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Hydrogen bond-driven columnar self-assembly of electroluminescent D-A-D configured cyanopyridones

D. R. Vinayakumara,[a] Hidayath Ulla, [b] Sandeep kumar,[c] Anup Pandith,[d] M. N. Satyanarayan,[e] D. S. Shankar Rao,[f] S. Krishna Prasad,[f] Airody Vasudeva Adhikari *[a]

[a] Organic Materials Laboratory, Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Mangalore-575 025, India. [b] Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati-781 039, India. [c] SCM group, Raman Research Institute, C.V. Raman Avenue, Sadashivanagar, Bangalore-560 080, India.[d] Department of Chemistry, Chonbuk National University, Jeonju, Republic of Korea-54398. [e] Department of Physics, National Institute of Technology Karnataka, Surathkal, Mangalore-575025, India. [f] Centre for Nano and Soft Matter Sciences, Jalahalli, Bangalore-560 013, India.

Supporting information

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1. Materials and methods

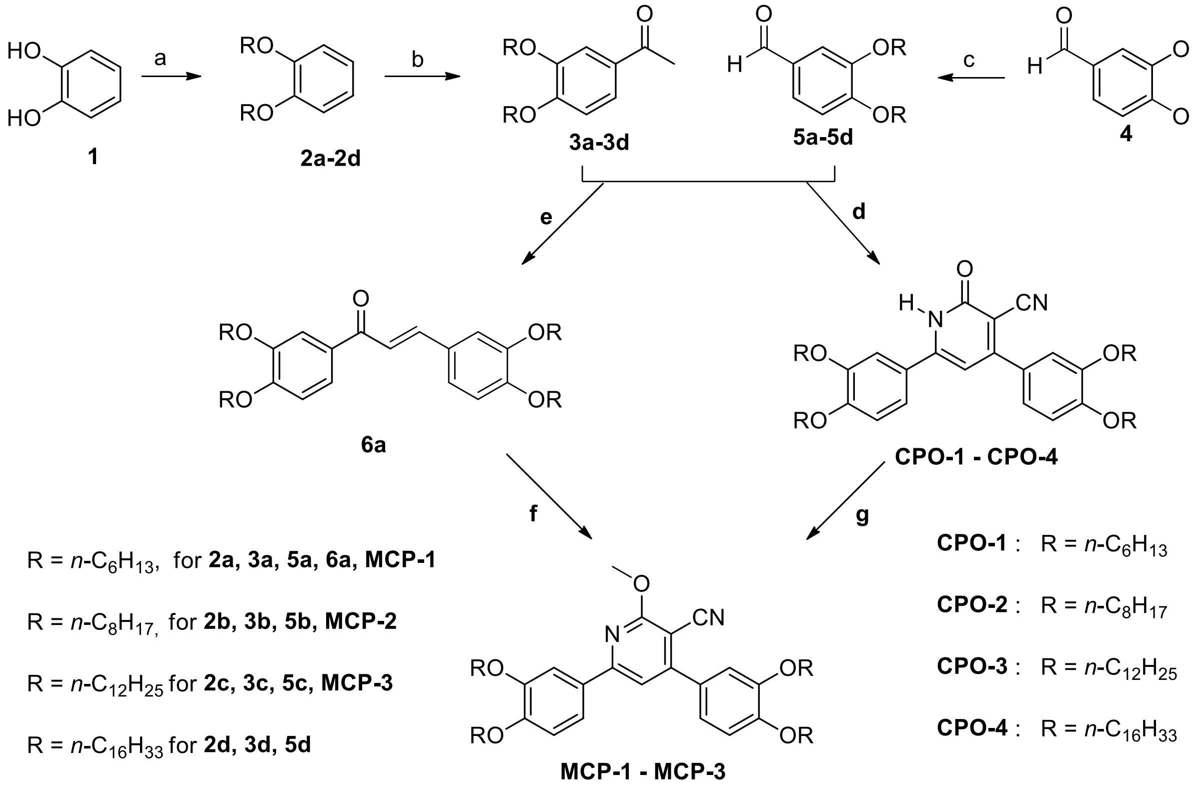
General: All the required chemicals such as catechol, 3,4-dihydroxybenzaldehyde, different *n*-alkylbromides, ethyl cyanoacetate, common organic and inorganic salts were purchased from Sigma Aldrich, Merck, Spectrochem and SD's Fine Chem. Ltd. and used without any further purifications. The solvents were purchased from local companies and dried using standard procedures. The reactions were performed under inert atmosphere and completion of the reaction was monitored by TLC technique. Chromatographic separations were carried out using silica gel of mesh size 100-200 and 230-400. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker AMX 500 MHz, in $CDCl_3$ and TMS was used as an internal standard. FT-IR spectra were obtained by Bruker alpha Fourier transform IR spectrometer using ATR method. Elemental analysis was performed on a Carlo-Erba Flash 1112 analyser. Differential Scanning Calorimetry (DSC) thermograms of final compounds were obtained at the temperature range of -60 ^{0}C to 70 ^{0}C using Parkin-Elmer Pyris-1 DSC. Optical textures of mesophases were observed using Olympus BX51 Polarized Optical Microscope (POM) in conjunction with a Mettler FP82HT hot stage and FP90 central processor. Variable temperature powder X-ray diffraction (XRD) measurements of unoriented samples filled in a Lindemann capillary of diameter of 1 mm (Hampton Research) were carried out on DY 1042-Empyrean XRD with Pixel 3D detector at Cu-Kα radiation. UV-visible spectra of all the liquid crystalline materials were recorded at room temperature using SPECORD S 600 spectrophotometer. Further, the Fluorescence spectra were acquired on a Perkin Elmer LS55 Fluorescence spectrophotometer. Electrochemical properties of LC materials were studied by using CH-instrument connected to CHI660E software. The CV experiments were carried out by employing Ag/AgCl as reference electrode; calibrated with ferrocene/ferrocenium (Fc/Fc^+) redox couple, which has the absolute energy 4.8 eV to vacuum, glassy carbon working electrode, platinum wire as counter electrode, Tetrabutyl ammonium perchlorate (0.1 M) as supporting electrolyte in dichloromethane solvent. Theoretical calculations were made using the SPARTAN 10 program. Geometry optimizations were performed using the Becke three-parameter exchange functional and the Lee-Yang-Parr B3LYP exchange correlation functionals with the 6-31+G* basis set for C, H, N, and O. Calculations were performed under vacuum.

Device Fabrication and Measurement:

Patterned indium tin oxide (ITO, Kintec, Hong Kong) coated glass substrates with a sheet resistance of 15 Ω/□ and ITO thickness of 120 nm were used as transparent anodes. Prior to the deposition of organic materials, the ITO substrates were treated by the UV-Ozone after a careful chemical cleaning process.[1] All the organic and cathode materials were used as received without further purification. A 50 nm thick poly(3,4-ethylenedioxy-thiophene)/poly(styrene-sulfonate) (PEDOT: PSS, Sigma Aldrich) film was used as hole injection material and was spin-coated on the ITO substrates from aqueous dispersion and baked at 120 °C for 30 min. Subsequently, **CPO-2** (**device A**) or a mixture of **CPO-2** (10 wt.%) and the Poly(9-vinylcarbazole) (PVK) host (device **B/C/D**) was spin-coated onto the PEDOT: PSS layer, the thickness of which was controlled as 80 nm by adjusting the solution concentration and the spin rate. The substrates after coating the emission layer was annealed at 140 ^{o}C for 2 h and slowly cooled at a rate of 1 ^{o}C/min. In case of device **D**, PVK was also used as a hole transport material. The substrates were then transferred into a deposition chamber to deposit the remaining layers with a base pressure of 10^{-5} torr. On the substrate, Bathocuproine (BCP, Sigma Aldrich) as the hole blocking material and tris-(8-hydroxyquinoline)aluminum (Alq_3, Sigma Aldrich) as the electron transport material were deposited in sequences and thicknesses appropriate for the intended device structure by thermal evaporation. Alq_3 is being widely used as a green emitting electron transporting material and in the present device architecture it was used as electron transporting material to facilitate electron injection into the emitting layer. Finally, to improve electron injection, a bilayer cathode consisting of lithium fluoride (LiF, Sigma Aldrich) and aluminum (Al, Alfa Aesar) layers were sequentially deposited on the electron transporting material as the cathode. Here, LiF works as electron injecting material. All organic materials and cathode layers were deposited by thermal evaporation at a chamber pressure of 5 x 10^{-6} Torr and the devices were never exposed to air during fabrication. The deposition rates of organic materials, LiF and Al were maintained at 0.5 Å s^{-1}, 0.1 Å s^{-1} and 6 Å s^{-1}, respectively. The deposition rate and thickness of the deposited layers were monitored and controlled *in situ* by a quartz crystal thickness monitor placed near the substrate. The cathode was deposited on the top of the structure through a shadow mask. The light-emitting area was 1.6 mm^2 as defined by the overlap of the cathode and anode. Electroluminescence spectra was acquired using a Horiba Jobin Yvon iHR320 spectrophotometer with an attached charge-coupled device (CCD) camera. Opto-electrical characteristics were recorded in a customized setup using a computer-controlled programmable Keithley 2400 SMU for recording the current-voltage characteristics while the luminance was measured by a Keithley 6485 picoammeter using a calibrated Si photodiode (SM1PD2A). CIE coordinates were calculated from the EL spectra. Devices were driven under DC conditions.

All the measurements were carried out at room temperature under dark and ambient conditions without any encapsulation.

2. Synthesis scheme



Scheme 1: a) RBr, K_2CO_3, KI, DMF, 70 °C, 70-85 %; b) CH_3COCl, anhydrous $AlCl_3$, dry DCM, -5-0 °C, 85-92%; c) K_2CO_3, RBr, DMF, 80 °C, 65-85%; d) Ethyl cyanoacetate, $AcONH_4$, EtOH, 70 °C, 25-40%; e) Aqueous KOH, EtOH, RT, 83 %; f) Malononitile, NaOMe, MeOH, RT, 40 %; g) MeI, K_2CO_3, DMF, 45 °C, 85-90%

3. Experimental methods

General procedure for the synthesis of compounds, **3a-d**

Under argon atmosphere, the compound 1,2-dihexyloxybenzene **2a** (2g, 7.18 mmol, 1 equv.) was dissolved in 30 mL of dry DCM and cooled to -5 °C using NaCl/ice bath. To the stirred reaction mixture, anhydrous $AlCl_3$ (1 g 7.9 mmol, 1.1 equiv.) was added in small portions. Then, acetyl chloride (0.56 mL, 7.9 mmol, 1.1 equiv.) was added drop-wise and the mixture was stirred at -5 °C. After 30 min, the mixture was warmed to room temperature and continue the stirring for another 30 min. The mixture was poured into 50 mL of ice cooled water and the separated compound was extracted with DCM (2×50 mL). The combined DCM layers were washed with saturated $NaHCO_3$, then with brine and evaporated to dryness. The crude product was recrystallized using methanol to get white solid product **3a**, (Yield, 92 %). IR (ATR): ν_{max} in cm^{-1} 2955, 2954, 2928 (Ar C-H), 2857 (Aliph C-H), 1669 (C=O), 1584 (Ar C=C).). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.55 (d, 1H, *J* = 8.0 Hz, Ar-$\underline{H}$), 7.52 (s, 1H, Ar-$\underline{H}$), 6.87 (d, 1H, *J* = 8.5 Hz, Ar-$\underline{H}$) 4.06 (m, 4H, $2\times OC\underline{H_2}$), 2.56 (s, 3H, $COC\underline{H_3}$), 1.88 – 1.81 (m, 4H, $2\times O\text{-}CH_2\text{-}C\underline{H_2}$), 1.49 (m, 4H, $2\times C\underline{H_2}$), 1.36 (m, 8H, $4\times C\underline{H_2}$), 0.92 (t, 6H, *J* = 6.5 Hz, $2\times C\underline{H_3}$). ^{13}C NMR ($CDCl_3$, 125 MHz): 196.87, 153.52, 148.84, 130.25, 123.18, 112.33, 111.52, 69.11, 31.55, 29.07, 26.20, 25.65, 22.59, 13.99. Elemental Anal. Calcd for $C_{20}H_{32}O_3$ (%): C, 74.96; H, 10.06; Found: C, 74.95, H, 10.08.

The compounds **3b**, **3c** and **3d** were synthesized by adopting similar procedure as described for the synthesis of **3a**.

For **3b**, (Yield, 89 %). IR (ATR): ν_{max} in cm^{-1} 2958, 2952, 2928 (Ar C-H), 2855 (Aliph C-H), 1669 (C=O), 1583 (Ar C=C).). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.54 (d, 1H, *J* = 8.0 Hz, Ar-$\underline{H}$), 7.52 (s, 1H, Ar-$\underline{H}$), 6.87 (d, 1H, *J* = 8.0 Hz, Ar-$\underline{H}$) 4.06 (m, 4H, $2\times O\text{-}C\underline{H_2}$), 2.56 (s, 3H, $COC\underline{H_3}$), 1.87 – 1.83 (m, 4H, $2\times OCH_2\text{-}C\underline{H_2}$), 1.48 (m, 4H, $2\times C\underline{H_2}$), 1.37- 1.30 (m, 16H, $8\times C\underline{H_2}$), 0.89 (t, 6H, *J* = 6.5 Hz, $2\times C\underline{H_3}$). ^{13}C NMR ($CDCl_3$, 125 MHz): 196.85, 153.53, 148.84, 130.26, 123.18, 112.36, 111.54, 69.17, 31.81, 29.23, 26.20, 26.00, 22.67, 14.09. Elemental Anal. Calcd for $C_{24}H_{40}O_3$ (%): C, 76.55; H, 10.71. Found: C, 76.58; H, 10.61.

For **3c**, (Yield, 90 %). IR (ATR): ν_{max} in cm^{-1} 2958, 2953, 2927 (Ar C-H), 2849 (Aliph C-H), 1666 (C=O), 1590 (Ar C=C).). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.55 (d, 1H, *J* = 8.5 Hz, Ar-$\underline{H}$), 7.52 (s, 1H, Ar-$\underline{H}$), 6.87 (d, 1H, *J* = 8.5 Hz, Ar-$\underline{H}$) 4.06 (m, 4H, $2\times OC\underline{H_2}$), 2.56 (s, 3H, $COC\underline{H_3}$), 1.87 – 1.81 (m, 4H, $2\times OCH_2\text{-}C\underline{H_2}$), 1.48 (m, 4H, $2\times C\underline{H_2}$), 1.33 (m, 32H, $16\times C\underline{H_2}$), 0.89 (t, 6H, *J* = 6.5 Hz, $2\times C\underline{H_3}$). ^{13}C NMR ($CDCl_3$, 125 MHz): 196.88, 153.54, 148.84, 130.26, 123.18, 112.37, 111.55, 69.13, 30.81, 29.50, 26.20, 26.01, 22.69, 14.11. Elemental Anal. Calcd for $C_{32}H_{56}O_3$ (%): C, 78.63; H, 11.55; O, 9.82. Found: C, 78.63; H, 11.58; O, 9.78.

