Electronic Supplementary Information

Effect of Fluorine Position and Content on Phenylene Spacer in Carbazole Based Organic Sensitizers for Dye Sensitized Solar Cells

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Content **page**

Materials and Characterization:

All the materials used in this work were purchased from different commercial sources and used as received. Precursor 3-bromo-9-hexyl-9H-carbazole was synthesized according to the reported literature.[1] All the reactions were performed under argon atmosphere. Moisture sensitive reactions were carried out with dried and freshly distilled solvents. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Varian AS400 (400 MHz) or Brucker Ascend 600 (600 MHz) spectrometers, using solvent $CDCl_3$ or DMSO-d_6. HRMS spectra were recorded on a Waters (Micro mass MSTechnologies) Q-Tof MS Analyzer spectrometer. The UV-vis absorption spectra for solution were recorded on a Perkin-Elmer Lambda 35 spectrometer and that for film/dye coated TiO_2 films on a Perkin-Elmer Lambda 75 spectrometer. Electrochemical measurements were carried out using a CH Instruments 760D electrochemical workstation at a scan rate of 50 mV/s. A three-electrode cell with platinum wire counter electrode, glassy carbon working electrode and Ag/Ag^{+} reference electrode was employed. Tetrabutylammonium hexafluorophosphate (0.1 M) in acetonitrile was used as supporting electrolyte and Fc^{+}/Fc couple was used as internal reference. A thin film was casted from 10 μL, 1 mM solution of dye in DCM on the working electrode and the measurements were performed at room temperature under inert atmosphere. Time-resolved fluorescence studies were performed using an Edinburgh Life Spec II instrument. Veeco Dektak 150 Surface Profilometer was used for the measurement of the TiO_2 film thickness. Oriel Sol 3A solar simulator from Newport, with a 500 W xenon lamp, connected to AM 1.5 Globe filter and a Keithley-2400 digital source meter were used for IV measurements. A Solartron 1287 gain phase analyser was used for Impedance Spectroscopy (EIS) measurements and analysis was performed by sweeping frequency from 120 KHz to 0.1Hz in dark condition under a bias of -0.65V DC with a small AC perturbation (10 mV). Open-circuit voltage decay (OCVD) and Tafel polarization plot were obtained using a Solartron electrochemical analyser by sweeping potential $\pm$0.65 in dark with 25mV/s scan rate. IPCE measurement was carried out on Optosolar SR 300, Gemany, where a 250 W xenon lamp was used as the light source. Electronic distribution of frontier molecular orbitals was investigated in Gaussian 09 software package. Calculations were carried out using Density functional theory (DFT) with B3LYP-631G (d,p) basis set.

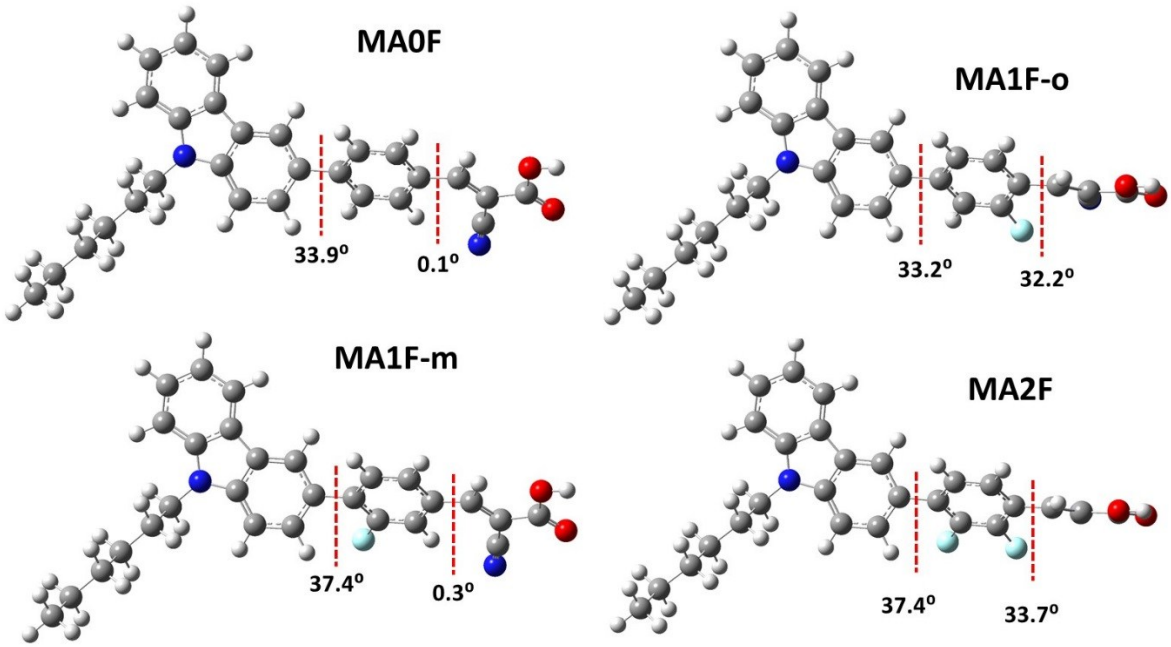

Fig. S1 Optimized structure of dyes showing dihedral angles

Table S1: Dipole moment of the sensitizers calculated using density functional theory

Dye	*Components of dipole moment (Debye)*		
	μ_x	μ_y	μ_z
MA0F	-1.5	-6.3	6.3
MA1F-o	-0.8	-5.6	7.0
MA1F-m	-0.9	-5.3	5.5
MA2F	-0.3	-4.6	6.2

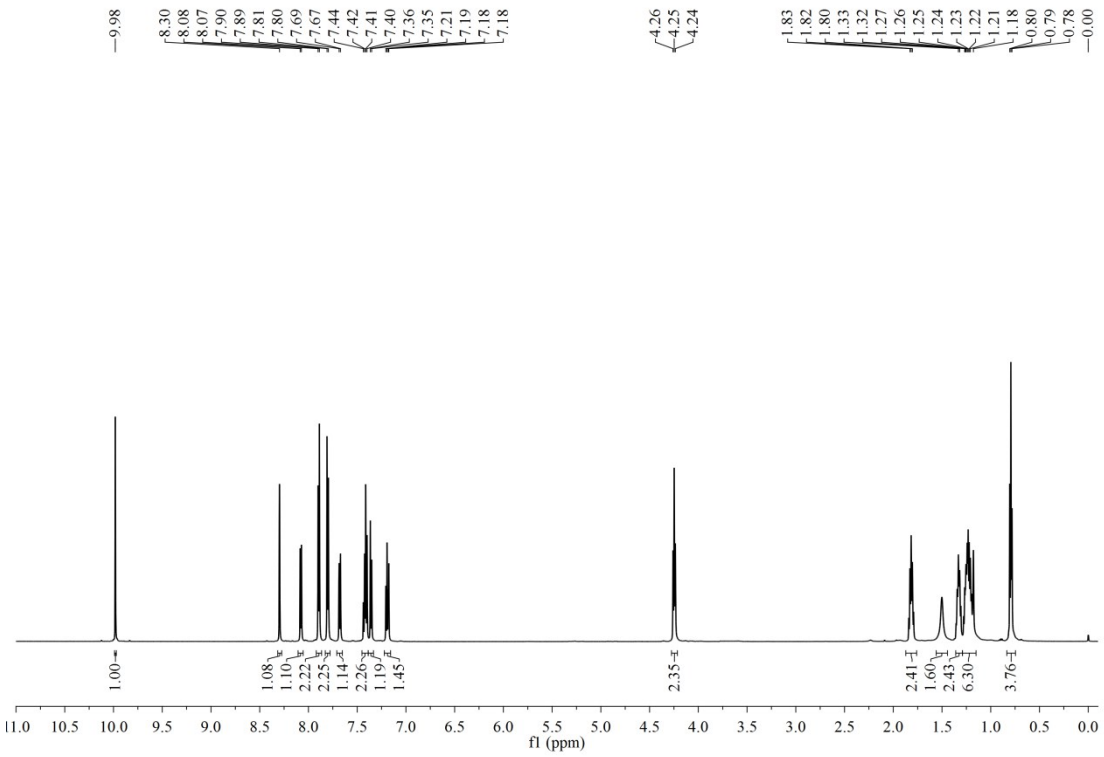

Fig. S2 ^{1}H NMR of 4-(9-hexyl-9H-carbazol-3-yl)benzaldehyde (2a)

