Supramolecular gels for the remediation of reactive organophosphorus compounds

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Electronic Supplementary Information

Experimental

General remarks: All reactions were performed under slight positive pressure of nitrogen using oven-dried glassware. All solvents and starting materials were purchased from chemical stores where available. Commercial grade reagents have been used without further purification. ^{1}H NMR (500 MHz) and ^{13}C{^{1}H} NMR (125 MHz) were determined on a Bruker AV III HD 500 spectrometer , ^{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 AV II 400 or AV III HD 400 spectrometer with the chemical shifts reported in parts per million (ppm), calibrated to the centre of the solvent peak set. Some ^{13}C peaks are missing due to overlapping signals. 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}). Low resolution mass spectra were recorded on a Waters Acquity UHPLC-MS system. High resolution mass spectra were recorded on a Bruker Maxis ESI-TOF system 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. SEM images were collected on a FEI XL30 ESEM in low pressure mode. Samples were prepared on aluminium stubs using self adhesive carbon tabs. Details of individual image collection can be seen in Figure S20.

Compound 2 Undecanoic acid (0.50 g, 2.68 mM) was heated at reflux with carbonyldiimidazole (CDI) (0.46 g, 2.82 mM) for 2 hrs in chloroform (40 mL). (1*R*,2*R*)-(-)-1,2-Cyclohexanediamine (0.15 g, 1.34 mM) was then added to the solution which was heated at reflux overnight under. The mixture was then washed with water (2 x 100 mL) and then dried with $MgSO_4$. The organic phase was then taken to dryness and dissolved in the minimum amount of hot methanol. A white solid formed as the solution cooled, this was isolated by filtration and washed with cold methanol (20 ml). Yield: 57 % (0.34 g, 0.79 mM); mp: 172 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ: 0.87 (t, J = 6.08 Hz, 6H), 1.25 (br s, 32H), 1.56 (br s, 4H), 1.74 (d, J = 8.16 Hz, 2H), 2.02 (d, J = 12.08 Hz, 2H), 2.10 (dd, J_1 = 11.60 Hz, J_2 = 6.96 Hz, 4H), 3.65 (br s, 2H), 5.93 (d, J = 4.40 Hz, 2H, amide NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ: 14.2 (CH_3), 22.8 (CH_2), 24.9 (CH_2), 26.0 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 32.0 (CH_2), 32.5 (CH_2), 37.1 (CH_2), 53.8 (CH), 174.0 (CO); IR (film): ν = 3270 (amide NH stretching), 3080 (amide NH stretching), 1640 (amide CO stretching), 1540 (amide CO stretching); LRMS (ESI^{+}): m/z: 451 [M+H]$^{+}$; HRMS (ESI^{+}) for $C_{28}H_{54}N_2NaO_2$: m/z: act: [M+Na]$^{+}$ 478.4068, cal: [M+Na]$^{+}$ 473.4078, Δδ (ppm) = 2.0.

Compound 1 was synthesised by the same general method given for compound **2**. Decanoic acid (0.50 g, 2.90 mM), CDI (0.49, 3.00 mM), (1*R*,2*R*)-(-)-1,2-Cyclohexanediamine (0.17 g, 1.45 mM). Yield: 38 % (0.24 g, 0.56 mM). ^{1}H NMR spectrum was found to match that previously published by Sato and co-workers.[1]

Compound 3 was synthesised by the same general method given for compound **2**. Dodecanoic acid (0.50 g, 2.50 mM), CDI (0.42, 2.60 mM), (1*R*,2*R*)-(-)-1,2-Cyclohexanediamine (0.14 g, 1.25 mM). Yield: 58 % (0.35 g, 0.73 mM). ^{1}H NMR spectrum was found to match that previously published by Esch and co-workers.[2]

Compound 4 was synthesised by the same general method given for compound **2**. Tridecanoic acid (0.50 g, 2.33 mM), CDI (0.40, 2.45 mM), (1*R*,2*R*)-(-)-1,2-Cyclohexanediamine (0.13 g, 1.17 mM). Yield: 79 % (0.47 g, 0.92 mM); mp: 168 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ: 0.88 (t, J = 6.00 Hz, 6H), 1.25 (br s, 40H), 1.57 (br s, 4H), 1.74 (d, J = 7.96 Hz, 2H), 2.02 (d, J = 12.24 Hz, 2H), 2.11 (dd, J_1 = 11.36 Hz, J_2 = 7.08 Hz, 4H), 3.65 (br s, 2H), 5.90 (br s, 2H, amide NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ: 14.6 (CH_3), 23.1 (CH_2), 25.2 (CH_2), 26.3 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.9 (CH_2), 30.0 (CH_2), 30.1 (CH_2), 30.1 (CH_2), 32.4 (CH_2), 37.4 (CH_2), 54.1 (CH), 174.4 (CO); IR (film): ν = 3270 (amide NH stretching), 3080 (amide NH stretching), 1640 (amide CO stretching), 1540 (amide CO stretching); LRMS (ESI$^+$): m/z: 507 $[M+H]^+$; HRMS (ESI$^+$) for $C_{32}H_{63}N_2O_2$: m/z: act: $[M+H]^+$ 507.4878, cal: $[M+H]^+$ 507.4884, Δδ (ppm) = 1.3. Although previously published by Kimura, Shirai and co-workers[3] full characterisation of this compound was performed.

