Electronic Supplementary Information

Design, synthesis and DSSC performance of o-fluorine substituted phenylene spacer sensitizers: Effect of TiO_2 thickness variation

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Characterization:

^{1}H and ^{13}C NMR spectra were recorded on Varian 400 MHz spectrometer. The residual signal of the solvent was taken in $CDCl_3$. The UV-vis absorption spectra experiments were done in Perkin-Elmer Lambda UV-vis spectrometer. Electro spray ionization mass (ESI-MS) spectra were recorded on a Waters (Micro mass MS-Technologies) Q-Tof MS Analyzer spectrometer. Cyclic Voltammetry were performed on CH instruments 611D model with three standard electrochemical cells. Thin film of dyes were coated on glassy carbon electrode, it was used as a working electrode, Ag/Ag^{+} electrode as the reference and Pt wire for counter electrode. 0.1 M tetrabutyl ammonium hexaflurophosphate (Bu_4NPF_6) for supporting electrolyte dissolve in acetonitrile solvent. CV curves were calibrated by using ferrocene as the standard. Time resolved PL measurement to determine the exciton lifetimes of dyes are recorded in LifeSpec II Edinburgh instrument. The J–V characteristics of the fabricated two different thickness based solar cell devices were measured using a Keithley-2400 digital source meter controlled a computer scan rate of 10 mV/s. Impedance Spectroscopy (EIS) measurements were carried out using Solartron 1287 gain phase analyser and recorded by sweeping frequency from 120 KHz to 0.1Hz in dark under -0.65V DC bias. A small AC perturbation (10mV) was imposed onto the system. Open-circuit voltage decay (OCVD) and Tafel polarization curves were obtained by using Solartron electrochemical analyser by sweeping potential ±0.65 in dark with 25mV/s scan rate. For IPCE characteristics model : SR 300, Optosolar, Gemany, where a 250 W, Xe lamp was used as the light source

Materials and synthesis:

All reactions were performed under argon atmosphere and appropriate solvents were distilled from drying agents prior to use. The starting materials of dyes 3-bromo-9-hexyl-9*H*-carbazole, 4-bromo-*N,N*-diphenylaniline, 3-bromo-10-hexyl-10*H*-phenothiazine were prepared according to the published references [1-3]. 2-Fluoro 4-formylphenyl boronic acid, and cyano acetic acid, Nano-crystalline TiO_2 semiconductor (<20 nm, 99.7%, anatase), ethyl cellulose (90.2%) and α-terpineol (90%) were purchased from Sigma-Aldrich and used as received. Compound 1a-3a

was synthesized by Suzuki-coupling reaction and 1b-3b was prepared by Knoevenagel condensation method according to the published journals. TCO (Transparent Conductive Oxide) glass (15Ω/cm^2) and Meltonix tape were procured from Solaronix, Switzerland. Solvents acetonitrile, ethanol and isopropanol, etc., were purchased from Merck and used without further purification.

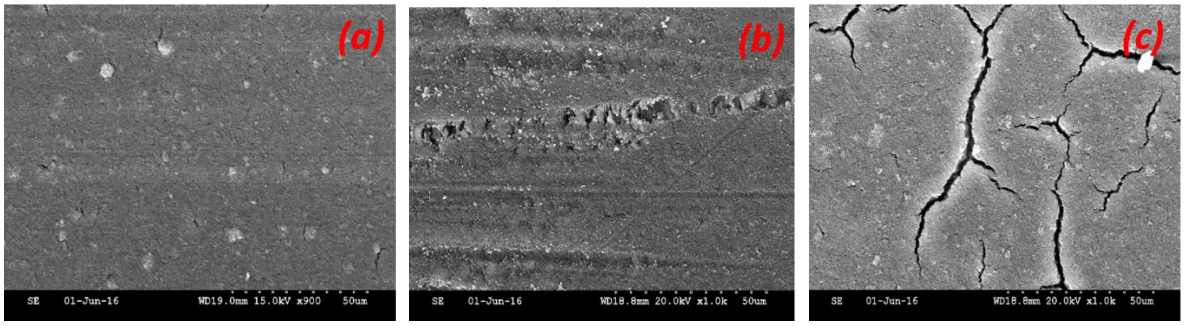

Figure S1. The SEM images of various thickness TiO_2 photoanode (a) 9µm, (b) 12µm and (c) 14µm

Table S1. amount of dye loading on 9µm and 12 µm titania surfaces

Dyes	Dye loading on 9µm TiO_2 thickness ($mol^{-1}.cm^{-1}$)	Dye loading on 12µm TiO_2 thickness ($mol^{-1}.cm^{-1}$)
1b	**1.1×10^{-6}**	**2.3×10^{-6}**
2b	**0.5×10^{-6}**	**0.8×10^{-6}**
3b	**0.8×10^{-6}**	**0.9×10^{-6}**

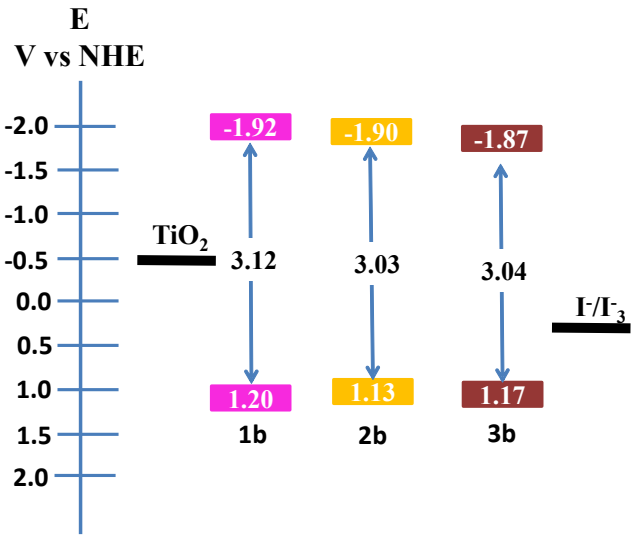

Figure S2. By cyclic voltammetry calculated energy level diagram of organic dyes.

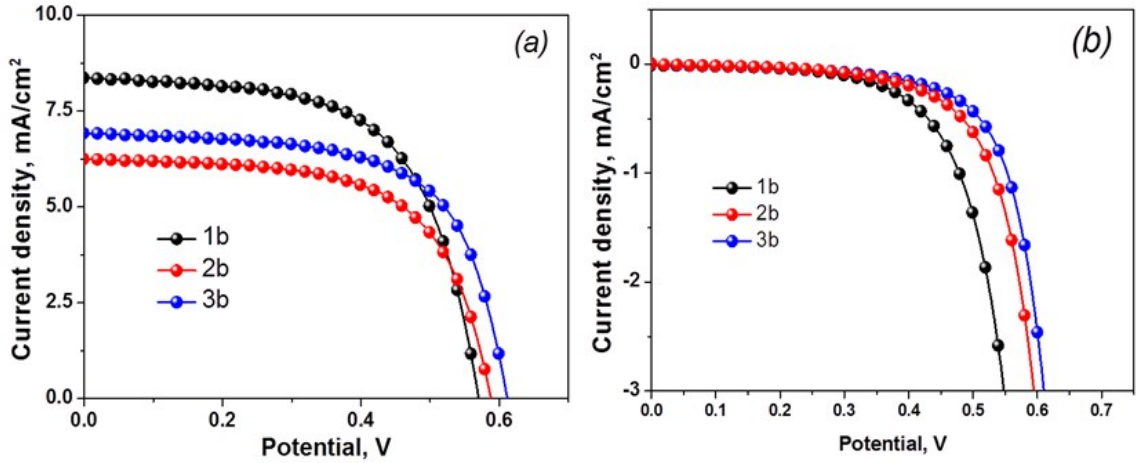

Figure S3. I-V measurement in light and dark condition (Photoanode thickness 9µm)

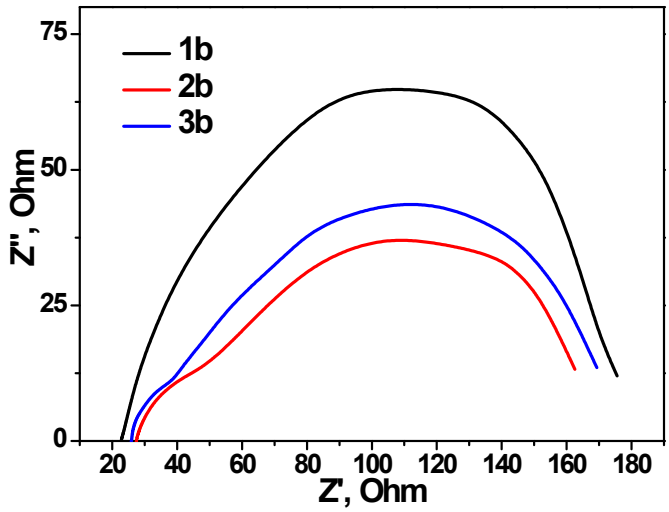

Figure S4. ESI measurements of 9 µm thickness device recorded in dark at -0.65V DC bias

Table S2. DSSC parameters R_{pt}, R_{rec}, τ_n and J_o extracted from EIS measurements and Tafel polarization study

Dye	R_{pt} (Ohm)[a]	R_{rec} (Ohm) [a]	CPE-P [a]	τ_n (ms)[a]	J_o ($\mu A/cm^2$)[b]
1b	22.5	150	0.68	0.159	0.52
2b	27.0	105	0.67	0.138	0.40
3b	25.5	132	0.63	0.140	0.39

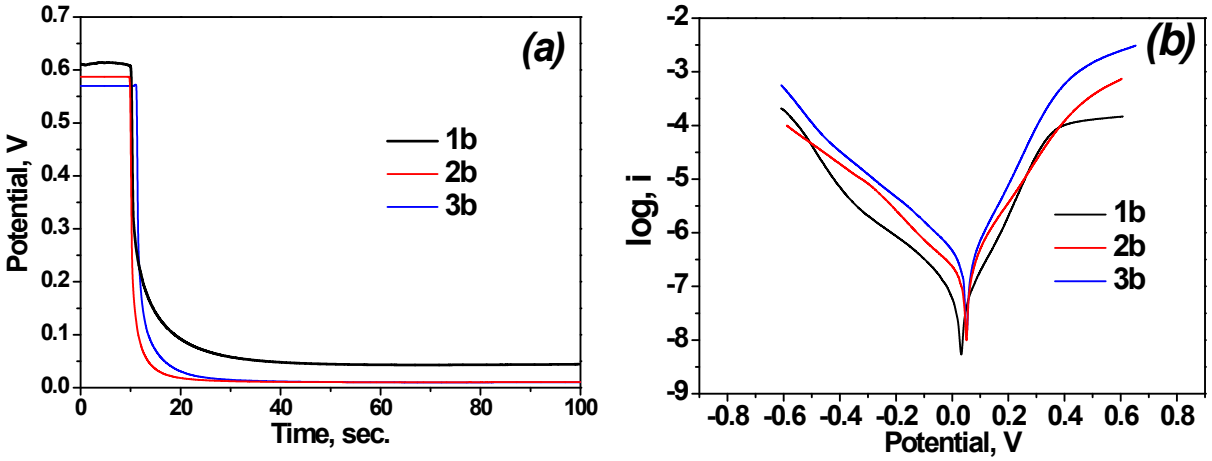

Figure S5. (a) OCVD spectra of 9 µm thickness device, decay curves after illumination are turned off, (b) Tafel polarization study of the device at 9 µm thickness

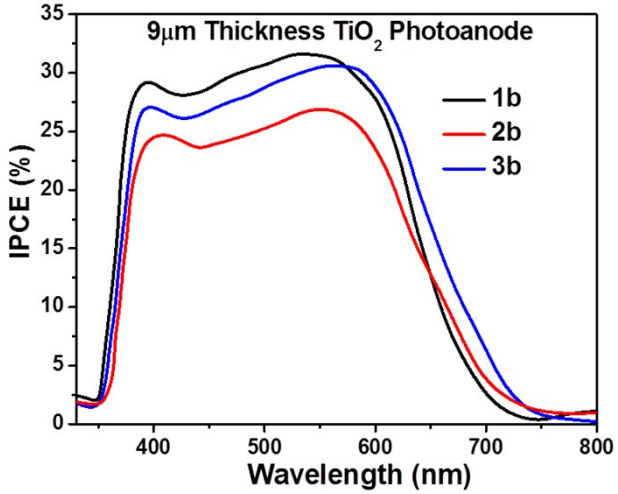

Figure S6. IPCE characteristics of the 9µm TiO_2 photoanode with various sensitizer.

