Electronic Supplementary Information (ESI)

for

A gelator-starch blend for dry powder based instant solidification of crude oil at room temperature

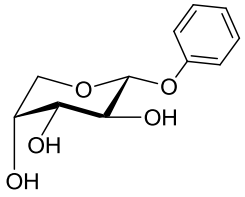
Department of Chemistry, Indian Institute of Technology (ISM), Dhanbad, 826004, Jharkhand, India. Corresponding author email: somnath@iitism.ac.in

Experimental Procedures

General Procedures

All chemicals, solvents and reagents were procured from commercial sources and were used as received. Column chromatography was performed by using silica gel (230-400 mesh) under medium pressure. TLC was performed on precoated aluminium plates of silica gel 60-F254. TLC spots were visualized by staining with a vaniline solution and subsequent heating on a hot plate. 1H and 13C NMR spectra were recorded on Bruker AC-400 NMR spectrometer at 400MHz (1H) and 100 MHz (13C) in solutions of $CDCl_3$ or DMSO-*d*6. δ Values are reported in parts per million (ppm) and coupling constants (J) in Hertz. The crude oil obtained in this study were procured from ONGC and soluble starch was procured from Rankem Fine Chemicals Limited.

Synthesis of 1-(phenoxy)-β-D-arabinopyranoside (2a)



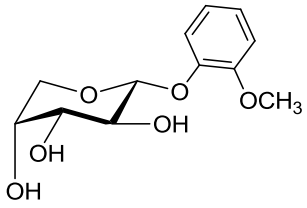
1,2,3,4-tetra-*O*-acetyl-D-arabinopyranose (5.95 g, 18.69 mmol) was dissolved in acetic acid (104 mL) followed by the drop wise addition of phosphorus tri-bromide (17.75 mL, 186.88 mmol) under nitrogen atmosphere. The solution was stirred at room temperature for 4 hours after which the reaction mixture was poured into ice/water (200 mL) and the aqueous phase was extracted thrice with dichloromethane (DCM, 80 mL each). The combined extract was then washed with brine and then dried over anhydrous (Na_2SO_4). Concentration of the extract in *vacuo* yielded a colorless solid of 2,3,4- tri-*O*-acetyl-1-bromo-□-D-arabinopyranoside (5.42 g, 85%).

Subsequently, the 2,3,4-tri-*O*-acetyl-1-bromo-α-D-arabinopyranoside (5.42 g, 15.98 mmol) was dissolved in anhydrous DMF (20 mL) and phenol derivatives (2.10 mL, 23.97 mmol) fallowed by Sodium hydride (0.95 g, 39.95 mmol) was added to the reaction mixture. The progress of the reaction was monitored by TLC. After 2 h, when the reaction was completed, the mixture was quenched with EA. Then the reaction mixture was extracted thrice with EA (40 mL x 3). The combined organic extract was then dried over Na_2SO_4, filtered and concentrated in *vacuo* to yield the crude product. The crude product was purified by column chromatography (20% EA/PE) to afford 2,3,4-tri-*O*-acetyl-1-phenoxy-β-D-arabinopyranoside (3.03 g, 54%, over two steps from **1**).

Subsequently, the 2,3,4-tri-*O*-acetyl-1-phenoxy-β-D-arabinopyranoside (3.03 g, 8.60 mmol) was dissolved in methanol (10 mL) fallowed by Sodium methoxide (0.139 g, 2.57 mmol) was added to the reaction mixture. The progress of the reaction was monitored by TLC. After 1 h, when the reaction was completed, the mixture was neutralized with amberlite IR 120 H^+. Then

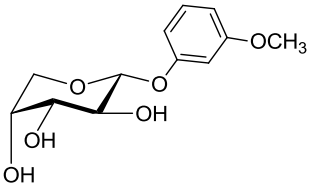
the reaction mixture was filtered and concentrated in *vacuo* to yield the crude product. The crude product was purified by column chromatography (8% MeOH/$CHCl_3$) to afford white solid phenoxy-β-D-arabinopyranoside (**2a**, 1.8 g, 93%, overall 43% from **1**) as a white solid. m.p. 148 – 150 °C $[\alpha]_D^{30}$ = –1.20 (c = 0.116 in MeOH); 1H NMR (400 MHz, d6-DMSO in CDCl3) δ (ppm) 7.30 – 7.25 (m, 2H), 7.02 – 6.97 (m, 3H), 5.17 (bs, 1H), 4.83 (d, J = 6.8 Hz, 1H), 4.77 (bs, 1H), 4.64 – 4.61 (bs, 1H), 3.78 (dd, J = 12.0 and 3.0 Hz, 1H), 3.74 (bs, 1H), 3.64 (m, 1H), 3.59 (dd, J = 11.9 and 1.3 Hz, 1H), 3.49 (dd, J = 8.7 and 3.2 Hz, 1H); 13C NMR (100 MHz, d6-DMSO in CDCl3) δ (ppm) 158.4, 130.4 (2C), 122.8, 117.5 (2C), 102.0, 73.7, 71.5, 68.7, 66.8; HRMS calcd. for C11H14O5Na+ (M + Na)+ 249.0739; found 249.0731.

