

# Coordination chemistry of *N*-picolyl-1,8-naphthalimides: colourful low molecular weight metallo-gelators and unique chelation behaviours

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## Experimental

### Materials and Methods

All reagents were used as received from commercial sources and used without further purification. NMR spectra were recorded using a Bruker Spectrospin DPX-400 instrument operating at 400 MHz for  $^1\text{H}$  and 100 MHz for  $^{13}\text{C}$ , or a Bruker AV-600 instrument operating at 600.1 MHz for  $^1\text{H}$  NMR and 150.9 MHz for  $^{13}\text{C}$  NMR. Chemical shifts are reported in ppm with the residual solvent as the internal reference. All NMR spectra were carried out at 293 K. Mass spectra were acquired using a Micromass time of flight mass spectrometer (tof), interfaced to a Waters 2690 HPLC. The instrument was operated in positive or negative mode as required. Leucine Enkephalin was used as an internal lock mass. Masses were recorded over the range 100-1000 m/z. Melting points were determined using an Electrothermal IA9000 digital melting point apparatus and are uncorrected. Infrared spectra were recorded on a PerkinElmer Spectrum One FTIR spectrometer in the range 4000 - 650  $\text{cm}^{-1}$ . Thermogravimetric analysis 4 was performed on Perkin Elmer Pyrus 1 TGA equipped with an ultra-micro balance with a sensitivity of 0.1 microgram. The temperature range is from 25-500  $^{\circ}\text{C}$  with a scan rate 5  $^{\circ}\text{C min}^{-1}$ . Phase purity of all crystalline materials was confirmed with X-ray powder diffraction patterns recorded with a Bruker D2 Phaser instrument using Cu-K $\alpha$  ( $\lambda$  = 1.5405 Å) radiation. Samples were finely ground and applied to a quartz sample holder. Raw data were compared with the simulated patterns from the single crystal data collections carried out at 100 K. Rheological measurements were carried out with an Anton Paar MCR 301 rheometer using a plate-plate geometry. All measurements were carried out in duplicate to ensure reproducibility.

### X-ray Crystallography

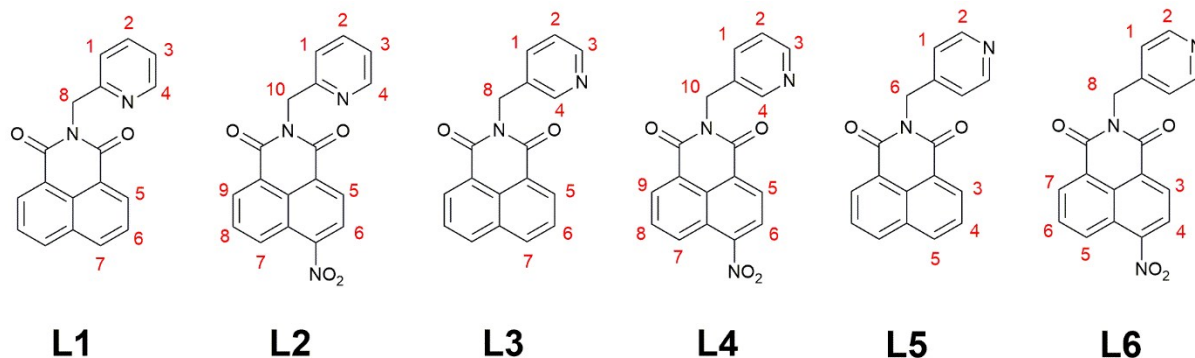
Structural and refinement parameters are presented in Tables S1 – S3. All diffraction data were collected using a Bruker APEX-II Duo dual-source instrument using graphite-monochromated Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) or microfocus Cu K $\alpha$  (1.5405 Å) radiation as specified. Datasets were collected using  $\omega$  and  $\phi$  scans with the samples immersed in oil and maintained at a constant temperature of 100 K using a Cobra cryostream. The data were reduced and processed using the Bruker APEX-3 suite of programs.<sup>S1</sup> Multi-scan absorption corrections were applied using SADABS.<sup>S2</sup> The diffraction data were solved using SHELXT and refined by full-matrix least squares procedures using SHELXL-2015 within the OLEX-2 GUI.<sup>S3-S5</sup> The functions minimized were  $\Sigma w(F_o^2 - F_c^2)$ , with  $w = [\sigma^2(F_o^2) + aP^2 + bP]^{-1}$ , where  $P = [\max(F_o^2) + 2F_c^2]/3$ . All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon-bound hydrogen atoms were placed in calculated positions and refined with a riding model, with isotropic displacement parameters equal to either 1.2 or 1.5 times the isotropic equivalent of their carrier atoms. Where appropriate, the positions of hydrogen atoms involved in hydrogen bonding interactions were refined to provide the best fit for the residual Fourier peaks and assigned a  $U_{\text{iso}}$  value equal to 1.5 times that of the nearest associated atom, with the appreciation that the exact positions of these atoms cannot be meaningfully inferred from X-ray diffraction data. Particular refinement strategies for each structure, including the specific use of restraints, are provided in the combined crystallographic information files. CCDC 1511748-1511758.

### Photophysical Measurements

Unless otherwise stated, all measurements were performed at 298K in acetonitrile (spectroscopic grade, Aldrich) solutions. UV-Vis absorption spectra were measured in 1 cm

quartz cuvettes (Hellma) on a Varian Cary 50 spectrophotometer. Baseline correction was applied for all spectra.

## Synthesis and Characterisation



**Figure S1** Structures and  $^1\text{H}$  NMR labelling scheme for ligands **L1** – **L6**

### N-(2-picolyl)-1,8-naphthalimide **L1**

To a suspension of 1,8-naphthalic anhydride (300 mg, 1.5 mmol,) and AcOH (5 mL), 2-picolylamine (0.31 mL, 3 mmol, 2 eq) was added and the mixture was heated under reflux for six hours. After cooling to room temperature the reaction mixture was poured into  $\text{H}_2\text{O}$  (100 mL), which produced a yellow precipitate. The mixture was then taken to pH 6 with aqueous KOH to aid precipitation. The resulting precipitate was filtered and washed with MeOH and  $\text{Et}_2\text{O}$ , and dried in air. Yield (309 mg, 71 %) m.p.  $171\text{ }^\circ\text{C} - 173\text{ }^\circ\text{C}$ . Found C, 74.83; H, 4.16; N, 9.66 %; Anal. calc. for  $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_2$ : C, 74.99; H, 4.20; N, 9.72 %;  $\delta_{\text{H}}$  (600 MHz,  $d_6$ -DMSO) 8.52 (m, 4H,  $\text{H}^5 + \text{H}^7$ ), 8.41 (d,  $^3J = 4.2\text{ Hz}$ , 1H,  $\text{H}^4$ ), 7.91 (t,  $^3J = 7.7\text{ Hz}$ , 2H,  $\text{H}^6$ ), 7.75 (t,  $^3J = 5.7\text{ Hz}$ , 1H,  $\text{H}^2$ ), 7.40 (d,  $^3J = 7.9\text{ Hz}$ , 1H,  $\text{H}^1$ ), 7.24 (dd,  $^3J_1 = 6.9$ ,  $^3J_2 = 5.0\text{ Hz}$ , 1H,  $\text{H}^3$ ), 5.40 (s, 2H,  $\text{H}^8$ );  $\delta_{\text{C}}$  (151 MHz,  $d_6$ -DMSO): 163.41, 155.92, 148.86, 136.67, 134.53, 131.38, 130.93, 127.53, 127.28, 122.08, 121.96, 120.92, 40.04.  $\nu_{\text{max}}$  (ATR)  $\text{cm}^{-1}$ : 3062w, 1704m, 1655s, 1585m, 1484m, 1438s, 1327s, 1233s, 1030m, 972s, 840m, 767s;  $m/z$  (ESI $^+$ ) 289.1 (M+H) $^+$ , calculated for  $\text{C}_{18}\text{H}_{13}\text{N}_2\text{O}_2$  289.1; UV-Vis ( $\text{CH}_3\text{CN}$ )  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon_{\text{max}}/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ): 232 (49000  $\pm$  3000); 333 (13000 $\pm$ 800)

### Synthesis and characterisation of N-(2-picolyl)-4-nitro-1,8-naphthalimide **L2**

To a suspension of 4-nitro-1,8-naphthalic anhydride (500 mg, 2.06 mmol, 1 eq) and AcOH (5 mL), 2-picolylamine (0.42 mL, 4.12 mmol, 2 eq) was added and the mixture was heated under reflux for six hours. After cooling to room temperature the green mixture was poured into  $\text{H}_2\text{O}$  (130 mL) which produced a beige suspension. The mixture was then taken to pH 6 with aqueous KOH to aid precipitation. The resulting orange precipitate was filtered and washed with MeOH and  $\text{Et}_2\text{O}$ , and dried under air, followed by recrystallisation from EtOAc. Yield 598 mg (87 %); m.p  $191\text{ }^\circ\text{C} - 193\text{ }^\circ\text{C}$ . Found C, 64.61; H, 3.12; N, 12.41; Anal. calc. for  $\text{C}_{18}\text{H}_{11}\text{N}_3\text{O}_4$  C, 64.87; H, 3.33; N, 12.61%;  $\delta_{\text{H}}$  (400 MHz,  $d_6$ -DMSO)  $\delta$  8.76 (d,  $^3J = 8.1\text{ Hz}$ , 1H,  $\text{H}^7$ ), 8.70-8.56 (m, 3H,  $\text{H}^5 + \text{H}^6 + \text{H}^9$ ), 8.41 (d,  $^3J = 4.5\text{ Hz}$ , 1H,  $\text{H}^4$ ), 8.14 (dd,  $^3J_1 = 8.7$ ,  $^3J_2 = 7.4\text{ Hz}$ , 1H,  $\text{H}^8$ ), 7.76 (td,  $^3J_1 = 7.7\text{ Hz}$ ,  $^3J_2 = 5.4\text{ Hz}$ , 1H,  $\text{H}^2$ ), 7.46 (d,  $^3J = 7.9\text{ Hz}$ , 1H,  $\text{H}^1$ ),

7.26 (dd,  $^3J_1 = 6.7$ ,  $^3J_2 = 4.6$  Hz, 1H, H<sup>3</sup>), 5.40 (s, 2H, H<sup>10</sup>);  $\delta_C$  (101 MHz, d<sub>6</sub>-DMSO):  $\delta$  162.99, 162.21, 155.47, 149.38, 148.93, 136.76, 132.01, 130.22, 129.97, 129.13, 128.53, 126.45, 124.37, 122.89, 122.25, 122.08, 121.07, 39.91.  $\nu_{\max}$  (ATR) cm<sup>-1</sup>: 3108w, 1708m, 1664s, 1627s, 1588m, 1523s, 1331s, 1236s, 984s, 941m, 829m, 758s;  $m/z$  (ESI<sup>+</sup>): 334.1 (M+H)<sup>+</sup>, calculated for C<sub>18</sub>H<sub>12</sub>N<sub>3</sub>O<sub>4</sub>  $m/z$  = 334.1; UV-Vis (CH<sub>3</sub>CN)  $\lambda_{\max}/nm$  ( $\epsilon_{\max}/L \cdot mol^{-1} \cdot cm^{-1}$ ) 232 (30200  $\pm$  1500); 348 (10000 $\pm$ 500)

### Synthesis and characterisation of N-(3-picolyl)-1,8-naphthalimide L3

To a suspension of 1,8-naphthalic anhydride (400mg, 2.02mmol, 1eq) and AcOH (5 mL) 3-picolylamine (0.41mL, 4.04mmol, 2 eq) was added and the mixture heated under reflux for six hours. After cooling to room temperature the reaction mixture was poured into H<sub>2</sub>O (100 mL) which produced a yellow precipitate. The mixture was then taken to pH 6 with aqueous KOH to aid precipitation. The resulting precipitate was filtered and washed with MeOH, Et<sub>2</sub>O and dried under air. Yield (497mg, 85%); m.p 166 °C – 168 °C. Found C, 74.73; H, 4.18; N, 9.61; Calculated for C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: C, 74.99; H, 4.20; N, 9.71%;  $\delta_H$  (400 MHz, d<sub>6</sub>-DMSO): 8.64 (s, 1H, H<sup>4</sup>), 8.59-8.47 (m, 4H, H<sup>5</sup>+H<sup>7</sup>), 8.46 (d,  $^3J=4.8$ , 1H, H<sup>3</sup>), 7.90 (t,  $^3J=7.7$  Hz, 2H, H<sup>6</sup>), 7.78 (d,  $^3J=7.7$  Hz, 1H, H<sup>1</sup>), 7.34 (dd,  $^3J_1 = 7.8$ ,  $^3J_2 = 4.8$  Hz, 1H, H<sup>2</sup>), 5.25 (s, 2H, H<sup>8</sup>);  $\delta_C$  (151 MHz, d<sub>6</sub>-DMSO): 164.05, 149.71, 148.79, 135.95, 135.10, 133.51, 131.82, 131.50, 127.98, 127.75, 124.02, 122.40, 39.83.  $\nu_{\max}$  (ATR) cm<sup>-1</sup>: 3075w, 2969 w, 2161w, 1980w, 1691m, 1657s, 1585s, 1529s, 1426m, 1332s, 1317s, 1229 s, 1092m, 1029m, 946 m, 781s, 712s.  $m/z$  (ESI<sup>+</sup>): 289.1 (M+H)<sup>+</sup> calculated for C<sub>18</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub> 289.1; UV-Vis (CH<sub>3</sub>CN)  $\lambda_{\max}/nm$  ( $\epsilon_{\max}/L \cdot mol^{-1} \cdot cm^{-1}$ ): 232 (59000  $\pm$  3000); 333(18000 $\pm$ 1000)

### Synthesis and characterisation of N-(3-picolyl)-4-nitro-1,8-naphthalimide L4

To a suspension of 4-nitro-1,8-naphthalic anhydride (600 mg, 2.5 mmol, 1 eq) and AcOH (6 mL), 3-picolylamine (0.5 mL, 5 mmol, 2 eq) was added and the mixture heated under reflux for six hours. After cooling to room temperature the brown/red mixture was poured into H<sub>2</sub>O (100 mL) which produced yellow/beige suspension. The mixture was then taken to pH 6 with aqueous KOH to aid precipitation. The excess H<sub>2</sub>O was decanted, MeOH added and the reaction mixture triturated to aid the formation of a pale yellow product. The resulting precipitate was filtered and washed with MeOH and Et<sub>2</sub>O and dried in air. Yield 593 mg (71 %); m.p 170 °C – 171 °C. Found C, 64.43; H, 3.20; N, 12.24; Anal. Calc. for C<sub>18</sub>H<sub>11</sub>N<sub>3</sub>O<sub>4</sub> C, 64.87; H, 3.33; N, 12.61%;  $\delta_H$  (400 MHz, d<sub>6</sub>- DMSO) 8.66 (s, 1H, H<sup>4</sup>), 8.54 (m, 2H, H<sup>6</sup> + H<sup>7</sup>), 8.49 (m, 2H, H<sup>5</sup> + H<sup>8</sup>), 8.46 (d,  $^3J=4.4$  Hz, 1H, H<sup>3</sup>), 7.86 (t,  $^3J=7.8$  Hz, 2H, H<sup>8</sup>), 7.74 (d,  $^3J=7.9$  Hz, 1H, H<sup>1</sup>), 7.30 (dd,  $^3J_1=7.8$   $^3J_2=4.8$  Hz, 1H, H<sup>2</sup>), 5.25 (s, 2H, H<sup>10</sup>);  $\delta_C$  (101 MHz, d<sub>6</sub>-DMSO): 163.64, 162.86, 149.78, 148.87, 136.05, 133.07, 132.38, 130.57, 130.32, 129.44, 129.04, 127.08, 124.67, 124.02, 123.22, 111.27, 110.67, 39.58;  $\nu_{\max}$  (ATR) cm<sup>-1</sup>: 3076 w, 2161w, 1703s, 1662s, 1619m, 1529s, 1427m, 1320s, 1319s, 1230s, 1098m, 1030m, 868m, 825s, 785s, 757s, 711s;  $m/z$  (ESI<sup>+</sup>): 334.1 (M+H)<sup>+</sup>, calculated for C<sub>18</sub>H<sub>12</sub>N<sub>3</sub>O<sub>4</sub> 334.1; UV-Vis (CH<sub>3</sub>CN)  $\lambda_{\max}/nm$  ( $\epsilon_{\max}/L \cdot mol^{-1} \cdot cm^{-1}$ ): 232 (30000  $\pm$  2000); 348 (11500 $\pm$ 800)

### Synthesis and characterisation of N-(4-picolyl)-1,8-naphthalimide L5

To a suspension of 1,8-naphthalic anhydride (300 mg, 1.5 mmol, 1 eq) and AcOH (4 mL) 4-picolylamine (0.30 mL, 3 mmol, 2 eq) was added and the reaction mixture was heated under reflux for six hours. After cooling to room temperature the reaction mixture was poured into H<sub>2</sub>O (100 mL) which produced a yellow precipitate. The mixture was then taken to pH 6 with aqueous KOH to aid precipitation. The resulting precipitate was filtered and washed with MeOH and Et<sub>2</sub>O and dried in air. Yield 396mg (90 %); m.p 201°C - 202°C;  $\delta_H$  (600 MHz, d<sub>6</sub>-

DMSO)  $\delta$  8.48 (m, 6H,  $H^4 + H^5 + H^2$ ), 7.90 (t,  $^3J = 7.6$  Hz, 2H,  $H^6$ ), 7.31 (d,  $^3J = 5.6$  Hz, 2H,  $H^1$ ), 5.27 (s, 2H,  $H^6$ );  $\delta_C$  (151 MHz,  $d_6$ -DMSO)  $\delta$  206.50, 163.53, 149.62, 146.23, 134.66, 131.38, 131.05, 127.28, 122.06, 121.87, 42.23.  $\nu_{\max}$ (ATR)  $\text{cm}^{-1}$ : 3050w, 2922w, 1710m, 1658s, 1597s, 1484m, 1447m, 1376s, 1327s, 1236s, 1165m, 1024w, 948m, 936m, 847m, 779s;  $m/z$  (ESI<sup>+</sup>) 289.1 (M+H)<sup>+</sup>, calculated for  $C_{18}H_{13}N_2O_2$  289.1

### Synthesis and characterisation of N-(4-picolyl)-4-nitro-1,8-naphthalimide L6

To a suspension of 4-nitro-1,8-naphthalic anhydride (600 mg, 2.4 mmol) and AcOH (20 mL) 4-picolylamine (0.30 mL, 3 mmol) was added and the reaction mixture heated under reflux for 8 hours. After cooling to room temperature the reaction mixture was poured into  $H_2O$  (100 mL). The solution was gradually taken to pH 6 with aqueous potassium hydroxide, and the orange solids were filtered, washed with  $H_2O$  and MeOH and Et<sub>2</sub>O and dried in air. Yield (708 mg, 88%). m.p. > 300 °C  $\delta_H$  (400 MHz,  $d_6$ -DMSO) 8.72 (d, 2H,  $^3J = 8.7$  Hz,  $H^6$ ), 8.62 – 8.66 (m, 2H,  $H^5 + H^8$ ), 8.56 (d, 1H,  $^3J = 7.8$  Hz,  $H^4$ ), 8.47 (d, 2H,  $^3J = 5.8$  Hz,  $H^1$ ), 8.11 (dd, 1H,  $^3J_1 = 8.7$  Hz,  $^3J_2 = 7.5$  Hz,  $H^7$ ), 7.37 (d, 2H,  $^3J = 5.8$  Hz,  $H^2$ ), 5.27 (s, 2H,  $H^3$ );  $\delta_C$  (100 MHz,  $d_6$ -DMSO) 42.58, 122.14, 122.70, 122.82, 124.22, 126.56, 128.67, 129.05, 129.93, 130.15, 132.00, 145.82, 149.40, 149.62, 162.39, 163.16;  $\nu_{\max}$ (ATR,  $\text{cm}^{-1}$ ) 3260w, 2747w, 2318w, 1701s, 1659s, 1621m, 1584s, 1518s, 1406m, 1380w, 1332s 1271m, 1237s, 1178s, 1132w, 1065w, 1004w, 978s, 938m, 873m, 833m, 788s, 757s;  $m/z$  (ESI<sup>+</sup>): 334. 1 (M+H)<sup>+</sup>, calculated for  $C_{18}H_{12}N_3O_4$   $m/z$  = 334.1

### Synthesis and characterisation of N-(3-picolyl)-4-(1-piperidiny)-1,8-naphthalimide L7

The title compound was synthesised through literature protocols<sup>S6-7</sup> All characterisation data were in accordance with the previously reported values.

### Synthesis and characterisation of [MnCl<sub>2</sub>(L1)<sub>2</sub>].2H<sub>2</sub>O 1

Ligand L1 (20 mg, 70  $\mu\text{mol}$ ) and MnCl<sub>2</sub>.4H<sub>2</sub>O (7mg, 35  $\mu\text{mol}$ , 0.5eq) were dissolved in MeCN (2.5mL) with the aid of sonication. The colourless solution deposited colourless crystals after being left to stand for 24 hours, which were isolated by filtration. Yield 6mg (24%). m.p >300 °C. Found C, 58.23; H, 3.64; N, 7.53; Anal. Calc. for  $C_{36}H_{28}Cl_2MnN_4O_6$ : C 58.55, H 3.82, N 7.59%;  $\nu_{\max}$  (ATR)  $\text{cm}^{-1}$  3526w, 3455w, 3077w, 2011w, 1696m, 1660s, 1585s, 1524s, 1442m, 1384m, 1337s, 1236s, 1182s, 1060 m, 1017m, 783s, 761s, 704m, 655m.

