

Synergy Effect of Electronic Characteristics and Spatial Configurations of Electron Donors on Photovoltaic Performance of Organic Dyes

Jinfeng Wang,^{a,b} Kai Chang,^a Siwei Liu,^a Qiuyan Liao,^a Sheng Li,^c Hongwei Han,^c Qianqian Li,^{*a} Zhen Li,^{*ab}

1. Additional graph

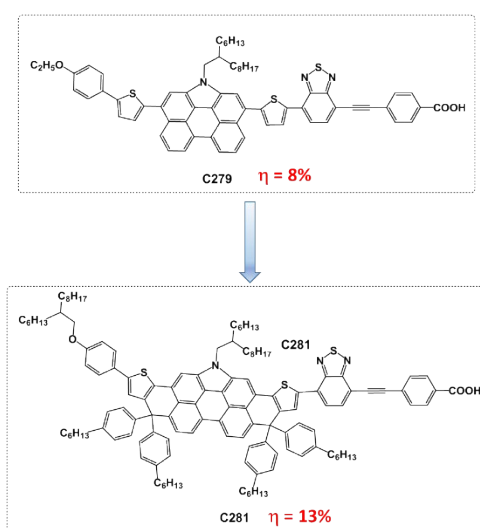


Figure S1 The structure of **C279** and **C281**

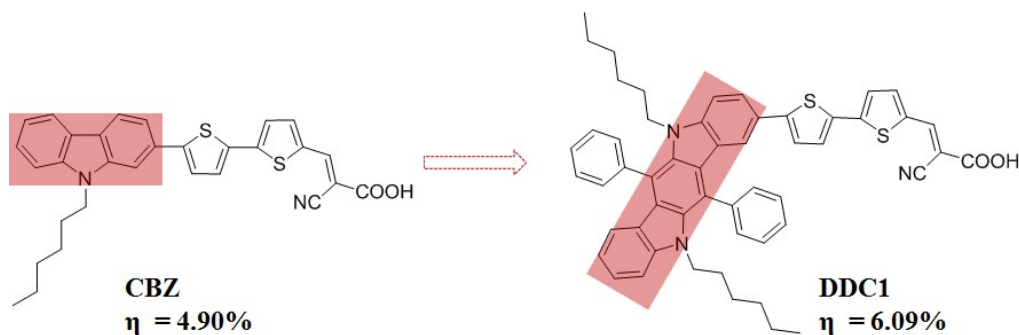


Figure S2 The structure of **CBZ** and **DDC1**

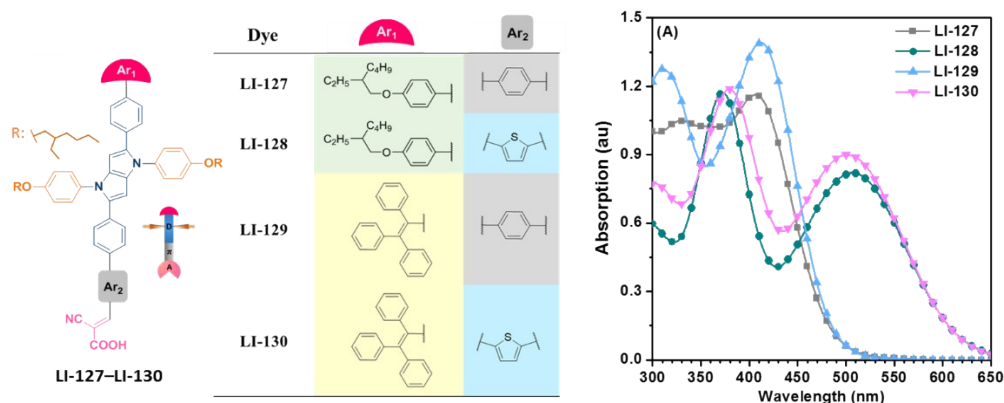


Figure S3 The structures of dye **LI-127-LI-130** based on **TAPP** unit and the corresponded UV-vis absorption spectra

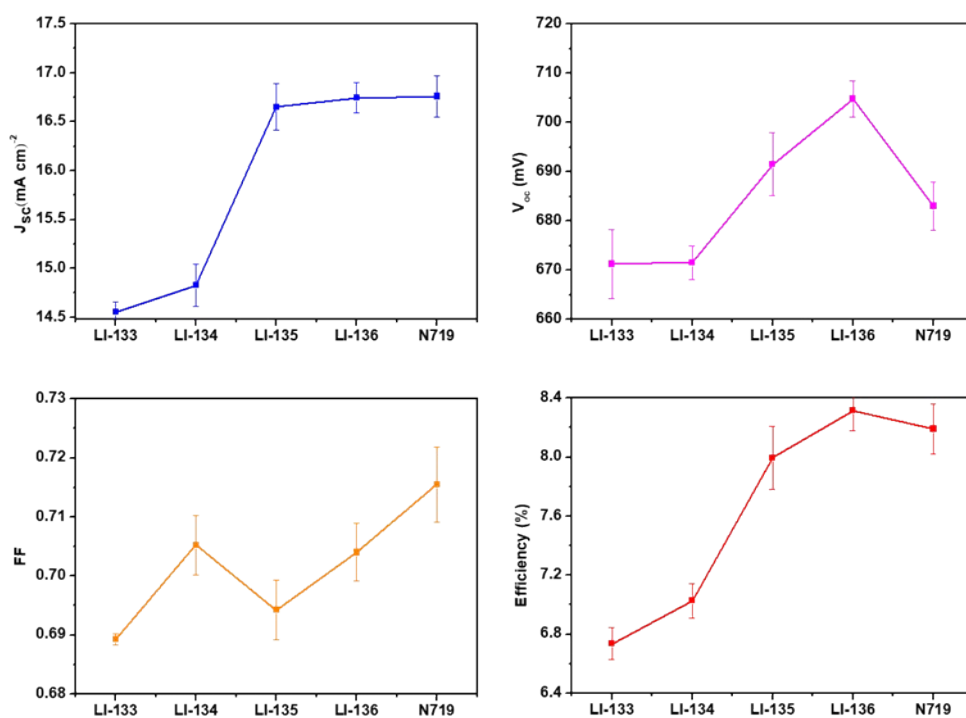


Figure S4 The photovoltaic parameters of DSCs based on dye LI-133-LI-136 with error bars

Table S1 Photovoltaic parameters of DSCs co-sensitized with CDCA

Dye	CDCA [mM]	J_{sc} [mA·cm ⁻²]	V_{oc} [mV]	FF	η [%]	Dye loading [mol cm ⁻² μm ⁻¹]
LI-133	0	14.56	672	0.689	6.73	1.25×10 ⁻⁸
	1	13.58	692	0.685	6.44	1.17×10 ⁻⁸
	5	12.60	692	0.694	6.05	8.96×10 ⁻⁹
LI-134	0	14.88	673	0.702	7.03	1.23×10 ⁻⁸
	1	14.92	730	0.653	7.11	1.13×10 ⁻⁸
	5	14.00	716	0.660	6.62	7.84×10 ⁻⁹

LI-135	0	16.66	697	0.697	8.09	1.78×10^{-8}
	1	14.60	720	0.681	7.16	1.56×10^{-8}
	5	14.20	718	0.680	6.93	1.22×10^{-8}
LI-136	0	16.75	705	0.706	8.34	1.18×10^{-8}
	1	16.94	718	0.636	7.73	1.05×10^{-8}
	5	15.25	718	0.655	7.17	8.45×10^{-9}

2. Experimental

2.1. Materials

Tetrahydrofuran (THF) was dried over and distilled from K-Na alloy under an atmosphere of dry argon. All solvents were analytical grade and were used without further purification. All reagents used in this work were purchased. ^1H and ^{13}C spectra were obtained with a Bruker 400 MHz spectrometer using tetramethylsilane (TMS, $\delta = 0$ ppm) as internal standard. Elemental analyses were performed by a 73 CARLOERBA-1106 micro-elemental analyzer. ESI-MS spectra were recorded with a Finnigan LCQ advantage mass spectrometer. UV-visible spectra were conducted on a Shimadzu UV-2550 spectrometer. Cyclic voltammograms were obtained at a CHI 660 voltammetric analyzer with a scanning rate of 100 mV/s in nitrogen-purged dichloromethane. In the test system, tetrabutylammonium hexafluorophosphate (TBAPF_6) is used as the supporting electrolyte, Pt disk, Pt plate, and Ag/AgCl electrode are acted as working electrode, counter electrode, and reference electrode, respectively. The ferrocene/ferrocenium redox couple was used for internal reference.

