

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI†)

FOR

Enantiomeric organogelators from D-/L- arabinose for phase selective gelation of crude oil and their gel as a photochemical micro reactor

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Experimental

1.1 General

Starting materials and solvents were purchased from commercial sources and were used as purchased, without further purification.

1.2 Synthesis of β -3,4-isopropylidene-D-arabinopyranoside (D-1) or β -3,4-isopropylidene-L-arabinopyranoside (L-1)

Compounds D-1 and L-1 were prepared following the procedure reported by Kiso and Hasegawa.¹ The spectroscopic data of D-1 corresponded well with those reported.²

To solution of D- or L- arabinose (2 g, 13.3 mmol) in 20 mL of DMF, was added *p*-toluenesulfonic acid monohydrate (30 mg, 0.15 mmol) and followed by addition of 2,2-dimethoxy propane (4.13 g, 39.60 mmol) and the resulting solution was stirred at ambient temperature for 2 h. Then amberlite-IR 400 (-OH) was added and the mixture stirred for 30 minutes to neutralize the acid following which it was filtered. The filtrate was concentrated *in vacuo* and the residue chromatographed over a column of silica-gel (60-120 mesh). Elution of the column with 5% methanol-benzene gave β -3,4-isopropylidene-D-arabinopyranoside (D-1) or β -3,4-isopropylidene-L-arabinopyranoside (L-1).

Characterization data for D-1: m.p. 83-85 °C (Lit. 84-85 °C)¹. ¹H NMR (500MHz, DMSO-d₆) δ 1.27 (s, 3H), 1.39 (s, 3H), 3.37-3.41 (m, 1H), 3.70 (d, *J* = 13.0 Hz, 1H), 3.96-4.03 (m, 2H), 4.23 (b, 1H), 4.84-4.88 (m, 2H), 6.28 (d, *J* = 4.8 Hz, 1H). ¹³C NMR (125 MHz, DMSO-d₆) δ 27.1 (CH₃), 29.0 (CH₃), 59.1 (CH₂), 70.9 (CH), 73.5 (CH), 76.7 (CH), 92.9 (CH), 108.4 (CH₂). HRMS calcd. for C₈H₁₄O₅Na⁺ 213.0733; found 213.0737.

Characterization data for L-1: m.p. 84-85 °C (Lit. 84-85 °C)¹. ¹H NMR (500MHz, DMSO-d₆) δ 1.27 (s, 3H), 1.39 (s, 3H), 3.37-3.41 (m, 1H), 3.70 (d, *J* = 13.0 Hz, 1H), 3.98-4.03 (m, 2H), 4.14-4.16 (m, 1H) 4.84-4.88 (m, 2H), 6.28 (d, *J* = 4.8 Hz, 1H). ¹³C NMR (125 MHz, DMSO-d₆) δ 27.0 (CH₃), 29.0 (CH₃), 59.1 (CH₂), 70.9 (CH), 73.5 (CH), 76.7 (CH), 92.9 (CH), 108.4 (CH₂). HRMS calcd. for C₈H₁₄O₅Na⁺ 213.0733; found 213.0737.

1.3 Gelation experiments

Gelation experiments were carried out by adding a weighed exact amount of the gelator D-1/L-1 to a 1 mL of appropriate solvent in a vial, following which the vial was sealed. The mixture was then warmed to dissolve the gelator and then set aside to cool. Gelation was tested by inverting the vial almost immediately.

1.4 Determination of Critical gelation concentration (CGC)

To 1 mL of solvent taken in a vial, 3 mg of D-1/L-1 was added and gelation was tested as mentioned before. If partial or no gelation was observed 1 mg of D-1 was added subsequently at each step and gelation test repeated until a stable gel was formed almost instantaneously.

1.5 Gelation temperature (T_g)

Gel samples at particular concentrations were prepared in sealed vials and then the vial was immersed in a water bath. The water bath was heated to maintain a temperature rise

of 2 °C per minute. The temperature range during which the gel started to flow and turned into a sol was noted.

1.6 Phase selective gelation of crude oil

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 D-/L-1 in petrol (0.5 mL) was added. The resulting biphasic mixture was set aside for 10 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.

1.6 Photochemical transformation of 3 to 5 in gel microreactor

A mixture of D-/L-1 (250 mg) and 3 (25 mg 0.093 mMol) and benzene (25 mL) was taken in a double walled quartz vessel which was then sealed. The mixture was warmed and subsequently allowed to cool where upon it formed a gel. The set-up was then irradiated in a Rayonet Photochemical reactor using lamps of 300 nm for 1 h. Cold water was passed through the outer wall of the double walled vessel to prevent the transformation of the gel to a solution. Then the reaction was stopped and the gel transformed into a sol by warming which was then poured out. Evaporation of the benzene *in vacuo* followed by column chromatography of the residue over silica gel (60-120 mesh) afforded 4³ (22 mg, 88%) using 10% ethyl acetate-petroleum ether (60-80). The column was then eluted with 5% methanol-benzene to recover D-/L-1.

2 Gel characterizations

2.1 Optical Microscopy

The experiments were carried out by placing a small amount of the gel sample at a particular concentration, on a glass slide and viewing it with the microscope.

2.2 Scanning Electron Microscopy

The experiments were performed by using xerogels prepared from the gel samples by drying them overnight in air inside a dessicator. The xerogel samples for SEM were prepared by placing a small amount of sample on a stub which was then sputter coated with Au.

2.3 Rheology

The rheological experiments were carried out using a Anton Paar rheometer (MCR 302) equipped with stainless steel cone and plate geometry (50 mm diameter). The temperature of the plate was controlled at 25 °C ($\pm 0.1^\circ\text{C}$). The gels were made in vial and subsequently transferred to the rheometer plate by scooping with spatula. The frequency sweep experiment was performed as a function of angular frequency (0.1–600 rad s⁻¹) at a fixed strain of 0.01% at 25 °C and the storage modulus (G') and the loss modulus (G'') were plotted against angular frequency (ω).

3 References

1. M. Kiso and A. Hasegawa, *Carbohydrate Res.*, 1976, **52**, 95. 2.
2. (a) B. N. Stacey and B. Tierney, *Carbohydrate Res.*, 1976, **49**, 129. (b) J. Gelas and D. Horton, *Carbohydrate Res.*, 1975, **45**, 181.
3. S. Yadav, S. Banerjee, D. Maji and S. Lahiri, *Tetrahedron*, 2007, **63**, 10979.

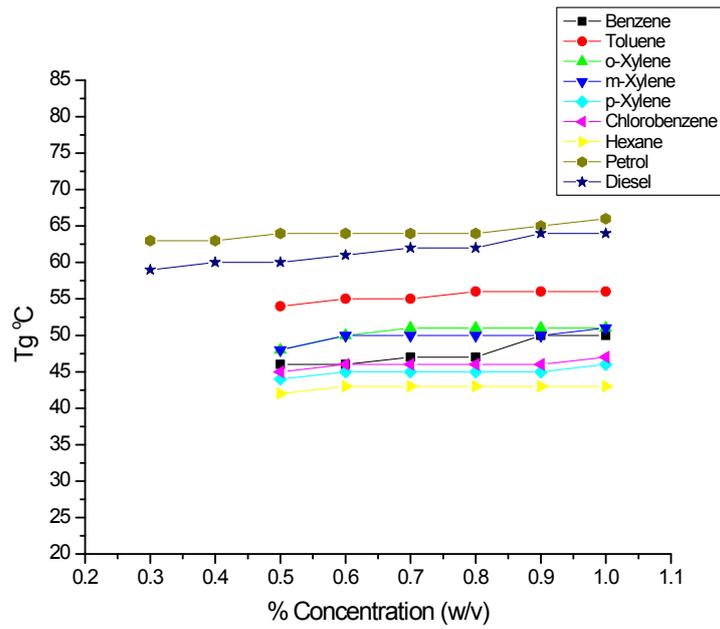
4 Tables and graph

Table S1 Gelation data for various solvents using gelator D-1

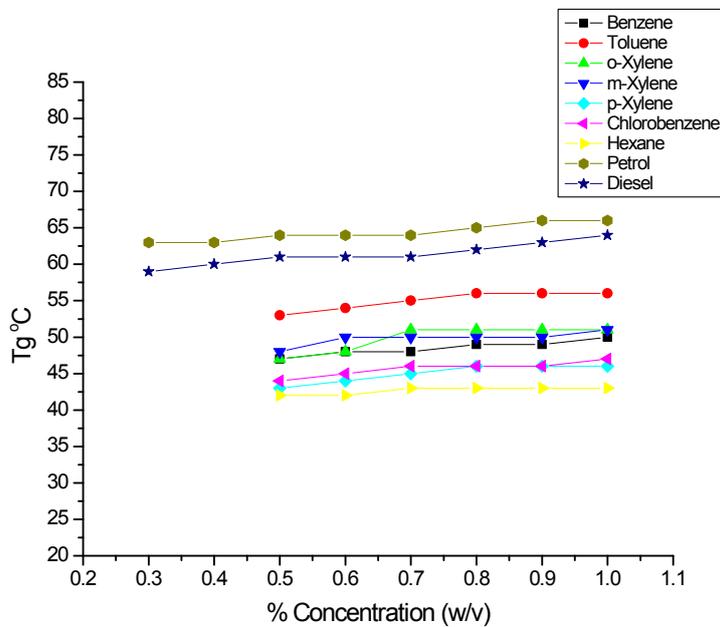
Solvent / Concentration	0.3% Tg °C	0.4% Tg °C	0.5% Tg °C	0.6% Tg °C	0.7% Tg °C	0.8% Tg °C	0.9% Tg °C	1.0% Tg °C
Benzene	S	PG	G 46-47	G 46-47	G 47-48	G 47-48	G 50-51	G 50-51
Toluene	S	PG	G 54- 55	G 55-56	G 55- 56	G 56-57	G 56-57	G 56-57
<i>o</i> -Xylene	S	PG	G 48 – 49	G 50 - 51	G 51-52	G 51- 52	G 51- 52	G 51 -52
<i>m</i> -Xylene	S	PG	G 48– 49	G 50- 51	G 50-51	G 50- 51	G 50-51	G 51- 52
<i>p</i> -Xylene	S	PG	G 44– 45	G 45- 46	G 45- 46	G 45- 46	G 45- 46	G 46- 47
Chloro benzene	S	PG	G 45- 46	G 46- 47	G 46- 47	G 46- 47	G 46- 47	G 47- 48
Nitro benzene	S	S	S	S	S	S	S	S
Hexane	S	PG	G 42- 43	G 43- 44	G 43- 44	G 43- 44	G 43- 44	G 43- 44
Dichloromethane	S	S	S	S	S	S	S	S
Chloroform	S	S	S	S	S	S	S	S
Ethyl acetate	S	S	S	S	S	S	S	S
Aceto nitrile	S	S	S	S	S	S	S	S
Methanol	S	S	S	S	S	S	S	S
Ethanol	S	S	S	S	S	S	S	S
<i>n</i> -Butyl alcohol	S	S	I	-	-	-	-	-
Amyl alcohol	S	S	S	S	S	S	S	S
Water	S	S	S	S	S	S	S	S
DMF	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S
Petrol	G 63-64	G 63- 64	G 64-65	G 64-65	G 64-65	G 64-66	G 65-66	G 66-67
Diesel	G 59-60	G 60- 61	G 60-61	G 61-62	G 62-63	G 62-64	G 64-65	G 64-65
Crude oil	PG	PG	G 45-47	G 45-47	G 46-48	G 46-47	G 47-48	G 47-48

