

Supporting Information

“Medium-Ring” Strategy Enables High-Performance Narrowband

Pure-Blue Multi-Resonance Emitters:

Boosted by a Unique Perpendicular Geometry[†]

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I. General Remarks

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

II. OLED Fabrication and Characterization

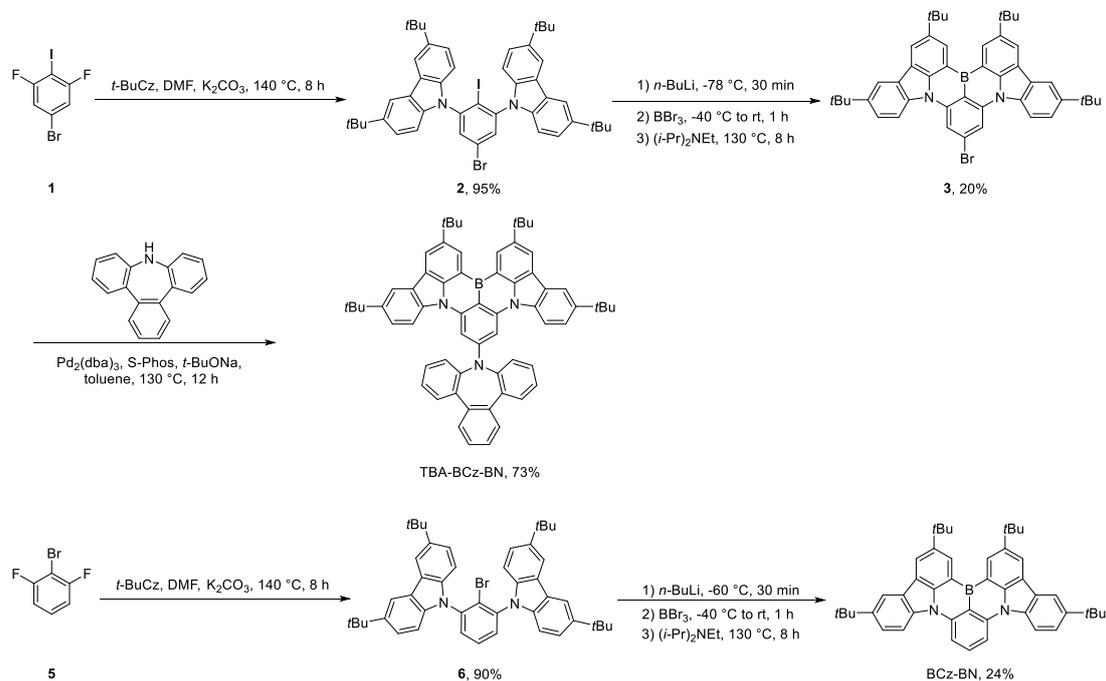
Indium-tin-oxide (ITO) coated glass with a sheet resistance of $15\ \Omega\ \text{sq}^{-1}$ was used as the anode substrate. Prior to film deposition, patterned ITO substrates were cleaned

with alkaline detergent, boiled deionized water, and deionized water thoroughly in ultrasonic bath, dried in an oven, and finally treated with oxygen plasma for 10 min to enhance the surface work function of ITO anode. The organic layers were deposited with the rate of $0.1 \text{ nm}\cdot\text{s}^{-1}$ under high vacuum. The doped and co-doped layers were prepared by co-evaporating dopant and host material from two individual sources, and the doping concentrations were modulated by controlling the evaporation rates of dopant.

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

III. Synthesis and Characterization

Scheme S1. Synthetic routes to BCz-BN and TBA-BCz-BN.



Synthesis of 2 (BCz-I-Br, 9,9'-(5-bromo-2-iodo-1,3-phenylene)bis(3,6-di-*tert*-butyl-9*H*-carbazole)): A dried round bottom flask with a magnetic stir bar was charged with 3,6-di-*tert*-butyl-9*H*-carbazole (6.14 g, 22.0 mmol), K₂CO₃ (6.07 g, 44.0 mmol),

5-bromo-1,3-difluoro-2-iodobenzene (3.12 g, 10.0 mmol) and DMF (*N,N*-dimethylformamide) 100 mL under an air atmosphere. After stirring for 10 min under room temperature, the reaction mixture was allowed to warm to 140 °C and stirred for 8 h. After cooling to room temperature, the solution was filtered through a celite pad and washed with dichloromethane. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/dichloromethane = 20:1, v/v) to provide **2** as white solid in 95% yield (7.9 g, 9.5 mmol). ¹H NMR (CDCl₃, 400 MHz): δ = 1.50 (s, 36H), 7.13 (d, *J* = 8.8 Hz, 4H), 7.54 (dd, *J*₁ = 8.4 Hz, *J*₂ = 1.6 Hz, 4H), 7.70 (s, 2H), 8.18 (d, *J* = 1.6 Hz, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 32.2, 35.0, 104.3, 109.2, 116.1, 122.7, 123.7, 124.5, 133.1, 139.1, 143.6, 144.8 ppm. HRMS (ESI⁺): calcd for C₄₆H₅₁⁷⁹BrIN₂⁺ [M+H]⁺, 837.2275, found 837.2273; calcd for C₄₆H₅₁⁸¹BrIN₂⁺ [M+H]⁺, 839.2254, found 839.2252.

Synthesis of 3 (BCz-BN-Br): In a dried round bottom flask with a magnetic stir bar, a solution of *n*-BuLi in hexane (2.2 mL, 2.5 M, 5.5 mmol) was added slowly to a solution of **2** (4.2 g, 5.0 mmol) in toluene (100 mL) at -78 °C under a nitrogen atmosphere. After stirring for 1.0 h the reaction mixture was allowed to warm to -40 °C. After addition of boron tribromide (0.71 mL, 7.5 mmol), the reaction mixture was stirred at room temperature for 1.0 h. *N,N*-Diisopropylethylamine (3.5 mL, 20.0 mmol) was added at 0 °C and then the reaction mixture was allowed to warm to 130 °C. After stirring for 8 h, the reaction mixture was cooled to room temperature. The solution was filtered through a celite pad and washed with dichloromethane. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/dichloromethane = 10:1, v/v) to provide **3** as yellow powder in 20% yield (720.0 mg, 1.0 mmol). ¹H NMR (400 MHz, CDCl₃): δ = 1.53 (s, 18H), 1.67 (s, 18H), 7.61 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.0 Hz, 2H), 8.15-8.18 (m, 4H), 8.23 (s, 2H), 8.39 (d, *J* = 1.6 Hz, 2H), 9.02 (d, *J* = 2.0 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 32.0, 32.3, 34.9, 35.3, 110.9, 114.2, 117.4, 121.0, 123.3, 124.6, 126.5, 127.8, 129.8, 138.6,

140.4, 143.8, 145.0, 145.7 ppm. HRMS (ESI⁺): calcd for C₄₆H₄₉B⁷⁹BrN₂ [M+H]⁺ 719.3167, found 719.3165; calcd for C₄₆H₄₉B⁸¹BrN₂ [M+H]⁺ 721.3146, found 721.3147.