2.2. DSC devices fabrication and measurement

The devices were fabricated according to our previous report. Firstly, fluorine doped tin oxide (FTO) conducting glasses (3.2 mm thickness, 7-8 ohms/sq) were cleaned with detergent, water, ethanol and acetone respectively, and irradiated at atmosphere of O_3 for 18 min, then immersed in TiCl_4 solution (40 mM) for 30 min at 70 °C. After being cooled to room temperature, they were washed with deionized water and ethanol for three times, and then dried. The TiO_2 films (16 μm thickness) were prepared by the screen printing technique and heated under airflow at 325 °C for 5 min, 375 °C for 5 min, 450 °C for 15 min and 500 °C for 1 h gradually, which consist of 12 μm layer of mesoporous

TiO₂ (18 NR-T, 18-20 nm, Dyesol) and 4 μm scatter layer (18 NR-AO, 20-450 nm, Dyesol). After the films cool to room temperature, they were immersed in TiCl₄ solution (40 mM) for 30 min at 70 °C once again, then washed clearly and annealed at 500 °C for 30 min. When the temperature of corresponding TiO₂ film cool to 80 °C, they were immersed in dye bathes (0.3 mM) in the mixture solvents (CH₃OH/CH₂Cl₂ = 1/1) for 18 h in dark condition. Then, the sensitized electrodes were washed with corresponding solvents and dried in air. Counter electrodes were prepared by thermal deposition: FTO glass (2.2 mm thickness, 7-8 ohms/sq) with two small hole were cleaned as counter electrode, 10 μL of H₂PtCl₆ (10 mM) solution in isopropyl alcohol were dispersed on FTO glass and heated at 400 °C for 30 min. After then, dye sensitized photoanodes and Pt-counter electrodes were assembled into a sandwich type cell and sealed with a hot-melt gasket (25 μm thickness, from the ionomer Surlyn 1702 (DuPont)). The electrolyte was injected into cells by the two small holes in after assembled. Lastly, the holes were sealed with a Surlyn sheet (50 μm thickness) and a thin ITO glass covered by heating.

Photovoltaic measurement were conducted under AM 1.5 solar simulator (Model 94023A equipped with a 450 W xenon arc lamp, Newport Co). It was calibrated with a normal silicon solar cells before measurement. The *J-V* curves is obtained by Keithley model 2400 digital source meter when applying an external bias to the cell. Incident photon-current conversion efficiency (IPCE) was recorded on a DC Power Meter (Model 2931-C equipped with a 300 W xenon arc lamp, Newport Co.) under irradiation with a motorized monochromator (Oriel). Some electrochemical properties were obtained by Modulab XM PhotoEchem system such as IMVS (intensity modulated photovoltage spectroscopy), CE (charge extraction), EIS (electrochemical impedance spectroscopy). IMVS and CE were measured under a white light emitting diode (LED) array. CE were conducted in dark with different potential biases with a frequency range from 0.1 Hz to 100 kHz.

