

Supporting Information

Mechanochemical synthesis of Cu₂S bonded 2D-sulfonated organic polymer: continuous production of dimethyl carbonate (DMC) *via* preheating of reactants

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EXPERIMENTAL

Materials and instruments

CuCl₂, benzene-1,3,5-tricarboxaldehyde (BTC), 2,5-diaminobenzene sulfonic acid (DABSA), DMSO, DMF, DCM, and THF were purchased from Sigma-Aldrich and used as received without further purification. Pressurized carbon dioxide gas cylinder was procured from the Messer Gases with 99.99 purity. Retsch ball mill (planetary motion) was used with 125 mL vessel and 26 balls (6 balls of 20 mm and 20 balls of 10 mm) of silicon nitride for the mechanochemical synthesis of catalyst. H-Cube and Phoenix flow reactors with loop holder for 8 mL coil (1/16" OD and 1 mm ID) (Thales Nano Inc.) were used for performing flow reactions

and preheating the gaseous mixture, respectively. Catalyst was filled in stainless steel CatCart with the help of CatCart packer connected to the vacuum pump.

Characterization techniques

Powder X-ray diffraction (XRD) patterns of material were determined by X'Pert PRO MPD diffractometer (PANalytical) in the Bragg–Brentano geometry, equipped with an X'Celerator detector, and programmable divergence and diffracted beam anti-scatter slits at room temperature using iron-filtered Co-K α radiation (40 kV, 30 mA, $\lambda = 0.1789$ nm). The angular range of measurement was set as $2\theta = 5\text{--}90^\circ$, with a step size of 0.017° . Microscopic TEM images were obtained by HRTEM TITAN 60-300 with X-FEG type emission gun, operating at 80 kV. This microscope is equipped with Cs image corrector and a STEM high-angle annular dark-field detector (HAADF). The point resolution is 0.06 nm in TEM mode. The elemental mappings were obtained by STEM-energy dispersive X-ray spectroscopy (EDS) with acquisition time 20 min. XPS surface investigation has been performed on the PHI 5000 Versa Probe II XPS system (Physical Electronics) with monochromatic Al-K α source (15 kV, 50 W) and photon energy of 1486.7 eV. Dual beam charge compensation was used for all measurements. All the spectra were measured in the vacuum of 1.3×10^{-7} Pa and at the room temperature of 21 °C. The analyzed area on each sample was a spot of 200 μm in diameter. The survey spectra were measured with pass energy of 187.850 eV and electronvolt step of 0.8 eV, while for the high-resolution spectra, pass energy of 23.500 eV, and electronvolt step of 0.2 eV were used. The spectra were evaluated with the MultiPak (Ulvac - PHI, Inc.) software. All binding energy (BE) values were referenced to the carbon peak C 1s at 284.80 eV. The conversion and selectivity of the reactions were analyzed by GC employing chromatograph Agilent 6820 (Agilent, United

States), equipped with flame ionization detector (FID) and chromatographic column DB5 (30×0.250×0.25). The surface area and porosity of the samples were examined by nitrogen adsorption at 77.4 K. The analyzer Autosorb-iQ-C (Quantachrome), which uses the static volumetric technique, was employed to measure the adsorption isotherms up to the saturation pressure of nitrogen. Prior to the measurements, all samples were outgassed at elevated temperature of 100 °C for at least 24 h. The surface areas were calculated by multipoint BET (Brunauer–Emmett–Teller) model. For ICP-MS analysis, samples were dissolved in a mixture of concentrated HNO₃ and HCl and filled up to defined volume with ultra-pure water. ICP-MS (Agilent 7700x, Agilent, Japan) instrument quantified all the elements using external calibration and appropriate isotopes. All NMR spectra were acquired by using the JNM-ECZ400R/S1 spectrometer (JEOL 400). Water vapor adsorption experiments were performed on a volumetric gas adsorption analyzer (3Flex, Micromeritics, USA), equipped with vapor source container. Prior to the analysis, the samples were degassed under high vacuum (10⁻⁴ Pa) at 80 °C for 12 hours. Water type 1 (Milli-Q Reference Water Purification System, USA) was used as the vapor source, while high purity (99.999%) N₂, He gases were used for the purification and measurement, respectively.

