Electronic Supplementary Information (ESI)

A facile approach to construct organic D-π-A dyes *via* sequential condensation reactions for dye-sensitized solar cells

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General

All chemicals and reagents were used as received from chemical company (Aldrich) without further purification. Column chromatography was performed using with silica gel (200 ~300 mesh) as a stationary phase. Cyclic voltammetry (CV) was performed on a CHI760E Electrochemical Workstation (CHI Instruments Co., Shanghai, China). All CV measurements were carried out in anhydrous CH_2Cl_2 containing 0.1 M TBAHFP as a supporting electrolyte, purging with argon prior to conduct the experiment. Platinum electrode was used as a working electrode, Ag/AgCl in saturated KCl (aq.) as a reference electrode, and a platinum wire as a counter electrode. UV-Vis spectra were measured in CH_2Cl_2 solution or TiO_2 film using UV-3600 Spectrophotometer (SHIMADZU). Fluorescence spectra were measured using FL6500 spectrophotometer (PerkinElmer). The ^{1}H- and ^{13}C-NMR measurements were performed by a DRX spectrometer (Bruker BioSpin). Mass spectra were measured on a Shimadzu Biotech matrix-assisted laser desorption ionization (MALDI) mass

spectrometer. Geometry optimization and Molecular orbital distributions of three dyes were performed using B3LYP functional and 6-31G (d,p) basis set implemented in the Gaussian 09 program package.[1] To estimate the dye-loading amount of each dye in DSSCs, dyes were desorbed from the nanocrystalline TiO_2 film by dipping in 0.1 M TBAOH solution of 1: 1 mixture of H_2O and ethanol. The content of uptake dye was estimated from the absorption peak of each resulting solution.

Cell fabrication and characterization

The device fabrication was performed as follows. TiO_2 paste was received from dyesol Ltd. A double-layered TiO_2 film as photoanode containing 11 μm main transparent layer with ca. 20 nm sized titania particles and a 5 μm scattering layer with ca. 400 nm sized titania particles were screen printed on the fluorine-doped tin oxide (FTO) conducting glass substrate (~10 Ohm^{-2}, Solaronix). The double-layered films were heated to 520 ^oC and sintered for 1 hour and then cooled to 80 ^oC, following additional treatment with 0.1 M HCl aqueous solution. The resuluted TiO_2 films were washed, dried and then dipped into a 3×10^{-4} M acetonitrile/n-BuOH (1/1, v/v) solution of the corresponding sensitizer in CH_3CN/n-BuOH (1/1, v/v) for 40 h. Afterwards, the dye-loaded TiO_2 film and a platinum coated conducting glass were assembled into a DSSC of a sandwich type and sealed by heating the Surlyn spacer (40 mm thick). An electrolyte consisting of 0.6 M dimethylpropylimidazolium iodide, 0.05 M I_2, 0.1 M LiI and 0.7 M TBP in acetonitrile was injected into the spacer from the counterelectrode side through a pre-drilled hole, and then the hole was sealed with a Bynel sheet and a thin-glass-slide cover by heating.

The *J-V* characteristics were carried out by using a black metal mask with an aperture area of 0.2304 cm^{-2} under standard AM 1.5 sunlight, 100 $mW \cdot cm^{-2}$ (WXS-155S-10: Wacom Denso Co. Japan). Monochromatic IPCE spectra were determined with monochromatic incident light of 1×10^{16} photons per cm^2 under 100 $mW \cdot cm^{-2}$ in director current mode (CEP-2000BX, Bunko-Keiki). The IMVS were characterized with a potentiostat (Solartron1287) equipped with a frequency response analyzer

(Solartron1255B) at an open-circuit condition based on a monochromatic illumination (420 nm) controlled by a Labview system to obtain the photovoltaic response induced by the modulated light.

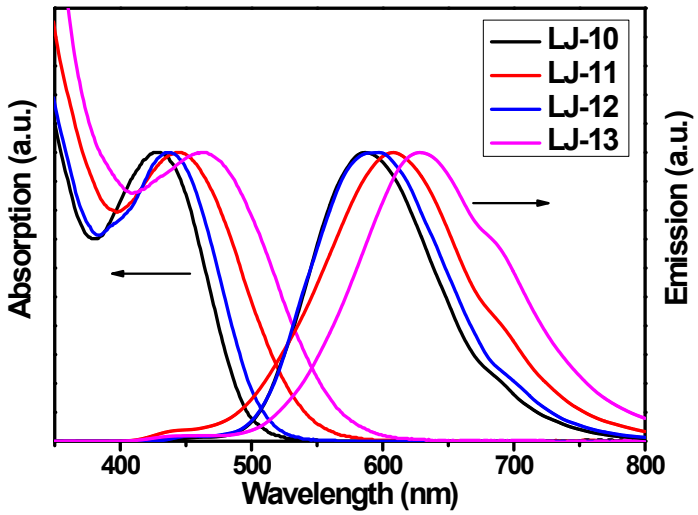

Fig. S1 Normalized UV-Vis and emission spectra of dyes **LJ-10**, **LJ-11**, **LJ-12** and **LJ-13** in CH_2Cl_2.

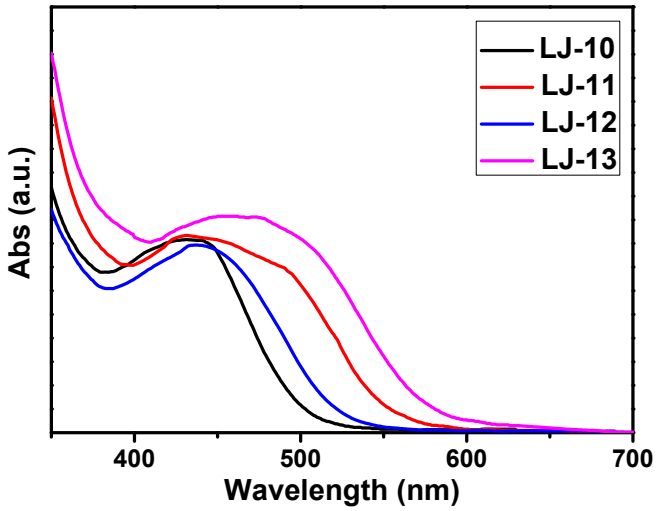

Fig. S2 Absorption spectra of dyes **LJ-10**, **LJ-11**, **LJ-12** and **LJ-13** anchored on a transparent TiO_2 films.

