Supporting Information

S1. Materials and general methods

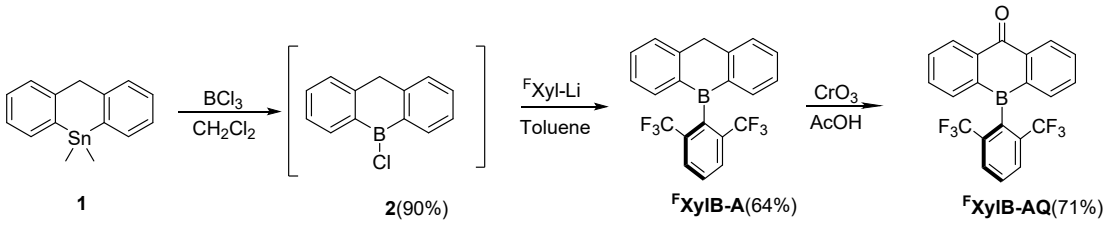
THF, ether, toluene and dichloromethane were dewatered and deoxygenated with a Solvent Purification System (FL-MD-5), and stored under nitrogen prior to use. All chemicals from commercial sources were used as received unless otherwise stated. 1-Bromo-4-fluoro-2-iodobenzene, 3,6-di-*tert*-butyl-9H-carbazole, 2-Bromobenzaldehyde were purchased from Bide PharmatechLtd. (Shanghai, China). Isopropylmagnesium chloride lithium chloride complex (1.3M in THF), 2,6-Bis(trifluoromethyl)bromobenzene were purchased from Energy Chemical (Shanghai, China). Hydriodic acid, *n*-BuLi (1.6M in Hexane) and BCl_3 (1 M in dichloromethane) were purchased from J&K Scientific (Beijing, China). Acetic Acid was purchased from Shanghai Titan Scientific Co., Ltd. 1,3,5-Tri-*tert*-butylbenzene was purchased from 9Ding Chemistry (Shanghai, China). Dimethyltin dichloride were purchased from TCI(Shanghai)Development Co., Ltd. N, N -Dimethylformamide, Petroleumeter, ethyl acetate, dichloromethane, tetrahydrofuran and hexane were purchased from Sinopharm Chemical Reagent Co., Ltd.

^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz, 176 MHz) and ^{11}B NMR (128 MHz, 225 MHz) spectra were recorded on Bruker Avance 400 MHz and 700 MHz spectrometer, respectively. 1H NMR chemical shifts were referenced to residual $CDCl_3$ (7.26 ppm) and THF-d_8 (1.72, 3.58 ppm). ^{13}C NMR (proton decoupled) chemical shifts were referenced to $CDCl_3$ (77.16 ppm) and THF-d_8 (25.31, 67.21 ppm). For ^{11}B NMR spectra, boron-free quartz NMR tubes were used and the spectra were referenced to external $BF_3{\cdot}Et_2O$ ($\delta = 0$). High resolution mass spectral data were obtained on an Agilent (Q-TOF 6520) mass spectrometer and MALDI-MS measurements were performed on a Bruker AutoFlex MAX in linear (+) mode.

UV-vis absorption spectra were recorded on a JASCO V-770 UV-vis-NIR spectrophotometer. The fluorescence spectra (including temperature-dependent emission spectra) and transient decay curves were measured on an Edinburgh Instruments FLS980 spectrophotometer. The phosphorescence spectra were also recorded on Edinburgh Instruments FLS980 spectrophotometer with delay of 0.1ms. Fluorescent quantum efficiencies were determined using a Hamamatsu Quantaurus-QY spectrometer(C11347-11). Cyclic voltammetry (CV) was recorded at room temperature on an AUTOLAB-CV-75W voltammetric analyzer with ferrocene as the internal standard and tetrabutyl ammonium hexafluorophosphate (0.1 M) in deaerated DCM or THF as the supporting electrolyte solvent. The cyclic voltammograms were obtained at scan rate of 0.1 V s^{-1}.

DFT calculations were performed with the Gaussian 16 program package.[1] Geometry optimizations and single point energies were conducted at the B3LYP-D3/6-311G* level of theory, and all optimized structures indicated no imaginary frequency. Vertical transitions and excited states were calculated using TD-DFT (PBE0/ def2-TZVP). Electron-hole analysis is conducted using multiwfn software. [2]

S2. Experimental section



Scheme S1 Synthetic route of **^{F}XylB-AQ**.

Synthesis of 5-(2,6-bis(trifluoromethyl)phenyl)-5,10-dihydrodibenzo[*b,e*]borinine(^{F}XylB-A)

To a stirring solution of **1** (1.98 g, 6.27 mmol) in dichloromethane at -78 °C was added BCl_3 (1 M; 9.4 mL, 9.40 mmol) dropwise. The reaction mixture was allowed to slowly come to room temperature. The volatile compounds were removed under dynamic vacuum. The resultant off white solid was transferred to a sublimation vessel and the residual Me_2SnCl_2 was removed at ambient temperature under dynamic vacuum, leaving a grey solid **2** (1.2 g, 90%). The product is extremely sensitive toward oxygen and water that should be handled accordingly. 2-bromo-1,3-bis(trifluoromethyl)benzene (2.75 g, 9.40 mmol) was charged into a flame-dried Schlenk flask under nitrogen atmosphere and 60 mL of dry ether were added. The flask was cooled to -78 °C and was added *n*-BuLi (1.6 M; 6.5 mL, 10.34 mmol) dropwise. The mixture was stirred for 0.5 h at -78 °C, then warmed to room temperature and stirred for 4 h. The solvent was removed under high vacuum to obtain the lithium salt of 2-bromo-1,3-bis(trifluoromethyl)benzene (^{F}XylLi) as light yellow solid. The ^{F}XylLi was redissolved in 30 mL of dry toluene and the mixture was cooled to -78 °C. A solution of **2** (1.2 g, 5.65 mmol) in 20 mL dry toluene was added to the above solution, then the mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by adding 40 mL of water. The aqueous layer was separated and extracted with dichloromethane (3 × 10 mL). The combined organic layers were washed with brine (30 mL), dried with Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by column chromatography on silica gel using petroleum ether as an eluent to give **^{F}XylB-A** as a light yellow solid (1.6 g, 64%).

Synthesis of 5-(2,6-bis(trifluoromethyl)phenyl)dibenzo[*b,e*]borinin-10(5H)-one(^{F}XylB-AQ)

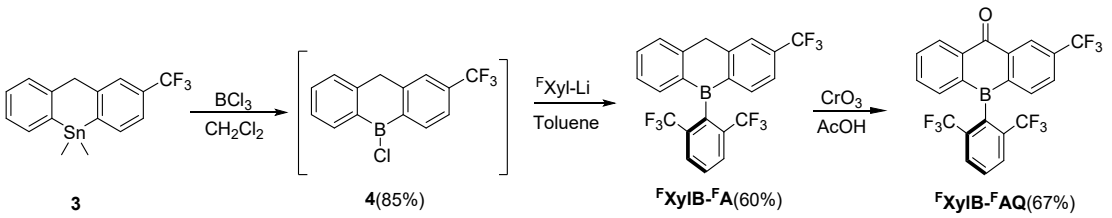
To a solution of **^{F}XylB-A** (1.63 g, 4.10mmol) in acetic acid (80 mL) was added chromium (VI) oxide (1.07 g, 10.66mmol). The mixture was refluxed with stirring for 12 h. After addition of water, the mixture was extracted with dichloromethane three times. The combined organic extract was washed with a saturated aqueous solution of $NaHCO_3$ and dried over Na_2SO_4. After filtration, the mixture was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using petroleum ether / dichloromethane (1:1) as an eluent to give **^{F}XylB-AQ** as pale yellow solid (1.2 g, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 8.0 Hz, 2H), 7.98 (d, J = 8.0 Hz, 2H), 7.79 (t, J = 8.0 Hz, 1H), 7.72 (t, J = 8.0 Hz, 2H), 7.56 (t, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.16, 138.42, 136.87, 134.37, 133.76, 133.29 (q, J = 32.3 Hz), 133.19, 129.44, 129.40, 129.35, 128.20, 124.29 (q, J = 275.7 Hz).

^{11}B NMR (225 MHz, $CDCl_3$) δ 61.6.

HR-ESIMS (m/z): $[M+H]^+$ calcd. for $C_{21}H_{11}BF_6O$, 405.0880; found: 405.0883.



Scheme S2. Synthetic route of **^{F}Xyl1B-^{F}AQ**.

Synthesis of 2-(trifluoromethyl)-5-(2,6-bis(trifluoromethyl)phenyl)-5,10-dihydrodibenzo[*b,e*]borinine(^{F}**XylB-**^{F}**A)**

To a stirring solution of **3** (2.91 g, 7.60 mmol) in dichloromethane at -78 °C was added BCl_3 (1 M; 11.4 mL, 11.4mmol) dropwise. The reaction mixture was allowed to slowly come to room temperature. The volatile compounds were removed under dynamic vacuum. The resultant off white solid was transferred to a sublimation vessel and the residual Me_2SnCl_2 was removed at ambient temperature under dynamic vacuum, leaving a grey solid **4** (1.8 g, 85%). The product is extremely sensitive toward oxygen and water that should be handled accordingly. 2-bromo-1,3-bis(trifluoromethyl)benzene (3.34 g, 11.4 mmol) was charged into a flame-dried Schlenk flask under nitrogen atmosphere and 120 mL of dry ether were added. The flask was cooled to -78 °C and was added *n*-BuLi (2.5 M; 5.02 mL, 12.54 mmol) dropwise. The mixture was stirred for 0.5 h at -78 °C, then warmed to room temperature and stirred for 4 h. The solvent was removed under high vacuum to obtain the lithium salt of 2-bromo-1,3-bis(trifluoromethyl)benzene (^{F}XylLi) as light yellow solid. The ^{F}XylLi was re-dissolved in 30 mL of dry toluene and the mixture was cooled to -78 °C. A solution of **4** (1.8 g, 6.42 mmol) in 20 mL dry toluene was added to the above solution, then the mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by adding 30 mL of water. The aqueous layer was separated and extracted with dichloromethane (3 × 10 mL). The combined organic layers were washed with brine (30 mL), dried with Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by column chromatography on silica gel using petroleum ether as an eluent to give **^{F}XylB-^{F}A** as a light yellow solid (2.1 g, 60%).

Synthesis of 5-(2,6-bis(trifluoromethyl)phenyl)-2-(trifluoromethyl)dibenzo [b,e]borinin-10(5H)-one (^{F}**XylB-**^{F}**AQ)**

To a solution of ^{F}XylB-^{F}A (2.1 g, 5.38 mmol) in acetic acid (120 mL) was added chromium (VI) oxide (1.4g, 14.00mmol). The mixture was refluxed with stirring for 12 h. After addition of water, the mixture was extracted with dichloromethane three times. The combined organic extract was washed with a saturated aqueous solution of $NaHCO_3$ and dried over Na_2SO_4. After filtration, the mixture was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using petroleum ether / dichloromethane (1:1) as an eluent to give ^{F}XylB-^{F}AQ as pale yellow solid (1.7 g, 71%).

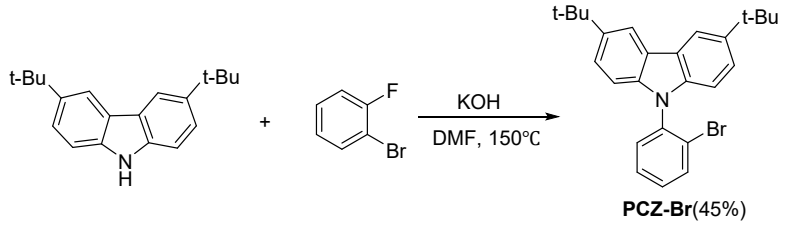
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 1.8 Hz, 1H), 8.45 (dd, *J* = 7.8, 1.1 Hz, 1H), 8.01 (d, *J* = 7.9 Hz, 2H), 7.87 – 7.82 (m, 1H), 7.82 – 7.74 (m, 2H), 7.61 (td, *J* = 7.4, 1.2 Hz, 1H), 7.44 (d, J = 7.7 Hz, 1H), 7.34 (dd, *J* = 7.4, 1.3 Hz, 1H).

^{13}C NMR (101 MHz, CDCl3) δ 186.62, 138.71, 137.92, 137.16, 136.92, 135.63, 135.44, 134.83, 133.51, 133.22, 133.04, 132.86, 129.67, 129.44, 129.17, 128.40, 126.64, 124.96, 124.24, 123.52, 122.69, 121,96.

^{11}B NMR (225 MHz, CDCl3) δ 62.5.

HR-ESIMS (m/z): $[M + H]^+$ calcd. for $C_{22}H_{10}BF_9O$, 473.0681; found: 473.0731.

Synthesis of 9-(2-bromophenyl)-3,6-di-tert-butyl-9H-carbazole (PCZ-Br)



Scheme S3 Synthetic route of **PCZ-Br**.

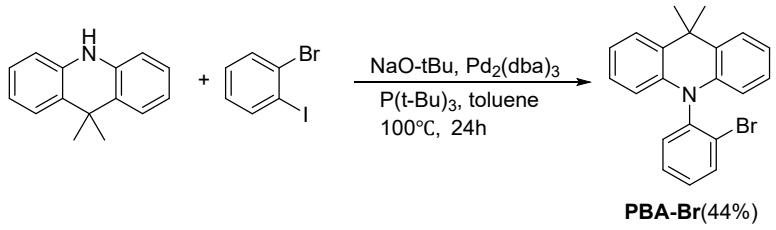
A mixture of 3,6-Di-*tert*-butyl-*9H*-carbazole (1 g, 3.58 mmol), 1-bromo-2-fluorobenzene (2.5 g, 14.32mmol) and KOH (2 g, 35.8 mmol) in 60 mL DMF was stirred at 150 ℃ for 12 h. After cooling to room temperature, the mixture was quenched with saturated saline, and extracted with ethyl acetate three times. Combined organic layer was dried over Na_2SO_4. After removal of the solvents, the residue was purified by silica gel column chromatography (eluent: petroleum ether/dichloromethane = 40/1) to obtain the title compound **PCZ-Br** (0.7g, yield = 45%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 2.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.46 – 7.41 (m, 3H), 7.38 (td, *J* = 7.7, 1.9 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 1.46 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.80, 139.39, 137.33, 134.16, 131.05, 129.83, 128.71, 123.73, 123,63, 123.23, 116.33, 109.50, 34.74, 32.09.

HR-ESIMS (m/z): $[M+H]^+$ calcd. for $C_{26}H_{28}BrN$, 436.1485; found: 436.1419.

Synthesis of 10-(2-bromophenyl)-9,9-dimethyl-9,10-dihydroacridine (PBA-Br)



Scheme S4 Synthetic route of **PBA-Br**.

A mixture of 9,9-dimethyl-9,10-dihydroacridine (2 g, 9.56 mmol), 1-bromo-2-iodobenzene (5.41 g, 19.11 mmol), tris(dibenzylideneacetone)dipalladium (0) [$Pd_2(dba)_3$, 0.44 g, 0.48 mmol], tri-tert-butylphosphine (0.17 g, 0.86 mmol), sodium tert-butoxide (NaO-tBu, 1.84 g, 19.12 mmol) in dry toluene (50 mL) was stirred at 100 °C for 24 h. After the mixture had been cooled to room temperature, water (100 mL) was slowly added and a turbid mixture was extracted with ethyl acetate three times. Combined organic layer was dried over Na_2SO_4. After removal of the solvents, the residue was purified by silica gel column chromatography (eluent: pure petroleum ether) to obtain the title compound **PBA-Br** (1.6g, yield = 44%) as a white solid.

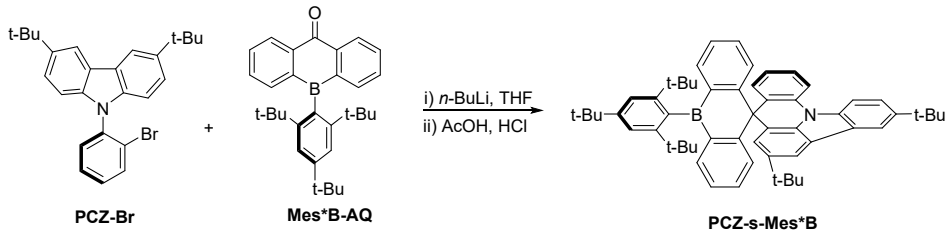
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.57 (dtd, *J* = 15.3, 7.6, 1.5 Hz, 1H), 7.48

(ddd, *J* = 7.4, 3.0, 1.8 Hz, 2H), 7.42 – 7.30 (m, 2H), 7.03 – 6.89 (m, 4H), 6.09 (ddd, *J* = 20.5, 7.6, 1.5 Hz, 2H), 1.77 (s, 3H), 1.67 (d, *J* = 1.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.27, 141.41, 139.70, 139.21, 139.06, 135.01, 133.54, 132.80, 130.82, 129.85, 126.56, 125.91, 125.70, 120.88, 113.49, 113.34, 35.98, 33.27, 31.11.

HR-ESIMS (m/z): $[M + H]^+$ calcd. for $C_{19}H_{14}BrN$,338.0289; found:338.3394.

Synthesis of 3',6'-di-tert-butyl-5-(2,4,6-tri-tert-butylphenyl)-5H-spiro[dibenzo[*b,e*]borinine-10,8'-indolo[3,2,1-de]acridine](PCZ-s-Mes*B)



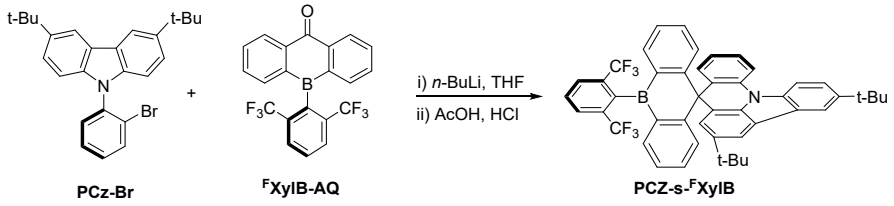
To a stirring solution of 9-(2-bromophenyl)-3,6-di-tert-butyl-9H-carbazole (0.20 g, 0.46 mmol) in THF at -78°C was added *n*-BuLi (1.6 M; 0.32 mL, 0.51 mmol) dropwise and the reaction mixture was stirred for 1.5 h at the same temperature. Then, **Mes*B-AQ** (0.25 g, 0.58 mmol) in THF (5 mL) was added dropwise at -78°C. After complete addition, the mixture was allowed to warm to room temperature overnight. After completion, the reaction was quenched with 5 mL water. The aqueous layer was separated and extracted with CH_2Cl_2 (3 ×20 mL). The combined organic layers were washed with brine, dried with Na_2SO_4 and concentrated *in vacuo* and the product was dissolved in 12 mL glacial acetic acid. The solution was heated to reflux added with 0.5 mL of concentrated hydrochloric acid and stirred for 6h. After cooling to room temperature, the mixture was poured into 100 mL ice water, and collected by filtration. The resulting precipitate was further purified via column chromatography with petroleum ether / dichloromethane (5:1) as eluents to afford a white solid (0.14 g, 39%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.15(dd, *J*=5.4 Hz, 2H), 8.12(d, *J*=2.5 Hz, 1H), 7.85(d, *J*=1.6 Hz, 1H), 7.63(d, *J*=2.1 Hz, 1H), 7.62-7.57(m, 2H), 7.50(s, 1H), 7,24-7.18(m, 1H), 7.15-7.04(m, 6H), 6.69(t, *J*=2.1 Hz, 1H), 6.66-6.58(m, 2H), 1.44(s, 10H), 1.37(s, 9H), 1.21(d, *J*=2.7 Hz, 18H), 1.09(s, 9H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 155.94, 152.48, 152.38, 148.32, 145.85, 143.88, 137.92, 137.22, 136.69, 135.97, 135.62, 134.12, 133.76, 132.42, 132.40, 131.93, 130.28, 127.14, 126.45, 125.78, 124.05, 123.94, 122.72, 122.69, 122.61, 122.16, 117.23, 114.06, 113.78, 113.07, 53.64, 38.62, 38.58, 35.51, 35.37, 35.03, 34.77, 34.73, 31.93, 31.90, 31.48.

HR-ESIMS (m/z): $[M+H]^+$ calcd. for $C_{57}H_{64}BN$, 774.5132; found: 774.5225.

Synthesis of 5-(2,6-bis(trifluoromethyl)phenyl)-3',6'-di-tert-butyl-5H-spiro[dibenzo[*b,e*]borinine-10,8'-indolo[3,2,1-de]acridine](PCZ-s-^{F}XylB)



To a stirring solution of 9-(2-bromophenyl)-3,6-di-*tert*-butyl-9H-carbazole (0.20 g, 0.46 mmol) in THF at -78°C was added *n*-BuLi (1.6 M; 0.32 mL, 0.51 mmol) dropwise and the reaction mixture was stirred for 1.5 h at the same temperature. Then, **^{F}XylB-AQ** (0.23 g, 0.58 mmol) in THF (5 mL) was added dropwise at -78°C. After complete addition, the mixture was allowed to warm to room temperature overnight. After completion, the reaction was quenched with 5 mL water. The aqueous layer was separated and extracted with CH_2Cl_2 (3 ×20 mL). The combined organic layers were washed with brine, dried with Na_2SO_4 and concentrated in vacuo and the product was dissolved in 12 mL glacial acetic acid. The solution was heated to reflux added with 0.5 mL of concentrated hydrochloric acid and stirred for 6h. After cooling to room temperature, the mixture was poured into 100 mL ice water, and collected by filtration. The resulting precipitate was further purified via column chromatography with petroleum ether / dichloromethane (5:1) as eluents to afford a white solid (0.13 g, 38%).

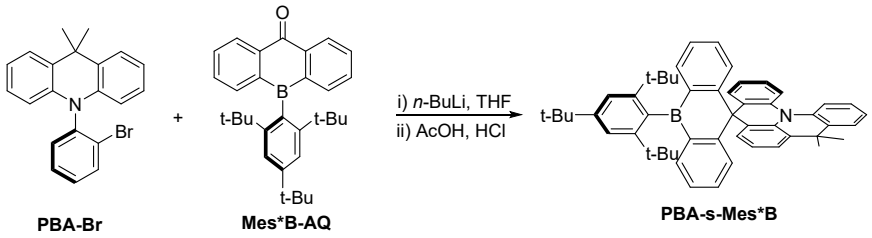
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22(s, 1H), 8.20 (d, *J* = 1.9 Hz, 2H), 8.05 (dd, *J* = 8.0, 3.1 Hz, 2H), 7.84 (d, *J* = 1.7 Hz, 1H), 7.80 (t, *J* = 7.9 Hz, 1H), 7.67 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.33 (d, *J* = 1.9 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.27 (dd, *J* = 3.8, 1.6 Hz, 1H), 7.23 (d, *J* = 1.6 Hz, 1H), 7.14 – 7.08 (m, 4H), 6.82 (dd, *J* = 7.6, 7.2, 1.1 Hz, 1H), 6.75 – 6.54 (m, 2H), 1.52 (s, 9H), 1.15 (s, 9H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 158.58, 146.02, 143.81, 136.77, 136.22, 136.03, 134.12, 133,95, 133.49 (d, *J* = 13.9 Hz), 133.18 (t, *J* = 6.8 Hz), 132.85, 132.52, 132.07, 129.16, 128.57, 127.92, 127.30, 126.32, 126.04 (d, *J* = 4.6 Hz), 125.60, 124.13, 123.73, 123.33, 123.10, 122.31, 117.24, 114.21, 113.59, 112.77, 53.36, 34.84, 34.76, 31.94, 31.59.

