Electronic Supplementary Material (ESI) for Materials Horizons.

Supporting Information

Spirobifluorene-Fused Strategy Enables Pure-Green Multiple Resonance Emitters with Low Efficiency Roll-Off

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I. General Remarks

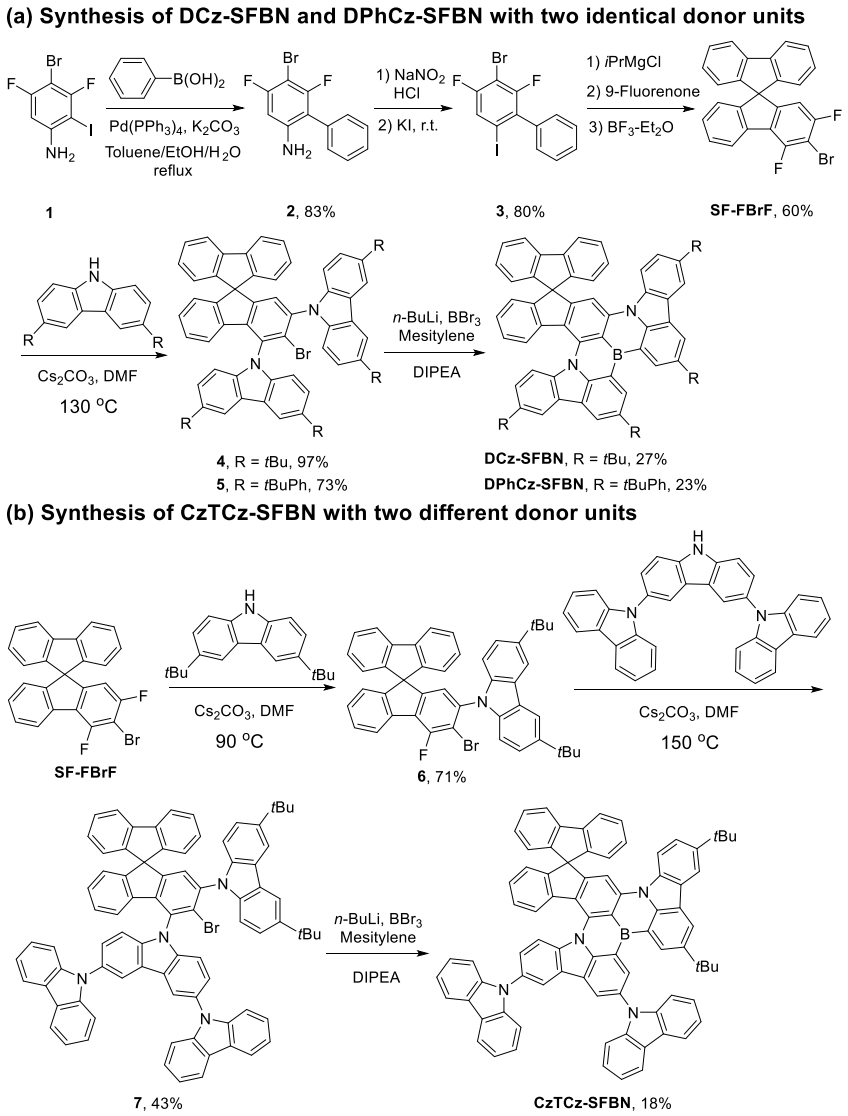
All commercially available chemical reagents were used directly without further purification. The solvents were dried and purified using an Innovative Technology PS-MD-5 Solvent Purification System. Unless otherwise noted, all reactions were carried out using Schlenk techniques under a nitrogen atmosphere. The NMR spectra were obtained on an Agilent 400-MR DD2 spectrometer. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ as the internal reference ($CDCl_3$: δ = 7.26 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ as the internal standard ($CDCl_3$: δ = 77.16 ppm). High-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-IT-TOF (ESI) or Shimadzu AXIMA Performance. X-Ray single-crystal diffraction data were collected on a Bruker D8 VENTURE single crystal diffraction. UV-vis spectra were measured on a HITACHI U-2910. Fluorescence spectra and photoluminescence quantum yield were collected on a Horiba Jobin Yvon-Edison Fluoromax-3 fluorescence spectrometer with a calibrated integrating sphere system. Phosphorescence spectra were collected on a HITACHI F-7100 fluorescence spectrophotometer and a Horiba Jobin Yvon-Edison Fluoromax-3 fluorescence spectrometer. Transient photoluminescence decay spectra were obtained with Horiba Single Photon Counting Controller: FluoroHub and Horiba TBX Picosecond Photon Detection. Thermogravimetric analysis (TGA) was carried out using DTG-60(H) at a rate of 10 ºC/min under nitrogen atmosphere. Cyclic voltammogram were performed on LK2005A with a solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) in dichloromethane as electrolyte and ferrocene/ferrocenium (Fc/Fc^+) as standard. Three-electrode system (Ag/Ag^+, platinum wire and glassy carbon electrode as reference, counter and work electrode respectively) was used in the CV measurement. HPLC analysis was conducted on a Shimadzu Prominence Modular HPLC system. HPLC traces were performed using a Daicel analytical column in hexane and isopropyl alcohol.

II. OLED Fabrication and Characterization

Indium-tin-oxide (ITO) coated glass with a sheet resistance of about 15 Ω sq^{-1} was used as the anode substrate. Ahead of film deposition, ITO substrates were cleaned with alkaline detergent, boiled deionized water, deionized water in ultrasonic bath, dried in an oven, and finally treated with oxygen plasma for 10 min to enhance the surface work function of ITO anode. All organic layers were deposited with the rate of 0.1 nm·s^{-1} under high vacuum. The doped and co-doped layers were prepared by co-evaporating dopant and host material from individual sources, and the doping concentrations were modulated by controlling the evaporation rates of dopant.

Current density-voltage-Luminance (*J*-*V*-*L*) characteristics were measured by using KEYSIGHT B1500A. The luminance and electroluminescence spectra were collected with model DLM-100Z photometer and OPT2000 spectrophotometer, respectively.

III. Synthesis and Characterization



Scheme S1. Synthetic routes to **DCz-SFBN**, **DPhCz-SFBN** and **CzTCz-SFBN**.

Synthesis of compound 2

To a dried round bottom flask was added compound **1** (13.36 g, 40.0 mmol), phenylboronic acid (1.1 equiv), $Pd(PPh_3)_4$ (2.5 mol%), K_2CO_3 (2.0 equiv). After being evacuated and backfilled with nitrogen for 3 times, and 100.0 mL of dry toluene was added under N_2 atmosphere. The reaction mixture was stirred at 120 ℃ for 36 h. After being cooled to room temperature, the reaction mixture was diluted with 100.0 mL of ethyl acetate, washed with brine (3 × 100.0 mL), and extracted with ethyl acetate (3 × 50.0 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered

and concentrated under reduced pressure. The crude product was isolated by silica gel column chromatography (petroleum ether/dichloromethane, *v*/*v* = 4/1) to give the pure product **2** as a white power (9.40 g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.88 (s, 2H), 6.38 (dd, J_1 = 10.4 Hz, J_2 = 2 Hz, 1H), 7.32 – 7.35(m, 2H), 7.39 – 7.44 (m, 1H), 7.46 – 7.51 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 85.1 (t, J = 25 Hz), 98.3 (dd, J_1 = 26 Hz, J_2 = 3 Hz), 112.5 (dd, J_1 = 21 Hz, J_2 = 4 Hz), 128.6, 129.3, 130.4, 131.2, 145.4 (dd, J_1 = 13 Hz, J_2 = 8 Hz), 156.2 (d, J = 7 Hz), 158.5 (dd, J_1 = 37 Hz, J_2 = 6 Hz), 160.7 (d, J = 7 Hz) ppm. HRMS (ESI$^+$): calcd for $C_{12}H_8BrF_2N$ $[M+H]^+$ 283.9881, 285.9861 found 283.9862, 285.9862.

Synthesis of compound 3

At 0°C, Compound **2** (8.49 g, 30.0 mmol) were suspended in 100.0 mL of 3M HCl. After slowly adding a solution of $NaNO_2$ (3.10 g, 45.0 mmol) in H_2O (20.0 mL) to the reaction mixture, stirring was continued for 1.0 hour at 0°C. A solution of KI (9.96 g, 60.0 mmol) in H_2O (20.0 mL) was slowly added by dropwise. Then, the reaction mixture was allowed to warm to room temperature overnight. The reaction was quenched by adding saturated Na_2SO_3 solution and extracted with ethyl acetate (4 × 100.0 mL) and the organic layers were washed with brine (3 ×100.0 mL). After being dried over Na_2SO_4 and concentrated in vacuo, the crude product was purified by column chromatography (petroleum ether) to obtain a light yellow solid (9.46 g, 80%) as the pure product **3**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 – 7.24 (m, 2H), 7.46 – 7.50 (m, 3H), 7.58 (dd, J_1 = 7.6 Hz, J_2 = 2 Hz 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 97.7 (d, J = 11 Hz), 99.0 (t, J = 16 Hz), 122.4 (dd, J_1 = 24 Hz, J_2 = 4 Hz), 128.6, 129.0, 129.9, 137.0, 154.8 (d, J = 4 Hz), 157.5 (dd, J_1 = 49 Hz, J_2 = 4 Hz), 160.3 (d, J = 4 Hz) ppm. MS (MALDI-TOF): calcd for $C_{12}H_6BrF_2I$ $[M+H]^+$, 394.8739; found, 394.2641.

Synthesis of SF-FBrF

To a flame dried 250 mL Schlenk flask was added compound **3** (9.46 g, 24.0 mmol) and 100.0 mL of dry THF under N_2 atmosphere. After being cooled to 0 ℃, a solution of *i*PrMgCl in hexane (13.0 mL, 2.0 M, 26.0 mmol) was added dropwise to the solution under N_2 atmosphere. After being stirred at 0 ℃ for 1.5 h, a solution of fluorenone (5.18

g, 28.8 mmol) in THF was added slowly to the reaction mixture under N_2 atmosphere. Then the reaction mixture was allowed to warm to 80 ℃. After being stirred for 12.0 h, the reaction was cooled to room temperature. The reaction was quenched with diluted HCl and extracted with ethyl acetate. The combined organic phases were dried over anhydrous Na_2SO_4, and filtered. Then, the solvent was removed under reduced pressure. Subsequently, the reaction system was dissolved in dichloromethane, and BF_3-Et_2O was introduced into it. After stirring at room temperature for 1.0 hour, the reaction was quenched with water and extracted with dichloromethane, and washed with brine. The combined organic phases were dried over anhydrous Na_2SO_4, and filtered. Then, the solvent was removed under reduced pressure. Finally, the crude product was purified by neutral silica gel column chromatography (petroleum ether) to afford the pure product SF-FBrF as a white solid (6.20 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.34 (dd, J_1= 7.6 Hz, J_2 = 1.2 Hz, 1H), 6.74 (d, J = 7.6 Hz, 3H), 7.12 – 7.17 (m, 3H), 7.38 – 7.43 (m, 3H), 7.85 (d, J = 7.6 Hz, 2H), 7.99 (d, J = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 66.6, 97.4 (t, J = 26 Hz), 108.1 (dd, J_1 = 24 Hz, J_2 = 4 Hz), 120.4, 123.3 (d, J = 5 Hz), 124.1, 128.3, 128.4 – 128.5 (m), 137.7, 141.8, 147.3, 148.1, 151.1 (dd, J_1 = 9 Hz, J_2 = 6 Hz), 153.4 (d, J = 4 Hz), 156.0 (d, J = 4 Hz), 158.1 (d, J = 3 Hz), 160.6 (d, J = 3 Hz) ppm. MS (MALDI-TOF): calcd for $C_{25}H_{13}BrF_2$ $[M]^+$, 430.0169; found, 430.5222.

