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Supporting Information

New D-A-A′-Configured Small Molecule Donors Employing Conjugation to Red-shift the Absorption for Photovoltaics

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Nuclear Magnetic Resonance (NMR) Spectroscopy. ^{1}H and ^{13}C NMR spectra of molecules were recorded on a Varian 400 Unity plus (400 MHz) spectrometer in deuterated chloroform (or other given solvents) as internal reference. The Chemical shift δ was reported in ppm. The definition of splitting pattern was: s, singlet; d, doublet; t, triplet; q, quartet; qn, quintet; sex, sextet; m, multiplet. Coupling constant was represented by *J* and reported in Hz.

Mass Spectrometry. Mass spectra were recorded using a Bruker timsTOF mass spectrometer and Bruker Daltonics autoflex speed with electrospray ionization (ESI) and matrix-assisted laser desorption/ionization (MALDI) as the ionization method.

Thermogravimetric analysis (TGA). Decomposed temperature (T_d, 5% weight loss) were measured with a Dynamic Q500 Thermo-Gravimetric Analyzer under a nitrogen atmosphere with heating and cooling rates of 10 °C·min^{-1}.

Differential Scanning Calorimetry (DSC). The melting and crystallization temperatures were measured using Perkin Elmer Jade DSC 4000 under nitrogen flow with heating and cooling rates of 10 °C·min^{-1}.

UV-Vis Absorption Measurement. The absorption spectra of in CH_2Cl_2 solutions (1 – 10 μM) were measured by spectrophotometers JASCO V-670 spectrophotometer.

Electrochemical Characterization. The electrochemical properties of molecules were investigated by cyclic voltammetry (CV). The measurement of oxidation potentials was carried out in anhydrous CH_2Cl_2 solution (1.0 mM) containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as a supporting electrolyte, while the measurement of the reduction potentials were conducted in an anhydrous THF solution (1.0 mM) containing 0.1 M tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte, purged with argon prior to conduct the measurements. A glassy carbon electrode and a platinum wire was used as the working electrode and counter electrode, respectively. All potentials were recorded versus Ag/AgCl (saturated) as a reference electrode and calibrated with the ferrocene/ferrocenium (Fc/Fc+) redox couple. All measurements were performed at a scan rate of 100 mVs^{-1}.

Single Crystal Structure Determinations. Crystallographic data were collected at 295(2) K on an Oxford Gemini A CCD diffractometer using graphite-monochromatized Cu-Kα radiation (λ = 1.54178 Å). Cell parameters were retrieved and refined using CrysAlis Pro software on all observed reflections. Data reduction was performed with the CrysAlis Pro software. The structures were solved and refined with SHELXL programs. The hydrogen atoms were included in calculated positions and refined using a riding mode.

OPV Device Fabrication. In this work, the D − A − A type donor materials were synthesized in the laboratory. Other materials, MoO_3, C_{70}, BCP, BPhen and Ag were purchased from commercially available resources. All organic materials had been sublimated twice by using our homemade graded purification system with a high vacuum of ~ 8×10^{-6} torr. Before the device fabrication, the ITO substrate was sequentially soaked in solutions (acetone, isopropyl, and deionized water) and carried out in the ultrasonic vibration tank for 5 min followed by drying by nitrogen with 5N pressure. For OPV device preparation, the thin films were deposited by thermal evaporation under a high pressure of < 5×10^{-6} torr. The thickness of each layer was monitored by an in-situ quartz crystal monitor, which was calibrated by a surface profiler (Dektak XT). The size of anode and cathode pads defined our device's active area of 4 mm^2. After the device fabrication process, the devices were transferred into a nitrogen-filled glovebox with low oxygen and moisture (<0.1ppm). Then, all devices were appropriately encapsulated using UV-curable epoxy resin (Everwide Chemical Corporation Limited EXC345) and getter-attached cover glass to protect our OPV devices.

OPV Device Measurement. The electrical characteristics of our OPV devices with 1 mm^2 shadow mask were measured by a source meter (Keithley 2401) under a AAA solar simulator with the intensity of 100 mW cm^{-2} (Enli Tech, SS-X100R) and KG2 reference (Enli Tech, SRC-2020-KG2) which was calibrated by ISO/IEC 17025 certified lab and traced to NREL. The spectral mismatch factor is 1.005 as according to IEC-60904-7 and NREL testing protocol. To confirm the repeatability, the data acquired from eight devices were utilized to give the averaged value and the standard deviation. The EQE spectrum was measured with a QE-R Solar Cell Spectral Response Measurement System (Enli Technology Co., Ltd., Taiwan). The reference spectrum (SS-X100R) of the solar simulator compared with the AM 1.5G solar spectrum is shown below.

Indoor OPV measurement. For evaluating the electrical characteristics of indoor OPVs, the devices were measured using a commercial indoor PV measurement system (CMS-PV101) with a fluorescent lamp (PHILIPS TLD 18W/840) and Keithley 2401, which was designed by the Center for Measurement Standards, Industrial Technology Research Institute (ITRI, Taiwan). In this measurement system, the fluorescent lamp was mounted on the top of a designed room-liked construction space with normal incidence, the light intensity of the fluorescent lamp can be easily controlled from 0 to 2500 lux by a programmed software, while the nonuniformity and temporal instability were kept < 2%. To check the irradiance and luminance qualities, the lux levels of the fluorescence lamps were measured using a lux meter (TES1332A DIGITAL LUX

METER) and the intensity calibration was carried out by using the spectrometer (BLUE – Wave UVNb-25 Spectrometer). The testing procedure of indoor OPV was followed as described in the previous work[11]. The spectrum and intensity of the fluorescent lamp (PHILIPS TLD 18W/840) at brightness of 500 and 1000 lux are shown below.

[1] Chen, C. H.; Ting, H. C.; Li, Y. Z.; Lo, Y. C.; Sher, P. H.; Wang, J. K.; Chiu, T. L.; Lin, C. F.; Hsu, I. S.; Lee, J. H.; Liu, S. W.; Wong, K. T. *ACS Appl. Mater. & Interfaces* **2019**, *11*, 8337-8349.

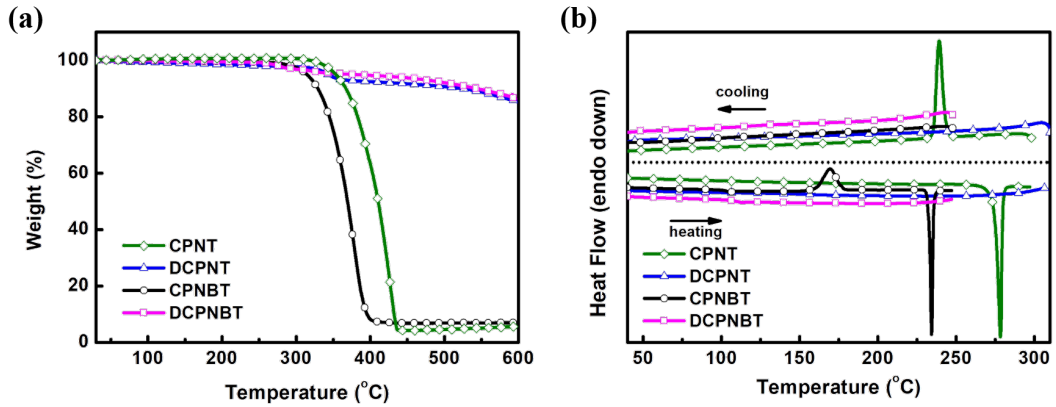


Figure S1. (a) TGA and (b) DSC analyses of **CPNT**, **DCPNT**, **CPNBT** and **DCPNBT**.

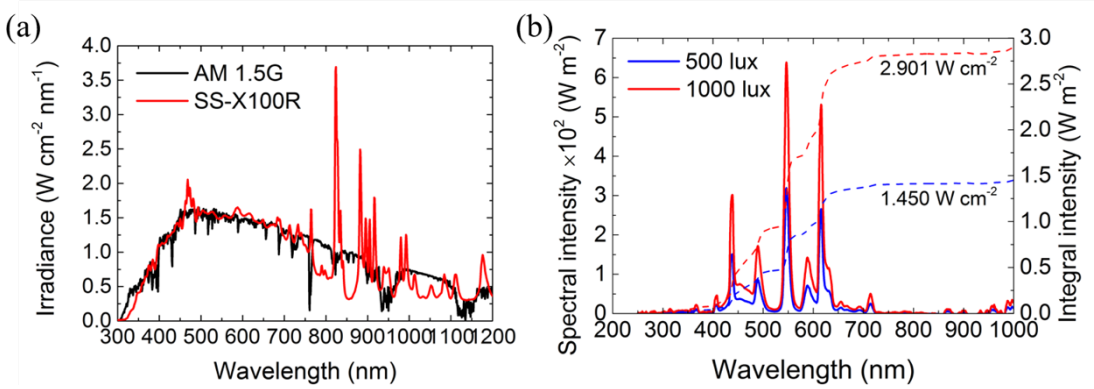
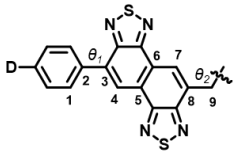
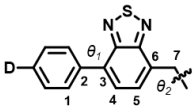
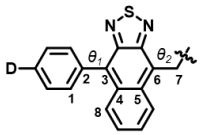


Figure S2. (a) The reference spectrum (SS-X100R) of the solar simulator compared with the AM 1.5G solar spectrum. (b) The spectral intensity of the fluorescent lamp (PHILIPS TLD 18W/840) based on 500 and 1000 lux. The dash line is the correlative integral intensity of the spectral.

Table S1. X-ray data and structure refinement parameters for **CPNT**, **DCPNT**, **CPNBT** and **DCPNBT** crystals.

