Novel Cross-linked Deep-blue Fluorene-based Emitters for Full solution-processed Organic Light-emitting Diodes

Xia Wang[a,b], Chuanxin Liao[a,b], Xianggao Li[a,b], HongLi Liu[a,b], Shirong Wang[a,b]**

[a] *School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China*

[b] *Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China*

E-mail: liuhongli@tju.edu.cn, wangshirong@tju.edu.cn

Experimental steps

Materials and Methods

All reagents and solvents used for synthesis and measurement were purchased from commercial suppliers and werw used without further purification unless otherwise specified. Proton nuclear magnetic resonance (^{1}H NMR) and carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were measured on a Bruker AVANCE III HD 400 MHz NMR spectrometer using chloroform-*d* as the solvent and tetramethylsilane (TMS) as the internal standard. High resolution mass spectrometry (HRMS) were measured using atmospheric pressure chemical ionization (APCI) source ionization on a Bruker MicroTOF-Q II high-resolution mass spectrometer. Fourier transform infrared (FTIR) spectra were recorded on an FTIR-650 Fourier transform infrared spectrometer and used high-purity potassium bromide (KBr) tabletting. Ultraviolet-visible (UV-vis) absorption spectra were recorded on a Thermo GENESYS 10S UV-vis spectrophotometer. Photoluminescence (PL) spectra, time-resolved photoluminescence (TRPL) spectra, and photoluminescence quantum yields (PLQYs) were recorded on a Horiba FluoroMax-4 spectrophotometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves were measured on a TA Q500 thermogravimetric analyzer and a TA Q20 differential scanning calorimeter at a heating rate of 10 °C min^{-1} under nitrogen flow. X-ray diffraction (XRD) results and atomic force microscopy (AFM) images were obtained on a MiniFlex 600 X-ray diffractometer and a Dimension icon atomic force microscope, respectively. Ultraviolet photo-electron spectroscopy (UPS) data were obtained using the K-Alpha+ model X-ray photoelectron spectroscopy analyzer from Thermo Technologies in the United States. Contact angle diagrams were obtained using the JC 2000D contact angle tester from Shanghai Zhongchen Digital Technology Equipment Co., Ltd.

Quantum chemical computation

All calculations performed to the emitters were implemented using the Gaussian 09 software package. The optimized ground state geometrical configurations, frontier molecular orbital (FMO) energy levels and electron cloud distributions were determined

using the density functional theory (DFT) calculations with the B3LYP/6-31G(d) basis set.

Device preparation and measurement

Etched patterned indium tin oxide (ITO) glass was used as the substrate. Before device manufacturing, the ITO glass substrates were cleaned with detergent, deionized water, and ethanol for 20 min, boiled and blown dry in ethanol, and then treated with O_2 plasma on a CIF CPC-a plasma cleaner for 10 minutes. 40 μL of poly (3,4-ethylenedioxythiophene)-poly(styrene sulfonic acid) (PEDOT: PSS) 4083 solution was taken and spin-coated on the ITO substrate at 4000 rpm for 30 seconds, and then annealed at 140 °C for 20 minutes in an air atmosphere. 40 μL of poly [(9,9-dioctylfluorene-2,7-diyl)-co-(4,4'-(*N*-(4-sec-butylphenyl)diphenylamine)] (TFB) in chlorobenzene solution (6 mg/mL) was takenand spin-coated on the obtained PEDOT: PSS film at 4000 rpm for 30 seconds, then annealed at 140 °C for 20 minutes in an air atmosphere. 40 μL of V-MFCz, V-HFCz, and V-SAFCz in chlorobenzene solution (15 mg/mL) was takenand spin-coated on the obtained TFB film at a speed of 3000 rpm for 30 seconds, annealed heated at 300 ℃, 180 ℃, and 280 ℃ for 30 minutes under an Ar atmosphere, respectively. 40 μL of 1,3,5-tris (1-phenyl-1H-benzimidazol-2-yl) benzene (TPBi) in toluene solution (20 mg/mL) was taken and spin-coated on the obtained EML at 4000 rpm for 30 seconds, then annealed at 100 °C for 20 minutes in an Ar atmosphere. The thickness of different spin-coated films were measured on the KLA Tencor Alpha Step D300 stylus profiler. TPBi, lithium fluoride (LiF), and aluminum (Al) were evaporated with the pressure of about 6×10^{-4} Pa at the rates of 1, 0.1, and 10 Å s^{-1}, respectively. During this process, the thickness of each sedimentary layer was monitored through quartz crystal oscillation. Electroluminescence (EL) spectrum was recorded on the Konicaminolta CS-2000 spectrometer. The curves of current density and luminance versus voltage (*J-V-L*), and external quantum efficiencies (EQEs) were recorded on a computer-controlled Keithley 2400 source meter equipped with a silicon photodiode in a glove box.

Synthesis route

The synthesis of 9-(4-bromophenyl)-9H-carbazole-3-carbaldehyde (**Cz-Br**) : 9- (4-bromophenyl) carbazole (3.22 g, 10.0 mmol) and anhydrous N,N-Dimethylformamide (50

mL) were added in a 250 mL double necked flask with an ice water. Under argon protection, phosphorus oxychloride (13.72 ml, 150 mmol) was slowly added dropwise to the flask, restored to room temperature, stirred for 2 hours, refluxed at 90 ℃ for 20 hours, monitored by thin layer chromatography (TLC). Then the reaction solution was poured into ice water and adjusted to neutral pH by adding sodium hydroxide solution. After filtration, extracted the solid from the Buchner funnel with dichloromethane and dried under vacuum, and the crude product was purified by silica gel column chromatography with the eluent of petroleum ether and dichloromethane (volume ratio: 2:1) to obtain **Cz-Br** with a yield of 70%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.13 (s, 1H), 8.67 (s, 1H), 8.21 (d, J = 7.6 Hz, 1H), 7.96 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 8.6 Hz, 2H), 7.52 – 7.36 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.72, 144.21, 141.57, 135.77, 133.44, 129.68, 128.81, 127.66, 127.19, 123.85, 123.74, 123.33, 122.01, 121.50, 120.81, 110.21, 109.94. HRMS (APCI^{+}) *m*/*z*: calculated value for $C_{19}H_{12}BrNO$ $[M+H]^{+}$ 350.0175, found value $[M+H]^{+}$ 350.0157.

The synthesis of 9,9'-((9,9-dimethyl-9H-fluorene-2,7-diyl)bis(4,1-phenylene))bis(9H-carbazole-3-carbaldehyde) (**MFCz-CHO**): **Cz-Br** (1.1 g, 3.14 mmol), 9,9-dimethylfluorene-2,7-bis(boronic acid pinacol ester) (0.61 g, 1.37 mmol), anhydrous potassium carbonate (2 mol/L), tetrakis(triphenylphosphine)palladium(0) (0.24 g, 0.2 mmol), 1,4-dioxane (90 mL) and water (22.5 mL) were added in a 250 mL double necked flask, stirred under Ar atmosphere, and refluxed at 120 °C overnight, monitored by TLC. Then, the reaction was cooled to room temperature, poured into water, and extracted with dichloromethane. The organic phase was washed with saturated sodium chloride/water solution, then dried with anhydrous magnesium sulfate. After solvent was remove by vacuum distillation, and finally crude product was purified by silica gel column chromatography with the eluent of dichloromethane and petroleum ether (volume ratio: 3:1) to obtain 0.565 g of **MFCz-CHO** as a white solid with yield of 56.5%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.15 (s, 2H), 8.71 (d, J = 1.6 Hz, 2H), 8.25 (d, J = 7.8 Hz, 2H), 8.06 – 7.85 (m, 8H), 7.80 (d, J = 1.7 Hz, 2H), 7.74 (dd, J = 7.8, 1.7 Hz, 2H), 7.70 – 7.48 (m, 10H), 7.41 (ddd, J = 8.0, 5.7, 2.4 Hz, 2H), 1.68 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.81, 154.84, 144.53, 141.89, 141.59, 139.41, 138.56, 135.76, 129.54, 128.85, 128.73, 127.52,

127.49, 127.42, 127.09, 126.48, 123.97, 123.70, 123.34, 121.54, 121.32, 120.78, 110.52, 110.23, 47.27, 27.40. HRMS (APCI$^+$) *m*/*z*: calculated value for $C_{53}H_{36}N_2O_2$ $[M+H]^+$ 733.2849, found value $[M+H]^+$ 733.2855.

The synthesis of **V-MFCz**: methyltriphenylphosphonium bromide (3.66 g, 10.23 mmol), potassium tert-butoxide (1.15 g, 10.23 mmol), and 50 mL anhydrous tetrahydrofuran were added in a 100 mL double necked flask, followed by a 2 hour ice water bath to generate Wittig reagent, **MFCz-CHO** (1.5 g, 2.05 mmol) and anhydrous tetrahydrofuran were added to a 250 mL double necked flask, stirred under Ar atmosphere, Wittig reagent was injected by a 10 mL syringe into the 250 mL double necked flask and refluxed at 65 °C for 20 hours monitored by TLC. Then, the reaction was cooled to room temperature, quenched the reaction with water, extracted with ethyl acetate. The organic phase was washed with saturated sodium chloride/water solution, then dried with anhydrous magnesium sulfate. After solvent was remove by vacuum distillation, and finally crude product was purified by alumina column chromatography with the eluent of dichloromethane and petroleum ether (volume ratio: 1:10) and then recrystallized from ethyl acetate and n-hexane to obtain 0.84 g of **V-MFCz** as a white solid with yield of 56.5%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (d, J = 8.4 Hz, 4H), 7.97 – 7.87 (m, 6H), 7.79 (s, 2H), 7.70 (dd, J = 18.4, 8.9 Hz, 6H), 7.56 (d, J = 10.3 Hz, 2H), 7.52 – 7.42 (m, 6H), 7.32 (t, J = 6.8 Hz, 2H), 6.95 (dd, J = 17.5, 10.9 Hz, 2H), 5.82 (d, J = 17.5 Hz, 2H), 5.24 (d, J = 11.0 Hz, 2H), 1.67 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.79, 141.29, 140.70, 140.67, 139.58, 138.44, 137.39, 136.70, 130.09, 128.62, 127.29, 126.40, 126.17, 124.36, 123.67, 123.52, 121.49, 120.69, 120.44, 120.20, 118.41, 111.58, 110.02, 109.91, 47.25, 27.42. HRMS (APCI$^+$) *m*/*z*: calculated value for $C_{55}H_{40}N_2$ $[M+H]^+$ 729.3264, found value $[M+H]^+$ 729.3259.

The synthesis of 9,9'-((9,9-dihexyl-9H-fluorene-2,7-diyl)bis(4,1-phenylene))bis(9H-carbazole-3-carbaldehyde) (**HFCz-CHO**): **Cz-Br** (1.4 g, 4 mmol), 2,2'-(9,9-dihexyl-9*H*-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (0.97 g, 1.67 mmol), anhydrous potassium carbonate (2 mol/L), tetrakis(triphenylphosphine)palladium(0) (0.24 g, 0.2 mmol), 1,4-dioxane (90 mL) and water (22.5 mL) were added in a 250 mL double necked flask, stirred under Ar atmosphere, and refluxed at 120 °C overnight, monitored by

TLC. Then, the reaction was cooled to room temperature, poured into water, and extracted with dichloromethane. The organic phase was washed with saturated sodium chloride/water solution, then dried with anhydrous magnesium sulfate. After solvent was remove by vacuum distillation, and finally crude product was purified by silica gel column chromatography with the eluent of dichloromethane and petroleum ether (volume ratio: 1:1) to obtain 1.1 g of **HFCz-CHO** as a white solid with yield of 75%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.15 (s, 2H), 8.71 (s, 2H), 8.25 (s, 2H), 8.00 (s, 2H), 7.96 (d, J = 8.8 Hz, 4H), 7.89 (d, J = 7.6 Hz, 2H), 7.73 (dd, J = 7.6, 1.7 Hz, 2H), 7.71 – 7.67 (m, 6H), 7.56 (d, J = 8.4 Hz, 2H), 7.50 (s, 4H), 7.41 (td, J = 5.8, 3.0 Hz, 2H), 2.14 (d, J = 7.8 Hz, 4H), 1.26 (s, 4H), 1.15 (s, 12H), 0.79 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.83, 152.00, 144.52, 141.88, 141.64, 140.51, 139.06, 135.69, 129.52, 128.83, 127.52, 127.47, 127.09, 126.28, 123.99, 123.70, 123.35, 121.53, 121.33, 120.78, 120.45, 110.52, 110.23, 55.52, 40.58, 31.56, 29.79, 23.92, 22.65, 14.07. HRMS (APCI^{+}) *m*/*z*: calculated value for $C_{63}H_{56}N_2O_2$ $[M+H]^+$ 873.4414, found value $[M+H]^+$ 873.4420.

The synthesis of **V-HFCz**: methyltriphenylphosphonium bromide (3.68 g, 10.31 mmol), potassium tert-butoxide (1.16 g, 10.31 mmol), and 50 mL anhydrous tetrahydrofuran were added in a 100 mL double necked flask, followed by a 2-hour ice water bath to generate Wittig reagent, **HFCz-CHO** (1.8 g, 2.06 mmol) and anhydrous tetrahydrofuran were added to a 250 mL double necked flask, stirred under Ar atmosphere, Wittig reagent was injected by a 10 mL syringe into the 250 mL double necked flask and refluxed at 65 °C for 20 hours monitored by TLC. Then, the reaction was cooled to room temperature, quenched the reaction with water, extracted with ethyl acetate. The organic phase was washed with saturated sodium chloride/water solution, then dried with anhydrous magnesium sulfate. After solvent was remove by vacuum distillation, and finally crude product was purified by alumina column chromatography with the eluent of dichloromethane and petroleum ether (volume ratio: 1:10) and then recrystallized from ethyl acetate and n-hexane to obtain 1.34 g of **V-HFCz** as a white solid with yield of 74.8 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 – 8.16 (m, 4H), 7.93 (d, J = 6.4 Hz, 4H), 7.88 (d, J = 7.6 Hz, 2H), 7.72 (dd, J = 7.6, 1.7 Hz, 2H), 7.71 – 7.67 (m, 6H), 7.57 – 7.55 (m, 2H), 7.51 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.7

Hz, 4H), 7.34 – 7.31 (m, 2H), 6.97 – 6.93 (m, 2H), 5.82 (d, J = 17.5 Hz, 2H), 5.25 (d, J = 10.9 Hz, 2H), 2.15 – 2.12 (m, 4H), 1.17 – 1.09 (m, 12H), 0.78 (t, J = 7.2 Hz, 10H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.95, 141.29, 140.76, 140.68, 140.39, 139.23, 137.39, 136.64, 130.09, 128.60, 127.28, 126.19, 126.17, 124.36, 123.68, 123.52, 121.48, 120.45, 120.36, 120.21, 118.42, 111.59, 110.02, 109.91, 55.49, 40.61, 31.57, 29.81, 23.92, 22.66, 14.08. HRMS (APCI$^+$) *m*/*z*: calculated value for $C_{65}H_{60}N_2$ $[M+H]^+$ 869.4829, found value $[M+H]^+$ 869.4837.

The synthesis of 2',7'-dibromo-10-phenyl-10*H*-spiro[acridine-9,9'-fluorene] **(SAF-Br)**: 2-bromotriphenylamine (3.23 g, 10 mmol) and 40 mL anhydrous tetrahydrofuran were added a 100 mL three necked flask, cooled to -78 ℃ through a low-temperature reactor. Slowly added 4.8 mL of n-butyllithium (n-BuLi, 2.5 M in hexane, 12 mmol) using a syringe, and stirred at -78 ℃ for 1 hour. Then droped 2,7-dibromo-9-fluorenone (3.70 g, 11 mmol) dissolved in 20 mL of tetrahydrofuran into the reaction system, stirred under Ar atmosphere, and refluxed at room temperature overnight, monitored by TLC. Then, the reaction was cooled to room temperature, added 5 mL of deionized water, extracted three times with dichloromethane, dried the organic phase with anhydrous sodium sulfate, filtered, and evaporated under reduced pressure to remove the solvent. The crude product was separated by silica gel column chromatography to obtain a yellow solid. Finally, yellow solid was dissolved in 50 mL of acetic acid and 5 mL of concentrated hydrochloric acid (36%), refluxed at 120 ℃ for 5 hours. The reaction was cooled to room temperature, filtered, and washed the filter cake with petroleum ether to obtain 3.64 g of **SAF-Br** as white solid with a yield of 64%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (t, J = 7.7 Hz, 2H), 7.66 – 7.58 (m, 3H), 7.55 – 7.44 (m, 6H), 7.01 – 6.93 (m, 2H), 6.66 – 6.58 (m, 2H), 6.38 (d, J = 11.7 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.15, 141.10, 140.69, 137.16, 131.20, 131.12, 131.08, 129.21, 128.66, 127.76, 122.99, 122.37, 121.38, 120.78, 115.04, 56.97. HRMS (APCI$^+$) *m*/*z*: calculated value for $C_{31}H_{19}Br_2N$ $[M+H]^+$ 565.9938, found value $[M+H]^+$ 565.9930.

