Supporting information

Solid State Packing and Photoreactivity of Alkali Metal Salts of *trans, trans*-Muconate

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Experimental Section

Trans,trans-H_2muco, LiOH, NaOH, KOH etc were purchased from various commercial sources. The alkali metal hydroxides were dissolved in water and their aqueous solutions were added drop wise to *tr,tr*-H_2muco in water until it dissolved to produce colorless solution. The diffraction quality single crystals were obtained by slowly evaporating the aqueous solutions.

^{1}H NMR spectra were recorded with a Bruker ACF 300 FT-NMR spectrometer by using D_2O as the solvent for all compounds. Elemental analyses were carried out at the Micro-analytical Laboratory, Department of Chemistry, National University of Singapore. Thermogravimetric analyses were recorded with a TA SDT 2960 TGA Thermal Analyzer. Samples were heated from room temperature to 600 °C with a heating rate of 5 °C min^{-1} under nitrogen gas flow. Powder X-ray diffraction (PXRD) patterns were obtained with a D5005 Bruker X-ray diffractometer and Cu-Kα radiation.

Single crystal X-ray diffraction data were collected for structure determination with a Bruker APEX diffractometer equipped with a CCD detector and graphite monochromated Mo-Kα (λ=0.71073 Å) radiation. Empirical absorption corrections were applied to the data by using the SADABS program[1] and the ShelxTL crystallographic package[2] was used for all calculations.

UV irradiation experiments were conducted with a Luzchem photoreactor at a wavelength of 354 nm and an intensity of 1.75 mW cm^{-2}. About 20 mg of each compound was packed between two Pyrex glass slides and the UV irradiation experiments were completed by turning the packed glass slides for each sample half-way during their irradiation to ensure uniform irradiation. ^{1}H NMR spectra were acquired to determine the percentages of various compounds in mixture by calculation on the integration values.

References

1. Sheldrick, G. M. SADABS Software for empirical absorption corrections, Version 2.05, University of Göttingen, Göttingen, **1996**.
2. (a) Sheldrick, G. M. *ActaCrystallogr. Sect. A* **2008**, *64*, 112-122; (b) Müller, P.; Herbst-Irmer, R.; Spek, A. L.; Schneider, T. R.; Sawaya, M. R. *Crystal Structure Refinement: A Crystallographers Guide to SHELXL*; Ed.: Müller, P.; Oxford University Press, Oxford: **2006**.

Table 1: Crystallographic data for **1** and **3**. CCDC numbers 1412301-1412302

Compounds	**1**	**3**
Formula	$C_6H_4O_4Li_2$	$C_6H_4O_4K_2$
M	153.97	218.29
T (K)	100(2)	100(2)
λ (Å)	0.71073	0.71073
Crystal syst.	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	7.763(1)	10.765(2)
b (Å)	5.0161(6)	3.9739(7)
c (Å)	8.7526(11)	11.261(2)
β (°)	115.232(3)	117.978(2)
Volume (Å^3)	308.31(7)	425.43(13)
Z	2	2
D_{calcd} (g cm^{-3})	1.659	1.704
μ (mm^{-1})	0.134	1.082
Reflns col.	2037	2695
Ind. Reflns.	708	962
Goof on F^2	1.068	1.261
Final R[$I>2\sigma$][a]	0.0392	0.0372
$R1$		
$wR2$[b]	0.1045	0.1183

[a] $R1 = \Sigma||F_o| - |F_c||/ \Sigma|F_o|$, [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Elemental Analysis data for 1 – 3.

Analysis found for **1** (%), C, 46.54, H, 3.15; $C_6H_4O_4Li_2$ requires C, 46.80, H, 2.62.

Analysis found for **2** (%), C, 38.86, H, 2.31; $C_6H_4O_4Na_2$ requires C, 38.73, H, 2.17.

Analysis found for **3** (%), C, 32.84, H, 2.06; $C_6H_4O_4K_2$ requires C, 33.01, H, 1.85.

