

## Supporting Information

### Efficient Deep-Blue Organic Light-Emitting Diodes Employing Difluoroboron-Enabled Thermally Activated Delayed Fluorescence Emitters

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## General Information.

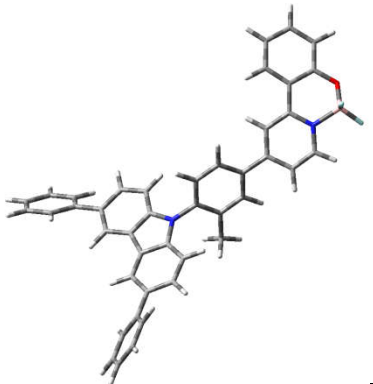
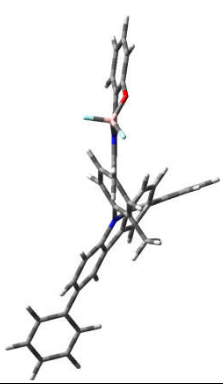
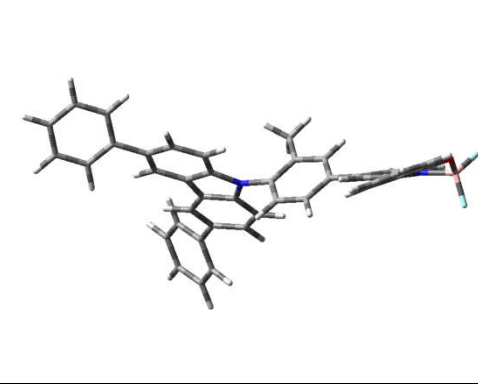
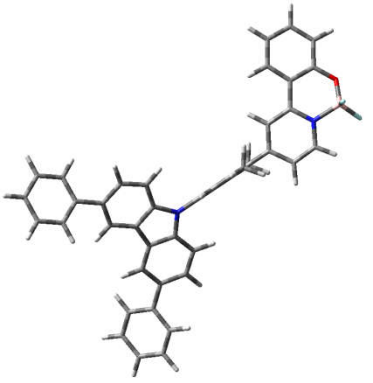
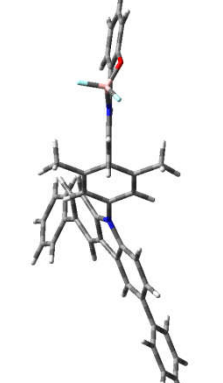
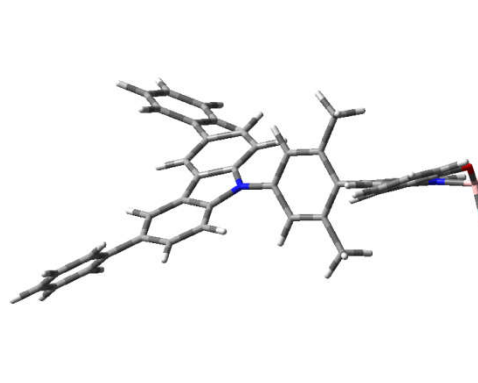
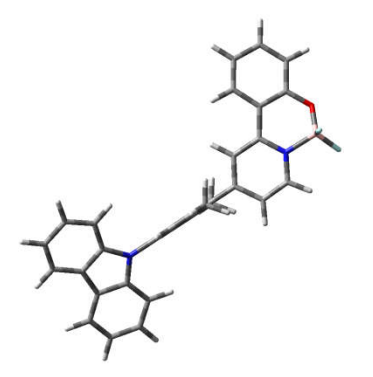
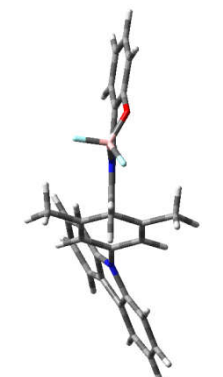
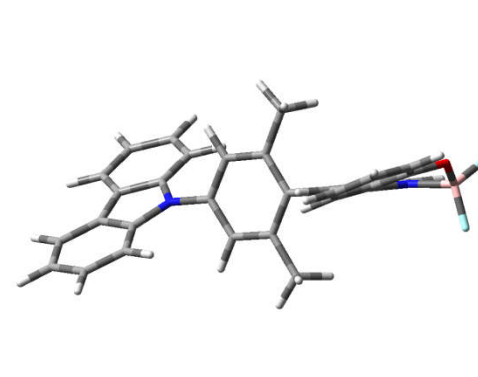
**Synthesis and Characterization.** Unless noted, all commercial reagents were purchased and used as received without further purification.  $^1\text{H}$  NMR spectra were recorded at 500 MHz, and  $^{13}\text{C}$  NMR spectra were recorded at 150 MHz NMR instruments in  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$  solutions and chemical shifts were referenced to tetramethylsilane (TMS) or residual protiated solvent. If  $\text{CDCl}_3$  was used as solvent,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with TMS ( $\delta = 0.00$  ppm) and  $\text{CDCl}_3$  ( $\delta = 77.00$  ppm) as internal references, respectively. If  $\text{DMSO-}d_6$  was used as solvent,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with TMS ( $\delta = 0.00$  ppm) and  $\text{DMSO-}d_6$  ( $\delta = 39.52$  ppm) as internal references, respectively. The following abbreviations (or combinations thereof) were used to explain  $^1\text{H}$  NMR multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet, br = broad. All of the new compounds were analyzed for HRMS on a mass spectrometer using electrospray ionization in positive ion mode on ESI-QTOF mass spectrometer from Applied Biosystems.

**Electrochemistry.** Cyclic voltammetry and different pulsed voltammetry were performed using a CH1760E electrochemical analyzer according previous report.<sup>1</sup> 0.1 M tetra-*n*-butylammonium hexafluorophosphate was used as the supporting electrolyte, anhydrous *N,N*-dimethylformamide, was used as the solvents for the  $E_{\text{ox}}$  and  $E_{\text{red}}$  measurements, and the solutions were bubbled with nitrogen for 15 min prior to the test. Silver wire, platinum wire and glassy carbon were used as pseudoreference electrode, counter electrode, and working electrode respectively. Scan rate was 300 mV/s. The redox potentials are based on the values measured from different pulsed voltammetry and are reported relative to an internal reference ferrocenium/ferrocene ( $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ ).<sup>2</sup> The reversibility of reduction or oxidation was determined using CV.<sup>3</sup> As defined, if the magnitudes of the peak anodic and the peak cathodic current have an equal magnitude as scan speeds of 100 mV/s or slower, then the process is considered reversible; if the magnitudes of the peak anodic and the peak cathodic currents are not equal, but the return sweeps are nonzero, the process is considered quasi-reversible; otherwise, the process is considered irreversible.<sup>2,3</sup>

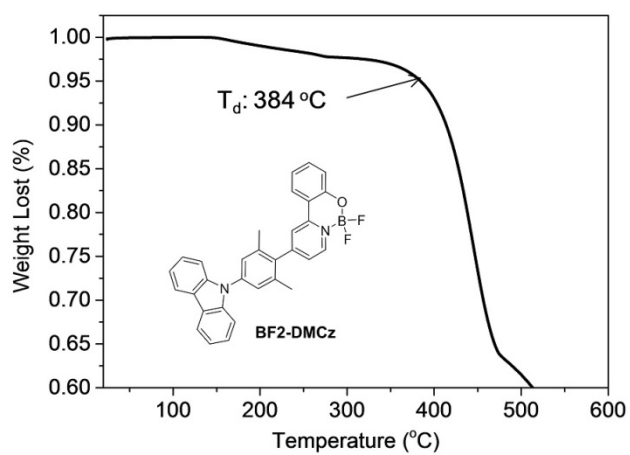
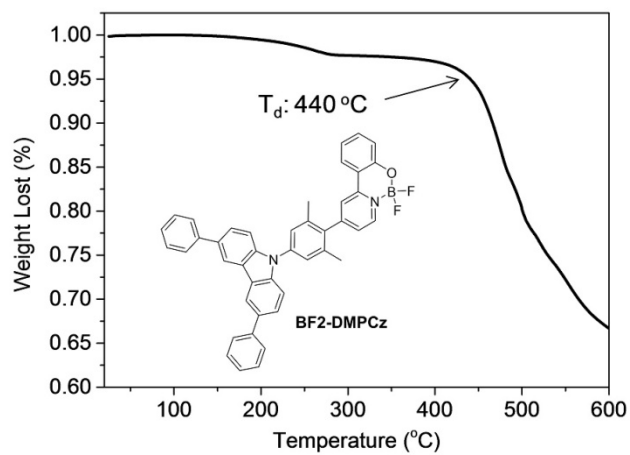
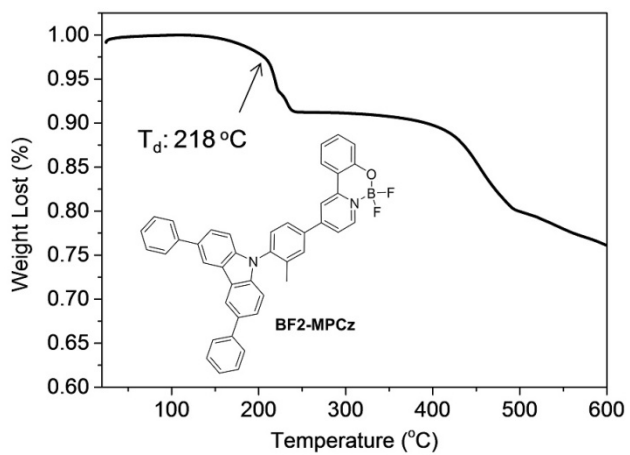
**DFT Calculations.** Gaussian 16 program package was used for all quantum chemical calculations. The molecular geometries of ground states ( $S_0$ ) were optimized with the density functional theory (DFT) method. The DFT calculations were performed using a B3LYP functional

with a basis set of 6-311G (d, p) for all atoms. TD-DFT was then employed to obtain the vertical transitions of the  $S_1$  and  $T_1$  states based on the corresponding  $S_0$  geometries at same theoretical level.<sup>4</sup>

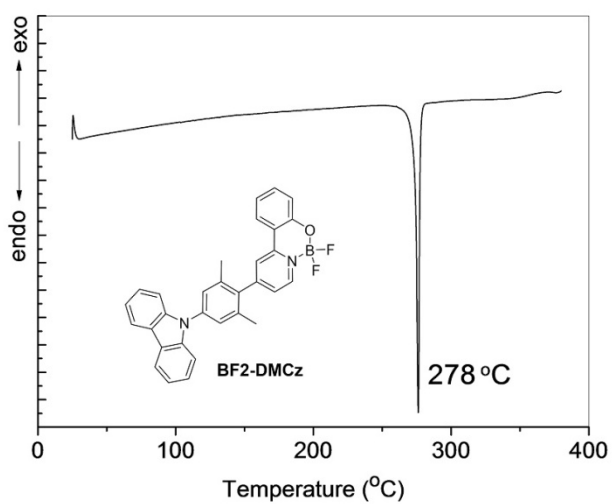
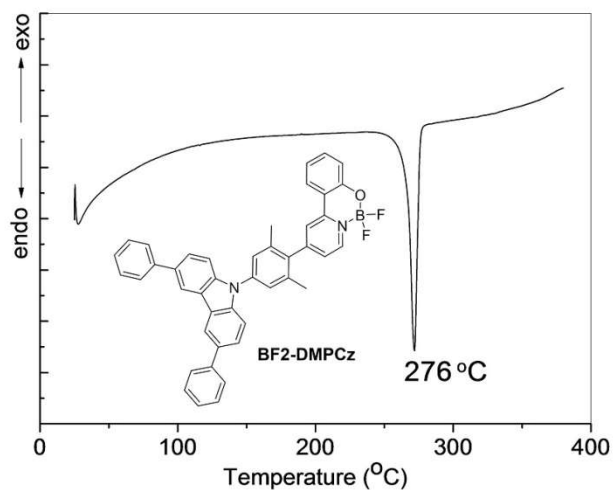
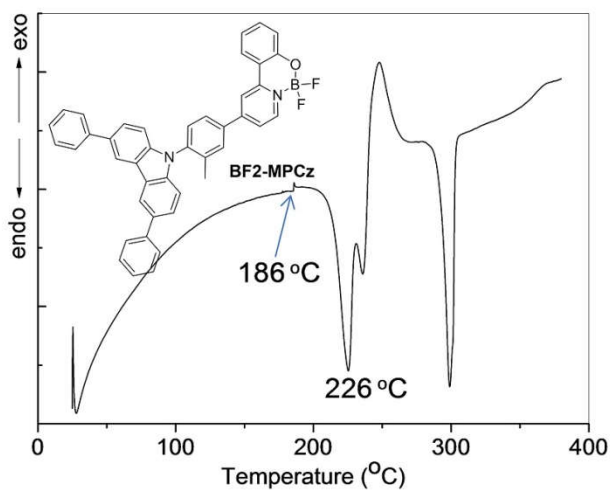
**Photophysical Measurements.** The absorption spectra were measured on an Agilent 8453 UV–VS Spectrometer. Steady state emission experiments and lifetime measurements were performed on a Horiba Jobin Yvon FluoroLog-3 spectrometer. Low temperature (77 K) emission spectra and lifetimes were measured in toluene cooled with liquid nitrogen.

Table S1. DFT Calculations for difluoroboron Complexes <sup>a</sup>			
complexes	Front view	Side view	Top view
BF2-MPCz			
BF2-DMPCz			
BF2-DMCz			

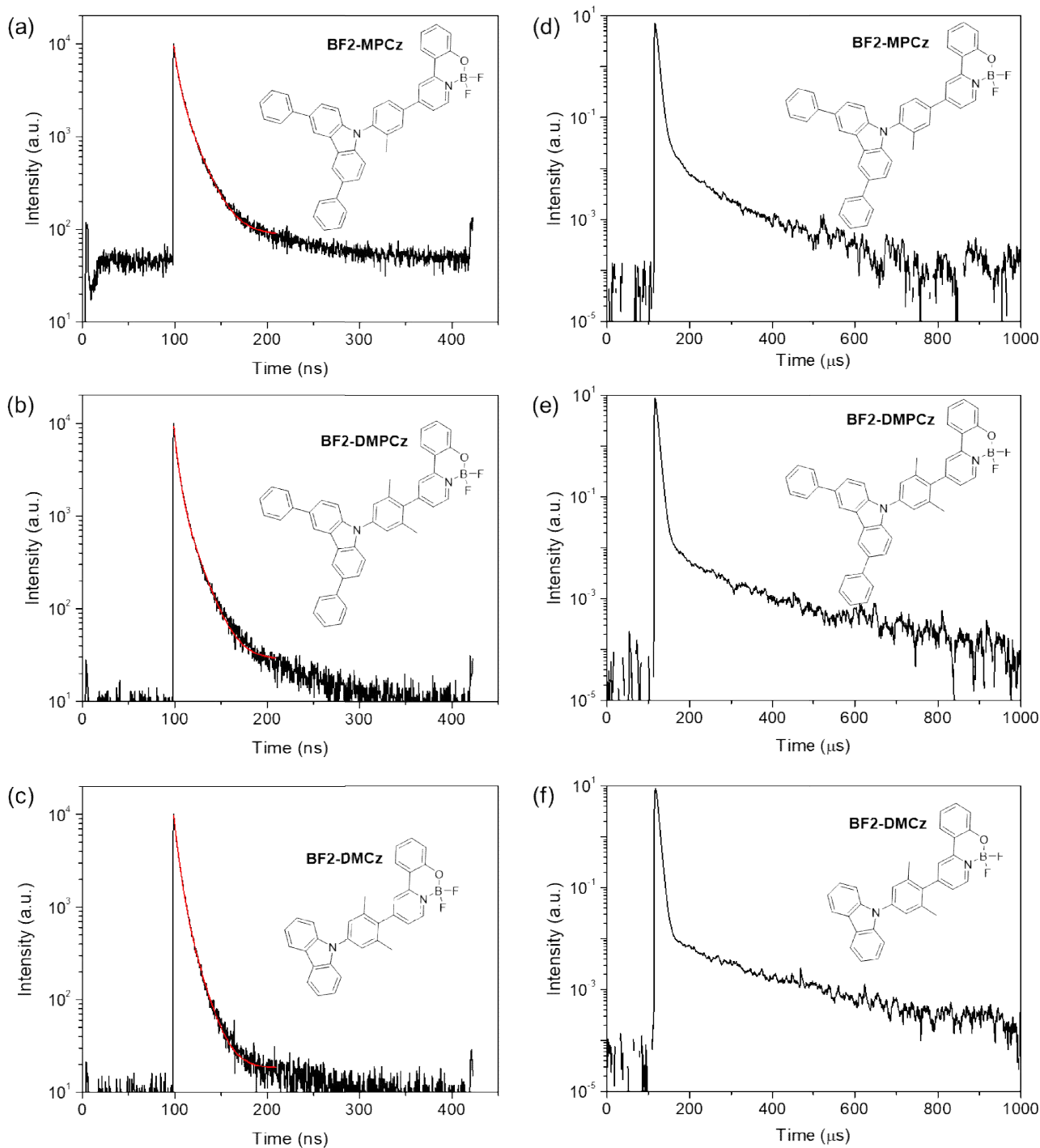
<sup>a</sup>Optimized  $S_0$  were calculated at the B3LYP/6-311G (d, p) level in the gas phase.



**Figure S1.** Thermogravimetric analysis ( TGA) of **BF2-MPCz**, **BF2-DMPCz** and **BF2-DMCz**.

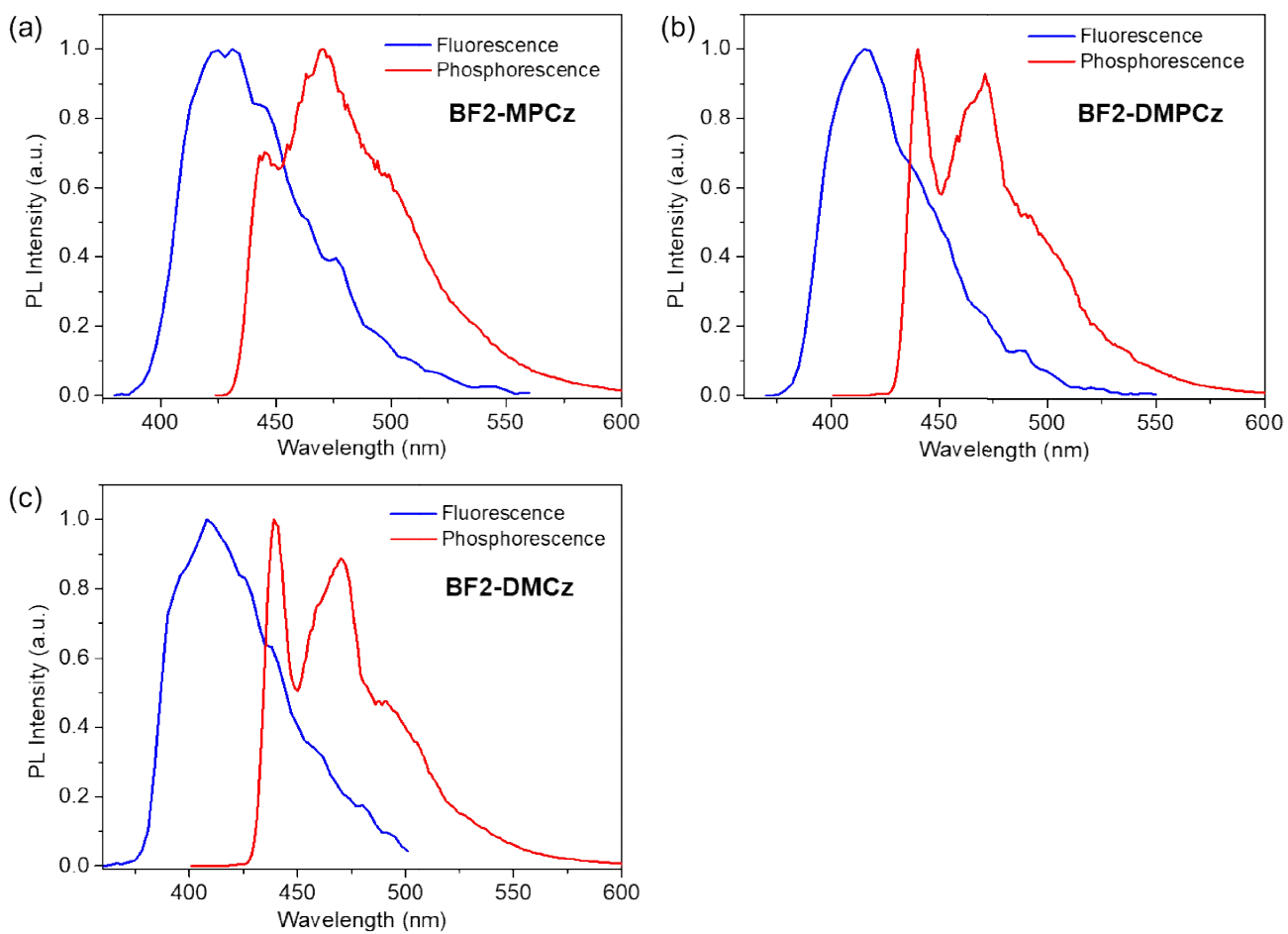


**Figure S2.** Differential scanning calorimetry (DSC) of BF2-MPCz, BF2-DMPCz and BF2-DMCz.

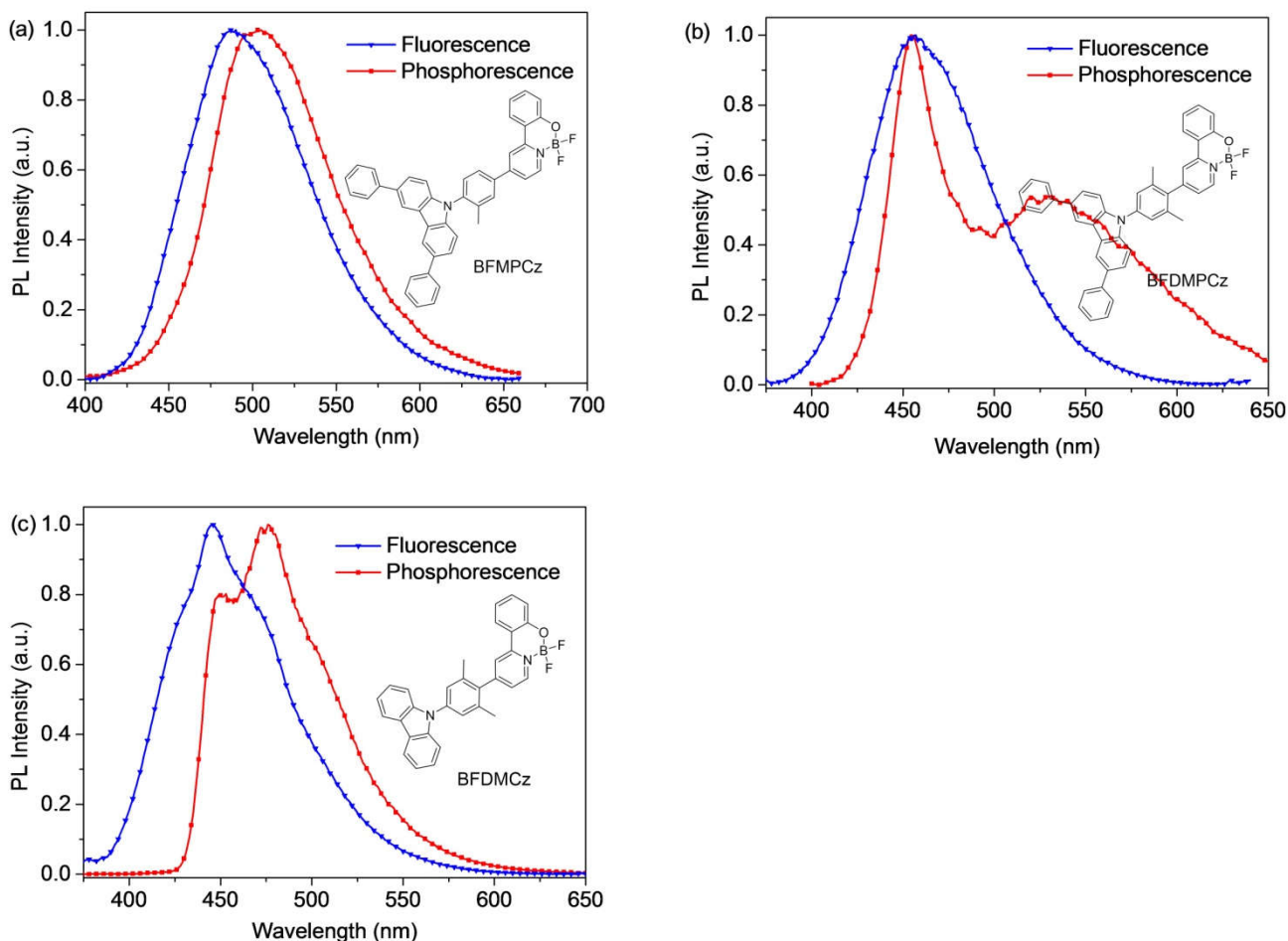


**Figure S3.** Prompt transient PL decay curves (black lines) and biexponential fitting curves (blackred lines) of (a) **BF2-MPCz** (8.9 ns), (b) **BF2-DMPCz** (6.4 ns) and (c) **BF2-DMCz** (6.0 ns) in 10 wt% emitter:DPEPO doped film measured at room temperature under  $N_2$  using semiconductor laser (371 nm) on Horiba deltaflex01 system via TCSPC technique. Delayed transient PL decay curves of (d) **BF2-MPCz** (70  $\mu$ s), (e) **BF2-DMPCz** (95  $\mu$ s) and (f) **BF2-DMCz** (130  $\mu$ s) in 10 wt% emitter:DPEPO doped film measured at room temperature under  $N_2$  using nitrogen laser (337 nm) on PTI QM-40 spectrofluorometer via strobe technique.





