Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

New cyanopyridone based unsymmetrical dyads: Effect of donor strength on their optoelectronic properties

D. R. Vinayakumara,[a] Rajalakshmi Kesavan [a] Sandeep Kumar,[b] Airody Vasudeva Adhikari.*[a]

Supporting information

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1. Material and methods

All the chemicals and reagents (AR grade) were purchased from Sigma-Aldrich and used without further purification. The solvents were procured 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 were reported in cm^{-1}. Proton magnetic resonance spectra 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 were reported in δ related to internal standard TMS. Elemental analysis was performed on a Carlo-Erba Flash 1112 analyzer.

The thermal phase transitions of all the final compounds were investigated by employing 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 ºC min^{-1} under continuous flow of nitrogen gas; thermal stability was established by Perkin Elmer TGA4000 analyser at the heating rate of 10 °C/min under nitrogen atmosphere.

The photophysical properties of target materials were studied by recording steady-state UV-visible and fluorescence spectra with the help of SPECORD S 600 UV-visible spectrophotometer and Fluoromax 4 HORIBA spectrofluorometer, respectively. Absolute quantum yields were determined by using an integrated sphere set-up EDINBURGH (UK) and FLS 980 TCSPC instrument. 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.

Theoretical calculations were carried out using the Gaussian 09 software. Geometry optimised structures of all the molecules were obtained using the Becke three-parameter exchange functional and Lee-Yang-Parr (B3LYP) exchange correlation functional with the 6-31G(d,p) basis set for C, H, N, and O. The calculations were performed under vacuum.

2. Structural characterization data

For precursor **A**,

FTIR (ATR, ν_{max} in cm^{-1}): 2915 (Ar C-H), 2847 (Aliph C-H), 2730 (aldehyde C-H), 1692 (aldehyde C=O), 1580 (Ar C=C); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS, δ in ppm): δ- 9.84 (s, 1H, CHO), 7.10 (s, 2H, Ar-H), 4.06 (m, 6H, OCH_2), 1.86-1.75 (m, 6H, CH_2), 1.64-1.28 (m, 54H, CH_2), 0.9 (t, 9H, *J* = 5.5 Hz, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS, δ in ppm): δ- 191.24, 153.53, 143.91, 131.46, 107.89, 73.63, 69.26, 31.93, 30.35, 29.58, 29.27, 26.03, 22.69, 14.09; Elemental Anal. Calcd (%) for $C_{43}H_{78}O_4$: C 78.36, H 11.93; Found: C 78.26, H 12.01.

For final compound **CP1**,

(Yield, 41 %) FTIR (ATR): ν_{max} in cm^{-1} 2916 (Ar C-H), 2849 (Aliph C-H), 2218 (C≡N), 1654 (C=O), 1587 (Ar-C=C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 12.29 (s, 1H, CONH), 8.01 (d, 2H, *J* = 8.5 Hz, Ar-H), 7.28 (d, 2H, *J* = 8.5 Hz, Ar-H), 6.84 (s, 2H, Ar-H), 6.67 (s, 1H, pyridone-H). 4.086 (t, 2H, *J* = 6.5 Hz, OCH_2), 4.022 (t, 4H, *J* = 6.5 Hz, OCH_2), 1.82-0.91 (m, 60H, CH_2), 0.91 (t, 9H, *J* = 6.0 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 163.97, 161.30, 160.43, 153.38, 150.88, 139.69, 131.30, 128.98, 122.78, 116.93, 106.53, 105.50, 97.68, 73.91, 69.37, 31.94, 30.32, 29.76 29.72 29.65, 26.10, 22.69 14.12. Elemental Anal. Calculated for $C_{54}H_{84}N_2O_5$ (%): C, 77.10; H, 10.06; N, 3.33. Found: C, 76.98; H, 10.25; N, 3.15.

For final compound **CP2**

(Yield, 44 %) FTIR (ATR): ν_{max} in cm^{-1} 2919 (Ar C-H), 2850 (Aliph C-H), 2217 (C≡N), 1654 (C=O), 1605 (Ar-C=C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 12.14 (s, 1H, CONH), 7.95 (d, 2H, *J* = 9.0 Hz, Ar-H), 7.11 (d, 2H, *J* = 8.5 Hz, Ar-H), 6.89 (s, 2H, Ar-H), 6.70 (s, 1H, pyridone-H), 4.06 (m, 6H, OCH_2), 3.91 (s, 3H, OCH_3), 1.88-1.77 (m, 6H, CH_2), 1.54-1.38 (m, 54H, CH_2), 0.91 (t, 9H, *J* = 6.0 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.66, 160.97, 153.38, 150.17, 140.49, 130.86, 128.90, 123.83, 116.10, 115.04, 106.94, 105.60, 98.23, 73.66, 69.49, 69.49, 55.62, 31.95, 31.93, 30.39, 29.52, 26.12, 22.10, 14.10. Elemental Anal. Calculated for $C_{55}H_{86}N_2O_5$ (%): C, 77.24; H, 10.14; N, 3.28. Found: C, 77.38; H, 10.07; N, 3.11.

For final compound **CP3**

(Yield, 29 %) FTIR (ATR): ν_{max} in cm^{-1} 3391 3357 (Ar-NH_2), 2917 (Ar C-H), 2849 (Aliph C-H), 2219 (C≡N), 1662 (C=O), 1588 (Ar-C=C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 12.27 (s, 1H, CONH), 7.76 (d, 2H, *J* = 9.0 Hz, Ar-H), 6.88 (s, 2H, Ar-H), 6.83 (d, 2H, *J* = 9.0 Hz, Ar-H), 6.64 (s, 1H, pyridone-H), 4.15 (s, 2H, NH_2) 4.05 (m, 6H, OCH_2), 1.88-1.76 (m, 6H, CH_2) 1.59-1.28 (m, 54H, CH_2), 0.92 (3, 9H, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.03, 160.77, 153.32, 150.62, 150.16, 140.29, 131.17, 128.79, 120.75, 116.45, 115.14, 106.90, 106.90, 104.61, 97.13, 73.65, 69.47, 31.94, 30.39, 29.62, 26.13, 22.69, 14.11. Elemental Anal. Calculated for $C_{54}H_{85}N_3O_4$ (%): C, 77.19; H, 10.20; N, 5.00. Found: C, 77.05; H, 10.33; N, 4.60.

For final compound **CP4**

(Yield, 33 %) FTIR (ATR): ν_{max} in cm^{-1} 2917 (Ar C-H), 2849 (Aliph C-H), 2211 (C≡N), 1631 (C=O), 1602 (Ar-C=C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 12.16 (s, 1H, CONH), 7.75 (d, 2H, *J* = 9.0 Hz, Ar-H), 6.79 (s, 2H, Ar-H), 6.74 (d, 2H, *J* = 9.0 Hz, Ar-H), 6.55 (s, 1H, pyridone-H), 3.96 (m, 6H, OCH_2), 3.0 (s, 6H, NCH_3), 1.78-1.67 (m, 6H, CH_2) 1.42-1.40 (m, 54H, CH_2), 0.81 (m, 9H, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 163.92, 160.60, 153.27, 152.61, 142.25 131.42, 128.32, 117.86, 116.52, 112.12, 106.85, 104.17, 96.37, 73.64, 69.43, 40.08, 31.95, 30.38, 29.51, 26.13, 22.70, 14.12. Elemental Anal. Calculated for $C_{56}H_{89}N_3O_4$ (%): C, 77.46; H, 10.33; N, 4.84. Found: C, 77.85; H, 10.12; N, 5.02.

For final compound **CP5**

(Yield, 40 %) FTIR (ATR): ν_{max} in cm^{-1} 2919 (Ar C-H), 2850 (Aliph C-H), 2212 (C≡N), 1631 (C=O), 1601 (Ar-C=C). ^1H NMR ($CDCl_3$, 500 MHz): δ 13.26 (s, 1H, CONH), 8.32 (d, 1H, *J* = 3.0 Hz, Ar-H), 7.59 (dd, *J* = 0.5, 5.0 Hz, 1H, Ar-H), 7.32 (m, 1H, Ar-H), 6.89 (m, 2H, Ar-H), 6.72 (s, 1H, pyridone-H), 4.05 (m, 6H, OCH_2), 1.89-1.78 (m, 6H, CH_2) 1.39-1.28 (m, 54H, CH_2), 0.91 (m, 9H, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): 163.82, 161.08, 153.40, 144.09, 134.31, 130.45, 130.08, 129.73, 115.96, 106.91, 105.61, 98.62, 73.69, 69.51, 31.94, 30.39, 29.65, 26.12, 22.70, 14.12. Elemental Anal. Calculated for $C_{52}H_{82}N_2O_4S$ (%): C, 75.13; H, 9.94; N, 3.37; S, 3.86. Found: C, 75.11; H, 10.07; N, 3.57; S, 3.42.

For final compound **CP6**

(Yield, 49 %) FTIR (ATR): ν_{max} in cm^{-1} 2919 (Ar C-H), 2850 (Aliph C-H), 2212 (C≡N), 1631 (C=O), 1601 (Ar-C=C). ^1H NMR ($CDCl_3$, 500 MHz): δ 13.25 (s, 1H, CONH), 8.07 (d, 2H, *J* = 8.5 Hz, Ar-H), 7.85 (d, 2H, *J* = 8.5 Hz, Ar-H), 7.68 (t, 2H, *J* = 7.0 Hz, Ar-H), 7.49 (m, 2H, Ar-H), 7.42 (t, 1H, *J* = 7.0 Hz, Ar-H), 6.92 (s, 2H, Ar-H), 6.83 (s, 1H, pyridone-H), 4.07 (m, 6H, OCH_2), 1.89-1.78 (m, 6H, CH_2) 1.64-1.28 (m, 54H, CH_2), 0.91 (m, 9H, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): 164.15, 161.00, 153.41, 150.05, 144.70, 140.52, 139.55, 130.70, 130.37, 128.99, 128.25, 128.15, 127.74, 127.28, 116.00, 106.91, 106.46, 99.30, 73.68, 69.48, 31.96, 31.94, 30.40, 29.54, 26.14, 22.71, 14.12. Elemental Anal. Calculated for $C_{60}H_{88}N_2O_4$ (%): C, 79.95; H, 9.84; N, 3.11. Found: C, 80.08; H, 9.74; N, 3.18.

