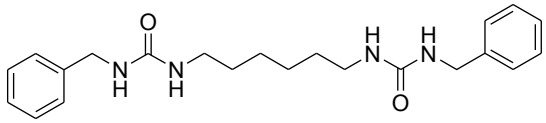
Electronic Supplementary Material (ESI) for Chemical Communications

Detection of nerve agent *via* perturbation of supramolecular gel formation

Jennifer R. Hiscock, Francesca Piana, Mark R. Sambrook, Neil J. Wells, Alistair J. Clark, Jack C. Vincent, Nathalie Busschaert, Richard C. D. Brown, and Philip A. Gale

Electronic Supplementary Information



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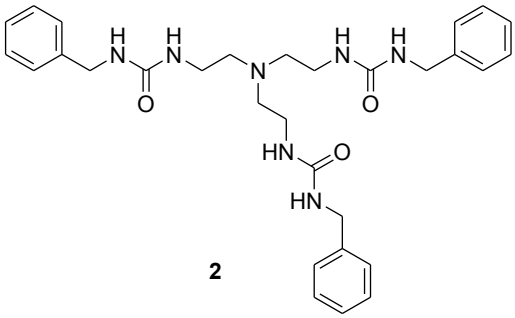

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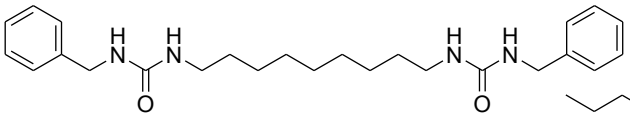

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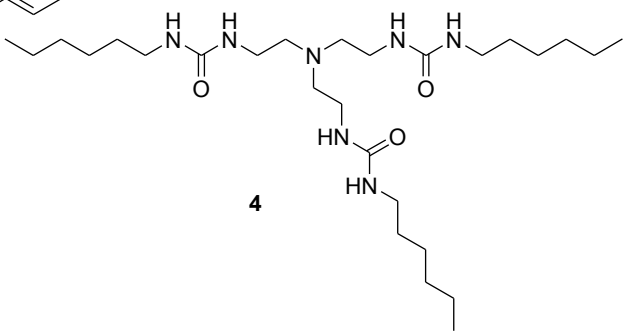

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Experimental

General remarks: ^{1}H NMR (300 MHz), ^{31}P{^{1}H} NMR (121 MHz) and ^{13}C{^{1}H} NMR (75 MHz) were determined on a Bruker AV300 spectrometer with the chemical shifts reported in parts per million (ppm), calibrated to the centre of the solvent peak set.^{1}H NMR (600 MHz) and ^{31}P{^{1}H} NMR (243 MHz) spectra were acquired at 14.1 Tesla using a Bruker AVIII 600 MHz spectrometer equipped with a QCI-P 5 mm cryoprobe operating at 600.13 and 242.93 MHz for ^{1}H and ^{31}P respectively. ^{1}H NMR (400 MHz), ^{31}P{^{1}H} NMR (162 MHz) and ^{13}C{^{1}H} NMR (100 MHz) were determined on a Bruker AV400 spectrometer with the chemical shifts reported in parts per million (ppm), calibrated to the centre of the solvent peak set. The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Infrared (IR) spectra were recorded on a Matterson Satellite (ATR), and reported in wavenumbers (cm^{-1}). All solvents and starting materials were purchased from chemical stores where available. Low resolution mass spectra were recorded on a Micromass Platform II Single Quadrupole mass spectrometer. High resolution mass spectra were recorded on a VG 70-250-SE normal geometry double focusing mass spectrometer by the mass spectrometry service at the University of Southampton. Melting points were recorded in open capillaries on a Gallenkamp melting point apparatus and are uncorrected. Compounds **1-3** have

been previously synthesised, [1-2] however full experimental details for compounds **1**-**3** are given. Commercial grade reagents have been used without further purification. All synthesis was performed under an inert atmosphere of nitrogen.

Compound **1** – A solution of benzyl isocyanate (0.46 mL, 3.76 mM) and hexane-1,6-diamine (0.25 g, 1.88 mM) in DCM (2 mL) was stirred at room temperature in a sealed vial overnight. The white solid was then collected by filtration and washed with DCM (10 mL). Yield: 82 % (0.59 g, 1.54 mM); mp: 210 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): δ: 1.25 (br s, 4H), 1.47 (t, J = 6.03 Hz, 4H), 4.64 (br s, 4H), 7.21-7.35 (m, 10H), 7.48 (br s, 2H, urea NH), 7.77 (br s, 2H, urea NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ: 26.1 (CH_2), 30.0 (CH_2), 42.9 (CH_2), 126.5 (ArCH), 127.0 (ArCH), 128.2 (ArCH), 141.0 (ArC), 158.1 (CO); IR (film): ν = 3330 (urea NH stretching), 1620 (urea CO stretching); LRMS (ESI$^+$): m/z: 405 $[M+Na]^+$; HRMS (ESI$^+$) for $C_{22}H_{30}N_4O_2$: m/z: act: $[M+Na]^+$ 405.2260, cal: $[M+Na]^+$ 405.2261, Δδ (ppm) = 0.4.

Compound **2** – A solution of benzyl isocyanate (0.46 mL, 3.76 mM) and tris(2-aminoethyl)amine (tren) (0.19 mL, 1.25 mM) in DCM (2 mL) was stirred at room temperature in a sealed vial overnight. The semi solid was then dissolved with DCM (10 mL) and purified with SCX(II) column chromatography. The column was flushed firstly with methanol (60 mL) and then 7N ammonia in methanol (25 mL). The ammonia fraction was then taken to dryness. This resulted in a white solid. Yield: 55 % (0.38 g, 0.69 mM); mp: 85 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): δ: 2.46-2.50 (m, 6H), 3.08 (dd, J_1 = 11.70 Hz, J_2 = 5.85 Hz, 6H), 4.18 (d, J = 5.85 Hz, 6H), 5.98 (t, J = 5.49 Hz, 3H, urea NH), 6.40 (t, J = 5.85 Hz, 3H, urea NH), 7.18-7.31 (m, 15H); ^{13}C NMR (75 MHz, DMSO-d_6): δ: 37.9 (CH_2), 42.9 (CH_2), 54.4 (CH_2), 126.5 (ArCH), 127.0 (ArCH), 128.2 (ArCH), 140.8 (ArC), 158.2 (CO); IR (film): ν = 3330 (urea NH stretching), 1620 (urea CO stretching); LRMS (ESI$^+$): m/z: 568 $[M+Na]^+$; HRMS (ESI$^+$) for $C_{30}H_{39}N_7O_3$: m/z: act: $[M+Na]^+$ 568.3008, cal: $[M+Na]^+$ 568.3007, Δδ (ppm) = -0.3.

Compound **3** – A solution of benzyl isocyanate (0.46 mL, 3.76 mM) and nonane-1,9-diamine (0.30 g, 1.88 mM) in DCM (2 mL) was stirred at room temperature in a sealed vial overnight. The white solid was then collected by filtration and washed with DCM (10 mL). Yield: 80 % (0.64 g, 1.51 mM); mp: 70 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): δ: 1.25 (br s, 10H), 1.46 (t, J = 6.78 Hz, 4H), 4.64 (br s, 4H), 7.21-7.34 (m, 10H), 7.46 (br s, 2H, urea NH), 7.76 (br s, 2H, urea NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ: 26.4 (CH_2), 28.7 (CH_2), 30.0 (CH_2), 42.9 (CH_2), 126.5 (ArCH), 127.0 (ArCH), 128.2 (ArCH), 141.0 (ArC), 158.1 (CO)(one missing CH_2 signal due to peak overlapping); IR (film): ν = 3330 (urea NH stretching), 1620 (urea CO stretching); LRMS (ESI$^+$): m/z: 447 $[M+Na]^+$; HRMS (ESI$^+$) for $C_{25}H_{36}N_4O_2$: m/z: act: $[M+Na]^+$ 447.2731, cal: $[M+Na]^+$ 447.2730, Δδ (ppm) = -0.2.

Compound **4 –** Tren (0.20 g, 1.37 mM) was dissolved in dry DCM (10 mL). To this solution was added hexylisocyanate (0.52 g, 4.10 mM) in dry DCM (10 mL) dropwise. The mixture was stirred overnight at room temperature. The gel-like precipitate was filtered off, washed with DCM and dried under reduced pressure. Yield: 59 % (0.42 g, 0.80 mM); mp: 132-134 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): δ: 0.85 (t, J = 7.17 Hz, 9H), 1.23-1.34 (m, 24H), 2.41 (t, J = 6.03 Hz, 6H), 2.92-3.01 (m, 12H), 5.79 (t, J = 5.28 Hz, 3H, urea NH), 5.86 (t, J = 5.64 Hz, 3H, urea NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ: 14.0 (CH_3), 22.6 (CH_2), 26.8 (CH_2), 30.5 (CH_2), 31.7 (CH_2), 38.4 (CH_2), 40.5 (CH_2), 55.0 (CH_2), 159.6 (CO); IR (film): ν = 3319 (urea NH stretching), 1626 (urea CO stretching); LRMS (ESI$^+$): m/z: 447 $[M+Na]^+$; HRMS (ESI$^+$) for $C_{27}H_{57}N_7O_3$: m/z: act: $[M+H]^+$ 528.4596, cal: $[M+H]^+$ 528.4596, Δδ (ppm) = -0.03.

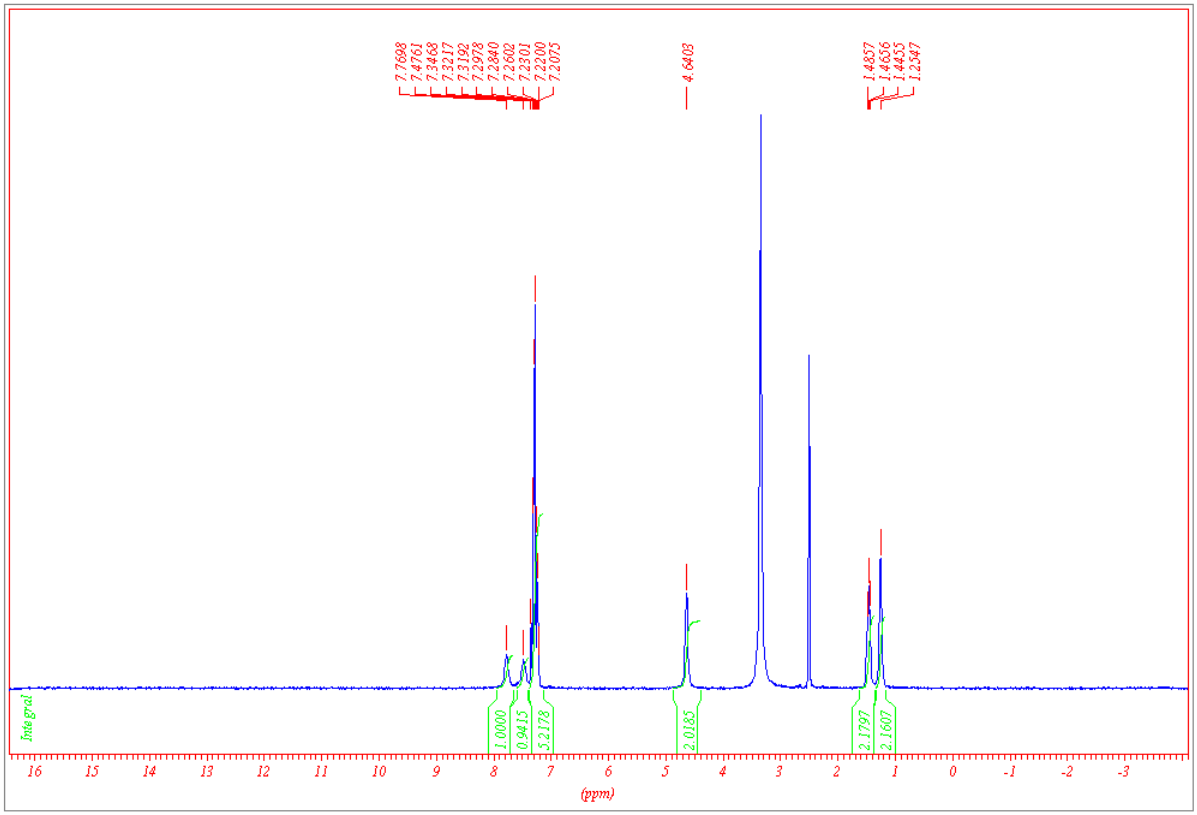

Figure S1a: ^{1}H NMR spectrum of compound **1** in DMSO-d_6.

