

## *Supporting Information*

### **Spirobifluorene-based hole-transporting materials for RGB**

#### **OLEDs with high efficiency and low efficiency roll-off**

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## I. General remarks

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. NMR spectra were recorded on an Agilent 400-MR DD2 spectrometer. The  $^1\text{H}$  NMR (400 MHz) chemical shifts were measured relative to  $\text{CDCl}_3$  as the internal reference ( $\text{CDCl}_3$ :  $\delta = 7.26$  ppm). The  $^{13}\text{C}$  NMR (100 MHz) chemical shifts were given using  $\text{CDCl}_3$  as the internal standard ( $\delta = 77.16$  ppm).  $^{19}\text{F}$  NMR (376 MHz) was recorded on Bruker AV II-400 MHz. High resolution mass spectra (HRMS) were collected on Shimadzu LCMS-ITTOF (ESI). X-Ray single-crystal diffraction data were collected on an Agilent Technologies Gemini single-crystal diffractometer. UV-visible absorption spectra experiments were conducted on a HITACHI U-2910 spectrometer. Fluorescence spectra were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer with a calibrated integrating sphere system. Phosphorescence spectra were collected on a HITACHI F-7100 fluorescence spectrophotometer. Thermogravimetric analysis (TGA) curves were carried out using DTG-60(H) at a rate of  $10\text{ }^\circ\text{C}/\text{min}$  under nitrogen atmosphere. Differential scanning calorimetry (DSC) thermograms were recorded on DSC 200PC equipment under nitrogen atmosphere at a rate of  $10\text{ }^\circ\text{C}/\text{min}$ . Cyclic voltammograms were performed on LK2005A with a solution of tetrabutylammonium hexafluorophosphate ( $\text{NBu}_4\text{PF}_6$ ,  $0.1\text{ M}$ ) in  $\text{CH}_2\text{Cl}_2$  as electrolyte and ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) as standard, the sweep rate is  $100\text{ mV}^{-1}$ . Three-electrode system ( $\text{Ag}/\text{Ag}^+$ , platinum wire and glassy carbon electrode as reference, counter and work electrode respectively) was used in the CV measurement.

## II. OLED fabrication and characterization

ITO (indium tin oxide) glass substrates with a sheet resistance of  $15\ \Omega$  per square were cleaned with alkaline detergent, boiled deionized water, and deionized water thoroughly in ultrasonic bath and then treated with  $\text{O}_2$  plasma for 10 min. Organic layers, LiF and Al were deposited on ITO substrates by thermal evaporation in a high vacuum chamber below  $6 \times 10^{-6}$  mbar in an inert gas glovebox. The quartz crystal oscillators controlled

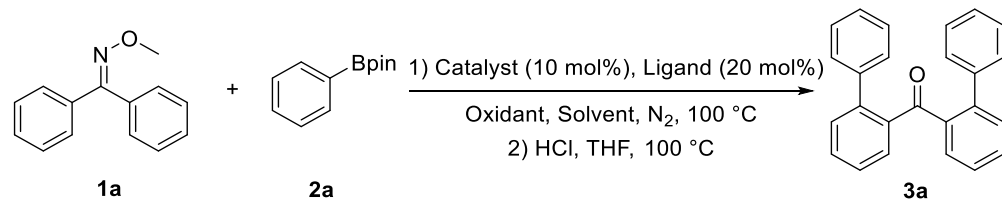
the thicknesses of deposited films. The as-fabricated OLEDs were measured in the inert gas glovebox without any encapsulation. Current density of OLEDs was measured by Keithley B1500A. The luminance and EL spectra were collected with model DLM-100Z photometer and OPT2000 spectrophotometer, respectively.

### III.Synthesis and Characterization

#### Condition optimization

A Schlenk tube with a magnetic stir bar was charged with **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), Pd(dba)<sub>2</sub> (0.02 mmol, 10.0 mol%), *N*-acetyl-*L*-phenylalanine (0.04 mmol, 20 mol%), Ag<sub>2</sub>CO<sub>3</sub> (0.3 mmol, 1.5 equiv) and HFIP (1.0 mL) under a nitrogen atmosphere. The reaction mixture was heated at 100 °C for 36 hours. The reaction mixture was cooled to room temperature and remove solvent under reduced pressure. Then add THF (1.0 mL) and HCl (0.2 mL) to Schlenk under an air atmosphere. The reaction mixture was heated at 100 °C for 12 hours. The reaction mixture was cooled to room temperature, diluted with 5 mL CH<sub>2</sub>Cl<sub>2</sub>, filtered through a celite pad, and washed with 20-30 mL CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) to give a white solid **3a**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.42 (dd, *J*<sub>1</sub> = 1.2, *J*<sub>2</sub> = 7.6, 2H), 7.33 (td, *J*<sub>1</sub> = 1.2, *J*<sub>2</sub> = 7.2, 2H), 7.22-7.16 (m, 8H), 7.12-7.10 (m, 6H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 200.50, 141.68, 140.64, 139.22, 130.85, 130.74, 130.41, 129.06, 128.00, 127.21, 126.81 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>25</sub>H<sub>18</sub>NaO [M+Na]<sup>+</sup> 357.1250, found 357.1254.

**Table S1.** Optimization of C–H diarylation<sup>a</sup>

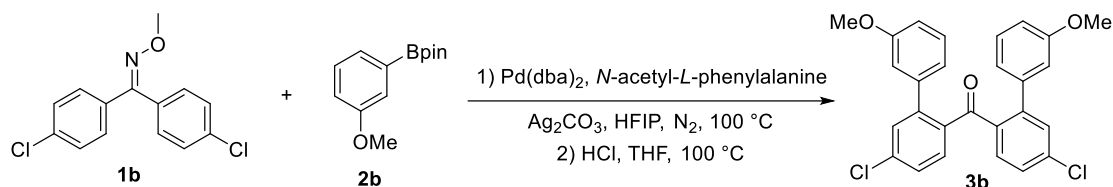


Entry	Catalyst	Ligand	Oxidant	Solvent	Yield of <b>3a</b> (%)
1	Pd(dba) <sub>2</sub>	<i>N</i> -acetyl-glycine	Ag <sub>2</sub> CO <sub>3</sub>	HFIP	53
2	Pd(dba) <sub>2</sub>	<i>N</i> -acetyl- <i>L</i> -valine	Ag <sub>2</sub> CO <sub>3</sub>	HFIP	55

3	Pd(dba) <sub>2</sub>	<i>N</i> -acetyl- <i>L</i> -isoleucine	Ag <sub>2</sub> CO <sub>3</sub>	HFIP	60
4	Pd(dba) <sub>2</sub>	<i>N</i> -acetyl- <i>L</i> -phenylalanine	Ag <sub>2</sub> CO <sub>3</sub>	HFIP	71
5	Pd(dba) <sub>2</sub>	none	Ag <sub>2</sub> CO <sub>3</sub>	HFIP	0
6	Pd(dba) <sub>2</sub>	<i>N</i> -acetyl- <i>L</i> -phenylalanine	AgTFA	HFIP	trace
7	Pd(dba) <sub>2</sub>	<i>N</i> -acetyl- <i>L</i> -phenylalanine	Ag <sub>2</sub> O	HFIP	64
8	Pd(dba) <sub>2</sub>	<i>N</i> -acetyl- <i>L</i> -phenylalanine	AgOAc	HFIP	trace
9	Pd(dba) <sub>2</sub>	<i>N</i> -acetyl- <i>L</i> -phenylalanine	none	HFIP	0
10	Pd <sub>2</sub> (dba) <sub>3</sub>	<i>N</i> -acetyl- <i>L</i> -phenylalanine	Ag <sub>2</sub> CO <sub>3</sub>	HFIP	68
11	Pd(acac) <sub>2</sub>	<i>N</i> -acetyl- <i>L</i> -phenylalanine	Ag <sub>2</sub> CO <sub>3</sub>	HFIP	trace
12	Pd(OAc) <sub>2</sub>	<i>N</i> -acetyl- <i>L</i> -phenylalanine	Ag <sub>2</sub> CO <sub>3</sub>	HFIP	trace
13	none	<i>N</i> -acetyl- <i>L</i> -phenylalanine	Ag <sub>2</sub> CO <sub>3</sub>	HFIP	0
14	Pd(dba) <sub>2</sub>	<i>N</i> -acetyl- <i>L</i> -phenylalanine	Ag <sub>2</sub> CO <sub>3</sub>	DCE	0
15	Pd(dba) <sub>2</sub>	<i>N</i> -acetyl- <i>L</i> -phenylalanine	Ag <sub>2</sub> CO <sub>3</sub>	DMF	0
16	Pd(dba) <sub>2</sub>	<i>N</i> -acetyl- <i>L</i> -phenylalanine	Ag <sub>2</sub> CO <sub>3</sub>	Toluene	0

<sup>a</sup>Reaction conditions: **1a** (0.20 mmol), **2a** (0.60 mmol), catalyst (10 mol %), ligand (20 mol %), oxidant (0.30 mmol) and solvent (1 mL) at 100 °C for 36 h under N<sub>2</sub>. HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

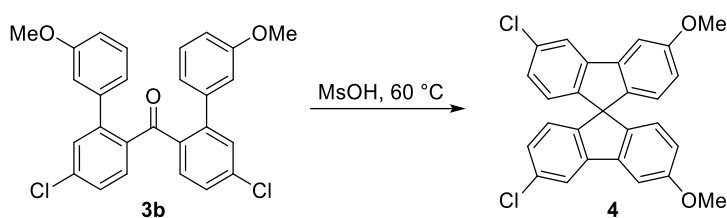
### Synthesis of compound **3b**



A 120 mL Schlenk tube with a magnetic stir bar was charged with **1b** (1.12 g, 4.0 mmol, 1.0 equiv), **2b** (2.81 g, 12.0 mmol, 3.0 equiv), Pd(dba)<sub>2</sub> (226.8 mg, 0.4 mmol, 10.0 mol%), *N*-acetyl-*L*-phenylalanine (165.8 mg, 0.8 mmol, 20 mol%), Ag<sub>2</sub>CO<sub>3</sub> (1.65 g, 6.0 mmol, 1.5 equiv) and HFIP (10.0 mL) under a nitrogen atmosphere. The reaction mixture was heated at 100 °C for 36 hours. The reaction mixture was cooled to room temperature and remove solvent under reduced pressure. Then add THF (10.0 mL) and HCl (4.0 mL) to Schlenk under an air atmosphere. The reaction mixture was heated at 100 °C for 12 hours. The reaction mixture was cooled to room temperature, diluted with 20 mL CH<sub>2</sub>Cl<sub>2</sub>, filtered through a celite pad, and washed with 50-60 mL CH<sub>2</sub>Cl<sub>2</sub>. The

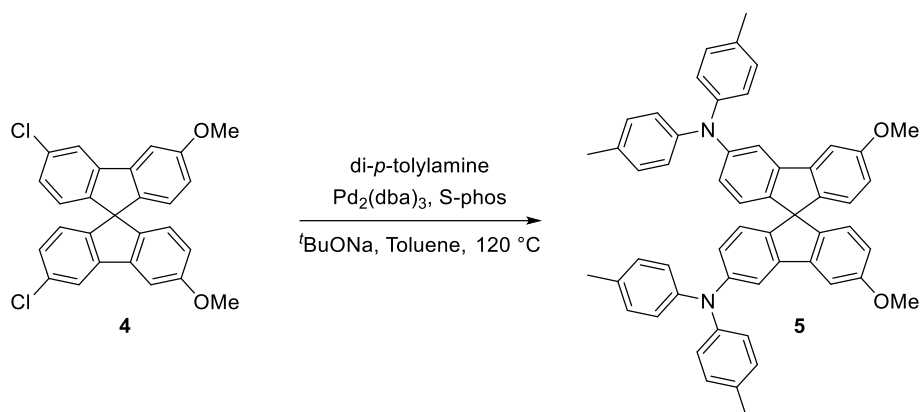
filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) to give a yellow solid **3b** (1.15 g, 62% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.24-7.22 (m, 2H), 7.13-7.09 (m, 6H), 6.75 (dd,  $J_1$  = 2.4,  $J_2$  = 8.4, 2H), 6.61 (d,  $J$  = 7.2, 2H), 6.54-6.53 (m, 2H), 3.76 (s, 6H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 198.95, 159.23, 142.68, 140.43, 137.64, 136.55, 131.88, 129.72, 129.29, 126.97, 121.49, 114.85, 113.24, 55.40 ppm. HRMS (ESI $^+$ ): calcd for  $\text{C}_{27}\text{H}_{20}\text{Cl}_2\text{NaO}_3$   $[\text{M}+\text{Na}]^+$  485.0682, 486.0715, 487.0652, found 485.0676, 486.0711, 487.0657.