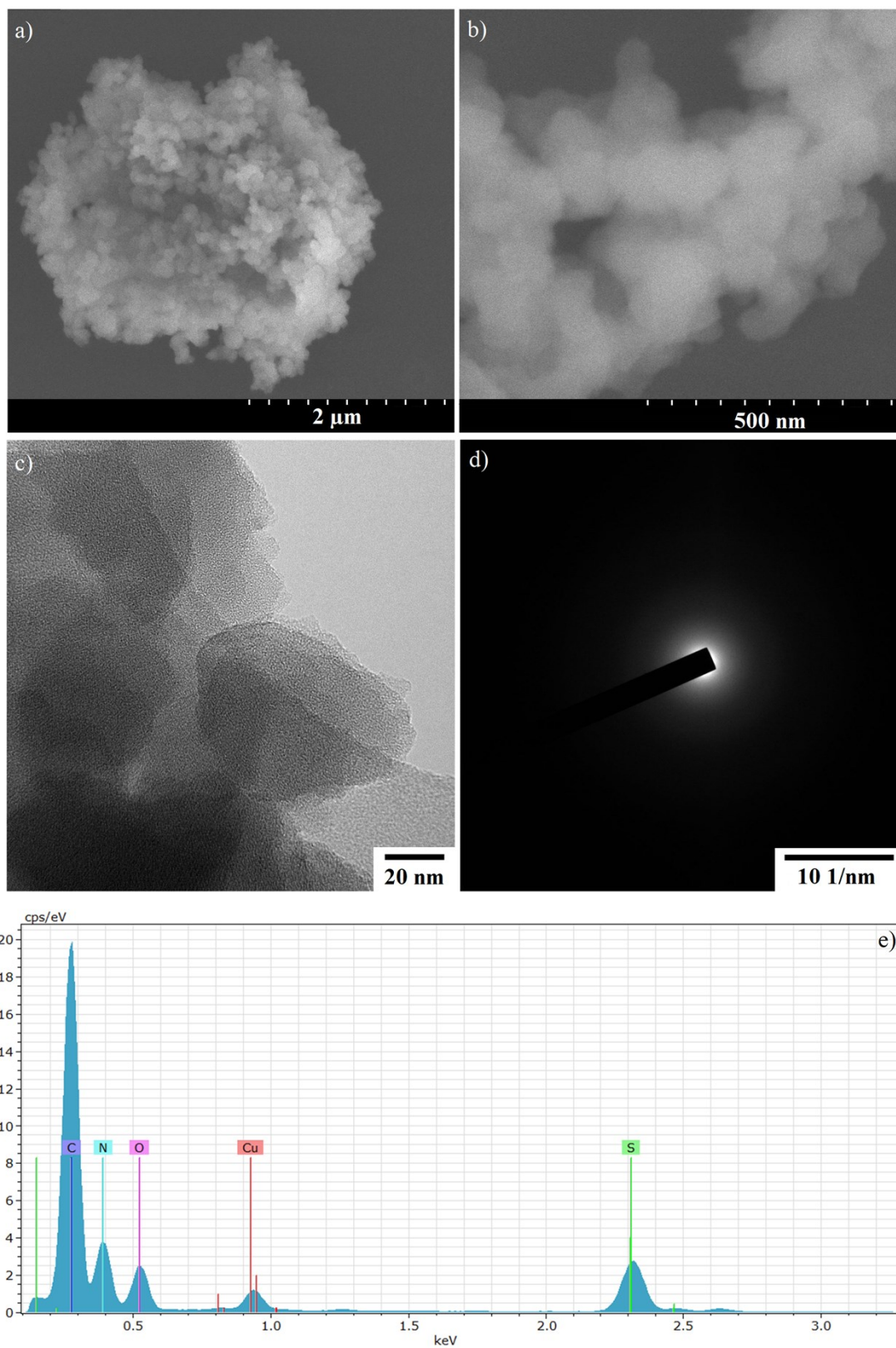


Fig. S1 a),b) SEM images; c) TEM image; d) SAED pattern; e) EDX of Cu-SOPm.