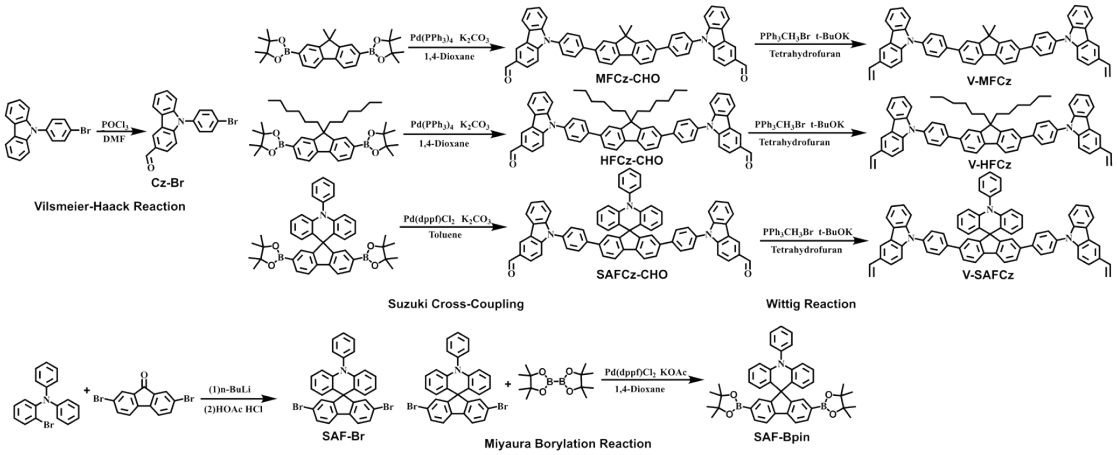
The synthesis of 10-phenyl-2',7'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10*H*-spiro[acridine-9,9'-fluorene] **(SAF-Bpin**): **SAF-Br** (3.50 g, 6.19 mmol),

4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (6.29 g, 24.77 mmol), 1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.68g, 0.93 mmol), acetic acid (4.86g, 49.53 mmol) and anhydrous 1,4-dioxane (100 mL) were added to a 250 mL two necked flask, stirred under Ar atmosphere, and refluxed at 80 °C or 10 hours, monitored by TLC. Then, the reaction was cooled to room temperature, poured into water, and extracted with dichloromethane. The organic phase was washed with saturated sodium chloride/water solution, then dried with anhydrous magnesium sulfate. After solvent was remove by vacuum distillation, and finally crude product was purified by silica gel column chromatography with the eluent of dichloromethane and petroleum ether (volume ratio: 1:3) to obtain 3.95 g of **SAF-Bpin** as a white solid with yield of 96.8%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (s, 2H), 7.83 (d, J = 4.6 Hz, 4H), 7.73 (d, J = 7.7 Hz, 2H), 7.63 – 7.55 (m, 3H), 6.93 (d, J = 7.1 Hz, 2H), 6.58 – 6.52 (m, 2H), 6.42 – 6.35 (m, 4H), 1.31 (s, 24H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.21, 141.89, 141.50, 141.12, 134.32, 132.21, 131.47, 130.99, 128.40, 127.94, 127.01, 124.90, 120.44, 119.62, 114.69, 83.75, 56.78, 24.98. HRMS (APCI^{+}) *m*/*z*: calculated value for $C_{43}H_{43}B_2NO_4$ $[M+H]^+$ 660.3465, found value $[M+H]^+$ 660.3466.

The synthesis of 9,9'-((10-phenyl-10*H*-spiro[acridine-9,9'-fluorene]-2',7'-diyl)bis(4,1-phenylene))bis(9*H*-carbazole-3-carbaldehyde (**SAFCz-CHO**): **Cz-Br** (1.4 g, 4 mmol), SAF-Bpin (1.1 g, 1.67 mmol), anhydrous potassium carbonate (2 mol/L), 1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.29 g, 0.25 mmol), toluene (60 mL) and water (12 mL) were added in a 250 mL double necked flask, stirred under Ar atmosphere, and refluxed at 120 °C overnight, monitored by TLC. Then, the reaction was cooled to room temperature, poured into water, and extracted with dichloromethane. The organic phase was washed with saturated sodium chloride/water solution, then dried with anhydrous magnesium sulfate. After solvent was remove by vacuum distillation, and finally crude product was purified by silica gel column chromatography with the eluent of dichloromethane and petroleum ether (volume ratio: 1:1) to obtain 0.95 g of **SAFCz-CHO** as a white solid with yield of 60%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.13 (s, 2H), 8.69 (s, 2H), 8.22 (d, J = 7.7 Hz, 2H), 8.00 (d, J = 5.1 Hz, 2H), 7.97 (d, J = 5.5 Hz, 3H), 7.84 (d,

J = 8.2 Hz, 4H), 7.79 (d, J = 7.6 Hz, 2H), 7.72 (t, J = 7.9 Hz, 3H), 7.60 (d, J = 8.7 Hz, 4H), 7.54 (d, J = 6.8 Hz, 3H), 7.49 (d, J = 3.9 Hz, 4H), 7.44 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 7.4 Hz, 2H), 7.00 – 6.98 (m, 2H), 6.68 – 6.66 (m, 2H), 6.61 (d, J = 9.6 Hz, 2H), 6.44 (d, J = 9.7 Hz, 2H). HRMS (APCI$^+$) *m*/*z*: calculated value for $C_{69}H_{43}N_3O_2$ $[M+H]^+$ 946.3428, found value $[M+H]^+$ 946.3427.

The synthesis of **V-SAFCz**: methyltriphenylphosphonium bromide (1.13 g, 3.17 mmol), potassium tert-butoxide (0.37 g, 3.17 mmol), and 50 mL anhydrous tetrahydrofuran were added in a 100 mL double necked flask, followed by a 2-hour ice water bath to generate Wittig reagent, **SAF-CHO** (0.6 g, 0.63 mmol) and anhydrous tetrahydrofuran were added to a 250 mL double necked flask. stirred under Ar atmosphere, Wittig reagent was injected by a 10 mL syringe into the 250 mL double necked flask and refluxed at 65 °C for 20 hours monitored by TLC. Then, the reaction was cooled to room temperature, quenched the reaction with water, extracted with ethyl acetate. The organic phase was washed with saturated sodium chloride/water solution, then dried with anhydrous magnesium sulfate. After solvent was remove by vacuum distillation, and finally crude product was purified by alumina column chromatography with the eluent of dichloromethane and petroleum ether (volume ratio: 1:10) and then recrystallized from ethyl acetate and n-hexane to obtain 0.32 g of **V-SAFCz** as a white solid with yield of 53 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 – 8.12 (m, 4H), 7.98 (d, J = 7.7 Hz, 2H), 7.81 (d, J = 7.5 Hz, 5H), 7.78 (d, J = 4.5 Hz, 2H), 7.73 (s, 2H), 7.62 – 7.57 (m, 5H), 7.56 – 7.52 (m, 4H), 7.44 – 7.40 (m, 4H), 7.38 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 6.4 Hz, 2H), 7.00 – 6.97 (m, 2H), 6.93 (dd, J = 17.5, 10.7 Hz, 2H), 6.66 (d, J = 7.0 Hz, 2H), 6.62 (d, J = 8.0 Hz, 2H), 6.44 (d, J = 8.5 Hz, 2H), 5.80 (d, J = 17.5 Hz, 2H), 5.30 (s, 1H), 5.23 (d, J = 10.9 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.64, 140.39, 140.19, 139.96, 139.58, 139.40, 139.24, 137.39, 136.31, 135.65, 130.13, 130.08, 129.00, 127.57, 127.45, 126.81, 126.41, 126.14, 125.81, 125.08, 123.63, 123.49, 123.27, 122.58, 122.42, 119.75, 119.56, 119.34, 119.11, 117.31, 113.83, 110.49, 108.90, 108.79, 56.17. HRMS (APCI$^+$) *m*/*z*: calculated value for $C_{71}H_{47}N_3$ $[M+H]^+$ 942.3842, found value $[M+H]^+$ 942.3850.



Scheme 1. Synthesis route of V-MFCz, V-HFCz, and V-SAFCz.

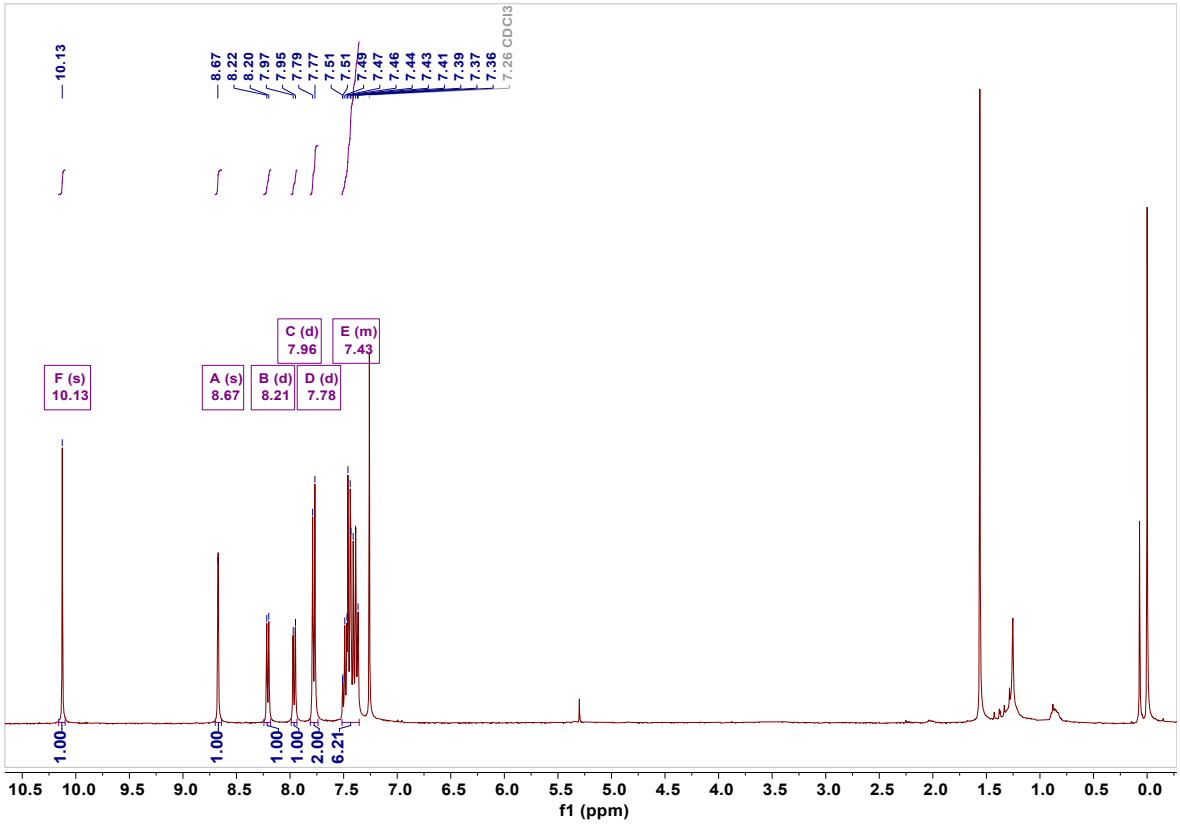


Figure S1. ^{1}H NMR spectrum of intermediate Cz-Br (solvent: Chloroform-*d*).

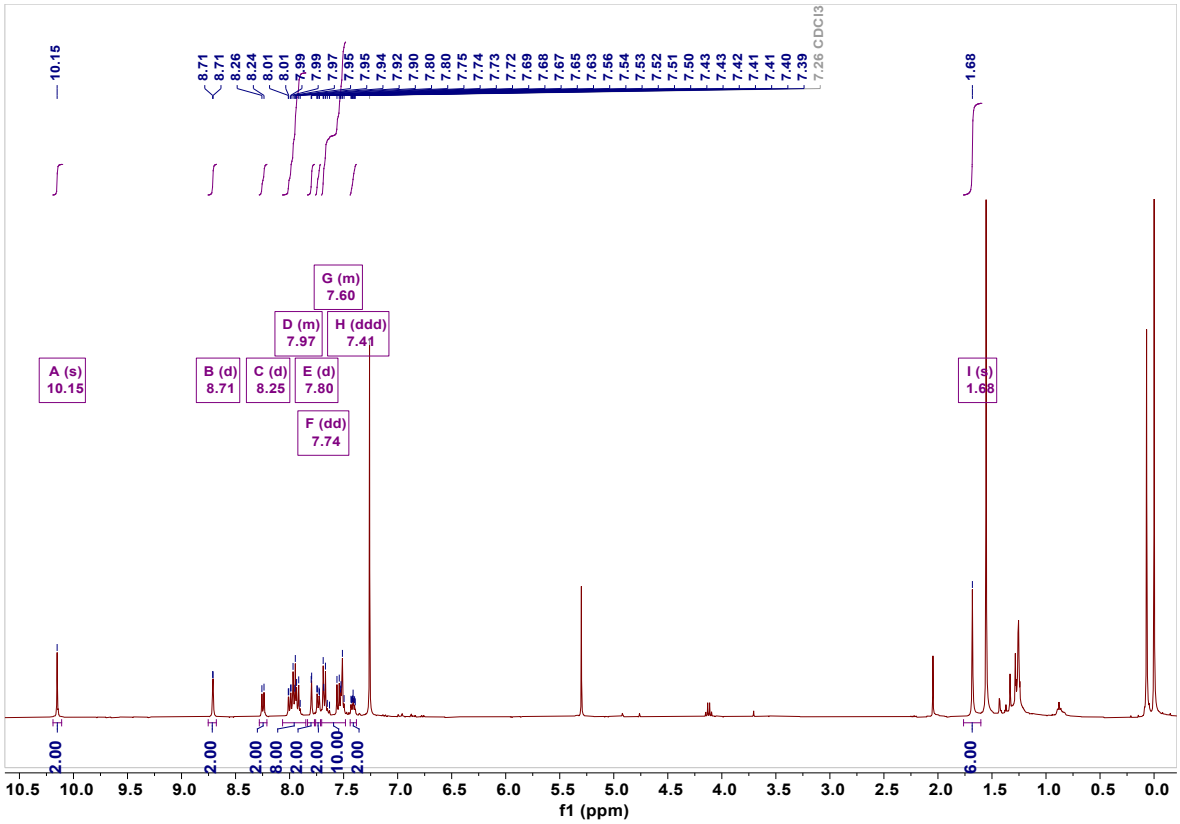


Figure S2. [1]H NMR spectrum of intermediate MFCz-CHO (solvent: Chloroform-*d*).

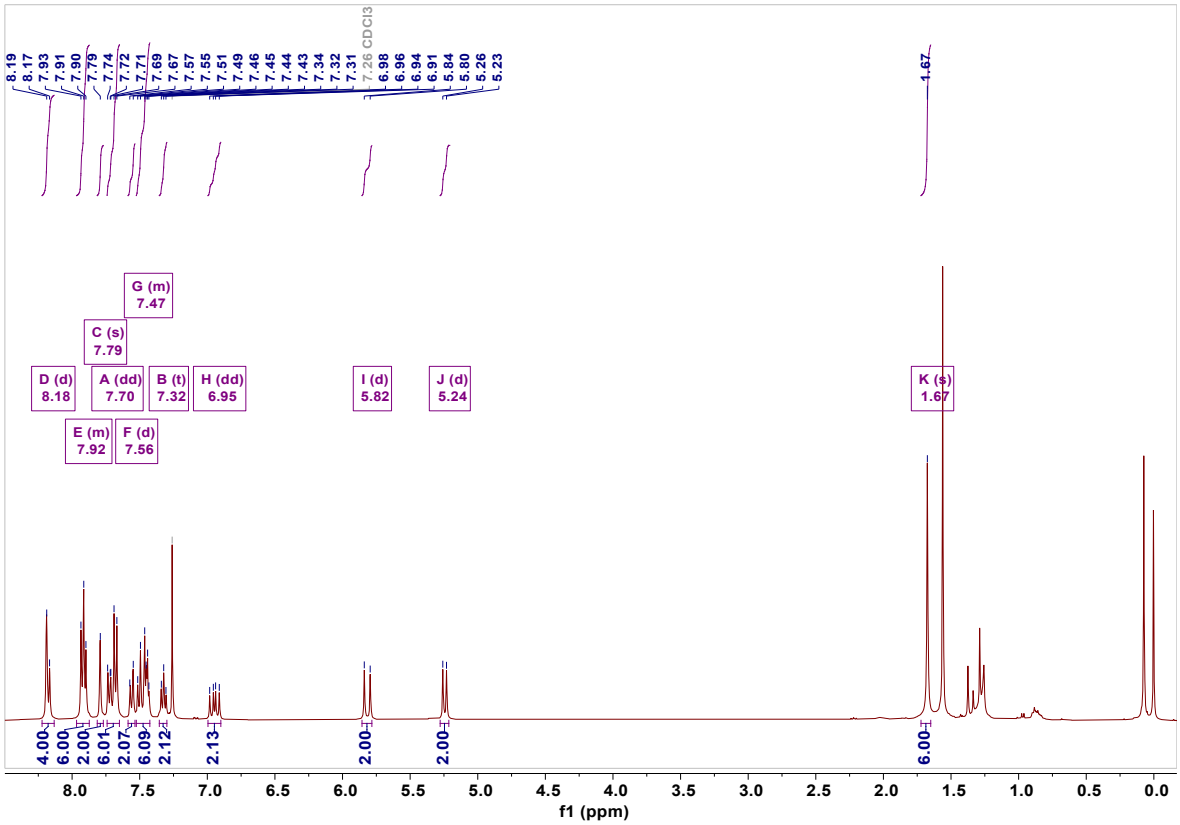


Figure S3. [1]H NMR spectrum of V-MFCz (solvent: Chloroform-*d*).

