

Supporting information

B/N/O-Participated Multi-Resonance TADF Emitters by Simple Peripheral Decoration Strategy Enable High-Efficiency Electroluminescence with EQEs up to 36.5%

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1. Experimental Section

1.1 General Information

^1H NMR (500 MHz), ^{13}C NMR (125 MHz), and ^{19}F NMR (470 MHz) spectra were recorded on Bruker AV 600 NMR instrument at ambient temperature using deuterated solvents. Chemical shifts were given parts per million (ppm) relative to tetramethylsilane ($\delta = 0$ ppm). High-resolution mass spectra (HRMS) were measured on a Bruker maxis UHR-TOF mass spectrometer. Thermogravimetric analysis (TGA) of final products were measured using a PerkinElmer Instruments (Pyris1 TGA) at a heating rate of 10 °C/ min from 30 to 800 °C under nitrogen atmosphere. The UV-vis absorption spectra were recorded using a UV-3100 spectrophotometer. Photoluminescence spectra and phosphorescence spectra were measured on a Hitachi F-7000 fluorescence spectrophotometer with xenon lamp as the light source. The absolute PL quantum yields were determined on a Quantaaurus-QY measurement system (C9920-02, Hamamatsu Photonics) using an integrating sphere system under nitrogen flow. The lifetimes of fluorescence and delayed fluorescence were undertaken on PicoQuant Fluotime300. Cyclic voltammetry experiments were performed on a CHI600 electrochemical analyzer (Chenhua, China) with a three-electrode cell configuration consisting of platinum counter electrode, an Ag/AgCl reference electrode and glassy carbon electrode used for the working electrode, respectively. During the electrochemical measurements, nitrogen-purged CH_3CN was used for the oxidation scan with tetra-*n*-butylammonium hexafluorophosphate (0.1 M

in CH₃CN) as the supporting electrolyte, and redox potentials were obtained at a scan rate of 100 mV s⁻¹.

1.2 Theoretical Calculations

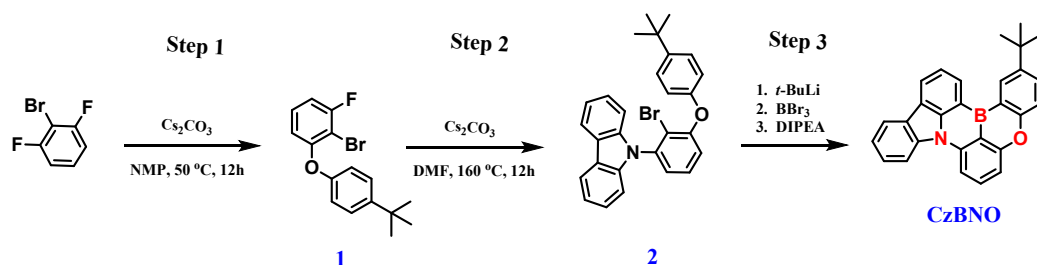
Geometrical and electronic properties of the ground-state were carried out by B3LYP density functional method including 6-31G (d) basis set using Gaussian 09 software package. HOMO and LUMO were visualized with Gaussview 5.0. The properties of excited states were calculated by time-dependent DFT (TD-DFT) calculations with PBE0 functional and basis set of def2-SVP.

1.3 Device Fabrication and Characterization

Patterned ITO glass substrates were cleaned sequentially with acetone, deionized water and isopropyl alcohol in an ultrasonic cleaner, then dried with N₂ flow and finally transferred into a vacuum chamber for deposition. The organic layers of 8-hydroxyquinolinolato-lithium (Liq) as electron injection layer and aluminum (Al) as cathode layer were deposited by thermal evaporation at 5×10⁻⁵ Pa with rates of 0.1 and 3 Å/s, respectively. The other organic layers were deposited at the rates of 0.2-3 Å/s. The emitting area of the device is about 0.09 cm². The current density-voltage-luminance (*J-V-L*), *L-EQE* curves and electroluminescence (EL) spectra were measured by using a Keithley 2400 source meter and an absolute EQE measurement system (C9920-12, Hamamatsu Photonics, Japan).

1.4 Synthesis

All reagents and solvents were purchased from commercial sources and used without further purification. All reactions were performed under nitrogen conditions using anhydrous solvents. The final products were first purified by column chromatography, and then further refined by temperature gradient vacuum sublimation. All reactions were heated by metal sand bath (WATTCAS, LAB-500, <https://www.wattcas.com>).



Scheme S1. Synthetic route to CzBNO.

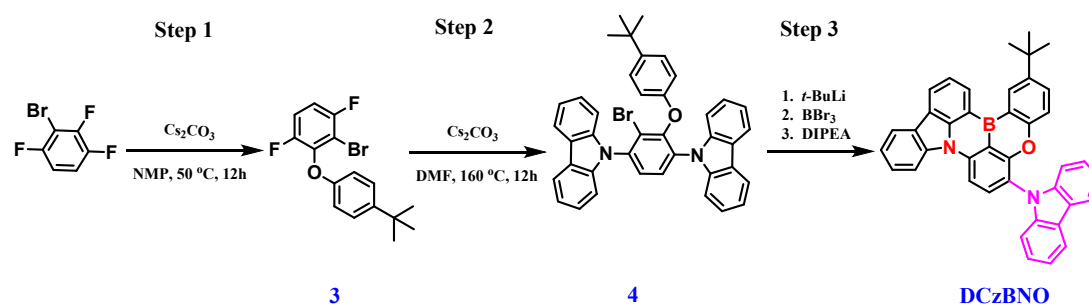
Step 1: A mixture of 2-bromo-1,3-difluorobenzene (7.2 g, 40.0 mmol), 4-tert-butylphenol (7.2 g, 48.0 mmol), and cesium carbonate (16.0 g, 50.0 mmol) in dry *N*-methylpyrrolidone (100 mL) was stirred and heated at 50 °C for 12 h under nitrogen. When cooling to room temperature, the reaction mixture was extracted with ethyl acetate:petroleum ether ($v:v=1:1$) and water. The collected organic layers were dried over anhydrous Na_2SO_4 and then evaporated under reduced pressure. The crude product was further purified using silica gel chromatography with petroleum ether as eluent to afford 2-bromo-1-(4-(tert-butyl)phenoxy)-3-fluorobenzene (compound **1**) as a white powder with a yield of 86%. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.45 – 7.33 (m, 2H), 7.18 (m, 1H), 6.99 – 6.93 (m, 2H), 6.89 (td, $J = 8.0, 1.5$ Hz, 1H), 6.69 (dt, $J = 8.5, 1.5$ Hz, 1H), 1.34 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 161.36, 159.40,

156.14, 156.12, 153.84, 147.07, 128.46, 128.38, 126.76, 118.43, 114.47, 114.45, 110.83, 110.65, 102.27, 102.09, 34.40, 31.49. ^{19}F NMR (470 MHz, CDCl_3 , δ): -104.82.

Step 2: A mixture of compound **1** (3.2 g, 10.0 mmol), 4-*tert*-butylphenol (1.8 g, 12.0 mmol), and cesium carbonate (4.0 g, 12.5 mmol) in dry *N,N*-dimethylformamide (100 mL) was stirred and heated at 160 °C for 12 h under nitrogen. When cooling to room temperature, the reaction mixture was extracted with ethyl acetate:petroleum ether (*v:v*=1:1) and water. The collected organic layers were dried over anhydrous Na_2SO_4 and then evaporated under reduced pressure. The crude product was further purified using silica gel chromatography with petroleum ether as eluent to afford 9-(2-bromo-3-(4-(*tert*-butyl)phenoxy)phenyl)-9H-carbazole (compound **2**) as a white powder with a yield of 72%. ^1H NMR (500 MHz, Chloroform-*d*) δ 8.16 (dt, $J = 7.5, 1.0$ Hz, 2H), 7.48 – 7.40 (m, 5H), 7.31 (m, 2H), 7.24 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.14 (dt, $J = 8.0, 1.0$ Hz, 2H), 7.09 (dd, $J = 8.5, 1.5$ Hz, 1H), 7.07 – 7.03 (m, 2H), 1.35 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 156.42, 153.81, 147.13, 140.73, 138.56, 128.76, 126.84, 125.93, 125.16, 123.26, 120.34, 120.00, 119.01, 118.49, 116.06, 110.11, 34.41, 31.48.

Step 3: To a solution of compound **2** (1.9 g, 4.0 mmol) in dry *tert*-butylbenzene (40 mL), *tert*-butyllithium (1.3 M, 6.2 mL, 8.0 mmol) was added drop by drop at 0 °C. After stirring for 2 h at 60 °C, the reaction mixture was cooled to 0 °C and boron tribromide (0.77 mL, 8.0 mmol) was added, then the reaction mixture was allowed to return to room temperature and stirred for another 1 h. *N,N*-diisopropyl-ethylamine (1.4 mL, 8.0 mmol) was added at 0 °C and then the mixture was allowed to room

temperature and stirred 1 h. After stirring for 24 h at 140 °C, the mixture was then quenched by slow addition of 5 mL *N,N*-diisopropyl-ethylamine. The resulting mixture was extracted with dichloromethane and water, and then the combined organic layer was concentrated by evaporation under reduced pressure. The residue was further purified by silica gel chromatography (eluent:dichloromethane/petroleum ether = 1:5) to give **CzBNO** as a yellow powder with yield of 30%. ¹H NMR (500 MHz, Chloroform-*d*) δ 8.84 (d, *J* = 7.5 Hz, 1H), 8.81 (d, *J* = 2.5 Hz, 1H), 8.43 (d, *J* = 8.5 Hz, 1H), 8.39 (d, *J* = 7.5 Hz, 1H), 8.22 (d, *J* = 8.5 Hz, 2H), 7.90 (t, *J* = 8.0 Hz, 1H), 7.79 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 1.52 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 159.06, 157.65, 144.91, 143.07, 142.21, 139.61, 133.83, 132.81, 131.12, 130.55, 126.93, 126.59, 123.74, 123.67, 122.22, 121.98, 120.77, 117.39, 114.31, 109.46, 107.36, 34.59, 31.70. HRMS (*m/z*): calcd. for C₂₈H₂₂BNO 399.1794; found 400.1862 (*M*+*H*)⁺

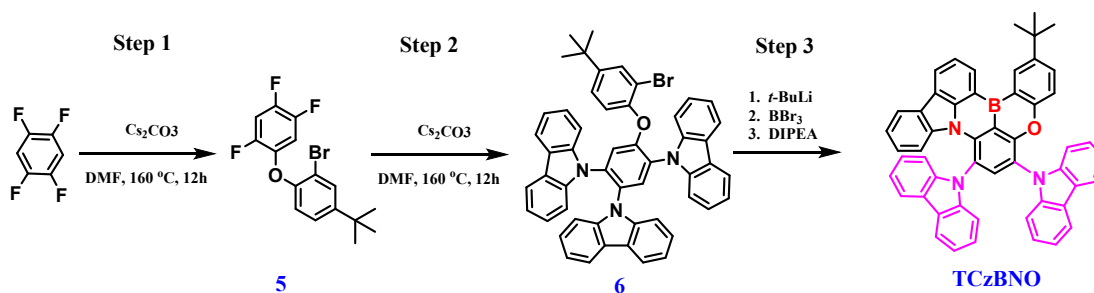


Scheme S2. Synthetic route to **DCzBNO**.