DFT Calculation

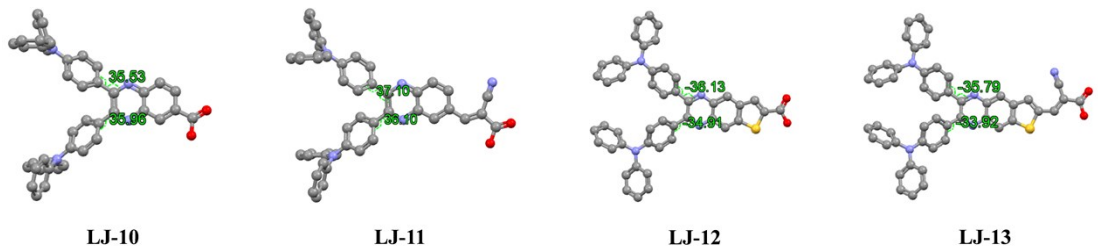

Fig. S3 Optimized ground-state geometries of dyes **LJ-10**, **LJ-11**, **LJ-12** and **LJ-13**.

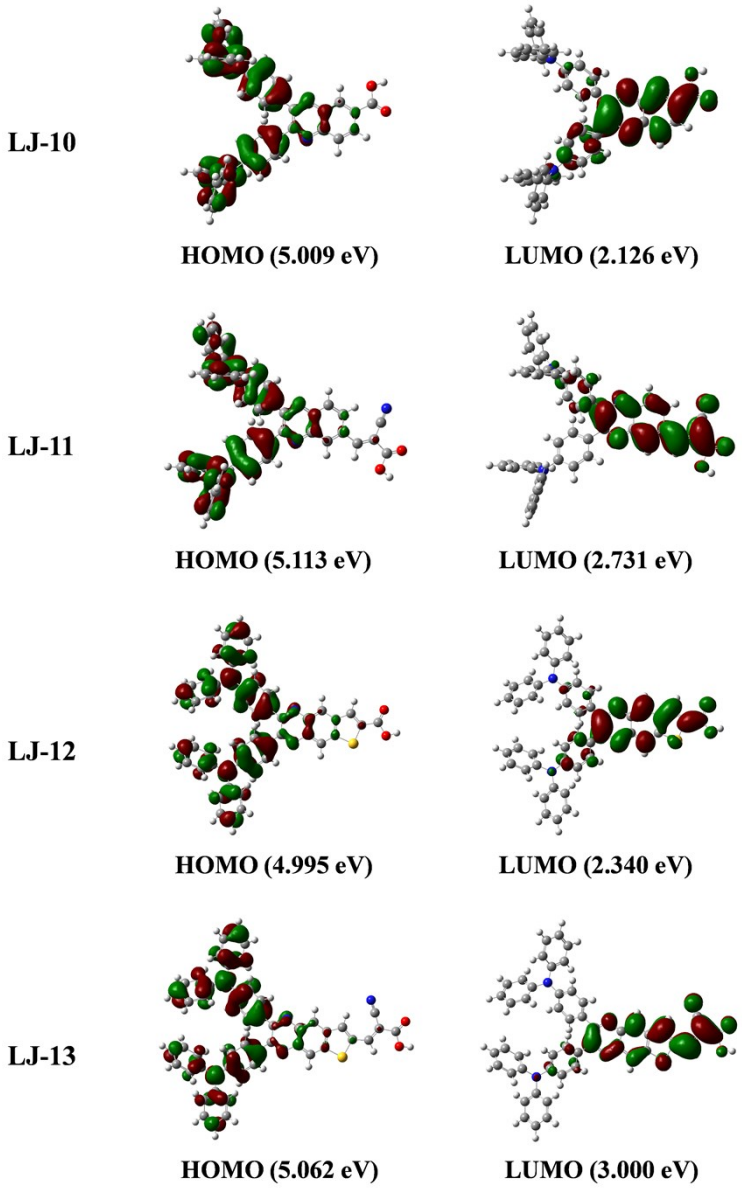

Fig. S4 The HOMO and LUMO of dyes **LJ-10**, **LJ-11**, **LJ-12** and **LJ-13** calculated at B3LYP/6-31G** level.

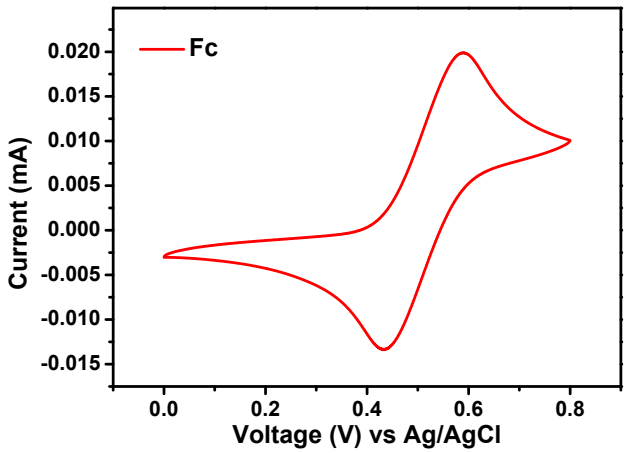

Fig. S5 Cyclic voltammograms of ferrocene in CH_2Cl_2/TBAHFP (0.1 M), [c] = 1×10^{-4} mol·L^{-1}, 293 K, scan rate = 100 mV·s^{-1}.

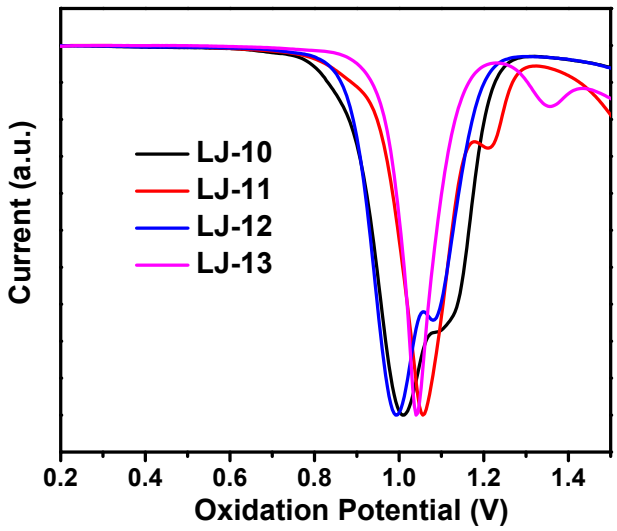

Fig. S6 Differential pulse voltammetry of dyes **LJ-10**, **LJ-11**, **LJ-12** and **LJ-13**.