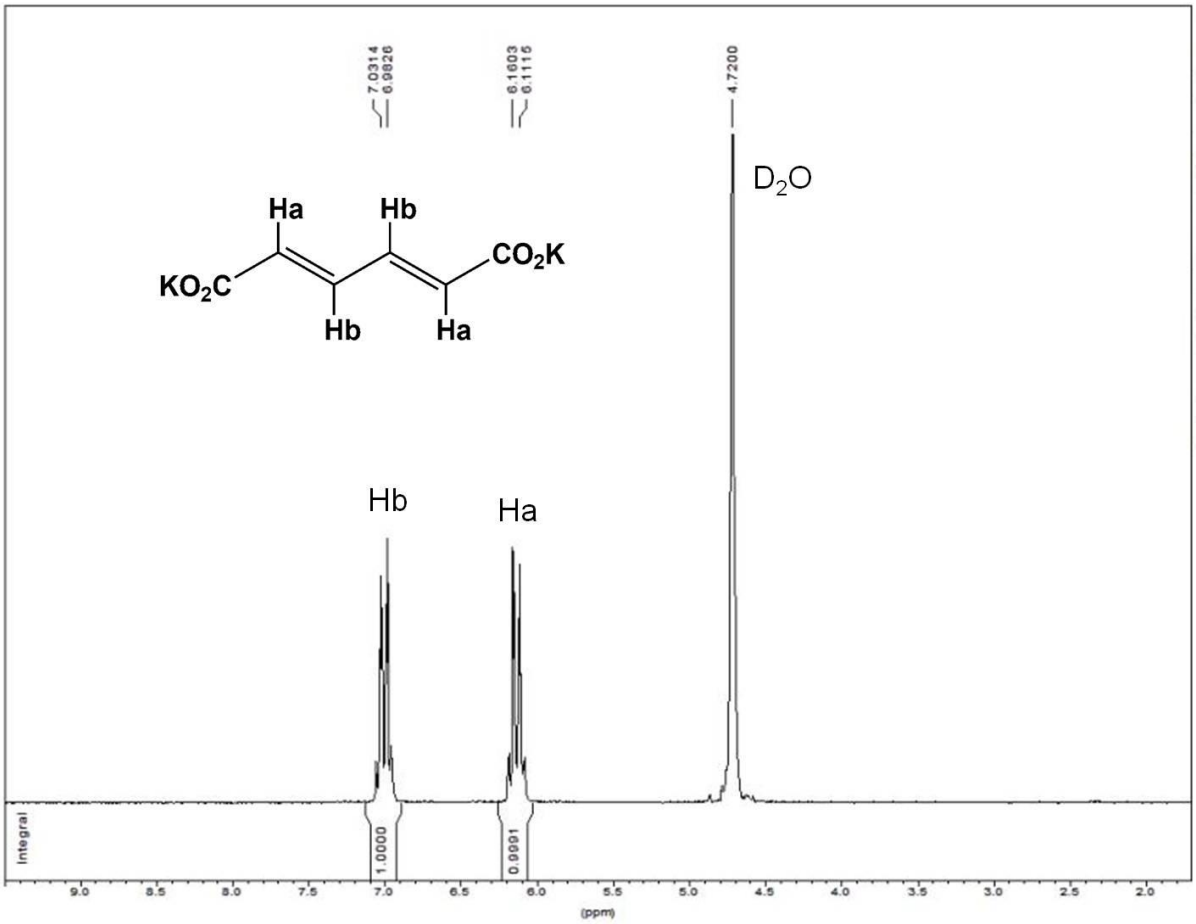

Figure S1: The ^{1}H NMR spectrum (300 MHz, D_2O) of K_2*muco*

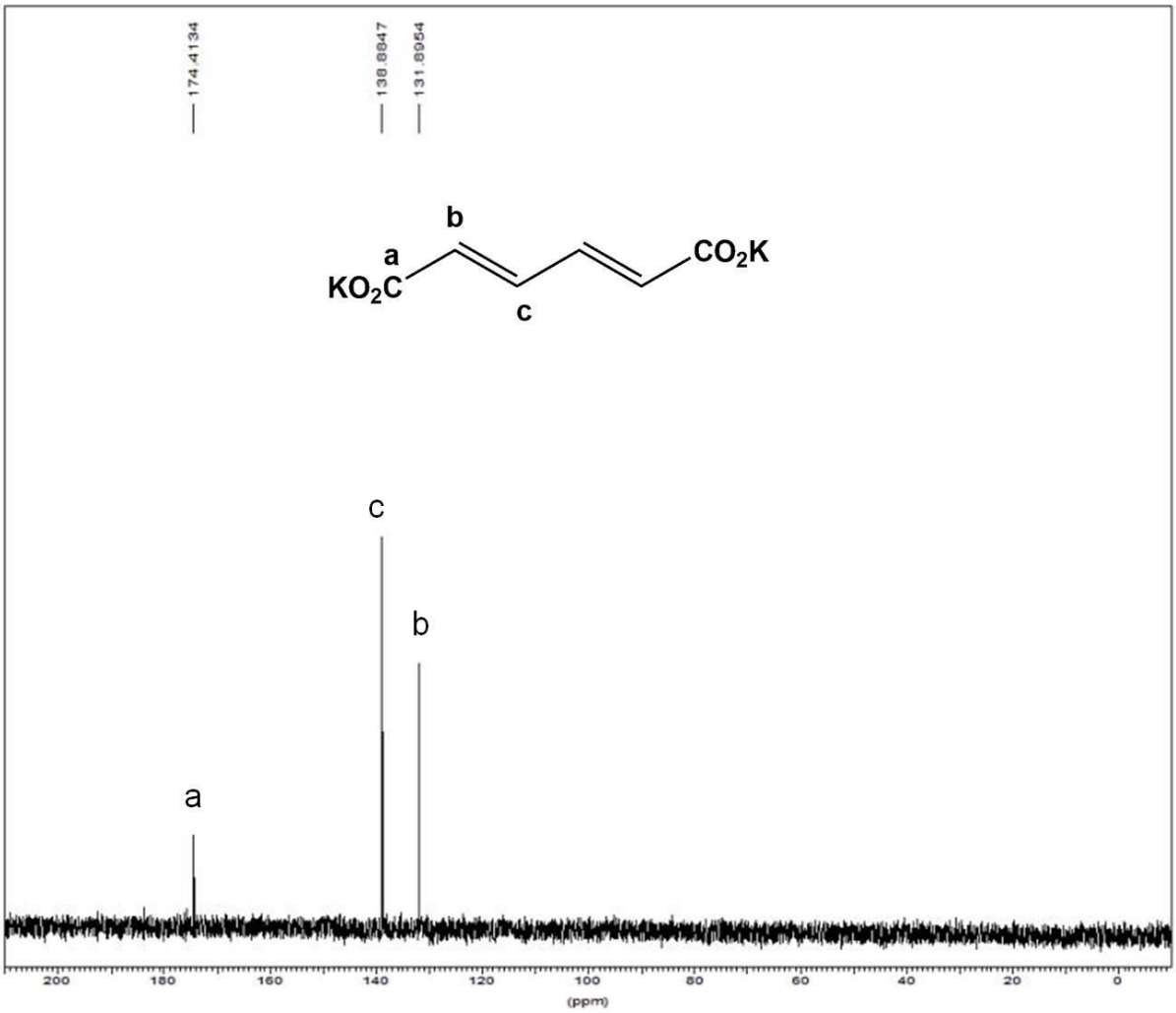

Figure S2: The ^{13}C NMR spectrum (300 MHz, D_2O) of K_2*muco*

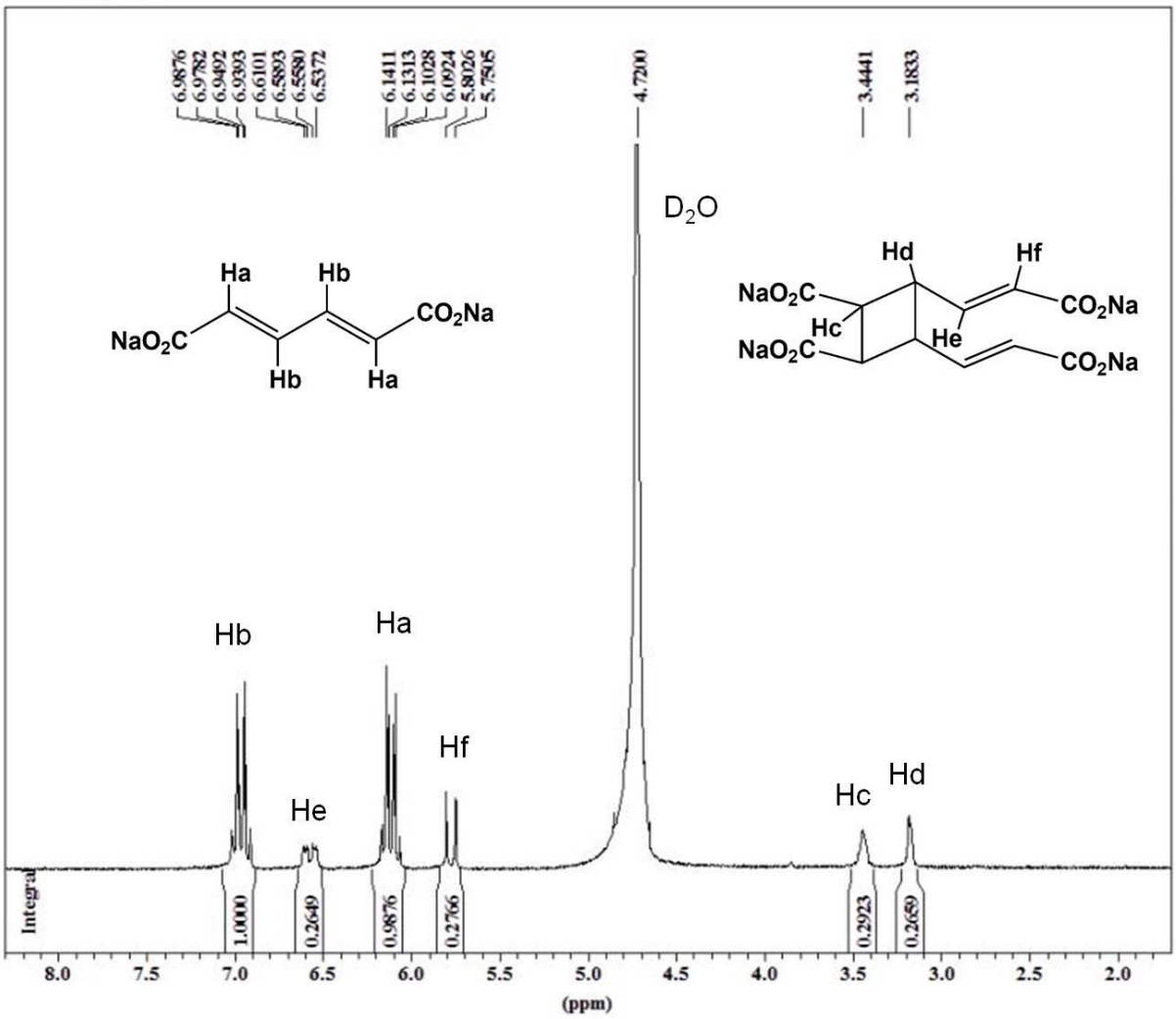

Figure S3: The ^{1}H NMR spectrum (300 MHz, D_2O) of Na_2*muco* after irradiation for 1 h under UV light. No cycloocta-3,7-diene-1,2,5,6-tetracarboxylate (**B**) was detected to form which supports stepwise mechanism.

