Electronic Supplementary Material (ESI) for Chemical Communications.


# Modulating nanostructure morphology and mesomorphic properties using unsaturation in cardanol – azo benzenes

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## MATERIALS AND METHODS

### General methods

All starting materials were obtained from commercial suppliers and used as received, except otherwise mentioned. 3-Pentadecyl phenol was purchased from TCI America. Cardanol was supplied by golden cashew Pvt Ltd and it was purified by double vacuum distillation of cashew-nut shell liquid at 3-4 mm Hg, the fraction distilled at 230-235 $^{\circ}$C was collected. Cardanol consists of a mixture of four phenolic lipids, with varying degree of unsaturation in the side chain: 5% of 3-(pentadecyl)phenol, 49% 3-(8Z-pentadecenyl)phenol, 17% of 3-(8Z,11Z-pentadecadienyl)- phenol and 29% of 3-(8Z,11Z,14Z-pentadecatrienyl)phenol.

$^{1}$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra of samples were recorded on a Bruker-400 MHz NMR spectrometer instrument with the chemical shift (δ) given in parts per million (ppm). Proton chemical shifts are reported in parts per million downfield from tetramethylsilane (TMS). The IR spectra were recorded on a Perkin Elmer Model 882 infrared spectrometer. Mass spectra were recorded on a Thermo Scientific Exactive mass spectrometer operating in ESI/HRMS mode. All the solvents used were purified by distillation before use. The progress of the reaction was monitored by looking TLC of the reaction mixture at various time intervals.

SEM images were obtained using a Jeol-JSM-6490-LA scanning electron microscope (SEM) with an accelerating voltage of 15 KV and an FE-SEM Gemini 300 Carlzeissinstrument. Samples were prepared by spinning the samples on glass slices and coating them with Au. The electronic absorption spectra were recorded on a Shimadzu UV-3101 spectrophotometer, DLS measurements were done by using HORIBA-SZ 100 Nano particle analyzer at 23 $^{0}$C.The compounds were investigated for liquid crystalline behaviour using a polarizing optical microscope (Nikon-Eclipse-LV100NPOL) equipped with a programmable hot stage (LINKAM-T96-S). DSC thermograms were recorded using Q2000 V24.11 Build 124 instrument. X-ray diffraction (XRD) studies were carried out on powder samples in Lindemann capillaries with CuK α (λ = 0.15418 nm) radiation using either an Image plate (IP) detector (GeniX3D, Xenocs) from a source operating at 50 kV and 0.6 mA in conjunction with a multilayer mirror was used to illuminate the sample or PANalytical X'Pert PRO MP machine consisting of a focusing elliptical mirror and a fast high-resolution

detector (PIXCEL). The energy minimised structure of the model was obtained using the software Avogadro 2.

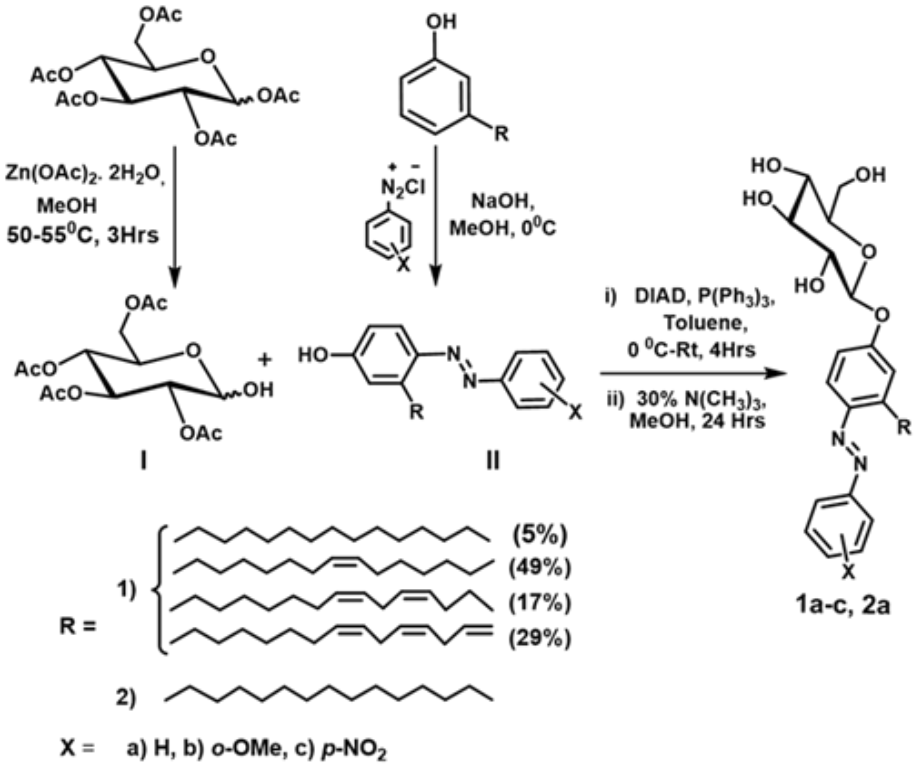
**Method of preparation of viscous phase and gel phase**

**Preparation of viscous phase**

The viscous phase is characterized by its flow and viscoelastic properties, which vary significantly from true solutions. The viscous phase is prepared by hot dissolving required amount of azo dyes (refer Table S1) in toluene or toluene-hexane (The composition of toluene can be 40-100% in the toluene-hexane mixture to obtain the viscous phase). The solution when cool to room temperature becomes viscous, and appeared elastic, which can be pulled into a 'wet string' using a glass rod.

**Preparation of gel phase**

The gelation experiments were carried out with various solvents using a test tube inversion method.The gelators and the solvents were put in a glass vial and heated (> 65 ºC) until the solid was dissolved. Then the sample vial was cooled to 25 ºC. It was then left for few minutes to obtain the gel at ambient conditions. Qualitatively, gelation was considered successful if no sample flow was observed upon inverting the container at room temperature.




**Scheme S1**. Synthesis of azodyes **1a-c** and **2a**.

**Synthesis of D-Glucopyranose,1,2,3,4,6-pentacetate[1]**

To a solution of 1 g D-Glucose (0.0055 mmol) in 5 ml acetic anhydride, added 0.45 g sodium acetate (0.0055 mol) and is heated at reflux for 4 hrs. After cooling to room temperature, the solution is poured into ice water and stirred for 2 hrs. The solid was collected by filtration, dried and recrystallized from water to obtain per acetylated glucose as colourless crystals. White solid (53%, mp 131-132 $^0$C).

$^1$H NMR (400 MHz, $CDCl_3$) δ = 5.72 (1H, d, J = 8.4), 5.26 (1H, t, J = 9.2), 5.14 (2H, m), 4.29 (1H, m), 4.12 (1H, m), 3.84 (1H, m), 2.10 (15H, m).

$^{13}$C NMR (400 MHz, $CDCl_3$). 20.5, 61.1, 67.5, 70.1, 72.6, 91.6, 160.1, 168.1, 169.3, 170.5

LC-MS: m/z = 390.

IR: 3472, 3251, 2966, 1743, 1430, 1381, 1371, 1167, 1080, 1070, 985, 949, 966, 915, 599, 546, 514, 546 and 542cm$^{-1}$.

**Synthesis of D-Glucopyranose,2,3,4,6-tetraacetate[2] (I)**

**General procedure:** 0.056 g Zinc acetate (0.256 mmol) was added to a solution of 1 g peracetylated glucose (2.56 mmol) in 25 mL of methanol, and stirred for 3 hrs at 50-55 $^0$C. The solvent was then evaporated from the mixture under reduced pressure, and the crude product was purified by column chromatography upon silica gel (100-200 mesh) using hexane and ethyl acetate (3:1). The product gave acceptable $^1$H NMR spectra that matched the data reported in the literature. Product was obtained in 60% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ = 2.02 - 2.09 (12 H, s), 3.74 (3H, m), 4.7 - 5.6 (5H, m).

$^{13}$C NMR (400 MHz, $CDCl_3$) δ = 170.9, 170.8, 170.19, 170.18, 170.16, 169.7, 169.5, 95.5, 90.1, 73.1, 72.1, 72.0, 71.0, 69.8, 68.4, 68.3, 67.1, 61.90, 61.88, 20.72, 20.69, 20.67, 20.60, 20.57, 20.56.

LC-MS; m/z = 348.11

**Synthesis of phenyl azocardanol derivatives[3] (II)**

i) 4-(Phenylazo)-3-pentadecyl phenol:

Aniline (0.093 g, 0.01 mol) was dissolved in a mixture of concentrated hydrochloric acid (3 ml) and distilled water (3 ml). A saturated solution of sodium nitrite (0.897 g, 0.013 mol) in distilled water was prepared and added drop wise to the acidic solution of amine over a period of 10 min at 0 °C and stirred for 20 min. To this mixture, a pre-cooled solution of 3-pentadecylphenol (3.04 g, 0.01mol) dissolved in methanol (10 ml) and 0.40 g NaOH (0.01 mol) was added drop-wise. The reaction mixture was stirred at 0 °C for 40 min. On

completion of the reaction, the water in-soluble layer was extracted with ethyl acetate, and washed (2-3 times) with 50 ml distilled water. Removal of the solvent gave a residue which was then subjected to column chromatography over silica gel using a mixture of ethyl acetate and hexane (1:9).

Yellowish-solid (Yield 63%). $^{1}$HNMR (400 MHz, $CDCl_3$) δ = 7.87 (2H, d, J = 8.8 Hz), 7.68 (1H, d, J = 8.8 Hz), 7.5 (2H, m), 7.42 (1H, m), 6.77 (1H, s), 6.70 (1H, d, J = 9), 5.42 (1H, s), 3.089 (2H, t, J = 7.6), 1.66 (2H, m), 1.31 (24H, m), 0.88 (3H, t).

$^{13}$C NMR (400 MHz, $CDCl_3$), δ = 158.26, 153.07, 146.00, 144.76, 130.17, 129.02, 122.72, 117.22, 117.22, 116.37, 113.70, 32.01, 31.94, 29.68, 22.71, 14.44.

LC-MS; m/z = 409.3.

IR: 3346, 3008, 2923, 2852, 1600, 1483, 1468, 1455, 1365, and 1225 $cm^{-1}$.

ii) 4-(Phenylazo)cardanol:

Aniline (0.093 g, 0.01 mol) was dissolved in a mixture of concentrated hydrochloric acid (3 ml) and distilled water (3 ml). A saturated solution of sodium nitrite (0.897 g, 0.013 mol) in distilled water was prepared and added drop wise to the acidic solution of amine over a period of 10 min at 0 °C and stirred for 20 min. To this mixture, a pre-cooled solution of cardanol (3.00 g, 0.01mol) dissolved in methanol (10 ml) and 0.40 g NaOH (0.01 mol) was added drop-wise. The reaction mixture was stirred at 0 °C for 40 min. On completion of the reaction, the water in-soluble layer was extracted with ethyl acetate, and washed (2-3 times) with 50 ml distilled water. Removal of the solvent gave a residue which was then subjected to column chromatography over silica gel using a mixture of ethyl acetate and hexane (1:9).

Yellowish-brown viscous liquid (Yield 62%). $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 7.87 (2H, d, J = 7.4), 7.69 (1H, d, J = 8.8 Hz), 7.50 (2H, m), 7.42 (1H, m), 6.78 (1H, s), 6.72 (1H, d, J = 8), 5.41 (1H, s), 5.22 (3H, m), 3.1 (2H, t, J = 7.6 Hz), 2.8 (2H, m), 2.05 (3H, m), 1.67 (3H, m), 1.34 (3H, m), 1.26 (14H, m), 0.88 (2H, m).

$^{13}$C NMR (400 MHz, $CDCl_3$). 158.85, 153.07, 145.95, 144.65, 136.86, 13.44, 130.16, 129.88, 129.34, 129.04, 128.18, 127.67, 126.83, 122.70, 117.97, 117.22, 116.37, 115.42, 114.73, 113.80, 32.37, 31.53, 29.49, 29.09, 27.24, 25.66, 22.81, 13.81.

LC-MS ; m/z = 409.3, 407.6, 405.3, 403.3.

IR: 3346, 3008, 2923, 2852, 1600, 1483, 1468, 1455, 1365, and 1225$cm^{-1}$.

iii) 4-(2-methoxyphenylazo)cardanol:

O-Anisidine (1.23 g, 0.01 mol) was dissolved in a mixture of concentrated hydrochloric acid (3 ml) and distilled water (3 ml). A saturated solution of sodium nitrite (0.897 g, 0.013 mol) in distilled water was prepared and added drop wise to the acidic solution of amine over a period of 10 min at 0 °C and stirred for 20 min. To this mixture, a pre-cooled solution of cardanol (3.00 g, 0.01mol) dissolved in methanol (10 ml) and 0.40 g NaOH (0.01 mol) was added drop-wise. The reaction mixture was stirred at 0 °C for 40 min. On completion of the reaction, the water in-soluble layer was extracted with ethyl acetate, and washed (2-3 times) with 50 ml distilled water. Removal of the solvent gave a residue which was then subjected to column chromatography over silica gel using a mixture of ethyl acetate and hexane (1:9).