### Synthesis and characterisation of [CoCl<sub>2</sub>(L1)<sub>2</sub>] 2

Ligand L1, (40 mg, 140  $\mu\text{mol}$ ) and CoCl<sub>2</sub>.6H<sub>2</sub>O (10 mg, 42  $\mu\text{mol}$ , 0.3 eq) were dissolved in MeCN (2.5 mL). The green solution was left to stand for 24 hours, producing orange/brown crystals which were isolated by filtration. Yield (5 mg, 17%) m.p. >300 °C; Found C, 60.97; H, 3.23; N, 7.87; Anal. Calc. for  $C_{36}H_{22}Cl_2CoN_6O_8$ : C, 61.21; H, 3.42; N, 7.93%;  $\nu_{\max}$  (ATR)  $\text{cm}^{-1}$  3017w, 2973w, 2163w, 1981w, 1693s, 1615s, 1592s, 1587s, 1484m, 1440s, 1390s, 1337s, 1301s, 1236s, 1177m, 1149m, 1091m, 1016m, 958m, 844m, 759s.

### Synthesis and characterisation of [Co(L1)<sub>2</sub>(OH)<sub>2</sub>][CoCl<sub>3</sub>(L1)]<sub>2</sub>.4MeCN 3

Ligand L1 (10 mg, 35  $\mu\text{mol}$ ) and CoCl<sub>2</sub>.6H<sub>2</sub>O (7 mg, 29  $\mu\text{mol}$ ) were dissolved in MeCN (2.5 mL) with sonication. After 24 hours, turquoise crystals formed in combination with a small amount of compound 2. m.p. >300 °C. Yield 10 mg (65 % on L1 basis)  $\nu_{\max}$  (ATR)  $\text{cm}^{-1}$  3021w, 2972w, 2163 w, 1981w, 1692s, 1614s 1585s, 1451m, 1441s, 1388s, 1337s, 1301s, 1237s, 1177s, 1148m, 1092m, 1018m, 958m, 845s, 771s. Due to the intractable presence of complex

**2** in the mixture, we were unable to obtain a satisfactory elemental analysis result for this material.

#### **Synthesis and characterisation of [CoCl<sub>2</sub>(L2)<sub>2</sub>] **4****

Ligand **L2** (20 mg, 60  $\mu$ mol) and CoCl<sub>2</sub>·6H<sub>2</sub>O (10 mg, 42  $\mu$ mol, 0.7 eq) were dissolved in MeCN (2.5 mL) with sonication. The green solution deposited orange/brown crystals after being left to stand for 24 hours. Yield (14 mg, 60 %). m.p. >300 °C; Found C, 54.25; H, 2.77; N, 10.58; Anal. Calc. for C<sub>36</sub>H<sub>22</sub>Cl<sub>2</sub>CoN<sub>6</sub>O<sub>8</sub> C, 54.29; H, 2.78; N, 10.55%;  $\nu_{\text{max}}$  (ATR) cm<sup>-1</sup> 3075w, 2967w, 2162w, 1979w, 1703 s, 1655s, 1583s, 1522s, 1484m, 1431s, 1330s, 1233s, 1184m, 1030s, 1049s, 977s, 826s, 784s, 704s

#### **Synthesis and characterisation of [ZnCl<sub>2</sub>L1] **5****

Ligand **L1** (20 mg, 70  $\mu$ mol) and ZnCl<sub>2</sub> (9.5mg, 71  $\mu$ mol, 1eq) were dissolved in MeCN (2.5mL). The colourless solution deposited colourless crystals within 24 hours. Yield (6 mg, 20 %) m.p.: > 300 °C; Found C, 50.90; H, 2.80; N, 6.45; Anal. Calc. for C<sub>18</sub>H<sub>12</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Zn C, 50.92; H, 2.50; N, 6.60 %;  $\delta_{\text{H}}$  (400 MHz, d<sub>3</sub>-CD<sub>3</sub>CN):  $\delta_{\text{H}}$  8.59 (d, <sup>3</sup>J= 7.3 Hz, 2H, H<sup>5</sup>), 8.54 (d, <sup>3</sup>J = 5.3 Hz, 1H, H<sup>4</sup>), 8.41 (d, <sup>3</sup>J = 8.3Hz, 2H, H<sup>7</sup>), 7.89 – 7.82 (m, 2H, H<sup>6</sup>), 7.81 (s, 1H, H<sup>2</sup>), 7.46 (d, <sup>3</sup>J= 8.0 Hz, 1H, H<sup>3</sup>), 7.33 (s, 1H, H<sup>1</sup>), 5.54 (s, 2H, H<sup>8</sup>),  $\nu_{\text{max}}$  (ATR) cm<sup>-1</sup> 3077 w, 2967w, 2869w, 2161w, 1980w, 1703m, 1656s, 1624m, 1656s, 1624m, 1583m, 1522s, 1431m, 1331s, 1233s, 1049s, 1027s, 968m, 827m, 783s, 732m, 704s

#### **Synthesis and characterisation of *poly*-[MnCl<sub>2</sub>(L3)(MeOH)] **6****

Ligand **L3** (20 mg, 70  $\mu$ mol) and MnCl<sub>2</sub>·4H<sub>2</sub>O (7mg, 35  $\mu$ mol, 0.5 eq) were dissolved in MeCN:MeOH (9:1) (2.5mL) with gentle heating and sonication. The colourless solution deposited colourless crystals after standing at room temperature for several days. Microanalysis on an air-dried sample suggested the labile methanol ligand is replaced by an aqua ligand on standing in air for several weeks; X-ray powder diffraction analysis confirms the crystal structure is effectively unchanged. Yield 13mg, 51%). Melting point: >300 °C Found C, 59.75; H, 3.70; N, 7.51; Anal. Calc. for C<sub>36</sub>H<sub>24</sub>N<sub>4</sub>O<sub>4</sub>Cl<sub>2</sub>Mn·H<sub>2</sub>O C, 60.01; H, 3.64; N, 7.78%;  $\nu_{\text{max}}$  (ATR) cm<sup>-1</sup> 3076w, 2967w, 2162w, 1980w, 1702m, 1655s, 1584m, 1522m, 1432m, 1333s, 1321s, 1234s, 1179m, 1050s, 1026s, 967m, 784s, 778s, 701m.

#### **Synthesis and characterisation of [ZnCl<sub>2</sub>(L3)<sub>2</sub>]·0.66MeCN **7****

Ligand **L3** (20 mg, 70  $\mu$ mol) and ZnCl<sub>2</sub> (9.5mg, 71  $\mu$ mol, 1eq) were dissolved in MeCN:MeOH (9:1) (2.5mL) with the aid of sonication. The colourless solution deposited colourless crystals after standing for 24 hours. Yield 13 mg (24%); m.p. >300 °C; Found C, 60.14; H, 3.44; N, 9.01 %; Anal. Calc. for C<sub>36</sub>H<sub>24</sub>N<sub>4</sub>O<sub>4</sub>ZnCl<sub>2</sub>·0.66 MeCN C, 60.57; H, 3.54; N, 8.83;  $\delta_{\text{H}}$  (400 MHz, d<sub>3</sub>-CD<sub>3</sub>CN)  $\delta$  8.74 (s, 1H, H<sup>4</sup>), 8.60 (d, <sup>3</sup>J= 7.3 Hz, 2H, H<sup>5</sup>), 8.50 (m, 2H, H<sup>1</sup> + H<sup>3</sup>), 8.39 (d, <sup>3</sup>J = 8.4 Hz, 2H, H<sup>7</sup>), 7.88-7.81 (m, 2H, H<sup>6</sup>), 7.32 (s, 1H, H<sup>2</sup>), 5.35 (s, 2H, H<sup>8</sup>)  $\nu_{\text{max}}$  (ATR) cm<sup>-1</sup>: 3019w, 2974w, 2601w, 2161w, 2007w, 1980w, 1692s, 1636s, 1611 s, 1587s, 1570s, 1483m, 1442s, 1388s, 1346s, 1301s, 1236s, 1176m, 1091m, 1017m, 959m, 885m, 843s, 771s

#### **Synthesis and characterisation of L4-Mn gel **8****

Ligand **L4** (20 mg, 60  $\mu$ mol) was dissolved in MeCN (2.5 mL) at room temperature affording a yellow solution (sol I). MnCl<sub>2</sub>·4H<sub>2</sub>O (12 mg, 60  $\mu$ mol) was suspended in MeCN (2.5 mL) at

room temperature with the aid of sonication affording a yellow suspension (sol II). Sol II was added rapidly at RT to sol I and left to stand overnight formed a yellow homogenous gel.

#### **Synthesis and characterisation L4-Co gel 9 (1:1 stoichiometry)**

Ligand **L4** (20 mg, 60  $\mu\text{mol}$ ) was dissolved in MeCN (2.5 mL) at room temperature affording a yellow solution (sol I).  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (12 mg, 51  $\mu\text{mol}$ ) was dissolved in MeCN (2.5 mL) at room temperature with the aid of sonication affording a deep-blue solution (sol II). Sol II was added rapidly at RT to sol I and left to stand overnight formed a deep green homogenous gel.

#### **Synthesis and characterisation of L4-Co gel (2:1 stoichiometry) (9a)**

Ligand **L4** (20 mg,  $6 \times 10^{-5}$  mol) was dissolved in MeCN (2.5 mL) at room temperature affording a yellow solution (sol I).  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (6 mg,  $2.5 \times 10^{-5}$  mol) was dissolved in MeCN (2.5 mL) at room temperature with the aid of sonication affording a deep-blue solution (sol II). Sol II was added rapidly at RT to sol I and left to stand overnight formed a deep green homogenous gel.

#### **Synthesis and characterisation of L4-Ni gel 10**

Ligand **L4** (20 mg, 60  $\mu\text{mol}$ ) was dissolved in MeCN (2.5 mL) at room temperature affording a yellow solution (sol I).  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (8 mg, 34  $\mu\text{mol}$ ) was suspended in MeCN (2.5 mL) at room temperature with the aid of sonication, affording a colourless suspension (sol II). Sol II was added rapidly at RT to sol I and left to stand overnight formed a weak, colourless gel.

#### **Synthesis and characterisation of L7-Co gel 11**

Ligand **L7** (20 mg, 54  $\mu\text{mol}$ ) was dissolved in MeCN (2.5 mL) at room temperature affording a yellow solution (sol III).  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (12 mg, 51  $\mu\text{mol}$ ) was dissolved in MeCN (2.5 mL) at room temperature with sonication, affording a deep blue solution (sol IV). Sol IV was added rapidly at RT to sol III and left to stand overnight formed a green homogenous gel.

#### **Synthesis and characterisation of L7-Mn gel 12**

Ligand **L7** (20 mg, 54  $\mu\text{mol}$ ) was dissolved in MeCN (2.5 mL) at room temperature affording a yellow solution (sol III).  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (6 mg, 30  $\mu\text{mol}$ ) was suspended in MeCN (2.5 mL) at room temperature with sonication, affording a pale yellow suspension (sol IV). Sol IV was added rapidly at RT to sol III and left to stand overnight formed a yellow homogenous gel.

**Table S1** Crystal and refinement parameters for compounds **L1 – L4**

| Identification code                                          | <b>L1</b>                                                                    | <b>L2</b>                                                                    | <b>L3</b>                                                                    | <b>L4</b>                                                                    |
|--------------------------------------------------------------|------------------------------------------------------------------------------|------------------------------------------------------------------------------|------------------------------------------------------------------------------|------------------------------------------------------------------------------|
| Empirical formula                                            | C <sub>18</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>                | C <sub>18</sub> H <sub>11</sub> N <sub>3</sub> O <sub>4</sub>                | C <sub>18</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>                | C <sub>18</sub> H <sub>11</sub> N <sub>3</sub> O <sub>4</sub>                |
| Formula weight                                               | 288.3                                                                        | 333.3                                                                        | 288.3                                                                        | 333.3                                                                        |
| Temperature/K                                                | 100(2)                                                                       | 100(2)                                                                       | 100(2)                                                                       | 100(2)                                                                       |
| Crystal system                                               | monoclinic                                                                   | orthorhombic                                                                 | triclinic                                                                    | orthorhombic                                                                 |
| Space group                                                  | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                           | <i>Pbca</i>                                                                  | <i>P</i> -1                                                                  | <i>Pbca</i>                                                                  |
| <i>a</i> /Å                                                  | 9.1815(6)                                                                    | 14.4265(6)                                                                   | 8.2040(3)                                                                    | 6.9920(4)                                                                    |
| <i>b</i> /Å                                                  | 14.4232(8)                                                                   | 11.5416(5)                                                                   | 9.0699(3)                                                                    | 18.0217(14)                                                                  |
| <i>c</i> /Å                                                  | 10.1911(7)                                                                   | 17.5201(8)                                                                   | 9.5149(4)                                                                    | 22.5014(16)                                                                  |
| $\alpha$ /°                                                  | 90                                                                           | 90                                                                           | 80.777(2)                                                                    | 90                                                                           |
| $\beta$ /°                                                   | 93.965(2)                                                                    | 90                                                                           | 79.653(2)                                                                    | 90                                                                           |
| $\gamma$ /°                                                  | 90                                                                           | 90                                                                           | 71.835(2)                                                                    | 90                                                                           |
| Volume/Å <sup>3</sup>                                        | 1346.34(15)                                                                  | 2917.2(2)                                                                    | 657.64(4)                                                                    | 2835.4(3)                                                                    |
| <i>Z</i>                                                     | 4                                                                            | 8                                                                            | 2                                                                            | 8                                                                            |
| $\rho_{\text{calc}}$ /g/cm <sup>3</sup>                      | 1.422                                                                        | 1.518                                                                        | 1.456                                                                        | 1.562                                                                        |
| $\mu$ /mm <sup>-1</sup>                                      | 0.095                                                                        | 0.11                                                                         | 0.785                                                                        | 0.948                                                                        |
| <i>F</i> (000)                                               | 600                                                                          | 1376                                                                         | 300                                                                          | 1376                                                                         |
| Crystal size/mm <sup>3</sup>                                 | 0.19 × 0.16 × 0.07                                                           | 0.15 × 0.15 × 0.08                                                           | 0.1 × 0.08 × 0.06                                                            | 0.13 × 0.13 × 0.04                                                           |
| Radiation                                                    | MoK $\alpha$ ( $\lambda$ = 0.71073)                                          | MoK $\alpha$ ( $\lambda$ = 0.71073)                                          | CuK $\alpha$ ( $\lambda$ = 1.54178)                                          | CuK $\alpha$ ( $\lambda$ = 1.54178)                                          |
| 2 $\theta$ range for data collection/°                       | 4.446 to 55.11                                                               | 4.65 to 55.828                                                               | 9.508 to 136.704                                                             | 7.858 to 136.89                                                              |
| Index ranges                                                 | -10 ≤ <i>h</i> ≤ 11, -18 ≤ <i>k</i> ≤ 18, -13 ≤ <i>l</i> ≤ 11                | -18 ≤ <i>h</i> ≤ 18, -15 ≤ <i>k</i> ≤ 12, -23 ≤ <i>l</i> ≤ 21                | -9 ≤ <i>h</i> ≤ 9, -10 ≤ <i>k</i> ≤ 10, -11 ≤ <i>l</i> ≤ 11                  | -8 ≤ <i>h</i> ≤ 8, -21 ≤ <i>k</i> ≤ 21, -27 ≤ <i>l</i> ≤ 27                  |
| Reflections collected                                        | 10516                                                                        | 24473                                                                        | 7989                                                                         | 23779                                                                        |
| Independent reflections                                      | 3089 [ <i>R</i> <sub>int</sub> = 0.0254, <i>R</i> <sub>sigma</sub> = 0.0309] | 3485 [ <i>R</i> <sub>int</sub> = 0.0638, <i>R</i> <sub>sigma</sub> = 0.0506] | 2390 [ <i>R</i> <sub>int</sub> = 0.0357, <i>R</i> <sub>sigma</sub> = 0.0339] | 2607 [ <i>R</i> <sub>int</sub> = 0.0904, <i>R</i> <sub>sigma</sub> = 0.0744] |
| Data/restraints/parameters                                   | 3089/0/199                                                                   | 3485/25/262                                                                  | 2390/0/199                                                                   | 2607/9/226                                                                   |
| Goodness-of-fit on <i>F</i> <sup>2</sup>                     | 1.029                                                                        | 1.058                                                                        | 0.995                                                                        | 1.04                                                                         |
| Final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )] | <i>R</i> <sub>1</sub> = 0.0398, <i>wR</i> <sub>2</sub> = 0.0923              | <i>R</i> <sub>1</sub> = 0.0588, <i>wR</i> <sub>2</sub> = 0.1346              | <i>R</i> <sub>1</sub> = 0.0447, <i>wR</i> <sub>2</sub> = 0.1268              | <i>R</i> <sub>1</sub> = 0.0825, <i>wR</i> <sub>2</sub> = 0.2255              |
| Final <i>R</i> indexes [all data]                            | <i>R</i> <sub>1</sub> = 0.0637, <i>wR</i> <sub>2</sub> = 0.1061              | <i>R</i> <sub>1</sub> = 0.0980, <i>wR</i> <sub>2</sub> = 0.1506              | <i>R</i> <sub>1</sub> = 0.0525, <i>wR</i> <sub>2</sub> = 0.1350              | <i>R</i> <sub>1</sub> = 0.1173, <i>wR</i> <sub>2</sub> = 0.2698              |
| Largest diff. peak/hole / e Å <sup>-3</sup>                  | 0.32/-0.23                                                                   | 0.58/-0.31                                                                   | 0.22/-0.24                                                                   | 0.63/-0.39                                                                   |
| CCDC No.                                                     | 1511748                                                                      | 1511749                                                                      | 1511750                                                                      | 1511751                                                                      |