**Figure S4.** Fluorescence and phosphorescence spectra of (a) **BF2-MPCz**, (b) **BF2-DMPCz** and (c) **BF2-DMCz** measured at 77 K in toluene solution.

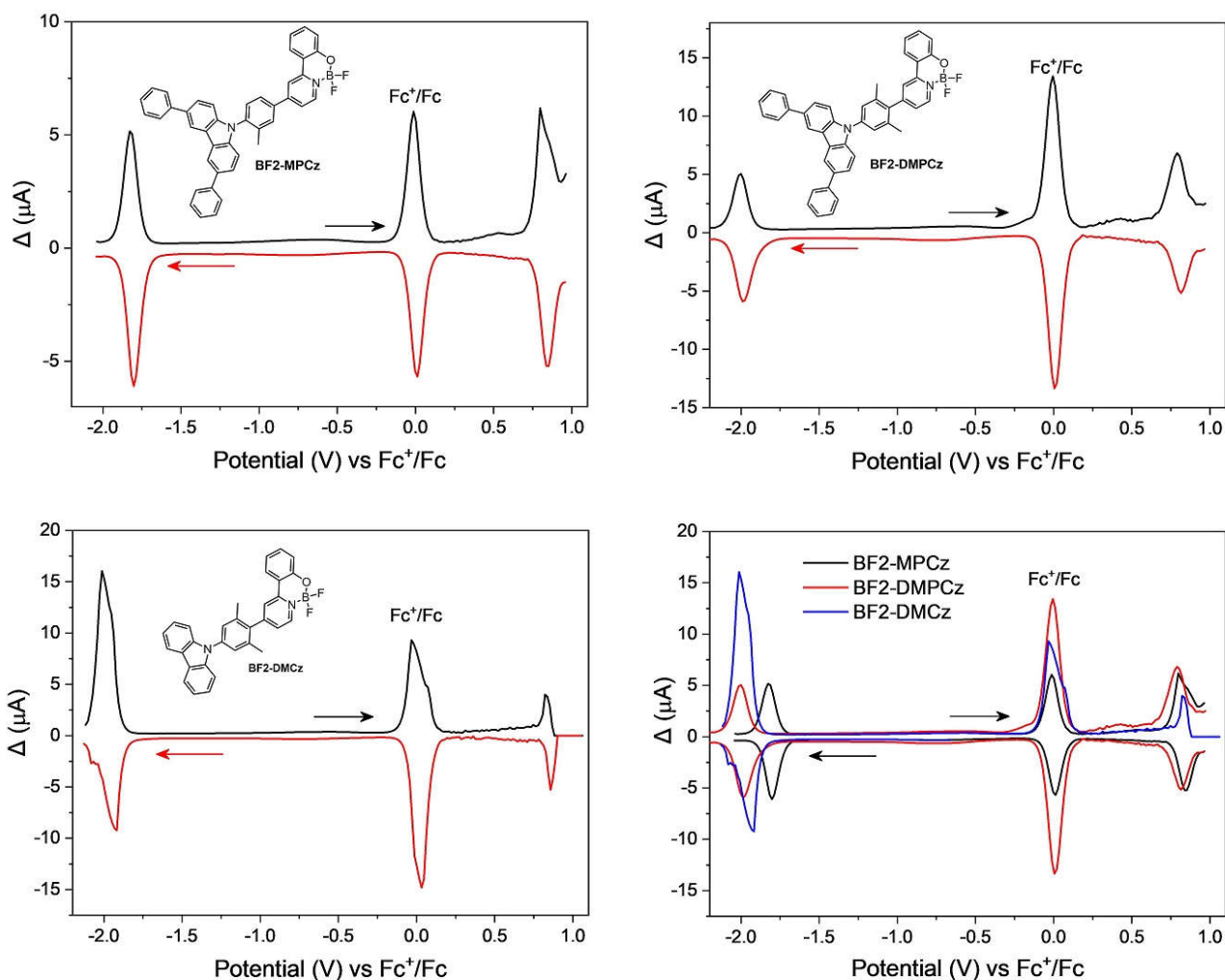


**Figure S5.** Fluorescence and phosphorescence spectra of (a) **BF2-MPCz**, (b) **BF2-DMPCz** and (c) **BF2-DMCz** measured at 77 K in 10 wt% doped DPEPO film.

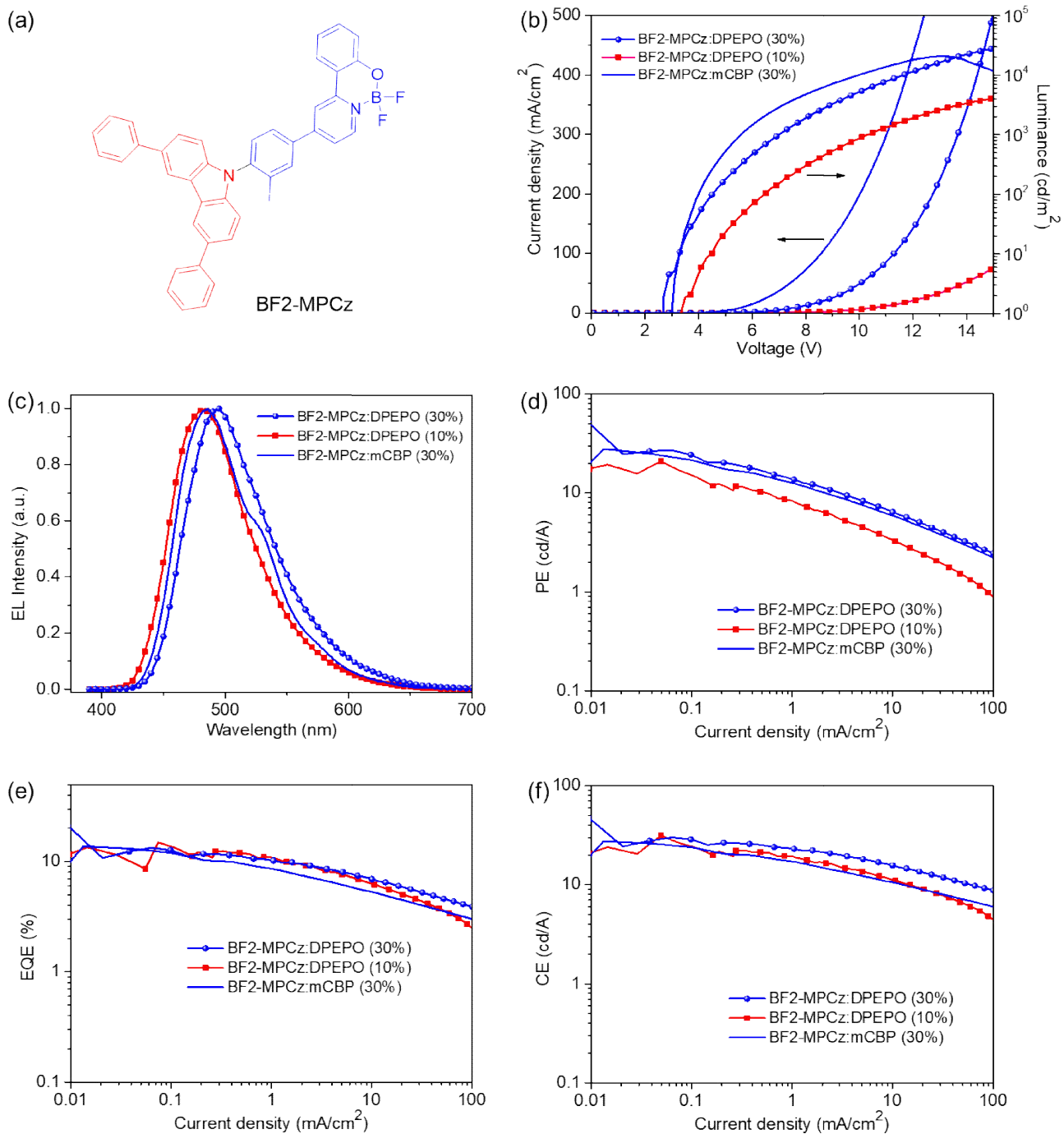
**Table S2. Electrochemical Properties of the Difluoroboron Compounds**

Compound	$E_{\text{ox}}$ (V)	$E_{\text{red}}$ (V)	HOMO/LUMO <sup>a)</sup> (eV)
<b>BF2-MPCz</b>	0.82	-1.82	-5.62/-2.99
<b>BF2-DMPCz</b>	0.83	-1.97	-5.63/-2.83
<b>BF2-DMCz</b>	0.84	-1.97	-5.64/-2.83

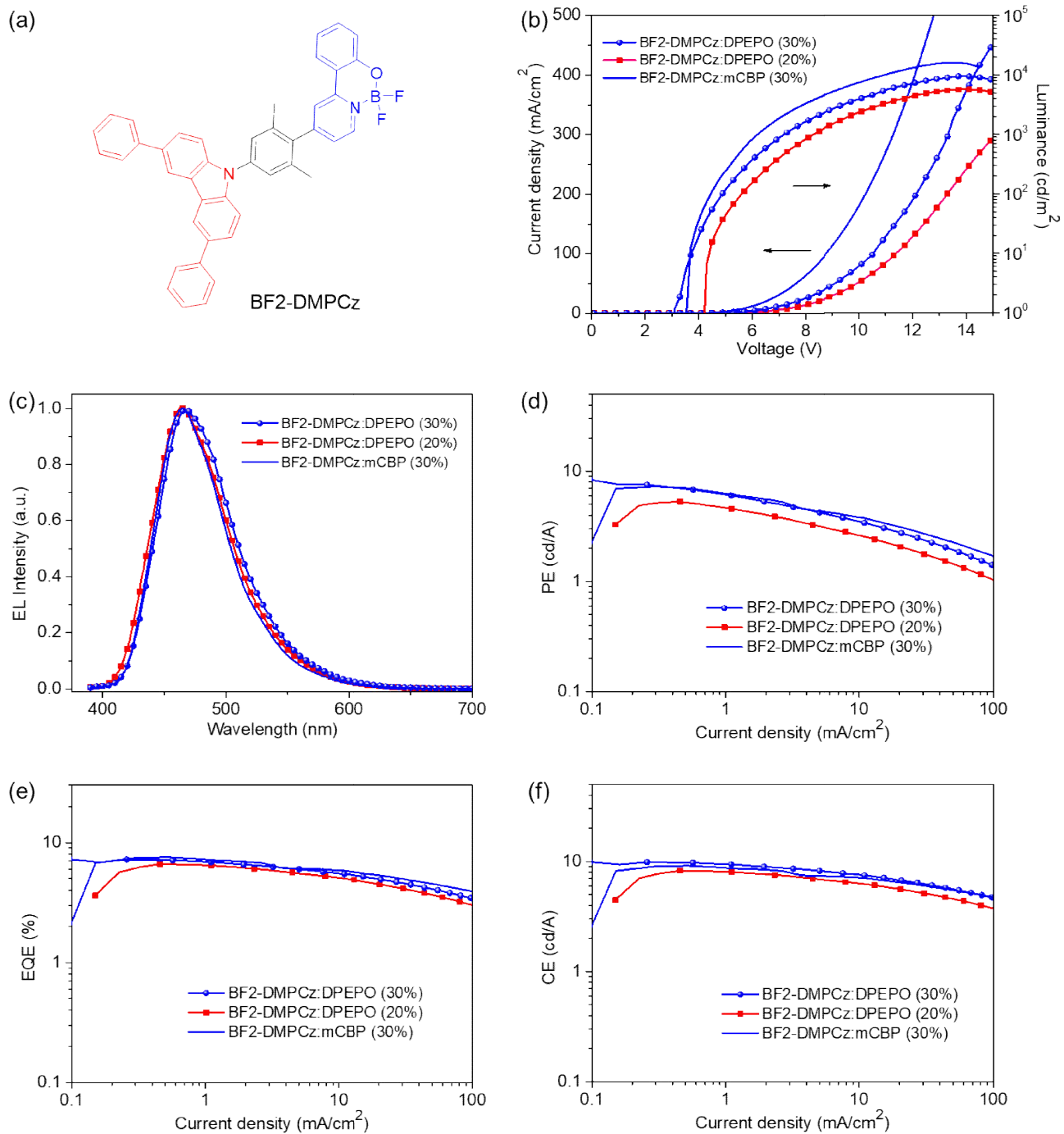
<sup>a)</sup>The HOMO and LUMO levels were estimated by using  $\text{Cp}_2\text{Fe}^+/\text{Cp}_2\text{Fe}$  values of 4.8 eV below the vacuum level. Differential pulsed voltammetry (DPV) of the difluoroboron compounds measured in anhydrous *N,N*-dimethylformamide (DMF); a silver wire was used as pseudoreference electrode; a platinum wire was used as counter electrode; glassy carbon was used as the working electrode; scan rate is 300 mV/s.



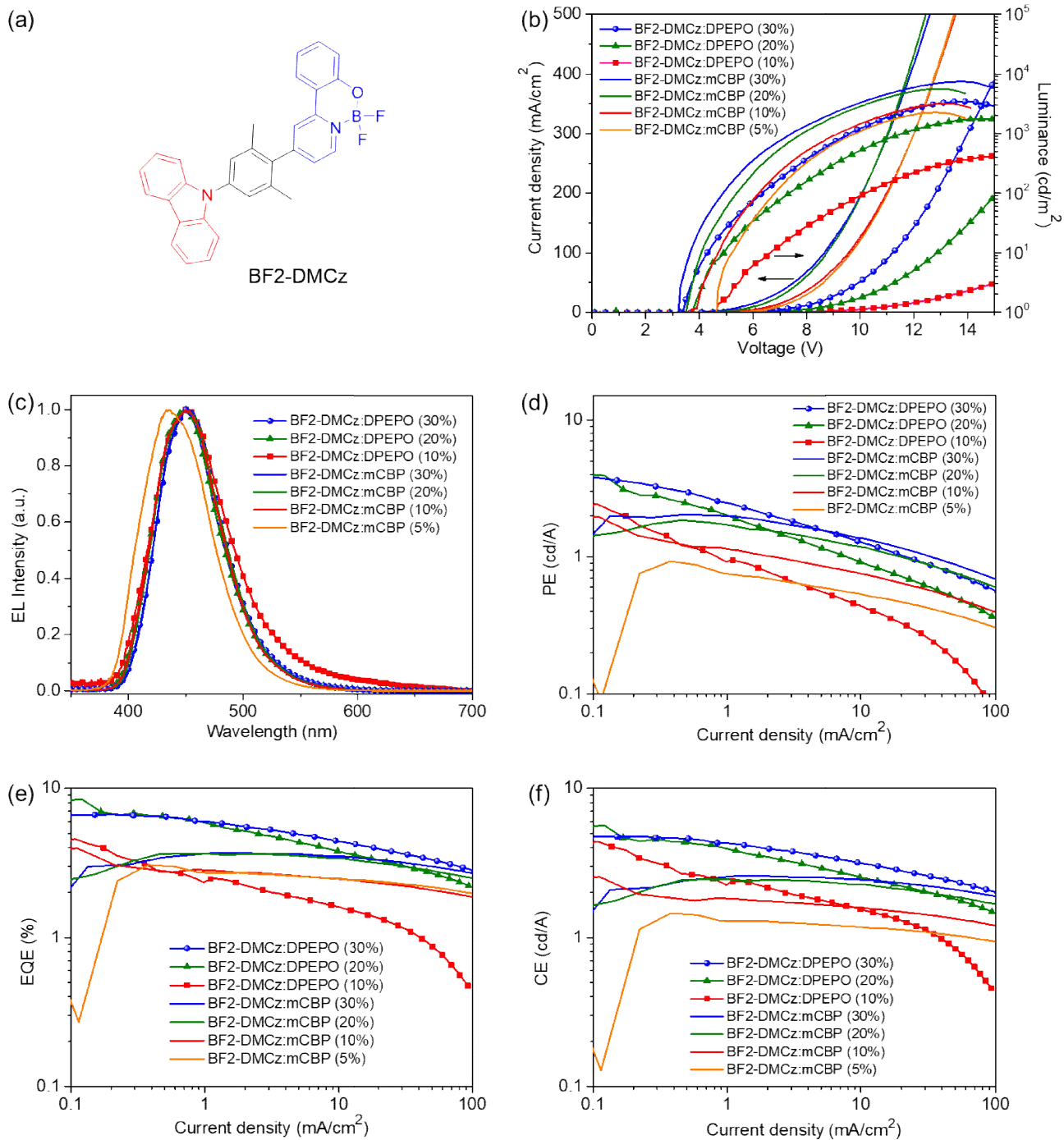
**Figure S6.** Differential pulsed voltammetry (DPV) of **BF2-MPCz**, **BF2-DMPCz** and **BF2-DMCz** measured in anhydrous *N,N*-dimethylformamide (DMF); a silver wire was used as pseudoreference electrode; a platinum wire was used as counter electrode; glassy carbon was used as the working electrode.



**Figure S7.** Device performances of **BF2-MPCz**-based OLEDs.



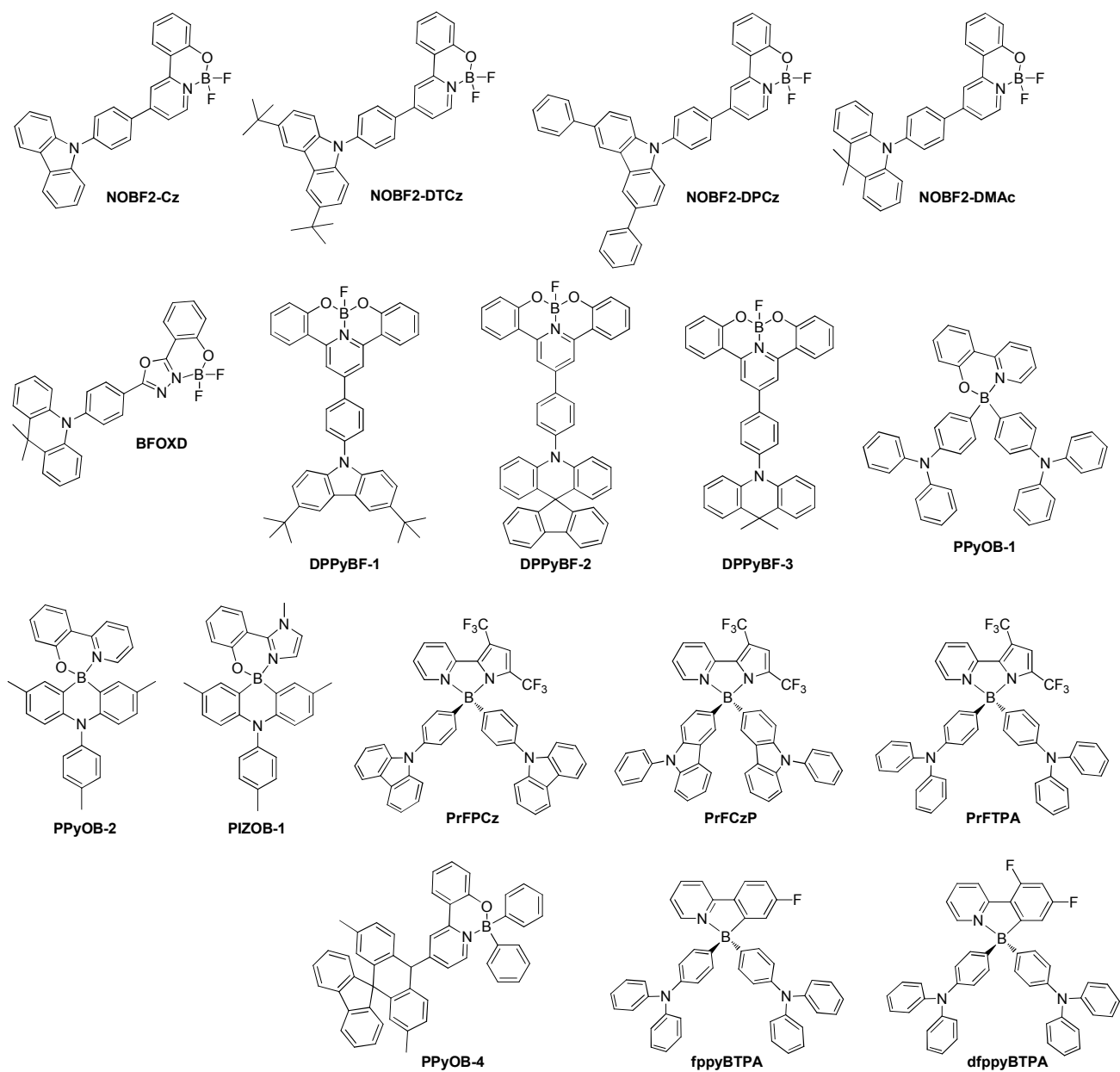
**Figure S8.** Device performances of **BF2-DMPCz**-based OLEDs.



**Figure S9.** Device performances of BF2-DMCz-based OLEDs.

**Table S3. Summarized Photophysical and Device Properties of Some Selected TADF Emitters Using Tetracoordinated Boron Units as Acceptors**

emitter	$\lambda_{\text{PL}}$ [nm]	$\Phi_{\text{PL}}$ [%]	Peak EQE (%)	CIE (x, y)	Ref.
<b>BF2-MPCz</b>	<b>471</b>	<b>94</b>	<b>13.8</b>	<b>(0.175, 0.354)</b>	<b>This work</b>
<b>BF2-DMPCz</b>	<b>443</b>	<b>99</b>	<b>7.5</b>	<b>(0.146, 0.174)</b>	<b>This work</b>
<b>BF2-DMCz</b>	<b>435</b>	<b>98</b>	<b>8.4</b>	<b>(0.149, 0.083)</b>	<b>This work</b>
NOBF2-Cz	467	99	11.0	(0.14, 0.16)	(4)
NOBF2-DTCz	471	74	12.7	(0.14, 0.21)	(4)
DPPyBF-1	480	65	8.8	(0.16, 0.31)	(5)
NOBF2-DPCz	483	70	15.8	(0.14, 0.28)	(4)
PIZOB-1	490	37	–	(0.223, 0.365)	(6)
BFOXD	492	66	20.1	(0.21, 0.38)	(7)
PrFPCz	495	40	7.6	–	(8)
PPyOB-4	504	97	22.7	(0.20, 0.42)	(9)
DPPyBF-2	508	89	18.0	(0.28, 0.54)	(5)
DPPyBF-3	512	82	5.6	(0.303, 0.519)	(5)
PrFTPA	515	60	13.5	–	(8)
PrFCzP	520	38	4.8	–	(8)
NOBF2-DMCz	523	65	13.2	(0.29, 0.60)	(4)
fppyBTPA	529	72	20.2	(0.27, 0.54)	(10)
dfppyBTPA	535	100	26.6	(0.26, 0.58)	(10)
PPyOB-1	544	42	17.5	(0.40, 0.56)	(6)
PPyOB-2	548	29	8.3	(0.450, 0.529)	(6)

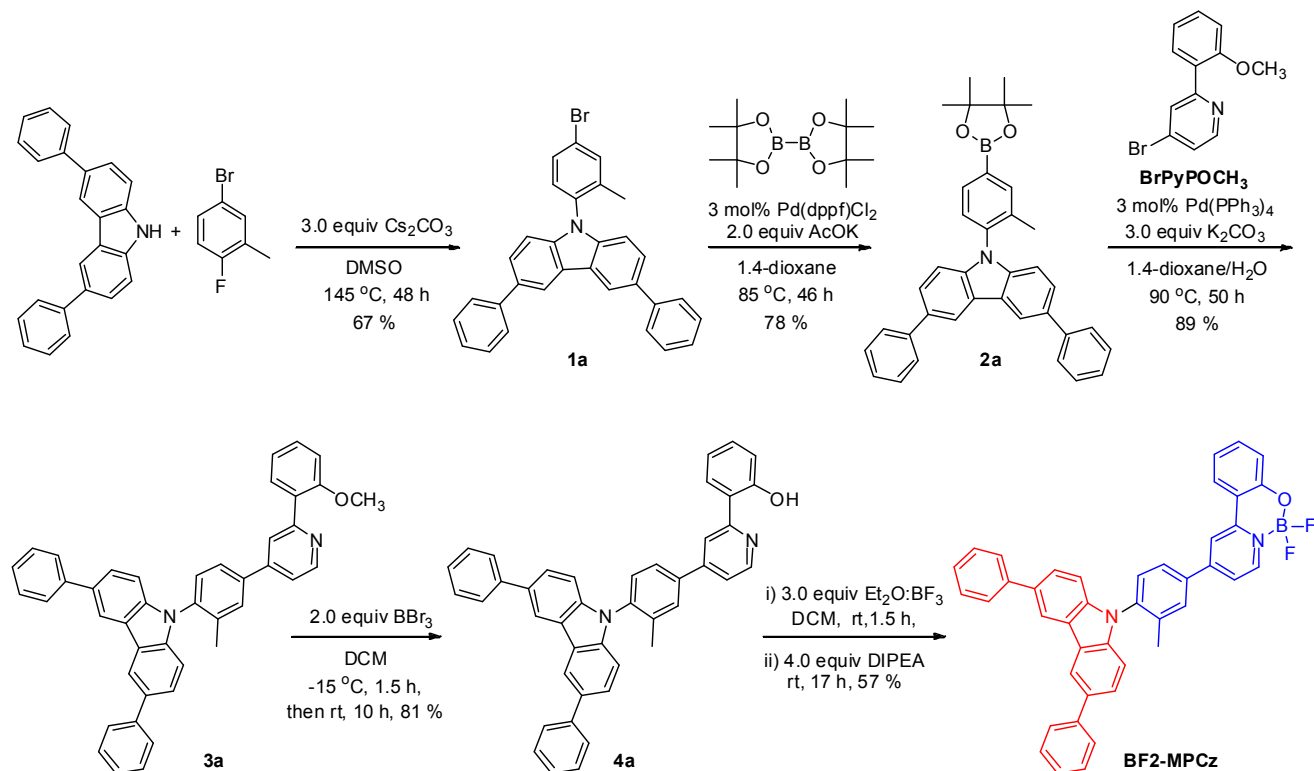


**Figure S10.** Molecular structures of some selected TADF emitters using tetracoordinated boron units as acceptors discussed in this study (Table S4).