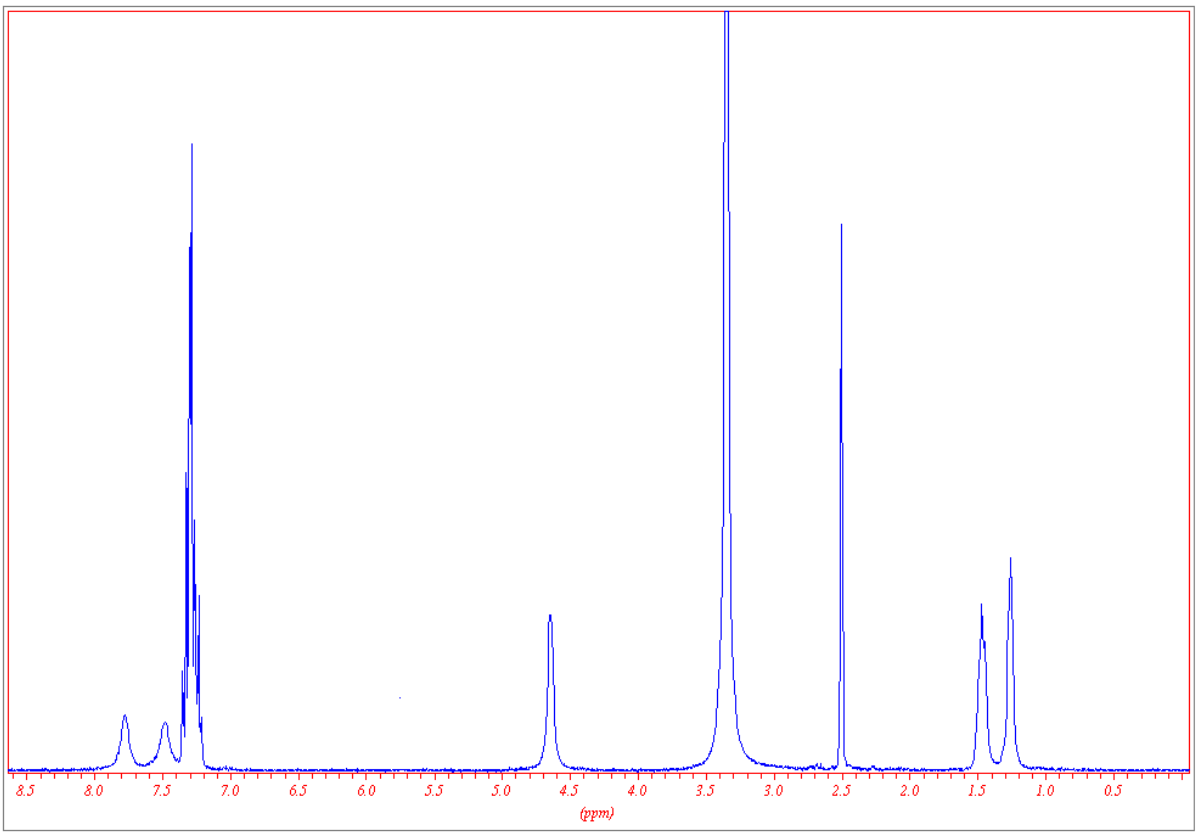

Figure S1b: ^{1}H NMR spectrum of compound **1** in DMSO-d_6.

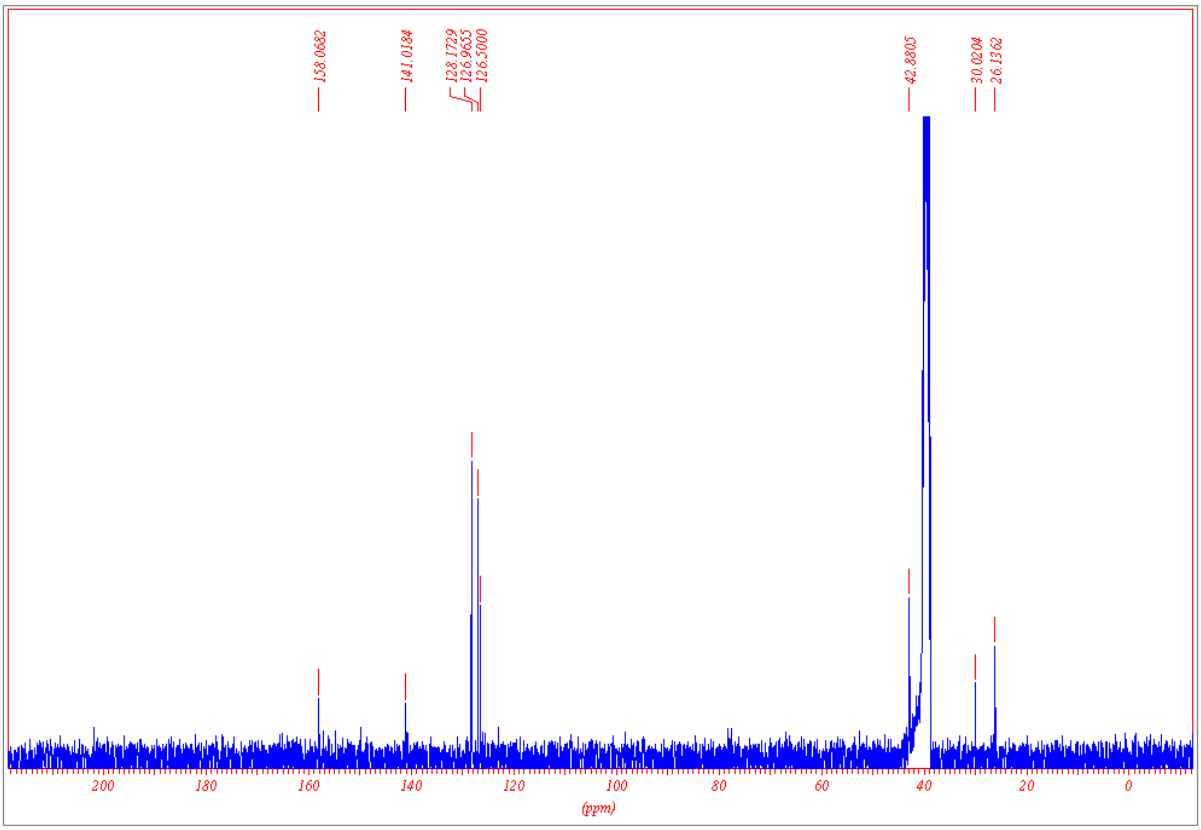

Figure S2: ^{13}C NMR spectrum of compound **1** in DMSO-d_6.

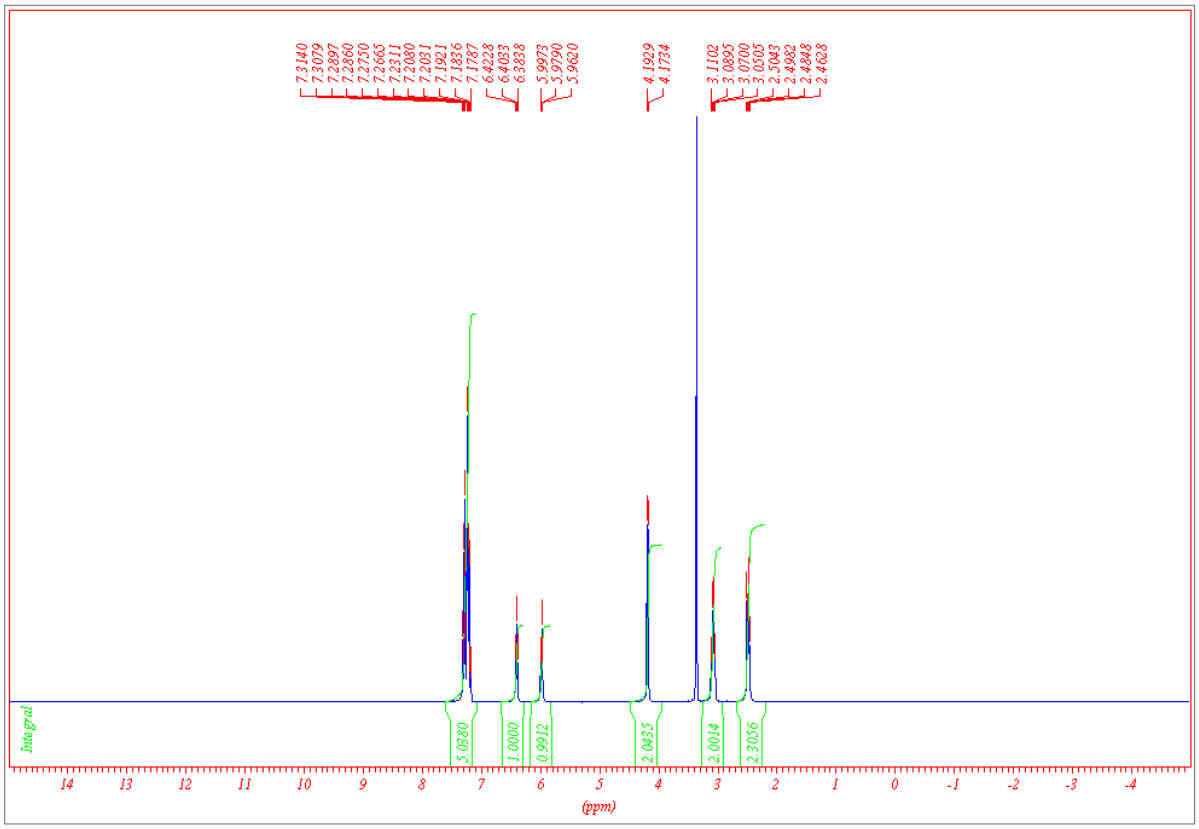

Figure S3a: ^{1}H NMR spectrum of compound **2** in DMSO-d_6.

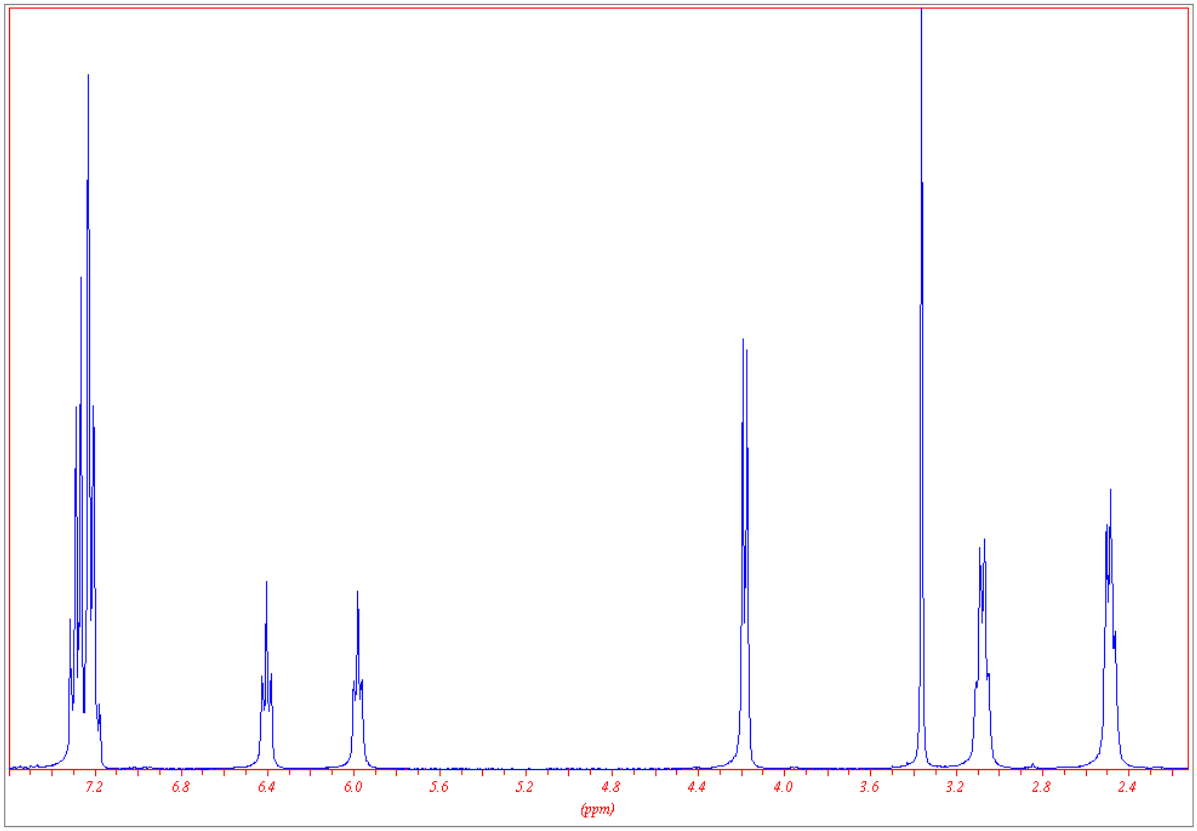

Figure S3b: ^{1}H NMR spectrum of compound **2** in DMSO-d_6.