	CPNT	**DCPNT**	**CPNBT**	**DCPNBT**
Emperical formula	$C_{63}H_{41}Cl_3N_{12}OS_4$, $C_{31}H_{20}N_6S_2$ (**CPNT** with 2 $CHCl_3$)	$C_{35}H_{22}Cl_3N_7S$, $C_{34}H_{21}N_7S_2$ (**DCPNT** with $CHCl_3$)	$C_{31.50}H_{23}ClN_4S$, $C_{31}H_{22}N_4S$ (**CPNBT** with 0.5 CH_2Cl_2)	$C_{37}H_{30}N_5S$, $C_{34}H_{23}N_5S$ (**DCPNBT** with 0.5 C_6H_{14})
Formula weight	1216.67	711.07	525.05	576.72
T /K	200(2)	150(2)	200(2)	200(2)
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Wavelength / Å	0.71073	1.54178	1.54178	1.54178
Space group	P-1	P-1	P-1	P-1
a /Å	10.8991(3)	7.2000(9)	6.9061(2)	10.5064(2)
b /Å	17.1289(8)	9.1357(9)	11.8760(3)	12.3880(3)
c /Å	18.5608(7)	25.837(3)	15.5321(4)	13.5519(3)
α /º	114.553(4)	82.973(9)	91.7206(8)	64.4687(7)
β /º	91.159(3)	87.501(9)	95.8705(8)	76.3120(7)
γ /º	104.132(3)	72.172(10)	95.4305(8)	70.6562(7)
V /Å^3	3027.2(2)	1605.7(3)	1260.51(6)	1492.58(6)
Z	2	2	2	2
ρ_c /g.cm^{-3}	1.335	1.471	1.383	1.283
μ /mm^{-1}	0.342	4.114	2.340	1.230
F (000)	1252	728	546	606
Reflections collected	18643	9569	6974	10406
Independent reflections (R_{int})	10613 (0.0413)	5791 (0.0799)	5092 (0.0210)	3839 (0.0119)
R_1, wR_2 [$I>2\sigma(I)$]	0.0953, 0.2471	0.0993, 0.2361	0.0533, 0.1433	0.0464, 0.1254
R_1, wR_2 [all data]	0.1485, 0.2854	0.1752, 0.2988	0.0560, 0.1461	0.0478, 0.1266
GooF on F^2	1.173	1.122	1.056	1.072
Largest diff. peak and hole/ e.Å^{-3}	1.715, -0.903	0.997, -0.926	0.658, -0.518	0.698, -0.381

Table S2. Structural data of **CPNT**, **DCPNT**, **DTCPB**, **DTDCPB**, **CPNBT** and **DCPNBT** crystals.

	CPNT	DCPNT	DTCPB	DTDCPB	CPNBT	DCPNBT
θ_1	40.37°	15.49°	28.34°	24.66°	40.43°	45.63°
θ_2	-	1.77°	-	9.36°	-	46.67°
C1-C2 (Å)	1.409	1.406	1.401	1.399	1.400	1.401
C2-C3 (Å)	1.462	1.460	1.471	1.471	1.479	1.477
BLA[a] of C2-C3 (Å)	0.070	0.061	0.081	0.083	0.072	0.070
C3-C4 (Å)	1.375	1.393	1.380	1.377	1.414	1.414
C4-C5 (Å)	1.416	1.402	1.411	1.408	1.452	1.452
C5-C6 (Å)	1.405	1.401	1.364	1.380	1.405	1.414
C6-C7 (Å)	1.416	1.404	1.435	1.442	1.436	1.455
C7-C8 (Å)	1.368	1.411				
C8-C9 (Å)	1.430	1.435				

[a] $\text{Bond length alternation (BLA)} = (\text{C2} - \text{C3}) - \frac{(C1-C2)+(C3-C4)}{2}$

*Synthesis of compound **4***

Hexyne (1.14 mL, 10 mmol) was added dropwise catecholborane (11.94 mL, 1 M in THF). After stirred and heated at reflux temperature under argon atmosphere for 1.5 h, the reaction mixture was added additional catecholborane (3.81 mL, 1M in THF) and then continued stirring for 2 h. The resulting alkene intermediate was cooled to room temperature and directly used into next step. A mixture of alkene intermediate (10 mmol), **1** (5 g, 12.4 mmol), $Pd(PPh_3)_4$ (431 mg, 0.37 mmol), and sodium carbonate (7.5 g , 24 mmol) in anhydrous toluene (620 mL) and nitrogen-bubbled distilled water (37 mL) was stirred and heated at reflux temperature under argon atmosphere for 12 h. After cooling to room temperature, the solvent was removed by rotary evaporation. The resulting mixture was extract with chloroform, washed with brine, dried over anhydrous $MgSO_4$, filtered, and then concentrated under reduced pressure. The crude product was purified by column chromatography with $CHCl_3$:hexanes = 1:4 (v/v) as eluent to yield **6** as a yellow solid (1.17 g, 29%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.08 (s, 1H), 8.69 (s, 1H), 7.33 (dt, J = 14.6, 7.2 Hz, 1H), 7.06 (d, *J* = 16.1 Hz, 1H), 2.43 (q, *J* = 8.1 Hz, 2H), 1.61 (m, 2H), 1.46 (dq, *J* = 14.3, 7.1 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.41, 153.26, 152.53, 152.45, 139.32, 131.30, 129.76, 125.55, 125.44,

124.66, 122.40, 113.16, 33.65, 31.28, 22.42, 14.00; HRMS (m/z, ESI^+) Calcd for $C_{16}H_{13}{}^{79}BrN_4S_2$ 403.9765, found 403.9760; Calcd for $C_{16}H_{13}{}^{81}BrN_4S_2$ 405.9745, found 405.9739.

*Synthesis of intermediate **5***

Hexyne (1.38 mL, 12 mmol) was added dropwise catecholborane (12.00 mL, 1 M in THF). After stirred and heated at reflux temperature under argon atmosphere for 1.5 h, the reaction mixture was added additional catecholborane (4.00 mL, 1M in THF) and then continued stirring for 2 h. The resulting alkene intermediate was cooled to room temperature and directly used into next step. A mixture of alkene intermediate (10 mmol), **2** (3.44 g, 10 mmol), $Pd(PPh_3)_4$ (924 mg, 0.8 mmol), and sodium carbonate (3.18 g, 30 mmol) in anhydrous toluene (100 mL) and nitrogen-bubbled distilled water (13 mL) was stirred and heated at reflux temperature under argon atmosphere for 12 h. After cooling to room temperature, the solution was filtered and the solid were washed by 100 mL of ethylacetate. The filtrate was washed with brine, water and the organic layer was dried over anhydrous $MgSO_4$, filtered, and then concentrated under reduced pressure. The crude product was purified by column chromatography with CH_2Cl_2:hexanes = 3:7 (v/v) as eluent to afford intermediate **5** and was used directly in the next step.

*Synthesis of compound **6***

A solution of **4** (1.27 g, 3.1 mmol) in anhydrous CH_2Cl_2 (400 mL) was stirred and bubbled with ozone at -78 °C for 30 min. The reaction mixture was added dimethyl sulfide (2 mL, 27 mmol) and then stirred at room temperature for 12 h. The resulting mixture was concentrated by rotary evaporation and purified by column chromatography with $CHCl_3$ as eluent to yield **8** as a light yellow solid (0.83 g, 75%). ^1H NMR (400 MHz, $CDCl_3$) δ 10.86 (s, 1H), 9.47 (s, 1H), 9.26 (s, 1H); ^{13}C NMR spectra of **8** is not available due to the low solubility; HRMS (m/z, EI^+) Calcd for $C_{11}H_3{}^{79}BrN_4OS_2$ 349.8932, found 349.8935; Calcd for $C_{11}H_3{}^{81}BrN_4OS_2$ 351.8911, found 351.8913.

Synthesis of compound 7

The intermediate **5** from the previous step was dissolved in anhydrous CH_2Cl_2 (100 mL) and was stirred and bubbled with ozone at -78 °C for 20 min. The reaction mixture was added dimethyl sulfide (7 mL, 100 mmol) and then stirred at room temperature for 12 h. The resulting mixture was concentrated by rotary evaporation and purified by column chromatography with $CHCl_3$:hexanes = 3:2 (v/v) as eluent to yield **7** as a orange solid (880 mg, 30% for 2 steps). ^1H NMR (400 MHz, $CDCl_3$) δ 11.60 (s, 1H), 9.60 (dd, J = 2, 1.2 Hz, 1H), 9.55 (dd, J = 10.0, 1.2 Hz, 1H), 7.78 – 7.66 (m 2H); ^{13}C NMR spectra

of **7** is not available due to the low solubility; HRMS (m/z, MALDI-TOF, $[M+H]^+$) Calcd for $C_{11}H_5{}^{79}BrN_2OS$ 292.9379, found 292.9391; Calcd for $C_{11}H_5{}^{81}BrN_2OS$ 294.9358, found 294.9448.

*Synthesis of compound **8***

A mixture of 4-methyl-*N*-(*p*-tolyl)-*N*-(4-(trimethylstannyl)-phenyl)aniline (2.1 mmol), **6** (0.60 g, 1.7 mmol), and $PdCl_2(PPh_3)_2$ (63 mg, 0.09 mmol) in anhydrous toluene (105 mL) was stirred and heated at reflux temperature under argon atmosphere for 2 h. After cooling to room temperature, the solvent was removed by rotary evaporation. The resulting mixture was extract with chloroform, washed with brine, dried over anhydrous $MgSO_4$, filtered, and then concentrated under reduced pressure. The crude product was purified by column chromatography with $CHCl_3$:hexanes = 1:1 (v/v) as eluent to yield **10** as a blue solid (0.70 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.81 (s, 1H), 9.51 (s, 1H), 9.02 (s, 1H), 8.05 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 8.8 Hz, 2H), 7.16 – 7.10 (m, 8H), 2.35 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.93, 153.87, 153.67, 149.69, 144.51, 136.99, 133.72, 132.26, 130.43, 130.12, 128.23, 126.12, 125.57, 123.28, 123.00, 120.85, 20.91.