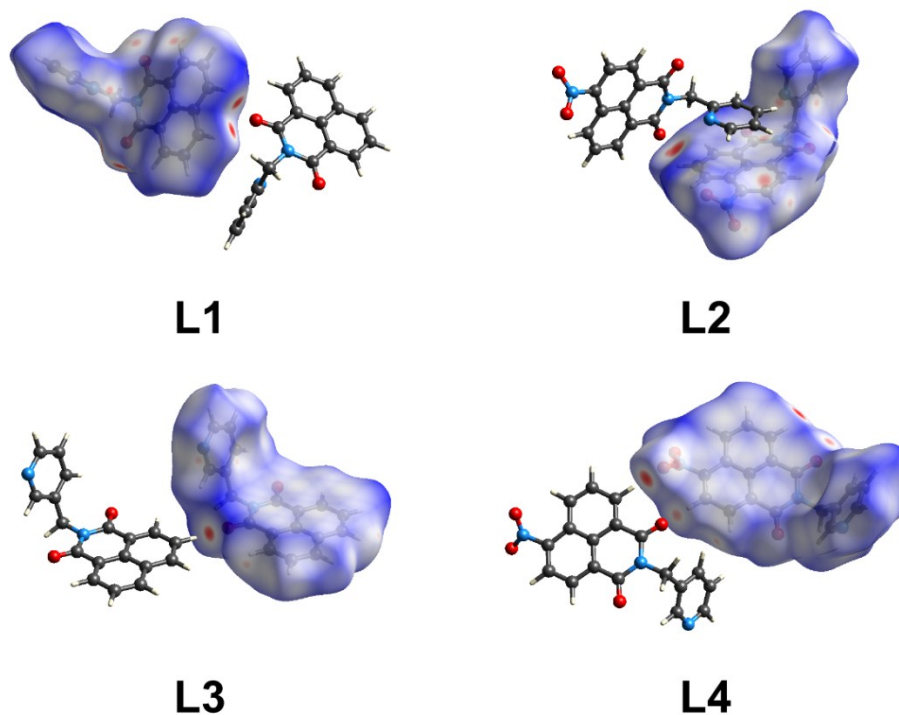


**Table S2** Crystal and refinement parameters for complexes **1 - 4**

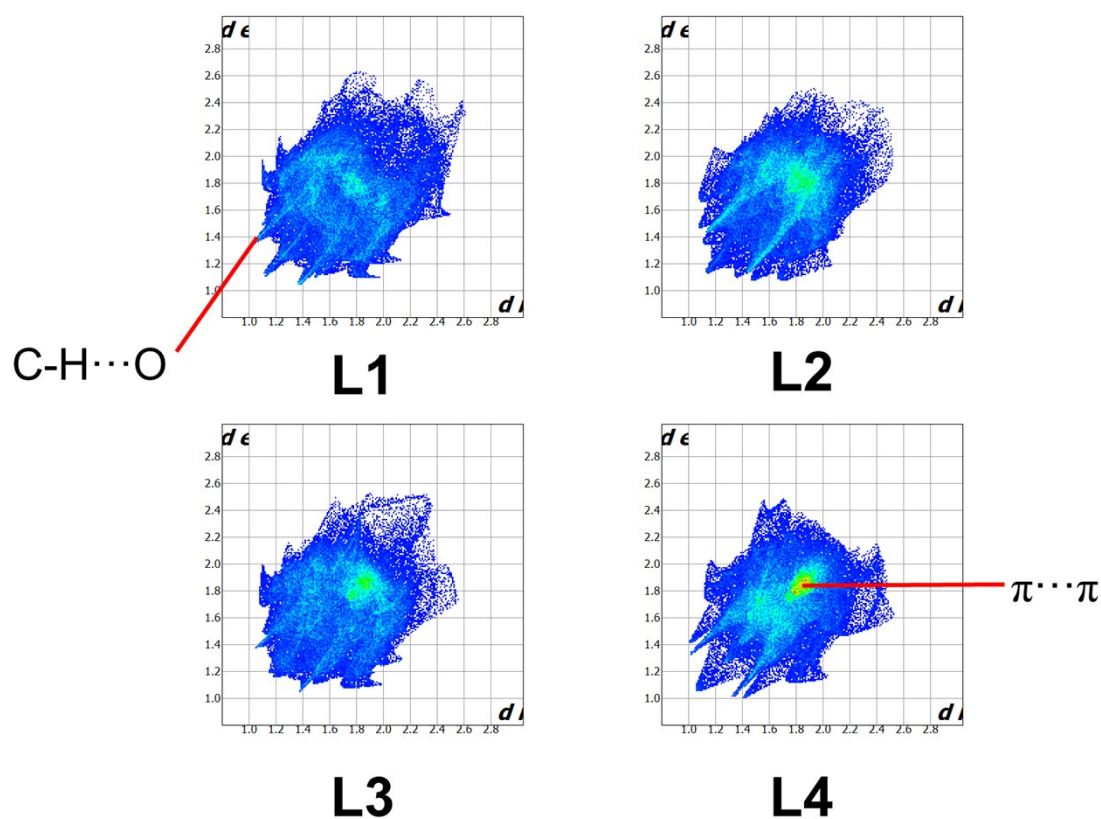
| Identification code                                             | <b>1</b>                                                                            | <b>2</b>                                                                           | <b>3</b>                                                                                          | <b>4</b>                                                                           |
|-----------------------------------------------------------------|-------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|
| Empirical formula                                               | C <sub>36</sub> H <sub>28</sub> Cl <sub>2</sub> Mn<br>N <sub>4</sub> O <sub>6</sub> | C <sub>36</sub> H <sub>24</sub> Cl <sub>2</sub> CoN<br>O <sub>4</sub>              | C <sub>80</sub> H <sub>64</sub> Cl <sub>6</sub> Co <sub>3</sub> N <sub>1</sub><br>O <sub>10</sub> | C <sub>36</sub> H <sub>22</sub> Cl <sub>2</sub> CoN<br>O <sub>8</sub>              |
| Formula weight                                                  | 738.46                                                                              | 706.42                                                                             | 1742.92                                                                                           | 796.42                                                                             |
| Temperature/K                                                   | 100(2)                                                                              | 100(2)                                                                             | 100(2)                                                                                            | 100(2)                                                                             |
| Crystal system                                                  | triclinic                                                                           | triclinic                                                                          | monoclinic                                                                                        | monoclinic                                                                         |
| Space group                                                     | <i>P</i> -1                                                                         | <i>P</i> -1                                                                        | <i>P</i> 2 <sub>1</sub> / <i>n</i>                                                                | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                                 |
| <i>a</i> /Å                                                     | 8.8451(4)                                                                           | 7.3935(4)                                                                          | 16.4021(5)                                                                                        | 9.1182(4)                                                                          |
| <i>b</i> /Å                                                     | 9.5894(4)                                                                           | 9.1136(6)                                                                          | 13.3749(4)                                                                                        | 23.7237(13)                                                                        |
| <i>c</i> /Å                                                     | 10.3016(4)                                                                          | 12.1362(7)                                                                         | 17.2099(6)                                                                                        | 7.2314(4)                                                                          |
| $\alpha$ /°                                                     | 77.4960(10)                                                                         | 90.411(2)                                                                          | 90                                                                                                | 90                                                                                 |
| $\beta$ /°                                                      | 80.6640(10)                                                                         | 104.798(2)                                                                         | 92.7917(10)                                                                                       | 103.296(4)                                                                         |
| $\gamma$ /°                                                     | 64.1630(10)                                                                         | 111.102(2)                                                                         | 90                                                                                                | 90                                                                                 |
| Volume/Å <sup>3</sup>                                           | 765.48(6)                                                                           | 733.14(8)                                                                          | 3771.0(2)                                                                                         | 1522.35(14)                                                                        |
| <i>Z</i>                                                        | 1                                                                                   | 1                                                                                  | 2                                                                                                 | 2                                                                                  |
| $\rho_{\text{calc}}$ /g/cm <sup>3</sup>                         | 1.602                                                                               | 1.6                                                                                | 1.535                                                                                             | 1.737                                                                              |
| $\mu$ /mm <sup>-1</sup>                                         | 0.664                                                                               | 0.819                                                                              | 0.934                                                                                             | 6.648                                                                              |
| <i>F</i> (000)                                                  | 379                                                                                 | 361                                                                                | 1782                                                                                              | 810                                                                                |
| Crystal size/mm <sup>3</sup>                                    | 0.23 × 0.13 ×<br>0.06                                                               | 0.11 × 0.06 ×<br>0.05                                                              | 0.27 × 0.17 ×<br>0.12                                                                             | 0.07 × 0.04 ×<br>0.04                                                              |
| Radiation                                                       | MoK $\alpha$ ( $\lambda$ =<br>0.71073)                                              | MoK $\alpha$ ( $\lambda$ =<br>0.71073)                                             | MoK $\alpha$ ( $\lambda$ =<br>0.71073)                                                            | CuK $\alpha$ ( $\lambda$ =<br>1.54178)                                             |
| 2 $\theta$ range for data<br>collection/°                       | 4.062 to<br>55.032                                                                  | 3.492 to 55                                                                        | 3.35 to 58.352                                                                                    | 7.452 to<br>136.518                                                                |
| Index ranges                                                    | -8 ≤ <i>h</i> ≤ 11, -<br>12 ≤ <i>k</i> ≤ 11, -<br>13 ≤ <i>l</i> ≤ 11                | -8 ≤ <i>h</i> ≤ 9, -11<br>≤ <i>k</i> ≤ 9, -15 ≤<br><i>l</i> ≤ 15                   | -22 ≤ <i>h</i> ≤ 20, -<br>18 ≤ <i>k</i> ≤ 17, -23<br>≤ <i>l</i> ≤ 16                              | -10 ≤ <i>h</i> ≤ 10, -<br>26 ≤ <i>k</i> ≤ 28, -<br>8 ≤ <i>l</i> ≤ 8                |
| Reflections collected                                           | 5680                                                                                | 5391                                                                               | 32344                                                                                             | 13787                                                                              |
| Independent<br>reflections                                      | 3524 [ <i>R</i> <sub>int</sub> =<br>0.0161, <i>R</i> <sub>sigma</sub><br>= 0.0312]  | 3362 [ <i>R</i> <sub>int</sub> =<br>0.0323, <i>R</i> <sub>sigma</sub><br>= 0.0740] | 10179 [ <i>R</i> <sub>int</sub> =<br>0.0540, <i>R</i> <sub>sigma</sub> =<br>0.0677]               | 2785 [ <i>R</i> <sub>int</sub> =<br>0.0632, <i>R</i> <sub>sigma</sub><br>= 0.0529] |
| Data/restraints/para<br>meters                                  | 3524/2/229                                                                          | 3362/0/214                                                                         | 10179/2/510                                                                                       | 2785/0/241                                                                         |
| Goodness-of-fit on<br><i>F</i> <sup>2</sup>                     | 1.025                                                                               | 1.036                                                                              | 1.005                                                                                             | 1.064                                                                              |
| Final <i>R</i> indexes<br>[ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )] | <i>R</i> <sub>1</sub> = 0.0297,<br><i>wR</i> <sub>2</sub> = 0.0706                  | <i>R</i> <sub>1</sub> = 0.0466,<br><i>wR</i> <sub>2</sub> = 0.0895                 | <i>R</i> <sub>1</sub> = 0.0406,<br><i>wR</i> <sub>2</sub> = 0.0705                                | <i>R</i> <sub>1</sub> = 0.0792,<br><i>wR</i> <sub>2</sub> = 0.2224                 |
| Final <i>R</i> indexes [all<br>data]                            | <i>R</i> <sub>1</sub> = 0.0405,<br><i>wR</i> <sub>2</sub> = 0.0760                  | <i>R</i> <sub>1</sub> = 0.0831,<br><i>wR</i> <sub>2</sub> = 0.1047                 | <i>R</i> <sub>1</sub> = 0.0830,<br><i>wR</i> <sub>2</sub> = 0.0824                                | <i>R</i> <sub>1</sub> = 0.0918,<br><i>wR</i> <sub>2</sub> = 0.2319                 |
| Largest diff.<br>peak/hole / e Å <sup>-3</sup>                  | 0.38/-0.33                                                                          | 0.62/-0.94                                                                         | 0.47/-0.81                                                                                        | 0.76/-0.99                                                                         |
| CCDC No.                                                        | 1511752                                                                             | 1511753                                                                            | 1511754                                                                                           | 1511755                                                                            |

**Table S3** Crystal and refinement parameters for complexes **5** - **7**

| Identification code                                          | <b>5</b>                                                                                     | <b>6</b>                                                                        | <b>7</b>                                                                                           |
|--------------------------------------------------------------|----------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|
| Empirical formula                                            | C <sub>18</sub> H <sub>12</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub> Z <sub>n</sub> | C <sub>37</sub> H <sub>28</sub> Cl <sub>2</sub> MnN <sub>4</sub> O <sub>5</sub> | C <sub>37.33</sub> H <sub>26</sub> Cl <sub>2</sub> N <sub>4.67</sub> O <sub>4</sub> Z <sub>n</sub> |
| Formula weight                                               | 424.57                                                                                       | 734.47                                                                          | 740.23                                                                                             |
| Temperature/K                                                | 100(2)                                                                                       | 100(2)                                                                          | 100(2)                                                                                             |
| Crystal system                                               | triclinic                                                                                    | monoclinic                                                                      | monoclinic                                                                                         |
| Space group                                                  | <i>P</i> -1                                                                                  | <i>C</i> 2/ <i>c</i>                                                            | <i>C</i> 2/ <i>c</i>                                                                               |
| <i>a</i> /Å                                                  | 7.3139(2)                                                                                    | 25.4298(13)                                                                     | 10.4255(8)                                                                                         |
| <i>b</i> /Å                                                  | 8.5996(3)                                                                                    | 4.6669(2)                                                                       | 11.0223(8)                                                                                         |
| <i>c</i> /Å                                                  | 14.4546(5)                                                                                   | 27.8832(12)                                                                     | 28.403(3)                                                                                          |
| $\alpha$ /°                                                  | 94.9430(10)                                                                                  | 90                                                                              | 90                                                                                                 |
| $\beta$ /°                                                   | 102.0330(10)                                                                                 | 109.266(3)                                                                      | 94.650(8)                                                                                          |
| $\gamma$ /°                                                  | 113.9780(10)                                                                                 | 90                                                                              | 90                                                                                                 |
| Volume/Å <sup>3</sup>                                        | 797.44(5)                                                                                    | 3123.8(3)                                                                       | 3253.2(4)                                                                                          |
| <i>Z</i>                                                     | 2                                                                                            | 4                                                                               | 4                                                                                                  |
| $\rho_{\text{calc}}$ /g/cm <sup>3</sup>                      | 1.768                                                                                        | 1.562                                                                           | 1.511                                                                                              |
| $\mu$ /mm <sup>-1</sup>                                      | 1.89                                                                                         | 5.46                                                                            | 2.971                                                                                              |
| F(000)                                                       | 428                                                                                          | 1508                                                                            | 1515                                                                                               |
| Crystal size/mm <sup>3</sup>                                 | 0.31 × 0.11 × 0.05                                                                           | 0.14 × 0.03 × 0.02                                                              | 0.05 × 0.05 × 0.01                                                                                 |
| Radiation                                                    | MoK $\alpha$ ( $\lambda$ = 0.71073)                                                          | CuK $\alpha$ ( $\lambda$ = 1.54178)                                             | CuK $\alpha$ ( $\lambda$ = 1.54178)                                                                |
| 2 $\Theta$ range for data collection/°                       | 5.282 to 56.694                                                                              | 6.716 to 134.954                                                                | 6.244 to 140.266                                                                                   |
| Index ranges                                                 | -9 ≤ <i>h</i> ≤ 9, -11 ≤ <i>k</i> ≤ 4, -19 ≤ <i>l</i> ≤ 18                                   | -30 ≤ <i>h</i> ≤ 30, -5 ≤ <i>k</i> ≤ 5, -29 ≤ <i>l</i> ≤ 33                     | -11 ≤ <i>h</i> ≤ 12, -13 ≤ <i>k</i> ≤ 13, -34 ≤ <i>l</i> ≤ 34                                      |
| Reflections collected                                        | 6138                                                                                         | 9538                                                                            | 16379                                                                                              |
| Independent reflections                                      | 3975 [ <i>R</i> <sub>int</sub> = 0.0141, <i>R</i> <sub>sigma</sub> = 0.0229]                 | 2815 [ <i>R</i> <sub>int</sub> = 0.0403, <i>R</i> <sub>sigma</sub> = 0.0386]    | 3074 [ <i>R</i> <sub>int</sub> = 0.0893, <i>R</i> <sub>sigma</sub> = 0.0638]                       |
| Data/restraints/parameters                                   | 3975/0/226                                                                                   | 2815/3/244                                                                      | 3074/21/240                                                                                        |
| Goodness-of-fit on F <sup>2</sup>                            | 1.063                                                                                        | 1.061                                                                           | 1.061                                                                                              |
| Final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )] | <i>R</i> <sub>1</sub> = 0.0214, <i>wR</i> <sub>2</sub> = 0.0530                              | <i>R</i> <sub>1</sub> = 0.0379, <i>wR</i> <sub>2</sub> = 0.1013                 | <i>R</i> <sub>1</sub> = 0.0773, <i>wR</i> <sub>2</sub> = 0.2085                                    |
| Final <i>R</i> indexes [all data]                            | <i>R</i> <sub>1</sub> = 0.0250, <i>wR</i> <sub>2</sub> = 0.0546                              | <i>R</i> <sub>1</sub> = 0.0435, <i>wR</i> <sub>2</sub> = 0.1057                 | <i>R</i> <sub>1</sub> = 0.1292, <i>wR</i> <sub>2</sub> = 0.2469                                    |
| Largest diff. peak/hole / e Å <sup>-3</sup>                  | 0.43/-0.35                                                                                   | 0.30/-0.64                                                                      | 0.54/-0.85                                                                                         |
| CCDC No.                                                     | 1511756                                                                                      | 1511757                                                                         | 1511758                                                                                            |



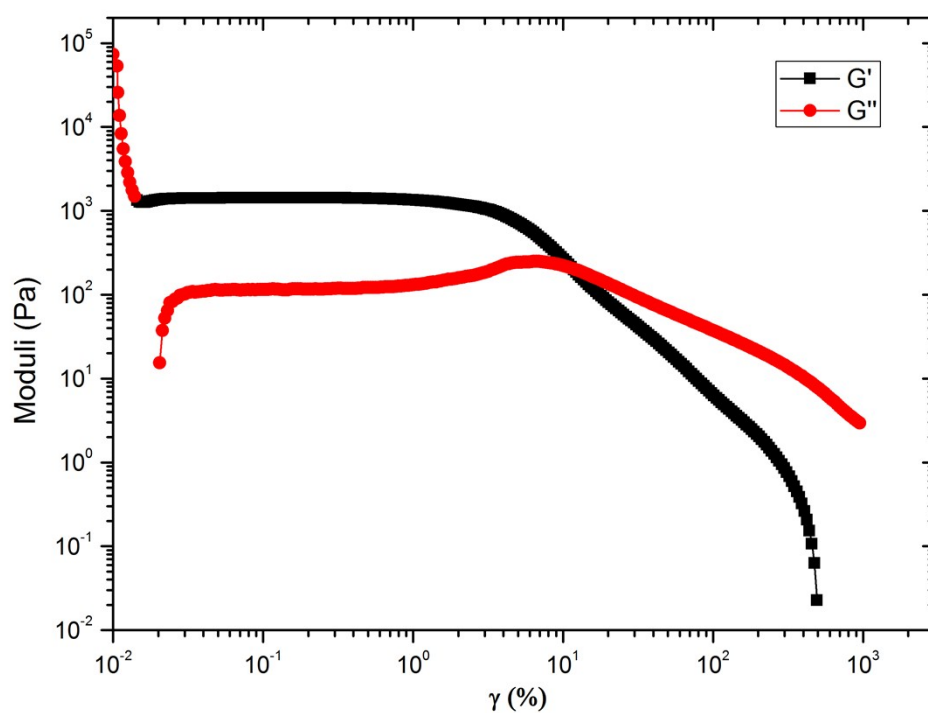
**Figure S2** Calculated Hirshfeld ( $d_{\text{norm}}$ ) surface areas for **L1** – **L4** showing main C-H $\cdots$ O interactions for each compound. Figures prepared with CrystalExplorer software<sup>S8-9</sup>, rendered with surface property in the range -0.16 - +1.25.



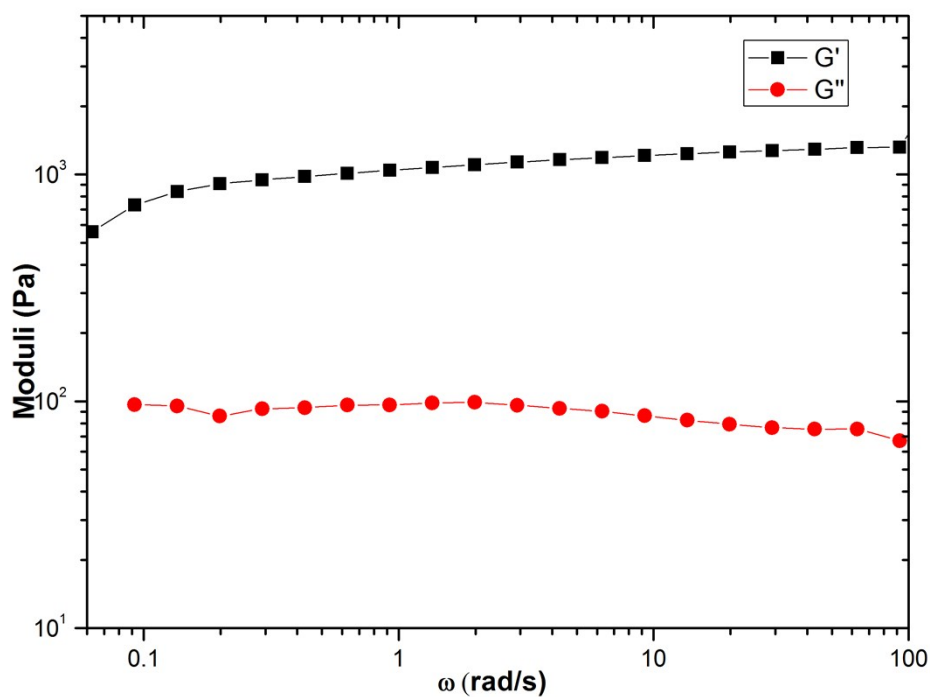
**Figure S3** Fingerprint plots for **L1** – **L4** with dominant features highlighted for two representative cases. Figures prepared with CrystalExplorer software<sup>S8-9</sup>



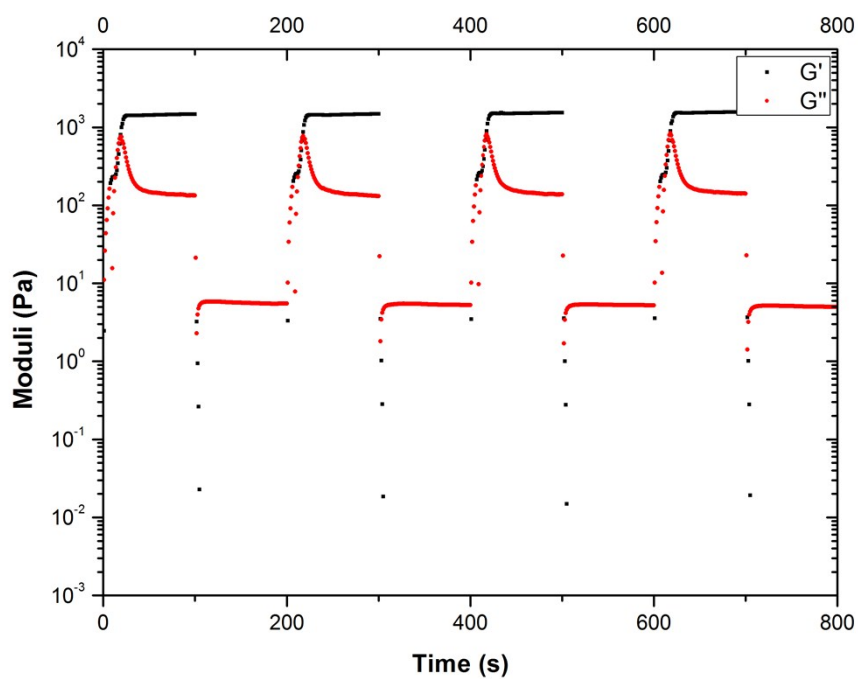
**Figure S4** The four gel samples used for rheology measurements (L-R, gel 9, 8, 9a and 11)



