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Aromatic π-π Driven Supergelation, Aggregation Induced Emission and Columnar Self-assembly of Star-shaped 1,2,4-Oxadiazole Derivatives

Suraj Kumar Pathak[a], Balaram Pradhan[a], Ravindra Kumar Gupta[a], Monika Gupta[b], Santanu Kumar Pal[b] and Ammathnadu S. Achalkumar[a]*

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

Supporting information

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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. Alluminium 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 charactreization 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. Steady State anisotropy experiment was performed on Horiba Scientific Fluoromax spectrofluorometer 4. Time resolved lifetime measurements were done on time correlated single photon counter from Horiba Jobin Yvon (excitation by 440 nm laser diode). Cyclic Voltammetry (CV) studies were carried out using a Versa Stat 3 (Princeton Applied Research) instrument.The X-ray diffraction data were collected at 296 K with Mo K_α radiation (λ = 0.71073 Å) using a Bruker Nonius SMART APEX II CCD diffractometer equipped with a graphite monochromator. Smart software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT software. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL software. All the non-H atoms were refined in the anisotropic approximation.

Atomic Force microscopy (AFM) images were obtained for the drop-casted films using Agilent 5500-STM instrument. TEM images were obtained on a JEM-2100 Transmission Electron Microscope operating at an accelerating voltage of 200 kV. SEM images were obtained on a JEOL 7600F FESEM instrument. Rheological data is obtained using Rheometer MCR-302 Anton Paar.

Experimental Section

Compounds **6c-d, 5c-d, 4b-d** were prepared as per the reported procedures.[1] Synthesis of compounds **3a-d, 2a-d** and **1a-d** are reported as below.

Procedure for the synthesis of ethyl 3,4,5-tris(decyloxy) benzoate (**6c**)[1]

A mixture of ethyl gallate (25.23 mmol, 1equiv.), anhyd K_2CO_3 (166.52 mmol, 6.6 equiv.), *n*-bromodecane (80.74 mmol, 3.2 equiv.) were taken in dry DMF (20 ml) and heated at 80 °C 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 anhyd. Na_2SO_4 and concentrated. The crude product was purified by column chromatography on neutral alumina. Elution with hexanes followed by 5-10% ethylacetate-hexanes yielded the desired product.

R_f = 0.58 (10% EtOAc-hexanes); Low melting colorless solid; yield: 70%; IR (KBr pellet): ν_{max} in cm^{-1}2920, 2850, 1710, 1597, 1516, 1466, 1424, 1347, 1213, 1103, 760, 613; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26 (s, 2H, Ar), 4.35-4.36 (m, 2H, $COOCH_2$), 4.01 (s, 6H, 3 × OCH_2),1.27-1.81 (m, 48H, 24 × CH_2), 0.89 (bs, 12H, 4 × CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): 166.67, 152.99, 145.31, 125.24, 108.19, 73.68, 69.37, 61.14, 32.12, 30.53, 29.93, 29.84, 29.79, 29.60, 29.56, 26.29, 22.89, 14.30; HRMS (ESI+) exact mass calculated for $C_{39}H_{71}O_5$ (M+1): 619.5296, Found: 619.5218

Procedure for the synthesis of ethyl 3,4,5-tris(dodecyloxy) benzoate (**6d**)[1]

A mixture of ethyl gallate (25.23 mmol, 1equiv.), anhyd K_2CO_3 (166.52 mmol, 6.6 equiv.), *n*-bromododecane (83.26 mmol, 3.3 equiv.) were taken in dry DMF (20 ml) and heated at 80 °C 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 anhyd Na_2SO_4 and concentrated. The crude product was purified by column chromatography on neutral alumina. Elution with hexanes followed by 5-10% ethylacetate-hexanes yielded the desired product.

R_f = 0.61(10% EtOAc-hexanes); Low melting colorless solid; yield: 90%; IR (KBr pellet): ν_{max} in cm^{-1} 2924, 2853, 1716, 1590, 1504, 1465, 1432, 1333, 1222, 1119; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.25 (s, 2H, Ar), 4.33 – 4.37 (m, 2H, $COOCH_2$), 4.01 (m, 6H, 3 × OCH_2), 1.23-1.83

(m, 60H, 30 × CH_2), 0.87-0.89 (m, 12H, 4 × CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): 166.66, 153.01, 142.57, 125.26, 108.24, 73.68, 69.40, 61.14, 32.14, 30.54, 29.95, 29.92, 29.85, 29.79, 29.61, 29.54, 26.30, 22.90, 14.30; HRMS (ESI+) exact mass calculated for $C_{45}H_{83}O_5$ (M+1): 703.6235, Found: 703.6199.

Procedure for the synthesis of (3,4,5-tris(decyloxy)phenyl)methanol (**5c**):[2]

To a stirred suspension of lithium aluminium hydride (LAH) (18.2 mmol, 1.5 equiv.) in dry THF (20 ml) under nitrogen atmosphere, added the solution of ethyl 3,4,5-tris(decyloxy) benzoate (12.13 mmol, 1 equiv.) drop wise at 0 °C. Then the reaction mixture was allowed to reach room temperature and stirred for 2 h. Excess LAH present was quenched by the addition of moist sodium sulphate. Reaction mixture was extracted with EtOAc (5 × 50 ml). The combined extracts were washed with water, dried over anhyd Na_2SO_4 and concentrated *in vaccuo*. Purification was done by column chromatography over silica gel (60-120) with 10% EtOAc-hexanes as eluent.

R_f = 0.12 (10% EtOAc-hexanes), white solid, m.p: 44 – 46°C; yield: 75%; IR (KBr pellet): ν_{max} in cm^{-1} 3412.64, 2922.60, 2852.97, 1592.66, 1466.88, 1440.35, 1335.89, 1233.54, 1121.80, 811.98, 723.09 and 455.56; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.55 (s, 2H, Ar), 4.58 (s, 2H, $ArCH_2$), 3.91- 3.98 (m, 6H, 3 × OCH_2), 1.27-1.82 (m, 48H, 24 × CH_2), 0.86 – 0.89 (m, 9H, 3 × CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): 153.46, 137.75, 136.27, 105.52, 73.65, 69.30, 65.84, 63.30, 33.01, 32.15, 32.12, 30.53, 29.95, 29.89, 29.86, 29.83, 29.80, 29.76, 29.63, 29.57, 26.34, 26.31, 25.94, 22.89, 14.31; HRMS (ESI+) exact mass calculated for $C_{37}H_{69}O_4$(M+1): 577.5190, Found: 577.5185.

Procedure for the synthesis of (3,4,5-tris(dodecyloxy)phenyl) methanol (**5d**):[2]

To a stirred suspension of lithium aluminium hydride (LAH) (21.33 mmol, 1.5 equiv.) in dry THF (20 ml) under nitrogen atmosphere, added the solution of ethyl 3,4,5-tris(dodecyloxy) benzoate (14.22 mmol, 1 equiv.) drop wise at 0 °C. Then the reaction mixture was allowed to reach room temperature and stirred for 2 h. Excess LAH present was quenched by the addition of moist sodium sulphate. Reaction mixture was extracted with EtOAc (6 × 30 ml). The combined extracts were washed with water, dried over anhyd $Na_2SO_4$and concentrated *in vaccuo*. Purification was done by column chromatography over silica gel (60-120) with 10% EtOAc-hexanes as eluent.

R_f= 0.15 (10% EtOAc-hexanes), white solid, m.p: 52 – 54°C;yield: 80%; IR (KBr pellet): ν_{max} in cm^{-1} 3417.27, 2922.36, 2852.51, 1590.29, 1467.09, 1438.45, 1334.39, 1231.90, 1124.64, 806.80, 722.27, and 466.28; ^1H NMR ($CDCl_3$, 400 MHz): δ 6.55 (s, 2H, Ar), 4.59 (s, 2H, $ArCH_2$), 3.91-3.98 (m, 6H, 3 × OCH_2), 1.26- 1.81 (m, 60H, 30 × CH_2), 0.86 – 0.89 (m, 9H, 3 × CH_3);^{13}C NMR ($CDCl_3$, 100 MHz): 153.46, 137.75, 136.27, 105.52, 73.65, 69.29, 65.86, 32.16, 32.14, 30.53, 29.97, 29.95, 29.92, 29.87, 29.84, 29.63, 29.58, 26.35, 26.32, 22.91, 14.33;HRMS (ESI+) exact mass calculated for $C_{43}H_{81}O_4$(M+1): 661.6129, Found: 661.6128.

Procedure for the synthesis of 3,4- bis(decyloxy)benzaldehyde (**4b**):

A mixture of 3,4-dihydroxybenzaldehyde (14.48 mmol, 1equiv.), anhyd K_2CO_3 (60.82 mmol, 4.2 equiv.), *n*-bromodecane (31.86 mmol, 2.2 equiv.) were taken in dry DMF (20 ml) and heated at 80 °C 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 anhyd Na_2SO_4 and concentrated. The crude product was recrystallised with ethanol to get the pure product.

R_f = 0.5 (10% EtOAc-hexanes);white solid, m.p: 62 – 64°C;yield: 80%; IR (KBr pellet): ν_{max} in cm^{-1} 3341.99, 3086.82, 2953.59, 2921.42, 2850.54, 2754.45, 1687.44, 1591.37, 1438.55, 1394.40, 1345.49, 1235.46, 1132.99, 723.43, 657.51, and 586.51; ^1H NMR ($CDCl_3$, 400 MHz): δ 9.83(s, 1H, CHO), 7.41 (d, 1H, *J* = 8 Hz Ar), 7.39(s,1H, Ar), 4.03-4.09 (m, 4H, 2× OCH_2), 1.32-1.87 (m, 32H, 16 × CH_2), 0.86 - 0.89 (m, 6H, 2 × CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): 191.24, 154.89, 149.64, 130.07, 126.82, 111.95, 111.15, 69.33, 32.12, 29.83, 29.80, 29.78, 29.76, 29.59, 29.56, 29.28, 29.18, 26.19, 26.16, 22.89, 14.32; HRMS (ESI+) exact mass calculated for $C_{27}H_{47}O_3$(M+1): 419.3520, Found: 419.3517.

Procedure for the synthesis of 3,4,5-tris(decyloxy)benzaldehyde **(4c)**:[2]

An appropriate (3,4,5-tris(decyloxy) phenyl)methanol (8.7 mmol,1 equiv.) was taken in CH_2Cl_2 (10 vol.). To this pyridinium chlorochromate (8.7 mmol, 1 equiv.) adsorbed over equal amount of silica gel is added and stirred at room temperature for 1h.The reaction mixture was filtered over celite bed and concentrated to get the crude product, which was further purified by column chromatography on silica gel (60-120) with 10% EtOAc-hexanes as eluent.

R_f = 0.51(10% EtOAc-hexanes), low melting white solid, yield: 70%; IR (KBr pellet): ν_{max} in cm^{-1} 3369.16, 2950.81, 2923.70, 2852.91, 2728.30, 1742.75, 1695.63, 1585.77, 1439.72, 1382.43, 1332.61, 1228.57, 1117.47, 720.99, 645.56 and 580.35 ; ^1H NMR ($CDCl_3$, 400 MHz): δ9.82 (s, 1H, CHO), 7.08 (s, 2H, Ar),4.01 - 4.07(m, 6H, 3 × OCH_2), 1.27 -1.84 (m, 48H, 24 × CH_2), 0.86 – 0.89 (m, 9H, 3 × CH_3);^{13}C NMR ($CDCl_3$, 100 MHz): 191.55, 153.72, 144.00, 131.63, 108.01, 73.84, 69.41, 32.15, 32.12, 30.54, 29.93, 29.88, 29.84, 29.79, 29.76, 29.59, 29.56, 29.45, 26.28, 26.23, 22.90, 14.33; HRMS (ESI+) exact mass calculated for $C_{37}H_{67}O_4$(M+1): 575.5034, Found: 575.5033.

Procedure for the synthesis of 3,4,5-tris(dodecyloxy)benzaldehyde (**4d**):[2]

An appropriate (3,4,5-tris(dodecyloxy) phenyl)methanol (11.3 mmol,1 equiv.) was taken in CH_2Cl_2 (10 vol.). To this pyridinium chlorochromate (11.3 mmol, 1 equiv.) adsorbed over equal amount of silica gel is added and stirred at room temperature for 1h.The reaction mixture was filtered over celite bed and concentrated to get the crude product, which was further purified by column chromatography on silica gel (60-120) with 10% EtOAc-hexanes as eluent.

R_f = 0.53 (10% EtOAc-hexanes), white solid, m.p: 49 – 51°C; yield: 81%; IR (KBr pellet): ν_{max} in cm^{-1} 3441.06, 2956.36, 2919.21, 2849.30, 2729.23, 1695.12, 1584.10, 1439.42, 1381.82, 1336.74, 1226.84, 1119.30,720.33, 645.33 and 579.48; ^1H NMR ($CDCl_3$, 400 MHz): δ 9.83(s, 1H, CHO), 7.08 (s, 2H, Ar), 4.01 - 4.07(m, 6H, 3 × OCH_2), 1.18-1.84 (m, 60H, 30 × CH_2), 0.86 – 0.89 (m, 9H, 3 × CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): 191.52, 153.74, 144.08, 131.66, 108.07, 73.85, 69.45, 32.14, 30.56, 29.97, 29.94, 29.92, 29.88, 29.85, 29.76, 29.60, 29.47, 26.29, 26.25, 22.92, 14.33; HRMS (ESI+) exact mass calculated for $C_{37}H_{79}O_4$(M+1): 659.5973, Found:659.5975.

Procedure for the synthesis of 4-decyloxy benzonitrile (**3a**):

A mixture of 4-dihydroxybenzaldehyde (41.97 mmol, 1equiv.), anhyd K_2CO_3 (92.34 mmol, 2.2 equiv.), *n*-bromodecane (46.17 mmol, 1.1 equiv.) were taken in dry DMF (20 ml) and heated at 80 °C 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 anhyd Na_2SO_4 and concentrated. The crude product was recrystallised with ethanol to get the pure product.

R_f = 0.53 (10% EtOAc-hexanes), low melting white solid, yield: 80%; IR (KBr pellet): ν_{max} in cm^{-1} 2920.38, 2851.64, 2556.48, 2218.96, 1606.75, 1573.82, 1508.08, 1470.06, 1396.50, 1258.77, 1118.93, 832.93, 808.98 and 715.49 ; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.57 (d, 2H, *J* = 6 Hz, Ar), 6.93 (d, 2H, *J* = 6 Hz, Ar), 3.99 (t, 2H, *J* = 6 Hz, 1 × OCH_2), 1.24-1.81 (m, 16H, 8 × CH_2), 0.88 (t, 3H, *J* = 6 Hz, 1 × CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): 162.67, 134.16, 119.55, 115.37, 103.82, 68.63, 32.08, 29.73, 29.51, 29.18, 26.13, 22.88, 14.31; HRMS (ESI+) exact mass calculated for $C_{17}H_{26}NO$(M+1): 260.2009, Found:260.1999.

Procedure for the synthesis of 3,4-bis(decyloxy) benzonitrile (**3b**):[3]

3,4-bis(decyloxy) benzaldehyde (9.55mmol, 1equiv.) was added to a solution of hydroxyl amine hydrochloride (17.68mmol, 1.85equiv.) in DMSO (19.1mL), and the resulting reaction solution was stirred and heated for 3hrs at 100°C. After cooling to room temperature, water was added to the reaction mixture , which was then extracted with Chloroform (5× 20mL). The combined chloroform layers were washed with water (4× 20mL) and dried with sodium sulfate. Removal of chloroform by rotatory evaporation and high vacuum yielded the desired product which was then recrystallised with ethanol to get the pure product.

R_f = 0.6 (10% EtOAc-hexanes), white solid, m.p: 77 – 78°C; yield: 70%; IR (KBr pellet): ν_{max} in cm^{-1} 2920.20, 2850.27, 2220.44, 1597.05, 1518.72, 1467.71, 1422.67, 1278.38, 1242.48, 1138.03, 988.18, 808.27 and 722.14;^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.23(dd, 1H, *J* = 1.2 Hz, *J* = 8Hz, Ar), 7.06-7.07 (m, 1H, Ar), 6.86 (d, 1H, *J* = 8 Hz, Ar), 3.96-4.04(m, 4H, 2 × OCH_2), 1.27-1.85 (m, 32H, 16 × CH_2), 0.86-0.89(m, 6H, 2 × CH_3); ^{13}C NMR ($CDCl_3$, 100MHz):153.30, 149.28, 126.52, 119.66, 116.27, 112.94, 103.71, 69.67, 69.33, 32.12, 29.80, 29.76, 29.55, 29.24, 29.16, 26.14, 22.89, 14.32; HRMS (ESI+) exact mass calculated for $C_{27}H_{46}NO_2$(M+1): 416.3523, Found:416.3419.

Procedure for the synthesis of 3,4,5-tris(decyloxy) benzonitrile (**3c**):[3]

3,4,5-tris(decyloxy) benzaldehyde (5.9mmol, 1equiv.) was added to a solution of hydroxyl amine hydrochloride (10.92mmol, 1.85equiv.) in DMSO(11.8mL), and the resulting reaction solution was stirred and heated for 3hrs at 100°C. After cooling to room temperature, water was added to the reaction mixture , which was then extracted with Chloroform (5× 20mL). The combined chloroform layers were washed with water (4× 20mL) and dried with sodium sulfate. Removal of chloroform by rotatory evaporation and high vacuum yielded the desired product which was then recrystallised with ethanol to get the pure product.

R$_f$ = 0.65 (10% EtOAc-hexanes), white solid, m.p: 50 – 52°C; yield: 80%; IR (KBr pellet): ν_{max} in cm^{-1} 2922.87, 2852.85, 2225.51, 1580.96, 1500.88, 1465.41, 1431.78, 1239.49, 1121.99, 813.75 and 720.49; ^{1}H NMR (CDCl$_3$, 600 MHz): δ 6.81(s, 2H, Ar), 4.00(t, 2H, *J* = 6 Hz, 1 × OCH$_2$), 3.95 (t, 4H, *J* = 6 Hz, 2 × OCH$_2$),1.24-1.82 (m, 48H, 24 × CH$_2$), 0.88(t, 9H,*J* = 6 Hz, 3 × CH$_3$); ^{13}C NMR (CDCl$_3$, 150MHz): 153.65, 142.71, 119.44, 110.69, 106.37, 73.90, 69.61, 32.12, 32.10, 30.48, 29.90, 29.85, 29.79, 29.76, 29.72, 29.57, 29.53, 29.37, 26.20, 22.88, 14.29; HRMS (ESI+) exact mass calculated for $C_{37}H_{66}NO_3$(M+1): 572.5025, Found:572.5037.

Procedure for the synthesis of 3,4,5-tris(dodecyloxy) benzonitrile (**3d**):[3]

3,4,5- tris(dodecyloxy)benzaldehyde (3.03mmol, 1equiv.) was added to a solution of hydroxyl amine hydrochloride (5.614mmol, 1.85equiv.) in DMSO(6mL), and the resulting reaction solution was stirred and heated for 3hrs at 100°C. After cooling to room temperature, water was added to the reaction mixture, which was then extracted with Chloroform (5× 20mL). The combined chloroform layers were washed with water (4× 20mL) and dried with sodium sulfate. Removal of chloroform by rotatory evaporation and high vacuum yielded the desired product which was then recrystallised with ethanol to get the pure product.

R$_f$ = 0.67 (10% EtOAc-hexanes), white solid, m.p: 62 – 63°C;yield: 78%;IR (KBr pellet): ν_{max} in cm^{-1} 2921.22, 2851.17, 2225.45, 1580.94, 1502.67, 1467.20, 1431.38, 1239.70, 1122.57, 832.19 and 720.40;^{1}H NMR (CDCl$_3$, 600 MHz): δ 6.81(s, 2H, Ar), 4.00(t, 2H, *J* = 6 Hz, 1 × OCH$_2$), 3.94 – 3.97 (m, 4H, 2 × OCH$_2$), 1.23-1.82 (m, 60H, 30 × CH$_2$), 0.88 (t, 9H, *J* = 6 Hz, 3 × CH$_3$); ^{13}C NMR (CDCl$_3$, 100MHz): 153.63, 142.62, 119.49, 110.61, 106.35, 73.91, 69.57, 32.14, 30.48, 29.95, 29.92, 29.89, 29.86, 29.82, 29.73, 29.60, 29.57, 29.55, 29.35, 26.21, 22.90, 14.32; HRMS (ESI+) exact mass calculated for $C_{43}H_{78}NO_3$(M+1): 656.5976, Found:656.5853.

Procedure for the synthesis of 4-bis(decyloxy)-*N*'-hydroxybenzamidine(**2a**):[4]

To a stirred solution of 4 -decyloxy benzonitrile (30.84 mmol, 1equiv.) in ethanol (20ml) was added hydroxylamine hydrochloride (67.85 mmol, 2.2 equiv.) and then triethylamine (70.94 mmol, 2.3 equiv.) was added. The solution was stirred under reflux for 18h and then diluted with water. Ethanol was removed under reduced pressure and the aqueous layer extracted 2 times with

DCM. The combined organic phases were dried over Na_2SO_4, evaporated under reduced pressure as the residue purified by recrystallization (ethanol) to afford the title compound as a white solid.

