Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Phenylene-Bridged Multi-Resonance Cyclic TADF Emitters for High Color Purity Sky-Blue OLEDs with EQE of 30%

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Contents

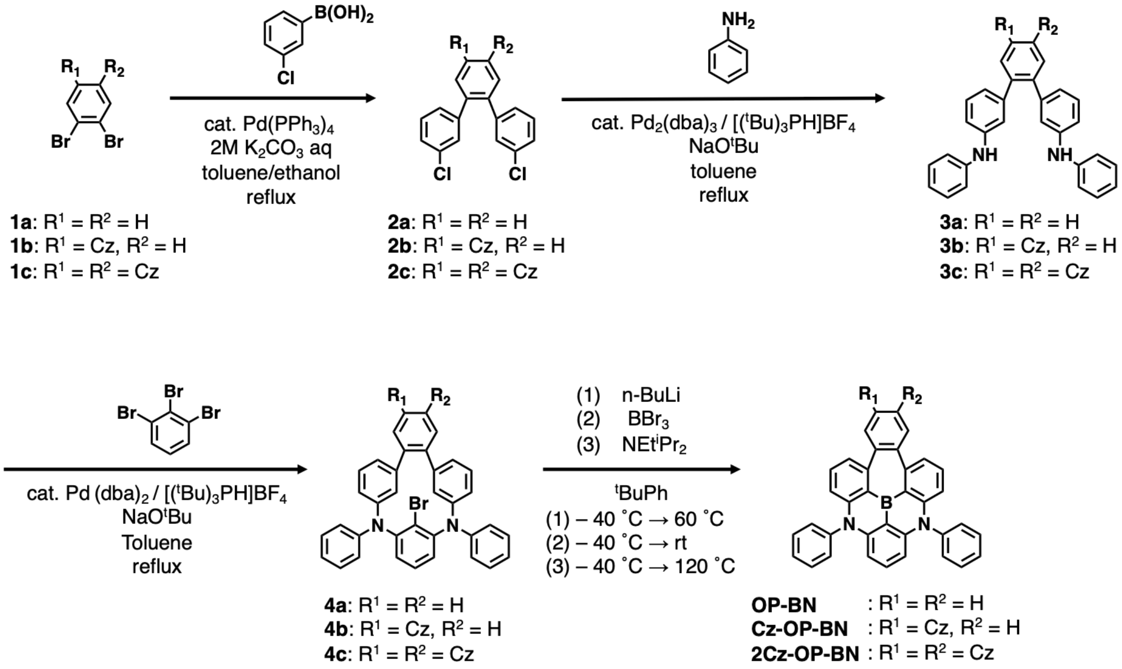
1. General Considerations

Quantum chemical calculations were performed using the hybrid DFT functional Becke and Hartree-Fock exchange and Lee Yang and Parr correlation (B3LYP) as implemented by the Gaussian 09 program packages. [1] Electrons were described by the Pople's 6-31G(d) and 6-31G(d) basis sets for molecular structure optimization and single-point energy calculations, respectively. ^{1}H NMR, ^{11}B NMR and ^{13}C NMR spectra were recorded on JEOL 400 (400MHz) as spectrometer. MS spectrum was obtained using a JEOL JMS-K9 mass spectrometer. TGA was undertaken using a SEIKO EXSTAR 6000 TG/DTA 6200 unit under nitrogen atmosphere at a heating rate of 10 ˚C min^{-1}. DSC was performed using a Perkin-Elmer Diamond DSC Pyris instrument under nitrogen atmosphere at a heating rate of 10 ˚C min^{-1}. UV–vis absorption spectra was measured using a Shimadzu UV-2600 spectrophotometer. Photoluminescence spectra were measured using a FluoroMax-2 (Jobin-Yvon-Spex) luminescence spectrometer. The I_p was determined by a PYS under the vacuum (=10^{-3} Pa). [2] Transient PL decay curves and time resolved photoluminescence spectra were measured by using a streak camera (C4334 from Hamamatsu Photonics) at 300 K and 6 K. Photoluminescence quantum yield were measured using a Hamamatsu C11347 absolute PL quantum yield spectrometer with an integral sphere at an excitation wavelength of each sample. Natural transition orbitals (NTO) of S_1 and T_n (n = 1, 2) states were calculated using B3LYP functional with 6-31G(d) basis set. SOC matrix elements (ζ) were calculated by using the Breit–Pauli Hamiltonian with an effective charge approximation implemented in the PySOC program [3] at the same level of theory. Using singlet-triplet (S_1-T_n) energy gap and corresponding ζ, the rate constants for RISC prosses (k_{RISC}) were calculated according to the reference method [4].

2. Device Fabrication and Characterization

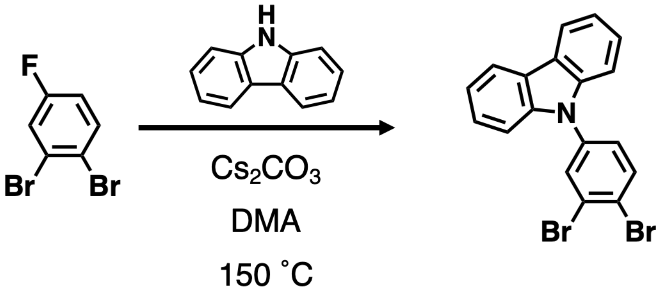
The substrates were cleaned with ultrapurified water and organic solvents, and then dry-cleaned for 30 minutes by exposure to UV-O_3. The organic layers were deposited onto the ITO substrates under the vacuum (=10^{-5} Pa), successively. LiF and Al was patterned using a shadow mask with an array of 2 mm × 2mm openings without breaking the vacuum (=10^{-5} Pa). The electroluminescent (EL) were taken using an optical multichannel analyzer Hamamatsu Photonics PMA-11. The current density–voltage and luminance–voltage characteristics were measured by using a Keithley source measure unit 2400 and a Minolta CS200 luminance meter, respectively.

3. Synthesis



Scheme S1. Synthesis of **OP-BN**, **Cz-OP-BN**, **2Cz-OP-BN**

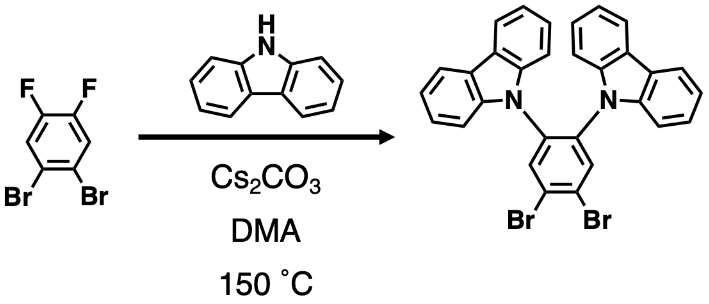
Synthesis of 1b



Carbazole (8.36 g, 50 mmol), cesium carbonate (48.9 g, 150 mmol), dry N,N-dimethylacetamide 100 mL were added to a round bottom flask and stirred 1 hour at room temperature under N_2 flow. Then, 1,2-dibromo-4-fluorobenzene (6.3 mL, 50 mmol) was added and the resultant mixture was stirred 20 hours at 150 ˚C under N_2 flow. The mixture was extracted with diethyl ether and washed with water. The combined organic extracts were dried over $MgSO_4$ and evaporated to dryness. The resulting solid was purified by chromatography on silica gel (eluent: hexane/toluene = 19 : 1) to obtain **1b** as a white solid. (16.8 g, 83.3 %)

^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.13 (d, J = 7.6 Hz, 2H), 7.87 (d, J = 2.8 Hz, 1H), 7.85 (d, J = 8.3 Hz, 1H), 7.44-7.38 (m, 5H), 7.31 (t, J = 6.9 Hz, 2H) ppm ; MS (ASAP) : m/z = 401 $[M+H]^+$

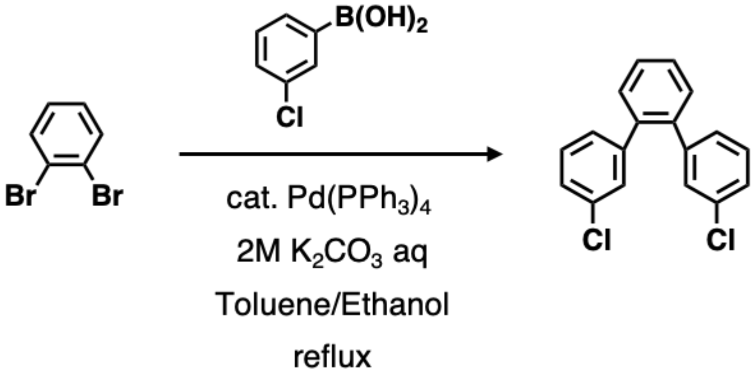
Synthesis of 1c



Carbazole (40.2 g, 100 mmol), cesium carbonate (81.5 g, 250 mmol), dry N,N-dimethylacetamide 500 mL were added to a round bottom flask and stirred 1 hour at room temperature under N_2 flow. Then, 1,2-dibromo-4,5-difluorobenzene (27.2 g, 100 mmol) was added and the resultant mixture was stirred 16 hours at 150 ˚C under N_2 flow. The mixture was extracted with diethyl ether and washed with water. The combined organic extracts were dried over $MgSO_4$ and evaporated to dryness. The resulting solid was purified by chromatography on silica gel (eluent: hexane/toluene = 9 : 1) to obtain **1c** as a white solid. (49.9 g, 88.1 %)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 2H), 7.77-7.74 (m, 4H), 7.13-7.11 (m, 4H), 7.07-7.02 (m, 8H) ppm ; MS (ASAP) : m/z = 566 $[M+H]^+$

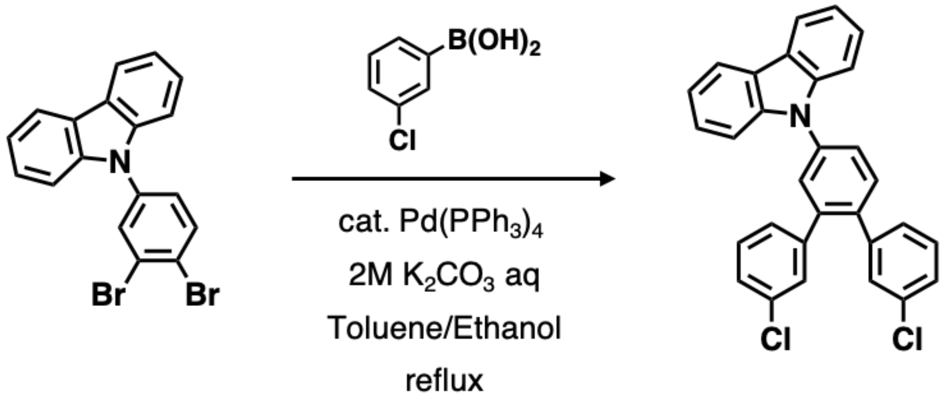
Synthesis of 2a



1,2-Dibromobenzene (5.9 mL, 50 mmol), 3-chlorobenzoic Acid (18.8 g, 120 mmol), 2M K_2CO_3 aq (100 mL), toluene 200 mL, ethanol 100 mL were added to a round bottom flask and nitrogen bubbled through the mixture for 1 hour. Then, Pd(PPh$_3$)$_4$ (2.89 g, 2.5 mmol) was added and the resultant mixture was stirred 23 hour at reflux temperature under N_2 flow. The mixture was extracted with toluene and washed with water. The combined organic extracts were dried over $MgSO_4$ and evaporated to dryness. The resulting solid was purified by chromatography on silica gel (eluent: hexane) to obtain **2a** as a white solid. (9.2 g, 61.1 %) a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.39 (m, 4H), 7.21-7.19 (m, 4H), 7.15-7.11 (m, 2H), 6.95-6.92 (m, 2H) ppm ; MS (ASAP) : m/z = 302 $[M+H]^+$

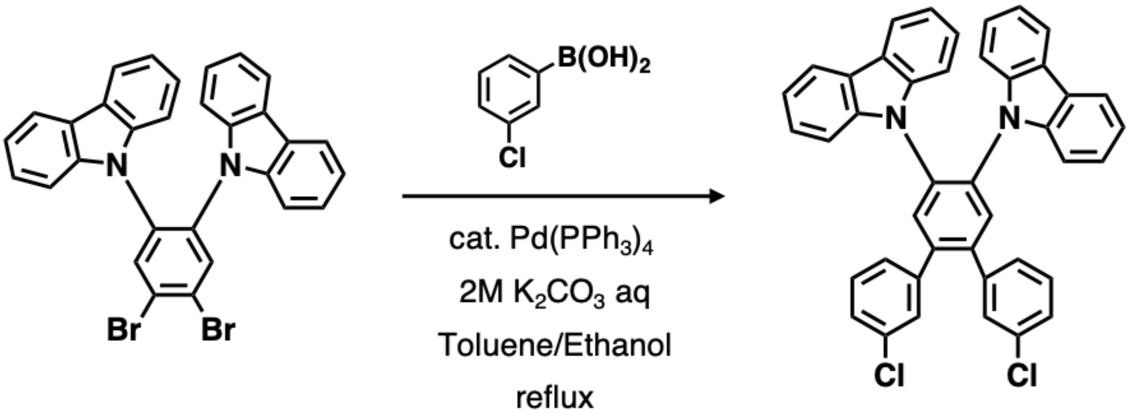
Synthesis of 2b



1b (20.7 g, 51.7 mmol), 3-chlorobenzoic Acid (19.4 g, 124 mmol), 2M K_2CO_3 aq (100 mL), toluene 200 mL, ethanol 100 mL were added to a round bottom flask and nitrogen bubbled through the mixture for 1 hour. Then, $Pd(PPh_3)_4$ (3.0 g, 2.6 mmol) was added and the resultant mixture was stirred 22 hour at reflux temperature under N_2 flow. The mixture was extracted with ethyl acetate and washed with water. The combined organic extracts were dried over MgSO4 and evaporated to dryness. The resulting solid was dissolved in reflux toluene and filtered through pad of silica gel. After the filtrate was concentrated, the resulting solid was purified by recrystallization using cyclohexane to obtain **2b** a white solid. (19.4 g, 80.6 %)

^{1}H NMR (400 MHz, $CDCl_3$) : 8.16 (d, J = 8.3 Hz, 2H), 7.67-7.63 (m, 3H), 7.53 (d, J = 8.3 Hz, 2H), 7.45 (t, J = 7.2 Hz, 2H), 7.33-7.31 (m, 3H), 7.27 (s, 1H), 7.25-7.16 (m, 4H), 7.04 (t, J = 6.5 Hz, 2H) ppm ; MS (ASAP) : m/z = 463 $[M+H]^+$

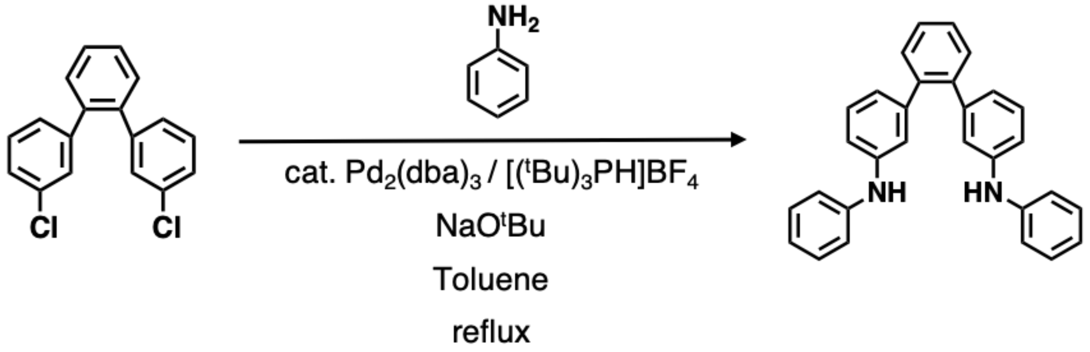
Synthesis of 2c



1c (49.8 g, 88 mmol), 3-chlorobenzoic Acid (34.4 g, 220 mmol), 2M K_2CO_3 aq (120 mL), toluene 240 mL, ethanol 120 mL were added to a round bottom flask and nitrogen bubbled through the mixture for 1 hour. Then, $Pd(PPh_3)_4$ (5.0 g, 4.4 mmol) was added and the resultant mixture was stirred 19 hour at reflux temperature under N_2 flow. **(5)** was purified according to the similar method to **2c** and obtained as white solid. (23.7 g, 42.7 %)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 2H), 7.81-7.77 (m, 6H), 7.16-7.13 (m, 6H), 7.07 (td, J = 6.6, 3.8 Hz, 12H) ppm ; MS (ASAP) : m/z = 628 $[M+H]^+$

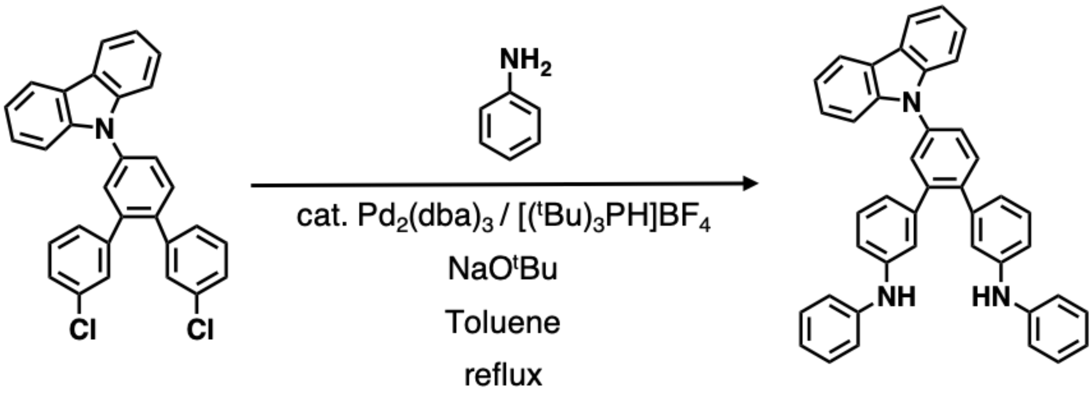
Synthesis of 3a



2a (9.17 g, 30.6 mmol), aniline (16.2 mL, 122.4 mmol), NaO^{t}Bu (8.82 g, 91.8 mmol), dry toluene 100 mL were added to a round bottom flask and nitrogen bubbled through the mixture for 1 hour. Then, $Pd_2(dba)_3$ (1.37 g, 1.5 mmol), $[(^tBu)_3PH]BF_4$ (1.31 g, 4.5 mmol) was added and the resultant mixture was stirred 23 hours at reflux temperature under N_2 flow. The mixture was extracted with ethyl acetate, and washed with water. The combined organic extracts were dried over $MgSO_4$, and evaporated to dryness. The resulting solid was purified by chromatography on silica gel (eluent: hexane/toluene = 2 : 1) to afford **3a** (7.64 g, 60.6 %) as a white solid.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.41-7.37 (m, 4H), 7.28 (t, J = 7.6 Hz, 2H), 7.16 (t, J = 7.4 Hz, 4H), 6.93-6.83 (m, 8H), 6.74 (d, J = 7.6 Hz, 4H), 5.78 (s, 2H) ppm ; MS (ASAP) : m/z = 413 $[M+H]^+$

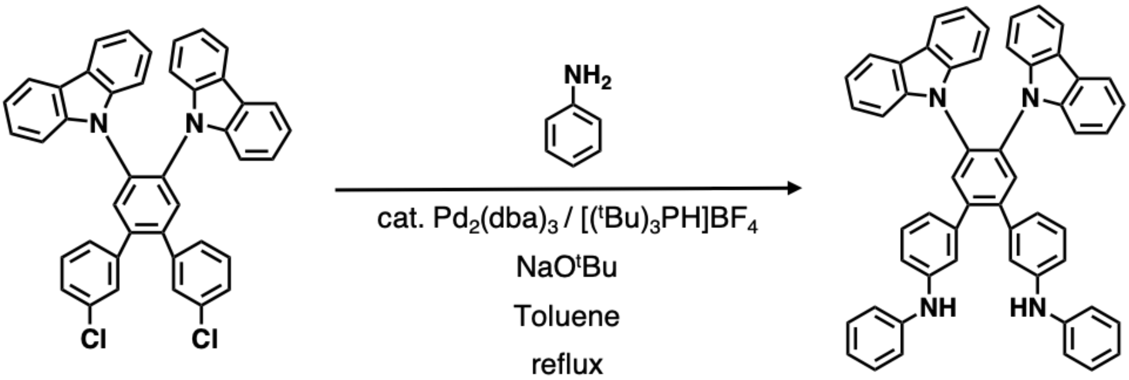
Synthesis of 3b



2b (18.6 g, 40 mmol), aniline (14.6 mL, 160 mmol), NaO^{t}Bu (15.4 g, 160 mmol), dry toluene 200 mL were added to a round bottom flask and nitrogen bubbled through the mixture for 1 hour. Then, $Pd_2(dba)_3$ (1.8 g, 2.0 mmol), $[(^tBu)_3PH]BF_4$ (1.74 g, 6.0 mmol) was added and the resultant mixture was stirred 64 hours at reflux temperature under N_2 flow. The mixture was extracted with ethyl acetate, and washed with water. The combined organic extracts were dried over $MgSO_4$, and evaporated to dryness. The resulting solid was washed by methanol to afford **3b** (11.6 g, 50.2 %) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 7.8 Hz, 2H), 7.62-7.60 (m, 2H), 7.55 (dd, J = 8.2, 2.3 Hz, 1H), 7.50 (d, J = 8.2 Hz, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.34-7.25 (m, 4H), 7.17 (m, 4H), 7.03-6.85 (m, 8H), 6.77-6.72 (m, 4H), 5.67 (s, 2H) ppm ; MS (ASAP) : m/z = 579 $[M+H]^+$

