Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Columnar self-assembly of luminescent bent-shaped hexacatenars with a central pyridine core connected with substituted 1,3,4-oxadiazole and thiadiazoles

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Supporting information

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1. Materials and methods

All commercially obtained chemicals were used as received. As required the solvents were dried as per the standard protocols. Silica gel or neutral alumina used as stationery phase for column chromatography. Aluminium sheets coated with silica gel were used for thin layer chromatography (TLC) to monitor the reactions and column purifications.Infrared spectra were measured on a Perkin Elmer IR spectrometer at room temperature by preparing the KBr pellet. ^{1}H and ^{13}C NMR spectra were recorded using Varian Mercury 400 MHz (at 298K) or Bruker 600 MHz NMR spectrometer. Mass spectrometry was carried out using MALDI-TOF mass spectrometer or High Resolution Mass Spectrometer. Polarizing optical microscope (POM) (Nikon Eclipse LV100POL) in conjunction with a controllable hot stage (Mettler Toledo FP90) was used for the characterization of mesogens. The phase transitions, associated enthalpy changes were obtained by differential scanning calorimeter (DSC) (Mettler Toledo DSC1). X-ray diffraction (XRD) studies were carried out using image plate and a detector. This setup had Cu Kα (λ =0.15418 nm) radiation from a source (GeniX3D, Xenocs) operating at 50 kV and 0.6 mA in conjunction with a multilayer mirror was used to irradiate the sample. Glass capillaries containing the sample were used for the measurements. Perkin-Elmer Lambda 750, UV/VIS/NIR spectrometer was used to obtain UV-Vis spectra, while Fluoromax-4 fluorescence spectrophotometer and Perkin Elmer LS 50B spectrometer were used to obtain emission spectra in solution state and solid thin film state respectively. Cyclic Voltammetry (CV) studies were carried out using a Versa Stat 3 (Princeton Applied Research) instrument. Atomic Force microscopy (AFM) images were obtained for the spin-coated films using Agilent 5500-STM instrument. SEM images were obtained on a JEOL 7600F FESEM instrument. Rheological data is obtained using Rheometer MCR-302 Anton Paar.

Gelation and photophysical studies[3]

The process of gelation involves generally three steps. The first step was mixing of the substrate with solvent in sealed glass vial at room temperature. The second step was to get a clear solution by heating it until the solid was dissolved completely. The last step was cooling the vial slowly to ambient temperature. The cooling step includes the gelation process. Then, the formation of the gel was confirmed by “stable to inversion of the glass vial” method. After the glass vial was inversed to observe the state, if the flow test was negative then it confirms the formation of stable

gel. Thermal stability or T_{gel} measurement was done by using dropping ball method. The gel thermal stability was measured by dropping ball method. A metallic ball was placed on the gel of a known concentration in a vial. This was gradually heated and noted the temperature, when the ball reaches the bottom of the vial due to the dissolution (gel-sol conversion). We could not do the UV-Vis spectroscopy of the gels because of the saturation. However we obtained the excitation spectra. The enhancement in the emission due to aggregation (AIEE) was proven by fluorescence spectroscopy. The solution at its critical gelation concentration or CGC in a quartz cuvette (Concentrations: 0.6 wt% for **1c** and 0.5 wt% for **2c** in decane) was kept inside the fluorimeter and fluorescence was taken by exciting at their solution absorption maxima at regular intervals as a function of time. Fluorescence intensity increases steadily as the solution becomes viscous and becomes stagnant when the gelation completes. This can also be done by keeping the gel in fluorimeter and gradual heating (as a function of temperature, controlled by a temperature controller attached to th espectrometer), which shows the reduction in emission intensity on becoming solution. This intensity is several folds higher than the solution state fluorescence. Visually, this change is apparent on irradiating the solution at these time intervals with long-wavelength UV light (λ = 365 nm) and by the 'stable to inversion' test.

Rheological studies

A controlled stress rheometer (Anton Paar, MCR 102) was used to perform dynamic and steady state rheological measurements. A parallel plate (8 mm diameter) with a gap of 25 micrometre between the upper and lower plates was taken as the sample geometry. The sample temperature was maintained by using a built-in Peltier temperature controller (precision 0.02°C). All the rheological experiments were carried out at 25 °C.

2. Experimental Section

Compounds **5a-d**, **4a-d** were prepared as per the reported procedures.[1] Synthesis of compound **2c** is reported earlier.[2] Synthesis of compounds **2a**, **2b**, **2d** and **1a-d** are reported as below.

Procedure for the synthesis of 2,6-bis(5-(4-(hexadecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)pyridine (**1a**):

Pyridine dicarboxyllic acid (0.7 mmol) in 4 ml of thionyl chloride and DMF (2-3 drops) was heated under reflux for 8 h. The excess of thionyl chloride was removed by distillation and

the crude product (pyridine diacid chloride) was dried in vacuo and used for the next reaction without further purification and characterization. The solution of pyridine diacid chloride (0.6 mmol, 1equiv.) in THF was added dropwise to a solution of 4-(hexadecyloxy) benzohydrazide (1.2 mmol, 2.05 equiv.) and triethylamine (1.2 mmol, 2 equiv.) in THF (15 mL). The reaction mixture was stirred at 55 ^{o}C for 12 h. After cooling, THF was removed through distillation and the residue was extracted with EtOAc. The extract was washed with water and brine, dried over Na_2SO_4 and concentrated. The resulting crude product (**3a**) was directly used for next reaction.

The solution of crude product **3a** (1.2 mmol, 1equiv.) in $POCl_3$ (10 mL) was refluxed for 24 h. After the reaction, the crude mixture was added dropwise to ice water. Then, it was extracted with DCM. After removal of solvent *in vacuo*, the crude product was further purified through column chromatography on neutral alumina. Elution with DCM yielded the desired product. Again, the product was recrystallized with DCM- ethanol system (2:1).

R_f = 0.6 (80% DCM-hexanes); white solid, yield: 72%; IR (KBr pellet): ν_{max} in cm^{-1} 3443, 2919, 2849, 1617, 1497, 1430, 1298, 1253, 1180, 835; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.45 (d, 2H, *J* =12Hz, H_{Ar}), 8.20 (d, 4H, *J* =12Hz, H_{Ar}), 8.10 (t, 1H, *J* =12Hz, H_{Ar}), 7.06 (d, 4H, *J* =12Hz, H_{Ar}), 4.05 (t, 4H, 2× OCH_2), 1.81 – 1.85 (m, 4H, 2 × CH_2), 1.47 – 1.48 (m, 4H, 2 × CH_2), 1.26 – 1.45 (m, 48H, 24 × CH_2), 0.87 (t, 6H, 2 × CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 166.25, 163.10, 162.63, 144.62, 138.67, 129.20, 125.04, 115.94, 115.25, 68.58, 32.14, 29.91, 29.80, 29.57, 29.36, 26.23, 22.90, 14.34; MALDI TOF MS: m/z for $C_{53}H_{78}N_5O_4$ [$M+H^+$], calculated: 848.605, Found: 848.987.

Procedure for the synthesis of 2,6-bis(5-(3,4-bis(hexadecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)pyridine (**1b**):

Pyridine dicarboxyllic acid (0.7 mmol) in 4 ml of thionyl chloride and DMF (2-3 drops) was heated under reflux for 8 h. The excess of thionyl chloride was removed by distillation and the crude product (pyridine diacidchloride) was dried in vacuo and used for the next reaction without further purification and characterization. The solution of pyridine diacidchloride (0.6 mmol, 1equiv.) in THF was added dropwise to a solution of solution of 3,4-bis(hexadecyloxy)benzohydrazide (1.2 mmol, 2.05 equiv.) and triethylamine (1.2 mmol, 2 equiv.) in THF (15 mL). The reaction mixture was stirred at 55 ^{o}C for 12 h. After cooling, THF was removed through distillation and the residue was extracted with EtOAc. The extract was

washed with water and brine, dried over Na_2SO_4 and concentrated. The resulting crude product (**3b**) was directly used for next reaction.

The solution of crude product **3b** (1.2 mmol, 1equiv.) in $POCl_3$ (10 mL) was refluxed for 24 h. After the reaction, the crude mixture was dropwise added to ice water. Then, it was extracted with DCM. After removal of solvent *in vacuo*, the crude product was further purified through column chromatography on neutral alumina. Elution with DCM yielded the desired product. Again, the product was recrystallized with DCM- ethanol system (2:1).

R_f = 0.63 (80% DCM-hexanes); white solid, yield: 68%; IR (KBr pellet): ν_{max} in cm^{-1} 3444, 2918, 2850, 1606, 1498, 1465, 1281, 1145, 1034, 821; ^1H NMR ($CDCl_3$, 600 MHz): δ 8.44 (d, 2H, *J* =12Hz, H_{Ar}), 8.11 (s, 1H, H_{Ar}), 7.80 (d, 2H, *J* =12Hz, H_{Ar}), 7.75 (s, 2H, H_{Ar}), 6.99 (d, 2H, *J* =12Hz, H_{Ar}), 4.09 – 4.13 (m, 8H, 4× OCH_2), 1.87 (m, 8H, 4 × CH_2), 1.50 (m, 8H, 4 × CH_2), 1.26 – 1.38 (m, 96H, 48 × CH_2), 0.88 (s, 12H, 4 × CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 166.31, 163.04, 152.91, 149.58, 144.60, 138.69, 125.04, 121.35, 115.99, 112.98, 112.14, 69.67, 69.36, 32.15, 29.94, 29.89, 29.64, 29.59, 29.45, 29.34, 26.27, 22.91, 14.33; MALDI TOF MS: m/z for $C_{85}H_{142}N_5O_6$ [$M+H^+$], calculated: 1329.095, Found: 1329.565.

Procedure for the synthesis of 2,6-bis(5-(3,4,5-tris(hexadecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)pyridine (**1c**):

Pyridine dicarboxyllic acid (0.7 mmol) in 4 ml of thionyl chloride and DMF (2-3 drops) was heated under reflux for 8 h. The excess of thionyl chloride was removed by distillation and the crude product (pyridine diacidchloride) was dried in vacuo and used for the next reaction without further purification and characterization. The solution of pyridine diacidchloride (0.6 mmol, 1equiv.) in THF was added dropwise to a solution of solution of 3,4,5-tris(hexadecyloxy)benzohydrazide (1.2 mmol, 2.05 equiv.) and triethylamine (1.2 mmol, 2 equiv.) in THF (15 mL). The reaction mixture was stirred at 55 ^oC for 12 h. After cooling, THF was removed through distillation and the residue was extracted with EtOAc. The extract was washed with water and brine, dried over Na_2SO_4 and concentrated. The resulting crude product (**3c**) was directly used for next reaction.

The solution of crude product **3c** (1.2 mmol, 1equiv.) in $POCl_3$ (10 mL) was refluxed for 24 h. After the reaction, the crude mixture was dropwise added to ice water. Then, it was extracted

with DCM. After removal of solvent *in vacuo*, the crude product was further purified through column chromatography on neutral alumina. Elution with DCM yielded the desired product. Again, the product was recrystallized with DCM- ethanol system (2:1).

R_f = 0.68 (80% DCM-hexanes); white solid, yield: 65%; IR (KBr pellet): ν_{max} in cm^{-1} 3438, 2961, 2917, 2849, 1640, 1593, 1467, 1123, 837, 720; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.43 (d, 2H, *J* =6Hz, H_{Ar}), 8.13 (t, 1H, H_{Ar}), 7.42 (s, 4H, H_{Ar}), 4.08 (t, 8H, 4× OCH_2), 4.05 (t, 4H, 2× OCH_2) 1.75 – 1.86 (m, 12H, 6 × CH_2), 1.46 – 1.50 (m, 12H, 6 × CH_2), 1.25 – 1.36 (m, 144H, 72 × CH_2), 0.87 (t, 18H, 6 × CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): 170.82, 168.56, 153.86, 149.63, 138.68, 125.12, 122.46, 106.98, 73.92, 69.75, 32.16, 30.59, 29.96, 29.82, 29.67, 29.60, 26.34, 22.91, 14.33; MALDI TOF MS: m/z for $C_{117}H_{206}N_5O_8$ [$M+H^+$], calculated: 1810.59, Found: 1810.197.

Procedure for the synthesis of 2,6-bis(5-(3,4,5-tris(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)pyridine (**1d**):

Pyridine dicarboxyllic acid (0.7 mmol) in 4 ml of thionyl chloride and DMF (2-3 drops) was heated under reflux for 8 h. The excess of thionyl chloride was removed by distillation and the crude product (pyridine diacidchloride) was dried in vacuo and used for the next reaction without further purification and characterization. The solution of pyridine diacidchloride (0.6 mmol, 1equiv.) in THF was added dropwise to a solution of solution of 3,4,5-tris(dodecyloxy)benzohydrazide (1.2 mmol, 2.05 equiv.) and triethylamine (1.2 mmol, 2 equiv.) in THF (15 mL). The reaction mixture was stirred at 55 ^oC for 12 h. After cooling, THF was removed through distillation and the residue was extracted with EtOAc. The extract was washed with water and brine, dried over Na_2SO_4 and concentrated. The resulting crude product (**3d**) was directly used for next reaction.

The solution of crude product **3d** (1.2 mmol, 1equiv.) in $POCl_3$ (10 mL) was refluxed for 24 h. After the reaction, the crude mixture was dropwise added to ice water. Then, it was extracted with DCM. After removal of solvent *in vacuo*, the crude product was further purified through column chromatography on neutral alumina. Elution with DCM yielded the desired product. Again, the product was recrystallized with DCM- ethanol system (2:1).

R_f = 0.66 (80% DCM-hexanes); white solid, yield: 65%; IR (KBr pellet): ν_{max} in cm^{-1} 3445, 2918, 2849, 1589, 1520, 1467, 1420, 1277, 1149, 808; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.43 (d, 2H, *J* =6Hz, H_{Ar}), 8.13 (t, 1H, *J* =6Hz, H_{Ar}), 7.42 (s, 4H, H_{Ar}), 4.08 (t, 8H, *J* =6Hz, 4× OCH_2), 4.05 (t, 4H, *J* =6Hz, 2× OCH_2) 1.76 – 1.85 (m, 8H, 4 × CH_2), 1.46 – 1.50 (m, 4H, 2 × CH_2), 1.35 – 1.36 (m, 12H, 6 × CH_2), 1.25 – 1.33 (m, 96H, 48 × CH_2), 0.87 (t, 18H, *J* =6Hz, 6 × CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 166.36, 163.14, 153.86, 144.56, 142.07, 138.79, 125.21, 118.10, 106.12, 73.87, 69.68, 32.13, 29.95, 29.90, 29.86, 29.80, 29.63, 29.56, 26.32, 26.29, 22.89, 14.31; MALDI TOF MS: m/z for $C_{93}H_{158}N_5O_8$ [M^+], calculated: 1473.2105, Found: 1473.762.

Procedure for the synthesis of 2,6-bis(5-(4-(hexadecyloxy)phenyl)-1,3,4-thiadiazol-2-yl)pyridine (**2a**):

Pyridine dicarboxyllic acid (0.7 mmol) in 4 ml of thionyl chloride and DMF (2-3 drops) was heated under reflux for 8 h. The excess of thionyl chloride was removed by distillation and the crude product (pyridine diacidchloride) was dried in vacuo and used for the next reaction without further purification and characterization. The solution of pyridine diacidchloride (0.6 mmol, 1equiv.) in THF was added dropwise to a solution of solution of 4-(hexadecyloxy) benzohydrazide (1.2 mmol, 2.05 equiv.) and triethylamine (1.2 mmol, 2 equiv.) in THF (15 mL). The reaction mixture was stirred at 55 ^oC for 12 h. After cooling, THF was removed through distillation and the residue was extracted with EtOAc. The extract was washed with water and brine, dried over Na_2SO_4 and concentrated. The resulting crude product (**3a**) was directly used for next reaction.

