Electronic Supplementary Material (ESI) for Soft Matter.

Self-assembly of luminescent *N*-annulated Perylene Tetraesters into Fluid Columnar phases

Ravindra Kumar Gupta[a], Suraj Kumar Pathak[a], Balaram Pradhan[a], D. S. Shankar Rao[b],
S. Krishna Prasad[b] and Ammathnadu S. Achalkumar*, [a]

[a] *Indian Institute of Technology Guwahati, Guwahati, 781039, Assam, India*
[b] *Centre for Nano and Soft Matter Sciences, Jalahalli, P. B. No. 1329, Bangalore, 560013, India.*

Supporting information

Table of Contents

Materials and methods

Commercially available chemicals were used without any purification; solvents were dried following the standard procedures. Chromatography was performed using either silica gel (60-120 and 100-200) or neutral aluminiun oxide. For thin layer chromatography, aluminium sheets pre-coated with silica gel were employed. IR spectra were recorded on a Perkin Elmer IR spectrometer at normal temperature by using KBr pellet. The spectral positions are given in wave number (cm^{-1}) unit. NMR spectra were recorded using Varian Mercury 400 MHz (at 298K) or Bruker 600 MHz NMR spectrometer. For ^1H NMR spectra, the chemical shifts are reported in ppm relative to TMS as an internal standard. Coupling constants are given in Hz. Mass spectra were determined from MALDI-TOF mass spectrometer using α-cyanocinnamic acid as a matrix or High Resolution Mass Spectrometer. The mesogenic compounds were investigated for their liquid crystalline behavior (birefringence and fluidity) by employing a polarizing optical microscope (Nikon Eclipse LV100POL) equipped with a programmable hot stage (Mettler Toledo FP90). Clean glass slides and coverslips were employed for the polarizing optical microscopic observations. The transition temperatures and associated enthalpy changes were determined by differential scanning calorimeter (Mettler Toledo DSC1) under nitrogen atmosphere. Peak temperatures obtained in DSC corresponding to transitions were in agreement with the polarizing optical microscopic observations. The transition temperatures obtained from calorimetric measurements of the first heating and cooling cycles at a rate of 5 °C/min are tabulated. In the cases where the DSC signatures are not observed for the phase transitions, the transition temperatures have been taken from microscopic observations. X-ray diffraction measurements were carried out using image plate (IP) and a solid state detector. In this apparatus Cu K_α (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 illuminate the sample, which was contained in a glass capillary tube (Capillary Tube Supplies Ltd). The temperature of the sample was varied using a Mettler hot stage/ programmer (FP82HT/FP90. The diffraction patterns were collected on a 2D IP detector of 345 mm diameter and 0.1 mm pixel size (Mar345, Mar Research). Thermogravimetric analysis (TGA) was performed using thermogravimetric analyzer (Mettler Toledo, model TG/SDTA 851 e) under a nitrogen flow at a heating rate of 10 °C/min. UV-Vis spectra were obtained by using Perkin-Elmer Lambda 750, UV/VIS/NIR spectrometer. Fluorescence emission spectra in solution state were recorded with Horiba Fluoromax-4 fluorescence spectrophotometer or Perkin Elmer LS 50B spectrometer. Cyclic Voltammetry studies were carried out using a Versa Stat 3 (Princeton Applied Research) Electrochemical workstation.

(i) Experimental Section

General procedure for synthesis of tetrakis(alkyl)perylene-3,4,9,10-tetracarboxylate **(3a-c)**[1]

Perylene tetracarboxylic dianhydride (2.5 mmol, 1 equiv.) was dissolved in 30 mL aqueous KOH (13.76 mmol, 5.4 equiv.) solution and stirred at 70 °C for 0.5 h. The solution was filtered and pH value of filterate was adjusted to 8-9 using 10% HCl. Then Aliquat 336 (0.9 mmol, 0.4 equiv.) and KI (1.4 mmol, 0.6 equiv.) were charged into the solution and then stirred vigorously for 10 min. *n*-Bromoalkane (15.3 mmol, 6 equiv.) was added to this reaction mixture. After the addition the reaction mixture was refluxed for 12 h until a red oil floats on the top and the rest of the solution becomes clear. Subsequently, chloroform (10 mL) was poured into the mixture and filtered through the celite bed to remove unreacted part and the celite bed was washed with chloroform. This chloroform layer was separated and washed twice with 15% sodium chloride solution, dried over sodium sulfate and concentrated *in vacuo* to get a viscous concentrate. Methanol was added to precipitate the compound from this concentrate. The solid was precipitated filtered and dried in vacuum. Yield varies from 69-75%.

3a[1a]**:** *Rf* = 0.56 (10% EtoAc-Hexanes); Yellow solid, yield: 70%; IR (KBr pellet) ν_{max} in cm^{-1} 2953, 2926, 2851, 1732, 1712, 1274, 1164; ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 8.21 (d, *J* = 8 Hz, 4H, H_{Ar}), 7.99 (d, *J* = 7.6 Hz, 4H, H_{Ar}), 4.33-4.3 (m, 8H, 4 ×-OCH$_2$), 1.80-1.77 (m, 8H, 4 ×-OCH$_2$-CH_2), 1.44-1.28 (m, 40H, 20 × CH$_2$), 0.87-0.86 (m, 12H, 4 × CH$_3$); ^{13}C NMR (150 MHz, CDCl$_3$, 301K): 168.7, 133.3, 130.7, 130.65, 129.3, 129.1, 121.6, 65.9, 32, 29.5, 29.4, 28.8, 26.3, 22.9, 14.3.

3b[1b]**:** *Rf* = 0.58 (10% EtoAc-Hexane); Yellow-orange solid, yield: 69%; IR (KBr pellet) ν_{max} in cm^{-1} 2956, 2920, 2850, 1731, 1719, 1468, 1281, 1172; ^{1}H NMR (400

MHz, $CDCl_3$, 298 K): δ 8.24 (d, *J* = 7.6 Hz, 4H, H_{Ar}), 8.01 (d, *J* = 8 Hz, 4H, H_{Ar}), 4.32 (t, *J* = 6.8 Hz, 8H, 4 × $-OCH_2$), 1.83-1.75 (m, 8H, 4 ×$-OCH_2-CH_2$), 1.44-1.27 (m, 56H, 28 × CH_2), 0.87 (t, *J* = 6.8 Hz, 12H, 4 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 301K): 168.7, 133.3, 130.8, 130.6, 129.3, 129.1, 121.6, 65.9, 32.1, 29.8, 29.6, 29.5, 28.8, 26.3, 22.9, 14.3.

3c[1a,c]**:** *Rf* = 0.6 (10% EtoAc-Hexane); Yellow solid, yield: 75%; IR (KBr pellet) *v*max in cm^{-1} 2954, 2919, 2850, 1731, 1720, 1593, 1292, 1173, 1025; ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.21 (d, *J* = 8.4 Hz, 4H, H_{Ar}), 7.99 (d, *J* = 7.6 Hz, 4H, H_{Ar}), 4.33-4.3 (m, 8H, $-OCH_2$), 1.82-1.75 (m, 8H, $-OCH_2-CH_2$), 1.46-1.25 (m, 72H, CH_2), 0.88-0.85 (m, 12H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 298K): 168.74, 132.89, 132.92, 130.46, 128.96, 128.75, 121.43, 65.83, 32.13, 29.89, 29.87, 29.85, 29.80, 29.6, 29.58, 28.86, 26.26, 22.89, 14.31.

General procedure for synthesis of tetrakis(alkyl)-1-nitroperylene-3,4,9,10-tetracarboxylate (**4a-4c**)[2]

To a solution of perylene tetraester (0.7 mmol, 1 equiv.) in dichloromethane (5 mL), added $NaNO_2$ (0.7 mmol, 1 equiv.) at 0 °C and stirred. To this well stirred suspension, 69% HNO_3 (3.42 mmol, 5 equiv., 10% solution in dichloromethane) was added dropwise. This mixture was stirred at 0 °C for 1 h. The reaction mixture was poured into water and extracted with dichloromethane (25 mL). The extract was washed with water and brine. Finally organic layer was dried over anhyd Na_2SO_4 and concentrated. The crude product was purified by column chromatography on neutral alumina. Elution with 50% dichloromethane-hexane yielded the desired product. Yields of these nitro compounds were in the range of 80-90%.

4a: *Rf* = 0.56 (10% EtoAc-Hexane); red viscous liquid, yield: 90%; IR (KBr pellet) *v*max in cm^{-1} 2956, 2926, 2855, 1721, 1534, 1280, 1169; ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.43-8.39 (m, 2H, H_{Ar}), 8.26 (s, 1H, H_{Ar}), 8.21 (d, *J* = 7.6 Hz, 1H, H_{Ar}), 8.14 (d, *J* = 8 Hz, 1H, H_{Ar}), 8.01-7.95 (m, 2H, H_{Ar}), 4.35-4.3 (m, 8H, 4 × $-OCH_2$), 1.8-1.75 (m, 8H, 4 × $-OCH_2-CH_2$), 1.44-1.28 (m, 40H, 20 ×CH_2), 0.88-0.86 (m, 12H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 298K): 168, 167.8, 167.7, 166.6, 145.9, 133.2, 132.1, 131.9, 131.2, 131, 130.6, 130.1, 129.7, 129.4, 128.8, 128.2, 128.1, 127.3, 126.3, 125.4, 123, 122.4, 66.3, 66, 65.8, 31.83, 31.8, 29.32, 29.3, 29.2, 28.6, 28.5,

26.04, 26, 25.9, 22.6, 14.1; HRMS (-APCI mode) exact mass calculated for $C_{56}H_{75}NO_{10}$ (M^-): 921.5396, Found: 921.5406.

4b: *Rf* = 0.58 (10% EtoAc-Hexane); red viscous liquid, yield: 82%; IR (KBr pellet) *v*max in cm^{-1} 2956, 2924, 2854, 1722, 1466, 1280, 1168; ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.25-8.21 (m, 3H, H_{Ar}), 8.15-8.12 (m, 1H, H_{Ar}), 8.06-8.03 (m, 1H, H_{Ar}), 7.90-7.87 (m, 1H, H_{Ar}), 7.77-7.74 (m, 1H, H_{Ar}), 4.38-4.31 (m, 8H, 4 ×-OCH_2), 1.81-1.69 (m, 8H, 4 ×-OCH_2-CH_2), 1.46-1.27 (m, 56H, 28 ×CH_2), 0.89-0.86 (m, 12H, 4 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 298K): 168.2, 168.04, 167.97, 166.8, 146.4, 133.8, 132.5, 132.1, 131.6, 130.9, 130.5, 130.1, 129.8, 129.2, 128.7, 128.5, 127.9, 127.6, 126.7, 125.8, 123.3, 122.7, 66.6, 66.2, 66.15, 66.1, 32.1, 29.6, 29.5, 28.8, 28.7, 26.23, 26.20, 26.17, 22.9, 14.3; HRMS (-APCI mode) exact mass calculated for $C_{64}H_{91}NO_{10}$ (M^-): 1033.6648, Found: 1033.6537.

4c: *Rf* = 0.6 (10% EtoAc-Hexane); red viscous liquid, yield: 80%; IR (KBr pellet) *v*max in cm^{-1} 2956, 2922, 2852, 1716, 1532, 1281, 1259, 1171, 1108; ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.19-8.1 (m, 4H, H_{Ar}), 8.02-7.98 (m, 1H, H_{Ar}), 7.86-7.82 (m, 1H, H_{Ar}), 7.71-7.64 (m, 1H, H_{Ar}), 4.37-4.31 (m, 8H, 4 × -OCH_2), 1.82-1.80 (m, 8H, 4 × -OCH_2-CH_2), 1.46-1.26 (m, 72H, 36 × CH_2), 0.88-0.85 (m, 12H, 4 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 298K): 168.14, 167.95, 167.90, 166.76,146.15, 133.47, 132.32, 132.03, 131.43, 131.23, 130.82, 130.35, 130.31, 129.89, 129.60, 129.03, 128.43, 128.37, 127.51, 127.47, 126.52, 127.64, 123.12, 122.59, 66.51, 66.14, 66, 32.1, 29.8, 29.8, 29.5, 28.8, 28.7, 26.22, 26.2, 26.16, 22.9, 14.3; HRMS (-APCI mode) exact mass calculated for $C_{72}H_{107}NO_{10}$ (M^-): 1145.79, Found: 1145.8093.

General procedure for synthesis of tetrakis(alkyl)-1H-phenanthro[1,10,9,8]carbazole-3,4,9,10-tetracarboxylate (**1a-1c**)[3]

A mixture of compound (**4a-4c**, 0.6 mmol) and triethyl phosphite (7 mL) were refluxed for 4 h under argon atmosphere. Reaction mixture was cooled to room temperature to precipitate the product. This precipitated product was filtered off and washed with water, dried in vacuum. Further purification was done by repeated recrystallization from (10%) dichloromethane-methanol system. Yields of these carbazoles were in range of 55-60%.

1a: *Rf* = 0.6 (20% EtoAc-Hexane); yellow solid, yield: 55%; IR (KBr pellet) ν_{max} in cm^{-1} 3353, 2954, 2922, 2852, 1711, 1593, 1278, 1194, 1156; ^1H NMR (600 MHz, $CDCl_3$, 299 K): δ 9.50 (s, 1H, NH), 8.04 (d, *J* = 12 Hz, 2H, H_{Ar}), 7.96-7.93 (m, 4H, H_{Ar}), 4.52-4.47 (m, 8H, 4 × $-OCH_2$), 1.98-1.92 (m, 8H, 4 × $-OCH_2-CH_2$), 1.58-1.31 (m, 40H, 20 ×CH_2), 0.90-0.88 (m, 12H, 4 × CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, 301K): 169.8, 131.4, 130.5, 128.7, 127.71, 127.6, 123.5, 123, 121.7, 119.4, 118.2, 66, 65.9, 32.1, 29.7, 29.5, 29.12, 29.1, 26.4, 23, 14.32; HRMS (+APCI mode) exact mass calculated for $C_{56}H_{76}NO_8$ (M+1): 890.5565, Found: 890.6854.