### Synthesis of compound **4**



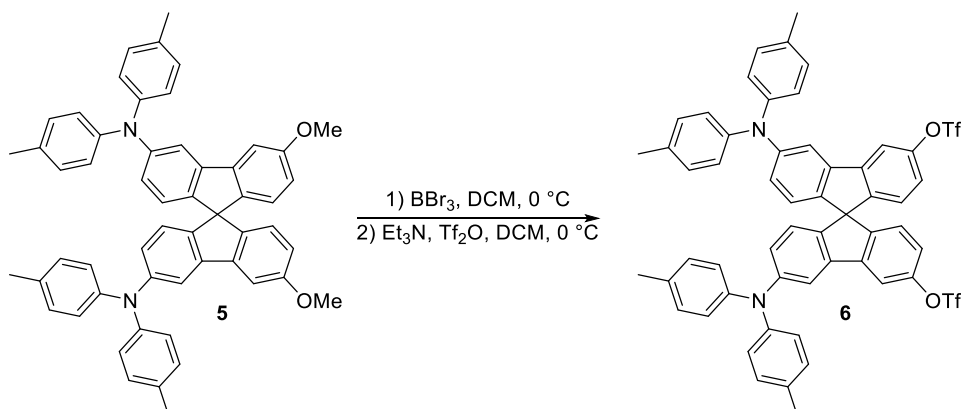
The preparation of **4** was carried out using the method described in the literature.<sup>2</sup> The compound **3b** (11.55 g, 25.0 mmol) was added to 100 mL of methanesulfonic acid and was stirred at 60 °C for 12 h. The reaction mixture was poured into ice-cold water, extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$  30 mL). The organic phase was washed with aqueous  $\text{NaHCO}_3$  and brine, dried over  $\text{MgSO}_4$ , and concentrated under reduced pressure. This solid was recrystallization in  $\text{CH}_2\text{Cl}_2$  to give a white solid **4** (9.10 g, 82%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.75 (d,  $J$  = 1.6, 2H), 7.30 (d,  $J$  = 2.4, 2H), 7.07 (dd,  $J_1$  = 2.0,  $J_2$  = 8.0, 2H), 6.72-6.70 (m, 2H), 6.64-6.61 (m, 4H), 3.88 (s, 6H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 160.19, 147.73, 143.38, 141.85, 140.66, 133.90, 128.02, 125.10, 124.89, 120.41, 115.08, 105.46, 64.03, 55.73 ppm. HRMS (ESI $^+$ ): calcd for  $\text{C}_{27}\text{H}_{19}\text{ClO}_3$   $[\text{M}+\text{H}]^+$  445.0757, 447.0727, 446.0790, found 445.0753, 447.0731, 446.0785.

## Synthesis of compound 5



A Schlenk tube with a magnetic stir bar was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (457.5 mg, 5 mol%), S-phos (615.8 mg, 15 mol%), <sup>t</sup>BuONa (3.84 g, 40.0 mmol, 4.0 equiv), compound 4 (4.44 g, 10.0 mmol, 1.0 equiv), di-*p*-tolylamine (4.14 g, 21.0 mmol, 2.1 equiv), toluene (30 mL) under a nitrogen atmosphere. The resulting mixture was heated to 120 °C and stirred for 24 h. The reaction mixture was cooled to room temperature, diluted with 30 mL CH<sub>2</sub>Cl<sub>2</sub>, filtered through a celite pad, and washed with 30 mL CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 3/1, v/v) to give a white solid 5 (6.44 g, 84% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.46 (d, *J* = 2.4, 2H), 7.15 (d, *J* = 2.0, 2H), 7.09-7.03 (m, 16H), 6.79 (dd, *J*<sub>1</sub> = 2.4, *J*<sub>2</sub> = 8.4, 2H), 6.70-6.65 (m, 4H), 6.61 (d, *J* = 8.4, 2H), 3.83 (s, 6H), 2.33 (s, 12H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 159.76, 147.96, 145.73, 143.52, 142.87, 142.47, 141.82, 132.30, 129.99, 124.68, 124.45, 123.44, 114.66, 114.26, 105.02, 63.98, 55.72, 20.96 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>55</sub>H<sub>47</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 767.3632, found 767.3632.

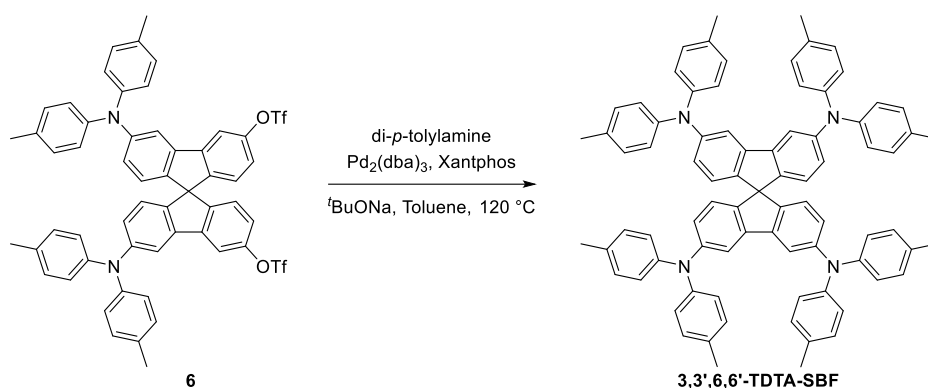
## Synthesis of compound 6



The preparation of **6** was carried out using the method described in the literature.<sup>3</sup> Compound **5** (6.13 g, 8.0 mmol, 1.0 equiv) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) and cooled down to 0 °C. Boron tribromide (3.10 mL, 32.0 mmol, 4.0 equiv) was then added dropwise to the solution at 0 °C. The reaction mixture was allowed to warm up to room temperature and stirred for 12 h, the mixture was then cooled to 0°C and quenched with cold water (50 mL). The organic layer was separated, washed with NaHCO<sub>3</sub> (aq.) then brine. The combined organic extracts were dried over sodium sulfate and concentrated under reduced pressure. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) before Et<sub>3</sub>N (2.80 mL, 20.0 mmol, 2.5 equiv) was added and the reaction mixture was stirred at 0 °C for 30 minutes. A solution of trifluoromethanesulfonic anhydride (4.00 mL, 24.0 mmol, 3.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (24 mL) was added to above mixture, then warmed to room temperature. After stirred for 12 h, cold water (100 mL) was added, and the organic layer was separated. The combined organic extracts were dried over sodium sulfate and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 4/1, v/v) to give a white solid **6** (6.17 g, 77% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.49 (d, *J* = 2.0, 2H), 7.45 (d, *J* = 1.6, 2H), 7.11 (d, *J* = 8.0, 8H), 7.05 (d, *J* = 8.0, 8H), 6.99 (dd, *J*<sub>1</sub> = 8.4, *J*<sub>2</sub> = 2.4, 2H), 6.88 (dd, *J*<sub>1</sub> = 8.4, *J*<sub>2</sub> = 2.0, 2H), 6.80 (d, *J* = 8.0, 2H), 6.62 (d, *J* = 8.4, 2H), 2.35 (s, 12 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 149.45, 148.90, 148.65, 145.17, 143.99, 140.85, 140.67, 132.97, 130.08, 125.37, 124.79, 122.02 (q, *J* = 342.0 Hz), 117.12, 114.09 (d, *J* = 4.0 Hz), 113.37 (d, *J* = 4.0 Hz), 64.18, 20.85 ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ = 72.92 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>55</sub>H<sub>44</sub>F<sub>6</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub> [M+H]<sup>+</sup> 1003.2305, found 1003.2306.

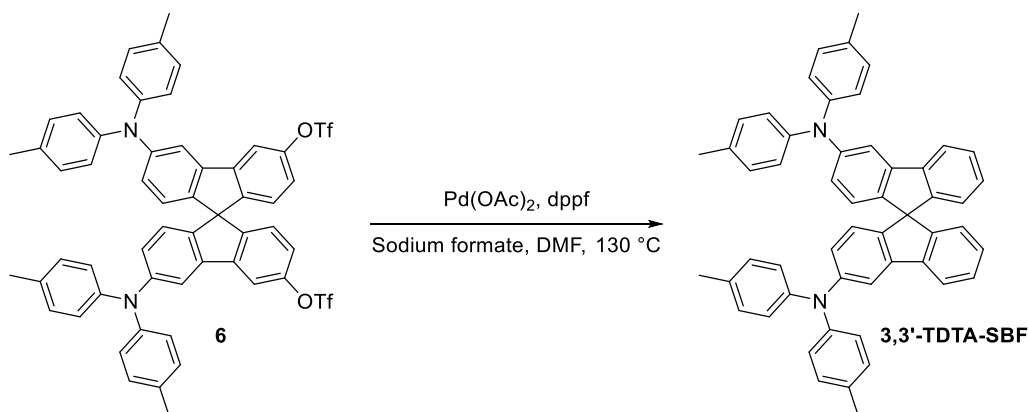


### Synthesis of compound 3,3',6,6'-TDTA-SBF



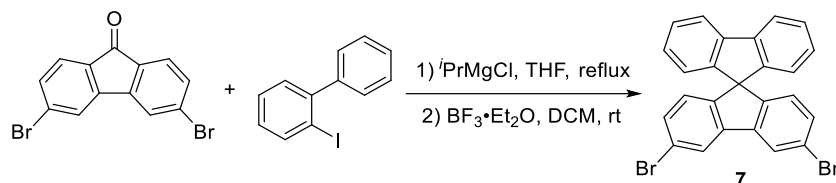
A Schlenk tube with a magnetic stir bar was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (137.3 mg, 5 mol%), Xantphos (260.4 mg, 15 mol%), <sup>t</sup>BuONa (1.15 g, 12.0 mmol, 4.0 equiv), compound **6** (3.00 g, 3.0 mmol, 1.0 equiv), di-*p*-tolylamine (1.24 g, 6.3 mmol, 2.1 equiv), toluene (10 mL) under a nitrogen atmosphere. The resulting mixture was heated to 120 °C and stirred for 24 h. The reaction mixture was cooled to room temperature, diluted with 10 mL CH<sub>2</sub>Cl<sub>2</sub>, filtered through a celite pad, and washed with 20 mL CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 8/1, v/v) to give a white solid **3,3',6,6'-TDTA-SBF** (2.47 g, 75% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.37 (d, *J* = 2.0, 4H), 7.07-6.99 (m, 32 H), 6.82 (dd, *J*<sub>1</sub> = 8.0, *J*<sub>2</sub> = 2.0, 4H), 6.69 (d, *J* = 8.0, 4H), 2.32 (s, 24 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 147.88, 145.79, 143.68, 142.62, 132.10, 129.98, 124.68, 124.14, 124.04, 115.55, 64.32, 20.93 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>81</sub>H<sub>69</sub>N<sub>4</sub> [M+H]<sup>+</sup> 1097.5517, found 1097.5509.