For final compound **CP7**

(Yield, 30 %) FTIR (ATR): ν_{max} in cm^{-1} 2919 (Ar C-H), 2850 (Aliph C-H), 2218 (C≡N), 1636 (C=O), 1589 (Ar-C=C). ^1H NMR ($CDCl_3$, 500 MHz): δ 11.88 (s, 1H, CONH), 7.58 (d, 2H, *J* = 9 Hz, Ar-H), 7.27-7.23 (m, 4H, Ar-H), 7.10 (3, 4H, Ar-H), 7.49 (m, 2H, Ar-H), 7.03 (m, 4H, Ar-H), 6.76 (s, 2H, Ar-H), 6.53 (s, 1H, pyridone-H), 3.95 (t, 6H, *J* = 6.5 Hz, OCH_2), 1.76-1.68 (m, 6H, CH_2) 1.40 (m, 6H, CH_2),1.22-1.18 (m, 48H, CH_2) 0.81 (m, 9H, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): 164.25, 160.83, 153.31, 146.35, 130.99, 129.69, 127.98, 125.86, 124.70, 123.23, 120.98, 106.83, 73.65, 69.43, 31.93, 30.38, 29.77, 29.37, 26.12, 22.70, 14.12.

Elemental Anal. Calculated for $C_{66}H_{93}N_3O_4$ (%): C, 79.87; H, 9.45; N, 4.23. Found: C, 79.01; H, 10.0; N, 4.32.

