

## **Co-facial through space charge transfer enables fast reverse intersystem crossing in sky-blue TADF emitters.**

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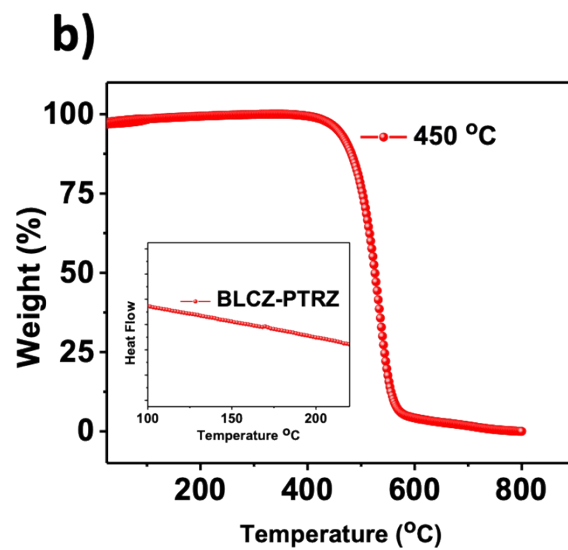
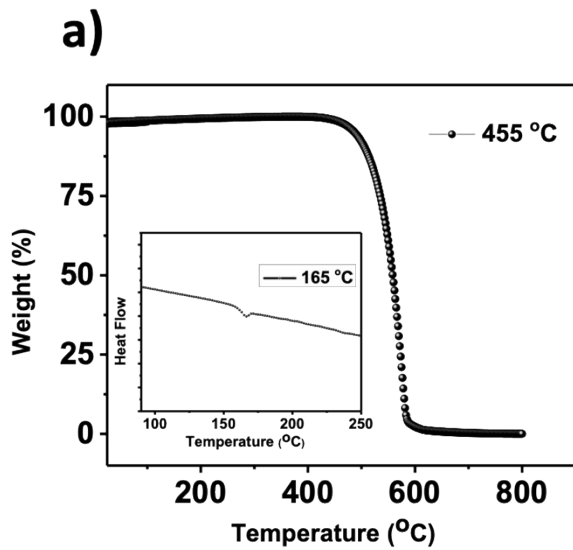
## 1. Chemicals and instruments

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.  $^1\text{H}$  NMR and  $^{13}\text{C}$  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  $10\text{ }^\circ\text{C}/\text{min}$  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  $10\text{ }^\circ\text{C}/\text{min}$  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  $\text{CH}_2\text{Cl}_2$ , and the supporting electrolyte was  $0.1\text{ M} [\text{Bu}_4\text{N}]\text{PF}_6$ . Ferrocene was added as a calibrant after each set of measurements, and all potentials reported were quoted with reference to the ferrocene-ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) couple at a scan rate of  $100\text{ mV}/\text{s}$ . 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.

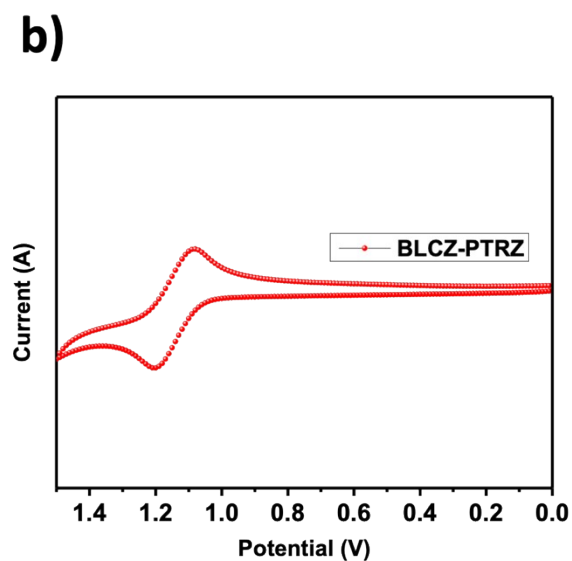
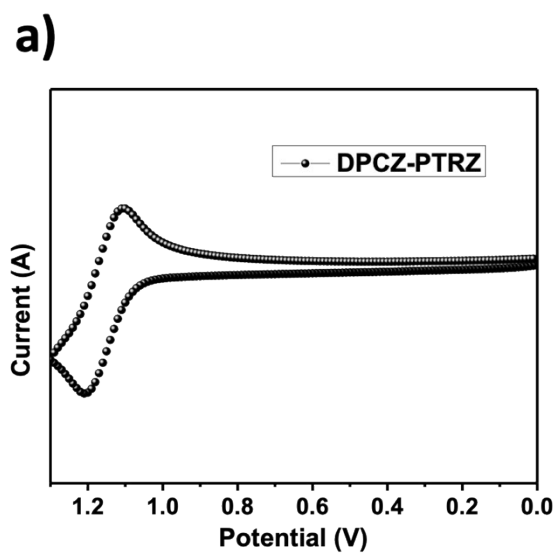
## 2. OLED fabrication and measurements

All the material except two novel synthesized emitters were acquired from commercial source without further purification. OLEDs were all fabricated under a base vacuum of  $4 \times 10^{-6}$  Torr and on ITO glass substrates (160 nm, 15  $\Omega/\text{sq}$ ). 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. Transient photoluminescence (PL) delay curves were obtained using FluoTime 300 (PicoQuant GmbH) with a Picosecond Pulsed UV-LASER (LASTER375) as the excitation source with a wavelength of 375 nm.



**Figure S1** The TGA, DSC (inset figure) plots of a) **DPCZ-PTRZ** and b) **BLCZ-PTRZ**



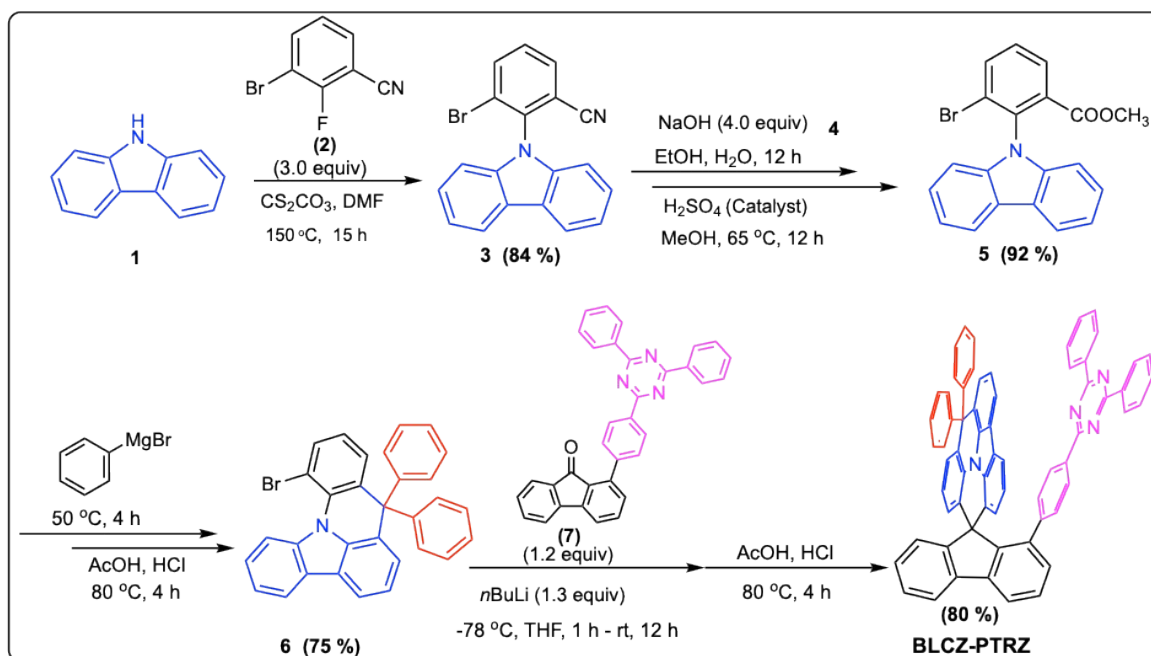
**Figure S2** Cyclic Voltammetry curves of a) **BLCZ-PTRZ** and b) **DPCZ-PTRZ** in DCM solution at room temperature.

