Supporting Information

Manipulating Matrix Stacking Modes for Ultralong Organic Room Temperature Phosphorescence in Trace Isomer Doping Systems

Shou Yuan,‡[a] QiKun Sun,‡[a] Yaguang Wang,[a] Lingtai Yue,[a] Jie Ma,[a] Yuefa Zhang,[a] Haichang Zhang,[a] Shanfeng Xue*[a] and Wenjun Yang*[a]

Key Laboratory of Rubber-plastics of Ministry of Education/Shandong Province (QUST), School of Polymer Science & Engineering, Qingdao University of Science & Technology, 53-Zhengzhou Road, Qingdao, 266042, P. R. China. E-mail: ywjph2004@qust.edu.cn, sfxue@qust.edu.cn.

General method

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC500 spectrometer at 500 MHz and 125 MHz, respectively, using deuterated chloroform or deuterated dimethyl sulfoxide as the solvent and tetramethylsilane (TMS) as the internal standard. Photo-luminescence spectra were recorded on a Hitachi F-4600 spectrophotometer. Time-resolved decay curves were recorded by a Hamamatsu compact fluorescence lifetime spectrometer (FLS-1000). The lifetimes (τ) of the luminescence were obtained by fitting the decay curve with a multi-exponential decay function of

$$R(t) = \sum_i B_i e^{-\frac{t}{\tau}} \quad \text{(S1)}$$

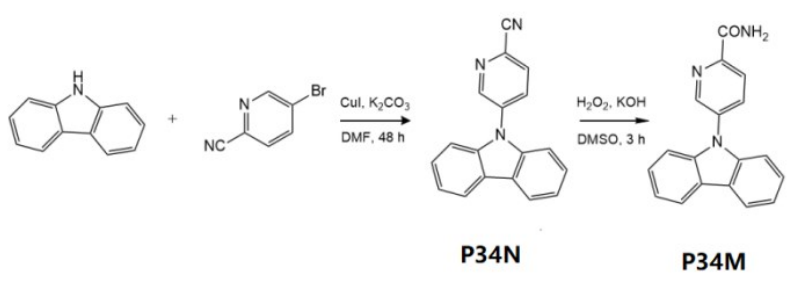
where and represent the amplitudes and lifetimes of the individual components for multi-exponential decay profiles, respectively. The digital photographs were captured by the FDR-AX700 4K HDR digital cameras (SONY, Japan). Absolute PL quantum yields (PLQY) were determined with a spectrometer C11347 (Hamamatsu, Japan). Elemental analysis was characterized using a Flash EA 1112 instrument. Photoluminescence spectra and photographs at 78 K were performed on a QE Pro spectrometer with a CCD array (Ocean Optics) as a power detector and 365 nm lamp as excitation light. The RTP yields were generally obtained by peak-differentiation-imitating analysis from the corresponding steady-state and transient PL spectra and the absolute total quantum yield (Φ_p). By peak-differentiation-imitating analysis, the RTP ratio can be identified, and from, both fluorescent and RTP yields can be figured out. As illustrated in Equation S2, Φ_p is obtained by photon counting from the excitation source into an integration sphere with the ratio of photons emitted:

$$\Phi = \frac{N^{em}}{N^{abs}} \quad \text{(S2)}$$

In this equation, N^{em} is the number of emitted photons and N^{abs} is the number of absorbed photons.

Synthesis and Characterization

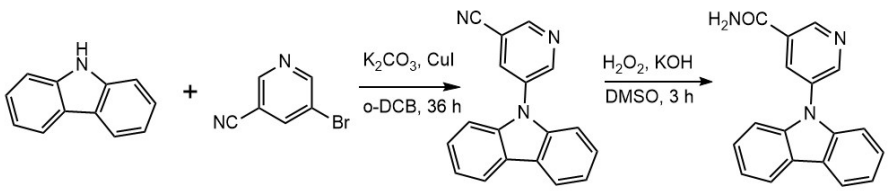
Scheme 1. The synthetic route of P34N and P34M.



