Supporting Information

Rechargeable self-healing safety fuel gel†

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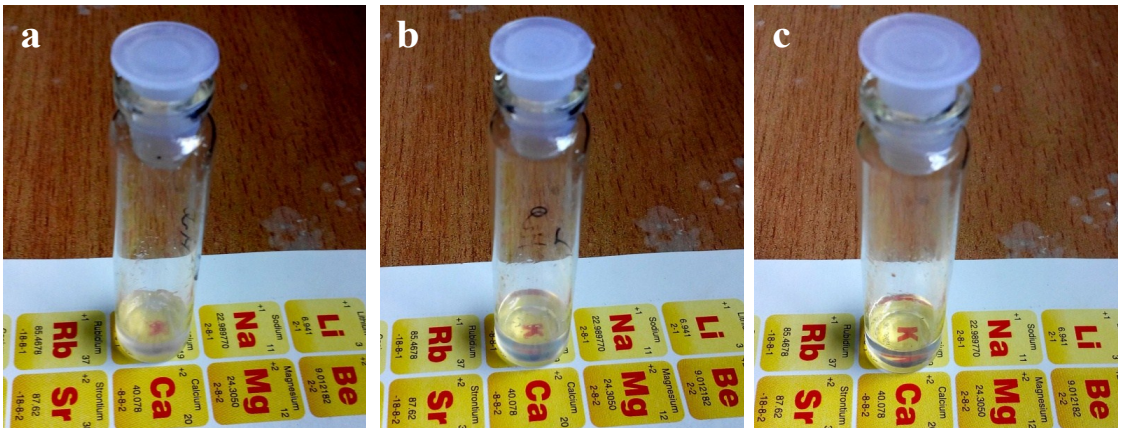
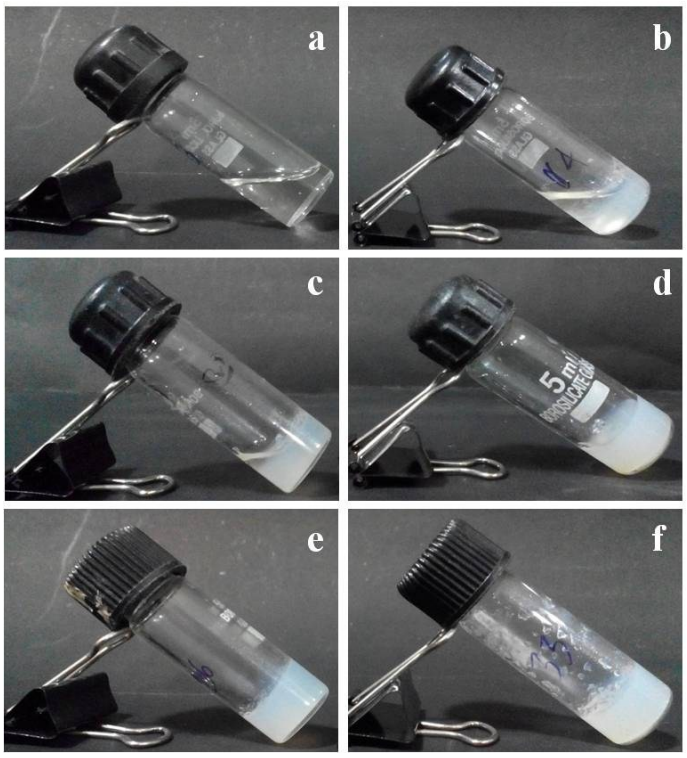
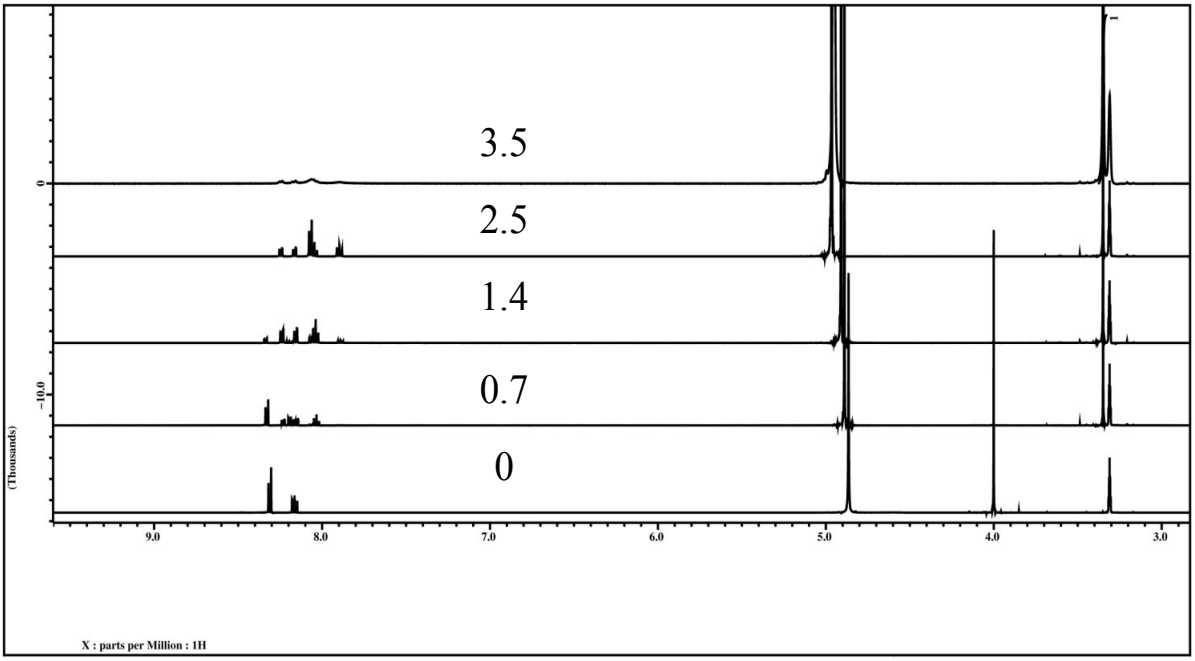