Synthesis of compound 4

A dried 100 mL Schlenk tube with a magnetic stir bar was charged with **SF-FBrF** (3.00 g, 7.0 mmol), 3,6-bis(*tert*-butyl)carbazole (4.90 g, 17.5 mmol) and Cs_2CO_3 (6.90 g, 21 mmol). After being evacuated and backfilled with N_2 (3 times), DMF (50.0 mL) was added under N_2 atmosphere. After the reaction mixture was stirred at 130°C for 12.0 hours, it was cooled to room temperature. the reaction mixture was diluted with 100.0 mL of ethyl acetate and filtered. Then, the solvent was removed under reduced pressure. Finally, the crude product was purified by column chromatography (petroleum ether/dichloromethane = 5:1, v/v) and the pure compound **4** was obtained

as a white powder (6.40 g, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42 (s, 18H), 1.52 (s, 18H), 6.15 (d, J = 7.6 Hz, 1H), 6.70 (d, J = 7.6 Hz, 1H), 6.88 (t, J = 8 Hz, 1 H), 6.95 (t, J = 9.2 Hz, 4 H), 6.99 – 7.05 (m, 2H), 7.19 – 7.26 (m, 4H), 7.38 – 7.42 (m, 4H), 7.56 (d, J = 8 Hz, 2H), 7.81 (d, J = 7.6 Hz, 2H), 8.07 (s, 2 H), 8.30 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.1, 32.2, 34.8, 35.0, 66.2, 109.3, 109.4, 116.5, 116.8, 120.6, 123.3, 123.4, 123.5, 123.7, 123.8, 123.9, 124.4, 126.6, 128.4, 128.5, 128.6, 129.3, 132.0, 137.7, 138.1, 139.0, 141.9, 142.8, 143.0, 143.2, 147.4, 149.6, 151.2 ppm. HRMS (ESI^+): calcd for $C_{65}H_{61}BrN_2$ $[M+H]^+$ 949.4091, 951.4071 found 949.4091, 951.4070.

Synthesis of compound 5

Compound **5** was synthesized according to the same procedure as for compound **4** by using 3,6-bis(4-(*tert*-butyl)phenyl)carbazole (7.56 g, 17.5 mmol) instead of 3,6-bis(*tert*-butyl)carbazole. The crude product was purified by neutral silica gel column chromatography (petroleum ether/dichloromethane = 4:1, v/v) to afford the pure compound **6** as a white solid (6.41 g, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39 (s, 18H), 1.43 (s, 18H), 6.27 (d, J = 8 Hz, 1H), 6.77 (d, J = 7.6 Hz, 1H), 6.93 (t, J = 8.4 Hz, 1H), 7.01 (d, J = 7.6 Hz, 2H), 7.07 (t, J = 7.6 Hz, 1H), 7.11 – 7.14 (m, 3H), 7.28 – 7.30 (m, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.49 (d, J = 8.8 Hz, 4H), 7.56 (d, J = 8.4 Hz, 4H), 7.61 – 7.63 (m, 6H), 7.75 (d, J = 8.4 Hz, 4H), 7.80 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 2H), 7.84 (d, J = 7.6 Hz, 2H), 8.30 (d, J = 1.6 Hz, 2H), 8.56 (d, J = 1.2 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.6, 34.6, 34.7, 66.3, 110.3, 110.4, 118.9, 119.4, 120.6, 123.9, 124.1, 124.3, 125.8, 125.9, 126.3, 126.4, 127.1, 127.2, 128.4, 128.6, 128.8, 129.6, 131.7, 134.0, 134.2, 137.4, 137.9, 139.1, 139.1, 139.5, 140.3, 142.0, 143.0, 147.3, 149.6, 149.7, 149.8, 151.7 ppm. MS (MALDI-TOF): calcd for $C_{89}H_{77}BrN_2$ $[M+H]^+$, 1255.5323; found, 1255.8442.

Synthesis of compound 6

Compound **6** was synthesized according to the same procedure as for compound **4** by using **SF-FBrF** (3.00 g, 7.0 mmol), 3,6-bis(*tert*-butyl)carbazole (1.96 g, 7.0 mmol) and stirred at 90 ºC instead of 130 ºC. The crude product was purified by neutral silica gel column chromatography (petroleum ether/dichloromethane = 10:1, v/v) to afford

the pure compound **6** as a white solid (3.42 g, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.51 (s, 18H), 6.05 (d, J = 7.8 Hz, 1H), 6.66 (d, J = 7.2 Hz, 1H), 6.71 (d, J = 7.6 Hz, 1H), 6.79 – 6.85 (m, 3H), 6.79 – 6.85 (m, 3H), 6.94 (t, J = 7.6 Hz, 1H), 7.06 (d, J = 8.4 Hz, 2H), 7.22 (t, J = 8.0 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.49 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 2H), 7.89 (d, J = 7.6 Hz, 2H), 8.29 (d, J = 1.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.2, 35.0, 66.2, 109.4, 112.3 (d, J = 21 Hz), 112.8 (d, J = 26 Hz), 116.7, 120.5, 123.4, 123.8, 124.1, 124.3, 128.3 – 128.5 (m), 131.7, 138.1, 138.5 (d, J = 3 Hz), 141.9, 143.3, 147.5, 148.7 (d, J = 2 Hz), 151.2 (d, J = 9 Hz), 158.3, 160.8 ppm. HRMS (ESI+): calcd for C45H37BrFN $[M+Na]^+$ 712.1986, 714.1966 found 712.1981, 714.1964.

Synthesis of compound 7

Compound **7** was synthesized according to the same procedure as for compound **4** by using compound **6** (3.00 g, 4.3 mmol), 3,6-di-(9-carbazole)carbazole (3.2 g, 6.5 mmol) and stirred at 150 ºC. The crude product was purified by neutral silica gel column chromatography (petroleum ether/dichloromethane = 4:1, v/v) to afford the pure compound **7** as a white solid (2.2 g, 43% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53 (s, 18H), 6.21 (d, J = 8.0 Hz, 1H), 6.76 (d, J = 7.6 Hz, 1H), 6.92 (t, J = 7.6 Hz, 1H), 7.01 (d, J = 7.6 Hz, 2H), 7.06 (t, J = 7.6 Hz, 1H), 7.23 (s, 1H), 7.24 – 7.25 (m, 3H), 7.26 – 7.30 (m, 7H), 7.33 – 7.39 (m, 8H), 7.45 (t, J = 7.6 Hz, 2H), 7.58 (ddd, J_1 = 10.4 Hz, J_2 = 8.8 Hz, J_3 = 2.0 Hz, 4H), 7.87 (d, J = 7.6 Hz, 2H), 8.14 (d, J = 8.0 Hz, 4H), 8.19 (d, J = 2.0 Hz, 2H), 8.34 (d, J = 1.2 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.2, 35.0, 66.3, 109.2, 109.9, 111.6, 117.0, 119.8, 119.9, 120.4, 120.6, 123.3, 123.5, 123.8, 123.9, 124.0, 124.0, 124.5, 126.0, 126.5, 126.6, 126.7, 128.5, 128.6, 128.8, 129.7, 130.7, 132.5, 136.5, 137.9, 138.1, 140.4, 141.9, 142.0, 143.5, 143.8, 147.3, 149.6, 151.7 ppm. MS (MALDI-TOF): calcd for $C_{81}H_{59}BrN_4$ $[M]^+$, 1166.39; found, 1166.77.

Synthesis of DCz-SFBN

To a flame dried 100 mL Schlenk flask was added compound **4** (3.00 g, 3.16 mmol) and 50 mL of dry mesitylene under N_2 atmosphere. After being cooled to 0 ℃, a solution of *n*-BuLi in hexane (2.5 mL, 2.5 M, 6.3 mmol) was added slowly to the

solution under N_2 atmosphere. After being stirred at 40 ℃ for 2 h, the reaction mixture was allowed to cooled to 0 ℃ again. Boron tribromide (1.3 mL, 13 mmol) was added slowly to the reaction mixture. After the reaction mixture was stirred at 40 ℃ for 2.0 h, *N*,*N*-diisopropylethylamine (DIPEA, 4.5 mL, 25 mmol) was added at 0 ℃. After being stirred at 0 ℃ for 0.5 h, the reaction mixture was allowed to warm to 150 ℃. After being stirred for 12.0 h, the reaction was cooled to room temperature. The reaction was quenched with water and extracted with dichloromethane. The combined organic phases were dried over anhydrous Na_2SO_4, and filtered. Then, the solvent was removed under reduced pressure. Finally, the crude product was purified by neutral silica gel column chromatography (petroleum ether/dichloromethane = 4:1, v/v), and recrystallized from dichloromethane /methanol as a yellow solid at 27% yield (**DCz-SFBN**, 749 mg, 0.85 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 9H), 1.53 (s, 9H), 1.65 (s, 9H), 1.72 (s, 9H), 6.76 – 6.83 (m, 3H), 6.99 – 7.05 (m, 2H), 7.17 (t, J = 7.6 Hz, 1H), 7.28 – 7.30 (m, 2H), 7.35 – 7.40 (m, 2H), 7.45 – 7.51 (m, 3H), 7.61 (d, J = 8.4 Hz, 1H), 7.74 (s, 1H), 8.01 (dd, J_1 = 7.6 Hz, J_2 = 4.0 Hz, 2H), 8.15 (d, J = 2.0 Hz, 1H), 8.30 (d, J = 2.0 Hz, 1H), 8.40 (d, J = 2.0 Hz, 1H), 8.56 (d, J = 2.0 Hz, 1H), 9.11 (dd, J_1 = 16.8 Hz, J_2 = 2.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.9, 32.1, 32.3, 32.4, 34.9, 35.1, 35.3, 35.5, 67.2, 104.9, 113.9 116.8, 117.0, 117.3, 120.2, 120.8, 121.0, 122.7, 123.1, 123.8, 124.0, 124.5, 124.8, 125.0, 125.9, 126.1, 126.2, 126.4, 127.1, 128.1, 128.2, 128.3, 128.5, 129.4, 130.2, 137.2, 137.6, 138.3, 141.5, 141.6, 142.5, 142.9, 143.6, 144.9, 145.4, 145.4, 145.6, 148.0, 148.7, 149.6, 158.0 ppm. HRMS (ESI$^+$): calcd for $C_{65}H_{59}BN_2$ $[M+Na]^+$ 901.4664 found 901.4663.

Synthesis of DPhCz-SFBN

DPhCz-SFBN was synthesized according to the same procedure as for DCz-SFBN by using compound **5** (6.26 g, 5.0 mmol) instead of compound **4**. The crude product was purified by neutral silica gel column chromatography (petroleum ether/ dichloromethane = 4:1, v/v) and recrystallized from dichloromethane /methanol as yellow solid at 23% yield (**DPhCz-SFBN**, 1.36 g, 1.15 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.41 (s, 9H), 1.45 (s, 9H), 1.47 (s, 9H), 1.49 (s, 9H), 6.77 (d, J = 7.6 Hz,

1H), 6.82 – 6.88 (m, 2H), 7.05 – 7.07 (m, 2H), 7.18 (t, J = 7.6 Hz, 1H), 7.31 – 7.39 (m, 2H), 7.48 – 7.68 (m, 14H), 7.71 – 7.75 (m, 2H), 7.80 – 7.85 (m, 5H), 7.92 (d, J = 8.4 Hz, 2H), 8.06 (t, J = 8.0 Hz, 2H), 8.38 (s, 1H), 8.56 (d, J = 2.0 Hz, 2H), 8.74 (s, 1H), 9.25 (d, J = 12.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.5, 31.6, 31.6, 34.7, 34.8, 34.8, 67.2, 105.7, 114.7, 117.5, 119.1, 119.2, 120.2, 120.9, 122.4, 122.6, 122.8, 123.2, 123.3, 123.4, 124.1, 124.3, 124.7, 124.9, 125.2, 126.0, 126.1, 126.2, 126.2, 126.6, 126.6, 126.9, ,127.0, 127.6, 127.7, 128.3, 128.5, ,128.6, 131.9, 132.6, 135.6, 135.8, 136.3, 136.9, 138.1, 138.4, 138.7, ,139.4, 139.5, 141.2, 141.6, 142.3, 142.5, 143.3, 143.9, 148.0, 148.5, 149.5, 150.1, 150.1, 150.2, 150.3, 158.3 ppm. HRMS (ESI$^+$): calcd for $C_{89}H_{75}BN_2$ $[M+H]^+$, 1183.6097; found, 1183.6110.