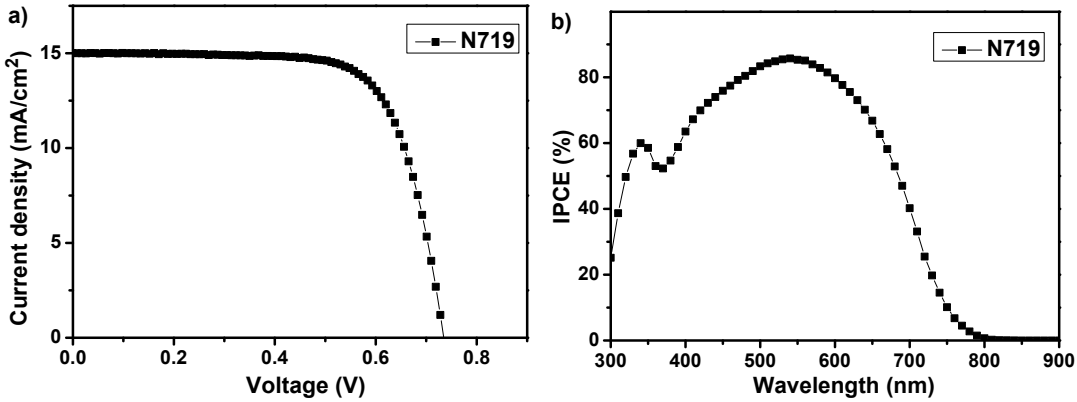

Fig. S7 *J-V* curve (a) and IPCE (b) of DSSC based on dye **N719**.

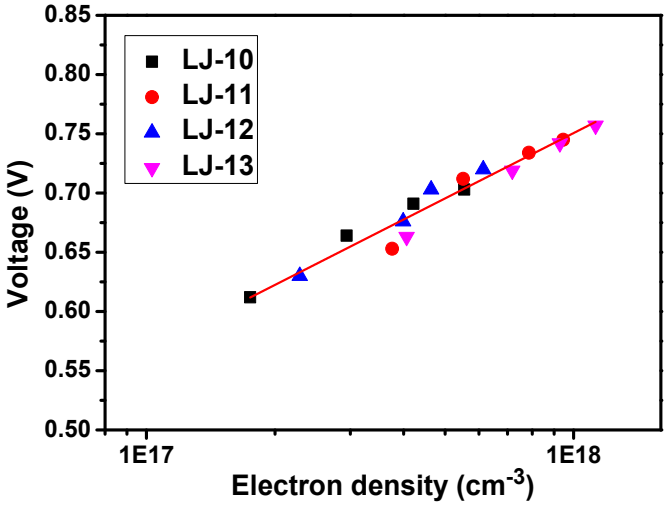

Fig. S8 V_{OC} as a function of extracted electron density for DSSCs based on dyes **LJ-10**, **LJ-11**, **LJ-12** and **LJ-13**, respectively.

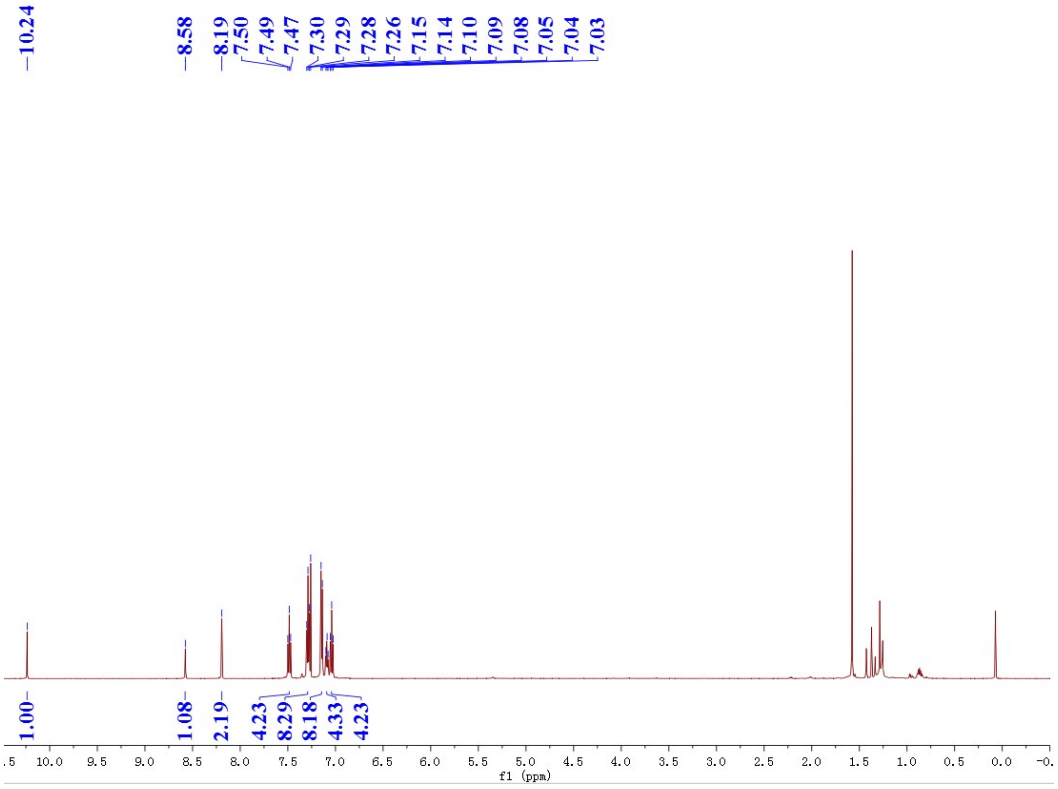

Fig. S9 ^{1}H NMR spectra of compound **3a**.

