

Optoelectronic Exploration of Novel Non-symmetrical Star-shaped Discotic Liquid Crystals Based on Cyanopyridine

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Supporting information

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1. Material and methods

All the chemicals and reagents are AR-grade quality purchased from Sigma-Aldrich and used without further purification. The solvents were also purchased from local companies (Loba chemi, Merck, S D fine) and dried using standard protocols. Chromatographic separations were performed using silica gel (100-200 and 230-400 mesh, Merck made) or neutral aluminium oxide. FTIR spectra were obtained from Bruker alpha Fourier Transform IR spectrophotometer using ATR method and only major peaks are reported in cm^{-1} . Nuclear magnetic resonance spectroscopy ^1H NMR were recorded on Bruker machine at 500 MHz and ^{13}C NMR at 125 MHz using CDCl_3 solvent (Sigma-Aldrich made) and chemical shifts are reported in δ related to TMS used as an internal standard. Elemental analysis was performed on a Carlo-Erba Flash 1112 analyzer.

The liquid crystalline behaviour of all the final compounds were investigated by employing Olympus BX51 Polarized Optical Microscope (POM) in conjunction with a Mettler FP82HT hot stage and FP90 central processor attached with a digital camera (Olympus, Tokyo, Japan); METTLER TOLEDO DSC 3 STAR^e system with PC system operating on STAR^e software. Prior to the use, the instrument was calibrated using pure indium and zinc. DSC traces were recorded at scan rate of $5\text{ }^\circ\text{C min}^{-1}$ under continuous flow of nitrogen gas; variable temperature X-ray diffraction (XRD) measurements were performed on unoriented samples filled in a Lindemann capillary of diameter of 1 mm (Hampton Research) with $\text{Cu } K\alpha$ ($\lambda = 1.54060\text{ \AA}$) radiation using DY 1042-Empyrean, X-ray diffractometer comprising a programmable divergence slit and PIXcel 3D detector.

The photophysical properties of liquid crystalline materials were studied by means of recording steady-state UV-visible and fluorescence spectra with the help of SPECORD S 600 UV-visible spectrophotometer and Fluoromax 4 HORIBA spectrofluorometer, respectively. Fluorescence quantum yields were determined by relative method using quinine sulphate monohydrate as a reference ($\Phi_{\text{F}} = 0.54$ in $0.1\text{ M H}_2\text{SO}_4$). Fluorescence life time was estimated by employing the Time Correlated Single Photon Counting (TCSPC) technique using a nano-LED with a spectral width of 1.2 nm as an excitation source and their decay profiles were best fitted using DAS6 software. 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 a reference electrode, calibrated with ferrocene/ferrocenium (Fc/Fc^+) redox couple which has the absolute energy 4.8 eV to

vacuum, glassy carbon as a working electrode, platinum wire as a counter electrode, tetrabutyl ammonium perchlorate (0.1 M) as the supporting electrolyte in dry dichloromethane solvent. Theoretical calculations were carried out using the SPARTAN 10 program. Geometry optimised structures of LC molecules were obtained by using the Becke three-parameter exchange functional and Lee-Yang-Parr (B3LYP) exchange correlation functional with the 6-31+G* basis set for C, H, N, and O. The calculations were performed under vacuum.

2. Experimental methods

Synthesis of 1-(3,4-bis(hexyloxy)phenyl)ethanone (3)

The compound **2** (2 g, 7.19 mmol, 1equiv.) was dissolved in 25 mL of dry DCM in two neck RB under a nitrogen atmosphere, which was cooled to -5 °C. Then, anhydrous AlCl₃ (1 g, 7.9 mmol, 1.1 equiv.) was added in small portions. After stirring for 5 minutes, acetyl chloride (0.62 g, 7.9 mmol, 1.1 equiv.) was added drop-wise. The stirring was continued at the same temperature for 30 minutes and at room temperature for 1.5 hours. The reaction mixture was quenched by adding ice at 0 °C and the mixture was then extracted with DCM (50 mL ×2). The organic layer was washed with brine and dried using anhydrous Na₂SO₄. The removal of solvent under reduced pressure yielded the desired product which was then recrystallized from cold methanol to obtain pure product as white solid (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). ¹H NMR (CDCl₃, 500 MHz): δ 7.55 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.52 (s, 1H, Ar-H), 6.87 (d, 1H, *J* = 8.5 Hz, Ar-H) 4.06 (m, 4H, 2×OCH₂), 2.56 (s, 3H, COCH₃), 1.88-1.81 (m, 4H, 2×CH₂), 1.49 (m, 4H, 2×CH₂), 1.36 (m, 8H, 4×CH₂), 0.92 (t, 6H, *J* = 6.5 Hz, 2×CH₃). ¹³C NMR (CDCl₃, 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 C₂₀H₃₂O₃: C, 74.96; H, 10.06, Found: C, 74.95, H, 10.08.

Synthesis of 3,4-bis(hexyloxy)benzaldehyde (5)

A mixture of 3,4-dihydroxybenzaldehyde (2 g, 14.48 mmol, 1 equiv.), anhydrous K₂CO₃ (8g, 57.92 mmol, 4 equiv.) and 1-bromohexane (5.26 g, 31.85 mmol, 2.2 equiv.) was taken in 40 mL of DMF, the mixture was heated at 80 °C for 12 hours under nitrogen atmosphere. The reaction mass was cooled to room temperature and poured into 120 mL of ice-cooled water. The product was then extracted with DCM (200 mL×3), combined organic fractions was evaporated to dryness and the obtained crude solid was purified by silica gel column

chromatography (100-200 mesh size) using 2 % ethyl acetate in pet-ether as eluent to offer **5** as pale white solid (yield, 82%) IR (ATR): ν_{\max} in cm^{-1} 2953, 2923 (Ar C-H), 2855 (Aliph C-H), 2754 (aldehyde C-H), 1684 (aldehyde C=O), 1595 (Ar C=C). ^1H NMR (CDCl_3 , 500 MHz): δ 9.84 (s, 1H, Ar-CHO), 7.42 (d, 2H, $J = 8.5$ Hz, Ar-H), 7.28 (s, 1H, Ar-H), 6.96 (d, 1H, $J = 8.5$ Hz, Ar-H), 4.0 (m, 4H, $2 \times \text{O-CH}_2$), 1.86 (m, 4H, $2 \times \text{CH}_2$), 1.48 (m, 8H, $4 \times \text{CH}_2$), 0.89 (t, 6H, $J = 6.5$ Hz, $2 \times \text{CH}_3$). ^{13}C NMR (CDCl_3 , 125 MHz): 190.98, 154.68, 149.44, 129.87, 126.59, 111.75, 110.96, 69.92, 31.91, 29.50, 25.97, 22.68, 14.11. Elemental Anal. Calcd (%) for $\text{C}_{19}\text{H}_{30}\text{O}_3$: C, 74.47; H, 9.87; C, 74.50, H, 10.00.

Synthesis of 4,6-bis(3,4-hexyloxyphenyl)-2-oxo-1,2-dihydropyridine-3-carbonitrile (6)

An equimolar mixture of **3** (2 g, 6.24 mmol, 1 equiv.), **5** (1.91 g, 6.24 mmol, 1 equiv.) and ethylcyanoacetate (0.8 mL, 6.9 mmol, 1 equiv.) was dissolved in 50 mL of absolute ethanol. Excess of ammonium acetate (7.2 g, 93.6 mmol, 15 equiv.) was then added to reaction mixture and refluxed for 12 h. The reaction mixture was allowed to cool to room temperature, obtained precipitate was filtered and washed with ethanol to get a yellow solid. The crude product was purified by column chromatography with silica gel of 100-200 mesh using 1:3 pet-ether (60-70 °C) and dichloromethane as eluents (Yield, 40 %). IR (ATR): ν_{\max} in cm^{-1} 2922 (Ar C-H), 2854 (Aliph C-H), 2217 ($\text{C}\equiv\text{N}$), 1653 (C=O), 1600 (Ar C=C). ^1H NMR (CDCl_3 , 500 MHz): δ 12.81 (s, 1H, CONH), 7.52 (dd, 1H, $J = 8.5, 2.0$ Hz, Ar-H), 7.39 (d, 1H, $J = 2.5$ Hz, Ar-H), 7.27 (dd, 1H, $J = 8.0, 2.0$ Hz, Ar-H), 7.26 (d, 1H, $J = 2.0$ Hz, Ar-H), 7.04 (d, 1H, $J = 8.5$ Hz, Ar-H), 7.01 (d, 1H, $J = 8.0$ Hz, Ar-H), 6.68 (s, 1H, pyridone-H), 4.22 (t, 2H, $J = 6.5$ Hz, $2 \times \text{O-CH}_2$), 4.08 (m, 6H, $3 \times \text{O-CH}_2$), 1.92-1.85 (m, 8H, $4 \times \text{CH}_2$), δ 1.53 (t, 8H, $J = 7.0$ Hz, $4 \times \text{CH}_2$), δ 1.39-1.36 (m, 16H, $8 \times \text{CH}_2$), δ 0.95 (t, 12H, $J = 6.5$ Hz, $4 \times \text{CH}_3$). ^{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 $\text{C}_{42}\text{H}_{60}\text{N}_2\text{O}_5$: C, 74.96; H, 8.99; N, 4.16, Found: C, 74.81; H, 9.261; N, 4.10.