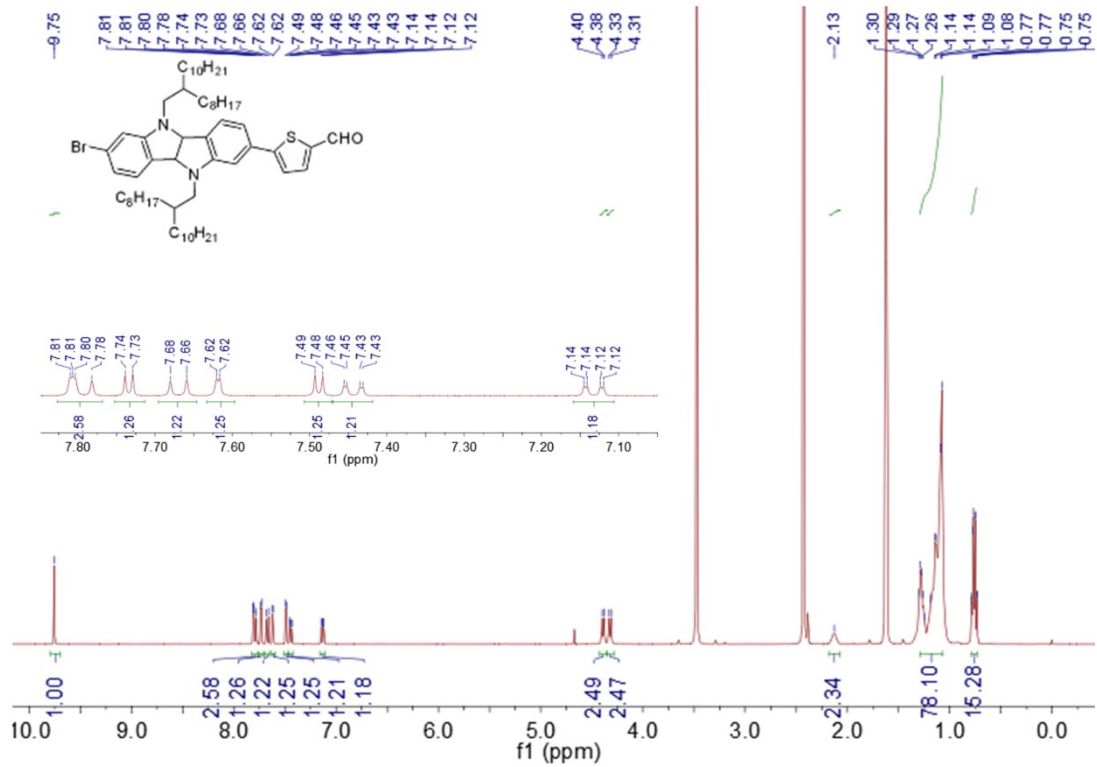


Figure S5. ¹H NMR spectrum of compound **7**

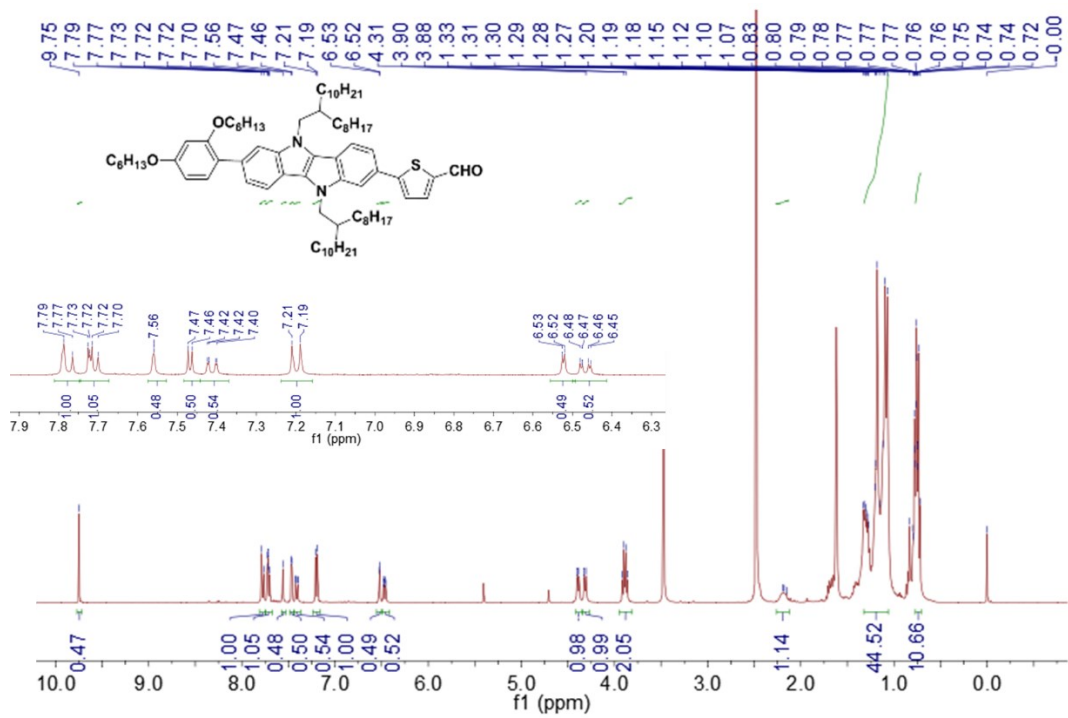


Figure S6. ¹H NMR spectrum of compound **8a**

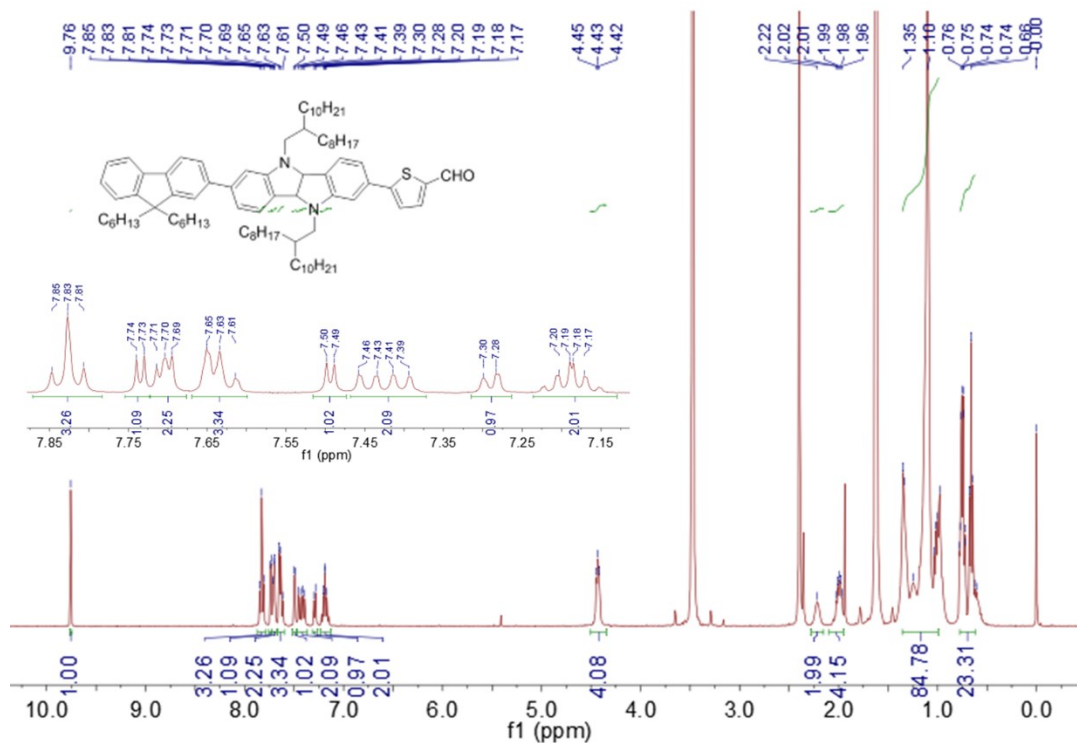


Figure S7. ¹H NMR spectrum of compound **8b**

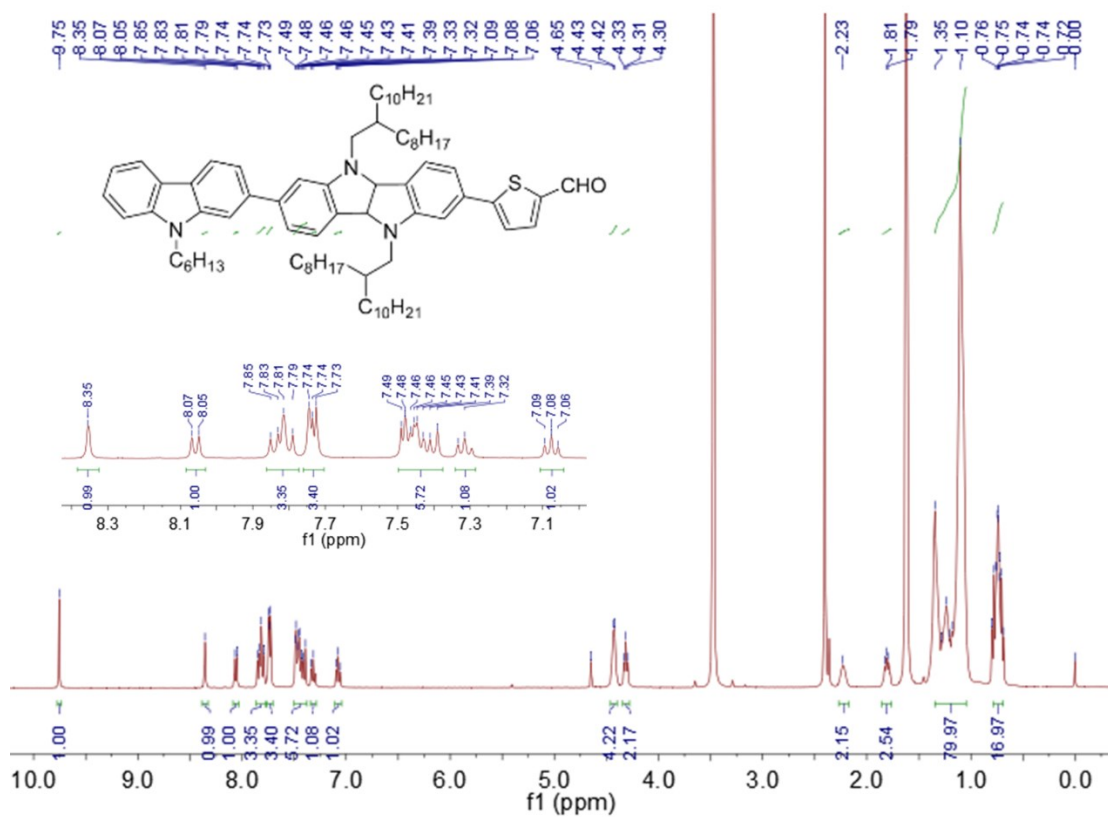