## Experimental Procedures

### Synthesis of BF<sub>2</sub>-MPCz:



### Synthesis of 9-(4-bromo-2-methylphenyl)-3,6-diphenyl-9H-carbazole **1a**:

3,6-Diphenyl-9H-carbazole (767 mg, 2.40 mmol, 1.0 equiv), Cs<sub>2</sub>CO<sub>3</sub> (2.35 g, 7.20 mmol, 3.0 equiv) were added to a dry sealed tube equipped with a magnetic stir bar. Then the sealed tube was evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then 4-bromo-1-fluoro-2-methylbenzene (1.36 g, 7.2 mmol, 3.0 equiv) and DMSO (20 mL) were added to the tube quickly under nitrogen atmosphere. The mixture was stirred at 145 °C for 48 h, and the reaction monitored by TLC until the reaction was completed. Then the resulting mixture was cooled down to room temperature, and diluted with ethyl acetate. The organic layer was washed with water, and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified through column chromatography on silica gel using petroleum ether/ethyl acetate = 50:1-20:1 as eluent to afford the desired product as a white solid 780 mg in 67% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.03 (s, 3H), 7.10 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.34–7.37 (m, 2H), 7.47–7.50 (m, 4H), 7.57 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 2.0 Hz, 2H), 7.72–7.74 (m, 4H), 8.41 (d, *J* = 1.0 Hz, 2H).

### Synthesis

of

**9-(2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-3,6-diphenyl-9H-carbazole**

**2a:** 9-(4-Bromo-2-methylphenyl)-3,6-diphenyl-9H-carbazole **1a** (940 mg, 1.92 mmol, 1.0 equiv), bis(pinacolato)diboron (586 mg, 2.31 mmol, 1.2 equiv), Pd(dppf)Cl<sub>2</sub> (42 mg, 0.06 mmol, 3 mol%), AcOK (376 mg, 3.84 mmol, 2.0 equiv) were added to a dry three-necked flask equipped with a magnetic stir bar. Then the flask was evacuated and backfilled with nitrogen, this evacuation and backfilled procedure was repeated twice. Then dry 1,4-dioxane (15 mL) was added under nitrogen atmosphere. The mixture was stirred at 85 °C for 46 h, and the reaction monitored by TLC until the reaction was completed. The resulting mixture was cooled down to room temperature, then the solvent was removed and the residue was diluted with ethyl acetate. The mixture was washed with water, separated and then the organic layer dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified through column chromatography on silica gel using petroleum ether/ethyl acetate = 100:1-50:1 as eluent to afford **2a** as white solid 807 mg in 78% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.43 (s, 12H), 2.08 (s, 3H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.34–7.37 (m, 2H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.47–7.50 (m, 4H), 7.66 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.73–7.75 (m, 4H), 7.89 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.98 (s, 1H), 8.42 (d, *J* = 1.5 Hz, 2H).

**Synthesis of 9-(4-(2-(2-methoxyphenyl)pyridin-4-yl)-2-methylphenyl)-3,6-diphenyl-9H-carbazole 3a:** **2a** (700 mg, 1.31 mmol, 1.0 equiv), 4-bromo-2-(2-methoxyphenyl)pyridine **BrPyPOCH<sub>3</sub>** (345 mg, 1.31 mmol, 1.0 equiv, which was synthesized according previous report.<sup>4</sup>), Pd(PPh<sub>3</sub>)<sub>4</sub> (46 mg, 0.04 mmol, 3 mol%), and K<sub>2</sub>CO<sub>3</sub> (543 mg, 3.93 mmol, 3.0 equiv) were added to a dry three-necked flask equipped with a magnetic stir bar. Then the flask was evacuated and backfilled with nitrogen, this evacuation and backfilled procedure was repeated twice. Then 1,4-dioxane (15 mL) and H<sub>2</sub>O (3 mL) were added to the mixture under nitrogen atmosphere. The mixture was stirred at 90 °C for 50 h, and the reaction monitored by TLC until the reaction was completed. Then the resulting mixture was cooled down to room temperature, then the solvent was removed and the residue was diluted with ethyl acetate. The mixture was washed with water, the organic layer was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified through column chromatography on silica gel using petroleum ether/ethyl acetate/dichloromethane = 10:2:1 as eluent to afford **3a** as green yellow solid 696 mg in 89% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.15 (s, 3H), 3.93 (s, 3H), 7.07 (d, *J* = 8.5 Hz,

1H), 7.14 (td,  $J = 7.5, 1.0$  Hz, 1H), 7.19 (d,  $J = 8.5$  Hz, 2H), 7.34–7.38 (m, 2H), 7.41–7.44 (m, 1H), 7.47–7.51 (m, 4H), 7.54–7.56 (m, 2H), 7.67 (d,  $J = 1.5$  Hz, 1H), 7.69 (d,  $J = 2.0$  Hz, 1H), 7.73–7.75 (m, 5H), 7.81 (d,  $J = 2.0$  Hz, 1H), 7.84 (dd,  $J = 7.5, 1.5$  Hz, 1H), 8.14 (d,  $J = 1.0$  Hz, 1H), 8.44 (d,  $J = 1.5$  Hz, 2H), 8.82 (dd,  $J = 5.0, 0.5$  Hz, 1H).

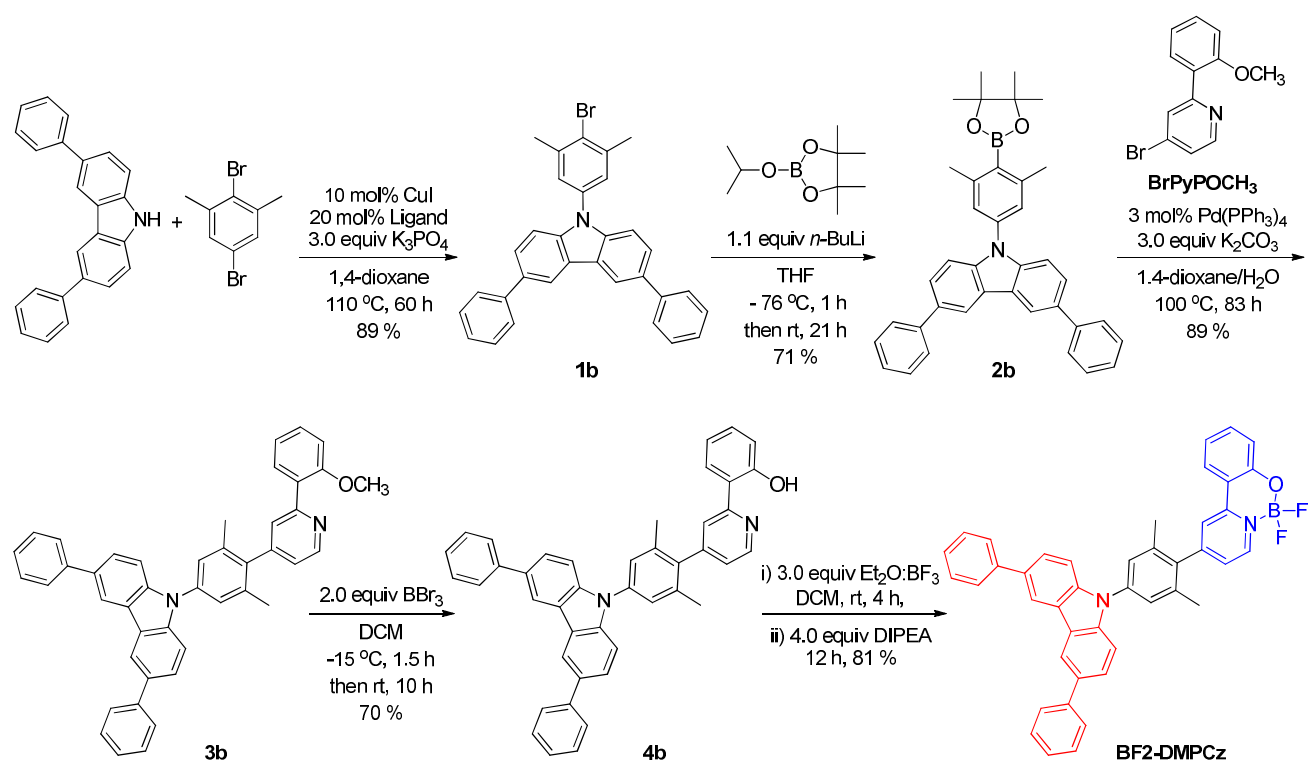
**Synthesis of 2-(4-(4-(3,6-diphenyl-9H-carbazol-9-yl)-3-methylphenyl)pyridin-2-yl)phenol**

**4a:** 9-(4-(2-(2-Methoxyphenyl)pyridin-4-yl)-2-methylphenyl)-3,6-diphenyl-9H-carbazole **3a** (750 mg, 1.27 mmol, 1.0 equiv) was added to a dry three-necked flask equipped with a magnetic stir bar. Then the flask was evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then dry  $\text{CH}_2\text{Cl}_2$  (20 mL) was added under nitrogen atmosphere. The mixture was stirred at  $-15$  °C for 10 min, then  $\text{BBr}_3$  (0.24 mL, 634 mg, 2.53 mmol, 2.0 equiv) was dropped slowly. The mixture was stirred at  $-15$  °C for 1.5 hours and then the temperature of the mixture allowed to raised to room temperature and stirred for further 10 hours. The reaction monitored by TLC until the reaction was completed. Then the reaction was quenched with  $\text{NaHCO}_3$  solution, and then extracted with  $\text{CH}_2\text{Cl}_2$  three times, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and the filtrate was concentrated under reduced pressure. The residue was purified through column chromatography on silica gel using petroleum ether/ethyl acetate/dichloromethane = 10:2:1 as eluent to afford **4a** as green yellow solid 596 mg in 81% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.19 (s, 3H), 6.96–6.99 (m, 1H), 7.09 (dd,  $J = 8.0, 1.0$  Hz, 1H), 7.18 (s, 1H), 7.19 (s, 1H), 7.34–7.38 (m, 3H), 7.47–7.51 (m, 4H), 7.57 (dd,  $J = 5.0, 1.5$  Hz, 1H), 7.59 (d,  $J = 8.0$  Hz, 1H), 7.69 (dd,  $J = 8.5, 1.5$  Hz, 2H), 7.73–7.77 (m, 5H), 7.83 (d,  $J = 2.0$  Hz, 1H), 7.98 (dd,  $J = 8.0, 1.5$  Hz, 1H), 8.22 (s, 1H), 8.44 (d,  $J = 1.5$  Hz, 2H), 8.64 (dd,  $J = 5.0, 1.0$  Hz, 1H), 14.37 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  17.93, 110.09, 117.20, 118.76, 118.87, 119.03, 119.74, 123.89, 125.79, 126.19, 126.21, 126.62, 127.29, 128.78, 130.00, 130.42, 131.71, 133.63, 137.21, 138.27, 138.62, 140.91, 141.83, 146.34, 149.50, 158.31, 160.14. HRMS (ESI): calcd for  $\text{C}_{42}\text{H}_{31}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$  579.2431, found 579.2428.

**Synthesis of BF2-MPCz:** **4a** (550 mg, 0.95 mmol, 1.0 equiv) was add to a dry three-necked flask equipped with a magnetic stir bar. The flask then evacuated and backfilled with nitrogen, this evacuation and backfill procedure repeated twice. Then dry  $\text{CH}_2\text{Cl}_2$  (20 mL) was added under nitrogen atmosphere, and then  $\text{Et}_2\text{O}:\text{BF}_3$  (0.36 mL, 404 mg, 2.85 mmol, 3.0 equiv) was added to the flask. The mixture was stirred at room temperature for 1.5 hour, after that,

*N,N*-diisopropylethylamine (DIPEA) (0.66 mL, 491 mg, 3.80 mmol, 4.0 equiv) was added. The mixture was stirred for further 17 hours, and the reaction monitored by TLC until the starting material was consumed completely. Then the reaction was quenched with NaHCO<sub>3</sub> solution, and then extracted with CH<sub>2</sub>Cl<sub>2</sub> three times, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and the filtrate was concentrated under reduced pressure. Then the mixture was concentrated and the residue was purified through column chromatography on silica gel using petroleum ether/dichloromethane/ethyl acetate = 10:4:1 as eluent to afford **BF2-MPCz** as light yellow solid 340 mg in 57% yield. m.p.: 201.5–202.6 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.23 (s, 3H), 7.10–7.13 (m, 1H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.25 (dd, *J* = 1.1 Hz, 1H), 7.35–7.39 (m, 2H), 7.49–7.52 (m, 4H), 7.53–7.57 (m, 1H), 7.67–7.71 (m, 3H), 7.74–7.76 (m, 4H), 7.83 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.88 (dd, *J* = 6.5, 2.0 Hz, 1H), 7.90 (d, *J* = 2.0 Hz, 1H), 8.01 (dd, *J* = 8.0, 1.0 Hz, 1H), 8.38 (d, *J* = 1.0 Hz, 1H), 8.45 (d, *J* = 1.0 Hz, 2H), 8.81 (d, *J* = 6.0 Hz, 1H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -146.59. <sup>11</sup>B NMR (192.5 MHz, CDCl<sub>3</sub>) δ 1.03. HRMS (ESI): calcd for C<sub>42</sub>H<sub>33</sub><sup>11</sup>BF<sub>2</sub>N<sub>3</sub>O [M+NH<sub>4</sub>]<sup>+</sup> 644.2679, found 644.2687.

#### Synthesis of **BF2-DMPCz**:



#### Synthesis of 9-(4-bromo-3,5-dimethylphenyl)-3,6-diphenyl-9H-carbazole **1b**:

3,6-Diphenyl-9H-carbazole (1.10 g, 3.45 mmol, 1.0 equiv), CuI (65 mg, 0.35 mmol, 10 mol%) and K<sub>3</sub>PO<sub>4</sub> (2.20 g, 10.35 mmol, 3.0 equiv) were added to a dry tube equipped with a magnetic stir bar.

Then the tube was evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then 2,5-dibromo-1,3-dimethylbenzene (1.00 g, 3.79 mmol, 1.1 equiv), *trans*-1,2-diaminocyclohexane (79 mg, 0.69 mmol, 20 mol%) and dry 1,4-dioxane (20 mL) were added to the tube rapidly under nitrogen atmosphere. The mixture was stirred at 110 °C for 60 hours, and the reaction monitored by TLC until the reaction was completed. The resulting mixture was cooled down to room temperature, then the solvent was removed and the residue was diluted with ethyl acetate. The mixture was washed with water, separated and then the organic layer dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified through column chromatography on silica gel using petroleum ether/dichloromethane = 30:1-10:1 as eluent to afford the desired product as light yellow solid 1.54 g in 89% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.55 (s, 6H), 7.34–7.37 (m, 4H), 7.45–7.50 (m, 6H), 7.68 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.72–7.74 (m, 4H), 8.39 (d, *J* = 2.0 Hz, 2H).

**Synthesis of 9-(3,5-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-3,6-diphenyl-9H-carbazole 2b:** 9-(4-Bromo-3,5-dimethylphenyl)-3,6-diphenyl-9H-carbazole **1b** (1.30 g, 2.59 mmol, 1.0 equiv) was added to a dry three-necked flask equipped with a magnetic stir bar. The flask was evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then anhydrous THF (40 mL) was added under nitrogen atmosphere. After cooling it to –76 °C using liquid nitrogen, *n*-BuLi (1.78 mL, 2.85 mmol, 1.1 equiv, 1.60 M in hexane) was dropped slowly, followed by stirring for 1 hour, and then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (579 mg, 3.11 mmol, 1.2 equiv) was added to the cold reaction mixture. The resulting solution was then allowed to raise to room temperature and stirred for further 21 hours. Then the mixture was quenched with a saturated solution of NH<sub>4</sub>Cl in water, and then extracted with ethyl acetate three times, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified through column chromatography on silica gel using petroleum ether/ethyl acetate = 100:1 as eluent to afford **2b** as white solid 1.0 g in 71% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.45 (s, 12H), 2.53 (s, 6H), 7.21 (s, 2H), 7.32–7.36 (m, 2H), 7.44–7.49 (m, 6H), 7.66 (dd, *J* = 8.5, 2.0 Hz, 2H), 7.72–7.74 (m, 4H), 8.38 (d, *J* = 1.5 Hz, 2H).

**Synthesis of 9-(4-(2-(2-methoxyphenyl)pyridin-4-yl)-3,5-dimethylphenyl)-3,6-diphenyl-9H-carbazole 3b:** **2b** (1.0 g, 1.83 mmol, 1.0 equiv), 4-bromo-2-(2-methoxyphenyl)pyridine

(**BrPyPOCH<sub>3</sub>**) (508 mg, 1.92 mmol, 1.05 equiv, which was synthesized according previous report.<sup>4</sup>), Pd(PPh<sub>3</sub>)<sub>4</sub> (63 mg, 0.055 mmol, 3 mol%), and K<sub>2</sub>CO<sub>3</sub> (759 mg, 5.49 mmol, 3.0 equiv) were added to a dry three-necked flask equipped with a magnetic stir bar. Then the flask was evacuated and backfilled with nitrogen, this evacuation and backfilled procedure was repeated twice. Then 1,4-dioxane (15 mL) and H<sub>2</sub>O (3 mL) were added to the mixture under nitrogen atmosphere. The mixture was stirred at 100 °C for 83 h, and the reaction monitored by TLC until the reaction was completed. Then the resulting mixture was cooled down to room temperature, then the solvent was removed and the residue was diluted with ethyl acetate. The mixture was washed with water, the organic layer was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified through column chromatography on silica gel using petroleum ether/ethyl acetate = 20:1–5:1 as eluent to afford **3b** as light yellow solid 986 mg in 89% yield. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 2.21 (s, 6H), 3.85 (s, 3H), 7.11 (td, *J* = 8.0, 1.0 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.32 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.35–7.38 (m, 2H), 7.42–7.46 (m, 1H), 7.49–7.53 (m, 6H), 7.58 (s, 1H), 7.60 (s, 1H), 7.78 (q, *J* = 1.5, 0.5 Hz, 1H), 7.80 (d, *J* = 1.8 Hz, 1H), 7.81–7.87 (m, 6H), 8.75 (d, *J* = 1.5 Hz, 2H), 8.80 (d, *J* = 5.0 Hz, 1H).

### Synthesis

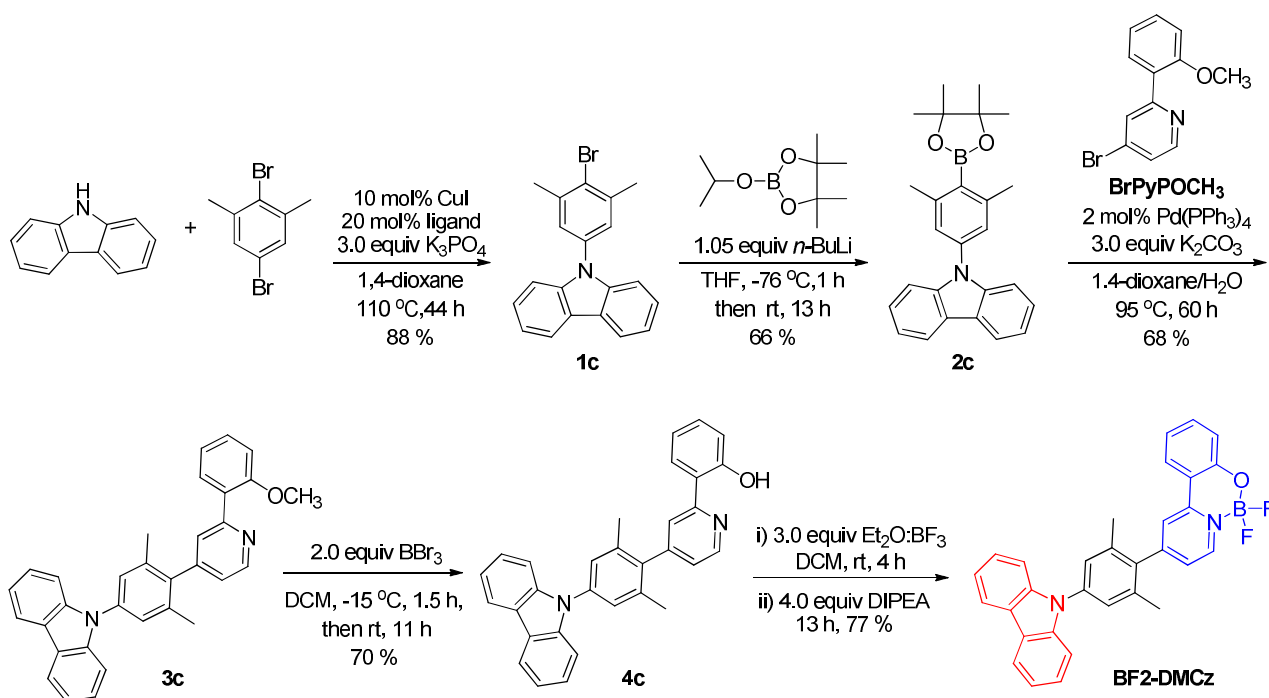
of

**2-(4-(4-(3,6-diphenyl-9H-carbazol-9-yl)-2,6-dimethylphenyl)pyridin-2-yl)phenol 4b**: **3b** (956 mg, 1.58 mmol, 1.0 equiv) was added to a dry three-necked flask equipped with a magnetic stir bar. Then the flask was evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then dry CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added under nitrogen atmosphere. The mixture was stirred at –15 °C for 10 min, then BBr<sub>3</sub> (791 mg (0.3 mL), 3.16 mmol, 2.0 equiv) was dropped slowly. The mixture was stirred at –15 °C for 1.5 hour and then the temperature of the mixture allowed to raised to room temperature and stirred for further 10 hours. The reaction monitored by TLC until the reaction was completed. Then the reaction was quenched with NaHCO<sub>3</sub> solution, and then extracted with CH<sub>2</sub>Cl<sub>2</sub> three times, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified through column chromatography on silica gel using petroleum ether/dichloromethane/ethyl acetate = 50:2:1 as eluent to afford **4b** as light yellow solid 652 mg in 70% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.21 (s, 6H), 6.92–6.95 (m, 1H), 7.09 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.22 (dd, *J* = 5.5, 1.0 Hz, 1H), 7.34–7.38 (m, 3H), 7.43 (s, 2H), 7.50 (t, *J* = 7.5 Hz, 4H), 7.59 (d, *J* =

8.0 Hz, 2H), 7.72 (dd,  $J = 8.5, 2.0$  Hz, 2H), 7.74–7.76 (m, 4H), 7.86 (dd,  $J = 8.0, 1.0$  Hz, 1H), 7.89 (s, 1H), 8.42 (d,  $J = 1.5$  Hz, 2H), 8.67 (d,  $J = 5.0$  Hz, 1H), 14.39 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  20.86, 110.25, 118.74, 118.78, 118.86, 118.91, 119.80, 122.31, 124.11, 125.67, 125.87, 126.24, 126.63, 127.29, 128.79, 131.77, 133.74, 137.27, 137.36, 138.07, 140.72, 141.85, 146.32, 150.80, 158.36, 160.13. HRMS (ESI): calcd for  $\text{C}_{43}\text{H}_{33}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$  593.2587, found 593.2582.

