Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Star-shaped π-Gelators based on Oxadiazole and Thiadiazoles: A Structure-property Correlation

Subrata Nath,[a] Suraj Kumar Pathak, [a] Joydip De,[b] Santanu Kumar Pal[b] and Ammathnadu S. Achalkumar[a]*

[a]Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, 781039, Assam, India. [b]Department of Chemical Sciences, Indian Institute of Science Education and Research Mohali, Sector-81, Knowledge City, Manauli 140306, Punjab, India.

Supporting information

Table of Contents

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. Thermogravimetric analysis (TGA) was accomplished with a thermogravimetric analyzer (Mettler Toledo, model TG/SDTA 851 e).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.

2. Experimental Section

Ethyl-3,5-dihydroxybenzoate (**1**)

3,5-dihydroxybenzoic acid (5g, 32.44mmol.)was dissolved in 20 mL ethanol and catalytic amount of sulphuric acid was added and the reaction mixture was refluxed for 24 h. Nearly 70% of ethanol was distilled off and the reaction mixture was diluted with water and sulphuric acid and unreacted benzoic acid were neutralised with saturated solution of sodium bicarbonate and then extracted with ethyl acetate, washed with water, brine and dried over anhydrous Na_2SO_4, concentrated and finally recrystallized from ethanol.

1: R_f = 0.5 (50% EtOAc-hexanes); a brownish solid; mp: 120-125 ^oC; yield: 70-75%; IR (KBr pellet): ν_{max} cm^{-1} 3304, 2997, 1690, 1680, 1607, 1465, 1372, 1338, 1163, 1029, 871, 766; ^1H NMR (CD_3OD, 600 MHz): δ 6.93 (s, 2H, Ar), 6.47 (s, 1H,Ar), 4.89 (s, 2H, 2 × OH), 4.31-4.27 (m, 2H, OCH_2), 1.33 (t, 3H, 1 × CH_3), ^{13}C NMR (CD_3OD, 150MHz): 168.20, 159.70, 133.32, 108.74, 108.15, 62.03, 14.53; HRMS (ESI+) exact Mass calculated for $C_9H_{11}O_4$ (M+1): 183.0652, found: 183.0658.

Procedure for the synthesis of ethy-l,3,5-bis(decyloxy)benzoate (**2**)[1]

A mixture of ethyl 3,5-dihydroxybenzoate (1equiv.), anhydrous K_2CO_3 (4.4 equiv.), *n*-bromodecane (2.2 equiv.) were taken in dry DMF (20 ml) and heated at 80 ^oC for 17 h under nitrogen atmosphere. Then the reaction mixture was poured into ice-water and extracted with CH_2Cl_2. The combined extract was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by column chromatography on silica gel. Elution with hexanes followed by 5-10% ethylacetate-hexanes yielded the desired product.

2: R_f = 0.8 (5% EtOAc-hexanes); a viscous colorless liquid; yield: 75-80%; IR (KBr pellet): ν_{max} cm^{-1} 2923, 2852, 1722, 1601, 1445, 1468, 1390, 1326, 1232, 1167, 1128, 1055, 858, 762, 720; ^1H NMR ($CDCl_3$, 600 MHz): δ 7.16 (s, 2H, Ar), 6.62 (s, 1H,Ar), 4.37-4.33 (m, 2H, OCH_2), 3.96 (t, 4H, 2 × OCH_2), 1.79 -1.27 (m, 35H, 16 × CH_2, 1 × CH_3), 0.88(t, 6H, 2 ×CH_3), ^{13}C NMR ($CDCl_3$, 150MHz): 166.75, 160.32, 132.38, 107.81, 106.47, 68.49, 61.27, 32.11, 29.77, 29.58, 29.54, 29.40, 26.22, 22.90, 14.53; HRMS (ESI+) exact Mass calculated for $C_{29}H_{51}O_4$ (M+1): 463.3782, found: 463.3782.

Procedure for the synthesis of 3,5-bis(decyloxy)benzohydrazide (**3**)[2]

A mixture of ethyl 3,5-bis(decyloxy)benzoate (10 mmol, 1equiv.), excess hydrazine hydrate (10 mL), *n*-butanol (20 mL) was refluxed for 40 h. Water (100 mL) was added and resulting

precipitate was collected, dried under vacuum, and recrystallized from ethanol to yield pure **3** as a white solid.

3: R_f = 0.3 (20% EtOAc-hexanes); a white solid; mp: 72-75 ^oC; yield: 65-70%; IR (KBr pellet): ν_{max} cm^{-1} 3368, 3312, 3129, 2942, 2920, 2851, 1642, 1594, 1517, 1468, 1392, 1358, 1304, 1178, 1077, 1052, 1035, 836, 764, 721, 684; ^1H NMR ($CDCl_3$, 600 MHz): δ 7.48 (broad s, 1H, CONH), 6.83 (s, 2H, Ar) 6.57 (s, 1H, Ar), 3.94 (t, 4H, 2 × OCH_2), 3.10 (broad s, 2H, NH_2), 1.78-1.26 (m, 32H, 16 × CH_2), 0.89-0.86 (m, 6H, 2 × CH_3), ^{13}C NMR ($CDCl_3$, 100MHz): 168.91, 160.64, 134.67, 105.31, 104.98, 68.53, 32.10, 29.78, 29.76, 29.57, 29.52, 29.35, 26.20, 22.89, 14.33; HRMS (ESI+) exact Mass calculated for $C_{27}H_{49}N_2O_3$ (M+1): 449.3738, found: 449.3744.

Procedure for the synthesis of 1,3,5-tris(5-(3,5-bis(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene **(4a)**[2]

Benzene-1,3,5-tricarboxylic acid (1 equiv.) in 4.5 ml of thionyl chloride and DMF (catalytic amount) was heated under reflux for 4 h. The excess of thionyl chloride was removed by distillation; the crude product (benzene-1,3,5-tricarbonyl trichloride) was dried in vacuo and used for the next reaction without further purification and characterization. The solution of benzene-1,3,5-tricarbonyl trichloride (1equiv.) in THF was added dropwise to a solution of 3,5-bis(decyloxy)benzohydrazide (3.3 equiv.) and triethylamine (3 equiv.) in THF (20 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 dichloromethane. The extract was washed with water and brine. Dried over anhydrous Na_2SO_4 and concentrated. The resulting crude product was directly used for next reaction where the crude product (1 equiv.) was taken in $POCl_3$ and refluxed for 24 h. The reaction mixture was cooled to room temperature and carefully added to ice-water and extracted with chloroform. After removal of solvent *in vacuo*, the crude product was purified through column chromatography on neutral alumina. Elution with 30-40% ethylacetate-hexanes yielded the desired product which was further recrystallized in ethanol.

4a: R_f = 0.85 (50% EtOAc-hexanes); a dirty white solid; yield: 55-60%; IR (KBr pellet): ν_{max} cm^{-1} 2921, 2851, 1599, 1551, 1541, 1467, 1441, 1386, 1362, 1290, 1175, 1060, 855, 834, 734, 721, 678; ^1H NMR ($CDCl_3$, 400 MHz): δ 9.04 (s,3H, Ar), 7.32 (d, *J* = 4 Hz, 6H, Ar), 6.66 (s, 3H, Ar), 4.07-4.04 (m, 12H, 6 × OCH_2), 1.86-1.22 (m, 96H, 48 × CH_2), 0.89-0.86 (m, 18H, 6 × CH_3), ^{13}C NMR ($CDCl_3$, 100MHz): 165.89, 163.00, 161.02, 127.56, 126.41, 124.77, 105.79,

105.57, 68.72, 32.12, 29.82, 29.81, 29.64, 29.56, 29.42, 26.27, 22.91, 14.36; MALDI Tof MS ES+ for $C_{90}H_{139}N_6O_9$ (M+1), Calculated :1448.059, Found: 1448.264.

Procedure for the synthesis of 1,4-bis(5-(3,5-bis(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (**5a**)[3]

Terephthalic acid (1 eqiv.) in 4.5 ml of thionyl chloride and DMF (catalytic amount) was heated under reflux for 4 h. The excess of thionyl chloride was removed by distillation; the crude product (terephthaloyl dichloride) was dried in vacuo and used for the next reaction without further purification and characterization. The solution of terephthaloyl dichloride (1 equiv.) in THF was added dropwise to a solution of 3,5-bis(decyloxy)benzohydrazide (2.2 equiv.) and triethylamine (2 equiv.) in THF (20 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 dichloromethane. The extract was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated. The resulting crude product was directly used for next reaction where the crude product (1equiv.) was taken in $POCl_3$ and refluxed for 24 h. The reaction mixture was cooled to room temperature and carefully added to ice-water and extracted with chloroform. After removal of solvent *in vacuo*, the crude product was purified through column chromatography on neutral alumina. Elution with 30-40% ethylacetate-hexanes yielded the desired product, which was further recrystallized in ethanol.

5a: R_f = 0.89 (50% EtOAc-hexanes); off white solid; yield: 47-52 %; IR (KBr pellet): ν_{max} cm^{-1} 2921, 2851, 1598, 1546, 1493, 1468, 1443, 1356, 1300, 1178, 1049, 838, 853, 731, 680; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.30 (s, 4H, Ar), 7.27-7.25 (m, 4H, Ar), 6.63 (s, 2H, Ar), 4.04-4.01 (m, 8H, 4 × OCH_2), 1.85-1.27 (m, 64H, 32 × CH_2) 0.89-0.86 (m, 12H, 4 × CH_3), ^{13}C NMR ($CDCl_3$, 100MHz): 165.35, 163.88, 160.96, 127.72, 126.77, 125.07, 105.48, 105.37, 68.67, 32.12, 29.81, 29.79, 29.61, 29.55, 29.40,26.25, 22.91, 14.36; MALDI Tof MS ES+ for $C_{62}H_{95}N_4O_6$ (M+1), Calculated: 991.724, Found: 991.503.