### Synthesis of compound 3,3'-DDTA-SBF



A Schlenk tube with a magnetic stir bar was charged with Pd(OAc)<sub>2</sub> (66.0 mg, 5 mol%), dppf (249.5 mg, 15 mol%), sodium formate (816.1 mg, 12.0 mmol, 4.0 equiv), compound **6** (3.00 g, 3.0 mmol, 1.0 equiv), DMF (20 mL) under a nitrogen atmosphere. The resulting mixture was heated to 130 °C and stirred for 24 h. The reaction mixture was cooled to room temperature, diluted with 10 mL CH<sub>2</sub>Cl<sub>2</sub>, filtered through a celite pad, and washed with 20 mL CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 8/1, v/v) to give a white solid **3,3'-DDTA-SBF** (1.86 g, 88% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.65 (d, *J* = 7.6, 2H), 7.52 (s, 2H), 7.30 (t, *J* = 7.2, 2H), 7.13-7.06 (m, 18H), 6.84-6.78 (m, 4H), 6.65 (d, *J* = 8.4, 2H), 2.35 (s, 12H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 149.82, 148.15, 145.71, 142.74, 142.26, 141.67, 132.37, 130.00, 127.80, 127.55, 124.56, 124.54, 124.11, 123.18, 120.12, 114.60, 65.22, 20.97 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>53</sub>H<sub>43</sub>N<sub>2</sub> [M+H]<sup>+</sup> 707.3421, found 707.3417.

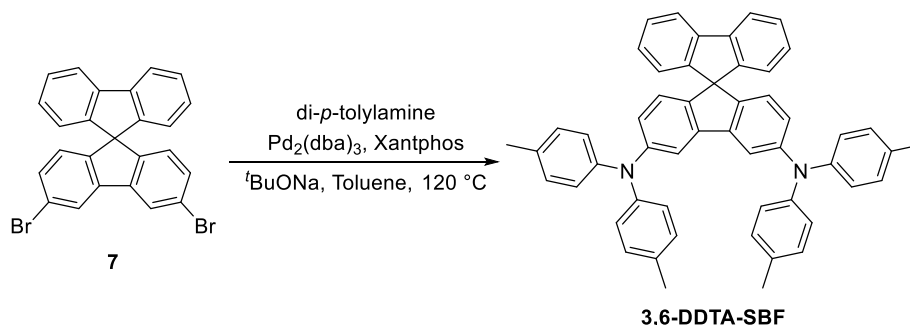
### Synthesis of compound **7**



2-Iodobiphenyl (1.40 g, 5.0 mmol, 1.0 equiv) was dissolved in dry THF (20 mL) and cooled down to 0 °C. A 2 M pentane solution of *i*-PrMgCl (1.1 equiv, 2.8 mL, 5.5 mmol, 1.1 equiv) was then added dropwise to the solution at 0 °C. The resulting mixture was stirred at the same temperature for one hour and the 3,6-dibromofluorene-9-one (1.69 g, 5.0 mmol, 1.0 equiv) dissolved in dry THF (20 mL) was added dropwise with a syringe. The reaction was allowed to stir at 0 °C for additional 30 minutes. The reaction mixture was allowed to warm up to 75 °C and stirred for 24 h. After cooling to room temperature, a saturated solution of ammonium chloride was added. The organic layer was extracted with ethyl acetate. The combined organic extracts were dried over sodium sulfate and concentrated under reduced pressure. The residue was dissolved in DCE (20 mL) before trifluoroboron etherate (3.1 mL, 25.0 mmol, 5.0 equiv) was added slowly and the solution was stirred for 3 h at room temperature. The reaction was quenched

with methanol and evaporated under reduced pressure. The residue was purified by column chromatography (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 6/1, v/v) to give the desired product. Compound **7** has been reported in the literature.<sup>4</sup>

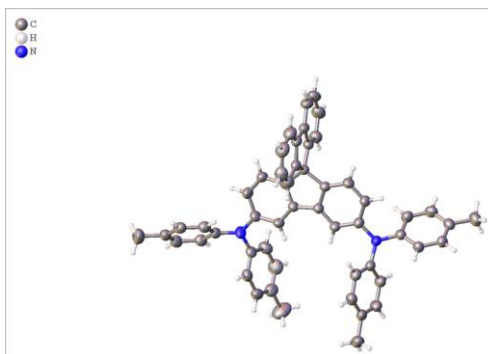
### Synthesis of compound **3,6-DDTA-SBF**



A Schlenk tube with a magnetic stir bar was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (109.8 mg, 5mol%), Xantphos (208.3 mg, 15mol%), <sup>t</sup>BuONa (920.1 mg, 9.6 mmol, 4.0 equiv), compound **7** (1.78 g, 2.4 mmol, 1.0 equiv), di-*p*-tolylamine (992.0 mg, 5.0 mmol, 2.1 equiv), toluene (10 mL) under a nitrogen atmosphere. The resulting mixture was heated to 120 °C and stirred for 24 h. The reaction mixture was cooled to room temperature, diluted with 10 mL CH<sub>2</sub>Cl<sub>2</sub>, filtered through a celite pad, and washed with 20 mL CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 8/1, v/v) to give a white solid **3,6-DDTA-SBF** (1.27 g, 75% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.82 (d, *J* = 7.6, 2H), 7.39-7.35 (m, 4 H), 7.18 (t, *J* = 8.0, 2H), 7.06-6.99 (m, 16 H), 6.91 (d, *J* = 7.6, 2H), 6.76 (dd, *J*<sub>1</sub> = 8.4, *J*<sub>2</sub> = 2.4, 2H), 6.54 (d, *J* = 8.4, 2H), 2.31 (s, 12 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 149.35, 148.00, 145.73, 143.14, 142.78, 141.71, 132.15, 129.97, 127.86, 127.69, 124.49, 124.27, 124.17, 124.01, 120.06, 115.45, 65.20, 20.93 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>53</sub>H<sub>43</sub>N<sub>2</sub> [M+H]<sup>+</sup> 707.3421, found 707.3421.

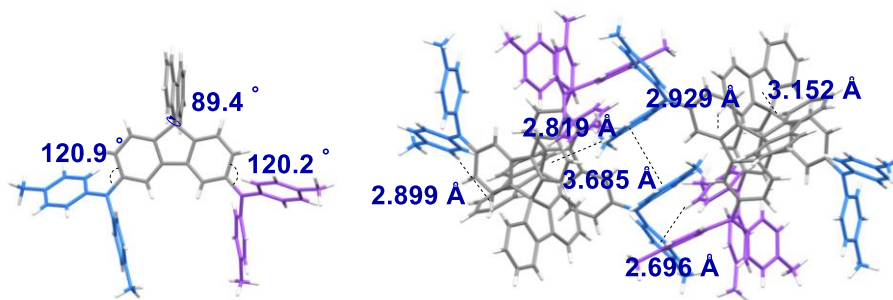
## IV. Crystal data

**Table S2.** Crystal Data for **3,6-DDTA-SBF** (CCDC 2370368)

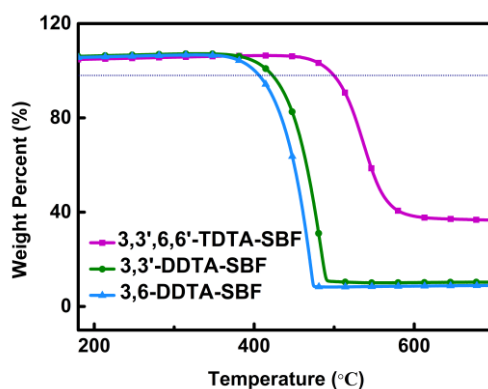


Identification code	<b>3,6-DDTA-SBF</b>
Empirical formula	C <sub>53</sub> H <sub>42</sub> N <sub>2</sub>
Formula weight	706.88
Temperature/K	150.0
Crystal system	orthorhombic
Space group	Pbca
a/Å	19.1121(13)
b/Å	13.8417(9)
c/Å	30.0202(17)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	7941.7(9)
Z	8
ρ <sub>calc</sub> /cm <sup>3</sup>	1.182
μ/mm <sup>-1</sup>	0.068
F(000)	2992.0
Crystal size/mm <sup>3</sup>	0.43 × 0.08 × 0.07
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.262 to 49.996
Index ranges	-22 ≤ h ≤ 22, -16 ≤ k ≤ 14, -35 ≤ l ≤ 35
Reflections collected	45883
Independent reflections	6971 [R <sub>int</sub> = 0.1295, R <sub>sigma</sub> = 0.0776]
Data/restraints/parameters	6971/0/501
Goodness-of-fit on F <sup>2</sup>	1.039
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0537, wR <sub>2</sub> = 0.1284
Final R indexes [all data]	R <sub>1</sub> = 0.0877, wR <sub>2</sub> = 0.1548
Largest diff. peak/hole / e Å <sup>-3</sup>	0.21/-0.19

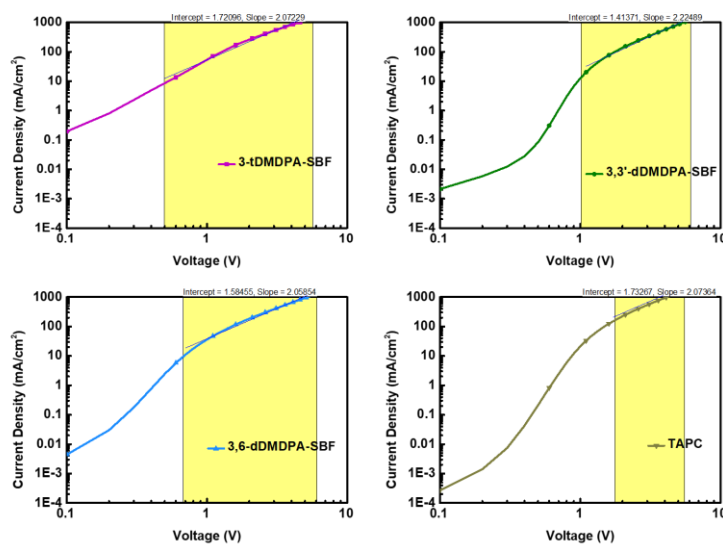
## V. Additional spectra and data



*Fig. S1* Single crystal X-ray structure and packing pattern of **3,6-DDTA-SBF**.



*Fig. S2* TGA curves of **3,3',6,6'-TDTA-SBF**, **3,3'-DDTA-SBF** and **3,6-DDTA-SBF**.



*Fig. S3* Current density ( $J$ )-voltage ( $V$ ) curves of **3,3',6,6'-TDTA-SBF**-, **3,3'-DDTA-SBF**-, **3,6-DDTA-SBF**- and **TAPC**-based hole-only devices (HODs) devices.