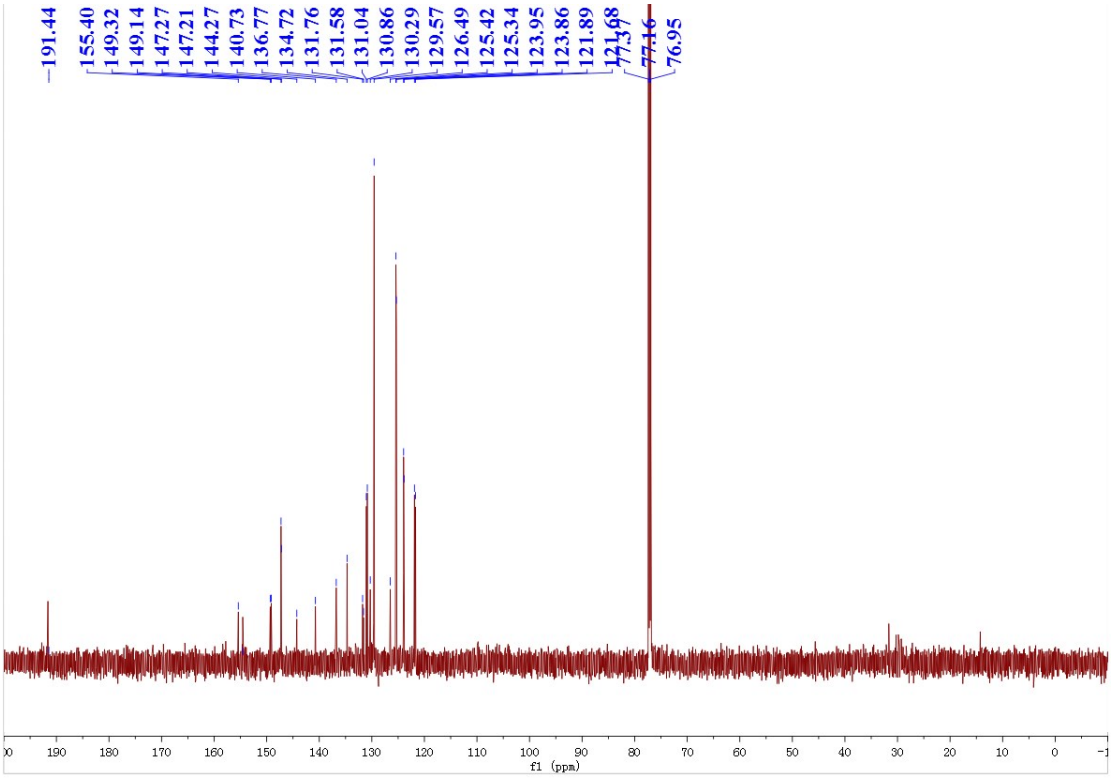

Fig. S10 ^{13}C NMR spectra of compound **3a**.

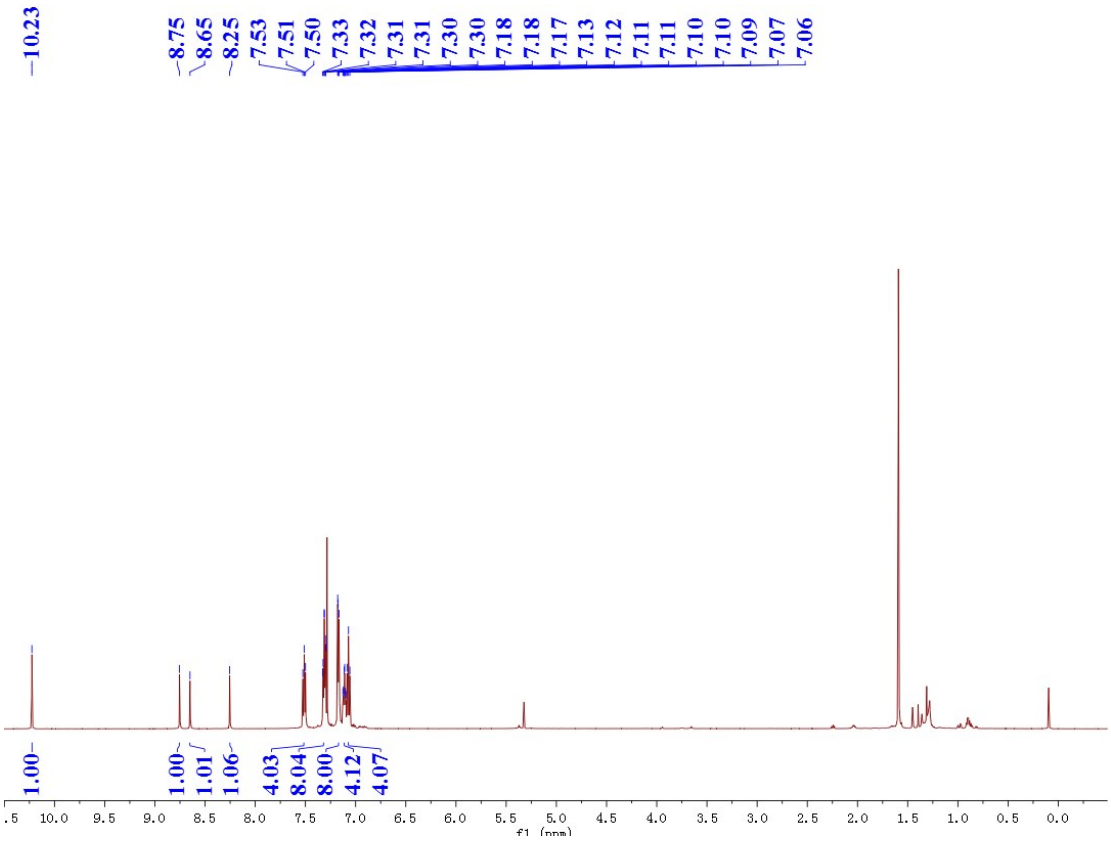

Fig. S11 ^{1}H NMR spectra of compound **3b**.

