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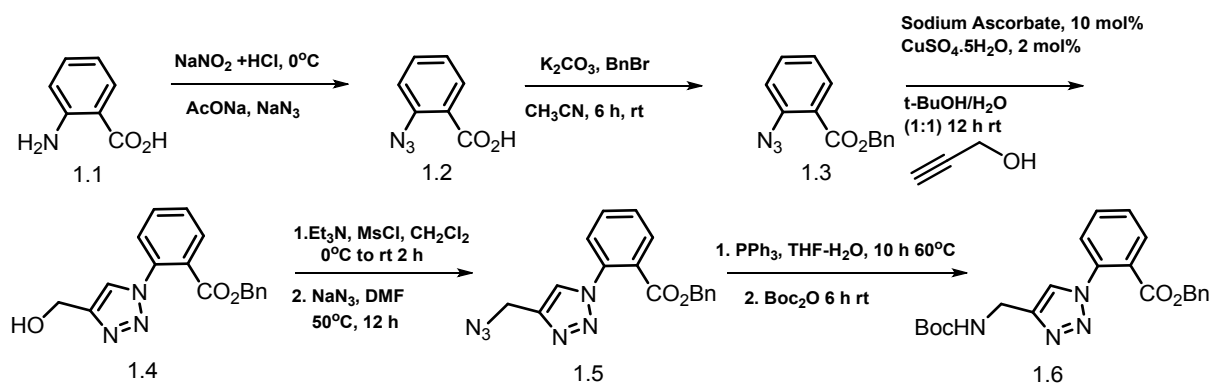
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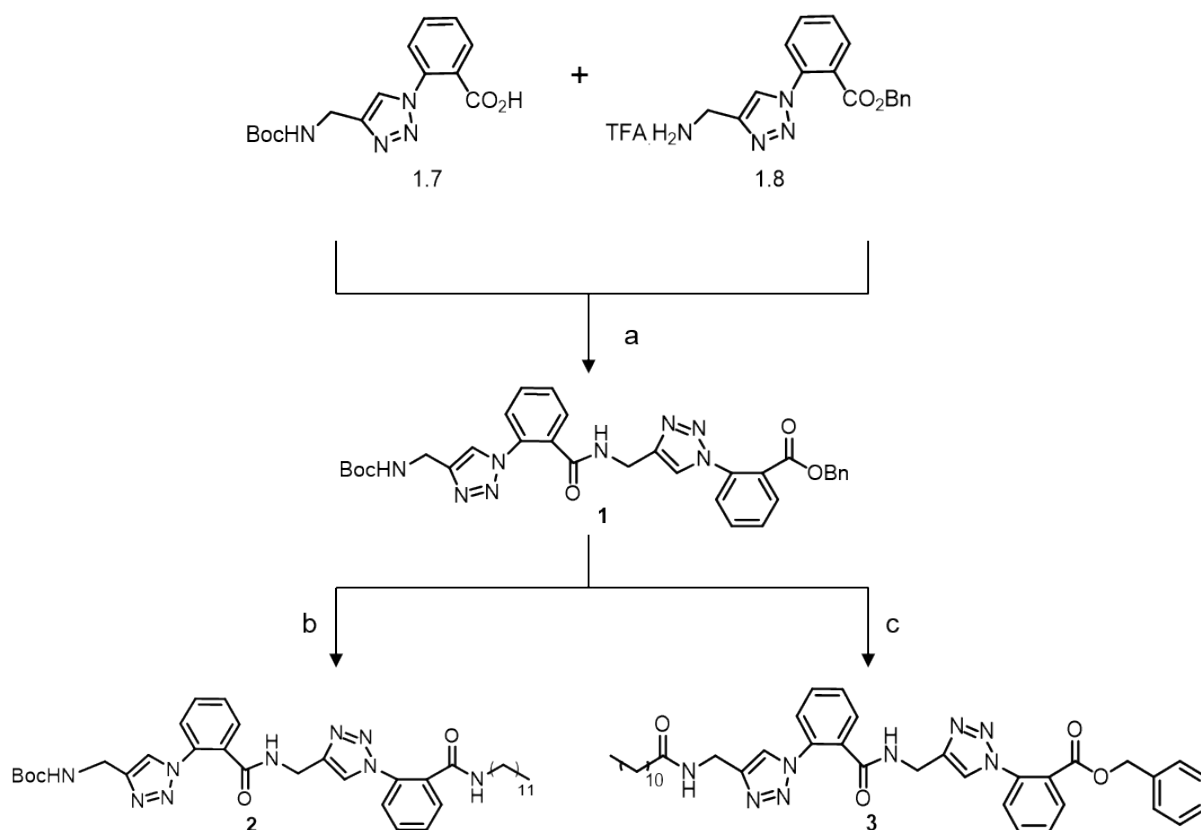
### **General experimental information:**

Experiments which required anhydrous conditions were carried out under nitrogen atmosphere in dry dichloromethane (DCM). Thin-layer chromatography (TLC) was performed on 0.25 mm silica gel plates (60 F254 grade) from Merck, and were analyzed using 254 nm UV light. Chromatographic separation was carried out on 100-200 mesh silica gel in gravity mode.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker Avance 400 MHz and 500 MHz instruments, and the chemical shifts ( $\delta$ ) are reported in parts per million (ppm) relative to tetramethylsilane (TMS) with coupling constant ( $J$ ) values in Hertz (Hz). The splitting patterns in  $^1\text{H}$  NMR spectra are reported as follows: s = singlet; d = doublet; t = triplet; dd = doublet of doublet; m = multiplet, bs = broad singlet.  $^{13}\text{C}$  NMR data are reported with the solvent peak ( $\text{CDCl}_3$ ,  $\delta = 77.0$  ppm) as the internal standard. Mass spectra were recorded under ESI/HRMS at 60000 resolution using ThermoScientific Exactive mass spectrometer. Infrared spectra were recorded using a Nicolet 6700 FT-IR spectrophotometer. Powder X-Ray diffraction data was obtained on BRUKER D8-Advance diffractometer using  $\text{CuK}\alpha$  radiation ( $\lambda=1.5418$  Å) over the range of  $0.5^\circ < 2\theta < 15^\circ$  at room temperature. Samples for SEM imaging were coated with Au-Pd (Gatan precision etching coating system (model No. 682) operating at 5 KeV) and analyzed by FEI Quanta FEG 200 High Resolution Scanning Electron Microscope operating at 10-30 kV. Rheological measurements were performed with a stress-controlled rheometer (MCR 301) equipped with steel-coated parallel-plate geometry (25 mm diameter). The gap distance was fixed at 1 mm and a solvent-trapping device was placed above the plate to prevent solvent evaporation. All measurements were done at 25°C. The synthetic strategy adopted to access various compounds reported here is presented in Schemes 1 and 2. Detailed experimental procedures are given subsequently.

## Synthesis of aryl-triazole peptide 1, and its derivatives 2 and 3



**Scheme 1.** Synthesis of Building-block 1.6



**Scheme 2.** Synthesis of compounds 1, 2 and 3; a) EDCI (1equiv.), HOBT (1 equiv.), DIPEA (3 equiv.), 24 h, 0°C to rt, 95% b) (i) H<sub>2</sub>, Pd/C (10%), 4 h, rt, (ii) Lauryl amine, EDCI (1 equiv.), HOBT (1 equiv.), DIPEA (3 equiv.), 24 h, 0°C to rt, 87%, c) (i) Trifluoroacetic acid, DCM, 0°C to rt 3 h (ii) Lauroyl chloride (1.5 equiv.), DIPEA (3 equiv.) 0°C to rt 12 h, 85%.

## General reaction procedures:

*Debenzylation of Benzyl esters 1.6 and 1:* To a solution of benzyl ester (1 equiv.) in methanol (10 mL) taken in an RB flask, was added 10% Pd/C (20% w/w), and the mixture was stirred under an atmosphere of hydrogen (H<sub>2</sub> balloon) at room temperature for 4 h. The catalyst was filtered through a celite bed, washed thoroughly with methanol and the filtrate was evaporated under reduced pressure. The resulting residue was washed with hexane and dried under high vacuum to get the corresponding acid as off-white solid.

*Boc-deprotection of 1.6 and 1:* To a solution of the Boc-protected precursor (1 equiv.) in dry dichloromethane at 0°C was added TFA (0.5 mL). The mixture was gradually allowed to warm to room temperature and was stirred until the starting material was completely consumed as per TLC (~3 h). Subsequently, all the volatiles were removed under a stream of nitrogen, toluene (1 mL) was added to the residue, and evaporated to dryness to get the amine as trifluoroacetate salt.

## Peptide coupling protocol

To a stirred mixture of the acid component (1.1 mmol), HOBt (1.2 mmol) and EDCI (1.2 mmol) in 5 mL of dry DCM was added DIPEA (3 mmol) at 0°C. After 1 h, the amine trifluoroacetate salt (1 mmol) in dry DCM (5 mL) was added to it and the mixture was continued to stir for 24 h at room temperature. Subsequently, the volatiles were removed under reduced pressure, the residue dissolved in ethyl acetate, and the organic layer was successively washed with 5% HCl (10 mL) and saturated sodium bicarbonate (10 mL). After drying with sodium sulphate, the organic layer was evaporated under reduced pressure to get the crude product which was further purified by column chromatography using ethyl acetate/Hexane mixture in a gradient mode. The intermediates **1.2** and **1.3** used in Scheme 1 were synthesized according to the literature protocol.<sup>1</sup>

## Synthesis of individual compounds and their spectral data

### Benzyl 2-(4-(hydroxymethyl)-1H-1,2,3-triazol-1-yl)benzoate (1.4):

To a solution of the azide **1.3** (8.8 g, 34.62 mmol) in 1:1 mixture of tBuOH/water (80 mL) in a round bottom flask was added propargyl alcohol (2.0 mL, 34.62 mmol) drop-wise. The mixture was stirred for 5 minutes and a solution of sodium ascorbate (2.05 g, 10.38 mmol) in water (5 mL) and copper sulphate pentahydrate (0.26 g, 1.04 mmol) in water (2 mL) were

sequentially added to it. Stirring was continued for ~12 h till the starting materials were completely consumed. After evaporating <sup>t</sup>BuOH, the residue was dissolved in ethyl acetate, washed with water (3 x 50 mL), the combined organic portion dried using anhydrous sodium sulphate, filtered, and evaporated to dryness. Purification of resulting residue was done by column chromatography using 50% Ethyl acetate-hexane solvent system in a gradient mode and the product was obtained as a viscous liquid (9.7 g, 90 %). Analytical data: R<sub>f</sub>: 0.35 (50 % Ethylacetate- Hexane); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.01 (dd, 1H, *J* = 7.7 Hz, 1.5 Hz), 7.73 (s, 1H) 7.63 (ddd, 1H, *J* = 7.6, 7.6, 1.6 Hz), 7.57 (ddd, 1H, *J* = 7.6, 7.6, 1.4 Hz), 7.42 (dd, 1H, *J* = 7.6, 1.2 Hz), 7.32-7.30 (m, 3H), 7.22-7.20 (m, 2H), 5.11 (s, 2H), 4.72 (s, 2H), 2.89 (bs, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 165, 147.5, 136.0, 134.8, 132.8, 131.4, 129.9, 128.6 (2C), 128.49, 128.46 (2C), 127.4, 126.8, 123.8, 67.6, 56.1 IR (neat): 3371, 3151, 3033, 2926, 2876, 1720, 1455, 1292, 1276, 1124, 1078, 1021, 760, 700; HRMS (ESI) exact mass calcd. for C<sub>17</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub>Na [M+Na]<sup>+</sup> 332.1011, found [M+Na]<sup>+</sup> 332.1004.

#### **Benzyl 2-(4-(azido methyl)-1H-1,2,3-triazol-1-yl)benzoate (1.5):**

To a stirred solution of the alcohol **1.4** (9 g, 29.09 mmol) in dry dichloromethane (80 mL) at 0°C under nitrogen atmosphere was added triethylamine (8.1 mL, 58.19 mmol), followed by mesyl chloride (3.38 mL, 43.63 mmol). The reaction was monitored by TLC, and after complete consumption of starting materials (2 h), the mixture was washed with 5% NaHCO<sub>3</sub> solution (50 mL) and brine (50 mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to get the mesylate as a gummy solid. To a stirred solution of this mesylate in DMF (40 mL) was added NaN<sub>3</sub> (3.8 g, 58.19 mmol) and the mixture was heated at 50°C for 12 h. The reaction mixture was diluted with ethyl acetate and washed with water (3 x 50 mL), followed by brine (50 mL) and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. It was filtered and concentrated under reduced pressure to get a residue which was purified by chromatography on silica gel using 30% ethyl acetate- hexane system to afford the azide **1.4** as a viscous liquid (6.8 g, 70 %). Analytical data: R<sub>f</sub>: 0.82 ( 50 % Ethyl acetate-Hexane); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.06 (d, 1H, *J* = 7.4 Hz, ), 7.74 (s, 1H), 7.68 (app. t, 1H, *J* = 7.0 Hz), 7.61 (app. t, 1H, *J* = 7.3 Hz), 7.47 (d, 1H, *J* = 7.0 Hz), 7.33 (m, 3H), 7.25-7.23 (m, 2H), 5.14 (s, 2H), 4.43 (s, 2H) <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 164.8, 142.4, 135.9, 134.8, 132.9, 131.5, 130.1, 128.62 (2C), 128.58, 128.51 (2C), 127.5, 126.9, 124.2, 67.6, 45.5; IR(neat): 3150, 3020, 2930, 2873, 2132, 1725, 1458, 1292, 1278, 1124, 1078, 1021, 766, 700; HRMS (ESI) exact mass calcd. for C<sub>17</sub>H<sub>14</sub>N<sub>6</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup> 357.1075, found [M+Na]<sup>+</sup> 357.1074.