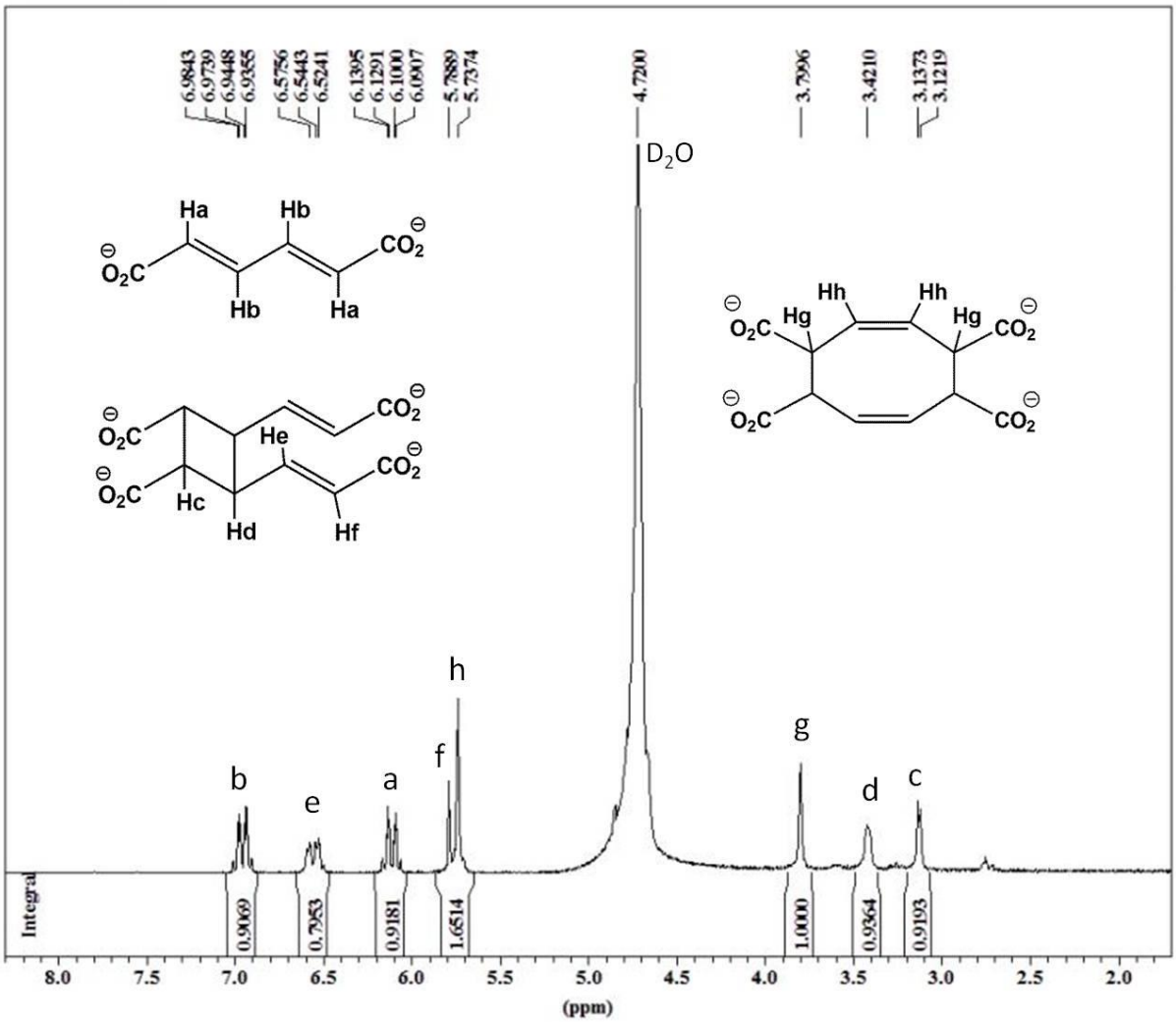

Figure S4: The ^{1}H NMR spectrum (300 MHz, D_2O) of Na_2*muco* after irradiation for 3 h under UV light. It shows the presence of both the dimer products.

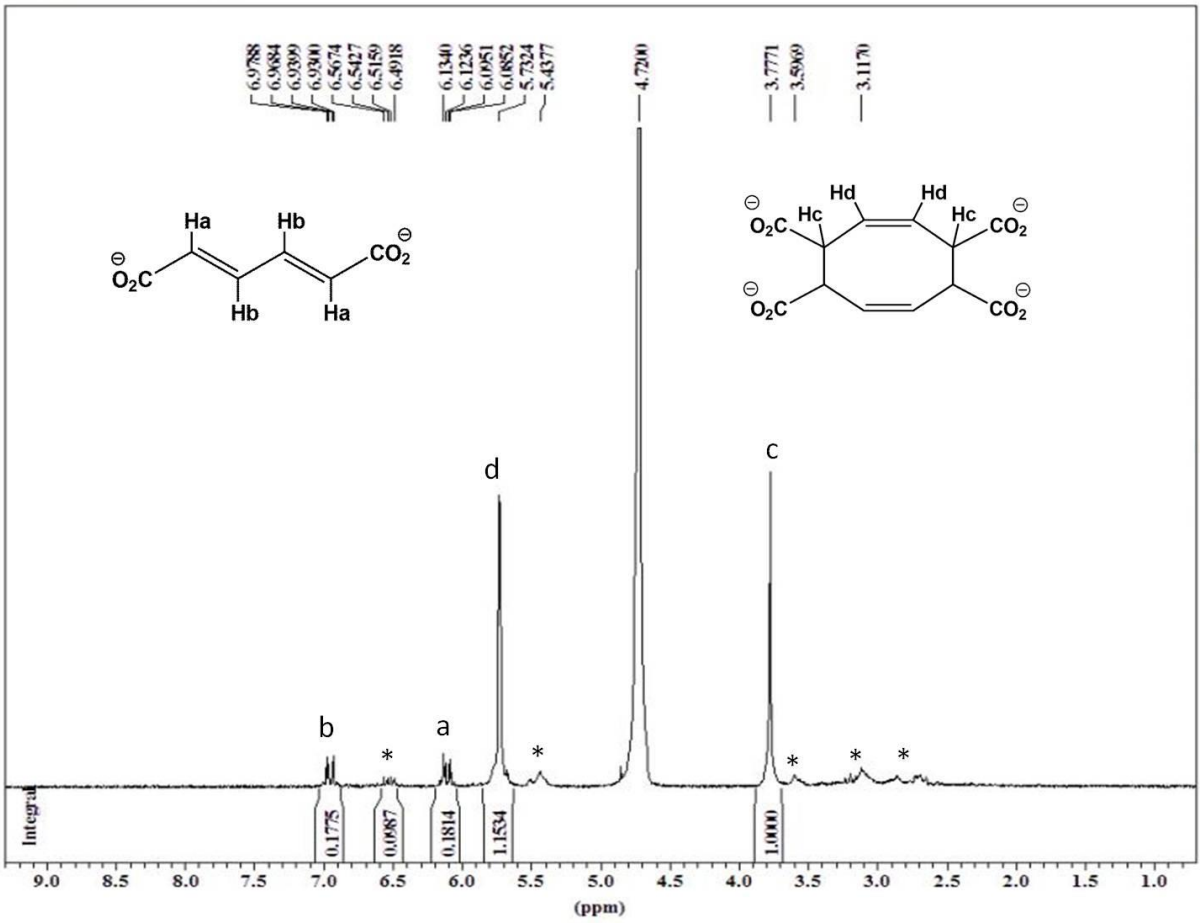

Figure S5: The ^{1}H NMR spectrum (300 MHz, D_2O) of Na_2*muco* after irradiation for 18 h under UV light. The asterisked peaks represent the minor products **C** and **D**.

