Supplementary Information

Spirocyclic Side Chain of Non-Fullerene Acceptor Enables Efficient Organic Solar Cells with Reduced Recombination Loss and Energetic Disorder

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Materials and synthesis. All the starting materials were purchased from commercial suppliers and used without further purification unless indicated otherwise. Polymeric donor **PM6** [1] was purchased from Solarmer Material (Beijing) Inc and **F-2F** [2] acceptor was synthesized based on our previously reported methods. All reactions and manipulations were carried out under argon atmosphere with the use of standard Schlenk techniques.

Synthesis of Compound 2. Adding 1.7 mL (15 mmol) of 2,3-dimethyl-l,3-buta-diene (1) in 20 mL of pentane to a mixture of 3.36 g (30 mmol) of potassium *tert*-butoxide, 40 mL pentane, and 14 mL (30 mmol) of 2.2 M *n*-butyllithium in hexane in a nitrogen-filled flask. After 10 min of stirring, the dianion salt was allowed to settle, and the liquid was removed and blown dry with nitrogen. For reaction, it was suspended in 20 mL of THF and added to the reaction via syringe. To the dianion flask prepared as previously described was added 5.81 g (30 mmol) of 1-bromooctane dissolved in 20 ml of THF

followed by dropwise. The solution was stirred while warming to room temperature. After 1 h, the solution was extracted with pentane. The organic phase was dried over $MgSO_4$, and the product was purified by column chromatography on silica gel in a 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.04 (s, 2H), 4.90 (s, 2H), 2.22 (t, 4H), 1.46-1.40 (m, 4H), 1.33-1.23 (m, 20H), 0.88 (t, J = 6.9 Hz, 6H).

Synthesis of Compound 3. 50 mmol *Compound 2*, was added to 50 mL of THF and placed in an ice bath, and then 25 mL of a 1 M solution B_2H_6 in THF was added dropwise. After warming to room temperature, the excess hydride was decomposed by dropwise addition of water. The organoborane was oxidized at 30-50 °C (water bath) by the addition of 12 mL of 3N NaOH, followed by dropwise addition of 12 mL of 30% H_2O_2. After 1 h 30 g of potassium carbonate was added. The THF layer was separated, and the aqueous phase was extracted with ether. The ether extracts were combined and dried. Following the removal of the solvent by rotary evaporation, the product was purified by column chromatography on silica gel in a 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.51-4.11 (m, 2H), 3.41-3.29 (m, 4H), 1.34-1.19 (m, 30H), 0.86 (t, J = 6.8 Hz, 6H).

Synthesis of Compound 4. *p*-Toluenesulfonyl chloride (53.38g, 280 mmol) was dissolved in pyridine (200 mL) at 0 °C. *Compound 3* (21.70g, 69 mmol) was then added as a solution in $CHCl_3$, (40 mL) and the resulting solution was allowed to stir for 2 h at 0 °C before it was transferred to a freezer and stored for 4.0h at –20 °C. The solution was poured into a slurry of HCl (400 mL of 10% sol) and crushed ice (100 g) and the

product extracted into $CHCl_3$ (3×200 mL). The combined organic extracts were washed further with HCl (10% sol, 3×100mL), water (3×200 mL), saturated $NaHCO_3$ (100 mL) and brine (100 mL), dried over $NaSO_4$, and concentrated in vacuo. The product was recrystalized from $CHCl_3$, to afford 30.0g (70%) of the title compound as white prisms. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 8.3, 1.7 Hz, 4H), 7.35 (d, *J* = 8 Hz, 4H), 3.91 (t, *J* = 4.5 Hz, 4H), 2.45 (s, 6H), 1.76-1.65 (m, 2H), 1.34-1.03 (m, 28H), 0.89 (t, *J* = 7.0 Hz, 6H).

Synthesis of Compound 5. Lithium bromide (5.99 g, 69 mmol) was dissolved in dry acetone (60 mL) and *Compound 4* (10.59 g, 17 mmol) was added. The resulting solution was refluxed in the dark for 8.0 h, after which the mixture was poured into water (200 mL) and extracted into EtOAc (4x50 mL). The organic layers were combined and treated with HCl (10% sol, 100 mL), followed by saturated $NaHCO_3$ (100 mL) and brine (50 mL). The resulting solution was dried over $NaSO_4$, filtered through a plug of silica, and concentrated in vacuo. Elution with hexanes through a short column of silica gel afforded 7.11g (95 %) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62-3.35 (m, 4H), 1.84-1.72 (m, 2H), 1.46-1.21 (m, 28H), 0.89 (t, *J* = 6.7 Hz, 6H).

Synthesis of Compound 7. To a solution of 3.24 g 2,7-dibromo-9H-fluorene (10 mmol) and 2.52 g potassium hydroxide (45 mmol) in 50 ml DMSO was added 4.4 g *Compound 5* (10 mmol) at room temperature and the reaction mixture was allowed to stir for 5 h. The reaction mixture was poured into water, and then the mixture was extracted with

ethyl acetate. The combined organic layers were washed with brine, dried over MgSO4 and filtered, and then the solvent was evaporated in vacuum. The residue was purified by flash column chromatography using petroleum ether as eluent to afford the product (5.24 g, yield 87 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.46 (m, 2H), 7.46-7.36 (m, 4H), 2.49-2.36 (m, 1H), 2.23 (dd, *J* = 12.7, 5.0 Hz, 1H), 2.03 (dd, *J* = 13.6, 6.4 Hz, 1H), 1.96-1.75 (m, 4H), 1.64-1.54 (m, 1H), 1.39-1.13 (m, 26H), 0.87 (t, *J* = 7.5, 5.1 Hz, 6H).

Synthesis of Compound 8. To a stirred solution of *Compound 7* (6.02 g, 10.0 mmol) in dry THF (40 mL) was added n-BuLi (22.0 mmol) (2.4 M in hexanes), at -78 °C (dry ice/ACN) under an argon atmosphere. After stirring at -78 °C for 1 hour, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.28g, 23.0 mmol) was added under -78 °C. The reaction mixture was slowly warmed to room temperature overnight, quenched by addition of water and extracted with hexanes. The combined extracts were washed with brine, dried over anhydrous MgSO4, and then filtered. The solvent was removed by rotary evaporation to give the *compound 8* as a white solid which was used without further purification.

Synthesis of Compound 9. To a three-necked round bottom flask were added *compound 8* (6.7 g, 9.62mmol), ethyl 2-bromothiophene-3-carboxylate (5.2 g, 22.12 mmol), $Pd(PPh_3)_4$ (2.3 g, 0.2 mmol), K_2CO_3 (7.98 g, 57.72 mmol) and toluene/water (100 mL, 4/1). The mixture was deoxygenated with nitrogen for 30 min and then stirred at 110 °C for 48 h. After cooled down to room temperature, Brine (60 mL) was added and the mixture was extracted with dichloromethane (3×30mL). The organic phase was dried

over anhydrous Na_2SO_4 and filtered. After removing the solvent from the filtrate, the residue was purified by column chromatography on silica gel using dichloromethane as the eluent yielding a yellow solid (7.24 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.65 (m, 2H), 7.62-7.43 (m, 6H), 7.25-7.22 (m, 2H), 4.19 (q, *J* = 7.1 Hz, 4H), 2.51-2.44 (m, 1H), 2.36-2.27 (m, 1H), 2.20-1.99 (m, 2H), 1.96-1.84 (m, 2H), 1.81-1.70 (m, 1H), 1.62-1.55 (m, 1H), 1.38-1.13 (m, 32H), 0.85 (t, *J* = 6.7, 4.3 Hz, 6H).

Synthesis of Compound 10. To a 250 mL two-neck flask was added *compound 9* (3.92 g, 5.18 mmol), sodium hydroxide (2.90 g, 72.5 mmol), ethanol (200 mL), and water (30 mL). The reaction mixture was refluxed at 90 °C for 12 h. The ethanol was removed under reduced pressure. 1M concentrated HCl was added to acidify the solution. The precipitate was collected by filtration and washed with water to afford *compound 10* crude product as a white solid (2.75 g, 76%) which was used without further purification.