Table S2 Gelation data for various solvents using gelator L-1

Solvent / Concentration	0.3% Tg °C	0.4% Tg °C	0.5% Tg °C	0.6% Tg °C	0.7% Tg °C	0.8% Tg °C	0.9% Tg °C	1.0% Tg °C
Benzene	S	PG	G 47-48	G 48-49	G 48-49	G 49-50	G 49-50	G 50-51
Toluene	S	PG	G 53-54	G 54-55	G 55-56	G 56-57	G 56-57	G 56-57
<i>o</i> -Xylene	S	PG	G 47-48	G 48-49	G 51-52	G 51-52	G 51-52	G 51-52
<i>m</i> -Xylene	S	PG	G 48-49	G 50-51	G 50-51	G 50-51	G 50-51	G 51-52
<i>p</i> -Xylene	S	PG	G 43-44	G 44-45	G 45-46	G 46-47	G 46-47	G 46-47
Chloro benzene	S	PG	G 44-45	G 45-46	G 46-47	G 46-47	G 46-47	G 47-48
Nitro benzene	S	S	S	S	S	S	S	S
Hexane	S	PG	G 42-43	G 42-44	G 43-44	G 43-44	G 43-44	G 43-44
Dichloromethane	S	S	S	S	S	S	S	S
Chloroform	S	S	S	S	S	S	S	S
Ethyl acetate	S	S	S	S	S	S	S	S
Aceto nitrile	S	S	S	S	S	S	S	S
Methanol	S	S	S	S	S	S	S	S
Ethanol	S	S	S	S	S	S	S	S
<i>n</i> -Butyl alcohol	S	S	I	-	-	-	-	-
Amyl alcohol	S	S	S	S	S	S	S	S
Water	S	S	S	S	S	S	S	S
DMF	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S
Petrol	G 63-64	G 63-65	G 64-65	G 64-65	G 64-65	G 65-66	G 66-67	G 66-67
Diesel	G 59-60	G 60-61	G 61-62	G 61-62	G 61-62	G 62-63	G 63-64	G 64-65
Crude oil	PG	PG	G 45-47	G 45-47	G 46-47	G 46-47	G 47-48	G 47-48



Graph S1. Variation of Tg with concentration for organogels of D-1



Graph S2. Variation of Tg with concentration for organogels of L-1

ISM_DHANBAD_RK_D in DMSO (13c)

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Current Data Parameters
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PROCNO   1

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PULPROG  zgpg30
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FIDRES   0.458222 Hz
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DM       16.650 usec
DE       6.00 usec
TE       304.8 K
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d11      0.03000000 sec
DELTA    1.89999998 sec
MCREST   0.00000000 sec
MCMARK   0.01500000 sec

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PL1      0.00 dB
SFO1     125.7703643 MHz

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PL12     16.12 dB
PL13     20.00 dB
SFO2     500.1320005 MHz

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SSB      0
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GB       0
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1D NMR plot parameters
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CY       20.00 cm
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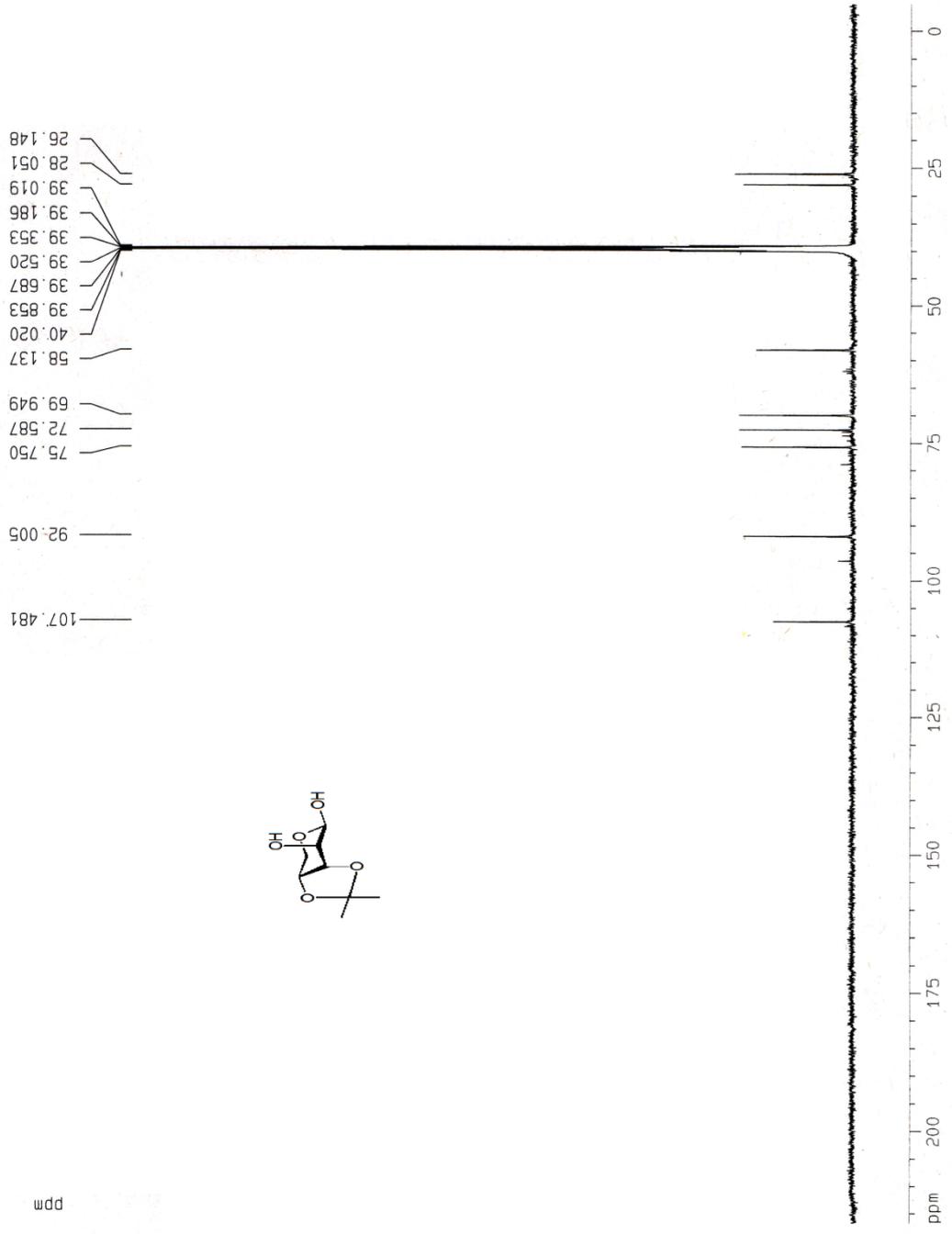


Figure S2. ¹³C-NMR of D-1 (125 MHz, DMSO-D₆)

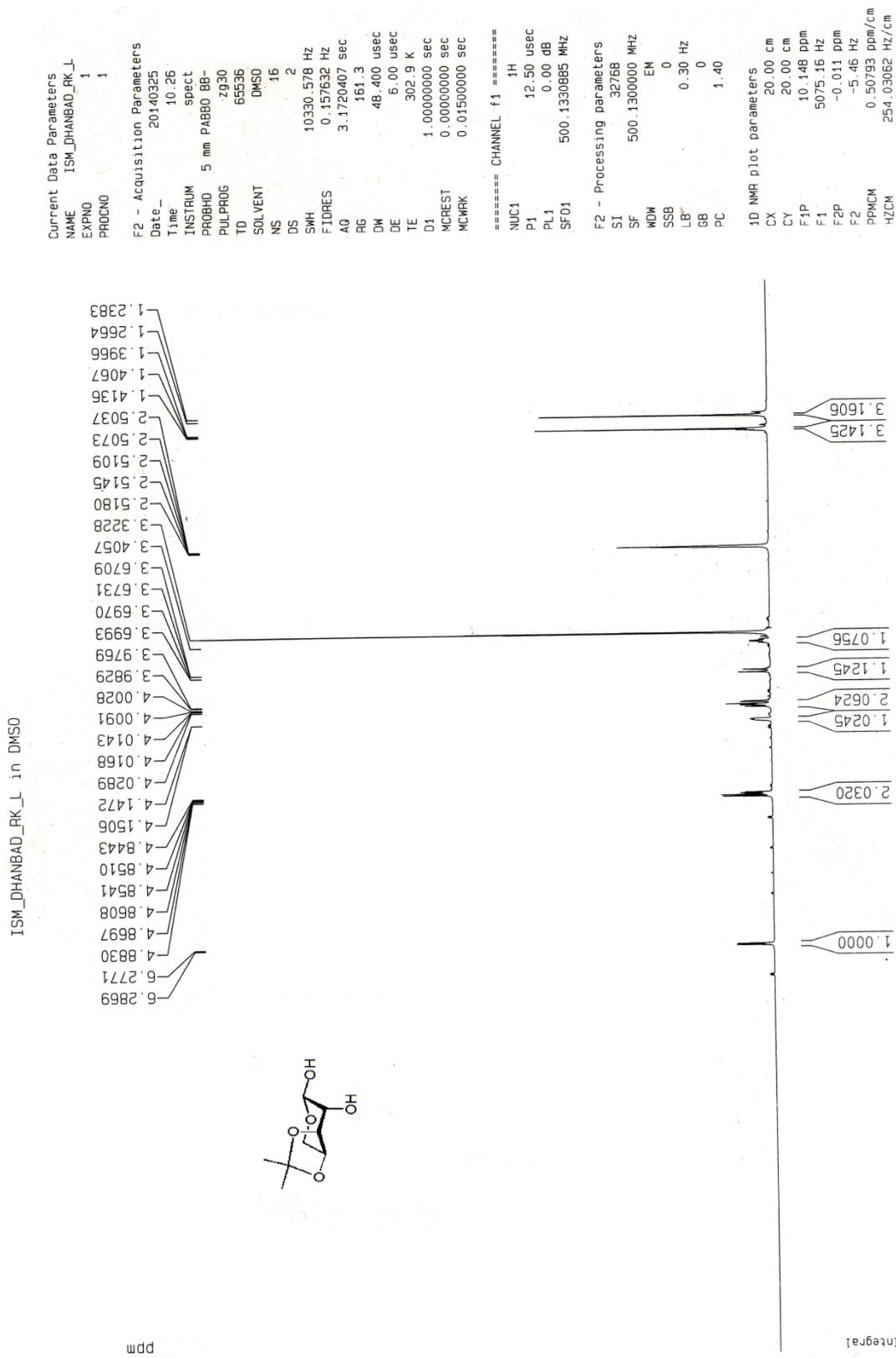


Figure S3. ¹H-NMR of L-1 (500 MHz, DMSO-D₆)

