Phenanthroimidazole-Based Bipolar Carbazoles Featuring Cyano Substituents to Realize Efficient Deep Blue Electroluminescence with External Quantum Efficiency Near 6%

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Electronic Supplementary Information

Experimental section

Materials and methods

All the starting materials and solvents used, were obtained from commercial sources and consumed as received. The essential solvents used for analytical measurements were carefully dried by following standard distillation procedures. The purification of compounds was carried out through column chromatography technique by using silica gel (100-200 mesh) as stationary phase. The NMR spectra such as ^{1}H and ^{13}C of the compounds were collected at 400 and 100.3 MHz of frequency. The deuterated chloroform ($CDCl_3$) or deuterated dimethyl sulfoxide (DMSO-D6) were used as solvents to record the NMR studies. The calibration of chemical shifts was performed by using TMS (δ = 0.00 ppm) as an internal standard. The electronic absorption measurements (UV/Vis) of the synthesized final dyes were recorded in Cary 300 spectrophotometer by taking solution sample in a quartz cuvette. The fluorescence spectral measurements were performed at room temperature in Horiba Scientific spectrofluorometer instrument (Fluoromax 4). The absolute fluorescence quantum yield of final dyes was measured by calibrated integrating sphere methods attached with spectrofluorometer. The electrochemical studies (CV and DPV) were recorded in BASi Epsilon CHI electrochemical analyzer through a three-electrode configuration (glassy carbon as a working electrode, $Ag/AgNO_3$ as a reference electrode, platinum wire counter as a counter electrode). The calibration of peak potentials was performed by using ferrocene (as an internal standard) at room temperature. The dried dichloromethane (DCM) solvent of 1×10^{-4} M concentration were used to record electrochemical measurements. The tetrabutylammonium perchlorate of 0.1 M concentration was used as a supporting electrolyte. The high-resolution mass spectroscopy of dyes was accomplished in HRMS ESI spectrometer of Brucker Daltonics at positive-ion mode. The thermal characteristics of dyes were measured over Perkin–Elmer Pyris Diamond analyzer for TGA and Shimadzu DSC-60 Plus for DSC at inert (N_2) atmosphere and heating rate of 10 °C min^{-1}. The methods used to perform theoretical calculations and procedures

followed in the fabrication of organic light-emitting diode (OLED) were employed as reported in our previous report[1].

Synthesis

4,4'-(3-Bromo-9-butyl-9*H*-carbazole-2,7-diyl)dibenzaldehyde (5)

4,4'-(9-butyl-9*H*-carbazole-2,7-diyl)dibenzaldehyde (**4**) (0.4 g, 0.92 mmol) was dissolved in 15 mL chloroform and added *N*-Bromosuccinimide (0.18 g, 1.08 mmol) portion-wise in dark condition. After completion of reaction, the content was poured into water and obtained compound was filtered to obtained the crude. It was further purified over silica gel column chromatography in chloroform and hexanes in 1:1 ratio. Off-white solid. Yield 0.45 g (95 %); mp 179-181 °C; IR (KBr): 1694 cm^{-1} ($\nu_{C=O}$); ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 10.12 (s, 1H), 10.09 (s, 1H), 8.41 (s, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 8.01 (dd, *J* = 8.2, 2.8 Hz, 4H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.65 – 7.61 (m, 1H), 7.55 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.36 (s, 1H), 4.35 (t, *J* = 7.1 Hz, 2H), 1.95 – 1.82 (m, 2H), 1.48 – 1.36 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 192.1, 192.1, 148.4, 148.1, 148.0, 141.8, 140.3, 139.4, 138.7, 135.6, 135.5, 135.3, 130.8, 130.5, 129.5, 128.3, 125.0, 123.9, 122.9, 121.8, 121.4, 119.5, 112.0, 111.0, 108.0, 43.3, 31.3, 20.7, 14.0; HRMS calcd for $C_{30}H_{24}BrNO_2Na$ $[M + Na]^+$ m/z 532.0882, found 532.0878.

4,4'-(3,6-Dibromo-9-butyl-9*H*-carbazole-2,7-diyl)dibenzaldehyde (6)

In a dry round bottom flask equipped with magnetic stirring, 4,4'-(9-butyl-9*H*-carbazole-2,7-diyl)dibenzaldehyde (**4**) (0.4 g, 0.92 mmol) was dissolved in chloroform (15 ml). Bromine (0.1 mL, 1.94 mmol) dissolved in 10 mL chloroform was then added dropwise to the vigorously stirred solution. After addition of the entire amount of bromine, the mixture was stirred for 6 h. After completion of reaction, it was further quenched with sodium hydrogen sulphite. The obtained solid was filtered and washed with hexanes. Off white solid. Yield 0.42 g (77 %).; mp 267-269 °C; IR

(KBr): 1694 cm^{-1} ($\nu_{C=O}$); ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 10.12 (s, 2H), 8.38 (s, 2H), 8.01 (d, *J* = 8.1 Hz, 4H), 7.70 (d, *J* = 8.2 Hz, 4H), 7.35 (s, 2H), 4.27 (t, *J* = 7.2 Hz, 2H), 1.90 – 1.77 (m, 2H), 1.44 – 1.30 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 192.1, 148.1, 140.4, 139.4, 135.6, 130.7, 129.5, 125.3, 125.2, 122.9, 112.4, 111.3, 111.2, 43.4, 31.1, 20.6, 13.9; HRMS calcd for $C_{30}H_{24}Br_2NO_2$ $[M + H]^+$ m/z 588.0168, found 588.0172.

2,2'-(3,6-Dibromo-9-butyl-9*H*-carbazole-2,7-diyl)bis(1-(*p*-tolyl)-1*H*-phenanthro[9,10-*d*]imidazole) (3)

A mixture of an 3,6-dibromo-9-butyl-9*H*-carbazole-2,7-dicarbaldehyde (2) (1.00 g, 2.28 mmol), 9,10-phenanthraquinone (0.95 g, 457 mmol), NH_4OAc (3.51 g, 45.6 mmol), *p*-toludine (1.22 g, 11.4 mmol), and acetic acid (25 mL) was refluxed for 2h under nitrogen atmosphere. The progress of reaction was monitored by TLC. After completion of reaction, the reaction mixture was diluted with methanol and filtered. The product was further purified over column chromatography by using hexanes and chloroform in 1:2 ratios. Light green solid. Yield 1.2 g (66 %); mp 262-264 °C; ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 8.86 (dd, *J* = 8.0, 1.5 Hz, 2H), 8.79 (d, *J* = 8.4 Hz, 2H), 8.73 (d, *J* = 8.3 Hz, 2H), 8.16 (s, 2H), 7.78 – 7.69 (m, 2H), 7.66 (ddd, *J* = 8.4, 7.1, 1.4 Hz, 2H), 7.54 (ddd, *J* = 8.4, 6.7, 1.6 Hz, 2H), 7.46 (s, 2H), 7.42 (d, *J* = 8.2 Hz, 4H), 7.35 – 7.26 (m, 6H), 7.21 (d, *J* = 8.0 Hz, 4H), 4.12 (t, *J* = 6.9 Hz, 2H), 2.38 (s, 6H), 1.70 – 1.64 (m, 2H), 1.23 – 1.09 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 151.0, 139.7, 139.4, 137.0, 135.2, 130.4, 130.2, 129.5, 128.5, 128.3, 127.5, 127.4, 126.4, 125.7, 125.2, 124.6, 124.2, 123.8, 123.3, 123.1, 122.9, 121.1, 114.6, 113.7, 43.4, 31.0, 21.5, 20.6, 14.0; HRMS calcd for $C_{60}H_{43}Br_2N_5$ $[M]^+$ m/z 991.1879, found 991.1883.

2,2'-((3-Bromo-9-butyl-9*H*-carbazole-2,7-diyl)bis(4,1-phenylene))bis(1-(*p*-tolyl)-1*H*-phenanthro[9,10-*d*]imidazole) (7)

A mixture of an 4,4'-(3-bromo-9-butyl-9*H*-carbazole-2,7-diyl)dibenzaldehyde (**5**) (0.4 g, 0.78 mmol), 9, 10-phenanthraquinone (0.36 g, 172 mmol), NH_4OAc (1.2 g, 15.66 mmol), *p*-toludine (0.42 g, 3.91 mmol), and acetic acid (30 mL) was refluxed for 2h under nitrogen atmosphere. The progress of reaction was monitored by TLC. After completion of reaction, the reaction mixture was diluted with methanol and filtered. The product was further purified over column chromatography by using hexanes and chloroform in 1:2 ratio. Off-white solid. Yield 0.49 g (59 %); mp 366-368 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.91 (d, *J* = 7.9 Hz, 2H), 8.78 (d, *J* = 8.4 Hz, 2H), 8.72 (d, *J* = 8.3 Hz, 2H), 8.35 (s, 1H), 8.09 (d, *J* = 8.1 Hz, 1H), 7.80 – 7.71 (m, 6H), 7.70 – 7.63 (m, 4H), 7.57 (d, *J* = 1.5 Hz, 1H), 7.56 – 7.41 (m, 14H), 7.33 – 7.27 (m, 3H), 7.24 (t, *J* = 1.4 Hz, 1H), 4.31 (t, *J* = 7.1 Hz, 2H), 2.57 (s, 6H), 1.87 (dq, *J* = 9.8, 7.3 Hz, 2H), 1.42 (dq, *J* = 10.0, 7.5 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 150.6, 142.9, 140.1, 140.0, 139.0, 138.9, 137.4, 137.1, 136.1, 135.8, 132.5, 130.9, 129.8, 129.7, 129.7, 129.5, 129.3, 128.8, 128.7, 128.4, 128.3, 127.3, 127.2, 126.3, 125.6, 124.8, 124.1, 120.9, 43.6, 31.1, 21.5, 20.5, 13.9; HRMS calcd for $C_{72}H_{52}BrN_5$ $[M + Na]^+$ m/z 1065.3400, found 1065.3419.

2,2'-((3,6-Dibromo-9-butyl-9*H*-carbazole-2,7-diyl)bis(4,1-phenylene))bis(1-(*p*-tolyl)-1*H*-phenanthro[9,10-*d*]imidazole) (8)

A mixture of an 4,4'-(3,6-dibromo-9-butyl-9*H*-carbazole-2,7-diyl)dibenzaldehyde (**6**) (0.45 g, 0.76 mmol), 9, 10 phenanthraquinone (0.35 g, 1.67 mmol), NH_4OAc (1.17 g, 15.26 mmol), *p*-toludine (0.81 g, 7.63 mmol), and acetic acid (30 mL) was refluxed for 2h under inert atmosphere. The progress of reaction was monitored by TLC. After completion of reaction, the reaction mixture was diluted with methanol and filtered. The product was further purified over column chromatography by using hexanes and chloroform in 1:2 ratio. Off-white solid. Yield 0.57 g (65 %); mp 388-390 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.91 (dd, *J* = 8.0, 1.5 Hz, 2H), 8.77 (d,

J = 8.4 Hz, 2H), 8.71 (d, *J* = 8.3 Hz, 2H), 8.30 (s, 2H), 7.80 – 7.70 (m, 6H), 7.66 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 2H), 7.56 – 7.40 (m, 15H), 7.36 – 7.21 (m, 7H), 4.20 (t, *J* = 7.2 Hz, 2H), 2.57 (s, 6H), 1.86 – 1.74 (m, 2H), 1.42 – 1.28 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 150.7, 142.4, 140.4, 140.2, 139.8, 137.6, 136.3, 131.0, 130.0, 129.9, 129.4, 128.9, 128.5, 128.4, 127.4, 126.4, 125.7, 125.0, 125.0, 124.2, 123.3, 123.3, 122.9, 122.6, 121.0, 112.7, 111.4, 43.3, 31.1, 21.7, 20.6, 14.0; HRMS calcd for $C_{72}H_{51}Br_2N_5K$ $[M + K]^+$ m/z 1182.2142, found 1182.2148.

2,7-Dibromo-9-butyl-9*H*-carbazole-3-carbaldehyde (10)

An oven-dried 250 mL round-bottomed flask equipped with a magnetic stirring bar is charged with 1 g of 2,7-dibromo-9-butyl-9*H*-carbazole (**9**) (2.6 mmol) and 15 mL of dimethylformamide under stirring and cooled to 0 °C. 3.2 mL of phosphoryl chloride (39.3 mmol) is added dropwise for 15 min. The reaction is allowed to warm to room temperature and heated at 100 ◦C for 12 h. The TLC was checked the confirm the completion of the reaction. The reaction is allowed to cool to room temperature and quenched with ice, neutralized with 5% aq. Sodium hydroxide and extracted with ethyl acetate. The organic layer is washed with water and brine, dried over anhydrous sodium sulfate and the solvent is removed under reduced pressure. The crude material is purified over column chromatography. White solid. Yield 0.48 g (64%); mp 149-151 °C; IR (KBr): 1667 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 10.42 (s, 1H), 8.62 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.41 (dd, *J* = 8.3, 1.6 Hz, 1H), 4.21 (t, *J* = 7.3 Hz, 2H), 1.92 – 1.78 (m, 2H), 1.50 – 1.34 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 191.7, 144.4, 142.3, 125.5, 124.6, 124.2, 122.7, 122.7, 122.3, 122.2, 121.8, 121.1, 113.4, 112.8, 43.6, 31.0, 20.6, 13.9; HRMS calcd for $C_{17}H_{16}Br_2NO$ $[M + H]^+$ m/z 407.9593, found 407.9595.

2-(2,7-Dibromo-9-butyl-9*H*-carbazol-3-yl)-1-(*p*-tolyl)-1*H*-phenanthro[9,10-*d*]imidazole (11)

A mixture of prepared aldehyde **10** (1.2 g, 2.93 mmol), a 9, 10-phenanthraquinone (0.61 g, 2.93 mmol), NH_4OAc (4.52 g, 58.6 mmol), *p*-toludine (1.57 g, 14.65 mmol), and acetic acid (30 mL) was refluxed for 2 h under inert atmosphere. The progress of reaction was monitored by TLC. After completion of reaction, the reaction mixture was diluted with methanol and filtered. The product was further purified over column chromatography by using hexanes and chloroform in 1:2 ratios. Off-white solid. Yield 1.3 g (65 %); mp 264-266 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.86 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.78 (d, *J* = 8.4 Hz, 1H), 8.72 (dd, *J* = 8.1, 1.0 Hz, 1H), 8.11 (s, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.72 (ddd, *J* = 7.9, 6.9, 1.1 Hz, 1H), 7.64 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.62 – 7.48 (m, 3H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.23 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.17 (t, *J* = 7.3 Hz, 2H), 2.35 (s, 3H), 1.86 – 1.74 (m, 2H), 1.45 – 1.29 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 151.3, 141.7, 141.6, 139.2, 136.9, 135.1, 130.1, 129.3, 128.2, 127.3, 126.2, 125.5, 124.9, 124.3, 124.0, 123.1, 122.9, 122.8, 121.8, 121.7, 121.1, 121.0, 120.1, 112.7, 112.2, 43.3, 30.8, 29.7, 21.3, 20.5, 13.8; HRMS calcd for $C_{38}H_{29}Br_2N_3$ $[M]^+$ m/z 685.0722, found 685.0728.

2,2'-(9-Butyl-9*H*-carbazole-2,7-diyl)bis(1-(*p*-tolyl)-1*H*-phenanthro[9,10-*d*]imidazole) (27PI)

A mixture of 9-butyl-9*H*-carbazole-2,7-dicarbaldehyde (1) (0.50 g, 1.78 mmol), phenanthrene-9,10-dione (0.74 g, 3.57 mmol), NH_4OAc (2.74 g, 35.6 mmol), *p*-toludine (0.95 g, 8.90 mmol), and acetic acid (25 mL) was heated at 120 °C for 2h under nitrogen atmosphere. The progress of reaction was monitored by TLC. After completion of reaction, the reaction mixture was poured into methanol solution and filtered. The obtained brown residue was purified over silica gel column chromatography. Light green solid. Yield 0.65 g (44%); mp 375-377 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.93 (dd, *J* = 8.0, 1.5 Hz, 2H), 8.79 (d, *J* = 8.4 Hz, 2H), 8.73 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.76 (ddd, *J* = 7.9, 7.0, 1.1 Hz, 2H), 7.67 (ddd, *J* = 8.4, 7.1, 1.5 Hz, 2H),

7.60 – 7.55 (m, 4H), 7.52 (ddd, *J* = 8.3, 6.6, 1.7 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 4H), 7.40 (d, *J* = 8.0 Hz, 4H), 7.33 – 7.27 (m, 4H), 4.04 (t, *J* = 7.2 Hz, 2H), 2.54 (s, 6H), 1.66 – 1.60 (m, 2H), 1.34 – 1.28 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 151.7, 140.6, 139.8, 137.4, 136.5, 130.8, 129.2, 129.0, 128.3, 128.3, 128.1, 127.3, 126.2, 125.5, 124.8, 124.1, 123.2, 123.1, 122.8, 122.6, 120.9, 120.8, 120.3, 109.9, 77.3, 77.0, 76.7, 42.8, 29.7, 21.4, 20.6, 10.4; HRMS calcd for $C_{60}H_{46}N_5$ $[M + H]^+$ m/z 836.3747, found 836.3751.