**Benzyl 2-(4-(((tert-butoxycarbonyl) amino) methyl)-1H-1,2,3-triazol-1-yl)benzoate (1.6):**

To a stirred solution of **1.5** (5 g, 14.95 mmol) in THF/H<sub>2</sub>O (3:1, 40 mL) was added triphenylphosphine (4.7 g, 17.94 mmol). The mixture was stirred at room temperature for 30 minutes, heated to 60°C and continued stirring at the same temperature for 10 h. After bringing it to room temperature, Boc<sub>2</sub>O (5.15 mL, 0.22 mmol) was added and stirring was continued for 6 h. Excess solvent was then evaporated and the residue was purified by column chromatography using 30% ethyl acetate-hexane solvent system to get **1.6** as a white solid (4.25 g, 70 %). Analytical data: R<sub>f</sub>: 0.56 ( 50 % Ethyl acetate- Hexane); m.p. 87-89 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 8.04-8.03 (d, 1H, *J* = 7.6 Hz), 7.69 (s, 1H), 7.68-7.59 (m, 2H), 7.44-7.42 (d, 1H, *J* = 7.6 Hz), 7.35-7.33 (m, 3H), 7.23-7.21 (m, 2H), 5.12 (s, 2H), 5.00 (broad s, 1H), 4.34 (s, 2H), 1.44 (s, 9H) <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 165.0, 155.8, 145.2, 136.1, 134.9, 132.8, 131.5, 129.9, 128.6 (2C), 128.55, 128.51 (2C), 127.5, 126.8, 123.8, 79.7, 67.6, 36, 28.4 (3C); IR(neat) : 3439, 3151, 3015, 2975, 2851, 1716, 1510, 1455, 1363, 1288, 1263 1163, 1124, 1081, 870, 763, 700; HRMS (ESI) exact mass calcd. for C<sub>22</sub>H<sub>24</sub>N<sub>4</sub>O<sub>4</sub>Na [M+Na]<sup>+</sup> 431.1695, found [M+Na]<sup>+</sup> 431.1699.

**Benzyl 2-(4-((2-(4-(((tert-butoxycarbonyl) amino)methyl)-1H-1,2,3-triazol-1-yl)benzamido)methyl)-1H-1,2,3-triazol-1-yl)benzoate (1):**

To a stirred mixture of the acid **1.7** (0.5 g, 1.57 mmol), HOBt (0.25 g, 1.88 mmol) and EDCI (0.36 g, 1.88 mmol) in dry dichloromethane (10 mL) at 0°C was added DIPEA (3 mmol). After stirring for 1 h, the amine trifluoroacetate salt **1.8** (0.63 g, 1.57 mmol) in 5 mL of dry dichloromethane was added, and stirring continued for 24 h at room temperature. All the volatiles were then removed under reduced pressure, the residue dissolved in ethyl acetate and washed successively with 5% HCl (3 x 10 mL) and saturated NaHCO<sub>3</sub> (3 x 10 mL). After drying with sodium sulphate, the organic layer was evaporated under reduced pressure to get a residue which was purified by column chromatography using 80% ethyl acetate/hexane system to get the product as a white solid (0.9 g, 95 %). Analytical data: R<sub>f</sub>: 0.13 ( 50 % Ethyl acetate- Hexane); mp 98-100 °C <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 8.07-8.05 (d, 1H, *J* = 7.6 Hz), 7.79 (s, 1H), 7.77 (s, 1H), 7.71-7.66 (m, 2H), 7.63-7.53 (m, 4H), 7.47-7.45 (d, 1H, *J* = 7.6 Hz), 7.28-7.25 (m, 3H), 7.18-7.16 (m, 2H) 6.39 (bs NH<sup>2</sup>, 1H), 5.31 (bs, 1H, NH<sup>1</sup>), 5.11 (s, 2H), 4.48 (s, 2H), 4.39 (s, 2H), 1.42 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 166.4, 164.9, 155.8, 146.0, 143.4, 136.1, 134.9, 134.3, 132.9, 132.4, 131.5, 131.2, 130.0, 129.9, 129.1,

128.5 (2C), 128.4 (2C), 128.4, 127.3, 127.1, 125.8, 124.7, 123.7, 79.7, 67.5, 36.0, 35.1, 28.3 (3C); IR(neat): 3449, 3151, 3015, 2975, 2926, 2855, 1734, 1705, 1627, 1606, 1502, 1455, 1399, 1288, 1249, 1166, 1120, 1046, 767, 700; HRMS (ESI) exact mass calcd. for  $C_{32}H_{32}N_8O_5Na$   $[M+Na]^+$  631.2393, found  $[M+Na]^+$  631.2407.

### **Preparation of dipeptide derivative 2:**

To a solution of **1** (1 mmol) in methanol (10 mL) in an RB flask was added 10% Pd/C (20% w/w), and the mixture was stirred under an atmosphere of hydrogen ( $H_2$  balloon) at room temperature for 6 h. The catalyst was filtered through a celite bed, washed thoroughly with methanol and the filtrate was evaporated under reduced pressure get the free acid which was directly used in the next step without further purification.

To a stirred solution containing mixture of the free acid generated above (0.5 g, 0.96 mmol), HOBt (0.15 g, 1.15 mmol) and EDCI (0.22 g, 1.15 mmol) in 10 mL dry dichloromethane was added DIPEA (0.5 mL, 2.88 mmol) at 0°C. After 1 h, lauryl amine (0.26 mL, 1.92 mmol) in dry dichloromethane (2 mL) was added to the mixture and stirring continued for 24h at room temperature. All the volatiles were then removed, the residue dissolved in ethyl acetate, and washed successively with 5% HCl (3 x 10 mL) and saturated  $NaHCO_3$  (3 x 10 mL). After drying with sodium sulphate, the organic layer was evaporated under reduced pressure to get a residue which was purified by column chromatography using 80% ethyl acetate/hexane solvent system to get the product as a solid (0.57 g, 87 %). Analytical data:  $R_f$ : 0.21 (50 % Ethyl acetate- Hexane); mp 118-120 °C  $^1H$  NMR ( $CDCl_3$ , 400 MHz): 7.83 (s, 1H), 7.79 (s, 1H), 7.74-7.64 (m, 2H), 7.61-7.50 (m, 5H), 7.45-7.38 (m, 1H), 6.84 (bs, 1H), 6.52 (br s, 1H), 5.40 (bs, 1H), 4.6 (s, 2H), 4.27 (s, 2H), 3.20 (m, 2H), 1.37 (m, 2H), 1.41 (s, 9H), 1.26-1.13 (m, 18H), 0.86 (t, 3H, 6.8 Hz);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz): 166.48, 166.43, 155.7, 146.0, 144.0, 134.1, 133.8, 133.0, 132.56, 131.1, 130.8, 130, 129.9, 129.21, 129.15, 125.8, 125.7, 124.7, 123.8, 79.7, 40.1, 36.0, 35.2, 31.9 29.6 (2C), 29.55, 29.51, 29.3, 29.2, 29.1, 28.4(3C), 26.8, 22.6, 14.1; IR (neat): 3442, 3287, 3149, 3017, 2925, 2856, 1700, 1663, 1654, 1640, 1606, 1557, 1539, 1525, 1508, 1459, 1214, 1165, 1045, 1019, 763, 669; HRMS (ESI) exact mass calcd. for  $C_{37}H_{51}N_9O_4Na$   $[M+Na]^+$  708.3961, found  $[M+Na]^+$  708.3973.

### **Preparation of dipeptide derivative 3:**

To a stirred solution of **2** (1 mmol) in dry dichloromethane (5 mL) at 0°C was added TFA (0.5 mL). The mixture was gradually allowed to warm to room temperature and stirred for

another 3h. After completion of the reaction as indicated by TLC, all the volatiles were removed under a stream of nitrogen. Toluene was then added to the residue, and evaporated to dryness to get the trifluoroacetate salt of the amine, which was used in the next step without further purification.

To a stirred solution of the amine trifluoroacetate salt generated above (0.5 g, 0.82 mmol) and DIPEA (0.42 mL, 2.47 mmol) in dry dichloromethane (10 mL) was added lauroyl chloride (0.28 mL, 1.23 mmol) drop wise at 0 °C under N<sub>2</sub> atmosphere. The reaction mixture was warmed to room temperature and allowed to stir for 12 h. After completion of the reaction (as per TLC), the mixture was washed with water and extracted with dichloromethane. The organic layer was dried using Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated under reduced pressure. The residue was then purified by column chromatography on silica gel using 80% ethylacetate-hexane solvent system in a gradient mode to get the product as a white solid (0.48 g, 85 %). Analytical data: R<sub>f</sub>: 0.21 (50 % Ethyl acetate- Hexane); mp 74-76 °C <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 8.10-8.01 (d, 1H, *J* = 6.8 Hz), 7.78 (s, 1H), 7.77 (s, 1H), 7.75-7.65 (m, 2H), 7.65-7.51 (m, 4H), 7.47-7.40 (d, 1H, *J* = 6.8 Hz), 7.27 (m, 3H), 7.21-7.14 (m, 2H) 6.66 (bs, 1H, NH<sup>2</sup>), 6.42 (bs, 1H, NH<sup>1</sup>), 5.11 (s, 2H), 4.49 (s, 2H), 4.46 (s, 2H), 2.15 (t, 2H, *J* = 7.6 Hz), 1.57 (m, 2H), 1.22 (m, 16H), 0.87 (t, 3H, *J* = 6.8 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 173.5, 166.2, 164.9, 145.4, 143.4, 136.1, 134.9, 134.2, 132.9, 132.3, 131.4, 131.2, 130.0, 129.9, 129.4, 128.48(2C), 128.45(2C), 128.42, 127.4, 127.1, 125.8, 124.8, 124.0, 67.5, 36.4, 35.1, 34.8, 31.9, 29.6 (2C), 29.5, 29.33 (2C), 29.3, 25.6, 22.7, 14.1. IR (neat): 3445, 3152, 3017, 2956, 2931, 2856, 1721, 1663, 1603, 1519, 1510, 1459, 1425, 1290, 1264, 1217, 1126, 1042, 1016, 930, 766, 666; HRMS (ESI) exact mass calcd. for C<sub>39</sub>H<sub>46</sub>N<sub>8</sub>O<sub>4</sub>Na [M+Na]<sup>+</sup> 713.3539, found [M+Na]<sup>+</sup> 713.3556.



## Gelation studies

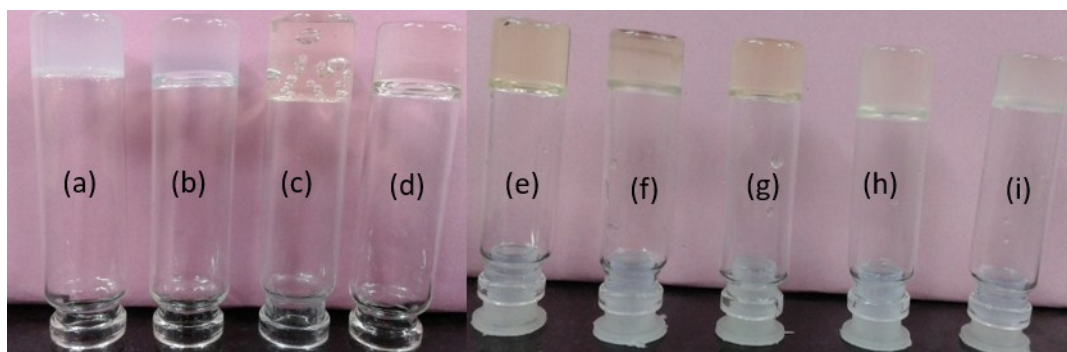
To perform the gelation test, a weighed amount of the gelator (mg) in a 5 mL vial was dissolved in appropriate solvent (measured volume) by gentle heating. It was then allowed to reach room temperature. Gelation is usually evident from the decreased mobility of the solvent which can be confirmed by inverting the vial; instead of flowing down, it remains stable on the top which can be taken as the sign of gelation. This procedure is usually called vial inversion method. Following this, Critical Gelation Concentration (CGC), which represent the minimum amount of the gelator required to immobilize 1 mL of the solvent was calculated.

**Table 1.** Critical gelation concentration values of organogelators **1** and **2** in different organic solvents; behaviour of **3** in these solvents is also shown. OG: opaque gel, TG: transparent gel, WG: weak gel, S: solution, P: precipitate

<b>Organic solvents</b>	<b>1(CGC/ wt. %)</b>	<b>2(CGC/ wt. %)</b>	<b>3</b>
<b>Benzene</b>	1.5 (OG)	1.2 (TG)	P
<b>Toluene</b>	0.6 (OG)	1.0 (TG)	P
<b>m-Xylene</b>	0.3 (OG)	0.8 (TG)	P
<b>Mesitylene</b>	0.1 (TG)	0.5 (TG)	P
<b>Carbon tetrachloride</b>	.08 (TG)	1.5 (TG)	I
<b>Ethylacetate-Hexane (1:1)</b>	0.5 (OG)	0.3 (TG)	P
<b>p-xylene</b>	0.7 (OG)	0.6 (TG)	S

<b>Chlorobenzene</b>	2.0 (OG)	S	S
<b>Bromobenzene</b>	2.0 (OG)	S	S
<b>Chloroform-hexane (1:1)</b>	P	0.1 (TG)	P
<b>Diesel</b>	I	0.3 (TG)	WG
<b>Petrol</b>	I	0.1(TG)	WG
<b>Coconut oil</b>	I	0.5 (TG)	P
<b>Almond oil</b>	I	1.0 (TG)	P
<b>Groundnut oil</b>	I	1.0 (TG)	P
<b>Olive oil</b>	I	1.2 (TG)	P
<b>Dichloromethane-Hexane (1:2)</b>	P	0.5(TG)	P
<b>THF-Heptane (1:4)</b>	P	0.25(TG)	P
<b>Methanol</b>	S	S	S
<b>Ethanol</b>	S	S	S

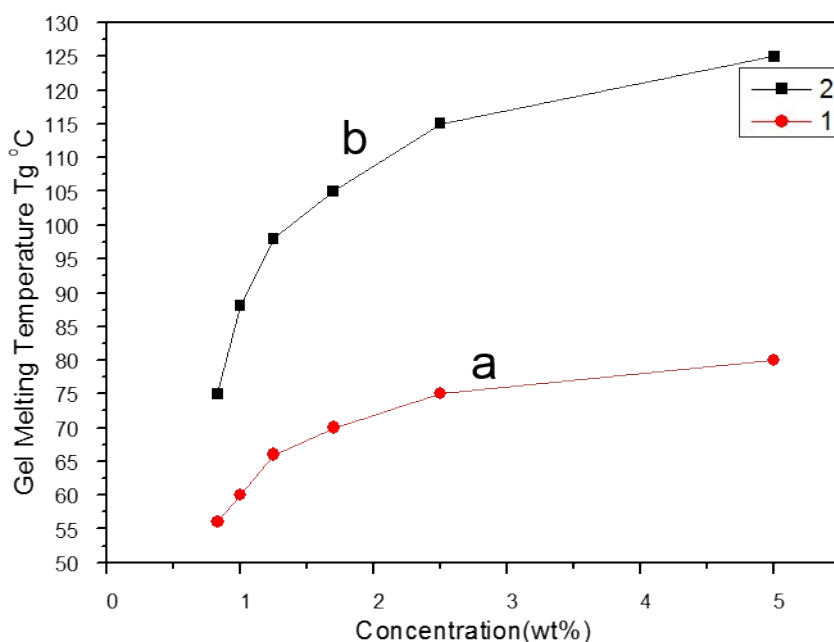
<b>Isopropanol</b>	2.5(OG)	S	S
<b>Dodecanol</b>	2(OG)	S	S



**Figure 1.** Gels of **1** and **2** in various solvents: a) **1** in  $\text{CCl}_4$ ; b) **1** in Mesitylene; c) **2** in DCM/Hexane (1:2); d) **2** in Mesitylene; e) **2** in Olive oil; f) **2** in Groundnut oil; g) **2** in Gingili oil; h) **2** in Almond oil; i) **2** in Coconut oil.