General procedure for the synthesis of 4,6-bis(3,4-bis(hexyloxy)phenyl)-2-((3,4,5-tris(alkoxy)benzyl)oxy)nicotinonitriles (**CPBz6**, **CPBz8** and **CPBz12**)

A mixture of compound **6** (0.3 g, 0.45 mmol, 1 equiv.) and anhydrous K_2CO_3 (0.92 g, 0.67 mmol, 1.5 equiv.) in 15 mL DMF was stirred at room temperature under inert atmosphere for 15 min. Then, trihexyloxybenzyl bromide **11a** (0.23 g, 0.49 mmol, 1.1 equiv.) was added to the mixture and heated to 60 °C for overnight. After completion of the reaction,

the reaction mass was added into 50 mL of ice-cold water. The crude product was extracted with dichloromethane (40 mL×2) and the combined organic layers was concentrated. The resulted crude product was purified by silica gel column chromatography (100-200 mesh size) using 3% ethyl acetate in petroleum ether (60-70 °C) as mobile phase to obtain pure white product. (Yield, 70 %). IR (ATR): ν_{\max} in cm^{-1} 2922 (Ar C-H), 2855 (Aliph C-H), 2216 ($\text{C}\equiv\text{N}$) and 1591 (Ar C=C). ^1H NMR (CDCl_3 , 500 MHz): δ 7.68-7.65 (m, 2H, 2×Ar-H), 7.38 (s, 1H, pyridine-H), 7.24-7.21 (m, 2H, 2×Ar-H), 7.0 (d, 1H, $J = 8.5$ Hz, Ar-H), 6.97 (d, 1H, $J = 8.5$ Hz, Ar-H), 6.79 (s, 2H, 2×Ar-H), 5.57 (s, 2H, 2×OCH₂-Ar), 4.0 (m, 8H, 4×OCH₂), 3.97 (m, 6H, 3×OCH₂), 1.88 (m, 8H, 4×CH₂), 1.77 (m, 6H, 3×CH₂) 1.49-1.28 (m, 42H, 2×CH₂), 0.95-0.9 (m, 21H, 7×CH₃). ^{13}C NMR (CDCl_3 , 125 MHz): 164.46, 157.47, 156.35, 153.15, 151.63, 150.83, 149.23 149.16, 137.93, 131.57, 130.20, 128.88, 121.39, 120.81, 116.04 114.02, 113.39, 113.06, 112.76, 106.71, 92.10, 73.41, 69.71, 69.62, 69.21, 69.12, 69.77, 31.71, 30.228, 29.70, 29.38, 29.24, 29.16, 29.51, 25.73, 25.65, 14.06. Elemental Anal. Calcd (%) for $\text{C}_{42}\text{H}_{60}\text{N}_2\text{O}_5$: C, 74.96; H, 8.99; N, 4.16; O, Found: C, 74.81; H, 9.261; N, 4.10.

CPBz8 and **CPBz12** were synthesized by adopting same procedure

CPBz8, pale white coloured product, (Yield, 66%). IR (ATR): ν_{\max} in cm^{-1} 2922 (Ar C-H), 2855 (Aliph C-H), 2216 ($\text{C}\equiv\text{N}$) and 1591 (Ar C=C). ^1H NMR (CDCl_3 , 500 MHz): δ 7.68-7.65 (m, 2H, 2×Ar-H), 7.38 (s, 1H, pyridine-H), 7.24-7.21 (m, 2H, 2×Ar-H), 7.0 (d, 1H, $J = 8.5$ Hz, Ar-H) 6.97 (d, 1H, $J = 8.5$ Hz, Ar-H), 6.80 (s, 2H, 2×Ar-H), 5.57 (s, 2H, 2×OCH₂-Ar), 4.0 (m, 8H, 4×OCH₂), 3.96 (m, 6H, 3×OCH₂), 1.87 (m, 8H, 4×OCH₂-CH₂), 1.74 (m, 6H, 3×CH₂) 1.51-1.27 (m, 54H, 27×CH₂), 0.95-0.88 (m, 21H, 7×CH₃). ^{13}C NMR (CDCl_3 , 125 MHz): 164.45, 157.48, 156.35, 153.14, 151.62, 150.82, 149.24 149.19, 137.94. 131.56, 130.20, 128.87, 121.39, 120.82, 114.0, 113.06, 106.70, 92.09, 73.43, 69.67, 69.04, 31.74, 29.41, 25.74, 25.64, 14.05. Elemental Anal. Calcd (%) for $\text{C}_{73}\text{H}_{114}\text{N}_2\text{O}_8$: C, 76.39; H, 10.01; N, 2.44; O, Found: C, 76.41; H, 10.42; N, 2.29.

CPBz12, pale white coloured product, (Yield, 62%). IR (ATR): ν_{\max} in cm^{-1} 2922 (Ar C-H), 2846 (Aliph C-H), 2216 ($\text{C}\equiv\text{N}$), 1591 (Ar C=C). ^1H NMR (CDCl_3 , 500 MHz): δ 7.68-7.65 (m, 2H, 2×Ar-H), 7.38 (s, 1H, pyridine-H), 7.24-7.21 (m, 2H, 2×Ar-H), 7.0 (d, 1H, $J = 8.5$ Hz, Ar-H) 6.97 (d, 1H, $J = 8.5$ Hz, Ar-H), 6.79 (s, 2H, 2×Ar-H), 5.57 (s, 2H, 2×OCH₂-Ar), 4.10 (m, 8H, 4×OCH₂), 3.96 (m, 6H, 3×OCH₂), 1.87 (m, 8H, 4×OCH₂-CH₂), 1.76 (m, 3H, 2×CH₂) 1.51-1.27 (m, 78H, 39×CH₂), 0.95-0.88 (m, 21H, 7×CH₃). ^{13}C NMR (CDCl_3 , 125 MHz): 164.46, 157.47, 156.35, 153.15, 151.62, 150.83, 149.23, 149.16, 137.94, 131.55,

130.20, 128.88, 121.39, 120.81, 114.01, 113.38 113.06, 112.75 106.71, 73.42, 69.71, 69.61, 69.20, 69.13, 68.79, 31.94, 31.65, 31.60, 31.58, 30.36, 29.43, 26.15, 26.12, 25.74, 22.66, 14.05. Elemental Anal. Calcd (%) for $C_{85}H_{138}N_2O_8$: C, 77.58; H, 10.57; N, 2.13; Found: C, 77.40; H, 10.64; N, 2.30.