For **3d**, (Yield, 90 %). IR (ATR): ν_{max} in cm^{-1} 2955, 2951, 2930 (Ar C-H), 2859 (Aliph C-H), 1668 (C=O), 1593 (Ar C=C).). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.55 (d, 1H, *J* = 8.5 Hz, Ar-$\underline{H}$), 7.53 (s, 1H, Ar-$\underline{H}$), 6.88 (d, 1H, *J* = 8.5 Hz, Ar-$\underline{H}$) 4.06 (m, 4H, $2\times OC\underline{H_2}$), 2.57 (s, 3H, $COC\underline{H_3}$), 1.89 – 1.82 (m, 4H, $2\times OCH_2\text{-}C\underline{H_2}$), 1.49 (m, 4H, $2\times C\underline{H_2}$), 1.34 (m, 48H, $24\times C\underline{H_2}$), 0.89 (t, 6H, *J* = 6.5 Hz, $2\times C\underline{H_3}$). ^{13}C NMR ($CDCl_3$, 125 MHz): 196.89, 153.54, 148.85, 130.26, 123.18, 112.37, 111.54, 69.14, 31.94, 29.65, 26.22, 25.99, 22.70, 14.12. Elemental Anal. Calcd for $C_{40}H_{72}O_3$ (%) C, 79.94; H, 12.08. Found: C, 79.86; H, 12.03.

General procedure for the synthesis of 4,6-bis(3,4-dialkoxyphenyl)-2-oxo-1,2-dihydropyridine-3-carbonitriles, **CPO-1 to COP-4**

An equimolar mixture of 1-(3,4-dihexyloxyphenyl)ethanone **3a** (2 g, 6.24 mmol, 1equiv.) and 3,4-dihexyloxybenzaldehyde **5a** (1.91 g, 6.24 mmol, 1 equiv.) was taken in 50 mL of ethanol. The mixture was warmed to 60 °C to get clear solution. Then, ethyl cyanoacetate (0.8 mL, 6.9 mmol, 1.1 equiv.) and ammonium acetate (7.2 g, 93.6 mmol, 15 equiv.) were added and the mixture was heated to 70 °C for 12 h. After completion of the reaction, the obtained precipitate was filtered and washed with ethanol to obtain yellow solid, **CPO-1**. The crude was purified by column chromatography with silica gel of 100-200 mesh using 1:3 pet-ether (60-70°C) and dichloromethane as eluent (Yield, 40 %) IR (ATR): ν_{max} in cm^{-1} 2922 (Ar C-H), 2854 (Aliph C-H), 2217 (C≡N), 1653 (C=O), 1600 (Ar C=C). ^1H NMR ($CDCl_3$, 500 MHz): δ 12.81 (s, 1H, CON$\underline{H}$), 7.52 (dd, 1H, *J* = 8.5, 2.0 Hz, Ar-$\underline{H}$), 7.39 (d, 1H, *J* = 2.5 Hz, Ar-$\underline{H}$), 7.27 (dd, 1H, *J* = 8.0, 2.0 Hz, Ar-$\underline{H}$), 7.26 (d, 1H, *J* = 2.0 Hz, Ar-$\underline{H}$), 7.04 (d, 1H, *J* = 8.5 Hz, Ar-$\underline{H}$), 7.01 (d, 1H, *J* = 8.0 Hz, Ar-$\underline{H}$), 6.68 (s, 1H, pyridone-$\underline{H}$), 4.22 (t, 2H, *J* = 6.5 Hz, $OC\underline{H}_2$), 4.08 (m, 6H, $3\times OC\underline{H}_2$), 1.92-1.85 (m, 8H, $4\times OCH_2\text{-}C\underline{H}_2$), 1.53 (t, 8H, *J* = 7.0 Hz, $4\times C\underline{H}_2$),1.39-1.36 (m, 16H, $8\times C\underline{H}_2$), 0.95 (t, 12H, *J* = 6.5 Hz, $4\times C\underline{H}_3$). ^{13}C NMR ($CDCl_3$, 125 MHz): 164.14, 160.57, 152.51, 151.44, 150.42, 149.79, 149.10, 128.52, 124.05, 121.46, 120.76, 116.45, 113.71, 113.23, 112.07, 105.79, 97.78, 69.56, 31.60, 29.14, 25.69, 22.61, 14.02. Elemental Anal. Calcd for $C_{42}H_{60}N_2O_5$ (%): C, 74.96; H, 8.99; N, 4.16. Found: C, 74.81; H, 9.261; N, 4.10.

The compounds **CPO-2**, **CPO-3** and **CPO-4** were synthesized by adopting similar procedure as described for the synthesis of **CPO-1**.

For **CPO-2**, yellow amorphous solid (Yield = 36 %). IR (ATR): ν_{max} in cm^{-1} 2915 (Ar C-H), 2851(Aliph C-H), 2216 (C≡N), 1653 (C=O), 1600 (Ar C=C). ^1H NMR ($CDCl_3$, 500 MHz): δ 12.95 (s, 1H, CON$\underline{H}$), 7.52 (dd, 1H, *J* = 8.5, 2.0 Hz, Ar-$\underline{H}$),7.40 (d, 1H, *J* = 2.0 Hz, Ar-$\underline{H}$), 7.28 (dd, 1H, *J* = 8.0 Hz, 2.0 Hz, Ar-$\underline{H}$), 7.25 (d, 1H, *J* = 2.0 Hz, Ar-$\underline{H}$),7.04 (d, 1H, *J* = 8.5 Hz, Ar-$\underline{H}$), 7.01 (d, 1H, *J* = 8.5 Hz, Ar-$\underline{H}$), 6.68 (s, 1H, pyridone-$\underline{H}$), 4.22 (t, 2H, *J* = 6.5 Hz, $OC\underline{H}_2$) 4.08 (m, 6H, $3\times OC\underline{H}_2$), 1.90-1.85 (m, 8H, $4\times OCH_2\text{-}C\underline{H}_2$), 1.54-1.48 (m, 8H, $4\times C\underline{H}_2$) 1.38-1.35 (m, 32H, $16\times C\underline{H}_2$), 0.95 (t, 12H, *J* = 6.5 Hz, $4\times C\underline{H}_3$). ^{13}C NMR ($CDCl_3$, 125 MHz): 164.24, 160.55, 152.51, 151.44, 150.48, 149.78. 149.10, 128.53, 124.05, 121.47, 120.81, 116.47, 113.72, 113.32, 112.14, 105.81, 97.74, 69.57, 31.83, 29.30, 26.00, 22.68, 14.11. Elemental

Anal. Calculated for $C_{50}H_{76}N_2O_5$ (%): C, 76.49; H, 9.76; N, 3.57. Found: C, 76.31; H, 10.364; N, 3.53.

For **CPO-3**, yellow amorphous solid (Yield = 36 %). IR (ATR): ν_{max} in cm^{-1} 2951 (Ar C-H), 2851 (Aliph C-H), 2217 (C≡N), 1654 (C=O), 1601 (Ar C=C). ^1H NMR ($CDCl_3$, 500 MHz): δ 12.60 (s, 1H, CON$\underline{H}$), 7.50 (dd, 1H, *J* = 8.5, 2.0 Hz, Ar-$\underline{H}$), 7.37 (d, 1H, *J* = 2.0 Hz, Ar-$\underline{H}$), 7.28 (dd, 1H, *J* = 8.0, 2.0 Hz, Ar-$\underline{H}$), 7.25 (d, 1H, *J* = 2.0 Hz, Ar-$\underline{H}$), 7.04 (d, 1H, *J* = 8.5 Hz, Ar-$\underline{H}$), 7.01 (d, 1H, *J* = 8.0 Hz, Ar-$\underline{H}$), 6.67 (s, 1H, pyridone-$\underline{H}$), 4.21 (t, 2H, *J* = 6.5 Hz, OC$\underline{H_2}$), 4.09 (m, 6H, 3×OC$\underline{H_2}$), 1.87 (t, 8H, *J* = 6.5 Hz, 4×OCH_2-C$\underline{H_2}$), 1.54-1.27 (m, 72H, 36×C$\underline{H_2}$), 0.90 (m, 12H, 4×C$\underline{H_3}$). ^{13}C NMR ($CDCl_3$, 125 MHz): 164.31, 160.53, 152.52, 151.44, 150.52, 149.78, 149.10, 128.54, 124.03, 121.47, 120.85, 116.49, 113.72, 113.23, 112.18, 105.83, 97.69, 69.56, 31.94, 21.45, 26.0, 22.70, 14.12. Elemental Anal. Calculated for $C_{66}H_{108}N_2O_5$ (%): C, 78.52; H, 10.78; N, 2.77. Found: C, 77.46; H, 10.925; N, 3.07.

For **CPO-3**, yellow amorphous solid (Yield 35 %). IR (ATR): ν_{max} in cm^{-1} 2915 (Ar C-H), 2850 (Aliph C-H), 2217 (C≡N), 1656 (C=O), 1602 (Ar C=C). ^1H NMR ($CDCl_3$, 500 MHz): δ 12.54 (s, 1H, CON$\underline{H}$), 7.40 (dd, 1H, *J* = 8.5, 2.0 Hz, Ar-$\underline{H}$), 7.28 (d, 1H, *J* = 2.0 Hz, Ar-$\underline{H}$), 7.18 (dd, 1H, *J* = 8.0, 2.0 Hz, Ar-$\underline{H}$), 7.15 (d, 1H, *J* = 2.0 Hz, Ar-$\underline{H}$), 6.93 (d, 1H, *J* = 8.5 Hz, Ar-$\underline{H}$), 6.54 (d, 1H, *J* = 8.5 Hz, Ar-$\underline{H}$), δ 6.57 (s, 1H, pyridone-$\underline{H}$), 4.11 (t, 2H, *J* = 6.5 Hz, O-C$\underline{H_2}$), 4.0 (t, 6H, *J* = 6.5 Hz, 3×OC$\underline{H_2}$), 1.78-1.74 (m, 8H, 4×OCH_2-C$\underline{H_2}$),1.41-1.18 (m, 104H, 52×C$\underline{H_2}$), 0.80 (m, 12H, 4×C$\underline{H_3}$).). ^{13}C NMR ($CDCl_3$, 125 MHz): 164.02, 160.58, 152.51, 151.47, 150.34, 149.79, 149.11, 124.06, 121.48, 120.69, 116.44, 113.73, 113.22, 112.03, 105.74, 97.81, 69.57, 31.94, 29.43, 26.0, 22.70, 14.12. Elemental Anal. Calculated for $C_{82}H_{140}N_2O_5$ (%): C, 79.81; H, 11.44; N, 2.27. Found: C, 79.56; H, 11.862; N, 2.30.

Synthesis of the intermediate **6a**

An equimolar mixture of **4a** (1g, 3.26 mmol, 1 equiv.) and **3a** (1 g, 3.26 mmol, 1 equiv.) was dissolved in ethanol, to which 50% of aqueous KOH (0.64 g, 11.42 mmol, 3.5 equiv.) was added drop-wise. After stirring at room temperature for 5 hours, the resulted greenish yellow precipitate was filtered and washed with ethanol. Finally recrystallization with DCM and methanol offered the tittle compound as greenish yellow solid (Yield 83 %). IR (ATR): ν_{max} in cm^{-1} 2951 (Ar C-H), 2923 (Ar C-H),, 2857 (Aliph C-H), 1657 (C=O), 1574 (Ar C=C). ^1H NMR ($CDCl_3$, 500 MHz): δ 7.75 (d, 1H, *J* = 15.5 Hz, Olefinic-$\underline{H}$), 7.66 (d, 1H, *J* = 8.0 Hz, Ar-$\underline{H}$), 7.62 (s, 1H, Ar-$\underline{H}$), 7.41 (d, 1H, *J* = 15.5 Hz, Olefinic-$\underline{H}$), 7.22 (d, 1H, *J* = 8.5 Hz, Ar-$\underline{H}$), 7.19 (s, 1H, Ar-$\underline{H}$), 6.93 (d, 1H, *J* = 8.0 Hz, Ar-$\underline{H}$), 6.90 (d, 1H, *J* = 8.5 Hz, Ar-$\underline{H}$), 4.1-4.0 (m, 8H, 4×OC$\underline{H}_2$), 1.89-1.85 (m, 8H, 4×OCH$_2$-C$\underline{H}_2$), 1.51 (m, 8H, 4×C$\underline{H}_2$), 1.37 (m, 16H, *J* = 6.5 Hz, 8×C$\underline{H}_2$), 0.93 (m, 12H, 4×CH$_3$). ^{13}C NMR (CDCl$_3$, 125 MHz): 188.79, 153.33, 151.57, 149.13, 144.12, 131.40, 128.01, 122.90, 69.24, 31.59, 29.15, 25.68, 22.61, 14.02. Elemental Anal. Calculated for $C_{39}H_{60}O_5$ (%): C, 76.93; H, 9.93. Found: C, 76.99; H, 10.95.

Synthesis of **MCP-1** from chalcone **6a** (method-1)

To a suspension of chalcone **6a** (1 g, 1.48 mmol, 1 equiv.) in 20 mL of anhydrous methanol, sodium methoxide (0.83g, 14.87mmol 10 equiv.) was added portion-wise. Malononitrile (0.11 g, 1.63 mmol, 1.1 equiv.) was then added to it and stirred for 10 hrs at ambient temperature. The obtained pale yellow precipitate was filtered and washed repeatedly with methanol. The crude solid was purified by silica gel (100-200 mesh size) column chromatography using 5% ethyl acetate in pet-ether (60-70 °C) as mobile phase to yield **MCP-1** as pale white solid (Yield = 40%). IR (ATR): ν_{max} in cm^{-1} 2917 (Ar C-H), 2848 (Aliph C-H), 2219 (C≡N), 1578 (Ar C=C). ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.7 (s, 1H, Ar-$\underline{H}$), 7.67 (d, *J* = 8.5 Hz, 1H, Ar-$\underline{H}$), 7.39 (s, 1H, Ar-$\underline{H}$), 7.24 (d, *J* = 8.5 Hz, 1H, Ar-$\underline{H}$), 7.22 (s, 1H, Ar-$\underline{H}$), 7.01 (d, *J* = 8.5 Hz, 1H, Ar-$\underline{H}$), 6.97 (d, *J* = 8.5 Hz, 1H, Ar-$\underline{H}$), 4.20 (s, 1H, OC$\underline{H}_3$), 4.13-4.07 (m, 8H, 4×OC$\underline{H}_2$), 1.88 (m, 8H, 4×OCH$_2$-C$\underline{H}_2$), 1.50 (m, 8H, 4×C$\underline{H}_2$), 1.38-1.28 (m, 8H, 8×C$\underline{H}_2$), 0.925 (m, 12H, 4× C$\underline{H}_3$). ^{13}C NMR (CDCl$_3$, 125 MHz): 165.08, 157.56, 156.21, 151.59, 150.82, 149.17, 130.17, 128.86, 121.41, 120.71, 116.21, 114.02, 113.40, 113.08, 112.54, 91.68, 69.41, 54.38, 31.93, 29.70, 29.60, 29.45, 29.36, 29.24, 26.05, 22.70, 14.12. Elemental Anal. Calculated for $C_{43}H_{62}N_2O_5$

Synthesis of **MCP-1** from cyanopyridone **CPO-1** (method-2)

A mixture of **CPO-1** (0.5 g, 0.821 mmol, 1 equiv.), anhydrous K_2CO_3 (0.17 g, 1.23mmol, 1.5 equiv.) and methyl iodide (0.041 g, 0.98 mmol, 1.1 equiv.) in 15 ml of dry DMF was stirred at 45 °C for overnight. After completion of the reaction, the mixture was poured into ice and obtained precipitate was filtered and washed with water. It was further purified by silica gel (100 -200 mesh size) column chromatography using 5% ethyl acetate in pet-ether as eluents offered white solid (Yield = 90 %). The spectroscopic properties were identical to the compound obtained by method-1

The compounds **MCP-2** was prepared as described in method-2 (Yield = 88%) IR (ATR): ν_{max} in cm^{-1} 2920 (Ar C-H), 2848 (Aliph C-H), 2218 (C≡N), 1578 (Ar C=C). ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.7 (s, 1H, Ar-$\underline{H}$), 7.67 (d, *J* = 8.5 Hz, 1H, Ar-$\underline{H}$), 7.39 (s, 1H, Ar-$\underline{H}$), 7.24 (d, *J* = 8.5 Hz, 1H, Ar-$\underline{H}$), 7.22 (s, 1H, Ar-$\underline{H}$), 7.01 (d, *J* = 8.5 Hz, 1H, Ar-$\underline{H}$), 6.97 (d, *J* = 8.5 Hz, 1H, Ar-$\underline{H}$), 4.20 (s, 1H, OC$\underline{H}_3$), 4.20-4.07 (m, 8H, 4×OC$\underline{H}_2$), 1.88 (m, 8H, 4×OCH$_2$-C$\underline{H}_2$), 1.51 (m, 8H, 4×$C\underline{H}_2$), 1.39-1.31 (m, 8H, 16× $C\underline{H}_2$), 0.925 (t, 12H, *J* = 5.0 Hz, 4× $C\underline{H}_3$). ^{13}C NMR ($CDCl_3$, 125 MHz): 165.07, 157.55, 156.21, 151.60, 150.83, 149.18, 130.18, 128.86, 121.41, 120.72, 116.20, 114.04, 113.41, 113.10, 112.53, 91.68, 69.33, 54.37, 31.84, 29.34, 26.06, 22.64, 14.11. Elemental Anal. Calculated for $C_{51}H_{78}N_2O_5$ (%): C, 76.65; H, 9.84; N, 3.51. Found: C, 76.66; H, 9.90; N, 3.52.