2,2'-((9-Butyl-9*H*-carbazole-2,7-diyl)bis(4,1-phenylene))bis(1-(*p*-tolyl)-1*H*-phenanthro[9,10-*d*]imidazole) (27PHPI)

A mixture of an 4,4'-(9-butyl-9*H*-carbazole-2,7-diyl)dibenzaldehyde (**4**) (0.15 g, 0.34 mmol), a 9, 10 phenanthraquinone (0.16 g, 0.76 mmol), NH_4OAc (0.53 g, 6.94 mmol), *p*-toludine (0.18 g, 1.73 mmol), and acetic acid (30 mL) was heated at 120 °C for 2h under nitrogen atmosphere. The progress of reaction was monitored by TLC. After completion of reaction, the reaction mixture was diluted with methanol and filtered. The products were purified over column chromatography. Light green solid. Yield 0.24 g (71 %); mp 381-383 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.91 (d, *J* = 7.9 Hz, 2H), 8.79 (d, *J* = 8.4 Hz, 2H), 8.76 – 8.69 (m, 2H), 8.13 (d, *J* = 8.1 Hz, 2H), 7.80 – 7.71 (m, 6H), 7.72 – 7.62 (m, 7H), 7.62 – 7.57 (m, 2H), 7.57 – 7.41 (m, 13H), 7.30 (ddd, *J* = 7.8, 6.7, 1.2 Hz, 2H), 4.41 (t, *J* = 7.1 Hz, 2H), 2.58 (s, 6H), 1.99 – 1.89 (m, 2H), 1.52 – 1.39 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H; ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 150.7, 142.4, 140.4, 140.2, 139.8, 137.6, 136.3, 131.0, 130.0, 129.9, 129.4, 128.9, 128.5, 128.4, 127.4, 126.4, 125.7, 125.0, 124.2, 123.3, 122.9, 122.6, 121.0, 112.7, 111.4, 43.3, 31.1, 21.7, 20.6, 14.0; HRMS calcd for $C_{72}H_{53}N_7$ $[M]^+$ m/z 1015.4356, found 1015.4361.

9-Butyl-2,7-bis(1-(*p*-tolyl)-1*H*-phenanthro[9,10-*d*]imidazol-2-yl)-9*H*-carbazole-3,6-dicarbonitrile (27PI36CN)

Compound **3** (0.5 g, 0.5 mmol) and cuprous cyanide (0.27 g, 3.0 mmol) were charged into a two neck RB, and then 10mL of dry DMF was injected by syringe under an N_2 atmosphere. After being stirred at 150°C for 24 h, the reaction mixture was poured into ammonia solution and extracted with ethyl acetate and dried over sodium sulphate. The obtained product was then purified over column chromatography. Light brown solid. Yield 0.4 g (90%); mp 415-417 °C; IR (KBr): 2221 cm^{-1} ($\nu_{C\equiv N}$); ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 8.76 (dd, *J* = 7.9, 1.5 Hz, 2H), 8.71 (d, *J* = 8.3 Hz, 2H), 8.64 (d, *J* = 8.2 Hz, 2H), 7.91 (s, 2H), 7.63 – 7.56 (m, 3H), 7.58 – 7.47 (m, 9H), 7.34 – 7.25 (m, 9H), 7.20 (dd, *J* = 8.5, 1.5 Hz, 2H), 3.87 (t, *J* = 7.2 Hz, 2H), 2.42 (s, 6H), 1.42 – 1.31 (m, 2H), 1.10 (dq, *J* = 14.7, 7.3 Hz, 2H), 0.87 (t, *J* = 6.9 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 147.8, 141.8, 140.1, 137.5, 135.2, 132.2, 131.5, 130.0, 129.6, 128.5, 128.4, 128.4, 127.5, 127.3, 127.2, 127.2, 126.8, 126.7, 126.5, 126.1, 126.1, 125.8, 125.3, 124.9, 124.3, 123.3, 122.9, 121.8, 121.4, 120.4, 118.9, 113.6, 105.5, 43.4, 30.6, 22.0, 20.5, 13.9; HRMS calcd for $C_{62}H_{44}N_7$ $[M + H]^+$ m/z 886.3652, found 886.3646.

9-Butyl-2,7-bis(4-(1-(*p*-tolyl)-1*H*-phenanthro[9,10-*d*]imidazol-2-yl)phenyl)-9*H*-carbazole-3-carbonitrile (27PHPI3CN)

Compound **7** (0.35 g, 0.32 mmol), copper cyanide (0.06 g, 0.72 mmol) and DMF (30 mL) were taken in a two neck round bottom flask equipped with condenser and purged nitrogen for 15 min. It was refluxed for 24 h under inert atmosphere. Checked TLC for confirming the completion of the reaction and then quenched with ammonia solution. The obtained crude product was extract with chloroform and brine water. The product was dried over sodium sulphate and chloroform was evaporated under high pressure. The obtained crude product was then purified over column chromatography with chloroform:hexanes (4:1). Off-white solid. Yield 0.21 g (65 %); mp 385-387 °C; IR (KBr): 2217 cm^{-1} ($\nu_{C\equiv N}$); ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 8.90 (dd, *J* = 8.0, 1.4 Hz,

2H), 8.78 (d, *J* = 8.4 Hz, 2H), 8.71 (d, *J* = 8.4 Hz, 2H), 8.46 (s, 1H), 8.13 (d, *J* = 8.1 Hz, 1H), 7.85 – 7.70 (m, 6H), 7.71 – 7.58 (m, 7H), 7.60 – 7.38 (m, 13H), 7.30 (t, *J* = 7.7 Hz, 5H), 4.37 (t, *J* = 7.3 Hz, 2H), 2.57 (s, 6H), 1.96 – 1.82 (m, 2H), 1.42 (dt, *J* = 15.2, 7.6 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 150.5, 142.8, 142.0, 141.8, 141.6, 140.1, 140.0, 139.8, 137.5, 136.0, 131.0, 130.9, 129.8, 129.4, 129.3, 129.3, 129.1, 128.8, 128.8, 128.5, 128.4, 128.3, 127.3, 126.9, 126.3, 125.6, 124.9, 124.1, 123.1, 122.7, 121.9, 121.2, 121.1, 120.9, 120.9, 120.1, 110.0, 107.7, 31.1, 29.7, 21.5, 20.5, 13.9; HRMS calcd for $C_{73}H_{52}N_6Na$ $[M + Na]^+$ m/z 1035.4145, found 1035.4148.

9-Butyl-2,7-bis(4-(1-(*p*-tolyl)-1*H*-phenanthro[9,10-*d*]imidazol-2-yl)phenyl)-9*H*-carbazole-3,6-dicarbonitrile (27PHPI36CN)

Compound **8** (0.30 g, 0.26 mmol), copper cyanide (0.05 g, 0.57 mmol) were added into dimethylformamide (DMF) (20 mL) and purged nitrogen for 15 min. The content was refluxed for 24 h. After completion of reaction, the content was poured into ammonia solution. The solution was then extract with ice-cold water and dichloromethane solution for three times then passed over sodium sulphate. The obtained solution was then dried over rotary evaporator and purified by silica gel column chromatography to give the final product. Off-white solid. Yield 0.19 g (70 %); mp 420-422 °C; IR (KBr): 2217 cm^{-1} ($\nu_{C\equiv N}$); ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.86 (d, *J* = 7.8 Hz, 2H), 8.72 (d, *J* = 8.4 Hz, 2H), 8.65 (d, *J* = 8.5 Hz, 2H), 8.37 (d, *J* = 2.5 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 4H), 7.73 (t, *J* = 7.4 Hz, 2H), 7.62 (dd, *J* = 15.8, 7.5 Hz, 6H), 7.53 – 7.42 (m, 10H), 7.37 (d, *J* = 2.0 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 4.24 (t, *J* = 7.7 Hz, 2H), 2.57 (s, 6H), 1.81 – 1.76 (m, 2H), 1.41 – 1.33 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 150.1, 143.3, 143.2, 140.3, 139.0, 137.6, 136.1, 131.1, 129.6, 129.4, 129.2, 128.9, 128.6, 128.4, 127.4, 127.3, 126.5, 125.7, 125.1, 124.2, 123.2, 123.2, 122.8, 121.1, 121.0, 119.6,

110.7, 103.0, 50.9, 43.5, 31.0, 21.7, 20.5, 13.9; HRMS calcd for $C_{74}H_{51}N_7K$ $[M + K]^+$ m/z 1076.3837, found 1076.3842.

9-Butyl-3-(1-(*p*-tolyl)-1*H*-phenanthro[9,10-*d*]imidazol-2-yl)-9*H*-carbazole-2,7-dicarbonitrile (27CN3PI)

Compound 10 (0.35 g, 0.50 mmol), copper(I) cyanide (0.1 g, 1.12 mmol) and DMF (20 mL) were charged in a two neck RB flask and purged nitrogen for 15 min. It was refluxed for 24 h and checked the TLC for confirming the completion of the reaction and then quenched with ammonia solution. The obtained solution was extracted with chloroform and water for three times and dried over sodium sulphate. The obtained product was then purified over column chromatography. Light brown solid. Yield 0.22 g (76%); mp 322-324 °C; IR (KBr): 2225 cm^{-1} ($\nu_{C\equiv N}$); ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 8.84 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.78 (d, *J* = 8.4 Hz, 1H), 8.71 (dd, *J* = 8.1, 1.2 Hz, 1H), 8.23 (s, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.77 (s, 1H), 7.78 – 7.67 (m, 2H), 7.66 (ddd, *J* = 8.4, 7.0, 1.6 Hz, 1H), 7.59 – 7.49 (m, 2H), 7.53 – 7.43 (m, 2H), 7.36 – 7.24 (m, 6H), 4.31 (t, *J* = 7.3 Hz, 2H), 2.40 (s, 3H), 1.84 (dq, *J* = 9.6, 7.4 Hz, 2H), 1.44 – 1.30 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 148.4, 140.9, 140.4, 140.0, 137.5, 135.1, 130.6, 129.6, 129.3, 128.9, 128.5, 128.2, 127.7, 127.6, 127.3, 126.5, 125.9, 125.4, 125.1, 124.9, 124.2, 123.3, 123.3, 123.0, 122.9, 122.5, 122.3, 121.1, 119.7, 119.6, 118.6, 114.8, 114.0, 112.3, 110.7, 43.8, 31.1, 21.5, 20.7, 13.9; HRMS calcd for $C_{40}H_{29}N_5Na$ $[M + Na]^+$ m/z 602.2315, found 602.2341.

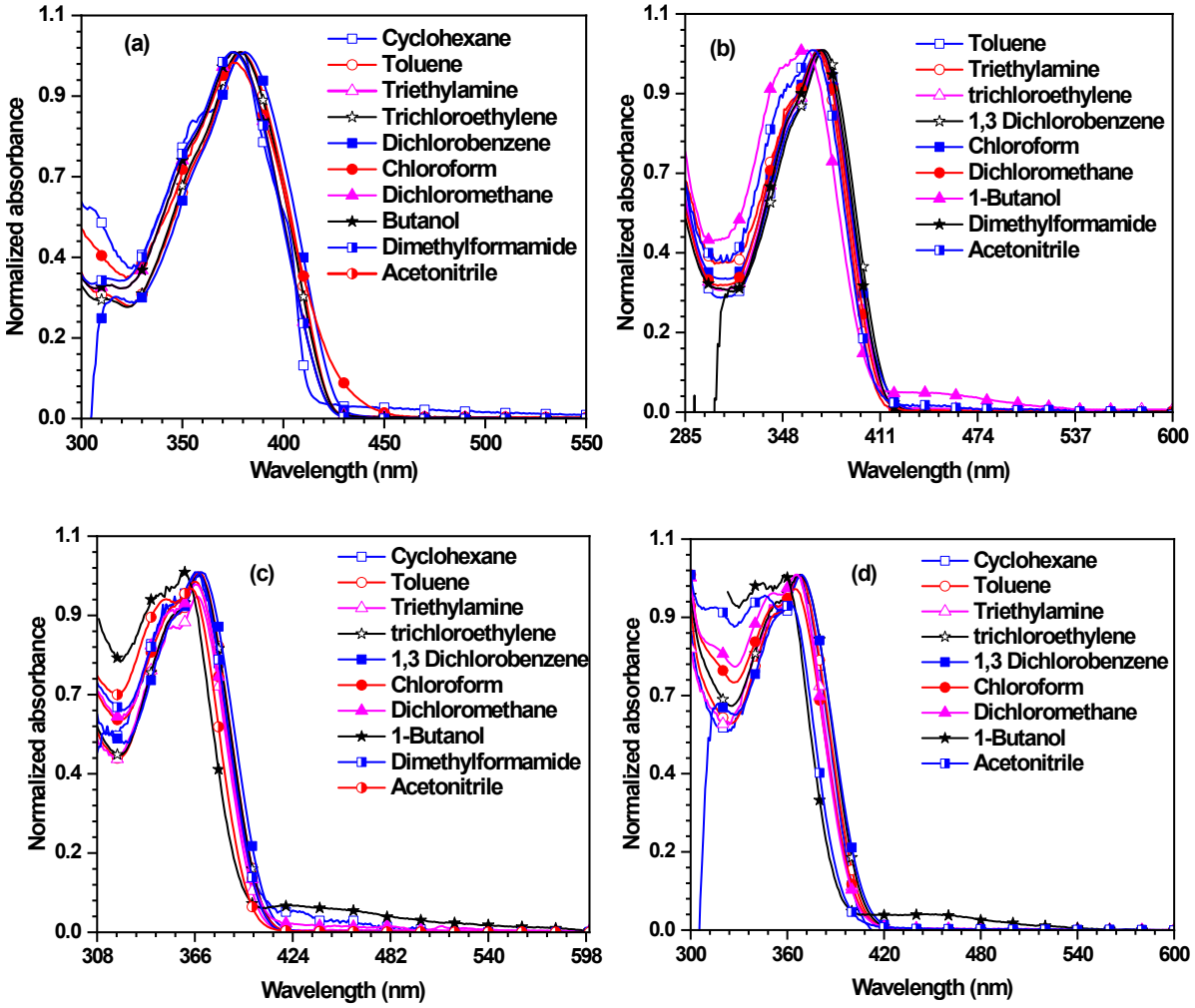
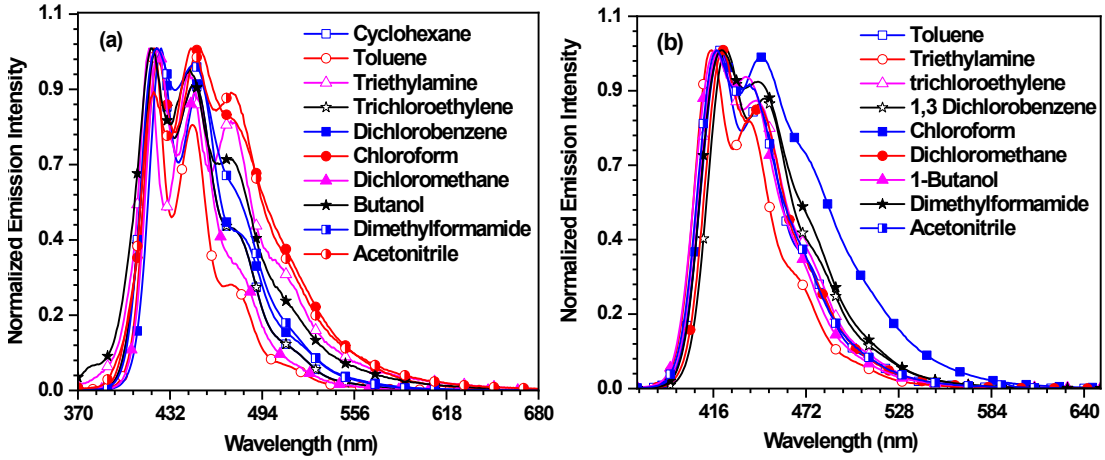


Fig. S1 Absorption spectra of the dye (a) **27PI**, (b) **27PHPI**, (c) **27PHPI36CN** and (d) **27PHPI3CN** recorded in different polarity solvents.