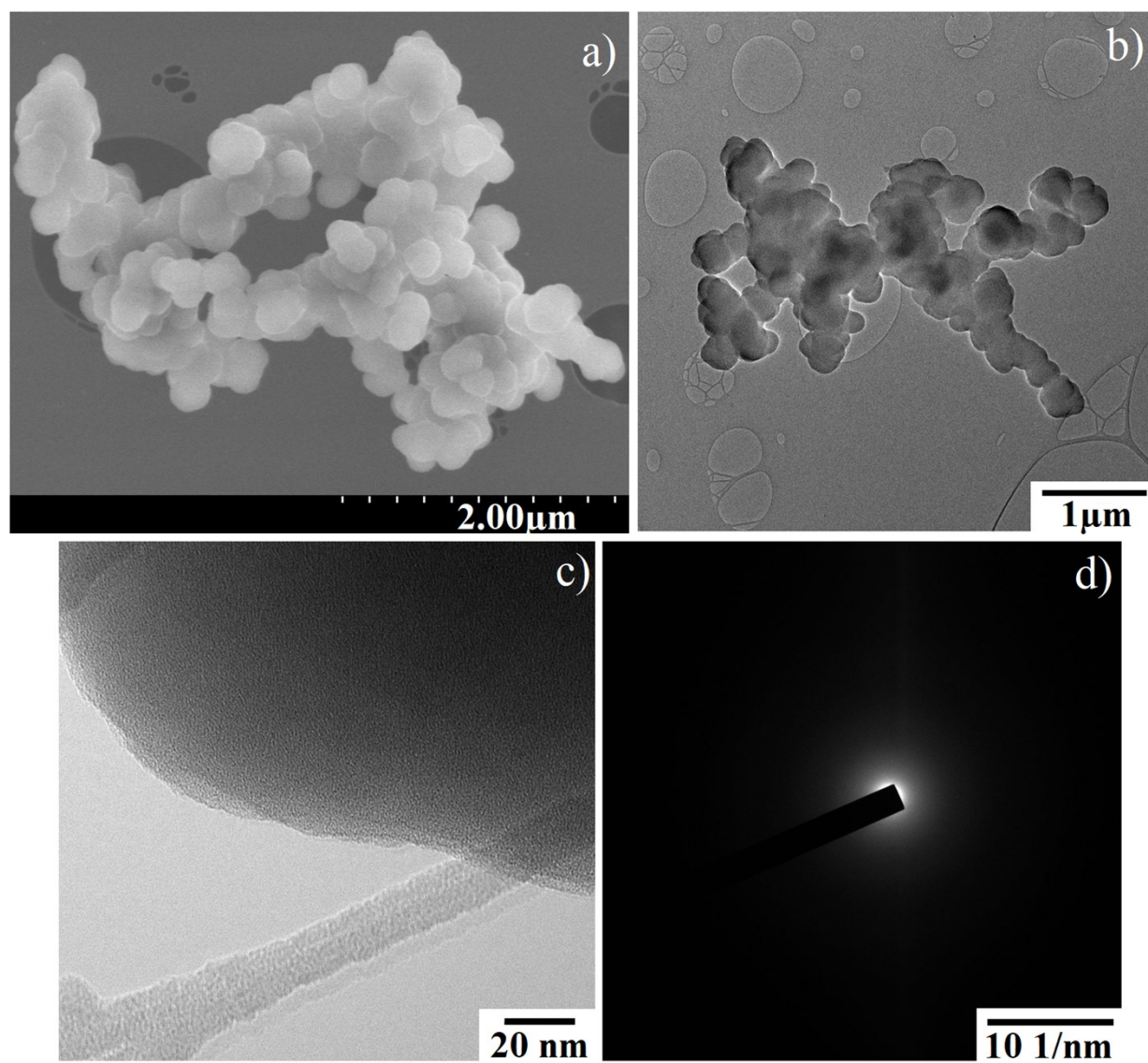


Fig. S2 a) SEM image; b) and c) TEM images; d) SAED pattern of Cu-SOPs.

Table S1 Solvent systems used for the solvothermal synthesis of Cu-SOP.

SN	Sample	Solvent system	Yield (%)
1.	Cu-SOP _{SDMA}	(Dioxane: Mesitylene: 3M Acetic Acid) 1:1:1	13
2.	Cu-SOP _{SDMF}	DMF	37
3.	Cu-SOPs	DMSO	89

Reaction conditions: benzene-1,3,5-tricarboxaldehyde (40.5 mg), 2,5-diaminobenzene sulfonic acid (47.0 mg) and CuCl₂ (33.5 mg), solvent (20 mL), temperature (140 °C) and time (12 h)

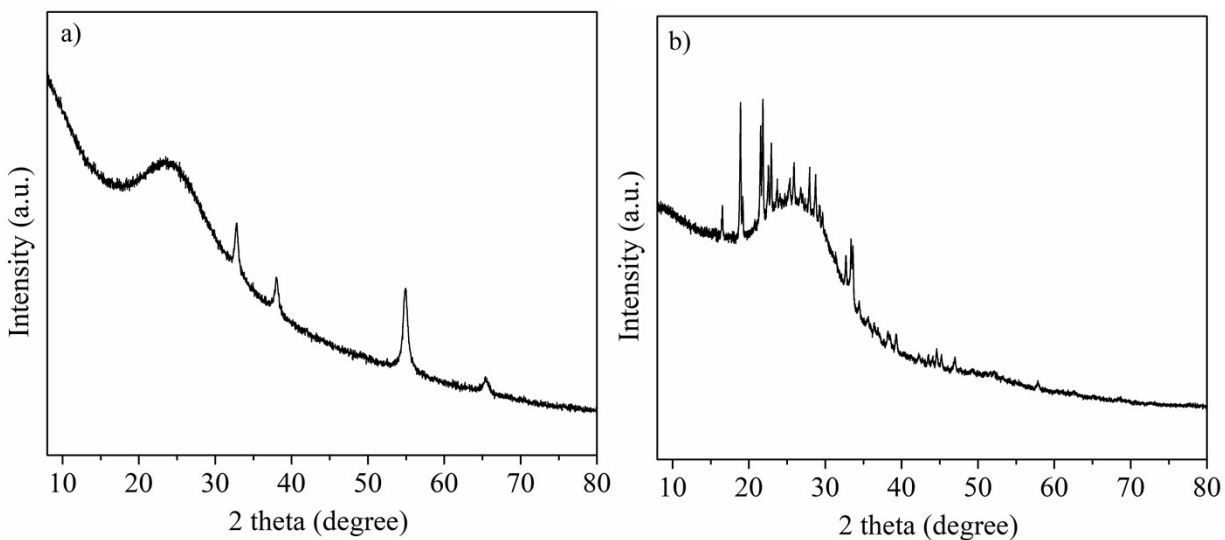


Fig. S3 a), b) XRD diffraction patterns of Cu-SOP_{SDMF} and Cu-SOP_{SDMA}, respectively.