3. FTIR characterization

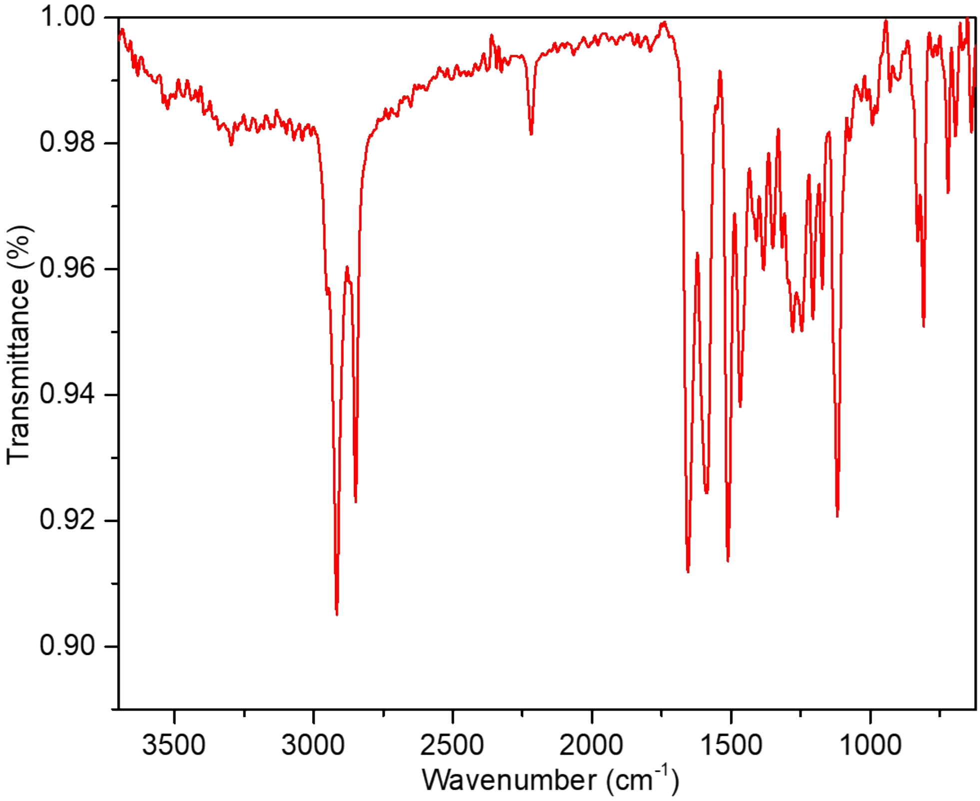

Figure S1: FTIR spectrum of **CP1**

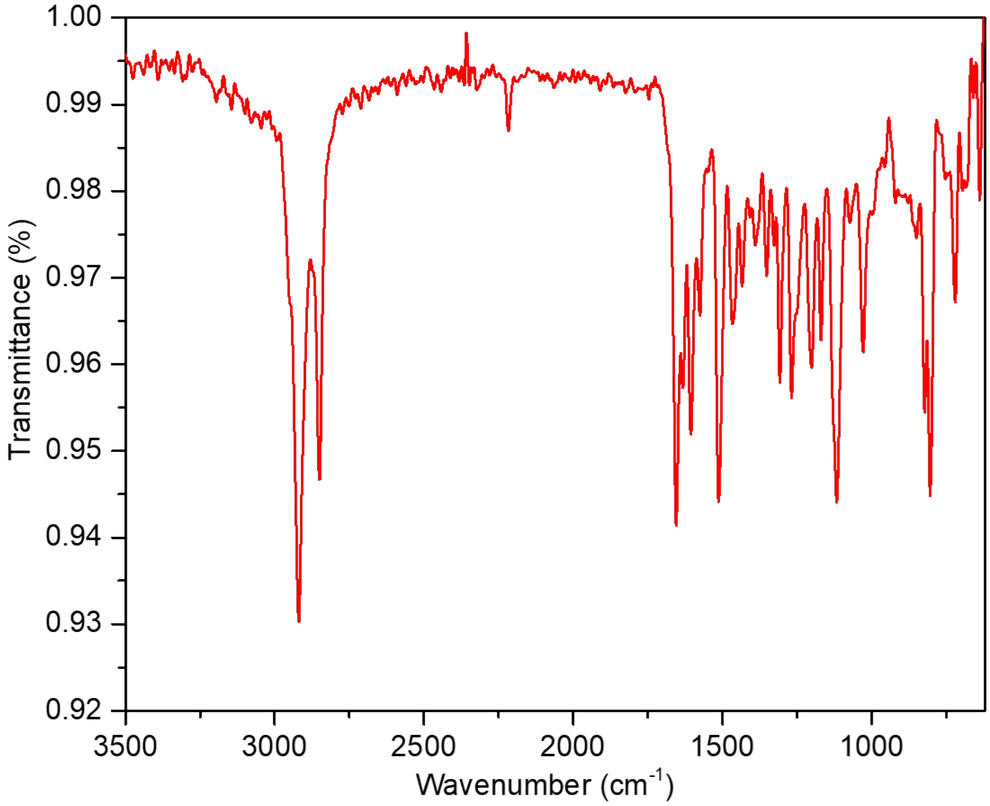

Figure S2: FTIR spectrum of **CP2**

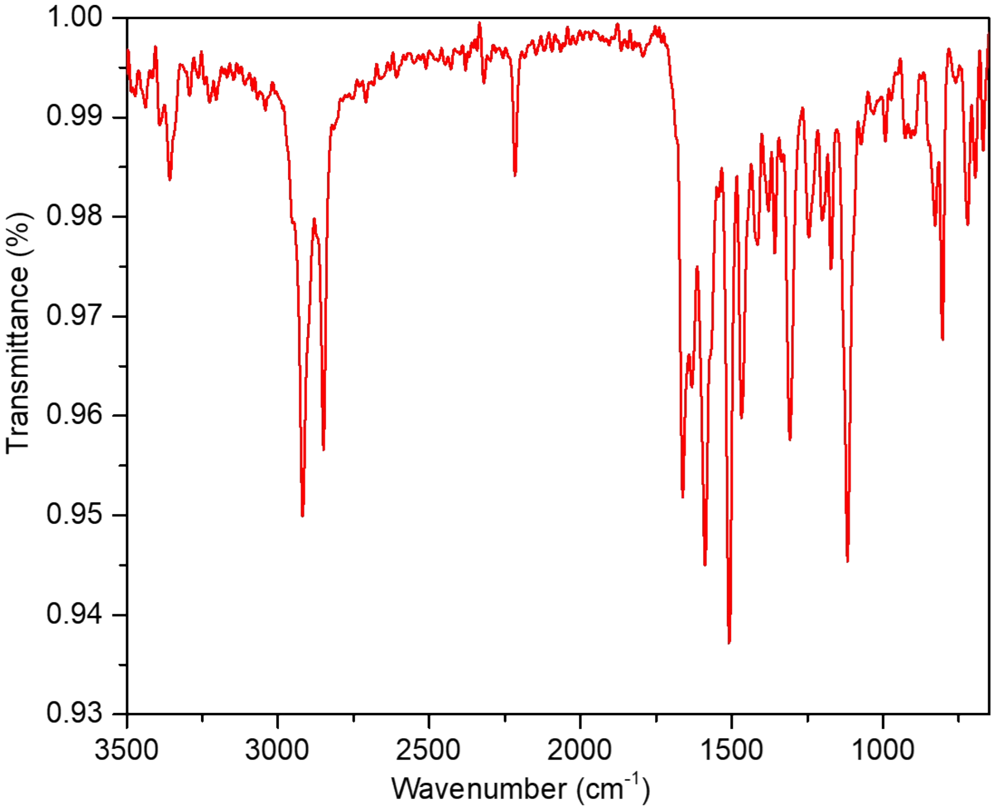

Figure S3: FTIR spectrum of **CP3**

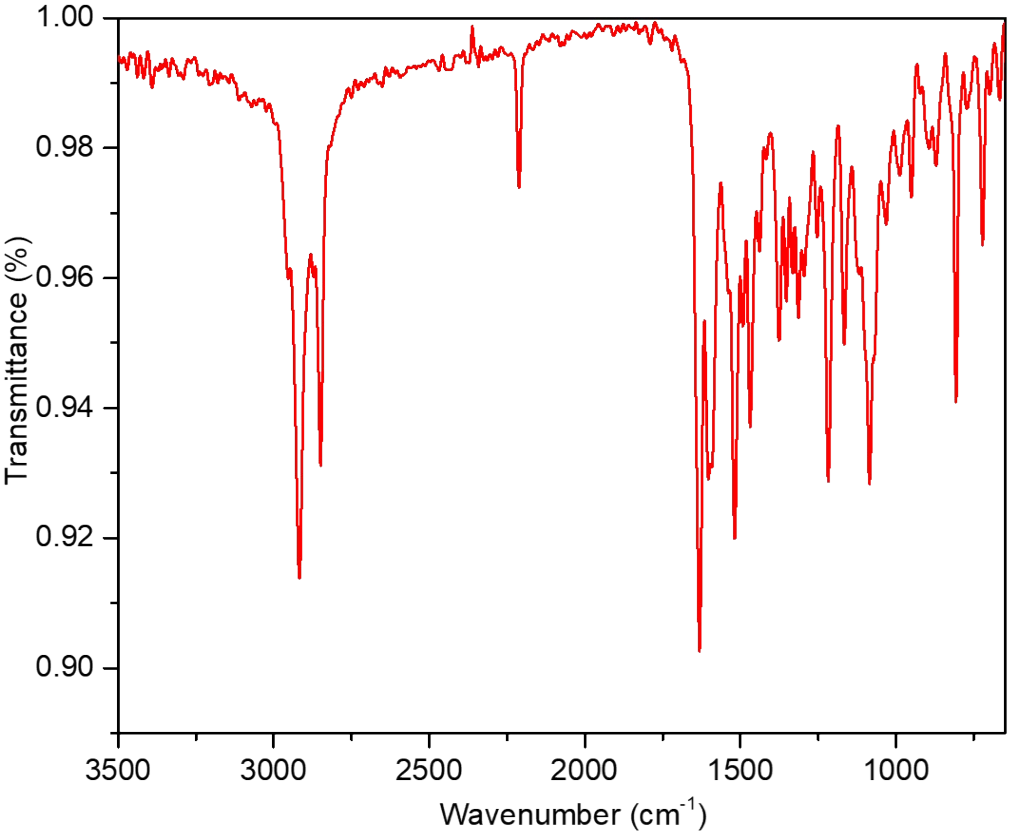

Figure S4: FTIR spectrum of **CP4**

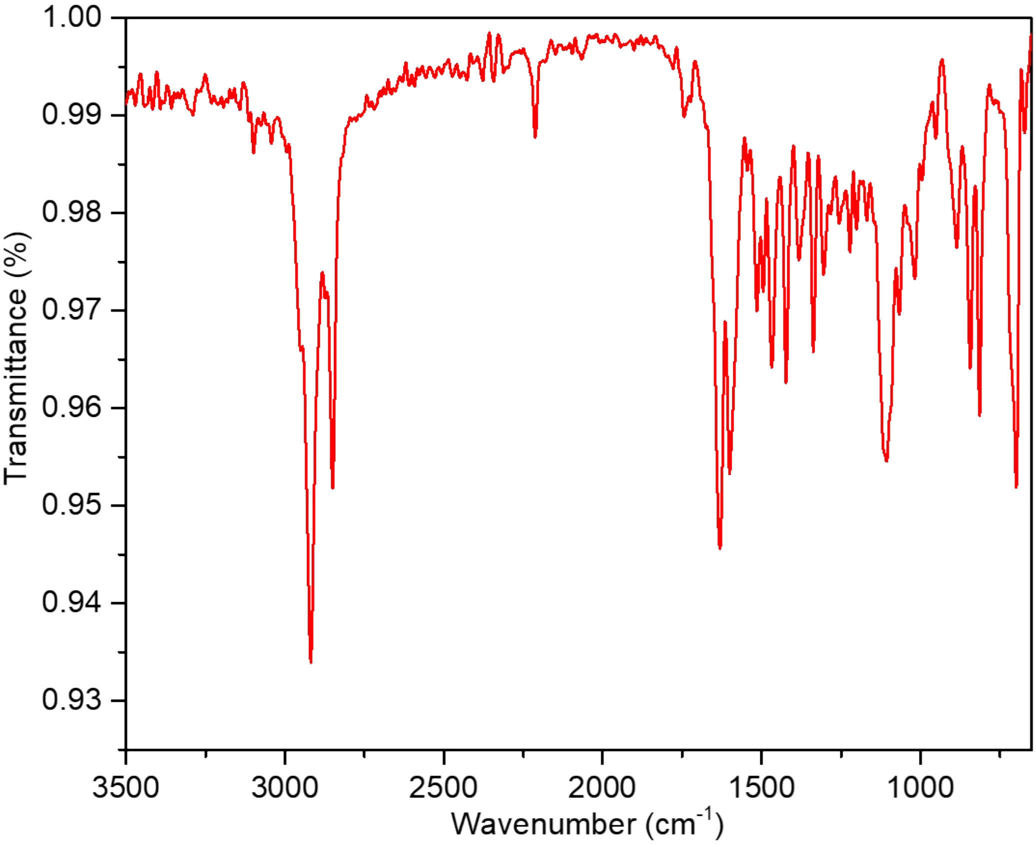

Figure S5: FTIR spectrum of **CP5**