Step 1: 2-bromo-1,3,4-trifluorobenzene (compound **3**) was synthesized according to the method of compound **1** as a white solid (72% yield). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 9.0 Hz, 2H), 7.17 – 7.09 (m, 1H), 7.04 – 6.96 (m, 1H), 6.82 (d, *J* = 9.0 Hz, 2H), 1.30 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 157.19, 157.17, 155.24, 155.22, 154.82, 153.40, 153.37, 151.41, 151.39, 145.85, 141.88, 141.86, 141.76, 141.74, 126.52, 115.87, 115.80, 115.70, 115.63, 114.69, 112.37, 112.31, 112.18, 112.12, 107.11, 107.09, 106.92, 106.90, 34.26, 31.49. ¹⁹F NMR (470 MHz, CDCl₃) δ -109.67, -109.70, -129.15, -129.18.

Step 2: 9,9'-(2-bromo-3-(4-(tert-butyl)phenoxy)-1,4-phenylene)bis(9H-carbazole) (compound **4**) was synthesized according to the method of compound **2** as a gray solid (63% yield).

Step 3: DCzBNO was synthesized according to the method of CzBNO as a yellow powder (yield 32%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.92 (d, *J* = 7.5 Hz, 1H), 8.83 (d, *J* = 2.5 Hz, 1H), 8.52 (d, *J* = 8.5 Hz, 1H), 8.48 – 8.42 (m, 2H), 8.29 (d, *J* = 7.5 Hz, 1H), 8.25 (d, *J* = 7.5 Hz, 2H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.59 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 1H), 1.47 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 157.05, 154.35, 145.70, 143.24, 141.97, 141.61, 139.73, 133.91, 133.16, 131.43, 130.44, 127.34, 126.89, 125.86, 124.23, 124.13, 123.50, 122.82, 122.59, 121.12, 120.23, 119.74, 118.09, 117.85, 114.45, 110.34, 107.98, 34.61, 31.63. HRMS (ESI) *m/z* calcd for C₄₀H₃₀BN₂O⁺ (M+H)⁺ 565.24457, found 565.24438.



Scheme S3. Synthetic route to **TCzBNO**.

Step 1: 1-(2-bromo-4-(tert-butyl)phenoxy)-2,4,5-trifluorobenzene (compound **5**) was synthesized according to the method of compound **2** as a crude white solid (80% yield) and directly used in the following step.

Step 2: 9,9',9''-(5-(2-bromo-4-(tert-butyl)phenoxy)benzene-1,2,4-triyl)tris(9H-carbazole) (compound **6**) was synthesized under the same conditions to that of compound **2**, using compound **1** (3.59 g, 10 mmol), cesium carbonate (3.58g, 11 mmol), and carbazole (6.69 g, 40 mmol) with a yield of 64%. ¹H NMR (500 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 8.0 Hz, 2H), 8.08 (d, *J* = 3.5 Hz, 1H), 7.82 (m, 4H), 7.69 (dd, *J* = 8.0, 3.0 Hz, 2H), 7.61 – 7.55 (m, 2H), 7.52 (t, *J* = 2.0 Hz, 1H), 7.43 – 7.32 (m, 5H), 7.31 – 7.27 (m, 2H), 7.22 (dt, *J* = 8.5, 2.0 Hz, 1H), 7.16 – 7.07 (m, 8H), 7.05 (d, *J* = 8.5 Hz, 1H), 1.23 (s, 9H).

Step 3: **TCzBNO** was synthesized under the same conditions to that of **CzBNO** as a orange powder (yield 25%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.87 (d, *J* = 7.5 Hz, 1H), 8.79 (d, *J* = 2.5 Hz, 1H), 8.42 – 8.29 (m, 2H), 8.22 (d, *J* = 7.5 Hz, 2H), 7.99 (dd, *J* = 7.0, 1.5 Hz, 2H), 7.78 (m, 2H), 7.66 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.40 (m, 2H), 7.37

– 7.30 (m, 4H), 7.22 – 7.14 (m, 4H), 7.10 (d, $J = 7.5$ Hz, 2H), 7.03 (d, $J = 8.5$ Hz, 1H), 6.88 (m, , 2H), 6.37 (td, $J = 7.5, 7.0, 1.0$ Hz, 1H), 1.49 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 156.96, 153.00, 146.18, 144.36, 141.36, 139.46, 138.75, 135.82, 133.98, 132.40, 131.66, 130.84, 126.24, 126.02, 125.32, 125.18, 125.13, 124.59, 123.86, 123.63, 123.07, 122.28, 120.35, 120.31, 120.18, 120.03, 119.64, 119.00, 117.79, 113.78, 110.30, 109.10, 34.67, 31.63. HRMS (ESI) m/z calcd for $\text{C}_{52}\text{H}_{37}\text{BN}_3\text{O}^+$ ($\text{M}+\text{H}$) $^+$ 730.30242, found 730.30237.

2. Supplementary Figures

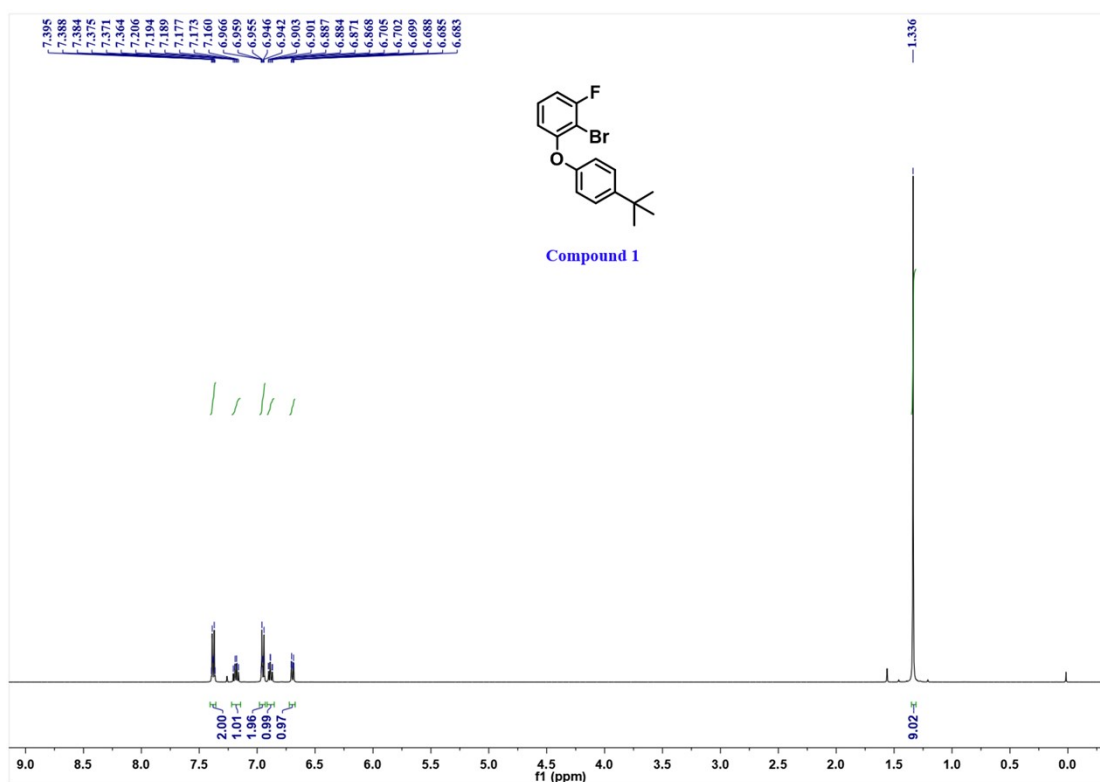


Figure S1. ^1H NMR of compound 1.

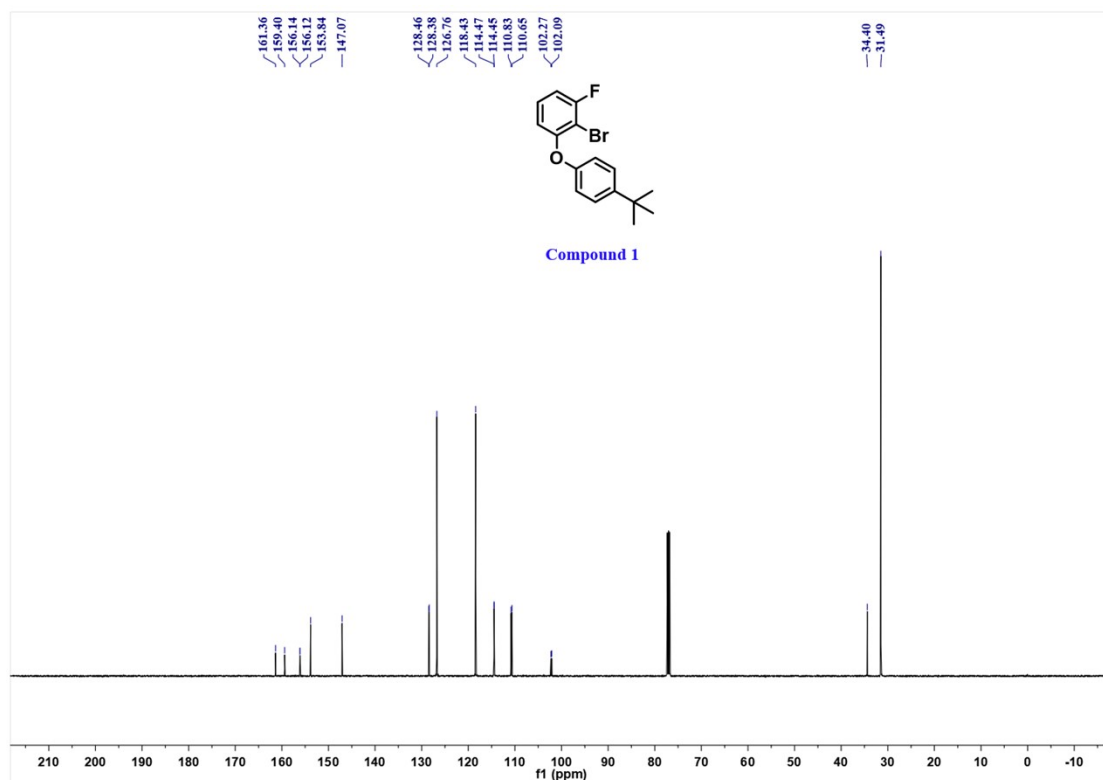


Figure S2. ^{13}C NMR of compound 1.

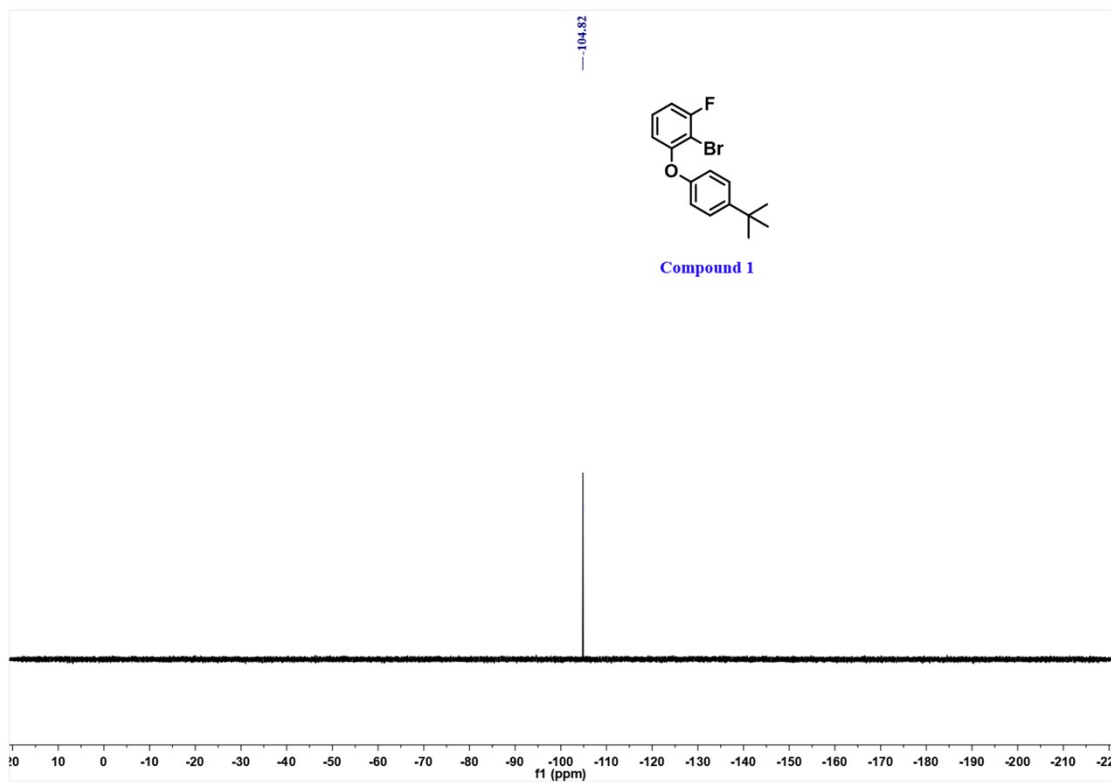


Figure S3. ^{19}F NMR of compound 1.