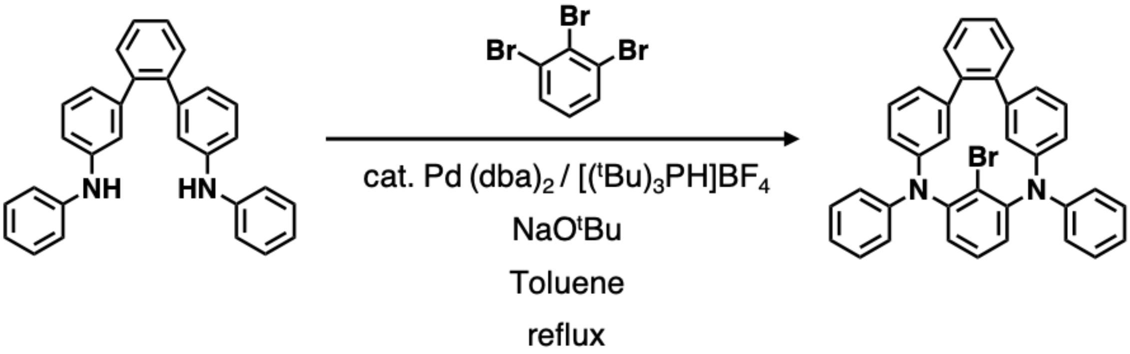
Synthesis of 3c



2c (23.7 g, 37.6 mmol), aniline (13.7 mL, 150 mmol), NaO^{t}Bu (14.4 g, 150 mmol), dry toluene 500 mL were added to a round bottom flask and nitrogen bubbled through the mixture for 1 hour. Then, $Pd_2(dba)_3$ (1.7 g, 1.9 mmol), $[(^tBu)_3PH]BF_4$ (1.6 g, 5.6 mmol) was added and the resultant mixture was stirred 17 hours at reflux temperature under N_2 flow. The mixture was extracted with ethyl acetate, and washed with water. The combined organic extracts were dried over $MgSO_4$, and evaporated to dryness. The resulting solid was purified by chromatography on silica gel (eluent: hexane/ethyl acetate = 4 : 1) to afford **3c** (22.3 g, 80.1 %) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 2H), 7.81-7.78 (m, 4H), 7.34 (t, J = 7.8 Hz, 2H), 7.28-7.26 (m, 2H), 7.20 (t, J = 7.8 Hz, 4H), 7.12-7.00 (m, 14H), 6.94-6.89 (m, 4H), 6.77 (d, J = 7.8 Hz, 4H), 5.72 (s, 2H) ppm ; MS (ASAP) : m/z = 743 $[M+H]^+$

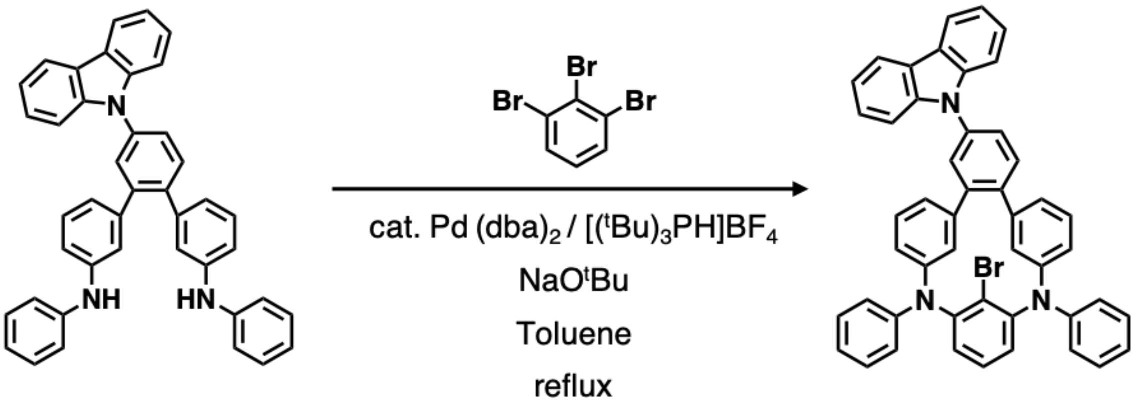
Synthesis of 4a



3a (4.13 g, 10 mmol), 1,2,3-tribromobenzene (3.15 g, 10 mmol), NaO^{t}Bu (2.88 g, 30 mmol), dry toluene 1000 mL were added to a round bottom flask and nitrogen bubbled through the mixture for 1 hour. Then, Pd(dba)$_2$ (230 mg, 0.4 mmol), [(^{t}Bu)$_3$PH]BF$_4$ (93 mg, 0.32 mmol) was added and the resultant mixture was stirred 18 hours at reflux temperature under N_2 flow. The mixture was extracted with ethyl acetate, and washed with water. The combined organic extracts were dried over $MgSO_4$, and evaporated to dryness. The resulting solid was purified by chromatography on silica gel (eluent: hexane/DCM = 4 : 1) to afford **4a** (2.4 g, 45.6 %) as a pale yellow solid.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.60 (t, J = 8.3 Hz, 1H), 7.30 (td, J = 16.5, 8.5 Hz, 12H), 7.15 (q, J = 7.8 Hz, 4H), 7.05 (q, J = 7.1 Hz, 2H), 7.00 (t, J = 8.3 Hz, 2H), 6.68 (d, J = 6.2 Hz, 2H), 6.33 (s, 2H) ppm ; MS : m/z 566 [M+H]$^+$

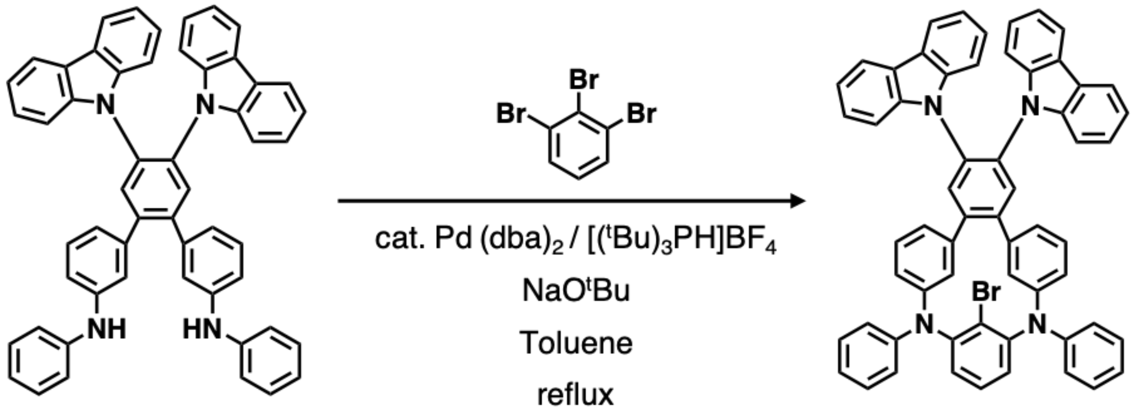
Synthesis of 4b



3b (5.8 g, 10 mmol), 1,2,3-tribromobenzene (3.15 g, 10 mmol), NaO^{t}Bu (2.9 g, 30 mmol), dry toluene 1000 mL were added to a round bottom flask and nitrogen bubbled through the mixture for 1 hour. Then, Pd(dba)$_2$ (230 mg, 0.4 mmol), [(^{t}Bu)$_3$PH]BF$_4$ (93 mg, 0.32 mmol) was added and the resultant mixture was stirred 17 hours at reflux temperature under N$_2$ flow. The mixture was extracted with ethyl acetate, and washed with water. The combined organic extracts were dried over MgSO$_4$, and evaporated to dryness. The resulting solid was purified by chromatography on silica gel (eluent: hexane/toluene = 4 : 1) to afford **4b** (1.25 g, 17.1 %) as a pale yellow solid.

^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 8.15 (d, J = 7.8 Hz, 2H), 7.60-7.51 (m, 5H), 7.45-7.41 (m, 2H), 7.37-7.15 (m, 15H), 7.11-7.04 (m, 4H), 6.86-6.76 (m, 2H), 6.46 (s, 2H) ppm ; MS : m/z 732 [M+H]$^+$

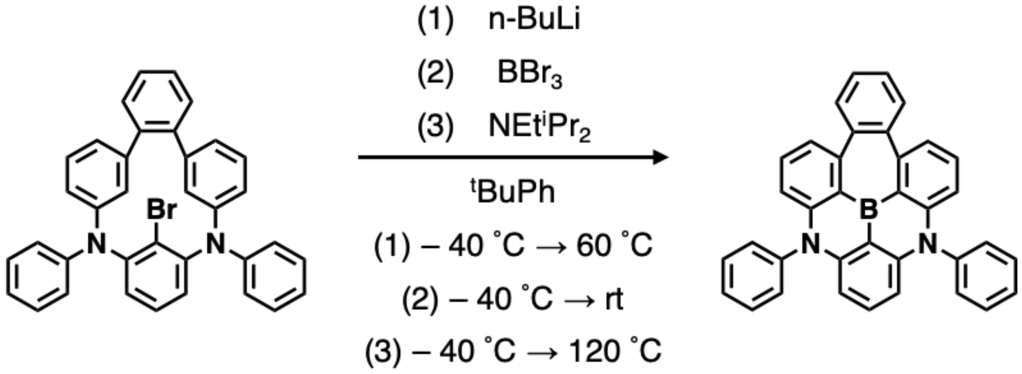
Synthesis of 4c



3c (7.43 g, 10 mmol), 1,2,3-tribromobenzene (3.15 g, 10 mmol), NaO^{t}Bu (2.9 g, 30 mmol), dry toluene 1000 mL were added to a round bottom flask and nitrogen bubbled through the mixture for 1 hour. Then, Pd(dba)$_2$ (230 mg, 0.4 mmol), [(^{t}Bu)$_3$PH]BF$_4$ (93 mg, 0.32mmol) was added and the resultant mixture was stirred 23 hours at reflux temperature under N$_2$ flow. The mixture was extracted with ethyl acetate, and washed with water. The combined organic extracts were dried over MgSO$_4$, and evaporated to dryness. The resulting solid was purified by chromatography on silica gel (eluent: hexane/DCM = 4 : 1) to afford **4c** (1.34 g, 15.0 %) as a pale yellow solid.

^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.90-7.82 (m, 4H), 7.75 (s, 2H), 7.40 (d, J = 8.2 Hz, 2H), 7.35-7.30 (m, 9H), 7.25-7.14 (m, 8H), 7.11-7.03 (m, 10H), 6.93-6.88 (m, 2H), 6.56 (s, 2H) ppm ; MS : m/z 897 [M+H]$^+$

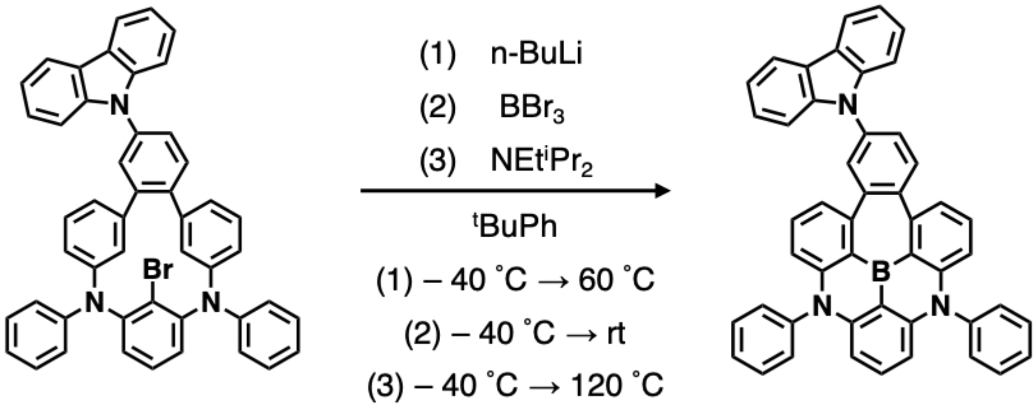
Synthesis of OP-BN



To a solution of **4a** (2.76 g, 4.88 mmol) in tert-butyl benzene was slowly added n-BuLi (1.58 M in hexane, 6.14 mL, 9.76 mmol) at –40 °C. After reacting for 30 minutes at room temperature and 3 h at 60 ˚C , BBr$_3$ (1.0 M in CH$_2$Cl$_2$, 9.76 mL, 9.76 mmol) was slowly added at –40 ˚C, and then the mixture was stirred at room temperature for 3 h. N,N-Diisopropylethylamine (1.70 mL, 9.76 mmol) was added at –40 ˚C and then the reaction mixture was allowed to warm to room temperature. After stirring at 120 ˚C for 64 h, the reaction mixture was cooled to room temperature. the solvent was removed in vacuo. The residue was dissolved in toluene and then filtered with a pad of silica gel (eluent: toluene). The resulting solid was purified by chromatography on silica gel (eluent: hexane/DCM = 4 : 1) to afford **OP-BN** (0.77 g, 32.0 %) as a yellow solid.

^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.72-7.69 (m, 4H), 7.61 (dd, J = 11.4, 7.2 Hz, 2H), 7.53 (q, J = 4.6 Hz, 2H), 7.49-7.41 (m, 6H), 7.38 (q, J = 2.5 Hz, 4H), 7.23 (td, J = 8.1, 4.6 Hz, 1H), 6.68 (q, J = 3.9 Hz, 2H), 6.04 (q, J = 4.4 Hz, 2H) ppm ; ^{13}C NMR (100 MHz, CD$_2$Cl$_2$) δ 147.9, 146.8, 146.7, 142.4, 140.4, 134.5, 132.3, 131.2, 130.8, 130.6, 128.6, 127.6, 121.9, 116.1, 104.4 ppm ; ^{11}B NMR (190 MHz, CD$_2$Cl$_2$) δ 45.7 ppm ; MS : m/z 494 [M+H]$^+$; Anal calcd for C$_{36}$H$_{23}$BN$_2$: C, 87.46; H, 4.69; N, 5.67 %. Found: C, 87.60; H, 4.83; N, 5.80 %

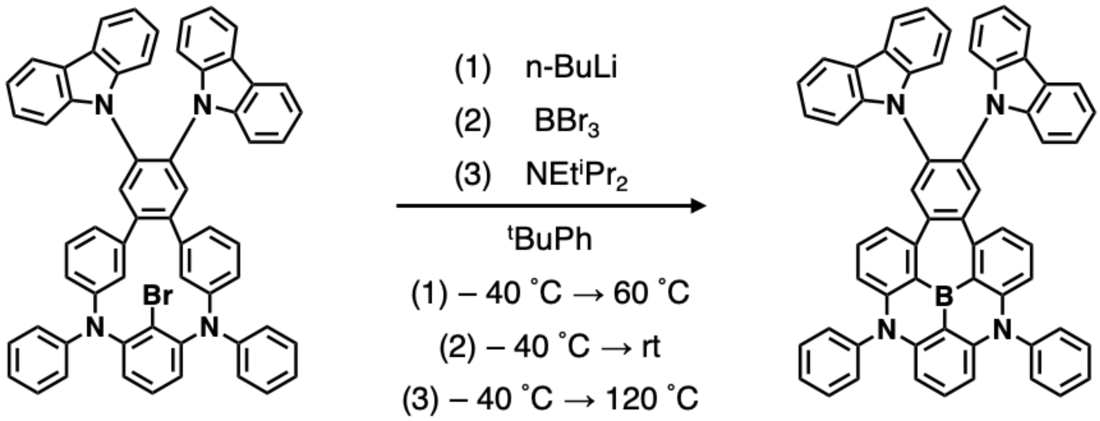
Synthesis of Cz-OP-BN



To a solution of **4b** (2.82 g, 3.86 mmol) in tert-butyl benzene was slowly added n-BuLi (2.6 M in hexane, 3.0 mL, 7.72 mmol) at –40 °C. After reacting for 30 minutes at room temperature and 3 h at 60 ˚C , BBr3 (1.0 M in CH2Cl2, 7.72 mL, 7.72 mmol) was slowly added at –40 ˚C, and then the mixture was stirred at room temperature for 3 h. N,N-Diisopropylethylamine (1.34 mL, 7.72 mmol) was added at –40 ˚C and then the reaction mixture was allowed to warm to room temperature. After stirring at 120 ˚C for 64 h, the reaction mixture was cooled to room temperature. the solvent was removed in vacuo. The residue was dissolved in toluene and then filtered with a pad of silica gel (eluent: toluene). The resulting solid was purified by chromatography on silica gel (eluent: hexane/toluene = 5 : 1) to afford **Cz-OP-BN** (0.88 g, 34.5 %) as a yellow solid.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.18 (s, 2H), 7.80-7.24 (m, 24H), 6.73 (d, J = 31.7 Hz, 2H), 6.08 (d, J = 15.8 Hz, 2H) ppm ; ^{13}C NMR (100 MHz, CD_2Cl_2) δ 147.2, 147.0, 146.8, 142.4, 142.3, 142.1, 141.0, 139.7, 136.8, 136.4, 132.5, 132.4, 131.2, 131.0, 130.6, 130.5, 128.7, 126.0, 125.7, 123.4, 122.1, 120.3, 120.0, 116.6, 116.4, 109.9, 104.6 ppm ; 11B-NMR (190 MHz, CD2Cl2) δ 42.4 ppm ; MS : m/z 659 $[M+H]^+$; Anal calcd for C48H30BN3: C, 87.41; H, 4.58; N, 6.37 %. Found: C, 87.61; H, 4.81; N, 6.50 %

Synthesis of 2Cz-OP-BN



To a solution of **4c** (1.34 g, 1.5 mmol) in tert-butyl benzene was slowly added n-BuLi (2.6 M in hexane, 1.2 mL, 3.0 mmol) at –40 °C. After reacting for 30 minutes at room temperature and 3 h at 60 ˚C , BBr3 (1.0 M in CH2Cl2, 3.p mL, 3.0 mmol) was slowly added at –40 ˚C, and then the mixture was stirred at room temperature for 3 h. N,N-Diisopropylethylamine (0.52 mL, 3.0 mmol) was added at –40 ˚C and then the reaction mixture was allowed to warm to room temperature. After stirring at 120 ˚C for 66 h, the reaction mixture was cooled to room temperature. the solvent was removed in vacuo. The residue was dissolved in toluene and then filtered with a pad of silica gel (eluent: toluene). The resulting solid was purified by chromatography on silica gel (eluent: hexane/toluene = 7 : 3) to afford **2Cz-OP-BN** (0.20 g, 18.0 %) as a yellow solid.

^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.99 (d, J = 8.3 Hz, 2H), 7.85 (t, J = 7.6 Hz, 4H), 7.71 (q, J = 7.8 Hz, 4H), 7.61 (q, J = 7.6 Hz, 2H), 7.56 (t, J = 7.9 Hz, 2H), 7.44-7.26 (m, 11H), 7.09 (q, J = 7.8 Hz, 8H), 6.73 (t, J = 8.3 Hz, 2H), 6.10 (t, J = 8.8 Hz, 2H) ppm ; ^{13}C NMR (100 MHz, CD$_2$Cl$_2$) δ 146.9, 146.8, 146.2, 142.3, 141.6, 140.1, 136.2, 133.1, 132.5, 131.2, 131.1, 130.5, 128.7, 125.6, 123.3, 122.2, 119.9, 116.9, 110.0, 104.7 ppm ; ^{11}B NMR (190 MHz, CD$_2$Cl$_2$) δ 42.2 ppm ; MS : m/z 825 [M+H]$^+$; Anal calcd for $C_{60}H_{37}BN_4$: C, 87.37; H, 4.52; N, 6.79 %. Found: C, 87.25; H, 5.72; N, 7.00 %

4. Molecular Design

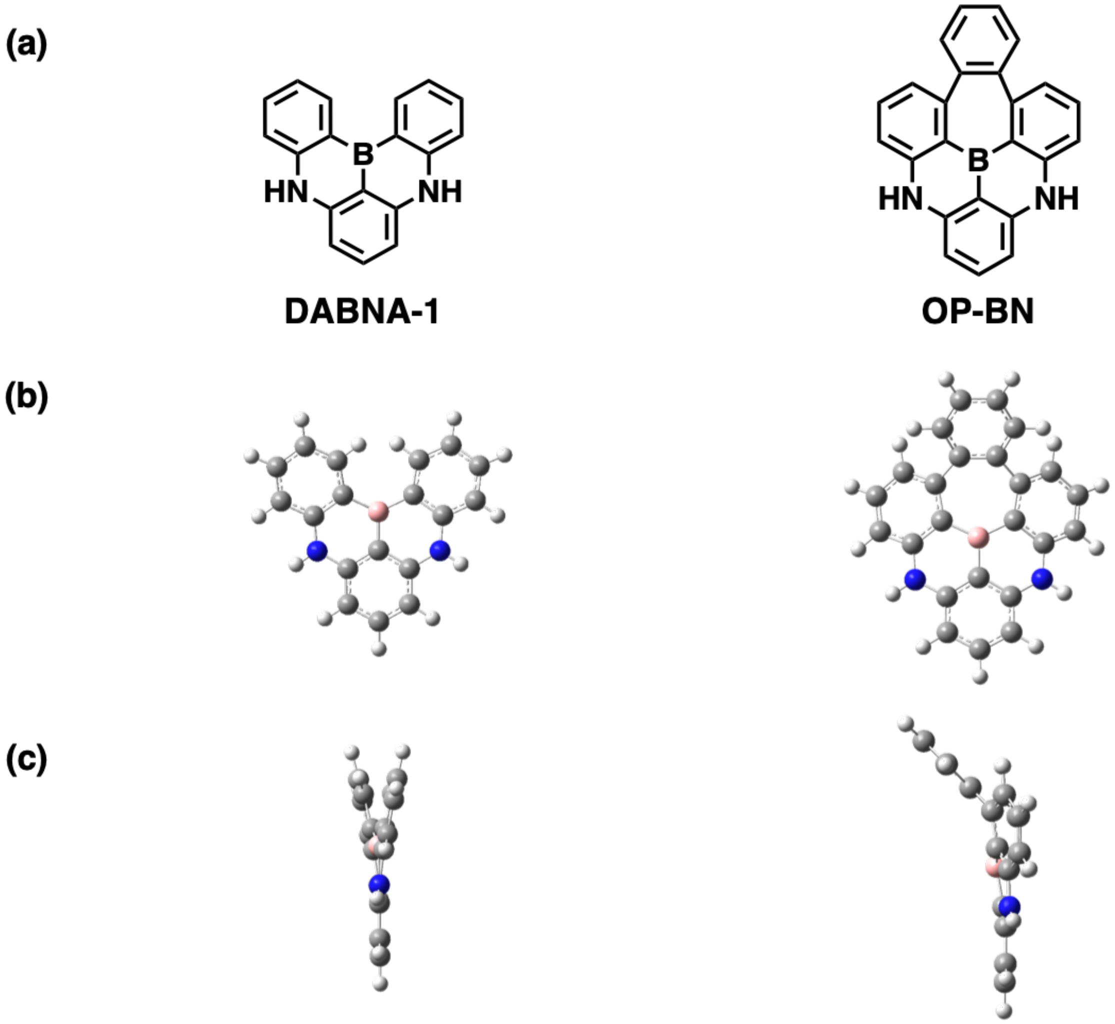


Figure S1. (a) Chemical structure and optimized structure of DABNA-1 and OP-BN, (b) front view, (c) side view