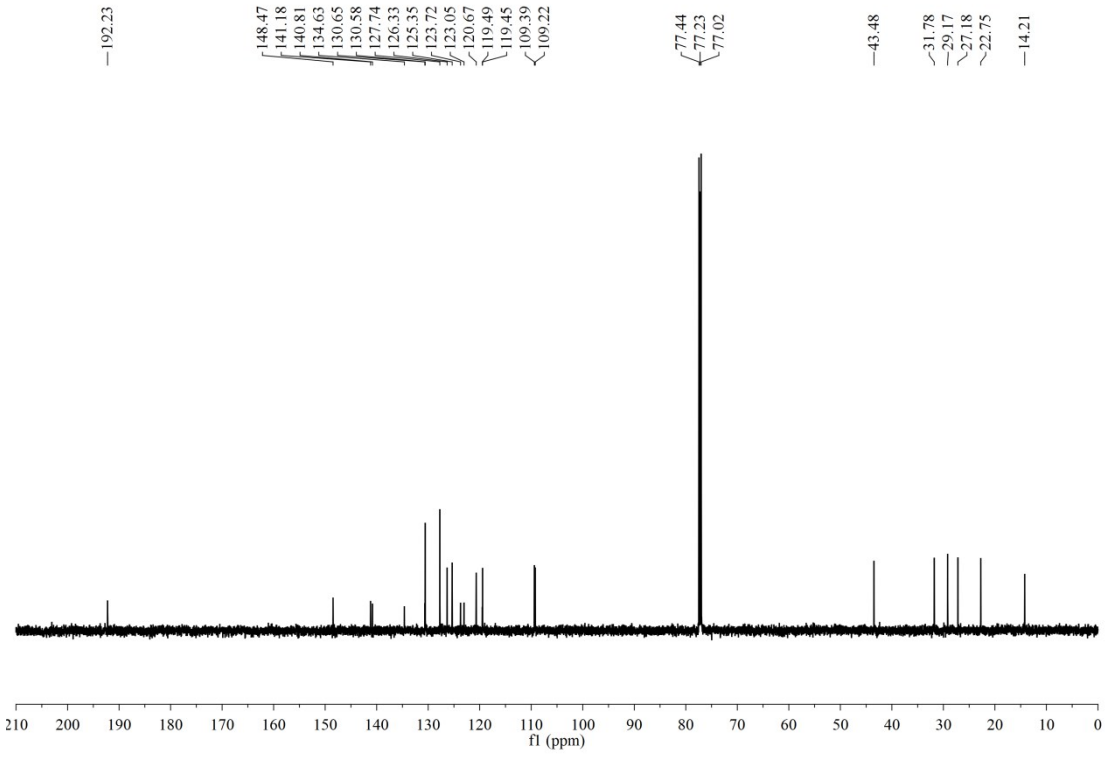

Fig. S3 ^{13}C NMR of 4-(9-hexyl-9H-carbazol-3-yl)benzaldehyde (2a)

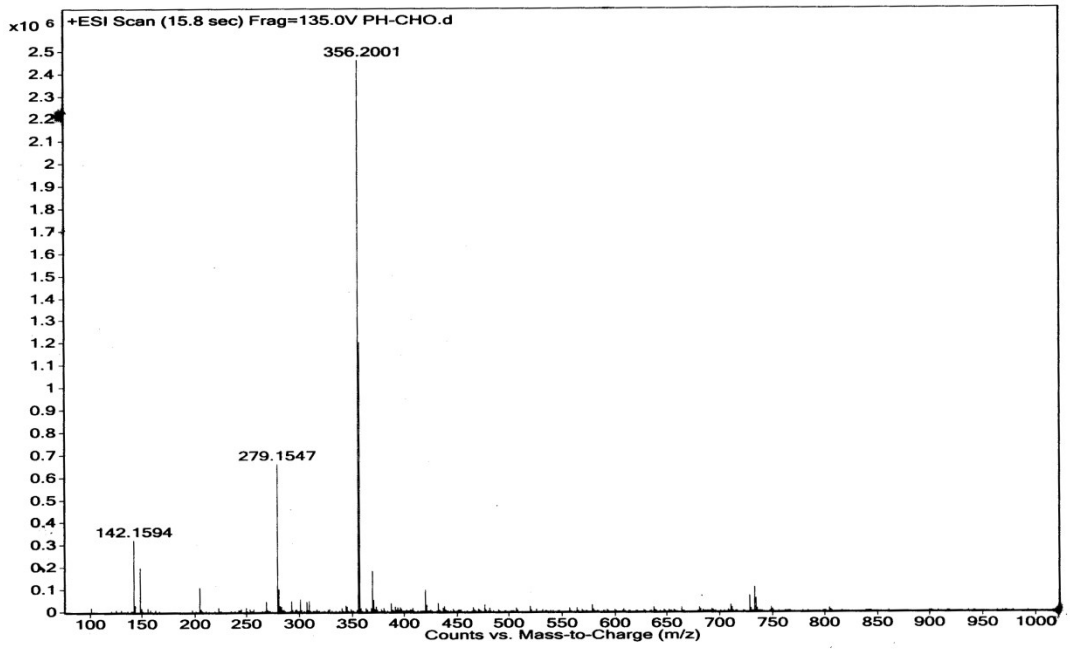

Fig. S4 HRMS (ESI) of 4-(9-hexyl-9H-carbazol-3-yl)benzaldehyde (2a)

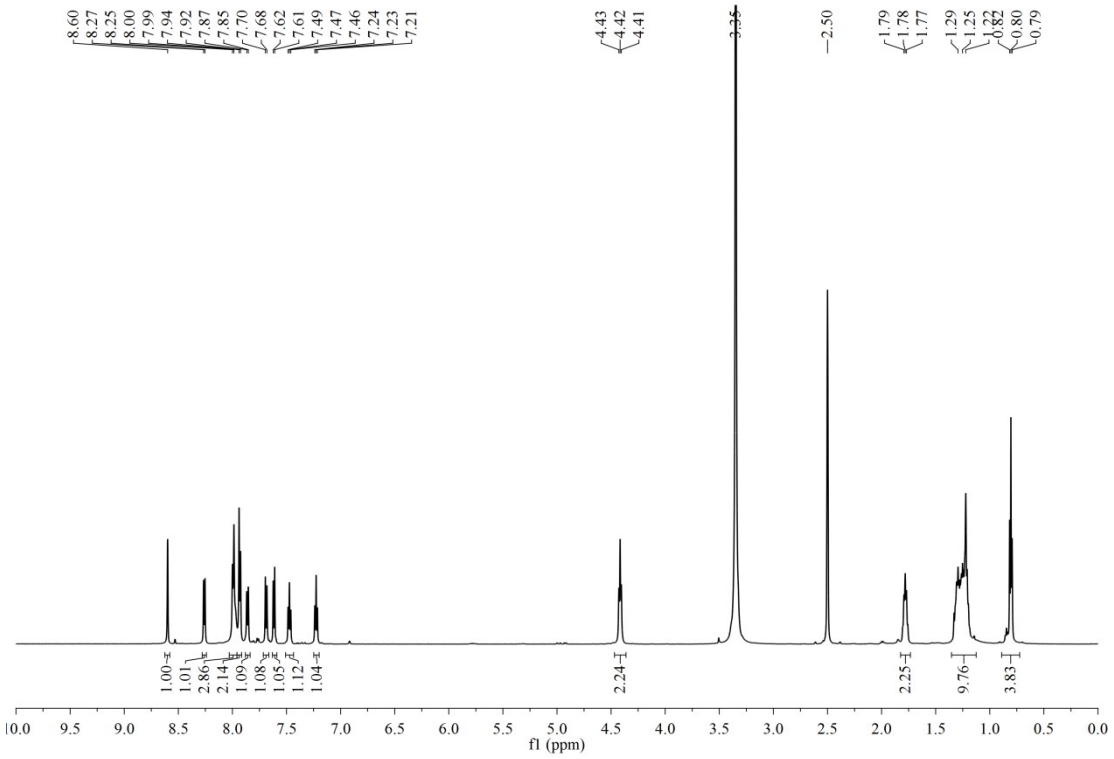

Fig. S5 ^{1}H NMR of 2-cyano-3-(4-(9-hexyl-9H-carbazol-3-yl)phenyl)acrylic acid (MA0F)