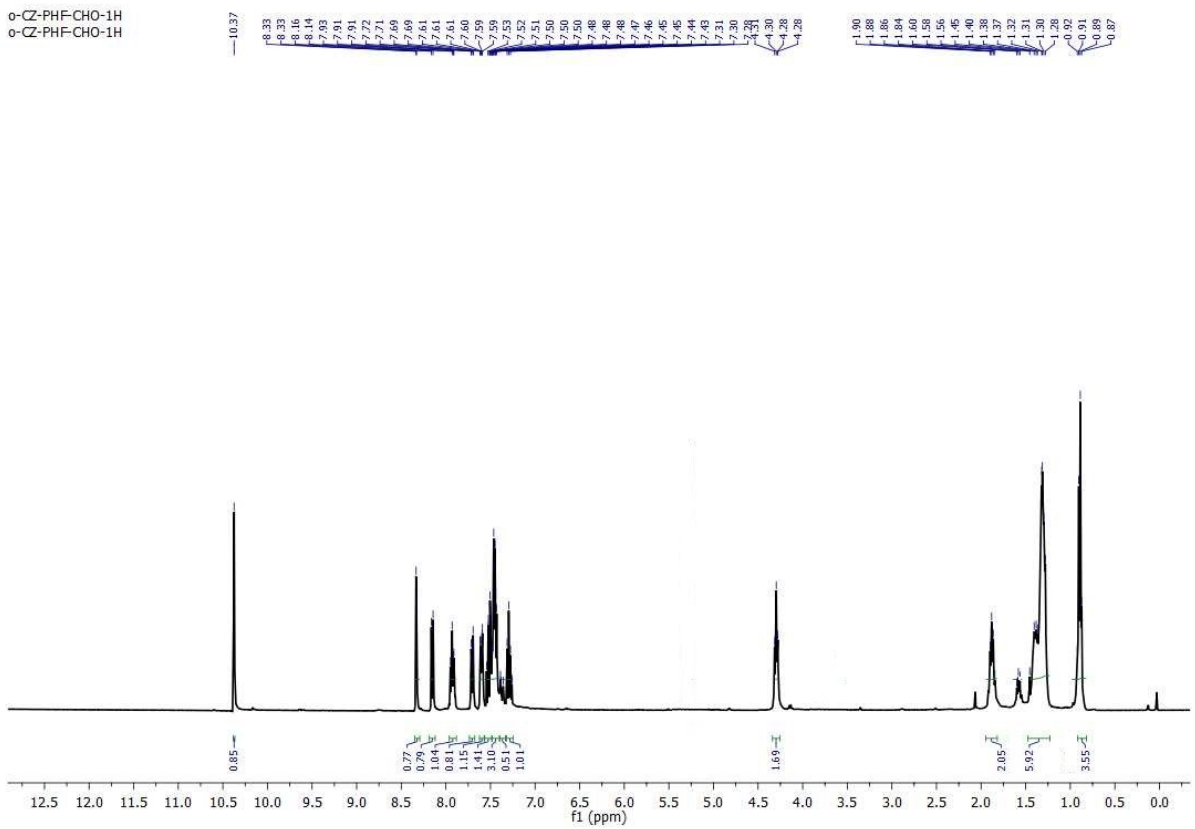

Figure S1a. ^{1}H NMR of 2-fluoro-4-(9-hexyl-9H-carbazol-3-yl)benzaldehyde (1a) in $CDCl_3$.

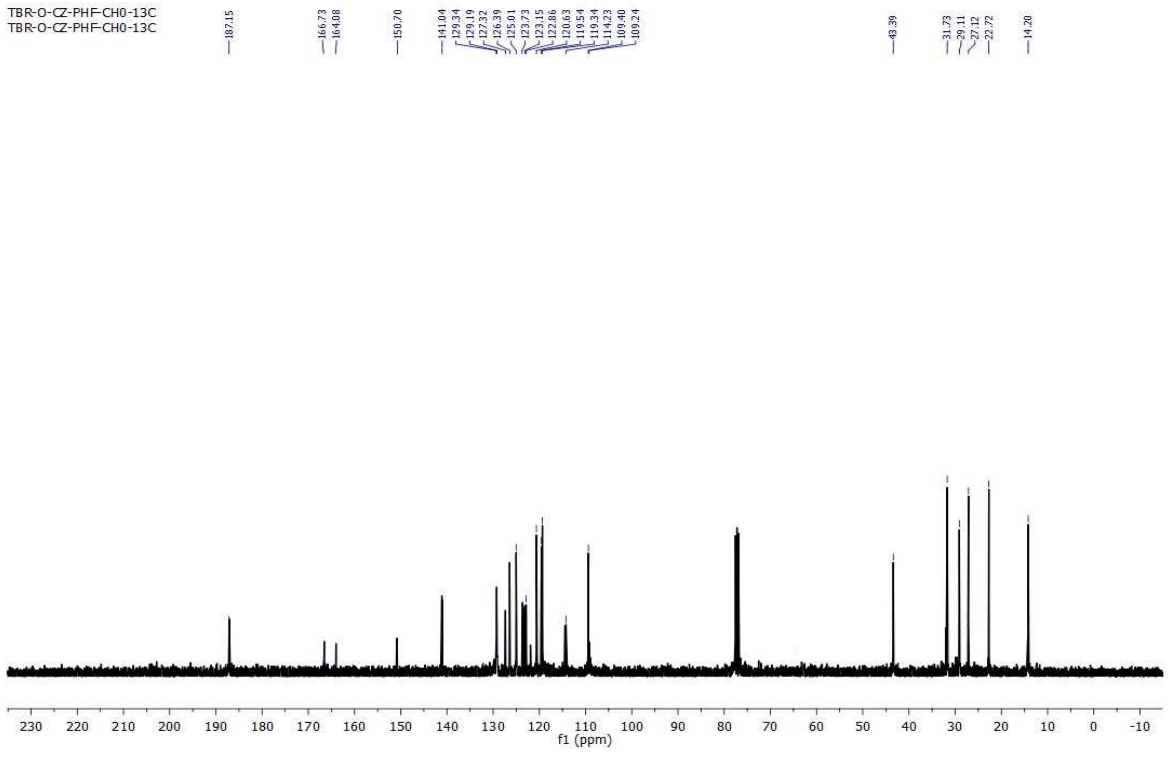

Figure S2b. ^{13}C NMR of 2-fluoro-4-(9-hexyl-9H-carbazol-3-yl)benzaldehyde (1a) in $CDCl_3$.

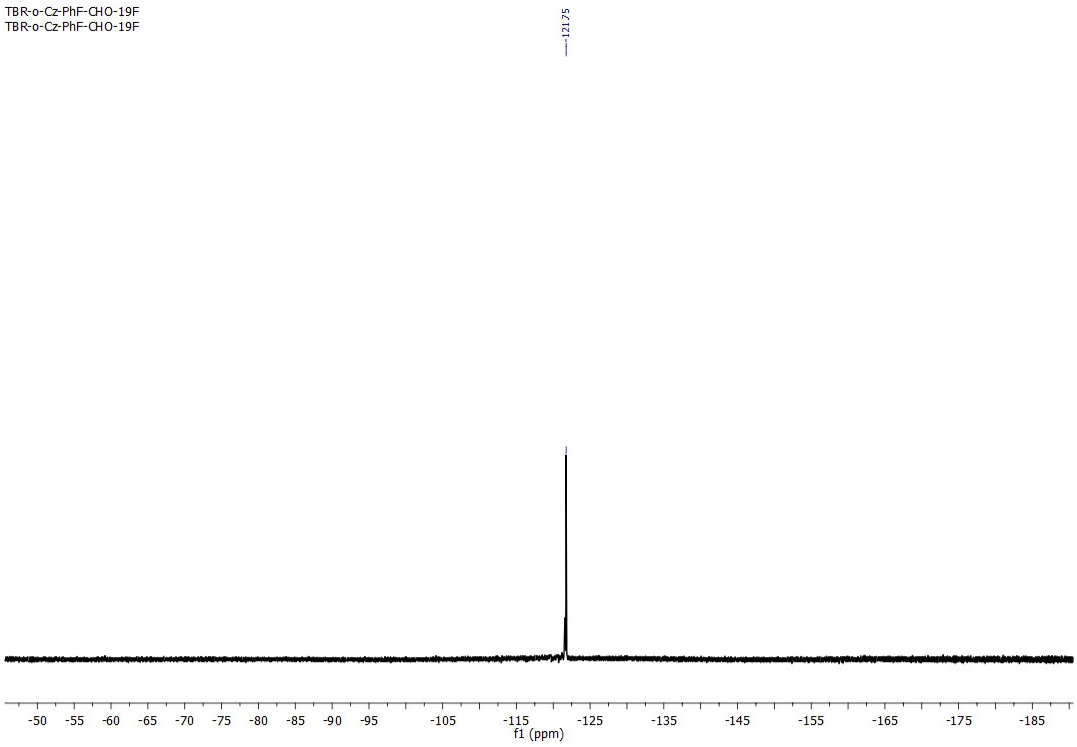

Figure S3c. ^{19}F NMR of 2-fluoro-4-(9-hexyl-9H-carbazol-3-yl)benzaldehyde (1a) in $CDCl_3$.