Dark red viscous liquid (Yield 60%). $^{1}$H NMR (400 MHz, $CDCl_3$), δ = 7.63 (2H, m), 7.4 (1H, t, J = 7.8), 7.01 (1H, t, J = 9.8), 6.75 (1H, s), 6.67 (1H, d, J = 8.8), 5.41 (1H, s), 5.38 (3H, m), 4.02 (3H, s), 3.1 (2H, t, J = 7.6 Hz), 2.8 (2H, m), 2.02 (3H, m), 1.65 (3H, m), 1.32 (14H, m), 0.88 (2H, m).

$^{13}$C NMR (400 MHz, $CDCl_3$).158.44, 156.64, 145.71, 142.61, 136.86, 131.51, 130.19, 129.34, 128.10, 127.50, 126.80, 120.84, 117.60, 116.16, 116.30, 114.72, 113.73, 112.61, 56.30, 31.80, 29.65, 27.24, 25.61, 22.74, 13.98.

LC-MS; m/z = 439.32, 437. 12, 435.29, 433.31,

IR: 3400, 3010, 3090, 2923, 2842, 1640, 1484, 1463, 1398, 1366, 1247, and 1181cm$^{-1}$.

iv) 4-(4-nitro-phenylazo)cardanol:

4-Nitroaniline (1.38 g, 0.01 mol) was dissolved in a mixture of concentrated hydrochloric acid (3 ml) and distilled water (3 ml). A saturated solution of sodium nitrite (0.897 g, 0.013 mol) in distilled water was prepared and added drop wise to the acidic solution of amine over a period of 10 min at 0 °C and stirred for 20 min. To this mixture, a pre-cooled solution of cardanol (3.00 g, 0.01mol) dissolved in methanol (10 ml) and 0.40 g NaOH (0.01 mol) was added drop-wise. The reaction mixture was stirred at 0 °C for 40 min. On completion of the reaction, the water in-soluble layer was extracted with ethyl acetate, and washed (2-3 times) with 50 ml distilled water. Removal of the solvent gave a residue which was then subjected to column chromatography over silica gel using a mixture of ethyl acetate and hexane (1:9).

Dark yellowish-brown viscous liquid (Yield 58%). $^{1}$H NMR (400 MHz, DMSO-d6), δ = 9.2 (s), 8.37 (2H, d), 7.95 (2H, d), 7.76 (1H, d), 6.84 (1H, d), 6.74 (1H, d, J = 2.4 Hz), 5.80

(1H, m), 5.34 (1H, m), 4.91 (1H, m), 3.03 (2H, t, J = 7.6 Hz), 2.73 (2H, m), 2.69 (3H, m), 1.9 (3H, m), 1.60 (3H, m), 1.20 (14H, m), 0.80 (2H, m).

$^{13}$C NMR (400 MHz, $CDCl_3$), 163.00, 156.39, 148.04, 144.78, 136.85, 130.42, 129.36, 127.65, 124.77, 120.87, 117.46, 116.63, 114.76, 112.61, 56.30, 31.80, 29.65, 27.04, 25.21, 22.14, 13.08.

LC-MS; m/z = 454.3, 452.8, 450.6, 448.5.

IR: 3380, 3013, 2899, 2827, 1600, 1529, 1485, 1480, 1463, 1402 , 1227, and 1339 $cm^{-1}$.

**Synthesis of phenyl azocardanolglucosides (1a-c, 2a)**

***1. Synthesis of 1-O-(4-phenylazo(3-pentadecylphenyl))glucopyranoside (2a)***

D-Glucopyranose,2,3,4,6-tetraacetate (1g, 0.0029 mol, 1 equiv), 4-(Phenylazo)-3-pentadecyl phenol (1.52g, 0.0037 mol, 1.3 equiv) and triphenyl phosphine (0.97g, 0.0037 mol, 1.3 equiv) were dissolved in 20 ml dry Toluene. The solution was cooled to 0 $^0$C, and a solution of Diisopropylazodicarboxylate (DIAD, 0.75g, 0.0037 mol, 1.3 equiv) in dry Toluene (5.00 mL) was added drop wise over 30 min. The reaction mixture was stirred at room temperature until the TLC showed no further consumption of the carbohydrate starting material. The solvent was evaporated in a vacuum, and the crude mixture was subjected to deprotection without further purification. To the crude product, 30% of triethylamine (10 ml) was added followed by 50 ml of methanol, and stirred at room temperature for 24 hrs. The reaction mixture was then washed with 10% sodium bicarbonate solution and purified by column chromatography using methanol and dichloromethane (1:9). The chromatography afforded the azodye as yellowish orange solid.

Orange yellow solid (Yield 62%, Melting range: 130-132 $^0$C).$^1$H NMR (400 MHz, DMSO-d6) δ = 7.84 (2H, d, J = 7.6), 7.65 (1H, d, J = 6.4), 7.58 (2H, m), 7.51 (1H, m), 7.06 (1H, s), 6.98 (1H, d, J = 9), 5.39 (1H, d, J = 4.8), 5.14 (1H, d, J = 4.8), 5.07 (1H, d, J = 5.2), 5.01 (1H, d, J = 7.2), 4.59 (1H, t, J = 5.6), 3.70 (1H, m), 3.57 (1H , m), 3.49 (1H, m), 3.29 (2H, m), 3.20 (1H, m), 3.09 (2H, t, J = 7.6), 1.63 (1H, t, J = 6.8), 1.23 (24H, m), 0.85 (3H, t, J = 6.8).

$^{13}$C NMR (400 MHz, DMSO-d6), δ = 160.43, 152.87, 145.38, 144.93, 131.18, 129.84, 122.77, 117.63, 116.84, 114.98, 100.31, 77.60, 77.10, 70.18, 73.68, 70.18, 61.06, 31.88, 29.28, 22.57, 14.43.

IR: 3287, 2919, 2849, 1605, 1577, 1418, 1379, 1238.77, 1159, 1103, 1072, 1053, 1070, 880, 830, 811, 719, 763, 684, 601, 552$cm^{-1}$ .

HRMS-ESI (m/z); $[M+Na]^+$**:** 593.35828 (cald 593.3597 for $C_{33}H_{50}N_2O_6$ )

***2. 1-O-(4-phenylazo(cardanyl))glucopyranoside (1a):***

D-Glucopyranose,2,3,4,6-tetraacetate (1g, 0.0029 mol, 1 equiv), 4-(Phenylazo)cardanol (1.45g, 0.0037 mol, 1.3 equiv) and triphenyl phosphine (0.97g, 0.0037 mol, 1.3 equiv) were dissolved in 20 mL dry Toluene. The solution was cooled to 0 $^0$C, and a solution of Diisopropylazodicarboxylate (DIAD, 0.75g, 0.0037 mol, 1.3 equiv) in dry Toluene (5.00 mL) was added drop wise over 30 min. The reaction mixture was stirred at room temperature until the TLC showed no further consumption of the carbohydrate starting material. The solvent was evaporated in a vacuum, and the crude mixture was subjected to deprotection without further purification. To the crude product, 30% of triethylamine (10 ml) was added followed by 50 ml of methanol, and stirred at room temperature for 24 hrs. The reaction mixture was then washed with 10% sodium bicarbonate solution and purified by column chromatography using methanol and dichloromethane (1:9). The chromatography afforded the azodye as orange red solid.

Orange red solid (yield 65%, Melting range: 167-173 $^0$C). $^1$H NMR (DMSO-d6), δ = 7.84 (2H, d, J = 7.6),7.65 (1H, d, J = 8.8), 7.58 (2H, m), 7.51 (1H, m), 7.06 (1H, s), 6.98 (1H, d, J = 9), 5.39 (1H, d, J = 4.8), 5.33 (3H, m), 5.14 (1H, d, J = 4.4), 5.07 (1H, d, J = 5.2), 5.00 (1H, d, J = 7.2), 4.59 (1H, t, J = 5.6), 3.71 (1H, m), 3.57(1H, m), 3.49 (1H, m), 3.30 (2H, m), 3.22 (1H, m), 3.09 (2H, t, J = 7.2), 2.74 (2H, m), 1.94 (3H, m), 1.62 (2H, m), 1.26 (14H, m), 0.82 (2H, m).

$^{13}$C NMR (100 MHz, DMSO-d6), δ = 160.43, 152.87, 145.36, 144.92, 137.14, 131.19, 129.90, 129.38, 128.18, 126.95, 122.76, 117.63, 116.85, 115.36, 114.98, 100.32, 77.60, 77.10, 73.68, 70.10, 61.07, 31.75, 29.06, 27.01, 25.62, 22.67, 14.43**.**

IR: 3315, 3009, 2922, 2852, 1713, 1603, 1577, 1483, 1463, 1399, 1375, 1294, 1235, 1164, 1144, 1105, 1074, 1050, 1020, 901, 877, 813, 762, 685, 658, 586, 569, 527, 500, 440 and 421cm.$^{-1}$.

HRMS-ESI (m/z); $[M+Na]^+$ peaks of saturated and unsaturated components**:** 593.3578 (Calcd 593.3587for $C_{33}H_{50}N_2O_6$), 591.3445 (Calcd 591.3397 for $C_{33}H_{48}N_2O_6$), 589.3254 (Calcd 589.3297 for $C_{33}H_{46}N_2O_6$) and 587.3103(Calcd 587.3097 for $C_{33}H_{44}N_2O_6$).

***3. 1-O-(4-2-methoxyphenylazo(cardanyl))glucopyranoside (1b):***

D-Glucopyranose,2,3,4,6-tetraacetate (1g, 0.0029 mol, 1 equiv), 4-(2-methoxyphenylazo)cardanol (1.61g, 0.0037 mol, 1.3 equiv) and triphenyl phosphine (0.97g,

0.0037 mol, 1.3 equiv) were dissolved in 20 ml dry Toluene. The solution was cooled to 0 $^0$C, and a solution of Diisopropylazodicarboxylate (DIAD, 0.75g, 0.0037 mol, 1.3 equiv) in dry Toluene (5.00 mL) was added drop wise over 30 min. The reaction mixture was stirred at room temperature until the TLC showed no further consumption of the carbohydrate starting material. The solvent was evaporated in a vacuum, and the crude mixture was subjected to deprotection without further purification. To the crude product, 30% of triethylamine (10 ml) was added followed by 50 ml of methanol, and stirred at room temperature for 24 hrs. The reaction mixture was then washed with 10% sodium bicarbonate solution and purified by column chromatography using methanol and dichloromethane (1:9). The chromatography afforded the azodye as orange red solid.

Orange red solid (Yield 67%, Melting range: 124-132 $^0$C).$^1$H NMR (400 MHz, DMSO-d6), δ = 7.56 (1H, d, J = 8), 7.48 (2H, m), 7.25 (1H, d, J = 8), 7.03 (2H, m), 6.97 (1H, J = 9), 5.38 (1H, d, J = 5.2), 5.34 (3H, m), 5.14 (1H, d, J = 4.4), 5.07 (1H, d, J = 5.2), 5.00 (1H, J = 7.2), 4.59 (1H, J = 5.6), 3.954 (3H, s), 3.71 (1H, m), 3.57 (1H, m), 3.49 (1H, m), 3.30 (2H, m), 3.22 (1H, m), 3.07 (2H, t, J = 7.6), 2.66 (2H, m), 1.94 (3H, m), 1.617 (2H, m), 1.28 (14H, m), 0.83(2H, m)**.**

$^{13}$C NMR (100 MHz, DMSO-d6), δ = 160.11, 156.97, 145.54, 144.92, 142.31, 132.62, 137.15, 129.91, 128.18, 126. 96, 120.96, 117.18, 116.68, 115.36, 114.90, 113.92, 100.36, 77.61, 77.10, 73.70, 70.13, 61.08, 56.47, 31.57, 29.16, 27.05, 25.60, 22.67, 14.38.

IR: 3332, 3006, 2922, 2851, 1591, 1485, 1458, 1308, 1278, 1234, 1184, 1158, 1073, 1043, 1019, 901, 824, 749, 647, 596, 509, 499, 450, 431, 419, and 405cm$^{-1}$ .

HRMS-ESI (m/z); $[M+Na]^+$ peaks of saturated and unsaturated components **:** 623.3684 (Calcd 623.3697 for $C_{34}H_{52}N_2O_7$), 621.3533 (Calcd 621.3497 for $C_{34}H_{50}N_2O_7$), 619.3387 (Calcd 619.3397 for $C_{34}H_{48}N_2O_7$) and 617.3221(Calcd 617.3197 for $C_{34}H_{46}N_2O_7$).

***4. 1-O-(4-4-nitrophenylazo(cardanyl))glucopyranoside (1c):***

D-Glucopyranose,2,3,4,6-tetraacetate (1g, 0.0029 mol, 1 equiv),4-(4-nitro-phenylazo)-cardanol (1.67g, 0.0037 mol, 1.3 equiv) and triphenyl phosphine (0.97g, 0.0037 mol, 1.3 equiv) was dissolved in 20 ml dry Toluene. The solution was cooled to 0 $^0$C, and a solution of Diisopropylazodicarboxylate (DIAD, 0.75g, 0.0037 mol, 1.3 equiv) in dry Toluene (5.00 mL) was added drop wise over 30 min. The reaction mixture was stirred at room temperature until the TLC showed no further consumption of the carbohydrate starting material. The solvent was evaporated in a vacuum, and the crude mixture was subjected to deprotection without further purification. To the crude product, 30% of triethylamine (10 ml)

was added followed by 50 ml of methanol, and stirred at room temperature for 24 hrs. The reaction mixture was then washed with 10% sodium bicarbonate solution and purified by column chromatography using methanol and dichloromethane (1:9). The chromatography afforded the azodye as red brown solid.