Figure S8. ¹H NMR spectrum of compound **8c**

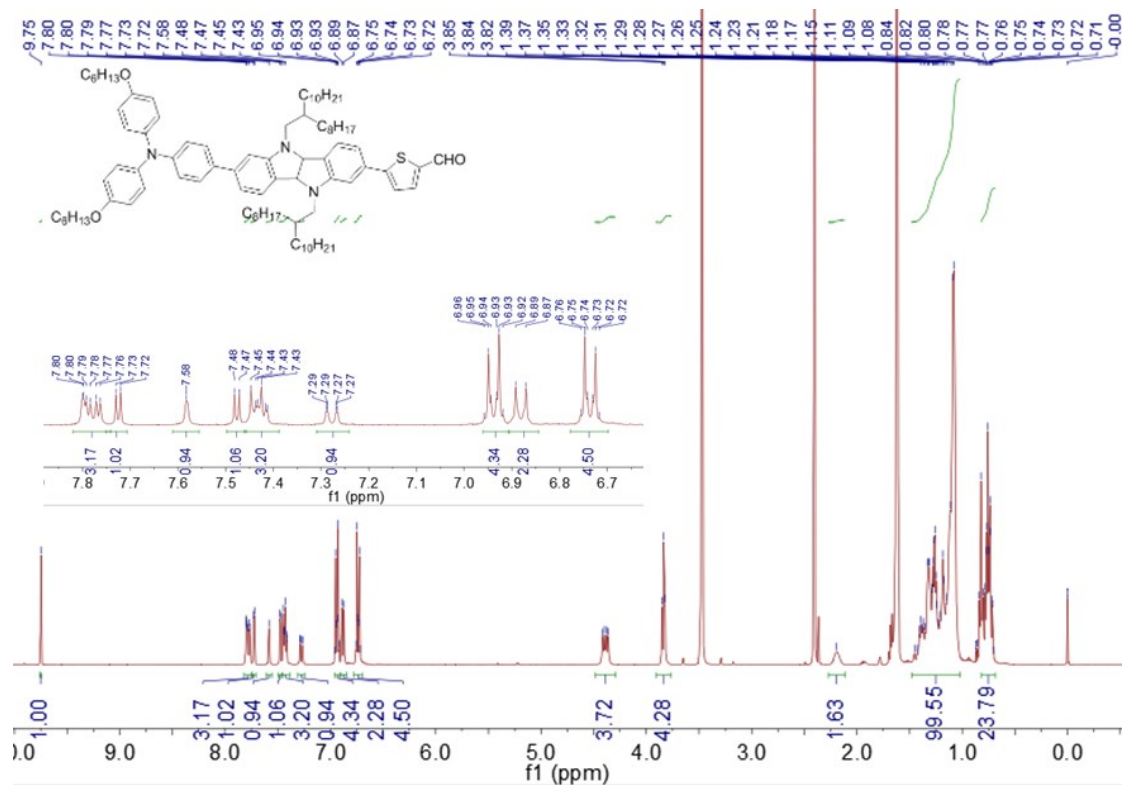


Figure S9. 1H NMR spectrum of compound **8d**

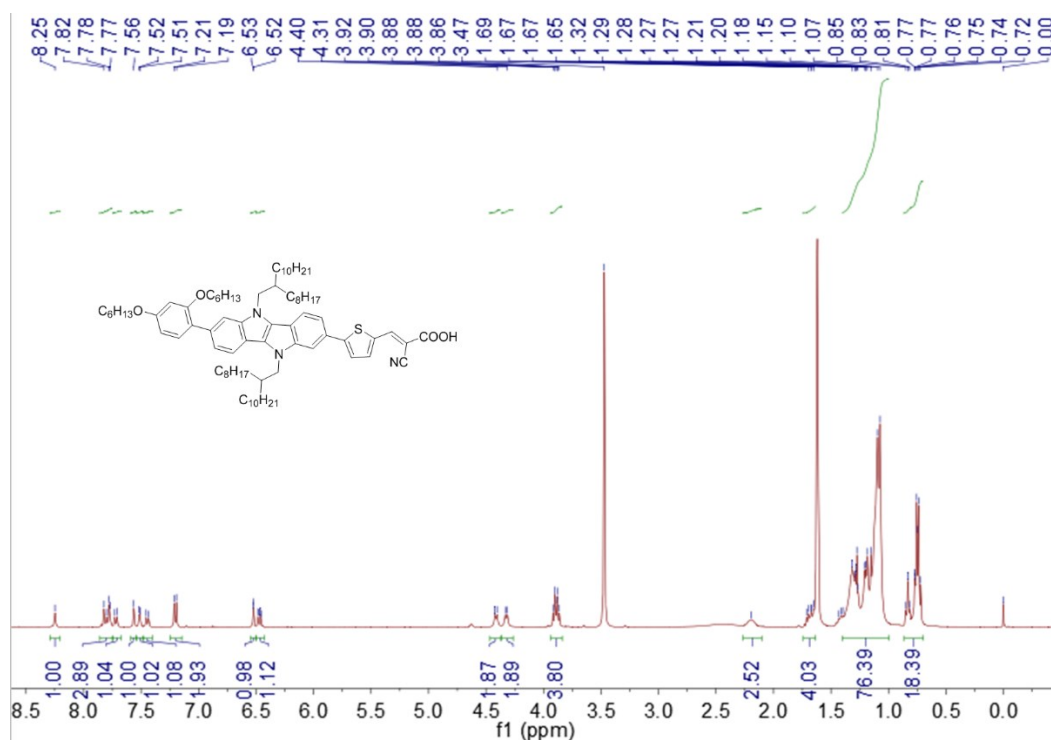


Figure S10. 1H NMR spectrum of compound **LI-133**

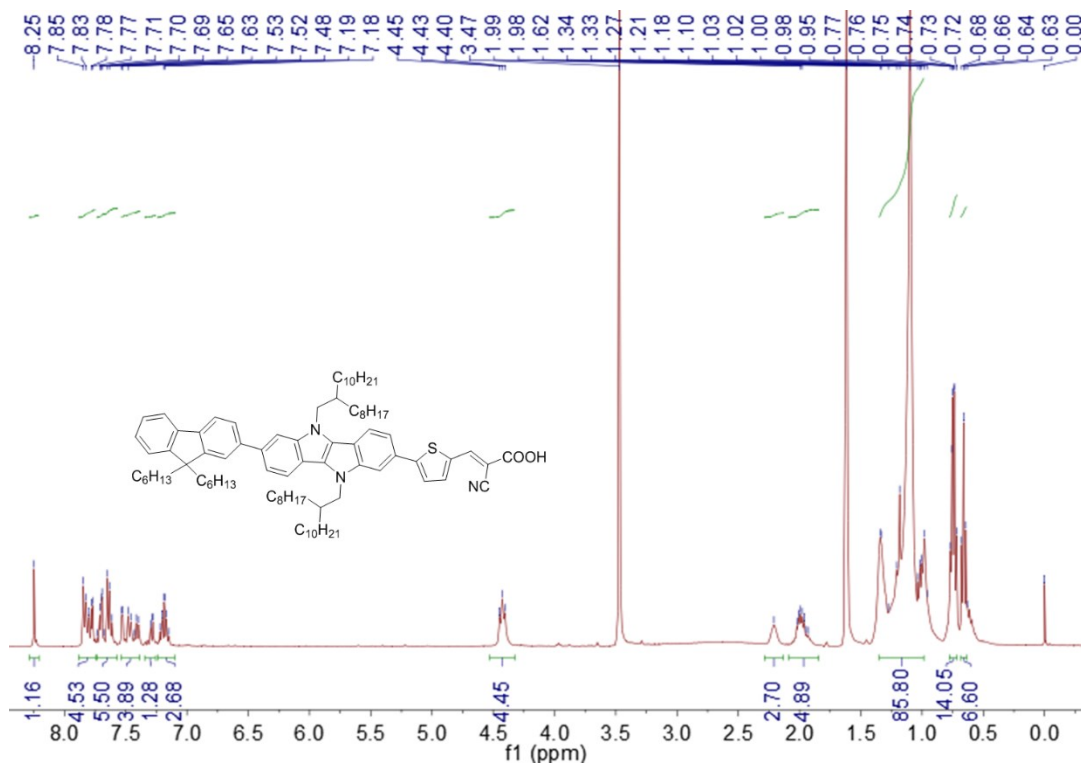


Figure S11. ¹H NMR spectrum of compound **LI-134**

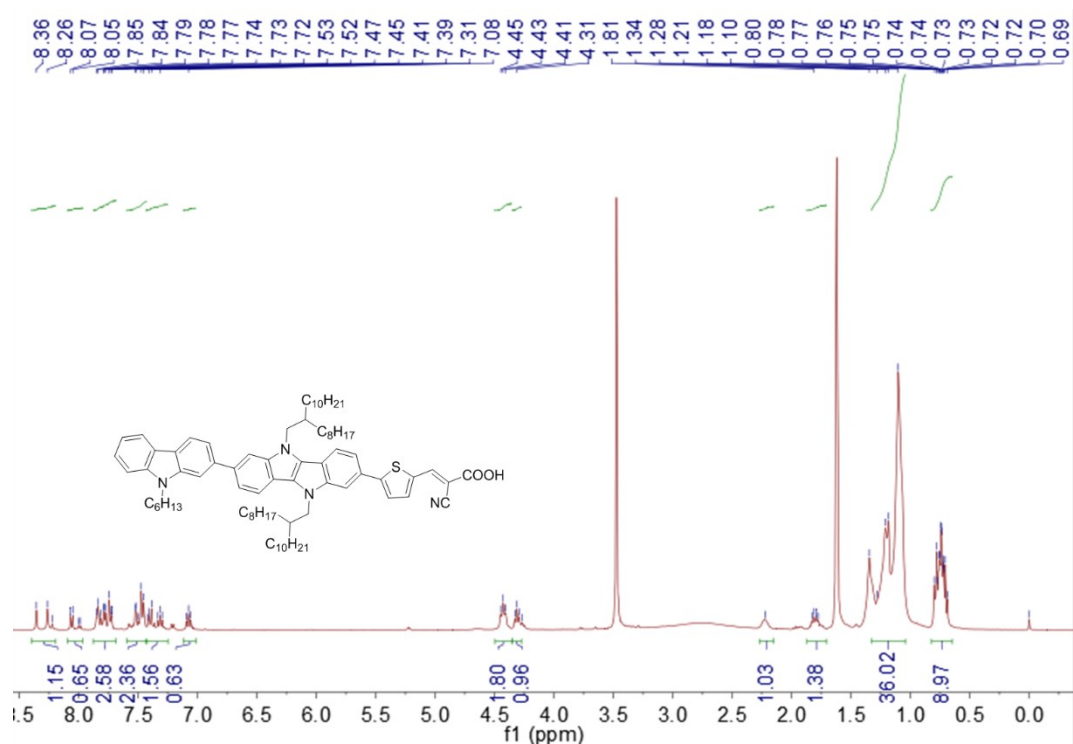