ISM_DHANBAD_RK_L in DMSO (13c)

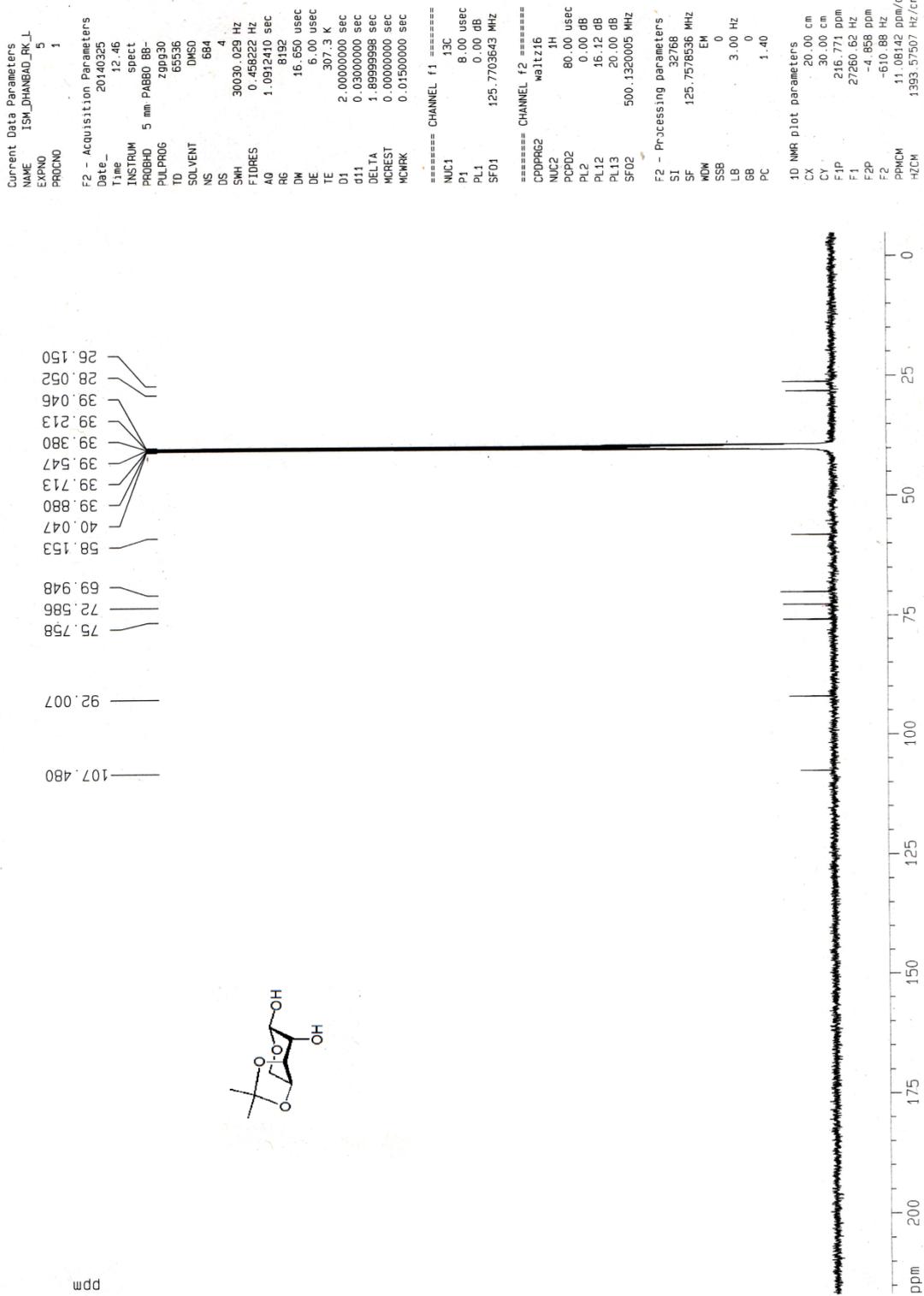


Figure S4. ^{13}C -NMR of L-1 (125 MHz, DMSO- D_6)

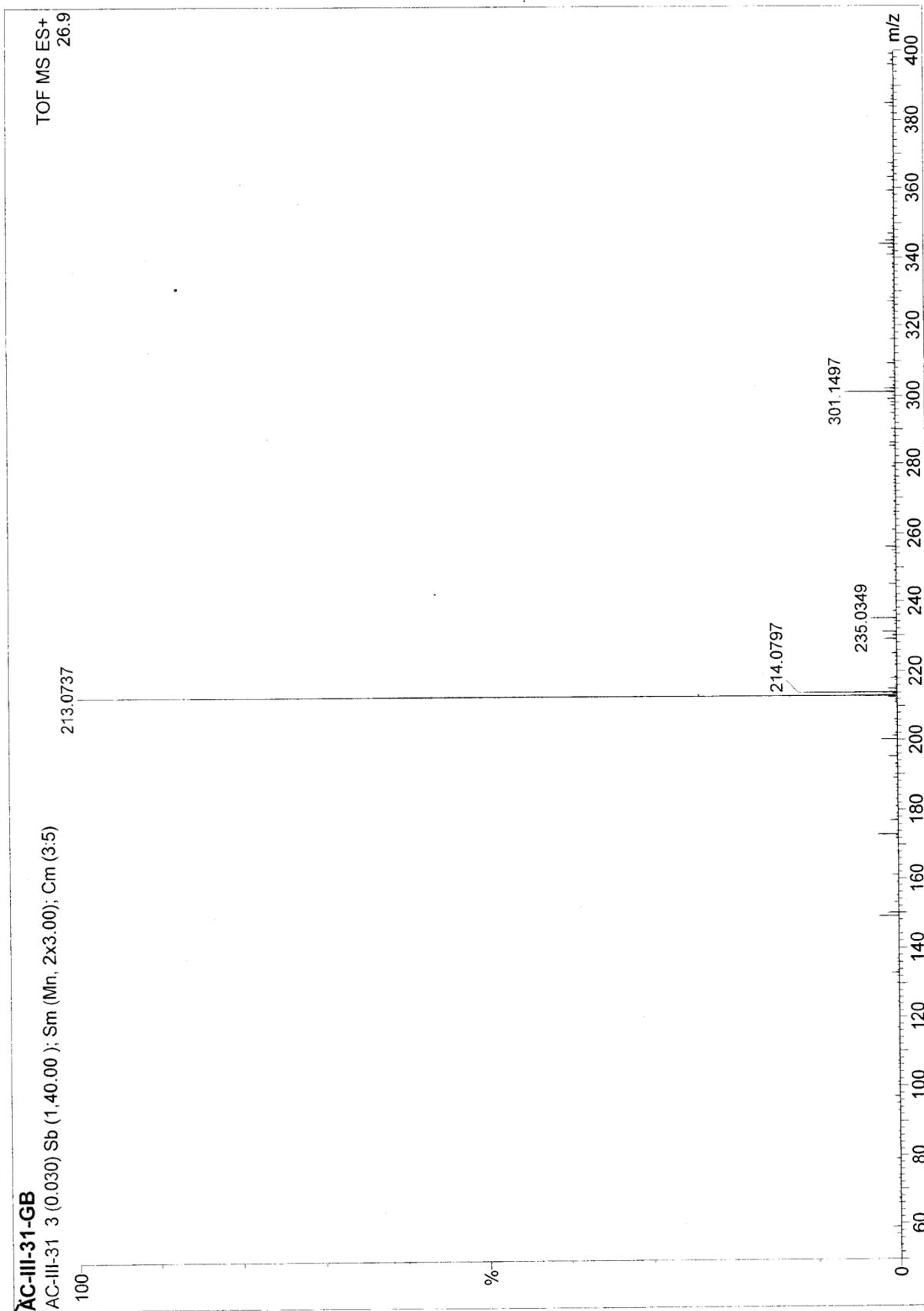


Figure S5. HRMS spectra of D-1.

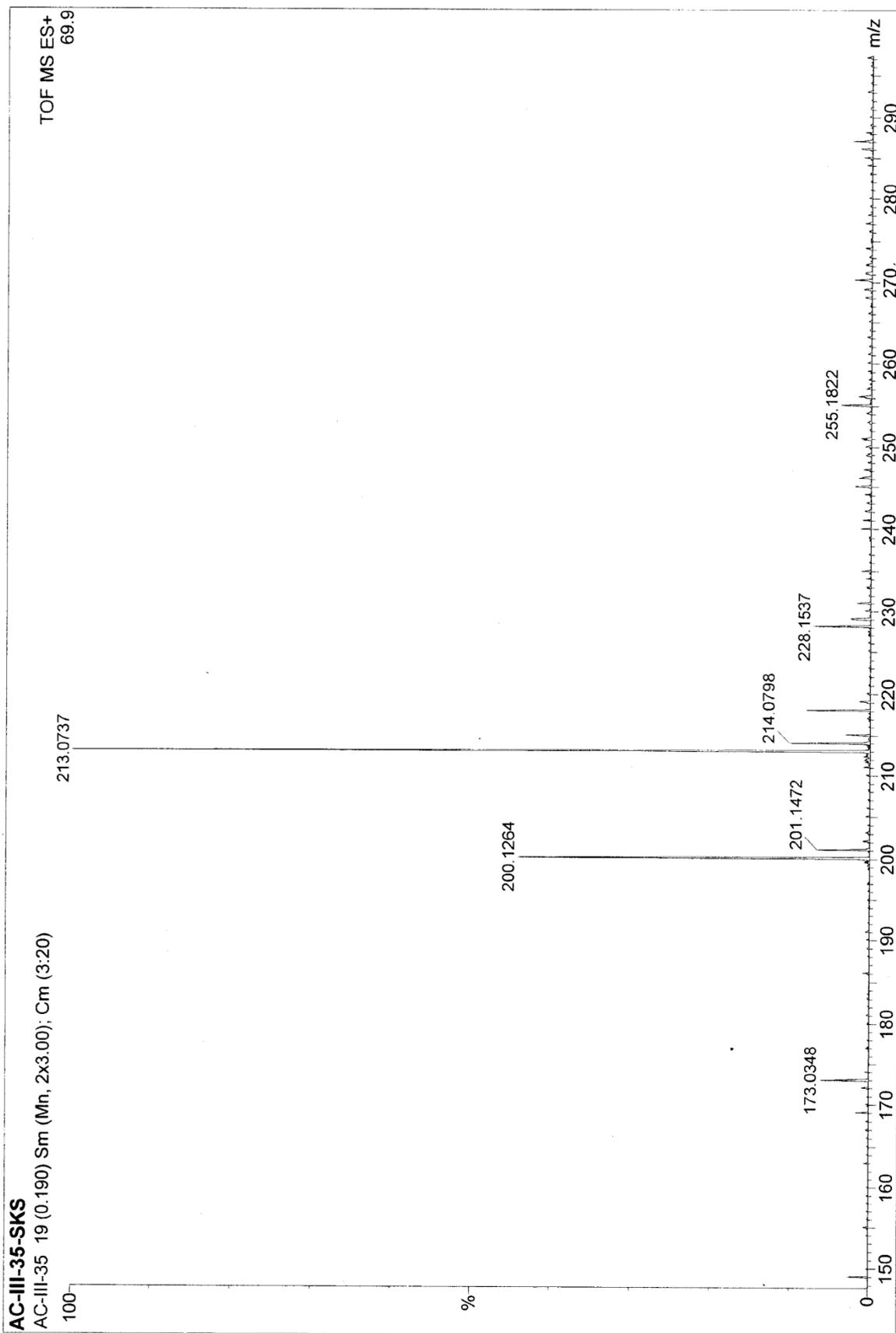


Figure S6. HRMS spectra of L-1.