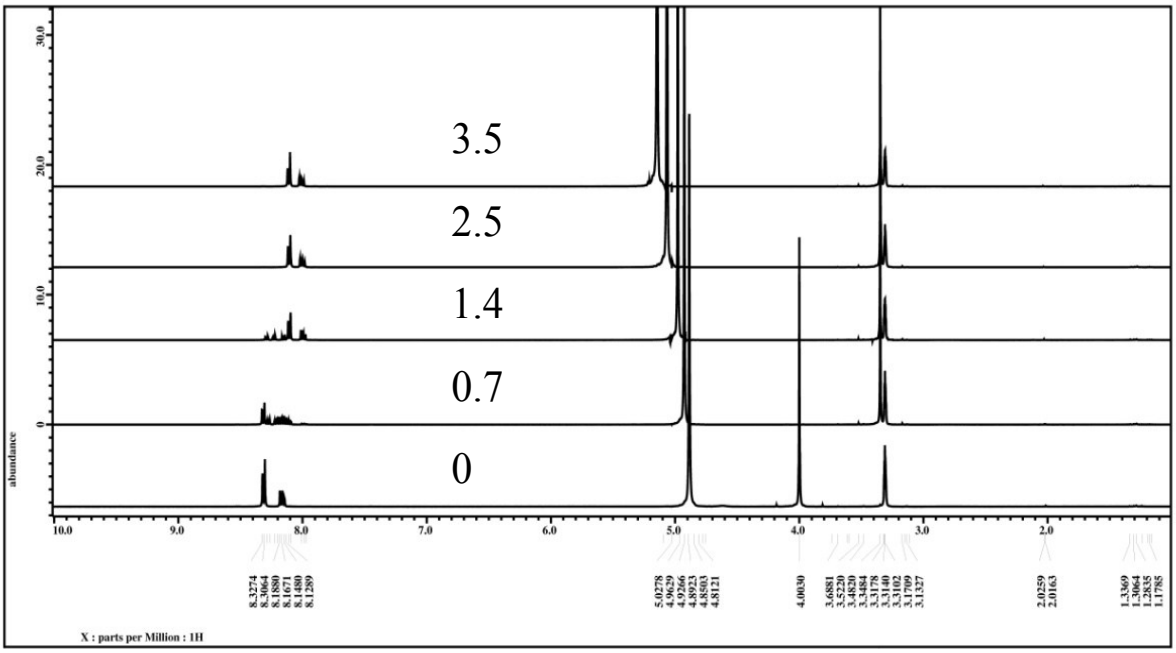
ESI Fig. 1 Transparency of the gel of compound **1** (6 mg, 1 equiv.) and KOH (5 equiv.) with increasing ratio of water in methanol (a) 0.5: 9.5, (b) 1: 9, (c) 1.2: 8.8.



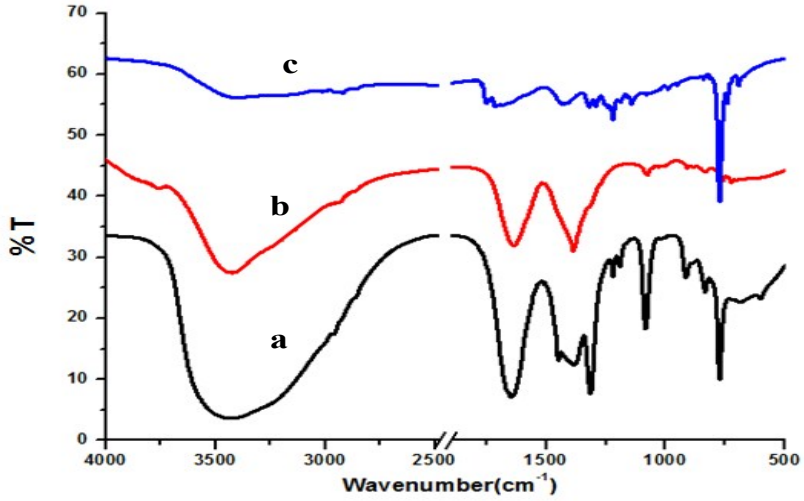
ESI Fig. 2 Gelation study of compound **1** (20mg, 1 equiv.) in water/methanol 1:9 with various equiv. Of KOH (a) 1 equiv., (b) 2 equiv., (c) 3 equiv., (d) 3.5 equiv., (e) 4.5 equiv., (f) 5.5 equiv.



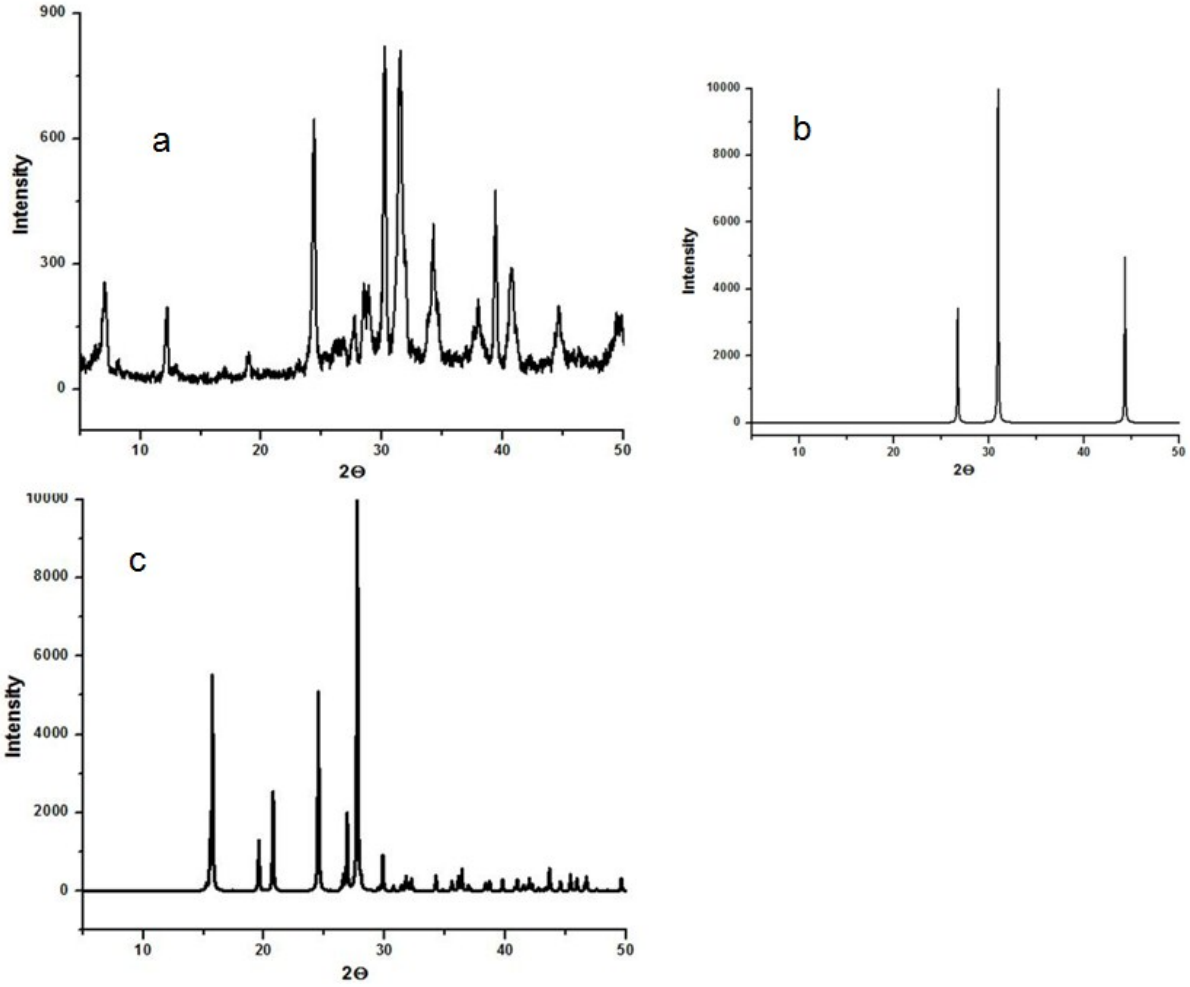
ESI Fig. 3 NMR titration study of compound **1**(0.5% w/v) in D_2O/MeOD 1:9 with increasing amount of KOH.