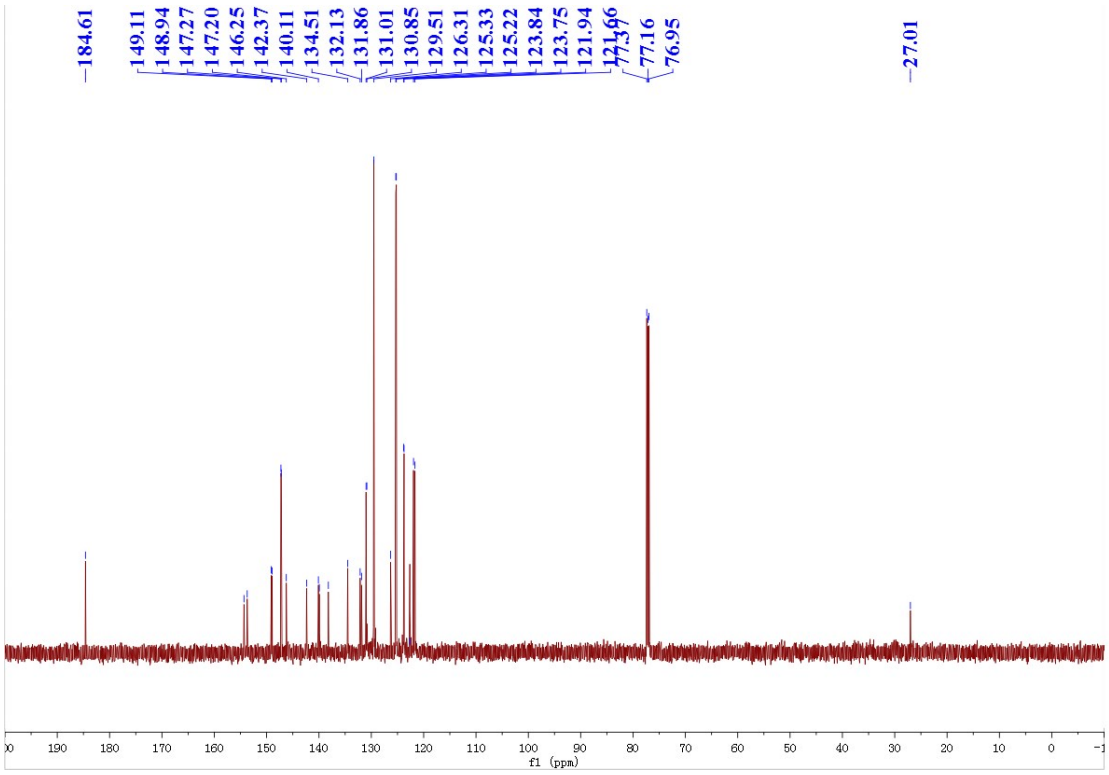

Fig. S12 ^{13}C NMR spectra of compound **3b**.

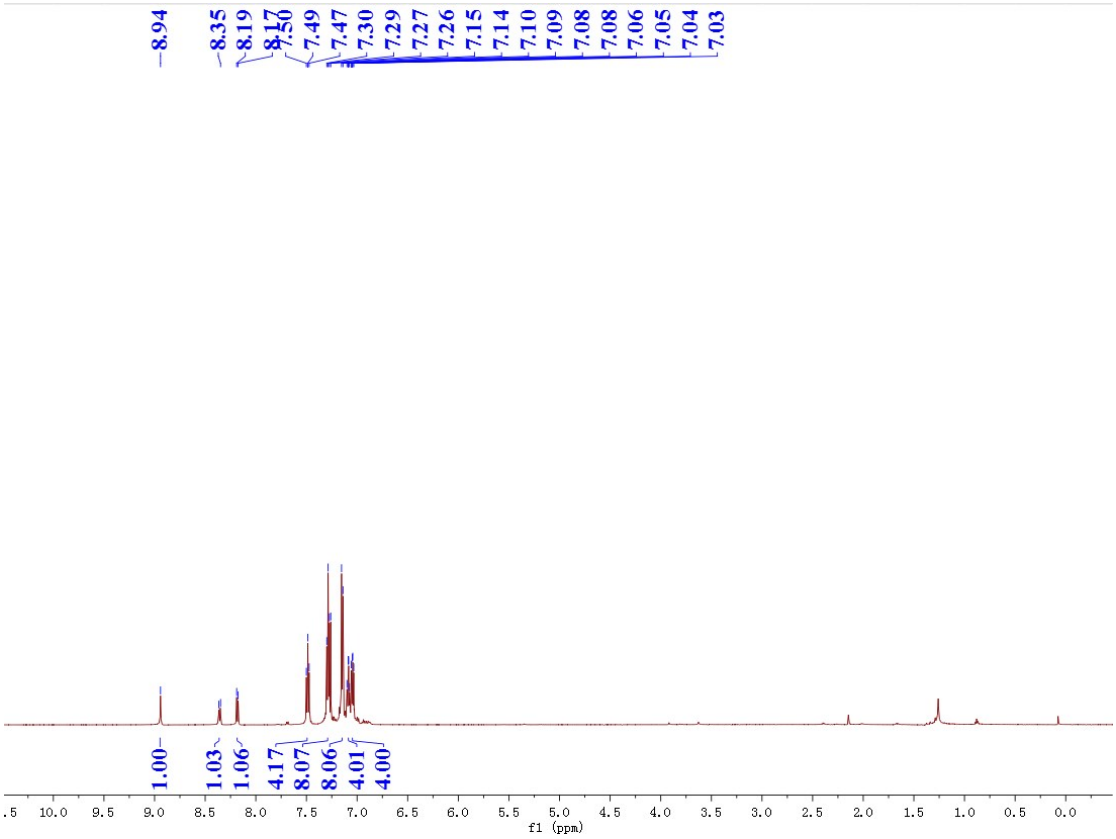

Fig. S13 ^{1}H NMR spectra of dye **LJ-10**.