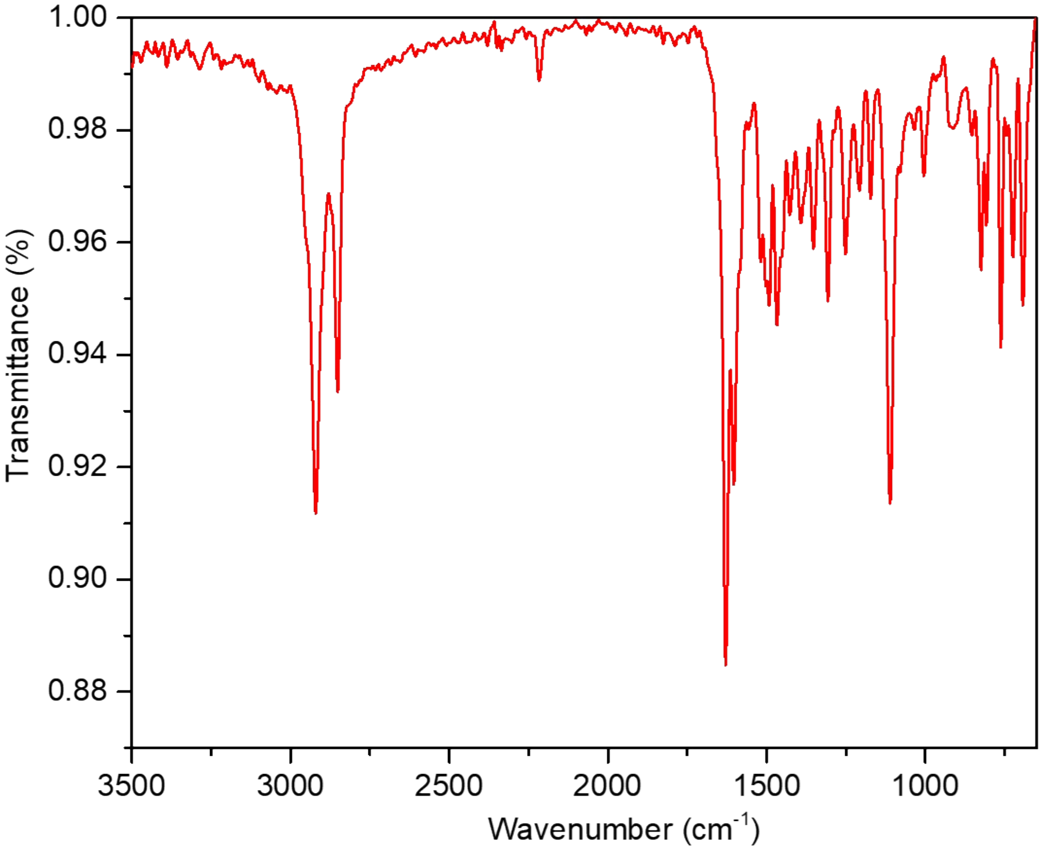

Figure S6: FTIR spectrum of **CP6**

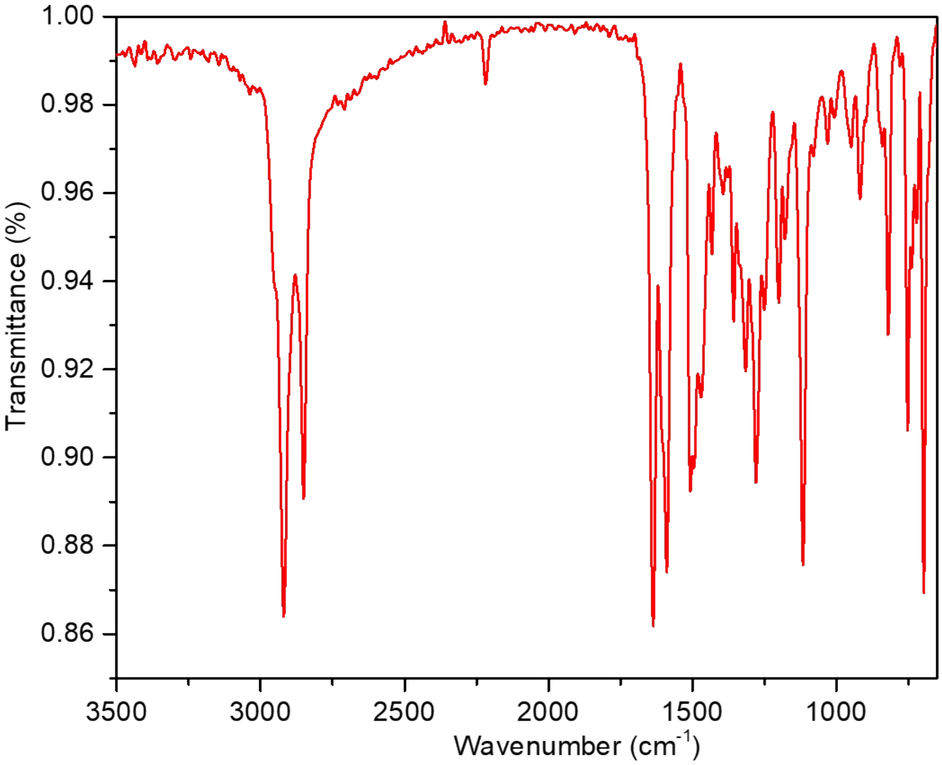

Figure S7: FTIR spectrum of **CP7**

4. NMR characterization

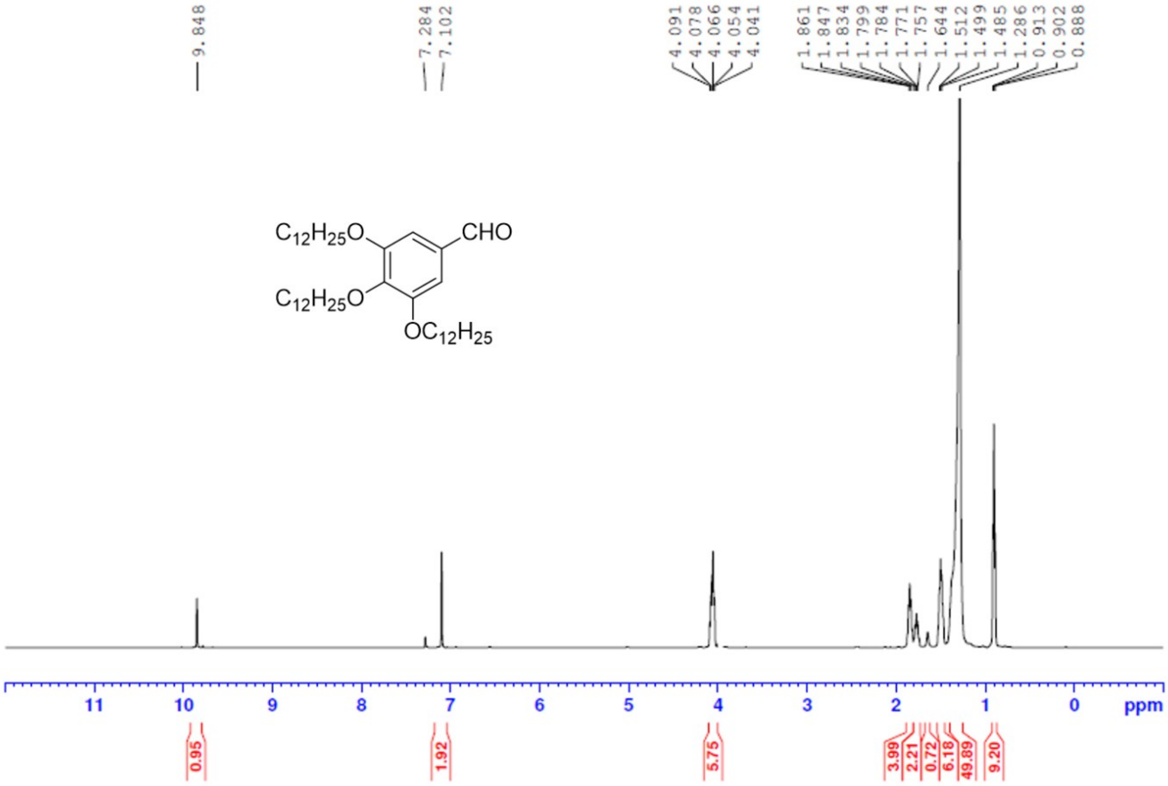

Figure S8: ^{1}H-NMR (500 MHz) spectrum of **A** recorded in CDCl$_3$

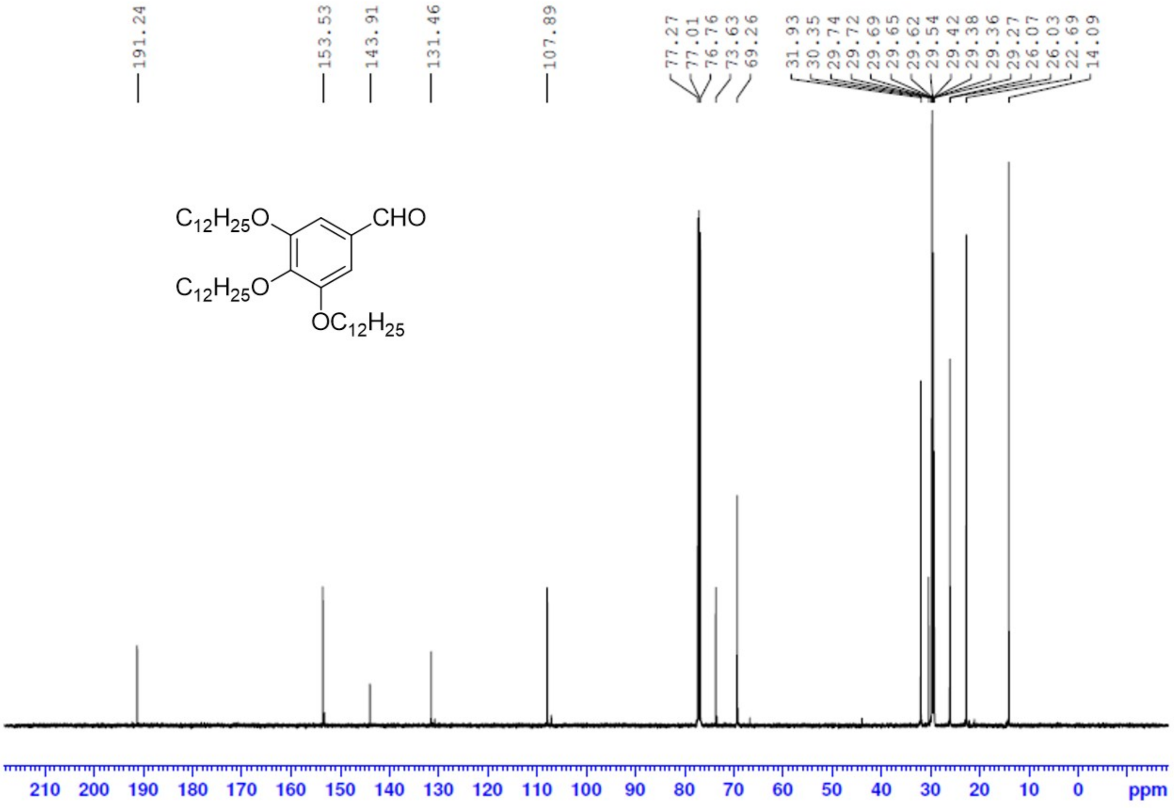

Figure S9: ^{13}C-NMR (125 MHz) spectrum of **A** recorded in CDCl$_3$

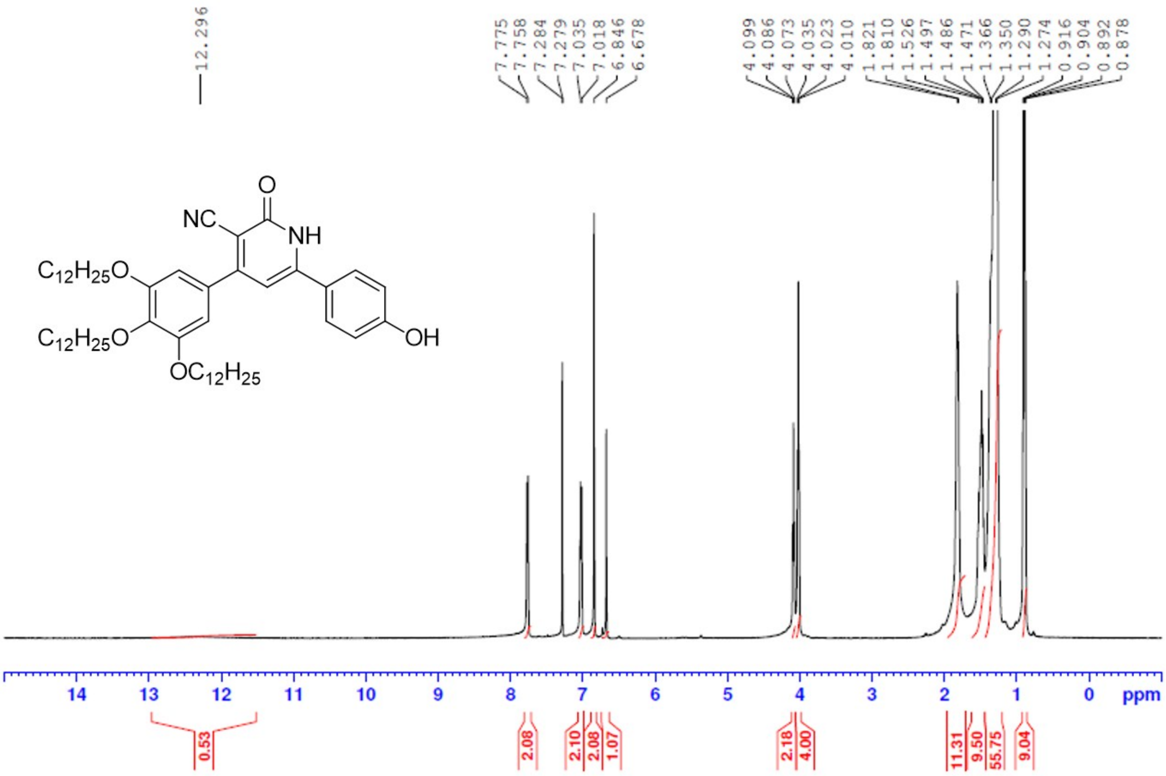

