Precision Design for High-Performance TADF Emitters with Novel Interlock D-A Frameworks

Aziz Khan,[1,2]† Fan-Cheng Kong,[2]† Jamal Kazmi,[1] Sarvendra Kumar,[2,4*] Tim Leydecker,[1*] Zhiming Wang [1,3*]

[1]Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 611731, P. R. China

[2]Institute.of Functional Nano & Soft Materials (FUNSOM) Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices Soochow University 199 Ren'ai Road, Suzhou, Jiangsu 215123, P. R. China

[3]Shimmer Center, Tianfu Jiangxi Laboratory, Chengdu 641419, P. R. China

[4]IndFlux Advance Materials Ltd, Chherat Chauraha, Anoopshahar Road, Aligarh, UP-202122, India

*Corresponding author. Tel.: +86 189 81930267;

Email: s.kumar@msn.com; tim_leydecker@uestc.edu.cn; zhmwang@uestc.edu.cn;

†*The authors contribute equally to this paper.*

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1. Chemicals and instruments

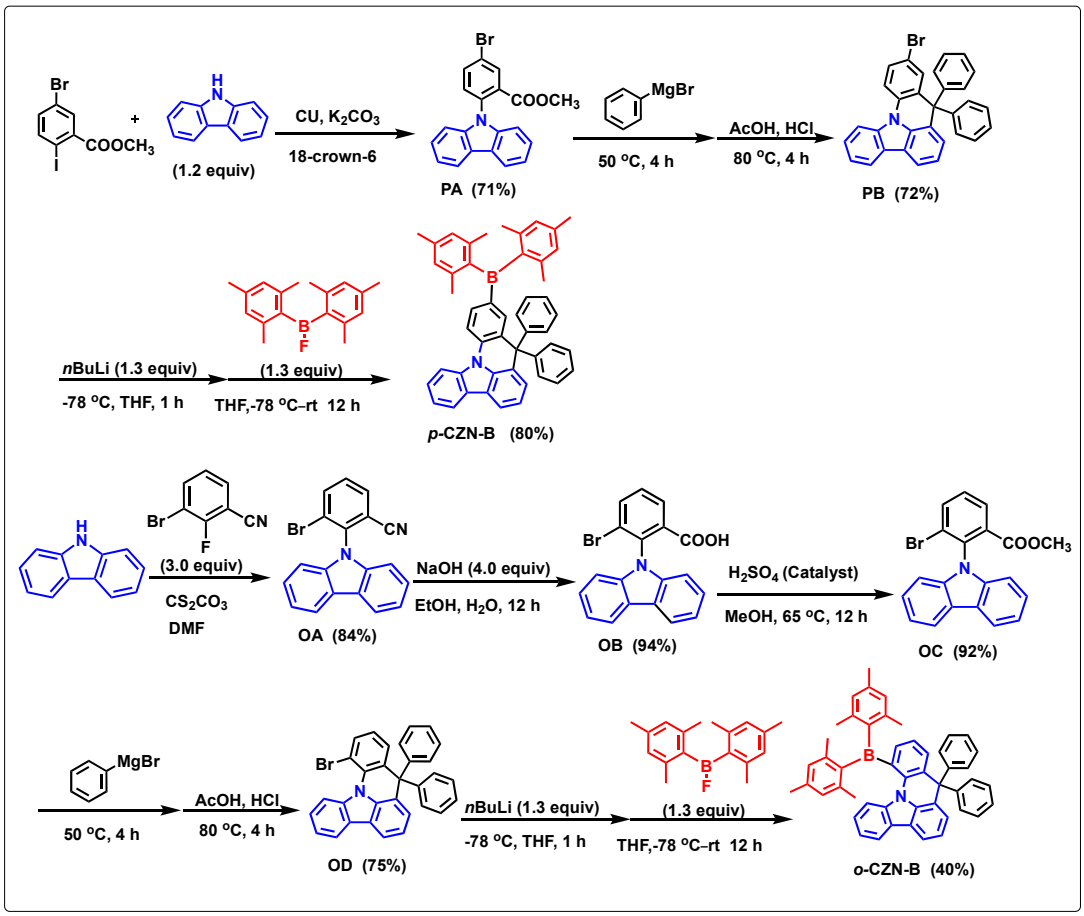
All chemicals and reagents were used as received from commercial resources without further purification. Tetrahydrofuran (THF), and 1,4-dioxane used in synthetic routes were purified by PURE SOLV (Innovative Technology) purification system. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker 400 and 600 spectrometers at room temperature. Mass spectra and time of Flight MS-MALDI (MALDI-TOF) were performed on a Thermo ISQ mass spectrometer using a direct exposure probe and Bruker Auto flex II/Compass 1.0, respectively. UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 750 spectrophotometer. Photoluminescence (PL) spectra and phosphorescent spectra were performed on Hitachi F-4600 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) was performed on a TA DSC 2010 unit at a heating rate of 10 ^{o}C/min under nitrogen. The glass transition temperature (*T*g) was determined from the second heating scan. Thermogravimetric analysis (TGA) was performed on TA SDT 2960 instrument at a heating rate of 10 ^{o}C/min under nitrogen, the temperature at 5% weight loss was used as the decomposition temperature (*T*d). The electrochemical measurement was made using a CHI600 voltammetric analyzer. A conventional three-electrode configuration consisting of a platinum working electrode, a Pt-wire counter electrode, and an Ag/AgCl reference electrode were used. The solvent in the measurement was CH_2Cl_2, and the supporting electrolyte was 0.1 M [Bu4N]PF6. Ferrocene was added as a calibrant after each set of measurements, and all potentials reported were quoted with reference to the ferrocene-ferrocenium (Fc/Fc+) couple at a scan rate of 100 mV/s. Theoretical calculations based on density functional theory (DFT) approach at the B3LYP/6-31G (d) level were performed with the use of the Gaussian 09 program.

2. OLED fabrication and measurements

All the material except two novel synthesized hosts were acquired from commercial source without further purification. OLEDs were all fabricated under a base vacuum of 4×10^{-6} Torr and on ITO glass substrates (160 nm, 15 Ω/sq). Before the evaporation, ITO glass substrates were ultrasonically cleaned sequentially with deionized water, acetone, ethanol, and deionized water, and dried in an oven at 110 °C for 6 h. After that, they were put in ultraviolet ozone for 15 mins. The charge injecting layers deposited rates were 0.2~0.4 Å/s, the charge transporting layers deposited rates were 2~3 Å/s and Al's is 6-8 Å/s. Quartz crystals would monitor all materials deposition rates and thicknesses.

The EL information such as current efficiency (CE), EL spectra, power efficiency (PE), CIE coordinate, values of driving voltages, *J-V* curves and luminance were all recorded via KEITHLEY 2400 source meter and programmable spectra scan photometer (PHOTO RESEARCH, PR 655). All the measurements were conducted in ambient air at a room temperature, and the external quantum efficiency was calculated assuming Lambertian distribution of light emission.

3. Synthesis



Scheme. S1 Synthetic routes for ***p*-CZN-B** and ***o*-CZN-B.**

3.1 Synthesis of methyl 5-bromo-2-(9H-carbazol-9-yl)benzoate (PA)

Methyl 5-bromo-2-iodobenzoate (5.0 g, 14.6 mmol), carbazole (3.0 g, 17.6 mmol), copper (0.1 g, 2.2 mmol), 18-Crown-6 (0.3 g, 1.5 mmol) and potassium carbonate (2.5 g, 18.0 mmol) was dissolved in 100 mL 1,2-dichlorobenzene in a 250 mL 2-neck round bottom flask under inert condition. After refluxed for 48 hours under stirring, the reaction was cooled to room temperature and then the solvent was removed under vacuum through rotary evaporator. The solid products dissolved in dichloromethane and washed three times with water. The organic layer was separated and the aqueous layer was extracted with 30 mL DCM twice. Then the extracts were combined, dried with sodium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by column chromatography using petroleum ether/ dichloromethane (7/3, v/v) as eluent to afford final product. The final product was a white powder (4.0 g, 71.7%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.7 Hz, 2H), 8.01 (dd, *J* = 7.9, 2.3 Hz, 2H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 6.96 (d, *J* = 8.1 Hz, 1H), 3.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.38, 141.33, 141.07, 137.44, 135.95, 133.74, 132.52, 130.70, 130.07, 129.72, 129.63, 127.20, 127.16, 126.36, 126.11, 126.04, 123.63, 123.44, 120.79, 120.58, 120.37, 120.16, 120.05, 109.64, 109.39, 77.38, 77.26, 77.06, 76.74, 52.38, 52.34. MS (EI) m/z: 379.0 [M+].