The solution of crude product **3a** (1.2 mmol, 1equiv.) in dry toluene (8 mL) was added dropwise to a solution of Lawesson's reagent (3 mmol, 2.4 equiv.) in toluene at room temperature under argon atmosphere and refluxed for 24 h. After the reaction, toluene was evaporated under reduced pressure. After removal of solvent *in vacuo*, the crude product was further purified through column chromatography on neutral alumina. Elution with DCM followed by 5-10% EtOAc-hexanes yielded the desired product. Again, the product was recrystallized with DCM-ethanol system (2:1).

R_f = 0.5 (50% DCM-hexanes); white solid, yield: 58%; IR (KBr pellet): ν_{max} in cm^{-1} 3417, 2919, 2849, 1606, 1516, 1432, 1407, 1310, 1256, 836; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.43 (d, 2H, *J* =12Hz, H_{Ar}), 8.02 (t, 1H, *J* =6Hz, H_{Ar}), 8.01 (d, 4H, *J* =6Hz, H_{Ar}), 7.00 (d, 4H, *J* =12Hz, H_{Ar}),

4.03 (t, 4H, 2× OCH_2), 1.79 – 1.86 (m, 4H, 2 × CH_2), 1.44 – 1.48 (m, 4H, 2 × CH_2), 1.26 – 1.34 (m, 48H, 24 × CH_2), 0.88 (t, 6H, 2 × CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.50, 168.19, 162.00, 149.53, 138.60, 129.80, 122.73, 122.12, 115.26, 68.51, 32.51, 29.93, 29.91, 29.88, 29.82, 29.79, 29.61, 29.59, 29.36, 26.22, 22.92, 14.36; MALDI TOF MS: m/z for $C_{53}H_{78}N_5O_2S_2$ [$M+H^+$], calculated: 880.560, Found: 880.941.

Procedure for the synthesis of 2,6-bis(5-(3,4-bis(hexadecyloxy)phenyl)-1,3,4-thiadiazol-2-yl)pyridine (**2b**):

Pyridine dicarboxyllic acid (0.7 mmol) in 4 ml of thionyl chloride and DMF (2-3 drops) was heated under reflux for 8 h. The excess of thionyl chloride was removed by distillation and the crude product (pyridine diacidchloride) was dried in vacuo and used for the next reaction without further purification and characterization. The solution of pyridine diacidchloride (0.6 mmol, 1equiv.) in THF was added dropwise to a solution of solution of 3,4-bis(hexadecyloxy)benzohydrazide (1.2 mmol, 2.05 equiv.) and triethylamine (1.2 mmol, 2 equiv.) in THF (15 mL). The reaction mixture was stirred at 55 ^oC for 12 h. After cooling, THF was removed through distillation and the residue was extracted with EtOAc. The extract was washed with water and brine, dried over Na_2SO_4 and concentrated. The resulting crude product (**3b**) was directly used for next reaction.

The solution of crude product **3b** (1.2 mmol, 1equiv.) in dry toluene (8 mL) was added dropwise to a solution of Lawesson's reagent (3 mmol, 2.4 equiv.) in toluene at room temperature under argon atmosphere and refluxed for 24 h. After the reaction, toluene was evaporated under reduced pressure. After removal of solvent *in vacuo*, the crude product was further purified through column chromatography on neutral alumina. Elution with DCM followed by 5-10% EtOAc-hexanes yielded the desired product. Again, the product was recrystallized with DCM-ethanol system (2:1).

R_f = 0.55 (50% DCM-hexanes); white solid, yield: 55%; IR (KBr pellet): ν_{max} in cm^{-1} 3417, 2918, 2848, 1637, 1520, 1420, 1387, 1277, 1149, 808; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.45 (d, 2H, J =12Hz, H_{Ar}), 8.03 (s, 1H, H_{Ar}), 7.71 (d, 2H, J =12Hz, H_{Ar}), 7.54 (d, 2H, J =12Hz, H_{Ar}), 6.95 (d, 2H, J =12Hz, H_{Ar}), 4.13 (t, 4H, 2× OCH_2), 4.08 (t, 4H, 2× OCH_2), 1.85 – 1.90 (m, 8H, 4 × CH_2), 1.51 (m, 8H, 4 × CH_2), 1.25 – 1.49 (m, 96H, 48 × CH_2), 0.87 (t, 12H, 4 × CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.69, 168.20, 152.31, 149.67, 149.62, 138.62, 123.03, 122.21,

122.08, 113.31, 112.46, 69.65, 69.43, 32.11, 29.90, 29.85, 29.60, 29.55, 29.42, 29.33, 26.23, 26.20, 22.87, 14.29; MALDI TOF MS: m/z for $C_{85}H_{142}N_5O_4S_2$ [M+H$^+$], calculated: 1361.050, Found: 1361.844.

Procedure for the synthesis of 2,6-bis(5-(3,4,5-tris(hexadecyloxy)phenyl)-1,3,4-thiadiazol-2-yl)pyridine (**2c**):

Pyridine dicarboxyllic acid (0.7 mmol) in 4 ml of thionyl chloride and DMF (2-3 drops) was heated under reflux for 8 h. The excess of thionyl chloride was removed by distillation and the crude product (pyridine diacidchloride) was dried in vacuo and used for the next reaction without further purification and characterization. The solution of pyridine diacidchloride (0.6 mmol, 1equiv.) in THF was added dropwise to a solution of solution of 3,4,5-tris(hexadecyloxy)benzohydrazide (1.2 mmol, 2.05 equiv.) and triethylamine (1.2 mmol, 2 equiv.) in THF (15 mL). The reaction mixture was stirred at 55 ^{o}C for 12 h. After cooling, THF was removed through distillation and the residue was extracted with EtOAc. The extract was washed with water and brine, dried over Na_2SO_4 and concentrated. The resulting crude product (**3c**) was directly used for next reaction.

The solution of crude product **3c** (1.2 mmol, 1equiv.) in dry toluene (8 mL) was added dropwise to a solution of Lawesson's reagent (3 mmol, 2.4 equiv.) in toluene at room temperature under argon atmosphere and refluxed for 24 h. After the reaction, toluene was evaporated under reduced pressure. After removal of solvent *in vacuo*, the crude product was further purified through column chromatography on neutral alumina. Elution with DCM followed by 5-10% EtOAc-hexanes yielded the desired product. Again, the product was recrystallized with DCM-ethanol system (2:1).

R_f = 0.58 (50% DCM-hexanes); white solid, yield: 55%; IR (KBr pellet): ν_{max} in cm^{-1} 3438, 2950, 2917, 2849, 1585, 1432, 1331, 1124, 813, 773; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.46 (d, 2H, *J* =12Hz, H_{Ar}), 8.04 (t, 1H, H_{Ar}), 7.28 (s, 4H, H_{Ar}), 4.10 (t, 8H, 4× OCH_2), 4.05 (t, 4H, 2× OCH_2), 1.75 – 1.88 (m, 12H, 6 × CH_2), 1.35 – 1.53 (m, 12H, 6 × CH_2), 1.25 – 1.29 (m, 144H, 72 × CH_2), 0.87 (m, 18H, 6 × CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): 169.11, 166.76, 153.83, 141.37, 131.55, 130.29, 130.12, 127.27, 124.93, 106.80, 73.89, 69.65, 32.15, 30.56, 29.94, 29.88, 29.81, 29.64, 29.59, 26.32, 22.91, 14.32; MALDI TOF MS: m/z for $C_{117}H_{206}N_5O_6S_2$ [M+H$^+$], calculated: 1841.5404, Found: 1841.835.

Procedure for the synthesis of 2,6-bis(5-(3,4,5-tris(dodecyloxy)phenyl)-1,3,4-thiadiazol-2-yl)pyridine (**2d**):

Pyridine dicarboxyllic acid (0.7 mmol) in 4 ml of thionyl chloride and DMF (2-3 drops) was heated under reflux for 8 h. The excess of thionyl chloride was removed by distillation and the crude product (pyridine diacidchloride) was dried in vacuo and used for the next reaction without further purification and characterization. The solution of pyridine diacidchloride (0.6 mmol, 1equiv.) in THF was added dropwise to a solution of solution of 3,4,5-tris(dodecyloxy)benzohydrazide (1.2 mmol, 2.05 equiv.) and triethylamine (1.2 mmol, 2 equiv.) in THF (15 mL). The reaction mixture was stirred at 55 ^{o}C for 12 h. After cooling, THF was removed through distillation and the residue was extracted with EtOAc. The extract was washed with water and brine, dried over Na_2SO_4 and concentrated. The resulting crude product (**3d**) was directly used for next reaction.

The solution of crude product **3d** (1.2 mmol, 1equiv.) in dry toluene (8 mL) was added dropwise to a solution of Lawesson's reagent (3 mmol, 2.4 equiv.) in toluene at room temperature under argon atmosphere and refluxed for 24 h. After the reaction, toluene was evaporated under reduced pressure. After removal of solvent *in vacuo*, the crude product was further purified through column chromatography on neutral alumina. Elution with DCM followed by 5-10% EtOAc-hexanes yielded the desired product. Again, the product was recrystallized with DCM-ethanol system (2:1).

R_f = 0.58 (50% DCM-hexanes); white solid, yield: 60%; IR (KBr pellet): ν_{max} in cm^{-1} 3444, 2919, 2849, 1606, 1516, 1432, 1407, 1310, 1256, 1024; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.46 (d, 2H, *J* =12Hz, H_{Ar}), 8.04 (t, 1H, *J* =12Hz, H_{Ar}), 7.29 (s, 4H, H_{Ar}), 4.10 (t, 8H, *J* =6Hz, 4× OCH_2), 4.05 (t, 4H, *J* =6Hz, 2× OCH_2) 1.86 – 1.87 (m, 8H, 4 × CH_2), 1.78 – 1.85 (m, 4H, 2 × CH_2), 1.36 – 1.52 (m, 12H, 6 × CH_2), 1.27 – 1.31 (m, 96H, 48 × CH_2), 0.88 (t, 18H, *J* =6Hz, 6 × CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.78, 168.54, 153.82, 149.56, 141.45, 138.64, 125.08, 122.42, 106.86, 73.87, 69.67, 32.13, 30.56, 29.88, 29.58, 26.31, 22.89, 14.31; MALDI TOF MS: m/z for $C_{93}H_{158}N_5O_6S_2$ [M+H$^+$], calculated: 1505.165, Found: 1505.834.