^{11}B NMR (225MHz, $CDCl_3$) δ 59.32.

HR-ESIMS (m/z): $[M+H]^+$ calcd. for $C_{47}H_{38}BF_6N$, 742.3001; found: 742.3054.

Synthesis of 9',9'-dimethyl-5-(2,4,6-tri-tert-butylphenyl)-5H,9'H-spiro[dibenzo[*b,e*]borinine-10,5'-quinolino[3,2,1-de]acridine](PBA-s-Mes*B)



PBA-Br **Mes*B-AQ** **PBA-s-Mes*B**

To a stirring solution of 10-(2-bromophenyl)-9,9-dimethyl-9,10-dihydroacridine (0.20 g, 0.55 mmol) in THF at -78°C was added *n*-BuLi (1.6 M; 0.38 mL, 0.61 mmol) dropwise and the reaction mixture was stirred for 1.5 h at the same temperature. Then, **Mes*B-AQ** (0.29 g, 0.66 mmol) in THF (5 mL) was added dropwise at -78°C. After complete addition, the mixture was allowed to warm to room temperature overnight. After completion, the reaction was quenched with 5 mL water. The aqueous layer was separated and extracted with CH_2Cl_2 (3 ×20 mL). The combined organic layers were washed with brine, dried with Na_2SO_4 and concentrated *in vacuo* and the product was dissolved in 12 mL glacial acetic acid. The solution was heated to reflux added with 0.5 mL of concentrated hydrochloric acid and stirred for 6h. After cooling to room temperature, the mixture was poured into 100 mL ice water, and collected by filtration. The resulting precipitate was further purified via column chromatography with petroleum ether

/ dichloromethane (5:1) as eluents to afford a white solid (0.14 g, 36%).

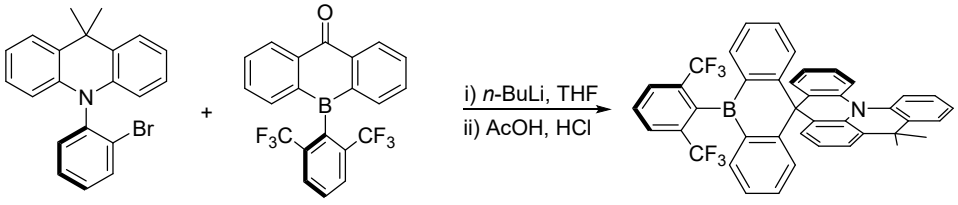
^{1}H NMR (400 MHz, THF-d_8) δ 7.63 (ddd, *J* = 11.4, 7.8, 1.4 Hz,2H), 7.49 (td, *J* = 5.4, 4.9, 1.6 Hz, 4H), 7.46 – 7.38 (m, 1H), 7.32 – 7.25 (m, 1H), 7.24 – 7.17 (m, 1H), 7.17 – 7.11 (m, 3H), 7.06 (td, *J* = 7.5, 1.2 Hz, 1H), 7.02 – 6.93 (m, 2H), 6.93 – 6.83 (m, 2H), 6.67 – 6.55 (m, 2H), 6.47 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.29 (dd, *J* = 7.9, 1.3 Hz, 1H), 1.85 (s, 3H), 1.33 (s, 9H), 1.31 (s, 3H), 1.18 (s, 9H), 1.11 (s, 9H).

^{13}C NMR (176 MHz, THF-d_8) δ 156.25, 154.37, 152.25 (d, *J* = 15.0 Hz), 148.25, 140.64, 139.67, 137.57, 137.42, 137.01, 136.82, 136.31, 136.24, 135.32, 135.02, 134.16, 133.99, 133.75, 132.84, 131.81, 131.15, 129.07, 127.83, 126.33, 126.09, 125.93, 125.57, 123.99, 123.14, 122.77, 122.61, 122.55, 122.53, 121.25, 119.02, 116.19, 53.37, 38.35, 38.34, 36.87, 34.83, 34.74, 34.39, 30.83, 29,96, 22.44.

^{11}B NMR (225MHz, THF-d_8) δ 62.11.

HR-ESIMS (m/z): $[M+H]^+$ calcd. for $C_{52}H_{54}BN$, 704.4349; found: 704.4455.

Synthesis of 5-(2,6-bis(trifluoromethyl)phenyl)-9',9'-dimethyl-5H,9'H-spiro[dibenzo[*b,e*]borinine-10,5'-quinolino[3,2,1-de]acridine](PBA-s-^{F}XylB)



PBA-Br **^{F}XylB-AQ** **PBA-s-^{F}XylB**(41%)

To a stirring solution of 10-(2-bromophenyl)-9,9-dimethyl-9,10-dihydroacridine (0.20 g, 0.55 mmol) in THF at -78°C was added *n*-BuLi (1.6 M; 0.38 mL, 0.61 mmol) dropwise and the reaction mixture was stirred for 1.5 h at the same temperature. Then, **^{F}XylB-AQ** (0.27 g, 0.66 mmol) in THF (5 mL) was added dropwise at -78°C. After complete addition, the mixture was allowed to warm to room temperature overnight. After completion, the reaction was quenched with 5 mL water. The aqueous layer was separated and extracted with CH_2Cl_2 (3 ×20 mL). The combined organic layers were washed with brine, dried with Na_2SO_4 and concentrated *in vacuo* and the product was dissolved in 12 mL glacial acetic acid. The solution was heated to reflux added with 0.5 mL of concentrated hydrochloric acid and stirred for 6h. After cooling to room temperature, the mixture was poured into 100 mL ice water, and collected by filtration. The resulting precipitate was further purified via column chromatography with petroleum ether / dichloromethane (5:1) as eluents to afford a yellow solid (0.15 g, 41%).

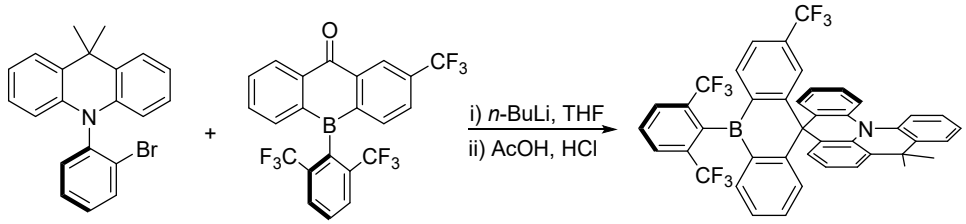
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30 (dd, *J* = 8.0, 3.0 Hz, 2H), 8.04 (t, *J* = 8.0 Hz, 1H), 7.66 – 7.56 (m, 3H), 7.51 (ddd, *J* = 8.4, 5.2, 3.6 Hz, 1H), 7.35 (td, *J* = 7.8, 1.5 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.28 – 7.16 (m, 6H), 7.12 (td, *J* = 7.5, 7.1, 1.4 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.85 (q, *J* = 7.1, 6.6 Hz, 2H), 6.41 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.23 (dd, *J* = 7.8, 1.2 Hz, 1H), 1.94 (s, 3H), 1.39 (s, 3H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 158.60, 157.35, 140.03, 137.25, 136.98, 136.43, 135.69, 135.63, 135.17, 134.65, 134.11, 133.74, 133.57, 133.45, 133.34, 133.28, 133.17, 132.95, 131.28, 129.46, 129.17, 128.57, 128.00, 126.37, 126.24, 125.73, 125.71, 125.40, 124.09, 123.84, 123.20, 123.18, 123.00, 121.31, 119.33, 116.48, 53.18, 37.13, 30.09, 23.14.

^{11}B NMR (225 MHz, $CDCl_3$) δ 59.09.

HR-ESIMS (m/z): $[M+H]^+$ calcd. for $C_{42}H_{28}BF_6N$, 672.2219; found: 672.2304.

Synthesis of (S)-5-(2,6-bis(trifluoromethyl)phenyl)-9',9'-dimethyl-2-(trifluoromethyl)-5H,9'H-spiro[dibenzo[*b,e*]borinine-10,5'-quinolino[3,2,1-de]acridine](PBA-s-^{F}XylBF)



PBA-Br **^{F}XylB-^{F}AQ** **PBA-s-^{F}XylBF**(39%)

To a stirring solution of 10-(2-bromophenyl)-9,9-dimethyl-9,10-dihydroacridine (0.20 g, 0.55 mmol) in THF at -78°C was added *n*-BuLi (1.6 M; 0.38 mL, 0.61 mmol) dropwise and the reaction mixture was stirred for 1.5 h at the same temperature. Then, **^{F}XylB-^{F}AQ** (0.31 g, 0.66 mmol) in THF (5 mL) was added dropwise at -78°C. After complete addition, the mixture was allowed to warm to room temperature overnight. After completion, the reaction was quenched with 5 mL water. The aqueous layer was separated and extracted with CH_2Cl_2 (3 ×20 mL). The combined organic layers were washed with brine, dried with Na_2SO_4 and concentrated *in vacuo* and the product was dissolved in 12 mL glacial acetic acid. The solution was heated to reflux added with 0.5 mL of concentrated hydrochloric acid and stirred for 6h. After cooling to room temperature, the mixture was poured into 100 mL ice water, and collected by filtration. The resulting precipitate was further purified via column chromatography with petroleum ether / dichloromethane (5:1) as eluents to afford a yellow solid (0.16 g, 39%).

^{1}H NMR (400 MHz, THF-d_8) δ 8.08 (dd, J = 7.9, 4.7 Hz, 2H), 7.86 (t, J = 7.9 Hz, 1H), 7.64 – 7.57 (m, 1H), 7.54 (dt, J = 8.3, 1.4 Hz, 1H), 7.48 (ddd, J = 8.6, 5.2, 2.5 Hz, 1H), 7.40 (dd, J = 8.0, 1.7 Hz, 1H), 7.31 (dddd, J = 17.0, 11.1, 7.9, 2.0 Hz, 2H), 7.23 – 7.12 (m, 4H), 7.11 – 6.99 (m, 2H), 6.95 (td, J = 7.3, 1.1 Hz, 1H), 6.74 – 6.60 (m, 2H), 6.41 (ddd, J = 13.6, 7.9, 1.4 Hz, 1H), 6.24 (ddd, J = 19.4, 7.9, 1.2 Hz, 1H), 2.31 (s, 3H), 1.87 (s, 3H).

^{13}C NMR (176 MHz, THF-d_8) δ 139.35, 137.28, 137.21, 136.99, 136.71, 135.86, 135.35, 135.07, 135.00, 134.67, 134.14, 133.83, 130.75, 129.61, 127.42, 126.83, 126.08, 126.05, 125.93, 125.90, 124.04, 123.85, 123.43, 123.02, 122.95, 121.70, 119.28, 116.41, 116.22, 53.55, 36.92, 29.63, 29.35.

^{11}B NMR (225 MHz, THF-d_8) δ 58.14.

HR-ESIMS (m/z): $[M + H]^+$ calcd. for $C_{43}H_{27}BF_9N$, 740.2093; found: 740.2174.

S3 Experimental data

S3.1 X-ray crystallographic analyses

Single-crystal X-ray diffraction data were collected on a Bruker D8 Venture 4-circle diffractometer using Mo/Cu- Kα (λ = 0.71073Å/1.54184 Å). The images were processed and corrected for Lorentz-polarization effects and absorptionas implemented in the Bruker software packages. The structures were solved using the intrinsic phasing method(SHELXT) [3] and Fourier expansion technique. All non-

hydrogen atoms were refined in anisotropic approximation, with hydrogen atoms 'riding' in idealized positions, by full-matrix least squares against F2 of all data, using SHELXL software.[4] Hydrogen atoms were refined with isotropic displacement parameters. Olex2[5] was used as a graphical user interface and for the preparation of the CIF files. Crystal data and experimental details are listed in Table S1.

Table S1 Crystal data and structure refinement for **PCZ-s-^{F}XylB(, PBA-s-Mes*B**, and **PBA-s-^{F}XylB**.

Identification code	**PCZ-s-^{F}XylB**	**PBA-s-Mes*B**	**PBA-s-^{F}XylB****
CCDC Deposit number	2426270	2426272	N/A
Empirical formula	$C_{47}H_{38}BF_6N$	$C_{52}H_{54}BN$	$C_{42}H_{28}NBF_6$
Formula weight	741.59	703.77	671.46
Temperature/K	179.99	180.0	298
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	P-1
a/Å	8.8760(4)	10.7285(7)	8.3507(18)
b/Å	31.8729(11)	14.2452 (9)	17.021(4)
c/Å	13.6461(5)	26.8675(15)	23.009(7)
α/°	90	90	90
β/°	95.507(2)	99.276(2)	82.924(9)
γ/°	90	90	90
Volume/Å^3	3842.7(3)	4052.5(4)	3245.6(15)
Z	4	4	4
ρcalcg/cm^3	1.282	1.154	1.374
μ/mm-1	0.094	0.065	0.103
F(000)	1544.0	1512.0	1384
Crystal size/mm^3	0.3 × 0.3 × 0.2	0.56 × 0.45 × 0.36	0.29 × 0.13 × 0.07
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.784 to 55.116	4.366 to 55.106	4.296 to 55.452
Index ranges	-11 ≤ h ≤ 10, -41 ≤ k ≤ 41, -17 ≤ l ≤ 17	-12 ≤ h ≤ 13, -18 ≤ k ≤ 18, -34 ≤ l ≤ 34	-10 ≤ h ≤ 10, -22 ≤ k ≤ 21, -30 ≤ l ≤ 29
Reflections collected	50654	52793	39510
Independent reflections	8853 [R_{int} = 0.0687, R_{sigma} = 0.0558]	9333 [R_{int} = 0.0475, R_{sigma} = 0.0384]	15012 [Rint = 0.4511, Rsigma = 0.6678]
Data/restraints/parameters	8853/84/533	9333/0/498	15012/0/905
Goodness-of-fit on F^2	1.041	1.042	0.912
Final R indexes [I>=2σ (I)]	R_1 = 0.0740, wR_2 = 0.1894	R_1 = 0.0642, wR_2 = 0.1557	R1 = 0.1061, wR2 = 0.2062
Final R indexes [all data]	R_1 = 0.1359, wR_2 = 0.2255	R_1 = 0.0929, wR_2 = 0.1738	R1 = 0.4326, wR2 = 0.3259
Largest diff. peak/hole / e Å^{-3}	0.57/-0.37	0.90/-0.73	0.61/-0.43

** The poor crystal quality of **PBA-s-^{F}XylB** resulted in low reliability of the single-crystal diffraction data, therefore, this information is provided for reference purposes only.

Table S2 Selected bond lengths [Å] and angles [°] of **PCZ-s-^{F}XylB**, **PBA-s-Mes*B** and **PBA-s-^{F}XylB**.

Compound	a /Å	b /Å	c / °
PCZ-s-^{F}XylB	B1-C4 1.590(4)	B1-C9 1.544(4) B1-C17 1.537 (4)	89.4
PBA-s-Mes*B	B1-C11 1.592(3)	B1-C10 1.560(3) B1-C19 1.556(3)	87.9
PBA-s-^{F}XylB**	B1-C35 1.563(10)	B1-C1 1.539(10) B1-C12 1.529(9)	89.0

a. The bond lengths of B-C^{F}Xyl/Mes*, b. the bond lengths of B-C_{Ar}, c. the dihedral angles between the planes of boraanthracene and donor moiety.

** The poor crystal quality of **PBA-s-^{F}XylB** resulted in low reliability of the single-crystal diffraction data, therefore, this information is provided for reference purposes only.

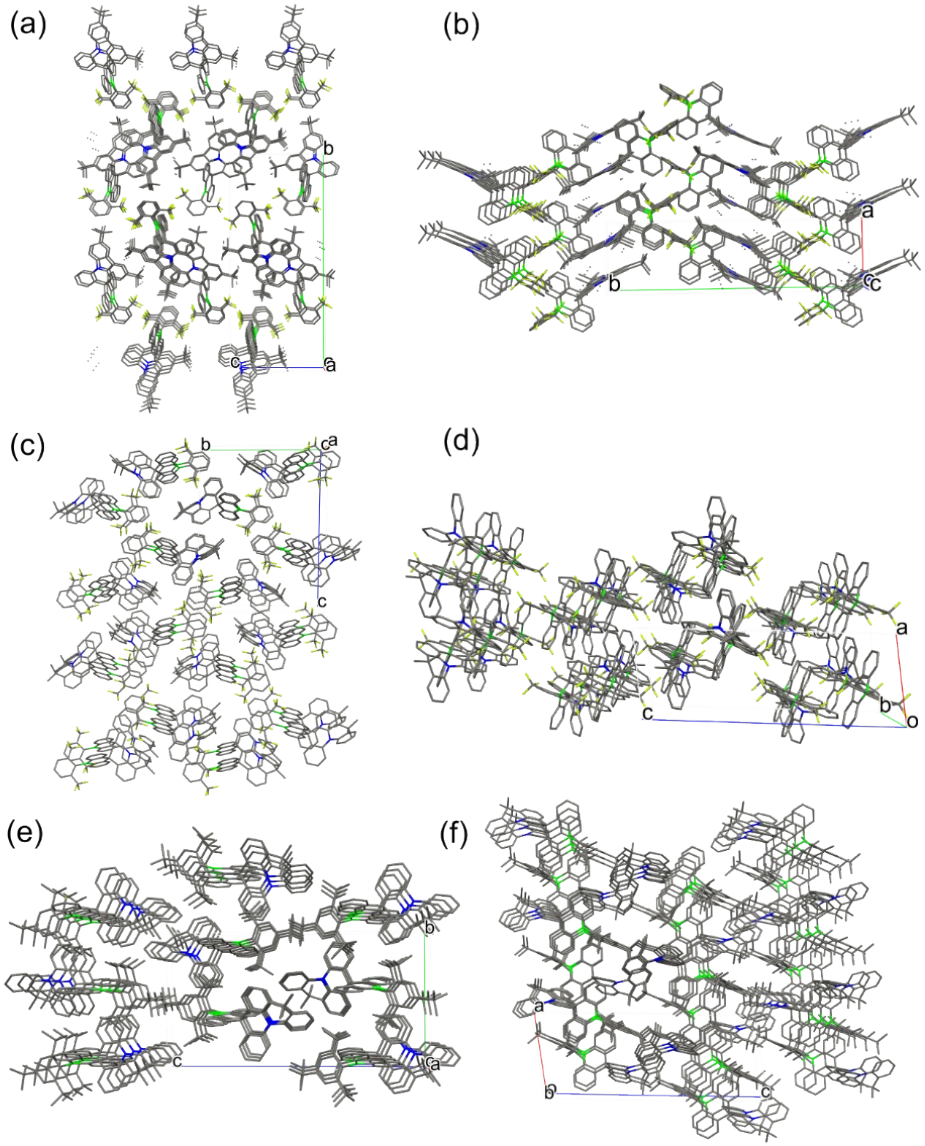


Figure S1. The stacking diagrams of the three molecules along different cell-axis: **PCZ-s-^{F}XylB** along a-axis (a) and c-axis; **PBA-s-^{F}XylB** along a-axis (c) and b-axis (d); **PBA-s-Mes*B** along a-axis (e) and b-axis (f).

S3.2 Photophysical properties

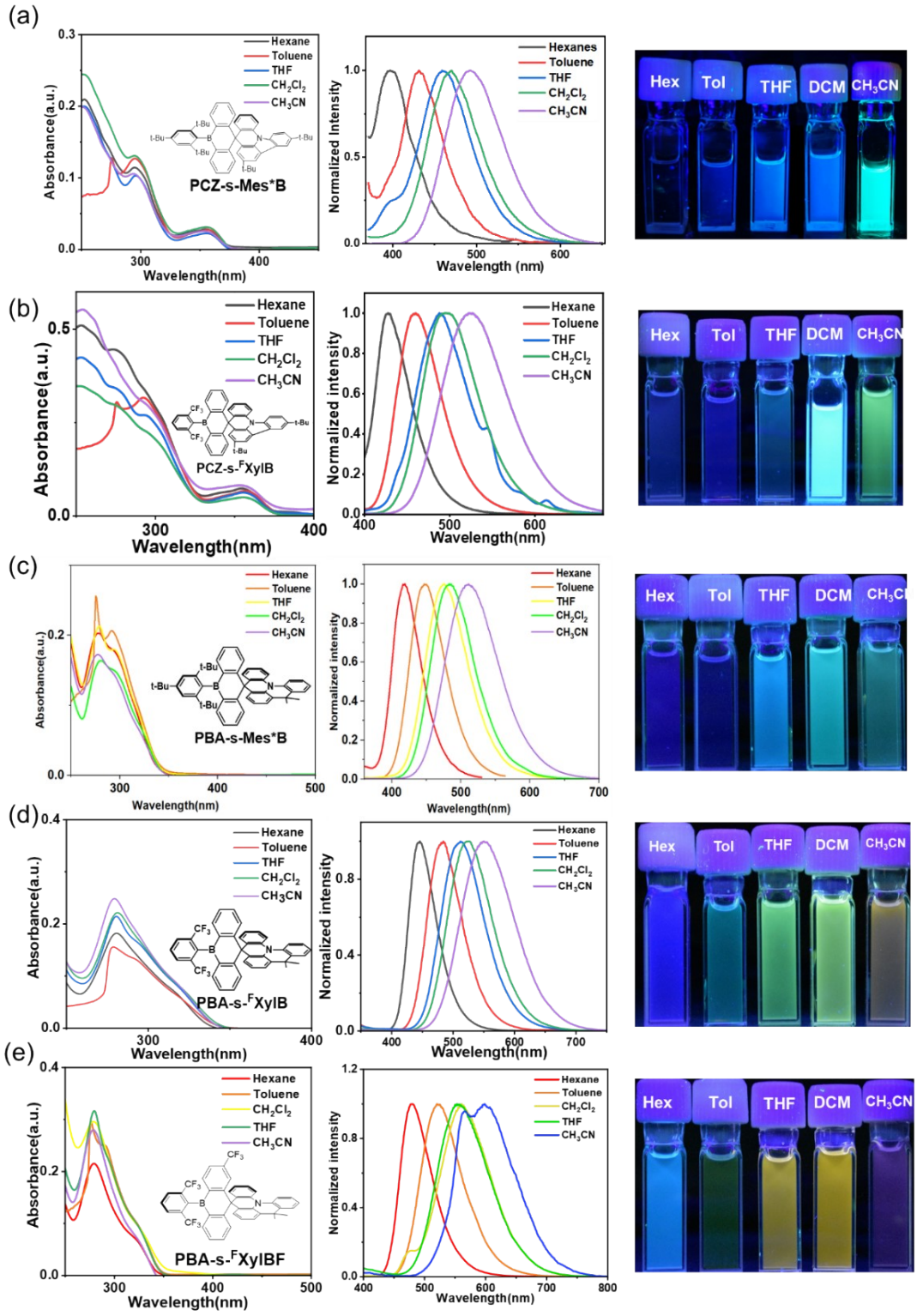


Figure S2. UV-Vis and Photoluminescent spectra of (a) **PCZ-s-Mes*B,** (b) **PCZ-s-^{F}XylB,** (c) **PBA-s-Mes*B,** (d) **PBA-s-^{F}XylB,** (e) **PBA-s-^{F}XylBF** in different solvents (1×10^{-5} M) at 298 K, and corresponding photos under UV lamp.