Synthesis of CzTCz-SFBN

CzTCz-SFBN was synthesized according to the same procedure as for **DCz-SFBN** by using compound **7** (5.80 g, 5.0 mmol) instead of compound **4**. The crude product was purified by neutral silica gel column chromatography (petroleum ether/ dichloromethane = 4:1, v/v) and recrystallized from dichloromethane/methanol as yellow solid at 18% yield (**CzTCz-SFBN**, 986 mg, 0.9 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.56 (s, 18H), 6.85 – 6.92 (m, 3H), 7.09 – 7.13 (m, 2H), 7.23 (t, J = 7.2 Hz, 1H), 7.27 – 7.40 (m, 11H), 7.46 – 7.58 (m, 7H), 7.72 (s, 1H), 7.86 (s, 1H), 7.95 (d, J = 8.8 Hz, 1H), 8.02 (dd, J_1 = 7.6 Hz, J_2 = 3.2 Hz, 2H), 8.15 (d, J = 7.6 Hz, 2H), 8.23 (d, J = 2.0 Hz, 1H), 8.31 (s, 1H), 8.35 (s, 1H), 8.52 (s, 1H), 8.62 (s, 1H), 8.97 (s, 1H), 9.27 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.1, 32.3, 35.2, 35.4, 67.4, 105.2, 109.8, 115.6, 117.0, 117.2, 120.1, 120.2, 120.3, 120.4, 120.5, 120.6, 121.0, 121.9, 122.0, 123.3, 123.4, 123.7, 123.8, 124.0, 124.5, 124.9, 125.1, 126.1, 126.2, 126.3, 126.4, 126.6, 126.8, 127.9, 128.3, 128.5, 128.6, 129.0, 132.4, 132.5, 132.7, 137.2, 137.6, 139.3, 141.3, 141.5, 141.5, 141.6, 141.8, 142.6, 142.9, 143.1, 146.1, 146.1, 148.0, 148.3, 149.4, 158.7 ppm. HRMS (ESI$^+$): calcd for $C_{81}H_{57}BN_4$ $[M+H]^+$, 1097.4750; found, 1097.4762.

IV. Method of Theoretical Calculations

All theoretical calculations were performed using Gaussian 09 serials software.[1] All theoretical calculations were calculated under wb97xd/def2svp level. The FMOs distributions were calculated on the basis of crystal structures and visualized using Gaussview 5.0 software.

The radiative decay rate (k_R) and reverse intersystem crossing rate (k_{RISC}) could be estimated using the following equations:[2]

$$\Phi_P = C_1\Phi_{PL}$$

$$\Phi_d = C_2\Phi_{PL}$$

$$k_R = \Phi_P/\tau_p = \Phi_{PL}C_1/\tau_p$$

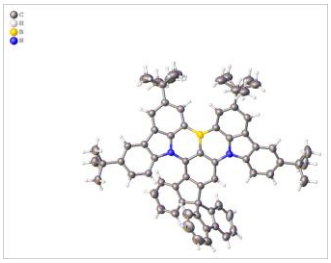
$$k_{ISC} = (1-\Phi_P)/\tau_p = (1-\Phi_{PL}C_1)/\tau_p$$

$$k_{RISC} = \Phi_d/(k_{ISC}\tau_p\tau_d\Phi_p) = C_2/[C_1\tau_d(1-\Phi_{PL}C_1)]$$

Where Φ_p and Φ_d represent prompt and delayed fluorescence components and can be distinguished from the total Φ_{PL} by comparing the integrated intensities of prompt (C_1) and delayed components (C_2) in the transient PL spectra.

V. Crystal Data

Table S1. Crystal Data for **DCz-SFBN** (CCDC: 2346375)



Identification code	**DCz-SFBN**
Empirical formula	$C_{65}H_{59}BN_2$
ρ_{calc}g/cm^3	1.142
μ/mm^{-1}	0.065
Formula weight	879.030
Colour	clear yellowish yellow
Shape	block-shaped
Size/mm^3	0.17 × 0.13 × 0.10
Temperature/K	150(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.0508(8)
b/Å	16.0816(11)
c/Å	28.825(2)
α/°	90
β/°	93.905(2)
γ/°	90
Volume/Å^3	5110.7(6)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	MoKα (λ = 0.71073)
Θmin/°	2.24
Θmax/°	25.00
Measured Refl's	35062
Indep't Refl's	8986
Refl's I≥2σ(I)	5519
R_{int}	0.1048
Parameters	688
Restraints	122
Largest Peak	0.3047
Deepest Hole	-0.3537
GooF	1.0913
wR_2 (all data)	0.1371
wR_2	0.1090
R_1 (all data)	0.1033
R_1	0.0527

VI. Additional Spectra and Data

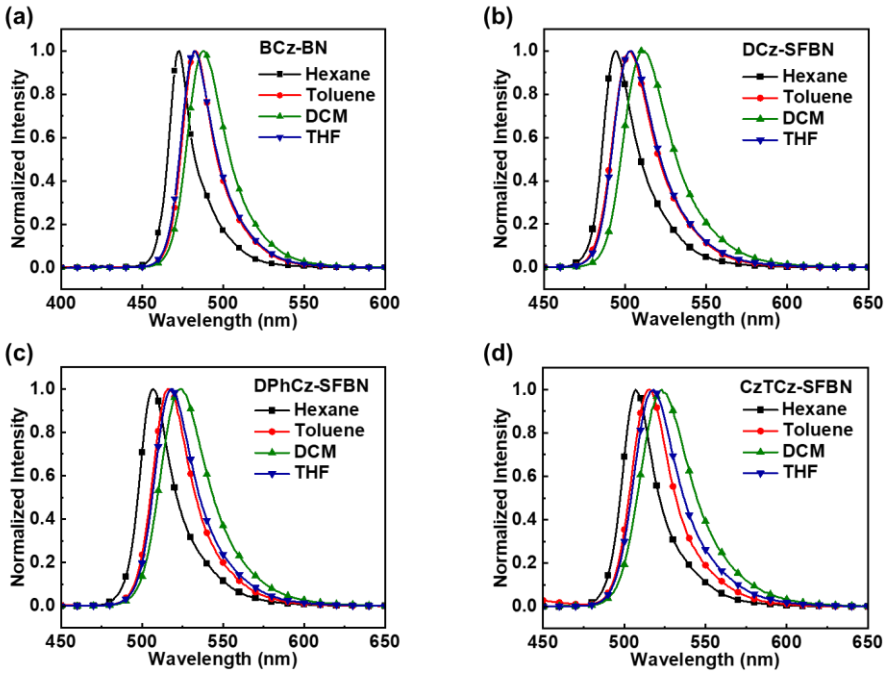


Fig. S1. Photoluminescence spectra measured in different polar solvents (1.0×10^{-5} M, 298 K) of (a) **BCz-BN**, (b) **DCz-SFBN**, (c) **DPhCz-SFBN** and (d) **CzTCz-SFBN**.

Table S2. Summary of photoluminescence spectra data in different polar solvents

Compound	**BCz-BN**		**DCz-SFBN**		**DPhCz-SFBN**		**CzTCz-SFBN**	
	λ_{em} [nm]	FWHM [nm]	λ_{em} [nm]	FWHM [nm]	λ_{em} [nm]	FWHM [nm]	λ_{em} [nm]	FWHM [nm]
n-hexane	473	17	494	25	507	24	507	24
toluene	481	23	503	33	516	26	515	28
DCM	488	29	510	35	524	34	523	37
THF	482	24	504	31	518	29	518	33

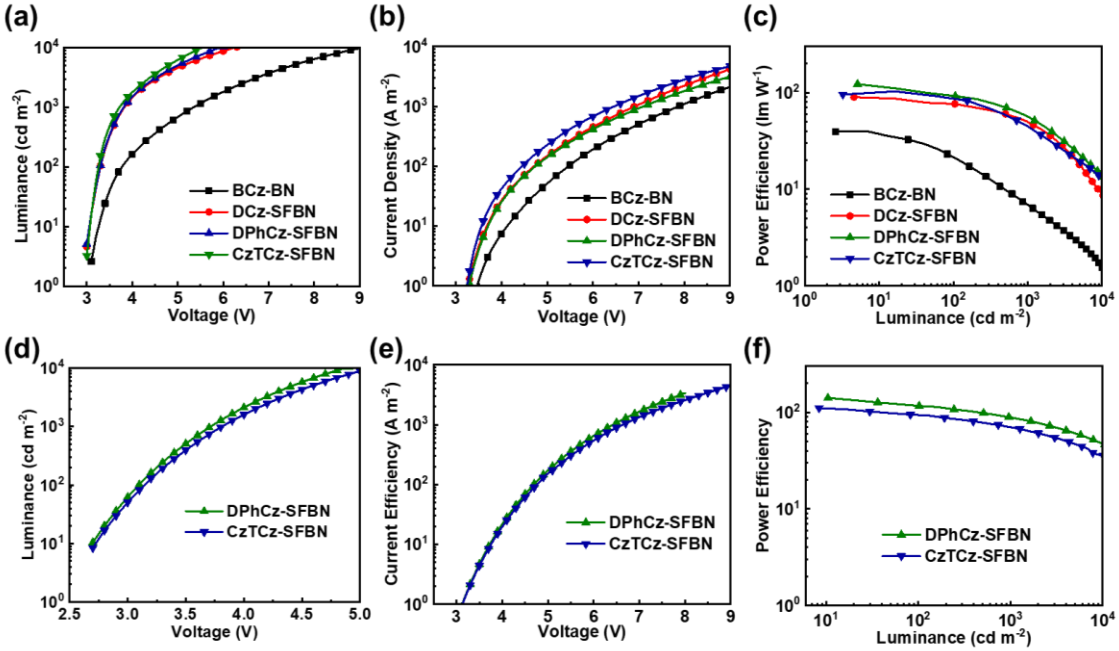


Fig. S2 (a) Luminance-voltage, (b) current density-voltage and (c) power efficiency-luminance curves of OLEDs without using TADF sensitizers. (d) Luminance-voltage, (e) current density-voltage and (f) power efficiency-luminance curves of OLEDs using **3CTF** as the TADF sensitizer.

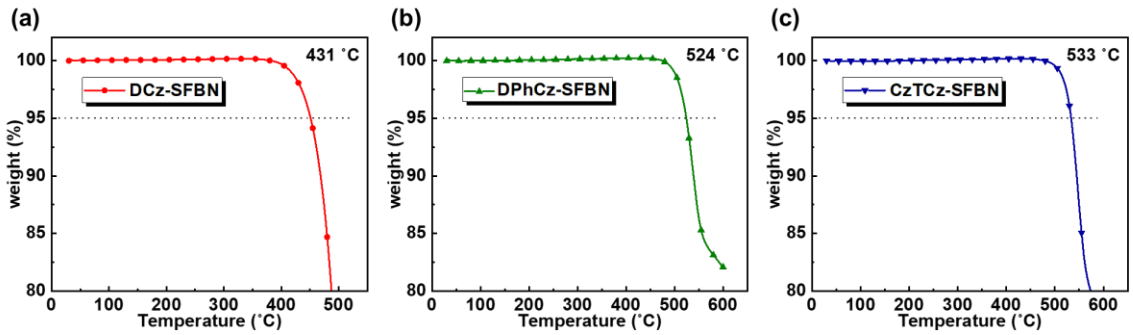


Fig. S3 Thermogravimetric analysis (TGA) curves of (a) **DCz-SFBN**, (b) **DPhCz-SFBN**, (c) **CzTCz-SFBN**.