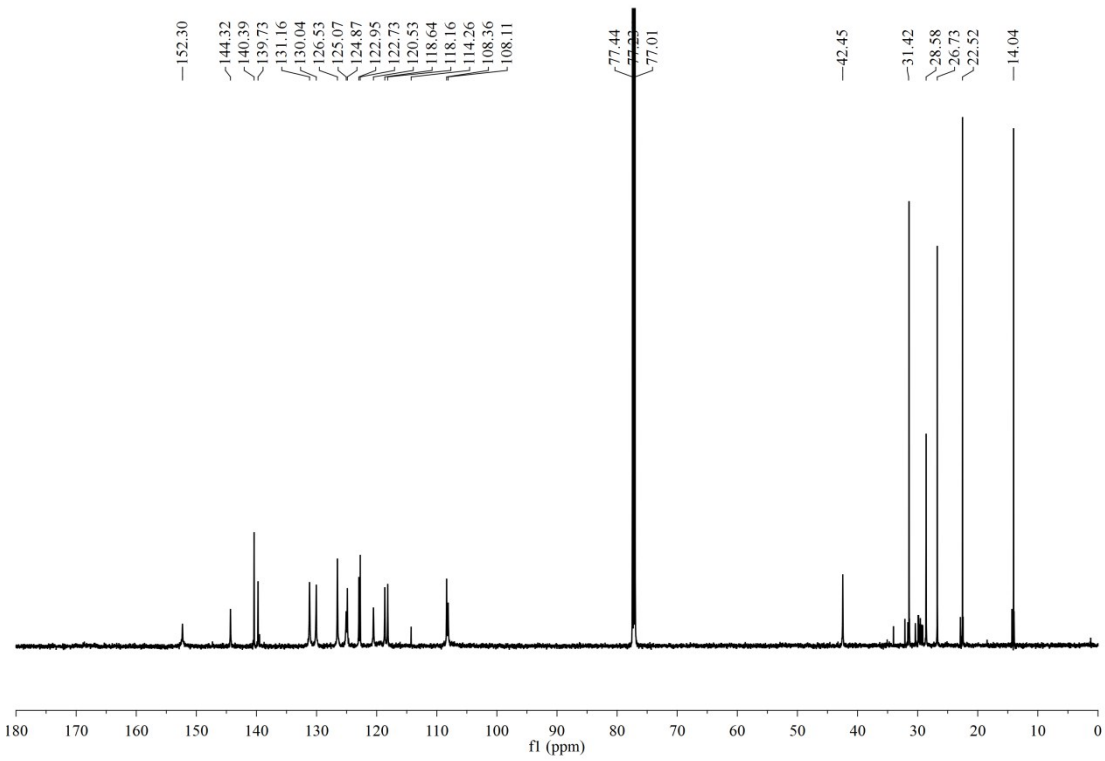

Fig. S6 ^{13}C NMR of 2-cyano-3-(4-(9-hexyl-9H-carbazol-3-yl)phenyl)acrylic acid (MA0F)

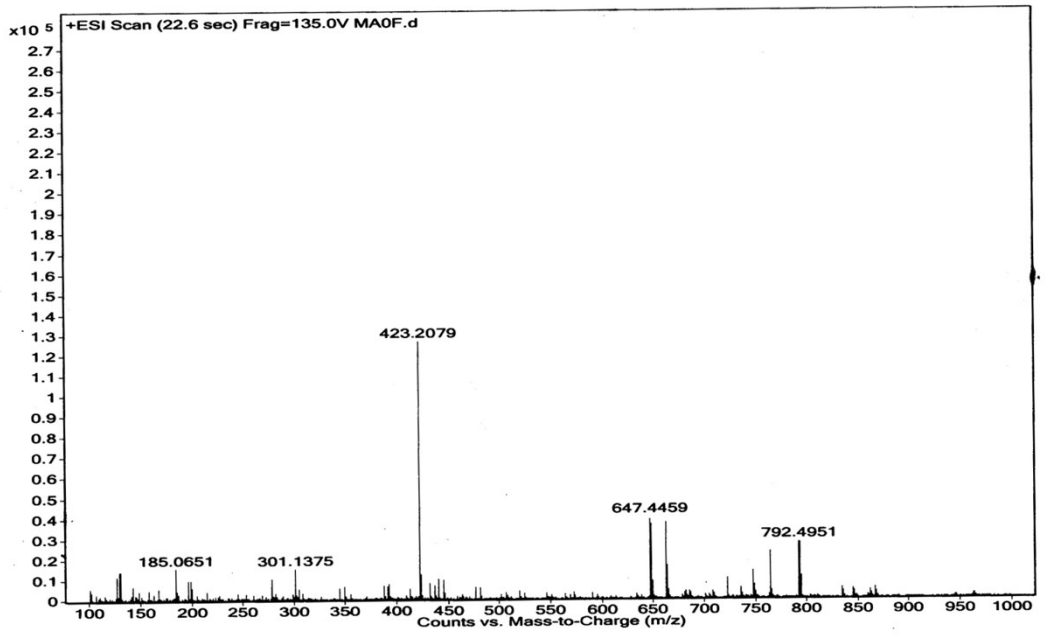

Fig. S7 HRMS (ESI) of 2-cyano-3-(4-(9-hexyl-9H-carbazol-3-yl)phenyl)acrylic acid (MA0F)

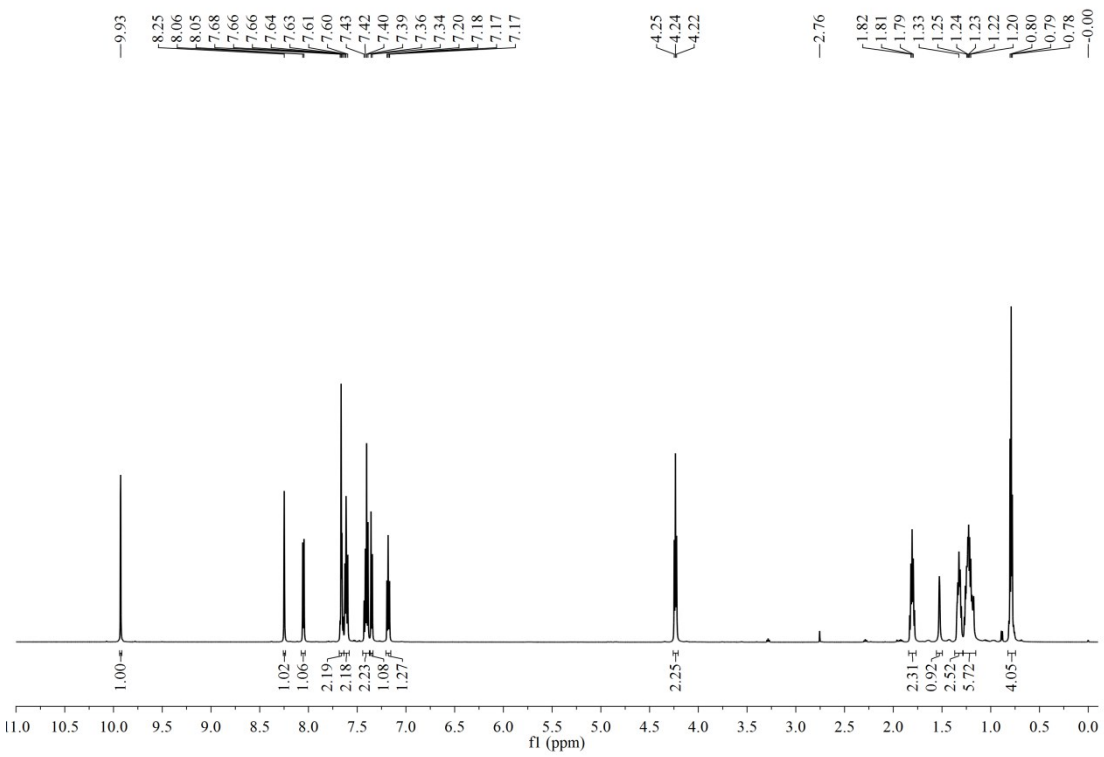

Fig. S8 ^{1}H NMR of 3-fluoro-4-(9-hexyl-9H-carbazol-3-yl)benzaldehyde (2c)