**Table S1.** Comparison with representative blue and sky-blue TSCT/TADF OLEDs reporting EL peak, CIE coordinates, EQEmax, and kRISC

Emitter	$\lambda$ EL (nm)	CIE (x, y)	EQEmax (%)	kRISC (s <sup>-1</sup> )	Reference
DPCZ-PTRZ	476	(0.15, 0.23)	18.4	$2.13 \times 10^7$	This work
BLCZ-PTRZ	470	(0.16, 0.24)	5.95	$5.3 \times 10^6$	This work
CzTPT-PA	476 / 481	(0.16, 0.27) /(0.17, 0.33)	24.0 / 25.0	$2.50 \times 10^5$	Wang et al., <i>ACS Appl. Mater. Interfaces</i> , 2025
CzTPT-CIA	472 / 474	(0.16, 0.24) /(0.16, 0.29)	17.9 / 18.9	$2.15 \times 10^5$	Wang et al., <i>ACS Appl. Mater. Interfaces</i> , 2025
CzTPT-IA	460 / 468	(0.15, 0.09) /(0.15, 0.18)	9.9 / 10.8	$1.02 \times 10^5$	Wang et al., <i>ACS Appl. Mater. Interfaces</i> , 2025
Emitter 1 (IPXZ-TRZ)	492	(0.29, 0.43)	24.3	$1.0 \times 10^6$	Song et al., <i>Chem. Eng. J.</i> , 2025
Emitter 2 (IPXZ-TRZ)	494	(0.29, 0.43)	22.2	$6.8 \times 10^5$	Song et al., <i>Chem. Eng. J.</i> , 2025
Emitter 3 (IPXZ-BO)	480	(0.15, 0.28)	23.8	$8.3 \times 10^4$	Song et al., <i>Chem. Eng. J.</i> , 2025
dCz-Xo-TRZ	477	(0.16, 0.29)	27.8	---	Huang et al., <i>Angew. Chem. Int. Ed.</i> , 2022
mCz-Xo-TRZ	464	(0.15, 0.20)	21.0	---	Huang et al., <i>Angew. Chem. Int. Ed.</i> , 2022
TSF-dCz	471	(0.13, 0.15)	34.7	---	Huang et al., <i>Angew. Chem. Int. Ed.</i> , 2022
TSF-mCz	471	(0.12, 0.14)	27.2	---	Huang et al., <i>Angew. Chem. Int. Ed.</i> , 2022
TRZ-STFMe	470	---	29.6	$5.23 \times 10^5$	Chen et al., <i>Chem. Eng. J.</i> , 2024
2tDMG	480	---	30.8	---	Peng et al., <i>Adv. Mater.</i> , 2020
8PhDM-B	---	---	33.1	---	Liu et al., <i>Adv. Mater.</i> , 2024
DCT-1	474	---	18.9	$6.19 \times 10^5$	Li et al., <i>Angew. Chem. Int. Ed.</i> , 2025, 64, e202506654
DCT-2	498	---	23.9	$1.05 \times 10^6$	Li et al., <i>Angew. Chem. Int. Ed.</i> , 2025, 64, e202506654
Emitter 1	~500	---	27.5	$1.3 \times 10^6$	Song et al., <i>Adv. Funct. Mater.</i> , 2025, 35, 2411957
Emitter 2	~500	---	27.5	$7.7 \times 10^5$	Song et al., <i>Adv. Funct. Mater.</i> , 2025, 35, 2411957

**Table S2.** Single-crystal X-ray crystal structure parameters for **DPCZ-PTRZ** and **BLCZ-PTRZ**

<b>DPCZ-PTRZ</b>		<b>BLCZ-PTRZ</b>	
<b>CCDC</b>	<b>1997554</b>	<b>CCDC</b>	<b>1997555</b>
Identification code	123_0m	Identification code	mo_0110_0m
Empirical formula	C <sub>64</sub> H <sub>40</sub> N <sub>4</sub>	Empirical formula	C <sub>65</sub> H <sub>40</sub> N <sub>4</sub>
Formula weight	864.77	Formula weight	877.01
Temperature/K	180.0	Temperature/K	170
Crystal system	monoclinic	Crystal system	triclinic
Space group	P2 <sub>1</sub> /c	Space group	P-1
a/Å	11.8659(7)	a/Å	13.1486(14)
b/Å	39.291(2)	b/Å	13.4543(13)
c/Å	21.8425(12)	c/Å	14.6650(12)
α/°	90	α/°	109.007(3)
β/°	103.985(2)	β/°	101.027(3)
γ/°	90	γ/°	103.177(4)
Volume/Å <sup>3</sup>	9881.6(10)	Volume/Å <sup>3</sup>	2286.8(4)
Z	4	Z	2
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.334	ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.274
μ/mm <sup>-1</sup>	0.234	μ/mm <sup>-1</sup>	0.074
F(000)	4120.0	F(000)	916.0
Crystal size/mm <sup>3</sup>	0.15 × 0.12 × 0.08	Crystal size/mm <sup>3</sup>	0.15 × 0.11 × 0.05
Radiation	MoKα (λ = 0.71073)	Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.98 to 50.052	2θ range for data collection/°	3.818 to 52.574
Index ranges	-14 ≤ h ≤ 14, -46 ≤ k ≤ 45, -25 ≤ l ≤ 25	Index ranges	-16 ≤ h ≤ 16, -16 ≤ k ≤ 18, -18 ≤ l ≤ 18
Reflections collected	64456	Reflections collected	25548
Independent reflections	17187 [R <sub>int</sub> = 0.1055, R <sub>sigma</sub> = 0.1045]	Independent reflections	9153 [R <sub>int</sub> = 0.0922, R <sub>sigma</sub> = 0.1080]
Data/restraints/parameters	17187/15/1306	Data/restraints/parameters	9153/0/622
Goodness-of-fit on F <sup>2</sup>	1.033	Goodness-of-fit on F <sup>2</sup>	0.997
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.1040, wR <sub>2</sub> = 0.2761	Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0662, wR <sub>2</sub> = 0.1800
Final R indexes [all data]	R <sub>1</sub> = 0.1931, wR <sub>2</sub> = 0.3487	Final R indexes [all data]	R <sub>1</sub> = 0.1211, wR <sub>2</sub> = 0.1800
Largest diff. peak/hole / e Å <sup>-3</sup>	2.87/-1.17	Largest diff. peak/hole / e Å <sup>-3</sup>	0.28/-0.30



**Scheme S1.** The synthetic routes for **BLCZ-PTRZ**.

## Experimental Section:

The compound **1**, **2**, **8**, **9** and the **11** purchased directly, while the compound **7** was synthesized according to the previously reported literature.

### 1. Synthesis of 3-bromo-2-(9H-carbazol-9-yl)benzonitrile (**3**)

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  $\text{Cs}_2\text{CO}_3$  (19.2 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 °C for 15 hrs, then the reaction mixture was diluted with water (100 mL). The obtained solid was extracted with DCM and washed with water ( $3 \times 50$  mL). The organic layer was collected and dried over  $\text{Na}_2\text{SO}_4$ . 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, 10.0 mmol 84 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  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)  $m/z$ : 346.07 [ $\text{M}^+$ ]. Calcd for  $\text{C}_{19}\text{H}_{11}\text{BrN}_2$ : 346.01

## 2. Synthesis of 3-bromo-2-(9H-carbazol-9-yl)benzoic acid (4)

Compound 3-bromo-2-(9H-carbazol-9-yl)benzotrile (3) (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  $\text{Na}_2\text{SO}_4$ , filtered and evaporated, resulting in yellow powder, which was process without purification for the next step (3.0 g, 8.1 mmol 94 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  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)  $m/z$ : 365.05 [ $\text{M}^+$ ]. Calcd for  $\text{C}_{19}\text{H}_{12}\text{BrNO}_2$ : 365.00

## 3. Synthesis of methyl 3-bromo-2-(9H-carbazol-9-yl)benzoate (5)

Compound 4 (2.8 g, 7.6 mmol) was dissolved in 30 mL methanol stirred and dissolved completely. After 10 minutes,  $\text{H}_2\text{SO}_4$  (8 mL) was added dropwise 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 ( $3 \times 50$  mL). The organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtered and evaporated, resulting in white powder, which was purified from column chromatography using petroleum ether/ dichloromethane (8/2, v/v) as eluent (2.7 g, 7.1 mmol 92 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  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)  $m/z$ : 379.05  $[\text{M}^+]$ . Calcd for  $\text{C}_{20}\text{H}_{14}\text{BrNO}_2$ : 379.02.