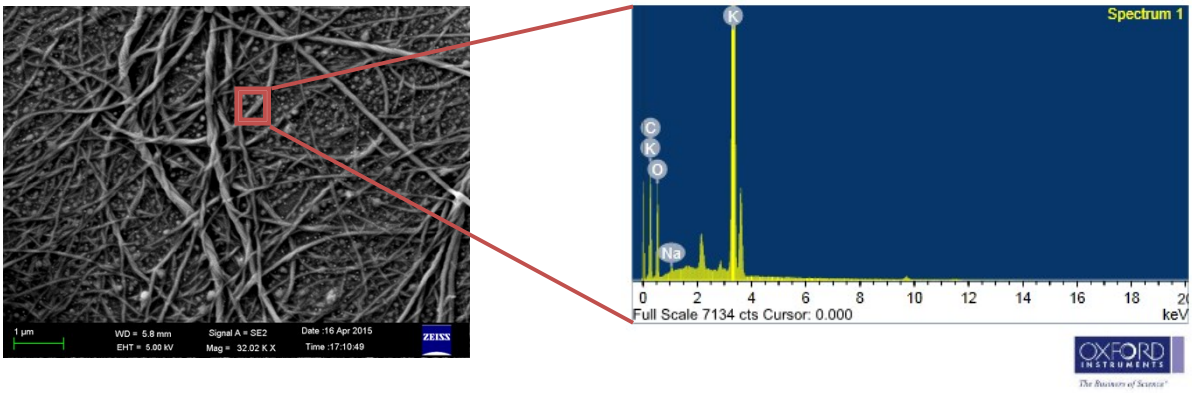
ESI Fig. 4 NMR titration study of compound **1**(0.5% w/v) in D_2O/MeOD 1:9 with increasing amount of LiOH.



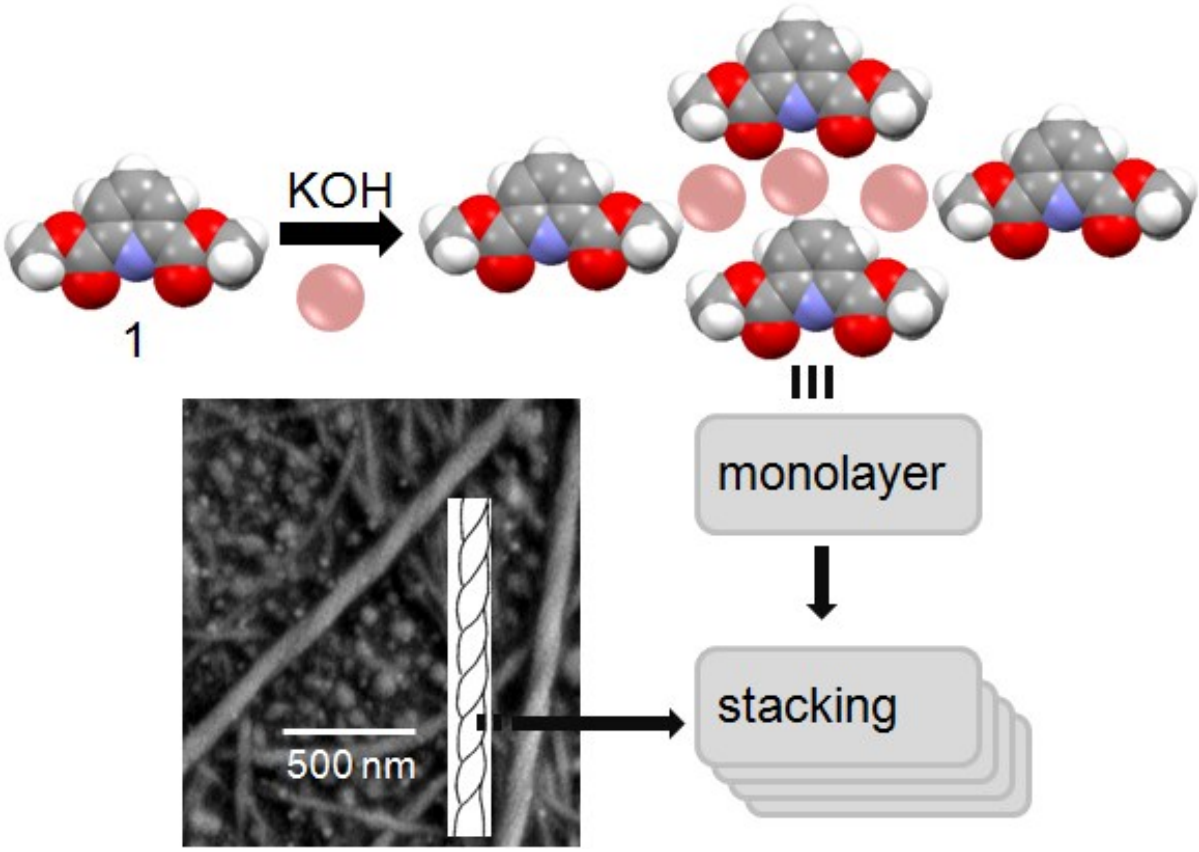
ESI Fig. 5 FT-IR spectra of compound **1** in (a) gelling solvent water/MeOH(1:9), (c) non-gelling solvent $CHCl_3$ and (b) solid state FT-IR spectra of the xero gel made from water/methanol(1:9).