Figure S10: ^{1}H-NMR (500 MHz) spectrum of **CP1** recorded in $CDCl_3$

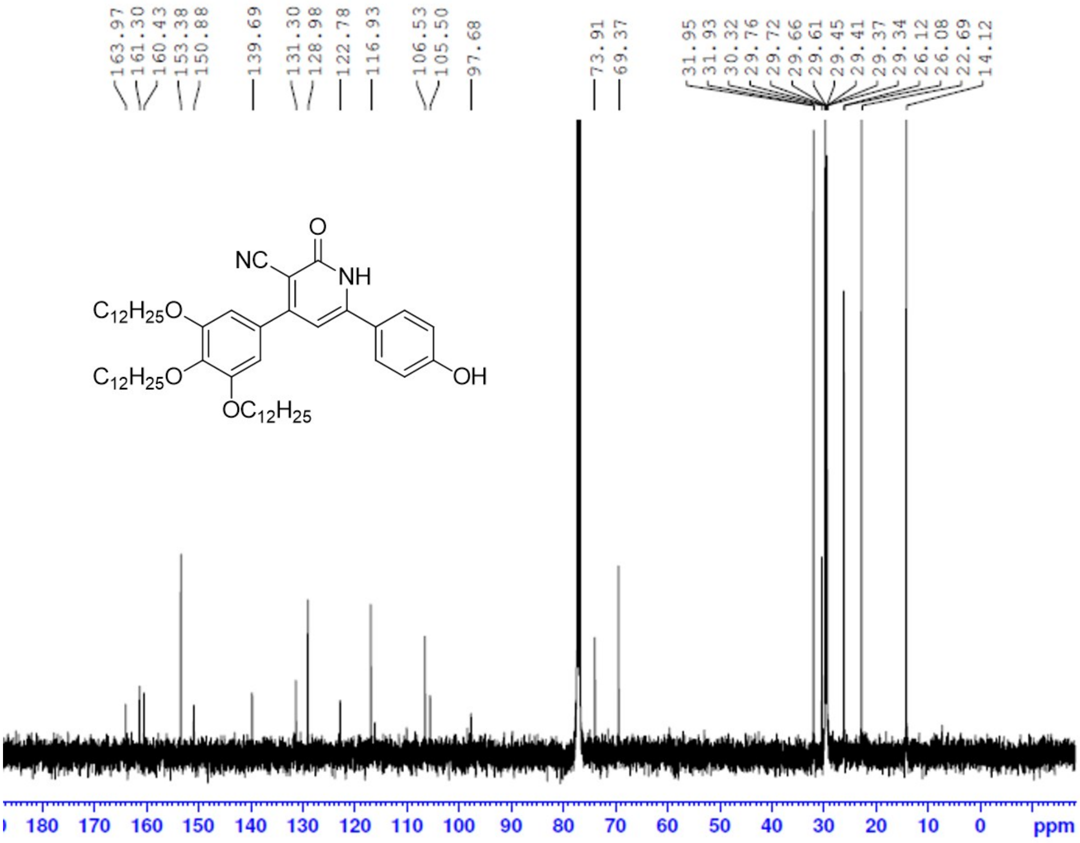

Figure S11: ^{13}C-NMR (125 MHz) spectrum of **CP1** recorded in $CDCl_3$

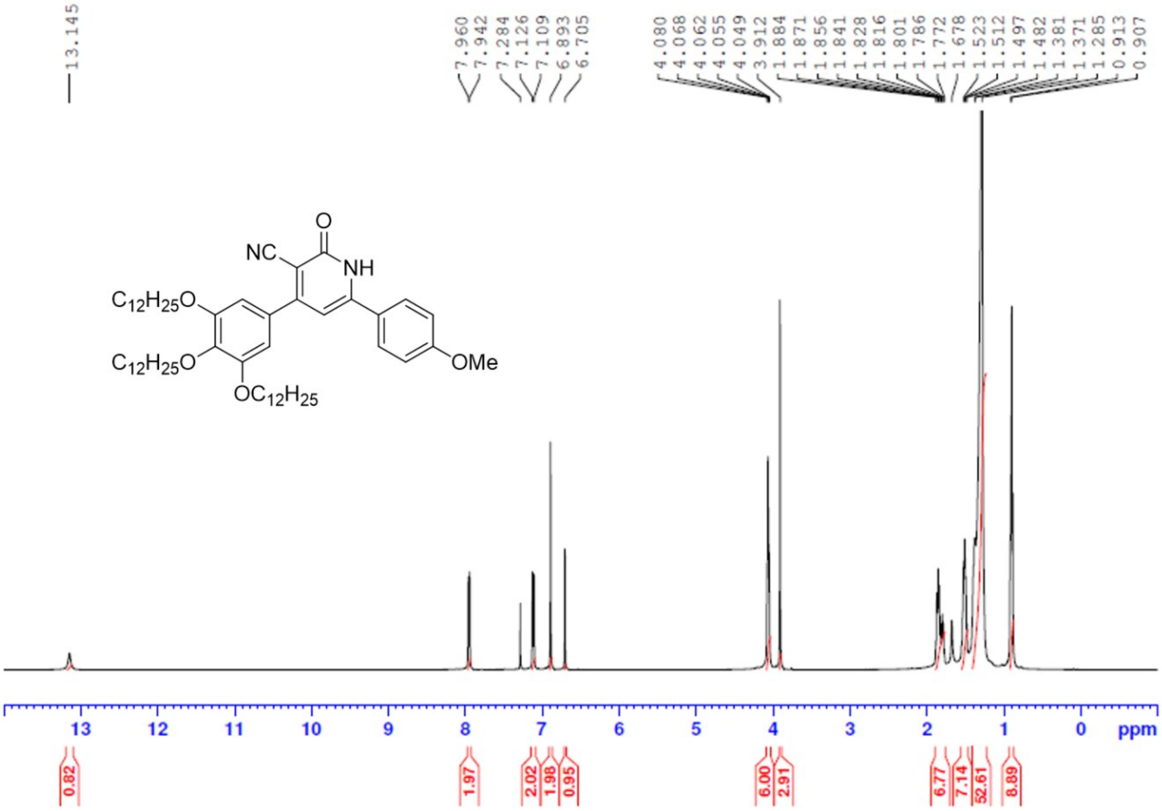

Figure S12: ^{1}H-NMR (500 MHz) spectrum of **CP2** recorded in $CDCl_3$

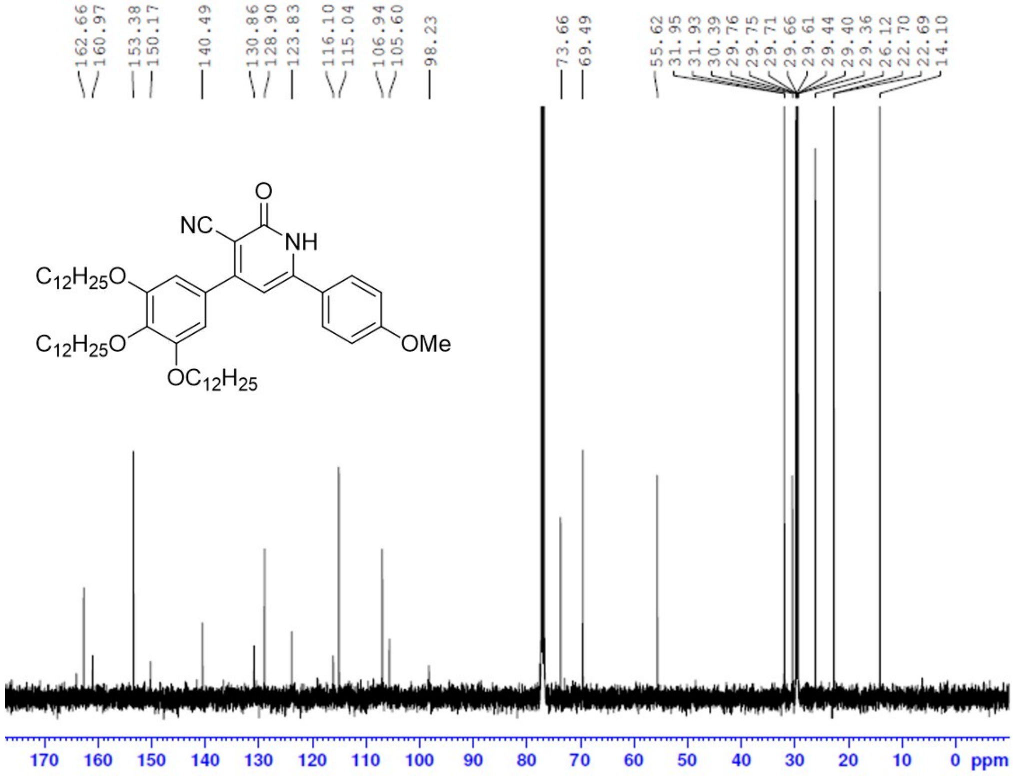

Figure S13: ^{13}C-NMR (125 MHz) spectrum of **CP2** recorded in $CDCl_3$