3.2 Synthesis of 10-bromo-8,8-diphenyl-8H-indolo[3,2,1-de]acridine (PB)

The phenyl magnesium bromide (9.0 g, 10.0 mmol) was taken and added to the flask under argon and stirred at room temperature. The THF solution of methyl 5-bromo-2-(9H-carbazol-9-yl) benzoate (3.8 g, 10.0 mmol) was added slowly to the reaction mixture. Further stirred at 50 ^{o}C for 4 hrs, then the reaction mixture was quenched with small amount of NH_4OH in water (5-8 mL) and THF was evaporated. The obtained solid was extracted with DCM and washed with water (3

× 50 mL). The organic layer was collected and dried over Na_2SO_4, resulting yellowish solid, which was direct used in the next reaction. The crude mixture was dissolved in 30 mL acetic acid while 8 mL hydrochloric acid (36%) was added drop-wise to the solution mixture. The reaction mixture was refluxed for 4 hours, then cooled to RT, extracted with DCM and water and evaporated. which was further purified from column chromatography with eluents: petroleum ether/ dichloromethane (7/3, v/v) (3.5 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 6.9 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.64 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.34 (ddd, *J* = 18.6, 13.9, 7.7 Hz, 4H), 7.24 – 7.14 (m, 7H), 6.98 (dt, *J* = 15.4, 8.0 Hz, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.13, 138.76, 137.69, 134.80, 131.08, 130.23, 128.09, 127.84, 127.77, 126.71, 125.99, 125.37, 123.70, 123.64, 122.85, 122.63, 121.25, 120.14, 119.25, 118.26, 110.06, 77.35, 77.23, 77.03, 76.71, 58.73. MS (EI) m/z: 485.0 [M+].

3.3 Synthesis of 10-(dimesitylboranyl)-8,8-diphenyl-8H-indolo[3,2,1-de]acridine (*p*-CZN-B).

Compound **PB** (2.0 g, 4.1 mmol) was dissolved in 30 mL freshly distilled THF and cooled to -78 °C. After 10 minutes, *n*-butyl lithium (3.0 mL, 4.9 mmol) was added drop-wise. The mixture was stirred for 1 hour at -78 °C, and then dimesitylborane (1.6 g, 6.1 mmol) in 30 mL THF was dissolved and added slowly to the reaction mixture. After 2 hours, the reaction mixture was slowly allowed to warm up to room temperature and stirred continued for 12 hrs. The reaction was monitored by TLC and after completion, 5 mL water was added to quench the reaction. The solvent was evaporated and the residue was dissolved in DCM and washed well with water (3 × 50 mL). The organic layer was dried over Na_2SO_4, filtered and evaporated, resulting in yellow powder, which was purified from column chromatography using petroleum ether/ dichloromethane (6/4, v/v) as an eluent (2.2 g, 80.1%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 15.2, 7.5 Hz, 3H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.58 – 7.47 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.18 – 7.09 (m, 7H), 7.04

(s, 1H), 7.01 – 6.93 (m, 4H), 6.71 (s, 4H), 2.28 (s, 6H), 1.96 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.17, 145.66, 141.44, 141.30, 140.43, 139.88, 139.52, 138.52, 138.01, 137.29, 136.50, 131.15, 129.97, 128.26, 128.00, 127.58, 127.07, 126.40, 126.33, 126.23, 122.66, 122.24, 121.65, 121.14, 118.05, 114.72, 112.77, 77.21, 77.00, 76.79, 56.88, 23.33, 21.17. MALDI-TOF (m/z) calculated for $C_{49}H_{42}BN$ [M+]: 655.69, found: 655.59.

3.4 Synthesis of 3-bromo-2-(9H-carbazol-9-yl)benzonitrile (OA)

The compound 3-bromo-2-(9H-carbazol-9-yl)benzonitrile was obtained by mixing carbazole (2.0 g, 11.9 mmol) and 3-bromo-2-fluorobenzonitrile (7.1 g, 35.6 mmol) in the presence of Cs_2CO_3 (8.1 g, 59.8 mmol) was taken and added to the flask under argon and stirred at room temperature. The DMF added slowly to the reaction mixture and refluxed at 150 ^{o}C for 15 hours, then the reaction mixture was diluted with water (100 mL). The obtained solid was extracted with DCM and washed with water (3 × 50 mL). The organic layer was collected and dried over Na_2SO_4. The solvent from the reaction mixture was evaporated and further purified from column chromatography with eluents: petroleum ether/ dichloromethane (7/2, v/v) (3.5 g, 84.2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.12 (m, 2H), 8.06 (d, *J* = 1.4 Hz, 1H), 7.86 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.43 (dd, *J* = 15.0, 7.0 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.32, 140.05, 139.42, 138.69, 133.24, 130.50, 130.03, 126.36, 126.00, 124.06, 123.88, 122.08, 121.11, 120.91, 120.75, 120.67, 116.50, 114.90, 109.64, 109.58. MS (EI) m/z: 346.0 [M+].

3.5 Synthesis of 3-bromo-2-(9H-carbazol-9-yl)benzoic acid (OB)

Compound 3-bromo-2-(9H-carbazol-9-yl)benzonitrile (**OA**) (3.0 g, 8.6 mmol) was dissolved in ethanol (50 mL) and followed by the NaOH (1.3 g, 34.5 mmol) dissolving in water (5-8 mL)

and refluxed overnight. The reaction mixture was monitored through TLC and after completion the reaction mixture was acidified and extracted with DCM (3 x 50 mL) and washed well with water thrice. The organic layer was dried over Na_2SO_4, filtered and evaporated, resulting in yellow powder, which was process without purification for the next step (3.0 g, 94.8%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 9.5 Hz, 2H), 8.06 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.98 – 7.90 (m, 2H), 7.51 (t, *J* = 7.9 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.35 – 7.29 (m, 2H), 6.99 (d, *J* = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.74, 140.91, 140.18, 137.48, 136.95, 136.74, 133.38, 130.99, 130.76, 130.72, 130.08, 126.81, 126.39, 125.93, 125.81, 123.64, 123.27, 120.98, 120.77, 120.20, 119.81, 109.69, 109.61, 77.38, 77.27, 77.06, 76.75. MS (EI) m/z: 365.0 [M^+].

3.6 Synthesis of methyl 3-bromo-2-(9H-carbazol-9-yl)benzoate (OC)

Compound **OB** (2.8 g, 7.6 mmol) was dissolved in 30 mL methanol stirred and dissolved completely. After 10 minutes, H_2SO_4 (8 mL) was added drop-wise as a catalyst. The reaction mixture was refluxed and stirred continuously for 12 hrs. The reaction was monitored by TLC and after completion, 100 mL water was added to quench the reaction. Then the residue was dissolved in DCM and washed well with water (3 × 50 mL). The organic layer was dried over Na_2SO_4, filtered and evaporated, resulting in white powder, which was purified from column chromatography using petroleum ether/ dichloromethane (8/2, v/v) as an eluent (2.7 g, 92.8%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.7 Hz, 2H), 8.01 (dd, *J* = 7.9, 2.3 Hz, 2H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.0 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 6.96 (d, *J* = 8.1 Hz, 2H), 3.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.38, 141.33, 141.07, 137.44, 135.95, 133.74, 132.52, 130.70, 130.07, 129.72, 129.63, 127.20, 127.16, 126.36, 126.11, 126.04, 123.63, 123.44, 120.79, 120.58, 120.37, 120.16, 120.05, 109.64, 109.39, 77.38, 77.26, 77.06, 76.74, 52.38, 52.34. MS (EI) m/z: 379.0 [M+].

3.7 Synthesis of 12-bromo-8,8-diphenyl-8H-indolo[3,2,1-de]acridine (OD).

The phenyl magnesium bromide (6.2 g, 34.1 mmol) was taken and added to the flask under argon and stirred at room temperature. The THF solution of methyl 3-bromo-2-(9H-carbazol-9-yl) benzoate (2.6 g, 6.8 mmol) was added slowly to the reaction mixture. Further stirred at 50 ^{o}C for 4 hours, then the reaction mixture was quenched with small amount of NH_4OH in water (5-8 mL) and THF was evaporated. The obtained solid was extracted with DCM and washed with water (3 × 50 mL). The organic layer was collected and dried over Na_2SO_4, resulting brownish solid, which was direct used in the next reaction. The crude mixture was dissolved in 30 mL acetic acid while 8 mL hydrochloric acid (36%) was added drop-wise to the solution mixture. The reaction mixture was refluxed for 4 hours, then cooled to RT, extracted with DCM and water. which was further purified from column chromatography with an eluents: petroleum ether/ dichloromethane (7/3, v/v) (2.5 g, 75%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.90 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.64 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.43 – 7.36 (m, 1H), 7.30 (dt, *J* = 19.2, 7.9 Hz, 3H), 7.23 – 7.16 (m, 7H), 7.04 – 6.93 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.13, 138.76, 137.69, 134.80, 131.08, 130.23, 128.09, 127.84, 127.77, 126.71, 125.99, 125.37, 123.70, 123.64, 122.85, 122.63, 121.25, 120.14, 119.25, 118.26, 110.06, 77.35, 77.23, 77.03, 76.71, 58.73. MS (EI) m/z: 485.0 [M+].