3. FTIR characterization

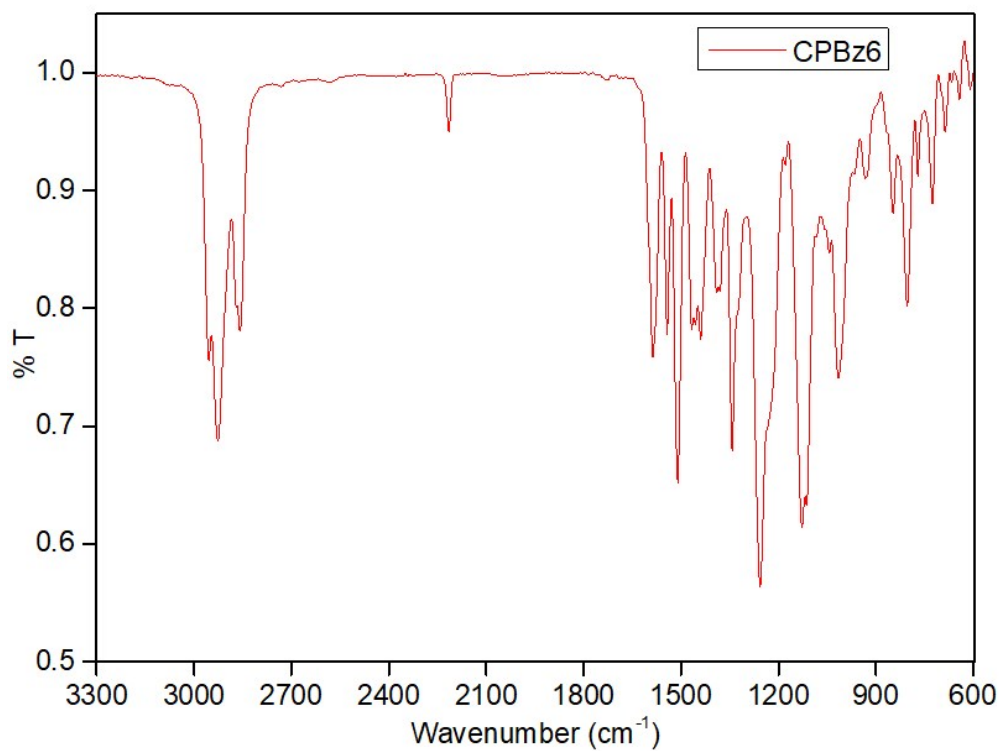


Figure S1. FTIR spectrum of **CPBz6**

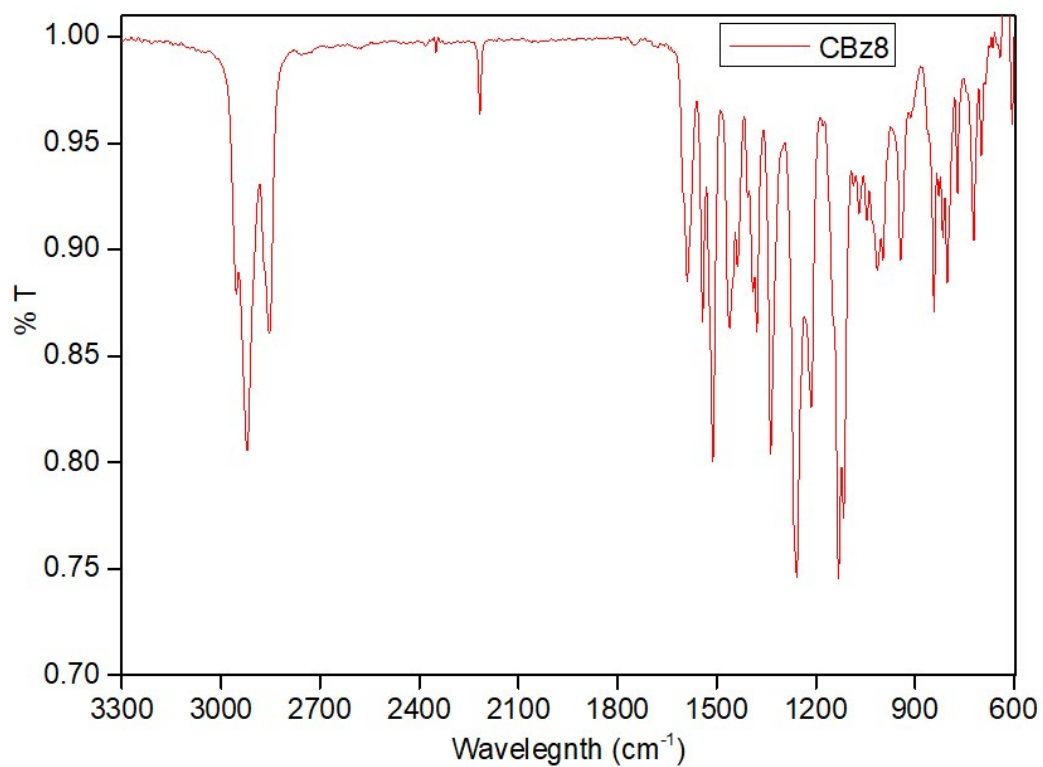


Figure S2. FTIR spectrum of **CPBz8**

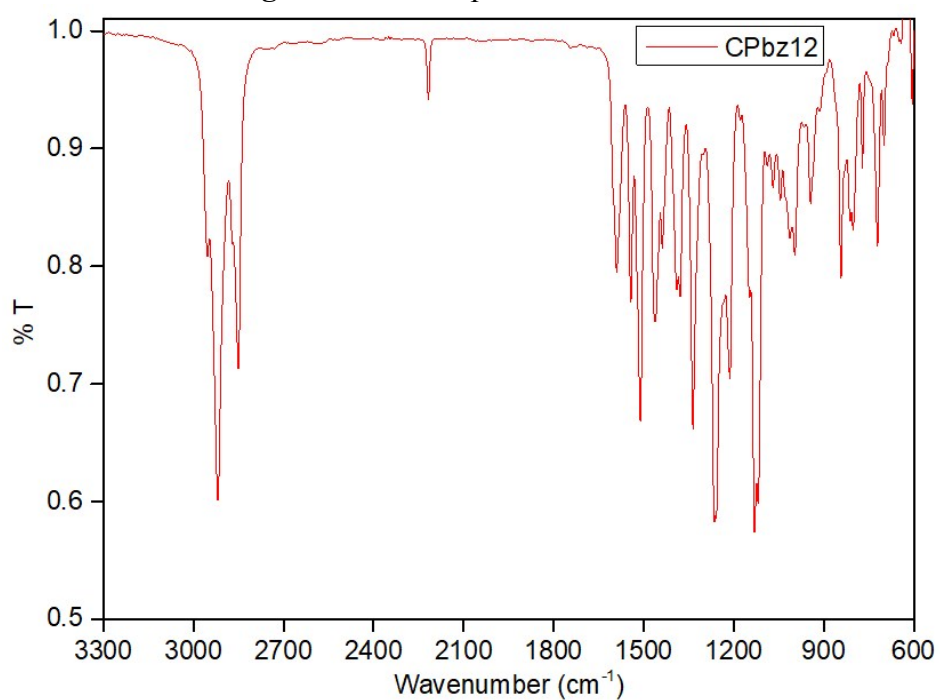


Figure S3. FTIR spectrum of **CPBz12**

4. NMR characterization

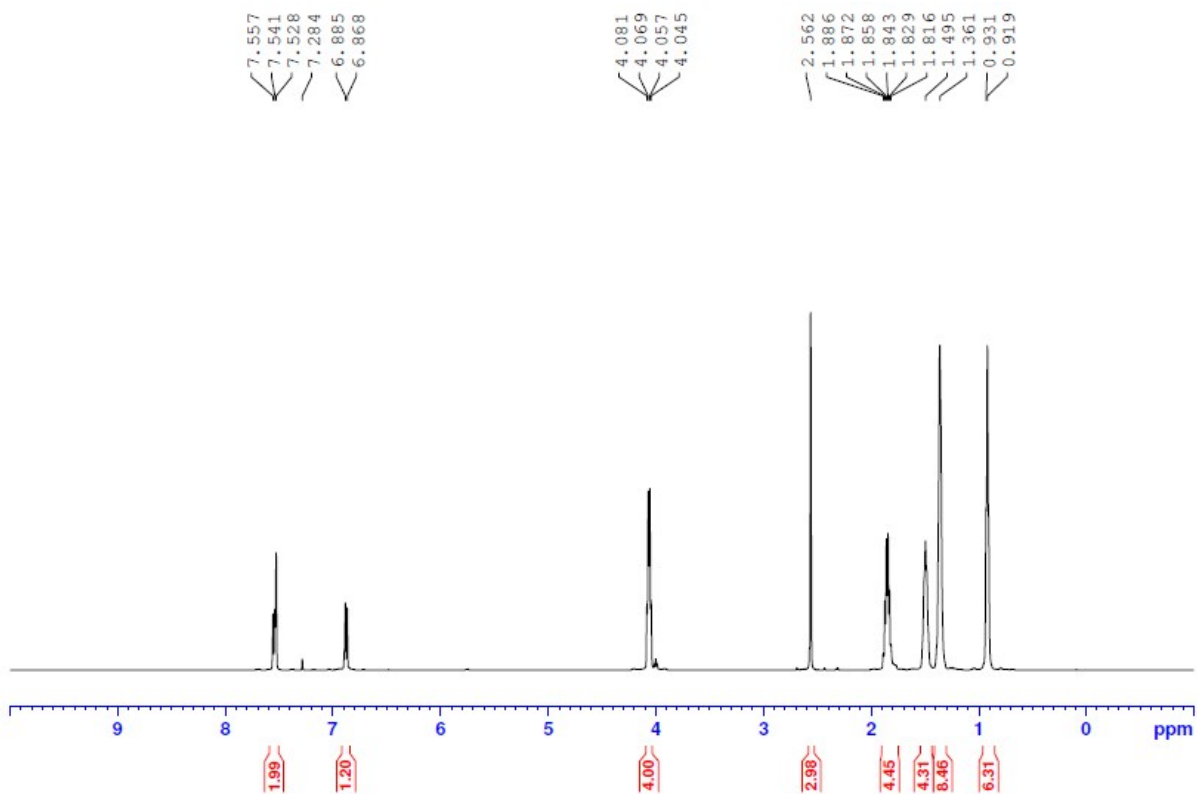