MCP-3 was also synthesized by adopting the method-2 (Yield = 85%) IR (ATR): ν_{max} in cm^{-1} 2955 (Ar C-H), 2849 (Aliph C-H), 2223 (C≡N), 1590 (Ar C=C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.6 (s, 1H, Ar-$\underline{H}$), 7.57 (d, *J* = 8.5 Hz, 1H, Ar-$\underline{H}$), 7.18 (s, 1H, pyridine-$\underline{H}$), 7.14 (d, *J* = 8.5 Hz, 1H, Ar-$\underline{H}$), 7.12 (s, 1H, Ar-$\underline{H}$), 7.91 (d, *J* = 8.5 Hz, 1H, Ar-$\underline{H}$), 6.88 (d, *J* = 8.5 Hz, 1H, Ar-$\underline{H}$), 4.10 (s, 1H, pyridine-$OC\underline{H}_3$), 4.10-3.97 (m, 8H, 4×$OC\underline{H}_2$), 1.78 (m, 8H, 4×OCH_2-$C\underline{H}_2$), 1.41 (m, 8H, 4×$C\underline{H}_2$), 1.39-1.31 (m, 64H, 32× $C\underline{H}_2$), 0.80 (m, 12H, 4× $C\underline{H}_3$). ^{13}C NMR ($CDCl_3$, 125 MHz): 165.08, 157.55, 156.21, 151.61, 150.84, 149.19, 130.18, 128.87, 121.41, 120.71, 116.20, 114.05, 113.42, 113.11, 112.53, 91.69, 69.34, 54.37, 31.94, 29.24, 27.57, 22.71, 14.12. Elemental Anal. Calculated for $C_{67}H_{110}N_2O_5$ (%): C, 78.59; H, 10.90; N, 2.71.