Synthesis of Compound 11. To a suspension mixture of *compound 10* (5.6 g, 8.0 mmol) in dry dichloromethane (100 mL) was slowly added oxalyl dichloride (4.1 g, 32 mmol) dropwise and dry N,N-dimethylformide (1 mL). The mixture was stirred under argon at rt for 12 h. The solvent was removed by reduced pressure to yield acid chloride compound as a yellow solid. Without further purification, it was dissolved with dry dichloromethane (70 mL). A solution of $AlCl_3$ (2.34 g, 17.55 mmol) in dry dichloromethane (40 mL) was added to the above solution by syringe at 0 °C. The mixture was stirred at rt for 5 h. After removal of the solvent by reduced pressure, the

residue was extracted with ethyl acetate (100 mL×3) and brine (100 mL×3). The collected organic layer was dried over $MgSO_4$, and then filtered. The solvent was removed by rotary evaporation to give the stannylated *compound 11* as a red solid which was used without further purification.

Synthesis of Compound 12. A mixture of *compound 11* (200 mg, 0.3 mmol), potassium hydroxide (345 mg, 6.16 mmol) in diethylene glycol (20 mL) and aniline (20 ml) was heated to 100 ºC for 30 min. Hydrazine monohydrate (300 mg, 6.16 mmol) was then slowly added to above solution dropwise. The mixture was heated to 180 °C for 24 h. After being cooled to r.t, the mixture was quenched by HCl (aq) followed by extraction with ethyl acetate (30 mL×3) and brine (100 mL×1). The collected organic layer was dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane) to yield a white solid (146 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.73 (m, 2H), 7.61-7.48 (m, 2H), 7.32 (dd, J = 4.8, 1.3 Hz, 2H), 7.14 (d, J = 4.8 Hz, 2H), 3.77 (s, 4H), 2.65-2.56 (m, 1H), 2.36 (dd, J = 12.4, 5.2 Hz, 1H), 2.23-1.92 (m, 5H), 1.74-1.66 (m, 1H), 1.40-1.24 (m, 26H), 0.88 (t, J = 8.8, 5.3 Hz, 6H).

Synthesis of Compound 13. A solution of *compound 12* (0.3 g, 0.47 mmol) in dry DMSO (20 mL) was heated at 80 °C. Sodium tert-butoxide (0.29 g, 3 mmol) dissolved in dry DMSO (15 ml) was added to the above mixture. After the reaction mixture was stirred at 80 ºC for 1 h, 1-bromooctane (0.54 g, 3 mmol) was added dropwise. The mixture was further stirred at 90 ºC for 4 h. The reaction was quenched by water and

extracted with ethyl ether (30 ml×3) and brine (50 ml×3). After being dried over $MgSO_4$, the organic layer was removed by reduced pressure and the residue was purified by column chromatography on silica gel to afford a sticky yellow product (0.45 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.51 (m, 2H), 7.49-7.31 (m, 2H), 7.29-7.24 (m, 2H), 6.98 (d, *J* = 4.9 Hz, 2H), 2.72-2.46 (m, 1H), 2.37-2.32 (m, 1H), 2.22-2.11 (m, 1H), 2.05-1.87 (m, 10H), 1.68-1.62 (m, 1H), 1.34-1.10 (m, 68H), 0.90-0.77 (m, 26H).

Synthesis of Compound 14. $POCl_3$ (0.22 mL) was added drop by drop to DMF (2 mL) at 0°C under the protection of argon and then stirred at room temperature for 5 h to gain the Vilsmerier reagent. The Vilsmerier reagent was added into a 1,2- dichloroethane (50 mL) solution of *compound 13* (0.43 g, 0.40 mmol). The above reaction mixture was stirred at room atmosphere for 1 h and then heated to 80 °C for 12 h. The mixture was quenched with CH_3COONa (aq), and then extracted with CH_2Cl_2 (50 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$ and purified by silica gel, yielding a yellow solid (0.30 g, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 2H), 7.71-7.61 (m, 4H), 7.53 (m, 2H), 2.64-2.53 (m, 1H), 2.37 (dd, *J* = 12.6, 5.3 Hz, 1H), 2.19 (dd, *J* = 13.5, 6.8 Hz, 1H), 2.12-1.90 (m, 10H), 1.72-1.65 (m, 1H), 1.51-1.07 (m, 68H), 0.94-0.78 (m, 26H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.91, 155.56, 155.14, 154.53, 154.49, 153.60, 153.56, 153.50, 153.28, 151.20, 151.11, 151.09, 143.97, 143.92, 138.59, 138.10, 138.07, 135.60, 135.53, 135.41, 129.45, 114.50, 114.20, 112.80, 55.57, 53.87, 53.04, 53.00, 52.98, 52.40, 47.10, 46.18, 44.25, 41.96, 38.16, 33.17, 30.91,

30.87, 30.71, 30.41, 29.71, 29.16, 29.11, 29.00, 28.67, 28.61, 28.35, 28.29, 28.25, 28.20, 27.66, 27.57, 23.33, 23.29, 21.69, 21.65, 21.55, 13.11, 13.09, 13.02.

Synthesis of Compound Spiro-F. Under the protection of argon, *Compound 14* (100 mg, 0.08 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (73.6 mg, 0.32 mmol) was dissolved in dry chloroform (30 mL), followed by the addition of pyridine (0.5 mL). After stirring at room temperature for 12 h, the mixture was poured into water and then extracted with $CHCl_3$ (30 mL×2), the organic layer was dried over anhydrous $MgSO_4$ for 3 h. After removal of solvent, the crude product was purified by silica gel, and then recrystallized from $CHCl_3$ and methanol to give Spiro-F as a dark blue solid (86 mg, 62%).^{1}H NMR (600 MHz, $CDCl_3$) δ 9.06-8.94 (m, 2H), 8.61-8.48 (m, 2H), 7.82-7.64 (m, 8H), 2.65 (s, 1H), 2.40 (dd, J = 13.3, 5.4 Hz, 1H), 2.21 (dd, J = 13.7, 6.4 Hz, 1H), 2.12-1.96 (m, 10H), 1.75 (s, 1H), 1.48-1.10 (m, 69H), 0.91-0.77 (m, 26H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 186.12, 163.02, 158.67, 157.69, 157.06, 156.33, 156.23, 155.21, 154.98, 153.58, 141.48, 141.01, 140.29, 138.88, 137.13, 136.49, 134.55, 120.26, 116.94, 116.49, 115.08, 114.52, 112.59, 68.76, 56.73, 54.76, 54.28, 54.25, 48.25, 47.44, 45.59, 42.69, 39.32, 39.26, 34.10, 31.96, 31.94, 31.73, 31.09, 30.18, 30.12, 29.99, 29.76, 29.66, 29.39, 29.33, 29.28, 29.24, 28.81, 28.59, 24.47, 22.74, 22.70, 22.58, 14.16, 14.14, 14.04.

Measurements and Instruments. The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were taken on a Bruker AV400 Spectrometer. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry were performed

on a Bruker Autoflex III instrument. Varian 7.0T FTMS was used to achieve the HR-MS data. UV-vis spectra were obtained with a Cary 5000 Spectrophotometers. Cyclic voltammogram (CV) was performed with a LK2010 Microcomputerbased Electrochemical Analyzer at a scan rate of 100 mV/s. The current density-voltage (J-V) curves of photovoltaic devices were obtained by a Keithley 2400 source-measure unit. The photocurrent was measured under simulated illumination of 100 mW cm^{-2} with AM1.5G irradiation using a xenon-lamp-based solar simulator [Oriel 96000] in an argon-filled glove box. External quantum efficiency values (EQEs) of the encapsulated devices were obtained with a halogen-tungsten lamp, monochromator, optical chopper, and lock-in amplifier in air and the photon flux was determined by a calibrated silicon photodiode. Atomic force microscopy (AFM) images were performed using in tapping mode on a Bruker MutiMode 8 atomic force microscope. Transmission electron microscopy (TEM) was performed on a Philips Technical G2 F20 at 200 kV. The GIWAXS (grazing incidence wide angle X-ray scattering) samples were prepared on ZnO-coated Si substrates using the same preparation conditions as for devices. Electroluminescence (EL) and electroluminescence quantum efficiency (EQE_{EL}) measurements were performed by an integrated system (REPS, Enli Technology Co., Ltd.). EQE_{EL} measurements were carried out from 1 to 4 V. Fourier-transform photocurrent spectroscopy external quantum efficiency (FTPS-EQE) was measured by an integrated system (PECT-600, Enli Technology Co., Ltd.), where the photocurrent was amplified and modulated by a lock-in instrument. SCLC was uesd to measure hole and electron mobilities, using a diode configuration of ITO/PEDOT:PSS/active

layer/Al for hole and glass/ZnO/active layer/Ag for electron by taking the dark current density in the range of 0–8 V and fitting the results to a space charge limited form.