3.8 Synthesis of 12-(dimesitylboranyl)-8,8-diphenyl-8H-indolo[3,2,1-de]acridine (*o*-CZN-B).

Compound **OD** (1.5 g, 3.0 mmol) was dissolved in 30 mL freshly distilled THF and cooled to -78 ^{o}C. After 10 minutes, *n*-butyl lithium 1.6 M (2.8 mL, 4.5 mmol) was added drop-wise. The

mixture was stirred for 1 hour at -78 °C, and then dimesitylborane (2.0 g, 7.7 mmol) in 30 mL THF was dissolved and added slowly to the reaction mixture. After 2 hours, the reaction mixture was slowly allowed to warm up to room temperature and stirred continued for 12 hrs. The reaction was monitored by TLC and after completion, 5 mL water was added to quench the reaction. The solvent was evaporated and the residue was dissolved in DCM (100 mL) and washed well with water (3 × 50 mL). The organic layer was dried over Na_2SO_4, filtered and evaporated, resulting in greenish powder, which was purified from column chromatography using petroleum ether/ dichloromethane (8/2, v/v) as eluent (0.8 g, 40.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.52 (dd, *J* = 15.7, 7.5 Hz, 3H), 7.27 (d, *J* = 7.7 Hz, 3H), 7.15 (dd, *J* = 18.5, 7.8 Hz, 6H), 7.08 – 7.00 (m, 4H), 6.94 (dd, *J* = 13.3, 7.3 Hz, 4H), 2.96 – 1.97 (m, 12H), 1.70 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.67, 141.77, 139.31, 138.22, 136.63, 134.92, 127.77, 127.17, 125.12, 124.98, 124.84, 122.94, 122.53, 122.07, 120.47, 119.97, 117.43, 112.18, 77.35, 77.24, 77.03, 76.72, 58.54. MALDI-TOF (m/z) calculated for $C_{49}H_{42}BN$ [M^+]: 655.69, found: 655.68.

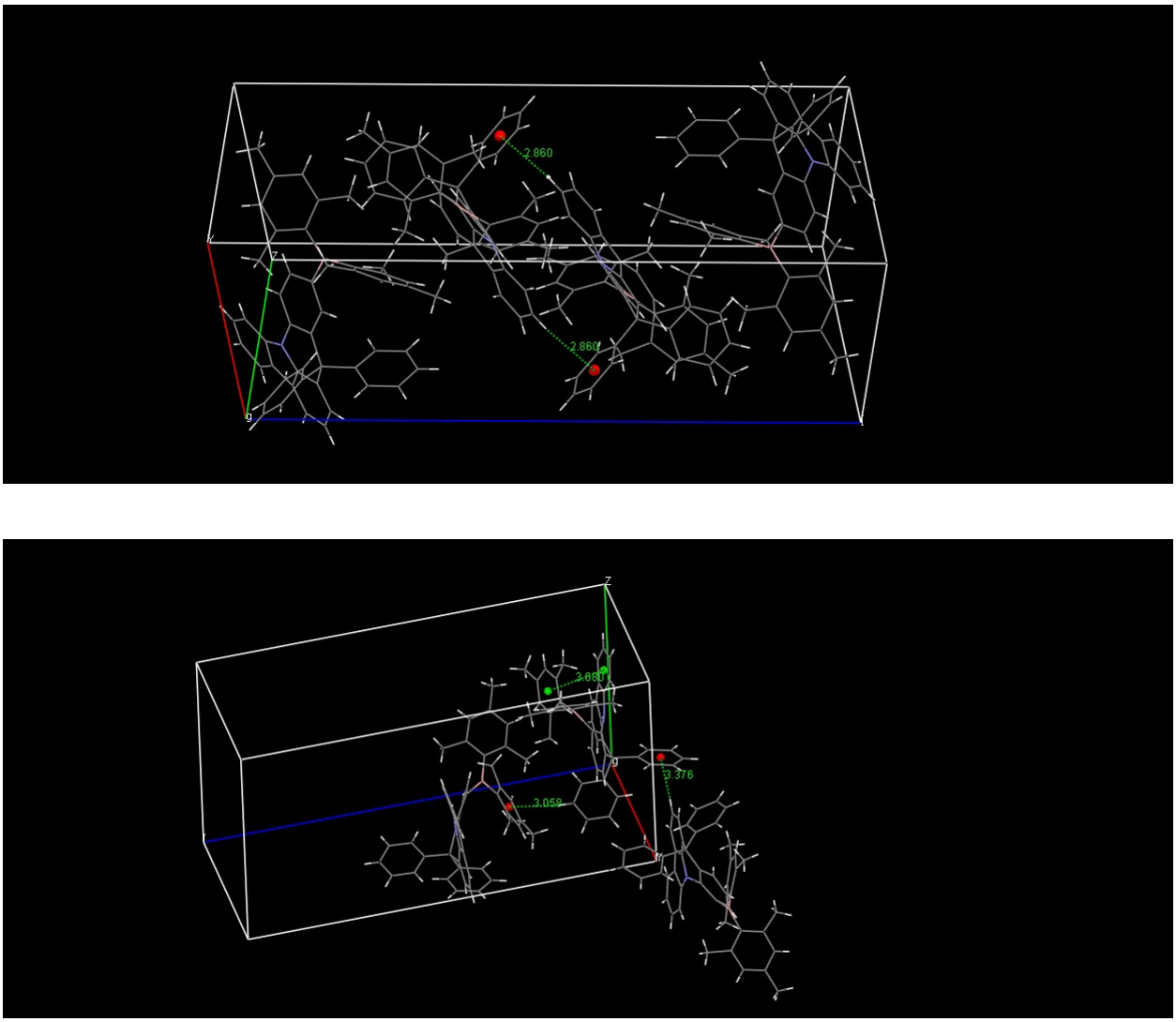


Figure S1. Packing diagrams for ***p*-CZN-B (top)** and ***o*-CZN-B** (bottom), in which molecules connected through C-H---π bonding and π---π stacking.

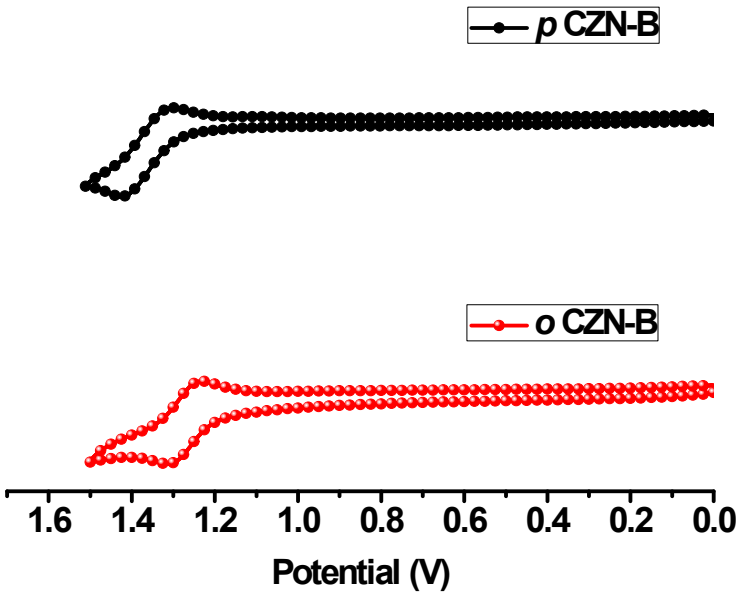


Figure S2. Cyclic Voltammetry curves of ***p*-CZN-B** and ***o*-CZN-B** in **DCM** solution at room temperature.