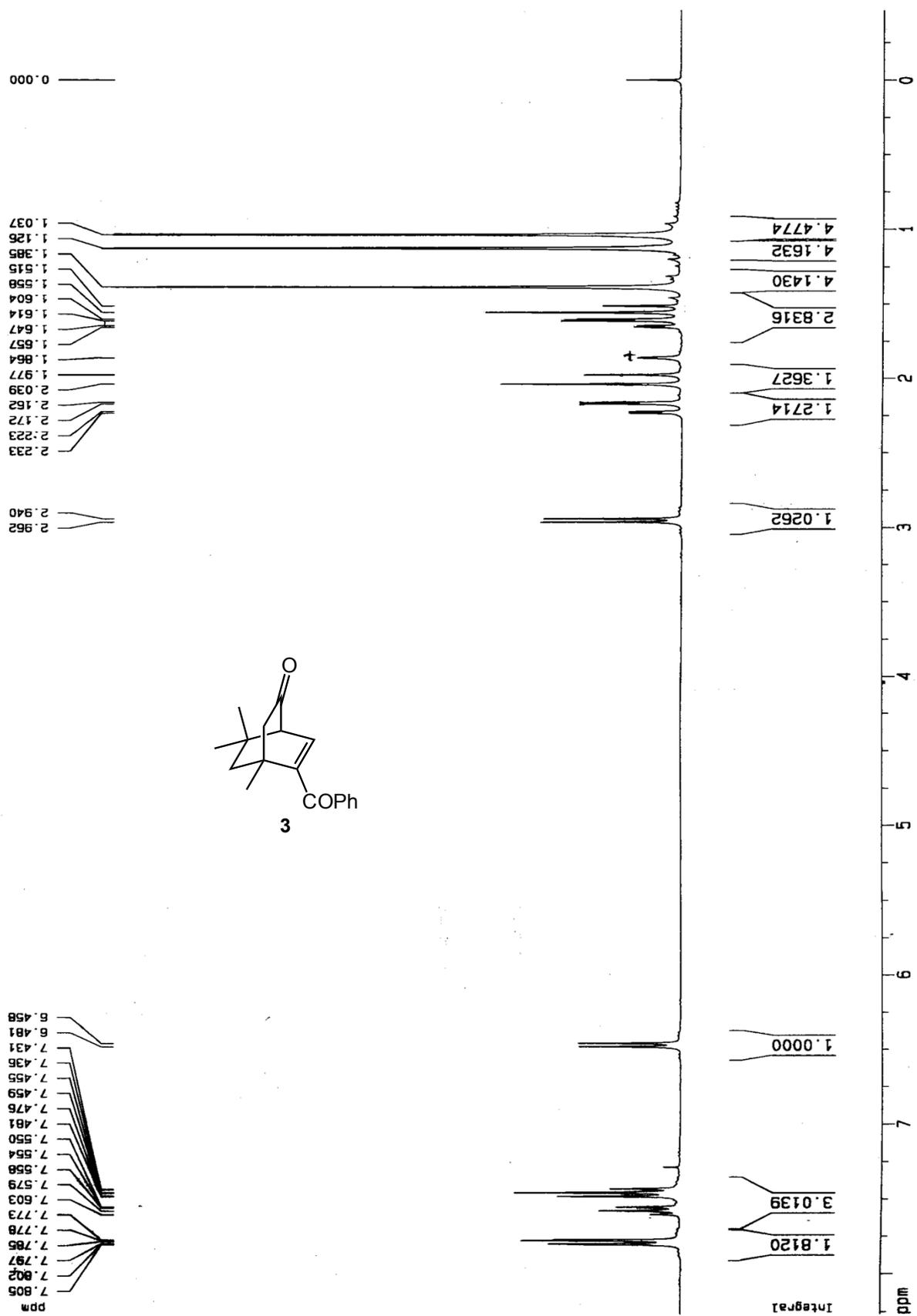


Figure S7. ¹H-NMR spectra of **3** (CDCl₃, 300 MHz).

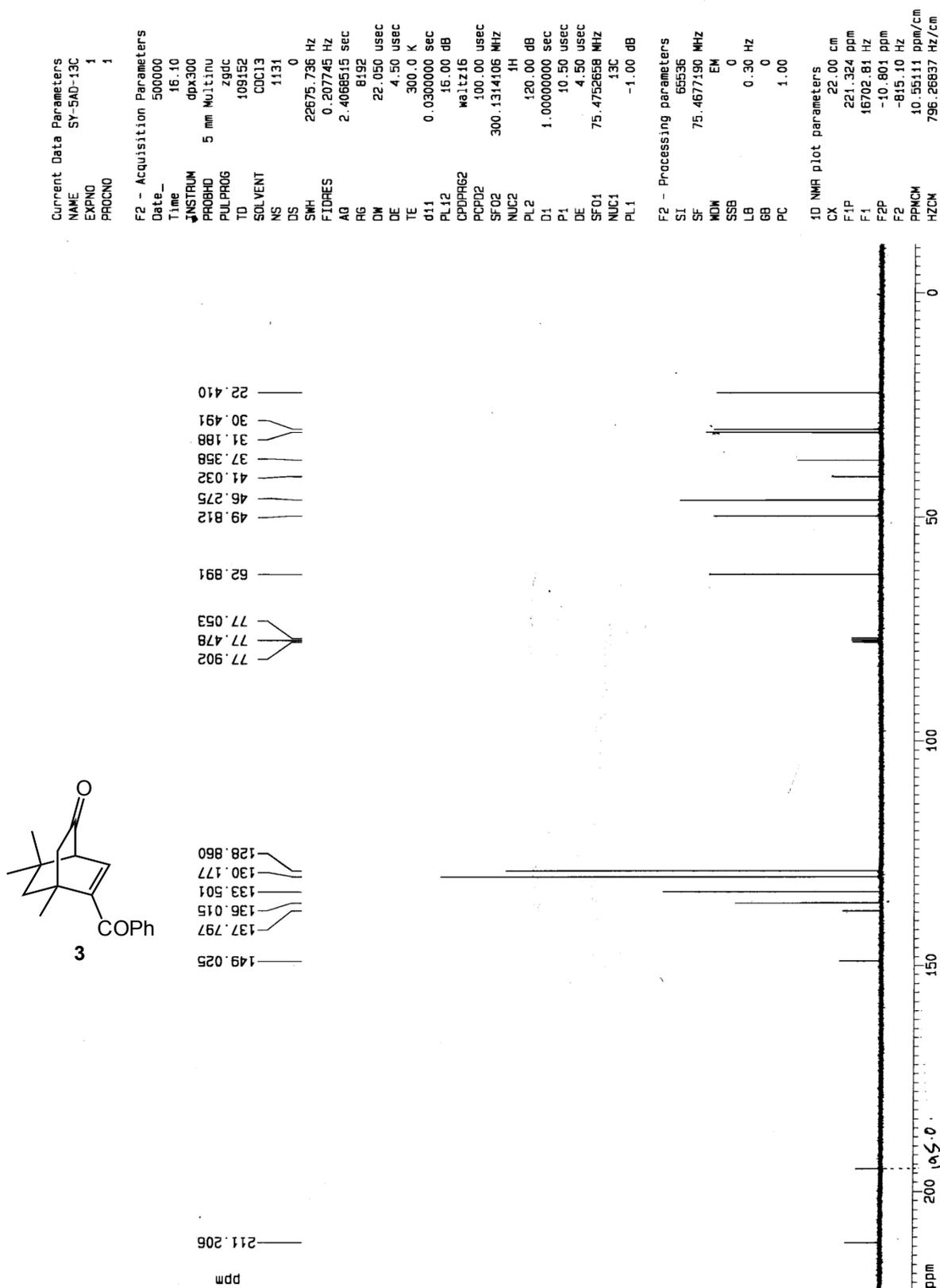


Figure S8. ¹³C-NMR spectra of **3** (CDCl₃, 300 MHz)

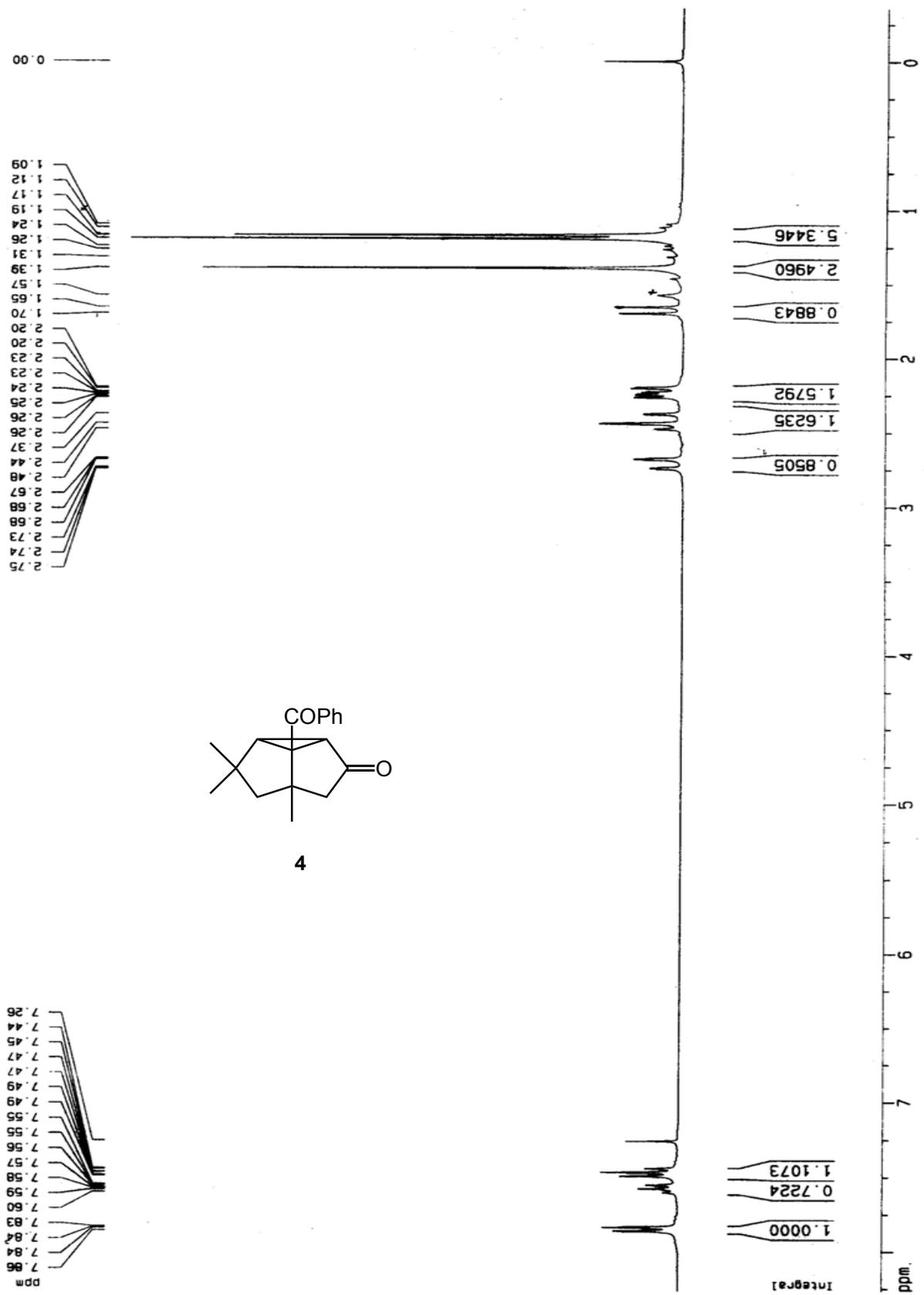


Figure S9. ¹H-NMR spectra of **4** (CDCl₃, 300 MHz)