Procedure for the synthesis of 1,3-bis(5-(3,5-bis(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (**6a**)[3]

Isophthalic acid (1 equiv.) in 4.5 ml of thionyl chloride and DMF (catalytic amount) was heated under reflux for 4 h. The excess of thionyl chloride was removed by distillation; the crude

product (isophthaloyl dichloride) was dried in vacuo and used for the next reaction without further purification and characterization. The solution of isophthaloyl dichloride (1equiv.) in THF was added dropwise to a solution of 3,5-bis(decyloxy)benzohydrazide (2.2 equiv.) and triethylamine (2 equiv.) in THF (20 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 dichloromethane. The extract was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated. The resulting crude product was directly used for next reaction where the crude product (0.4 mmol, 1equiv.) was taken in $POCl_3$ and refluxed for 24 h. The reaction mixture was cooled to room temperature and carefully added to ice-water and extracted with chloroform. After removal of solvent *in vacuo*, the crude product was purified through column chromatography on neutral alumina. Elution with 30-40% ethylacetate-hexanes yielded the desired product which was further recrystallized in ethanol.

6a: R_f = 0.88 (50% EtOAc-hexanes); off white solid; yield: 51-56%; IR (KBr pellet): ν_{max} cm^{-1} 2921, 2851, 1601, 1551, 1467, 1442, 1299, 1174, 1058, 857, 834, 731; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.89 (s, 1H, Ar), 8.33 (d, *J* =4 Hz, 2H, Ar), 7.73 (t, 1H, Ar), 7.29 (s, 4H, Ar), 6.54 (s, 2H, Ar), 4.04 (t, 8H, 4 × OCH_2) 1.83-1.28 (m, 64H, 32 × CH_2) 0.88 (t, 12H, 4 × CH_3), ^{13}C NMR ($CDCl_3$, 150MHz): 165.42, 163.84, 161.00, 130.20, 130.02, 125.33, 125.29, 125.12, 105.52, 68.70, 32.11, 29.79, 29.61, 29.54, 29.42, 26.25, 22.90, 14.34; MALDI Tof MS ES+ for $C_{62}H_{95}N_4O_6$ (M+1), Calculated: 991.724, Found: 991.894.

Procedure for the synthesis of 1,3,5-tris(5-(3,5-bis(decyloxy)phenyl)-1,3,4-thiadiazol-2-yl)benzene **(4b)**[2]

Benzene-1,3,5-tricarboxylic acid (1 equiv.) in 4.5 ml of thionyl chloride and DMF (catalytic amount) was heated under reflux for 4 h. The excess of thionyl chloride was removed by distillation; the crude product (benzene-1,3,5-tricarbonyl trichloride) was dried in vacuo and used for the next reaction as such. The solution of benzene-1,3,5-tricarbonyl trichloride (1equiv.) in THF was added dropwise to a solution of 3,5-bis(decyloxy)benzohydrazide (3.3 equiv.) and triethylamine (3 equiv.) in THF (20 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 dichloromethane. The extract was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated. The resulting crude product was directly used for next reaction. The crude

product (1equiv.) was taken in dry toluene (8 mL) was added dropwise to a solution of Lawesson's reagent (3.6 equiv.) at room temperature under Argon atmosphere and refluxed for 24 h. Toluene was removed by distillation. After removal of solvent *in vacuo*, the crude product was purified through column chromatography on neutral alumina. Elution with 30-40% ethylacetate-hexanes yielded the desired product which was further recrystallized in ethanol.

4b: R_f = 0.7 (50% EtOAc-hexanes); a brown solid; yield: 45-50 %; IR (KBr pellet): ν_{max} cm^{-1} 2924, 2853, 1600, 1458, 1422, 1389, 1345, 1169, 1057, 840, 739, 675; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.73 (s, 3H, Ar), 7.16 (s 6H, Ar), 6.60 (s, 3H, Ar), 4.04-4.01 (m, 12H, 6 × OCH_2), 1.84-1.24 (m, 96H, 48 × CH_2), 0.88 (t, 18H, 6 × CH_3), ^{13}C NMR ($CDCl_3$, 100MHz): 169.48, 165.97, 160.85, 132.29, 131.25, 128.57, 106.40, 104.78, 68.60, 32.13, 29.84, 29.82, 29.62, 29.57, 29.44, 26.25, 22.91, 14.35. MALDI Tof MS ES+ for $C_{90}H_{139}N_6O_6S_3$ (M+1), calculated: 1495.9913, Found: 1496.623.

Procedure for the synthesis of 1,4-bis(5-(3,5-bis(decyloxy)phenyl)-1,3,4-thiadiazol-2-yl)benzene (**5b**)[3]

Terephthalic acid (1equiv.) in 4.5 ml of thionyl chloride and DMF (catalytic amount) was heated under reflux for 4 h. The excess of thionyl chloride was removed by distillation; the crude product (terephthaloyl dichloride) was dried in vacuo and used for the next reaction as such. The solution of terephthaloyl dichloride (1 equiv.) in THF was added dropwise to a solution of 3,5-bis(decyloxy)benzohydrazide (2.2 equiv.) and triethylamine (2 equiv.) in THF (20 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 dichloromethane. The extract was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated. The resulting crude product was directly used for next reaction. Here the crude product (1 equiv.) was taken in dry toluene (8 mL) to which a solution of Lawesson's reagent (2.4 equiv.) was added dropwise at room temperature under Argon atmosphere and then refluxed for 24 h. Toluene was removed by distillation. After removal of solvent *in vacuo*, the crude product was purified through column chromatography on neutral alumina. Elution with 30-40% ethylacetate-hexanes yielded the desired product which was further recrystallized in ethanol.

5b: R_f = 0.7 (50% EtOAc-hexanes); off white solid; yield: 47-52%; IR (KBr pellet): ν_{max} cm^{-1} 2920, 2851, 1595, 1463, 1421, 1388, 1345, 1291, 1060, 987, 839, 772, 722, 678; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.13 (s, 4H, Ar), 7.15 (s, 4H, Ar), 6.59 (s, 2H, Ar), 4.02 (t, 8H, 4 × OCH_2) 1.88-1.28 (m, 64H, 32 × CH_2), 0.88 (t, 12H, 4 × CH_3), ^{13}C NMR ($CDCl_3$, 100MHz): 168.48, 166.52, 160.34, 132.00, 130.95, 128.16, 105.94, 104.18, 68.06, 31.56, 29.25, 29.23, 29.05, 28.99, 28.84, 25.68, 22.35, 13.79. MALDI Tof MS ES+: m/z for $C_{62}H_{95}N_4O_4S_2$(M+1), Calculated: 1024.6828 Found: 1024.606.

Procedure for the synthesis of 1,3-bis(5-(3,5-bis(decyloxy)phenyl)-1,3,4-thiadiazol-2-yl)benzene (**6b**)[3]

Isophthalic acid (1 equiv.) in 4.5 ml of thionyl chloride and DMF (catalytic amount) was heated under reflux for 4 h. The excess of thionyl chloride was removed by distillation; the crude product (isophthaloyl dichloride) was dried in vacuo and used for the next reaction as such. The solution of isophthaloyl dichloride (1equiv.) in THF was added dropwise to a solution of 3,5-bis(decyloxy)benzohydrazide (2.2 equiv.) and triethylamine (2 equiv.) in THF (20 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 dichloromethane. The extract was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated. The resulting crude product was directly used for next reaction. Here the crude product (1equiv.) was taken in dry toluene (8 mL) to which to a solution of Lawesson's reagent (2.4 equiv.) was added dropwise at room temperature under Argon atmosphere and refluxed for 24 h. Toluene was removed by distillation. After removal of solvent *in vacuo*, the crude product was purified through column chromatography on neutral alumina. Elution with 30-40% ethylacetate-hexanes yielded the desired product which was further recrystallized in ethanol.

6b: R_f = 0.69 (50% EtOAc-hexanes); dirty white solid; yield: 52-55%; IR (KBr pellet): ν_{max} cm^{-1} 2921, 2852, 1594, 1452, 1432, 1389, 1344, 1056, 836, 721; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.58 (s, 1H, Ar), 8.14 (d, *J* =12Hz, 2H, Ar), 7.63 (t, 1H, Ar), 7.15 (s, 4H, Ar), 6.59 (s, 2H, Ar), 4.02 (t, 8H, 4 × OCH_2), 1.83-1.28 (m, 64H, 32 × CH_2) 0.88 (t, 12H, 4 × CH_3), ^{13}C NMR ($CDCl_3$, 100 MHz): 169.02, 167.05, 160.87, 160.81, 131.48, 131.37, 130.20, 127.25, 106.45, 104.58, 68.58, 32.11, 29.80, 29.78, 29.60, 29.54, 29.39, 26.22, 22.89, 14.34. MALDI Tof MS ES+ : m/z for $C_{62}H_{95}N_4O_4S_2$(M+1), Calculated: 1024.6828 Found: 1024.606.