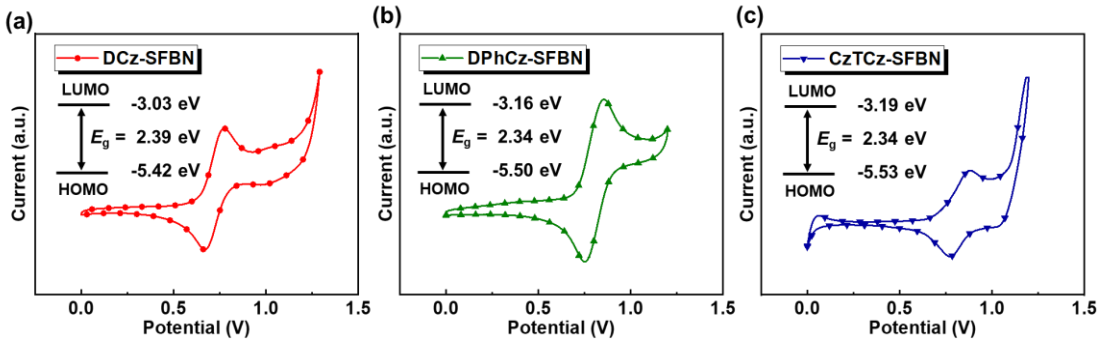


Fig. S4 Cyclic voltammograms of (a) **DCz-SFBN**, (b) **DPhCz-SFBN**, (c) **CzTCz-SFBN** measured in dry dichloromethane containing tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) as electrolyte and ferrocene/ferrocenium (Fc/Fc^+, 1.0×10^{-3} M) as standard. The HOMO energy levels were determined from cyclic voltammetry by formula: E_{HOMO} = -4.8 - (E_{OX} - $E_{1/2,Fe}$), while the LUMO energy levels were determined from formula: $E_{LUMO} = E_{HOMO} + E_g$, where E_g values were estimated from the absorption edges in the UV–vis spectra (Fig. 2a).

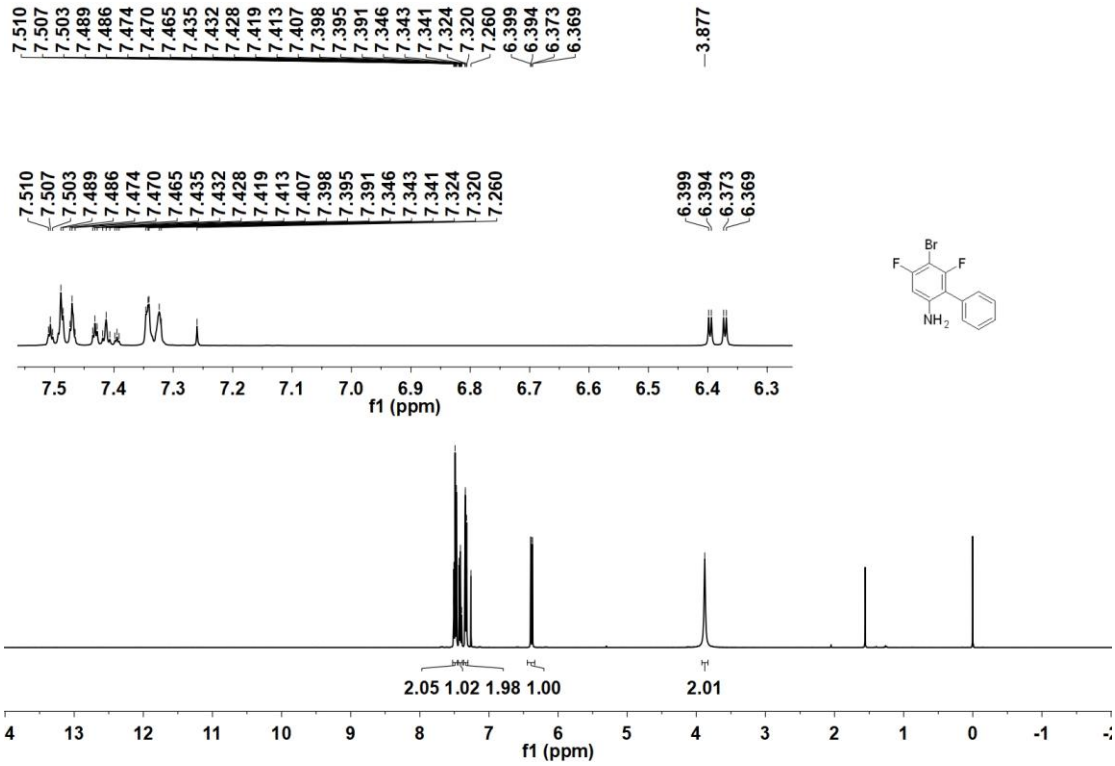
VII. References

[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. Jr. Montgomery, 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, N. J. 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, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision D. 01, Gaussian, Inc., Wallingford CT, 2009.

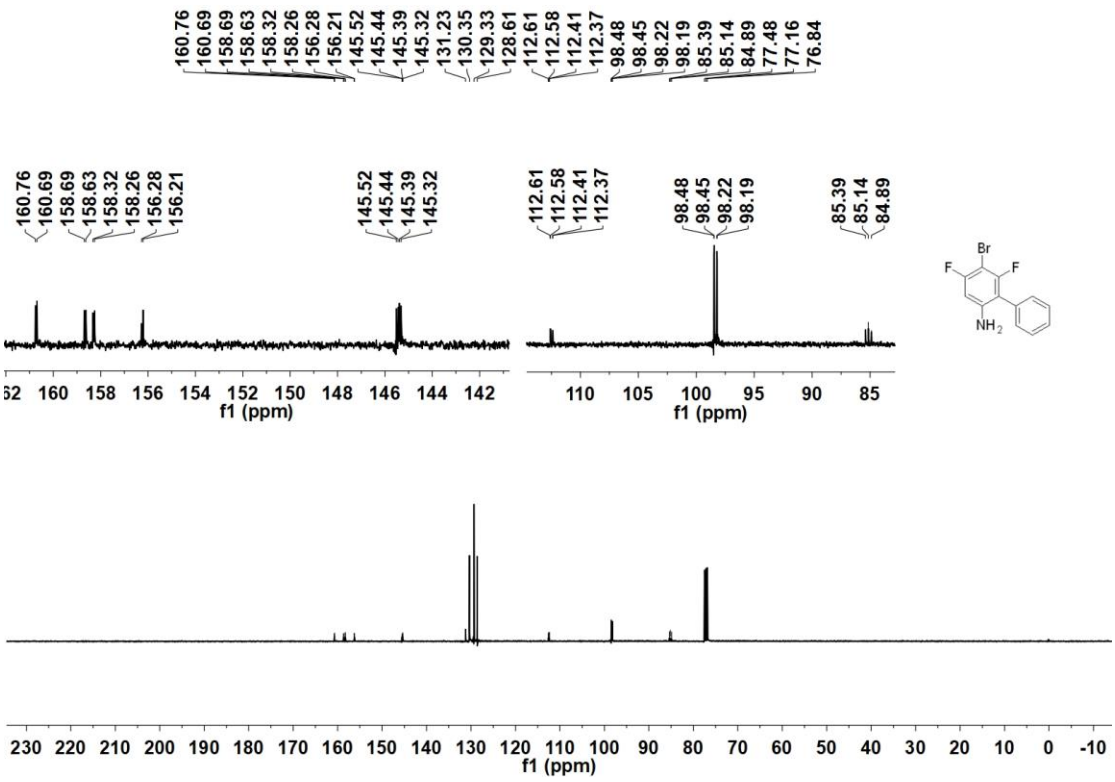
[2]. K. Masui, H. Nakanotani, C. Adachi, *Org. Electron*. 2013, **14**, 2721.

VIII. Copies of NMR spectra

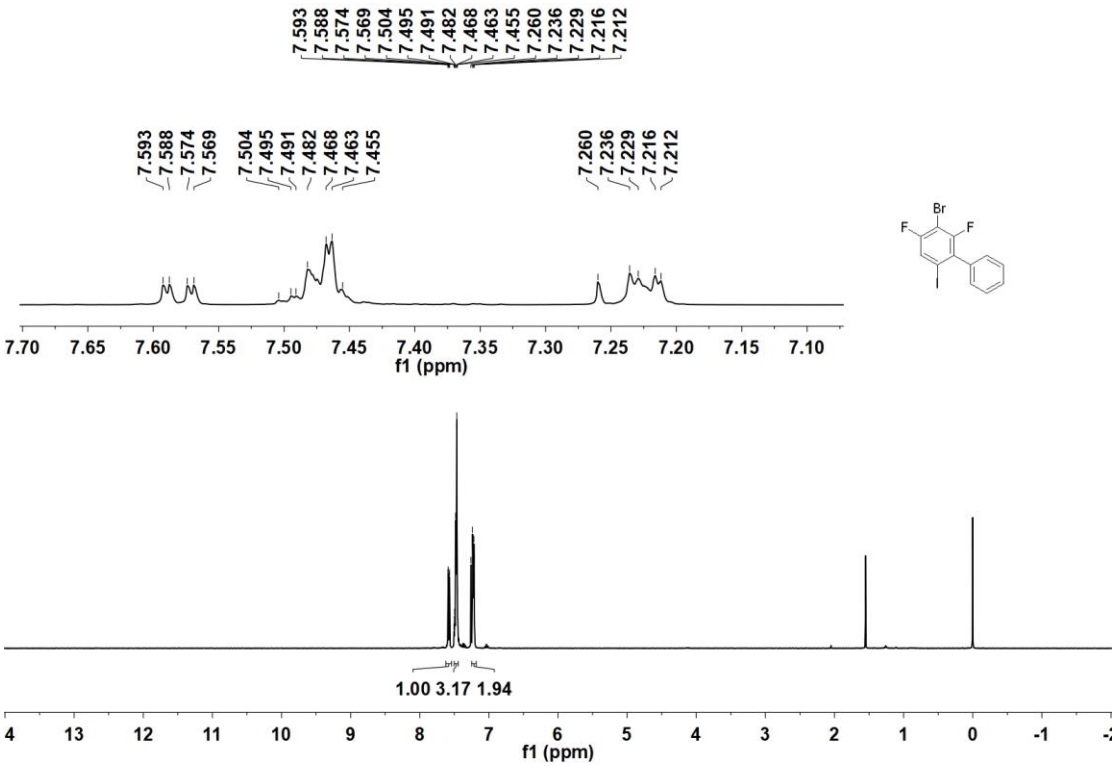
^{1}H NMR spectrum of **2** ($CDCl_3$)



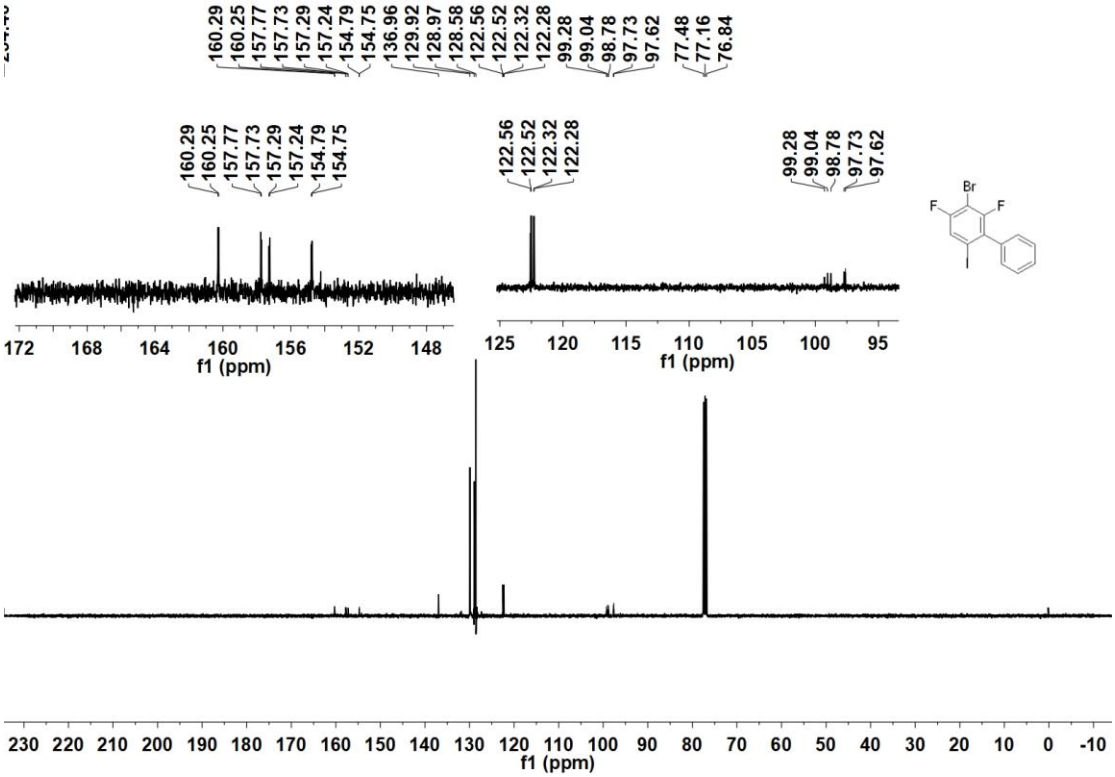
^{13}C NMR spectrum of **2** ($CDCl_3$)