R_f

R_f = 0.5 (40% EtOAc-hexanes), white solid, m.p: 112 – 114°C, yield: 85%;IR (KBr pellet): ν_{max} in cm^{-1} 3448.41, 3350.58, 2921.52, 2852.69, 1652.88, 1610.28, 1519.12, 1390.54, 1251.93 and 826.64;^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.55(d, 2H, *J* = 6 Hz, Ar), 6.90 (d, 2H, *J* = 12 Hz, Ar), 4.82 (s, 2H, NH_2), 3.97(t, 2H, *J* = 6 Hz, 1 × OCH_2), 1.25 -1.81 (m, 16H, 8 × CH_2), 0.88(t, 3H, *J* = 6Hz, 1 × CH_3); ^{13}C NMR ($CDCl_3$, 100MHz): 160.78, 152.80, 127.37, 124.82, 114.73, 68.32, 32.11, 29.79, 29.60, 29.54, 29.40, 26.23, 22.90, 14.34; HRMS (ESI+) exact mass calculated for $C_{17}H_{29}N_2O_4$(M+1): 293.2224, Found:293.2220.

Procedure for the synthesis of 3,4-bis(decyloxy)-N'-hydroxybenzamidine(**2b**):[4]

To a stirred solution of 3,4-bis(decyloxy) benzonitrile (6.01 mmol, 1equiv.) in ethanol (10ml) was added hydroxylamine hydrochloride (13.23 mmol, 2.2 equiv.) and then triethylamine (13.82 mmol, 2.3 equiv.) was added. The solution was stirred under reflux for 18h and then diluted with water. Ethanol was removed under reduced pressure and the aqueous layer extracted 2 times with DCM. The combined organic phases were dried over Na_2SO_4, evaporated under reduced pressure as the residue purified by recrystallization (ethanol) to afford the title compound as a white solid.

R_f = 0.58 (40% EtOAc-hexanes), white solid, m.p: 77 – 78°C; yield: 82%; IR (KBr pellet): ν_{max} in cm^{-1} 3452.31, 2953.80, 2922.91, 2852.18, 1638.91, 1522.08, 1384.51, 1264.04 and 807.26;^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.18(s, 1H, Ar), 7.12 (d,1H, *J* = 8 Hz, Ar), 6.86 (d,1H, *J* = 8.4 Hz, Ar) 4.85(s, 2H, NH_2), 3.99 -4.02 (m, 4H, 2 × OCH_2),1.26-1.81 (m, 32H, 16 × CH_2), 0.86 – 0.89 (m, 6H, 2× CH_3); ^{13}C NMR ($CDCl_3$, 100MHz):153.05, 150.97, 149.33, 125.32, 118.67, 113.37, 111.63, 69.56, 69.44, 32.13, 29.85, 29.80, 29.63, 29.57, 29.47, 29.41, 26.25, 26.22, 22.90, 14.31; HRMS (ESI+) exact mass calculated for $C_{27}H_{49}N_2O_3$(M+1): 449.3738, Found:449.3661.

Procedure for the synthesis of 3,4,5-tris(decyloxy)–N'- hydroxybenzamidine (**2c**):[4]

To a stirred solution of 3,4,5–tris(decyloxy)benzonitrile (3.5 mmol, 1equiv.) in ethanol (5ml) was added hydroxylamine hydrochloride (7.69 mmol, 2.2 equiv.) and then triethylamine (8.05 mmol, 2.3 equiv.) was added. The solution was stirred under reflux for 18h and then diluted with water. Ethanol was removed under reduced pressure and the aqueous layer extracted 2 times with

DCM. The combined organic phases were dried over Na_2SO_4, evaporated under reduced pressure as the residue purified by recrystallization (ethanol) to afford the title compound as a white solid.

R$_f$ = 0.6 (40% EtOAc-hexanes), white solid, m.p: 66 - 68°C; yield: 72%; ν_{max} in cm^{-1} 3440.43, 2922.26, 2851.53, 1633.54, 1583.77, 1512.26, 1379.12, 1239.39 and 942.71;^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.80 (s, 2H, Ar), 4.83 (s, 2H, NH_2), 3.94-3.99 (m, 6H, 3 × OCH_2), 1.27-1.81(m, 48H, 24 × CH_2), 0.86 – 0.89 (m, 9H, 3 × CH_3);^{13}C NMR ($CDCl_3$, 100MHz):153.43, 153.28, 139.99, 127.69, 104.79, 73.69, 69.44, 32.15, 32.12, 30.52, 29.95, 29.89, 29.86, 29.81, 29.63, 29.57, 26.30, 22.90, 14.32; HRMS (ESI+) exact mass calculated for $C_{37}H_{69}N_2O_4$(M+1): 605.5252, Found:605.5289.

Procedure for the synthesis of 3,4,5-tris(dodecyloxy)–N'- hydroxybenzamidine (**2d**):[4]

To a stirred solution of 3,4,5–tris(dodecyloxy) benzonitrile (2.29 mmol, 1equiv.) in ethanol (5ml) was added hydroxylamine hydrochloride (5.04 mmol, 2.2 equiv.) and then triethylamine (5.27 mmol, 2.3 equiv.) was added. The solution was stirred under reflux for 18h and then diluted with water. Ethanol was removed under reduced pressure and the aqueous layer extracted 2 times with DCM. The combined organic phases were dried over Na_2SO_4, evaporated under reduced pressure as the residue purified by recrystallization (ethanol) to afford the title compound as a white solid.

R$_f$ = 0.62(40% EtOAc-hexanes), white solid, m.p: 74 – 75°C; yield: 70%; ν_{max} in cm^{-1}3440.88, 3354.89, 2945.26, 2921.07, 2850.12, 1634.03, 1582.24, 1511.82, 1371.52, 1240.11, 941.74; 1H NMR ($CDCl_3$, 600 MHz): δ 6.81 (s, 2H, Ar), 4.81 (s, 2H, NH_2), 3.95-3.99 (m, 6H, 3 × OCH_2), 1.23 - 1.82 (m, 60H, 30 × CH_2), 0.88 (t, 9H, *J* = 6 Hz, 3 × CH_3); ^{13}C NMR ($CDCl_3$, 100MHz): 153.44, 153.26, 139.98, 127.69, 104.78, 73.69, 69.44, 32.16, 32.14, 30.53, 29.97, 29.95, 29.92, 29.87, 29.82, 29.63, 29.61, 29.59, 26.32, 22.91, 14.34; HRMS (ESI+) exact mass calculated for $C_{43}H_{81}N_2O_4$(M+1): 689.6191, Found:689.6191.

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

A mixture of 4-(decyloxy)-N'-hydroxybenzamidine (1.11 mmol, 3.1 equiv.) and dry pyridine (8ml) was stirred under Ar atmosphere at 0 °C. To this, a solution of benzene-1,3,5-tricarboyl trichloride (0.36 mmol, 1 equiv.) in dry THF was added drop wise. The reaction mixture was refluxed for 12 h and then poured into cold water. The whole mass (a mixture of solid and water) was extracted with Chloroform (2 × 100 ml). The combined extracts were washed with water, brine, dried over anhyd.Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on neutral alumina. Elution with 20% CH_2Cl_2 hexanes yielded the desired product. Recrystallization with ethylacetate gives the pure product.

R_f = 0.5 (60%CH_2Cl_2-hexane), colorless crystals, m.p: 128 – 130^{o}C; yield: 60%; ν_{max} in cm^{-1}2922.62, 2851.59, 1609.91, 1543.21, 1471.52, 1355.16, 1252.64, 1171.24, 759.28;^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.15 (s, 3H, Ar), 8.13 (d, 6H, J = 8.8 Hz, Ar), 7.01 (d, 6H, J = 8.8 Hz, Ar), 4.02(t, 6H, J = 6.4 Hz, 3 × OCH_2), 1.23-1.84(m, 48H, 24 × CH_2), 0.89(t, 9H, J = 6.4 Hz, 3 × CH_3);^{13}C NMR ($CDCl_3$, 100MHz): 173.28, 169.31, 162.06, 130.71, 129.46, 126.85, 118.72, 115.05, 68.43, 32.12, 29.79, 29.63, 29.55, 29.41, 26.25, 22.91, 14.34; MALDI-TOF exact mass calculated for $C_{60}H_{81}N_6O_6$(M+3H): 981.6207, Found:981.6210.

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

A mixture of 3,4-bis(decyloxy)-N'-hydroxybenzamidine (1.11 mmol, 3.1 equiv.) and dry pyridine (8ml) was stirred under Ar atmosphere at 0 ^{o}C. To this, a solution of benzene-1,3,5-tricarboyl trichloride (0.36 mmol, 1 equiv.) in dry THF was added drop wise. The reaction mixture was refluxed for 12 h and then poured into cold water. The whole mass (a mixture of solid and water) was extracted with Chloroform (2 × 100 ml). The combined extracts were washed with water, brine, dried over anhyd.Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on neutral alumina. Elution with 20% CH_2Cl_2 hexanes yielded the desired product. Recrystallization with ethylacetate gives the pure product.

R_f = 0.58 (60%CH_2Cl_2-hexane), white solid, yield: 60%; ν_{max} in cm^{-1}2922.30, 2851.61, 1607.97, 1546.77, 1462.74, 1386.22, 1262.72, 1131.83 and 752.12;^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.24(s, 3H, Ar), 7.80 – 7.82 (m, 3H, Ar), 7.70 (s, 3H, Ar), 7.00 (d, 3H, J = 8.4 Hz, Ar), 4.13 – 4.16(m, 6H, 3× OCH_2), 4.09(t, 6H, J = 8Hz, 3 × OCH_2), 1.29-1.91(m, 96H, 48 × CH_2), 0.86-0.89(m,18H, 6 × CH_3);^{13}C NMR ($CDCl_3$, 100MHz): 173.30, 169.47, 152.25, 149.52, 130.75, 126.82, 121.35, 118.86, 113.18, 112.30, 69.59, 69.32, 32.15, 29.88, 29.84, 29.71, 29.66, 29.60, 29.51, 29.40, 26.31, 26.25, 22.92, 14.33. MALDI-TOF exact mass calculated for $C_{90}H_{141}N_6O_9$(M+3H): 1450.0744, Found:1450.0170.

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

A mixture of 3,4,5-tris(decyloxy) –N'- hydroxybenzamidine (0.9 mmol, 3.1 equiv.) and dry pyridine (7ml) was stirred under Ar atmosphere at 0 ^oC. To this, a solution of benzene-1,3,5-tricarboyl trichloride (0.29 mmol, 1 equiv.) in dry THF was added drop wise. The reaction mixture was refluxed for 12 h and then poured into cold water. The whole mass (a mixture of solid and water) was extracted with Chloroform (2 × 100 ml). The combined extracts were washed with water, brine, dried over anhyd.Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on neutral alumina. Elution with 20% CH_2Cl_2 hexanes yielded the desired product. Recrystallization with ethylacetate gives the pure product.

R_f = 0.6 (60%CH_2Cl_2-hexane), white solid, yield: 56%; ν_{max} in cm^{-1} 2921.00, 2850.86, 1603.26, 1551.65, 1441.02, 1396.59, 1353.69, 1235.95, 1125.41 and 750.74;^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.27(s, 3H, Ar), 7.43 (s, 6H, Ar), 4.11 – 4.14(m, 12H, 6× OCH_2), 4.04 – 4.07(m, 6H, 3 × OCH_2), 1.28-1.89 (m, 144H, 72 × CH_2), 0.86-0.88(m, 27H, 9 × CH_3);^{13}C NMR ($CDCl_3$, 150MHz): 173.49, 169.76, 153.88, 141.42, 131.03, 126.93, 121.14, 106.26, 73.83, 69.59, 32.16, 30.61, 29.89, 29.84, 29.64, 29.39, 26.39, 22.91, 14.32. MALDI-TOF exact mass calculated for$C_{120}H_{200}N_6O_{12}$(M+2H): 1917.5213, Found:1917.285.

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

A mixture of 3,4,5-tris(dodecyloxy) –N'- hydroxybenzamidine(0.91 mmol, 3.1 equiv.) and dry pyridine (4ml) was stirred under Ar atmosphere at 0 ^oC. To this, a solution of benzene-1,3,5-tricarboyl trichloride (0.29 mmol, 1 equiv.) in dry THF was added drop wise. The reaction mixture was refluxed for 12 h and then poured into cold water. The whole mass (a mixture of solid and water) was extracted with Chloroform (2 × 100 ml). The combined extracts were washed with water, brine, dried over anhyd.Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on neutral alumina. Elution with

20% CH_2Cl_2 hexanes yielded the desired product. Recrystallization with ethylacetate gives the pure product.

R_f = 0.65(60%CH_2Cl_2-hexane), white solid, yield: 55%; ;ν_{max} in cm^{-1}2920.97, 2850.96, 1603.54, 1551.60, 1466.76, 1396.15, 1235.37, 1125.00 and 750.33;^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.27(s, 3H, Ar), 7.43 (s, 6H, Ar), 4.06 – 4.14(m, 18H, 9× OCH_2), 1.27-1.88 (m, 180H, 90 × CH_2), 0.86-0.89 (m, 27H, 9 × CH_3); ^{13}C NMR ($CDCl_3$, 100MHz): 173.47, 169.73, 153.84, 141.28, 126.89, 121.12, 110.23, 106.11, 73.81, 69.51, 32.15, 30.60, 29.99, 29.95, 29.93, 29.89, 29.84, 29.69, 29.60, 26.39, 26.34, 22.92, 14.34. MALDI-TOF exact mass calculated for$C_{138}H_{237}N_6O_{12}$(M+3H): 2170.8109, Found:2170.6540.