Fabrication of OPV devices. The photovoltaic devices were fabricated with a structure of indium tinoxide (ITO)/ZnO/PFN-Br/donor:acceptor/MoOx/Ag. The ITO-coated glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 minutes each time and subsequently dried by a nitrogen flow. A 30 nm thick layer of ZnO precursor solution was spin-coated (3000 rpm) onto the ITO surface. After baked at 200 °C for 60 min, the substrates were transferred into an argon-filled glove box. A thin film of PFN-Br (0.5mg/mL methol solution) was spin-coated with 5000 rpm for 15s on ZnO. Subsequently, a solution of PM6:Spiro-F blend (1:1, CB:DIO=100:0.3, v:v) was spincoated with different spincoating speed and then treated with different thermal annealing (TA) temperature. A MoOx (~2 nm) and Ag (~150 nm) was successively evaporated onto the active layer through a shadow mask to define the active area of the devices (~0.04 cm^2) in a vacuum chamber (<1x10^{-4} Pa). The device of PM6:F-2F was fabricated followed the previous report method.

The calculation of ΔE_1, ΔE_2 and ΔE_3.

The detailed components of E_{loss} can be categorized into two parts based on the SQ limit, as shown in Equation (1):

$$E_{loss} = (E_{gap} - qV_{OC}^{SQ}) + (qV_{OC}^{SQ} - qV_{OC}^{rad}) + (qV_{OC}^{rad} - qV_{OC})$$

Where

$$V_{OC}^{SQ} = \frac{kT}{q}\ln\left(\frac{J_{SC}^{SQ}}{J_0^{SQ}} + 1\right) \cong \frac{kT}{q}\ln\left(\frac{q \cdot \int_{E_g}^{+\infty} \emptyset_{AM1.5G}(E)dE}{q \cdot \int_{E_g}^{+\infty} \emptyset_{BB}(E)dE}\right)$$

Where $\emptyset_{BB}(E)$ is black body emission at room temperature,

thus,for the unavoidable radiative recombination ΔE_1

$$\Delta E_1 = E_{gap} - qV_{OC}^{SQ}$$

$$V_{OC}^{rad} = \frac{kT}{q}\ln\left(\frac{J_{SC}}{J_0^{rad}} + 1\right) \cong \frac{kT}{q}\ln\left(\frac{q \cdot \int_0^{+\infty} EQE(E)\emptyset_{AM1.5G}(E)dE}{q \cdot \int_0^{+\infty} EQE(E)\emptyset_{BB}(E)dE}\right)$$

Thus, for the unavoidable radiative recombination ΔE_2

$$\Delta E_2 = qV_{OC}^{SQ} - qV_{OC}^{rad}$$

Finally, for the non-radiative recombination loss ΔE_3

$$\Delta E_3 = qV_{OC}^{rad} - qV_{OC}$$

Where V_{oc} is the open circuit voltage of the PSC.

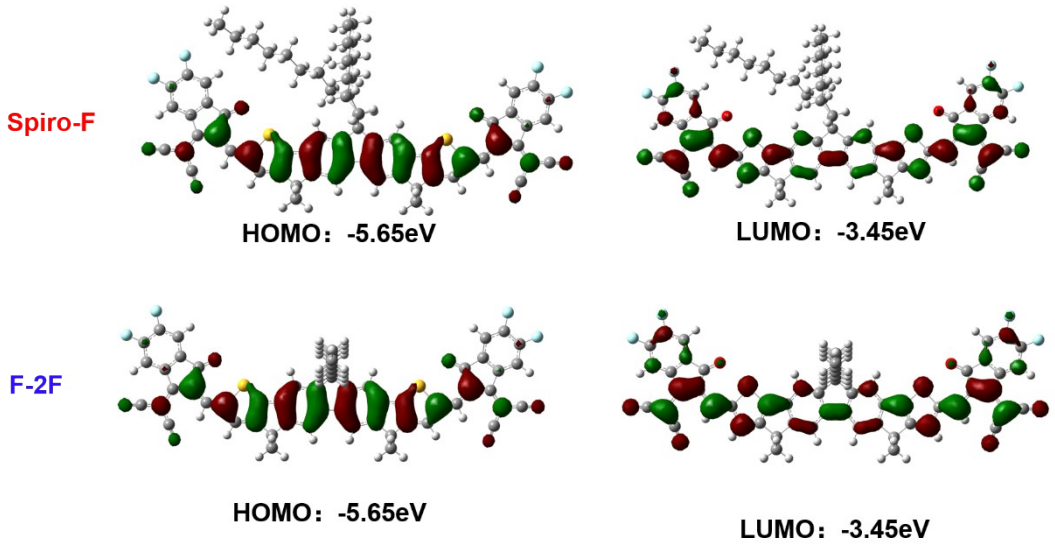

Fig.S1 Theoretical density distribution for the frontier molecular orbits of **F-2F** and

Spiro-F. All calculations were carried out using Gaussian 16.

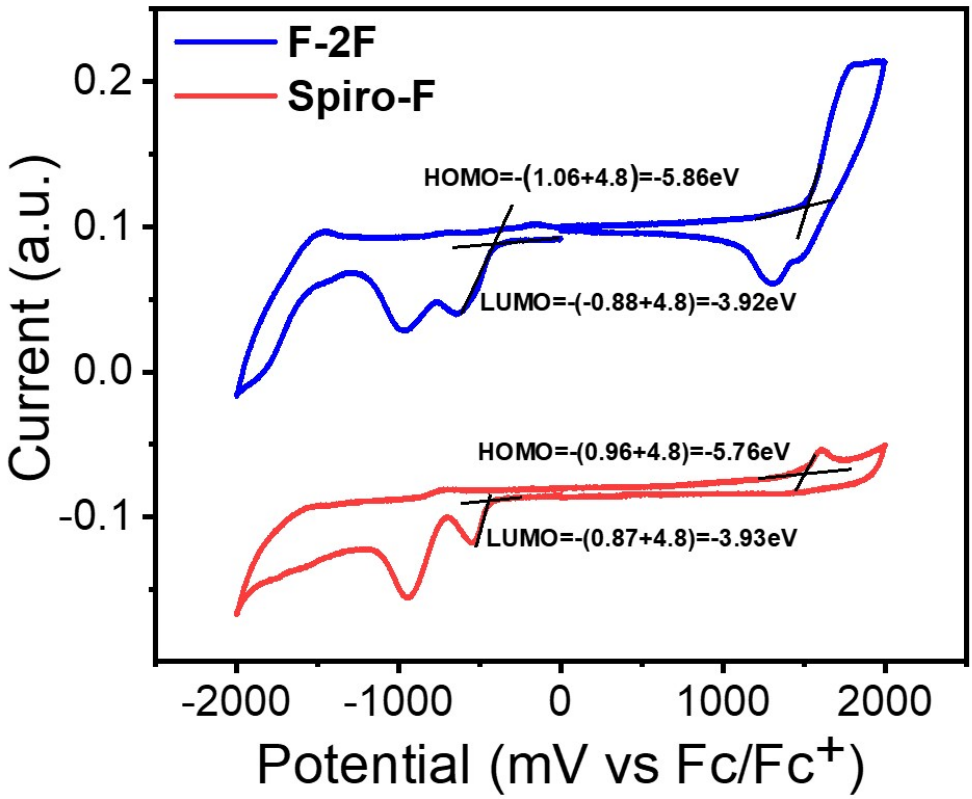

Fig. S2 Cyclic voltammogram of **F-2F** and **Spiro-F** film in acetonitrile solution with 0.1 mol L^{-1} *n*-Bu_4NPF_6 at a scan rate of 100 mV s^{-1}. The HOMO/LUMO energy levels were calculated from the onset oxidation potential and the onset reduction potential vs FC/FC+, using the equation $E_{HOMO} = -(4.80 + E_{onset\ vs\ FC/FC+}^{ox})$, $E_{LUMO} = -(4.80 + E_{onset\ vs\ FC/FC+}^{re})$.

Table S1. Photovoltaic performance of the solar cells based on **PM6**:**Spiro-F** (1:1, *w*/*w*) blend films with different spincoating speed under illumination of AM 1.5 G, 100 mW cm^{-2}.

Spincoating speed (rpm/min)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
1000	0.898	18.18	71.95	11.75
1500	0.912	19.69	74.16	13.30
2000	0.914	19.50	75.81	13.49
2500	0.913	17.97	77.00	12.61

Table S2. Photovoltaic performance of the solar cells based on **PM6**:**Spiro-F** (1:1, *w*/*w*) blend films with different TA temperature under illumination of AM 1.5 G, 100 mW cm^{-2}.