Based on the Schottky thermionic region and space-charge-limited current (SCLC)

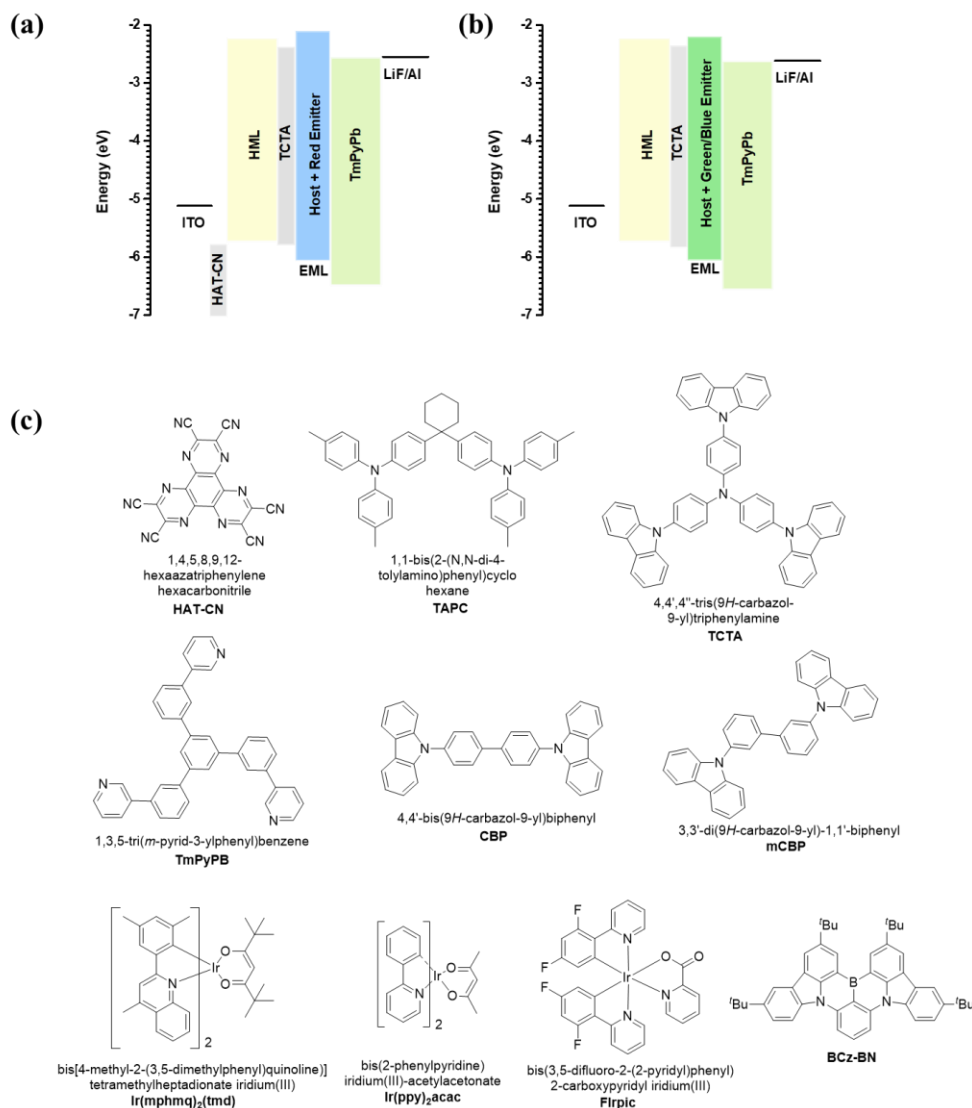
model, the curves can be divided into two parts under low bias. We assign the second region of the  $J$ - $V$  curve as assigned as the SCLC region, which then can be described by an equation:

$$J = \frac{9}{8} \varepsilon \varepsilon_0 \mu \frac{V^2}{L^3}$$

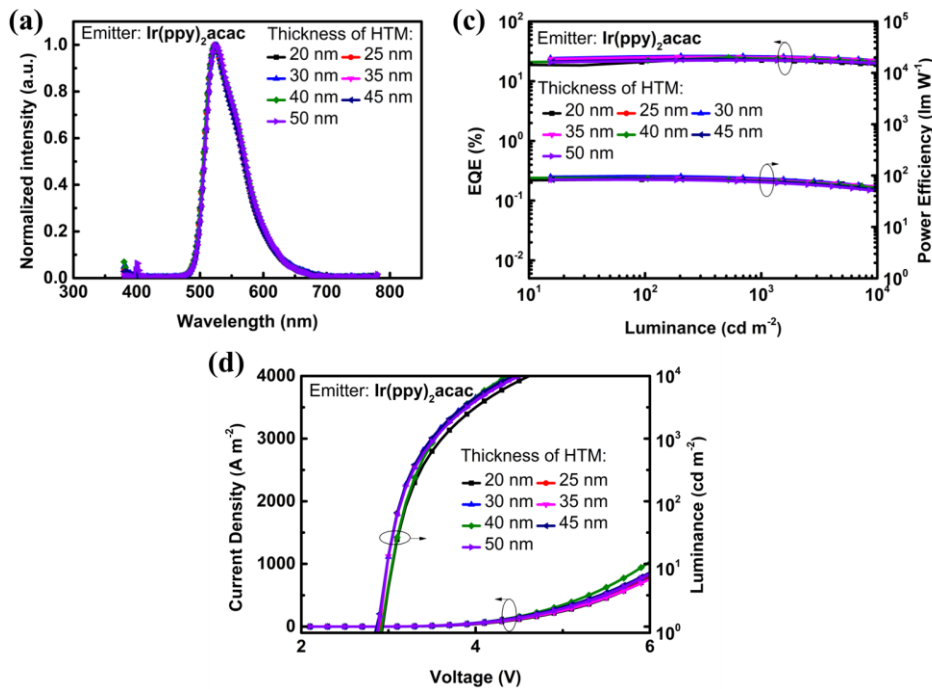
in which  $V$  is the driving voltage,  $L$  is the thickness of the thin layer,  $\varepsilon_0$  the permittivity of the free space,  $\varepsilon$  is the relative dielectric constant (estimated to be 3.0 here). The thickness  $L$  equals to 120 nm, and the hole mobilities of these compounds were calculated and summarized in Table 1.

## VI. OLED characteristics

The device configuration of red PhOLEDs is ITO/HAT-CN (10 nm)/HML (25 nm)/TCTA (10 nm)/CBP: 1 wt% Ir(mphmq)<sub>2</sub>tmd (10 nm)/TmPyPB (50 nm) LiF (0.8 nm)/Al (100 nm). The device configuration of green PhOLEDs is ITO/ HML (30 nm)/TCTA (10 nm)/CBP: 10 wt% Ir(ppy)<sub>2</sub>acac (20 nm)/TmPyPB (40 nm)/LiF (0.8 nm)/Al (100 nm). The device configuration of blue PhOLEDs is ITO/HML (30 nm)/TCTA (10 nm)/mCBP: 15 wt% Flrpic (23 nm)/TmPyPB (40 nm)/LiF (0.8 nm)/Al (100 nm). The device configuration of BN-MR OLEDs is ITO/HML (30 nm)/TCTA (10 nm) /mCBP: 15 wt% Flrpic: 0.5 wt% BCz-BN (23 nm)/TmPyPB (40 nm)/LiF (0.8 nm)/Al (100 nm).



**Fig. S4** Device structure and energy-level diagram of OLED devices. (a) Red OLED devices structure with corresponding energy levels. (b) green and blue OLED devices structure with corresponding energy levels. (c) Molecular structures of the materials used in OLEDs.



**Fig. S5** OLED device performances. (a) Electroluminescence spectra at the luminance of  $1000 \text{ cd m}^{-2}$ , (b) luminance and current density versus voltage curves, and (c) EQE and power efficiency versus luminance curves of green PhOLEDs with different **3,3',6,6'-TDTA-SBF** thicknesses.

**Table S3.** Performance of green PhOLED devices with different HTM thicknesses<sup>a</sup>.

Thickness [nm]	EL <sub>peak</sub> [nm]	V <sub>on</sub> <sup>b</sup> [V]	CIE <sup>c</sup> [x, y]	EQE <sub>max/1000/5000</sub> <sup>d</sup> [%]	PE <sub>max/1000/5000</sub> <sup>e</sup> [lm W <sup>-1</sup> ]
20	524	3.0	[0.32,0.63]	22.9/22.3/20.5	85.0/82.4/68.9
25	523	3.0	[0.32,0.63]	25.4/24.7/22.8	92.1/82.9/68.1
30	524	3.0	[0.32,0.63]	26.4/26.0/24.3	97.6/87.1/71.4
35	524	3.0	[0.32,0.63]	25.6/25.1/23.4	89.2/82.5/67.2
40	524	3.0	[0.32,0.63]	24.9/23.9/22.6	90.5/79.3/66.2
45	524	3.0	[0.32,0.63]	23.5/22.7/21.4	86.1/76.1/62.8
50	524	3.0	[0.32,0.63]	22.0/21.6/20.0	83.2/74.4/58.5

<sup>a</sup>Green PhOLEDs device structure is ITO/ **3,3',6,6'-TDTA-SBF** (x nm)/TCTA (10 nm)/CBP: 10 wt% Ir(ppy)<sub>2</sub>acac (20 nm)/TmPyPB (40 nm)/LiF (0.8 nm)/Al (100 nm).

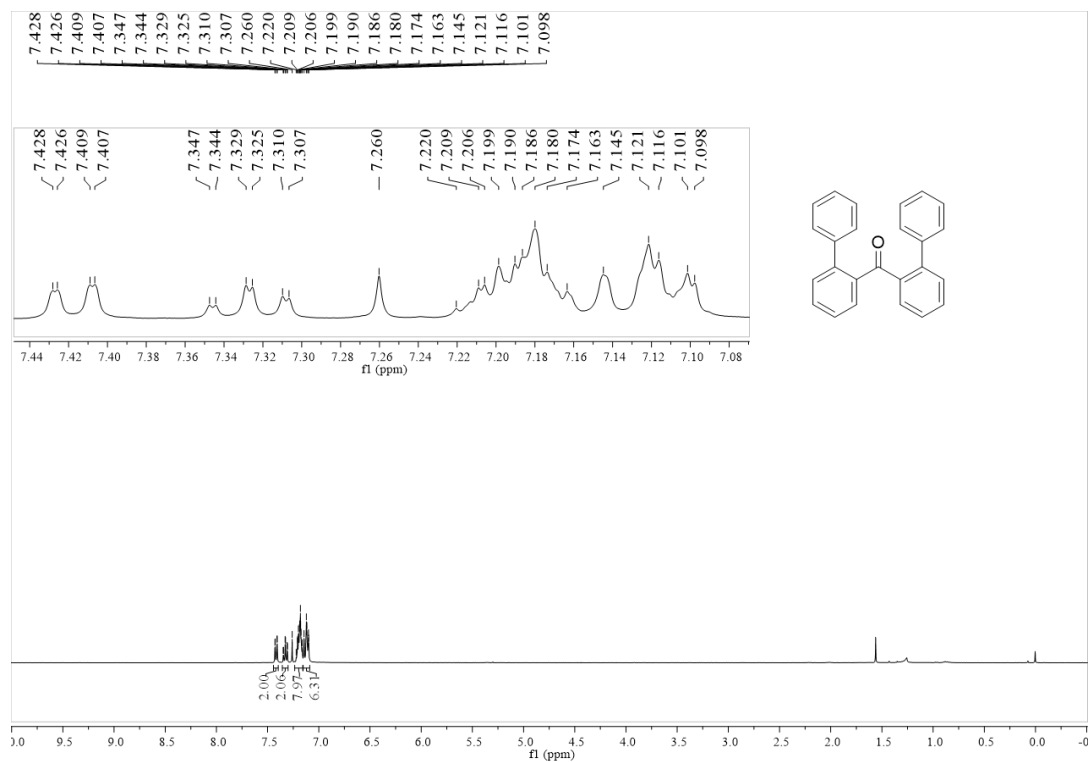
<sup>b</sup>Turn-on voltage. <sup>c</sup>Commission Internationale de l'Éclairage (CIE). <sup>d</sup>Maximum external quantum efficiency and external quantum efficiencies at the luminance of  $1000 \text{ cd m}^{-2}$  and  $5000 \text{ cd m}^{-2}$ . <sup>e</sup>Maximum power efficiency and power efficiencies at the luminance of  $1000 \text{ cd m}^{-2}$  and  $5000 \text{ cd m}^{-2}$ .