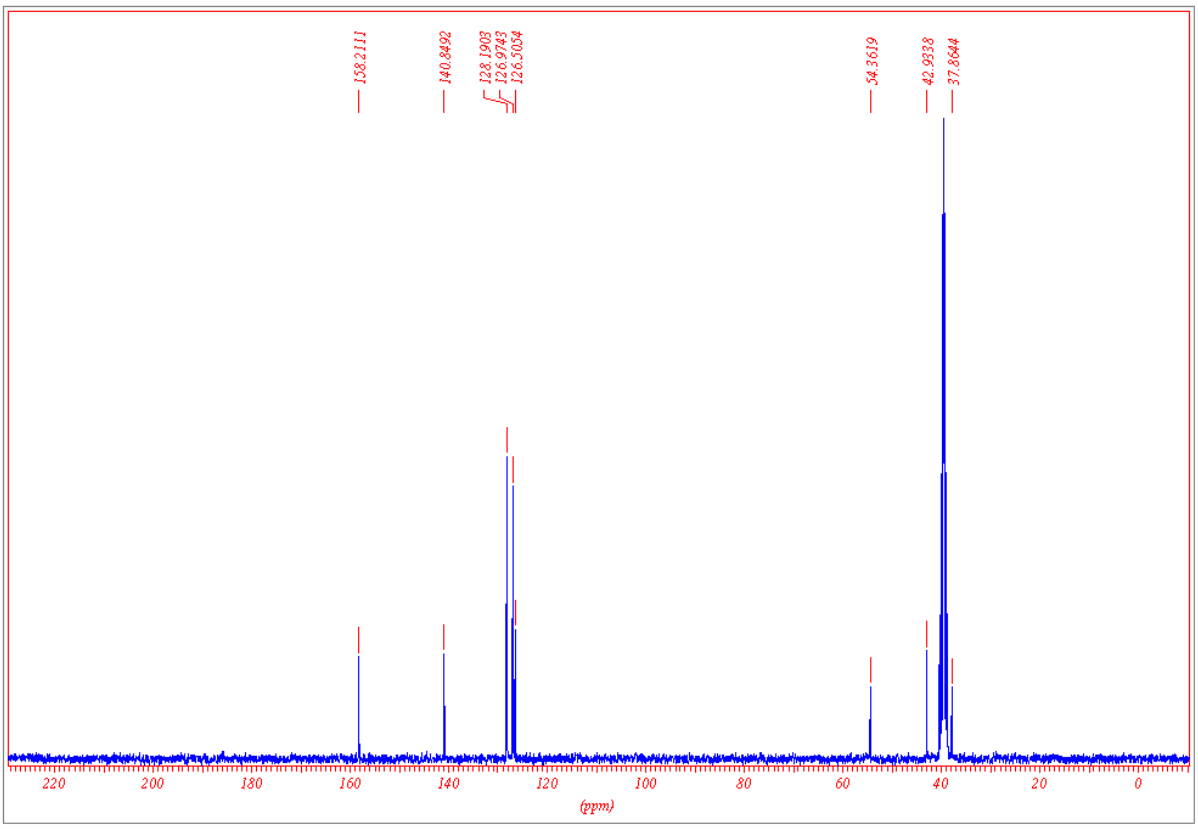

Figure S4: ^{13}C NMR spectrum of compound **2** in DMSO-d_6.

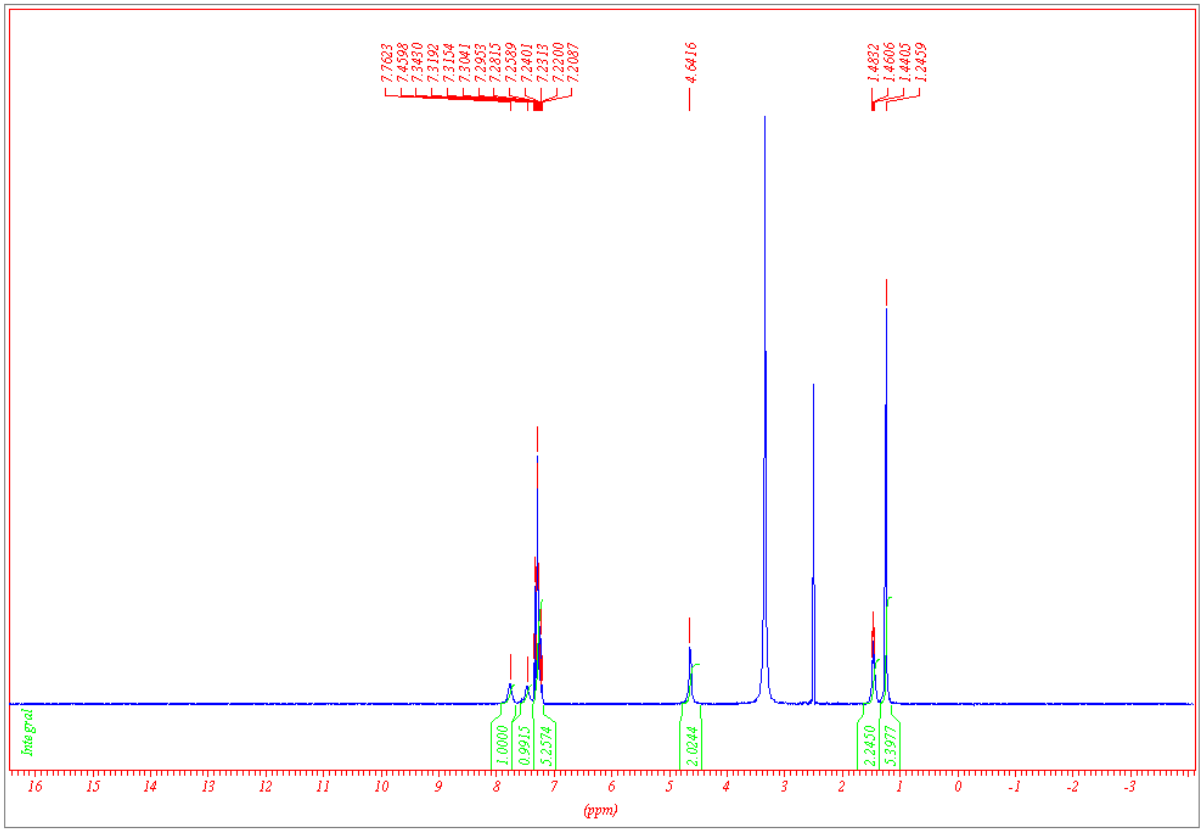

Figure S5a: ^{1}H NMR spectrum of compound **3** in DMSO-d_6.

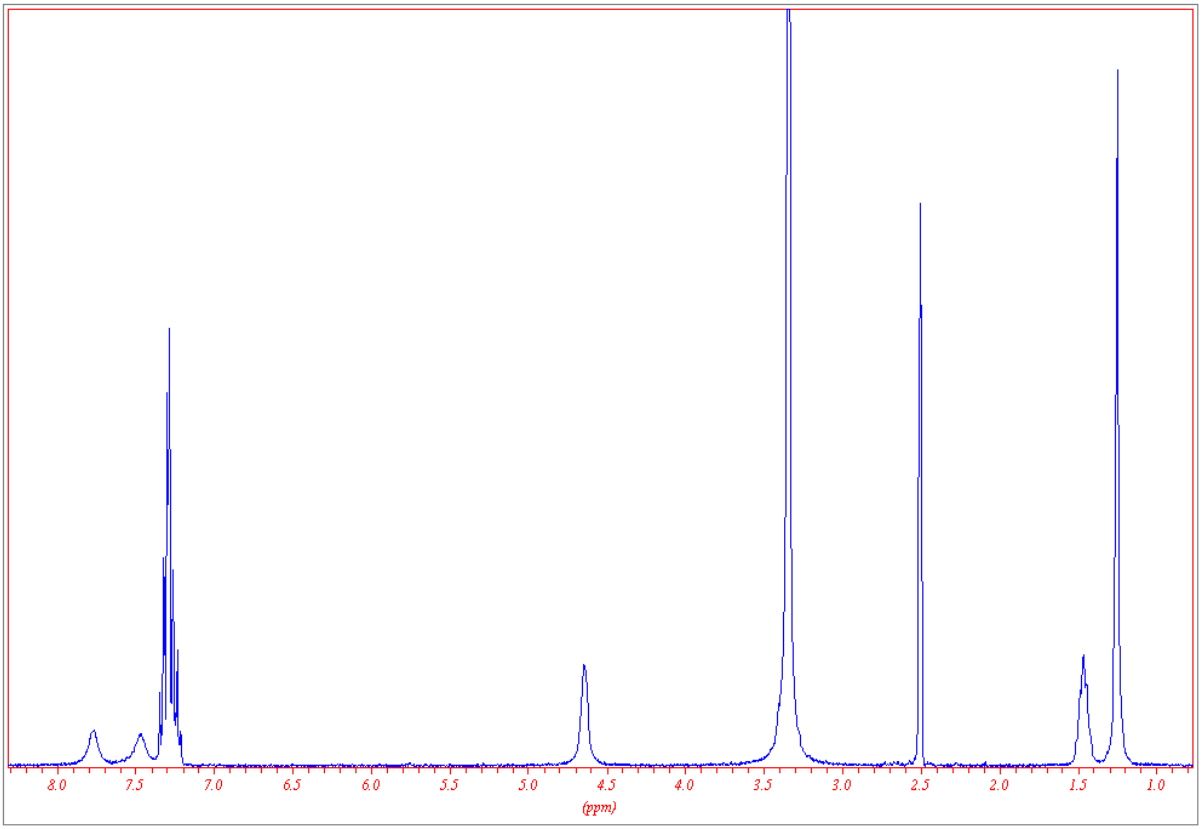

Figure S5b: ^{1}H NMR spectrum of compound **3** in DMSO-d_6.

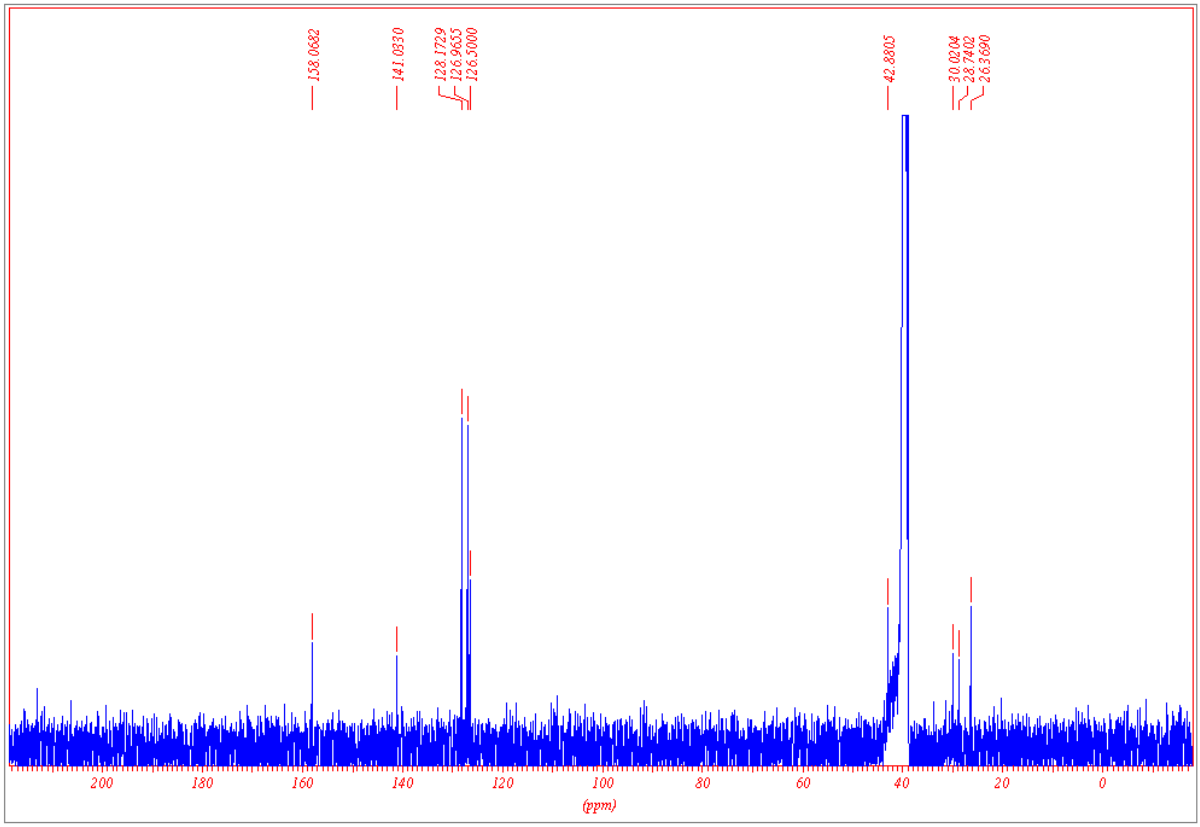

Figure S6: ^{13}C NMR spectrum of compound **3** in DMSO-d_6.