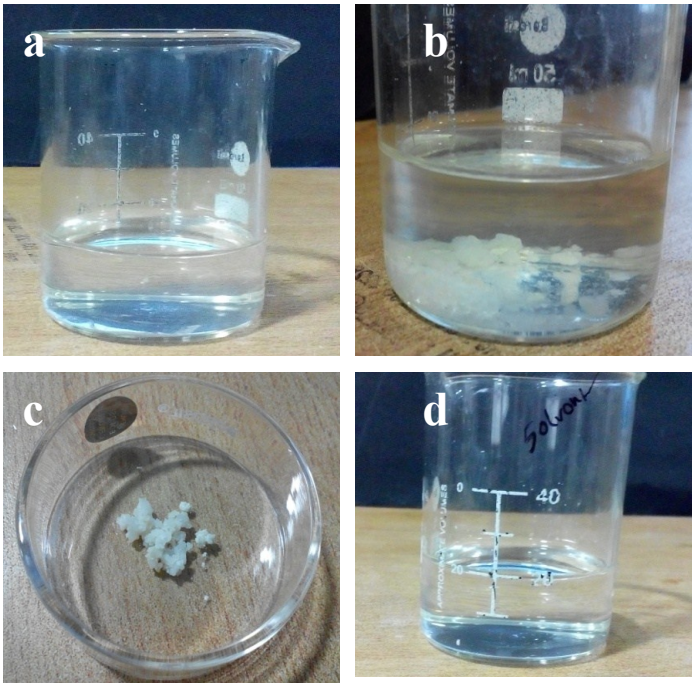
ESI Fig. 6 PXRD pattern of (a) xerogel of compound **1**, (b) obtained from single crystal diffraction of KOH and (c) single crystal diffraction of compound **1.**



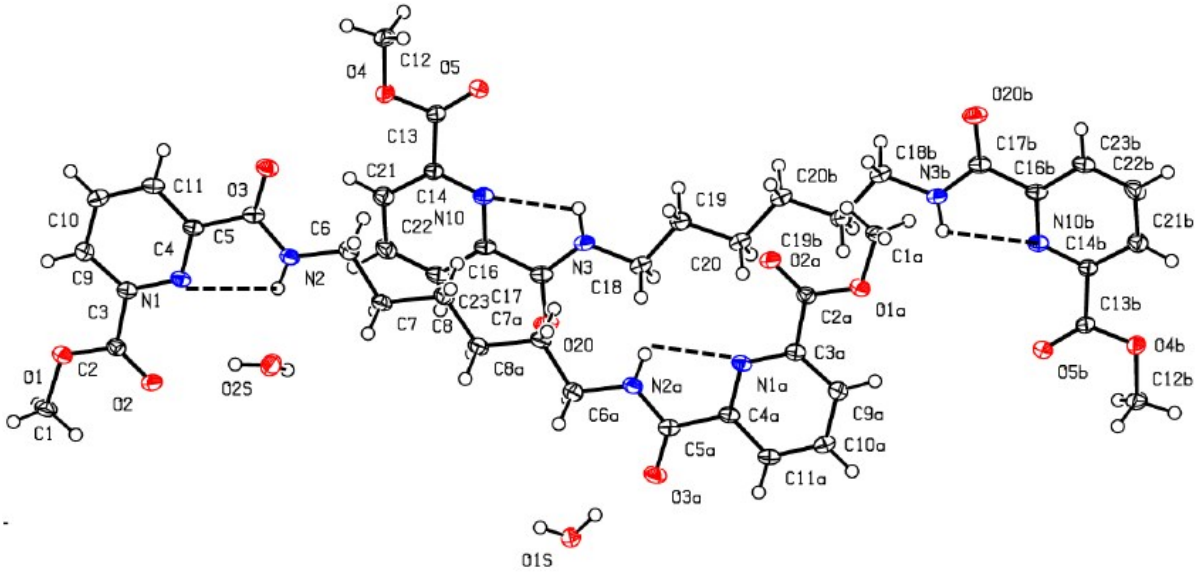
ESI Fig. 7 EDS data of gel made from compound **1** and KOH.



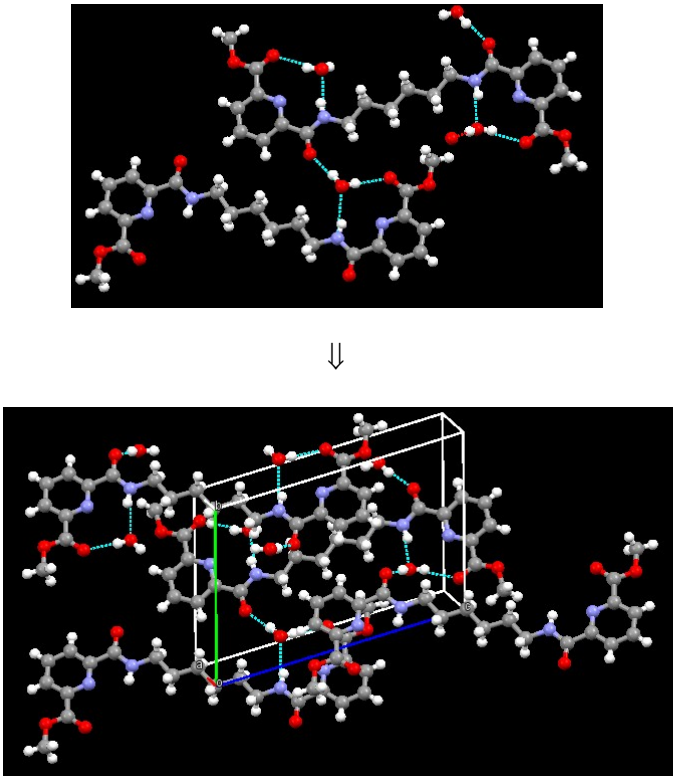
ESI Fig. 8 Probable model of interaction between compound **1** and KOH to form helical fiber.