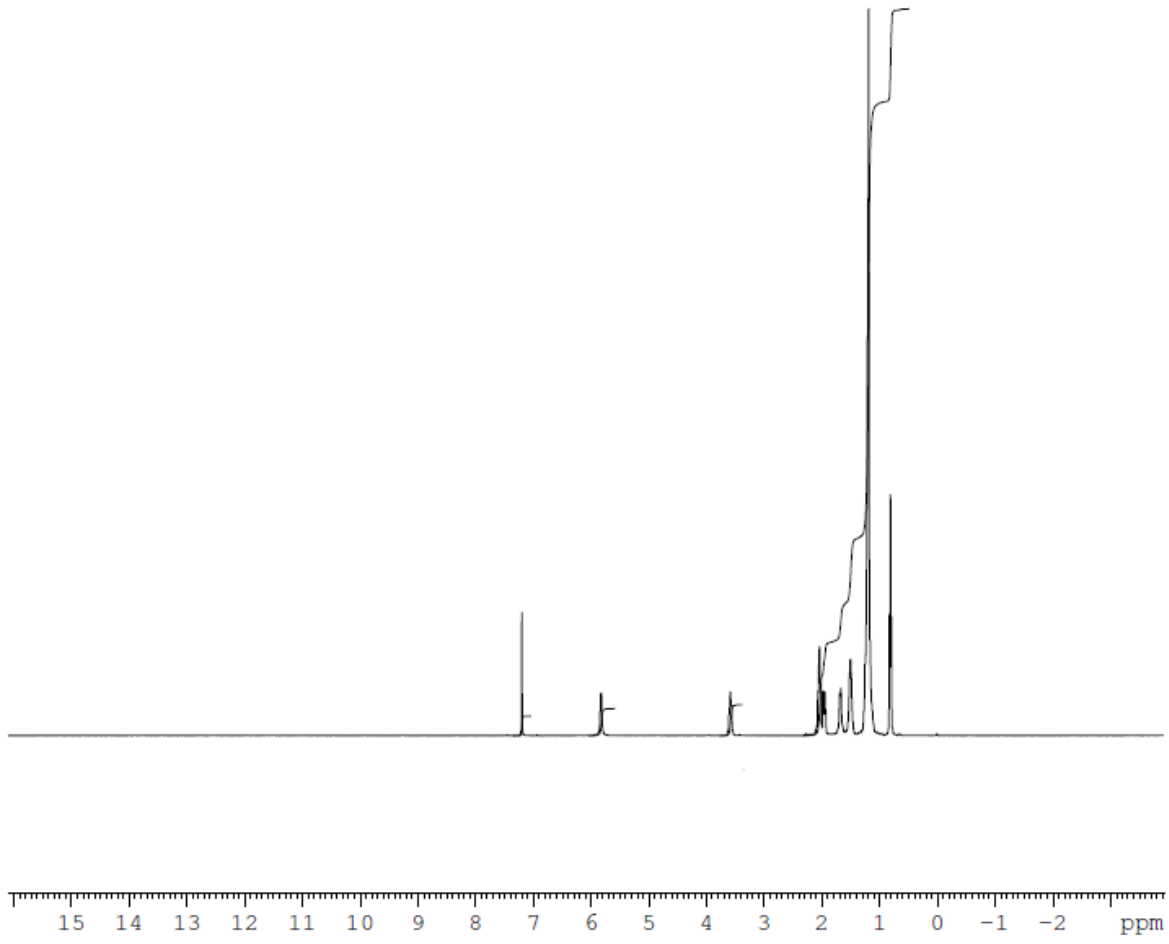

Figure S1 ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

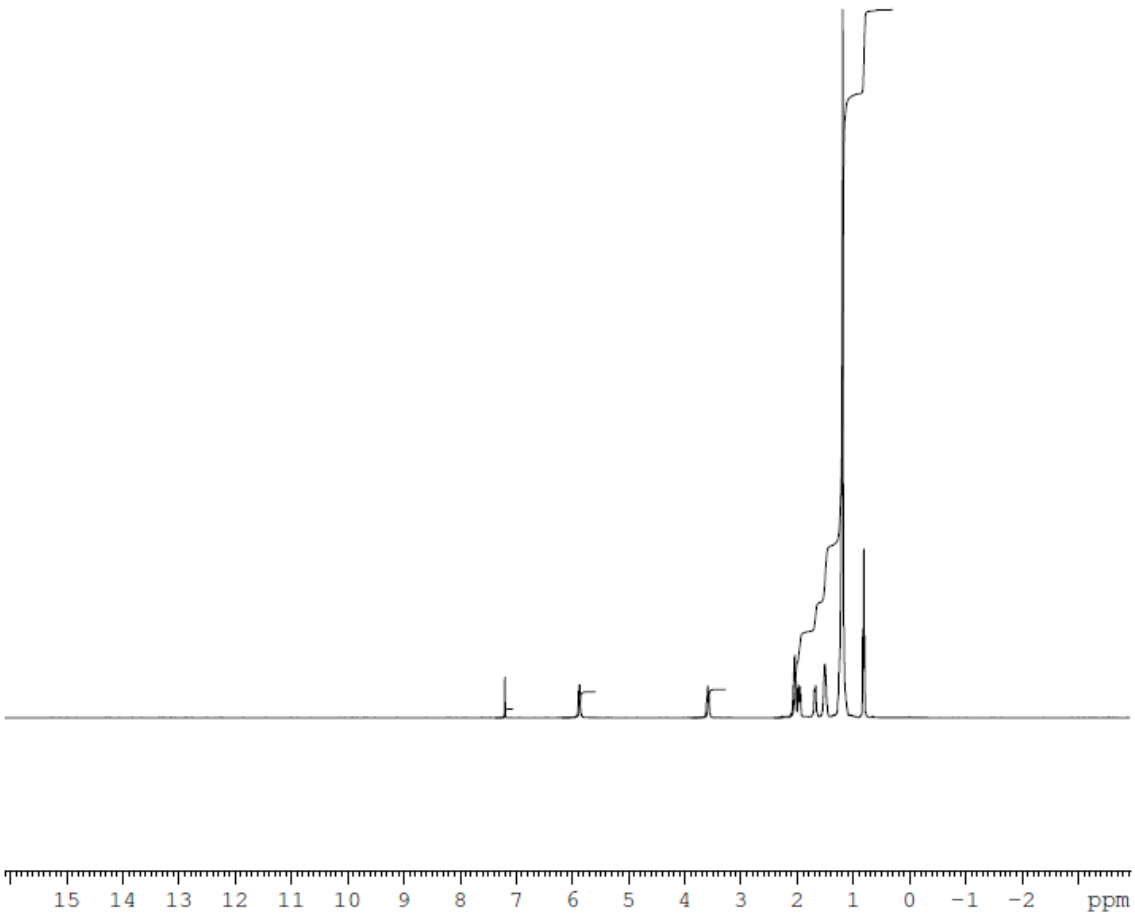

Figure S2 ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

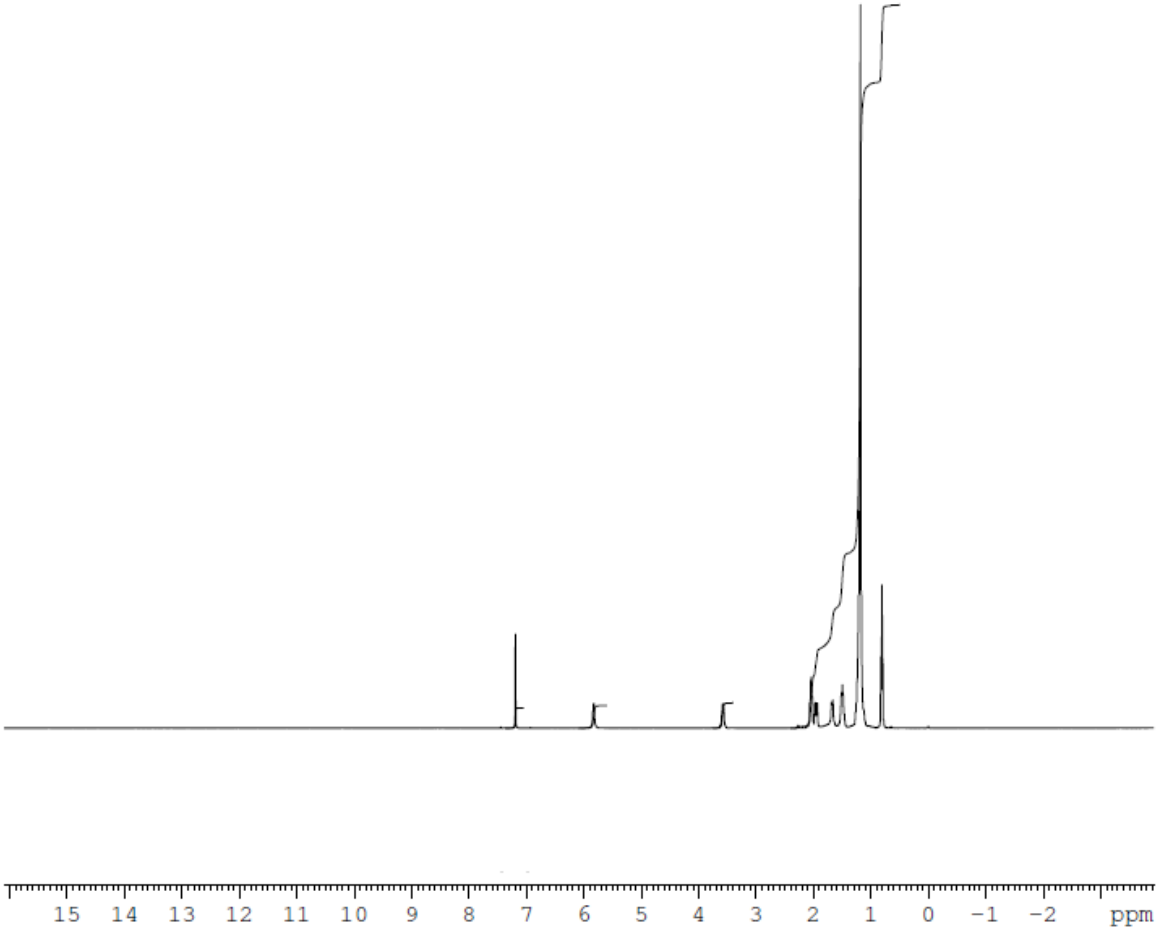

Figure S3 ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

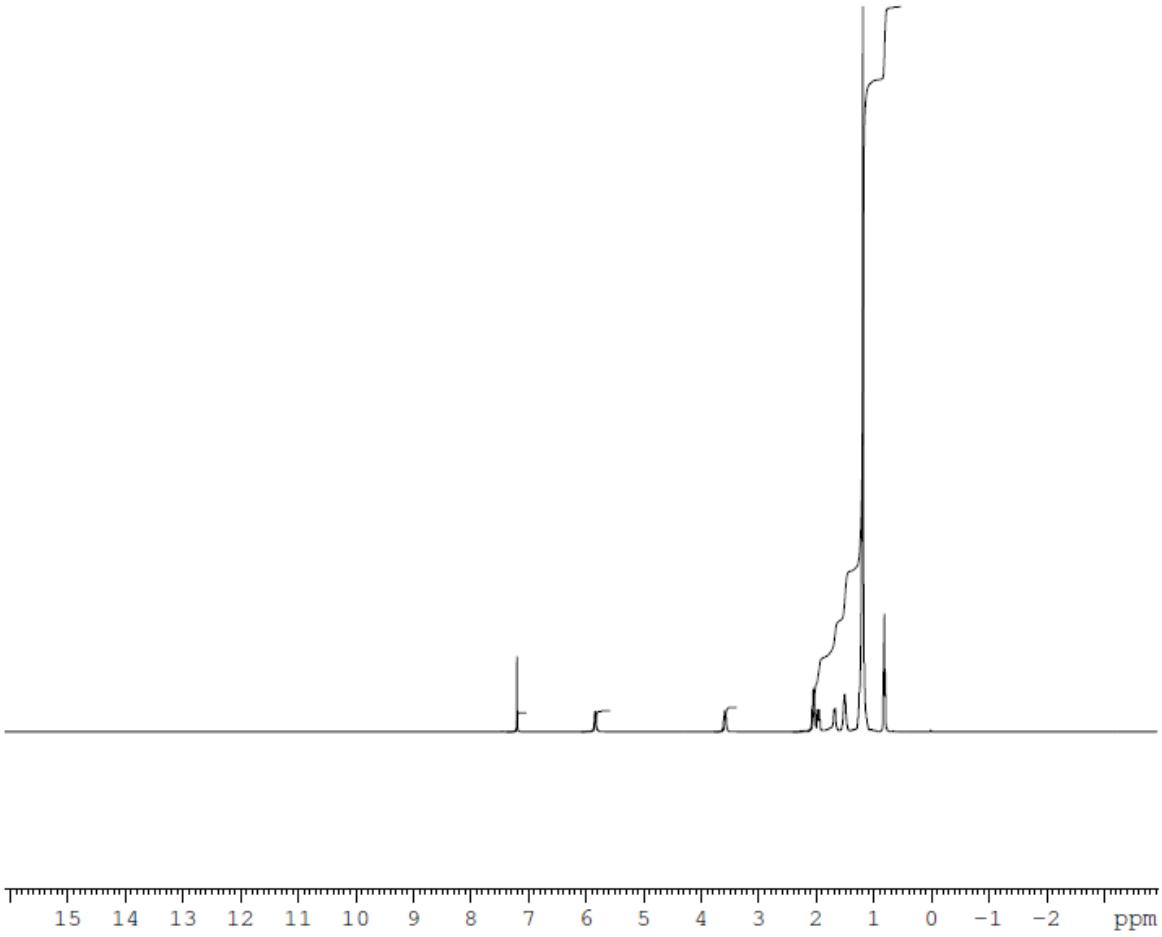

Figure S4 ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

Addition of DCP/HCl/EP to warmed gelation solutions of compounds 1-4 in pyridine. The pyridine gels were prepared using a standard method. The gelator was heated in a sealed vial with pyridine until all the solid had dissolved. The gel solution was then allowed to cool to 30-40 ºC, at this point just before gelation occurs the DCP/HCl/EP was added to the solution. The gels were then cooled to room temperature and inverted to check to see if a gel had formed. The results of these experiments are shown in Tables S10-S15.

Table S1 Amount of gelator, compound **1** (mmol) and added phosphonate (mmol).

Gelator	**Amount of gelator in 1 mL of gel (mmol)**								
	25 mg	20 mg	15 mg	10 mg	5.0 mg	4.0 mg	3.0 mg	2.5 mg	2.0 mg
1	0.059	0.047	0.035	0.024	0.012	0.009	0.007	0.006	0.005
2	0.055	0.044	0.033	0.022	0.011	0.009	0.007	0.006	0.004
3	0.052	0.042	0.031	0.021	0.010	0.008	0.006	0.005	0.004
4	0.049	0.039	0.029	0.020	0.010	0.008	0.006	0.005	0.004
Phosphonate	**Amount of phosphonate added (mmol)**								
	1.000 mL		0.100 mL		0.050 mL		0.010 mL		0.001 mL
DCP	6.955		0.695		0.348		0.070		0.007
DMMP	9.228		0.923		0.461		0.092		0.009

Table S2: Formation of gels with compound **1**, all experiments were performed with 1 mL of the solvent stated.

Concentration of gelator (mg/mL)	Solvent	
	Pyridine	TEA
25.0	No gel	NA
20.0	No gel	Gel
15.0	NA	NA
12.0	NA	NA
10.0	NA	Gel
9.0	NA	NA
8.0	NA	NA
7.0	NA	NA
6.0	NA	NA
5.0	NA	Gel
4.0	NA	Gel
3.0	NA	Partial gel
2.5	NA	Partial gel
2.0	NA	NA
1.0	NA	NA

Table S3: Formation of gels with compound **2**, all experiments were performed with 1 mL of the solvent stated.

Concentration of gelator (mg/mL)	Solvent	
	Pyridine	TEA
25.0	No gel	NA
20.0	No gel	Gel
15.0	NA	NA
12.0	NA	NA
10.0	NA	Gel
9.0	NA	NA
8.0	NA	NA
7.0	NA	NA
6.0	NA	NA
5.0	NA	Gel
4.0	NA	Partial gel
3.0	NA	Partial gel
2.5	NA	Partial gel
2.0	NA	NA
1.0	NA	NA

Table S4: Formation of gels with compound **3**, all experiments were performed with 1 mL of the solvent stated.

Concentration of gelator (mg/mL)	Solvent	
	Pyridine	TEA
25.0	Gel	NA
20.0	Gel	Gel
15.0	Gel	Gel
14.0	Gel	NA
13.0	Gel	NA
12.0	Partial gel	NA
11.0	Partial gel	NA
10.0	No gel	Gel
9.0	NA	NA
8.0	NA	Gel
7.0	NA	NA
6.0	NA	Gel
5.0	NA	NA
4.0	NA	Gel
3.0	NA	Gel
2.5	NA	NA
2.0	NA	Partial gel
1.0	NA	NA

Table S5: Formation of gels with compound **4**, all experiments were performed with 1 mL of the solvent stated.

Concentration of gelator (mg/mL)	Solvent	
	Pyridine	TEA
25.0	NA	NA
20.0	Gel	Gel
15.0	NA	NA
12.0	NA	NA
10.0	Gel	Gel
9.0	Gel	NA
8.0	Gel	NA
7.0	Gel	NA
6.0	Partial gel	NA
5.0	No gel	Gel
4.0	NA	Gel
3.0	NA	Partial gel
2.5	NA	Partial gel
2.0	NA	NA
1.0	NA	NA

Table S6: Formation of gels with compound **1**, all experiments were performed with 1 mL of the solvent stated.