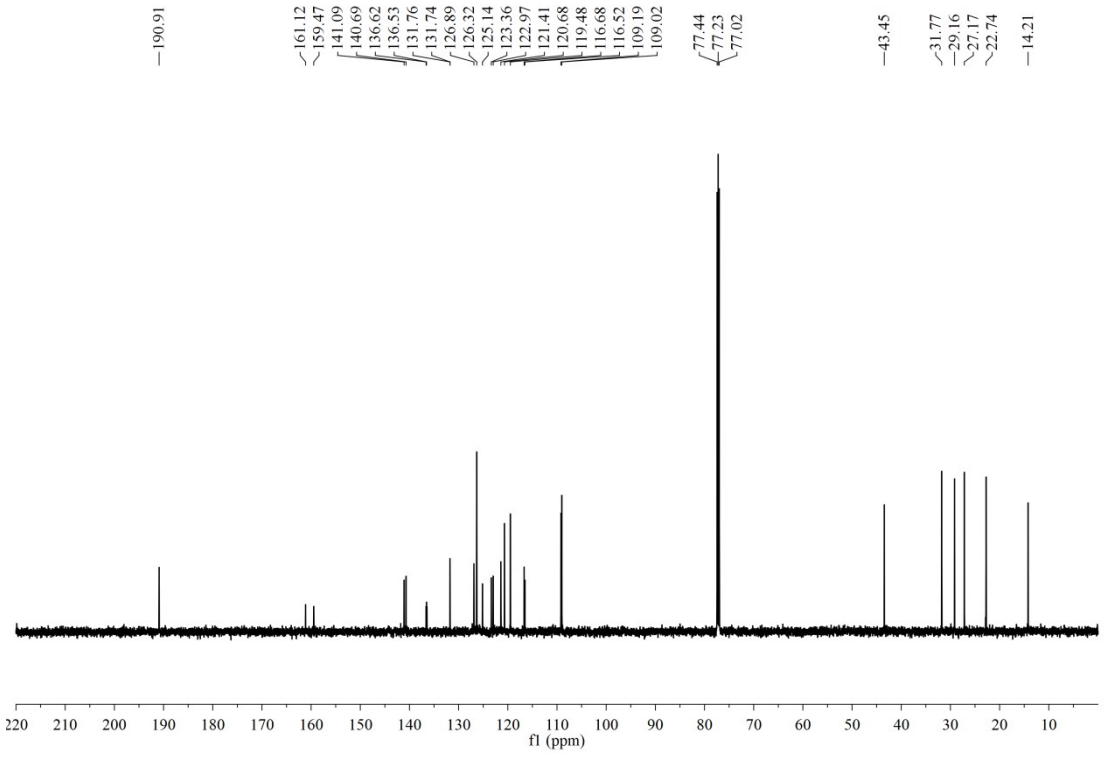

Fig. S9 ^{13}C NMR of 3-fluoro-4-(9-hexyl-9H-carbazol-3-yl)benzaldehyde (2c)

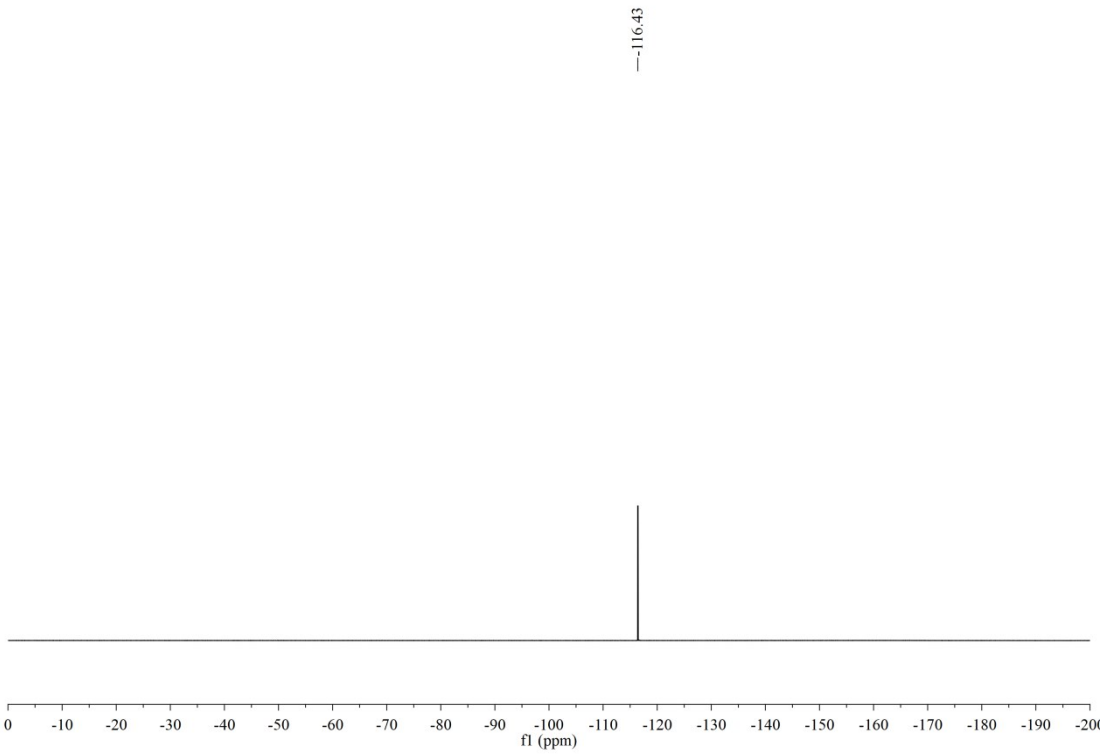

Fig. S10 ^{19}F NMR of 3-fluoro-4-(9-hexyl-9H-carbazol-3-yl)benzaldehyde (2c)

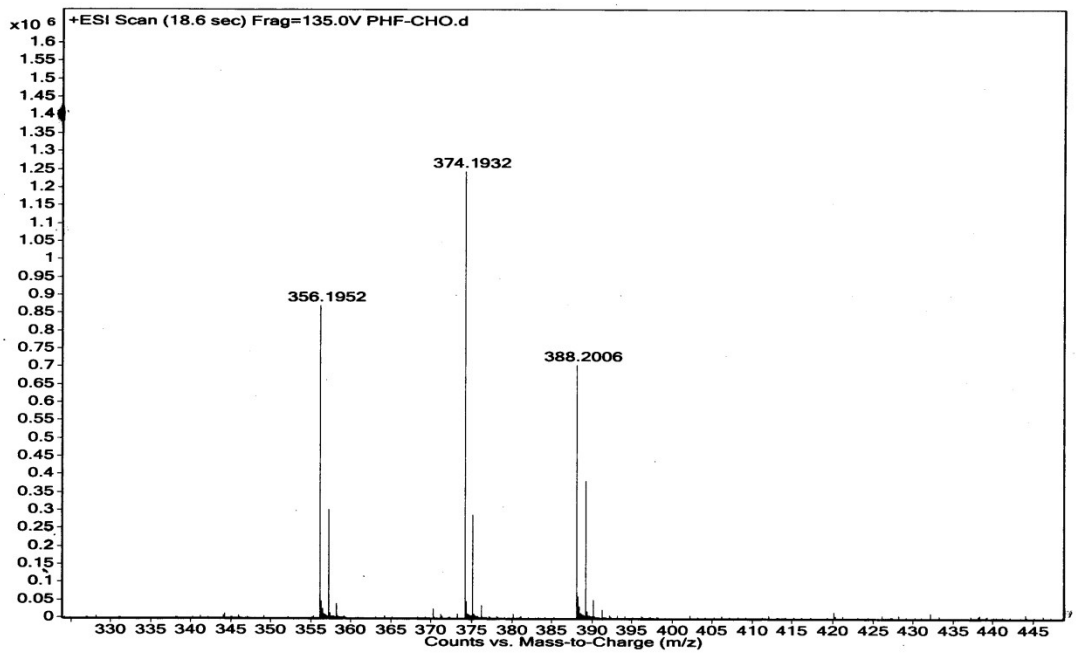

Fig. S11 HRMS (ESI) of 3-fluoro-4-(9-hexyl-9H-carbazol-3-yl)benzaldehyde (2c)