4. IR spectra

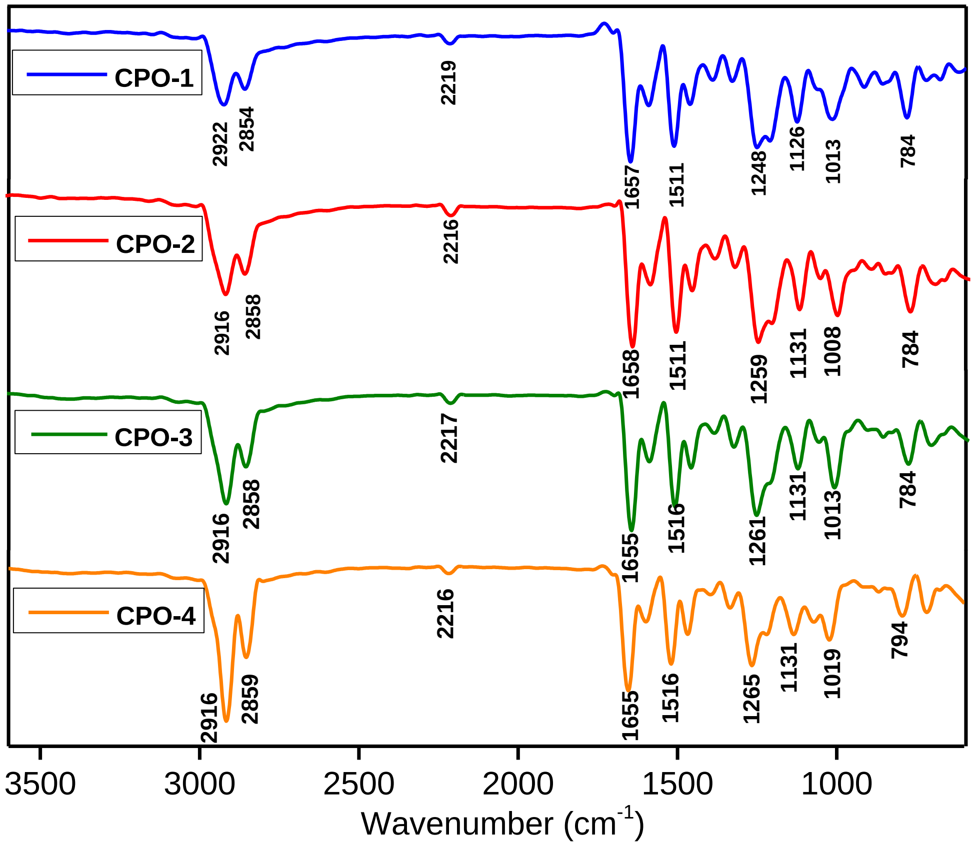


Figure S1: FTIR spectrum of **CPO-1** to **CPO-4**

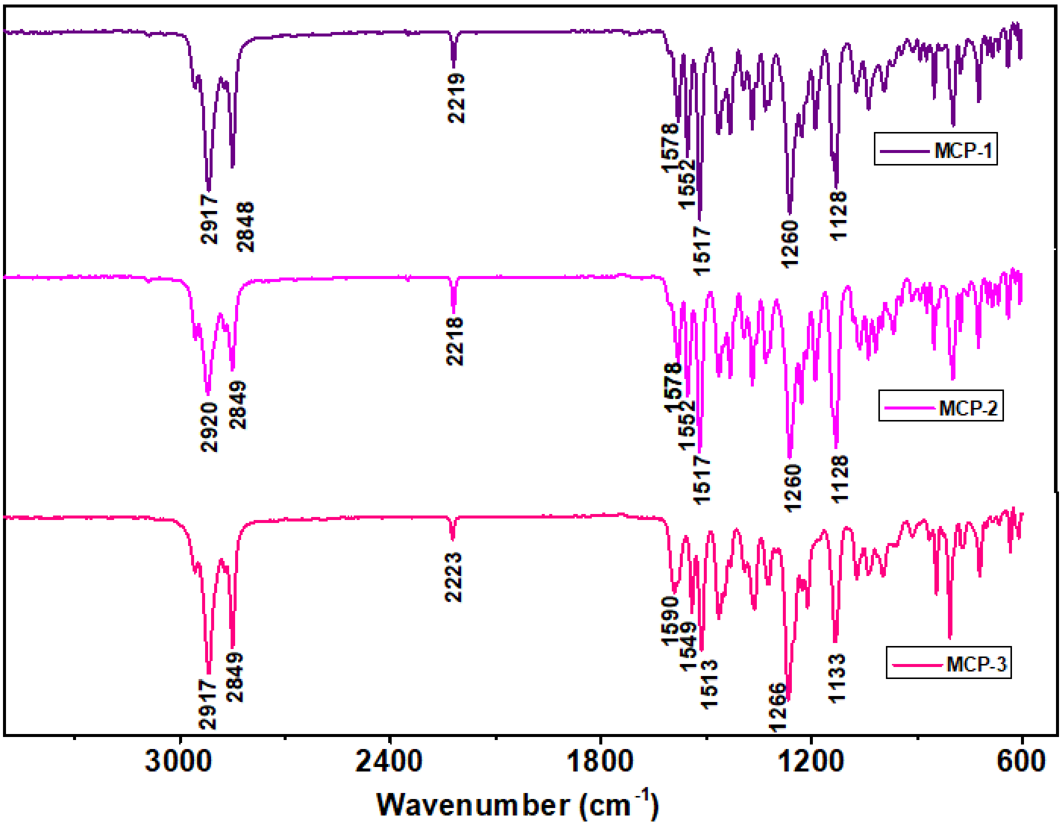


Figure S2: FTIR spectrum of **MCP-1** – **MCP-3**

5. NMR spectra

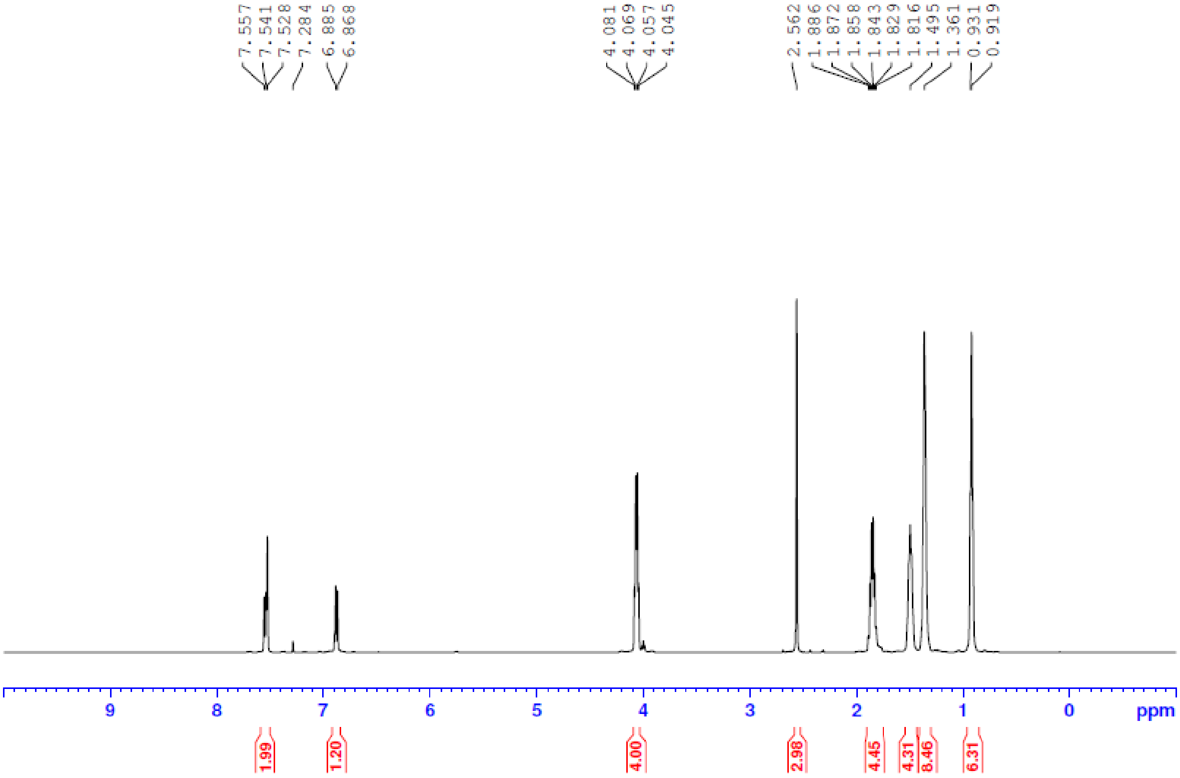


Figure S3: ^{1}H NMR spectrum of **3a** recorded in $CDCl_3$

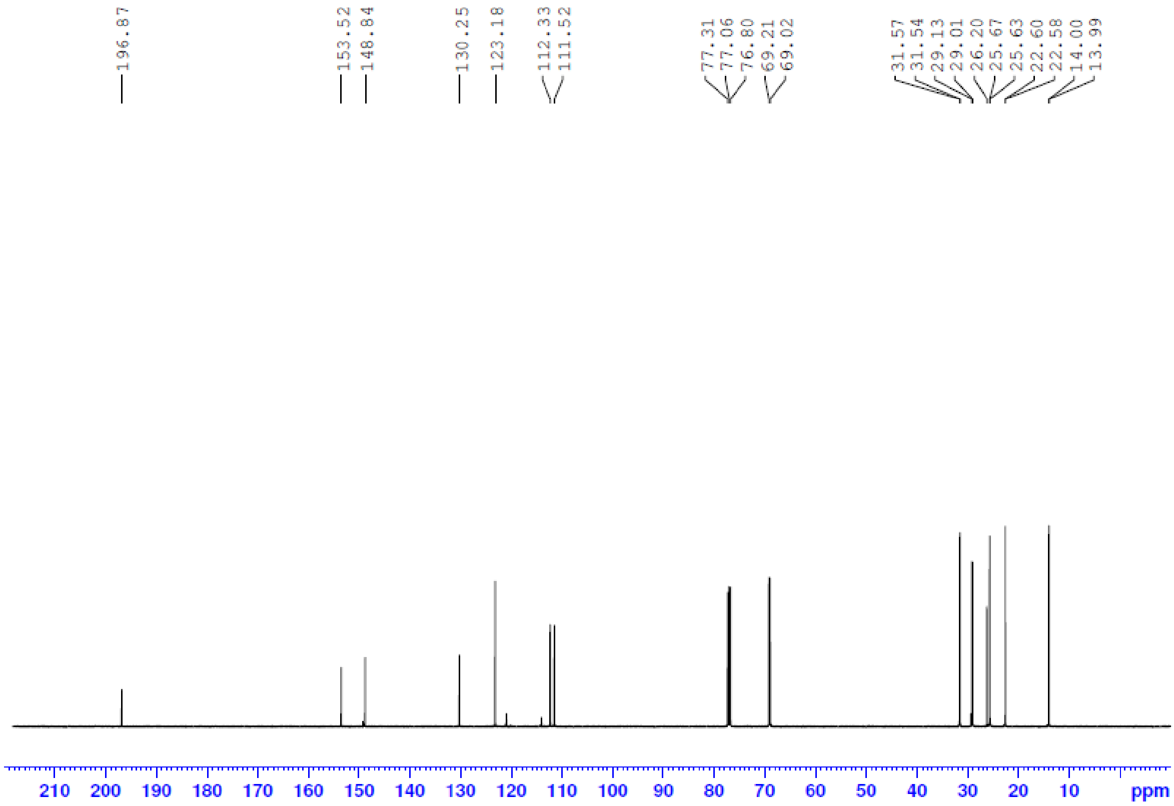


Figure S4: ^{13}C NMR spectrum of **3a** recorded in CDCl$_3$

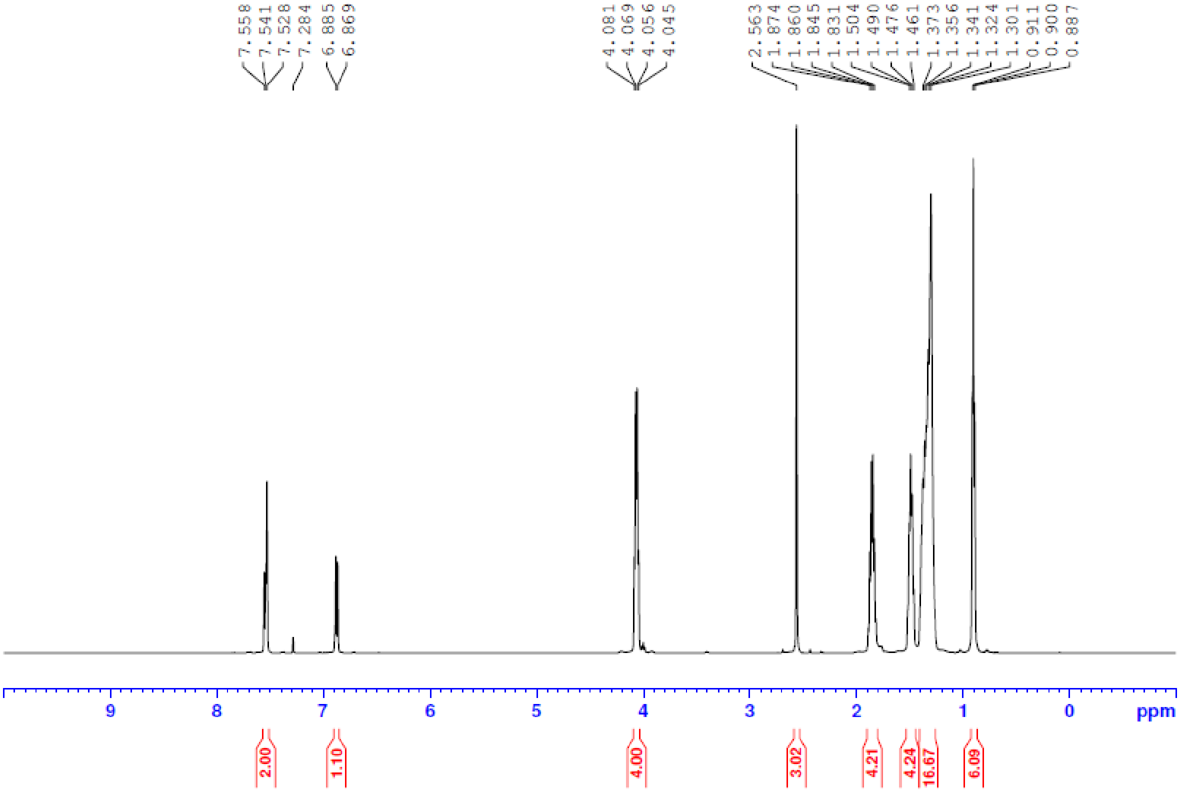


Figure S5: ^{1}H NMR spectrum of **3b** recorded in CDCl$_3$

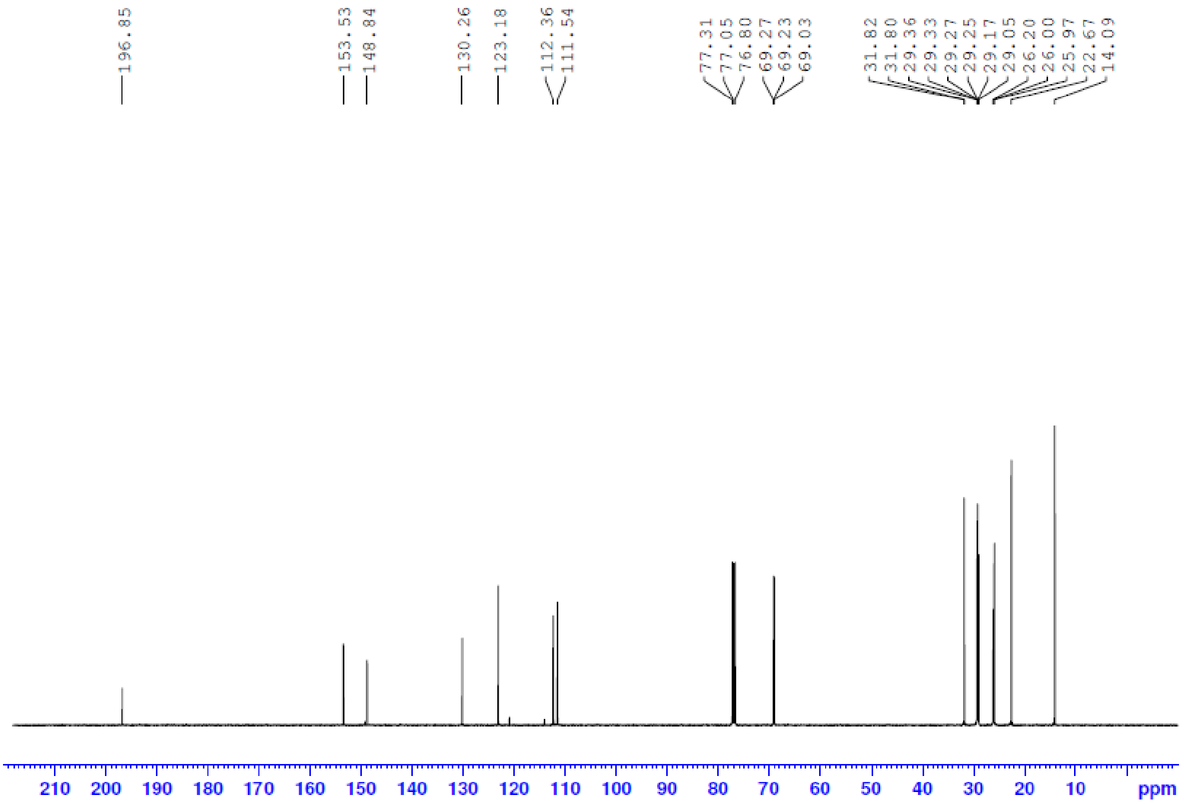


Figure S6: ^{13}C NMR spectrum of **3b** recorded in $CDCl_3$

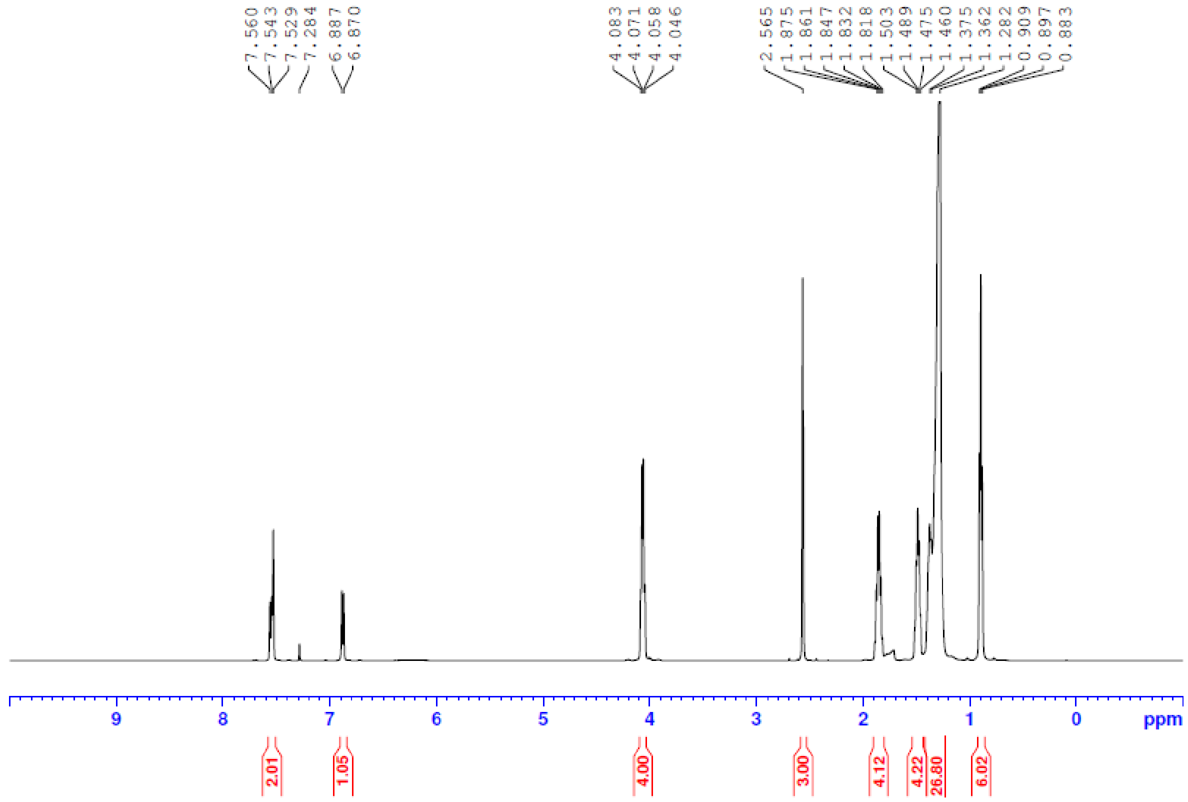


Figure S7: ^{1}H NMR spectrum of **3c** recorded in $CDCl_3$

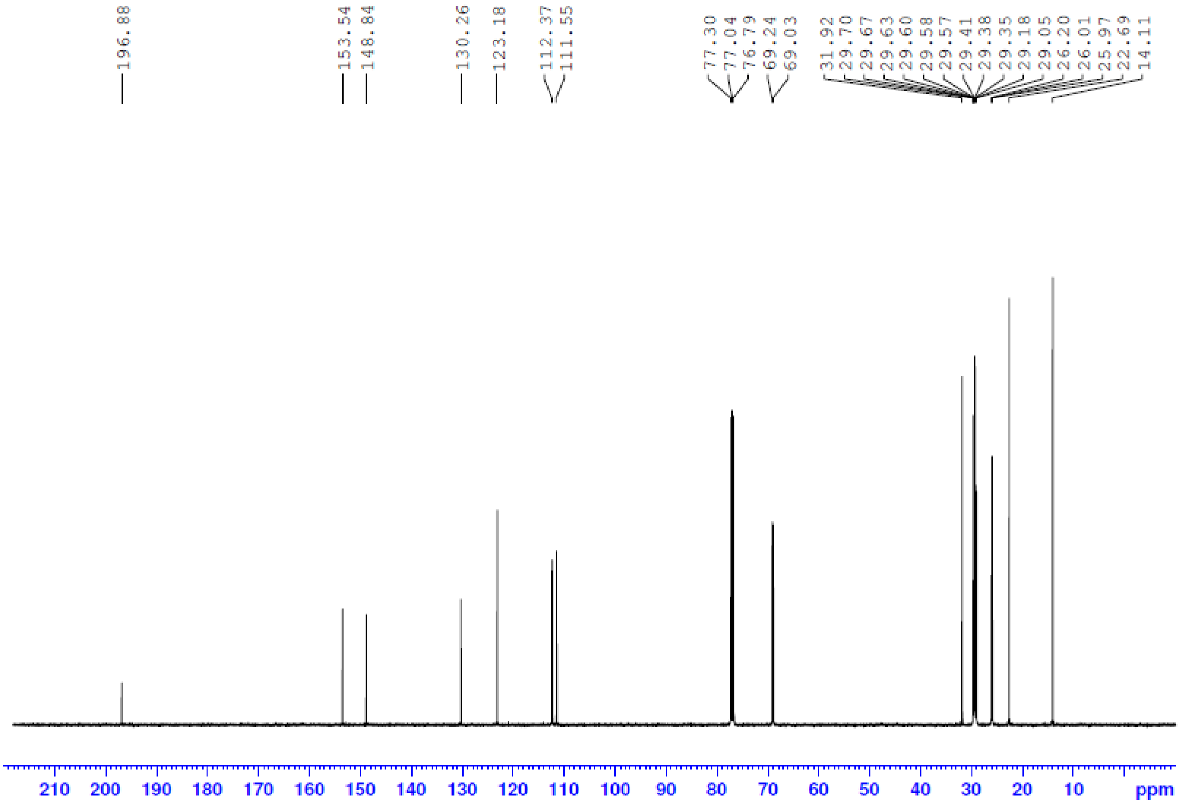


Figure S8: ^{13}C NMR spectrum of **3c** recorded in CDCl$_3$