(ii) NMR spectra

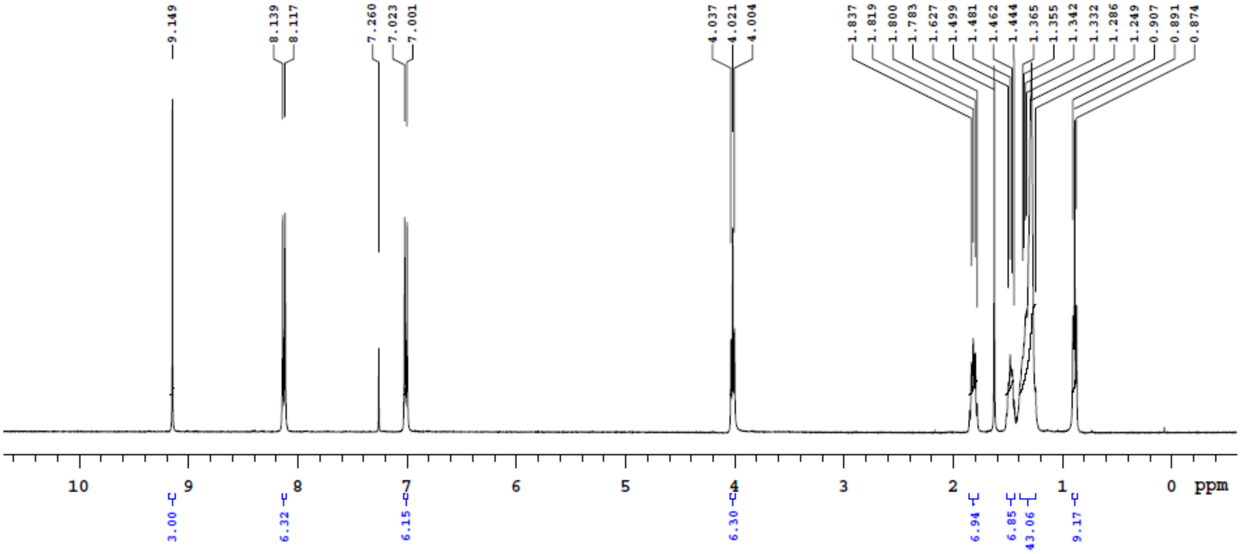

Figure S1. ^{1}H NMR (400 MHz) spectra of **1a** in CDCl$_3$

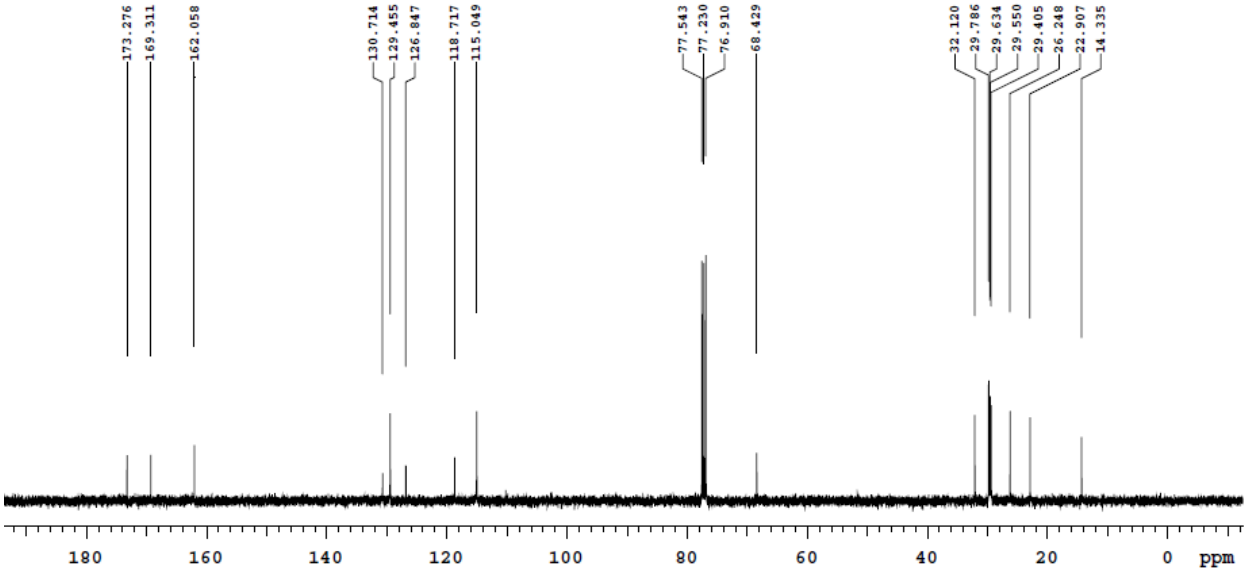

Figure S2. ^{13}C NMR (100 MHz) spectra of **1a** in CDCl$_3$

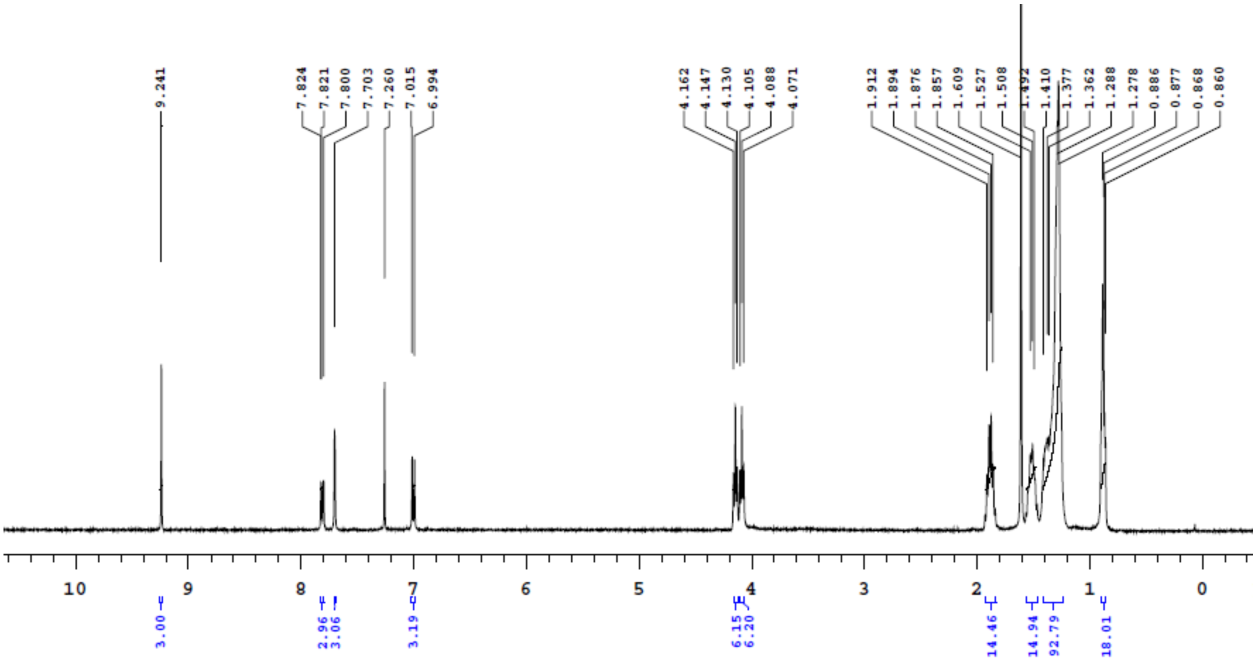

Figure S3.^{1}H NMR (400 MHz) spectra of **1b** in $CDCl_3$

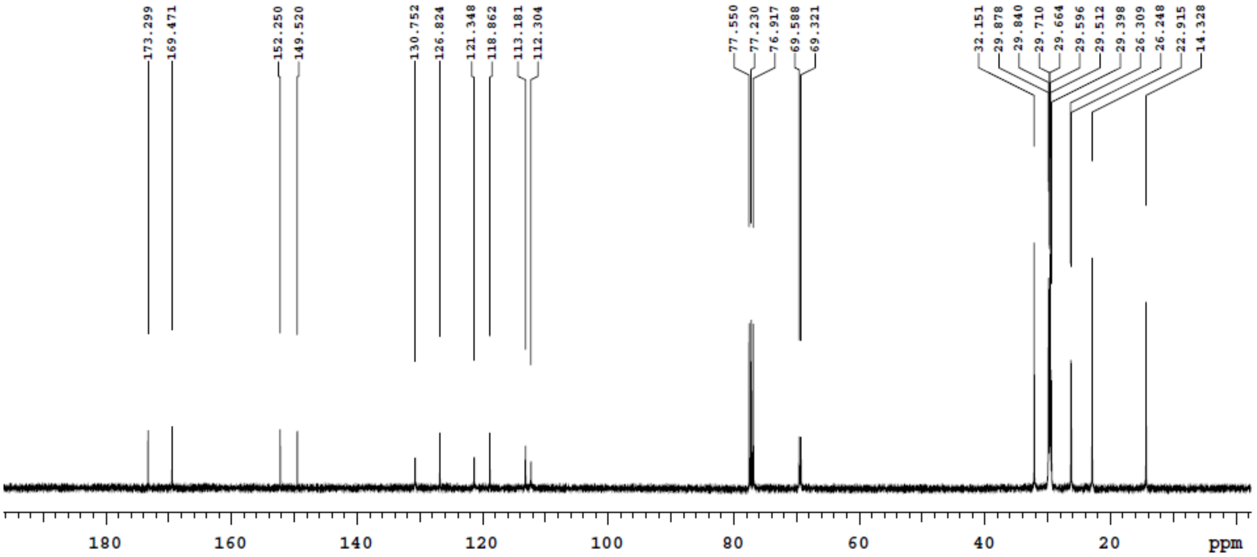

Figure S4.^{13}C NMR (100 MHz) spectra of **1b** in $CDCl_3$

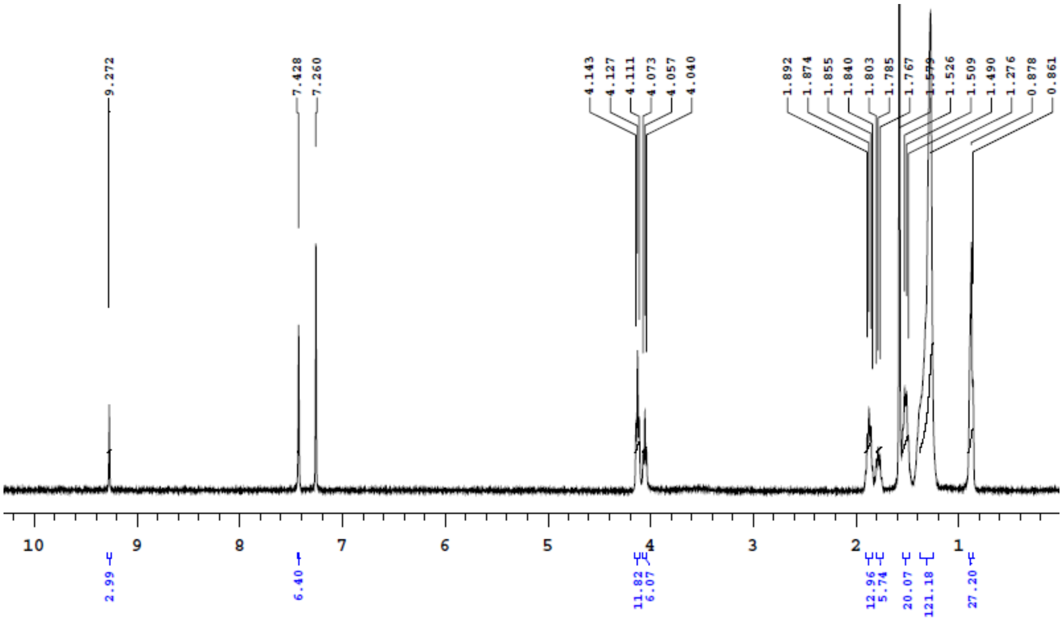

Figure S5. ^{1}H NMR (400 MHz) spectra of **1c** in $CDCl_3$

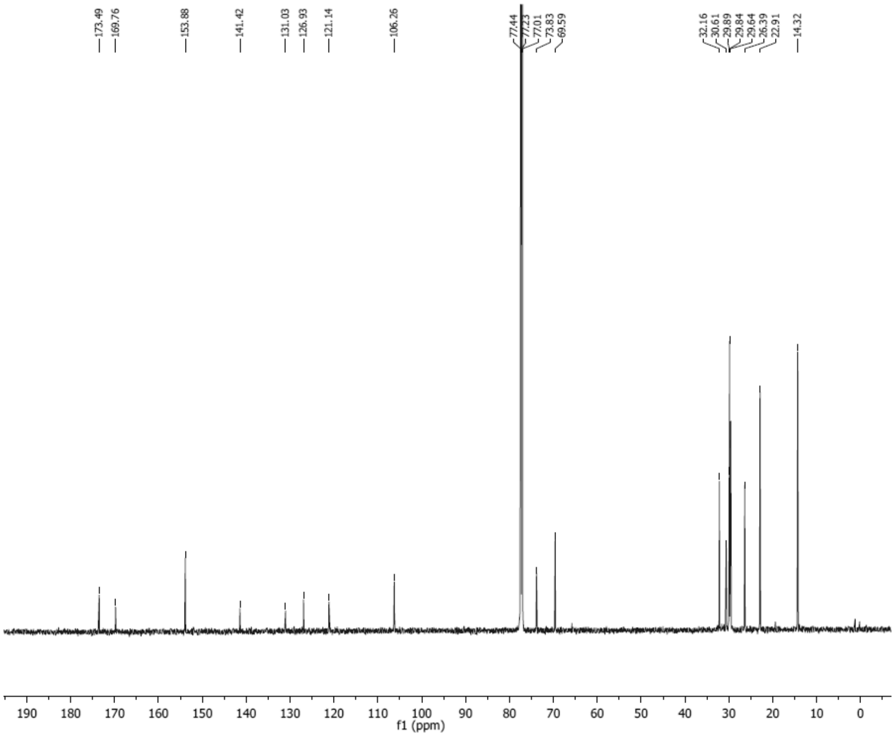

Figure S6. ^{13}C NMR (150 MHz) spectra of **1c** in $CDCl_3$

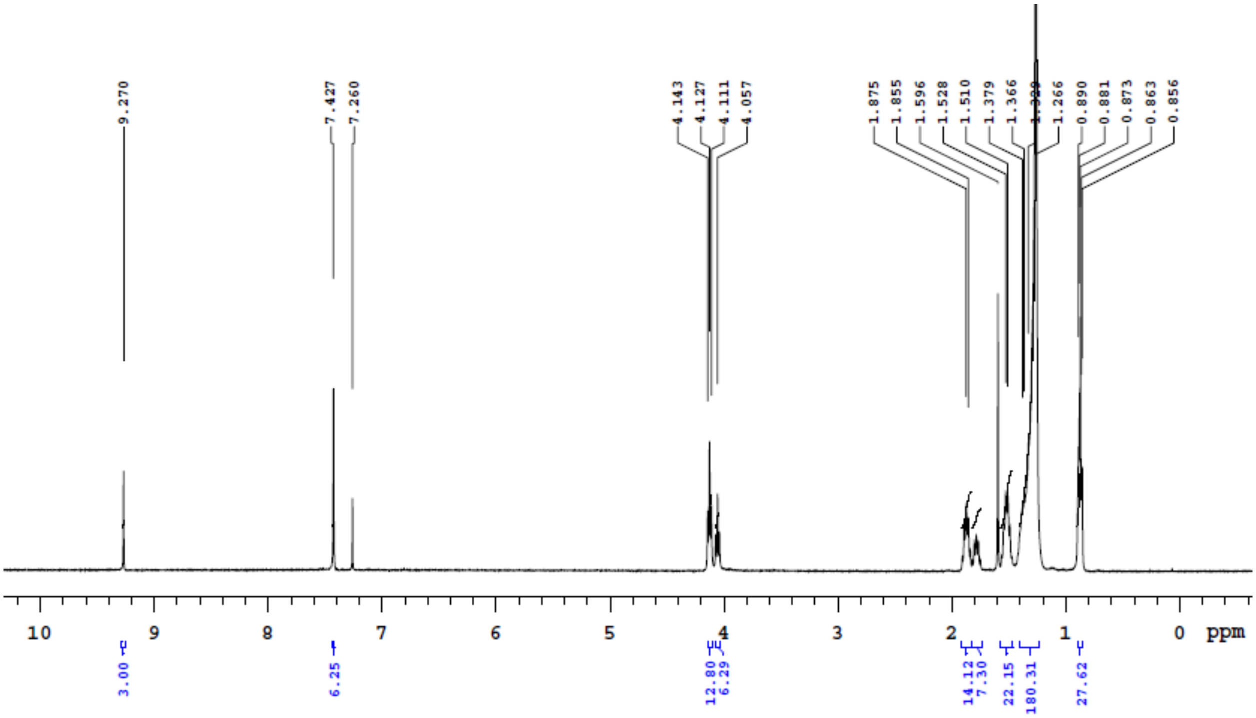

Figure S7. ^{1}H NMR (400 MHz) spectra of **1d** in CDCl$_3$

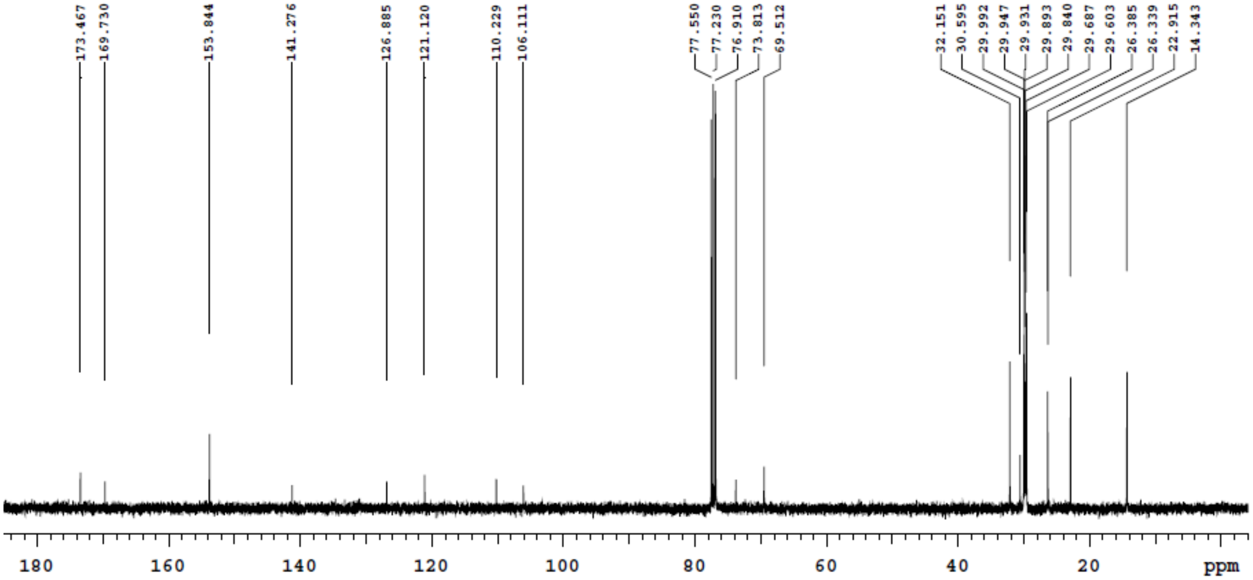

Figure S8. ^{13}C NMR (100 MHz) spectra of **1d** in CDCl$_3$

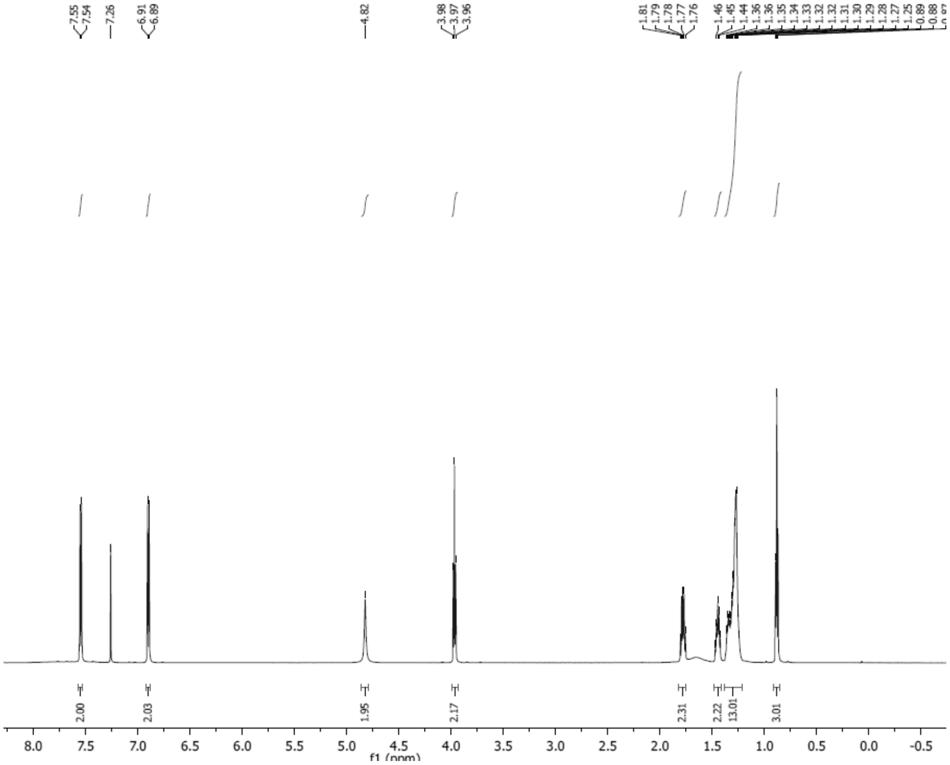

Figure S9. ^{1}H NMR (600 MHz) spectra of **2a** in CDCl$_3$

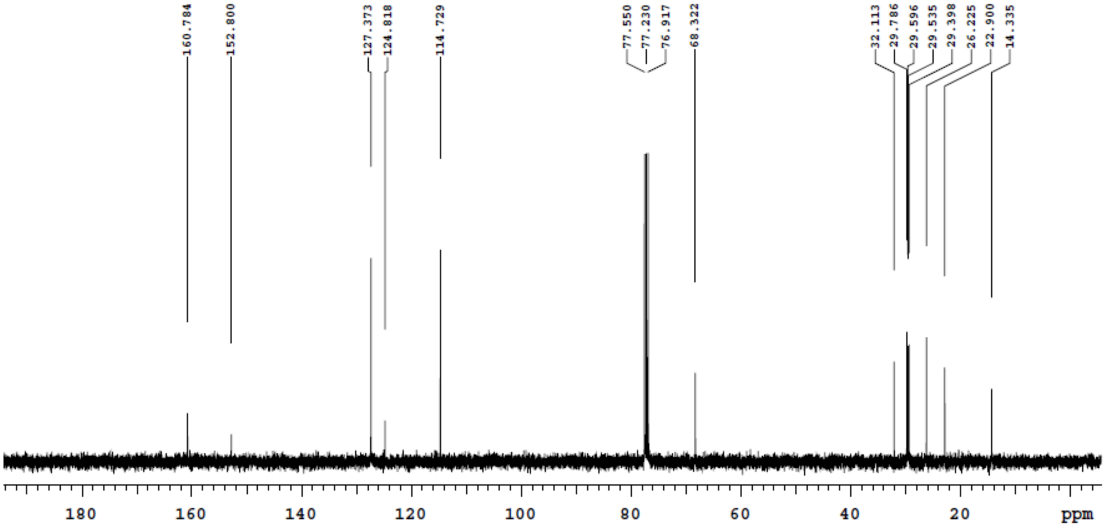

Figure S10. ^{13}C NMR (100 MHz) spectra of **2a** in CDCl$_3$

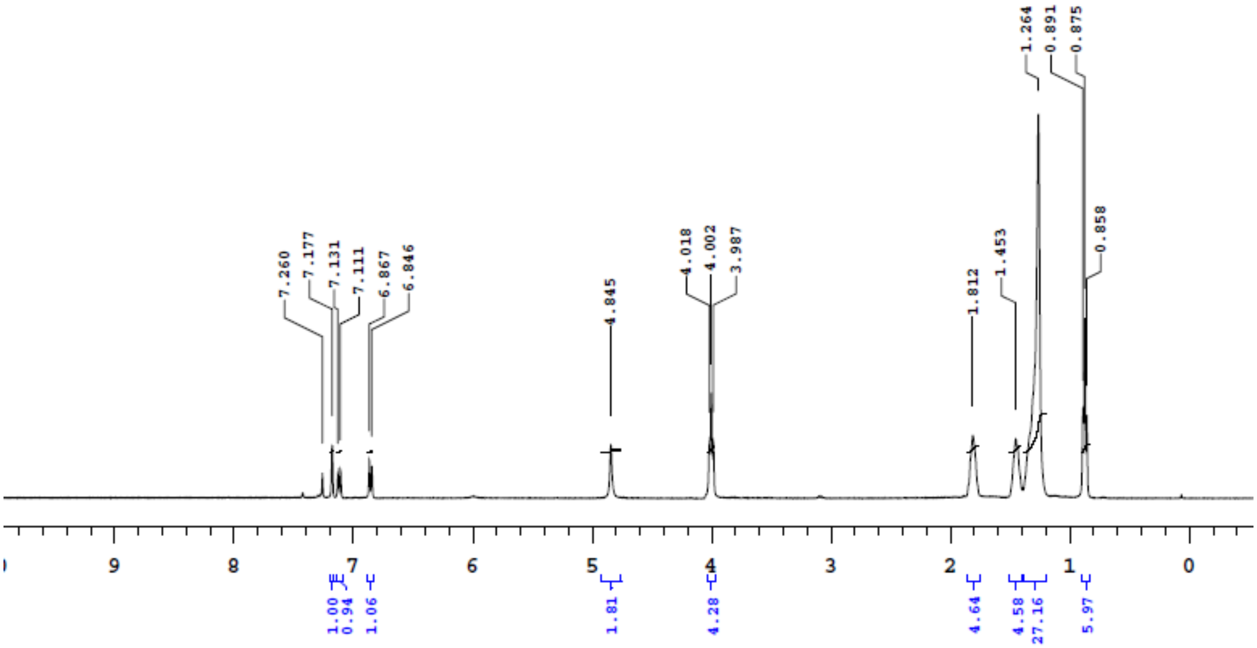