**Synthesis of BF2-DMPCz: 4b** (622 mg, 1.05 mmol, 1.0 equiv) was added to a dry three-necked flask equipped with a magnetic stir bar. The flask then evacuated and backfilled with nitrogen, this evacuation and backfill procedure repeated twice. Then dry  $\text{CH}_2\text{Cl}_2$  (15 mL) was added under nitrogen atmosphere, and then  $\text{Et}_2\text{O}:\text{BF}_3$  (0.39 mL, 448 mg, 3.15 mmol, 3.0 equiv) was added to the flask. The mixture was stirred at room temperature for 4 hours, after that, *N,N*-Diisopropylethylamine (DIPEA) (0.73 mL, 543 mg, 4.2 mmol, 4.0 equiv) was added, and the mixture was stirred for further 12 hours, the reaction monitored by TLC until the starting material was consumed completely. Then the reaction was quenched with  $\text{NaHCO}_3$  solution, and then extracted with  $\text{CH}_2\text{Cl}_2$  three times, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and the filtrate was concentrated under reduced pressure. Then the mixture was concentrated and the residue was purified through column chromatography on silica gel using petroleum ether/dichloromethane = 10:1–3:1 as eluent to afford **BF2-DMPCz** as green yellow solid 542 mg in 81% yield. m.p.: 235.3–236.1 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.24 (s, 6H), 7.06–7.10 (m, 1H), 7.26 (dd,  $J = 8.5, 1.0$  Hz 1H), 7.36–7.39 (m, 2H), 7.48–7.52 (m, 6H), 7.53–7.58 (m, 4H), 7.72 (dd,  $J = 8.5, 2.0$  Hz, 2H), 7.74–7.76 (m, 4H), 7.89 (dd,  $J = 8.5, 1.5$  Hz, 1H), 8.07 (s, 1H), 8.42 (d,  $J = 1.4$  Hz, 2H), 8.85 (d,  $J = 6.0$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  20.93, 110.15, 115.94, 119.00, 120.72, 121.00, 121.22, 124.13, 124.24, 125.33, 125.77, 126.22, 126.74, 127.30, 128.81, 128.84, 133.99, 135.00, 136.07, 137.01, 138.41, 140.54, 141.59, 141.75, 150.68, 156.06.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -146.41.  $^{11}\text{B}$  NMR (192.5 MHz,  $\text{CDCl}_3$ )  $\delta$  1.09. HRMS (ESI): calcd for  $\text{C}_{43}\text{H}_{35}^{11}\text{BF}_2\text{N}_3\text{O}$   $[\text{M}+\text{NH}_4]^+$  658.2836, found 658.2843.

## Synthesis of BF2-DMCz:



**Synthesis of 9-(4-bromo-3,5-dimethylphenyl)-9H-carbazole 1c:** 9H-carbazole (1.65 g, 9.85 mmol, 1.3 equiv), CuI (144 mg, 0.76 mmol, 10 mol%) and K<sub>3</sub>PO<sub>4</sub> (4.82 g, 22.73 mmol, 3.0 equiv) were added to a dry sealed tube equipped with a magnetic stir bar. Then the sealed tube was evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then 2,5-dibromo-1,3-dimethylbenzene (2.0 g, 7.58 mmol, 1.0 equiv), *trans*-1,2-diaminocyclohexane (173 mg, 1.52 mmol, 20 mol%) and dry 1,4-dioxane (30 mL) were added to the tube rapidly under nitrogen atmosphere. The mixture was stirred at 110 °C for 44 h, and the reaction monitored by TLC until the reaction was completed. The resulting mixture was cooled down to room temperature, then the solvent was removed and the residue was diluted with ethyl acetate. The mixture was washed with water, separated and then the organic layer dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified through column chromatography on silica gel using petroleum ether/ethyl acetate = 100:1 as eluent to afford the desired product as yellow white solid 2.34 g in 88% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.52 (s, 6H), 7.27–7.30 (m, 4H), 7.37–7.43 (m, 4H), 8.13 (d, *J* = 7.5 Hz, 2H).

**Synthesis of 9-(3,5-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole 2c:** 9-(4-Bromo-3,5-dimethylphenyl)-9H-carbazole **1c** (1.70 g, 4.85 mmol, 1.0 equiv) was added to a dry three-necked flask equipped with a magnetic stir bar. The flask was evacuated and



backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then anhydrous THF (70 mL) was added under nitrogen atmosphere. After cooling it to  $-76\text{ }^{\circ}\text{C}$  using liquid nitrogen, *n*-BuLi (3.18 mL, 5.09 mmol, 1.05 equiv, 1.60 M in hexane) was dropped slowly, followed by stirring for 1 hour, and then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.08 g, 5.82 mmol, 1.2 equiv) was added to the cold reaction mixture. The resulting solution was then allowed to raise to room temperature and stirred for further 13 hours. Then the mixture was quenched with a saturated solution of  $\text{NH}_4\text{Cl}$  in water, and then extracted with ethyl acetate three times, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and the filtrate was concentrated under reduced pressure. The residue was purified through column chromatography on silica gel using petroleum ether/ethyl acetate = 100:1 as eluent to afford the desired product as white solid 1.28 g in 66% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.45 (s, 12H), 2.51 (s, 6H), 7.16 (s, 2H), 7.25–7.28 (m, 2H), 7.37–7.41 (m, 4H), 8.12 (dt,  $J = 8.0, 1.0$  Hz, 2H).

**Synthesis of 9-(4-(2-(2-methoxyphenyl)pyridin-4-yl)-3,5-dimethylphenyl)-9H-carbazole 3c:**

9-(3,5-Dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole **2c** (1.28 g, 3.22 mmol, 1.0 equiv), 4-bromo-2-(2-methoxyphenyl)pyridine **BrPyPOCH<sub>3</sub>** (936 mg, 3.54 mmol, 1.1 equiv, which was synthesized according previous report.<sup>4</sup>),  $\text{Pd}(\text{PPh}_3)_4$  (74 mg, 0.064 mmol, 2 mol%), and  $\text{K}_2\text{CO}_3$  (1.33 g, 9.66 mmol, 3.0 equiv) were added to a dry three-necked flask equipped with a magnetic stir bar. Then the flask was evacuated and backfilled with nitrogen, this evacuation and backfilled procedure was repeated twice. Then 1,4-dioxane (20 mL) and  $\text{H}_2\text{O}$  (4 mL) were added to the mixture under nitrogen atmosphere. The mixture was stirred at  $95\text{ }^{\circ}\text{C}$  for 60 h, and the reaction monitored by TLC until the reaction was completed. Then the resulting mixture was cooled down to room temperature, then the solvent was removed and the residue was diluted with ethyl acetate. The mixture was washed with water, the organic layer was separated, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and the filtrate was concentrated under reduced pressure. The residue was purified through column chromatography on silica gel using petroleum ether/dichloromethane/ethyl acetate = 20:1:1 as eluent to afford **3c** as white solid 1.00 g in 68% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ )  $\delta$  2.19 (s, 6H), 3.85 (s, 3H), 7.11 (td,  $J = 7.5, 1.0$  Hz, 1H), 7.18 (dd,  $J = 8.0, 1.0$  Hz, 1H), 7.29–7.32 (m, 3H), 7.42–7.44 (m, 1H), 7.45–7.48 (m, 4H), 7.51 (dt,  $J = 8.0, 1.0$  Hz, 2H), 7.77 (q,  $J = 1.0$  Hz, 1H), 7.85 (dd,  $J = 7.5, 2.0$  Hz, 1H), 8.26 (dt,  $J = 7.5, 1.0$  Hz, 2H), 8.80 (dd,  $J = 5.0, 1.0$  Hz, 1H).

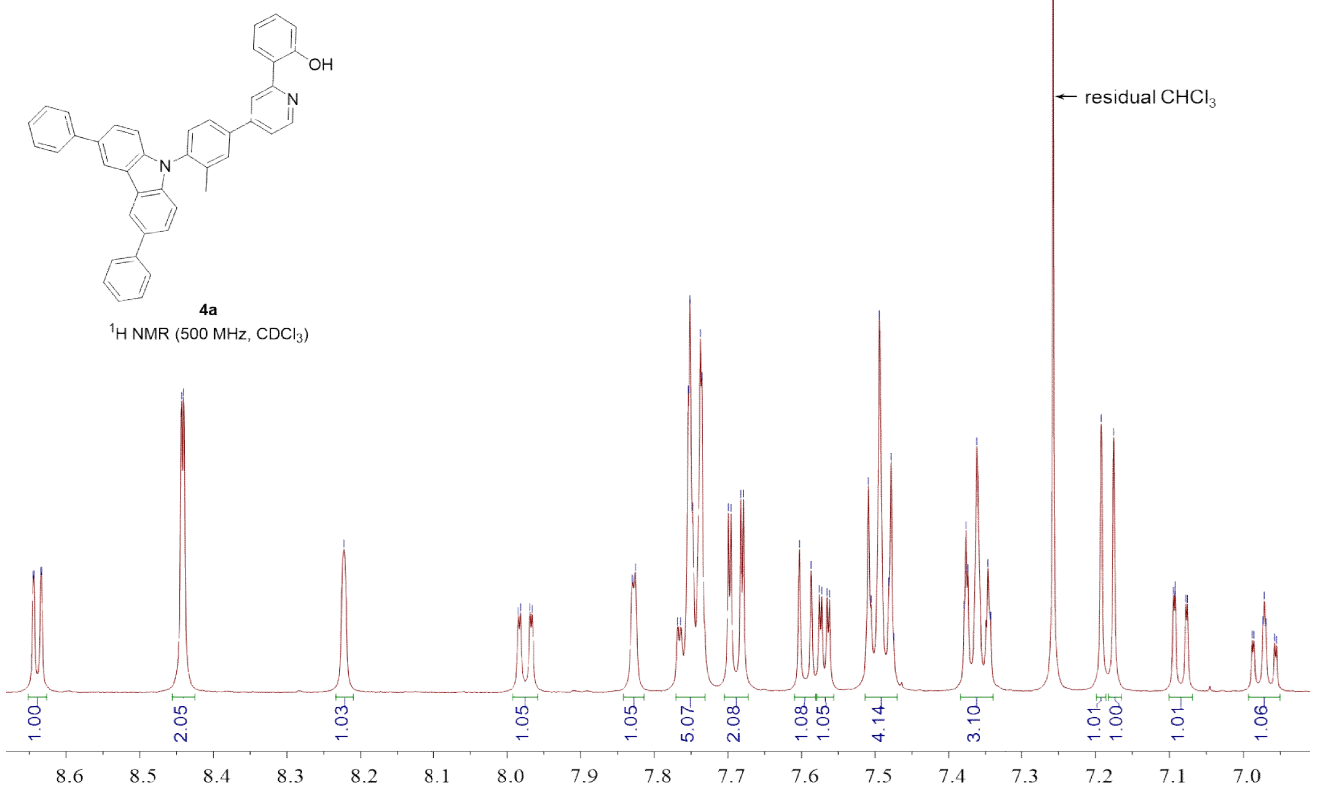
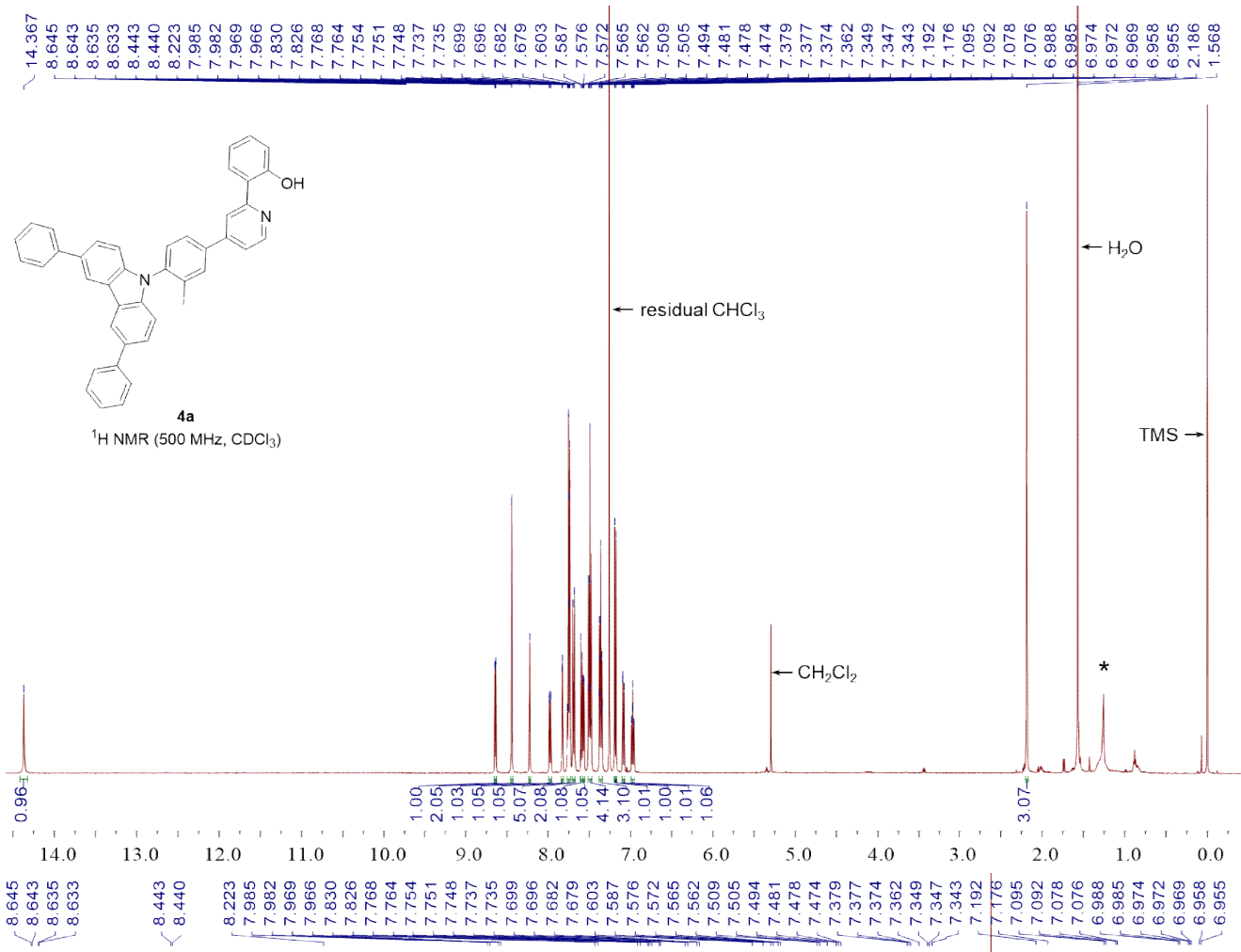
**Synthesis of 2-(4-(4-(9*H*-carbazol-9-yl)-2,6-dimethylphenyl)pyridin-2-yl)phenol 4c:** 9-(4-(2-(2-Methoxyphenyl)pyridin-4-yl)-3,5-dimethylphenyl)-9*H*-carbazole **3c** (1.00 g, 2.20 mmol, 1.0 equiv) was added to a dry three-necked flask equipped with a magnetic stir bar. Then the flask was evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice. Then dry CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added under nitrogen atmosphere. The mixture was stirred at -15 °C for 10 min, then BBr<sub>3</sub> (0.42 mL, 1.10 g, 4.40 mmol, 2.0 equiv) was dropped slowly. The mixture was stirred at -15 °C for 1.5 hour and then the temperature of the mixture allowed to raised to room temperature and stirred for further 11 hours. The reaction monitored by TLC until the reaction was completed. Then the reaction was quenched with NaHCO<sub>3</sub> solution, and then extracted with CH<sub>2</sub>Cl<sub>2</sub> three times, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified through column chromatography on silica gel using petroleum ether/dichloromethane/ethyl acetate = 50:2:1 as eluent to afford **4c** as yellow white solid 680 mg in 70% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.18 (s, 6H), 6.91–6.94 (m, *J* = 1H), 7.08 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.20 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.30–7.37 (m, 3H), 7.38 (s, 2H), 7.43–7.46 (m, 2H), 7.51 (dt, *J* = 8.5, 1.0 Hz, 2H), 7.85 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.87 (s, 1H), 8.17 (dt, *J* = 7.5, 1.0 Hz, 2H), 8.66 (dd, *J* = 5.0, 1.0 Hz, 1H), 14.40 (s, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 20.81, 109.83, 118.74, 118.83, 119.78, 119.96, 120.33, 122.32, 123.42, 125.91, 126.02, 126.22, 131.72, 137.12, 137.43, 137.93, 140.80, 146.29, 150.83, 158.33, 160.11. HRMS (ESI): calcd for C<sub>31</sub>H<sub>25</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 441.1961, found 441.1961.

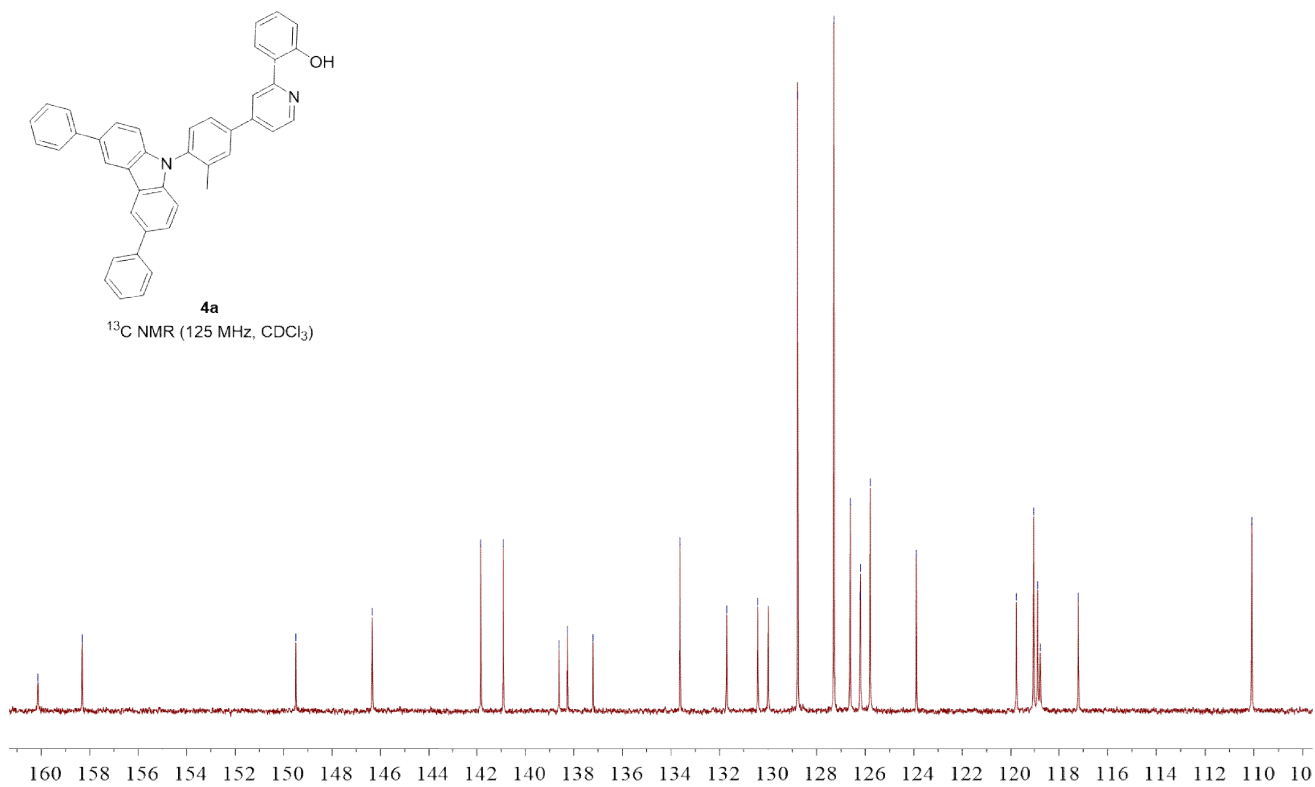
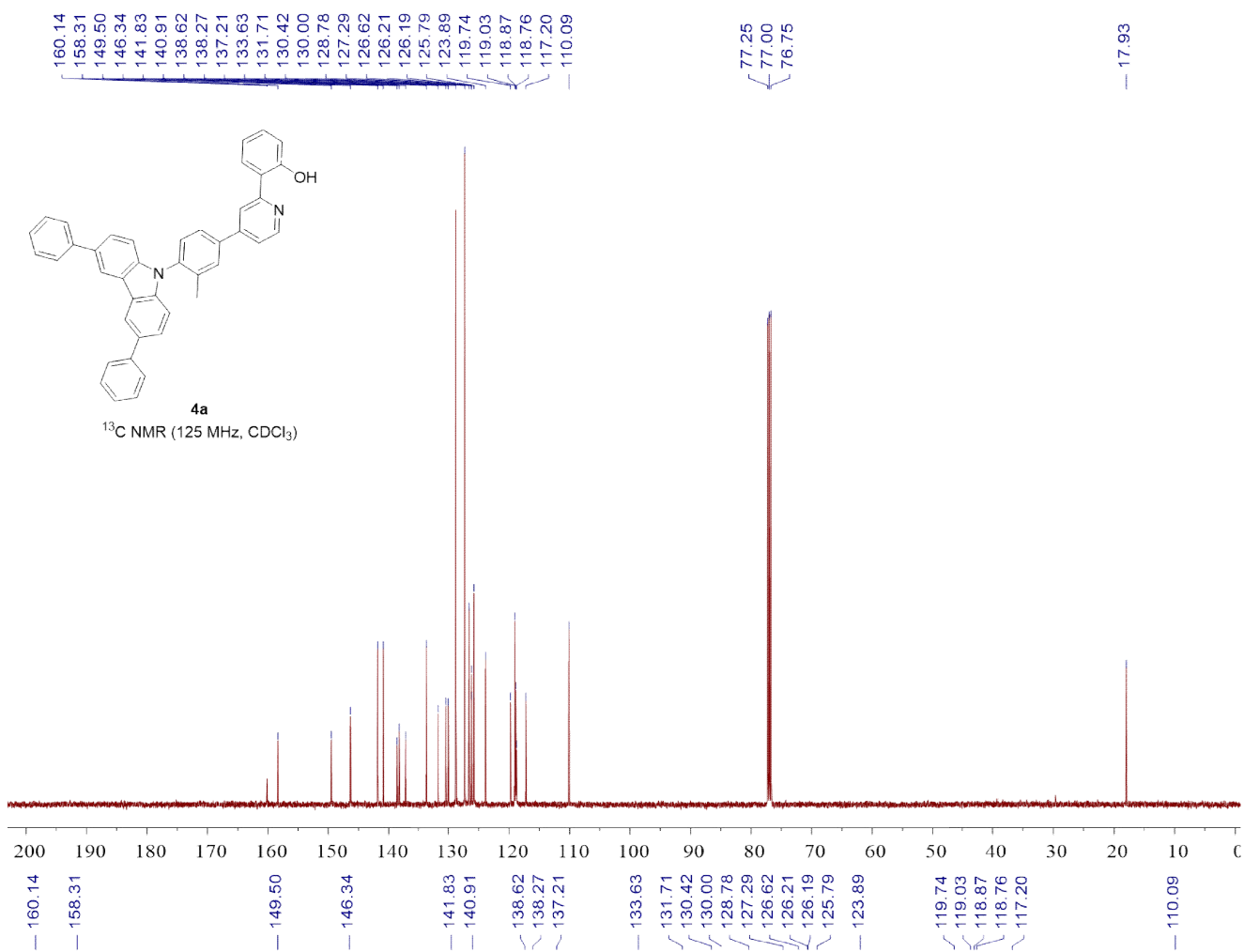
**Synthesis of BF<sub>2</sub>-DMCz:** 2-(4-(4-(9*H*-Carbazol-9-yl)-2,6-dimethylphenyl)pyridin-2-yl)phenol **4c** (640 mg, 1.45 mmol, 1.0 equiv) was add to a dry three-necked flask equipped with a magnetic stir bar. The flask then evacuated and backfilled with nitrogen, this evacuation and backfill procedure repeated twice. Then dry CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added under nitrogen atmosphere, and then Et<sub>2</sub>O·BF<sub>3</sub> (0.55 mL, 617 mg, 4.35 mmol, 3.0 equiv) was added to the flask. The mixture was stirred at room temperature for 4 hours, after that, *N,N*-Diisopropylethylamine (DIPEA) (1.01 mL, 749 mg, 5.80 mmol, 4.0 equiv) was added, and the mixture was stirred for further 13 hours, the reaction monitored by TLC until the starting material was consumed completely. Then the reaction was quenched with NaHCO<sub>3</sub> solution, and then extracted with CH<sub>2</sub>Cl<sub>2</sub> three times, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and the filtrate was concentrated under reduced pressure. Then the mixture was concentrated and the residue

was purified through column chromatography on silica gel using petroleum ether/dichloromethane = 10:1–1:3 as eluent to afford **BF2-DMCz** as white solid 545 mg in 77% yield. m.p.: 240.1–241.0 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.21 (s, 6H), 7.05–7.09 (m, 1H), 7.26 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.31–7.34 (m, 2H), 7.43–7.47 (m, 4H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.53–7.56 (m, 2H), 7.88 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.06 (s, 1H), 8.17 (d, *J* = 7.5 Hz, 2H), 8.84 (d, *J* = 6.0 Hz, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 20.87, 109.72, 115.93, 120.22, 120.44, 120.70, 120.97, 121.22, 123.56, 124.15, 125.33, 126.03, 126.36, 134.96, 135.94, 136.86, 138.49, 140.63, 141.55, 150.63, 156.12, 156.19. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ –146.38. <sup>11</sup>B NMR (192.5 MHz, CDCl<sub>3</sub>) δ 1.07. HRMS (ESI): calcd for C<sub>31</sub>H<sub>27</sub><sup>11</sup>BF<sub>2</sub>N<sub>3</sub>O [M+NH<sub>4</sub>]<sup>+</sup> 506.2210, found 506.2221.

