Supporting Information

Modulatory Spin-Flip of Triplet Excitons via Diversiform Electron-Donating Units for MR-TADF Emitters towards Solution-Processed Narrowband OLEDs

Shengyu Li, Zhi Yang, Yanchao Xie, Lei Hua, Shian Ying, Yuchao Liu, Zhongjie Ren, Shouke Yan**

S. Li, Z. Yang, Y. Xie, Dr. S. Ying, Dr. Y. Liu, Prof. S. Yan,

Department Key Laboratory of Rubber-Plastics, Ministry of Education/Shandong Provincial Key Laboratory of Rubber-Plastics, School of Polymer Science and Engineering, Qingdao University of Science & Technology, Qingdao 266042, P. R. China.

E-mail: *Dr. Y. Liu* liuyc@qust.edu.cn; *Prof. S. Yan* skyan@qust.edu.cn

Dr. L. Hua,

School of Materials Science & Engineering, Changzhou University, Changzhou 213164, P. R. China.

Prof. Z. Ren,

State Key Laboratory of Chemical Resource Engineering, College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China.

Contents

S1. Materials and experimental procedures

All the reagents were purchased from *J&K Scientific*, *Energy Chemical, Sigma-Aldrich* and used without further purification, unless otherwise noted. The solvents were purchased from *Sinopharm Chemical Reagent Co., Ltd.*, and anhydrous toluene was gained through sodium reflux. The NMR spectra were performed using a Bruker AVAN CE NEO 400 spectrometer (400MHz). ^{1}H NMR and ^{13}C NMR spectra were obtained with chloroform-*d* was adopted as slovent and TMS as internal standard, respectively. High-resolution mass spectra data (MALDI-TOF) were collected on Xevo G2. Cyclic voltammetry (CV) was performed in nitrogen-bubbled acetonitrile solvent using CHI voltammetric analyser at room temperature. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$ 0.1 M) was adopeted as the electrolyte, and a glassy carbon working electrode, a platinum wire auxiliary electrode, and an $Ag/AgNO_3$ pseudo-reference electrode were used in the conventional three-electrode system. Cyclic voltammograms were performed from 0 V to 1.5 V at scan rate of 100 mV s^{-1}, and ferrocene power as external standard.[1,2] Then the HOMO energy levels could be calculated according to the reference ferroceneredox couple in acetonitrile by using the following formula:[3]

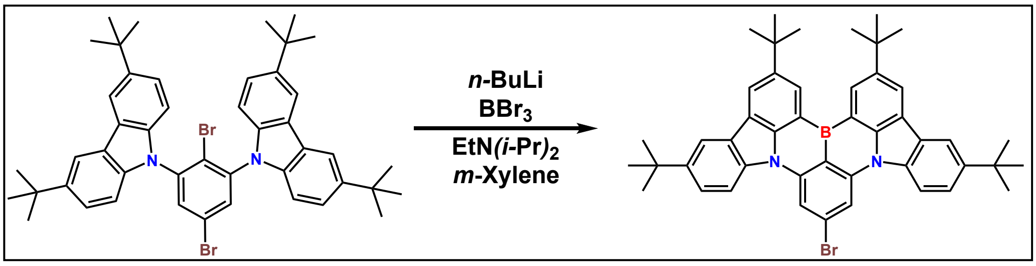
$$E_{HOMO} = -\left(E_{\left(onset,ox\ vs\ Fc^{+}/Fc\right)} + 4.8\right)$$

The LUMO energy levels could be calculated by the HOMO values and the energy gap (E_gs) obtained from the onset of the absorption spectra of the polymeric emitters. Differential scanning calorimetry (DSC) was performed on a TA Q2000 differential scanning calorimeter at a heating rate of 10 °C min^{-1} from 30 to 300 °C and a cooling rate of 10 °C min^{-1} from 300 to 30 °C under nitrogen atmosphere. The glass transition temperature (T_g) and the melting temperature (T_m) were determined from the second heating scan. Thermogravimetric analysis (TGA) was performed with a METTLER TOLEDO TGA/DSC 1/1100SF instrument. The thermal stability of the samples was obtained by measuring their 5% weight loss while heating at a rate of 10 °C min^{-1} from 25 to 800 °C under a nitrogen atmosphere.

UV/Vis absorption spectra were recorded on a Hitachi U-2910 spectrophotometer. PL spectra, including fluorescence at 77 K, and phorescence at 77 K, were recorded on a Hitachi F-7000 fluorescence spectrophotometer, and the energy gap (ΔE_{ST}) between lowest singlet (S_1) and triplet excited states (T_1) were determined from the difference values of the onset positions of fluorescencent and phorescencent spectra. To gain the proportion of delayed fluorescence (DF), the steady-state PL spectra in vacuum and in air, were performed using FS-5 spectrometer from Edinburgh Instruments Limited with Xe lamp source. The photoluminance quantum yields of the blended films were measured on FLS-980 with an integrating sphere (φ = 150 mm) under nitrogen gas. The transient-state PL spectra in vacuum and in air, including prompt fluorescence (PF) and DF spectra, and the temperature dependence of transient PL decay curves were determined using nanosecond gated luminescence and lifetime measurements with a high-energy pulsed Nd:YAG laser emitting at 320 nm.

Based on the optimized S_0 molecular geometries, the spin orbit coupling matrix elements (SOCEMs) between excited singlet and triplet states were calculated in B3LYP/6-31G (d) level using Orca 4.1.2 package and five states were considered in the analog computations to guarantee data reliability.

S2. Synthesis route and characteristic

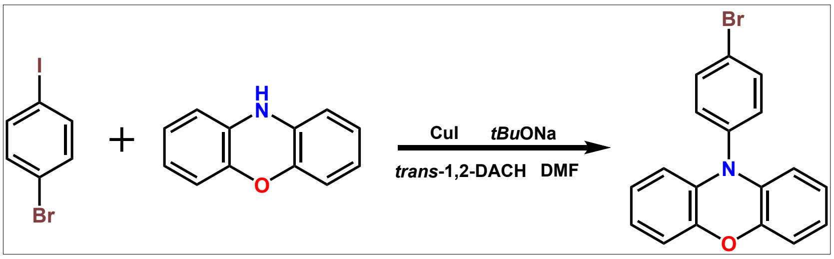


Scheme S1. Synthesis route of ***tBuCzBN-Br.***

DtBuCz-Ph-Br was synthesized according to the literature[xx]. D*t*BuCz-Ph-Br (738 mg, 1 mmol) was added into a two-necked flask under nitrogen atmosphere, and then 30 mL anhydrous m-xylene was injected into system. After stirring for 15 minutes, n-butyl lithium (0.7 mL, 1.1 mmol) was slowly added to the reaction system under ice bath, and keep stirring for another 20 minutes. Then the *n*-hexane was removed from the system. After that, boron tribromide (300.6 mg, 1.2 mmol) was injected into the reaction system at one time under ice bath for 20 minutes, and then keep stirring for30 minutes at room temperature. Finally, *N*, *N*-diisopropylethylamine (232.7 mg, 1.8 mmol) was slowly injected into reaction system, and then the system was heated to 150°C, and the reaction was carried out overnight. After the reaction is processed, the product is washed and spun dry with a mixture of petroleum ether and dichloromethane (10:1) and filtered to obtain a dark yellow solid. After purification by column chromatography with eluent of petroleum ether: dichloromethane = 20:1, and 244.7 mg bright yellow solid ***tBuCzBN-Br*** was obtained with a yield of 34%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.06 (d, *J* = 2.0 Hz, 2H), 8.42 (d, *J* = 1.8 Hz, 2H), 8.33 (d, *J* = 1.5 Hz, 2H), 8.27-8.18 (m, 4H), 7.65 (dd, *J* = 8.8, 2.1 Hz, 2H), 1.66 (s, 18H), 1.53 (s, 18H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.77, 145.03, 144.69, 141.41, 137.99, 129.76, 127.80, 127.15, 124.58, 123.74, 120.88, 117.33, 114.02, 110.89, 35.19, 34.82, 32.16, 31.80.

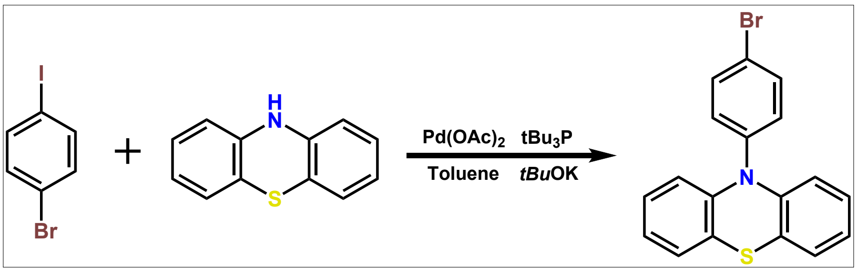


Scheme S2. Synthesis route of ***PXZ-Ph-Br***.

The mixture of CuI (190.5 mg, 1 mmol), sodium tert-butanol (2883 mg, 30 mmol), *p*-bromoiodobenzene (4243.5 mg, 15 mmol) and phenoxazine (1832.1 mg, 10 mmol) were added to 250 mL double-necked flask under nitrogen atmosphere. Then the *trans*-1, 2-cyclohexanediamine (228.4 mg, 2 mmol) and 40 mL anhydrous *N*, *N*-dimethylformamide were injected into system. After the mixture are fully dissolved, reaction temperature is raised to 100°C and the reaction is carried out overnight. Finally, the reaction was quenched, and after post-treatment, the product was purified with by column chromatography eluent of petroleum ether: dichloromethane = 5:1, and 1894 mg white solid PXZ-Ph-Br was obtained, with a yield of 56%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77-7.63 (m, 2H), 7.34-7.09 (m, 2H), 6.88 - 6.43 (m, 6H), 5.90 (dd, *J* = 7.8, 1.5 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.94, 138.12, 134.46, 134.00, 132.77, 123.31, 122.39, 121.64, 115.61, 113.20.

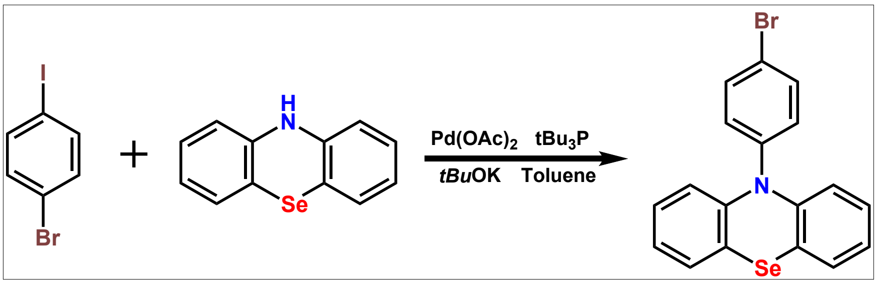


Scheme S3. Synthesis route of ***PTZ-Ph-Br***.

The mixture of *p*-bromoiodobenzene (8487.3 mg, 20 mmol), phenothiazine (3985.6 mg, 20 mmol), palladium acetate (224.5 mg, 1 mmol) and potassium tert-butanol (2693 mg, 24 mmol) were added to 250 mL double-necked flask under nitrogen atmosphere. Then the tri-tert-butylphosphine (25 mL, 2.5 mmol) and 60 mL anhydrous toluene were added, and the reaction temperature was raised to 110°C, and the reaction was carried out overnight. After post-treatment, the product was separated by column chromatography with eluent of petroleum ether: dichloromethane = 5:1. Finally, 4700 mg of white solid ***PTZ-Ph-Br*** was obtained, and the yield was 67%.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.84-7.78 (m, 1H), 7.40-7.32 (m, 1H), 7.12 (dd, J = 7.5, 1.7 Hz, 1H), 7.04-6.94 (m, 1H), 6.90 (td, J = 7.5, 1.3 Hz, 1H), 6.28 (dd, J = 8.2, 1.3 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 143.60, 140.56, 134.41, 132.10, 127.87, 127.36, 123.66, 121.26, 121.04, 117.40.

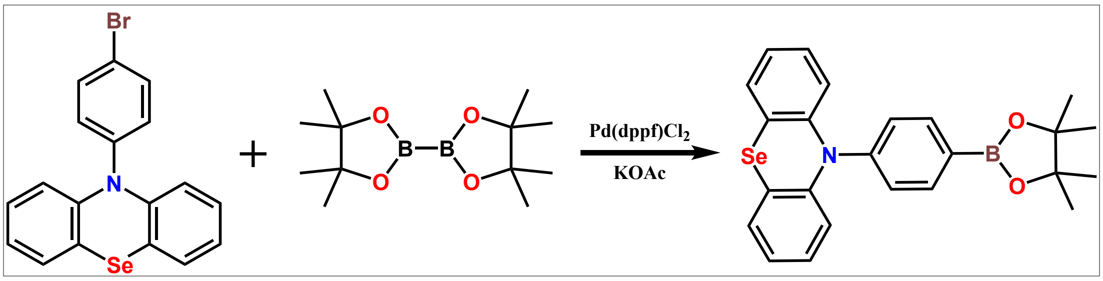


Scheme S4. Synthesis route of ***PSeZ-Ph-Br***.

The synthesis procedure is similar with that for ***PTZ-Ph-Br***. Finally, 5854 mg of white solid ***PSeZ-Ph-Br*** was obtained, and the yield was 73%.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.49 (dd, J = 8.6, 1.7 Hz, 2H), 7.38 (dd, J = 7.6, 1.7 Hz, 2H), 7.16 – 7.03 (m, 4H), 7.00 (td, J = 7.5, 1.4 Hz, 2H), 6.87 (dt, J = 8.0, 1.8 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-d) δ 143.18, 142.97, 138.70, 132.89, 130.41, 127.50, 125.66, 124.67, 122.33, 117.75.

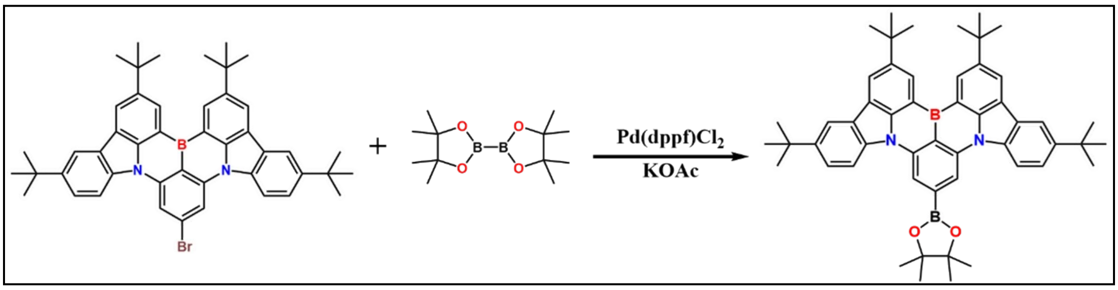


Scheme S5. Synthesis route of ***PSeZ-Ph-Bpin***.

The synthesis procedure is similar with that for ***PTZ-Ph-Bpin***. Finally, 1600 mg of white solid ***PSeZ-Ph-Bpin*** was obtained, and the yield was 65%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84-7.74 (m, 2H), 7.42 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.13 (dd, *J* = 8.0, 4.8 Hz, 4H), 7.00 (d, *J* = 8.0 Hz, 4H), 1.34 (s, 12H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.18, 142.97, 138.70, 132.89, 130.41, 127.50, 125.66, 124.67, 122.33, 117.75.

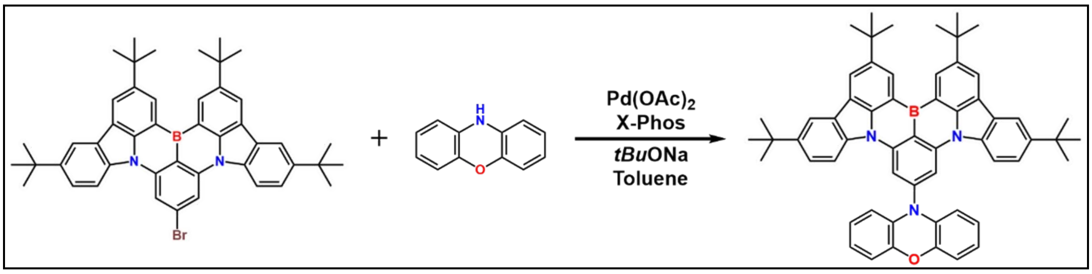


Scheme S6. Synthesis route of ***tBuCzBN-Bpin.***

The synthesis procedure is similar with that for ***PSeZ-Ph-Bpin***. Finally, 2700 mg of yellow solid ***tBuCzBN-Bpin*** was obtained, and the yield was 63%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.14 (d, *J* = 1.8 Hz, 2H), 8.79 (s, 2H), 8.54 (d, *J* = 8.8 Hz, 2H), 8.48 (d, *J* = 1.8 Hz, 2H), 8.27 (d, *J* = 2.0 Hz, 2H), 7.74 (dd, *J*= 8.8, 2.1 Hz, 2H), 1.67 (s, 18H), 1.55 (s, 18H), 1.50 (s, 12H).

^{13}C NMR (101 MHz, CDCl3) δ 144.12, 143.48, 142.62, 140.57, 137.43, 128.71, 125.88, 123.54, 122.70, 119.70, 116.06, 113.41, 112.72, 83.32, 34.14, 33.78, 31.17, 30.83, 24.05.



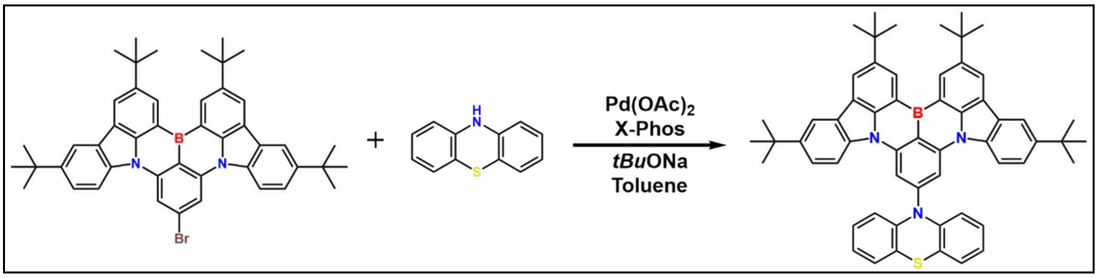
Scheme S7. Synthesis route of ***tBuCzBN-PXZ.***

The mixture of ***tBuCzBN-Br*** (719 mg, 1 mmol), phenoxazine (183.2 mg, 1 mmol), palladium acetate (11.2 mg, 0.05 mmol), tertiary butyl alcohol sodium (240.2 mg, 2.5 mmol) and 2-dicyclohexyl phosphine-2, 4, 6-triisopropyl biphenyl (47.7 mg, 0.1mmol) were added to 100 mL two-necked flask under nitrogen atmosphere, followed by adding 20 mL of anhydrous toluene. After stirring at 110°C for overnight reaction, the reaction was quenched, and the product was purified by column chromatography with eluent of petroleum ether/dichloromethane = 7:1 after post-treatment, and 641.1 mg bright yellow solid ***tBuCzBN-PXZ*** was obtained with a yield of 78%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.16 (d, *J* = 1.9 Hz, 2H), 8.49 (d, *J* = 1.8 Hz, 2H), 8.30 – 8.15 (m, 6H), 7.61 (dd, *J* = 8.7, 2.1 Hz, 2H), 6.81 (dd, *J* = 7.9, 1.5 Hz, 2H), 6.62 (td, *J* = 7.7, 1.5 Hz, 2H), 6.29 (d, *J* = 7.4 Hz, 2H), 1.69 (s, 18H), 1.49 (s, 18H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.41, 145.87, 145.17, 144.08, 141.59, 138.10, 134.23, 129.89, 127.11, 124.73, 123.86, 123.60, 121.66, 121.61, 121.00, 117.30, 115.61, 114.19, 113.57, 109.35, 35.23, 34.80, 32.18, 31.76.

TOF-MS m/z [M+H] calculated for C58H56BN3O+H 821.4516; observed 821.4521.



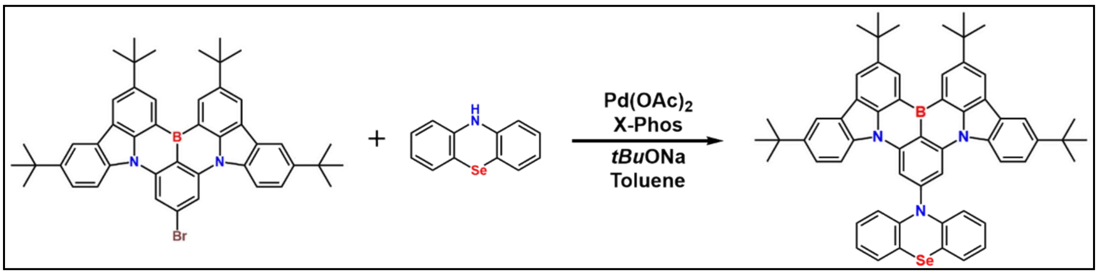
Scheme S8. Synthesis route of ***tBuCzBN-PTZ.***

The synthesis procedure is similar with that for ***tBuCzBN-PXZ***. Finally, 435 mg of yellow solid ***tBuCzBN-PTZ*** was obtained, and the yield was 52%.

[1]H NMR (400 MHz, Chloroform-*d*) δ 9.16-9.08 (s, 2H), 8.46-8.40 (s, 2H), 8.23 (d, *J* = 2.1 Hz, 2H), 8.11 (s, 2H), 7.97 (d, *J* = 8.8 Hz, 2H), 7.50 (dt, *J* = 8.8, 1.7 Hz, 2H), 7.38 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.27 (d, *J* = 1.6 Hz, 2H), 7.25-7.21 (m, 2H), 7.19-7.11 (m, 2H), 1.67 (s, *J* = 2.5 Hz, 18H), 1.50 (s, *J* = 2.0 Hz, 18H).

[13]C NMR (101 MHz, Chloroform-*d*) δ 148.39, 145.77, 145.42, 144.78, 142.81, 141.72, 138.05, 129.80, 128.10, 127.97, 127.23, 127.13, 124.78, 124.27, 123.56, 122.36, 120.47, 117.25, 114.03, 102.07, 35.18, 34.76, 32.19, 31.80.

TOF-MS m/z [M+H] calculated for C58H56BN3S+H 837.4288; observed 837.4286.



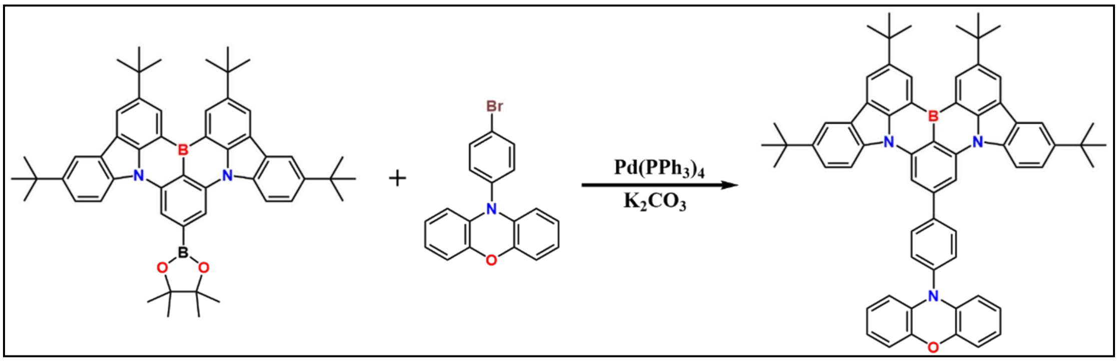
Scheme S9. Synthesis route of ***tBuCzBN-PSeZ.***

The synthesis procedure is similar with that for ***tBuCzBN-PXZ***. Finally, 761 mg of yellow solid ***tBuCzBN-PSeZ*** was obtained, and the yield was 86%.