#### 4. Synthesis of 12-bromo-8,8-diphenyl-8H-indolo[3,2,1-de]acridine (6).

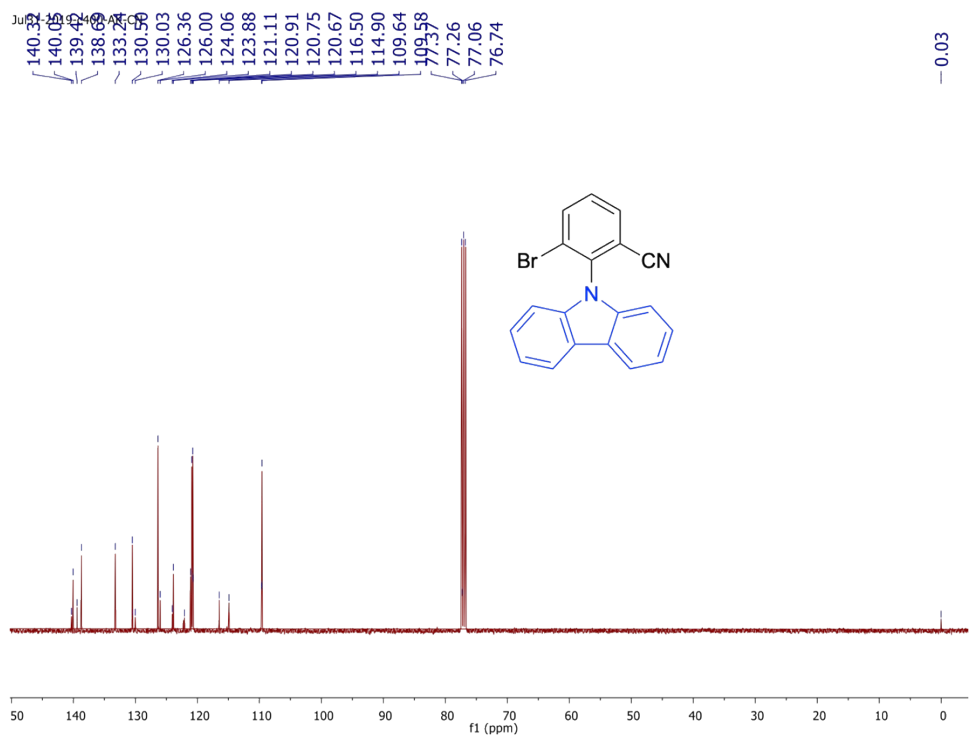
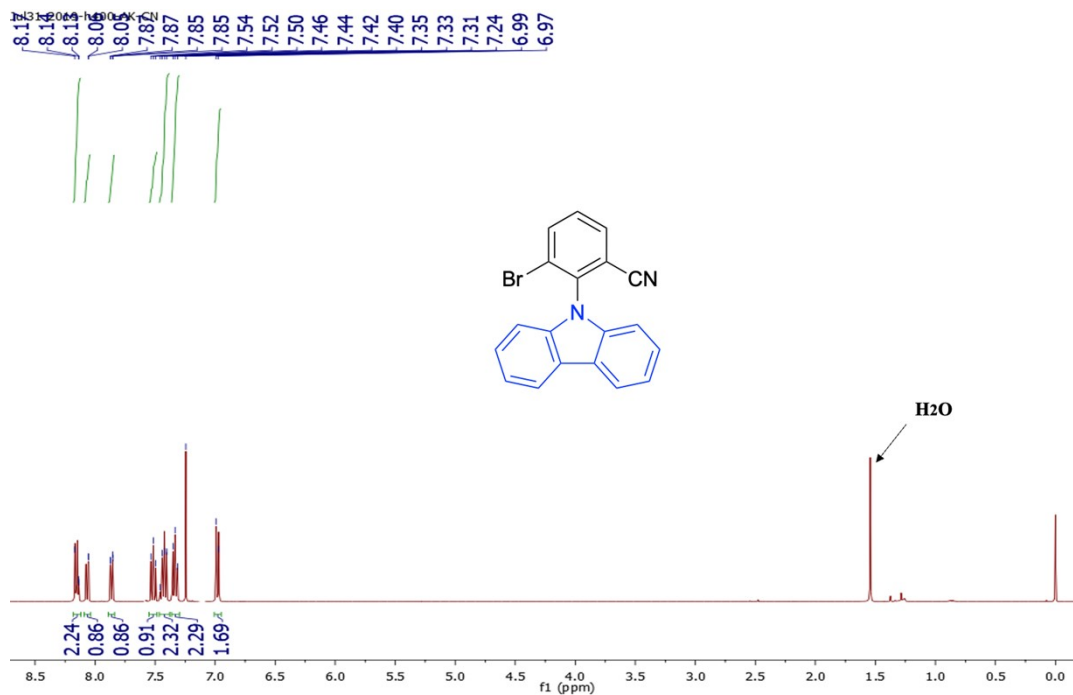
The phenyl magnesium bromide (6.2 g, 34.1 mmol) was taken and added to the flask under argon and stirred at room temperature. The THF solution of methyl 3-bromo-2-(9H-carbazol-9-yl) benzoate (2.6 g, 6.8 mmol) was added slowly to the reaction mixture. Further stirred at 50 °C for 4 hrs, then the reaction mixture was quenched with small amount of  $\text{NH}_4\text{OH}$  in water (5-8 mL) and THF was evaporated. The obtained solid was extracted with DCM and washed with water ( $3 \times 50$  mL). The organic layer was collected and dried over  $\text{Na}_2\text{SO}_4$ , 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 dropwise 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 eluents: petroleum ether/ dichloromethane (7/3, v/v) (2.5 g, 5.1 mmol 75 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  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)  $m/z$ : 485.13 [M+]. Calcd for  $\text{C}_{31}\text{H}_{20}\text{BrN}$ : 485.07

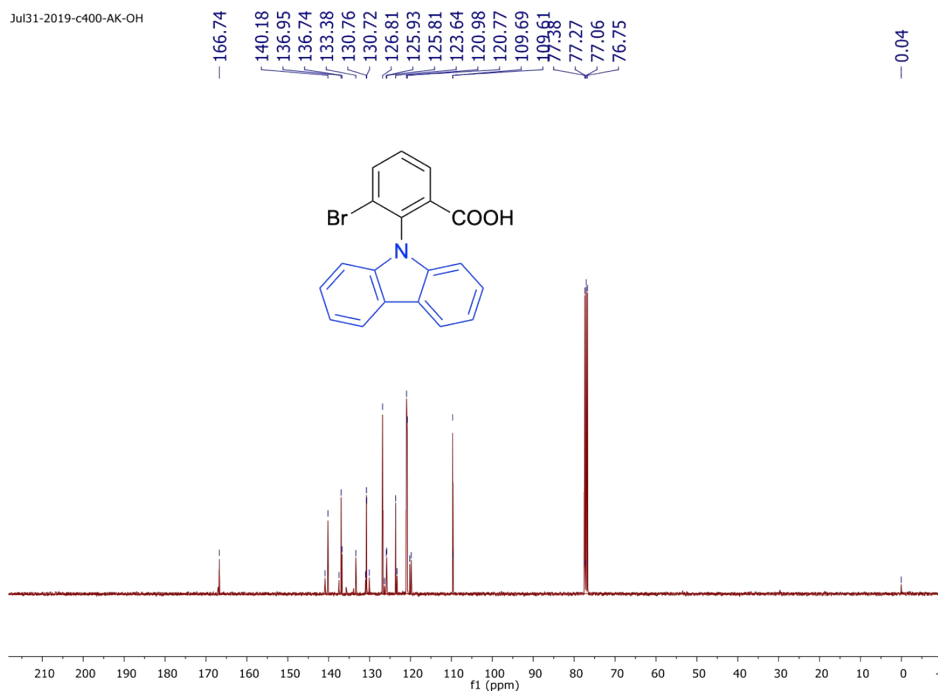
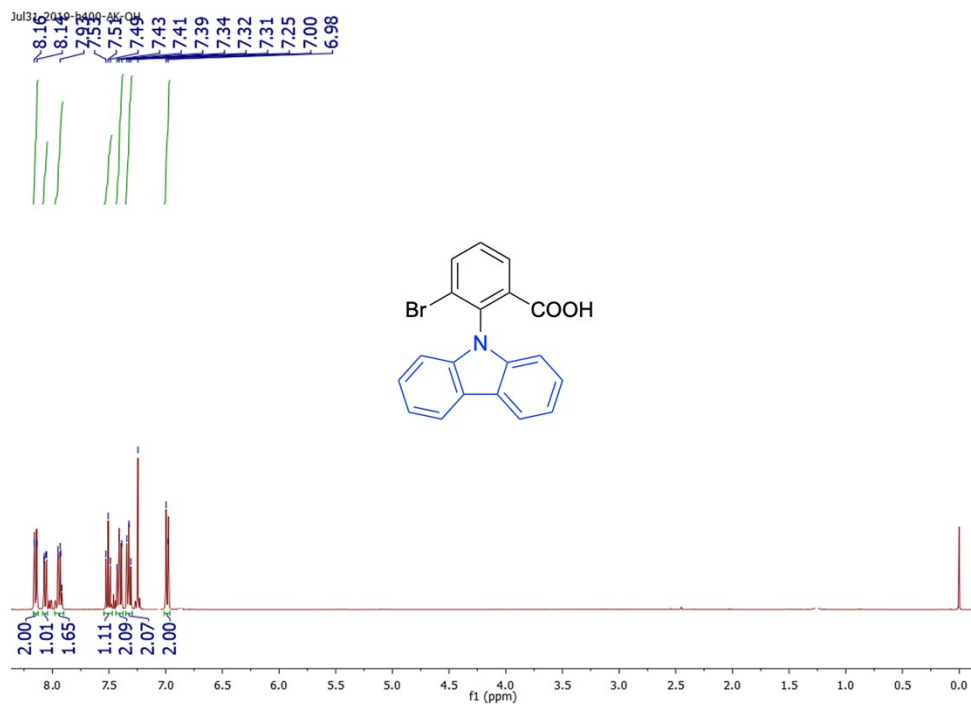
**5. Synthesis of (S)-1'-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-11,11-diphenyl-11H-spiro[benzo[8,1]indolizino[2,3,4,5,6-defg]acridine-7,9'-fluorene] (BLCZ-PTRZ).**