*Synthesis of compound **9***

A mixture of (4-(di-p-tolylamino)phenyl)boronic acid (1.8 mmol), **7** (440 mg, 1.5 mmol), potassium carbonate (622 mg, 4.5 mmol) and $Pd(PPh_3)_4$ (173 mg, 0.15 mmol) in anhydrous toluene (15 mL) and nitrogen-bubbled distilled water (2.5 mL) was stirred and heated at reflux temperature under argon atmosphere for 12 h. After cooling to room temperature, the solvent was removed by rotary evaporation. The resulting mixture was extract with chloroform, washed with brine, dried over anhydrous $MgSO_4$, filtered, and then concentrated under reduced pressure. The crude product was purified by column chromatography with CH_2Cl_2:hexanes = 1:1 (v/v) as eluent to yield **9** as a dark blue solid (490 mg, 67%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 11.60 (s, 1H), 9.62 (d, *J* = 9.2 Hz, 1H), 8.26 (d, *J* = 8.8 Hz, 1H), 7.75 – 7.71 (m, 1H), 7.52-7.47 (m, 3H), 7.19 – 7.14 (m, 10H), 2.35 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 191.80, 191.71, 155.85, 152.39, 149.79, 145.16, 140.48, 134.53, 134.06, 133.00, 131.97, 130.70, 128.63, 128.01, 126.99, 126.48, 126.28, 120.38, 117.54, 21.17; HRMS (m/z, MALDI-TOF, $[M]^+$) Calcd for $C_{31}H_{23}N_3OS$ 485.1562, found 485.1577.

*Synthesis of **DCPNT***

A mixture of **8** (0.70 g, 1.3 mmol), malononitrile (0.34 g, 5.2 mmol) in anhydrous CH_2Cl_2 (65 mL) was added five drops of trimethylamine and then stirred at room temperature for 20 min. The resulting mixture was poured into methanol and then

filtered. The collecting solid was purified by column chromatography with $CHCl_3$ as eluent to yield **DCPNT** as a blue solid (0.36 g, 47%). M.p. 297 °C (DSC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.97 (s, 1H), 8.91 (s, 1H), 8.07 (d, *J* = 8.8 Hz, 2H), 7.22 – 7.05 (m, 10H), 2.36 (s, 6H); HRMS (m/z, FAB$^+$) Calcd for $C_{34}H_{21}N_7S_2$ 591.1300, found 591.1285.

*Synthesis of **DCPNT***

A mixture of **9** (490 mg, 1 mmol), malononitrile (120 mg, 1.8 mmol) in anhydrous CH_2Cl_2 (20 mL) was added five drops of trimethylamine and then stirred at room temperature for 20 min. The resulting mixture was poured into methanol and then filtered to yield **DCPNBT** as a brown solid (460 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.30 (d, *J* = 9.2 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.53-7.50 (m, 3H), 7.20 – 7.14 (m, 10H), 2.36 (s, 6H); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.30 (d, *J* = 9.2 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.53-7.50 (m, 3H), 7.20 – 7.14 (m, 10H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.39, 151.36, 150.26, 149.35, 144.43, 138.61, 133.92, 133.41, 132.46, 131.05, 130.19, 129.99, 129.26, 126.61, 125.86, 124.33, 119.75, 116.45, 114.09, 112.51, 89.57, 20.91; HRMS (m/z, ESI, [M+H]$^+$) Calcd for $C_{34}H_{24}N_5S$ 534.1747, found 534.1715.

*Synthesis of intermediate **10***

A mixture of (4-(di-*p*-tolylamino)phenyl)boronic acid (2.03 g, 6.4 mmol), **1** (3.22 g, 8 mmol), $Pd(PPh_3)_4$ (280 mg, 0.24 mmol), and potassium carbonate (3.31 g , 24 mmol) in anhydrous toluene (450 mL) and nitrogen-bubbled distilled water (15 mL) was stirred and heated at reflux temperature under argon atmosphere for 12 h. After cooling to room temperature, the solvent was removed by rotary evaporation. The resulting mixture was extract with chloroform, washed with brine, dried over anhydrous $MgSO_4$, filtered, and then concentrated under reduced pressure. The crude product was purified by column chromatography with $CHCl_3$:hexanes = 1:1 (v/v) to afford intermediate **3** directly used into next step.

*Synthesis of compound **11***

A mixture of (4-(di-*p*-tolylamino)phenyl)boronic acid (1.38g, 4.4mmol), **2** (1.00 g, 2.9 mmol), $Pd(PPh_3)_4$ (168 mg, 0.14 mmol), and potassium carbonate (2 g , 14.5 mmol) in anhydrous toluene (30 mL) and nitrogen-bubbled distilled water (7.5 mL) was stirred and heated at reflux temperature under argon atmosphere for 12 h. After cooling to room temperature, the solvent was removed by rotary evaporation. The resulting mixture was extract with chloroform, washed with brine, dried over anhydrous $MgSO_4$, filtered, and then concentrated under reduced pressure. The crude product was purified

by column chromatography with CH_2Cl_2:hexanes = 3:7 (v/v) to afford 11 as purple solid (825 mg, 53%).^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.44 (d, *J* = 9.2 Hz, 1H), 8.13 (d, *J* = 8.8 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.45 – 7.38 (m, 3H), 7.20-7.12 (m, 10H), 2.35 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.36, 151.29, 148.71, 145.06, 135.66, 133.59, 133.32, 132.67, 132.22, 131.36, 130.30, 128.90, 128.45, 128.04, 127.80, 127.62, 126.68, 125.75, 120.78, 110.97, 21.10; HRMS (m/z, MALDI-TOF, $[M]^+$) Calcd for $C_{30}H_{22}{}^{79}BrN_3S$ 535.0712, found 535.0738; Calcd for $C_{30}H_{22}{}^{81}BrN_3S$ 537.0695, found 537.0832.

Synthesis of ***CPNT***

A mixture of intermediate **10** (1.74 g, 3 mmol), copper(I) cyanide (0.8 g, 9 mmol) in 1-methyl-2-pyrrolidone (30 mL) was stirred and heated to 190 °C by microwave reactor for 2 h. After cooling to room temperature, the resulting mixture was stirred with ferric chloride hydrochloric acid at 60 °C for 30 min, extracted with chloroform, washed with brine, dried over anhydrous $MgSO_4$, filtered, and then concentrated under reduced pressure. The crude product was purified by column chromatography with $CHCl_3$:hexanes = 1:1 (v/v) as eluent to yield **CPNT** as a purple solid (0.78 g, 48%). M.p. 278 °C (DSC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.94 (s, 1H), 8.02 (d, *J* = 7.8 Hz, 2H), 7.19 – 7.11 (m, 10H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.44, 153.18, 152.54, 152.29, 149.76, 144.42, 137.15, 134.44, 133.79, 130.40, 130.13, 129.06, 127.90, 125.60, 122.78, 122.61, 120.70, 115.44, 103.74, 20.92; HRMS (m/z, ESI, $[M+H]^+$) Calcd for $C_{31}H_{21}N_6S_2$ 541.1264, found 541.1228.

Synthesis of ***CPNBT***

A mixture of **1** (825 mg, 1.54 mmol), copper(I) cyanide (413 mg, 4.61 mmol) in 1-methyl-2-pyrrolidone (15 mL) was stirred and heated to 190 °C by microwave reactor for 2 h. After cooling to room temperature, the resulting mixture was stirred with ferric chloride in hydrochloric acid at 60 °C for 30 min, extracted with chloroform, washed with brine, dried over anhydrous $MgSO_4$, filtered, and then concentrated under reduced pressure. The crude product was purified by column chromatography with $CHCl_3$:hexanes = 2:1 (v/v) as eluent to yield **CPNBT** as a purple solid (480 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.4 Hz, 1H), 8.26 (d, *J* = 9.2 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.51 – 7.48 (m, 3H), 7.20 – 7.14 (m, 10H), 2.35 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.62, 151.23, 149.37, 144.43, 138.23, 137.11, 133.91, 132.31, 130.74, 130.37, 130.18, 128.58, 126.76, 126.27, 125.84, 119.79, 115.80, 97.43, 20.91; HRMS (m/z, MALDI-TOF, $[M]^+$) Calcd for $C_{31}H_{22}N_4S$ 482.1560, found 482.1581.

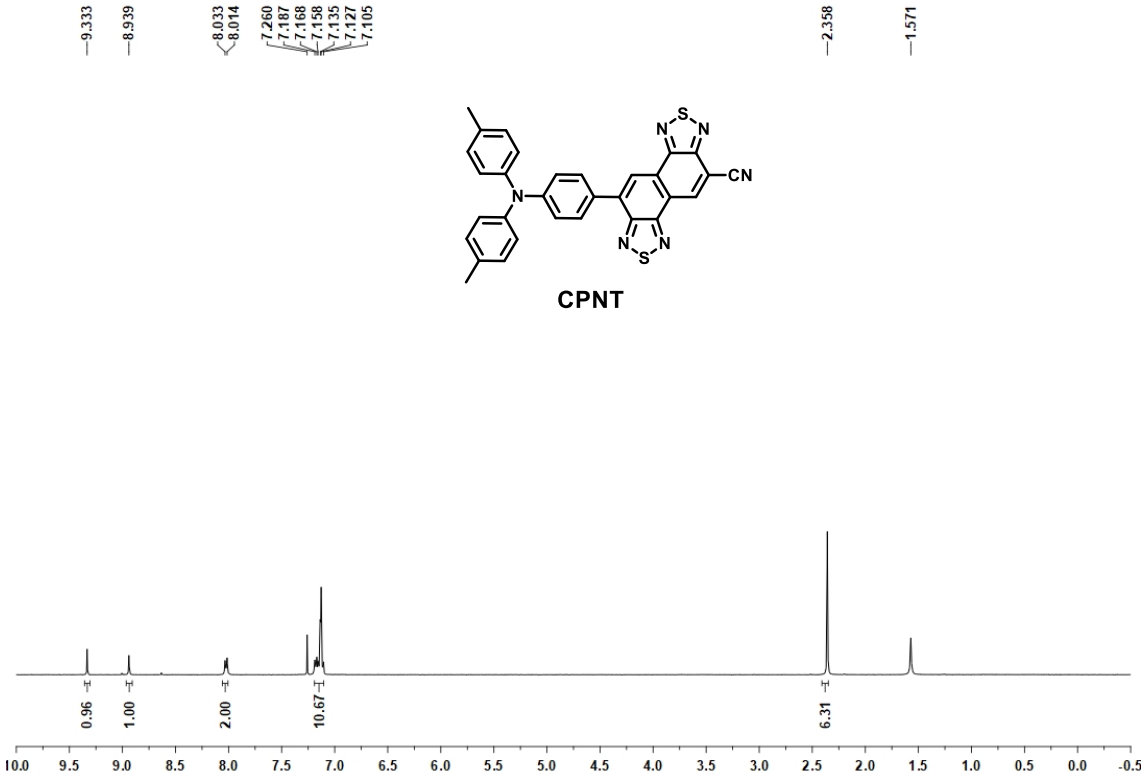


Figure S3. ^{1}H NMR spectra of **CPNT**.