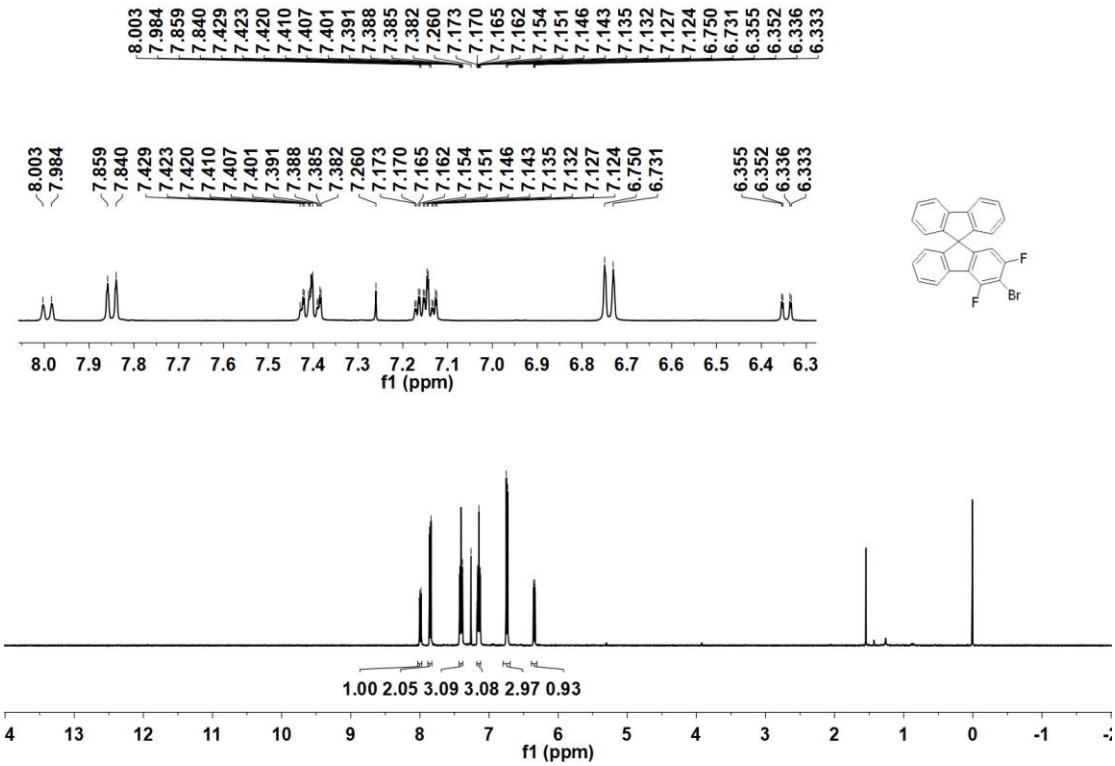
^{1}H NMR spectrum of **3** ($CDCl_3$)



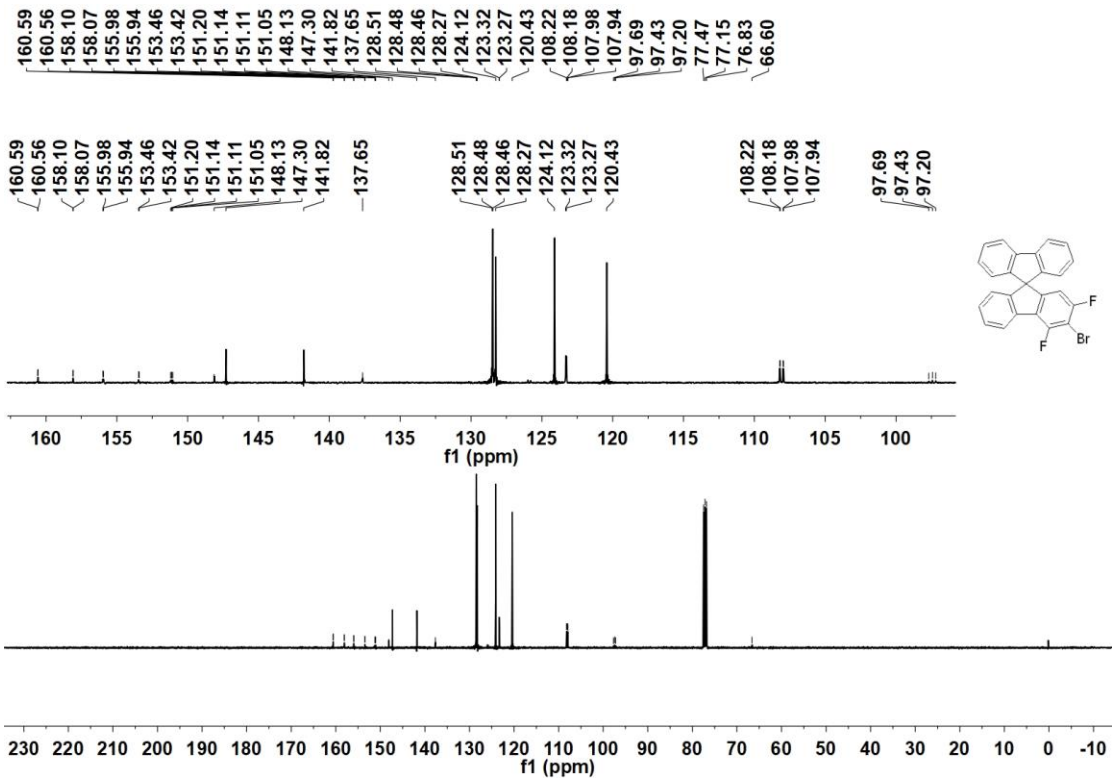
^{13}C NMR spectrum of **3** ($CDCl_3$)



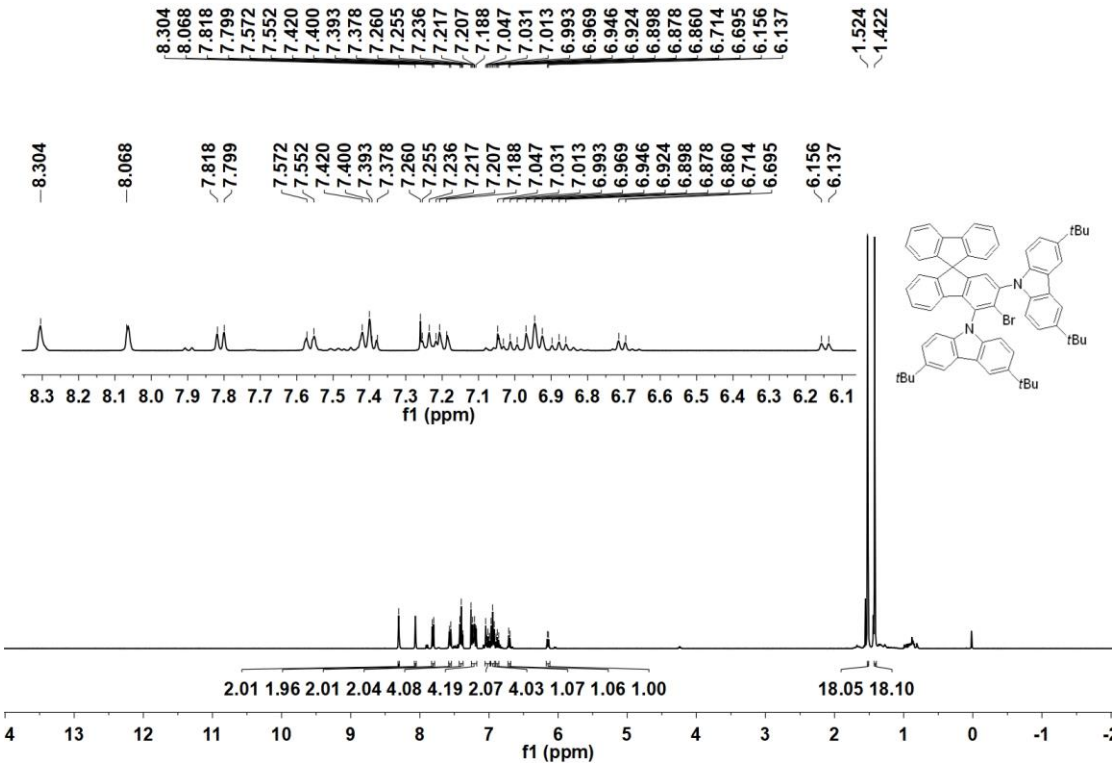
^{1}H NMR spectrum of **SF-FBrF** ($CDCl_3$)



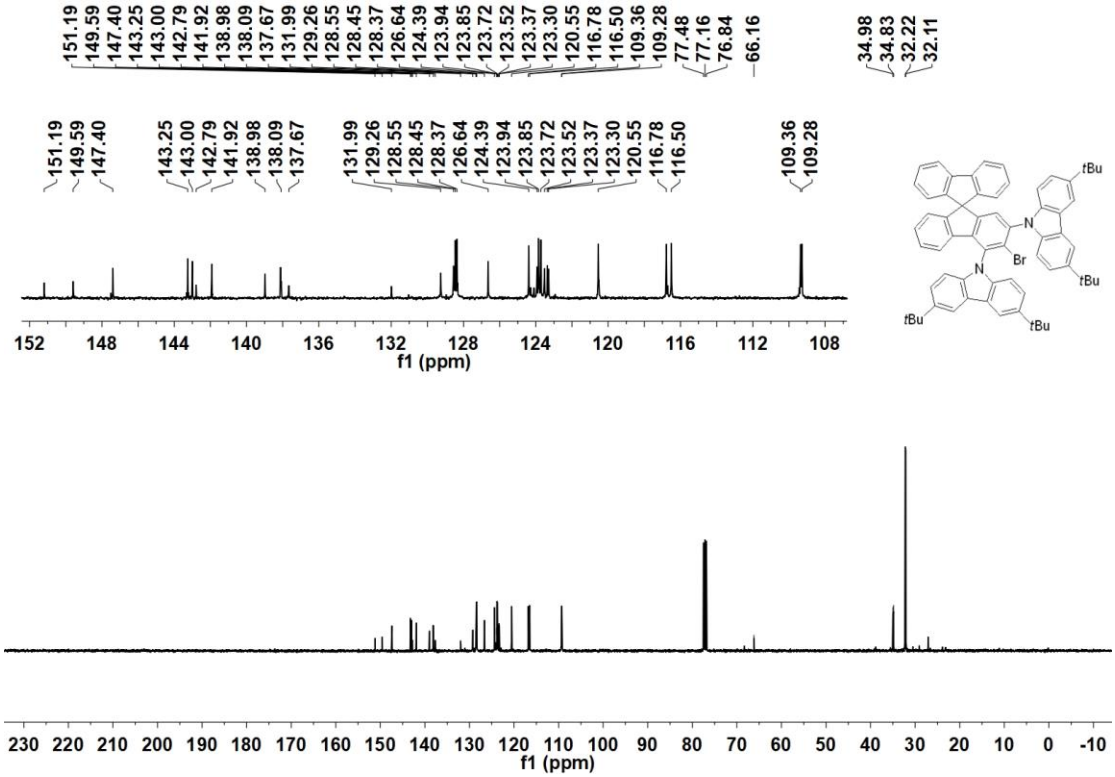
^{13}C NMR spectrum of **SF-FBrF** ($CDCl_3$)