(9*H*-carbazol-9-yl)isonicotinonitrile (P34N).
A mixture of K_2CO_3 (0.75 g, 5.46 mmol), 9*H*-carbazole (0.91 g, 5.45 mmol), 3-bromoisonicotinonitrile (1.0 g, 5.46 mmol) and 1,10-phenanthroline monohydrate (0.06 g, 0.55 mmol) in DMF (30 mL) was stirred at room temperature. CuI (0.4 g, 1.10 mmol) was added to the mixture and stirred at 128 ℃ for 48 h. After cooling to room temperature, the reaction mixture was extracted with dichloromethane. The combined organic layer was dried with anhydrous $MgSO_4$, and filtered and concentrated in vacuo. The crude product was purified by silica-gel column chromatography using petroleum ether/dichloromethane (1:1, v/v), yielding a yellow-green solid (0.45 g, yield 28.4 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.05 (d, *J* = 2.5 Hz, 1H), 8.23–8.05 (m, 3H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.53–7.40 (m, 4H), 7.37 (ddd, *J* = 8.0, 5.8, 2.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 148.55, 139.11, 137.29, 133.46, 130.59, 128.88, 126.21, 123.85, 121.18, 120.30, 116.41, 108.62. Anal. Calcd. For $C_{18}H_{11}N_3$: C, 80.28; H, 4.12; N, 15.60. Found: C, 80.33; H, 4.09; N, 15.58.

3-(9*H*-carbazol-9-yl)isonicotinamide (P34M).
A mixture of 3-(9*H*-carbazol-9-yl)isonicotinonitrile (0.4 g, 1.50 mmol), 30 % H_2O_2 (1.25 g, 37.5 mmol), KOH (0.74 g, 18.5 mmol), and DMSO (30 mL) was stirred for 3 h at 40 ℃. After cooling to room temperature, the mixture was extracted with dichloromethane, and the combined organic layer was dried with anhydrous $MgSO_4$ and filtered and then concentrated in vacuo. The crude product was purified by silica-gel column chromatography using dichloromethane as the eluent to give the compound as a white solid (0.4 g, yield 90 %). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.94 (d, *J* = 2.3 Hz, 1H), 8.40–8.18 (m, 5H), 7.83 (s, 1H), 7.46 (dd, *J* = 6.1, 1.4 Hz, 4H), 7.33 (ddd, *J* = 7.9, 6.1, 2.0 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 165.39, 148.78, 146.24, 139.72, 135.97, 135.41, 126.55, 123.37, 123.16, 120.78, 120.63, 109.56. Anal. Calcd. For $C_{18}H_{11}N_3O$: C, 75.25; H, 4.56; N, 14.63. Found: C, 75.30; H, 4.52; N, 14.65.

Scheme 2. The synthetic route of P35N and P35M.

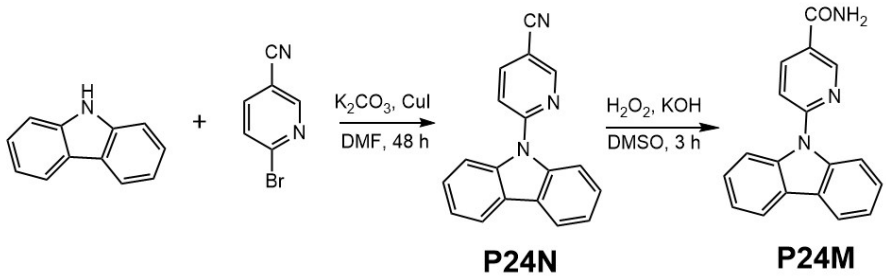


P35N **P35M**

5-(9*H*-carbazol-9-yl)nicotinonitrile (P35N).
A mixture of 9*H*-carbazole (1.0 g, 6.00 mmol), 3-bromo-5-fluoropyridine (1.2 g, 6.56 mmol), copper powder (0.25 g, 3.94 mmol), K_2CO_3 (3.31 g, 24.0 mmol), and 18-crown-6 (0.53 g, 1.97 mmol) in o-dichlorobenzene (40 mL) was stirred and refluxed for 36 h. The excessive o-dichlorobenzene was removed under reduced pressure. The crude product was purified by silica-gel column chromatography using dichloromethane as the eluent to give the white compound (0.35 g, yield 19.4 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.13 (d, *J* = 2.5 Hz, 1H), 8.96 (d, *J* = 1.8 Hz, 1H), 8.22 (t, *J* = 2.2 Hz, 1H), 8.16 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.47 (ddd, *J* = 8.3, 6.9, 1.3 Hz), 7.41–7.32 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.71, 150.23, 139.92, 136.65, 135.01, 126.70, 124.14, 121.51, 120.81, 115.67, 111.01, 108.90. Anal. Calcd. For $C_{18}H_{11}N_3$: C, 80.28; H, 4.12; N, 15.60. Found: C, 80.29; H, 4.09; N, 15.62.