Figure S12. ¹H NMR spectrum of compound **LI-135**

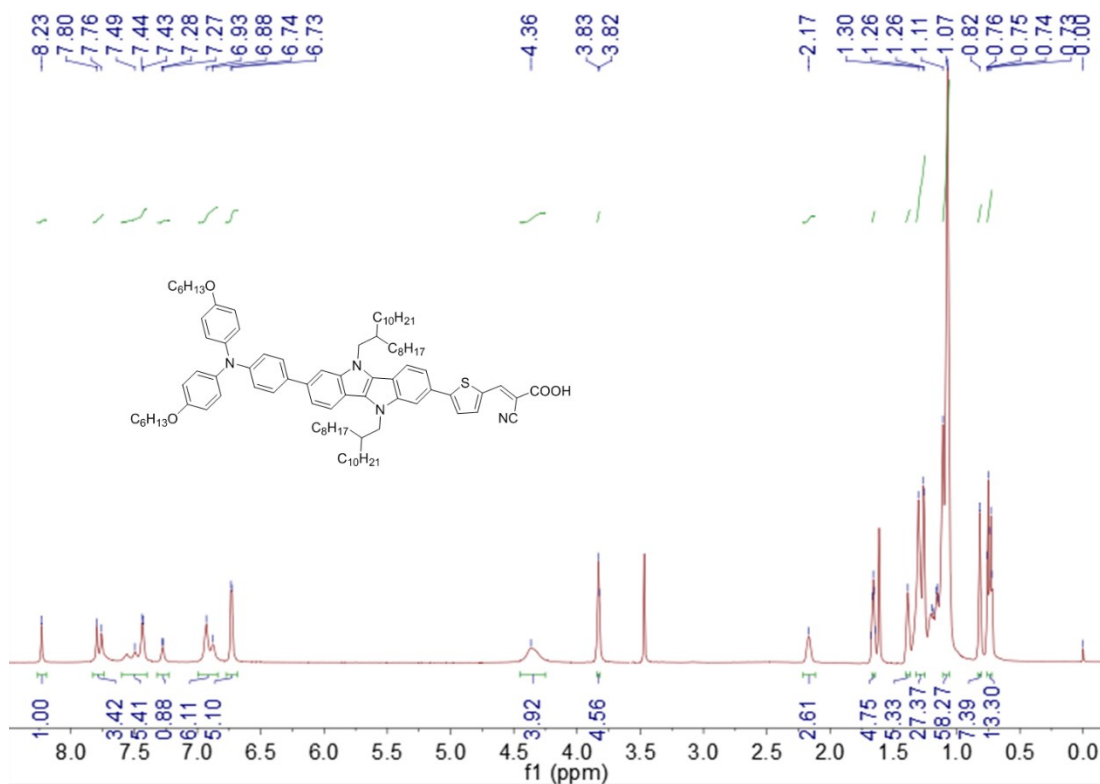


Figure S13. ¹H NMR spectrum of compound LI-136

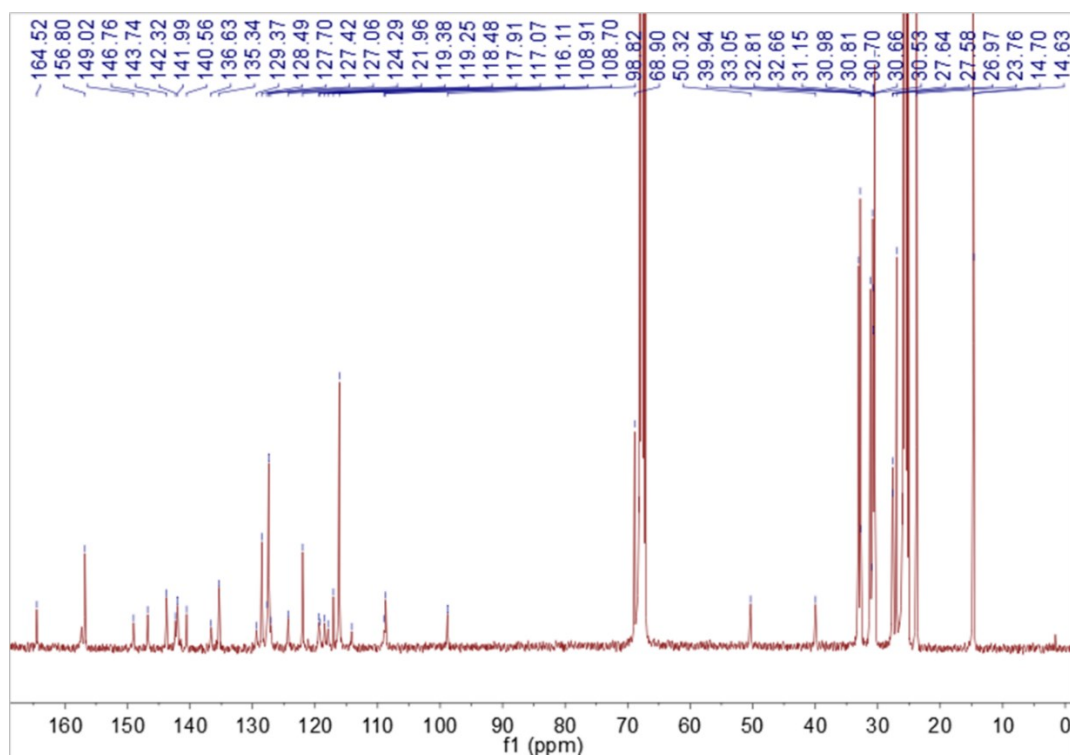


Figure S14. ¹³C NMR spectrum of compound LI-133

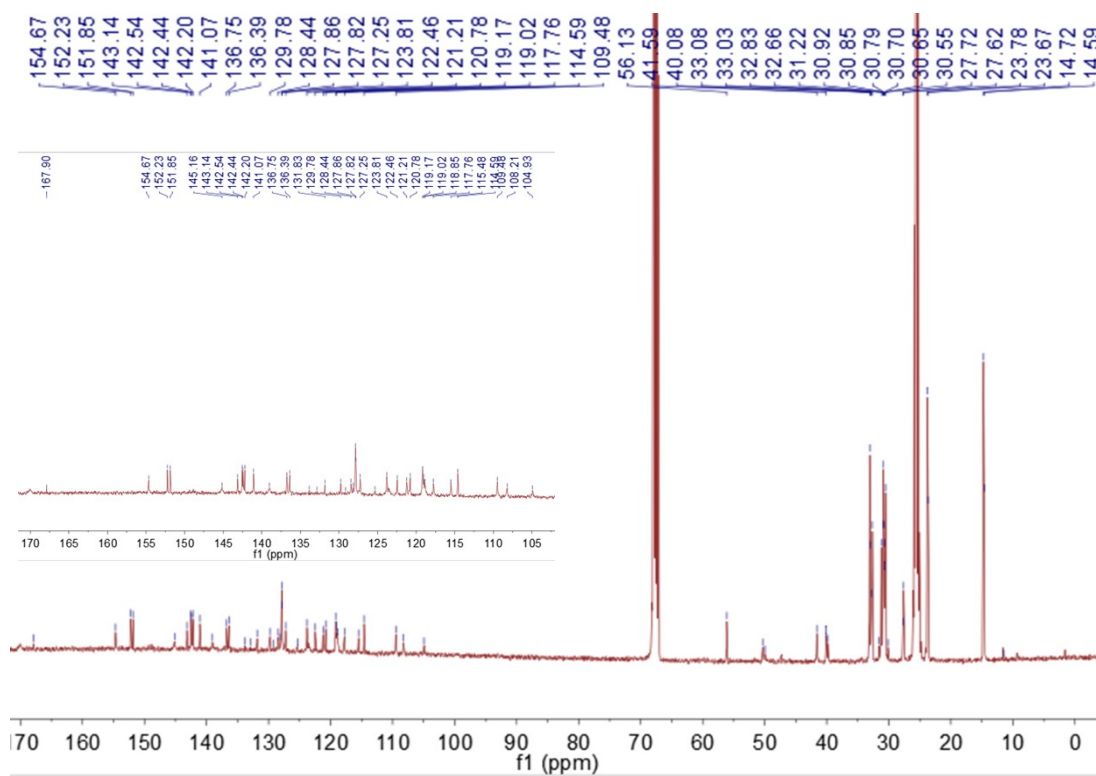


Figure S15. ^{13}C NMR spectrum of compound **LI-134**