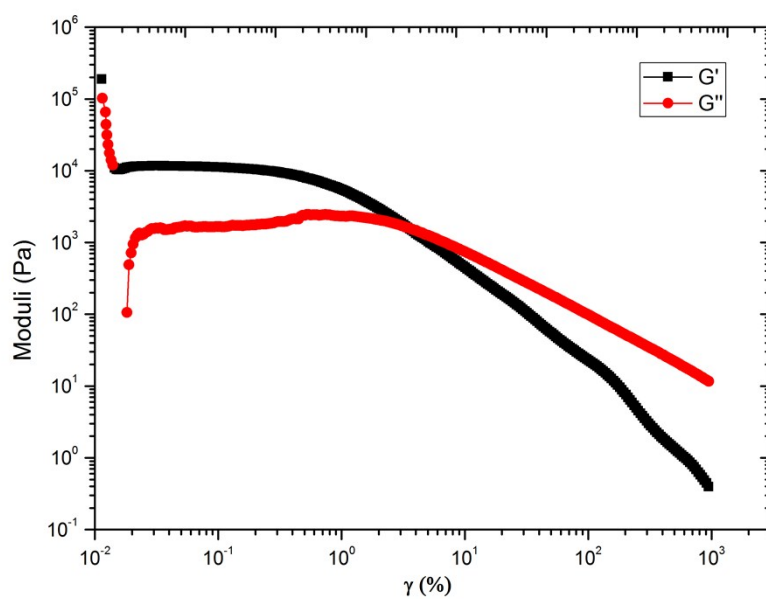
**Figure S5** Rheological measurements for gel 9a; amplitude sweep ( $\omega = 1$  rad/s)



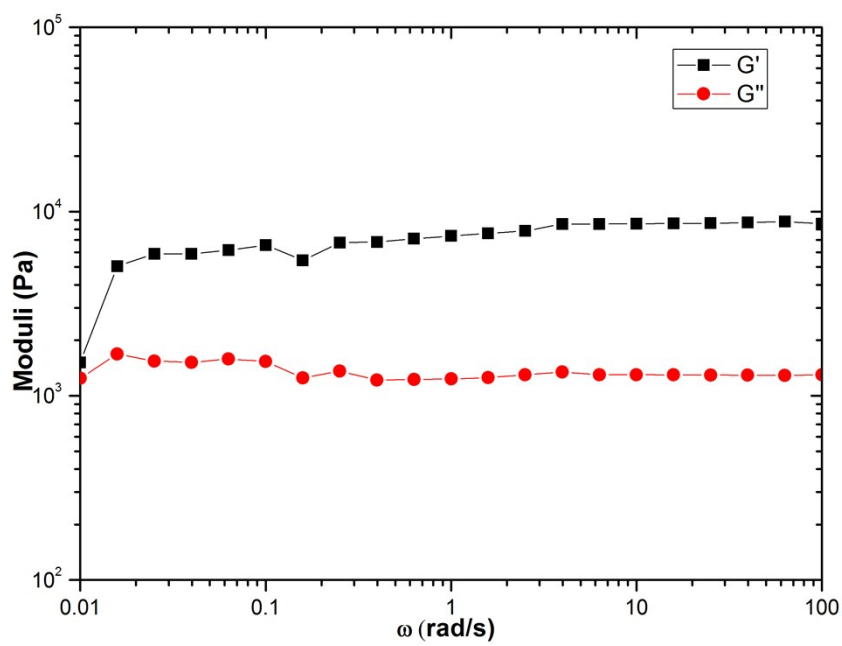
**Figure S6** Rheological measurements for gel **9a**; frequency sweep over consecutive cycles ( $\gamma = 0.1\%$ )



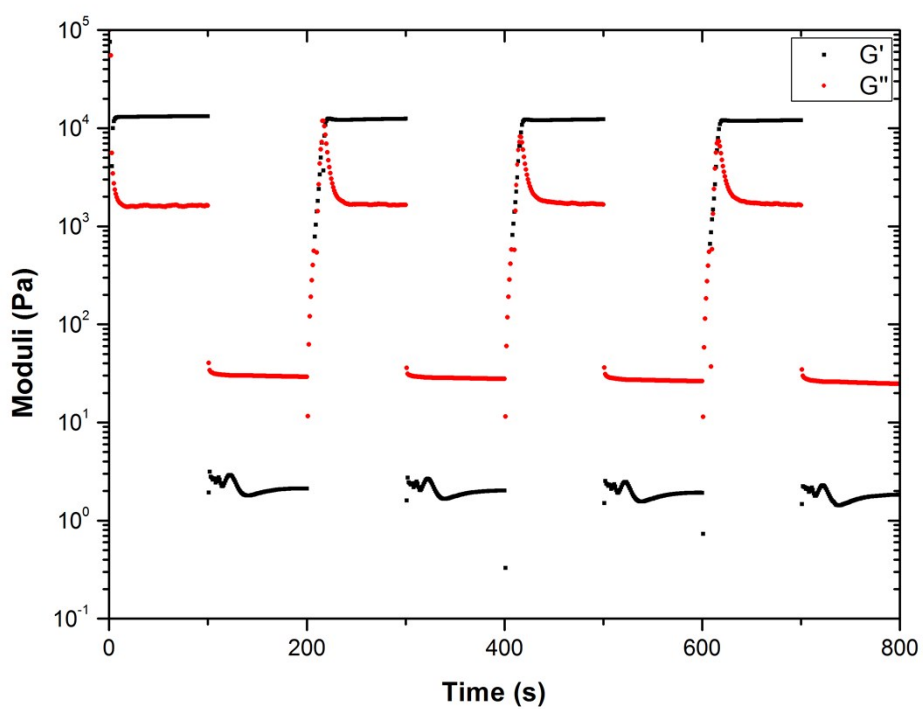
**Figure S7** Rheological measurements for gel **9a**; recovery test at alternating 0.1% and 500% strain amplitude.



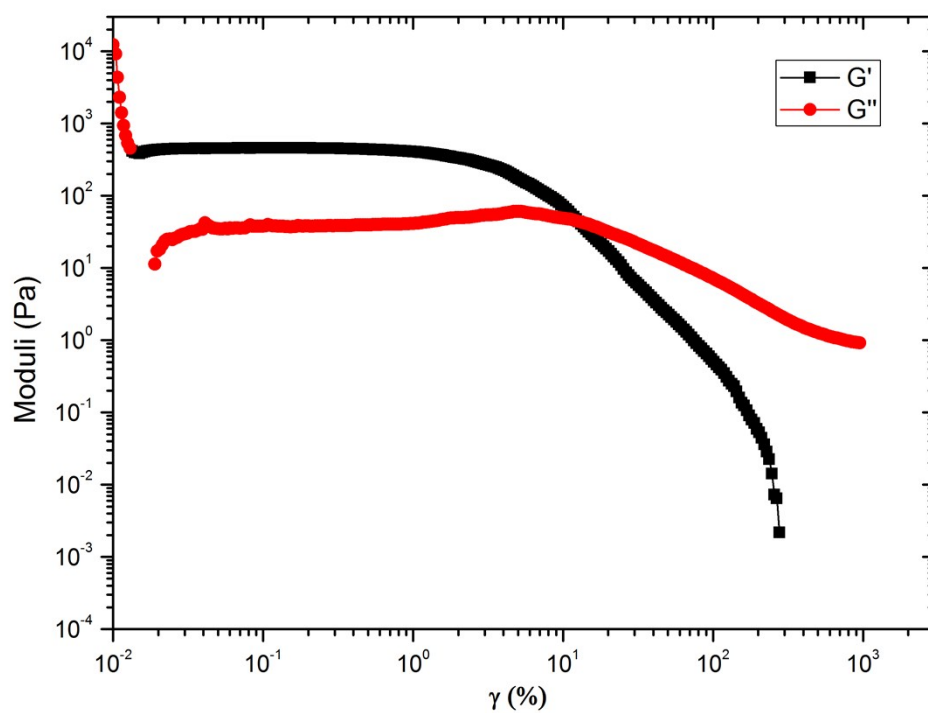
**Figure S8** Rheological measurements for gel **8**; amplitude sweep ( $\omega = 1$  rad/s)



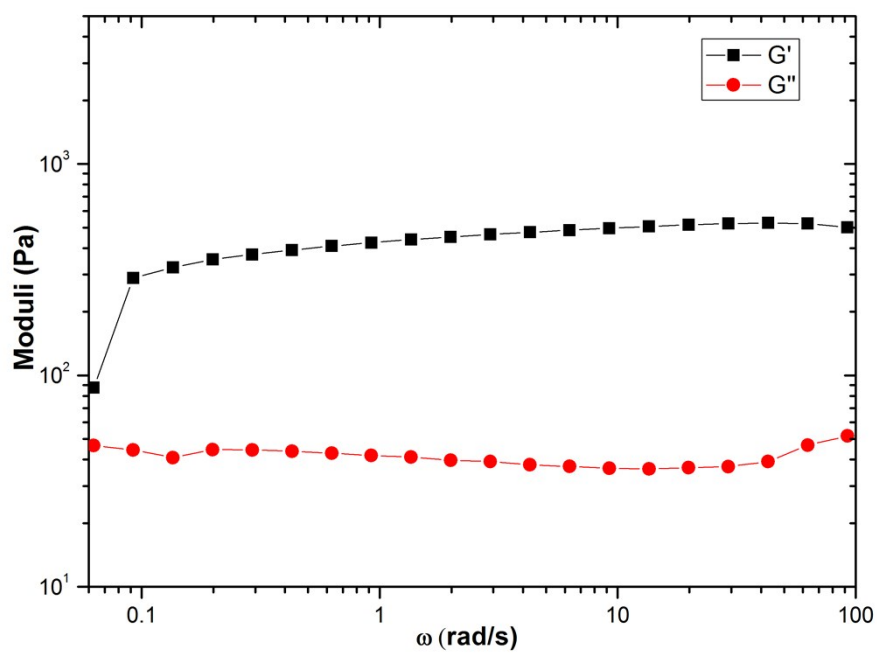
**Figure S9** Rheological measurements for gel **8**; frequency sweep over consecutive cycles ( $\gamma = 0.1$  %)



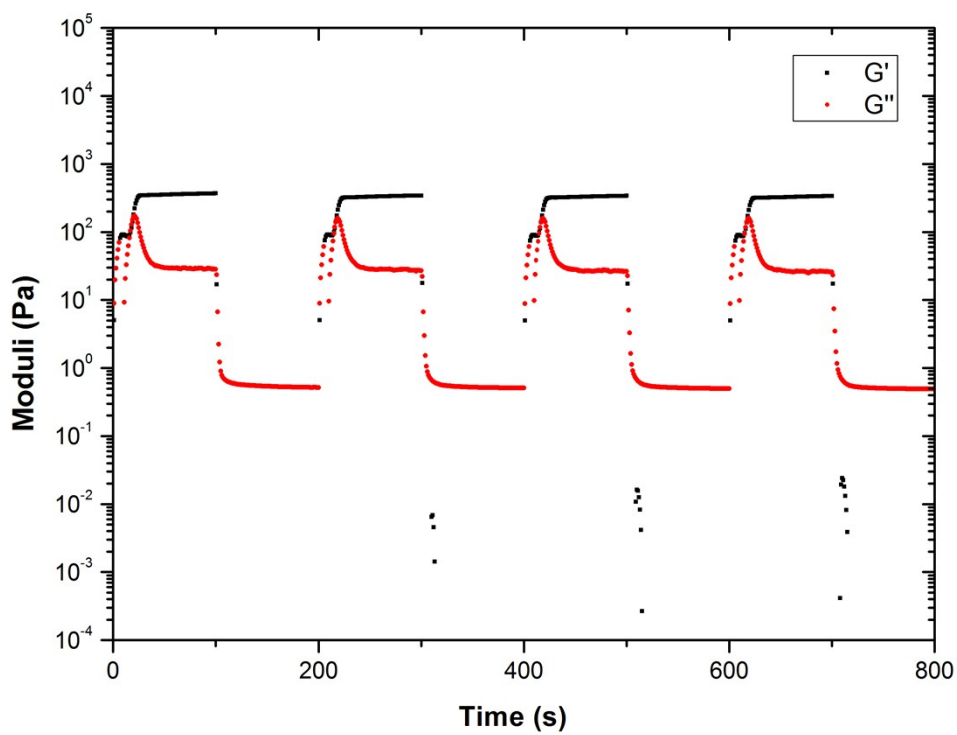
**Figure S10** Rheological measurements for gel **8**; Recovery test at alternating 0.1% and 500% strain amplitude.



**Figure S11** Rheological measurements for gel **11**; amplitude sweep ( $\omega = 1$  rad/s)

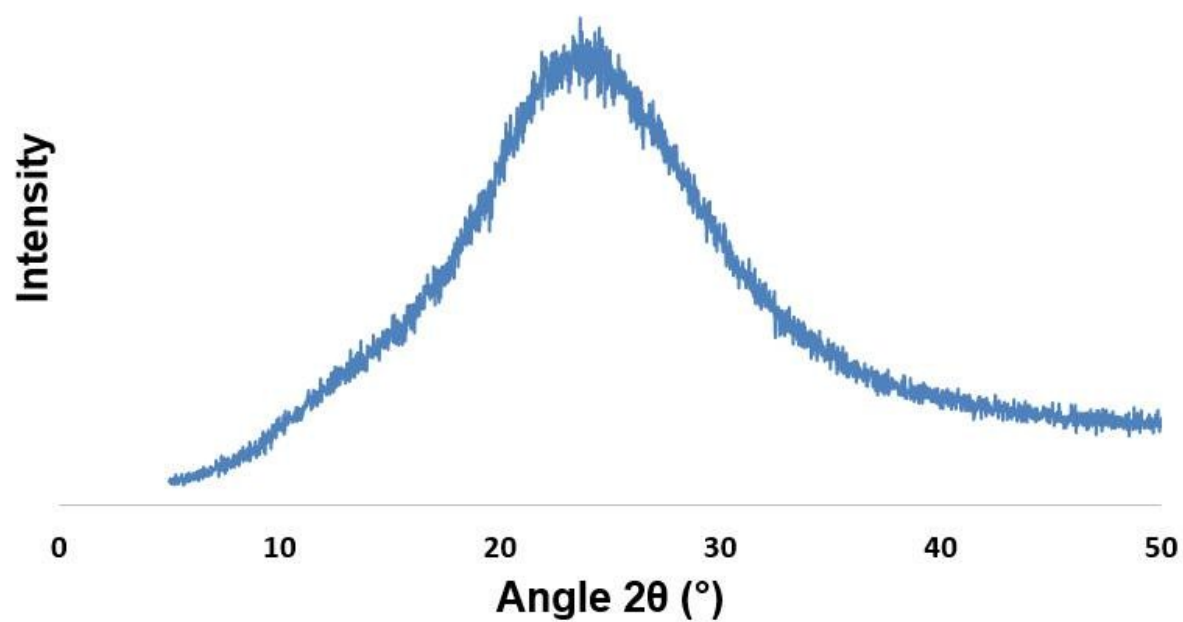


**Figure S12** Rheological measurements for gel **11**; frequency sweep over consecutive cycles ( $\gamma = 0.1\%$ );

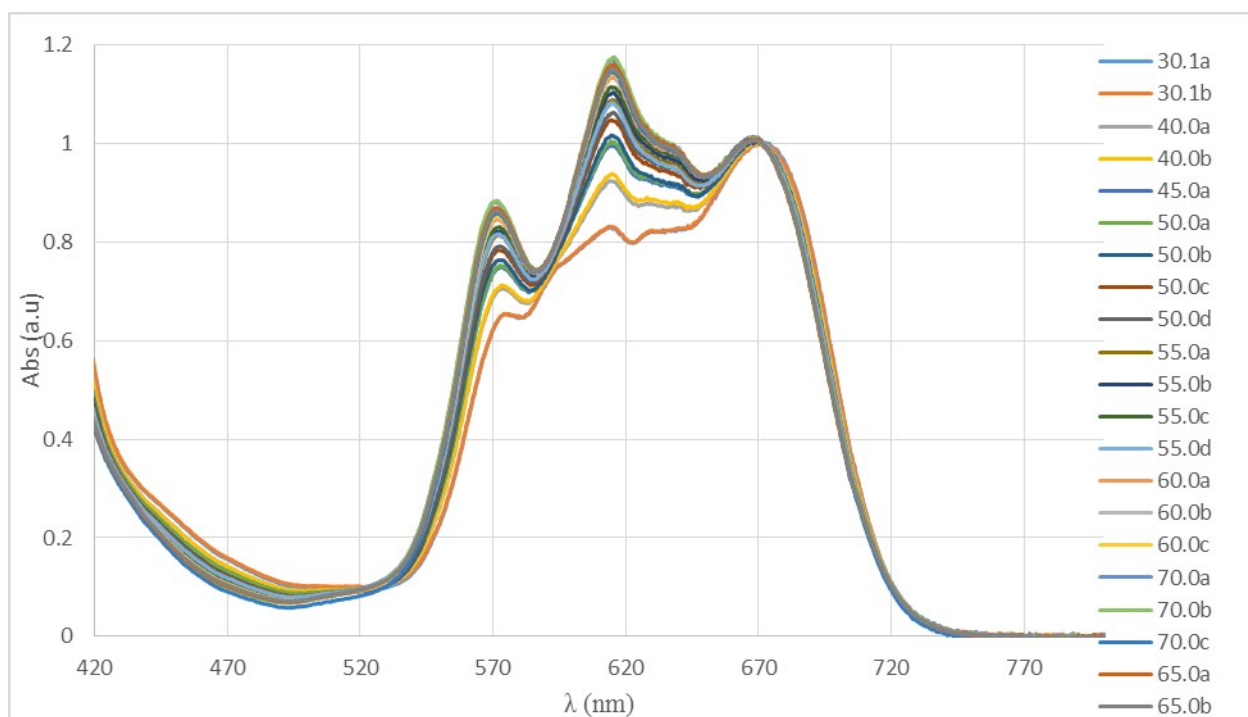


**Figure S13** Rheological measurements for gel **11**; recovery test at alternating 0.1% and 500% strain amplitude.

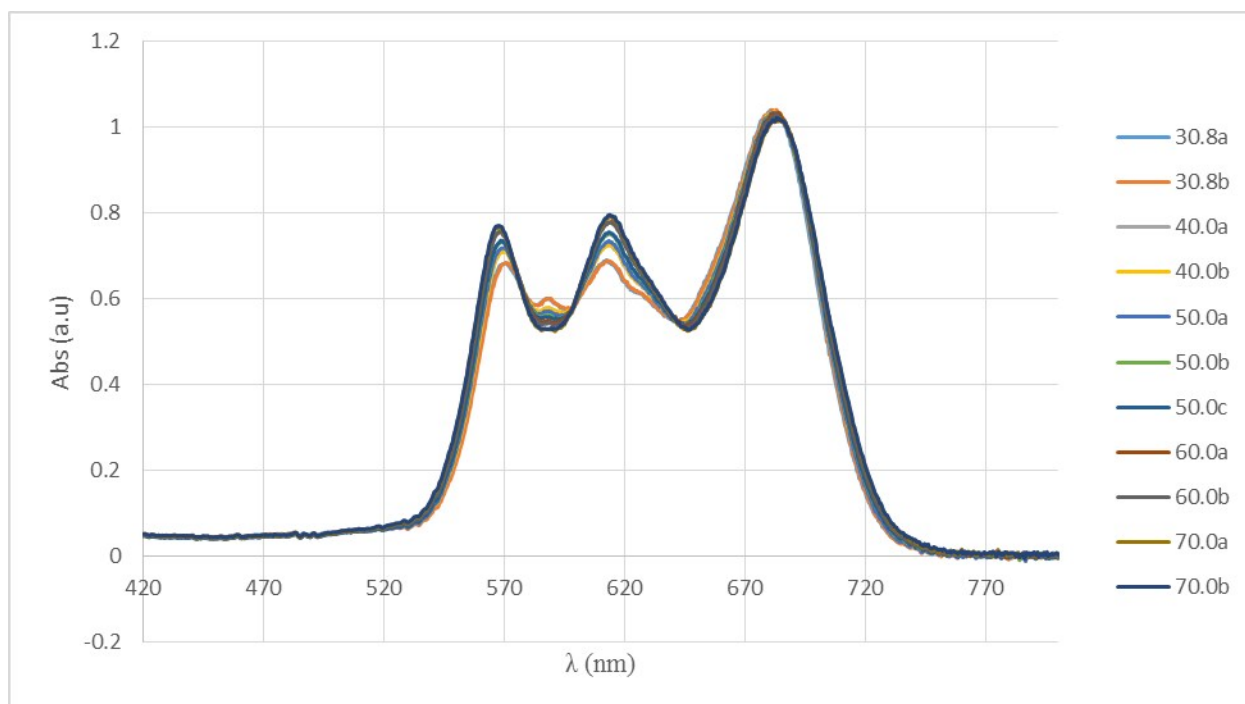




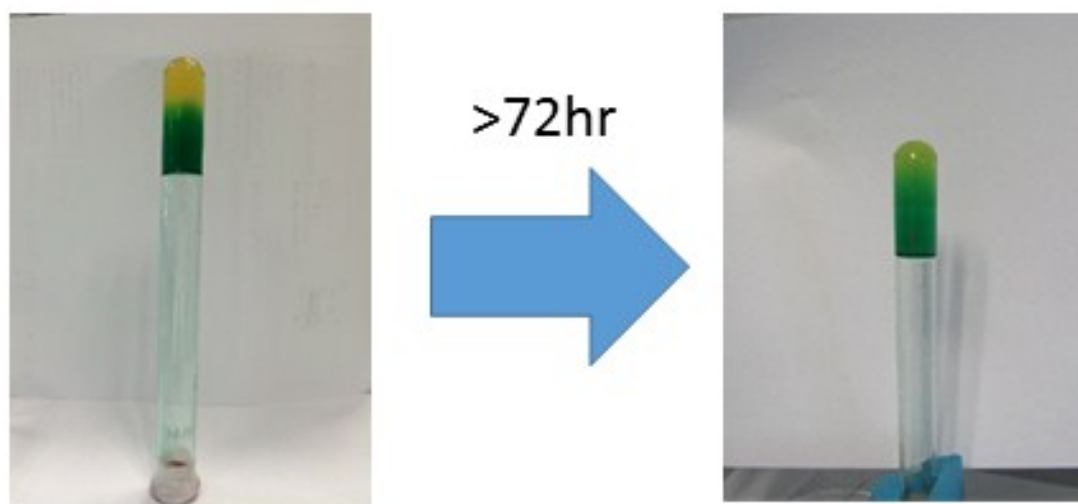
**Figure S14** X-ray diffraction pattern of the solvated gel **9**.