Concentration of gelator (mg/mL)	Solvent	
	DMMP	DCP
40.0	NA	No Gel
20.0	Gel	NA
10.0	Gel	NA
5.0	Gel	NA
4.0	Partial Gel	NA
3.0	Partial Gel	NA
2.5	No Gel	NA

Table S7: Formation of gels with compound **2**, all experiments were performed with 1 mL of the solvent stated.

Concentration of gelator (mg/mL)	Solvent	
	DMMP	DCP
40.0	NA	No Gel
20.0	Gel	NA
10.0	Gel	NA
5.0	Gel	NA
4.0	Gel	NA
3.0	Gel	NA
2.5	Partial Gel	NA

Table S8: Formation of gels with compound **3**, all experiments were performed with 1 mL of the solvent stated.

Concentration of gelator (mg/mL)	Solvent	
	DMMP	DCP
40.0	NA	Partial Gel/ Precipitation
20.0	Gel	Partial Gel
10.0	Gel	NA
5.0	Gel	NA
4.0	Gel	NA
3.0	Gel	NA
2.5	Partial Gel	NA

Table S9: Formation of gels with compound **4**, all experiments were performed with 1 mL of the solvent stated.

Concentration of gelator (mg/mL)	Solvent	
	DMMP	DCP
40.0	NA	No Gel
20.0	Gel	NA
10.0	Gel	NA
5.0	Gel	NA
4.0	Gel	NA
3.0	Gel	NA
2.5	Partial Gel	NA

Table S10: Reactions containing compounds **2/3** and/or pyridine with the addition of various additives, as well as the reactions of the solvents TEA and pyridine with the addition of various additives. Reactions were carried out over a time frame > 12 hrs.

Solvent	Gelator	Conc. (mg/mL)	Additive (mL)	Response
TEA	NA		HCl (0.1)	White solid produced (HCl salt)
TEA	NA		EP (0.1)	Immiscible
TEA	NA		DCP (0.1)	Solid/gel produced, yellow in colour, no solution, passed inversion test
Pyridine	NA		HCl (0.1)	No visible changes
Pyridine	NA		EP (0.1)	No visible changes
Pyridine	NA		DCP (0.1)	Very slight yellowing of the solution
Pyridine	**3**	20	EP (0.1)	Colourless gel formed with the incorporation in EP into the gel. No change noted over time.
Pyridine	**4**	20	EP (0.1)	Colourless gel formed with the incorporation in EP into the gel. No change noted over time.
NA	**2**	40	DCP (1.0)	Slight yellowing of the solution when left at room temperature overnight
NA	**3**	40	DCP (1.0)	Slight yellowing of the solution when left at room temperature overnight

Table S11: DCP (0.1 mL) addition to a warmed solution of compounds **1**, **2, 3** and **4** (20 mg) in pyridine (1 mL). Time (T=0) is considered to be the point at which the DCP is added to the warmed pyridine/gelator solution. All experiments were run for a minimum of 18 hrs. At the end of the experiment each gel was found to have degraded into a solution and all samples were red in colour.

Compound/ Gelator	DCP (mL)	Time (mins)	Observation
1	0.1	< 1	Light pink solution
1	0.1	5	Light pink solution
1	0.1	20	Light pink solution
2	0.1	<1	Light yellow solution
2	0.1	5	Light yellow solution
2	0.1	20	Light yellow solution
3	0.1	0	DCP added to warmed solution
3	0.1	3	Colourless gel formed
3	0.1	30	Yellow gel formed
3	0.1	60	Orange solution most of the gel dissolved
3	0.1	90	Darkening of orange solution – no gel
3	0.1	1080	Dark red solution
4	0.1	< 1	Almost immediate colourless, clear gel formation
4	0.1	5	Slight clouding of gel
4	0.1	20	Slight yellowing of gel
4	0.1	30	Increasing strength of colour
4	0.1	60	Increasing strength of colour
4	0.2	< 1	Almost immediate colourless, slightly opaque gel formation
4	0.2	5	Slight yellowing of gel
4	0.2	20	Increasing strength of colour
4	0.2	30	Increasing strength of colour
4	0.2	60	Orange gel some degradation into an orange solution
4	0.3	< 1	Immediate clear, colourless gel formation upon DCP addition
4	0.3	5	Slight yellowing of gel
4	0.3	20	Increasing strength of colour
4	0.3	30	Increasing strength of colour, some gel degradation
4	0.3	60	Orange gel approx. 2/3 degradation into an orange solution
4	0.4	< 1	Immediate clear, colourless gel formation upon DCP addition
4	0.4	5	Slight yellowing of gel
4	0.4	20	Increasing strength of colour
4	0.4	30	Increasing strength of colour, some gel degradation
4	0.4	60	Most of the gel degraded into an orange solution, orange gel
4	0.5	< 1	Immediate clear, colourless gel formation upon DCP addition
4	0.5	5	Slight yellowing of gel
4	0.5	20	Increasing strength of colour
4	0.5	30	Increasing strength of colour, some gel degradation
4	0.5	60	Complete degradation of orange gel into orange solution
4	1.0	< 1	Immediate clear, colourless gel formation upon DCP addition
4	1.0	5	Slight yellowing of gel
4	1.0	20	Partial gel only, some yellowing of solution and partial gel
4	1.0	30	Most of the gel degraded into an orange solution, orange gel
4	1.0	60	Complete degradation of orange gel into orange solution, some solid

Table S12: Conc. HCl addition to a warmed solution of compound **1** in pyridine (1 mL). Time (T=0) is considered to be the point at which the HCl is added to the warmed pyridine/gelator solution.

Compound/ Gelator	Amount (mg/mL)	HCl (mL)	Time (mins)	Observation
1	20	0.05	5	Yellow gel
1	20	0.1	5	Yellow solution
1	20	0.05	30	Yellow gel
1	20	0.1	30	Partial yellow gel
1	20	0.05	60	Yellow gel
1	20	0.1	60	Yellow gel
1	20	0.05	1360	Yellow gel
1	20	0.1	1360	Yellow gel

Table S13: Conc. HCl addition to a warmed solution of compound **2** in pyridine (1 mL). Time (T=0) is considered to be the point at which the HCl is added to the warmed pyridine/gelator solution.

Compound/ Gelator	Amount (mg/mL)	HCl (mL)	Time (mins)	Observation
2	20	0.05	5	Yellow gel
2	20	0.1	5	Yellow gel
2	20	0.05	1040	Yellow gel
2	20	0.1	1040	Yellow gel

Table S14: Conc. HCl addition to a warmed solution of compound **3** in pyridine (1 mL). Time (T=0) is considered to be the point at which the HCl is added to the warmed pyridine/gelator solution.

Compound/ Gelator	Amount (mg/mL)	HCl (mL)	Time (mins)	Observation
3	20	0.05	5	Yellow gel
3	20	0.1	5	Yellow gel
3	20	0.05	1230	Yellow gel
3	20	0.1	1230	Yellow gel

Table S15: Conc. HCl addition to a warmed solution of compound **4** in pyridine (1 mL). Time (T=0) is considered to be the point at which the HCl is added to the warmed pyridine/gelator solution.

Compound/ Gelator	Amount (mg/mL)	HCl (mL)	Time (mins)	Observation
4	20	0.05	5	Yellow gel
4	20	0.1	5	Yellow gel
4	20	0.05	1040	Yellow gel
4	20	0.1	1040	Yellow gel

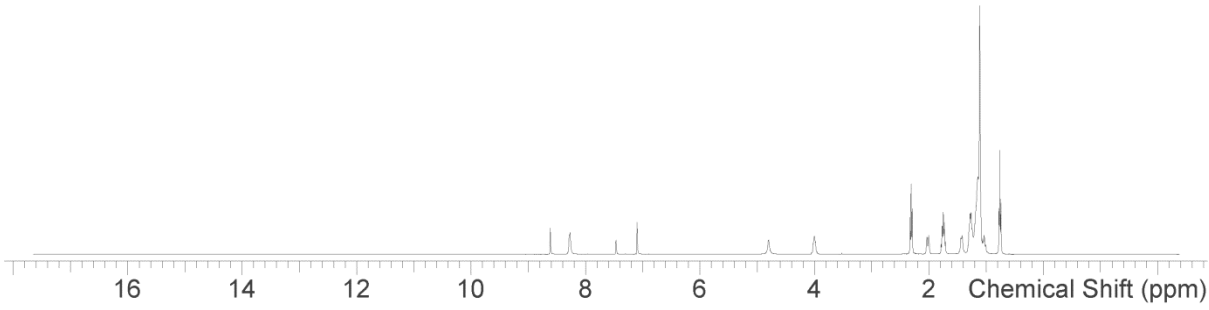

Figure S5 ^{1}H NMR spectrum compound **3** (25 mg/mL) in pyridine-d_5.

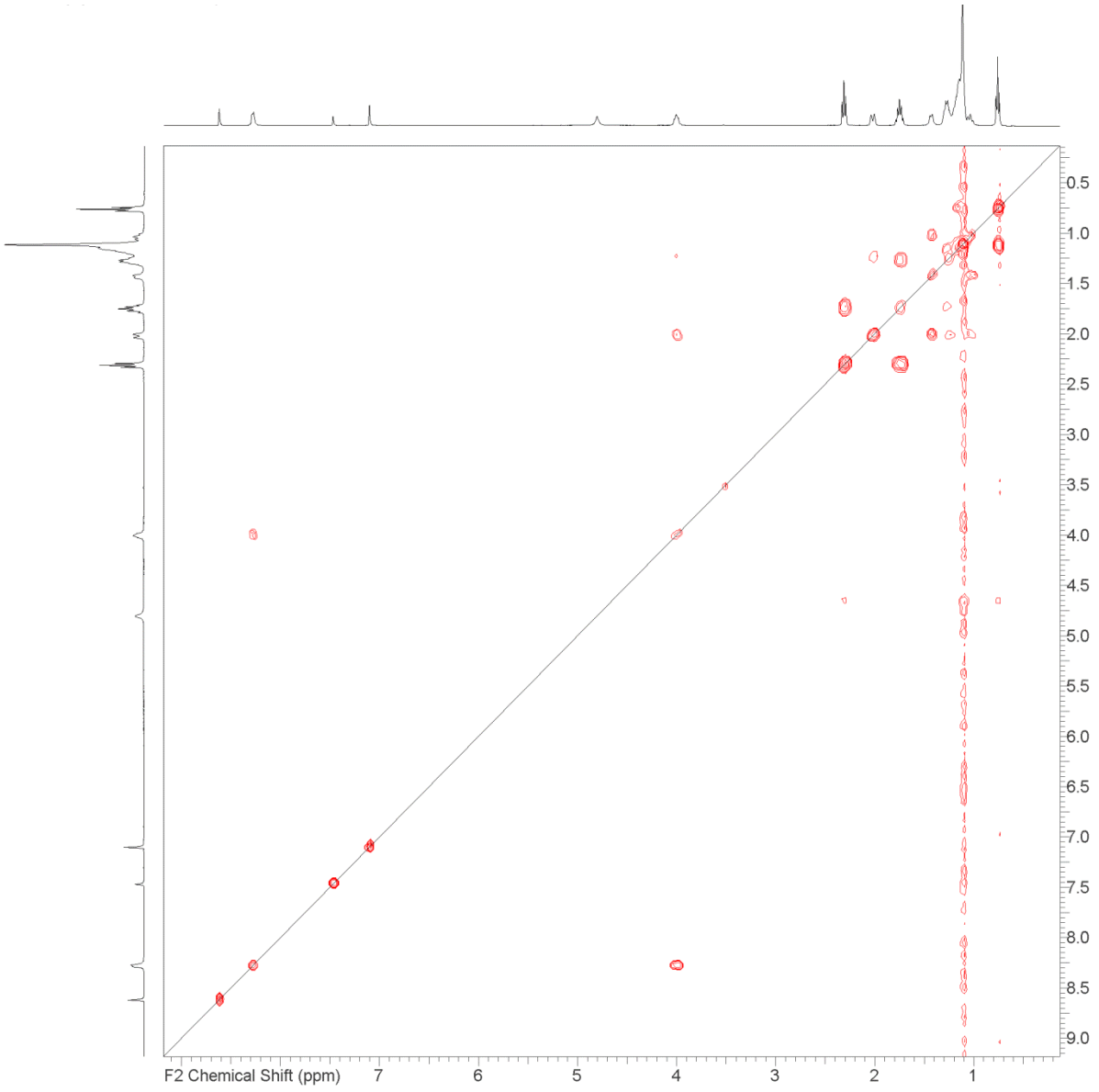

Figure S6 ^{1}H COSY NMR spectrum compound **3** (25 mg/mL) in pyridine-d_5.