3. NMR Spectra

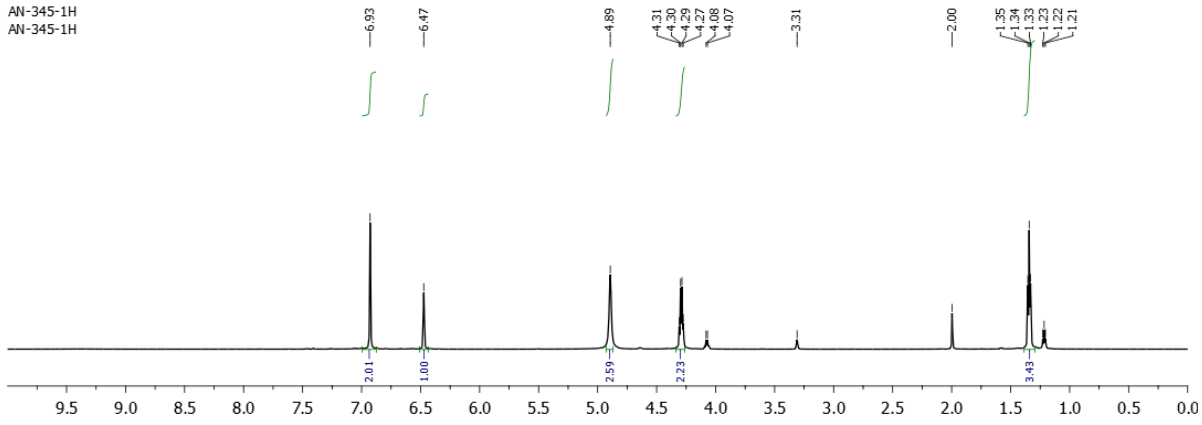

Figure S1. ^{1}H NMR (600 MHz) spectra of **1** in CD_3OD.

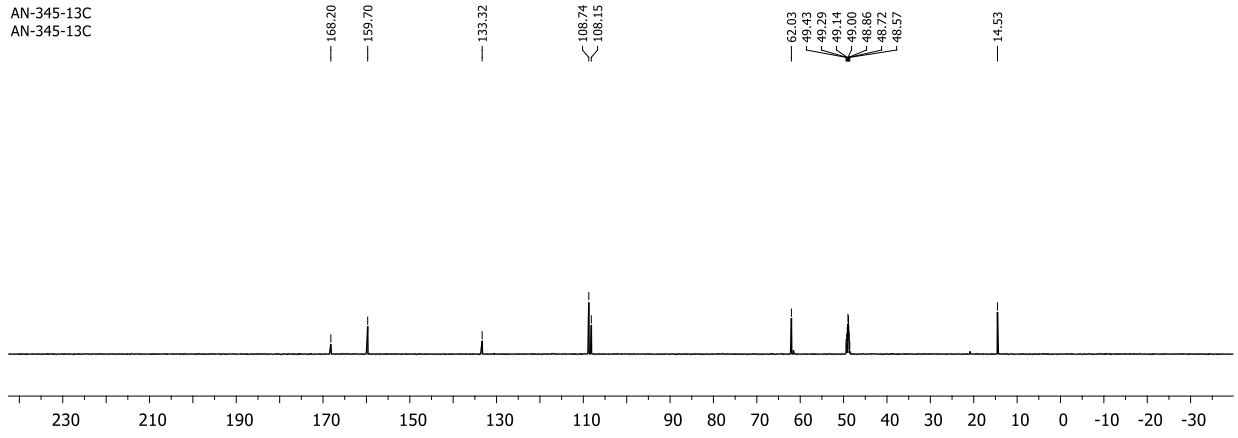

Figure S2. ^{1}H NMR (600 MHz) spectra of **1** in CD_3OD.

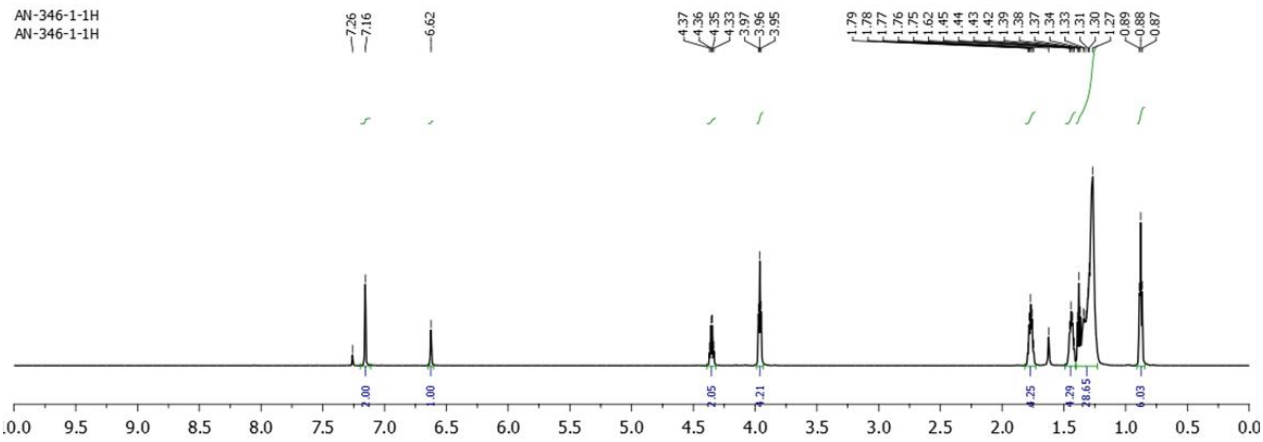

Figure S3. ^{1}H NMR (600 MHz) spectra of **2** in $CDCl_3$.

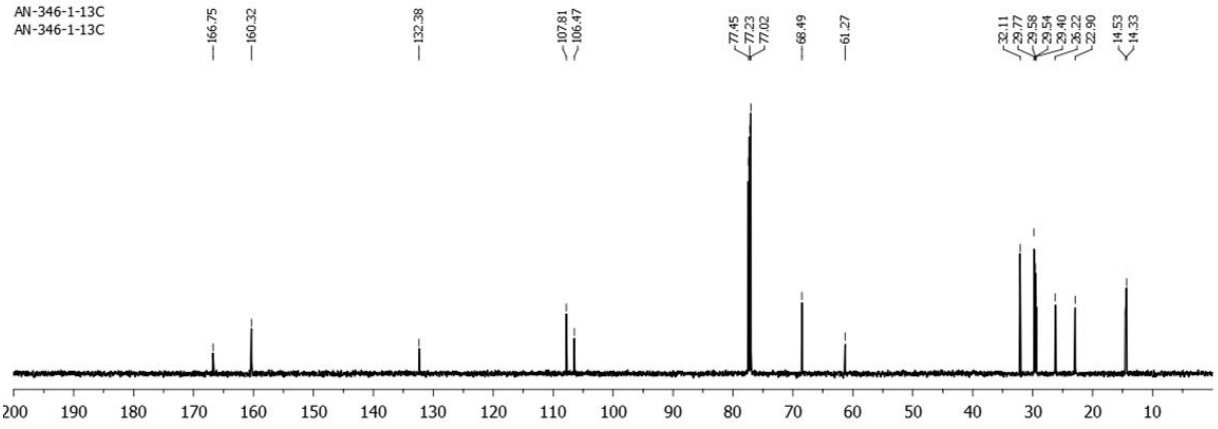

Figure S4. ^{13}C NMR (600 MHz) spectra of **2** in $CDCl_3$.

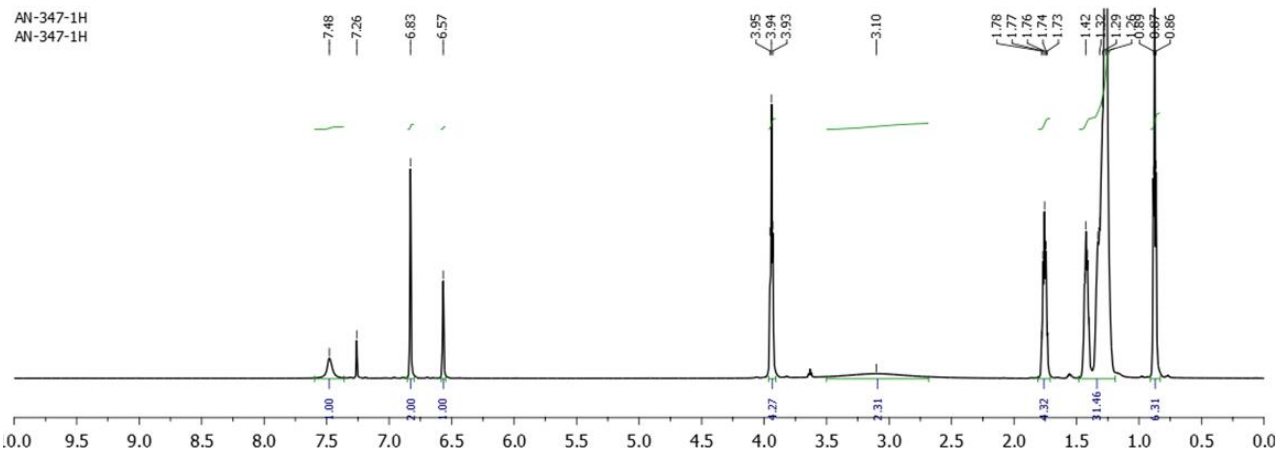

Figure S5. ^{1}H NMR (600 MHz) spectra of **3** in $CDCl_3$.