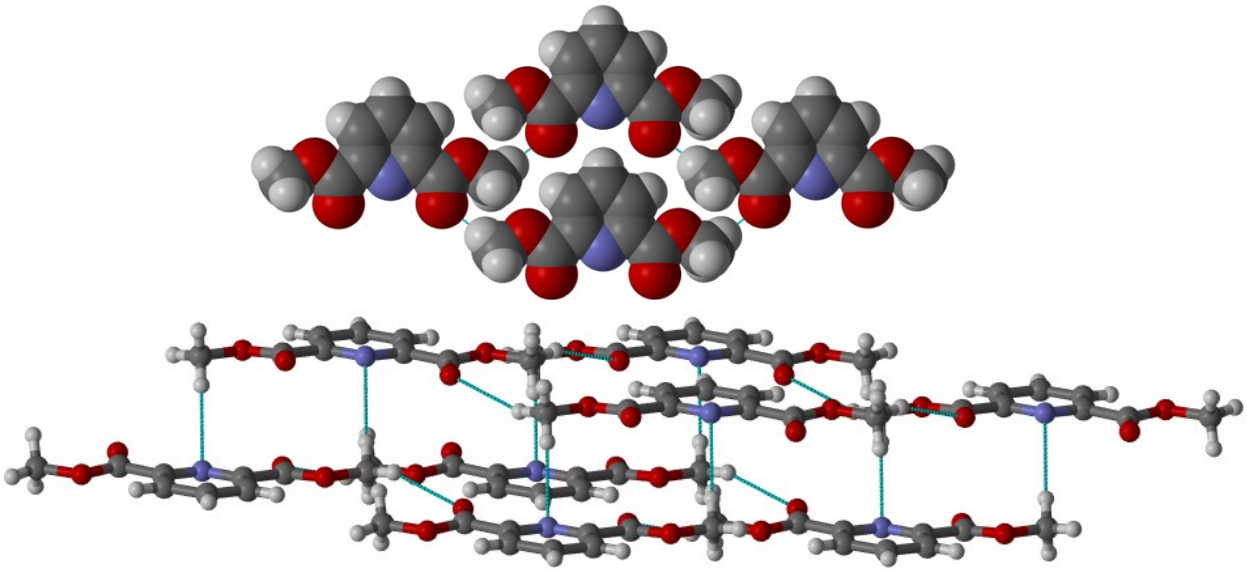
ESI Fig. 9 Solvent purification (a) ethyl acetate with little impurity methanol, (b) addition of compound **1** and aqueous KOH causes gelation of methanol which precipitated out from the solvent, (c) the precipitated gel which can be separated out by simple decantation or filtration, (d) recovered ethyl acetate.



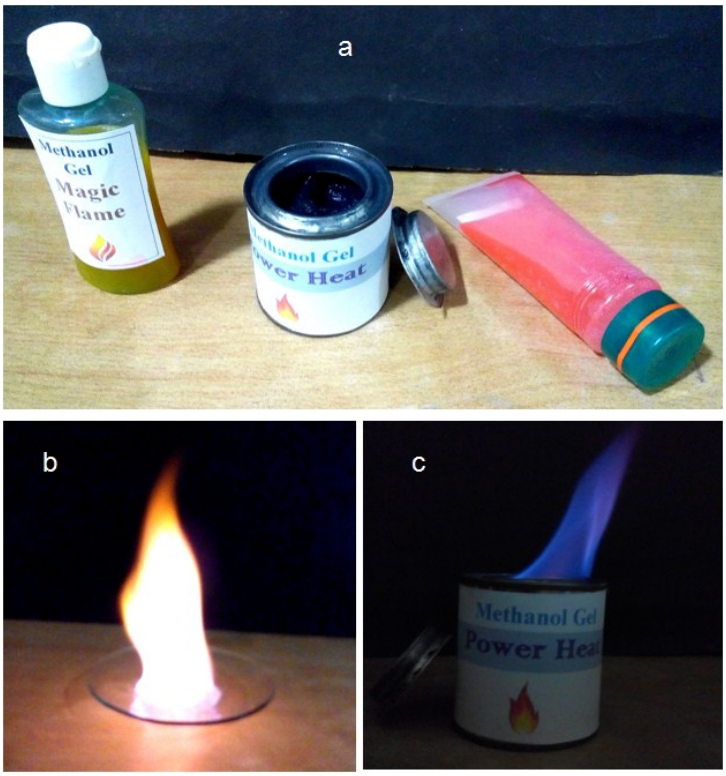
ESI Fig. 10 The ORTEP diagram of compound **2** showing atom numbering scheme. 50% probability level. Intramolecular hydrogen bonds are shown as dotted lines.



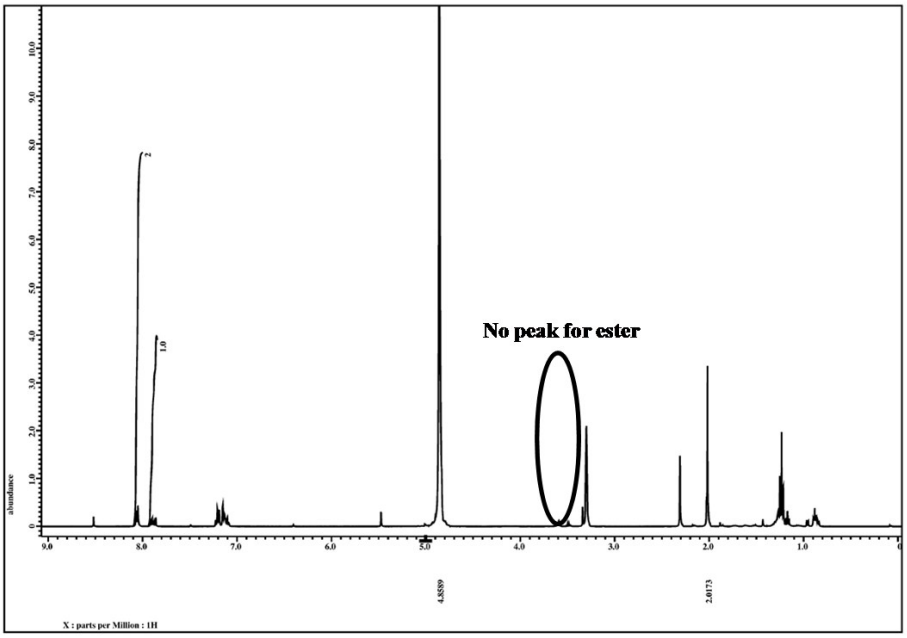
ESI Fig. 11 The water mediated hydrogen bonds between compound **2** molecules and the sheet like structure at higher order assembly. Hydrogen bonds are shown as dotted lines.