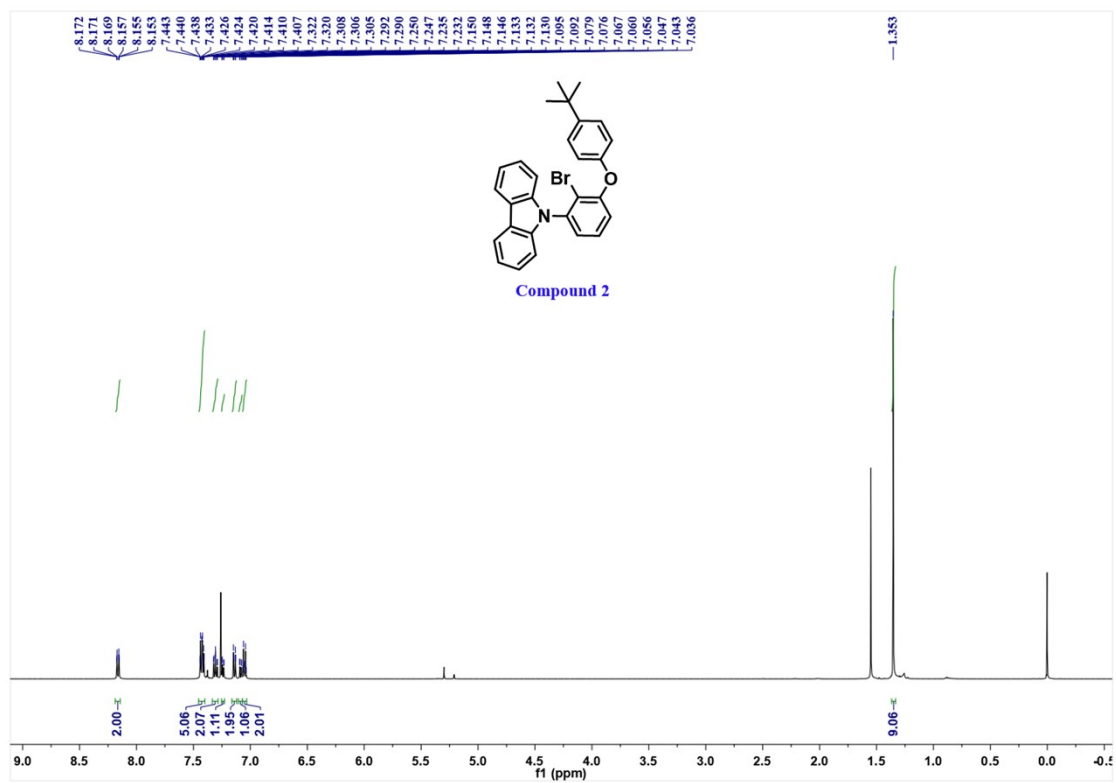


Figure S4. ¹H NMR of compound 2.

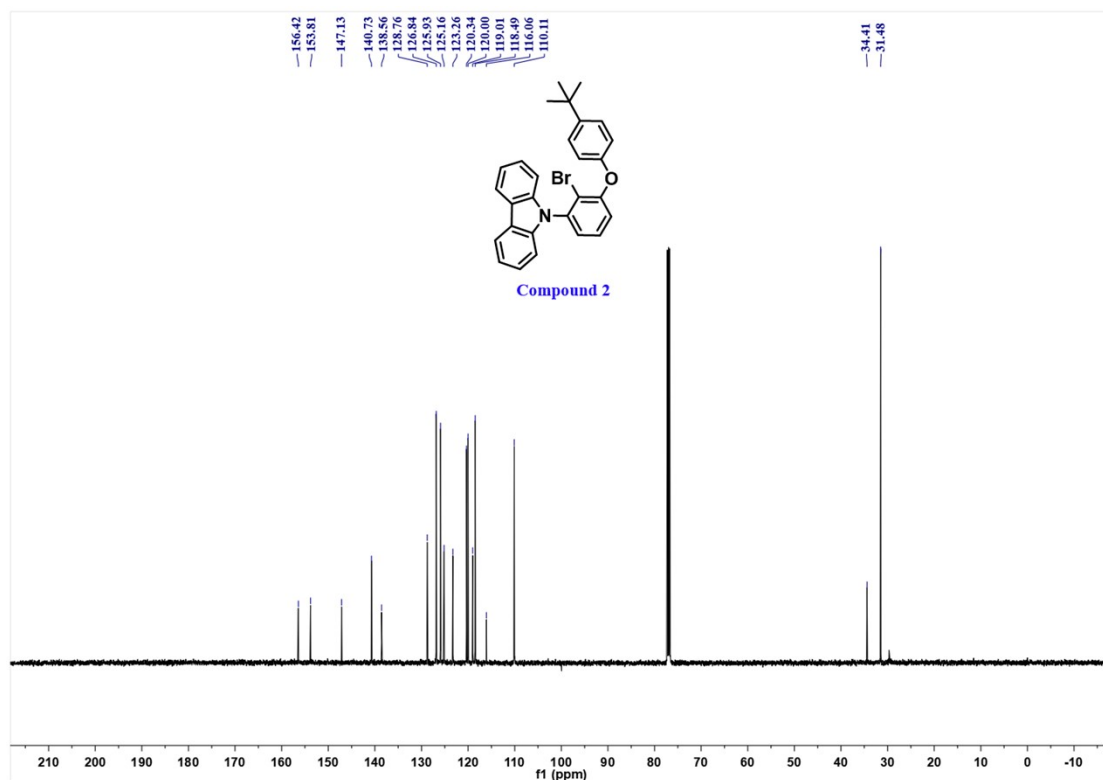


Figure S5. ¹³C NMR of compound 2.

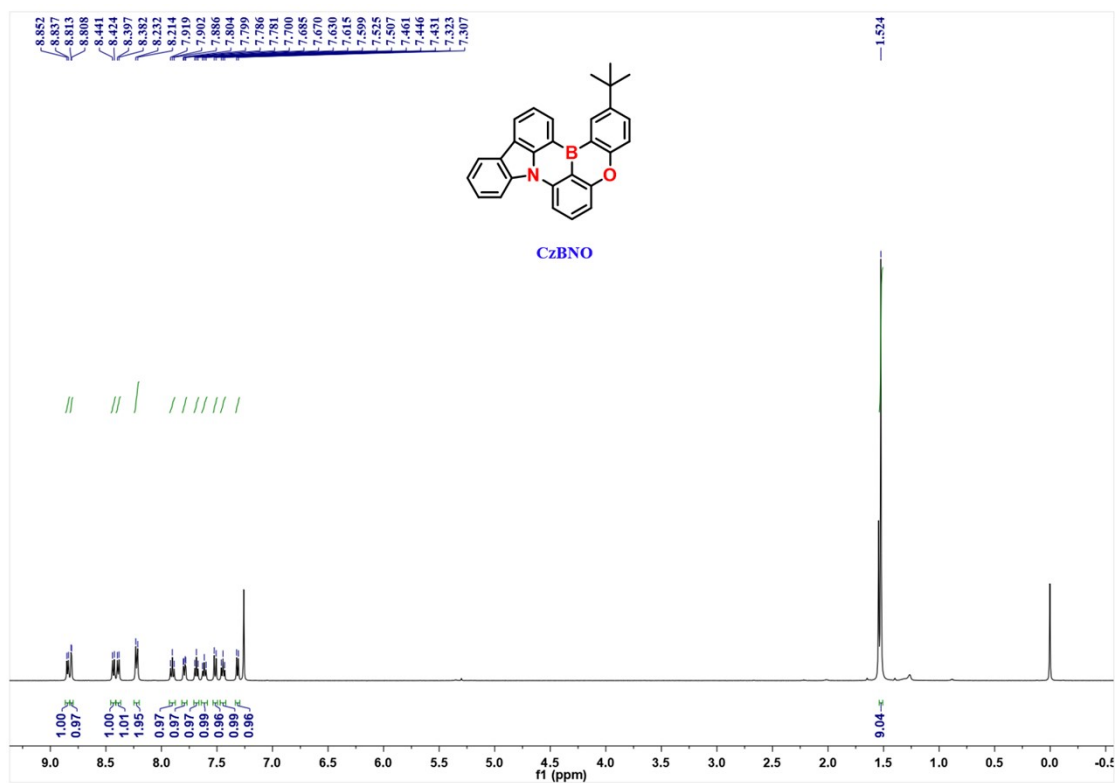


Figure S6. ¹H NMR of CzBNO.

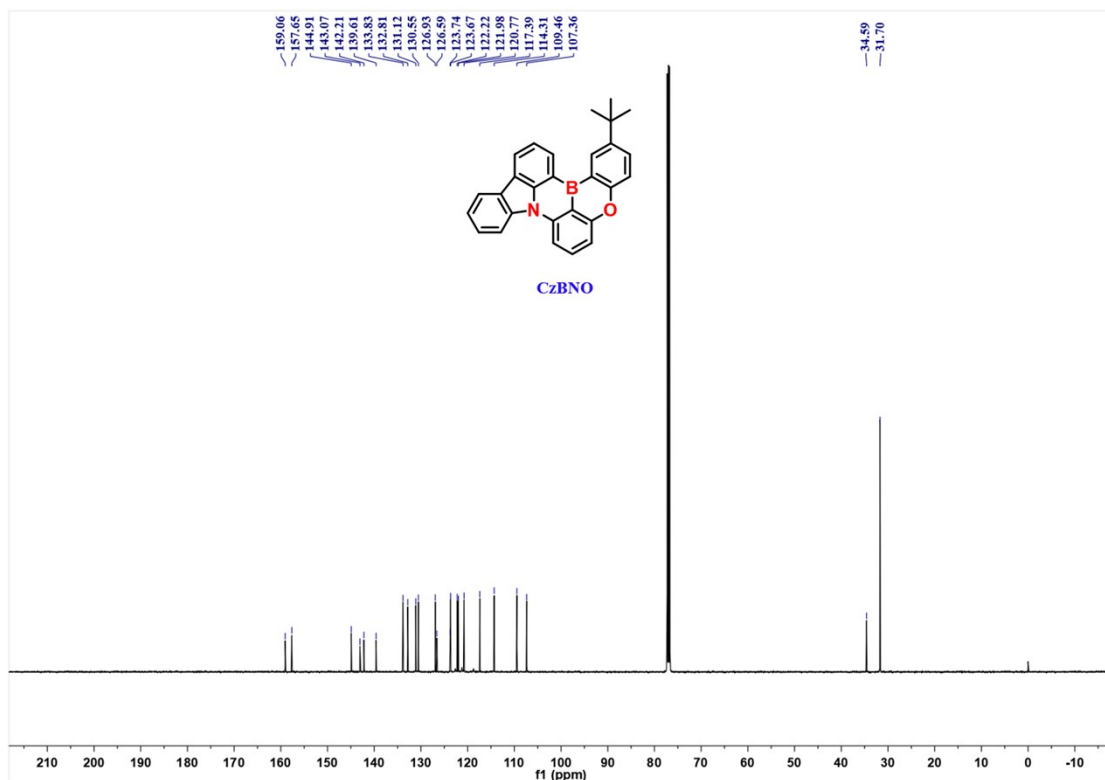


Figure S7. ¹³C NMR of CzBNO.