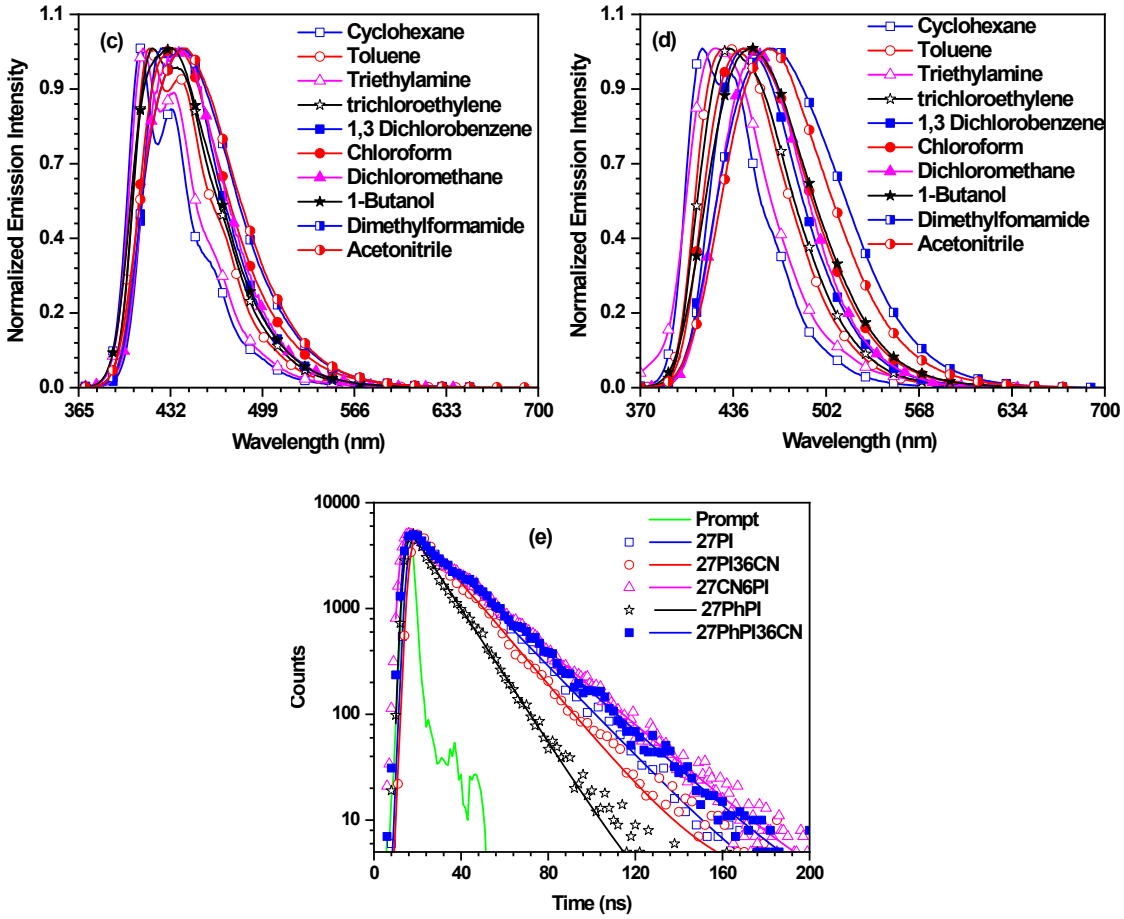


Fig. S2 Emission spectra of the dye(a) **27PI**, (b) **27PHPI**, (c) **27PHPI3CN** and (d) **27PHPI36CN** recorded in different polarity solvents. (e) Lifetime measurement of the compounds measured in toluene dilute solution.

References

1. A. Sharma, R. Balasaravanan, K. R. J. Thomas, M. Ram, D. K. Dubey, R. A. K. Yadav and J. H. Jou, *Dyes Pigm.*, 2021, **184**, 108830.

Table ST1 Solvatochromism data of the dyes recorded in various solvents

Solvent	**27PHPI**			**27PHPI3CN**			**27PHPI36CN**			**27PI36CN**			**27PI**			**27CN3PI**		
	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift
CH	373	414	2655	367	410	2858	365	416	3359	-	-	-	-	-	-	-	-	-
TOL	373	419	2943	369	417	3119	368	431	3972	358	428	4568	379	421	2632	389	445	3235
TEA	370	415	2931	367	412	2976	367	422	3551	359	429	4545	-	-	-	384	434	3000
TCE	372	420	3072	368	419	3308	368	433	4079	359	430	4599	379	423	2745	-	-	-
DCB	374	424	3153	370	425	3498	369	443	4527	362	434	4583	380	426	2842	389	454	3681
$CHCL_3$	371	420	3145	367	435	4259	366	445	4850	359	431	4653	376	423	2955	389	461	4015
DCM	372	422	3185	367	440	4521	366	452	5199	361	442	5076	376	424	3011	389	469	4385
BUOH	364	417	3492	360	432	4630	358	450	5711	352	435	5421	-	-	-	389	461	4015
DMF	373	421	3057	367	441	4572	-	-	-	356	446	5668	374	423	3097	389	475	4654
ACN	367	418	3325	363	442	4924	362	462	5979	356	447	5719	-	-	-	389	477	4743

Cyclohexane (CH), Toluene (TOL), Triethylamine (TEA), trichloroethylene (TCE), 1,3 dichlorobenzene (DCB), Chloroform ($CHCl_3$), Dichlorobenzene (DCM), Butanol (BUOH), dimethylformamide (DMF), Acetonitrile (ACN)

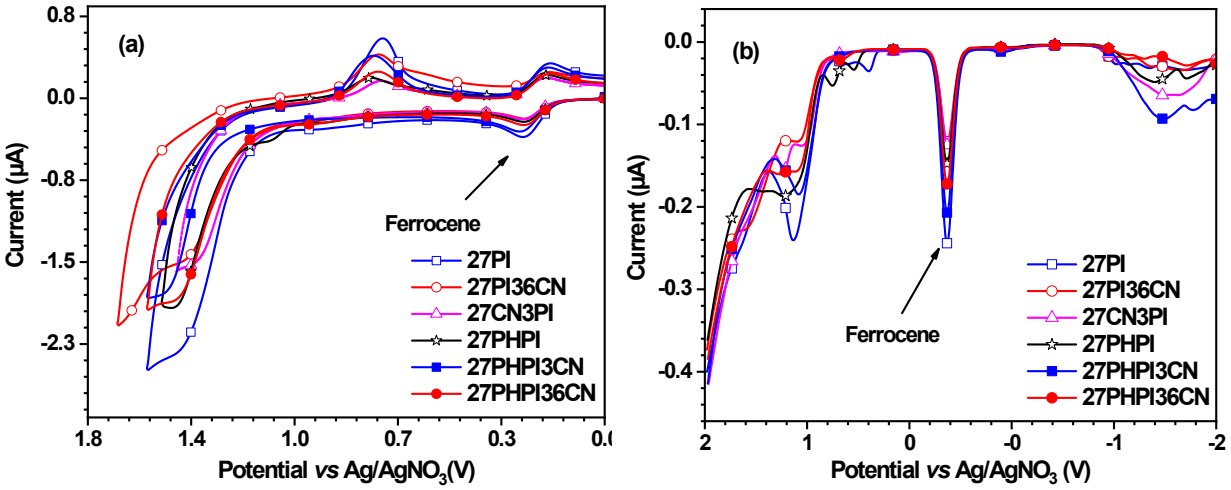


Fig. S3 (a) Cyclic voltammograms of dyes measured in dichloromethane (1 X 10^{-4} M solution).

(b) DPV of all the dyes recorded in dichloromethane solution.

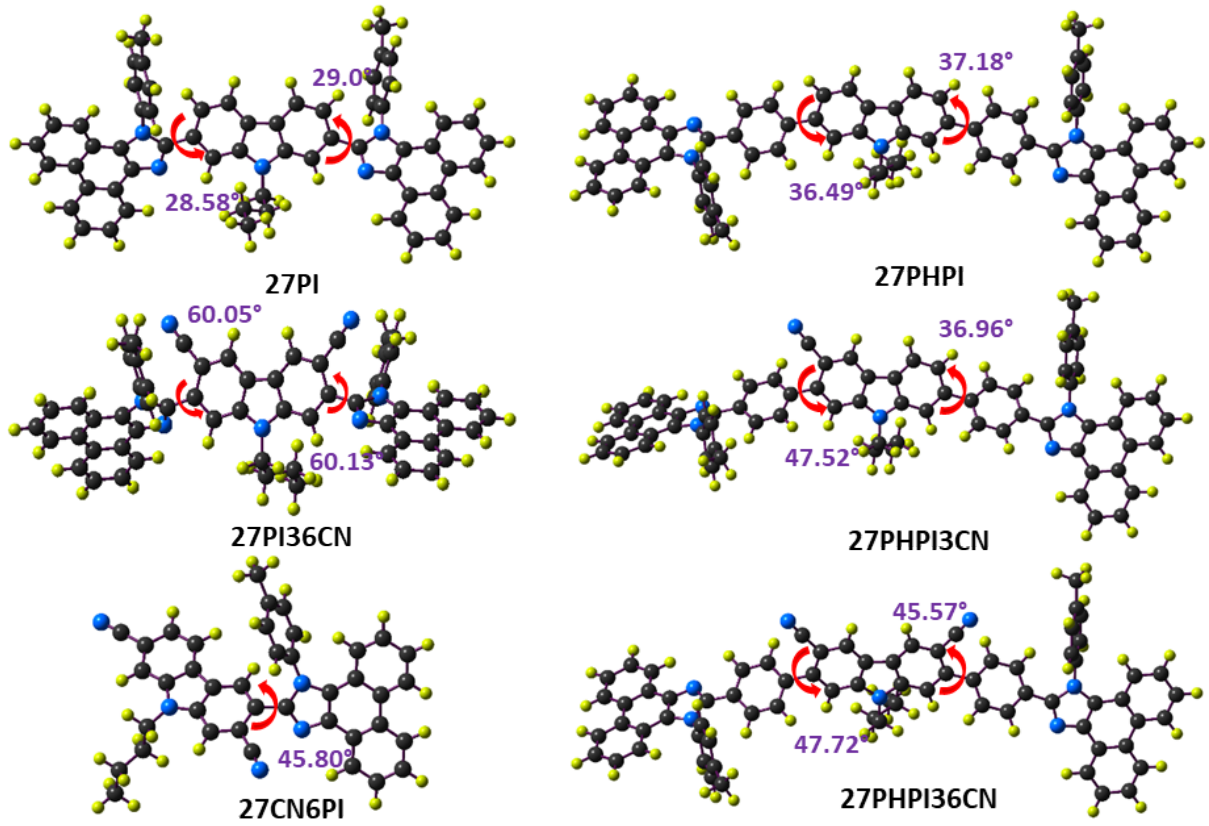


Fig. S4 Optimized geometries of the dyes with dihedral angles obtained by DFT studies.

Table ST2 Calculated vertical transitions and their oscillator strengths (*f*) (greater than 0.1) of the dyes.

Dye	Longest distance	State	λ_{abs} (nm)	*f*	Assignment (%)	HOMO (eV)	LUMO (eV)	E_g (eV)
27PI	24.70	S1	392.7	1.6390	HOMO→LUMO (+97%)	-4.91	-1.35	3.56
27PI36CN	24.29	S1	397.6	0.5244	HOMO→LUMO (+98%)	-5.38	-1.83	3.55
27PHPI	32.69	S1	391.0	2.4201	HOMO→LUMO (+93%)	-5.01	-1.44	3.57
27PHPI3CN	32.22	S1	394.8	1.8178	HOMO→LUMO (+87%), HOMO-1→LUMO (6%)	-5.13	-1.63	3.50
27PHPI36CN	32.52	S1	409.3	1.2979	HOMO→LUMO (+94%)	-5.23	-1.86	3.37
27CN3PI	17.43	S1	448.2	0.0199	HOMO→LUMO(+99%)	-5.33	-2.14	3.18
		S3	345.6	0.1113	HOMO-2→LUMO (+52%), HOMO→LUMO+1 (+42%)			
		S4	342.8	0.4559	HOMO→LUMO+1 (+54%), HOMO-2→LUMO (40%)			

Table ST3 Calculated dipole moments of the compounds.

Dye	Slope	μ_g[a]	μ_e	Δμ
27PI	1299.5002	5.89	17.05	11.16
27PI36CN	766.6642 (1st)	4.22	12.58	8.36
	11981.6149 (2nd)	4.22	37.28	33.06
27PhPI	1237.2881	3.78	20.37	16.59
27PhPI3CN	7516.9316	5.97	45.98	40.01
27PhPI36CN	8619.7540	5.74	49.18	43.44
27CN3PI	5191.3761	3.52	16.75	13.23

[a]Estimated from the B3LYP/6-31G(d,p) calculations.

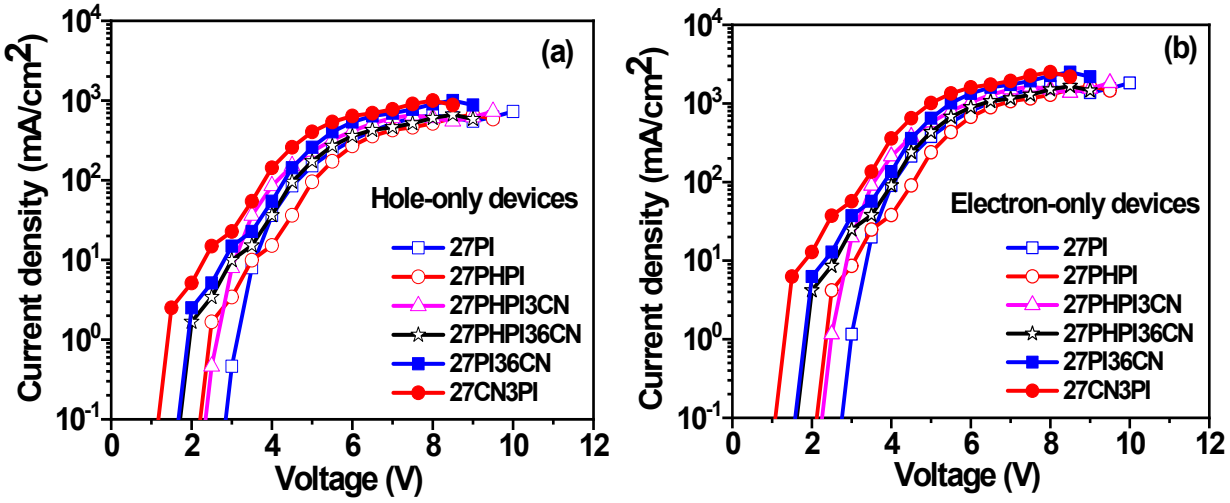
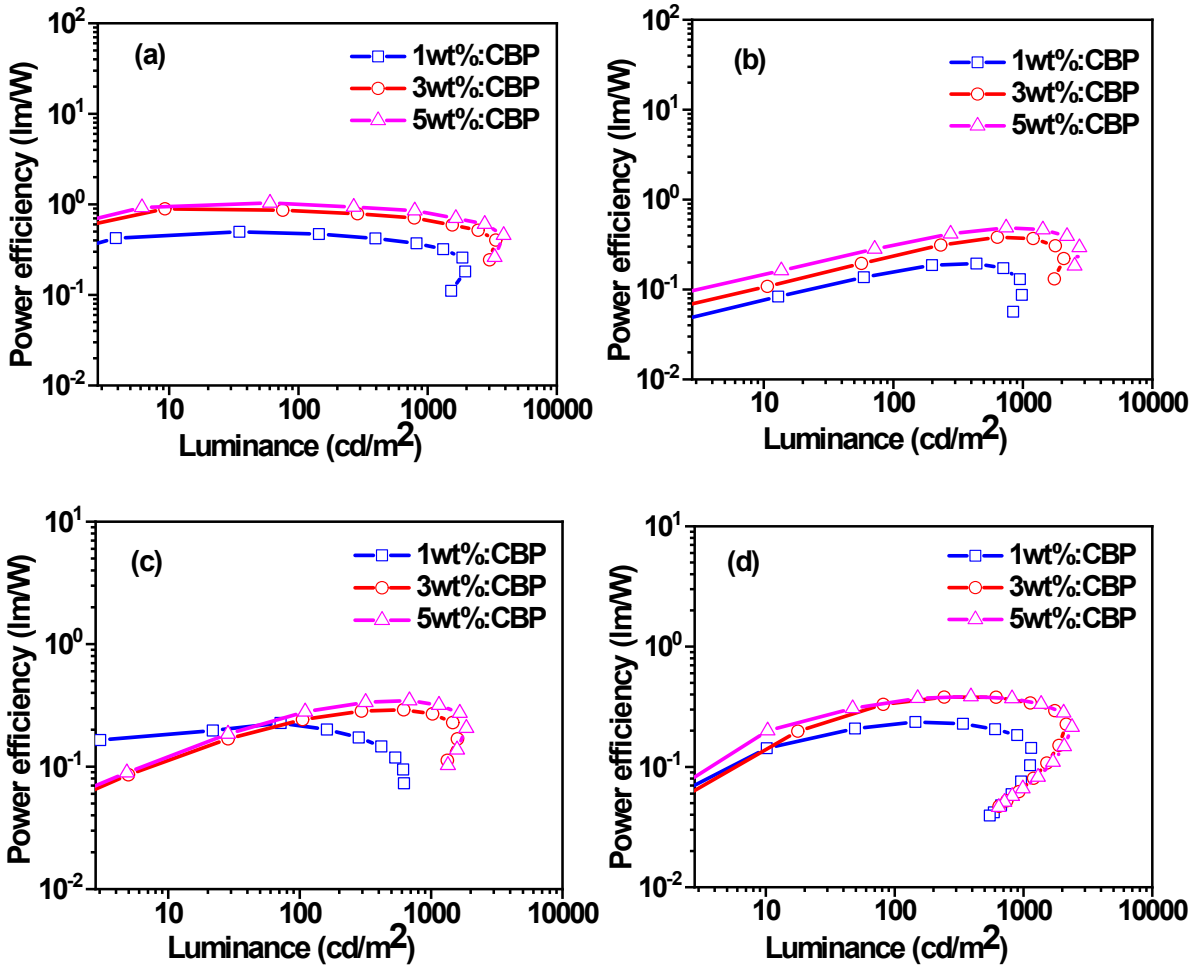


Fig. S5 Current density vs voltage plots of the a) hole-only and b) electron-only devices.