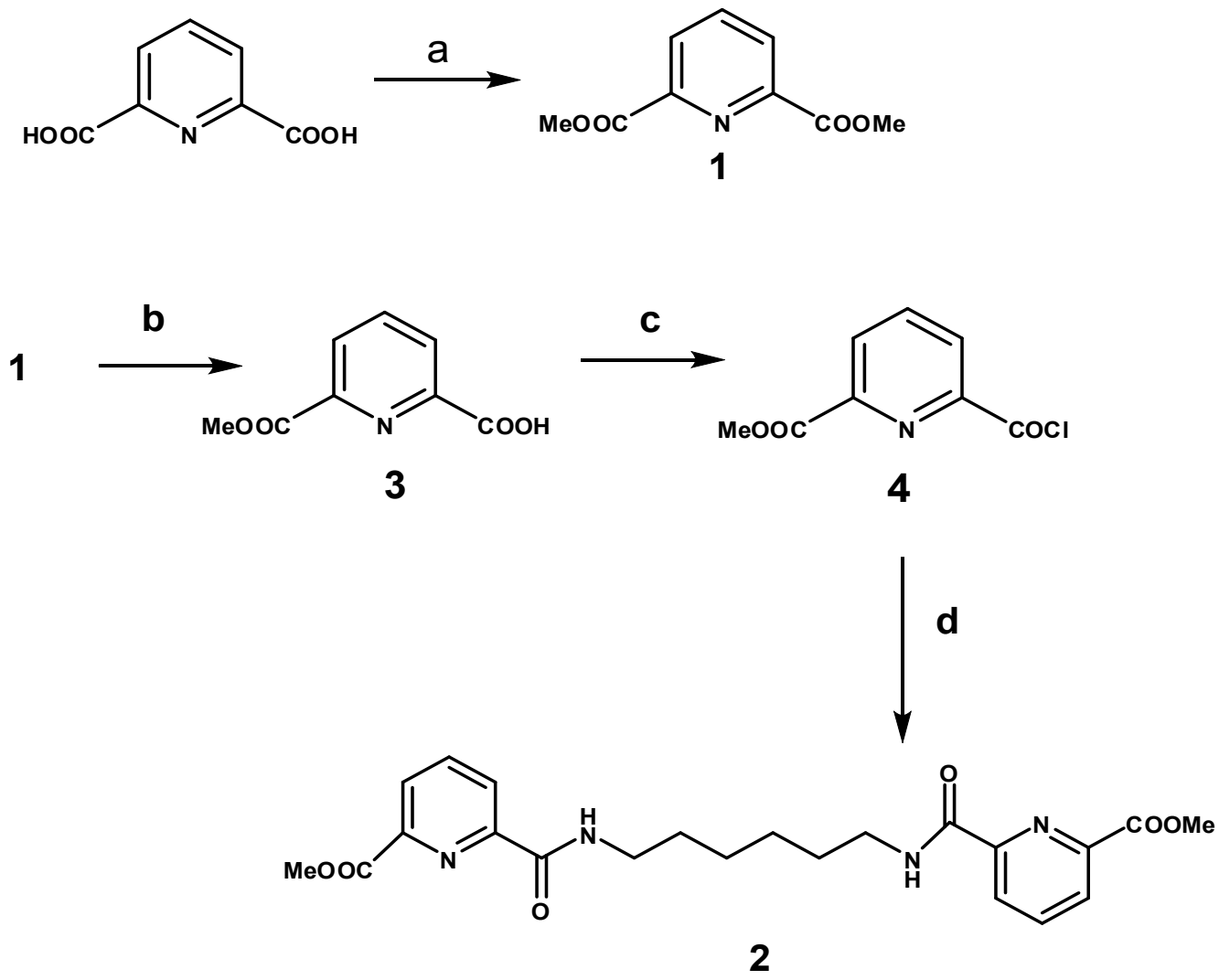
ESI Fig. 12 The sheet like packing of compound **1** in crystal.



ESI Fig. 13 (a) The KOH responsive compound **1** gel in portable plastic bottle, tin container and soft polymer tube. The gels have coloured with rhodamine 6G, methyl violet, methyl orange respectively. (b) The burning ethanol gel on a watch glass. (c) The methanol gel chafing fuel in a tin container.



ESI Fig. 14 ^{1}H NMR spectra of compound **1** recovered after five burning cycles, showing absence of OMe peak. The compound **1** has hydrolyzed by KOH in the burning process with high temperature.



Scheme 1. The synthesis of compound **1** and **2**. *Reagents and conditions*: (a) MeOH, $SOCl_2$, 0°C; (b) NaOH (1 eqv.), MeOH: H_2O (9:1); (c) $SOCl_2$, reflux; (d) $H_2NCH_2CH_2CH_2CH_2CH_2CH_2NH_2$, Et_3N, DCM.

Synthesis of compound 1

Dimethyl pyridine 2,6 dicarboxylate(1): 1.67g (10 mmol) pyridine 2,6 dicarboxylic acid was dissolved in 30 mL methanol, cooled in ice-bath, 2 mL of $SOCl_2$ was added dropwise and stirred for 8h. After completion of reaction the total liquid was evaporated under reduced pressure, the product was then dissolved in ethyl acetate and washed with fresh water repeatedly.The ethyl acetate layer was dried in anhydrous Na_2SO_4 and evaporated under reduce pressure to obtained di-ester as white crystalline solid.

Yield: 1.687g (8.65 mmol, 86.5%)

^{1}H NMR ($CDCl_3$, 500 MHz, δ_{ppm}): 8.274-8.258 (d, 2H, J= 7 Hz, aromatic protons), 8.005-7.974 (t, 1H, J_1=7.5 Hz, J_2= 8.0 Hz, aromatic proton), 3.974 (s, 6H, 2 x COOMe). ^{13}C NMR ($CDCl_3$, 125 MHz, δ_{ppm}): 164.91, 148.07, 138.29, 127.92, 53.068.

Synthesis of compound 2

(a) 6-(Methoxycarbonyl) picolinic acid (3): 1.66 g (8.51 mmol) compound **1** was dissolved in 50 mL of methanol water mixture, cooled and 340 mg of NaOH was added and stirred for 6h. Then methanol was evaporated under reduced pressure, about 20 mL water was added and washed with diethylether. The water portion was acidified with dilute HCL solution, the compound was extracted with ethyl acetate. The organic layer was then dried over anhydrous Na_2SO_4 and dried under reduced pressure. The crude was purified with column chromatography using DCM: Methanol as eluent.

Yield: 838 mg (4.63 mmol, 54.4%)

^{1}H NMR ($CDCl_3$, 500 MHz, δ_{ppm}): 8.237-8.200 (m, 2H, aromatic protons), 8.167-8.143 (m, 1H, aromatic proton), 3.917 (s, 3H, COOMe). ^{13}C NMR ($CDCl_3$, 125 MHz, δ_{ppm}): 165.80, 164.91, 138.97, 127.69, 127.08, 52.64

(b) dimethyl 6,6'-(hexane-1,6-diylbis(azanediyl))bis(oxomethylene)dipicolinate (2): Acid chloride derivative of compound **3** was prepared by refluxing 815mg compound **3** in 10 mL thionyl chloride. 895 mg (4.5 mmol) of acid chloride derivative was dissolved in dry DCM, cooled in ice-bath. Then 625µL of dry triethylamine was added dropwise with stirring

followed by the addition of 309 µL hexamethylene diamine (2.25 mmol). After 12h the solution was taken in separating funnel, washed with water, the organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography using ethyl acetate:hexane (1:1) as eluent.