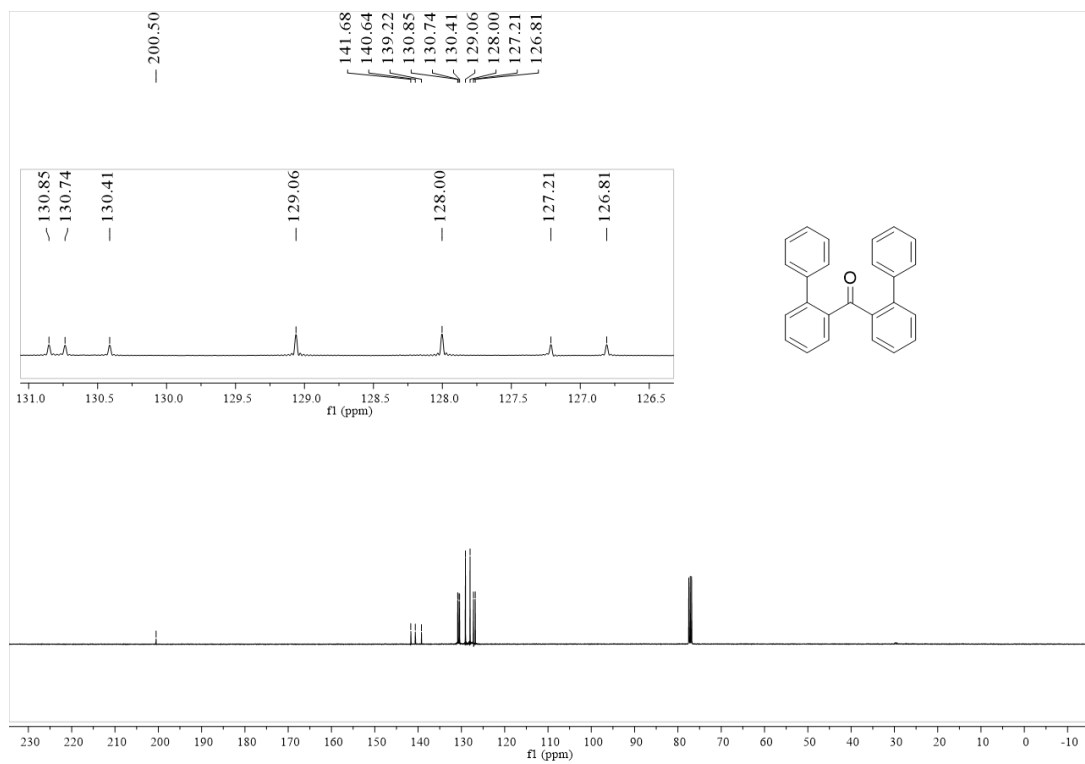
## VII. References

1. Q. Gao and S. Xu, *Org. Biomol. Chem.* 2018, **16**, 208-212.
2. X. Cheng, G.-H. Hou, J.-H. Xie and Q.-L. Zhou, *Org. Lett.* 2004, **6**, 2381-2383.
3. M. Lin, L. Bian, Q. Chen, H. Xu, Z. Liu and K. Zhu, *Angew. Chem. Int. Ed.* 2023, **62**, e202303035.
4. L. Wang, B. Pan, L. Zhu, B. Wang, Y. Wang, Y. Liu, J. Jin, J. Chen and D. Ma, *Dyes and Pigments* 2015, **114**, 222-230.

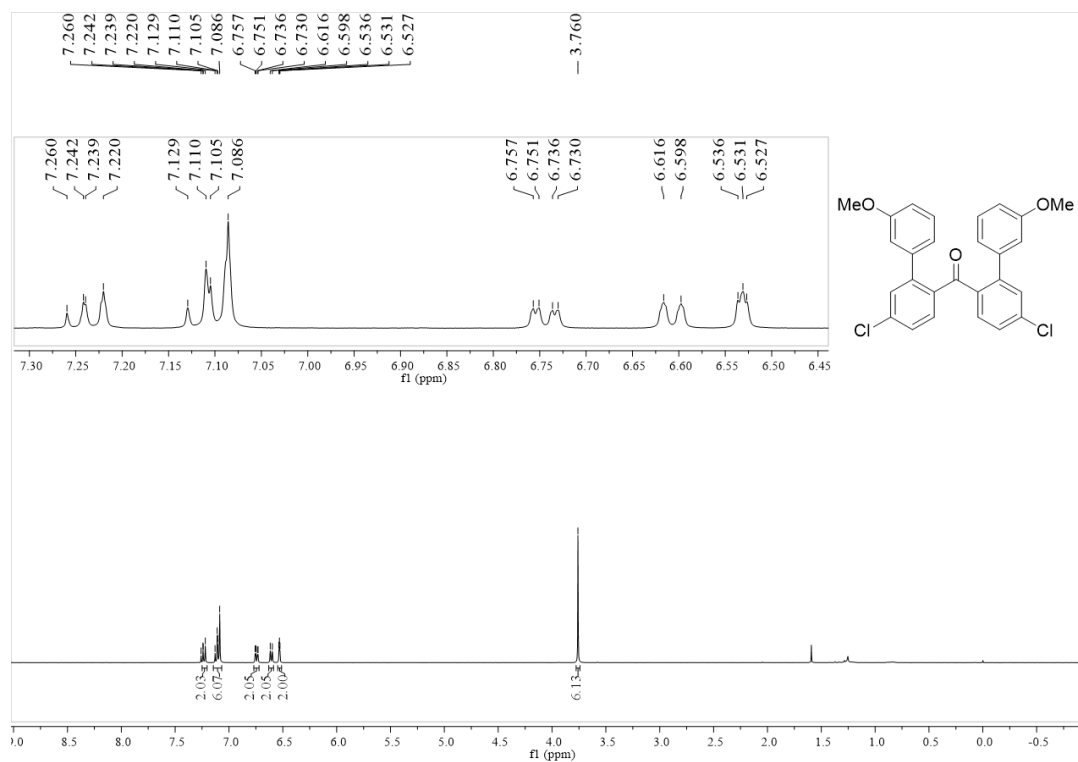
## VIII. Copies of NMR spectra



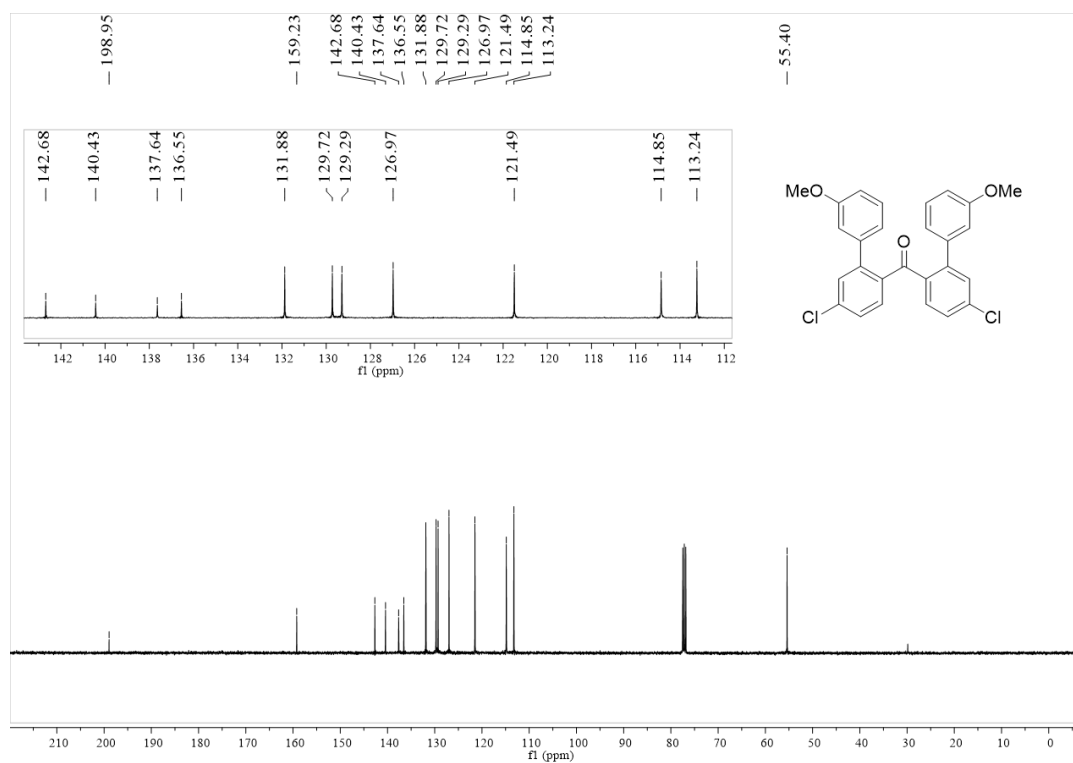
**Fig. S6** <sup>1</sup>H NMR spectrum of compound 3a in CDCl<sub>3</sub>.



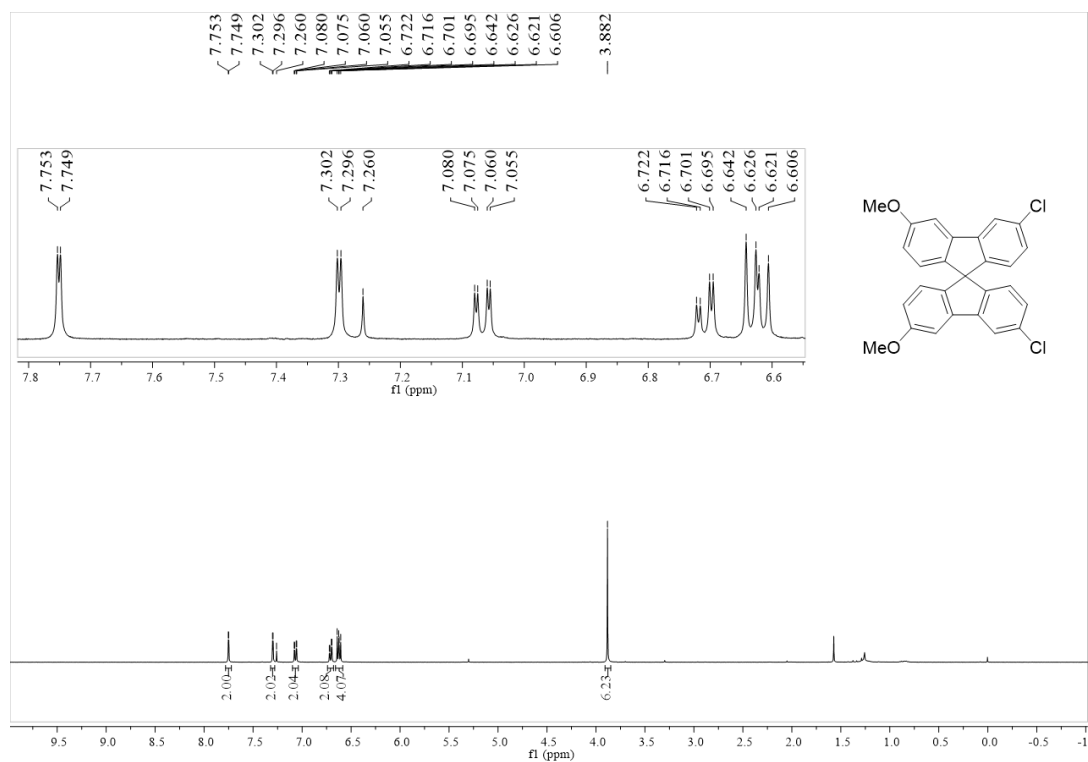
**Fig. S7** <sup>13</sup>C NMR spectrum of compound 3a in CDCl<sub>3</sub>.