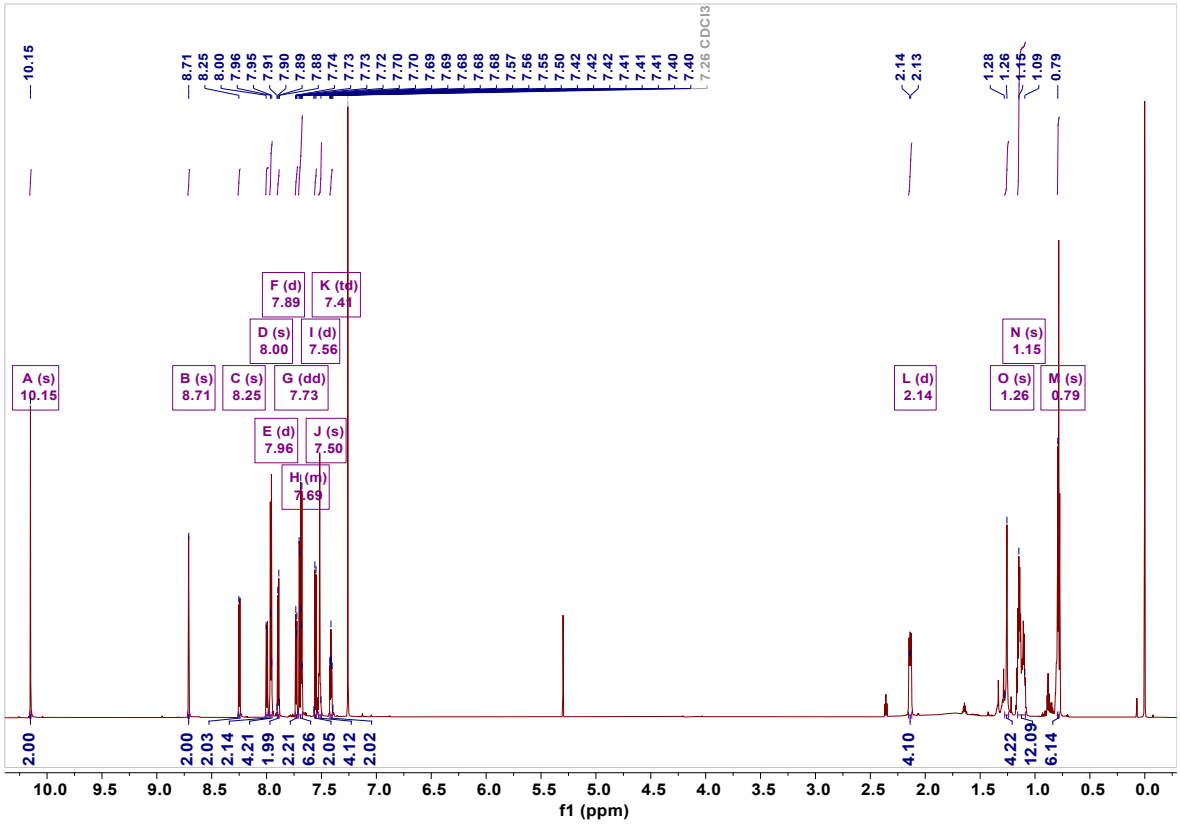


Figure S4. [1]H NMR spectrum of intermediate HFCz-CHO (solvent: Chloroform-*d*).

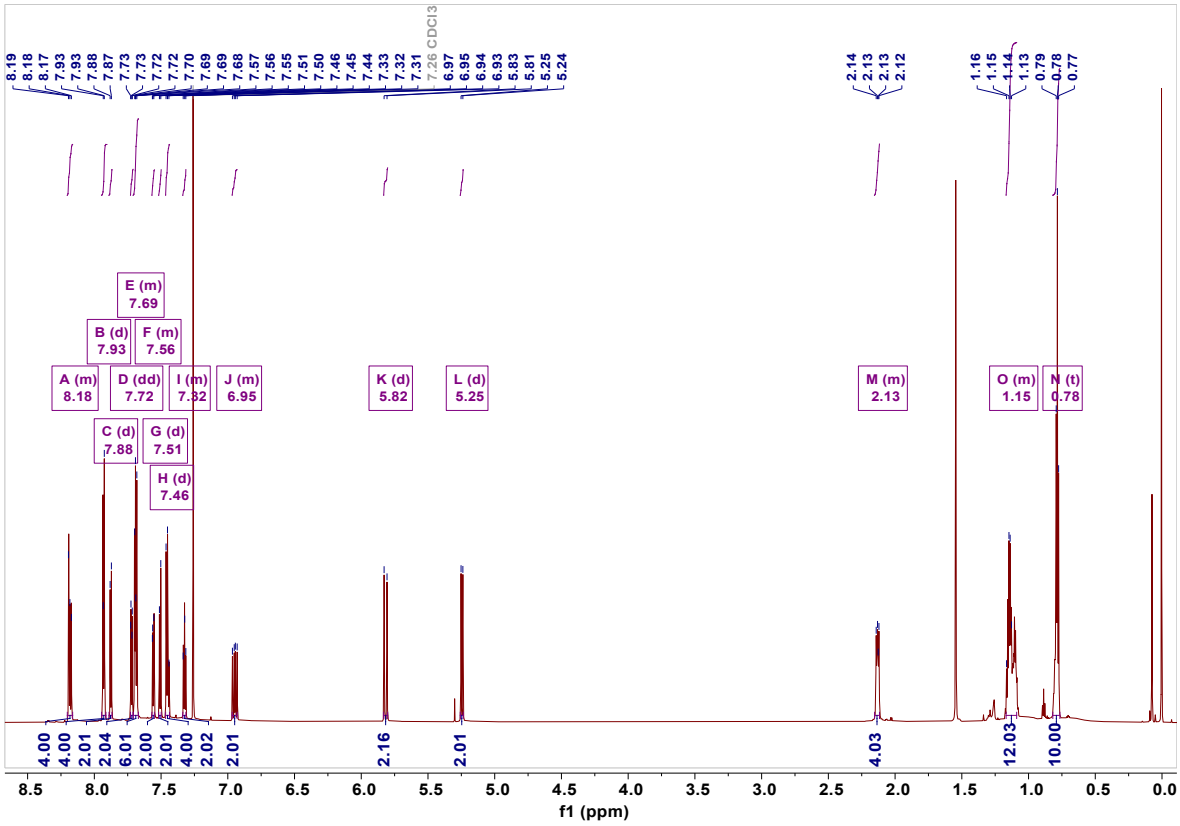


Figure S5. [1]H NMR spectrum of V-HFCz (solvent: Chloroform-*d*).

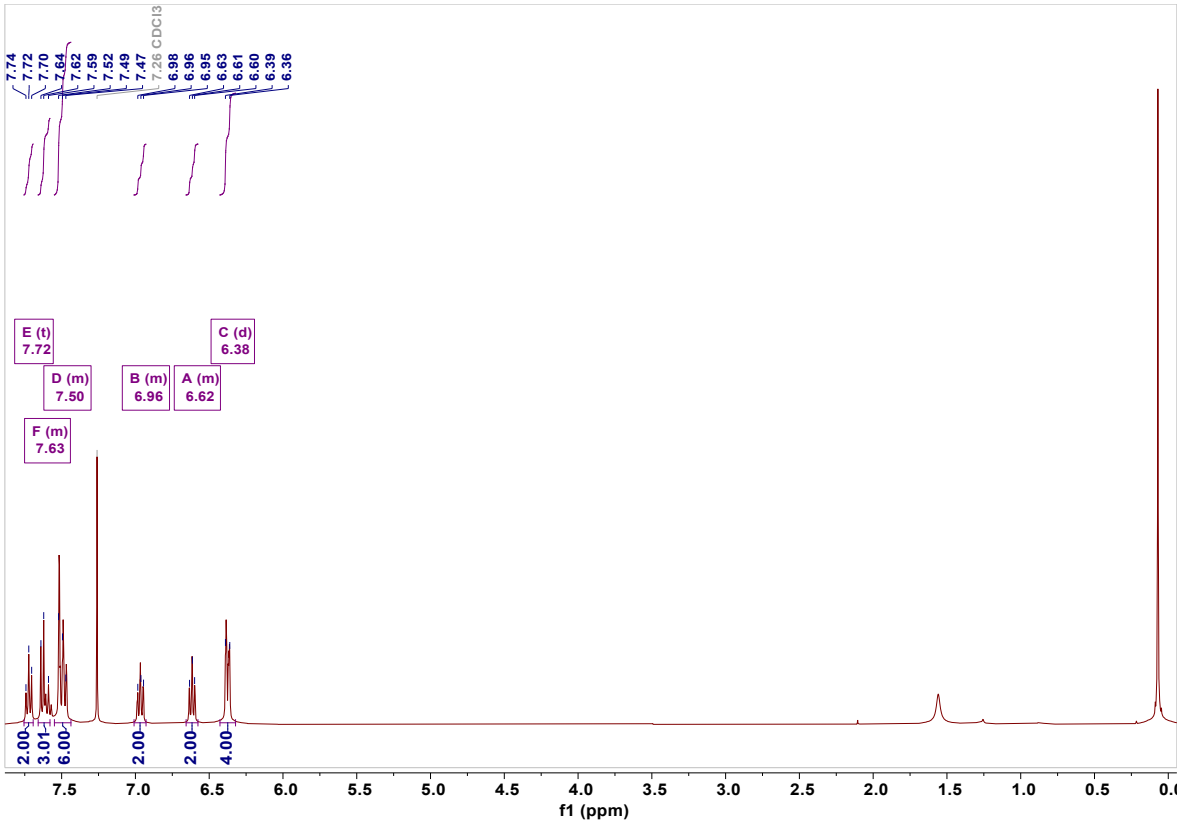


Figure S6. [1]H NMR spectrum of intermediate SAF-Br (solvent: Chloroform-*d*).

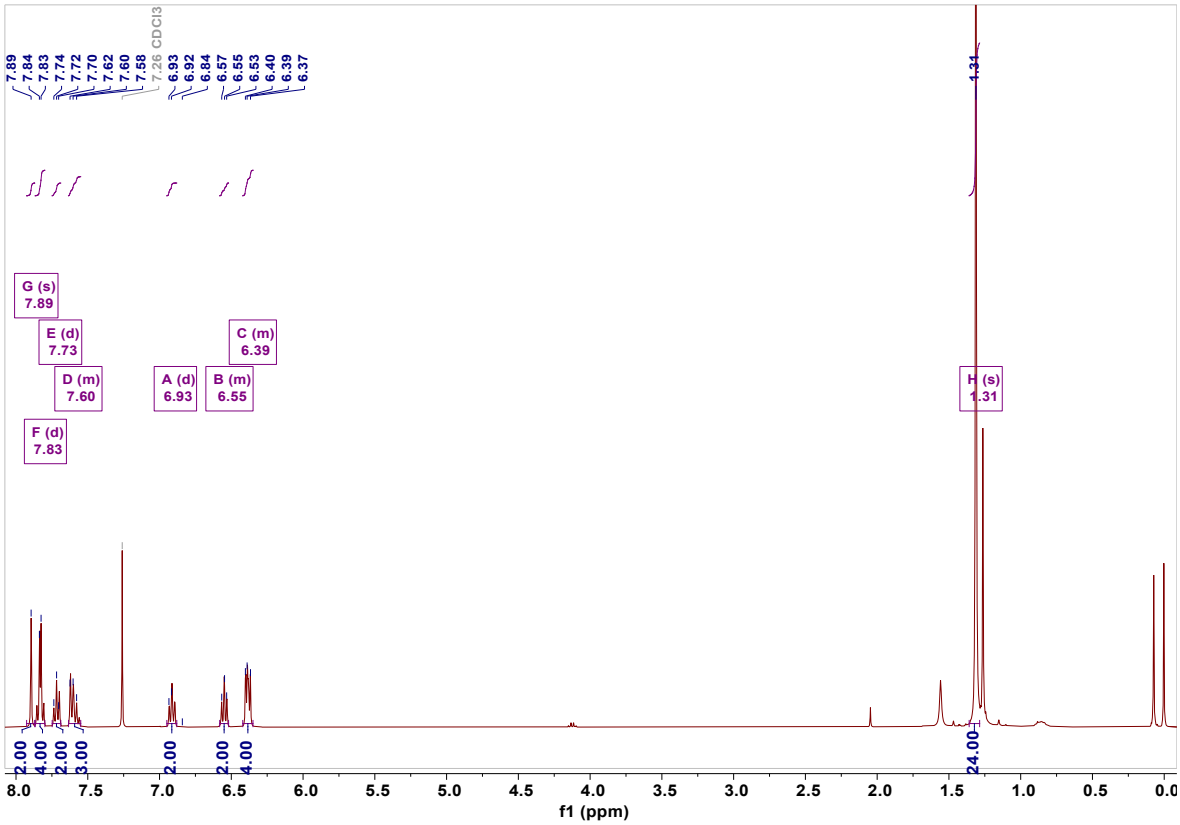


Figure S7. [1]H NMR spectrum of intermediate SAF-Bpin (solvent: Chloroform-*d*).

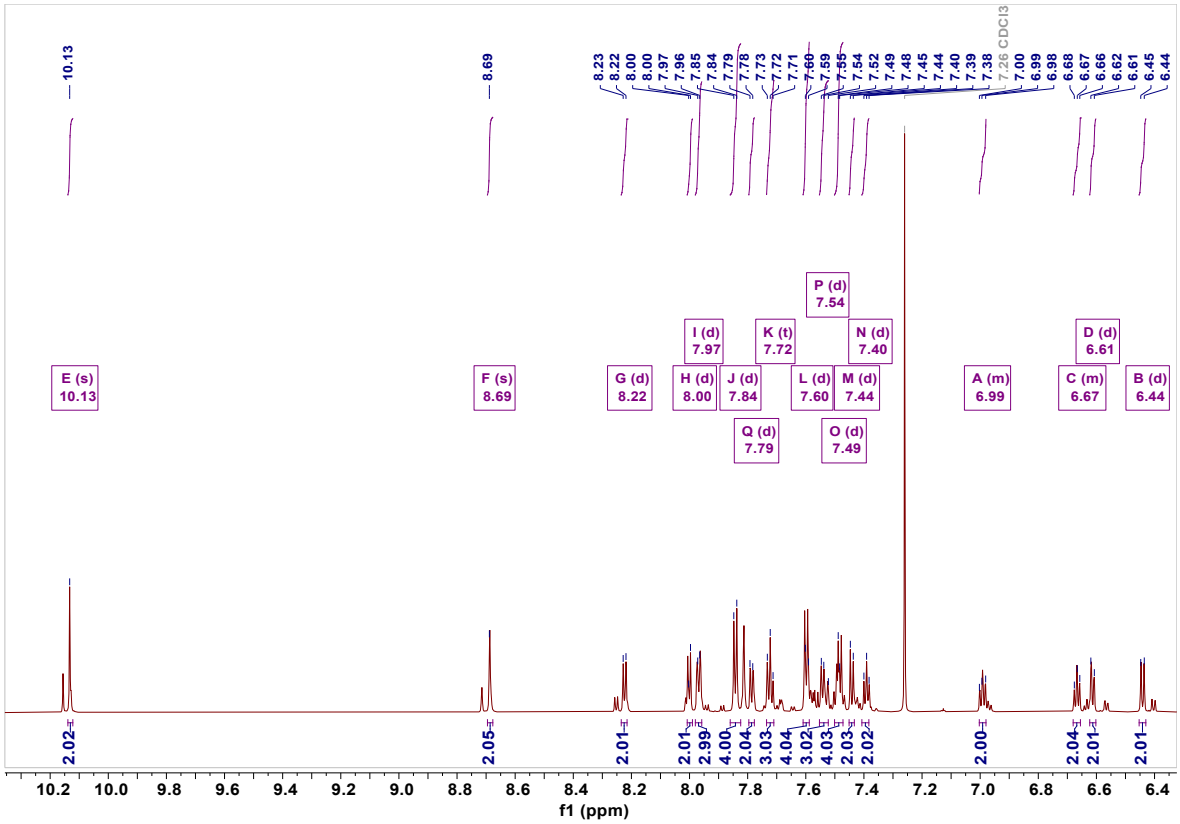


Figure S8. [1]H NMR spectrum of intermediate SAFCz-CHO (solvent: Chloroform-*d*).