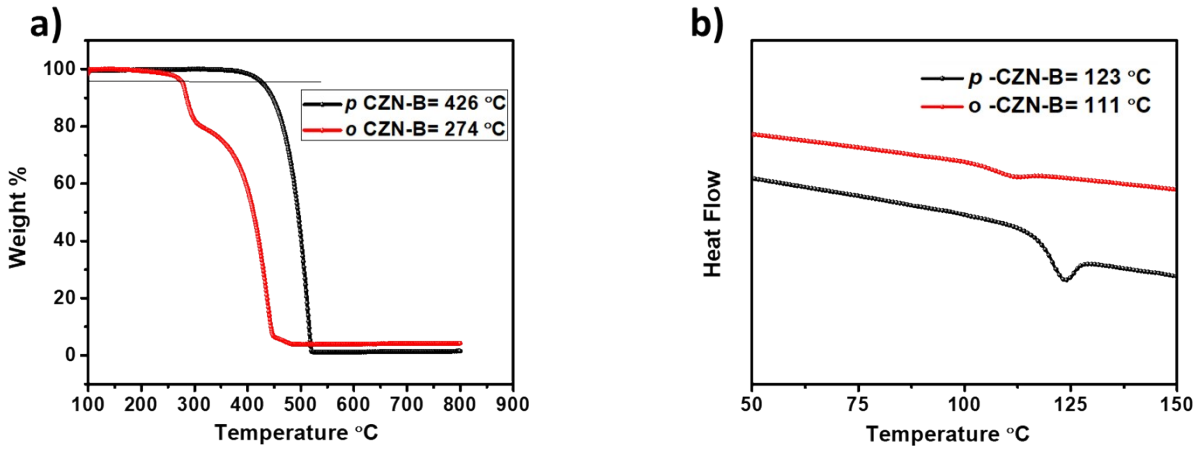


Figure S3. a) The TGA and **b)** DSC plots of ***p*-CZN-B and *o*-CZN-B.**

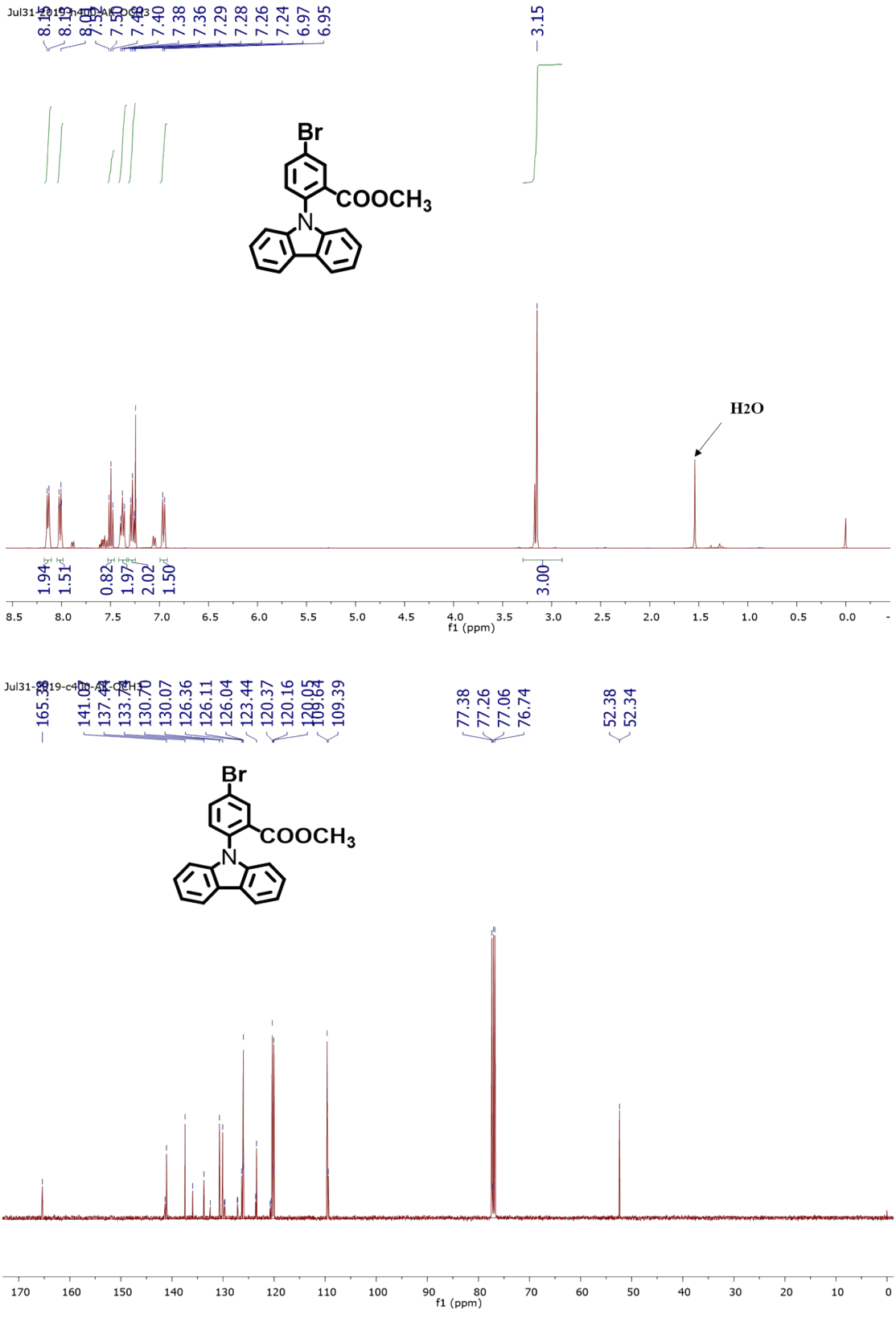


Figure S4. ^{1}H NMR and ^{13}C NMR spectra of compound (**PA**) in deuterated $CDCl_3$

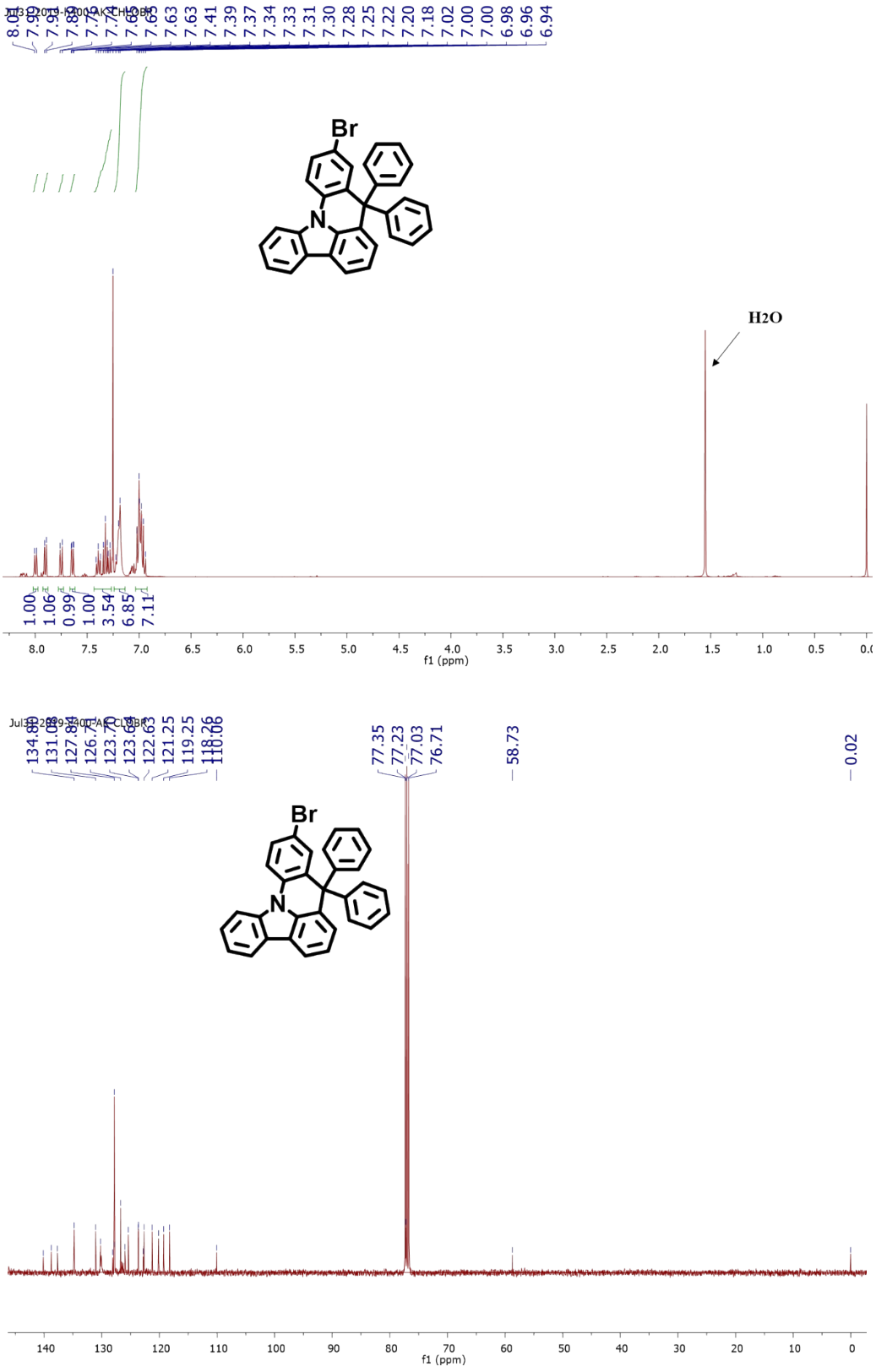


Figure S5. ^{1}H NMR and ^{13}C NMR spectra of compound (**PB**) in deuterated $CDCl_3$