### **Gel Melting Temperature ( $T_{\text{gel}}$ )**

The melting temperature/stability of gels formed by compounds **1** and **2** in different solvents were determined by ‘ball dropping method’. Here, a small steel ball which weights 100 mg was placed on the top of the specific gel formed from 1 mL of the solvent in a stoppered glass vial. It was slowly heated with an eye on the ball situated on the top. Softening of the gel under heat initiates downward movement of the ball and the temperature at which it reaches the bottom of the vial is noted as the sol-gel phase transition temperature ( $T_g$ ).



**Figure 2.** Variation of T<sub>g</sub> of Mesitylene gel from 1 and 2 with increasing concentration

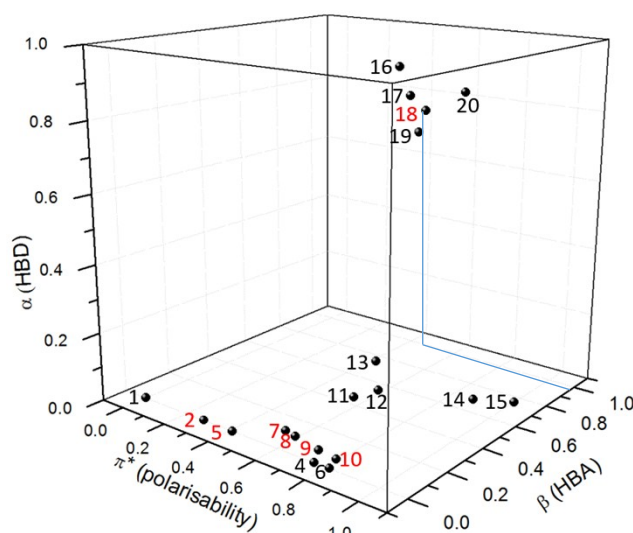
Gel melting temperature ( $T_m$ ) is the temperature at which the gel transforms completely into a liquid. This was measured as a function of concentration of the gelators in mesitylene which is a high boiling liquid and with good gelation propensity with **1** and **2**. As evident from Figure 2, increase in gelator concentration leads to an increase in  $T_m$  value as well. Beyond 2.5% w/v there was a reduction in the rate at which the  $T_m$  increased. Comparison of curves **a** and **b** shows that the strength of mesitylene gel from **2** is better than that of the gel from **1**. Additional contribution of the long chain attached at the C-terminus of **1** to the stability of the supramolecular network is the likely reason.

### Solvatochromic Parameters

Gel forming ability of chemical compounds can be correlated with the solvatochromic parameters of solvents to understand the relative influences of hydrogen bond donation ability ( $\alpha$ ), hydrogen bond acceptor ability ( $\beta$ ) and dipolarisability ( $\pi^*$ ). A compilation of these parameters<sup>2</sup> and the gelation profile of compounds **1** and **2** are presented in Table 2.

**Table 2.** Solvatochromic parameters of different solvents and gelation profiles of **1** and **2**; G = Gel; S = sol; I = insoluble

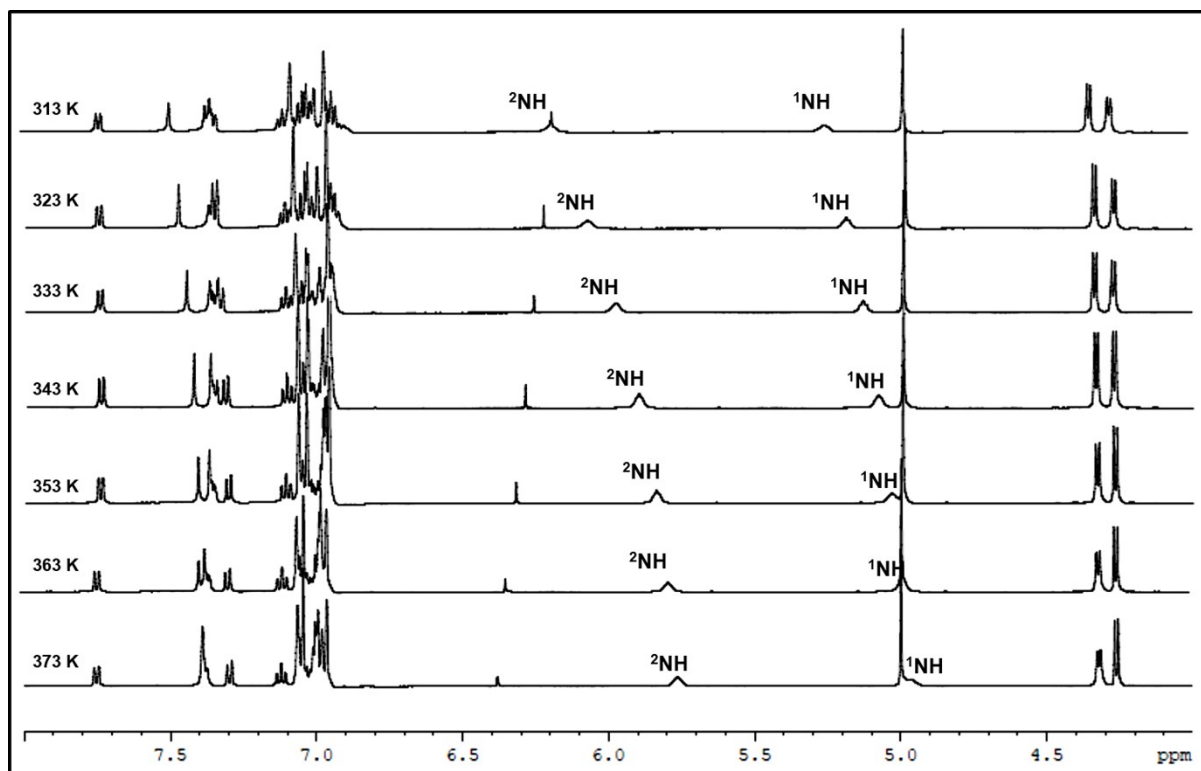
S.No.	solvents	$\pi^*$ (solvent polarizability)	$\beta$ (HBA)	$\alpha$ (HBD)	<b>1</b>	<b>2</b>
1	cyclohexane	0.00	0.00	0.00	I	G
2	Carbon tetrachloride	0.28	0.00	0.00	G (0.08)	G (1.5)
3	Dichloroethane	0.81	0.00	0.00	S	S
4	Dibromoethane	0.75	0.00	0.00	S	S
5	Mesitylene	0.41		0.00	G (0.1)	G
6	Iodobenzene	0.81		0.00	G	G
7	Toluene	0.54	0.11	0.00	G (0.6)	G
8	Benzene	0.59	0.10	0.00	G (1.5)	G
9	Chlorobenzene	0.71	0.07	0.00	G (2)	S
10	Bromobenzene	0.79	0.06	0.00	G (2)	S
11	Ethyl acetate	0.55	0.45	0.00	S	S
12	Tetrahydrofuran	0.58	0.55	0.00	S	S
13	Acetonitrile	0.75	0.31	0.19	S	S
14	DMF	0.88	0.69	0.00	S	S
15	DMSO	1.00	0.76	0.00	S	S
16	Methanol	0.60	0.62	0.93	S	S
17	Ethanol	0.54	0.77	0.83	S	S
18	Isopropanol	0.48	0.95	0.76	G(2.5)	S
19	t-butanol	0.41	1.01	0.68	S	S
20	Ethylene glycol	0.92	0.52	0.90	S	S



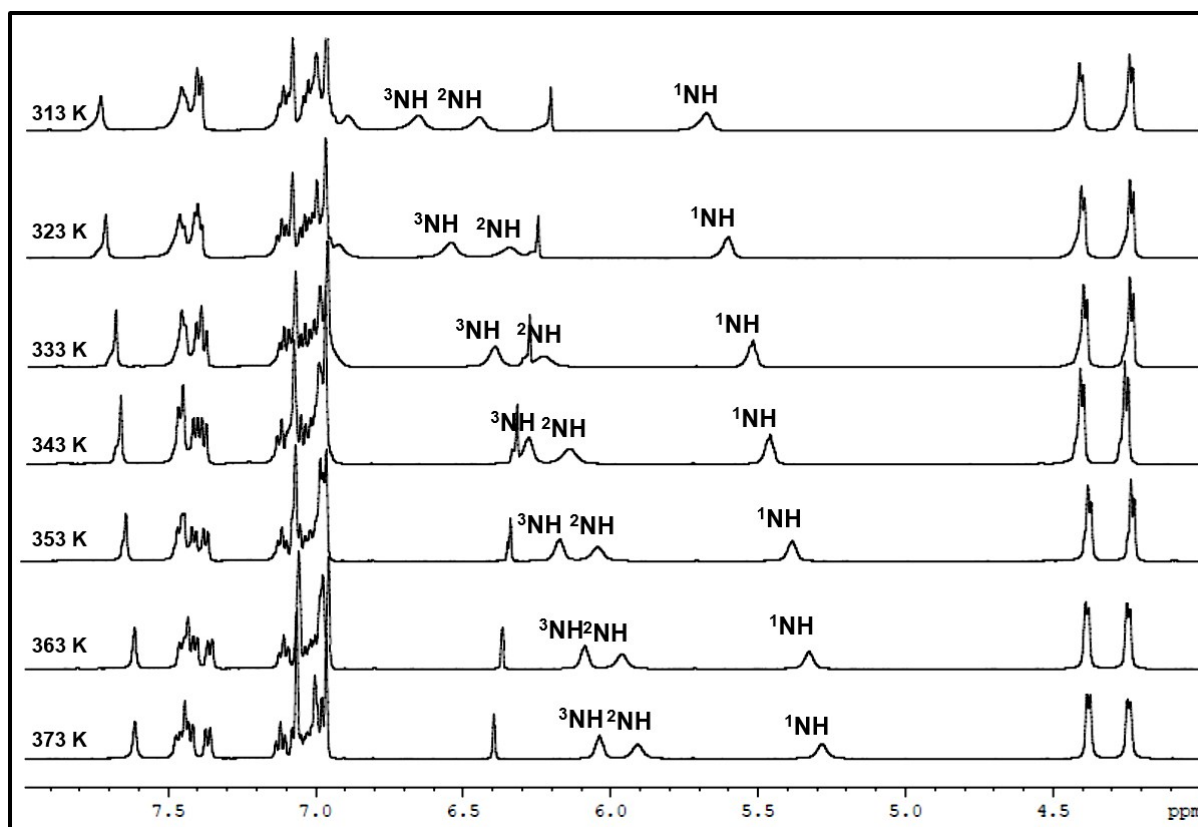
**Figure 3.** 3D Kamlet-Taft plot for compound **1** with various organic solvents mentioned in Table 2, gels has been coded with red colour.

### Variable temperature $^1\text{H}$ NMR experiments:

Gel network is stable only below a certain temperature. This can be correlated with the stability of secondary interactions which hold the supramolecular network responsible for gelation. As can be anticipated,  $^1\text{H}$  NMR signals of protons involved in hydrogen bonded interactions appear relatively downfield in  $^1\text{H}$  NMR spectrum. At higher temperatures, such secondary interactions break down, which results in the upfield shifting of these signals. To get a closer look into these, temperature-dependant  $^1\text{H}$  NMR study of **1** and **2** in Toluene- $\text{D}_8$  was carried out and the results are presented in Figures 4 and 5. In general, the signals were relatively sharper at temperatures above  $T_g$ .



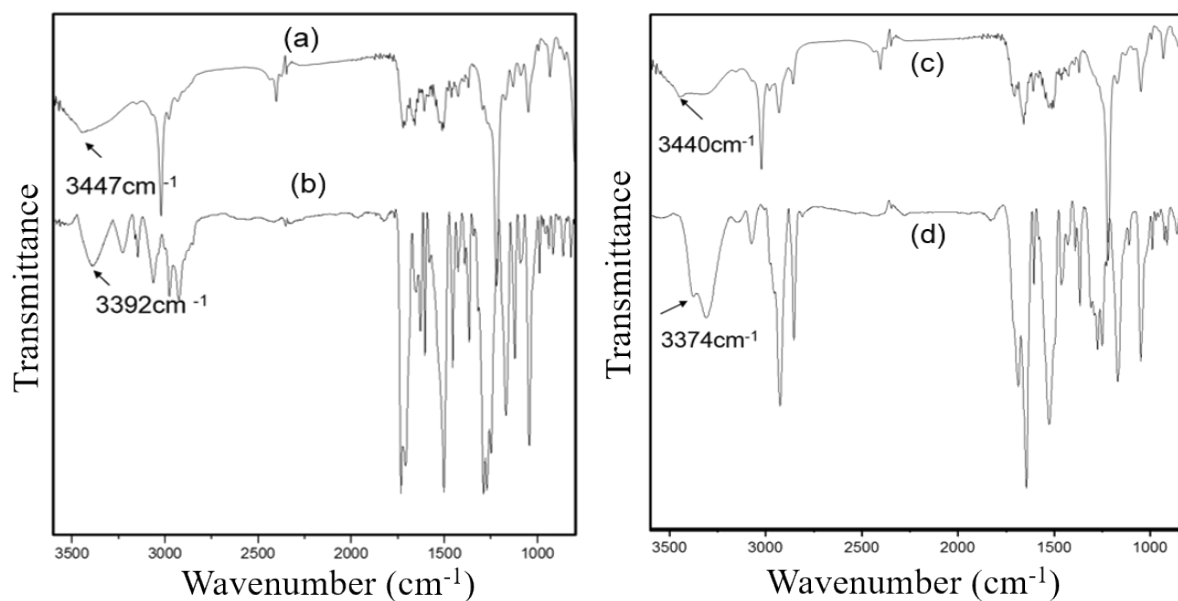
**Figure 4.** Variable temperature  $^1\text{H}$  NMR (500 MHz) spectra of **1** in Toluene- $\text{d}_8$ .