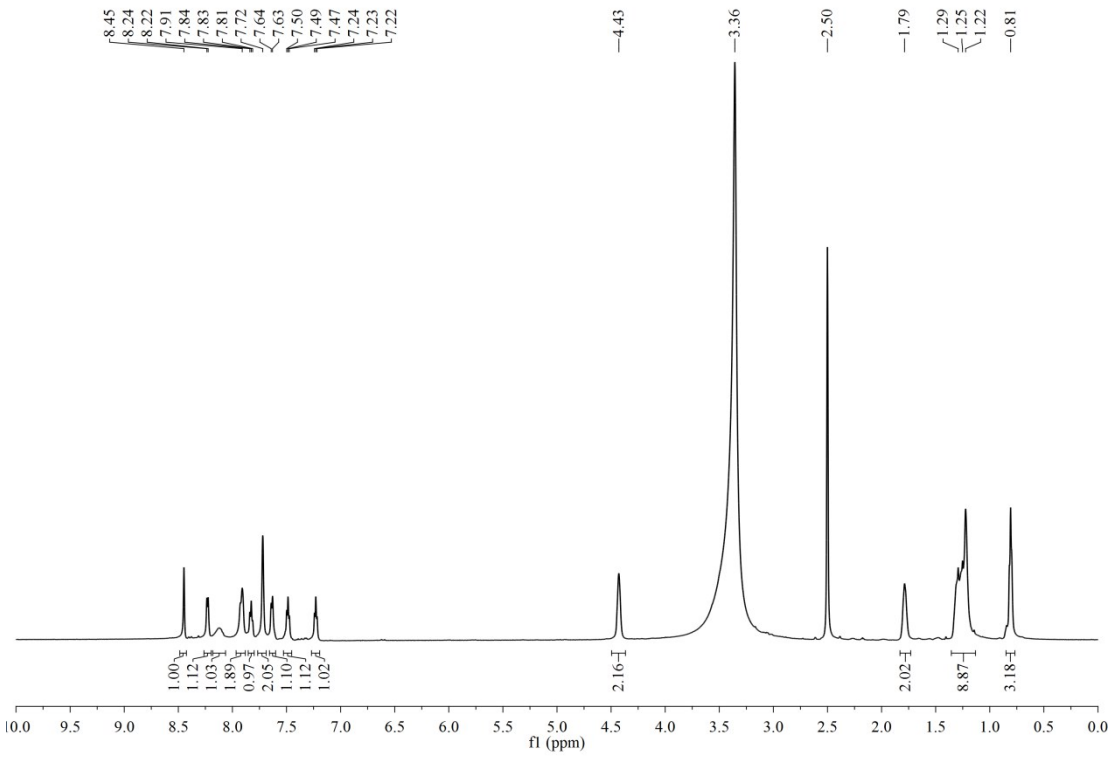

Fig. S12 ^{1}H NMR of 2-cyano-3-(3-fluoro-4-(9-hexyl-9H-carbazol-3-yl)phenyl)acrylic acid (MA1F-m)

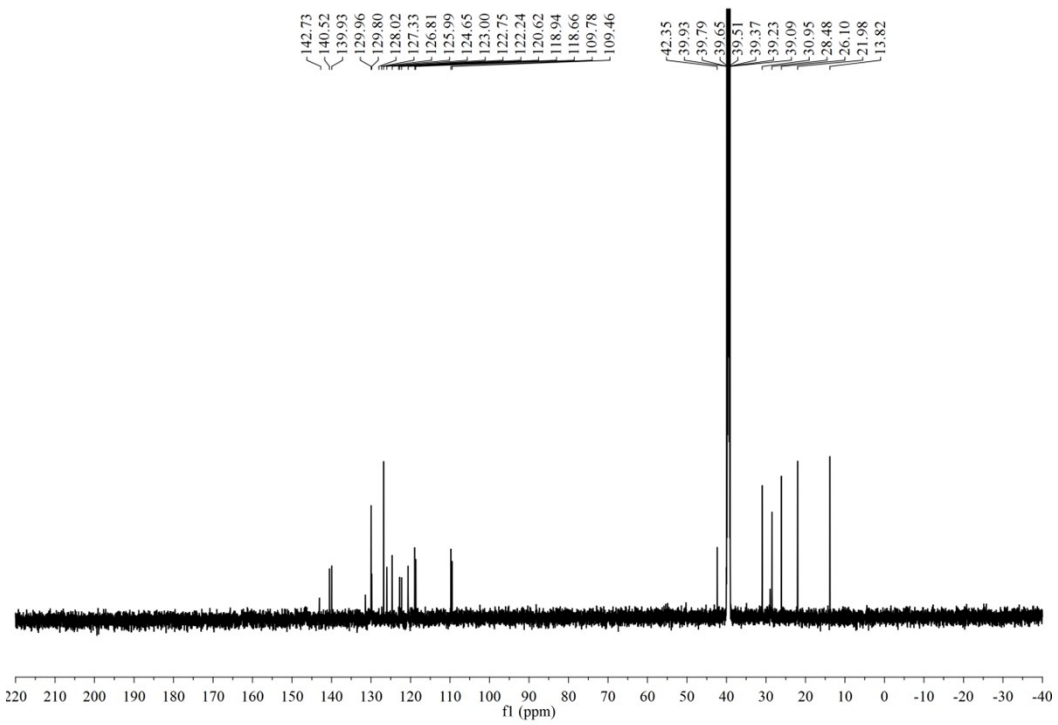

Fig. S13 ^{13}C NMR of 2-cyano-3-(3-fluoro-4-(9-hexyl-9H-carbazol-3-yl)phenyl)acrylic acid (MA1F-m)

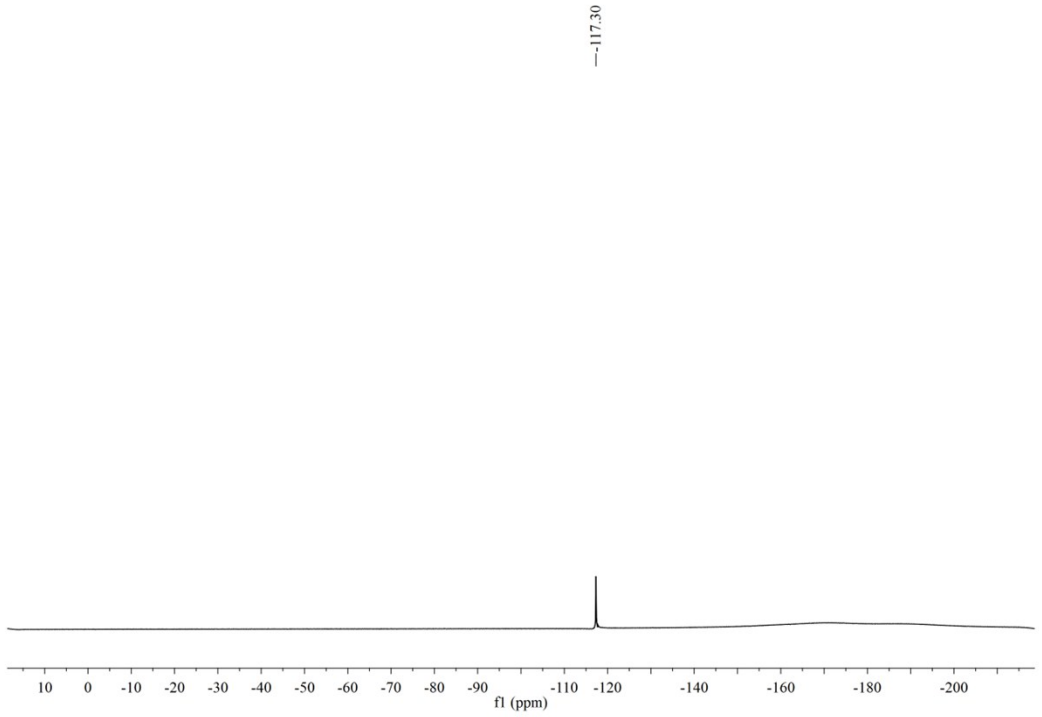

Fig. S14 ^{19}F NMR of 2-cyano-3-(3-fluoro-4-(9-hexyl-9H-carbazol-3-yl)phenyl)acrylic acid (MA1F-m)