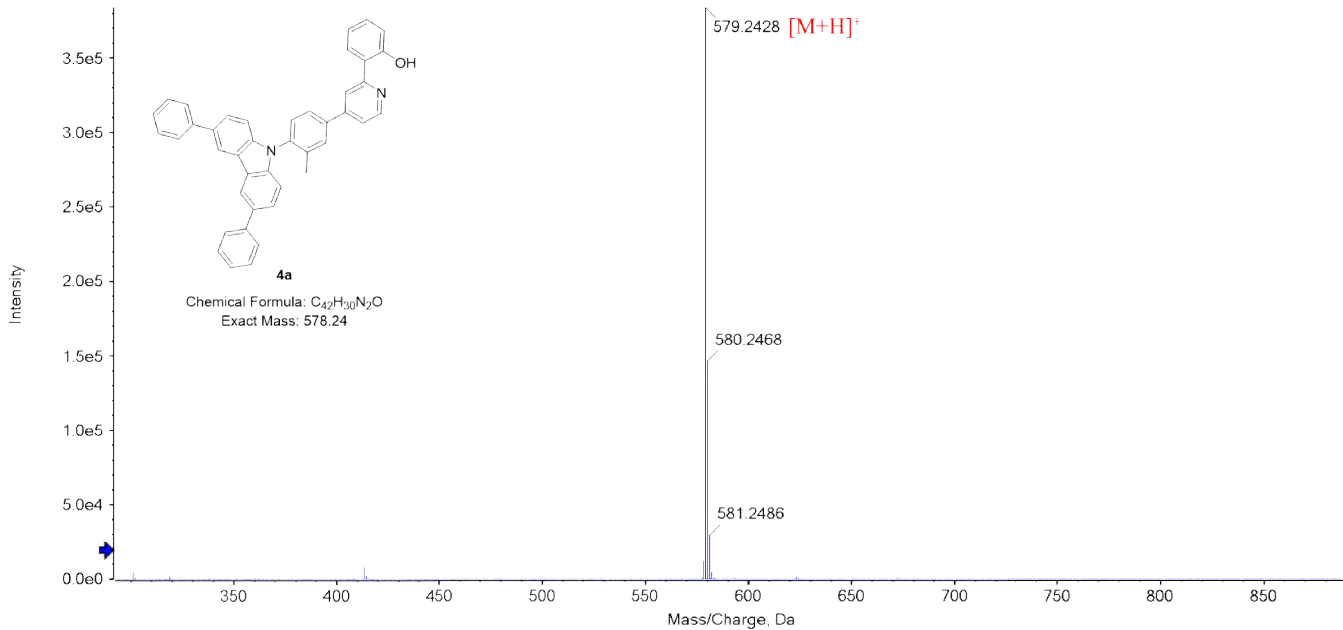
### References:

- (1) G. Li, A. Wolfe, J. Brooks, Z.-Q. Zhu, and J. Li, *Inorg. Chem.*, 2017, **56**, 8244–8256.
- (2) N. G. Connelly, and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877–910.
- (3) D. C. Harris, In *Quantitative Chemical Analysis*, 6th ed.; W. H. Freeman: New York, 2002; pp 394–396.
- (4) G. Li, W. Lou, D. Wang, C. Deng and Q. Zhang, *ACS Appl. Mater. Interfaces*, 2019, **11**, 32209–32217.
- (5) P. Li, H. Chan, S.-L. Lai, M. Ng, M.-Y. Chan and V. W.-W. Yam, *Angew. Chem., Int. Ed.*, 2019, **58**, 90
- (6) Y.-J. Shiu, Y.-C. Cheng, W.-L. Tsai, C.-C. Wu, C.-T. Chao, C.-W. Lu, Y. Chi, Y.-T. Chen, S.-H. Liu and P.-T. Chou, *Angew. Chem., Int. Ed.*, 2016, **55**, 3017–3021.
- (7) B. M. Bell, T. P. Clark, T. S. De Vries, Y. Lai, D. S. Laitar, T. J. Gallagher, J.-H. Jeon, K. L. Kearns, T. McIntire, S. Mukhopadhyay, H.-Y. Na, T. D. Paine and A. A. Rachford, *Dyes Pigm.*, 2017, **141**, 83–92.
- (8) D. Zhou, D. H. Liu, X. Gong, H. L. Ma, G. W. Qian, S. L. Gong, G. H. Xie, W. G. Zhu and Y. F. Wang, *ACS Appl. Mater. Interfaces*, 2019, **11**, 24339–24348.
- (9) K. Matsuo, T. Yasuda and C. Adachi, *Chem. Commun.*, 2017, **53**, 8723–8726.
- (10) Y.-J. Shiu, Y.-T. Chen, W.-K. Lee, C.-C. Wu, T.-C. Lin, S.-H. Liu, P.-T. Chou, C.-W. Lu, I.-C. Cheng, Y.-J. Lien, Y. Chi, *J. Mater. Chem. C* **2017**, **5**, 1452–1462.

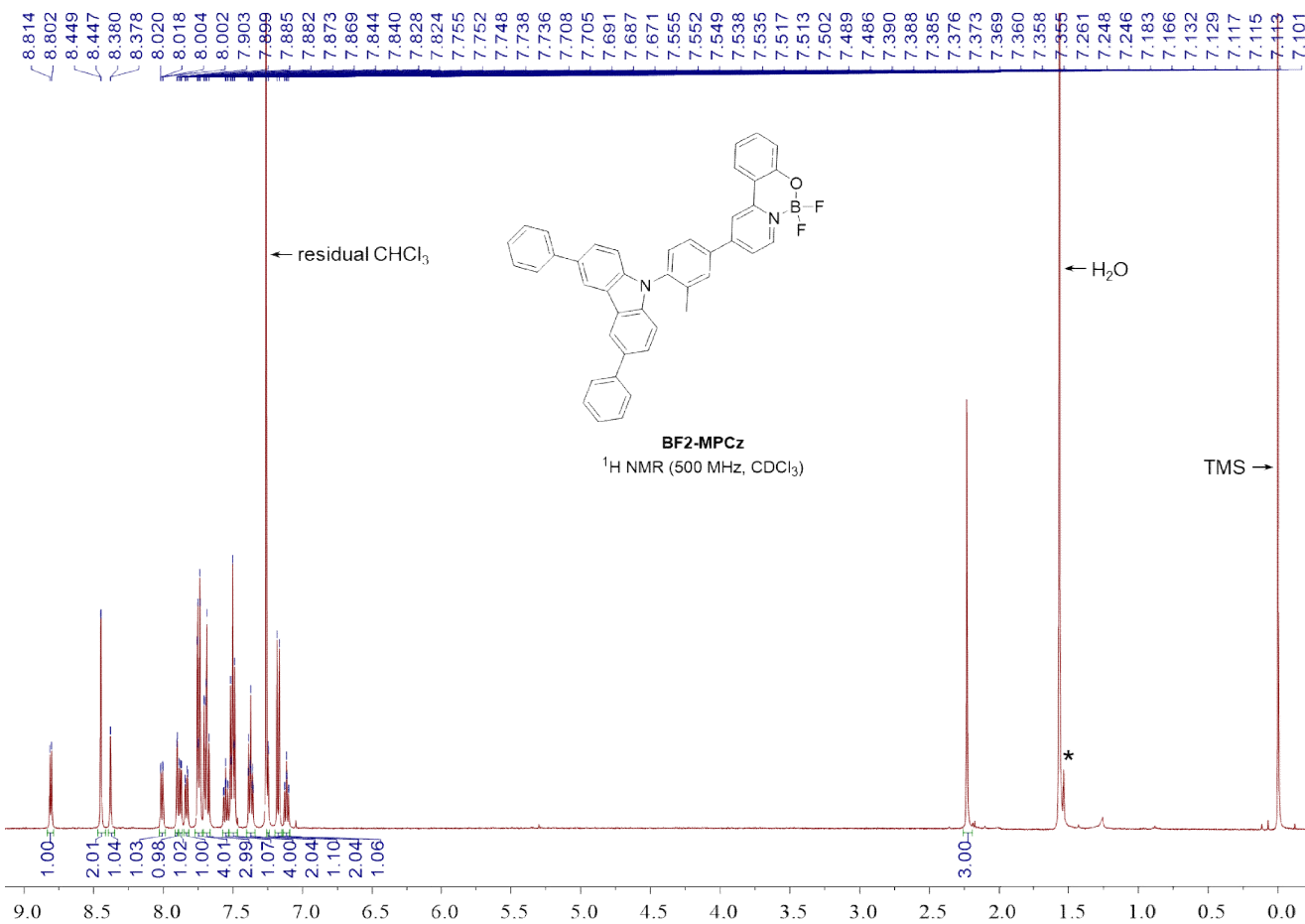


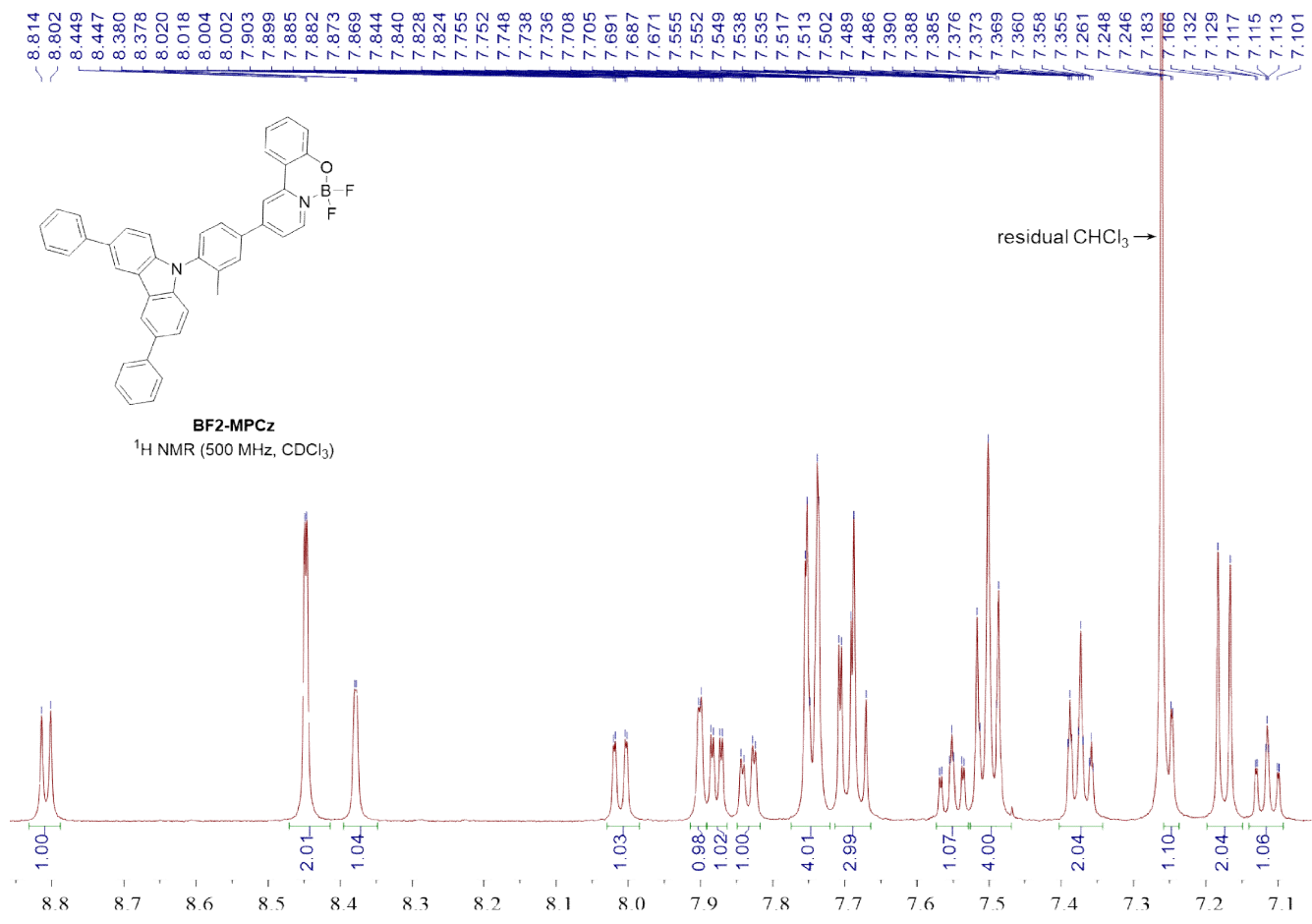


Spectrum from 0812.wiff (sample 24) - BFMPcZ-OH, +TOF MS (100 - 2000) from 0.149 to 0.0...from 0812.wiff (sample 24) - BFMPcZ-OH, +TOF MS (100 - 2000) from 0.372 to 0.418 min)



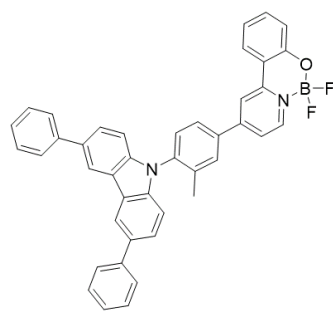
Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
C <sub>42</sub> H <sub>30</sub> N <sub>2</sub> O	C <sub>42</sub> H <sub>31</sub> N <sub>2</sub> O	579.2428	579.2431	-0.6



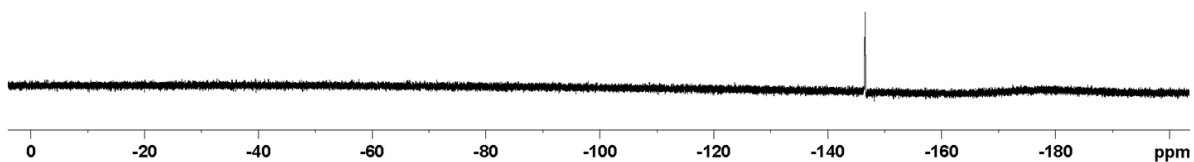


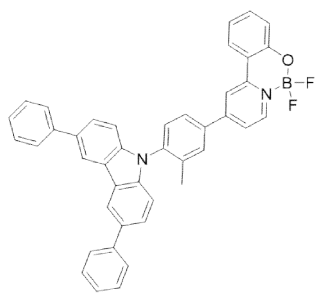
BF2 CDCl3

— -146.59



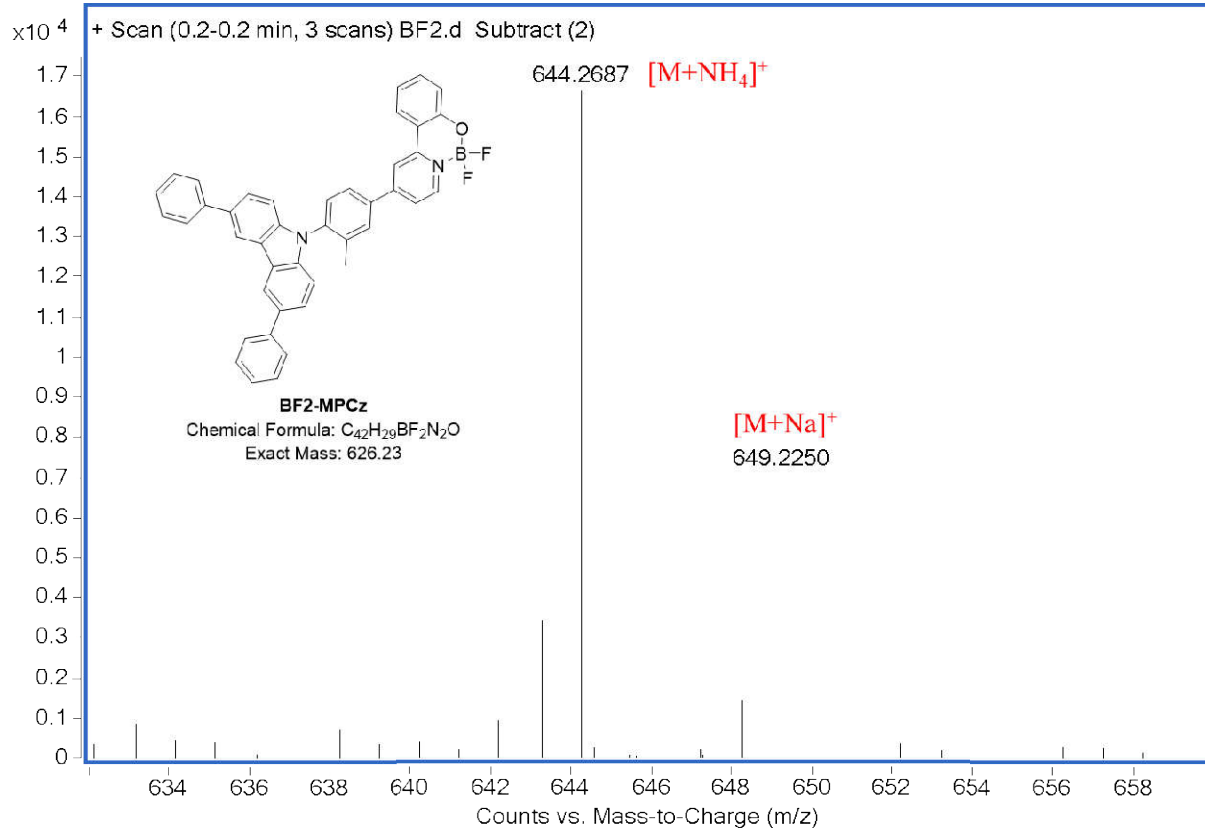
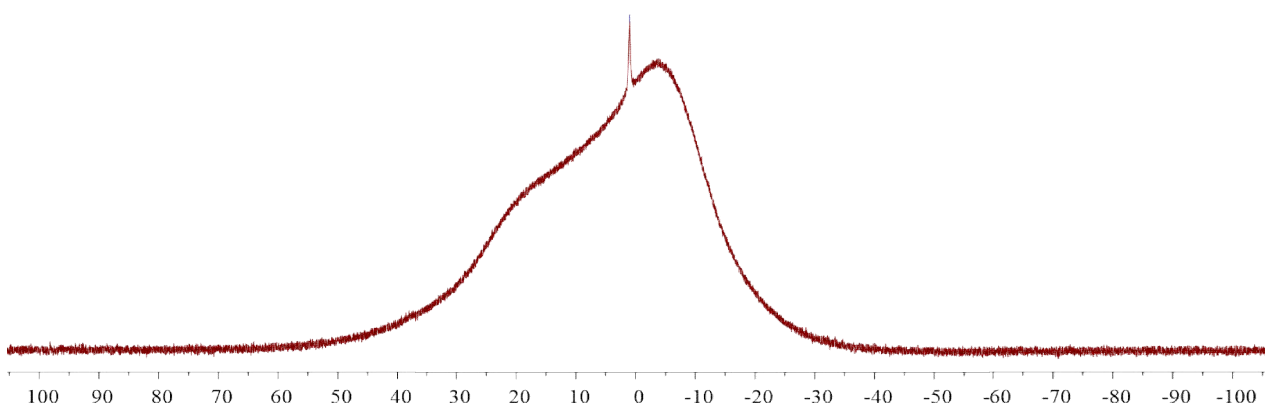
**BF2-MPCz**  
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)





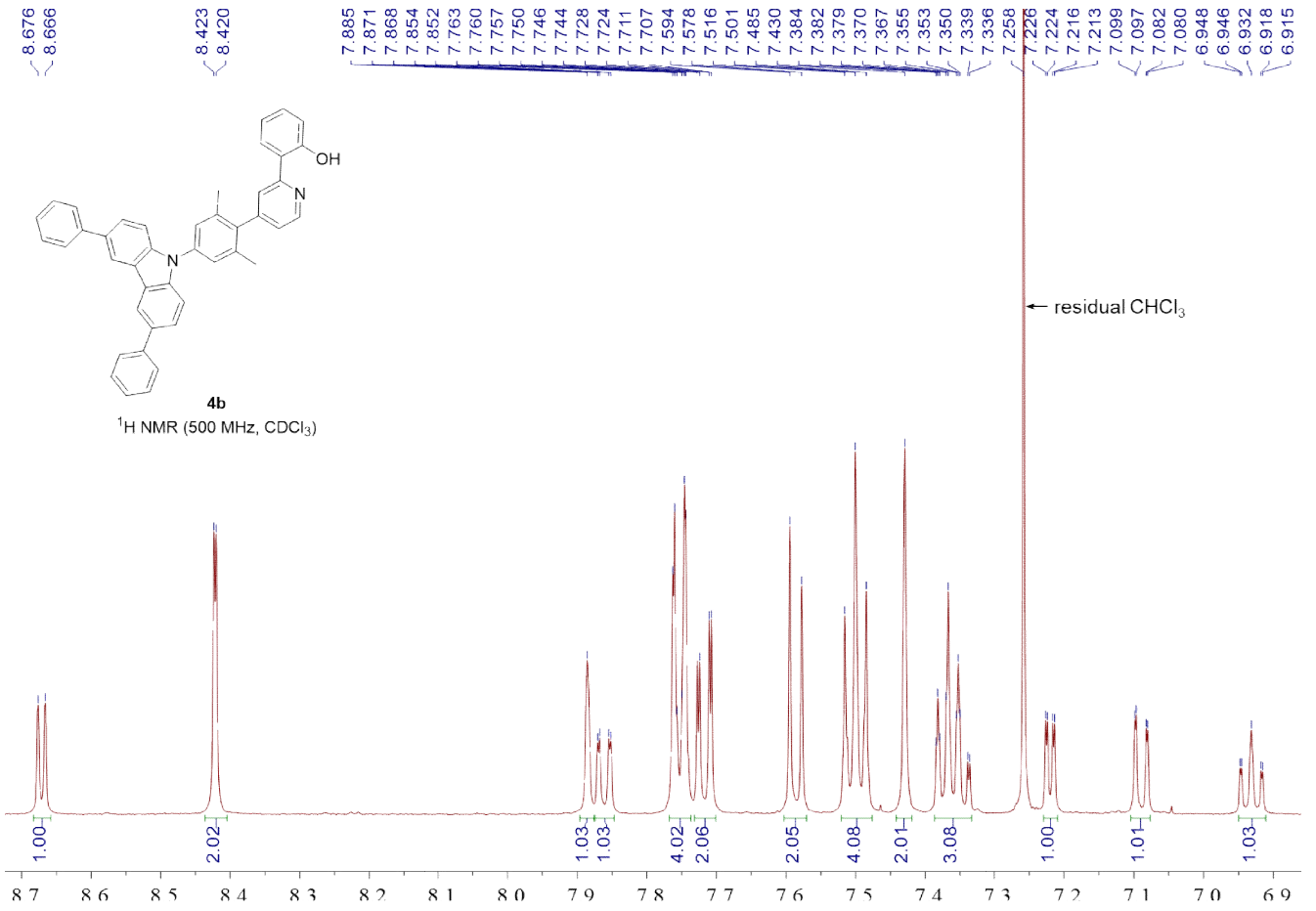
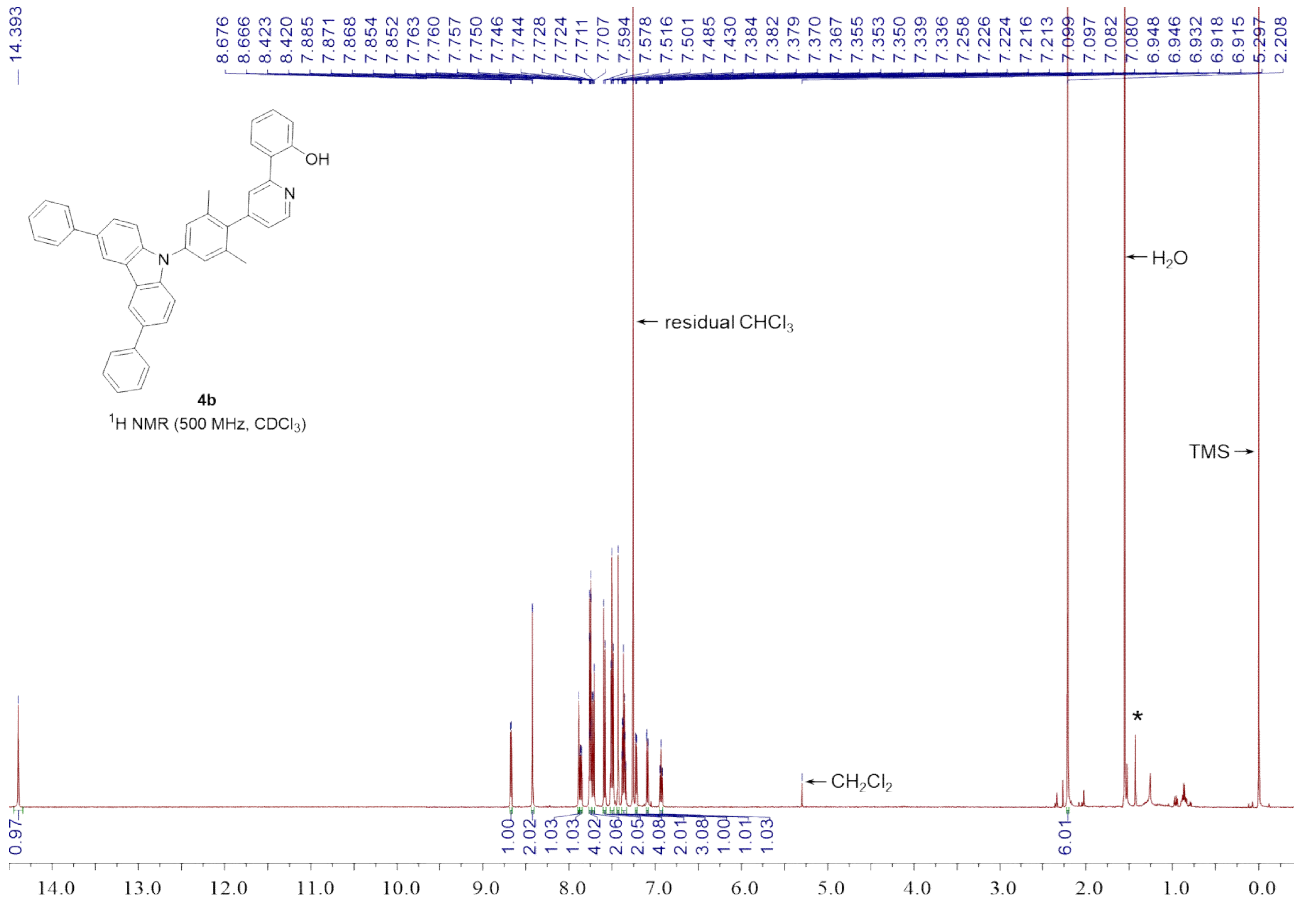
**BF2-MPCz**  
 $^{11}\text{B}$  NMR (192.5 MHz,  $\text{CDCl}_3$ )