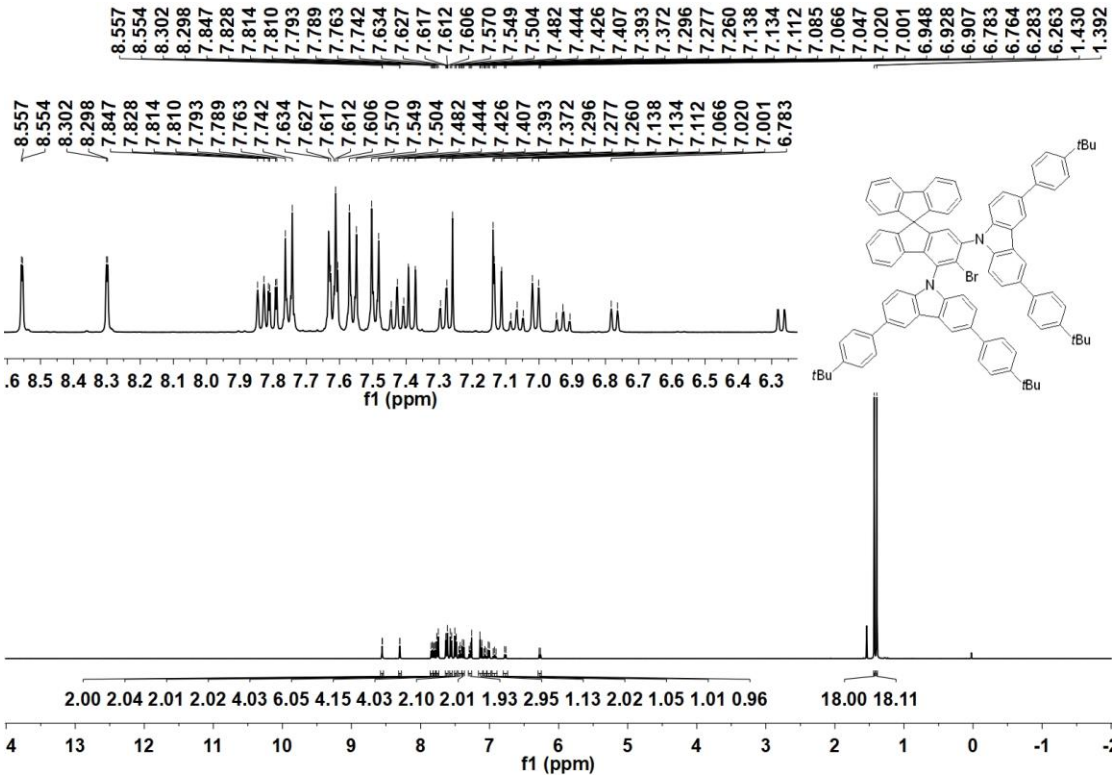
^{1}H NMR spectrum of **4** ($CDCl_3$)



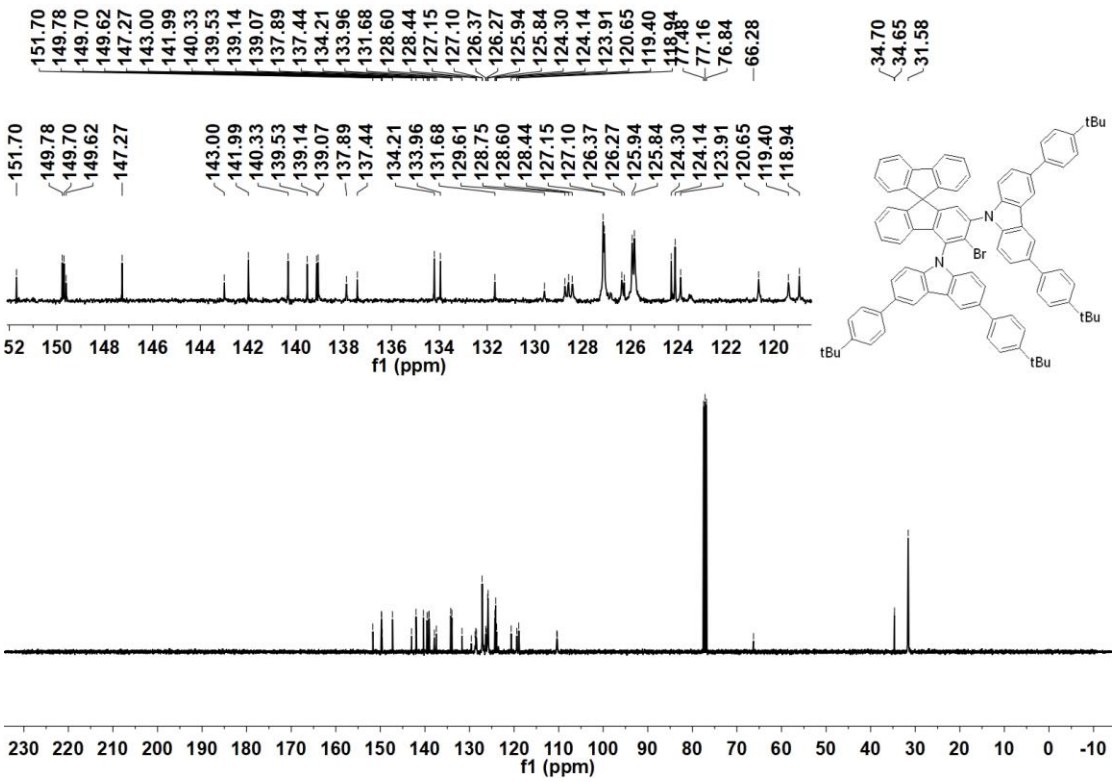
^{13}C NMR spectrum of **4** ($CDCl_3$)



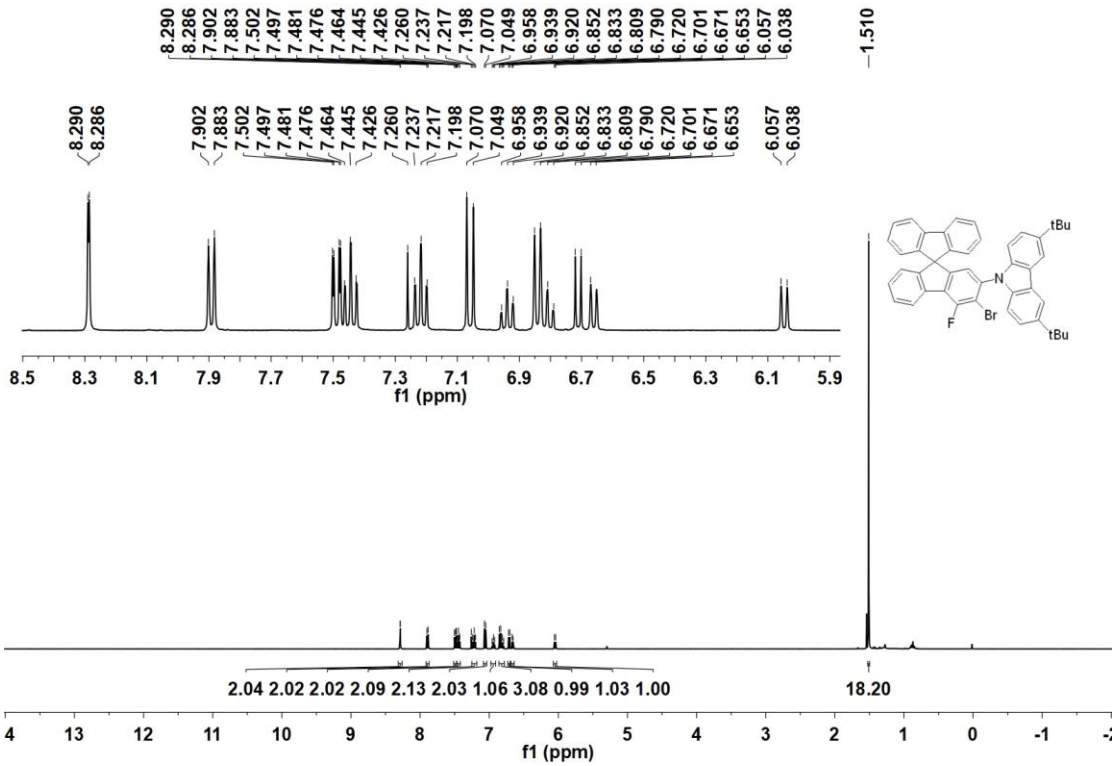
^{1}H NMR spectrum of **5** ($CDCl_3$)



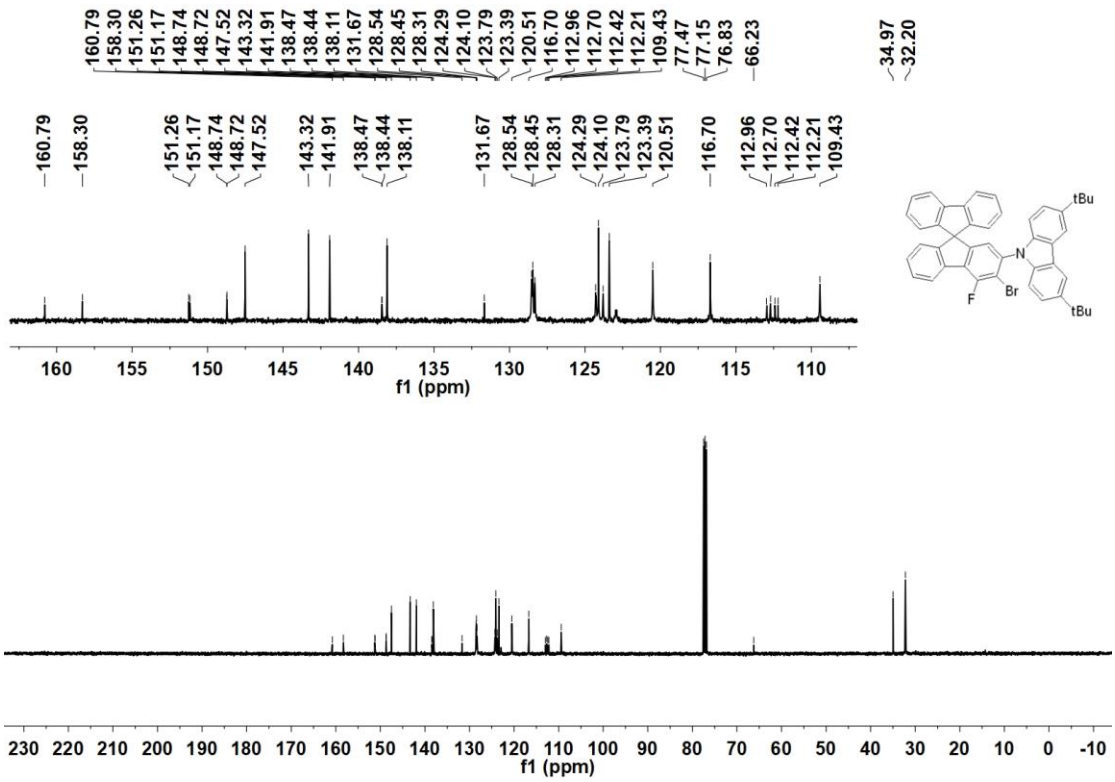
^{13}C NMR spectrum of **5** ($CDCl_3$)



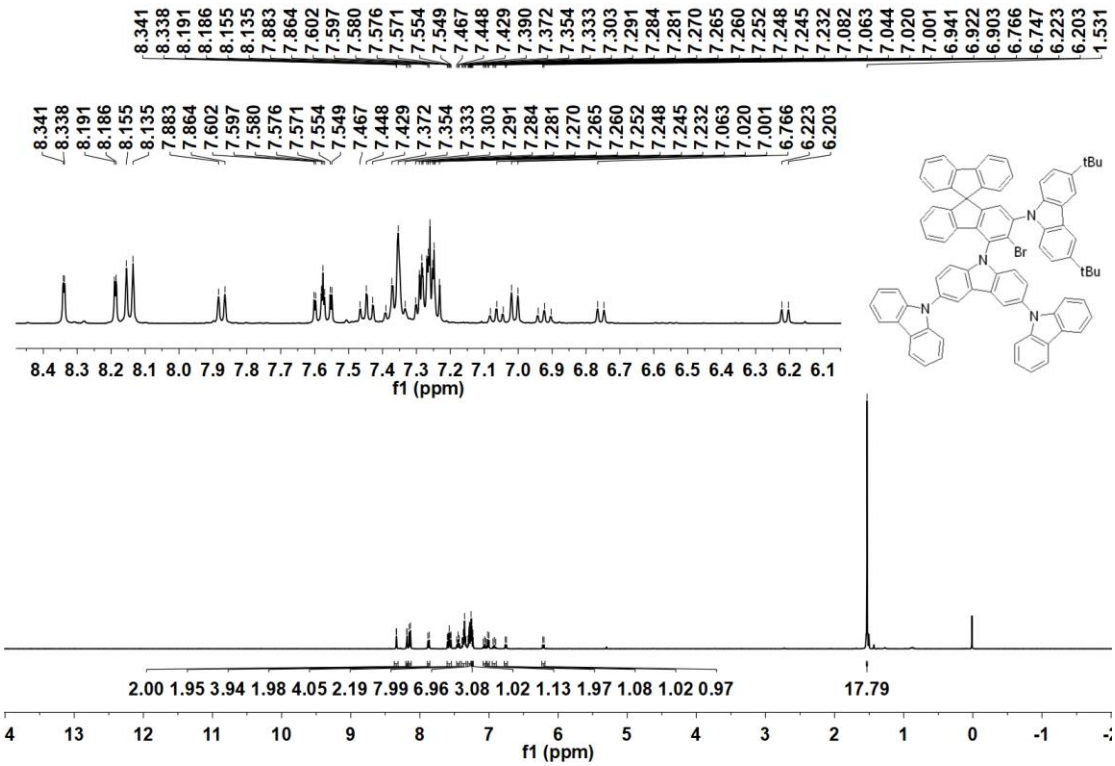
^{1}H NMR spectrum of **6** ($CDCl_3$)