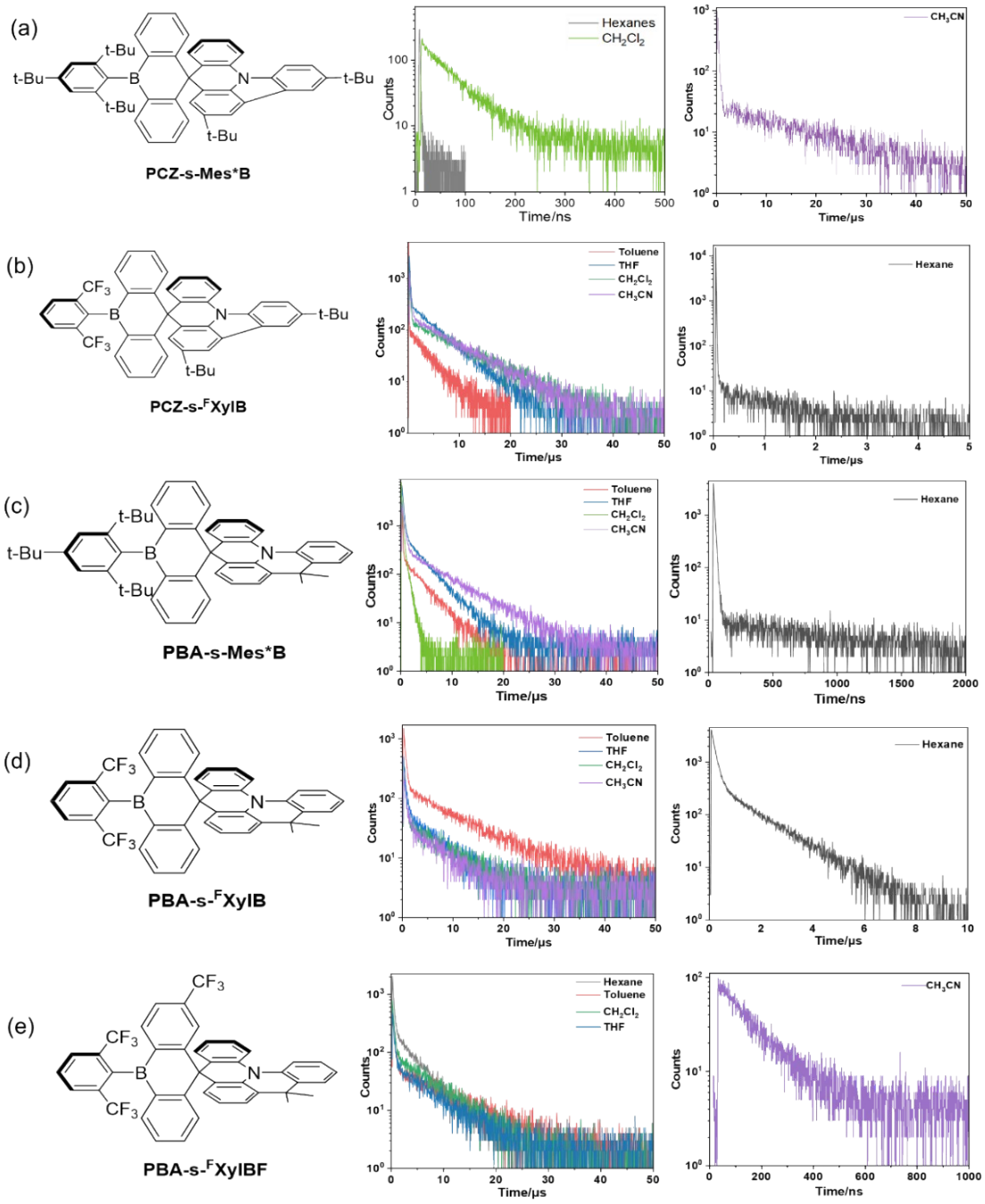
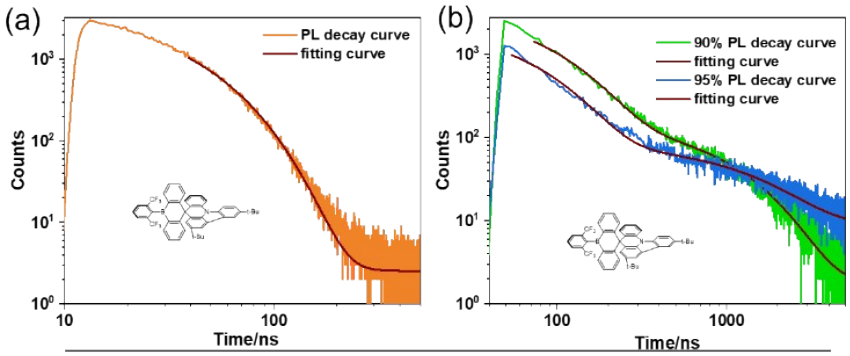


Figure S3. Structure of (a) **PCZ-s-Mes*B,** (b) **PCZ-s-^{F}XylB,** (c) **PBA-s-Mes*B,** (d) **PBA-s-^{F}XylB,** (e) **PBA-s-^{F}XylBF**, and corresponding transient PL decay curves in oxygen-free solvents (1×10^{-5} M) at 298 K.

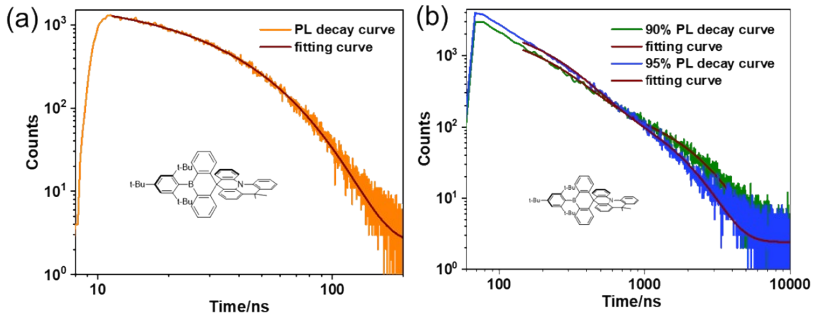
Table S3. Photophysical parameters of spiro compounds in different solvents under oxygen-free condition.

Compounds	Solvents	λ_{abs}[nm]	λ_{em}[nm]	PLQY	τ_{PF}[ns]/τ_{DF}[μs]
PCZ-s-Mes*B	Hexane	295,357	397	0.016	1.5/-
	Toluene	275,295,357	430	0.022	6.1/-
	THF	296,356	460	0.016	30.8/-
	CH_2Cl_2	296,358	470	0.087	56.5/-
	CH_3CN	296,356	492	0.74	1.9/16.9
PCZ-s-^{F}XylB	Hexane	275,353	428	0.03	4.9/0.16
	Toluene	292,356	459	1.00	13.9/2.22
	THF	294,357	486	0.96	3.1/3.95
	CH_2Cl_2	276,357	495	1.00	21.4/7.70
	CH_3CN	357	523	1.00	37.8/6.53
PBA-s-Mes*B	Hexane	278,296	418	0.06	8.3/0.12
	Toluene	276,292	447	1.00	29.2/2.39
	THF	279,295	476	1.00	124.7/2.01
	CH_2Cl_2	281,294	483	0.82	130.1/0.23
	CH_3CN	278	511	1.00	128.0/4.70
PBA-s-^{F}XylB	Hexane	280	447	1.00	73.5/0.70
	Toluene	279	486	1.00	87.2/6.71
	THF	280	512	1.00	115.8/3.84
	CH_2Cl_2	281	525	1.00	92.9/5.39
	CH_3CN	279	550	1.00	106.6/4.10
PBA-s-^{F}XylBF	Hexane	280	480	1.00	84.5/2.73
	Toluene	276,290	522	1.00	66.8/7.04
	THF	280	557	0.90	64.9/4.59
	CH_2Cl_2	279	563	1.00	73.6/4.77
	CH_3CN	279	599	0.20	8.4/0.12



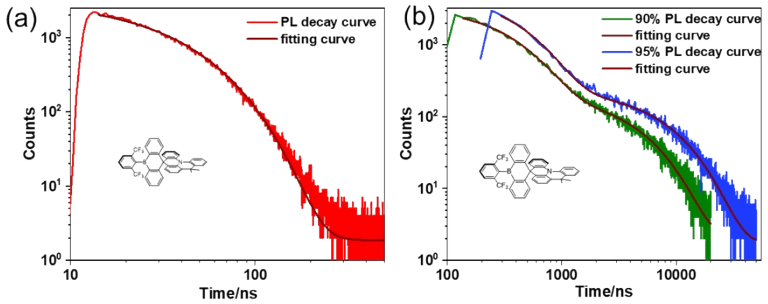
Water fraction (fw)	τ_{PF}[ns]/τ_{DF}[μs]	PLQY(100%)
0%	28.5/-	2.4
90%	33.3/0.5	9.6
95%	22.7/0.8	5.8

Figure S4. Transient decay curves and PLQY of **PCZ-s-^{F}XylB** in H_2O/THF with different water fraction



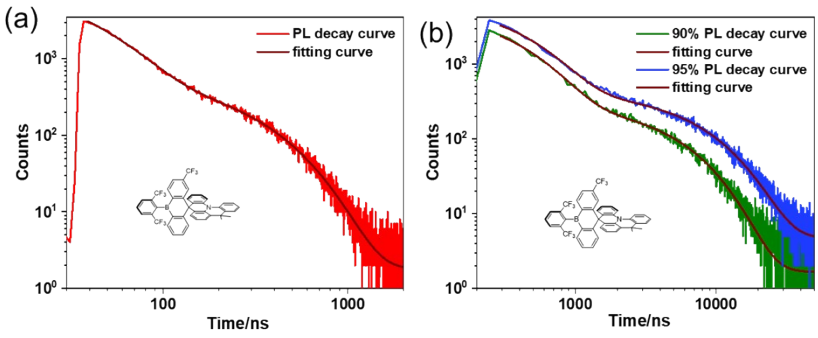
Water fraction (fw)	τ_{PF}[ns]/τ_{DF}[μs]	PLQY(100%)
0%	23.7/-	3.6
90%	62.3/0.7	16.4
95%	81.3/0.4	11.0

Figure S5. Transient decay curves and PLQY of **PBA-s-Mes*B** in H_2O/THF with different water fraction



water fraction (fw)	τ_{PF}[ns]/τ_{DF}[μs]	PLQY(100%)
0%	29.6/-	5.5
90%	152.1/2.0	15.6
95%	129.1/4.4	53.2

Figure S6. Transient decay curves and PLQY of **PBA-s-^{F}XylB** in H_2O/THF with different water fraction



Water fraction (fw)	τ_{PF}[ns]/τ_{DF}[μs]	PLQY(100%)
0%	10.9/0.1	7.3
90%	124.1/2.8	15.0
95%	104.1/4.7	49.5

Figure S7. Transient decay curves and PLQY of **PBA-s-^{F}XylBF** in H_2O/THF with different water fraction

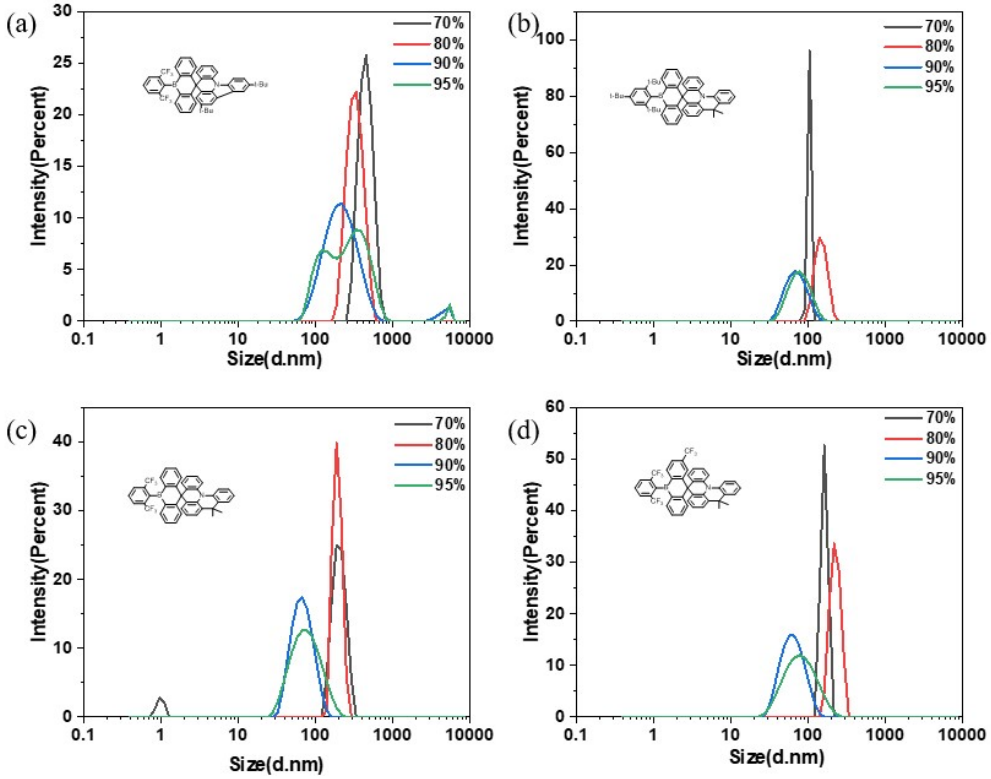


Figure S8. Dynamic light scattering (DLS) of compounds (a) **PCZ-s-^{F}XylB**, (b) **PBA-s-Mes*B**, (c) **PBA-s-^{F}XylB**, (d) **PBA-s-^{F}XylBF**

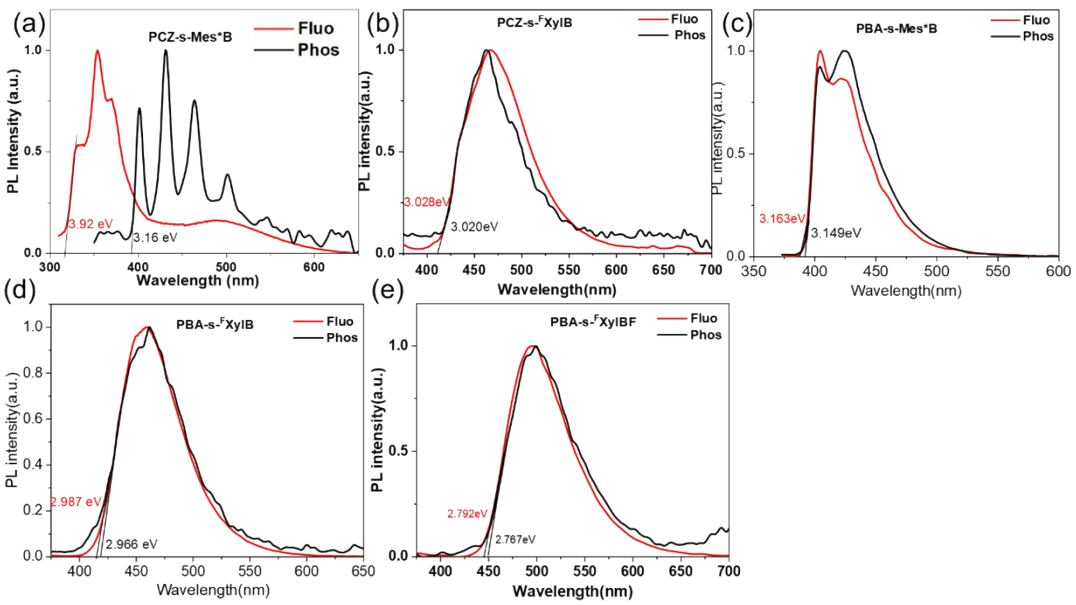


Figure S9. Normalized fluorescence and phosphorescence spectra at 77 K of **PCZ-s-Mes*B**, **PCZ-s-^{F}XylB**, **PBA-s-Mes*B**, **PBA-s-^{F}XylB** and **PBA-s-^{F}XylBF** in degassed toluene (1×10^{-5} M).

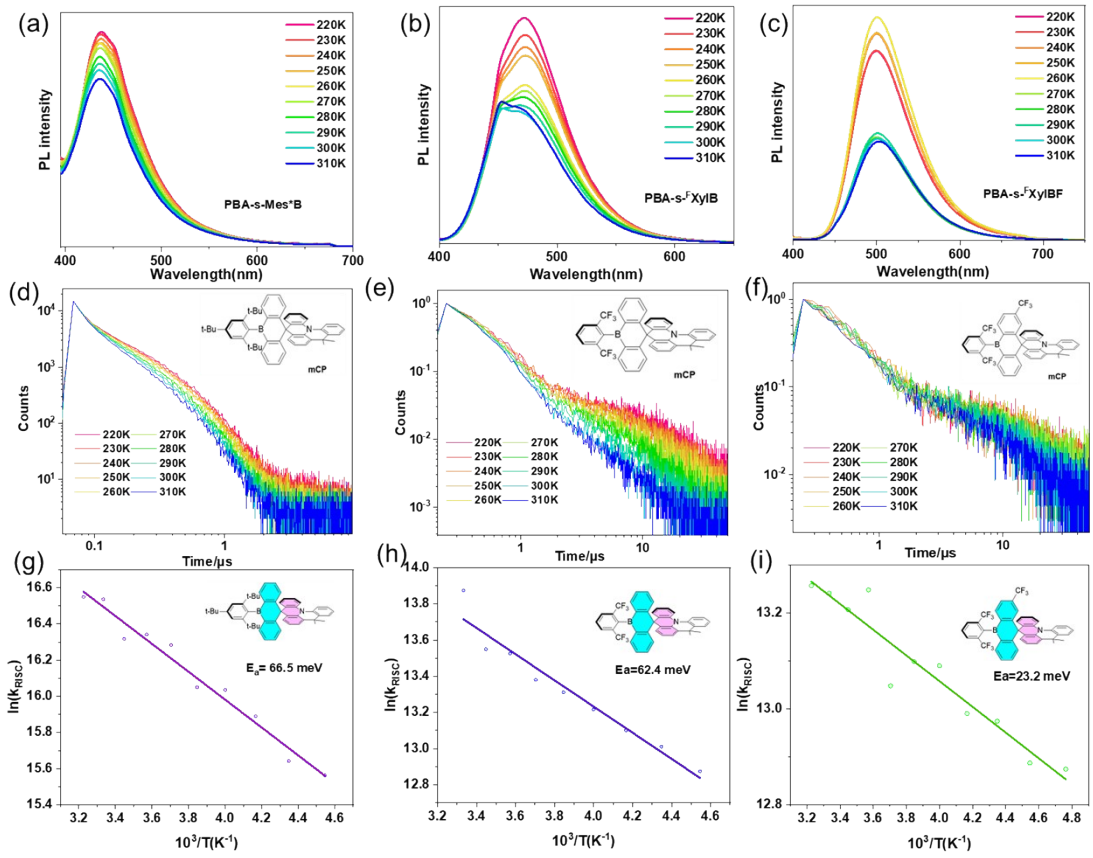


Figure S10. (a-c) Temperature dependent PL spectra of spiro B-N compounds in doped films (5 wt % **PBA-s-Mes*B** , **PBA-s-^{F}XylB** and **PBA-s-^{F}XylBF** doped in mCP); (d-f) Temperature dependent

transient PL decay curves with log-log diagram of spiro B-N compounds in doped films: 5 wt % **PBA-s-Mes*B**, **PBA-s-^{F}XylB** and **PBA-s-^{F}XylBF** doped in mCP; (g-i) Arrhenius plots of k_{RISC} in doped films.

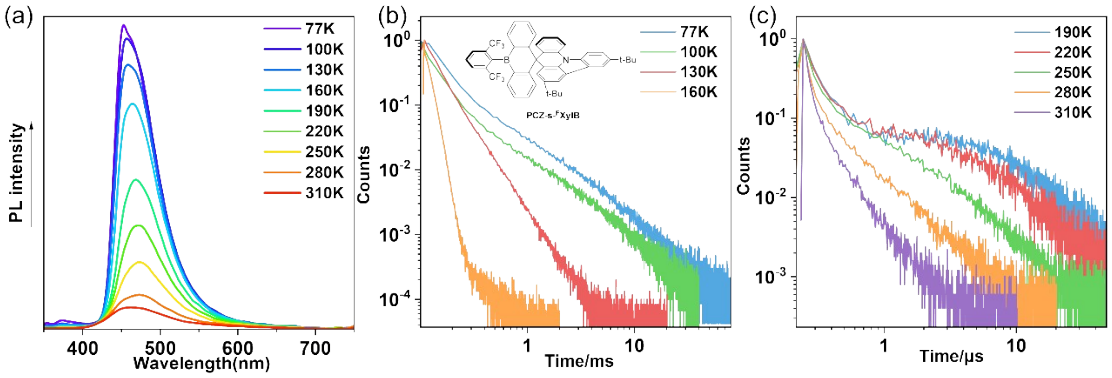


Figure S11. (a) Temperature dependent PL spectra of **PCZ-s-^{F}XylB** in doped films (5 wt % in mCP); (b-c) Temperature dependent transient PL decay curves with log-log diagram of **PCZ-s-^{F}XylB** in doped films (5 wt % in mCP).