Synthesis of 1-(2-methoxyphenoxy)-β-D-arabinopyranoside (2b)



It was synthesized following the general procedure and elution of the column with 8% methanol (MeOH) in Chloroform ($CHCl_3$) to afford **2b** (2.10 g, 44%) from compound **1** (over three steps) as a white solid. m.p. 152 – 154 °C $[\alpha]_D^{30}$ = 10.801 (*c* = 0.833 in MeOH); ^{1}H NMR (400 MHz, d_6-DMSO in $CDCl_3$) δ (ppm) 7.06 – 7.03 (m, 1H), 6.97 – 6.92 (m, 2H), 6.89 – 6.83 (m, 1H), 5.12 (d, *J* = 5.0 Hz, 1H), 4.89 (d, *J* = 6.2 Hz, 1H), 4.67 (d, *J* = 6.0 Hz, 1H), 4.59 (d, *J* = 4.4 Hz, 1H), 3.78 (s, 3H), 3.77 (bs, 1H), 3.75 – 3.73 (m, 1H), 3.72 – 3.67 (m, 1H), 3.54 – 3.50 (m, 2H); ^{13}C NMR (100 MHz, d_6-DMSO in $CDCl_3$) δ (ppm) 150.8, 147.2, 123.5, 121.7, 117.9, 113.8, 101.9, 73.6, 71.4, 68.2, 66.1, 56.8; HRMS calcd. for $C_{12}H_{16}O_6Na^+$ $(M + Na)^+$ 279.0845; found 279.0841.

Synthesis of 1-(3-methoxyphenoxy)-β-D-arabinopyranoside (2c)



It was synthesized following the general procedure and elution of the column with 8% methanol (MeOH) in Chloroform ($CHCl_3$) to afford **2c** (1.71 g; 36%) from compound **1** (over three steps) as a white solid. m.p. 149 – 151 °C $[\alpha]_D^{30}$ = 2.357 (*c* = 0.467 in MeOH); ^{1}H NMR (400 MHz, d_6-DMSO in $CDCl_3$) δ (ppm) 7.10 – 7.06 (m, 1H), 6.55 – 6.46 (m, 3H), 5.09 (d, *J* = 4.8 Hz, 1H), 4.74 (d, *J* = 6.9 Hz, 1H), 4.63 (d, *J* = 5.6 Hz, 1H), 4.48 (d, *J* = 4.0 Hz, 1H), 3.79 (dd, *J* = 12.1 and 2.9 Hz, 1H), 3.74 (bs,

1H), 3.68 (s, 3H), 3.64 (ddd, *J* = 10.1, 5.3 and 5.2 Hz, 1H), 3.53 – 3.46 (m, 2H); ^{13}C NMR (100 MHz, d_6-DMSO in $CDCl_3$) δ (ppm) 160.1, 158.3, 129.5, 108.4, 107.1, 102.7, 100.9, 72.6, 70.3, 67.4, 65.5, 54.8; HRMS calcd. for $C_{12}H_{16}O_6Na^+$ $(M + Na)^+$ 279.0845; found 279.0842.

Gelation Tests (Heating-cooling cycle)

Gelation test were carried out by adding exact weights of compounds **2a-2d** individually to 1 ml of appropriate solvent in a vial. The vial was sealed and the mixture was heated to dissolve the compound to get a clear solution. The solution was allowed to cool after which gelation was tested by inverting the sample vial. If the inverted vial was able to hold the system, it was considered as a gel. Apart from **2b** and **2d** the other phenolic arabinoside derivatives **2a**, **2c** were also tested in the same manner but they were not able to form gels in any solvent at 1% (w/v) concentration.

Determination of Gelation time by the dry powder method

Measured amounts of the powder gelator (2.5 mg, 5.0 mg, 10 mg or 20 mg) were added to separate sample vials containing 1 mL of the crude oil. The resultant mixture was left undisturbed and ckecked for gelation by the inversion method after designated regular intervals of time.

Solidification of crude oil from biphasic oil-water mixture using carrier solvent

Over a sample of saline water (4 mL) in a vial, 1.5 mL of crude oil was poured. Then to the floating crude oil layer a hot solution of **2b** in petrol (0.5 mL) was added. The resulting biphasic mixture was set aside for 2 minutes after which the crude oil layer formed a gel. The vial was inverted to visualize the formation of the gel when the crude oil gel layer was able to support the weight of the saline water.

Determination of the maximum gellable volume of crude oil by gelator-starch composite.

25 mg of the gelator-starch composite of different compositions was added to 1 mL of crude oil in a sample vial and the mixture was allowed to stand undisturbed for 30 s at room temperature. Then the vial was inverted to check for gelation. If the mixture passed the test, the experiment was repeated with fresh crude oil by 0.5 mL increments of volume each time until the maximum volume was reached when the gelation test was successful and beyond which the gelation test failed.

Determination of MGC

In a sample vial, gelator **2b** (1 mg) was added to the solvent (1 mL). The mixture was then heated until a clear solution was obtained. Then the solution was cooled and the vial was inverted to

confirm gelation. If partial or no gelation was observed, the cycle was repeated by adding 1 mg of **2b** at the beginning of each heating–cooling cycle until complete gelation of the solvent was observed upon inversion of the vial.

Field Emission Scanning Electron Micrographs (FESEM)

The experiments were performed by using a Zeiss supra-55 FESEM. The xerogels of the samples were prepared by drop casting the hot 1% (w/v) solution of gelator **2b** in benzene on a glass slide (2mm x 2mm) and drying them overnight in air inside a vacuum dessicator. The xerogel was then placed on a stub which was then coated with gold by a Quorum -Q150RES sputter coater under vacuum of 5 x 10^{-5} millibar and a current of 20 mA for 2 minutes.

Rheological experiments

Rheological properties of gel sample were determined by using a Bohlin Gemini-2 Malvern rheometer using parallel plates (25 mm, stainless steel). The gap between the parallel plates was 500 micron. The experiments were carried out for gels of **2b** at 1.0% (w/v) concentration. The gel samples were placed on parallel plates by spatula in such a way that it covered the surface of the parallel plates. The different tests Dynamic strain sweep (DSS) and Dynamic Frequency sweep (DFS) were performed to determine the viscoelastic nature of the gels. DSS experiment were carried out at a constant frequency of 1 Hz at temperature 25 °C. The strain value was determined at a point where tan δ = 1 (G" = G'). Variation of storage modulus (G') and loss modulus (G") was tested within frequency range of 1Hz to 100 Hz at strain of 0. 01 % by DFS experiments.