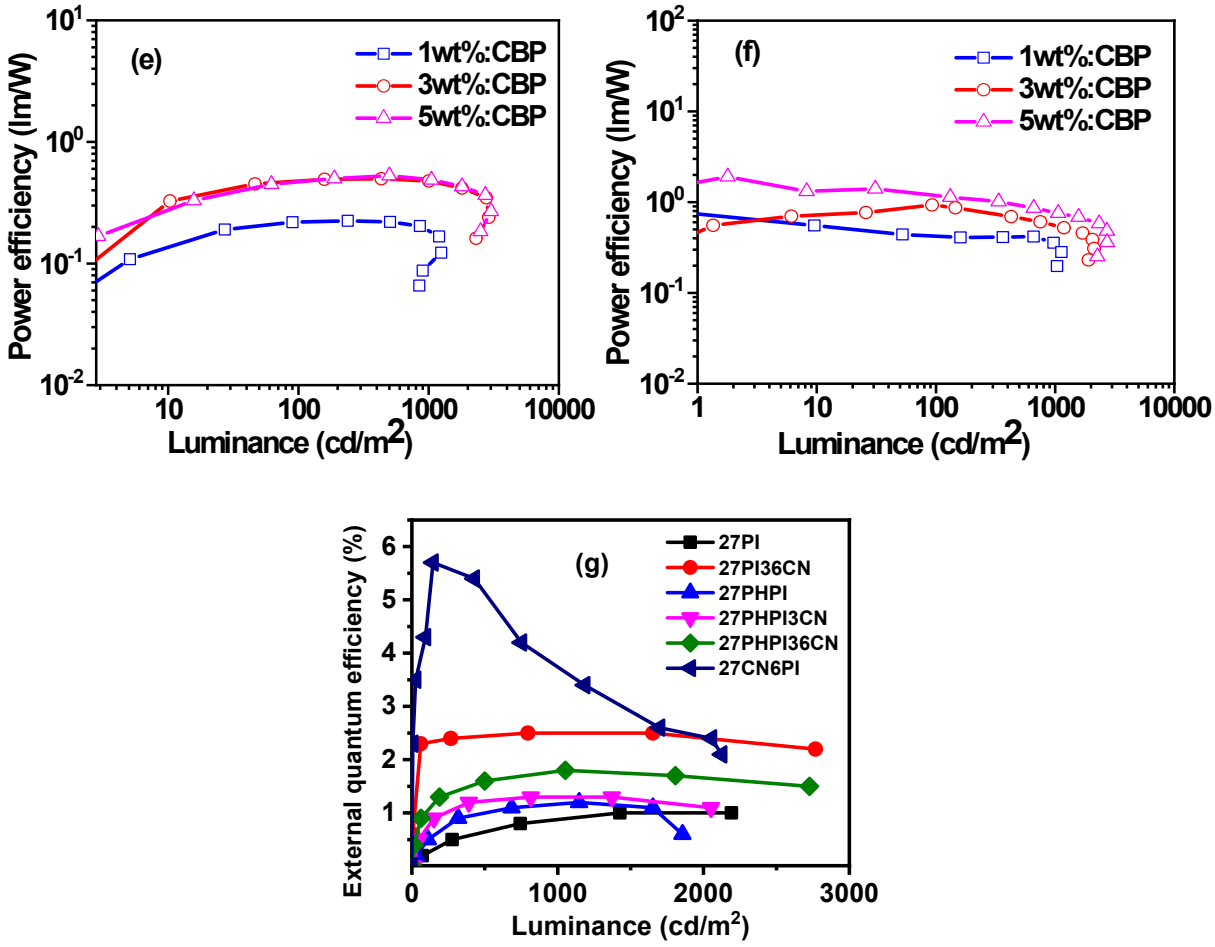


Fig. S6 Power efficiency vs Luminance plot of the device (a) **27PI36CN** (b) **27PI** (c) **27PHPI** (d) **27PHPI3CN** (e) **27PHPI36CN** (f) **27CN3PI**. (g) External quantum efficiency vs Luminance plot of the devices.

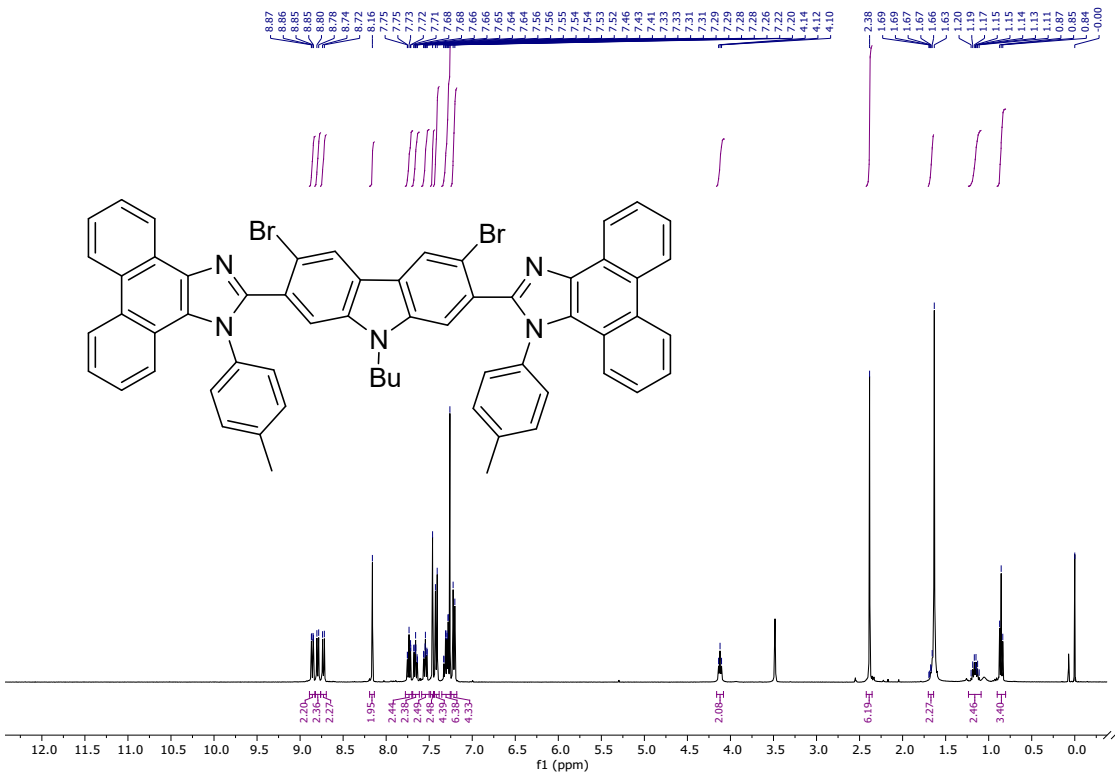


Fig. S7 ^{1}H NMR spectrum of **3** recorded in $CDCl_3$.

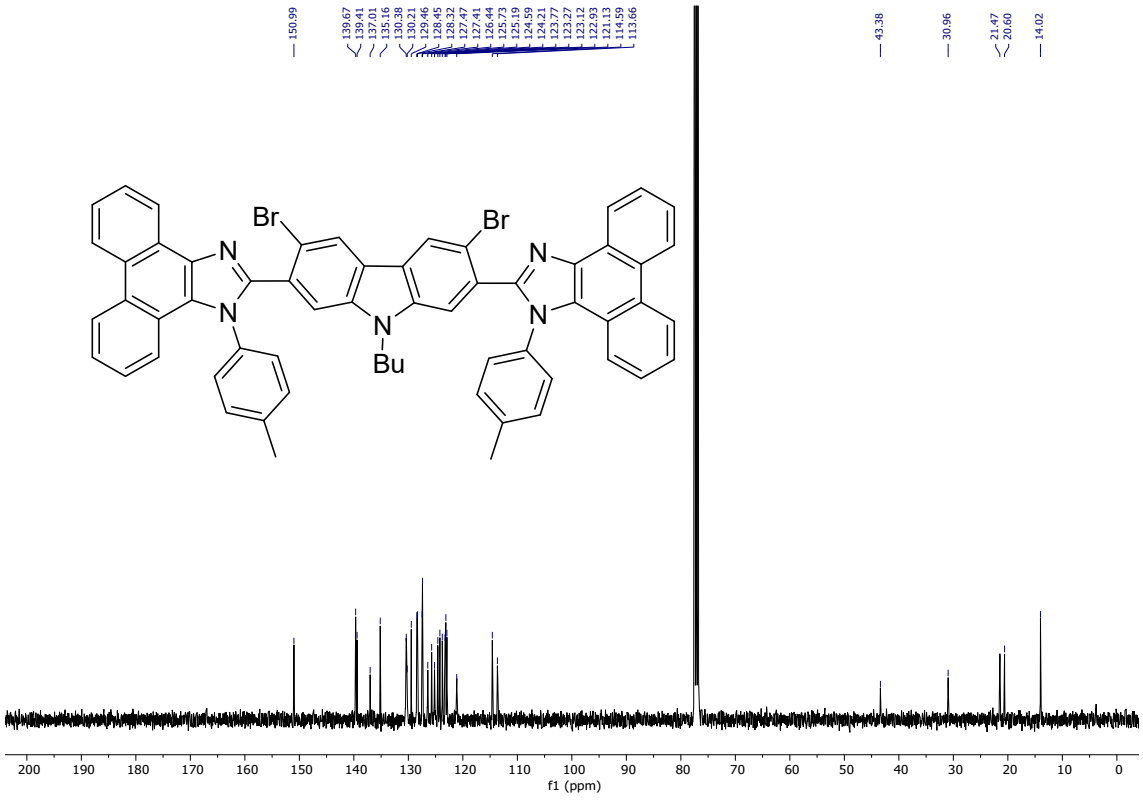


Fig. S8 ^{13}C NMR spectrum of **3** recorded in $CDCl_3$.

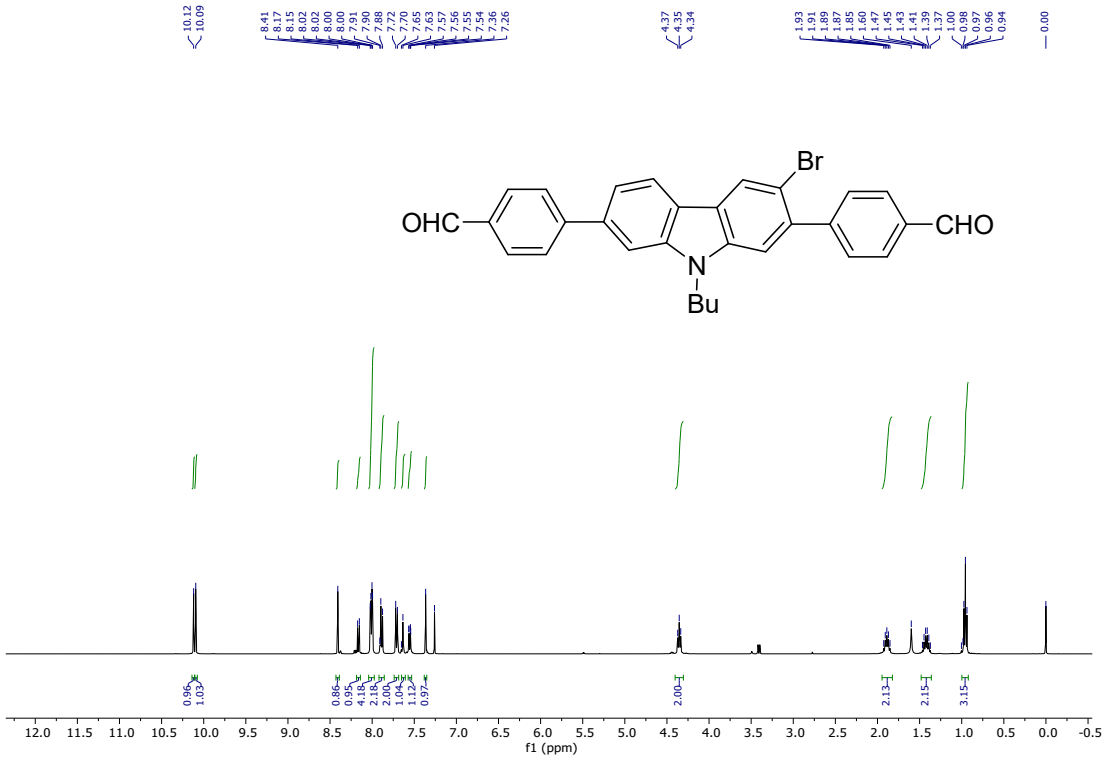


Fig. S9 ^{1}H NMR spectrum of **5** recorded in $CDCl_3$.

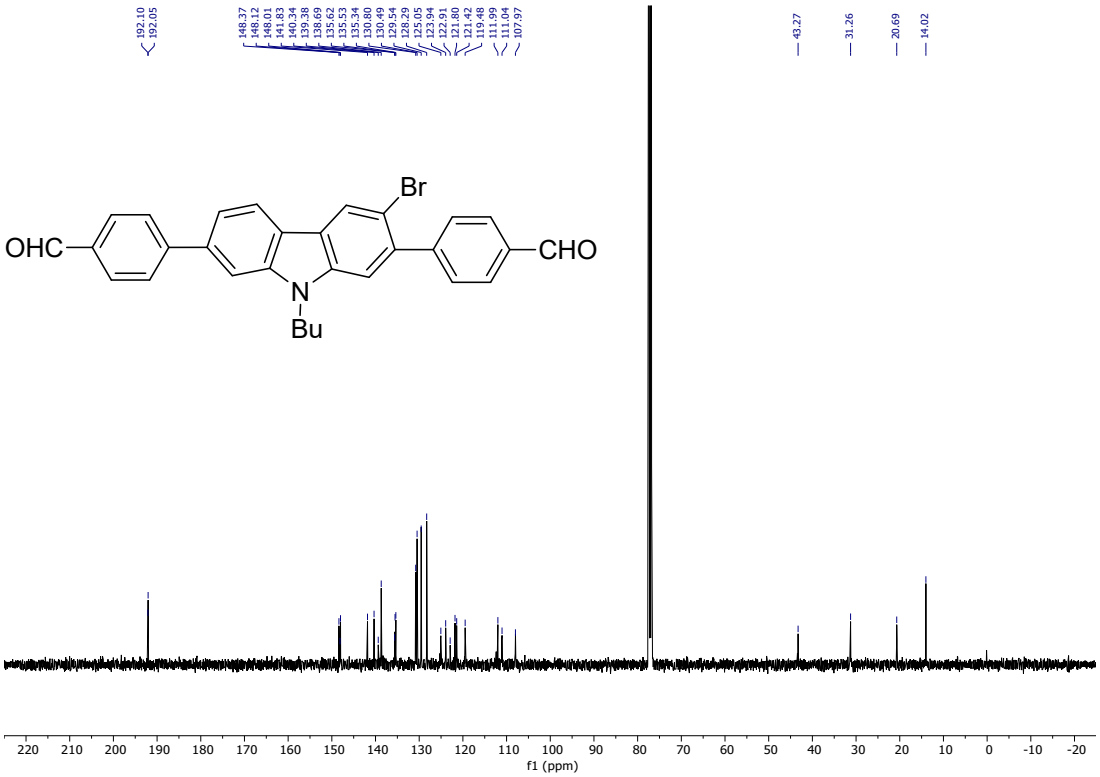


Fig. S10 ^{13}C NMR spectrum of **5** recorded in $CDCl_3$.