Figure S11. ^{1}H NMR (400 MHz) spectra of **2b** in $CDCl_3$

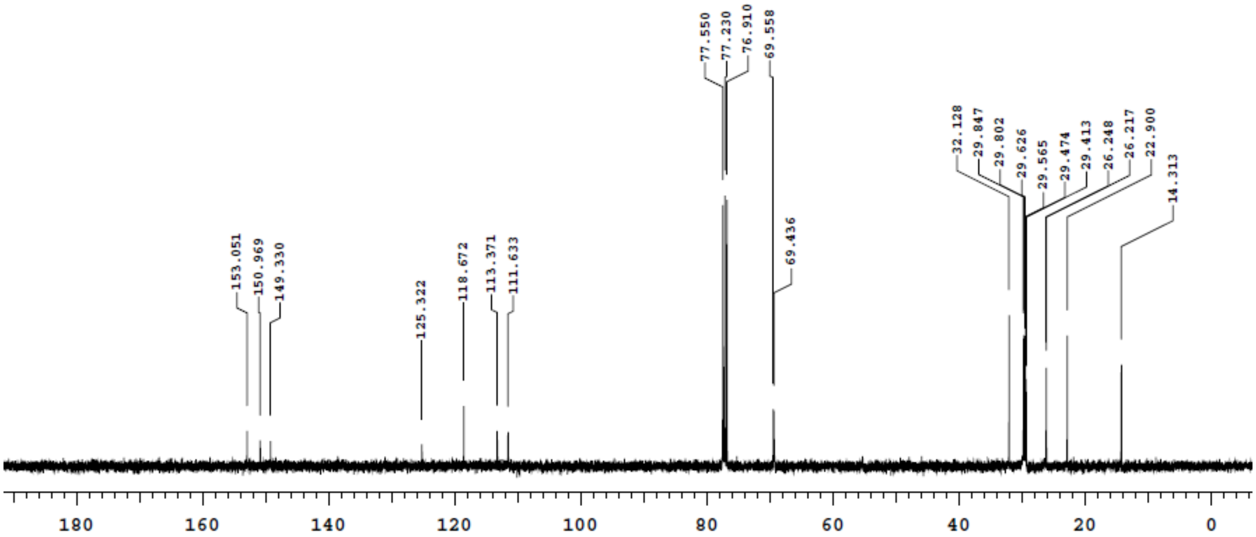

Figure S12. ^{13}C NMR (100 MHz) spectra of **2b** in $CDCl_3$

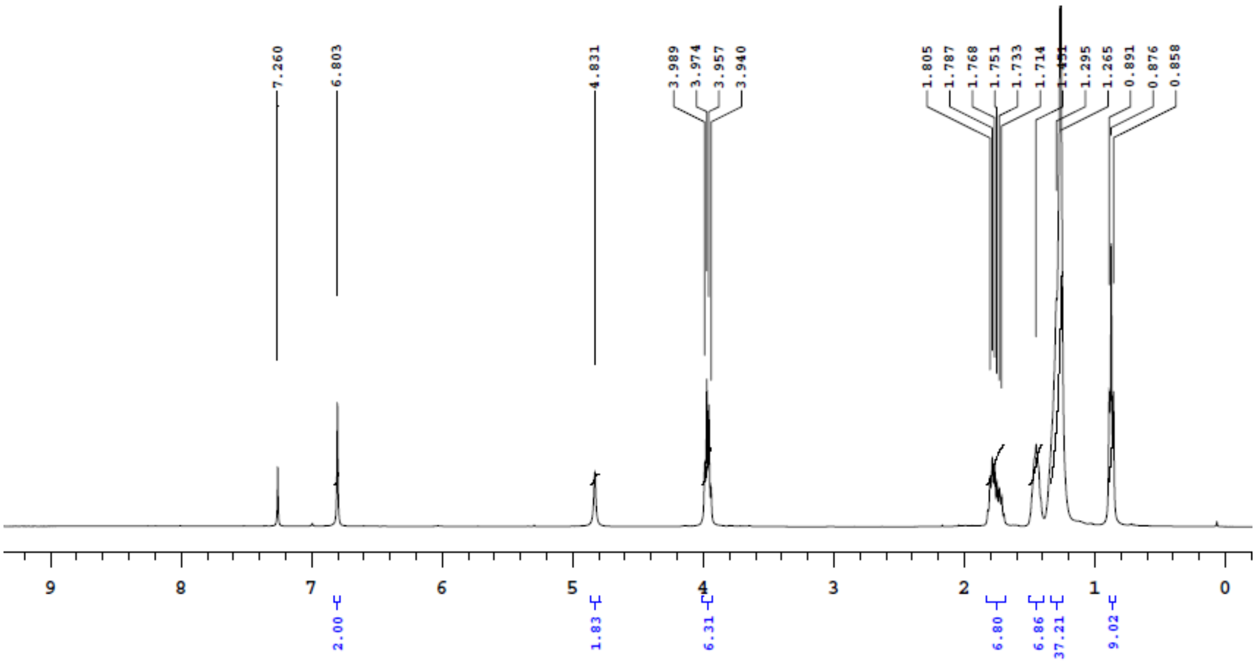

Figure S13. ^{1}H NMR (400 MHz) spectra of **2c** in CDCl$_3$

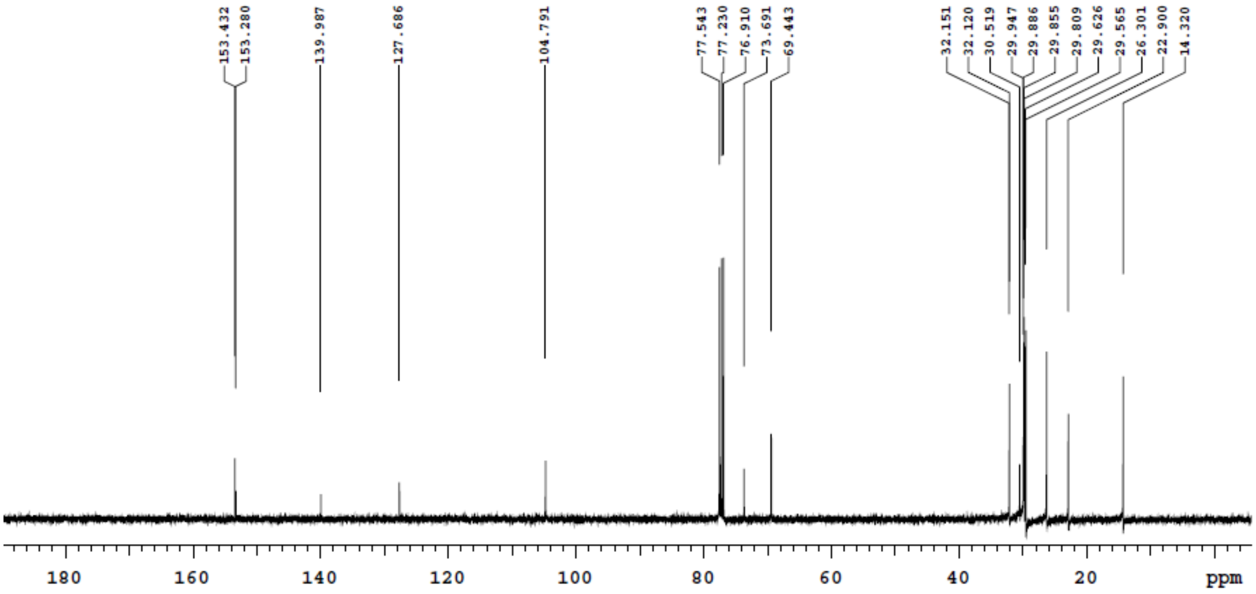

Figure S14. ^{13}C NMR (100 MHz) spectra of **2c** in CDCl$_3$

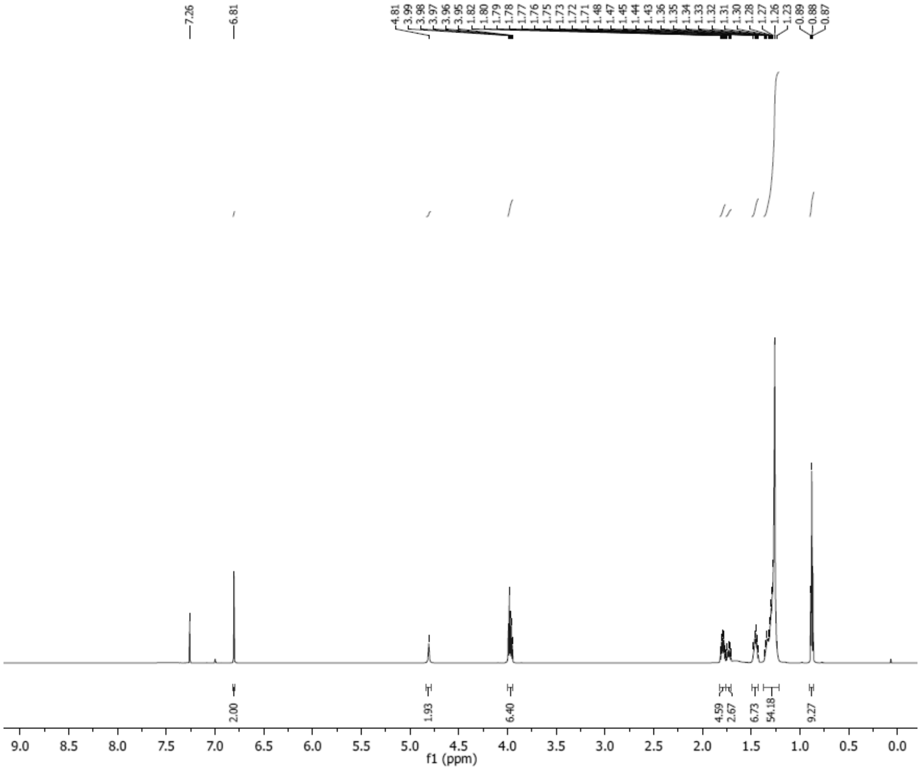

Figure S15. ^{1}H NMR (600 MHz) spectra of **2d** in $CDCl_3$

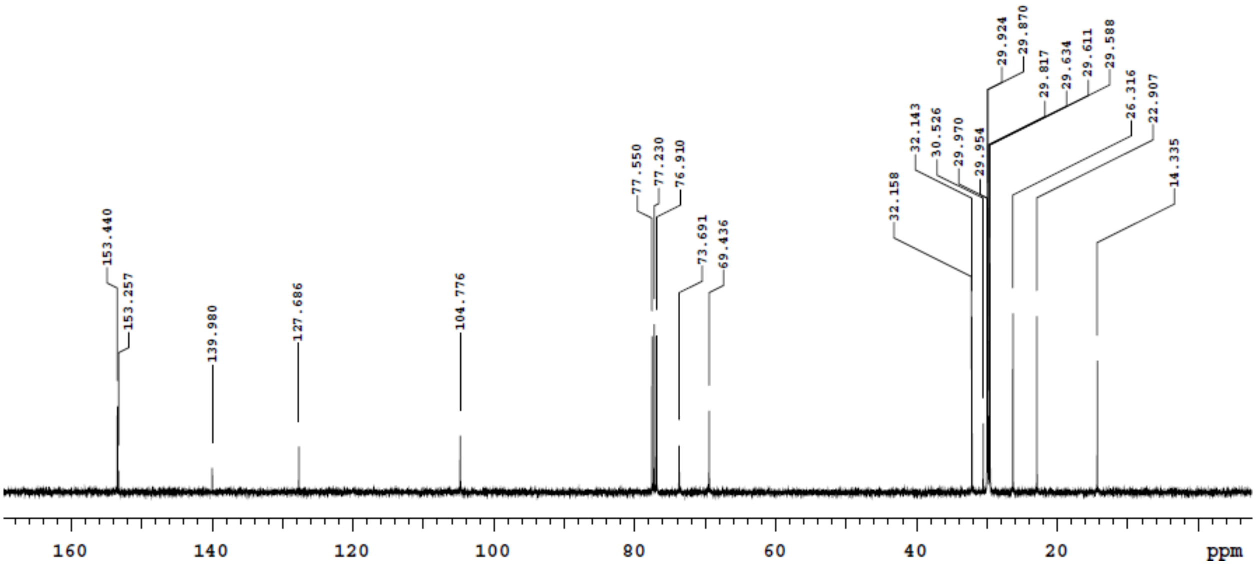

Figure S16. ^{13}C NMR (100 MHz) spectra of **2d** in $CDCl_3$

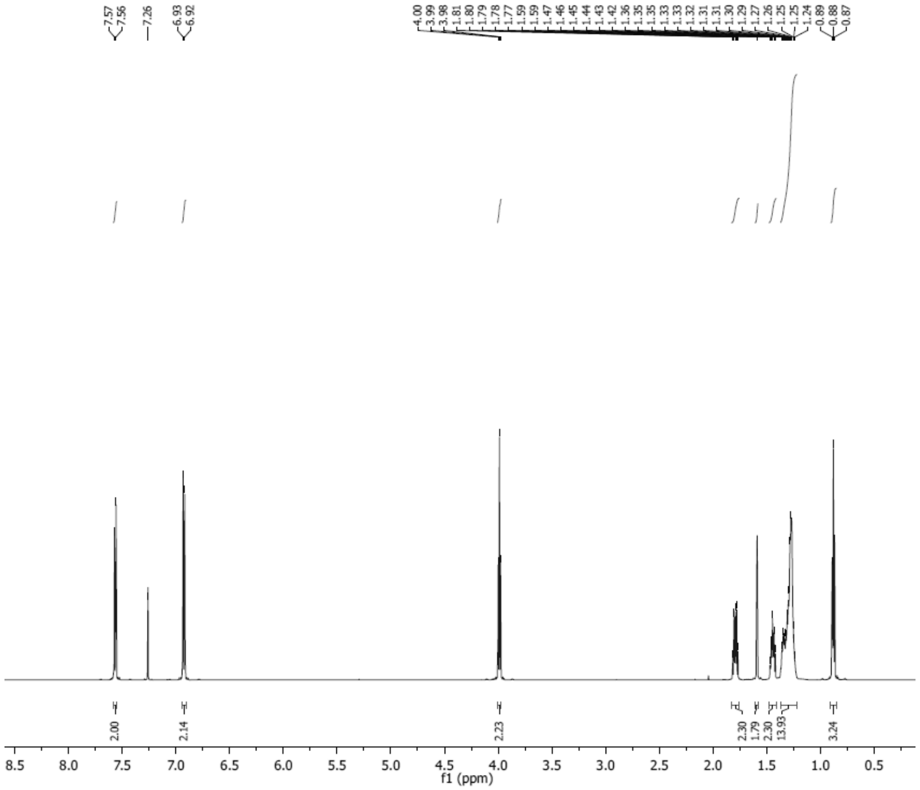

Figure S17.^{1}H NMR (600 MHz) spectra of **3a** in $CDCl_3$

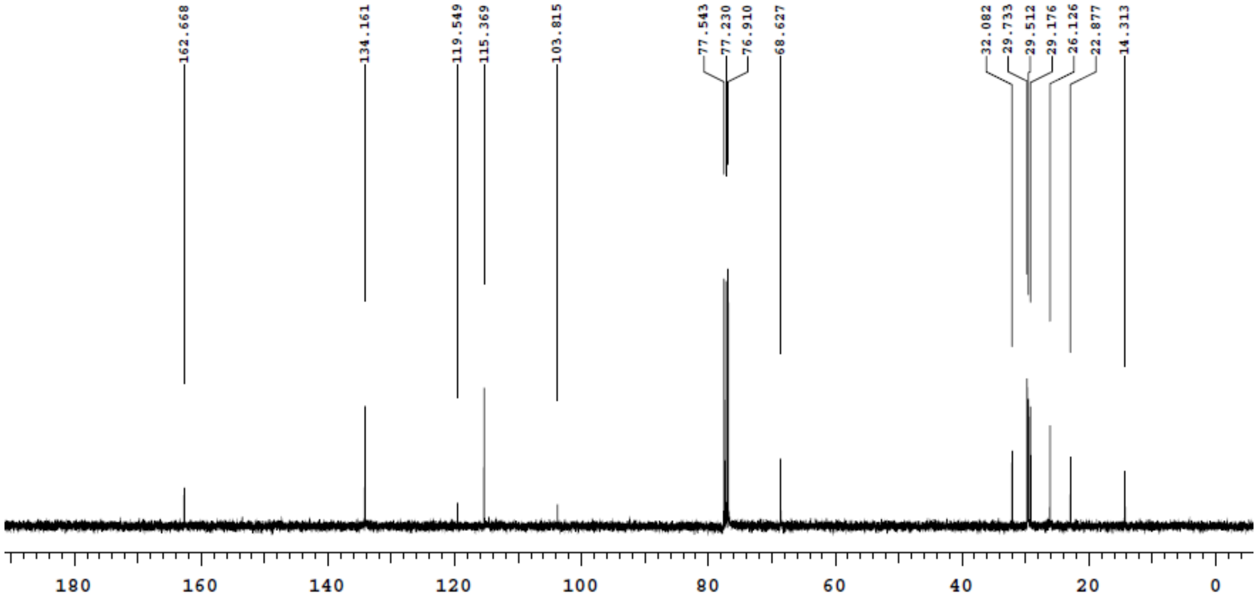

Figure S18.^{13}C NMR (100 MHz) spectra of **3a** in $CDCl_3$

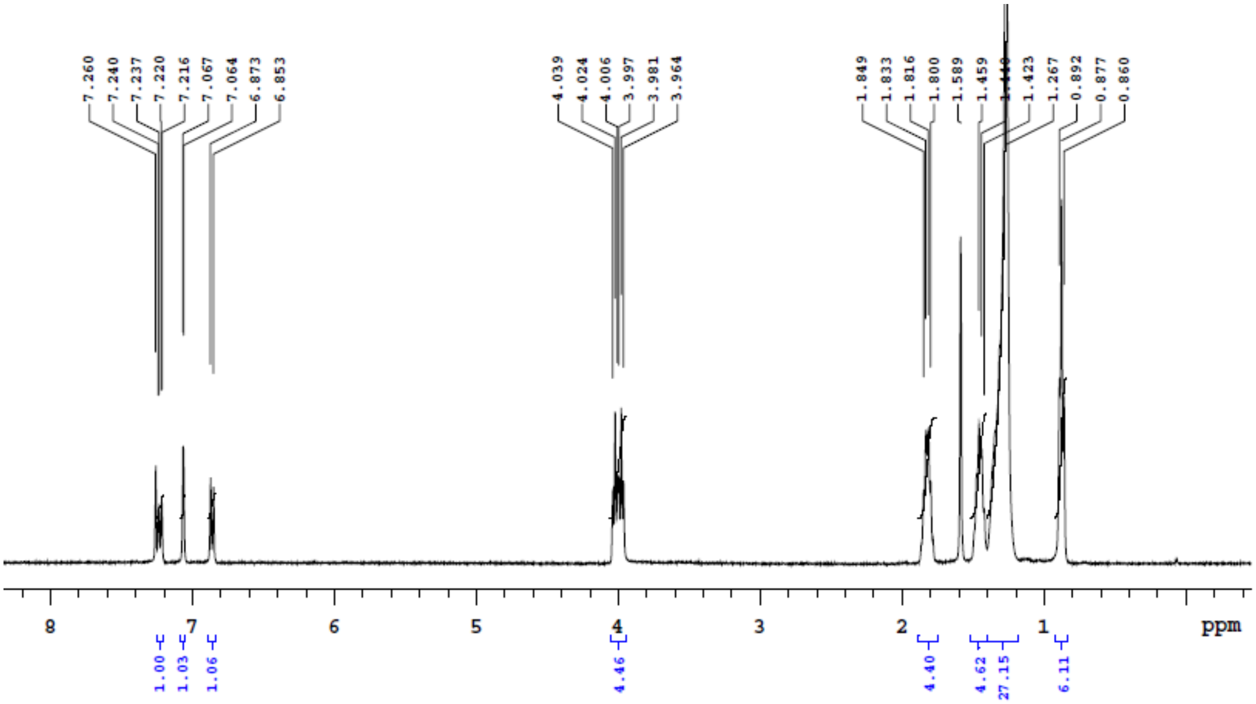

Figure S19.^{1}H NMR (400 MHz) spectra of **3b** in $CDCl_3$

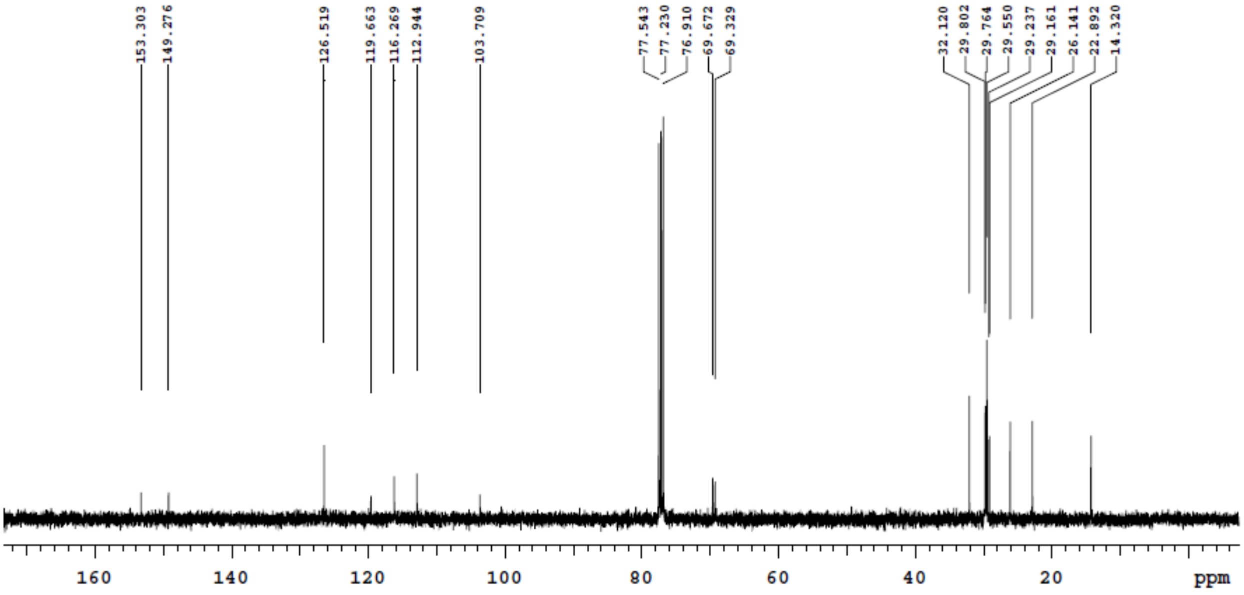

Figure S20.^{13}C NMR (100 MHz) spectra of **3b** in $CDCl_3$

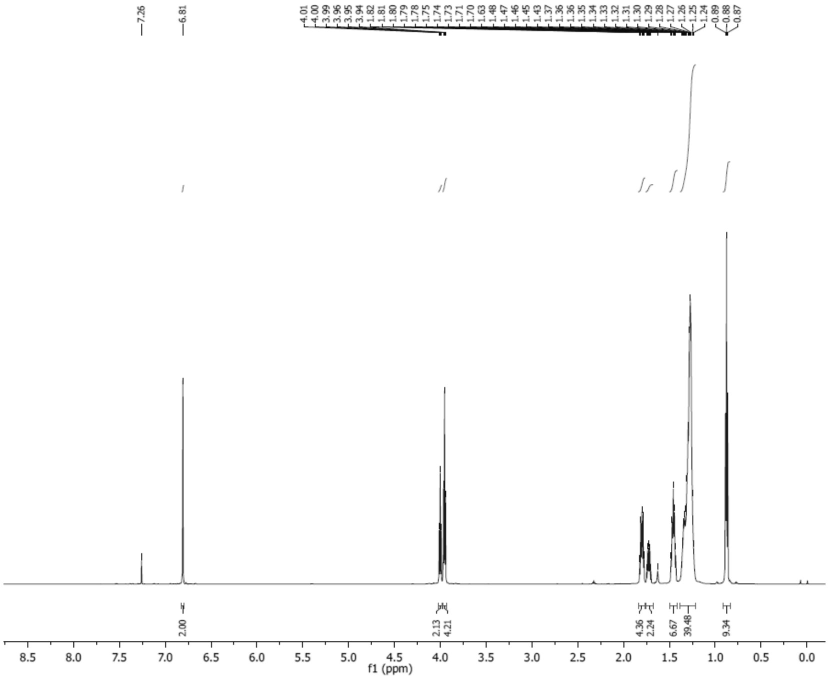