Red brown solid (Yield 68%, Melting range: 125-132 $^{0}$C).$^{1}$H NMR (400 MHz, DMSO-d6), δ = 8.42 (2H, d, J = 8.4), 8.03 (2H, d, J = 7.2), 7.72 (1H, d, J = 8.8), 7.11 (1H, s), 7.02 (1H, d, J = 9), 5.41 (1H, d, J = 4.8), 5.29 (3H, s), 5.16 (1H, d, J = 4), 5.08 (1H, d, J = 5.2), 5.05 (1H, d, J = 7.2), 4.56 (1H, t, J = 5.6), 3.70 (1H,d, J = 4.8), 3.49 (1H, m), 3.41 (1H, m ), 3.29 (2H, m), 3.20 (1H, m), 3.13 (2H, t, J = 7.2), 2.71 (2H, m), 1.92 (3H, m), 1.64 (2H, m), 1.25 (14H, m), 0.82 (2H, m).

$^{13}$C NMR (100 MHz, DMSO-d6), δ = 161.58, 156.17, 148.39, 147.00, 145.08, 137.13, 130.01, 129.34, 127, 125.55, 123.66, 117.73, 117. 78, 115.23, 100.20, 77.64, 77.09, 73.66, 70.09, 61.06, 31.43, 29.10, 27.03, 25.60, 22.59, 14.38.

IR: 3315, 3009, 2922, 2852, 1713, 1603, 1577, 1483, 1463, 1399, 1375, 1294, 1235, 1164, 1144, 1105, 1074, 1050, 1073, 1043, 1019, 901, 824, 749, 647, 596, 509, 499, 440, 421, 412, and 408cm$^{-1}$.

HRMS-ESI (m/z); $[M+Na]^{+}$ peaks of saturated and unsaturated components: 638.3431 (Calcd 638.3397 for $C_{33}H_{49}N_3O_8$), 636.3280 (Calcd 636.3297 for $C_{33}H_{47}N_3O_8$), 634.3129 (Calcd 634.3097 for$C_{33}H_{45}N_3O_8$) and 632.2977 (Calcd 632.2997 for $C_{33}H_{43}N_3O_8$).

**Study of aggregation**

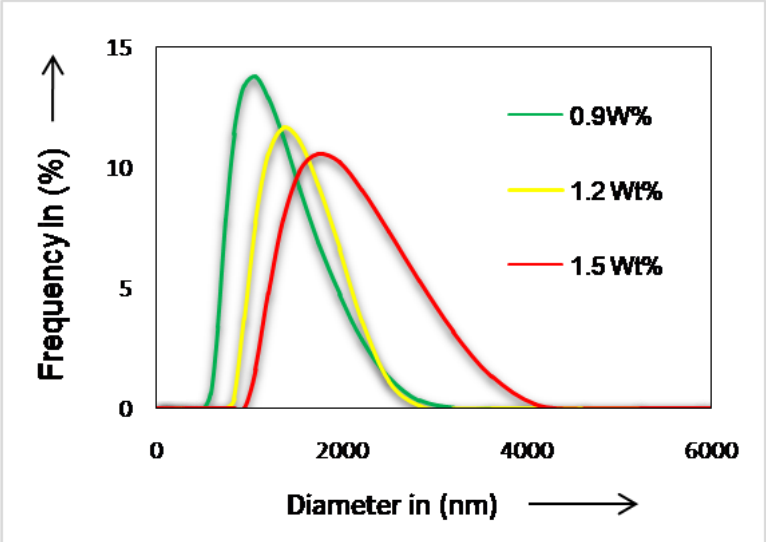



**Figure S1.** DLS graph showing the increase in the size of aggregates with an increase in the concentration of **1a** in toluene**.**

| **Solvent/ solvent mixture** | **Azodye 2a (1wt%)** | **Azodye 1a (2wt%)** | **Azodye 1b (2wt%)** | **Azodye 1c (1wt%)** |
|---|---|---|---|---|
| Chloroform/ Hexane (1:4) | Gel | Viscous liquid | Sticky viscous mass | Partial gel |
| Toluene/Hexane (1:1) | Gel | Viscous liquid | Sticky viscous mass | Insoluble |
| DCM/Hexane (1:4) | Gel | Viscous liquid | Sticky viscous mass | Partial Gel |
| Ethyl acetate/ Hexane (1:4) | Gel | Viscous liquid | Sticky viscous mass | Gel |
| Diethyl ether/ Hexane (1:4) | Gel | Viscous liqid | Sticky viscous mass | Partial gel |
| Toluene | Gel | Viscous liquid | Sticky viscous mass | Insoluble |
| Acetonitrile | Gel | Gel | Insoluble | Insoluble |
| Tertiary butanol | Gel | Gel | Gel | Insoluble |

**Table S1**. Gelation behaviour of azodyes **1a-c** and **2a** in various solvents and solvent mixtures at 25 $^{0}$C.

| Sl. No. | Solvent/Solvent mixture | Critical gelation concentration (CGC) | | | |
|---|---|---|---|---|---|
| | | **2a** | **1a** | **1b** | **1c** |
| 1. | Toluene | 0.75 Wt% | 5 Wt % | 4 Wt% | * |
| 2. | Toluene/ Hexane (1:1) | 0.25 Wt% | 3 Wt % | 2.5 Wt% | * |
| 3. | Chloroform/ Hexane (1:5) | 0.75 Wt % | 1.5 Wt % | 1.5 Wt% | 1 Wt% |
| 4. | Ethyl acetate/ Hexane (1:5) | 0.75 Wt % | 1.5 Wt% | 1.25 Wt% | 1 Wt% |
| 5. | Dichloromethane/ Hexane (1:5) | 0.5 Wt % | 1 Wt% | 1 Wt % | 0.75Wt % |
| 6. | Acetonitrile | 0.5 Wt% | 1 Wt% | Insoluble | * |

**Table S2.** Critical gelation concentration of different azodyes**. * 1c** forms random aggregates.

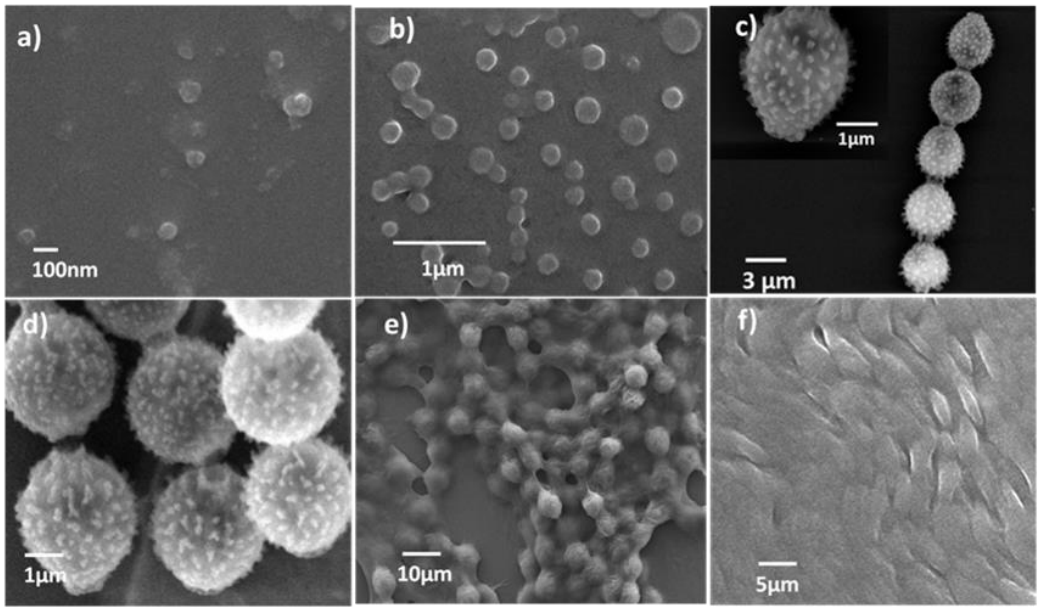



**Figure S2**. Characterization of morphology of viscous phase of **1a.** a-b) SEM images of nano gel structures in toluene-hexane (1:1) at different concentrations; c-d) SEM image of microgel-like structures in toluene-hexane (1:4); e) SEM image of microge-like structure in chloroform; f) SEM image showing string-like morphology of viscous phase in toluene-hexane (1:1).

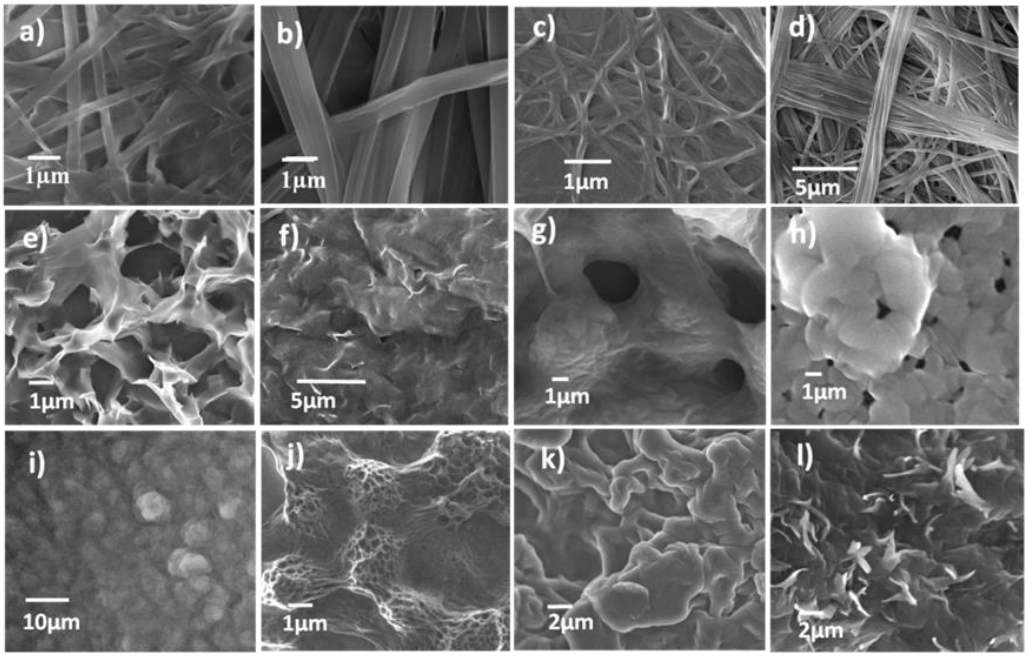



**Figure S3**. SEM images of dry Gels of **2a**, **1a, 1b** and **1c .** a-d**)** SEM images of dry gel of **2a** obtained from, acetonitrile, toluene, toluene-hexane (1:1), and chloroform-hexane (1:1) respectively; e-g) SEM images of dry gel of **1a** obtained from, acetonitrile, toluene, Chloroform-hexane (1:5); h-i) SEM images of dry gel of **1b** obtained from, toluene, toluene-hexane (1:5) respectively; j-l) SEM images of dry gel of **1c** obtained from, chloroform-hexane (1:5), ethyl acetate-hexane (1:5), chloroform respectively.