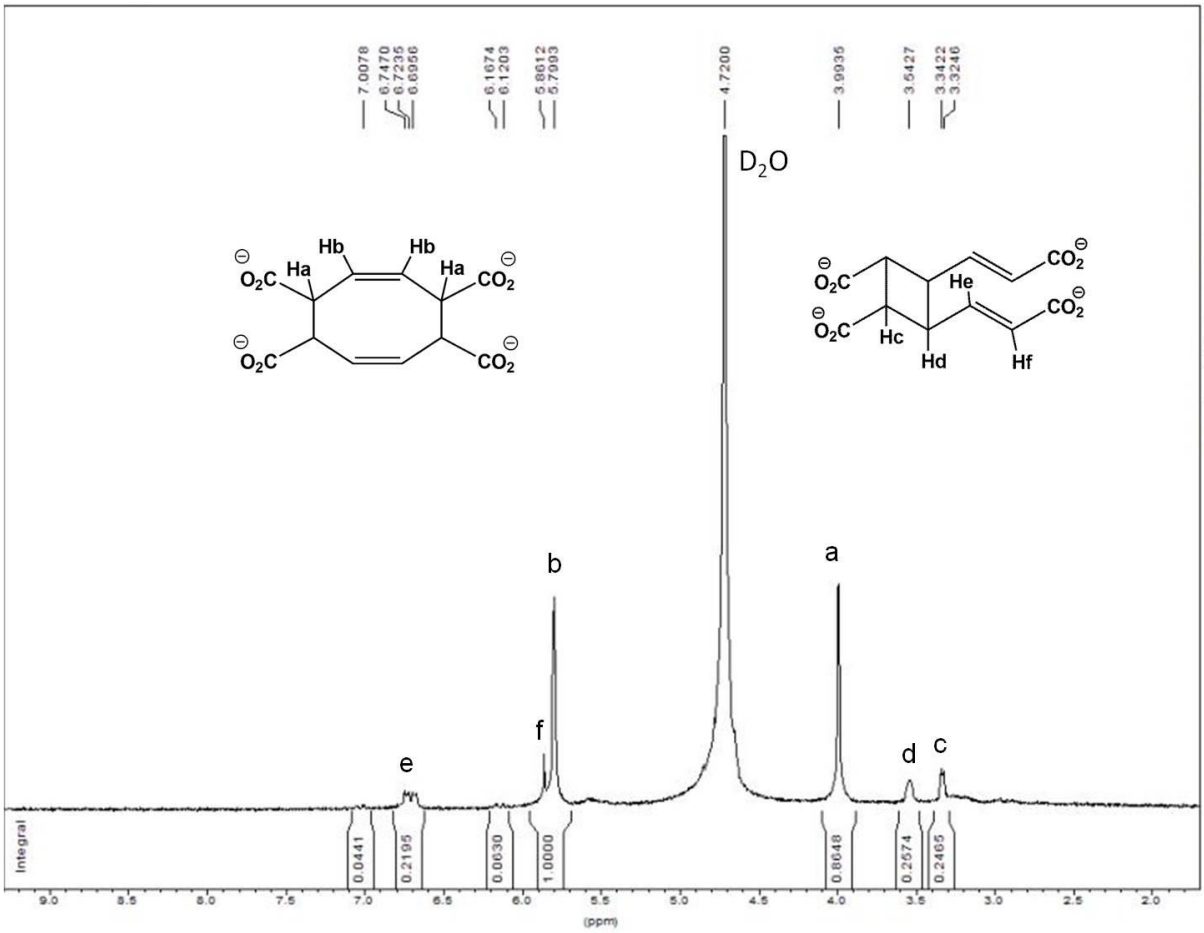

Figure S6: The ^{1}H NMR spectrum (300 MHz, D_2O) of K_2*muco* after irradiation for 10 h under UV light. The minor dimer products (**C**, **D**) are not yet observed.

