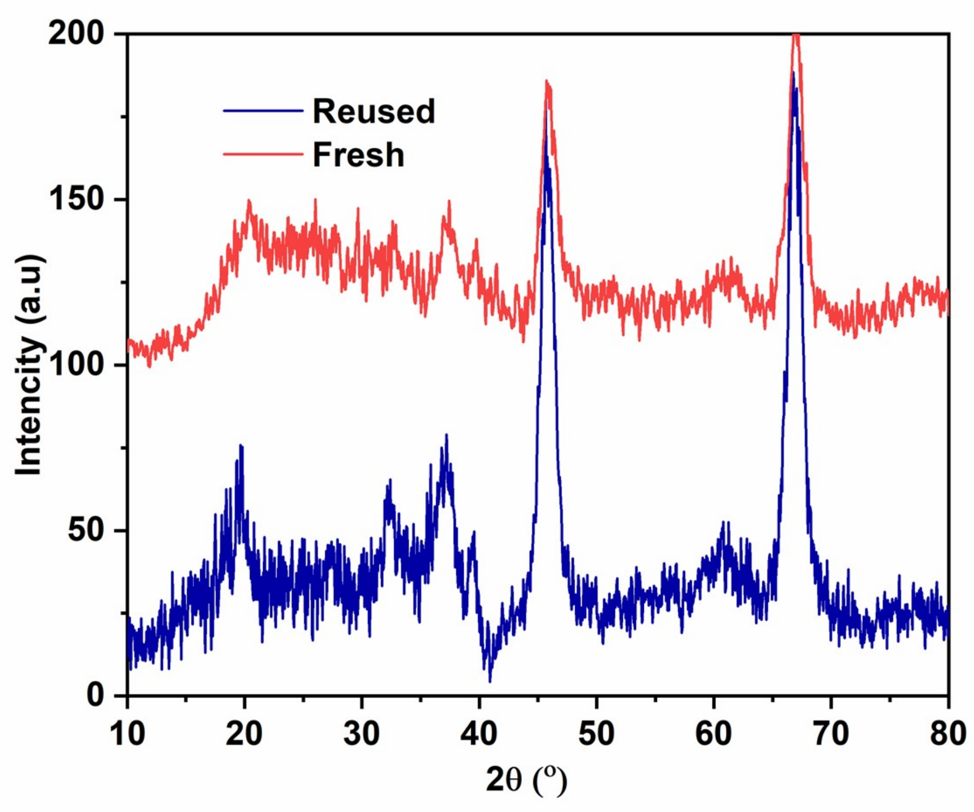
(xii). ^{13}C NMR spectra of **16b**

S9. A comparison of catalytic activities using different protocols for the acetalization of glycerol using benzaldehyde

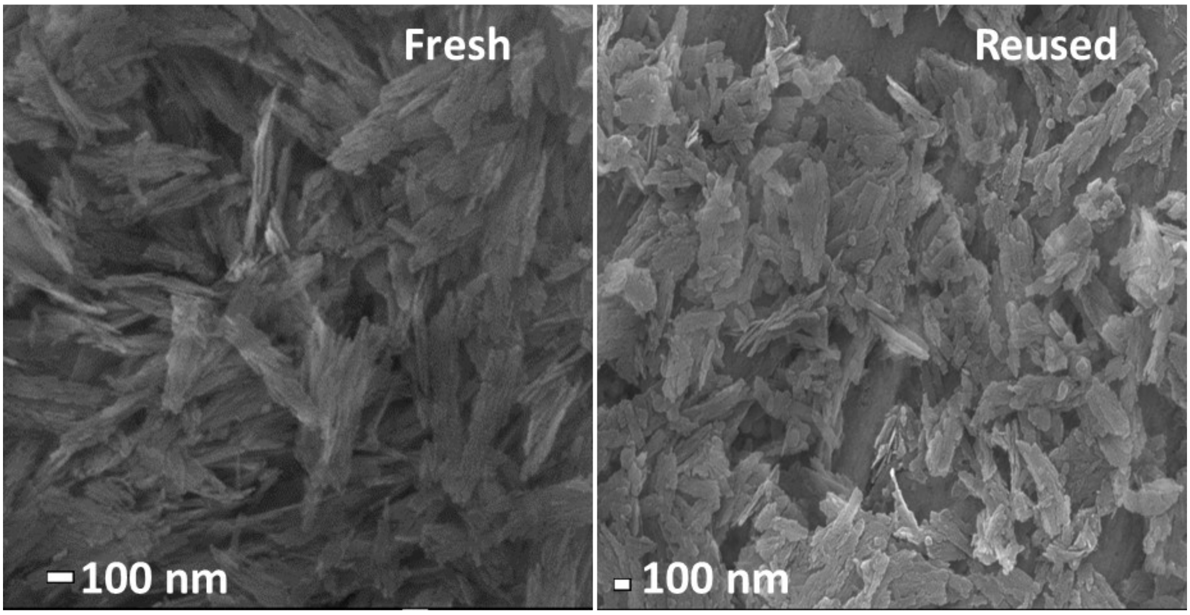
S. No.	Reaction conditions					Conversion (%)	Maximum Selectivity Achieved[a] (Dioxolane/ dioxane)	Ref.
	Catalyst	Substrate amount	Temp. (^oC)	Solvent	Time (h)			
1	BBnU	2:1	60	Solvent free	1	88	63/37	[1]
2	SiW_{11}/MCM-41	1:1.2	30	Solvent free	1	85	82:18	[2]
3	M_OO_x-TiO_2-ZrO_2	1:1	100	Toluene	1/2	74	50:50	[3]
4	$Cu_3(BTC)_2$	1:1	RT	ACN	24	25	86:14	[4]
5	Fe/Al-SBA-15	1:1	100	Solvent free	8	72	84:16	[5]
6	SO4 2-/CeO_2 -ZrO_2 catalyst	1:3	100	Toluene	8	91	87:13	[6]
7	zeolite USY-2	2:1	147	Toluene	1	93	58:42	[7]
8	MoO_3/SiO_2	1.1:1	100	Toluene	8	72	40:60	[8]
9	Al-SBA-15	1:1	100	Solvent free	8	82	83:17	[9]
10	$FeCl_3.6H_2O$	0.3:2	60	THF	3	51	39:61	[10]
11	MZrP-1	1:1	100	Solvent free	8	98	63:37	[11]
12	AnPOP-SO3H c	1:4	40	Solvent free	1.5	97	63:37	[12]
13	WO_3@Boehmite	1:1.5	100	Toluene	20	97	96	This work

[a] The table compares the activity of different catalysts reported in the literature for the acetalization of glycerol with benzaldehyde derivative. The representative example of benzaldehyde derivative is showed based on the report where the selectivity of dioxolane is maximum.

S10. XRD of fresh and reused catalyst



S11. SEM images of fresh and reusable WO_3@boehmite catalyst



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