5. Thermal property

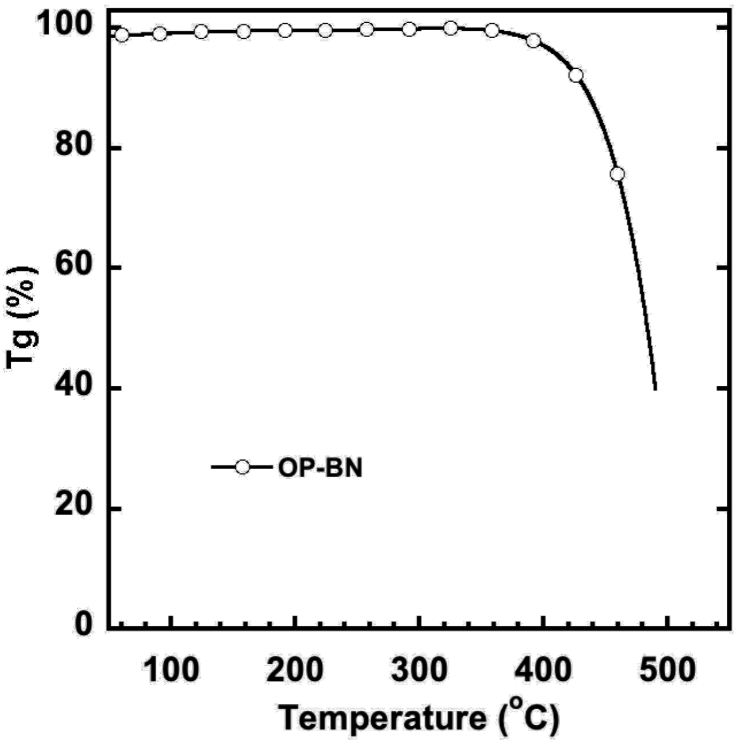


Figure S2. TGA curve of **OP-BN**

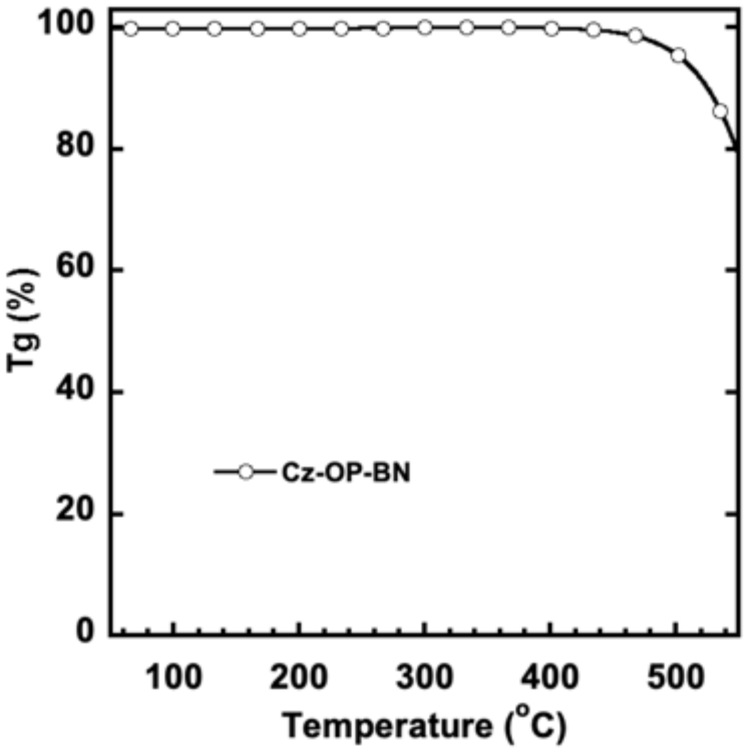


Figure S3. TGA curve of **Cz-OP-BN**

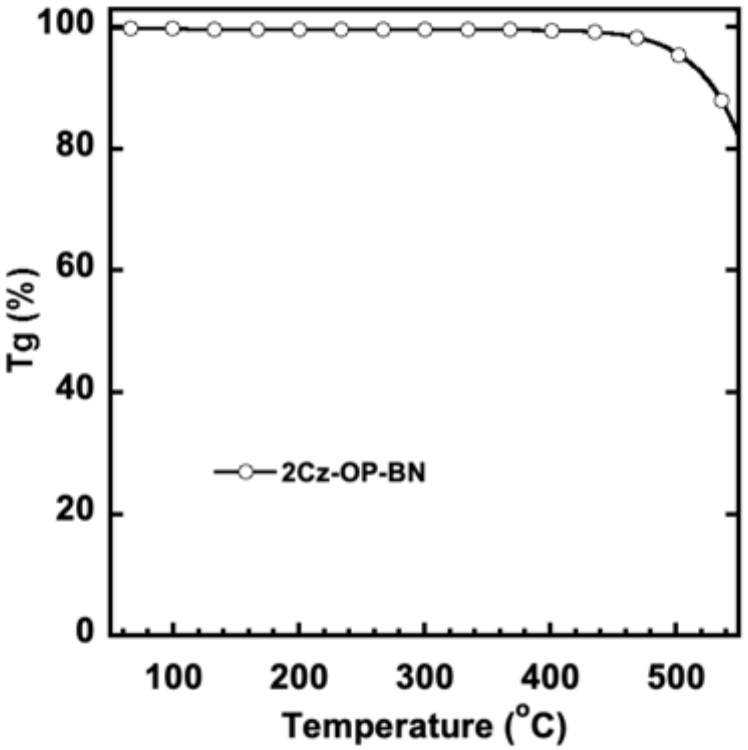


Figure S4. TGA curve of **2Cz-OP-BN**

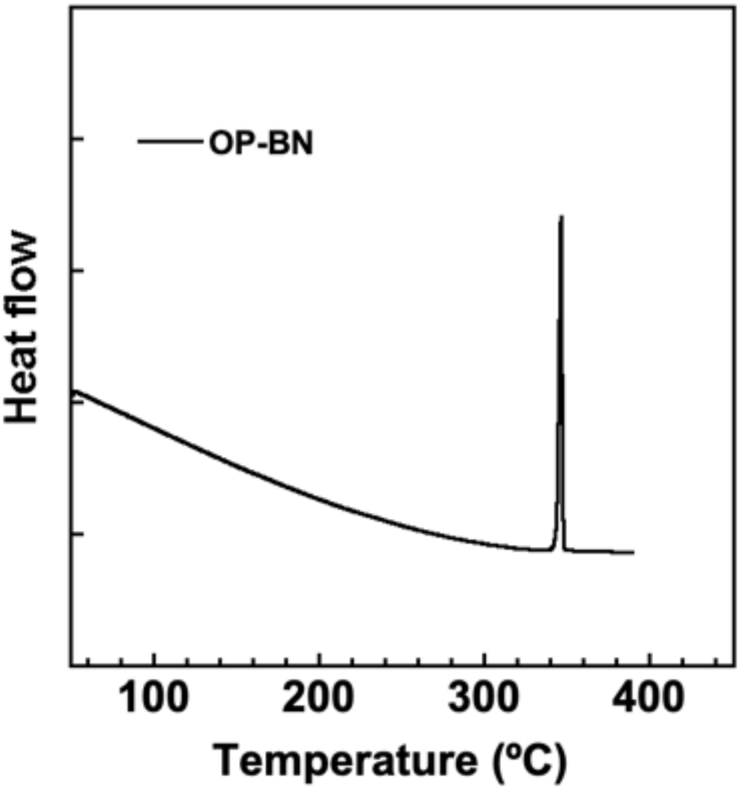


Figure S5. DSC curve of **OP-BN**

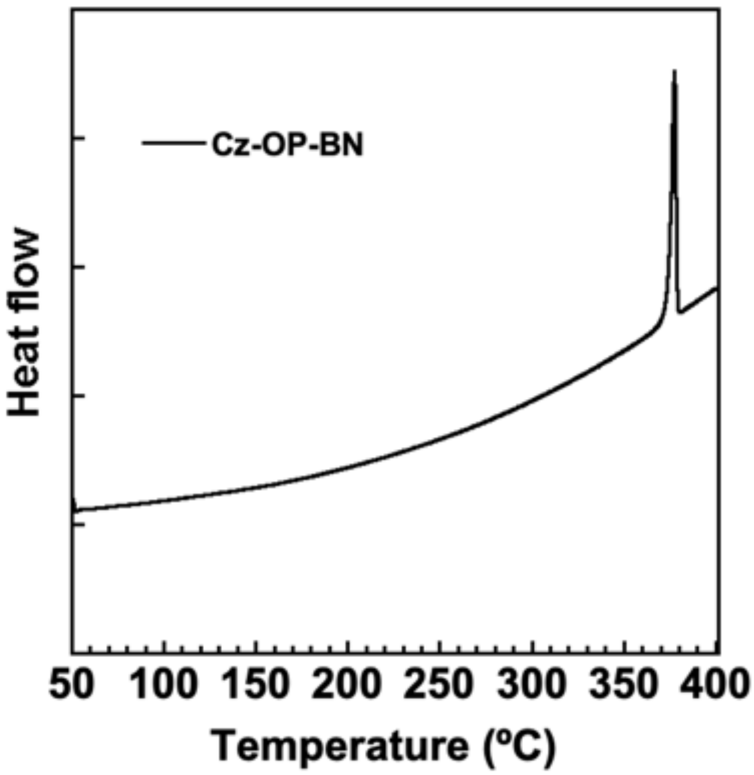


Figure S6. DSC curve of **Cz-OP-BN**

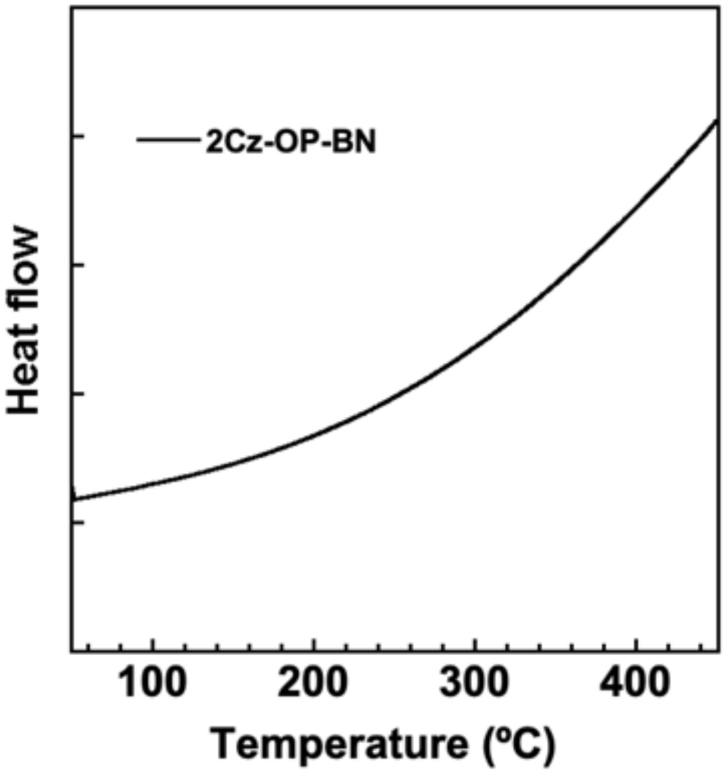


Figure S7. DSC curve of **2Cz-OP-BN**

6. Photophysical property

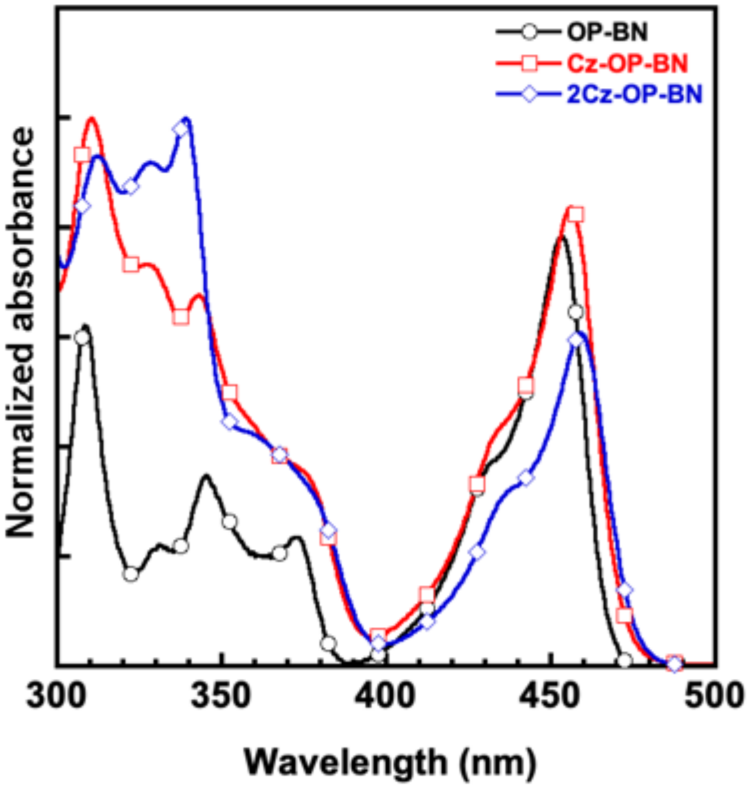


Figure S8. UV-vis absorption spectra of toluene solution

Table S1. Summary of photophysical properties in toluene

	λ_{abs} [nm]	λ_{PL} [nm]	FWHM [nm]	PLQY[a] [%]
OP-BN	453	466	31	84.0
Cz-OP-BN	456	467	27	65.7
2Cz-OP-BN	459	470	26	61.4

[a] Photoluminescence quantum yield of 10^{-5} M toluene solution.

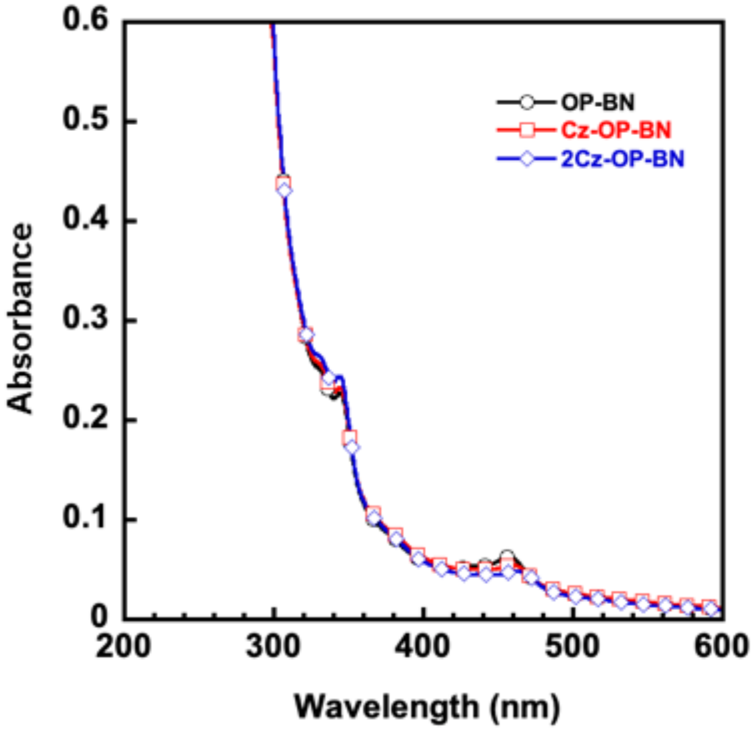


Figure S9. UV-vis absorption spectra of 8wt% emitter doped-mCBPCN film (Thickness : 30 nm)

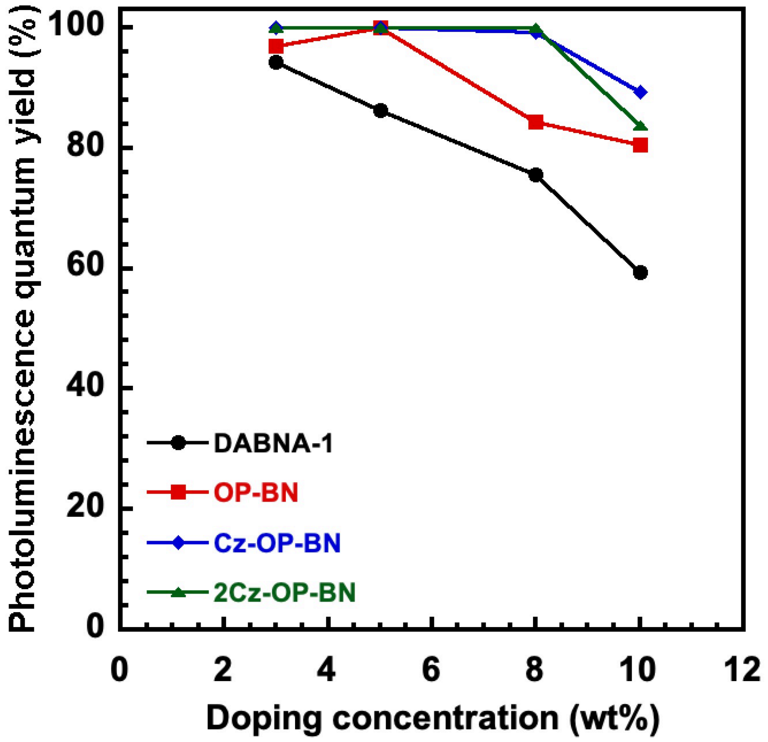


Figure S10. PLQYs of **DABNA-1, OP-BN, Cz-OP-BN** and **2Cz-OP-BN** doped mCBPCN films. (Thickness : 30 nm, λ_{ex} : 340 nm)

Table S2. PLQYs of **DABNA-1, OP-BN, Cz-OP-BN** and **2Cz-OP-BN** doped mCBPCN films. (Thickness : 30 nm, λ_{ex} : 340 nm)

	DABNA-1	**OP-BN**	**Cz-OP-BN**	**2Cz-OP-BN**
3 wt%	94.3 %	97.0 %	100 %	100 %
5 wt%	86.2 %	100 %	100 %	100 %
8 wt%	75.6 %	84.2 %	99.2 %	100 %
10 wt%	59.4 %	80.6 %	89.2 %	83.7 %

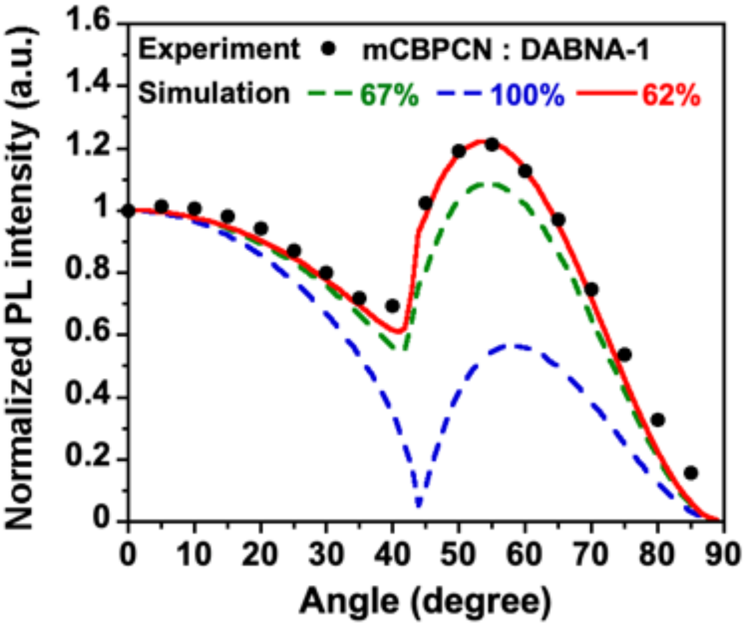


Figure S11. Angle dependent p-polarized PL characteristics of 3wt% **DABNA-1** doped-mCBPCN films. (Thickness : 30 nm, λex : 340 nm)

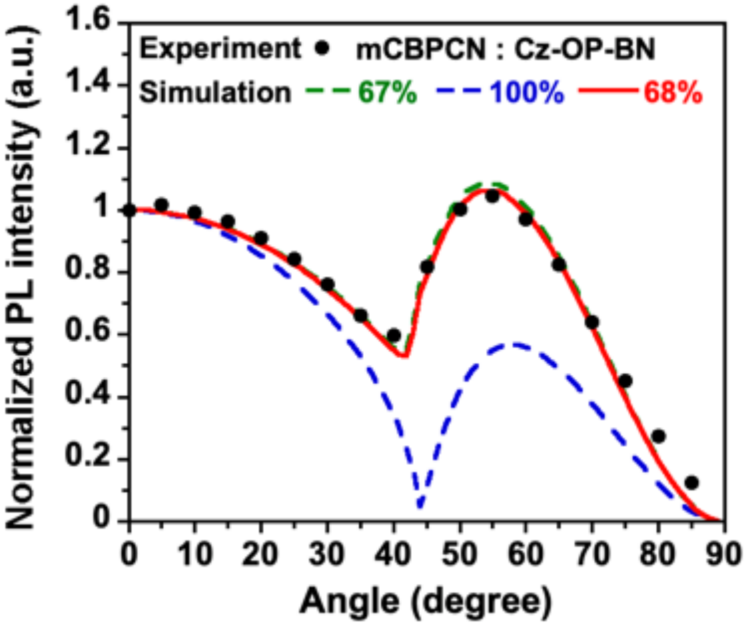


Figure S12. Angle dependent p-polarized PL characteristics of 3wt% **Cz-OP-BN** doped-mCBPCN films. (Thickness : 30 nm, λ_{ex} : 340 nm)

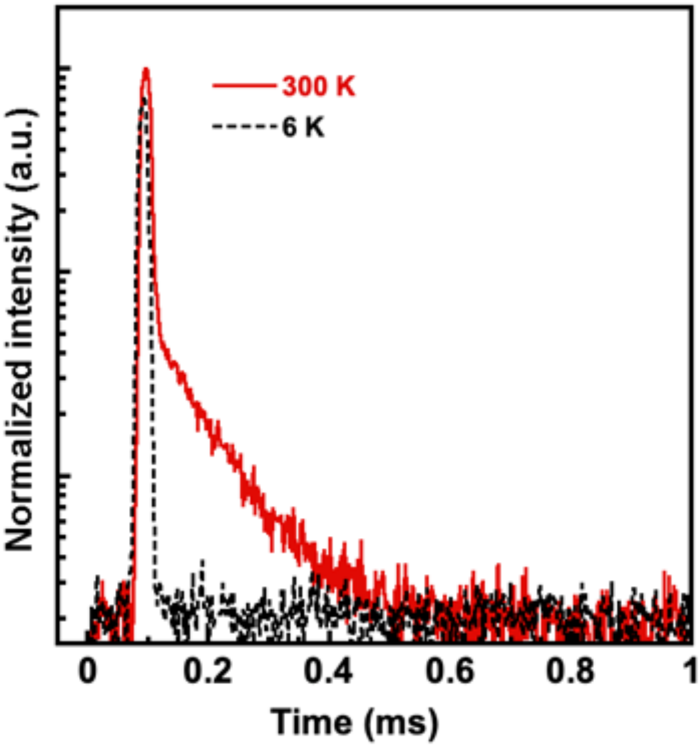


Figure S13. Transient PL decays curves of 8 wt% **OP-BN** doped-mCBPCN film at 300 K and 6 K (Thickness : 100 nm, λ_{ex} : 355 nm)