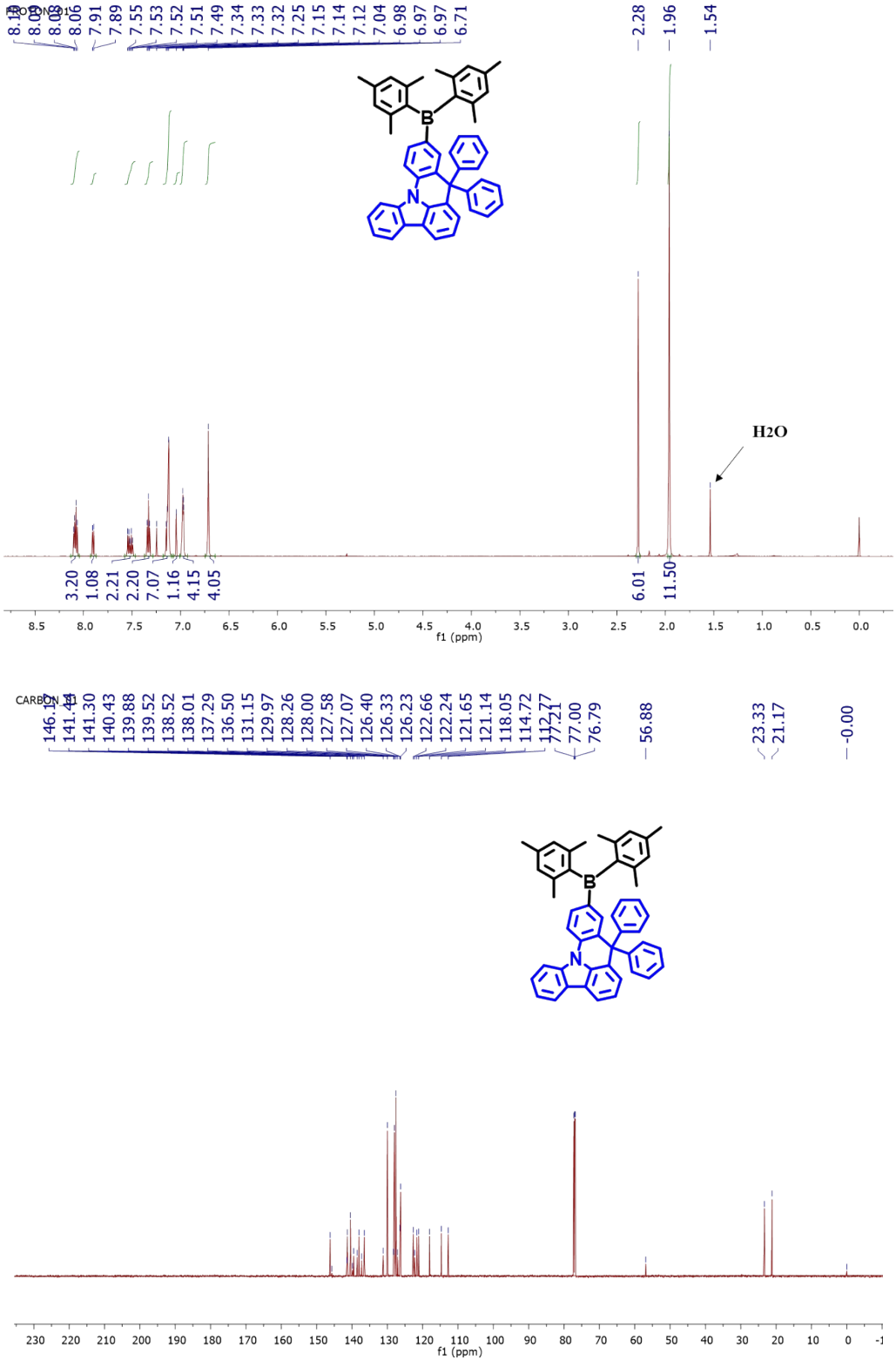


Figure S6. ^{1}H NMR and ^{13}C NMR spectra of compound (***p*-CZN-B**) in deuterated $CDCl_3$

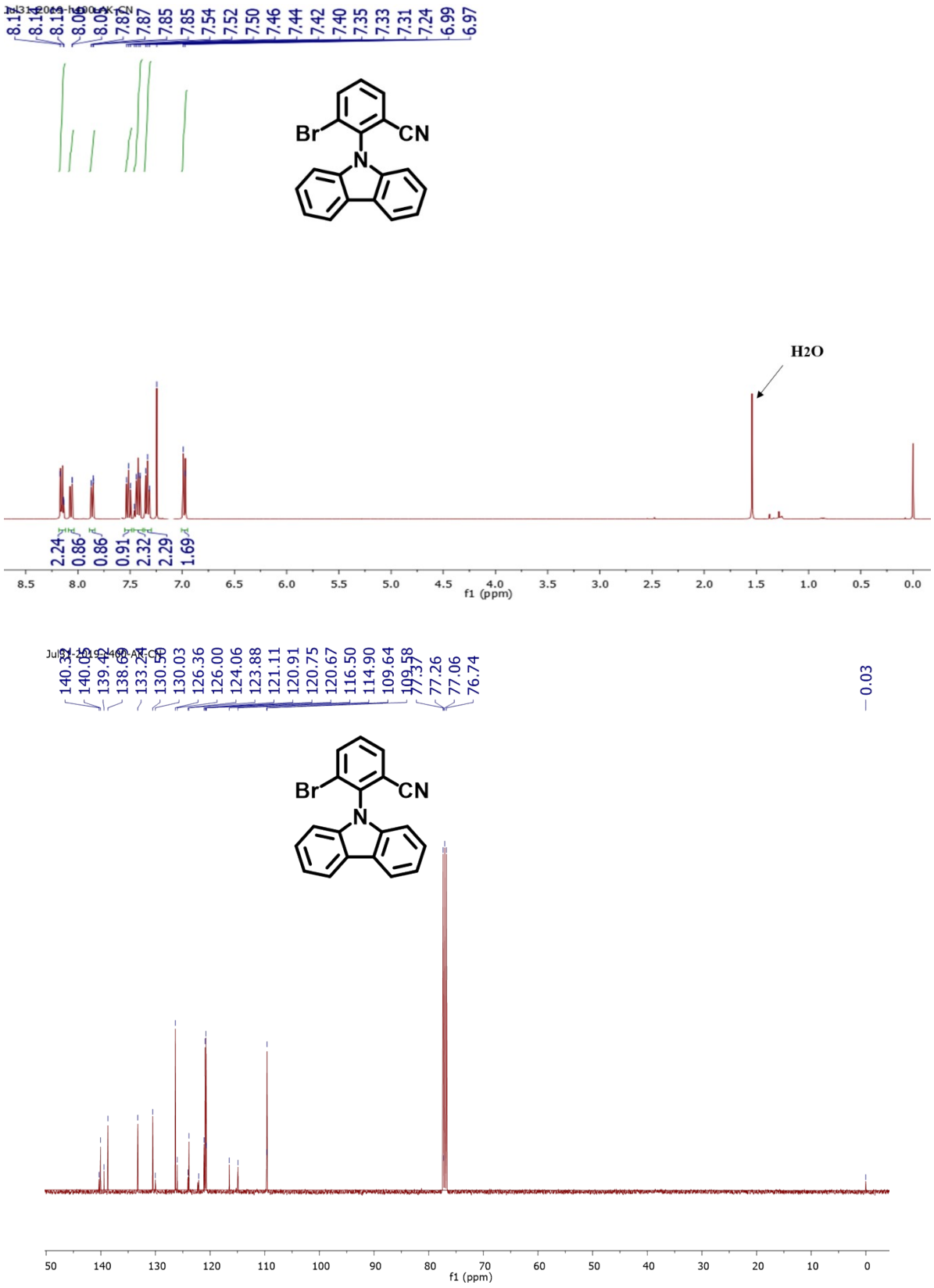


Figure S7. ^{1}H NMR and ^{13}C NMR spectra of compound (**OA**) in deuterated $CDCl_3$