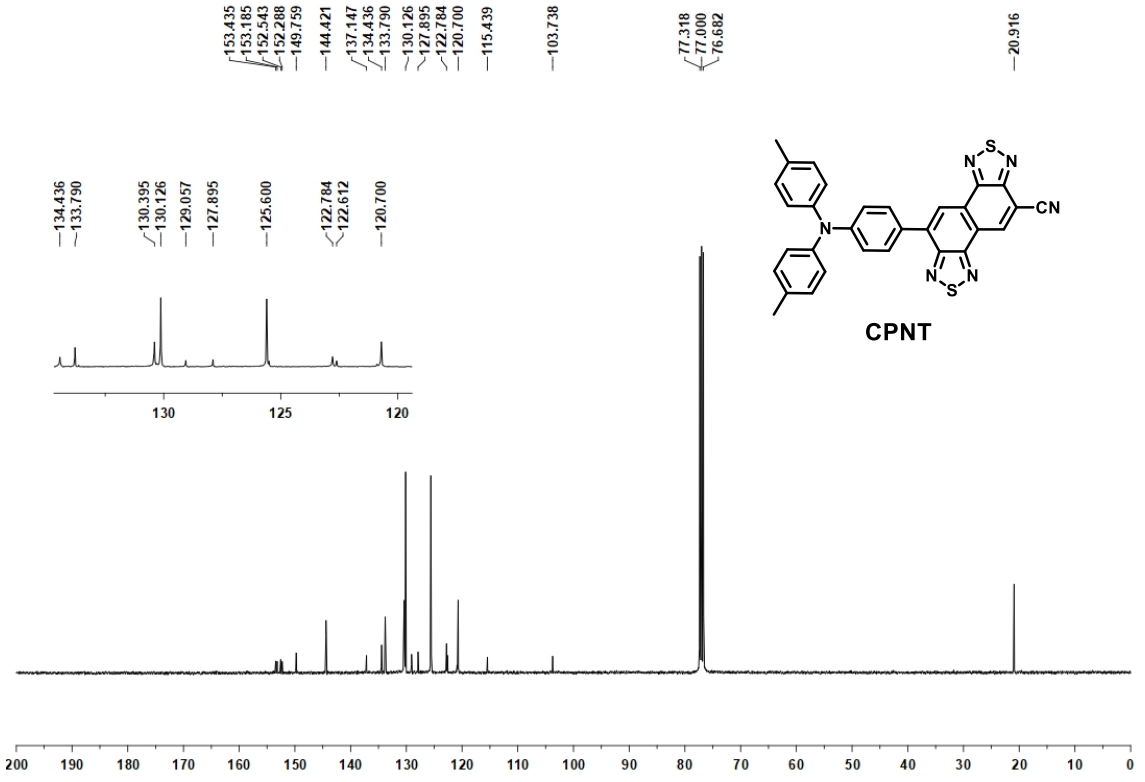


Figure S4. ^{13}C NMR spectra of **CPNT**.

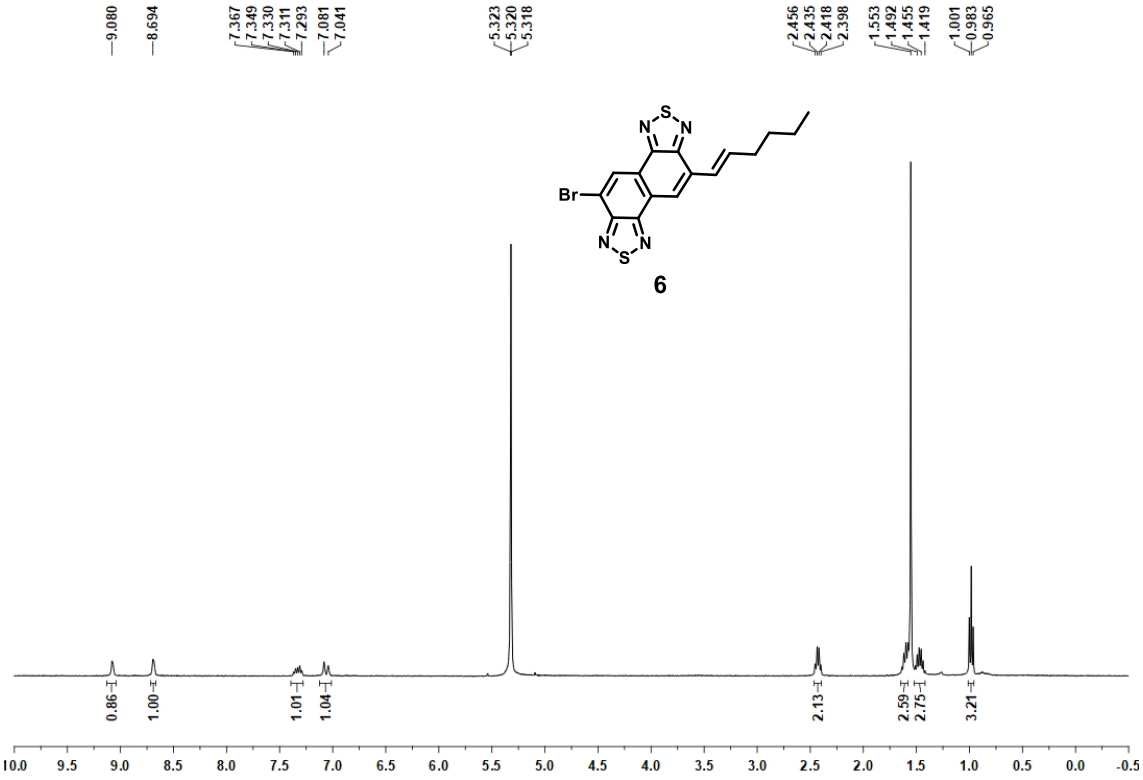


Figure S5. ^{1}H NMR spectra of **6**.

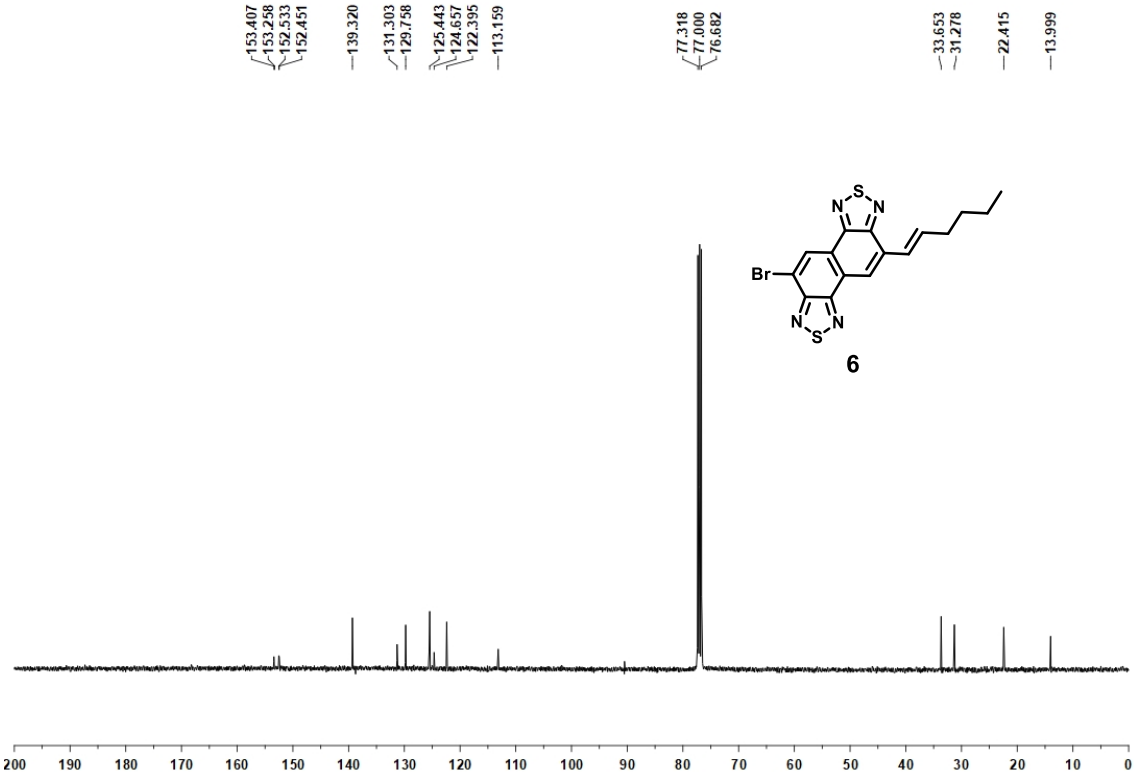


Figure S6. ^{13}C NMR spectra of **6**.