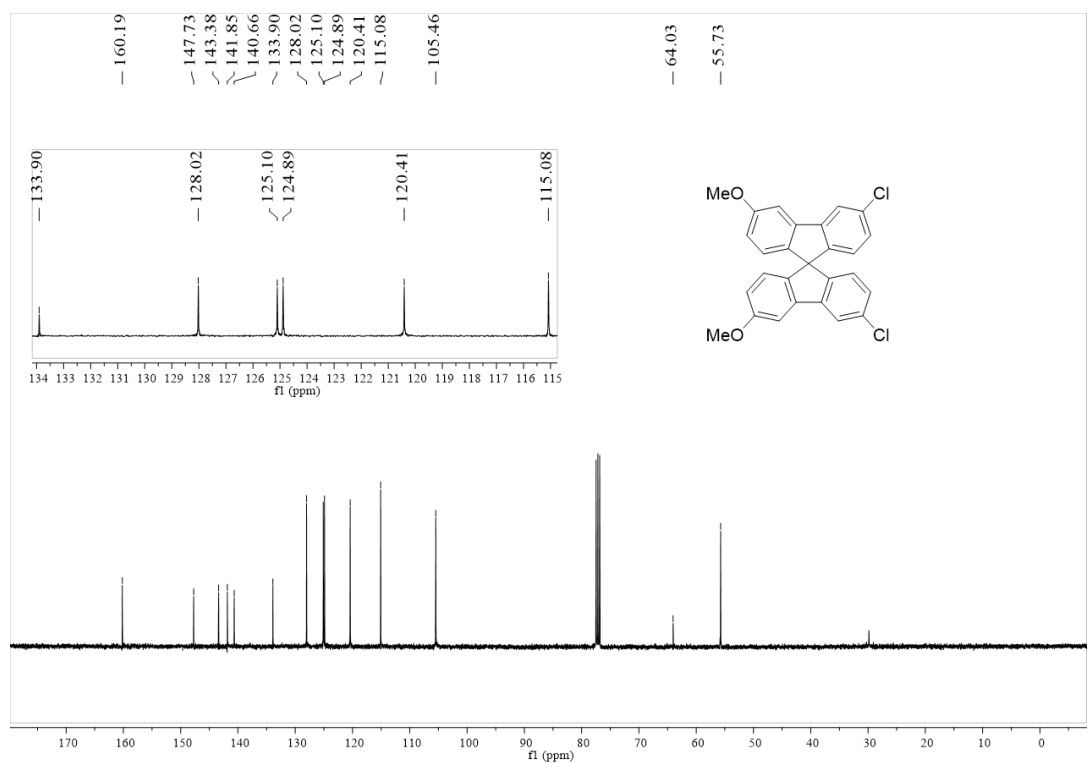
**Fig. S8** <sup>1</sup>H NMR spectrum of compound **3b** in CDCl<sub>3</sub>.



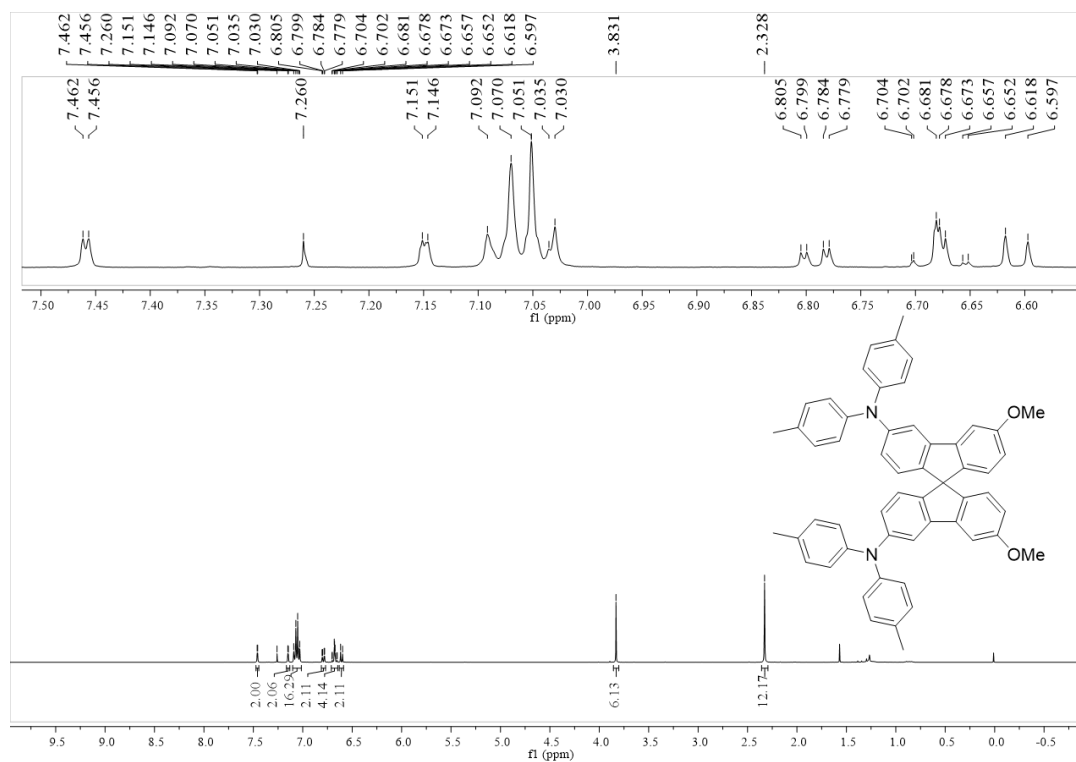
**Fig. S9** <sup>13</sup>C NMR spectrum of compound **3b** in CDCl<sub>3</sub>.



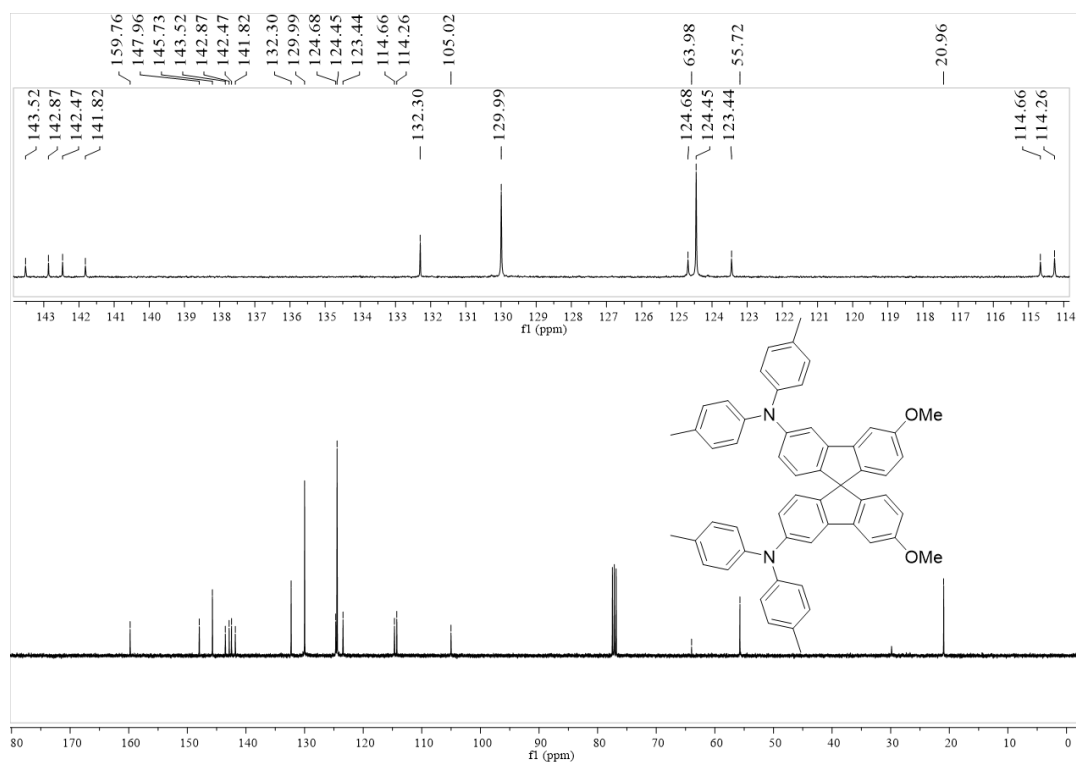
**Fig. S10** <sup>1</sup>H NMR spectrum of compound **4** in CDCl<sub>3</sub>.



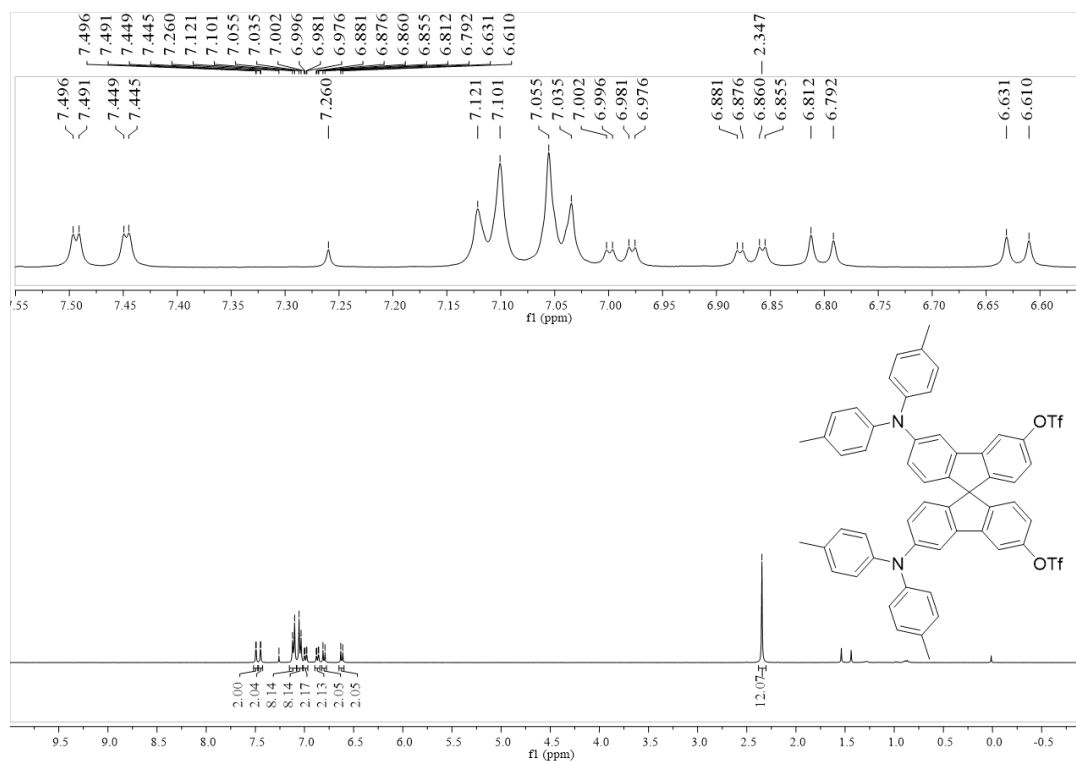
**Fig. S11** <sup>13</sup>C NMR spectrum of compound **4** in CDCl<sub>3</sub>.