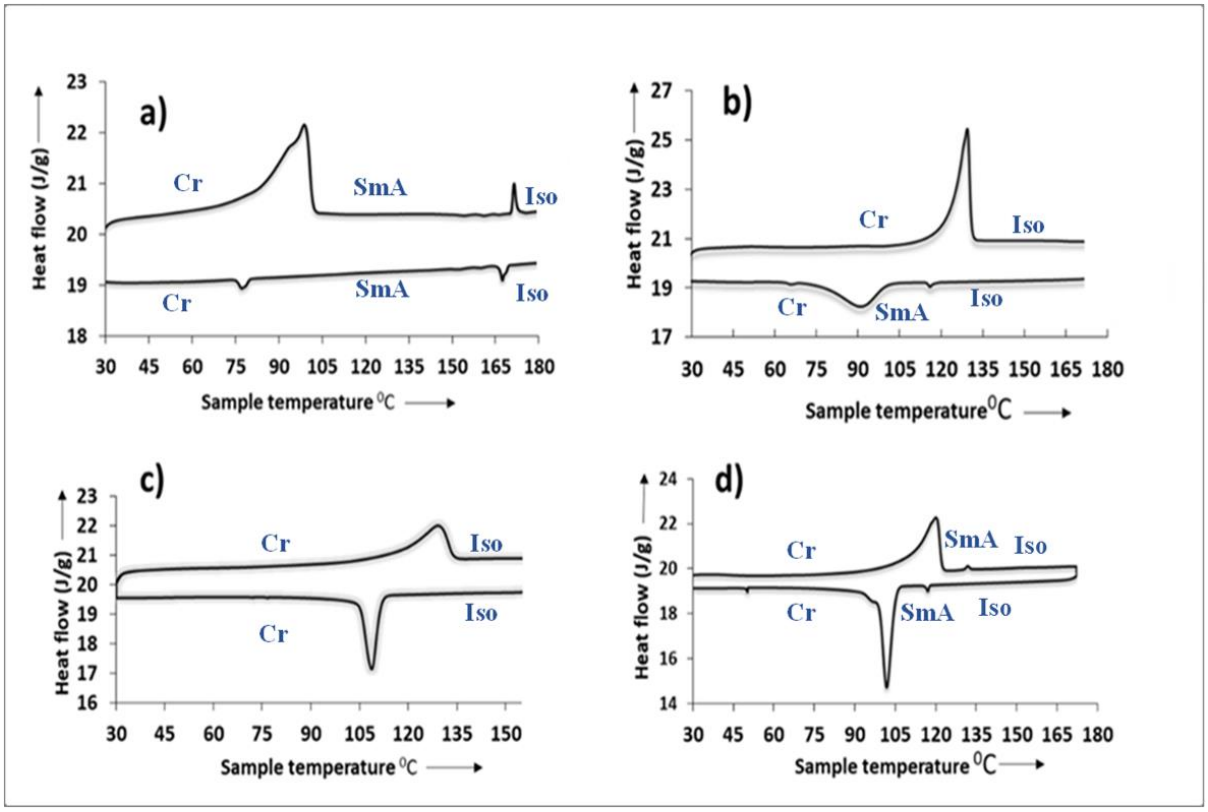



**Figure S4**. DSC thermogram of azo dyes in the first heating and cooling cycles (Endo up). a) **1a**, b) **1b**, c) **1c** and d) **2a.**

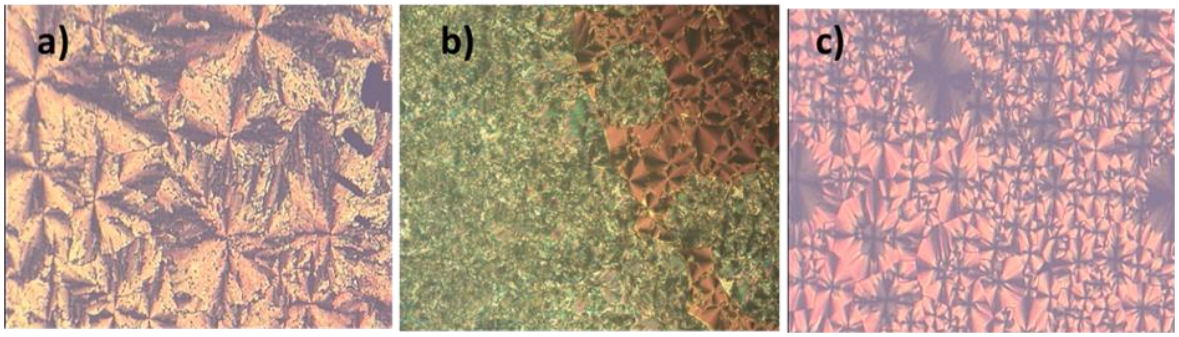



**Figure S5.** POM textures of crystal phases of a) **1a**, b) **1b** and c) **1c**.

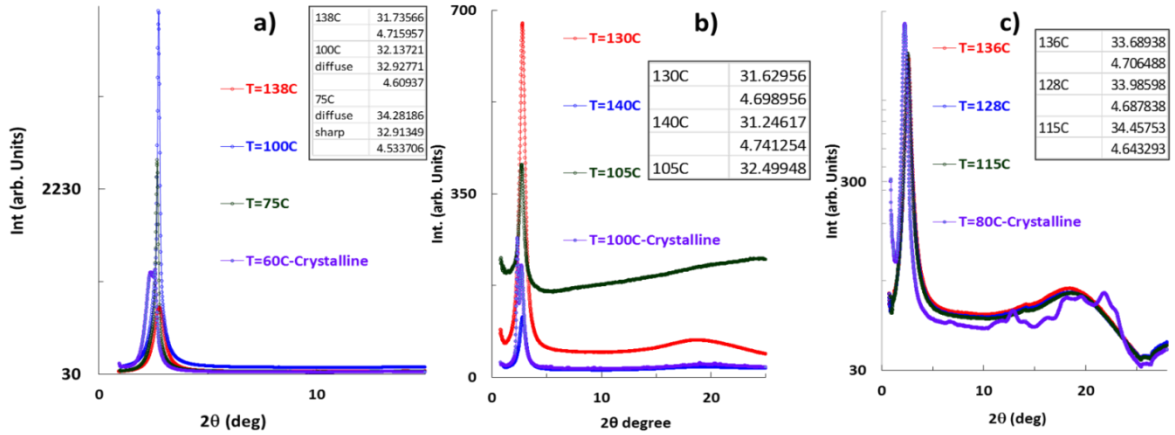



**Figure S6**. Variable temperature XRD analysis of a) **1a** b)**1b** and c) **2a** in their mesophases.

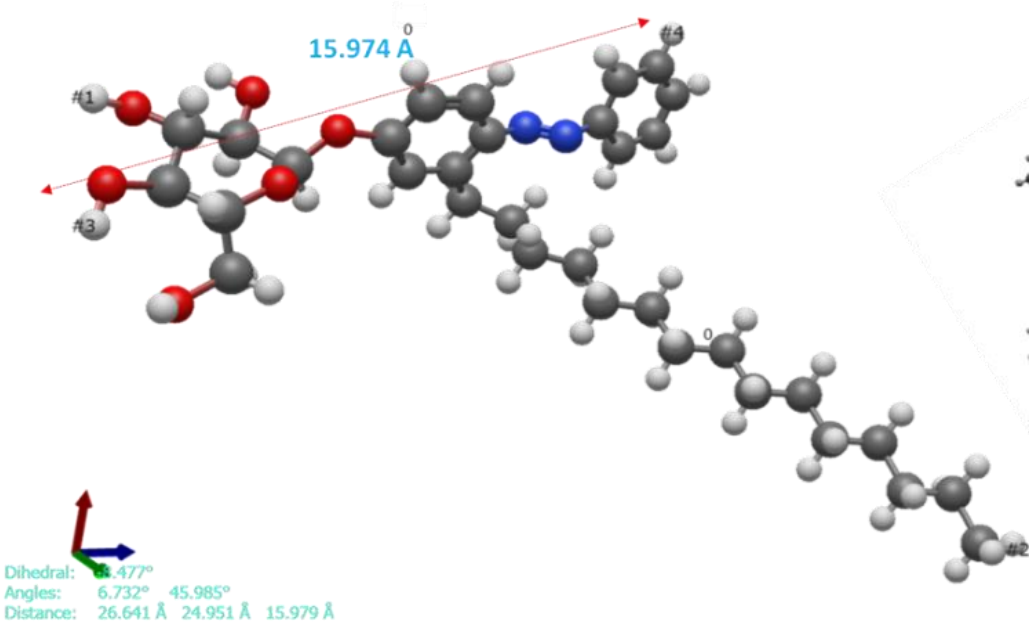



**Figure S7**. Geometry optimized structure of **2a.**

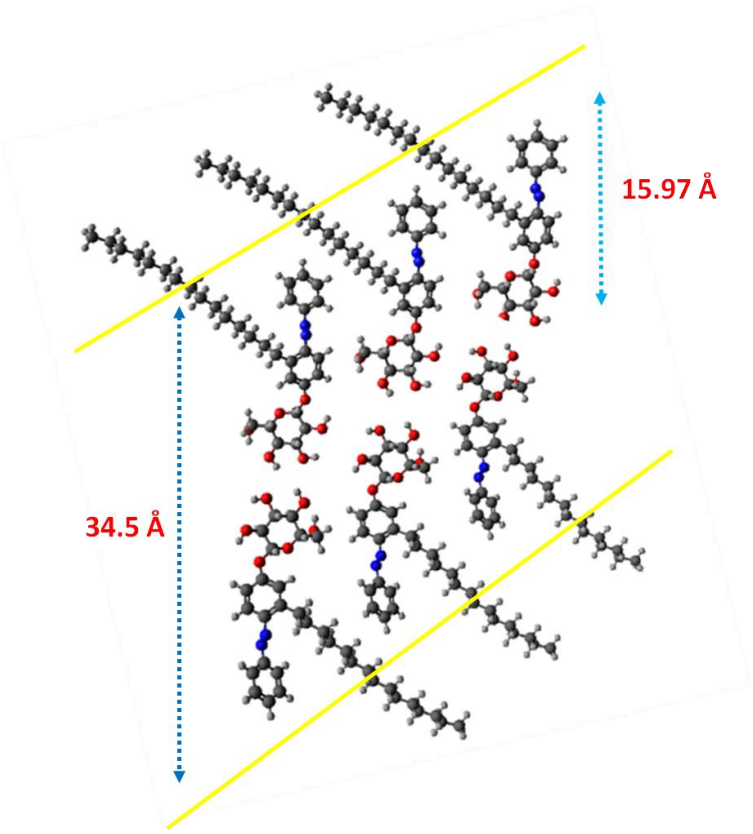



**Figure S8**. Proposed model showing the arrangement of azo dye **2a** in the SmA phase.

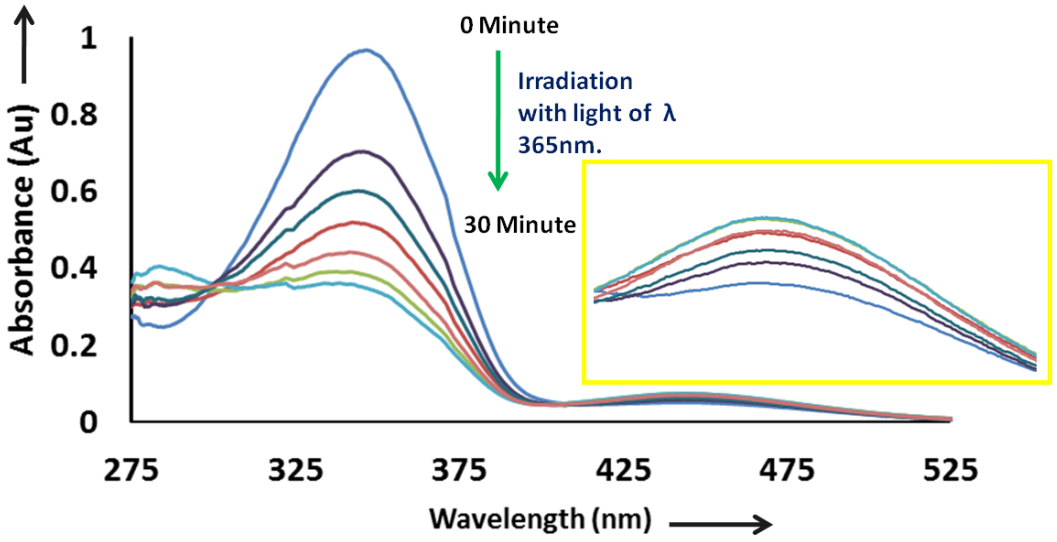



**Figure S9.** The UV spectral changes of **1a** upon photoirradiation using 365 nm light in toluene.

**Procedure for Photoirradiation experiments**

Sample solutions of azo dyes in a UV transperant cuvette were kept in ice bath, and irradiated for 5 – 60 minutes. The sample solutions after irradiation were drop casted on glass slide for SEM analysis. A reference sample is prepared by covering with aluminium foil, and kept in the same UV chamber. The SEM image of irradiated sample is compared with its corresponding reference to confirm the change due to irradiation.

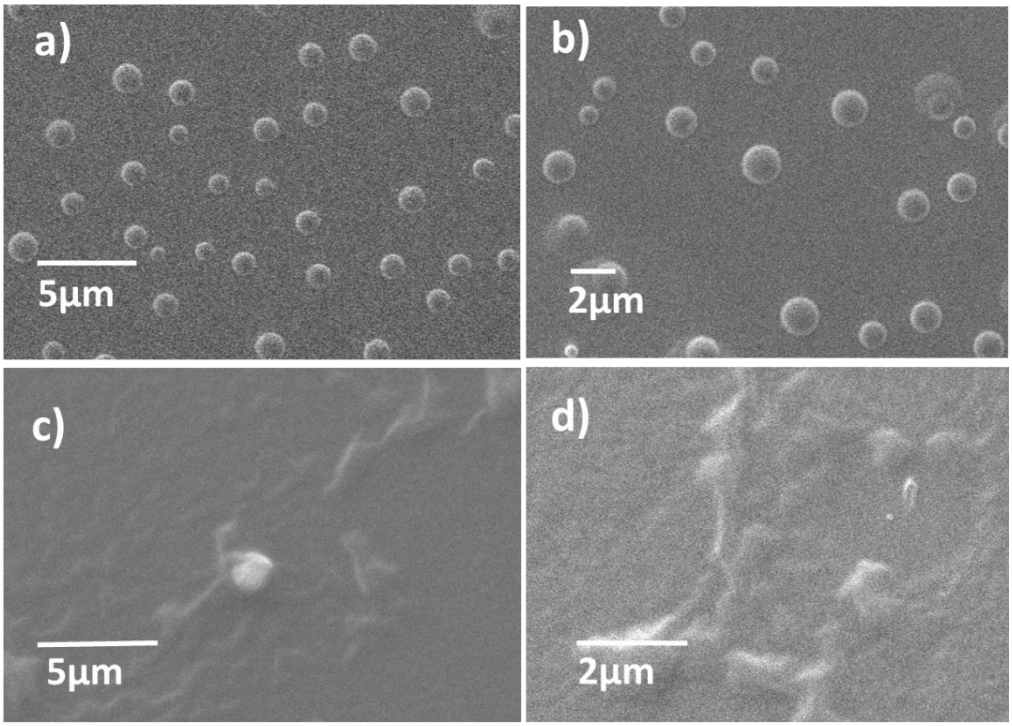



**Figure S10**. SEM image showing breaking of spherical assemblies of **1a** (1Wt% in toluene) upon photoirradiation using 365 nm light for 15 minutes. a-b) without irradiation and c-d) with irradiation.