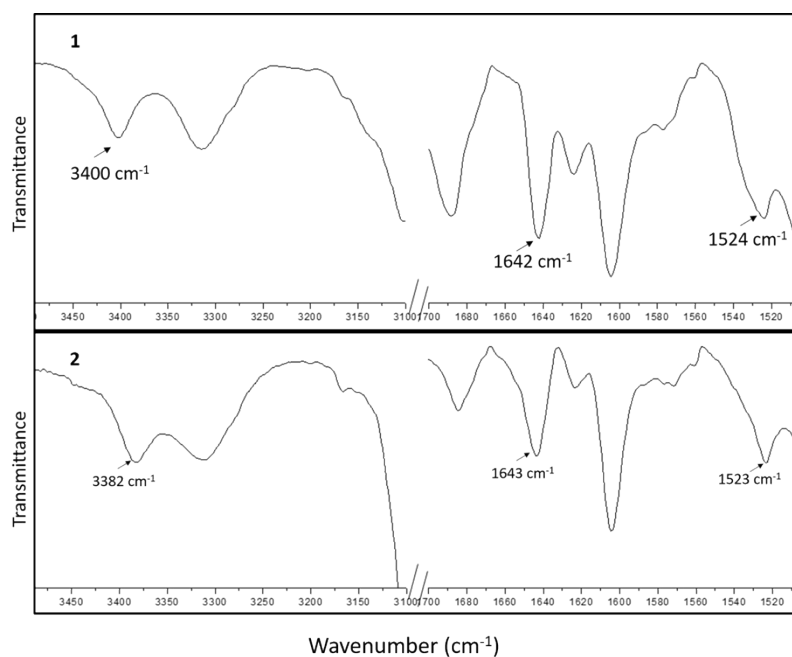
**Figure 5.** Variable temperature  $^1\text{H}$ NMR (500 MHz) spectra of **2** in Toluene- $d_8$ .

### IR experiments:

FT-IR is useful for understanding the hydrogen bonding pattern in self-assembled systems. The FT-IR spectrum of **1** drop-casted from chloroform solution showed transmission bands at 3447, 1656, and 1510  $\text{cm}^{-1}$  (Figure 6(a)) which are characteristic of nonhydrogen bonded NH (stretching), carbonyl (stretching), and NH (bending) whereas its xerogel (from toluene) had these bands at 3392, 1630, and 1533  $\text{cm}^{-1}$  (Figure 6(b)). Lowering of stretching frequencies of NH and amide carbonyl and a slight increase in NH bending frequency are clear indications of hydrogen bonding effects. Similarly FTIR of **2** from chloroform (neat) showed transmission bands at 3440, 1655, and 1518  $\text{cm}^{-1}$  which shifted to 3374, 1644 and 1526  $\text{cm}^{-1}$  in the case of xerogel from toluene (Figure 6(c) and (d)). In addition to this asymmetric and symmetric  $\text{CH}_2$  stretching frequencies appeared at 2927 and 2855  $\text{cm}^{-1}$  in the case of neat sample whereas the toluene xerogel had these bands at 2925 and 2853  $\text{cm}^{-1}$ . This lowering of frequency indicates some rigidity of the alkyl chain because of the Van der Waals association of  $\text{CH}_2$  units in the xerogel compared to that in the neat sample. Thus, hydrogen bonding as well as Van der Waals interactions are playing crucial roles in the self-assembly of **2**.



**Figure 6.** a) IR spectrum of **1** (neat) from  $\text{CHCl}_3$ , b) IR spectrum (KBr pellet) of the xerogel of **1** from Toluene c) IR spectrum of **2** (neat) from  $\text{CHCl}_3$  d) IR spectrum (KBr pellet) of the xerogel of **2** from Toluene.

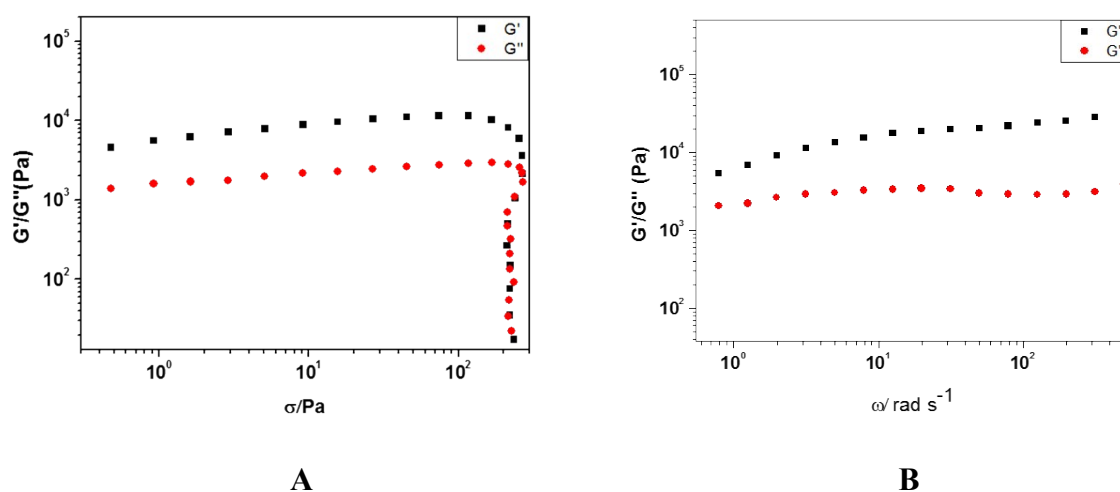


**Figure 7.** 1) IR spectrum of toluene gel of **1** showing NH stretching transmission at  $3400\text{cm}^{-1}$ , carbonyl stretching transmission at  $1642\text{ cm}^{-1}$ , and NH bending transmission band at  $1524\text{ cm}^{-1}$ , 2) IR spectrum of toluene gel of **2** showing NH stretching transmission at  $3382\text{cm}^{-1}$ , carbonyl stretching transmission at  $1643\text{ cm}^{-1}$ , and NH bending transmission band at  $1523\text{ cm}^{-1}$

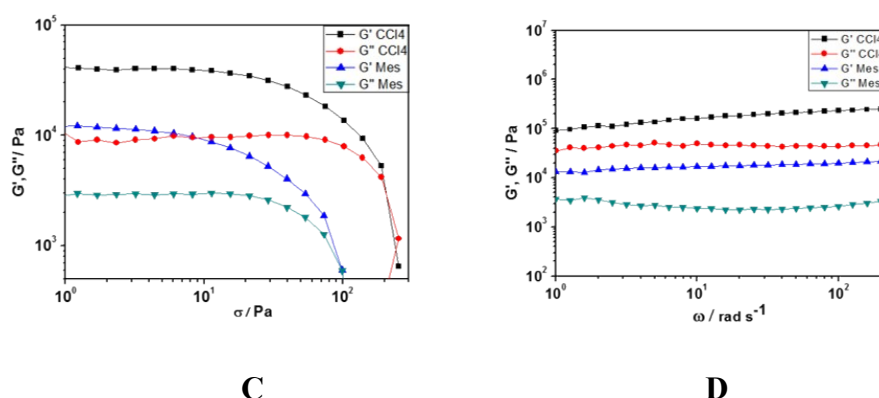


## Rheological experiments (Flow behaviour of Organogels)

Stress sweep experiment showing high yield stress value (269 Pa) for Petrol gel of 2 (2 % w/v) is shown in Figure 8A, whereas the results from its frequency sweep experiment indicating high strength over a wide range of frequency is shown in Figure 8B. Figure 9D shows the frequency dependence of the storage modulus ( $G'$ ) and loss modulus ( $G''$ ) of carbon tetrachloride- and mesitylene gels of 1 observed in an oscillatory frequency sweep experiment. For both the gels,  $G'$  was higher than  $G''$  over the entire frequency range (0-200 rad/s). The storage modulus ( $G'$ ) in carbon tetrachloride gel was in the order of  $10^5$  Pa whereas that for mesitylene gel, of the order of  $10^4$  Pa, indicating that the former is one order magnitude stronger than the latter. The yield stress value ( $\sigma$ ) of  $>100$  Pa for these gels is also an indication of their higher strength (Figure 9C).



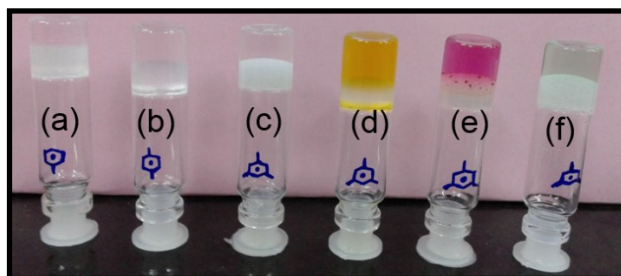
**Figure 8.** Results from stress sweep experiment (A) and frequency sweep experiment (B) with the petrol gel of 2 (2 wt%).



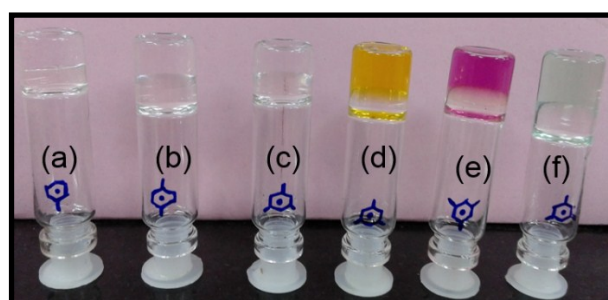
**Figure 9.** Results from stress sweep experiment (C) and frequency sweep experiment (D) with carbon tetrachloride and Mesitylene gels of 1.

## Phase selective gelation Studies

10 mg of the gelator (**1** or **2**) was added to a mixture of water (1 mL) and appropriate aromatic solvent (toluene, p-xylene or mesitylene; 1 mL) in a vial. The mixture was heated gently to dissolve the gelator and then allowed to cool to room temperature. This led to gelation of the organic phase (stable to vial inversion), leaving the aqueous portion intact (Figure 10). To know whether presence of metal salts/additives can affect phase selective gelation, we have carried out a series of tests using aqueous solutions of potassium dichromate, Potassium permanganate, and Nickel (II) chloride. As evident from images shown in Figure 10A and Figure 10B, gelation was efficient in all cases without any noticeable influence from these additives.



**Figure 10A.** Phase selective gelation of **1** with (a) Toluene from water, (b) p-xylene from water, (c) Mesitylene from water, (d) Mesitylene from aqueous solution of  $K_2Cr_2O_7$ , (e) Mesitylene from aqueous solution of  $KMnO_4$ , (f) Mesitylene from aqueous solution of Nickel (II) chloride.

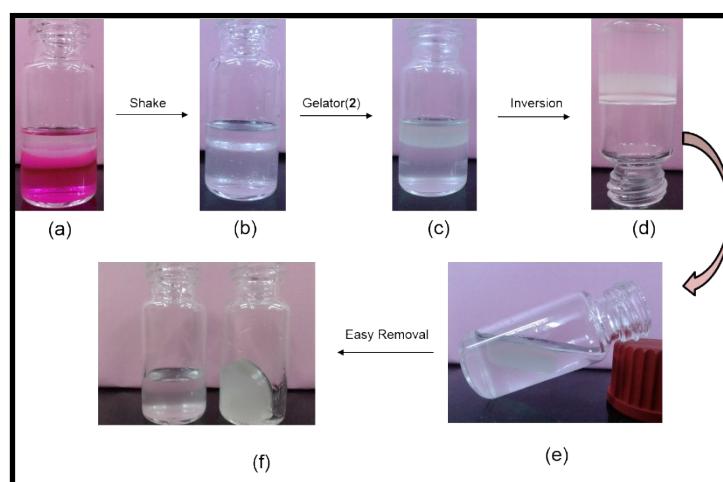


**Figure 10B.** Phase selective gelation of **2** with (a) Toluene from water, (b) p-xylene from water, (c) Mesitylene from water, (d) Mesitylene from aqueous solution of  $K_2Cr_2O_7$ , (e) Mesitylene from aqueous solution of  $KMnO_4$ , (f) Mesitylene from aqueous solution of Nickel (II) chloride.

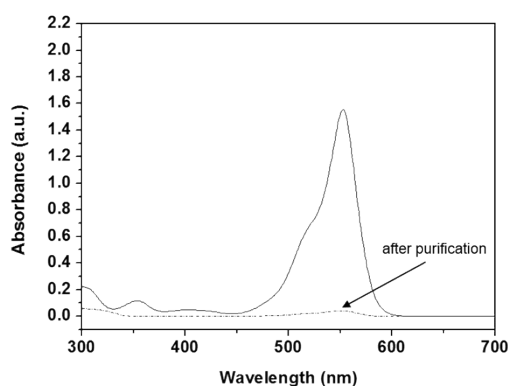
## Removal of Rhodamine B dye from water.

Dye removal experiments were done under three different conditions.

i) *Gelation with 2 after the dye is partitioned into mesitylene*: Mesitylene (1 mL) was added to a solution of Rhodamine B dye in tap water (2 mL, 0.047 mM, Figure-11a) and shaken well. This led to partitioning of the dye in the mesitylene layer as shown in Figure 11b. A solution of **2** (15 mg in 0.1 mL THF) was then added to it, which led to gelation of the mesitylene layer in less than 30 minutes (Figure 11c). The gel was stable on vial inversion as shown in Figure 11d. It was possible to decant the water layer leaving the dye entrapped gel in the vial as shown in Figure 11e and 11f. UV-Vis spectra presented in Figure 12 show the absorbance of the aqueous portion before (solid line) and after (dashed line) dye removal.