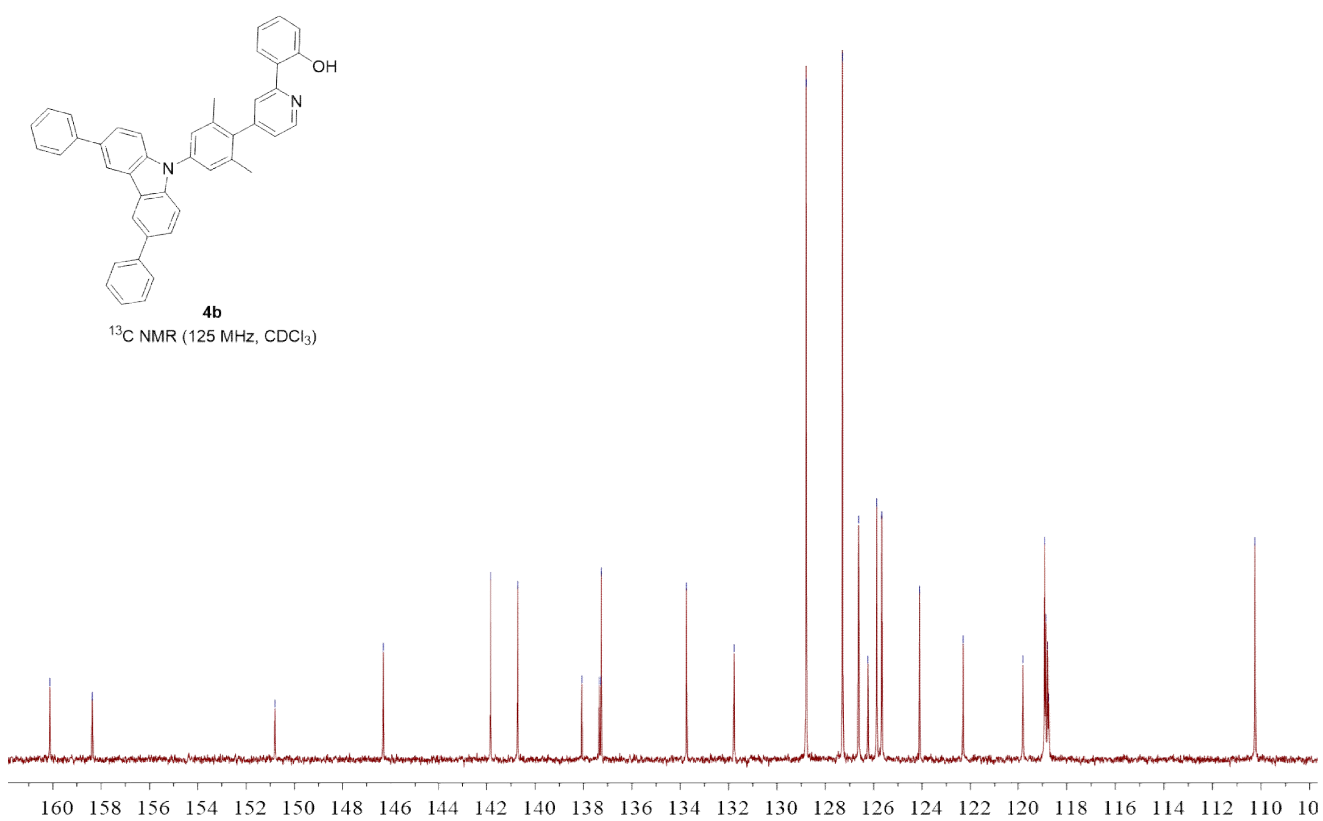
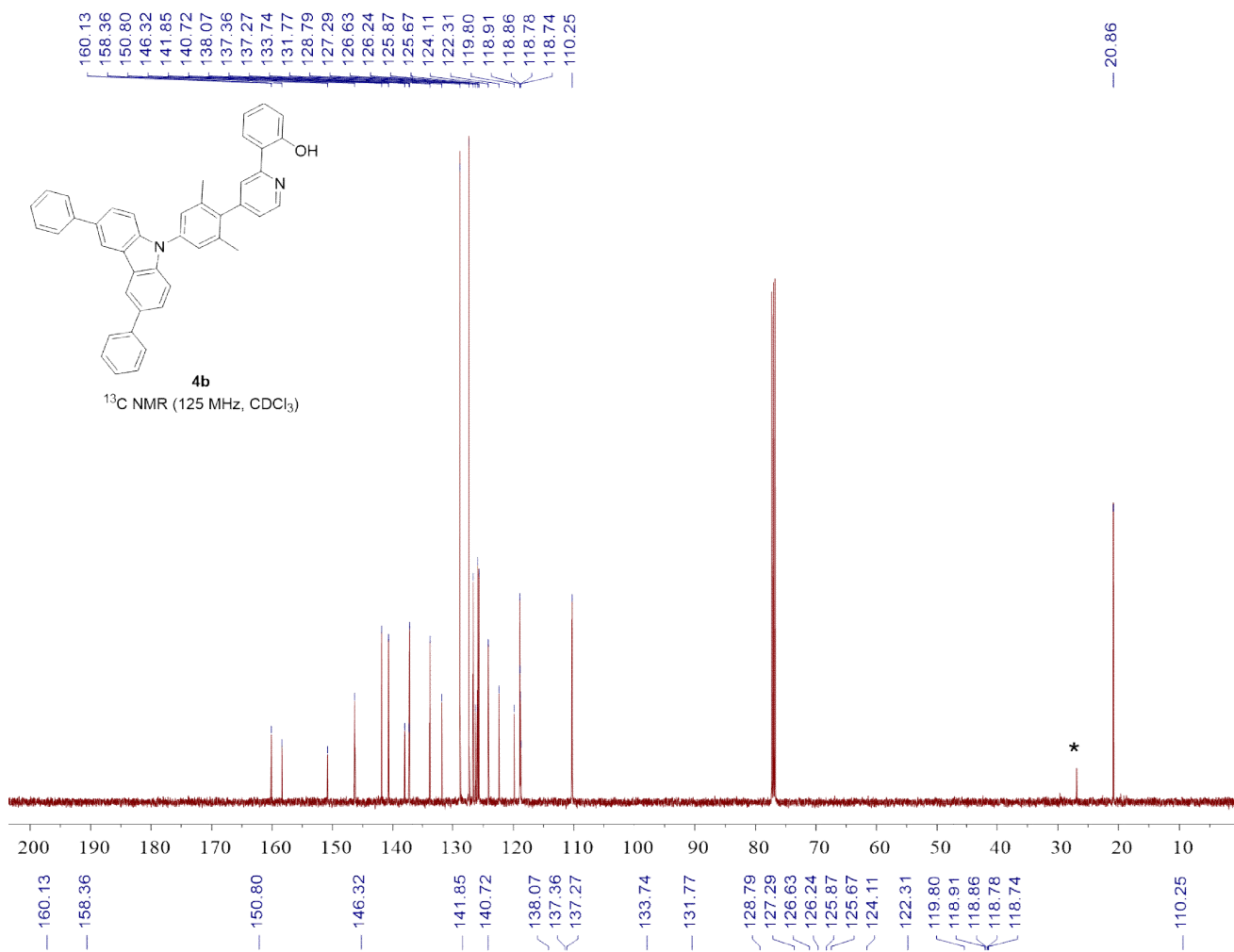
1.031



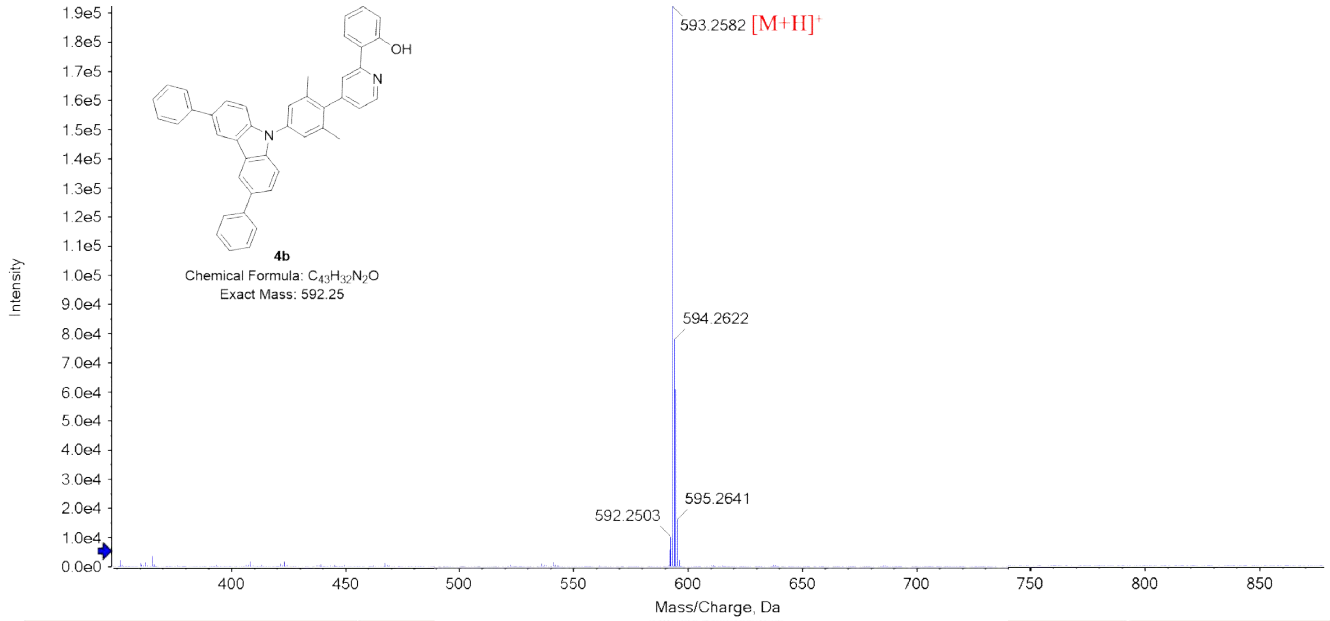
Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
$\text{C}_{42}\text{H}_{29}[^{11}\text{B}]\text{F}_2\text{N}_2\text{O}$	$\text{C}_{42}\text{H}_{33}[^{11}\text{B}]\text{F}_2\text{N}_3\text{O}$	644.2687	644.2679	-1.24



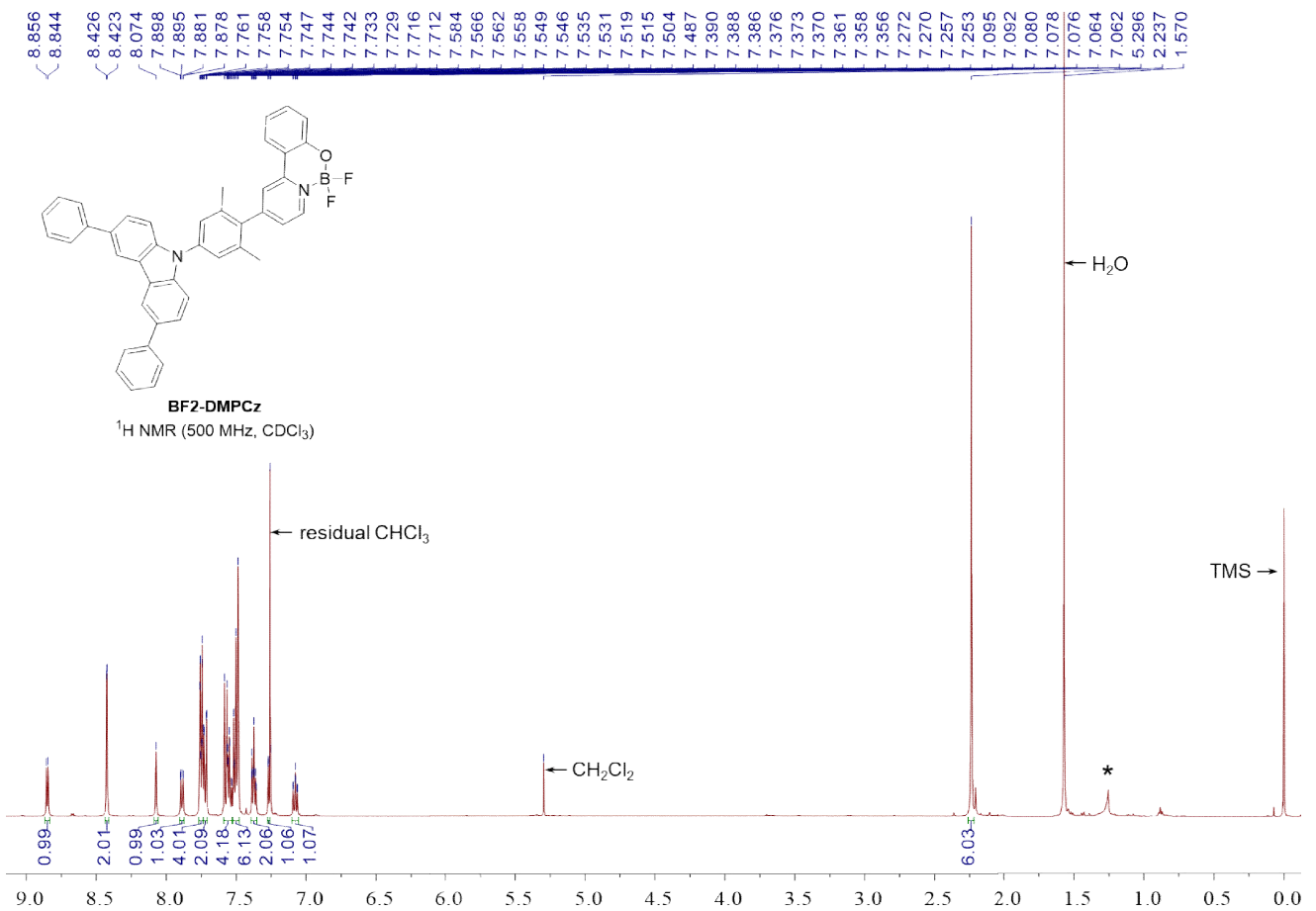


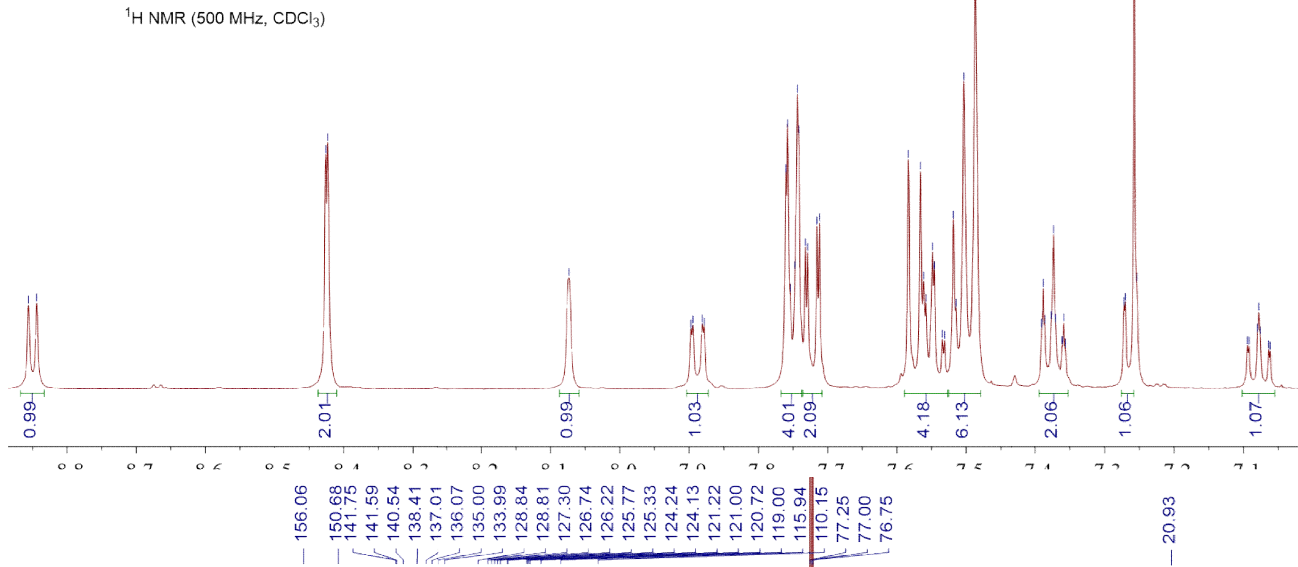
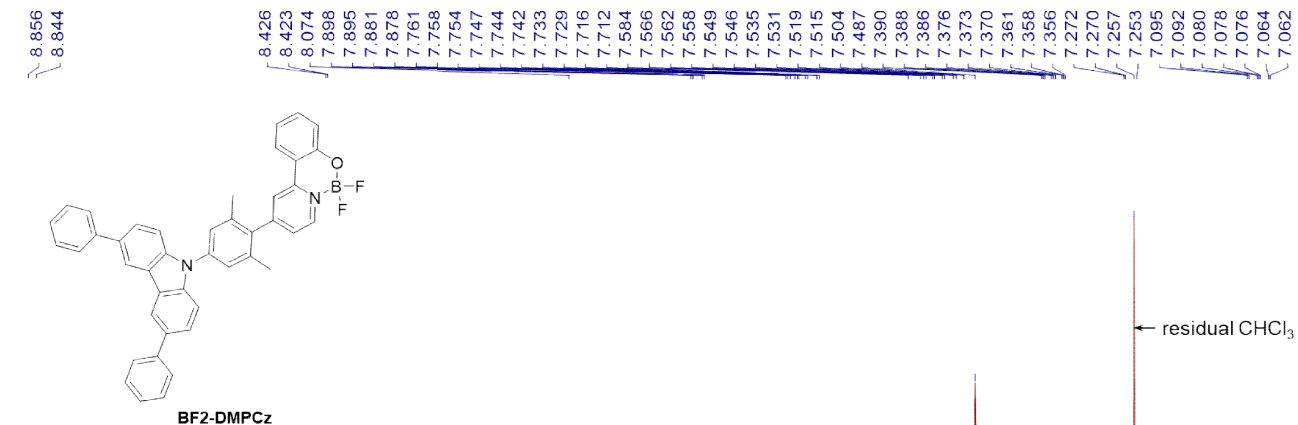


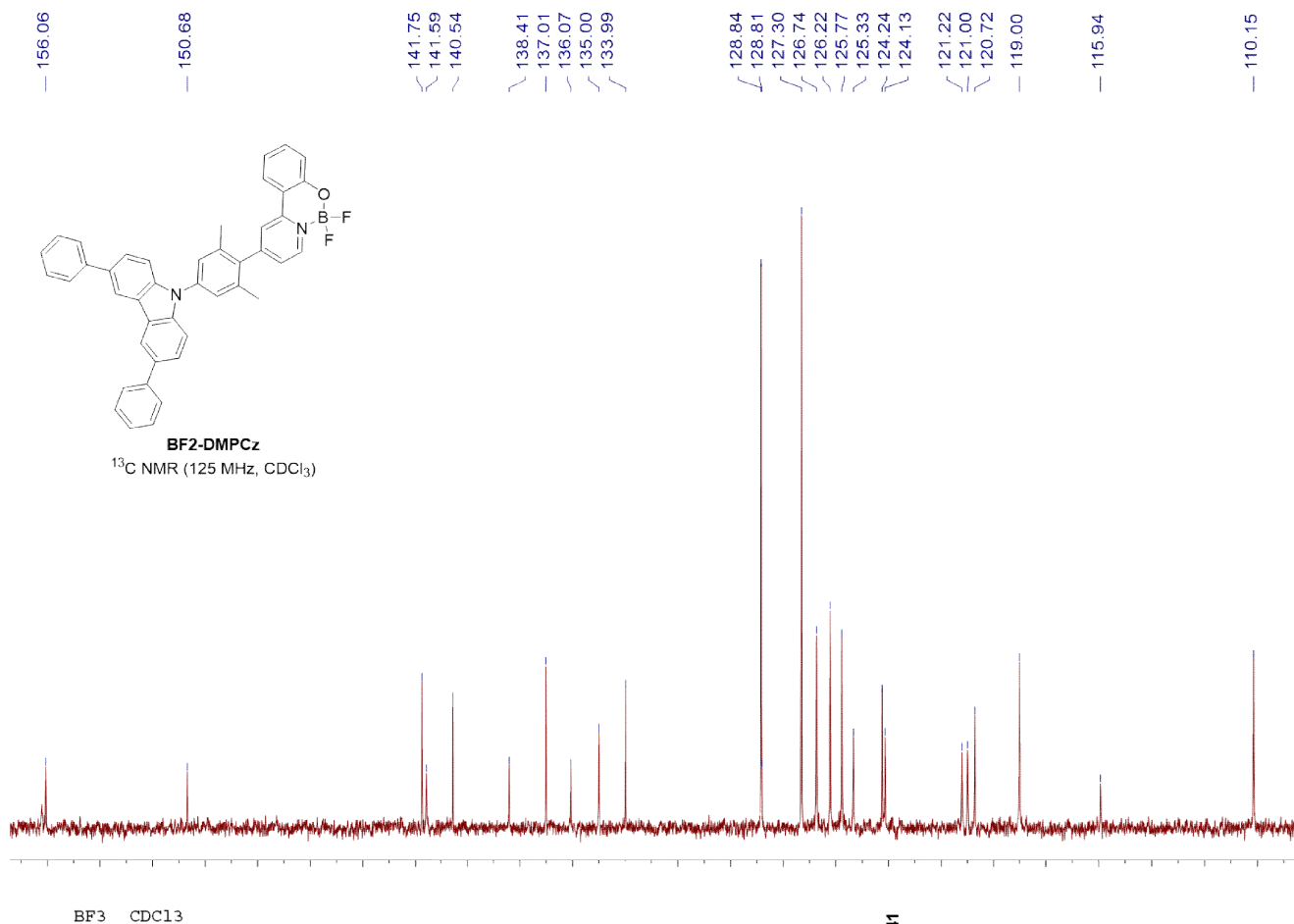
Spectrum from 0812.wiff (sample 22) - BFDMPCz-OH, +TOF MS (100 - 2000) from 0.126 to 0.200 min



Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
C <sub>43</sub> H <sub>32</sub> N <sub>2</sub> O	C <sub>43</sub> H <sub>33</sub> N <sub>2</sub> O	593.2582	593.2587	-0.8