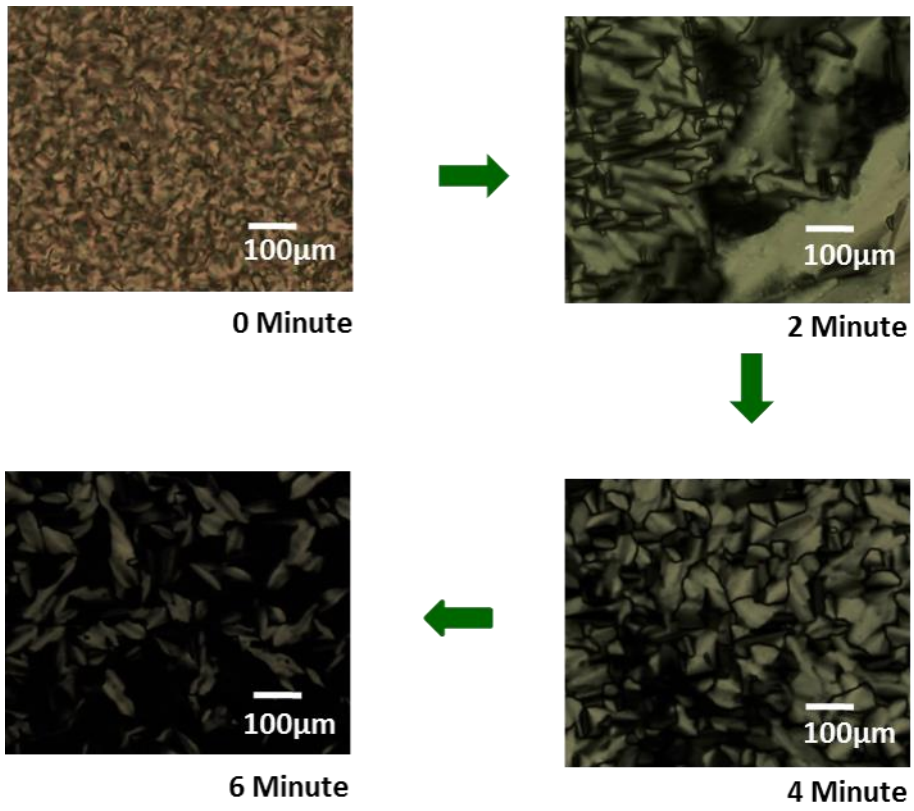
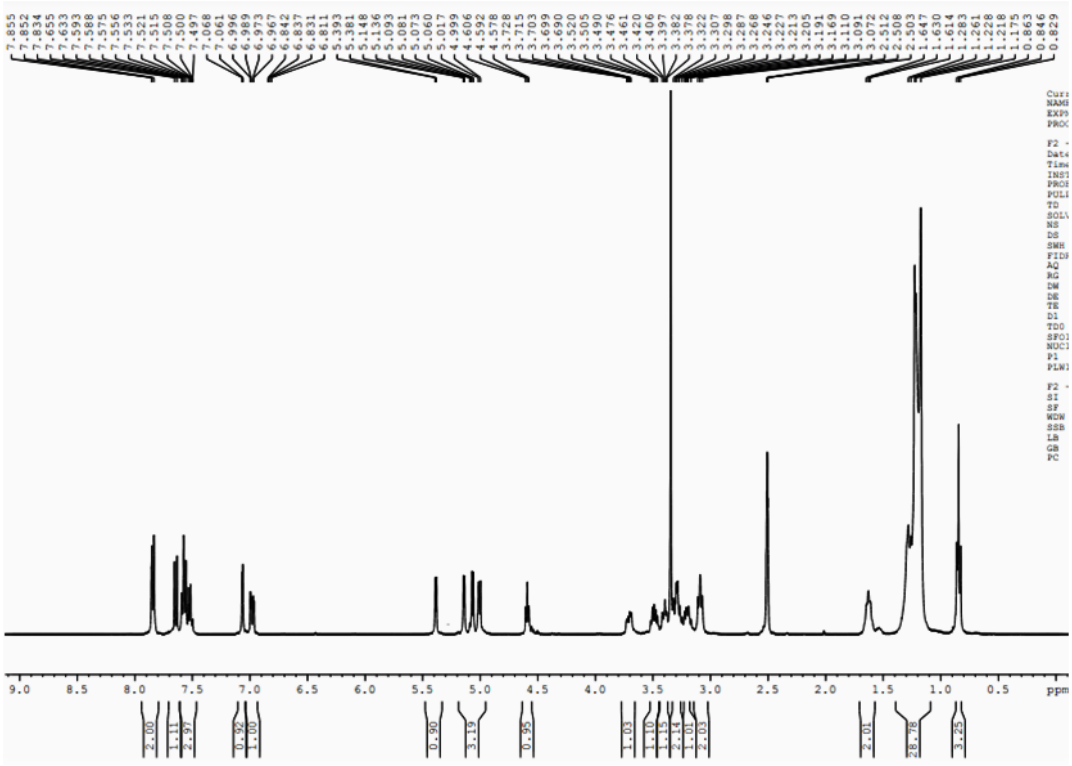



**Figure S11**. POM image showing degradation of gel of **1a** in toluene upon photoirradiation using 365nm light.

**A)**



**B)**

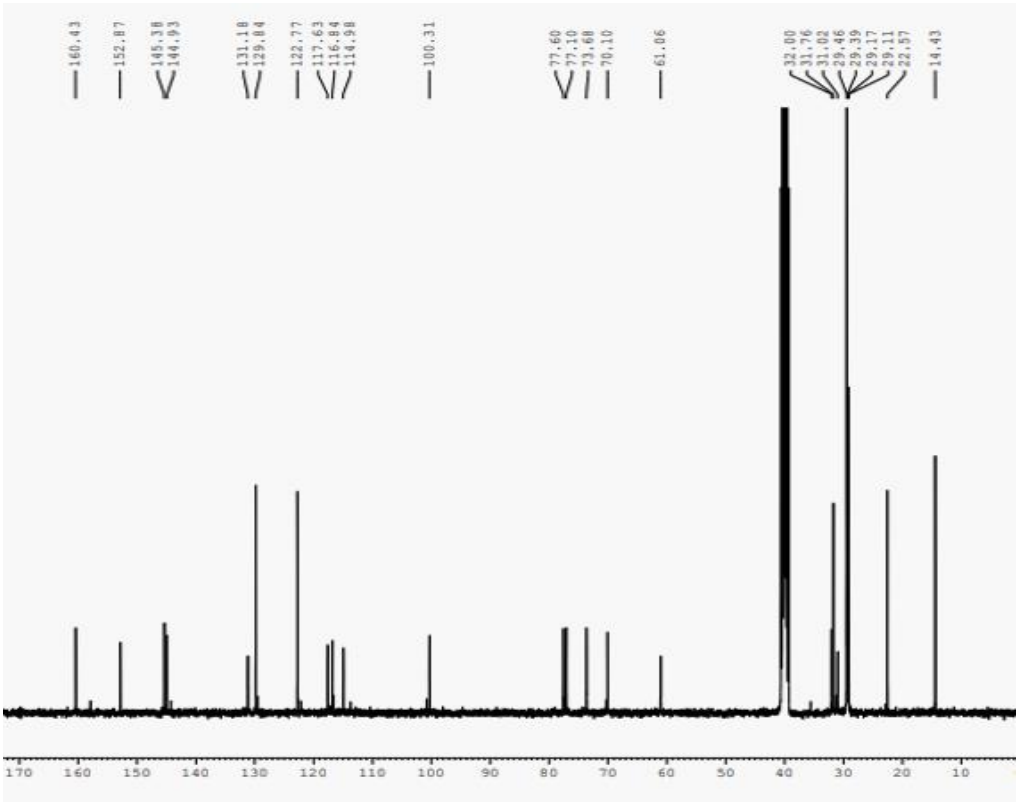
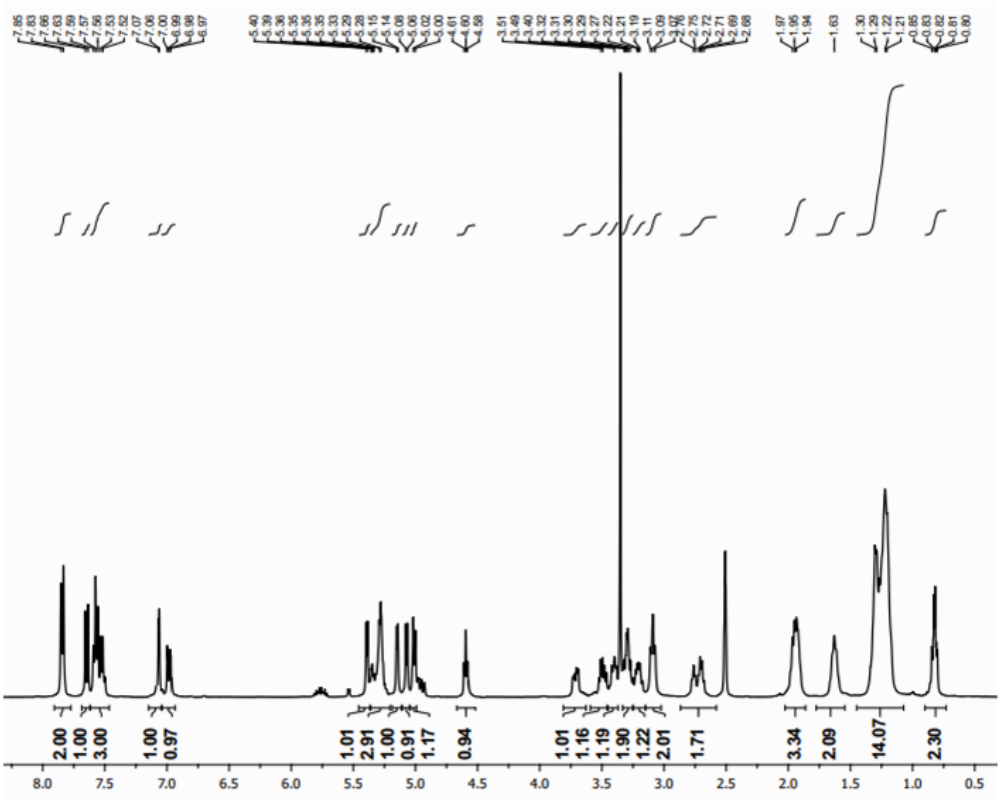