[1]H NMR (400 MHz, Chloroform-d) δ 9.06 (t, J = 2.9 Hz, 2H), 8.37 (t, J = 2.3 Hz, 2H), 8.19 (t, J = 2.2 Hz, 2H), 7.84 (ddd, J = 7.9, 2.6, 1.3 Hz, 2H), 7.80-7.71 (m, 4H), 7.69-7.58 (m, 4H), 7.39 (td, J = 8.0, 1.6 Hz, 4H), 1.67-1.61 (m, 18H), 1.50 (d, J = 5.4 Hz, 18H).

[13]C NMR (101 MHz, Chloroform-d) δ 151.08, 145.36, 144.97, 144.40, 141.91, 141.82, 138.02, 132.17, 131.80, 129.72, 128.68, 127.80, 127.14, 126.84, 123.84, 123.30, 119.98, 117.19, 113.89, 95.28, 35.15, 34.74, 32.23, 31.87.

TOF-MS m/z [M+H] calculated for C58H56BN3Se+H 885.3733;observed 885.3727.



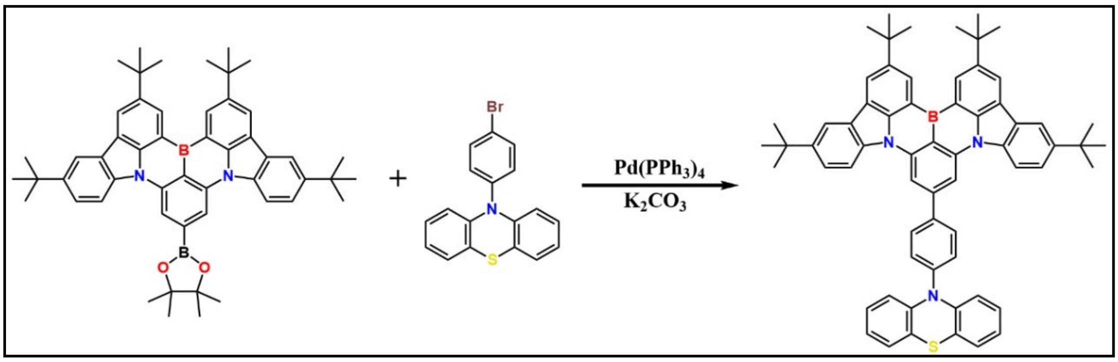
Scheme S10. Synthesis route of ***tBuCzBN-Ph-PXZ.***

The mixture of ***tBuCzBN-Bpin*** (345 mg, 0.45 mmol), ***PXZ-Ph-Br*** (167.4 mg, 0.5 mmol), potassium carbonate (124mg, 0.45mmol) and tetra-(triphenylphosphine) palladium (26 mg, 0.05 mmol) were added to 250 mL double-necked flask under nitrogen atmosphere. Then ethanol/water (v/v=2:1) and 20 mL anhydrous toluene were added into reaction system. After siring at 105°C for 12 hours, the reaction was cooled down to room temperature. Then the post-treatment was carried out, and column chromatography with eluent of petroleum ether/dichloromethane (v/v=10/1) was adopt to purify the product, and finally 237 mg bright yellow solid ***tBuCzBN-Ph-PXZ*** was obtained, with a yield of 53%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.05 (d, *J* = 1.9 Hz, 2H), 8.51-8.33 (m, 6H), 8.24 (d, *J* = 2.1 Hz, 2H), 8.08 (d, *J* = 8.2 Hz, 2H), 7.69 (dd, *J* = 8.8, 2.1 Hz, 2H), 7.62 - 7.51 (m, 2H), 6.78-6.62 (m, 6H), 6.21-6.10 (m, 2H), 1.66 (s, 18H), 1.54 (s, 18H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.41, 144.73, 144.67, 144.64, 144.08, 142.00, 141.73, 139.02, 138.27, 134.39, 131.58, 130.42, 129.73, 127.17, 124.56, 123.62, 123.35, 122.29, 122.25, 121.67, 121.54, 120.71, 117.35, 115.58, 114.21, 113.47, 106.94, 35.18, 34.85, 32.20, 31.87.

TOF-MS: C64H60BON3 [M+H] Calculated: 897.4829; Experimental: 897.4841.



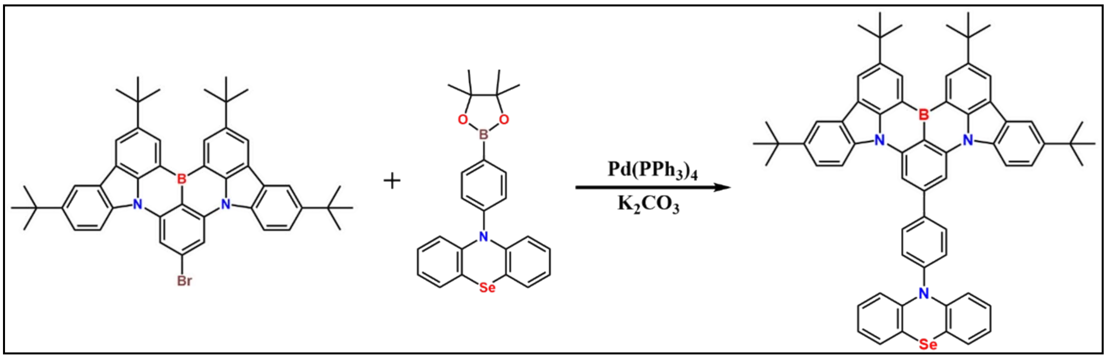
Scheme S11. Synthesis route of ***tBuCzBN-Ph-PTZ.***

The synthesis procedure is similar with that for ***tBuCzBN-Ph-PXZ***. Finally, 191 mg of bright yellow solid ***tBuCzBN-Ph-PTZ*** was obtained, and the yield was 42%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.02 (d, *J* = 1.9 Hz, 2H), 8.45-8.31 (m, 6H), 8.23 (d, *J* = 2.0 Hz, 2H), 8.05 (d, *J* = 8.1 Hz, 2H), 7.67 (dd, *J* = 8.8, 2.1 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.11 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.04-6.84 (m, 4H), 6.51 (d, *J* = 8.1 Hz, 2H), 1.65 (s, 18H), 1.54 (s, 18H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.34, 144.69, 144.59, 144.13, 141.72, 141.38, 141.14, 138.26, 130.53, 129.98, 129.68, 127.15, 127.00, 124.52, 123.59, 122.94, 121.66, 121.41, 120.67, 117.33, 117.03, 114.24, 106.85, 35.17, 34.84, 32.21, 31.88.

TOF-MS: C64H60BSN3 [M+H] Calculated: 913.4601; Experimental: 913.1956.



Scheme S12. Synthesis route of ***tBuCzBN-Ph-PSeZ.***

The mixture of ***tBuCzBN-Br*** (329 mg, 0.45 mmol), ***PSeZ-Ph-Bpin*** (224.1 mg, 0.5 mmol), potassium carbonate (124mg, 0.45mmol) and tetra-(triphenylphosphine) palladium (26 mg, 0.05 mmol) were added to 250 mL double-necked flask under nitrogen atmosphere. Then ethanol/water (v/v=2:1) and 20 mL anhydrous toluene were added into reaction system. After siring at 105°C for 12 hours, the reaction was cooled down to room temperature. Then the post-treatment was carried out, and column chromatography with eluent of petroleum ether/dichloromethane (v/v=10/1) was adopt to purify the product, and finally, 297.6 mg of bright yellow solid ***tBuCzBN-Ph-PSeZ*** was obtained, and the yield was 62%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.91 (d, *J* = 1.9 Hz, 2H), 8.35-8.18 (m, 6H), 8.13 (d, *J* = 2.2 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.54 (dd, *J* = 8.8, 2.1 Hz, 2H), 7.43-

7.23 (m, 4H), 7.17-7.11 (m, 2H), 7.09 – 7.02 (m, 2H), 7.02-6.94 (m, 2H), 1.55 (s, 18H), 1.44 (s, 18H).

^{13}C NMR (101 MHz, CDCl3) δ 144.19, 144.08, 143.64, 143.49, 143.24, 142.22, 140.68, 137.23, 136.35, 129.51, 128.66, 128.06, 126.51, 126.07, 123.80, 123.39, 123.29, 122.50, 122.27, 122.24, 119.52, 116.23, 113.16, 105.57, 34.11, 33.76, 31.15, 30.81.

TOF-MS: C64H60BSeN3 [M+H] Calculated: 961.4046; Experimental: 961.4055.