Synthesis of 4 (TBA-BCz-BN): A dried round bottom flask with a magnetic stir bar was charged with Pd₂(dba)₃ (18.3 mg, 0.02 mmol), S-Phos (24.7 mg, 0.06 mmol), *t*-BuONa (76.8 mg, 0.8 mmol), **3** (287.2 mg, 0.4 mmol), 9*H*-tribenzo[*b,d,f*]azepine (121.5 mg, 0.5 mmol) (TBA). After being evacuated and backfilled with nitrogen (3 times), toluene (10 mL) was added under N₂ atmosphere. The reaction mixture was stirred at 130 °C for 12 h. After being cooled down to room temperature, the solution was filtered through a celite pad and washed with dichloromethane. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/dichloromethane = 5:1, v/v) to provide compound **4** as yellow powder in 73% yield (255.7 mg, 0.29 mmol). ¹H NMR (400 MHz, CDCl₃): δ = 1.53 (s, 18H), 1.65 (s, 18H), 7.32-7.34 (m, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.46 (s, 2H), 7.63-7.71 (m, 6H), 7.76 (t, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 7.6 Hz, 2H), 8.21 (s, 2H), 8.36 (s, 2H), 9.03 (s, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 32.0, 32.3, 34.9, 35.2, 93.4, 112.7, 117.3, 119.1, 122.7, 123.9, 127.2, 128.2, 128.4, 128.8, 129.4, 129.7, 129.9, 131.5, 137.3, 138.2, 139.3, 141.8, 144.3, 144.8, 145.4, 145.5, 152.0 ppm. HRMS (ESI⁺): calcd for C₆₄H₆₁BN₃⁺ [M+H]⁺ 882.4959, found 882.4953.

Synthesis of 6 (BCz-Br, (9,9'-(2-bromo-1,3-phenylene)bis(3,6-di-*tert*-butyl-9*H*-carbazole)): A dried round bottom flask with a magnetic stir bar was charged with 3,6-di-*tert*-butyl-9*H*-carbazole (8.37 g, 30.0 mmol), K₂CO₃ (8.28 g, 60.0 mmol), 2-bromo-1,3-difluorobenzene (1.93 g, 10.0 mmol) and DMF 150 mL under an air atmosphere. After stirring for 10 min under room temperature, the reaction mixture was allowed to warm to 140 °C and stirred for 8 h. After cooling to room temperature, the solution was filtered through a celite pad and washed with dichloromethane. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum

ether/dichloromethane = 10:1, v/v) to provide **6** as a white solid in 90% yield (6.4 g, 9.0 mmol). ^1H NMR (400 MHz, CDCl_3): δ = 1.48 (s, 36H), 7.12 (d, J = 8.8 Hz, 4H), 7.51 (d, J = 8.4 Hz, 4H), 7.62 (d, J = 8.0 Hz, 2H), 7.68 (t, J = 8.8 Hz, 1H), 8.17 (s, 4H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 32.2, 34.9, 109.5, 116.6, 123.5, 123.9, 125.9, 129.4, 131.0, 139.3, 139.7, 143.2 ppm. HRMS (ESI⁺): calcd for $\text{C}_{46}\text{H}_{51}^{79}\text{BrN}_2\text{Na}^+$ [M+Na]⁺ 733.3128, found 733.3130; $\text{C}_{46}\text{H}_{51}^{81}\text{BrN}_2\text{Na}^+$ [M+Na]⁺ 735.3107, found 735.3108.

Synthesis of 7 (BCz-BN): In a dried round bottom flask with a magnetic stir bar, a solution of *n*-BuLi in hexane (4.0 mL, 2.5 M, 10.0 mmol) was added slowly to a solution of **6** (6.4 g, 9.0 mmol) in toluene (100 mL) at -60 °C under a nitrogen atmosphere. After stirring for 1.0 h at -60 °C, the reaction mixture was allowed to warm to -40 °C. After addition of boron tribromide (1.29 mL, 13.5 mmol), the reaction mixture was stirred at room temperature for 1.0 h. *N,N*-Diisopropylethylamine (6.3 mL, 36.0 mmol) was added at 0 °C and then the reaction mixture was allowed to warm to 130 °C. After stirring for 12 h, the reaction mixture was cooled to room temperature. The solution was filtered through a celite pad and washed with dichloromethane. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/dichloromethane = 20:1, v/v) to provide a bright yellow solid in 24% yield (1.39 g, 2.2 mmol). ^1H NMR (400 MHz, CDCl_3): δ = 1.54 (s, 18H), 1.68 (s, 18H), 7.65 (dd, J_1 = 8.8 Hz, J_2 = 2 Hz, 2H), 7.99 (t, J = 8 Hz, 1H), 8.26 (d, J = 2 Hz, 2H), 8.31 (d, J = 8 Hz, 2H), 8.39 (d, J = 8.8 Hz, 2H), 8.47 (d, J = 1.6 Hz, 2H), 9.13 (d, J = 1.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 32.0, 32.4, 34.9, 35.3, 108.1, 114.2, 117.4, 120.8, 123.7, 124.5, 127.2, 129.9, 133.1, 138.5, 141.7, 144.4, 144.7, 145.4 ppm. HRMS (ESI⁺): calcd for $\text{C}_{46}\text{H}_{50}\text{BN}_2^+$ [M+H]⁺ 641.4062, found 641.4061.