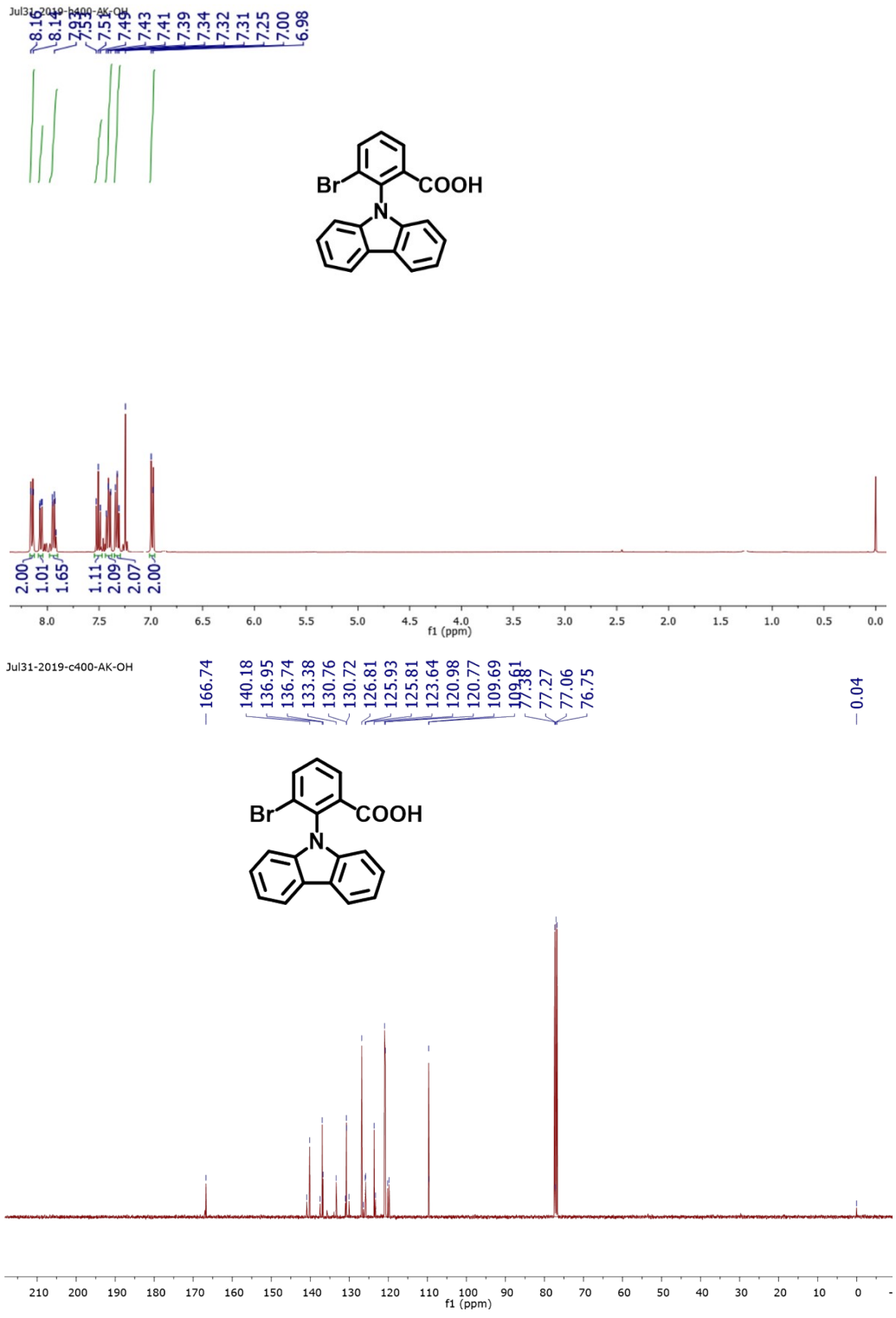


Figure S8. ^{1}H NMR and ^{13}C NMR spectra of compound (**OB**) in deuterated $CDCl_3$

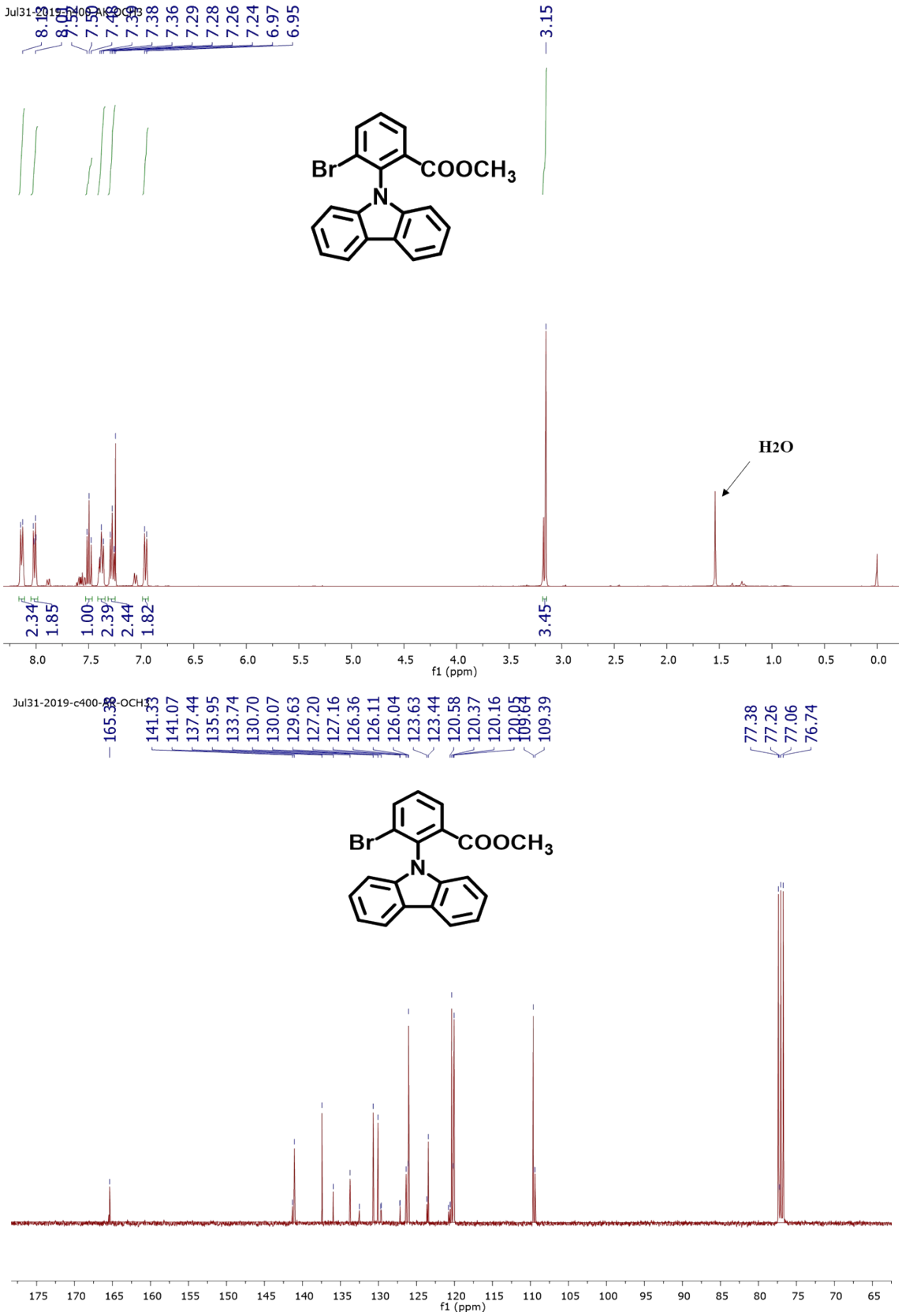


Figure S9. ^{1}H NMR and ^{13}C NMR spectra of compound (**OC**) in deuterated $CDCl_3$