**Figure S12**. A) $^{1}$H NMR, and B) $^{13}$C NMR spectra of **2a** in DMSO.

**A)**



**B)**

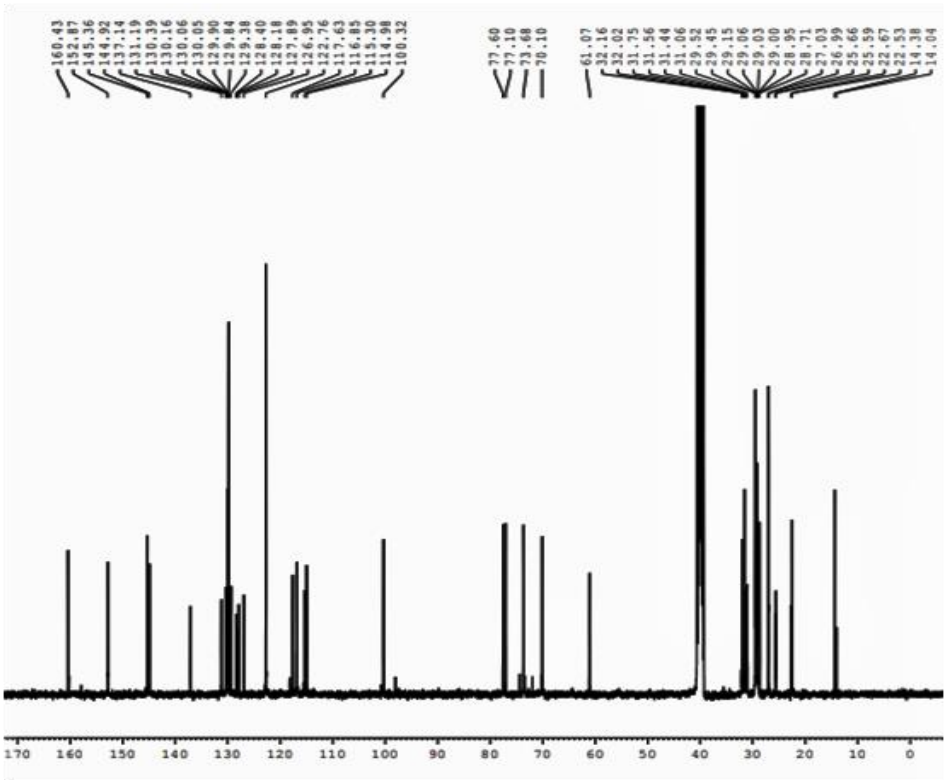
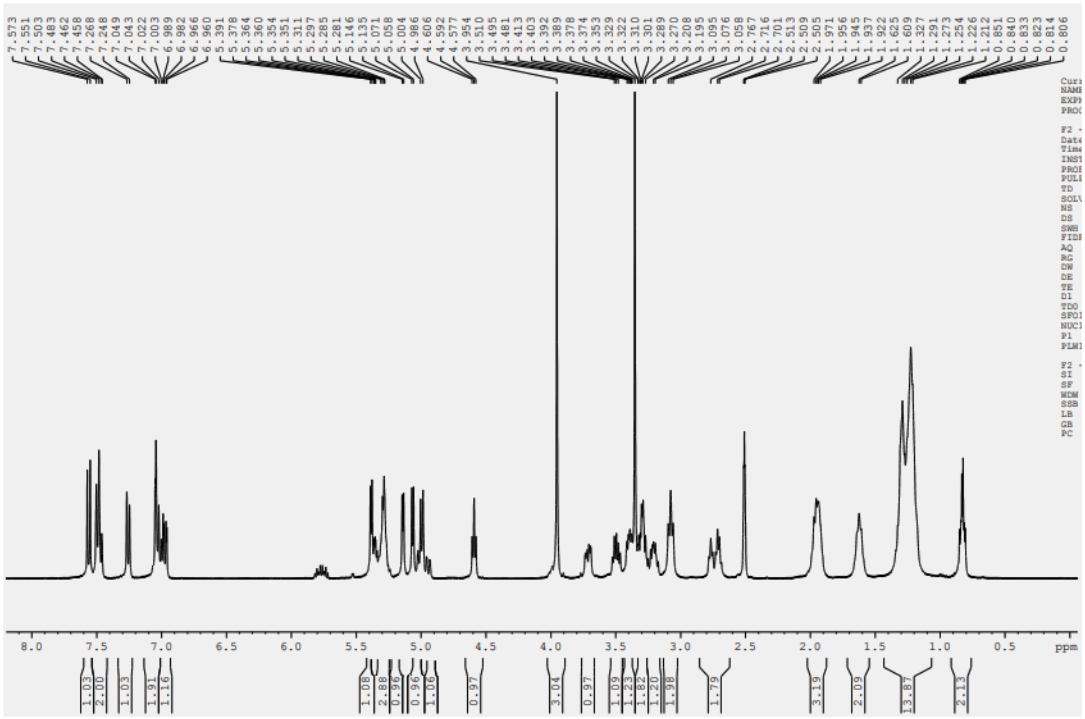


**Figure S13**. A) $^{1}$H NMR, and B) $^{13}$C NMR spectra of **1a** in DMSO.

**A)**



**B)**

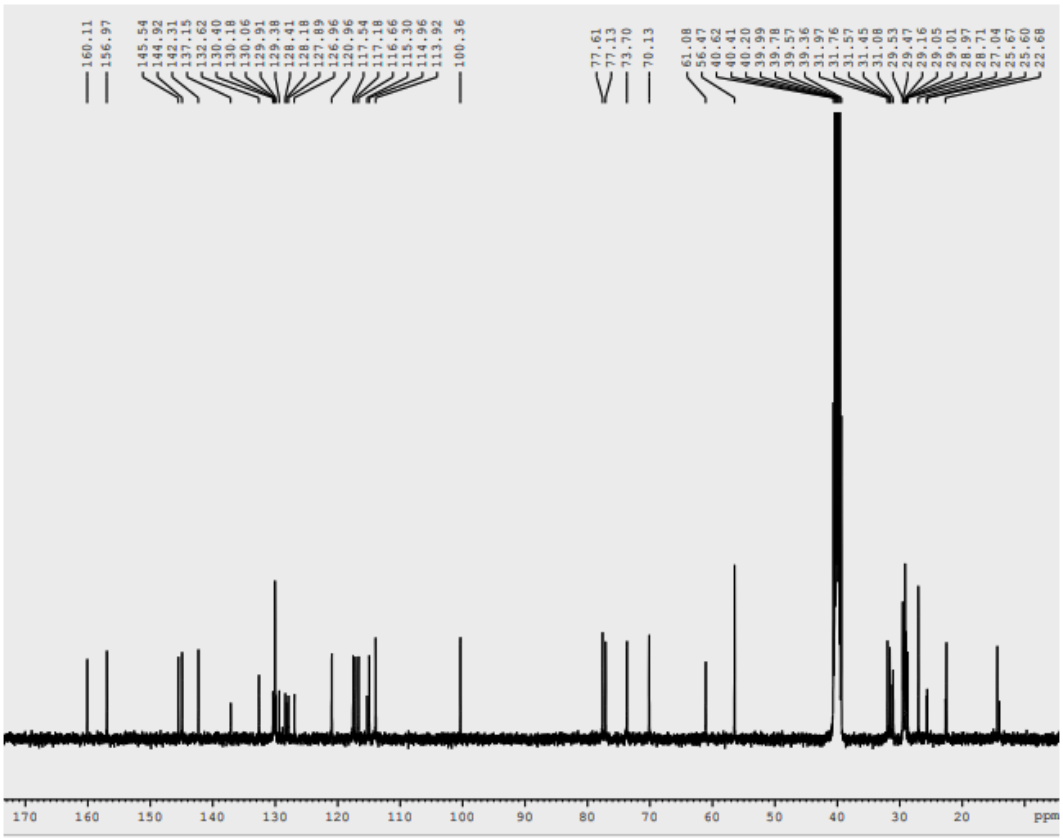
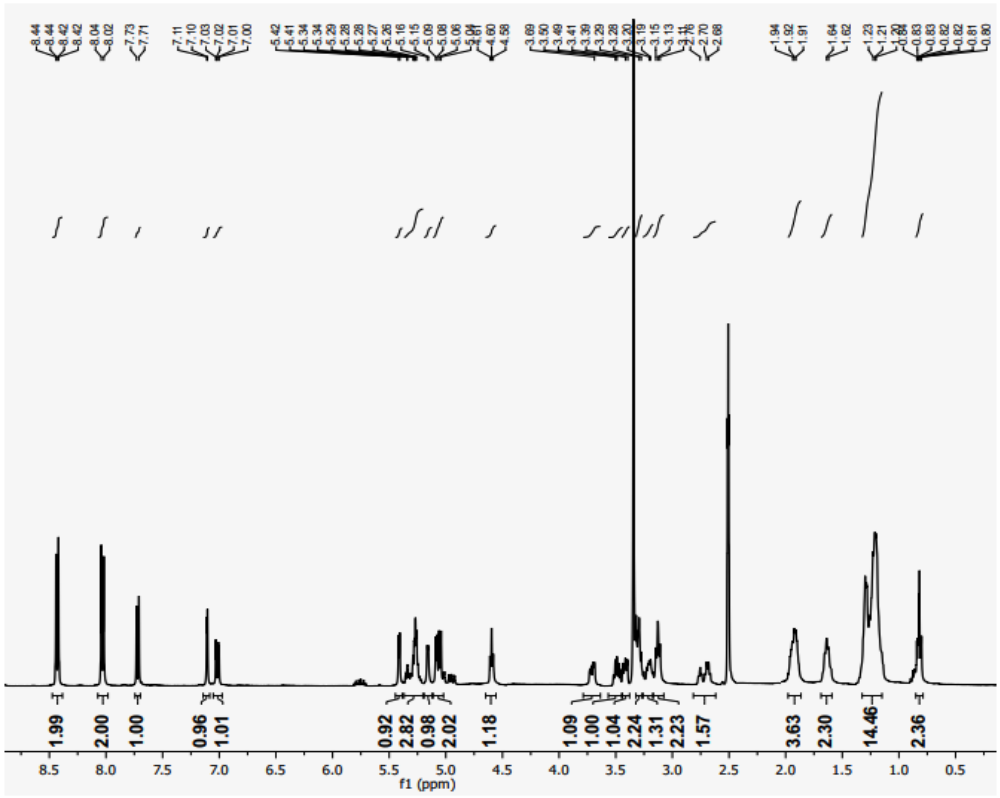


**Figure S14**. A) $^{1}$H NMR, and B) $^{13}$C NMR spectra of **1b** in DMSO.

**A)**




**B)**

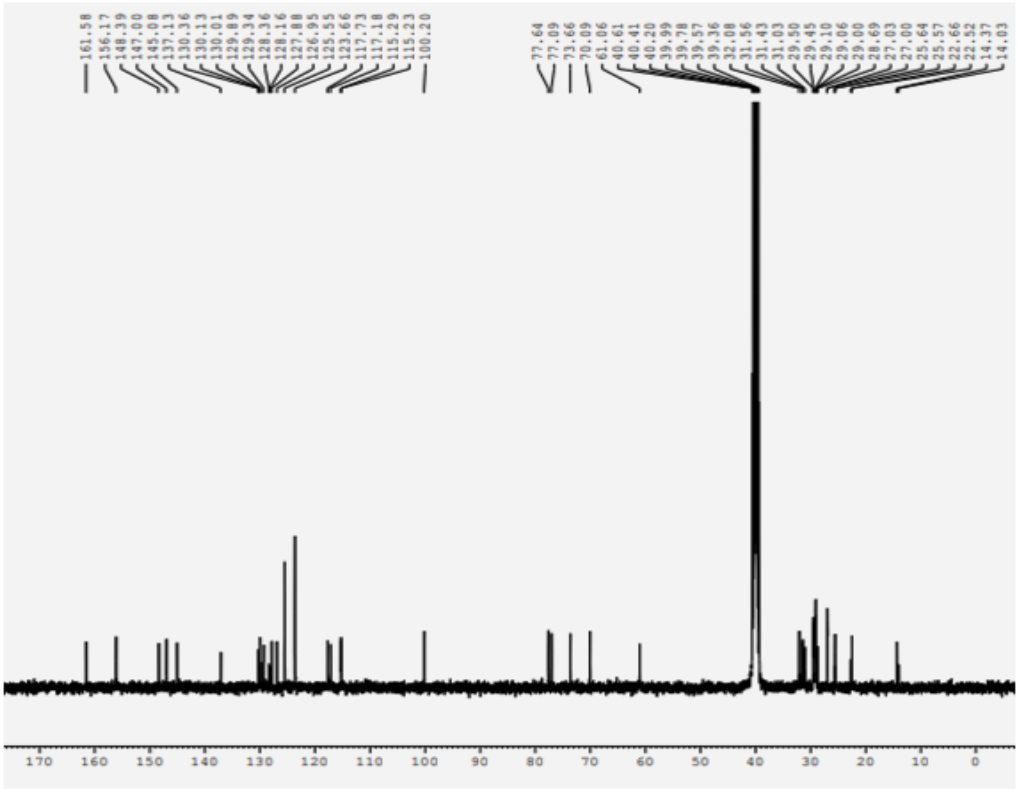
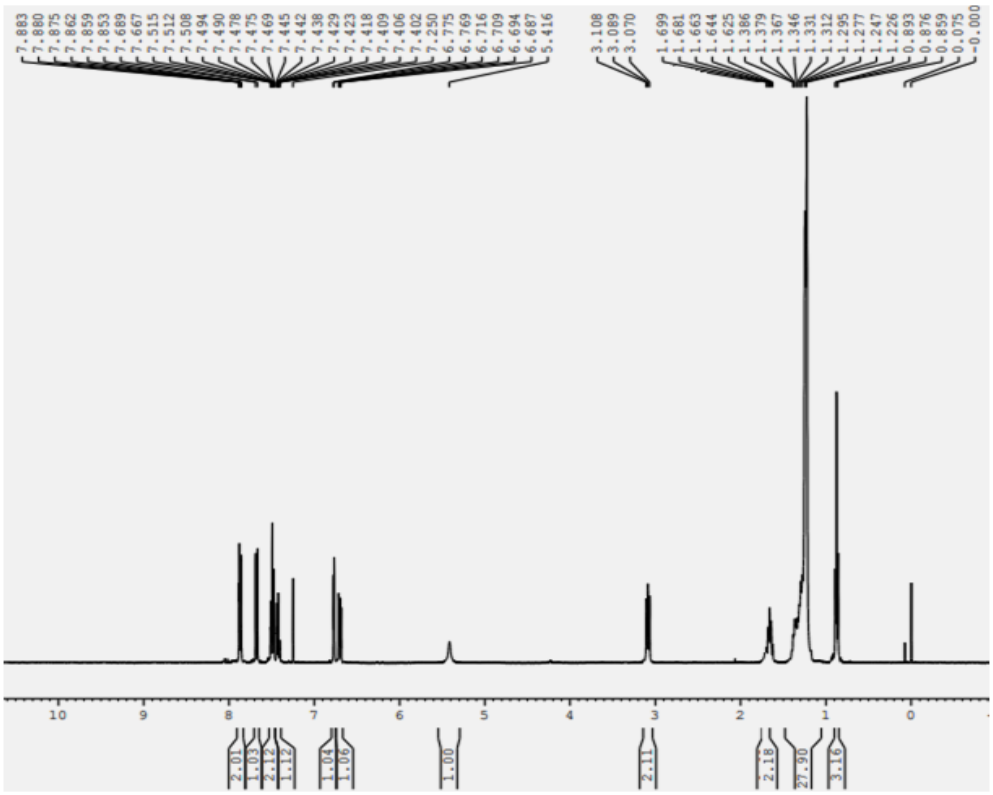