Compound 12-bromo-8,8-diphenyl-8H-indolo[3,2,1-de]acridine (0.7 g, 1.44 mmol) was dissolved in 30 mL freshly distilled THF and cooled to  $-78$  °C. After 10 minutes, *n*-butyl lithium (1.2 mL, 1.72 mmol) was added dropwise. The mixture was stirred for 1 hour at  $-78$  °C, and then 1-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9H-fluoren-9-one (0.77 g, 1.6 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 ( $3 \times 50$  mL). The organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtered and evaporated, resulting in yellow powder, which was used directly in the next step. The crude mixture was dissolved in 30 mL acetic acid while 8 mL hydrochloric acid (36%) was added dropwise 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 eluents: petroleum ether/ dichloromethane (7/4, v/v) (1.0 g, 1.2 mmol 80 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66 (d,  $J = 7.8$  Hz, 4H), 7.93 (t,  $J = 8.5$  Hz, 2H), 7.73 (d,  $J = 7.9$  Hz, 3H), 7.68-7.49 (m, 7H), 7.48-7.35 (m, 2H), 7.30-6.90 (m, 14H), 6.72 (s, 3H), 6.64 (t,  $J = 7.6$  Hz, 1H), 6.54 (d,  $J = 7.5$  Hz, 1H), 6.48-6.40 (m, 1H), 6.10 (d,  $J = 8.1$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.14, 170.61, 156.66, 154.22, 146.59, 146.35,

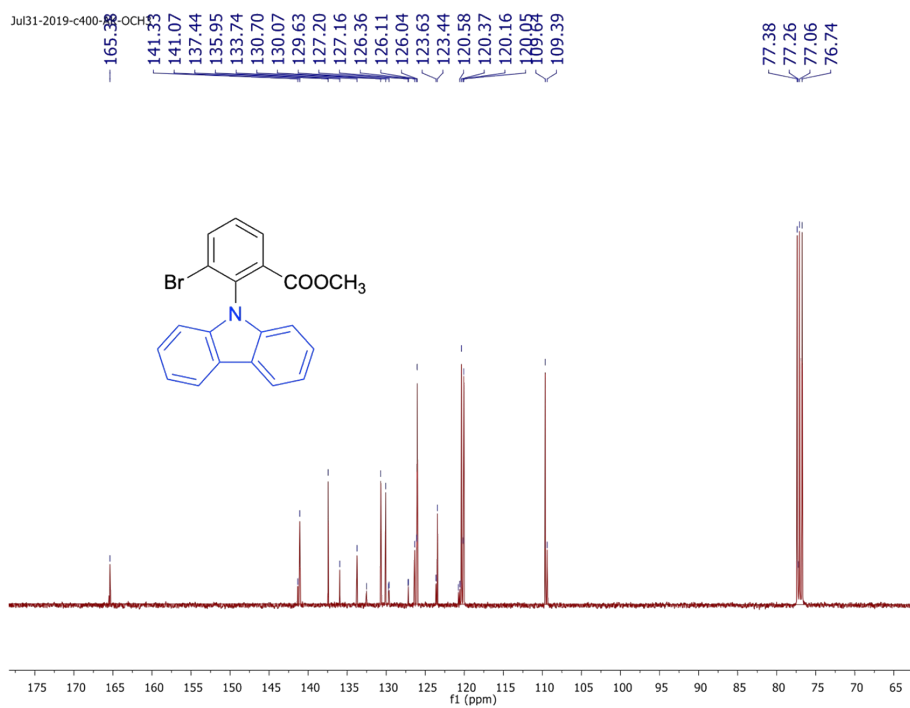
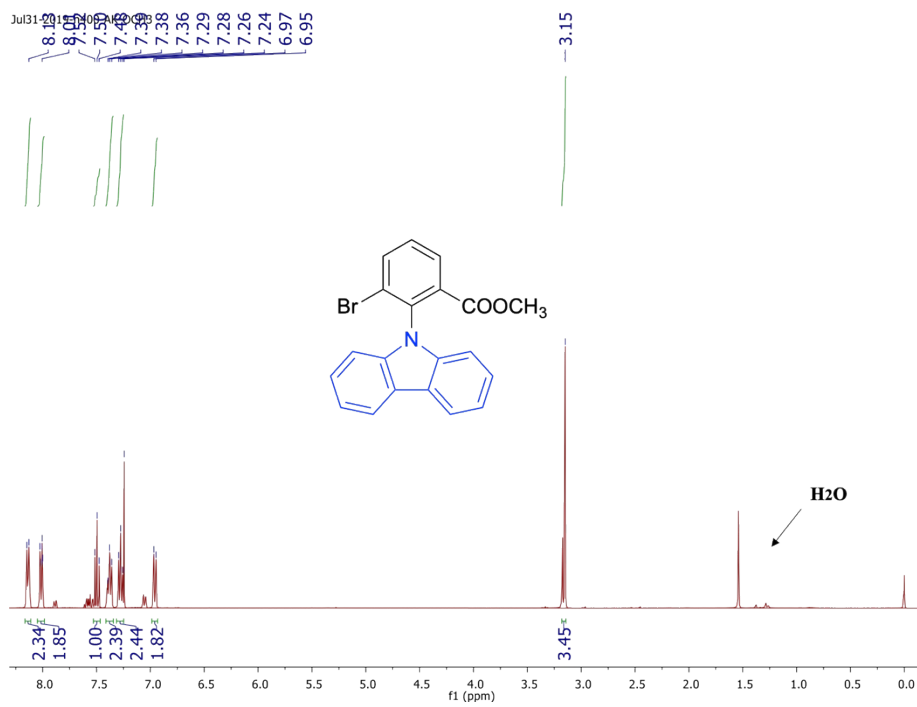
143.83, 140.47, 140.36, 138.81, 136.38, 135.47, 134.74, 133.27, 132.35, 131.10, 130.48, 129.44, 129.17, 129.04, 128.82, 128.70, 128.58, 128.40, 128.27, 127.86, 127.71, 127.11, 126.56, 126.47, 126.16, 125.95, 125.90, 125.29, 123.64, 123.47, 123.22, 123.02, 122.32, 122.05, 121.73, 120.27, 119.88, 119.40, 119.27, 77.35, 77.04, 76.72, 57.86, 56.78. MALDI-TOF (m/z) calculated for  $C_{65}H_{40}N_4$  [M<sup>+</sup>]: 876.32, found: 876.41.