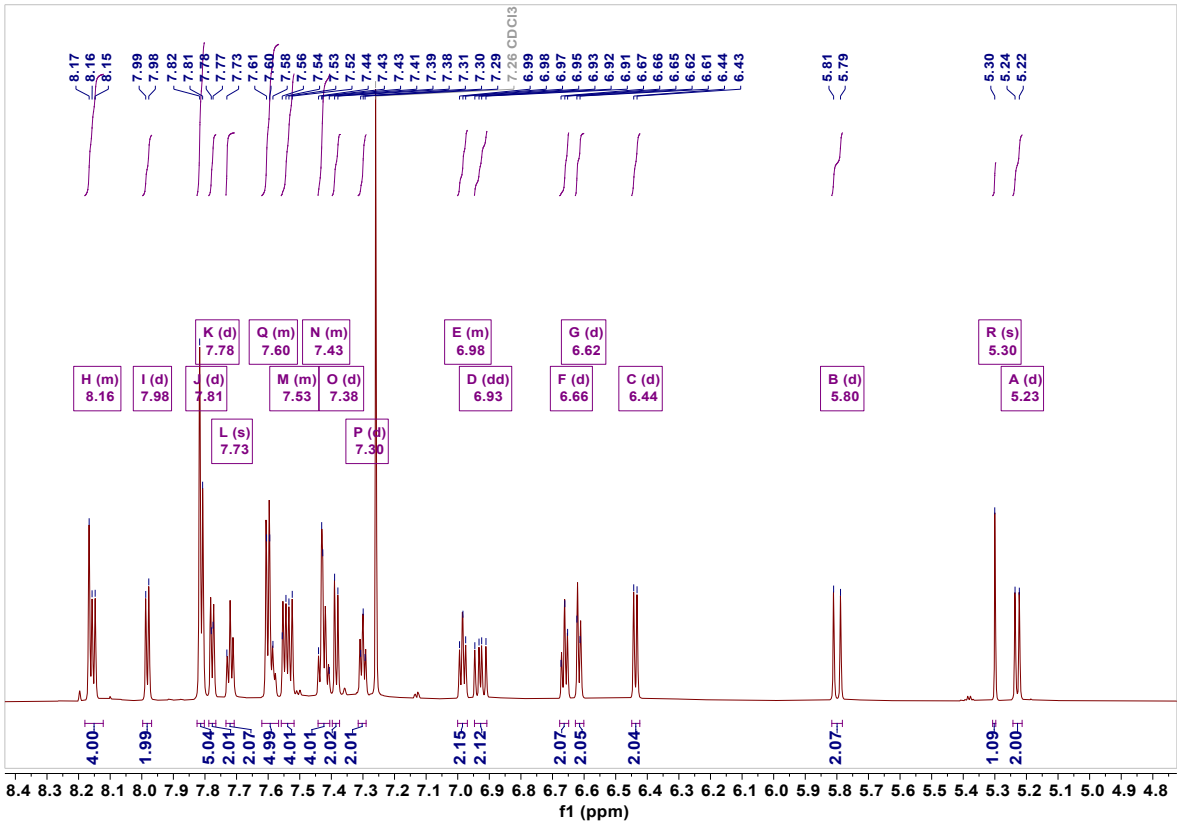


Figure S9. [1]H NMR spectrum of V-SAFCz (solvent: Chloroform-*d*).

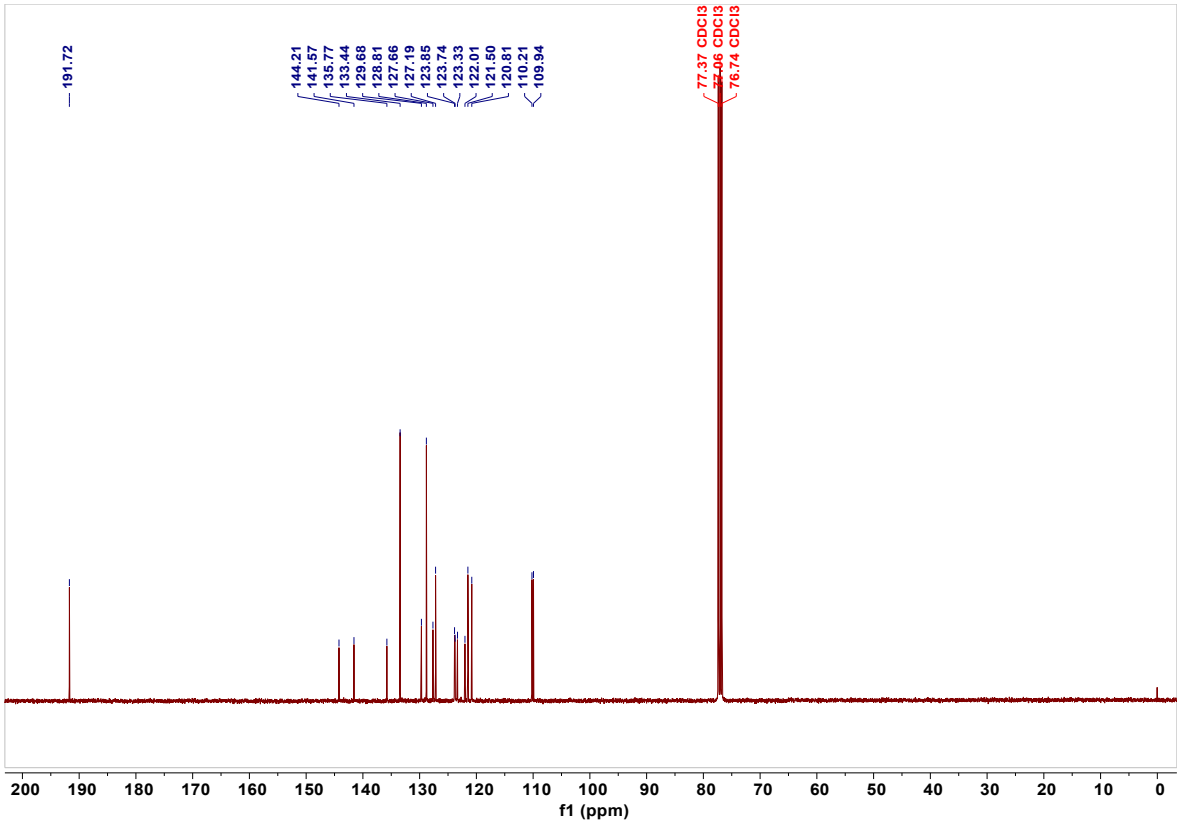


Figure S10. ^{13}C NMR spectrum of intermediate Cz-Br (solvent: Chloroform-*d*).

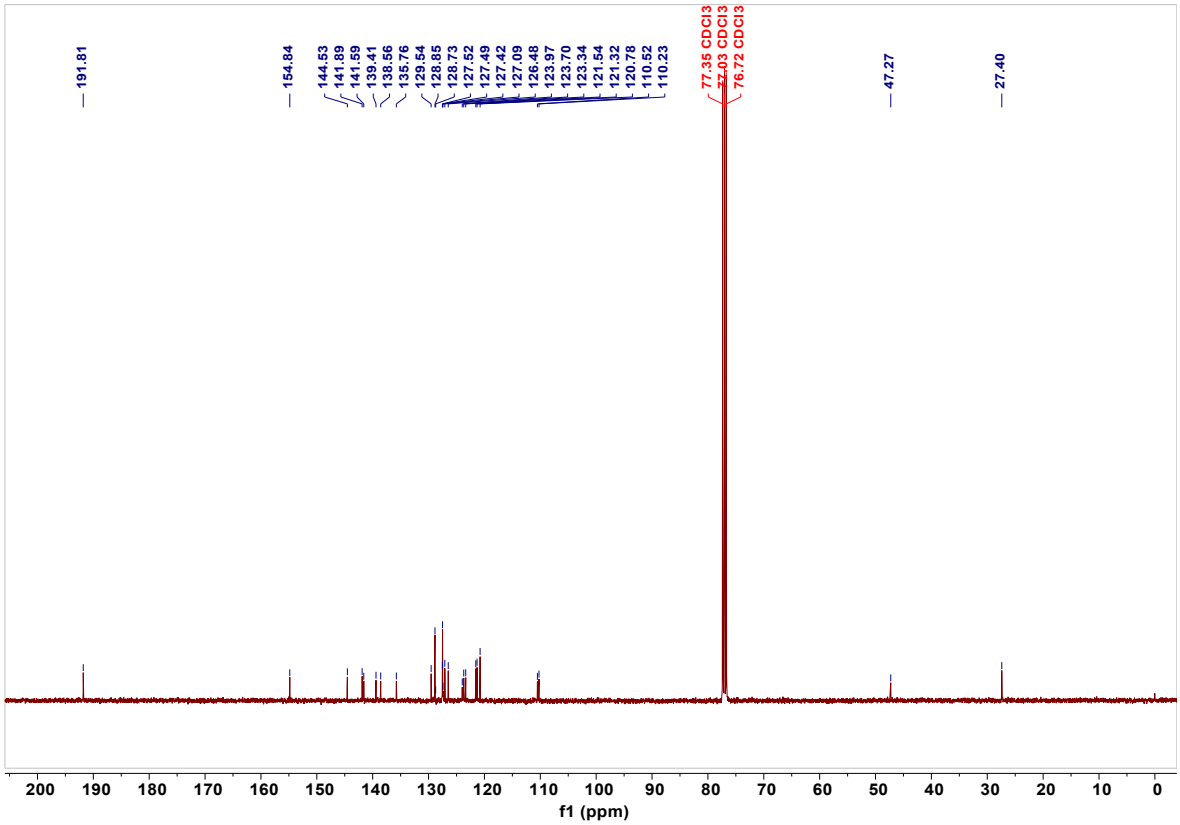


Figure S11. ^{13}C NMR spectrum of intermediate MFCz-CHO (solvent: Chloroform-*d*).

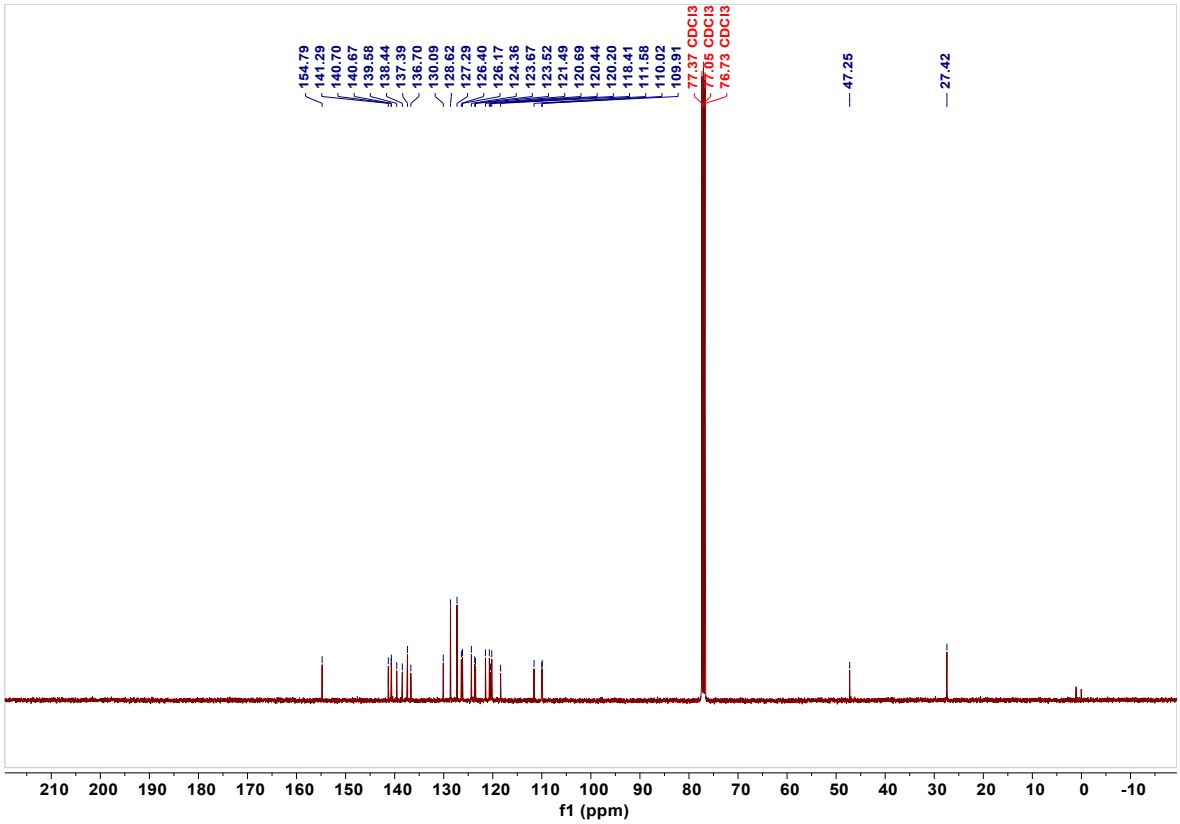


Figure S12. ^{13}C NMR spectrum of V-MFCz (solvent: Chloroform-*d*).

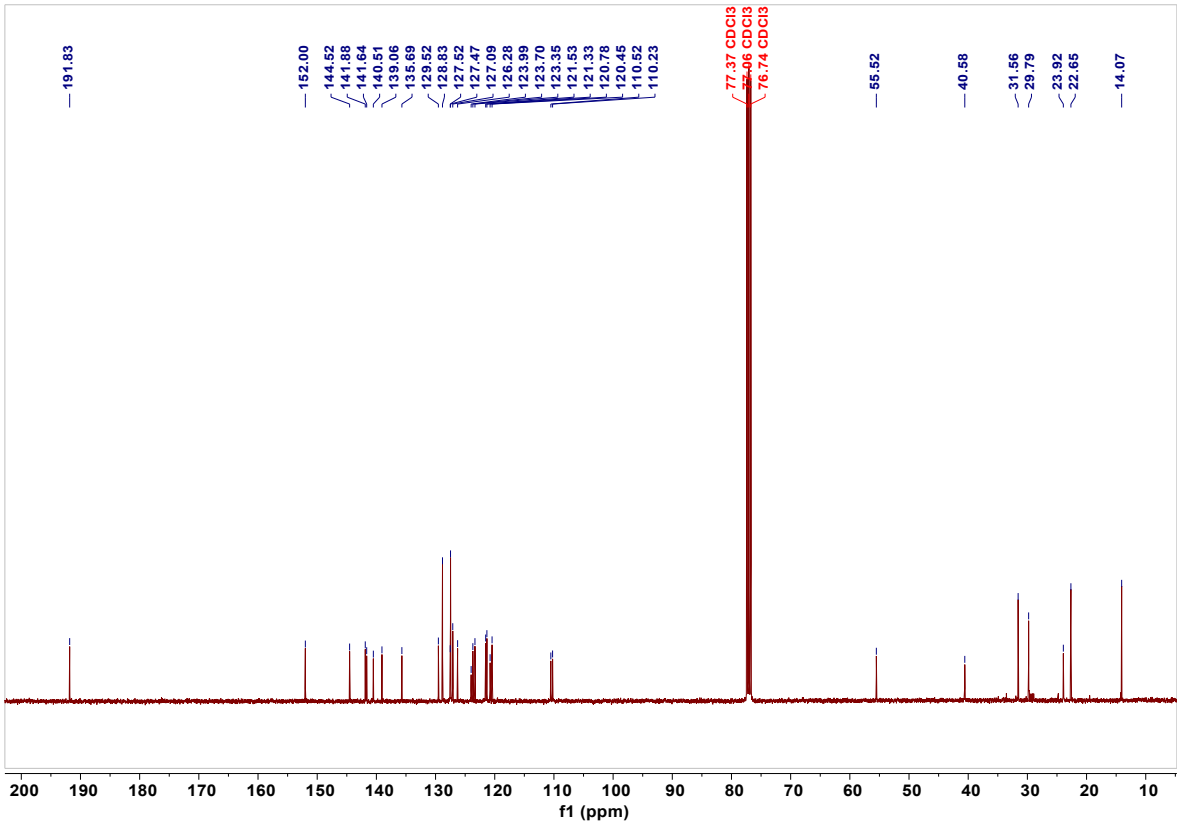


Figure S13. ^{13}C NMR spectrum of intermediate HFCz-CHO (solvent: Chloroform-*d*).

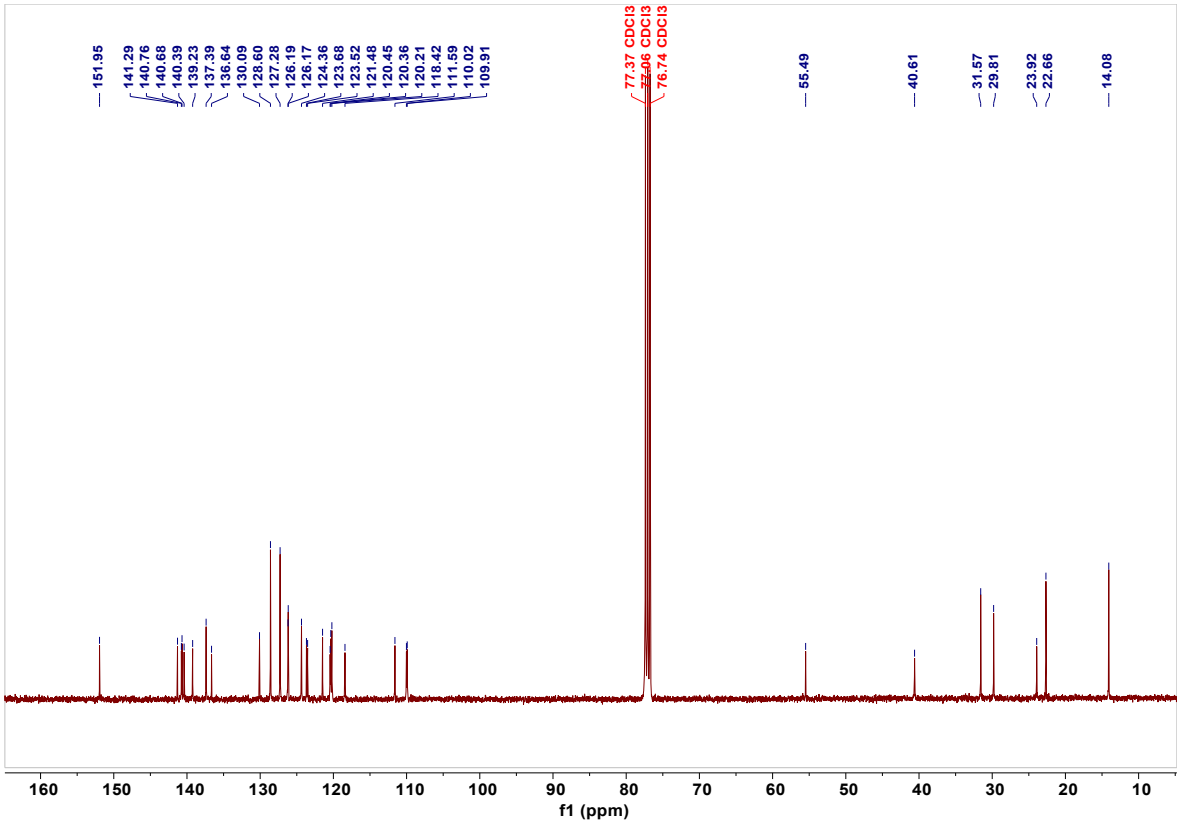


Figure S14. ^{13}C NMR spectrum of V-HFCz (solvent: Chloroform-*d*).