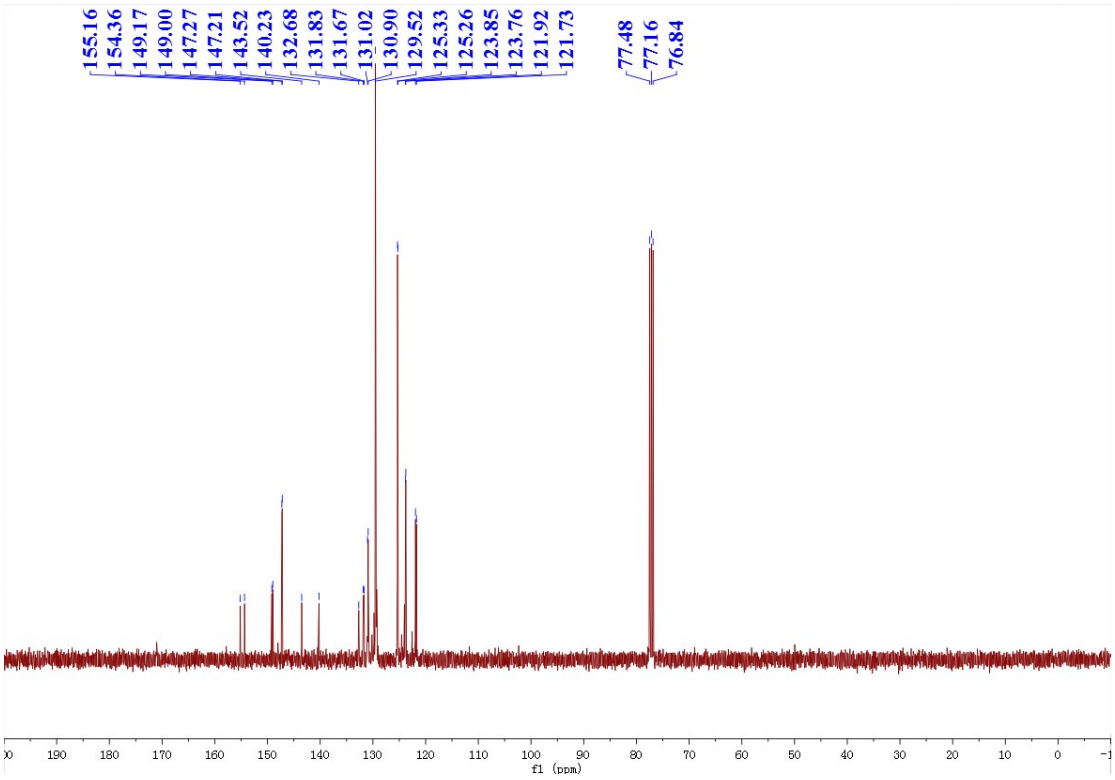

Fig. S14 ^{13}C NMR spectra of dye **LJ-10**.

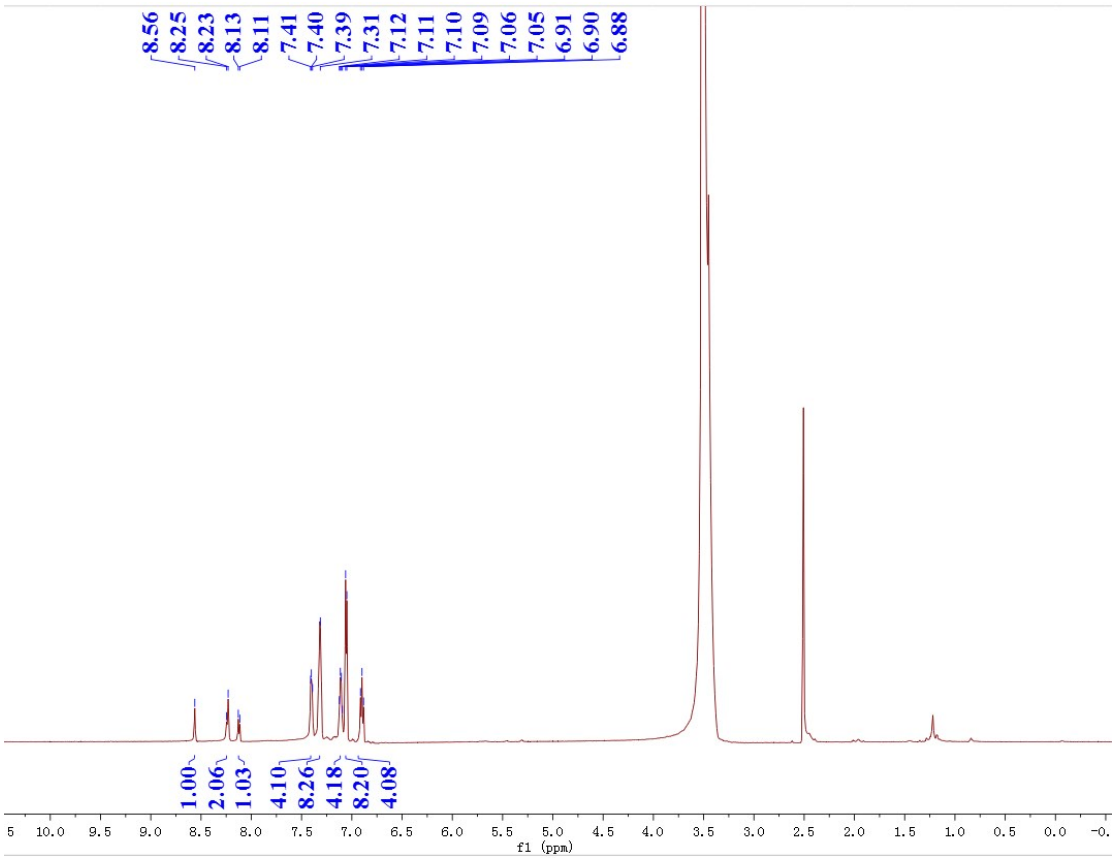

Fig. S15 ^{1}H NMR spectra of dye **LJ-11**.

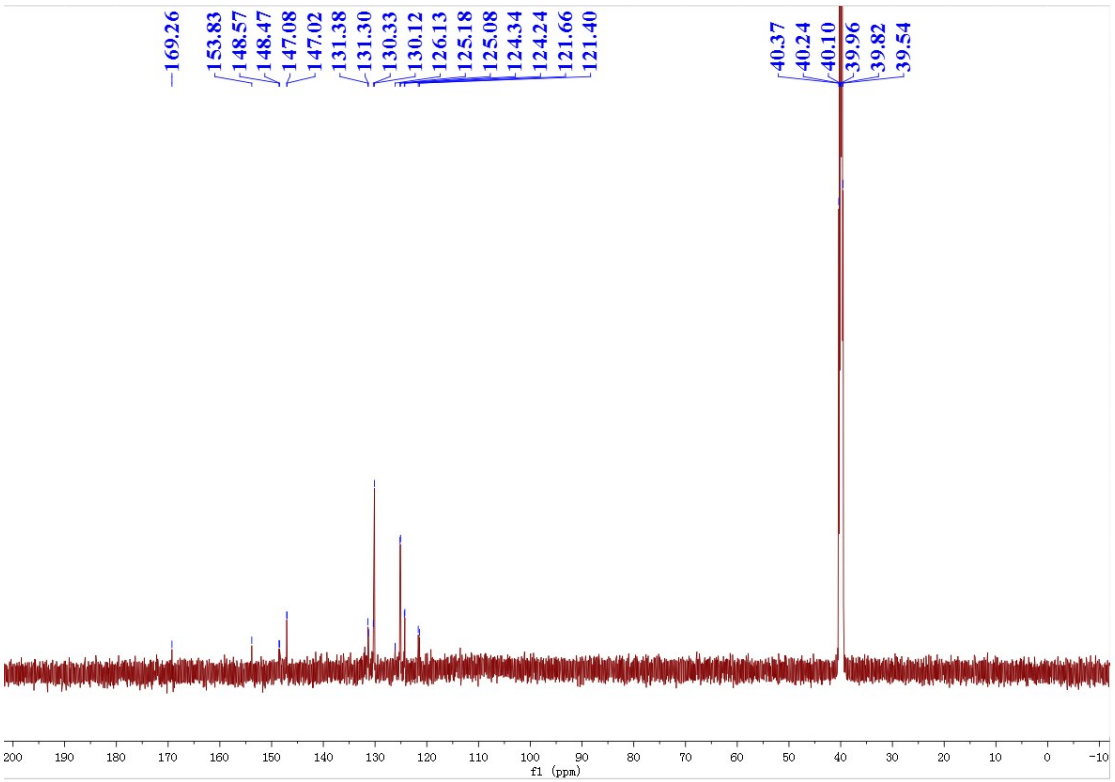

Fig. S16 ^{13}C NMR spectra of dye **LJ-11**.