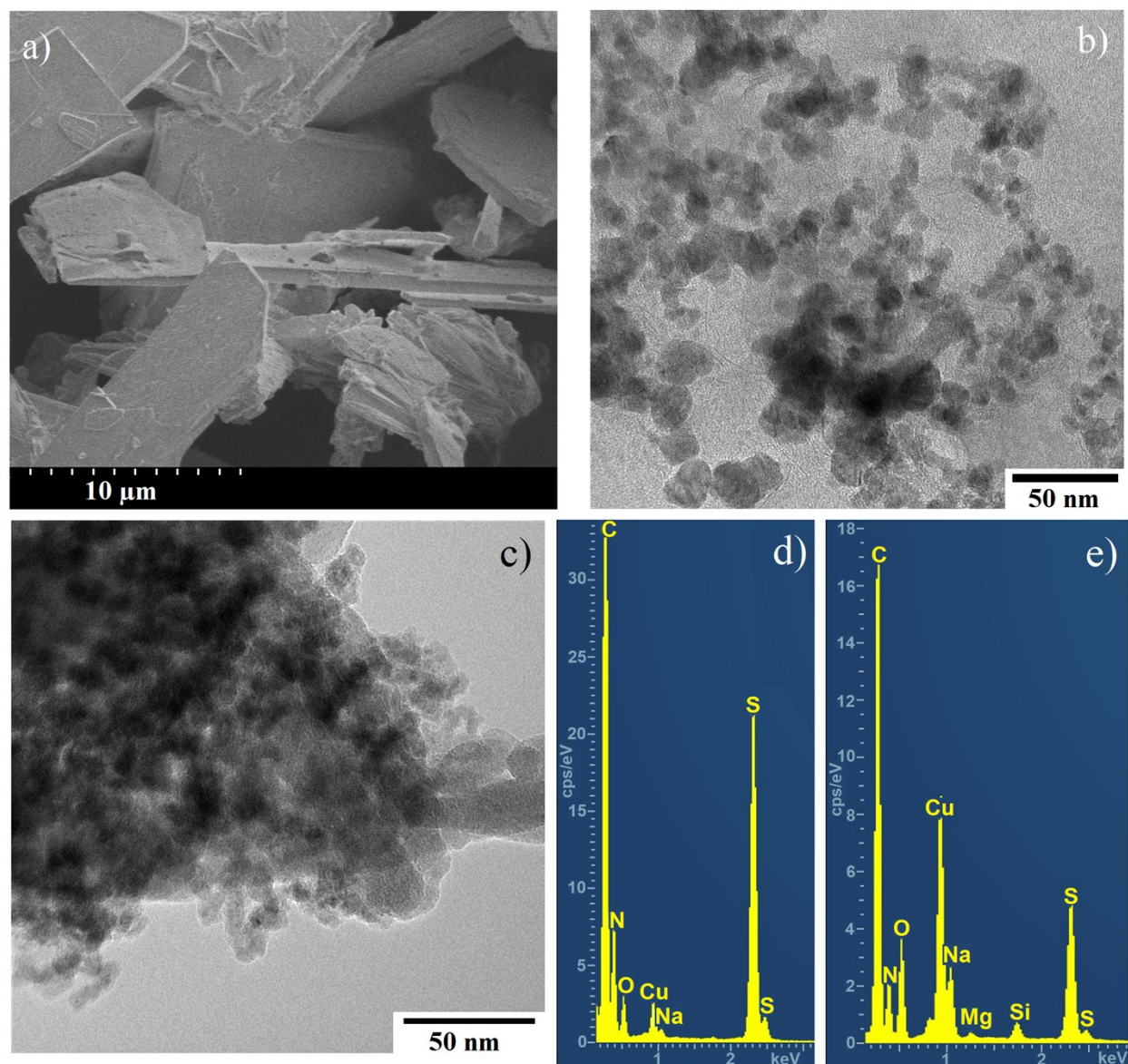


Fig. S4 a) SEM image of DABSA; b),c) TEM images and d),e) EDX spectra of Cu-SOP_{SDMF} and Cu-SOP_{SDMA}, respectively.