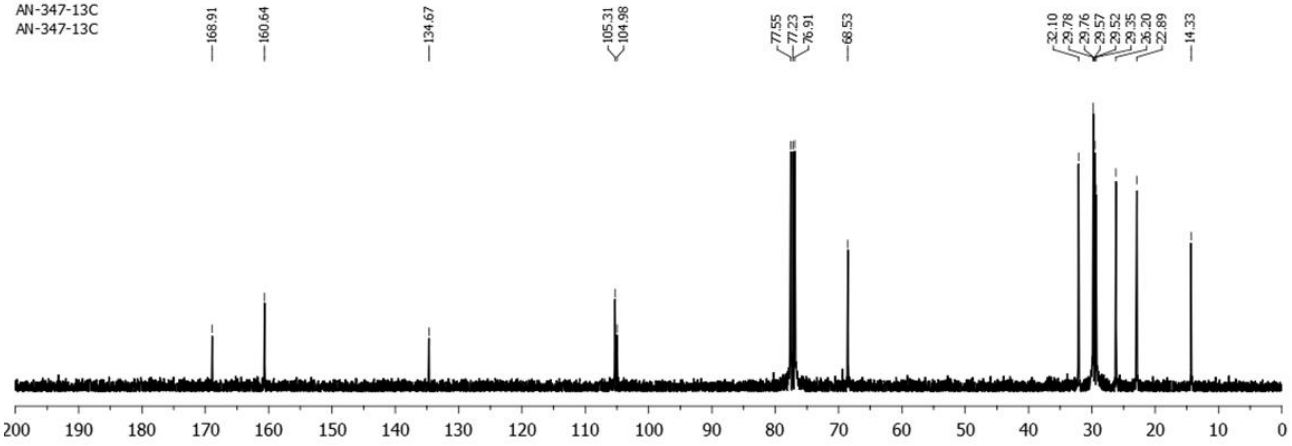

Figure S6. ^{13}C NMR (400 MHz) spectra of **3** in $CDCl_3$

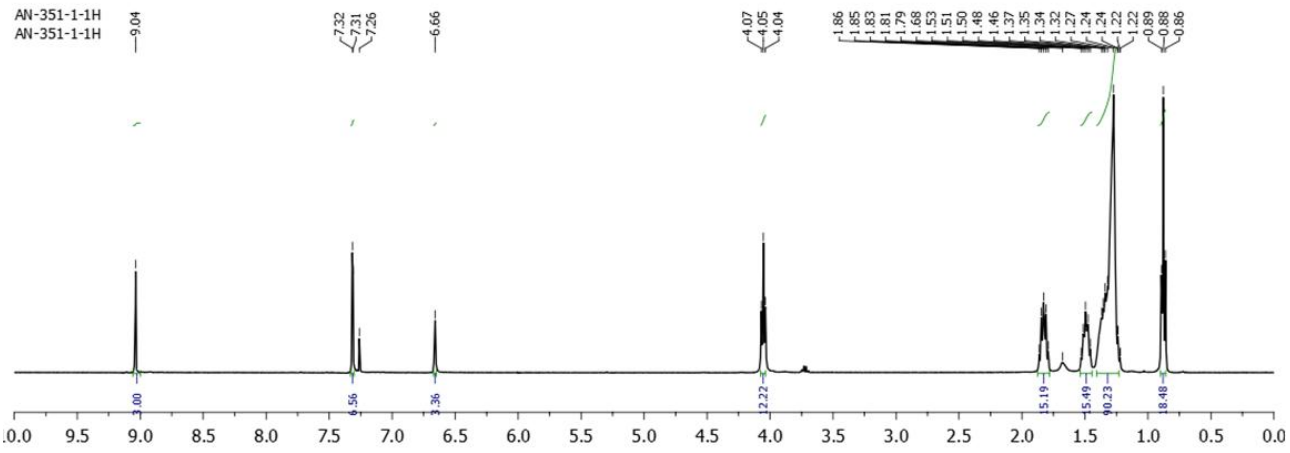

Figure S7. ^{1}H NMR (400 MHz) spectra of **4a** in $CDCl_3$.

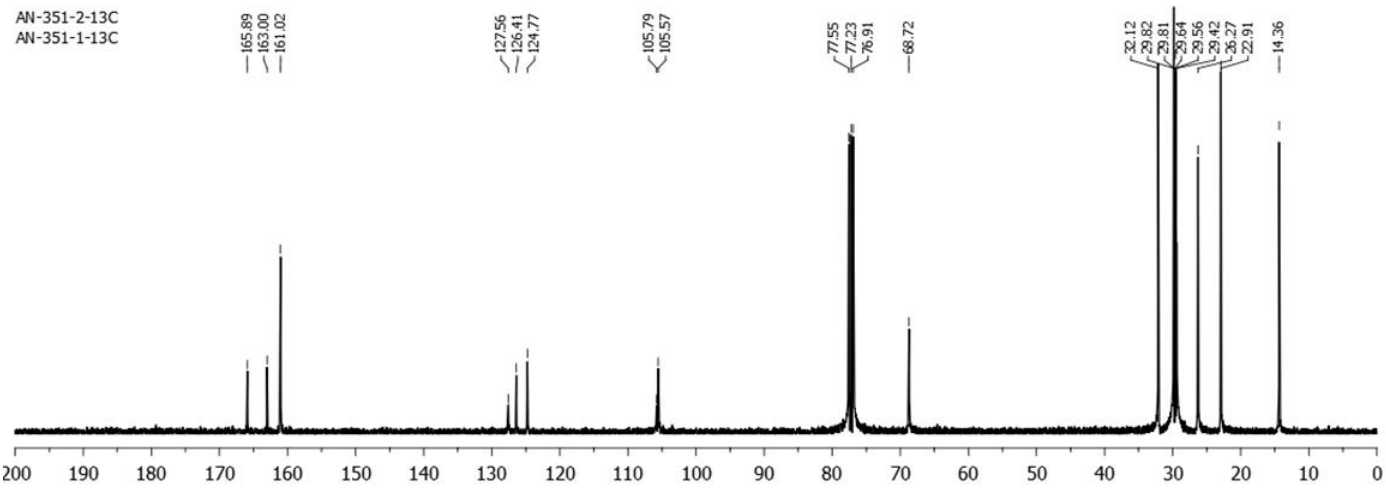

Figure S8. ^{13}C NMR (400 MHz) spectra of **4a** in $CDCl_3$.

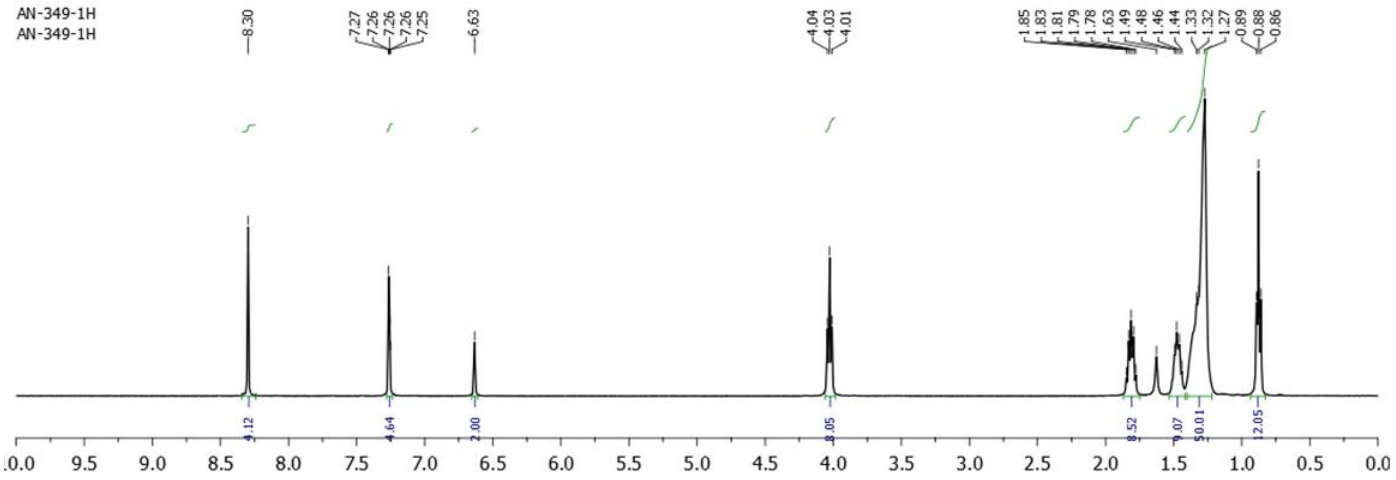

Figure S9. ^{1}H NMR (400 MHz) spectra of **5a** in $CDCl_3$.

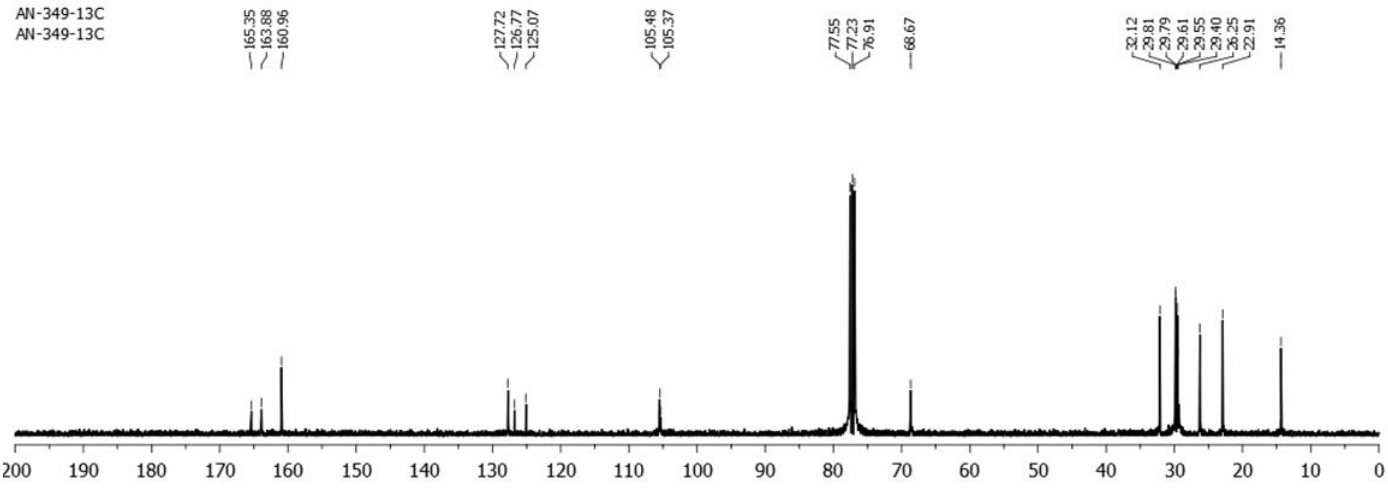

Figure S10. ^{13}C NMR (400 MHz) spectra of **5a** in $CDCl_3$.