FTIR experiments

FTIR experiments were carried out on an Agilent Cary 600 series FTIR spectrometer. Samples for IR experiments in the crystalline states were prepared by crystallization from $CHCl_3$-Petroleum ether mixtures. For FTIR experiments in the gel state, the benzene gel of 2b was analyzed directly in the ATR mode.

Wide Angle X-ray Diffraction (WXRD)

The xerogels of the sample were prepared by drying a benzene gel of **2b** overnight in a vacuum dessicator. The WXRD diffractogram of the samples were recorded on a Proro-AXRD diffractometer. X-rays of wavelength 1.54 Å were used.

Additional Figures

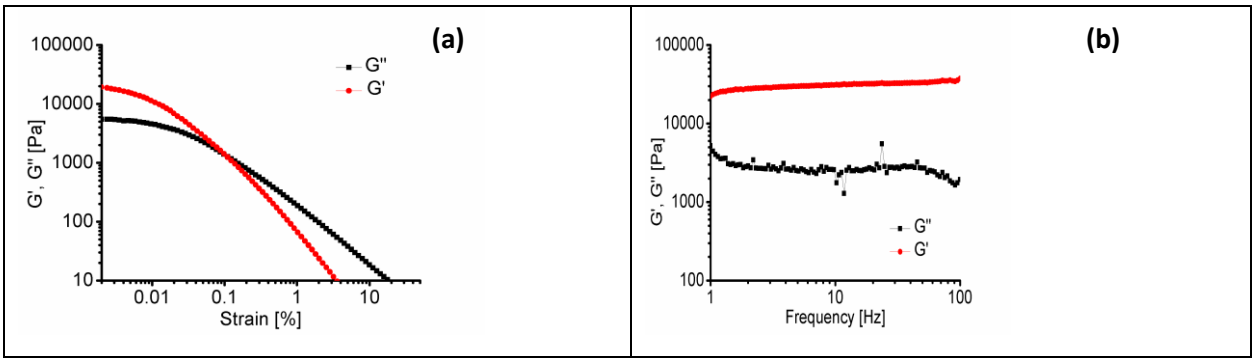


Figure S1 Rheology of **2b** gel with benzene at 1% (w/v) at 25°C (a) DSS curve at frequency 1 Hz (b) DFS curve at strain 0.001%.

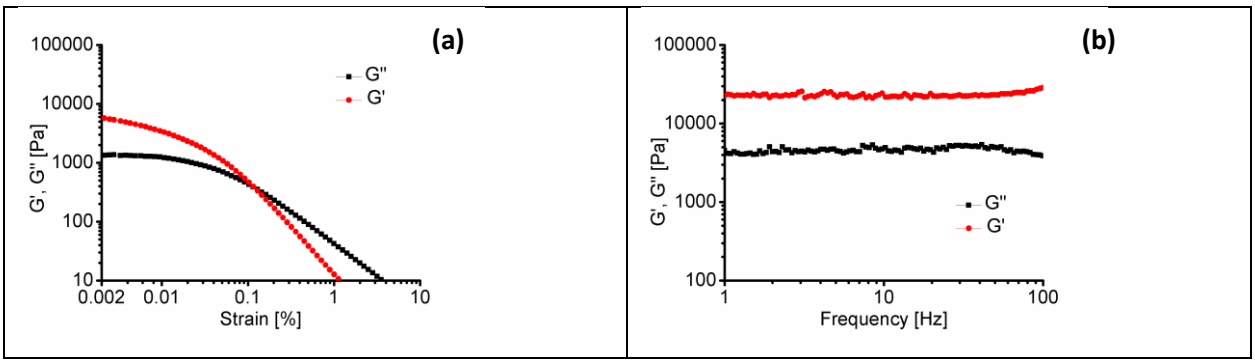


Figure S2. Rheology of **2b** gel with petrol at 1% (w/v) at 25°C (a) DSS curve at frequency 1 Hz (b) DFS curve at strain 0.001%.

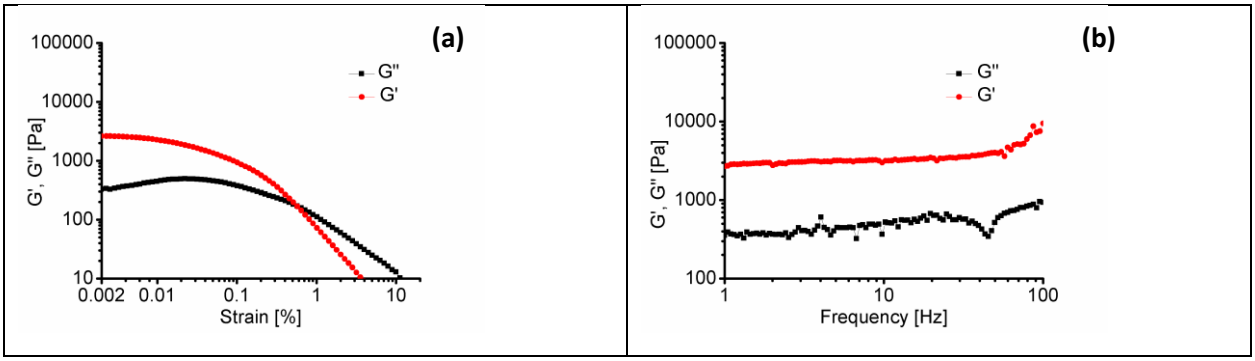


Figure S3 Rheology of **2b** gel with diesel at 1% (w/v) at 25°C (a) DSS curve at frequency 1 Hz (b) DFS curve at strain 0.001%.