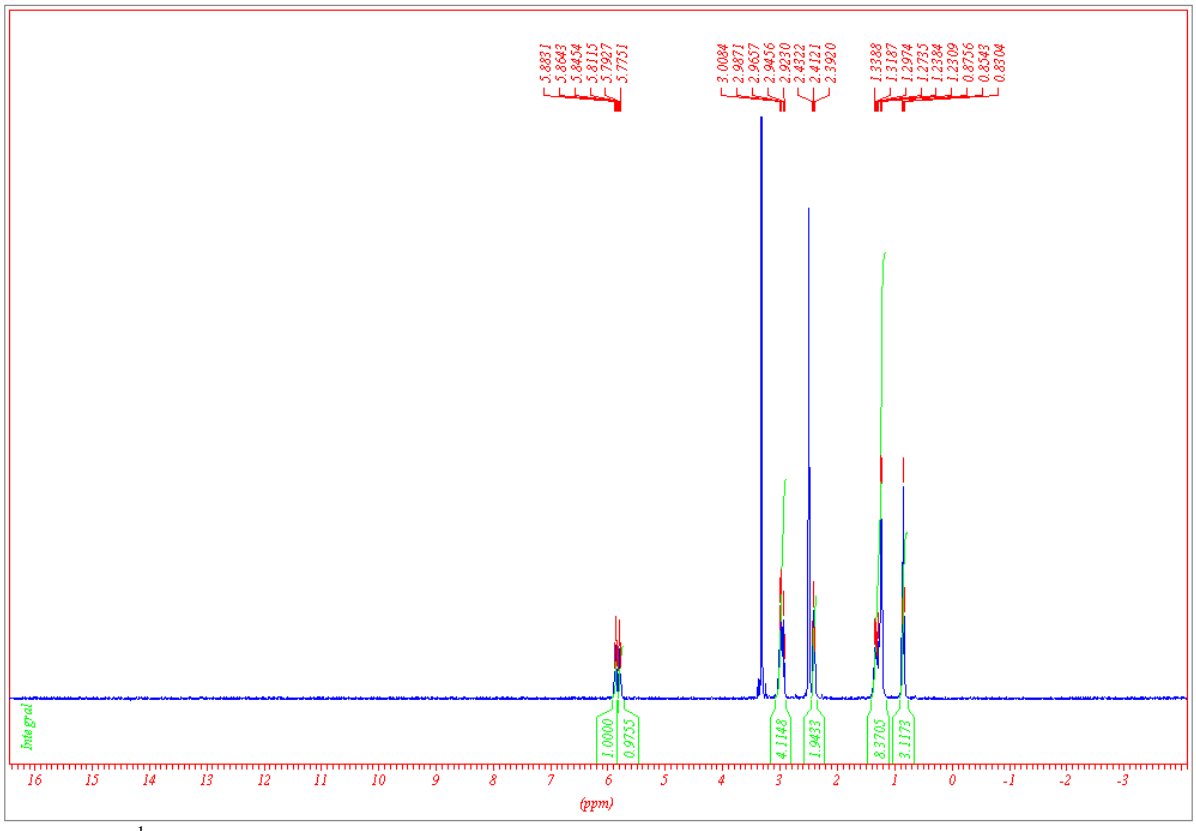

Figure S7a: ^{1}H NMR spectrum of compound **4** in DMSO-d_6.

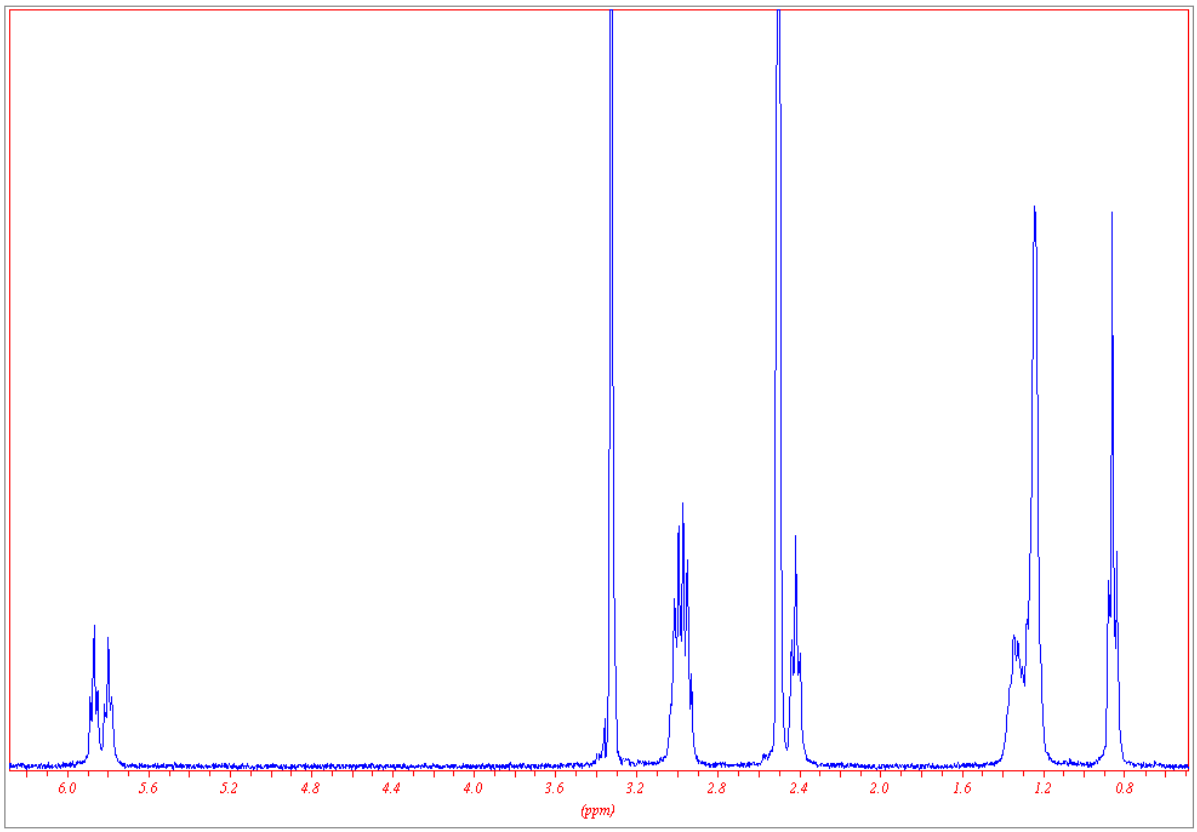

Figure S7b: ^{1}H NMR spectrum of compound **4** in DMSO-d_6.

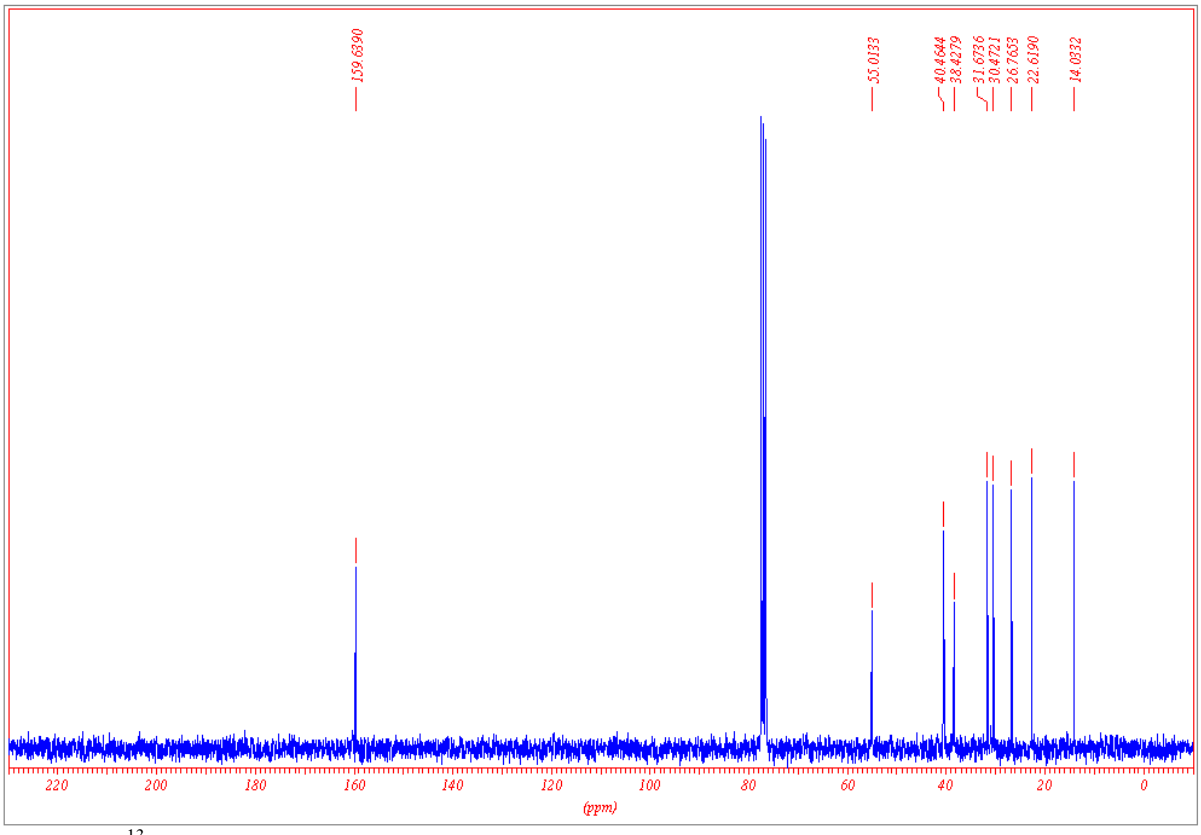

Figure S8: ^{13}C NMR spectrum of compound **4** in $CDCl_3$.

Gel synthesis

The gelator and solvent mixture was heated in a sealed vial until all the solid had dissolved. The solution was then inverted twice and allowed to cool to room temperature. To check that the gel was formed the vial was inverted. If the potential gel retained a solid structure at the bottom of the vial with no loss of solvent upon inversion a gel was considered to have formed.

The re-synthesis of some of the gels previously reported seemed to be very sensitive to experimental conditions. If we could not reliably reproduce the gel we did not report the result. We found that gel formation is susceptible to small changes in chemical composition of the components used to form the gel for example water concentration of stock solvents.

Sol-gel transition experiments – perturbation of the formation of a gel

A solution of the appropriate amine in toluene or tetralin (10 mL) was prepared. A solution of the appropriate isocyanate in toluene or tetralin (10 mL) was also prepared. Aliquots (0.5 mL) of these solutions were added to a vial. For certain experiments DMMP was added to an aliquot (0.5 mL) (either amine or isocyanate solution) before an aliquot (0.5 mL) of the second solution was added. These samples were checked for gel formation at various time intervals. Time = 0 was recorded as the time at which the amine and isocyanate solutions were added together. The experiments conducted with compounds **2** and **4** were repeated a minimum of two times to check for the reproducibility of the results. All experiments were observed for a maximum of 10 minutes. Initial gelation time results for the various solutions of amine and isocyanate were repeated three times to give a reliable maximum gelation time under these conditions (Table 1). All experiments were carried out at an ambient temperature of 20-21 ºC.

Sol-gel transition experiments with nerve agent

These experiments were not repeated; however the results were produced by the same methods as used for studies with DMMP.

Scanning Electron Microscopy (SEM)

Xerogels for SEM were produced by drying 0.3 mL of a gel containing 15 mg/mL gelator. The xerogels originally containing ethyl acetate and cyclohexanone were obtained by air drying the samples over a 48 hr period. The xerogel originally containing toluene was obtained by freezing the sample for 20 mins with liquid nitrogen under reduced pressure. The sample was then allowed to come to room temperature and the solvent removed further under reduced pressure at room temperature for 16hrs.

The SEM imaging was done with a JEOL-JSM5910. The samples were gold coated to an approximately. thickness of 20 nm using an anatech hummer 6.2 spatter coater. The Samples were mounted to an aluminium stub using a self adhesive carbon tab. The accelerating voltage for the experiments given was 7 kV.