TA temperature (°C)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
as cast	0.913	19.45	76.35	13.56
80℃	0.899	19.54	74.66	13.12
100℃	0.903	19.90	74.08	13.32
120℃	0.855	20.17	67.32	11.61

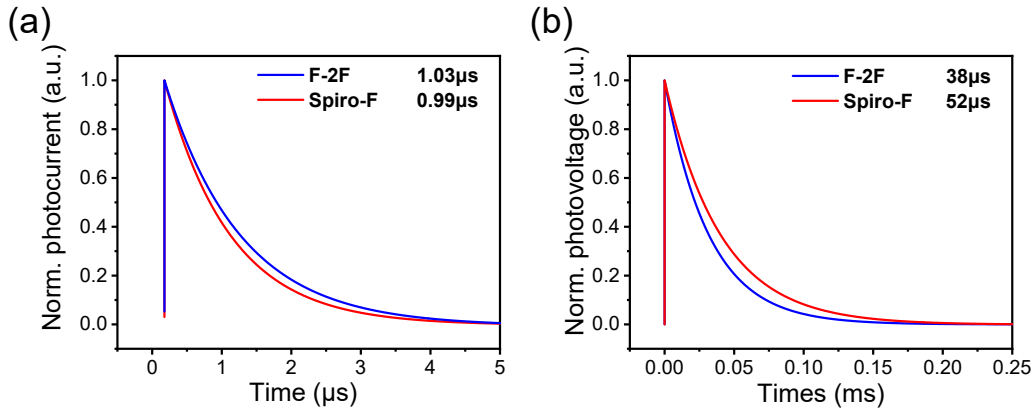

Fig. S3 TPC (a) and (b) TPV measurements of **PM6**:**F-2F** and **PM6**:**Spiro-F** devices.

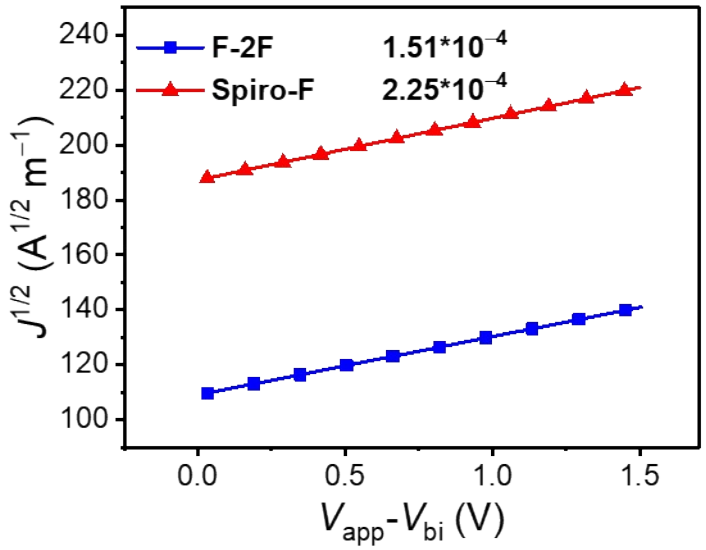

Fig. S4 The electron (μ_e) mobilities of **F-2F** and **Spiro-F** devices.

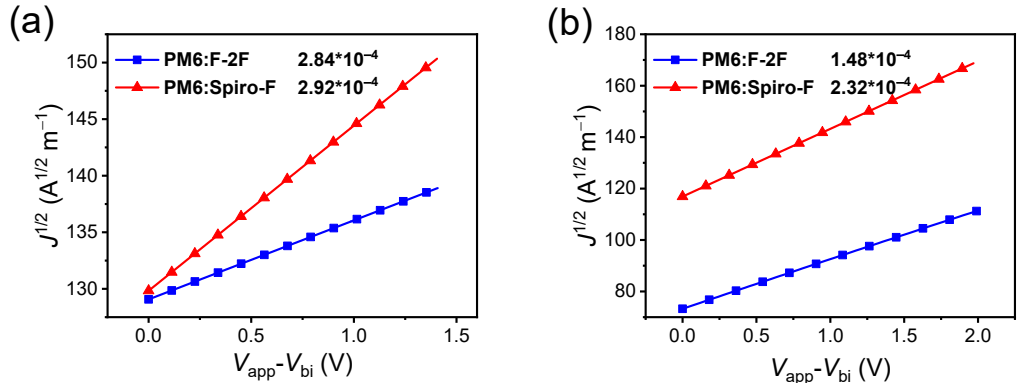

Fig. S5 The hole (μ_h) and electron (μ_e) mobilities of **PM6**:**F-2F** and **PM6**:**Spiro-F** devices.

Table S3 The detailed data of physical dynamic characterizations for devices.

Acceptors	V_{eff}-J_{ph}	α	S/(kT/q)	TPV (μs)	TPC (μs)	μ_h (10^{-4} cm^2 V^{-1} s^{-1})	μ_e (10^{-4} cm^2 V^{-1} s^{-1})	μ_h/μ_e
F-2F	97%	0.961	1.35	38	0.99	2.84	1.48	1.92
Spiro-F	96%	0.968	1.26	52	1.03	2.92	2.32	1.26

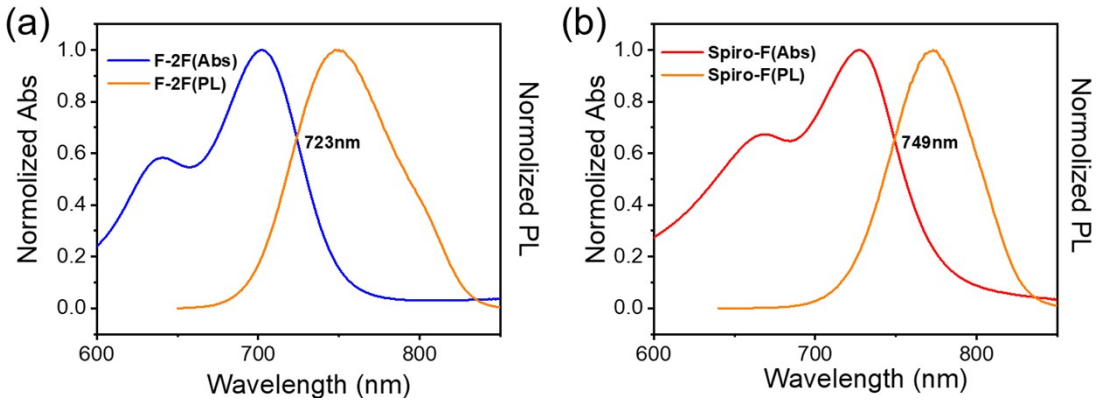

Fig. S6 Normalized absorption and PL spectra of **F-2F**, and **Spiro-F** neat films.

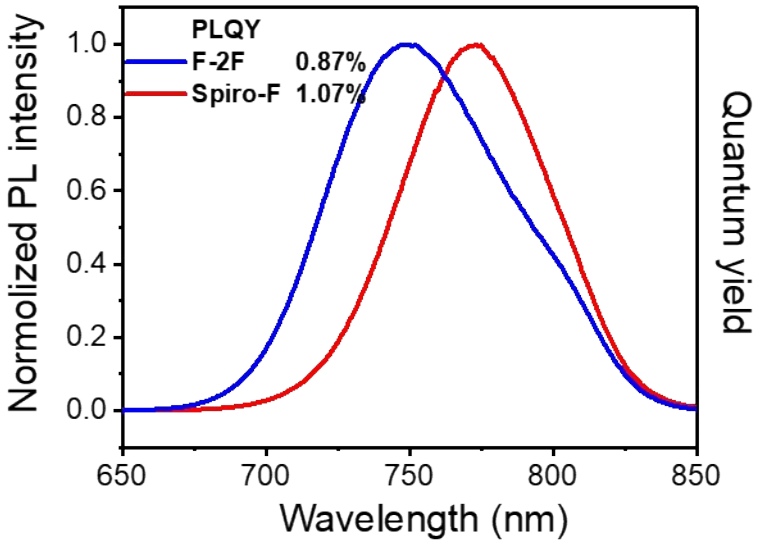

Figure S7 Photoluminescence spectra of the F-2F, Spiro-F films excited at 620 nm together with their quantum efficiencies