IV. Crystal Data

Table S1. Crystal Data for TBA-BCz-BN (CCDC: 2247576)

Identification code	TBA-BCz-BN
Empirical formula	C ₆₅ H ₆₁ BCl ₃ N ₃
Formula weight	1001.32
Temperature/K	231.0
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	15.1246(12)
b/Å	15.3418(9)
c/Å	23.6578(18)
α/°	90
β/°	99.404(3)
γ/°	90
Volume/Å ³	5415.7(7)
Z	4
ρ _{calc} /cm ³	1.228
μ/mm ⁻¹	0.213
F(000)	2112.0
Crystal size/mm ³	0.38 × 0.36 × 0.29
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.37 to 49.998
Index ranges	-17 ≤ h ≤ 17, -16 ≤ k ≤ 18, -28 ≤ l ≤ 28
Reflections collected	29947
Independent reflections	9482 [R _{int} = 0.0552, R _{sigma} = 0.0541]
Data/restraints/parameters	9482/10/682
Goodness-of-fit on F ²	1.017
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0696, wR ₂ = 0.1783
Final R indexes [all data]	R ₁ = 0.1001, wR ₂ = 0.2068
Largest diff. peak/hole / e Å ⁻³	0.64/-0.92

V. Additional Spectra and Data

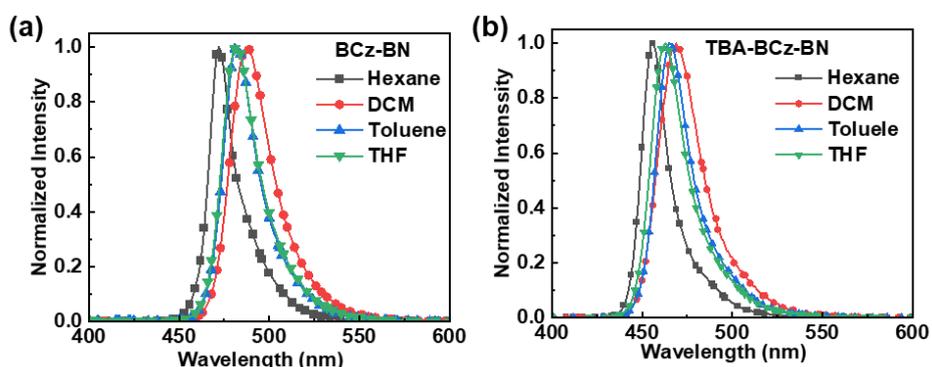


Figure S1. Photoluminescence spectra measured in different polar solvents (1.0×10^{-5} M, 298 K) of (a) BCz-BN and (b) TBA-BCz-BN.

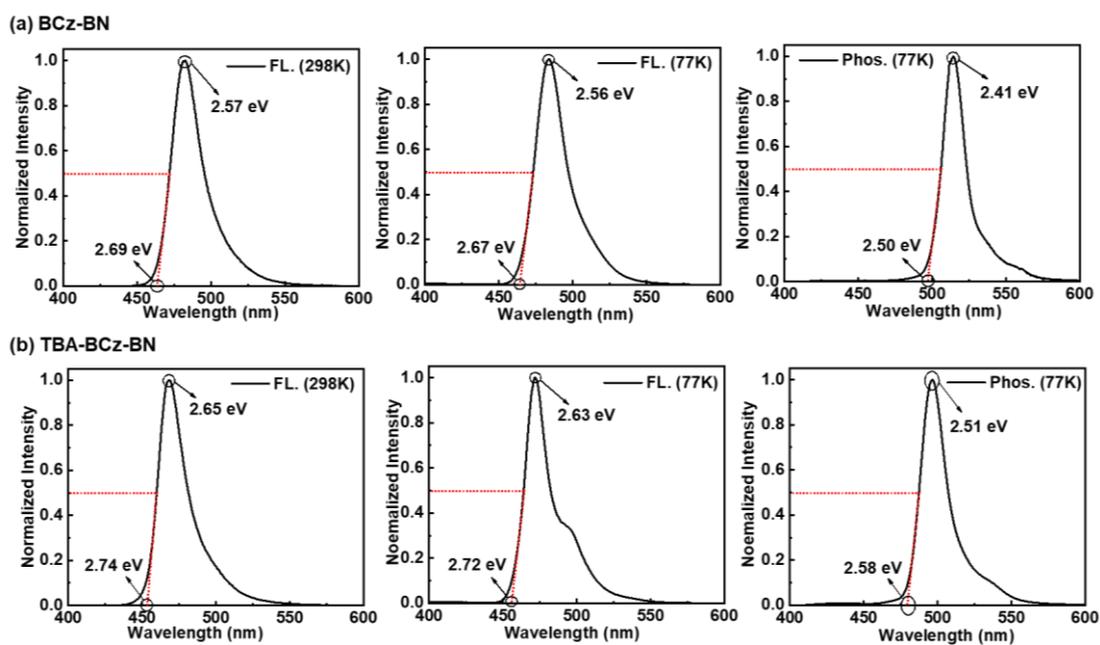


Figure S2. The singlet energy (E_{S1}) values and triplet energy (E_{T1}) values measured by the onset wavelengths and peaks of the FL.(at 298K and 77K) and Phos.(77K) spectra for (a) BCz-BN and (b) TBA-BCz-BN.

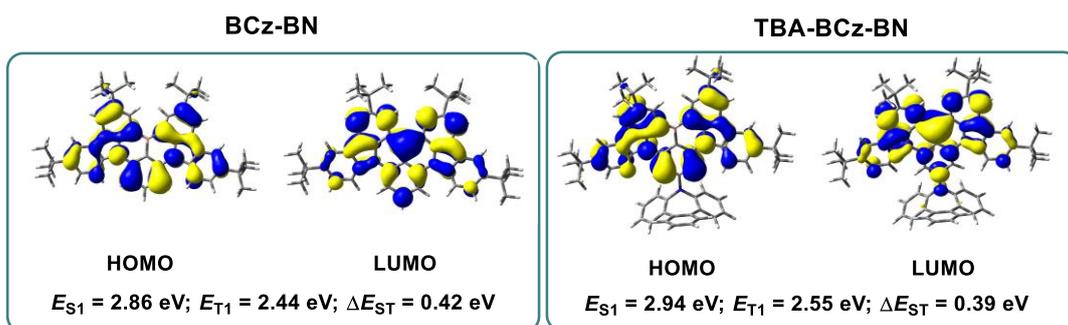


Figure S3. Theoretical calculation results of the FMOs distributions and energy level alignments of (a) BCz-BN and (b) TBA-BCz-BN.