S3.3 Electrochemical properties

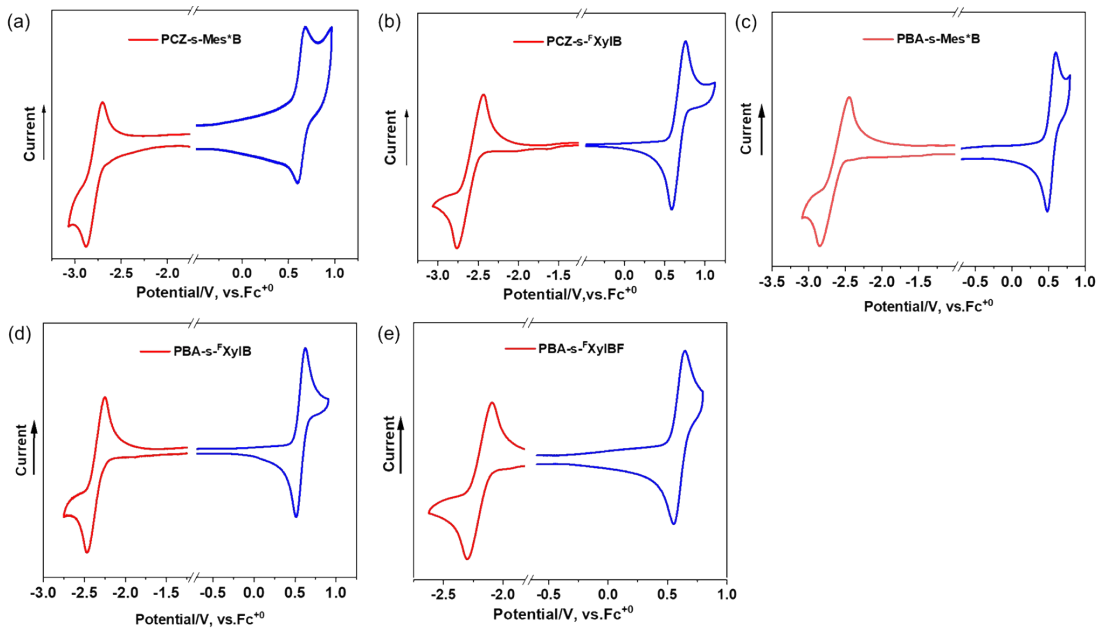


Figure S12. Cyclic voltammogram (CV) diagrams of **PCZ-s-Mes*B** (a), **PCZ-s-^{F}XylB** (b), **PBA-s-Mes*B** (c), **PBA-s-^{F}XylB** (d) and **PBA-s-^{F}XylBF** (e) showing the reduction (recorded in THF) and oxidation waves (recorded in CH_2Cl_2) vs Fc/Fc^+, using n-Bu_4NPF_6 (0.1 M) as the electrolyte, ν = 100 mV/s.

S3.4 Theoretical calculations

Table S4. Coordinates of optimized structure of **PCZ-s-Mes*B**, **PCZ-s-^{F}XylB**, **PBA-s-Mes*B**, **PBA-s-^{F}XylB**, **PBA-s-^{F}XylBF**

PCZ-s-Mes*B							
Element	Coordinates (angstroms)			Element	Coordinates (angstroms)		
	X	Y	Z		X	Y	Z
C	0.62151	-0.63931	0.57953	H	2.74019	-5.57652	1.48454
C	1.70721	0.4427	0.55777	H	0.3082	-5.13699	1.84752
C	3.01027	0.06451	0.30989	H	-0.57149	-2.86841	1.48627
N	3.46678	-1.24437	0.15962	H	0.46311	2.13208	0.91626
C	2.64039	-2.29692	0.59159	H	4.60442	3.05319	0.18119
C	1.27424	-2.02743	0.82713	H	1.86712	-1.03341	-1.78621
C	-0.03094	-0.68991	-0.81832	H	0.94726	-1.1598	-4.04533
C	-1.41591	-0.53675	-1.02109	H	-1.50056	-0.89517	-4.42516
B	-2.37153	-0.27347	0.17091	H	-2.98813	-0.49674	-2.48323
C	-1.72386	-0.17967	1.57609	H	-3.58023	0.20577	2.58573
C	-0.33893	-0.34181	1.73793	H	-2.5725	0.38174	4.84424
C	3.15215	-3.57374	0.85267	H	-0.11273	0.0931	5.10727
C	2.32064	-4.59499	1.29149	H	1.2925	-0.36628	3.1398
C	0.96812	-4.34956	1.50101	H	-6.80841	-1.88775	-0.39928
C	0.47023	-3.07102	1.28355	H	-6.23136	2.27225	-0.90361
C	1.47343	1.81175	0.70447	H	6.82789	1.57215	-0.46654
C	2.50119	2.76606	0.58963	H	7.74661	-2.57418	-1.11297
C	3.80123	2.33369	0.2926	H	5.46665	-3.21428	-0.61388
C	4.06679	0.97587	0.14853	H	-10.1007	-0.0808	-0.02612
C	0.79999	-0.91376	-1.92274	H	-8.81967	0.43899	1.0808
C	0.27936	-0.98642	-3.2076	H	-8.81377	-1.20033	0.43035
C	-1.0918	-0.83799	-3.42168	H	-8.43416	2.44754	-0.46695
C	-1.92043	-0.61607	-2.33417	H	-9.68072	1.82353	-1.54567
C	-2.51008	0.08041	2.71628	H	-8.07776	2.18682	-2.18155
C	-1.95008	0.18027	3.97845	H	-7.93725	-0.19822	-3.11251
C	-0.56931	0.01841	4.12551	H	-9.58024	-0.45373	-2.50315
C	0.22259	-0.23992	3.01681	H	-8.29098	-1.58089	-2.07586
C	-3.92558	-0.09513	-0.06928	H	-4.31224	-4.50462	-1.08025
C	-4.80863	-1.21621	-0.07571	H	-3.82714	-3.02787	-1.92436
C	-6.15725	-1.02484	-0.37872	H	-5.53675	-3.35343	-1.6308
C	-6.707	0.21594	-0.67797	H	-2.86368	-2.50299	1.66916
C	-5.84089	1.29659	-0.66046	H	-2.24188	-2.60022	0.00911
C	-4.47607	1.18269	-0.36301	H	-2.8562	-4.03128	0.79468
C	4.83512	-1.18451	-0.16196	H	-5.07878	-4.38374	1.37095
C	5.23826	0.17711	-0.16315	H	-6.42088	-3.38693	0.83213
C	6.55219	0.52535	-0.47493	H	-5.36579	-2.80846	2.12162

C	7.48611	-0.45551	-0.80337	H	-3.14969	3.88514	-2.09483
C	7.04883	-1.7937	-0.83162	H	-4.63965	2.98698	-2.41216
C	5.74784	-2.17491	-0.52534	H	-3.07729	2.17523	-2.54099
C	-8.19854	0.33762	-1.01091	H	-1.61196	1.84404	-0.48283
C	-9.03061	-0.15752	0.18948	H	-2.21116	2.32109	1.11665
C	-8.61255	1.78432	-1.3173	H	-1.84756	3.53031	-0.10489
C	-8.51886	-0.52677	-2.24728	H	-3.85923	4.55917	0.28196
C	-4.4248	-2.70428	0.1511	H	-4.55131	3.34457	1.36414
C	-4.5364	-3.44026	-1.20235	H	-5.42944	3.85983	-0.07647
C	-3.01471	-2.95414	0.68932	H	2.95265	5.85444	2.10747
C	-5.38622	-3.35279	1.17392	H	4.18519	4.64103	1.75526
C	-3.70308	2.52542	-0.47761	H	2.87738	4.26101	2.8762
C	-3.64347	2.91612	-1.97117	H	2.43772	6.09873	-0.38892
C	-2.26513	2.53321	0.05008	H	2.01615	4.67181	-1.34943
C	-4.43818	3.63201	0.31559	H	3.6682	4.89316	-0.77236
C	2.24867	4.26894	0.78443	H	0.45194	4.07717	2.02733
C	3.12004	4.78491	1.94811	H	0.11683	4.28231	0.30377
C	2.61702	5.02585	-0.50785	H	0.65796	5.65448	1.26644
C	0.783	4.57928	1.11494	H	10.29194	-0.37738	-2.84623
C	8.94505	-0.13044	-1.14766	H	8.60331	-0.10655	-3.30541
C	9.25459	-0.60435	-2.58249	H	9.1128	-1.68123	-2.69517
C	9.87847	-0.85491	-0.15619	H	9.7518	-1.93882	-0.19673
C	9.23923	1.37471	-1.06782	H	9.67882	-0.5359	0.86995
H	4.21011	-3.75995	0.7539	H	10.92574	-0.63426	-0.3836
H	9.06175	1.77151	-0.06489	H	10.28801	1.55991	-1.31286
H	8.6323	1.94676	-1.77438				

PCZ-s-^{F}XylB

Element	Coordinates (angstroms)			Element	Coordinates (angstroms)		
	X	Y	Z		X	Y	Z
F	4.07232	-2.57483	0.48054	C	2.51119	-0.70409	-3.70682
N	-2.81431	-1.32953	-0.04331	H	3.08681	-0.64581	-4.62449
F	5.28675	-2.59208	-1.31927	C	4.56239	0.18358	0.17461
F	6.1934	-3.0232	0.60109	F	3.45538	2.81628	1.58961
F	2.8603	2.36378	-0.44717	C	-0.28144	-4.69846	-0.10411
C	-2.24625	-0.06292	-0.17558	H	0.38286	-5.55511	-0.09934
C	-0.89756	0.22628	-0.22346	C	-2.50303	-3.76386	-0.1575
C	0.11909	-0.90786	-0.0934	H	-3.56607	-3.91658	-0.24582
C	-3.23993	0.92576	-0.22236	C	-5.25259	-2.06004	0.27258
C	1.0173	-0.85422	-1.33487	H	-5.08691	-3.11233	0.44554
C	-0.58362	-2.28335	-0.07477	C	-6.55211	-1.57033	0.32536
C	0.82712	-0.70896	1.25194	H	-7.34783	-2.28406	0.50624
C	-1.98331	-2.46368	-0.08146	C	5.59382	-0.77112	0.16542
C	-4.50146	0.22479	-0.08751	C	-1.6617	-4.86726	-0.16335
C	0.06241	-0.85758	2.41303	H	-2.09257	-5.86114	-0.22081

H	-0.9828	-1.13528	2.33732	C	4.96308	1.52862	0.28081
C	2.18195	-0.34539	1.35353	C	-1.00698	4.04665	-0.50009
C	-4.2096	-1.16111	0.0417	C	5.28541	-2.23568	-0.01426
C	2.38402	-0.53056	-1.2781	B	3.03351	-0.2338	0.08104
C	-0.54481	1.56487	-0.33628	C	3.93394	2.62861	0.33889
H	0.50781	1.81349	-0.36356	C	6.93821	-0.4113	0.26245
F	4.42974	3.81483	-0.06817	H	7.6998	-1.18128	0.25949
C	0.62492	-0.65229	3.6644	C	7.29614	0.92505	0.36747
H	0.01391	-0.77241	4.55324	H	8.33944	1.20816	0.44216
C	-5.81804	0.68198	-0.03261	C	6.30426	1.8969	0.37337
H	-6.00189	1.74367	-0.13731	H	6.56862	2.94435	0.44535
C	-6.87063	-0.20854	0.16513	C	-8.49058	1.75367	0.03574
C	0.23696	-3.41163	-0.07413	H	-8.10944	2.08091	-0.93504
H	1.31175	-3.26494	-0.05906	H	-7.97206	2.3187	0.81463
C	1.97008	-0.29357	3.78237	H	-9.54775	2.02682	0.08214
H	2.41005	-0.13403	4.76104	C	-9.13728	-0.47129	-0.88199
C	-2.85787	2.26485	-0.33887	H	-10.187	-0.16369	-0.85496
H	-3.6182	3.03426	-0.37272	H	-9.1074	-1.55759	-0.7742
C	0.41598	-1.09859	-2.57338	H	-8.73596	-0.22479	-1.86829
H	-0.63874	-1.34613	-2.61712	C	-8.92891	-0.13292	1.6041
C	-1.50163	2.59752	-0.39781	H	-8.37606	0.35607	2.41022
C	3.11059	-0.45806	-2.48423	H	-8.89532	-1.20938	1.78475
H	4.1642	-0.20359	-2.44862	H	-9.97489	0.18172	1.66895
C	2.73127	-0.14521	2.63644	C	-0.18109	4.39041	0.75746
H	3.77671	0.13041	2.72289	H	0.1784	5.42293	0.70851
C	1.15238	-1.02769	-3.7466	H	0.68925	3.74098	0.86316
H	0.66714	-1.22269	-4.69755	H	-0.7868	4.28373	1.66115
C	-8.33644	0.23803	0.22914	C	-2.16427	5.04996	-0.60593
C	-0.11787	4.2029	-1.75125	H	-2.80974	5.02349	0.27597
H	0.22436	5.23776	-1.84791	H	-2.78296	4.86559	-1.48834
H	-0.67044	3.94146	-2.65748	H	-1.76714	6.06474	-0.68894
H	0.76731	3.56702	-1.70404	□	□	□	□

PBA-s-Mes*B

Element	Coordinates (angstroms)			Element	Coordinates (angstroms)		
	X	Y	Z		X	Y	Z
C	-0.05975	0.34538	4.16612	C	8.32911	0.26705	0.37543
C	1.3243	0.20773	4.02677	H	-0.50399	0.42031	5.1535
C	1.86785	0.11836	2.7568	H	1.96223	0.17162	4.90377
C	1.06251	0.16123	1.60054	H	2.93923	0.00175	2.63377
C	-0.32706	0.28127	1.75606	H	-1.9453	0.47379	3.16008
C	-0.87167	0.37806	3.04279	H	2.27041	-0.17919	-2.47309
C	-0.67815	0.14902	-0.81749	H	0.74974	-0.21371	-4.4292
C	0.70961	0.02883	-1.01415	H	-1.70881	-0.01493	-4.0582
C	1.19844	-0.09795	-2.32887	H	-2.59853	0.21004	-1.80318

C	0.35174	-0.11411	-3.42465	H	-3.99457	5.01827	0.71871
C	-1.02366	-6.40E-04	-3.21658	H	-1.54811	4.94573	1.20992
C	-1.52821	0.12993	-1.93033	H	-0.37388	2.78106	1.19884
B	1.68931	0.04041	0.18751	H	-5.19673	2.93092	0.1821
C	-3.4533	4.07884	0.68272	H	-0.78213	-2.24784	1.42354
C	-2.08822	4.03811	0.96449	H	-2.31658	-4.17631	1.58538
C	-1.42565	2.81872	0.94758	H	-4.71538	-3.89122	1.0937
C	-2.08383	1.63046	0.62145	H	-7.84121	-1.51637	-1.74418
C	-3.45026	1.68526	0.31852	H	-7.96433	0.06854	-3.61838
C	-4.13156	2.90983	0.37573	H	-6.28911	1.902	-3.80064
C	-1.31493	0.29771	0.58105	H	-4.50947	2.11473	-2.10537
C	-2.29321	-0.87387	0.7756	H	-5.99642	0.19937	1.79859
C	-3.65152	-0.72986	0.48583	H	-6.46262	-1.33547	2.54197
N	-4.15363	0.50204	0.01736	H	-7.61088	-0.46149	1.50632
C	-1.83091	-2.12474	1.18705	H	-6.55193	-3.37571	-0.59944
C	-2.69449	-3.20611	1.28187	H	-7.9275	-2.5345	0.13322
C	-4.04988	-3.04271	0.99896	H	-6.79599	-3.39303	1.15411
C	-4.55203	-1.80212	0.62031	H	6.05862	1.81279	-0.42959
C	-6.03585	-1.50186	0.40588	H	5.69288	-2.39861	-0.54752
C	-6.13859	-0.59239	-0.8175	H	3.9803	4.52741	-0.75695
C	-5.201	0.44839	-0.93167	H	4.52773	3.23235	-1.82776
C	-7.11553	-0.71522	-1.80474	H	5.45222	3.65877	-0.38091
C	-7.18738	0.17901	-2.86986	H	4.71119	2.78007	1.88897
C	-6.25493	1.2074	-2.968	H	3.01944	2.34138	2.14223
C	-5.25587	1.33645	-2.01114	H	3.43727	3.98863	1.66325
C	-6.558	-0.72214	1.64231	H	1.88151	3.83781	-0.30775
C	-6.8706	-2.77677	0.25673	H	1.41434	2.22778	0.16454
C	3.25041	-0.08199	-0.02854	H	1.98853	2.51448	-1.47485
C	4.07304	1.08273	-0.14321	H	3.45039	-4.65249	0.91254
C	5.44039	0.93026	-0.36506	H	4.13821	-3.2865	1.79978
C	6.05731	-0.30833	-0.52058	H	4.97068	-3.94858	0.39203
C	5.24726	-1.42522	-0.41628	H	1.04783	-2.17702	-0.0971
C	3.87147	-1.35288	-0.15238	H	1.73163	-2.38778	1.52547
C	3.58148	2.54673	0.0323	H	1.3798	-3.77857	0.50391
C	4.44461	3.53851	-0.782	H	2.66194	-4.31795	-1.50743
C	3.69297	2.93326	1.52239	H	4.07787	-3.3706	-1.98383
C	2.13825	2.78156	-0.42839	H	2.45923	-2.68444	-2.15194
C	3.17161	-2.74033	-0.08677	H	8.95811	0.32757	-2.31444
C	3.9898	-3.7078	0.80209	H	7.59868	1.4211	-2.04227
C	1.75457	-2.751	0.49844	H	7.3529	-0.07357	-2.9457
C	3.09131	-3.31115	-1.51906	H	9.13401	-1.83794	-1.13402
C	7.56398	-0.38522	-0.7941	H	7.57302	-2.34457	-1.77634
C	7.88581	0.36918	-2.10019	H	7.88327	-2.41613	-0.03464
C	8.05805	-1.83173	-0.94168	H	9.4085	0.22298	0.20109

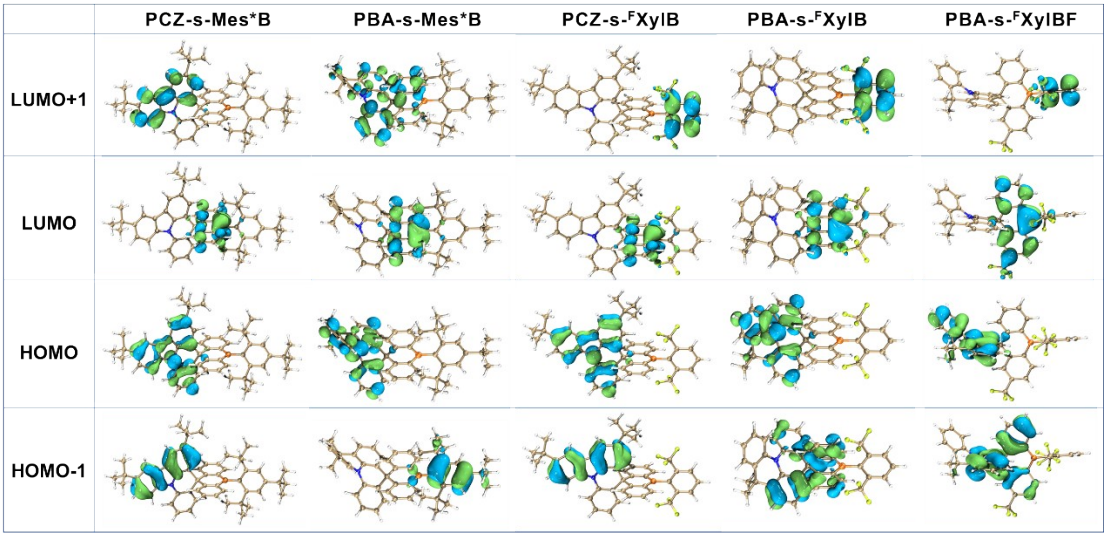
H	8.0564	1.31666	0.50359	H	8.11527	-0.24855	1.31526

PBA-s-^{F}XylB

Element	Coordinates (angstroms)			Element	Coordinates (angstroms)		
	X	Y	Z		X	Y	Z
F	-3.03008	2.38846	-0.52744	H	3.88121	2.12732	-2.00782
F	-2.65562	-2.65561	0.29454	C	6.19663	-2.56889	0.75826
F	-3.33417	-3.09206	-1.72184	H	7.24897	-2.27995	0.74489
F	-5.03059	3.18308	-0.8147	H	6.00249	-3.203	-0.10976
F	-4.37318	2.59557	1.16483	H	6.04932	-3.16602	1.65968
F	-4.45291	-3.83286	-0.02068	C	-3.75991	-2.7684	-0.48015
N	3.38362	0.57679	0.1369	C	-2.2625	0.28028	3.77526
C	2.59198	1.73276	0.29554	H	-2.93531	0.28822	4.62626
C	-0.0608	0.02388	-0.97418	C	-0.88651	0.43709	3.96293
C	2.88601	-0.66662	0.58114	H	-0.48506	0.56838	4.96265
C	-1.43655	-0.13553	-1.22389	C	6.7092	0.30125	-2.41872
C	1.20516	1.62246	0.44135	H	7.56408	0.20418	-3.07897
C	0.50739	0.25241	0.43556	C	-5.96146	-1.65409	-0.70352
C	1.51362	-0.8712	0.7231	H	-6.38469	-2.64414	-0.82013
C	4.52212	0.53952	-0.70366	C	-6.77749	-0.53317	-0.76878
C	5.48818	-0.4513	-0.45663	H	-7.84149	-0.64029	-0.94396
C	-4.59211	-1.51168	-0.48113	C	-6.21726	0.72636	-0.60556
C	-0.51797	0.25552	1.57542	H	-6.83982	1.61099	-0.6578
C	-1.89892	0.10521	1.37071	C	-4.32065	2.25158	-0.14292
C	1.05846	-2.14128	1.08059	C	3.81127	-1.69638	0.83429
H	-0.00763	-2.31182	1.17631	C	5.29483	-1.33173	0.77699
C	3.19894	2.99642	0.355	C	-0.02736	0.42347	2.87456
H	4.27755	3.06773	0.2914	H	1.03897	0.54211	3.03044
C	3.32355	-2.95474	1.16938	C	0.83999	-0.01306	-2.04407
H	4.01069	-3.77094	1.35253	H	1.90205	0.09799	-1.86698
C	-4.84796	0.8595	-0.37824	C	-3.98982	-0.25256	-0.31233
C	0.44598	2.78754	0.5788	C	5.6431	-0.49746	2.03851
H	-0.63011	2.70224	0.67343	H	5.02884	0.40097	2.10439
C	-2.75371	0.11708	2.49222	H	6.6924	-0.19223	2.01033
H	-3.82081	-0.00377	2.34104	H	5.47579	-1.09153	2.9406
C	-1.86588	-0.31412	-2.55458	C	1.04069	4.04084	0.58948
H	-2.92559	-0.43235	-2.75283	H	0.42947	4.93102	0.68716
C	0.3931	-0.19712	-3.3448	C	5.74524	1.27752	-2.6517
H	1.11255	-0.22434	-4.15693	H	5.83299	1.94354	-3.50358
C	1.95217	-3.1811	1.28728	C	-0.96997	-0.34589	-3.60878
H	1.58573	-4.16775	1.54853	H	-1.31956	-0.48716	-4.62597
C	6.56707	-0.5593	-1.33325	B	-2.43171	-0.09366	-0.05627
H	7.31695	-1.32257	-1.16825	H	2.91411	5.10998	0.53078
C	2.42897	4.14045	0.49143	C	4.64789	1.39026	-1.80701