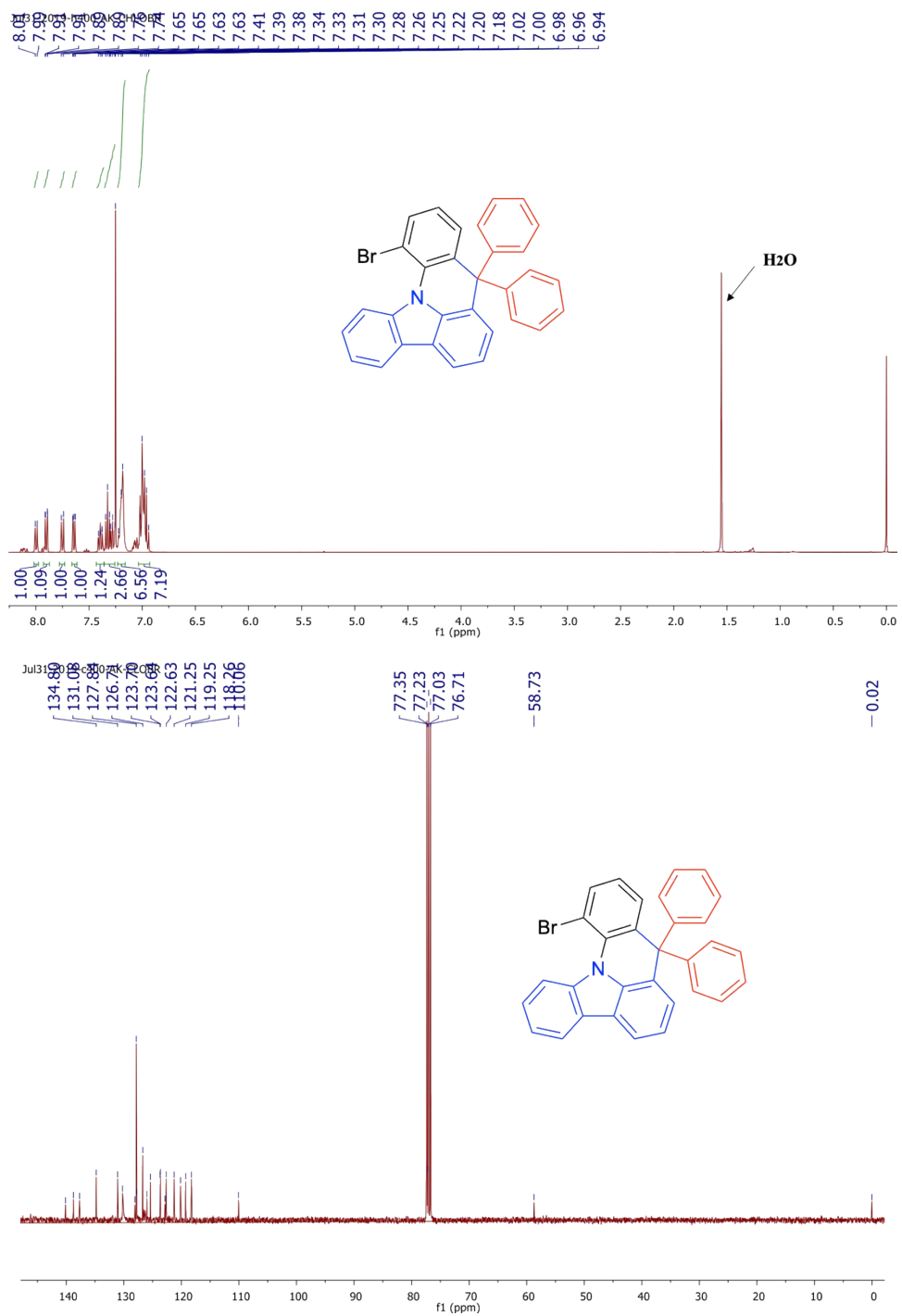
**Figure S3.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of compound (3) in deuterated CDCl<sub>3</sub>



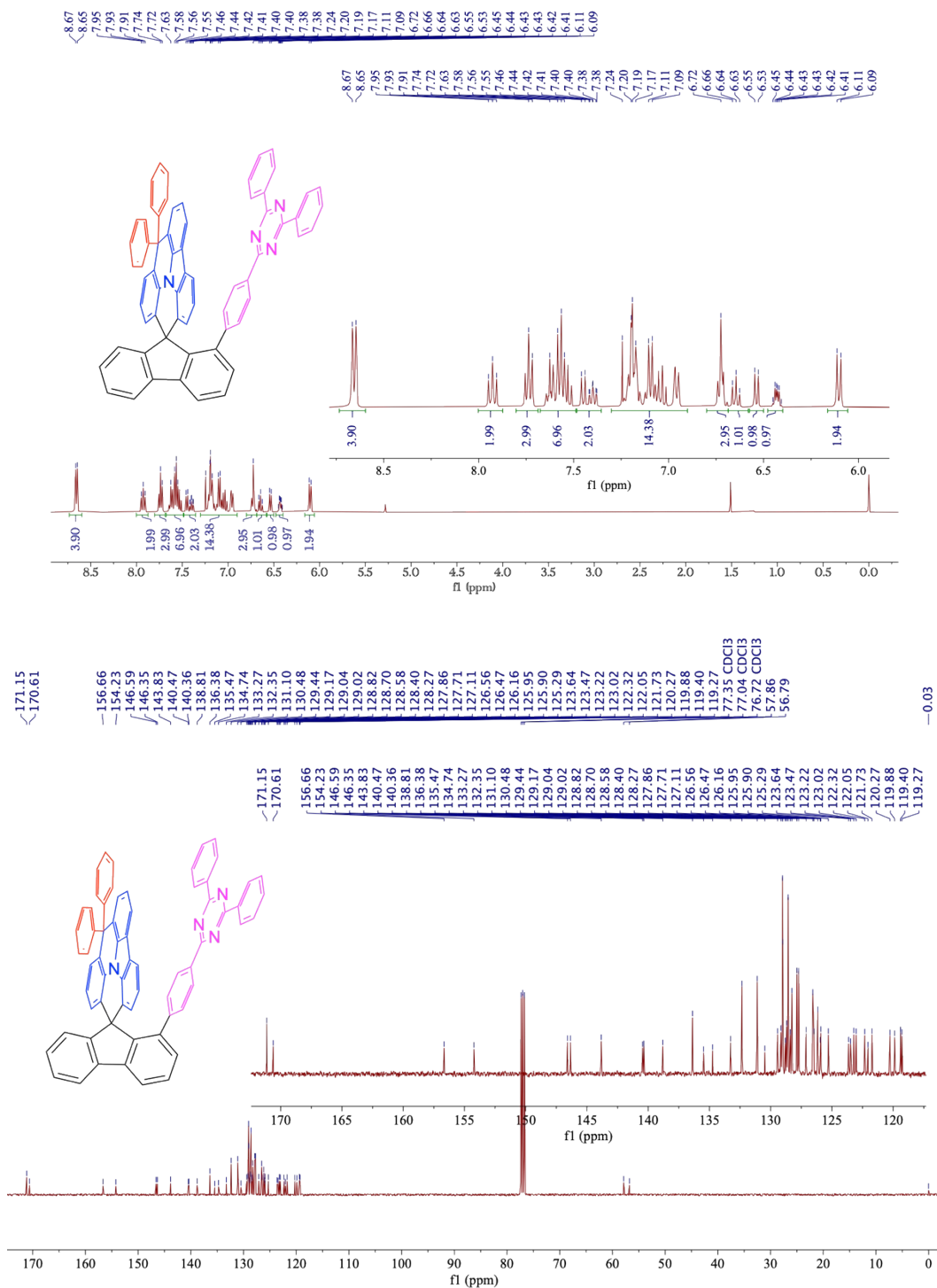
**Figure S4.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound (4) in deuterated  $\text{CDCl}_3$