3. NMR Spectra

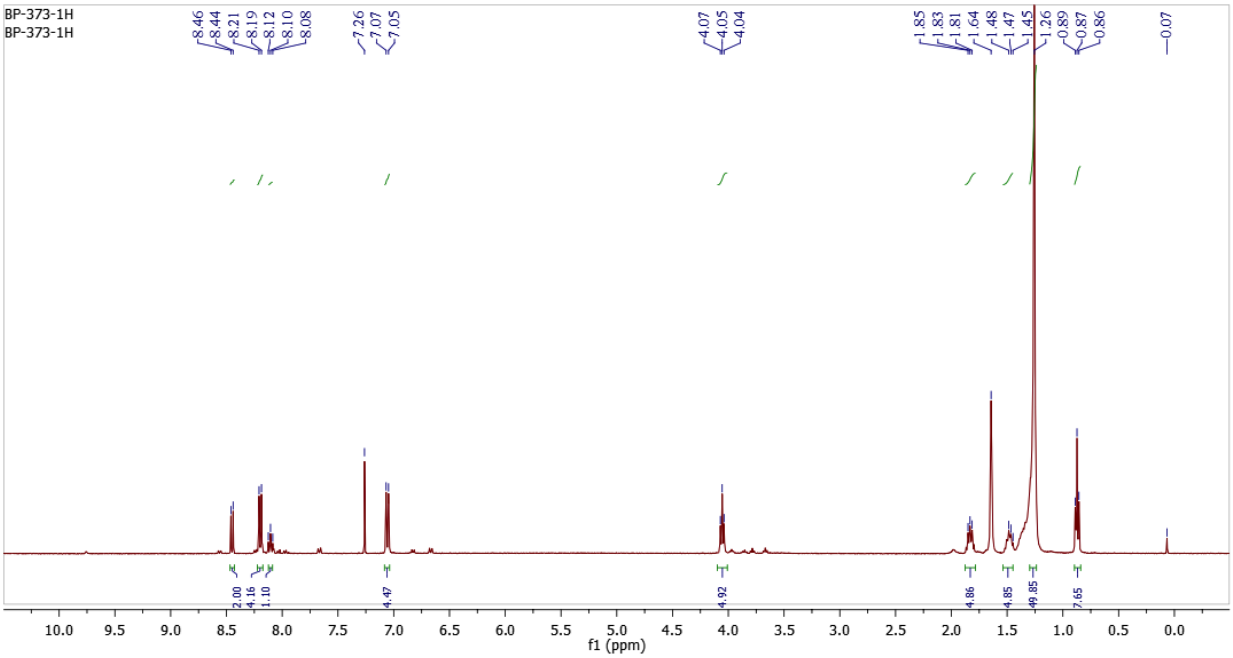

Figure S1. ^{1}H NMR (600 MHz) spectra of **1a** in $CDCl_3$

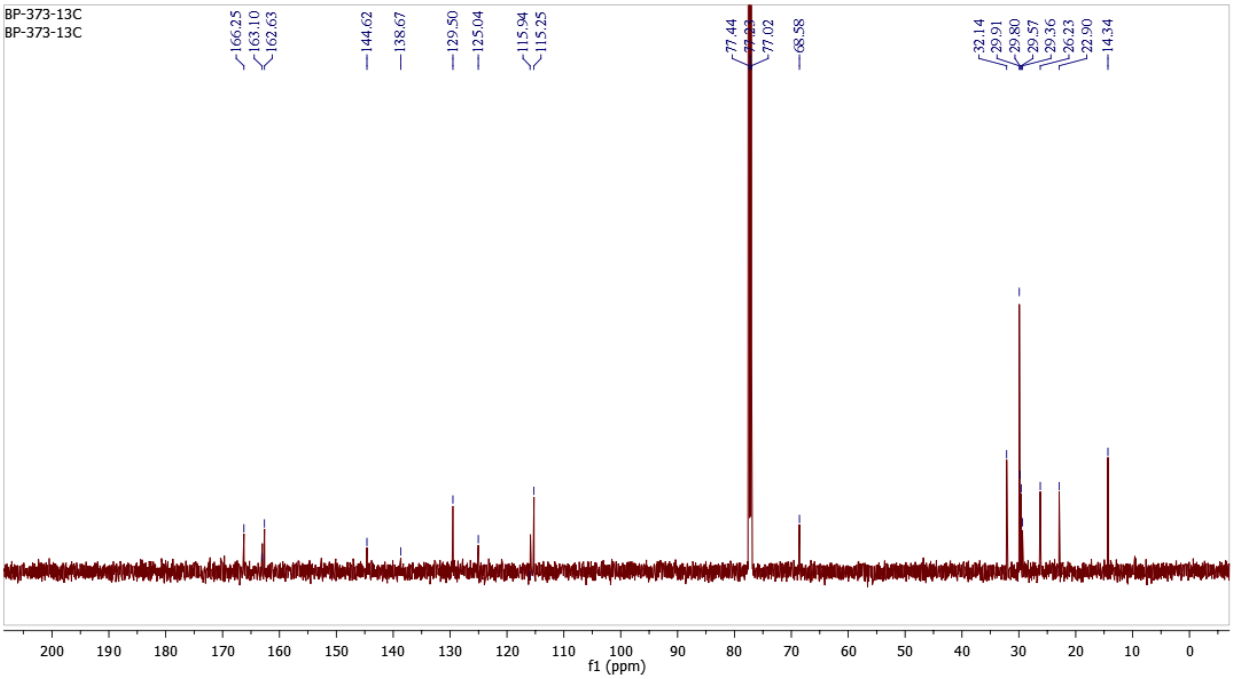

Figure S2. ^{13}C NMR (150 MHz) spectra of **1a** in $CDCl_3$

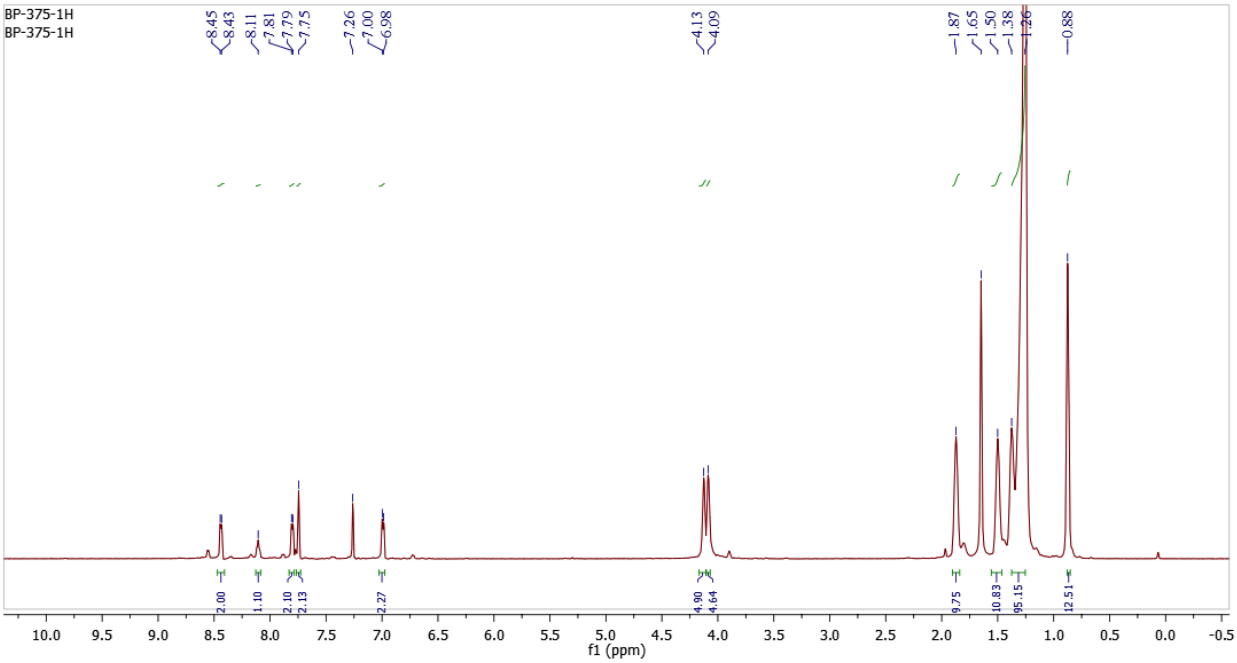

Figure S3. ^{1}H NMR (600 MHz) spectra of **1b** in $CDCl_3$

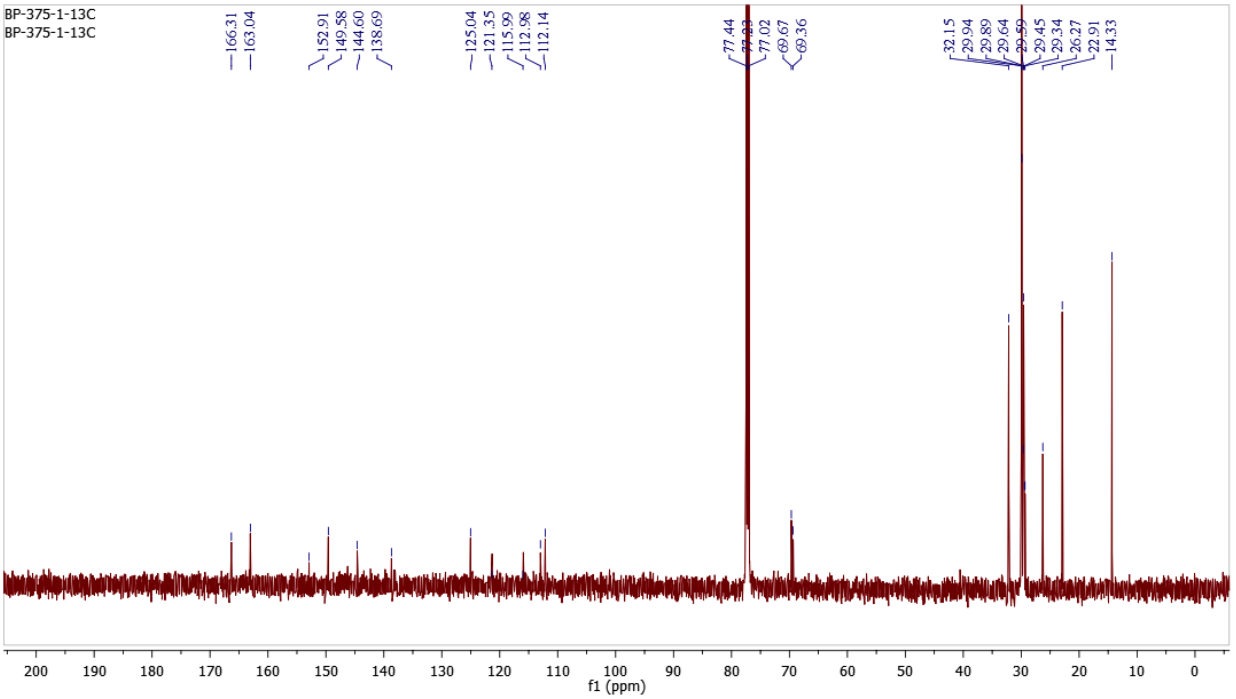

Figure S4. ^{13}C NMR (150 MHz) spectra of **1b** in $CDCl_3$

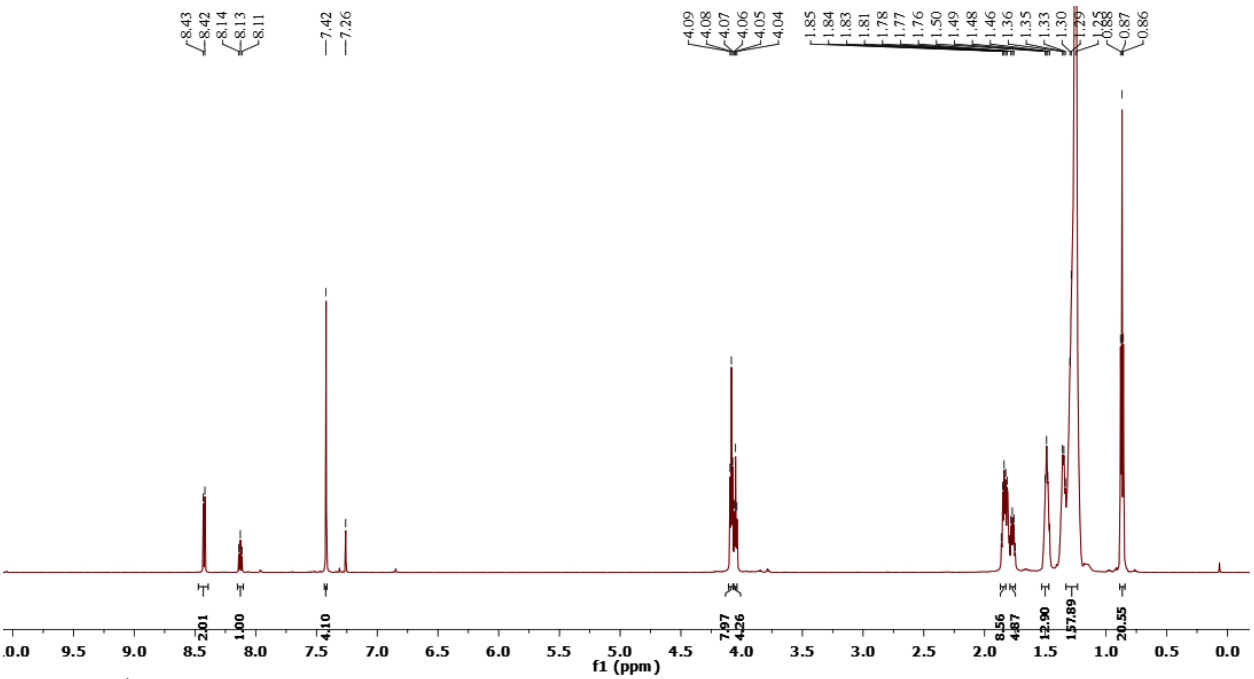

Figure S5. ^{1}H NMR (600 MHz) spectra of **1c** in $CDCl_3$

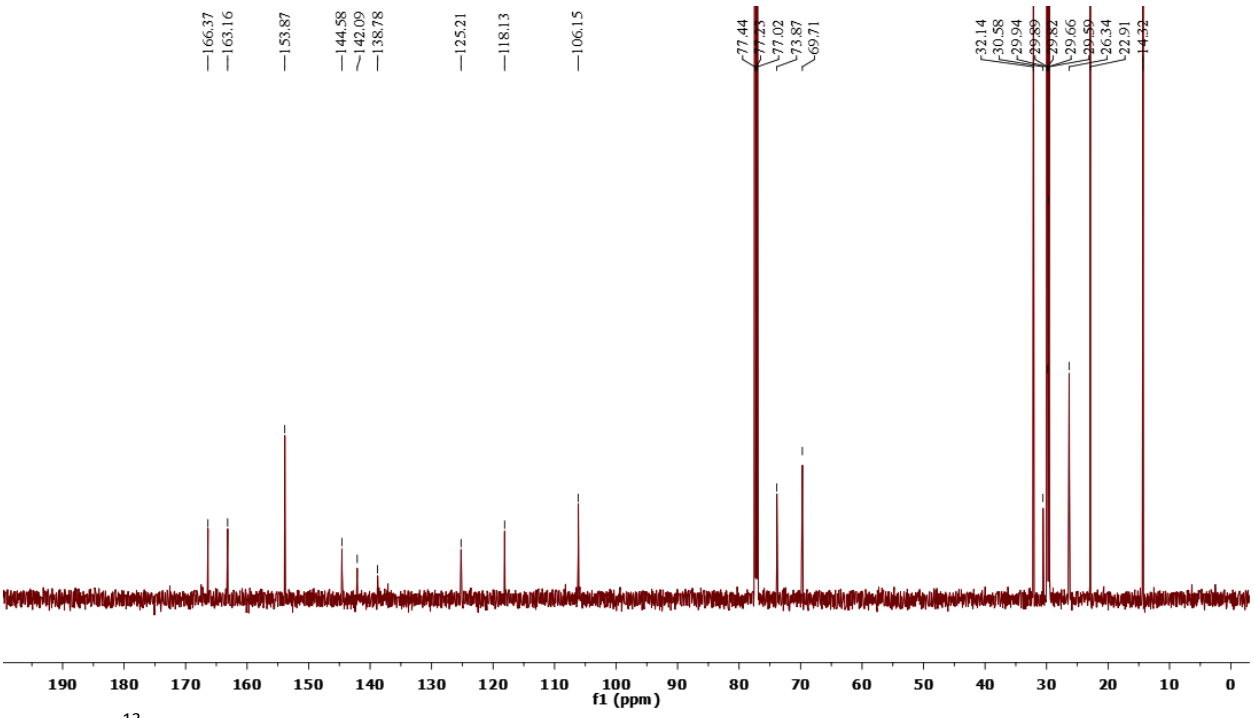

Figure S6. ^{13}C NMR (150 MHz) spectra of **1c** in $CDCl_3$