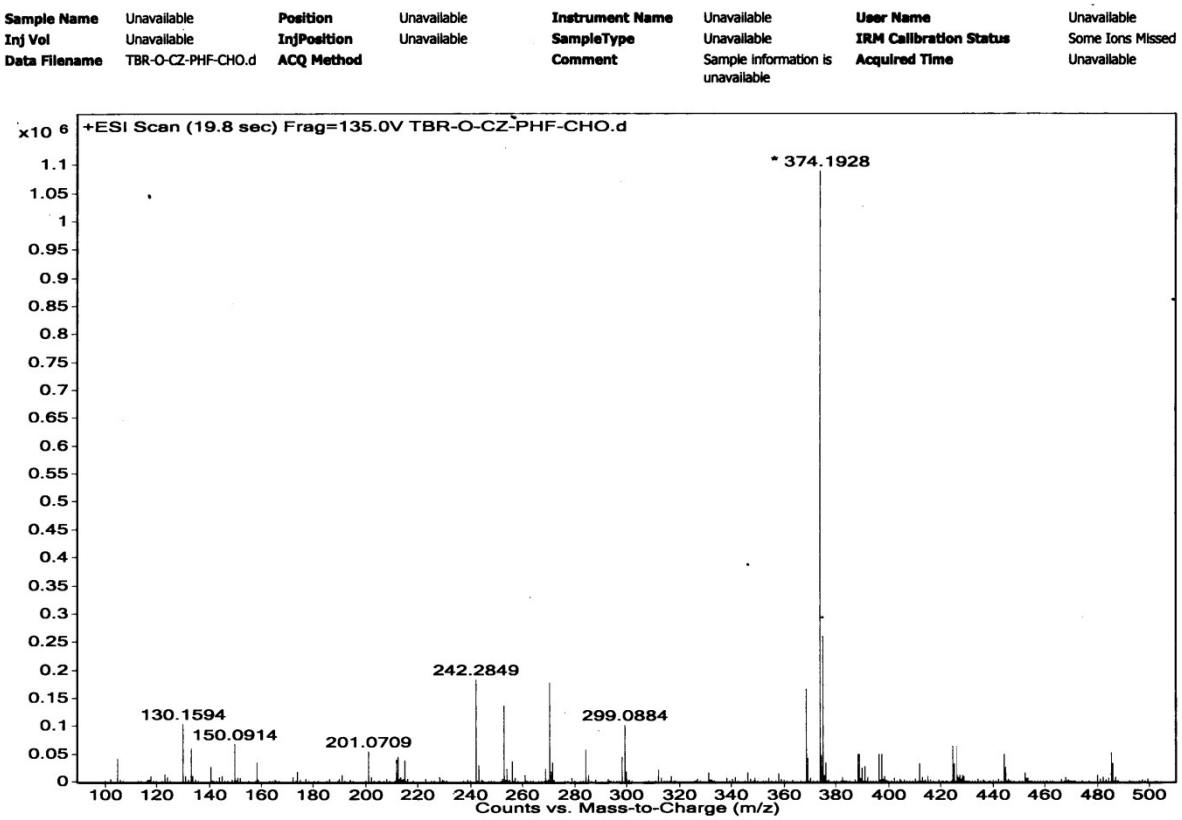

Figure S4d. HRMS (ESI) of 2-fluoro-4-(9-hexyl-9H-carbazol-3-yl)benzaldehyde (1a) (ESI) m/z: $[M+H]^+$calcd for $C_{25}H_{25}FNO$ 374.1920, found 374.1928..

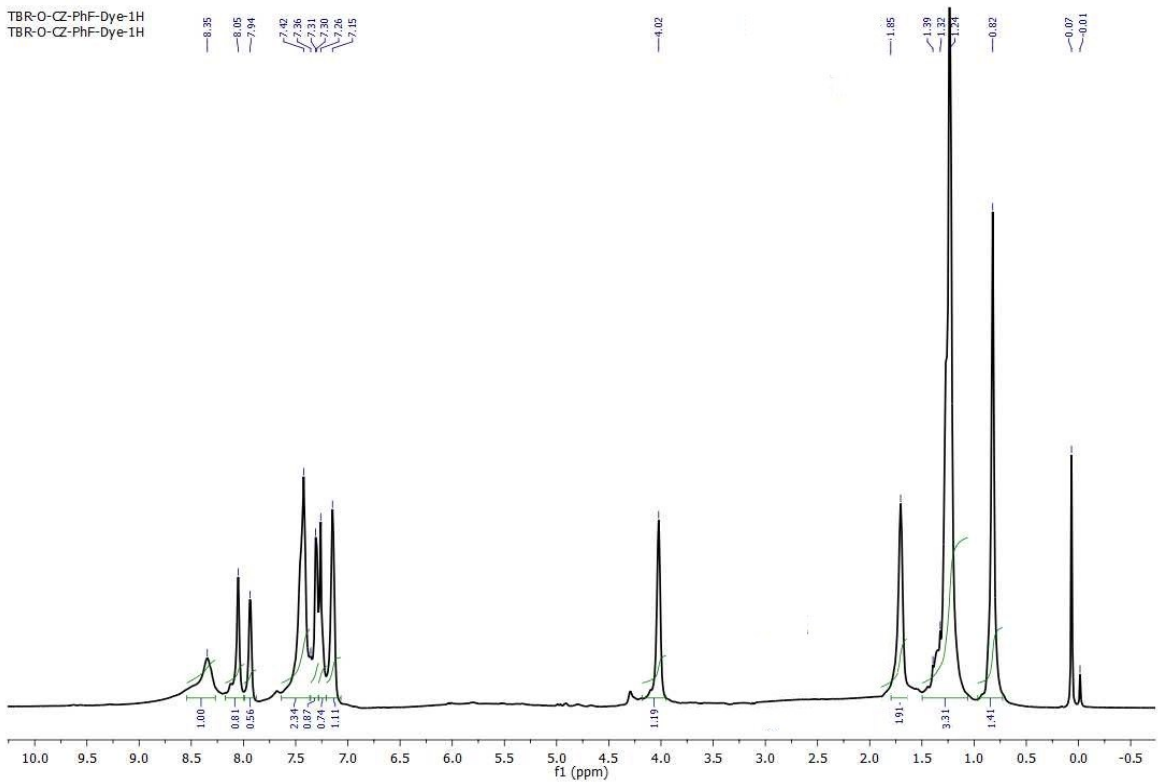

Figure S5a. ^{1}H NMR of (E)-2-cyano-3-(2-fluoro-4-(9-hexyl-9H-carbazol-3-yl)phenyl)acrylic acid (1b) in $CDCl_3$.

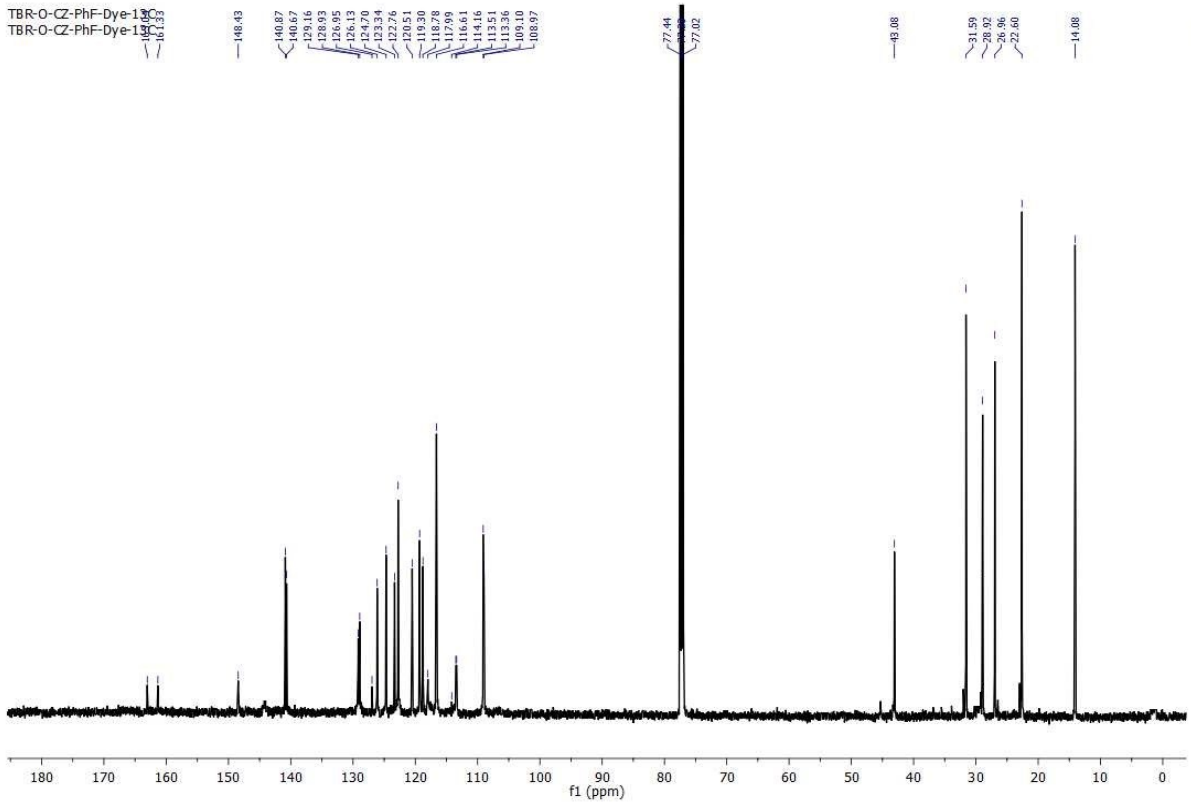

Figure S6b. ^{13}C NMR of (E)-2-cyano-3-(2-fluoro-4-(9-hexyl-9H-carbazol-3-yl)phenyl)acrylic acid (1b) in $CDCl_3$.

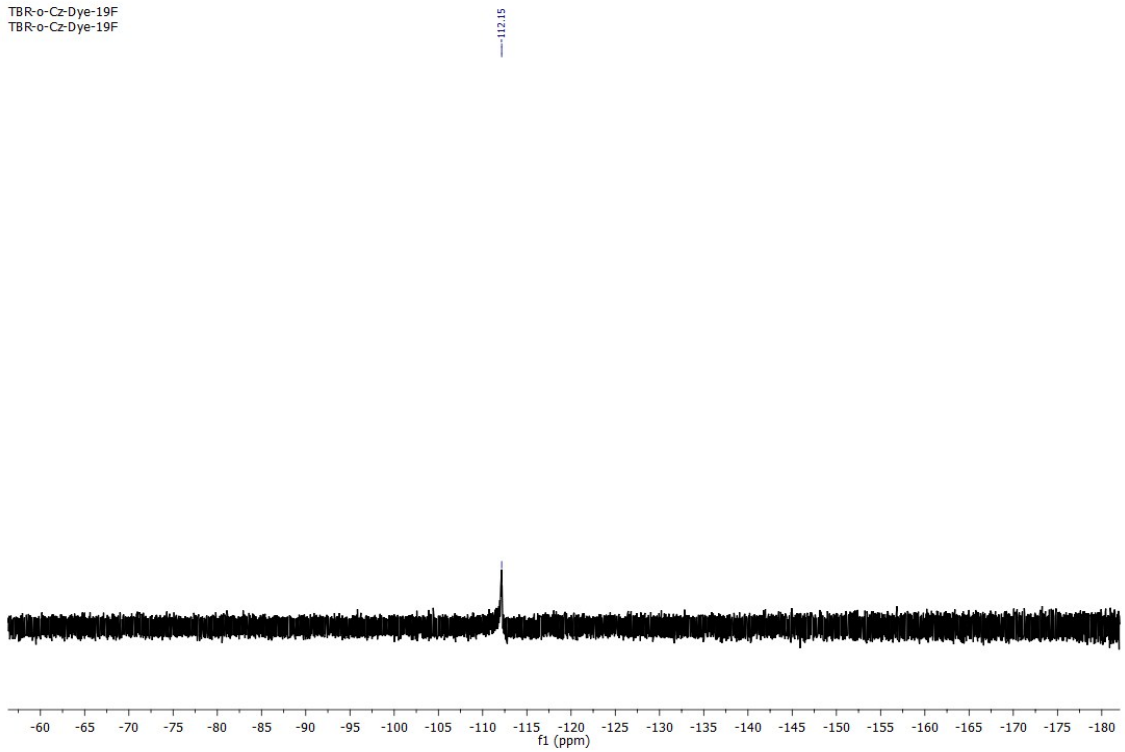

Figure S7c. ^{13}C NMR of (E)-2-cyano-3-(2-fluoro-4-(9-hexyl-9H-carbazol-3-yl)phenyl)acrylic acid (1b) in $CDCl_3$.