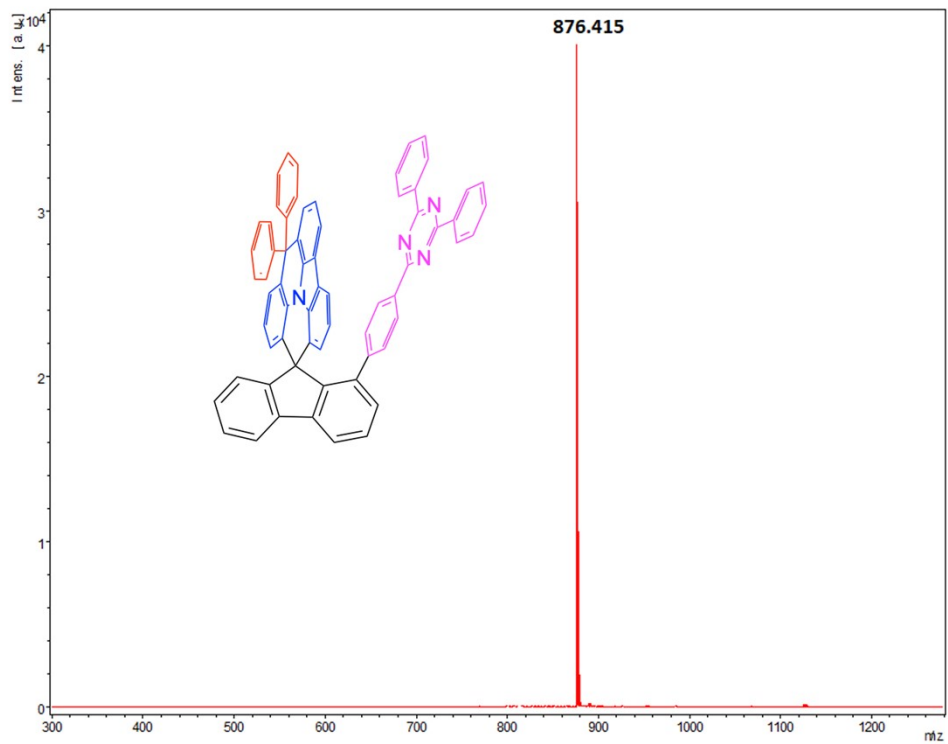
**Figure S5.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of compound (5) in deuterated CDCl<sub>3</sub>



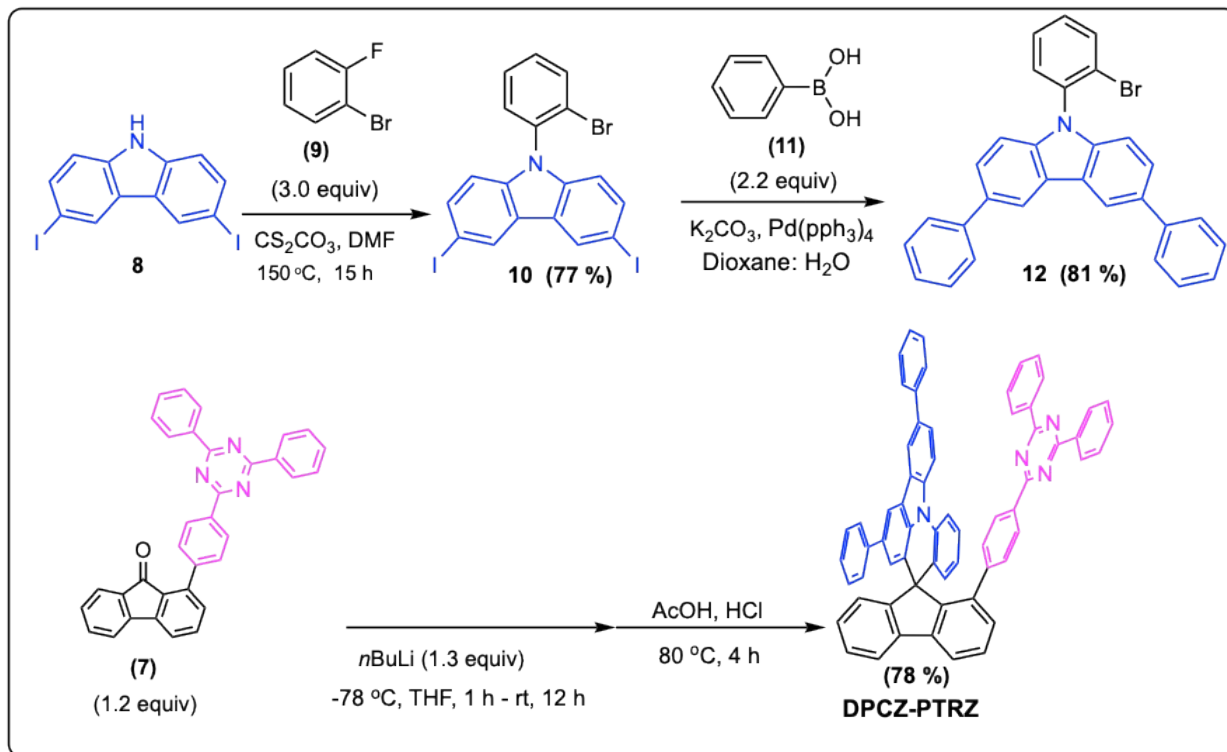
**Figure S6.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound (6) in deuterated  $\text{CDCl}_3$



**Figure S7.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of compound (**BLCZ-PTRZ**) in deuterated CDCl<sub>3</sub>



**Figure S8.** MALDI TOF spectrum of **BLCZ-PTRZ**.



**Scheme S2.** The synthetic routes for **DPCZ-PTRZ**.

## 6. Synthesis of 9-(2-bromophenyl)-3,6-diiodo-9H-carbazole (10)

The compound 9-(2-bromophenyl)-3,6-diiodo-9H-carbazole was obtained by mixing 3,6-diiodo-9H-carbazole (2.1 g, 5.0 mmol) and 1-bromo-2-fluorobenzene (2.6 g, 15.0 mmol) in the presence of  $\text{Cs}_2\text{CO}_3$  (8.1 g, 25 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°C for 15 hrs, then the reaction mixture was diluted with water (100 mL). The obtained solid was extracted with DCM and washed with water ( $3 \times 50$  mL). The organic layer was collected and dried over  $\text{Na}_2\text{SO}_4$ . The solvent from the reaction mixture was evaporated and further purified from column chromatography with eluents: petroleum ether/ dichloromethane (7/3, v/v) (2.2 g, 3.9 mmol 77 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.37 (d,  $J = 1.8$  Hz, 2H), 7.81 (dd,  $J = 7.9, 1.6$  Hz, 1H), 7.62 (dd,  $J = 8.5, 1.8$  Hz, 2H), 7.49 (td,  $J = 7.6, 1.6$  Hz, 1H), 7.36-7.42 (m, 2H), 6.79 (d,  $J = 8.5$  Hz, 2H).  $^{13}\text{C}$

NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  140.04, 135.67, 135.02, 134.45, 130.86, 130.79, 129.45, 129.08, 124.36, 123.59, 112.27, 83.30. MS (EI)  $m/z$ : 572.87 [M<sup>+</sup>]. Calcd for C<sub>18</sub>H<sub>10</sub>BrI<sub>2</sub>N: 572.80