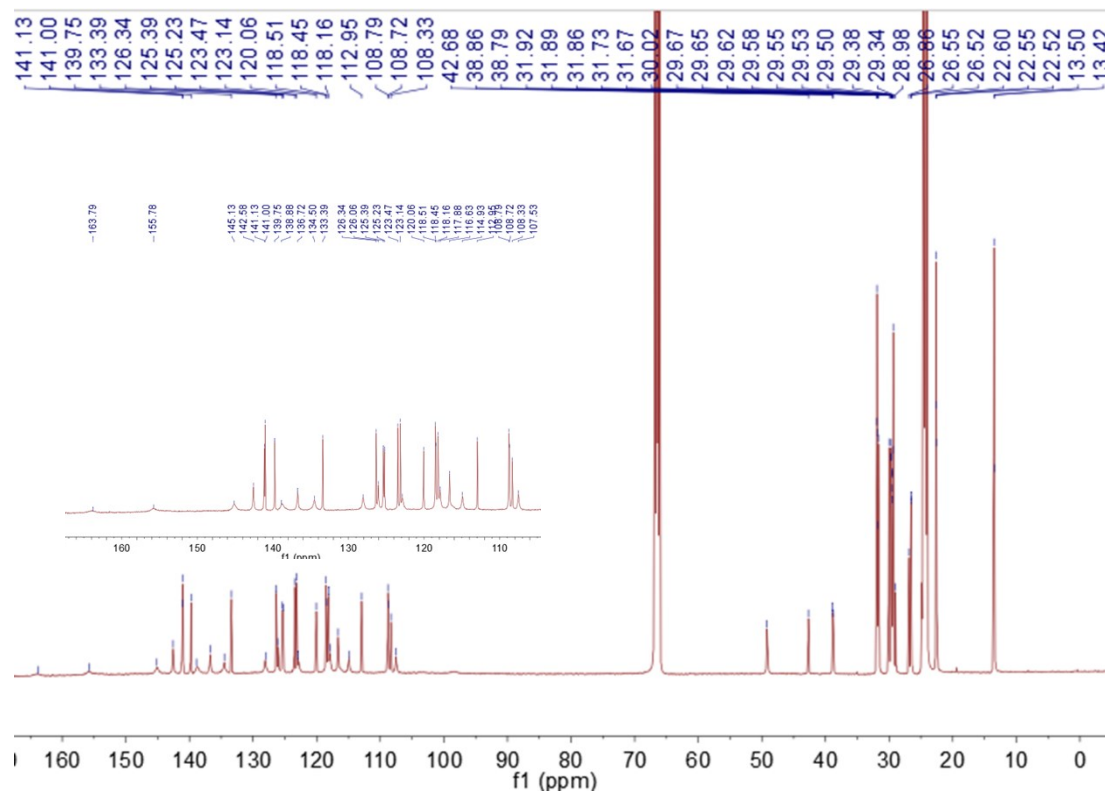


Figure S16. ^{13}C NMR spectrum of compound **LI-135**

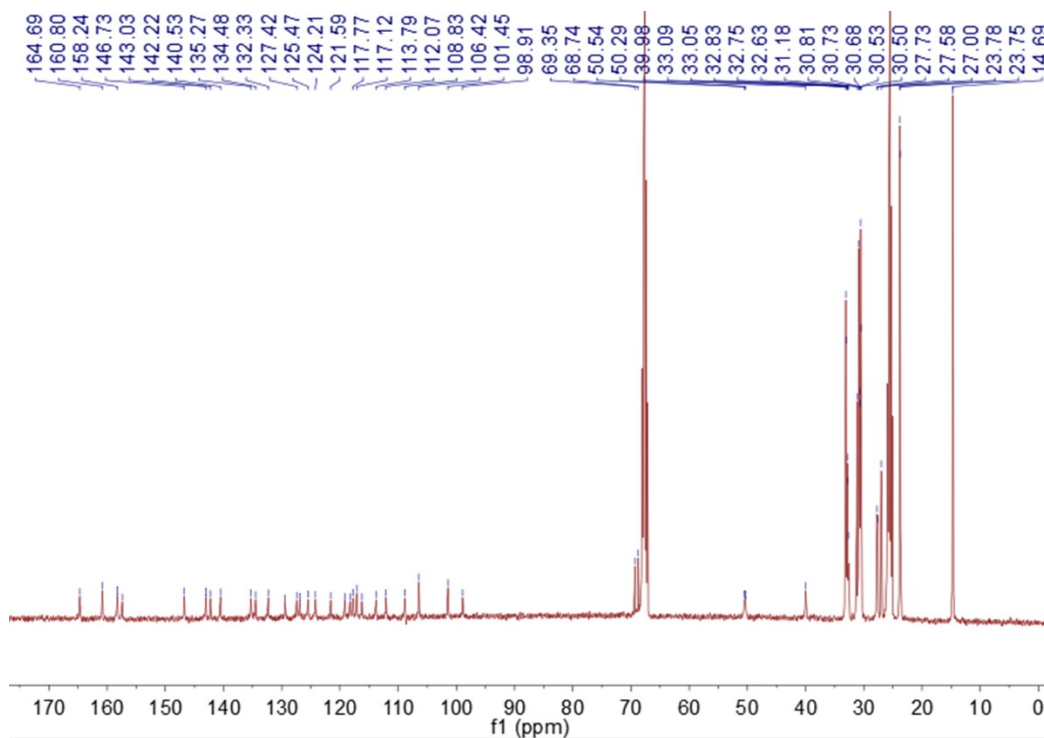


Figure S17. ^{13}C NMR spectrum of compound LI-136

ESI-2018-N007-136 #18-19 RT: 0.55-0.58 AV: 2 NL: 5.96E6
T: + c ESI Full ms [50.00-2000.00]

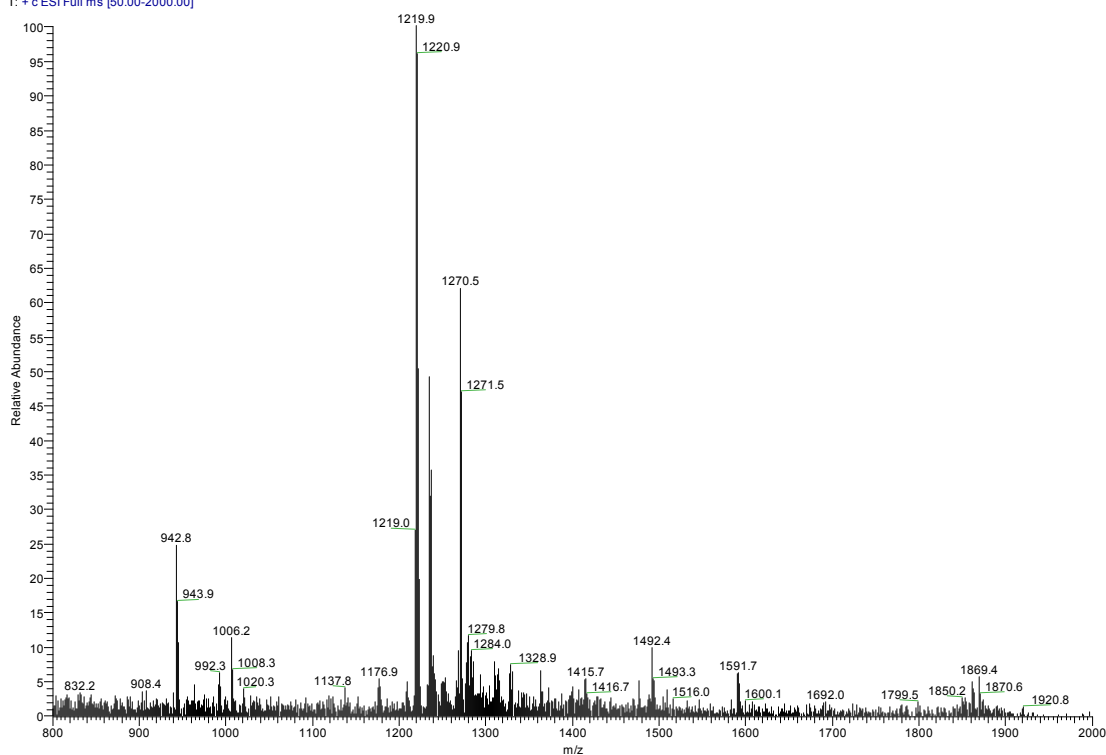