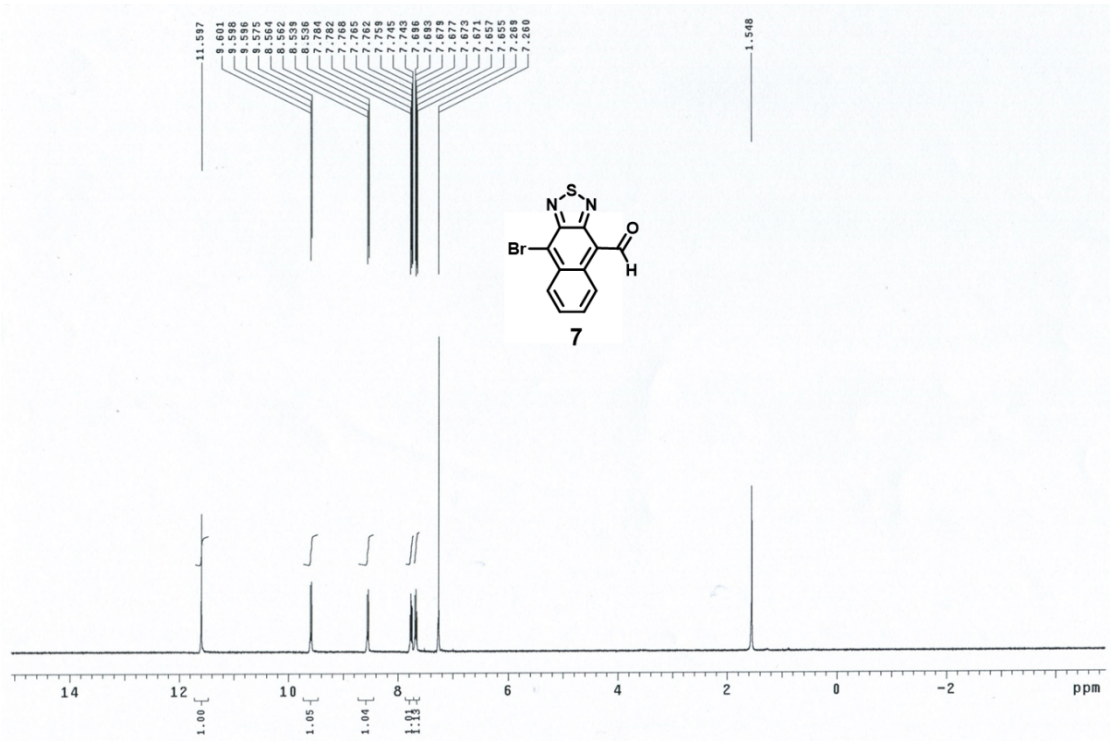


Figure S7. ^{1}H NMR spectra of **7**.

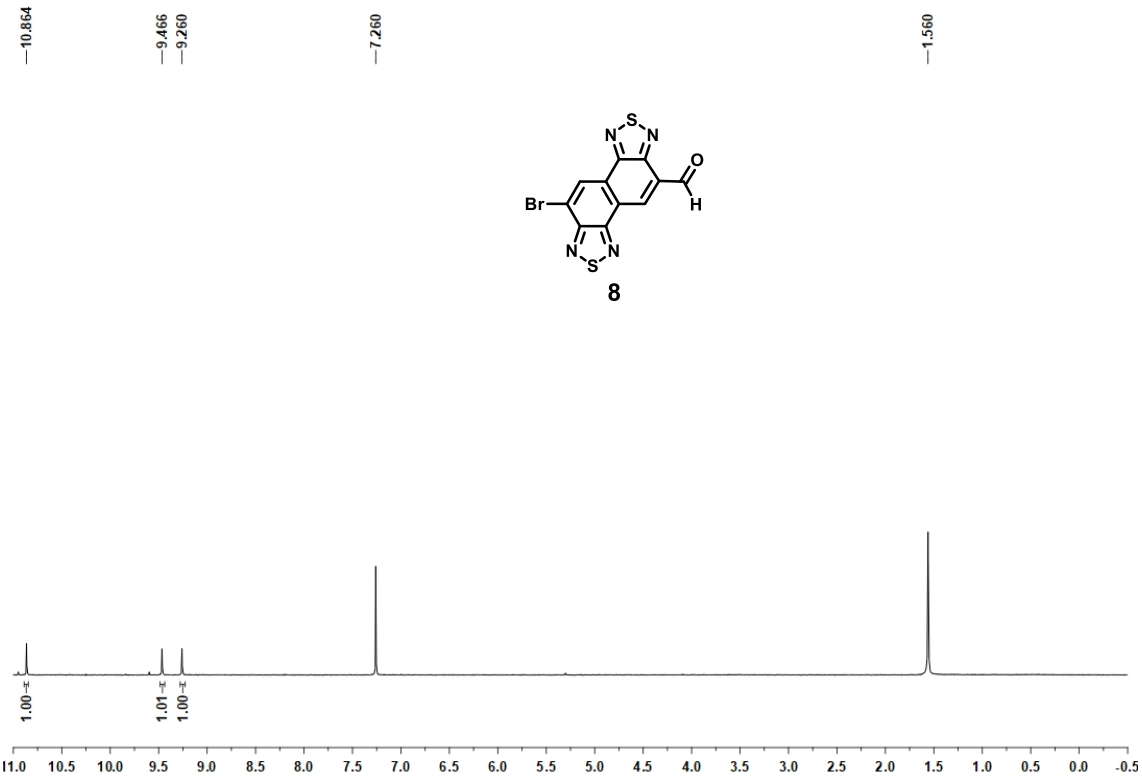


Figure S8. ^{1}H NMR spectra of **8**.

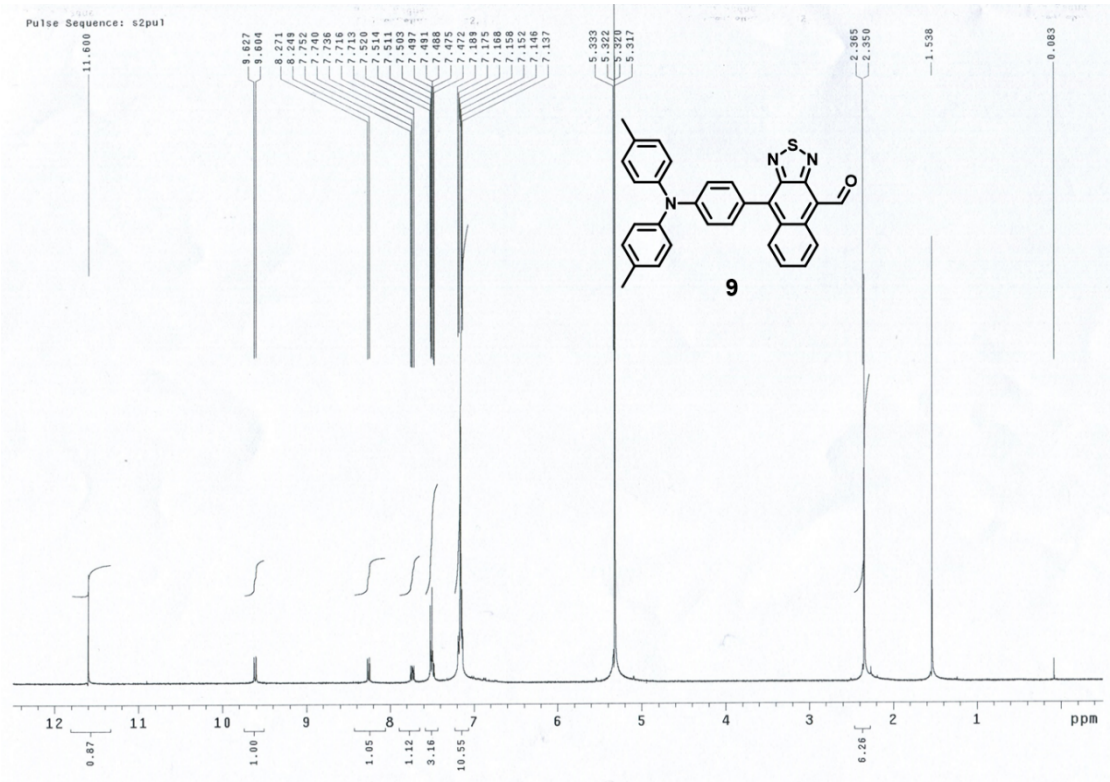


Figure S9. ^{1}H NMR spectra of **9**.

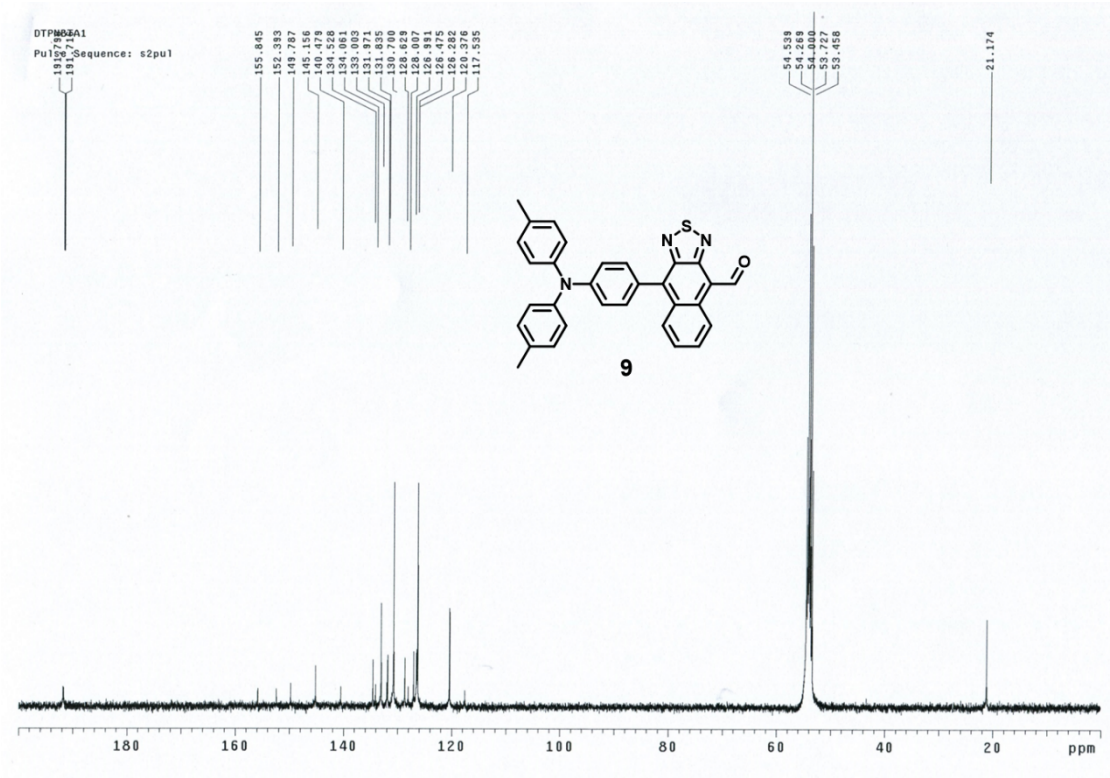


Figure S10. ^{13}C NMR spectra of **9**.