NMR and MS spectra

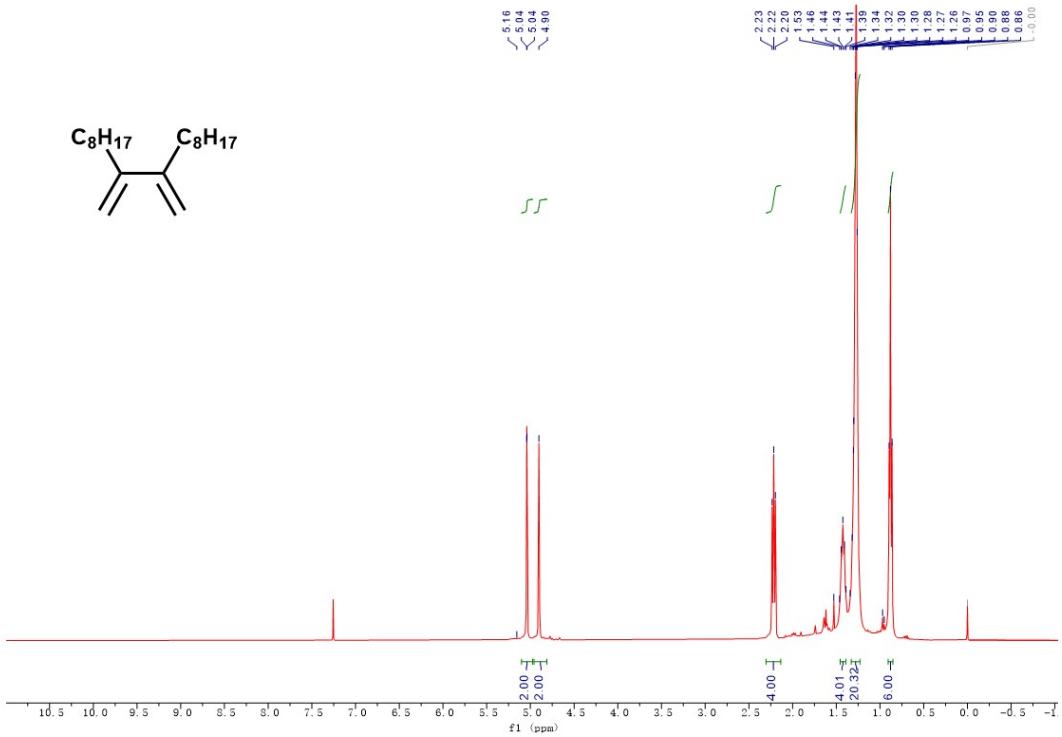

Fig. S8 ^{1}H NMR spectra of *compound 2* in $CDCl_3$.

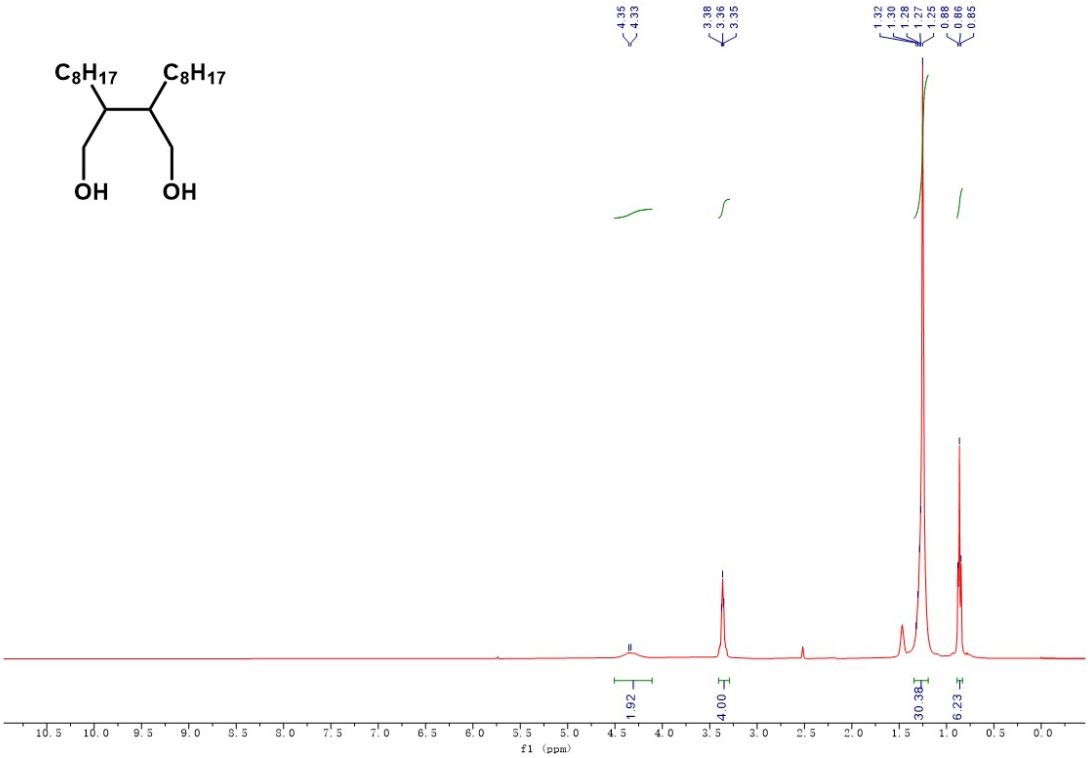

Fig. S9 ^{1}H NMR spectra of *compound 3* in $CDCl_3$.

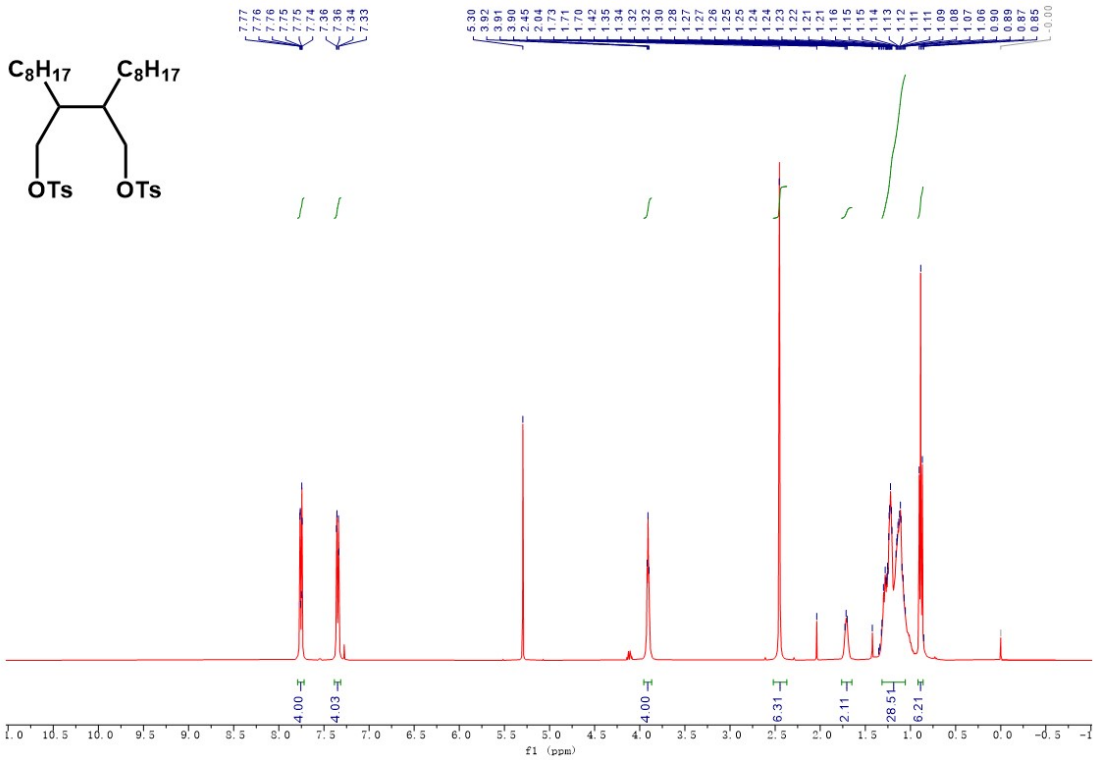

Fig. S10 ^{1}H NMR spectra of *compound 4* in $CDCl_3$.