#### 7. Synthesis of 9-(2-bromophenyl)-3,6-diphenyl-9H-carbazole (**12**)

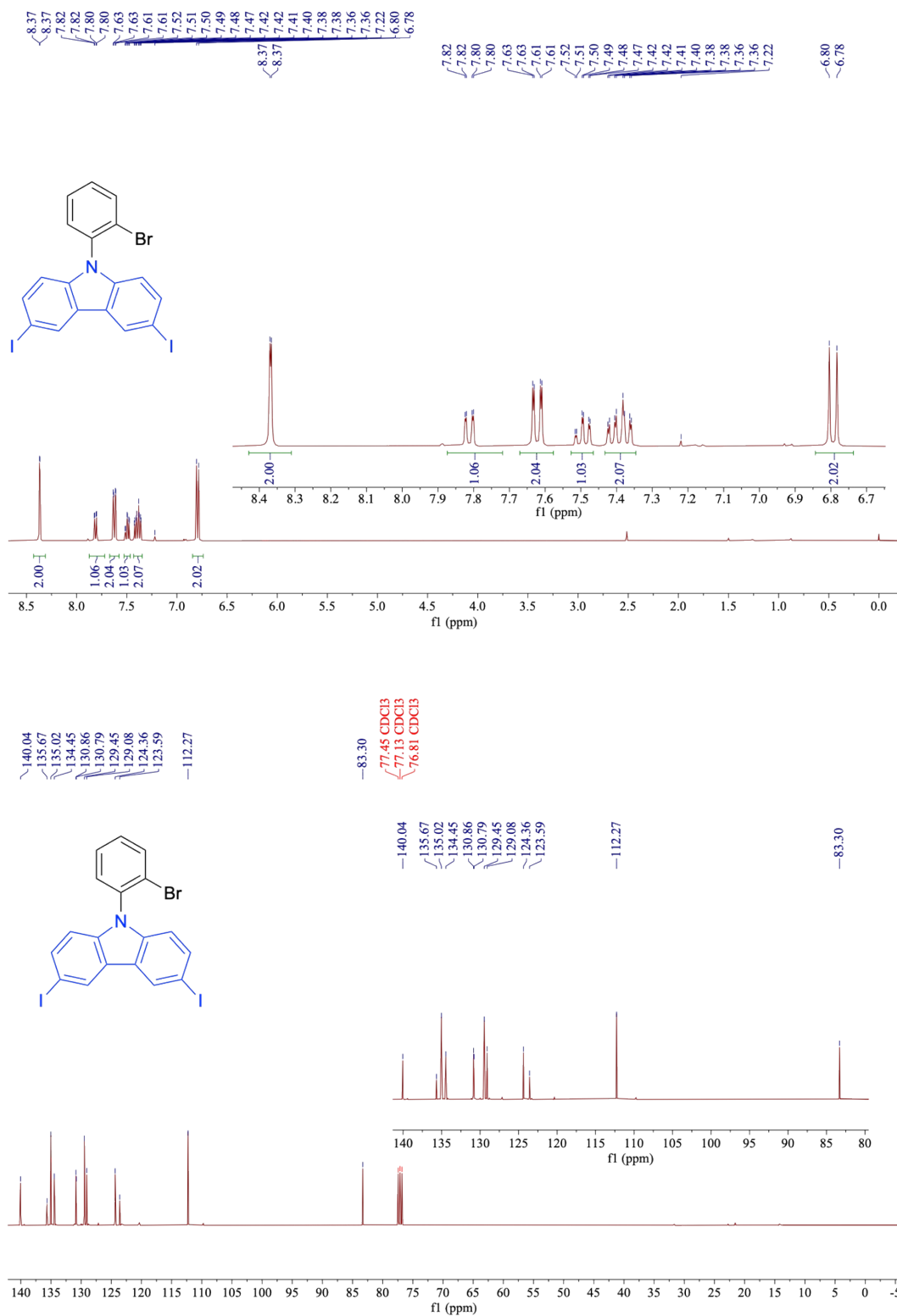
A mixture of 9-(2-bromophenyl)-3,6-diiodo-9H-carbazole (2.0 g, 3.5 mmol), phenylboronic acid (0.9 g, 7.7 mmol), tetrakis (triphenylphosphine) palladium (0) (138.0 mg, 0.12 mmol) and potassium carbonate (1.0 g, 7.5 mmol) was dissolved in 1,4-dioxane/H<sub>2</sub>O (60: 6) refluxed over night at 85 °C. The crude organic layer was subjected to column chromatography for further purification using PE/DCM (7/4, v/v) (1.34 g, 81%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.40 (d,  $J$  = 1.8 Hz, 2H), 7.76-7.39 (m, 14H), 7.34 (td,  $J$  = 7.2, 1.4 Hz, 2H), 7.14 (d,  $J$  = 8.5 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  141.94, 141.91, 140.81, 137.63, 136.65, 134.31, 133.76, 133.63, 131.03, 130.29, 129.96, 128.90, 128.78, 127.57, 127.37, 127.32, 126.99, 126.59, 125.73, 125.67, 124.02, 123.91, 123.75, 118.98, 118.87, 110.41, 110.16. MS (EI)  $m/z$ : 473.15 [M<sup>+</sup>]. Calcd for C<sub>30</sub>H<sub>20</sub>BrN: 473.07

#### 8. Synthesis of (R)-1-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-3',6'-

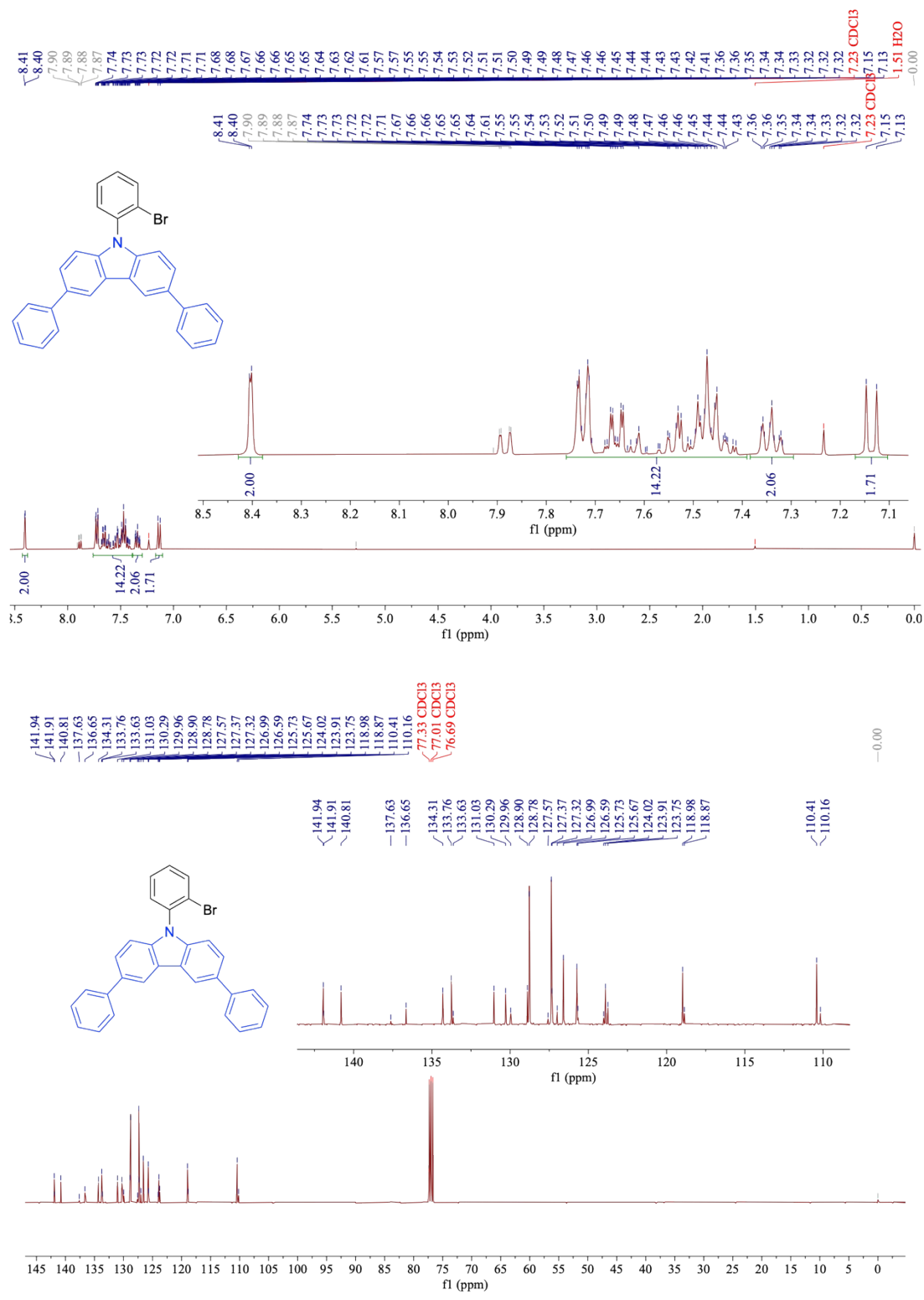
##### diphenylspiro[fluorene-9,8'-indolo[3,2,1-de]acridine] (DPCZ-PTRZ)

Compound 9-(2-bromophenyl)-3,6-diphenyl-9H-carbazole (**12**) (1.0 g, 2.11 mmol) was dissolved in 40 mL freshly distilled THF and cooled to -78 °C. After 30 minutes, *n*-butyl lithium (1.5 mL, 2.53 mmol) was added dropwise. The mixture was stirred for 1 hour at -78 °C, and then 1-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9H-fluoren-9-one (1.13 g, 2.32 mmol) in 50 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  $\text{Na}_2\text{SO}_4$ , filtered and evaporated, resulting in yellow powder, which was used directly in the next step. The crude mixture was dissolved in 30 mL acetic acid while 8 mL hydrochloric acid (36%) was added dropwise 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 eluents: petroleum ether/ dichloromethane (7/3, v/v) (1.43 g, 1.65 mmol 78 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.55 (dt,  $J = 8.6, 1.4$  Hz, 4H), 8.03 (dt,  $J = 6.1, 1.8$  Hz, 2H), 7.93 (dd,  $J = 7.7, 1.3$  Hz, 2H), 7.91-7.83 (m, 3H), 7.78-7.71 (m, 1H), 7.59-7.54 (m, 2H), 7.53-7.45 (m, 7H), 7.45-7.31 (m, 4H), 7.30-7.13 (m, 7H), 7.11-7.03 (m, 3H), 6.89-6.80 (m, 1H), 6.70 (t,  $J = 1.5$  Hz, 1H), 6.60 (dt,  $J = 7.9, 1.8$  Hz, 1H), 6.28 (dd,  $J = 8.1, 1.9$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.87, 170.55, 157.79, 155.07, 143.22, 141.92, 140.63, 140.10, 139.79, 139.41, 137.76, 137.23, 136.55, 136.37, 135.79, 133.94, 133.04, 132.18, 130.47, 128.94, 128.86, 128.68, 128.46, 128.34, 128.10, 127.85, 127.79, 127.33, 126.85, 126.69, 126.63, 126.44, 126.29, 125.89, 125.20, 123.80, 123.25, 122.96, 122.92, 119.95, 119.63, 118.38, 116.64, 114.33, 112.98, 56.27. MALDI-TOF (m/z) calculated for  $\text{C}_{64}\text{H}_{40}\text{N}_4$  [ $\text{M}^+$ ]: 864.33, found: 864.48.