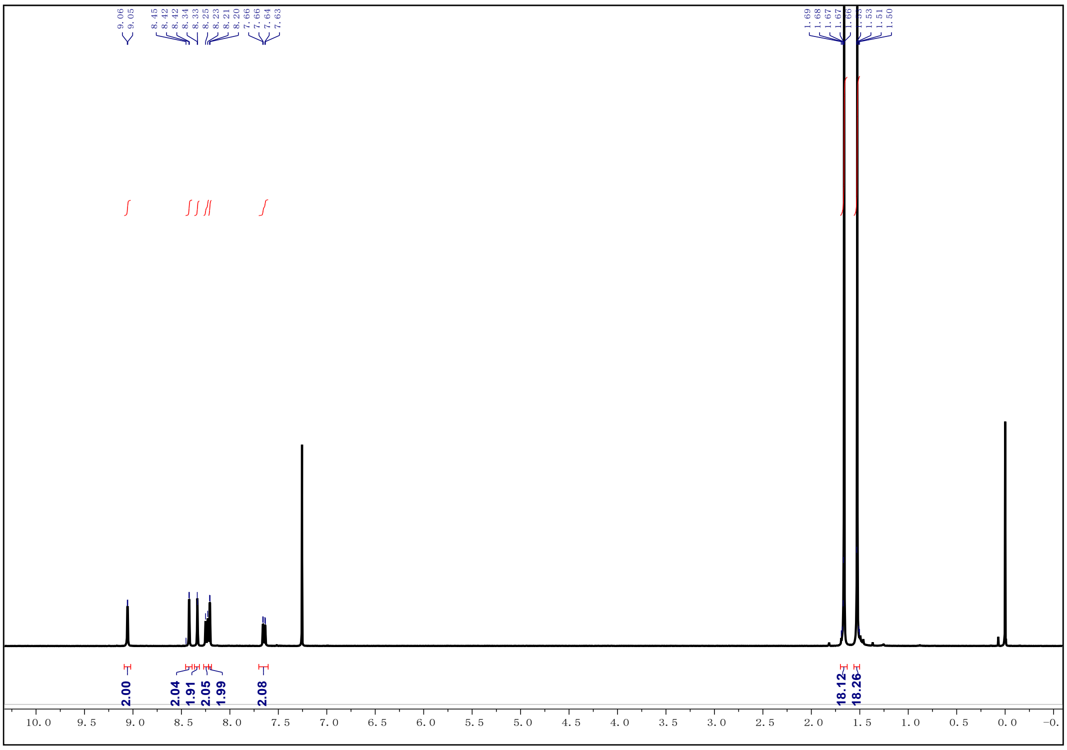


Figure S1. The ^{1}H NMR of ***tBuCzBN-Br***

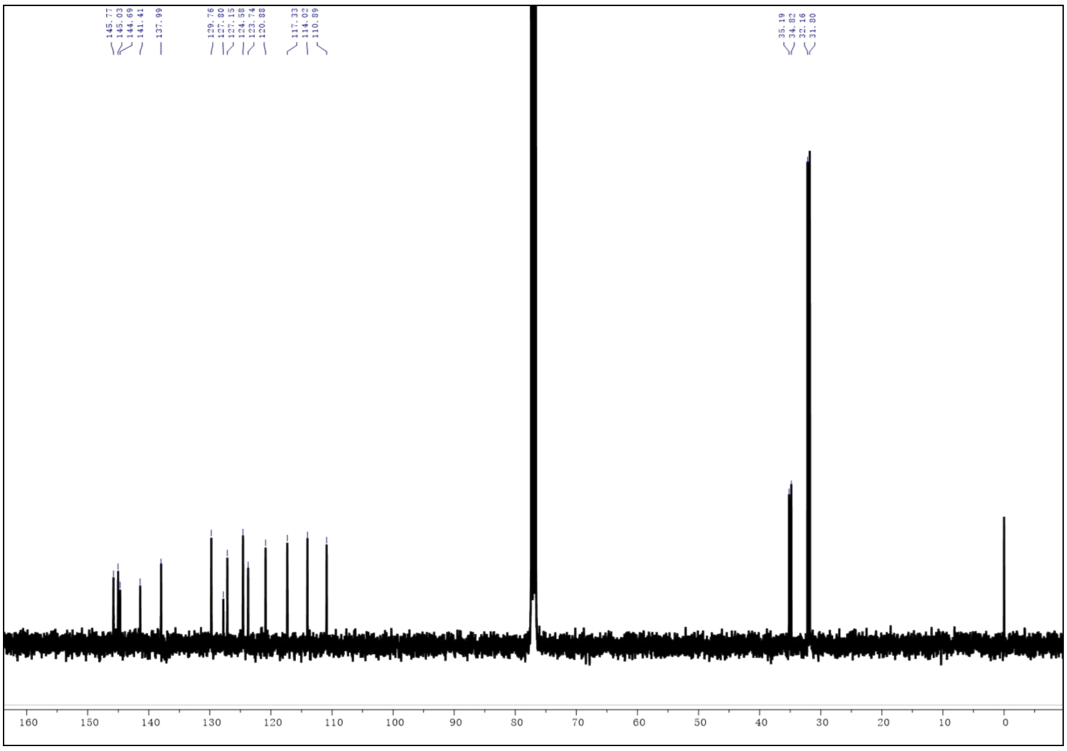


Figure S2. The ^{13}C NMR of ***tBuCzBN-Br***

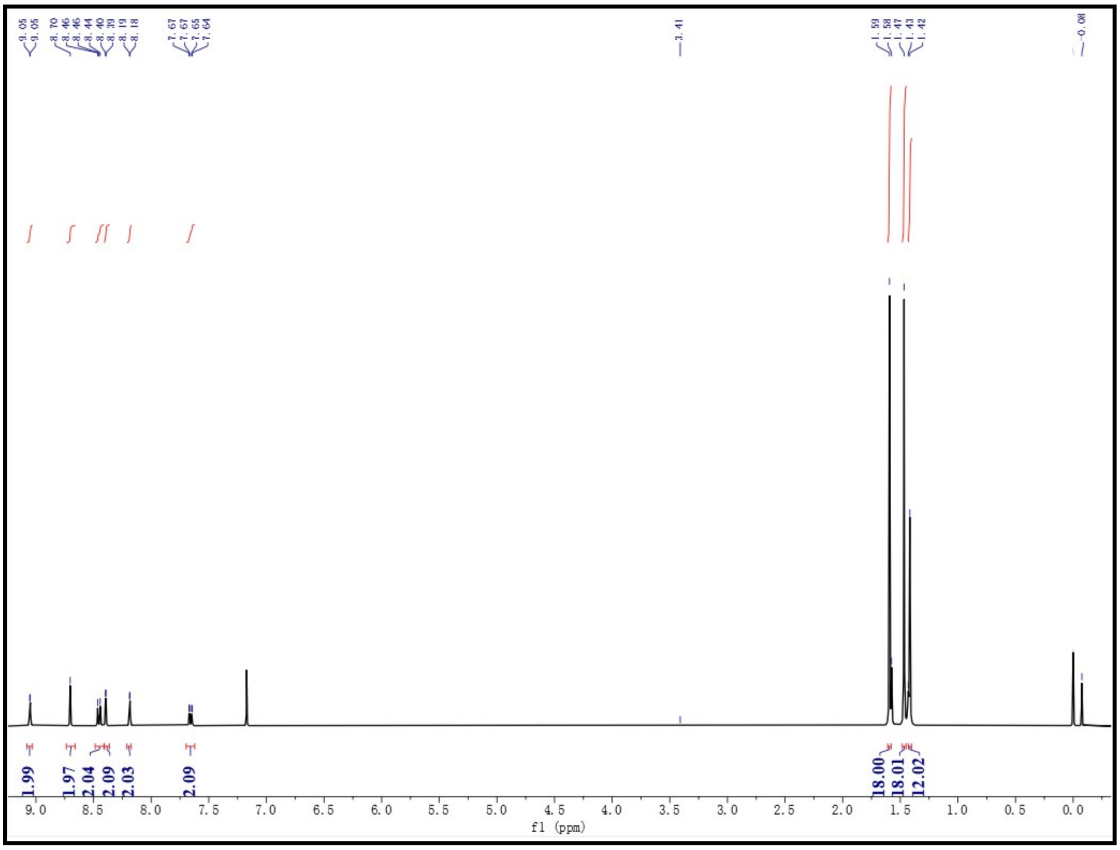


Figure S3. The ^{1}H NMR of ***tBuCzBN-Bpin***

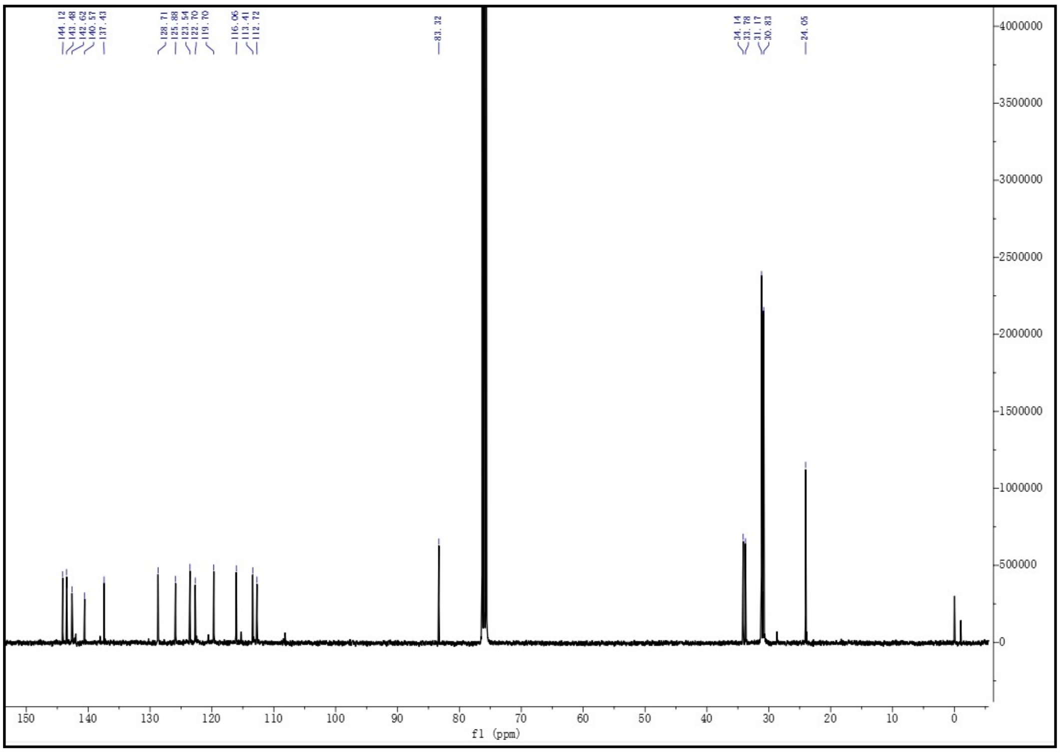


Figure S4. The ^{13}C NMR of ***tBuCzBN-Bpin***

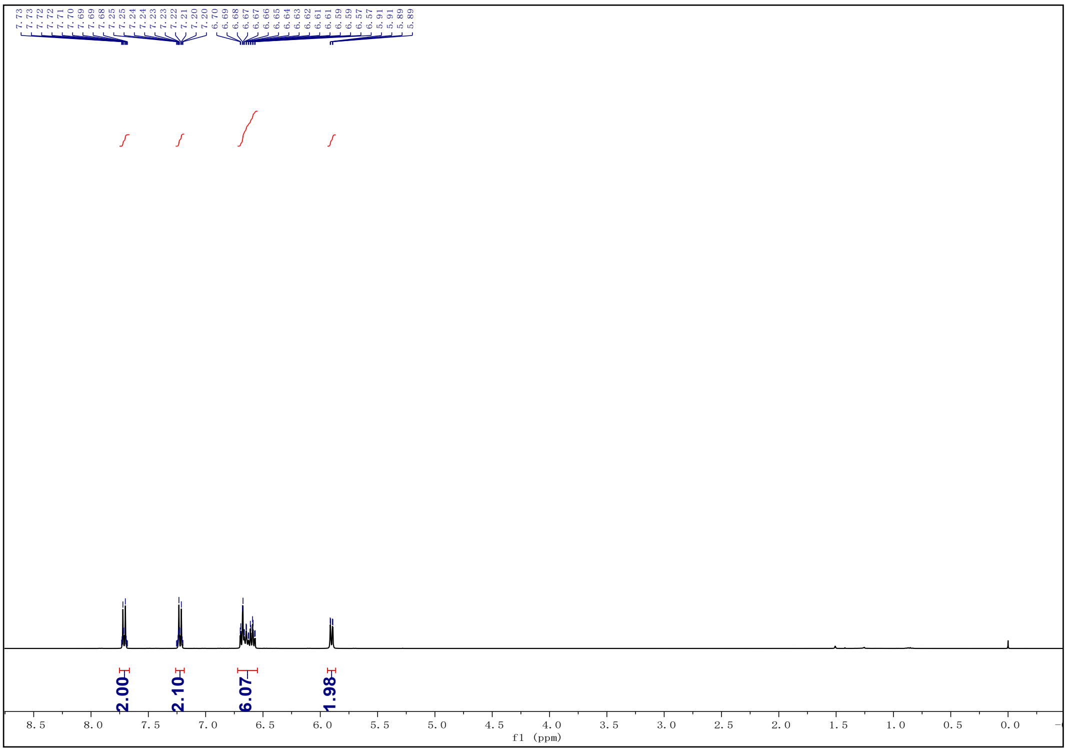


Figure S5. The ^{1}H NMR of ***PXZ-Ph-Br***

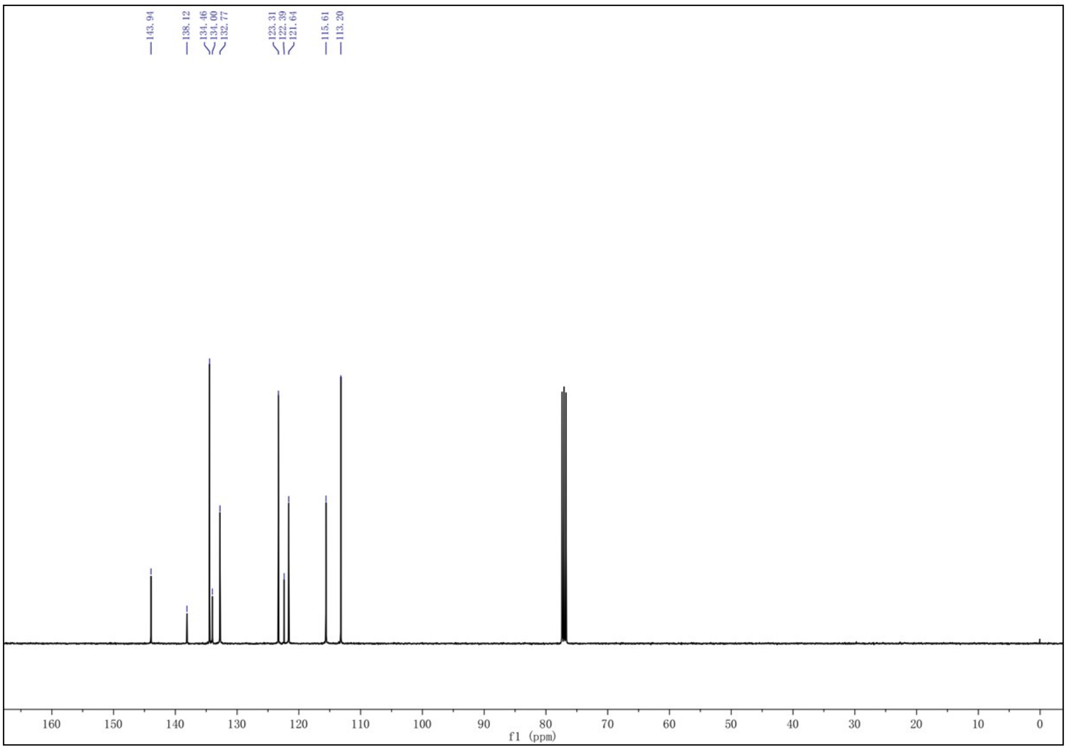


Figure S6. The ^{13}C NMR of ***PXZ-Ph-Br***

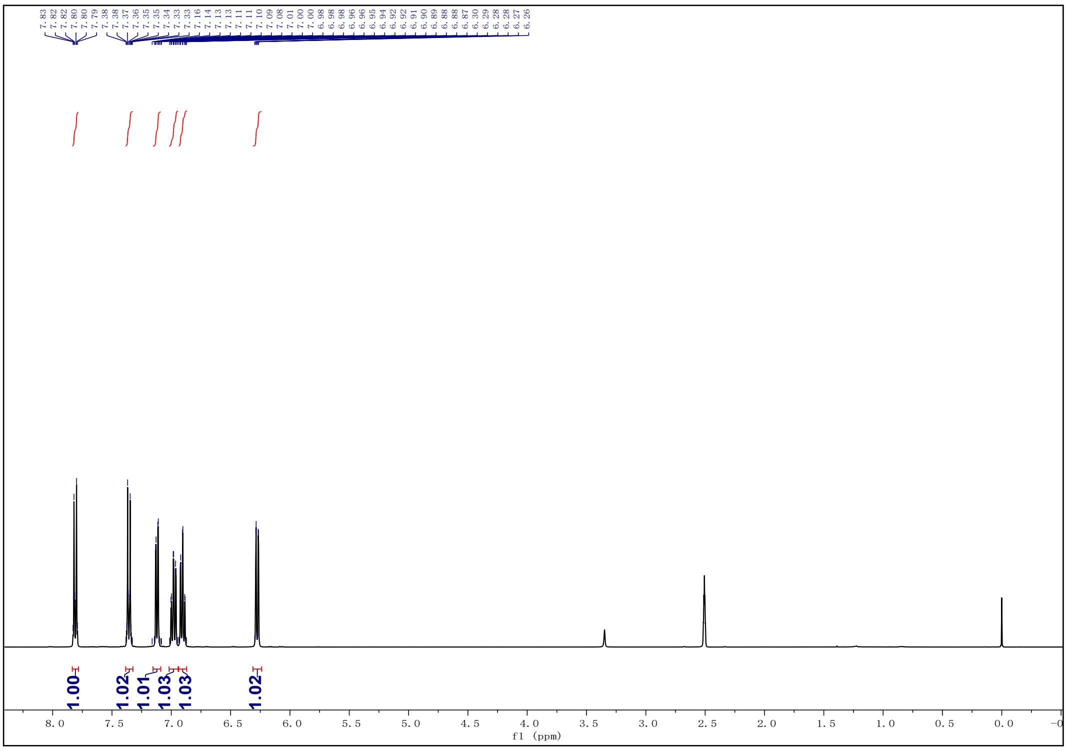


Figure S7. The ^{1}H NMR of ***PTZ-Ph-Br***

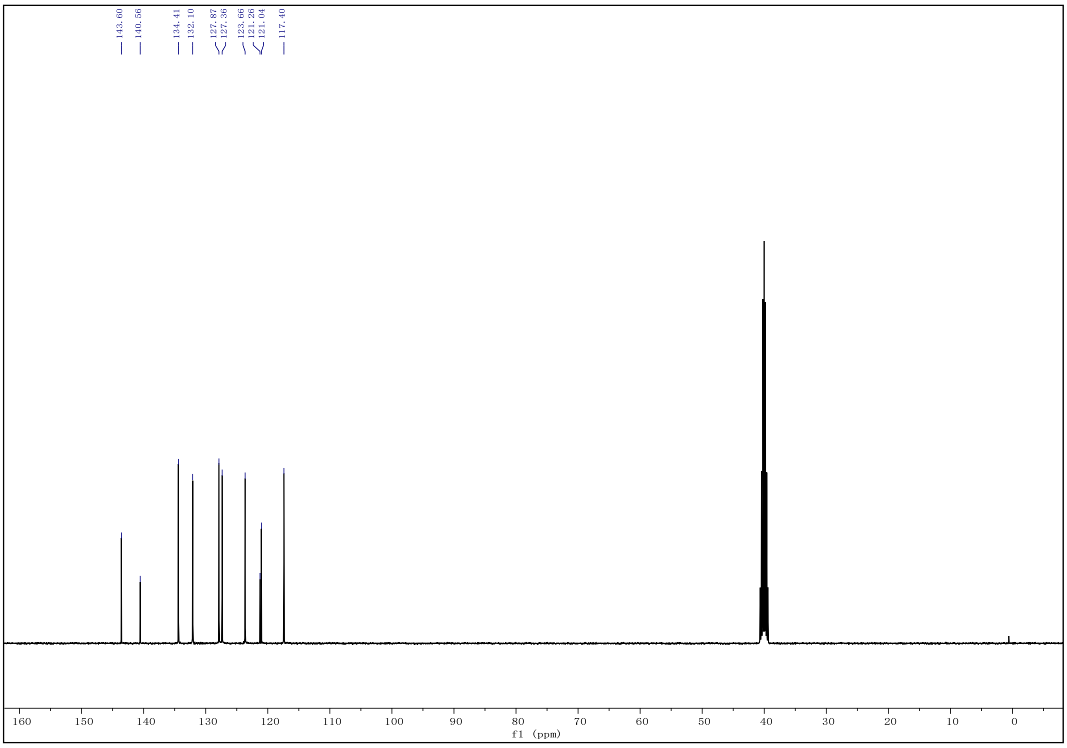


Figure S8. The ^{13}C NMR of ***PTZ-Ph-Br***

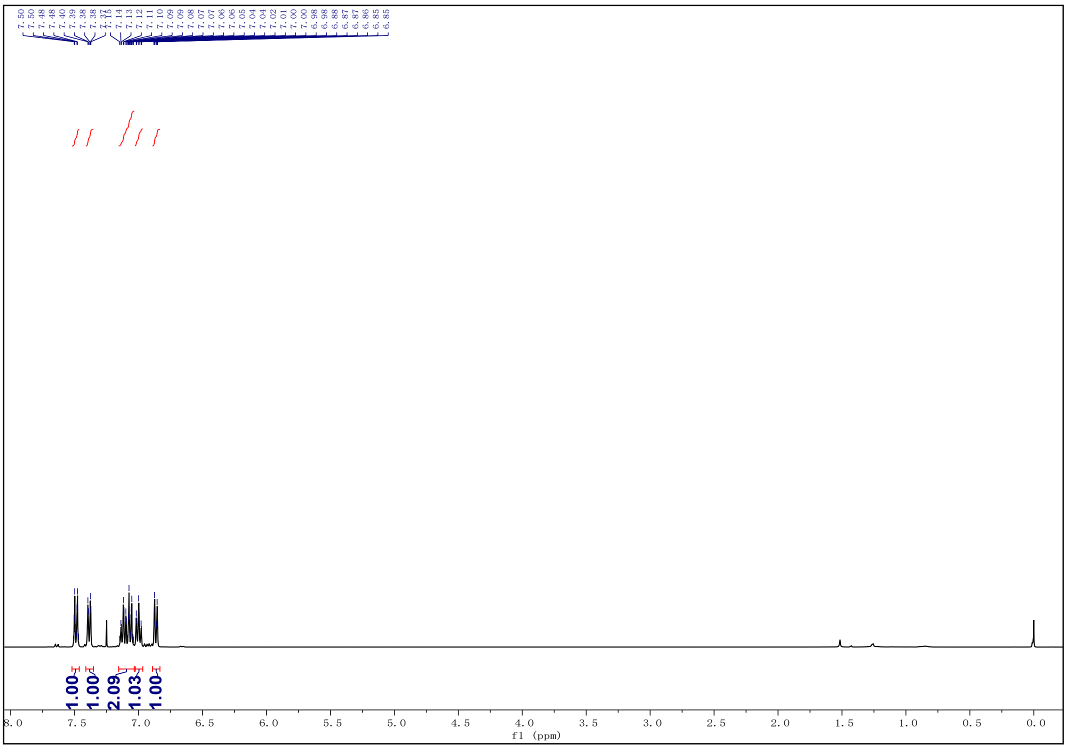


Figure S9. The ^{1}H NMR of ***PSeZ-Ph-Br***

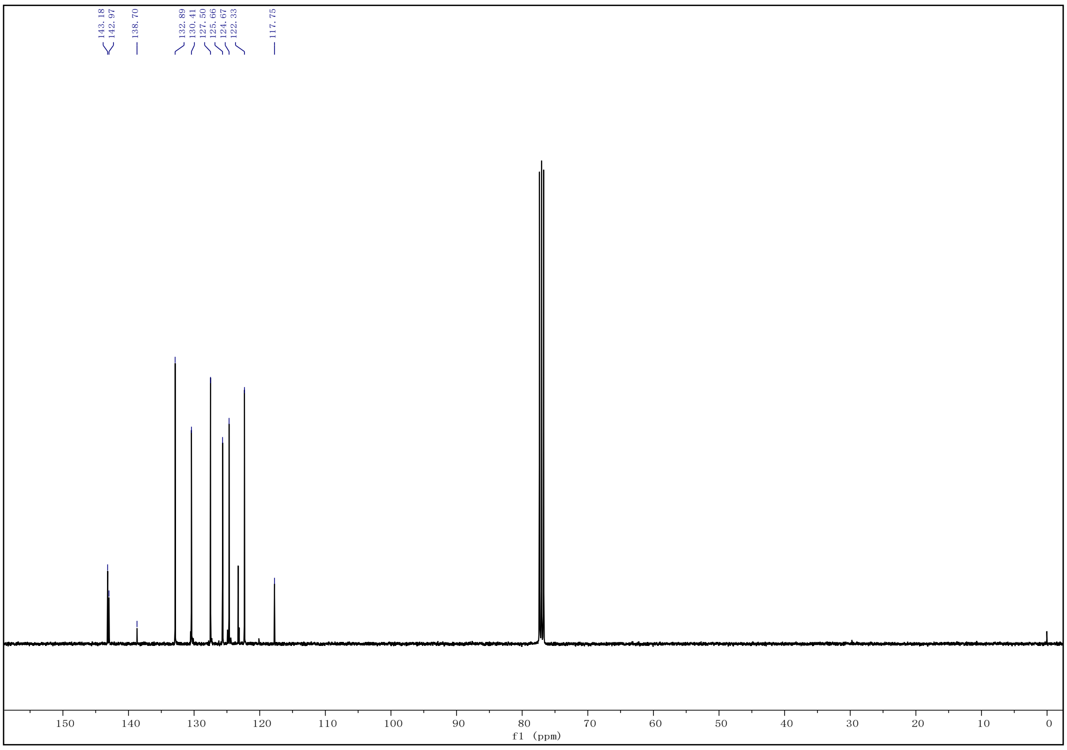


Figure S10. The ^{13}C NMR of ***PSeZ-Ph-Br***

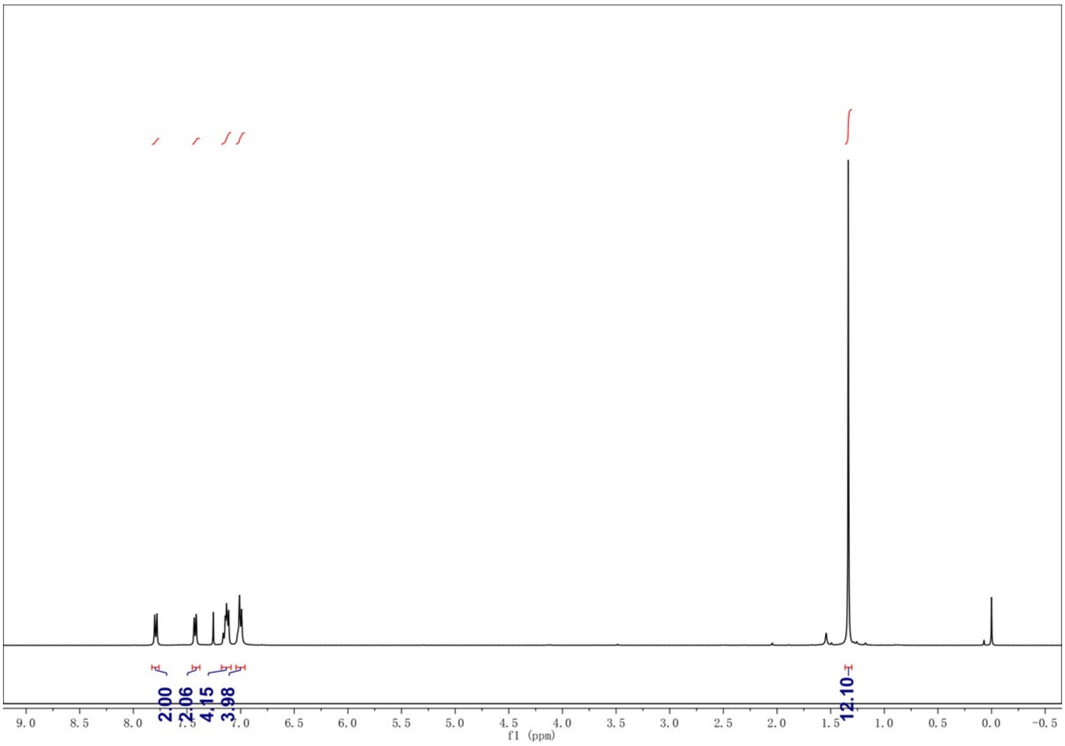


Figure S11. The ^{1}H NMR of ***PSeZ-Ph-Bpin***

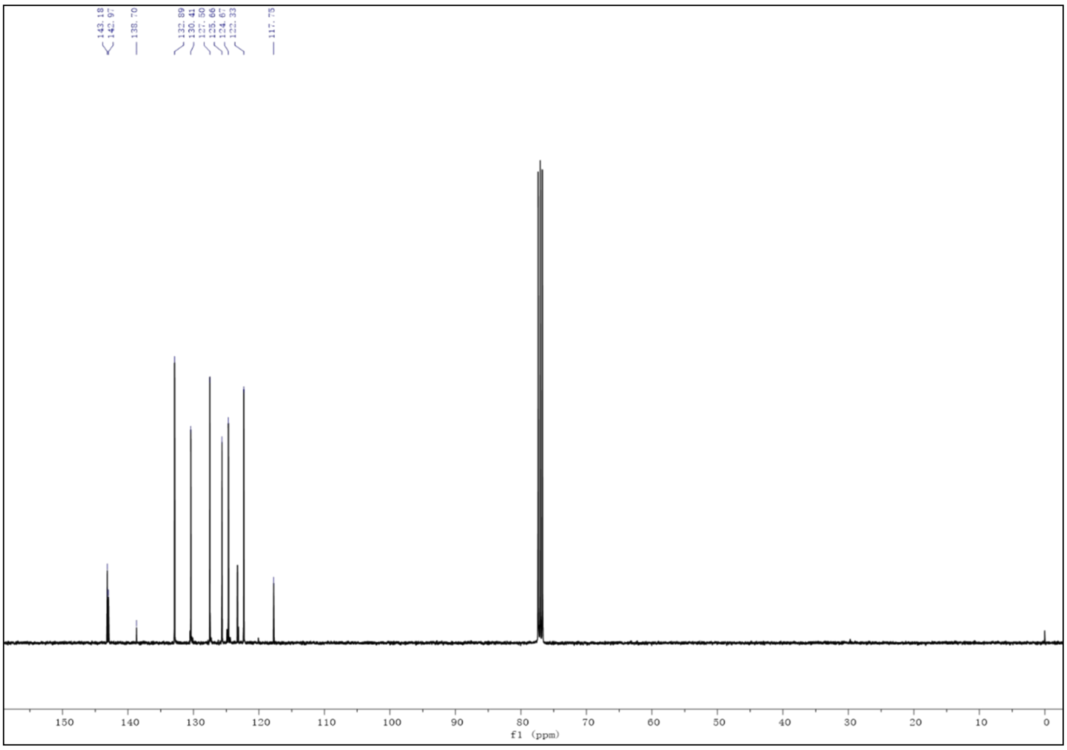


Figure S12. The ^{13}C NMR of ***PSeZ-Ph-Bpin***

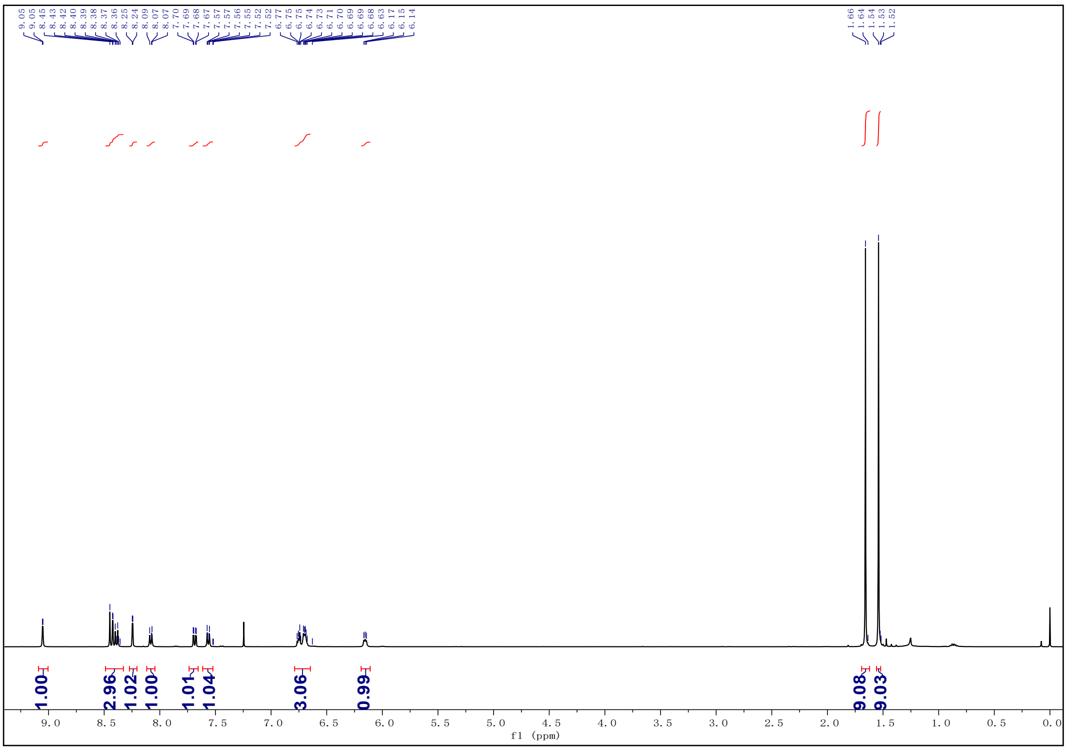