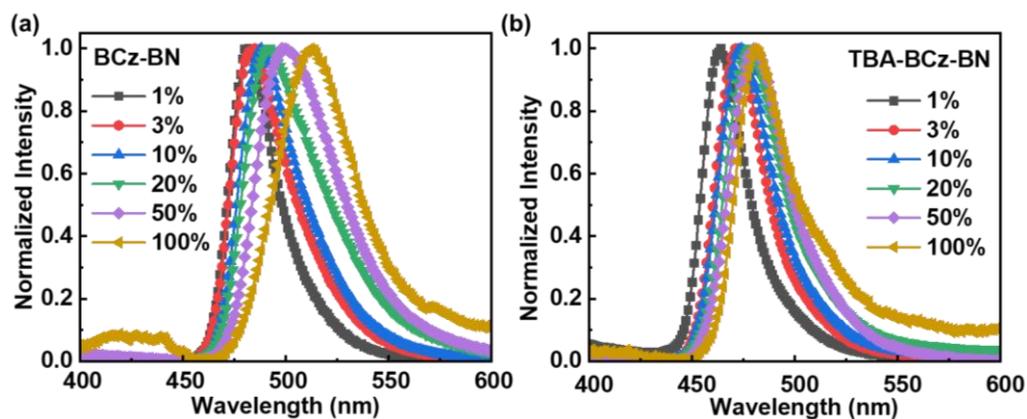


Figure S4. Normalized photoluminescence spectra of (a) BCz-BN and (b) TBA-BCz-BN in mCBP host at different concentrations.

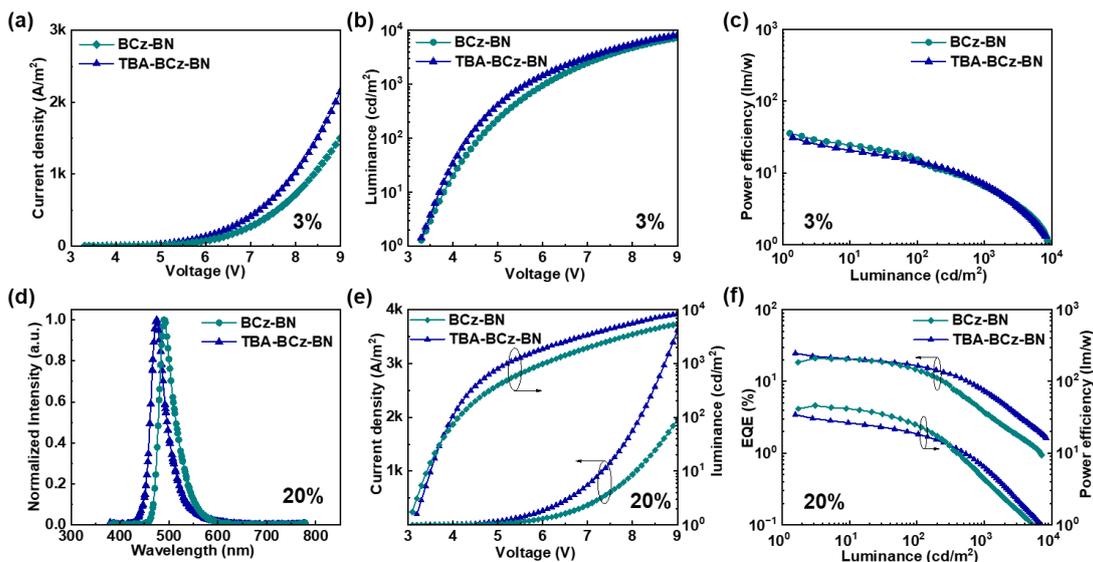


Figure S5. EL performances of OLEDs with the emitter at different doping concentrations. (a) Current density versus voltage curves, (b) luminance versus voltage curves and (c) power efficiency versus luminance curves of 3% BCz-BN- and TBA-BCz-BN-based OLEDs. (d) EL spectra versus wavelength curves, (e) current density and luminance versus voltage curves and (f) EQE and power efficiency versus luminance curves of 20% BCz-BN- and TBA-BCz-BN-based OLEDs.

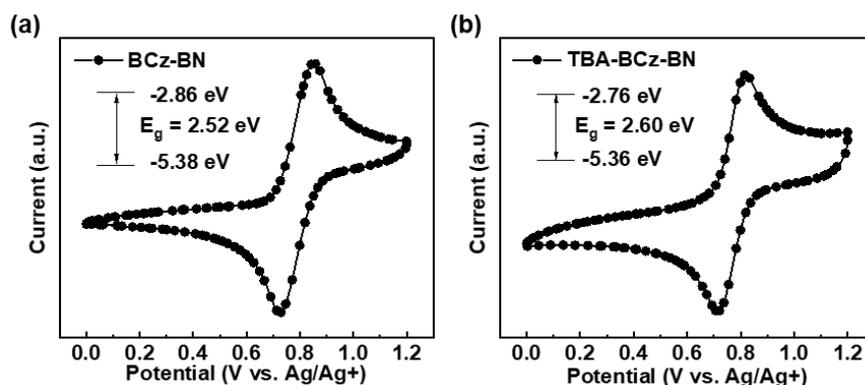


Figure S6. Cyclic voltammograms of (a) BCz-BN and (b) TBA-BCz-BN measured in dry dichloromethane containing 0.1 M of tetrabutylammonium hexafluorophosphate.

Table S2. Summary of photophysical properties for BCz-BN and TBA-BCz-BN in mCBP doped films.

Emitter	doping ratio [x wt%]	λ [nm]	FWHM [nm]	PLQY [%]
TBA-BCz-BN	1	464	25	95
	3	472	28	86
	10	474	31	78
	20	478	33	61
	50	480	34	51
	100	480	34	39
BCz-BN	1	482	27	91
	3	485	33	86
	10	488	35	65
	20	492	43	56
	50	498	46	42
	100	512	46	34