PBA-s-^{F}XylBF

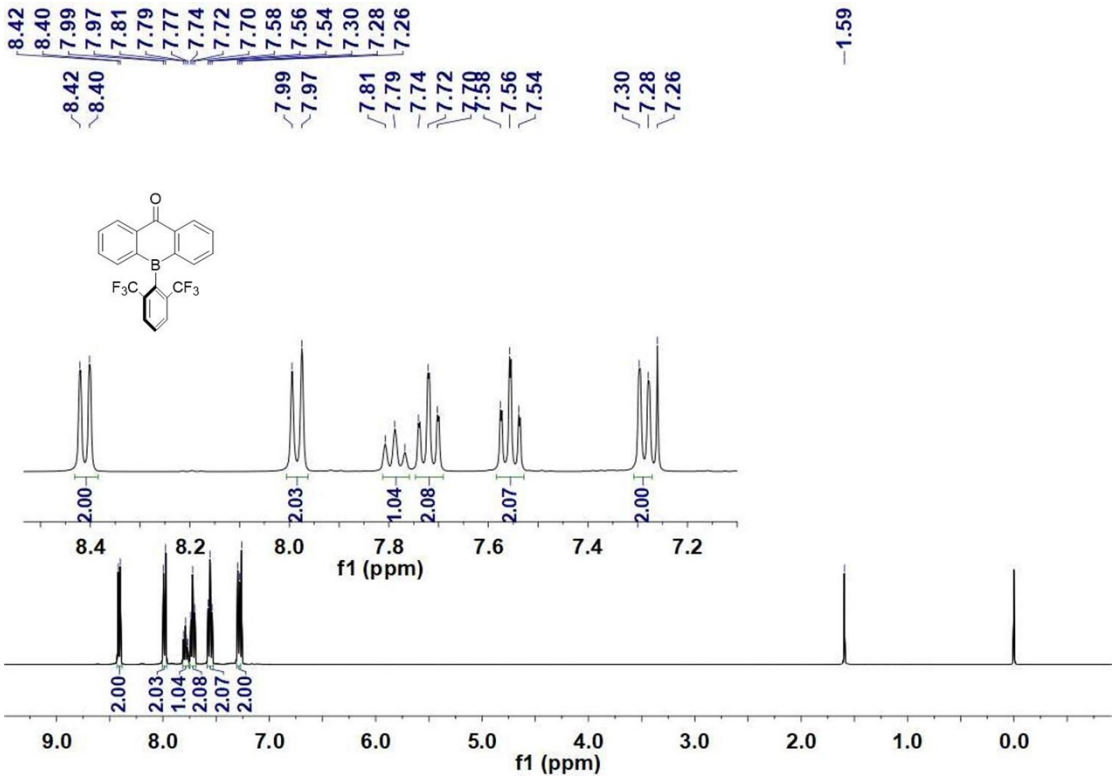
Element	Coordinates (angstroms)			Element	Coordinates (angstroms)		
	X	Y	Z		X	Y	Z
B	2.42862	-0.5933	-0.03636	C	4.30849	-0.15232	2.26072
C	1.43037	-1.74556	0.14494	F	5.03539	-0.56464	3.3199
C	0.05325	-1.46787	0.26046	F	3.02538	-0.53731	2.48359
C	-0.5156	-0.04153	0.21112	F	4.31467	1.2005	2.2813
C	0.50941	1.07749	-0.00674	C	3.73712	-1.56099	-2.556
C	1.89103	0.85112	-0.11448	F	3.24909	-2.82119	-2.57091
C	-1.51783	0.02658	-0.95018	F	2.66766	-0.72602	-2.61599
C	-2.89507	-0.03552	-0.72473	F	4.43287	-1.39515	-3.70063
N	-3.40373	-0.2078	0.58112	C	0.32293	4.84833	-0.42949
C	-2.60364	0.14503	1.68743	F	-0.91287	4.97043	0.09918
C	-1.21155	0.23482	1.55393	F	0.23645	5.20964	-1.73142
C	-3.20542	0.45826	2.91828	F	1.11676	5.76117	0.17565
C	-2.42658	0.78676	4.01929	H	-4.28585	0.43628	2.99726
C	-1.03422	0.82747	3.90617	H	-2.90805	1.02068	4.9636
C	-0.44315	0.56548	2.67616	H	-0.41773	1.07349	4.76426
C	-1.05355	0.10275	-2.26681	H	0.63619	0.60847	2.57581
C	-1.94455	0.12197	-3.33213	H	0.01618	0.12571	-2.44712
C	-3.32028	0.09476	-3.09011	H	-1.57323	0.16828	-4.35055
C	-3.8158	0.03221	-1.79001	H	-4.00628	0.13352	-3.92764
C	-4.56547	-1.01131	0.70534	H	-7.38139	-1.74953	-1.03865
C	-5.30059	0.09358	-1.42692	H	-7.67848	-3.32029	0.83482
C	-5.52766	-0.93598	-0.31978	H	-5.95032	-3.44857	2.62785
C	-6.63356	-1.786	-0.25548	H	-3.95296	-1.998	2.51989
C	-6.80343	-2.67935	0.802	H	-6.03595	-1.13031	-3.08651
C	-5.84081	-2.74553	1.80795	H	-6.0291	0.6155	-3.4046
C	-4.7173	-1.92575	1.75586	H	-7.25756	-0.07001	-2.35611
C	-6.20523	-0.14587	-2.64085	H	-5.41429	2.26729	-1.62339
C	-5.60857	1.50713	-0.86055	H	-6.6592	1.56943	-0.56028
C	1.85671	-3.08908	0.22075	H	-4.98885	1.72977	0.01042
C	0.95745	-4.12894	0.39755	H	2.91617	-3.30691	0.13361
C	-0.40665	-3.83722	0.50397	H	1.30465	-5.15593	0.45164
C	-0.85223	-2.52237	0.43737	H	-1.12663	-4.6389	0.63985
C	0.01091	2.38402	-0.09109	H	-1.9136	-2.31896	0.52052
C	0.8714	3.45569	-0.28326	H	-1.05398	2.56174	-0.00191
C	2.25276	3.24897	-0.3967	H	2.91775	4.0932	-0.53994
C	2.74433	1.95825	-0.31213	H	3.81279	1.78999	-0.39311
C	3.98564	-0.86906	-0.14008	H	6.83829	-0.80188	1.75385
C	4.84504	-0.69271	0.96033	H	7.84001	-1.56455	-0.39146
C	6.21636	-0.94239	0.87732	H	6.37599	-1.86893	-2.37942
C	6.77513	-1.37132	-0.32228	C	4.58551	-1.30036	-1.33775
C	5.95654	-1.54635	-1.43347	□	□	□	□



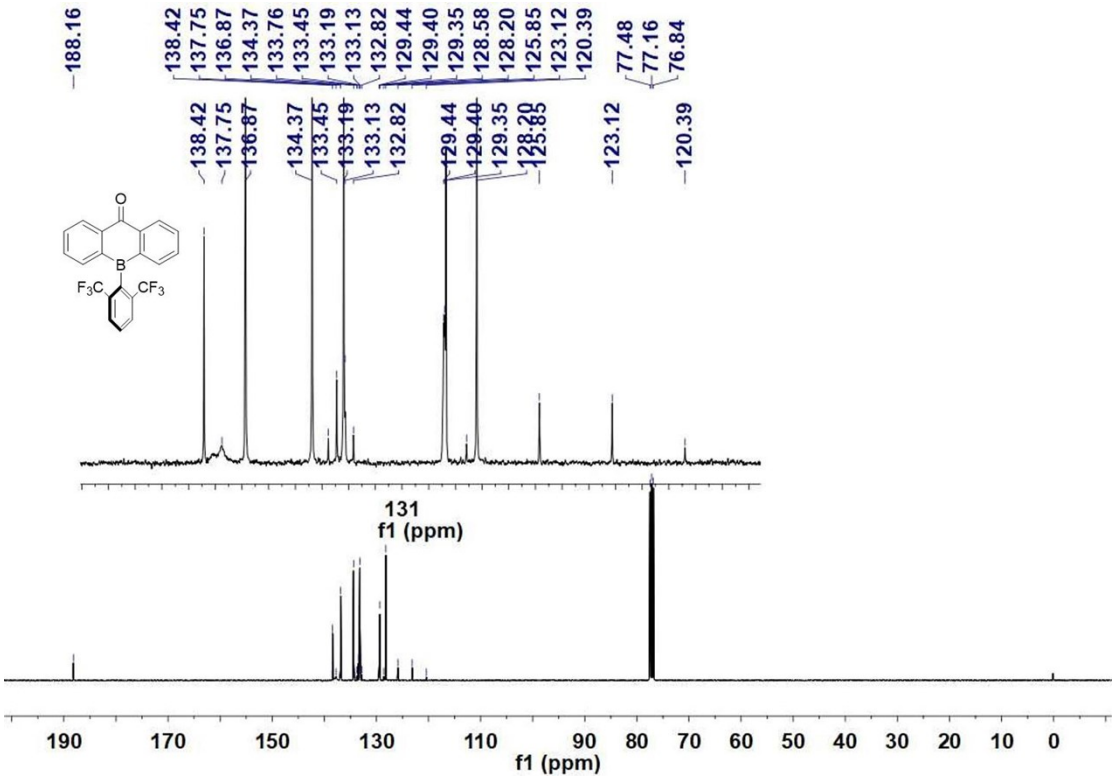
	PCZ-s-Mes*B	PBA-s-Mes*B	PCZ-s-^{F}XylB	PBA-s-^{F}XylB	PBA-s-^{F}XylBF
LUMO+1 /eV	-1.097	-0.824	-1.534	-1.479	-1.629
LUMO /eV	-1.770	-1.745	-1.974	-1.911	-2.245
HOMO /eV	-5.372	-5.282	-5.312	-5.238	-5.333
HOMO-1 /eV	-5.967	-6.180	-5.824	-6.293	-6.462

Figure S13. Plots and energy levels of frontier orbitals of **PCZ-s-Mes*B**, **PCZ-s-^{F}XylB**, **PBA-s-Mes*B**, **PBA-s-^{F}XylB**, **PBA-s-^{F}XylBF**.

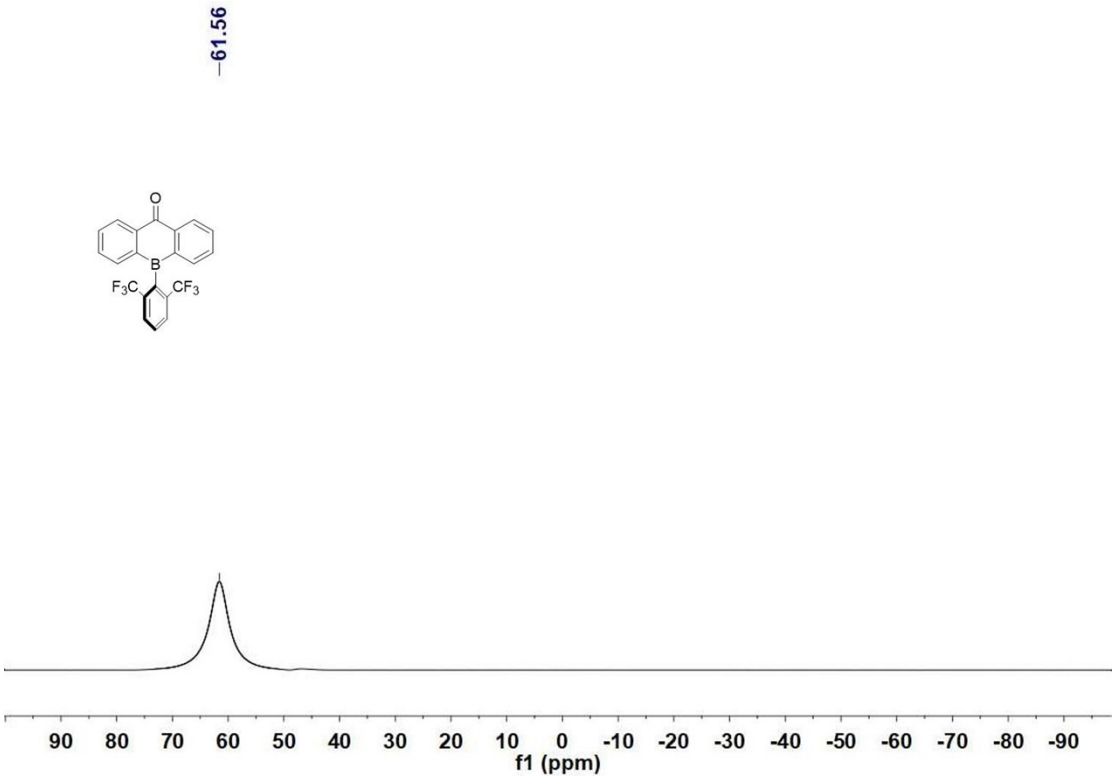
S3.5 Plots of ^{1}H, ^{13}C and ^{11}B NMR spectra



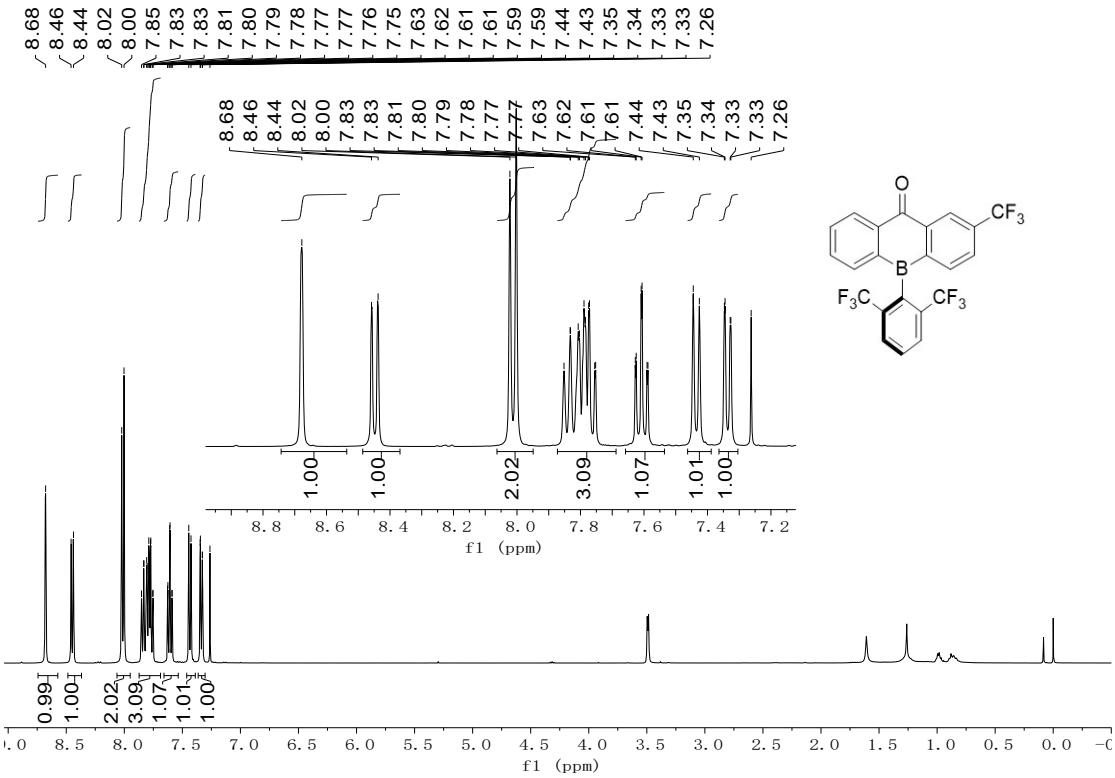
^{1}H NMR spectrum of **^{F}XylB-AQ** in $CDCl_3$.



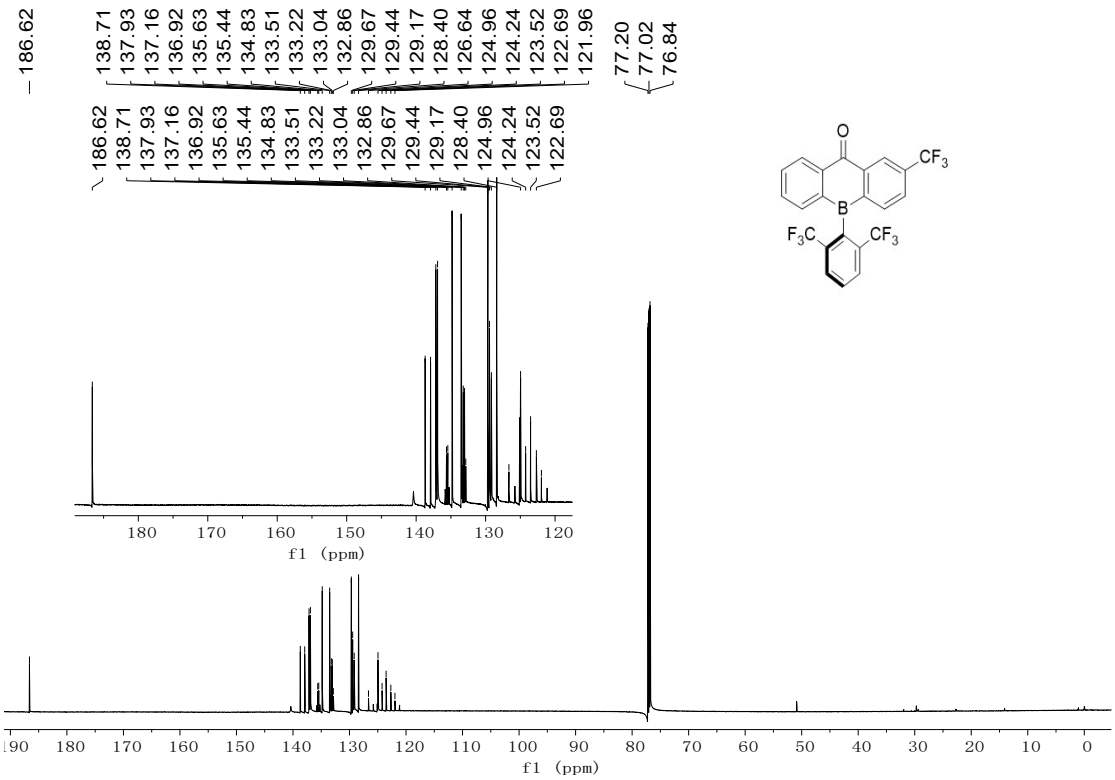
^{13}C NMR spectrum of **^{F}XylB-AQ** in $CDCl_3$



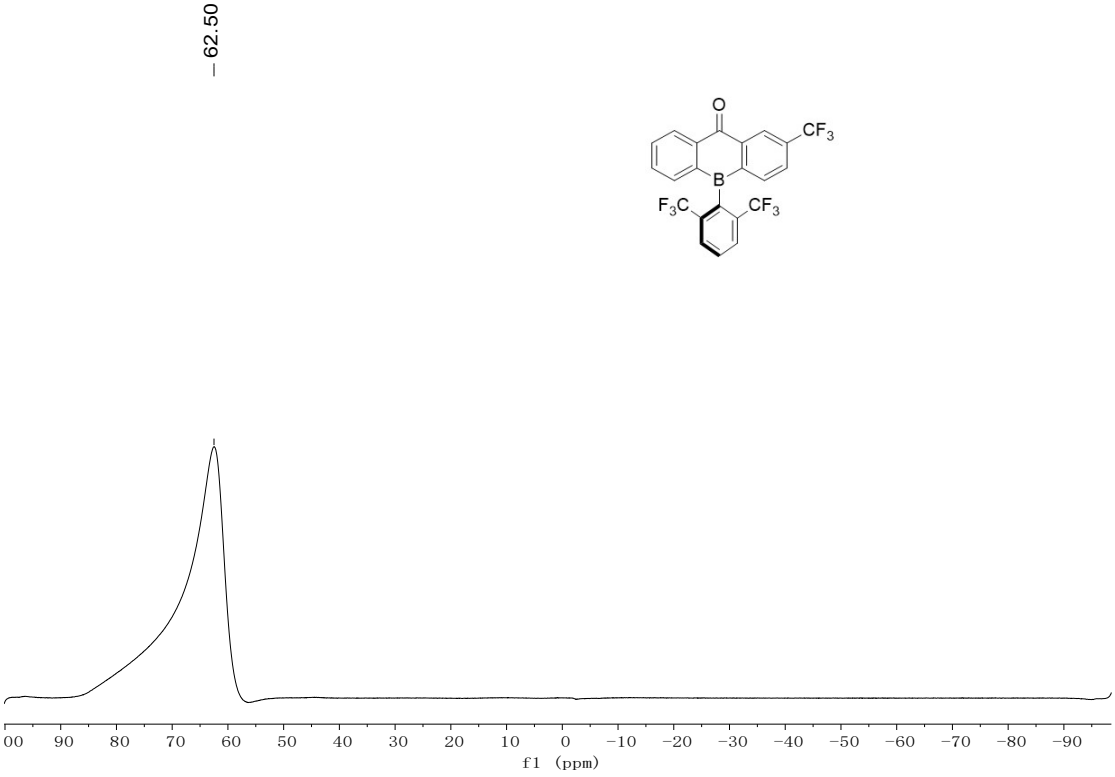
^{11}B NMR spectrum of **^{F}XylB-AQ** in $CDCl_3$.



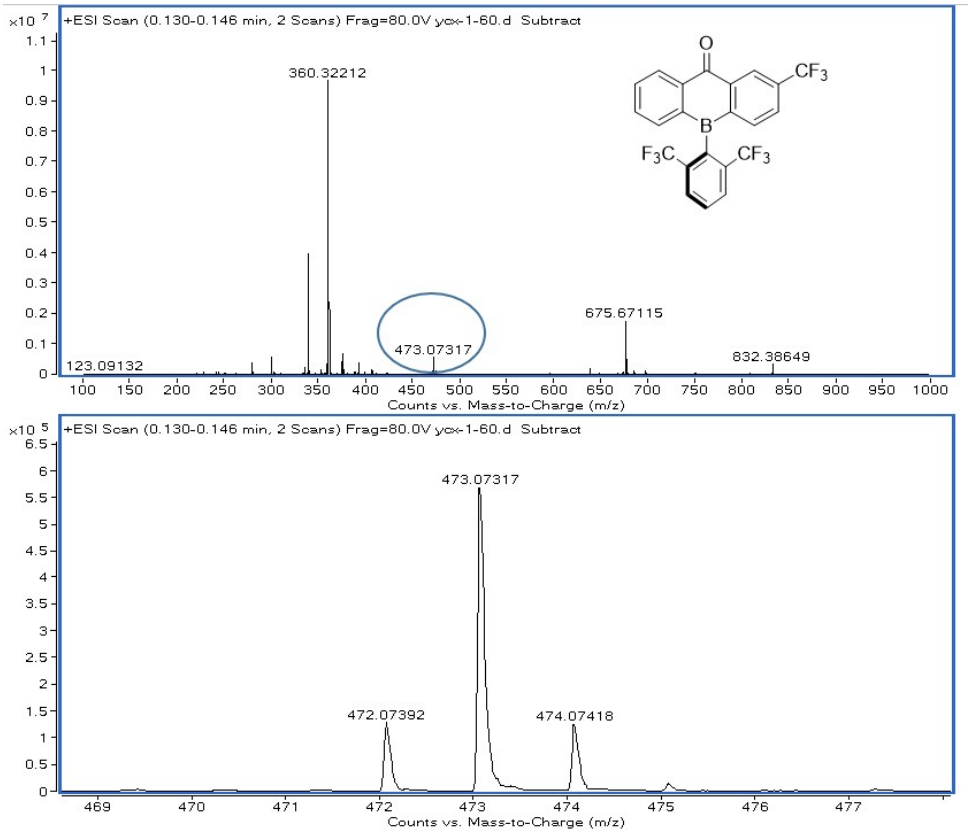
^{1}H NMR spectrum of **^{F}XylB-^{F}AQ** in $CDCl_3$.