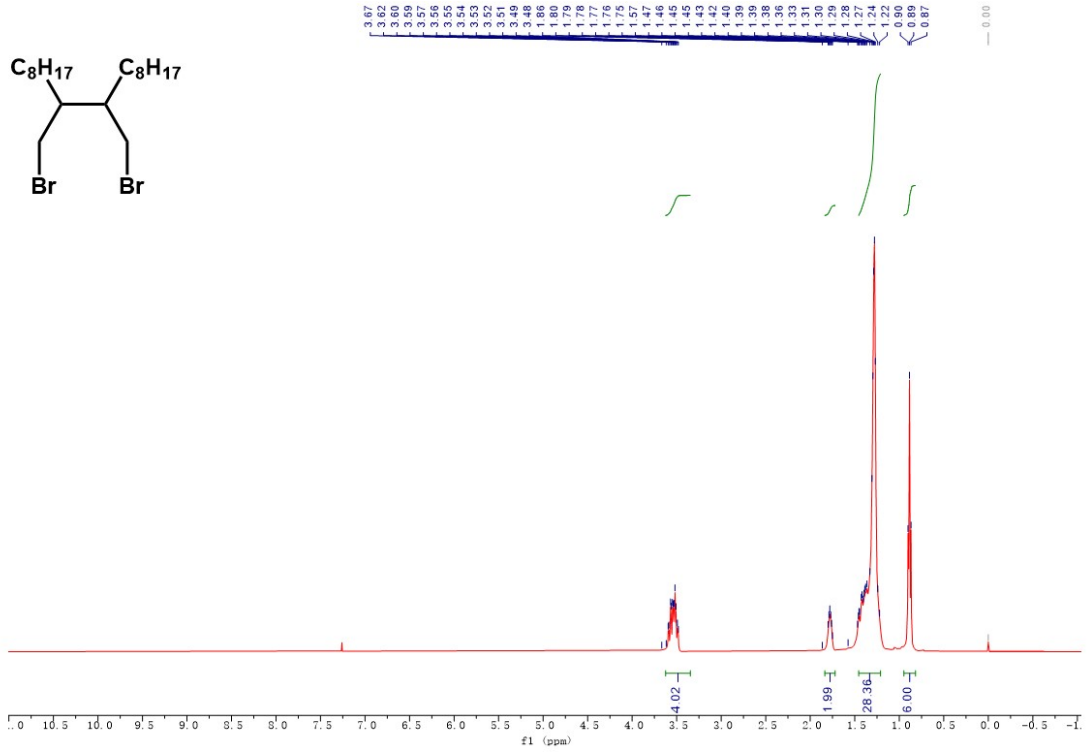

Fig. S11 ^{1}H NMR spectra of *compound 5* in $CDCl_3$.

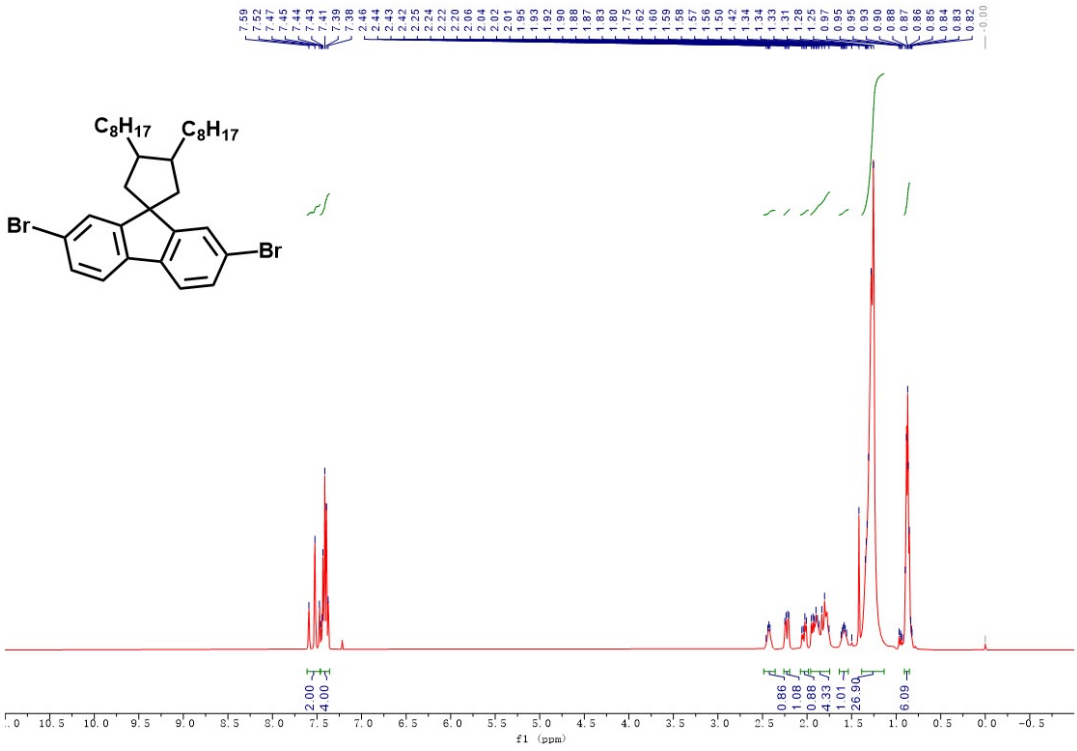

Fig. S12 ^{1}H NMR spectra of *compound 7* in $CDCl_3$.

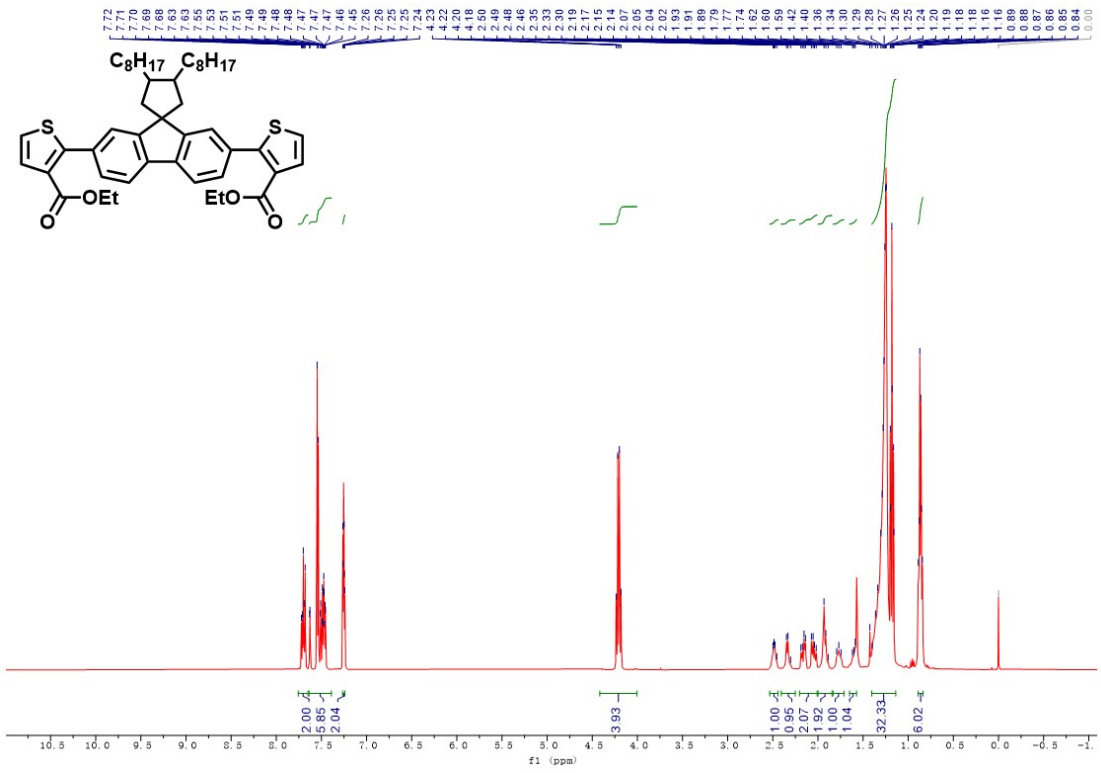

Fig. S13 ^{1}H NMR spectra of *compound 9* in $CDCl_3$.