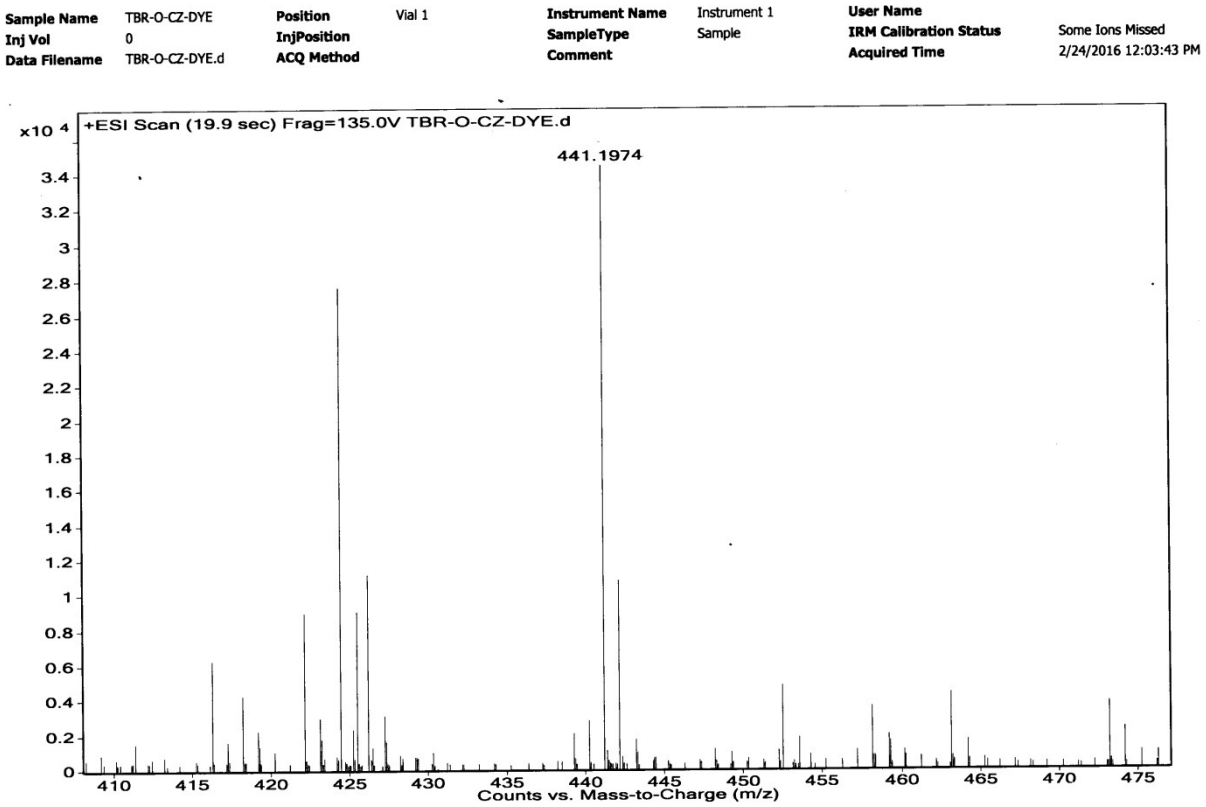

Figure S8d. HRMS of (E)-2-cyano-3-(2-fluoro-4-(9-hexyl-9H-carbazol-3-yl)phenyl)acrylic acid (1b) (ESI) m/z: $[M+H]^+$calcd for $C_{28}H_{26}FN_2O_2$ 441.1978, found 441.1974.

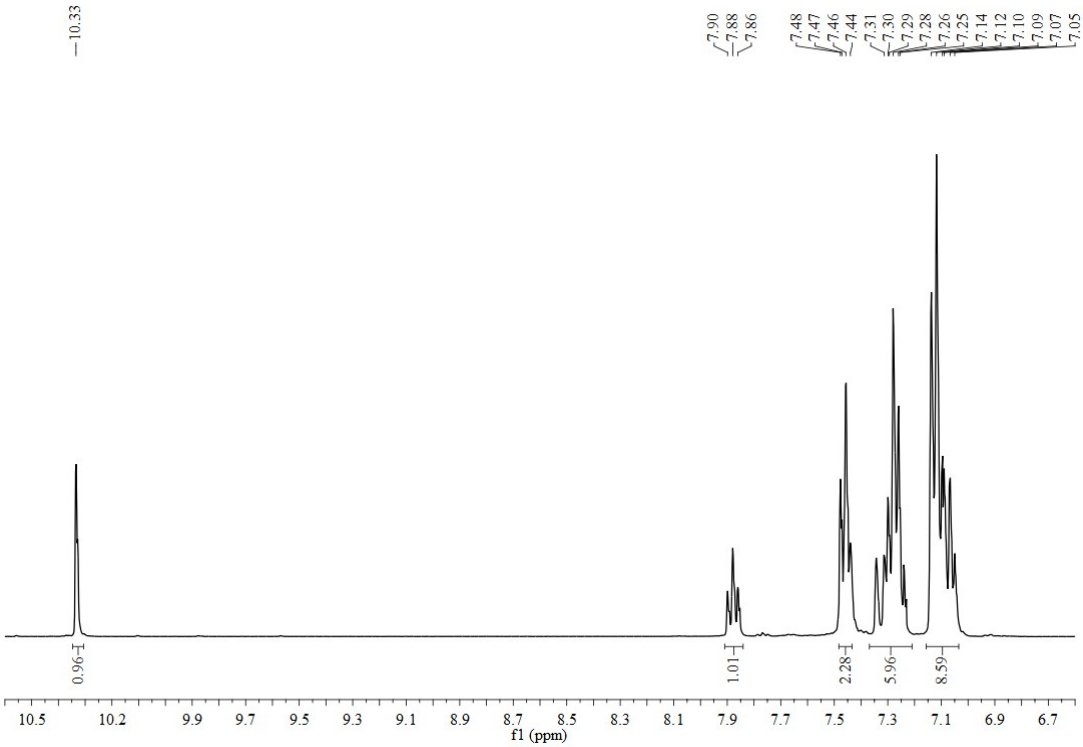

Figure S9a. ^{1}H NMR of 4'-(diphenylamino)-3-fluoro-[1,1'-biphenyl]-4-carbaldehyde (2a) in $CDCl_3$.

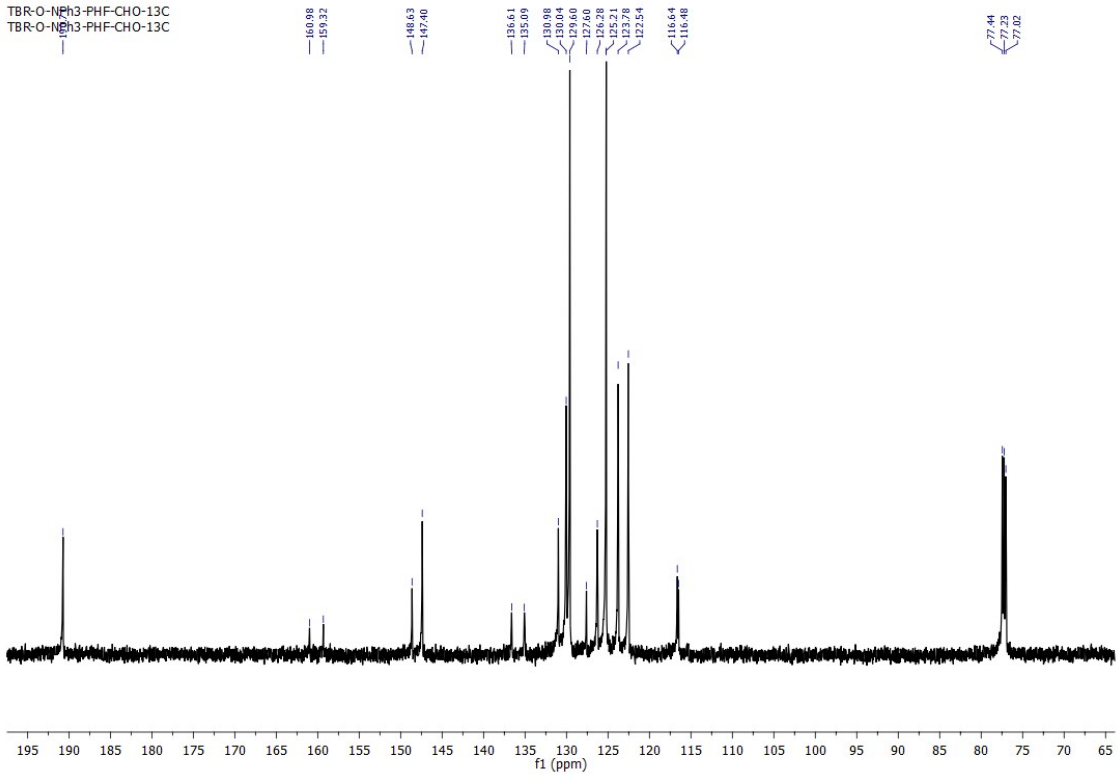

Figure S10b. ^{13}C NMR of 4'-(diphenylamino)-3-fluoro-[1,1'-biphenyl]-4-carbaldehyde (2a) in $CDCl_3$.