Figure S21. ^{1}H NMR (600 MHz) spectra of **3c** in $CDCl_3$

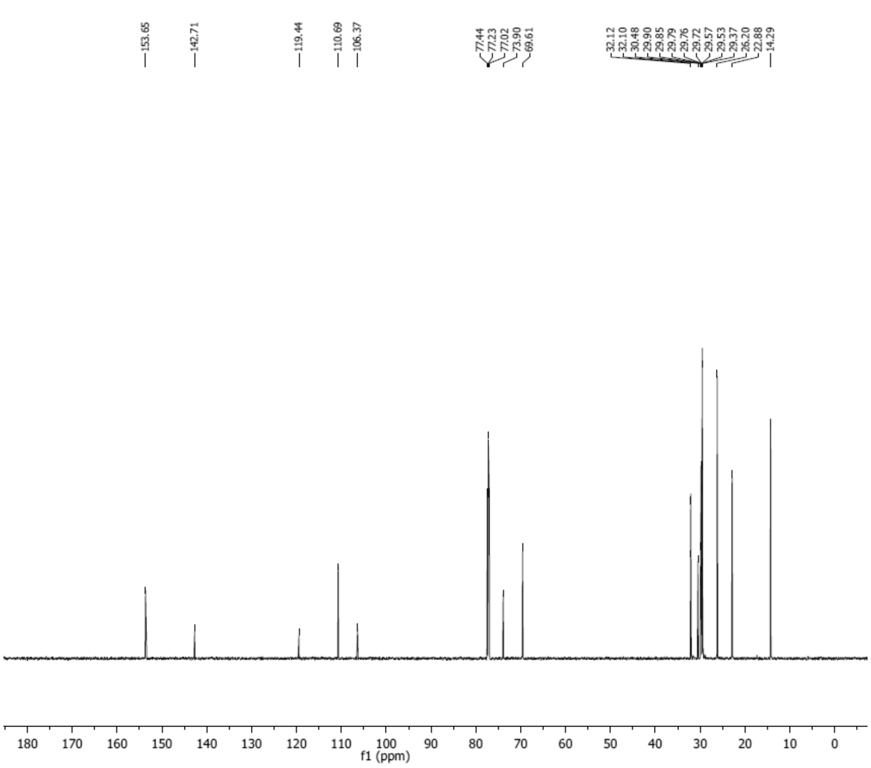

Figure S22. ^{13}C NMR (150 MHz) spectra of **3c** in $CDCl_3$

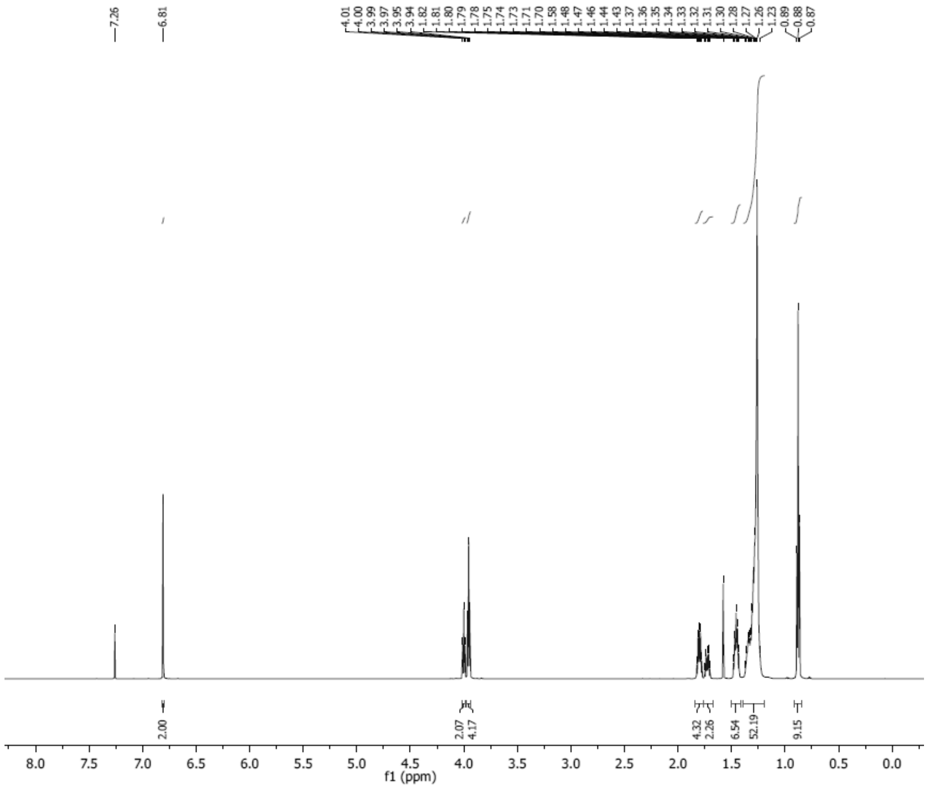

Figure S23. ^{1}H NMR (600 MHz) spectra of **3d** in $CDCl_3$

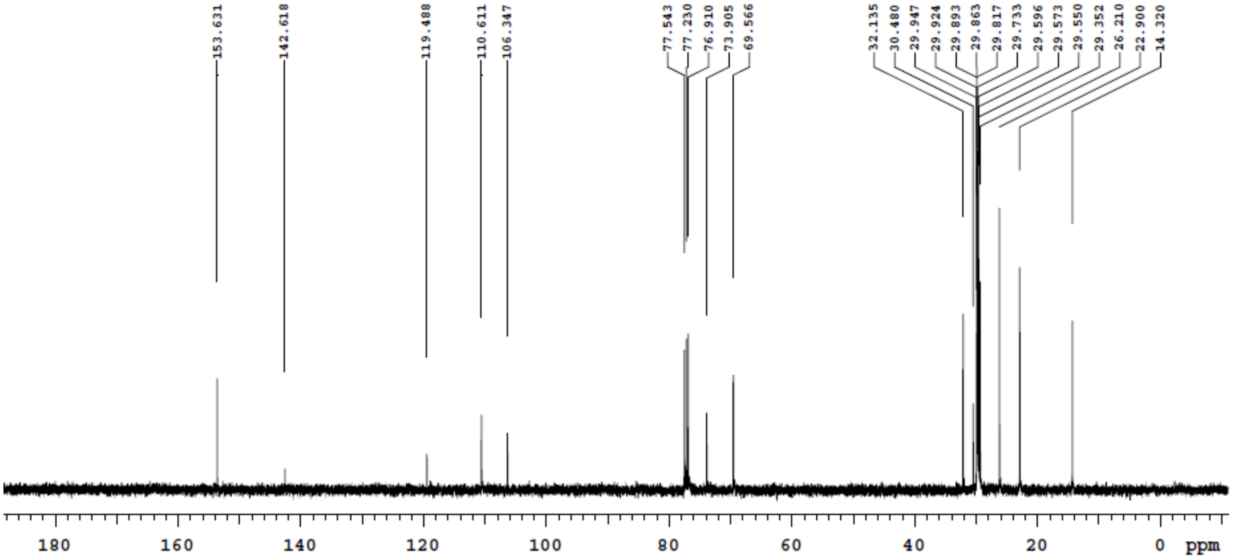

Figure S24. ^{13}C NMR (100 MHz) spectra of **3d** in $CDCl_3$

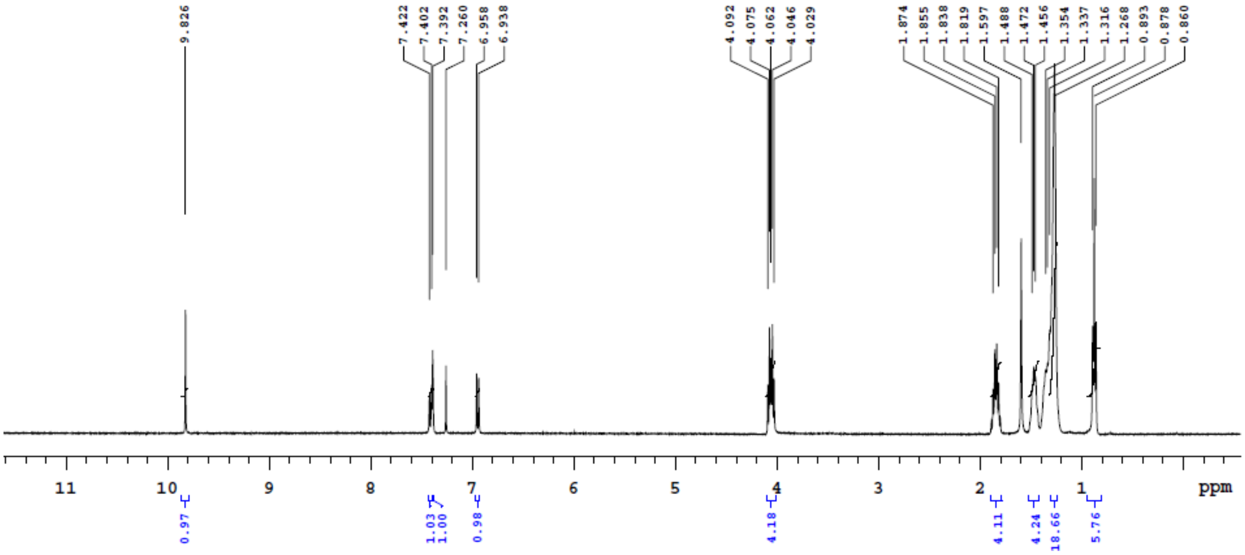

Figure S25. ^{1}H NMR (400 MHz) spectra of **4b** in CDCl$_3$

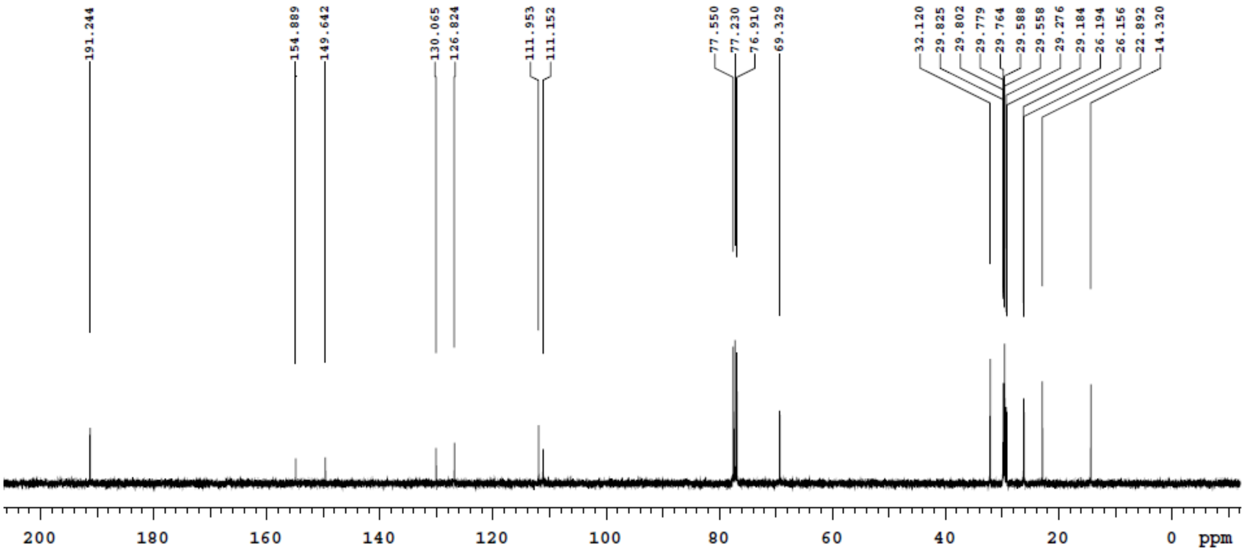

Figure S26. ^{13}C NMR (100 MHz) spectra of **4b** in CDCl$_3$

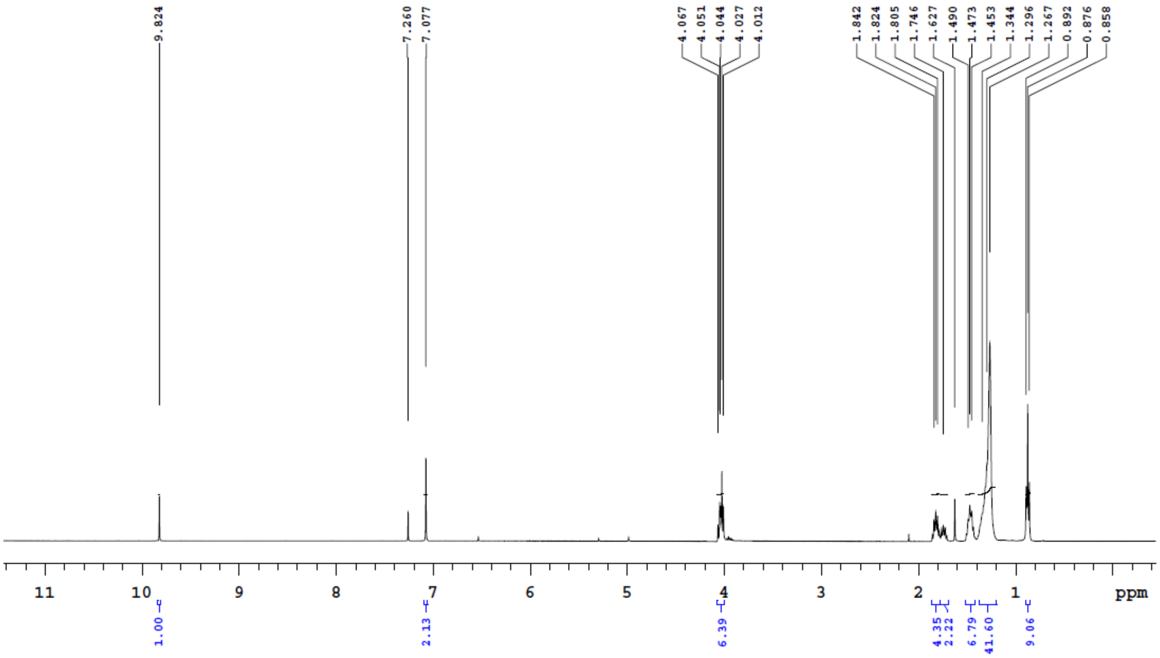

Figure S27. ^{1}H NMR (400 MHz) spectra of **4c** in CDCl$_3$

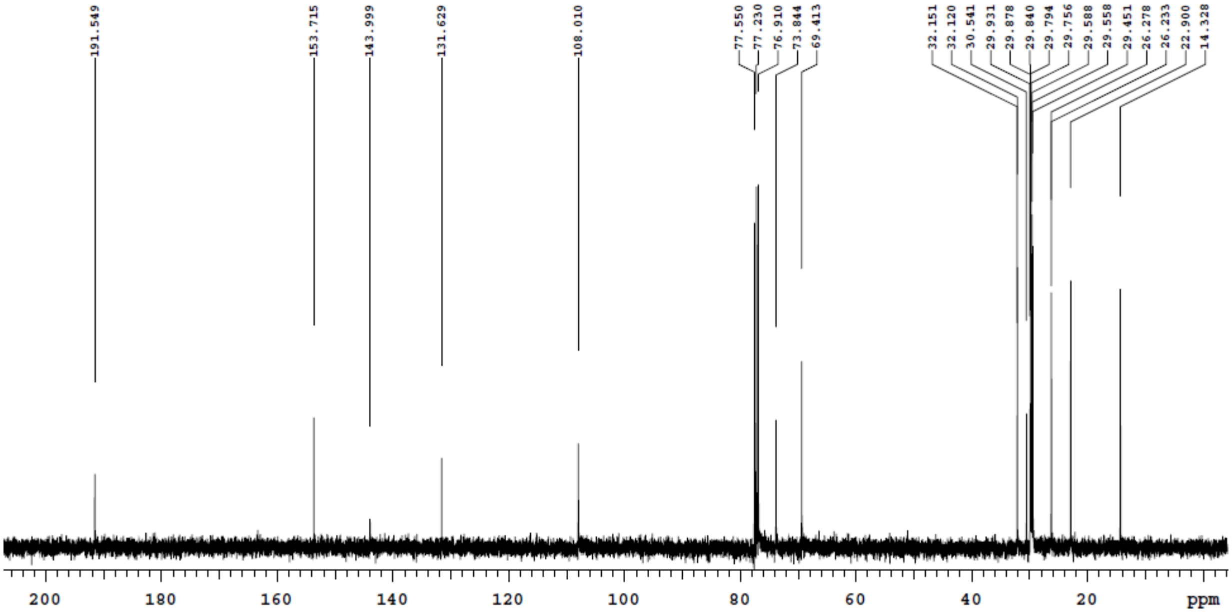

Figure S28. ^{13}C NMR (100 MHz) spectra of **4c** in CDCl$_3$

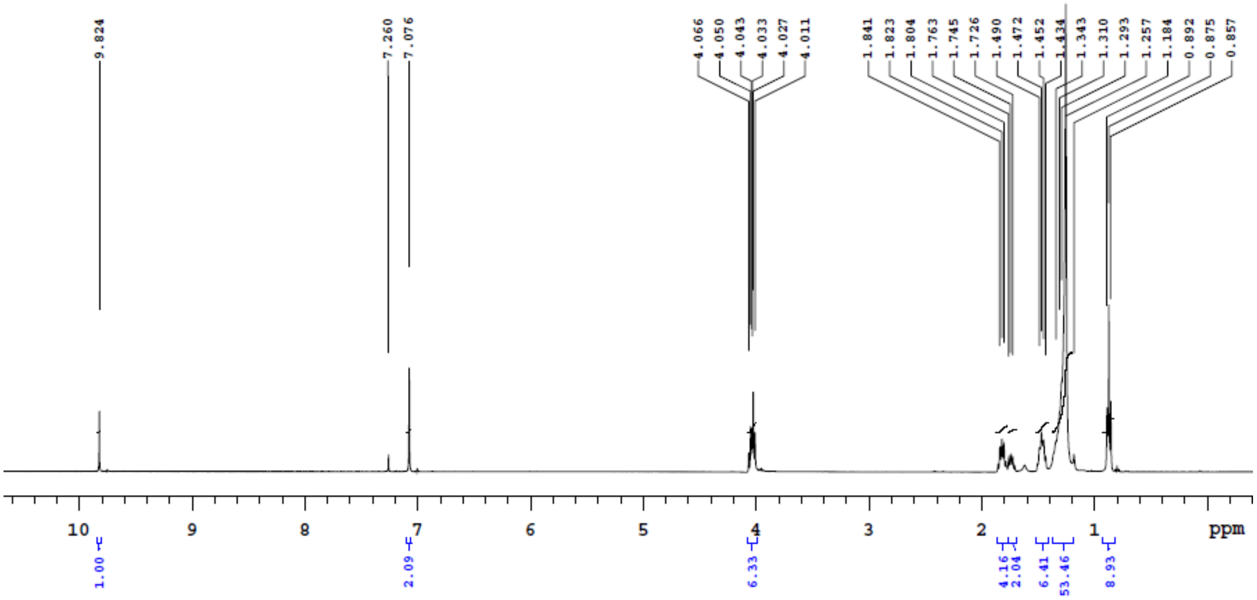

Figure S29. ^{1}H NMR (400 MHz) spectra of **4d** in CDCl$_3$

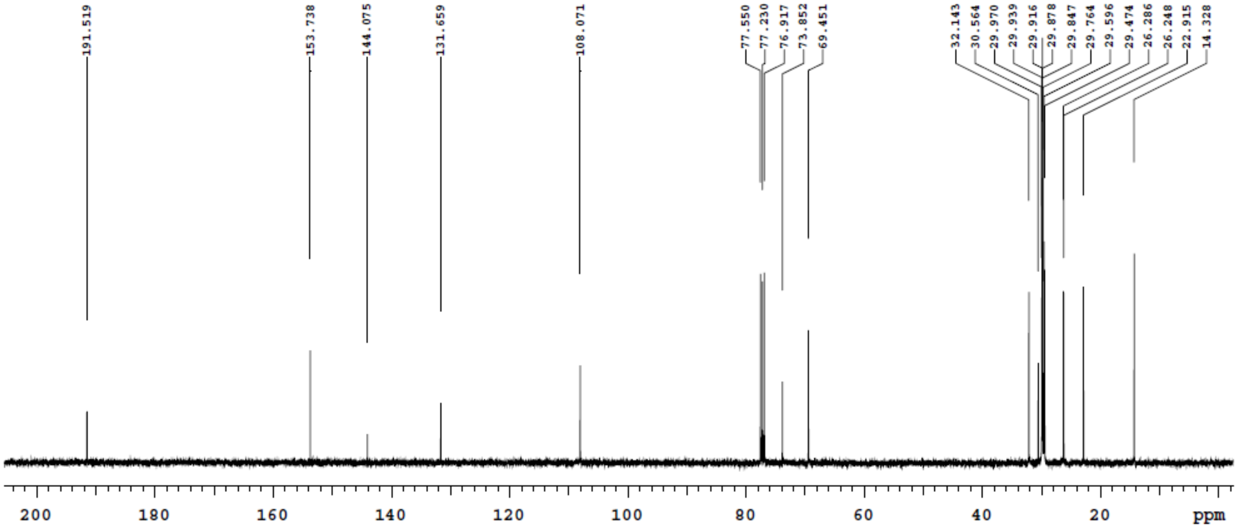

Figure S30. ^{13}C NMR (100 MHz) spectra of **4d** in CDCl$_3$

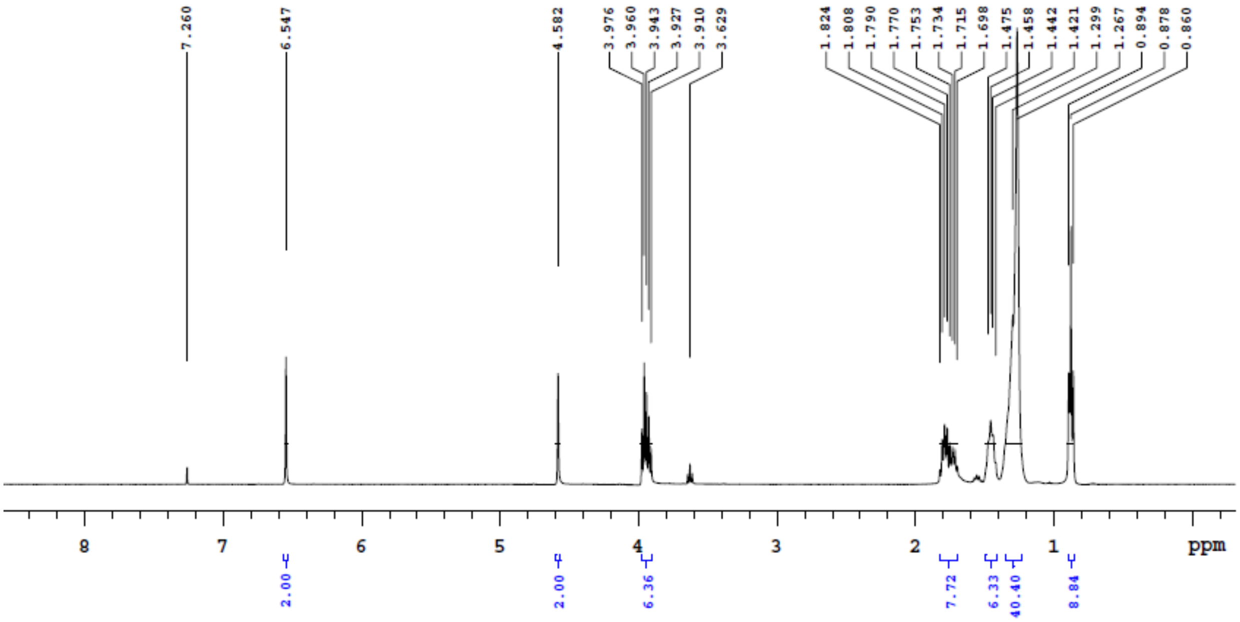

Figure S31. ^{1}H NMR (400 MHz) spectra of **5c** in $CDCl_3$