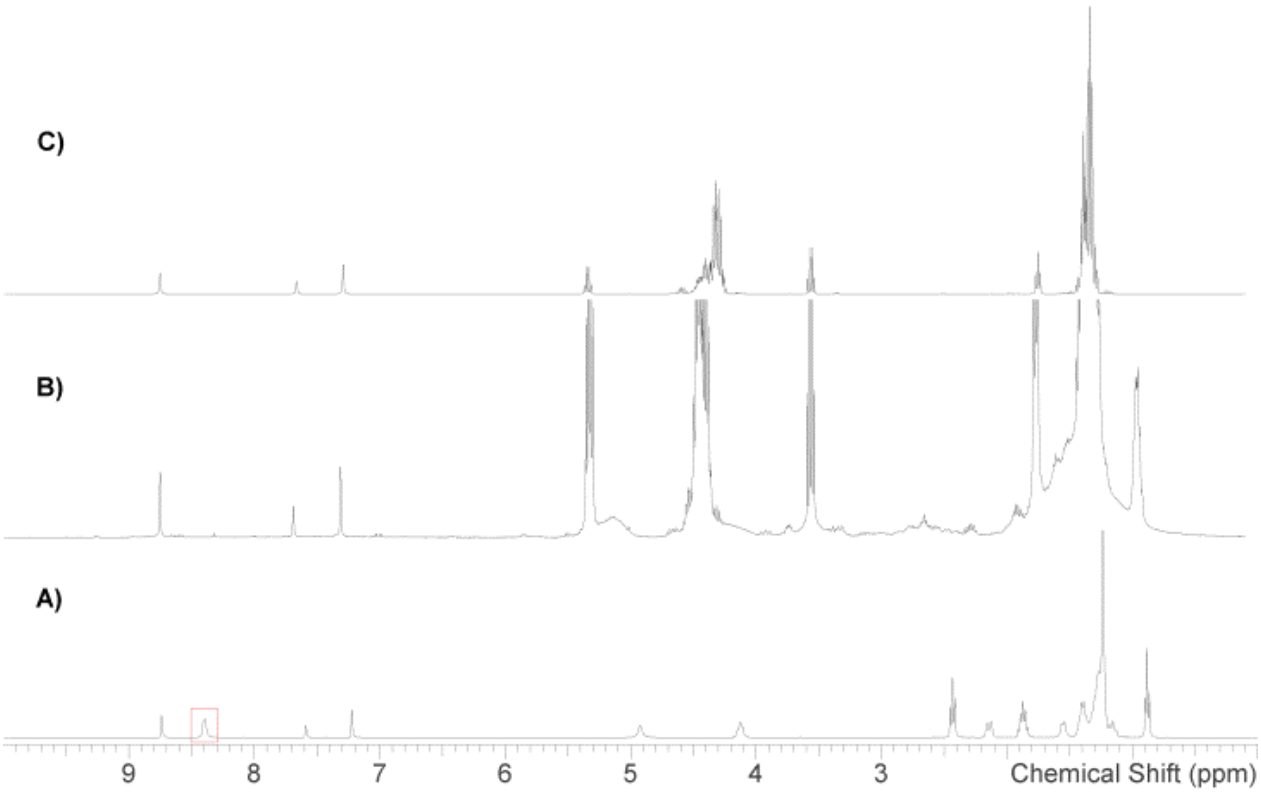

Figure S7 ^{1}H NMR spectra in pyridine-d_5 (1 mL) A) with compound **3** (25 mg/mL) the amide NH signal has been highlighted, B) same sample as A reacted with DCP (0.1 mL), C) with DCP only (0.1 mL).

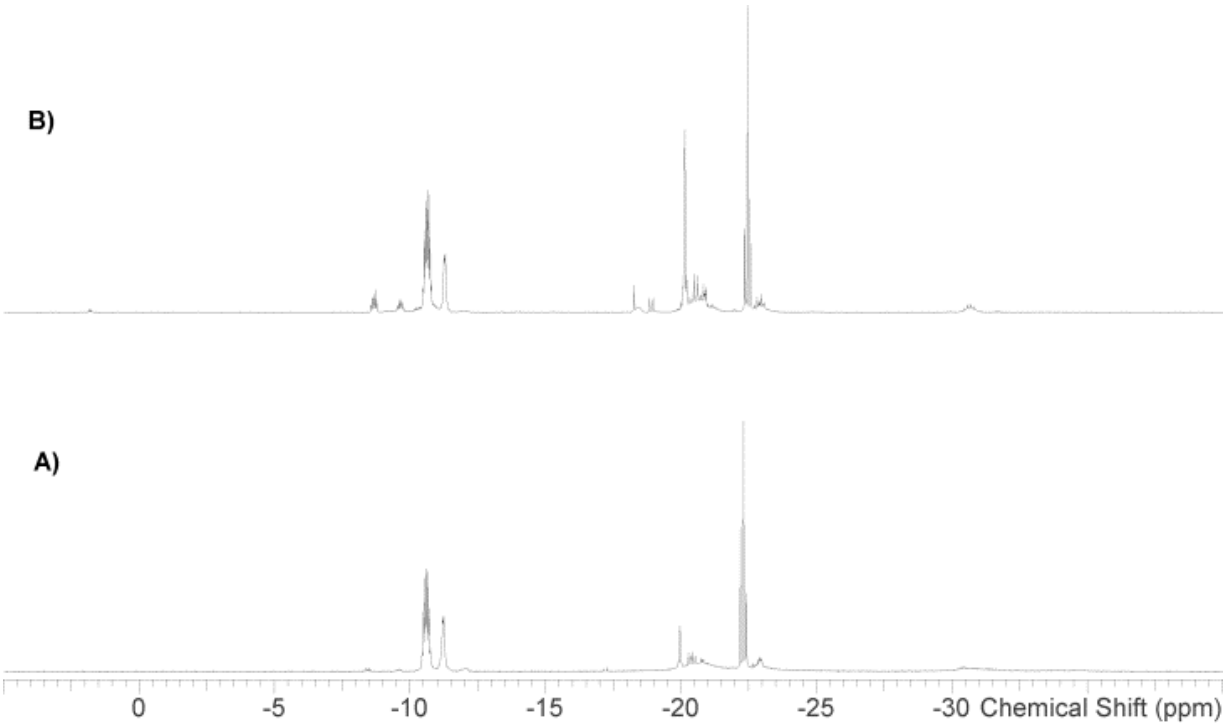

Figure S8 ^{31}P NMR spectra in pyridine-d_5 (1 mL) A) with DCP only (0.1 mL) B) with compound **3** (25 mg/mL) reacted with DCP (0.1 mL).

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Chemistry - maXis HPLC-ESI Accurate Mass Report

Analysis Info

Analysis Name	D:\Data\Chemistry\2014\Feb14\JH 7191 + DCP diluted_BC7_01_10532.d	Acquisition Date	07/02/2014 17:30:16
Method	soton lcms pos 120 to 1500.m	Operator	MSWEB@SOTON.AC.UK
Sample Name	JH 7191 + DCP diluted	Instrument / Ser#	maXis 17
Comment	Analyst: JMH		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
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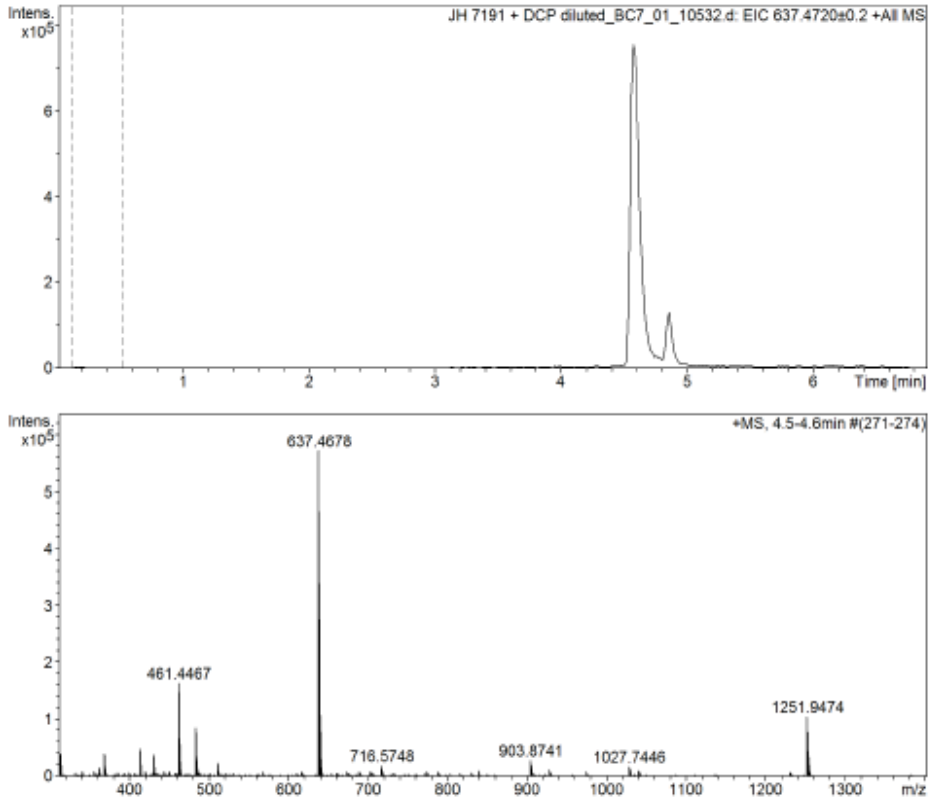
Scan End	1500 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

+MS, 4.5-4.6min #(271-274)



Chemistry - maXis HPLC-ESI Accurate Mass Report

Meas. m/z	Formula	m/z	err [ppm]	err [mDa]	# Sigma	mSigma	rdb	e⁻ Conf	N-Rule
637.4678	C 37 H 58 N 8 Na	637.4677	-0.2	-0.2	1	86.6	12.5	even	ok
	C 38 H 61 N 4 O 4	637.4687	1.4	0.9	2	86.7	10.5	even	ok
	C 37 H 65 O 8	637.4674	-0.7	-0.4	3	98.7	5.5	even	ok
	C 34 H 67 N 2 Na O 5 P	637.4680	0.2	0.2	4	113.3	2.5	even	ok
	C 32 H 62 N 8 O 3 P	637.4677	-0.2	-0.1	5	114.2	6.5	even	ok
	C 22 H 54 N 20 Na O	637.4682	0.5	0.3	6	172.8	5.5	even	ok
	C 21 H 58 N 16 Na O 5	637.4668	-1.6	-1.0	7	185.4	0.5	even	ok
	C 19 H 53 N 22 O 3	637.4666	-2.0	-1.3	8	186.6	4.5	even	ok

Samples were analysed using a MaXis (Bruker Daltonics, Bremen, Germany) mass spectrometer equipped with a Time of Flight (TOF) analyser. Samples were introduced to the mass spectrometer via a Dionex Ultimate 3000 autosampler and uHPLC pump. Gradient 20% acetonitrile (0.1% formic acid) to 100% acetonitrile (0.1% formic acid) in five minutes. Column, Acquity UPLC BEH C18 (Waters) 1.7 micron 50 x 2.1mm. High resolution mass spectra were recorded using positive/negative ion electrospray ionisation.