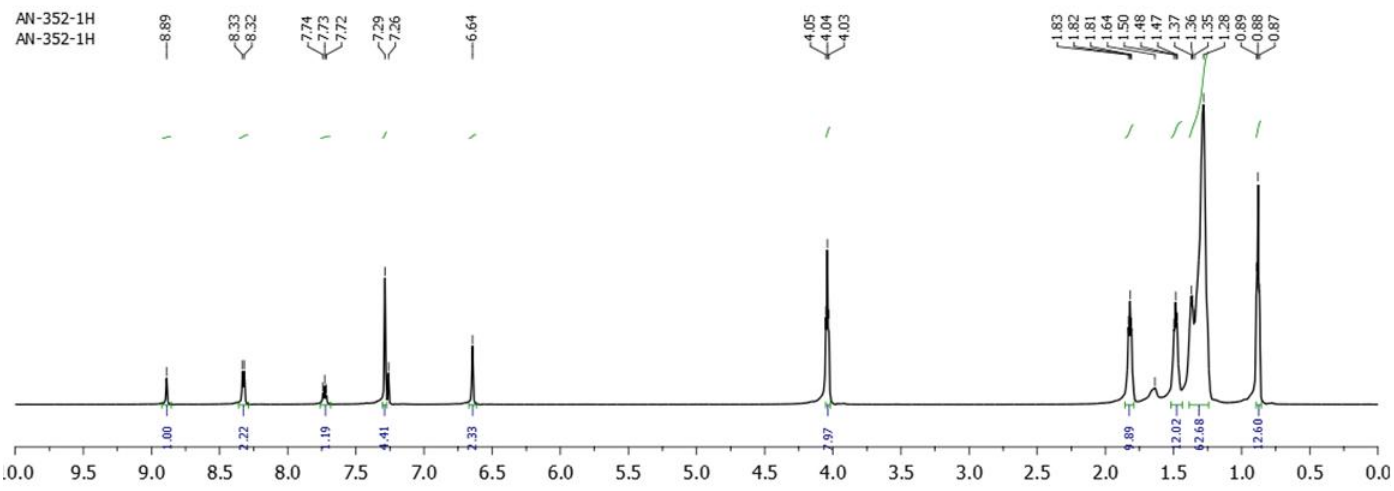

Figure S11. ^{1}H NMR (600 MHz) spectra of **6a** in $CDCl_3$.

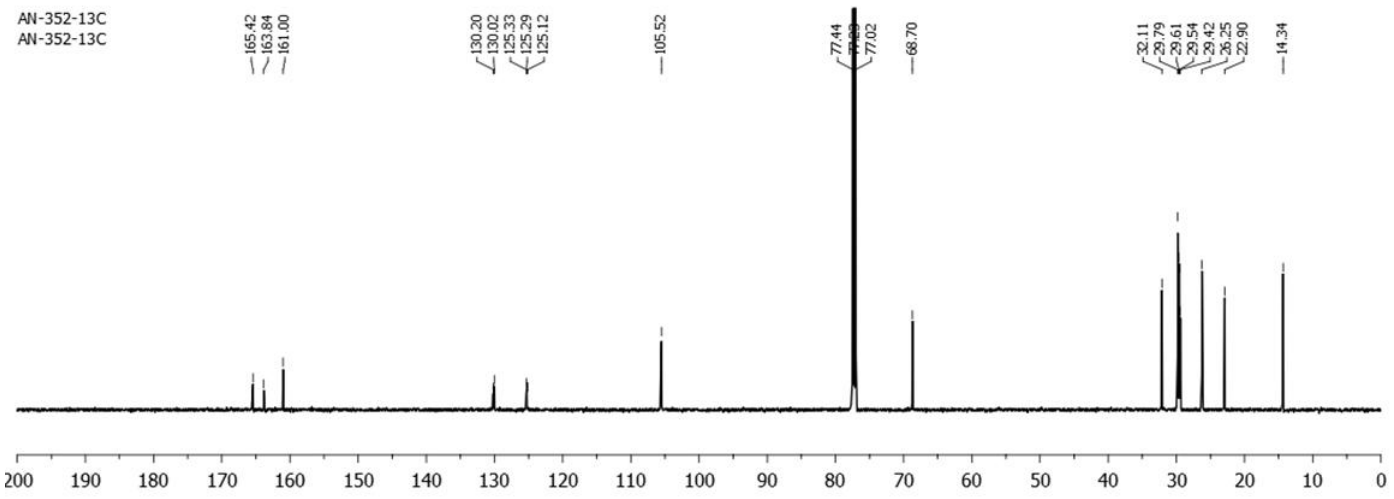

Figure S12. ^{13}C NMR (600 MHz) spectra of **6a** in $CDCl_3$.

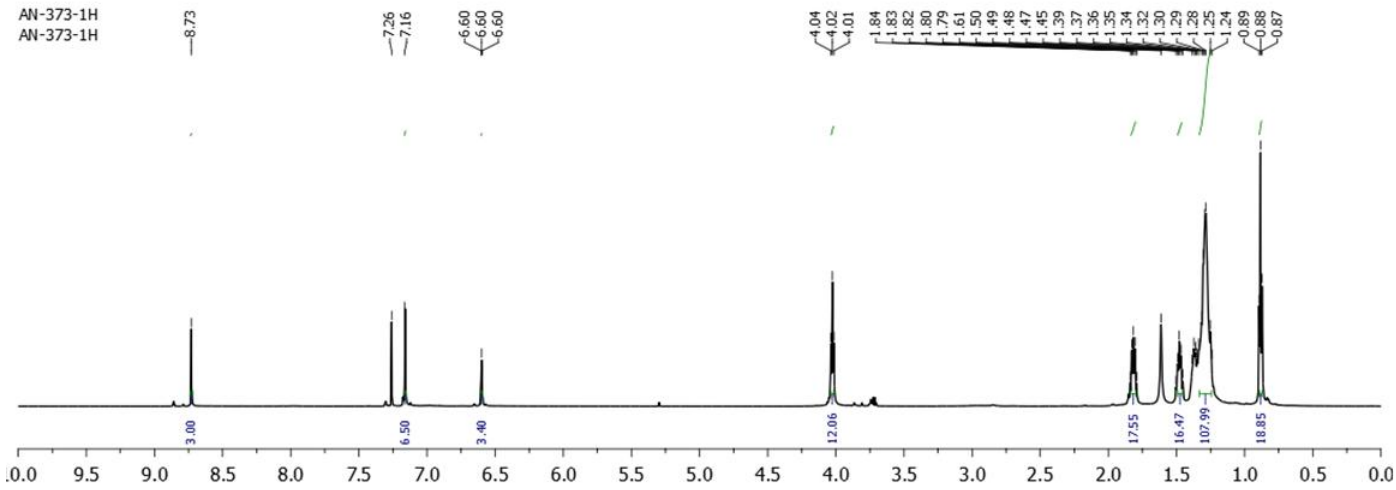

Figure S13. ^{1}H NMR (600 MHz) spectra of **4b** in $CDCl_3$.

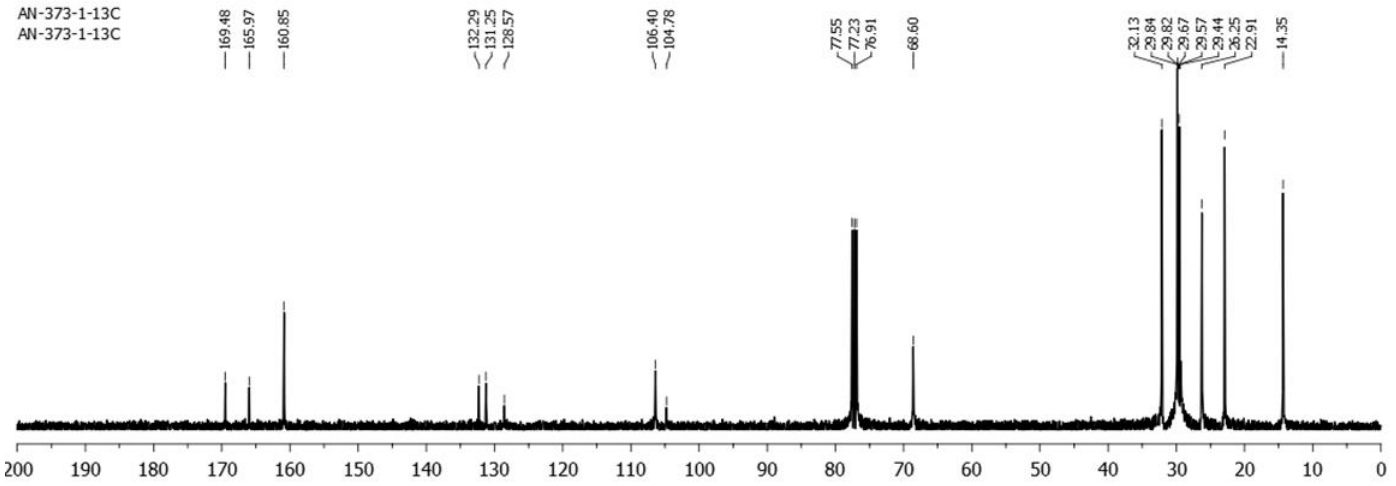

Figure S14. ^{13}C NMR (400 MHz) spectra of **4b** in $CDCl_3$.