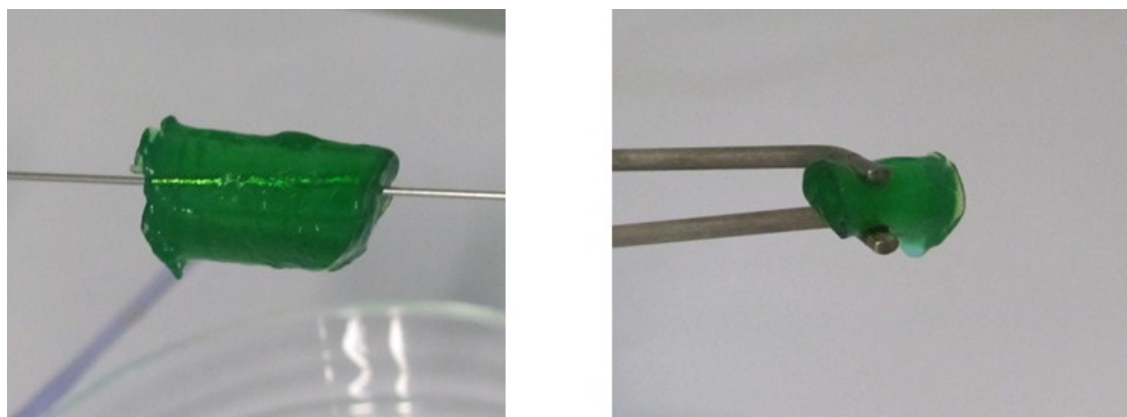
**Figure S15** Variable-temperature UV-Visible absorption spectra for gel **9**, with temperatures labelled



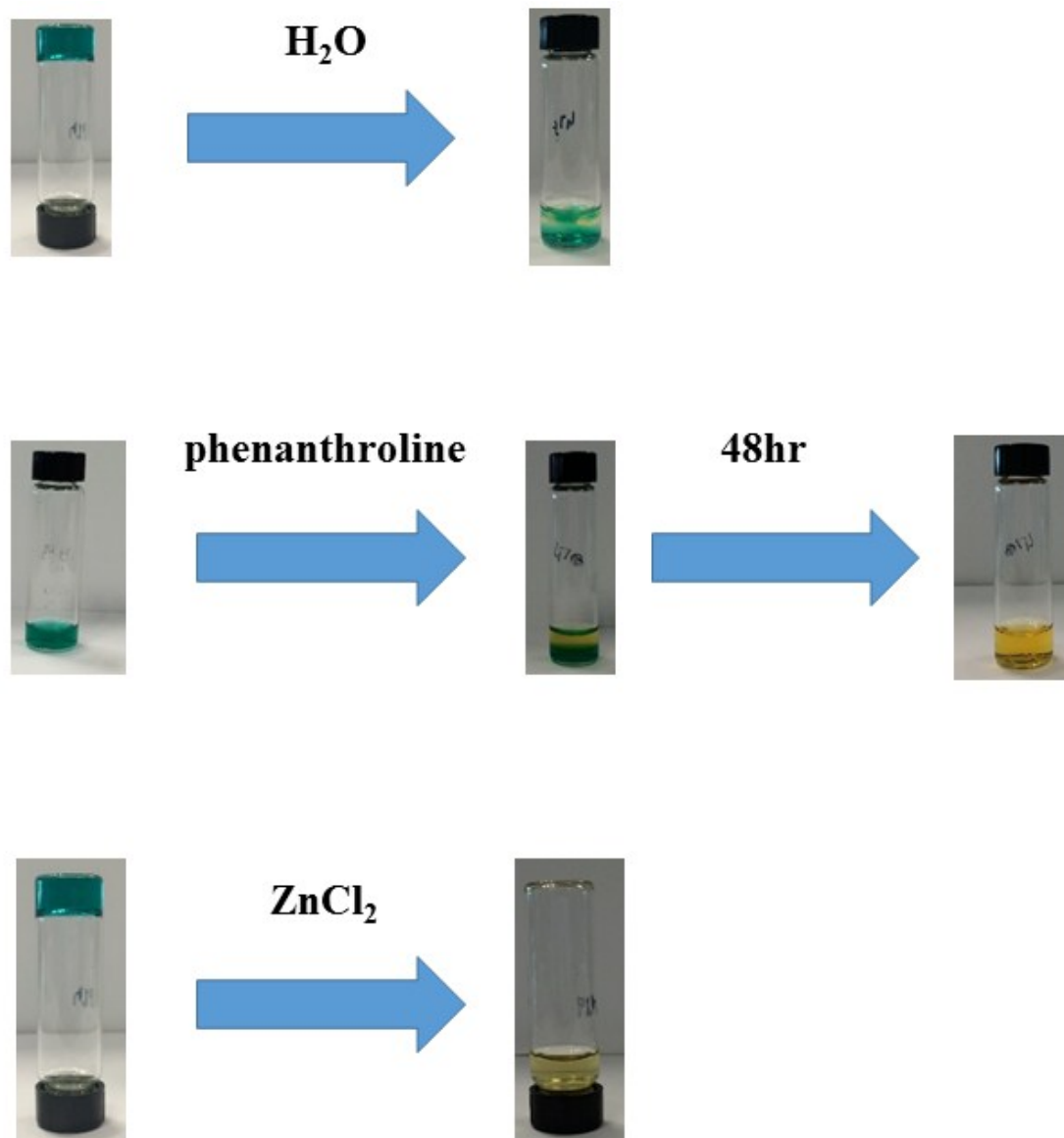
**Figure S16** Variable-temperature UV-Visible absorption spectra for pure cobalt(II) chloride in acetonitrile, with temperatures labelled



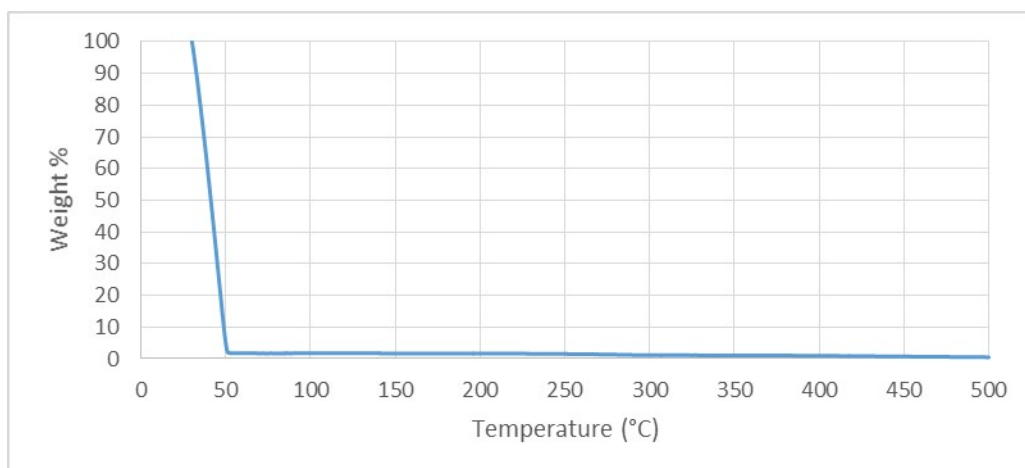
**Figure S17** The alternating mixed metal gel formed from layering gel 9 above gel 8, and subsequent ageing.



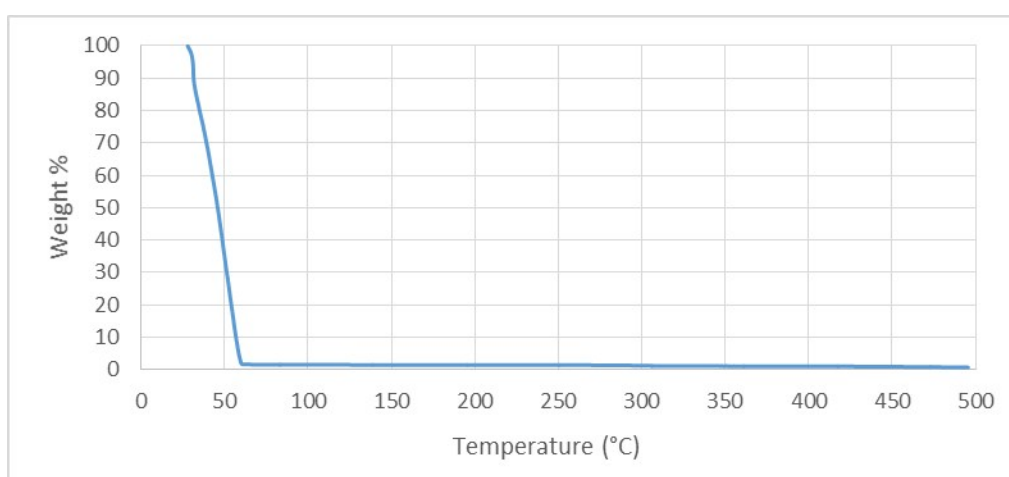
**Figure S18** Mechanical stability of the layered mixed-metal gel **9/8**



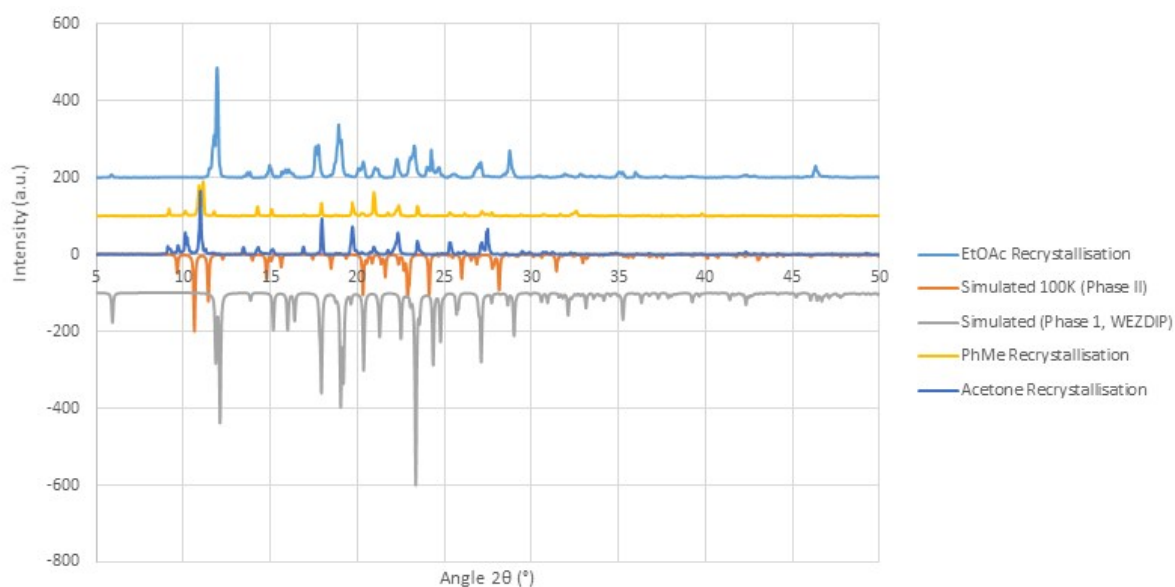
**Figure S19** Chemical destruction of gel **9** in the presence of competitive ligands or metals



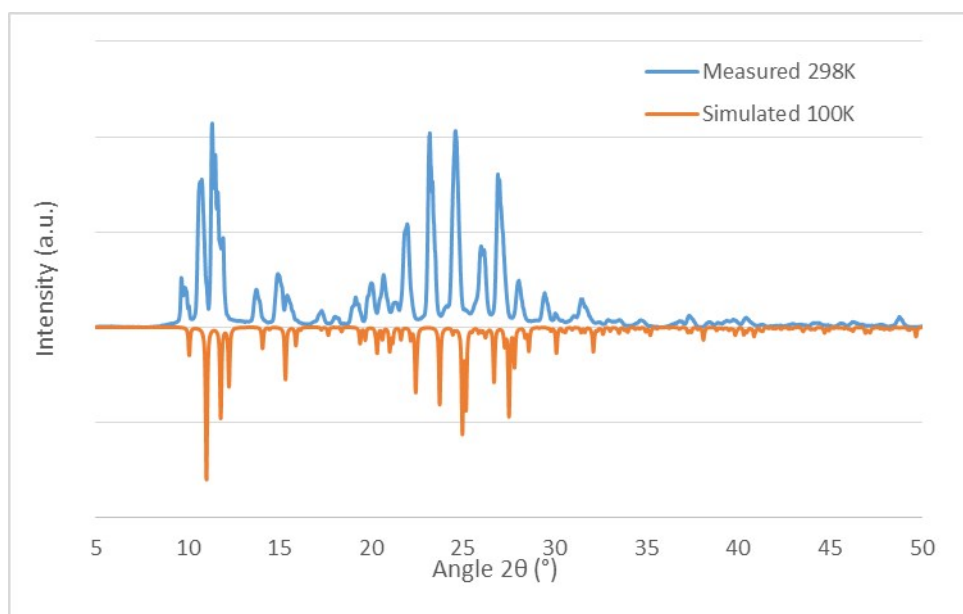
**Figure S20:** Thermogravimetric analysis for gel 8



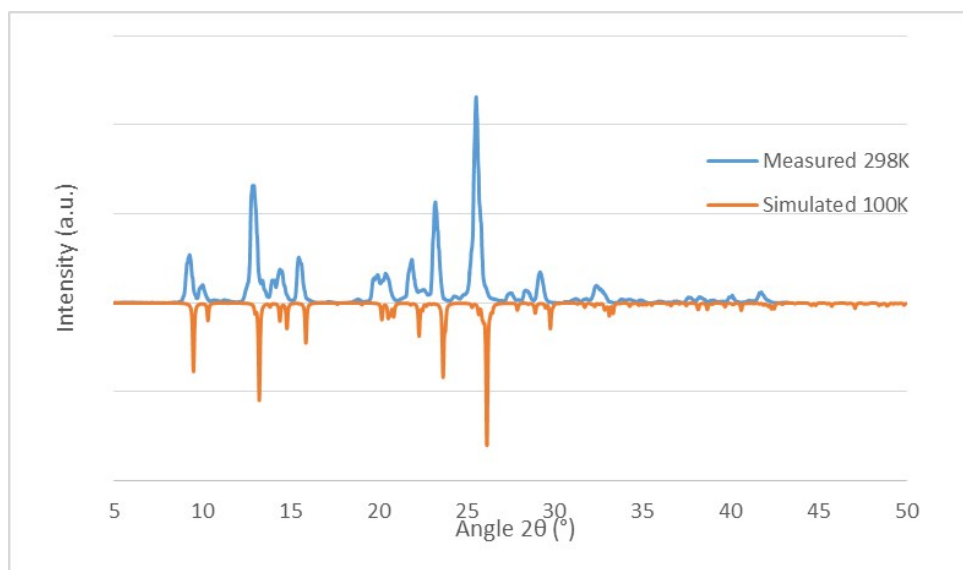
**Figure S21:** Thermogravimetric analysis for gel 9



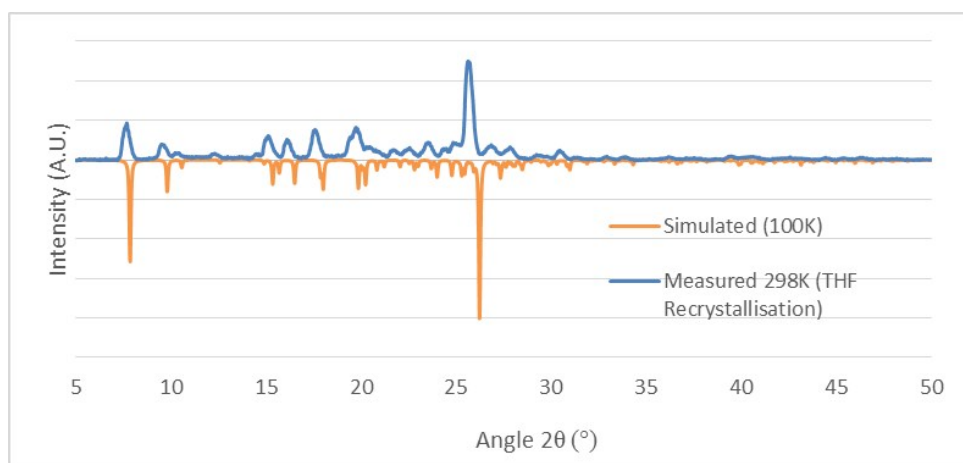
**Figure S22** X-ray powder diffraction patterns for **L1** (298K) and comparison to the simulated pattern for the reported  $\beta$ -phase (100K) and the phase previously reported by Baruah *et al.*<sup>S10</sup> (CCDC refcode WEZDIP, 298K)



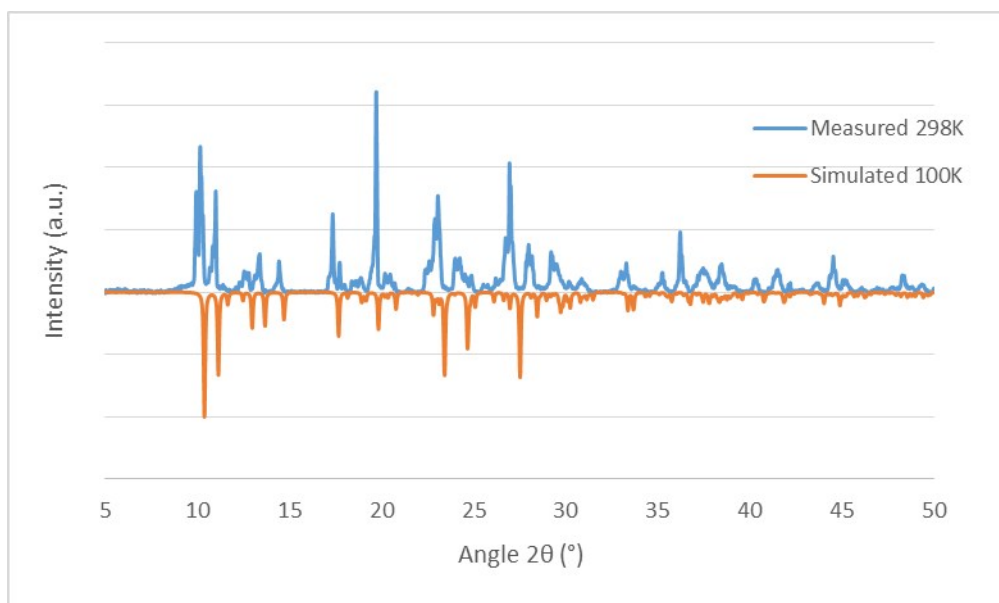
**Figure S23** X ray powder diffraction pattern for **L2**



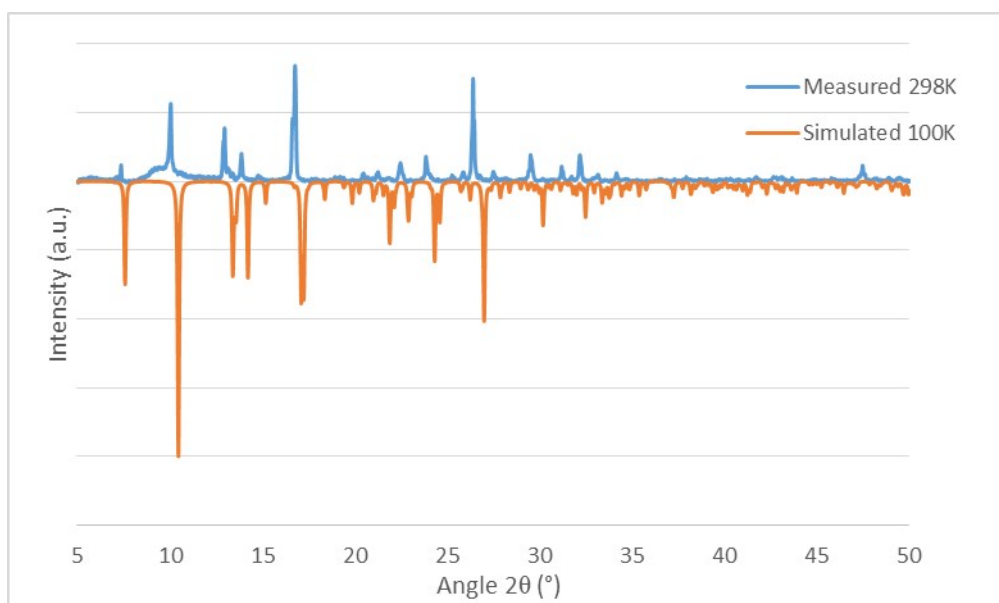
**Figure S24** X-ray powder diffraction pattern for **L3**