Figure S18. MS spectrum of compound LI-133

ESI-2018-N007-135 #61-67 RT: 1.75-1.92 AV: 7 NL: 1.15E8
T: - c ESI Full ms [50.00-2000.00]

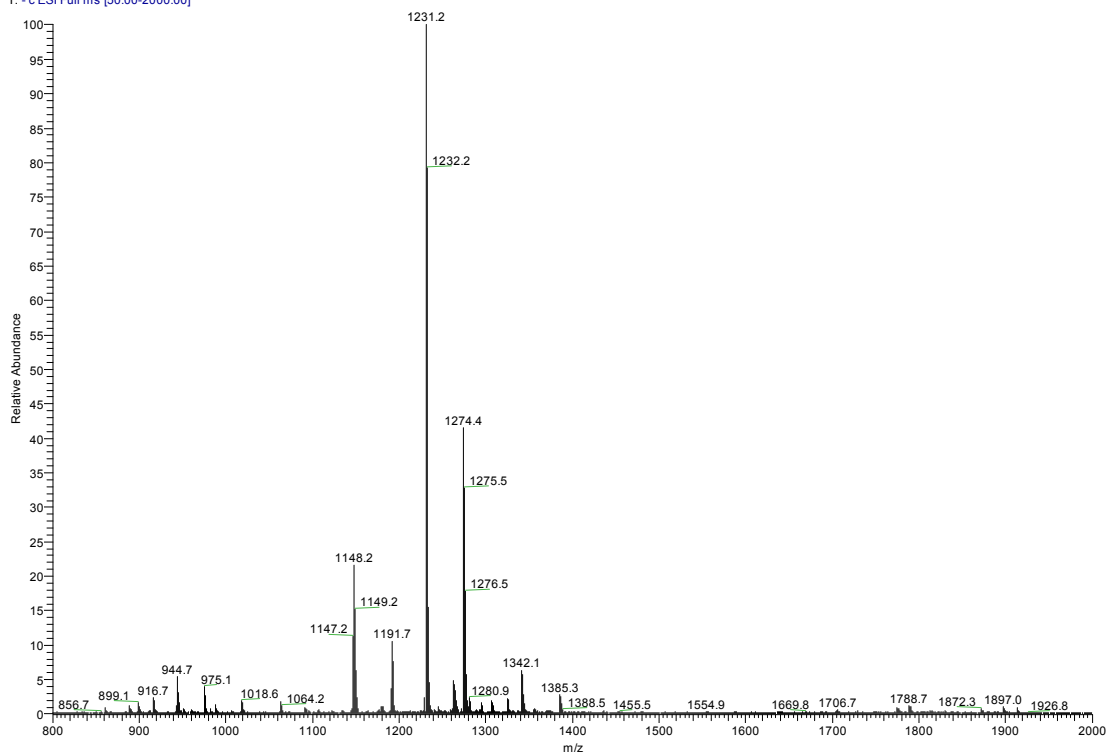


Figure S19. MS spectrum of compound LI-134

ESI-2018-N007-134 #21-24 RT: 0.62-0.71 AV: 4 NL: 9.88E7
T: - c ESI Full ms [50.00-2000.00]