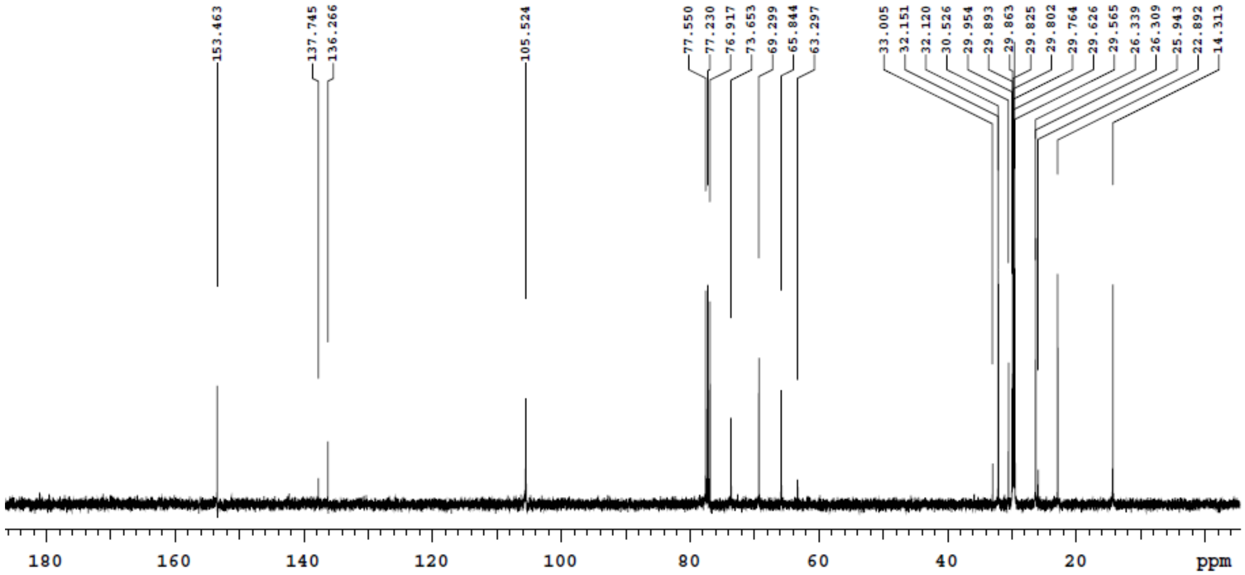

Figure S32. ^{13}C NMR (100 MHz) spectra of **5c** in $CDCl_3$

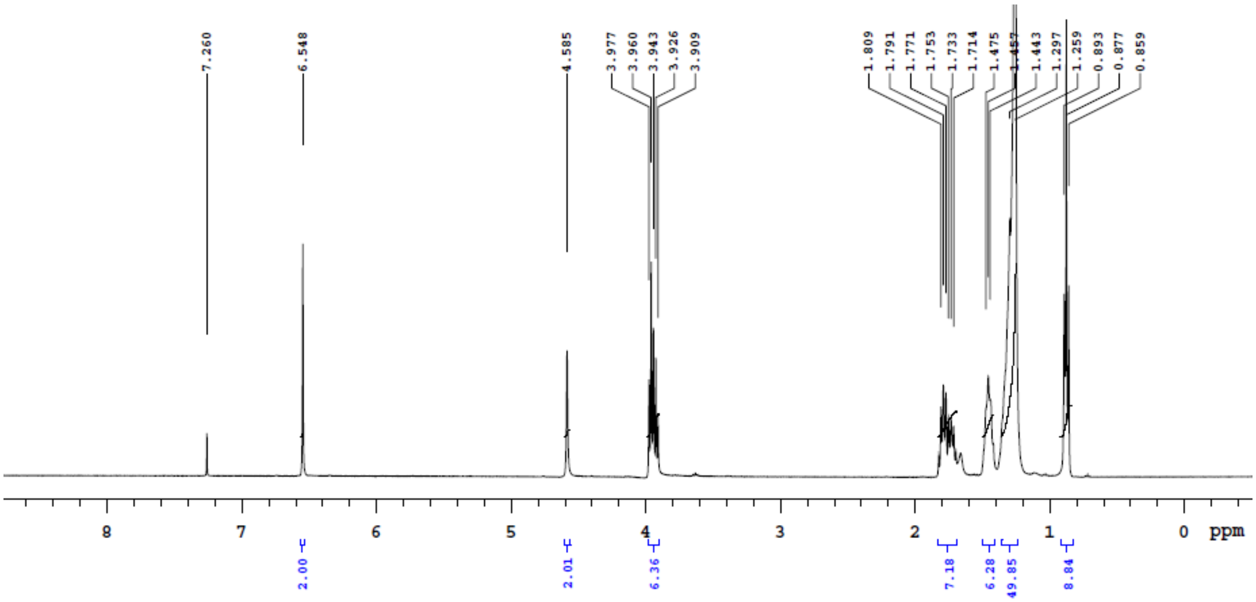

Figure S33. ^{1}H NMR (400 MHz) spectra of **5d** in $CDCl_3$

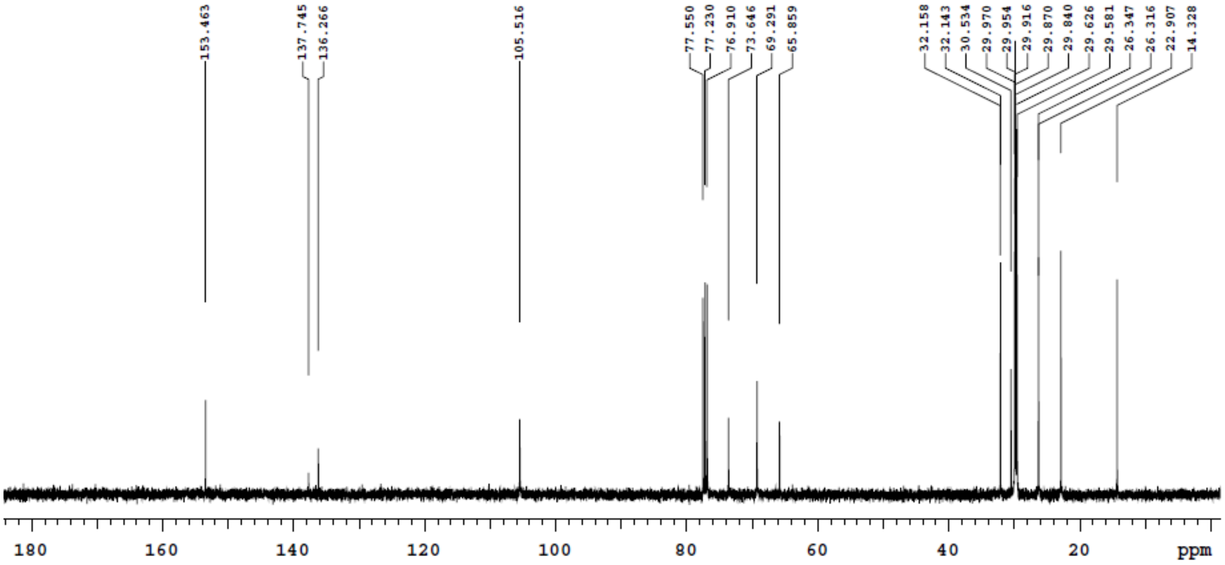

Figure S34. ^{13}C NMR (100 MHz) spectra of **5d** in $CDCl_3$

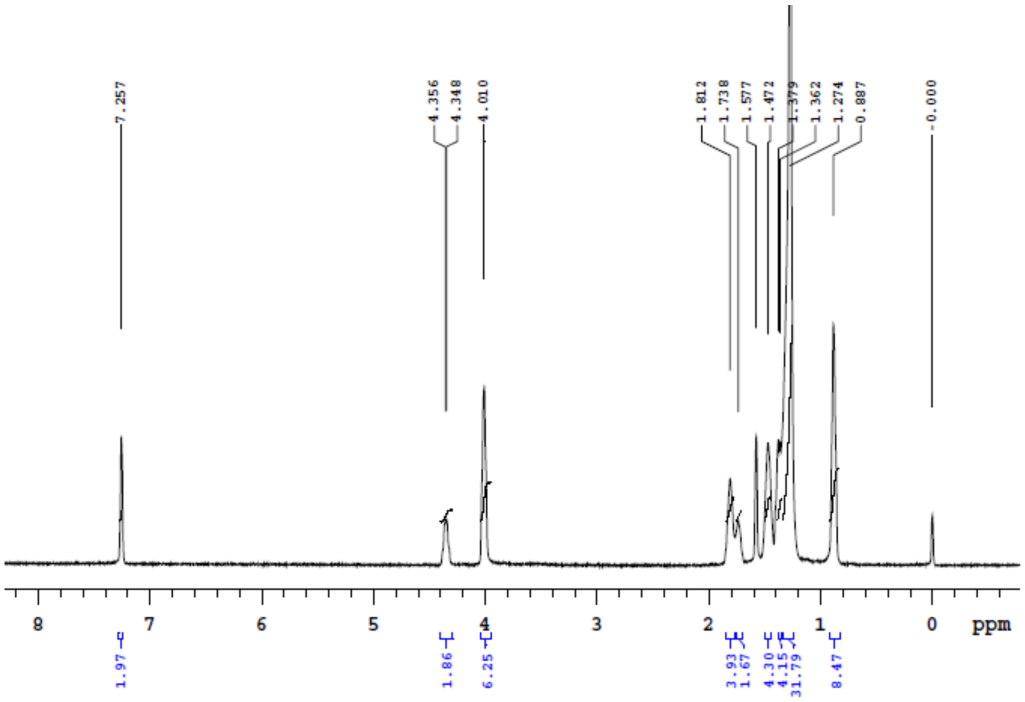

Figure S35. ^{1}H NMR (400 MHz) spectra of **6c** in CDCl$_3$

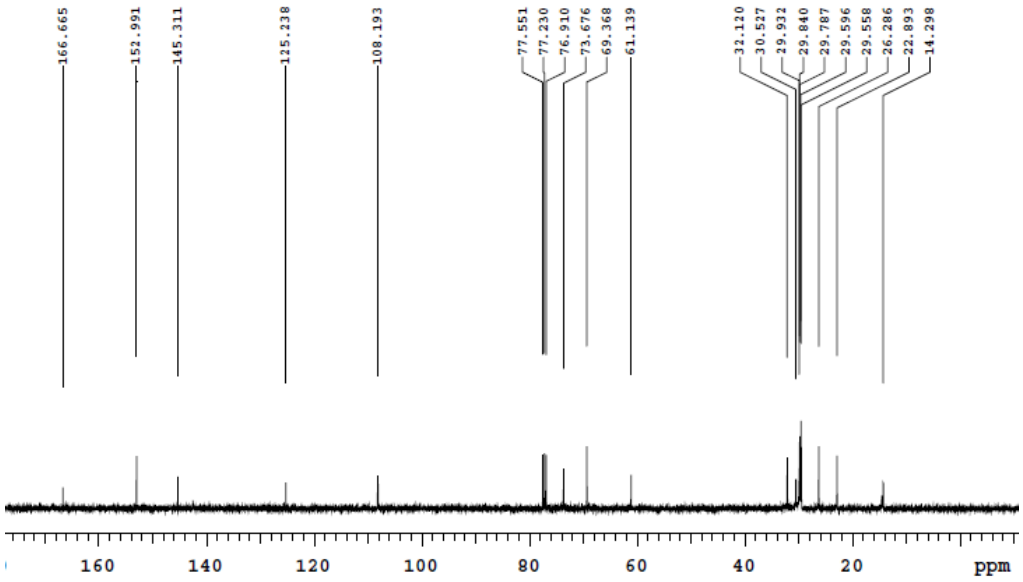

Figure S36. ^{13}C NMR (100 MHz) spectra of **6c** in CDCl$_3$

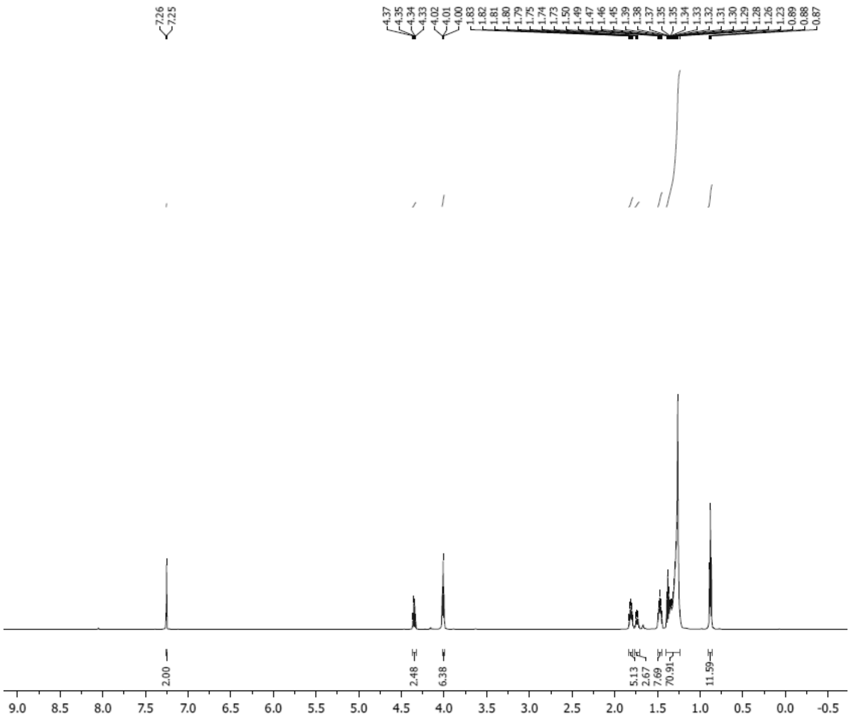

Figure S37. ^{1}H NMR (600 MHz) spectra of **6d** in $CDCl_3$

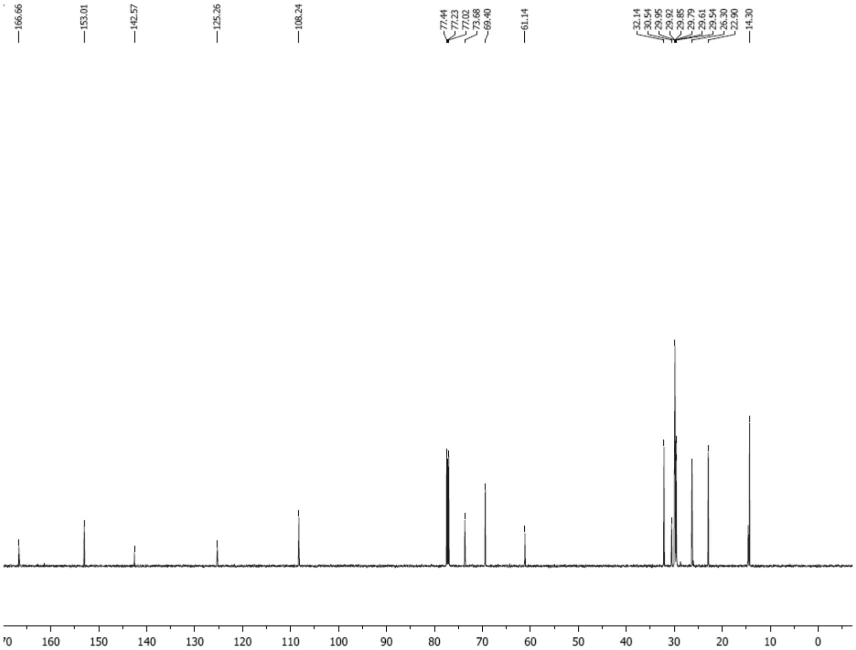

Figure S38. ^{13}C NMR (150 MHz) spectra of **6d** in $CDCl_3$

(iii) Polarizing Optical Microscopy

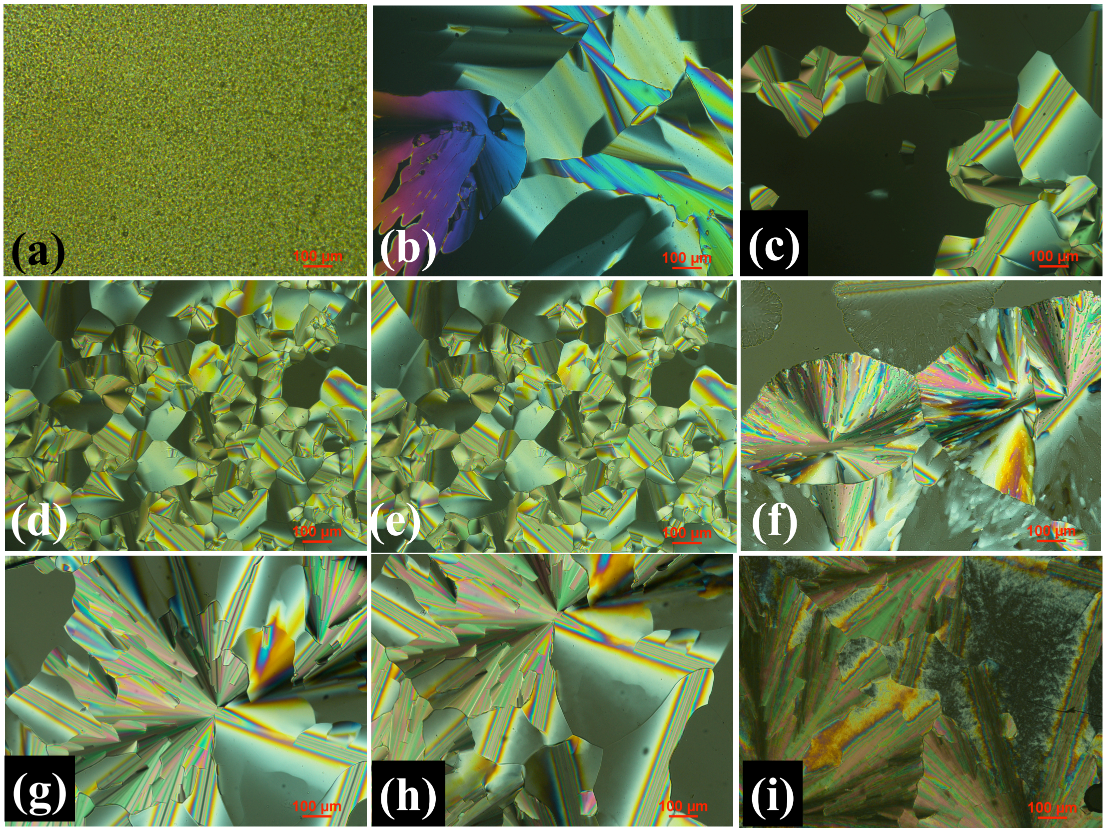

Figure S39.POM images of compound**1a**at 87 ^{o}C (a); **1b** at 111 ^{o}C (b); **1c** at 135 ^{o}C (c); at 111 ^{o}C (d); at 25 ^{o}C (e); **1d** at 148 ^{o}C (f); at 125 ^{o}C (g); at 40 ^{o}C (h) and at 30 ^{o}C (i) on a cooling process from isotropic melt.