Figure S13. The ^{1}H NMR of ***tBuCzBN-Ph-PXZ***

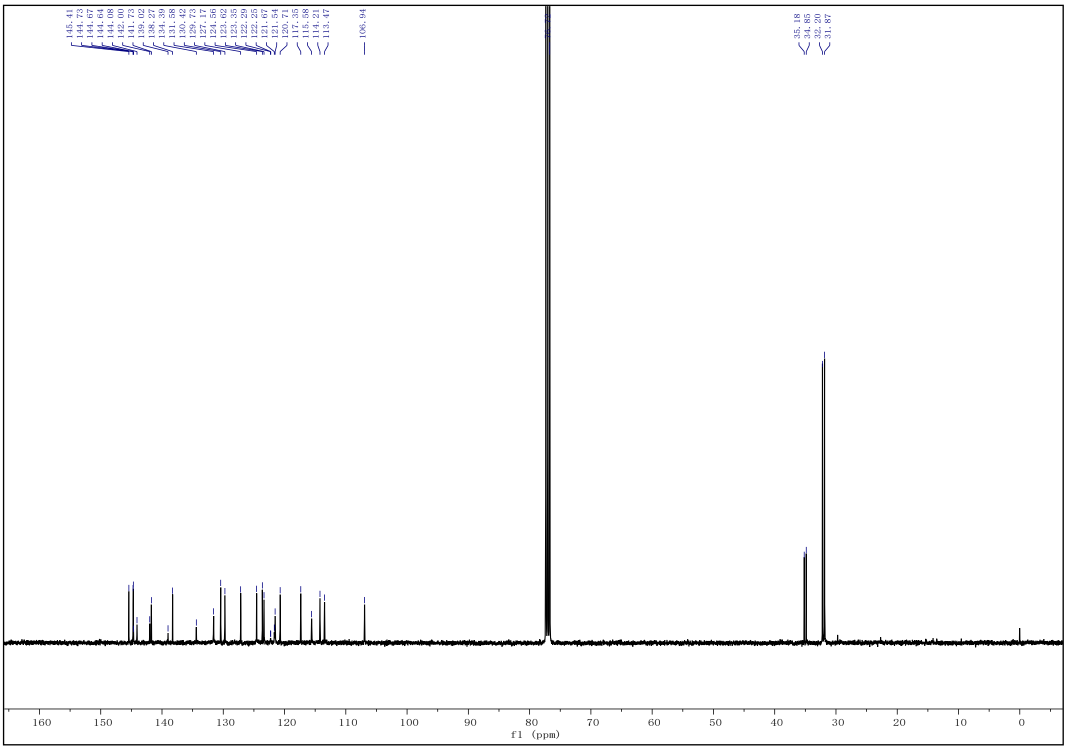


Figure S14. The ^{13}C NMR of ***tBuCzBN-Ph-PXZ***

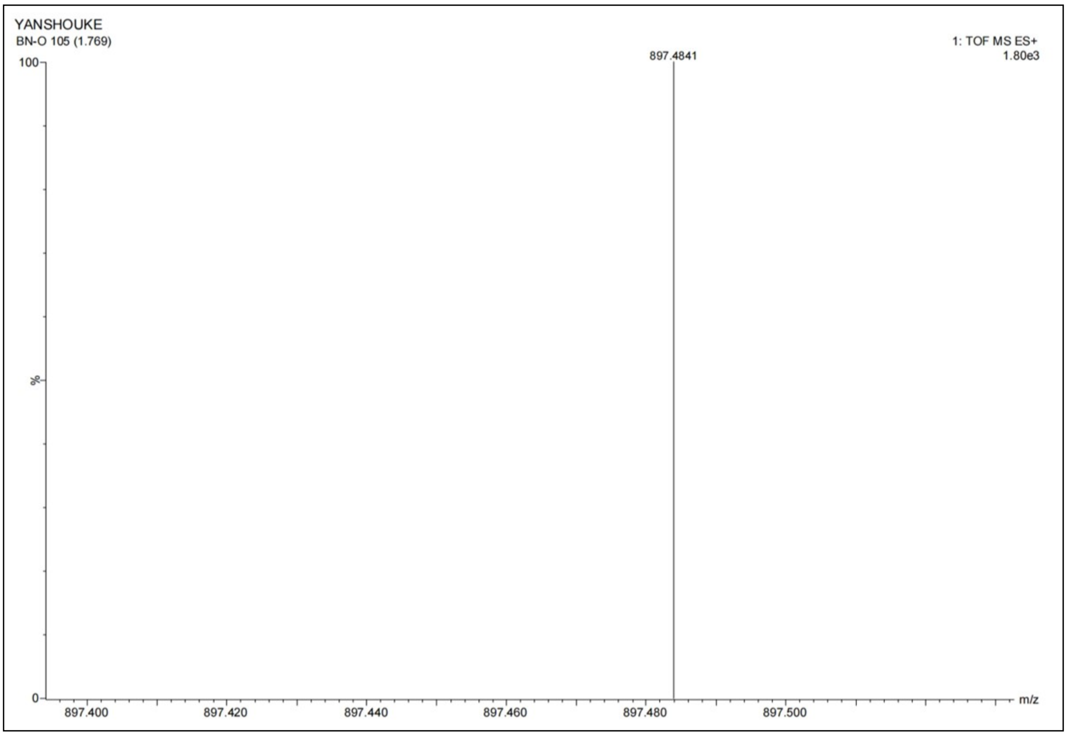


Figure S15. The MS spectrum of ***tBuCzBN-Ph-PXZ***

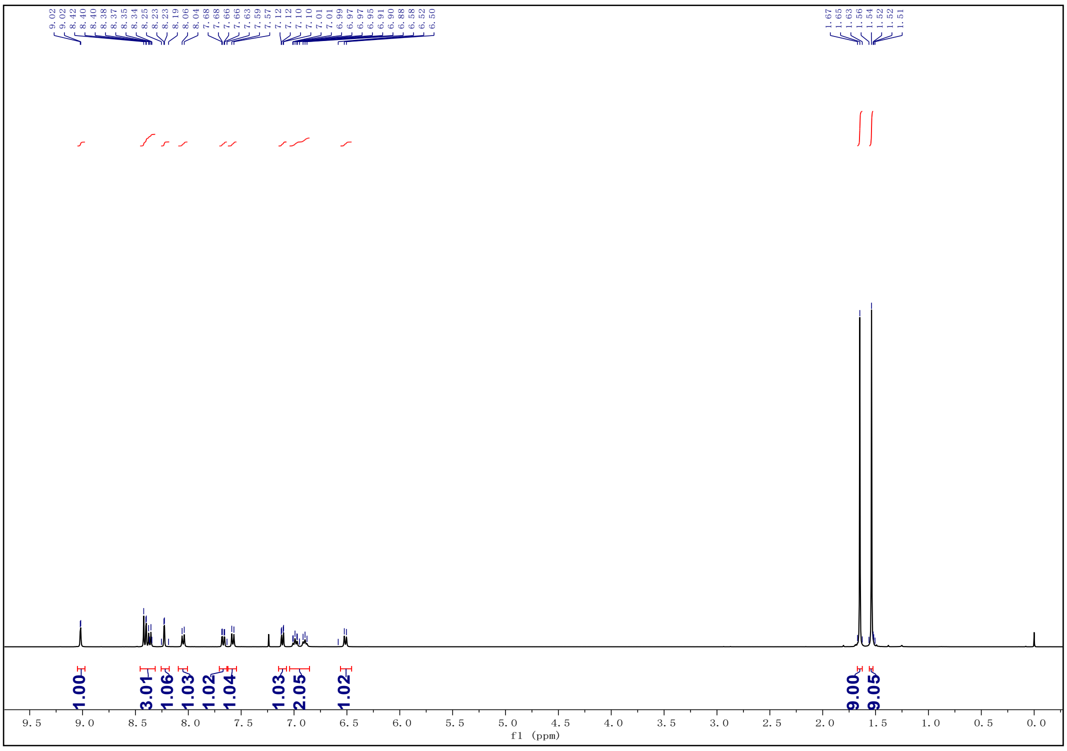


Figure S16. The ^{1}H NMR of ***tBuCzBN-Ph-PTZ***

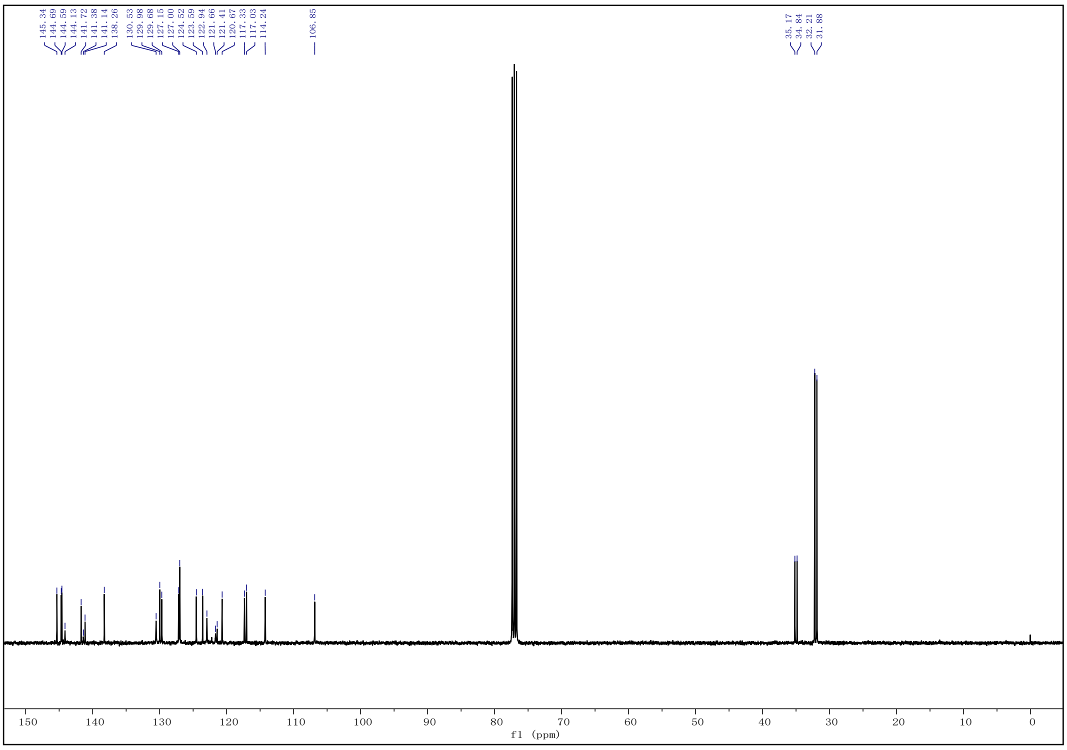


Figure S17. The ^{13}C NMR of ***tBuCzBN-Ph-PTZ***

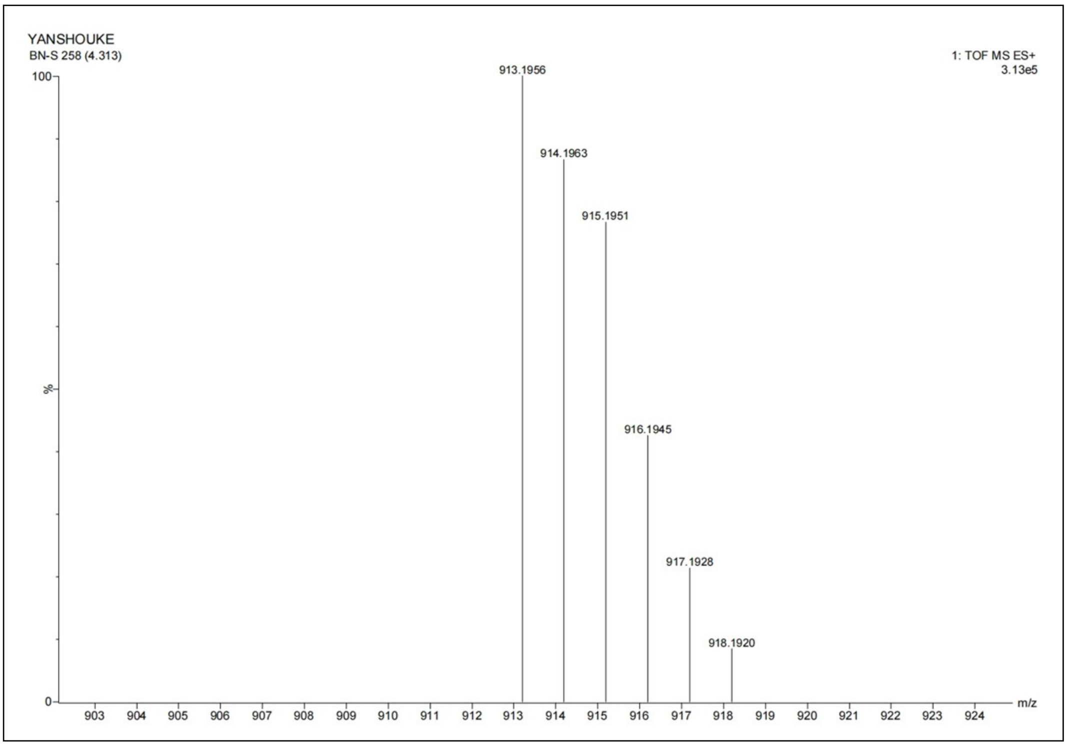


Figure S18. The MS spectrum of ***tBuCzBN-Ph-PTZ***

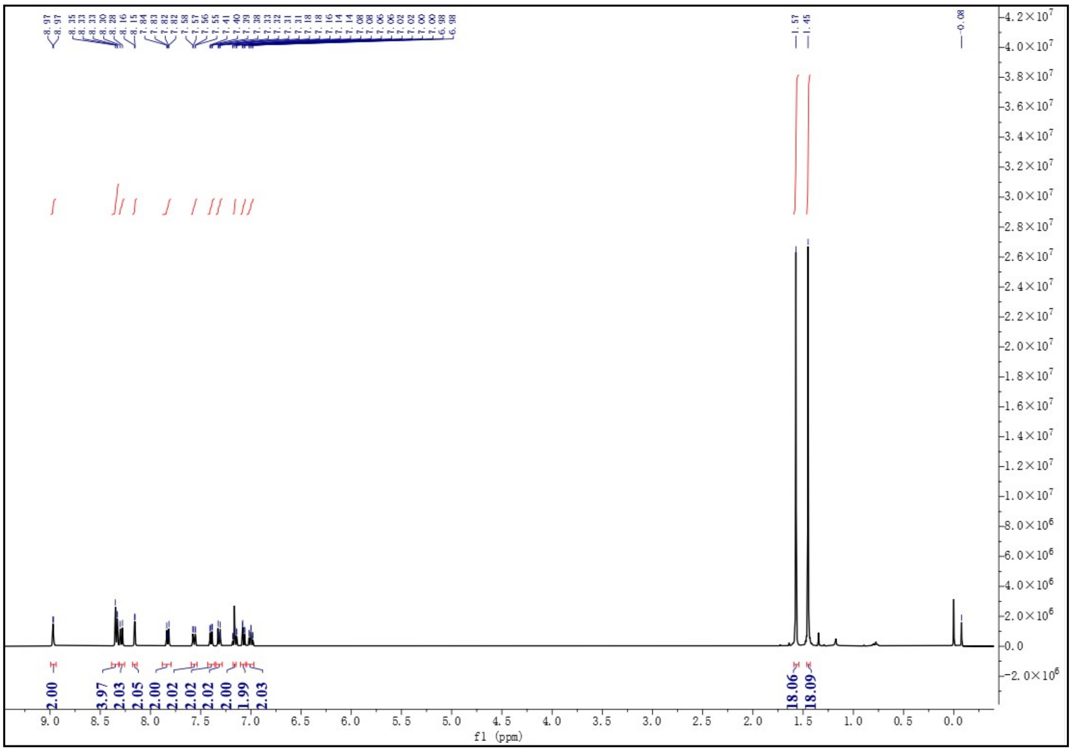


Figure S19. The ^{1}H NMR of ***tBuCzBN-Ph-PSeZ***

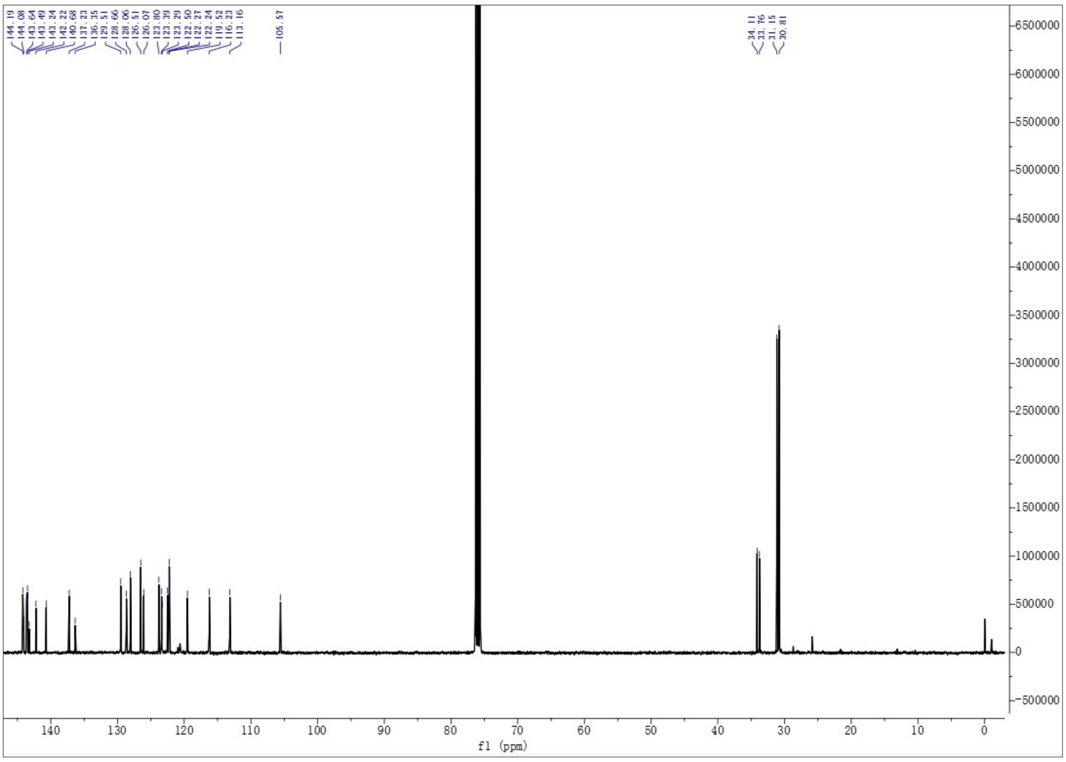


Figure S20. The ^{13}C NMR of ***tBuCzBN-Ph-PSeZ***

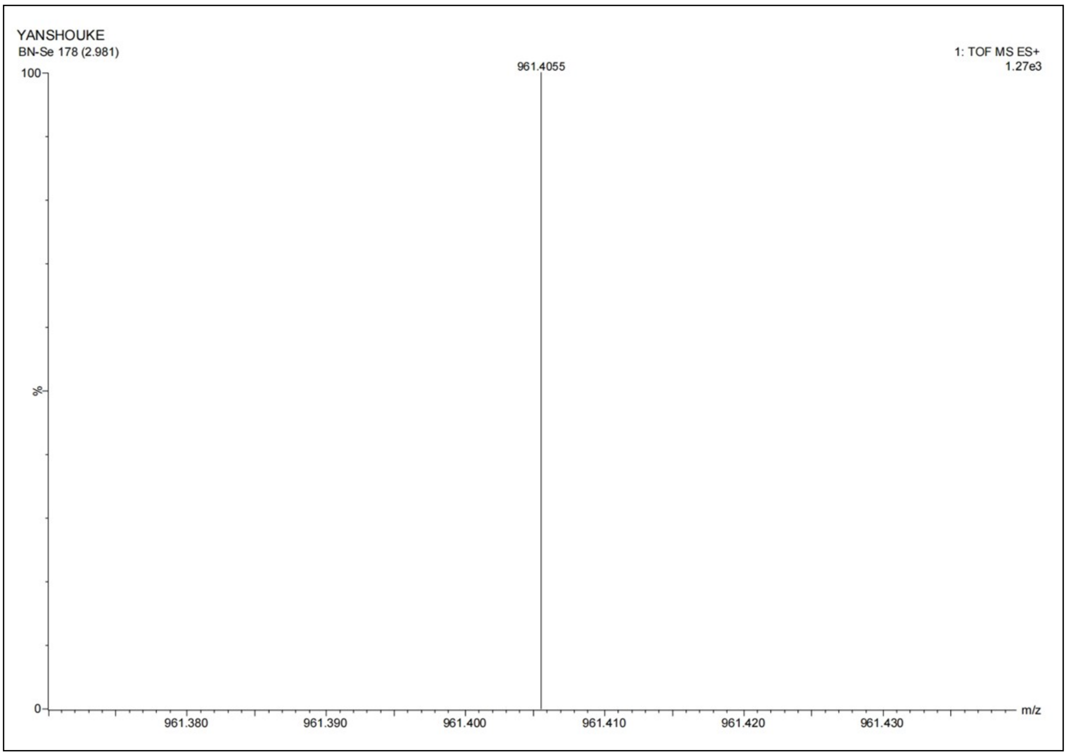


Figure S21. The MS spectrum of ***tBuCzBN-Ph-PSeZ***

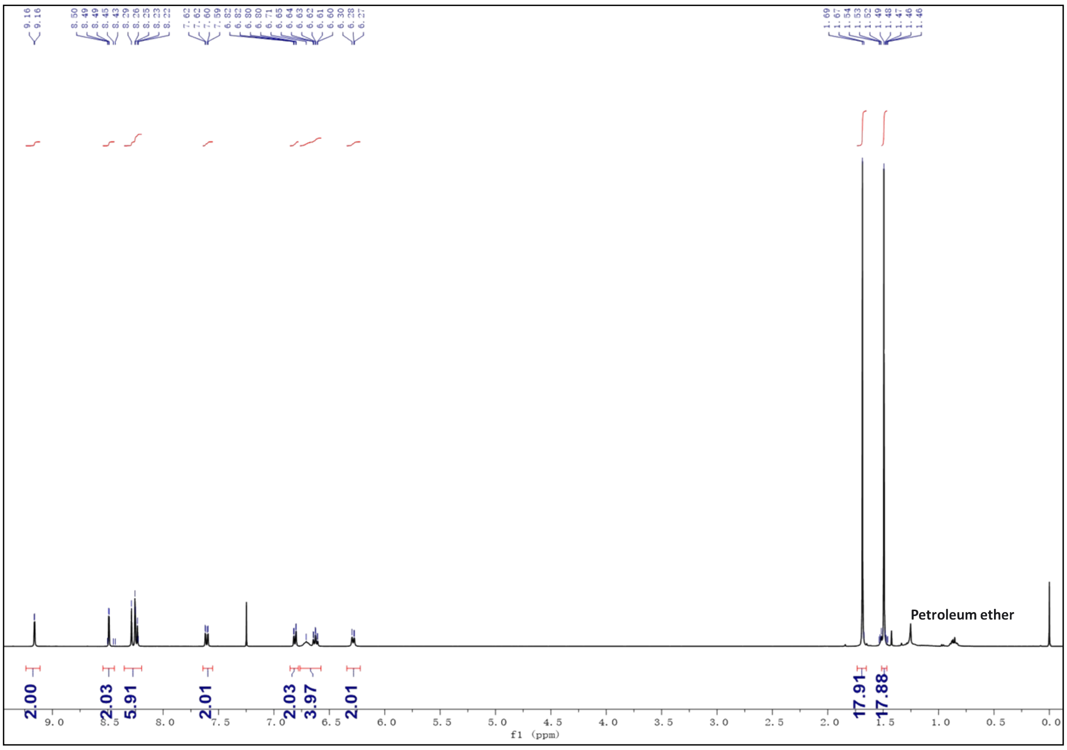


Figure S22. The ^{1}H NMR of ***tBuCzBN-PXZ***

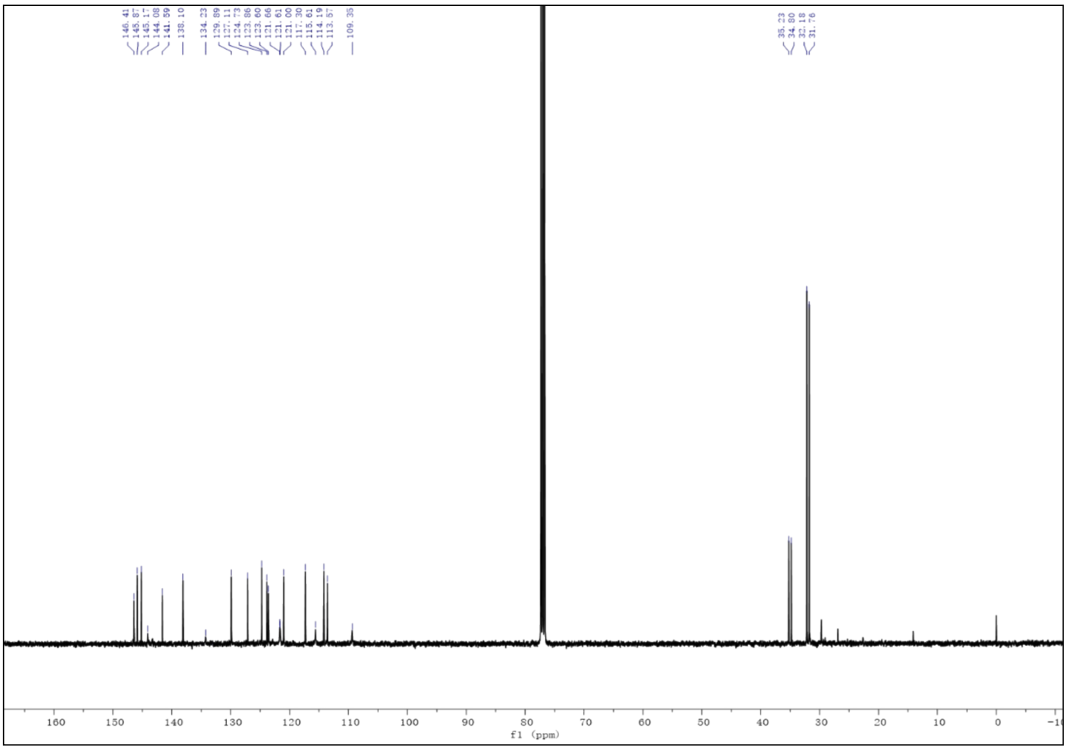


Figure S23. The ^{13}C NMR of ***tBuCzBN-PXZ***

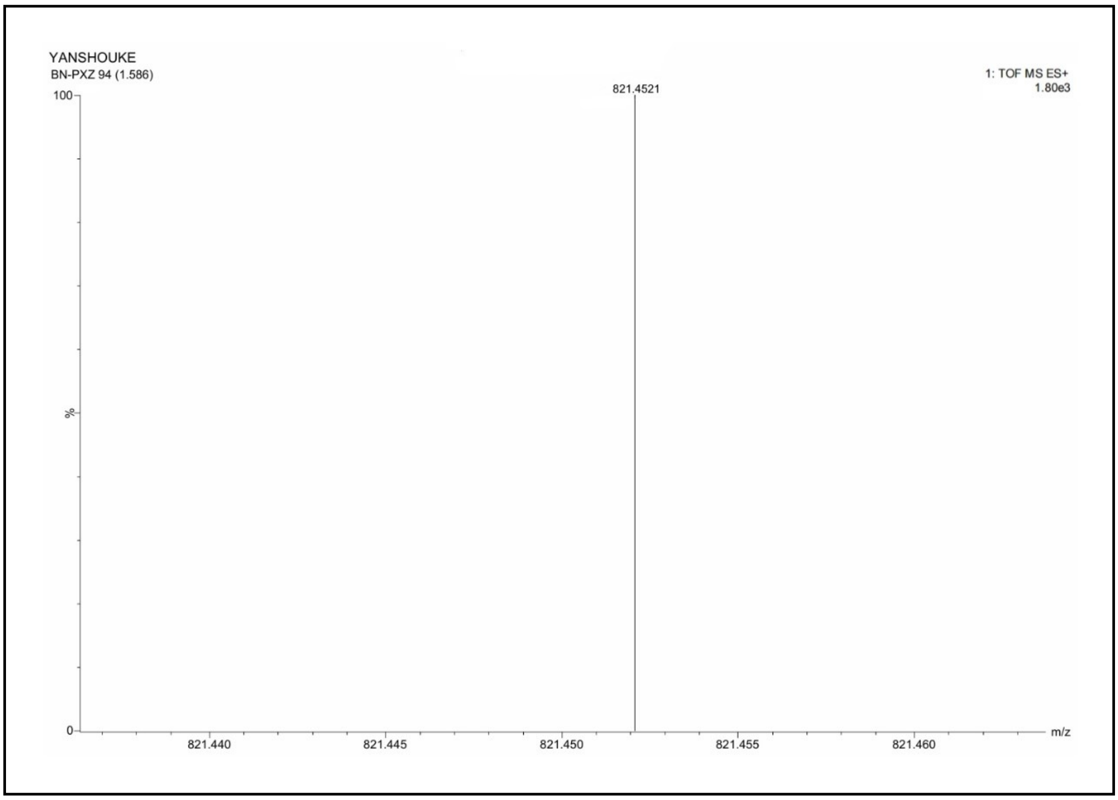


Figure S24. The MS spectrum of ***tBuCzBN-PXZ***

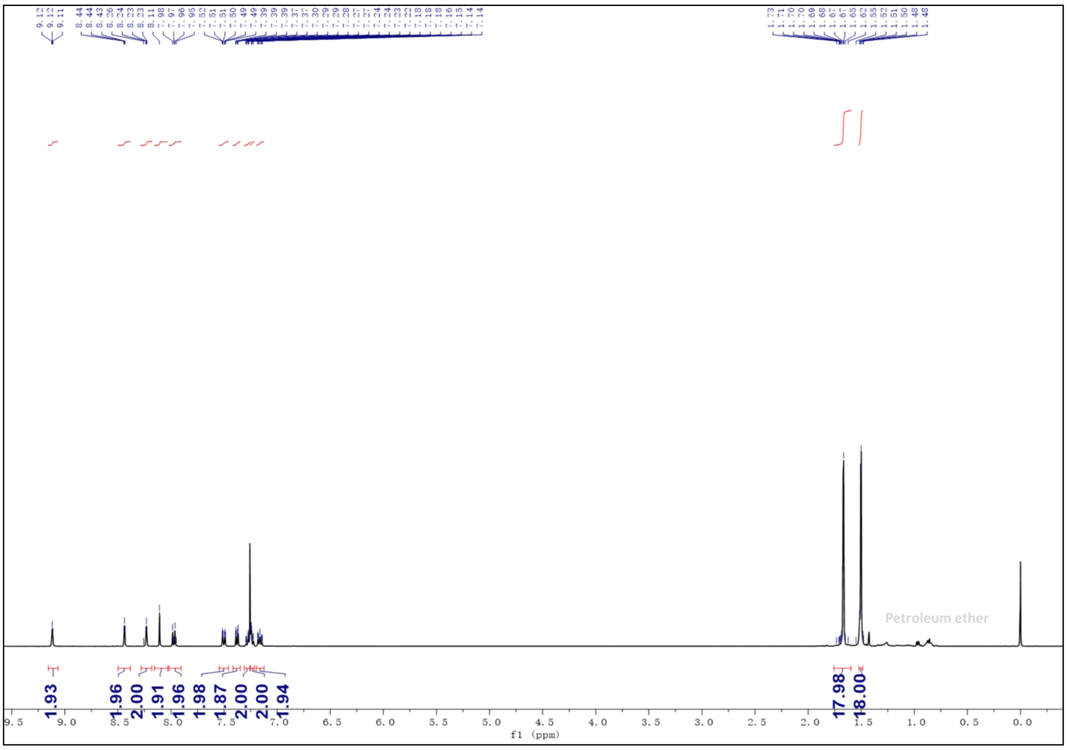