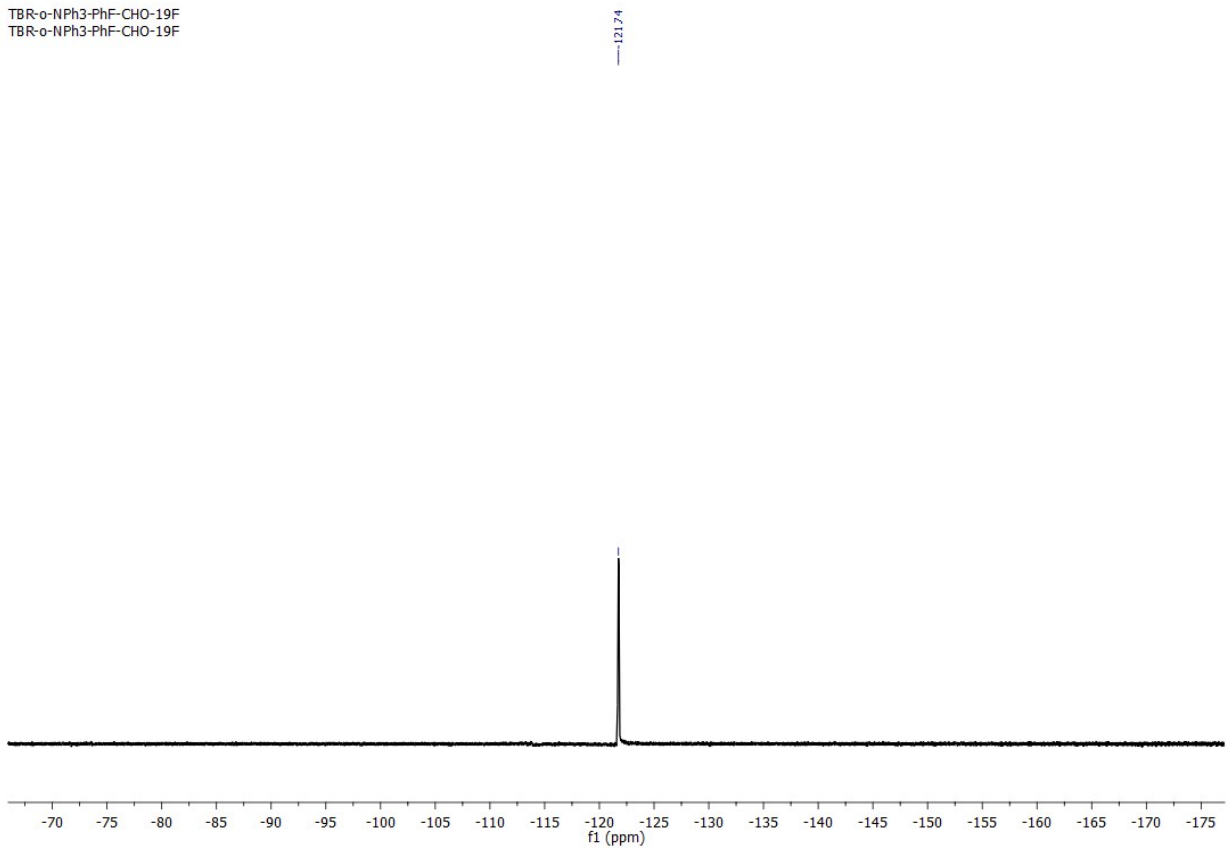

Figure S11c. ^{19}F NMR of 4'-(diphenylamino)-3-fluoro-[1,1'-biphenyl]-4-carbaldehyde (2a) in $CDCl_3$.

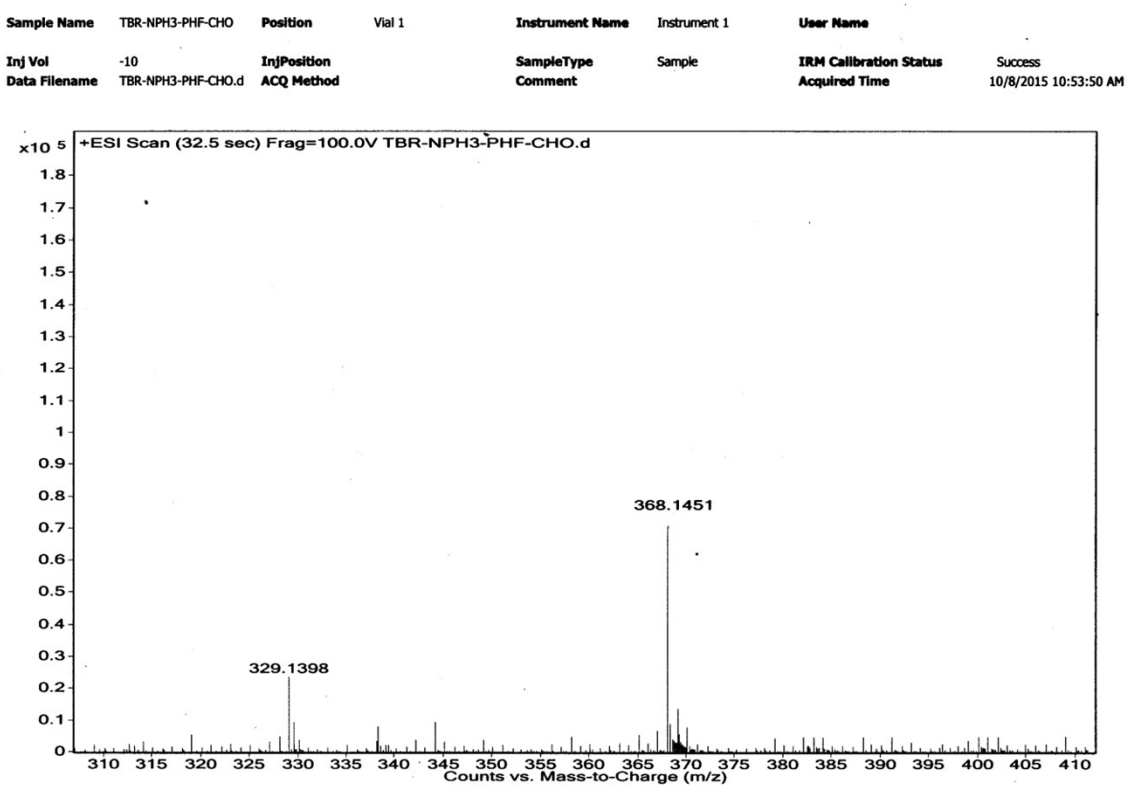

Figure S12d. HRMS (ESI) of 4'-(diphenylamino)-3-fluoro-[1,1'-biphenyl]-4-carbaldehyde (2a) (ESI) m/z: $[M+H]^+$calcd for $C_{25}H_{19}FNO$ 368.1451, found 368.1451.

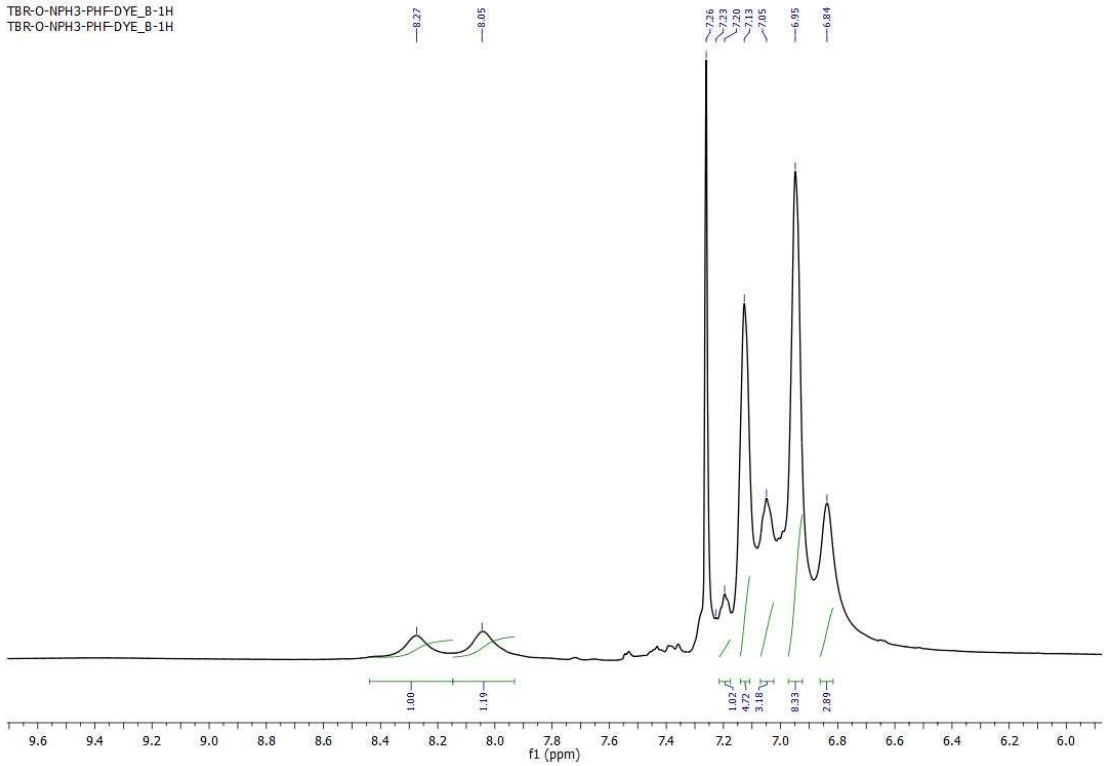

Figure S13a. ^{1}H NMR of (E)-2-cyano-3-(4'-(diphenylamino)-3-fluoro-[1,1'-biphenyl]-4-yl)acrylic acid (2b) in $CDCl_3$.

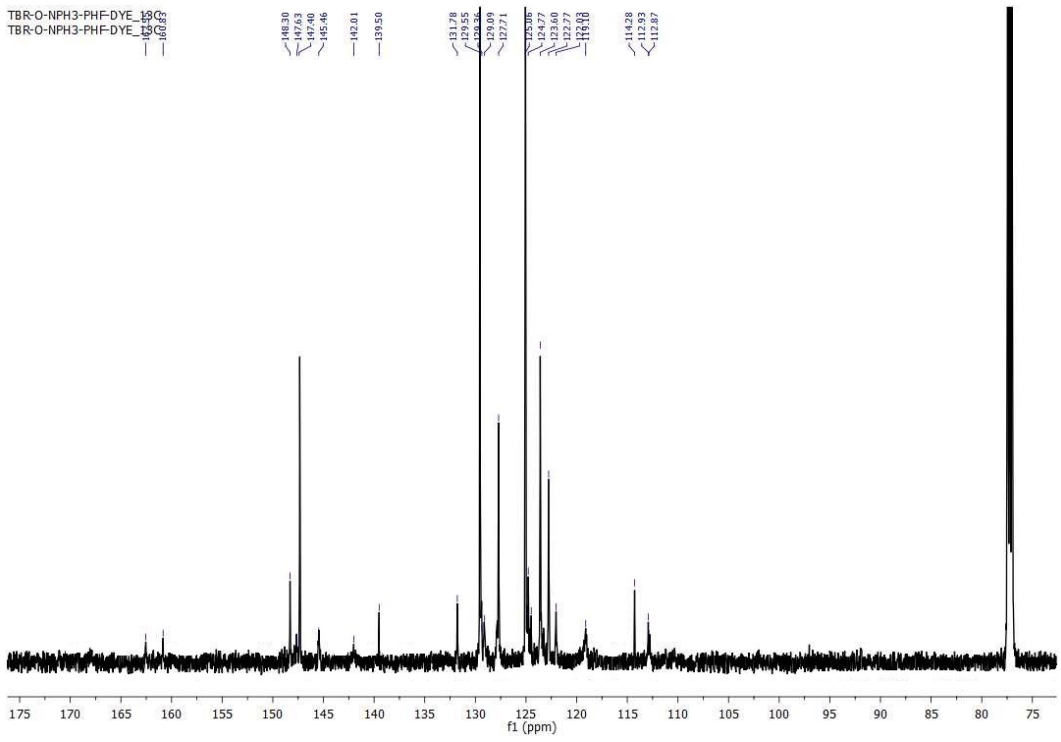

Figure S14b. ^{13}C NMR of (E)-2-cyano-3-(4'-(diphenylamino)-3-fluoro-[1,1'-biphenyl]-4-yl)acrylic acid (2b) in $CDCl_3$.