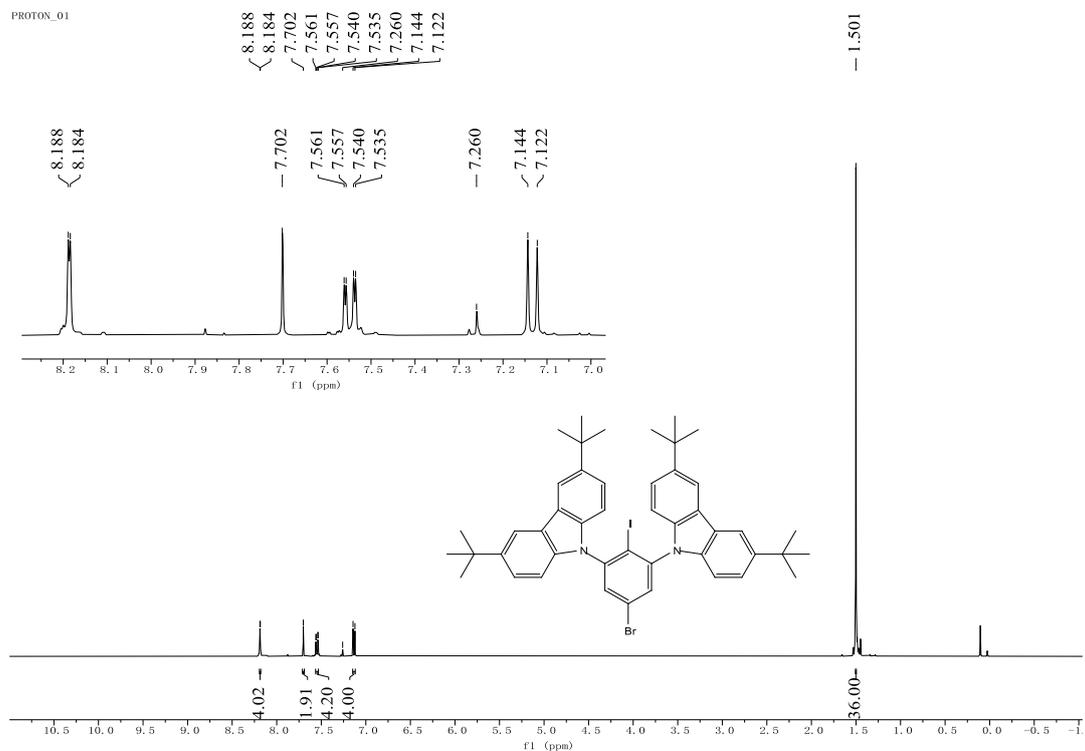
Table S3. EL performances of 20% BCz-BN- and TBA-BCz-BN-based OLEDs.

Emitter	EL _{peak} [nm]	V _{on} ^a [V]	FWHM [nm]	EQE _{max/100/1000} ^b [%]	PE _{max/100/1000} ^c [lm W ⁻¹]	CIE ^d [x, y]
BCz-BN	490	3.1	36	18.4%/13.8%/3.5%	41.6/23.0/4.1	[0.12,0.48]
TBA-BCz-BN	475	3.2	34	24.7%/16.5%/7.5%	34.5/18.4/6.5	[0.13,0.22]

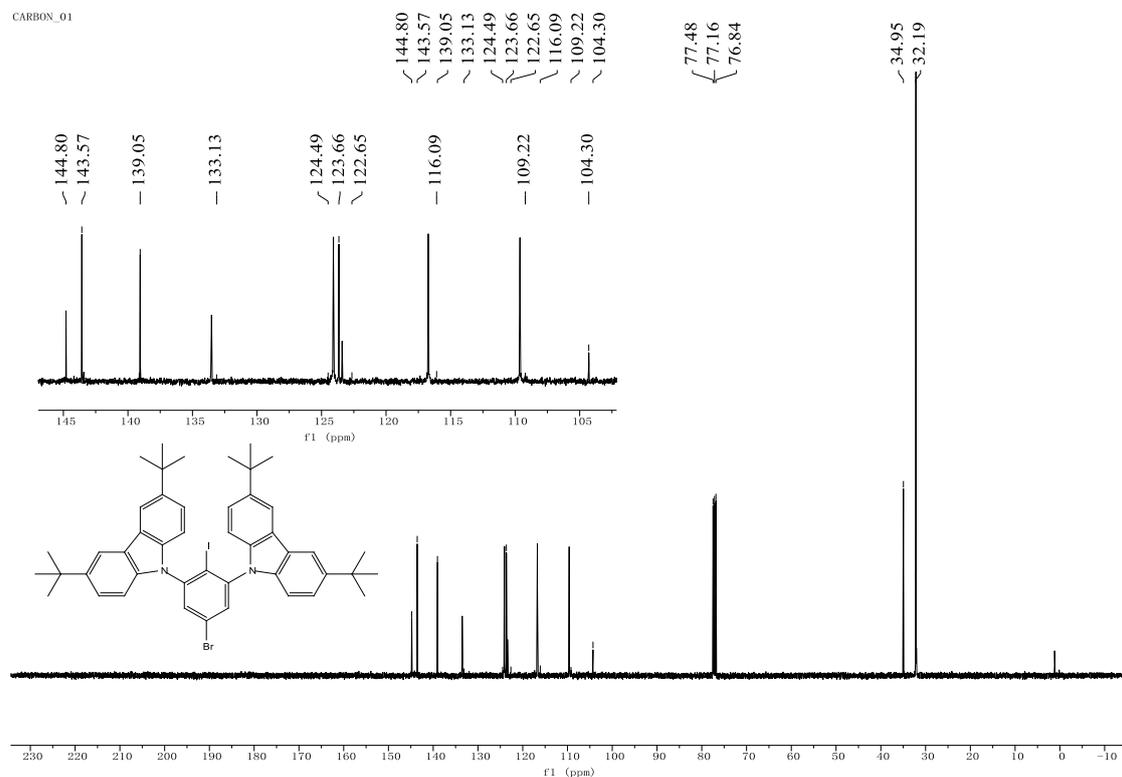
^aTurn-on voltage. ^bExternal quantum efficiency of maximum/at 100 cd m⁻²/1000 cd m⁻². ^cPower efficiency of maximum/at 100 cd m⁻²/1000 cd m⁻². ^dCommission Internationale de l'Eclairage (CIE) coordinates.