Figure S4. ^1H NMR (500 MHz) spectrum of **3** recorded in CDCl_3

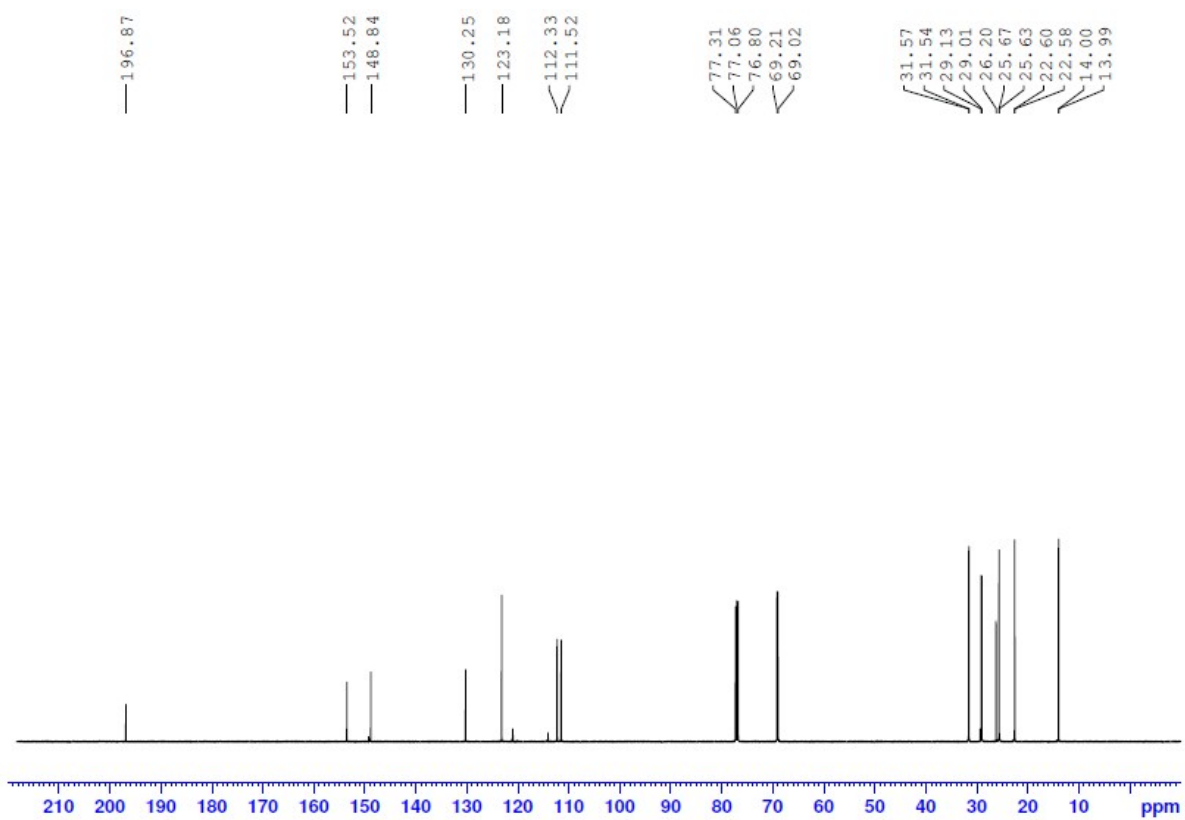


Figure S5. ^{13}C NMR (125 MHz) spectrum of **3** recorded in CDCl_3

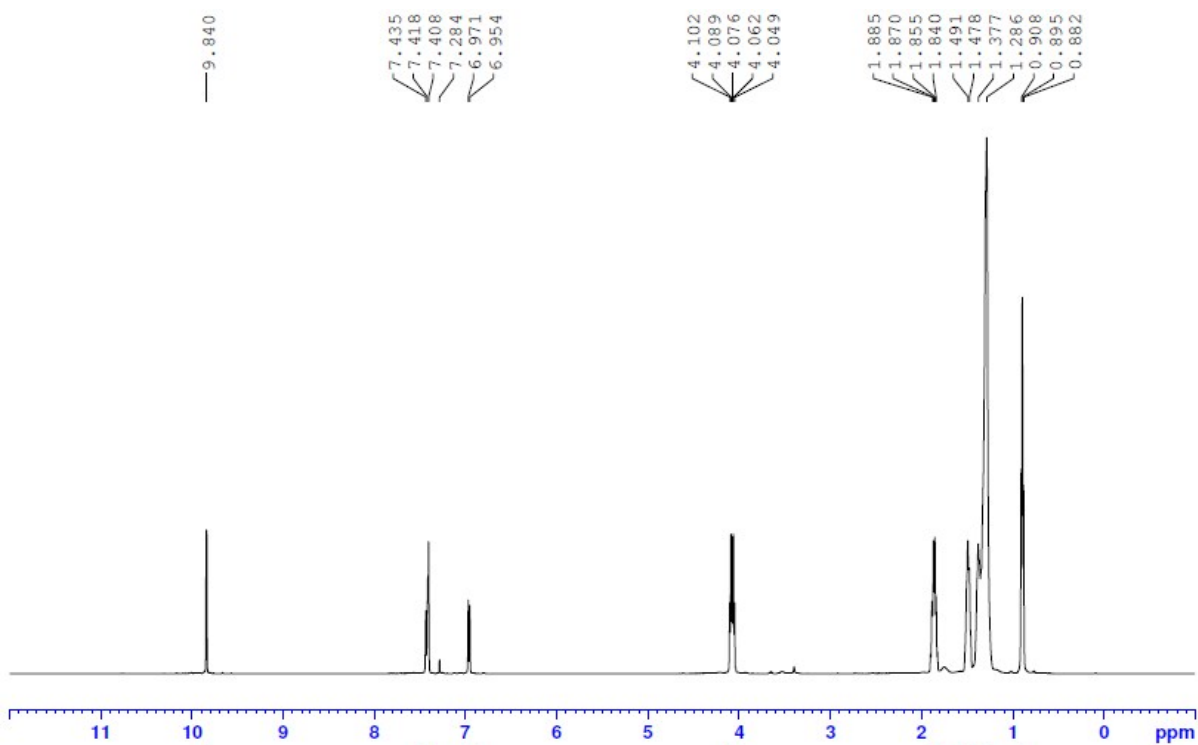


Figure S6. ^1H NMR (500 MHz) spectrum of **5** recorded in CDCl_3

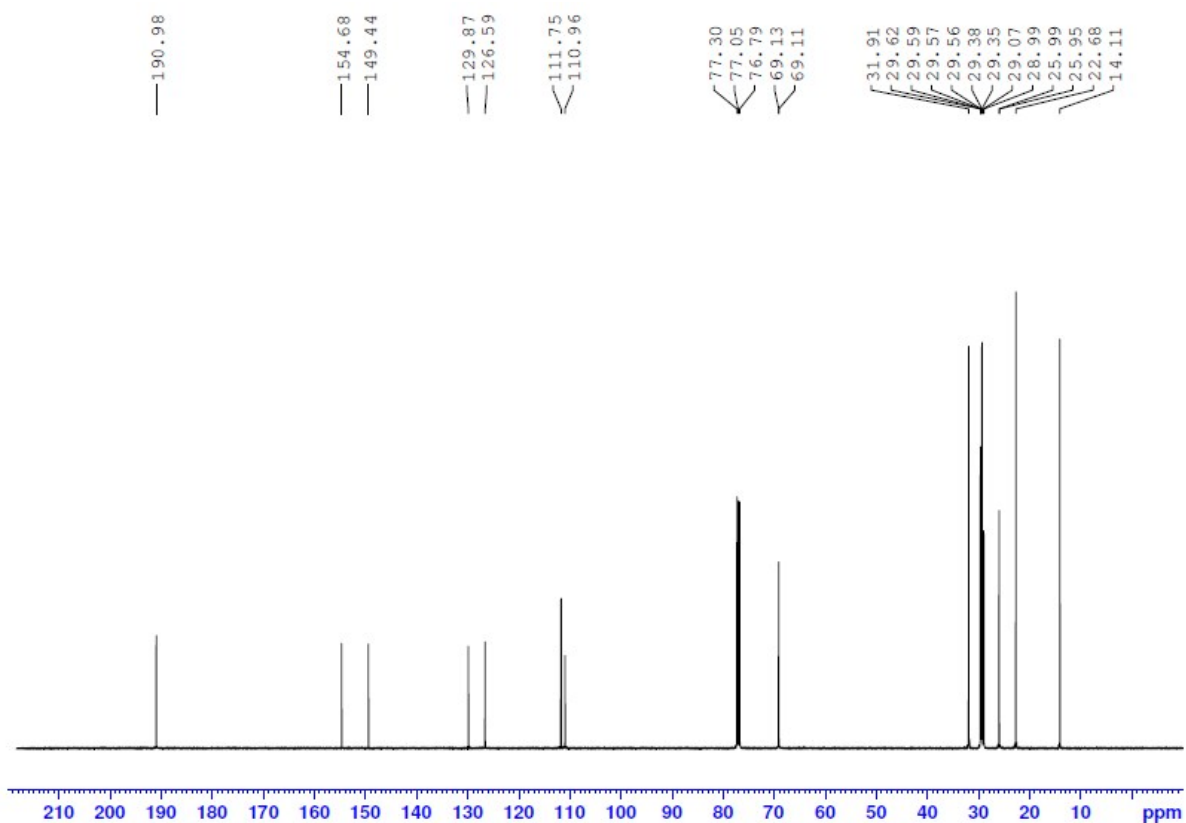


Figure S7. ^{13}C NMR (125 MHz) spectrum of **5** recorded in CDCl_3