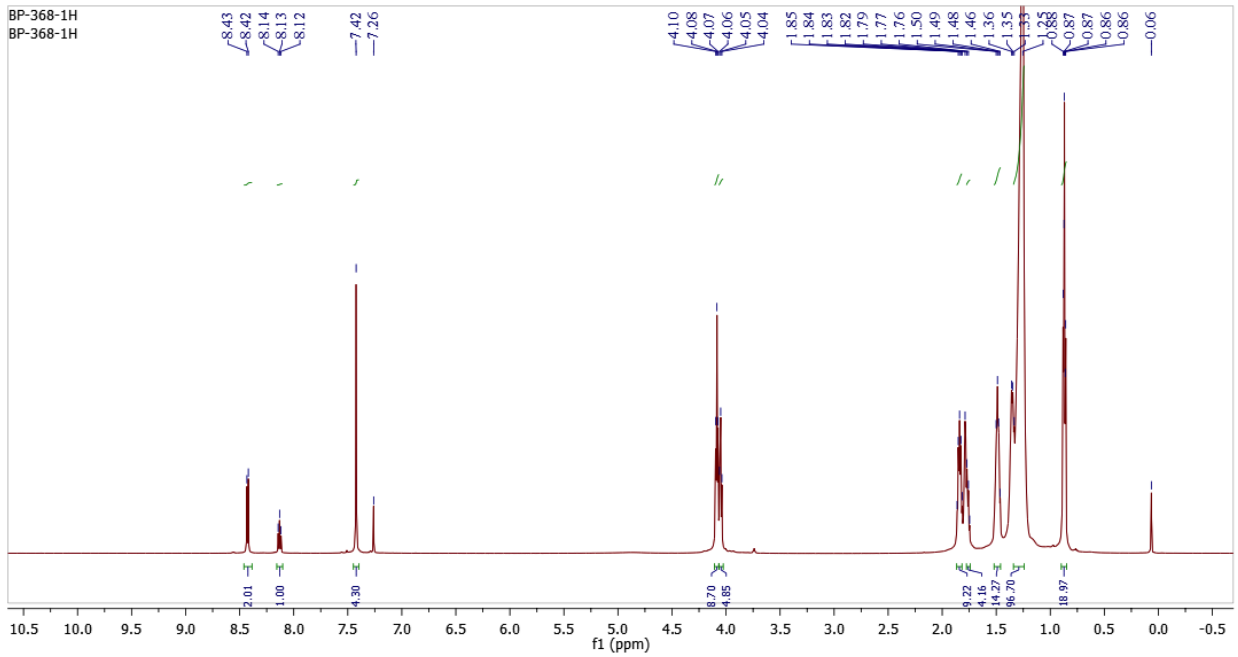

Figure S7. ^{1}H NMR (600 MHz) spectra of **1d** in $CDCl_3$

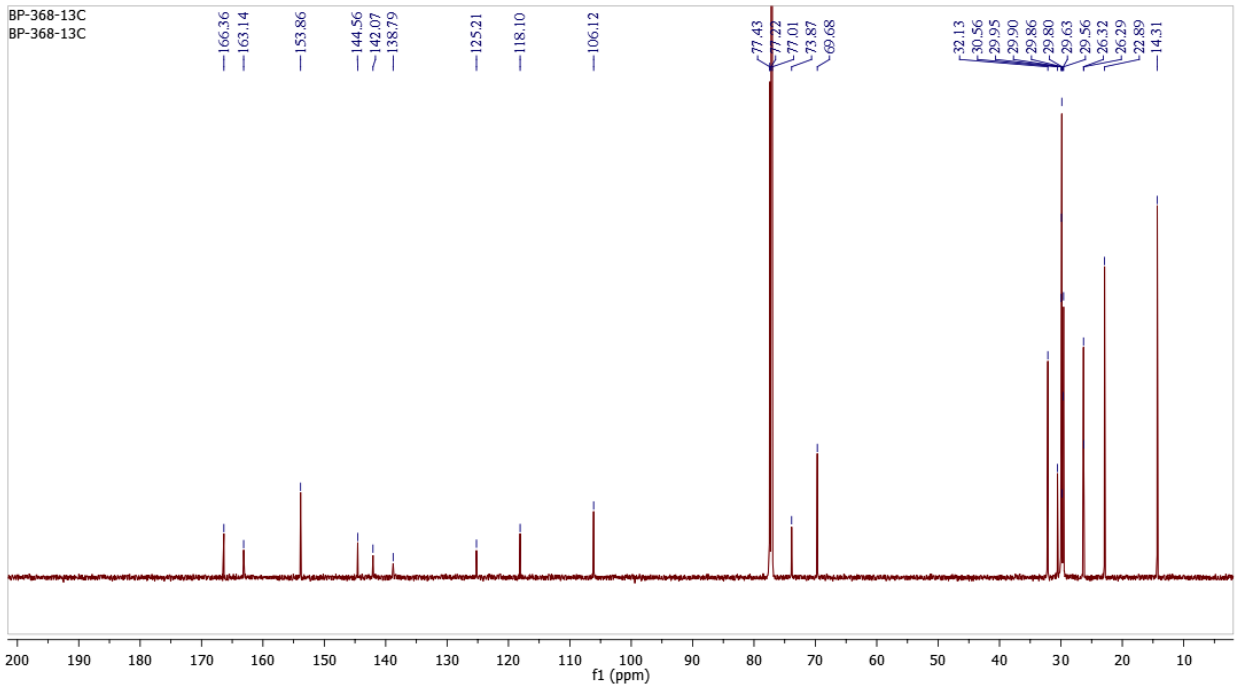

Figure S8. ^{13}C NMR (150 MHz) spectra of **1d** in $CDCl_3$

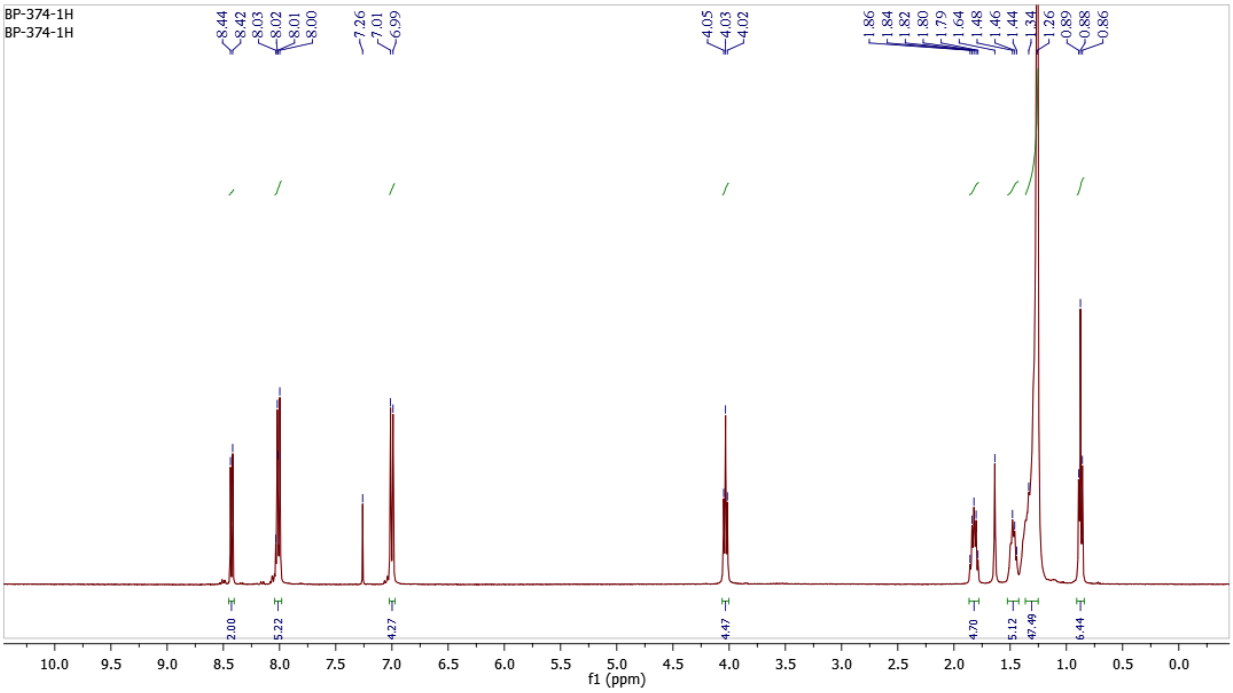

Figure S9. ^{1}H NMR (600 MHz) spectra of **2a** in $CDCl_3$

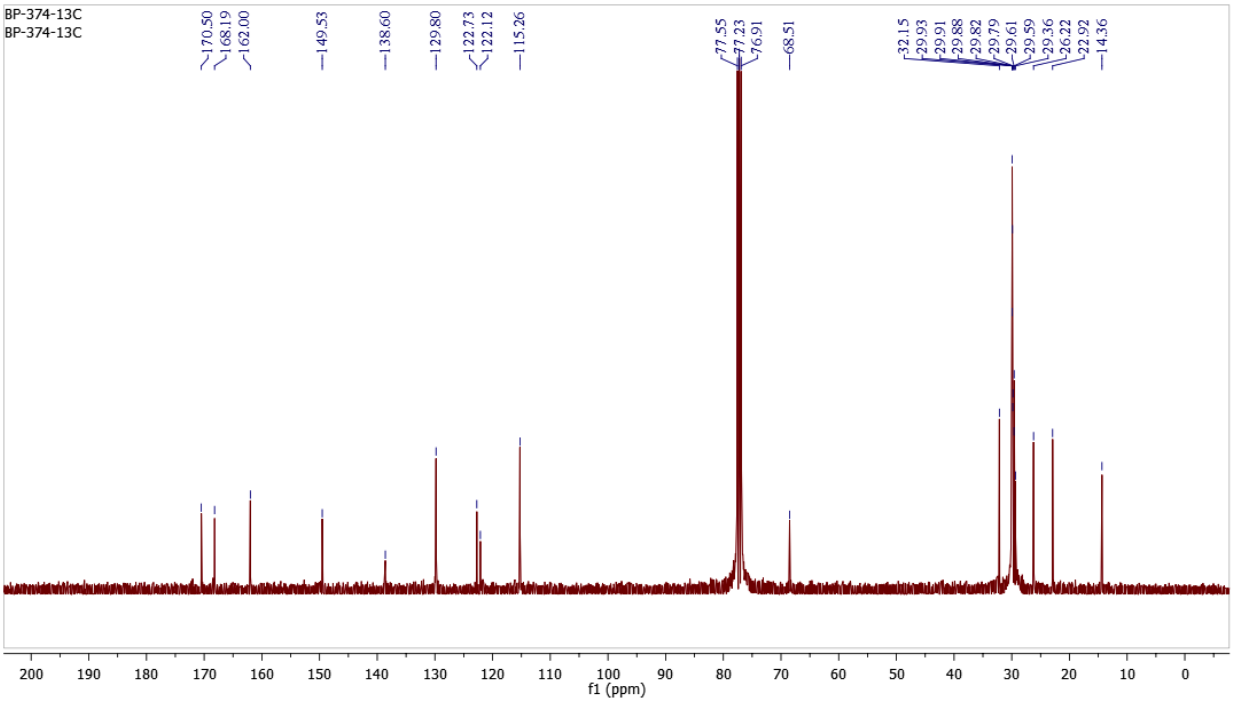

Figure S10. ^{13}C NMR (150 MHz) spectra of **2a** in $CDCl_3$

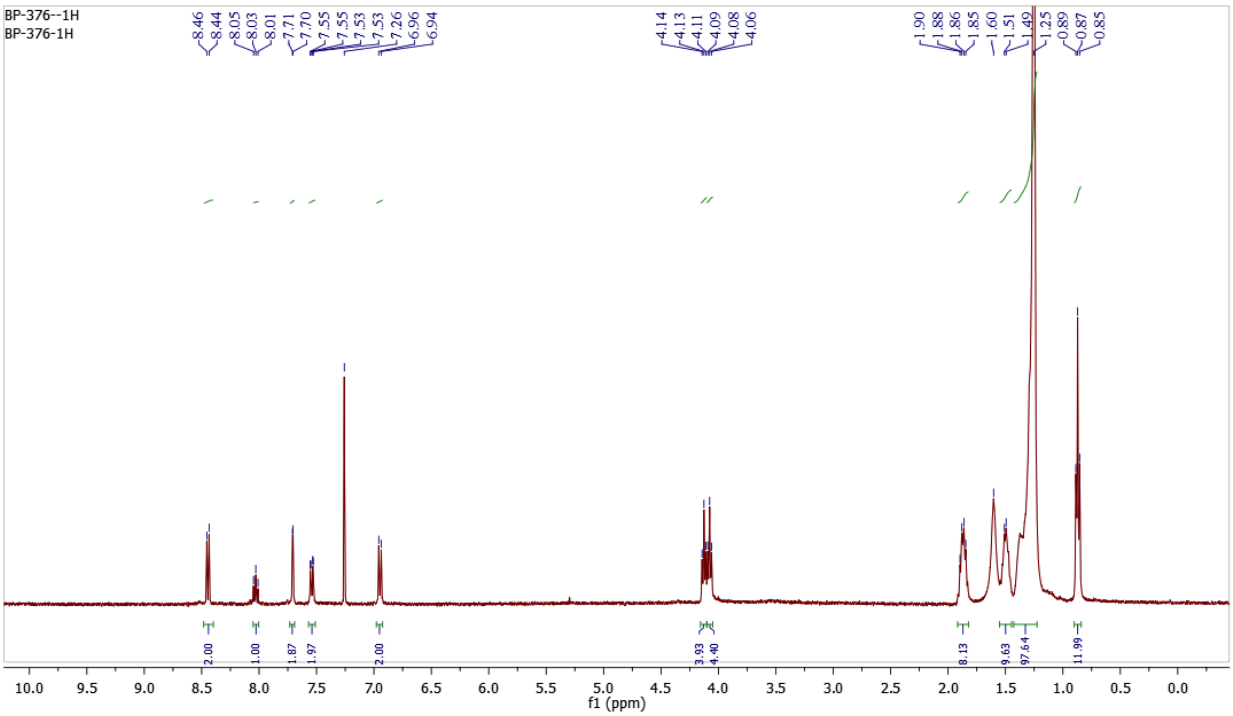

Figure S11. ^{1}H NMR (600 MHz) spectra of **2b** in $CDCl_3$

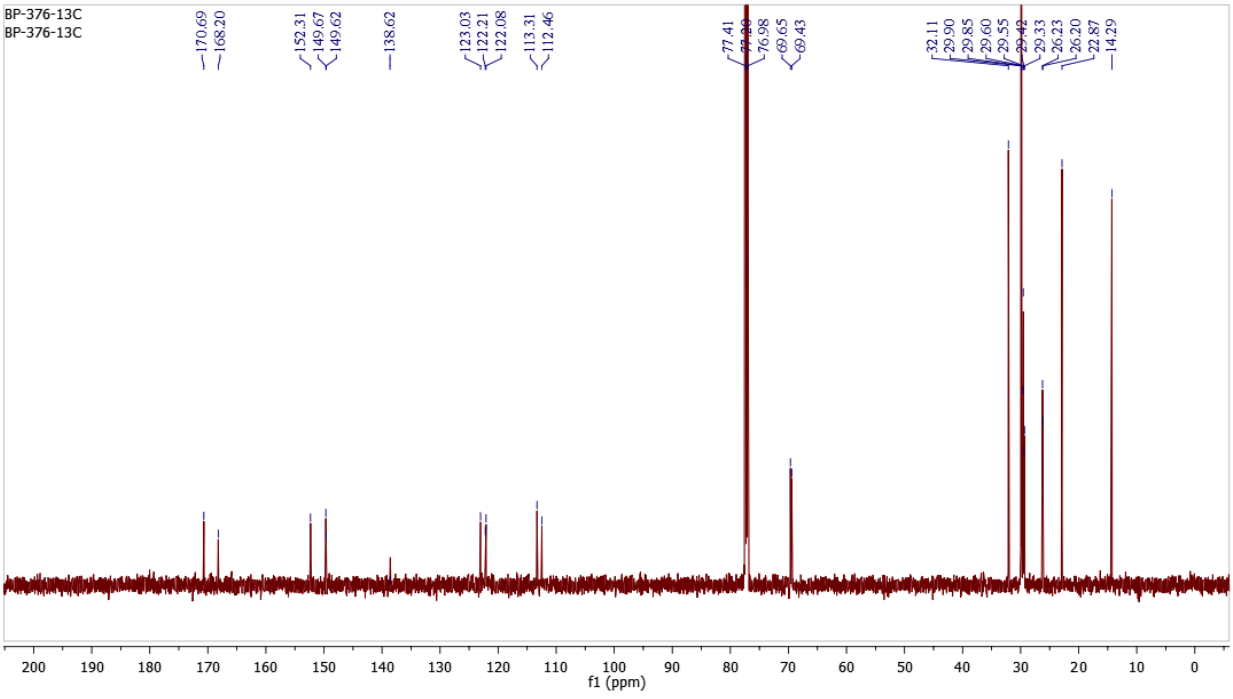

Figure S12. ^{13}C NMR (150 MHz) spectra of **2b** in $CDCl_3$

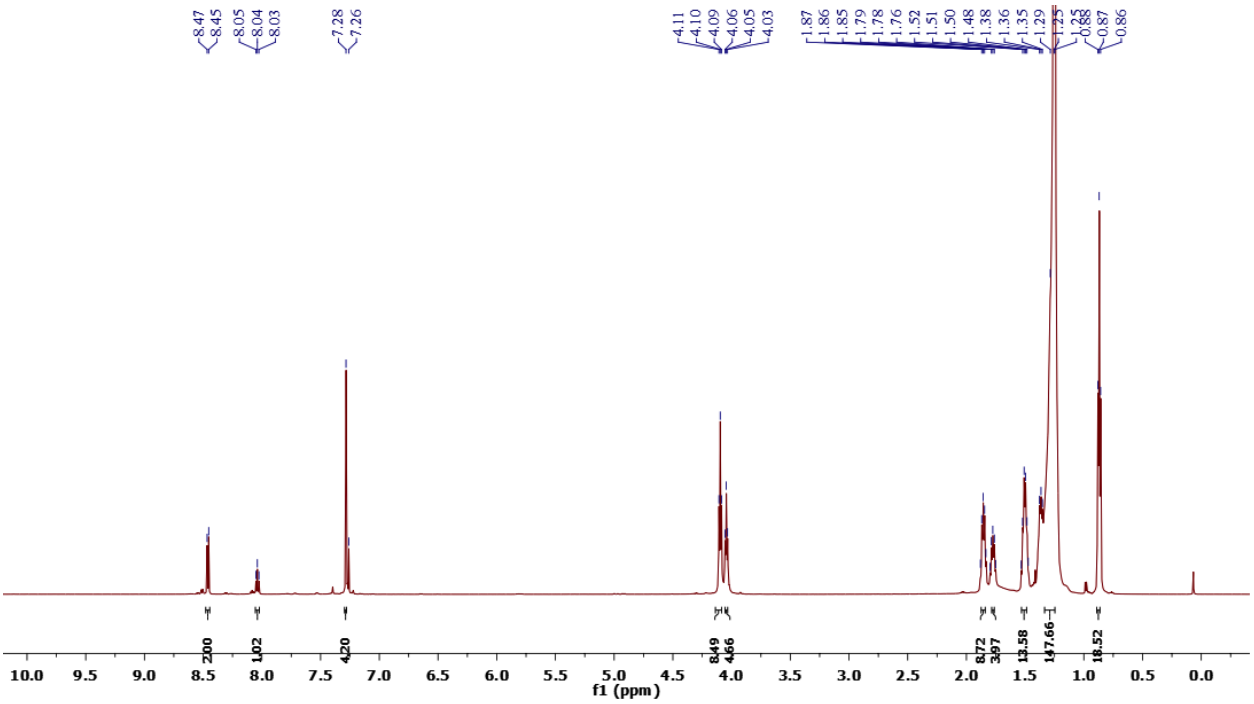