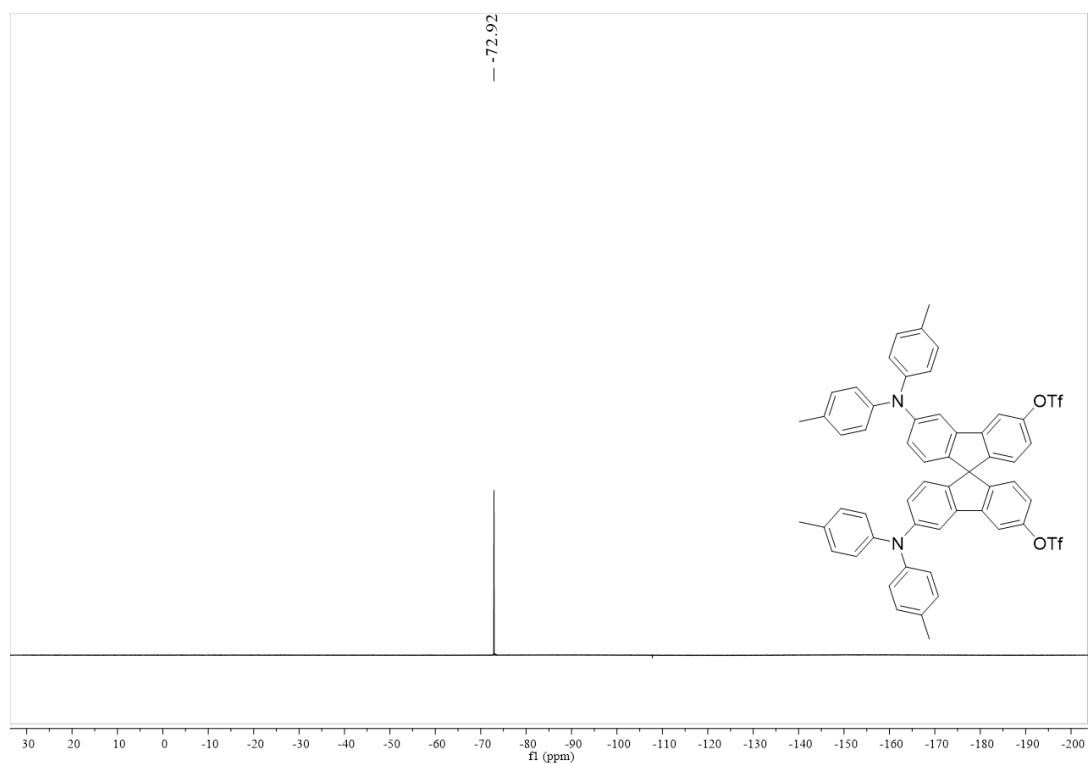
**Fig. S12** <sup>1</sup>H NMR spectrum of compound **5** in CDCl<sub>3</sub>.



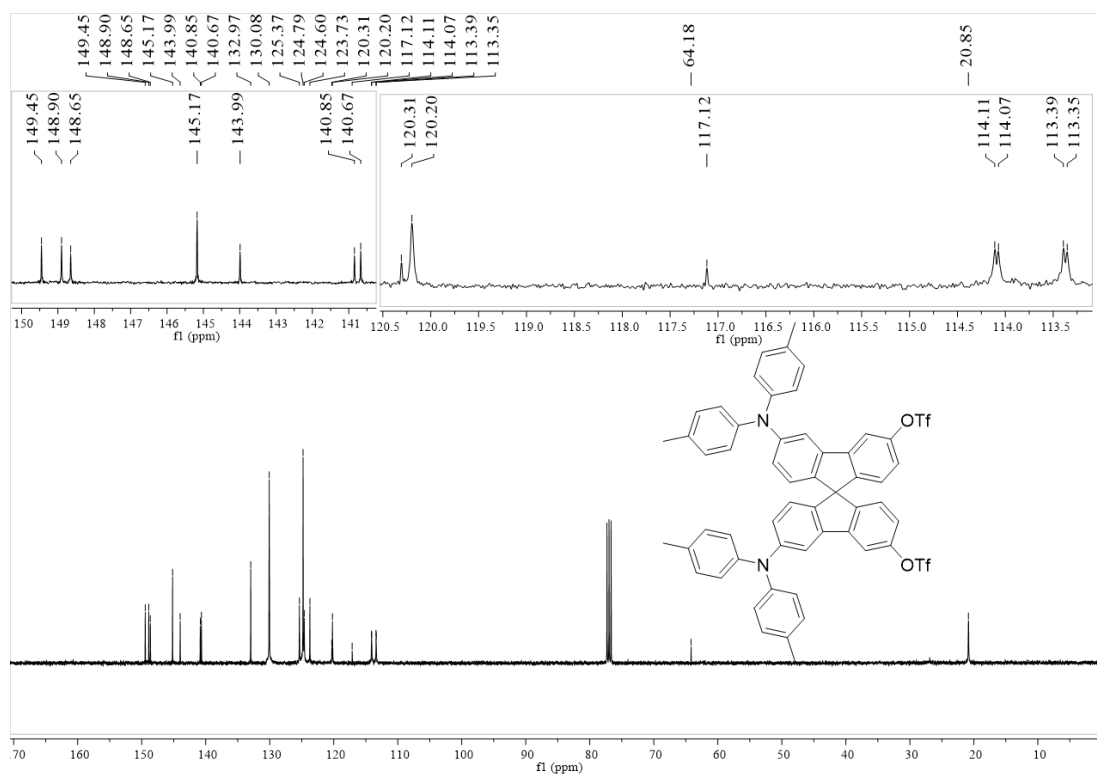
**Fig. S13** <sup>13</sup>C NMR spectrum of compound **5** in CDCl<sub>3</sub>.



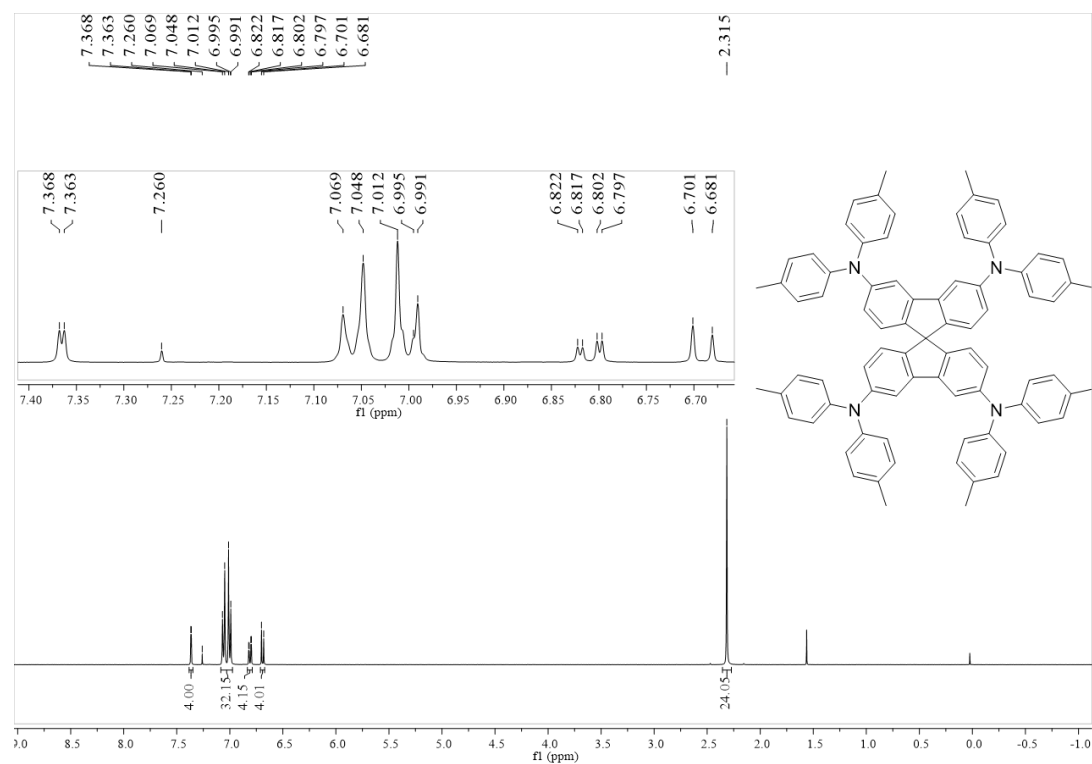
**Fig. S14**  $^1\text{H}$  NMR spectrum of compound **6** in  $\text{CDCl}_3$ .



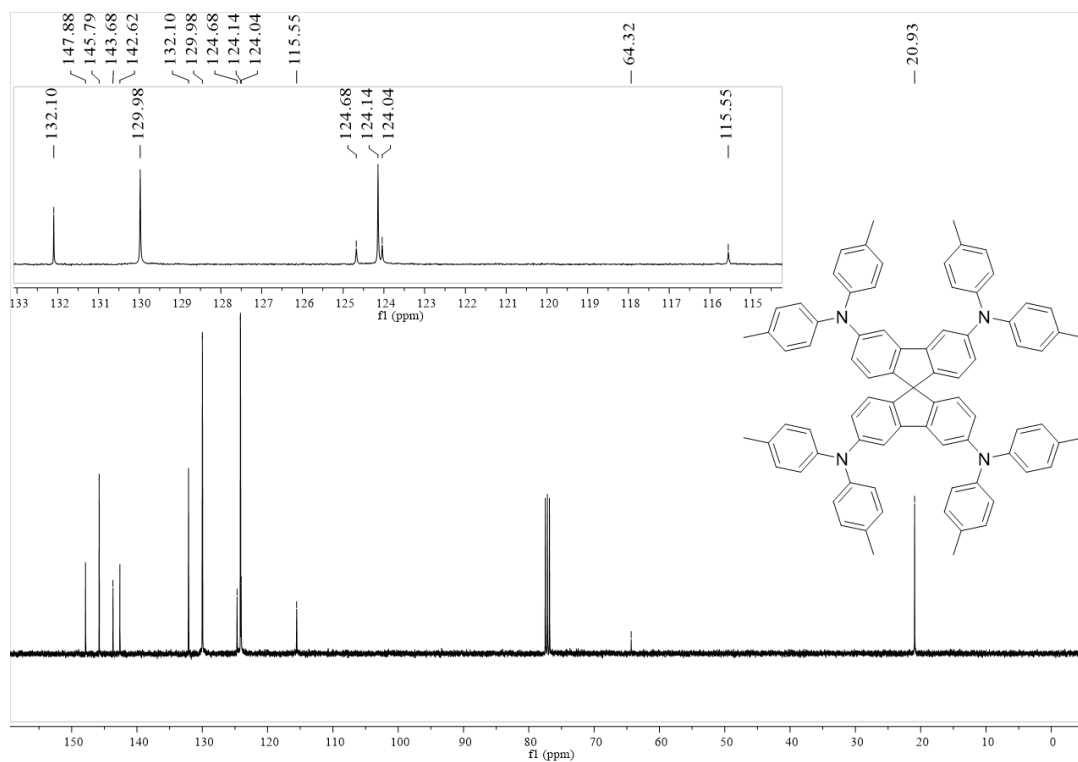
**Fig. S15**  $^{19}\text{F}$  NMR spectrum of compound **6** in  $\text{CDCl}_3$ .