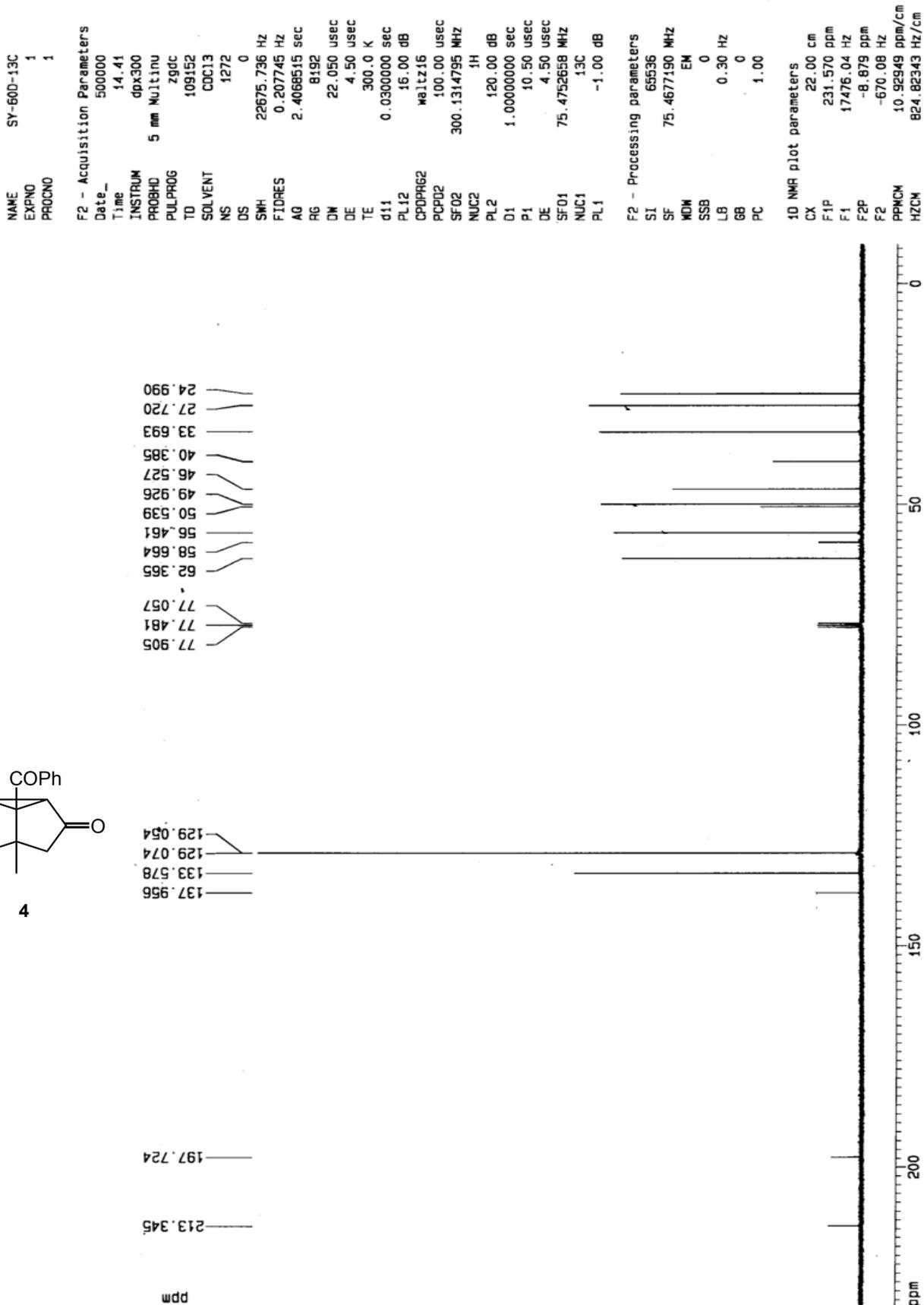
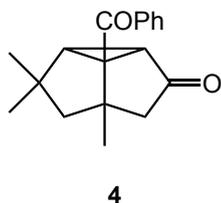


Figure S10. ¹³C-NMR spectra of 4 (CDCl₃, 300 MHz)

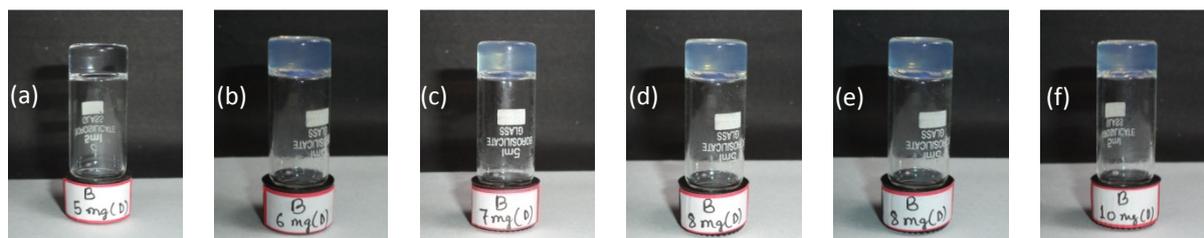


Figure S11. Gels from benzene and D-1 at various concentrations of D-1 (a) at 0.5% (w/v) concentration (b) at 0.6% (w/v) concentration (c) at 0.7% (w/v) concentration (d) at 0.8% (w/v) concentration (e) at 0.9% (w/v) concentration and (f) at 1.0% (w/v) concentration

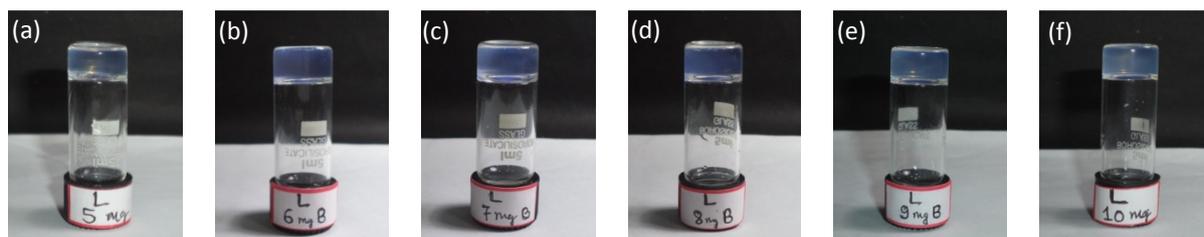


Figure S12. Gels from benzene and L-1 at various concentrations of L-1 (a) at 0.5% (w/v) concentration (b) at 0.6% (w/v) concentration (c) at 0.7% (w/v) concentration (d) at 0.8% (w/v) concentration (e) at 0.9% (w/v) concentration and (f) at 1.0% (w/v) concentration

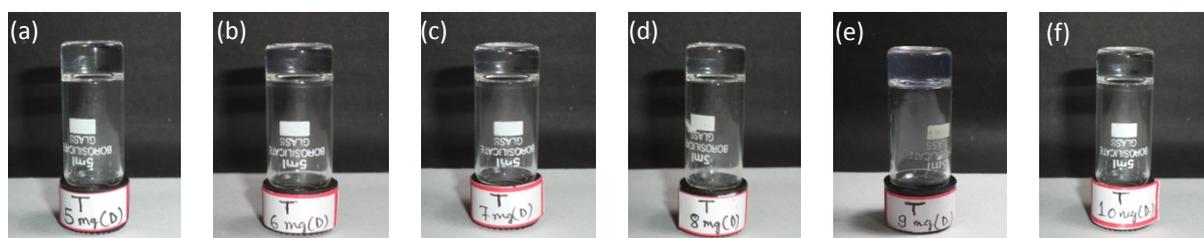


Figure S13. Gels from toluene and D-1 at various concentrations of D-1 (a) at 0.5% (w/v) concentration (b) at 0.6% (w/v) concentration (c) at 0.7% (w/v) concentration (d) at 0.8% (w/v) concentration (e) at 0.9% (w/v) concentration and (f) at 1.0% (w/v) concentration

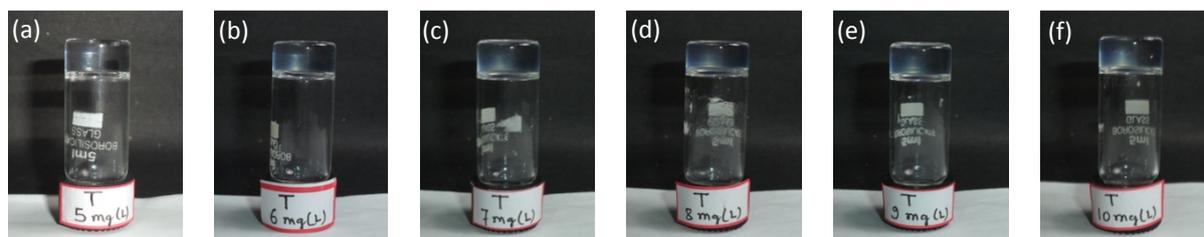


Figure S14. Gels from toluene and L-1 at various concentrations of L-1 (a) at 0.5% (w/v) concentration (b) at 0.6% (w/v) concentration (c) at 0.7% (w/v) concentration (d) at 0.8% (w/v) concentration (e) at 0.9% (w/v) concentration and (f) at 1.0% (w/v) concentration