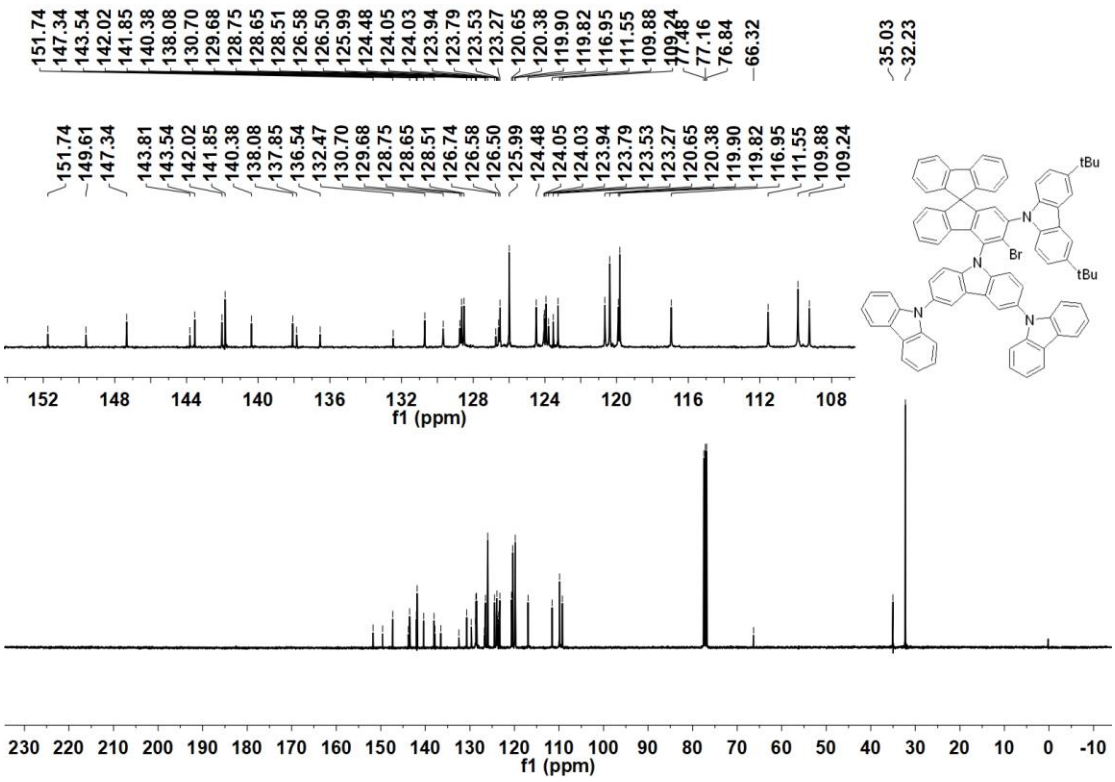
^{13}C NMR spectrum of **6** ($CDCl_3$)



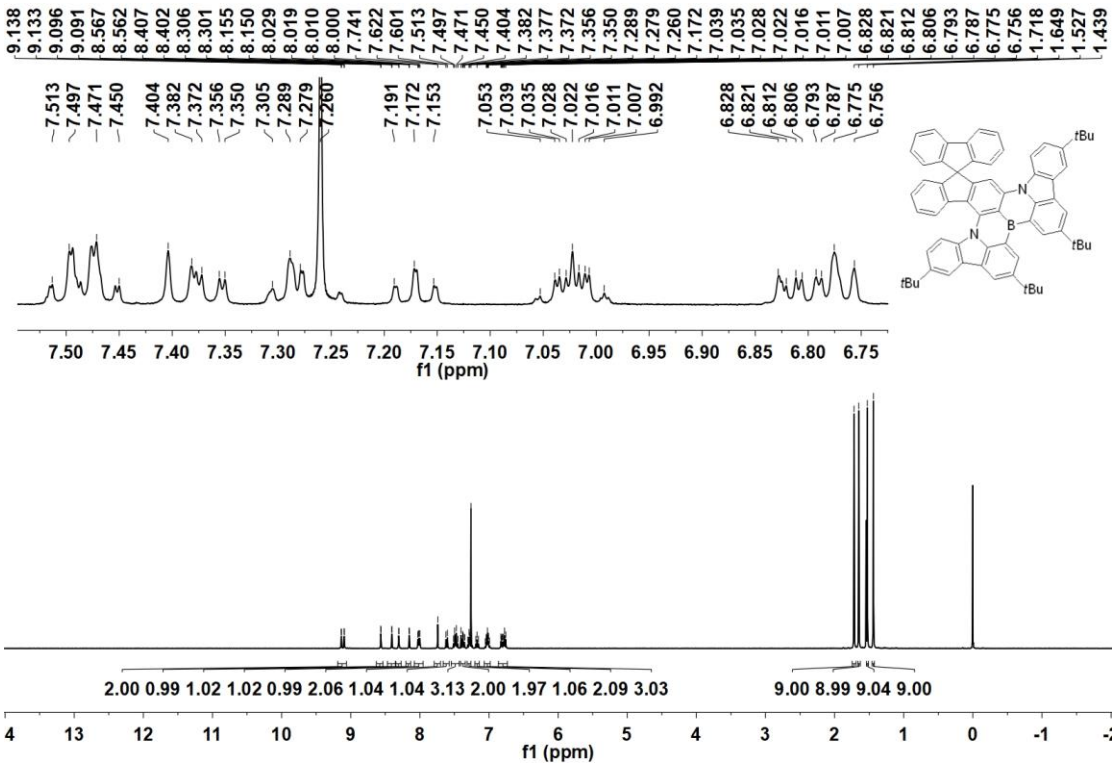
^{1}H NMR spectrum of **7** ($CDCl_3$)



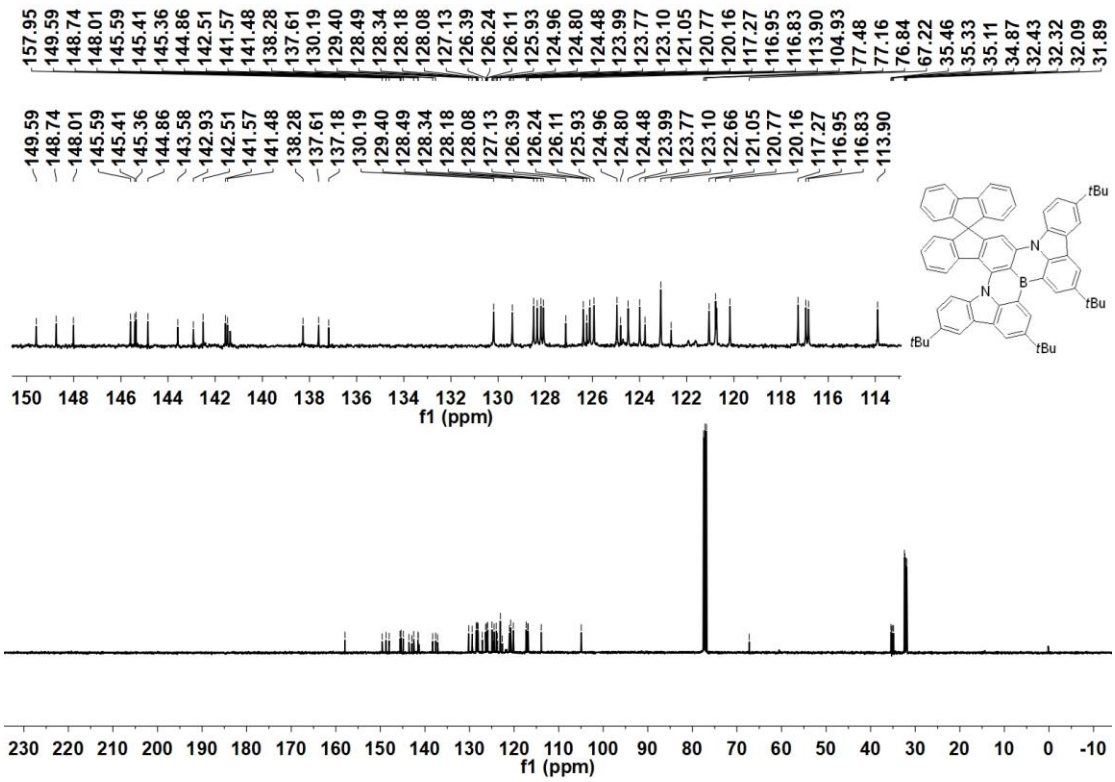
^{13}C NMR spectrum of **7** ($CDCl_3$)



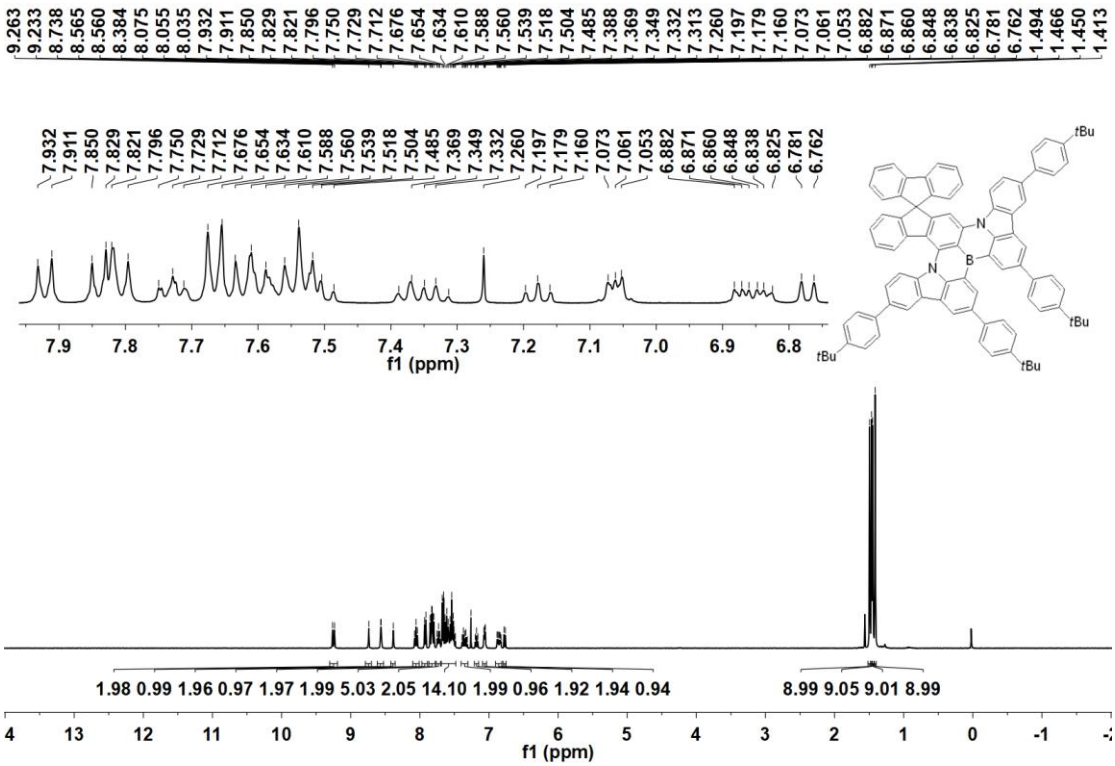
^{1}H NMR spectrum of **DCz-SFBN** ($CDCl_3$)