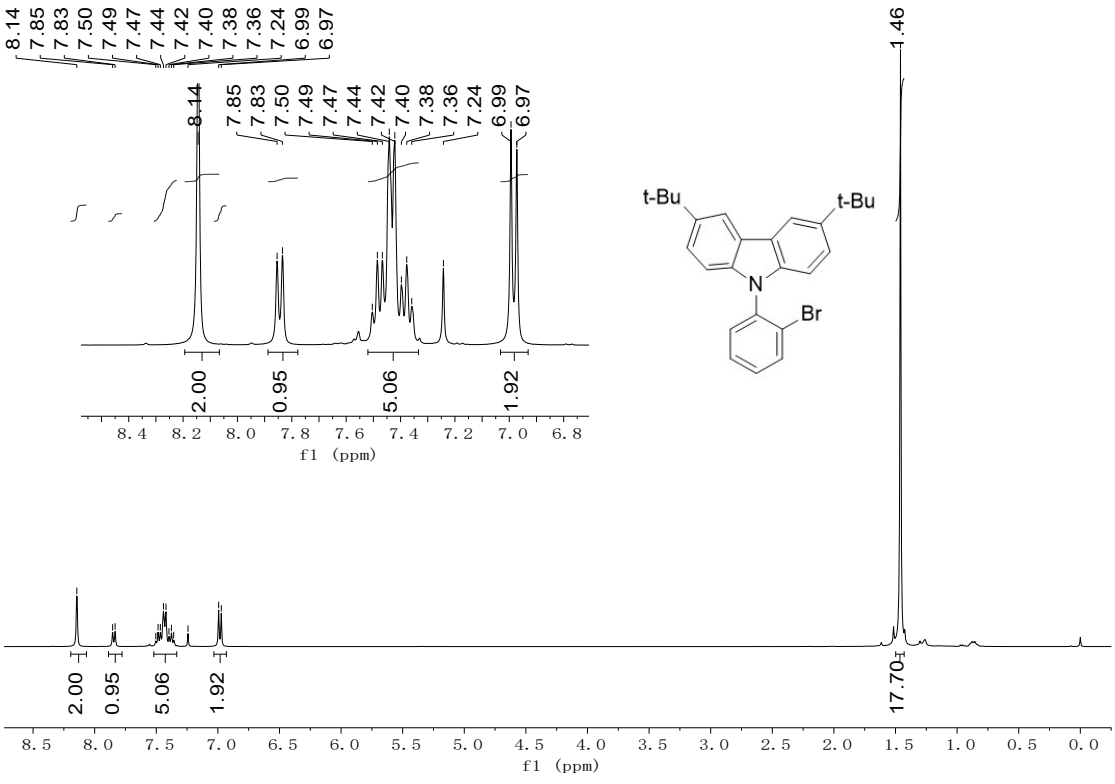
^{13}C NMR spectrum of **^{F}XylB-^{F}AQ** in $CDCl_3$



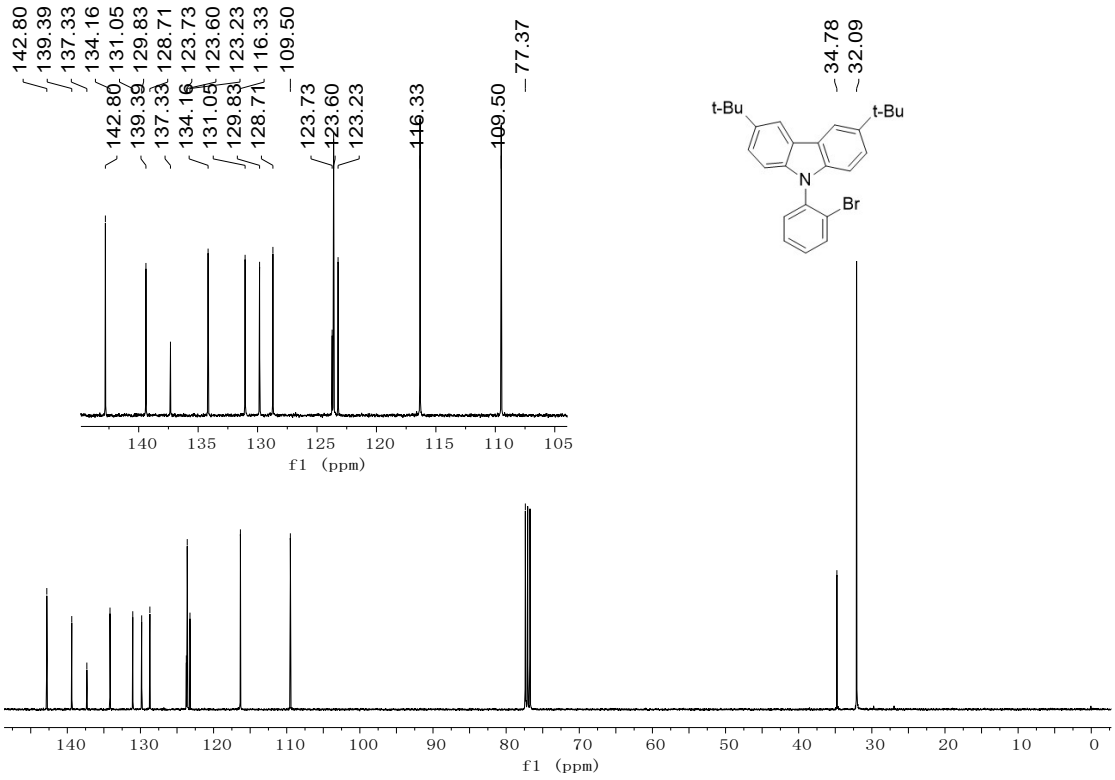
^{11}B NMR spectrum of **^{F}XylB-^{F}AQ** in $CDCl_3$.



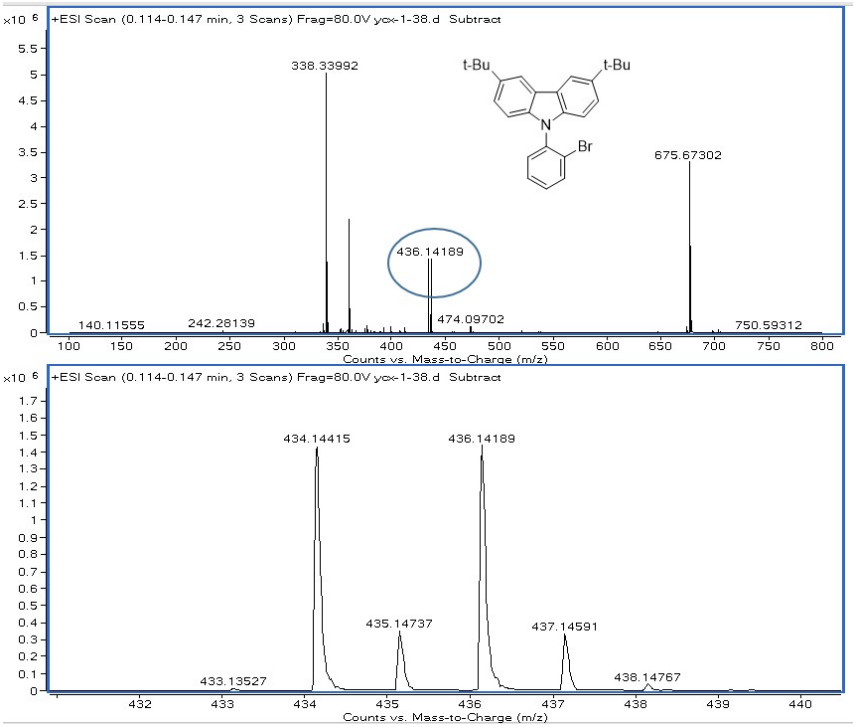
HRMS spectrum of **^{F}XylB-^{F}AQ**.



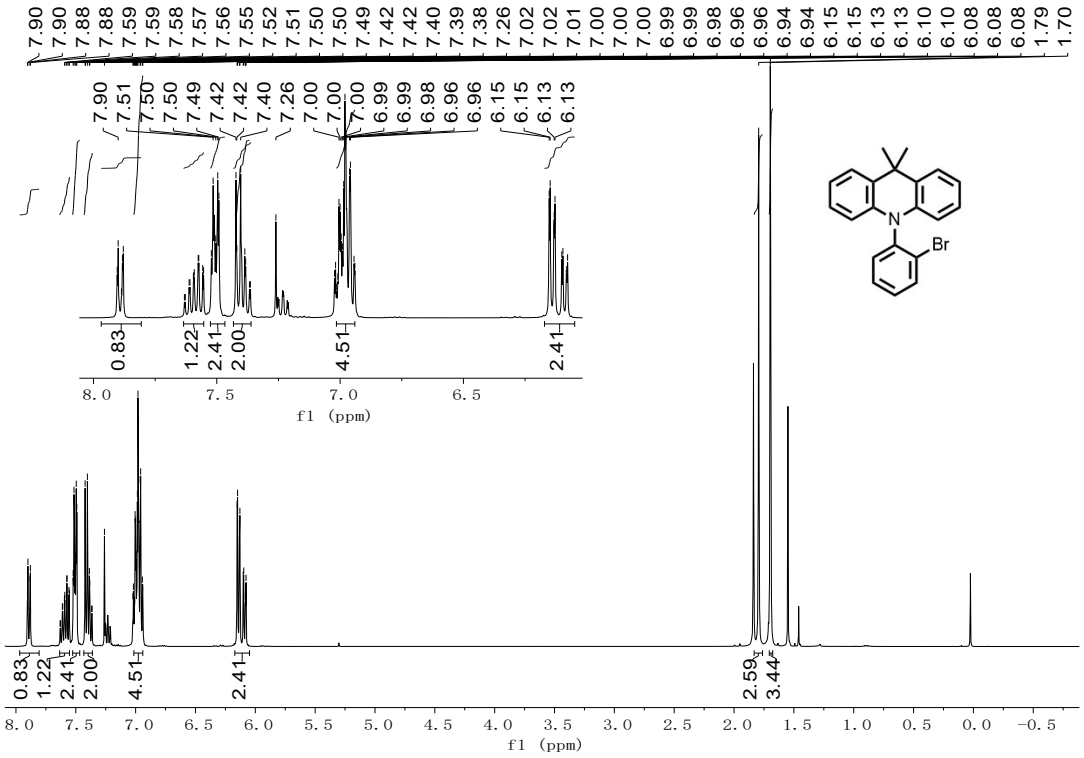
^{1}H NMR spectrum of **PCZ-Br** in $CDCl_3$.



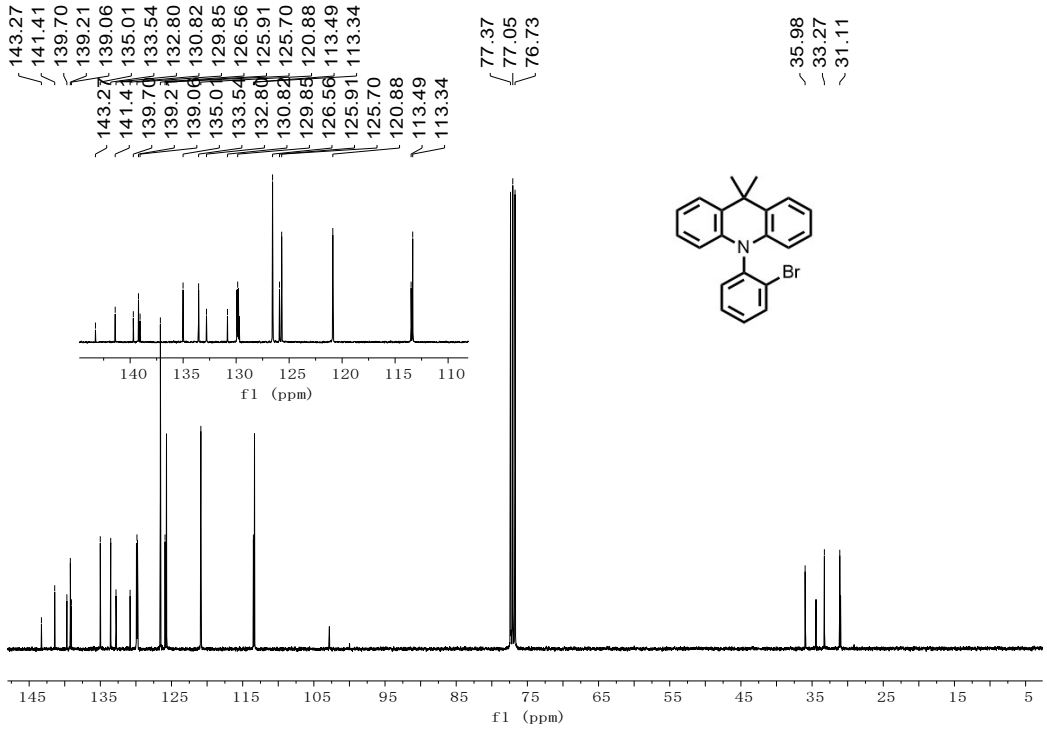
^{13}C NMR spectrum of **PCZ-Br** in $CDCl_3$.



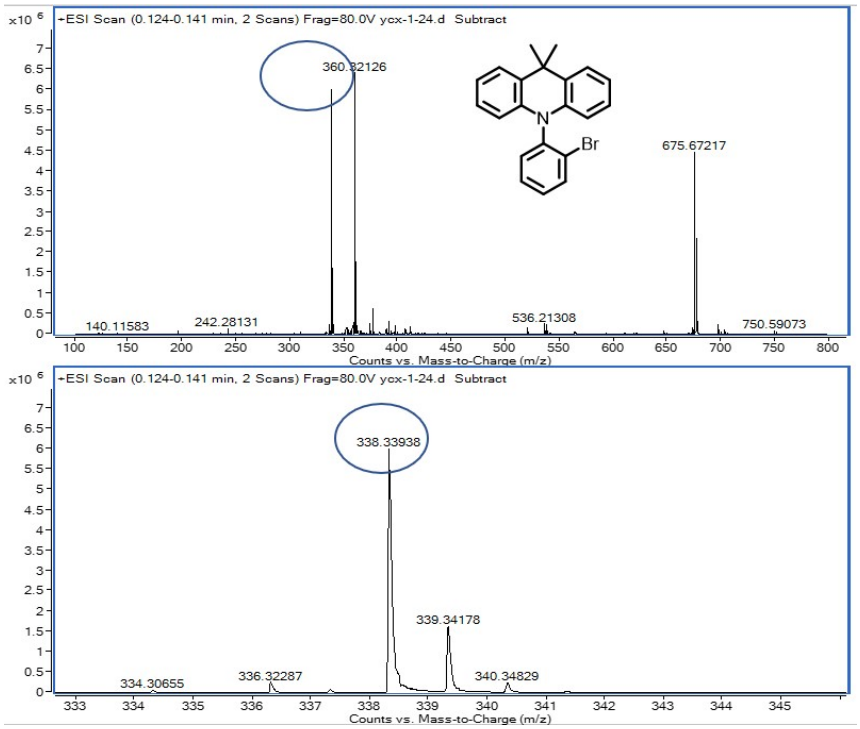
HRMS spectrum of **PCZ-Br**.



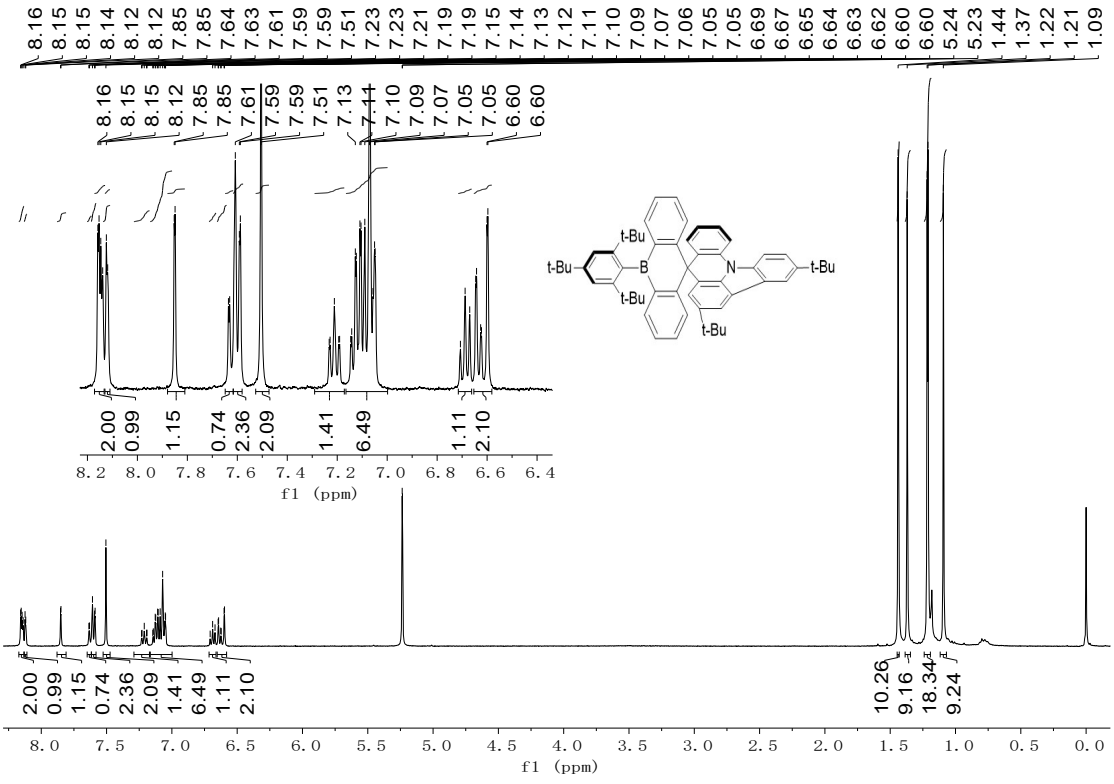
^{1}H NMR spectrum of **PBA-Br** in $CDCl_3$.



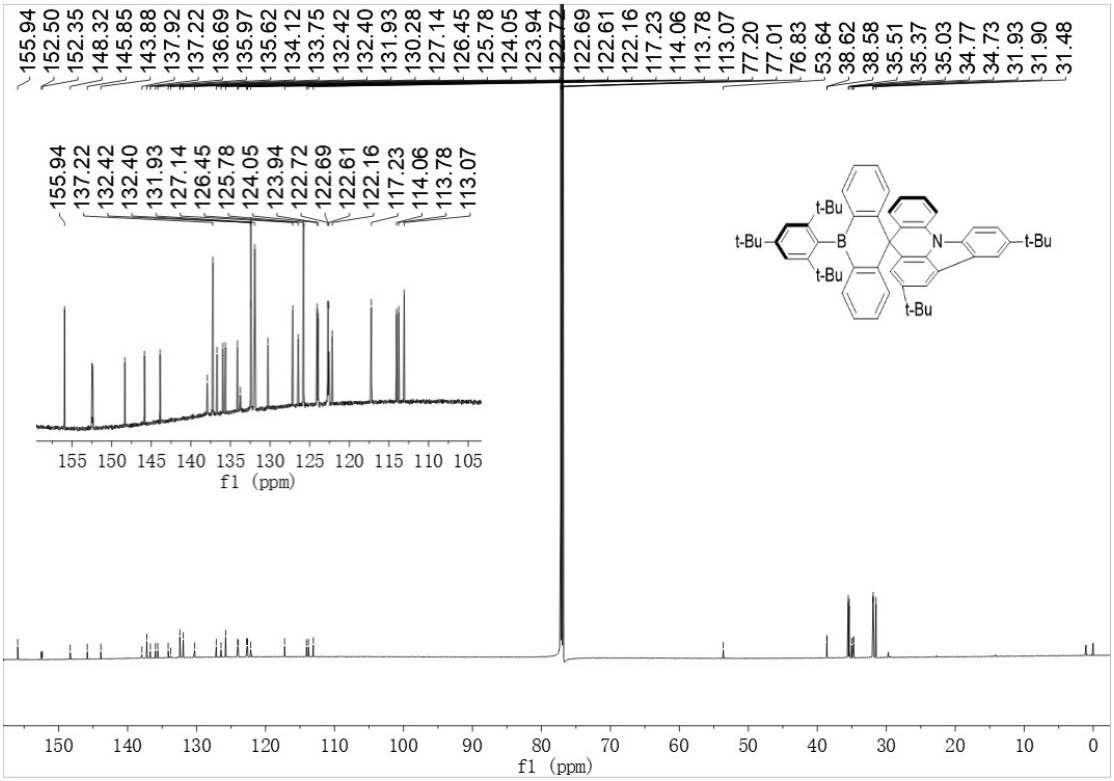
^{13}C NMR spectrum of **PBA-Br** in $CDCl_3$.



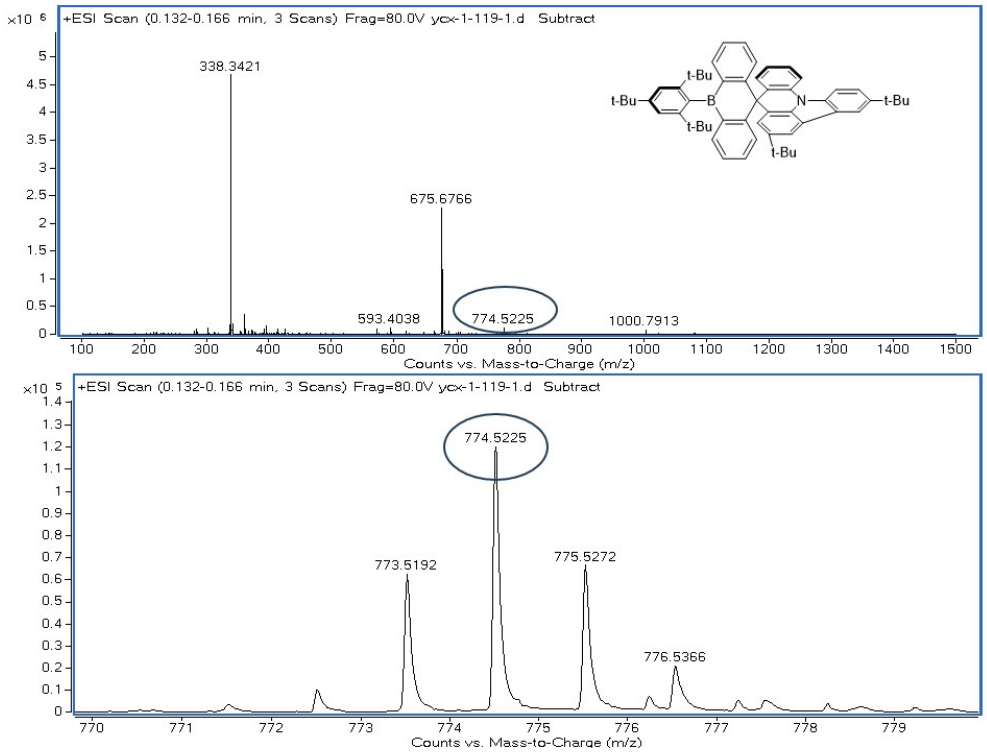
HRMS spectrum of **PBA-Br**.