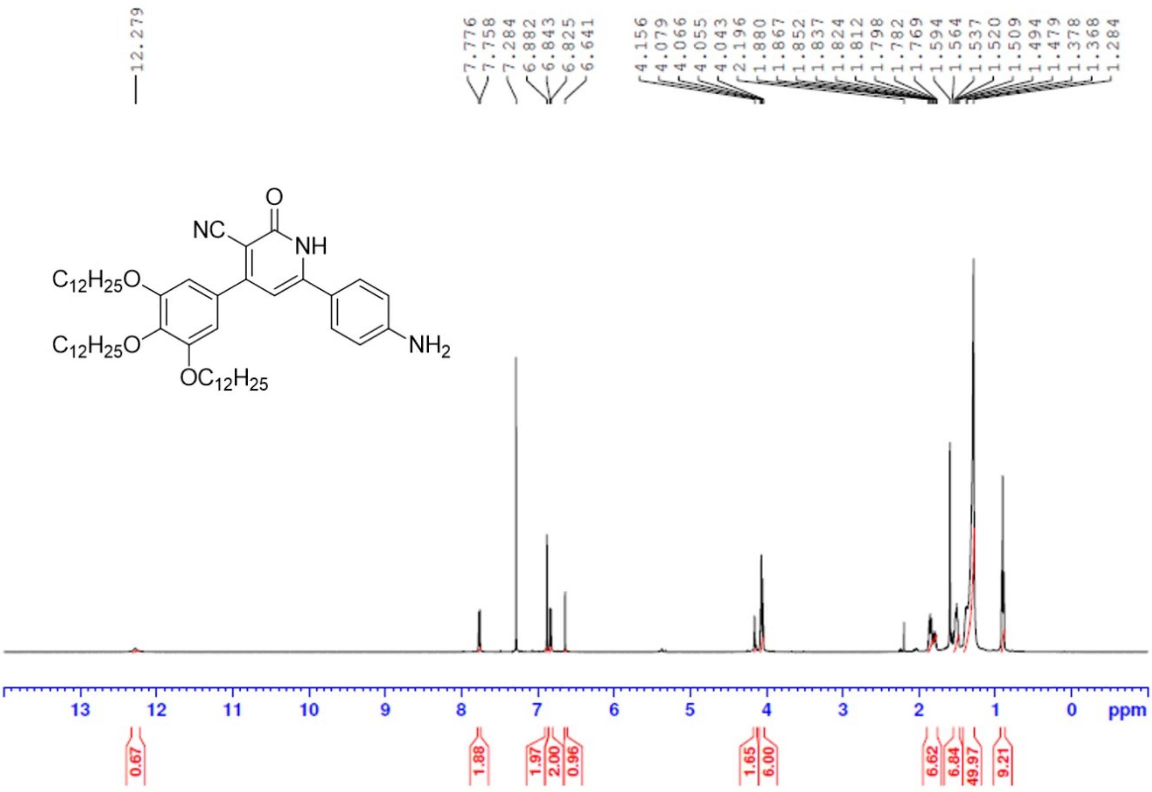

Figure S14: ^{1}H-NMR (500 MHz) spectrum of **CP3** recorded in $CDCl_3$

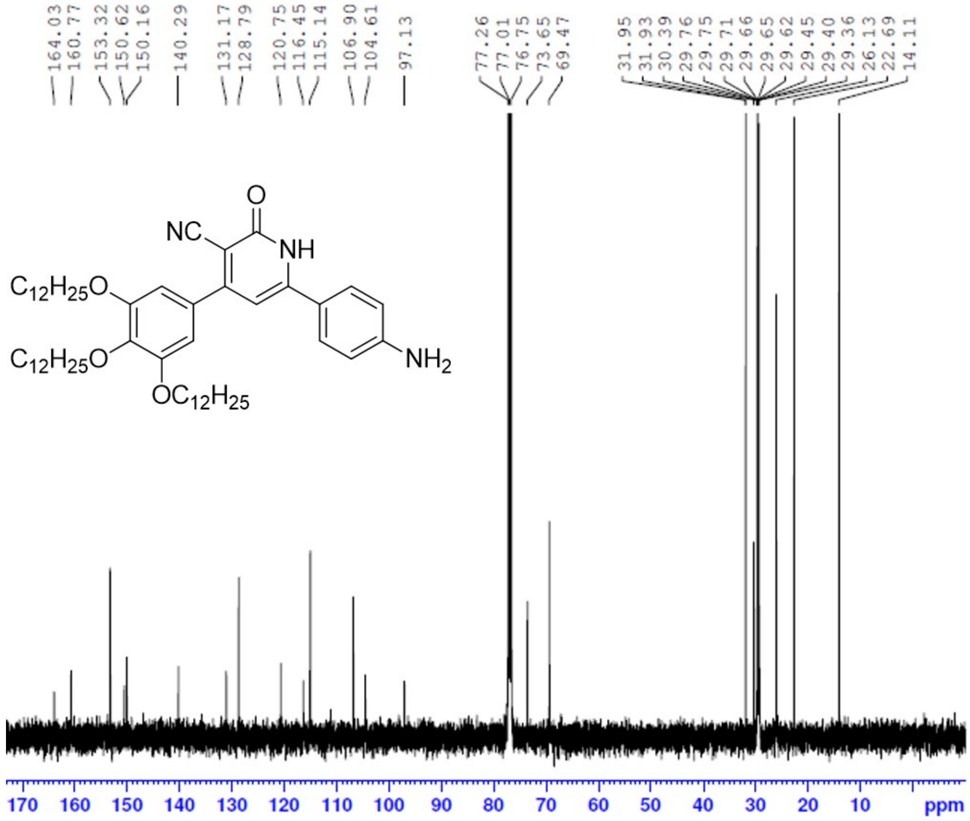

Figure S15: ^{13}C-NMR (125 MHz) spectrum of **CP3** recorded in CDCl$_3$

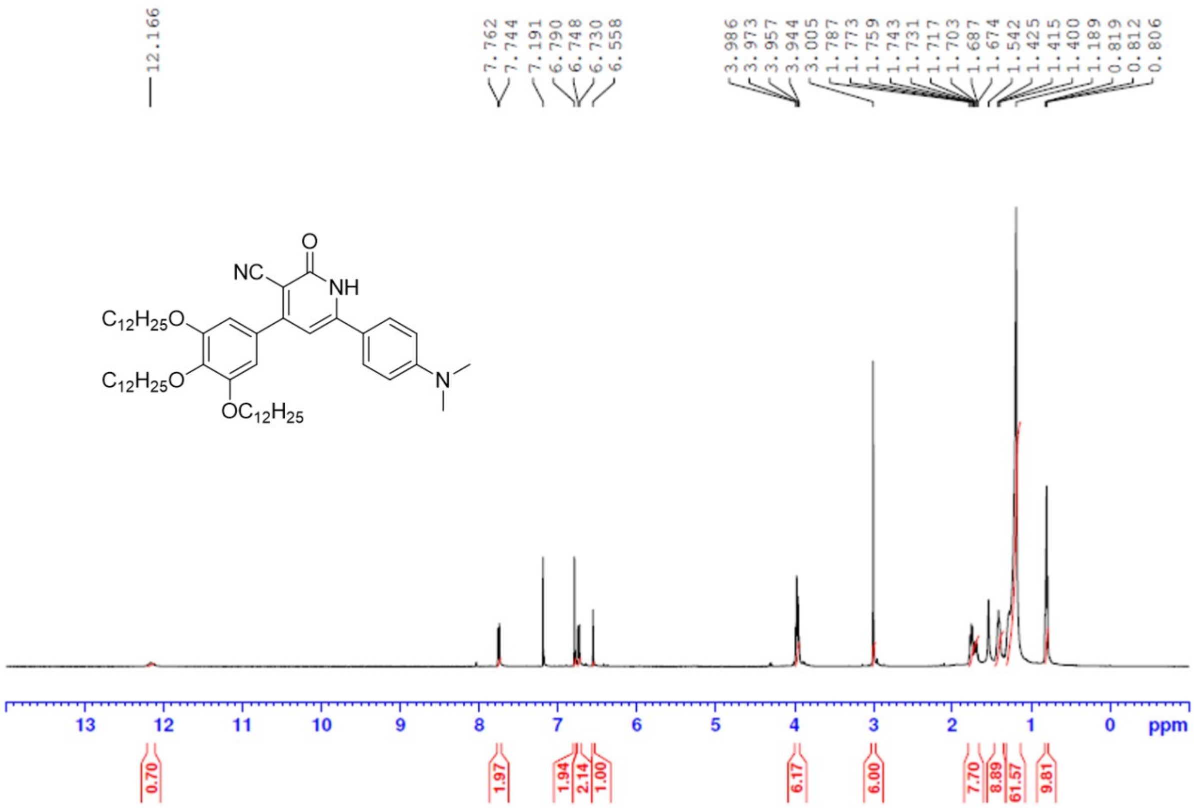

Figure S16: ^{1}H-NMR (500 MHz) spectrum of **CP4** recorded in CDCl$_3$

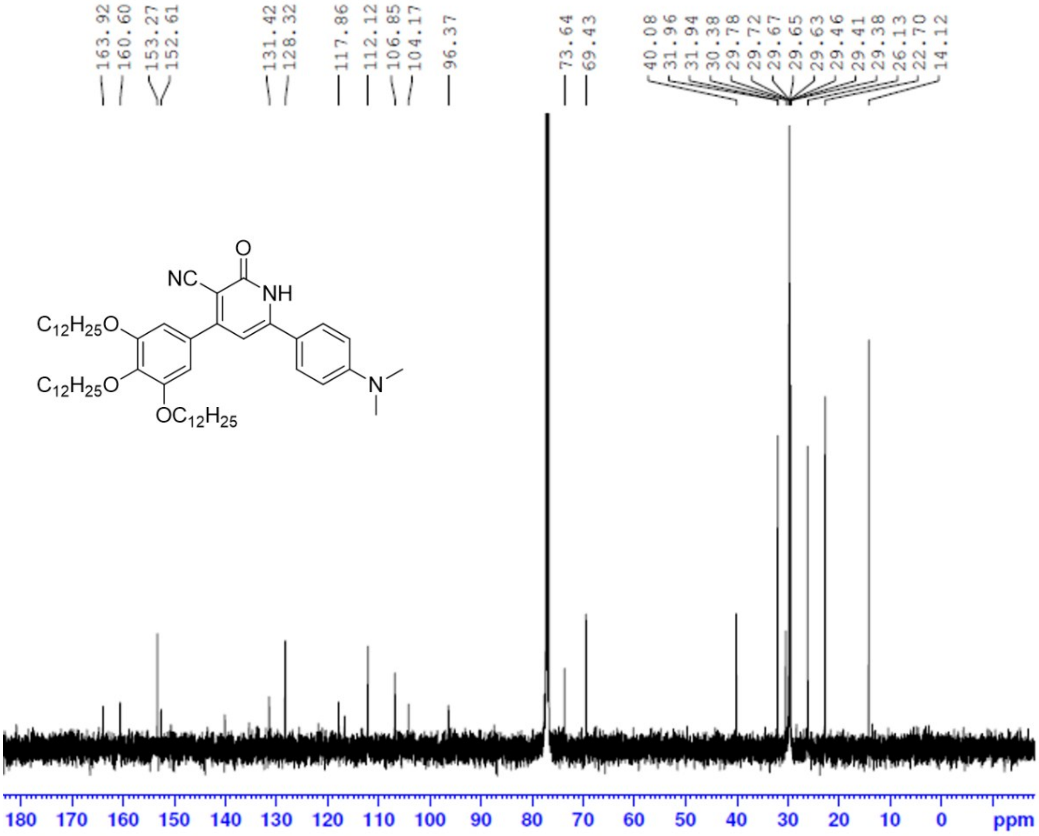

Figure S17: ^{13}C-NMR (125 MHz) spectrum of **CP4** recorded in CDCl$_3$