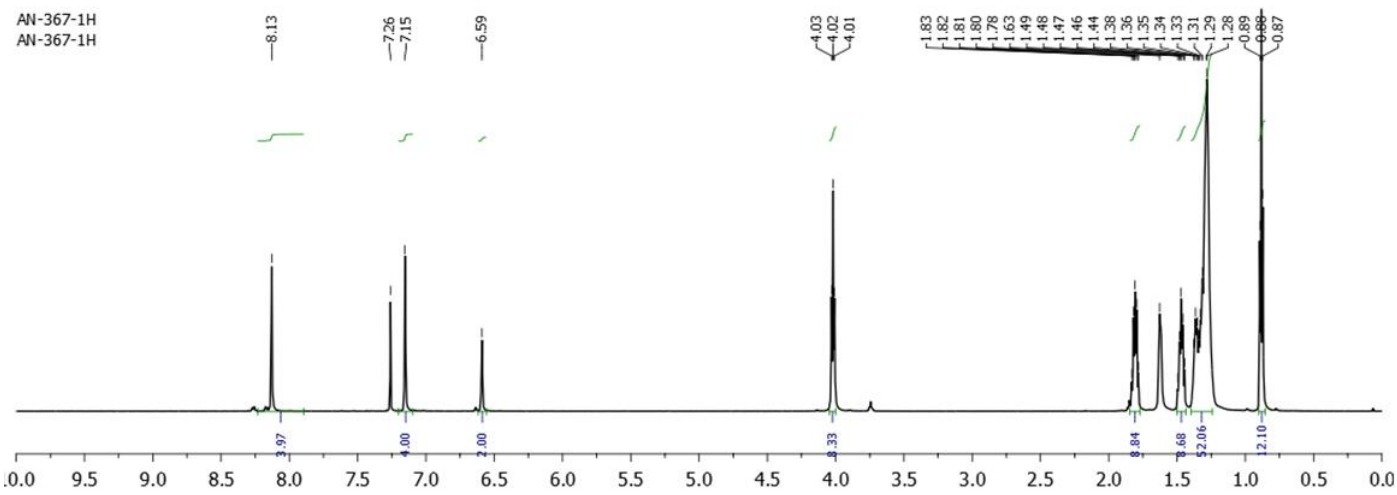

Figure S15. ^{1}H NMR (600 MHz) spectra of **5b** in $CDCl_3$.

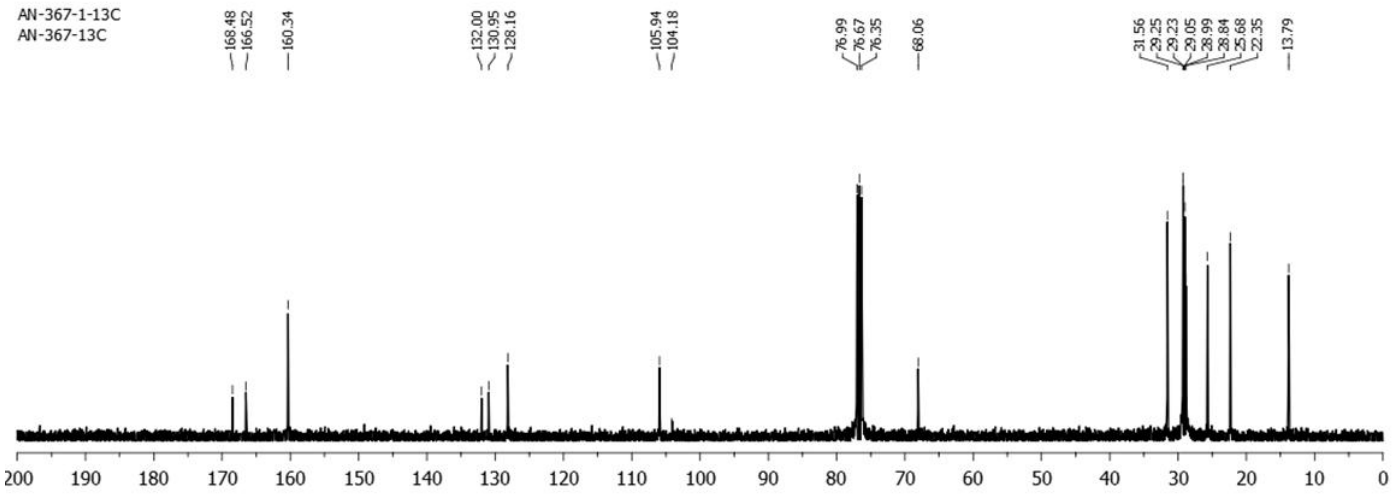

Figure S16. ^{13}C NMR (400 MHz) spectra of **5b** in $CDCl_3$.

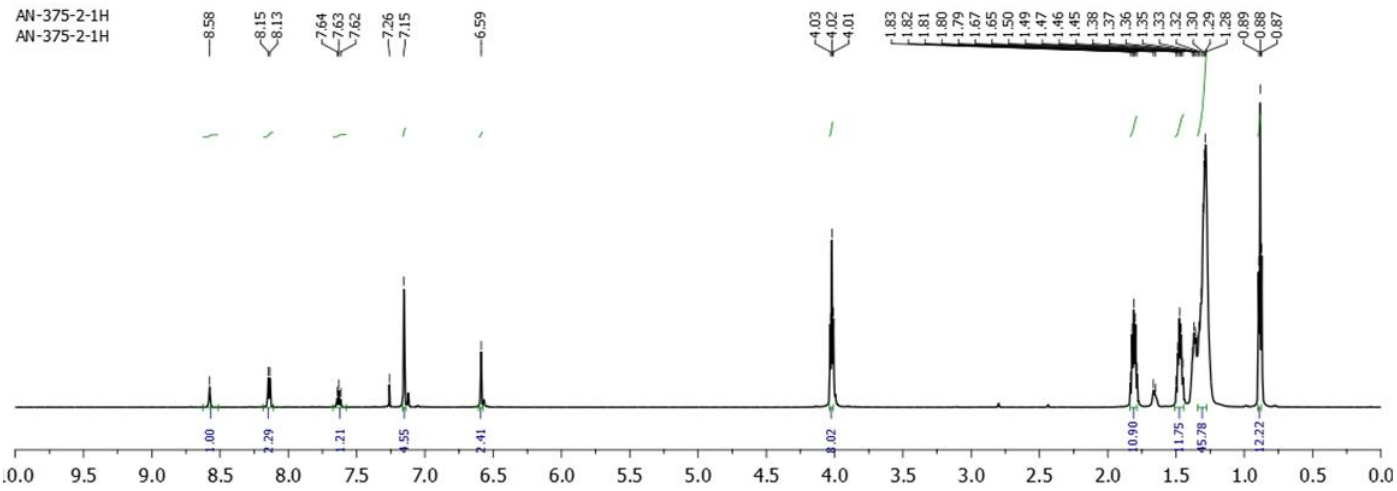

Figure S17. ^{1}H NMR (600 MHz) spectra of **6b** in $CDCl_3$.

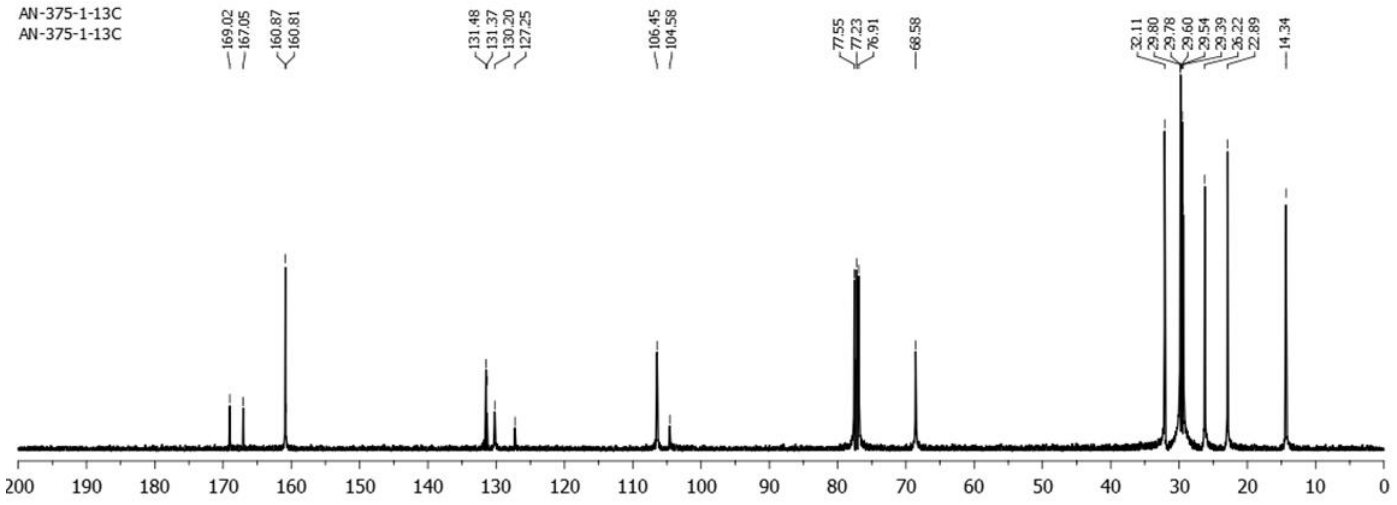

Figure S18. ^{13}C NMR (400 MHz) spectra of **6b** in $CDCl_3$.