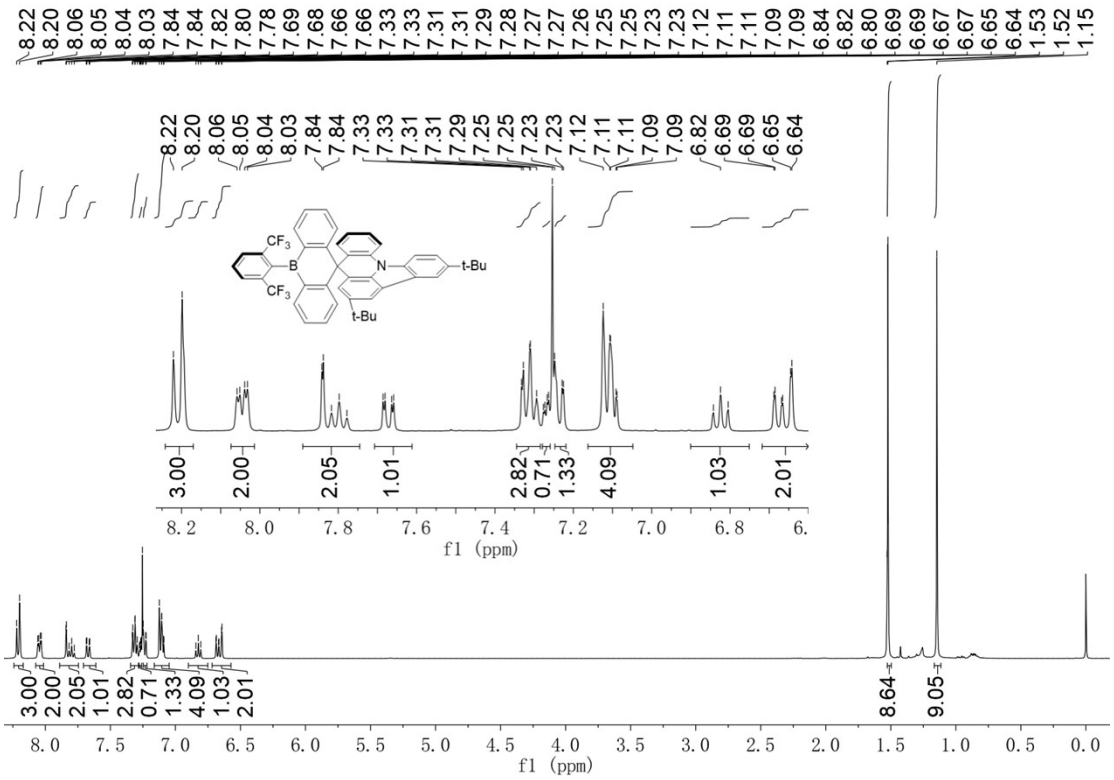
^{1}H NMR spectrum of **PCZ-s-Mes*B** in CD_2Cl_2.



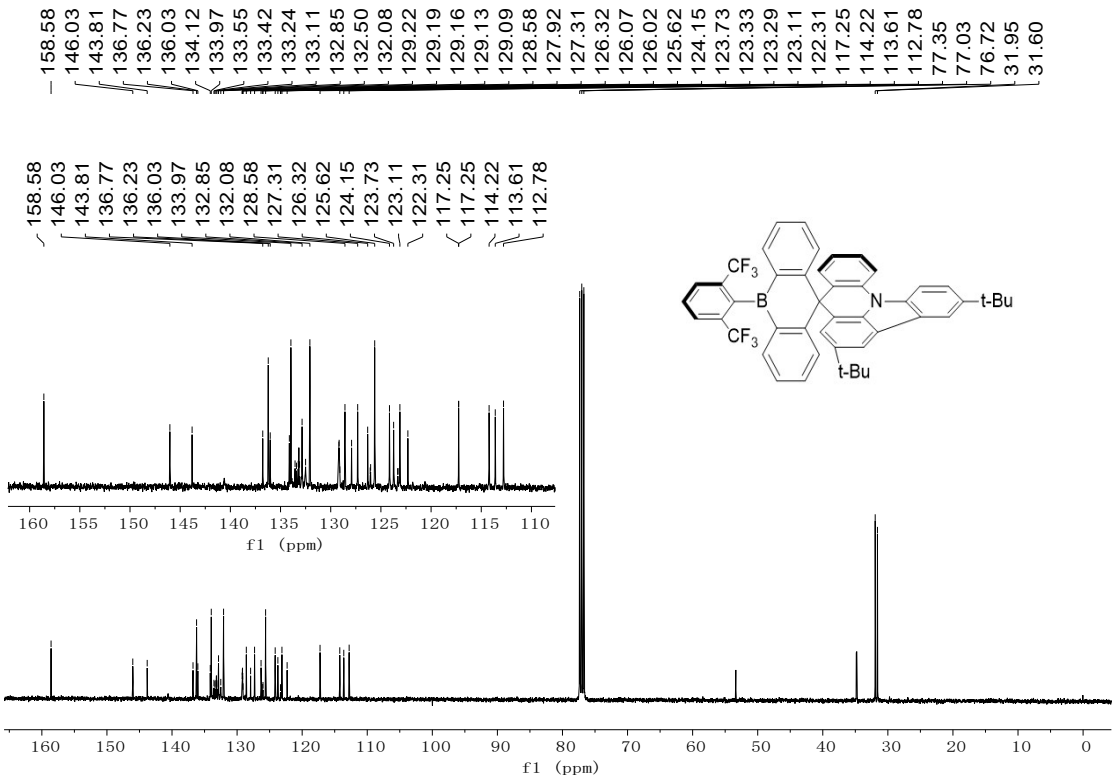
^{13}C NMR spectrum of **PCZ-s-Mes*B** in $CDCl_3$.



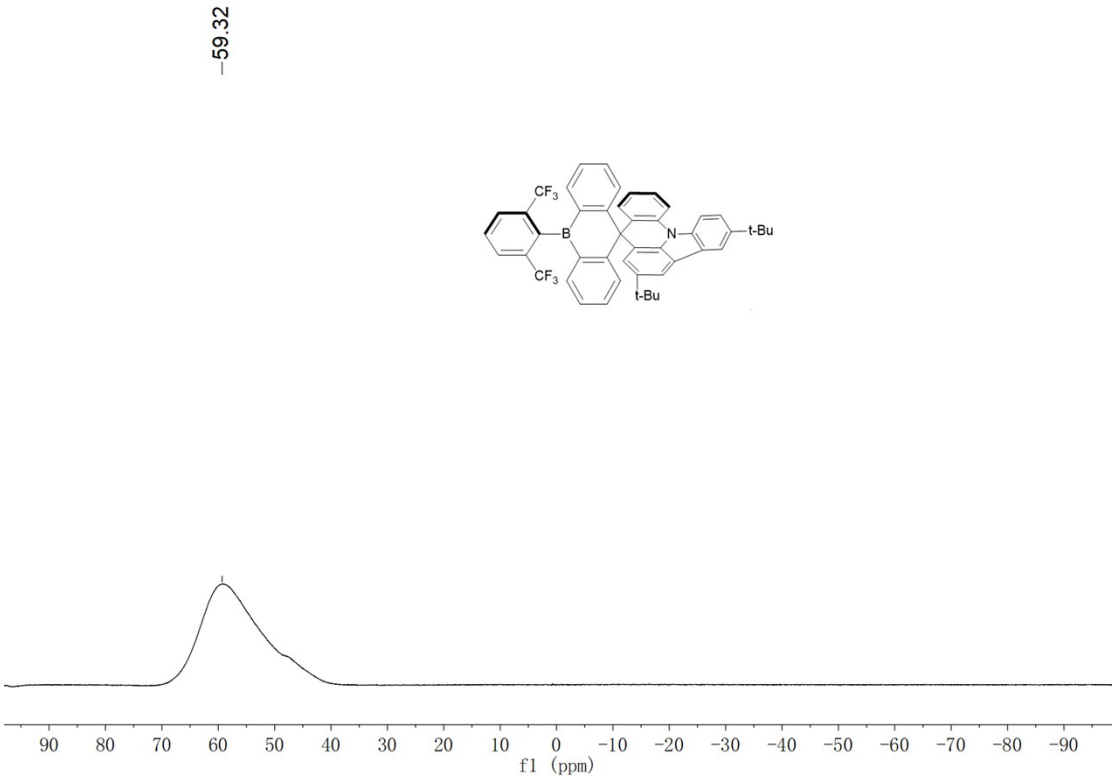
HRMS spectrum of **PCZ-s- Mes*B**.



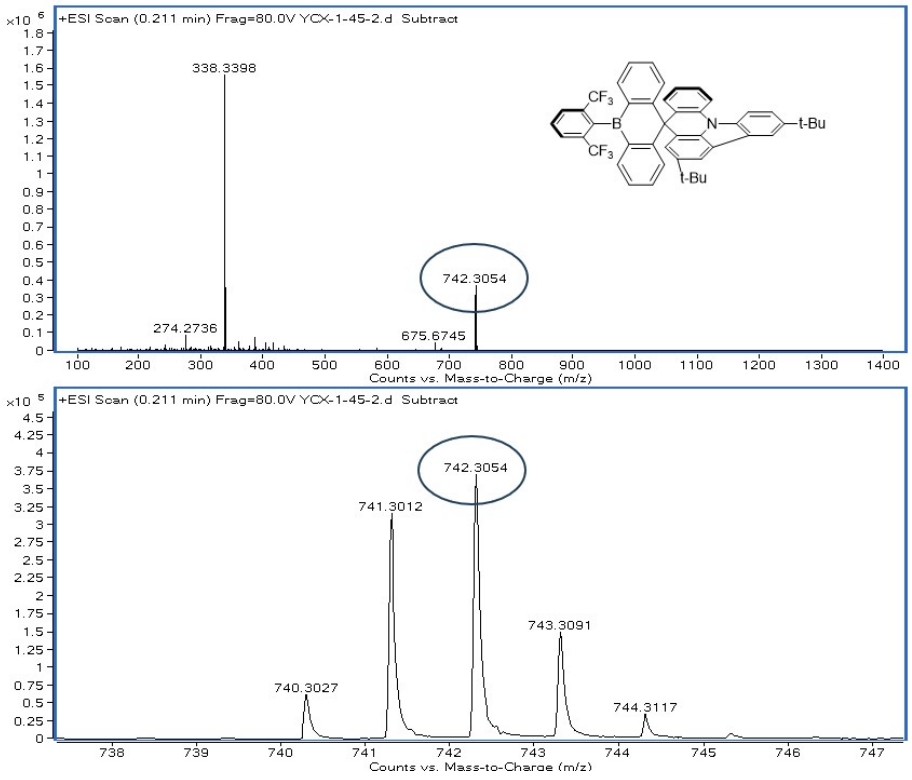
^{1}H NMR spectrum of **PCZ-s-^{F}XylB** in $CDCl_3$.



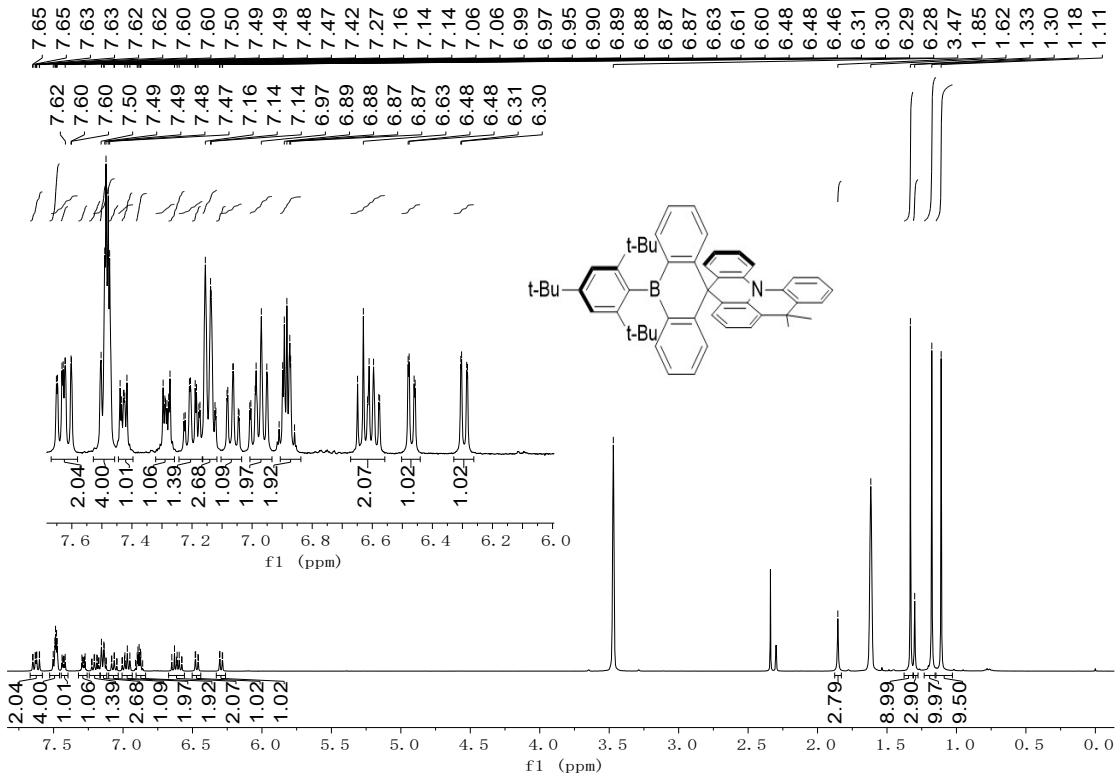
^{13}C NMR spectrum of **PCZ-s-^{F}XylB** in $CDCl_3$.



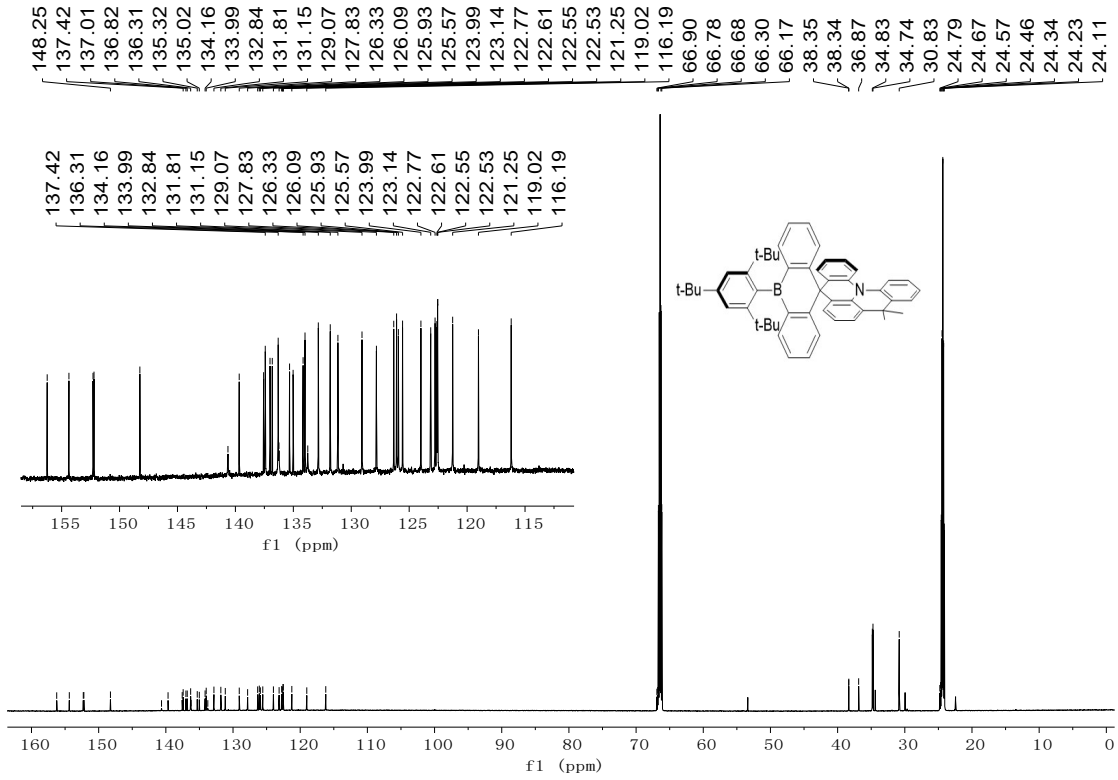
^{11}B NMR spectrum of **PCZ-s-^{F}XylB** in $CDCl_3$.



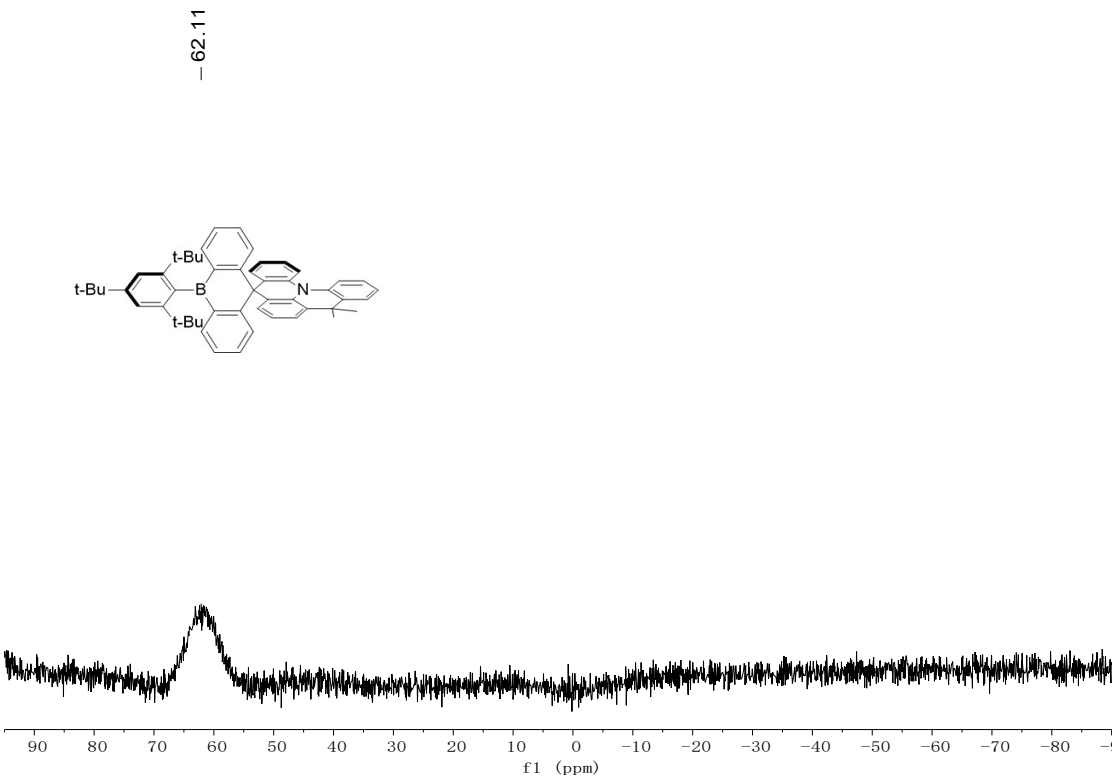
HRMS spectrum of **PCZ-s-^{F}XylB**.



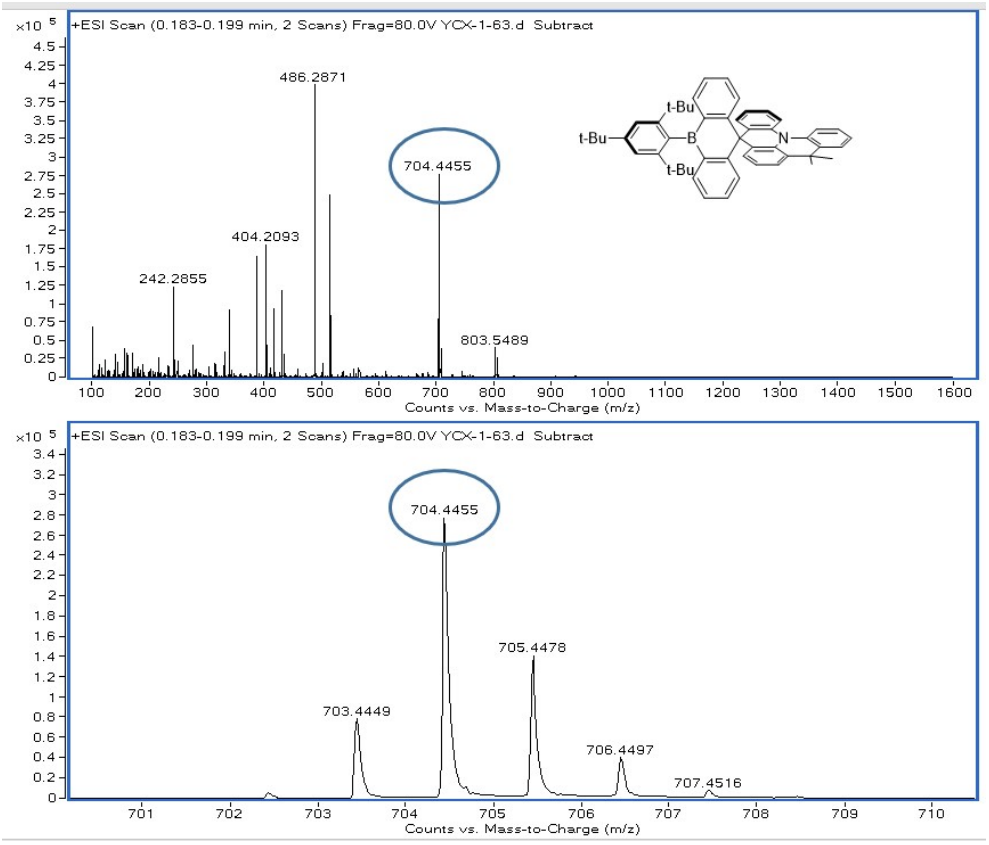
^{1}H NMR spectrum of **PBA-s-Mes*B** in THF-d_8.