1b: *Rf* = 0.59 (20% EtoAc-Hexane); yellow solid, yield: 60%; IR (KBr pellet) ν_{max} in cm^{-1} 3353, 2954, 2923, 2852, 1713, 1592, 1467, 1278, 1156, 1019; ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 9.55 (s, 1H, NH), 8.05 (d, *J* = 8 Hz, 2H, H_{Ar}), 7.96-7.94 (m, 4H, H_{Ar}), 4.52-4.46 (m, 8H, 4 × $-OCH_2$), 1.96-1.91 (m, 8H, 4 × $-OCH_2-CH_2$), 1.57-1.25 (m, 56H, 28 × CH_2), 0.88-0.85 (m, 12H, 4 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 298K): 169.9, 131.4, 130.5, 128.7, 127.7, 127.5, 123.4, 123, 121.7, 119.4, 118.1, 66, 65.95, 32.1, 29.9, 29.7, 29.6, 29.1, 29.09, 26.4, 22.9, 14.3; HRMS (+APCI mode) exact mass calculated for $C_{64}H_{92}NO_8$ (M+1): 1002.6817, Found: 1002.7582.

1c: *Rf* = 0.6 (20% EtoAc-Hexane); yellow solid, yield: 62%; IR (KBr pellet) *v*max in cm^{-1} 3353, 2953, 2920, 2850, 1711, 1640, 1279, 1196, 1158, 1047; ^1H NMR (600 MHz, $CDCl_3$, 299 K): δ 9.50 (s, 1H, NH), 8.07 (d, *J* = 6 Hz, 2H, H_{Ar}), 7.97-7.95 (m, 4H, H_{Ar}), 4.50-4.48 (m, 8H, 4 × $-OCH_2$), 1.95-1.94 (m, 8H, 4 × $-OCH_2-CH_2$), 1.57-1.26 (m, 72H, 4 × CH_2), 0.86 (brs, 12H, 4 × CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, 301K): 169.9, 131.23, 130.4, 128.62, 127.64, 127.4, 123.3, 122.9, 121.7, 119.4, 118, 66.04, 65.9, 32.2, 29.94, 29.9, 29.7, 29.6, 29.13, 29.1, 26.4, 22.9, 14.3; MALDI TOF MS: *m/z* for $C_{72}H_{108}NO_8$ [M+1] , Calcd: 1115.811. Found: 1115.754.

General procedure for synthesis of tetraalkyl 1-alkyl-1H-phenanthro[1,10,9,8-cdefg]carbazole-3,4,9,10-tetracarboxylate (**2a-2c**) [4]

A mixture of compound (**1a-c,** 0.12 mmol, 1 equiv.), sodium hydride (0.36 mmol, 3 equiv.) and alkyl bromide (0.18 mmol, 1.53 equiv.) in a dry THF was refluxed for overnight under argon atmosphere. After cooling to room temperature, water (2 mL) was added to the mixture and stirred for 10 min at 0 °C. The resulting mixture was extracted with dichloromethane, the extract was washed with water and brine. Finally organic layer was dried over anhyd. Na_2SO_4 and concentrated. The crude residue obtained was purified by column chromatography on neutral alumina. Elution with hexane followed by 10-50% dichloromethane-hexane solution to yield the desired product with 70-80% yield.

2a: *Rf* = 0.8 (10% EtoAc-Hexane); yellow liquid, yield: 80%; IR (KBr pellet) *v*max in cm^{-1} 2954, 2926, 2855, 1717, 1260, 1185, 1150; ^1H NMR (600 MHz, $CDCl_3$, 299 K): δ 8.74 (d, *J* = 6 Hz, 2H, H_{Ar}), 8.40 (s, 2H, H_{Ar}), 8.31 (d, *J* = 6 Hz, 2H, H_{Ar}), 4.76-4.73 (m, 2H, N-CH_2), 4.42-4.39 (m, 8H, 4 × -OCH_2), 2.11-2.08 (m, 2H, N-CH_2-CH_2), 1.84-1.82 (m, 8H, 4 ×-OCH_2-CH_2), 1.48-1.22 (m, 50H, 25 × CH_2), 0.89-0.86 (m, 12H, 4 × CH_3), 0.84-0.82 (m, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, 299K): 169.7, 169.3, 131.8, 129.11, 128.1, 127.7, 124.2, 123.2, 121.8, 118, 117.84, 117.8, 65.9, 65.8, 46, 32.1, 31.9, 31.4, 29.6, 29.5, 29.4, 29.3, 29, 27.3, 26.3, 22.9, 22.7, 14.3; MALDI TOF MS: *m/z* for $C_{64}H_{111}NO_8$ [M+3H], Calcd: 1004.6979. Found: 1004.6476.

2b: *Rf* = 0.75 (10% EtoAc-Hexane); yellow liquid, yield: 75%; IR (KBr pellet) *v*max in cm^{-1} 2953, 2925, 2854, 1718, 1586, 1463, 1260, 1185, 1151; ^1H NMR (400 MHz, $CDCl_3$, 299 K): δ 8.33 (d, *J* = 8 Hz, 2H, H_{Ar}), 8.11-8.09 (m, 4H, H_{Ar}), 4.61-4.58 (m, 2H, N-CH_2), 4.45-4.43 (m, 8H, 4 ×-OCH_2), 1.89-1.87 (m, 10H, N-CH_2-CH_2, 4 ×-OCH_2-CH_2), 1.52-1.16 (m, 70H, 35 ×CH_2), 0.89-0.87 (m, 12H, 4 × CH_3), 0.83-0.80 (m, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, 299K):169.7, 169.3, 131.6, 129, 127.9, 127.6, 124, 123.1, 121.7, 117.8, 117.6, 65.9, 65.8, 45.9, 32.1, 32, 31.4, 29.8, 29.7, 29.6, 29.5, 29.46, 29.38, 28.9, 27.3, 26.34, 22.9, 22.8, 14.3, 14.2; MALDI TOF MS: *m/z* for $C_{74}H_{114}NO_8Na$ [M+3H+Na] , Calcd: 1168.8515. Found: 1168.1365.

2c: *Rf* = 0.76 (10% EtoAc-Hexane); yellow solid, yield: 74%; IR (KBr pellet) *v*max in cm^{-1} 2954, 2920, 2852, 1727, 1628, 1468, 1260, 1151, 1022; ^1H NMR (600 MHz, $CDCl_3$, 299 K): δ 8.76 (d, *J* = 6 Hz, 2H, H_{Ar}), 8.42 (s, 2H, H_{Ar}), 8.32 (d, *J* = 6 Hz, 2H, H_{Ar}), 4.75 (t, *J* = 6 Hz, 2H, N-CH_2), 4.42-4.39 (m, 8H, 4 ×-OCH_2), 2.13-2.08 (m, 2H, N-CH_2-CH_2), 1.85-1.80 (m, 8H, 4 ×-OCH_2-CH_2), 1.46-1.21 (m, 90H, 45 × CH_2), 0.88-0.84 (m, 15H, 5 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 298K): 169.72, 169.27, 132.09, 132, 129.3, 128.3, 127.9, 124.53, 123.5, 121.9, 118.1, 65.9, 65.87, 32.14, 32.1, 31.5, 29.91, 29.88, 29.84, 29.82, 29.79, 29.66, 29.6, 29.5, 29.47, 29, 28.92, 27.4, 26.3, 22.9, 22.87, 14.3; MALDI TOF MS: *m/z* for $C_{84}H_{134}NO_8$ [M+3H] , Calcd: 1285.0109. Found: 1285.027.