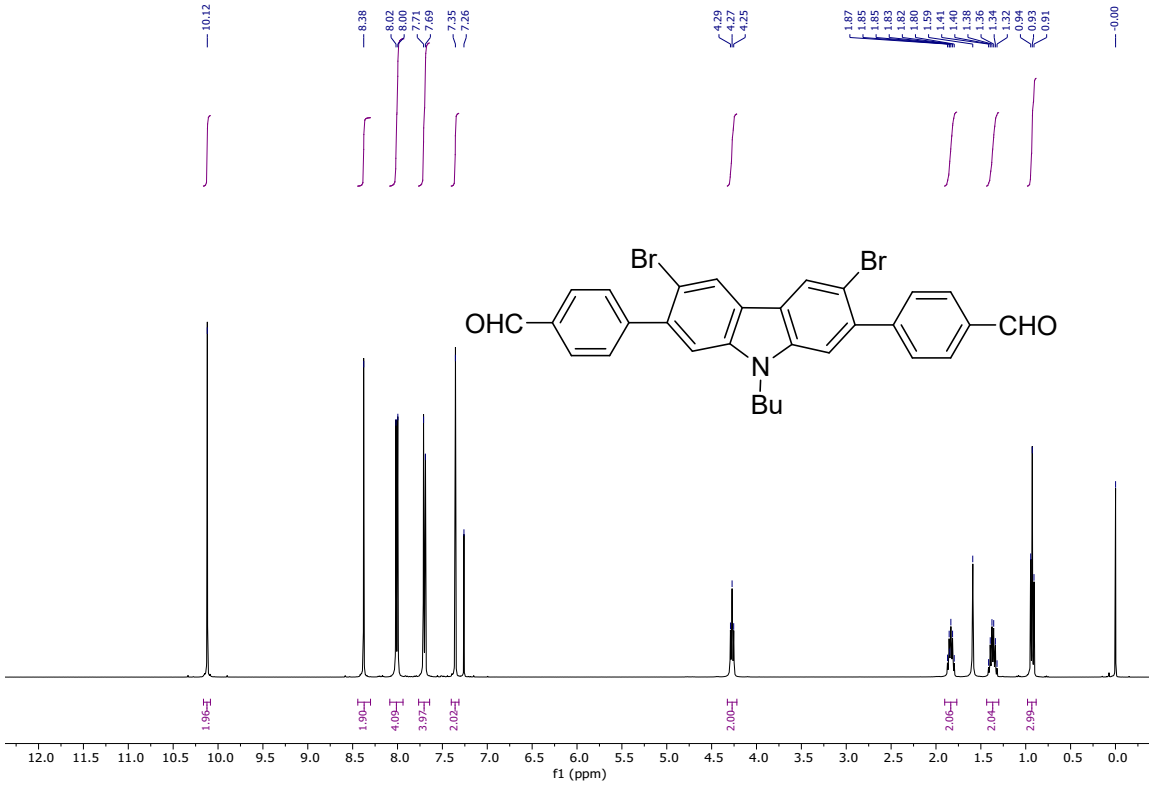


Fig. S11 ^{1}H NMR spectrum of **6** recorded in $CDCl_3$.

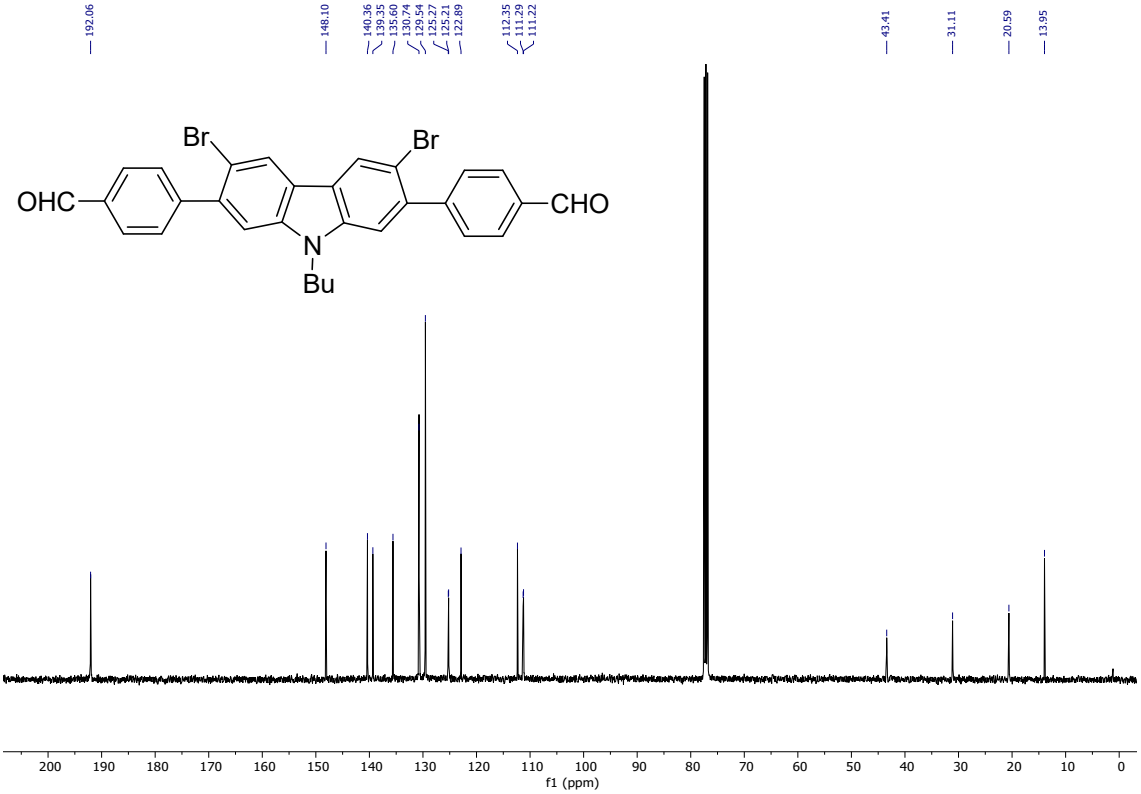


Fig. S12 ^{13}C NMR spectrum of **6** recorded in $CDCl_3$.

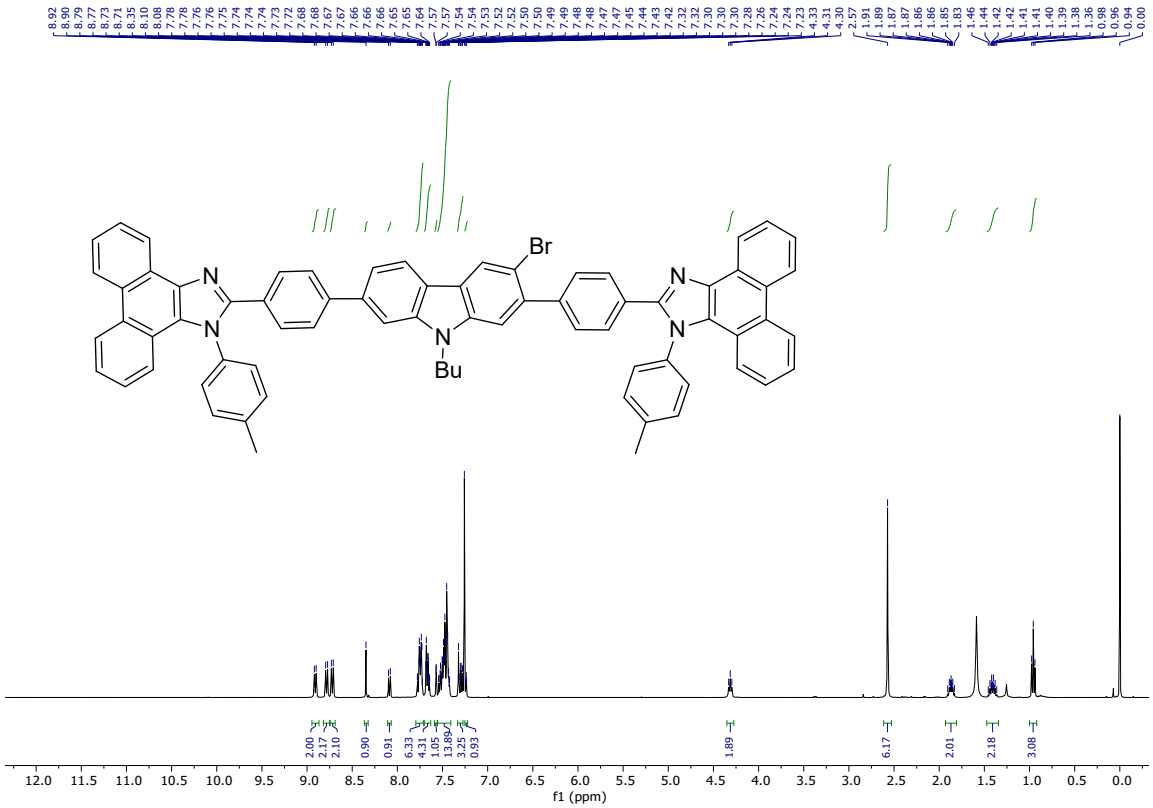


Fig. S13 ^{1}H NMR spectrum of **7** recorded in $CDCl_3$.

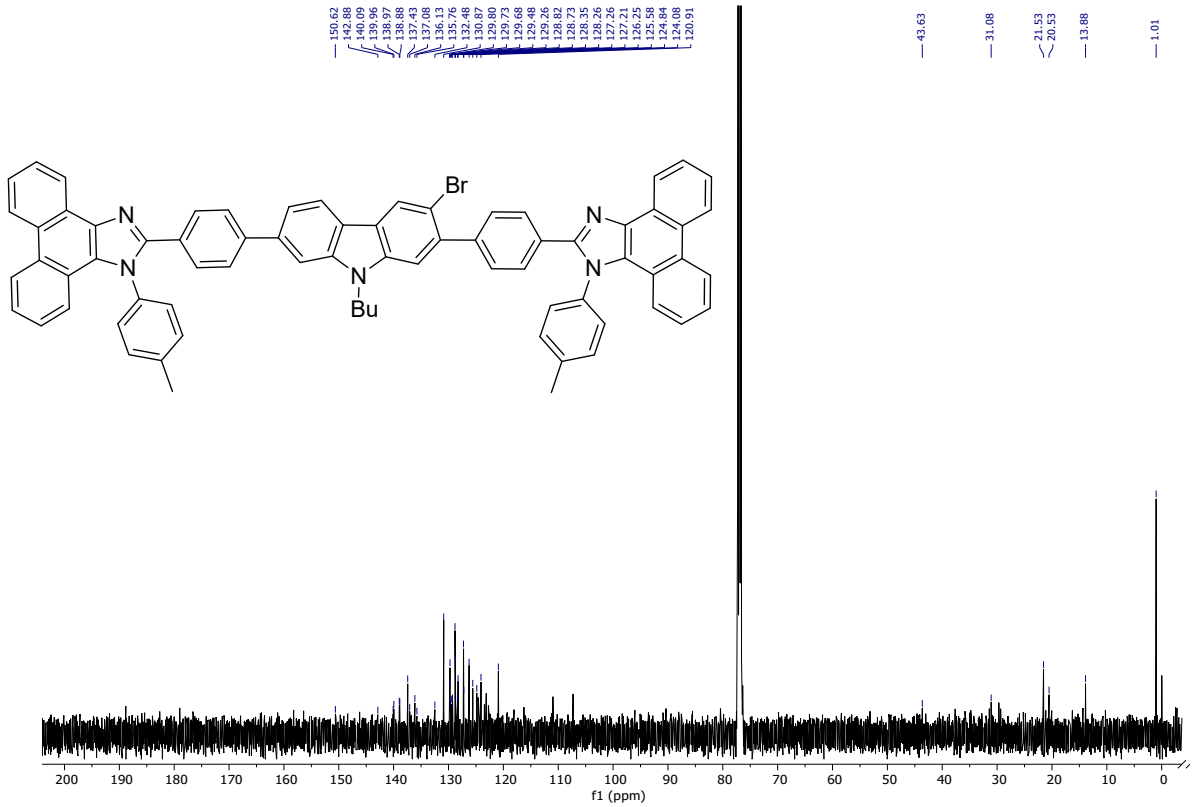


Fig. S14 ^{13}C NMR spectrum of **7** recorded in $CDCl_3$.

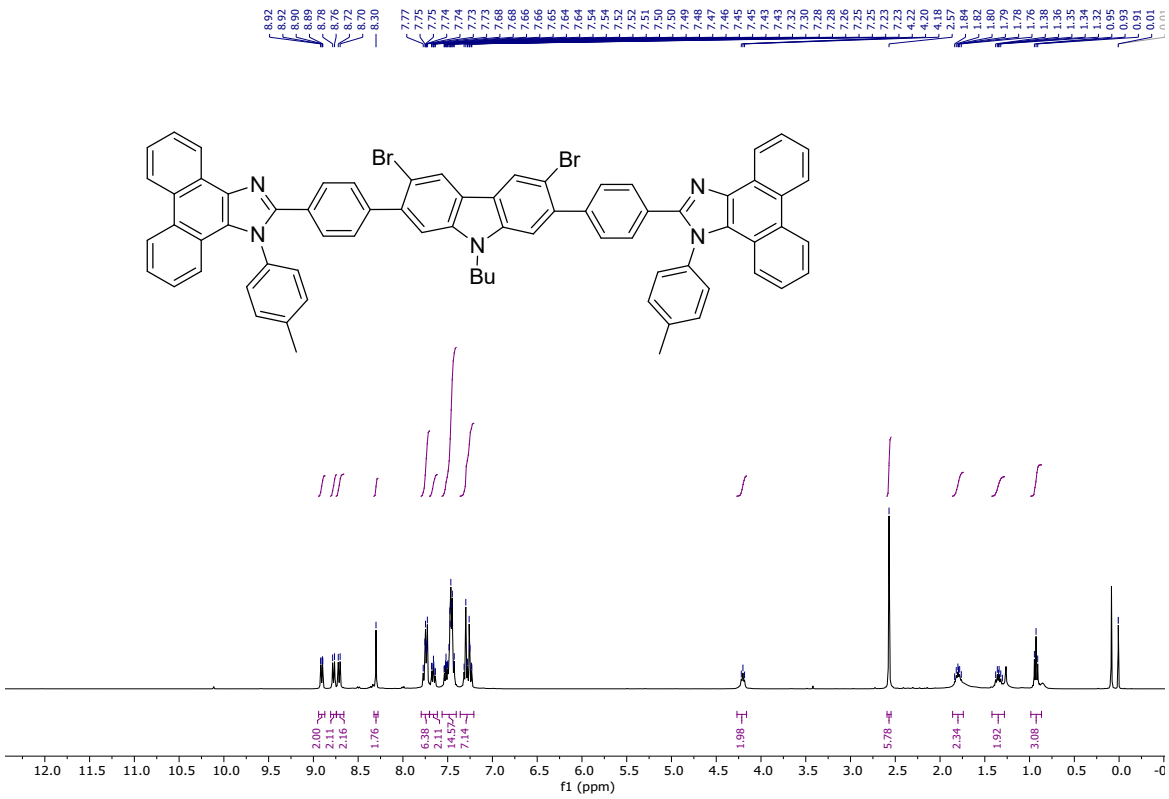


Fig. S15 ^{1}H NMR spectrum of **8** recorded in $CDCl_3$.