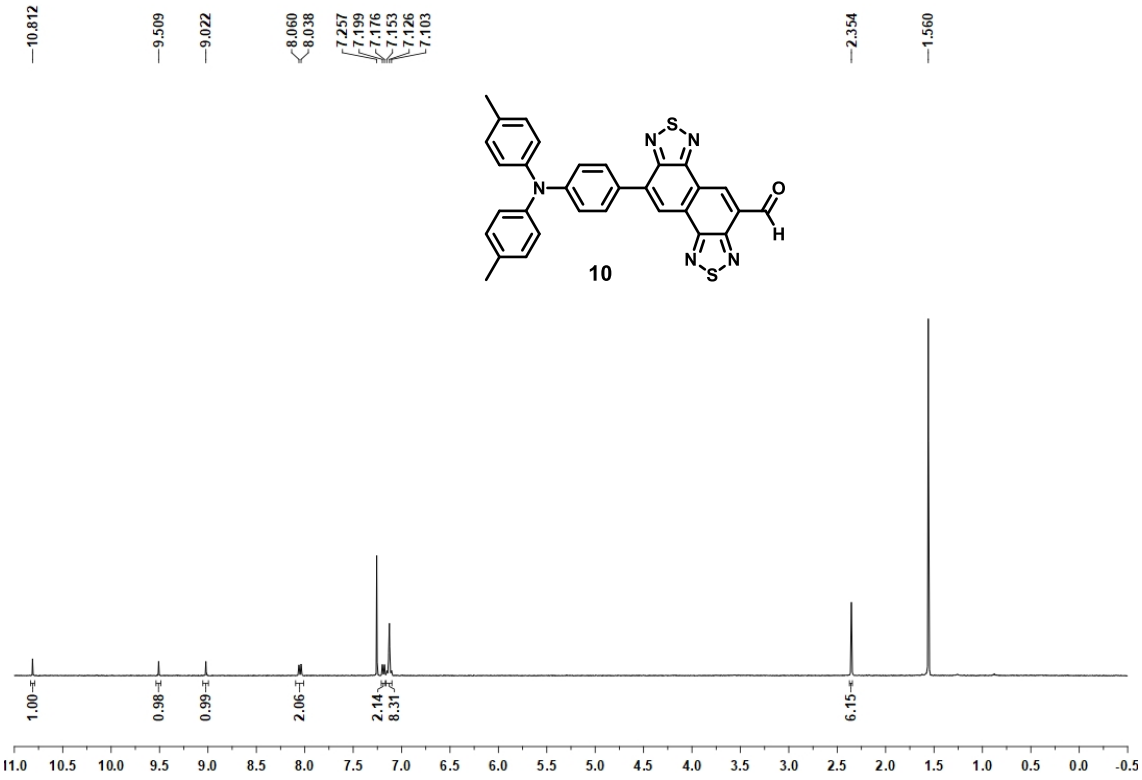


Figure S11. ^{1}H NMR spectra of **10**.

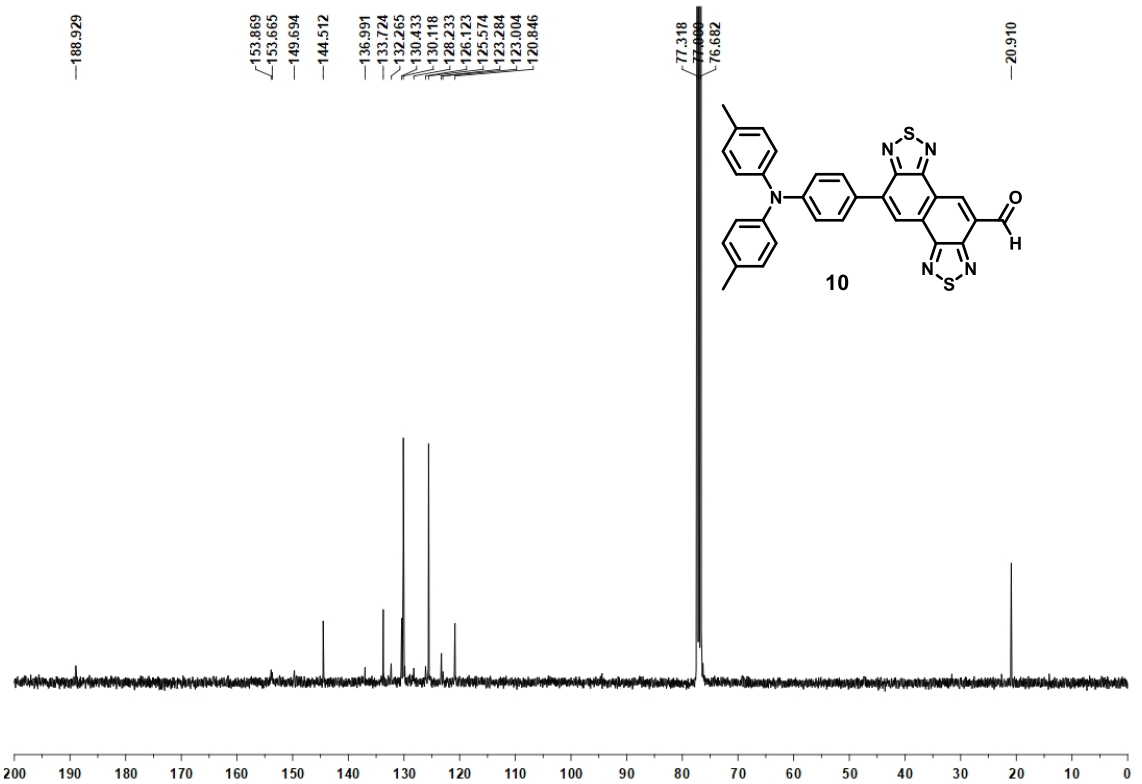


Figure S12. ^{13}C NMR spectra of **10**.

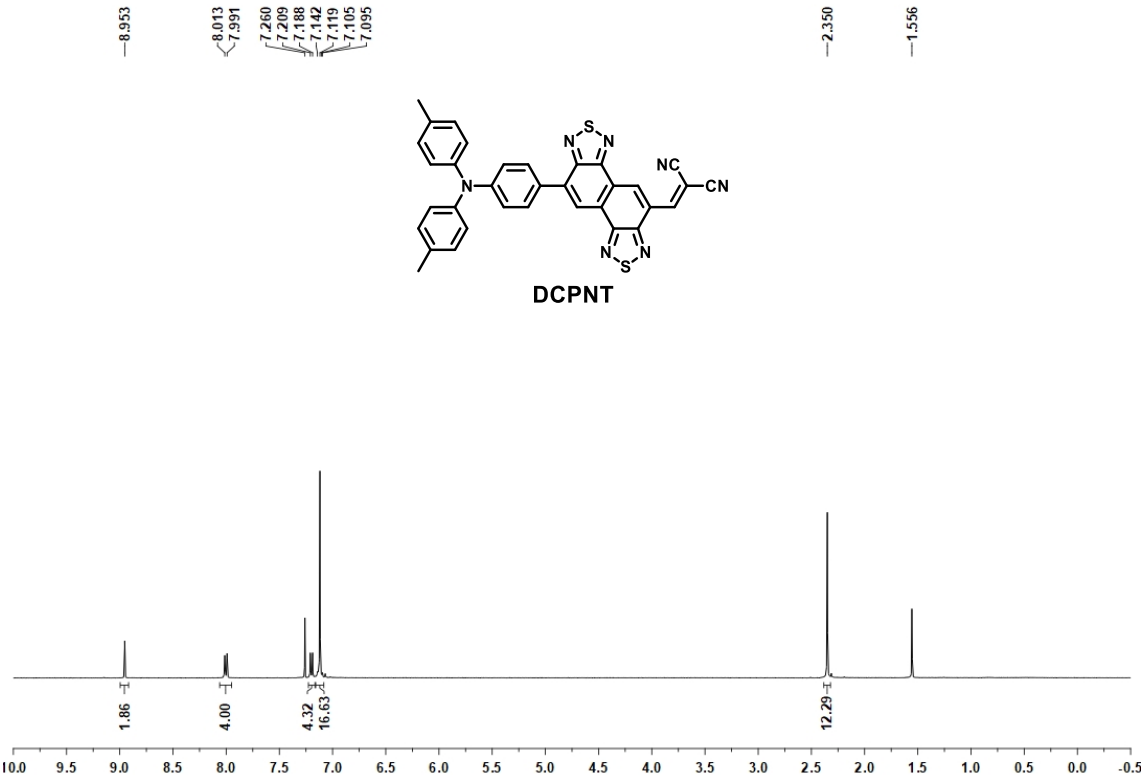


Figure S13. ^{13}C NMR spectra of **DCPNT**.