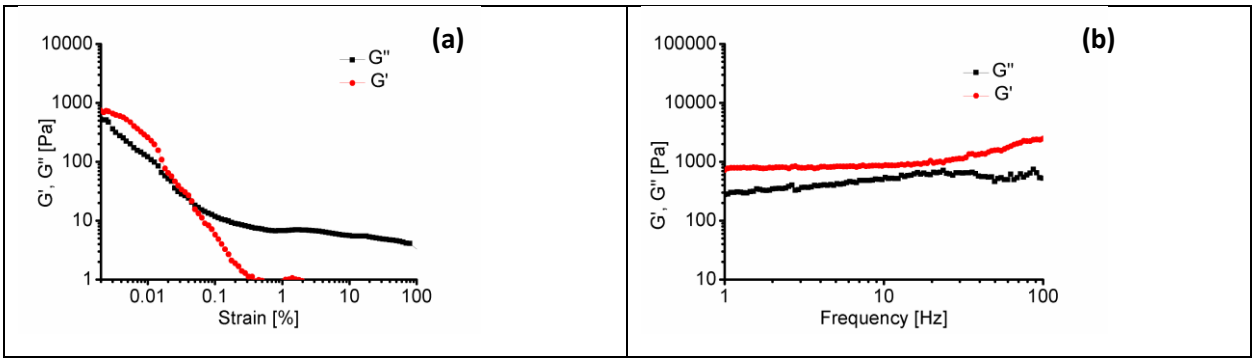


Figure S4. Rheology of **2b** gel with crude-oil at 1% (w/v) at 25 °C (a) DSS curve at frequency 1 Hz (b) DFS curve at strain 0.002%.

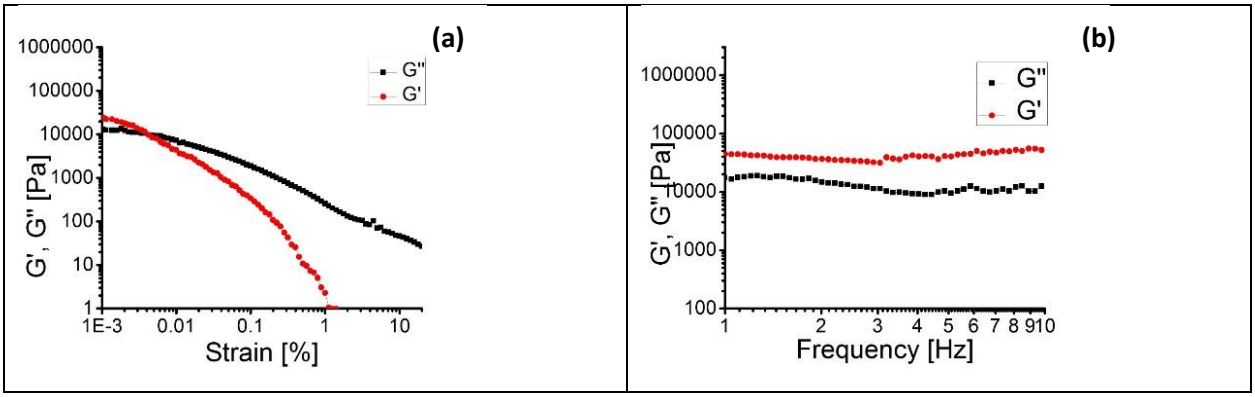


Figure S5. Rheology of **GSB-1** gel with crude-oil at 1% (w/v) at 25 °C (a) DSS curve at frequency 1 Hz (b) DFS curve at strain 0.002%.

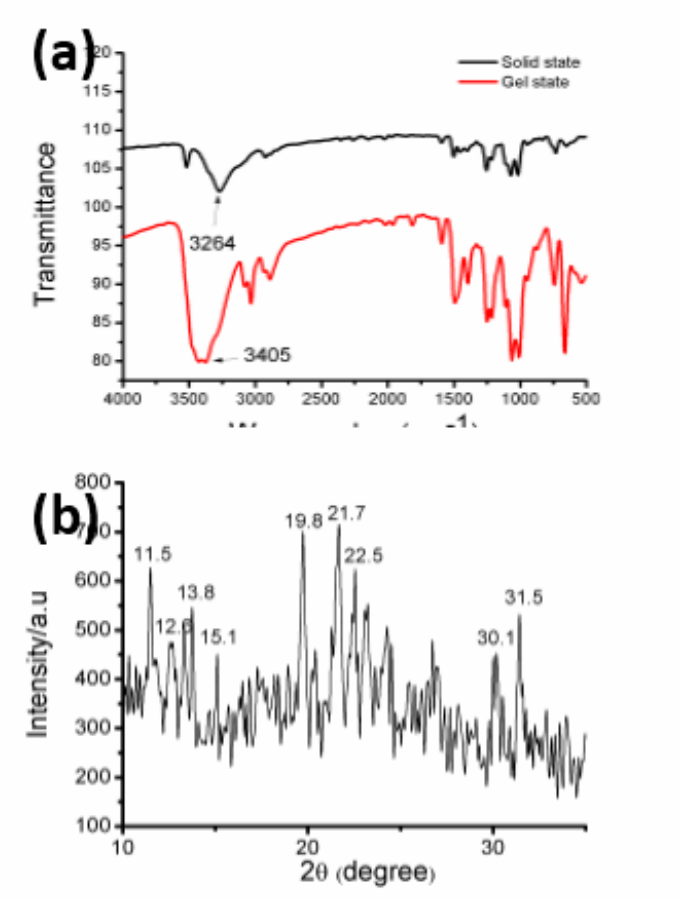


Figure S6. (a) FTIR spectra of crystalline (black) and benzene gel (red) of **2b**. (b) WXRD diffractogram of xerogel of **2b.**