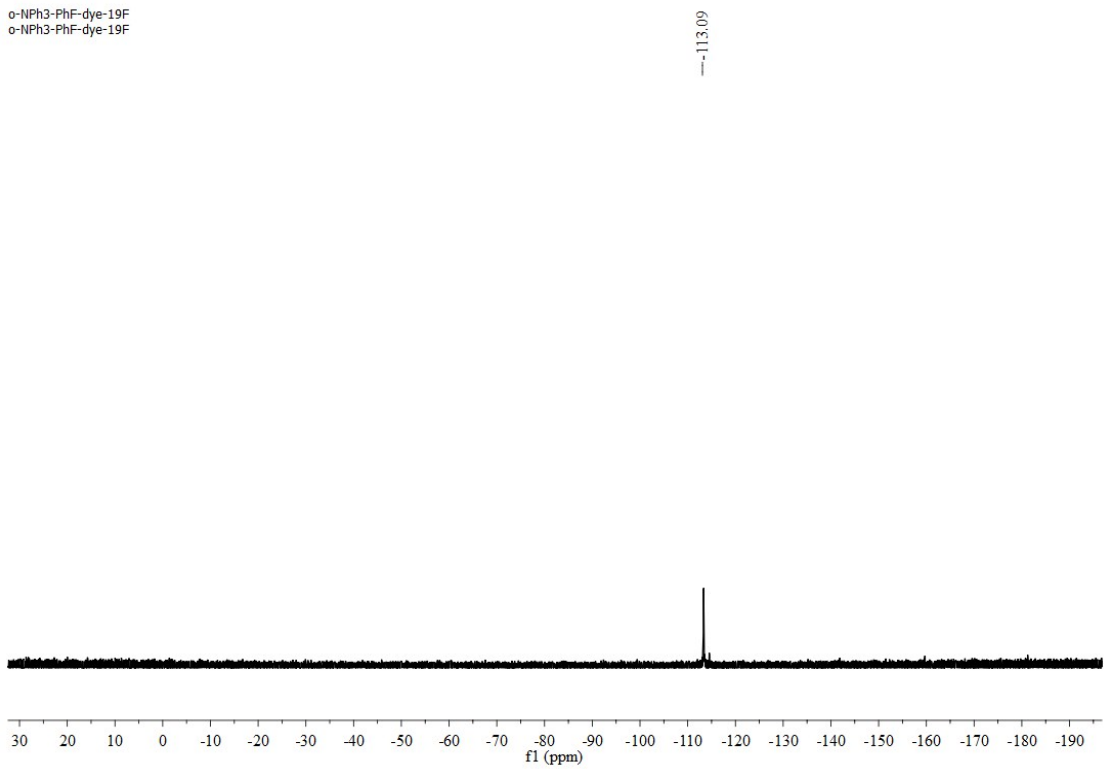

Figure S15c. ^{19}F NMR of (E)-2-cyano-3-(4'-(diphenylamino)-3-fluoro-[1,1'-biphenyl]-4-yl)acrylic acid (2b) in $CDCl_3$

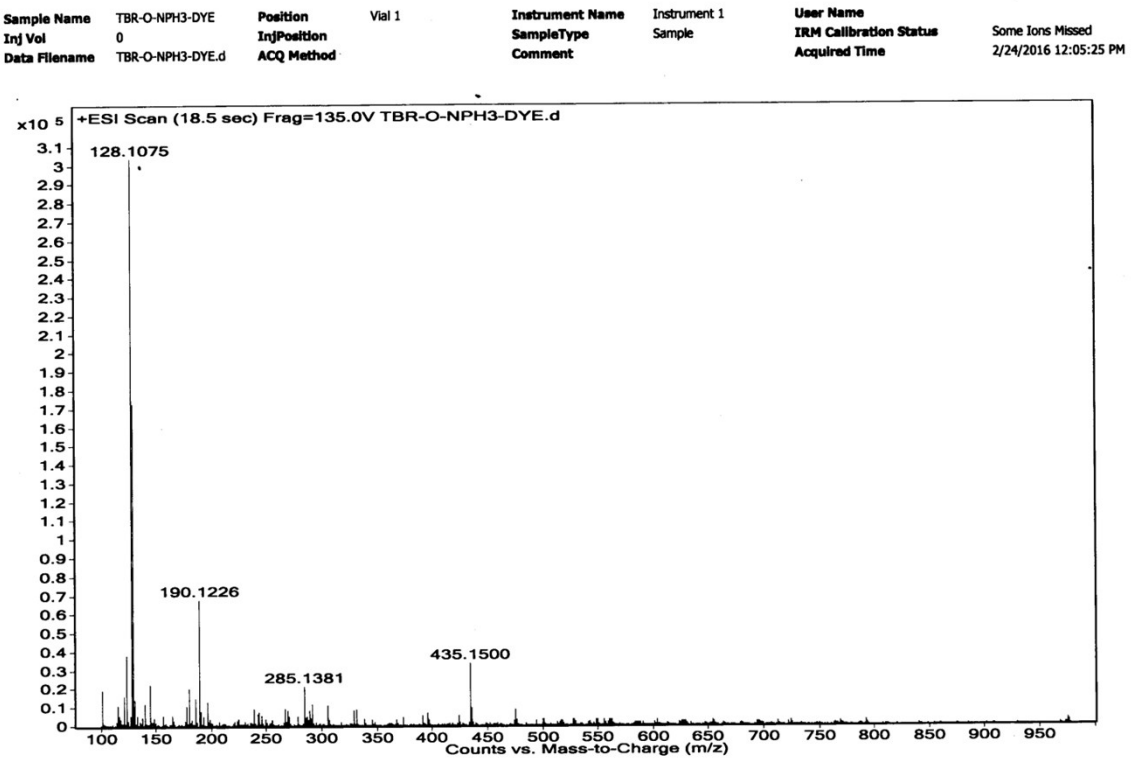

Figure S16d. HRMS of (E)-2-cyano-3-(4'-(diphenylamino)-3-fluoro-[1,1'-biphenyl]-4-yl)acrylic acid (2b) (ESI) m/z: $[M+H]^+$calcd for $C_{28}H_{20}FN_2O_2$ 435.1509, found 435.1500.

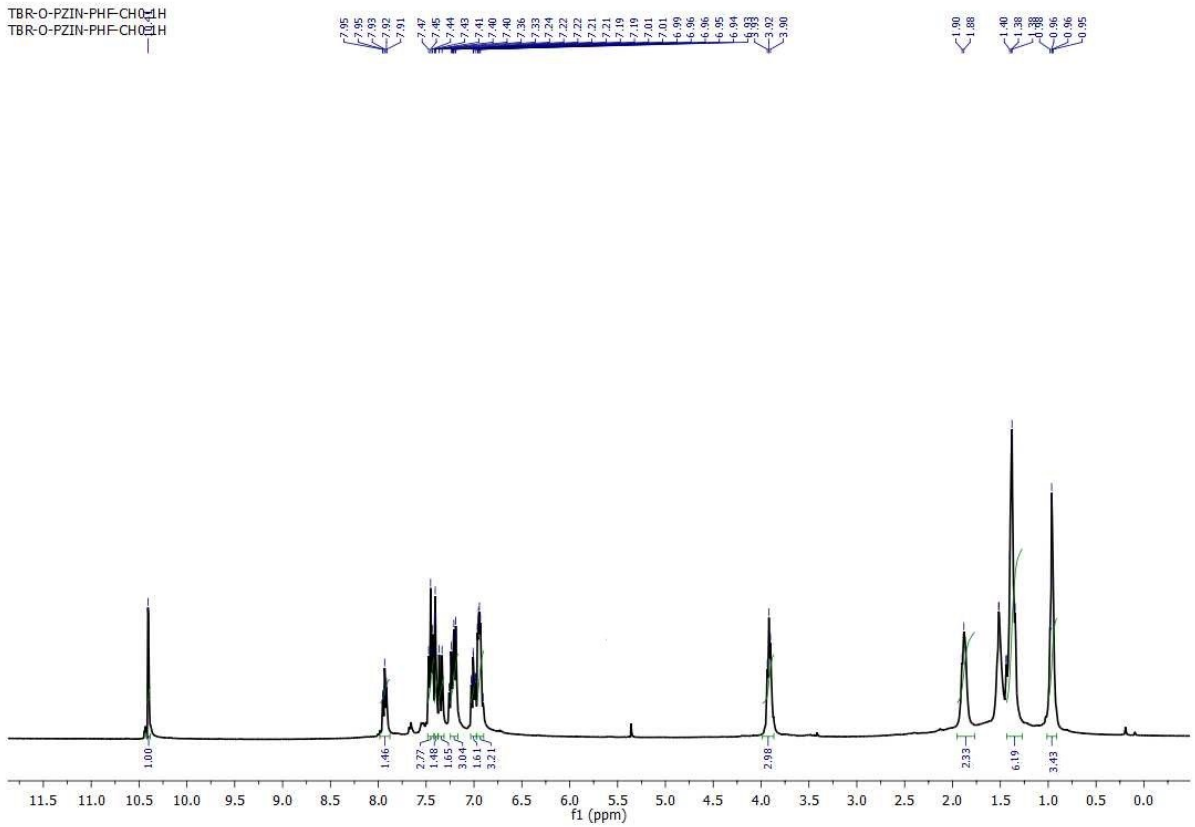

Figure S17a. ^{1}H NMR of 2-fluoro-4-(10-hexyl-10H-phenothiazin-3-yl)benzaldehyde (3a) in $CDCl_3$.