Table S1: Formation of gels with compound **1**

solvent	Concentration of gelator in mg/mL				
	100 mg/mL	20 mg/mL	15 mg/mL	10 mg/mL	5 mg/mL
tetralin	Not tried	Gelation	Gelation	Gelation	Gelation
toluene	Not tried	Not soluble	Not soluble	Not soluble	Not soluble
DMSO	Precipitation	Precipitation	Precipitation	Precipitation	Not gelation
ethyl acetate	Not tried	Not soluble	Not soluble	Not soluble	Not soluble
ethanol	Not tried	Not soluble	Not soluble	Not soluble	Not soluble
DCM	Not tried	Not soluble	Not soluble	Not soluble	Not soluble
hexane	Not tried	Not soluble	Not soluble	Not soluble	Not soluble
H_2O	Not tried	Not soluble	Not soluble	Not soluble	Not soluble
cyclohexanone	Not tried	Precipitation	Precipitation	Precipitation	Precipitation

Table S2: Formation of gels with compound **2**

solvent	Concentration of gelator in mg/mL				
	100 mg/mL	20 mg/mL	15 mg/mL	10 mg/mL	5 mg/mL
tetralin	Not tried	Gelation	Gelation	Gelation	Gelation
toluene	Not tried	Gelation	Gelation	Gelation	Partial Gel
DMSO	No gelation	No gelation	No gelation	No gelation	No gelation
ethanol	Not tried	Gelation	Gelation	Gelation	Partial Gel
DCM	Not tried	Gelation	No gelation	No gelation	No gelation
2-octanol	Not tried	Precipitation	Precipitation	Precipitation	Precipitation
cyclohexanone	Not tried	Precipitation	Precipitation	Precipitation	No gelation

Table S3: Formation of gels with compound **3**

Solvent	Concentration of gelator in mg/mL				
	100 mg/mL	20 mg/mL	15 mg/mL	10 mg/mL	5 mg/mL
tetralin	No tried	Gelation	Gelation	Partially Gel	Partial Gel
toluene	No tried	No gel	Gelation	Partial Gel	Partial Gel
DMSO	Gelation	Precipitation	Precipitation	Precipitation	Precipitation
ethanol	No tried	Gelation	Gelation	Precipitation	Precipitation
DCM	No tried	No soluble	No soluble	No soluble	No soluble
2-octanol	No tried	Gelation	Gelation	Gelation	No gelation
cyclohexanone	No tried	Precipitation	Precipitation	Precipitation	Precipitation
hexane	Not tried	No soluble	No soluble	No soluble	No soluble
Ethyl acetate	Not tried	No soluble	No soluble	No soluble	No soluble
H_2O	Not tried	No soluble	No soluble	No soluble	No soluble

Table S4: Formation of gels with compound **4**

solvent	Concentration of gelator in mg/mL				
	100 mg/mL	20 mg/mL	15 mg/mL	10 mg/mL	5 mg/mL
Tetralin	Not tried	Gelation	Gelation	Gelation	No gel
Toluene	Not tried	Gelation	Gelation	No gel	No gel
DMSO	Gelation dependent on H_2O concentration	No gel	No gel	No gel	No gel
Cyclohexanone	Not tried	Partial gelation	Gelation	No gel	No gel
2-Octanol	No gel	No gel	No gel	No gel	No gel
Hexane	No gel	No gel	No gel	No gel	No gel
Ethyl acetate	No tried	Gelation (room temp)	Gelation (room temp)	No gel	No gel
Ethanol	No gel	No gel	No gel	No gel	No gel
Water	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble

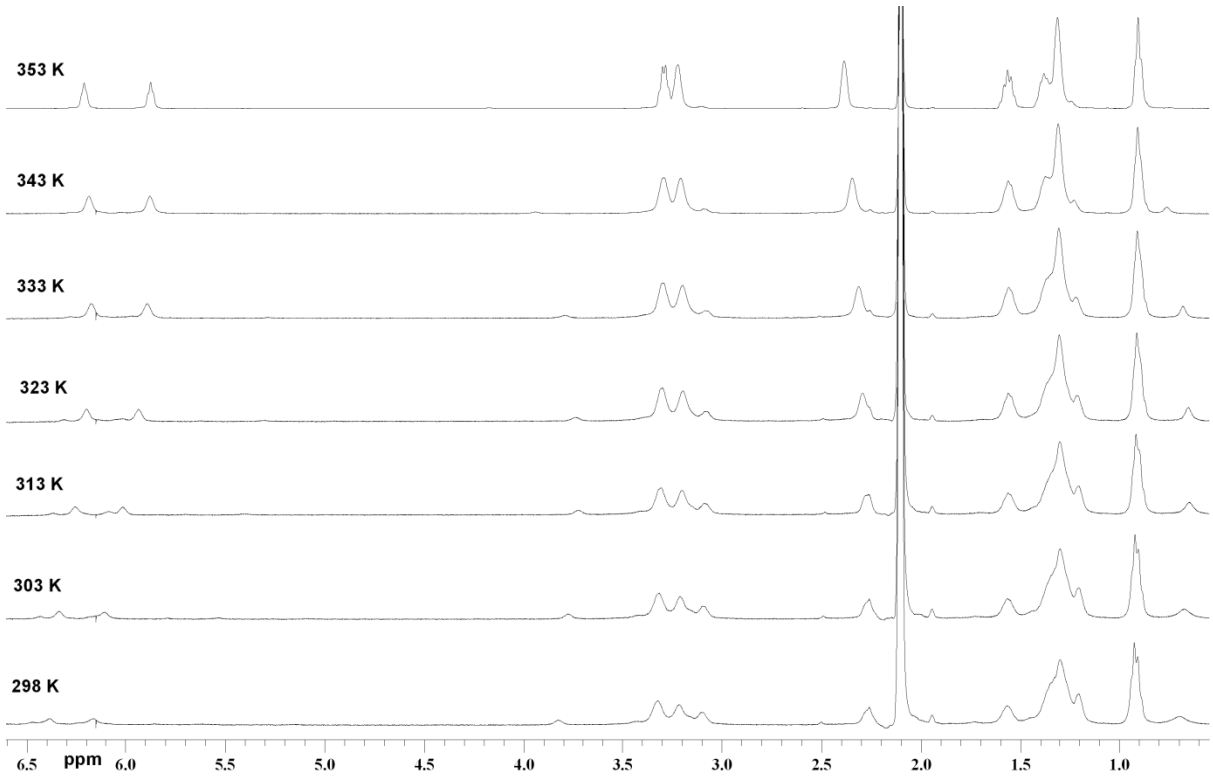

Figure S9: Stack plot of ^{1}H NMR spectra in toluene-d_8 showing the breakdown of 0.5 mL of 15 mg/mL gel **4** with increasing temperature from 298 K to 353 K.

Table S5: The time taken for gelators **1-4** to gel 1 mL of solvent. The gelators were synthesised *in situ* with a solution of the amine added to a solution of the isocyanate or vice versa. The solutions were checked for complete gelation at 30 sec intervals. a – Amine was insoluble at these concentrations; b – No gelation was observed using this method. These experiments were repeated three times and the results identical in each case. * Experiments conducted at DSTL before experiments with the nerve agent GD. This results in slightly longer gelation times at 5 mg/mL gelator concentrations.

Gelator	**Solvent**	**Time taken for gel formation (1 mL) (mins)**			
		20 mg/mL	**15 mg/mL**	**10 mg/mL**	**5 mg/mL**
4*	Toluene*			Within 0.5*	Between 1.17* and 1.33*
4	Toluene	Within 0.5	Within 0.5	Within 0.5	Within 1.0
4	Tetralin	a	a	Within 0.5	Within 1.0
4	Ethyl acetate	b			
4	Cyclohexanone	b			
2	Toluene	Within 0.5	Within 0.5	Within 0.5	No Gel
2	Tetralin	a	a	Within 0.5	Within 0.5
2	DCM	b			
1	Tetralin	Within 0.5	Within 0.5	Within 0.5	Within 0.5
3	Toluene	Within 0.5	Within 0.5	Within 0.5	Within 0.5
3	Toluene	Within 0.5	Within 0.5	Within 0.5	Within 0.5

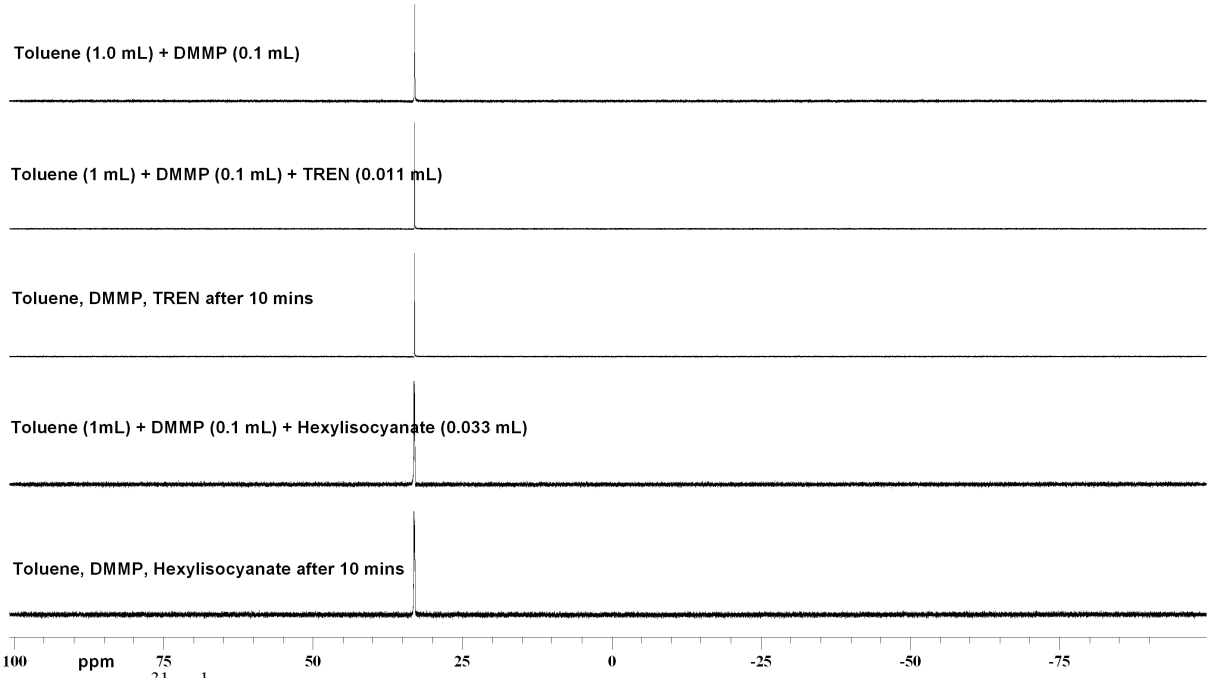

Figure S10: $^{31}P\{^{1}H\}$ NMR spectrum of DMMP in toluene with both the amine and isocyanate externally locked to D_2O showing no reaction with DMMP and either the amine or the isocyanate.

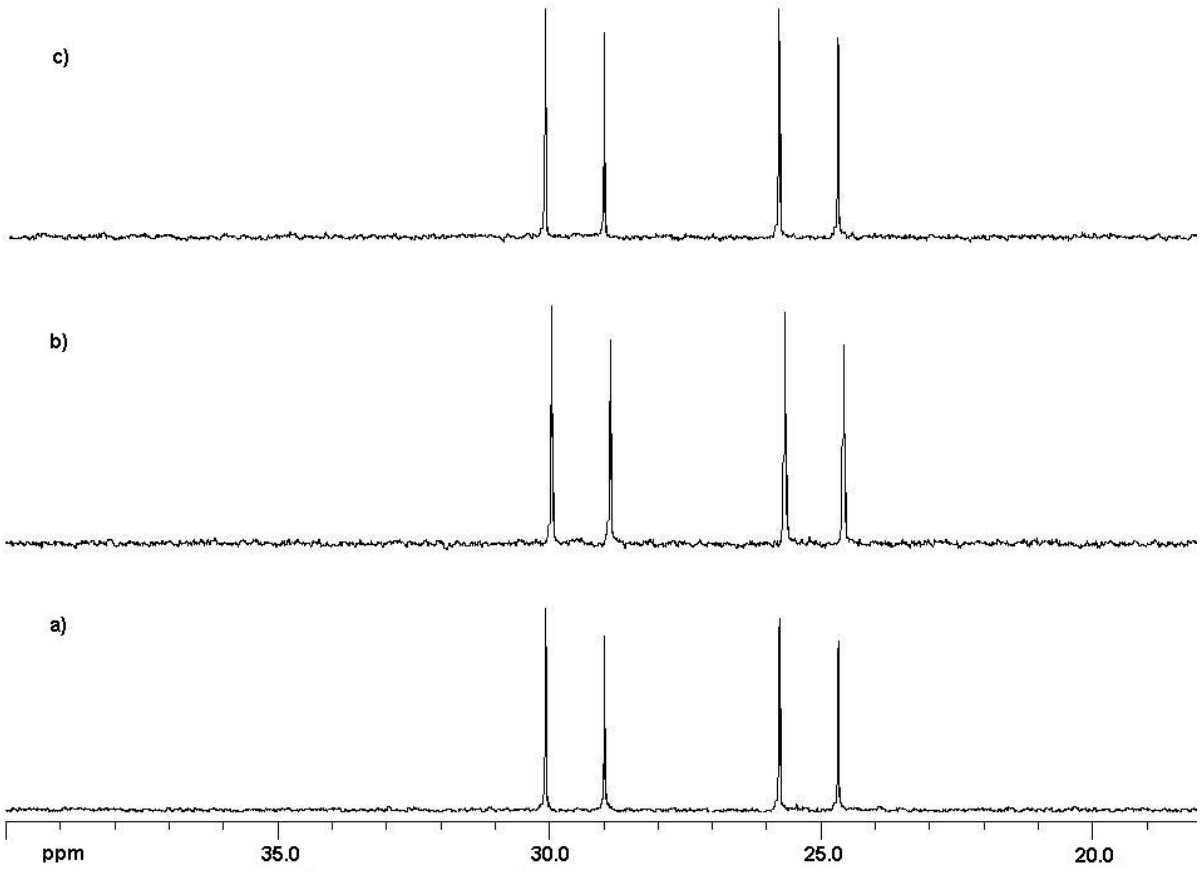

Figure S11: $^{31}P\{^{1}H\}$ NMR spectrum of GD in toluene/toluene-d_8 (9:1) with both the amine and isocyanate showing no reaction with GD and either the tren or hexylisocyanate. Spectra were recorded approximately 15 minutes after the solutions were dosed with GD. a) 0.9 mL of the stock hexylisocyanate solution used for making 10 mg/mL gels (compound **4**) plus 0.1 mL toluene-d_8; addition of 2 µL/mL GD, b) 0.9 mL of the stock tren solution used for making 10 mg/mL gels (compound **4**) plus 0.1 mL toluene-d_8; addition of 2 µL/mL GD, c) Control – 2 µL/mL GD.