Figure S25. The ^{1}H NMR of ***tBuCzBN-PTZ***

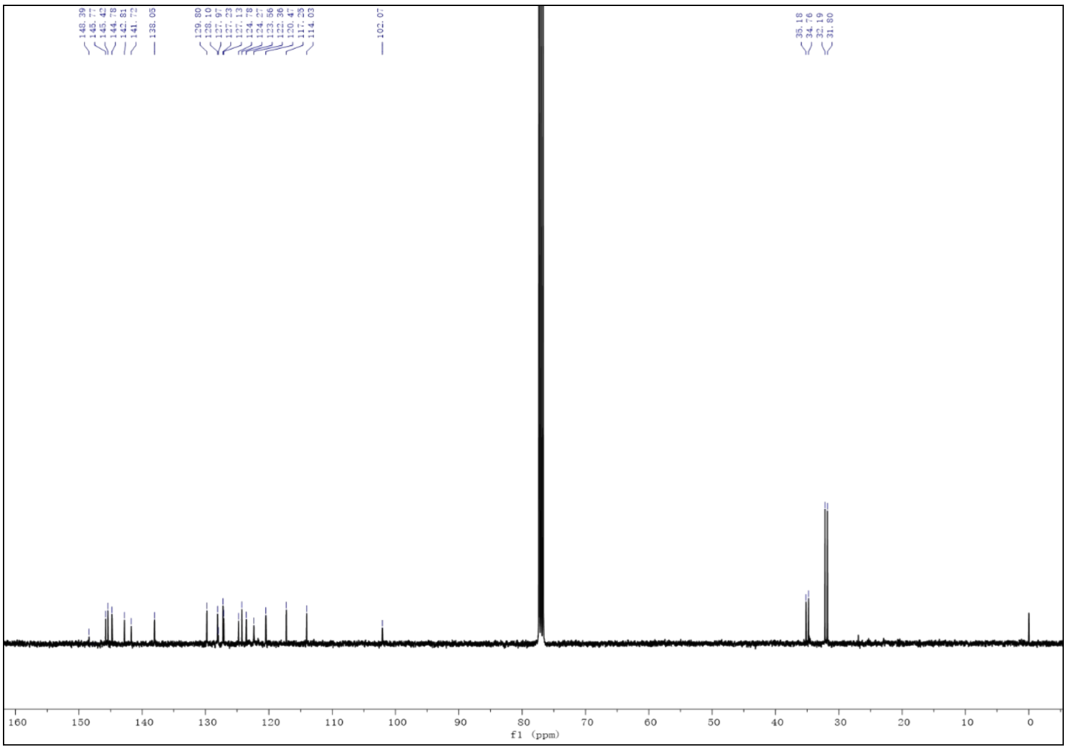


Figure S26. The [13]C NMR of ***tBuCzBN-PTZ***

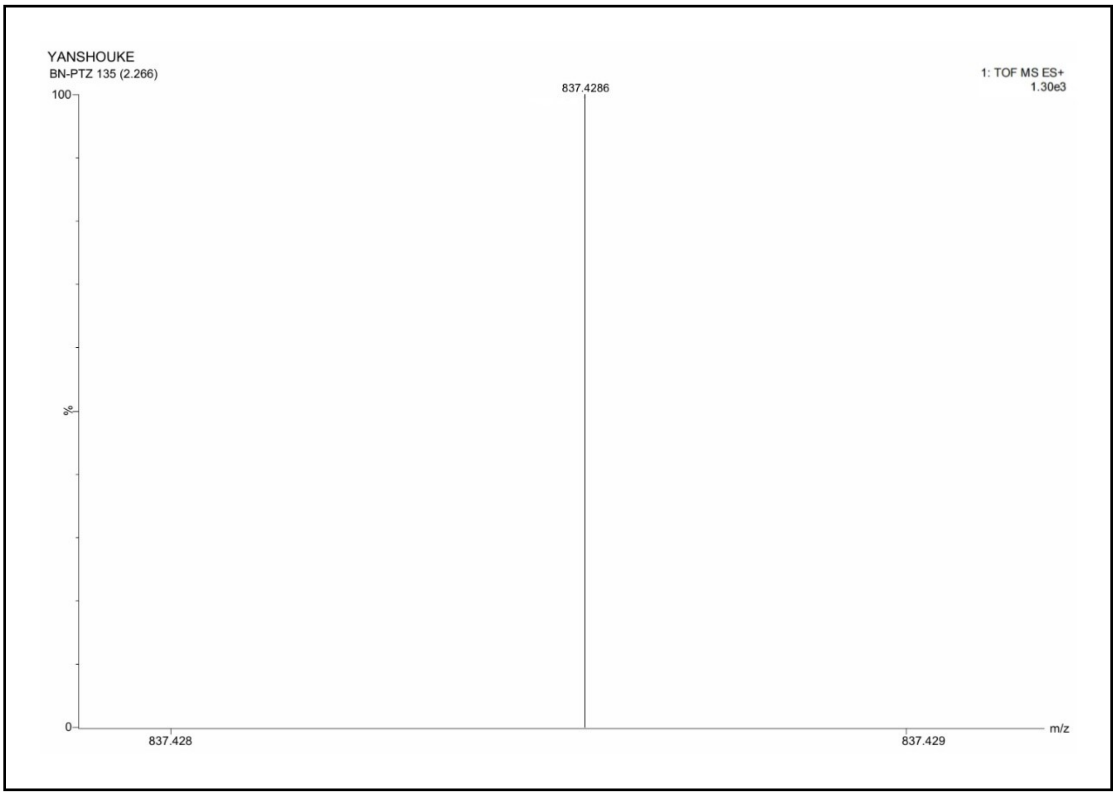


Figure S27. The MS spectrum of ***tBuCzBN-PTZ***

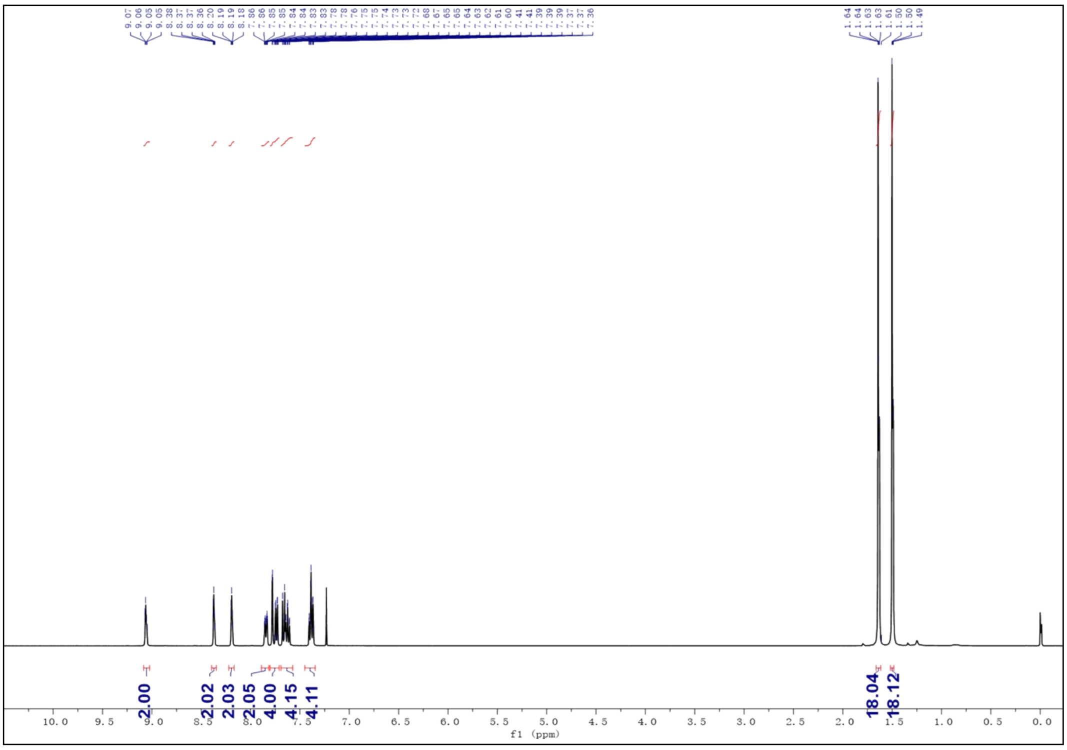


Figure S28. The ^{1}H NMR of ***tBuCzBN-PSeZ***

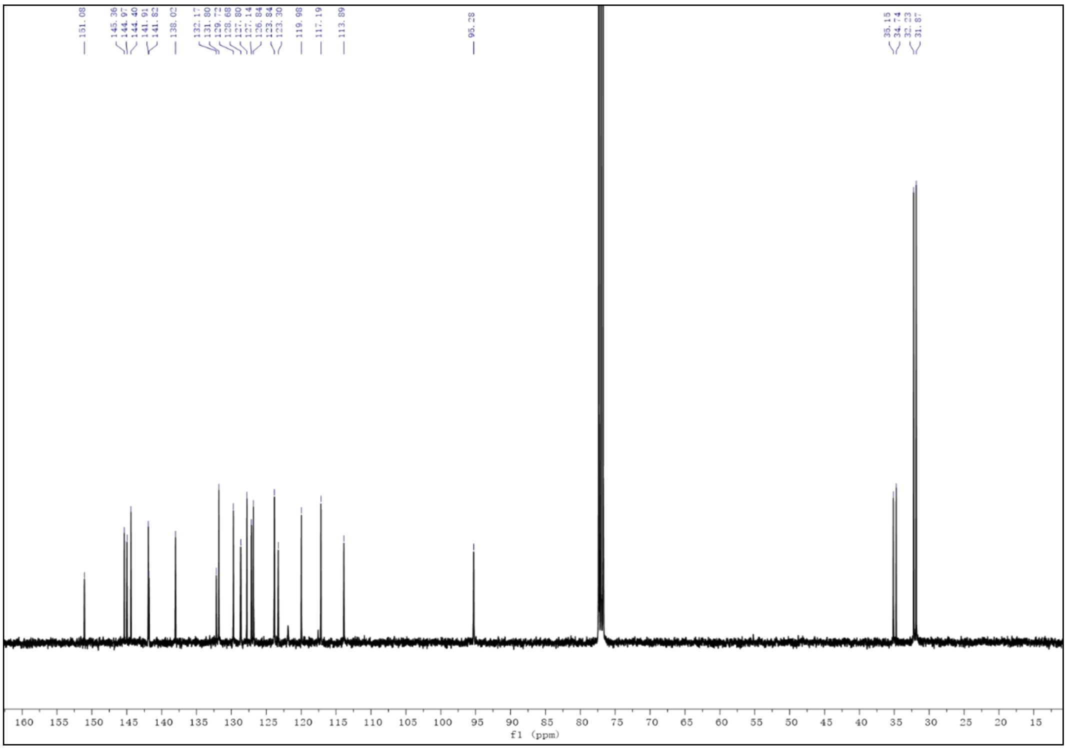


Figure S29. The ^{13}C NMR of ***tBuCzBN-PSeZ***

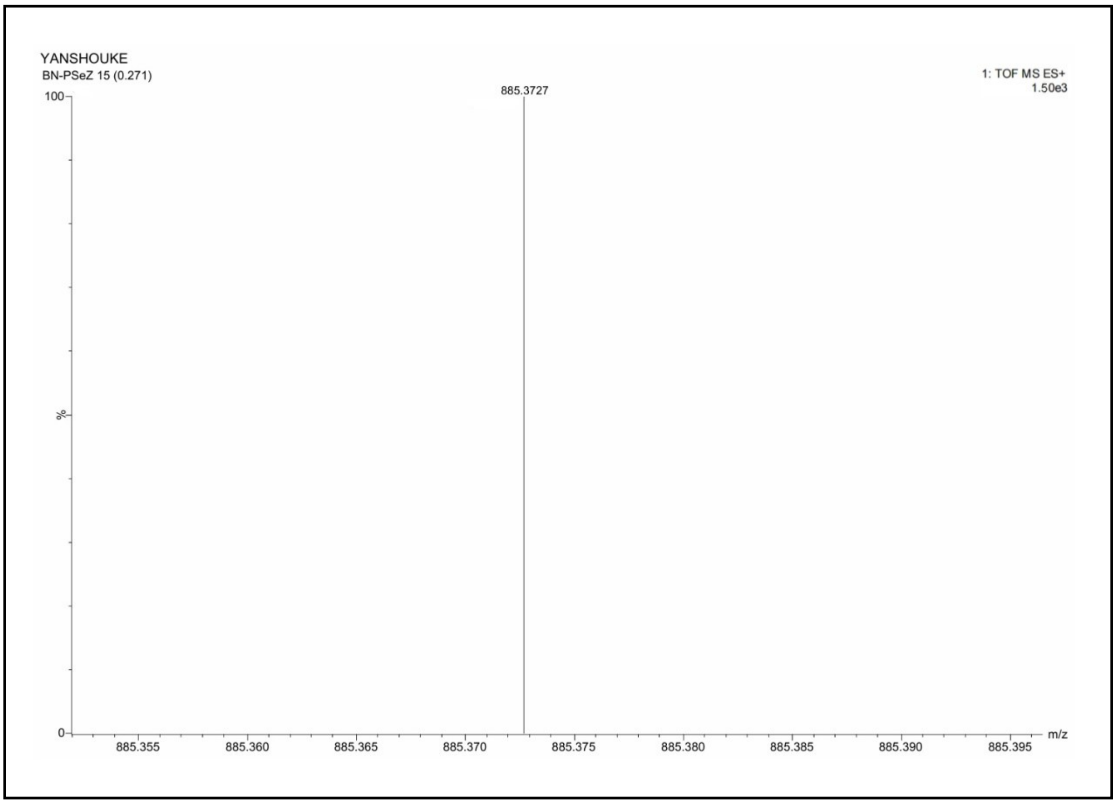


Figure S30. The MS spectrum of ***tBuCzBN-PSeZ***

S3. Thermal analysis

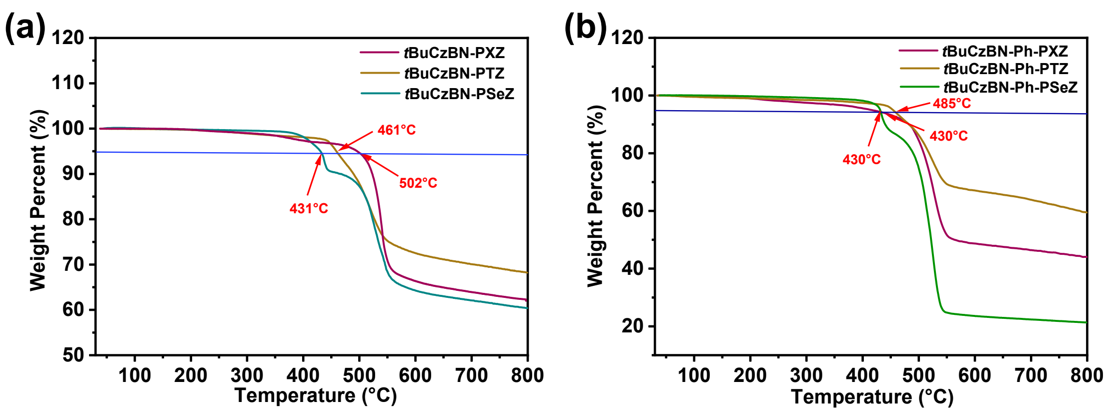


Figure S31. TGA curves of (a) ***t*BuCzBN-PXZ**, ***t*BuCzBN-PTZ**, and ***t*BuCzBN-PSeZ**; (b) ***t*BuCzBN-Ph-PXZ**, ***t*BuCzBN-Ph-PTZ**, and ***t*BuCzBN-Ph-PSeZ**.

S4. Quantum chemical calculation

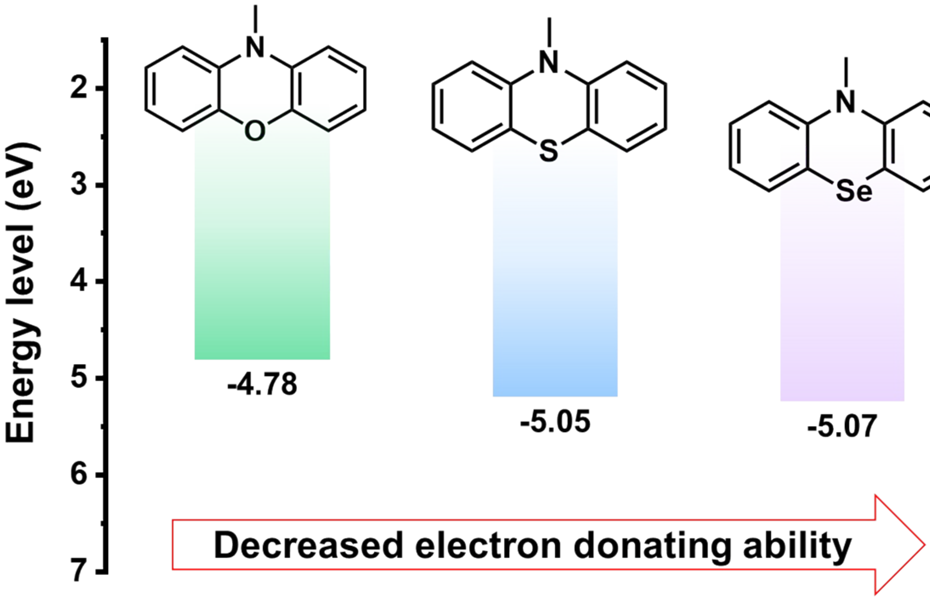


Figure S32. The HOMO levels of methyl-substituted **PXZ**, **PTZ** and **PSeZ** segments.

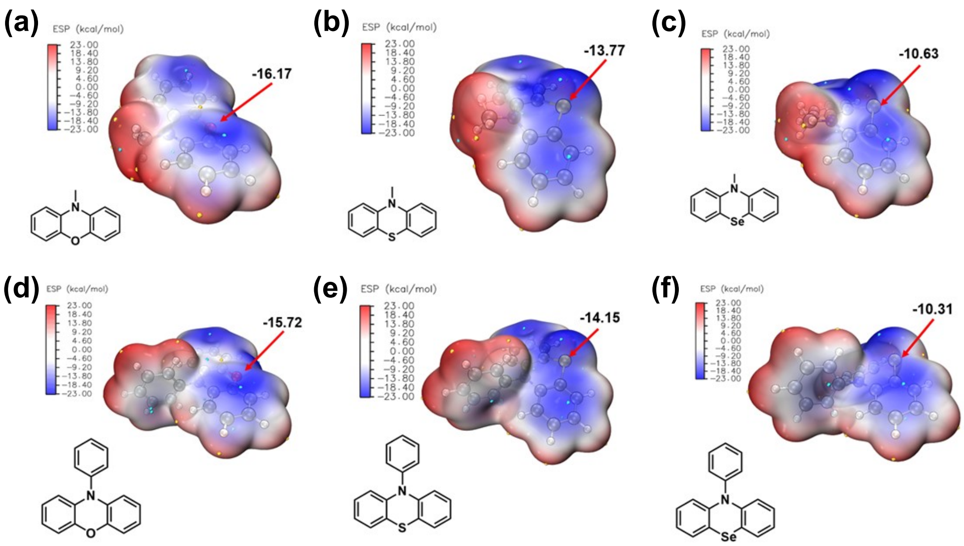


Figure S33. The surface electrostatic distributions of (a) **PXZ**, (b) **PTZ**, (c) **PSeZ**, (d) **Ph-PXZ**, (e) **Ph-PTZ**, and (f) **Ph-PSeZ**.