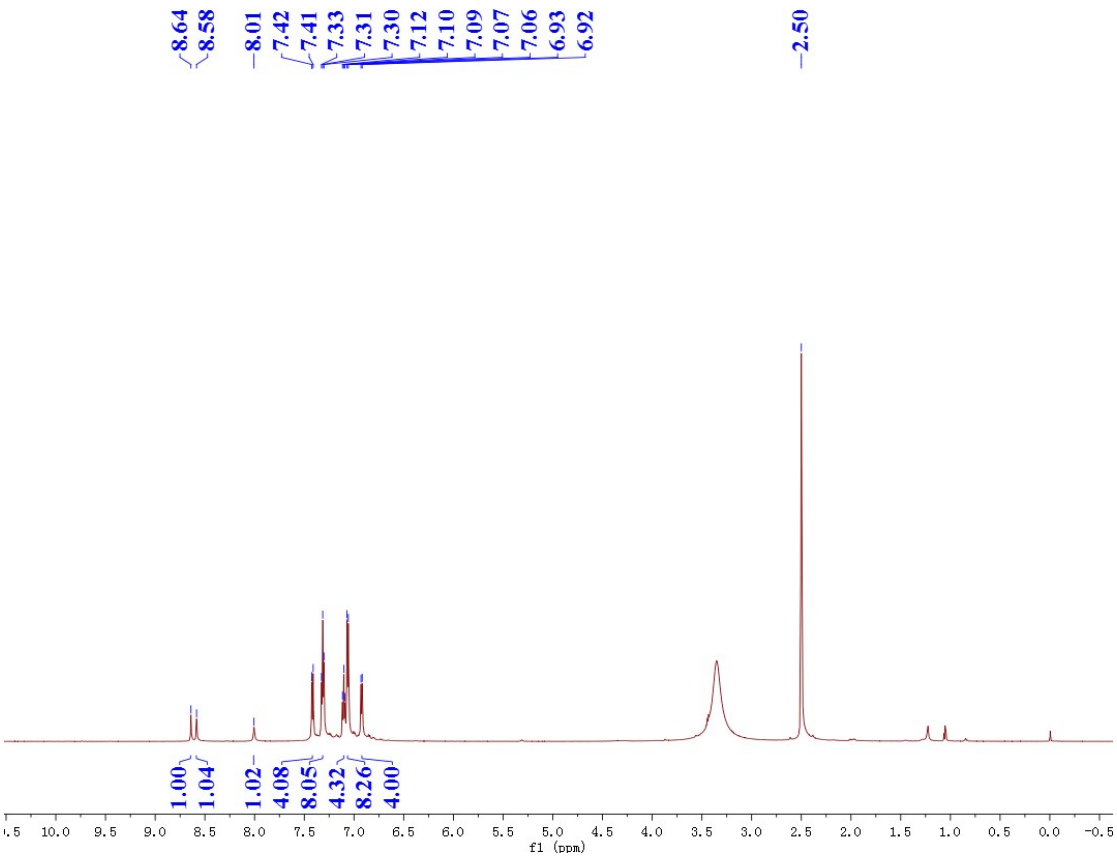

Fig. S17 ^{1}H NMR spectra of dye **LJ-12**.

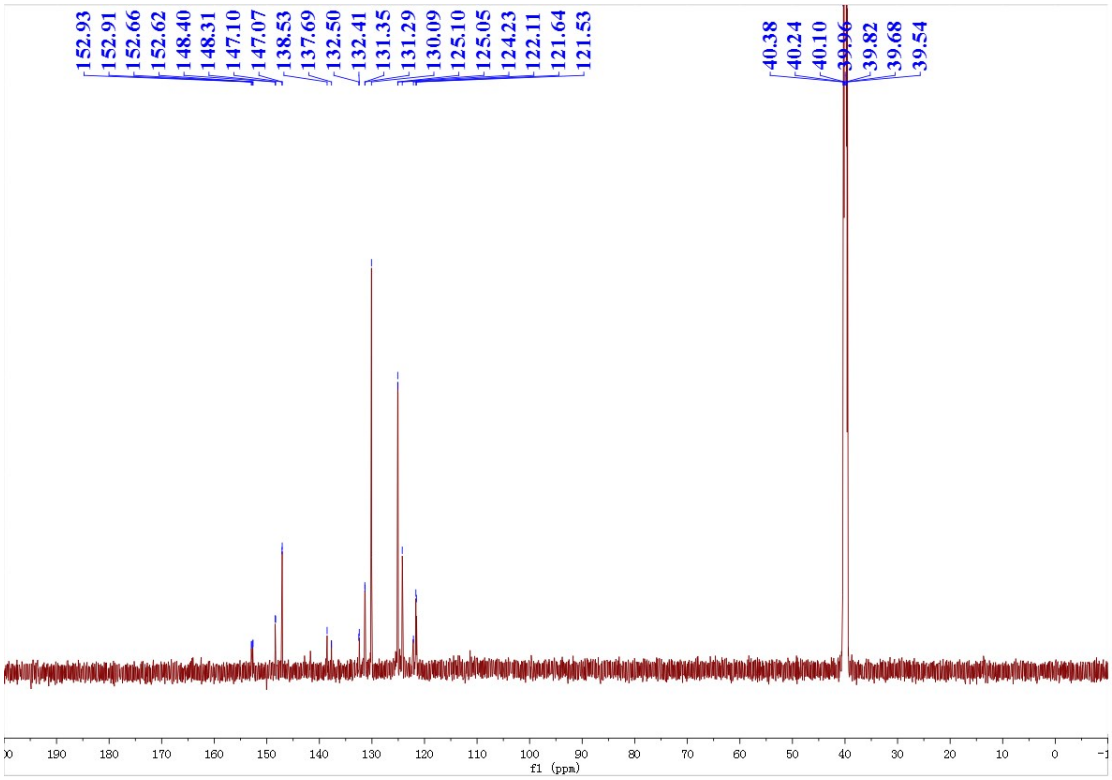

Fig. S18 ^{13}C NMR spectra of dye **LJ-12**.