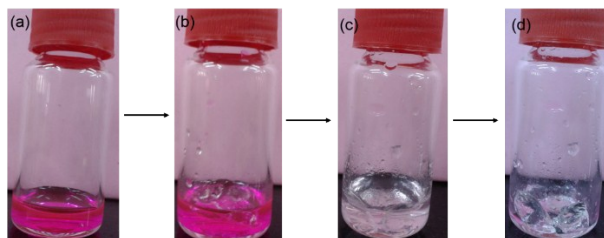
**Figure 11.** Removal of rhodamine B dye from water using organogelator **2** in mesitylene



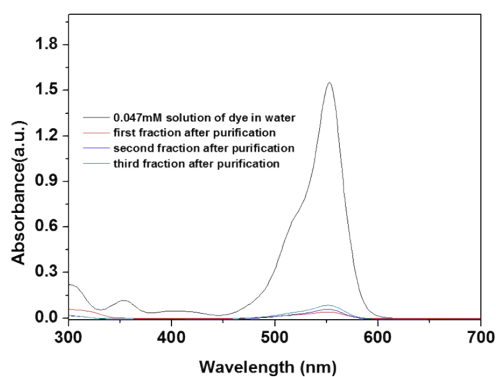
**Figure 12.** UV-Vis spectrum absorbance of the aqueous portion before (solid line) and after (dashed line) dye removal; 0.047 mM solution of Rhodamine B dye was used.

ii) *Partitioning of the dye to the pre-formed mesitylene gel of 2*: The gel formed from 1 mL of mesitylene and 1 % w/v of **2** was placed in the aqueous solution of the dye (0.047 mM, 1 mL)

in a vial. As shown in Figure 13, the colour of the aqueous layer disappeared in 4 h, after which it was decanted. The UV-Vis spectra of the aqueous layer before and after the dye removal are shown in Figure 14. It was possible to use the same gel multiple times, in present case we used it three times (Figure 14)

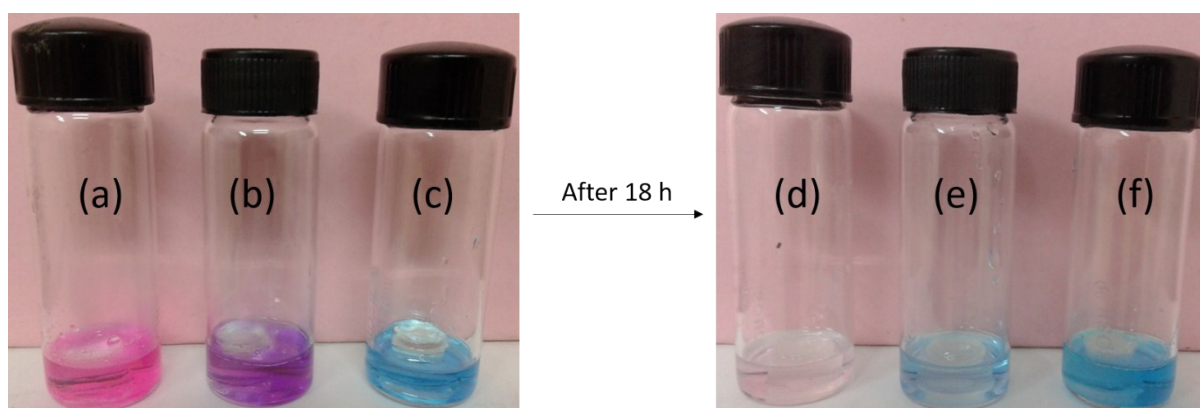


**Figure 13.** a) 1mL of 0.047 mM Rhodamine in water, b) preformed Mesitylene gel (1 % w/v) was added, c) after 4 hours complete removal of dye, d) removal of water leaving transparent gel containing dye



**Figure 14.** Absorption spectra of 0.047 mM rhodamine B in water (black), first fraction after purification (red), second fraction after purification from same gel (blue), third fraction (green).

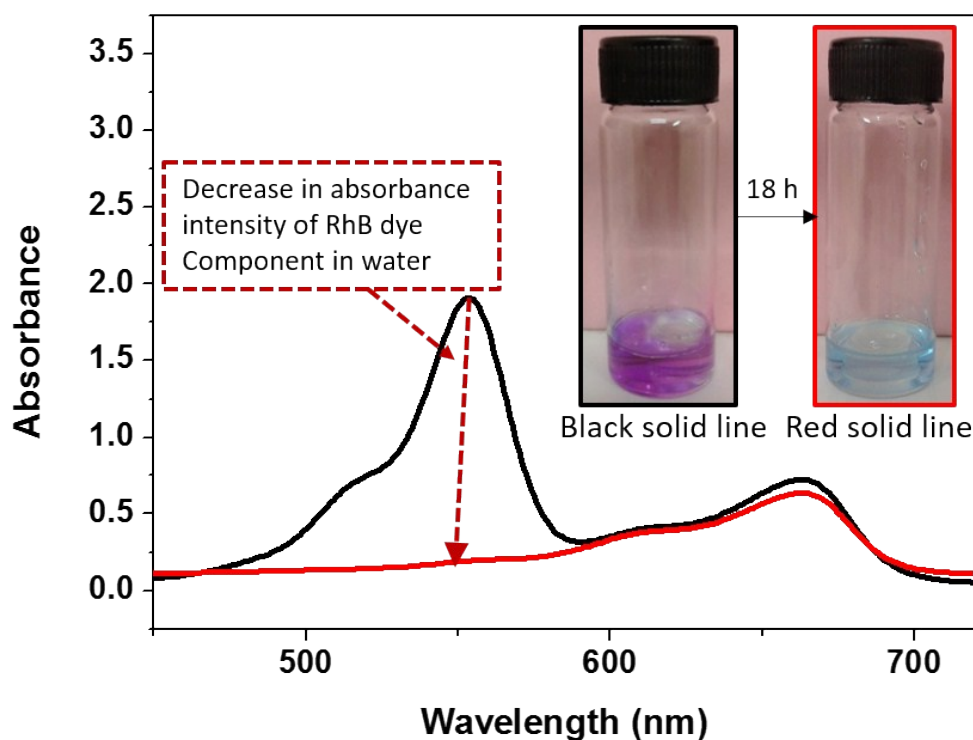
### Selective removal of Rhodamine B dye from a mixture of Rhodamine B and Methylene blue



**Figure 15.** (a) Rhodamine B dye in water (0.03 mM, 2 mL) with mesitylene gel of **2** (1 wt%), (b) mixture of Rhodamine B dye (0.03 mM, 1 mL) and methylene blue (0.03 mM, 1mL) with

mesitylene gel of **2** (1 wt%), (c) methylene blue dye in water (0.03 mM, 2 mL) with mesitylene gel of **2** (1 wt%); d-f represent the status of a-c respectively after 18h.

Figure 15d and 15e clearly indicate trapping of dye by the mesitylene gel block whereas 15f doesn't show any colour change after same amount of time. Interestingly from a mixture of two dyes, only one was selectively removed as is evident from Figure 15e, which was further confirmed by UV-spectra recorded after 18 h (Figure 16).



**Figure 16.** UV spectrum of mixture of Rhodamine B dye (0.03 mM, 1 mL) and methylene blue (0.03 mM, 1mL) dye (black solid line) and UV spectrum of the same mixture after 18 h of addition of 1wt% mesitylene gel of **2** (red solid line).

### Powder XRD details

Powder X-ray diffraction (PXRD) analysis of xerogels of **1** and **2** were done to get an insight into the molecular packing which is responsible for solvent entrapment. Figure 17 and 18 shows the PXRD patterns of xerogels of **1** from  $\text{CCl}_4$  and **2** from toluene. The xerogel of **1** displayed three peaks at  $2\theta$  3.66, 7.6, 10.95 corresponding to d-spacings of 24.14, 11.7, and 8.07 nm, respectively. The values fall in the ratio 1: 1/2: 1/3, indicating a layered structure. The xerogel of **2** displayed three reflection peaks at  $2\theta$  values 3.5, 7.5, 10.3 respectively corresponding to d-spacings: 25.3(d), 11.86( $\sim d/2$ ), 8.5( $d/3$ ) which again indicates a layered structure.

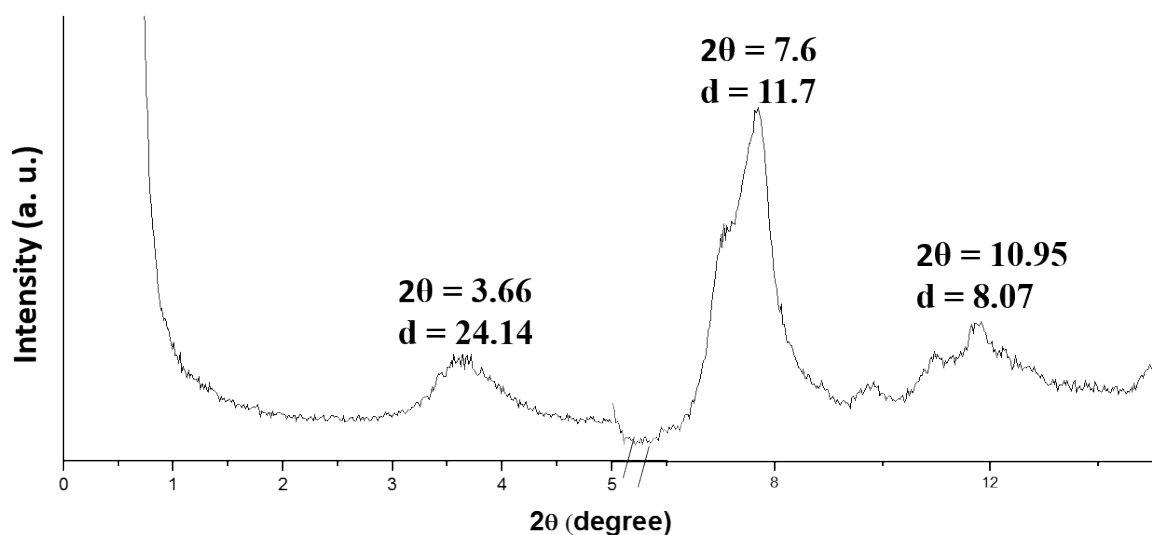


Figure 17. PXRD spectrum of xerogel of **1** from  $\text{CCl}_4$

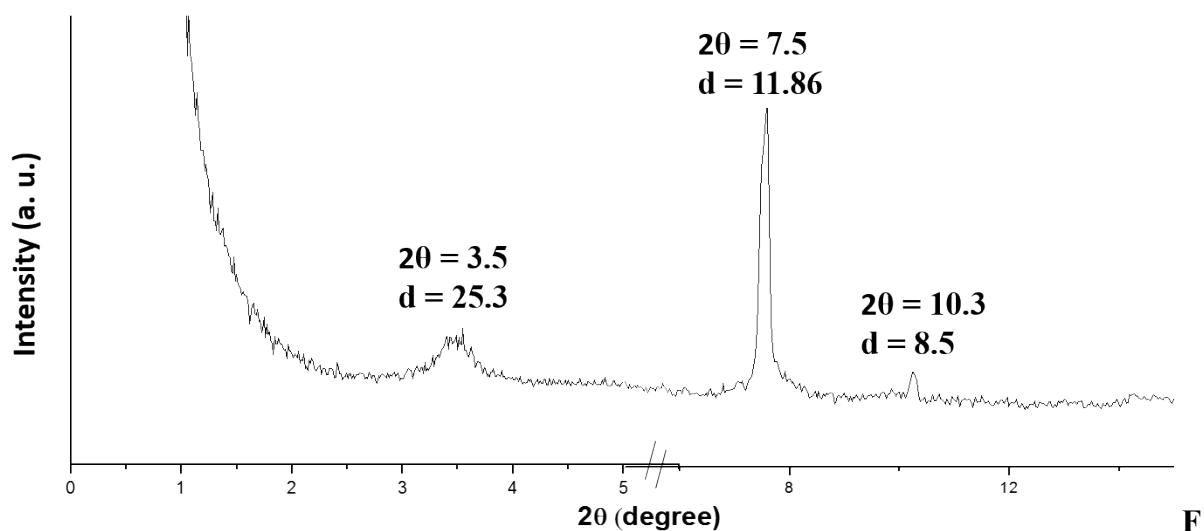


figure 18. XRD pattern of xerogel of 2 from Toluene

### Scanning Electron Microscopic images

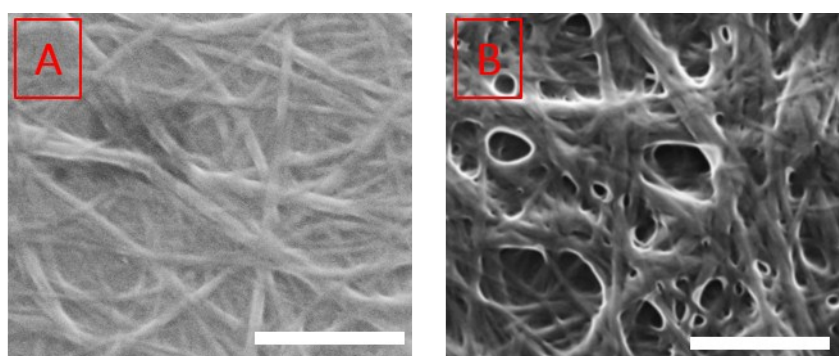


Figure 19. SEM images of xerogel of 1 from  $\text{CCl}_4$  (A), Toluene (B); scale bar 1  $\mu\text{m}$

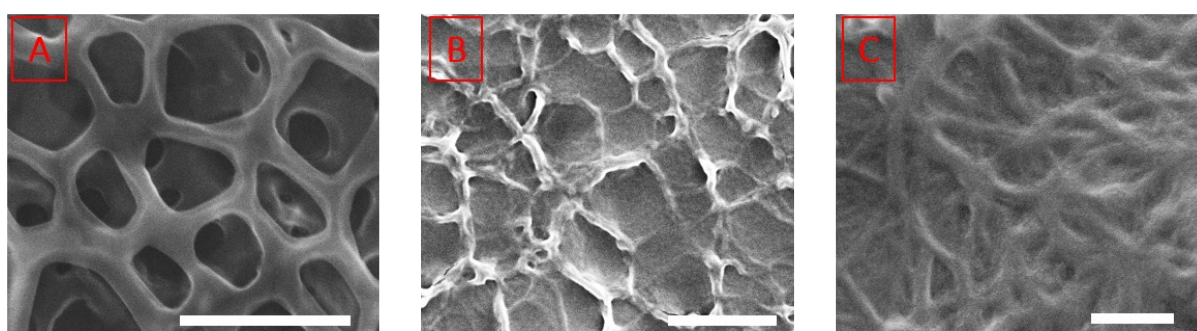
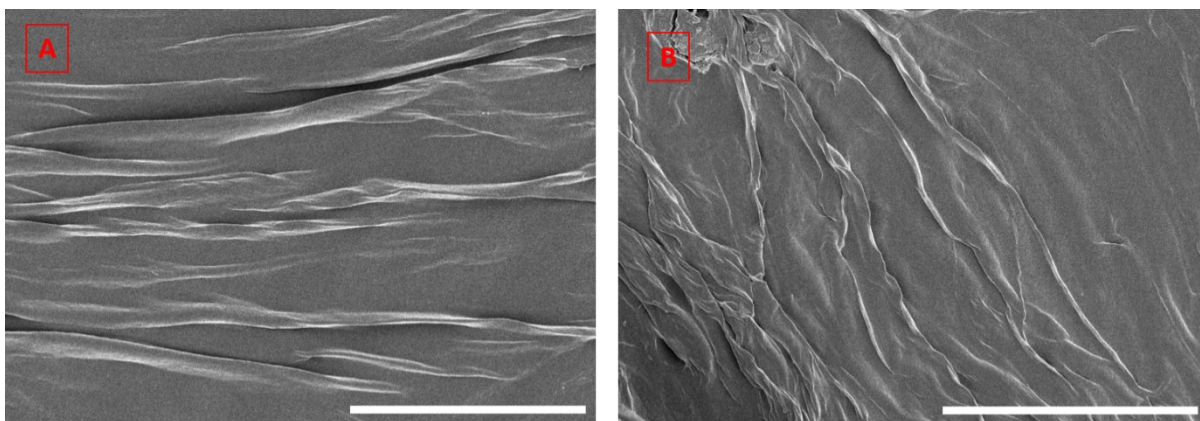