**Figure S15**.A) $^{1}$H NMR, and B) $^{13}$C NMR spectra of **1c** in DMSO.

**A)**



**B)**

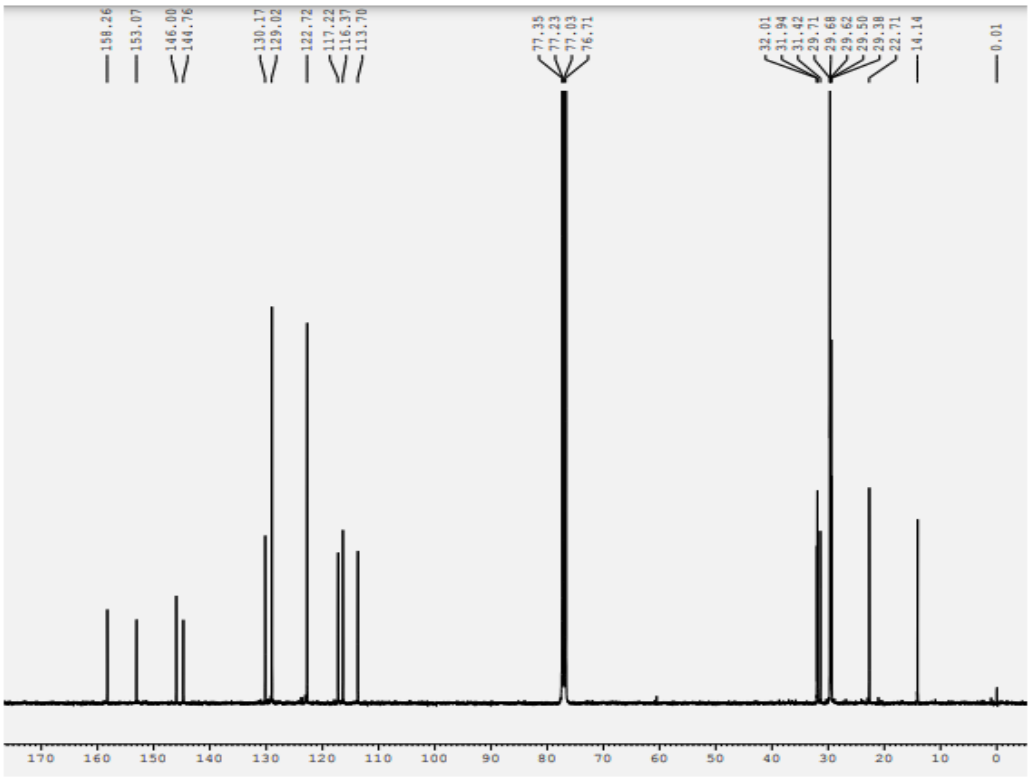
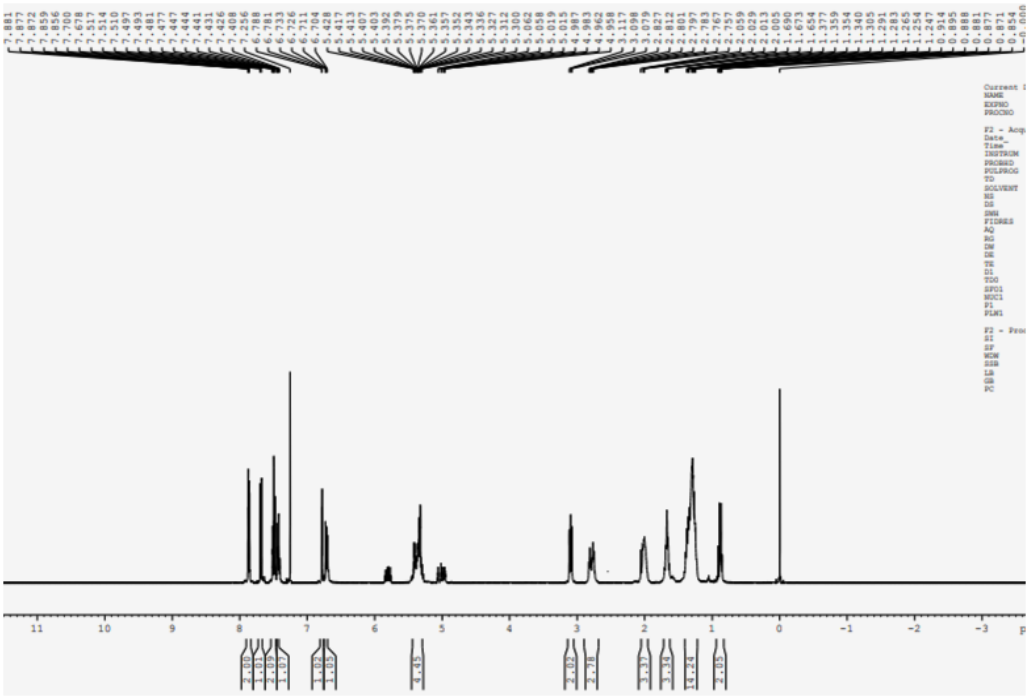


**Figure S16**. A) $^{1}H$ NMR, and B) $^{13}C$ NMR Spectra of 4-(Phenylazo)-3-pentadecyl phenol in $CDCl_3$.

**A)**



**B)**

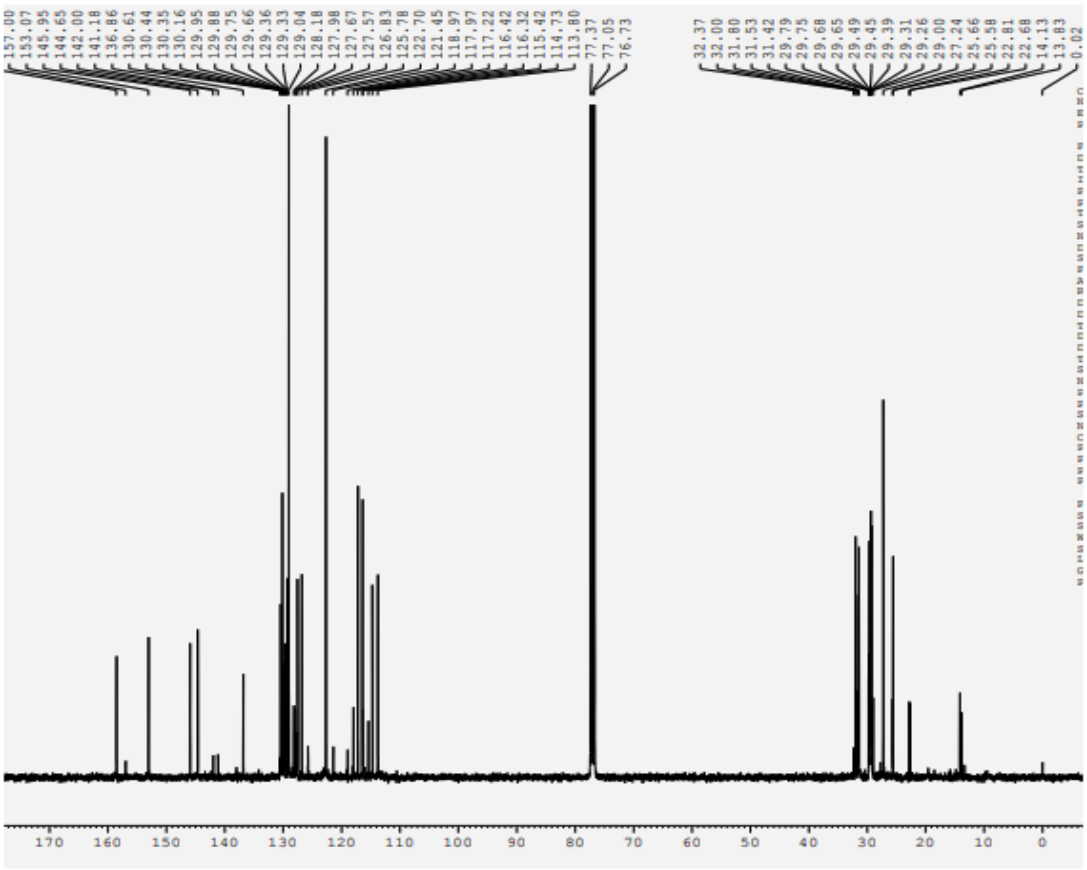
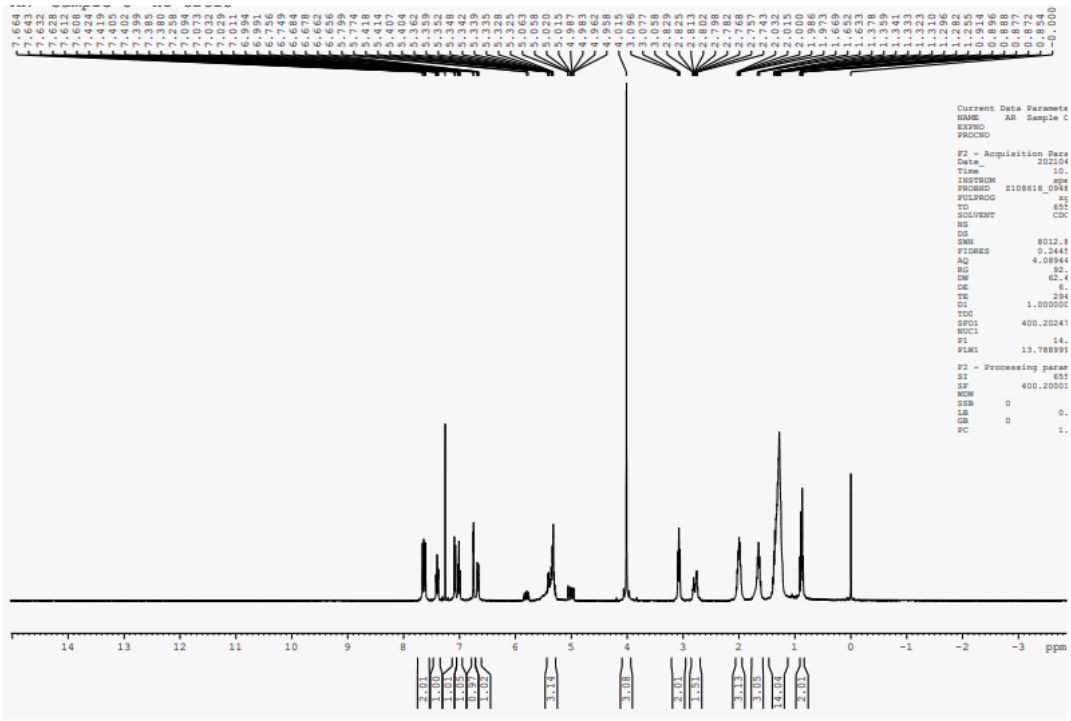