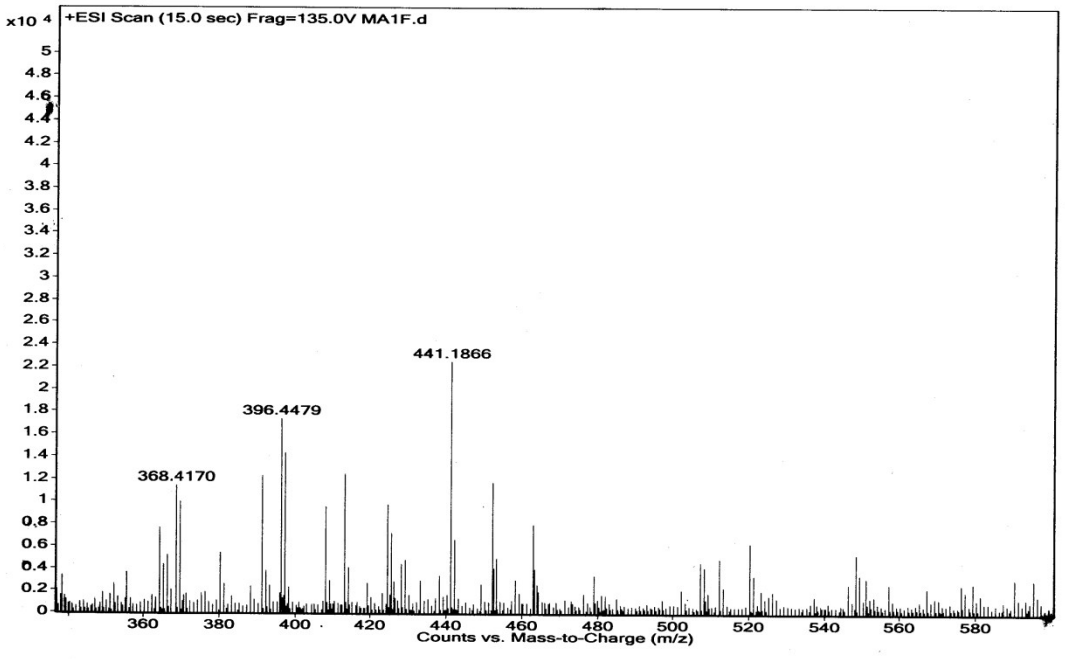

Fig. S15 HRMS (ESI) of 2-cyano-3-(3-fluoro-4-(9-hexyl-9H-carbazol-3-yl)phenyl)acrylic acid (MA1F-m)

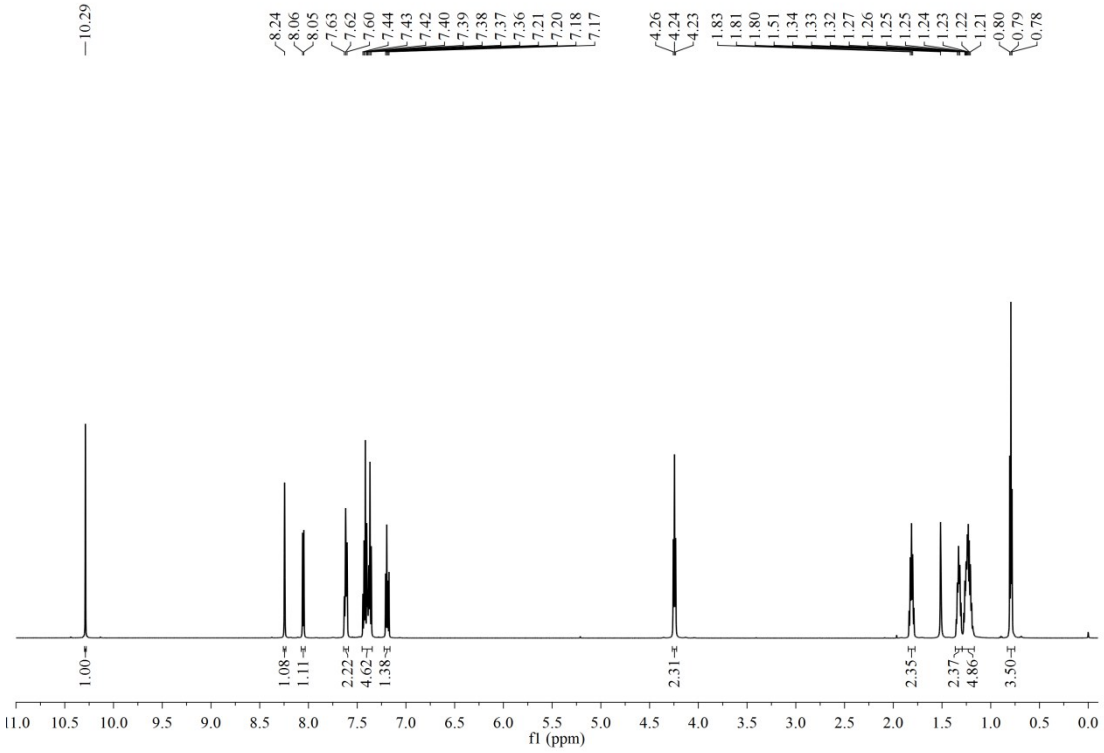

Fig. S16 ^{1}H NMR of 2,3-difluoro-4-(9-hexyl-9H-carbazol-3-yl)benzaldehyde (2d)

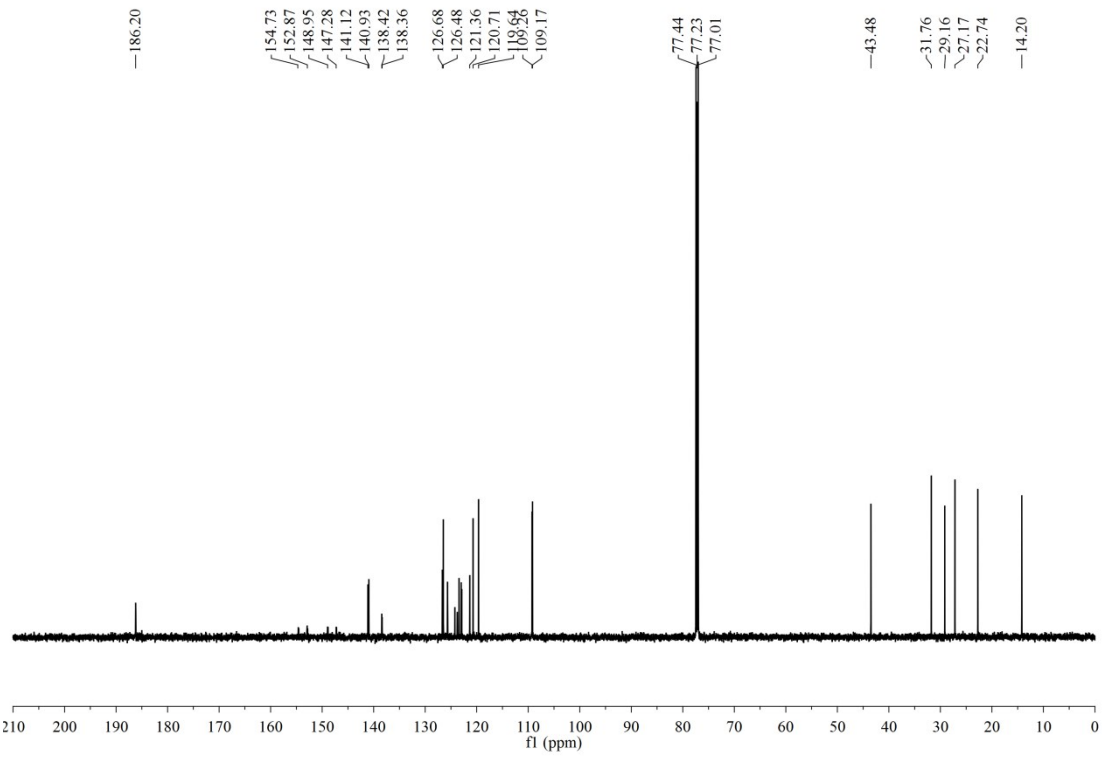

Fig. S17 ^{13}C NMR of 2,3-difluoro-4-(9-hexyl-9H-carbazol-3-yl)benzaldehyde (2d)