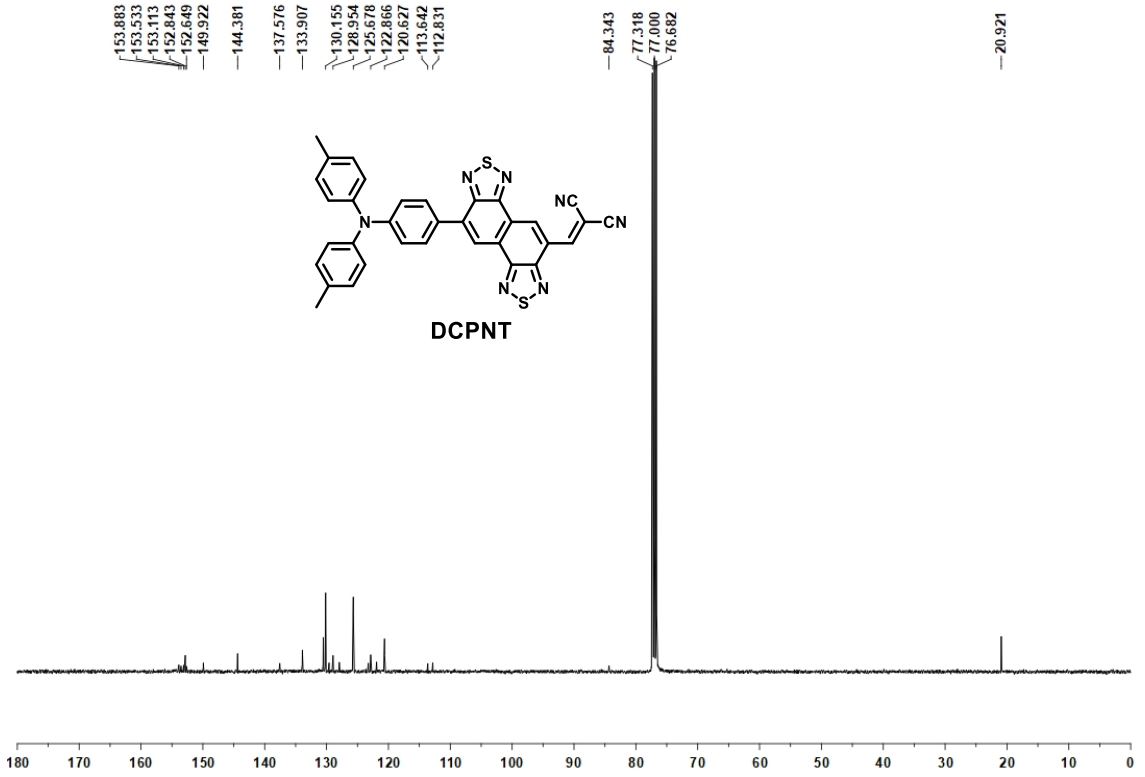


Figure S14. ^{13}C NMR spectra of **DCPNT**.

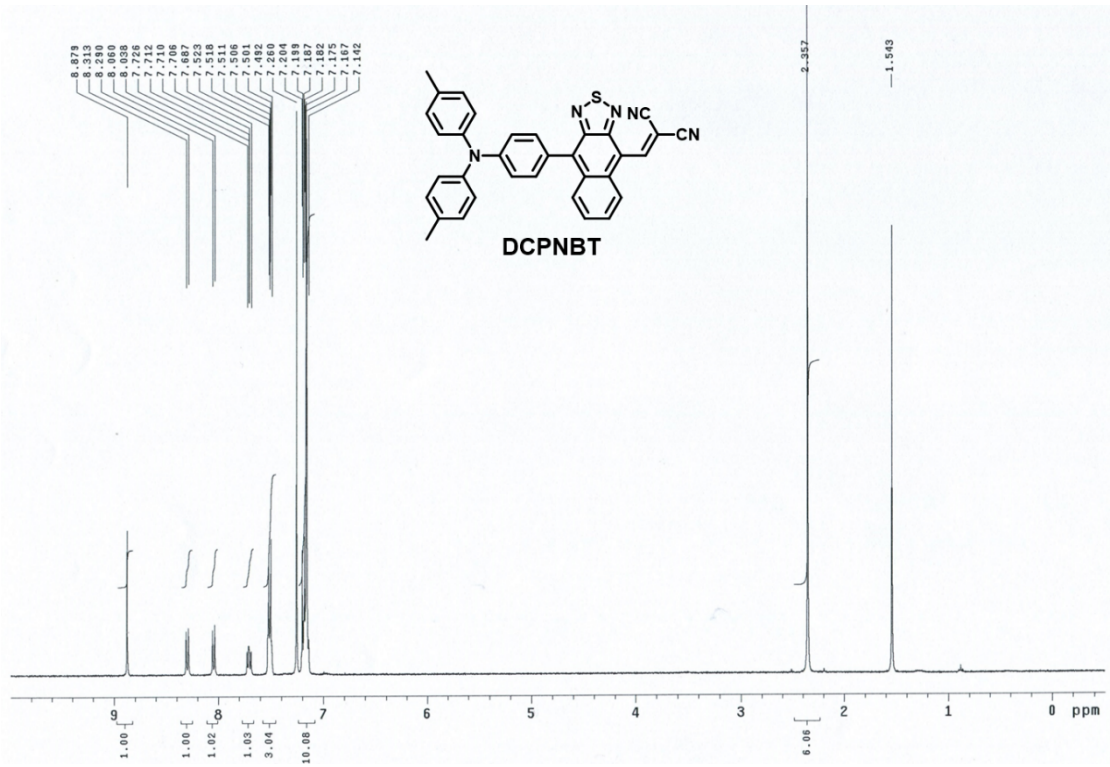


Figure S15. ^{1}H NMR spectra of **DCPNBT**.

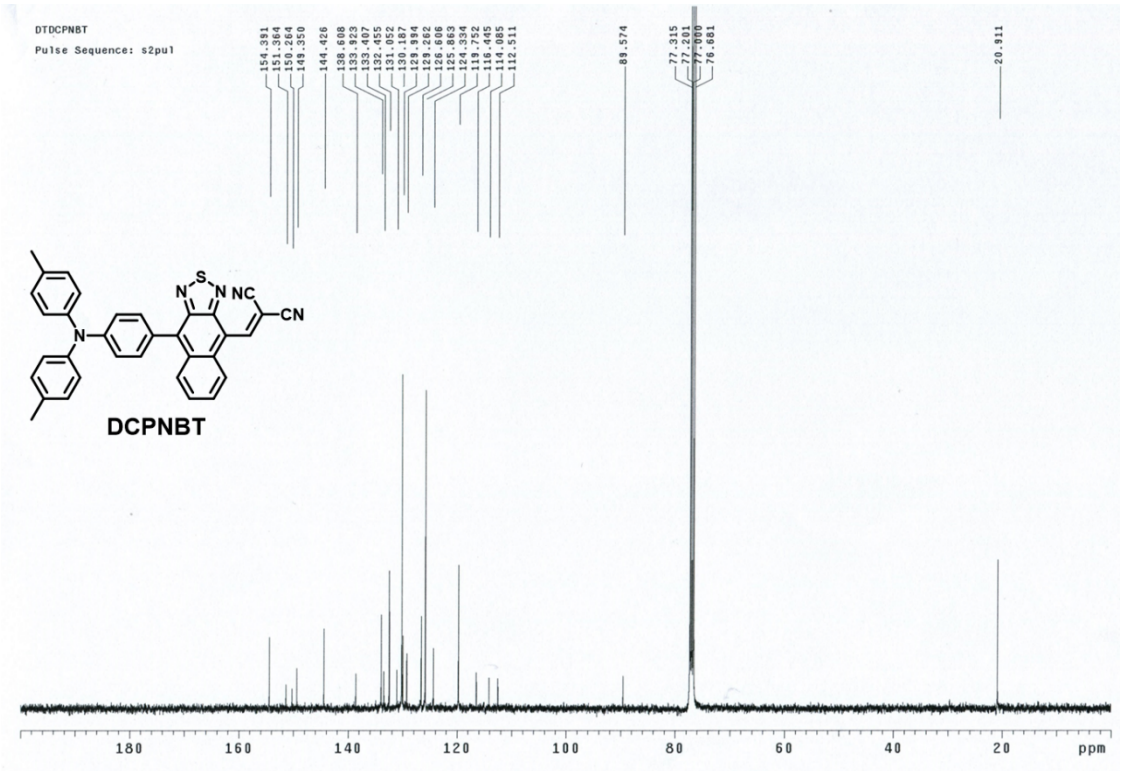


Figure S16. ^{13}C NMR spectra of **DCPNBT**.