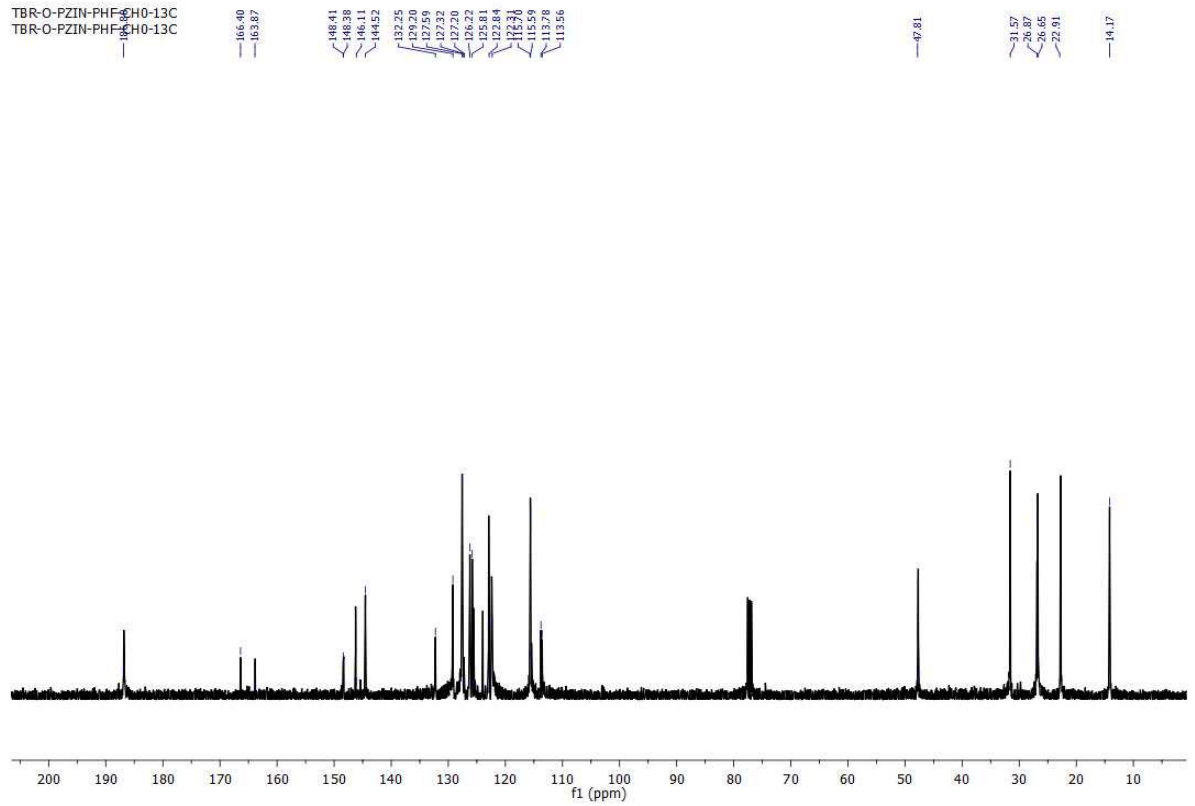

Figure S18b. ^{13}C NMR of 2-fluoro-4-(10-hexyl-10H-phenothiazin-3-yl)benzaldehyde (3a) in $CDCl_3$.

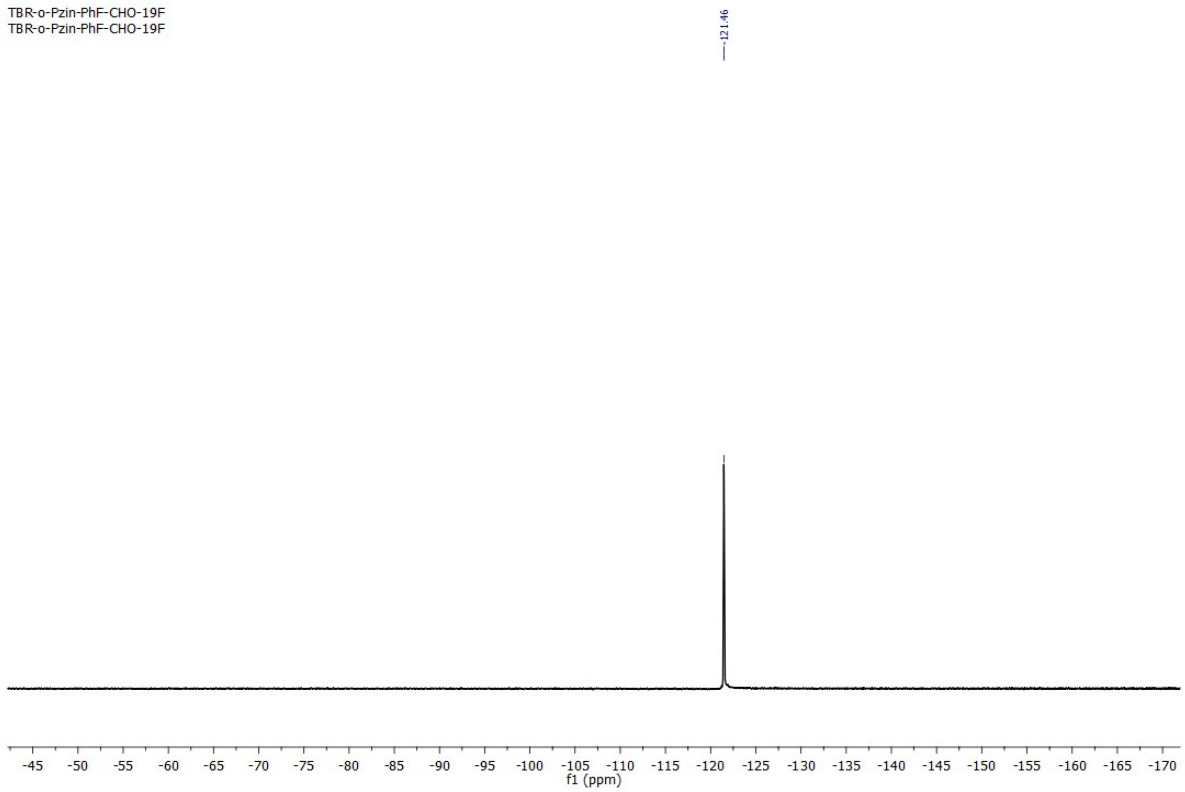

Figure S19c. ^{19}F NMR of 2-fluoro-4-(10-hexyl-10H-phenothiazin-3-yl)benzaldehyde (3a) in $CDCl_3$.

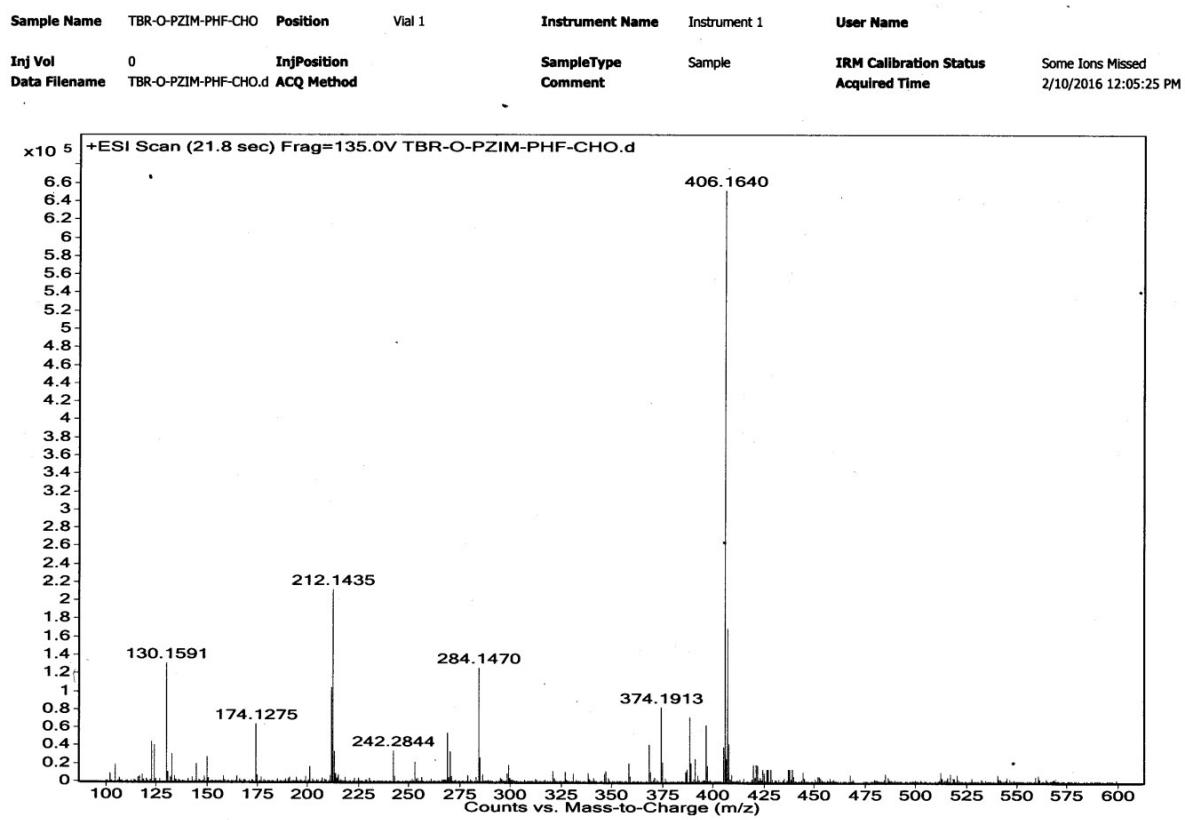

Figure S20d. HRMS of 2-fluoro-4-(10-hexyl-10H-phenothiazin-3-yl)benzaldehyde (3a) (ESI) m/z: $[M+H]^+$calcd for $C_{25}H_{25}FNOS$ 406.1640, found 406.1641.

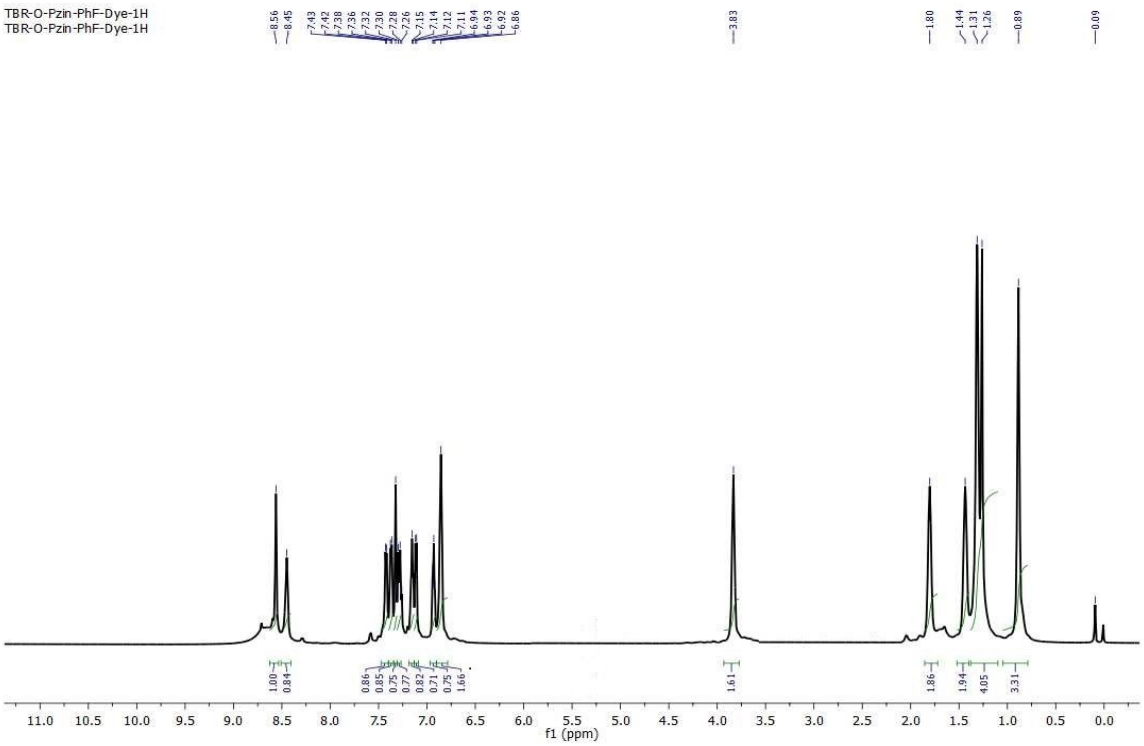

Figure S21a. ^{1}H NMR of (E)-2-cyano-3-(2-fluoro-4-(10-hexyl-10H-phenothiazin-3-yl)phenyl)acrylic acid (3b) in $CDCl_3$.