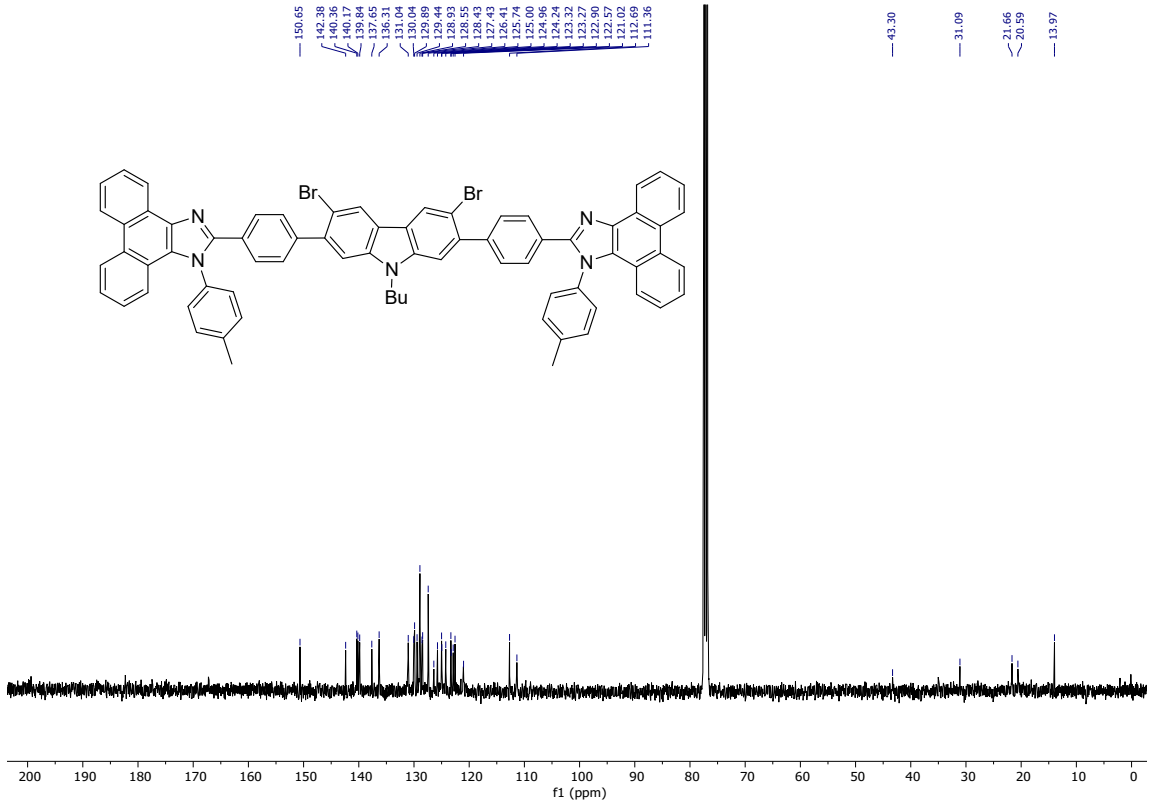


Fig. S16 ^{13}C NMR spectrum of **8** recorded in $CDCl_3$.

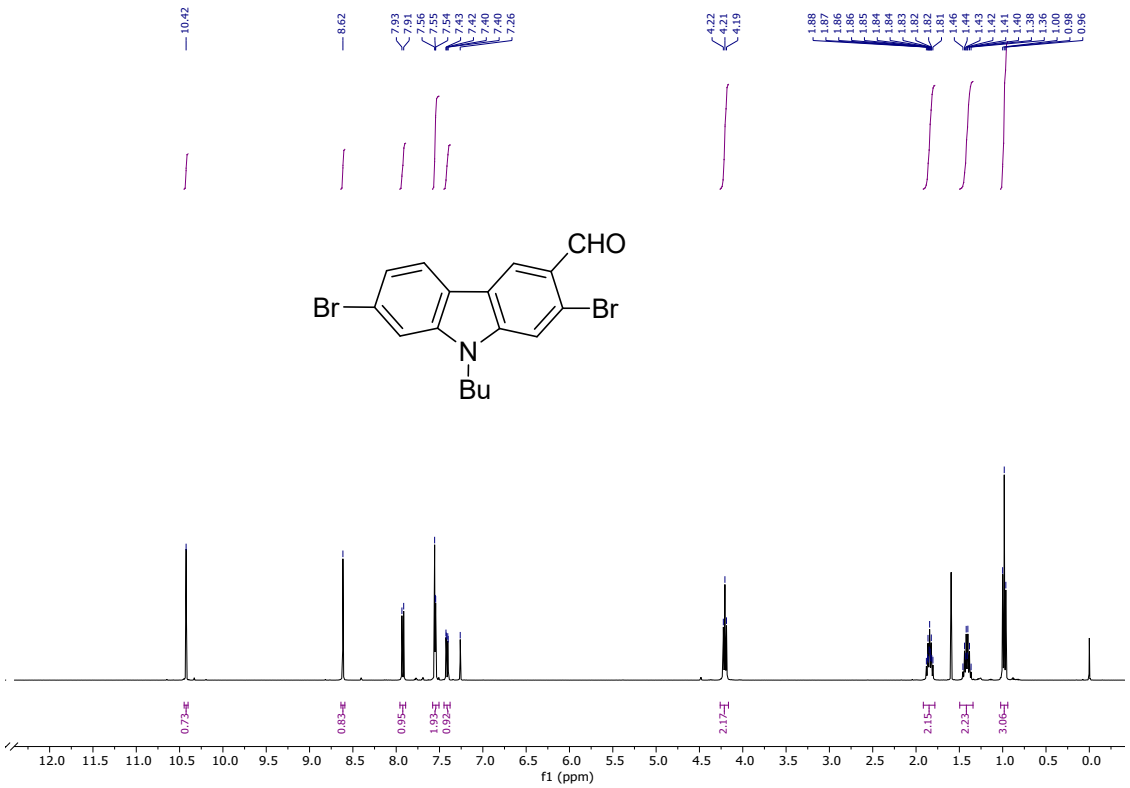


Fig. S17 ^{1}H NMR spectrum of **10** recorded in $CDCl_3$.

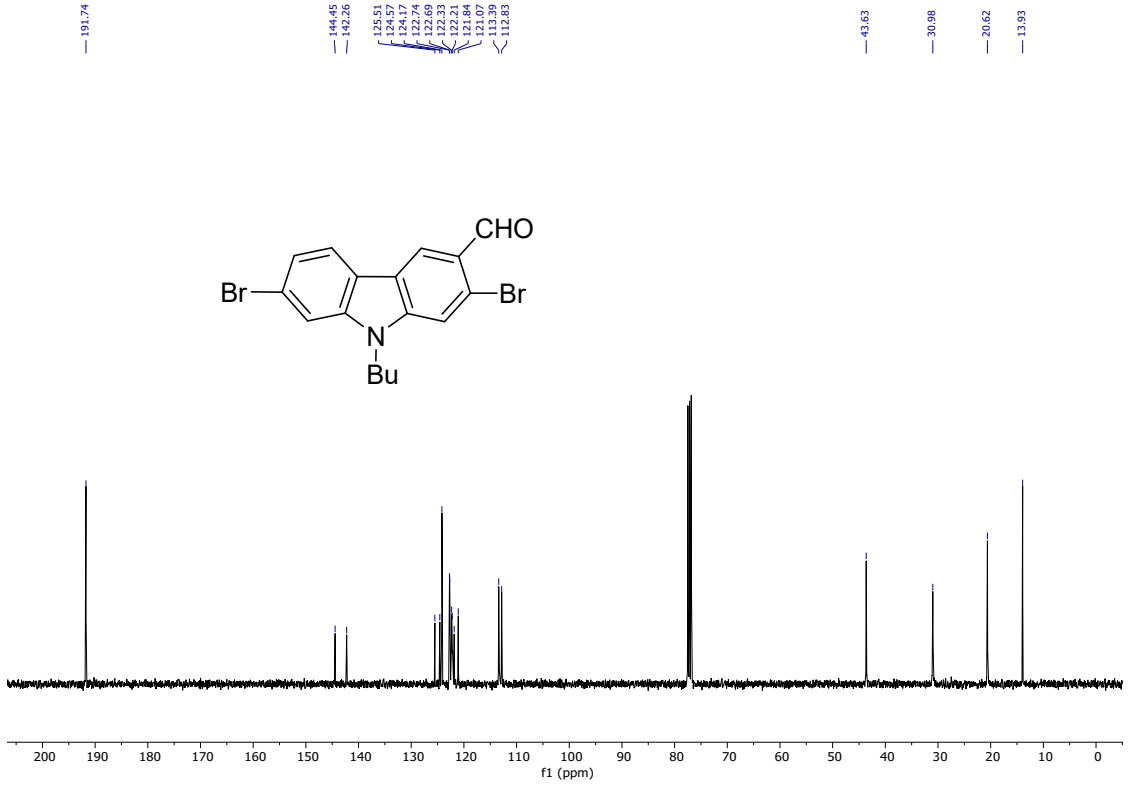


Fig. S18 ^{13}C NMR spectrum of **10** recorded in $CDCl_3$.

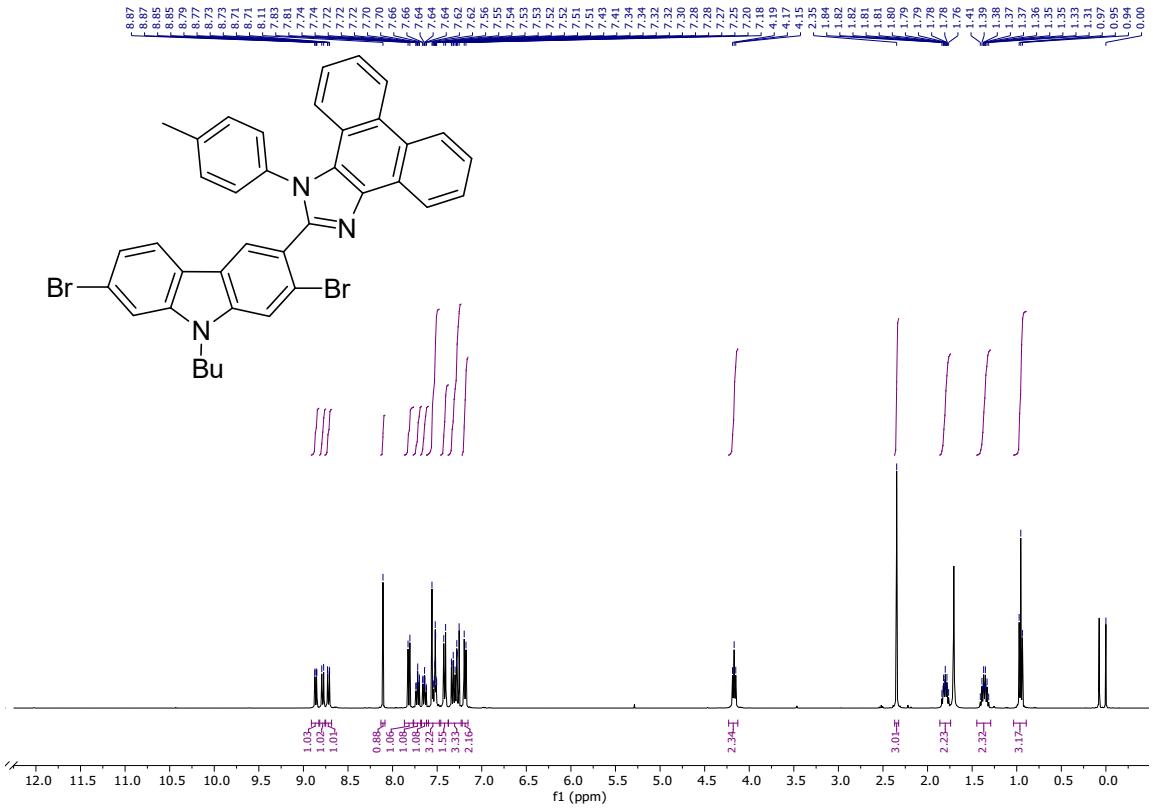


Fig. S19 ^{1}H NMR spectrum of **11** recorded in $CDCl_3$.

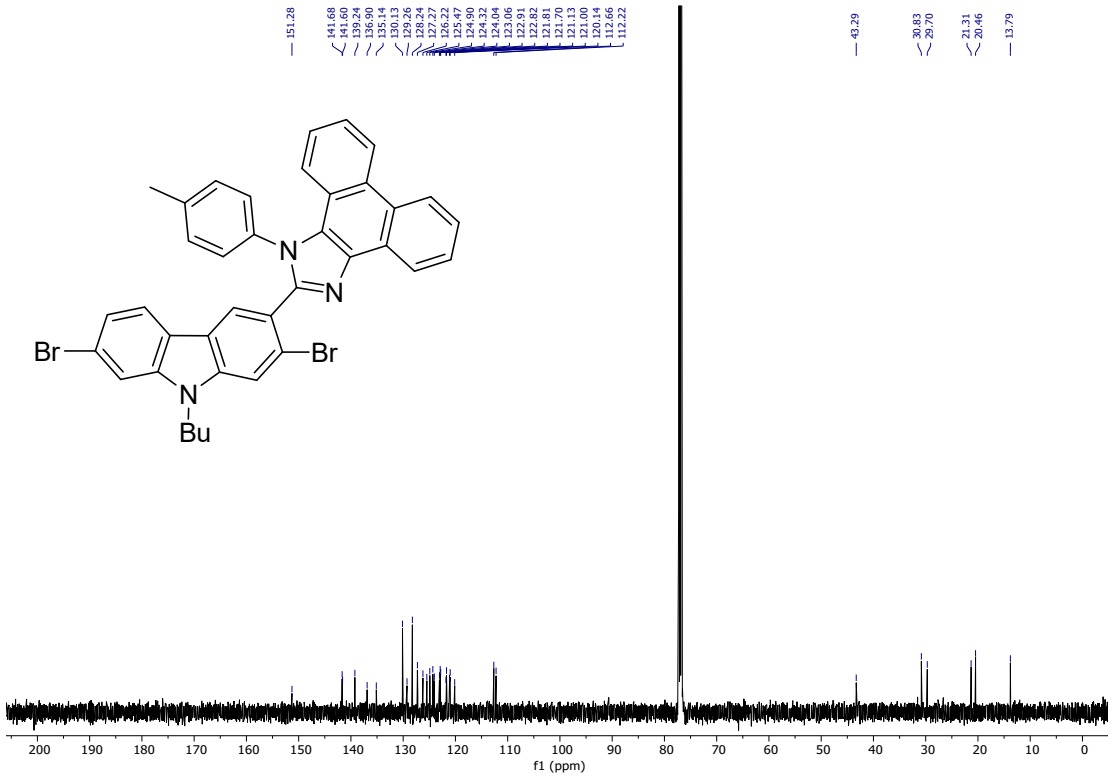


Fig. S20 ^{13}C NMR spectrum of **11** recorded in $CDCl_3$.

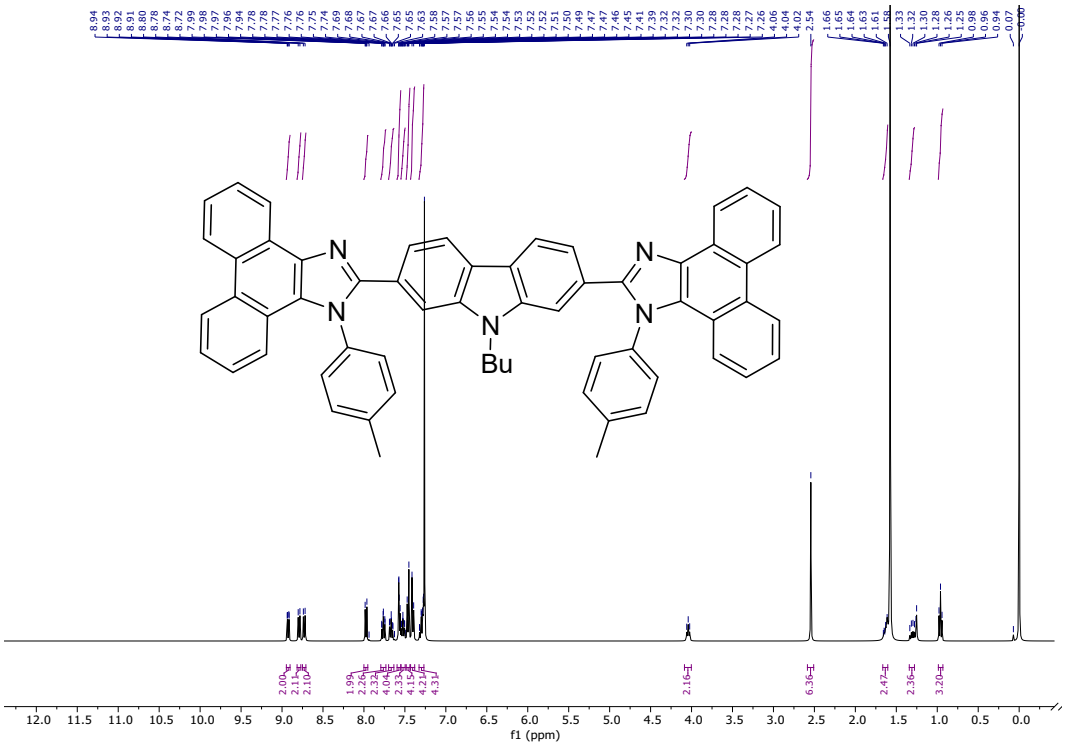


Fig. S21 ^{1}H NMR spectrum of **27PI** recorded in $CDCl_3$.