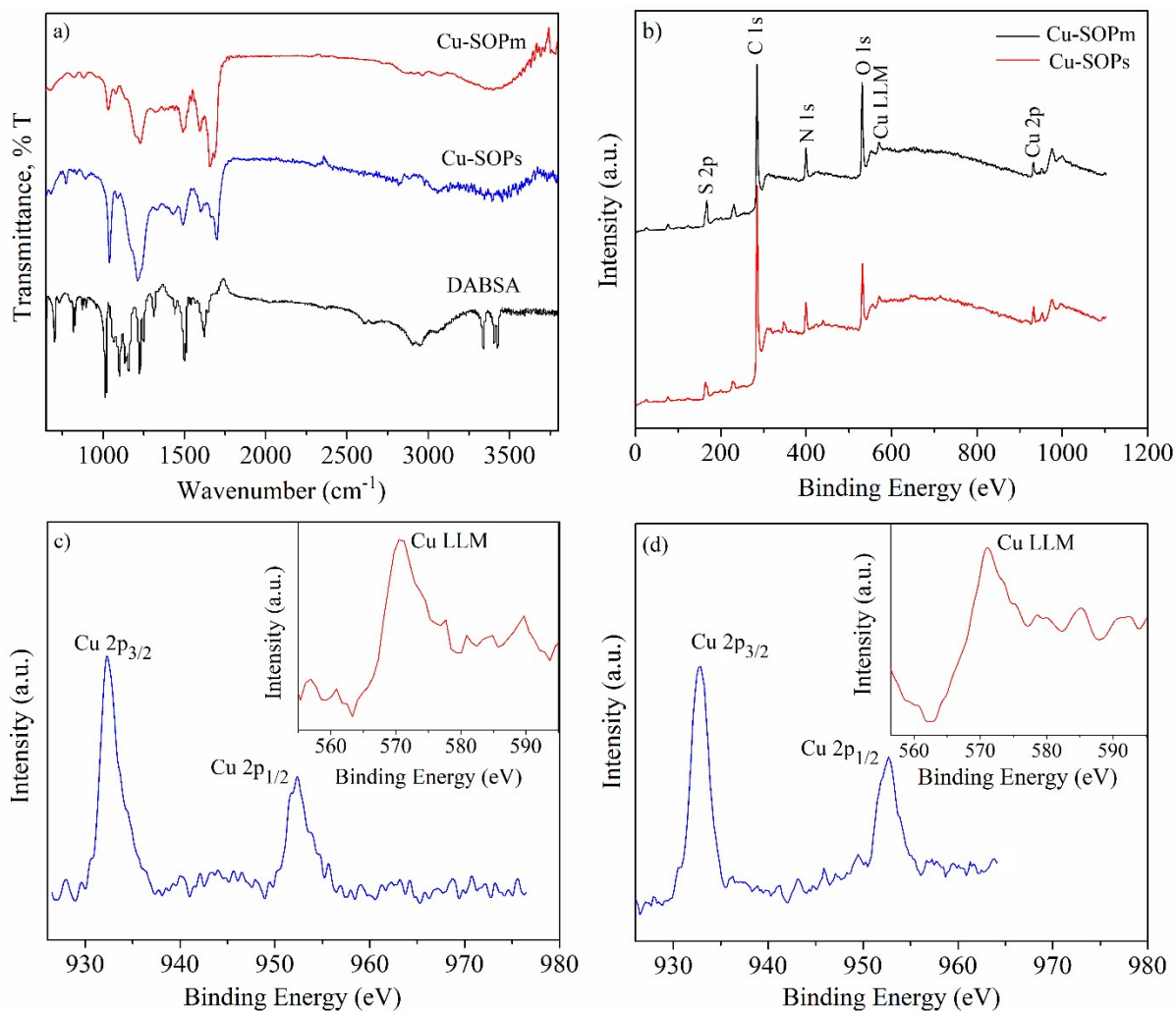


Fig. S5 a) FT-IR spectra; b) Survey scans; c) and d) High-resolution Cu2p XPS spectra with Cu LLM Auger XPS spectra (inset) of Cu-SOPm and Cu-SOPs, respectively.

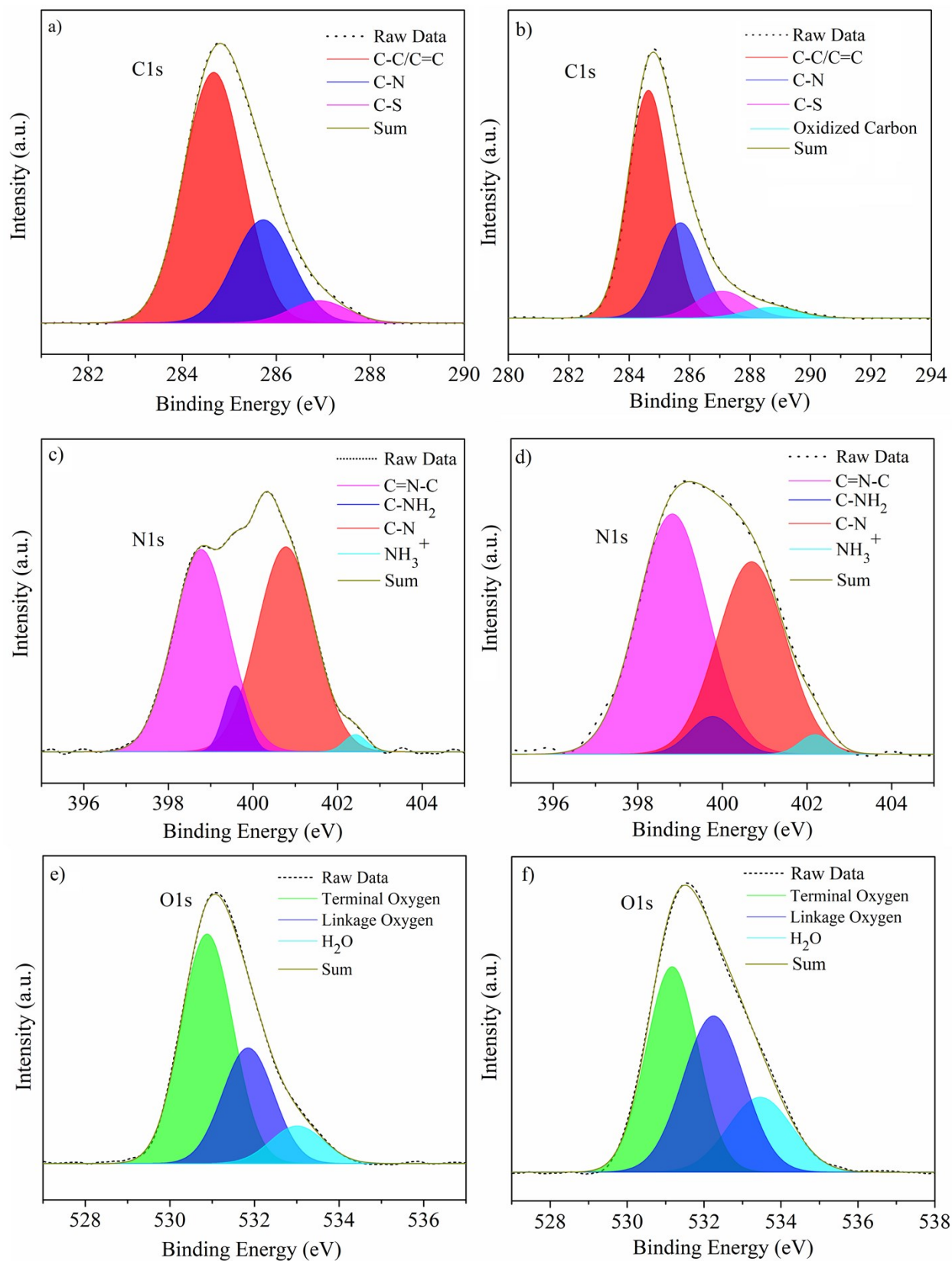
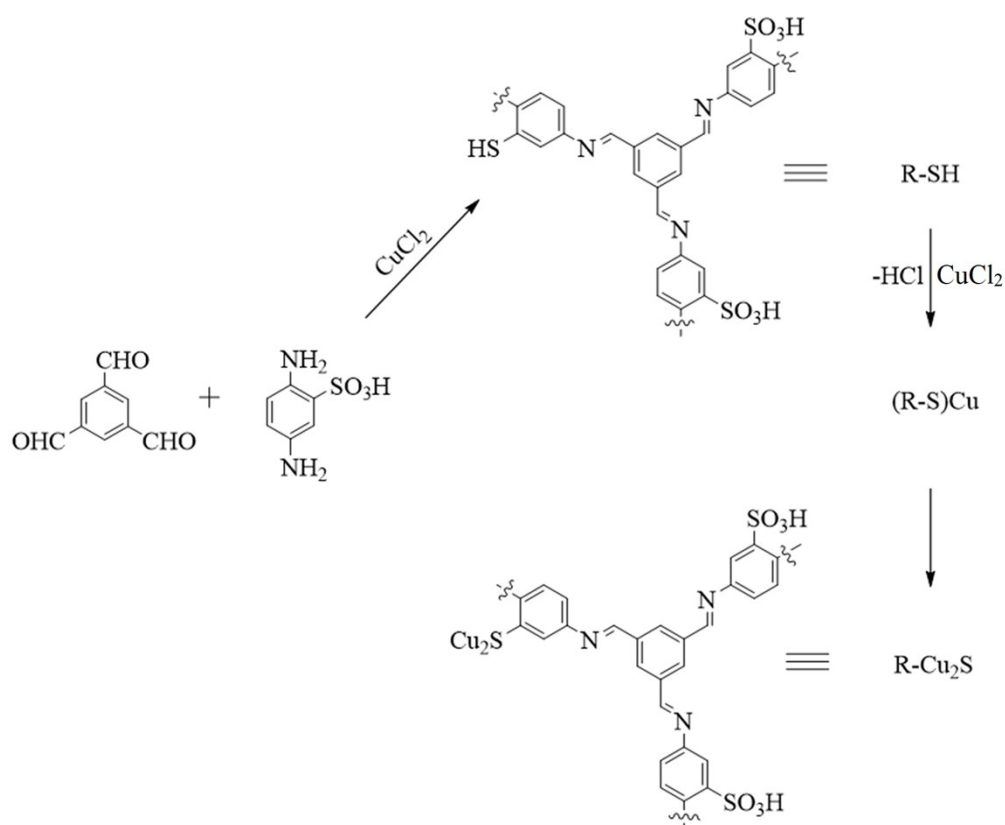