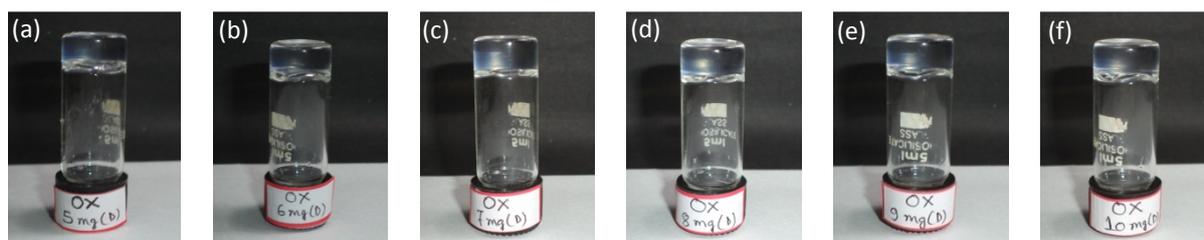


Figure S15. Gels from *o*-xylene and D-1 at various concentrations of D-1 (a) at 0.5% (w/v) concentration (b) at 0.6% (w/v) concentration (c) at 0.7% (w/v) concentration (d) at 0.8% (w/v) concentration (e) at 0.9% (w/v) concentration and (f) at 1.0% (w/v) concentration

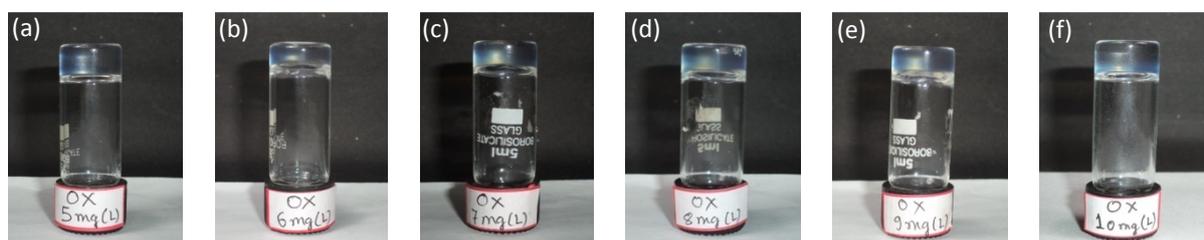


Figure S16. Gels from *o*-xylene and L-1 at various concentrations of L-1 (a) at 0.5% (w/v) concentration (b) at 0.6% (w/v) concentration (c) at 0.7% (w/v) concentration (d) at 0.8% (w/v) concentration (e) at 0.9% (w/v) concentration and (f) at 1.0% (w/v) concentration

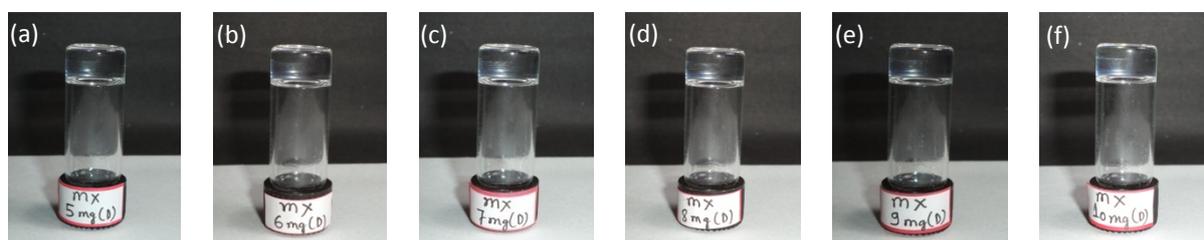


Figure S17. Gels from *m*-xylene and D-1 at various concentrations of D-1 (a) at 0.5% (w/v) concentration (b) at 0.6% (w/v) concentration (c) at 0.7% (w/v) concentration (d) at 0.8% (w/v) concentration (e) at 0.9% (w/v) concentration and (f) at 1.0% (w/v) concentration

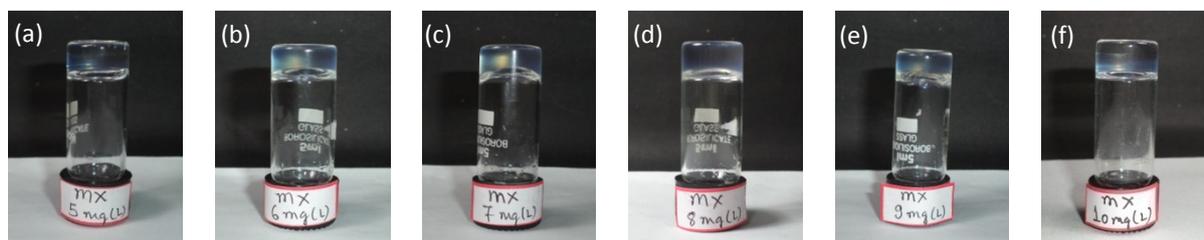


Figure S18. Gels from *m*-xylene and L-1 at various concentrations of L-1 (a) at 0.5% (w/v) concentration (b) at 0.6% (w/v) concentration (c) at 0.7% (w/v) concentration (d) at 0.8% (w/v) concentration (e) at 0.9% (w/v) concentration and (f) at 1.0% (w/v) concentration

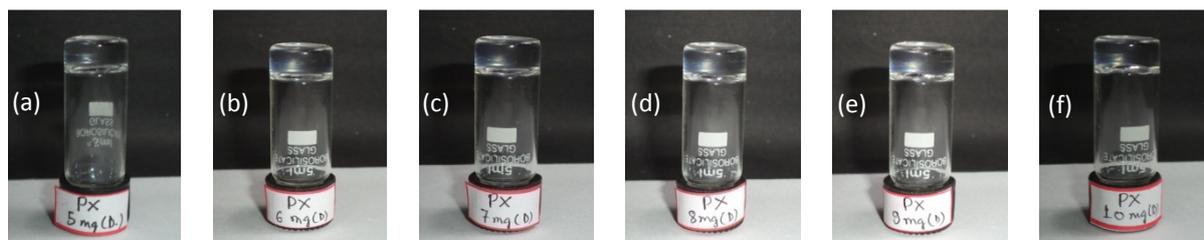


Figure S19. Gels from *p*-xylene and D-1 at various concentrations of D-1 (a) at 0.5% (w/v) concentration (b) at 0.6% (w/v) concentration (c) at 0.7% (w/v) concentration (d) at 0.8% (w/v) concentration (e) at 0.9% (w/v) concentration and (f) at 1.0% (w/v) concentration

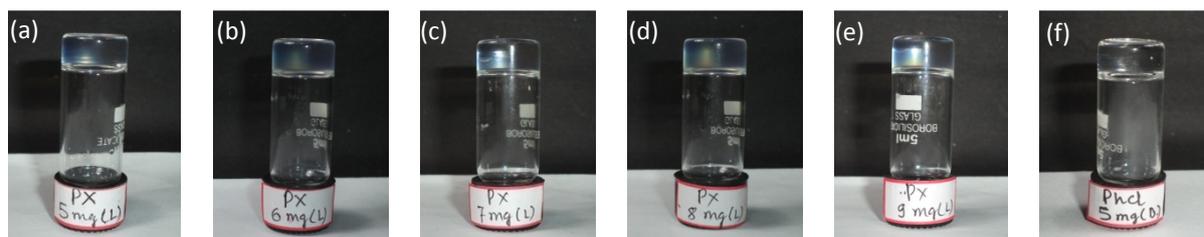


Figure S20. Gels from *p*-xylene and L-1 at various concentrations of L-1 (a) at 0.5% (w/v) concentration (b) at 0.6% (w/v) concentration (c) at 0.7% (w/v) concentration (d) at 0.8% (w/v) concentration (e) at 0.9% (w/v) concentration and (f) at 1.0% (w/v) concentration

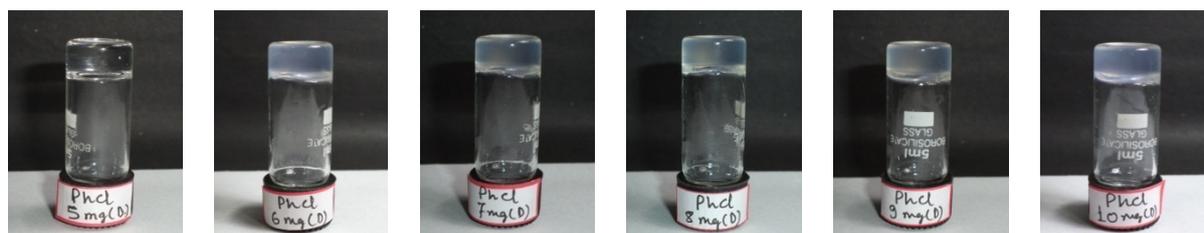


Figure S21. Gels from chlorobenzene and D-1 at various concentrations of D-1 (a) at 0.5% (w/v) concentration (b) at 0.6% (w/v) concentration (c) at 0.7% (w/v) concentration (d) at 0.8% (w/v) concentration (e) at 0.9% (w/v) concentration and (f) at 1.0% (w/v) concentration

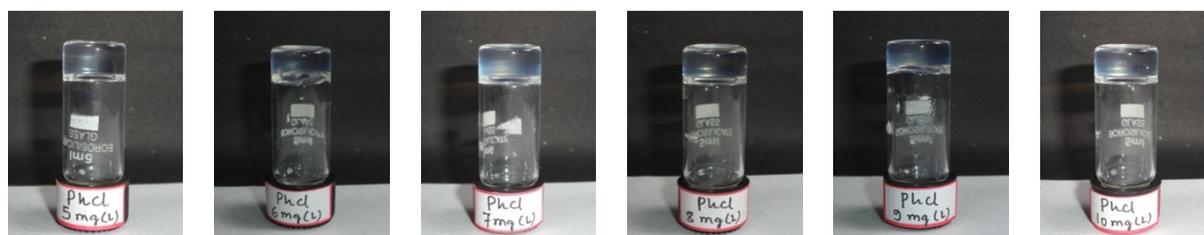


Figure S22. Gels from chlorobenzene and L-1 at various concentrations of L-1 (a) at 0.5% (w/v) concentration (b) at 0.6% (w/v) concentration (c) at 0.7% (w/v) concentration (d) at 0.8% (w/v) concentration (e) at 0.9% (w/v) concentration and (f) at 1.0% (w/v) concentration

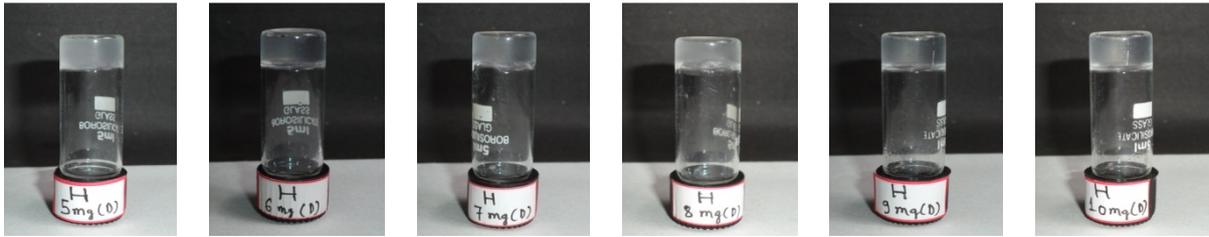


Figure S23. Gels from hexane and D-1 at various concentrations of D-1 (a) at 0.5% (w/v) concentration (b) at 0.6% (w/v) concentration (c) at 0.7% (w/v) concentration (d) at 0.8% (w/v) concentration (e) at 0.9% (w/v) concentration and (f) at 1.0% (w/v) concentration