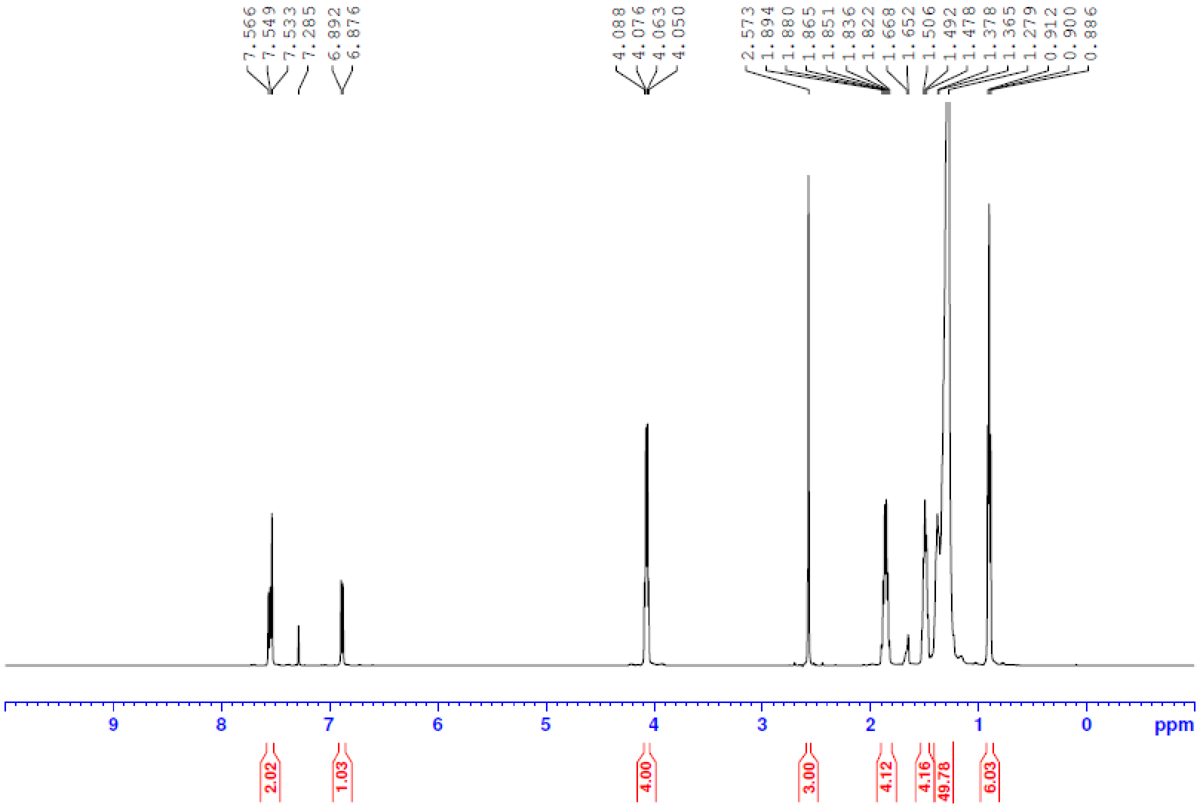


Figure S9: ^{1}H NMR spectrum of **3d** recorded in CDCl$_3$

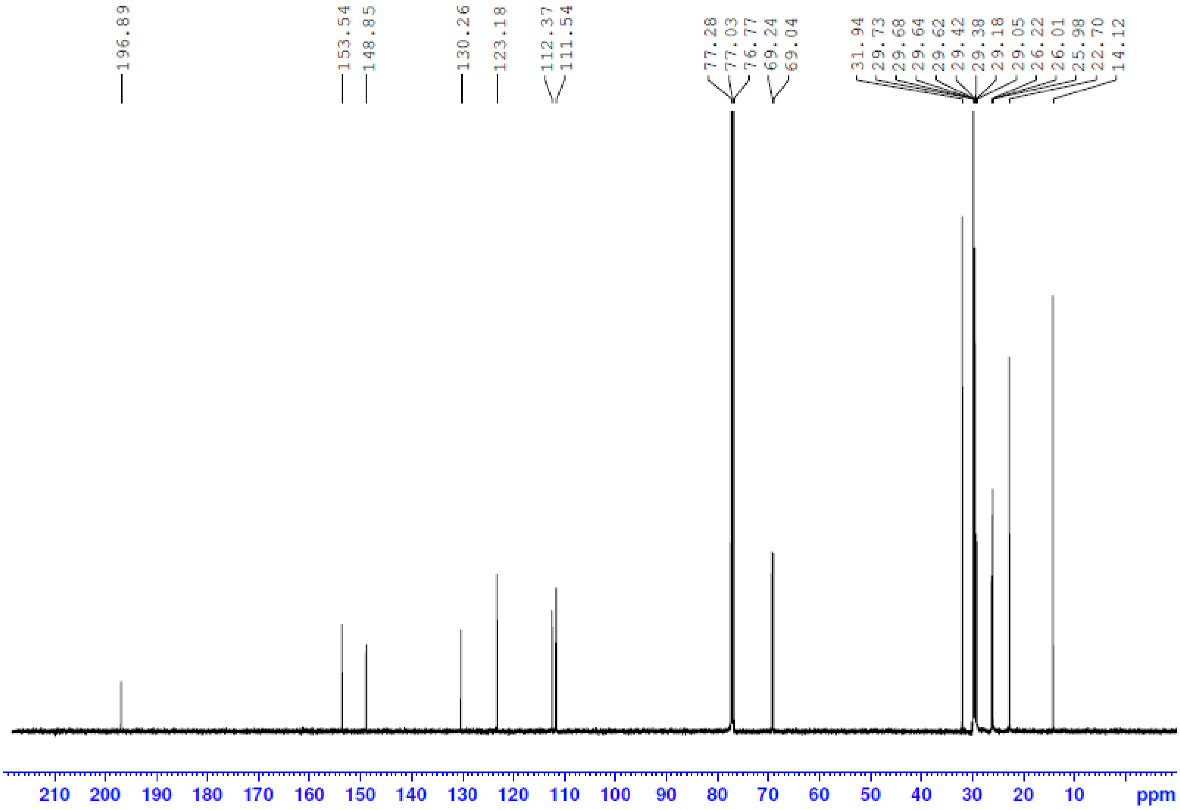


Figure S10: ^{13}C NMR spectrum of **3d** recorded in CDCl$_3$

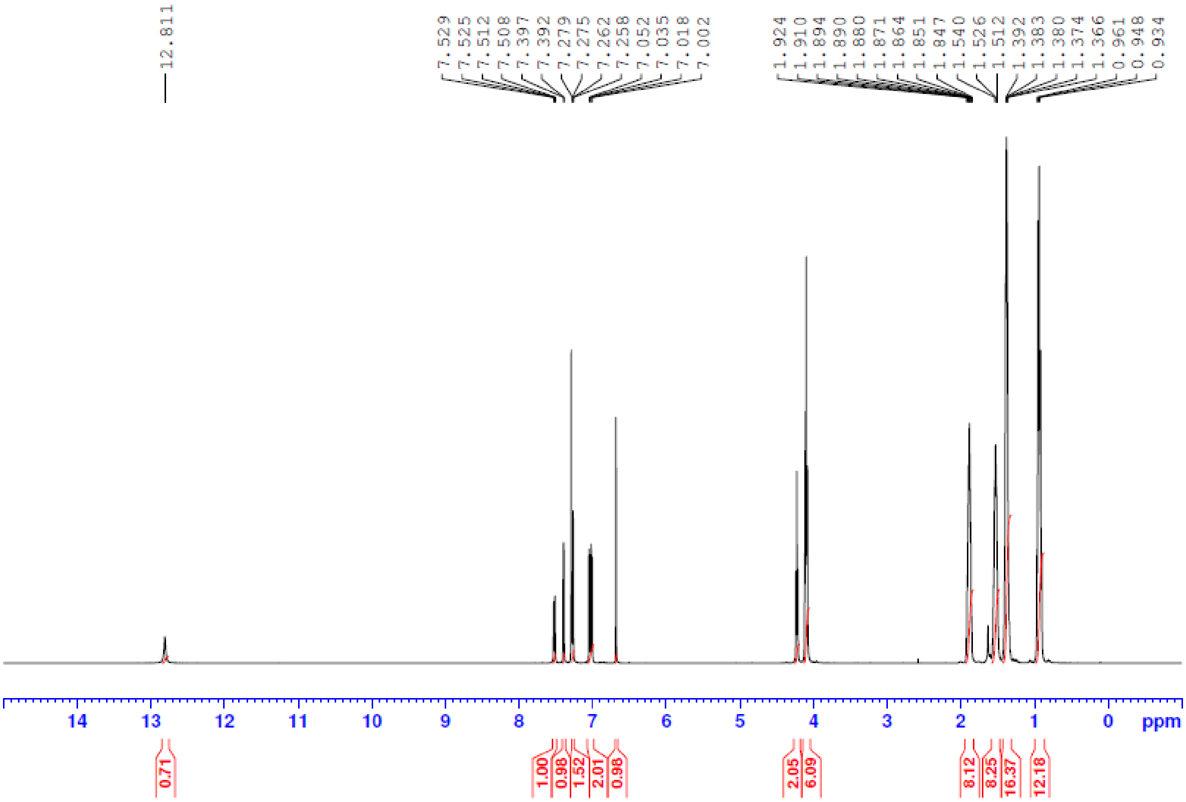


Figure S11: ^{1}H NMR spectrum of **CPO-1** recorded in CDCl$_3$

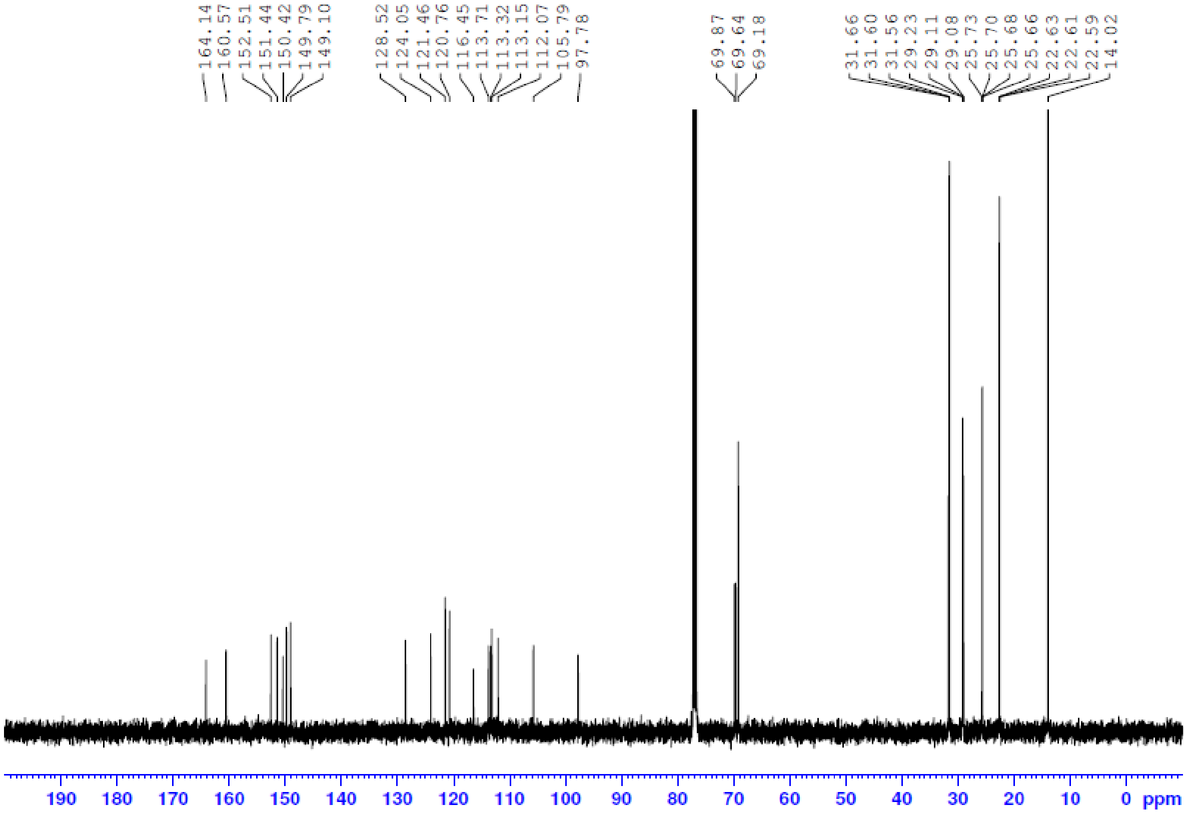


Figure S12: ^{13}C NMR spectra of **CPO-1** recorded in CDCl$_3$

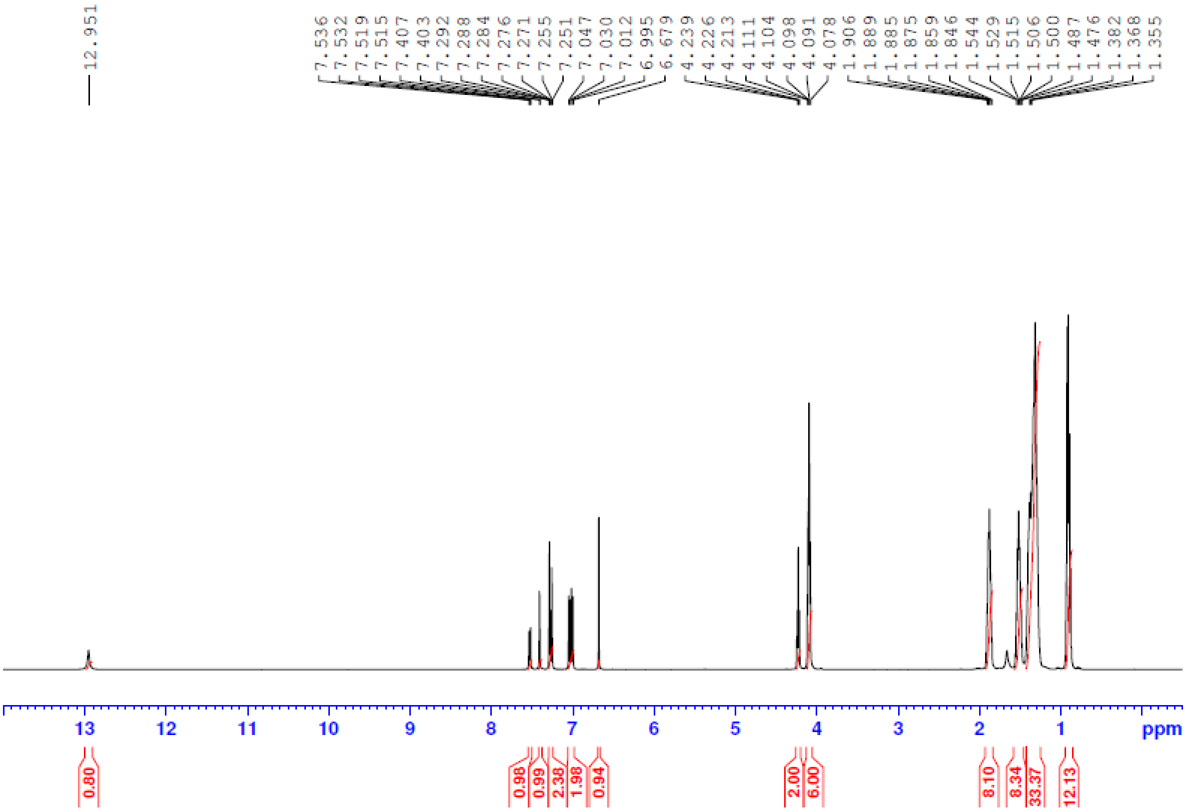


Figure S13: ^{1}H NMR spectrum of **CPO-2** recorded in CDCl$_3$

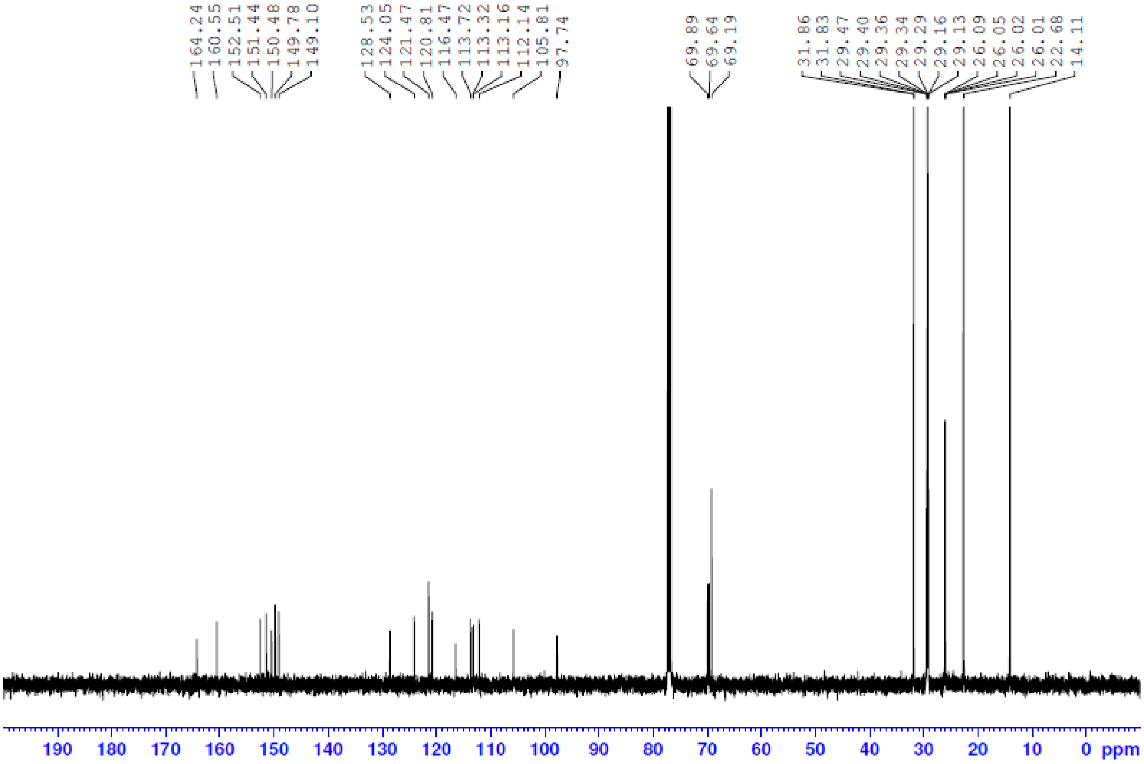


Figure S14: ^{13}C NMR spectrum of **CPO-2** recorded in $CDCl_3$

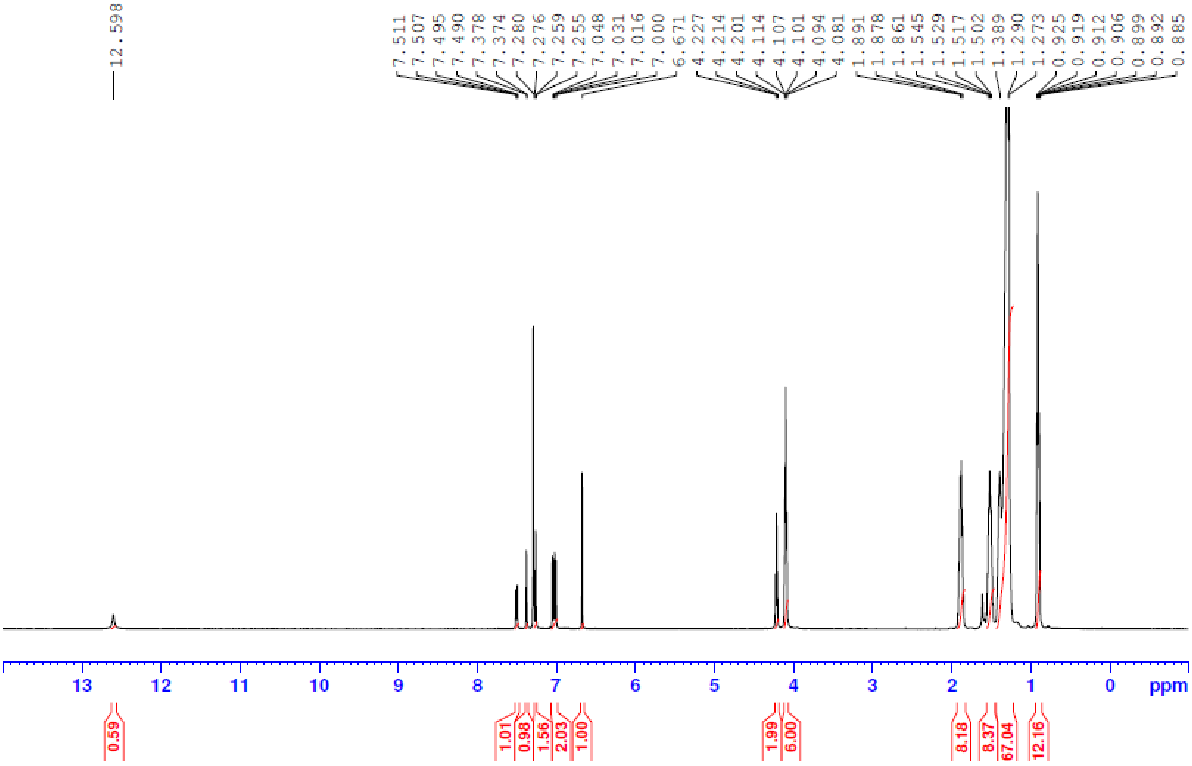


Figure S15: ^{1}H NMR spectrum of **CPO-3** recorded in $CDCl_3$

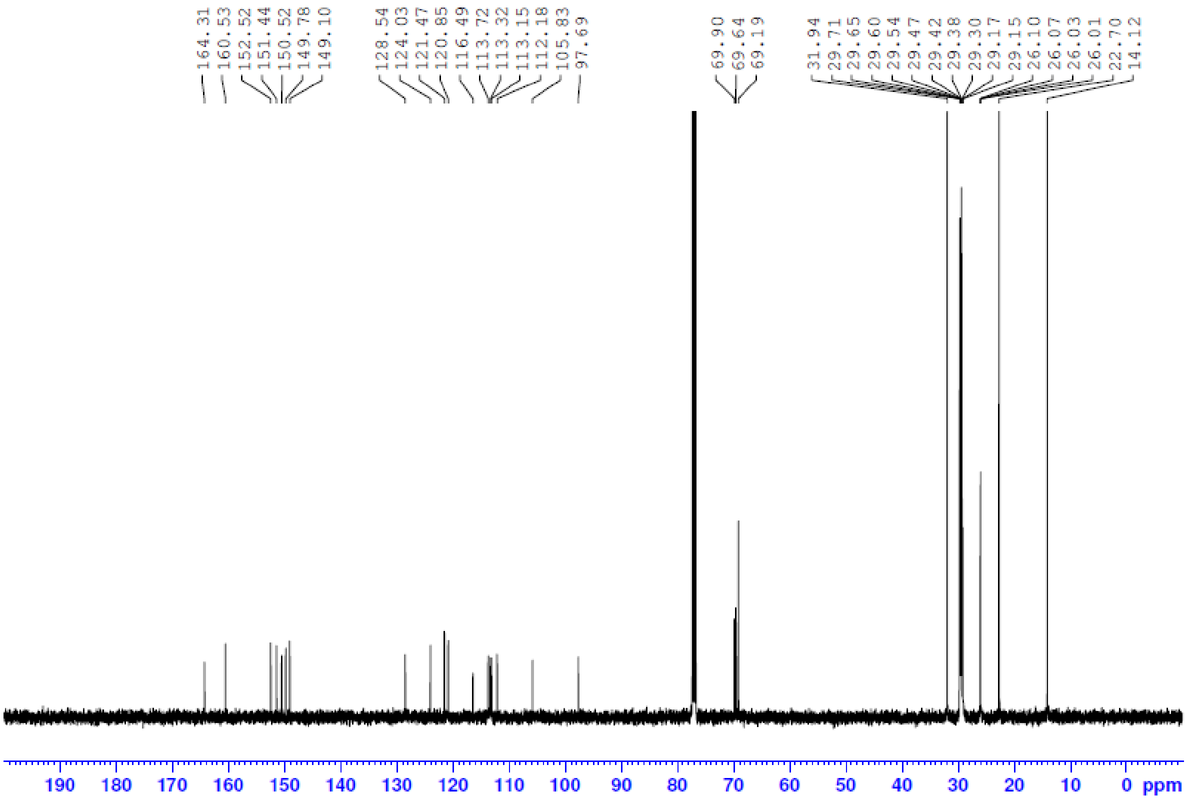


Figure S16: ^{13}C NMR spectrum of **CPO-3** recorded in $CDCl_3$