VI. Copies of NMR spectra

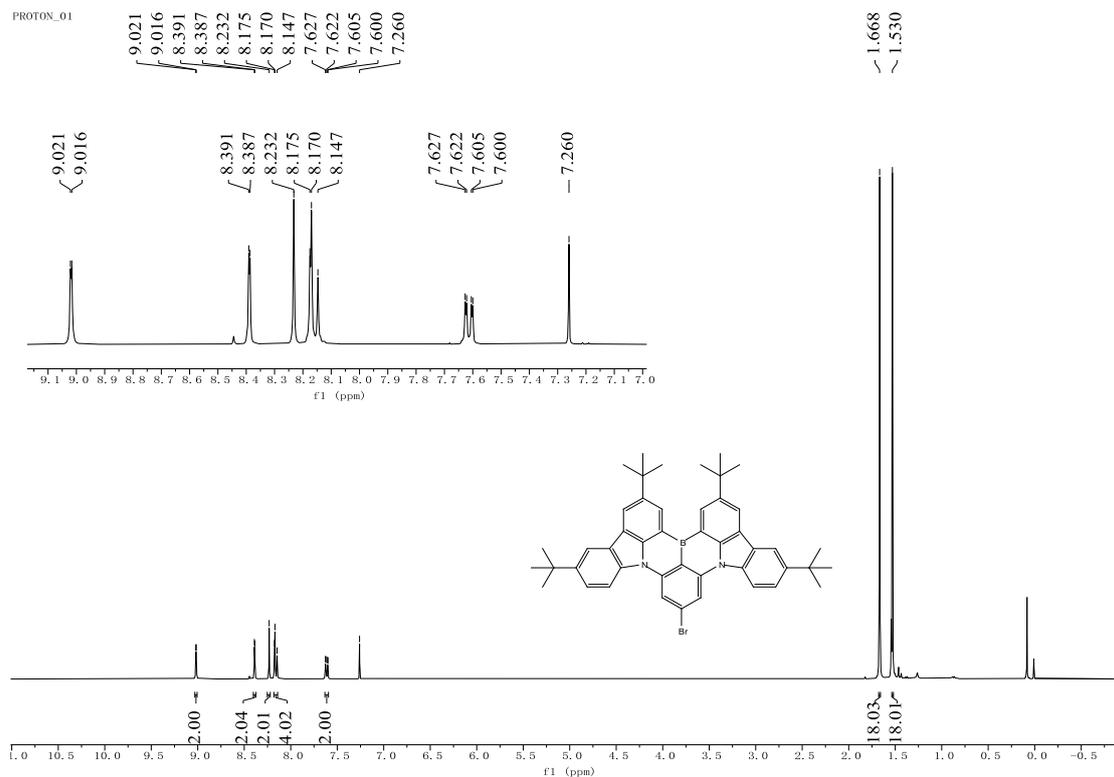
¹H NMR spectrum of **2** (CDCl₃)



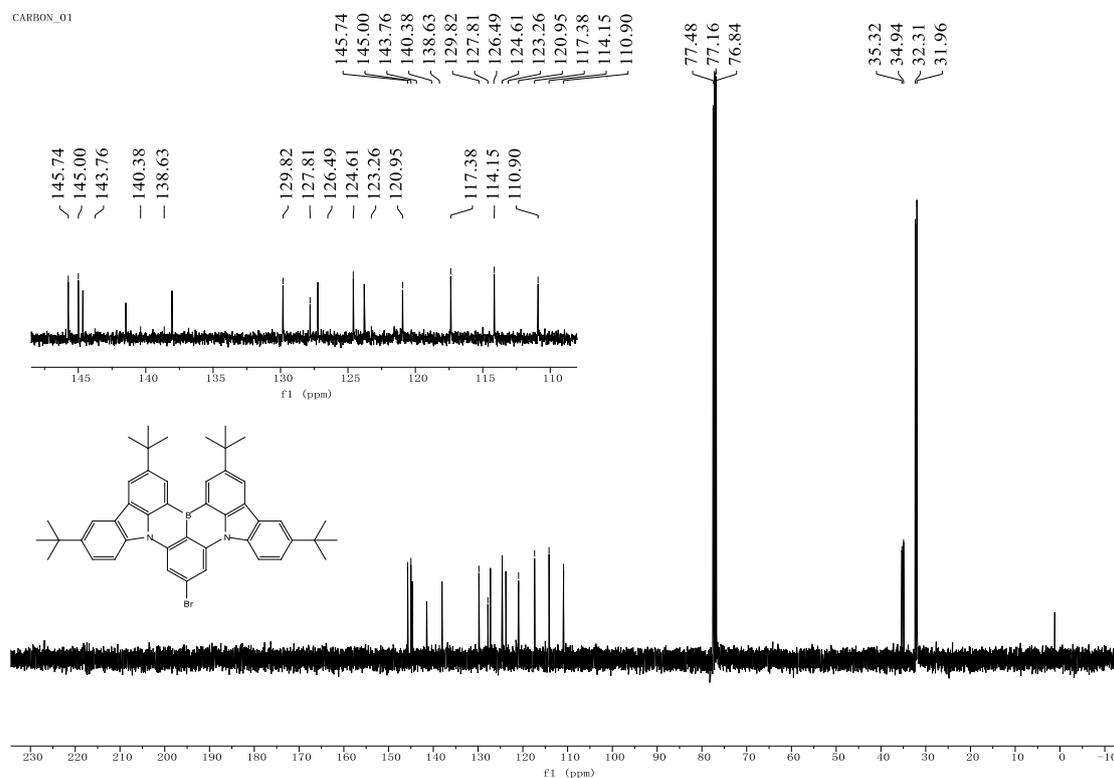
¹³C NMR spectrum of **2** (CDCl₃)



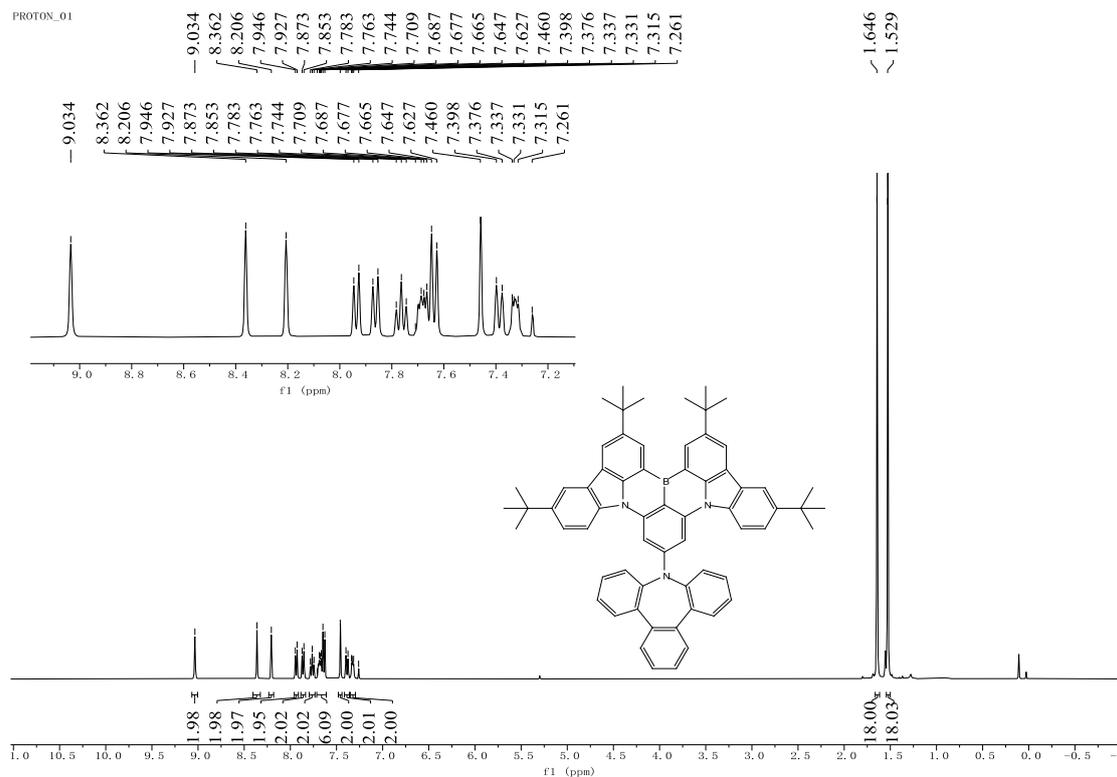
¹H NMR spectrum of **3** (CDCl₃)