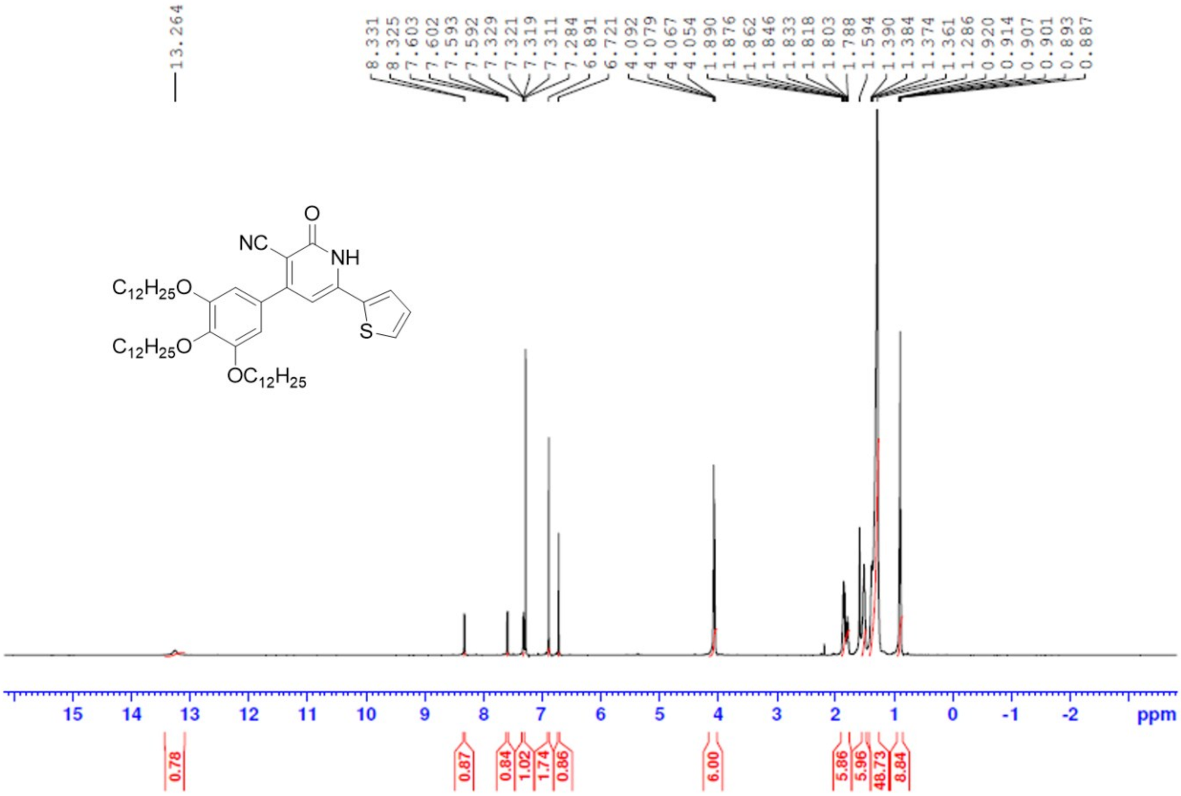

Figure S18: ^{1}H-NMR (500 MHz) spectrum of **CP5** recorded in CDCl$_3$

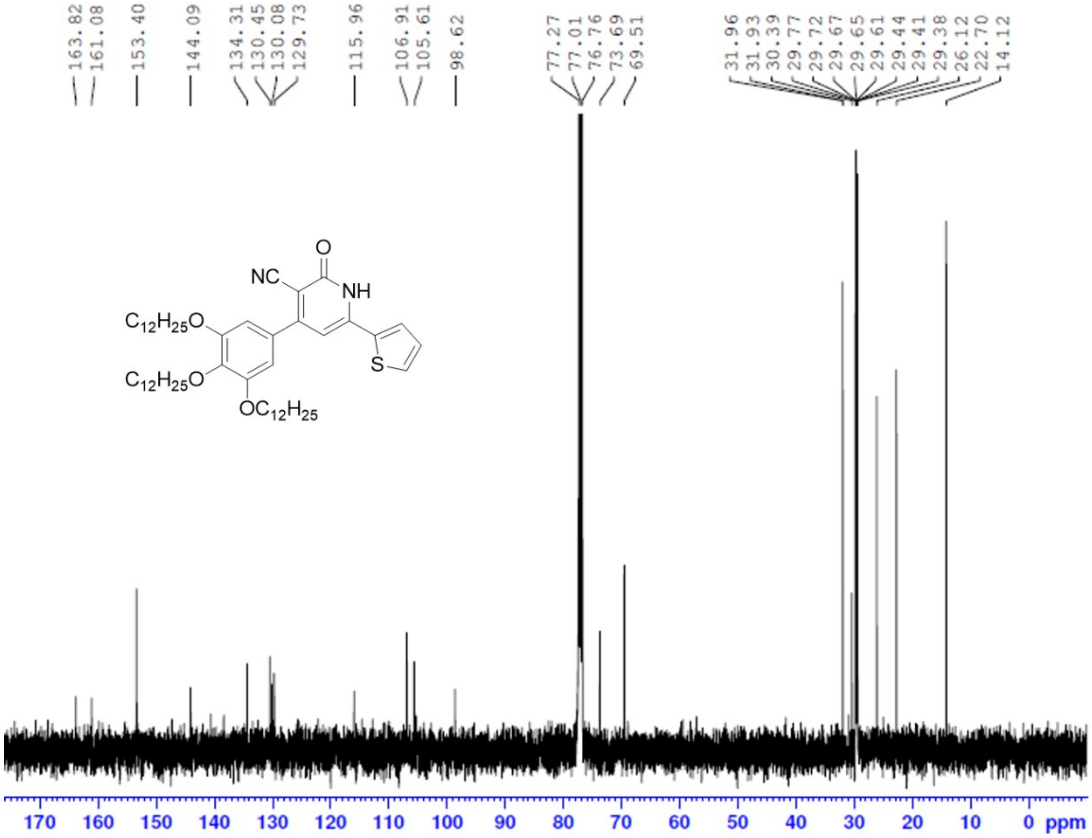

Figure S19: ^{13}C-NMR (125 MHz) spectrum of **CP5** recorded in $CDCl_3$

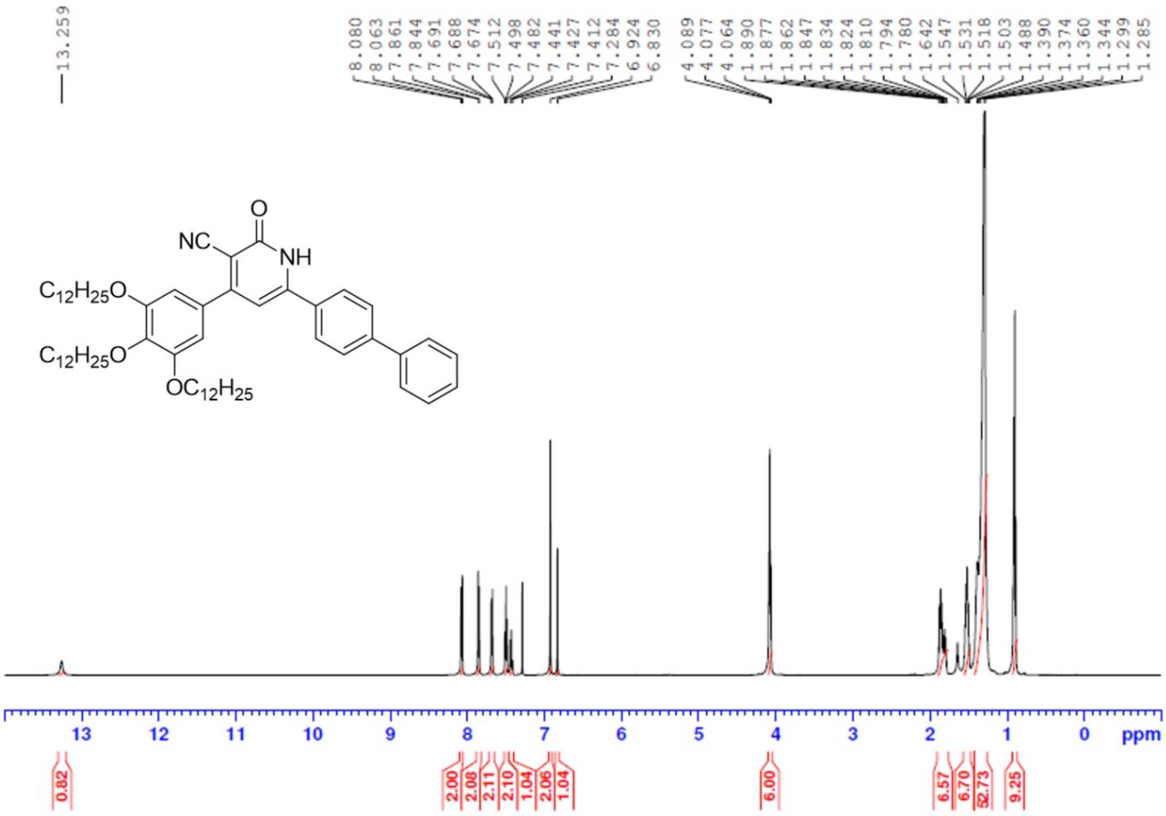

Figure S20: ^{1}H-NMR (500 MHz) spectrum of **CP6** recorded in $CDCl_3$

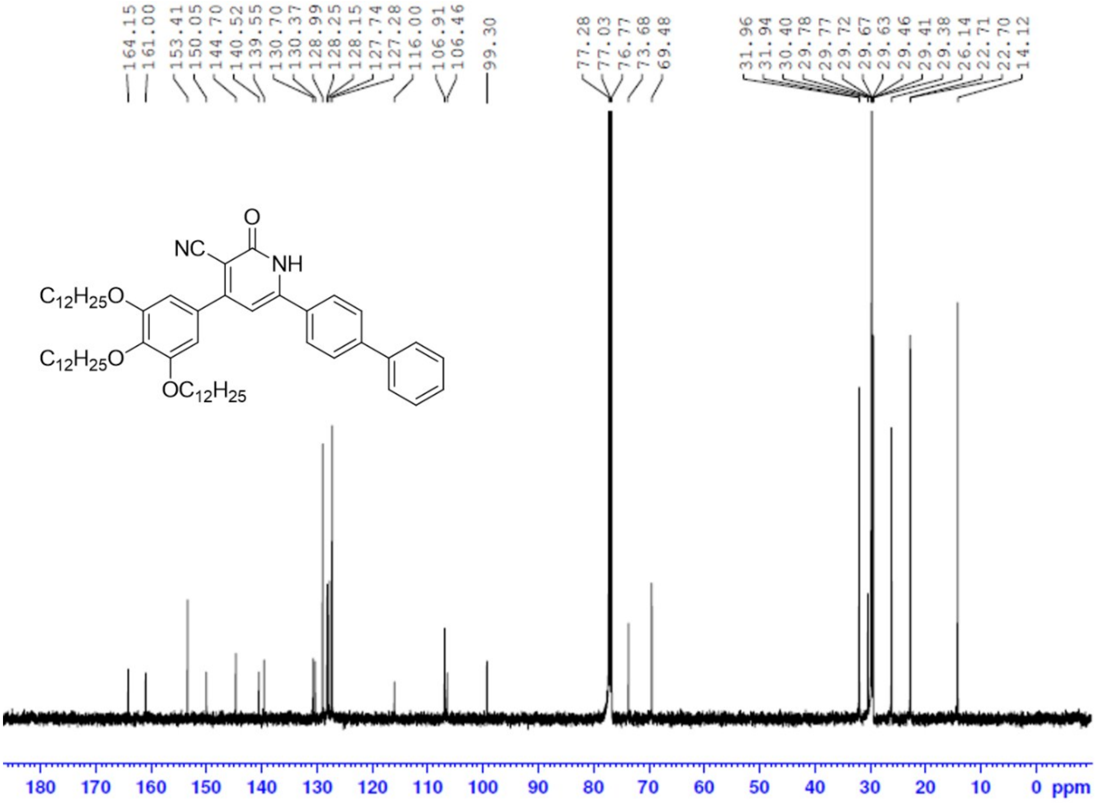