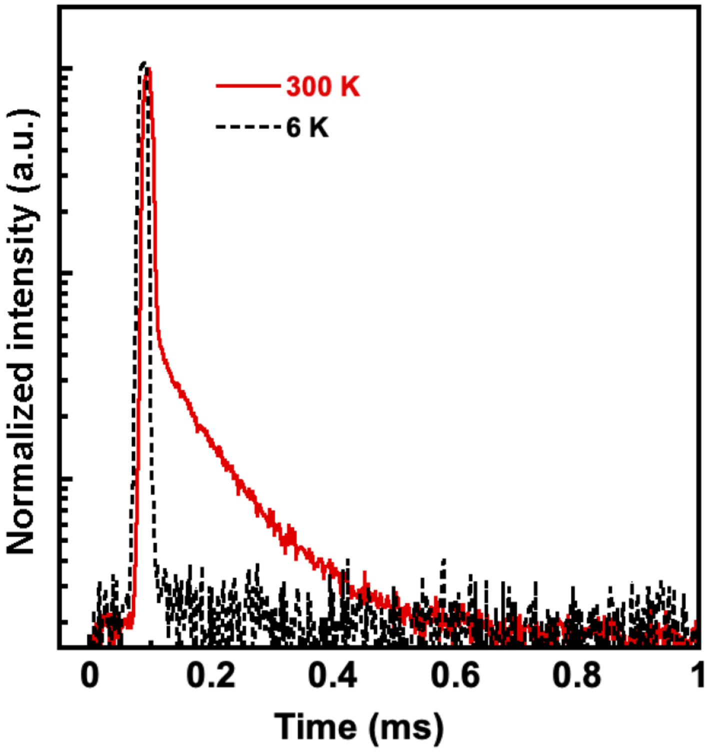


Figure S14. Transient PL decays curves of 8 wt% **Cz-OP-BN** doped-mCBPCN films at 300 K and 6 K (Thickness : 100 nm, λ_{ex} : 355 nm)

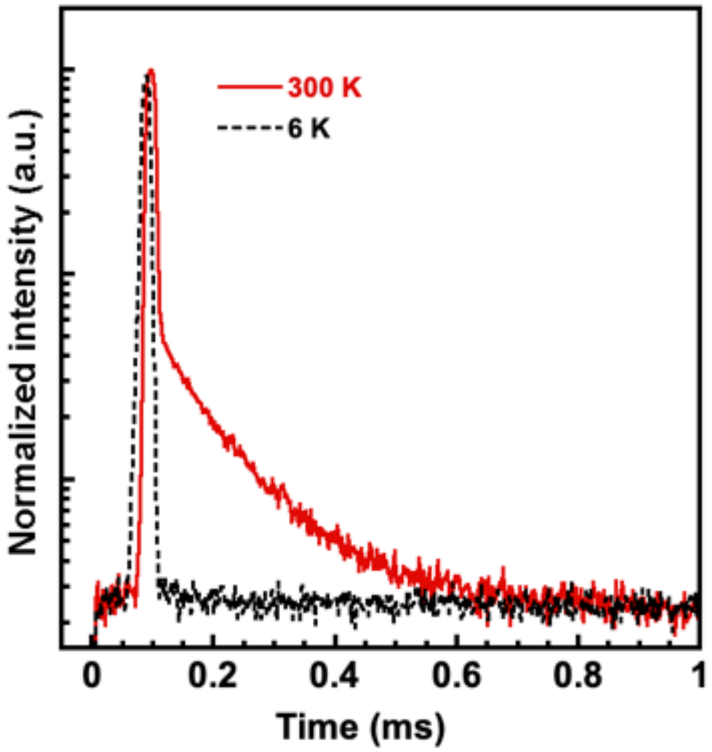


Figure S15. Transient PL decays curves of 8 wt% **2Cz-OP-BN** doped-mCBPCN films at 300 K and 6 K (Thickness : 100 nm, λ_{ex} : 355 nm)

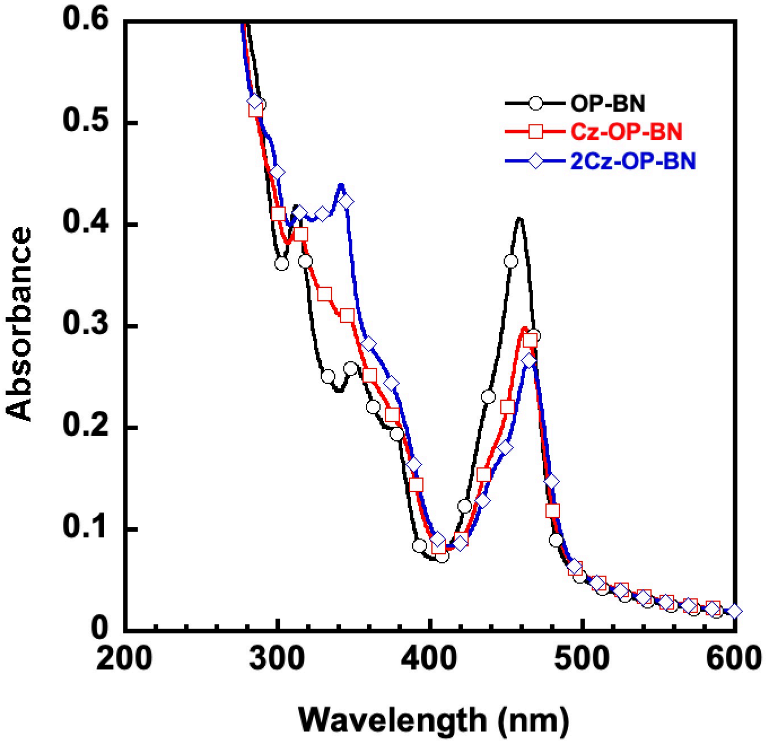


Figure S16. UV-vis absorption spectra of neat film (Thickness : 30 nm)

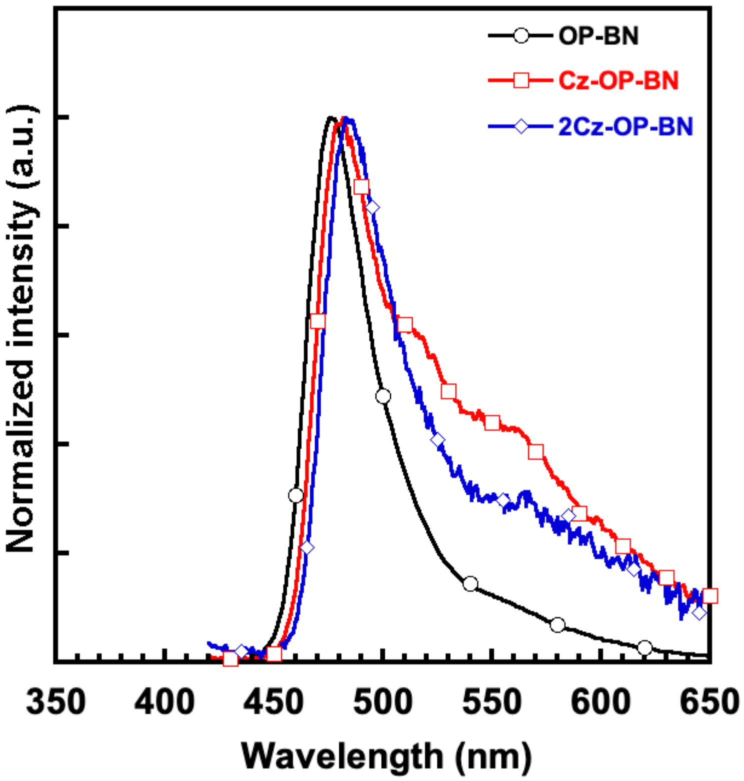


Figure S17. PL spectra of neat film (Thickness : 30 nm, λex : 400 nm)

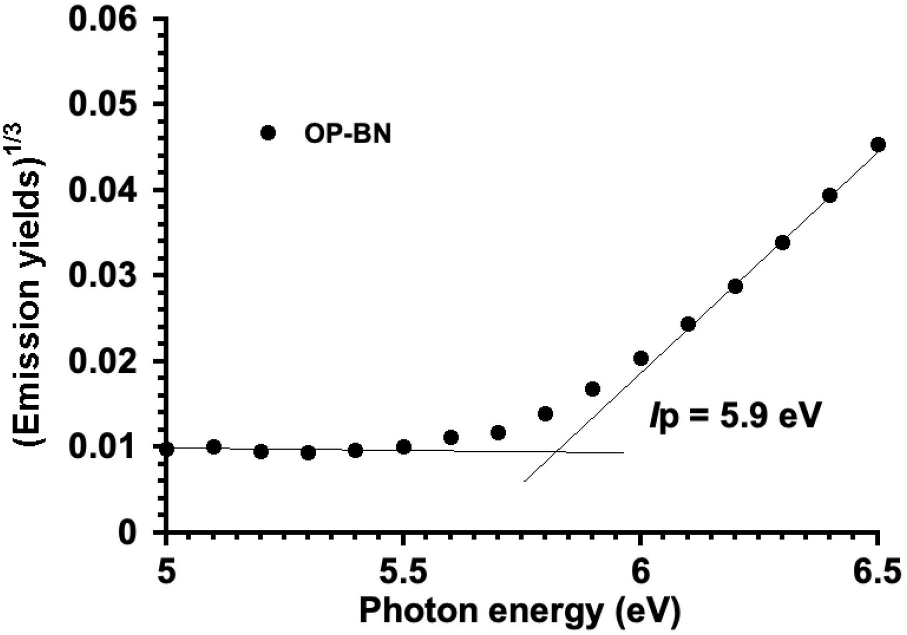


Figure S18. PYS plot of **OP-BN**

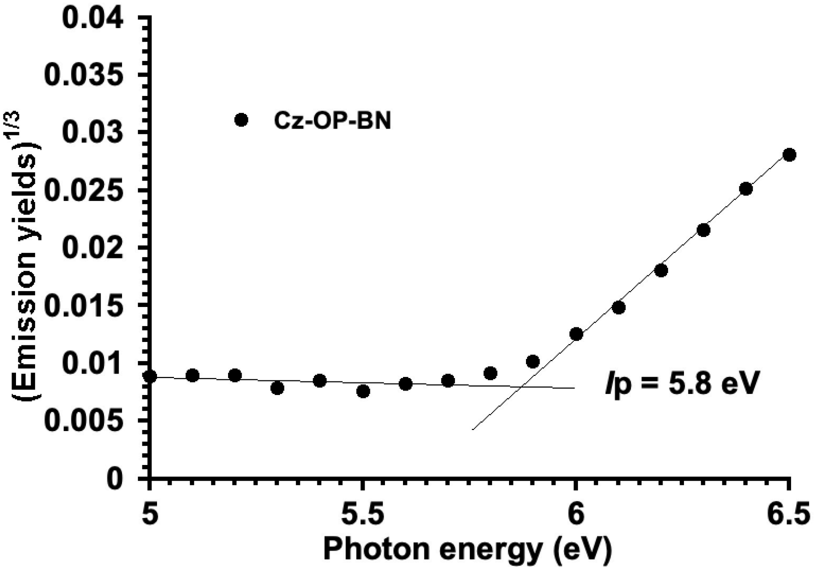


Figure S19. PYS plot of **Cz-OP-BN**

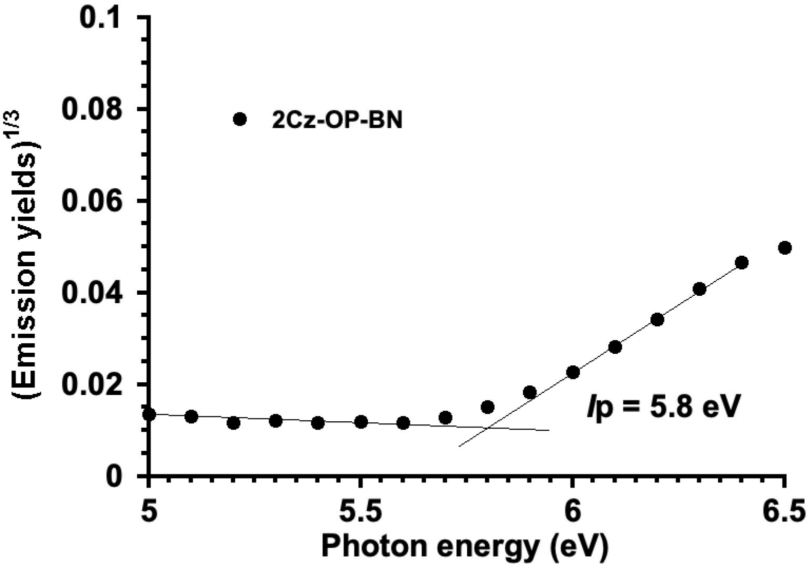


Figure S20. PYS plot of **2Cz-OP-BN**

Rate constants were determined from the measurements of quantum yields and lifetimes of the fluorescence and TADF components according to the equations 1-4[5].

$$k_P \qquad k_P = 1/\tau_P \qquad (1)$$

$$k_D \qquad k_D = 1/\tau_D \qquad (2)$$

$$k_{ISC} \qquad k_{ISC} = \Phi_D/(\Phi_P + \Phi_D)\ \tau_P \qquad (3)$$

$$k_{RISC} \qquad k_{RISC} = (1/\tau_D)(\Phi_P + \Phi_D)/\Phi_D \qquad (4)$$

Table S3. Photophysical properties of 8 wt% emitter doped mCBPCN films.

Compound	ΔE_{ST}[a] [eV]	Φ_{PL}[b] [%]	Φ_P[c] [%]	Φ_D[c] [%]	τ_P[d] [ns]	τ_D[d] [μs]	k_P[e] [$10^7 s^{-1}$]	k_D[e] [$10^3 s^{-1}$]	k_{ISC}[e] [$10^7 s^{-1}$]	k_{RISC}[e] [$10^3 s^{-1}$]
OP-BN	0.16	84.2	68.0	16.2	9.97	104	10.0	7.97	3.21	7.16
Cz-OP-BN	0.18	99.2	82.5	16.7	10.1	122	9.90	8.14	1.73	9.48
2Cz-OP-BN	0.15	100	79.2	20.8	11.4	144	8.77	6.94	2.45	9.63

[a] These values were defined as the energy difference between E_S and E_T as obtained from the onset of fluorescence and the phosphorescence spectra of the 8 wt% emitter-doped mCBPCN film, respectively.

[b] Absolute photoluminescence quantum yield.

[c] Fluorescent and TADF components determined from the total Φ_{PL} and contribution of the integrated area of each component in the transient spectra to the total integrated area.

[d] Lifetimes calculated from fluorescence decay.

[e] Decay rates of fluorescence (k_P), Decay rates of delayed fluorescence (k_D), intersystem crossing from S_1 to T_1 (k_{ISC}), and reverse intersystem crossing from T_1 to S_1 (k_{RISC}) were calculated from Φ_{PL}, Φ_P, Φ_D, τ_P, and τ_D.

7. NTO and SOC calculation

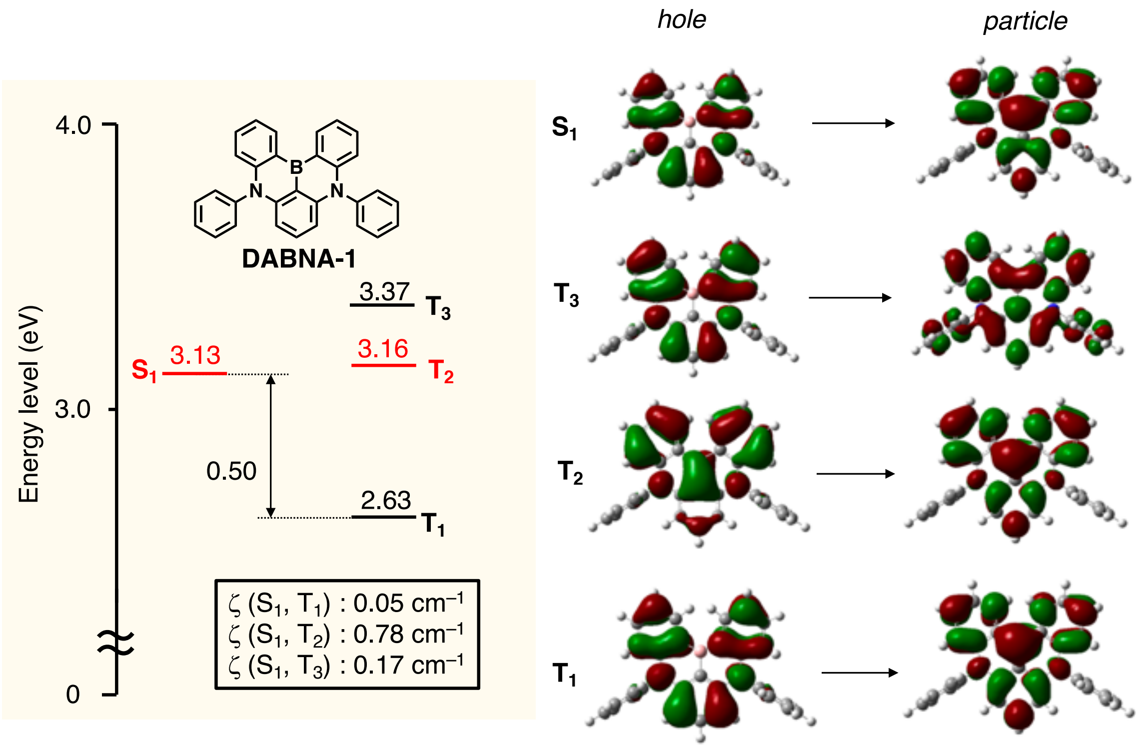


Figure S21. Energy levels of singlet and triplet states, SOC matrix elements, and representative NTOs of **DABNA-1**

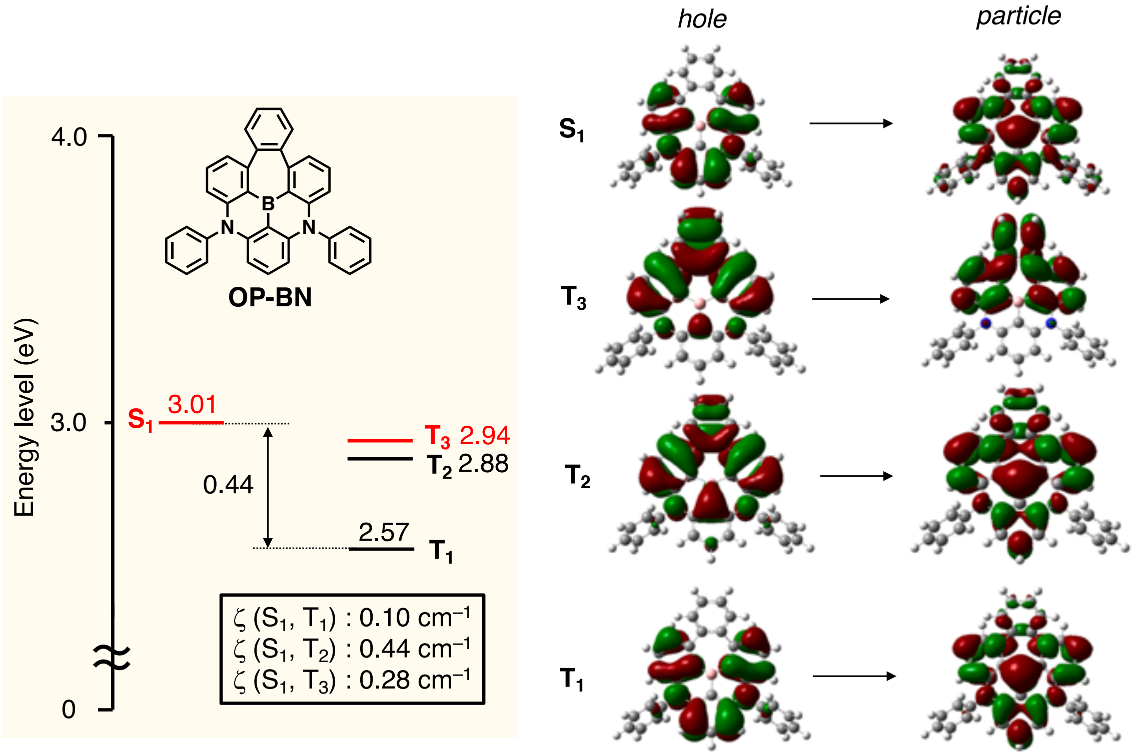


Figure S22. Energy levels of singlet and triplet states, SOC matrix elements, and representative NTOs of **OP-BN**

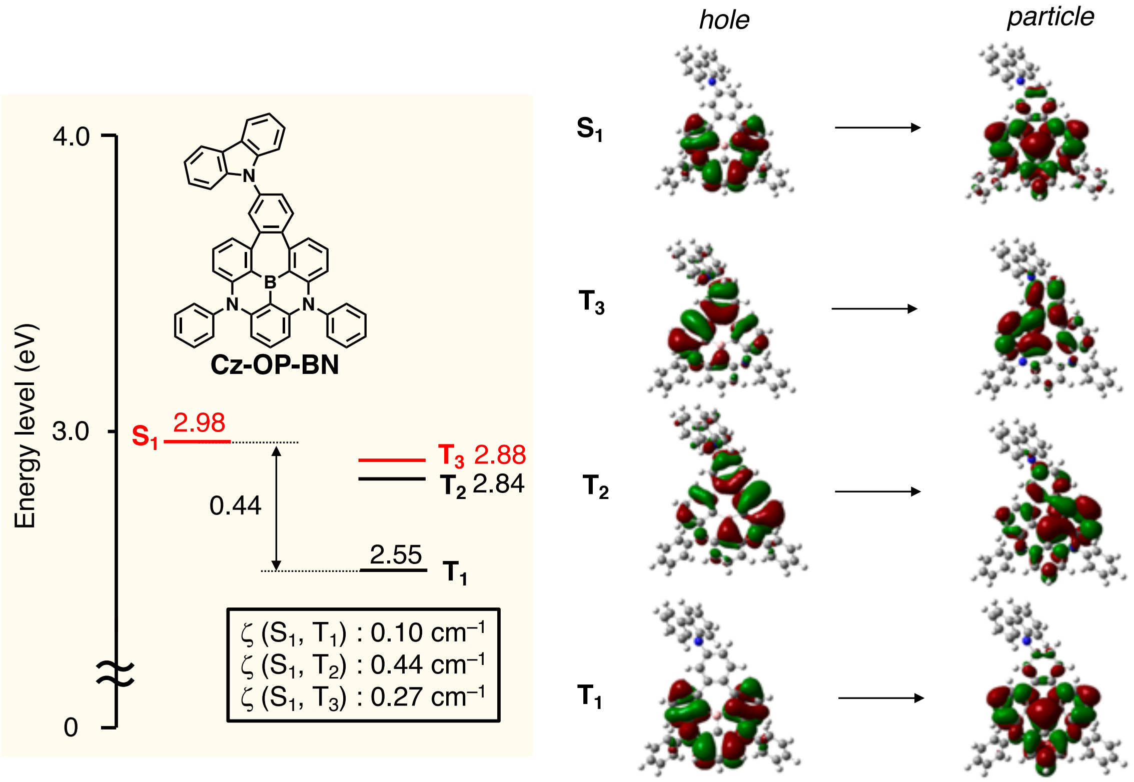


Figure S23. Energy levels of singlet and triplet states, SOC matrix elements, and representative NTOs of **Cz-OP-BN**