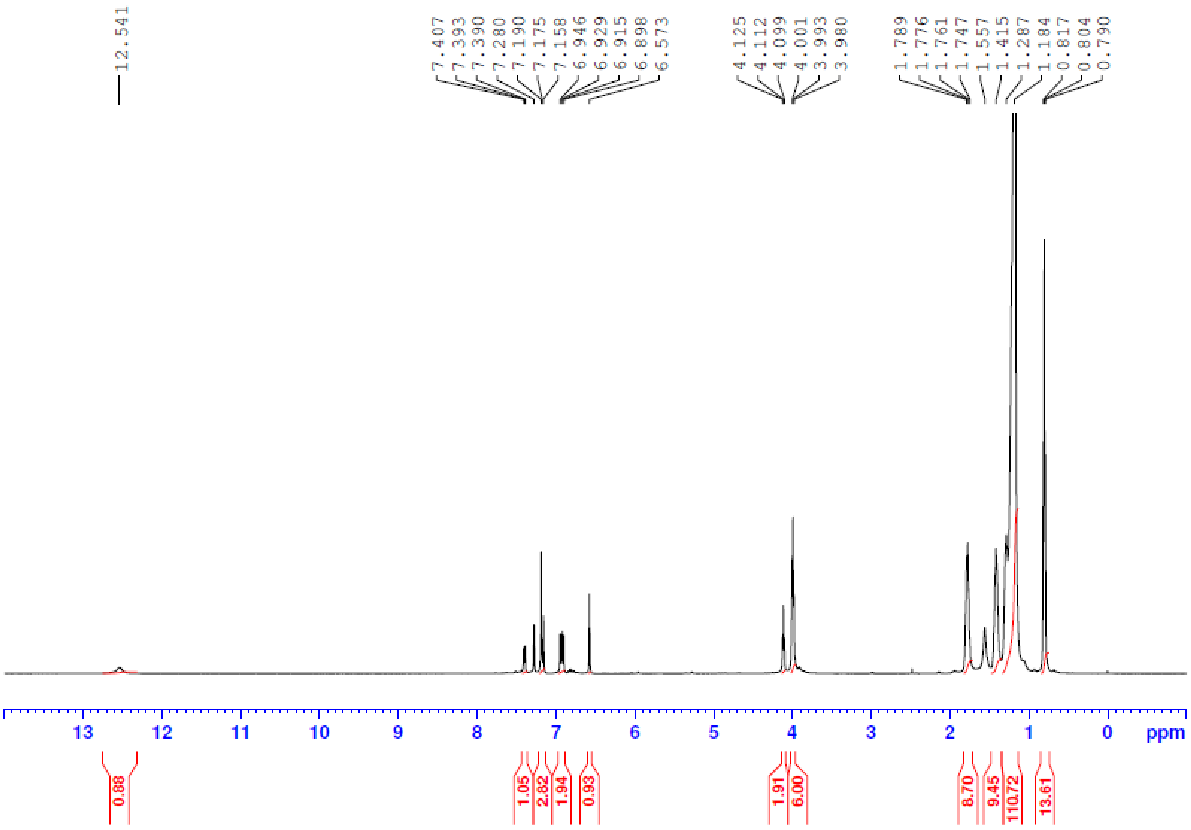


Figure S17: ^{1}H NMR spectrum of **CPO-4** recorded in $CDCl_3$

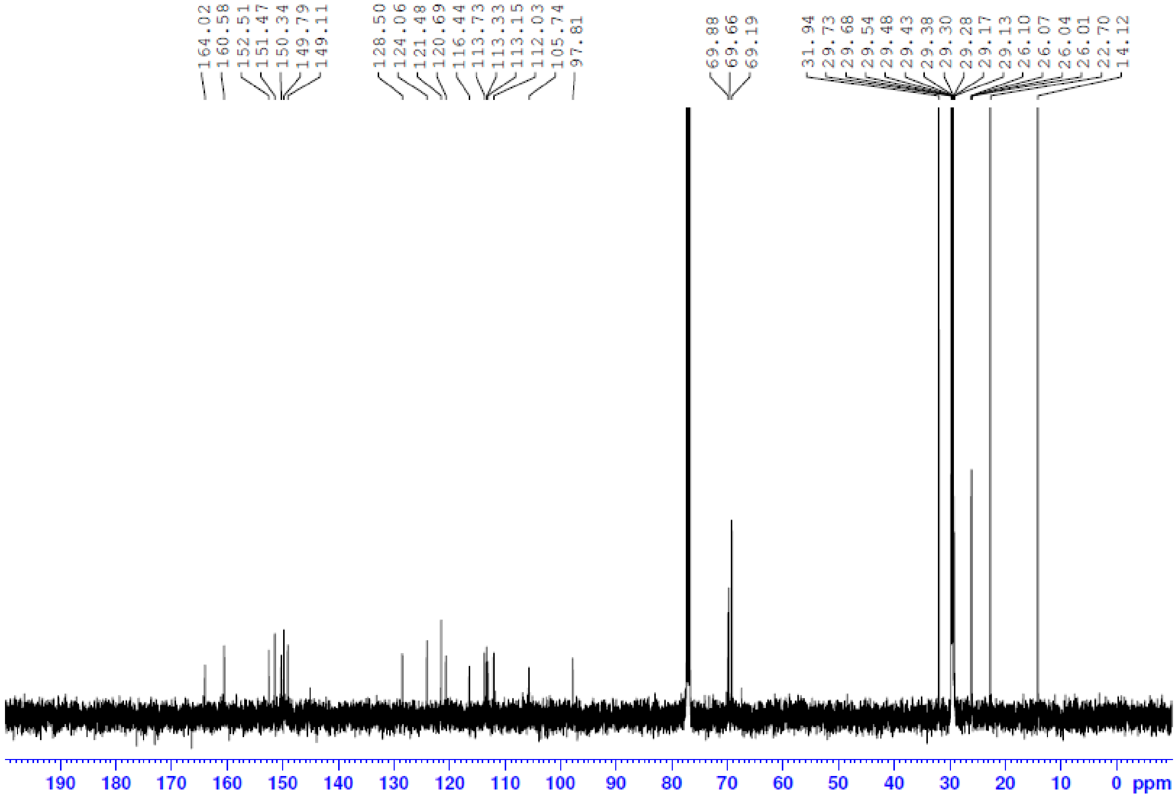


Figure S18: ^{13}C NMR spectrum of **CPO-4** recorded in $CDCl_3$

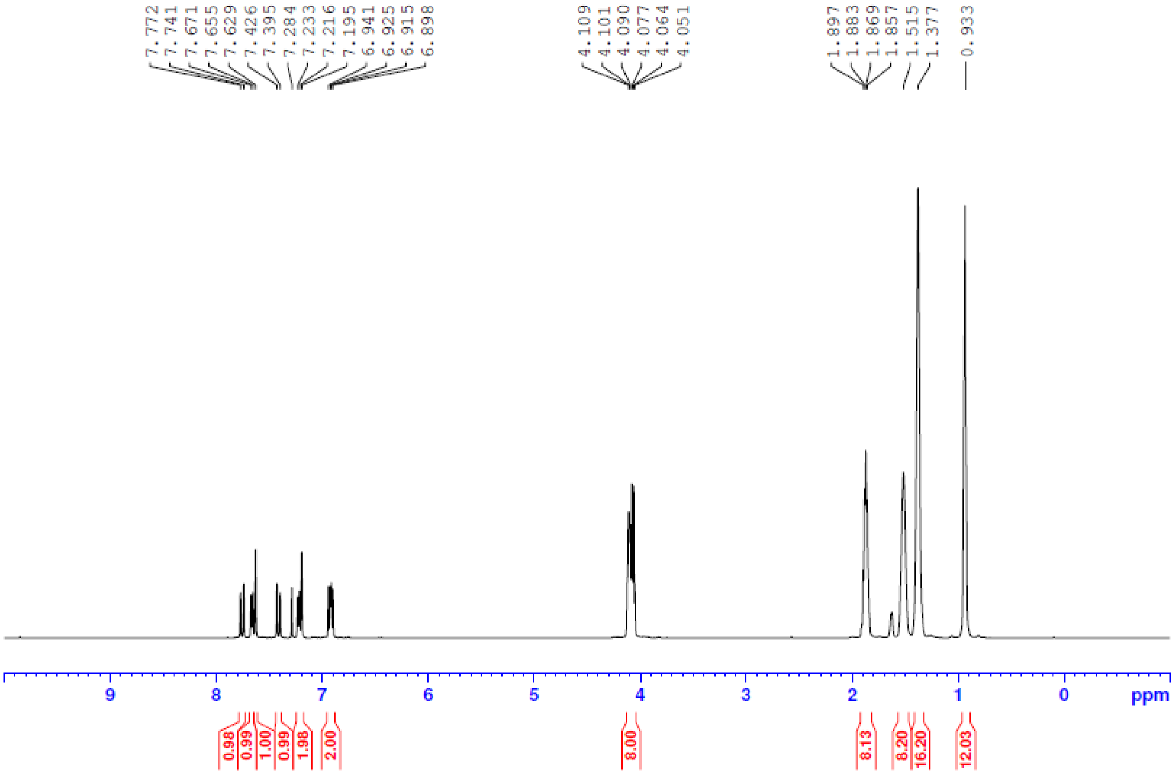


Figure S19: ^{1}H NMR spectrum of **6a** recorded in $CDCl_3$

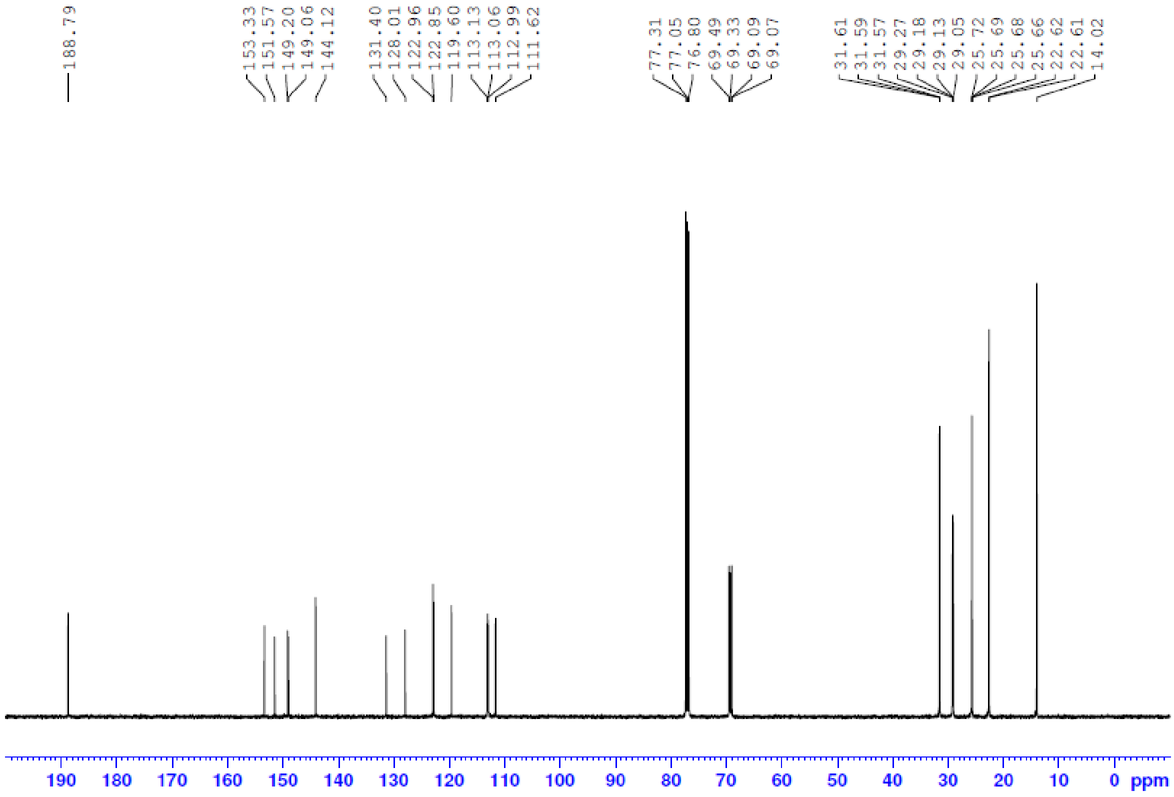


Figure S20: ^{13}C NMR spectrum of **6a** recorded in $CDCl_3$

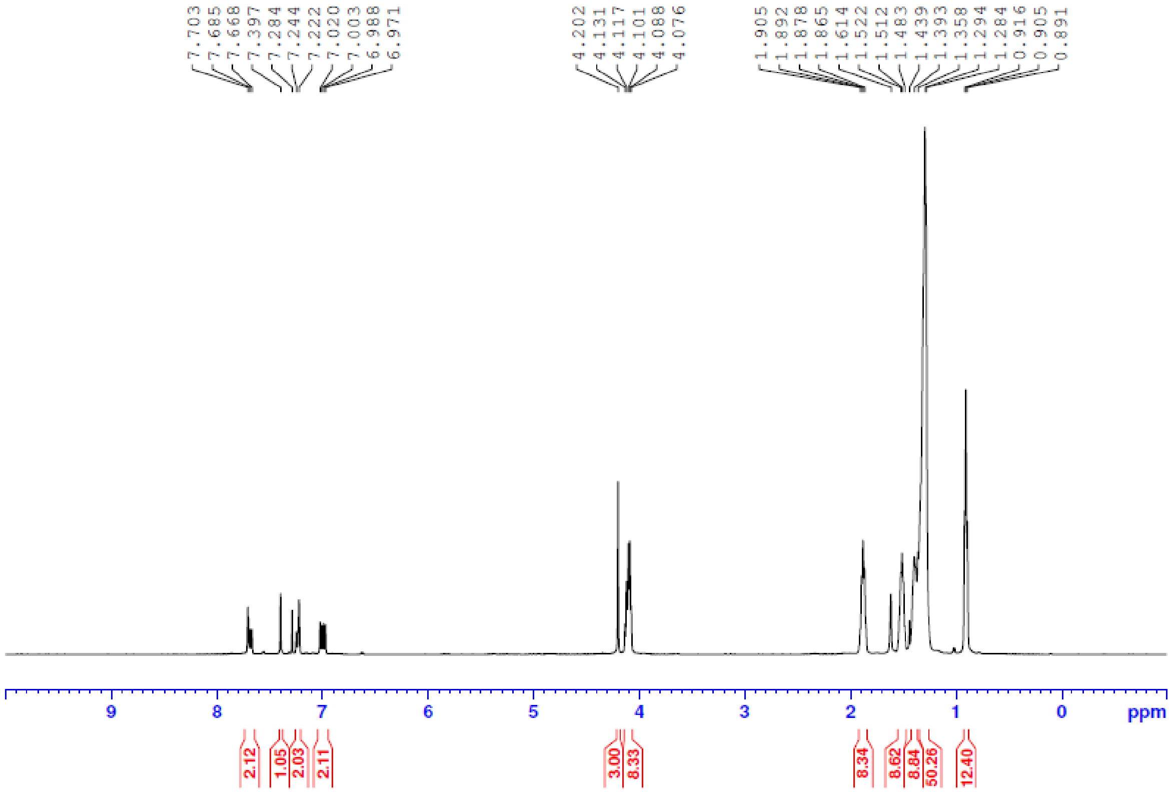


Figure S21: ^{1}H NMR spectrum of **MCA-1** recorded in $CDCl_3$

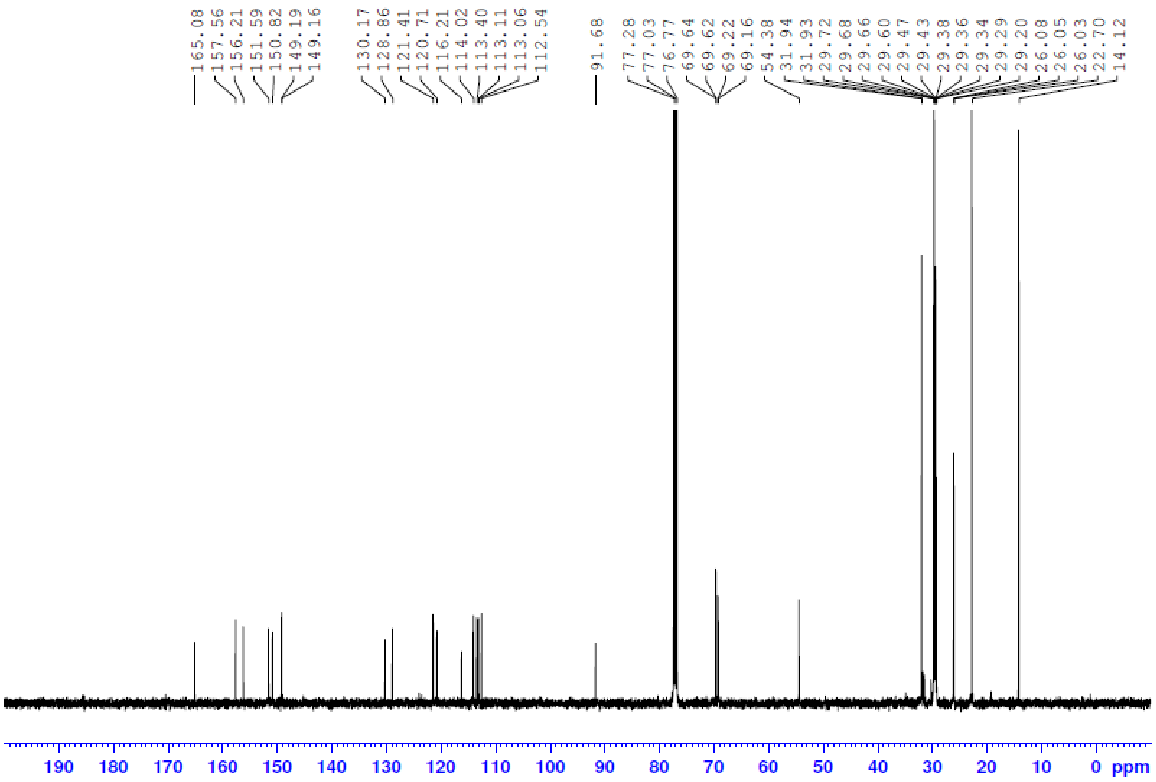


Figure S22: ^{13}C NMR spectrum of **MCA-1** recorded in $CDCl_3$

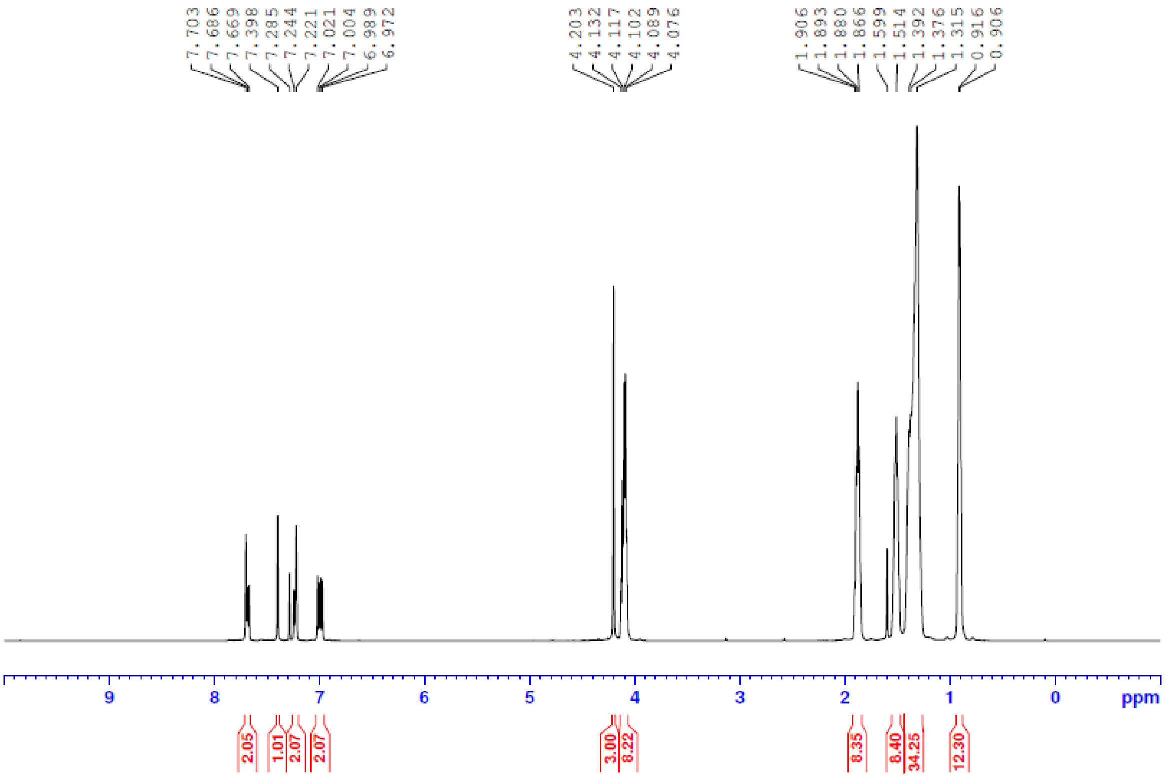


Figure S23: ^{1}H NMR spectrum of **MCA-2** recorded in $CDCl_3$

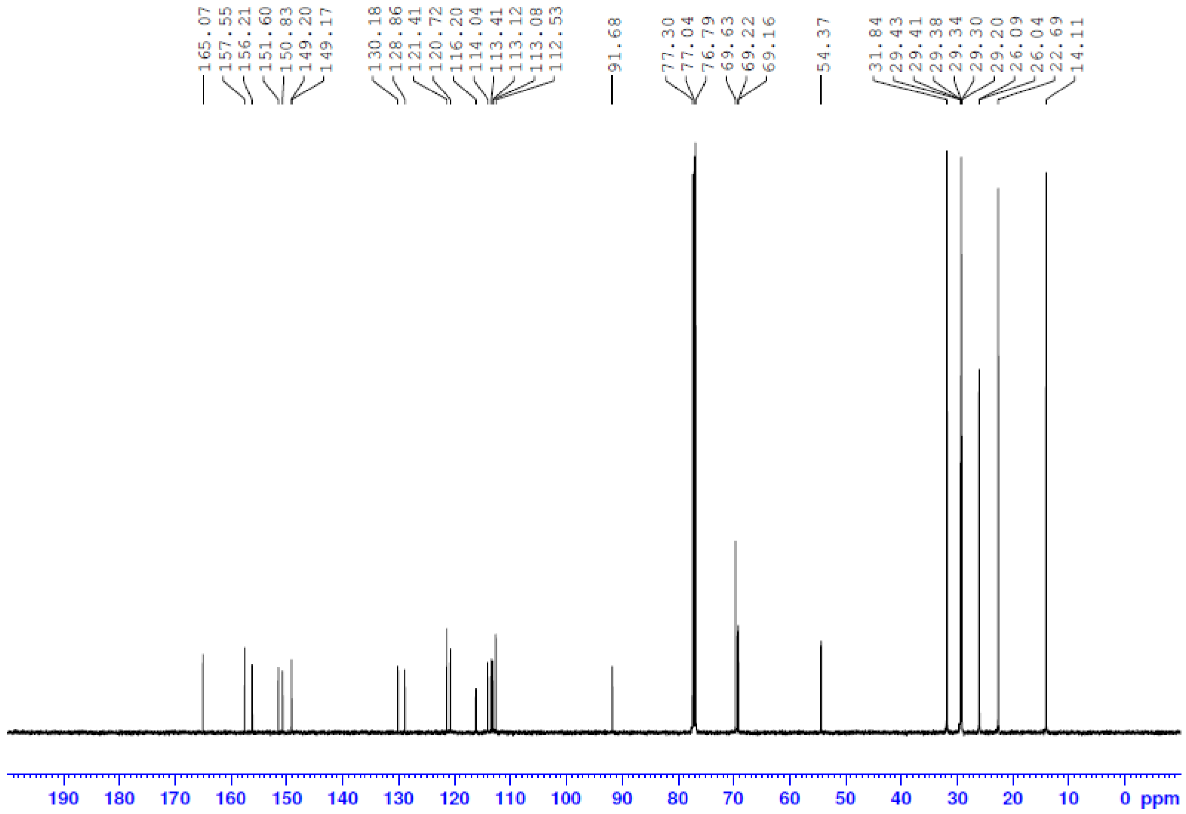


Figure S24: ^{13}C NMR spectrum of **MCA-2** recorded in $CDCl_3$