Figure S21: ^{13}C-NMR (125 MHz) spectrum of **CP6** recorded in CDCl$_3$

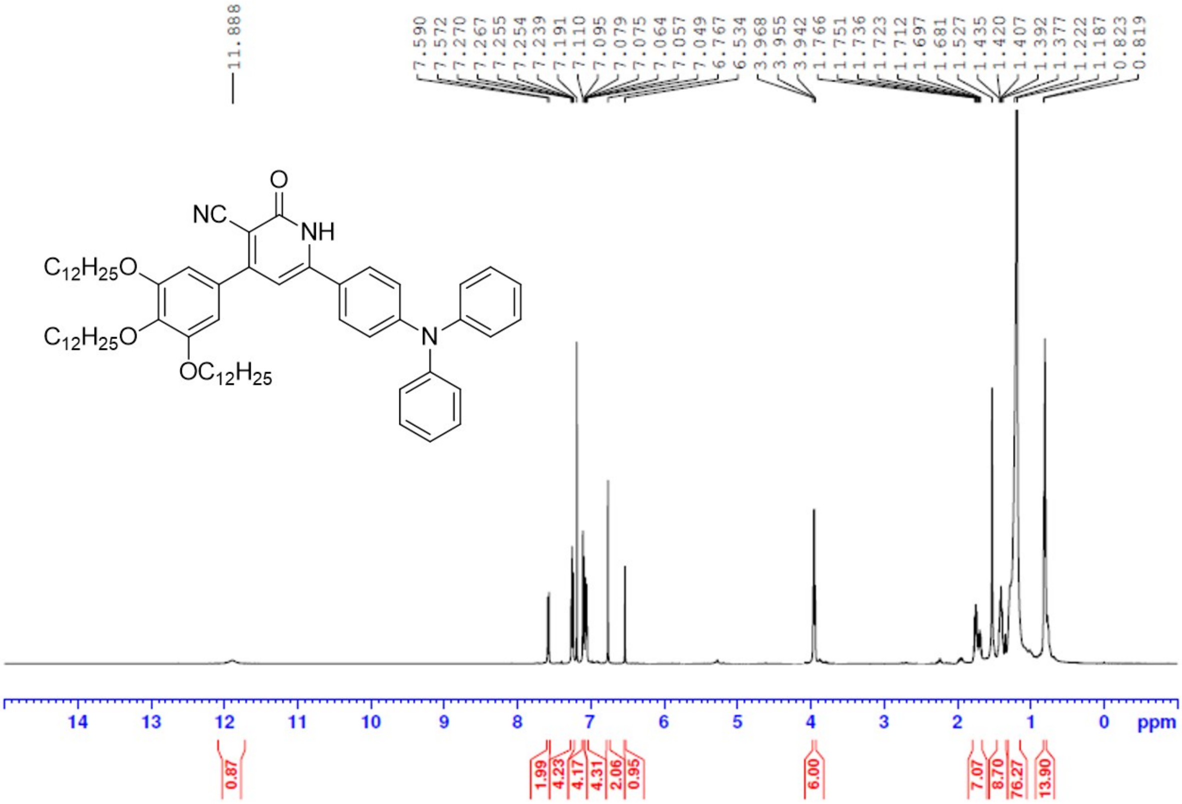

Figure S22: ^{13}C-NMR (125 MHz) spectrum of **CP7** recorded in CDCl$_3$

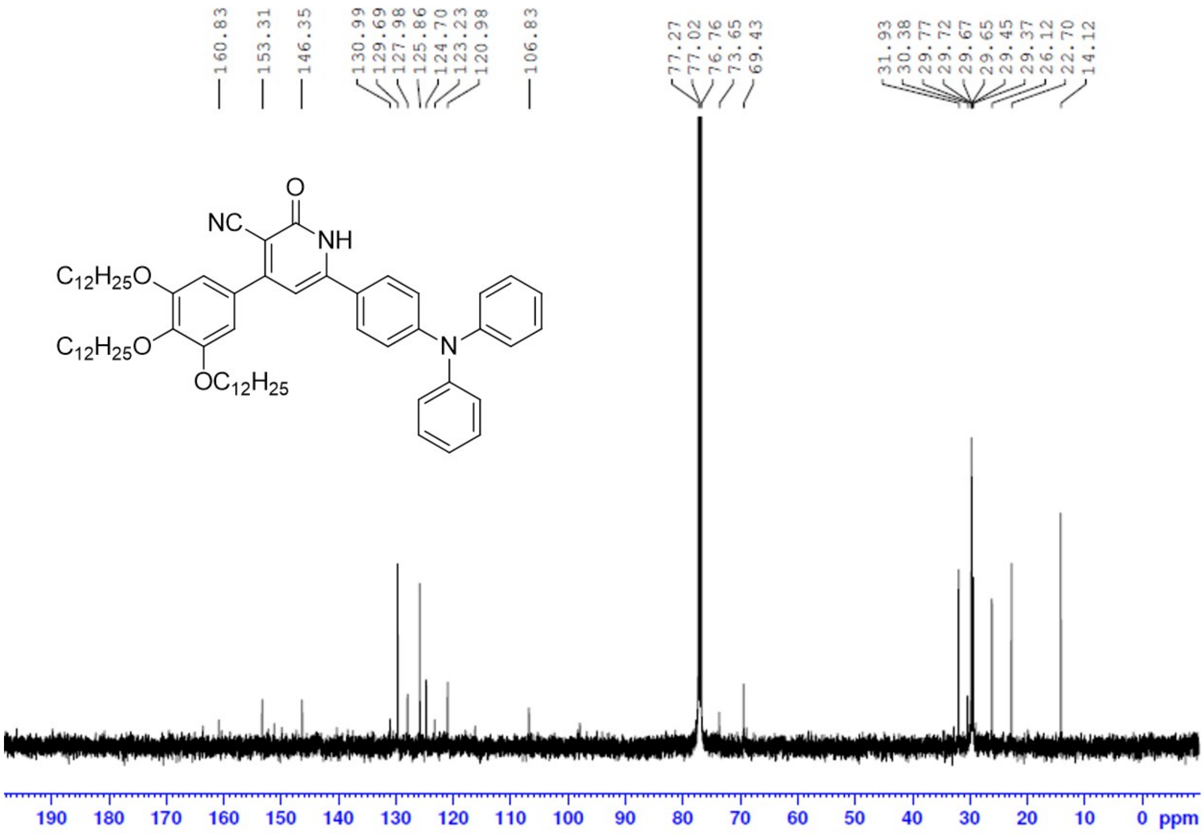

Figure S21: ^{13}C-NMR (125 MHz) spectrum of **CP7** recorded in $CDCl_3$

5. NMR characterization

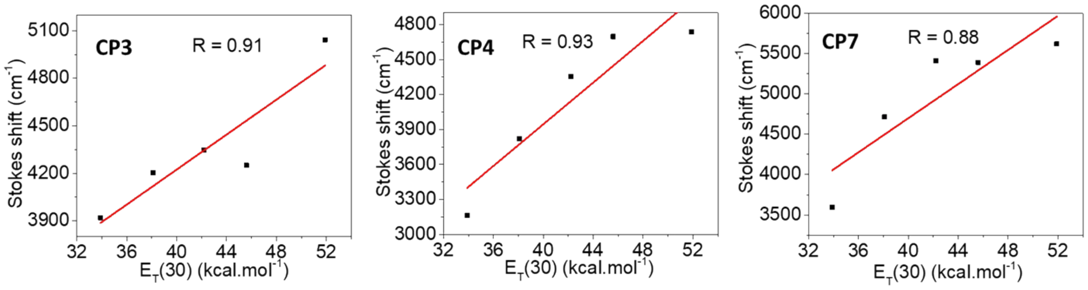

Figure S22 E_T (30) index of solvent *versus* Stokes shift of selected dyes