Figure S9 HRMS of compound **5** obtained from a reaction mixture of compound **3** (10 mg), DCP (0.1 mL) in Pyridine (1 mL).

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Chemistry - maXis ESI Accurate Mass Report

Analysis Info

Analysis Name	D:\Data\Chemistry\2014\Feb14\JH 7191 + DCP diluted_BC7_01_10532.d	Acquisition Date	07/02/2014 17:30:16
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Sample Name	JH 7191 + DCP diluted	Instrument / Ser#	maXis 17
Comment	Analyst: JMH		

Acquisition Parameter

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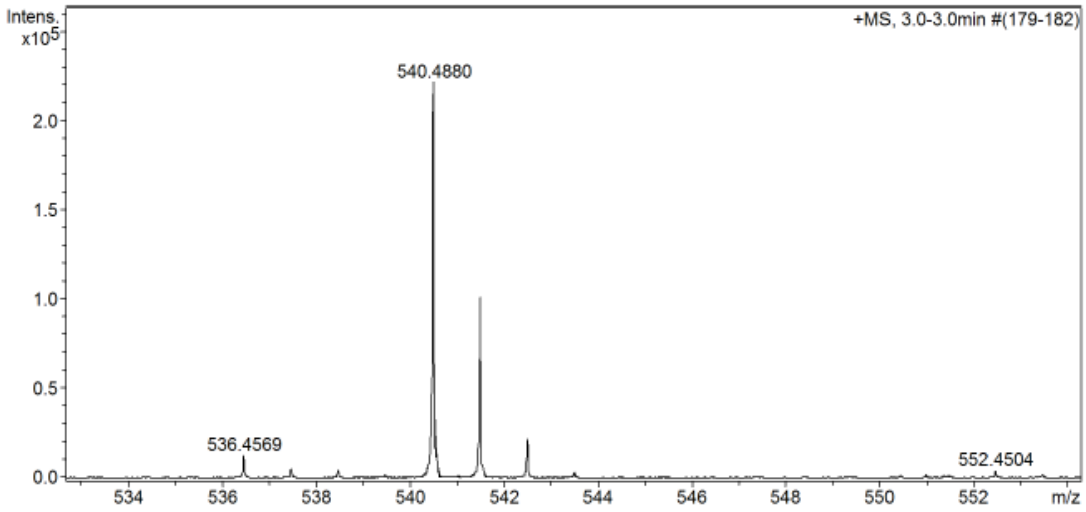
Scan End	1500 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

+MS, 3.0-3.0min #(179-182)



Meas. m/z	Formula	m/z	err [ppm]	err [mDa]	# Sigma	mSigma	rdb	e⁻ Conf	N-Rule
540.4880	C 35 H 62 N 3 O	540.4887	1.4	0.8	1	32.1	6.5	even	ok

Chemistry - maXis ESI Accurate Mass Report

Samples were analysed using a MaXis (Bruker Daltonics, Bremen, Germany) mass spectrometer equipped with a Time of Flight (TOF) analyser.High resolution mass spectra were recorded using positive/negative ion electrospray ionisation.

Figure S10 HRMS of compound **6** obtained from a reaction mixture of compound **3** (10 mg), DCP (0.1 mL) in Pyridine (1 mL).

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Chemistry - maXis ESI Accurate Mass Report

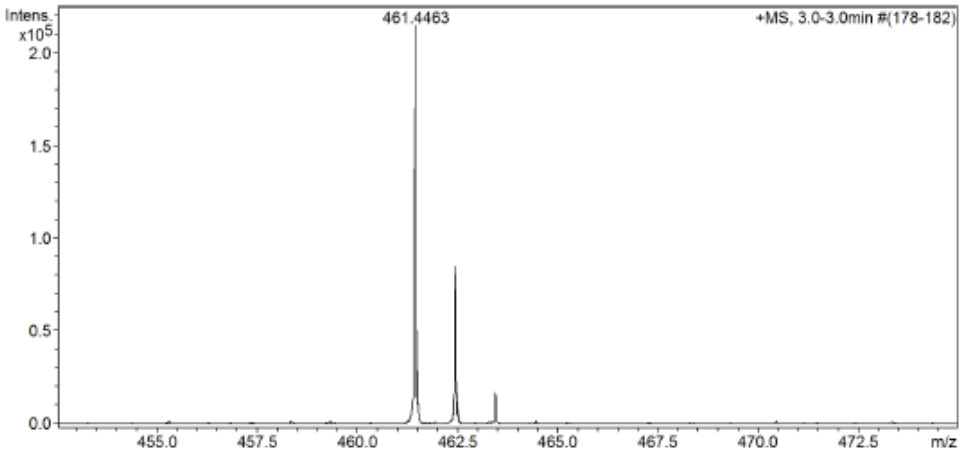
Analysis Info

Analysis Name	D:\Data\Chemistry\2014\Feb14\JH 7191 + DCP diluted_BC7_01_10532.d	Acquisition Date	07/02/2014 17:30:16
Method	soton lcms pos 120 to 1500.m	Operator	MSWEB@SOTON.AC.UK
Sample Name	JH 7191 + DCP diluted	Instrument / Ser#	maXis 17
Comment	Analyst: JMH		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	120 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

+MS, 3.0-3.0min #(178-182)



Meas. m/z	Formula	m/z	err [ppm]	err [mDa]	# Sigma	mSigma	rdb	e⁻ Conf	N-Rule
461.4463	C 30 H 57 N 2 O	461.4465	0.5	0.2	1	30.5	3.5	even	ok
	C 28 H 58 N 2 Na O	461.4441	-4.7	-2.2	2	41.9	0.5	even	ok

Chemistry - maXis ESI Accurate Mass Report

Samples were analysed using a MaXis (Bruker Daltonics, Bremen, Germany) mass spectrometer equipped with a Time of Flight (TOF) analyser.High resolution mass spectra were recorded using positive/negative ion electrospray ionisation.

Figure S11 HRMS of compound **7** obtained from a reaction mixture of compound **3** (10 mg), DCP (0.1 mL) in Pyridine (1 mL).

University of Southampton

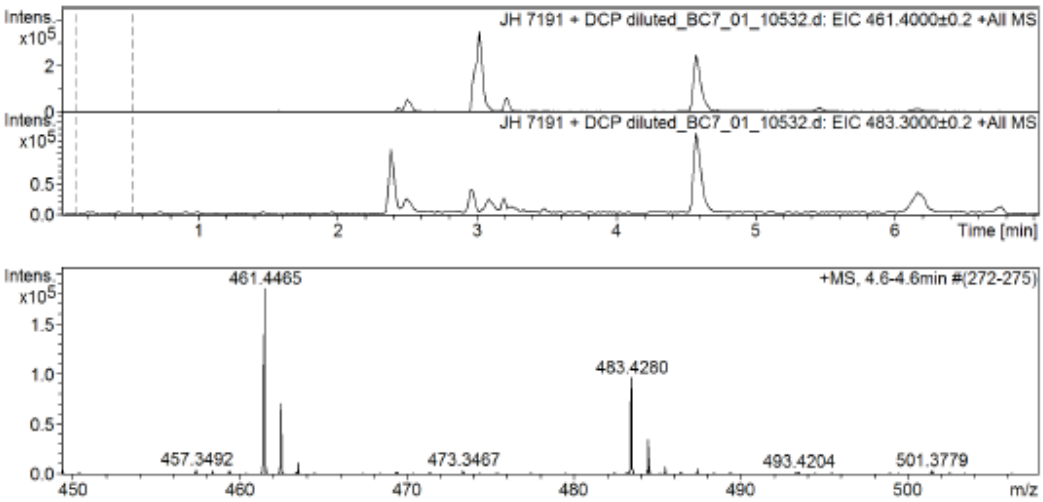
Chemistry - maXis ESI Accurate Mass Report

Analysis Info			
Analysis Name	D:\Data\Chemistry\2014\Feb14\JH 7191 + DCP diluted_BC7_01_10532.d	Acquisition Date	07/02/2014 17:30:16
Method	soton lcms pos 120 to 1500.m	Operator	MSWEB@SOTON.AC.UK
Sample Name	JH 7191 + DCP diluted	Instrument / Ser#	maXis 17
Comment	Analyst: JMH		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	120 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

+MS, 4.6-4.6min #(272-275)



Meas. m/z	Formula	m/z	err [ppm]	err [mDa]	# Sigma	mSigma	rdb	e⁻ Conf	N-Rule
461.4465	C 30 H 57 N 2 O	461.4465	0.1	0.0	1	23.7	3.5	even	ok
	C 28 H 58 N 2 Na O	461.4441	-5.1	-2.4	2	35.0	0.5	even	ok
483.4280	C 32 H 55 N 2 O	483.4309	6.0	2.9	1	7.0	6.5	even	ok
	C 30 H 56 N 2 Na O	483.4285	1.0	0.5	2	16.4	3.5	even	ok
	C 27 H 55 N 4 O 3	483.4269	-2.4	-1.1	3	27.7	2.5	even	ok

Chemistry - maXis ESI Accurate Mass Report

Samples were analysed using a MaXis (Bruker Daltonics, Bremen, Germany) mass spectrometer equipped with a Time of Flight (TOF) analyser.High resolution mass spectra were recorded using positive/negative ion electrospray ionisation.

Figure S12 HRMS of compound **8** obtained from a reaction mixture of compound **3** (10 mg), DCP (0.1 mL) in Pyridine (1 mL).

University of Southampton

Chemistry - maXis HPLC-ESI Accurate Mass Report

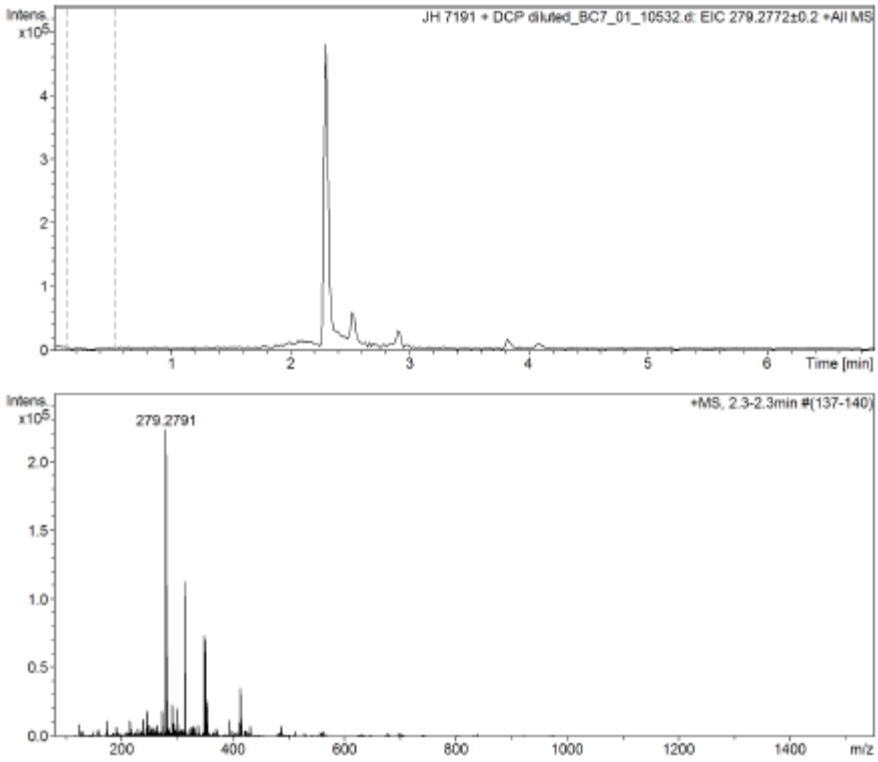
Analysis Info

Analysis Name	D:\Data\Chemistry\2014\Feb14\JH 7191 + DCP diluted_BC7_01_10532.d	Acquisition Date	07/02/2014 17:30:16
Method	soton icms pos 120 to 1500.m	Operator	MSWEB@SOTON.AC.UK
Sample Name	JH 7191 + DCP diluted	Instrument / Ser#	maXis 17
Comment	Analyst: JMH		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	120 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