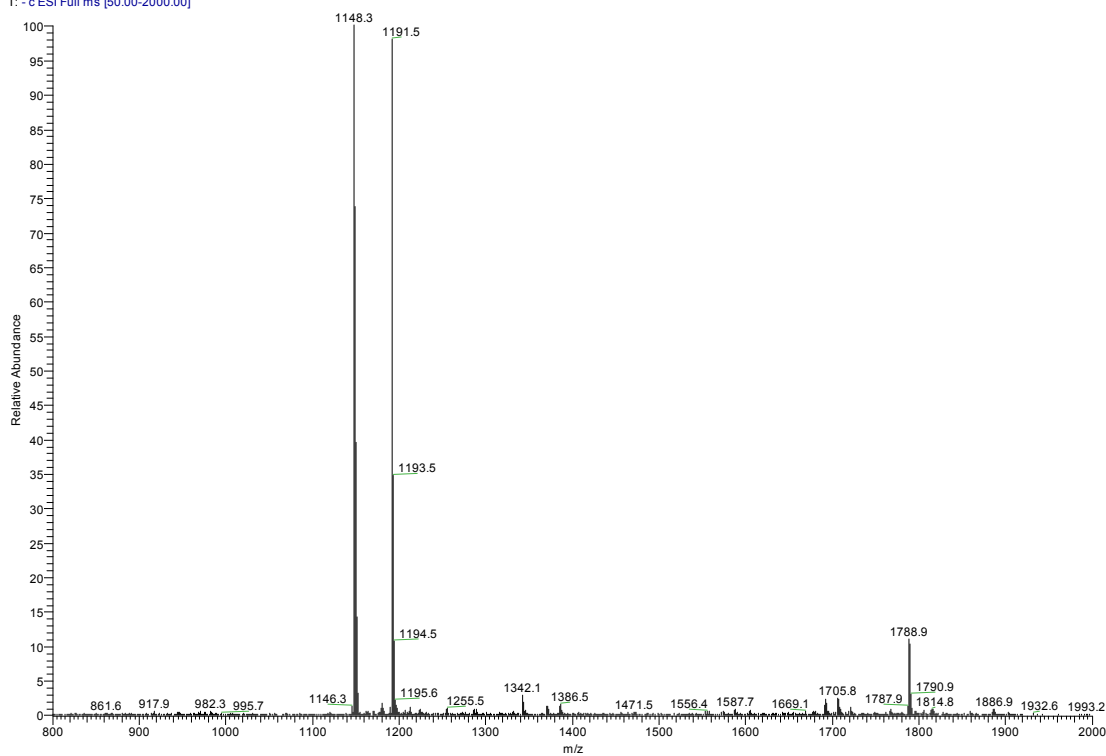


Figure S20. MS spectrum of compound LI-135

ESI-2018-N007-133 #11-12 RT: 0.33-0.36 AV: 2 NL: 9.53E7
T: - c ESI Full ms [50.00-2000.00]

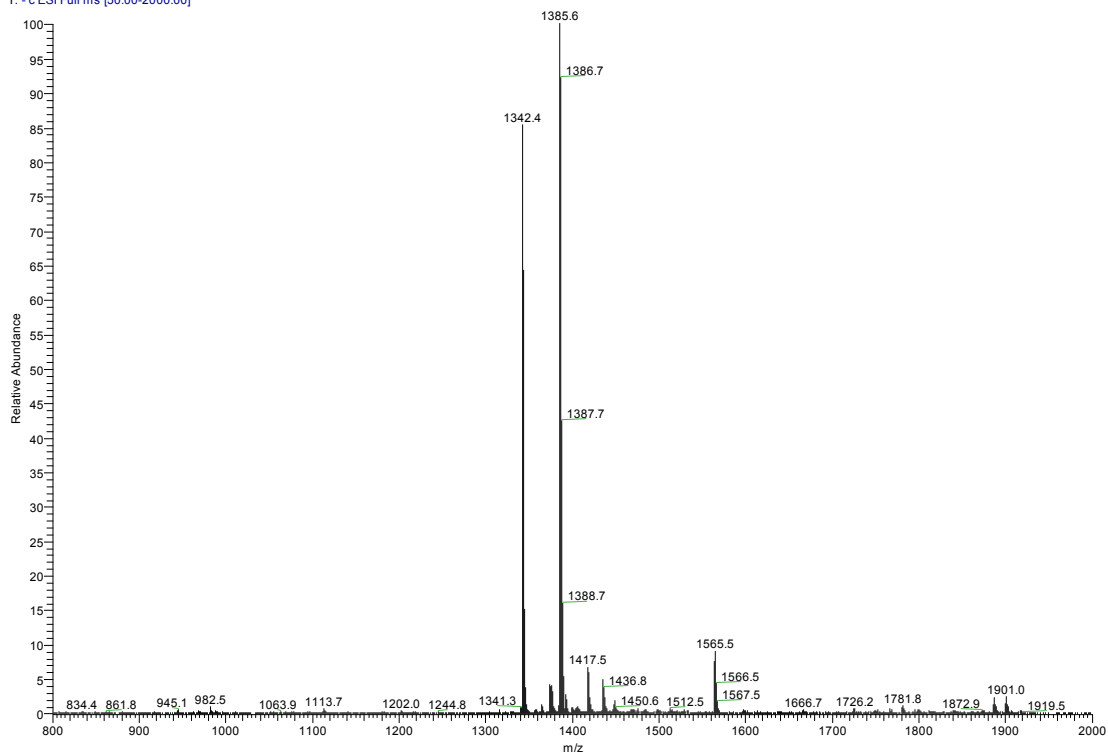


Figure S21. MS spectrum of compound **LI-136**

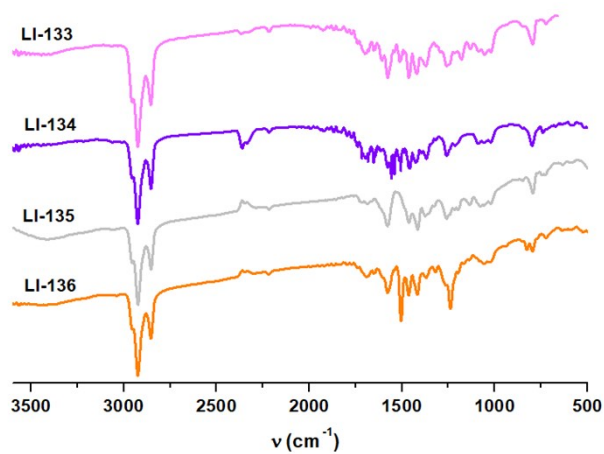


Figure S22. The IR spectra of organic dyes