**Figure S17**. A) $^{1}H$ NMR, and B) $^{13}C$ NMR Spectra of 4-(Phenylazo)cardanol in $CDCl_3$.

**A)**



**B)**

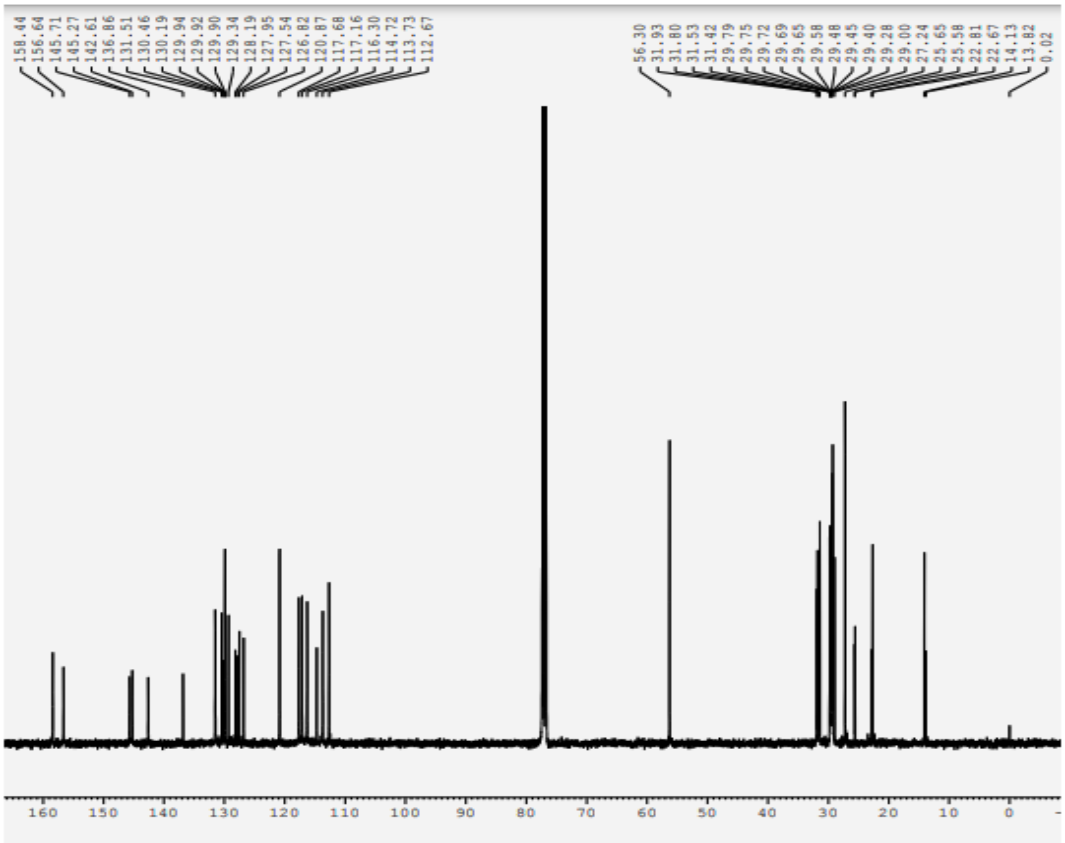
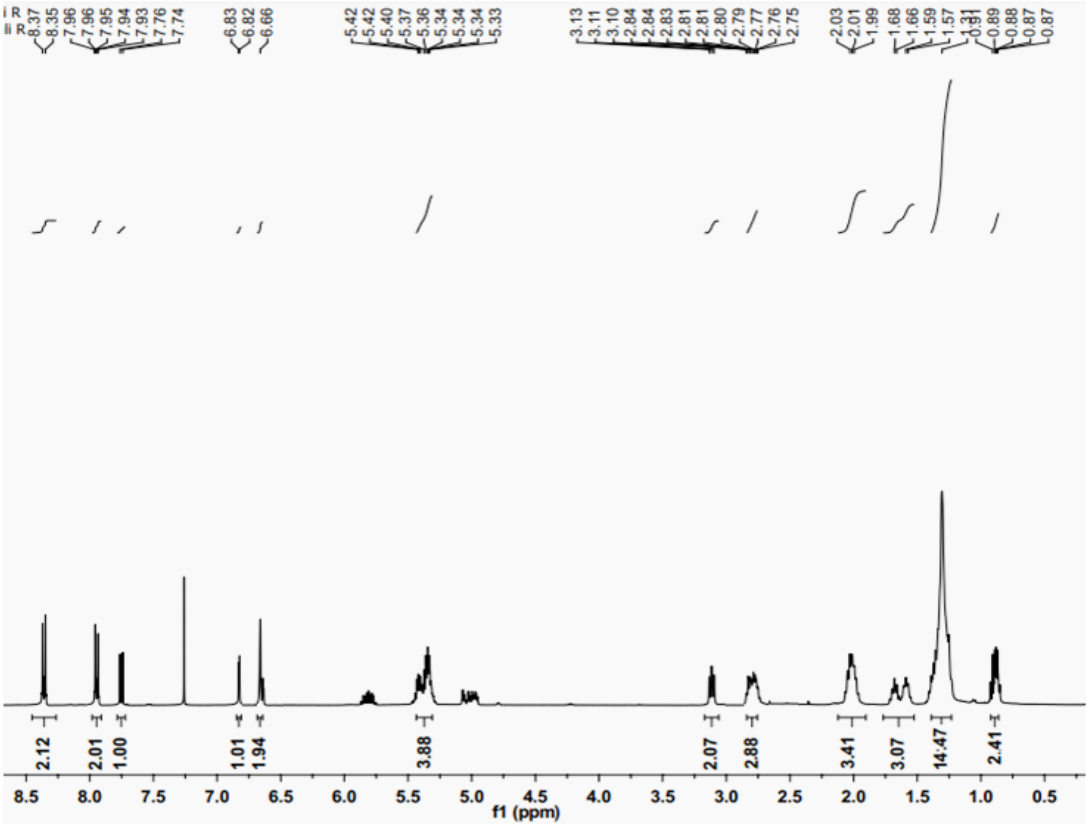


**Figure S18**. A) $^{1}$H NMR, and B) $^{13}$C NMR Spectra of 4-(2-methoxyphenylazo)cardanol in $CDCl_3$.

**A)**




**B)**

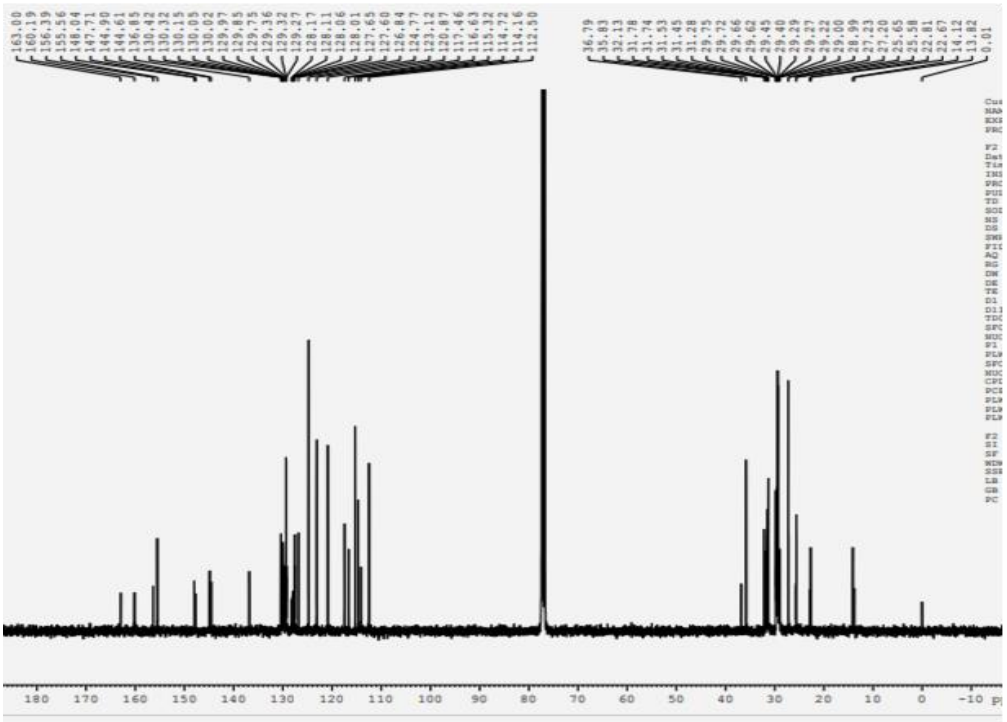
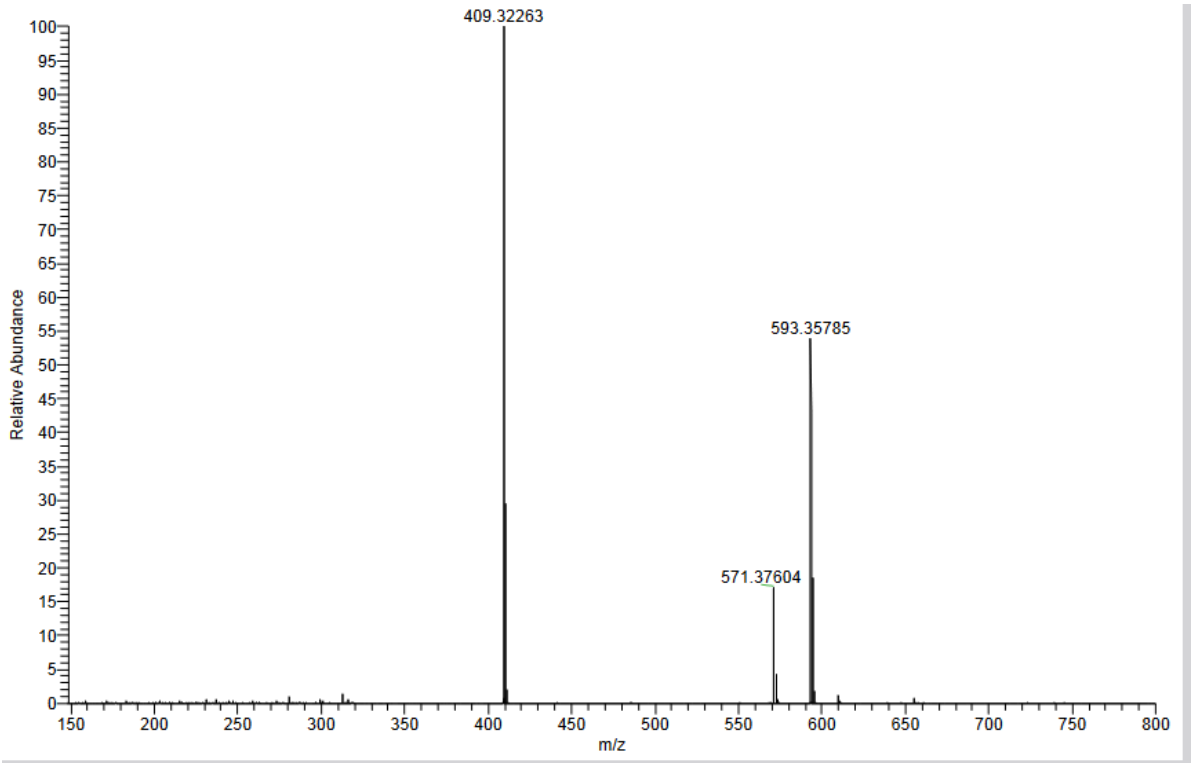



**Figure S19**. A) $^{1}$H NMR, and B) $^{13}$C NMR Spectra of 4-(4-nitro-phenylazo)cardanol in $CDCl_3$.

**A)**




**B)**

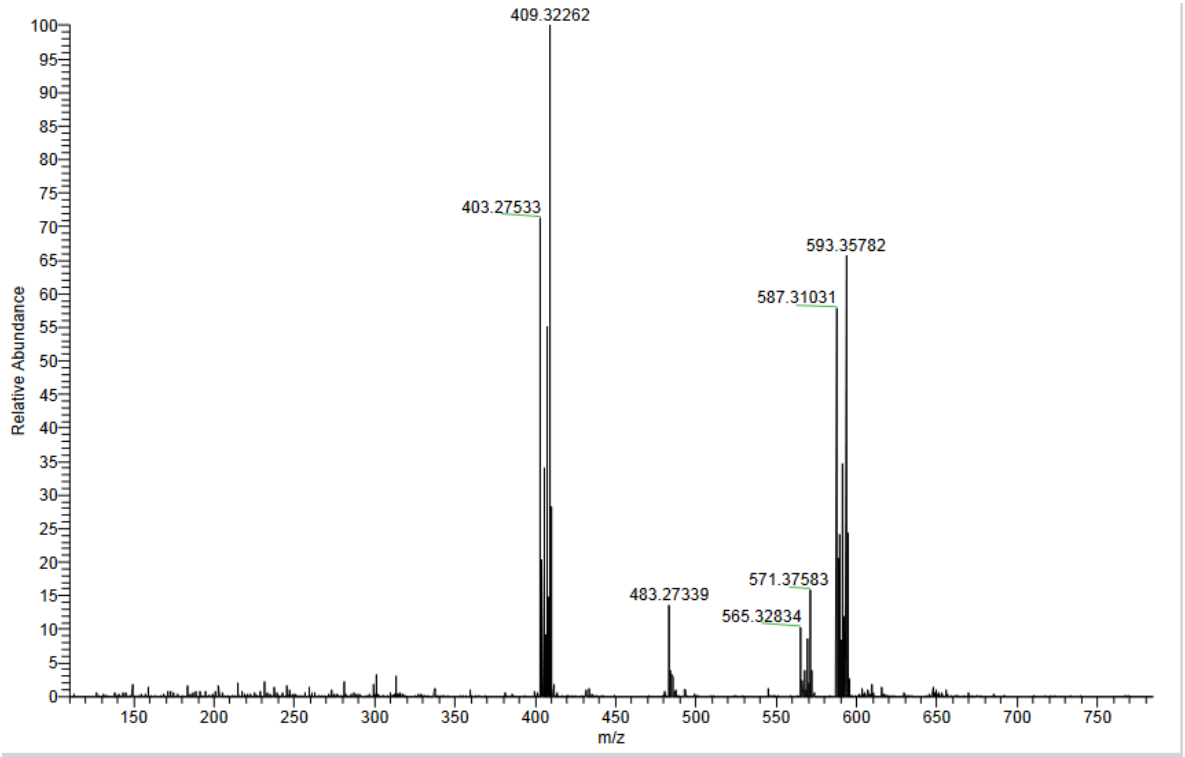



**Figure S20.** HRMS spectra of A) **2a** and B) **1a.**

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3. D. Mahata, S. M. Mandal, R. Bharti, V. K. Gupta, M. Mandal, A. Nag and G. Nando, *International Journal of Biological Macromolecules*, 2014, **69**, 5–11.
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