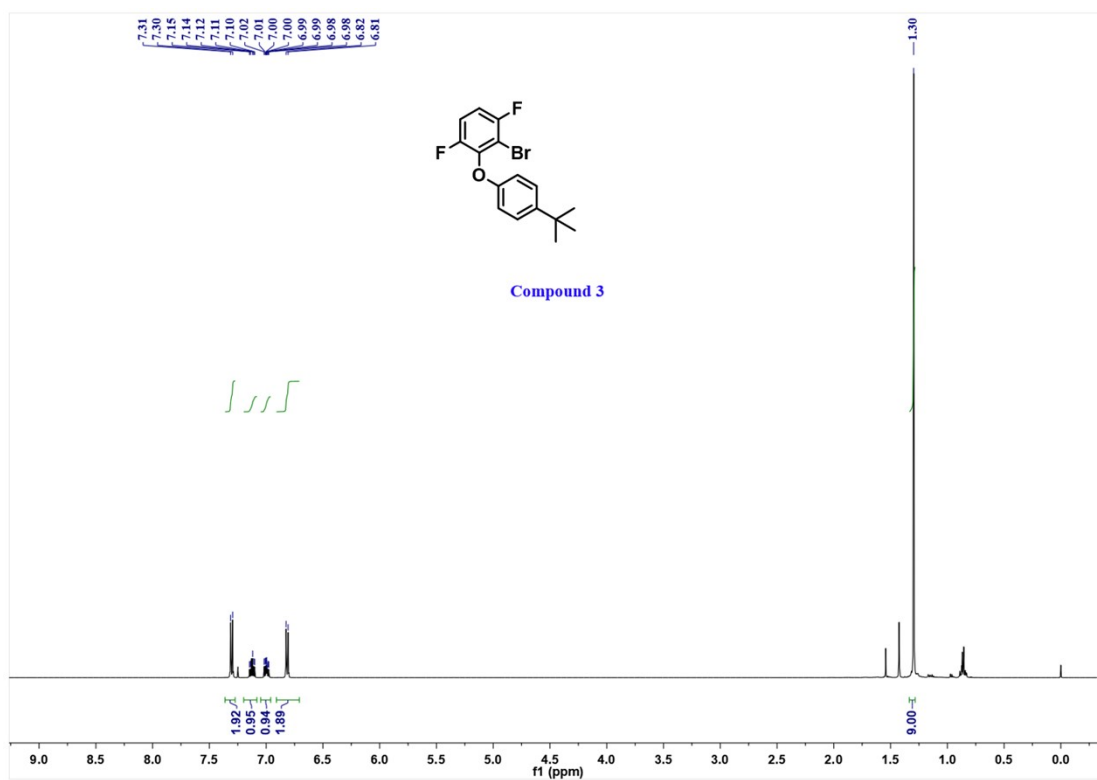


Figure S8. ¹H NMR of compound 3.

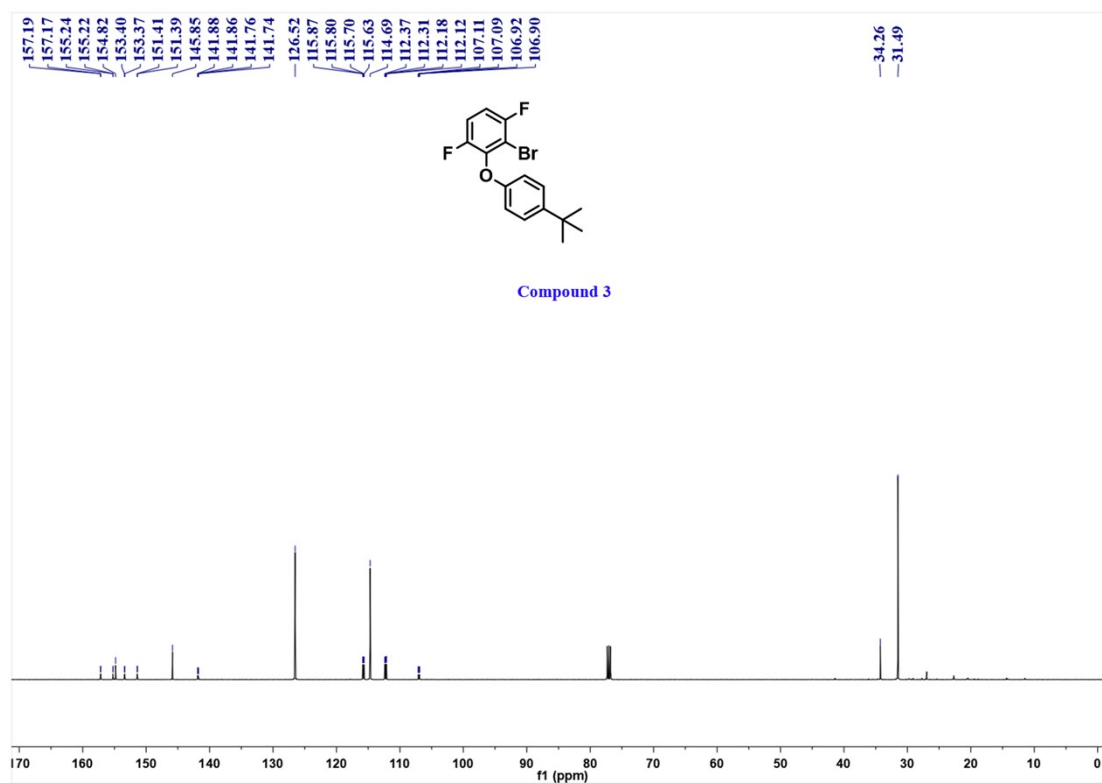


Figure S9. ¹³C NMR of compound 3.

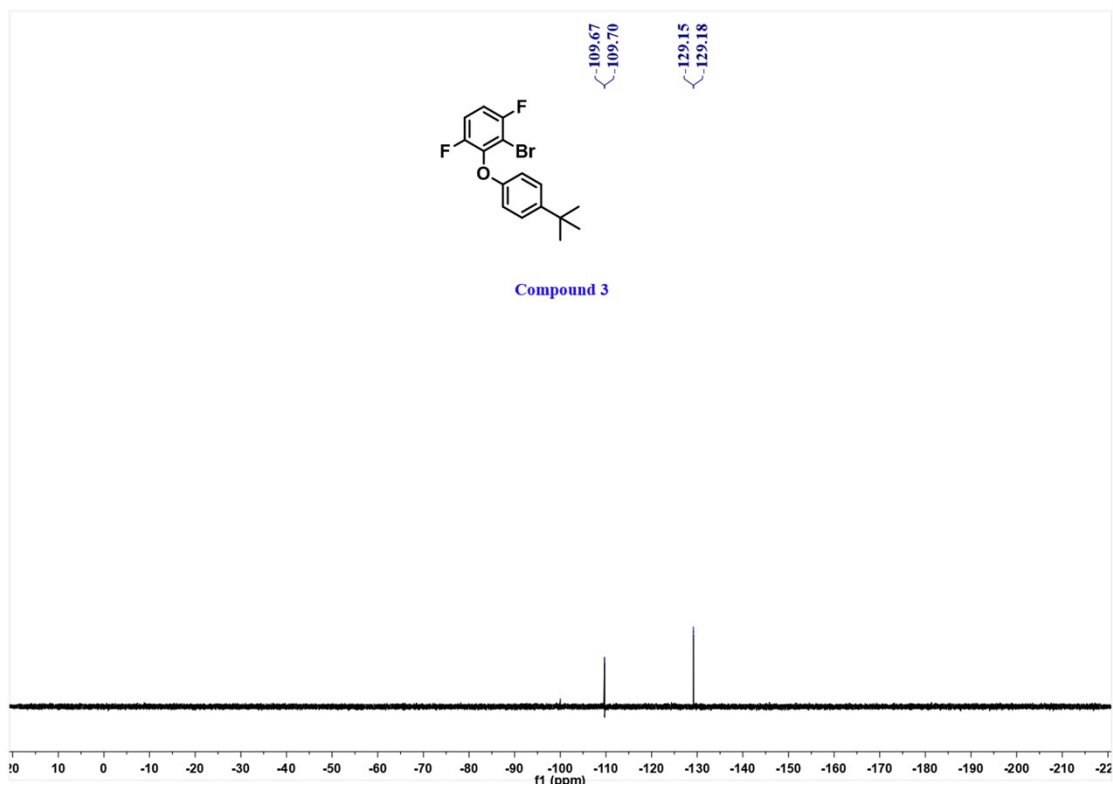


Figure S10. ¹⁹F NMR of compound 3.

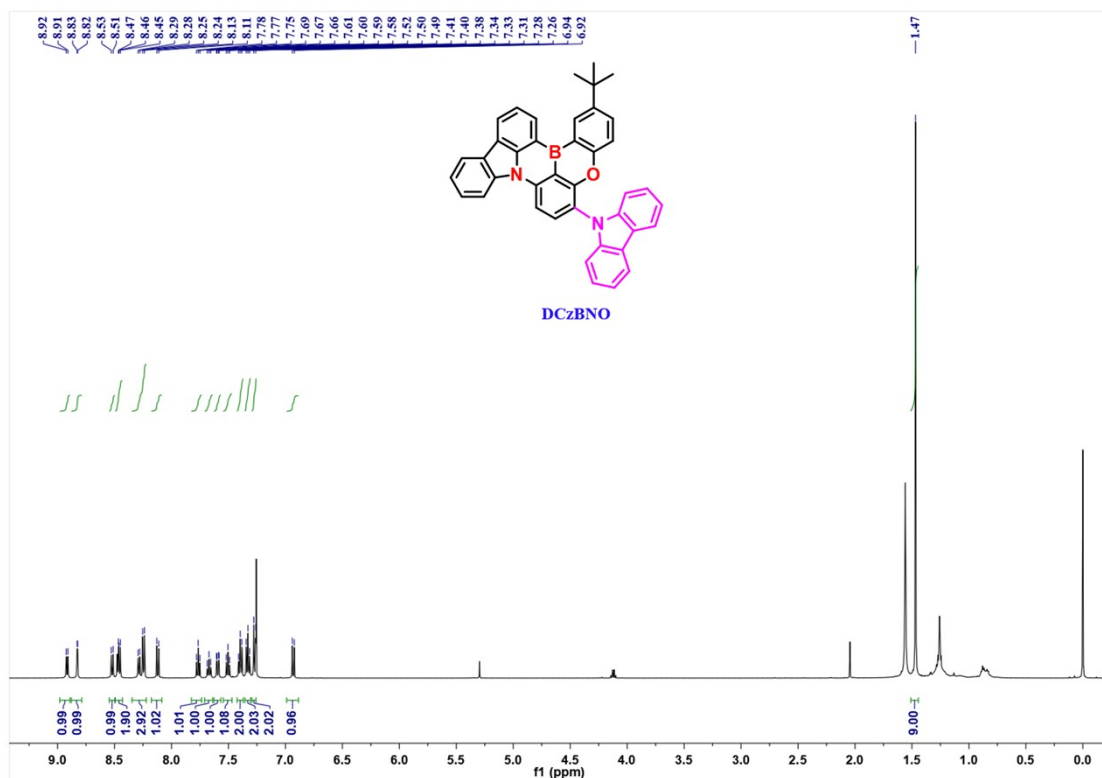


Figure S11. ¹H NMR of DCzBNO.