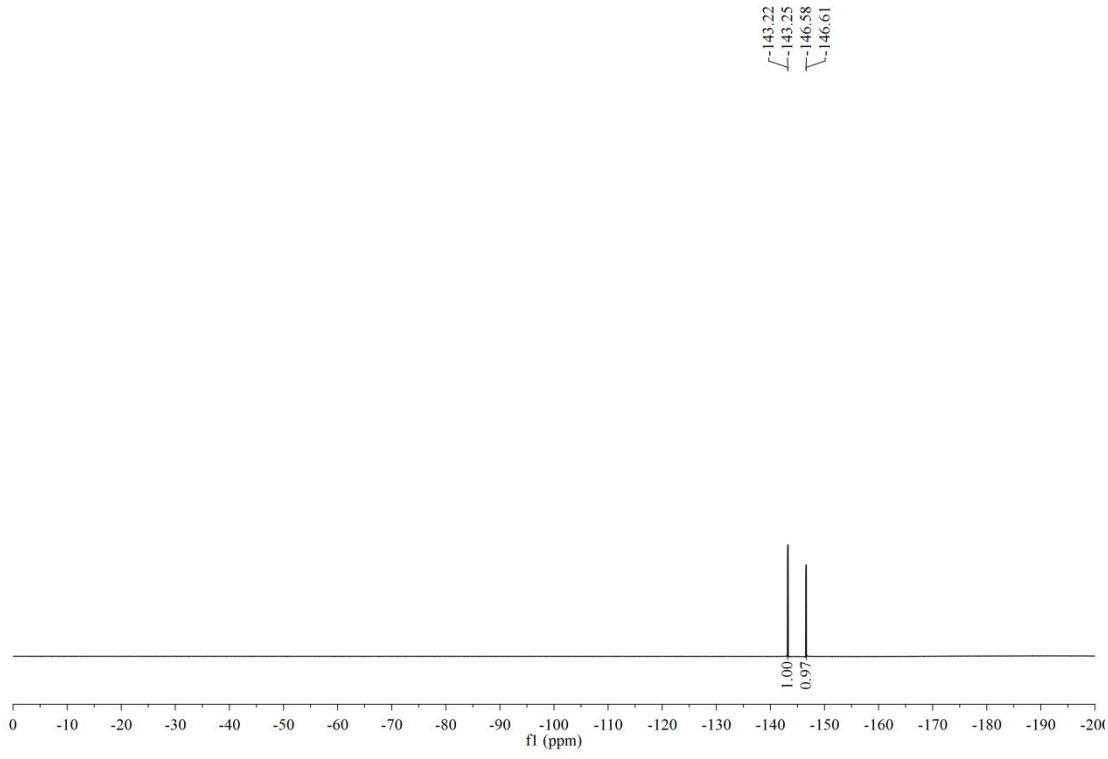

Fig. S18 ^{19}F NMR of 2,3-difluoro-4-(9-hexyl-9H-carbazol-3-yl)benzaldehyde (2d)

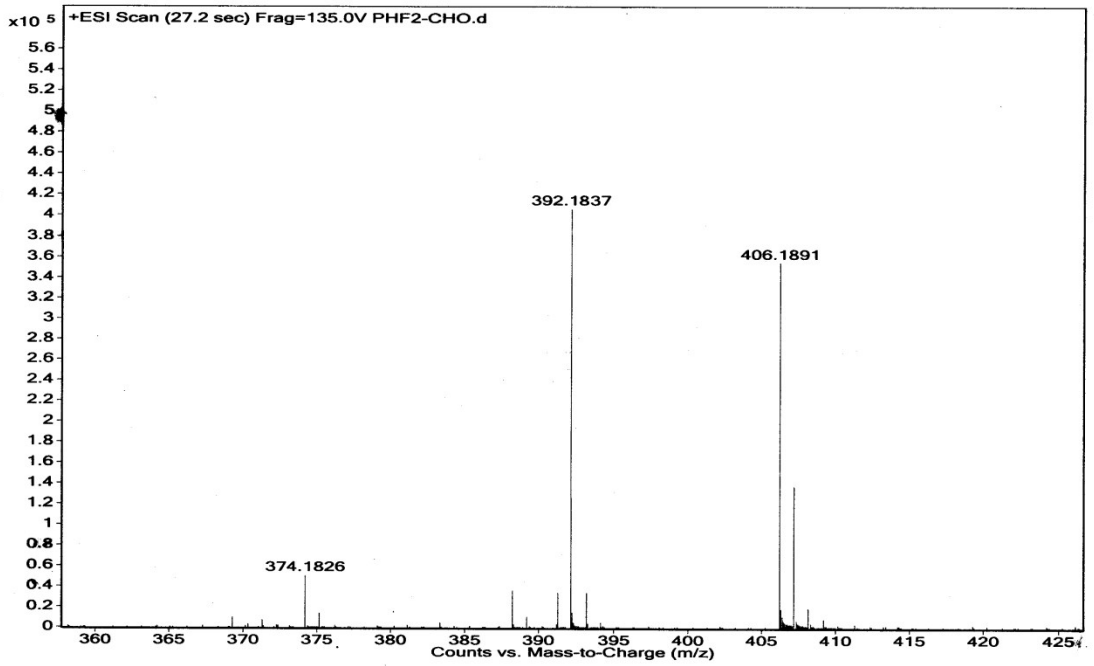

Fig. S19 HRMS (ESI) of 2,3-difluoro-4-(9-hexyl-9H-carbazol-3-yl)benzaldehyde (2d)

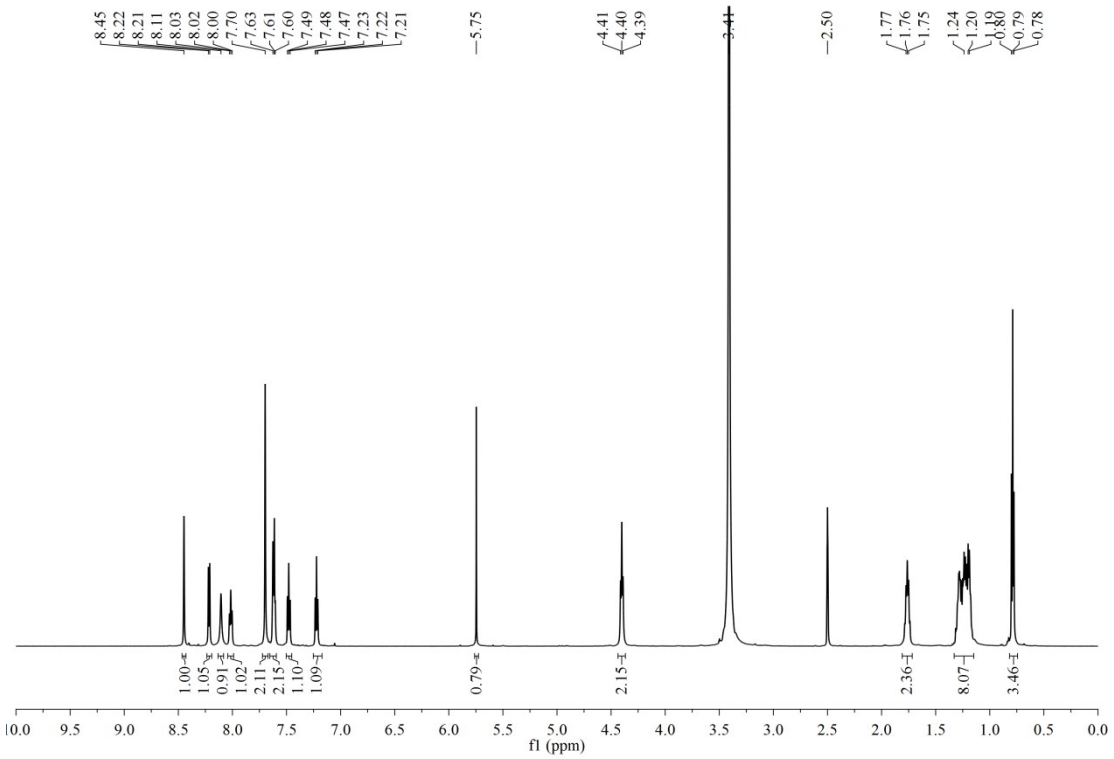

Fig. S20 ^{1}H NMR of 2-cyano-3-(2,3-difluoro-4-(9-hexyl-9H-carbazol-3-yl)phenyl)acrylic acid (MA2F)