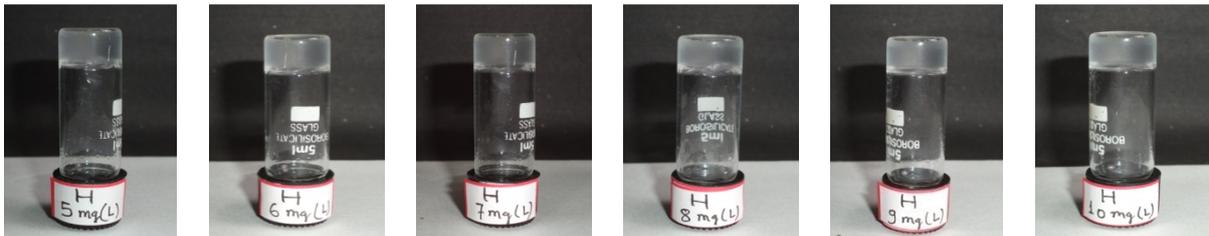


Figure S24. Gels from hexane and L-1 at various concentrations of L-1 (a) at 0.5% (w/v) concentration (b) at 0.6% (w/v) concentration (c) at 0.7% (w/v) concentration (d) at 0.8% (w/v) concentration (e) at 0.9% (w/v) concentration and (f) at 1.0% (w/v) concentration



Figure S25. Gels from petrol and D-1 at various concentrations of D-1 (a) at 0.3% (w/v) concentration (b) at 0.4% (w/v) concentration (c) at 0.5% (w/v) concentration (d) at 0.6% (w/v) concentration and (e) at 0.7% (w/v) concentration

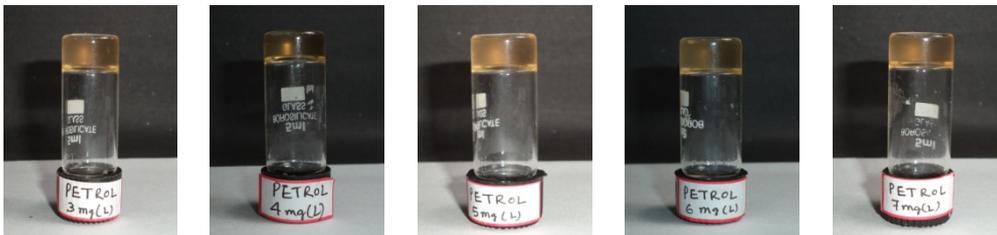


Figure S26. Gels from petrol and L-1 at various concentrations of L-1 (a) at 0.3% (w/v) concentration (b) at 0.4% (w/v) concentration (c) at 0.5% (w/v) concentration (d) at 0.6% (w/v) concentration and (e) at 0.7% (w/v) concentration



Figure S27. Gels from diesel and D-1 at various concentrations of D-1 (a) at 0.3% (w/v) concentration (b) at 0.4% (w/v) concentration (c) at 0.5% (w/v) concentration (d) at 0.6% (w/v) concentration and (e) at 0.7% (w/v) concentration



Figure S28. Gels from diesel and L-1 at various concentrations of L-1 (a) at 0.3% (w/v) concentration (b) at 0.4% (w/v) concentration (c) at 0.5% (w/v) concentration (d) at 0.6% (w/v) concentration and (e) at 0.7% (w/v) concentration

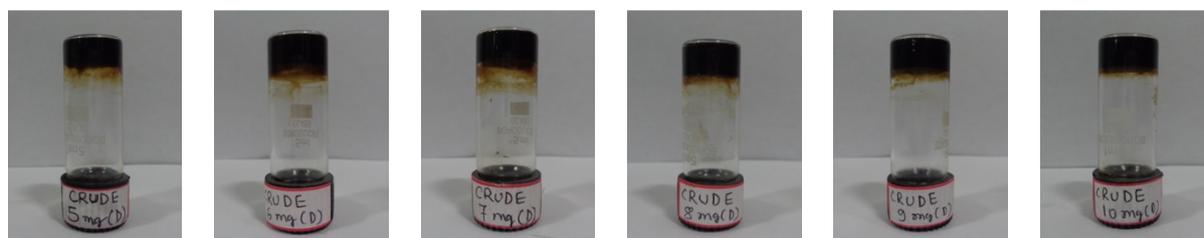


Figure S29. Gels from crude oil and D-1 at various concentrations of D-1 (a) at 0.5% (w/v) concentration (b) at 0.6% (w/v) concentration (c) at 0.7% (w/v) concentration (d) at 0.8% (w/v) concentration (e) at 0.9% (w/v) concentration and (f) at 1.0% (w/v) concentration



Figure S30. Gels from crude oil and L-1 at various concentrations of L-1 (a) at 0.5% (w/v) concentration (b) at 0.6% (w/v) concentration (c) at 0.7% (w/v) concentration (d) at 0.8% (w/v) concentration (e) at 0.9% (w/v) concentration and (f) at 1.0% (w/v) concentration

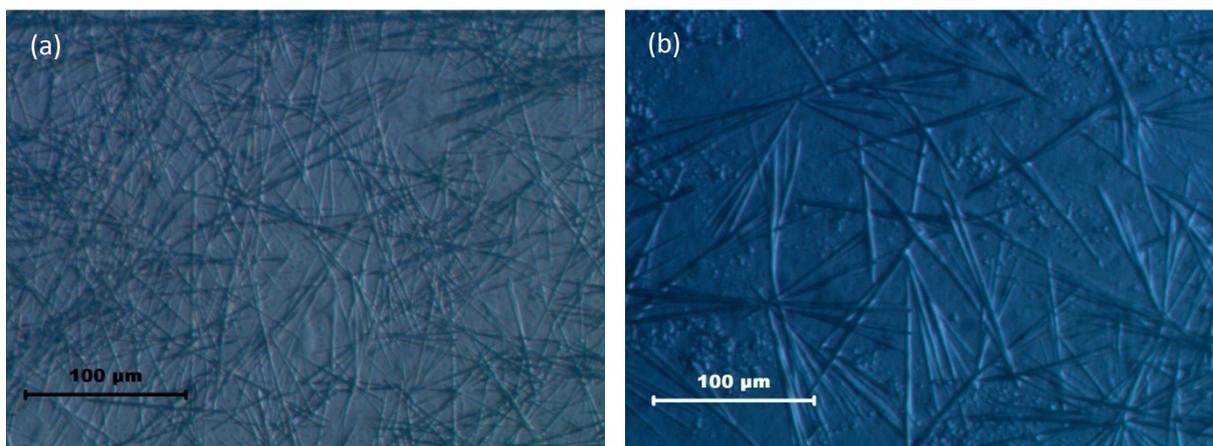


Figure S31. Optical microscopy images for D-1 and (a) benzene gel and (b) petrol gel at 0.8% (w/v) concentrations.

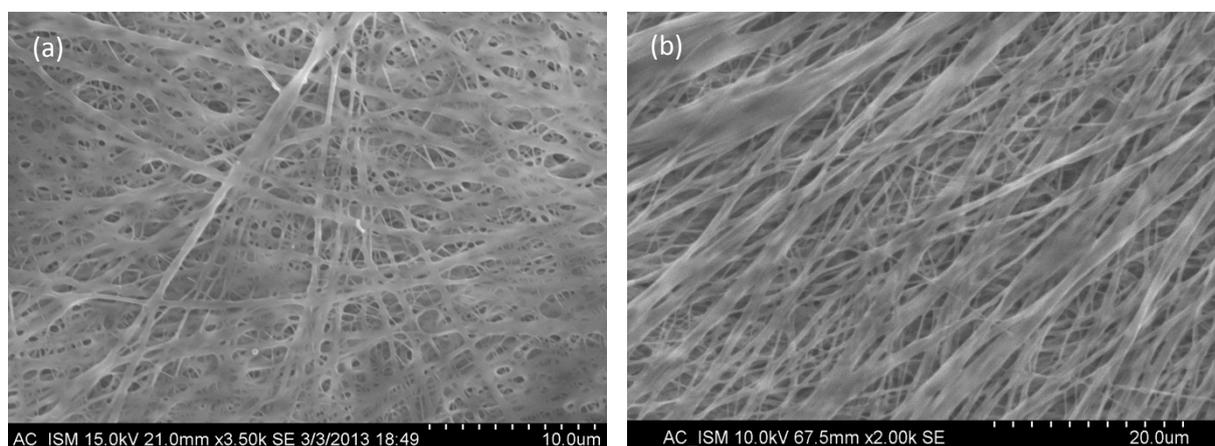


Figure S32. SEM image of the xerogel from benzene and (a) D-1 and (b) L-1 at 1.0% (w/v) concentrations.

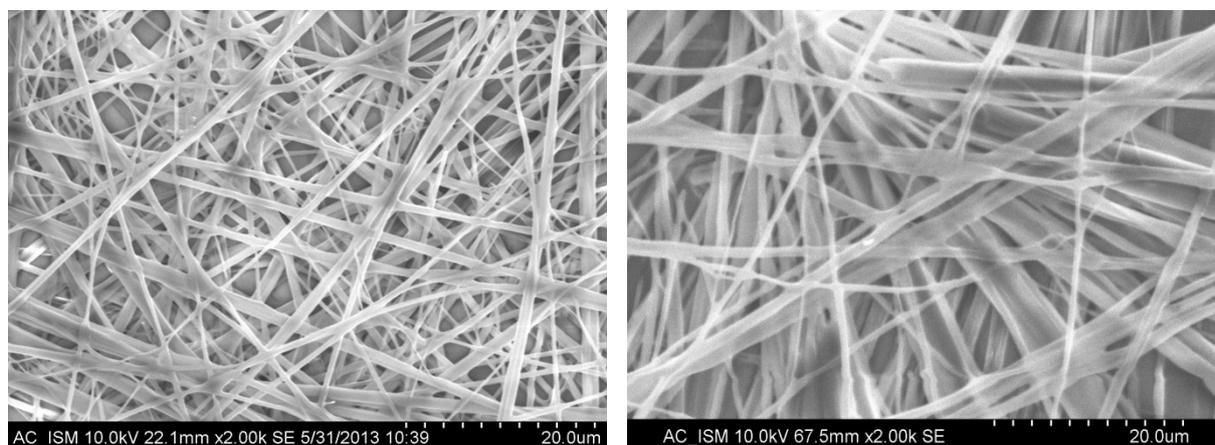


Figure S33. SEM image of the xerogel from toluene and (a) D-1 and (b) L-1 at 1.0% (w/v) concentrations.