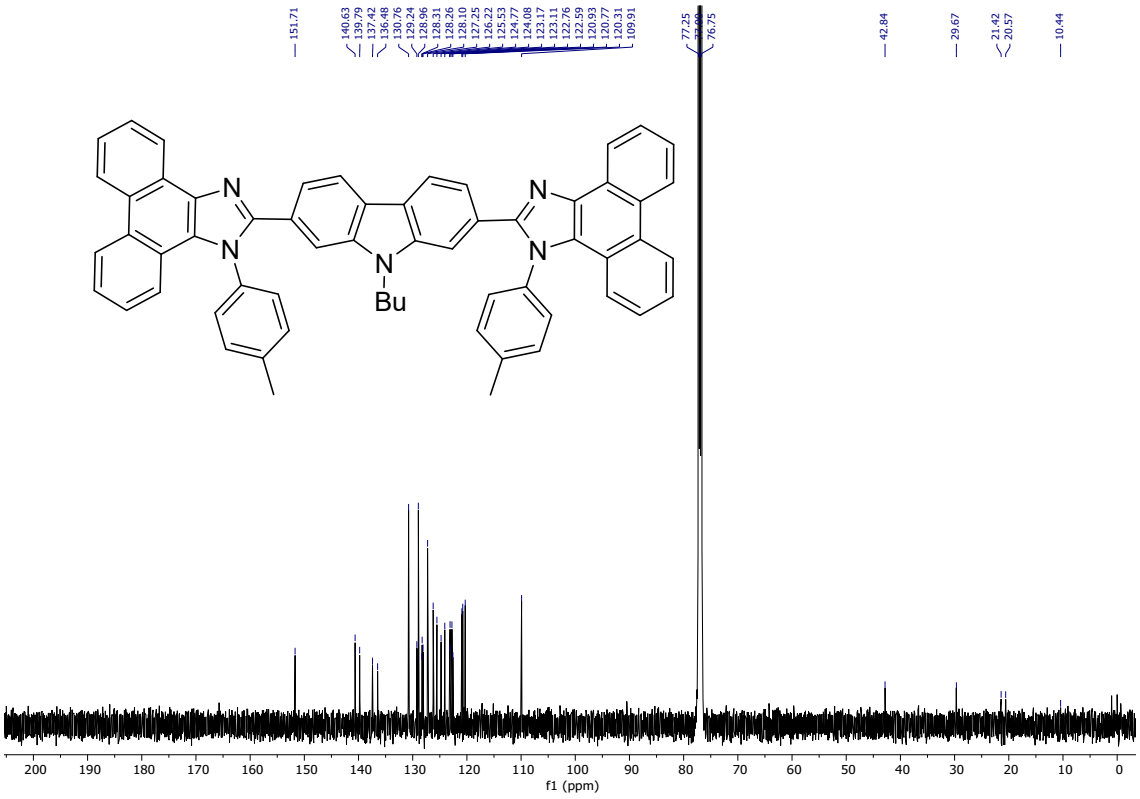


Fig. S22 ^{13}C NMR spectrum of **27PI** recorded in $CDCl_3$.

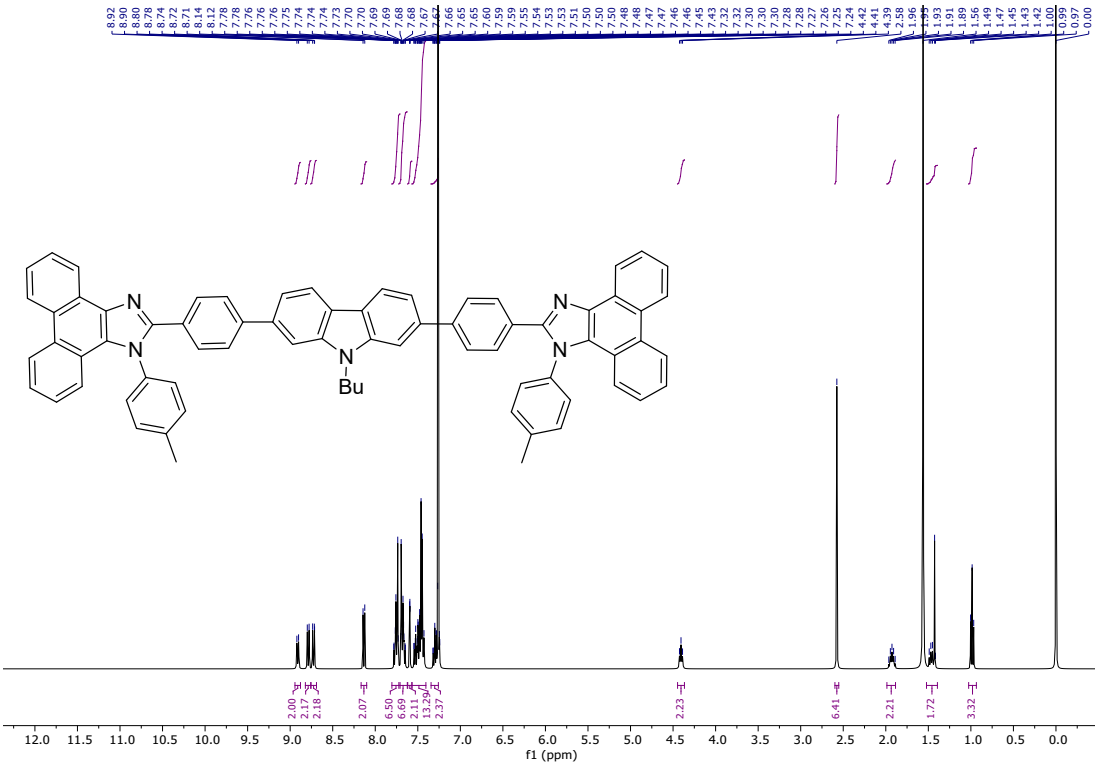


Fig. S23 ^{1}H NMR spectrum of **27PHPI** recorded in $CDCl_3$.

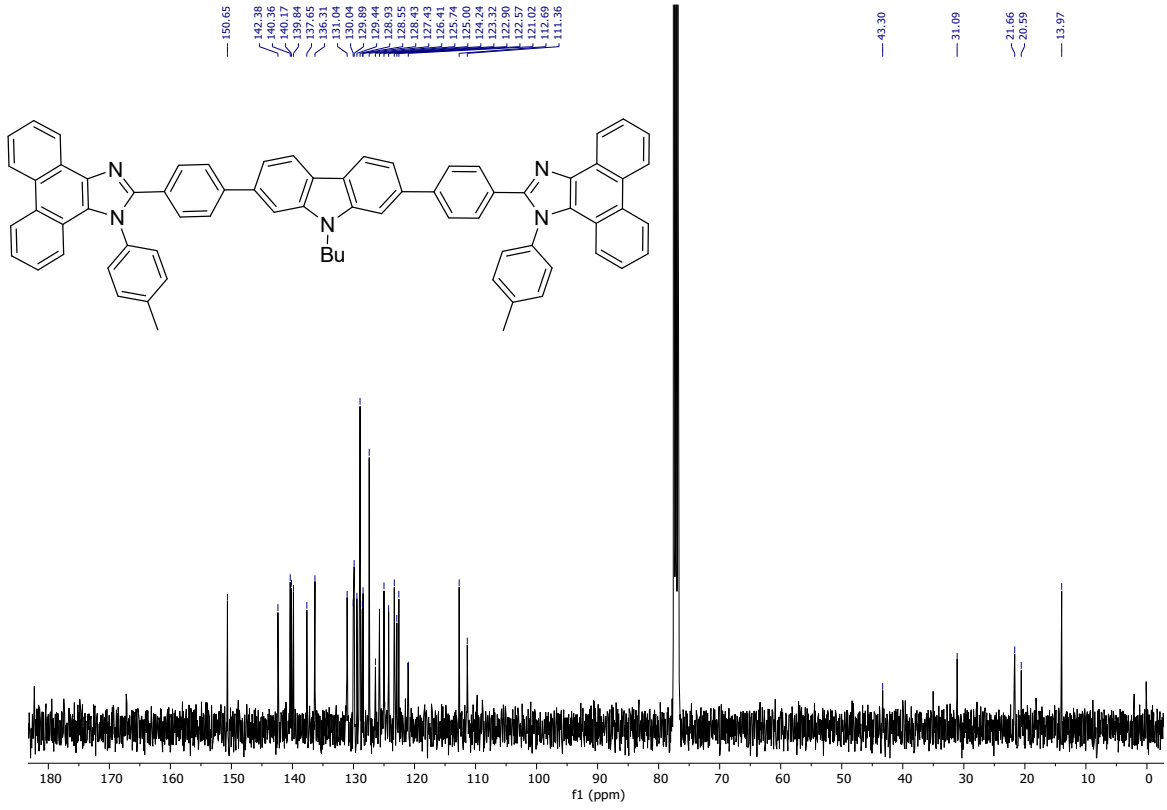


Fig. S24 ^{13}C NMR spectrum of **27PHPI** recorded in $CDCl_3$.

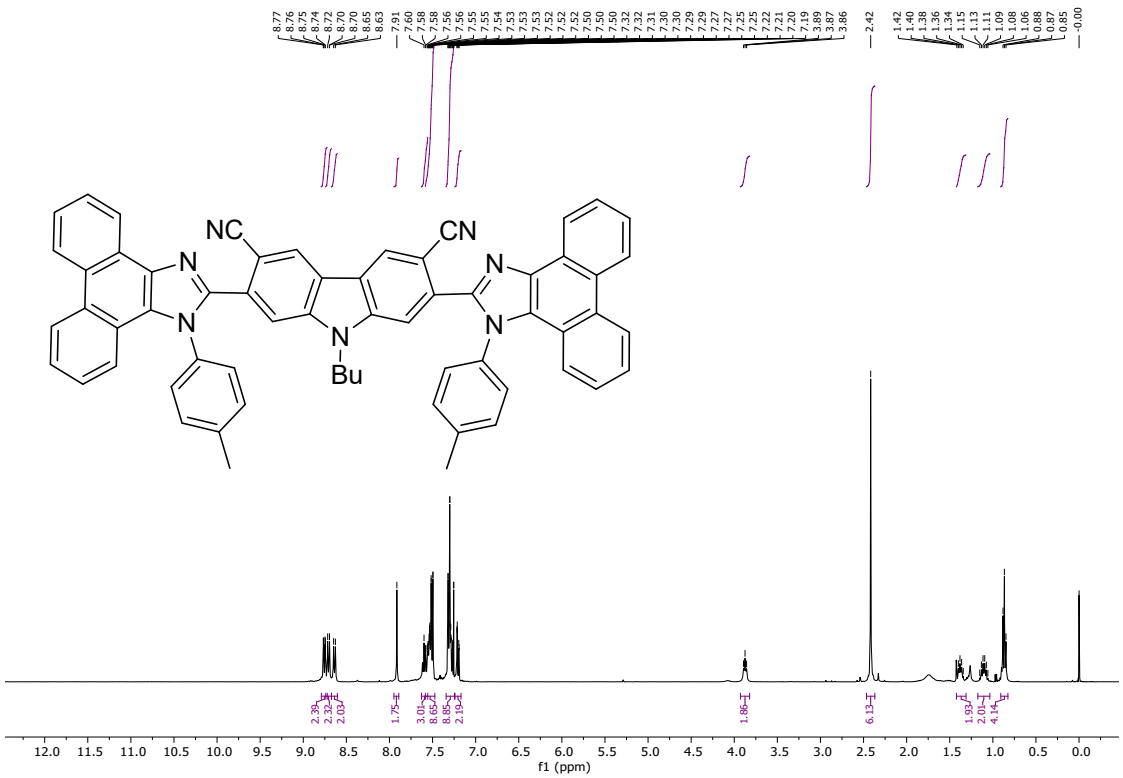


Fig. S25 ^{1}H NMR spectrum of **27PI36CN** recorded in $CDCl_3$.

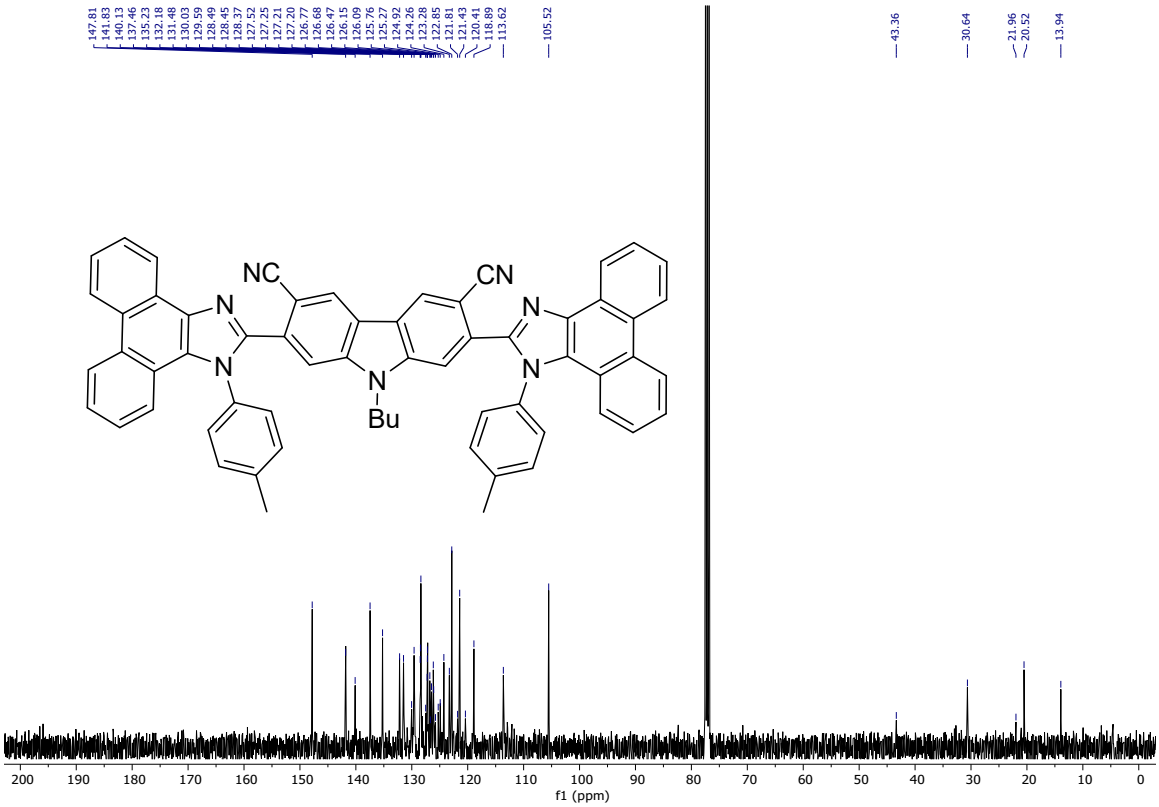


Fig. S26 ^{13}C NMR spectrum of **27PI36CN** recorded in $CDCl_3$.