Figure S13. ^{1}H NMR (600 MHz) spectra of **2c** in $CDCl_3$

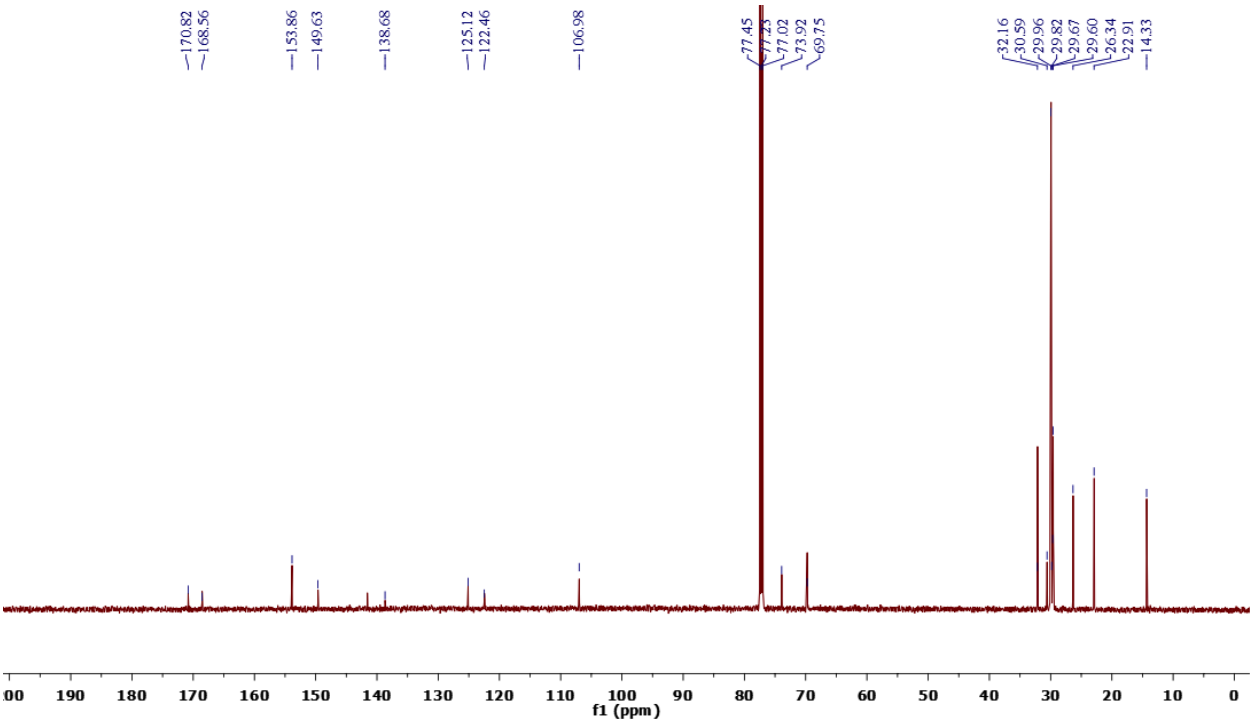

Figure S14. ^{13}C NMR (150 MHz) spectra of **2c** in $CDCl_3$

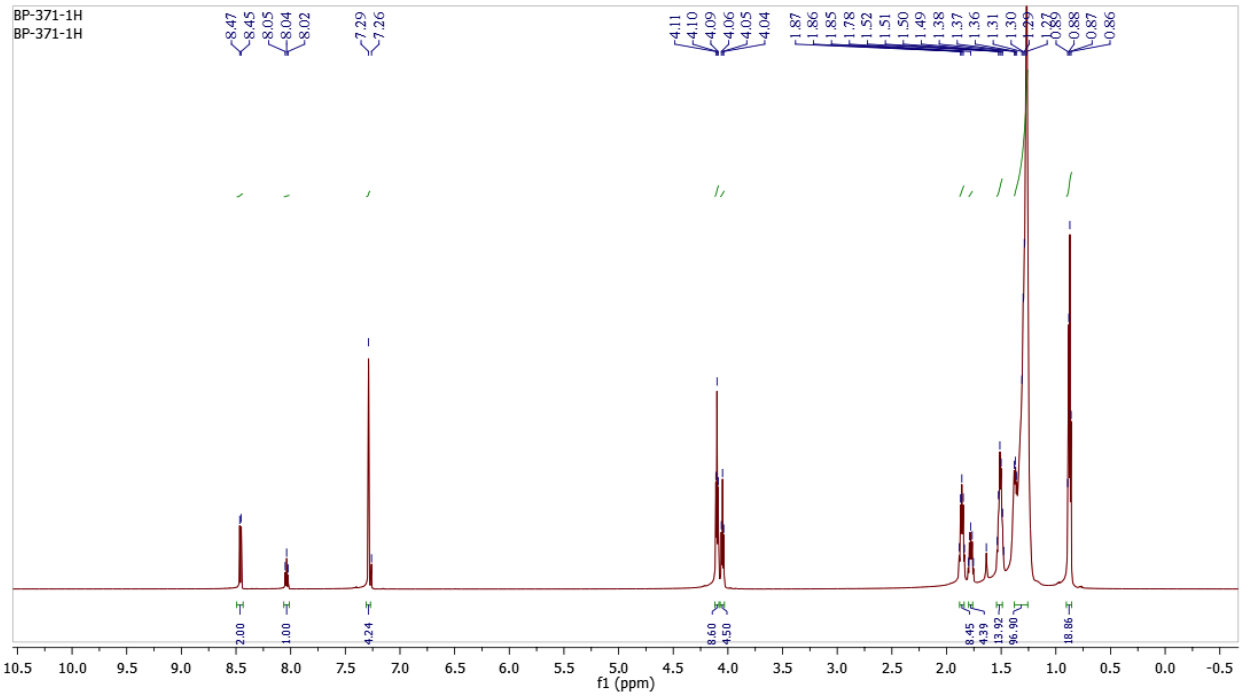

Figure S15. ^{1}H NMR (600 MHz) spectra of **2d** in $CDCl_3$

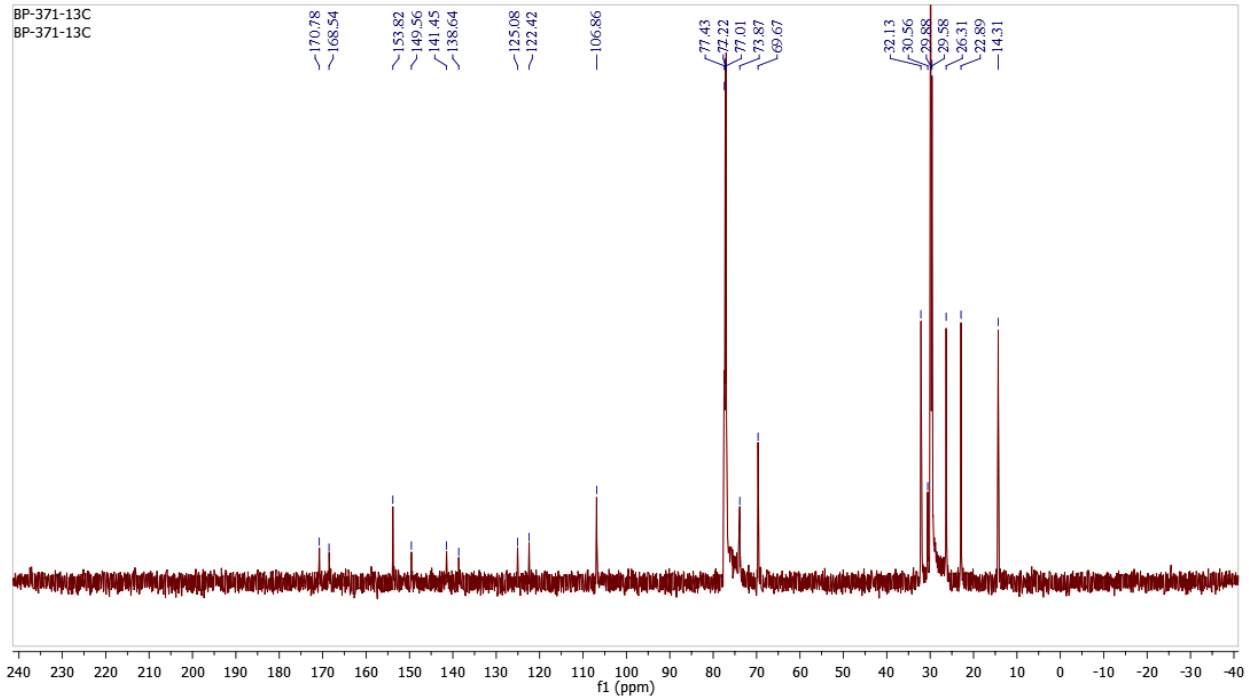

Figure S16. ^{13}C NMR (150 MHz) spectra of **2d** in $CDCl_3$

4. MALDI-TOF Spectra

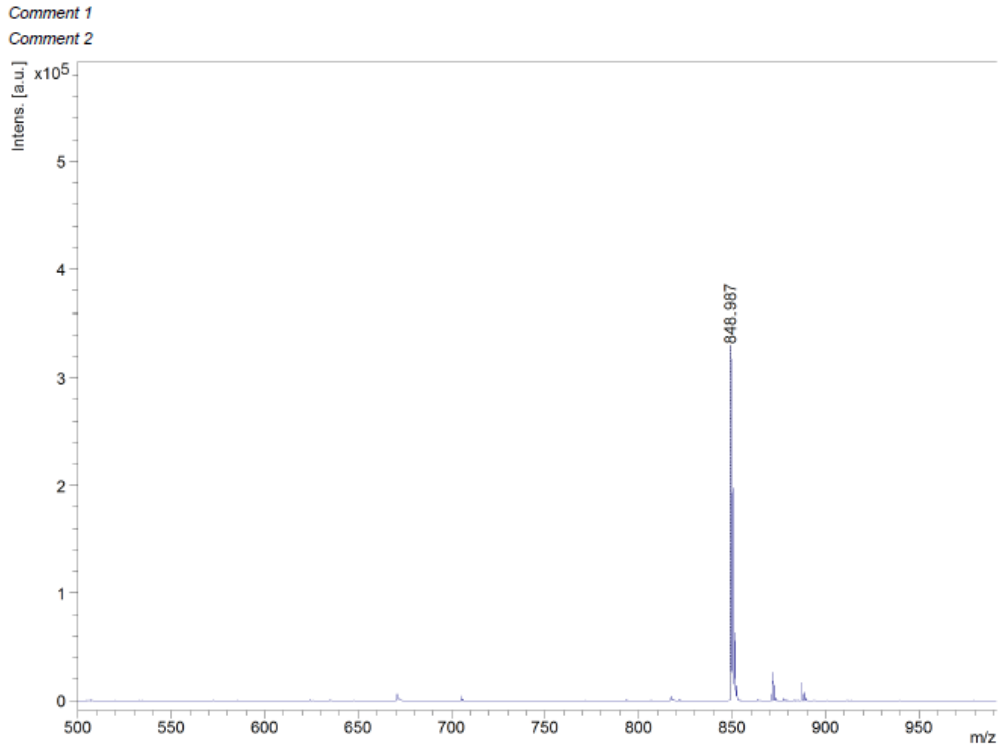

Figure S17. MALDI-TOF spectra of **1a**.

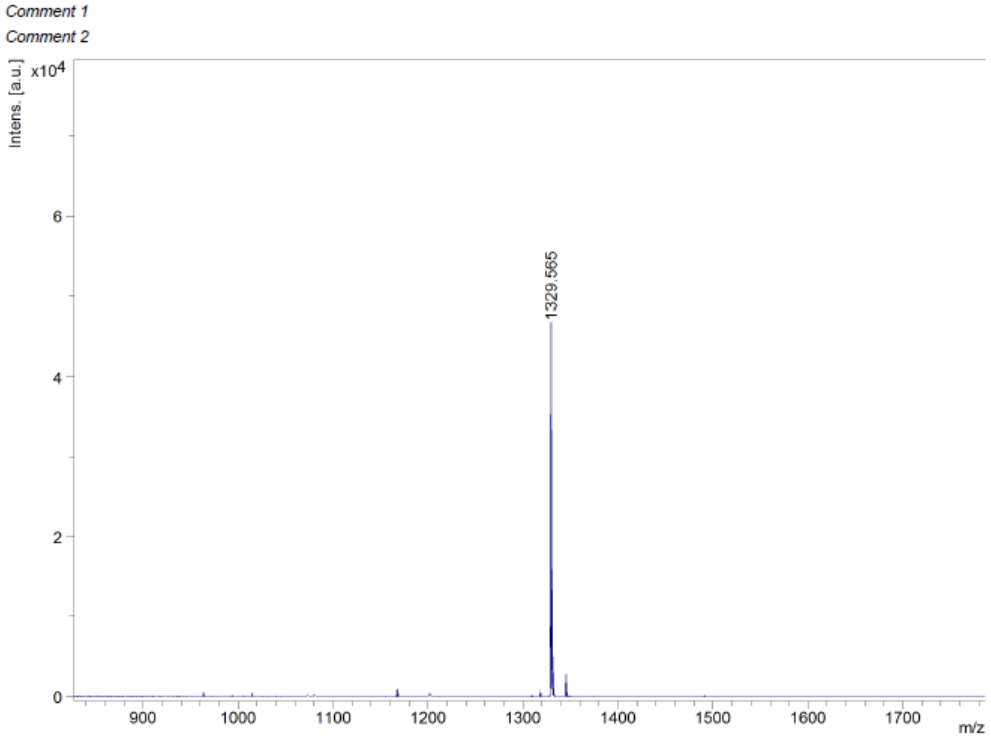

Figure S18. MALDI-TOF spectra of **1b**.

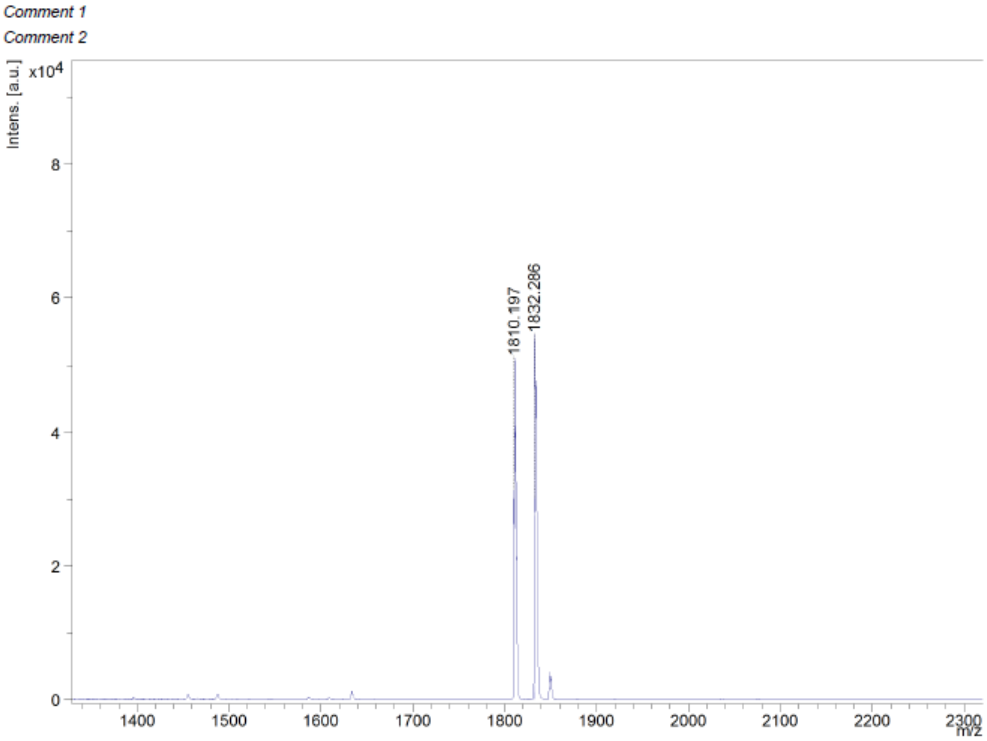

Figure S19. MALDI-TOF spectra of **1c**.