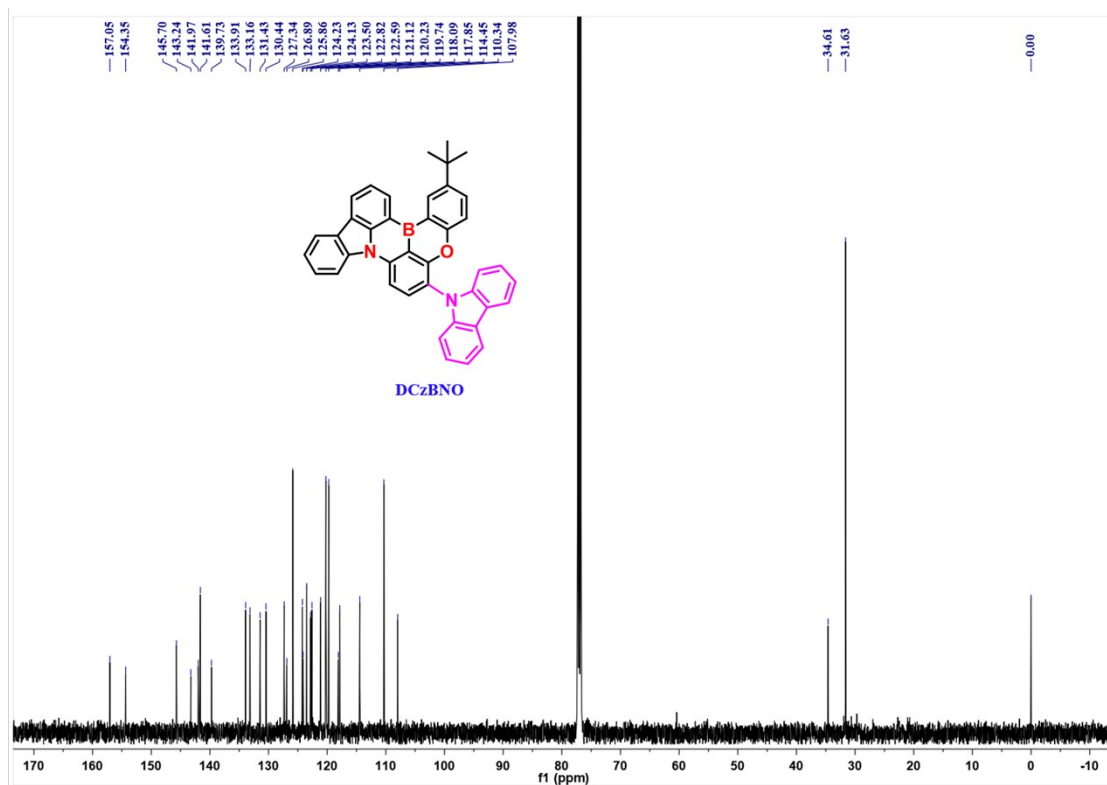


Figure S12. ^{13}C NMR of DCzBNO.

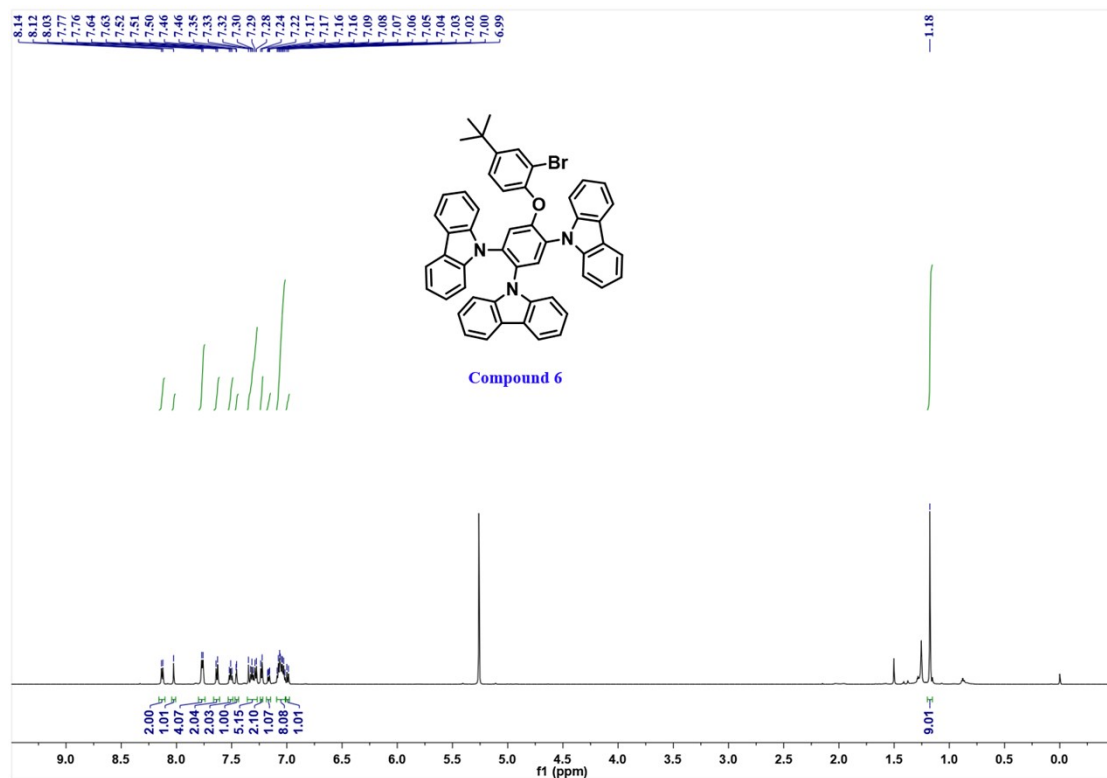


Figure S13. ^1H NMR of compound 6.

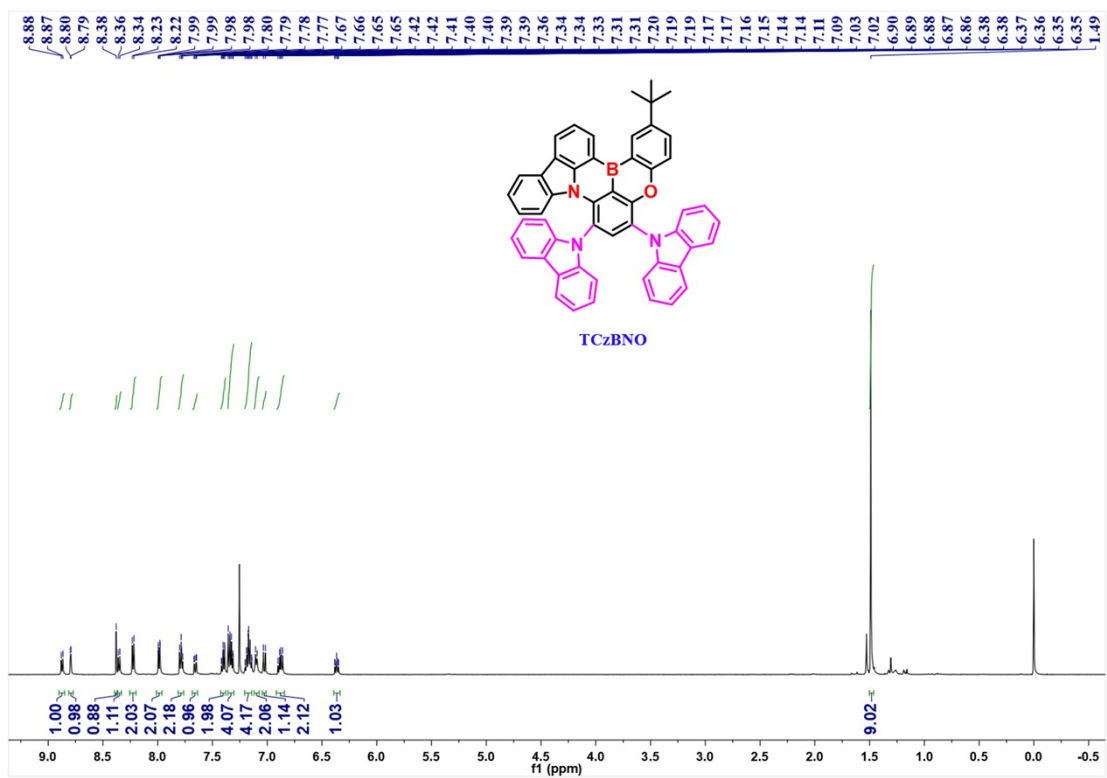


Figure S14. ^1H NMR of TCzBNO.

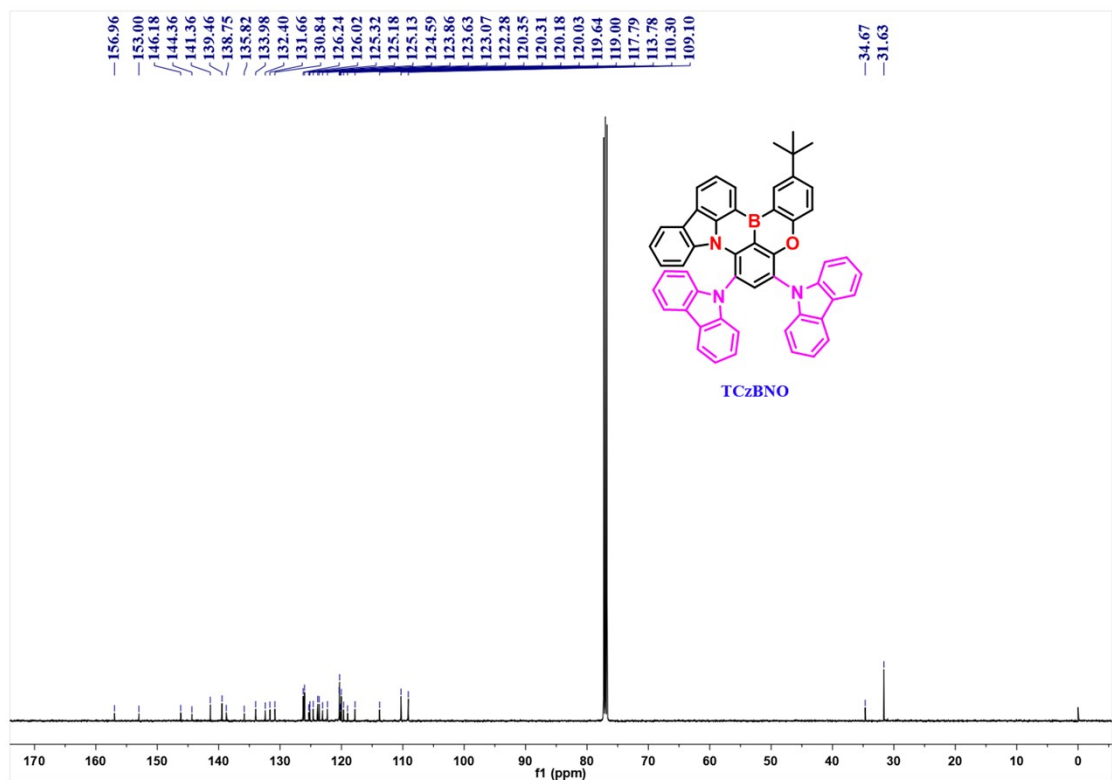


Figure S15. ^{13}C NMR of TCzBNO.