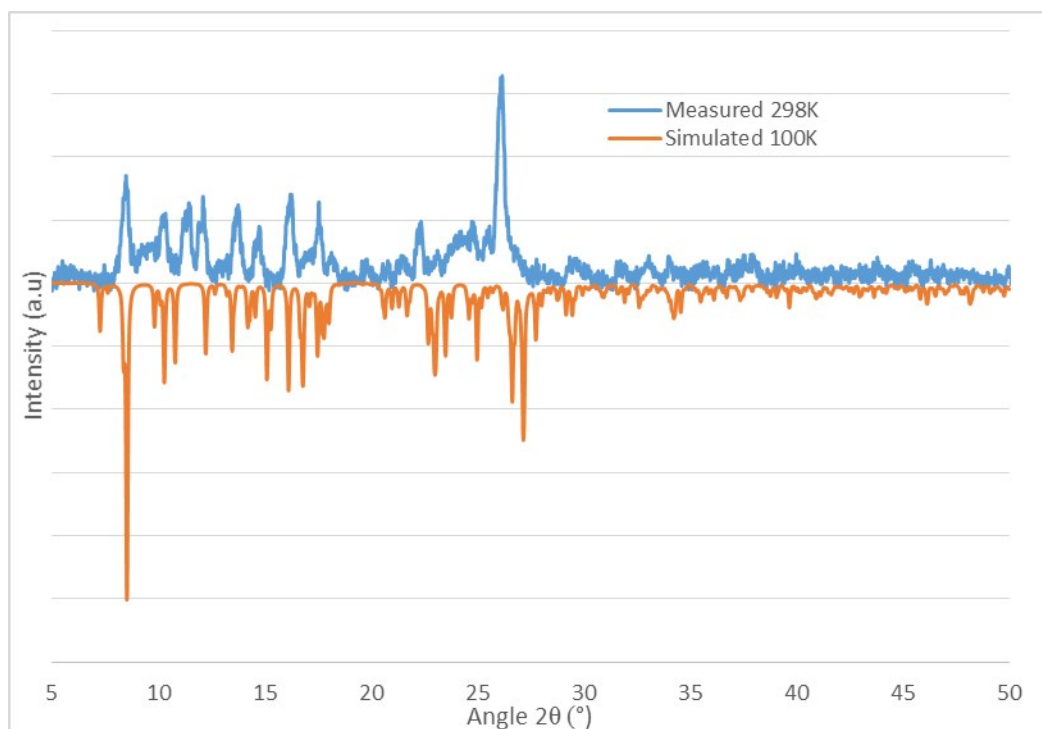
**Figure S25** X-ray powder diffraction pattern for **L4**



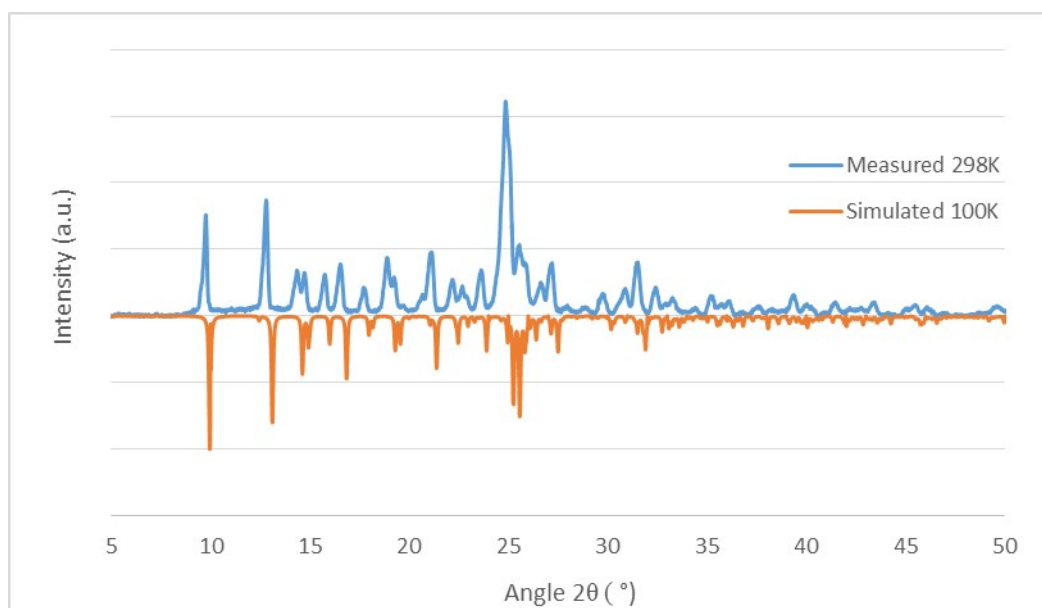
**Figure S26:** X-ray powder diffraction pattern for complex 1



**Figure S27:** X-ray powder diffraction pattern for complex 2

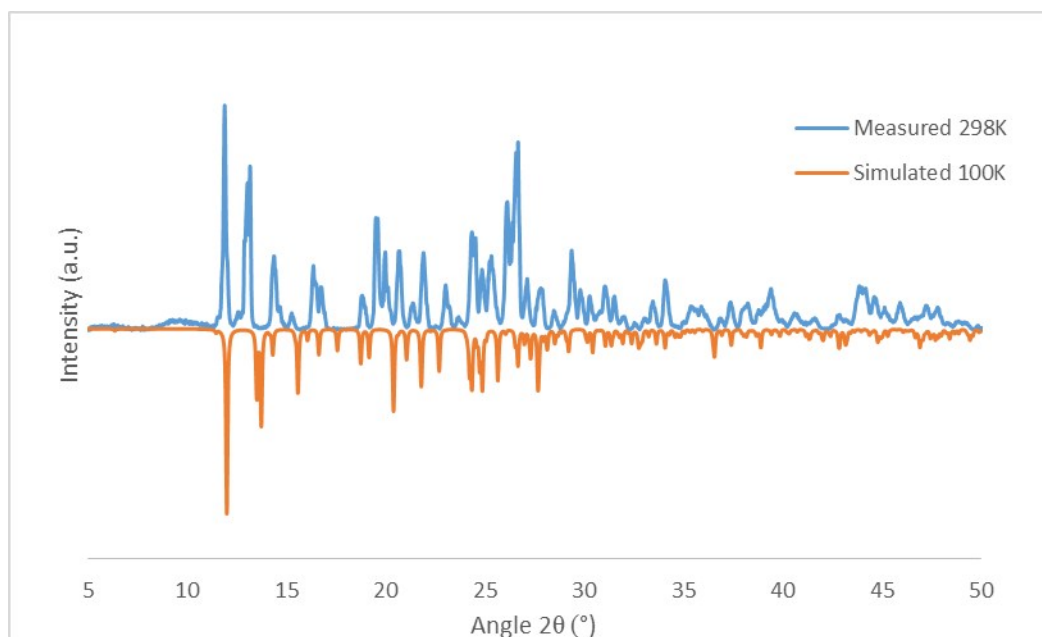


**Figure S28:** X-ray powder diffraction pattern for compound **3**, comprising a mixed phase of **2** and **3**

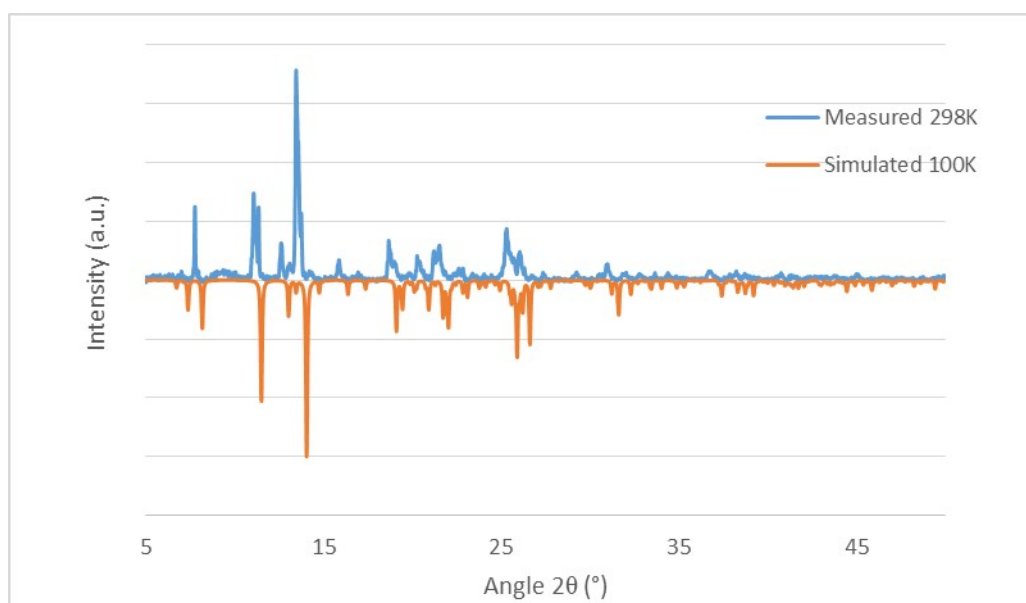


**Figure S29:** X ray powder diffraction pattern for complex **4**

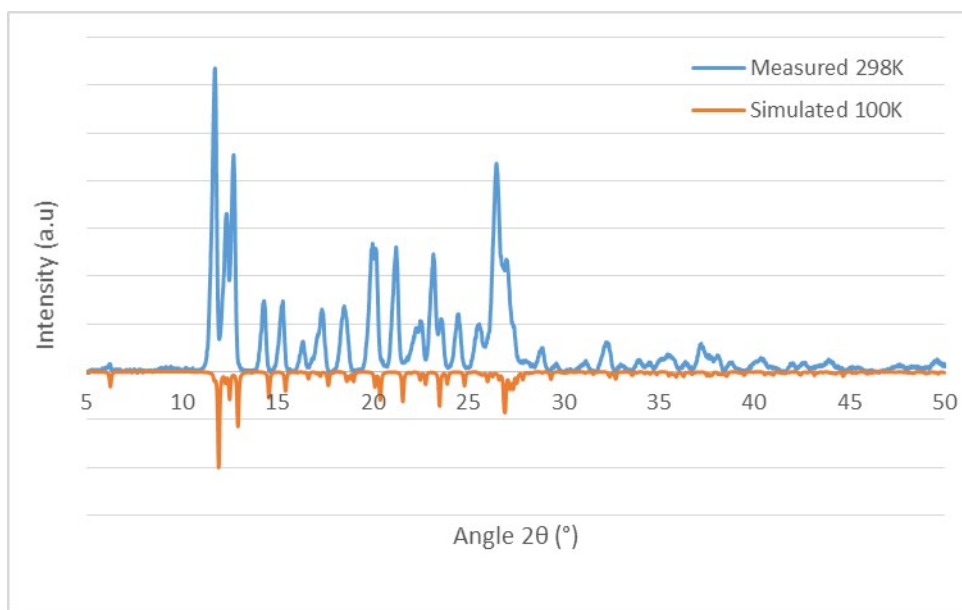




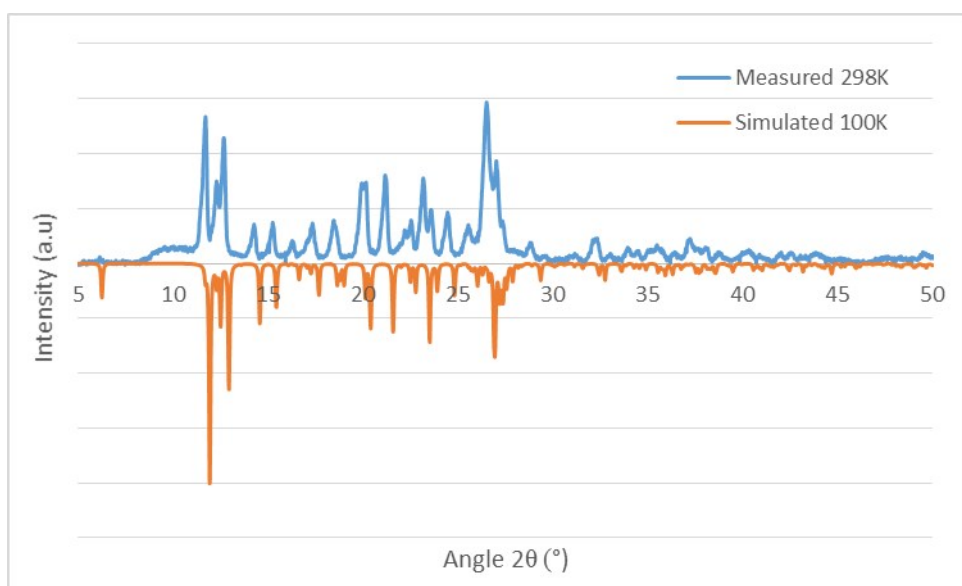
**Figure S30** X-ray powder diffraction pattern for complex **5**



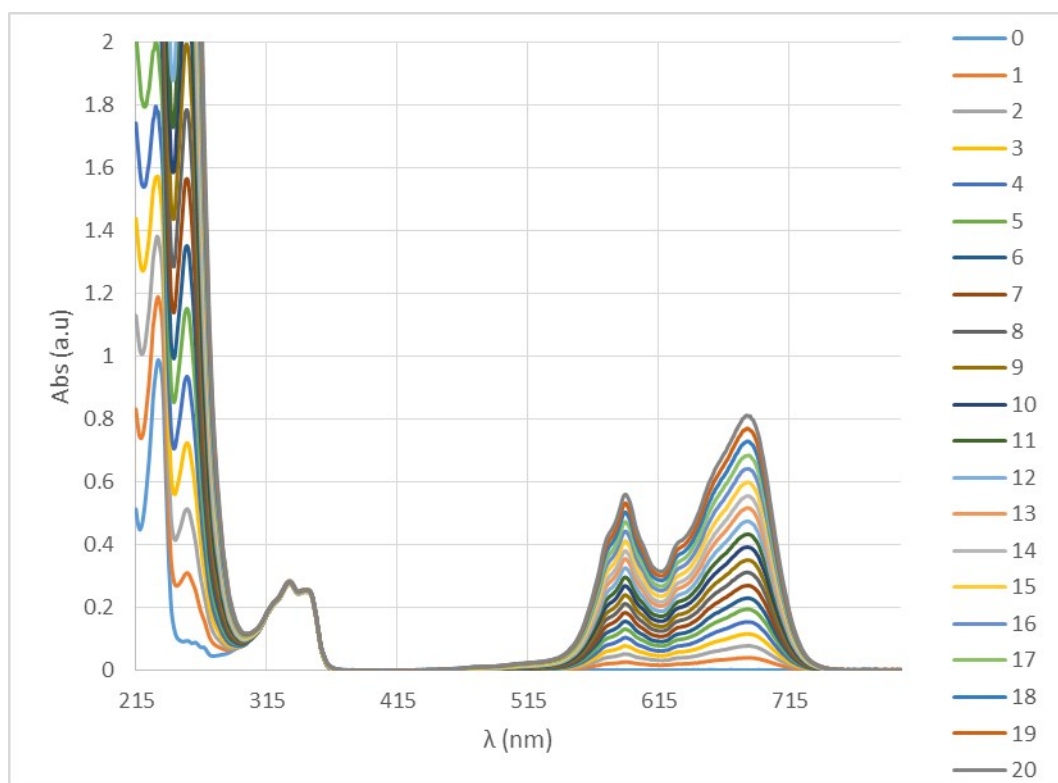
**Figure S31:** X ray powder diffraction for **6**



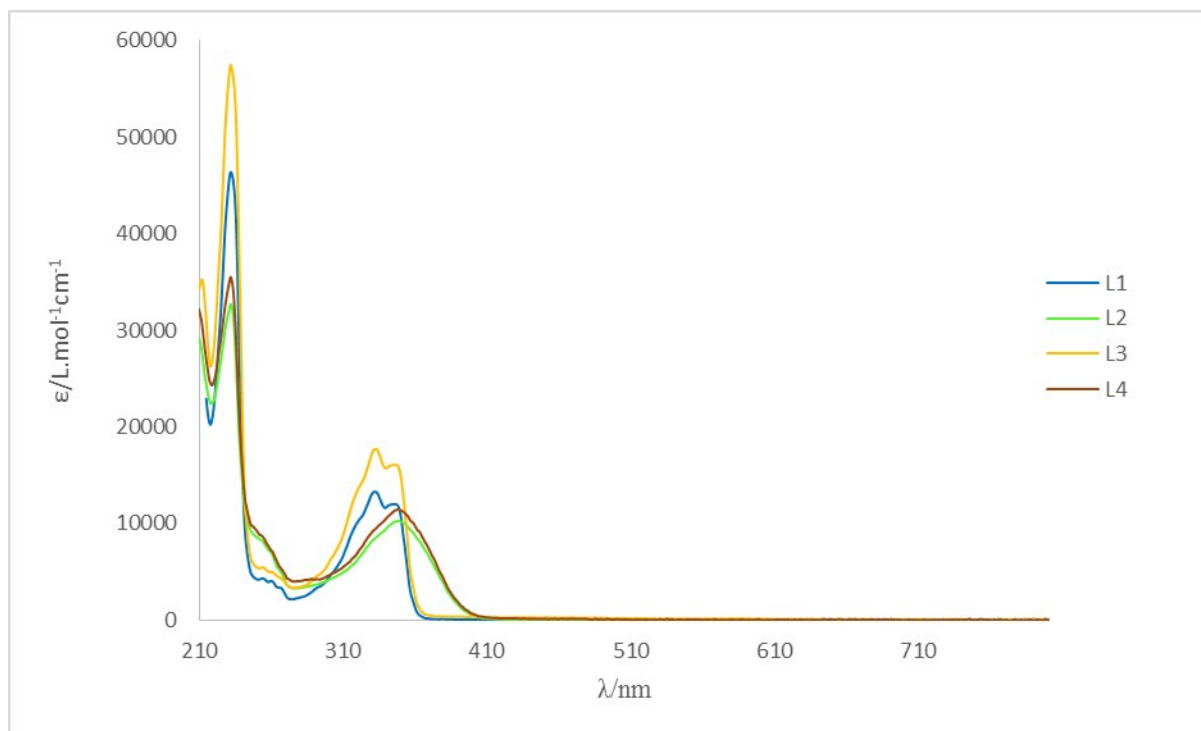
**Figure S32:** X ray powder diffraction for complex **7**



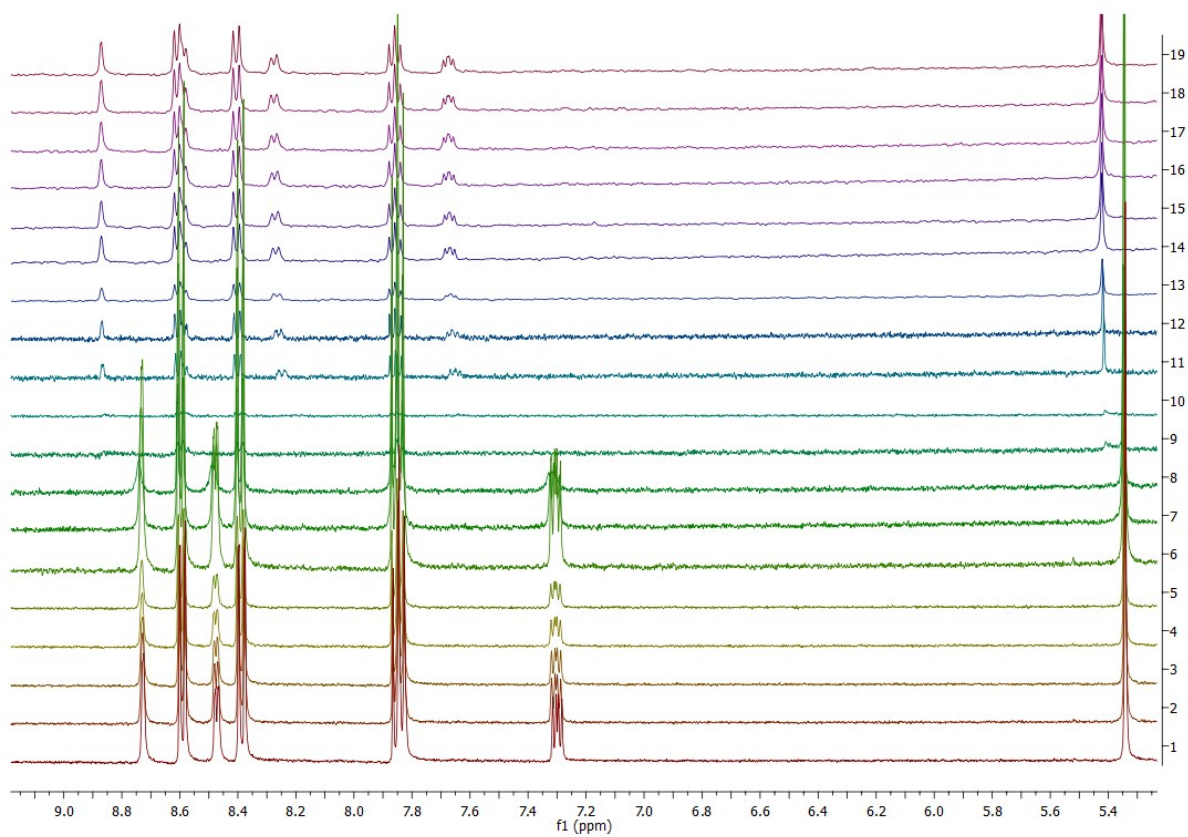
**Figure S33:** X-ray powder diffraction pattern for the cobalt equivalent of complex **7**, complex **7-Co**, compared to the simulated pattern for complex **7**.