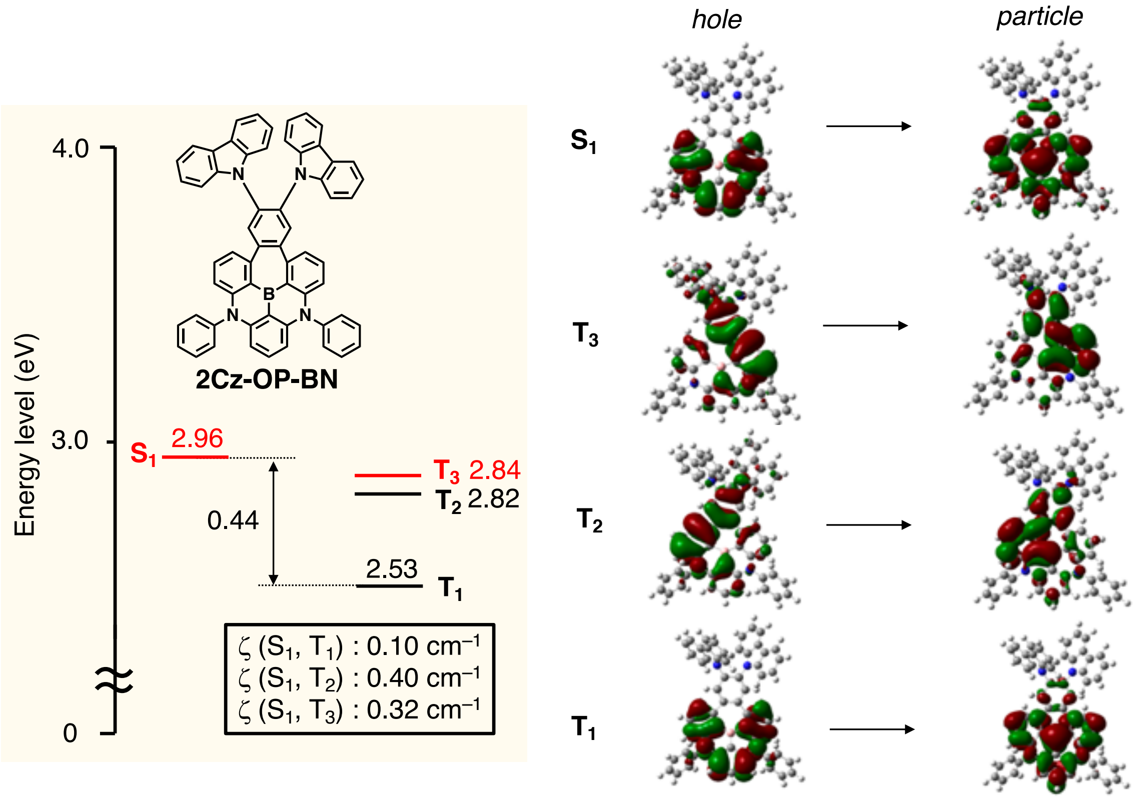


Figure S24. Energy levels of singlet and triplet states, SOC matrix elements, and representative NTOs of **2Cz-OP-BN**

8. Device perfoemance

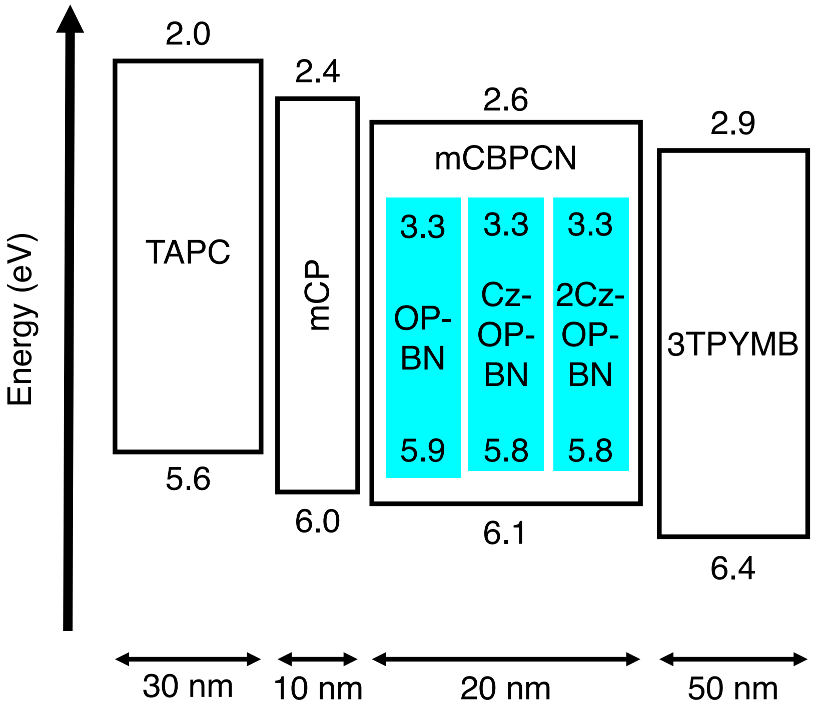


Figure S25. Energy diagram of the devices.

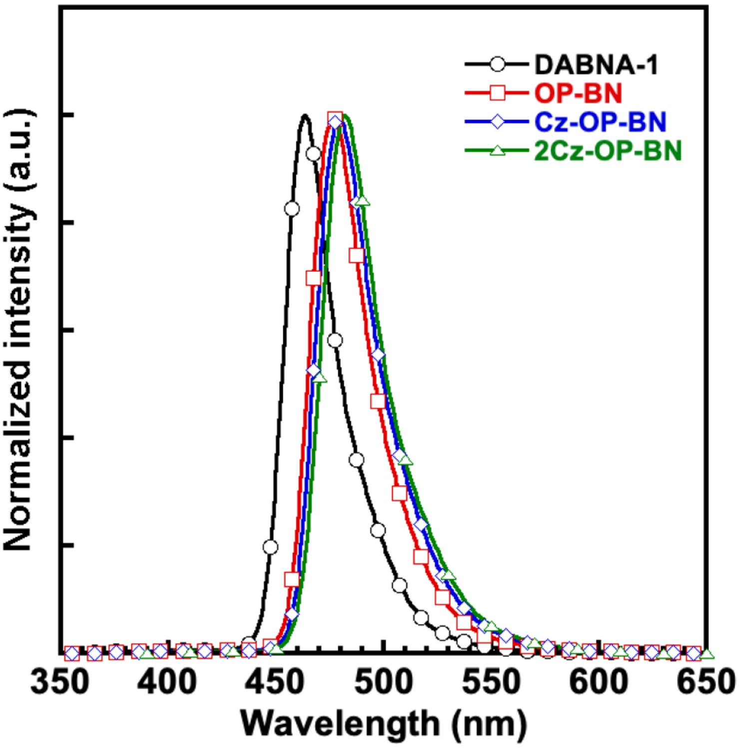


Figure S26. EL spectra at 100 cd/m^2

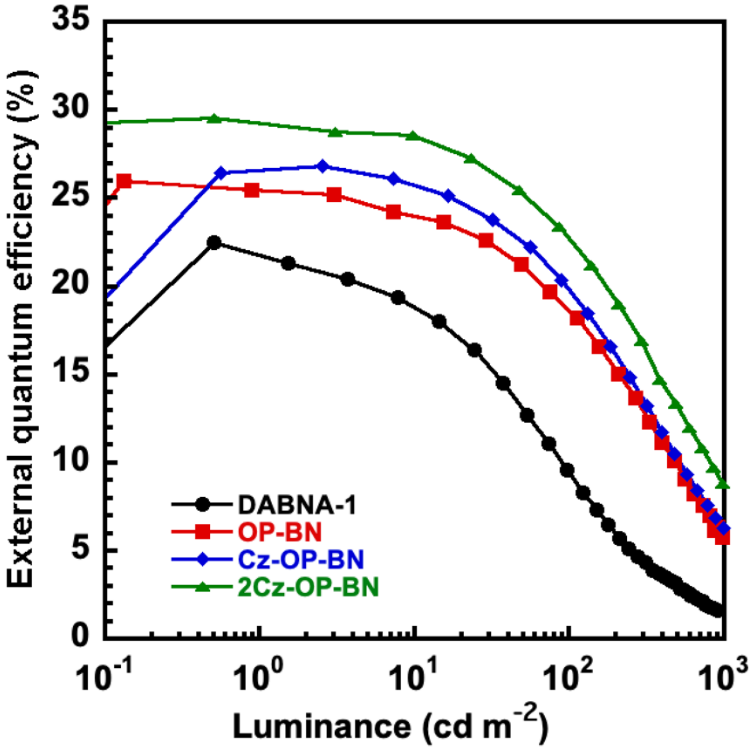


Figure S27. External quantum efficiency-luminance characteristics

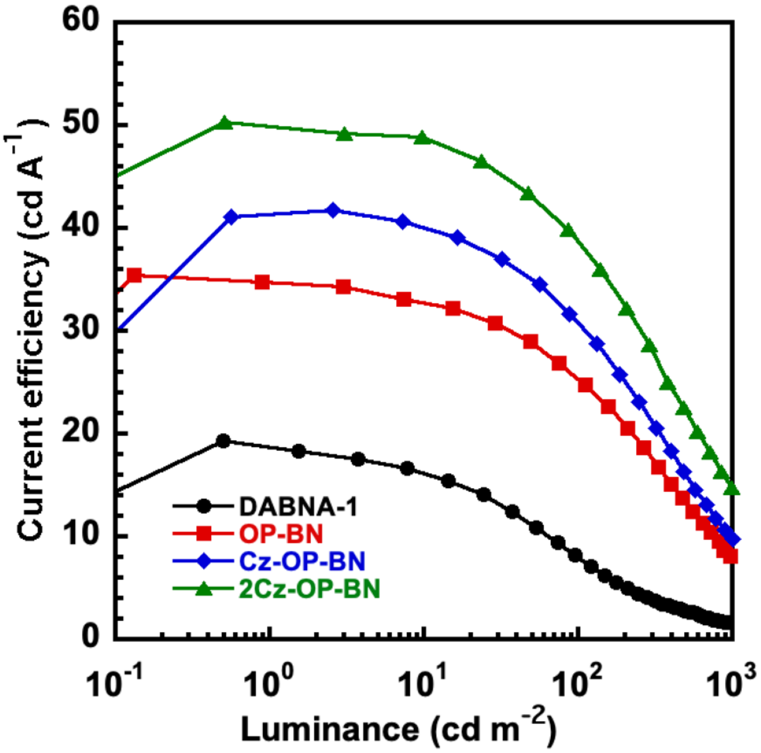


Figure S28. Current efficiency-luminance characteristics

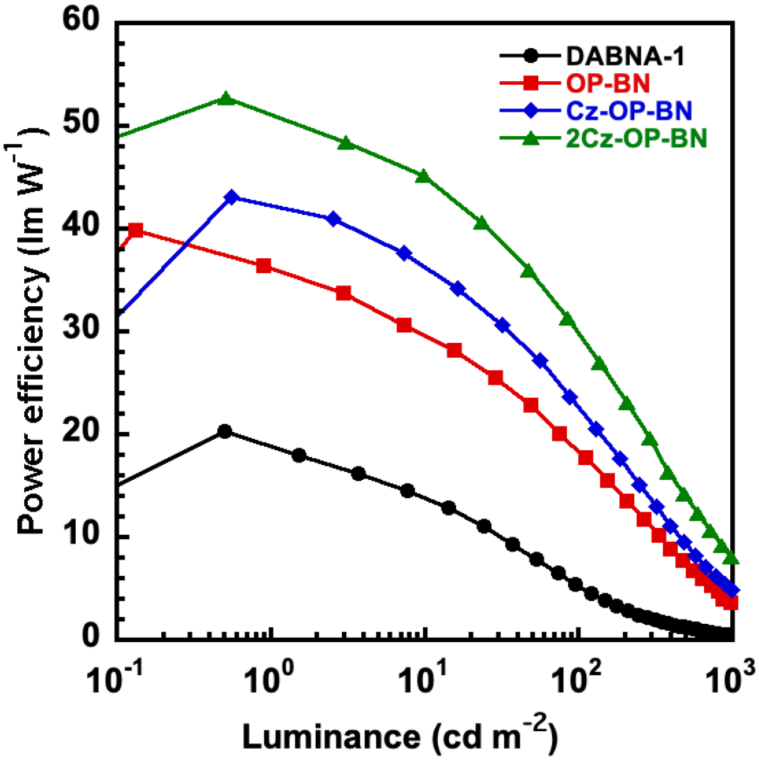


Figure S29. Power efficiency-luminance characteristics

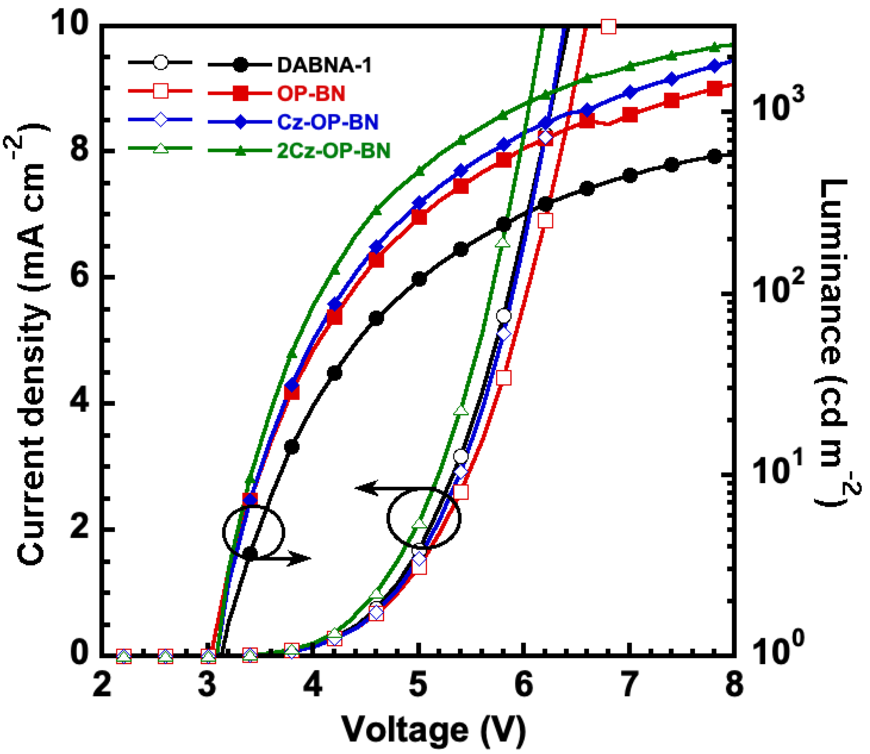


Figure S30. Current density-voltage-luminance characteristics

9. Spectral data

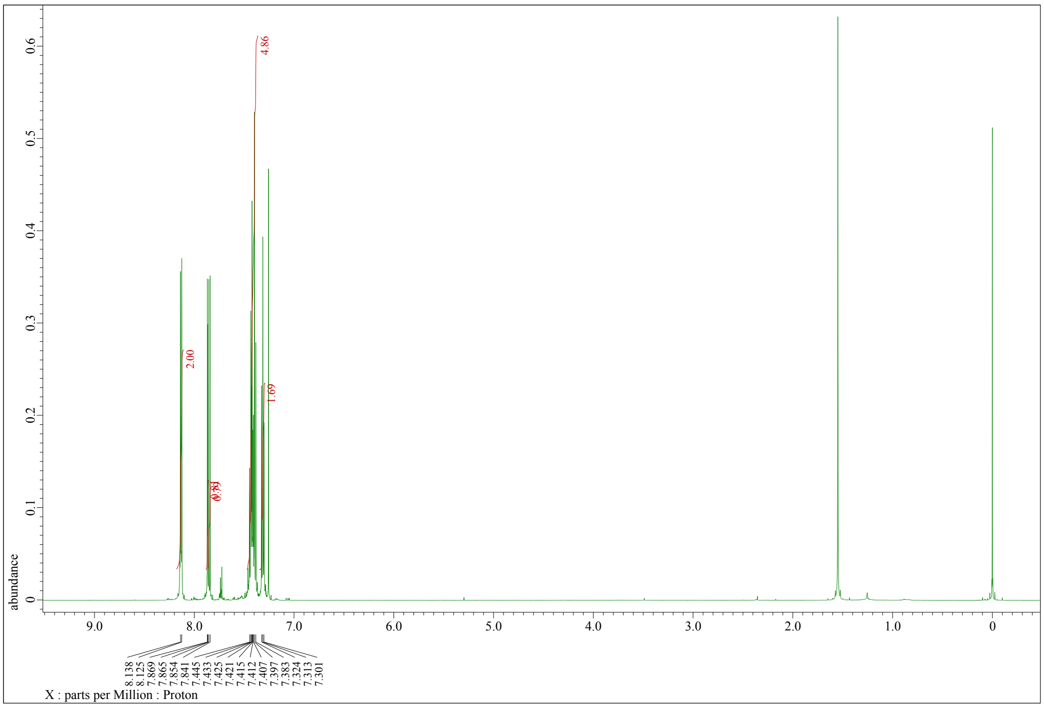


Chart S1. ^{1}H NMR spectrum of **1b** (400 MHz, $CDCl_3$, RT)

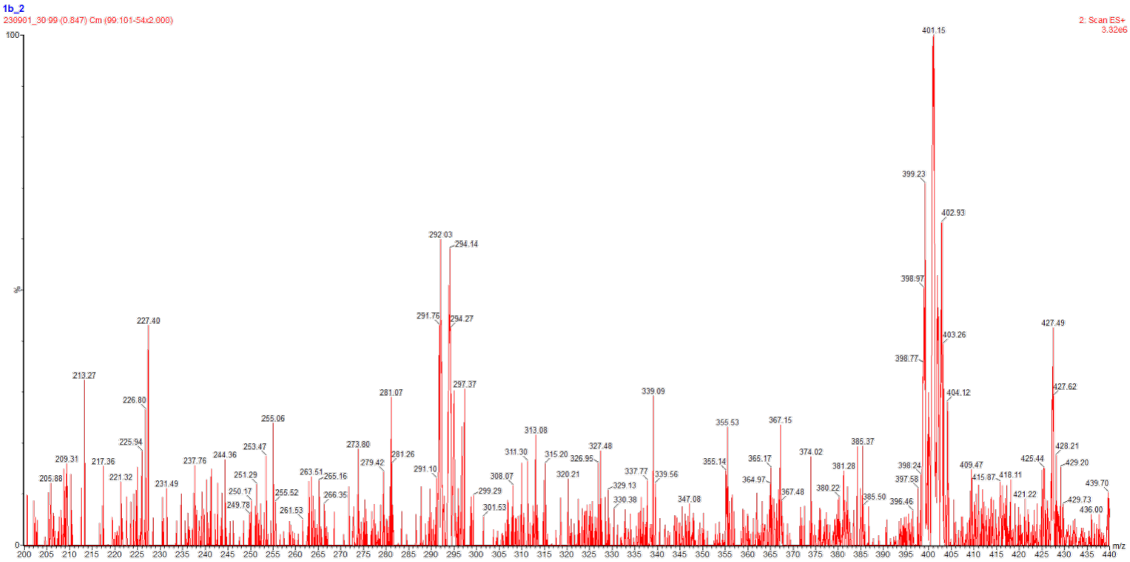


Chart S2. MS spectrum of **1b**

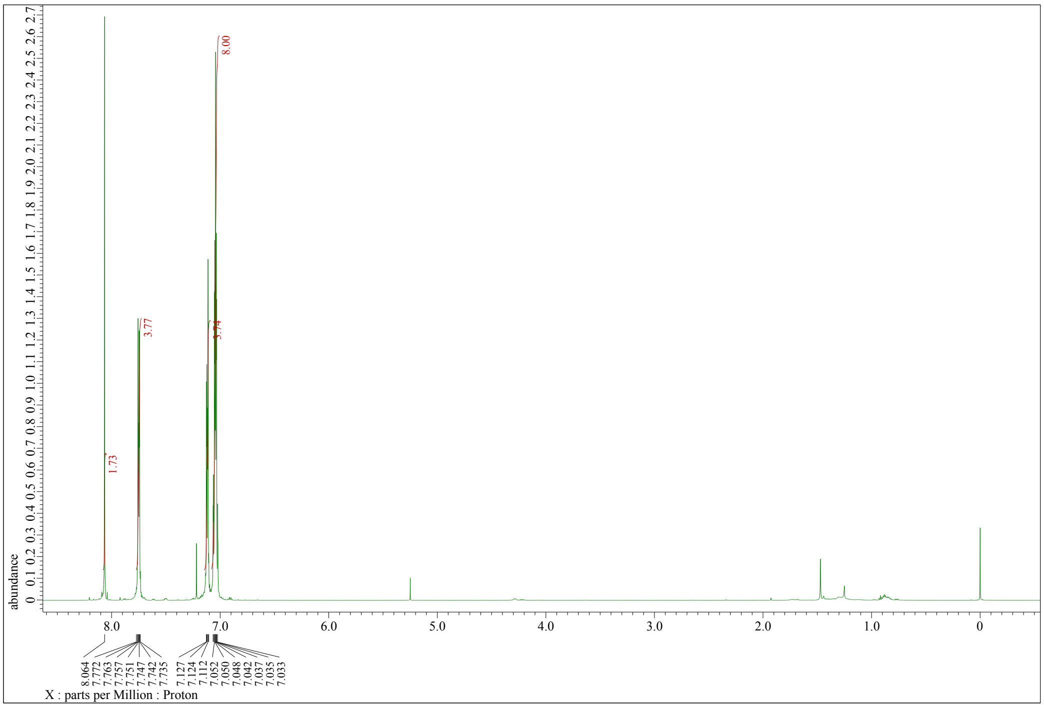


Chart S3. ^{1}H NMR spectrum of **1c** (400 MHz, $CDCl_3$, RT)