Yield: 689 mg (1.56 mmol, 69.3 %)

^{1}H NMR (DMSO-d_6, 500 MHz, δ_{ppm}): 8.516 (b, 2H, 2 x NH), 8.218-8.184 (m, 6H, aromatic proton), 3.920 (s, 6H, 2 x COOMe), 3.345-3.309(m,4H,aliphatic protons), 1.570-1.543(m, 4H, aliphatic protons), 1.334-1.317 (m,4H,aliphaticprotons). ^{13}C NMR ($CDCl_3$, 125 MHz, δ_{ppm}): 165.03,163.44,150.36,146.37,138.47,127.09,125.43,52.89,39.46,29.47,26.58.

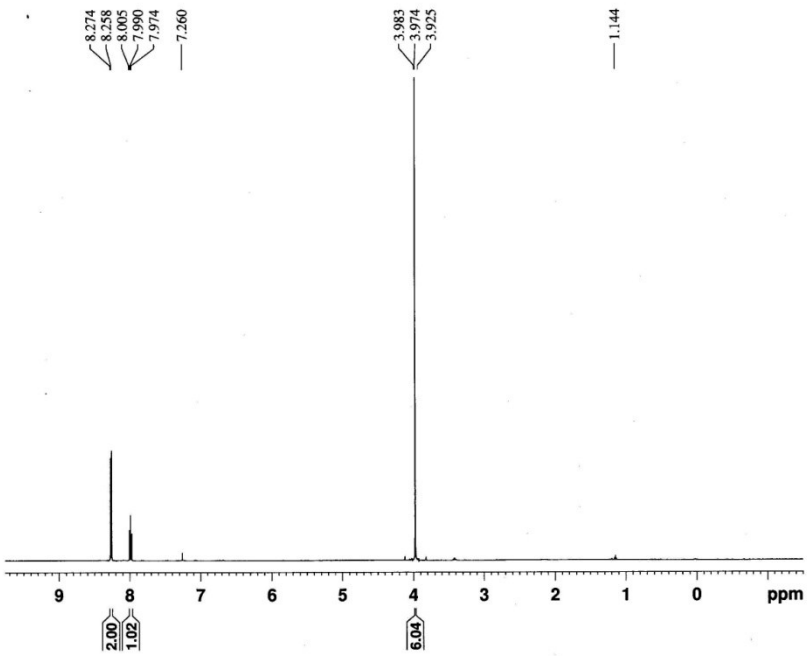


Fig. **S1**: ^{1}H NMR ($CDCl_3$, 500MHz, δ_{ppm}) spectra of compound **1.**

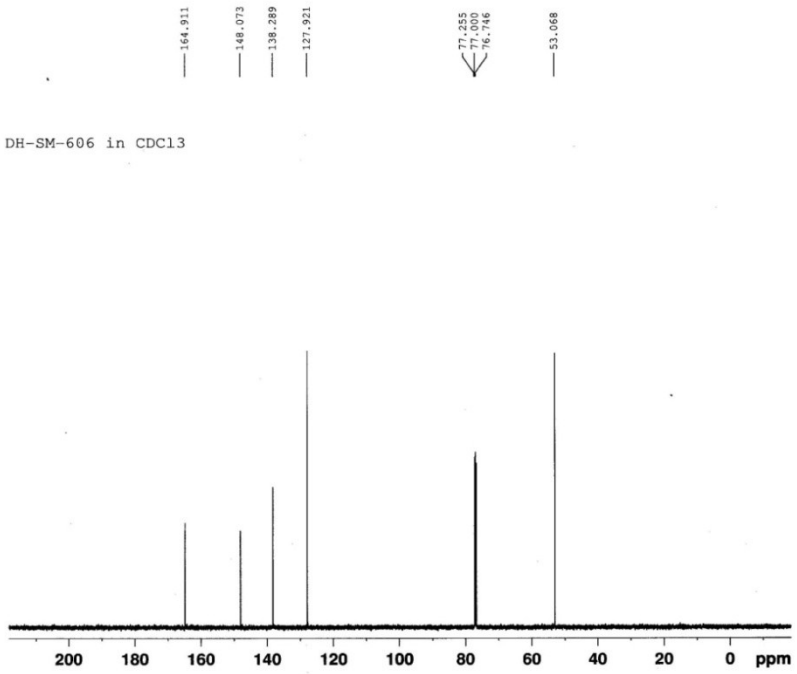


Fig. **S2**: ^{13}C NMR ($CDCl_3$, 125MHz, δ_{ppm}) spectra of compound **1.**

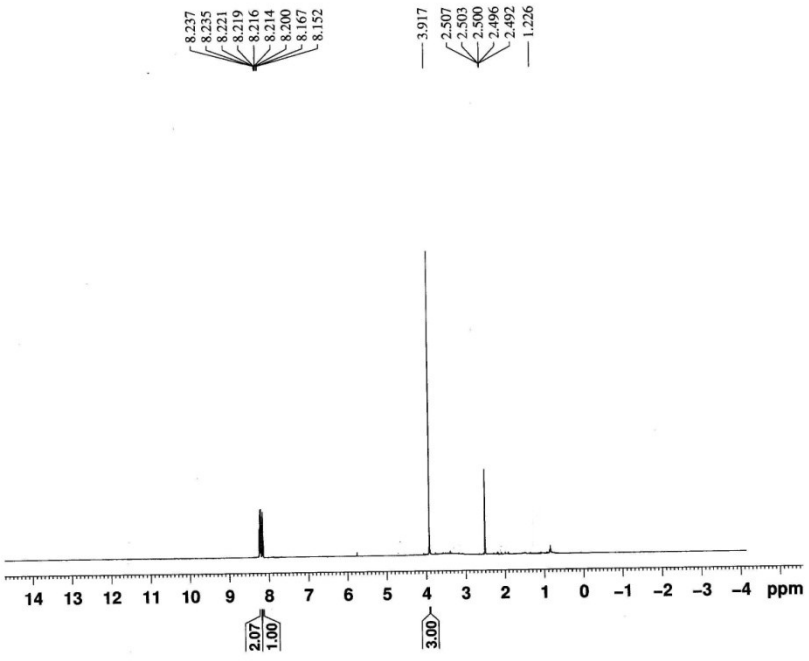


Fig. S 3: ^{1}H NMR (DMSO-*d6*, 500 MHz, δ_{ppm}) spectra of compound **3**.