Fig. S6 a),b) High-resolution C1s XPS spectra; c),d) High-resolution N1s XPS spectra and e),f) High-resolution O1s XPS spectra of Cu-SOPm and Cu-SOPs, respectively.

Comment: The bonding pattern of the C1s, N1s, and O1s for Cu-SOPs is similar to Cu-SOPm except the C1s XPS spectra that shows one extra broad peak at 288.8 eV corresponding to the oxidized carbon. Moreover, the peak intensities of the respective bonding pattern are also similar for C1s and O1s but differ for the N1s. The peak intensity associated with the C=N-C is higher for Cu-SOPs, which indicates improved imine condensation.



Scheme S1 Plausible reaction mechanism of catalyst formation.

Calculation for $\text{MeOH}_{\text{Conversion}}$, $\text{DMC}_{\text{Yield}}$ and $\text{DMC}_{\text{Selectivity}}$

$$\text{MeOH}_{\text{Conversion}} (\%) = \frac{\text{mmol of MeOH consumed}}{\text{mmol of MeOH taken}} \times 100$$

$$\text{DMC}_{\text{Selectivity}} (\%) = \frac{\text{mmol of DMC formed}}{\text{mmol of all products formed}} \times 100$$

$$\text{DMC}_{\text{Yield}} (\%) = \text{MeOH}_{\text{Conversion}} \times \text{DMC}_{\text{Selectivity}} \times 100$$

Determination of TON, TOF and Space velocity

$$\text{Turnover number (TON)} = \frac{\text{mmol of DMC formed}}{\text{mmol of catalyst (active sites)}}$$

$$\text{Turnover frequency (TOF)} = \frac{\text{Turnover number (TON)}}{\text{Time of reaction}}$$

$$\text{Gas Hour Space Velocity (GHSV)} = \frac{\text{Feed flow rate (mL/h)}}{\text{Weight of the catalyst (g)}}$$

Calculation for $\text{MeOH}_{\text{Mass Loss}}$

$$\text{MeOH}_{\text{Mass Loss}} (\%) = \frac{\text{mmol of MeOH taken} - \left[\begin{array}{c} \text{mmol of unreacted MeOH} \\ + \\ 2 \times \text{mmol of DMC formed} \end{array} \right]}{\text{mmol of MeOH taken}} \times 100$$

Preferential water adsorption over Cu-SOPm

The preferential adsorption of water molecules over Cu-SOPm was evaluated using ^1H -NMR technique. First, 100 μL of water, 100 μL of methanol and 1000 μL of THF were taken in a 5 mL vial and then 20 mg of Cu-SOPm, catalyst was added to it. Vial was sealed and the resulting mixture was stirred for 12 h at room temperature. 20 μL of the water-methanol-THF mixture (untreated and treated with Cu-SOPm catalyst) were used to record the ^1H -NMR spectra using 500 μL D_2O solvent.