(ii) NMR spectra

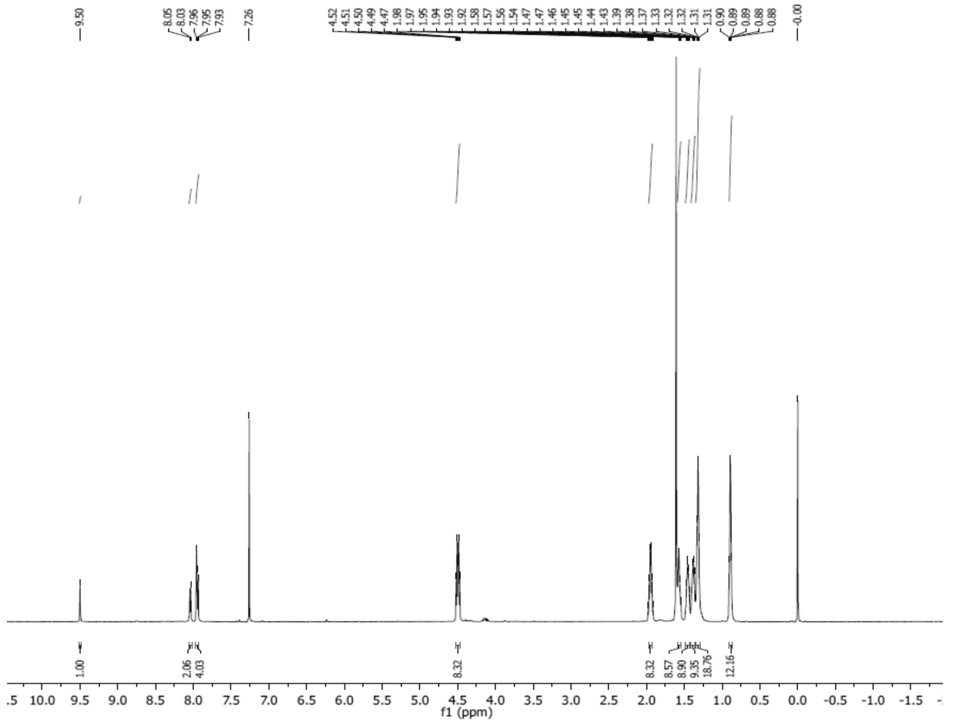

Figure S1. ^{1}H NMR (600 MHz) spectrum of **1a** in $CDCl_3$

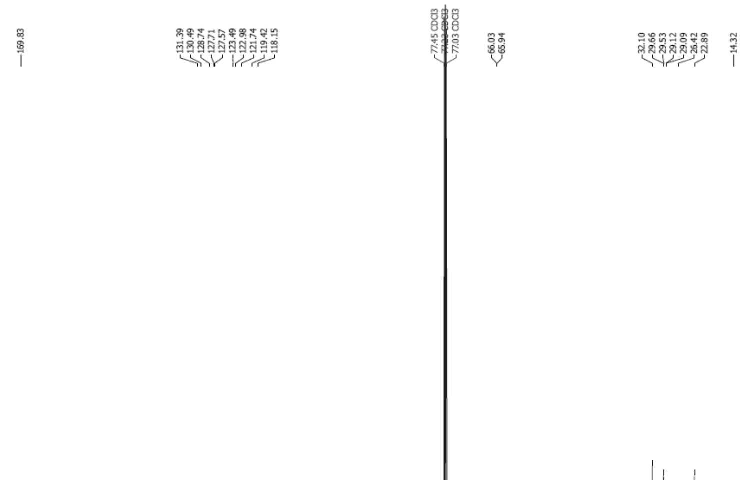

Figure S2. ^{13}C NMR (150 MHz) spectra of **1a** in $CDCl_3$

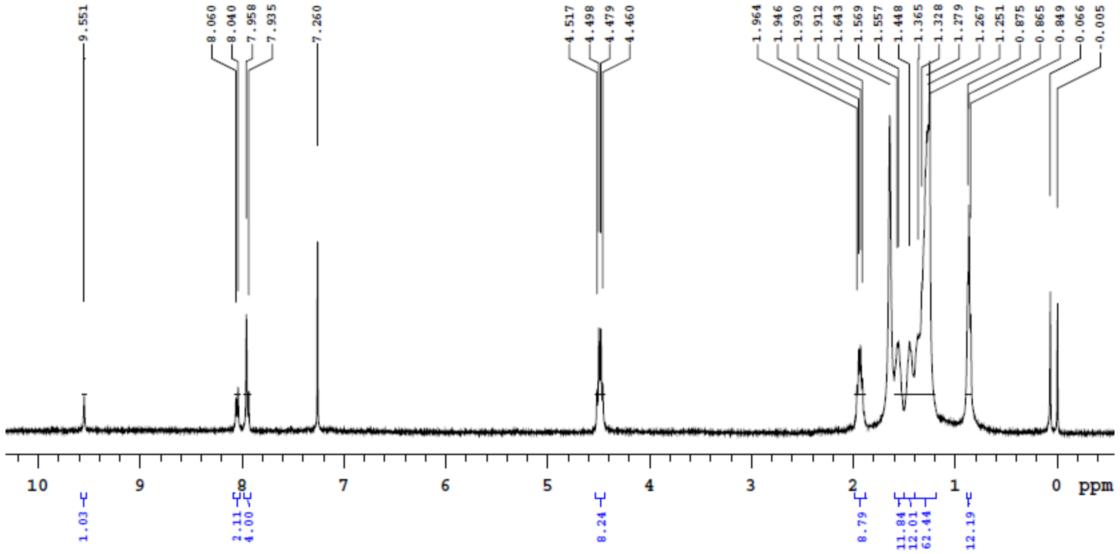

Figure S3. ^{1}H NMR (400 MHz) spectra of **1b** in $CDCl_3$

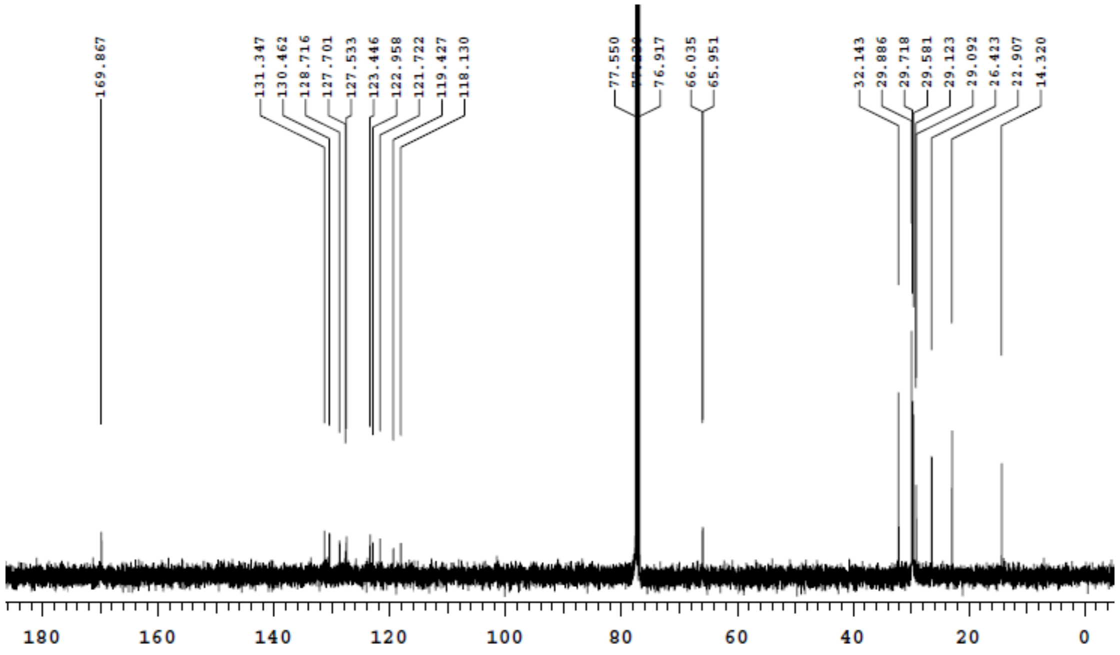

Figure S4. ^{13}C NMR (100 MHz) spectra of **1b** in $CDCl_3$

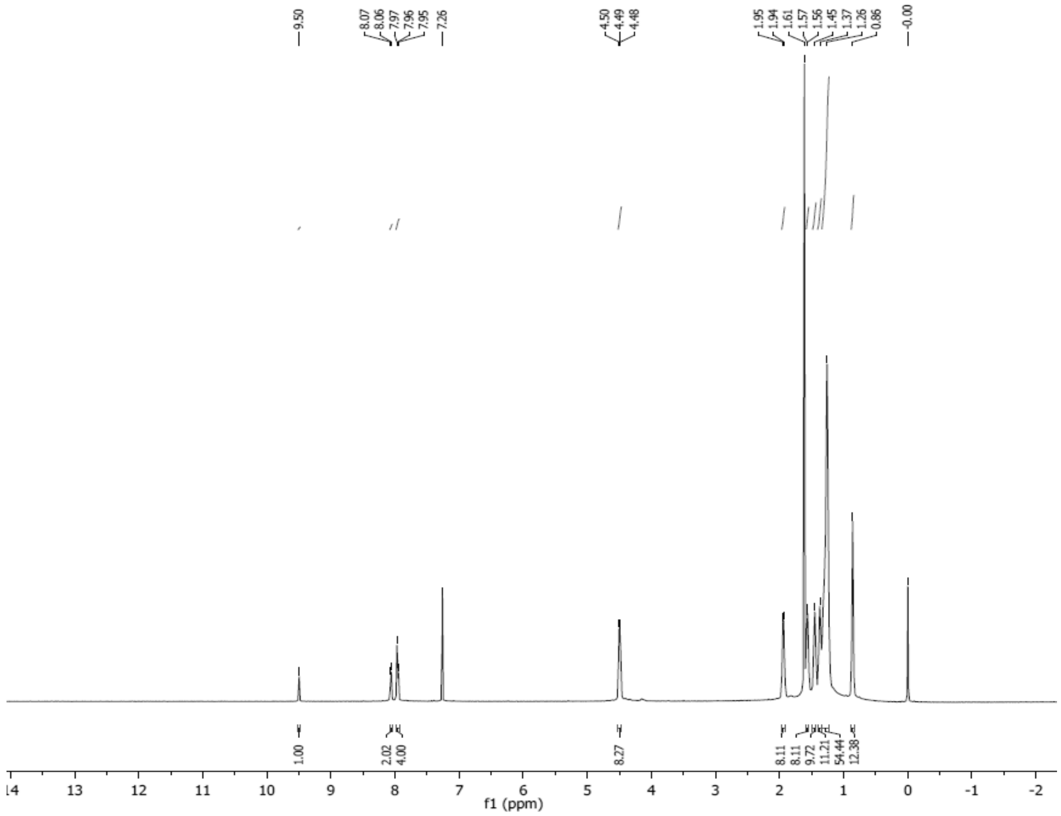

Figure S5. ^{1}H NMR (600 MHz) spectra of **1c** in CDCl$_3$

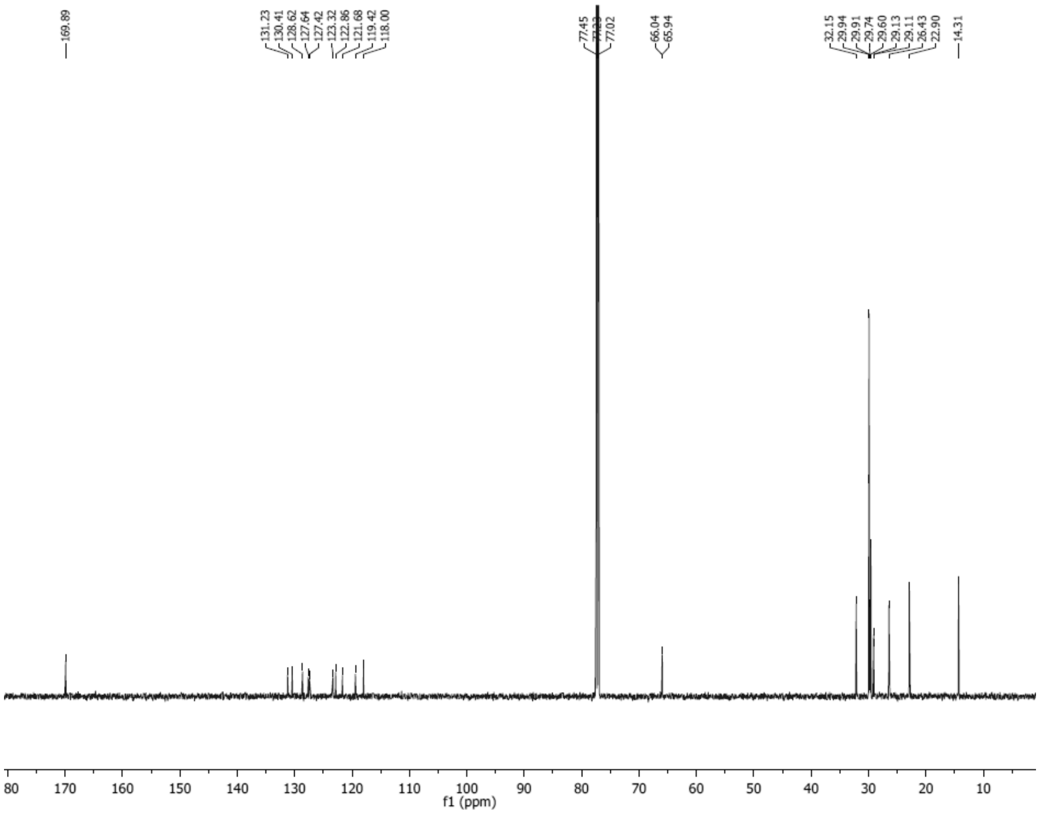

Figure S6. ^{13}C NMR (150 MHz) spectra of **1c** in CDCl$_3$

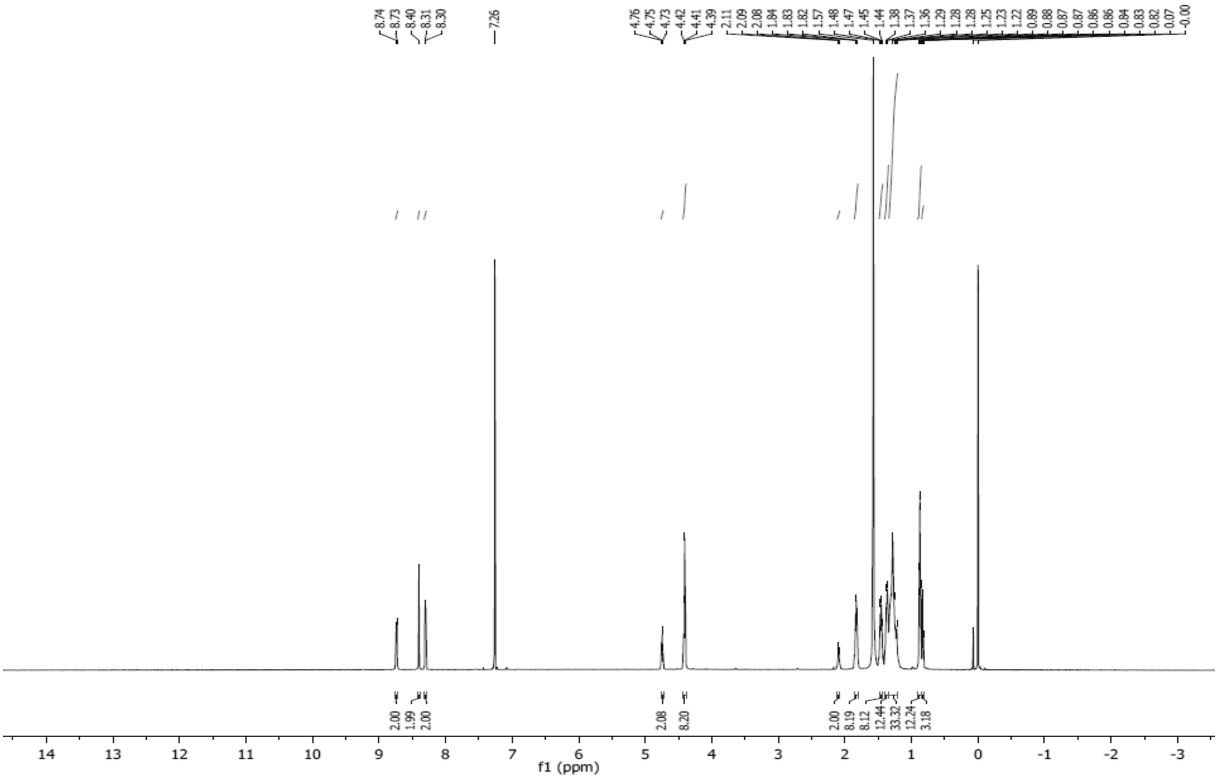

Figure S7. ^{1}H NMR (600 MHz) spectra of **2a** in $CDCl_3$