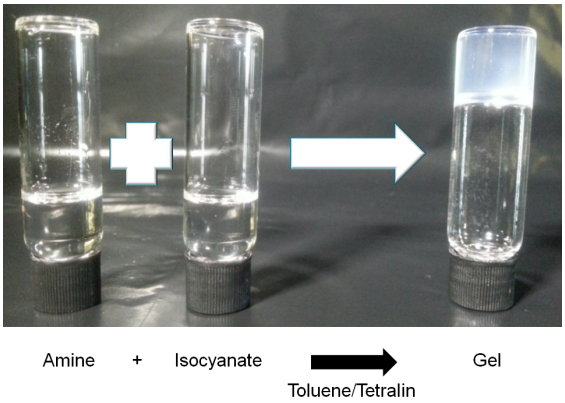

Figure S12: *In situ* gel synthesis (shown for the formation of a gel from the precursors to compound **4** and toluene (15 mg/mL)).

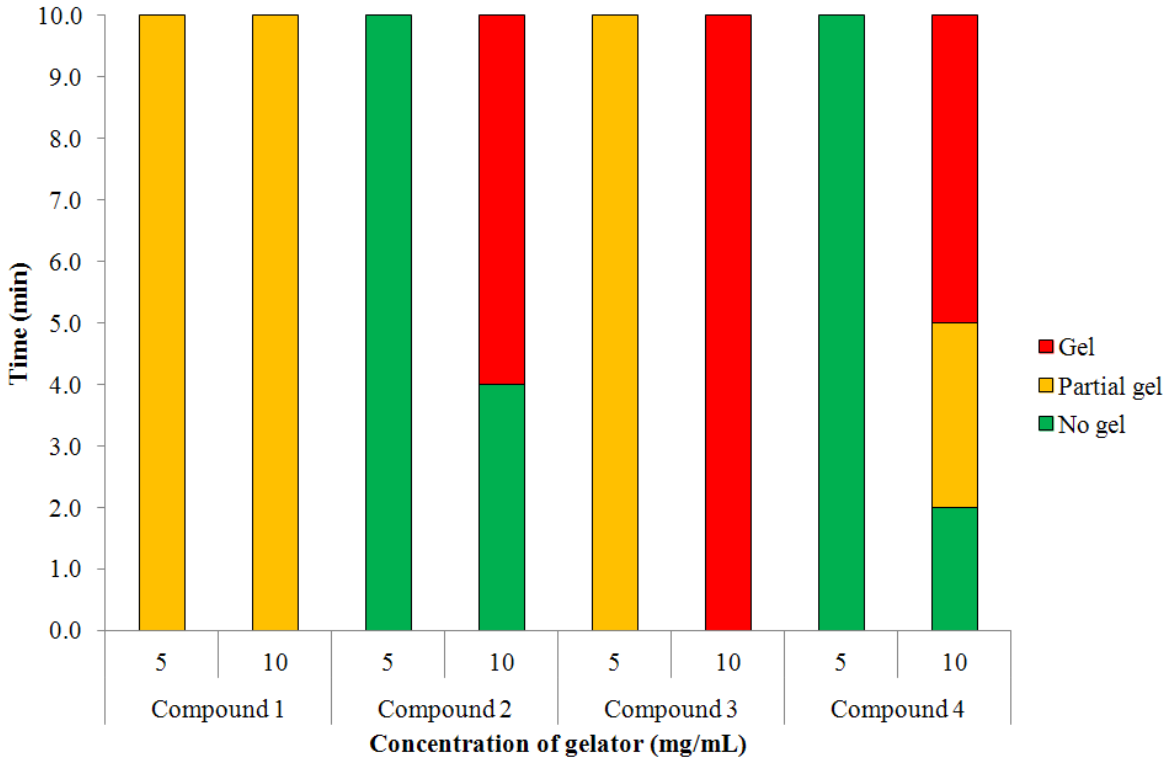

Figure S13: The time required for complete/partial gel formation (1 mL) by compounds **1-4** at 5 and 10 mg/mL in tetralin with 0.1 mL of DMMP present. Gelation experiments were first observed after 0.5 min.

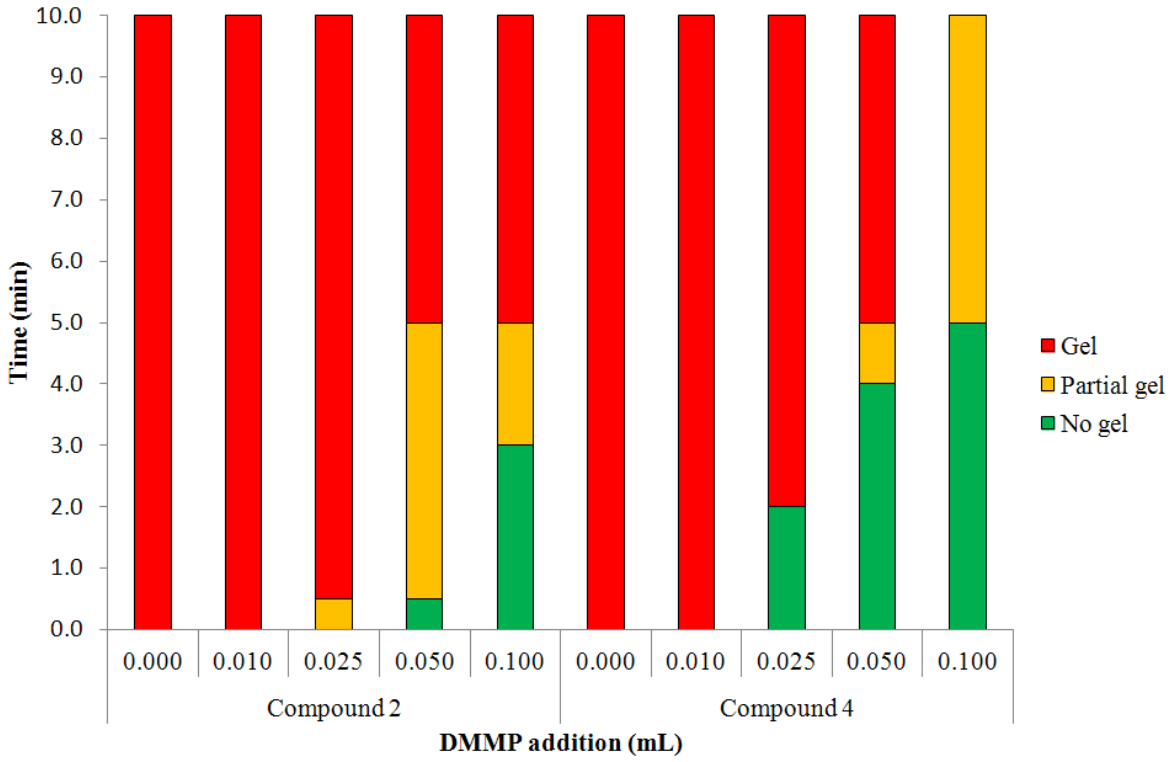

Figure S14: The time required for complete/ partial gel formation (1mL) by compounds **2** and **4** and in toluene with 10 mg/mL gelator in the presence of DMMP. Gelation experiments were first observed after 0.5 min.

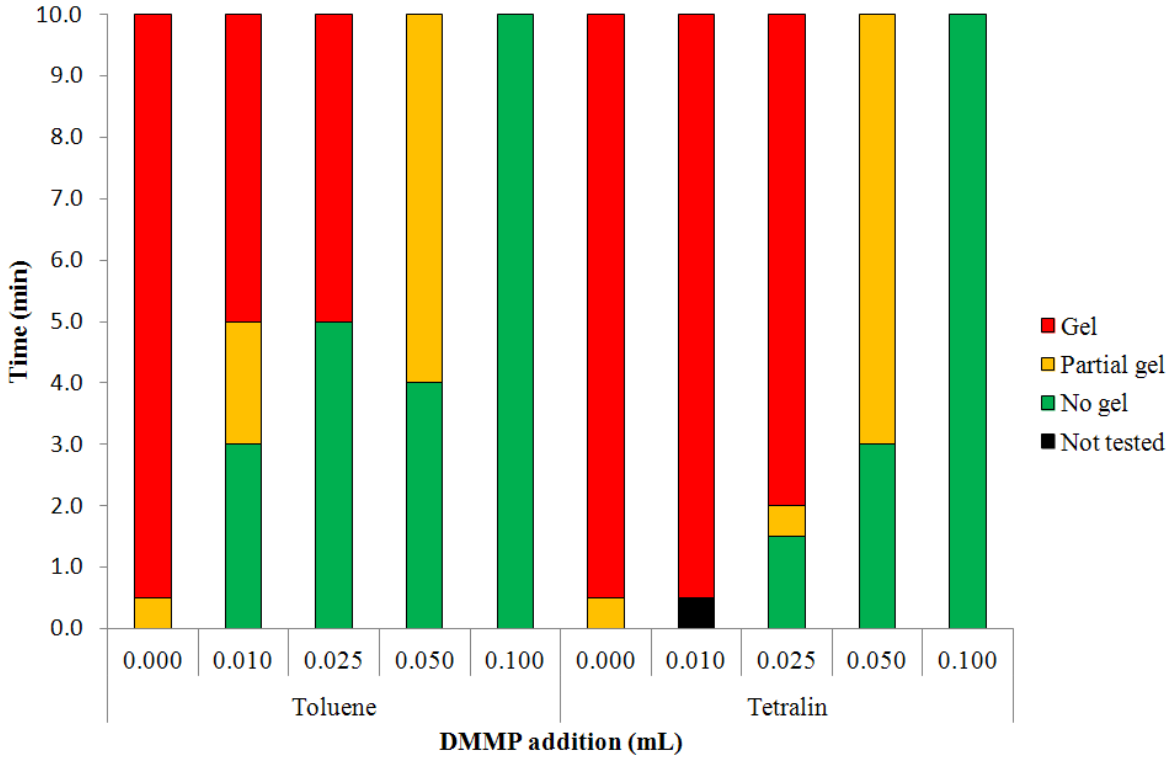

Figure S15: The time required for complete/ partial gel formation (1mL) by compound **4** (5 mg/mL) in toluene and tetralin in the presence of DMMP. Since only partial gels were found to form after 30 seconds the experiments conducted containing DMMP were not tested for gel formation between 0-30 seconds.

Dimethyl methylphosphonate (DMMP) addition

Time in mins.	**Table S6:** Concentration of gel **4** in toluene (1 mL, 20 mg/mL) – isocyanate addition to amine and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
0.5	No gel	No gel	Partial gel	Gel
1.0	No gel	No gel	Gel	Gel
1.5	No gel	No gel	Gel	Gel
2.0	No gel	No gel	Gel	Gel
3.0	No gel	Gel	Gel	Gel
4.0	No gel	Gel	Gel	Gel
5.0	No gel	Gel	Gel	Gel
10.0	Partial gel	Gel	Gel	Gel

Time in mins.	**Table S7:** Concentration of gel **4** in toluene (1 mL, 20 mg/mL) – amine addition to isocyanate and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
0.5	No gel	No gel	Partial gel	Gel
1.0	No gel	No gel	Gel	Gel
1.5	No gel	No gel	Gel	Gel
2.0	No gel	No gel	Gel	Gel
3.0	No gel	Gel	Gel	Gel
4.0	No gel	Gel	Gel	Gel
5.0	No gel	Gel	Gel	Gel
10.0	Partial gel	Gel	Gel	Gel

Time in mins.	**Table S8:** Concentration of gel **4** in toluene (1 mL, 15 mg/mL) – isocyanate addition to amine and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
0.5	No gel	No gel	No gel	Gel
1.0	No gel	No gel	No gel	Gel
1.5	No gel	No gel	Partial gel	Gel
2.0	No gel	No gel	Gel	Gel
3.0	Partial gel	Partial gel	Gel	Gel
4.0	Partial gel	Gel	Gel	Gel
5.0	Partial gel	Gel	Gel	Gel
10.0	Partial gel	Gel	Gel	Gel

Time in mins.	**Table S9:** Concentration of gel **4** in toluene (1 mL, 15 mg/mL) – amine addition to isocyanate and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
0.5	No gel	No gel	No gel	Gel
1.0	No gel	No gel	Partial gel	Gel
1.5	No gel	No gel	Gel	Gel
2.0	No gel	No gel	Gel	Gel
3.0	No gel	Partial gel	Gel	Gel
4.0	Partial gel	Gel	Gel	Gel
5.0	Partial gel	Gel	Gel	Gel
10.0	Partial gel	Gel	Gel	Gel