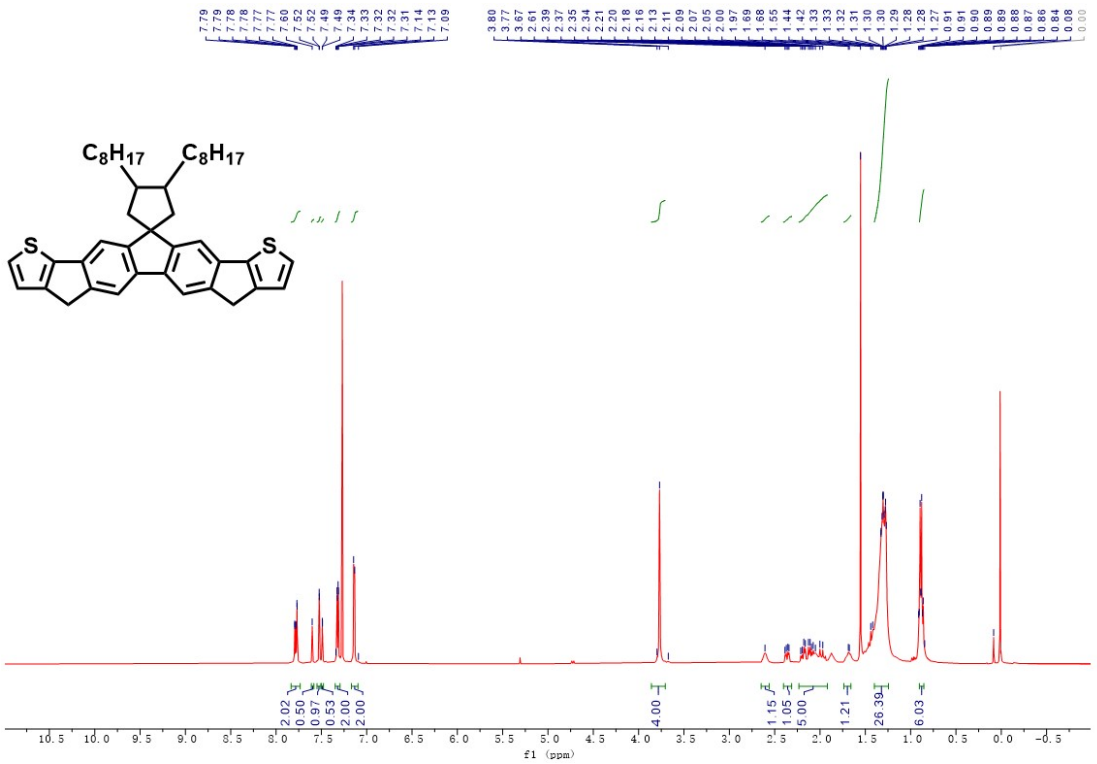

Fig. S14 ^{1}H NMR spectra of *compound 12* in $CDCl_3$.

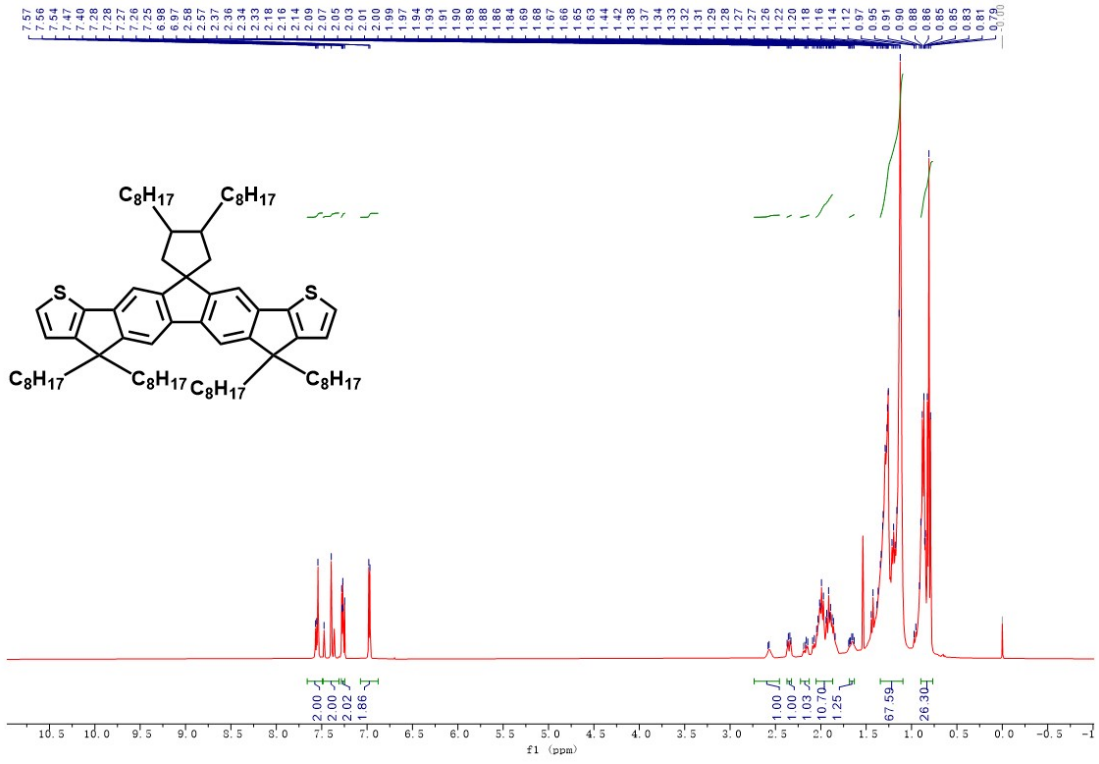

Fig. S15 ^{1}H NMR spectra of *compound 13* in $CDCl_3$.

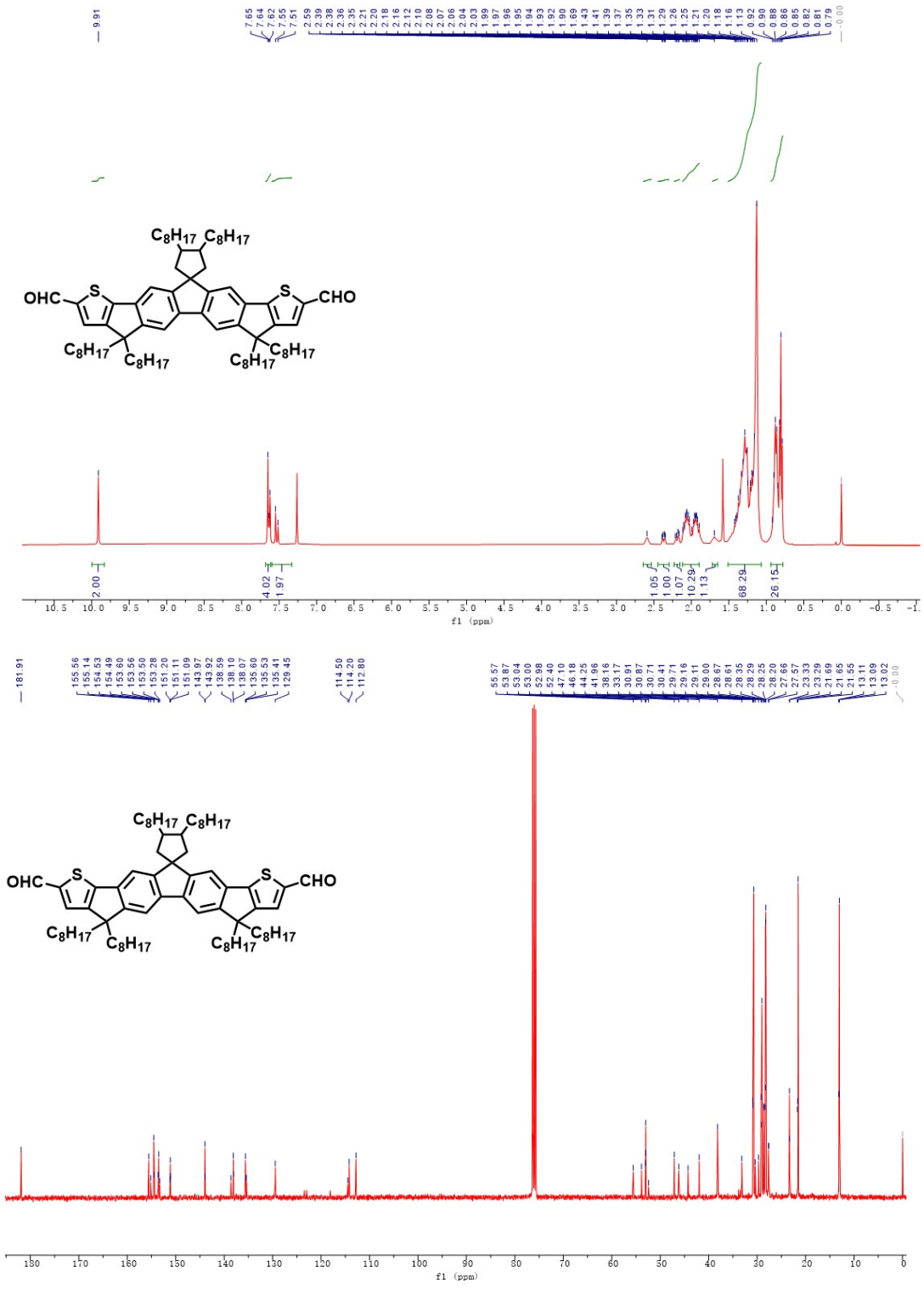

Fig. S16 ^{1}H NMR and ^{13}C NMR spectra of *compound 14* in $CDCl_3$.