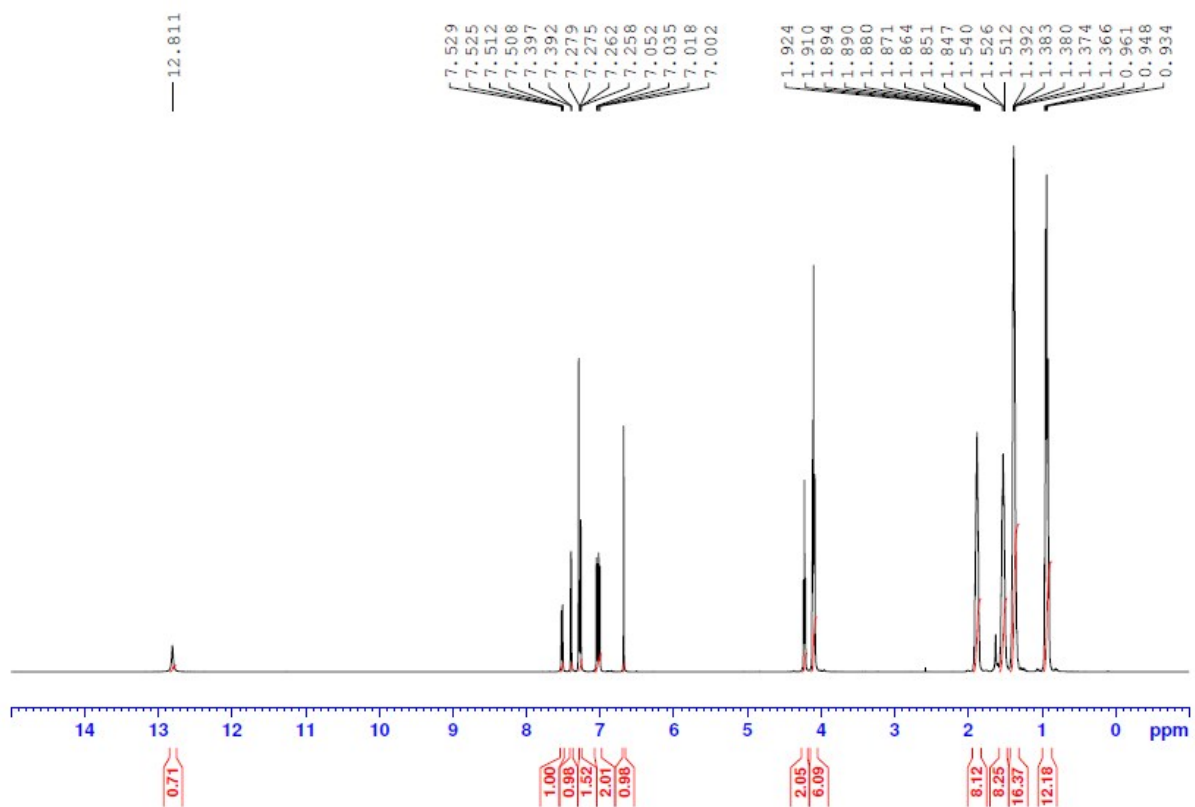


Figure S8. ^1H NMR (500 MHz) spectrum of **6** recorded in CDCl_3

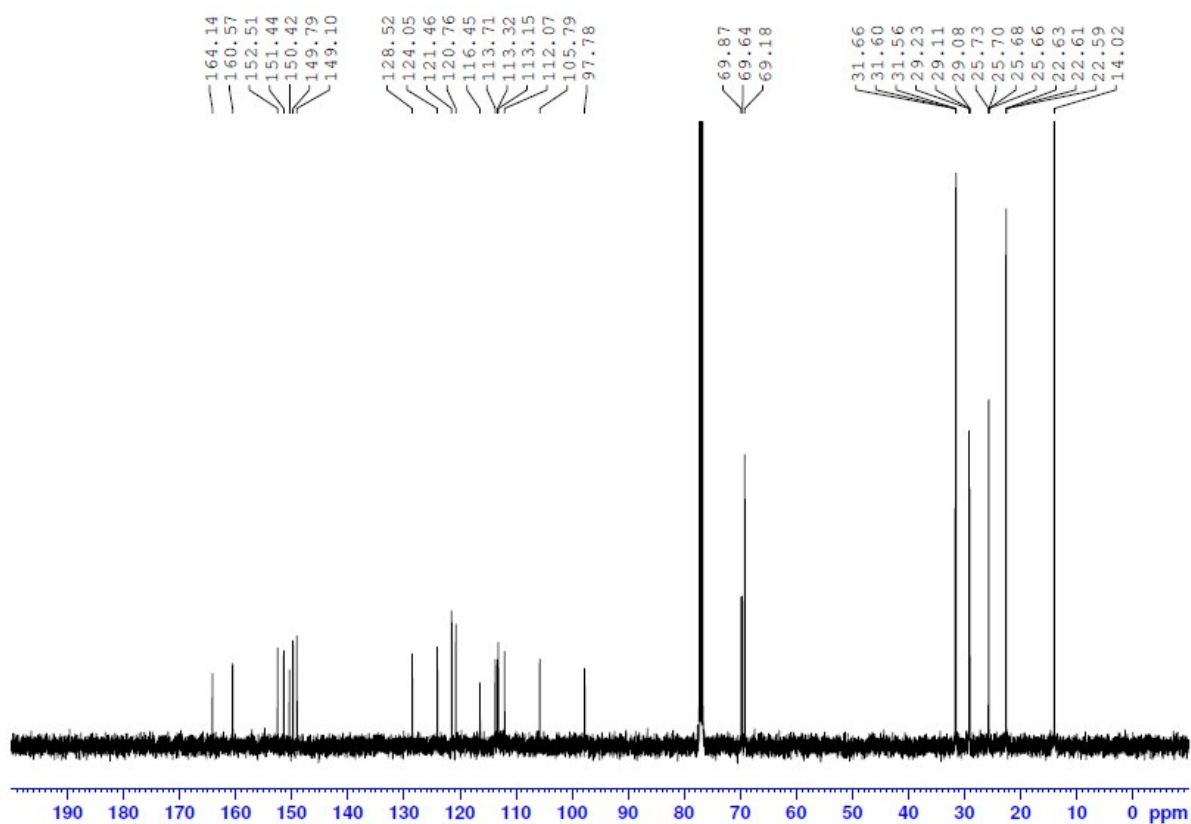


Figure S9. ^{13}C NMR (125 MHz) spectra of **6** recorded in CDCl_3

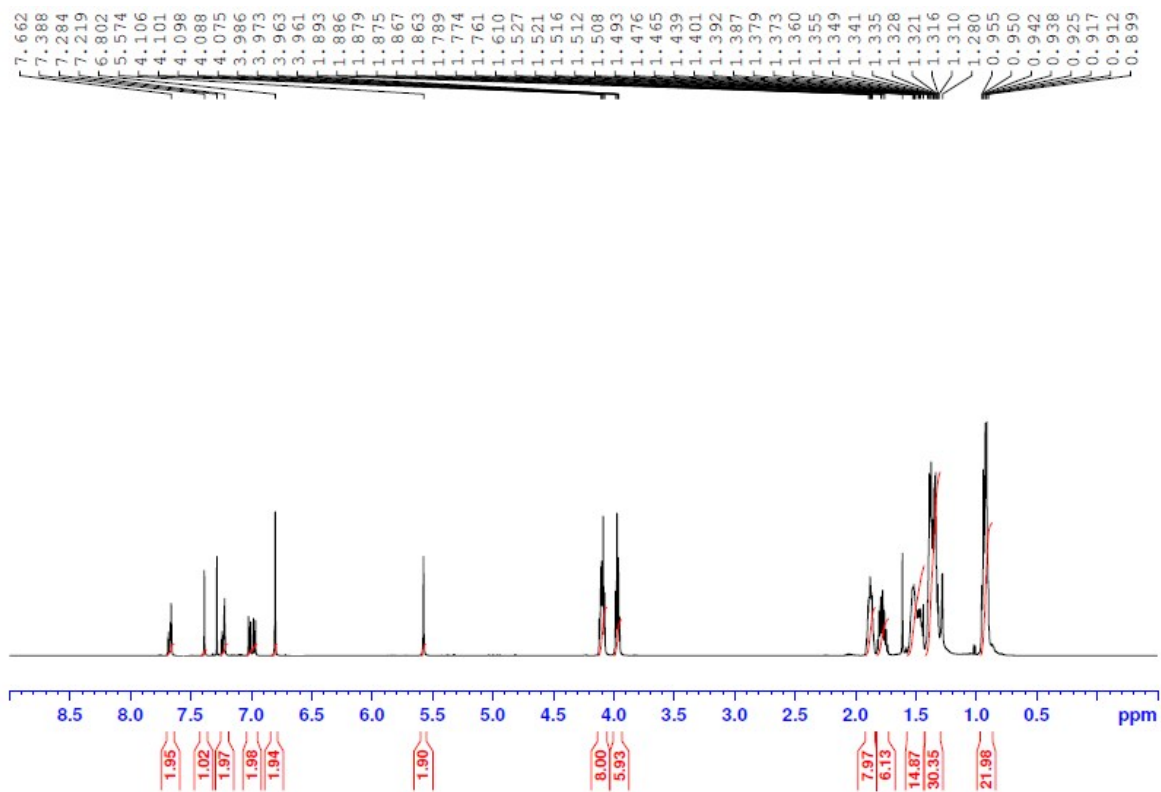


Figure S10. ^1H NMR (500 MHz) spectrum of CPBz6 recorded in CDCl_3

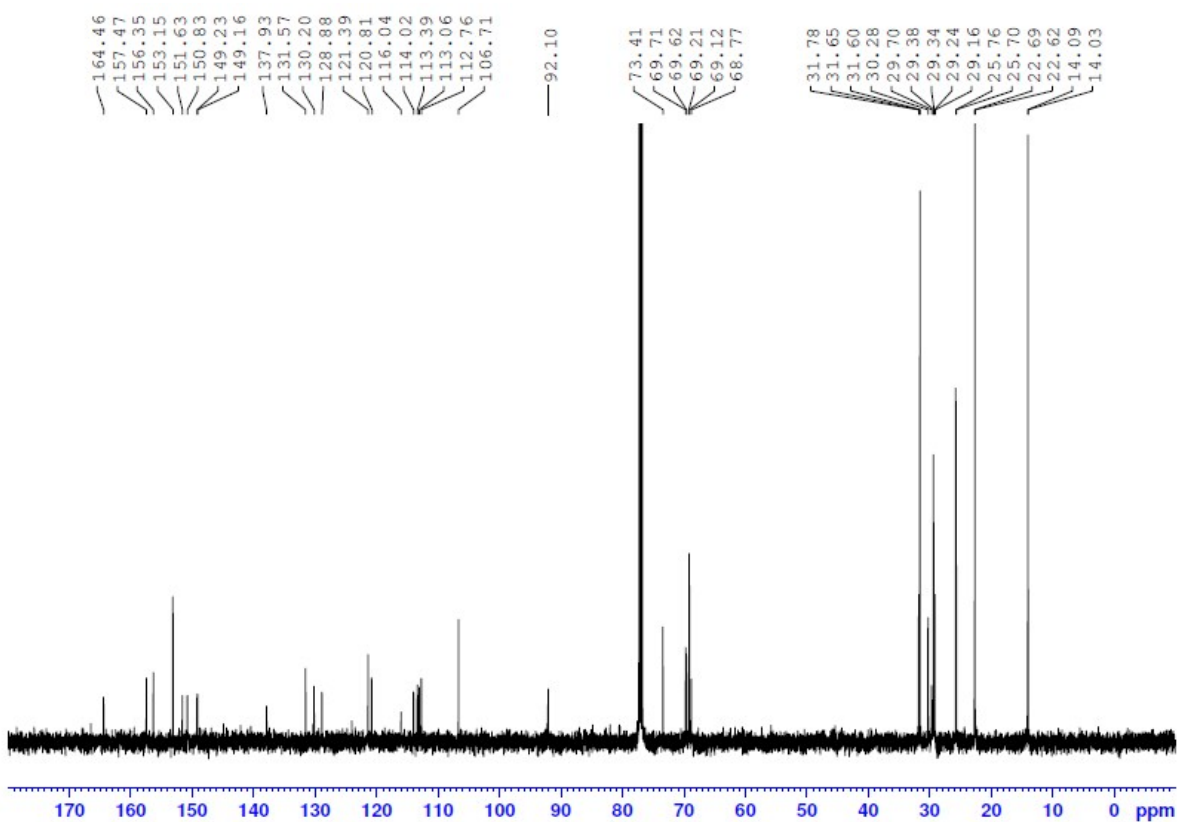