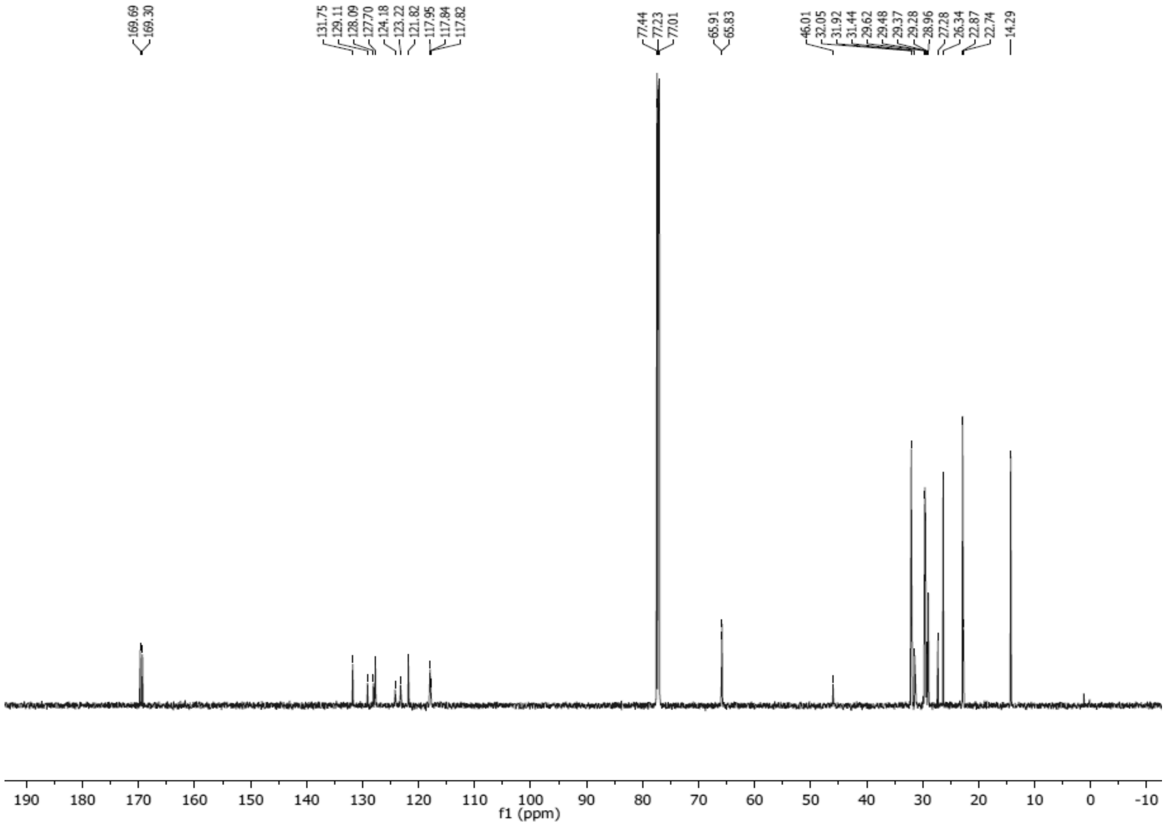

Figure S8. ^{13}C NMR (150 MHz) spectra of **2a** in $CDCl_3$

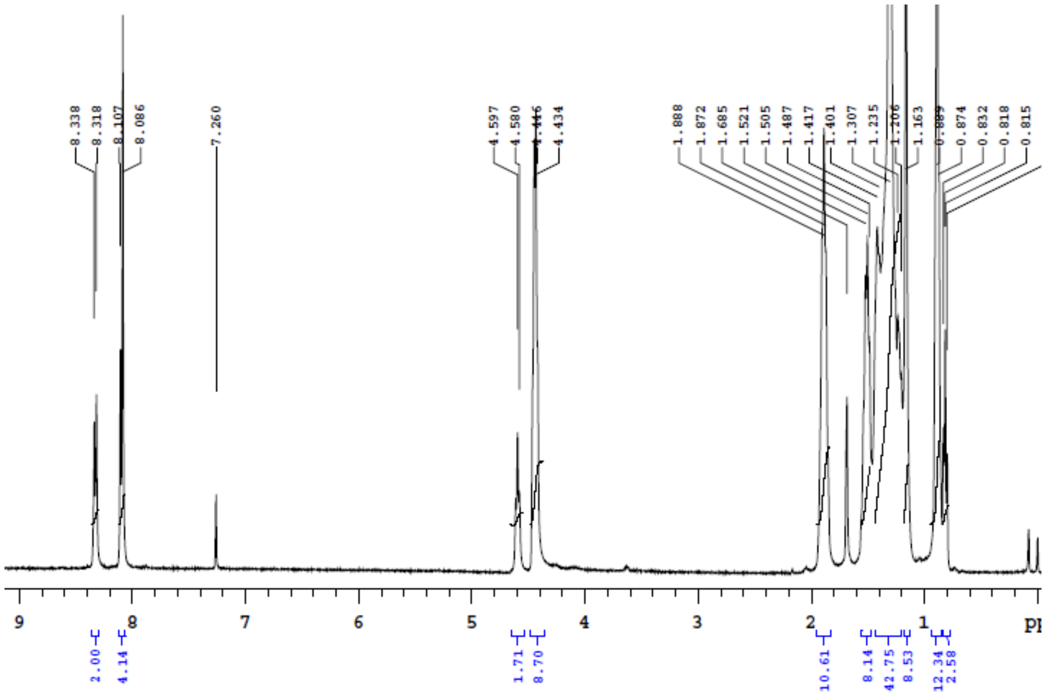

Figure S9. ^{1}H NMR (400 MHz) spectra of **2b** in $CDCl_3$

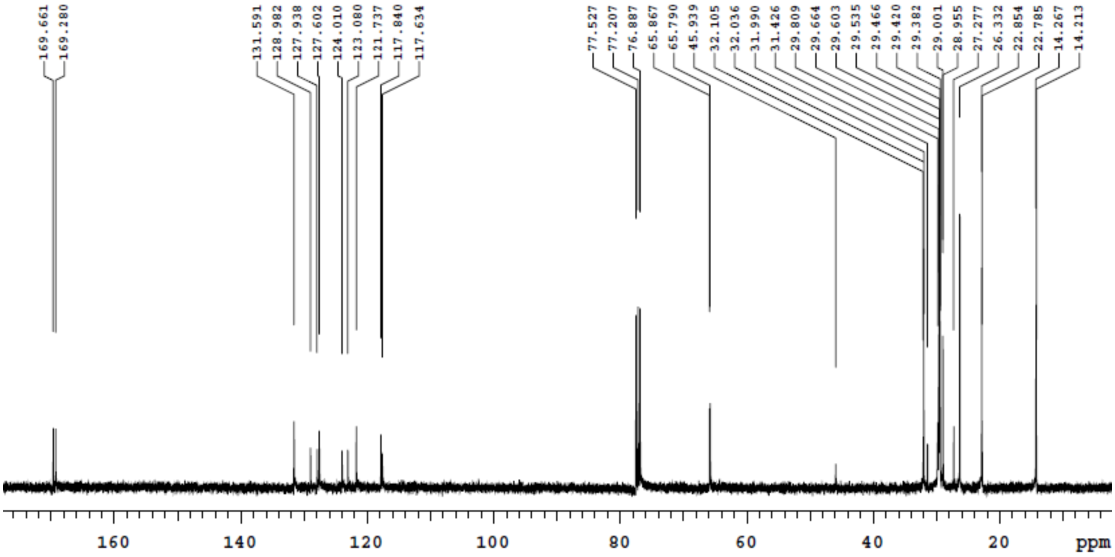

Figure S10. ^{13}C NMR (150 MHz) spectra of **2b** in $CDCl_3$

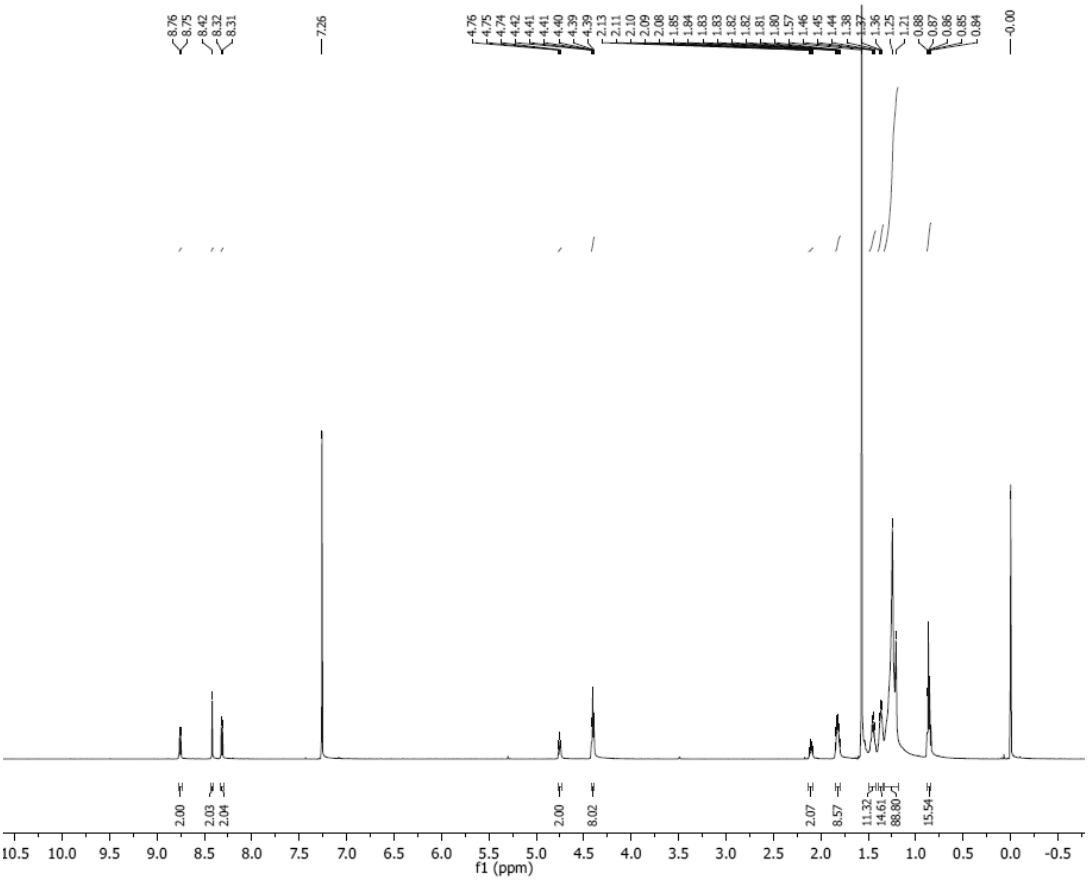

Figure S11. ^{1}H NMR (600 MHz) spectra of **2c** in $CDCl_3$

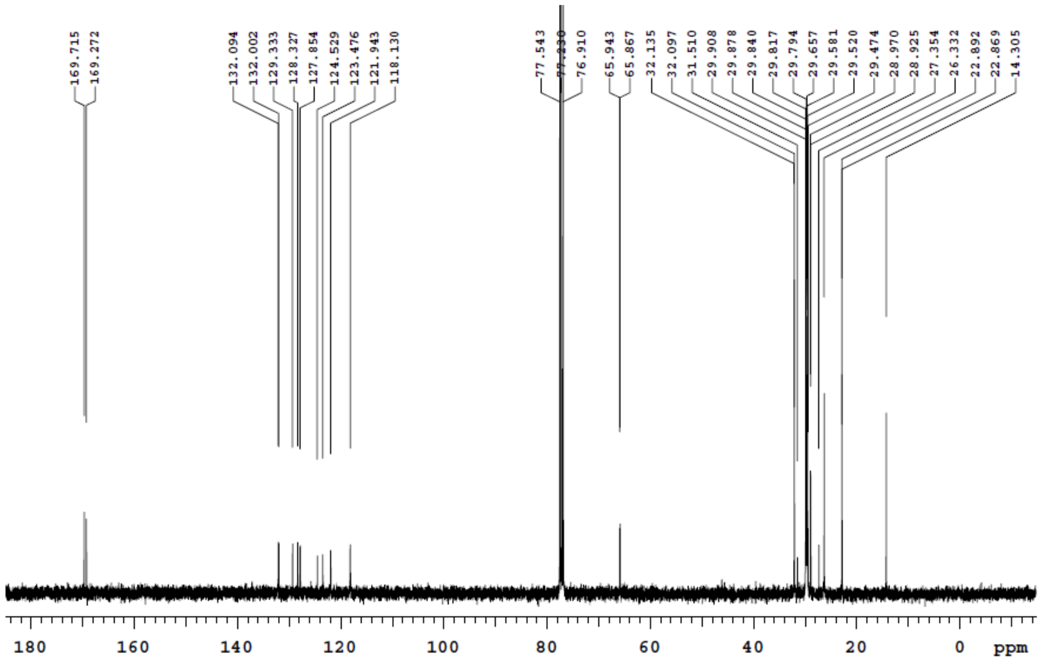

Figure S12. ^{13}C NMR (100 MHz) spectra of **2c** in $CDCl_3$

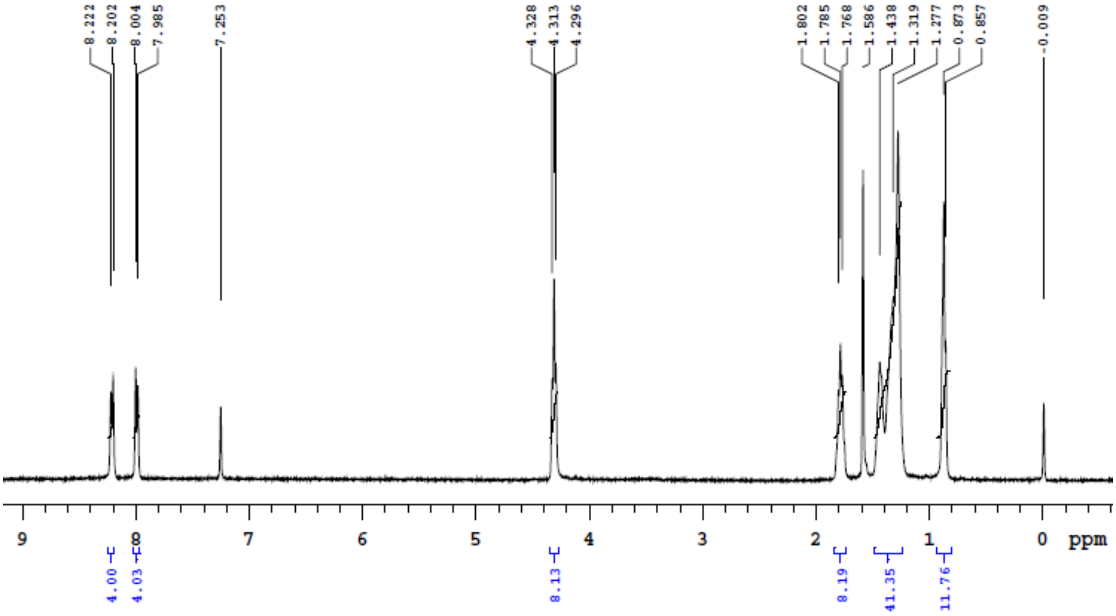

Figure S13. ^{1}H NMR (400 MHz) spectra of **3a** in $CDCl_3$

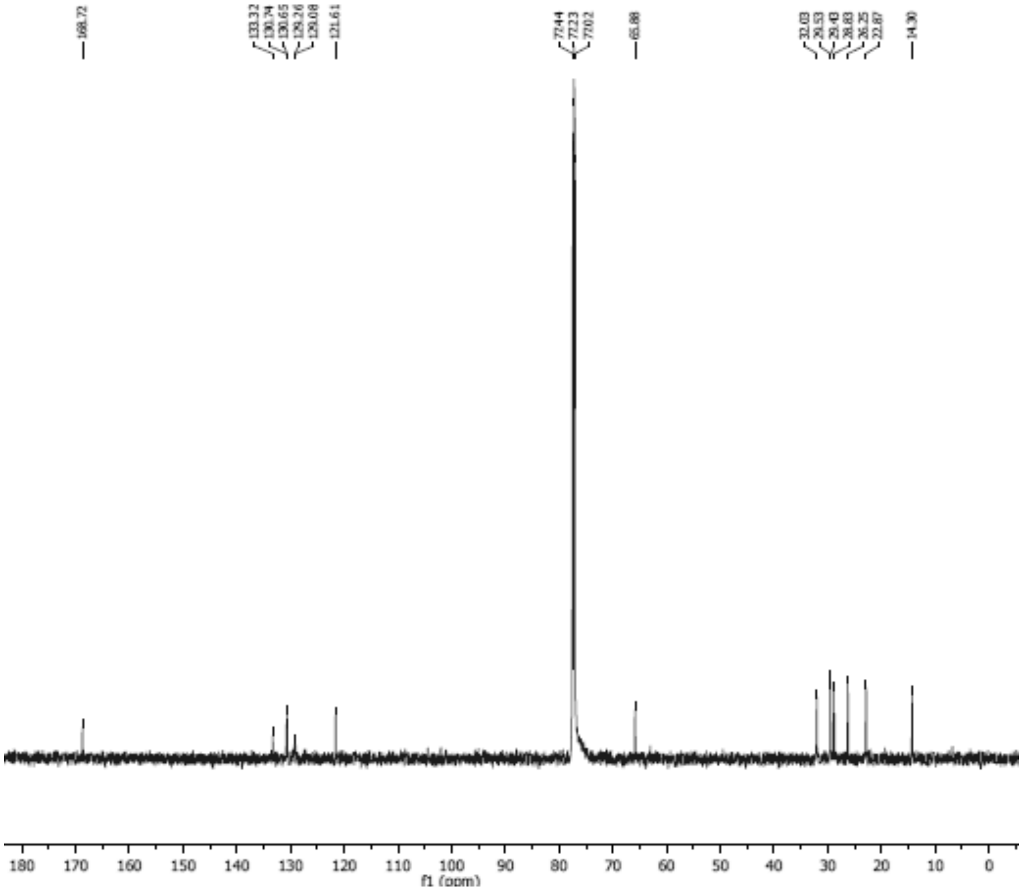

Figure S14. ^{13}C NMR (150 MHz) spectra of **3a** in $CDCl_3$