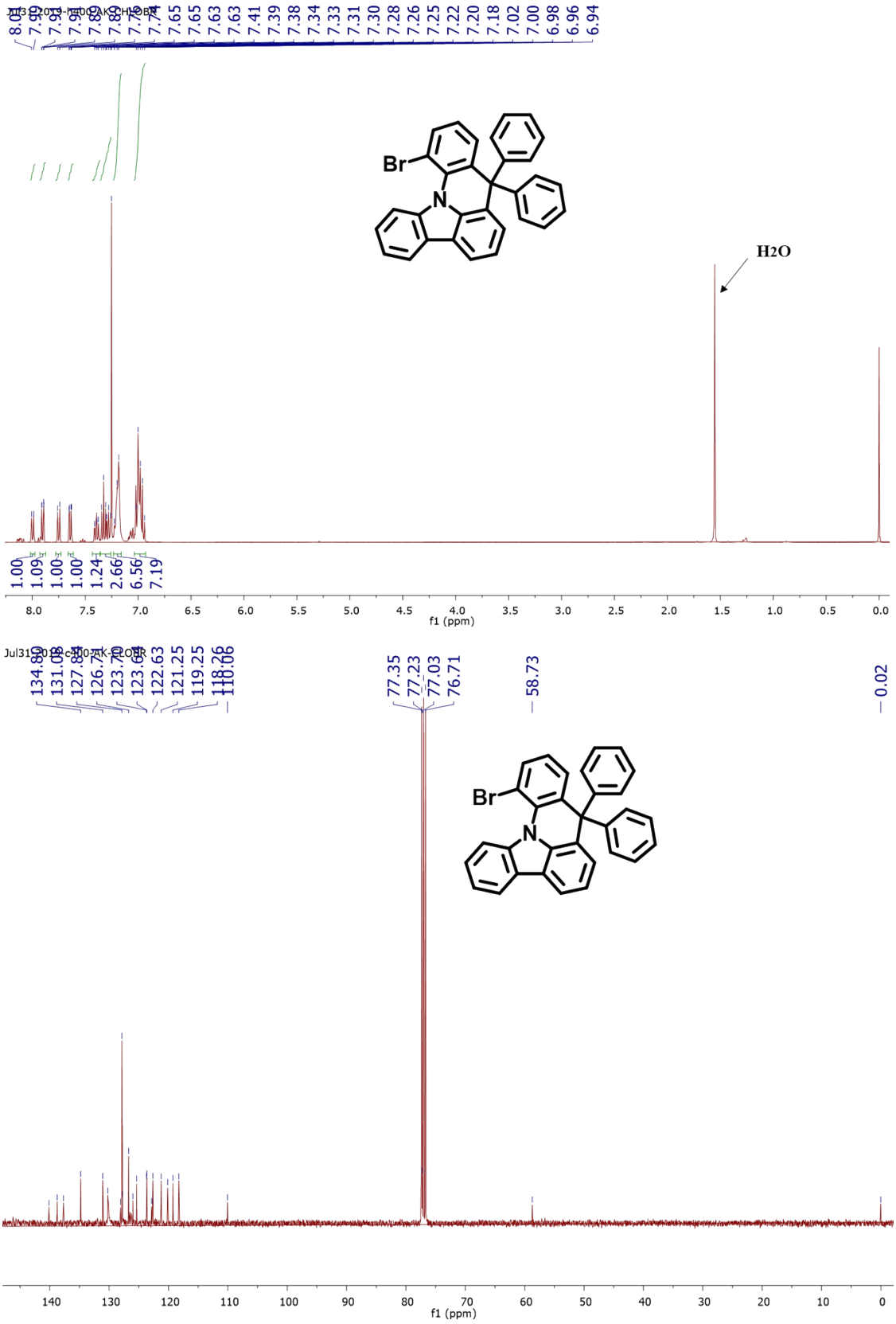


Figure S10. ^{1}H NMR and ^{13}C NMR spectra of compound (**OD**) in deuterated $CDCl_3$

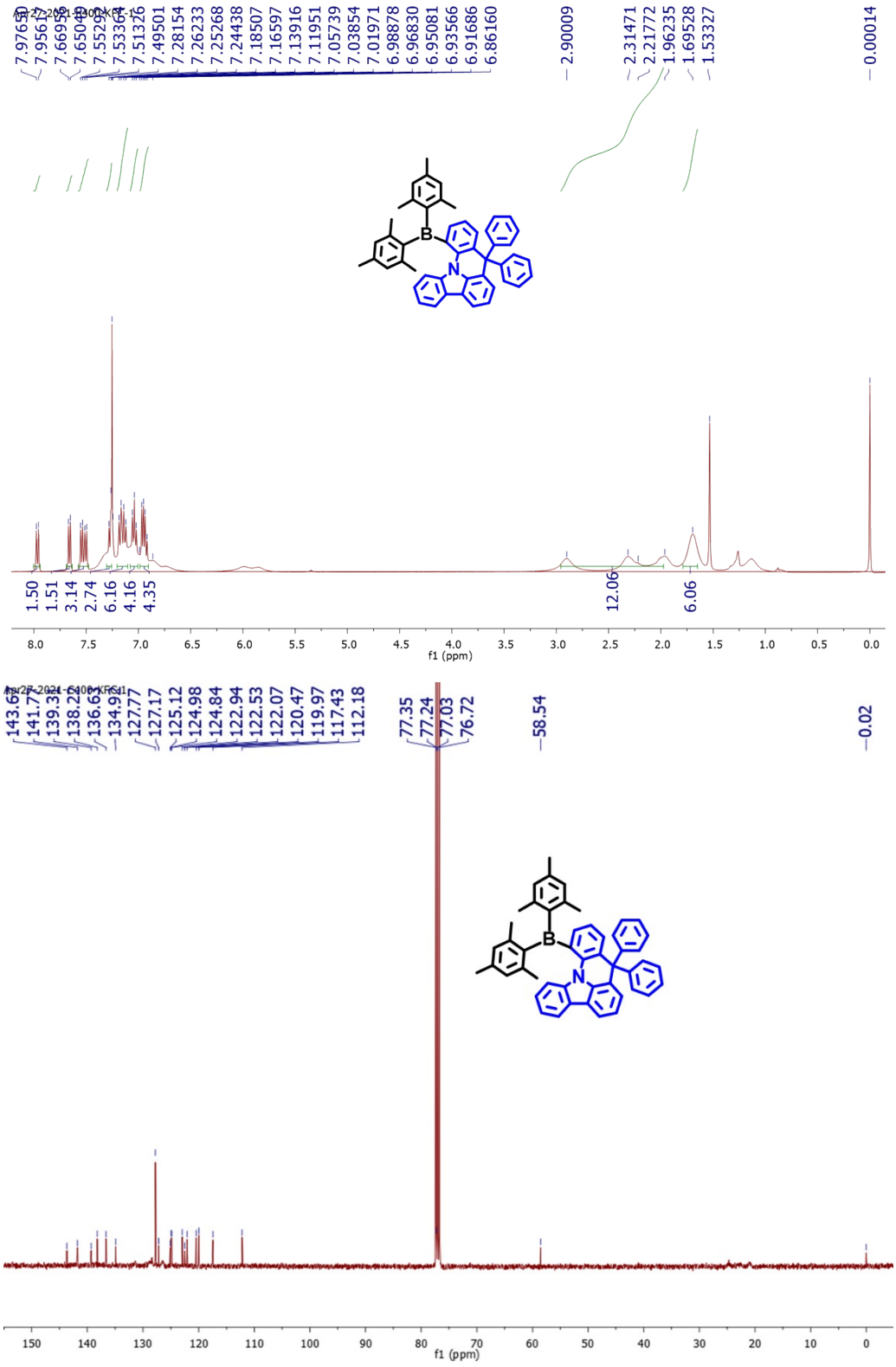


Figure S11. ^{1}H NMR and ^{13}C NMR spectra of compound (***o*-CZN-B**) in deuterated $CDCl_3$