Figure S11. ^{13}C NMR (125 MHz) spectrum of CPBz6 recorded in CDCl_3

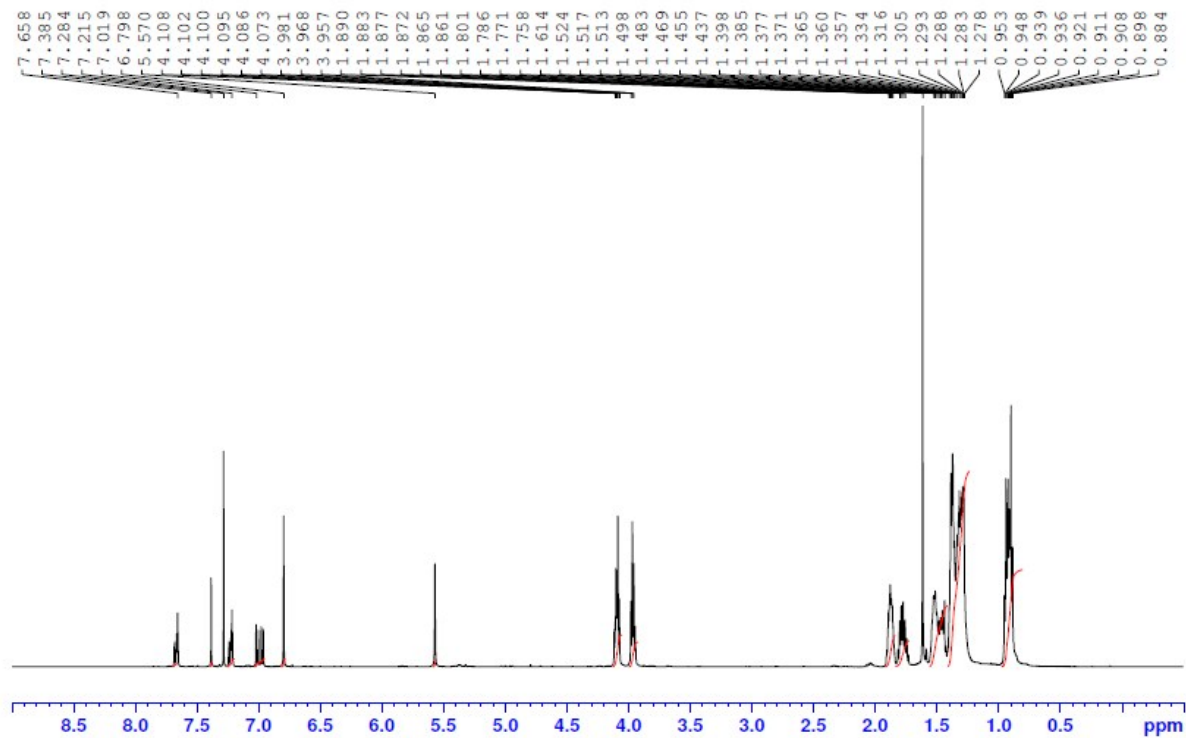


Figure S12. ^1H NMR (500 MHz) spectrum of CPBz8 recorded in CDCl_3

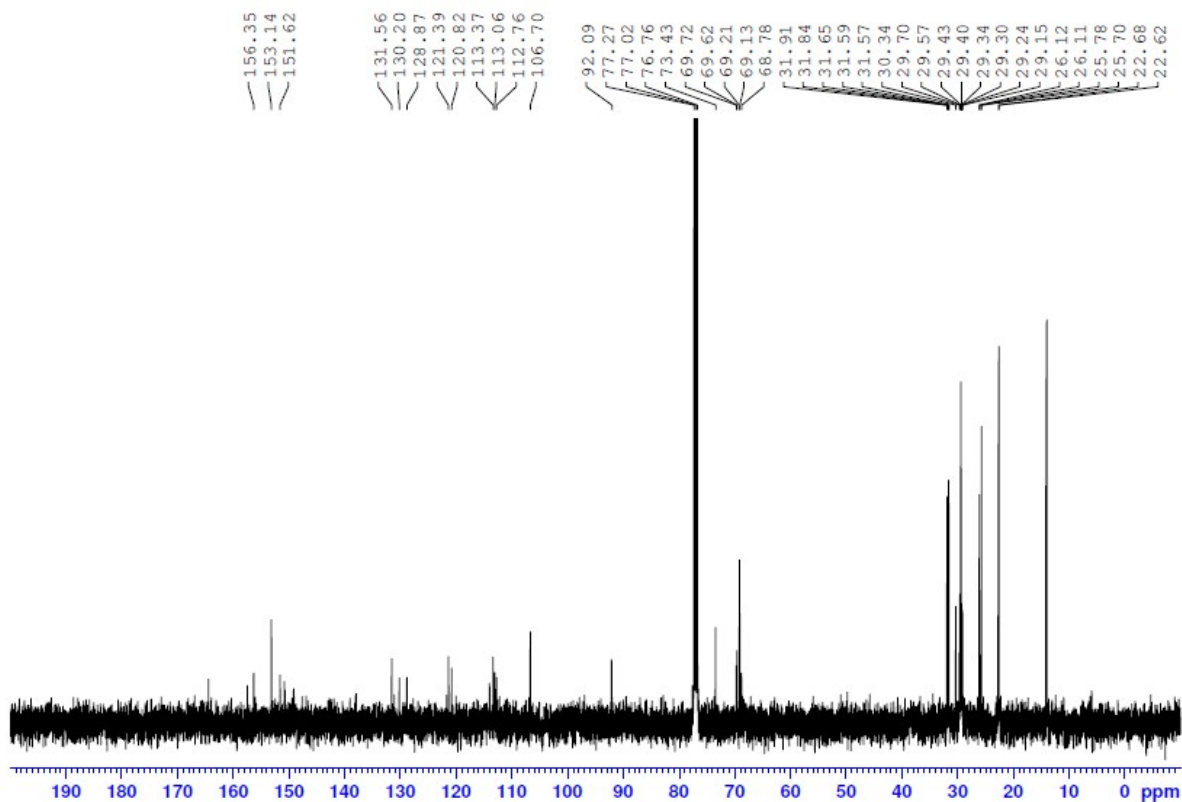


Figure S13. ^{13}C NMR (125 MHz) spectrum of CPBz8 recorded in CDCl_3

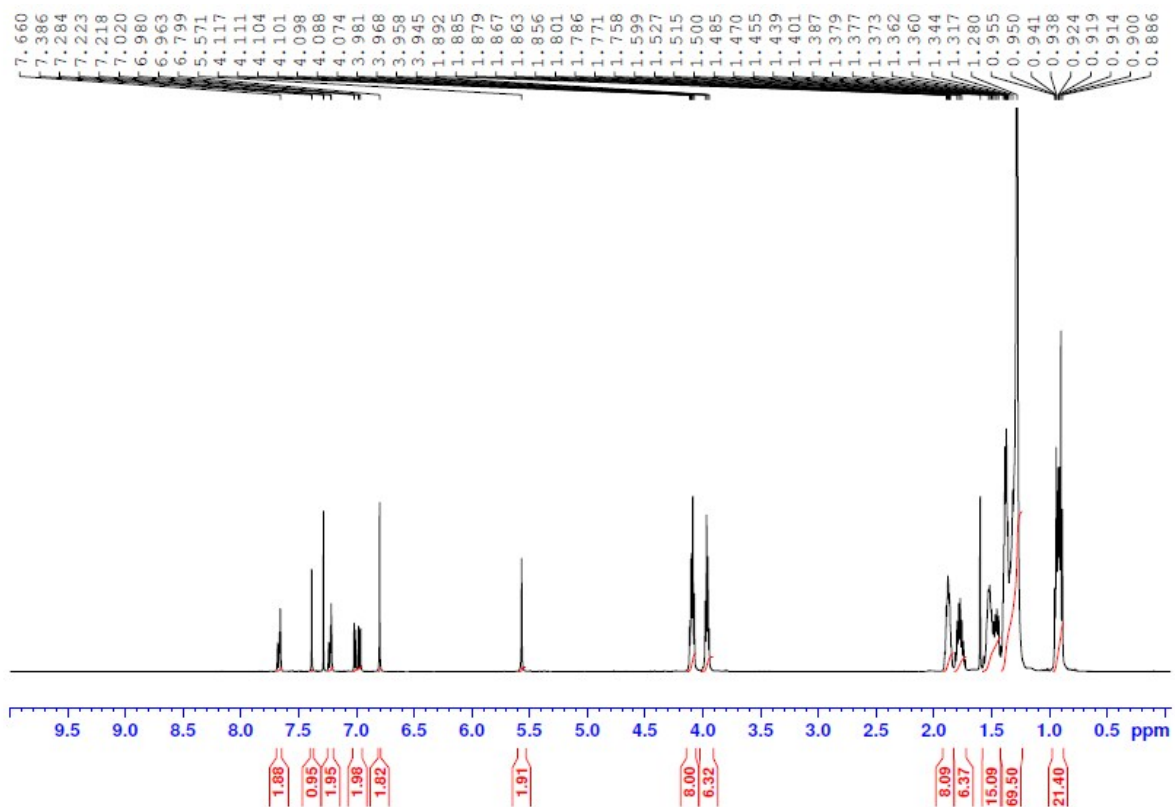