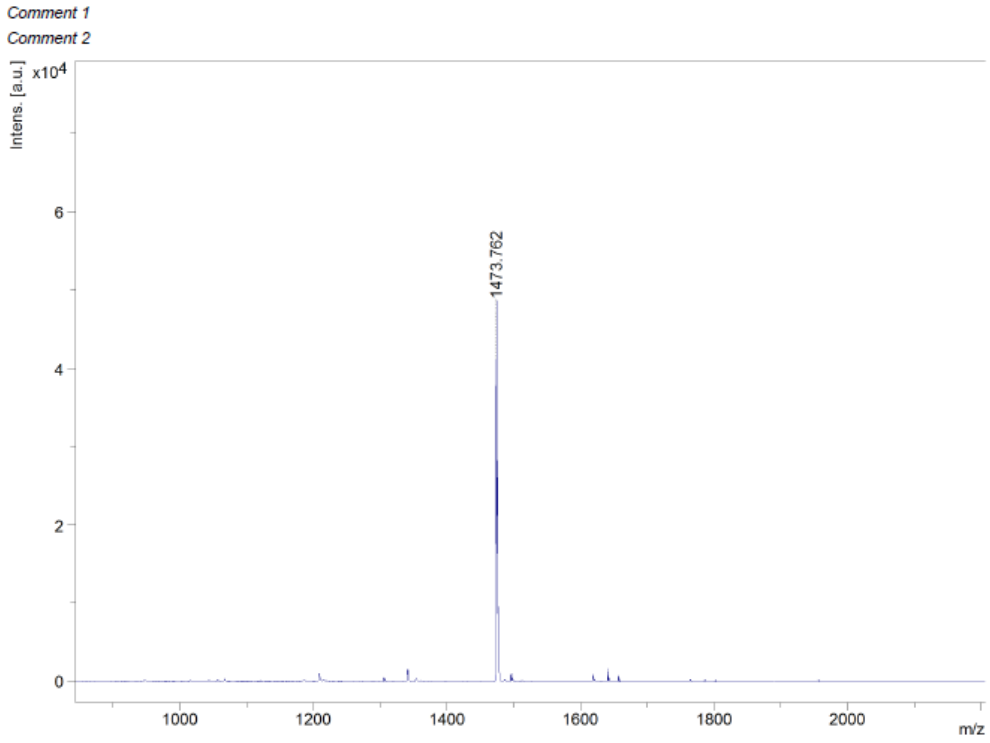

Figure S20. MALDI-TOF spectra of **1d**.

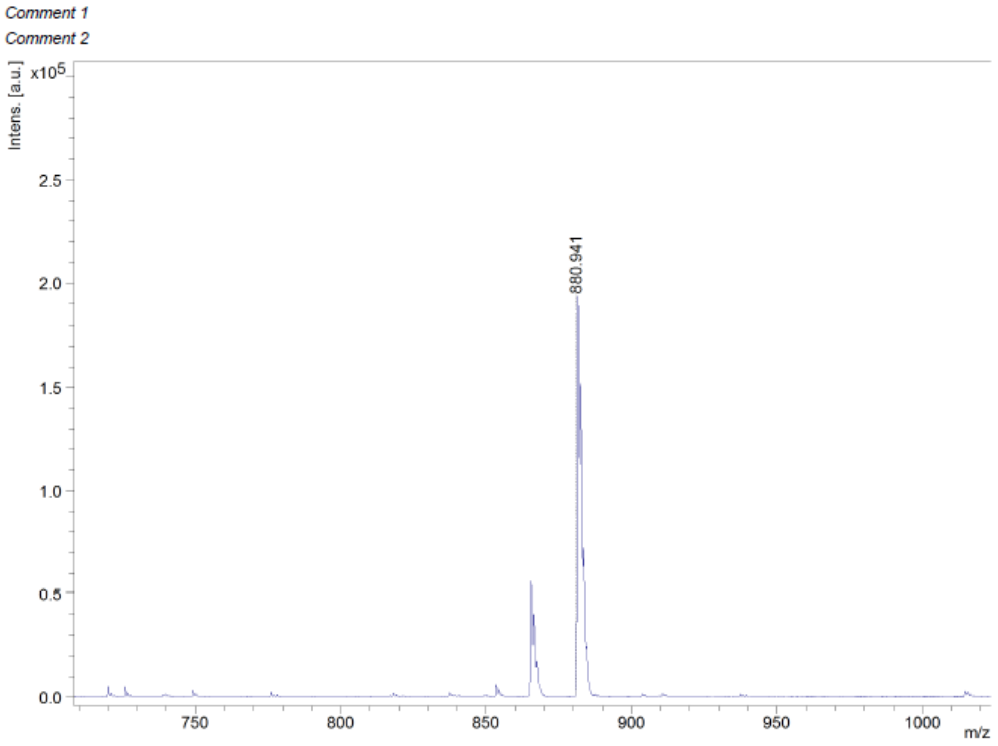

Figure S21. MALDI-TOF spectra of **2a**.

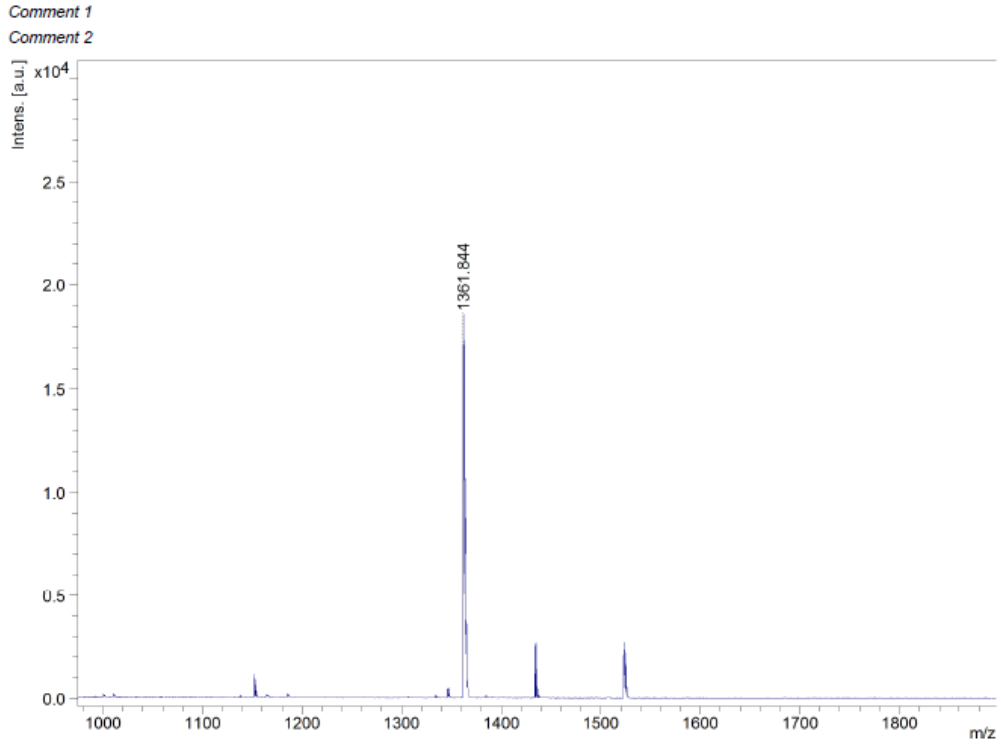

Figure S22. MALDI-TOF spectra of **2b**.

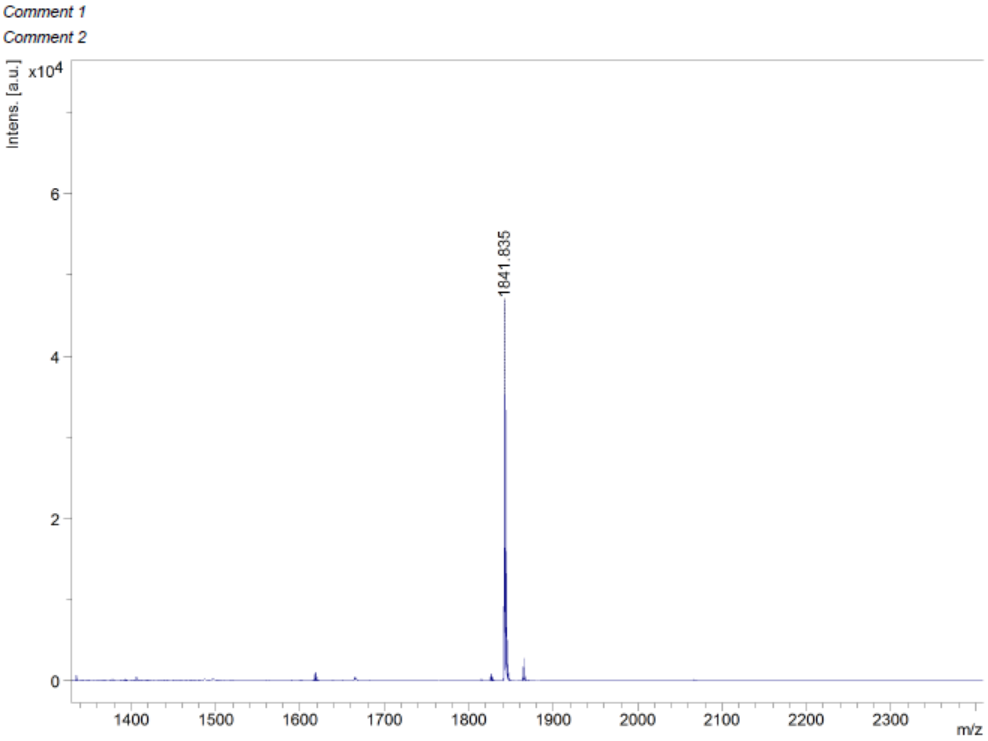

Figure S23. MALDI-TOF spectra of **2c**.

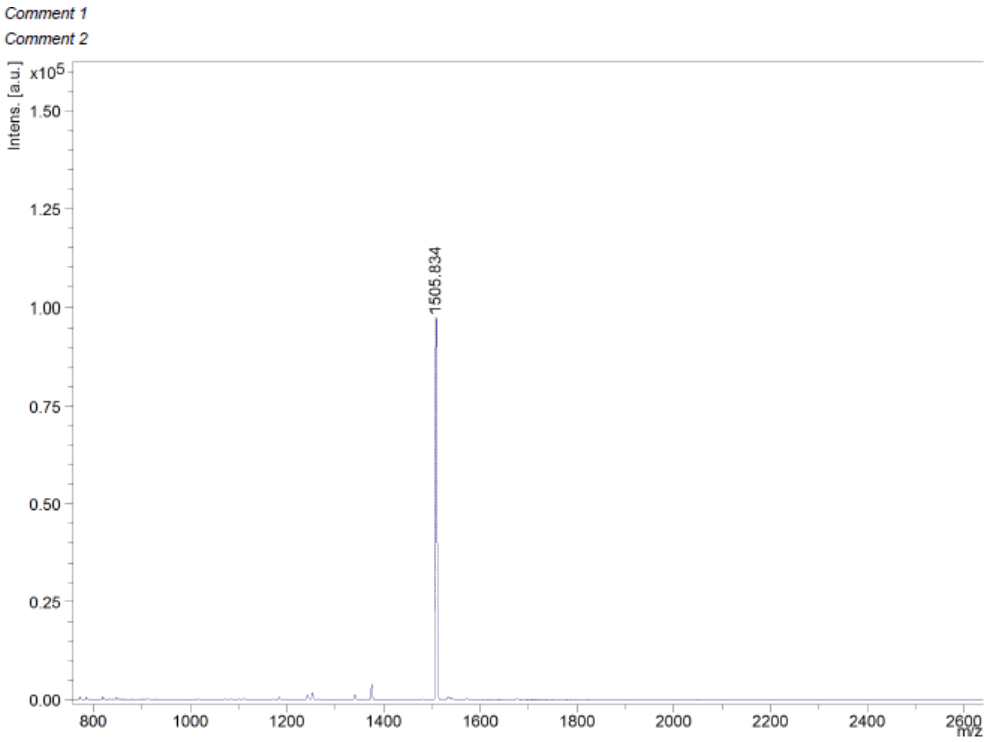

Figure S24. MALDI-TOF spectra of **2d**.

5. Polarizing Optical Microscopy

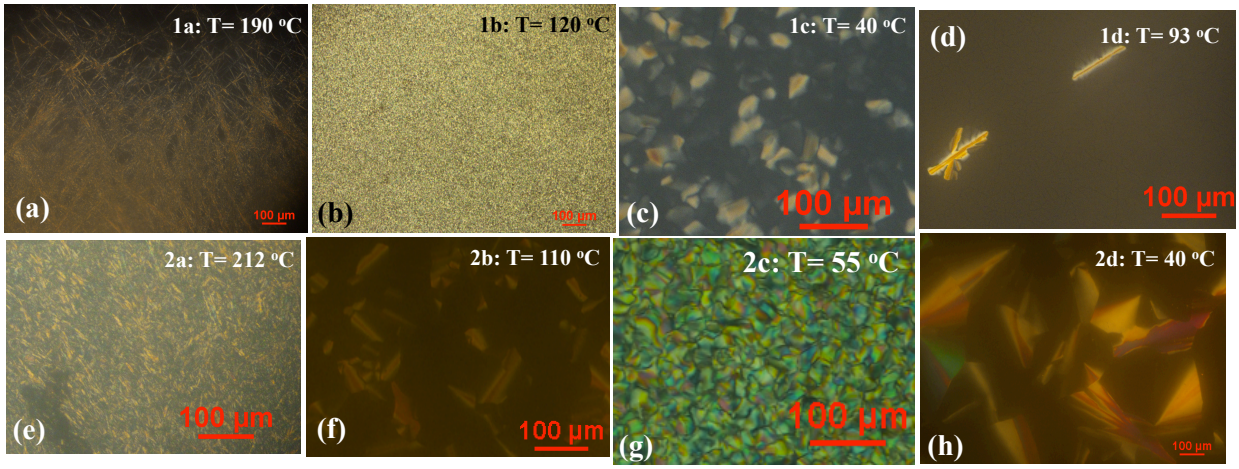

Figure S25. POM images obtained for the Cr phase of **1a** (a); Cr phase of **1b** (b); Col_r phase of **1c** (c); Col_h phase of **1d** (d); Cr phase of **2a** (e); Col_h phase of **2b** (f); Col_r phase of **2c** (g) and Col_r phase of **2d** (h).

6. Differental Scanning calorimetry

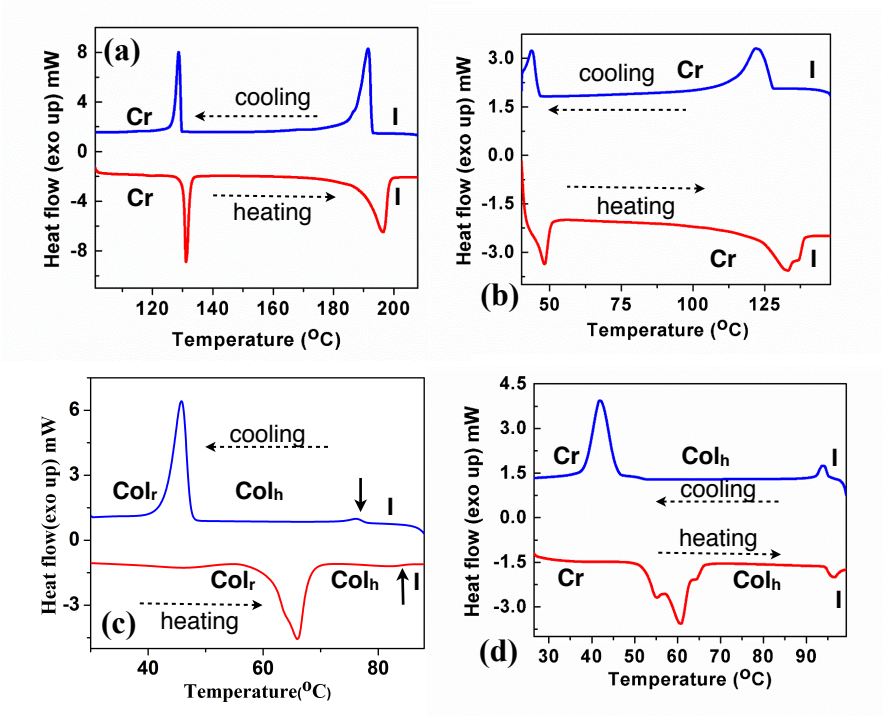

Figure S26. DSC scans obtained for the first cooling (blue trace) and second heating (red trace) cycle of compound **1a** (a); **1b** (b); **1c** (c) and **1d** (d).