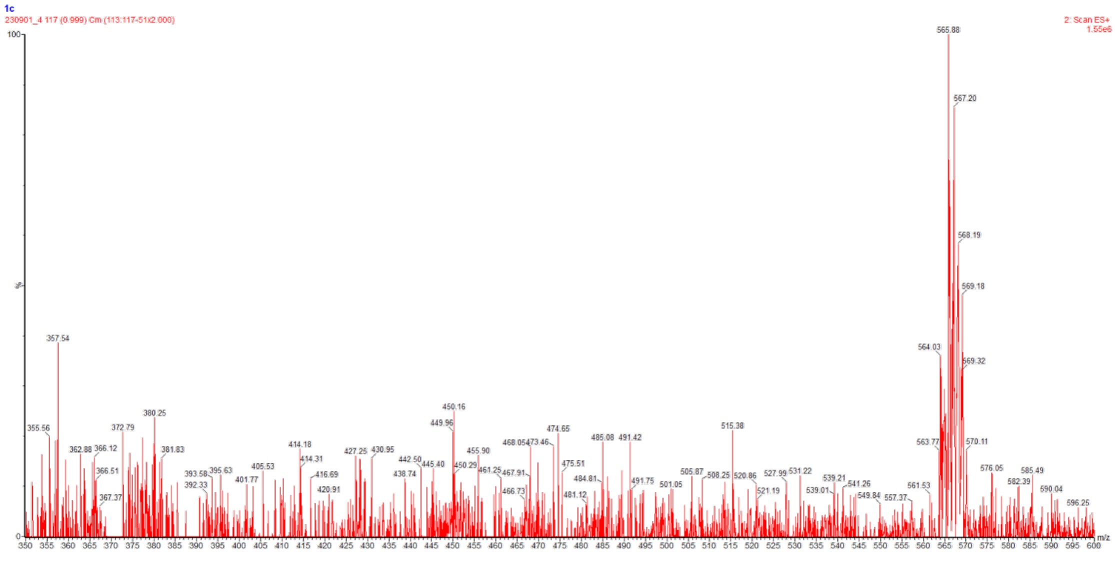


Chart S4. MS spectrum of **1c**

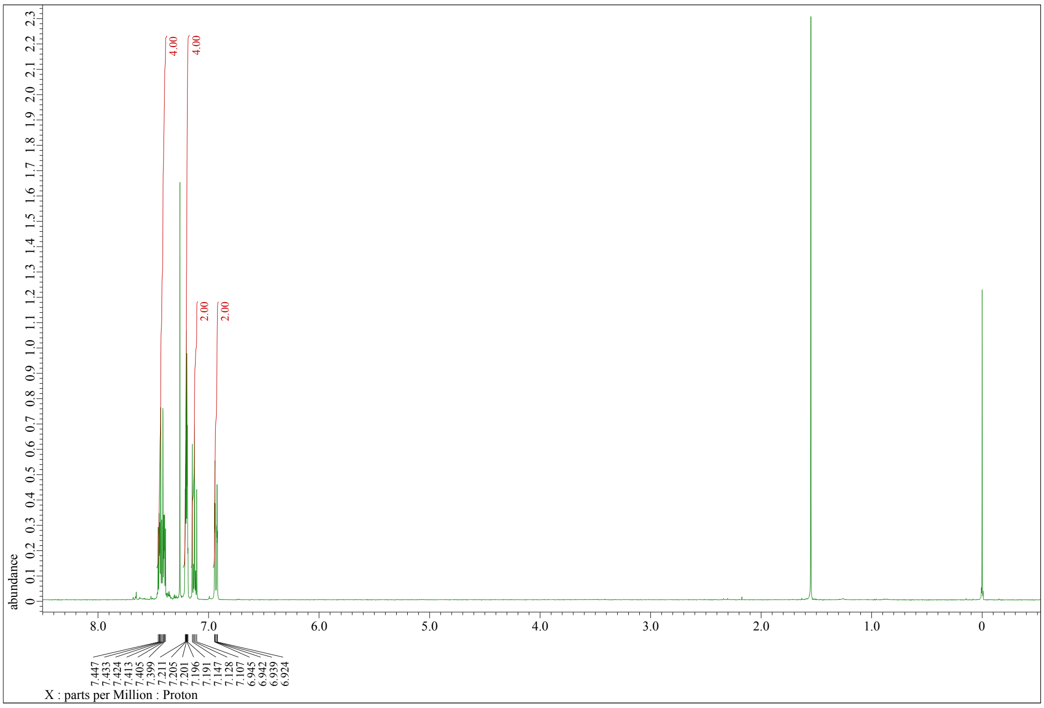


Chart S5. ^{1}H NMR spectrum of **2a** (400 MHz, $CDCl_3$, RT)

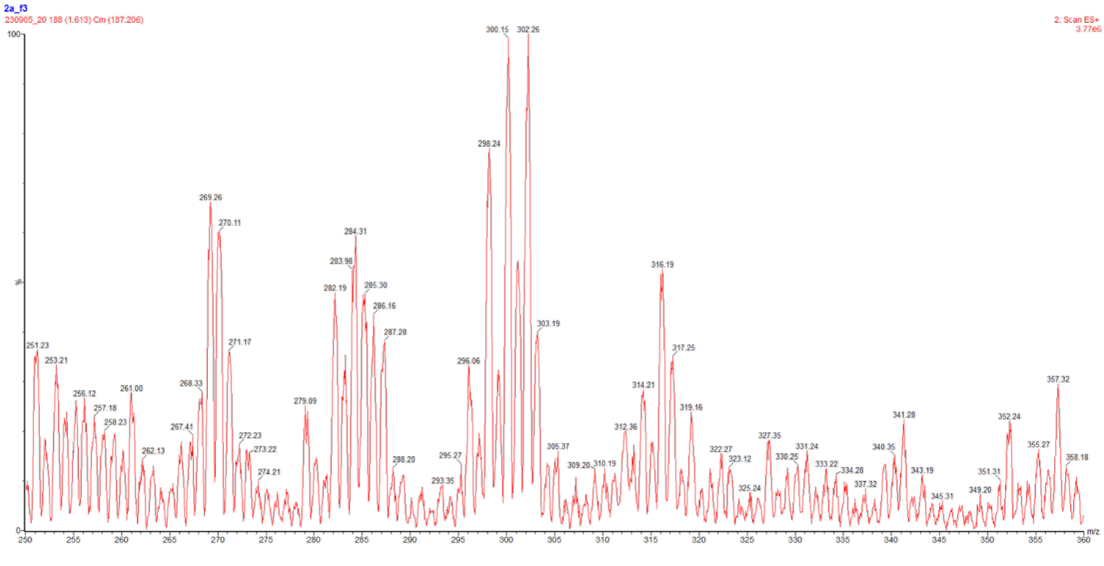


Chart S6. MS spectrum of **2a**

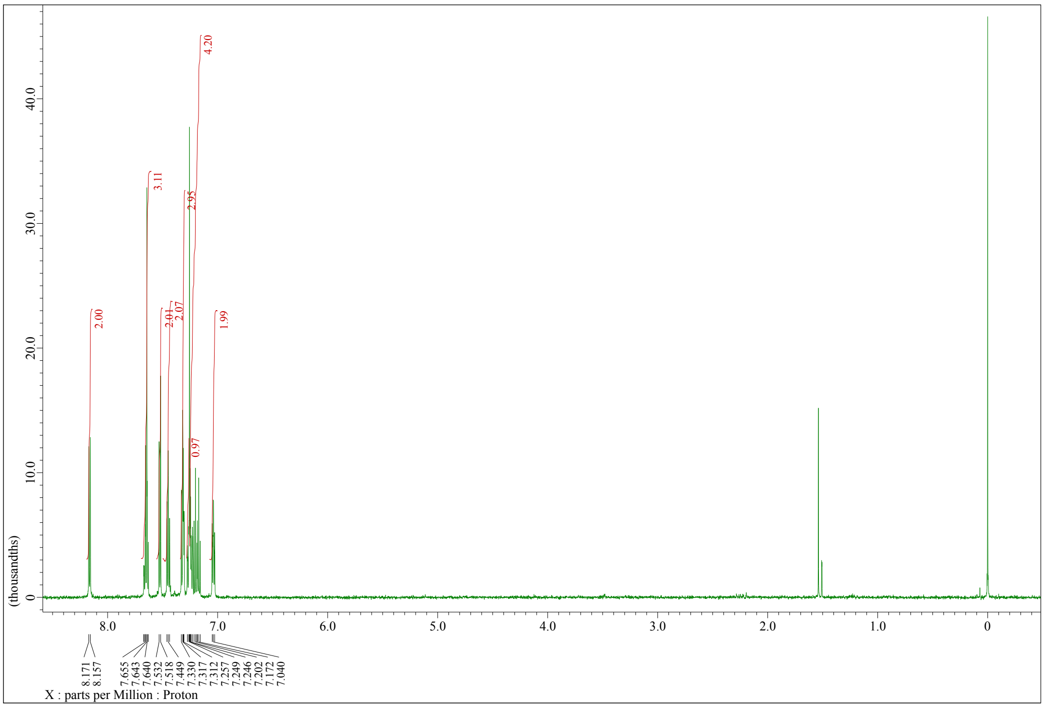


Chart S7. ^{1}H NMR spectrum of **2b** (400 MHz, CDCl$_3$, RT)

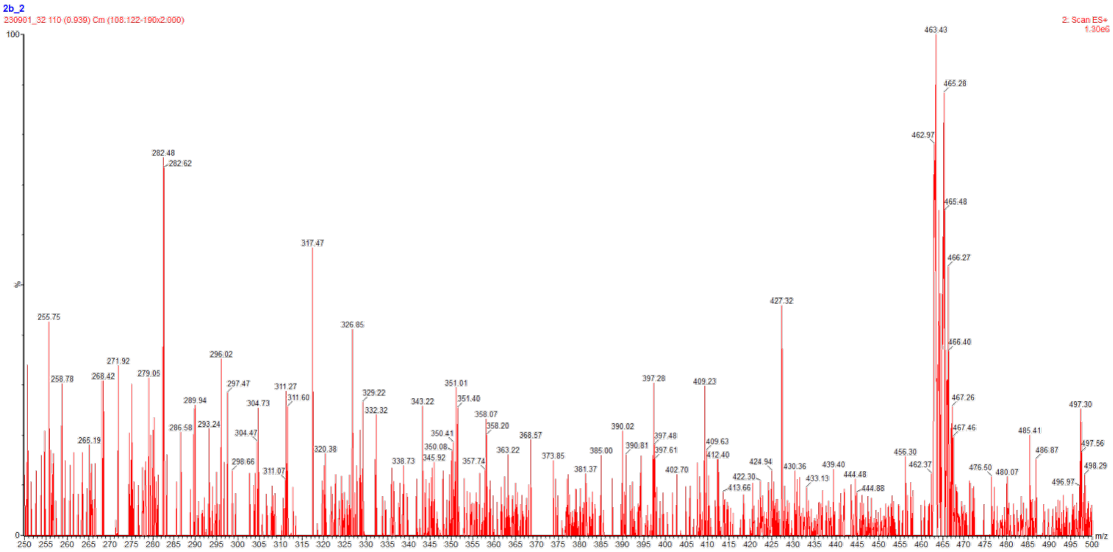


Chart S8. MS spectrum of **2b**

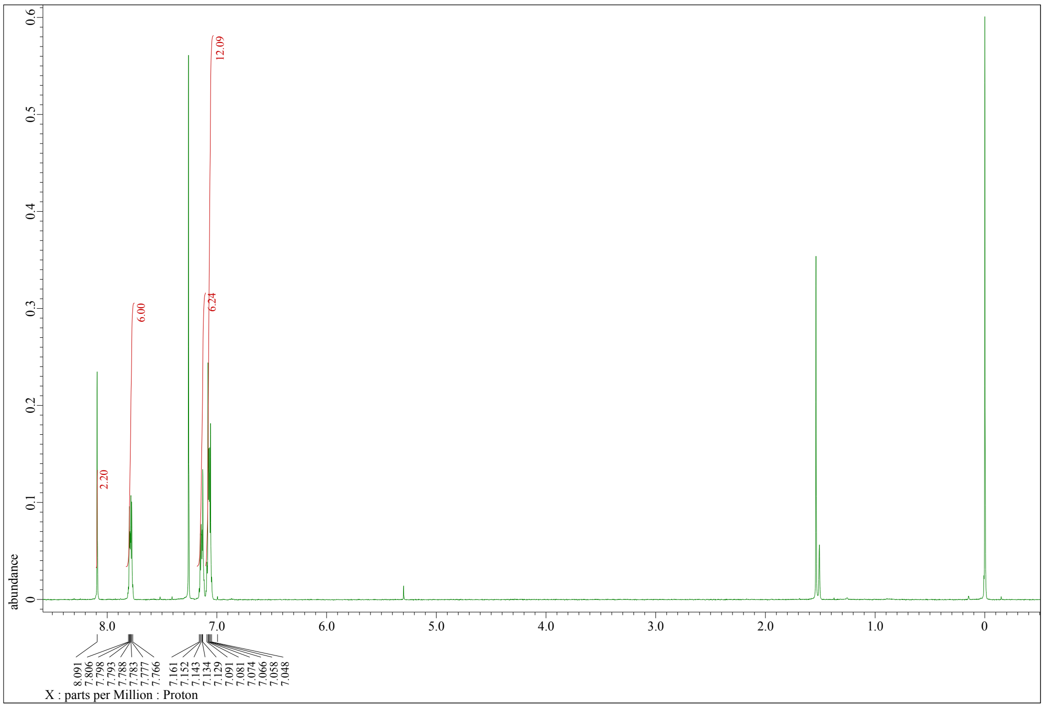


Chart S9. ^{1}H NMR spectrum of **2c** (400 MHz, $CDCl_3$, RT)

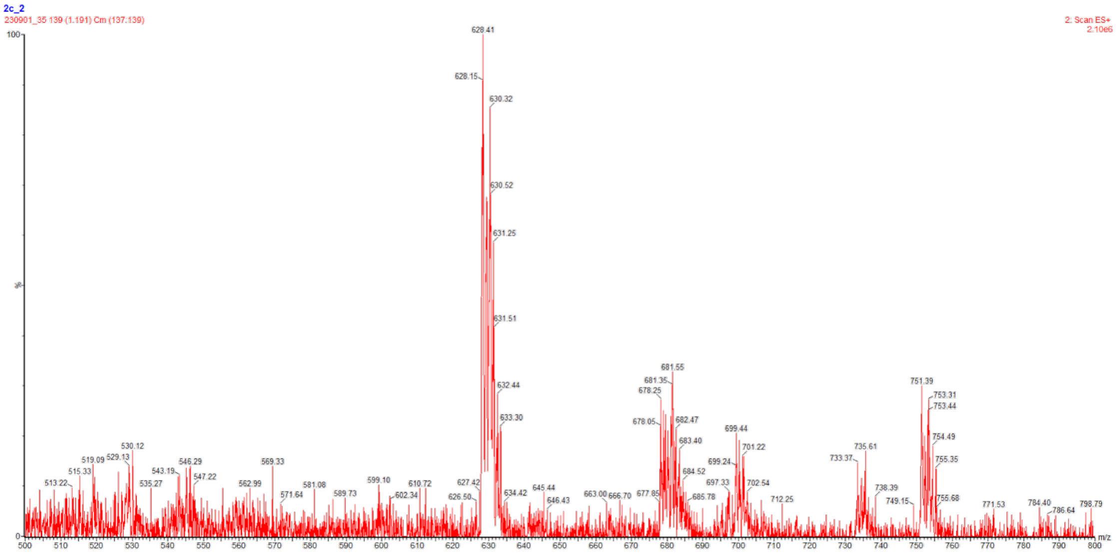


Chart S10. MS spectrum of **2c**

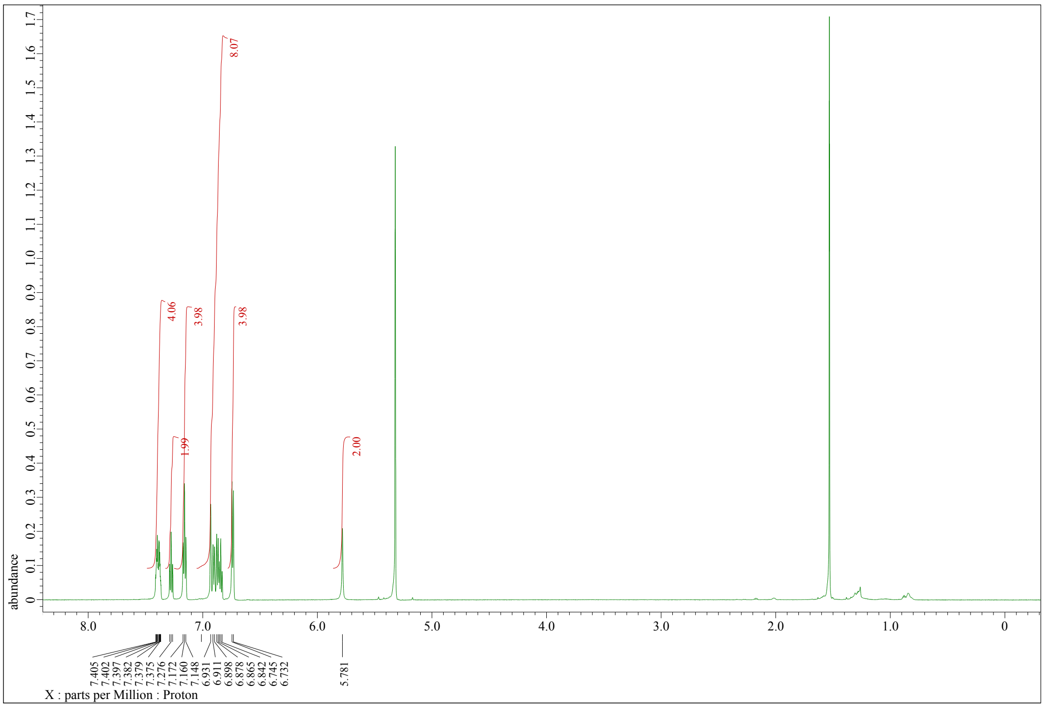


Chart S11. ^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$, RT)

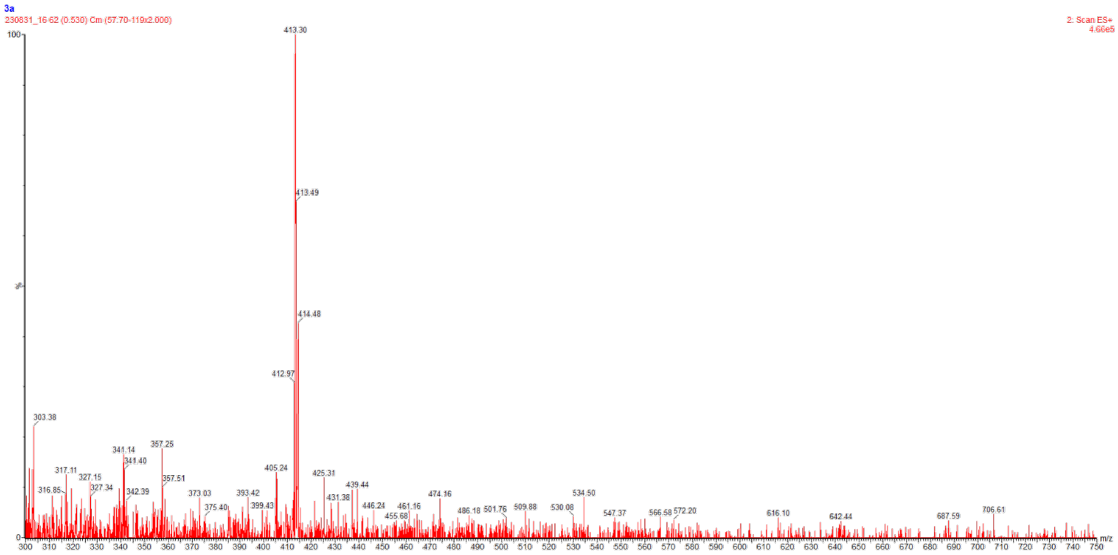


Chart S12. MS spectrum of **3a**

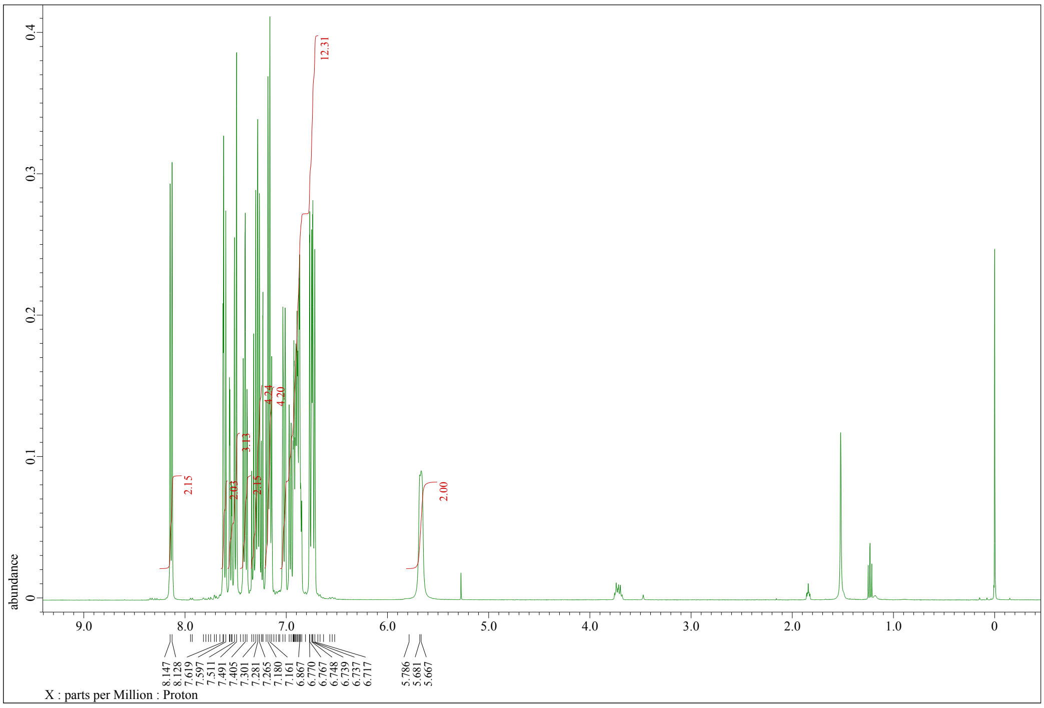


Chart S13. ^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$, RT)