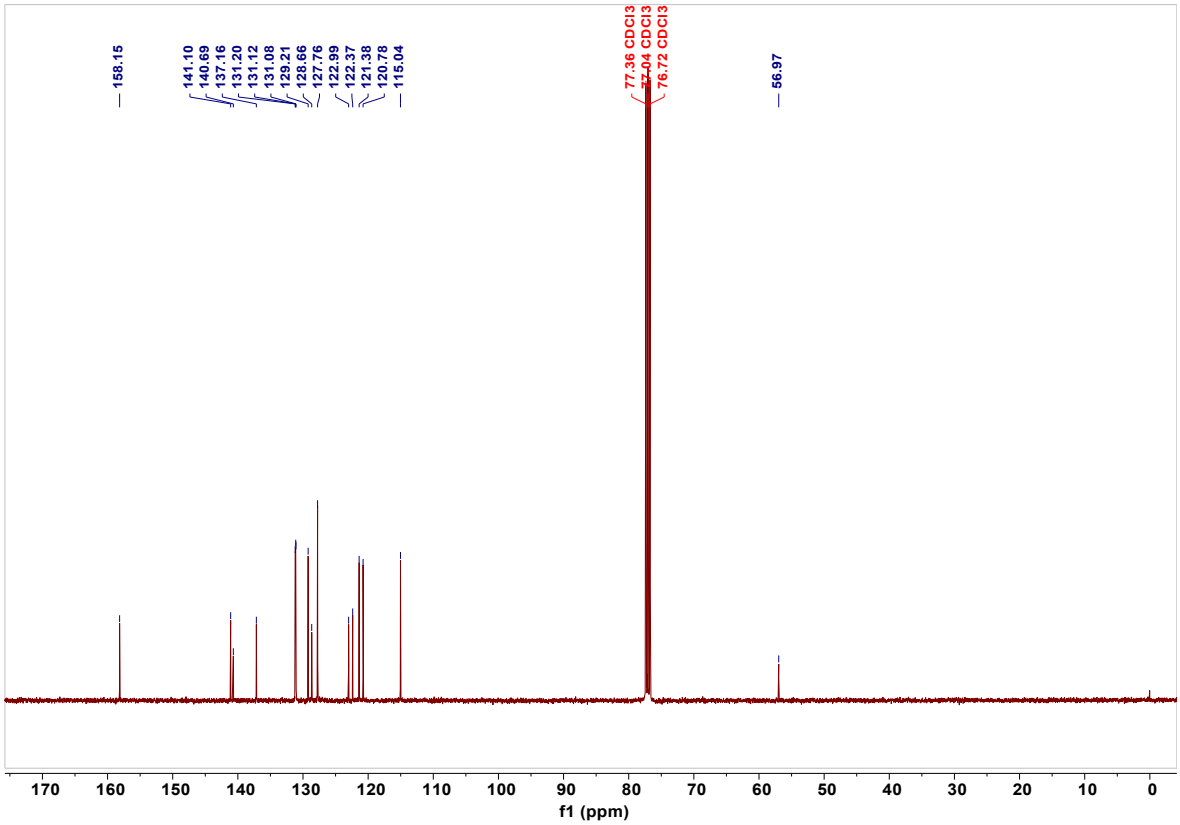


Figure S15. ^{13}C NMR spectrum of intermediate SAF-Br (solvent: Chloroform-*d*).

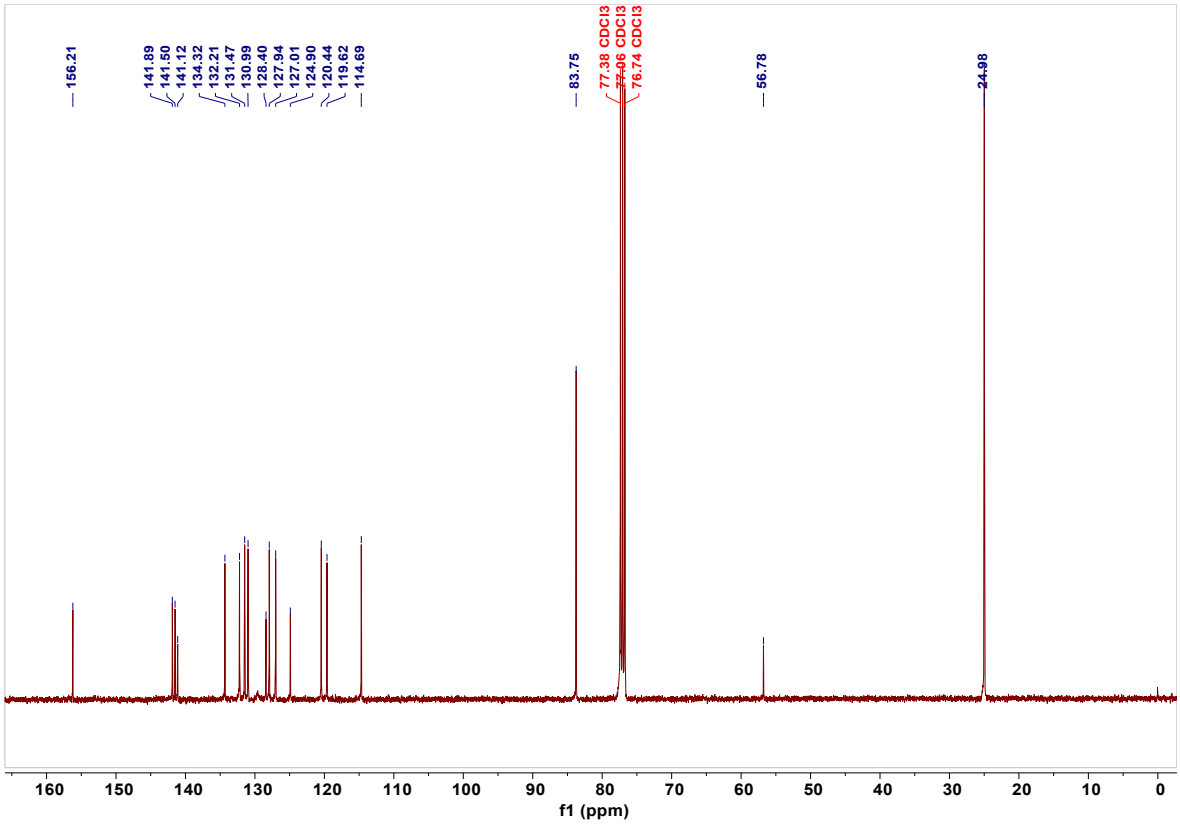


Figure S16. ^{13}C NMR spectrum of intermediate SAF-Bpin (solvent: Chloroform-*d*).

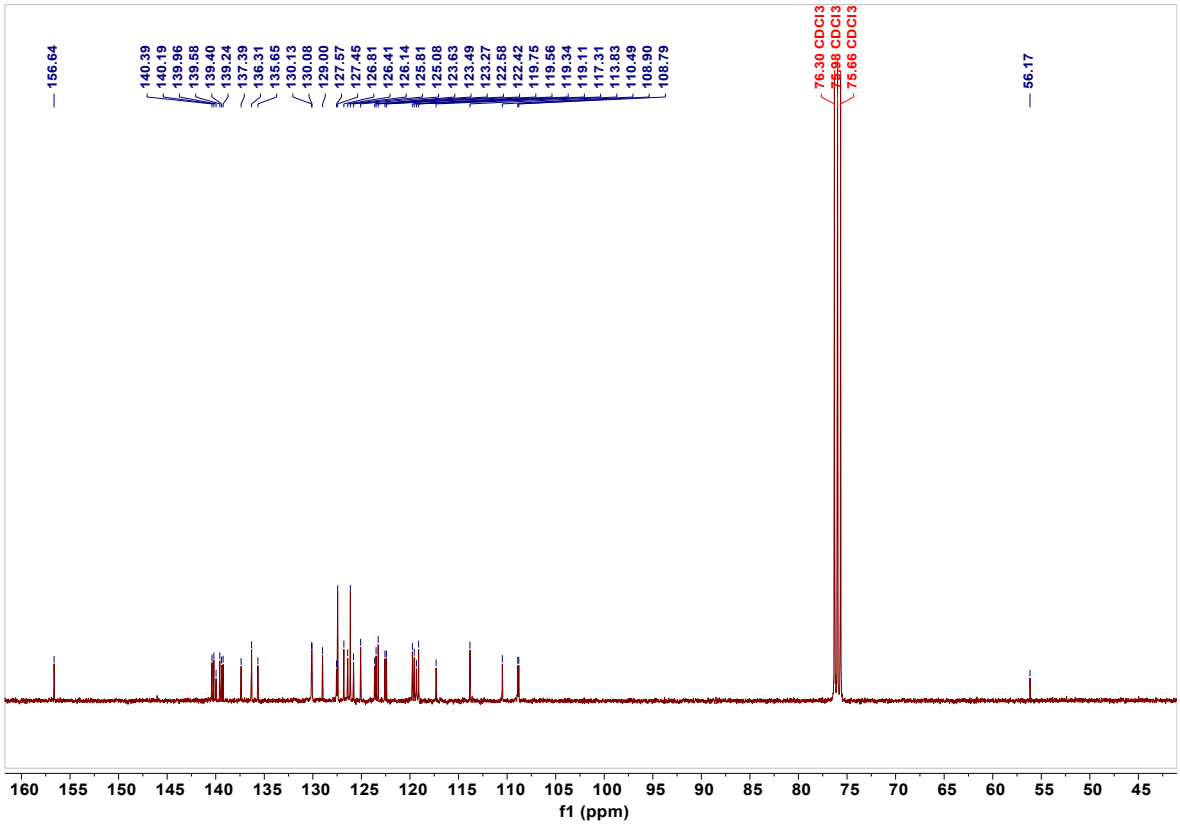


Figure S17. ^{13}C NMR spectrum of V-SAFCz (solvent: Chloroform-*d*).

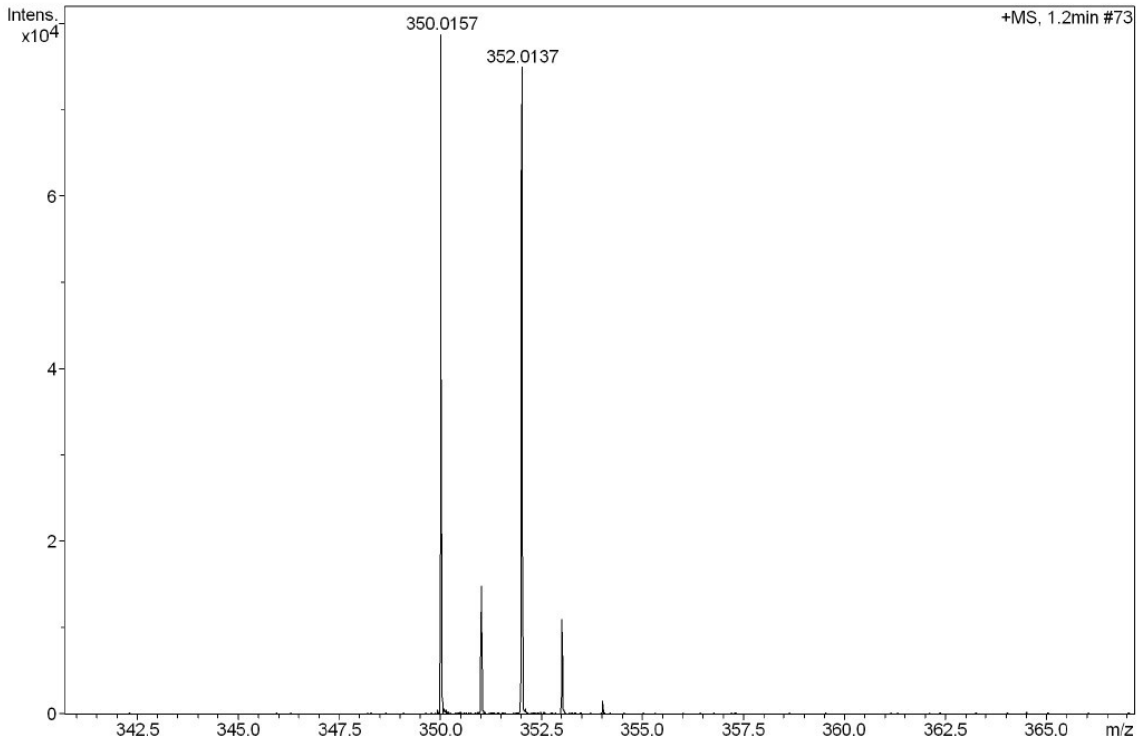


Figure S18. The HRMS spectrum of the intermediate Cz-Br.

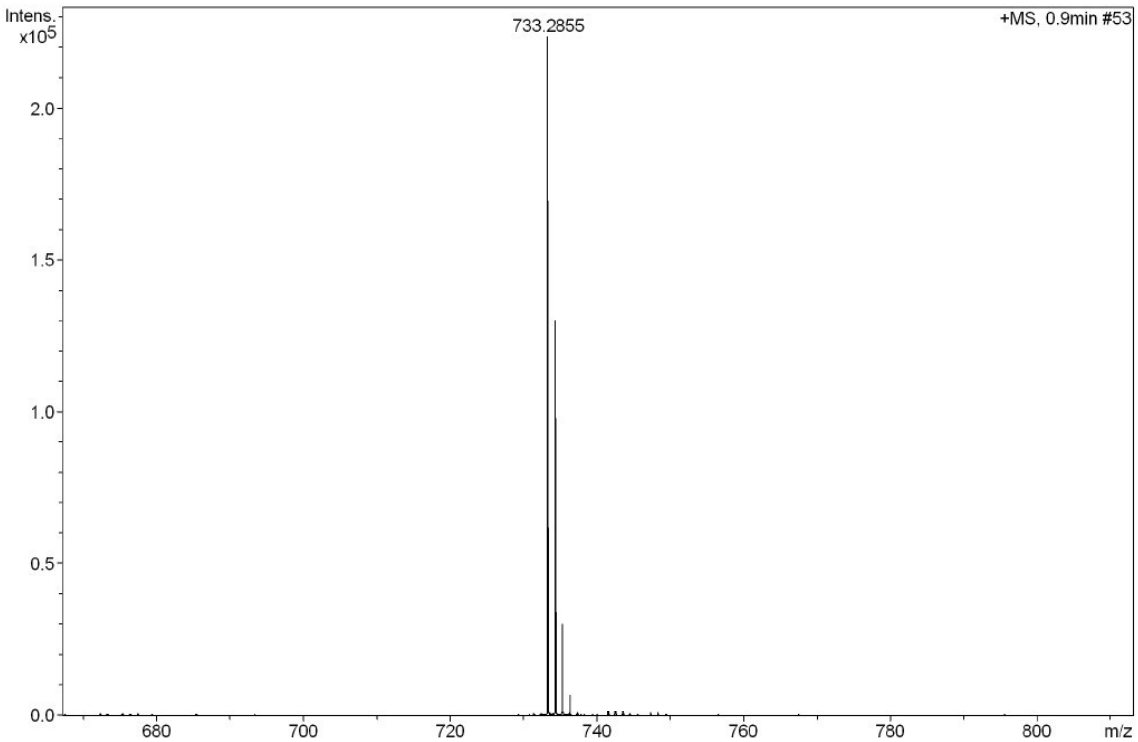


Figure S19. The HRMS spectrum of the intermediate MFCz-CHO.