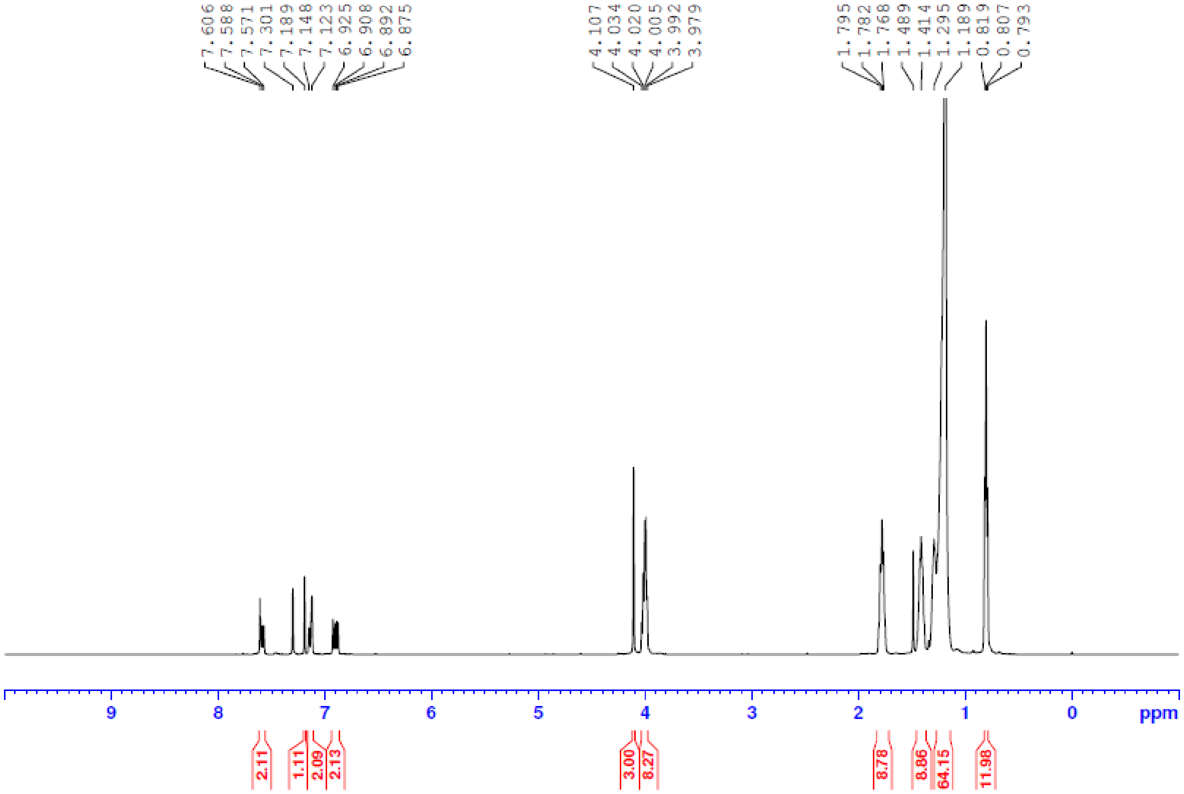


Figure S25: ^{1}H NMR spectrum of **MCA-3** recorded in $CDCl_3$

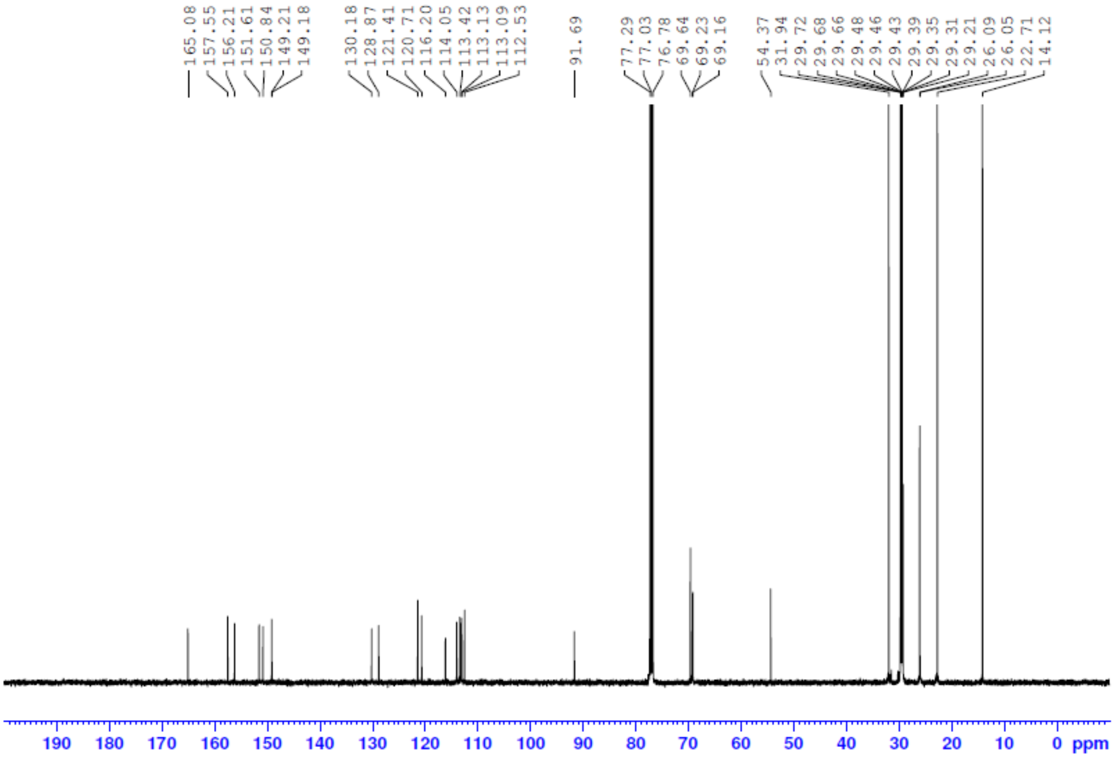


Figure S26: ^{13}C NMR spectrum of **MCA-3** recorded in $CDCl_3$

6. XRD and DSC thermograms

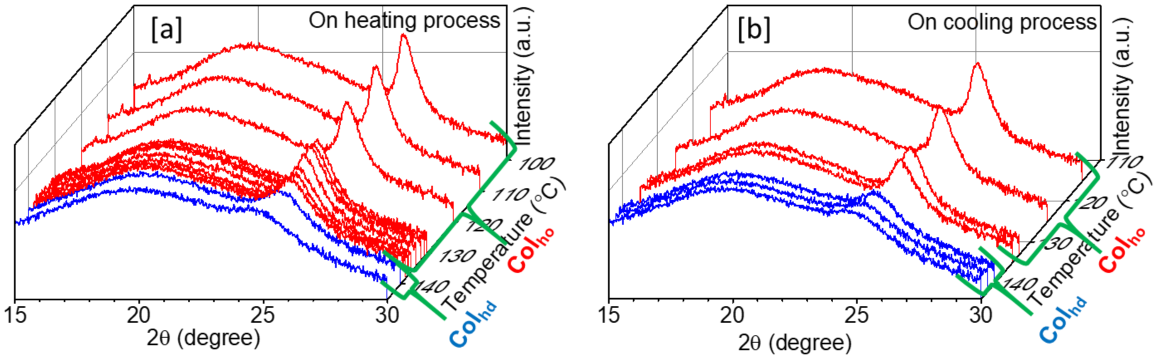


Figure S27: Wide angle XRD pattern of **CPO-2** at different temperatures: (a) on heating from crystalline state and (b) on cooling from isotropic temperature

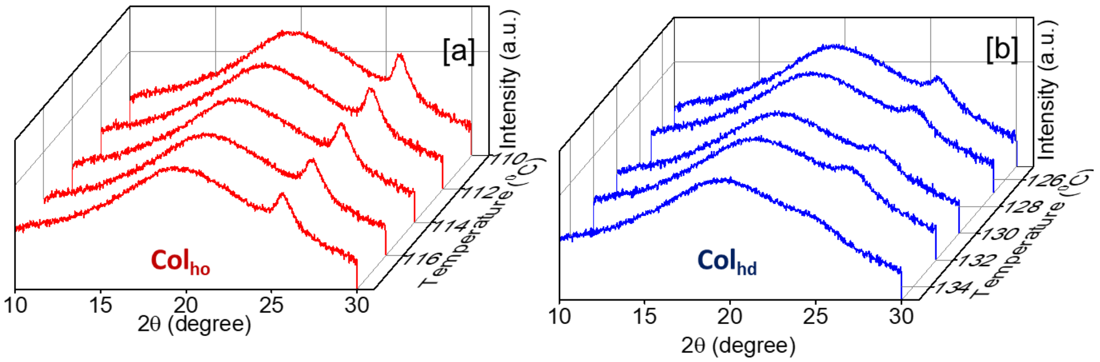


Figure S28: wide angle XRD pattern of **CPO-3** at different temperatures in (c) Col$_{ho}$ and (b) Col$_{hd}$ regions

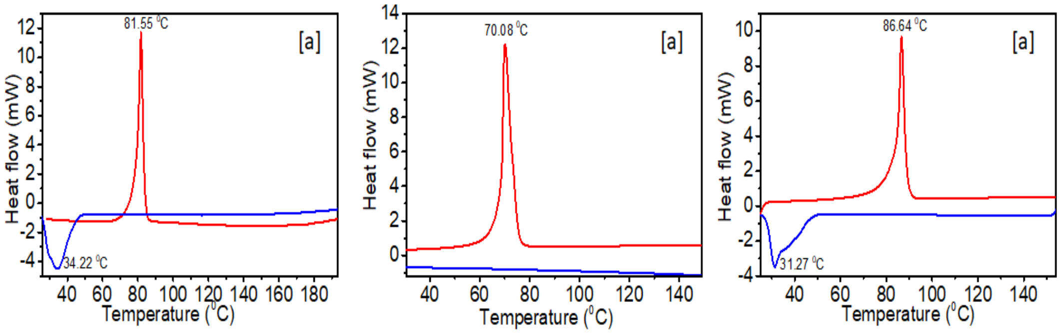


Figure S29: DSC curves of (a) **MCP-1**; (b) **MCP-2** and (c) **MCP-3** (red trace is heating cycle and blue trace is cooling cycle obtained at rate of 5 °C /min under nitrogen atmosphere)