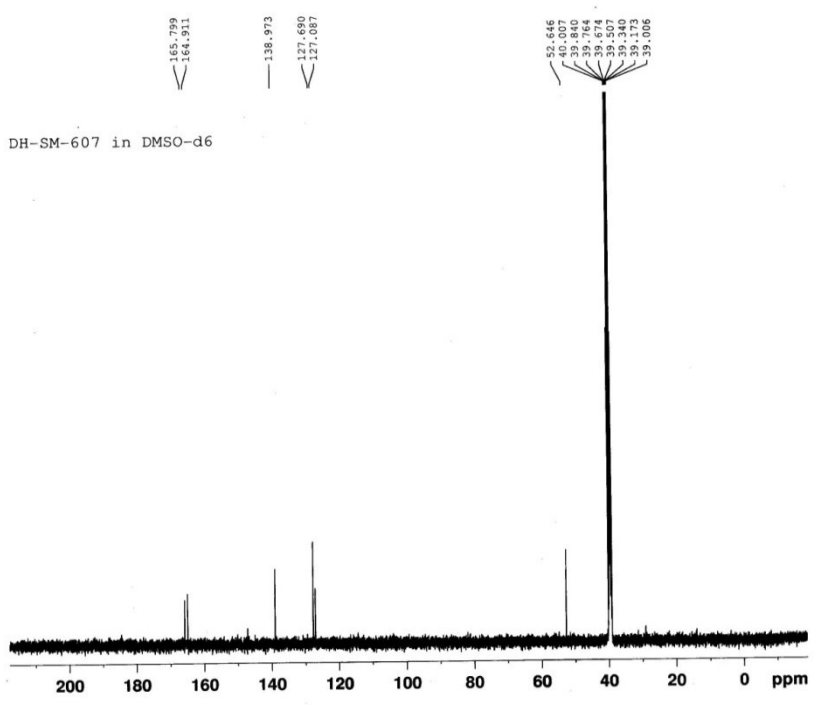


Fig. S4: ^{13}C NMR (DMSO-*d6*, 125MHz, δ_{ppm}) spectra of compound **3.**

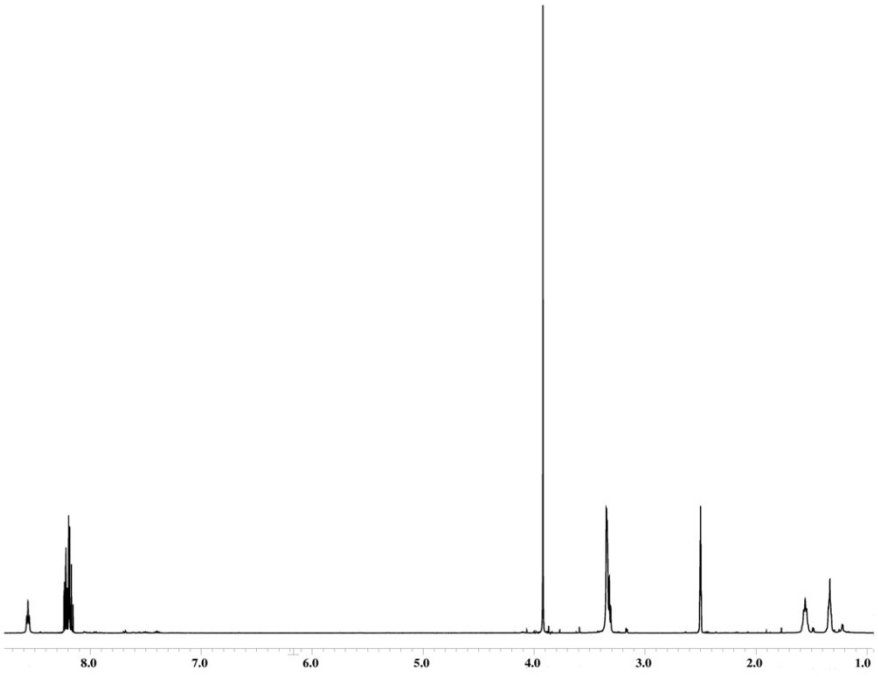


Fig. **5**: ^{1}H NMR (DMSO-d_6, 500MHz, δ_{ppm}) spectra of compound **2.**

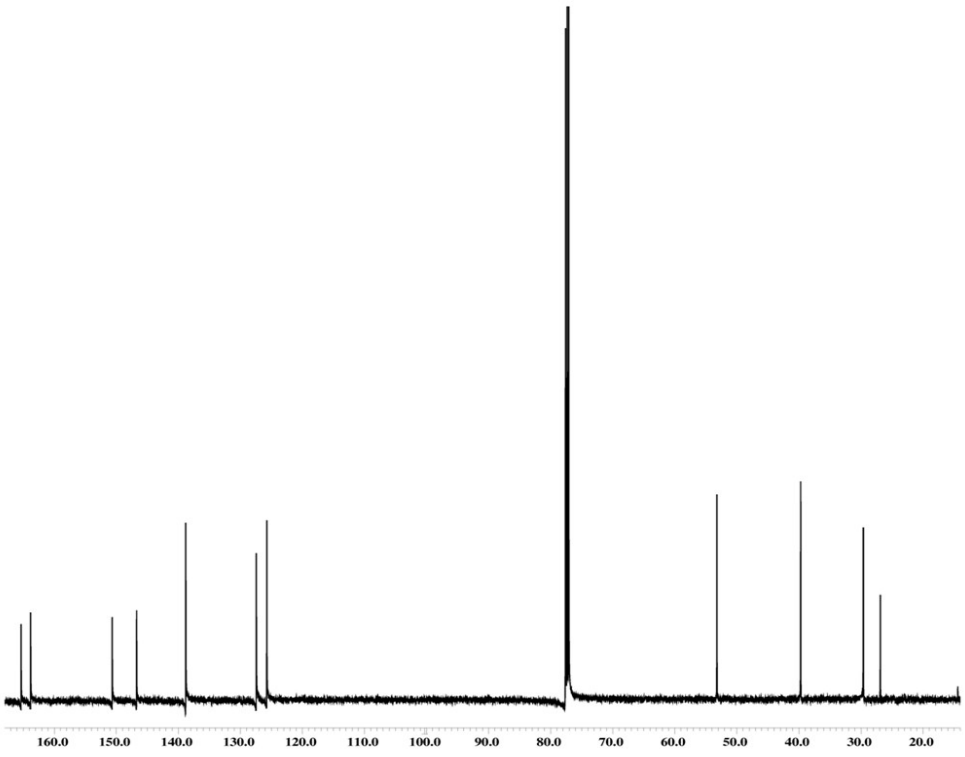


Fig. S6: ^{13}C NMR ($CDCl_3$, 125MHz, δ_{ppm}) spectra of compound **2.**