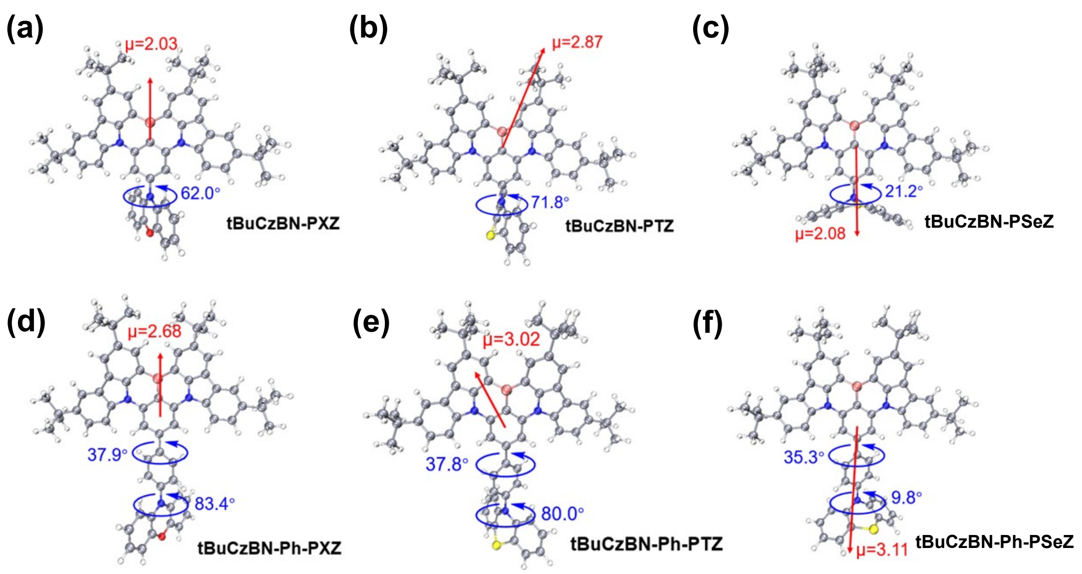


Figure S34. The optmized molecualr structures and the calculated ground-states dipole moments of (a) ***t*BuCzBN-PXZ**, (b) ***t*BuCzBN-PTZ**, (c) ***t*BuCzBN-PSeZ**, (d) ***t*BuCzBN-Ph-PXZ**, (e) ***t*BuCzBN-Ph-PTZ**, and (f) ***t*BuCzBN-Ph-PSeZ**.

S5. Electrochemical and photophysical properties

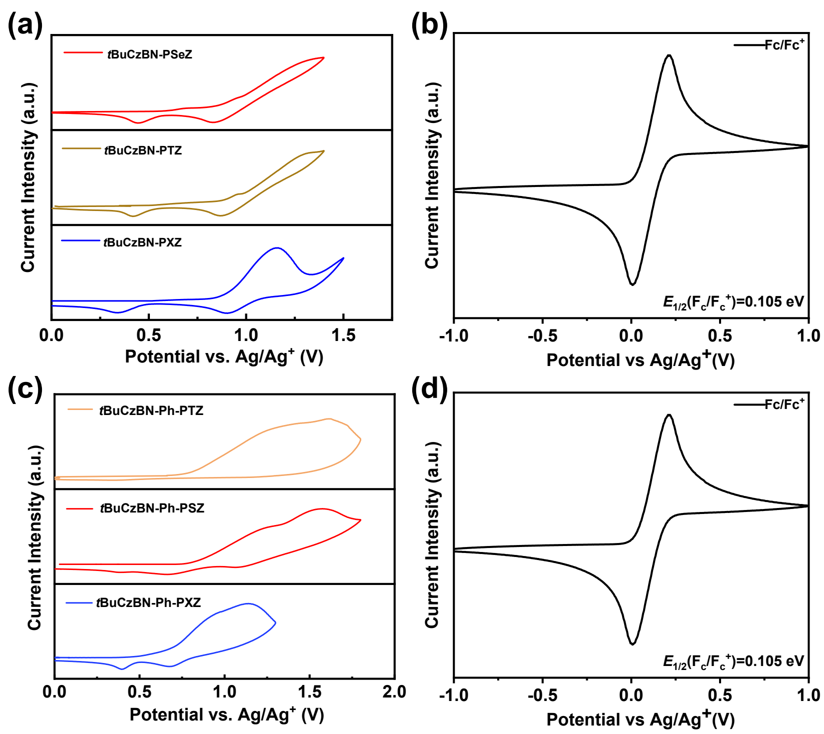


Figure S35. Cyclic voltammetry curves of (a) ***t*BuCzBN-PXZ**, ***t*BuCzBN-PTZ**, and ***t*BuCzBN-PSeZ**; (c) ***t*BuCzBN-Ph-PXZ**, ***t*BuCzBN-Ph-PTZ**, and ***t*BuCzBN-Ph-**

PSeZ, (b) (d) corresponding ferrocene as external reference.

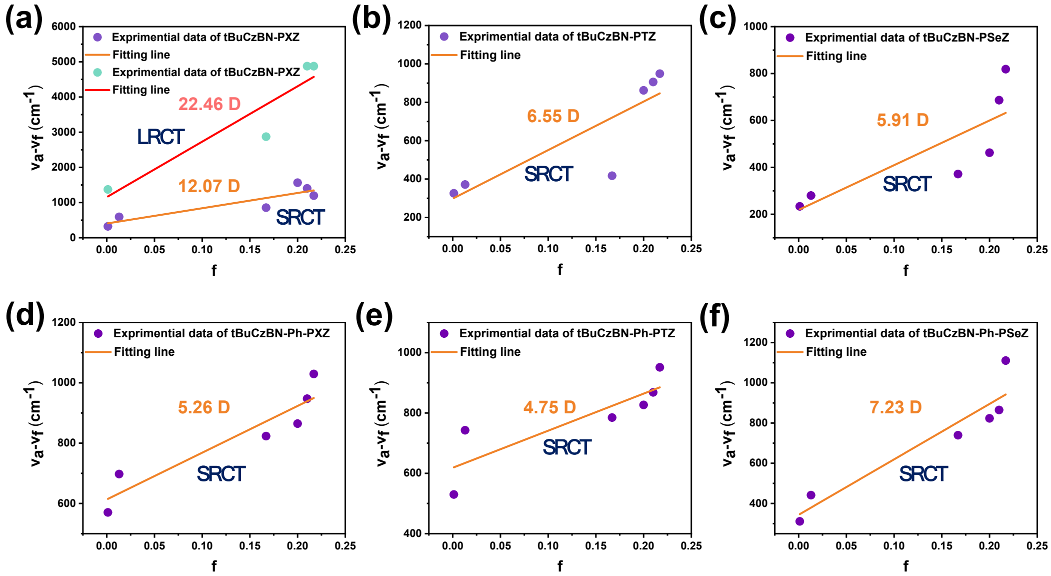


Figure S36. The analysis of solvation effect by the Lippert-Mataga solvatochromic model for (a) ***t*BuCzBN-PTZ**, (b) ***t*BuCzBN-PTZ**, (c) ***t*BuCzBN-PSeZ**, (d) ***t*BuCzBN-Ph-PXZ**, (e) ***t*BuCzBN-Ph-PTZ**, (f) ***t*BuCzBN-Ph-PSeZ**, respectively. The calculated dipole moments are also presented.

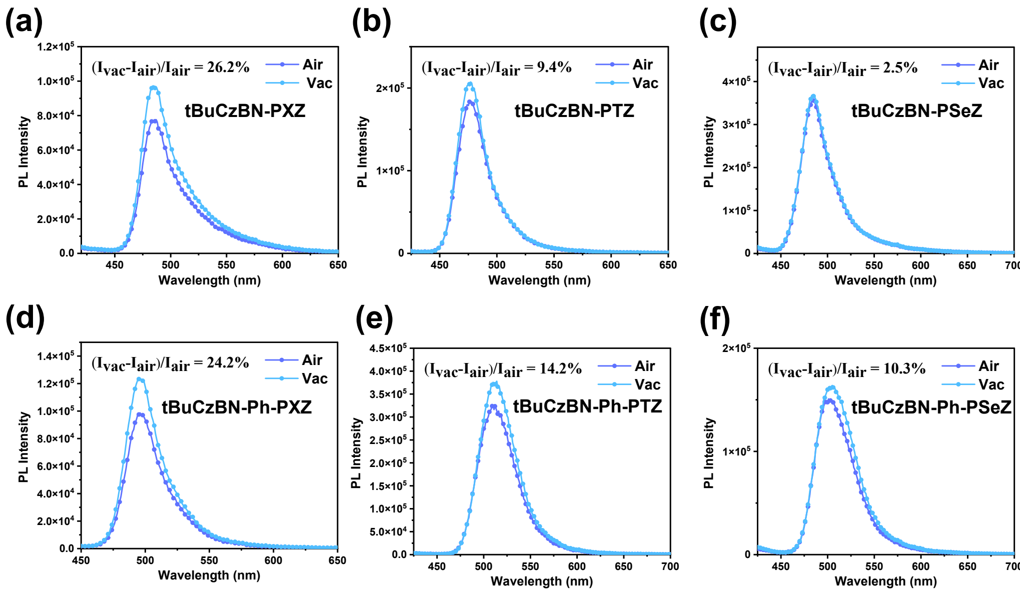


Figure S37. The steady-state PL spectra under air and vacuum of 2 wt% MR-TADF emitters doped in PhCzBCz for (a) ***t*BuCzBN-PTZ**, (b) ***t*BuCzBN-PTZ**, (c) ***t*BuCzBN-PSeZ**, (d) ***t*BuCzBN-Ph-PXZ**, (e) ***t*BuCzBN-Ph-PTZ**, (f) ***t*BuCzBN-Ph-PSeZ**, respectively. The calculated participations of triplet exciton are also presented.

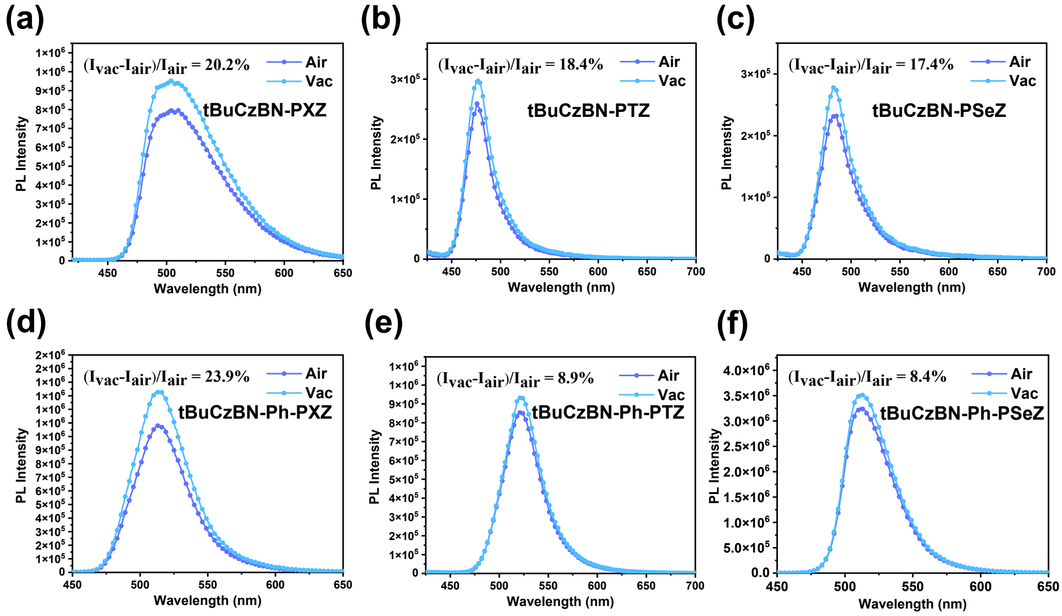


Figure S38. The steady-state PL spectra under air and vacuum of 2 wt% MR-TADF emitters doped in PhCzBCz for (a) ***t*BuCzBN-PTZ**, (b) ***t*BuCzBN-PTZ**, (c) ***t*BuCzBN-PSeZ**, (d) ***t*BuCzBN-Ph-PXZ**, (e) ***t*BuCzBN-Ph-PTZ**, (f) ***t*BuCzBN-Ph-PSeZ**, respectively. The calculated participations of triplet exciton are also presented.

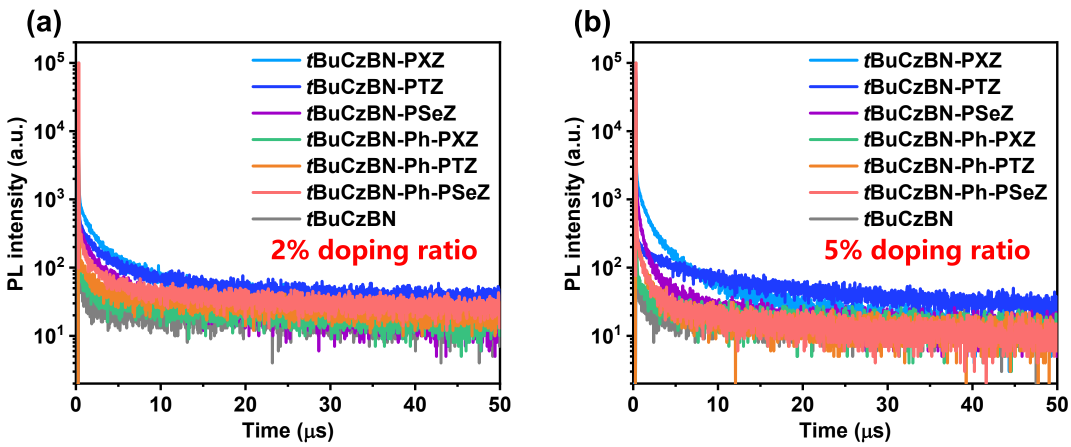


Figure S39. The transient PL decay spectra under vacuum of (a) 2 wt% MR-TADF emitters and (b) 5 wt% MR-TADF emitters doped in PhCzBCz.

Table S1. Photophysical data for Emitters (2 wt% in PhCzBCz).

Emitter	λ_{PL} [nm][b]	FWHM [nm][c]	Φ_{PL} [%][e]	τ_p/τ_d [ns]/ [μs][f]	φ_{DF} [%][g]	k_r^S [10^7 s^{-1}][h]	k_{RISC} [10^5 s^{-1}][i]	k_{ISC} [10^6 s^{-1}][j]
*t*BuCzBN-PXZ	484	36	96	27.1/5.7	83	3.1	1.6	4.8

*t*BuCzBN-PTZ	485	35	93	23.8/6.7	83	3.4	1.3	5.5
*t*BuCzBN-PSeZ	480	32	90	15.2/5.8	89	5.2	1.4	8.5
*t*BuCzBN-Ph-PXZ	496	32	96	12.5/21.7	61	6.6	0.4	10.4
*t*BuCzBN-Ph-PTZ	511	45	95	14.7/13.6	47	5.6	0.7	8.8
*t*BuCzBN-Ph-PSeZ	504	52	95	11.4/7.07	40	7.3	1.3	11.4

Table S2. Photophysical data for Emitters (5 wt% in PhCzBCz).

Emitter	λ_{PL} [nm][b]	FWHM [nm][c]	Φ_{PL} [%][e]	τ_p/τ_d [ns]/ [μs][f]	φ_{DF} [%][g]	k_r^S [10^7 s^{-1}][h]	k_{RISC} [10^5 s^{-1}][i]	k_{ISC} [10^6 s^{-1}][j]
*t*BuCzBN-PXZ	504	70	92	13.1/0.9	49	5.9	2.3	9.9
*t*BuCzBN-PTZ	477	36	91	16.2/13.3	50	4.8	0.9	8.0
*t*BuCzBN-PSeZ	474	24	90	17.3/6.74	30	4.5	1.2	7.5
*t*BuCzBN-Ph-PXZ	514	44	95	14.7/0.14	47	5.6	0.7	8.8
*t*BuCzBN-Ph-PTZ	523	45	94	11.6/16.0	53	4.0	1.4	4.6
*t*BuCzBN-Ph-PSeZ	514	42	96	12.0/5.46	56	6.1	2.7	9.5

S6. Morphologic analysis

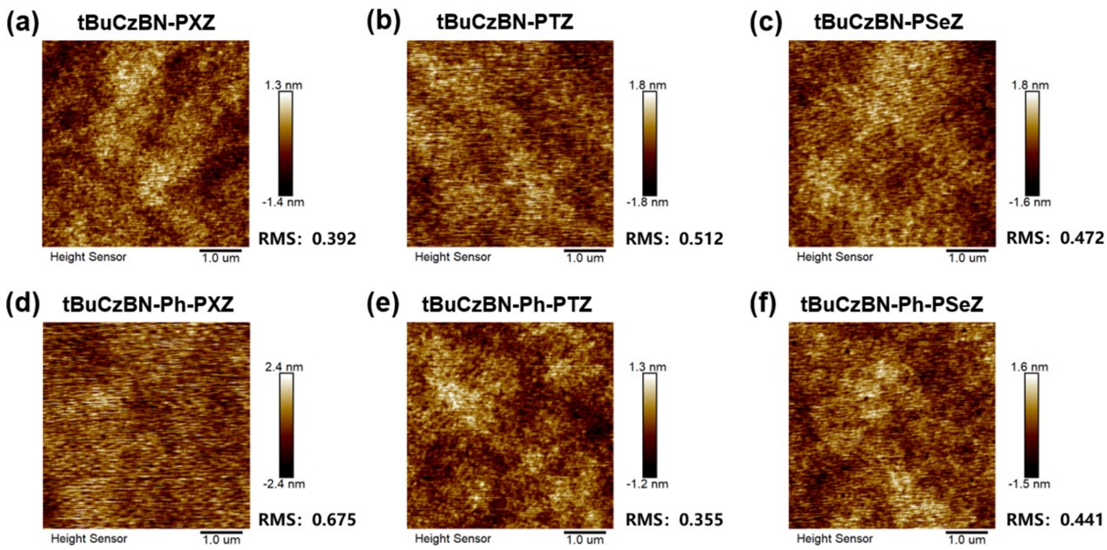


Figure S40. The AFM height images and their RMS values of spin-coating thin films: (a) ***t*BuCzBN-PXZ**, (b) ***t*BuCzBN-PTZ**, (c) ***t*BuCzBN-PSeZ**, (d) ***t*BuCzBN-Ph-PXZ**,

(e) ***t*BuCzBN-Ph-PTZ**, and (f) ***t*BuCzBN-Ph-PSeZ** based blended films. RMS values of the whole scanning area are shown in the images.

S7. OLED device and electroluminescent performances

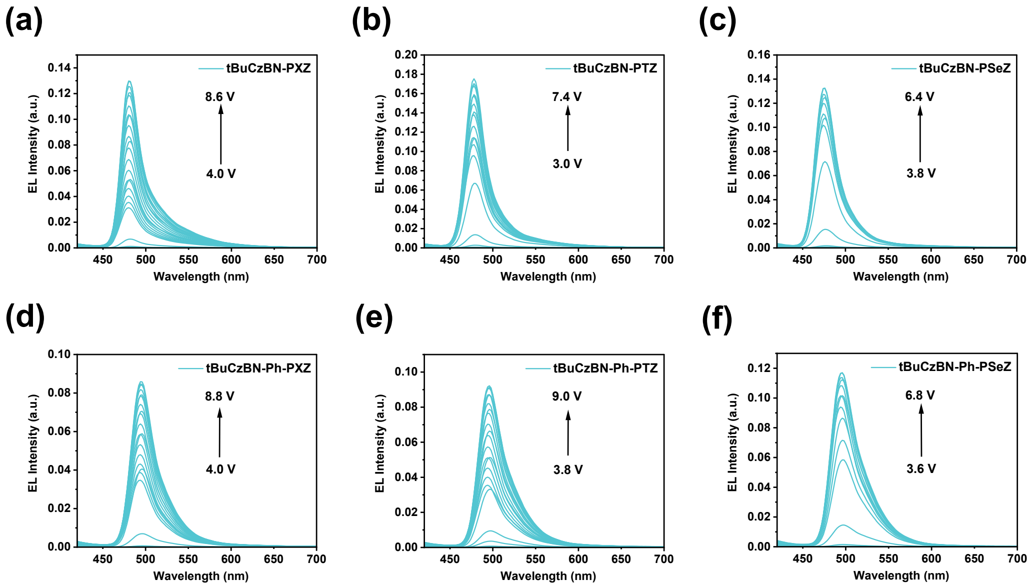


Figure S41. The EL spectral stability of the devices for (a) ***t*BuCzBN-PXZ**, (b) ***t*BuCzBN-PTZ**, (c) ***t*BuCzBN-PSeZ**, (d) ***t*BuCzBN-Ph-PXZ**, (e) ***t*BuCzBN-Ph-PTZ**, and (f) ***t*BuCzBN-Ph-PSeZ**.

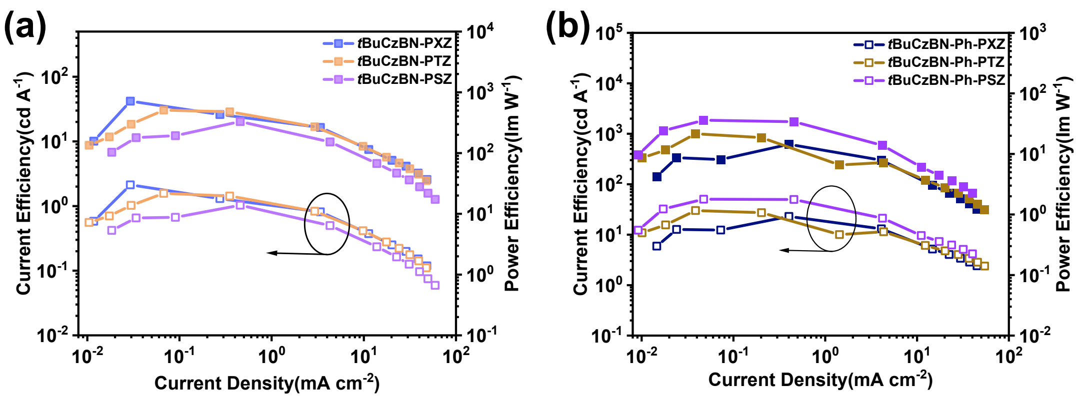


Figure S42. Current Efficiency-Current Density curves and Power Efficiency-Current Density curves of (a) ***t*BuCzBN-PXZ**, ***t*BuCzBN-PTZ**, and ***t*BuCzBN-PSeZ**; (b) ***t*BuCzBN-Ph-PXZ**, ***t*BuCzBN-Ph-PTZ**, and ***t*BuCzBN-Ph-PSeZ**.