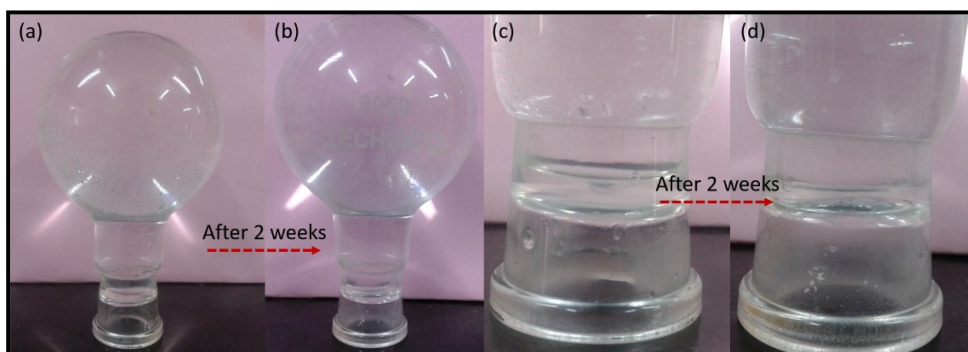
Figure 20 (a). SEM images of xerogel of 2 from  $\text{CCl}_4$  (A),  $\text{CHCl}_3$ -hexane (B), Toluene (C); scale bar 2  $\mu\text{m}$  for A, B and 1  $\mu\text{m}$  for C.





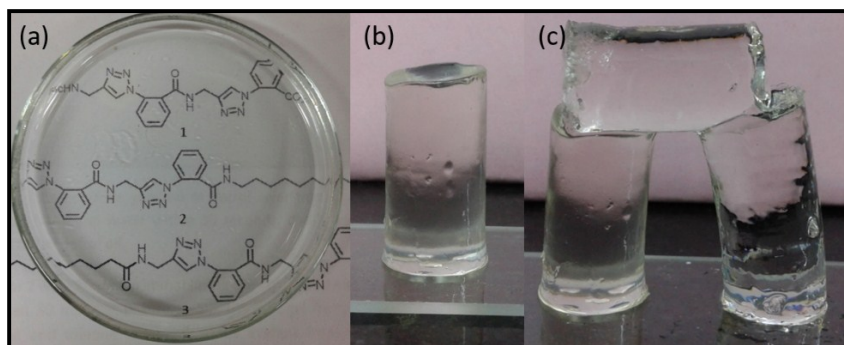
**Figure 21 (b).** SEM images of Rhodamine B dye entrapped xerogel of **2** from Mesitylene under condition 1 (A), under condition 2 (B); scale bar is 50  $\mu\text{m}$  for A and B.

### Load bearing Property and Transparent gel images



**Figure 22.** (a) Water ( $\sim 250$  mL) in a 250 mL RB flask kept upside down sealed with 1.5 mL (0.9% w/v) Mesitylene gel of **2**, (b) same RB flask (as in (a)) after 2 weeks, (c) Mesitylene layer responsible for Load bearing (zoom in of (a)), (d) Contraction of mesitylene layer after 2 weeks (still able to bear load of 250 mL of water).





**Figure 23.** (a) Thin layer of Mesitylene gel of **2** in a petri dish showing its transparent nature (b) Transparent cylinder formed from 3 mL (2% w/v) Mesitylene gel of **2** , (c) Transparent pillars made from 3 mL (2% w/v) Mesitylene gel of **2** showing its excellent strength.

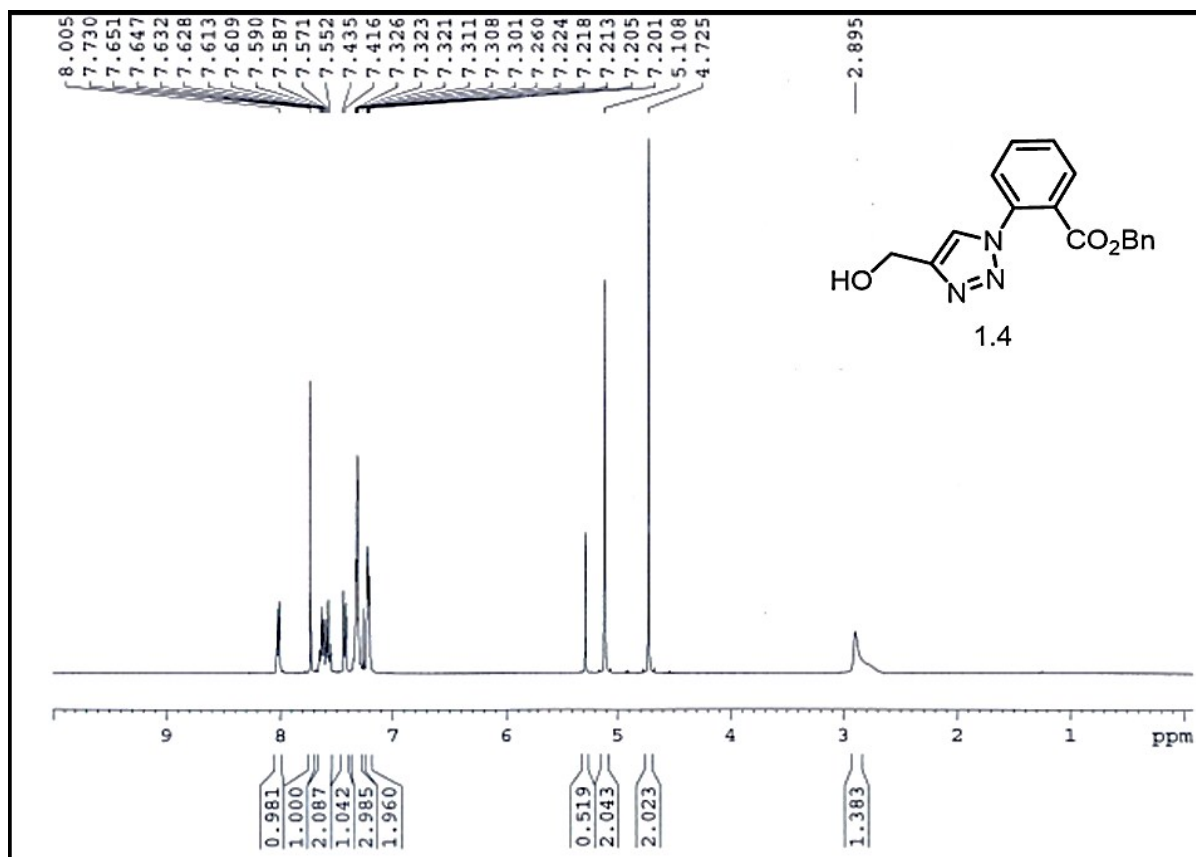


Figure 24.  $^1\text{H}$  NMR (400 MHz) spectra of **1.4** in  $\text{CDCl}_3$

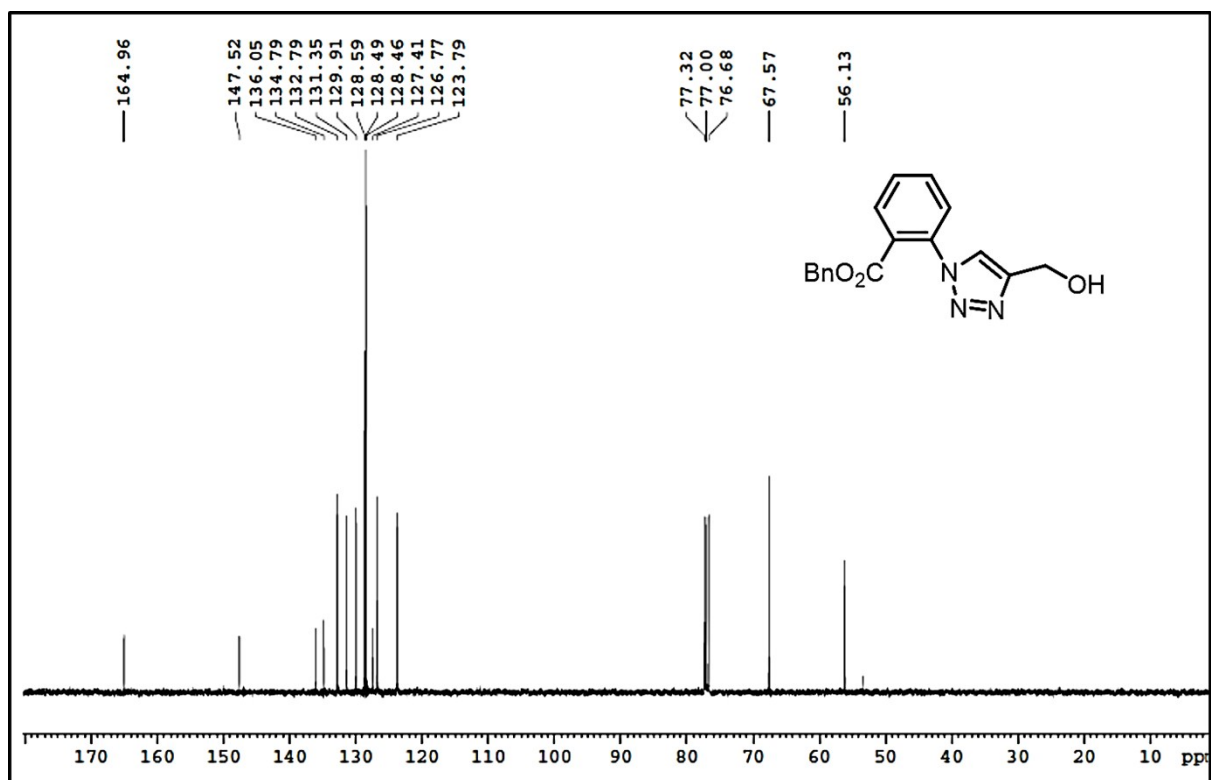


Figure 25.  $^{13}\text{C}$  NMR (100 MHz) spectra of **1.4** in  $\text{CDCl}_3$