Time in mins.	**Table S10:** Concentration of gel **4** in toluene (1 mL, 10 mg/mL) – isocyanate addition to amine and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
0.5	No gel	No gel	No gel	Gel
1.0	No gel	No gel	No gel	Gel
1.5	No gel	No gel	No gel	Gel
2.0	No gel	No gel	No gel	Gel
3.0	No gel	No gel	Gel	Gel
4.0	No gel	No gel	Gel	Gel
5.0	No gel	Partial gel	Gel	Gel
10.0	Partial gel	Gel	Gel	Gel

Time in mins.	**Table S11:** Concentration of gel **4** in toluene (1 mL, 10 mg/mL) – amine addition to isocyanate and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
0.5	No gel	No gel	No gel	Gel
1.0	No gel	No gel	No gel	Gel
1.5	No gel	No gel	No gel	Gel
2.0	No gel	No gel	No gel	Gel
3.0	No gel	No gel	Gel	Gel
4.0	No gel	No gel	Gel	Gel
5.0	No gel	No gel	Gel	Gel
10.0	Partial gel	Gel	Gel	Gel

Time in mins.	**Table S12:** Concentration of gel **4** in toluene (1 mL, 5 mg/mL) – isocyanate addition to amine and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
1.0	No gel	No gel	No gel	No gel
1.5	No gel	No gel	No gel	No gel
2.0	No gel	No gel	No gel	No gel
2.5	No gel	No gel	No gel	No gel
3.0	No gel	No gel	No gel	No gel
4.0	No gel	No gel	No gel	Partial gel
5.0	No gel	Partial gel	No gel	Partial gel
10.0	No gel	Partial gel	Gel	Gel

Time in mins.	**Table S13:** Concentration of gel **4** in toluene (1 mL, 5 mg/mL) – amine addition to isocyanate and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
1.0	No gel	No gel	No gel	No gel
1.5	No gel	No gel	No gel	No gel
2.0	No gel	No gel	No gel	No gel
2.5	No gel	No gel	No gel	No gel
3.0	No gel	No gel	No gel	No gel
4.0	No gel	No gel	No gel	No gel
5.0	No gel	No gel	No gel	Partial gel
10.0	No gel	Partial gel	Gel	Gel

Time in mins.	**Table S14:** Concentration of gel **4** in tetralin (1 mL, 10 mg/mL) – isocyanate addition to amine and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
0.5	No gel	No gel	Gel	Gel
1.0	No gel	No gel	Gel	Gel
1.5	No gel	No gel	Gel	Gel
2.0	No gel	No gel	Gel	Gel
3.0	Partial gel	Gel	Gel	Gel
4.0	Partial gel	Gel	Gel	Gel
5.0	Partial gel	Gel	Gel	Gel
10.0	Gel	Gel	Gel	Gel

Time in mins.	**Table S15:** Concentration of gel **4** in tetralin (1 mL, 10 mg/mL) – amine addition to isocyanate and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
0.5	No gel	No gel	Gel	Gel
1.0	No gel	No gel	Gel	Gel
1.5	No gel	No gel	Gel	Gel
2.0	No gel	No gel	Gel	Gel
3.0	No gel	Gel	Gel	Gel
4.0	Partial gel	Gel	Gel	Gel
5.0	Partial gel	Gel	Gel	Gel
10.0	Gel	Gel	Gel	Gel

Time in mins.	**Table S16:** Concentration of gel **4** in tetralin (1 mL, 5 mg/mL) – isocyanate addition to amine and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
1.0	No gel	No gel	No gel	Gel
1.5	No gel	No gel	No gel	Gel
2.0	No gel	No gel	No gel	Gel
2.5	No gel	No gel	No gel	Gel
3.0	No gel	No gel	Partial gel	Gel
4.0	No gel	No gel	Gel	Gel
5.0	No gel	No gel	Gel	Gel
10.0	No gel	No gel	Gel	Gel

Time in mins.	**Table S17:** Concentration of gel **4** in tetralin (1 mL, 5 mg/mL) – amine addition to isocyanate and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
1.0	No gel	No gel	No gel	Gel
1.5	No gel	No gel	No gel	Gel
2.0	No gel	No gel	Partial gel	Gel
2.5	No gel	No gel	Gel	Gel
3.0	No gel	No gel	Gel	Gel
4.0	No gel	Partial gel	Gel	Gel
5.0	No gel	Partial gel	Gel	Gel
10.0	No gel	Partial gel	Gel	Gel

Time in mins.	**Table S18:** Concentration of gel **2** in tetralin (1 mL, 10 mg/mL) – isocyanate addition to amine and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
0.5	No gel	No gel	Gel	Gel
1.0	No gel	Gel	Gel	Gel
1.5	No gel	Gel	Gel	Gel
2.0	No gel	Gel	Gel	Gel
3.0	No gel	Gel	Gel	Gel
4.0	No gel	Gel	Gel	Gel
5.0	Gel	Gel	Gel	Gel
10.0	Gel	Gel	Gel	Gel

Time in mins.	**Table S19:** Concentration of gel **2** in tetralin (1 mL, 10 mg/mL) – amine addition to isocyanate and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
0.5	No gel	No gel	Gel	Gel
1.0	No gel	Gel	Gel	Gel
1.5	No gel	Gel	Gel	Gel
2.0	No gel	Gel	Gel	Gel
3.0	No gel	Gel	Gel	Gel
4.0	No gel	Gel	Gel	Gel
5.0	Partial gel	Gel	Gel	Gel
10.0	Gel	Gel	Gel	Gel

Time in mins.	**Table S20:** Concentration of gel **2** in tetralin (1 mL, 5 mg/mL) – isocyanate addition to amine and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
0.5	No gel	No gel	No gel	Gel
1.0	No gel	No gel	Gel	Gel
1.5	No gel	No gel	Gel	Gel
2.0	No gel	No gel	Gel	Gel
3.0	No gel	Partial gel	Gel	Gel
4.0	No gel	Partial gel	Gel	Gel
5.0	No gel	Gel	Gel	Gel
10.0	No gel	Gel	Gel	Gel

Time in mins.	**Table S21:** Concentration of gel **2** in tetralin (1 mL, 5 mg/mL) – amine addition to isocyanate and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
0.5	No gel	No gel	No gel	Gel
1.0	No gel	No gel	Partial gel	Gel
1.5	No gel	No gel	Gel	Gel
2.0	No gel	No gel	Gel	Gel
3.0	No gel	No gel	Gel	Gel
4.0	No gel	No gel	Gel	Gel
5.0	No gel	Partial gel	Gel	Gel
10.0	No gel	Gel	Gel	Gel

Time in mins.	**Table S22:** Concentration of gel **2** in toluene (1 mL, 20 mg/mL) – isocyanate addition to amine and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
0.5	Partial gel	Gel	Gel	Gel
1.0	Gel	Gel	Gel	Gel
1.5	Gel	Gel	Gel	Gel
2.0	Gel	Gel	Gel	Gel
3.0	Gel	Gel	Gel	Gel
4.0	Gel	Gel	Gel	Gel
5.0	Gel	Gel	Gel	Gel
10.0	Gel	Gel	Gel	Gel

Time in mins.	**Table S23:** Concentration of gel **2** in toluene (1 mL, 20 mg/mL) – amine addition to isocyanate and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
0.5	Partial gel	Gel	Gel	Gel
1.0	Gel	Gel	Gel	Gel
1.5	Gel	Gel	Gel	Gel
2.0	Gel	Gel	Gel	Gel
3.0	Gel	Gel	Gel	Gel
4.0	Gel	Gel	Gel	Gel
5.0	Gel	Gel	Gel	Gel
10.0	Gel	Gel	Gel	Gel

Time in mins.	**Table S24:** Concentration of gel **2** in toluene (1 mL, 15 mg/mL) – isocyanate addition to amine and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
0.5	No gel	Gel	Gel	Gel
1.0	Partial gel	Gel	Gel	Gel
1.5	Partial gel	Gel	Gel	Gel
2.0	Gel	Gel	Gel	Gel
3.0	Gel	Gel	Gel	Gel
4.0	Gel	Gel	Gel	Gel
5.0	Gel	Gel	Gel	Gel
10.0	Gel	Gel	Gel	Gel

Time in mins.	**Table S25:** Concentration of gel **2** in toluene (1 mL, 15 mg/mL) – amine addition to isocyanate and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
0.5	No gel	Gel	Gel	Gel
1.0	Partial gel	Gel	Gel	Gel
1.5	Gel	Gel	Gel	Gel
2.0	Gel	Gel	Gel	Gel
3.0	Gel	Gel	Gel	Gel
4.0	Gel	Gel	Gel	Gel
5.0	Gel	Gel	Gel	Gel
10.0	Gel	Gel	Gel	Gel

Time in mins.	**Table S26:** Concentration of gel **2** in toluene (1 mL, 10 mg/mL) – isocyanate addition to amine and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
0.5	No gel	No gel	Partial gel	Gel
1.0	No gel	Partial gel	Gel	Gel
1.5	No gel	Partial gel	Gel	Gel
2.0	No gel	Partial gel	Gel	Gel
3.0	No gel	Partial gel	Gel	Gel
4.0	Partial gel	Partial gel	Gel	Gel
5.0	Partial gel	Partial gel	Gel	Gel
10.0	Gel	Gel	Gel	Gel

Time in mins.	**Table S27:** Concentration of gel **2** in toluene (1 mL, 10 mg/mL) – amine addition to isocyanate and DMMP solution			
	0.1 mL DMMP	0.05 mL DMMP	0.025 mL DMMP	0.01 mL DMMP
0.5	No gel	No gel	Partial gel	Gel
1.0	No gel	Partial gel	Gel	Gel
1.5	No gel	Partial gel	Gel	Gel
2.0	No gel	Partial gel	Gel	Gel
3.0	No gel	Partial gel	Gel	Gel
4.0	Partial gel	Partial gel	Gel	Gel
5.0	Partial gel	Partial gel	Gel	Gel
10.0	Gel	Gel	Gel	Gel

Time in mins.	**Table S28:** Concentration of gel **1** in tetralin (1 mL) in mg/mL – 0.1 mL DMMP			
	20 mg/mL	15 mg/mL	10 mg/mL	5 mg/mL
0.5	Gel	Gel	Partial gel	Partial gel
1.0	Gel	Gel	Partial gel	Partial gel
1.5	Gel	Gel	Partial gel	Partial gel
2.0	Gel	Gel	Partial gel	Partial gel
3.0	Gel	Gel	Partial gel	Partial gel
4.0	Gel	Gel	Partial gel	Partial gel
5.0	Gel	Gel	Partial gel	Partial gel
10.0	Gel	Gel	Partial gel	Partial gel

Time in mins.	**Table S29:** Concentration of gel **1** in tetralin (1 mL) in mg/mL – 0.05 mL DMMP			
	20 mg/mL	15 mg/mL	10 mg/mL	5 mg/mL
0.5	NA	NA	Gel	Gel
1.0	NA	NA	Gel	Gel
1.5	NA	NA	Gel	Gel
2.0	NA	NA	Gel	Gel
3.0	NA	NA	Gel	Gel
4.0	NA	NA	Gel	Gel
5.0	NA	NA	Gel	Gel
10.0	NA	NA	Gel	Gel

Time in mins.	**Table S30:** Concentration of gel **1** in tetralin (1 mL) in mg/mL – 0.025 mL DMMP			
	20 mg/mL	15 mg/mL	10 mg/mL	5 mg/mL
0.5	NA	NA	NA	NA
1.0	NA	NA	NA	NA
1.5	NA	NA	NA	NA
2.0	NA	NA	NA	NA
3.0	NA	NA	NA	NA
4.0	NA	NA	NA	NA
5.0	NA	NA	NA	NA
10.0	NA	NA	NA	NA

Time in mins.	**Table S31:** Concentration of gel **1** in tetralin (1 mL) in mg/mL – 0.01 mL DMMP			
	20 mg/mL	15 mg/mL	10 mg/mL	5 mg/mL
0.5	NA	NA	NA	NA
1.0	NA	NA	NA	NA
1.5	NA	NA	NA	NA
2.0	NA	NA	NA	NA
3.0	NA	NA	NA	NA
4.0	NA	NA	NA	NA
5.0	NA	NA	NA	NA
10.0	NA	NA	NA	NA

Time in mins.	**Table S32:** Concentration of gel **3** in tetralin (1 mL) in mg/mL – 0.1 mL DMMP			
	20 mg/mL	15 mg/mL	10 mg/mL	5 mg/mL
0.5	Gel	Gel	Gel	Partial gel
1.0	Gel	Gel	Gel	Partial gel
1.5	Gel	Gel	Gel	Partial gel
2.0	Gel	Gel	Gel	Partial gel
3.0	Gel	Gel	Gel	Partial gel
4.0	Gel	Gel	Gel	Partial gel
5.0	Gel	Gel	Gel	Partial gel
10.0	Gel	Gel	Gel	Partial gel

Time in mins.	**Table S33:** Concentration of gel **3** in tetralin (1 mL) in mg/mL – 0.05 mL DMMP			
	20 mg/mL	15 mg/mL	10 mg/mL	5 mg/mL
0.5	NA	NA	NA	Gel
1.0	NA	NA	NA	Gel
1.5	NA	NA	NA	Gel
2.0	NA	NA	NA	Gel
3.0	NA	NA	NA	Gel
4.0	NA	NA	NA	Gel
5.0	NA	NA	NA	Gel
10.0	NA	NA	NA	Gel