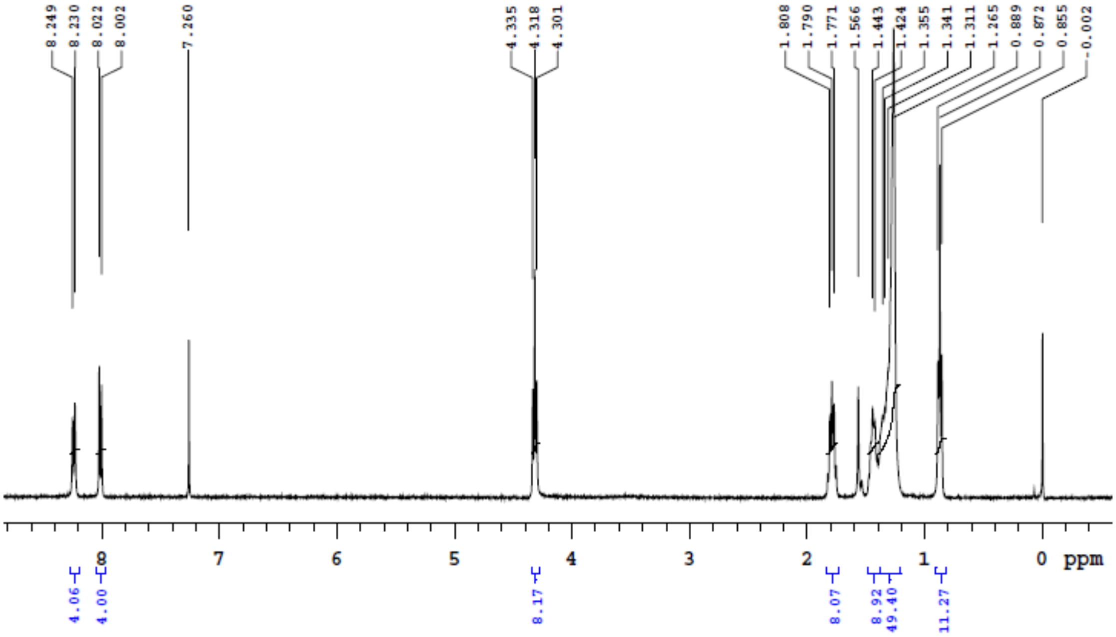

Figure S15. ^{1}H NMR (400 MHz) spectra of **3b** in $CDCl_3$

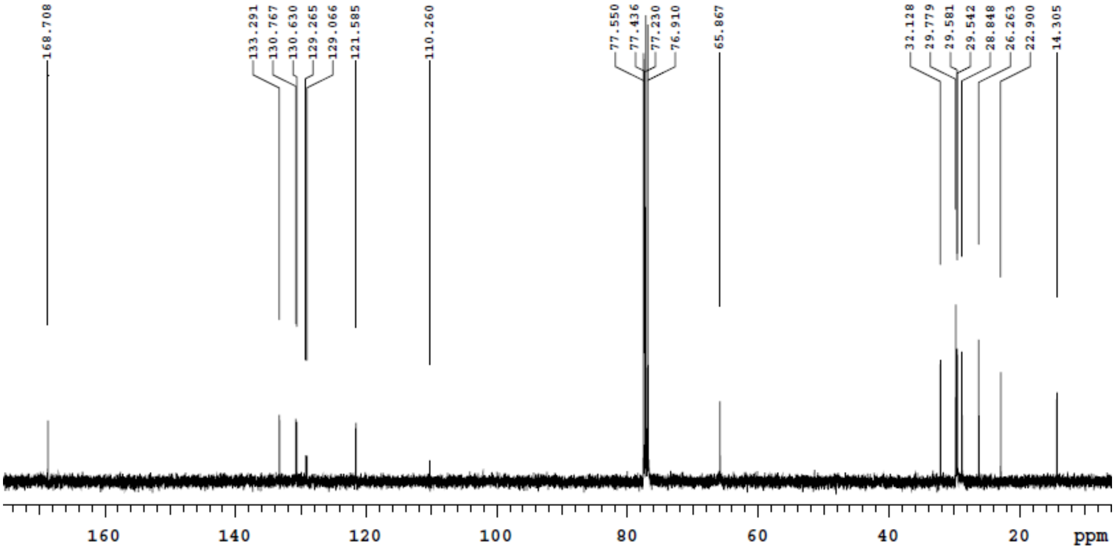

Figure S16. ^{13}C NMR (100 MHz) spectra of **3b** in $CDCl_3$

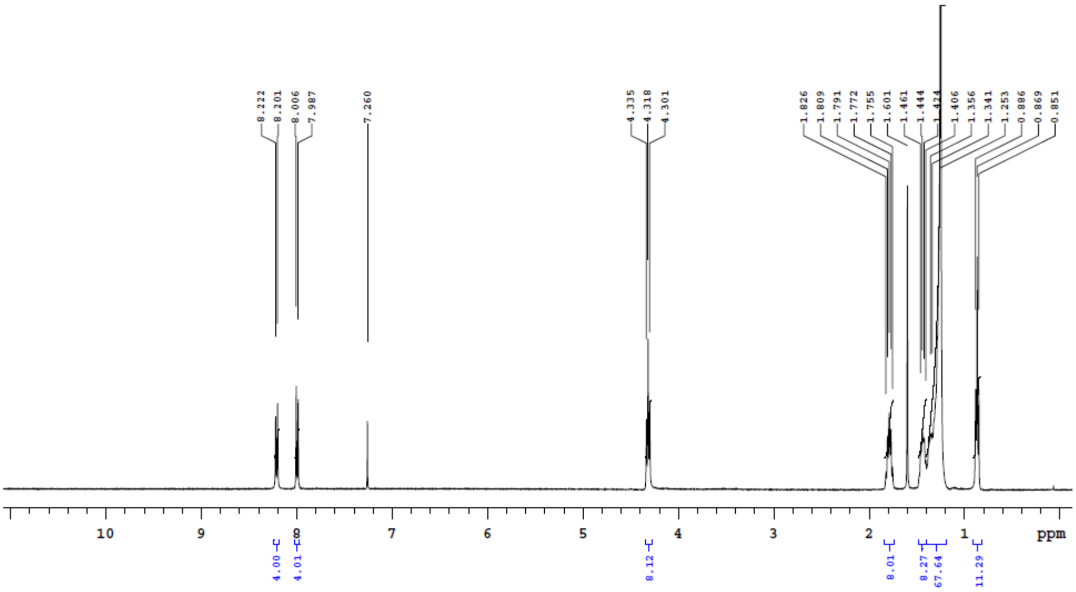

Figure S17. ^{1}H NMR (400 MHz) spectra of **3c** in CDCl$_3$

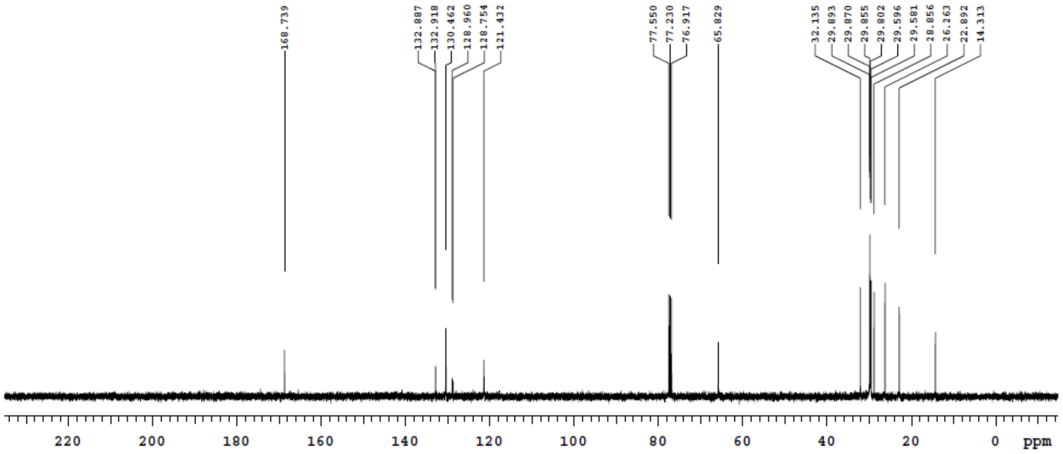

Figure S18. ^{13}C NMR (100 MHz) spectra of **3c** in CDCl$_3$

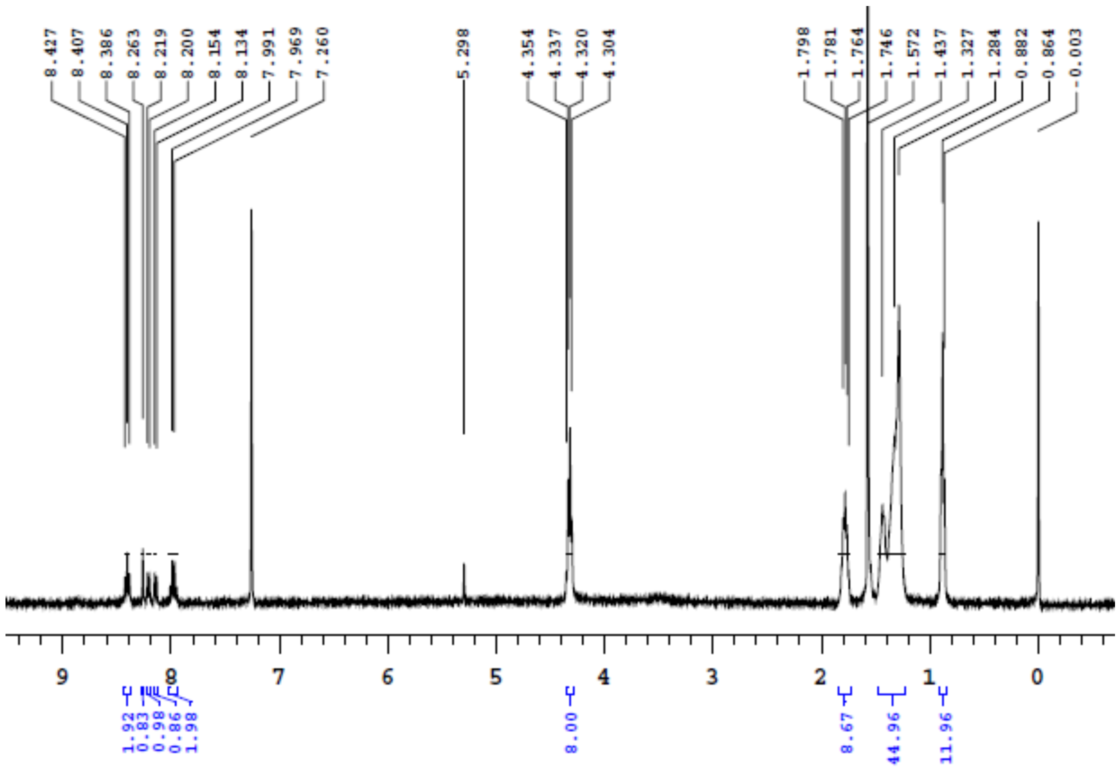

Figure S19. ^{1}H NMR (400 MHz) spectra of **4a** in $CDCl_3$

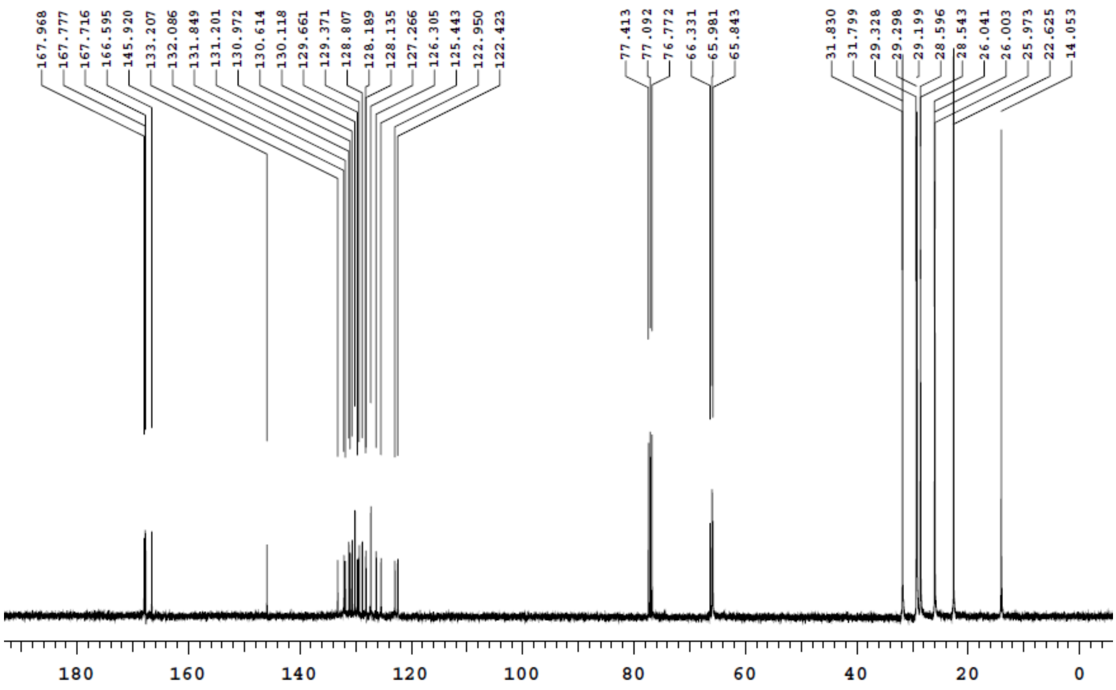

Figure S20. ^{13}C NMR (100 MHz) spectra of **4a** in $CDCl_3$

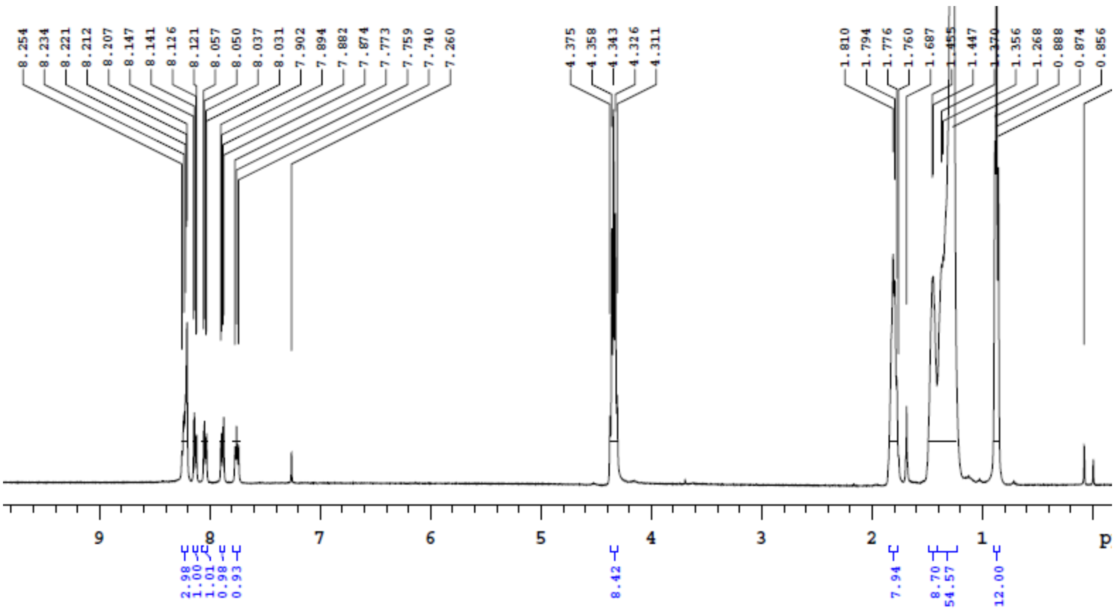