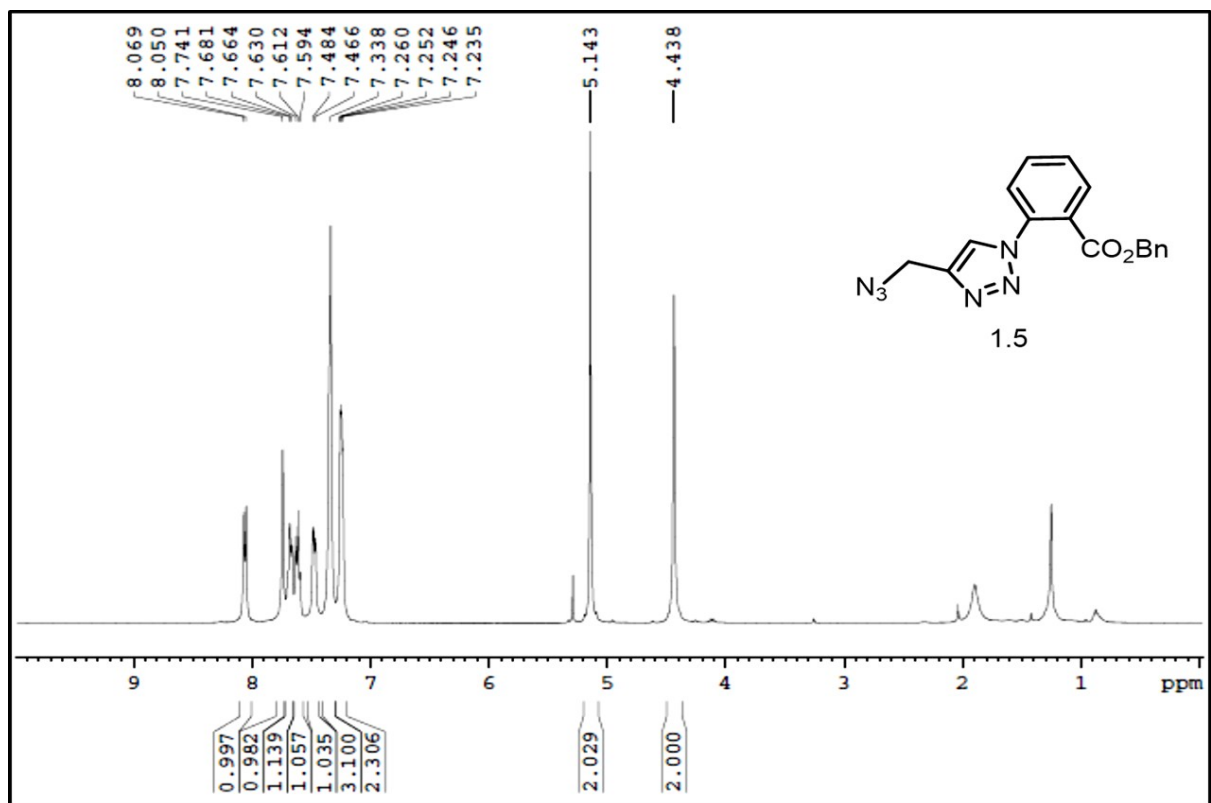
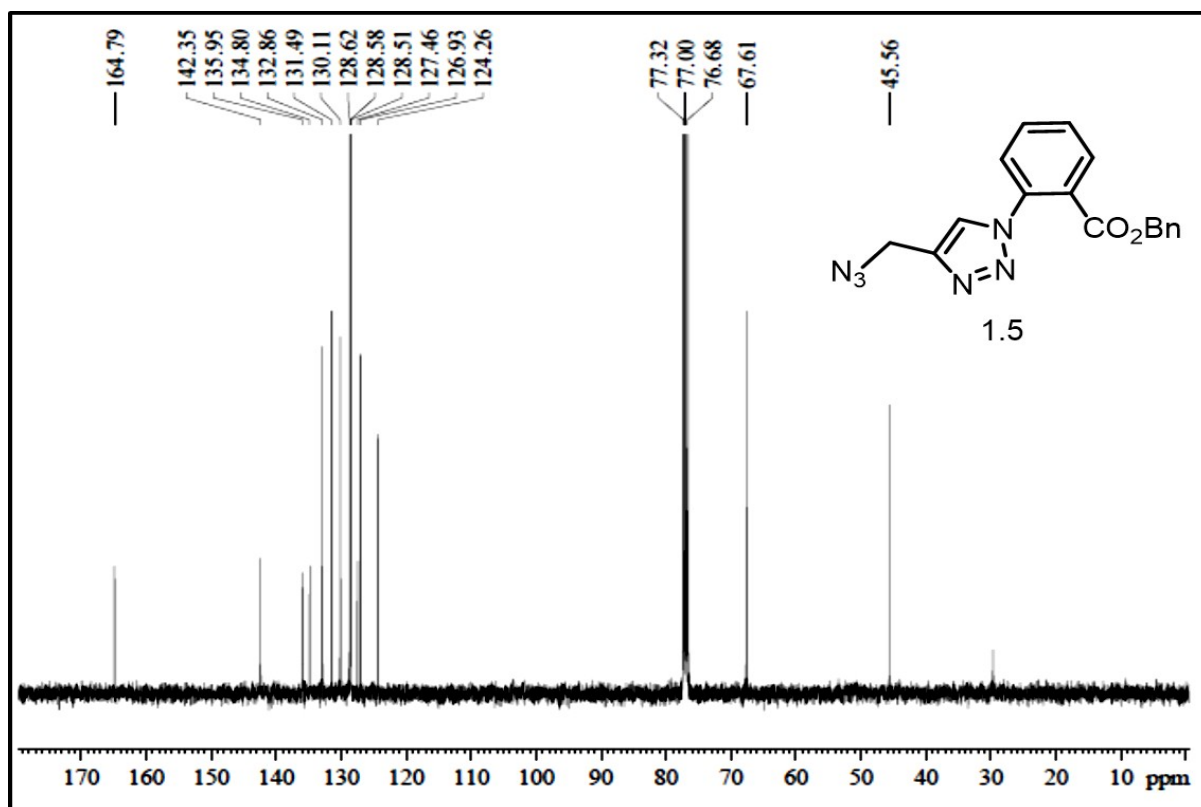
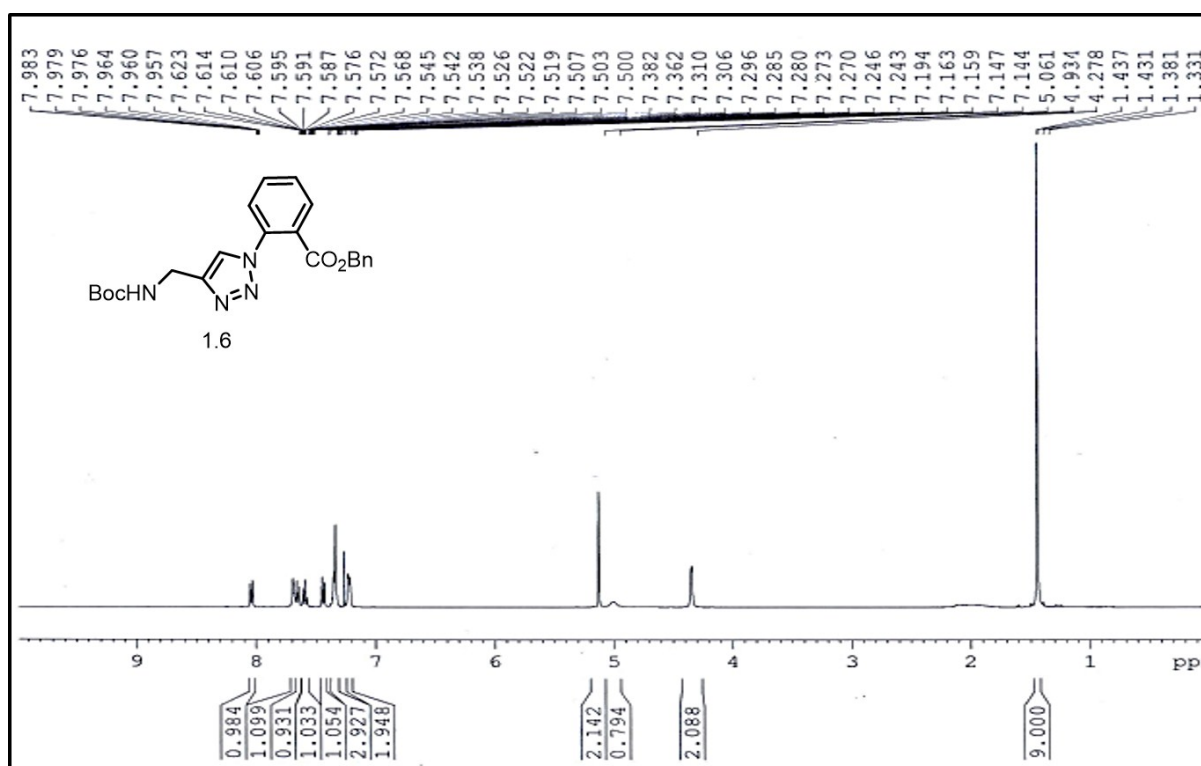


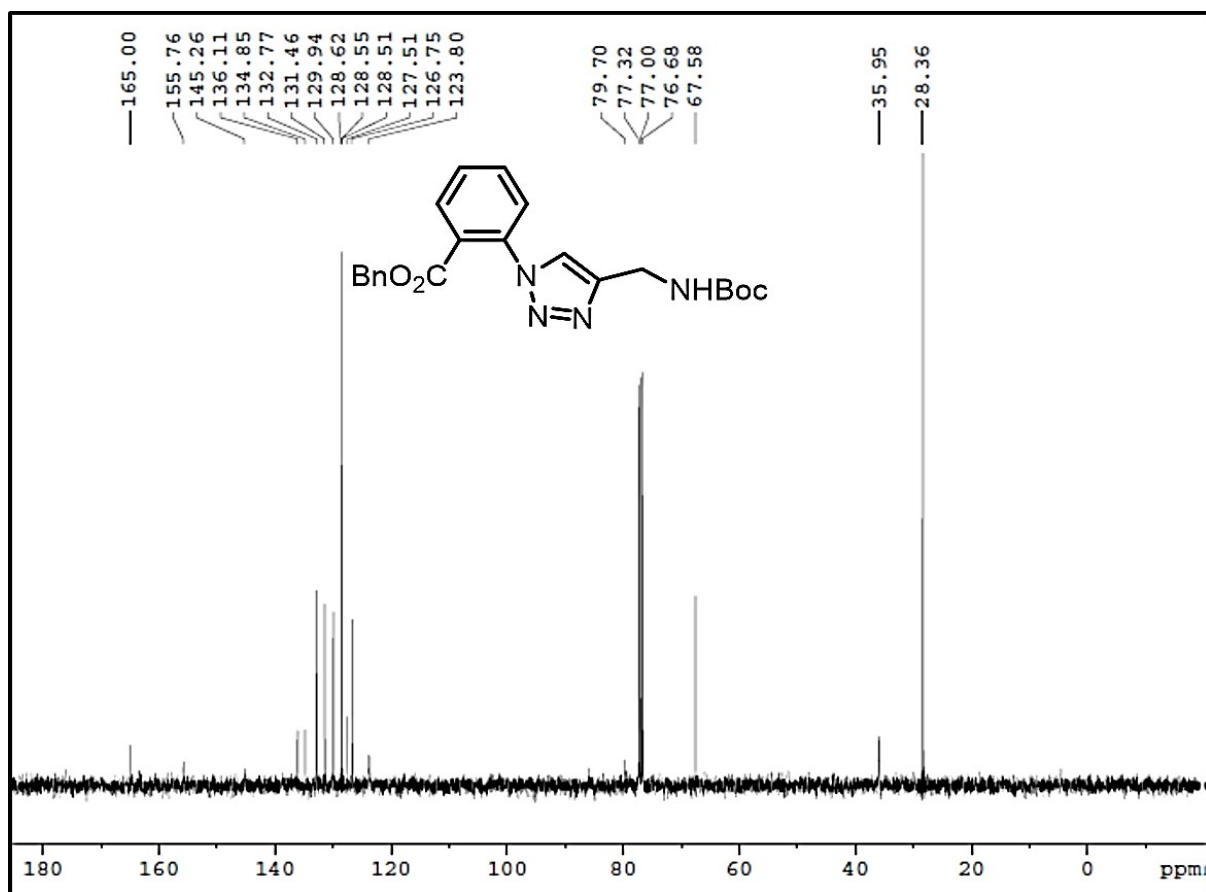
Figure 26.  $^1\text{H}$  NMR (400 MHz) spectra of **1.5** in  $\text{CDCl}_3$