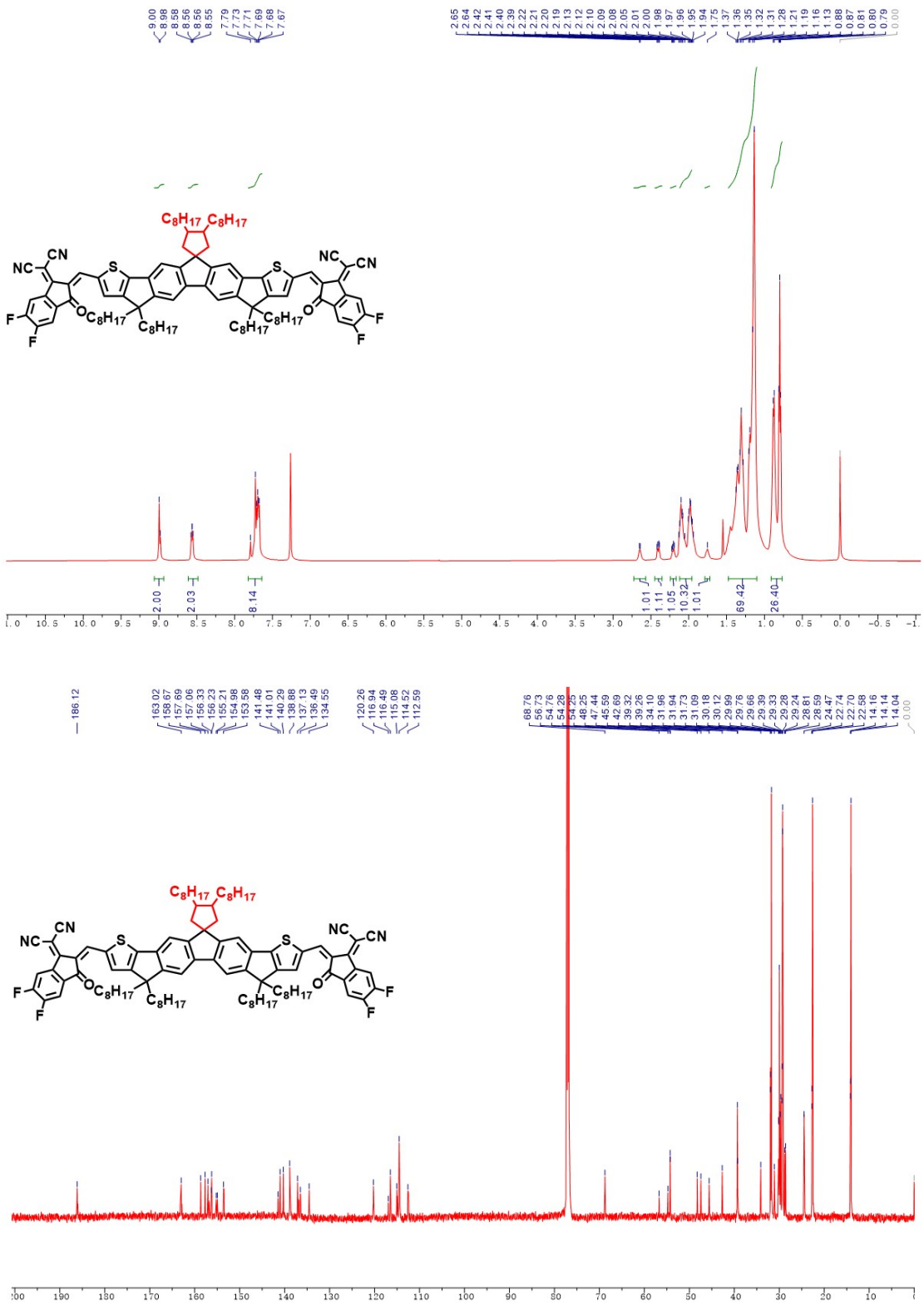

Fig. S17 ^{1}H NMR and ^{13}C NMR spectra of *Spiro-F* in $CDCl_3$.

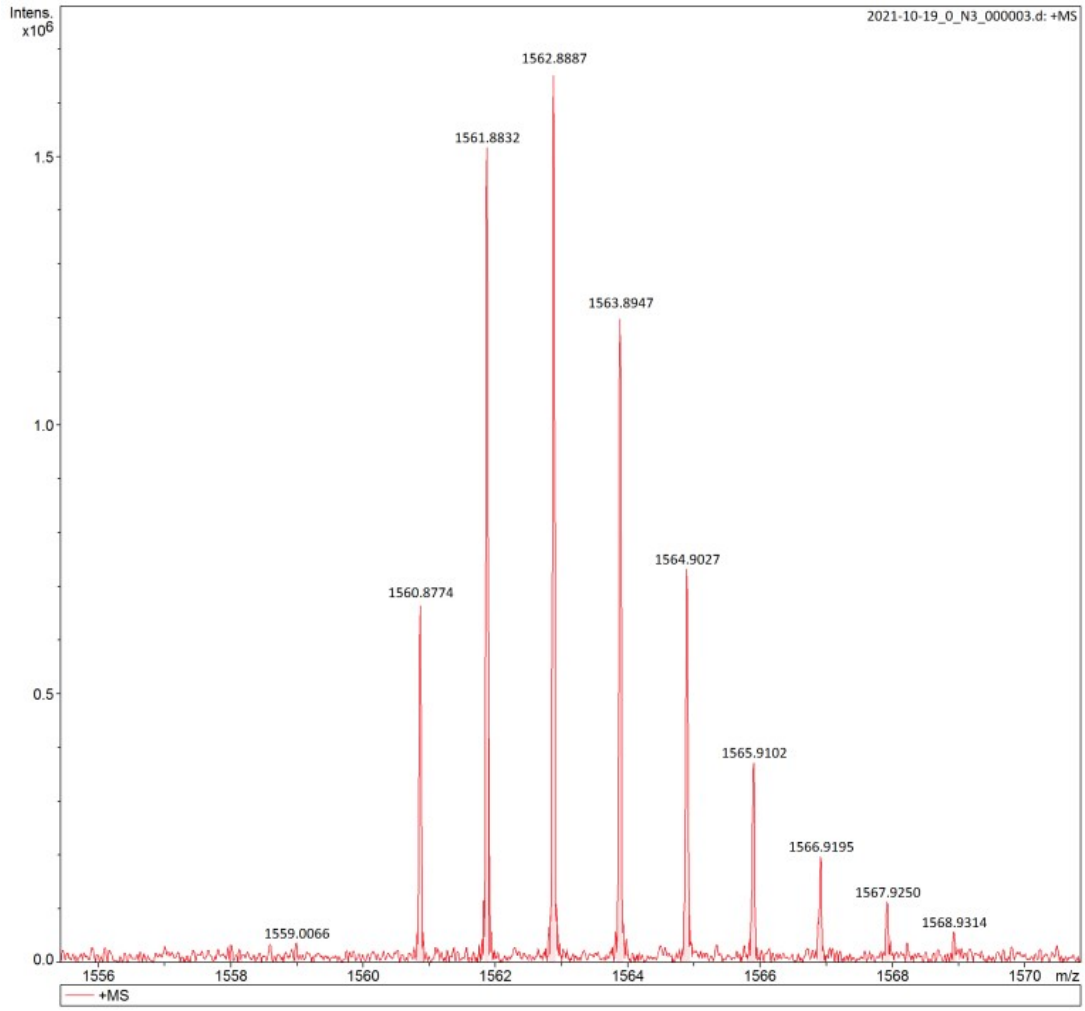

Fig. S18 HR-MS plots of compound Spiro-F.

References

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