Figure S21. ^{1}H NMR (400 MHz) spectra of **4b** in $CDCl_3$

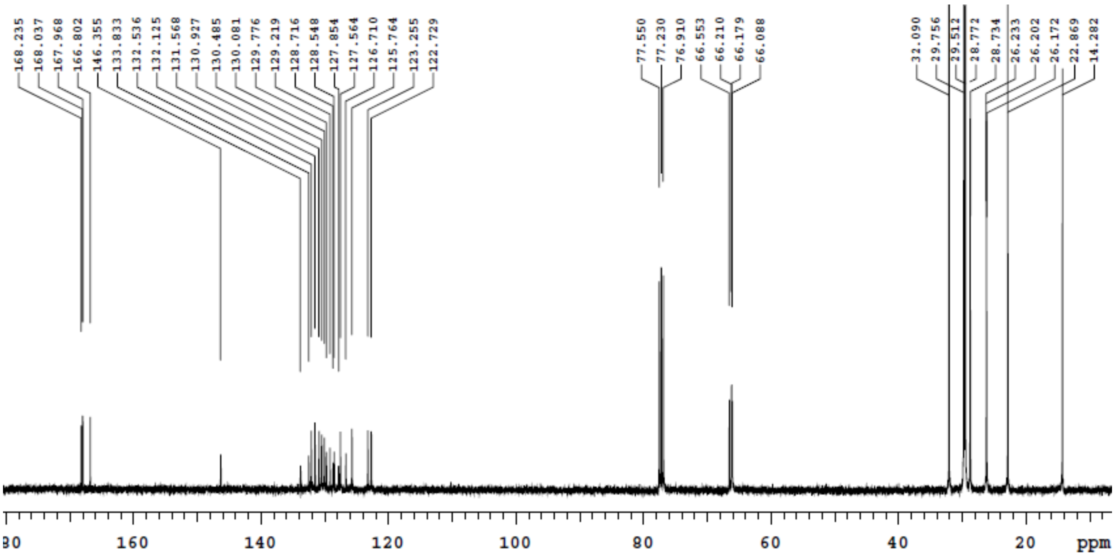

Figure S22. ^{13}C NMR (100 MHz) spectra of **4b** in $CDCl_3$

Figure S23. ^{1}H NMR (400 MHz) spectra of **4c** in $CDCl_3$

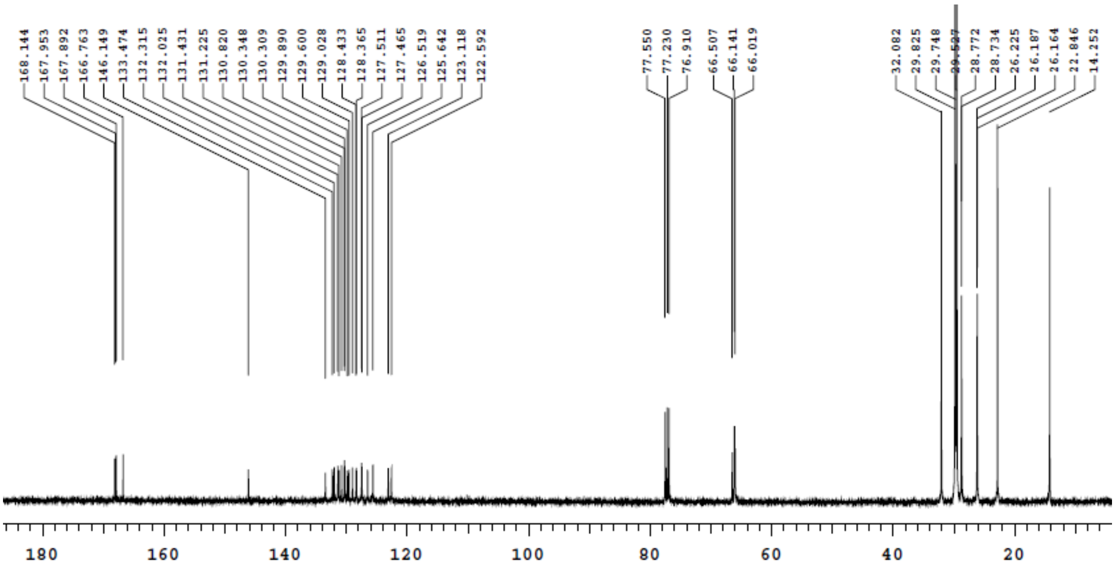

Figure S24. ^{13}C NMR (100 MHz) spectra of **4c** in $CDCl_3$

iii) Polarized Optical Microscopy

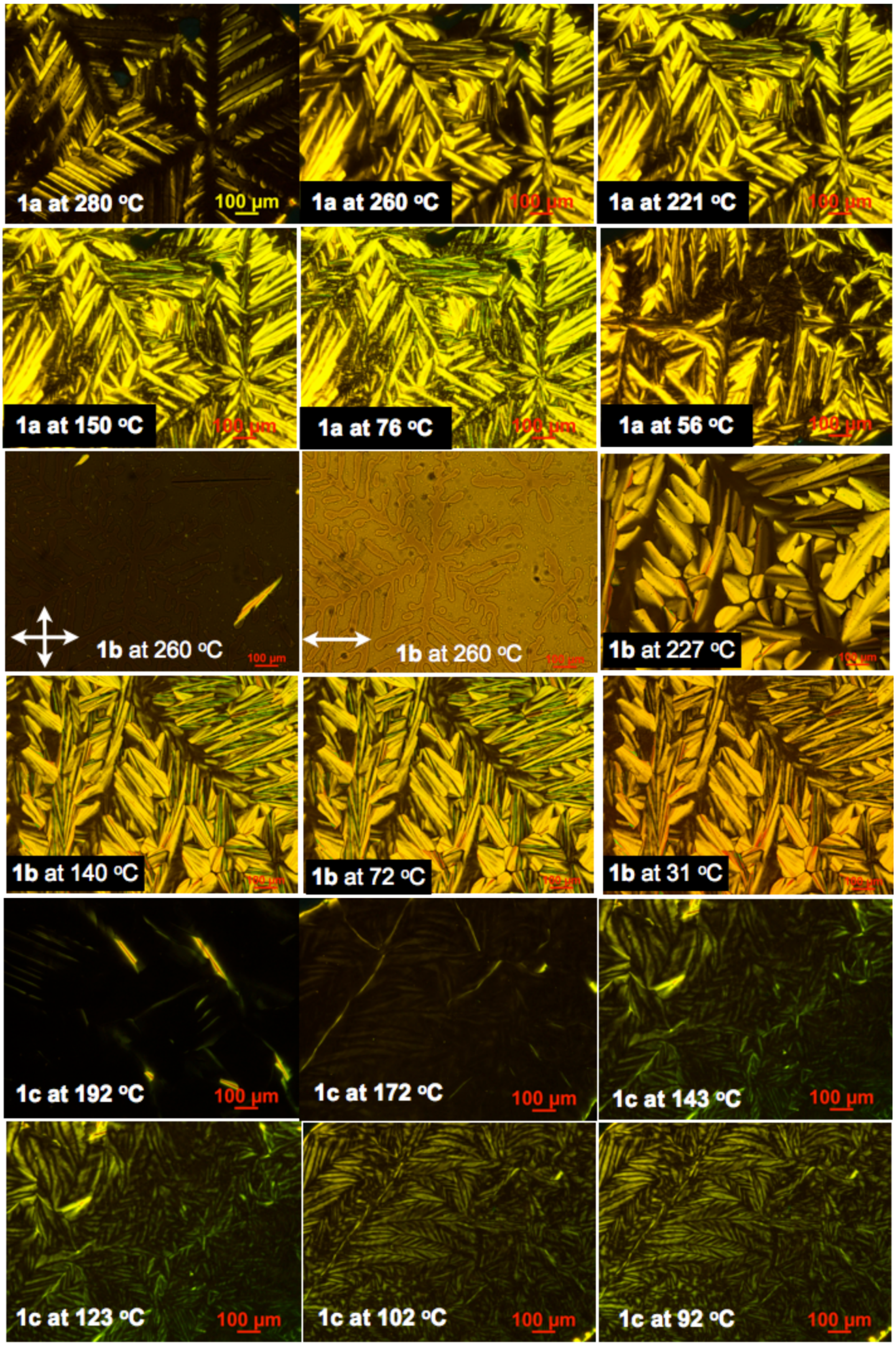

Figure S25. POM images of discotics **1a-c** on a cooling process from isotropic melt.

(iv) Differential Scanning Calorimetry

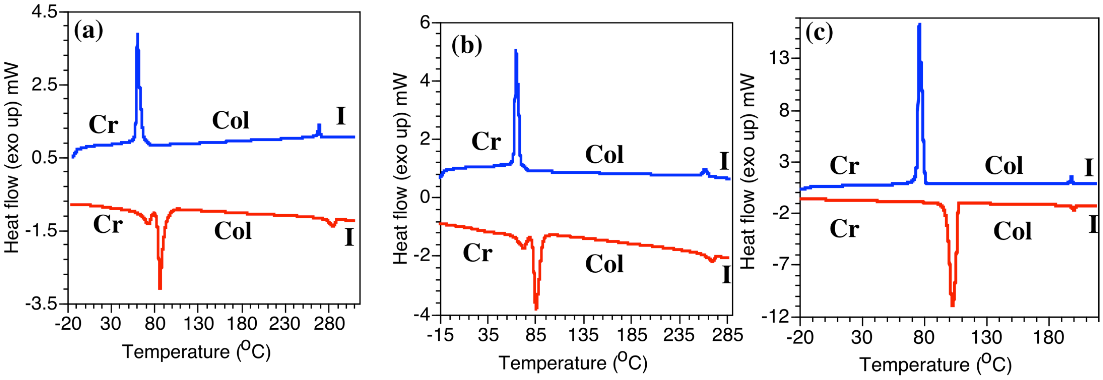

Figure S26. DSC thermograms of discotics **1a-c** showing the second heating (red trace) and the first cooling (blue trace) scans at a scanning rate of 5.0 ˚C min^{-1}.