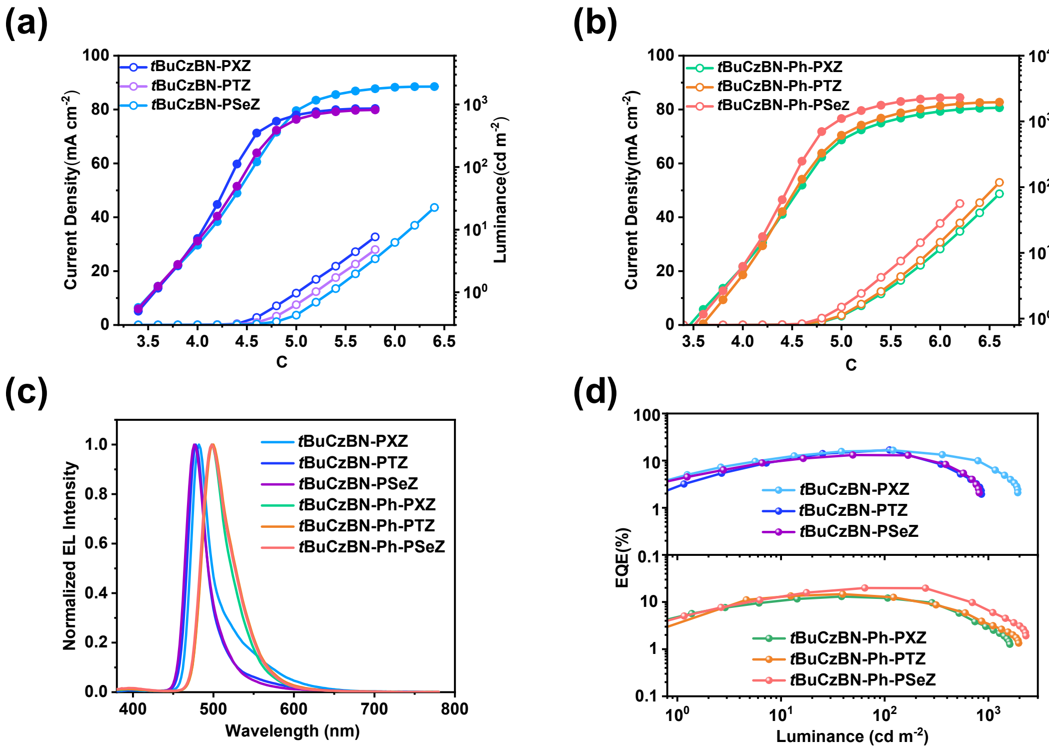


Figure S43. (a) Current density and luminance versus voltage (*J-V-L*) characteristics for ***t*BuCzBN-PXZ**, ***t*BuCzBN-PTZ**, and ***t*BuCzBN-PSeZ** (2 wt% in PhCzBCz); (b) Current density and luminance versus voltage (*J-V-L*) characteristics for ***t*BuCzBN-Ph-PXZ**, ***t*BuCzBN-Ph-PTZ**, and ***t*BuCzBN-Ph-PSeZ** (2 wt% in PhCzBCz); (c) the EL spectra detected at 6 V; (d) external quantum efficiency-luminance (*EQE-L*) plots.

Table S3. The EL properties of solution-processable OLEDs withou TADF sensitizer (2 wt% emitter in PhCzBCz).

Emitter (2 wt.% in PhCzBCz)	V_{on} [V][a]	*EL/FWHM* [nm][b]	L_{max} [cd m^{-2}][c]	CE_{max} [cd A^{-1}][d]	PE_{max} [lm W^{-1}][e]	EQE_{max} [%][f]	CIE_g
*t*BuCzBN-PXZ	3.8	482/28	1923	36.4	24.8	16.6	(0.18, 0.38)
*t*BuCzBN-PTZ	3.8	478/28	858	25.8	18.4	16.8	(0.14, 0.22)
*t*BuCzBN-PSeZ	4.0	476/29	816	19.2	13.7	13.2	(0.12, 0.23)
*t*BuCzBN-Ph-PXZ	3.6	496/36	1612	36.7	26.2	13.1	(0.15, 0.58)
*t*BuCzBN-Ph-PTZ	3.8	500/44	1959	42.07	30.0	14.3	(0.16, 0.58)
*t*BuCzBN-Ph-PSeZ	3.6	500/46	2304	57.4	41.0	19.8	(0.13, 0.51)

[a] The turn-on voltages; [b] the electronluminance spectral peaks and full width at half maximum detected at 6 V; [c] the maximum luminance; [d] the maximum current efficiencies; [e] the maximum power efficiencies; [f] the maximum

external quantum efficiency; [g] the coordinates of CIE.

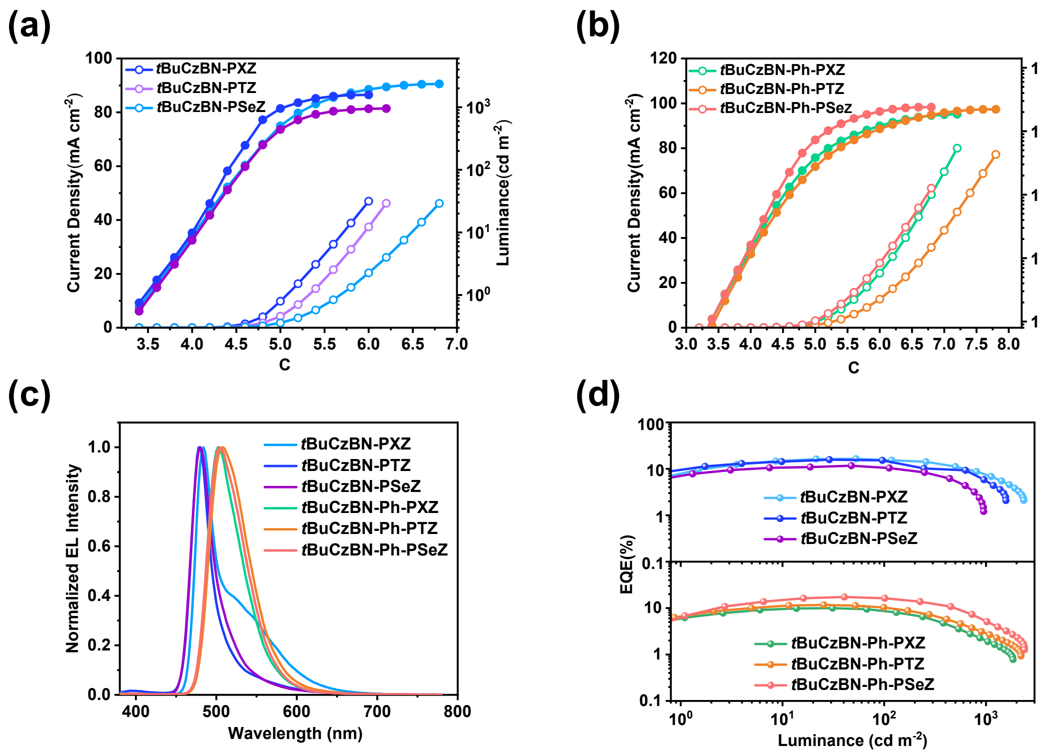


Figure S44. (a) Current density and luminance versus voltage (*J-V-L*) characteristics for ***t*****BuCzBN-PXZ**, ***t*****BuCzBN-PTZ**, and ***t*****BuCzBN-PSeZ** (5 wt% in PhCzBCz); (b) Current density and luminance versus voltage (*J-V-L*) characteristics for ***t*****BuCzBN-Ph-PXZ**, ***t*****BuCzBN-Ph-PTZ**, and ***t*****BuCzBN-Ph-PSeZ** (5 wt% in PhCzBCz); (c) the EL spectra detected at 6 V; (d) external quantum efficiency-luminance (*EQE-L*) plots.

Table S4. The EL properties of solution-processable OLEDs withou TADF sensitizer (2 wt% emitter in PhCzBCz).

Emitter (5 wt.% in PhCzBCz)	V_{on} [V][a]	*EL/FWHM* [nm][b]	L_{max} [cd m^{-2}][c]	CE_{max} [cd A^{-1}][d]	PE_{max} [lm W^{-1}][e]	EQE_{max} [%][f]	CIE_g
*t*BuCzBN-PXZ	3.6	480/30	2356	42.2	31.2	16.5	(0.22, 0.43)
*t*BuCzBN-PTZ	3.6	478/28	1572	26.6	19.9	15.8	(0.14, 0.27)
*t*BuCzBN-PSeZ	3.6	480/33	950	20.0	14.3	11.7	(0.13, 0.29)
*t*BuCzBN-Ph-PXZ	3.4	504/48	1849	31.4	24.2	10.0	(0.18, 0.63)
*t*BuCzBN-Ph-PTZ	3.6	508/54	2212	38.7	29.5	11.7	(0.20, 0.64)
*t*BuCzBN-Ph-PSeZ	3.4	504/52	2394	56.5	42.3	17.3	(0.18, 0.62)

[a] The turn-on voltages; [b] the electronluminance spectral peaks and full width at half maximum detected at 6 V; [c] the maximum luminance; [d] the maximum current efficiencies; [e] the maximum power efficiencies; [f] the maximum external quantum efficiency; [g] the coordinates of CIE.

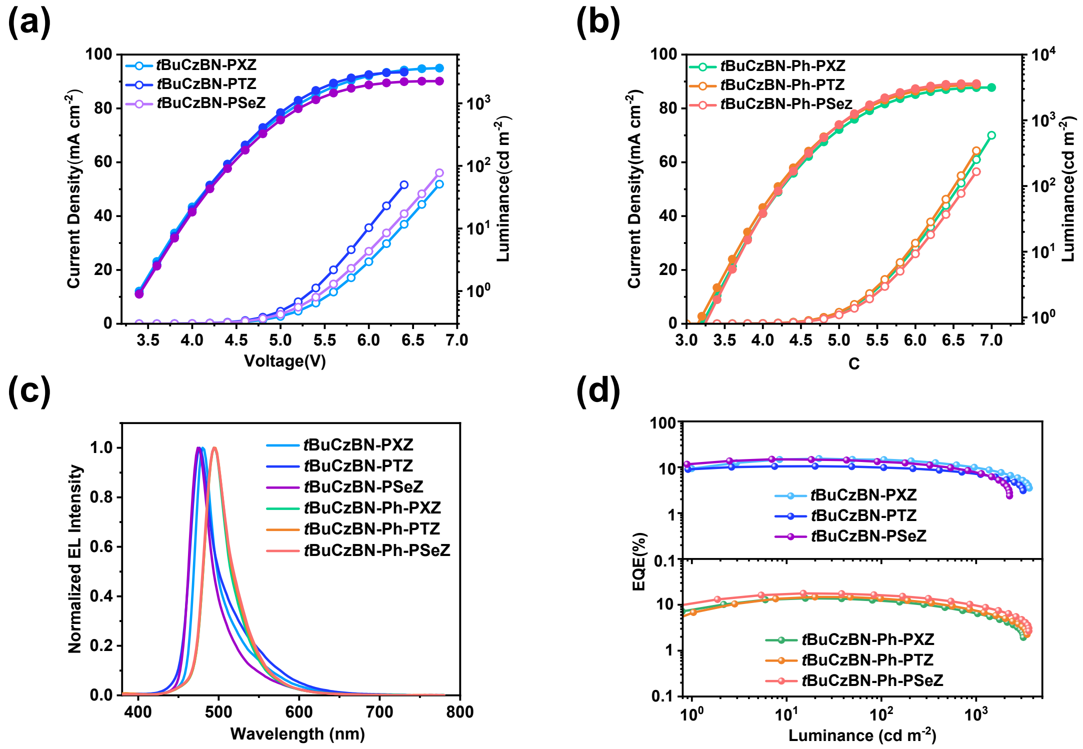


Figure S45. (a) Current density and luminance versus voltage (*J-V-L*) characteristics for ***t*BuCzBN-PXZ**, ***t*BuCzBN-PTZ**, and ***t*BuCzBN-PSeZ**; (b) Current density and luminance versus voltage (*J-V-L*) characteristics for ***t*BuCzBN-Ph-PXZ**, ***t*BuCzBN-Ph-PTZ**, and ***t*BuCzBN-Ph-PSeZ**; (c) the EL spectra detected at 6 V; (d) external quantum efficiency-luminance (*EQE-L*) plots.

Table S5. The EL properties of solution-processable OLEDs withou TADF sensitizer.

Emitter (1 wt.% and 10 wt.%5Cz-TRZ in PhCzBCz)	V_{on} [V][a]	*EL/FWHM* [nm][b]	L_{max} [cd m^{-2}][c]	CE_{max} [cd A^{-1}][d]	PE_{max} [lm W^{-1}][e]	EQE_{max} [%][f]	CIE_g
*t*BuCzBN-PXZ	3.6	482/29	3644	31.7	25.1	15.4	(0.17, 0.37)
*t*BuCzBN-PTZ	3.6	474/31	1572	20.4	17.3	10.4	(0.17, 0.31)
*t*BuCzBN-PSeZ	3.6	480/33	2258	20.0	19.5	14.8	(0.15, 0.26)

*t*BuCzBN-Ph-PXZ	3.4	496/34	3153	34.1	28.2	13.9	(0.14, 0.49)
*t*BuCzBN-Ph-PTZ	3.2	496/37	3458	36.7	31.3	14.8	(0.14, 0.48)
*t*BuCzBN-Ph-PSeZ	3.4	494/39	3611	45.9	38.0	17.7	(0.14, 0.52)

[a] The turn-on voltages; [b] the electronluminance spectral peaks and full width at half maximum detected at 6 V; [c] the maximum luminance; [d] the maximum current efficiencies; [e] the maximum power efficiencies; [f] the maximum external quantum efficiency; [g] the coordinates of CIE.

S8 Optimized structure of molecules

(1) *t*BuCzBN-PXZ

Atom	X	Y	Z
C	1.22239	-0.45612	-0.08373
C	1.22944	-1.85113	-0.18091
C	0.03803	-2.54998	-0.00727
C	-1.17357	-1.88697	0.16637
C	-1.20802	-0.49206	0.07019
C	-0.00383	0.27142	-0.00703
B	-0.02639	1.81208	-0.00785
N	2.41721	0.26838	-0.09913
N	-2.42364	0.19659	0.08784
C	2.43462	1.65166	-0.27942
C	3.76364	2.10308	-0.41451
C	4.61385	0.93665	-0.2516
C	3.76315	-0.17555	-0.02507
C	-3.75604	-0.28819	0.01843
C	-4.63957	0.80141	0.24916
C	-3.82217	1.99234	0.40787
C	-2.48151	1.57926	0.26765
C	1.32217	2.49497	-0.28658
C	1.60715	3.85911	-0.51579
C	2.90408	4.35755	-0.68745

C	3.98881	3.45789	-0.62177
C	6.00115	0.78916	-0.22681
C	6.57424	-0.45506	0.04557
C	5.70663	-1.53026	0.31986
C	4.31831	-1.41562	0.29808
C	-4.08634	3.33958	0.61589
C	-3.02817	4.27088	0.67778
C	-1.71821	3.81027	0.50183
C	-1.39428	2.45485	0.27162
C	-4.27551	-1.54105	-0.29998
C	-5.66421	-1.70159	-0.31484
C	-6.55768	-0.65513	-0.03746
C	-6.01678	0.60948	0.23067
C	3.18431	5.84849	-0.93069
C	1.89684	6.68949	-0.95922
C	4.0862	6.39088	0.19921
C	3.90154	6.01938	-2.28719
C	-3.35103	5.75297	0.92183
C	-4.07003	5.90294	2.27987
C	-2.08839	6.63088	0.94764
C	-4.27073	6.26888	-0.20613
C	-8.08147	-0.84237	-0.04115
C	-8.49166	-2.29109	-0.3509
C	-8.64265	-0.46825	1.34776
C	-8.70823	0.0766	-1.11201
C	8.09178	-0.68123	0.07845
C	8.87663	0.6018	-0.23885
C	8.50942	-1.16769	1.48312
C	8.47018	-1.75074	-0.96894
H	2.12942	-2.40291	-0.39431

H	-2.05671	-2.46523	0.37982
H	0.77312	4.54413	-0.57158
H	5.00547	3.82187	-0.73292
H	6.62163	1.65852	-0.40775
H	6.12524	-2.49901	0.5713
H	3.71932	-2.27167	0.57341
H	-5.11284	3.67354	0.73086
H	-0.9041	4.51904	0.55513
H	-3.65349	-2.37975	-0.57748
H	-6.04694	-2.68368	-0.56215
H	-6.66896	1.45772	0.41305
H	2.14872	7.74008	-1.13288
H	1.22328	6.37299	-1.76176
H	1.35245	6.63159	-0.01134
H	4.29923	7.45369	0.041
H	5.04272	5.86263	0.24419
H	3.59721	6.28033	1.17203
H	3.27871	5.64376	-3.1049
H	4.11548	7.07692	-2.47667
H	4.85068	5.47666	-2.31394
H	-4.31415	6.95381	2.46989
H	-5.00301	5.33297	2.30861
H	-3.43488	5.54549	3.09624
H	-2.37021	7.67371	1.12203
H	-1.54469	6.58881	-0.00146
H	-1.40414	6.3339	1.7486
H	-3.78073	6.17279	-1.17997
H	-5.21148	5.71284	-0.24925
H	-4.51449	7.32497	-0.04732
H	-9.5824	-2.37619	-0.33186

H	-8.15264	-2.60557	-1.34287
H	-8.09091	-2.99212	0.38782
H	-9.73124	-0.58925	1.36517
H	-8.41722	0.56959	1.60858
H	-8.21413	-1.10872	2.1248
H	-8.48916	1.13058	-0.91958
H	-8.32387	-0.16859	-2.1069
H	-9.79718	-0.04145	-1.12626
H	9.95029	0.39257	-0.21267
H	8.63741	0.98624	-1.23533
H	8.67522	1.39108	0.49228
H	9.59122	-1.33533	1.52238
H	8.01656	-2.10645	1.75045
H	8.24992	-0.42491	2.24382
H	8.18676	-1.42602	-1.97488
H	9.5508	-1.93001	-0.95805
H	7.97088	-2.70349	-0.77241
C	-0.64856	-4.7	-0.98764
C	0.79173	-4.67652	0.97389
C	-0.61556	-6.10541	-0.95472
C	-1.36108	-4.08721	-2.02485
C	0.80725	-6.08218	0.93919
C	1.48173	-4.04088	2.01262
C	-1.30228	-6.86406	-1.89108
C	-2.05267	-4.85027	-2.96899
H	-1.37042	-3.00782	-2.09666
C	1.51901	-6.81788	1.87518
C	2.19862	-4.7808	2.9563
H	1.45352	-2.96192	2.08596
C	-2.0339	-6.23926	-2.90351

H	-1.24415	-7.94406	-1.81122
H	-2.59896	-4.34319	-3.75751
H	1.49828	-7.89914	1.79386
C	2.2279	-6.16954	2.88898
H	2.72636	-4.25619	3.74599
H	-2.57096	-6.8379	-3.63121
H	2.78475	-6.75025	3.61634
N	0.05975	-3.97304	-0.00672
O	0.10851	-6.80033	-0.00856

(2) *t*BuCzBN-PTZ

Atom	**X**	**Y**	**Z**
C	-0.05599	-3.79225	2.42283
C	0.07866	-4.41159	3.66176
C	0.38562	-5.76487	3.7466
C	0.57551	-6.49221	2.57464
C	-0.74042	-6.67898	-2.3716
C	-1.47587	-6.03528	-3.36311
C	-1.693	-4.66669	-3.25953
C	-1.21269	-3.95211	-2.16553
C	0.14486	-4.51012	1.23667
C	0.48165	-5.86673	1.338
C	-0.2246	-5.96109	-1.30036
C	-0.47977	-4.58866	-1.15478
N	0.01785	-3.88644	-0.02999
C	-8.5282	-1.95476	-0.55758
C	-8.65621	0.4186	-1.31605
C	-8.65964	-0.13347	1.14224
C	-8.08081	-0.52064	-0.23503
C	8.90966	0.51887	-0.15504

C	8.46664	-1.81587	-0.91538
C	8.50147	-1.26279	1.54307
C	8.101	-0.75325	0.14242
C	2.07809	6.73299	-0.89925
C	4.06363	6.01402	-2.22815
C	4.25902	6.38425	0.25691
C	3.34439	5.86207	-0.87123
C	-4.60228	6.30543	1.00261
C	-2.49794	6.73803	-0.2639
C	-2.42299	6.31088	2.21757
C	-3.11721	5.92638	0.8939
C	6.03977	0.75441	-0.15611
C	6.58876	-0.50013	0.1038
C	5.70155	-1.56075	0.35816
C	4.31805	-1.41972	0.33032
C	1.40575	2.55235	-0.25119
C	1.72207	3.90983	-0.47309
C	3.02848	4.37917	-0.62781
C	4.09044	3.45666	-0.55106
C	-4.29785	-1.33332	-0.41236
C	-5.6882	-1.45192	-0.45614
C	-6.55319	-0.38025	-0.19859
C	-5.9798	0.86399	0.08276
C	-3.99165	3.53061	0.53394
C	-2.91567	4.42591	0.63339
C	-1.61285	3.92994	0.48221
C	-1.31799	2.57603	0.24368
C	2.4958	1.68506	-0.2292
C	3.83337	2.1097	-0.34856
C	4.65741	0.92658	-0.18703

C	3.78507	-0.16883	0.02295
C	-3.74469	-0.09945	-0.0865
C	-4.59991	1.01368	0.13025
C	-3.75372	2.17758	0.31551
C	-2.42737	1.7294	0.2029
N	2.447	0.3027	-0.05521
N	-2.40092	0.34822	0.01022
B	0.03878	1.9	-0.00769
C	0.02441	0.35931	-0.01997
C	1.23593	-0.39387	-0.06253
C	1.2095	-1.79001	-0.1401
C	-0.00291	-2.45156	-0.04331
C	-1.20432	-1.76527	0.07474
C	-1.20218	-0.3702	0.01312
H	-0.30938	-2.74292	2.37412
H	-0.07068	-3.82722	4.56181
H	0.47899	-6.25251	4.70906
H	0.81715	-7.54757	2.61125
H	-0.53999	-7.74175	-2.43369
H	-1.86064	-6.59655	-4.2055
H	-2.24615	-4.14034	-4.0283
H	-1.39283	-2.88922	-2.1074
H	-8.16752	-2.66789	0.18796
H	-9.61982	-2.00421	-0.56359
H	-8.17679	-2.27692	-1.54107
H	-8.41271	1.46372	-1.11384
H	-9.74585	0.32989	-1.35561
H	-8.25524	0.16569	-2.30077
H	-8.2638	-0.78562	1.92479
H	-8.4122	0.89638	1.40818

H	-9.74965	-0.22623	1.13641
H	8.71828	1.30158	0.58359
H	9.97751	0.28919	-0.12459
H	8.68415	0.91779	-1.1474
H	7.95342	-2.76174	-0.73068
H	9.54323	-2.00966	-0.90272
H	8.19087	-1.47529	-1.91658
H	9.57915	-1.44566	1.58648
H	8.24718	-0.52614	2.30933
H	7.99354	-2.1961	1.79418
H	1.53621	6.68851	0.04912
H	2.35587	7.77545	-1.073
H	1.39704	6.43369	-1.69979
H	4.99924	5.45122	-2.25325
H	4.29917	7.06511	-2.41937
H	3.43214	5.64988	-3.04238
H	3.77009	6.28147	1.22897
H	5.20379	5.83819	0.29826
H	4.4912	7.44155	0.09916
H	-5.093	5.78596	1.82977
H	-4.69362	7.37882	1.18567
H	-5.14583	6.07905	0.08155
H	-1.42549	6.55571	-0.3574
H	-2.64115	7.80951	-0.09588
H	-2.96681	6.47417	-1.21525
H	-2.55476	7.37783	2.42068
H	-2.84547	5.74753	3.0534
H	-1.35116	6.10507	2.18405
H	6.6751	1.6133	-0.32399
H	6.09857	-2.53931	0.59785

H	3.70553	-2.26875	0.58577
H	0.90549	4.61154	-0.54036
H	5.11443	3.79624	-0.6523
H	-3.70131	-2.1935	-0.66964
H	-6.09399	-2.42107	-0.70965
H	-6.60729	1.73048	0.25418
H	-5.01021	3.88208	0.6271
H	-0.78686	4.62277	0.56472
H	2.09637	-2.37853	-0.28897
H	-2.10749	-2.32652	0.23278
S	0.91392	-6.79	-0.15906