Recycling study

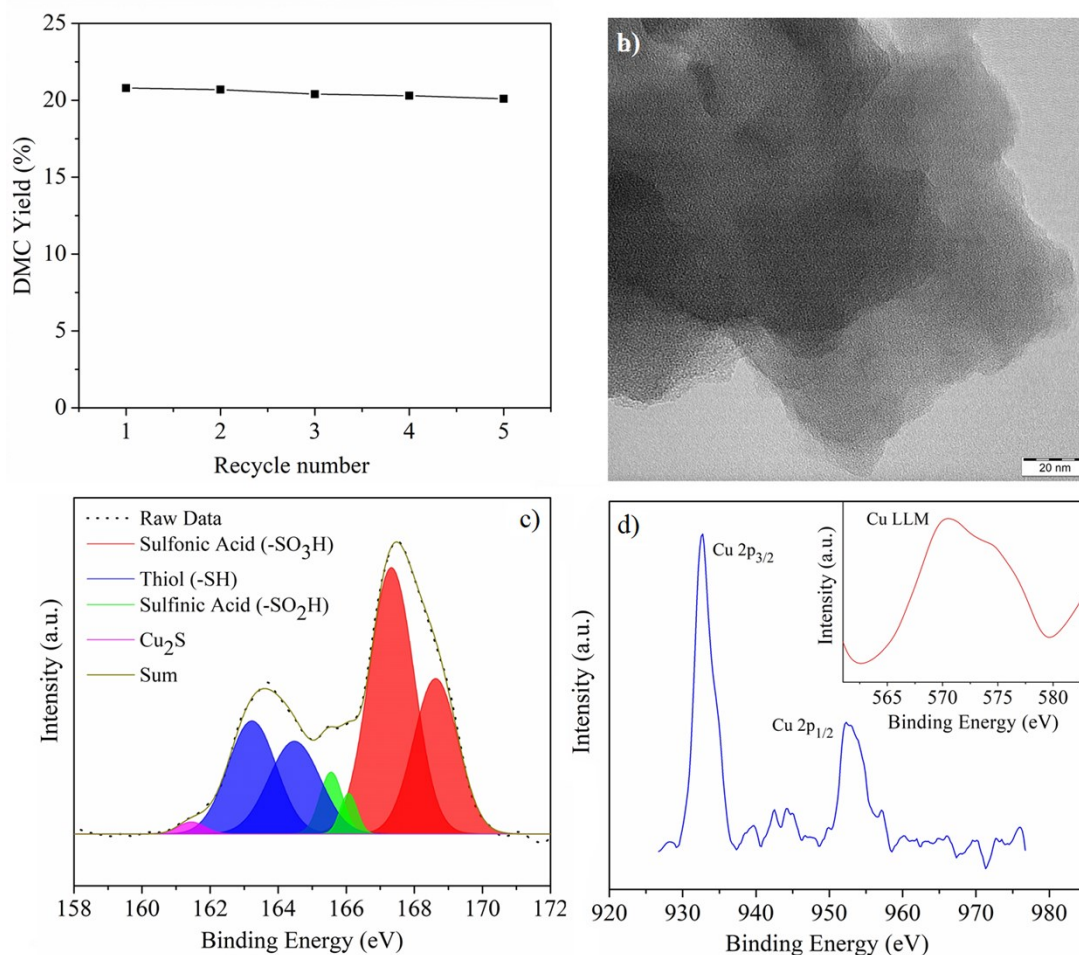


Fig. S7 a) Recycling test of Cu-SOPm for each 24 h under the similar reaction conditions; b) TEM image; c) S2p XPS spectra and d) Cu2p XPS spectrum with Cu LLM Auger XPS spectrum (inset) of Cu-SOPm reused catalyst.