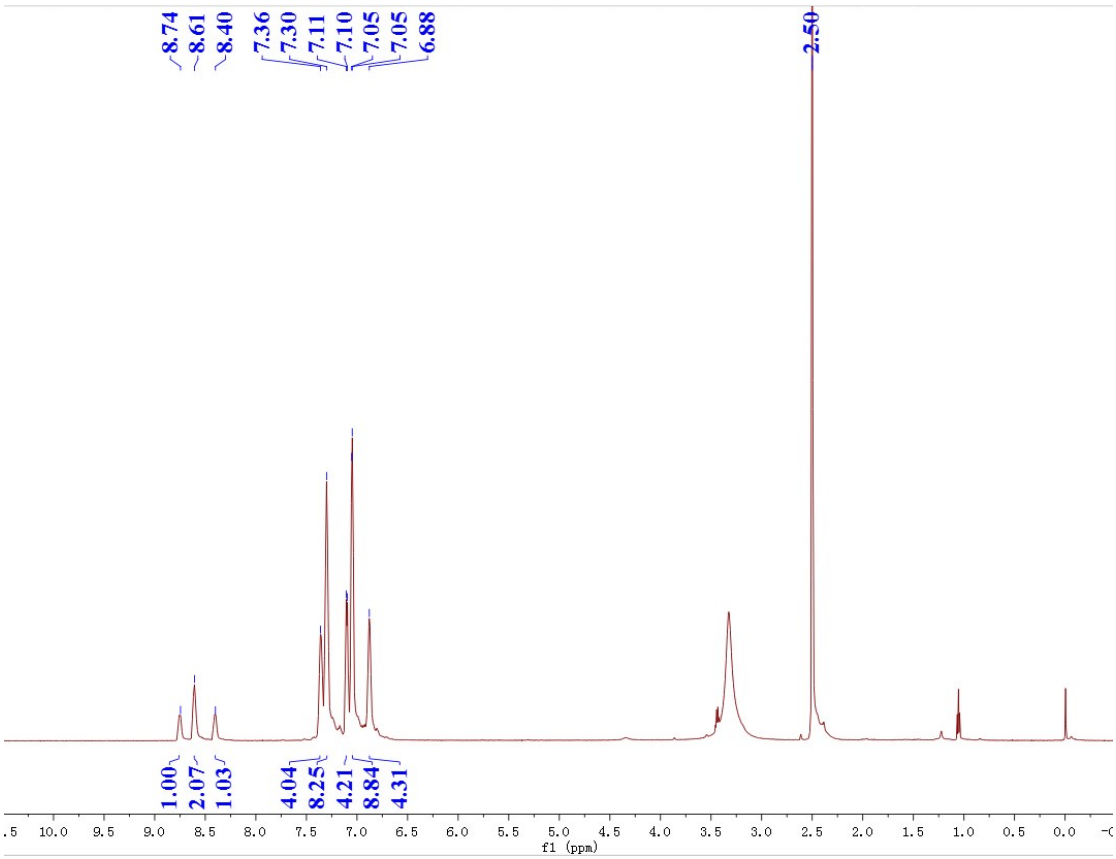

Fig. S19 ^{1}H NMR spectra of dye **LJ-13**.

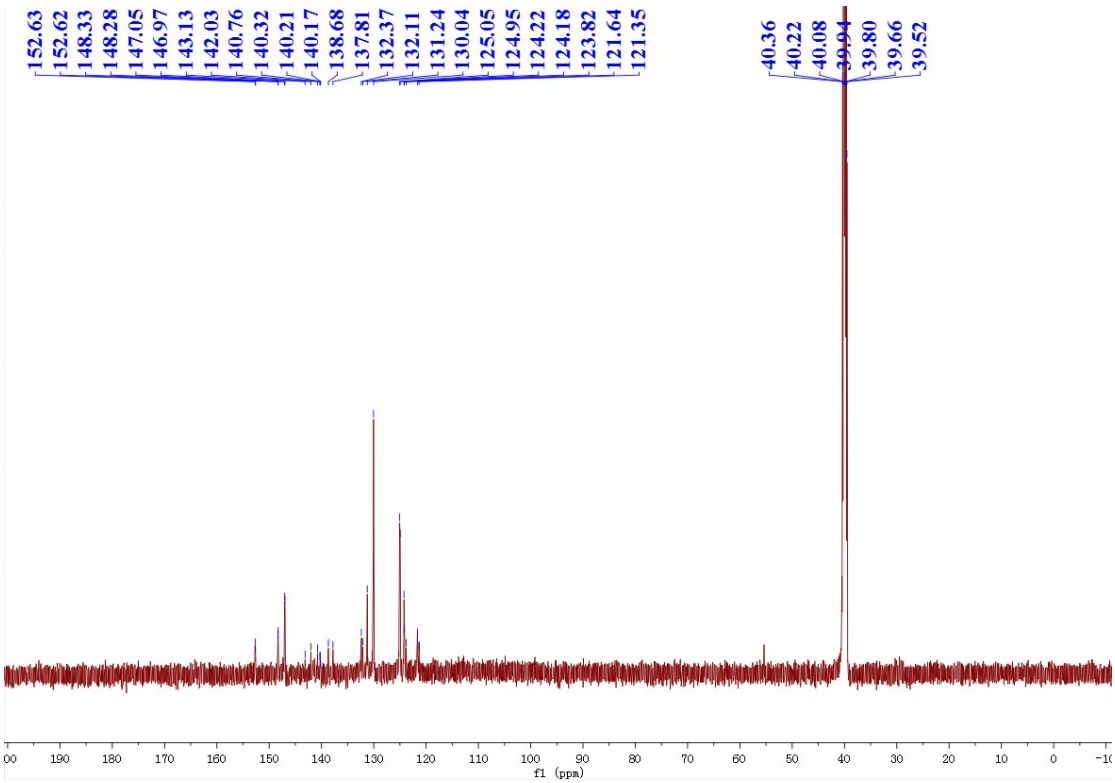

Fig. S20 ^{13}C NMR spectra of dye **LJ-13**.

Reference

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision A.02; Gaussian, Inc.: Wallingford, CT, **2009**.