(3) *t*BuCzBN-PSeZ

Atom	X	Y	Z
Se	-0.25954	-5.16617	1.93149
N	-2.38318	0.52757	-0.26019
N	2.46438	0.49188	-0.22589
N	0.01392	-3.66759	-0.74236
C	-1.31474	2.73769	0.16708
C	-1.17563	-0.1812	-0.32271
C	-2.41806	1.88994	0.04623
C	-3.75264	2.31891	0.19598
C	-1.22656	-4.36819	-0.66472
C	-1.17988	-1.57322	-0.41202
H	-2.09286	-2.12662	-0.30717
C	-4.58997	1.16454	-0.07657
C	0.02518	-2.26496	-0.57506
C	1.24781	-0.19386	-0.34473
C	1.27738	-5.15858	0.73786
C	-3.99784	3.64664	0.52383

H	-5.02103	3.98884	0.64652
C	-5.97117	1.00494	-0.1166
H	-6.6054	1.85207	0.12621
C	1.23866	-1.56926	-0.56533
H	2.15449	-2.0971	-0.7437
C	3.86708	2.31063	-0.28593
C	-4.27299	-1.13902	-0.78608
H	-3.67549	-1.97797	-1.10786
C	-1.6191	4.07115	0.51684
H	-0.79265	4.75191	0.66404
C	2.52586	1.8862	-0.25733
C	1.43311	2.76012	-0.23289
C	0.04078	0.5643	-0.26047
C	1.1893	-4.426	-0.45214
C	-3.72385	0.07789	-0.38344
C	3.08706	4.60422	-0.36326
C	-2.92464	4.54399	0.70053
C	-5.66462	-1.26876	-0.81777
H	-6.0637	-2.22689	-1.12738
C	-2.13454	-4.31063	-1.72734
H	-1.86265	-3.74455	-2.612
C	1.76627	4.12481	-0.30682
H	0.95727	4.84509	-0.33333
C	-1.55202	-5.10662	0.47793
C	2.26328	-4.44523	-1.3476
H	2.17098	-3.90516	-2.2838
C	-6.53848	-0.22505	-0.47611
C	3.79342	0.00354	-0.15365
C	4.1419	3.67673	-0.34053
H	5.1722	4.01156	-0.36633

C	6.59796	-0.35997	-0.03334
C	-3.69565	-5.66688	-0.47547
H	-4.65464	-6.16942	-0.39856
C	4.68051	1.11081	-0.22048
C	6.06301	0.92286	-0.17094
H	6.70905	1.79075	-0.22973
C	-2.77831	-5.76743	0.56991
H	-3.01303	-6.35319	1.4529
C	-3.22336	6.00265	1.07937
C	4.31239	-1.28143	0.03227
H	3.6899	-2.15103	0.18065
C	-3.37287	-4.94148	-1.62584
H	-4.07902	-4.87806	-2.44761
C	2.4387	-5.86544	1.0516
H	2.48967	-6.443	1.96908
C	3.3257	6.12048	-0.44045
C	3.43809	-5.12195	-1.02233
H	4.27545	-5.10861	-1.71241
C	5.69607	-1.43618	0.08148
H	6.08076	-2.44088	0.22494
C	8.10778	-0.6301	0.01718
C	-8.0656	-0.3789	-0.50001
B	0.0527	2.08828	-0.10518
C	3.52794	-5.82549	0.18075
H	4.43664	-6.36322	0.43247
C	-1.94374	6.84376	1.22674
H	-1.2894	6.4532	2.01249
H	-2.20825	7.8712	1.49546
H	-1.37387	6.8818	0.29267
C	-8.66653	0.62565	-1.50714

H	-8.42473	1.6584	-1.24067
H	-9.75799	0.53363	-1.53472
H	-8.28123	0.44189	-2.515
C	-8.50388	-1.79372	-0.91242
H	-8.16299	-2.04544	-1.92173
H	-9.59647	-1.85706	-0.90642
H	-8.12303	-2.55247	-0.22142
C	-3.97954	6.0374	2.42529
H	-4.92451	5.48906	2.37209
H	-4.20761	7.07037	2.71083
H	-3.37646	5.58705	3.21989
C	8.93358	0.65912	-0.12261
H	8.73563	1.1647	-1.07309
H	10.00084	0.41899	-0.08956
H	8.72677	1.36232	0.69034
C	-4.09782	6.64794	-0.01775
H	-3.58073	6.6354	-0.98237
H	-4.32498	7.6892	0.23656
H	-5.04769	6.11998	-0.14143
C	-8.62848	-0.09111	0.90889
H	-8.21753	-0.79281	1.6415
H	-9.71967	-0.19014	0.91299
H	-8.3829	0.92105	1.24245
C	8.49527	-1.57878	-1.13808
H	7.96683	-2.53395	-1.07035
H	9.57057	-1.78811	-1.11733
H	8.25206	-1.13001	-2.10634
C	2.6784	6.67427	-1.72855
H	3.11659	6.20553	-2.61531
H	2.83329	7.75668	-1.80035

H	1.60103	6.48757	-1.75074
C	8.46785	-1.29044	1.36589
H	8.20179	-0.63521	2.20119
H	9.54341	-1.49302	1.41754
H	7.94182	-2.23906	1.50518
C	2.68741	6.80612	0.78782
H	1.60793	6.63594	0.83205
H	2.85317	7.88857	0.75034
H	3.12407	6.42428	1.71602
C	4.82149	6.47547	-0.46327
H	5.33385	6.12804	0.43967
H	4.94206	7.56199	-0.51579
H	5.32691	6.04379	-1.33312

(4) *t*BuCzBN-Ph-PXZ

Atom	**X**	**Y**	**Z**
C	-0.81444	1.22473	0.03685
C	0.58187	1.2043	-0.02364
C	1.2669	-0.01297	-0.00024
C	0.55932	-1.21716	0.02369
C	-0.83731	-1.21153	-0.03585
C	-1.57113	0.01362	0.00053
B	-3.11121	0.02819	-0.00045
N	-1.51457	2.43713	0.10049
N	-1.55971	-2.41055	-0.09941
C	-2.89664	2.49617	-0.08782
C	-3.32183	3.83922	-0.14077
C	-2.14089	4.65372	0.07684
C	-1.04587	3.76869	0.25341
C	-1.11481	-3.75055	-0.25283

C	-2.22965	-4.61593	-0.07712
C	-3.39494	-3.77782	0.13928
C	-2.94328	-2.44365	0.08691
C	-3.76364	1.40657	-0.17958
C	-5.11926	1.73375	-0.40134
C	-5.59081	3.04895	-0.48883
C	-4.66961	4.10686	-0.34357
C	-1.96936	6.03462	0.17714
C	-0.71543	6.57157	0.47573
C	0.34445	5.67112	0.69627
C	0.20365	4.28849	0.59861
C	-4.74747	-4.01973	0.34023
C	-5.64868	-2.94433	0.48448
C	-5.1516	-1.63883	0.39765
C	-3.78949	-1.33775	0.17755
C	0.12189	-4.29359	-0.59472
C	0.24097	-5.68297	-0.69331
C	-0.83352	-6.55893	-0.47593
C	-2.08094	-5.99469	-0.17867
C	-7.07323	3.37577	-0.72533
C	-7.93889	2.11088	-0.85236
C	-7.60912	4.20677	0.46065
C	-7.21591	4.19035	-2.02913
C	-7.13734	-3.24263	0.71903
C	-7.29737	-4.05484	2.02231
C	-7.97856	-1.96129	0.84559
C	-7.68766	-4.06261	-0.468
C	-0.6942	-8.08465	-0.57237
C	0.74222	-8.52075	-0.90325
C	-1.09197	-8.71776	0.77854

C	-1.62781	-8.61503	-1.68194
C	-0.46309	8.08095	0.58975
C	-1.73291	8.90325	0.31705
C	0.03144	8.41404	2.01401
C	0.61172	8.49729	-0.43763
C	2.74788	-0.02659	-0.00149
C	3.45772	-0.99845	-0.72483
C	4.84909	-1.01082	-0.73037
C	5.55936	-0.0512	-0.00557
C	4.86806	0.9205	0.7216
C	3.47673	0.93246	0.7201
N	6.98575	-0.06336	-0.00827
C	7.69871	0.77478	-0.88308
C	9.10483	0.74789	-0.86083
O	9.80676	-0.0808	-0.00751
C	9.09419	-0.89719	0.84886
C	7.68783	-0.90666	0.87039
C	7.06574	1.63251	-1.7867
C	7.81516	2.44818	-2.6392
C	9.20477	2.41574	-2.60234
C	9.84809	1.55678	-1.70583
C	9.82696	-1.71228	1.69706
C	9.17258	-2.56047	2.59582
C	7.78267	-2.57573	2.63189
C	7.04382	-1.75357	1.77638
H	1.14455	2.11407	-0.14749
H	1.10487	-2.13739	0.14659
H	-5.819	0.91912	-0.52238
H	-5.01043	5.13645	-0.39129
H	-2.82848	6.67815	0.03133

H	1.32199	6.05809	0.96422
H	1.05048	3.66102	0.83145
H	-5.10784	-5.04268	0.38737
H	-5.83542	-0.81069	0.51786
H	0.98144	-3.68306	-0.82575
H	1.21271	-6.08045	-0.95801
H	-2.95023	-6.62892	-0.0364
H	-8.98235	2.39556	-1.0182
H	-7.62655	1.48882	-1.69699
H	-7.90212	1.5006	0.05559
H	-8.66567	4.45278	0.3084
H	-7.0618	5.1463	0.57789
H	-7.51867	3.64815	1.39739
H	-6.84428	3.61924	-2.88551
H	-8.26698	4.43883	-2.21238
H	-6.65427	5.12774	-1.98384
H	-8.35329	-4.28289	2.20413
H	-6.75405	-5.00298	1.97732
H	-6.91578	-3.49143	2.8794
H	-9.02747	-2.22585	1.01034
H	-7.9292	-1.35155	-0.06212
H	-7.65511	-1.34561	1.69071
H	-7.58514	-3.50551	-1.40439
H	-7.15852	-5.01253	-0.58491
H	-8.74897	-4.28816	-0.31724
H	0.79283	-9.61269	-0.95184
H	1.07162	-8.13102	-1.8715
H	1.45221	-8.18928	-0.13909
H	-1.00574	-9.80867	0.72928
H	-2.12323	-8.47561	1.05016

H	-0.44164	-8.35847	1.58205
H	-2.67505	-8.37425	-1.47903
H	-1.36609	-8.17861	-2.65079
H	-1.54452	-9.7043	-1.76251
H	-1.5055	9.97028	0.40023
H	-2.12213	8.72414	-0.69014
H	-2.52493	8.67641	1.03766
H	0.21752	9.48912	2.1113
H	0.96193	7.89161	2.25267
H	-0.71487	8.12639	2.76095
H	0.28185	8.27298	-1.45673
H	0.80837	9.57276	-0.36958
H	1.55663	7.97331	-0.26932
H	2.91085	-1.72732	-1.31379
H	5.39764	-1.75351	-1.29992
H	5.43114	1.65358	1.28944
H	2.94438	1.67083	1.31054
H	5.98349	1.65793	-1.82051
H	7.29886	3.10558	-3.3311
H	9.7922	3.0463	-3.26093
H	10.92953	1.49832	-1.64796
H	10.90906	-1.66725	1.63974
H	9.75183	-3.19614	3.25676
H	7.25792	-3.2246	3.32548
H	5.96132	-1.76563	1.80954

(5) *t*BuCzBN-Ph-PTZ

Atom	**X**	**Y**	**Z**
C	6.82503	1.0642	2.22296
C	7.48201	1.67213	3.29196

C	8.83982	1.97159	3.2129
C	9.53162	1.67411	2.03876
C	9.56916	-1.44687	-2.05304
C	8.89381	-2.50549	-2.66039
C	7.53385	-2.6716	-2.41074
C	6.85872	-1.80786	-1.54926
C	7.50848	0.76503	1.03402
C	8.86948	1.10405	0.95538
S	9.75731	0.91165	-0.61421
C	8.88914	-0.55917	-1.22439
C	7.52577	-0.73639	-0.9351
N	6.85001	0.15463	-0.06343
C	3.33926	-0.88668	0.69006
C	4.73047	-0.86996	0.68401
C	5.41683	0.11081	-0.03996
C	4.69923	1.07059	-0.75346
C	3.30682	1.04992	-0.74632
C	2.60311	0.07236	-0.0256
C	0.54103	8.55685	-0.92358
C	-1.28801	8.74388	0.76546
C	-1.83294	8.63457	-1.69315
C	-0.8914	8.11161	-0.58644
C	-1.82614	-8.88522	0.27168
C	-0.06111	-8.39321	1.96772
C	0.51499	-8.46245	-0.48581
C	-0.56032	-8.05673	0.54563
C	-8.07416	-2.11941	-0.84739
C	-7.73014	-4.22816	0.4417
C	-7.34006	-4.18155	-2.04869
C	-7.20065	-3.38071	-0.73576

C	-7.70179	4.6346	0.78891
C	-7.68774	2.51618	2.11094
C	-8.11616	2.46418	-0.37195
C	-7.30945	3.14843	0.75373
C	-2.0796	-6.0172	0.14592
C	-0.82148	-6.54833	0.43882
C	0.23413	-5.64275	0.6607
C	0.08508	-4.26013	0.56964
C	-3.90072	-1.39685	-0.18391
C	-5.2553	-1.73006	-0.40467
C	-5.71989	-3.04752	-0.49819
C	-4.79251	-4.10156	-0.36003
C	-0.05008	4.32571	-0.60819
C	0.05959	5.71595	-0.70843
C	-1.02048	6.58509	-0.48765
C	-2.26322	6.01335	-0.18475
C	-4.9178	4.02627	0.3508
C	-5.80676	2.94772	0.50208
C	-5.29904	1.64096	0.41295
C	-3.94189	1.34516	0.1841
C	-3.02742	-2.4823	-0.09982
C	-3.44551	-3.8277	-0.15839
C	-2.25929	-4.6366	0.05246
C	-1.1686	-3.74583	0.23028
C	-1.2824	3.7748	-0.26145
C	-2.40292	4.63312	-0.08152
C	-3.56098	3.78765	0.1415
C	-3.10172	2.45901	0.0881
N	-1.64525	-2.41634	0.0847
N	-1.71874	2.43271	-0.10561

B	-3.25546	-0.0164	-0.00092
C	-1.71596	0.00751	-0.00721
C	-0.95218	-1.19951	0.0227
C	0.44409	-1.17093	-0.04273
C	1.1222	0.05054	-0.0193
C	0.40748	1.25097	0.00931
C	-0.98945	1.23751	-0.04514
H	5.77196	0.83062	2.30791
H	6.92193	1.90048	4.19346
H	9.35673	2.43392	4.04729
H	10.58851	1.90278	1.9457
H	10.6271	-1.28749	-2.23562
H	9.42476	-3.18284	-3.32102
H	6.98591	-3.4837	-2.87851
H	5.80395	-1.95931	-1.36194
H	2.81265	-1.63094	1.27862
H	5.29553	-1.60643	1.2463
H	5.24514	1.81945	-1.31736
H	2.75546	1.78025	-1.32952
H	0.86927	8.16802	-1.89272
H	0.58425	9.64919	-0.97378
H	1.25634	8.23105	-0.16178
H	-2.31663	8.49504	1.04153
H	-1.20925	9.83542	0.71466
H	-0.63196	8.38987	1.56684
H	-1.57201	8.19862	-2.66258
H	-2.87784	8.38693	-1.48584
H	-1.75725	9.7244	-1.77549
H	-2.21852	-8.70374	-0.73398
H	-1.59241	-9.95143	0.3495

H	-2.61806	-8.6663	0.99501
H	0.8668	-7.86621	2.20697
H	0.1315	-9.46769	2.06011
H	-0.80779	-8.11317	2.71736
H	0.71811	-9.53714	-0.4229
H	0.18178	-8.23563	-1.5034
H	1.45728	-7.93361	-0.31705
H	-7.768	-1.48586	-1.6858
H	-9.11659	-2.40814	-1.01341
H	-8.03845	-1.51952	0.06785
H	-7.17753	-5.16607	0.54755
H	-8.78564	-4.47837	0.28824
H	-7.64141	-3.67971	1.38475
H	-6.97342	-3.59831	-2.89917
H	-6.77181	-5.11557	-2.01447
H	-8.38979	-4.43509	-2.23339
H	-7.47837	5.13507	-0.15882
H	-8.77749	4.7277	0.9672
H	-7.18584	5.17108	1.59164
H	-7.46955	1.4447	2.13152
H	-8.75786	2.64473	2.30787
H	-7.13008	2.98619	2.92709
H	-9.19079	2.60185	-0.20918
H	-7.86	2.8896	-1.34735
H	-7.92132	1.38879	-0.41499
H	-2.93547	-6.66517	-0.00059
H	1.21467	-6.0255	0.92444
H	0.92899	-3.62863	0.80311
H	-5.95918	-0.91808	-0.52084
H	-5.12805	-5.13279	-0.41301

H	0.8129	3.72063	-0.84176
H	1.02781	6.1197	-0.97708
H	-3.13601	6.64233	-0.03933
H	-5.27702	5.04753	0.39717
H	-5.98522	0.81198	0.53891
H	1.01162	-2.0773	-0.17071
H	0.94825	2.17447	0.13044

(6) *t*BuCzBN-Ph-PSeZ

Atom	X	Y	Z
C	-7.1146	-3.03042	0.28352
C	-7.778	-4.02219	-0.43573
C	-8.585	-3.67794	-1.52293
C	-8.73527	-2.33987	-1.88608
C	-8.96273	2.15577	0.66558
C	-8.9034	2.53527	2.00625
C	-8.08287	1.83746	2.89578
C	-7.31422	0.76684	2.44384
C	-7.22058	-1.68971	-0.10225
C	-8.04433	-1.35258	-1.18289
Se	-8.20951	0.53054	-1.6498
C	-8.16777	1.10332	0.21066
C	-7.32801	0.41039	1.09092
N	-6.52775	-0.66924	0.61335
C	-3.07172	0.6656	0.98497
C	-4.45337	0.55753	1.07676
C	-5.12515	-0.54526	0.51817
C	-4.35581	-1.51372	-0.1528
C	-2.9749	-1.39009	-0.23309
C	-2.29288	-0.30435	0.33658

C	0.28746	-8.66717	-0.27121
C	2.2134	-8.64806	1.31688
C	2.61589	-8.63285	-1.17106
C	1.7029	-8.11362	-0.039
C	1.52621	8.92866	-0.08705
C	-0.11497	8.41251	1.72195
C	-0.81534	8.31469	-0.69786
C	0.33483	8.03465	0.2938
C	8.14784	2.53314	-1.23676
C	7.7346	4.68019	-0.03439
C	7.21045	4.47694	-2.49194
C	7.19847	3.73932	-1.13536
C	8.33032	-4.13189	0.7575
C	8.2477	-1.94794	1.96493
C	8.52802	-2.00815	-0.53864
C	7.83572	-2.67885	0.66844
C	1.9661	6.08033	-0.08971
C	0.69224	6.54296	0.24754
C	-0.28611	5.58337	0.57306
C	-0.04846	4.21064	0.54281
C	4.07683	1.5775	-0.29114
C	5.39103	1.98593	-0.60701
C	5.75914	3.32405	-0.79457
C	4.77152	4.32129	-0.65577
C	0.6082	-4.39615	-0.19465
C	0.58731	-5.79375	-0.221
C	1.73423	-6.5788	-0.02223
C	2.95052	-5.91319	0.17889
C	5.49104	-3.73191	0.45603
C	6.31087	-2.59116	0.49879

C	5.71051	-1.32673	0.37426
C	4.32601	-1.13255	0.21322
C	3.13693	2.60659	-0.21254
C	3.45917	3.97138	-0.36274
C	2.23416	4.7113	-0.12441
C	1.21784	3.76157	0.15982
C	1.81813	-3.74924	0.05131
C	3.00267	-4.52316	0.20605
C	4.11111	-3.59374	0.31743
C	3.55962	-2.30253	0.22557
N	1.77494	2.46084	0.05436
N	2.16983	-2.37669	0.11463
B	3.53732	0.16957	-0.00006
C	2.00743	0.04526	0.08641
C	1.16326	1.19829	0.0977
C	-0.22796	1.07453	0.11499
C	-0.82322	-0.18423	0.24999
C	-0.02177	-1.32995	0.30206
C	1.36367	-1.22861	0.15797
H	-6.49515	-3.27916	1.13878
H	-7.6773	-5.06118	-0.13865
H	-9.11374	-4.44785	-2.076
H	-9.38799	-2.06228	-2.70748
H	-9.62567	2.66952	-0.02318
H	-9.51353	3.36083	2.35897
H	-8.05309	2.11675	3.94411
H	-6.68412	0.20445	3.1248
H	-2.58347	1.51416	1.45433
H	-5.0107	1.33399	1.58363
H	-4.83965	-2.35352	-0.63384

H	-2.41589	-2.13835	-0.78662
H	-0.11828	-8.35055	-1.23729
H	0.31485	-9.76127	-0.26623
H	-0.40541	-8.34859	0.51405
H	3.2365	-8.31974	1.52065
H	2.20494	-9.74368	1.32412
H	1.57988	-8.29482	2.13656
H	2.27431	-8.26582	-2.14397
H	3.65138	-8.30776	-1.03644
H	2.60935	-9.72821	-1.19573
H	1.87906	8.72116	-1.10227
H	1.22513	9.98011	-0.04841
H	2.36648	8.79903	0.60246
H	-0.99177	7.83909	2.03564
H	-0.37535	9.47559	1.7716
H	0.68535	8.2215	2.44372
H	-1.08838	9.37557	-0.67688
H	-0.51793	8.05733	-1.71925
H	-1.70941	7.73395	-0.4542
H	7.83799	1.83734	-2.02282
H	9.15735	2.87943	-1.47912
H	8.20462	1.98159	-0.29264
H	7.12607	5.5843	0.05816
H	8.76055	4.99013	-0.26198
H	7.73589	4.17741	0.93785
H	6.8371	3.82692	-3.28944
H	6.58302	5.37267	-2.47023
H	8.22878	4.78767	-2.75074
H	8.08786	-4.69835	-0.14744
H	9.41834	-4.14452	0.87497

H	7.89845	-4.65484	1.61681
H	7.95808	-0.89357	1.94276
H	9.33376	-1.99515	2.10253
H	7.77127	-2.40663	2.83708
H	9.61725	-2.06606	-0.43497
H	8.24575	-2.50372	-1.47286
H	8.25763	-0.952	-0.62607
H	2.7669	6.77391	-0.31699
H	-1.2756	5.91455	0.87119
H	-0.83411	3.53827	0.85248
H	6.14131	1.21648	-0.72258
H	5.03259	5.36794	-0.7797
H	-0.30456	-3.85949	-0.40511
H	-0.36494	-6.27261	-0.4127
H	3.87054	-6.47609	0.30313
H	5.9212	-4.72366	0.53142
H	6.34481	-0.44928	0.41592
H	-0.86183	1.93268	-0.03185
H	-0.48835	-2.27827	0.5094

S9. Reference

[1] Y. Liu, Y. Wang, C. Li, Z. Ren, D. Ma, S. Yan, *Macromolecules* **2018**, *51*, 4615.

[2] W. L. Tsai, M. H. Huang, W. K. Lee, Y. J. Hsu, K. C. Pan, Y. H. Huang, H. C. Ting, M. Sarm, Y. Y. Ho, H. C. Hu, C. C. Chen, M. T. Lee, K. T. Wong, C. C. Wu, *Chem. Commun.* **2015**, *51*, 13662.

[3] Y. Liu, G. Xie, Z. Ren, S. Yan, *ACS Appl. Polym. Mater*. **2019**, *8*, 2204.