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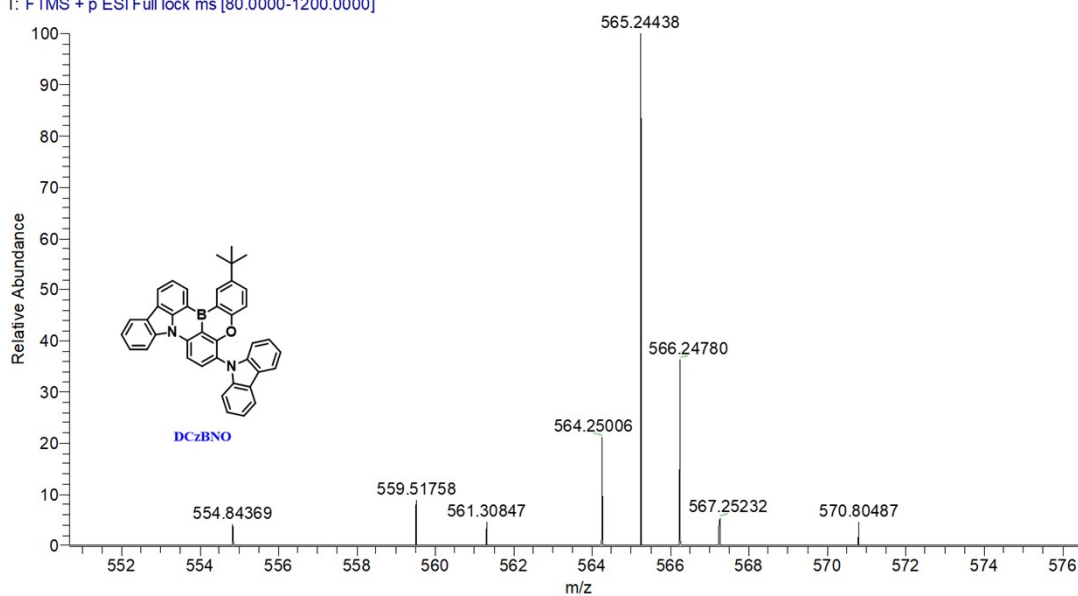


Figure S16. HRMS of DCzBNO.

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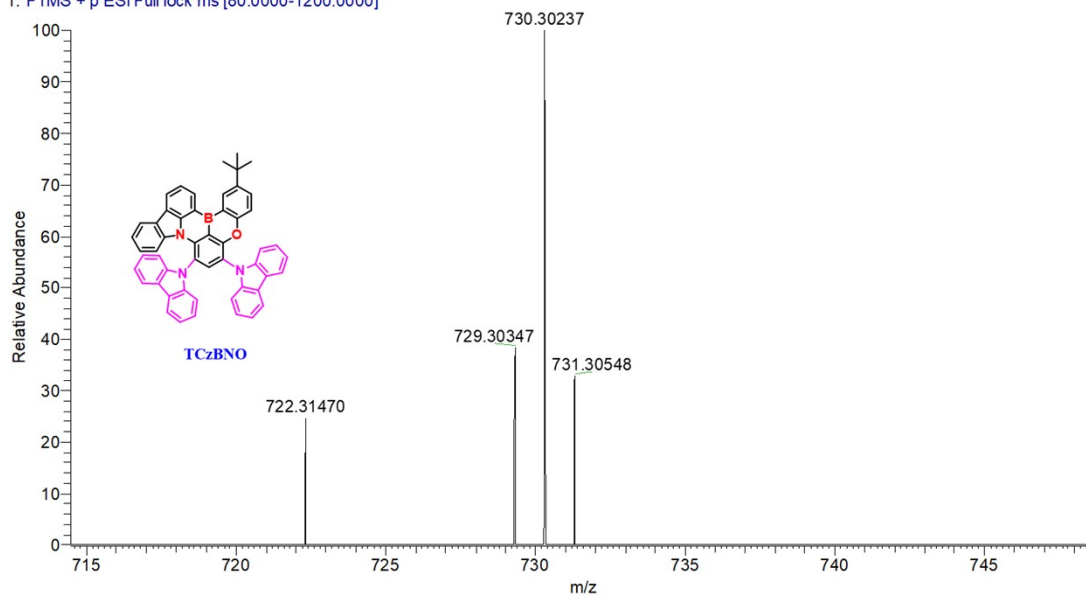


Figure S17. HRMS of DCzBNO.

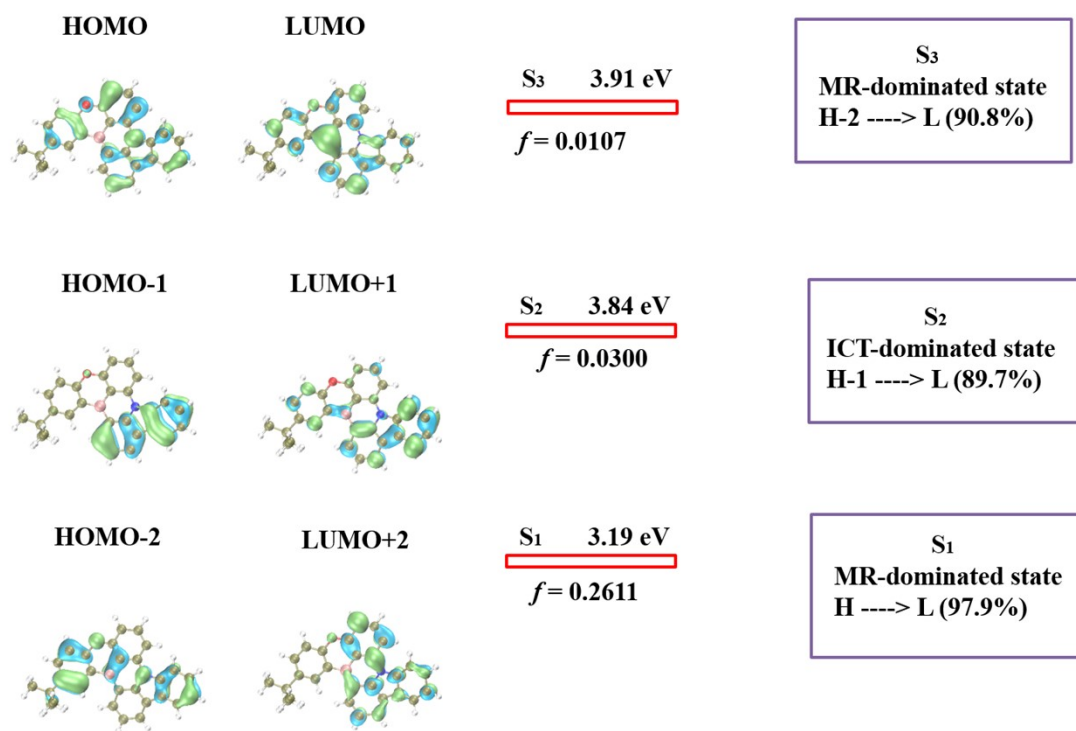


Figure S18. Frontier molecular orbitals of CzBNO.

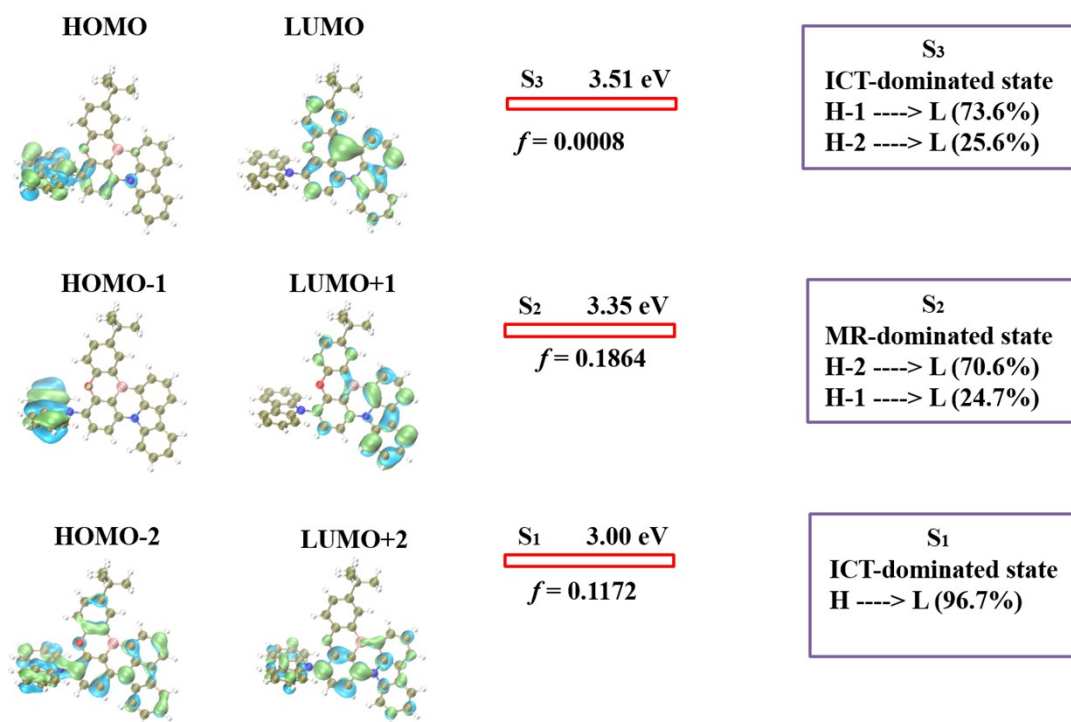


Figure S19. Frontier molecular orbitals of DCzBNO.

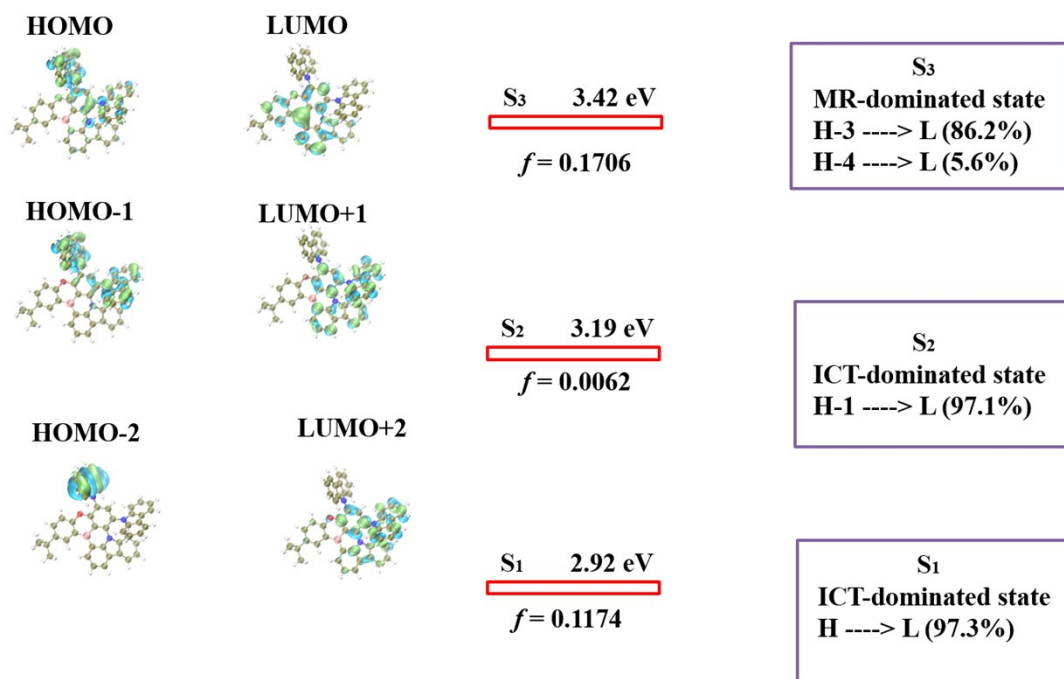


Figure S20. Frontier molecular orbitals of TCzBNO.