+MS, 2.3-2.3min #(137-140)



Chemistry - maXis HPLC-ESI Accurate Mass Report

Meas. m/z	Formula	m/z	err [ppm]	err [mDa]	# Sigma	mSigma	rdb	e⁻ Conf	N-Rule
279.2791	C 18 H 35 N 2	279.2795	1.2	0.3	1	47.0	2.5	even	ok

Samples were analysed using a MaXis (Bruker Daltonics, Bremen, Germany) mass spectrometer equipped with a Time of Flight (TOF) analyser. Samples were introduced to the mass spectrometer via a Dionex Ultimate 3000 autosampler and uHPLC pump. Gradient 20% acetonitrile (0.1% formic acid) to 100% acetonitrile (0.1% formic acid) in five minutes. Column, Acquity UPLC BEH C18 (Waters) 1.7 micron 50 x 2.1mm. High resolution mass spectra were recorded using positive/negative ion electrospray ionisation.

Figure S13 HRMS of compound **9** obtained from a reaction mixture of compound **3** (10 mg), DCP (0.1 mL) in Pyridine (1 mL).

Table 2 High resolution mass spectrometry data obtained from the reaction of gelator **3** (10 mg/mL) and DCP (0.1 mg) in pyridine (1 mL).

Ion	Experimental value (m/z)	Calculated value (m/z)	Retention time (min.)
[5 + Na]$^+$	637.4678	637.4680	4.5-4.6
[6]$^+$	540.4880	540.4887	3.0
[7]$^+$	461.4463	461.4465	3.0
[8 + H]$^+$	461.4465	461.4465	4.6
[8 + Na]$^+$	483.4280	483.4285	4.6
[9a^a + H]$^+$	279.2791	279.2795	2.3

[a] – compound **9a** is to be taken as the neutral form of compound **9**.

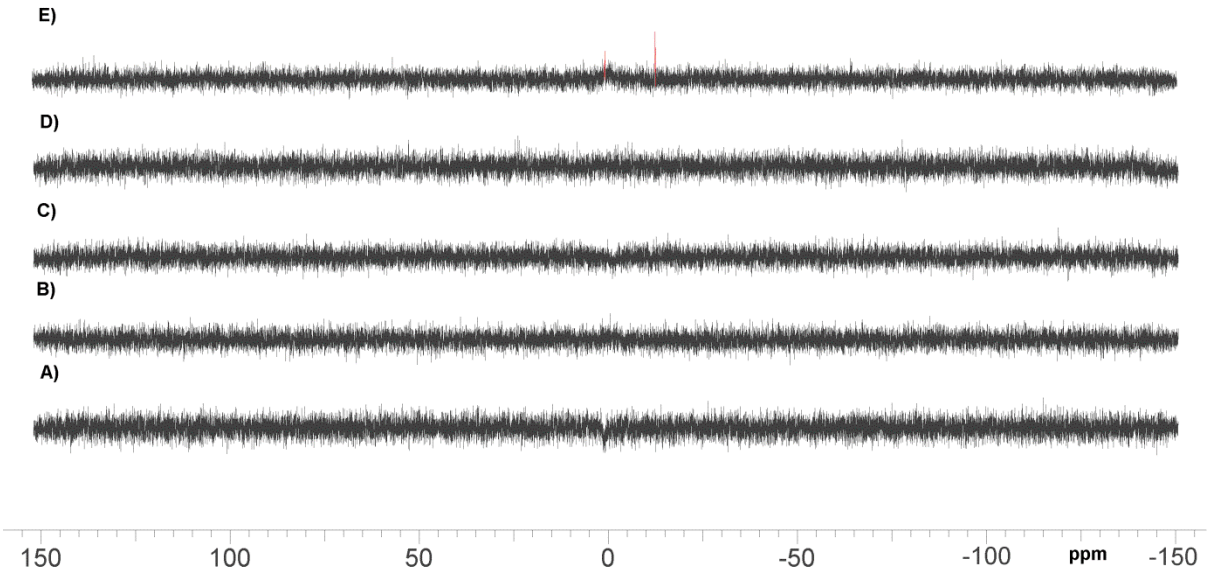
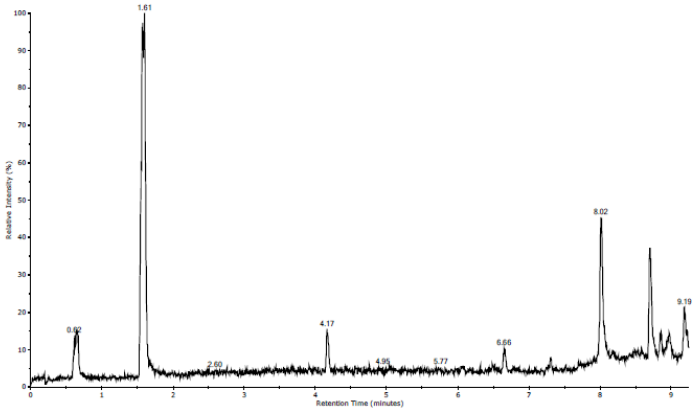


Figure S14a ^{31}P NMR of five coloured fractions isolated by preparative TLC from the reaction of compound **3** (20 mg), pyridine (1 mL) and DCP (0.1 mL) in a mixture of $CDCl_3$:DMSO-d_6 9:1. The phosphorus signals are highlighted in red.

TIC, NL 8.518E07, MS2 (150:1500) ES+



	RT Mins	Height	Height %	Area	Area %
1	1.58	7991246	10.14	4842489	4.56
2	1.61	78783206	100.00	106279002	100.00
3	4.17	9962302	12.65	15884584	14.95
4	6.66	4592669	5.83	5113631	4.81
5	8.02	31019375	39.37	34165145	32.15
6	8.70	22711975	28.83	63579695	59.82
7	9.19	8443399	10.72	22656482	21.32
8	9.22	4167935	5.29	4246435	4.00

Peak 2, RT 1.605, Scan 602, NL 4.017E07, MS2 (150:1500) ES+

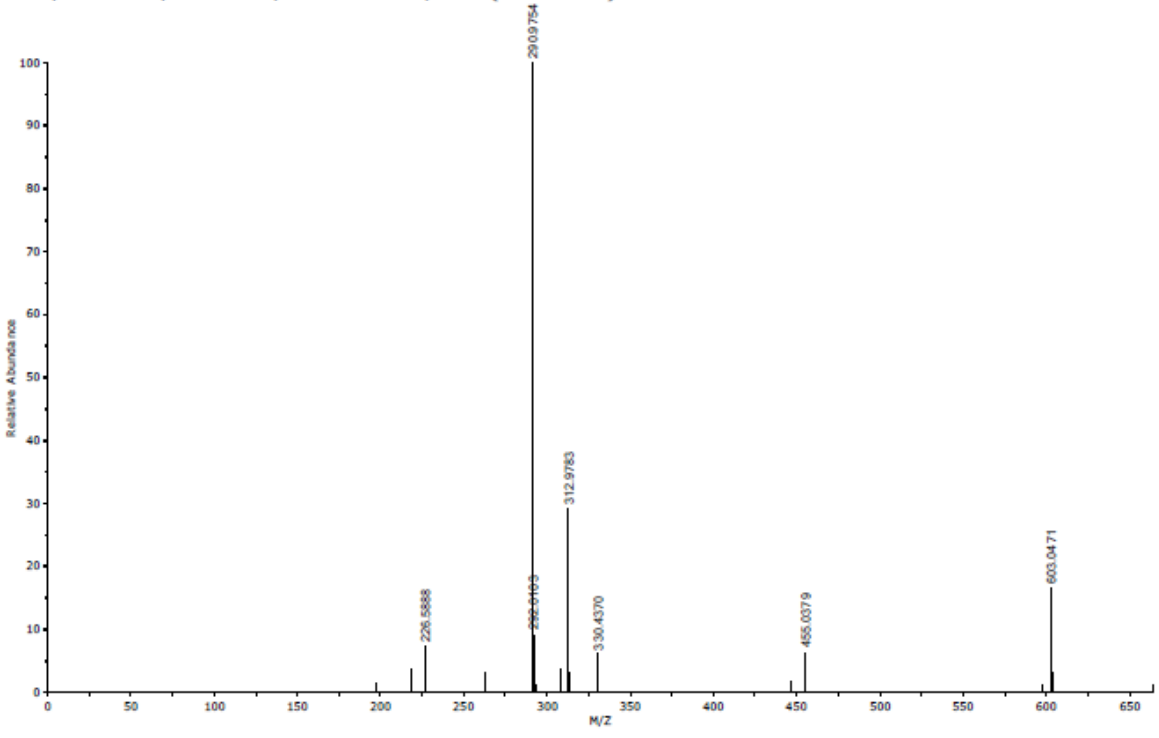


Figure S14b LRMS of fraction diethylphosphate isolated by preparative TLC (fraction E) from the reaction of compound **3** (20 mg), pyridine (1 mL) and DCP (0.1 mL).