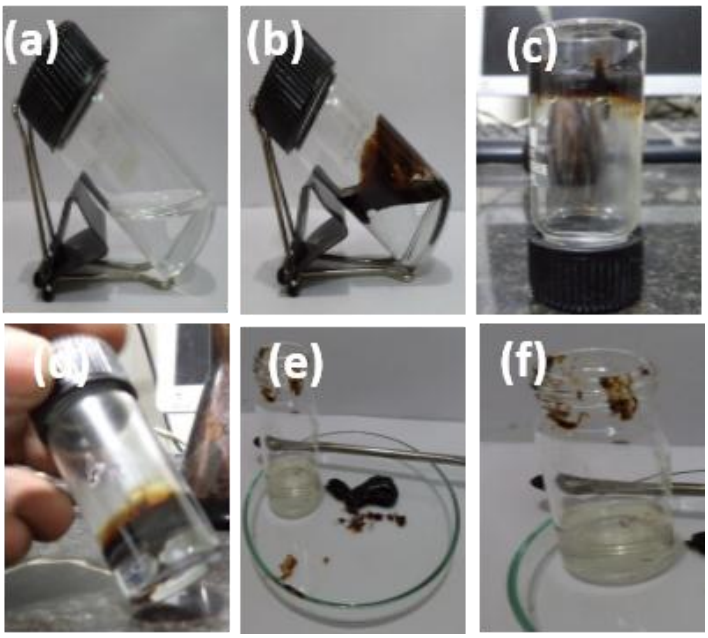


Figure S7. Phase selective organogelation of crude oil by using carrier solvent (a) water (b) biphasic mixture of crude oil and water (c & d) gelled crude oil layer on water (e) recovered solidified crude oil (f) water after removal of solidified crude oil.

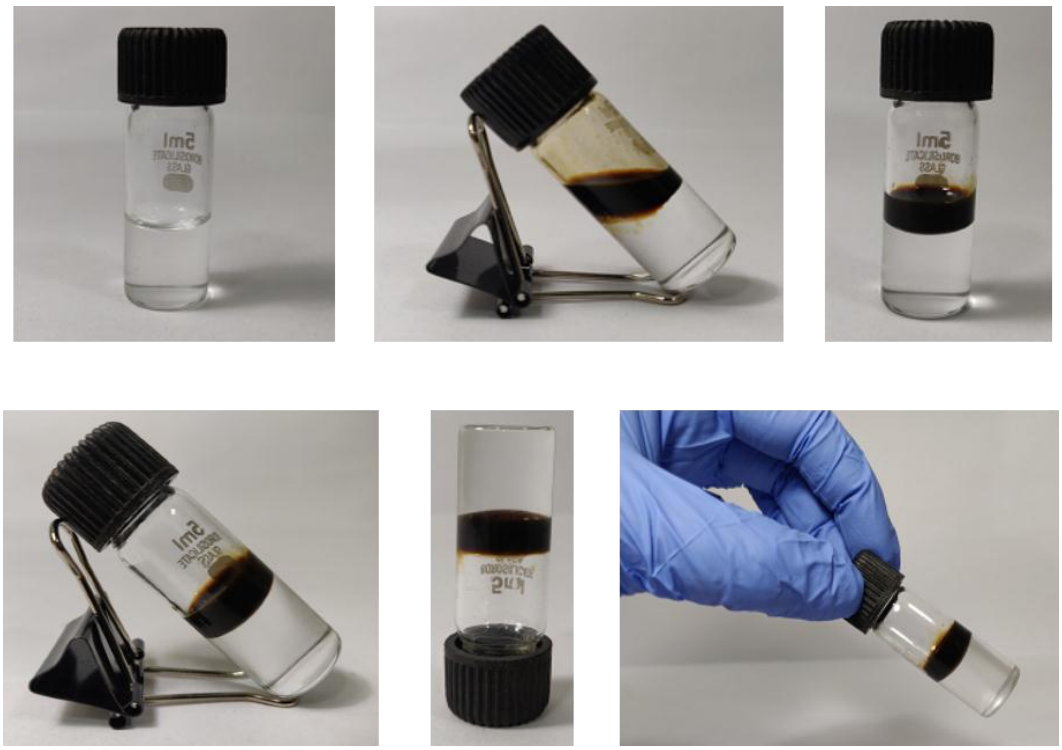


Figure S8. PSOG experiment on a small scale using GSB-1.