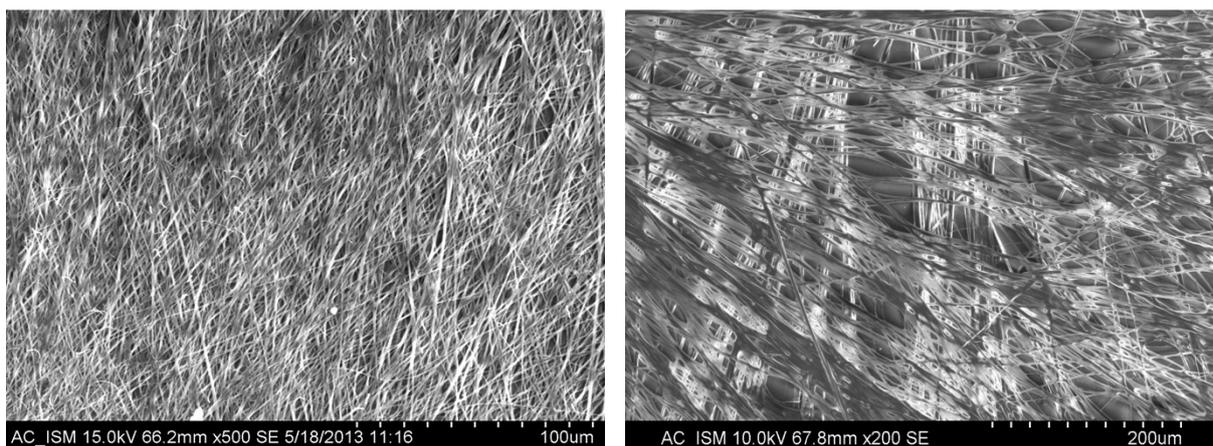


Figure S34. SEM image of the xerogel from *o*-xylene and (a) D-1 and (b) L-1 at 1.0% (w/v) concentrations

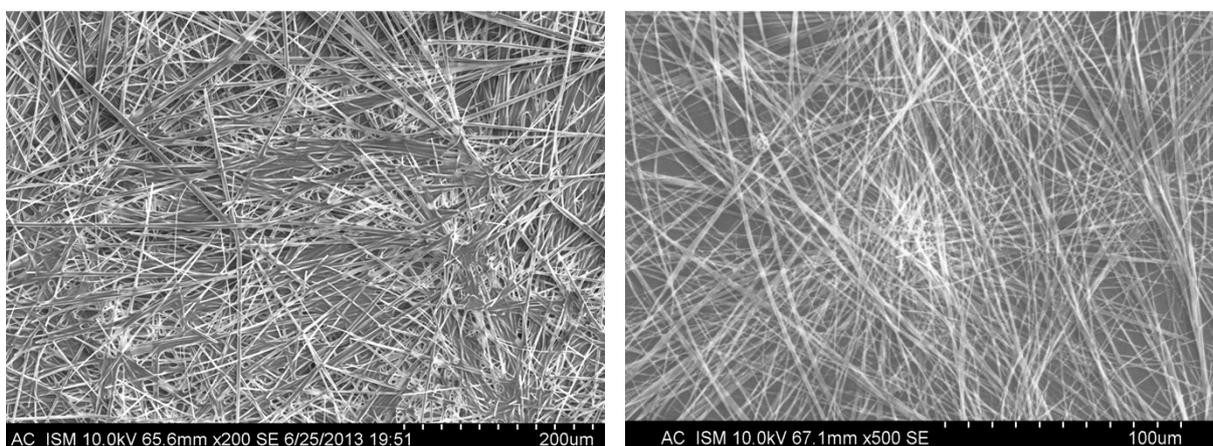


Figure S35. SEM image of the xerogel from *m*-xylene and (a) D-1 and (b) L-1 at 1.0% (w/v) concentrations

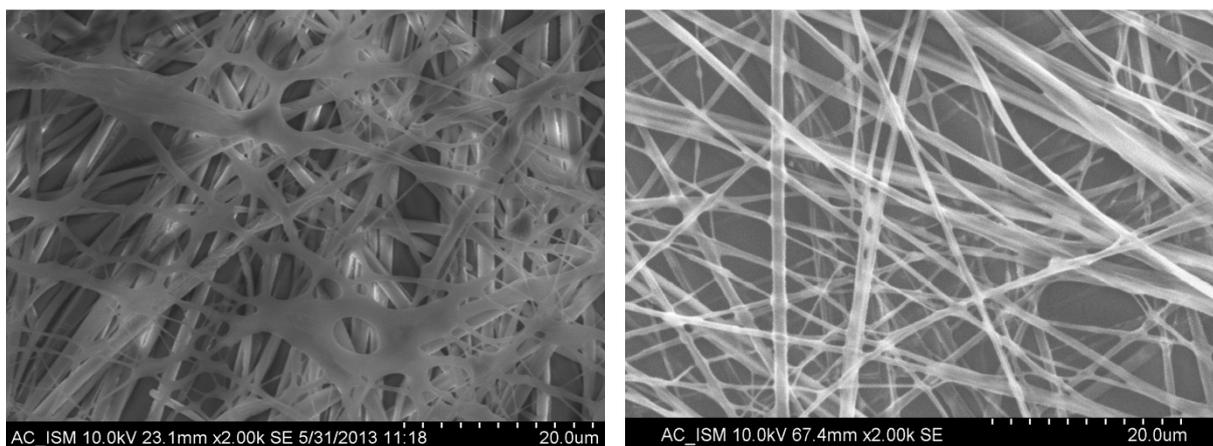


Figure S36. SEM image of the xerogel from *p*-xylene and (a) D-1 and (b) L-1 at 1.0% (w/v) concentrations

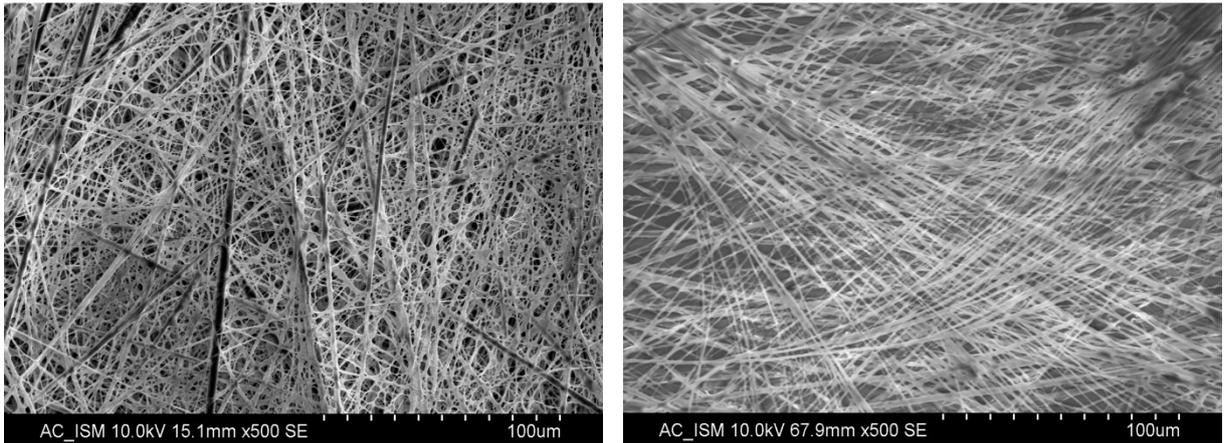


Figure S37. SEM image of the xerogel from chlorobenzene and (a) D-1 and (b) L-1 at 1.0% (w/v) concentrations

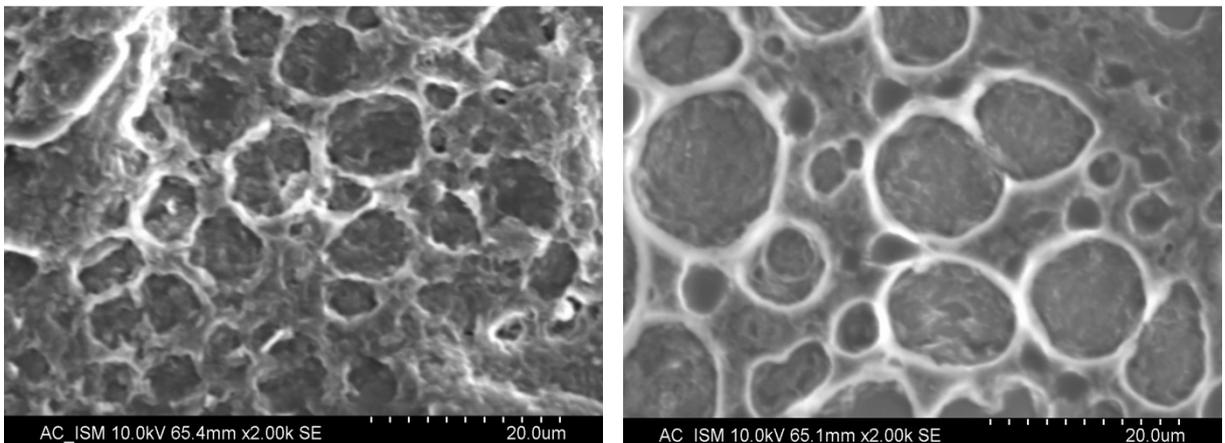


Figure S38. SEM image of the xerogel from hexane and (a) D-1 and (b) L-1 at 1.0% (w/v) concentrations

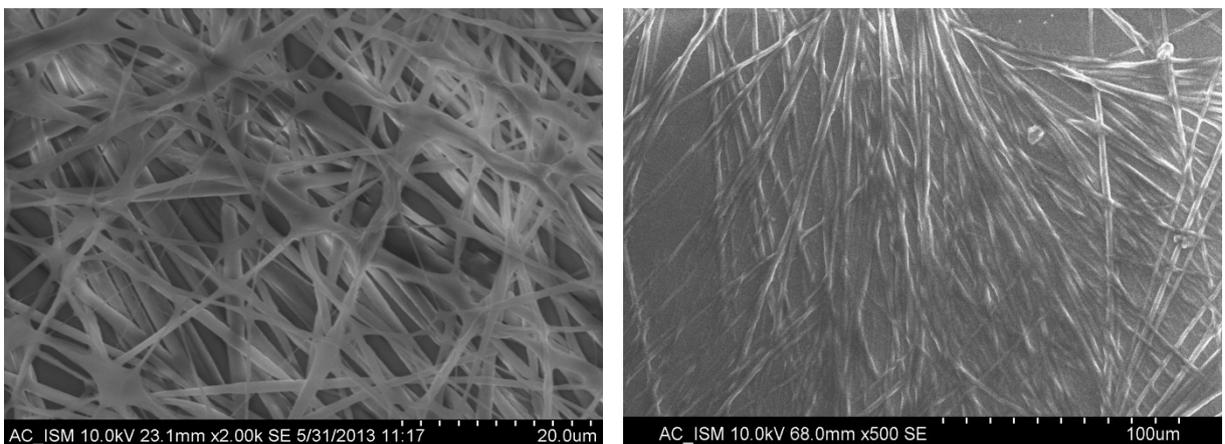


Figure S39. SEM image of the xerogel from petrol and (a) D-1 and (b) L-1 at 1.0% (w/v) concentrations