Figure S14. ^1H NMR (500 MHz) spectrum of **CPBz12** recorded in CDCl_3

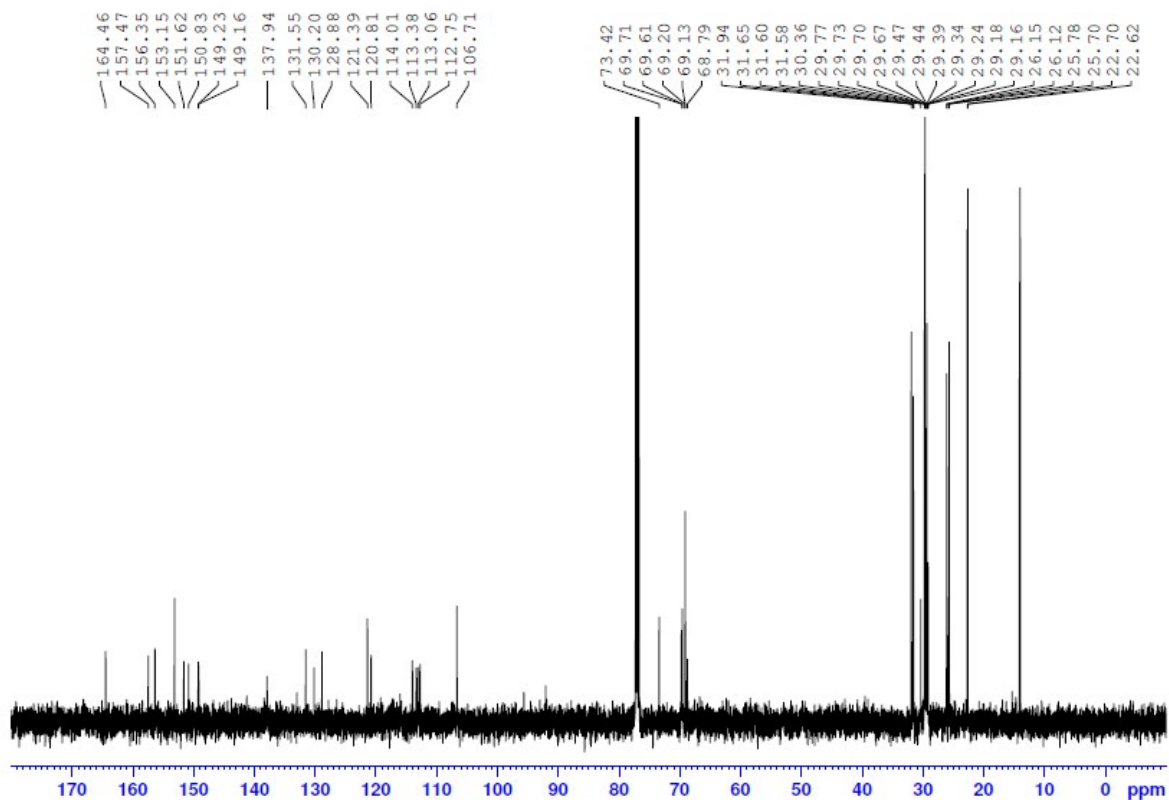


Figure S15. ^{13}C NMR (125 MHz) spectrum of **CPBz12** recorded in CDCl_3

5. XRD and POM characterization

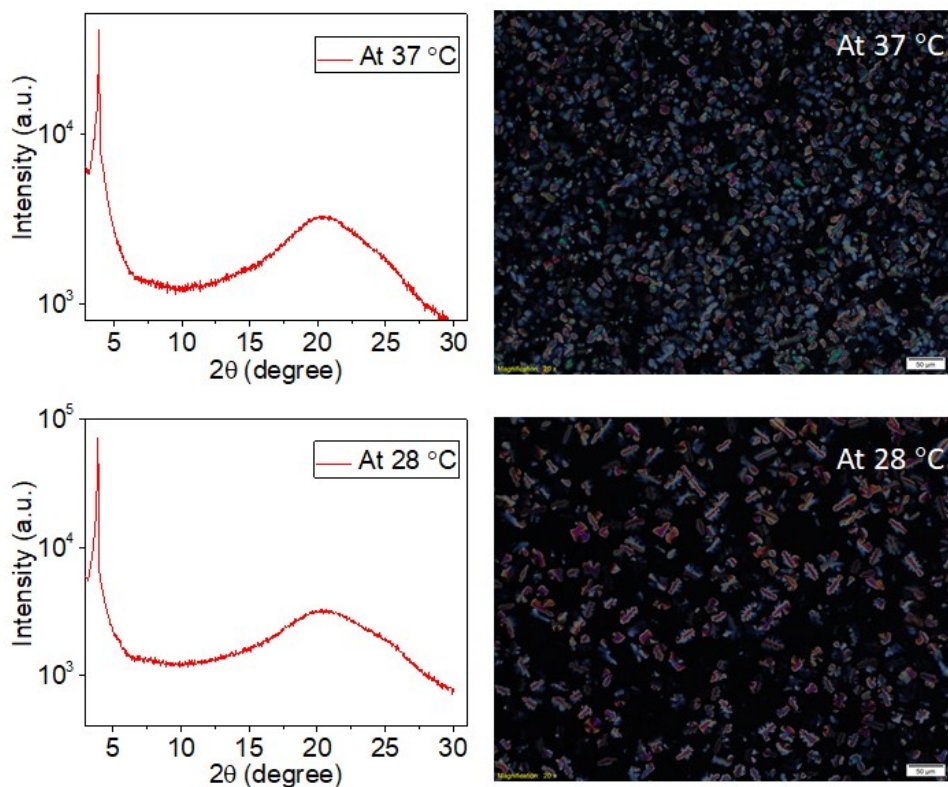


Figure S16. XRD spectra obtained at different temperatures and the corresponding POM textures of **CPBz8**