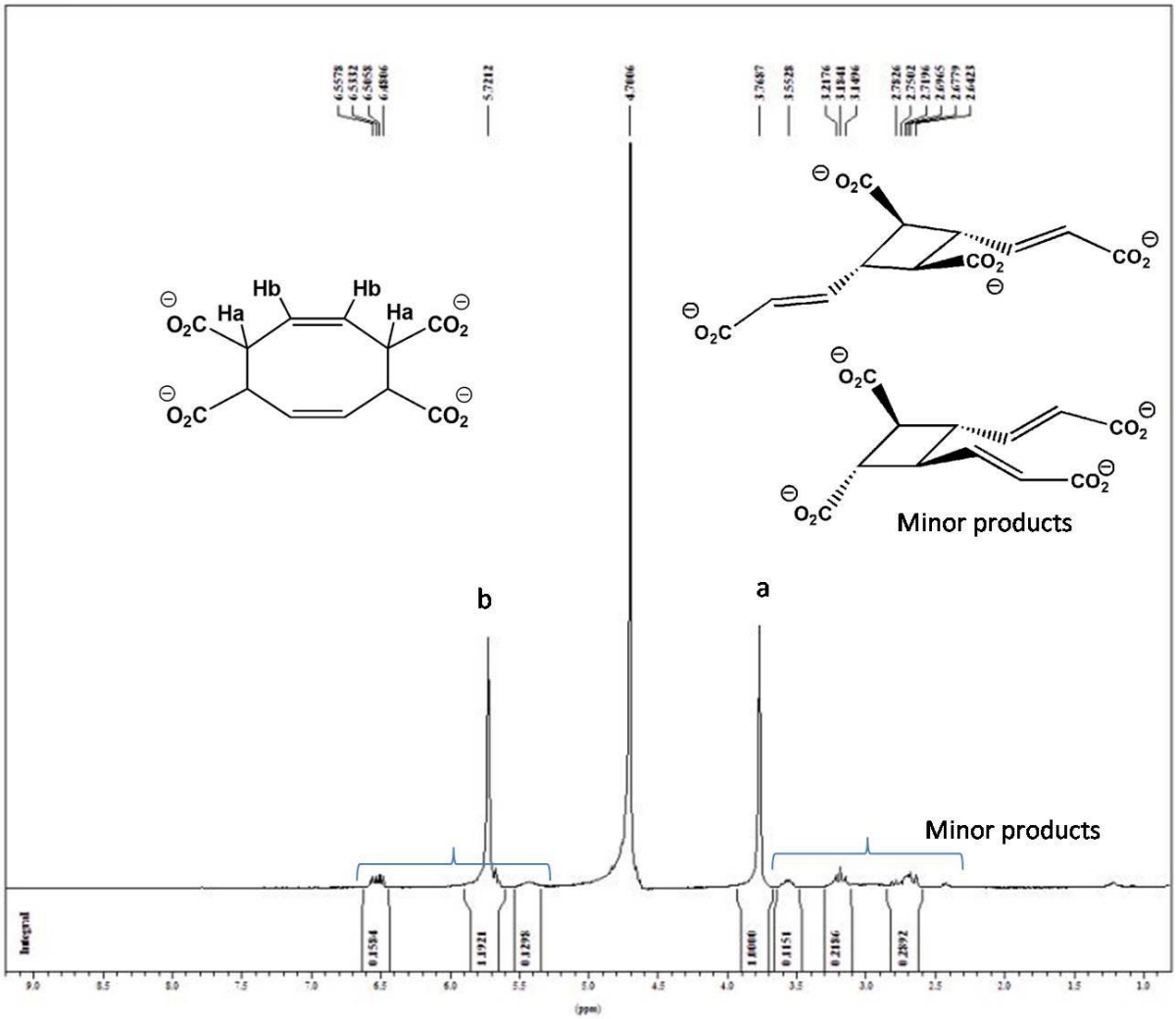

Figure S7: The ^{1}H NMR spectrum (300 MHz, D_2O) of K_2*muco* after irradiation for 18 h under UV light and then mild heating. All the *muco* is converted to various products as shown.

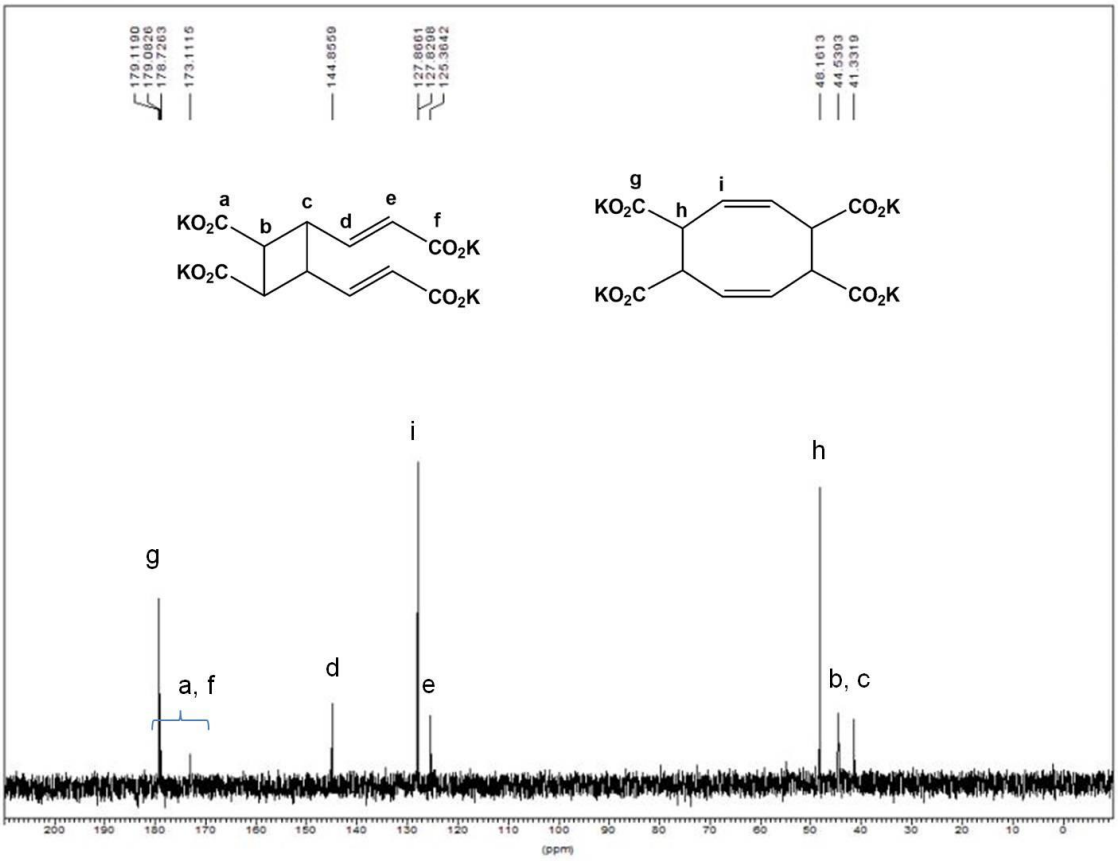

Figure S8: The ^{13}C NMR spectrum (300 MHz, D_2O) of K_2*muco* after irradiation for 18 h under UV light. It shows both the products **A** and **B**.

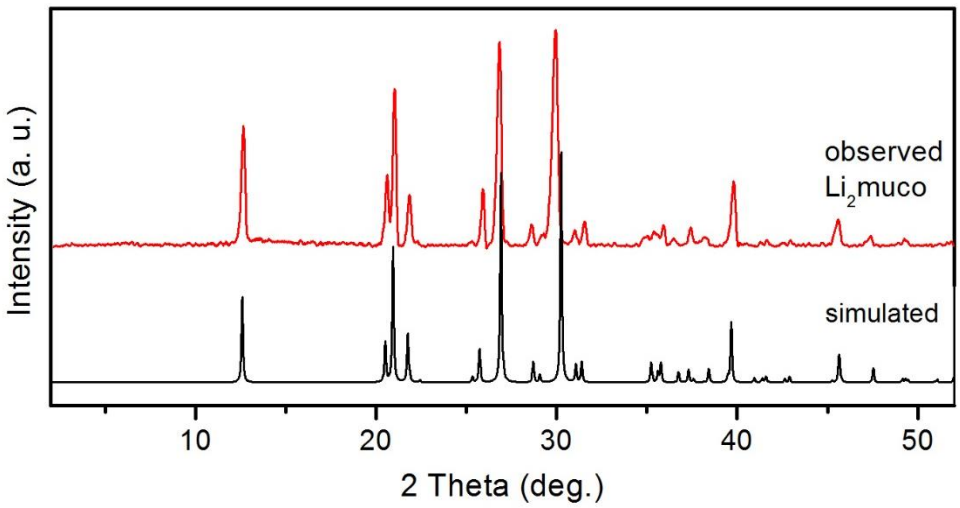

Figure S9: The overlay plot of the simulated and observed PXRD patterns for Li_2*muco*.