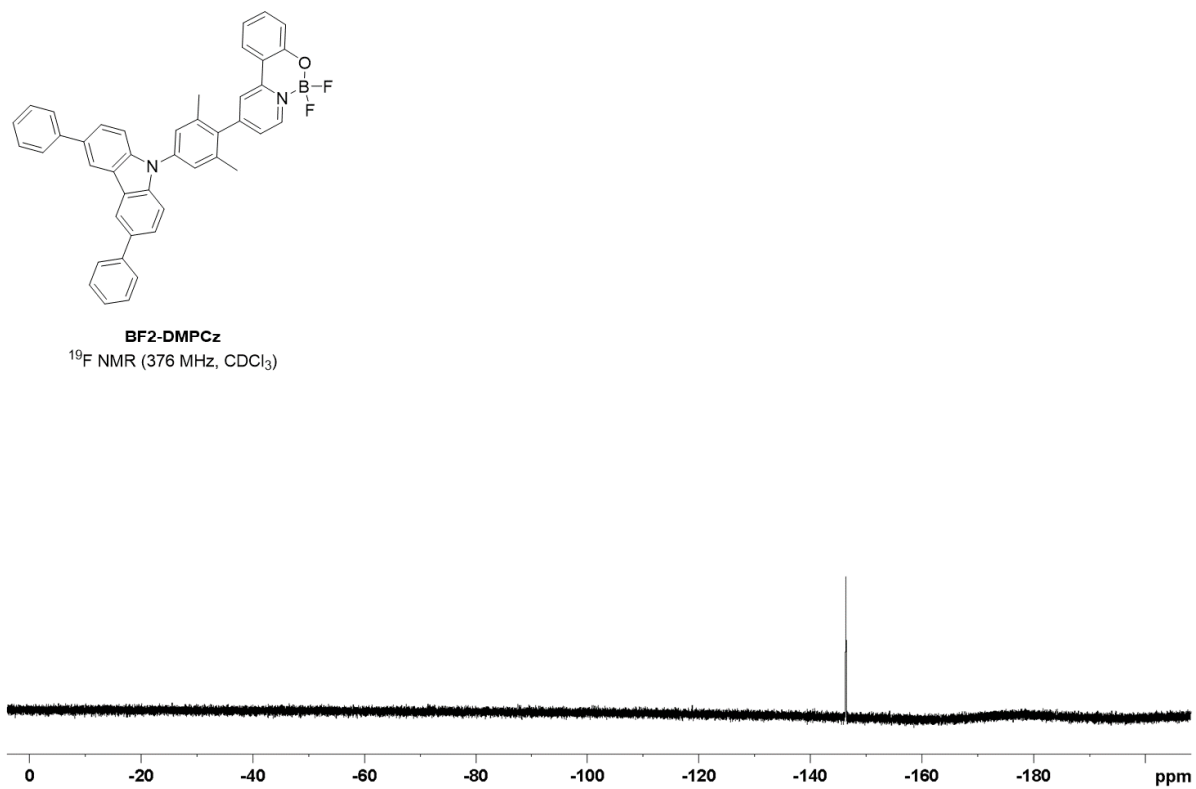


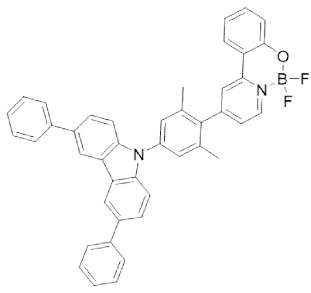




$\text{BF}_3 \quad \text{CDCl}_3$

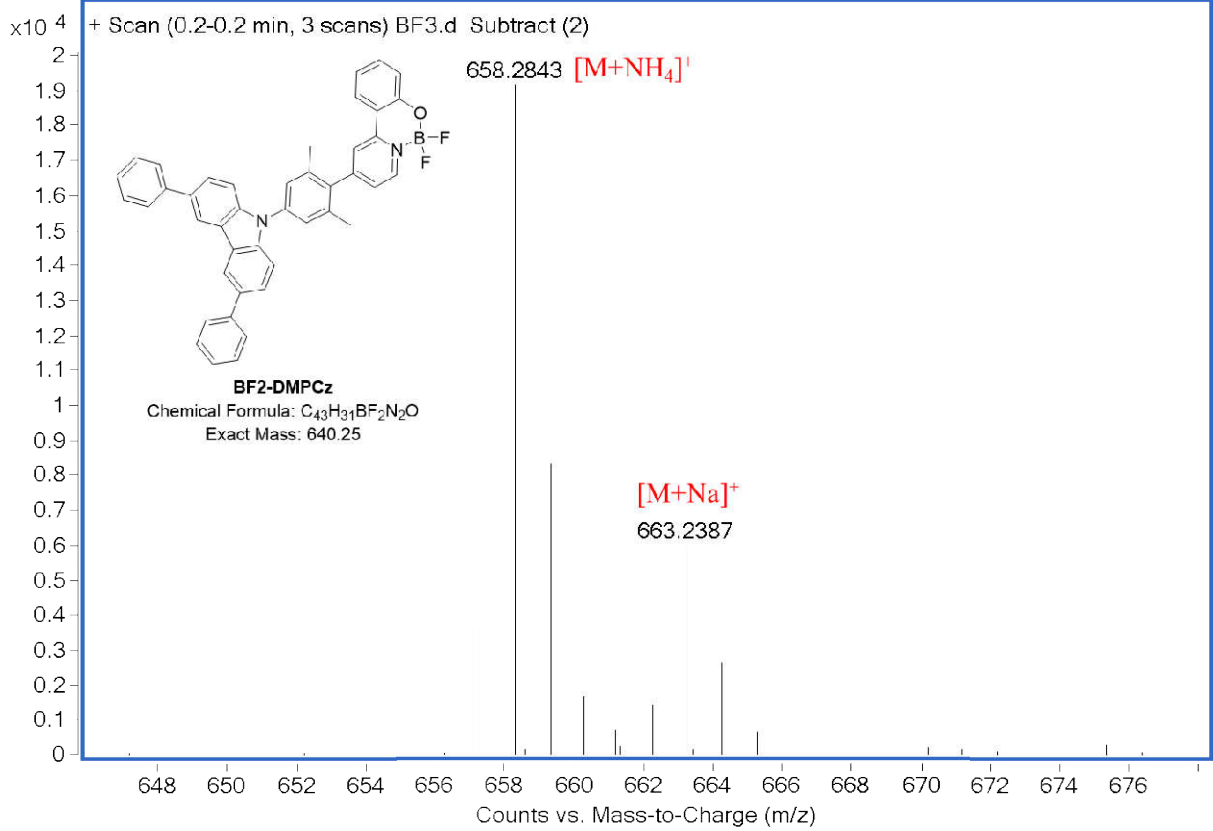
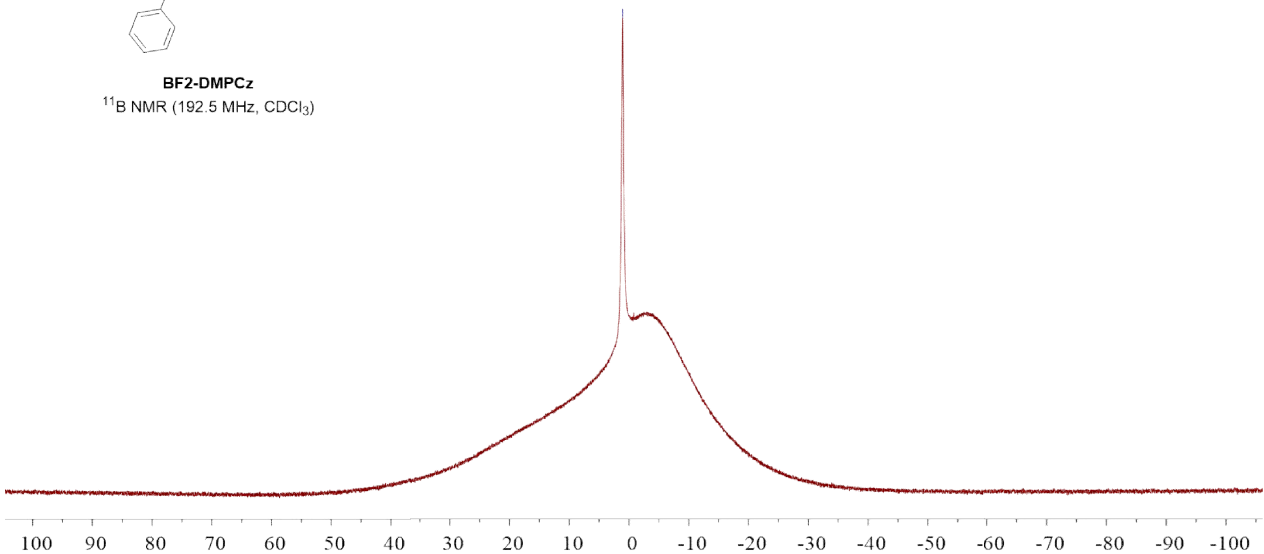
-146.41



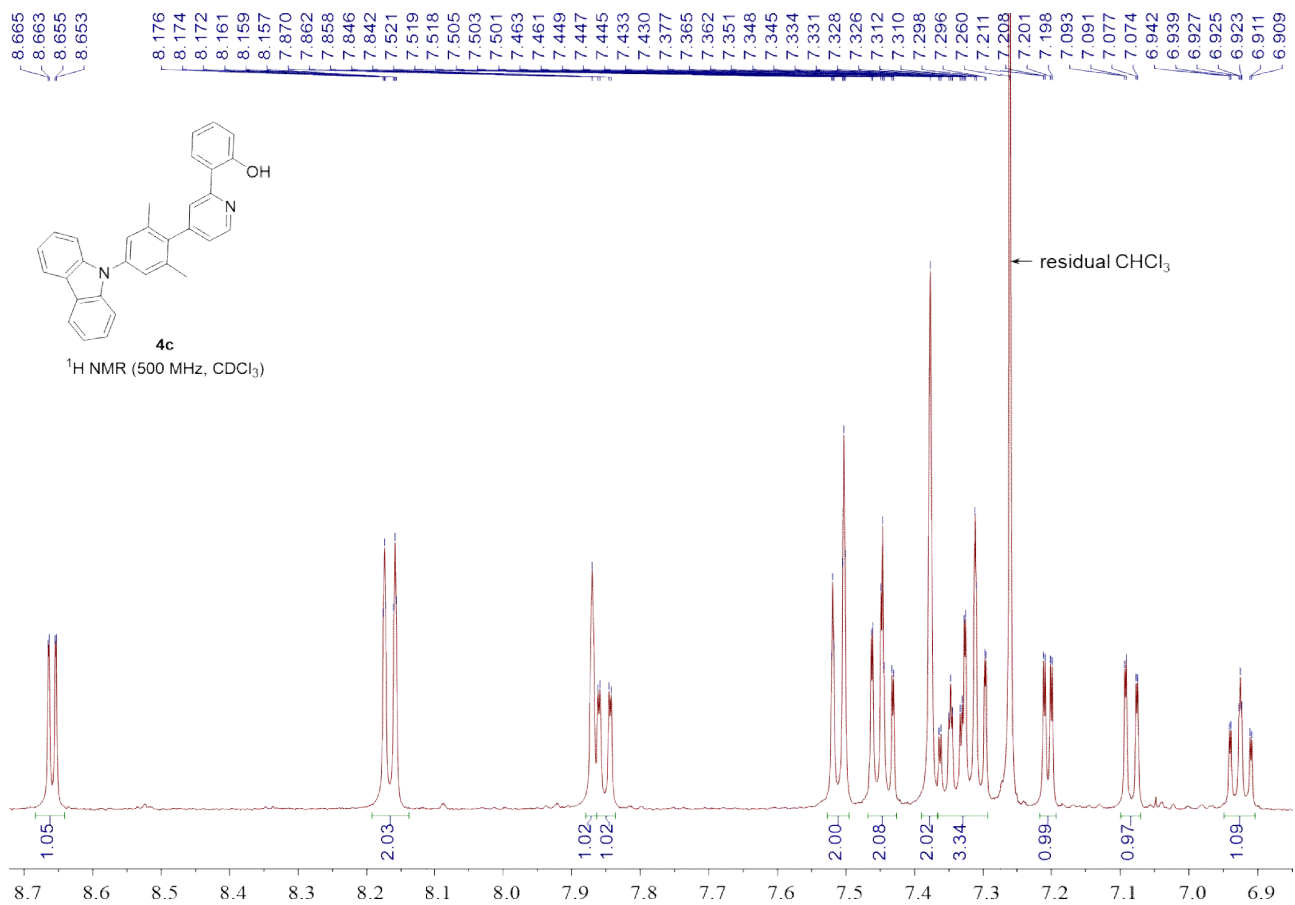
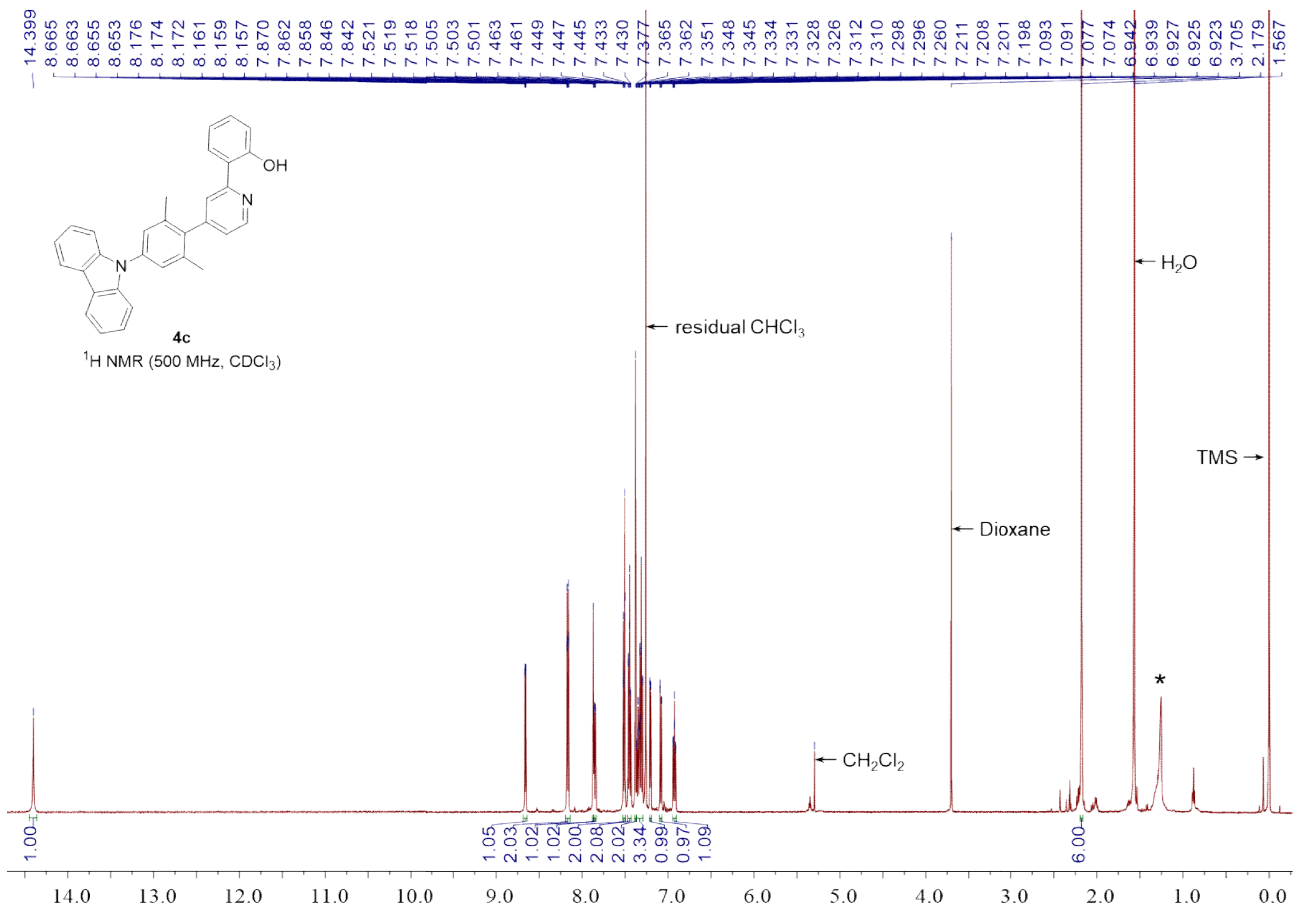


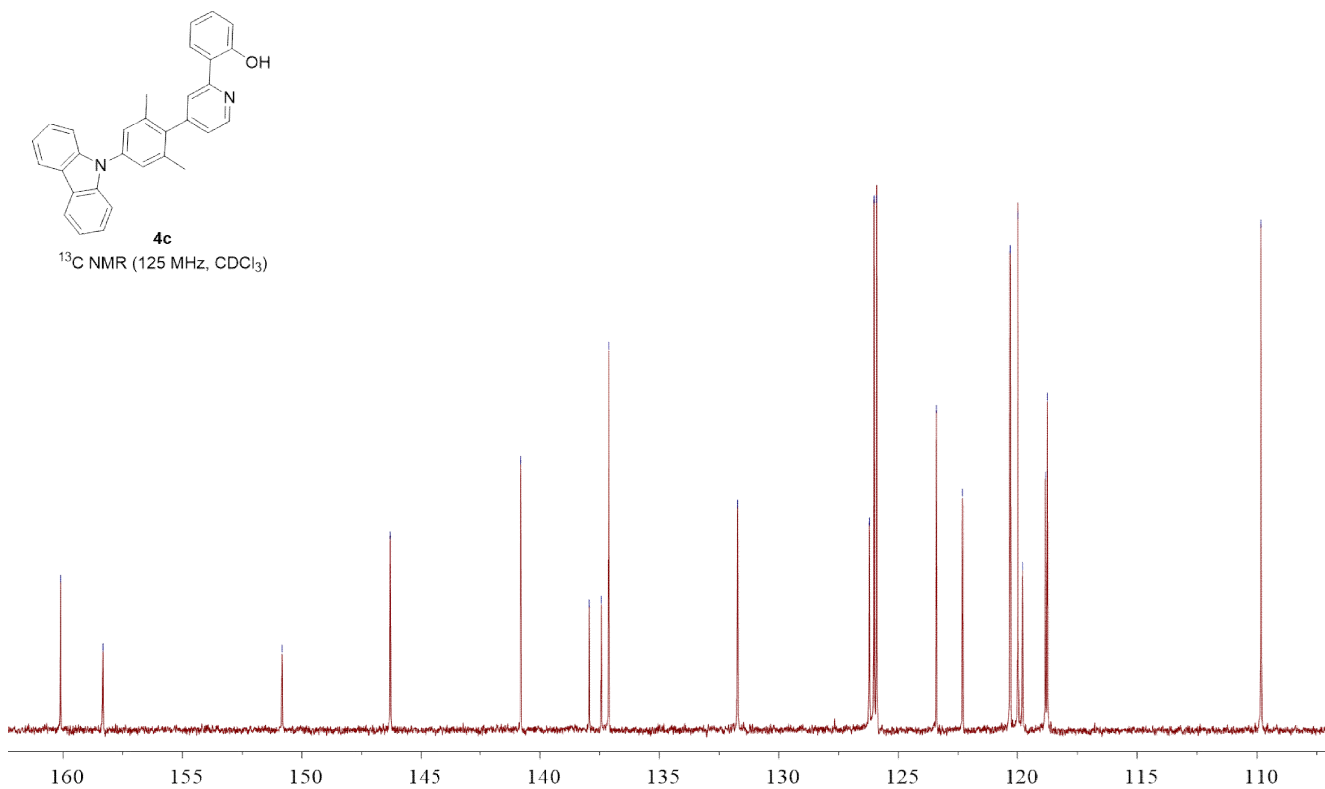
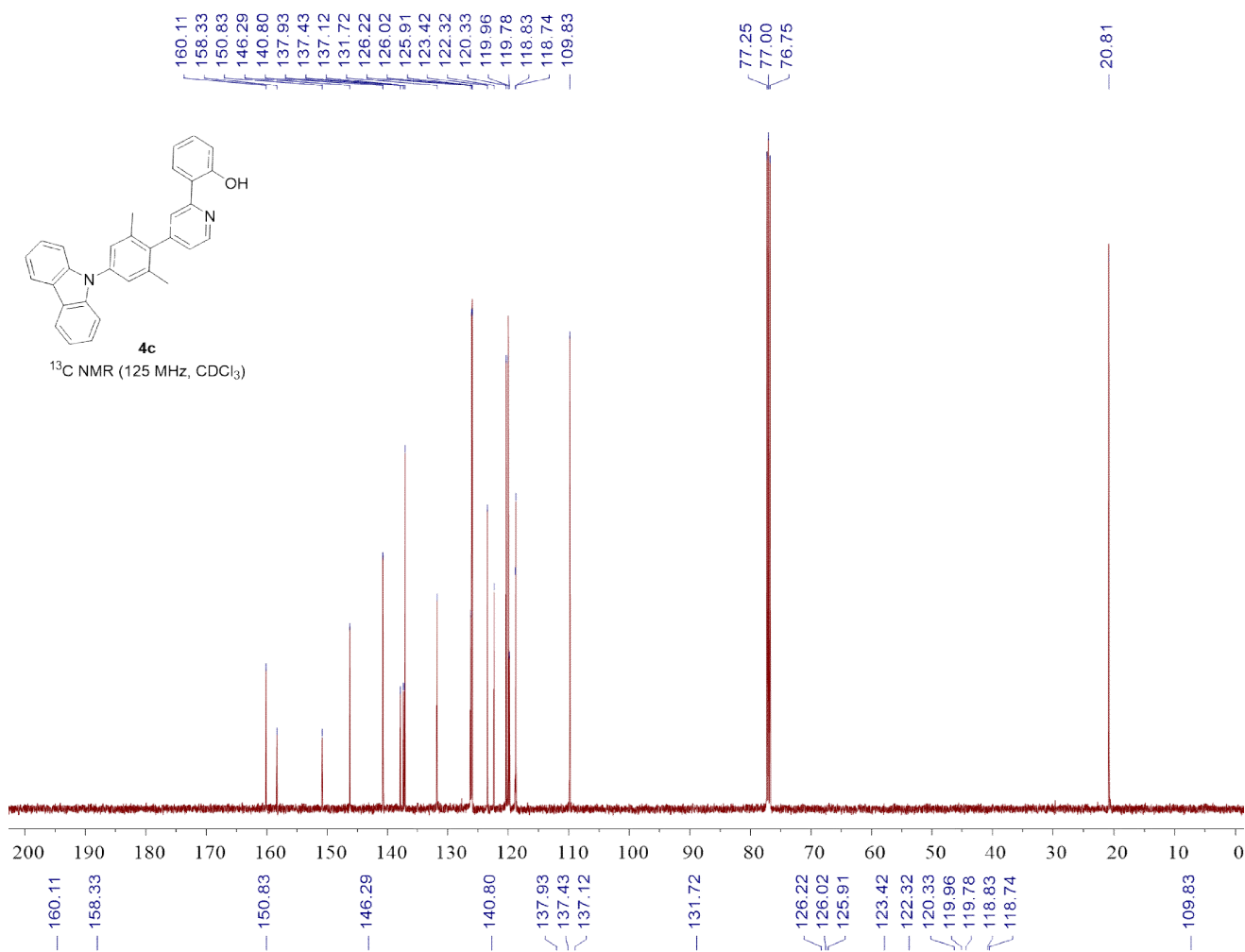
**BF2-DMPCz**  
 $^{11}\text{B}$  NMR (192.5 MHz,  $\text{CDCl}_3$ )

— 1.09



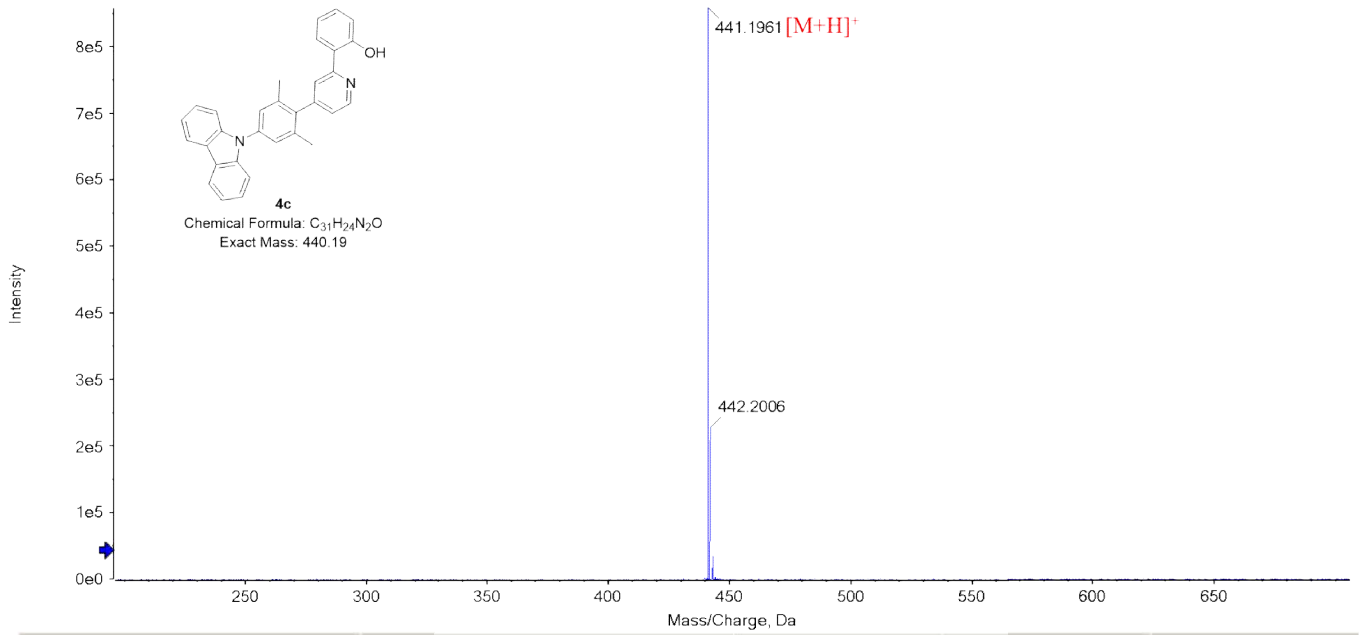
Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
$\text{C}_{43}\text{H}_{31}[^{11}\text{B}]\text{F}_2\text{N}_2\text{O}$	$\text{C}_{43}\text{H}_{35}[^{11}\text{B}]\text{F}_2\text{N}_3\text{O}$	658.2843	658.2836	-1.13