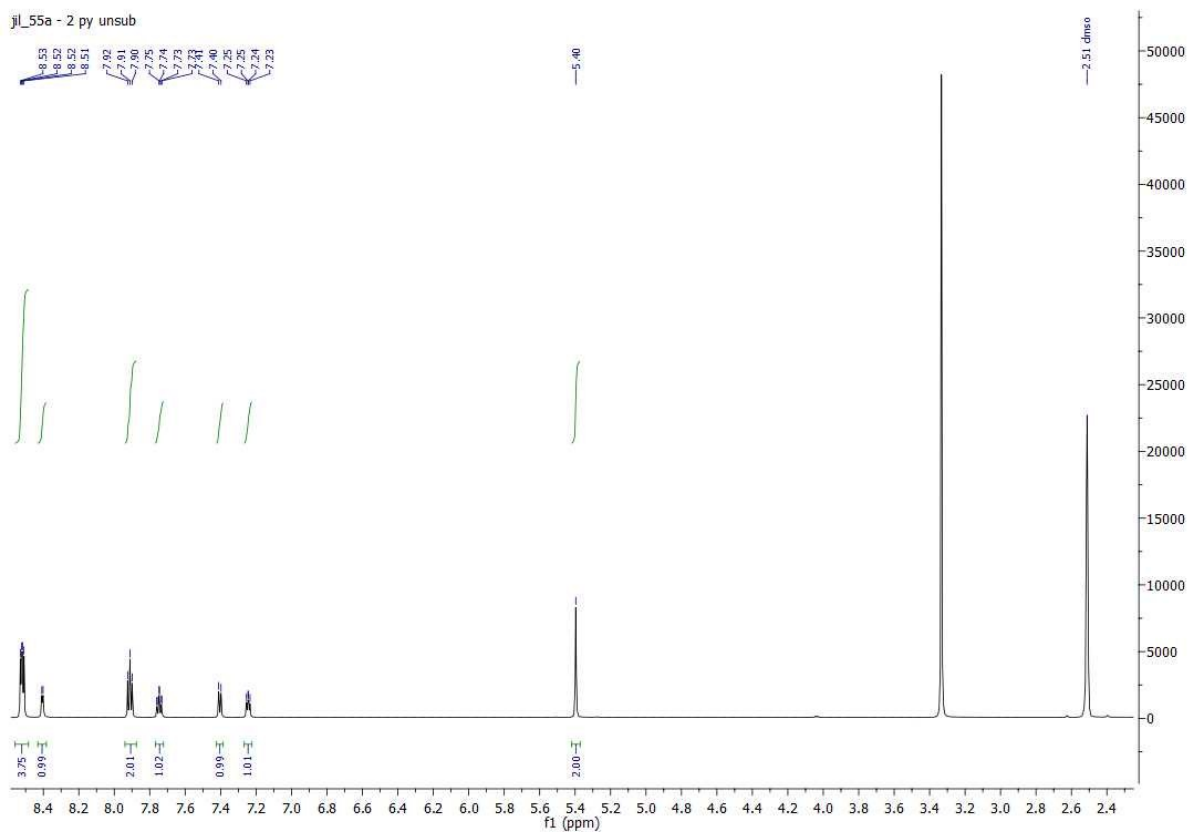
**Figure S34:** Representative UV Vis titration of the addition of  $\text{CoCl}_2$  to N-(2-picolyl)-1,8-naphthalimide **L1** in acetonitrile. Each addition represents 0.1 equivalents of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ .



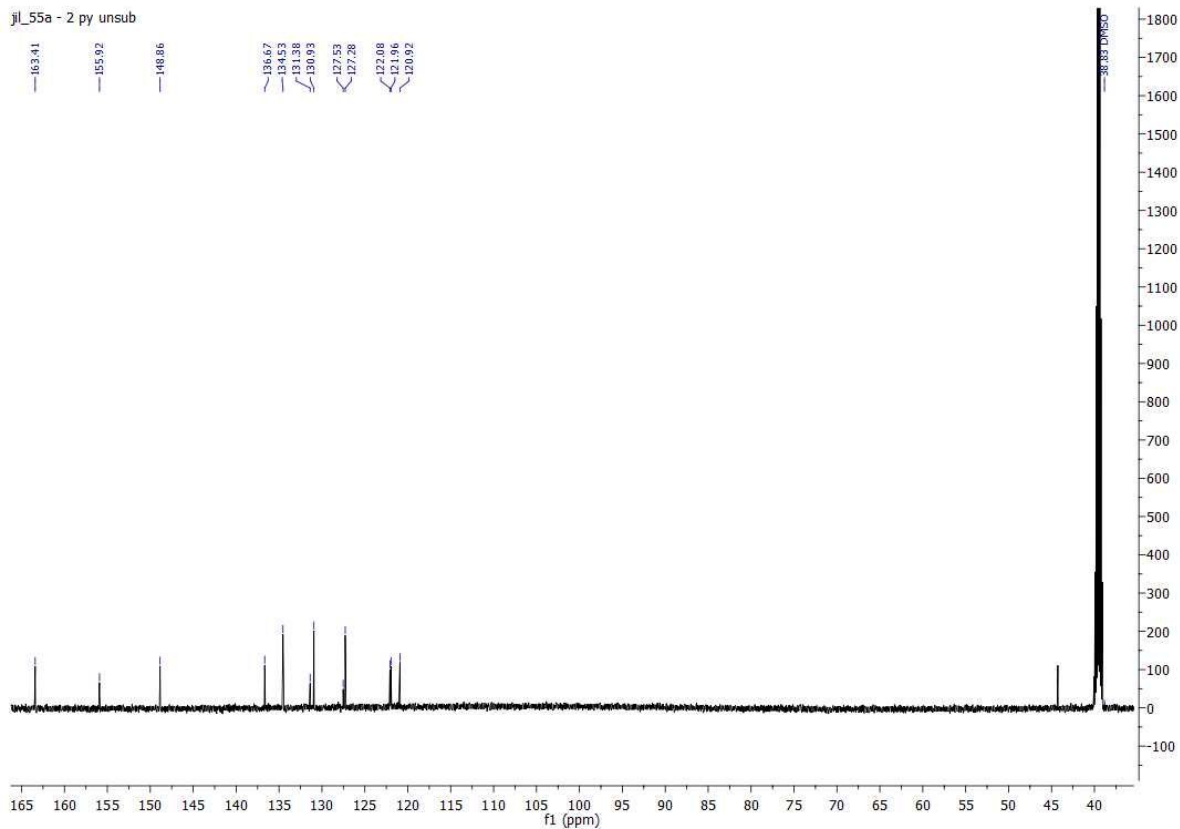
**Figure S35:** UV absorption spectra of **L1-L4** at  $1.5 \times 10^{-5} \text{ M}$  concentration (MeCN)



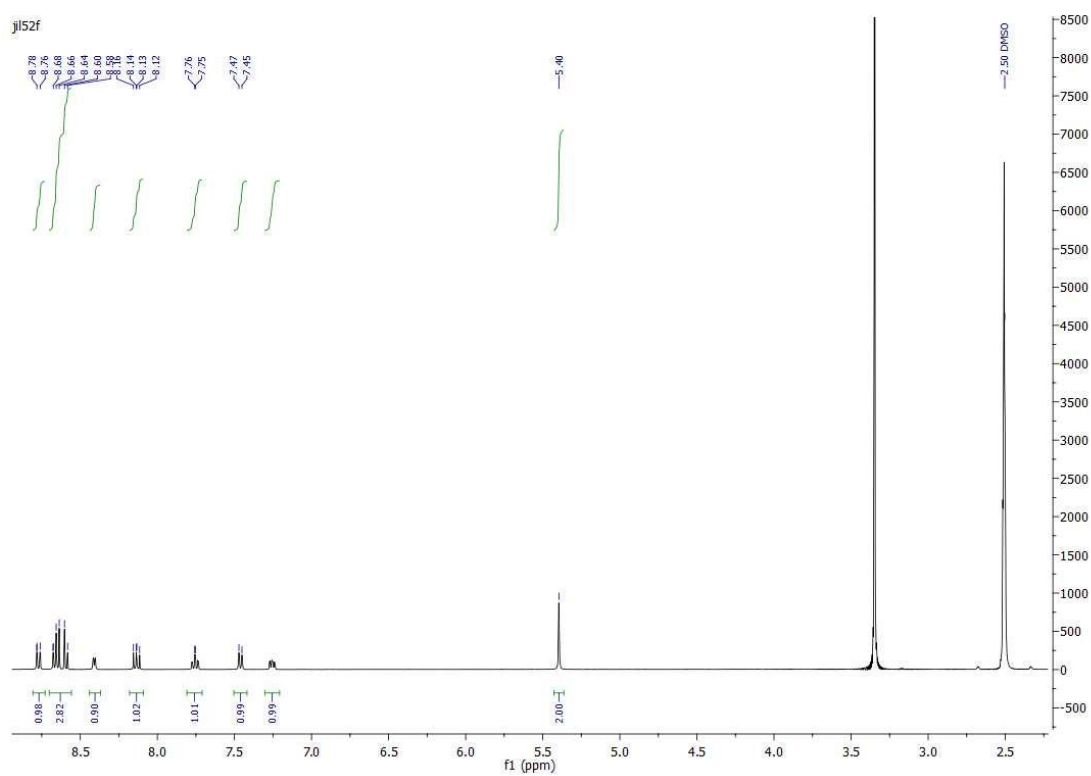
**Figure S36:** <sup>1</sup>H NMR titration of ZnCl<sub>2</sub> addition to **L4**



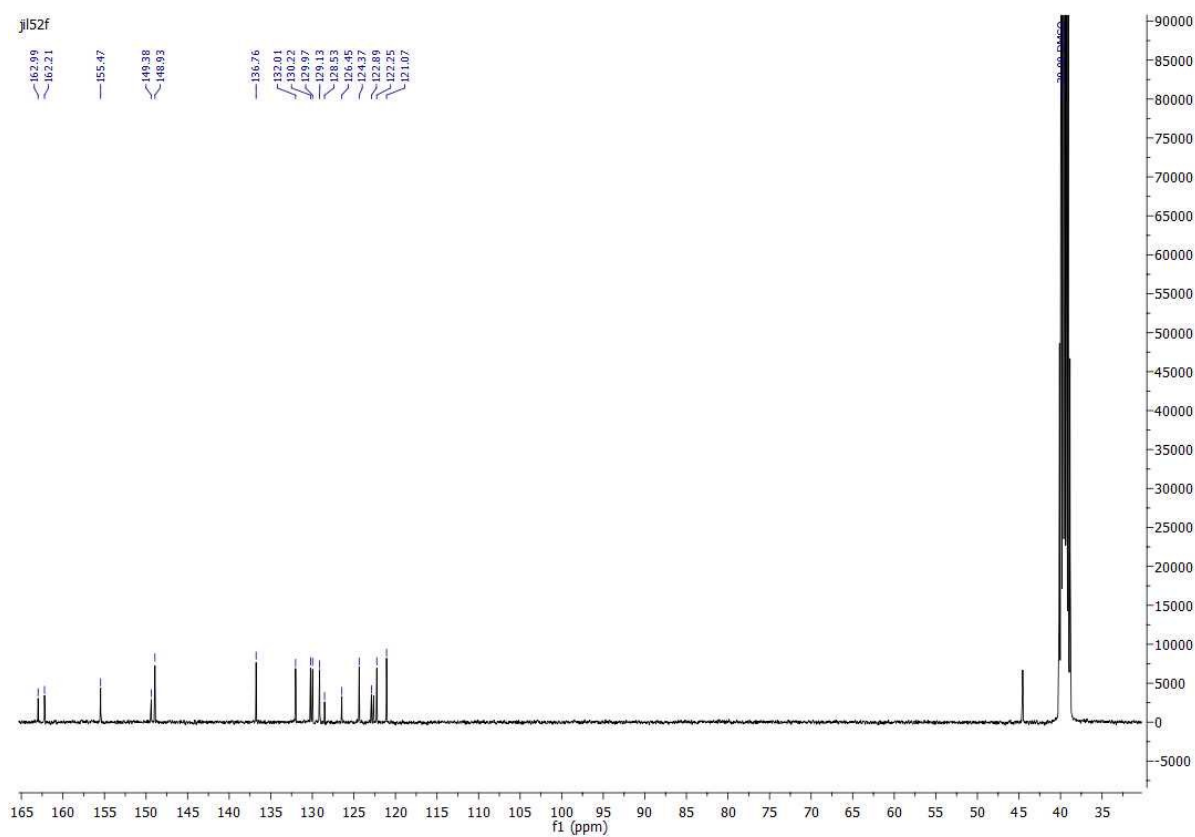
**Figure S37:**  $^1\text{H}$  NMR Spectra for L1



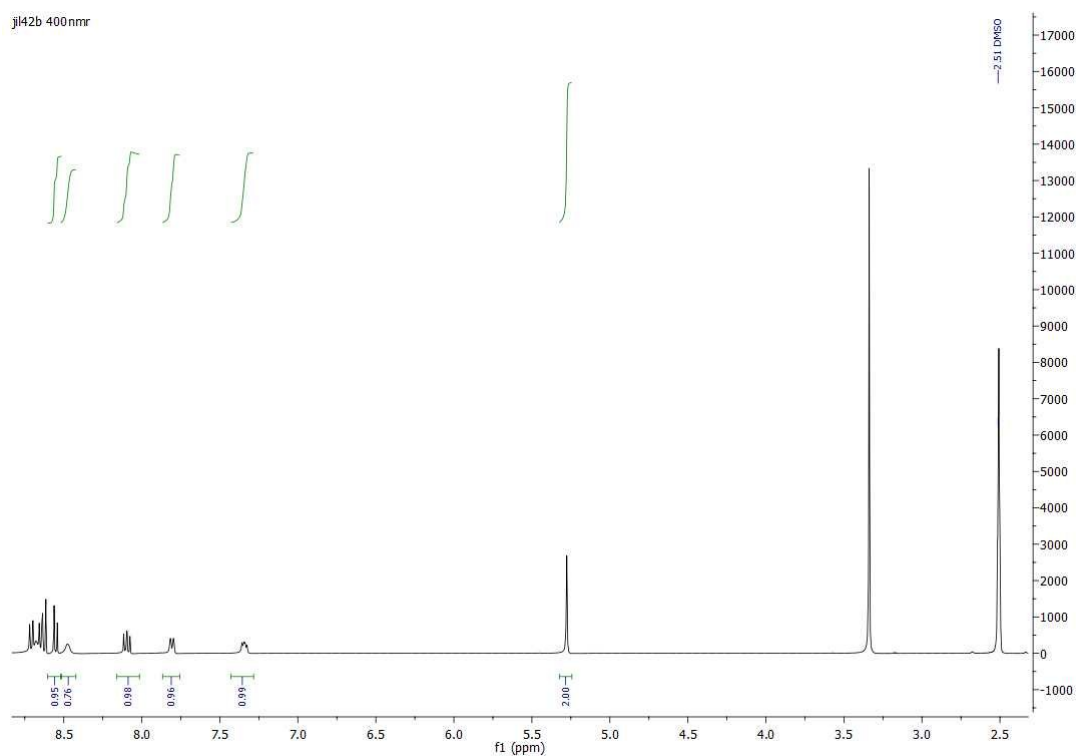
**Figure S38:**  $^{13}\text{C}$  NMR spectra for L1



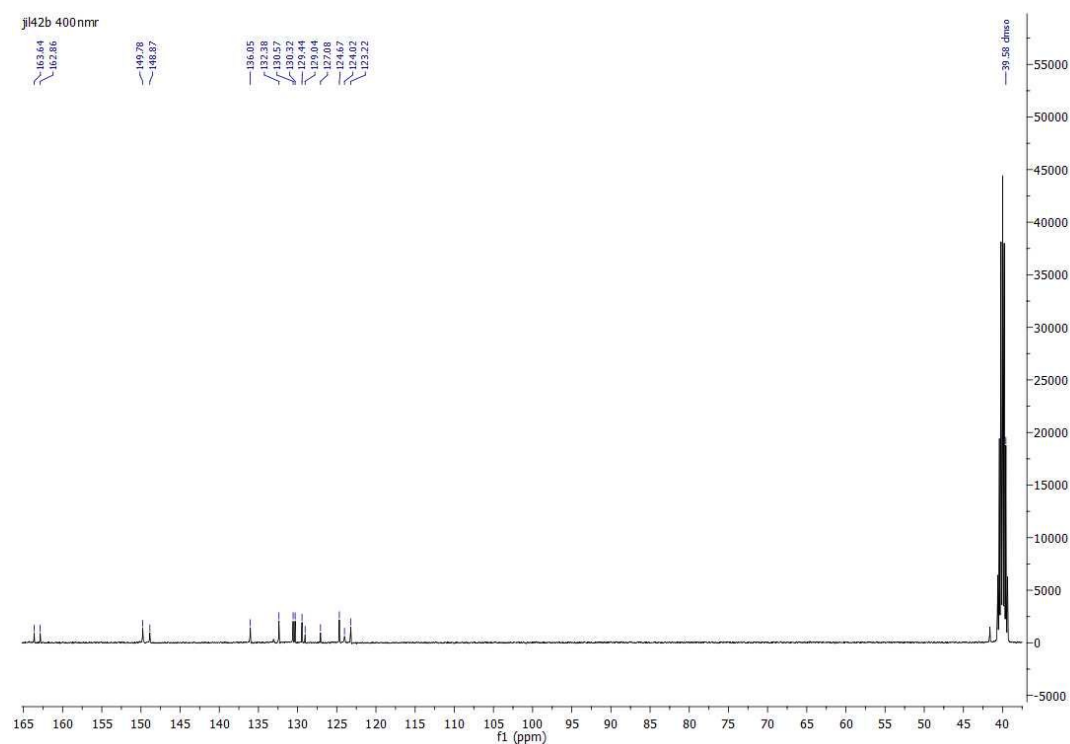
**Figure S39:** <sup>1</sup>H NMR Spectra for **L2**



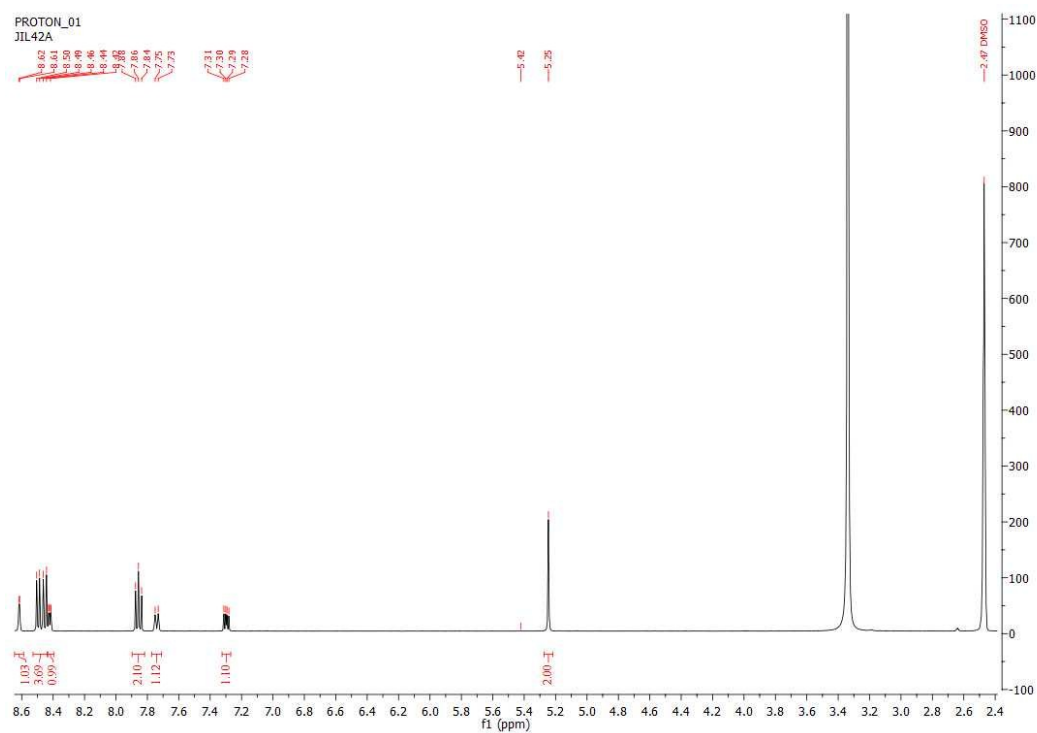
**Figure S40:** <sup>13</sup>C NMR Spectra for **L2**