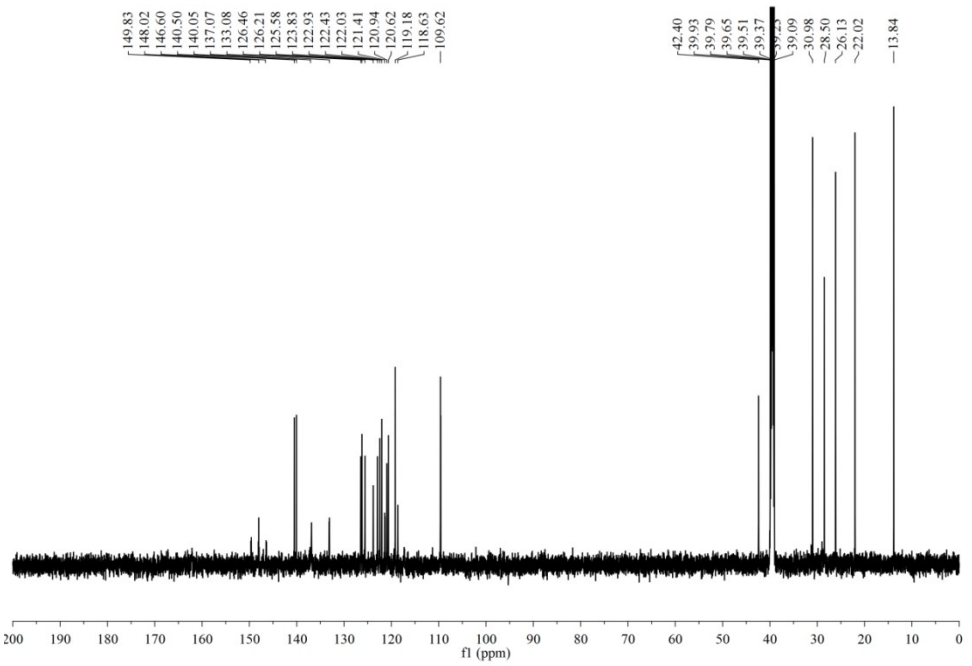

Fig. S21 ^{13}C NMR of 2-cyano-3-(2,3-difluoro-4-(9-hexyl-9H-carbazol-3-yl)phenyl)acrylic acid (MA2F)

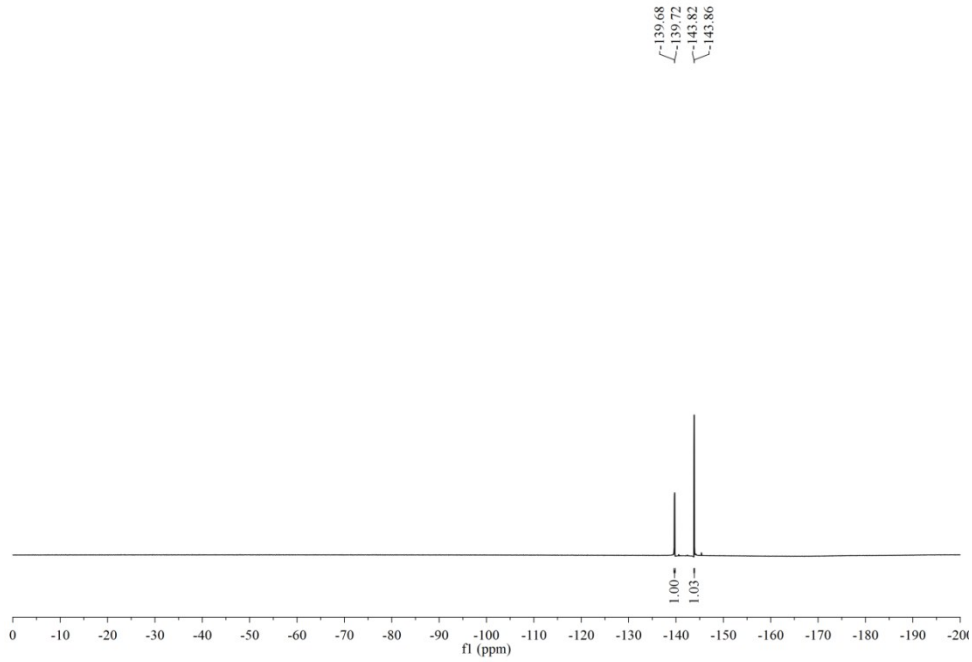

Fig. S22 ^{19}F NMR of 2-cyano-3-(2,3-difluoro-4-(9-hexyl-9H-carbazol-3-yl)phenyl)acrylic acid (MA2F)

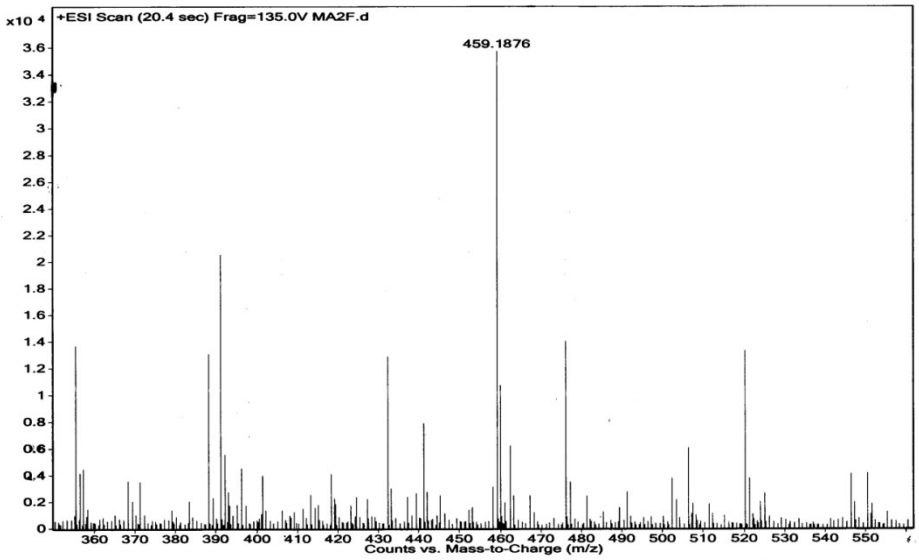

Fig. S23 HRMS (ESI) of 2-cyano-3-(2,3-difluoro-4-(9-hexyl-9H-carbazol-3-yl)phenyl)acrylic acid (MA2F)

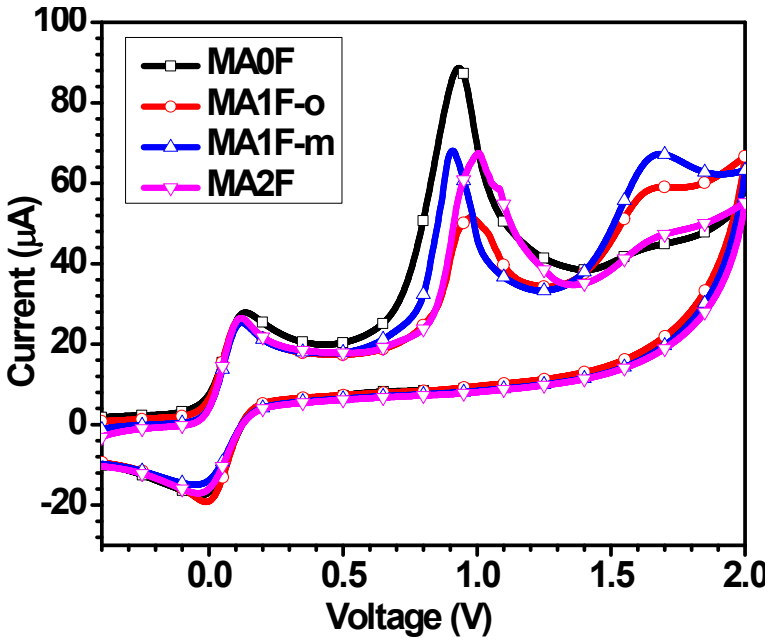

Fig. S24: CV spectra of the dyes

Reference:

(1) Feng, G. L.; Lai, W. Y.; Ji, S. J.; Huang, W. Synthesis of Novel Star-Shaped Carbazole-Functionalized Triazatruxenes. *Tetrahedron Lett.* **2006**, *47* (39), 7089–7092.