(v) Thermogravimetric Analysis

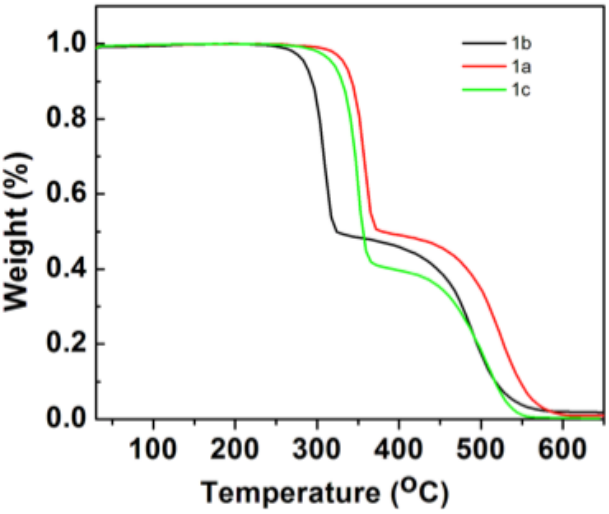

Figure S27. TGA plots of compound **1a-c** (heating rate of 10 °C/min, Nitrogen atmosphere)

(vi) Photophysical properties

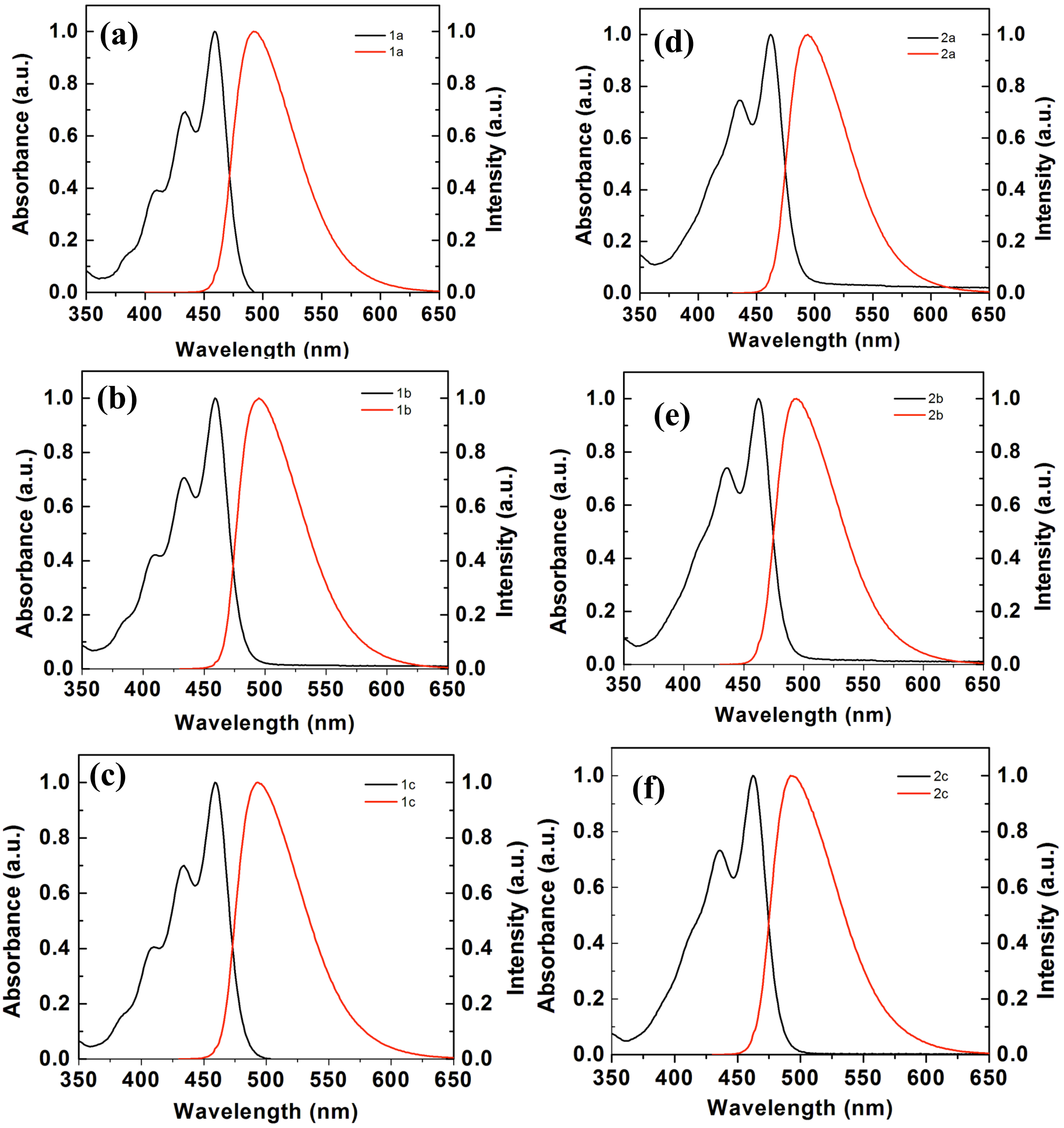

Figure S28. Absorption (black trace) and emission (red trace) spectra of compounds **1a-c (a-c)** and **2a-c (d-f)** in THF solution

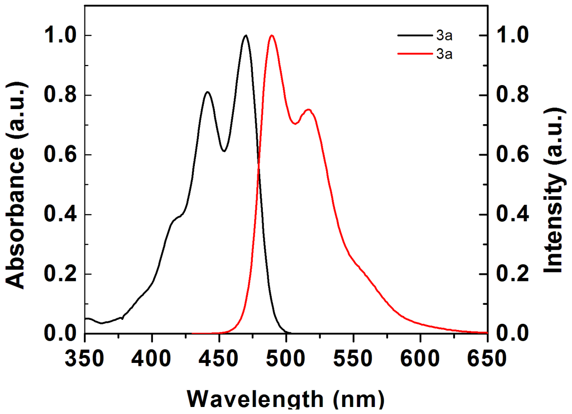

Figure S29. (a) Absorption (LHS) emission (RHS) spectra of compound **3a** in THF solution.

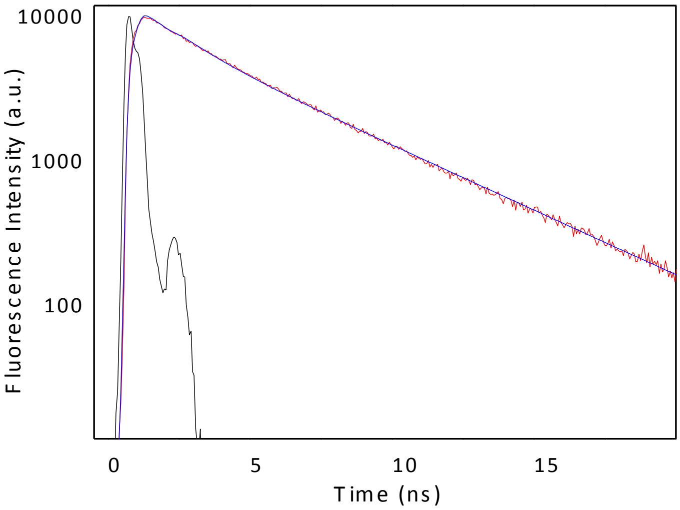

Figure S30. Plot showing the fluorescence life time decay profiles of compound **1a**

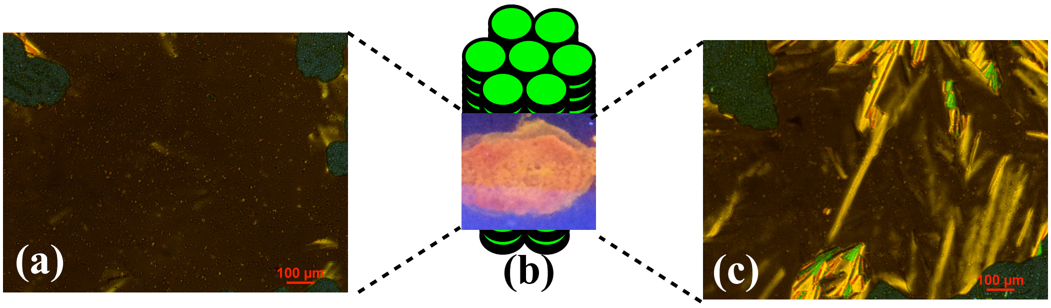

Figure S31. POM images of compound **1a** at 253 ^{o}C obtained on cooling from isotropic liquid (a); After sudden cooling to 0 ^{o}C (c); the frozen sample film under UV light of 365 nm (b).

Quantum Yield Calculation (Relative)[5]

Quantum yield was measured according to established procedure by using fluorescein in 0.1 M NaOH 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 (Calculated from Fig.S31)

n: refractive index (1.407 for THF and 1.33 for distilled water).

The subscript R refers to the reference fluorophore *i.e.* fluorescein solution in 0.1 M NaOH 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 459, 462, 470 nm.

Quantum Yield of fluorescein in 0.1 M NaOH solution is 0.79. Simplified equation for the calculation after substituting the appropriate values is given below and values obtained are given in table 1.

$$Q_S = 0.79 \times (m_S / m_R) \times (1.407/1.33)^2$$

$$= 0.88401 \text{ X } (m_S / m_R)$$

Entry	m_S	m_R	Q_S[a,b,c]
1a	2.285×10^9	2.001×10^9	1.00
1b	2.215×10^9	2.001×10^9	0.97
1c	2.230×10^9	2.001×10^9	0.98
2a	2.158×10^9	1.961×10^9	0.97
2b	1.922×10^9	1.961×10^9	0.86
2c	1.970×10^9	1.961×10^9	0.88
3a	2.278×10^9	1.959×10^9	1.00

[a] Measured in THF.

[b] Excited at absorption maxima .

[c] Standard fluorescein (**Q_f** = 0.79) in 0.1M NaOH.

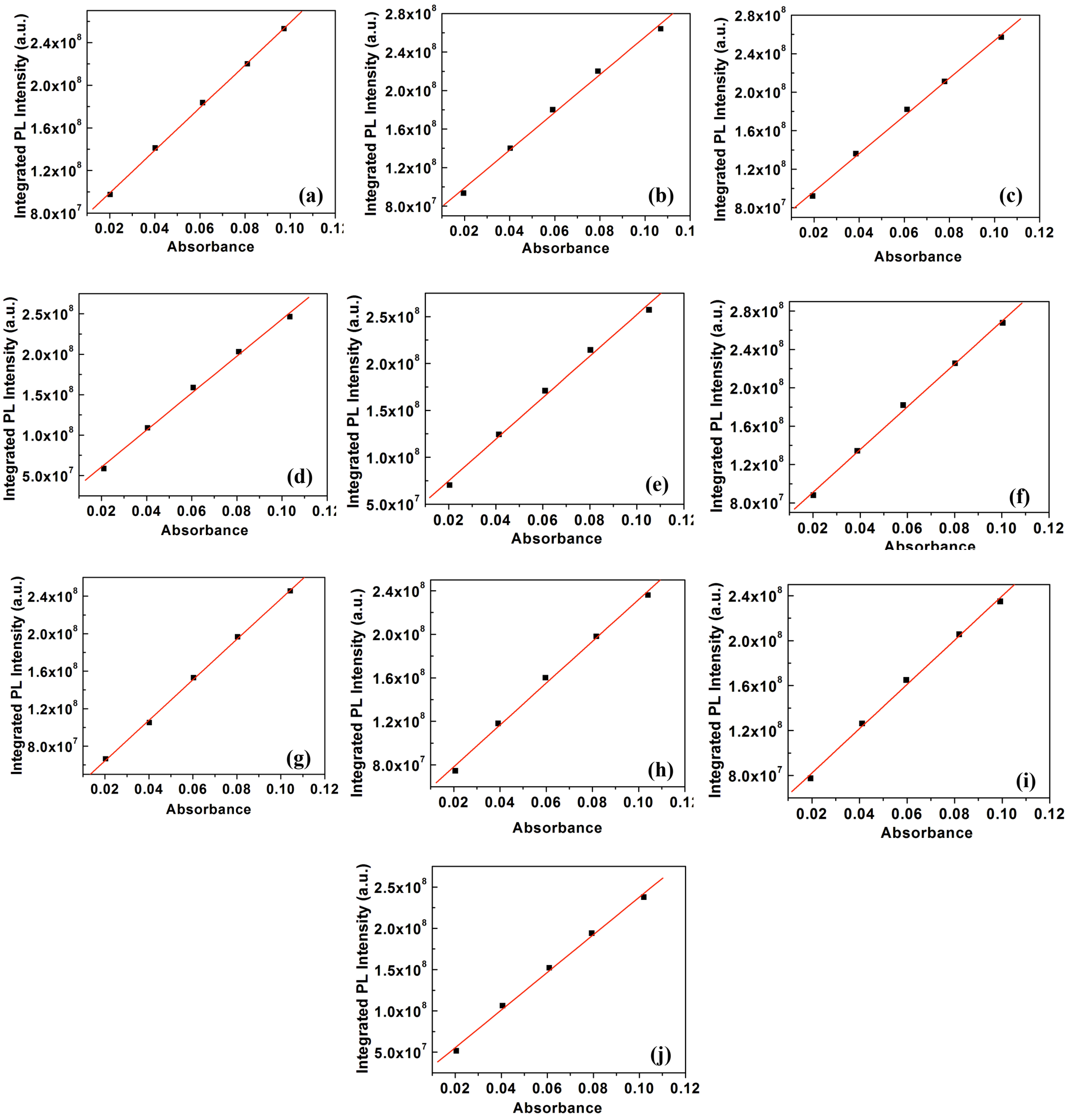

Figure S32. Plots of integrated photoluminescence intensity vs absorbance of Fluorescein (0.1M NaOH solution) excited at 459 nm (a); 462 nm (b); 470 nm (c) and for compounds **1a-c** (d-f); for compounds **2a-c** (g-i) and for compound **3a** (j).