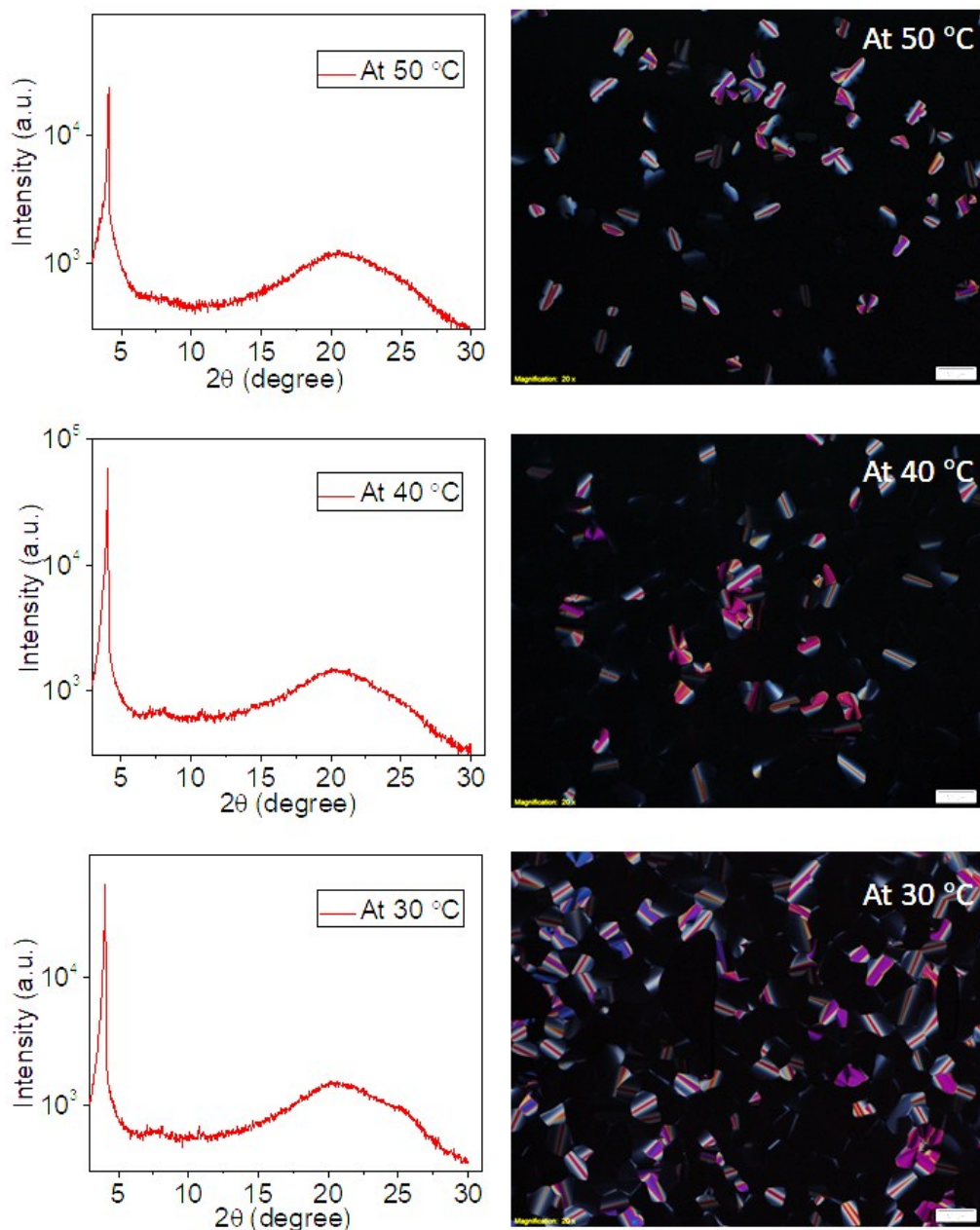


Figure S17. XRD spectra obtained at different temperature and the corresponding POM textures of CPBz6

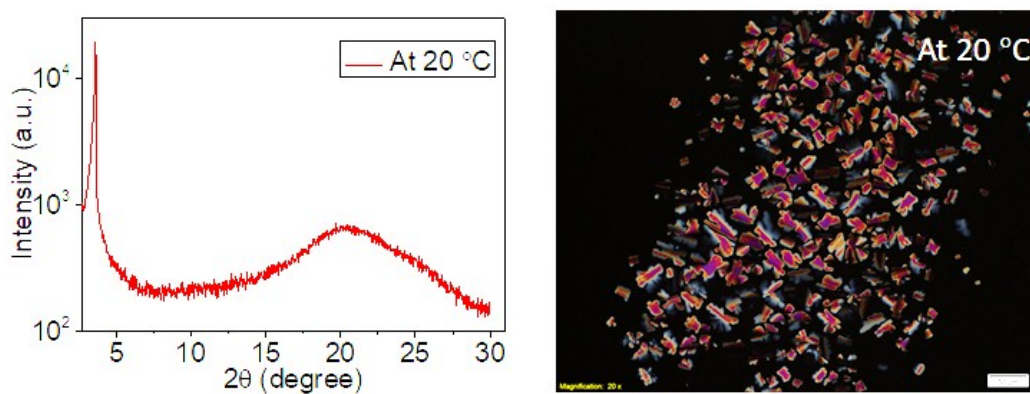


Figure S18. XRD spectra obtained at 20 °C and the corresponding POM textures of CPBz12

Table S1: XRD characterization data of spin-coated thin films of new mesogens

Compd.	Phase ($T/^\circ\text{C}$)	d_{obs} [\AA]	d_{cal} [\AA]	Miller Indices (hk)	Lattice parameter a [\AA], Lattice area S [\AA^2], Molecular volume V [\AA^3], Number of molecules per lattice site Z
CPBz6	Col _h (25)	21.41	21.41	(10)	$a = 24.72$ $S = 529.3$ $V = 1958.4$ $Z = 1.1$
		10.73	10.70	(20)	
		3.70 (h_a)			
CPBz8	Col _h (25)	22.26	22.26	(10)	$a = 25.70$ $S = 572.2$ $V = 2157$ $Z = 1.1$
		11.17	11.13	(20)	
		3.77 (h_a)			
CPBz12	Col _h (25)	23.72	23.39	(10)	$a = 27.39$ $S = 649.7$ $V = 2563$ $Z = 1.0$
		11.96	11.86	(20)	
		3.95 (h_a)			

d_{obs} , observed spacings; d_{cal} , calculated spacings from the lattice parameter a for the hexagonal lattice; h_a , alkyl chains correlation peak value; h_c , core-core spacing; Z , number of molecules per columnar slice; S , lattice area; V , molecular volume

6. Cyclic voltametric characterization

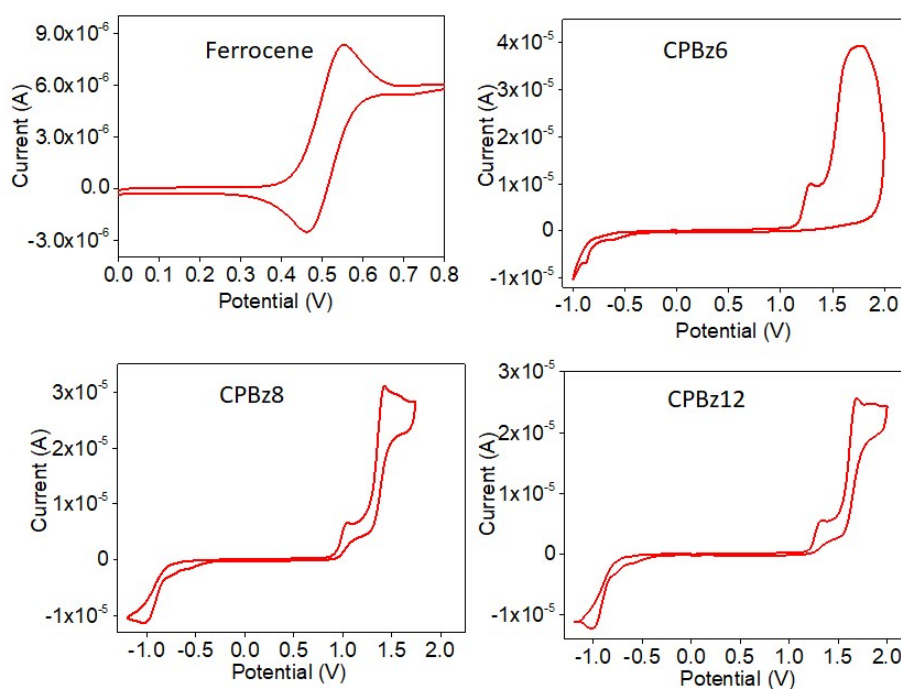


Figure S19. Cyclic voltamograms of CPBz DLCs