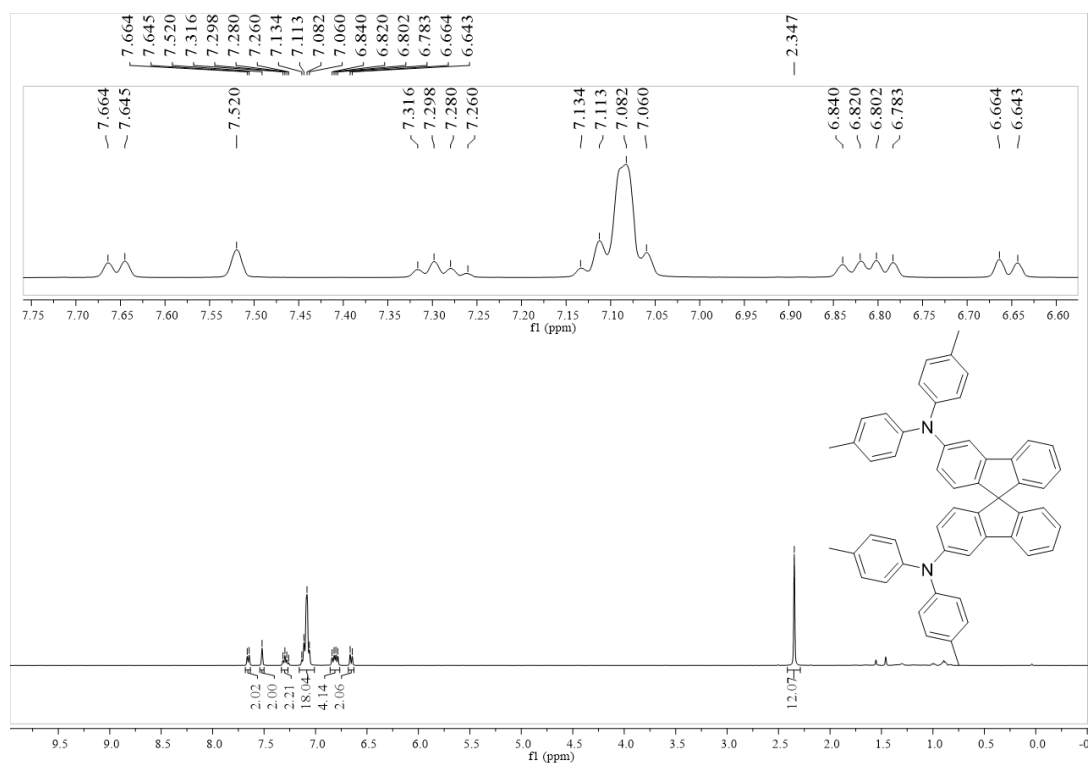
**Fig. S16** <sup>13</sup>C NMR spectrum of compound **6** in CDCl<sub>3</sub>.



**Fig. S17** <sup>1</sup>H NMR spectrum of compound **3,3',6,6'-TDTA-SBF** in CDCl<sub>3</sub>.

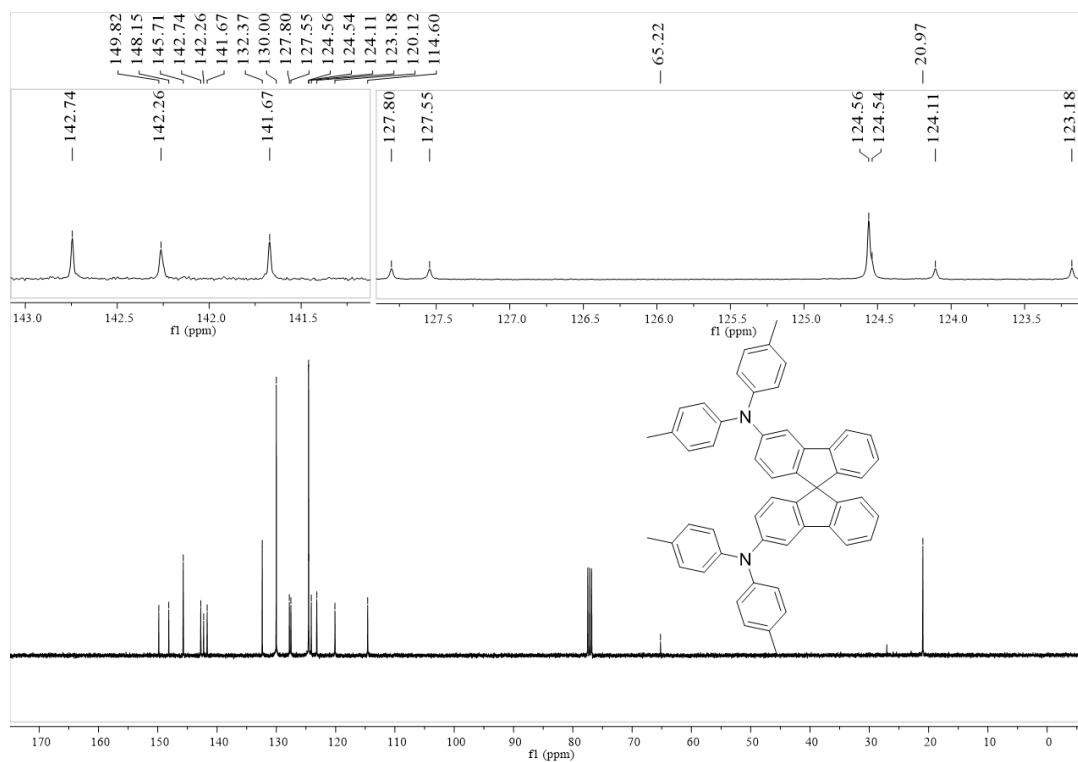


**Fig. S18** <sup>13</sup>C NMR spectrum of compound 3,3',6,6'-TDTA-SBF in CDCl<sub>3</sub>.

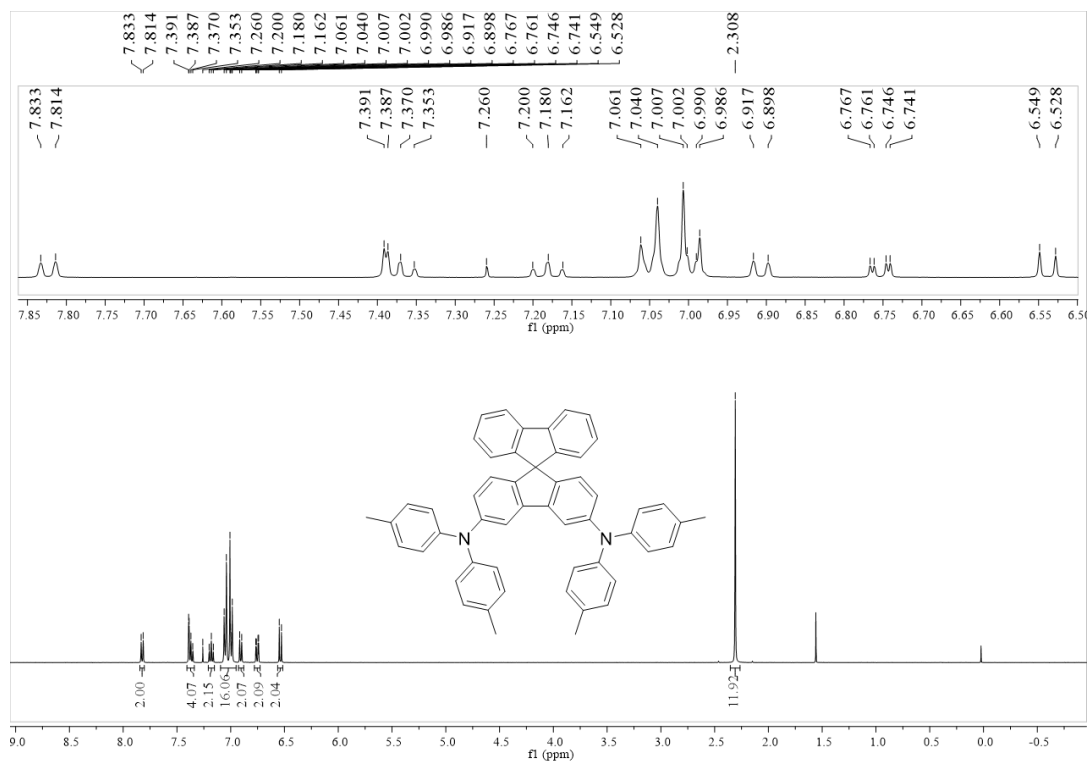


**Fig. S19** <sup>1</sup>H NMR spectrum of compound 3,3'-DDTA-SBF in CDCl<sub>3</sub>.

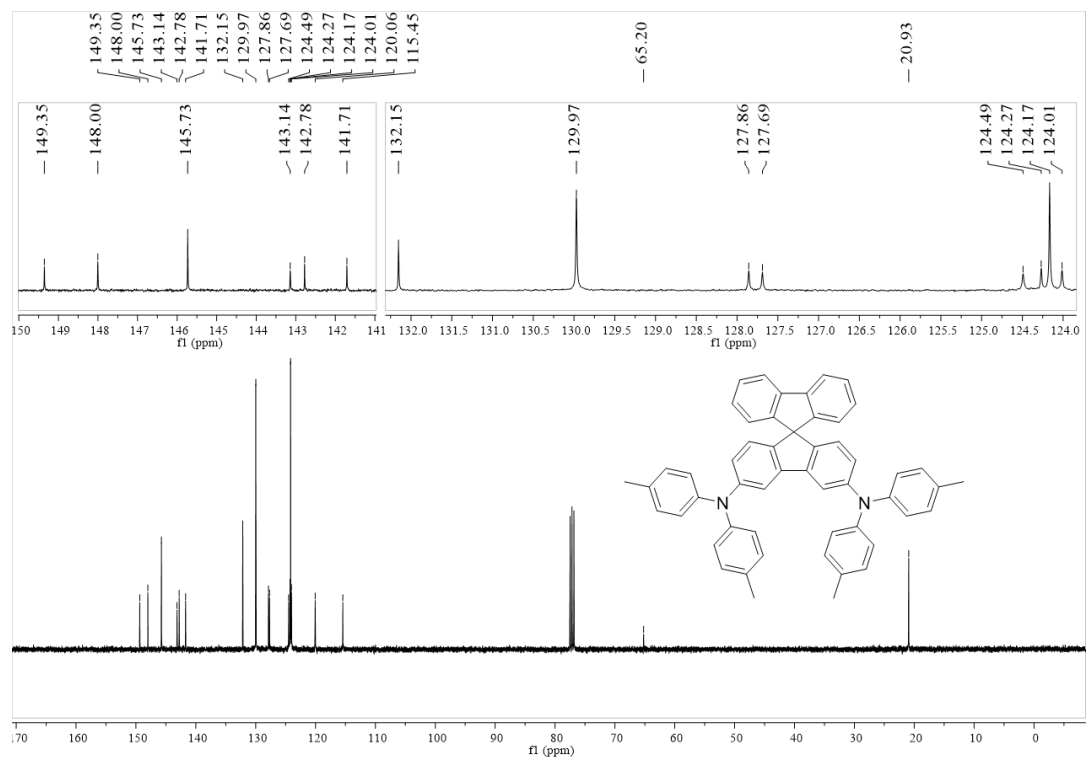




**Fig. S20** <sup>13</sup>C NMR spectrum of compound 3,3'-DDTA-SBF in CDCl<sub>3</sub>.



**Fig. S21** <sup>1</sup>H NMR spectrum of compound 3,6-DDTA-SBF in CDCl<sub>3</sub>.



**Fig. S22**  $^{13}\text{C}$  NMR spectrum of compound **3,6-DDTA-SBF** in  $\text{CDCl}_3$ .