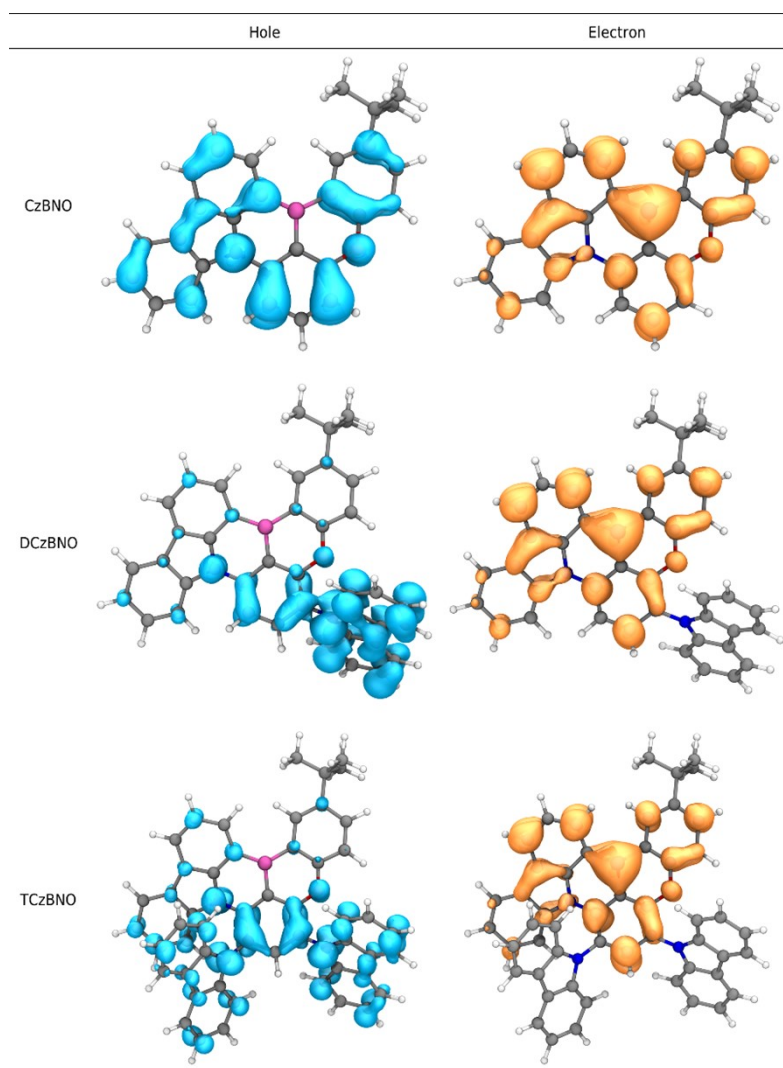


Figure S21. Natural transition orbitals (NTO) of CzBNO, DCzBNO, and TCzBNO.

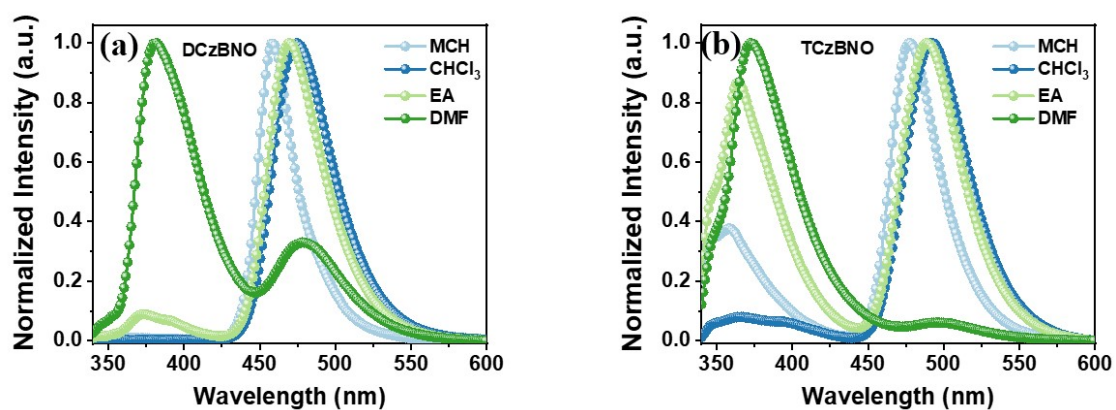


Figure S22. Solvatochromic effects of (a) DCzBNO and (b) TCzBNO: PL spectra in different solvents.

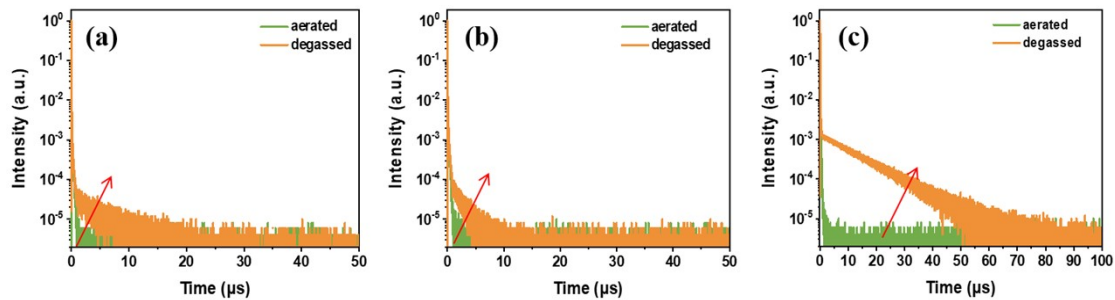


Figure S23. Transient photoluminescence spectra of (a) CzBNO, (b) DCzBNO, and (c) TCzBNO in toluene (1×10^{-5} M) at room temperature.

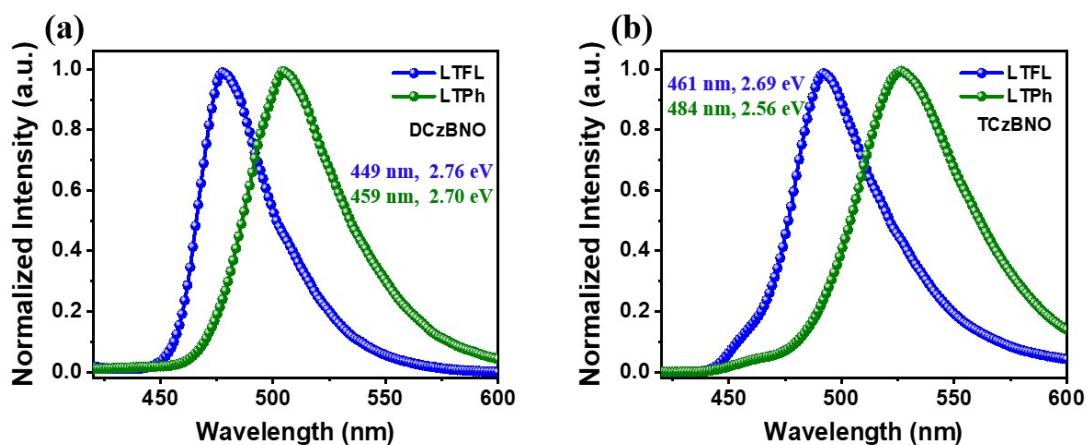


Figure S24. Low-temperature (77 K) fluorescence and phosphorescence spectra of (a) 26DCzPPy: 5 wt% DCzBNO and (b) 26DCzPPy: 5 wt% TCzBNO doped films.

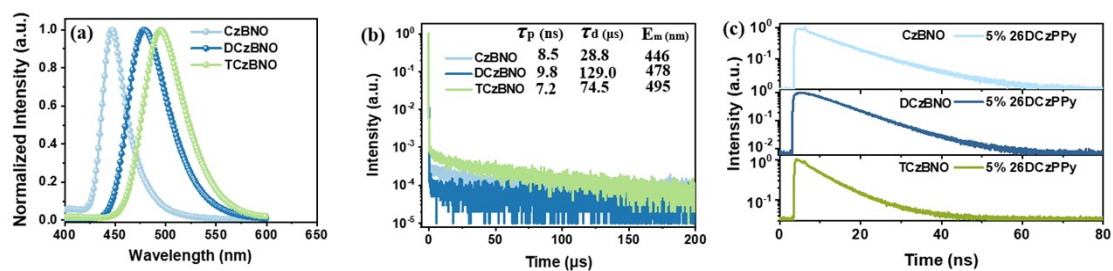


Figure S25. (a) PL, (b) (c) transient PL spectra of CzBNO, DCzBNO, and TCzBNO doped in 26DCzPPy host with 5 wt% concentration.

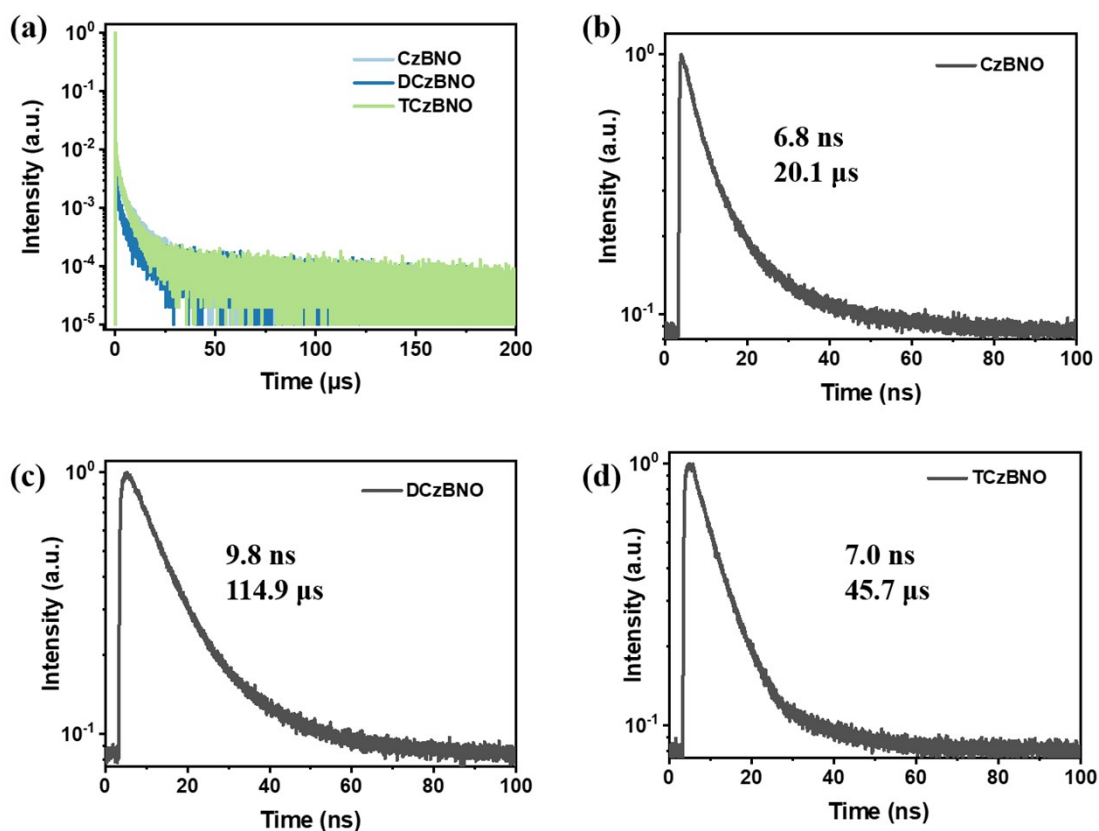


Figure S26. Transient PL spectra of CzBNO, DCzBNO, and TCzBNO ternary film consisting of 26DCzPPy host (79 wt%), 3Cz2CN sensitizer (20 wt%), and the corresponding emitter (1 wt%).