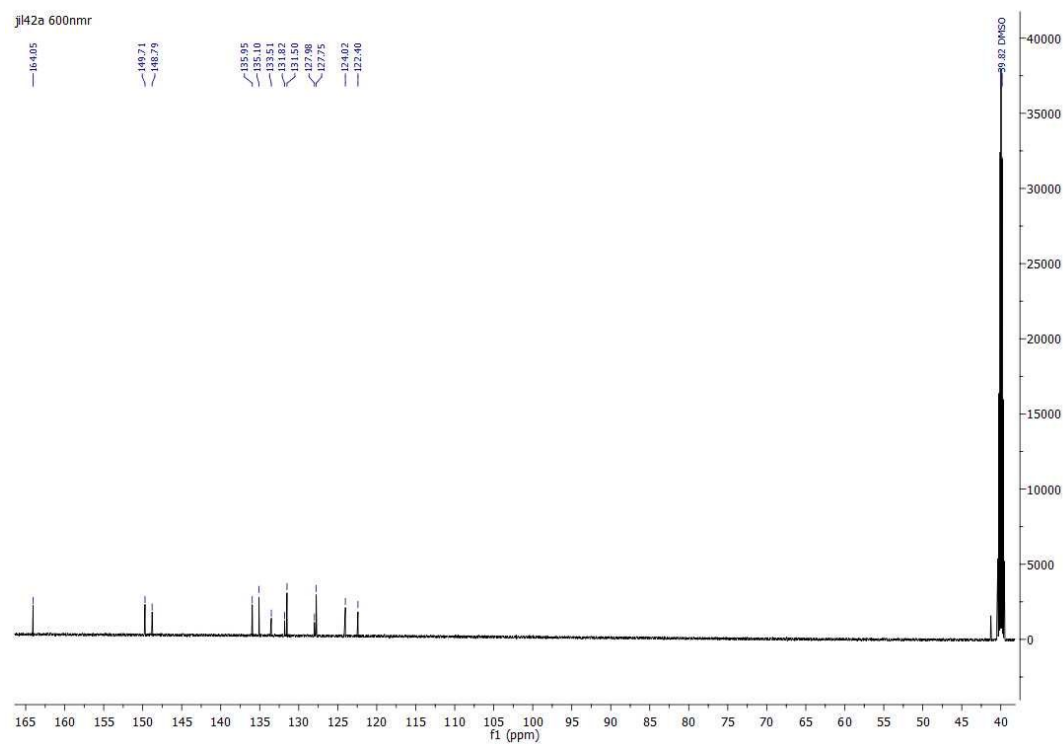
**Figure S41:**  $^1\text{H}$  NMR Spectra for L3



**Figure S42:**  $^{13}\text{C}$  NMR Spectra for L3

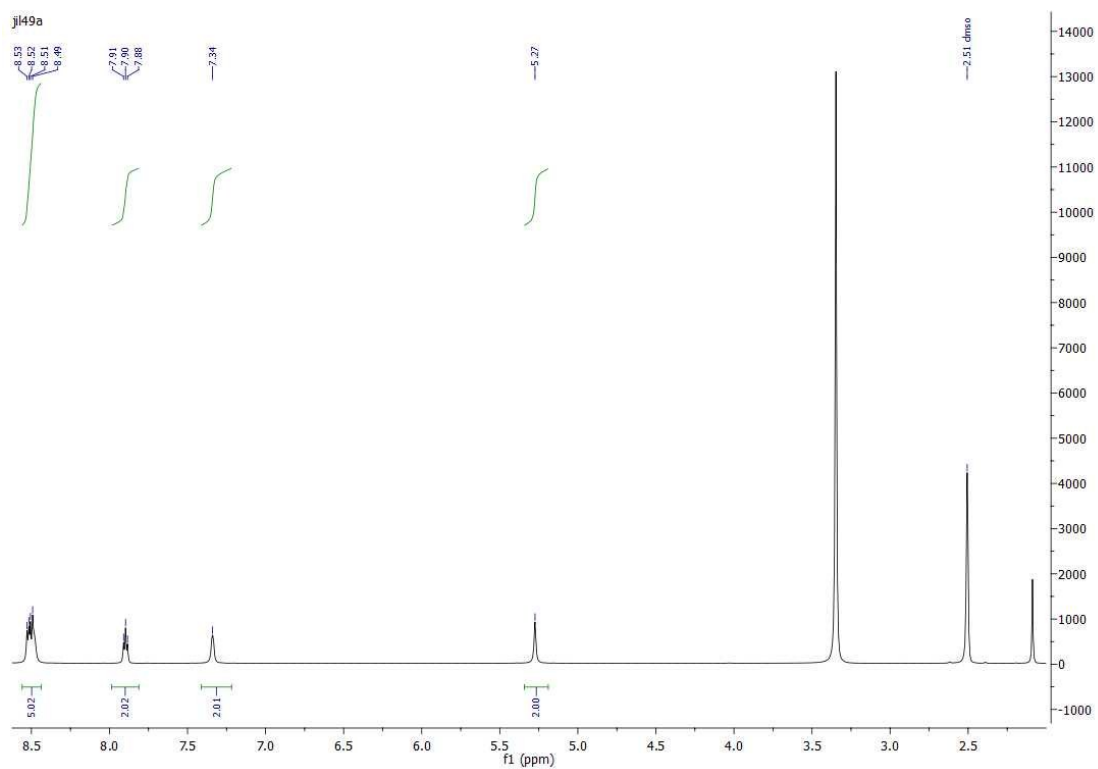


**Figure S43:**  $^1\text{H}$  NMR Spectra for L4

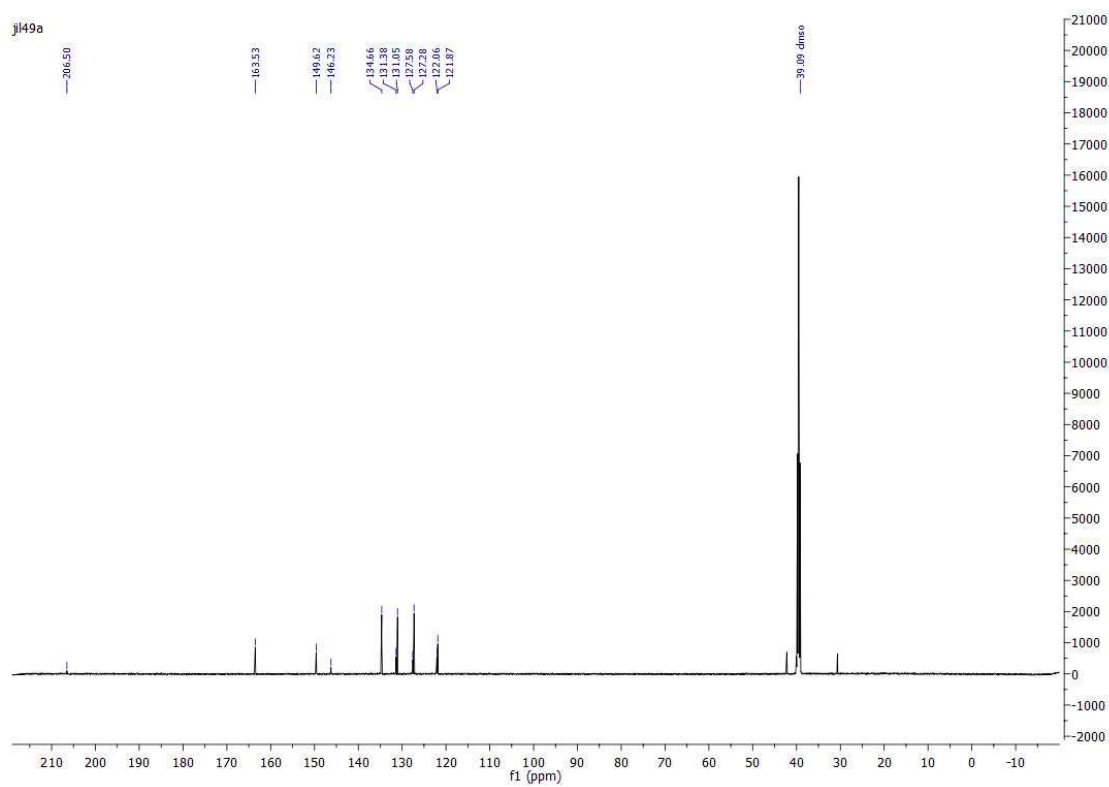


**Figure S44:**  $^{13}\text{C}$  NMR Spectra for L4

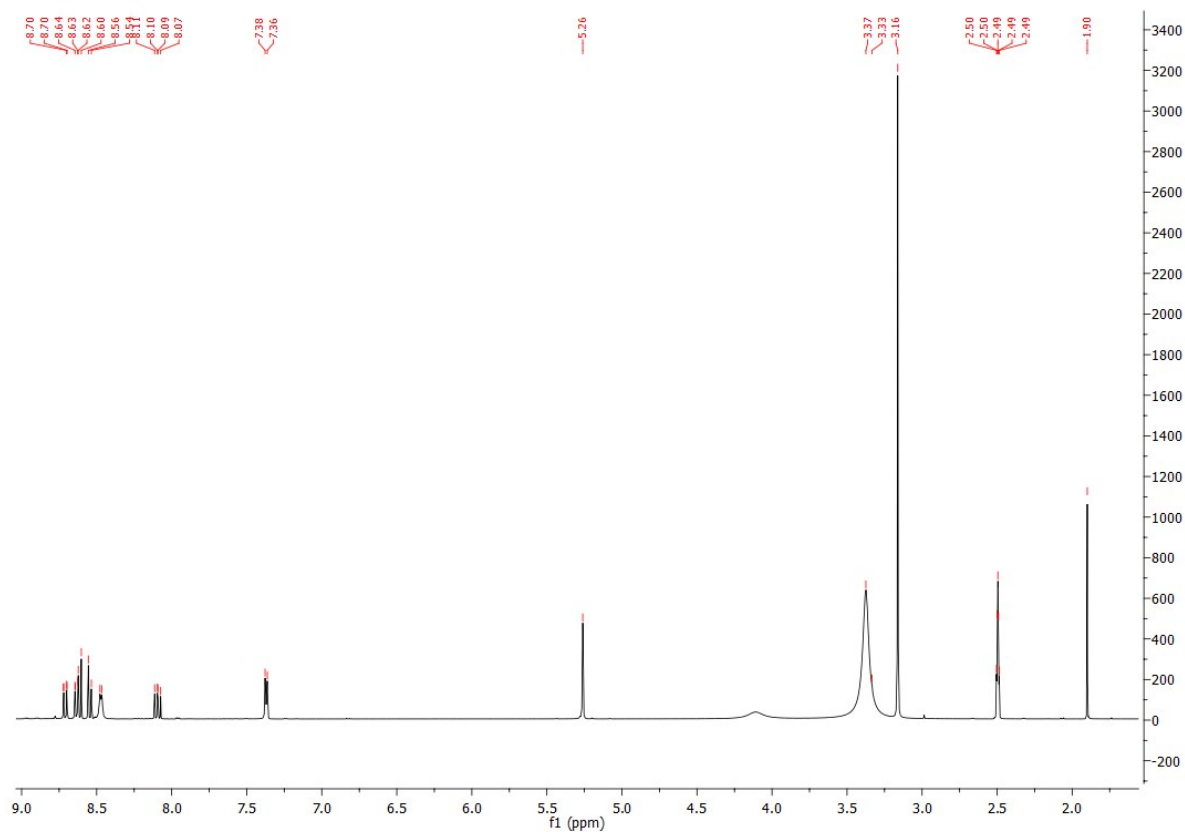




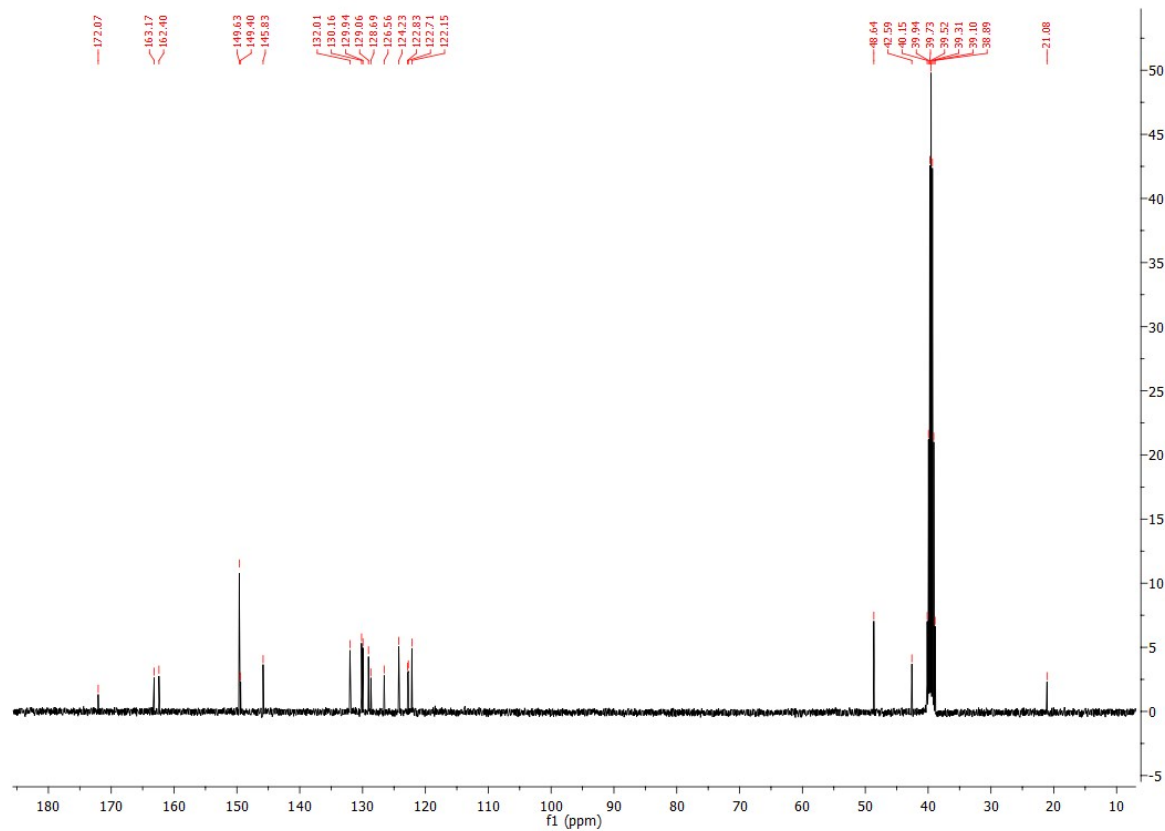
**Figure S45:  $^1\text{H}$  NMR Spectra for L5**



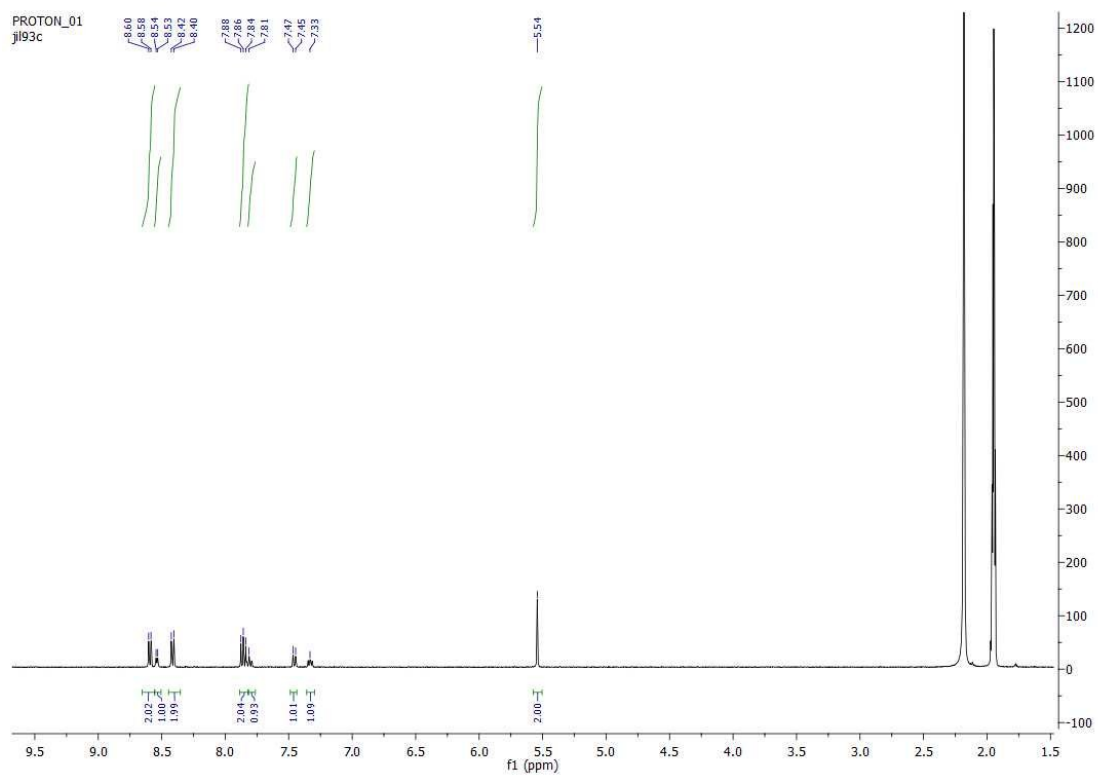
**Figure S46:  $^{13}\text{C}$  NMR Spectra for L5**



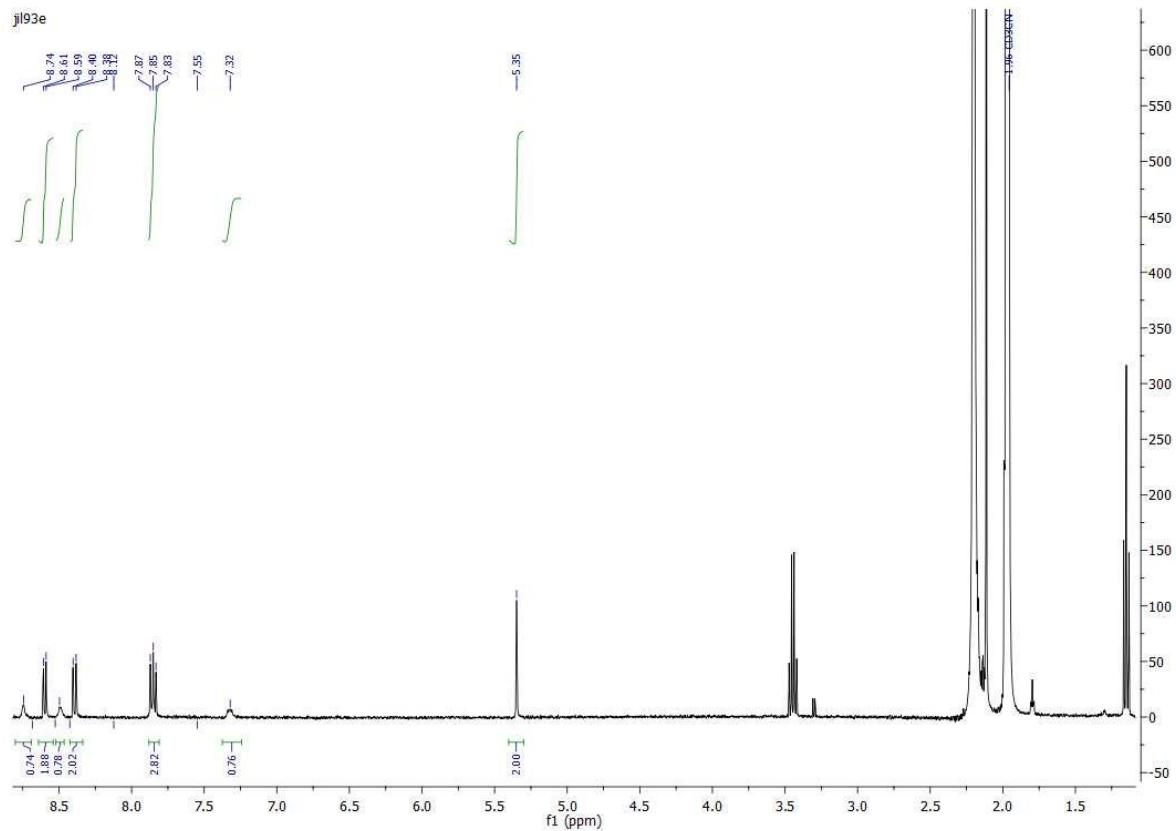
**Figure S47:** <sup>1</sup>H NMR Spectra for L6



**Figure S48:** <sup>13</sup>C NMR Spectra for L6



**Figure S49:**  $^1\text{H}$  NMR of complex **5**



**Figure S50:**  $^1\text{H}$  NMR of complex **7**

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- S4     G. M. Sheldrick *Acta Crystallogr. Sect. C*, 2015, **71**, 3-8.
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