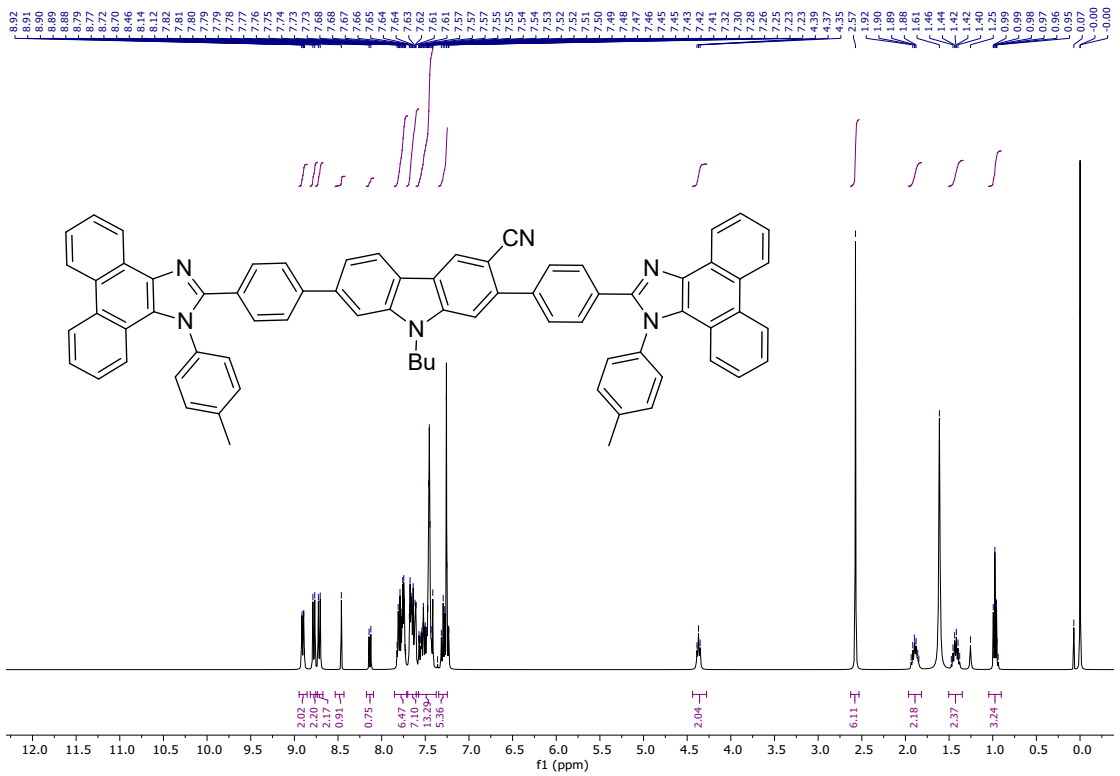


Fig. S27 ^{1}H NMR spectrum of **27PHPI3CN** recorded in $CDCl_3$.

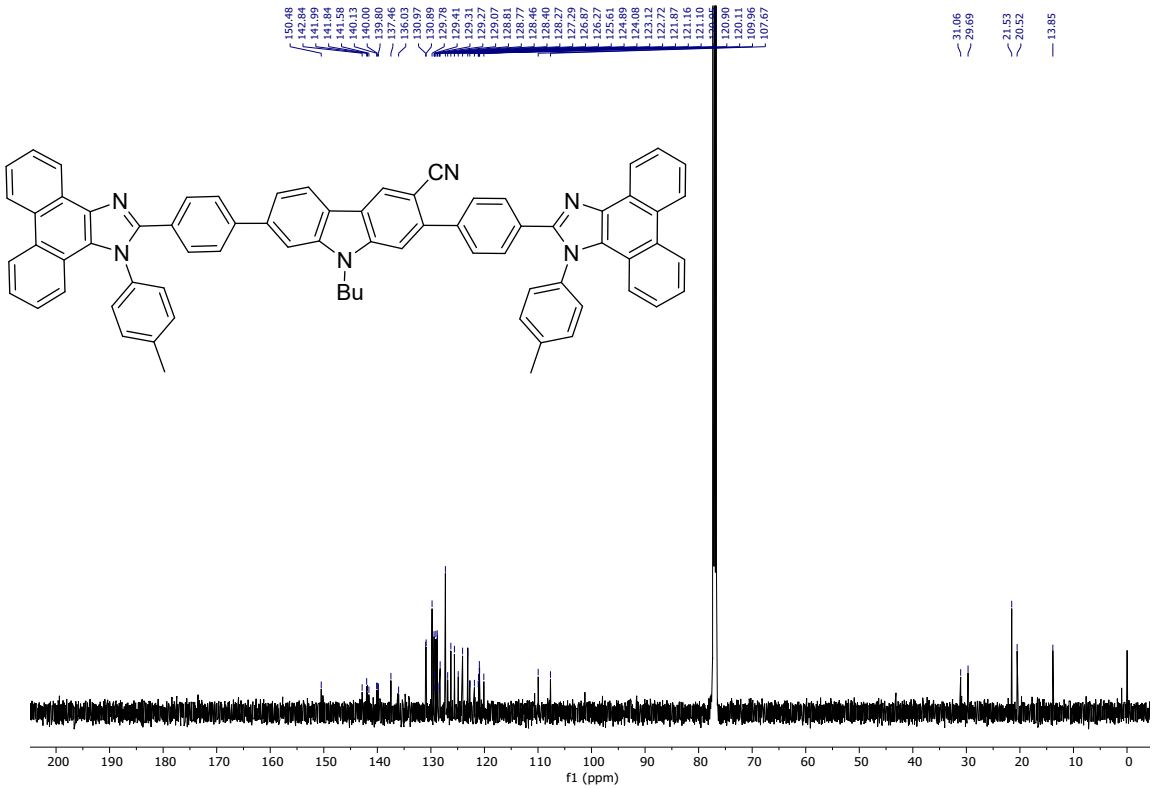


Fig. S28 ^{13}C NMR spectrum of **27PHPI3CN** recorded in $CDCl_3$.

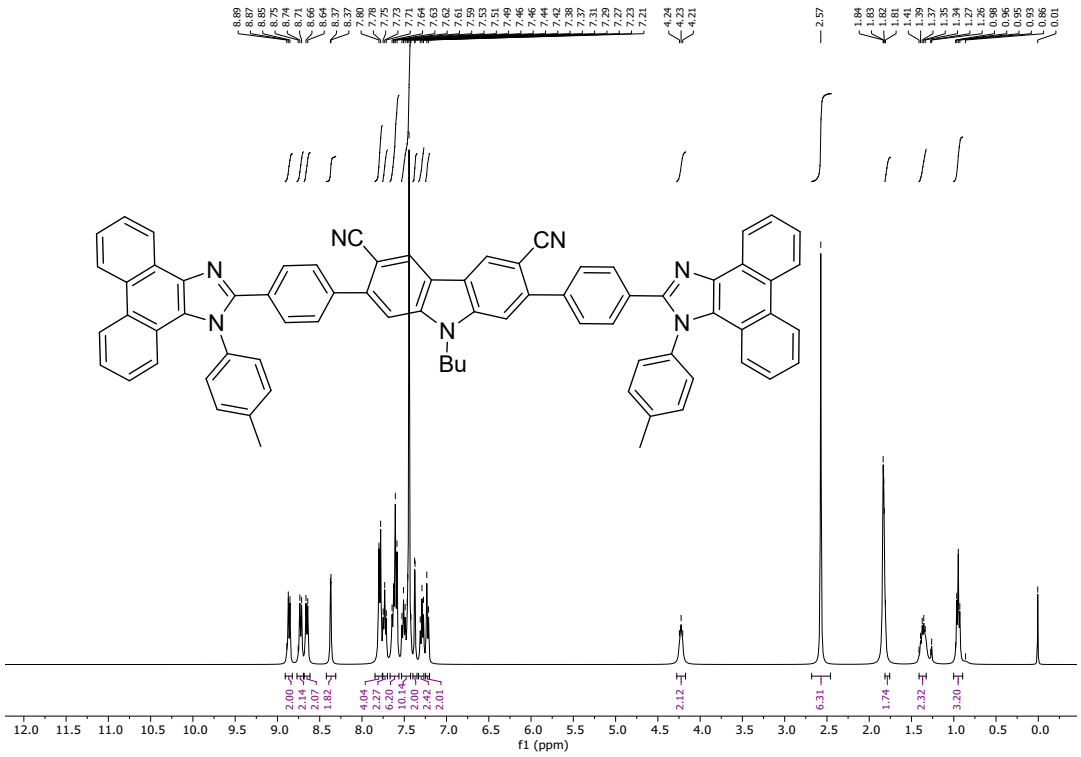


Fig. S29 ^{1}H NMR spectrum of **27PHPI36CN** recorded in $CDCl_3$.

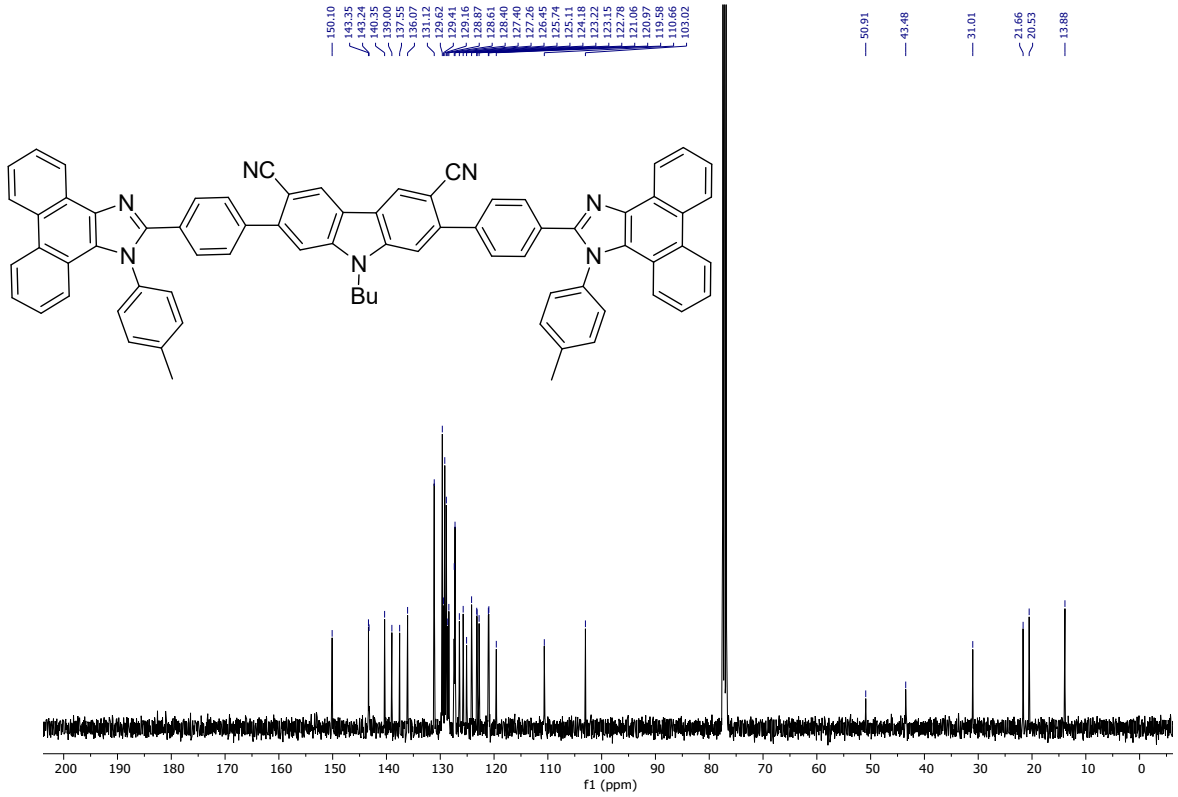


Fig. S30 ^{13}C NMR spectrum of **27PHPI36CN** recorded in $CDCl_3$.

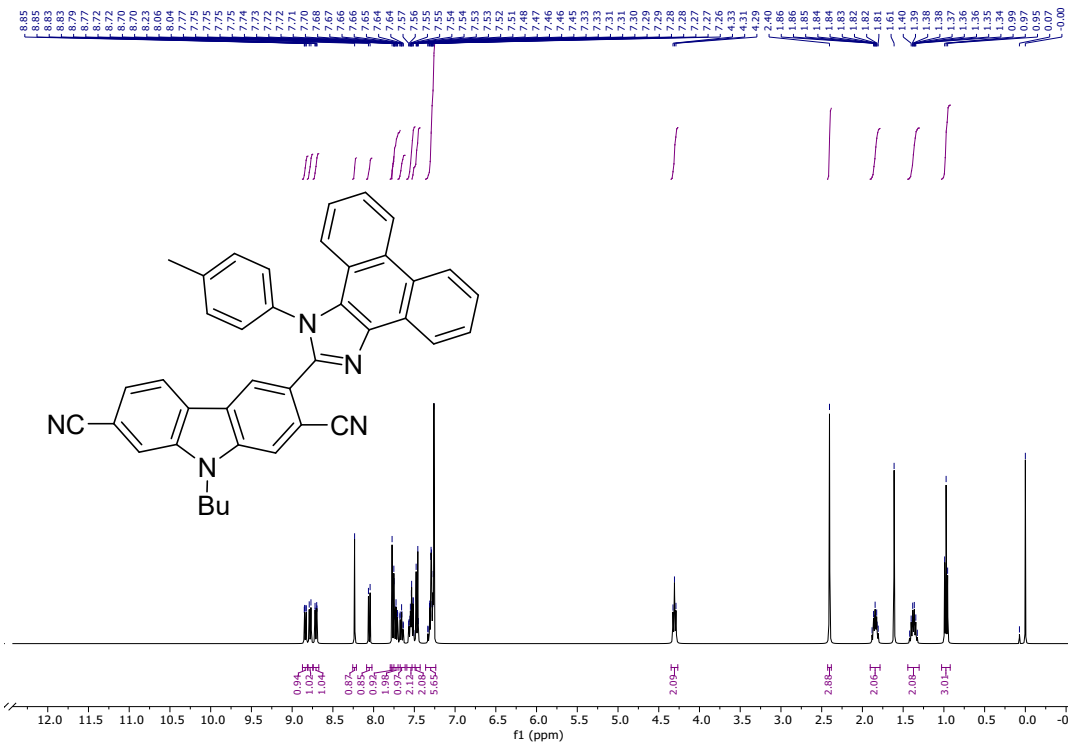


Fig. S31 ^{1}H NMR spectrum of **27CN3PI** recorded in $CDCl_3$.

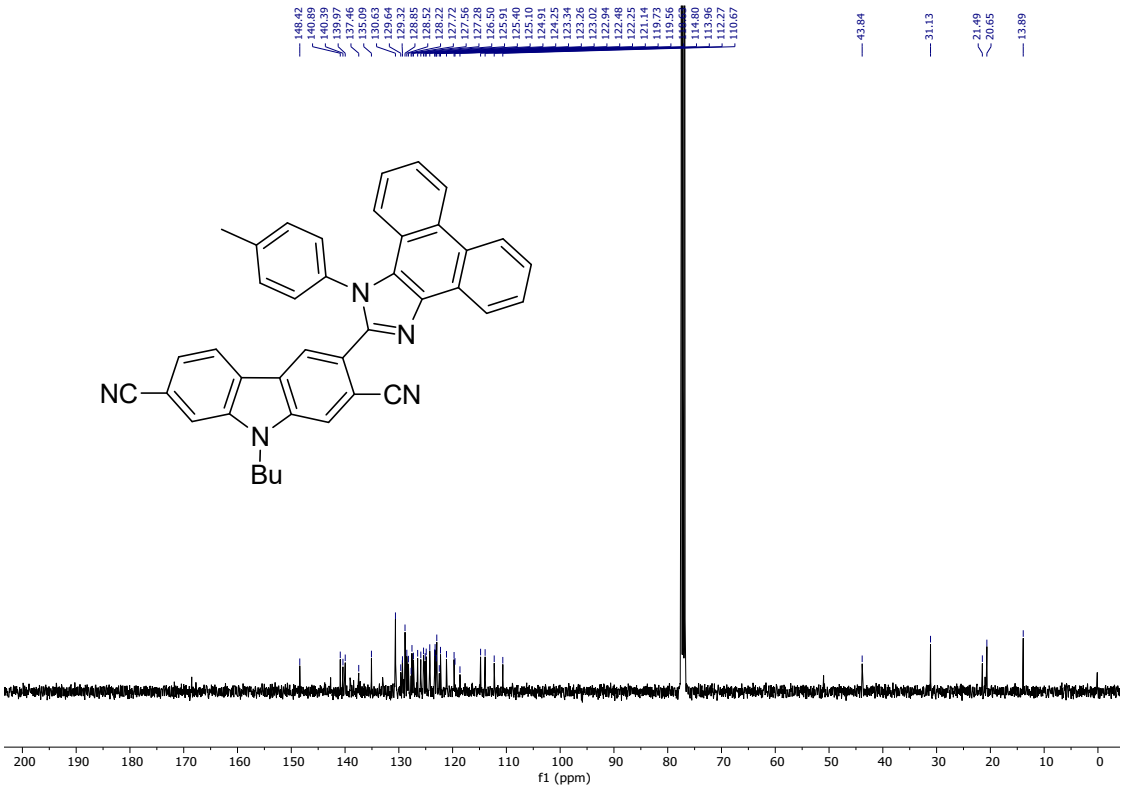


Fig. S32 ^{13}C NMR spectrum of **27CN3PI** recorded in $CDCl_3$.