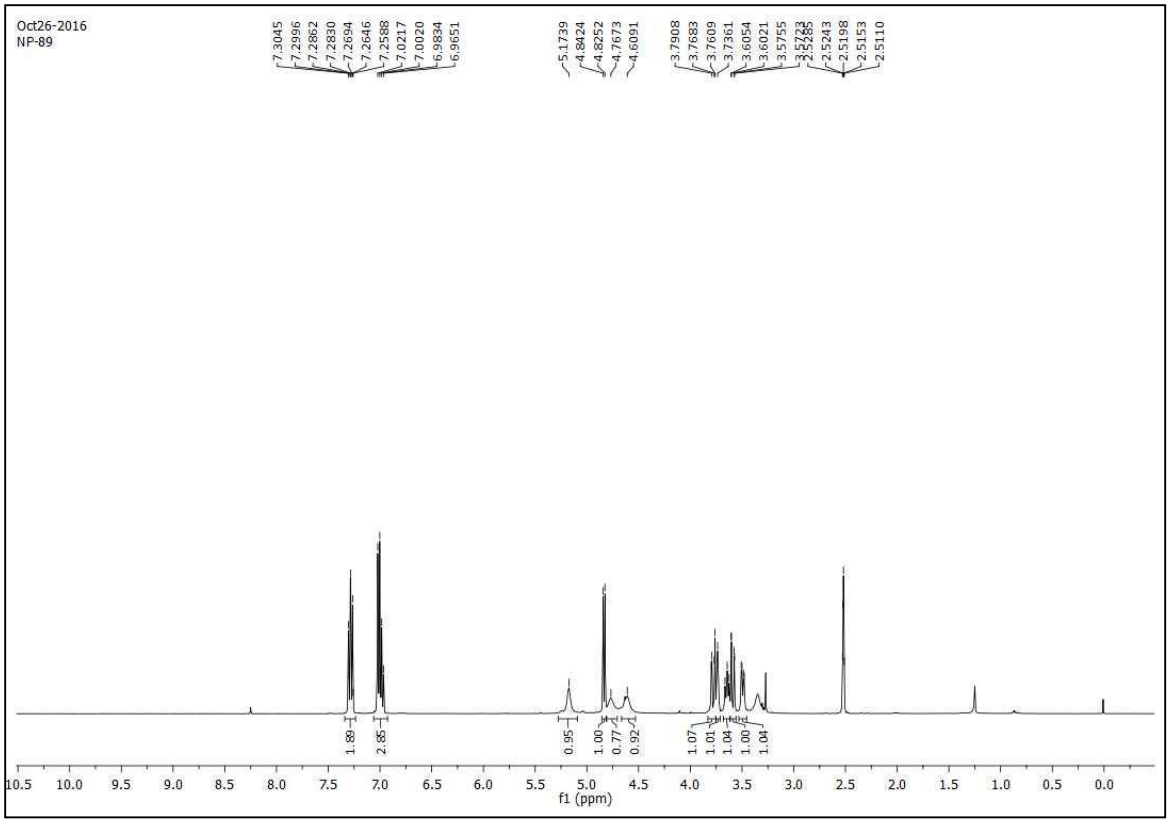


Figure S9. ^{1}H-NMR (400 MHz, DMSO-d6) spectra of **2a**.

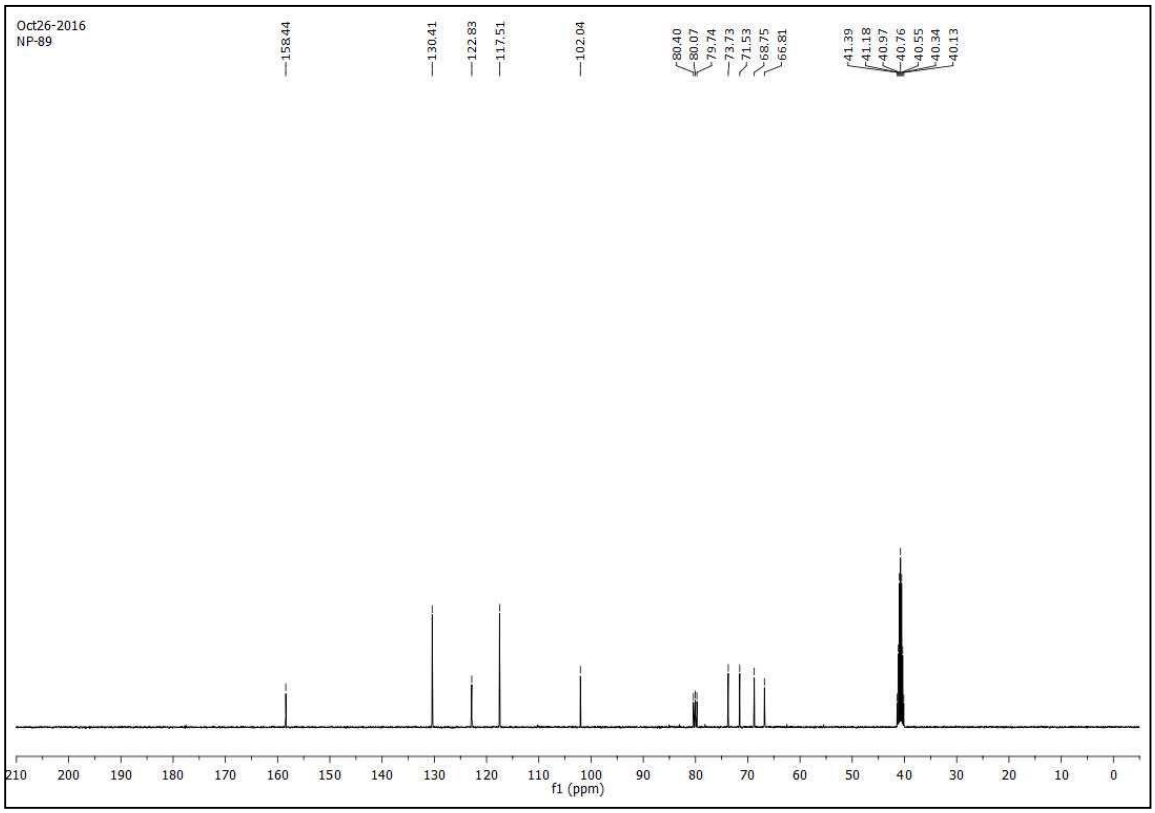


Figure S10. ^{13}C-NMR (100 MHz, DMSO-d6) spectra of **2a**.