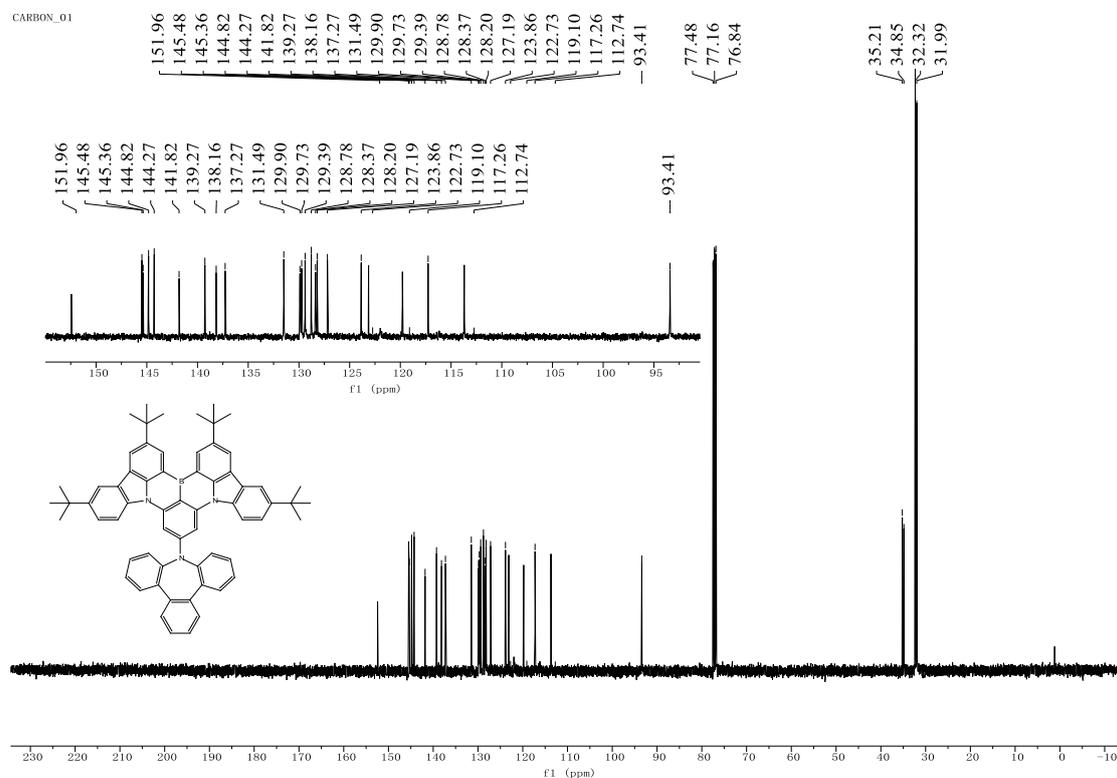
¹³C NMR spectrum of **3** (CDCl₃)



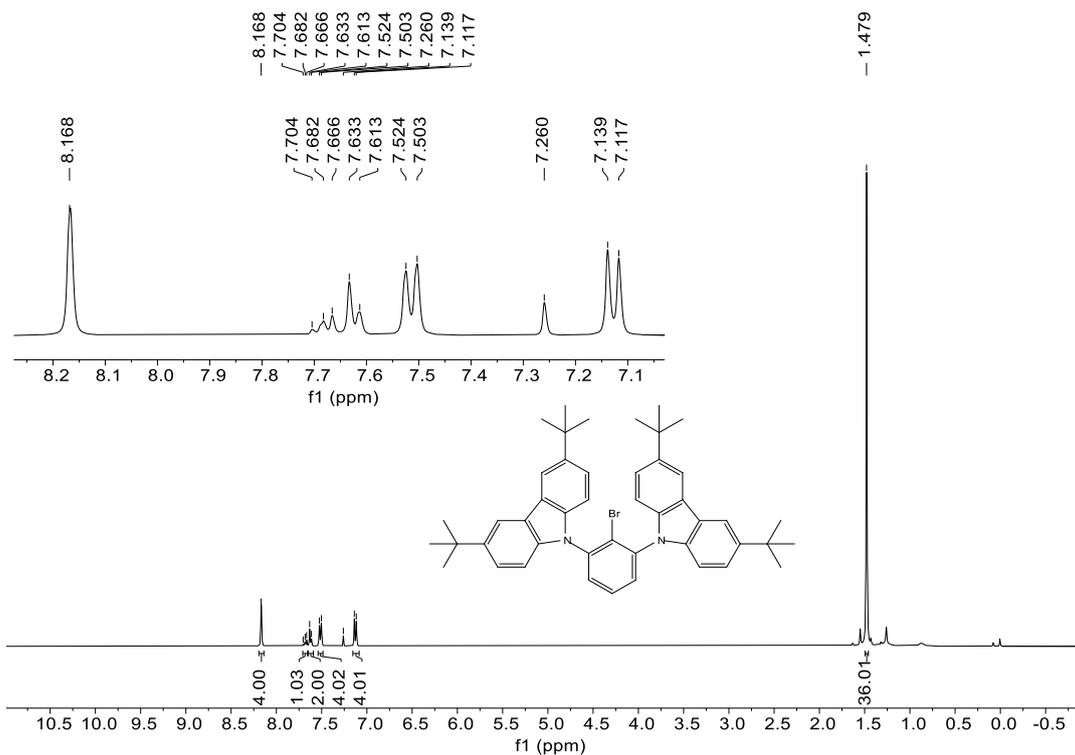
¹H NMR spectrum of TBA-BCz-BN (CDCl₃)