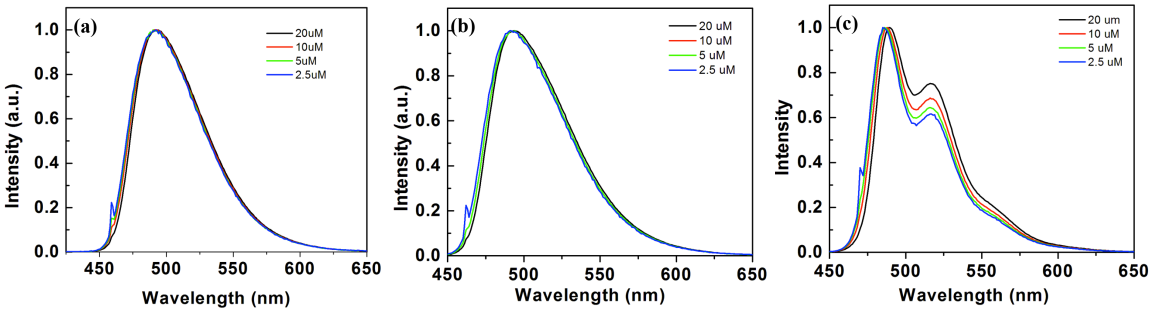

Figure S33. Normalized emission spectra of compounds **1a** (a), **2a** (b) and **3a** (c) as a function of concentration in THF solution.

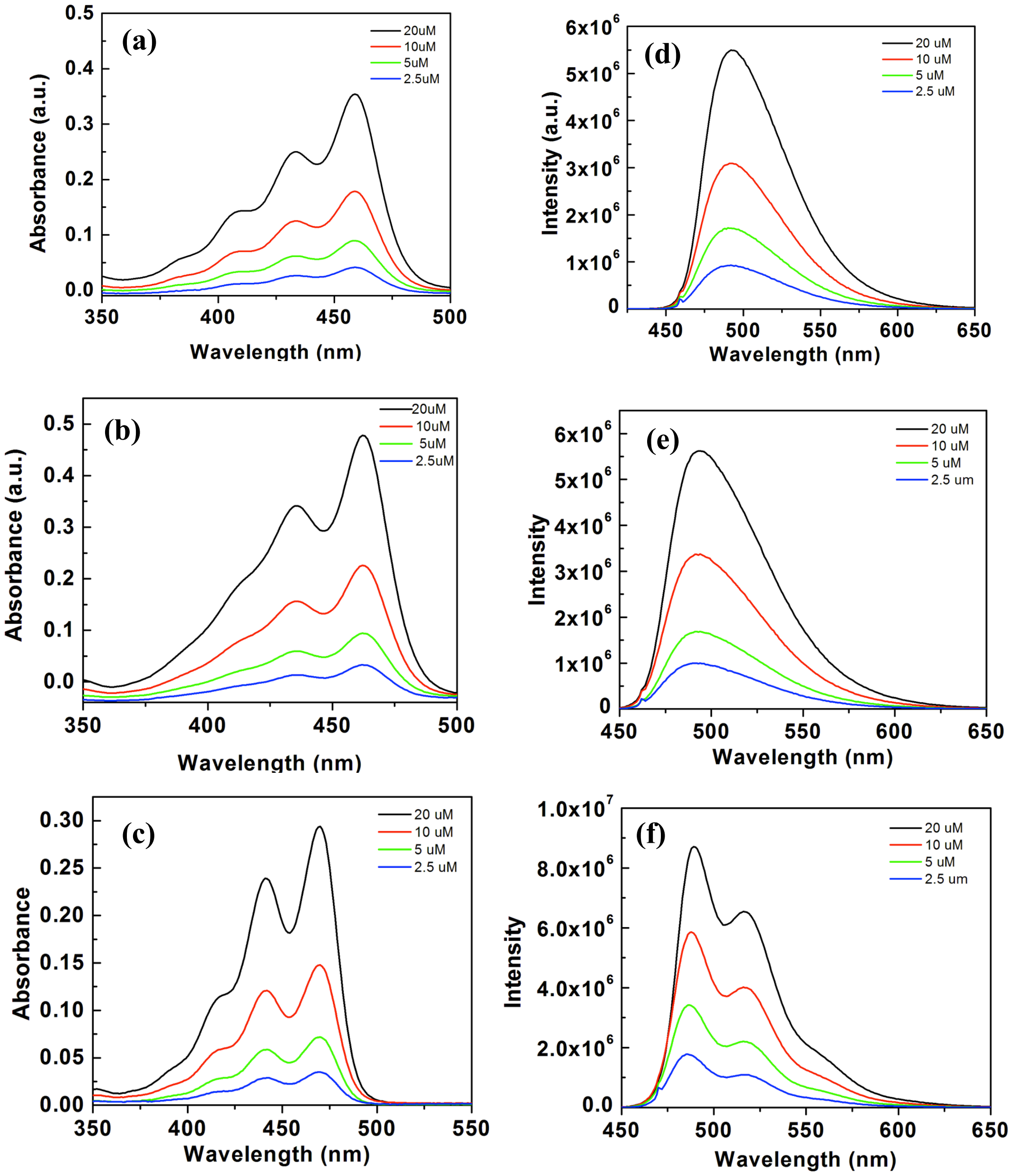

Figure S34. Absorption spectra of compounds **1a** (a)**, 2a** (b) and **3a** (c); emission spectra of compounds **1a** (d)**, 2a** (e) and **3a** (f) as a function of concentration in THF solution.

(vii) Electrochemical properties

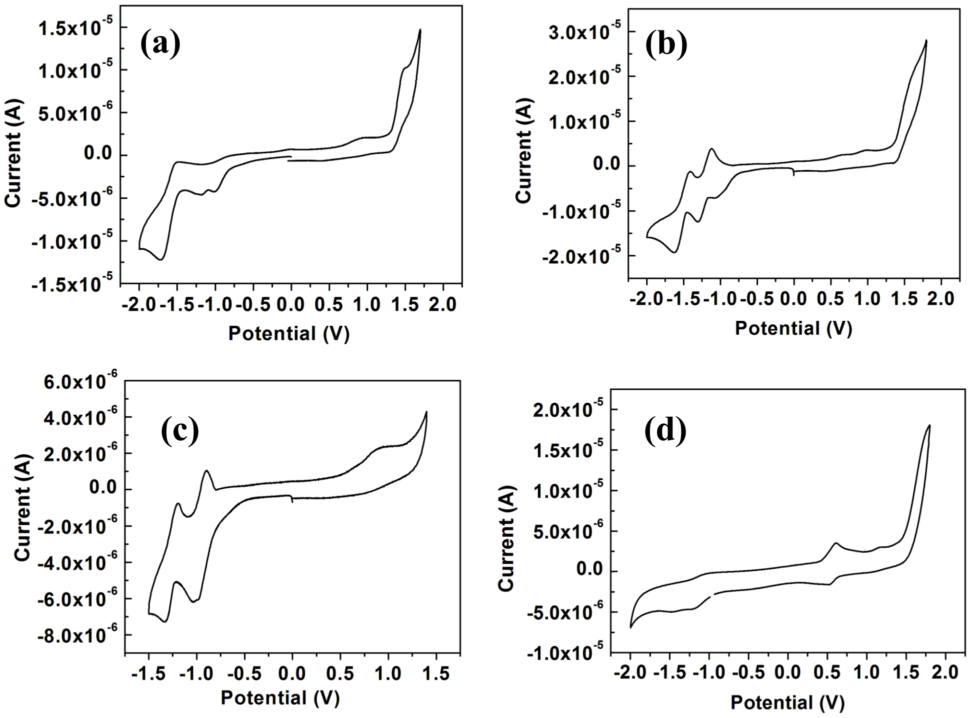

Figure S35. Cyclic voltammograms of the compounds **1a** (a), **2a** (b) and **3a** (c) in anhydrous THF solution of tetra-*n*-butylammonium perchlorate (TBAP) (0.1 M) at a scanning rate 0.5 mV/s; (d) Cyclic voltammogram of ferrocene in anhydrous THF solution of TBAP (0.1 M). The half-wave potential of the ferrocene/ ferrocenium (Fc/Fc$^+$) redox couple ($E_{1/2,\ \mathrm{Fc,Fc}^+}$) was found to be 0.56 V relative to the Ag/Ag$^+$ reference electrode.

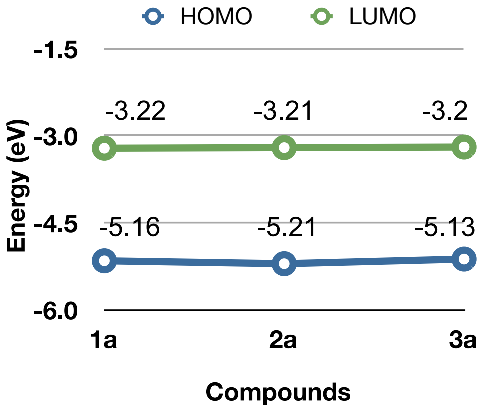

Figure S36. Schematic showing the bandgaps of compounds **1a**, **2a** and **3a** obtained from CV.

viii) Powder XRD studies

Table 1. Results of (*hkl*) indexation of XRD profiles of the compounds at a given temperature (T) of mesophases[a]

Compounds (*D*/Å)	Phase (T/°C)	d_{obs} (Å)	d_{cal} (Å)	Miller indices *hkl*	lattice parameters (Å), lattice area S (Å^2), molecular volume V (Å^3)
1a (32.81)	150 °C	19.37 11.19 9.69 5.78 (h_a) 4.53 (h_c)	19.37 11.19 9.69	100 110 200 001	$a = 22.37$, $c = 4.53$ $S = 433.3$, $V = 1965.3$ $Z = 1.33$
1b (37.63)	250 °C	20.28 11.71 10.14 5.82 (h_a) 4.73 (h_c)	20.28 11.71 10.14	100 110 200 001	$a = 23.42$, $c = 4.73$ $S = 475.0$, $V = 2245.2$ $Z = 1.35$
	227 °C	20.13 11.62 10.07 5.79 (h_a) 4.60 (h_c)	20.13 11.62 10.07	100 110 200 001	$a = 23.24$, $c = 4.60$ $S = 468.0$, $V = 2154.8$ $Z = 1.29$
	100 °C	19.60 11.33 9.81 5.76 (h_a) 4.50 (h_c)	19.61 11.32 9.80	100 110 200 001	$a = 22.64$, $c = 4.50$ $S = 444$, $V = 1996.8$ $Z = 1.2$
1c (42.39)	180 °C	22.49 12.98 11.25 5.56 (h_a) 4.65 (h_c)	22.49 12.98 11.24	100 110 200 001	$a = 25.97$, $c = 4.65$ $S = 584.0$, $V = 2716.7$ $Z = 1.47$
	150 °C	22.33 12.90 11.17 5.54 (h_a) 4.61 (h_c)	22.34 12.90 11.17	100 110 200 001	$a = 25.79$, $c = 4.61$ $S = 576.0$, $V = 2658.4$ $Z = 1.44$

[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. *Z* indicates the number of molecules per columnar slice of thickness h_c (When h_c is not observed then h_a is taken into account), estimated from the lattice area *S* and the volume *V*.)

References

(1) (a) X. Mo, H. -Z. Chen, M.-M. Shi and M. Wang, *Chemical Physics Letters*, 2006, **417**, 457–460; (b) C. Xue, R. Sun, R. Annab, D. Abadi and S. Jin, *Tetrahedron Lett.*, 2009, **50**, 853-856; (c) A. Wicklein, M.-A. Muth, and M. Thelakkat, *J. Mat. Chem.*, 2010, **20**, 8646–8652; (d) S. K. Gupta, S. Setia, S.

Sidiq, M. Gupta, S. Kumar, and S. K. Pal, *RSC Adv.*, 2013, **3**, 12060; (e) S. Benning, H. S. Kitzerow, H. Bock, and M. F. Achard, *Liq. Cryst.*, 2000, **27**, 901–906; (f) X. Mo, M. -M. Shi, J. -C. Huang, M. Wang, H. -Z. Chen, *Dyes and Pigments*, 2008, **76**, 236-242.

(2) C. V. Yelamaggad, A. S. Achalkumar, D. S. S. Rao, and S. K. Prasad, *J. Org. Chem.*, 2007, **72**, 8308–8318.

(3) (a) J. J. Looker, *J. Org. Chem.*, 1972, 37, 21, 3379-3381; (b) W. Jiang, H. Qian, Y. Li, and Z. Wang, *J. Org. Chem.*, 2008, **73**, 7369–7372.

(4) Y. Li and Z. Wang, *Org. Lett.*, 2009, **11**, 1385–1387.

(5) Brouwer, A. M. *Pure Appl. Chem*., **2011**, *83*, 12, 2213–2228.