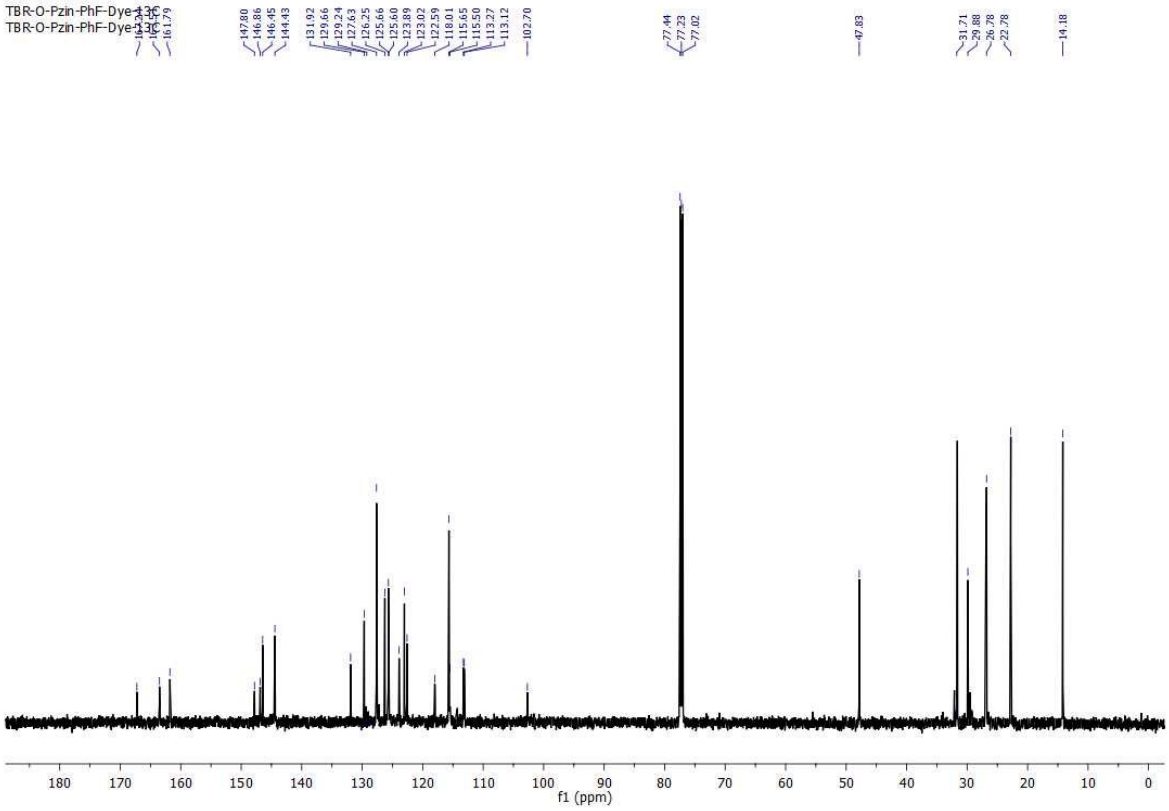

Figure S22b. ^{13}C NMR of (E)-2-cyano-3-(2-fluoro-4-(10-hexyl-10H-phenothiazin-3-yl)phenyl)acrylic acid (3b) in $CDCl_3$.

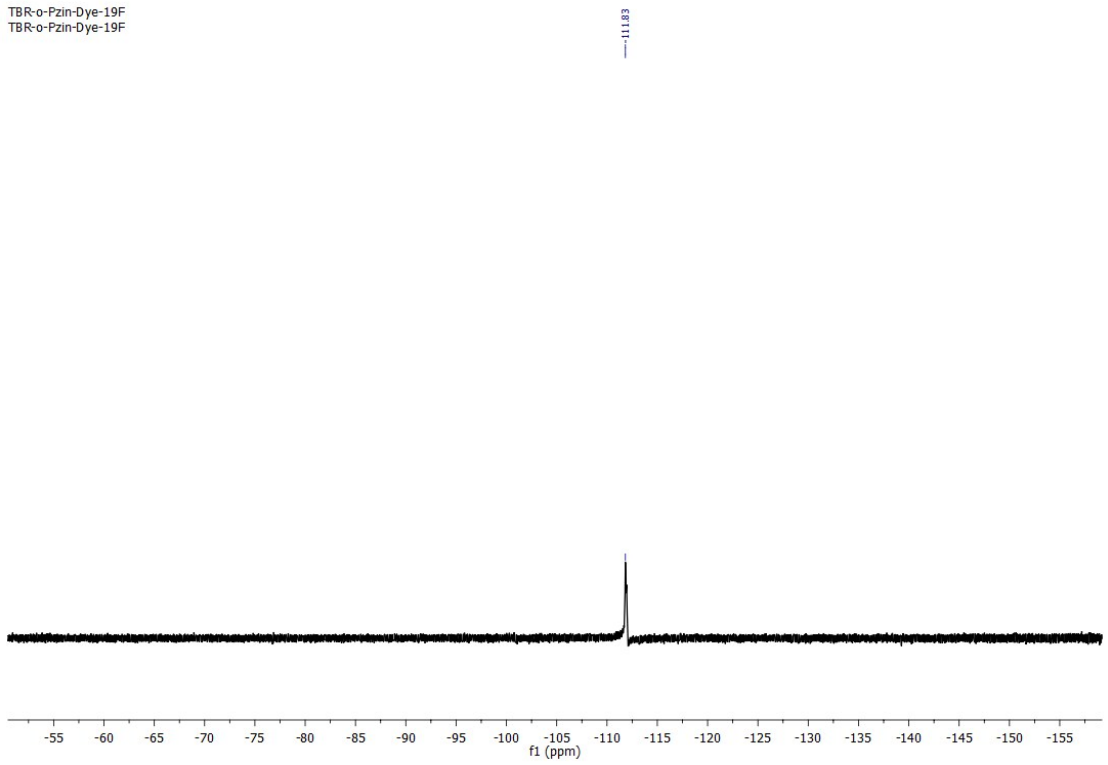

Figure S23c. ^{19}F NMR of (E)-2-cyano-3-(2-fluoro-4-(10-hexyl-10H-phenothiazin-3-yl)phenyl)acrylic acid (3b) in $CDCl_3$.

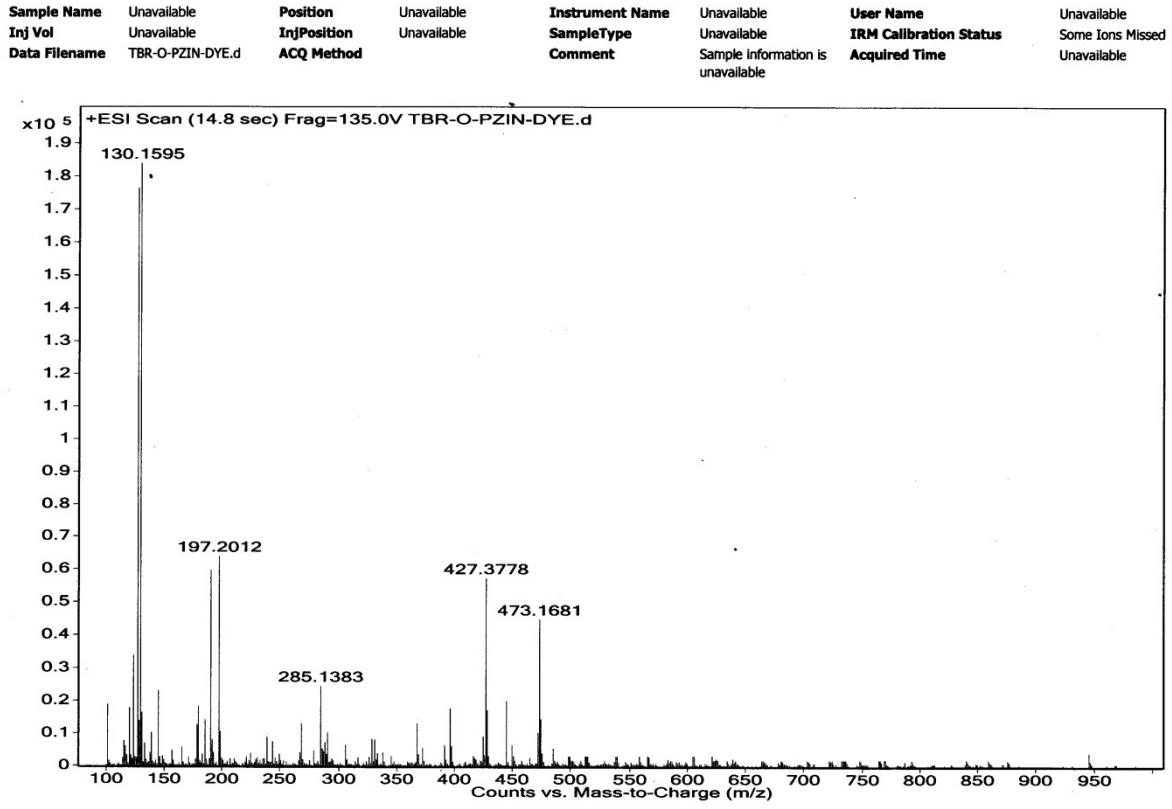

Figure S24d. HRMS of (E)-2-cyano-3-(2-fluoro-4-(10-hexyl-10H-phenothiazin-3-yl) phenyl) acrylic acid (3b) (ESI) m/z: $[M+H]^+$calcd for $C_{28}H_{26}FN_2O_2S$ 473.1699, found 473.1681.

References:

[1] G. Marotta, C. P. Kumar, M. G. Lobello, F. Cavazzini, P. Salvatori, K. Ganesh, M. K. Nazeeruddin, M. Chandrasekharam and F. De Angelis, *Dalton Trans.*, **2015**, 44, 5369-5378.

[2] D. Gudeika, J. V. Grazulevicius, D. Volyniuk, G. Juska, V. Jankauskas and G. Sini, *J. Phys. Chem. C*, **2015**, 119, 28335-28346.

[3] Y. S. Yang, H. Do Kim, J. H. Ryu, K. K. Kim, S. S. Park, K. S. Ahn and J. H. Kim, *Synthetic Met.*, **2011**, 161, 850-855.