**Figure 27.** <sup>13</sup>C NMR (100 MHz) spectra of **1.5** in CDCl<sub>3</sub>



**Figure 28.** <sup>1</sup>H NMR (400 MHz) spectra of **1.6** in CDCl<sub>3</sub>



**Figure 29.** <sup>13</sup>C NMR (100 MHz) spectra of **1.6** in CDCl<sub>3</sub>

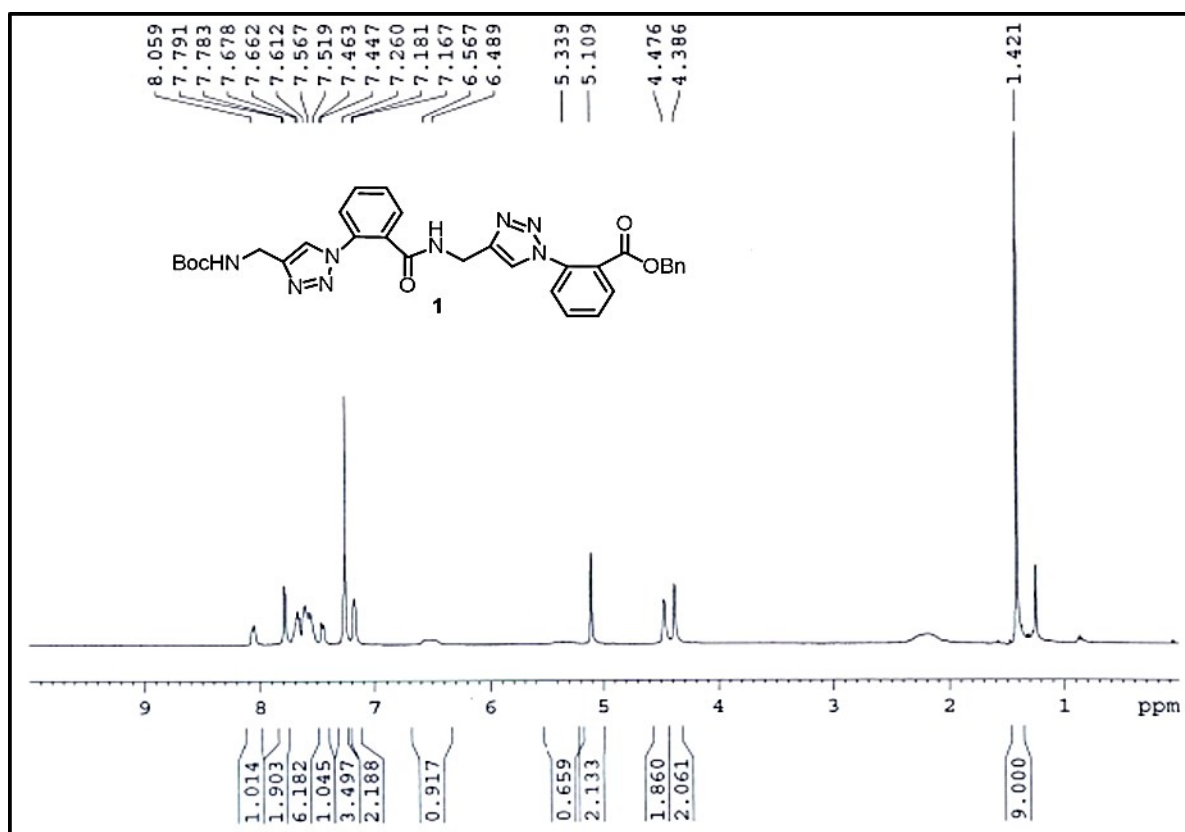


Figure 30.  $^1\text{H}$  NMR (400 MHz) spectra of **1** in  $\text{CDCl}_3$

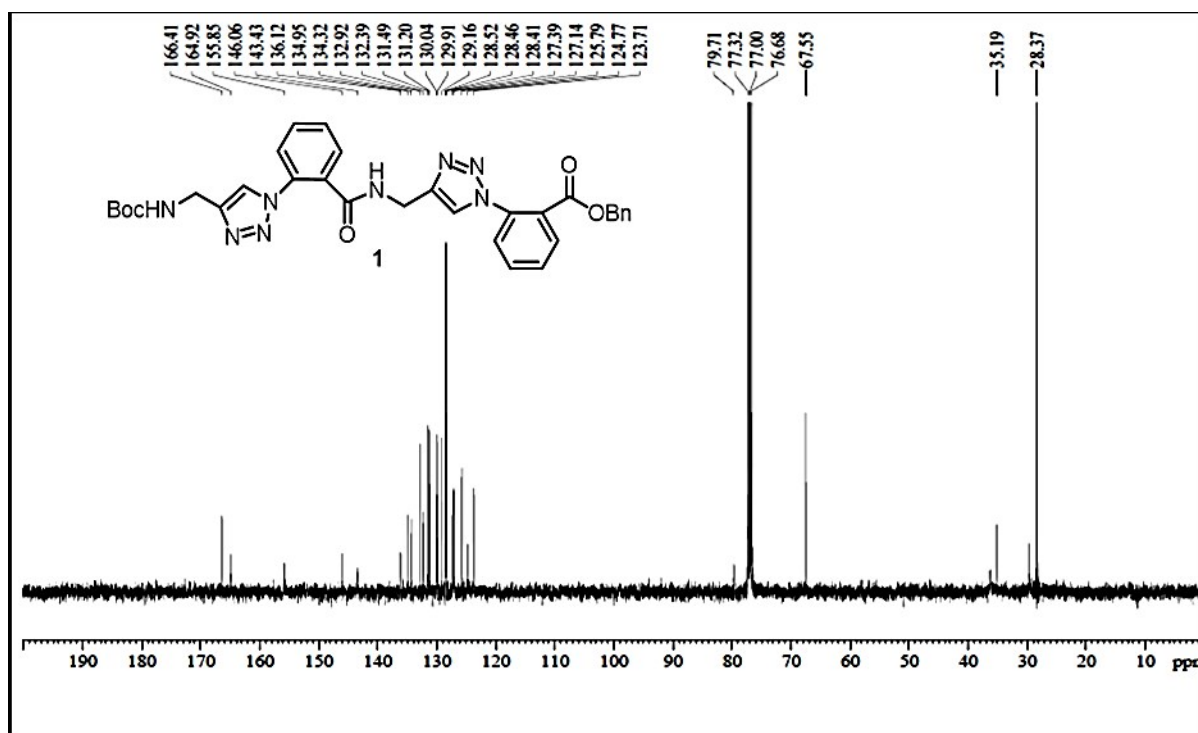


Figure 31.  $^{13}\text{C}$  NMR (100 MHz) spectra of **1** in  $\text{CDCl}_3$

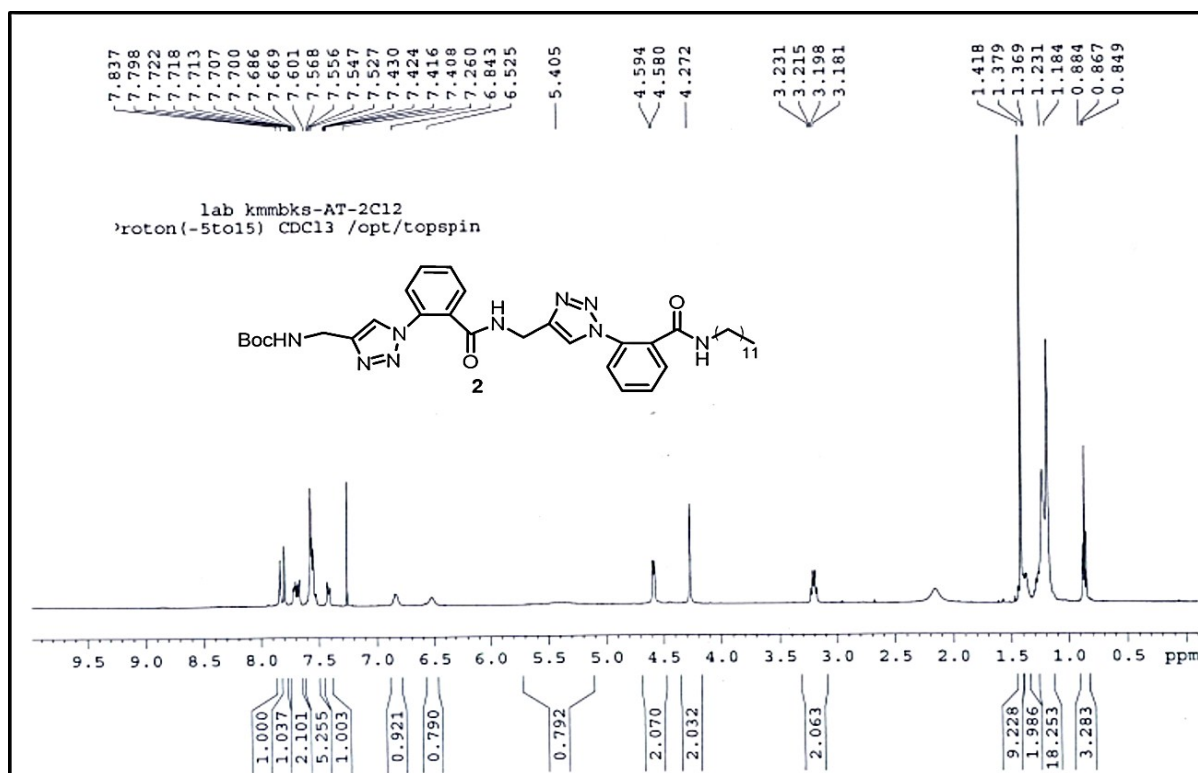
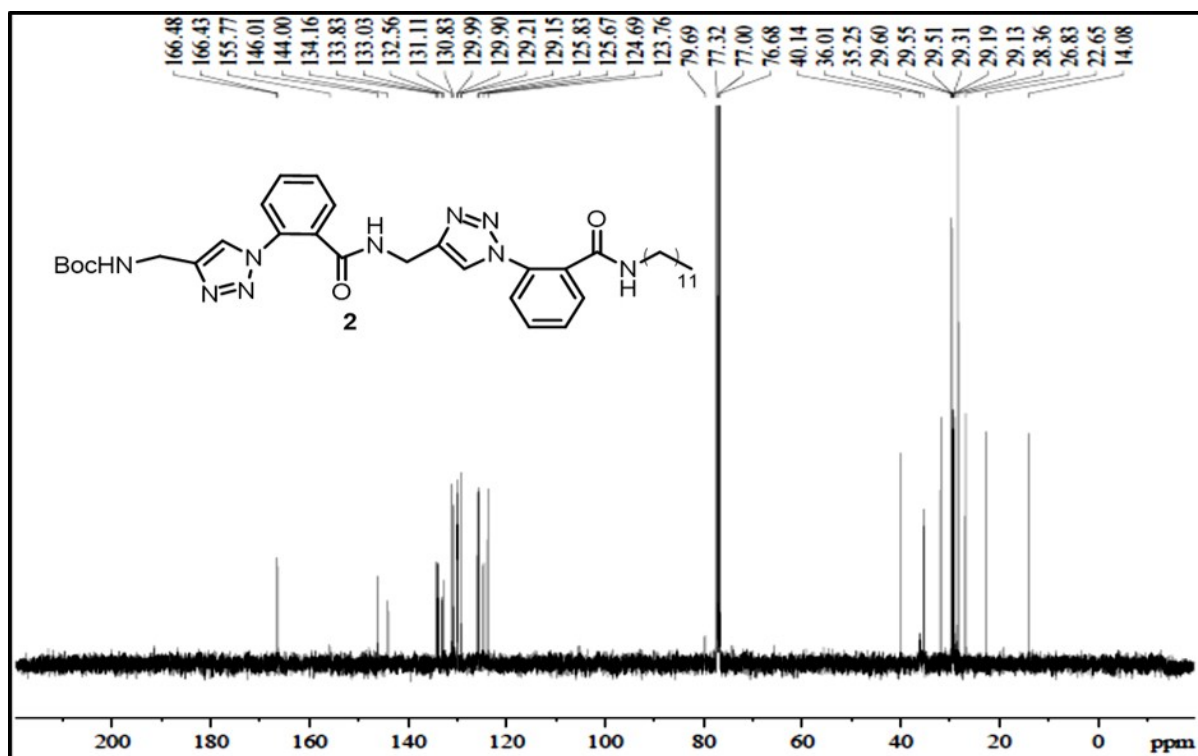
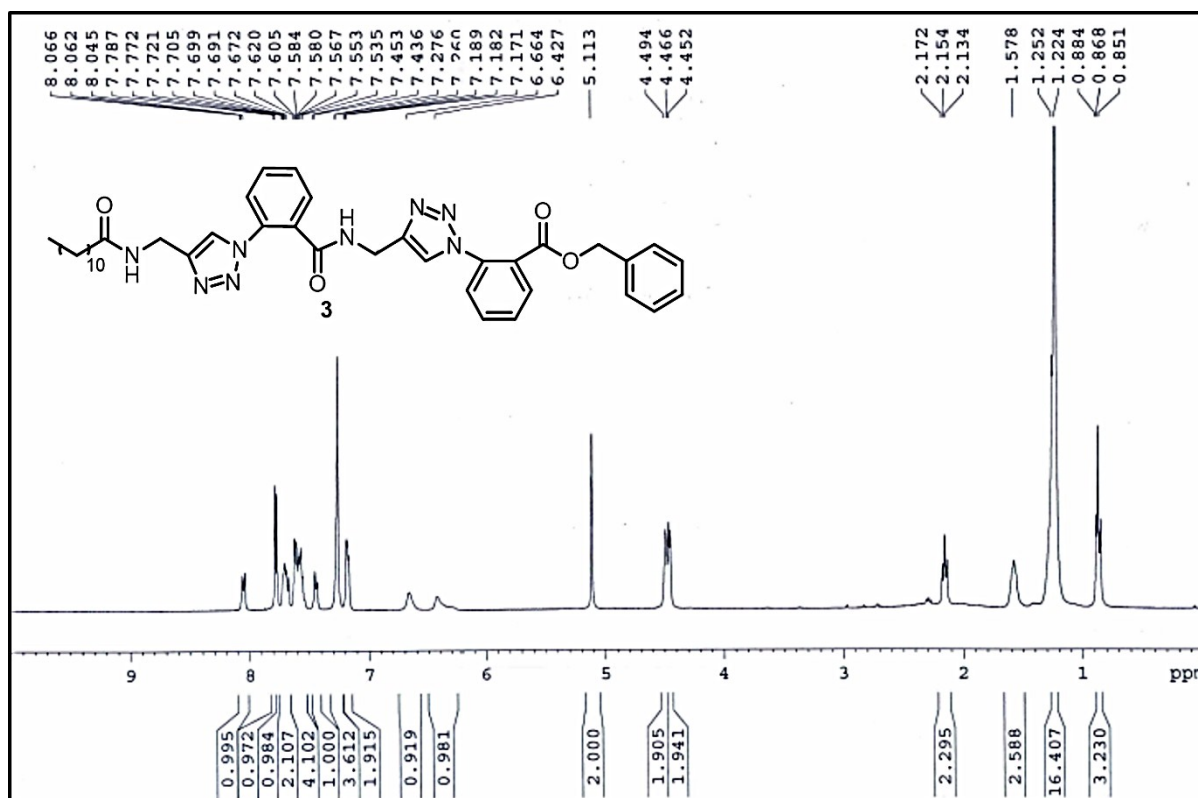


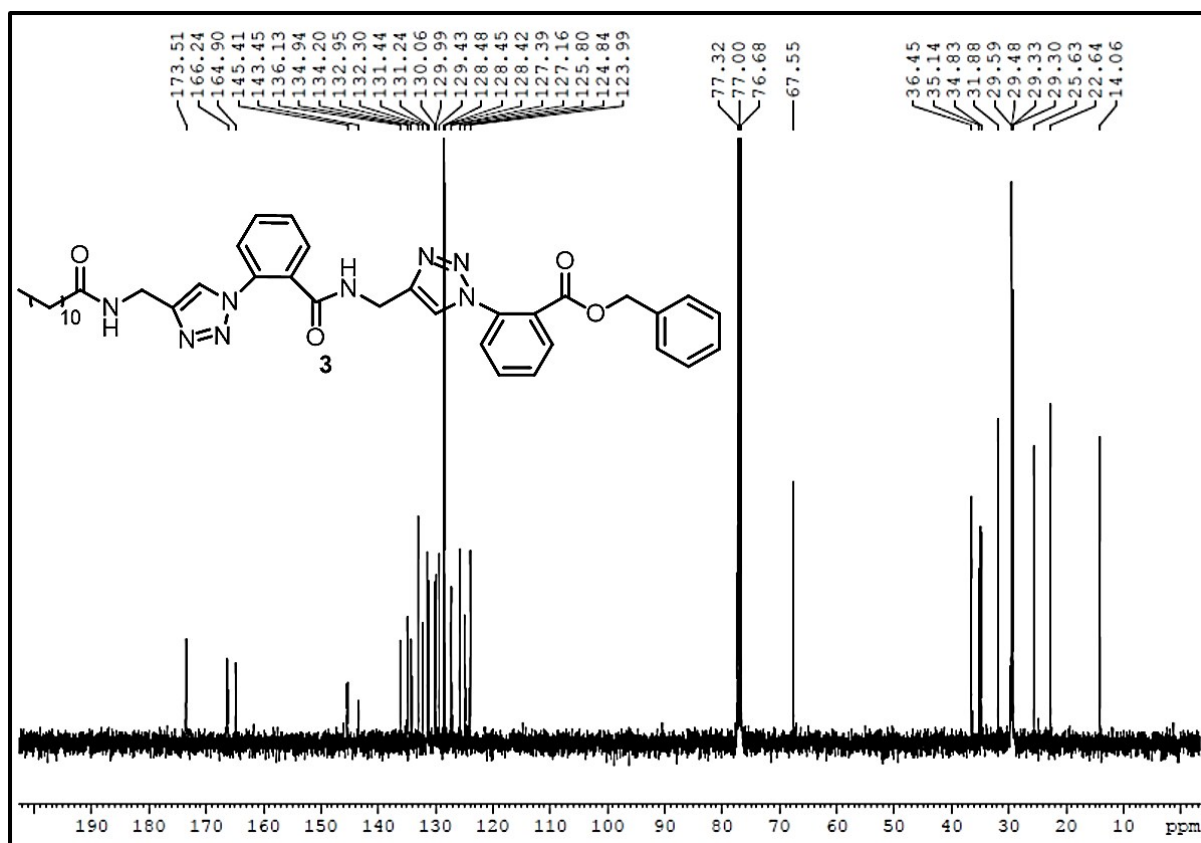
Figure 32.  $^1\text{H}$  NMR (400 MHz) spectra of **2** in  $\text{CDCl}_3$



**Figure 33.**  $^{13}\text{C}$  NMR (100 MHz) spectra of **2** in  $\text{CDCl}_3$



**Figure 34.**  $^1\text{H}$  NMR (400 MHz) spectra of **3** in  $\text{CDCl}_3$



**Figure 35.**  $^{13}\text{C}$  NMR (100 MHz) spectra of **3** in  $\text{CDCl}_3$

References:

- 1) S. S. More , D. Shanmughapriya , Y. Lingam and N. B. Patel, *Synthetic Communications*, 2009, **39**, 2058.