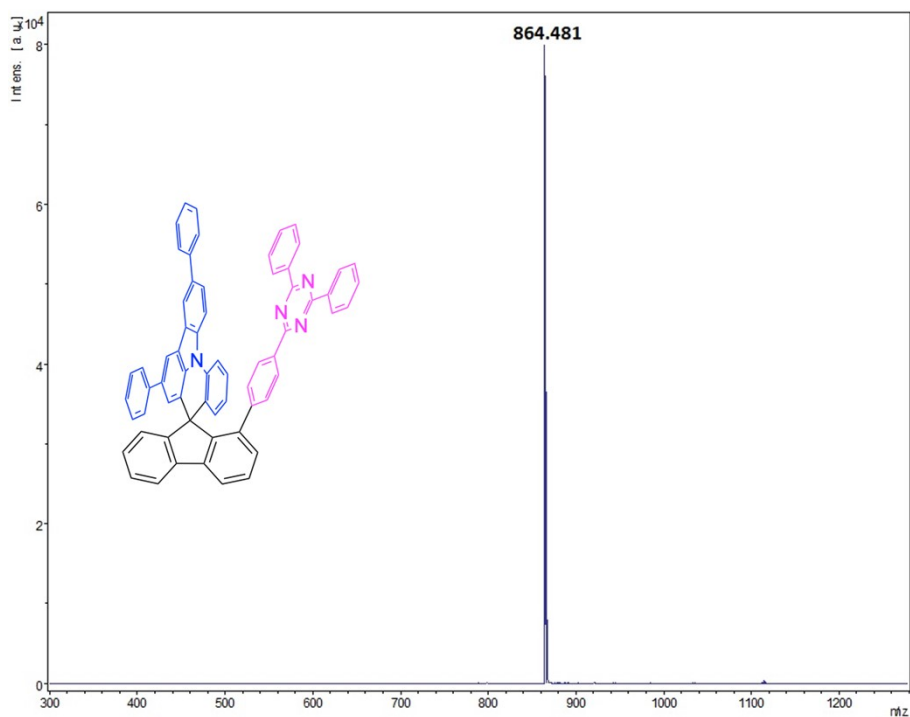


**Figure S9.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of compound (10) in deuterated CDCl<sub>3</sub>

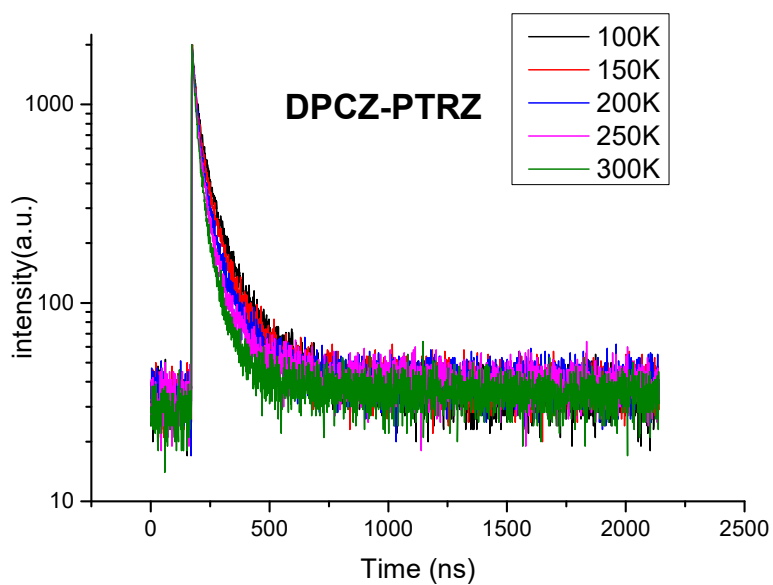


**Figure S10.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of compound (12) in deuterated CDCl<sub>3</sub>

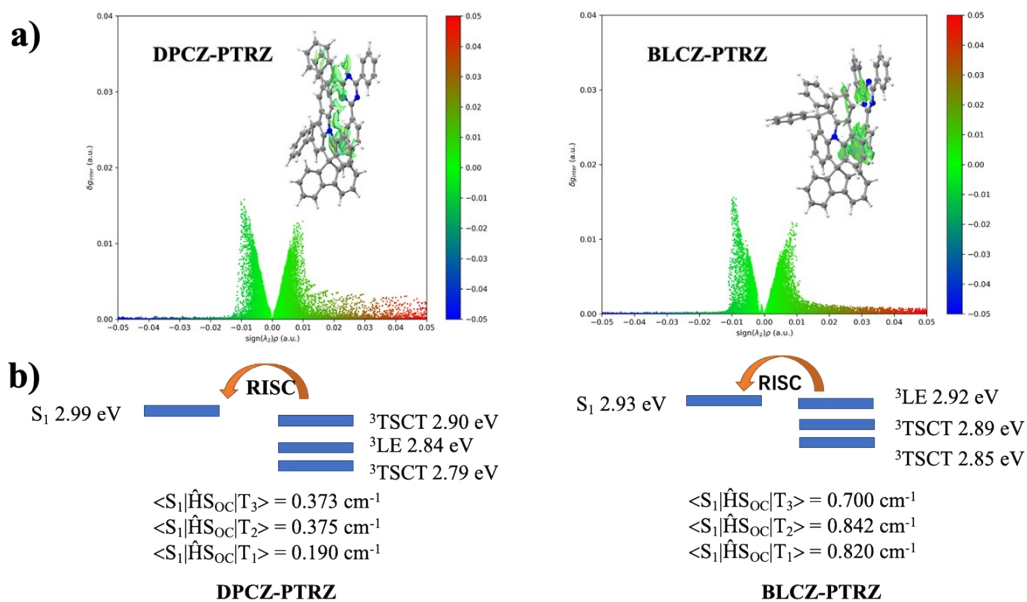




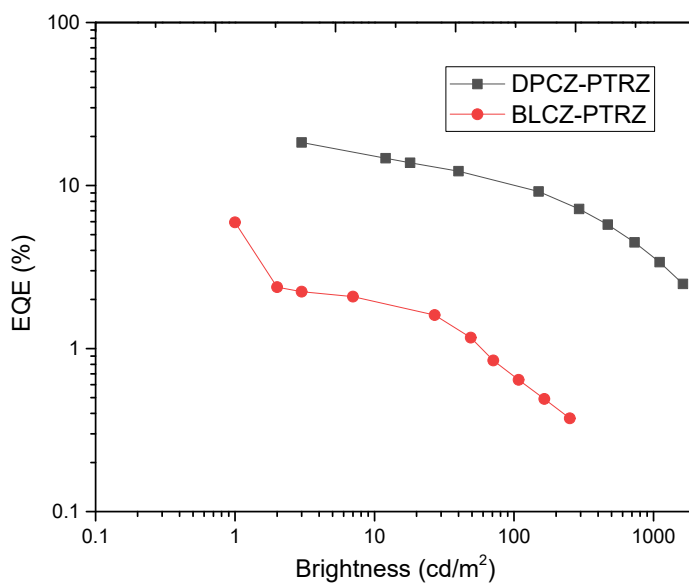
**Figure S12.** MALDI TOF spectrum of **DPCZ-PTRZ**.



**Figure S13.** Transient photoluminescence spectrum for **DPCZ-PTRZ** at different temperature.



**Figure S14 (a)** IGMH calculation of **DPCZ-PTRZ** and **BLCZ-PTRZ**. **(b)** Natural transition orbits (NTO) calculation about excited states energy level of **DPCZ-PTRZ** and **BLCZ-PTRZ**.



**Figure S15:** EQE vs brightness of **DPCZ-PTRZ** and **BLCZ-PTRZ**.