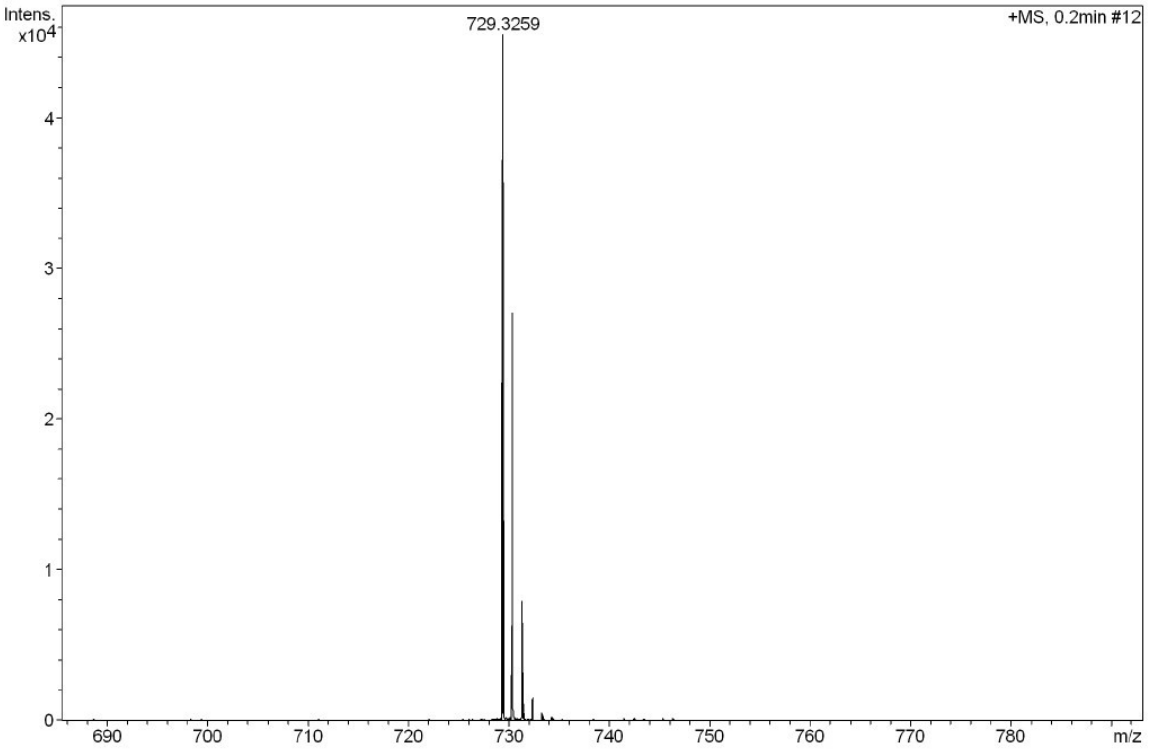


Figure S20. The HRMS spectrum of the V-MFCz.

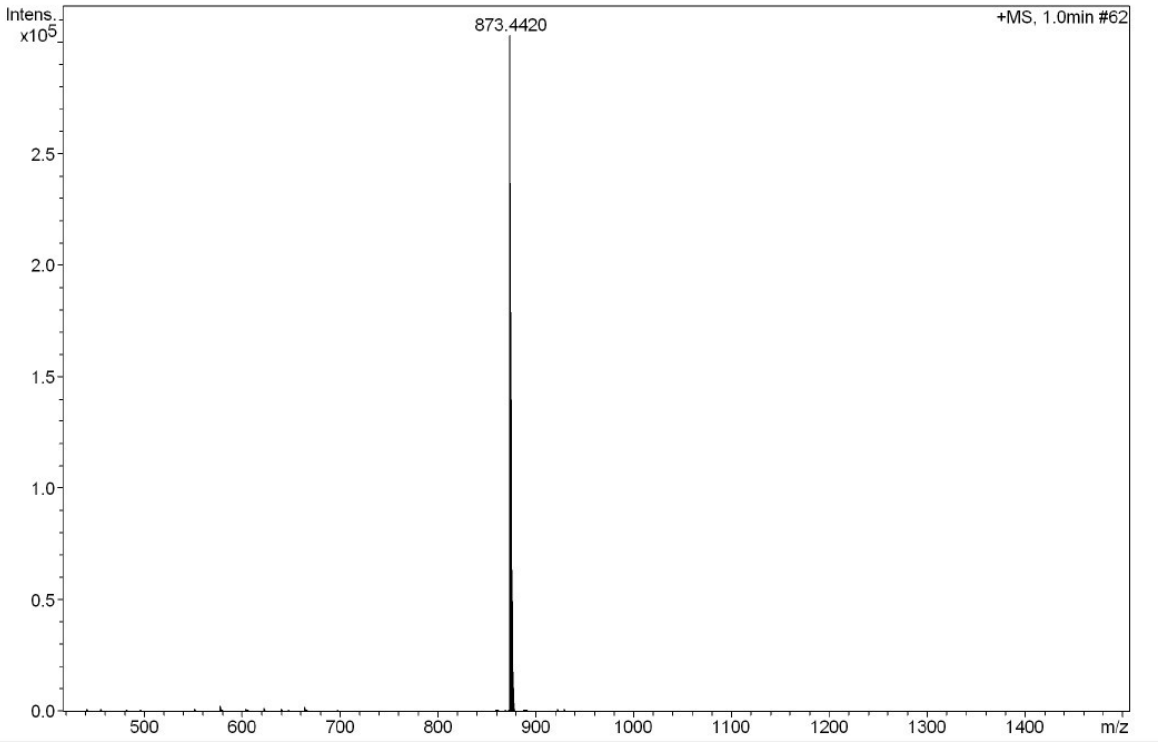


Figure S21. The HRMS spectrum of the intermediate HFCz-CHO.

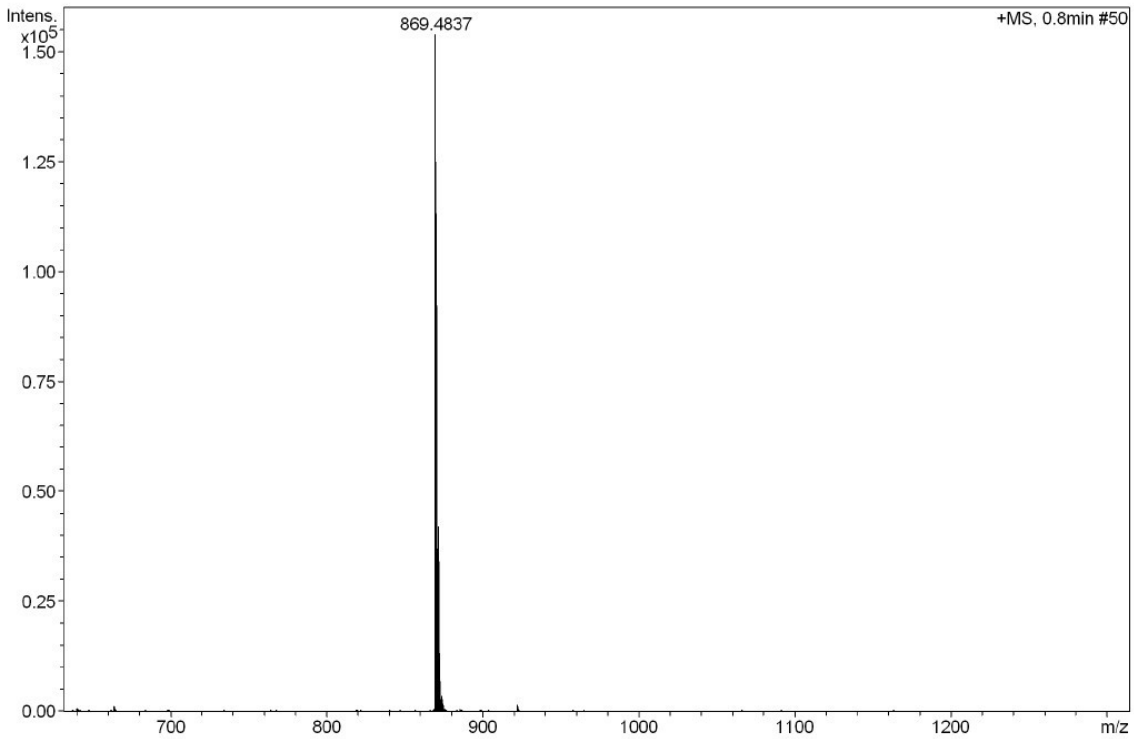


Figure S22. The HRMS spectrum of the V-HFCz.

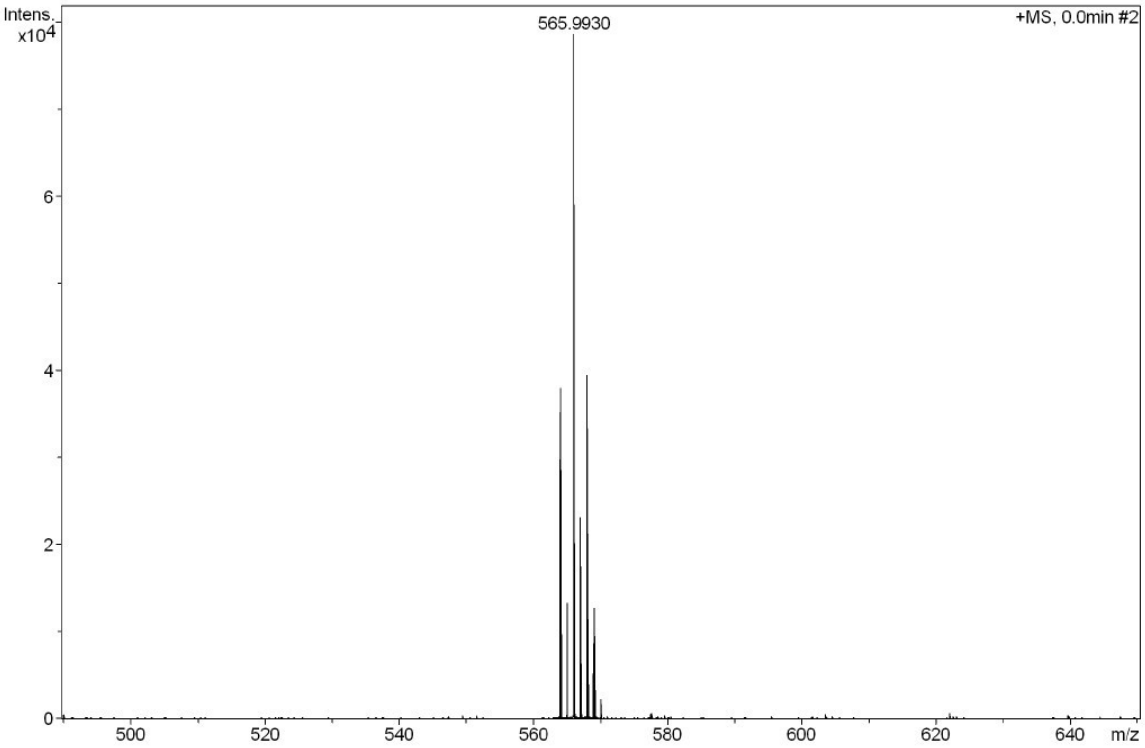


Figure S23. The HRMS spectrum of the intermediate SAF-Br.

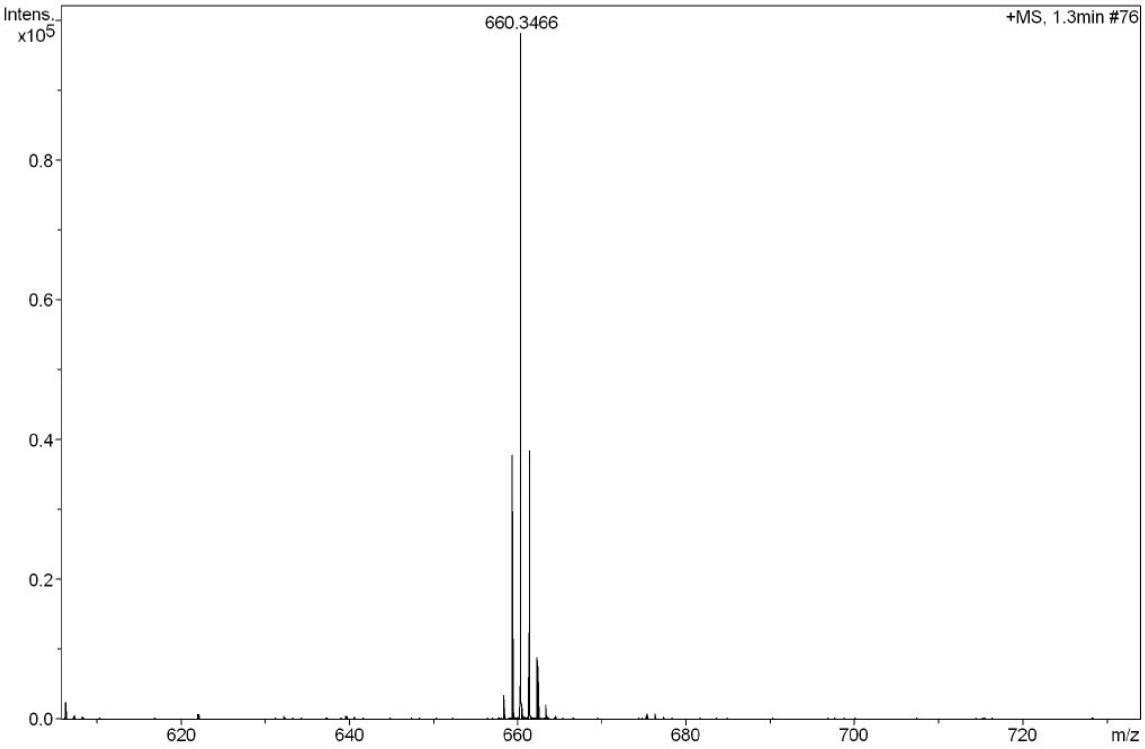


Figure S24. The HRMS spectrum of the intermediate SAF-Bpin.

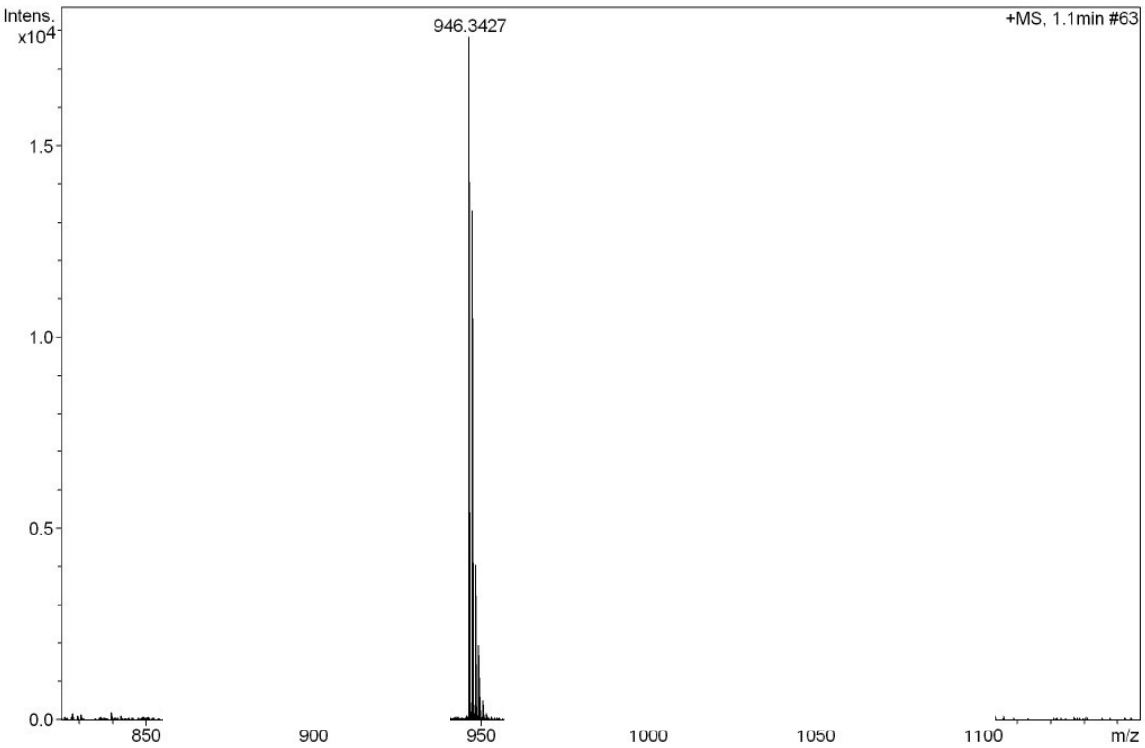


Figure S25. The HRMS spectrum of the intermediate SAFCz-CHO.

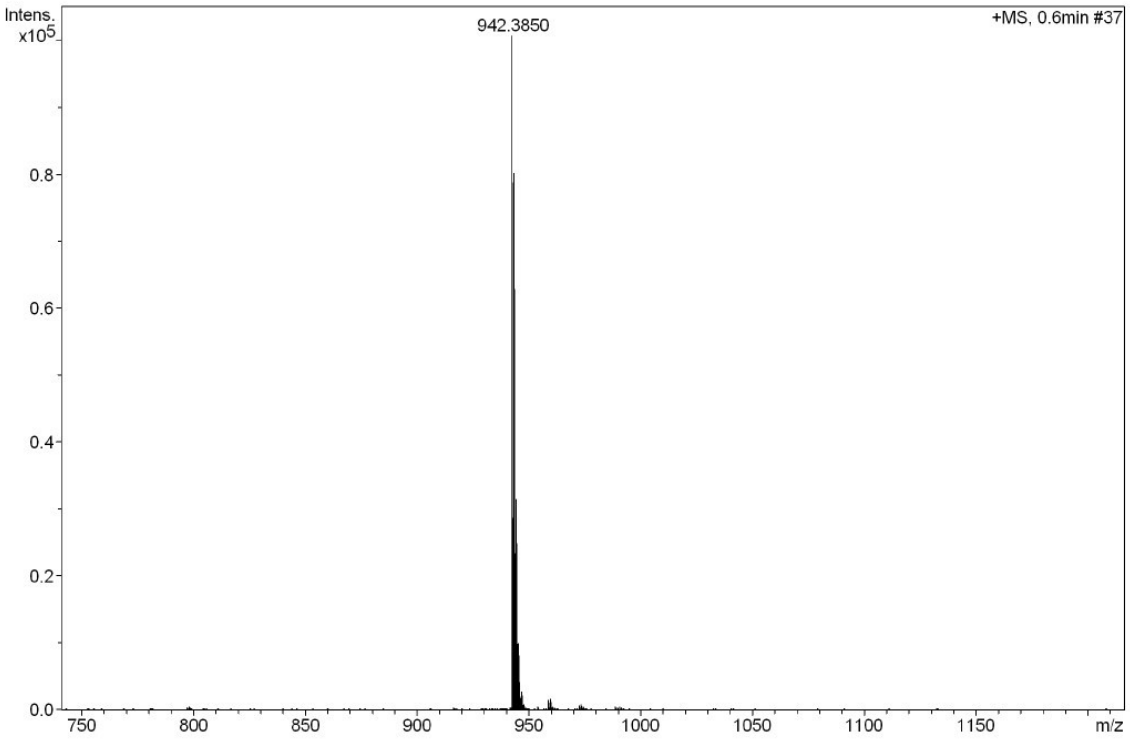


Figure S26. The HRMS spectrum of the V-SAFCz.