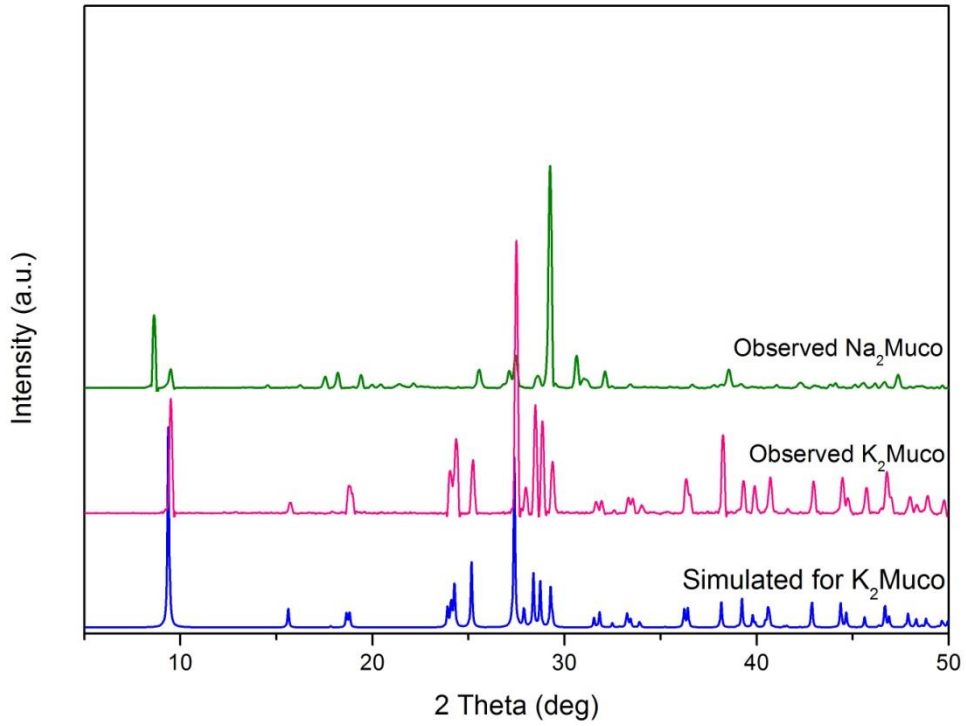

Figure S10: The overlay plot of the simulated and observed PXRD patterns for K$_2$*muco* and observed pattern for Na$_2$*muco*.

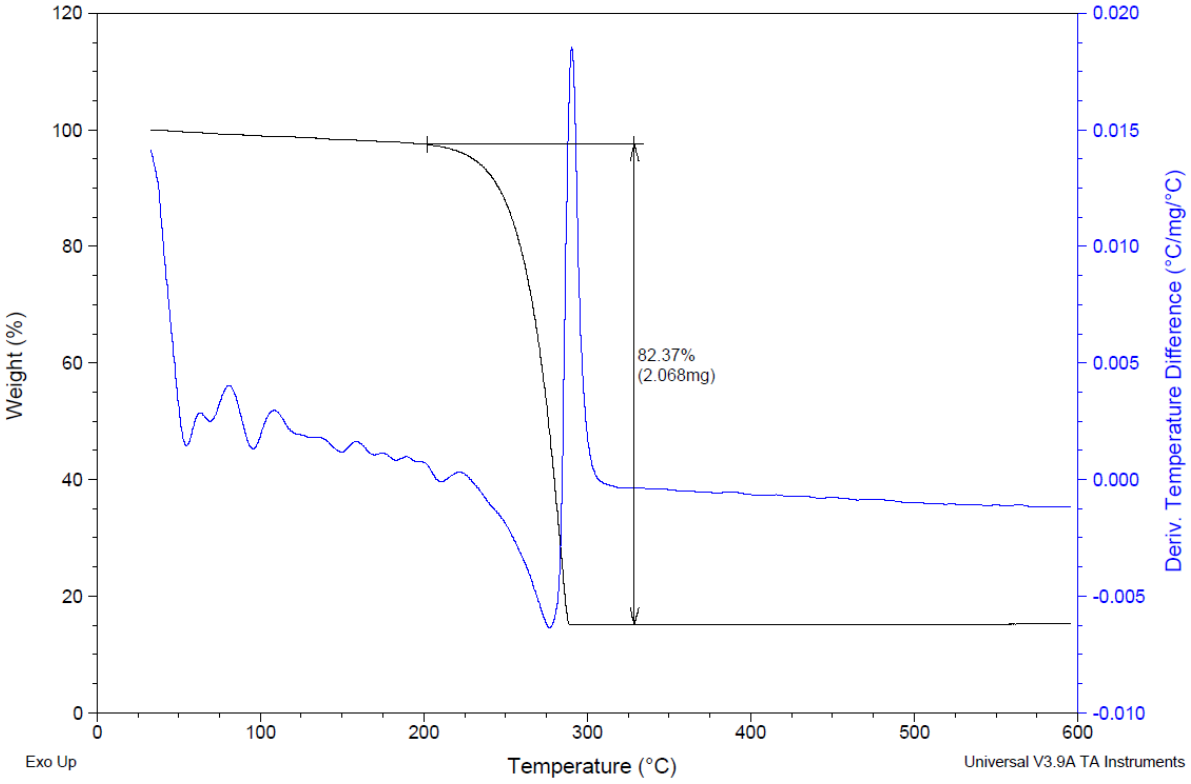

Figure S11: TGA plot for Li$_2$*muco*.