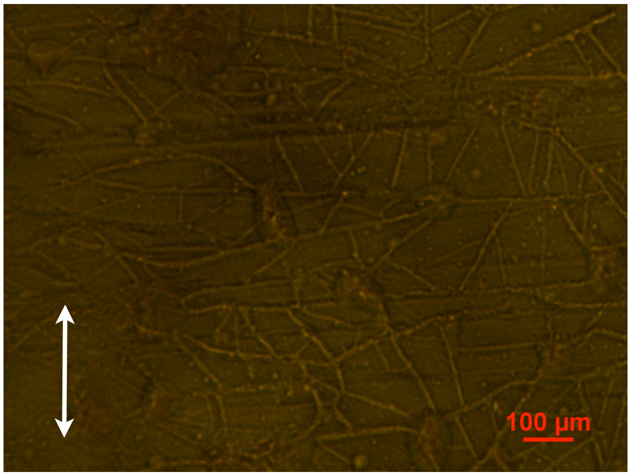

Figure S40.POM image of the thin film of compound**1b** in xerogel state under parallel polarizers (obtained from the dropcasting of 4mM dodecane solution)

(iv) Thermogravimetric Analysis

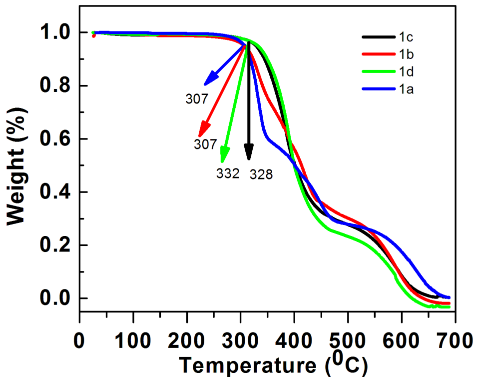

Figure S41. TGA curves of the compounds **1a-d (a)** and **2a-d (b)** carried out at a rate of 10 ^{o}C/min

(v) Differential Scanning Calorimetry

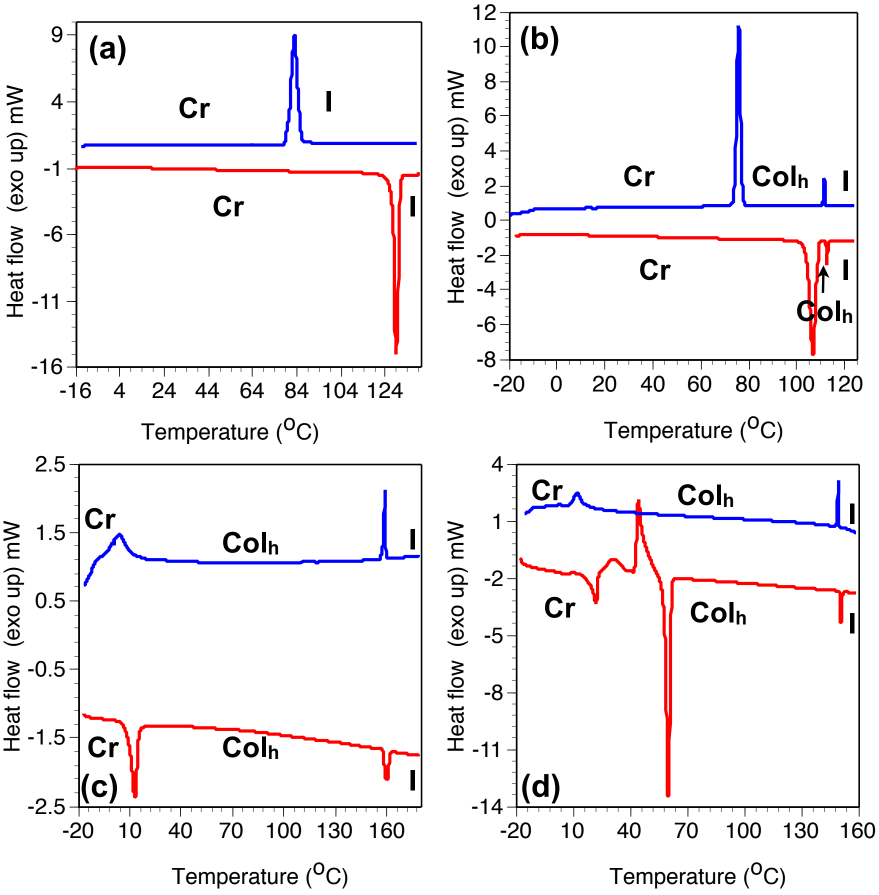

Figure S42. DSC thermograms of compounds **1a-d** showing the second heating (red trace) and the first cooling (blue trace) scans at a scanning rate of 5.0 ˚C min^{-1}.

(vi) X-ray Diffraction studies

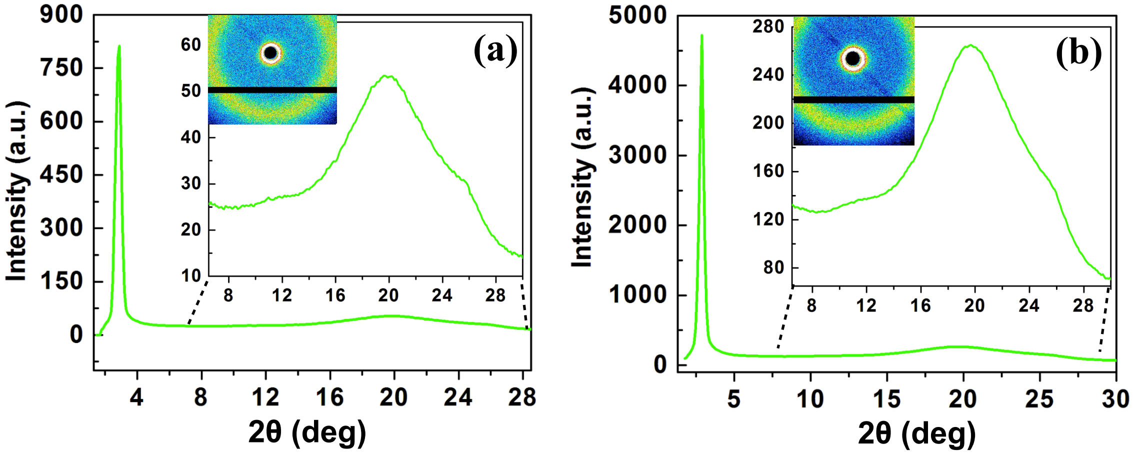

Figure S43. XRD profiles depicting the intensity against the 2θ obtained for the Col$_h$ phase of compound 1b at 85 ^{o}C (a) and at 100 ^{o}C (a) (inset shows the XRD image pattern obtained)

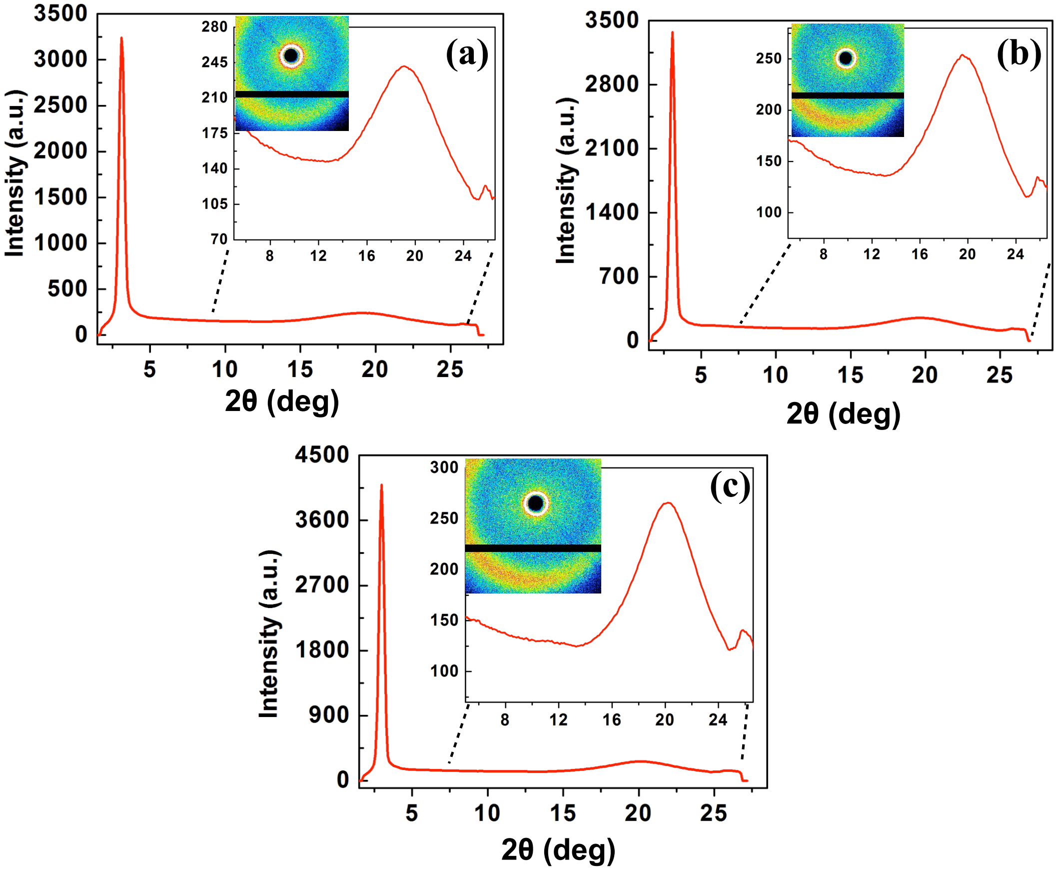

Figure S44. XRD profiles depicting the intensity against the 2θ obtained for the Col$_h$ phase of compound **1c** at 145 ^{o}C (a); at85^{o}C (b) and at 25^{o}C (c) (inset shows the XRD image pattern obtained)

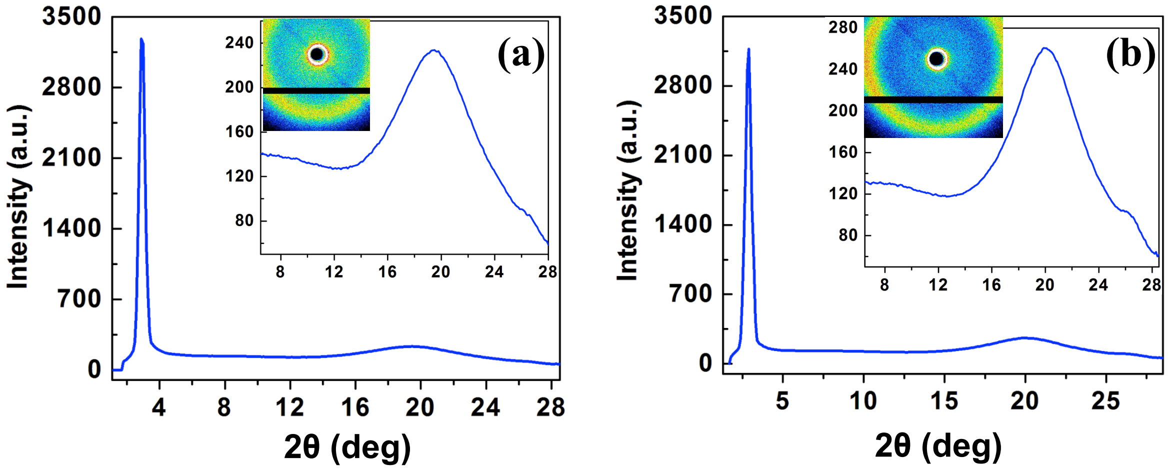

Figure S45. XRD profiles depicting the intensity against the 2θ obtained for the Col$_h$ phase of compound **1d** at 130°C (a) and at 50°C (b) (inset shows the XRD image pattern obtained)

Table 1. Results of (hkl) indexation of XRD profiles of the compound **1b** in xerogel state at room temperature

Compounds (*D*/Å)	Phase (T/°C)	d_{obs} (Å)	d_{cal} (Å)	Miller indices *hkl*	Lattice parameters (Å)
1b (42.21)	Col$_r$ (RT)	30.61	30.61	200	*a* = 61.22 *b* = 27.26
		24.91	24.91	110	
		10.67	11.33	320	
		9.11	9.08	330	
		7.11	6.65	240	
		6.18	6.22	440	
		5.96	5.95	540	
		5.42	5.66	640	
		5.05	4.98	500	
		3.79	3.91	400	

(vii) Photophysical properties

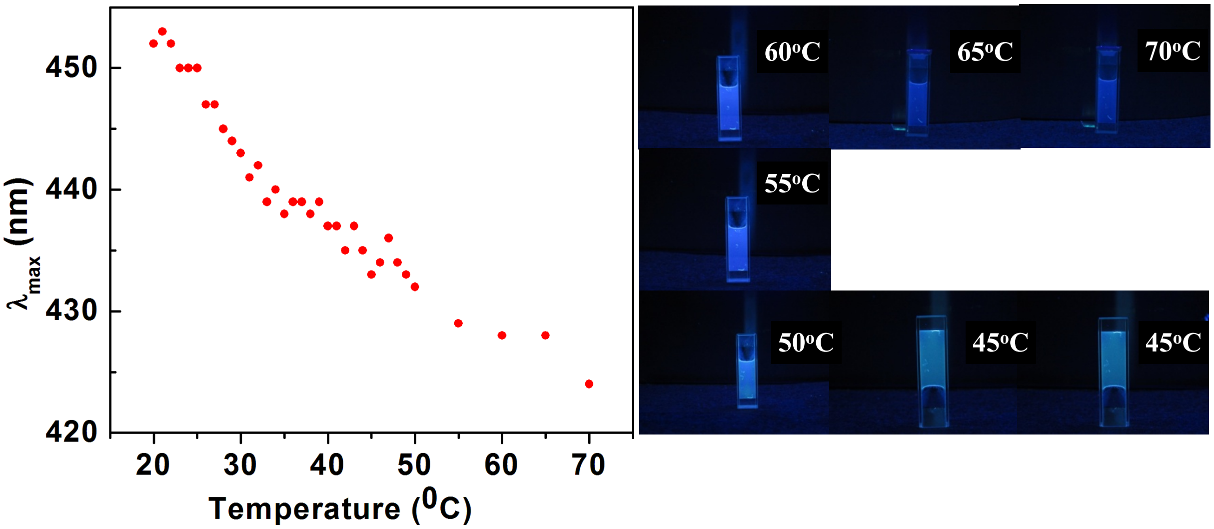

Figure S46. Variation in the emission wavelength with respect to temperature for compound **1b** (4mM solution in dodecane, on the right hand side note the change in the emission on irradiation of long wavelength UV light with the change of temperature)

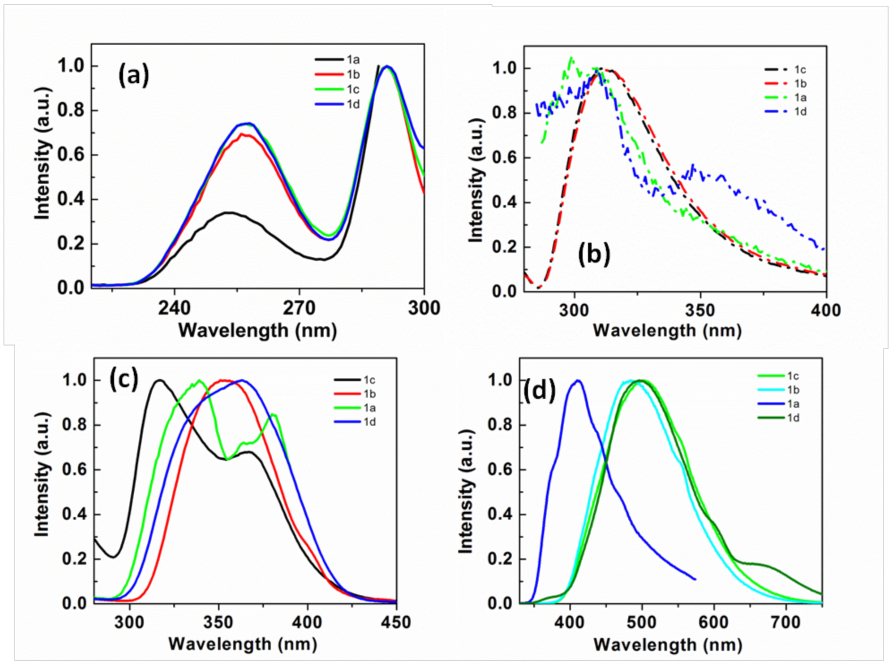

Figure S47. Excitation and emission spectra of compounds **1a-d** in micromolar THF solution (a), (b) and the same in thin film state (c), (d).

Table 2. Photophysical properties of star-shaped molecules in solution and thin film

	Solution^a		Thin film	
Entry	Excitation^b (nm)	Emission (nm)	Excitation^b (nm)	Emission^c (nm)
1a	255	299	339, 380	410
1b	255, 291	314	351	484
1c	256, 291	311	317, 367	502
1d	258, 291	309	363	496

^{a}Micromolar THF solution; ^{b}Emission monitored at λ_{max} ; ^{c}Excitation monitored at λ_{max}

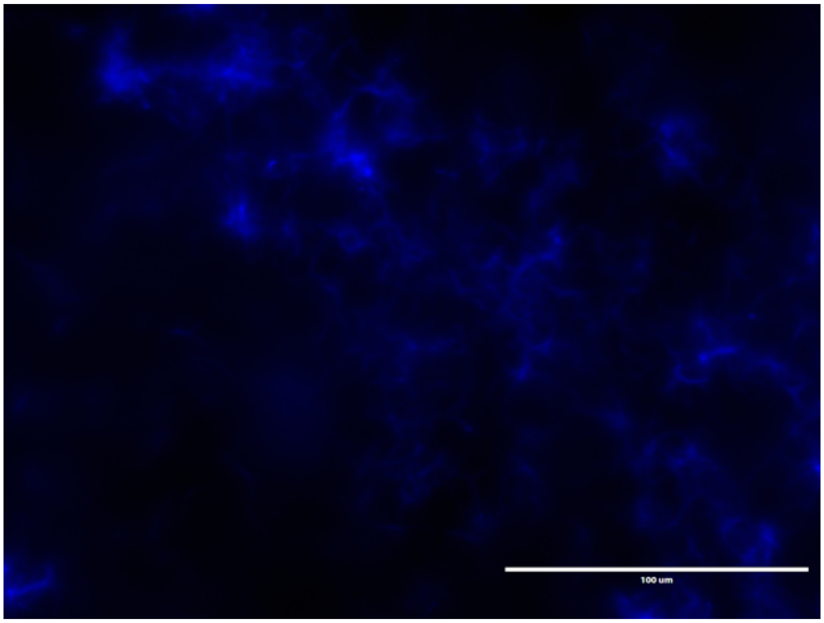

Figure S48. Fluorescent Microscopy Image of the thin film of the xerogel obtained for compound **1b** (4mM solution in dodecane, scale bar 100 µm)

(viii) Cyclic Voltammetry

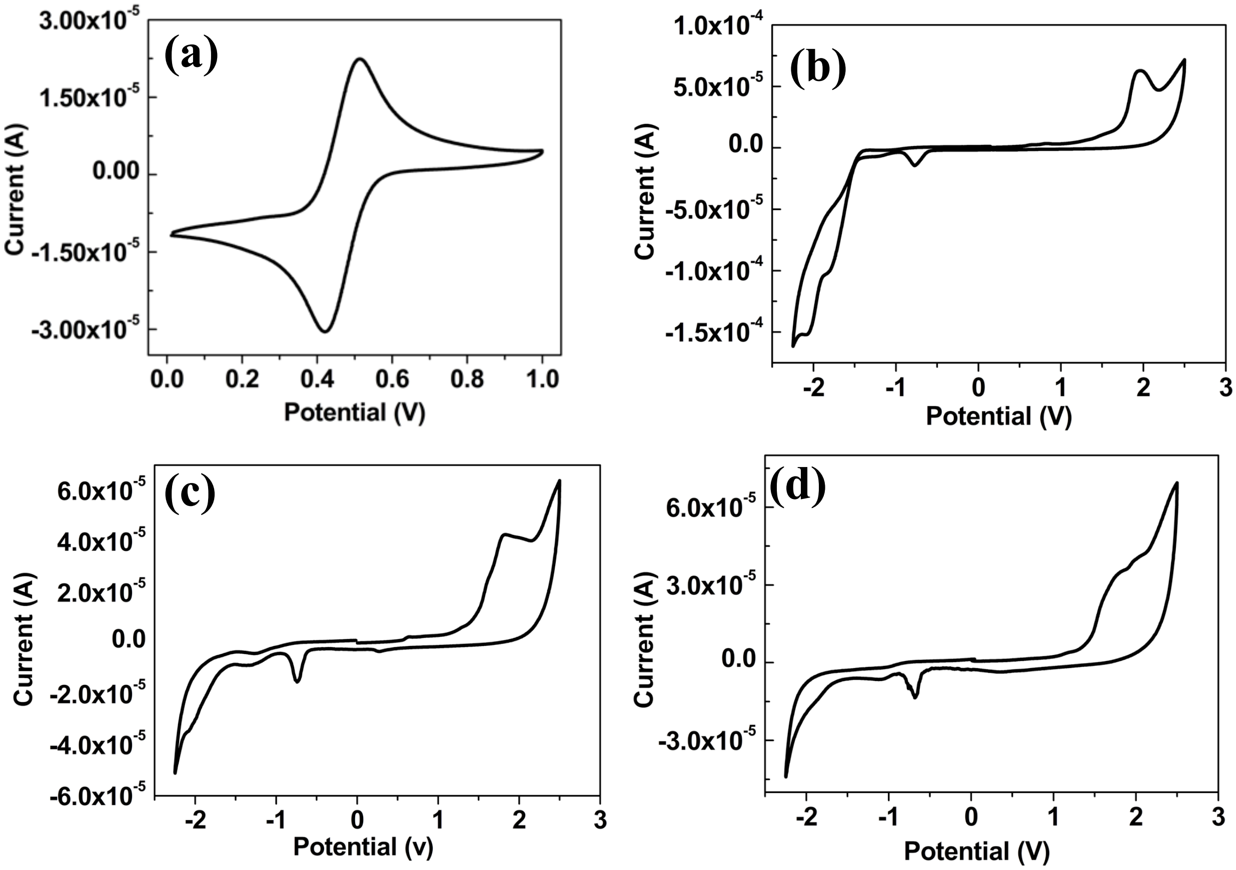

Figure S49. Cyclic voltammograms of ferrocene (a); compound **1a** (b); **1b** (c) and **1c** (d) in anhydrous DCM solution of tetra-*n*-butylammonium perchlorate (0.1 M)(The half-wave potential of the ferrocene/ ferrocenium (Fc/Fc$^+$) redox couple ($E_{1/2,\ \mathrm{Fc,Fc}^+}$) was found to be 0.46 V relative to the Ag/Ag$^+$ reference electrode).