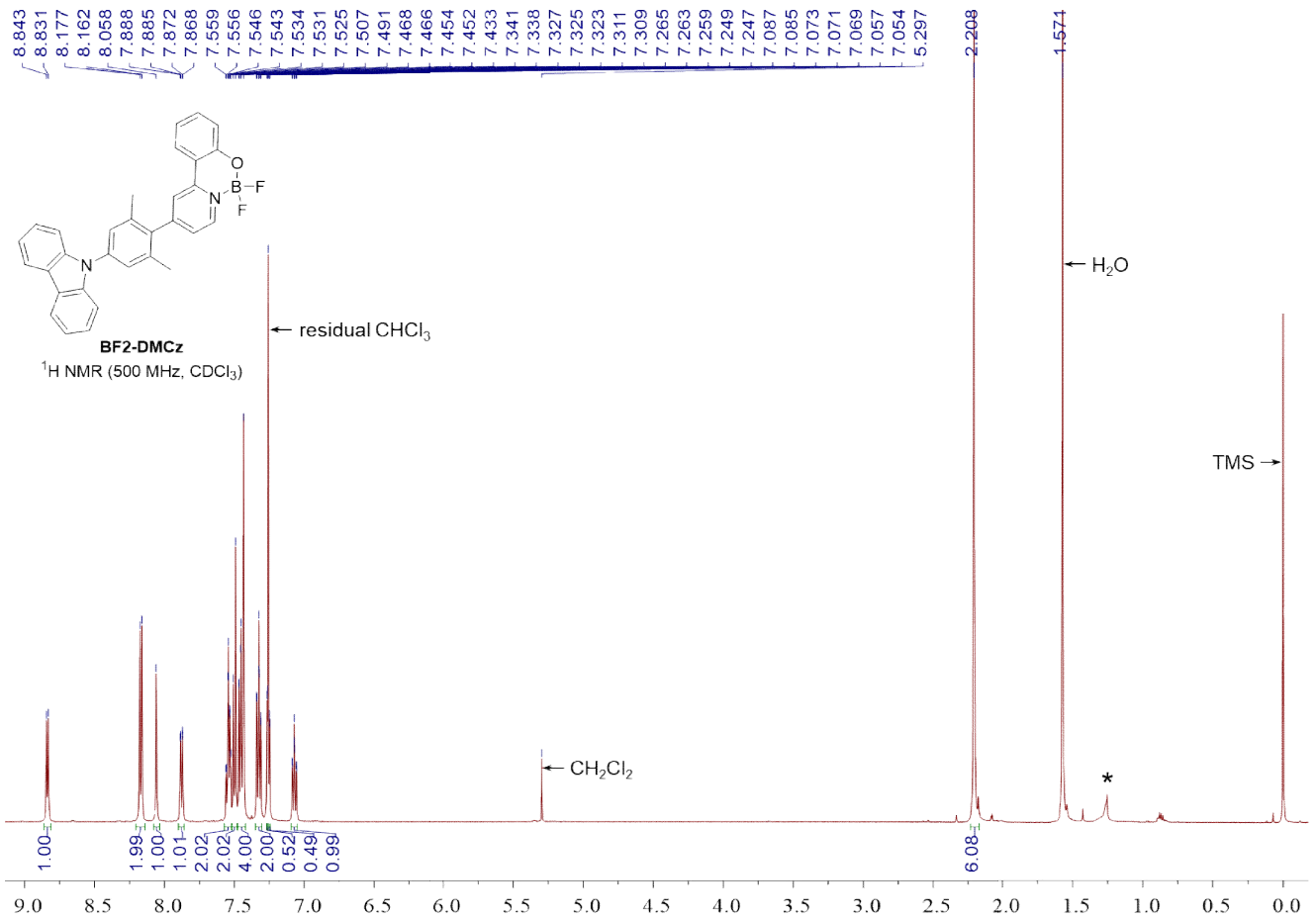


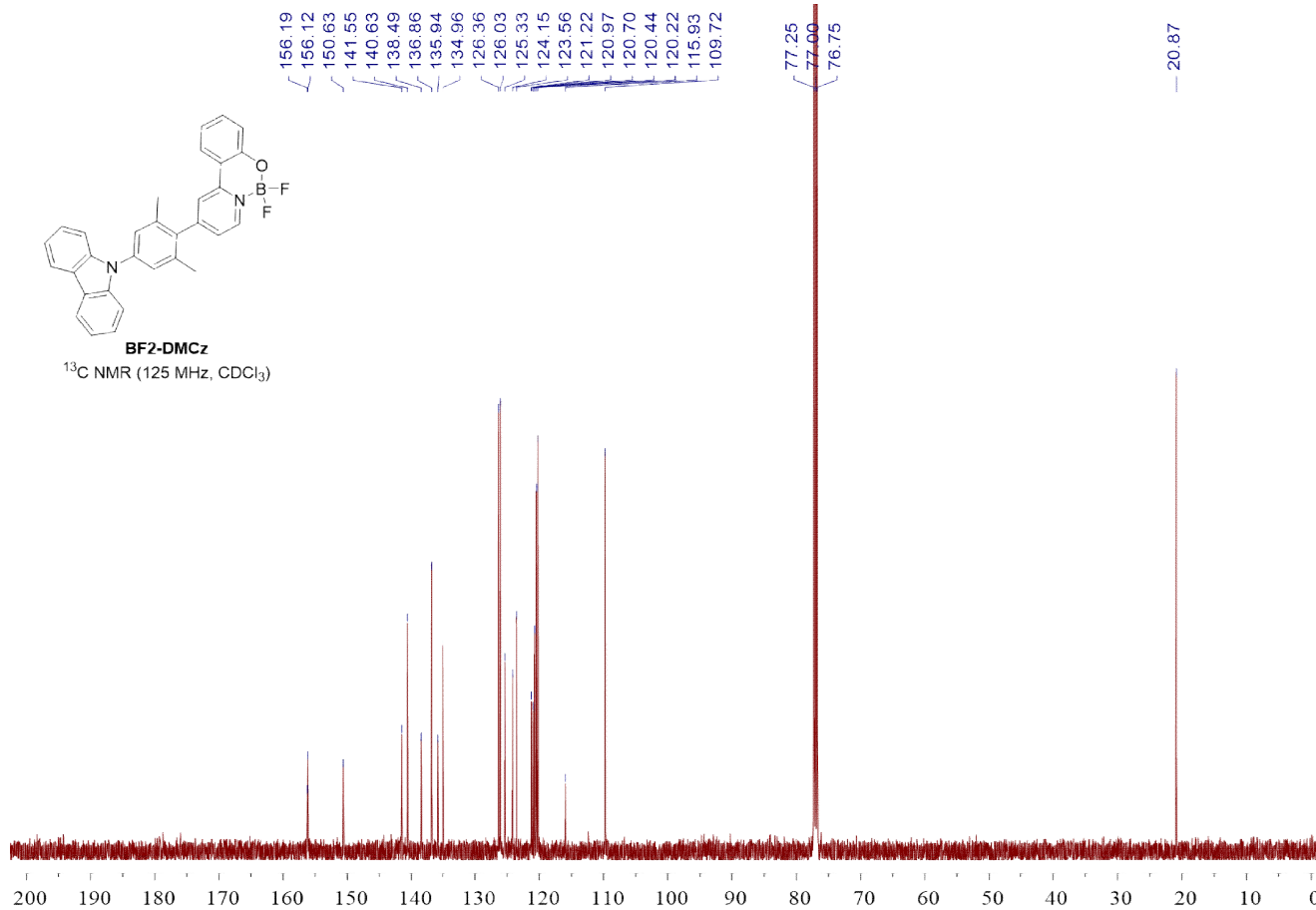
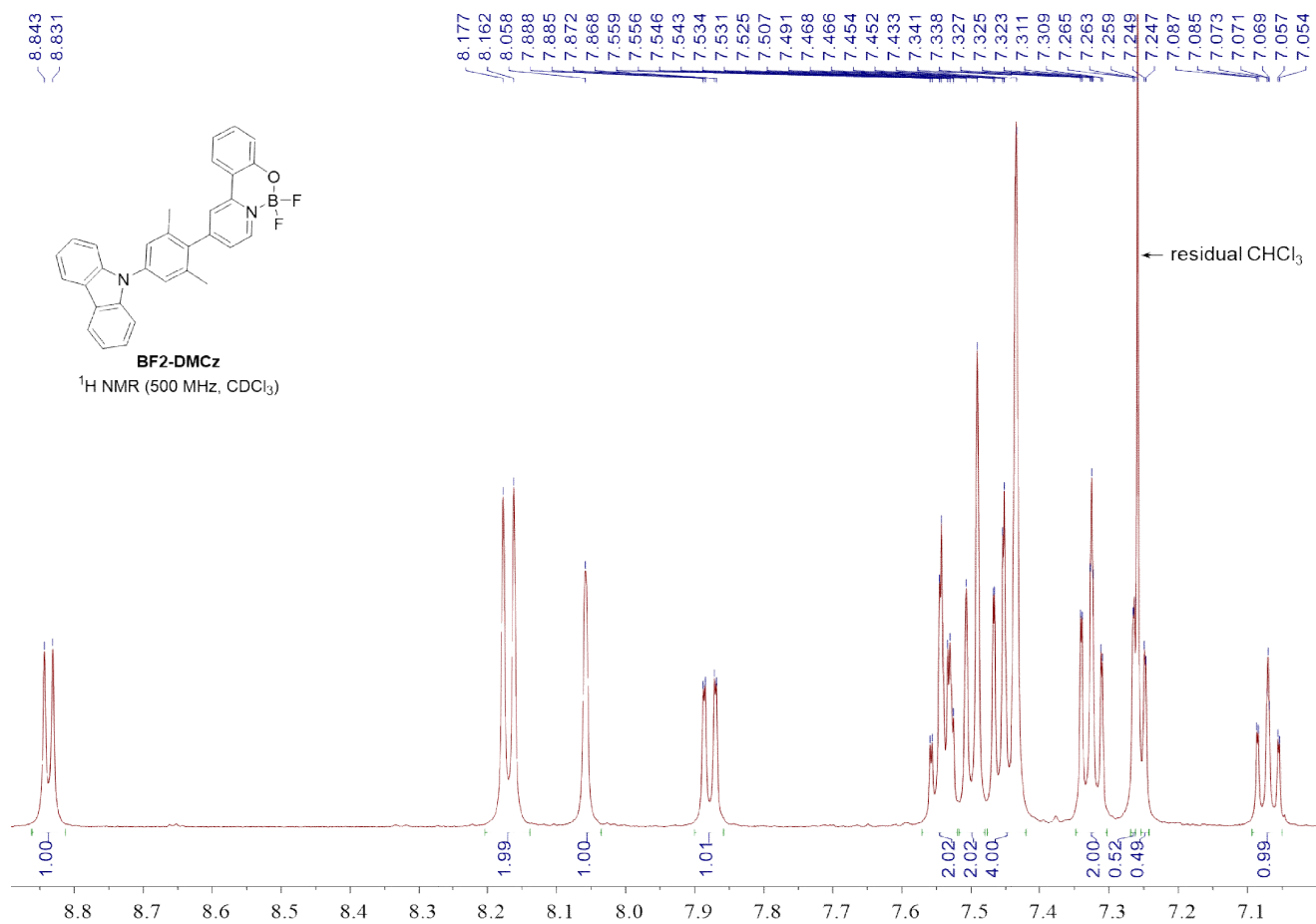


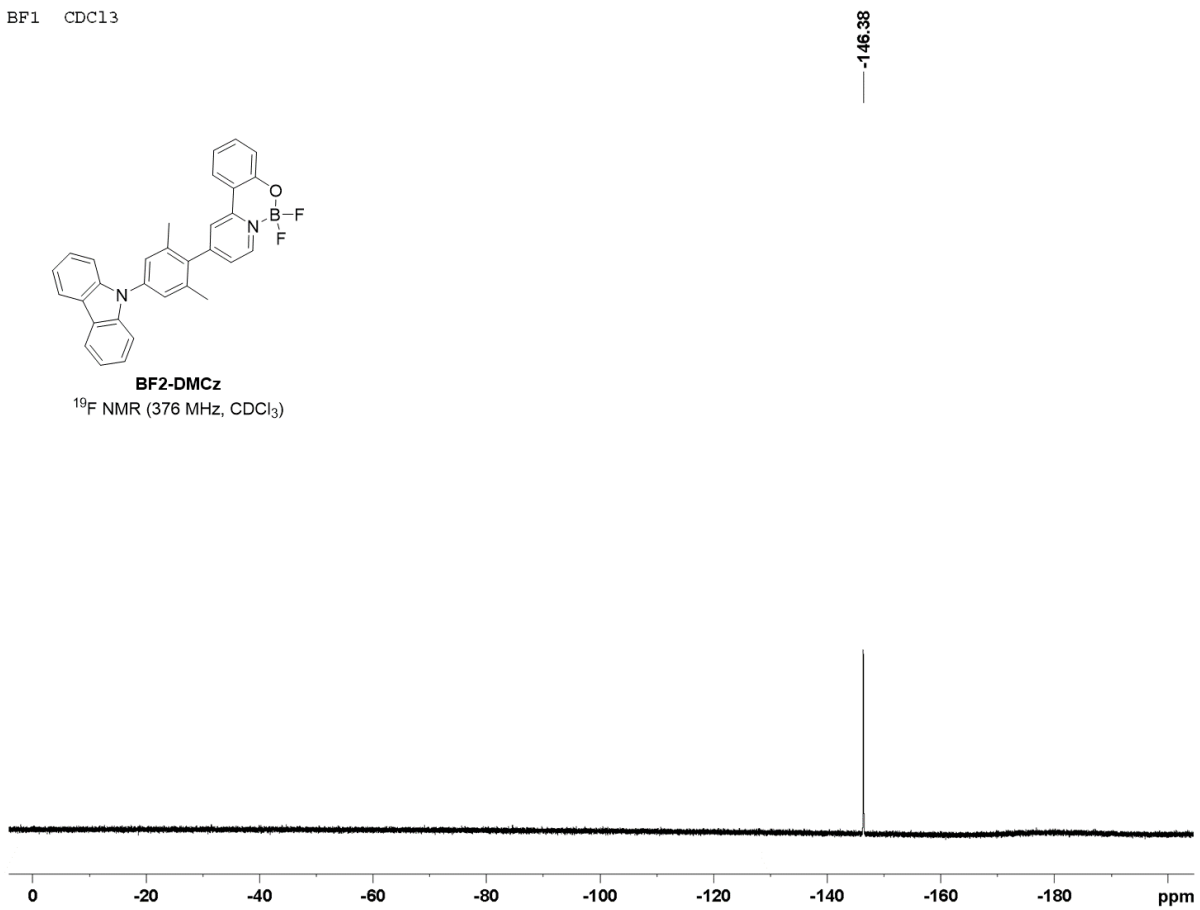
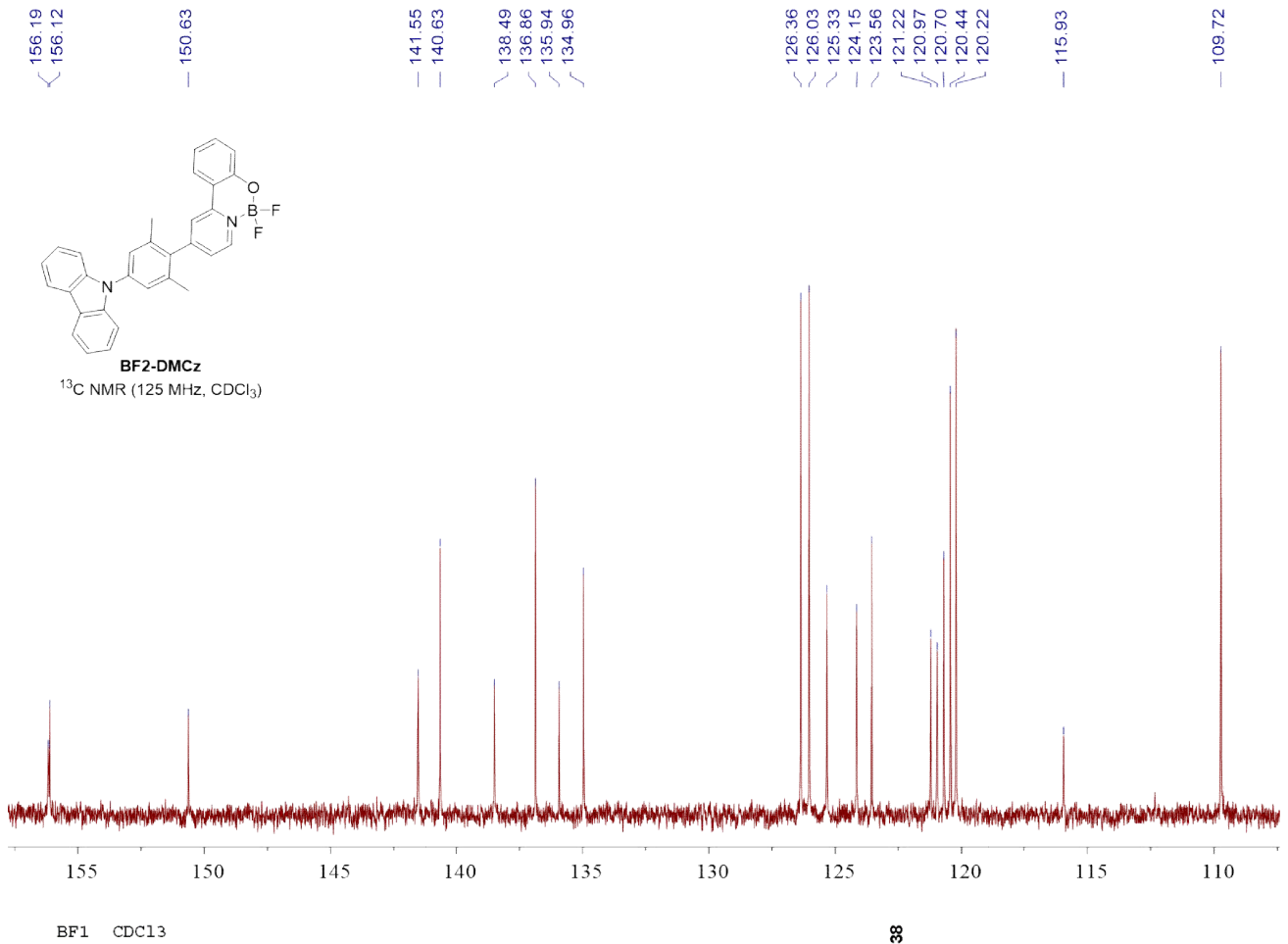
Spectrum from 0812sample.wiff (sample 18) - BFDMCz-OH, +TOF MS (100 - 2000) from 1.2...12sample.wiff (sample 18) - BFDMCz-OH, +TOF MS (100 - 2000) from 1.679 to 1.730 min)

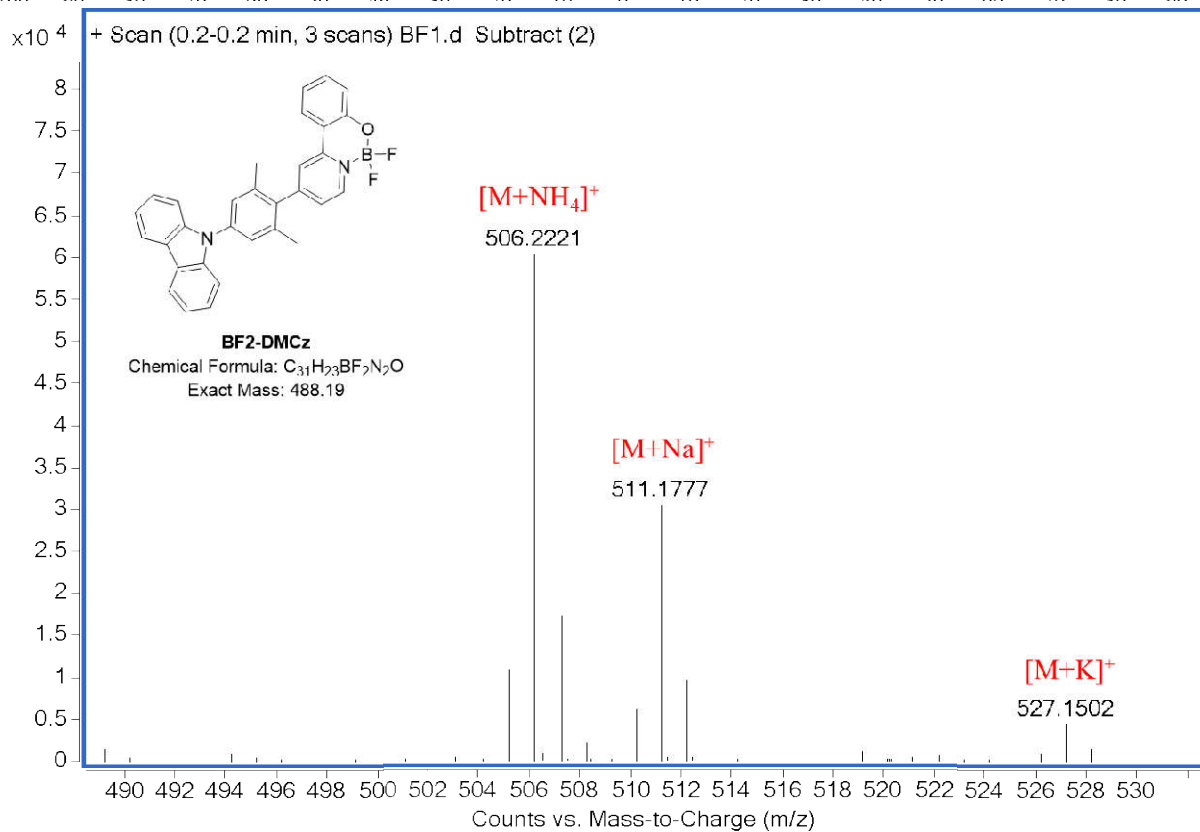
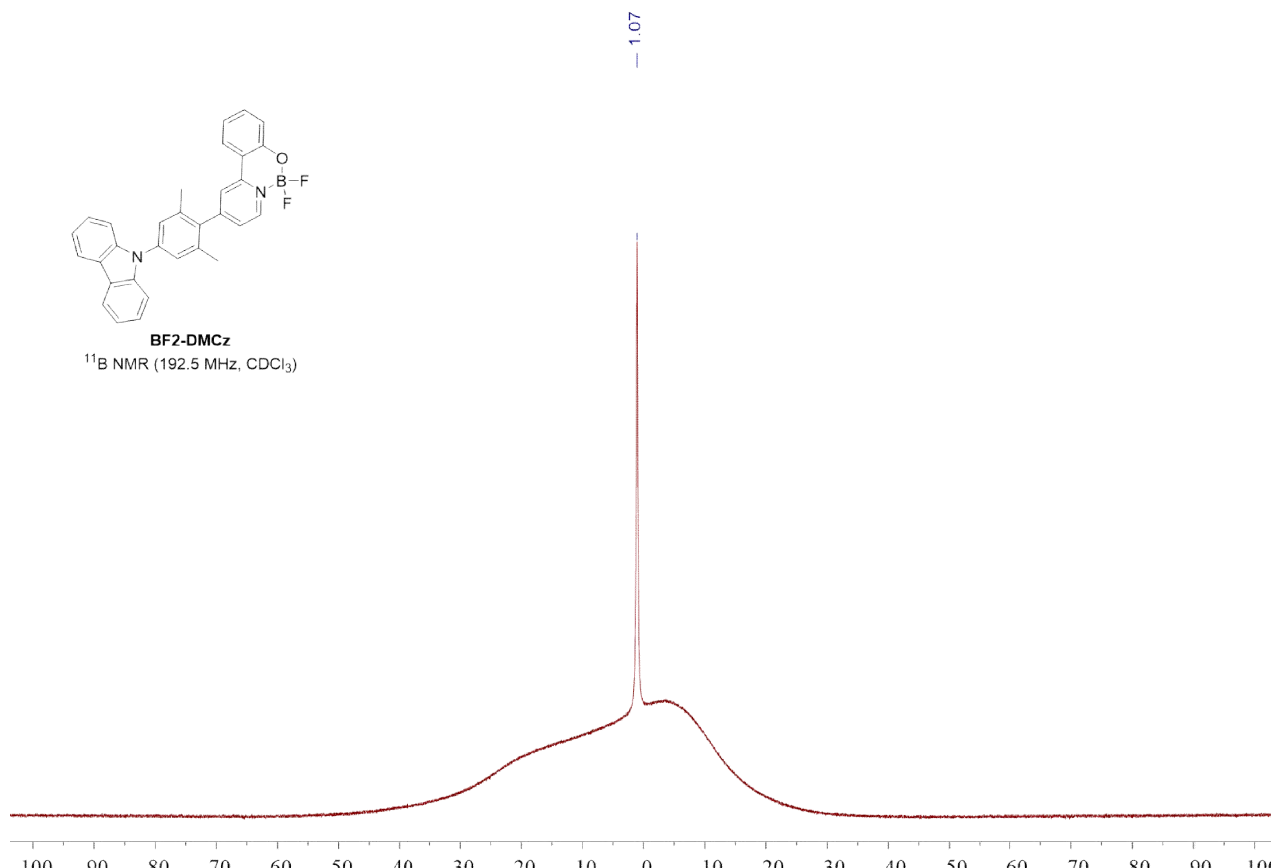
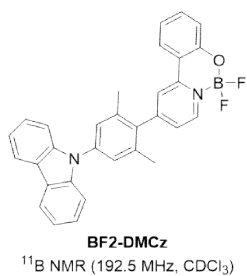


Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
$C_{31}H_{24}N_2O$	$C_{31}H_{25}N_2O$	441.1961	441.1961	-0.2









Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)
C <sub>31</sub> H <sub>23</sub> [ <sup>11</sup> B]F <sub>2</sub> N <sub>2</sub> O	C <sub>31</sub> H <sub>27</sub> [ <sup>11</sup> B]F <sub>2</sub> N <sub>3</sub> O	506.2221	506.221	-2.3