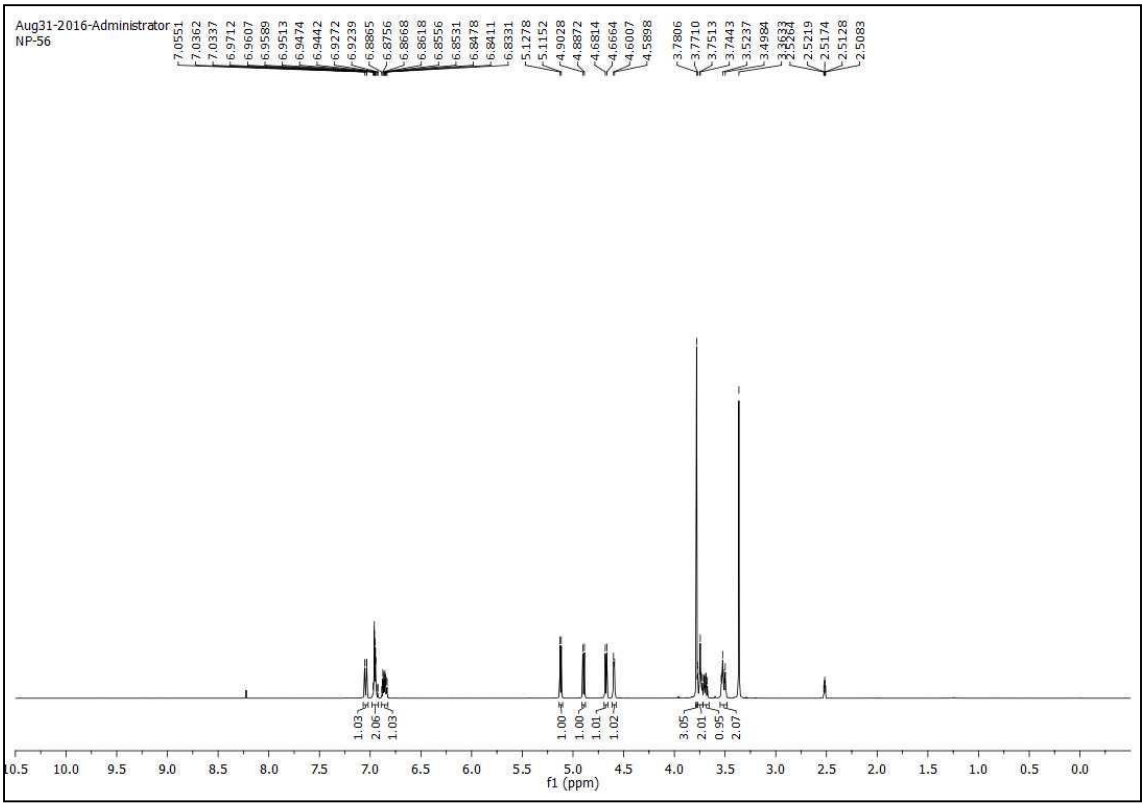


Figure S11. ^{1}H-NMR (400 MHz, DMSO-d6) spectra of **2b**.

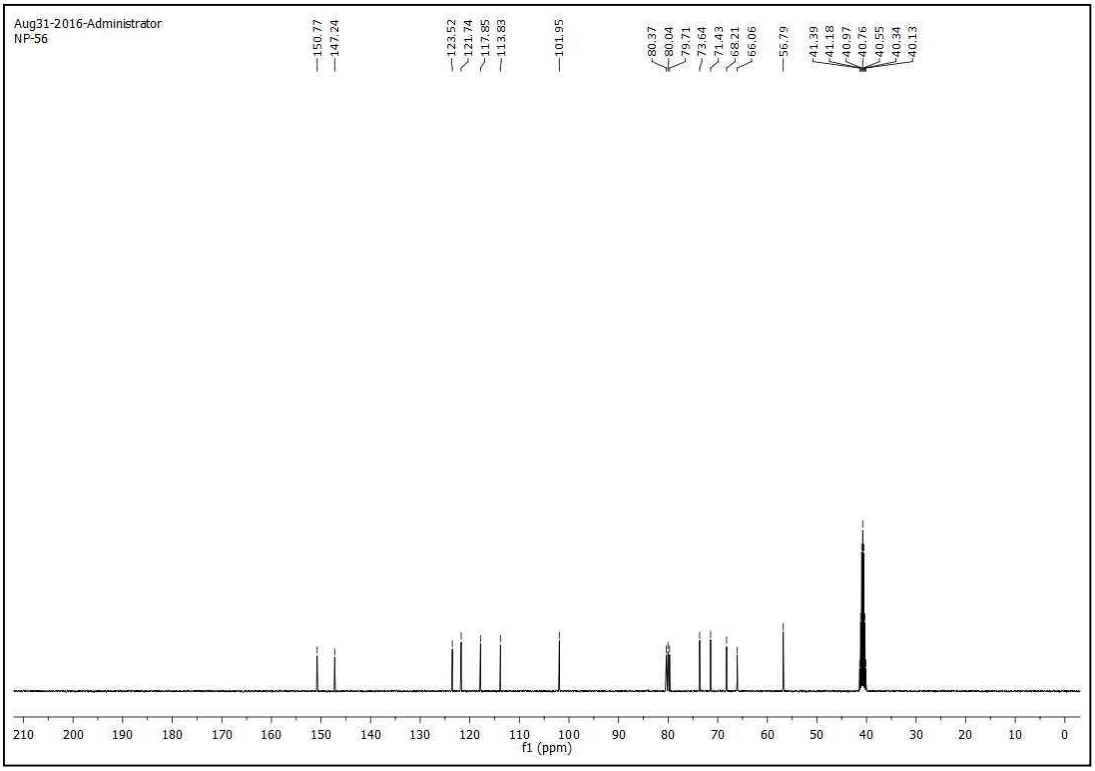


Figure S12. ^{13}C-NMR (100 MHz, DMSO-d6) spectra of **2b**.