4. Differential Scanning Calorimetry

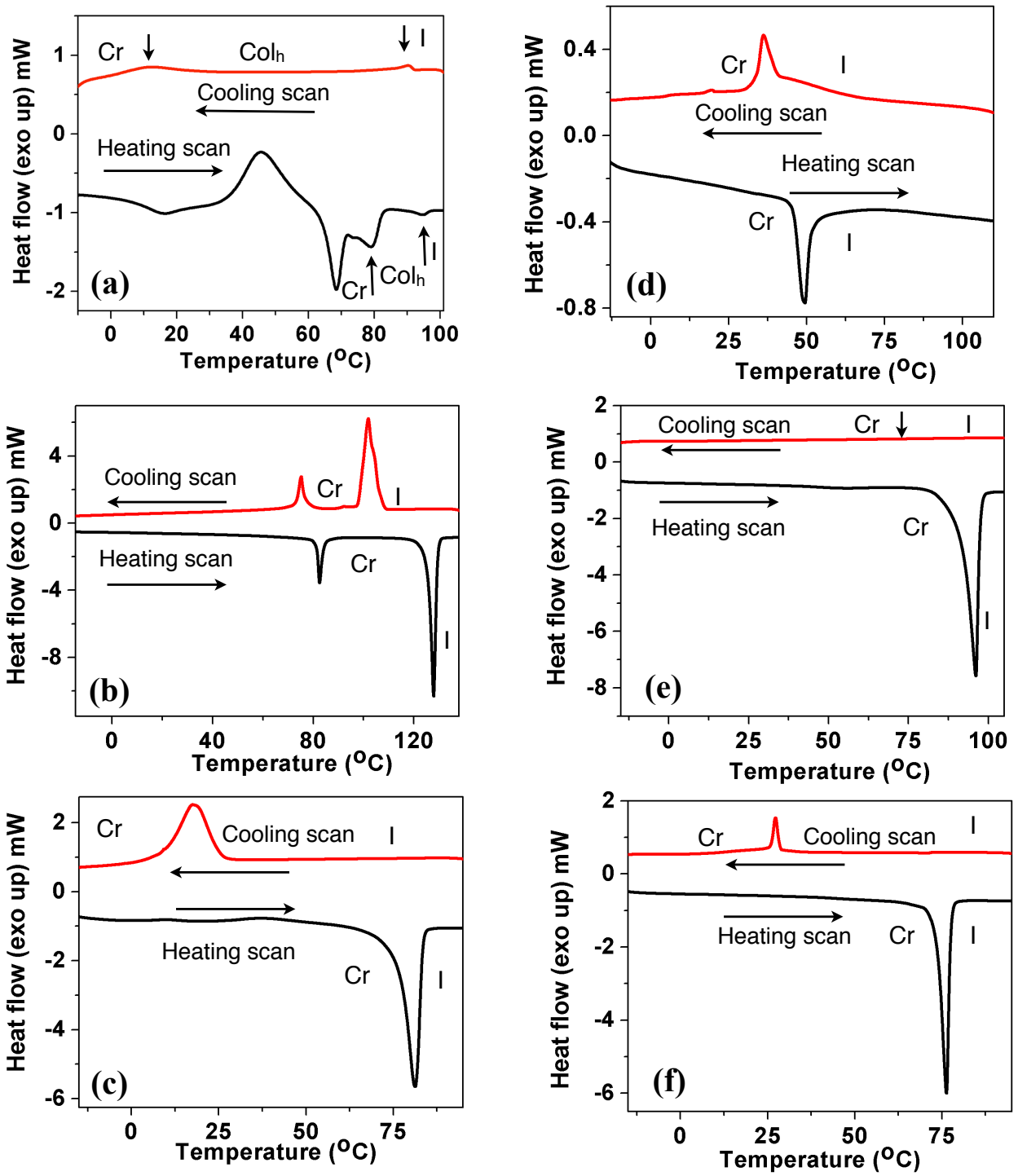

Figure S19. DSC scans obtained for the first cooling (red trace) and second heating (black trace) cycle of compound **4a** (a); **5a** (b); **6a** (c); **4b** (d); **5b** (e) and **6b** (f).

5. Photophysical properties

Quantum yield measurement: 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.

$Q_S = 0.54 \times (m_S / 2.71) \times (1.407/1.33)^2 = 0.223 \times m_S$

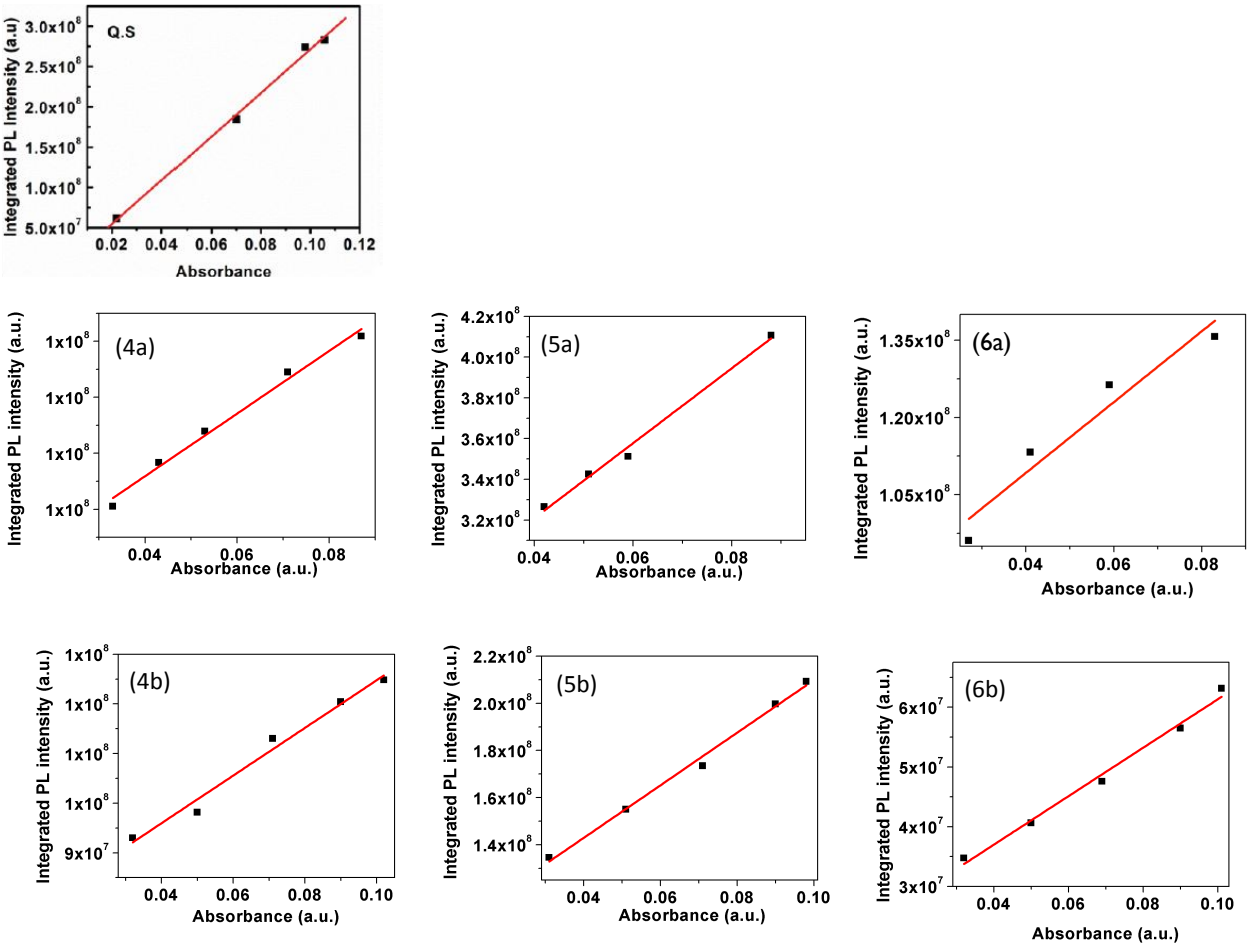

Figure S20. Plots of integrated photoluminescence intensity *vs* absorbance of Quinine sulphate (0.1M H_2SO_4 solution) and compounds **4a-b, 5a-b** and **6a-b** (micromolar THF solution).

Entry	m_s	m_r	Q_s[a,b,c]
4a	5.59×10^8	2.71×10^9	0.206
5a	1.83×10^9	2.71×10^9	0.675
6a	6.88×10^8	2.71×10^9	0.254
4b	4.80×10^8	2.71×10^9	0.177
5b	1.12×10^9	2.71×10^9	0.413
6b	4.05×10^8	2.71×10^9	0.149
[a] Measured in THF; [b]Excited at absorption maxima; [c]Standard quinine sulphate (Q_f= 0.54) in 0.1M H_2SO_4.			