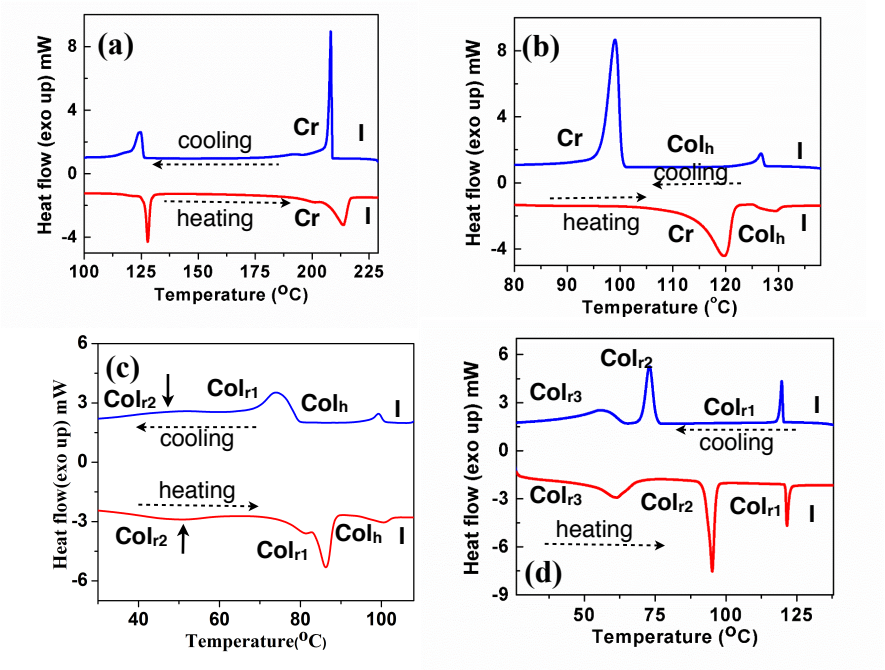

Figure S27. DSC scans obtained for the first cooling (blue trace) and second heating (red trace) cycle of compound **2a** (a); **2b** (b); **2c** (c) and **2d** (d)

7. Photophysical studies

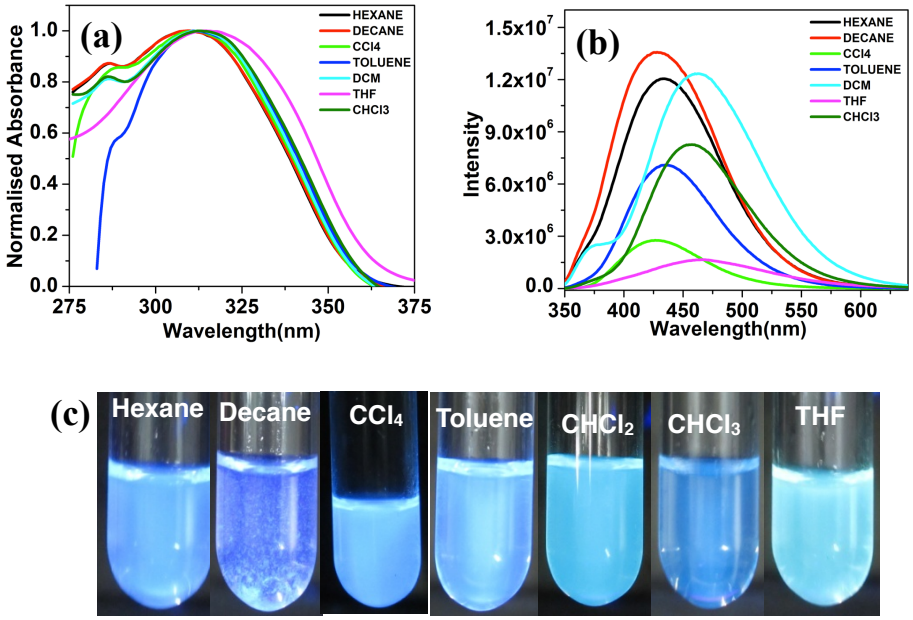

Figure S28. Noramalized absorption spectra (a) and emission spectra (b) of compound **1c** in micromolar concentration in different solvents; Images of the same solutions under the light of long wavelength (λ_{exc} = 365 nm) (c).

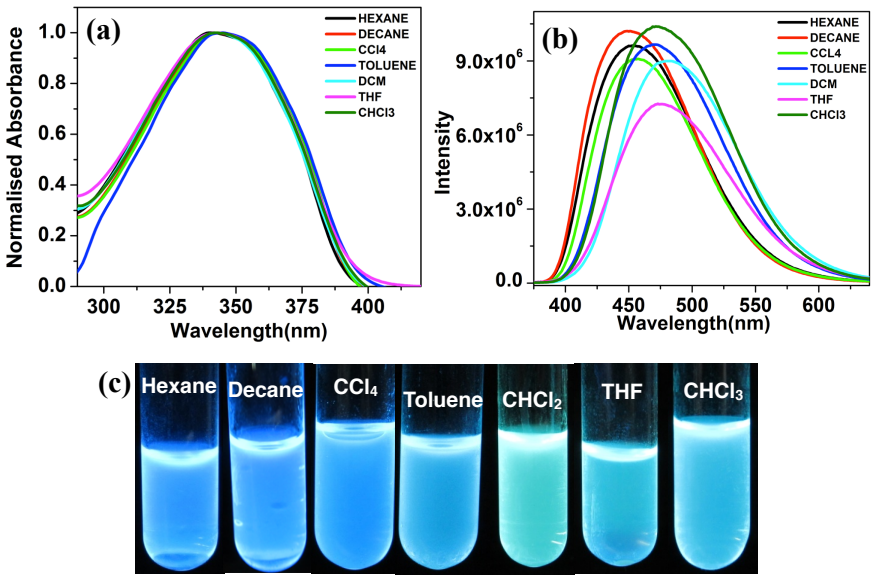

Figure S29. Noramalized absorption spectra (a) and emission spectra (b) of compound **2c** in micromolar concentration; Images of the same solutions under the light of long wavelength (λ_{exc} = 365 nm) (c).

Quantum yield calculation

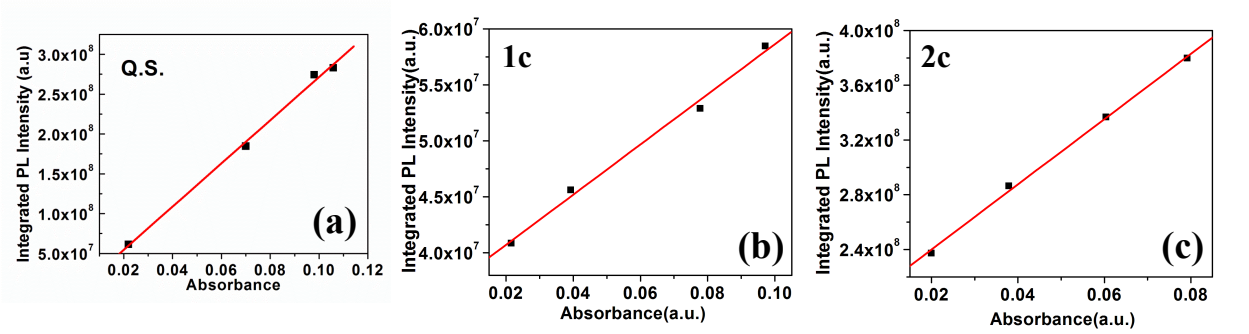

Figure S30. Plots of integrated photoluminescence intensity vs absorbance of quinine sulphate solution (a) (0.1 M H_2SO_4 solution) and compounds **1c** (b) and **2c** (c)(micromolar THF solution)

Quantum yield was measured according to established procedure by using quinine sulfate in 0.1 M H_2SO_4 solution as the standard. Absolute values were calculated according to the following equation: $Q_S = Q_R \times (m_S / m_R) \times (n_S / n_R)^2$

Where, Q: Quantum yield, m: Slope of the plot of integrated fluorescence intensity *vs* absorbance n: refractive index (1.407 for THF and 1.33 for distilled water). The subscript R refers to the

reference fluorophore *i.e.* quinine sulphate solution in 0.1 M H_2SO_4 and subscript S refers to the sample under investigation. In order to minimize re-absorption effects, absorbance was kept below 0.15 at the excitation wavelength of 347 nm.

Quantum Yield of quinine sulphate is 0.54. Simplified equation for the calculation after substituting the appropriate values is given below and values obtained are given in table 1.

$$Q_S = 0.54 \times (m_S / 2.71) \times (1.407/1.33)^2$$

$$= 0.223 \times m_S$$

Entry	m_S	m_R	Q_s [a,b,c]
1c	2.24	2.71	0.50
2c	2.38	2.71	0.53

[a] Measured in THF; [b]Excited at absorption maxima; [c]Standard quinine sulphate (Q_f = 0.54) in 0.1M H_2SO_4.

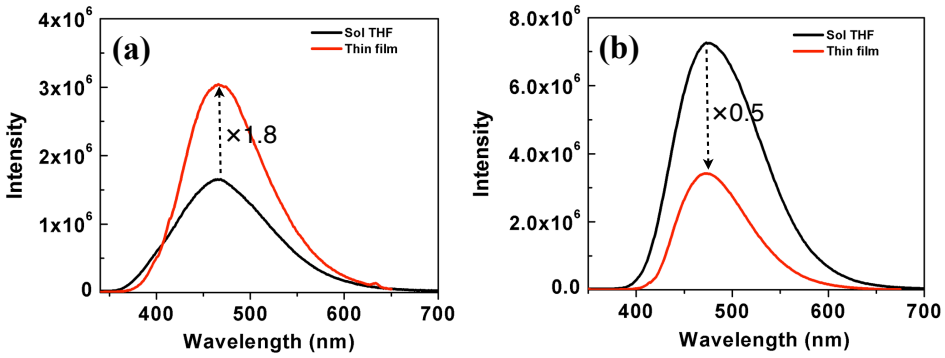

Figure S31. Comparison of the emission spectra of compounds **1c** (a) and **2c** (b) in micromolar THF solution and thin film state.

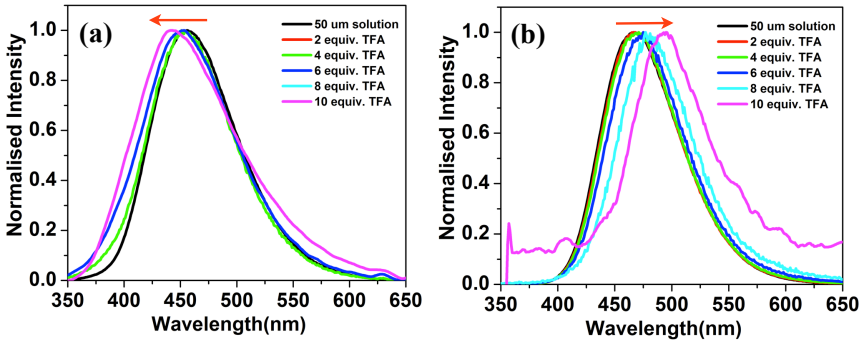

Figure S32. Comparison of the emission spectra of compounds **1c** (a) and **2c** (b) in micromolar THF solution on gradual addition of TFA.

8. Gelation studies

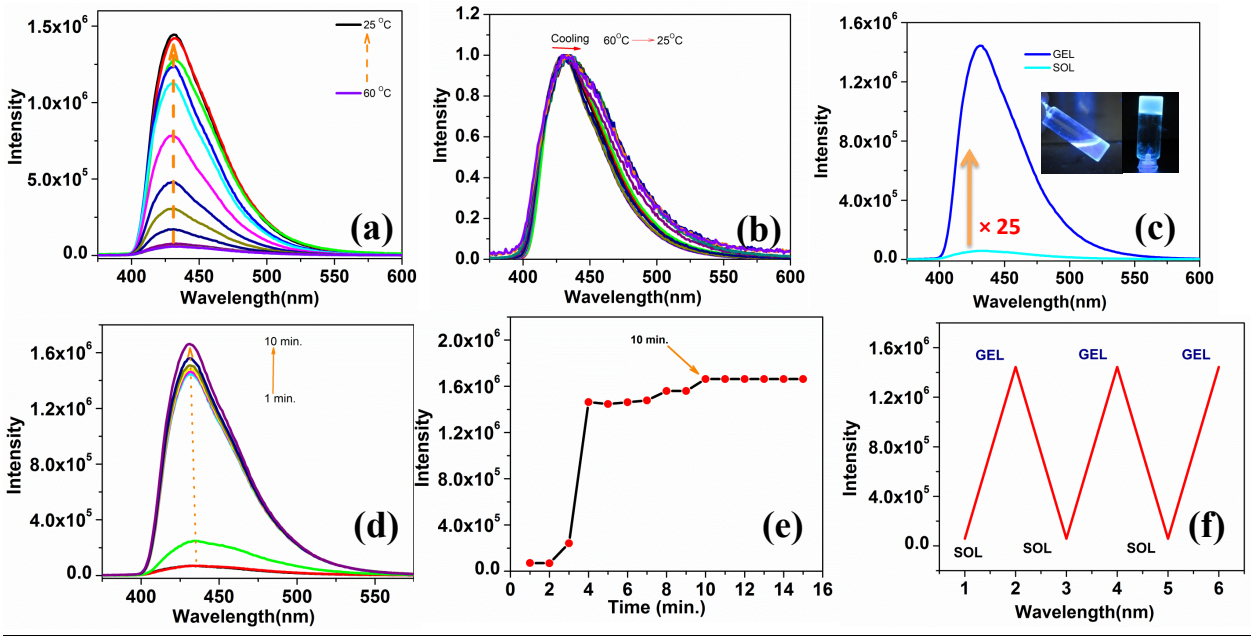

Figure S33. Emission spectra of compound **2c** in decane (0.27 mmol) on cooling from 60 °C to 25 °C (a); Normalized emission spectra on cooling from 60 °C to 25 °C (b); Emission spectra obtained as a function of time (c); Plot showing the emission intensity at 431 nm as a function of time (d); Reversible change in the emission intensity at 431nm by repeated sol-gel transition (e).

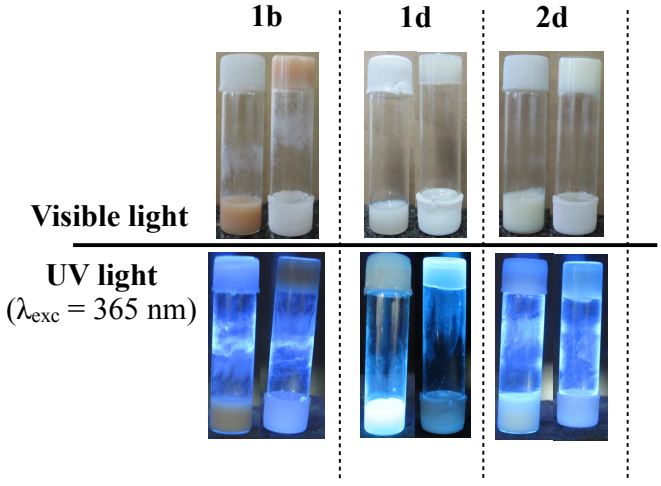

Figure S34. Images of solutions (left side) and gels (right side) seen under visible light and UV light of long wavelength.