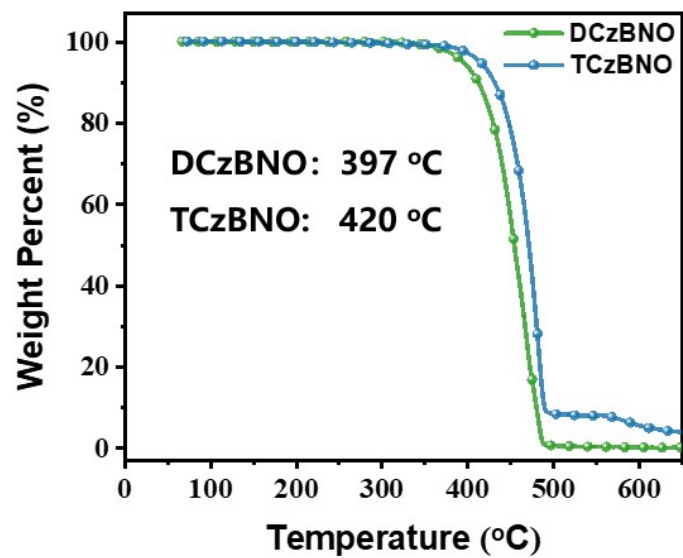


Figure S27. TGA curves of DCzBNO and TCzBNO.

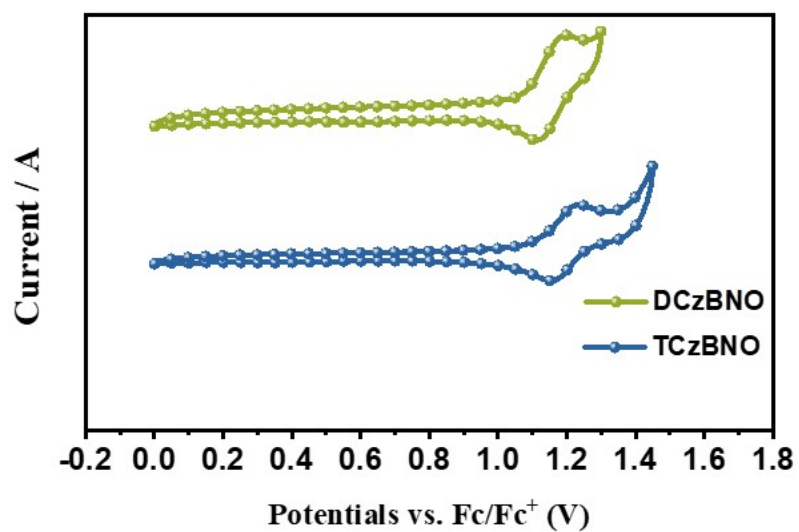


Figure S28. CV curves of DCzBNO and TCzBNO.

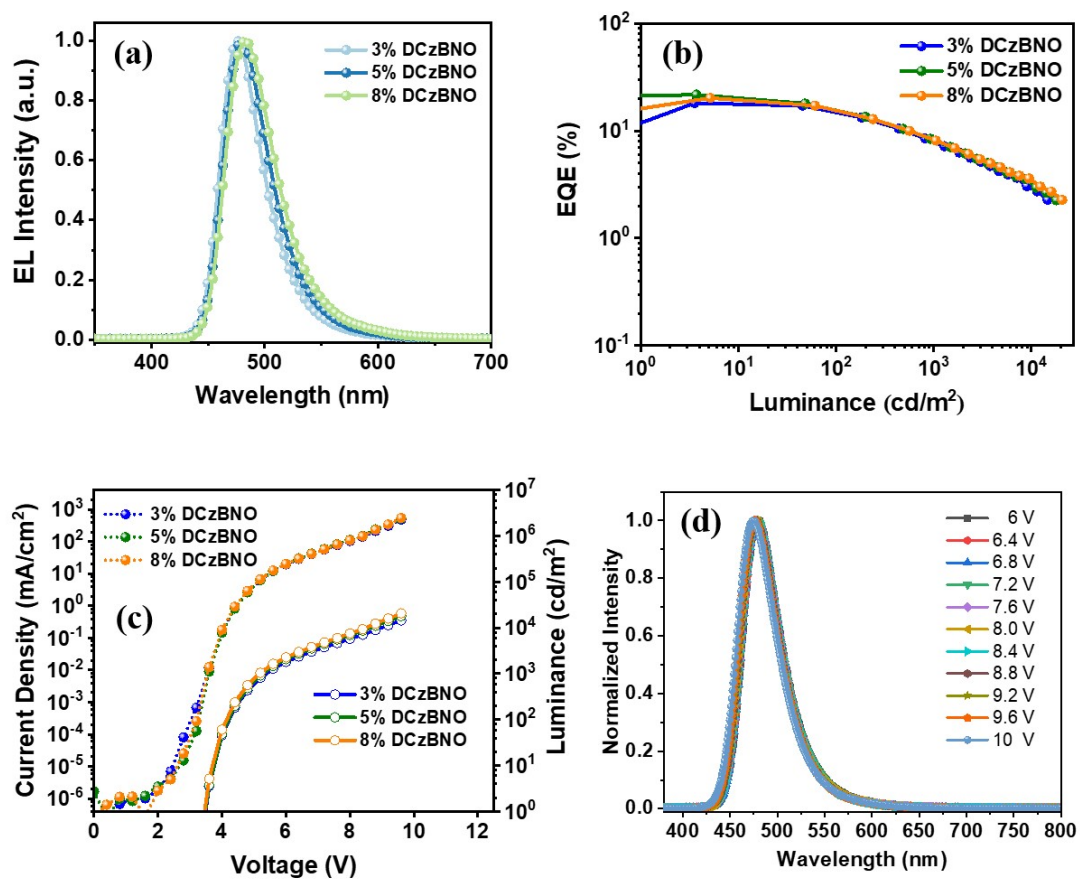


Figure S29. EL performance of non-sensitized device based on DCzBNO emitter with different doping concentrations: (a) EL spectra with different doping concentrations recorded at 7 V, (b) EQE-luminance curve, (c) J-V-L curve, (d) EL spectra with 5% concentration at different driving voltages.

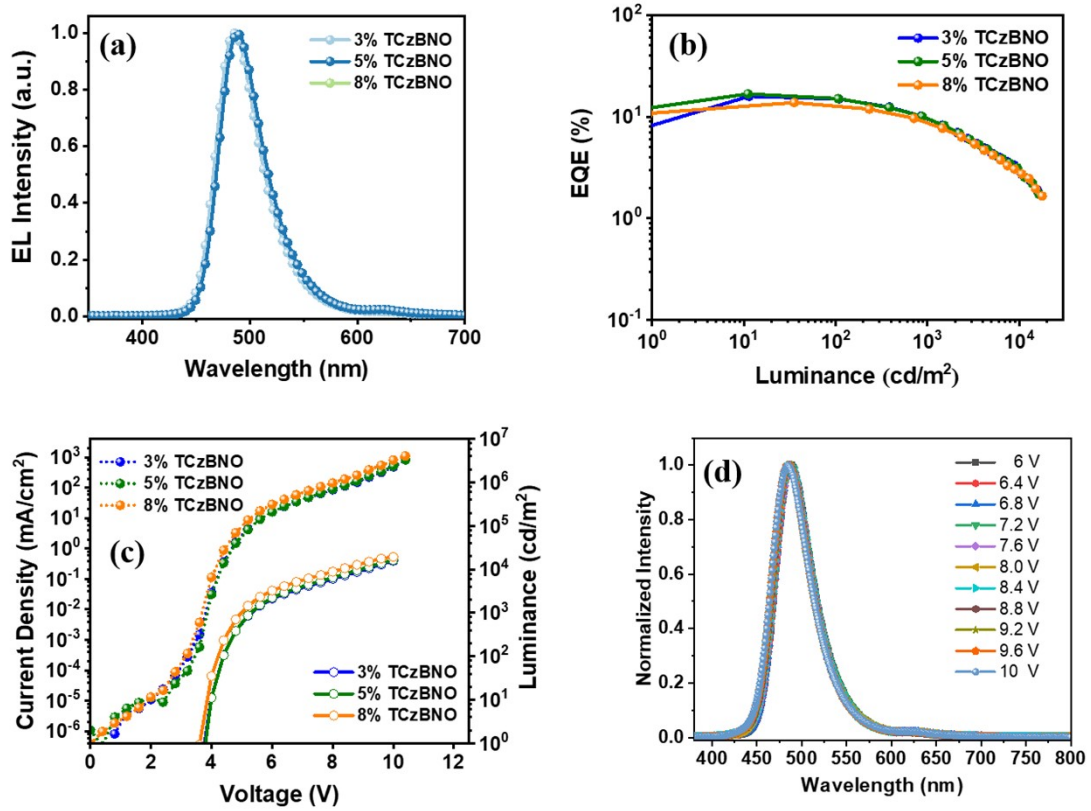
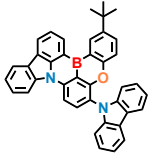
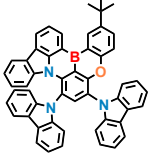
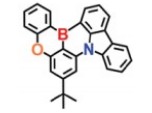
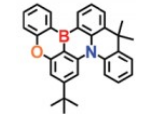
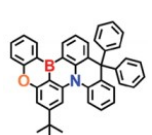
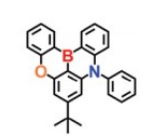
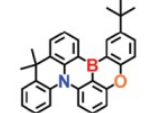
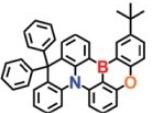
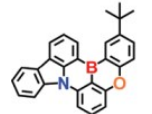
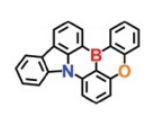
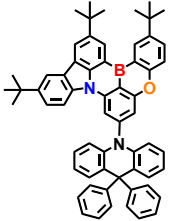
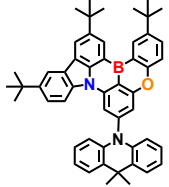
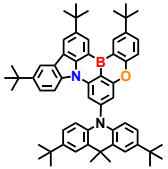


Figure S30. EL performance of non-sensitized device based on TCzBNO emitter with different doping concentrations: (a) EL spectra with different doping concentrations recorded at 7 V, (b) EQE-luminance curve, (c) J-V-L curve, (d) EL spectra with 5% concentration at different driving voltages.

3. Table

Table S1. FWHM values of the representative B/N/O type MR-TADF emitters with single boron.

compound	Molecular structure	FWHM (nm) ^[a]	Ref.
DCzBNO		36/ 47 /48	This work
TCzBNO		48/ 48 / 48	This work
B-O-Cz		27/ - /63	[1]
B-O-dmAc		38/ - /44	[1]
B-O-dpAc		38/ - /42	[1]
B-O-dpa		28/ - /32	[1]
DMAcBNO		34/ 41 /41	[2]
DPAcBNO		33/ 39 /37	[2]
CzBNO		23/ 30 /36	[2]
CzBO		26/ 29 / 30	[3]

BNO-DPAC		20/ 42 / 30	[4]
BNO-DMAC		21/ 56/ 45	[4]
BNO- <i>t</i> BuDMAC		81/ 92/ 75	[4]

[a] The values represent the FWHMs of the reported emitters in dilute solution, doped film, and EL devices, respectively.

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