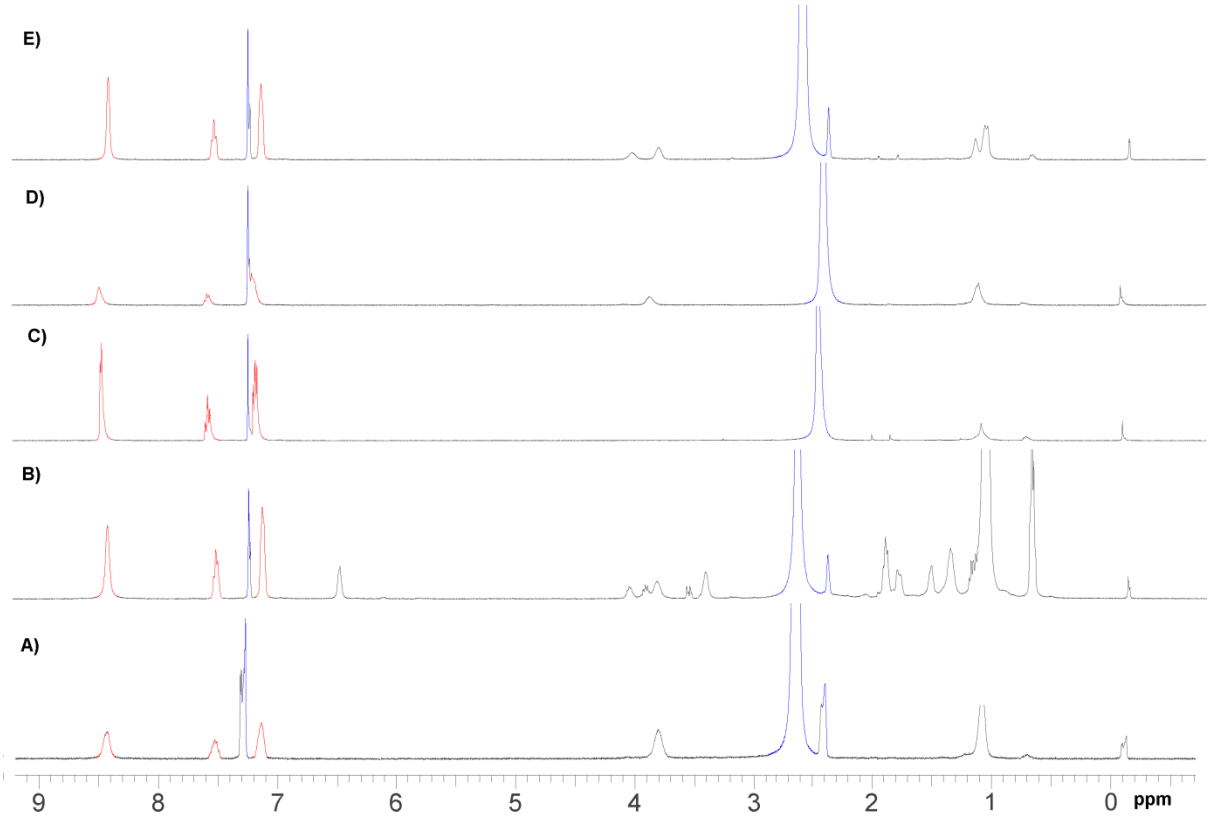


Figure S14c ^{1}H NMR of five coloured fractions isolated by preparative TLC from the reaction of compound **3** (20 mg), pyridine (1 mL) and DCP (0.1 mL) in a mixture of $CDCl_3$:DMSO-d_6 9:1. The pyridyl signals are highlighted in red and the solvent signals are highlighted in blue.

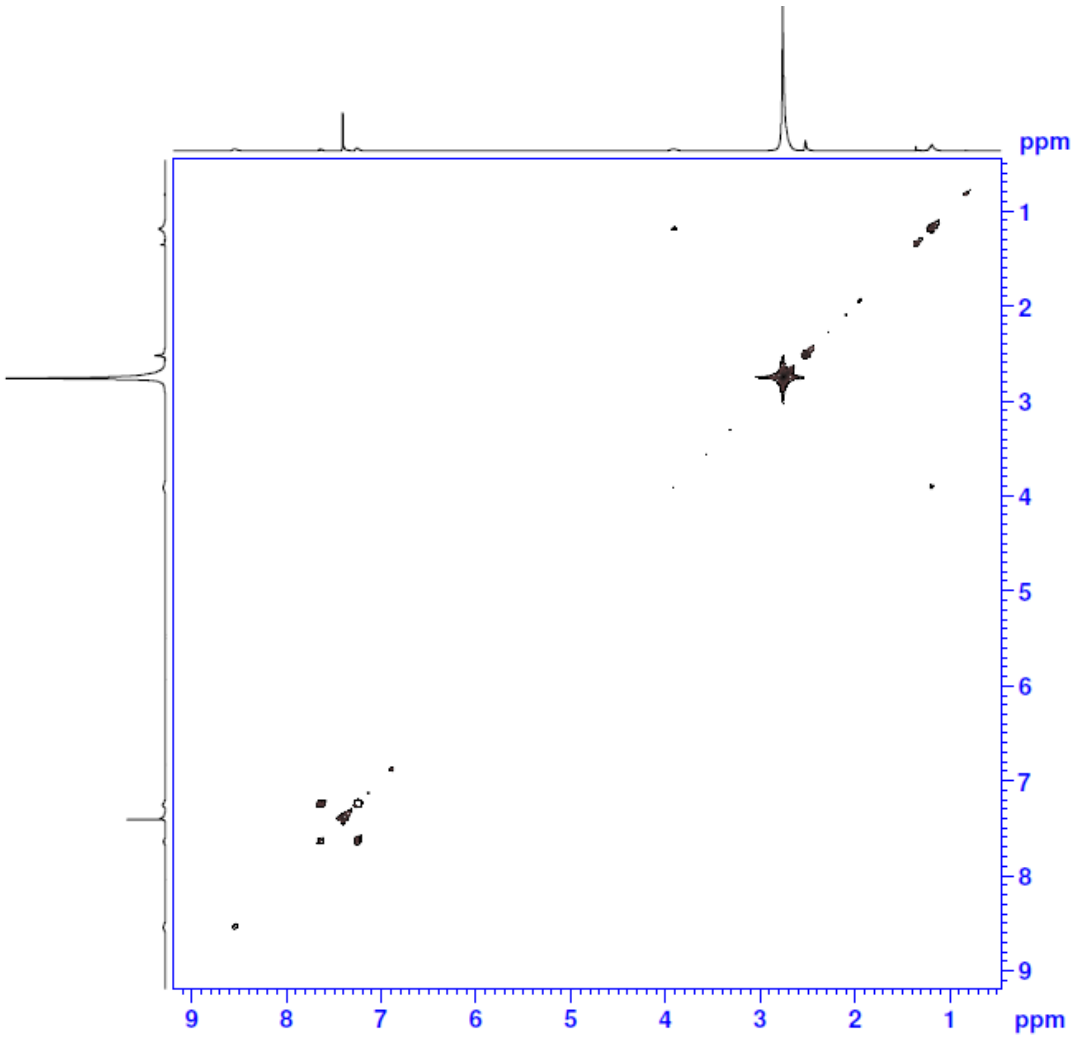


Figure S15a COSY of fraction A as described in Figure 14a.

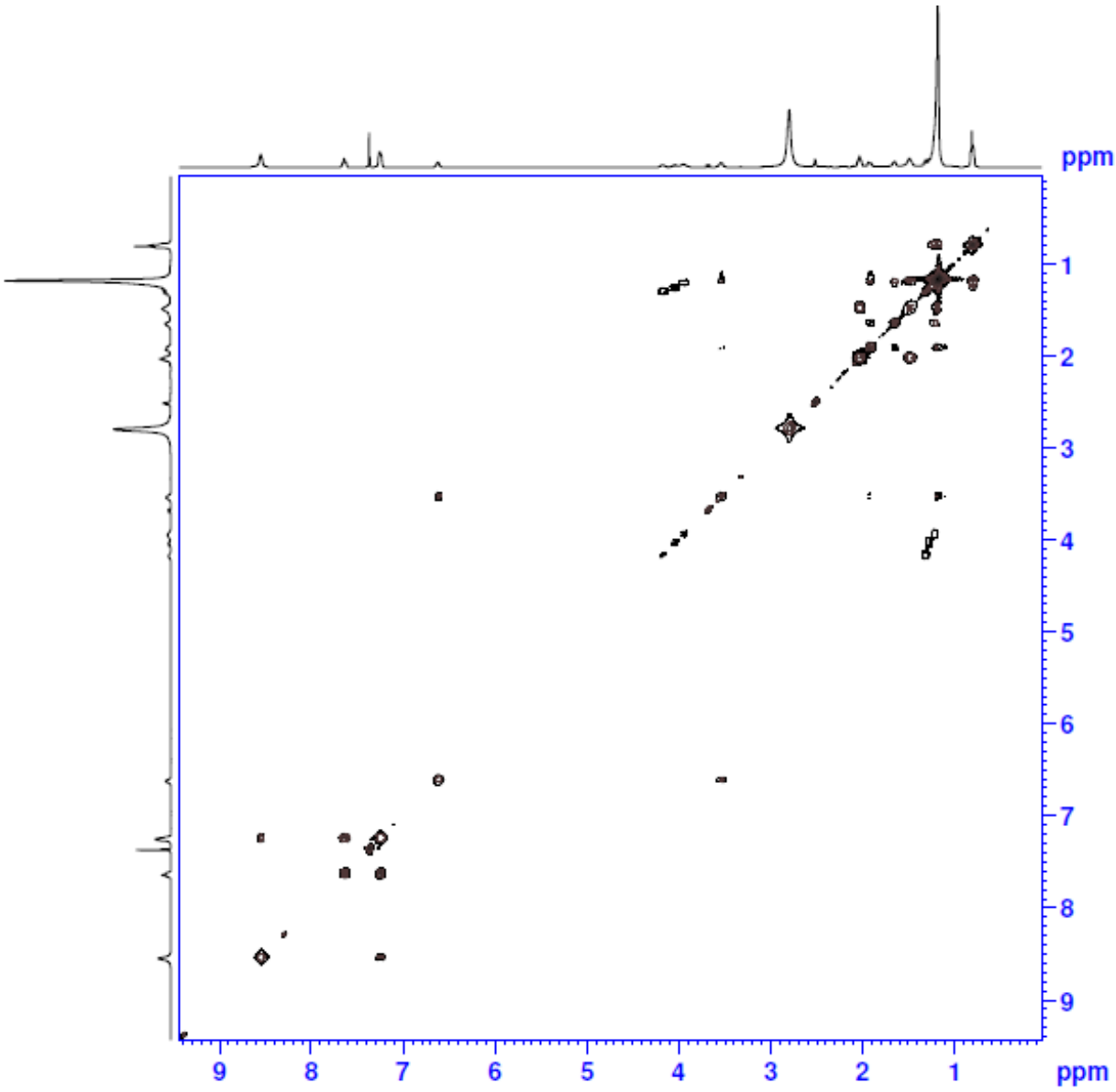


Figure S15b COSY of fraction B as described in Figure 14a.

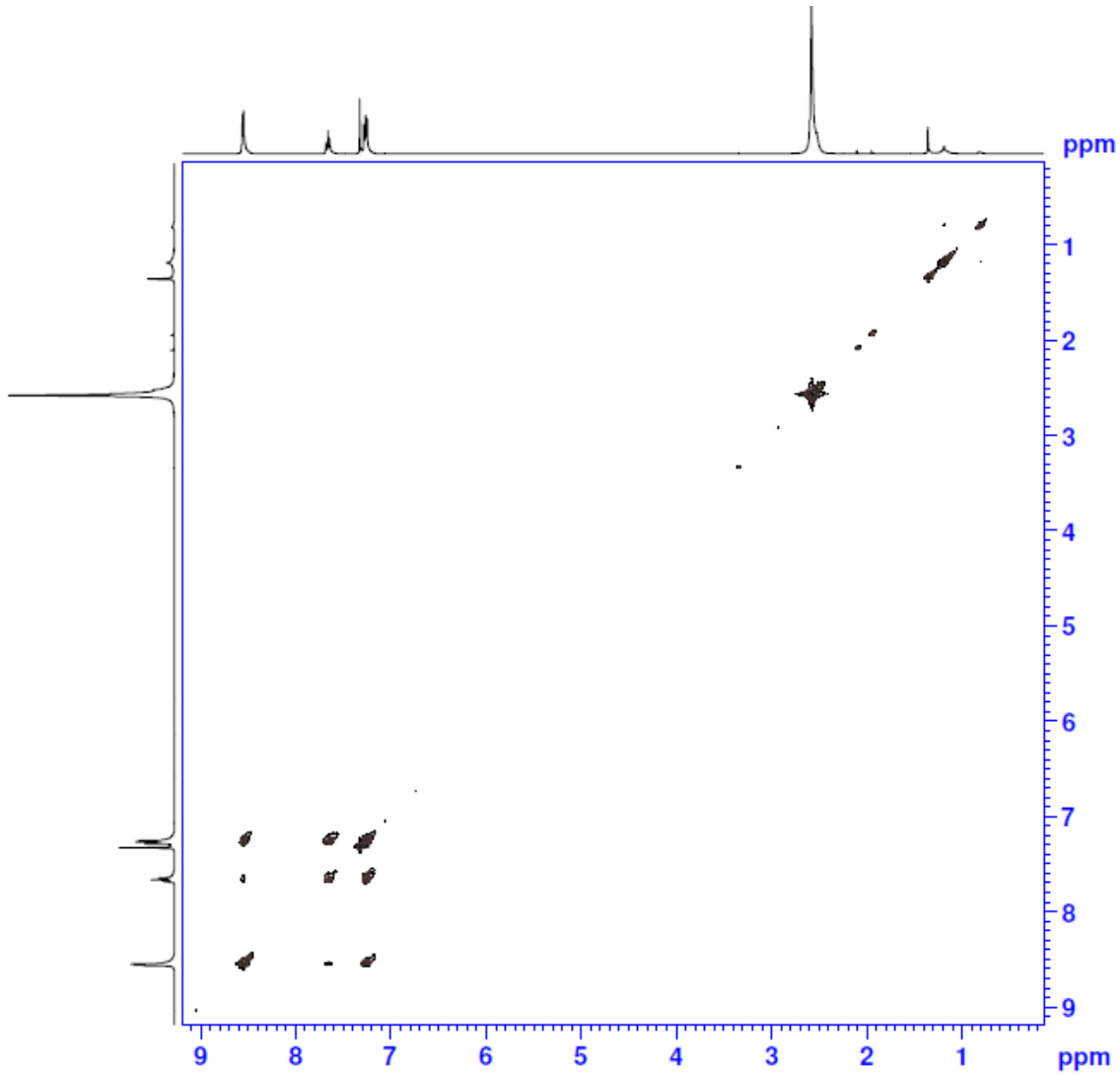


Figure S15c COSY of fraction C as described in Figure 14a.