Table S1. The Cartesian coordinates of V-MFCz：

Center number	Atom	Coordinate [Å]		
		X	Y	Z
1	C	-0.164488	1.817775	-1.817775
2	C	-0.094076	0.677938	0.184304
3	C	1.135885	-0.204048	-0.034984
4	C	0.757853	-1.528213	-0.334556
5	C	-0.704953	-1.608563	-0.326189
6	C	-1.222287	-0.333713	-0.021205
7	C	2.475778	0.150272	0.018559
8	C	3.473181	-0.815172	-0.225716
9	C	3.077768	-2.133592	-0.522839
10	C	1.733692	-2.496254	-0.579878
11	C	-1.571424	-2.677879	-0.561256
12	C	-2.946428	-2.464720	-0.489354
13	C	-3.480635	-1.197191	-0.187722
14	C	-2.592290	-0.128272	0.047137
15	C	4.909680	-0.450019	-0.171371

16	C	-4.947818	-0.990582	-0.119574
17	C	5.390849	0.472714	0.773717
18	C	6.738452	0.814373	0.832413
19	C	7.647943	0.250308	-0.070565
20	C	7.185191	-0.665718	-1.023412
21	C	5.838395	-1.012937	-1.064133
22	C	-5.818516	-1.655515	-1.000561
23	C	-7.194592	-1.456749	-0.946637
24	C	-7.744405	-0.591949	0.007730
25	C	-6.892821	0.072871	0.898558
26	C	-5.516695	-0.120643	0.826917
27	N	9.022137	0.602606	-0.020598
28	N	-9.148324	-0.390995	0.070239
29	C	9.538580	1.904203	-0.081904
30	C	10.952717	1.843320	-0.001555
31	C	11.307385	0.442588	0.114295
32	C	10.091489	-0.289859	0.098020
33	C	-9.801729	0.842605	0.000097
34	C	-11.202502	0.631778	0.093335
35	C	-11.401455	-0.797875	0.227966
36	C	-10.115904	-1.395469	0.208630
37	C	8.866167	3.119263	-0.235735
38	C	9.632722	4.281655	-0.287650
39	C	11.033996	4.240753	-0.194911
40	C	11.698625	3.025716	-0.056116
41	C	12.522187	-0.229002	0.242072
42	C	12.543261	-1.626719	0.358196
43	C	11.311796	-2.322776	0.357655
44	C	10.085398	-1.679893	0.231247
45	C	-9.275394	2.124000	-0.175273
46	C	-10.169004	3.187611	-0.234369
47	C	-11.569090	3.016461	-0.127330
48	C	-12.074496	1.717567	0.031131
49	C	-12.535048	-1.604918	0.373549

50	C	-12.375068	-2.981484	0.503317
51	C	-11.092725	-3.555524	0.495946
52	C	-9.947511	-2.775042	0.351694
53	C	13.787291	-2.401343	0.487582
54	C	-12.428584	4.208526	-0.194645
55	C	15.046637	-1.950942	0.422656
56	C	-13.758642	4.273094	-0.053830
57	C	-0.117899	1.265408	1.613081
58	H	0.683044	2.501347	-0.740580
59	H	-0.147505	1.422442	-1.875889
60	H	-1.083890	2.398924	-0.730242
61	H	2.765988	1.177626	0.220878
62	H	3.839496	-2.890159	-0.684056
63	H	1.457957	-3.523058	-0.803034
64	H	-1.187178	-3.668403	-0.788034
65	H	-3.622146	-3.300457	-0.642719
66	H	-2.990814	0.861317	0.253594
67	H	4.706440	0.899040	1.500529
68	H	7.096803	1.502069	1.591235
69	H	7.880813	-1.084743	-1.742992
70	H	5.493989	-1.702716	-1.828343
71	H	-5.408713	-2.307207	-1.765801
72	H	-7.848351	-1.952341	-1.656674
73	H	-7.316413	0.722259	1.657574
74	H	-4.874840	0.381498	1.544020
75	H	7.785741	3.158727	-0.318084
76	H	9.132893	5.238597	-0.405639
77	H	11.601337	5.165312	-0.237024
78	H	12.782708	2.994088	0.004497
79	H	13.449567	0.335193	0.261871
80	H	11.327355	-3.404600	0.460409
81	H	9.158655	-2.242468	0.242818
82	H	-8.207842	2.288262	-0.269256
83	H	-9.778121	4.192714	-0.369062

84	H	-13.145469	1.551925	0.096464
85	H	-13.526465	-1.161394	0.389719
86	H	-13.246885	-3.618478	0.615701
87	H	-10.988107	-4.630719	0.607670
88	H	-8.960678	-3.224308	0.356168
89	H	13.637483	-3.468458	0.650655
90	H	-11.892231	5.139107	-0.379317
91	H	15.886472	-2.627875	0.537586
92	H	15.290715	-0.906625	0.251669
93	H	-14.280624	5.221134	-0.128190
94	H	-14.374068	3.399630	0.140484
95	H	-1.033656	1.842593	1.778399
96	H	-0.072130	0.473429	2.365743
97	H	0.733365	1.936148	1.769600

Table S2. The Cartesian coordinates of V-HFCz：

Center number	Atom	Coordinate [Å]		
		X	Y	Z
1	C	-0.200809	1.033901	-1.140320
2	C	-0.047523	-0.018041	0.002568
3	C	1.185317	-0.916389	-0.175553
4	C	0.805042	-2.254978	-0.401151
5	C	-0.654585	-2.337067	-0.379693
6	C	-1.176804	-1.050039	-0.137089
7	C	2.532784	-0.585547	-0.098034
8	C	3.522271	-1.572224	-0.282349
9	C	3.119227	-2.897228	-0.531357
10	C	1.771839	-3.245168	-0.585312
11	C	-1.508594	-3.425252	-0.567506
12	C	-2.885445	-3.223371	-0.521491
13	C	-3.430198	-1.943948	-0.305022
14	C	-2.553052	-0.855759	-0.119771
15	C	4.961424	-1.219374	-0.210722
16	C	-4.899601	-1.743556	-0.278050

17	C	5.434154	-0.274103	0.716171
18	C	6.783612	0.057105	0.789616
19	C	7.703820	-0.540158	-0.080615
20	C	7.249782	-1.479724	-1.014519
21	C	5.900744	-1.816740	-1.069128
22	C	-5.747654	-2.465985	-1.135806
23	C	-7.126223	-2.278948	-1.118379
24	C	-7.702082	-1.368057	-0.224104
25	C	-6.873392	-0.643841	0.641725
26	C	-5.494307	-0.826401	0.605811
27	N	9.079757	-0.196661	-0.017194
28	N	-9.109202	-1.182083	-0.195623
29	C	9.606735	1.099383	-0.102634
30	C	11.019068	1.030558	0.000186
31	C	11.361625	-0.369357	0.155187
32	C	10.140692	-1.093418	0.138844
33	C	-9.776557	0.037962	-0.336039
34	C	-11.175766	-0.185679	-0.249455
35	C	-11.359200	-1.609103	-0.045295
36	C	-10.066405	-2.190448	-0.017892
37	C	8.945854	2.315176	-0.296004
38	C	9.721759	3.470459	-0.364790
39	C	11.121184	3.421903	-0.250236
40	C	11.774534	2.205921	-0.072042
41	C	12.569536	-1.046056	0.316903
42	C	12.578807	-2.440647	0.466941
43	C	11.342385	-3.127878	0.465535
44	C	10.122667	-2.479756	0.305736
45	C	-9.263772	1.315595	-0.569568
46	C	-10.169399	2.363443	-0.692601
47	C	-11.568536	2.180111	-0.593510
48	C	-12.060057	0.884360	-0.376580
49	C	-12.484973	-2.421862	0.126688
50	C	-12.310441	-3.787923	0.328576

51	C	-11.021304	-4.345226	0.367200
52	C	-9.883668	-3.558749	0.197827
53	C	13.815199	-3.220564	0.632580
54	C	-12.441528	3.356372	-0.729648
55	C	15.078596	-2.780780	0.573707
56	C	-13.773682	3.411233	-0.605478
57	C	0.017091	0.625599	1.422404
58	C	0.844005	2.154256	-1.223913
59	C	0.537226	3.160331	-2.343025
60	C	1.587793	4.270656	-2.462189
61	C	1.294262	5.280351	-3.578858
62	C	2.354686	6.379324	-3.693135
63	C	-1.123625	1.562768	1.839655
64	C	-0.893297	2.172546	3.229858
65	C	-2.021824	3.106634	3.683071
66	C	-1.793285	3.716271	5.071640
67	C	-2.923831	4.648920	5.516256
68	H	-0.214502	0.488731	-2.092147
69	H	-1.194545	1.489172	-1.045281
70	H	2.840812	0.437739	0.087168
71	H	3.874339	-4.279445	0.752217
72	H	1.484514	-1.952341	-1.656674
73	H	-1.111125	-4.420885	-0.743489
74	H	-3.552870	-4.071808	-0.636539
75	H	-2.969229	0.139053	-0.001235
76	H	4.740917	0.179336	1.417802
77	H	7.134578	0.763224	1.534832
78	H	7.954000	-1.925231	-1.709400
79	H	5.563492	-2.526039	-1.818577
80	H	-5.317308	-3.155642	0.460409
81	H	-1.855067	-2.820678	-1.810910
82	H	-7.316978	0.042607	1.355308
83	H	-4.870890	-0.277477	1.304639
84	H	7.867095	2.360416	-0.395230

85	H	9.230849	4.427777	-0.513282
86	H	11.695963	4.341115	-0.306311
87	H	12.857342	2.168037	0.005468
88	H	13.500616	-0.487972	0.336514
89	H	11.348561	-4.206964	0.594716
90	H	9.191872	-3.035563	0.317661
91	H	-8.197245	1.488558	-0.659182
92	H	-9.789019	3.365441	-0.872796
93	H	-13.129655	0.708387	-0.315832
94	H	-13.481670	-1.990422	0.107374
95	H	-13.176004	-4.429344	0.462128
96	H	-10.905252	-5.411900	0.535188
97	H	-8.891802	-3.994884	0.238209
98	H	13.655285	-4.282215	0.819892
99	H	-11.914449	4.283175	-0.955451
100	H	15.911821	-3.460503	0.716821
101	H	15.332600	-1.742777	0.380206
102	H	-14.306248	4.347690	-0.732729
103	H	-14.380521	2.540980	-0.373367
104	H	0.962622	1.177560	1.496221
105	H	0.092241	-0.190413	2.151905
106	H	0.903475	2.693681	-0.269360
107	H	1.836941	1.725545	-1.401628
108	H	0.462992	2.626453	-3.300903
109	H	-0.450813	3.610288	-2.170068
110	H	1.663975	4.803827	-1.503453
111	H	2.574878	3.818315	-2.634874
112	H	1.214997	4.747286	-4.536050
113	H	0.310352	5.736830	-3.404693
114	H	2.117572	7.082807	-4.497726
115	H	2.433281	6.952979	-2.762577
116	H	3.343292	5.955364	-3.902840
117	H	-2.073335	1.015204	1.847512
118	H	-1.238137	2.374699	1.109570

119	H	0.057042	2.725313	3.231712
120	H	-0.773803	1.364206	3.964972
121	H	-2.972921	2.554843	3.682828
122	H	-2.142113	3.915549	2.948062
123	H	-0.842706	4.266867	5.072509
124	H	-1.674983	2.907937	5.805908
125	H	-2.731341	5.066900	6.509595
126	H	-3.881793	4.118299	5.559176
127	H	-3.042857	5.487174	4.820349

Table S3. The Cartesian coordinates of V-SAFCz：

Center number	Atom	Coordinate [Å]		
		X	Y	Z
1	C	-0.802892	6.300242	-0.823361
2	C	-0.902140	4.914639	-0.692976
3	C	0.256638	4.136567	-0.604922
4	C	1.512904	4.748621	-0.646771
5	C	1.608671	6.134823	-0.776306
6	C	0.451900	6.911569	-0.864887
7	N	0.157574	2.708995	-0.471859
8	C	0.078566	2.142071	0.813282
9	C	0.081475	1.913909	-1.629890
10	C	0.113224	2.517833	-2.904646
11	C	0.038301	1.751848	-4.060042
12	C	-0.071339	0.362661	-3.979152
13	C	-0.100824	-0.233615	-2.724360
14	C	-0.025359	0.512176	-1.540810
15	C	-0.026901	0.748059	0.984924
16	C	-0.106697	0.234628	2.286038
17	C	-0.083758	1.053344	3.408543
18	C	0.023582	2.433704	3.230996
19	C	0.103124	2.972148	1.953895
20	C	-0.036087	-0.226359	-0.197999
21	C	1.142887	-1.214662	-0.106831

22	C	0.684178	-2.539051	0.020978
23	C	-0.782420	-2.530369	0.016148
24	C	-1.224902	-1.199927	-0.106006
25	C	-1.713120	-3.568274	0.106209
26	C	-3.072231	-3.263899	0.074142
27	C	-3.528173	-1.936323	-0.047241
28	C	-2.577944	-0.901097	-0.137646
29	C	2.499369	-0.931906	-0.130780
30	C	3.436533	-1.977770	-0.027298
31	C	2.964592	-3.298870	0.101701
32	C	1.601658	-3.586917	0.126783
33	C	4.892551	-1.693798	-0.058420
34	C	-4.980560	-1.634676	-0.078266
35	C	5.792044	-2.407168	0.752251
36	C	7.159370	-2.149934	0.716353
37	C	7.665267	-1.149932	-0.122887
38	C	6.782171	-0.422319	-0.929665
39	C	5.418894	-0.700442	-0.902113
40	C	-5.497625	-0.489144	0.550980
41	C	-6.857134	-0.194103	0.513460
42	C	-7.746626	-1.054739	-0.141196
43	C	-7.250176	-2.206470	-0.763558
44	C	-5.886311	-2.482056	-0.739240
45	N	9.058930	-0.876500	-0.155577
46	N	-9.136230	-0.762439	-0.174232
47	C	9.871128	-0.891318	-1.297211
48	C	11.199073	-0.564304	-0.922927
49	C	11.188754	-0.340575	0.509337
50	C	9.852736	-0.543092	0.944911
51	C	-9.950032	-0.530433	0.937948
52	C	-11.274750	-0.271510	0.497678
53	C	-11.256522	-0.349962	-0.949600
54	C	-9.924287	-0.653901	-1.328016
55	C	9.537460	-1.199845	-2.618432

56	C	10.554610	-1.157652	-3.569727
57	C	11.873132	-0.822168	-3.218938
58	C	12.201385	-0.528518	-1.898539
59	C	12.172644	0.019441	1.428966
60	C	11.842740	0.185085	2.782226
61	C	10.498191	-0.007496	3.177673
62	C	9.496092	-0.367273	2.283495
63	C	-9.636009	-0.563638	2.298250
64	C	-10.660139	-0.312680	3.204560
65	C	-11.986805	-0.032857	2.800988
66	C	-12.281346	-0.023645	1.429647
67	C	-12.232354	-0.179010	-1.937612
68	C	-11.871426	-0.305302	-3.275943
69	C	-10.543502	-0.592772	-3.633634
70	C	-9.552478	-0.768019	-2.670051
71	C	12.829145	0.556155	3.808614
72	C	-12.995234	0.229001	3.839594
73	C	14.150609	0.714689	3.661240
74	C	-14.276431	0.580798	3.672842
75	H	-1.704726	6.901138	-0.891916
76	H	-1.871018	4.426483	-0.659036
77	H	2.404032	4.132896	-0.576914
78	H	2.586048	6.606824	-0.808194
79	H	0.527922	7.990046	-0.965862
80	H	0.195972	3.594127	-2.983565
81	H	0.064675	2.246915	-5.026444
82	H	-0.131617	-0.244752	-4.876414
83	H	-0.183074	-1.313589	-2.647506
84	H	-0.187329	-0.840978	2.410779
85	H	-0.146405	0.622640	4.402651
86	H	0.045157	3.099416	4.088938
87	H	0.184368	4.044509	1.831733
88	H	-1.389915	-4.600253	0.209854
89	H	-3.798021	-4.065355	0.172030