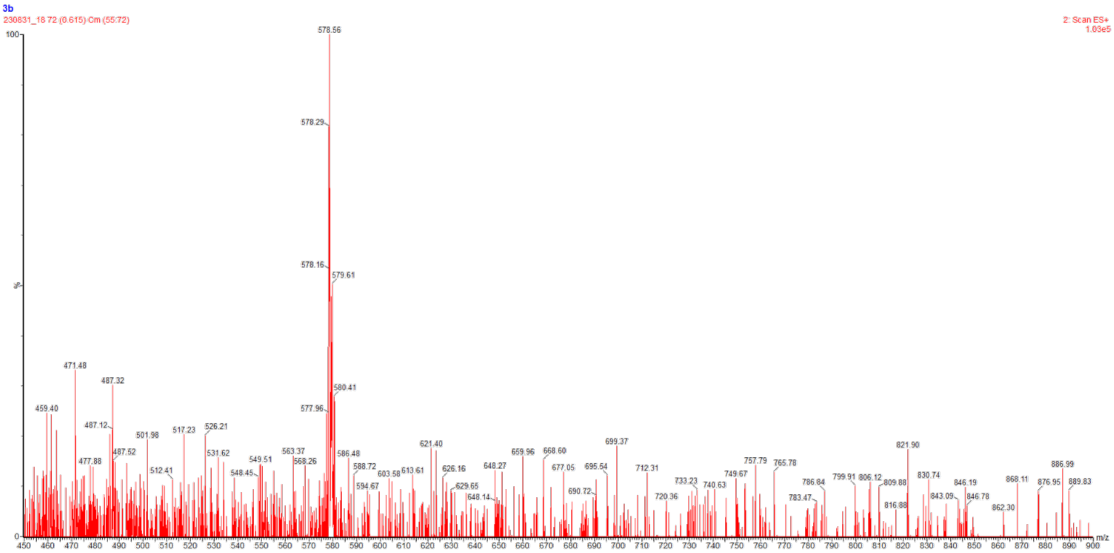


Chart S14. MS spectrum of **3b**

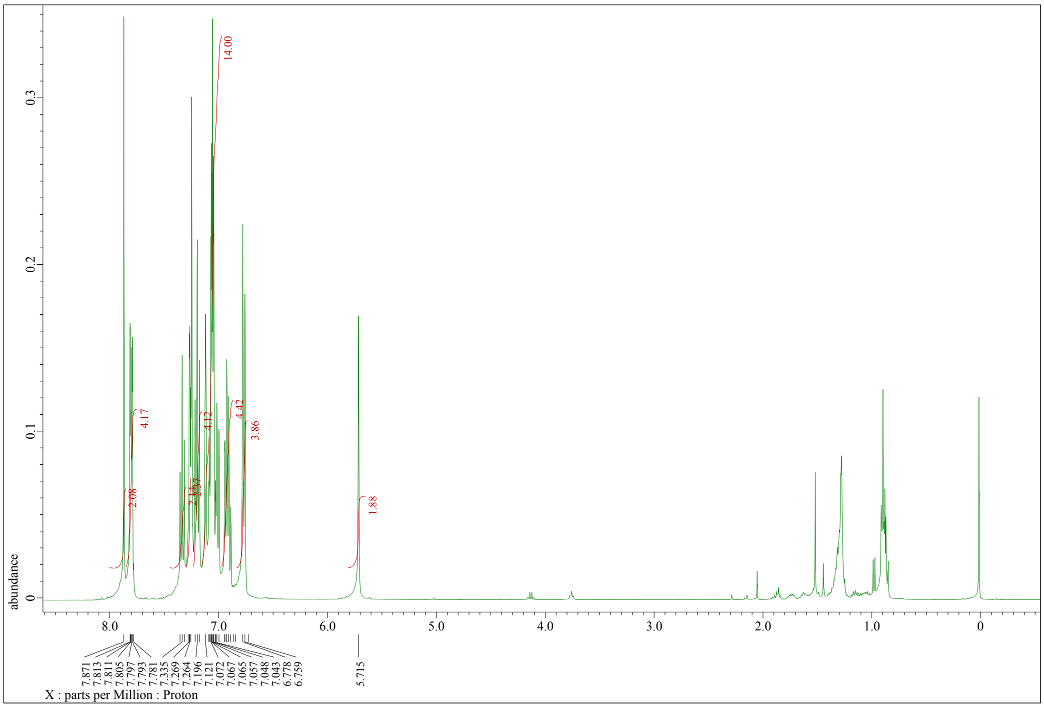


Chart S15. ^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$, RT)

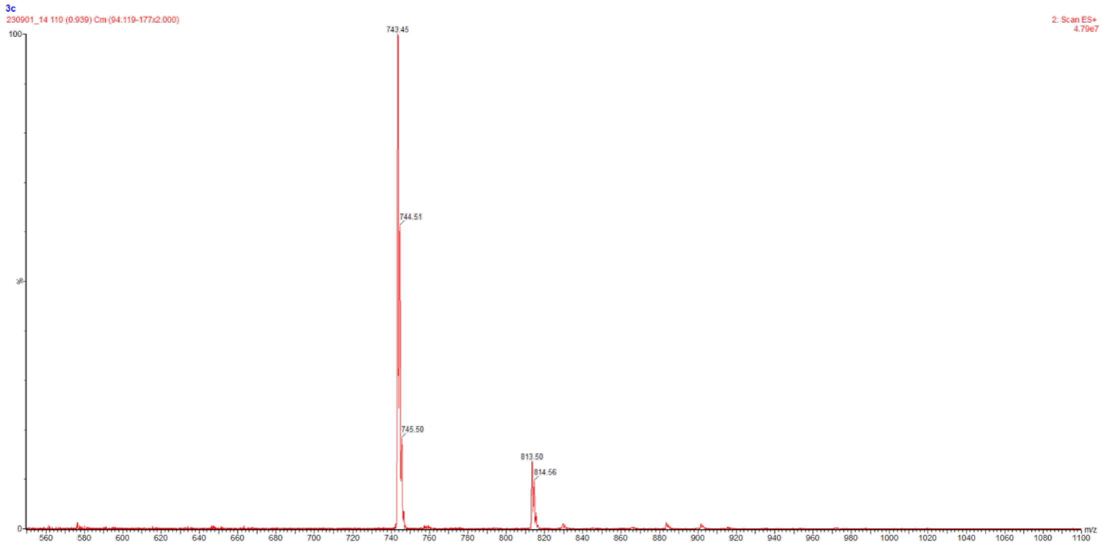


Chart S16. MS spectrum of **3c**

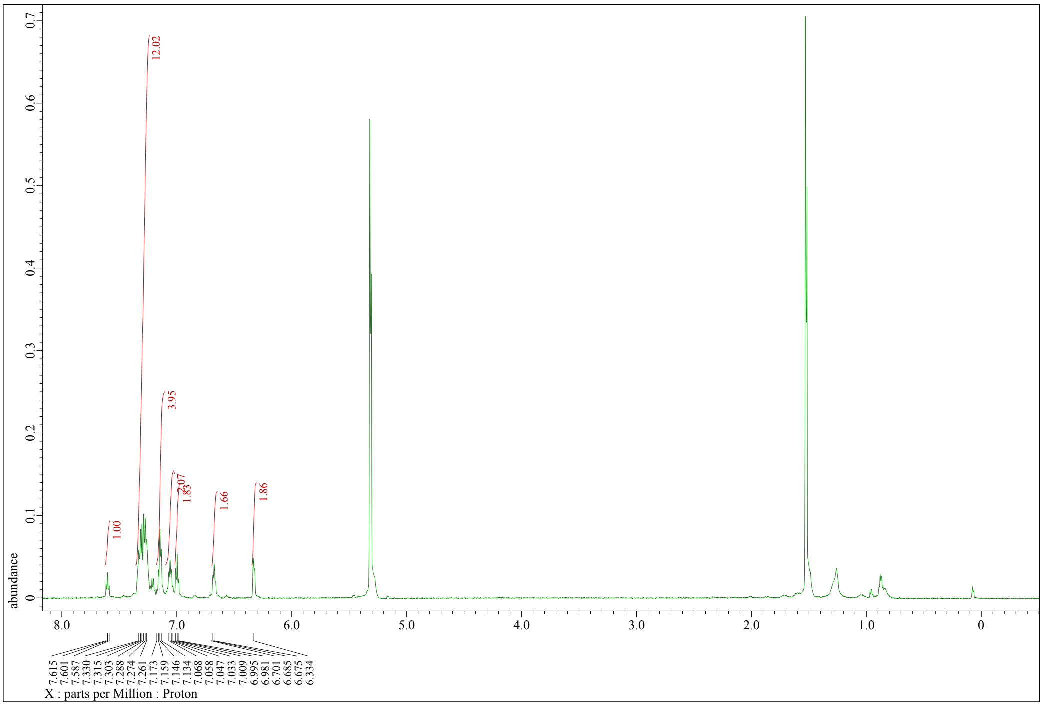


Chart S17. ^{1}H NMR spectrum of **4a** (400 MHz, CD_2Cl_2, RT)

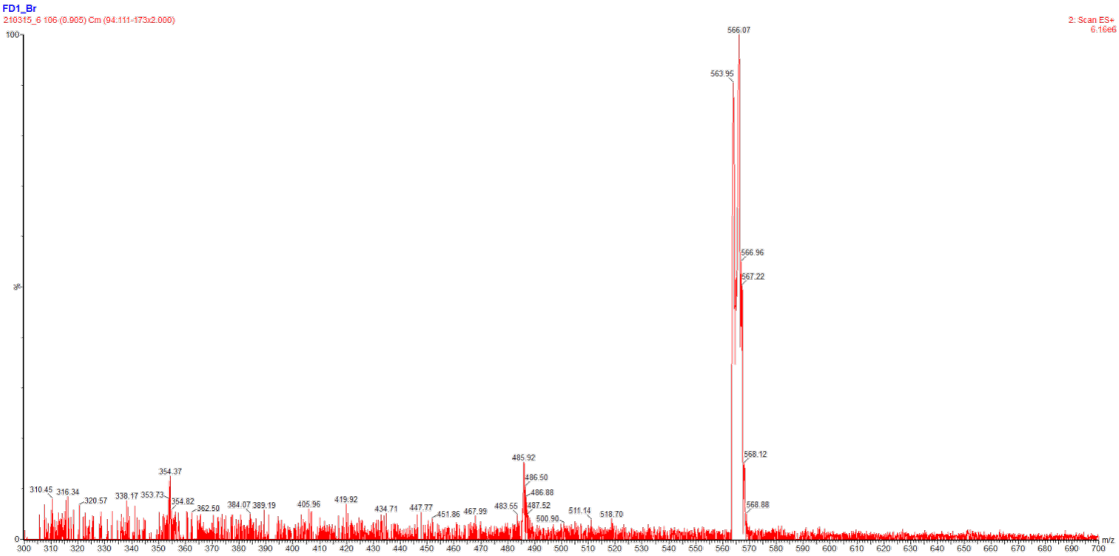


Chart S18. MS spectrum of **4a**

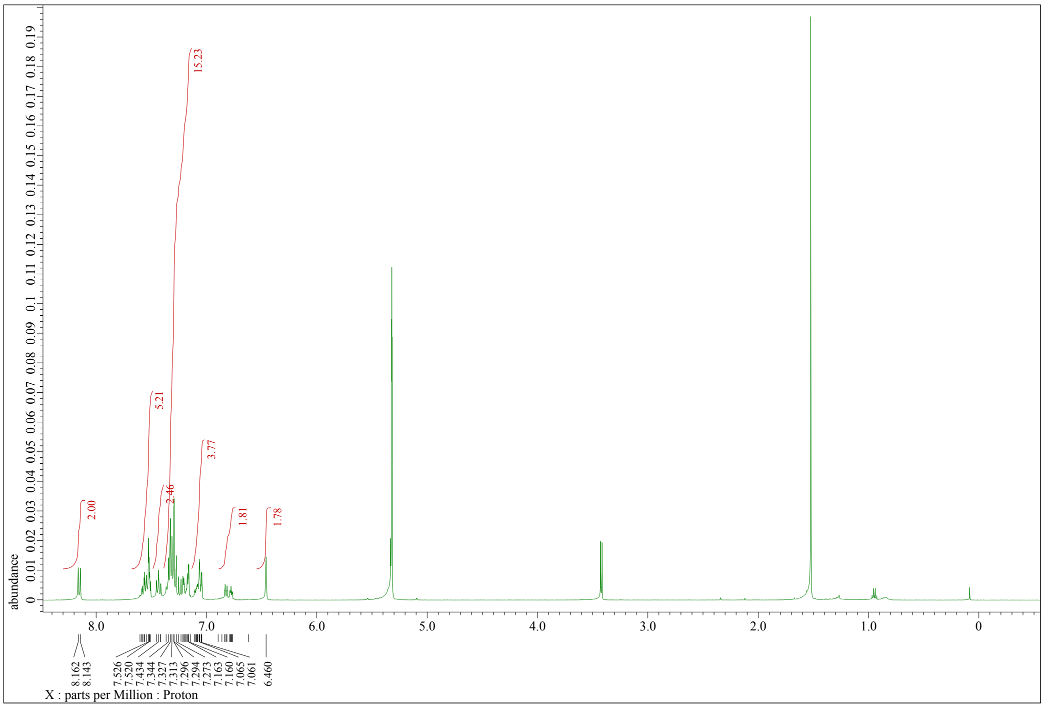


Chart S19. ^{1}H NMR spectrum of **4b** (400 MHz, CD_2Cl_2, RT)

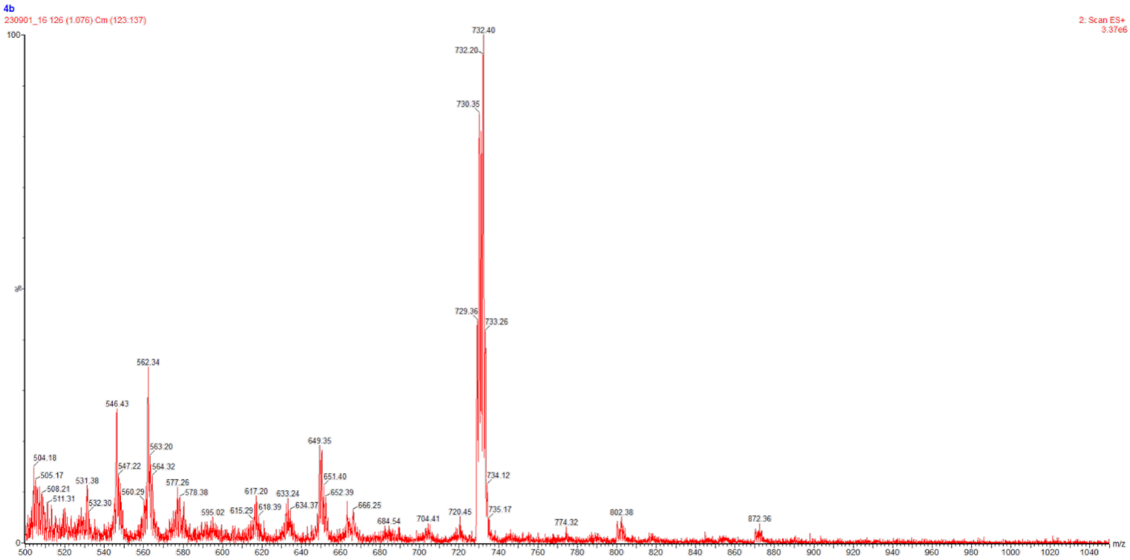


Chart S20. MS spectrum of **4b**

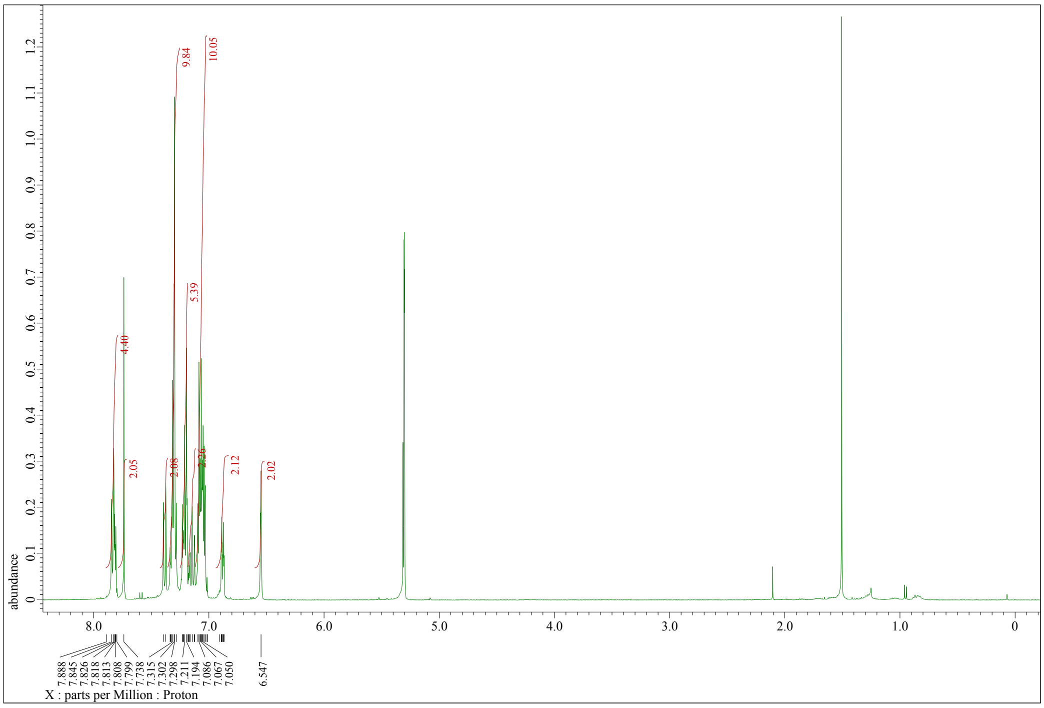


Chart S21. ^{1}H NMR spectrum of **4c** (400 MHz, CD_2Cl_2, RT)

Chart S22. MS spectrum of **4c**

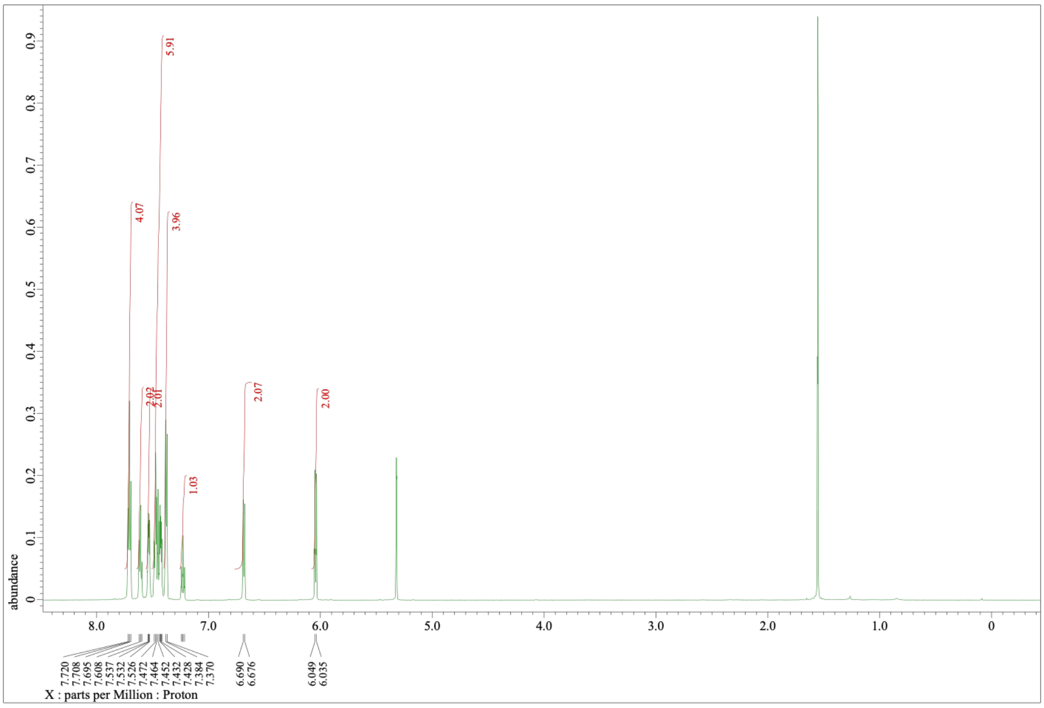


Chart S23. ^{1}H NMR spectrum of **OP-BN** (400 MHz, CD_2Cl_2, RT)

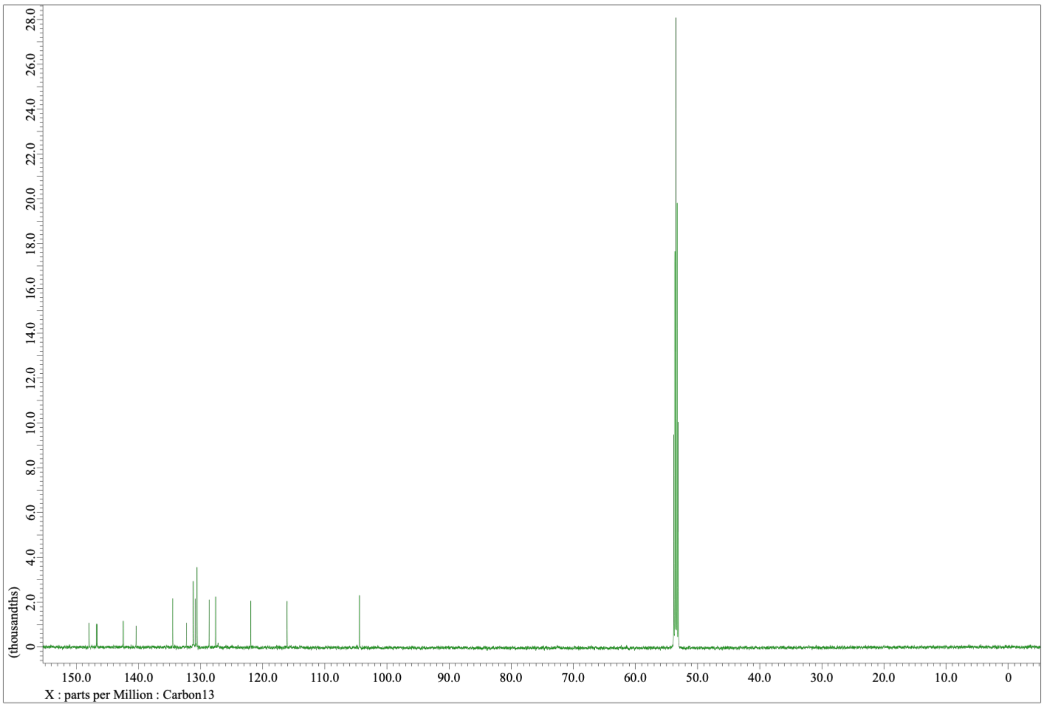


Chart S24. ^{13}C NMR spectrum of **OP-BN** (100 MHz, CD_2Cl_2, RT)