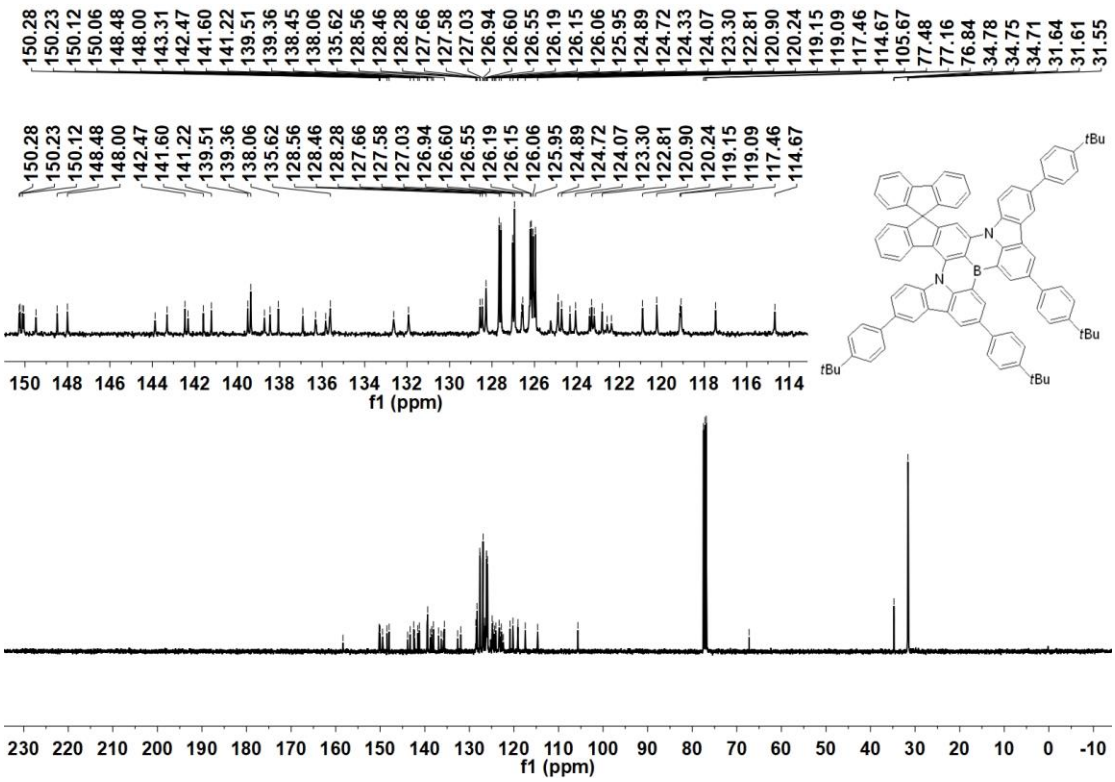
^{13}C NMR spectrum of **DCz-SFBN** ($CDCl_3$)



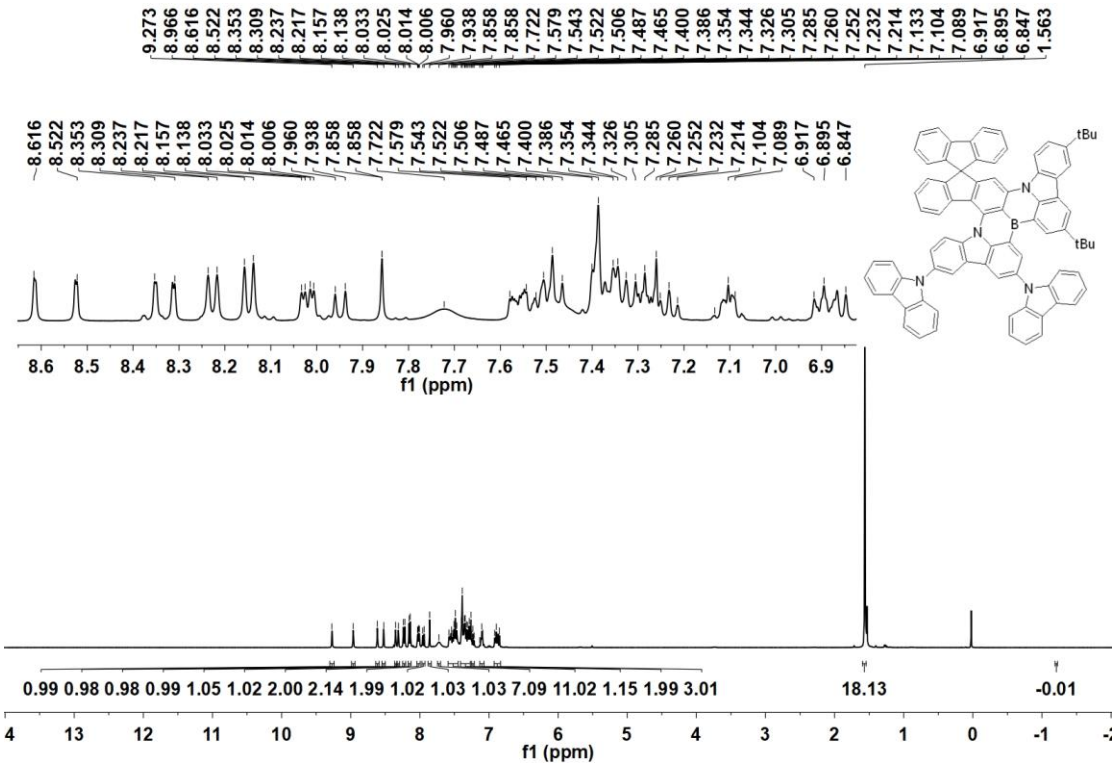
^{1}H NMR spectrum of **DPhCZ-SFBN** ($CDCl_3$)



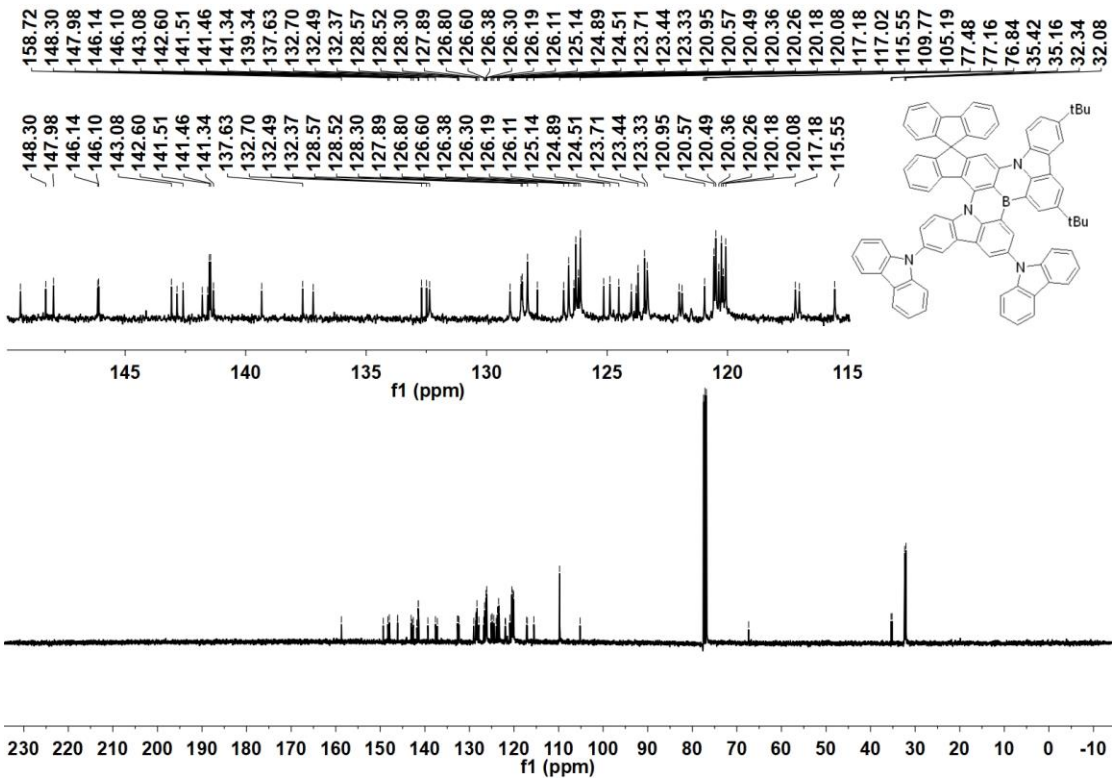
^{13}C NMR spectrum of **DPhCZ-SFBN** ($CDCl_3$)



^{1}H NMR spectrum of **CZTCz-SFBN** ($CDCl_3$)

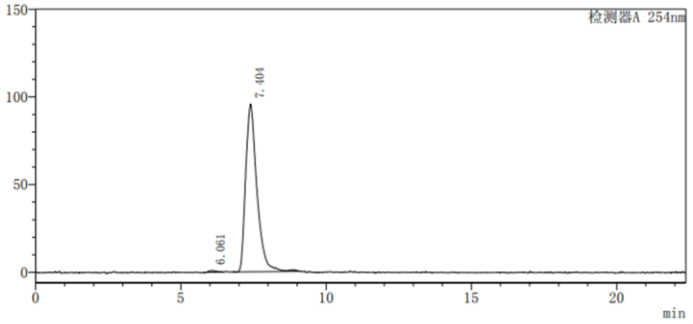


^{13}C NMR spectrum of **CZTCz-SFBN** ($CDCl_3$)



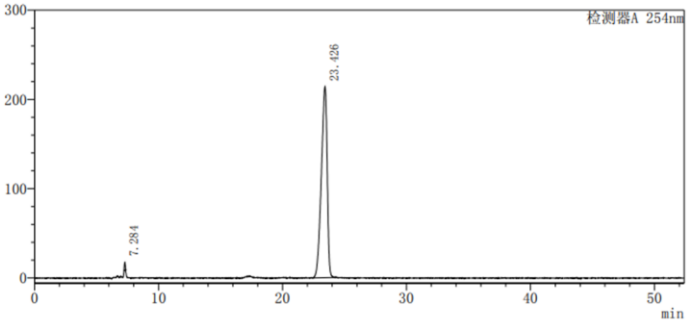
IX. Copies of HPLC Chromatogram

HPLC chromatogram of **DCz-SFBN** (99.353%)



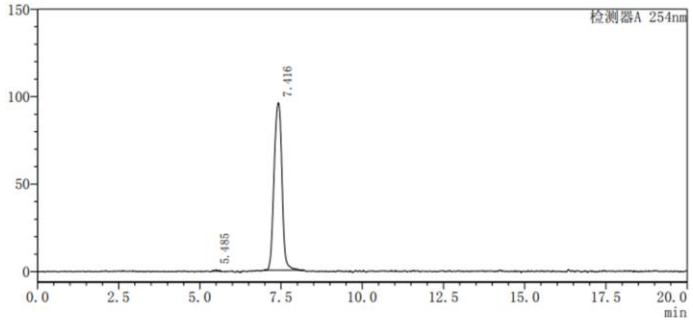
Peak#	Ret. Time	Area	Height	Area%
1	6.061	16763	1000	0.647
2	7.404	2573373	95634	99.353
Total		2590136	96634	

HPLC chromatogram of **DPhCz-SFBN** (99.381%)



Peak#	Ret. Time	Area	Height	Area%
1	7.284	43693	8943	0.619
2	23.426	7010689	213755	99.381
Total		7054382	222698	

HPLC chromatogram of **CzTCz-SFBN** (99.659%)



Peak#	Ret. Time	Area	Height	Area%
1	5.485	5528	642	0.341
2	7.416	1614614	95738	99.659
Total		1620142	96380	