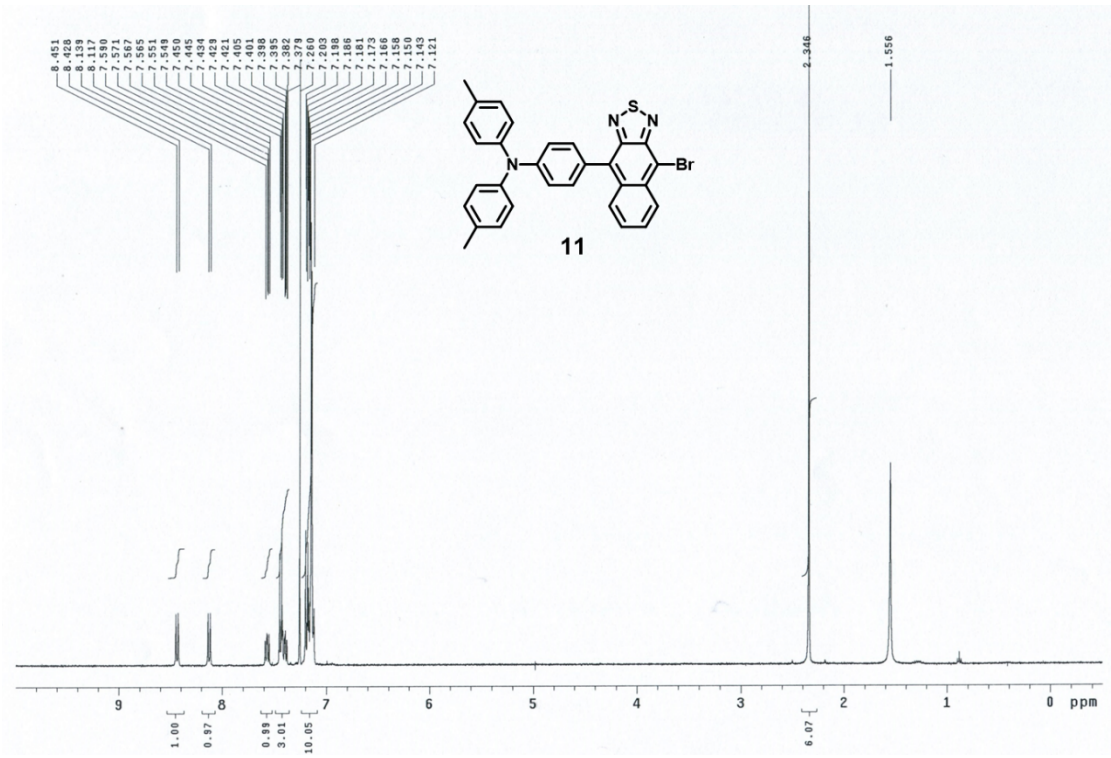


Figure S17. ^{1}H NMR spectra of **11**.

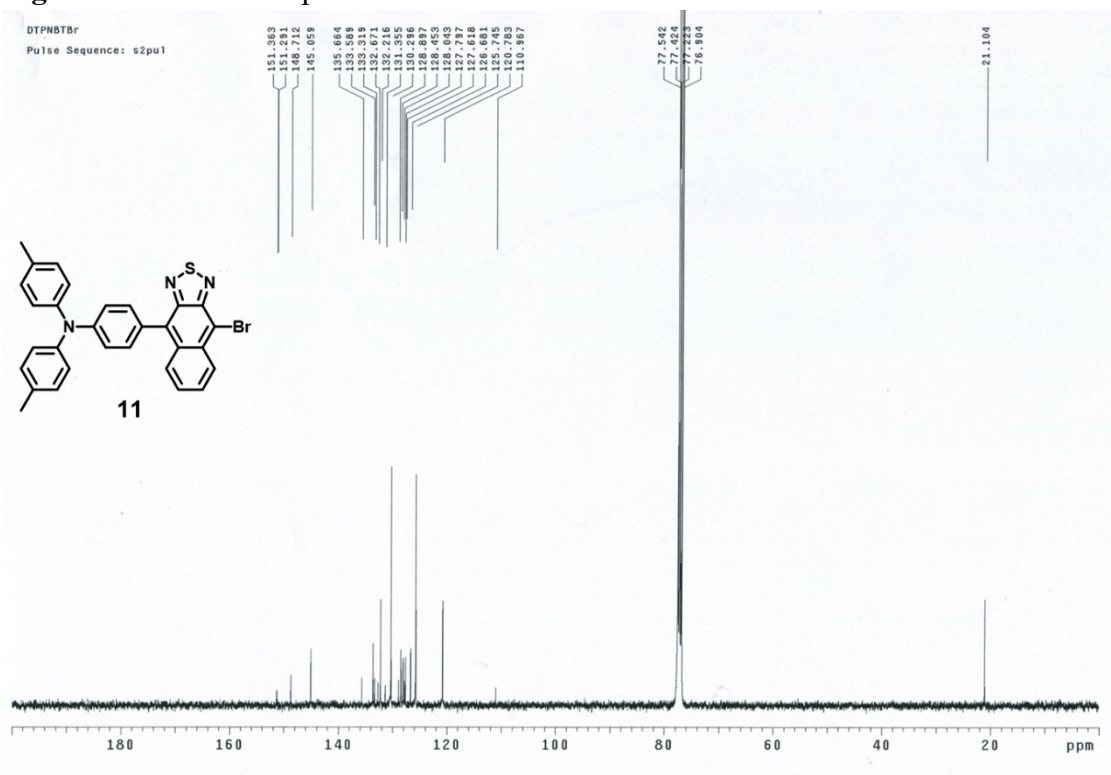


Figure S18. ^{13}C NMR spectra of **11**.

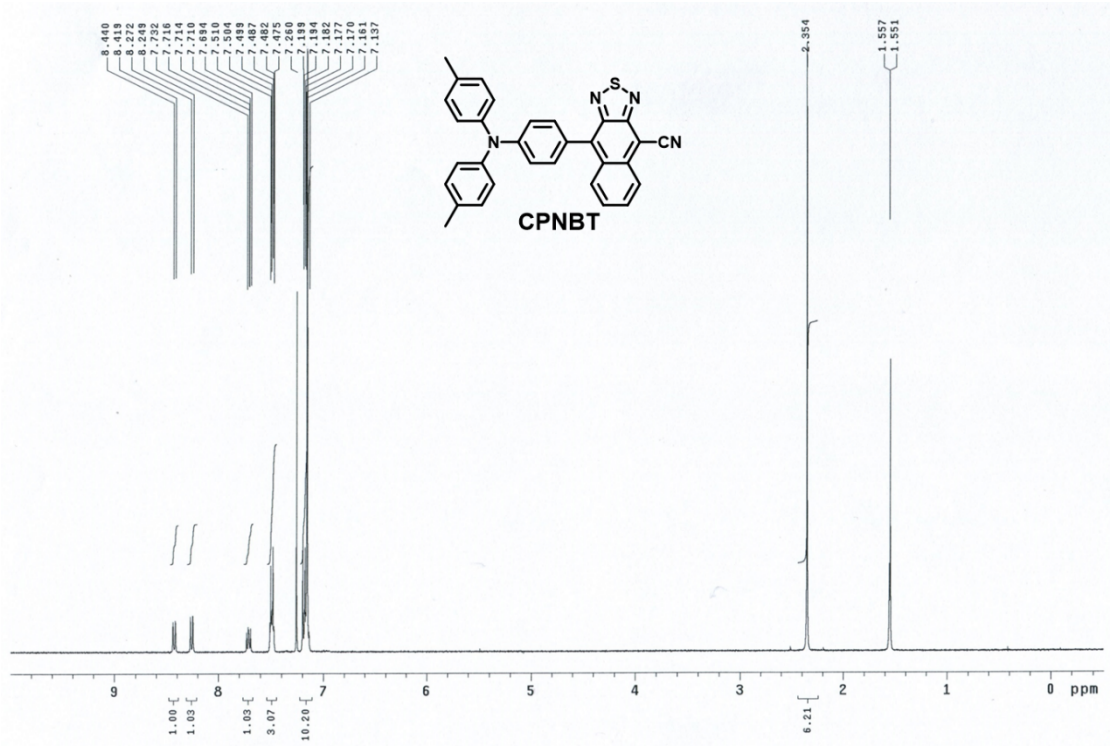


Figure S19. ^{1}H NMR spectra of **CPNBT**.

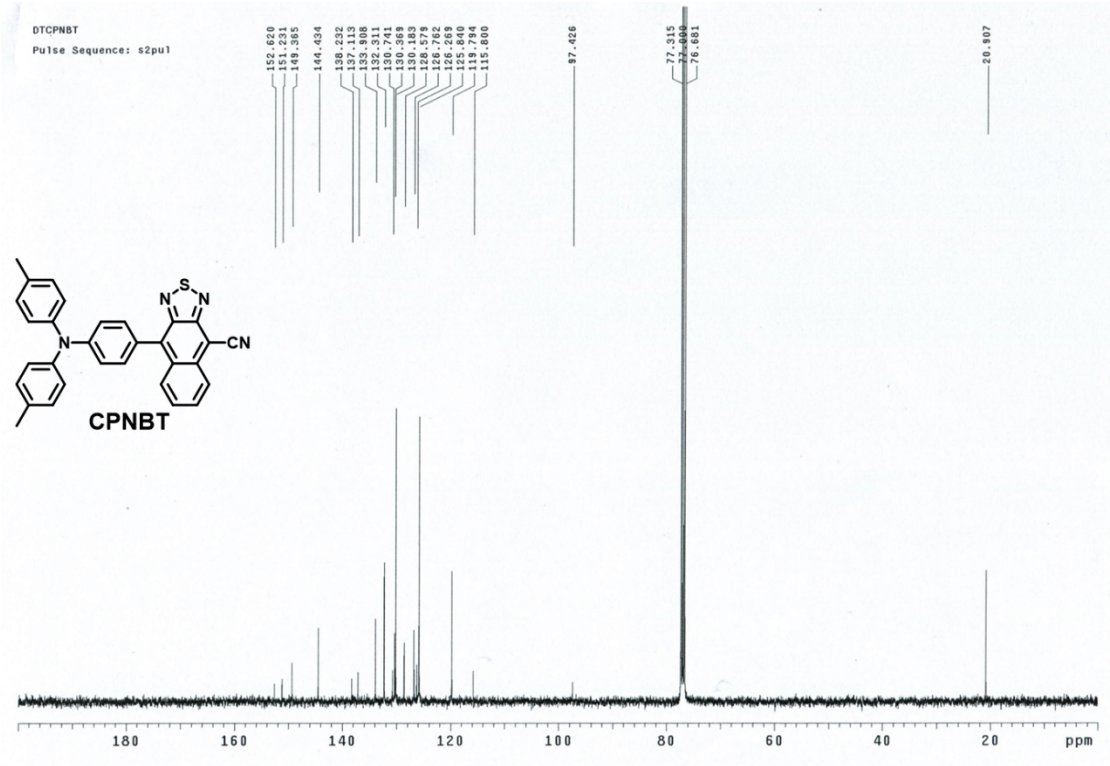


Figure S20. ^{13}C NMR spectra of **CPNBT**.