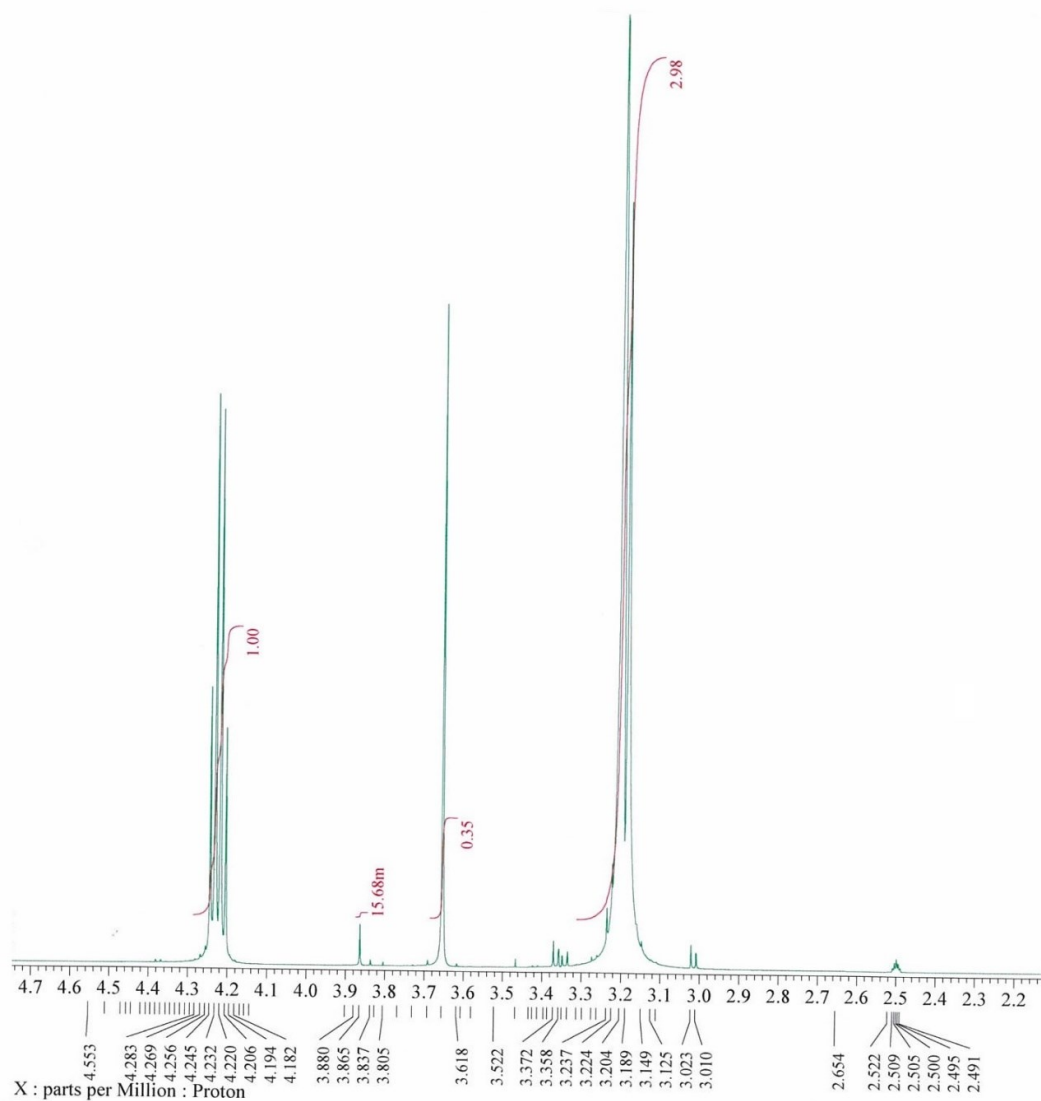


Fig. S8 ^1H -NMR of reaction mixture using DMSO- d_6 solvent.

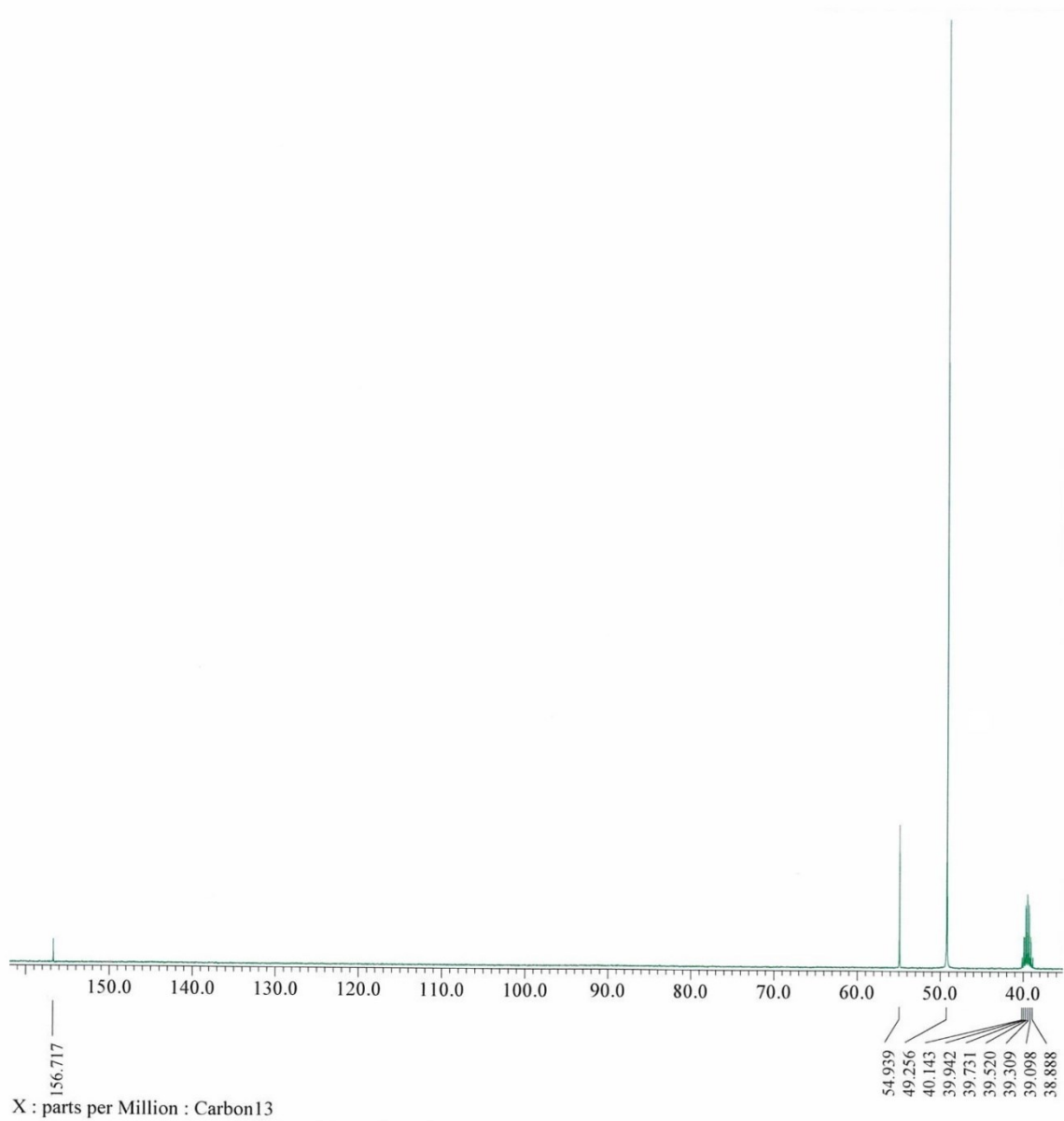


Fig. S9 C^{13} -NMR of reaction mixture using DMSO- d_6 solvent.