6. Electrochemical studies

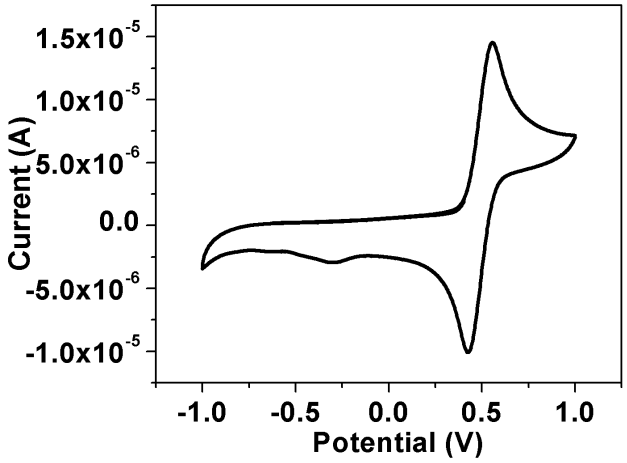

Figure S21. Cyclic voltammograms of ferrocene

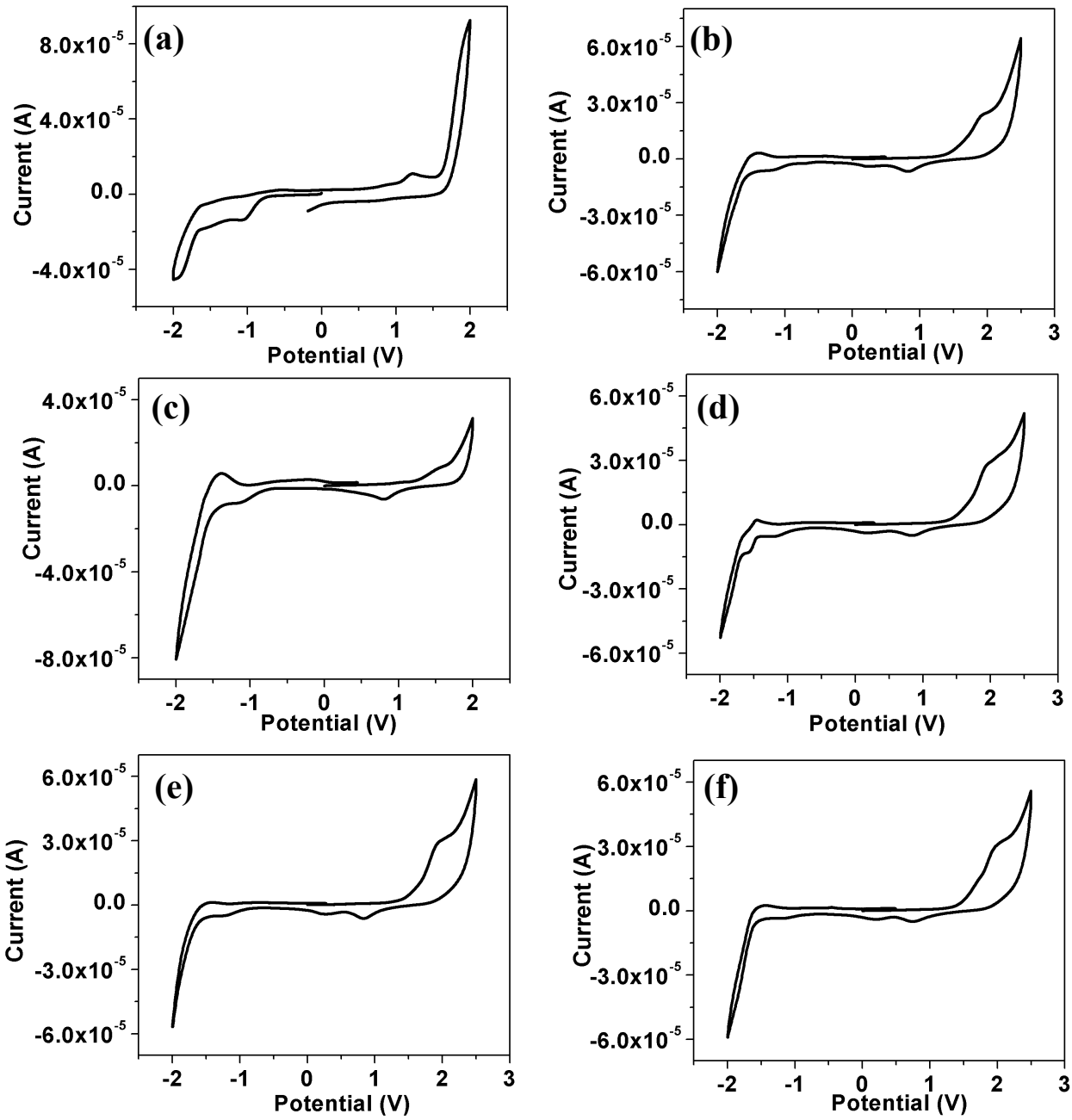

Figure S22. Cyclic Voltammogram of compound **4a** (a); **4b** (b); **5a** (c); **5b** (d); **6a** (e); **6b** (f).

7. Gelation studies

Table 1. Results of the (*hkl*) indexation of the XRD profiles of the xerogels at room temperature.[a]

Compounds (*D*/Å)	Phase	d_{obs} (Å)	d_{cal} (Å)	Miller indices (*hk)*	Lattice parameters (Å)
4a (41.1)	Cr	31.74 15.74 12.47 11.53 10.49 9.50 7.88 7.27 6.70 6.30 5.91 5.08 4.65 4.17 3.88 3.76 3.34 3.23			
7a (47.7)	Col_r *P2mm*	38.27 13.58 8.61 4.95 4.02(h_a) 3.68 (h_c)	38.27 13.58 7.99 4.84	01 11 14 30	a = 14.55; b = 38.27.
7b (48.4)	Cr	31.83 22.33 15.68 13.67 10.50 9.45 7.96 7.52 6.34 5.78 5.32 4.96 4.47 4.04 3.83 3.52 3.20 2.94 2.72			

[a]The diameter (*D*) of the disk (estimated from Chem 3D Pro 8.0 molecular model software from Cambridge Soft). d_{obs}: spacing observed; d_{cal}: spacing calculated (deduced from the lattice parameters; a for Col_h phase). The spacings marked h_a and h_c correspond to diffuse reflections in the wide-angle region arising from correlations between the alkyl chains and core regions, respectively.

8. Rheological studies

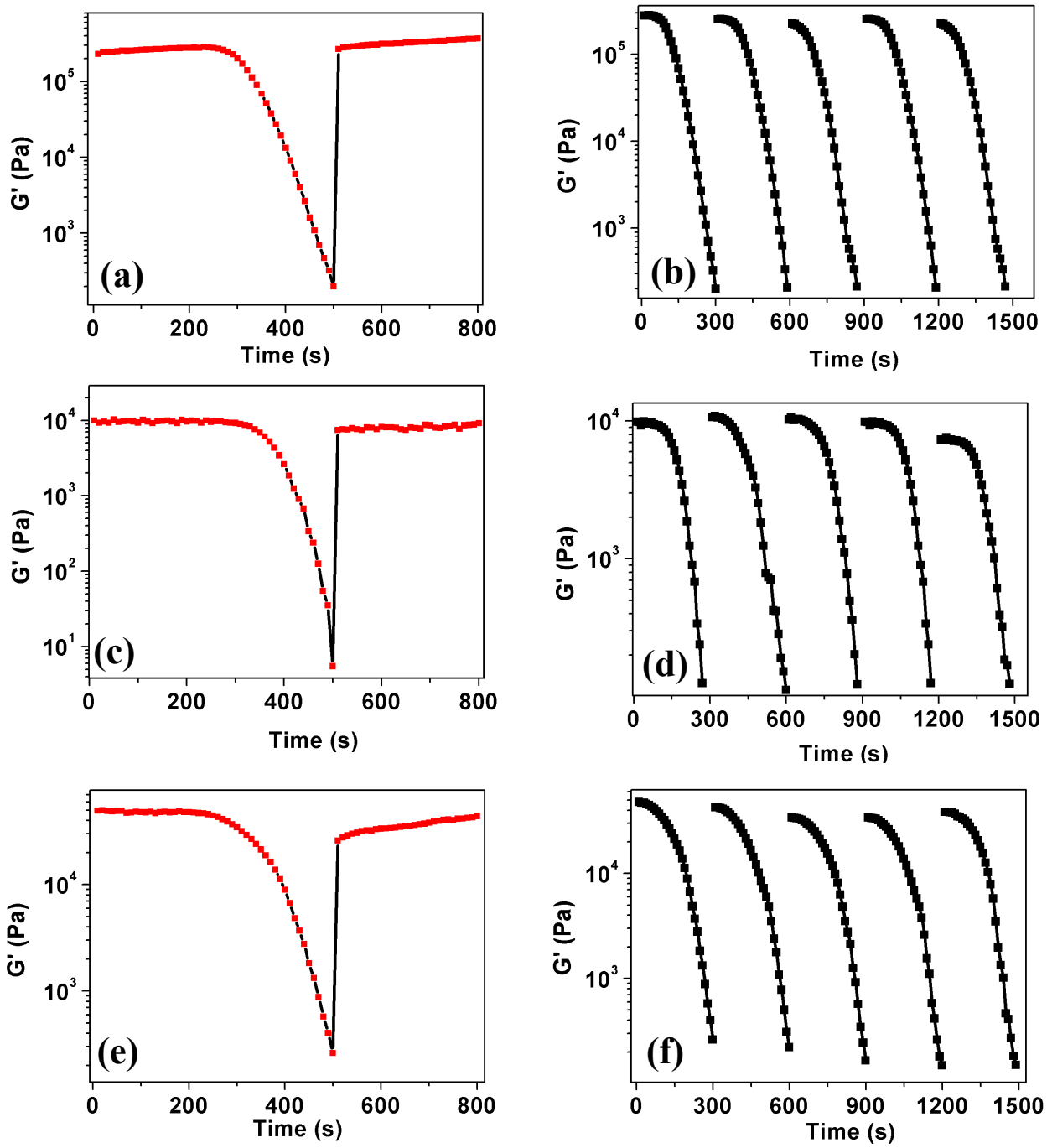

Figure S23. Thixotropic nature of organogel at their CGC, for **4a** (a), **7a** (c) and **7b** (e) in *n*-dodecane at 25 °C (Deformation; stress: 0.1 to 100 Pa, time: 300 s, angular frequency: 10 Hz; Recovery; Stress: 1 Pa, time: 300 s; angular frequency: 10 Hz.); Five continuous cycles of measurement for **4a** (b), **7a** (d) and **7b** (f) (at CGC) to prove that gel is thixotropic.

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) S. K. Pathak, R. K. Gupta, S. Nath, D. S. Shankar Rao, S. K. Prasad and A. S. Achalkumar, *J. Mater. Chem. C*, 2015, **3**, 2940-2952.

(3) S. K. Pathak, R. K. Gupta, S. Nath, D. S. Shankar Rao, S. K. Prasad and A. S. Achalkumar, *J. Mater. Chem. C*, 2015, **3**, 8166–8182.