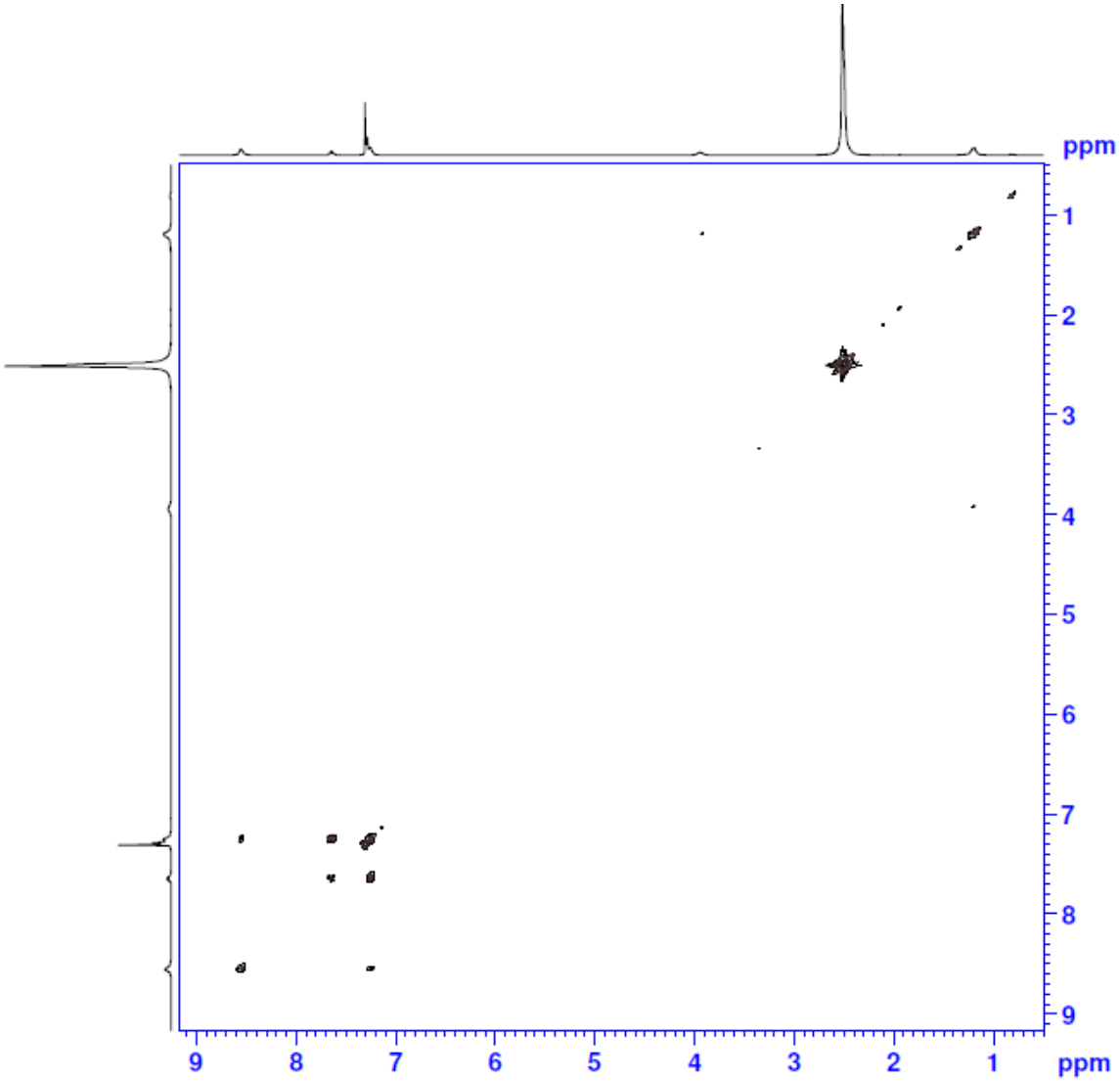


Figure S15d COSY of fraction D as described in Figure 14a.

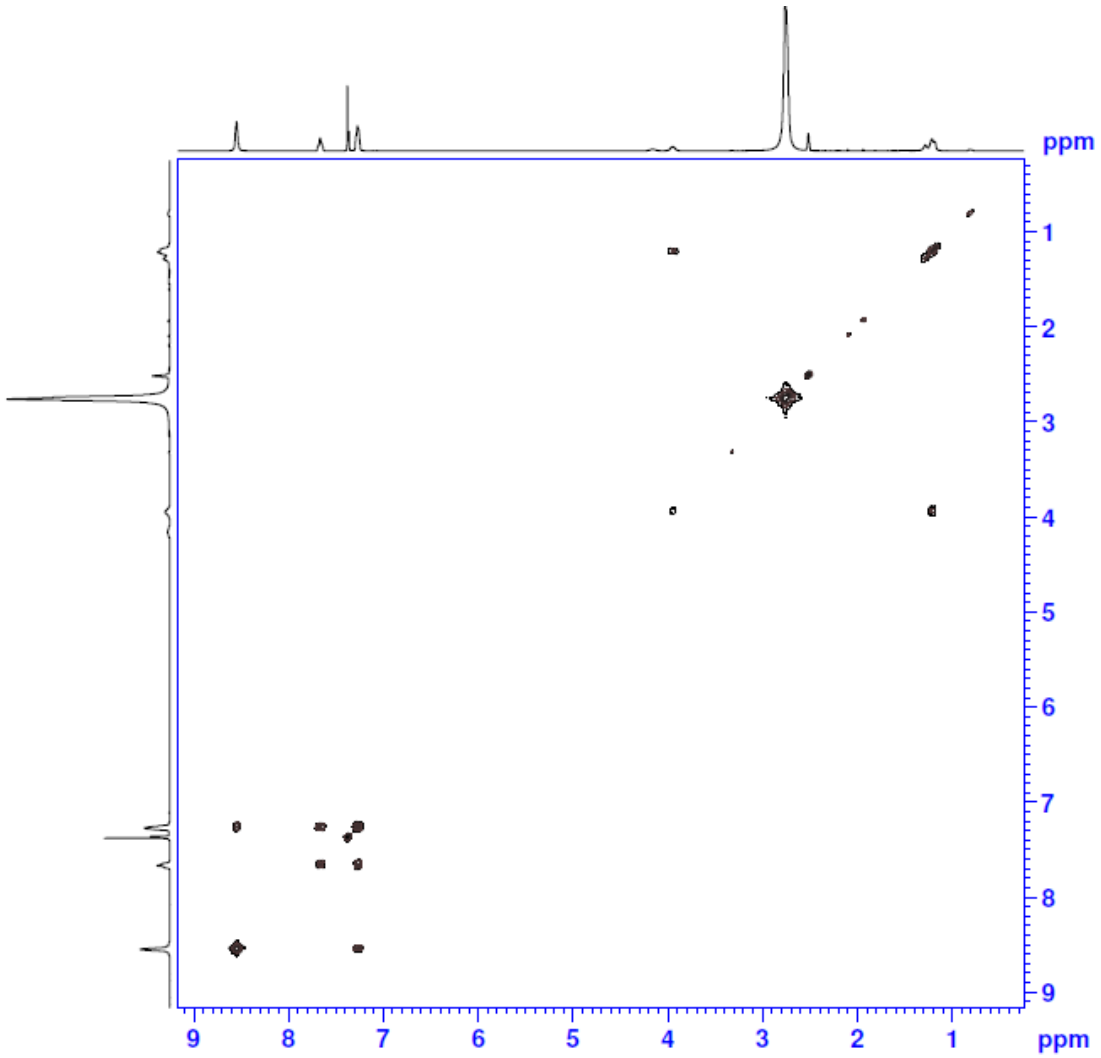


Figure S15e COSY of fraction E as described in Figure 14a.

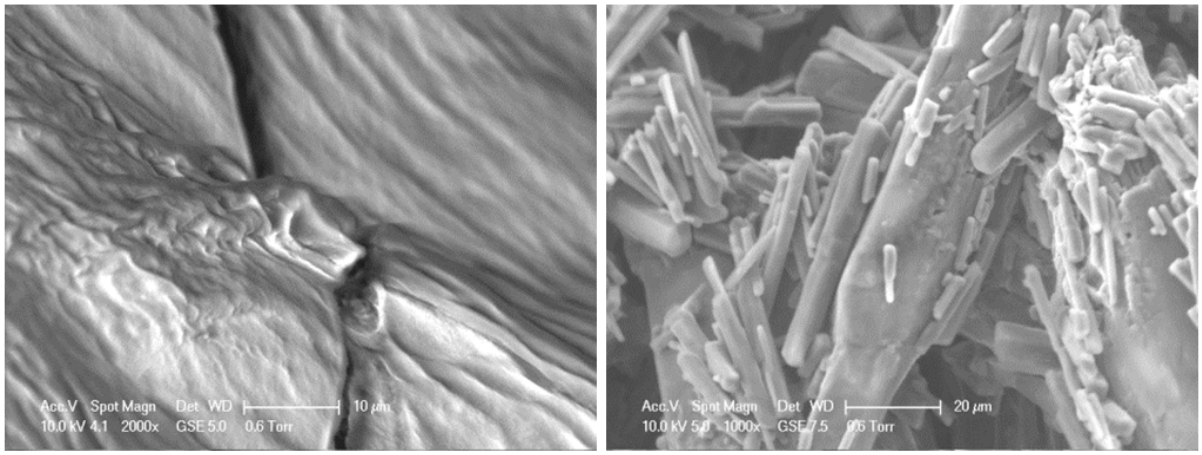


Figure S16 Enlargement of Figure 1 giving experimental details of individual experiments.

References

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2. N. Zweep, A. Hopkinson, A. Meetsma, W. R. Browne, B. L. Feringa and J. H. van Esch, *Langmuir*, 2009, **25**, 8802-8809.
3. M. Kimura, T. Kitamura, T. Muto, K. Hanabusa, H. Shirai and N. Kobayashi, *Chem. Lett.*, 2000, 1088-1089.