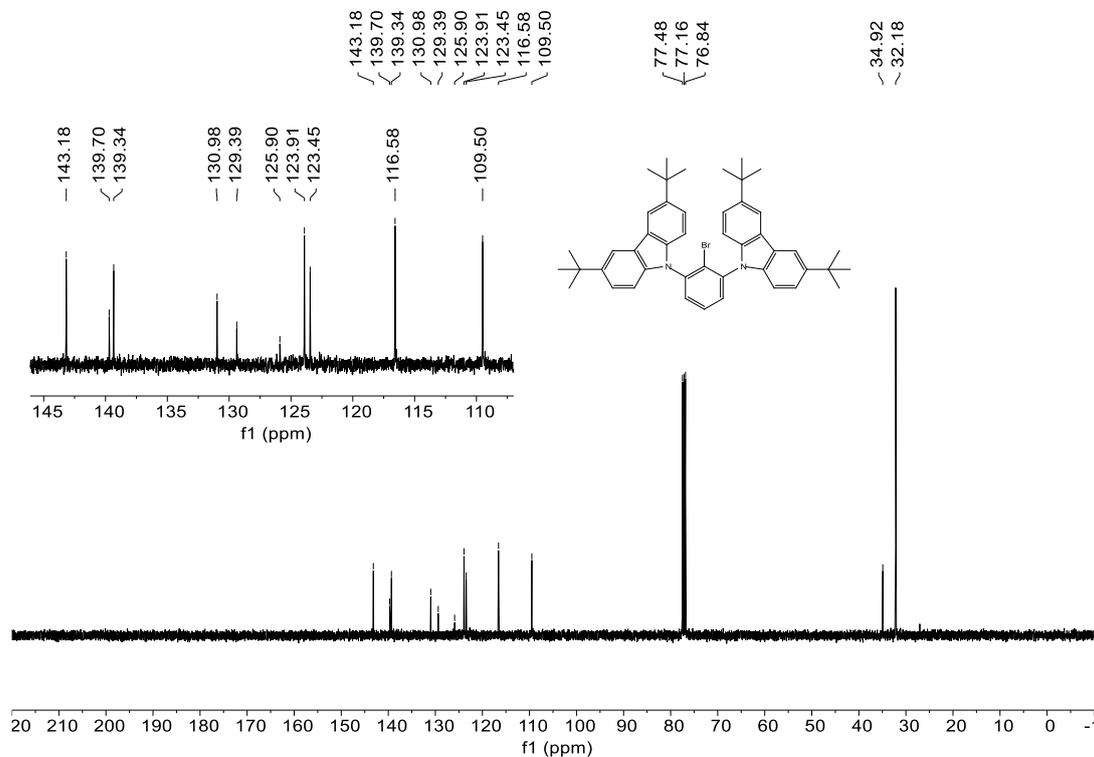
¹³C NMR spectrum of TBA-BCz-BN (CDCl₃)



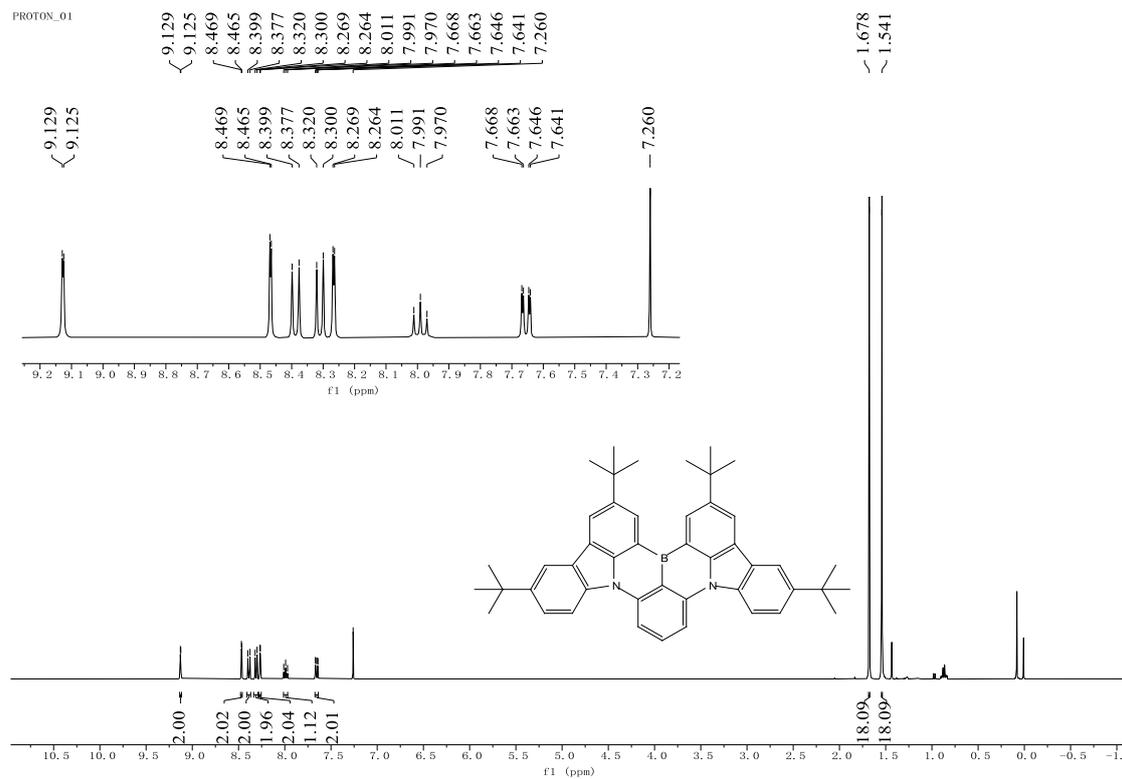
^1H NMR spectrum of **5** (CDCl_3)



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



¹H NMR spectrum of BCz-BN (CDCl₃)



¹³C NMR spectrum of BCz-BN (CDCl₃)