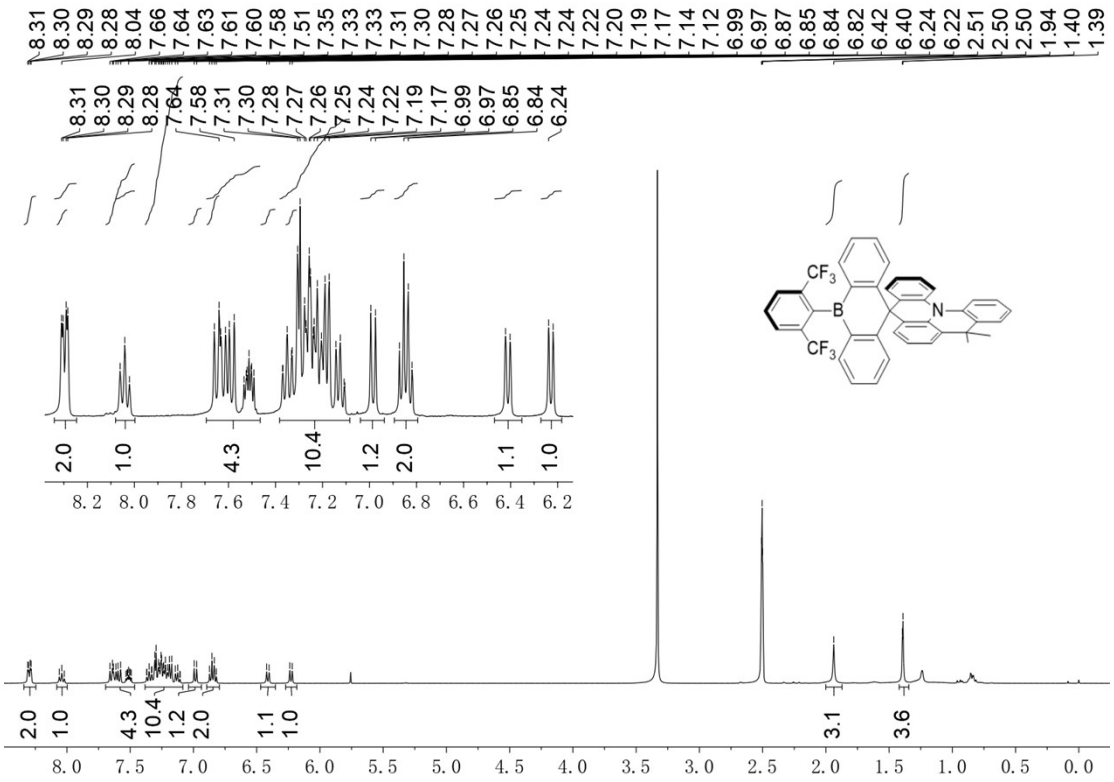
^{13}C NMR spectrum of **PBA-s-Mes*B** in THF-d_8.



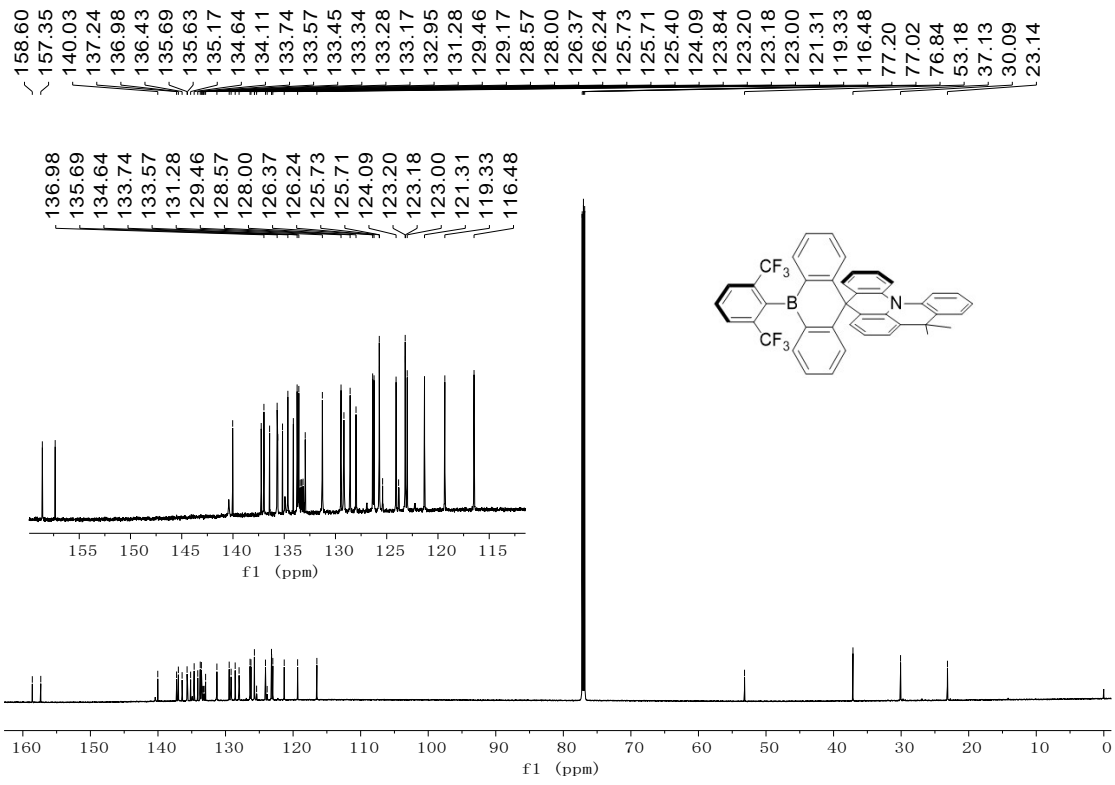
^{11}B NMR spectrum of **PBA-s-Mes*B** in THF-d_8.



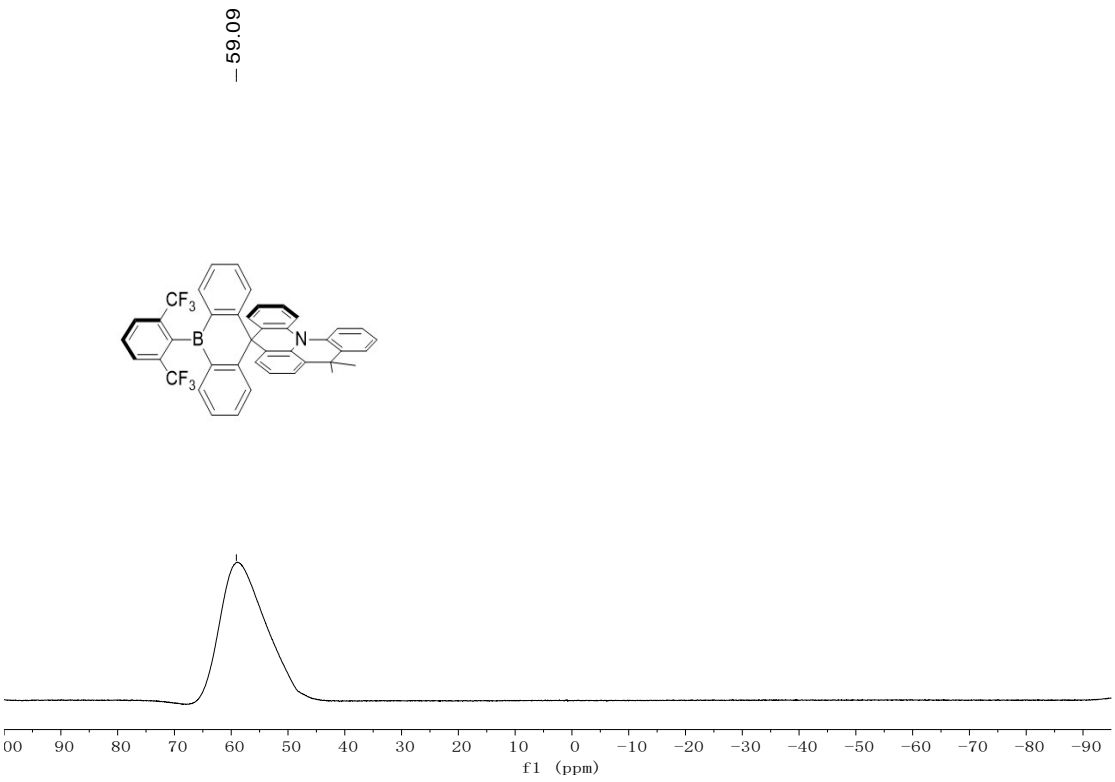
HRMS spectrum of **PBA-s-Mes*B**.



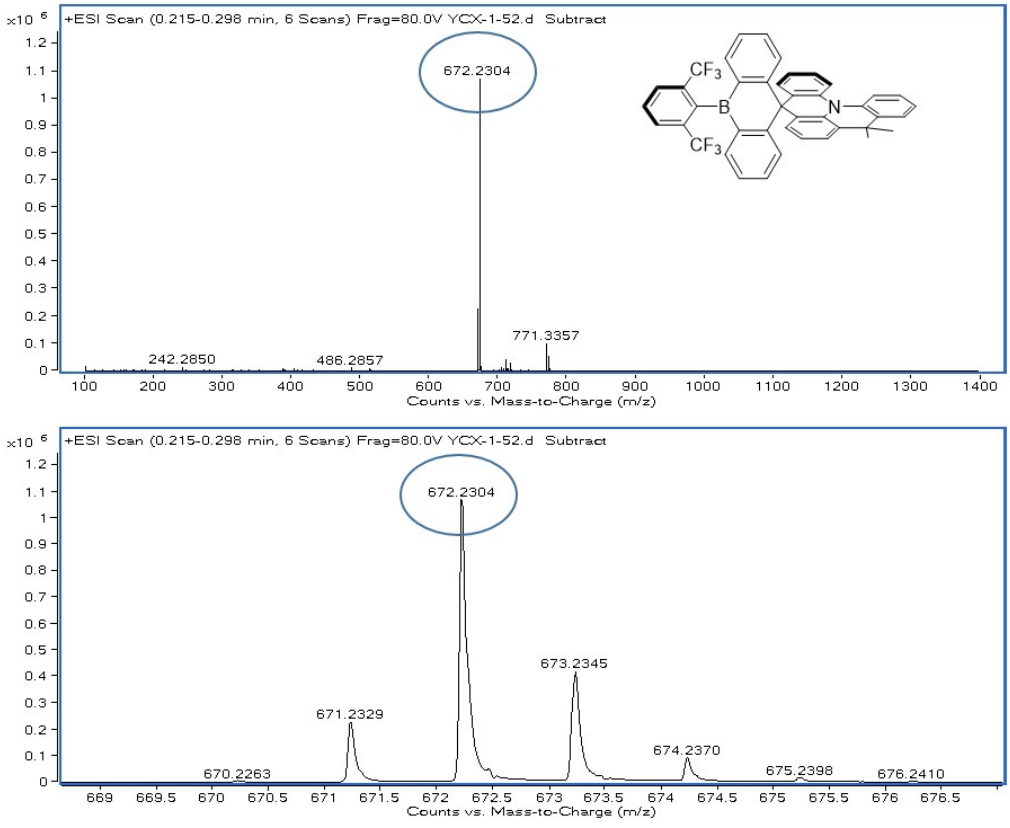
^{1}H NMR spectrum of **PBA-s-^{F}XylB** in $(CD_3)_2SO$.



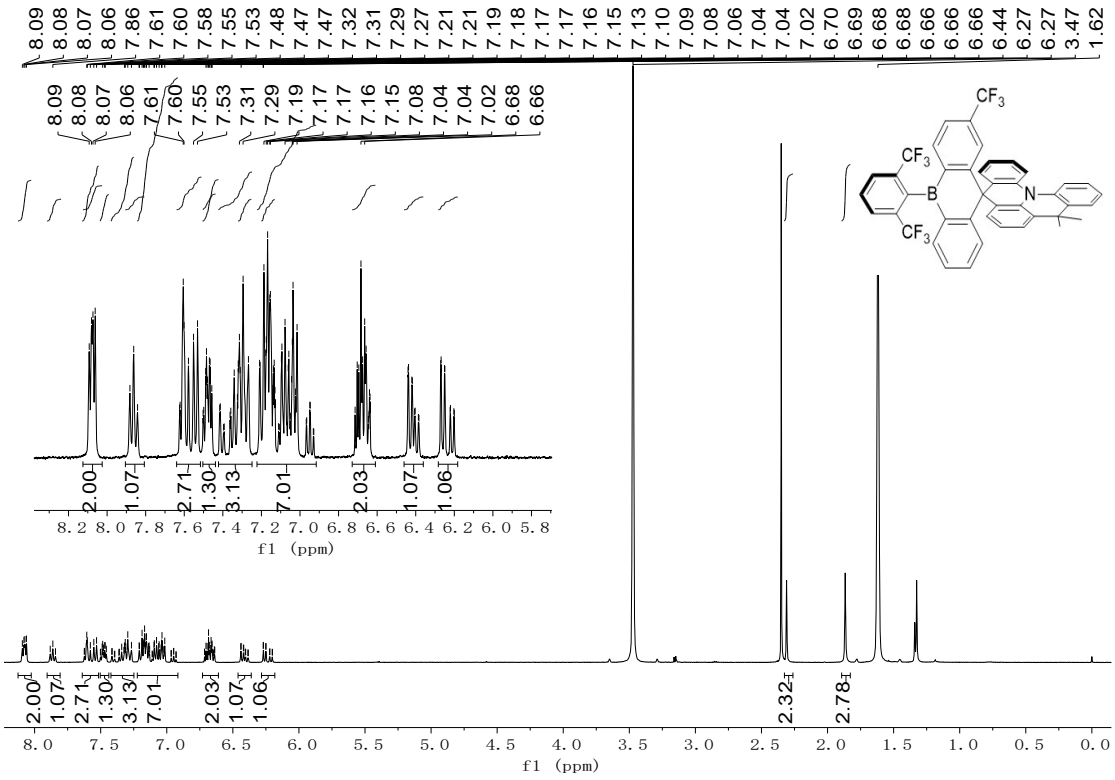
^{13}C NMR spectrum of **PBA-s-^{F}XylB** in $CDCl_3$.



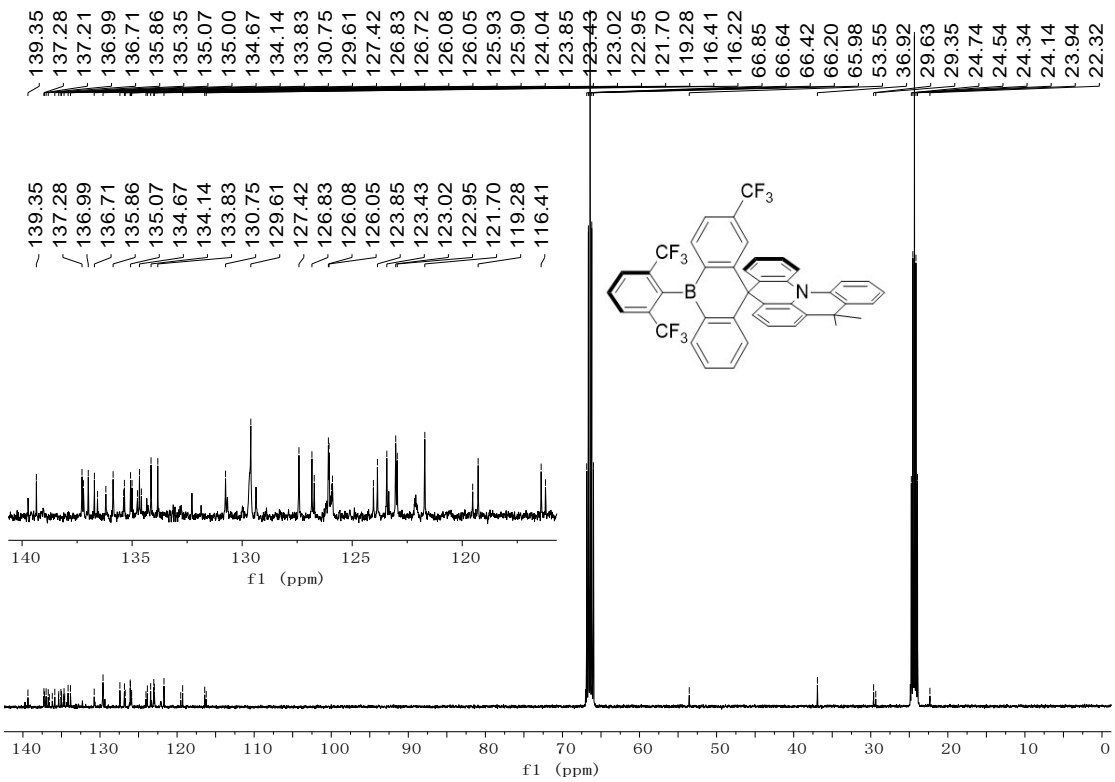
^{11}B NMR spectrum of **PBA-s-^{F}XylB** in $CDCl_3$.



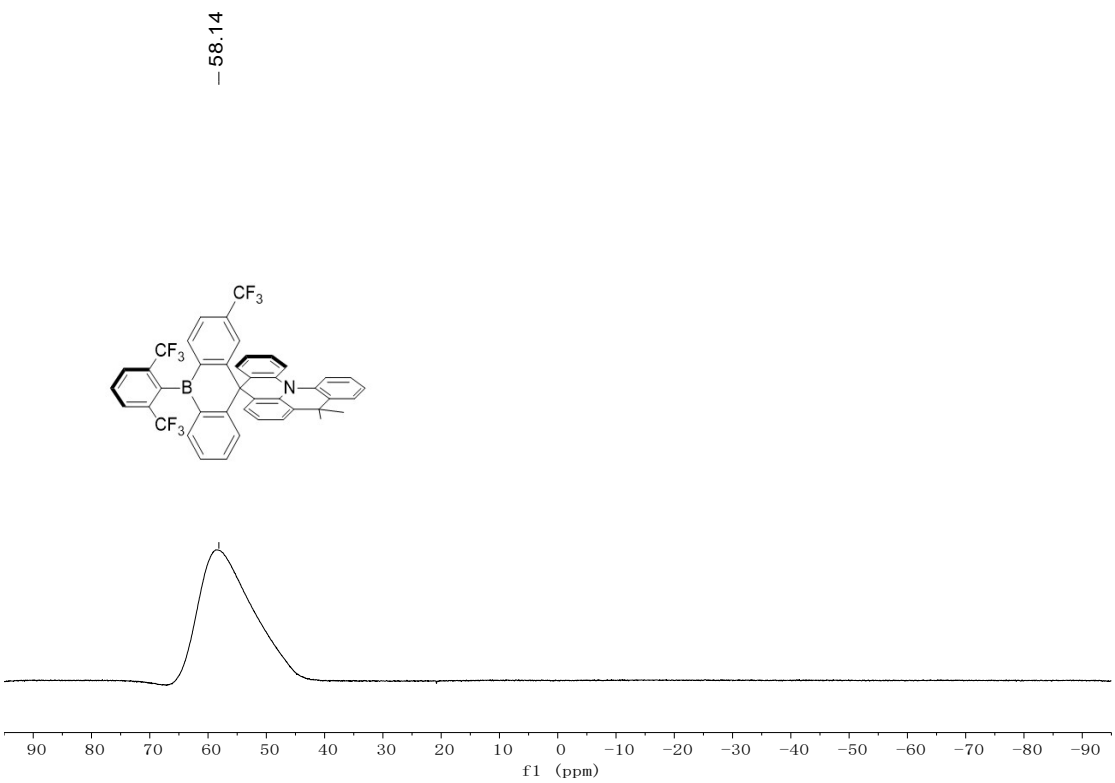
HRMS spectrum of **PBA-s-^{F}XylB**.



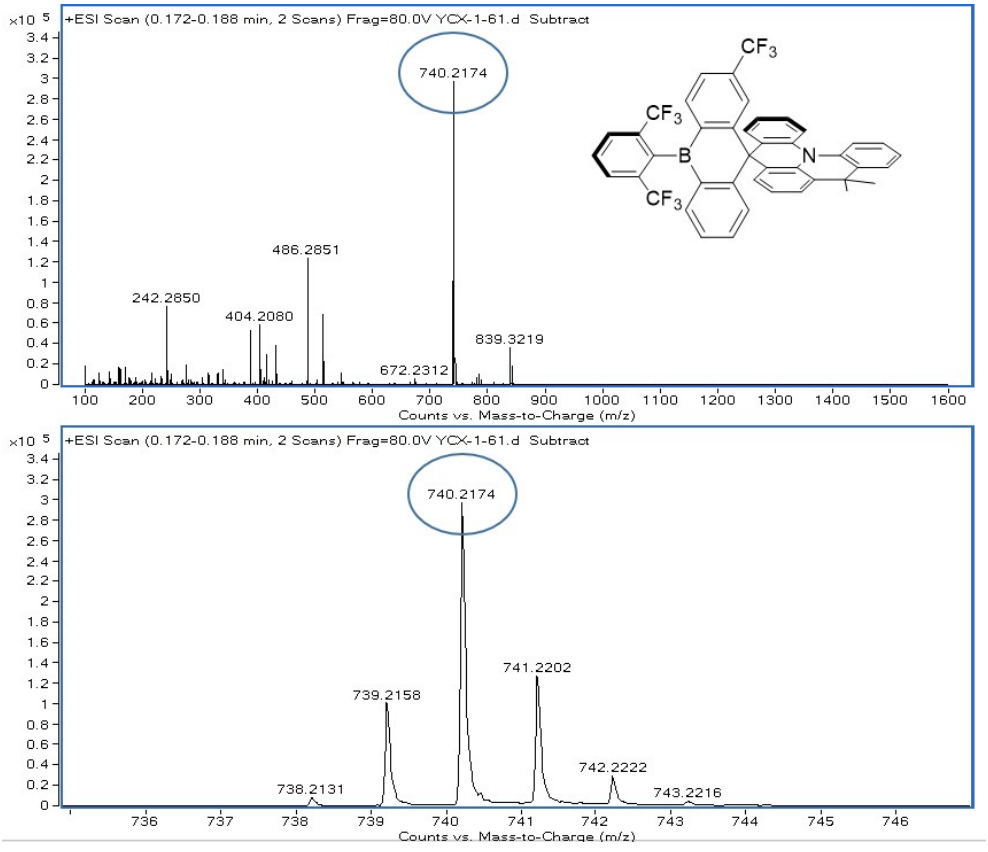
^{1}H NMR spectrum of **PBA-s-^{F}XylBF** in THF-d_8.



^{13}C NMR spectrum of **PBA-s-^{F}XylBF** in THF-d_8.



^{11}B NMR spectrum of **PBA-s-^{F}XylBF** in $CDCl_3$.



HRMS spectrum of **PBA-s-^{F}XylBF**

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