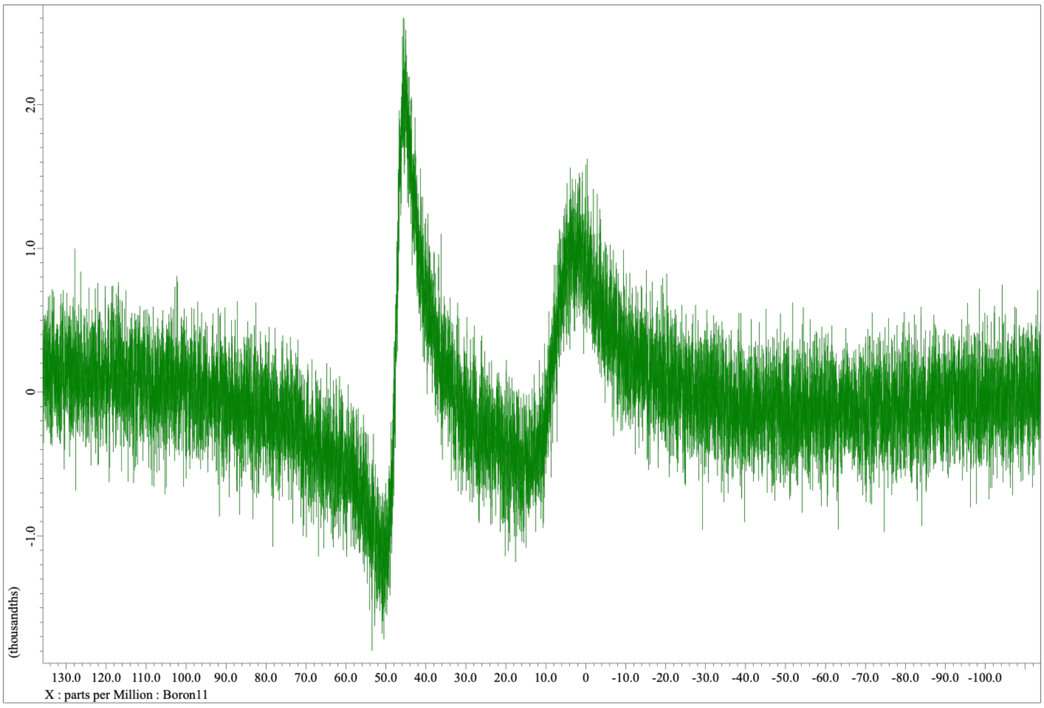


Chart S25. ^{11}B NMR spectrum of **OP-BN** (190 MHz, CD_2Cl_2, RT)

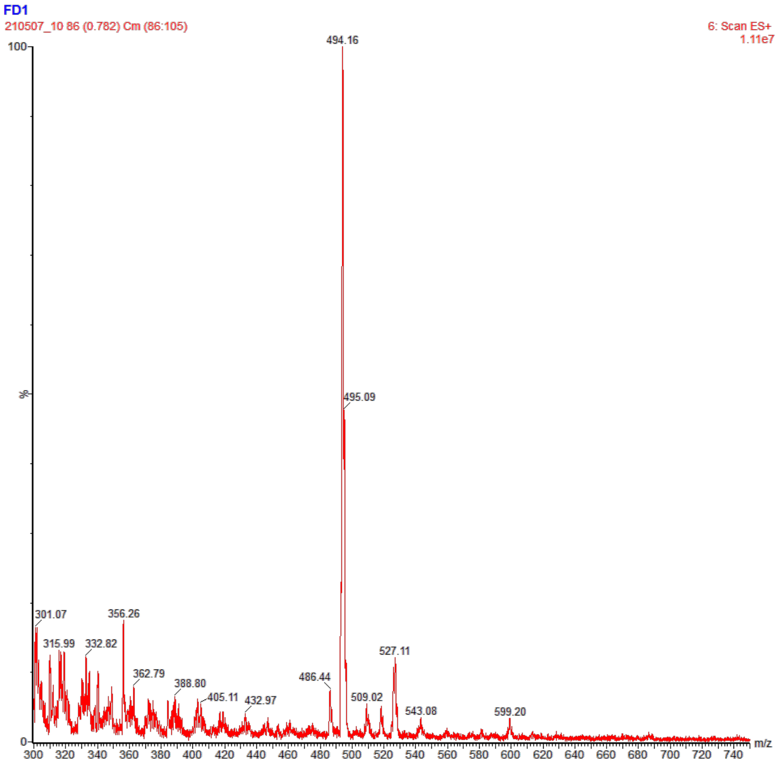


Chart S26. MS spectrum of **OP-BN**

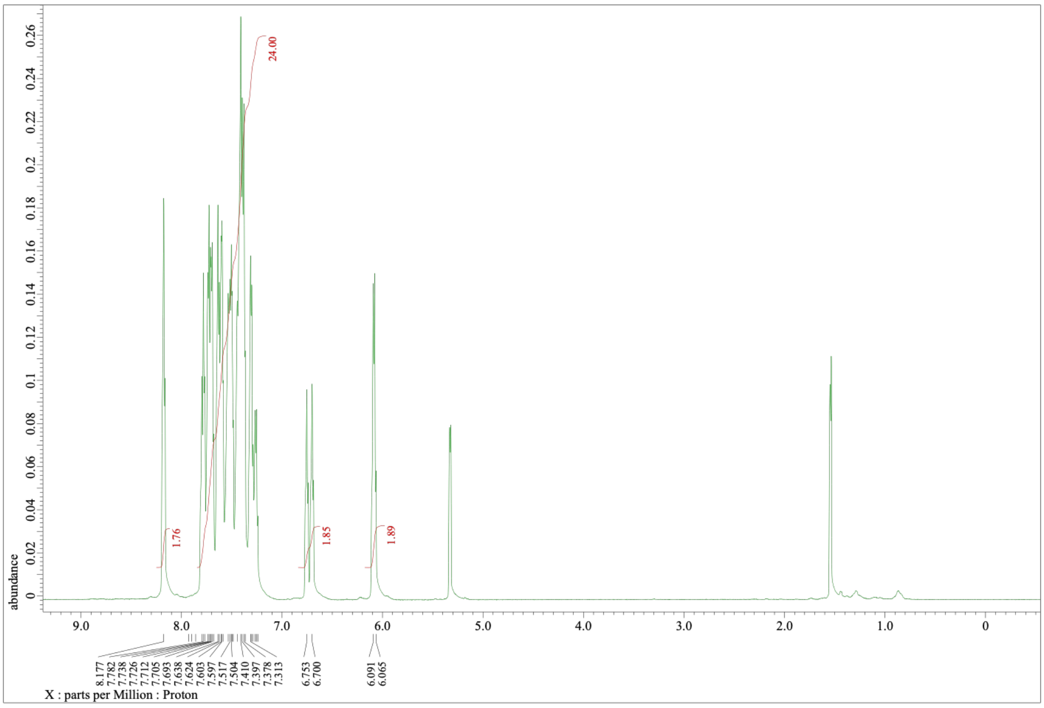


Chart S27. ^{1}H NMR spectrum of **Cz-OP-BN** (400 MHz, CD_2Cl_2, RT)

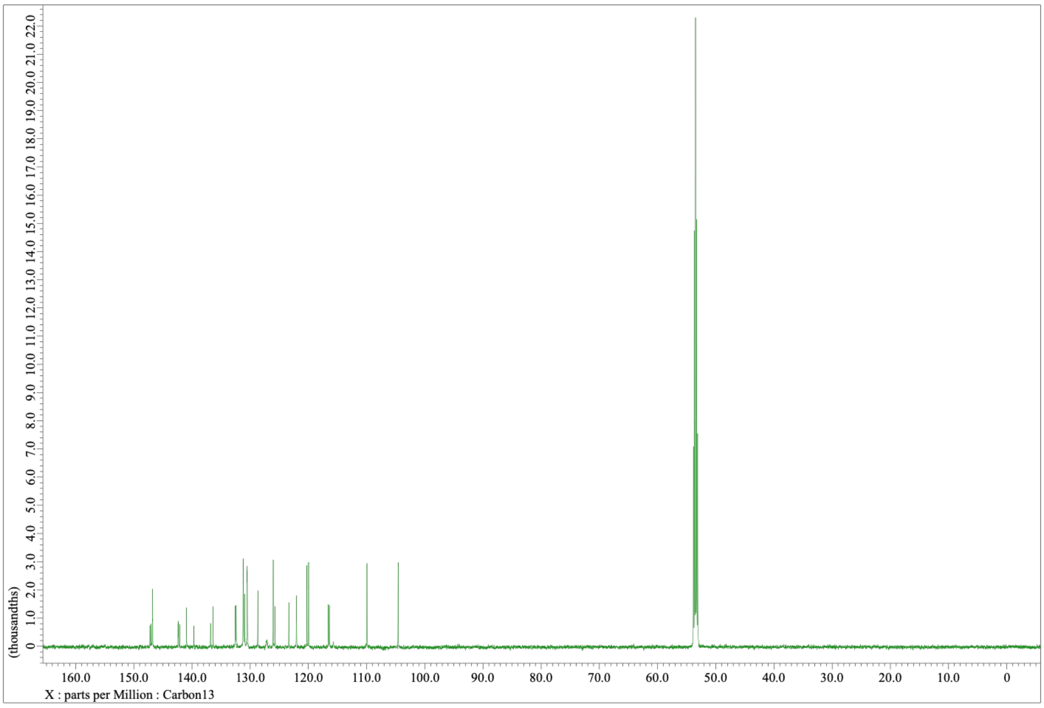


Chart S28. ^{13}C NMR spectrum of **Cz-OP-BN** (100 MHz, CD_2Cl_2, RT)

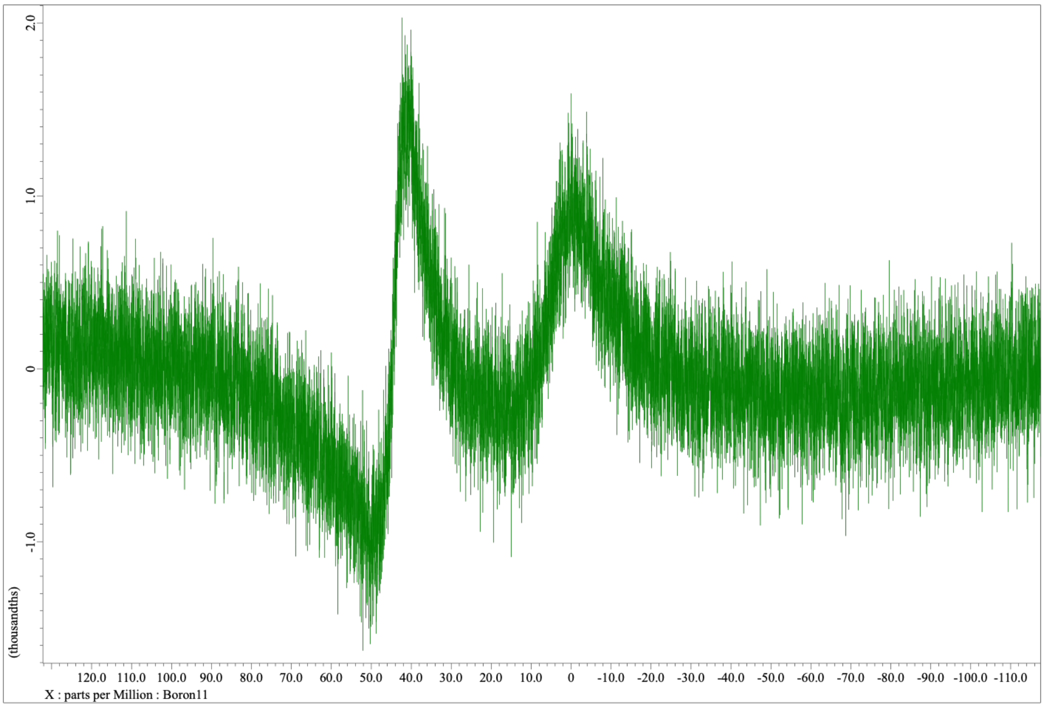


Chart S29. ^{11}B NMR spectrum of **Cz-OP-BN** (190 MHz, CD_2Cl_2, RT)

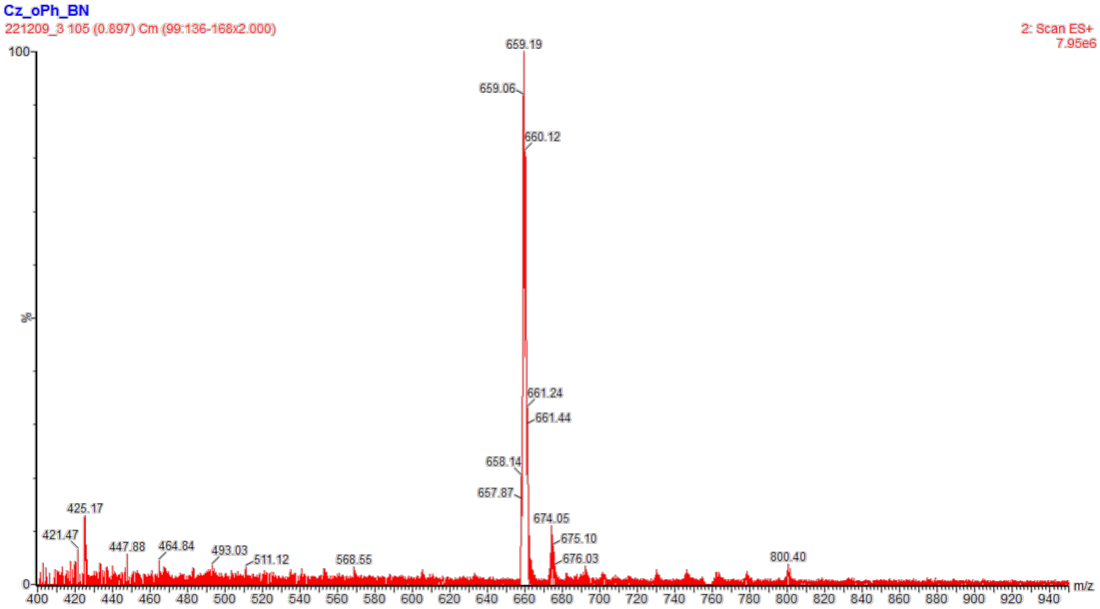


Chart S30. MS spectrum of **Cz-OP-BN**

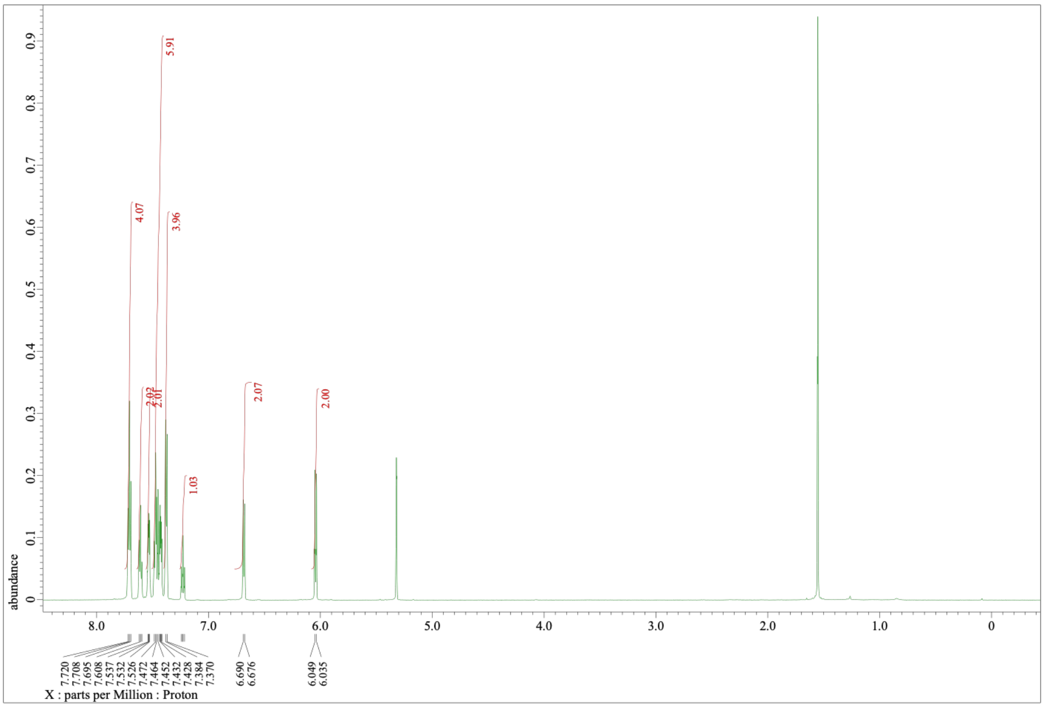


Chart S31. ^{1}H NMR spectrum of **2Cz-OP-BN** (400 MHz, CD_2Cl_2, RT)

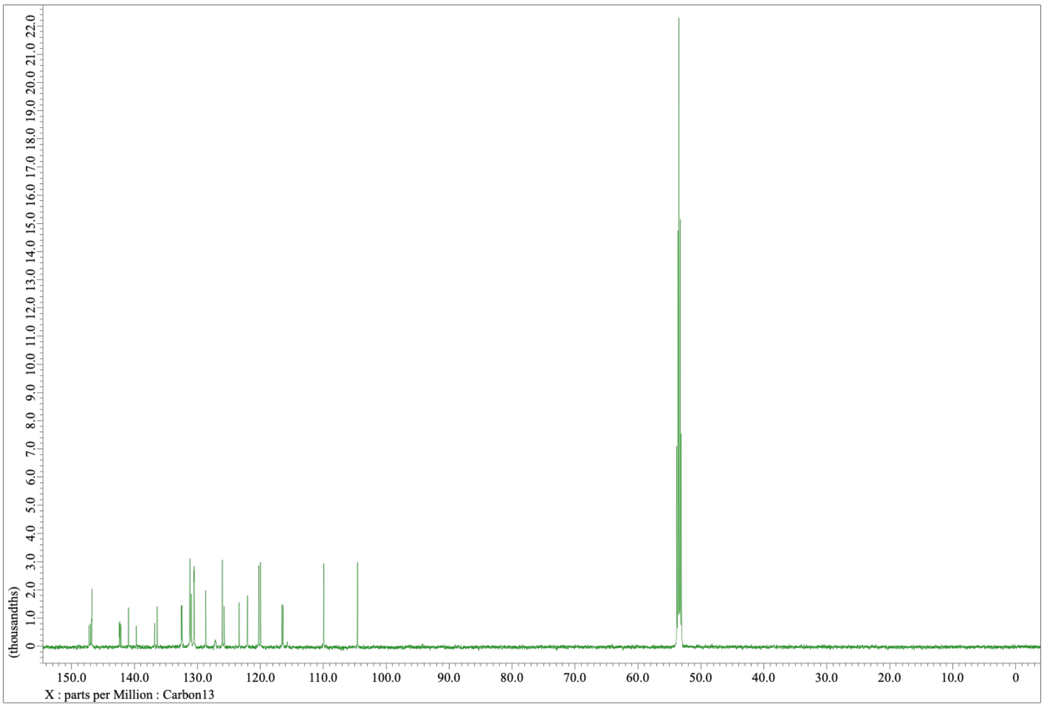


Chart S32. ^{13}C NMR spectrum of **2Cz-OP-BN** (100 MHz, CD_2Cl_2, RT)

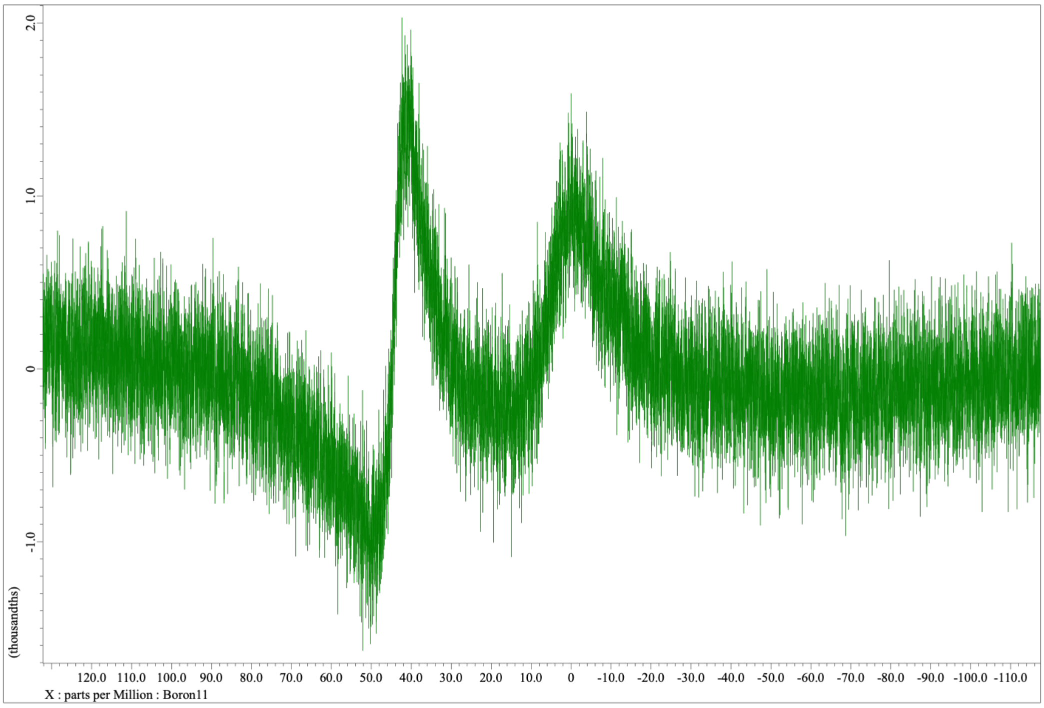


Chart S33. ^{11}B NMR spectrum of **2Cz-OP-BN** (190 MHz, CD_2Cl_2, RT)

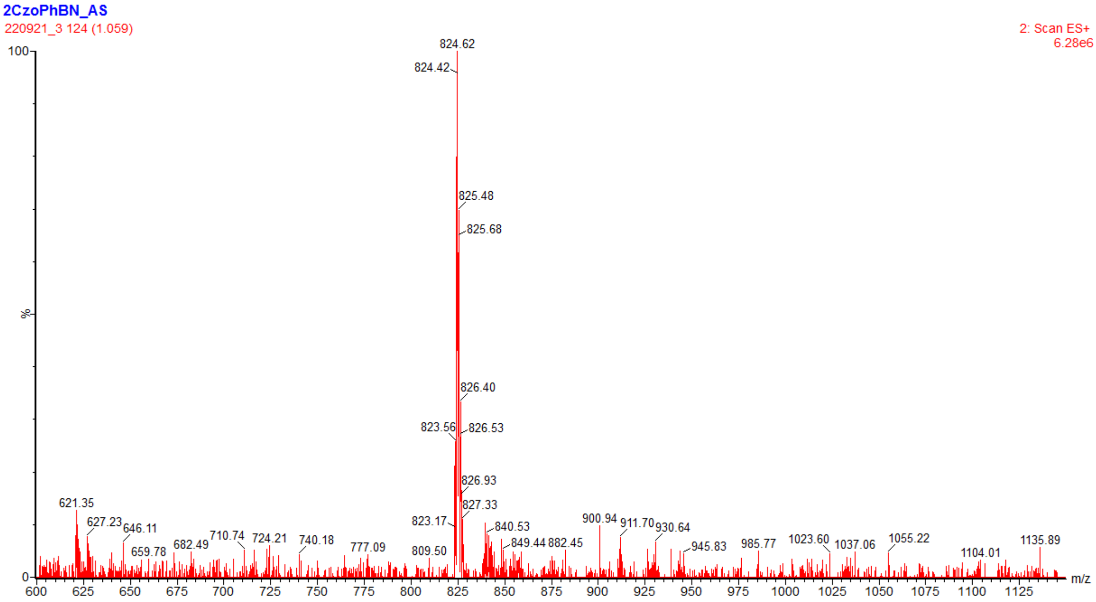


Chart S34. MS spectrum of **2Cz-OP-BN**

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