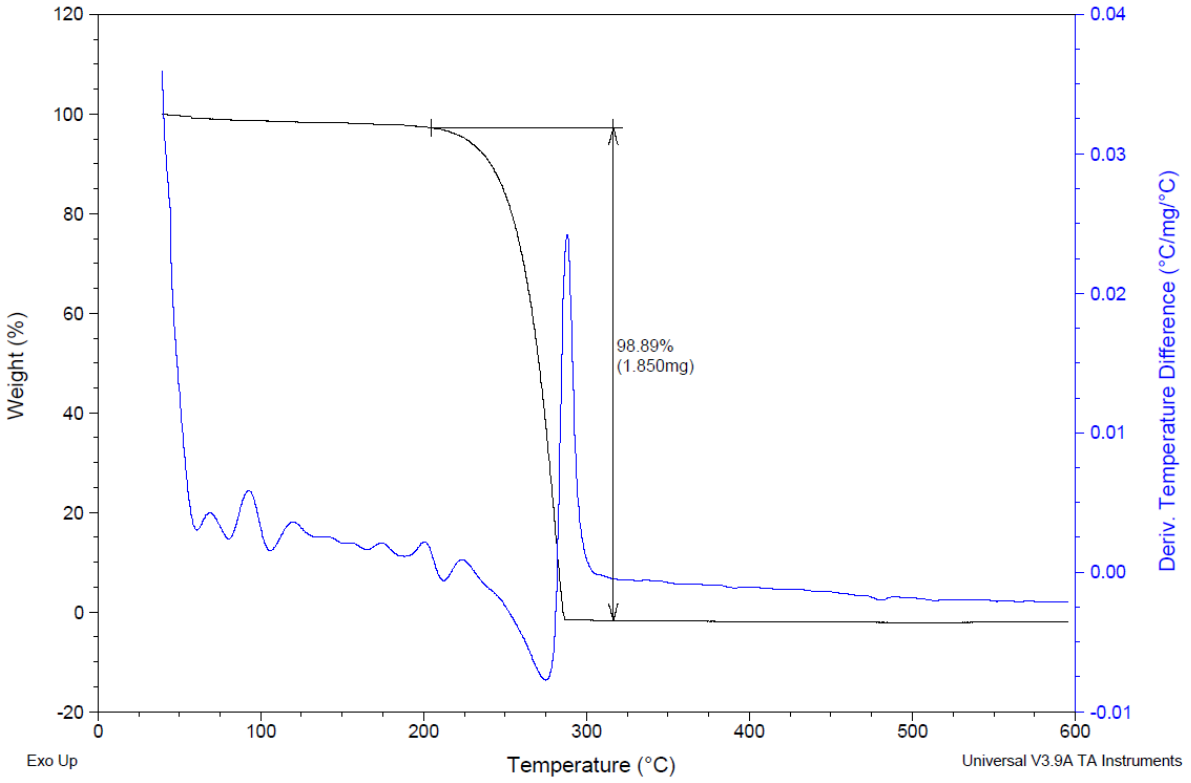

Figure S12: TGA plot for Na_2*muco*.

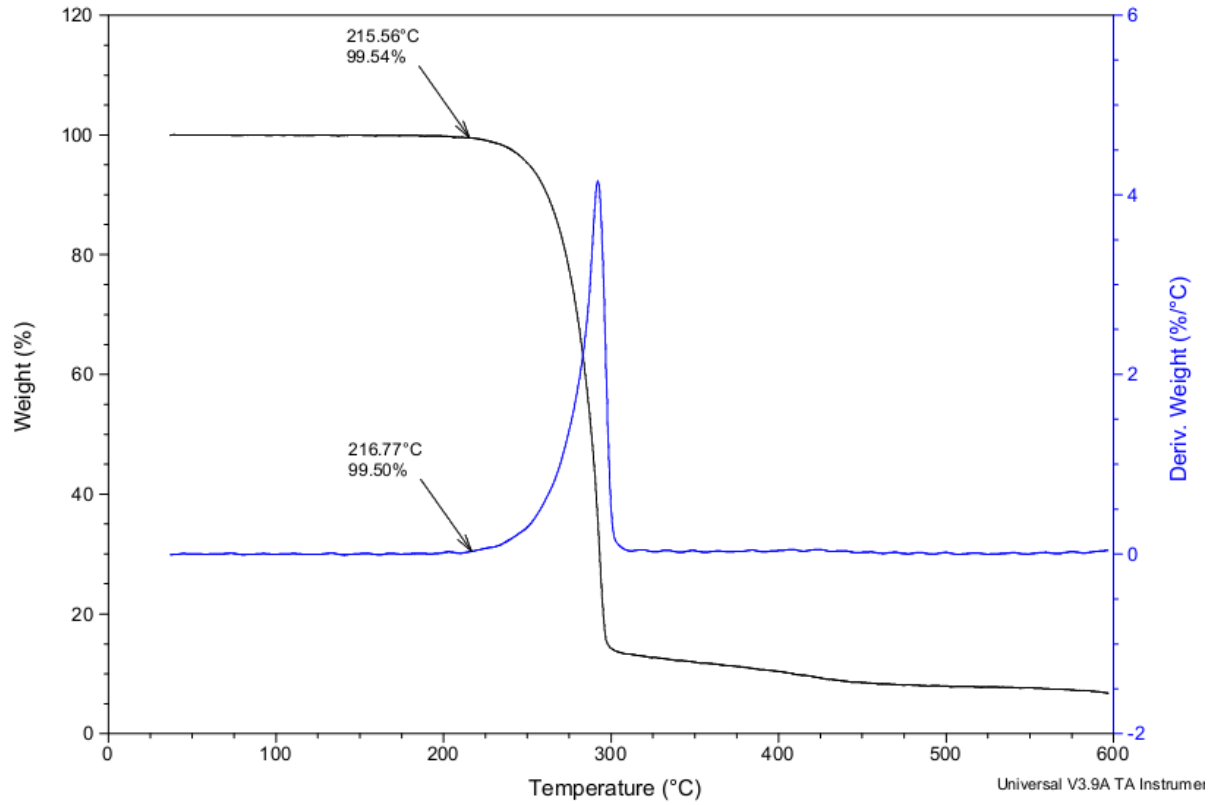

Figure S13: TGA plot for K_2*muco*.