Time in mins.	**Table S34:** Concentration of gel **3** in tetralin (1 mL) in mg/mL – 0.025 mL DMMP			
	20 mg/mL	15 mg/mL	10 mg/mL	5 mg/mL
0.5	NA	NA	NA	NA
1.0	NA	NA	NA	NA
1.5	NA	NA	NA	NA
2.0	NA	NA	NA	NA
3.0	NA	NA	NA	NA
4.0	NA	NA	NA	NA
5.0	NA	NA	NA	NA
10.0	NA	NA	NA	NA

Time in mins.	**Table S35:** Concentration of gel **3** in tetralin (1 mL) in mg/mL – 0.01 mL DMMP			
	20 mg/mL	15 mg/mL	10 mg/mL	5 mg/mL
0.5	NA	NA	NA	NA
1.0	NA	NA	NA	NA
1.5	NA	NA	NA	NA
2.0	NA	NA	NA	NA
3.0	NA	NA	NA	NA
4.0	NA	NA	NA	NA
5.0	NA	NA	NA	NA
10.0	NA	NA	NA	NA

Time in mins.	**Table S36:** Concentration of gel **3** in toluene (1 mL) in mg/mL – 0.1 mL DMMP			
	20 mg/mL	15 mg/mL	10 mg/mL	5 mg/mL
0.5	Gel	Gel	Partial gel	Partial gel
1.0	Gel	Gel	Partial gel	Partial gel
1.5	Gel	Gel	Partial gel	Partial gel
2.0	Gel	Gel	Partial gel	Partial gel
3.0	Gel	Gel	Partial gel	Partial gel
4.0	Gel	Gel	Partial gel	Partial gel
5.0	Gel	Gel	Partial gel	Partial gel
10.0	Gel	Gel	Partial gel	Partial gel

Time in mins.	**Table S37:** Concentration of gel **3** in toluene (1 mL) in mg/mL – 0.05 mL DMMP			
	20 mg/mL	15 mg/mL	10 mg/mL	5 mg/mL
0.5	NA	NA	Gel	Partial gel
1.0	NA	NA	Gel	Partial gel
1.5	NA	NA	Gel	Partial gel
2.0	NA	NA	Gel	Partial gel
3.0	NA	NA	Gel	Partial gel
4.0	NA	NA	Gel	Partial gel
5.0	NA	NA	Gel	Partial gel
10.0	NA	NA	Gel	Partial gel

Time in mins.	**Table S38:** Concentration of gel **3** in toluene (1 mL) in mg/mL – 0.025 mL DMMP			
	20 mg/mL	15 mg/mL	10 mg/mL	5 mg/mL
0.5	NA	NA	NA	Gel
1.0	NA	NA	NA	Gel
1.5	NA	NA	NA	Gel
2.0	NA	NA	NA	Gel
3.0	NA	NA	NA	Gel
4.0	NA	NA	NA	Gel
5.0	NA	NA	NA	Gel
10.0	NA	NA	NA	Gel

Time in mins.	**Table S39:** Concentration of gel **3** in toluene (1 mL) in mg/mL – 0.01 mL DMMP			
	20 mg/mL	15 mg/mL	10 mg/mL	5 mg/mL
0.5	NA	NA	NA	NA
1.0	NA	NA	NA	NA
1.5	NA	NA	NA	NA
2.0	NA	NA	NA	NA
3.0	NA	NA	NA	NA
4.0	NA	NA	NA	NA
5.0	NA	NA	NA	NA
10.0	NA	NA	NA	NA

Soman (GD) addition

Time in mins.	**Table S40:** Concentration of gel **4** in toluene (1 mL) in mg/mL – 0.025 mL GD	
	10 mg/mL	5 mg/mL
0.5	No Gel	No Gel
1.0	No Gel	No Gel
1.5	Gel	No Gel
2.0	Gel	No Gel
3.0	Gel	No Gel
4.0	Gel	No Gel
5.0	Gel	No Gel
10.0	Gel	No Gel

Time in mins.	**Table S41:** Concentration of gel **4** in toluene (1 mL) in mg/mL – 0.010 mL GD	
	10 mg/mL	5 mg/mL
1.0	No Gel	No Gel
1.5	No Gel	No Gel
2.0	No Gel	No Gel
3.0	No Gel	No Gel
4.0	Partial Gel	No Gel
5.0	Partial Gel	No Gel
6.0	Gel	No Gel
10.0	Gel	No Gel

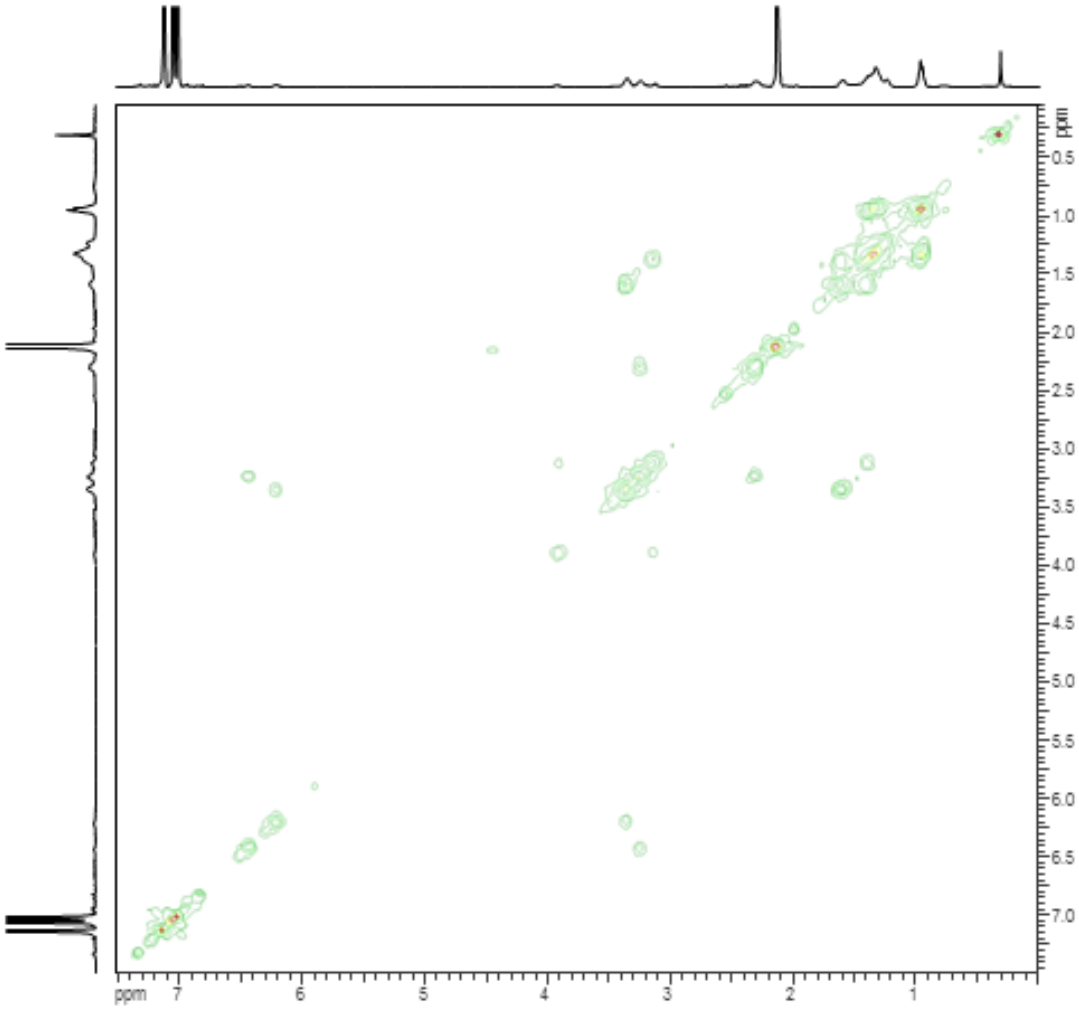

Figure S16: COSY NMR spectrum in toluene-d_8 showing the 0.5 mL of 15 mg/mL gel **4**.

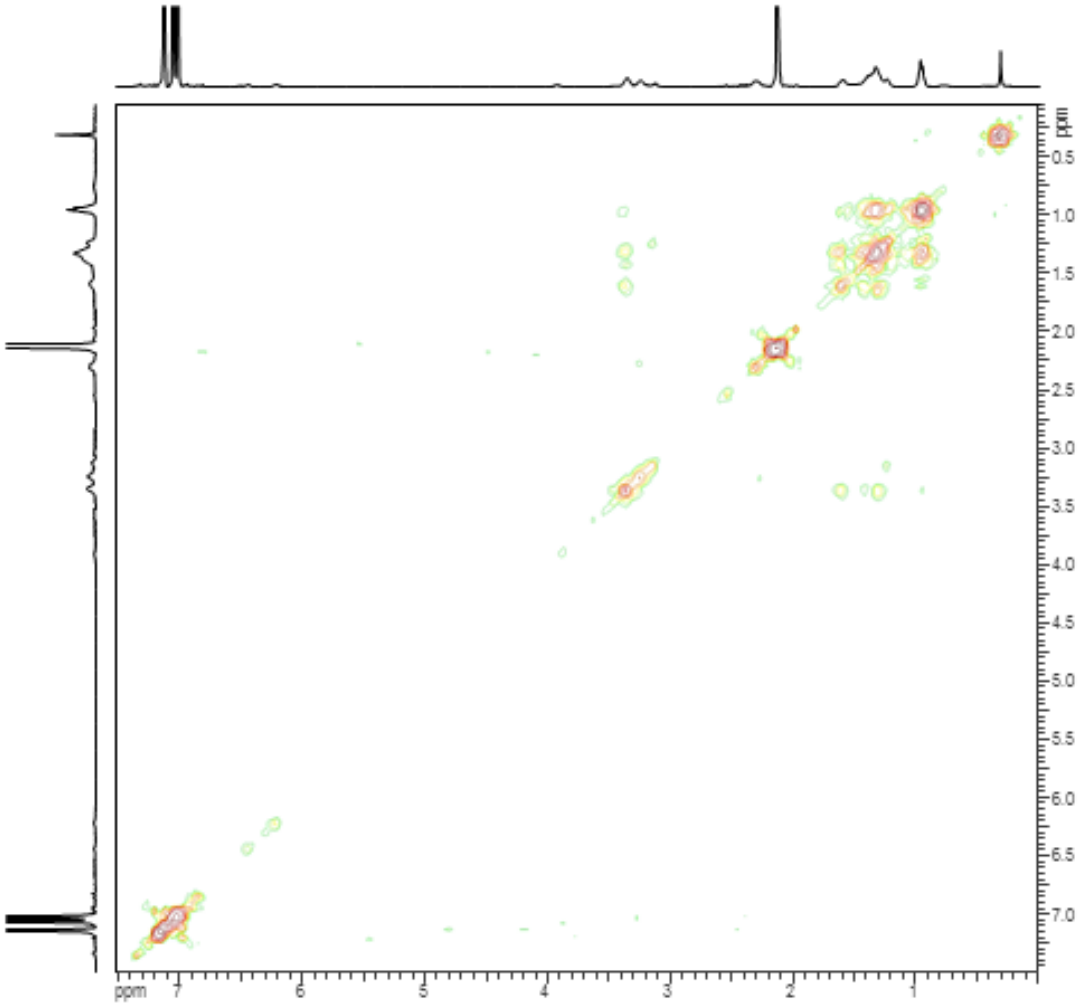

Figure S17: TOCSY NMR spectrum in toluene-d_8 showing the 0.5 mL of 15 mg/mL gel **4**.

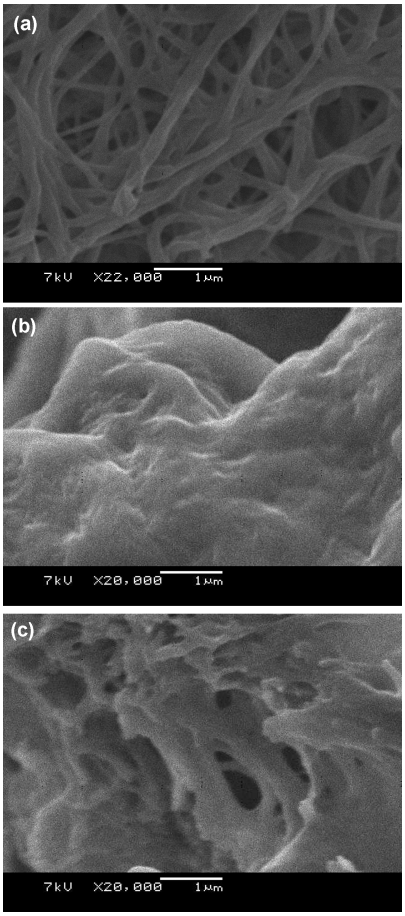

Figure S18: Scanning electron microscope images of the xerogels formed by compound **4** and (a) toluene, (b) cyclohexanone and (c) ethyl acetate after drying from samples prepared from 15mg/ml of gelator.

References

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