7. Solvatochromism

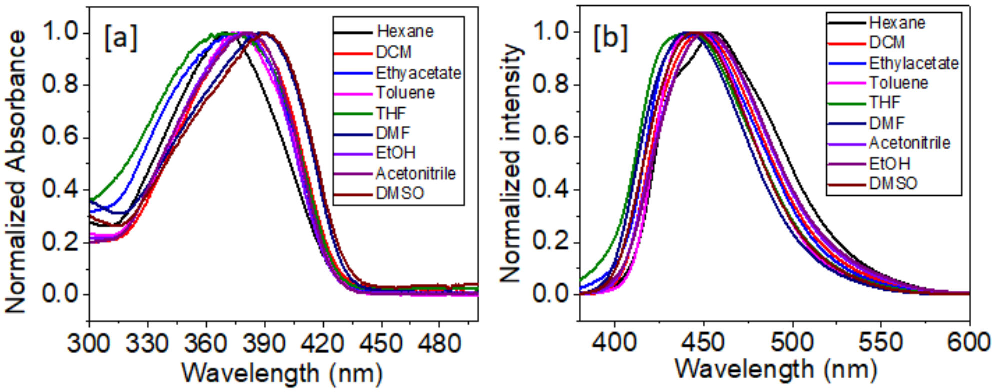


Figure S30: (a) Absorbance and (b) emission spectra of **CPO-1** in various solvents

Table 1. Photophysical properties of **CPO-1** in different solvents.

Solvent	$^{a}\lambda_{abs}$ **(nm)**	$^{b}\lambda_{em}$ **(nm)**	^{a} **Stokes shift (cm^{-1})**
Hexane	368	456	5244
DCM	383	454	4083
Ethyl acetate	375	449	4394
Toluene	378	444	3932
THF	371	443	4380
DMF	388	440	3045
Acetonitrile	379	451	4212
EtOH	381	452	4122
DMSO	390	455	3663

^{a} Micromolar solutions in different solvents; ^{b} Excited at their respective absorption maxima.

8. Cyclic voltamograms

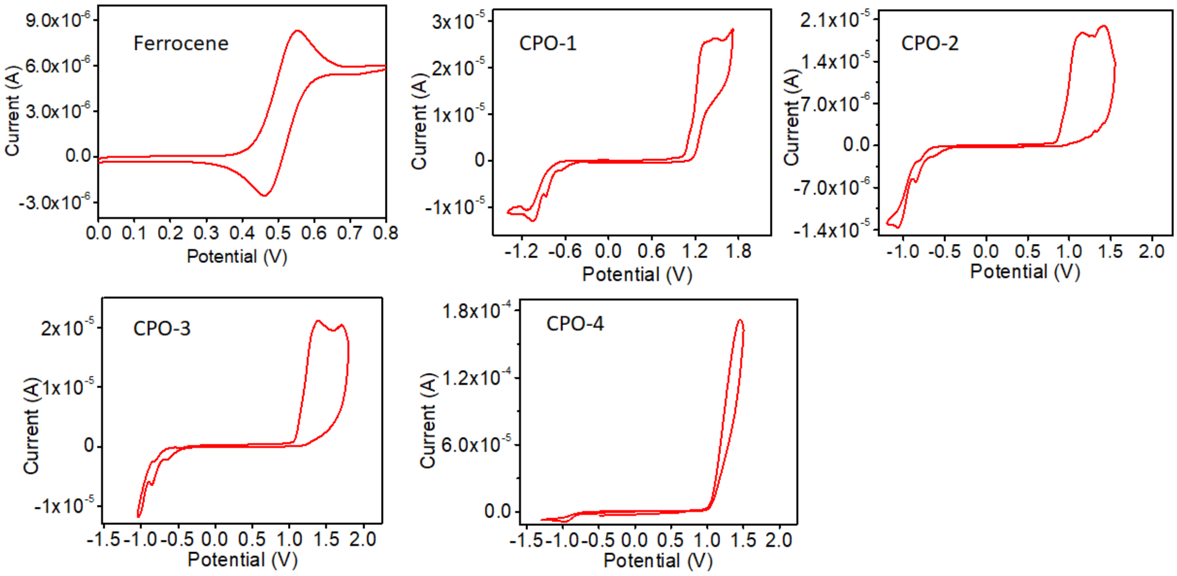


Figure S31: Cyclic voltamograms

1. H. Ulla, M. R. Kiran, B. Garudachari, T. N. Ahipa, K. Tarafder, A. V. Adhikari, G. Umesh and M. N. Satyanarayan, *J. Mol. Struct.*, 2017, **1143**, 344–354.