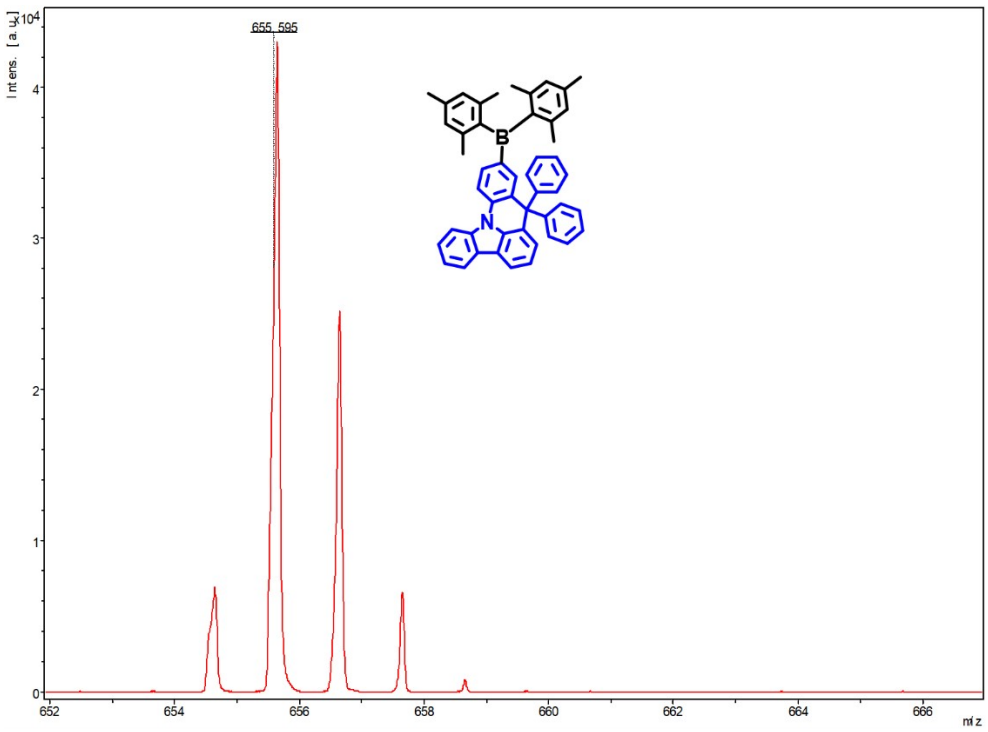


Figure S12. TOF spectrum for ***p*-CZN-B**

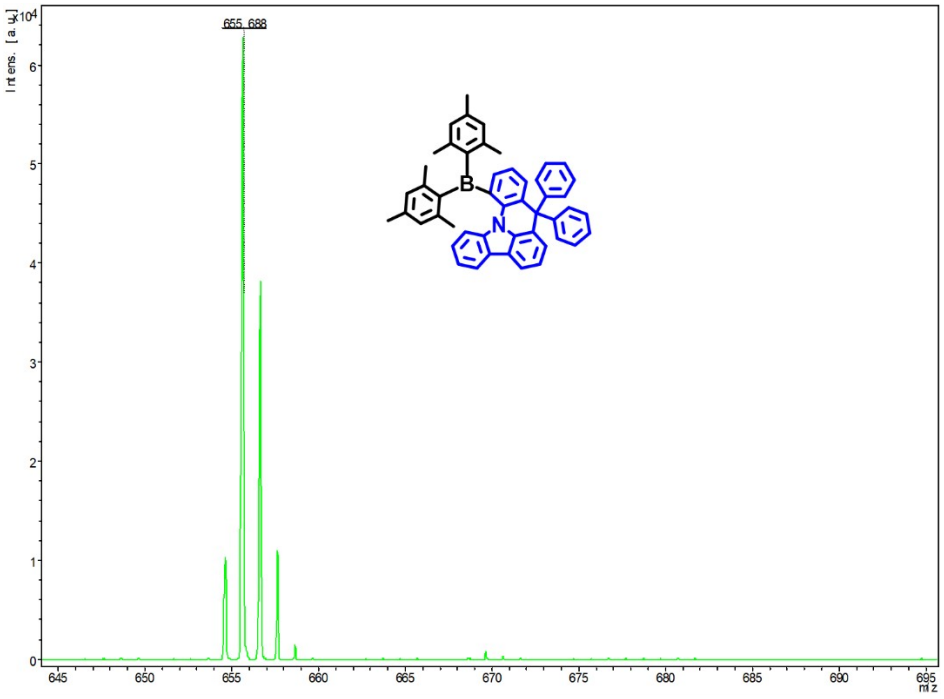


Figure S13. TOF spectrum for ***o*-CZN-B**

Table S1. Crystal data and structure refinement data for of ***p*-CZN-B** and ***o*-CZN-B**

***p*-CZN-B**		***o*-CZN-B**	
CCDC	**1994992**	**CCDC**	**1994991**
Empirical formula	$C_{49}H_{42}BN$	Empirical formula	$C_{49}H_{42}BN$
Formula weight	655.64	Formula weight	655.71
Temperature/K	100.0	Temperature/K	100.0
Crystal system	monoclinic	Crystal system	orthorhombic
Space group	$P2_1/c$	Space group	$P2_12_12_1$
a/Å	8.9930(4)	a/Å	10.3226(4)
b/Å	14.8759(7)	b/Å	13.8391(5)
c/Å	27.3786(15)	c/Å	25.9787(9)
α/°	90	α/°	90
β/°	98.882(2)	β/°	90
γ/°	90	γ/°	90
Volume/Å^3	3618.8(3)	Volume/Å^3	3711.2(2)
Z	4	Z	4
ρ_{calc}g/cm^3	1.203	ρ_{calc}g/cm^3	1.1734
μ/mm^{-1}	0.068	μ/mm^{-1}	0.066
F(000)	1392.0	F(000)	1392.5
Crystal size/mm^3	0.15 × 0.12 × 0.08	Crystal size/mm^3	0.35 × 0.25 × 0.25
Radiation	MoKα (λ = 0.71073)	Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.584 to 52.858	2Θ range for data collection/°	4.92 to 53
Index ranges	$-10 \le h \le 11$, $-18 \le k \le 18$, $-34 \le l \le 32$	Index ranges	$-13 \le h \le 13$, $-18 \le k \le 18$, $-33 \le l \le 33$
Reflections collected	36945	Reflections collected	196235
Independent reflections	7334 [R_{int} = 0.0847, R_{sigma} = 0.0669]	Independent reflections	7693 [R_{int} = 0.2018, R_{sigma} = 0.0861]
Data/restraints/parameters	7334/0/466	Data/restraints/parameters	7693/0/466
Goodness-of-fit on F^2	1.026	Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0560, wR_2 = 0.1208	Final R indexes [I>=2σ (I)]	R_1 = 0.0571, wR_2 = 0.1094
Final R indexes [all data]	R_1 = 0.0995, wR_2 = 0.1449	Final R indexes [all data]	R_1 = 0.1265, wR_2 = 0.1321
Largest diff. peak/hole / e Å^{-3}	0.24/-0.32	Largest diff. peak/hole / e Å^{-3}	0.32/-0.32
		Flack parameter	0(6)

Table S2. Summarized photophysical data and rate constants of ***o*-CZN-B**

Compound	τ_F (ns)	τ_{TADF} (μs)	ϕ_{PLQY} (%)	ϕ_F (%)	ϕ_{TADF} (%)	k_F $10^7 s^{-1}$	k_{ISC} $10^6 s^{-1}$	k_{TADF} $10^4 s^{-1}$	k_{RISC} $10^4 s^{-1}$	k_{nr} $10^5 s^{-1}$
o-CZN-B	31.99	2.12	94	93.83	0.17	3.13	1.93	1.33	1.42	4.58

Table S3. OLED and ASE device parameters comparison of of ***p*-CZN-B** and ***o*-CZN-B** with reported skeleton

Compounds	Doping Ratios (%)	EQE_{max} (%)	Host	*FWHM* (nm) device	*FWHM* (nm) ASE	$EL\lambda_{max}$ (nm)	$ASE\ \lambda_{max}$ (nm)	PLQ Y (%)	Threshold ($\mu J/cm^2$)	references
PXZN-B	10	12.7	mCP	48	8.1	468	470	93	0.82	[1]
DMACN-B	5	10.0	mCP	44	11.3	444	436	90	2.75	[1]
DABNA1	6	13.5	mCBP	28	/	459	476	/	2.8	[2]
DABNA2	6	20.2	mCBP	28	80	467	494	83	1.6	[3]
TPA-BCm	6	9.7	CBP	/	17	721	747	70	6.67	[4]
DTPA-BC	2	5.1	CBP	/	16.4	758	801	45	7.5	[5]
***p*-CZN-B**	10	2.6	mCP	24	4.7	416	412	45	5.79	This work
***o*-CZN-B**	20	23.3	mCP	51	/	484	/	94	/	This work

References

1. A. Khan, X. Tang, C. Zhong, Q. Wang, S. Yang, F. Kong, S. Yuan, A. S. D. Sandanayaka, C. Adachi, Z. Jiang and L. Liao, *Adv Funct Mater*, DOI:10.1002/adfm.202009488.
2. T. Hatakeyama, K. Shiren, K. Nakajima, S. Nomura, S. Nakatsuka, K. Kinoshita, J. Ni, Y. Ono and T. Ikuta, *Advanced Materials*, 2016, **28**, 2777–2781.
3. H. Nakanotani, T. Furukawa, T. Hosokai, T. Hatakeyama and C. Adachi, Adv Opt Mater, 2017, 5, 1–5.
4. D. H. Kim, A. D'Aléo, X. K. Chen, A. D. S. Sandanayaka, D. Yao, L. Zhao, T. Komino, E. Zaborova, G. Canard, Y. Tsuchiya, E. Choi, J. W. Wu, F. Fages, J. L. Brédas, J. C. Ribierre and C. Adachi, *Nat Photonics*, 2018, **12**, 98–104.
5. H. Ye, D. H. Kim, X. Chen, A. S. D. Sandanayaka, J. U. Kim, E. Zaborova, G. Canard, Y. Tsuchiya, E. Y. Choi and J. W. Wu, DOI:10.1021/acs.chemmater.8b02247.