(ix) Gelation studies

Table 3. Gelation properties of compound **1b**

Entry	Solvent	Properties	Critical Gel Concentration (wt.%)	T_{gel} (^{O}C)
1	Hexane	G (O)	0.67	66
2	Decane	G (O)	0.62	68
3	Dodecane	G (O)	0.52	70
4	Hexadecane	G (O)	0.47	75
5	Toluene	S	----	---
6	Benzene	S	----	---
7	*m*-xylene	S	----	---
8	DCM	S	----	---
9	Chloroform	S	----	---
10	THF	S	----	---
11	*n*-butanol	P	----	---
12	Ethanol	P	----	---
13	DMSO	I	----	---

G = stable gel; S = soluble; P = precipitate; I = insoluble; O = opaque; The critical gelation concentration (wt. %) is the minimum concentration necessary for gelation; T_{gel} (^{o}C) is the thermal stability of the gels determined by 'dropping ball' method (weight of the ball is 68.5 mg)

Compound **1b** with six decyloxy chains stabilized the gel formation in *n*-hexane, *n*-decane, *n*-dodecane and *n*-hexadecane with very low critical gelation concentration (CGC) of 0.67 wt %, 0.62 wt %, 0.52 wt % and 0.47 wt % respectively. The gel was prepared by dissolving 6.7 mg of gelator molecule **1b** in 1ml of *n*-hexane at higher temperatures and allowing the solution to cool to room temperature in a closed vial. Gel formation was confirmed by the failure of soft mass to flow on inverting the glass vial. Similarly the gel were prepared by dissolving 6.2 mg, 5.2 mg and 4.7 mg in 1ml of *n*-decane, *n*-dodecane and *n*-hexadecane respectively at higher temperatures and allowing the solution to cool to room temperature in a closed vial. The thermal stability of the gels was measured by dropping ball method (Fig.10g).

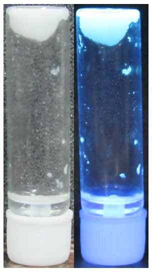

Figure S50. Photograph of the gel after keeping inverted for 25 days showing the formation of xerogel under daylight and UV light (λ_{max} = 365 nm)

(x) Single Crystal XRD studies

Table 4. Crystal data and structure refinement for 1a, $[C_{60} H_{78} N_6 O_6]$.[6]

Empirical formula	$C_{60} H_{78} N_6 O_6$
Formula weight	979.28
Crystal habit, colour	needle, colorless
Crystal size, mm^3	0.36 × 0.20 × 0.18
Temperature, T	296(2) K
Wavelength, λ	0.71073 Å
Crystal system	triclinic
Space group	$P -1$
Unit cell dimensions	a = 9.5084(6) Å
	b = 10.1887(6) Å
	c = 29.8085(17) Å
	α = 87.885(4)°
	β = 83.205(4)°
	γ = 80.832(4)°
Volume, V	2830.4(3) $Å^3$
Z	2
Calculated density, $Mg \cdot m^{-3}$	1.149 Mg/m^3
Absorption coefficient, μ	0.074 mm^{-1}
$F(000)$	1056
θ range for data collection	0.69° to 25.00°
Limiting indices	$-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $-35 \leq l \leq 35$
Reflection collected / unique	41914/ 9375 [R(int) = 0.0694]
Completeness to θ	0.941 %
Max. and min. transmission	0.987 and 0.982
Refinement method	Full−matrix least−squares on F^2
Data / restraints / parameters	9375 / 0 / 652
Goodness−of−fit on F^2	1.029
Final R indices [I>2sigma(I)]	$R1$ = 0.0674, $wR2$ = 0.1695
R indices (all data)	$R1$ = 0.1543, $wR2$ = 0.2203
Largest diff. peak and hole	0.232 and −0.249 e.$Å^{-3}$

Bond distances							
Bond distance	(Å)	Bond distance	(Å)	Bond distance	(Å)	Bond distance	(Å)
C1−C2	1.388(4)	C2−C3	1.389(4)	C3 −C4	1.408(4)	C4−C5	1.382(4)
C5 −C6	1.395(4)	C6 −C1	1.395(4)	C3 −C7	1.471(4)	C7 −N1	1.294(4)
C7 −O2	1.345(3)	N1− C8	1.382(4)	O2− N2	1.424(3)	N2− C8	1.305(4)
C8−C9	1.465(4)	C9−C10	1.387(4)	C10−C11	1.373(4)	C11−C12	1.390(4)
C12−C13	1.379(4)	C13−C14	1.381(4)	C14−C9	1.385(4)	C12−O4	1.362(4)
O4−C15	1.440(4)	C5−C25	1.459(4)	C25−O1	1.344(3)	C25−N3	1.296(4)
O1−N4	1.427(3)	N3−C25	1.296(4)	C26−N3	1.390(3)	C26−N4	1.311(4)
C26−C27	1.458(4)	C27−C28	1.379(4)	C28−C29	1.376(4)	C29−C30	1.387(4)
C30−C31	1.394(4)	C31−C32	1.372(4)	C27−C32	1.388(4)	C30−O6	1.366(3)
O6−C33	1.436(3)	C1−C43	1.460(4)	C43−O3	1.338(4)	C43−N6	1.294(4)
N5−C44	1.300(4)	N6−C44	1.378(4)	C44−C45	1.472(4)	C45−C46	1.379(4)
C46−C47	1.369(5)	C47−C48	1.381(5)	C48−C49	1.368(4)	C49−C50	1.390(4)
C50−C45	1.369(4)	C48−O5	1.371(4)	O5−C51	1.422(4)		

Bond angles							
Bond angle	(◦)	Bond angle	(◦)	Bond angle	(◦)	Bond angle	(◦)
C2− C1− C6	119.0(3)	C2− C1− C43	119.1(3)	C1− C2− C3	121.1(3)	C2 −C3− C4	119.7(3)
C2−C3 −C7	117.0(3)	C4 −C3− C7	123.2(3)	C5 −C4 −C3	119.2(3)	C4− C5 −C6	120.7(3)
C4−C5−C25	122.3(3)	C6 −C5 −C25	117.0(3)	C1 −C6− C5	120.3(3)	N1 C7O2	113.7(3)
N1− C7− C3	126.3(3)	O2 −C7− C3	119.9(3)	C7 −N1− C8	102.6(3)	N2 −C8−N1	114.6(3)
N2 −C8− C9	124.2(3)	N1− C8 −C9	121.2(3)	C7− O2− N2	105.8(2)	C14−C9−C10	117.8(3)
C14 −C9− C8	122.6(3)	C10− C9− C8	119.6(3)	C11−C10−C9	121.3(3)	C10−C11−C12	120.1(3)
O4 −C12−C13	125.3(3)	O4− C12−C11	115.2(3)	C13−C12−C11	119.5(3)	C12−C13−C14	119.6(3)
C13− C14− C9	121.7(3)	C12− O4−C15	119.1(3)	N3 −C25−O1	113.5(3)	N3− C25− C5	126.7(3)
O1 −C25− C5	119.8(3)	C25− O1− N4	105.9(2)	C26− N4− O1	103.8(2)	N4− C26− N3	113.5(3)
N4− C26−C27	124.3(3)	N3 −C26−C27	122.2(3)	C25− N3−C26	103.3(3)	C28−C27−C32	118.1(3)
C28−C27−C26	121.6(3)	C32−C27−C26	120.3(3)	C29−C28−C27	121.6(3)	C28−C29−C30	119.6(3)
O6 −C30−C29	125.1(3)	O6 −C30−C31	115.3(3)	C29−C30−C31	119.6(3)	C32−C31−C30	119.5(3)
C31−C32−C27	121.5(3)	C30− O6−C33	117.8(2)	N6− C43− O3	113.5(3)	N6− C43−C1	128.8(3)
O3 −C43− C1	117.7(3)	C43− O3− N5	105.8(2)	C44− N5− O3	103.7(3)	N5− C44− N6	114.0(3)
N5 −C44−C45	121.9(3)	N6− C44−C45	124.0(3)	C43− N6−C44	103.0(3)	C50−C45−C46	118.3(3)
C50−C45−C44	120.7(3)	C46−C45−C44	120.8(3)	C47−C46−C45	121.3(4)	C46−C47−C48	120.2(3)
C49− C48−O5	125.8(4)	C49−C48−C47	119.1(3)	O5− C48−C47	115.0(3)	C48−C49−C50	120.2(3)
C45−C50−C49	120.9(3)	C48− O5−C51	118.8(3)				

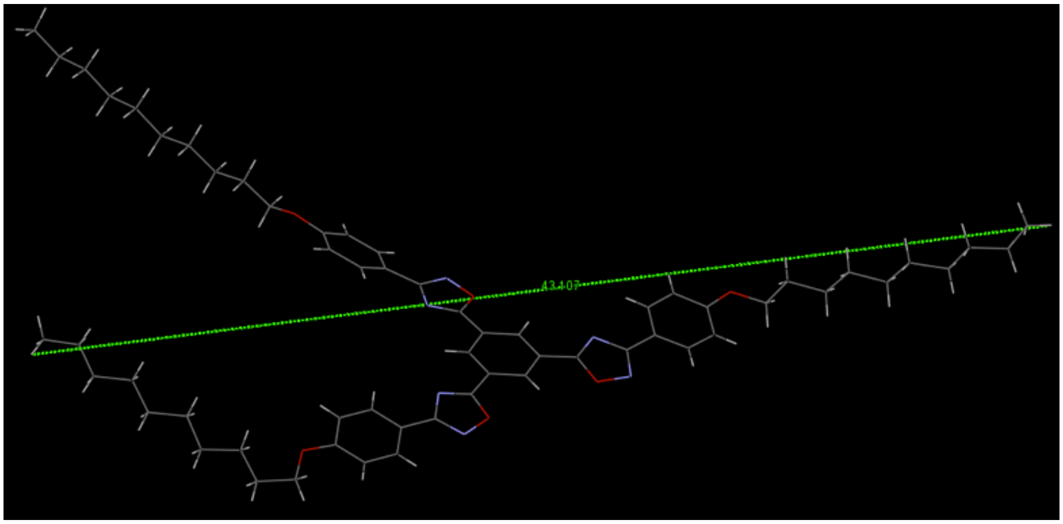

Figure S51.Molecular diameter of compound **1a**.

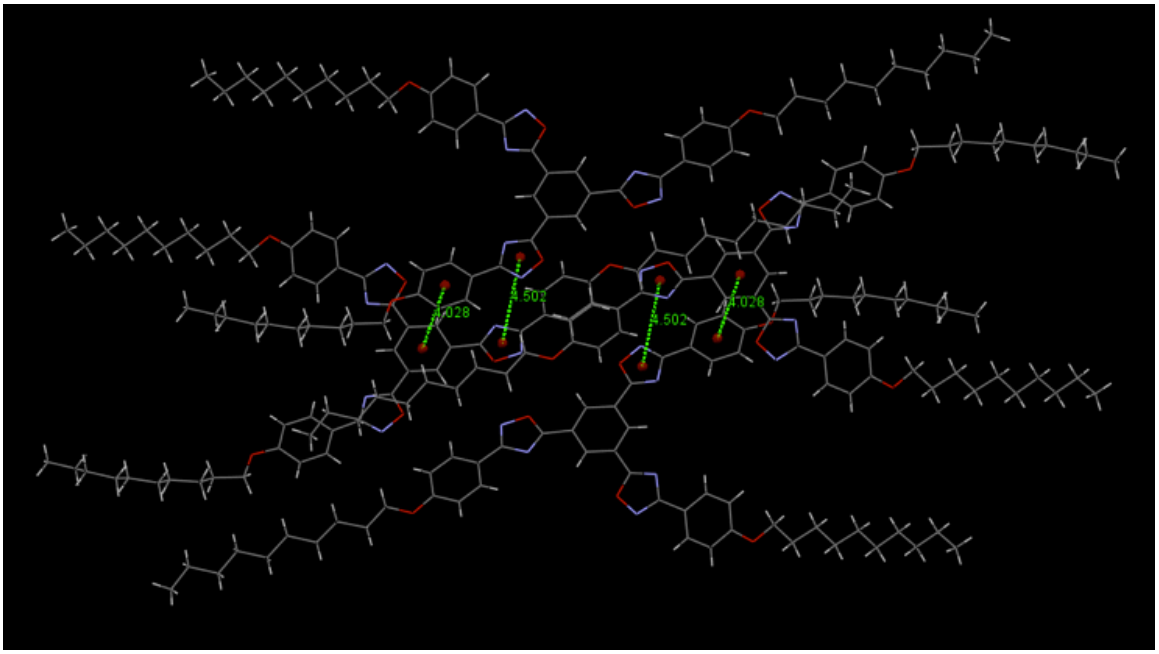

Figure S52.π–Interactions between the centroid of the oxadiazole ring of one molecule and the centroid of the oxadiazole ring of the neighboring molecule and centroid of the central benzene ring of one molecule and centroid of the peripheral benzene ring of other molecule.

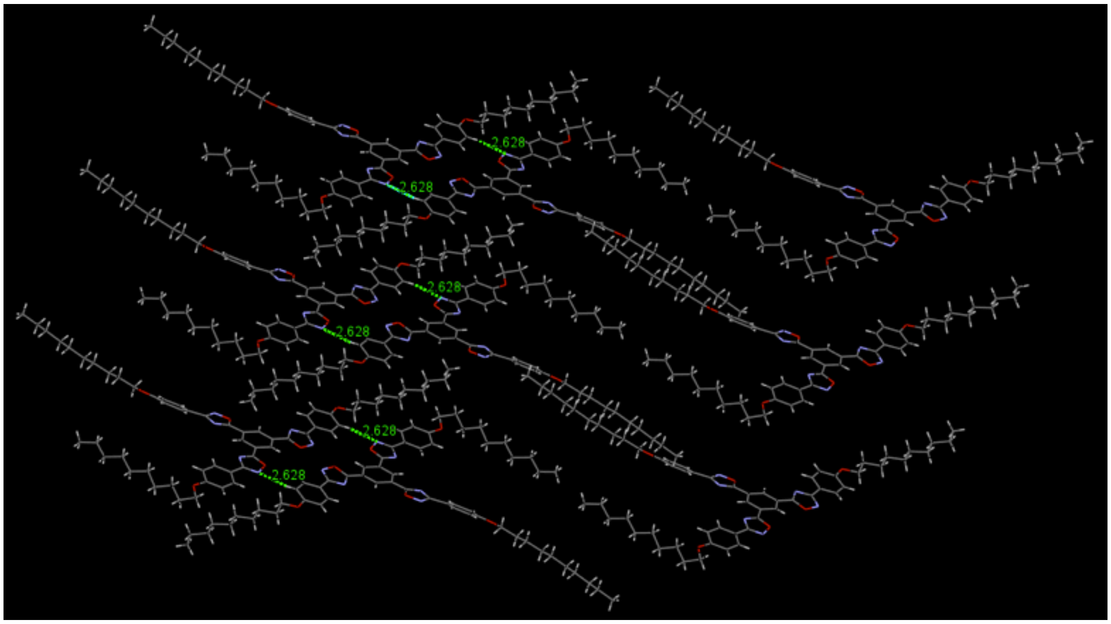

Figure S53.Non-covalent C-H·····N hydrogen bonding interaction between the hydrogen atom (H29) of the peripheral benzene ring and the (N2) of the oxadiazole ring

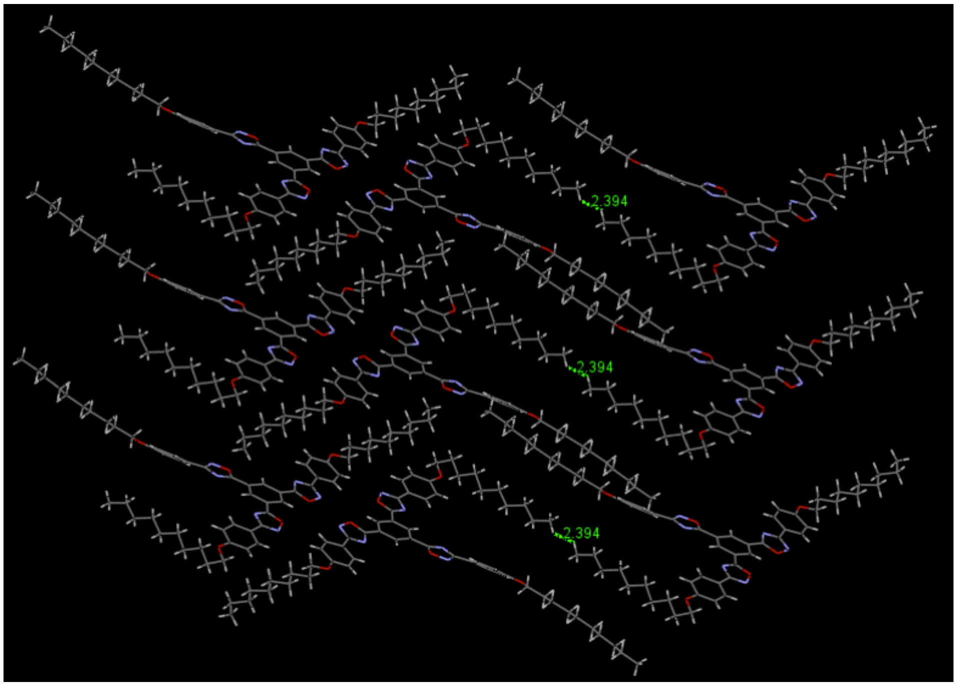

Figure S54. Vanderwaals' interaction between the peripheral alkyl chains of two molecules.

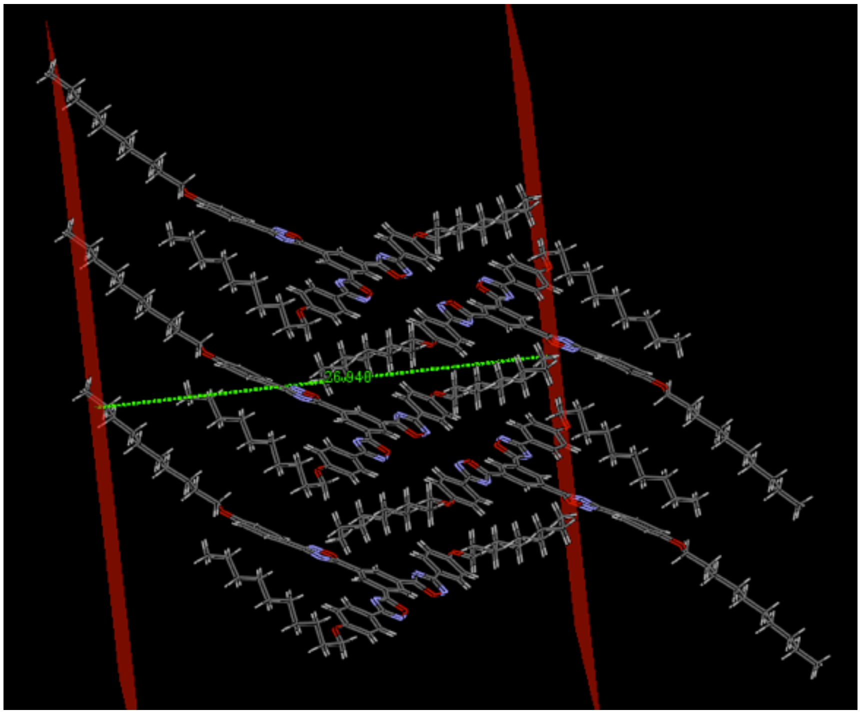

Figure S55. Lamellar arrangement of molecules of compound **1b**

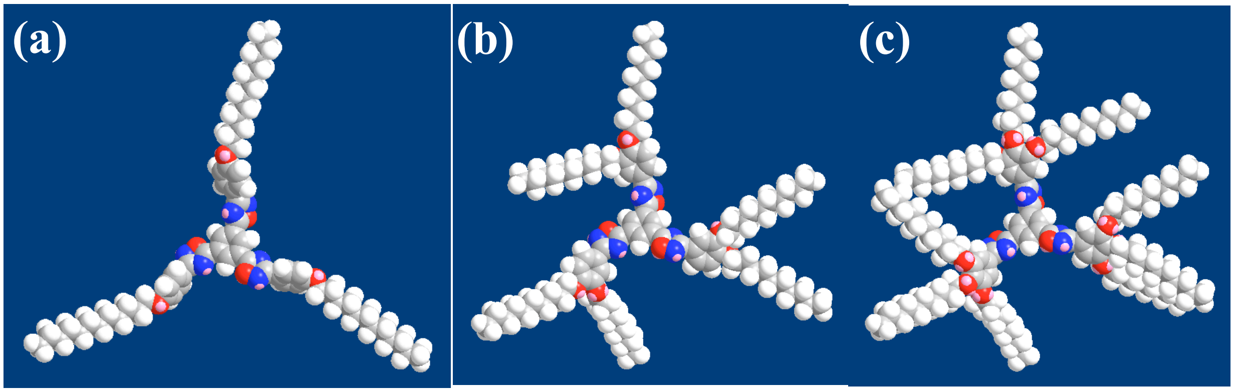

Figure S56. Energy minimized structures of compounds **1a** (a); **1b** (b) and **1c** (c)

References

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6. CCDC 1058790 contains the supplementary crystallographic data for compound **1a.** These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html