90	H	-2.906121	0.126982	-0.258558
91	H	2.841194	0.096309	-0.203234
92	H	3.680658	-4.113222	0.154671
93	H	1.265583	-4.616060	0.217219
94	H	5.414022	-3.166507	1.429587
95	H	7.841250	-2.721537	1.337302
96	H	7.169515	0.358563	-1.575743
97	H	4.752123	-0.146348	-1.555325
98	H	-4.826392	0.175079	1.086310
99	H	-7.235949	0.704205	0.989632
100	H	0.989632	-2.881109	-1.264422
101	H	-5.516114	-3.364060	-1.252415
102	H	8.523942	-1.468080	-2.895084
103	H	10.320147	-1.392389	-4.603851
104	H	12.641702	-0.796557	-3.985186
105	H	13.223169	-0.278839	-1.627187
106	H	13.191924	0.179221	1.090796
107	H	10.240309	0.132061	4.224177
108	H	8.473216	-0.499234	2.618008
109	H	-8.631191	-0.782914	2.641425
110	H	-10.434536	-0.332098	4.267525
111	H	-13.294487	0.167210	1.089291
112	H	-13.257213	0.053648	-1.662823
113	H	-12.619716	-0.176455	-4.051812
114	H	-10.279574	-0.677939	-4.683667
115	H	-8.527859	-0.979537	-2.954577
116	H	12.407213	0.711244	4.801474
117	H	-12.627668	0.120495	4.859843
118	H	14.774691	0.994757	4.503194
119	H	14.659332	0.571844	2.712426
120	H	-14.924291	0.744234	4.527455
121	H	-14.726710	0.721258	2.694572

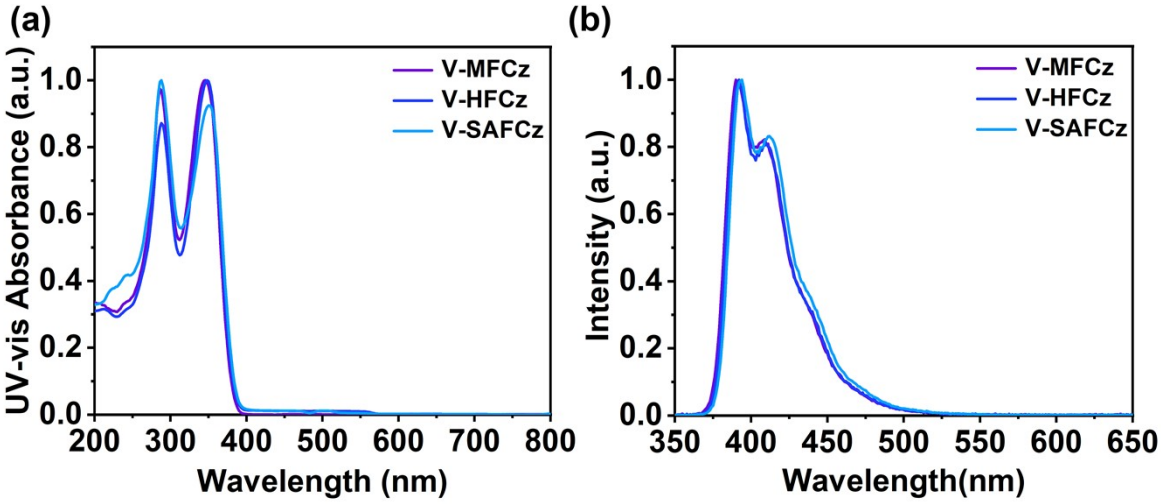


Figure S27. The UV-vis absorption and fluorescence spectra of V-MFCz, V-HFCz, and V-SAFCz in toluene solution.

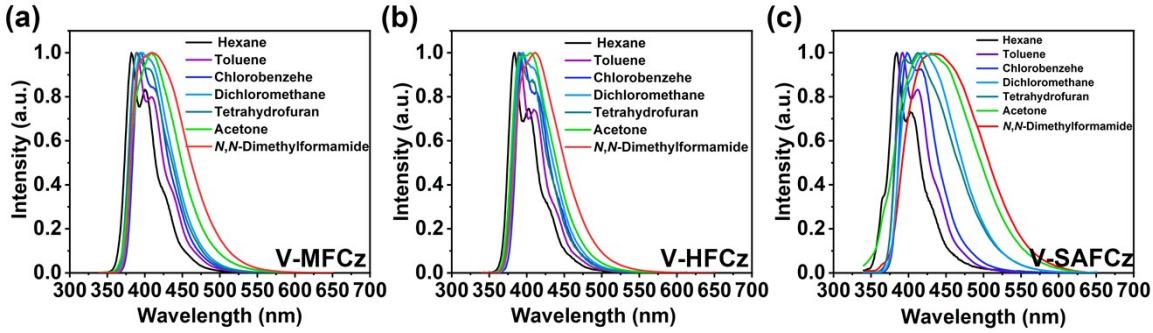


Figure S28. Fluorescence spectra of V-MFCz, V-HFCz, and V-SAFCz in different polar solutions.

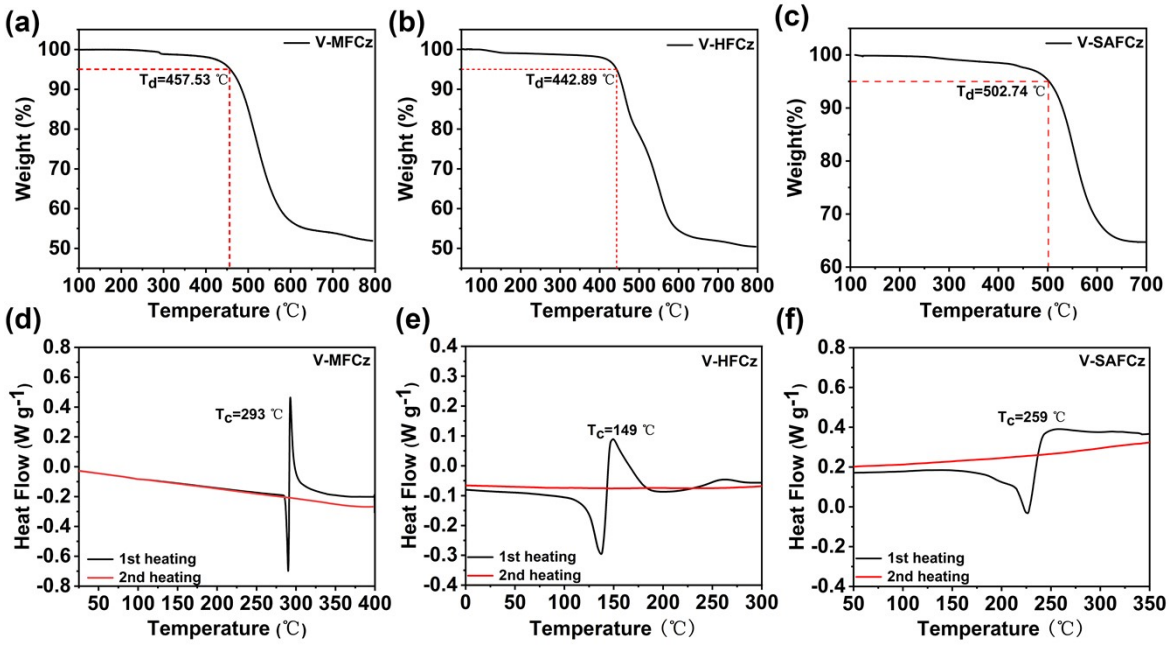


Figure S29. (a) TGA curves of V-MFCz (b) V-HFCz (c) V-SAFCz; (d) DSC curves of V-MFCz (e) V-HFCz and (f) V-SAFCz.

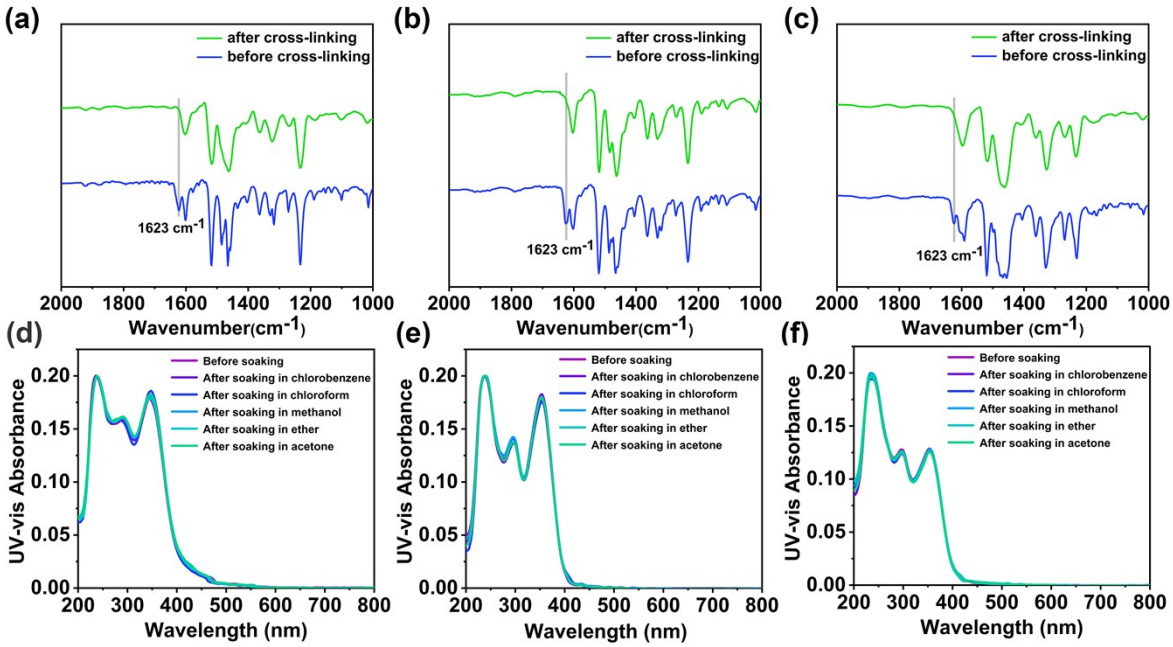


Figure S30 (a) FTIR spectra of V-MFCz (b) V-HFCz (c) V-SAFCz before and after cross-linking; (d) The solvent resistance of V-MFCz (e) V-HFCz (f) V-SAFCz cross-linked films in different solvents.

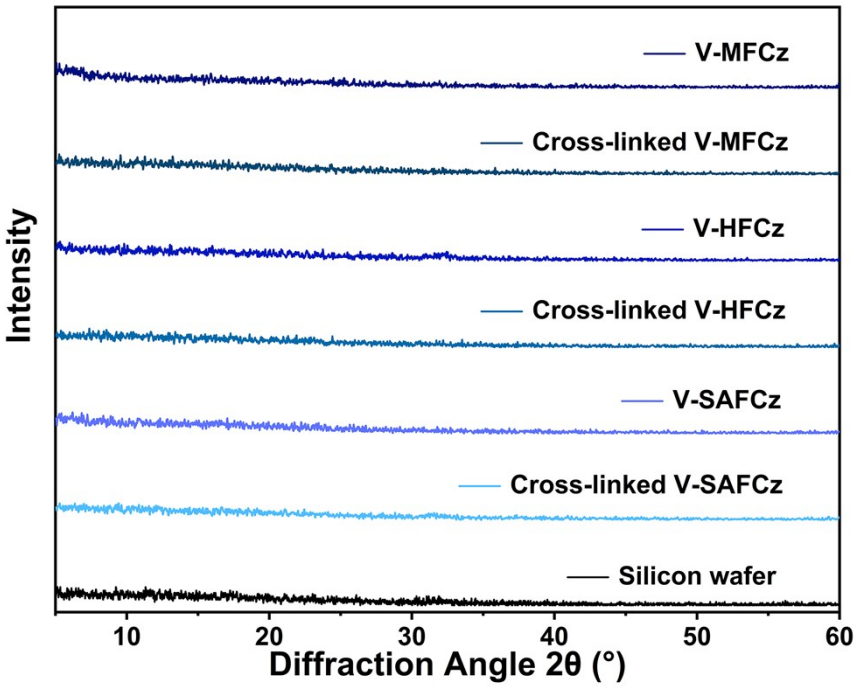


Figure S31. XRD patterns of V-MFCz, V-HFCz, and V-SAFCz films before and after cross-linking.

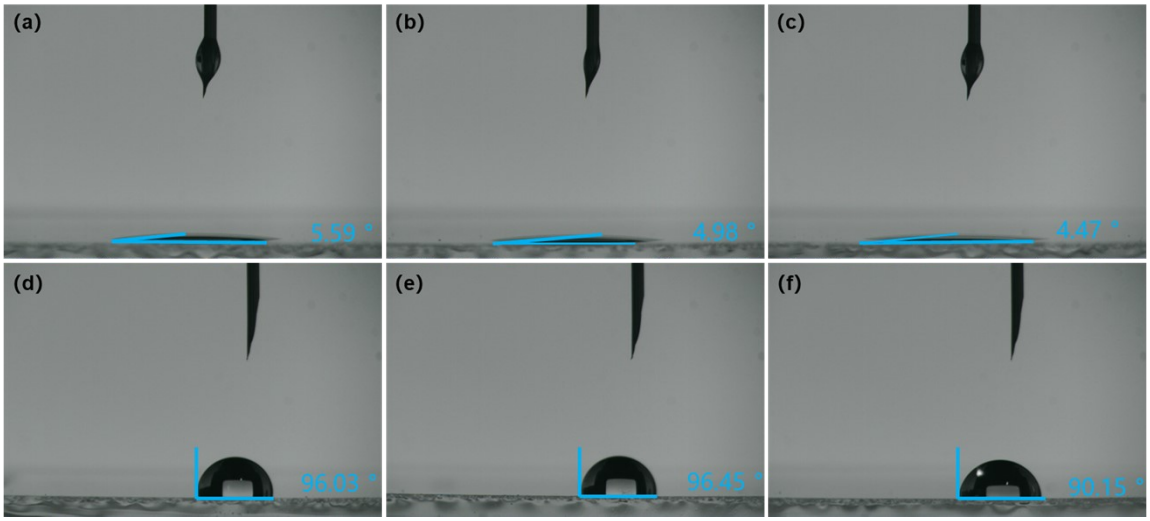


Figure S32. (a) Contact angles of V-MFCz, (b) V-HFCz, (c) V-SAFCz cross-linked films with toluene; (d) The contact angle between V-MFCz, (e) V-HFCz, (f) V-SAFCz cross-linked films and water.

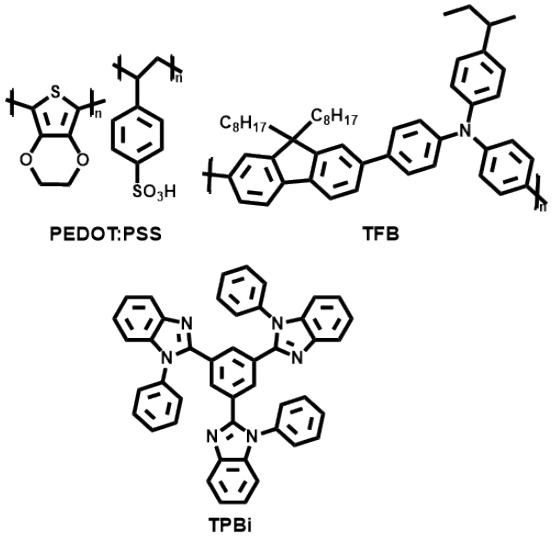


Figure S33. Chemical structures of the materials used for the non-doped deep-blue OLED devices.

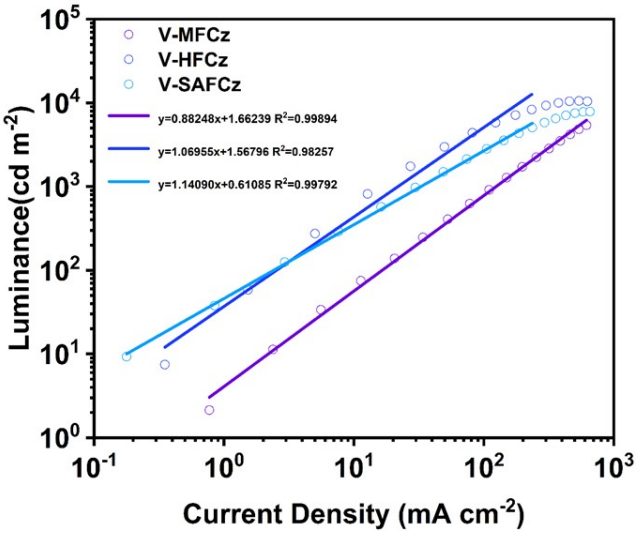


Figure S34. Luminance versus current density and the fitted curve plots.

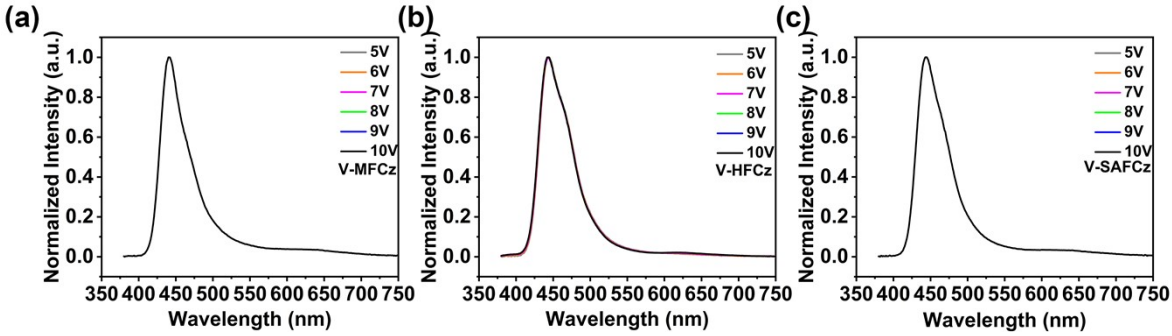


Figure S35. (a) EL spectra of V-MFCz, (b) V-HFCz, and (c) V-SAFCz at different voltages.