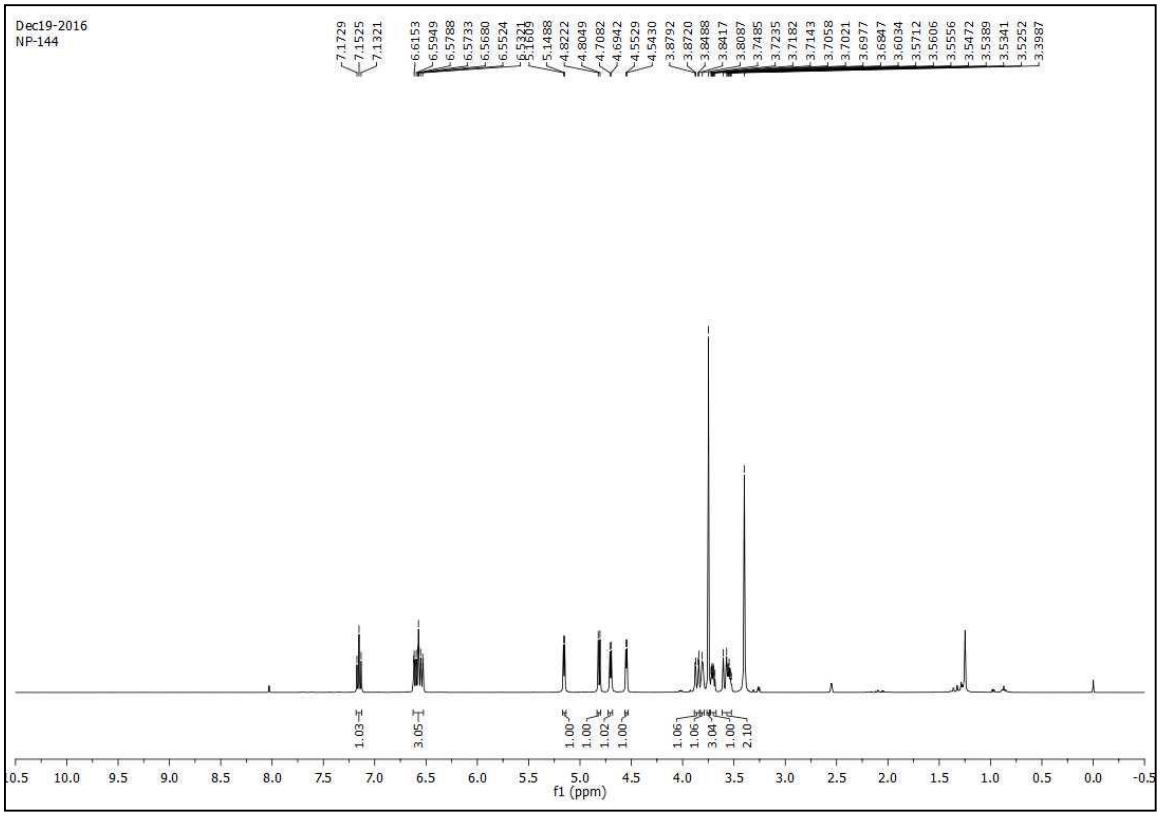


Figure S13. ^{1}H-NMR (400 MHz, DMSO-d6) spectra of **2c**.

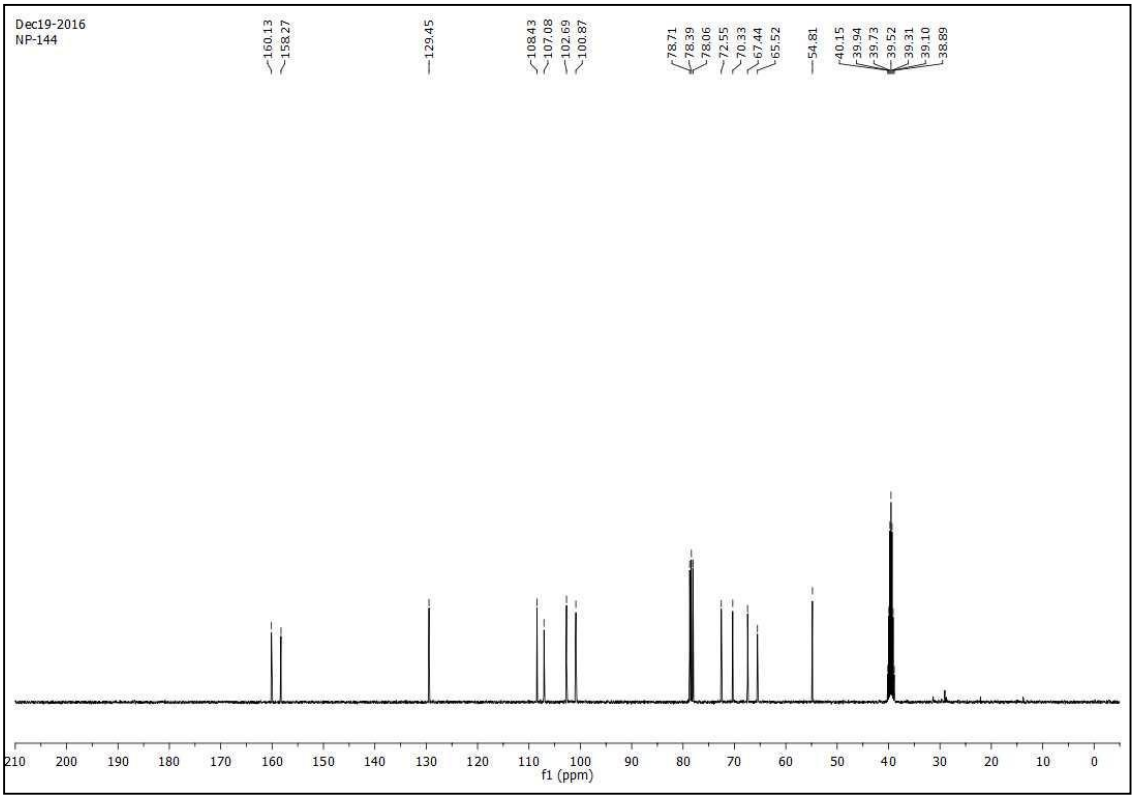


Figure S14. ^{13}C-NMR (100 MHz, DMSO-d6) spectra of **2c**.