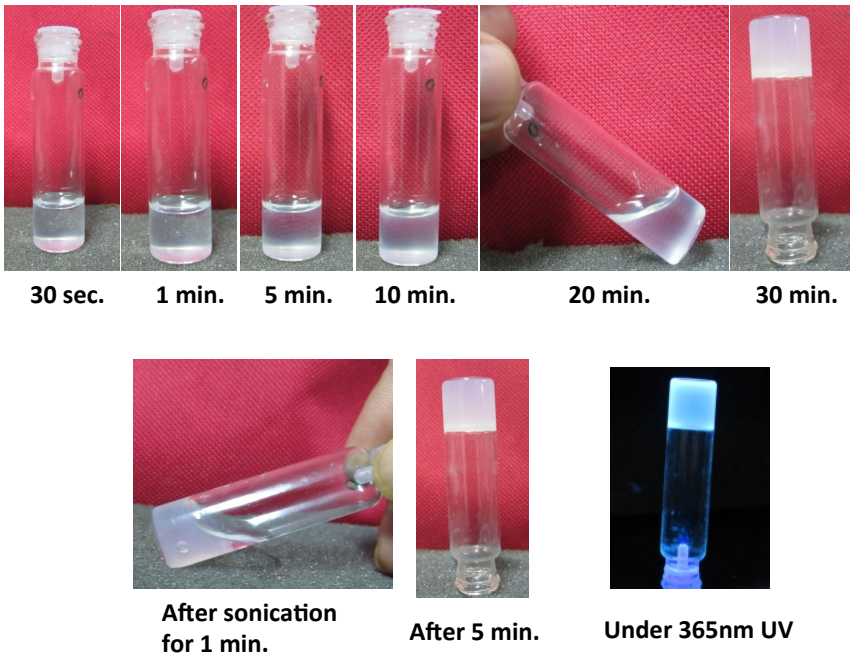

Figure S35. Images showing the transformation of solution to gel for compound **1c**

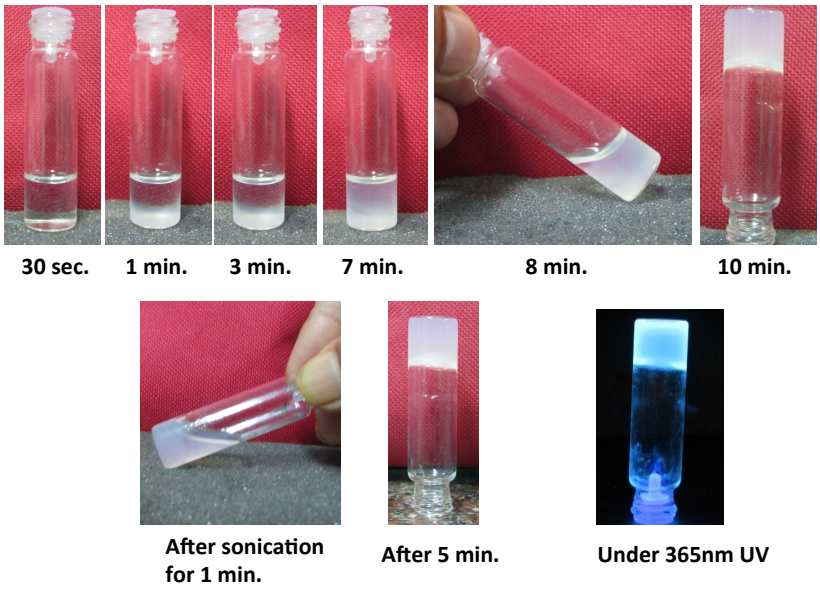

Figure S36. Images showing the transformation of solution to gel for compound **2c**

Table S1. Gelation properties of **1c** and **2c**

S. No.	Solvent	**1c**			**2c**		
		Properties	CGC (wt.%)	T_{gel} (°C)	Properties	CGC (wt.%)	T_{gel} (°C)
1	Hexane	G(O)	0.78	48	G(O)	0.56	43
2	Decane	G(O)	0.60	56	G(O)	0.50	47
3	Dodecane	G(O)	0.60	57	G(O)	0.48	52
4	Hexadecane	G(O)	0.58	59	G(O)	0.41	56
5	Toluene	S	----	---	S	----	---
6	Benzene	S	----	---	S	----	---
7	*m*-xylene	S	----	---	S	----	---
8	DCM	S	----	---	S	----	---
9	Chloroform	S	----	---	S	----	---
10	CCl_4	S	----	---	S	----	---
11	THF	S	----	---	S	----	---
12	*n*-butanol	P	----	---	P	----	---
13	Ethanol	P	----	---	P	----	---
14	DMSO	I	----	---	I	----	---
G = stable gel; P = precipitate; I = insoluble; O = opaque. The critical gelation concentration (wt. %) is the minimum concentration necessary for gelation. T_{gel} (°C) is the thermal stability of the gels.							

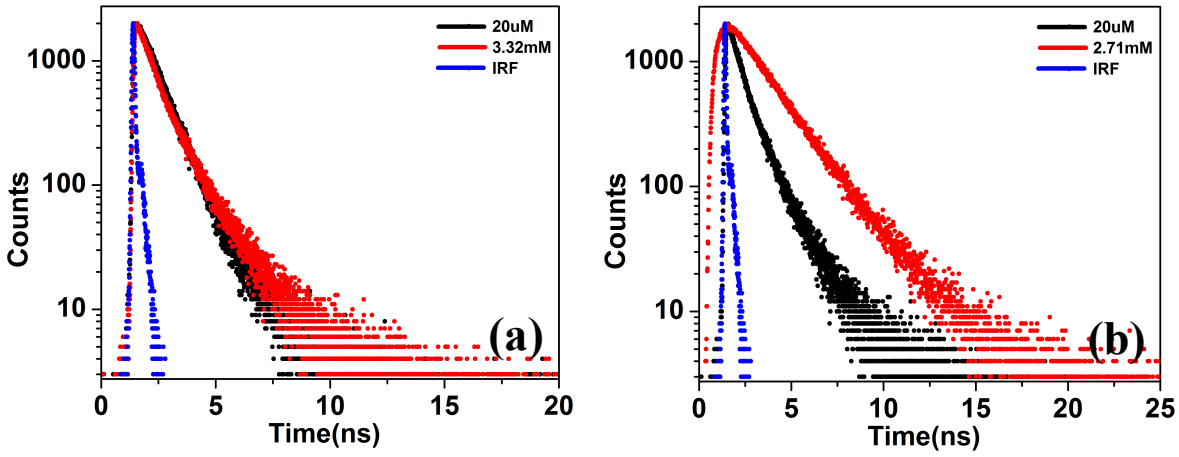

Figure S37. The fluorescence decay profiles of compound **1c** in decane at 20 μM (black trace) and 3.32 mM (red trace) concentrations (blue trace is instrument response function: IRF; λ_{exc} = 375 nm) (a); The fluorescence decay profiles of compound **2c** in decane at 20 μM (black trace) and 2.71 mM (red trace) concentrations (blue trace is instrument response function: IRF; λ_{exc} = 375 nm)

Table S2. Data obtained from time resolved photoluminescence studies

Compound	State of matter	Fraction of molecule	Life time (ns)
1c	Sol	55% 45%	0.6 1.5
	Gel	88% 12%	0.8 1.8
2c	Sol	83% 17%	1.9 3.1
	Gel	45% 55%	1.8 6.1

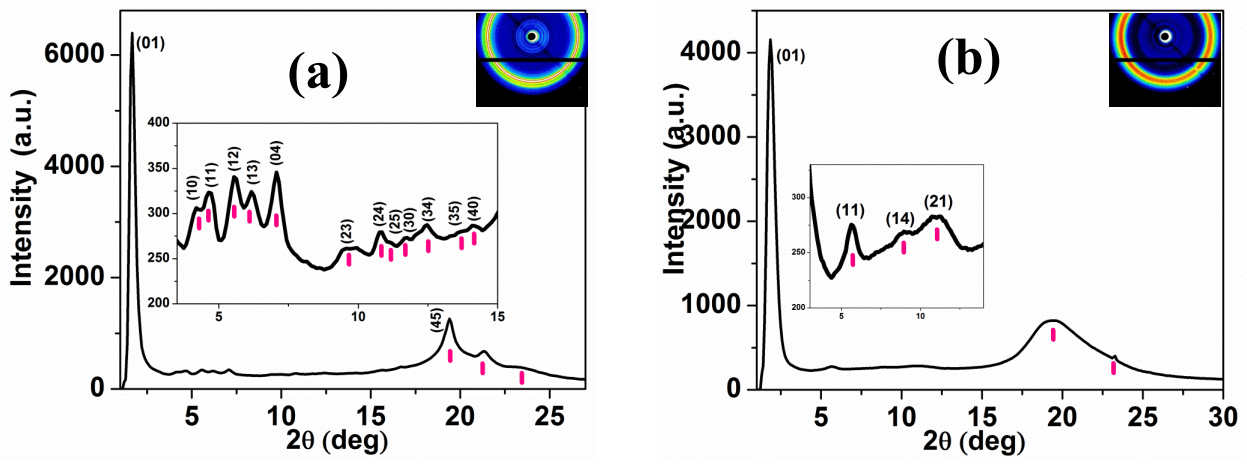

Figure S38. Intensity *vs* 2θ profiles obtained from the XRD pattern for the Col_r phase of the xerogel of compound **1c** (a); Col_r phase of the xerogel of compound **2c** (b)

8. XRD studies

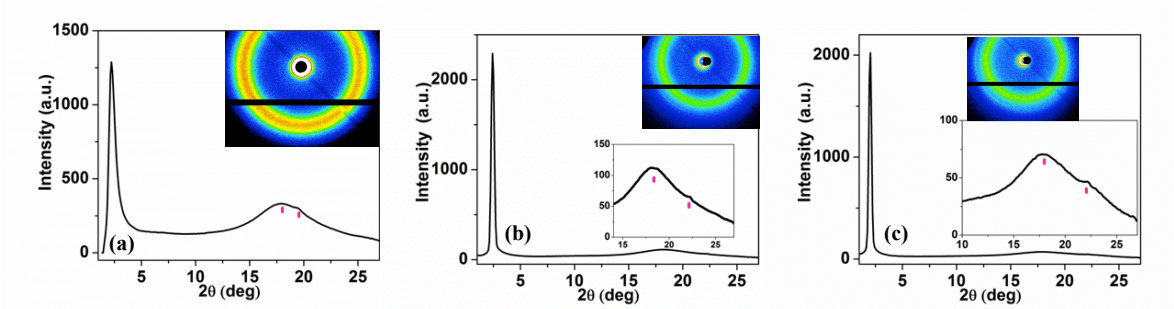

Figure S39. Intensity *vs* 2θ profiles obtained from the XRD pattern for compound **1c** at 65 ^{o}C (a); compound **1d** at 65 ^{o}C (b) and compound **2b** at 110 ^{o}C (c).

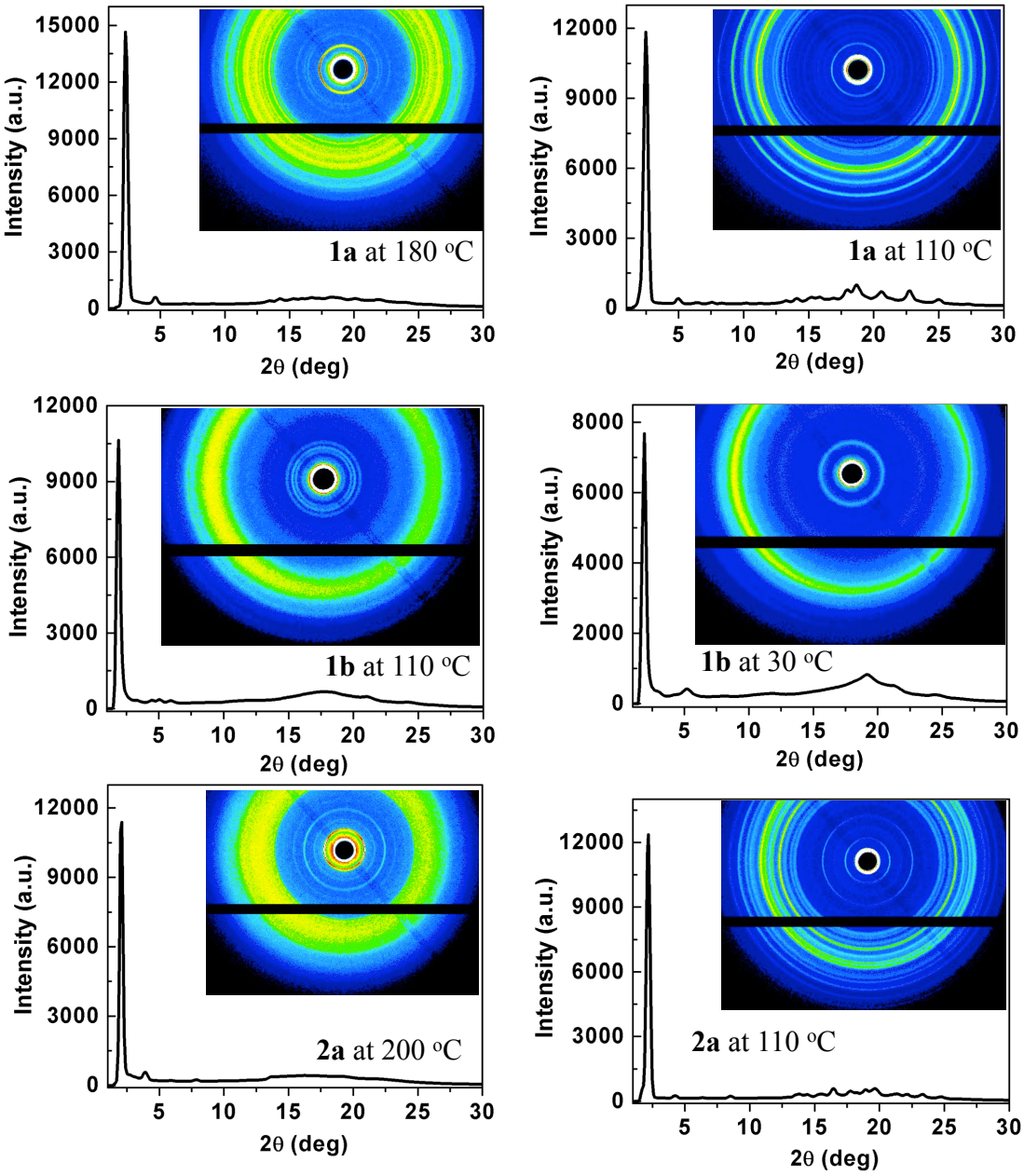

Figure S40. Intensity *vs* 2θ profiles obtained from the XRD patterns for compounds **1a, 1b** and **2b** at specified temperatures (insets show the image patterns obtained).

9. References

1. B. Pradhan, S. K. Pathak, R. K. Gupta, M. Gupta, S. K. Pal and A. S. Achalkumar, *J. Mater. Chem. C*, 2016, **4**, 6117-6130.
2. B. Pradhan, M. Gupta, S. K. Pal and A. S. Achalkumar, *J.Mater.Chem.C*, 2016, **4**, 9669-9673.
3. B. Pradhan, V. M. Vaisakh, G. G. Nair, D. S. S. Rao, S. K. Prasad and A. S. Achalkumar, *Chem. – Eur. J.*, 2016, **22**, 17843–17856