5-(9*H*-carbazol-9-yl)nicotinamide (P35M).
A mixture of 5-(9*H*-carbazol-9-yl)nicotinamide (0.4 g, 1.50 mmol), 30 % H_2O_2 (1.25 g, 37.5 mmol), KOH (0.74 g, 18.5 mmol), and DMSO (30 mL) was stirred for 3 h at 40 ℃. After cooling to room temperature, the mixture was extracted with dichloromethane. The combined organic layer was dried with anhydrous $MgSO_4$, and filtered and concentrated in vacuo. The crude product was purified by silica-gel column chromatography using dichloromethane as the eluent to give the compound as a white solid (0.4 g, yield 90 %). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.23 (t, *J* = 1.5 Hz, 1H), 9.13–9.05 (m, 1H), 8.54 (q, *J* = 2.1, 1.6 Hz, 1H), 8.41–8.26 (m, 3H), 7.84 (s, 1H), 7.57–7.43 (m, 4H), 7.43–7.33 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 165.51, 150.09, 147.65, 140.00, 133.49, 133.08, 130.87, 126.50, 123.02, 120.60, 109.51. Anal. Calcd. For $C_{18}H_{11}N_3O$: C, 75.25; H, 4.56; N, 14.63. Found: C, 75.32; H, 4.49; N, 14.61.

Scheme 3. The synthetic route of P24N and P24M.



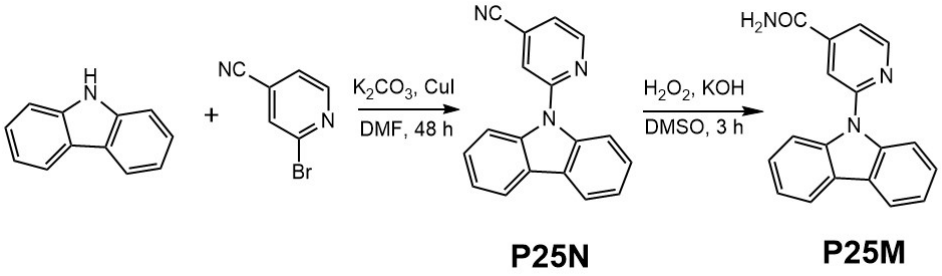
6-(9*H*-carbazol-9-yl)nicotinonitrile (P24N).

A mixture of K_2CO_3 (0.75 g, 5.46 mmol), 9*H*-carbazole (0.91 g, 5.45 mmol), 2-bromo-5-fluoropyridine (1.0 g, 5.46 mmol) and 1,10-phenanthroline monohydrate (0.06 g, 0.55 mmol) in DMF (30 mL) was stirred at room temperature. CuI (0.4 g, 1.10 mmol) was added to the mixture and stirred at 128 ℃ for 48 h. After cooling to room temperature, the reaction mixture was extracted with dichloromethane. The combined organic layer was dried with anhydrous $MgSO_4$, and filtered and concentrated in vacuo. The crude product was purified by silica-gel column chromatography using petroleum ether/dichloromethane (1:1, v/v), yielding a white solid (0.3 g, yield 18.7 %). ^{1}H NMR (500 MHz, Chloroform-d) δ 8.98 (d, *J* = 2.3 Hz, 1H), 8.21–8.06 (m, 3H), 7.98 (d, *J* = 8.3 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 154.07, 152.26, 140.72, 138.26, 126.22, 124.75, 121.88, 119.90, 116.94, 116.17, 111.41, 105.17. Anal. Calcd. For $C_{18}H_{11}N_3$: C, 80.28; H, 4.12; N, 15.60. Found: C, 80.29; H, 4.09; N, 15.62.

6-(9*H*-carbazol-9-yl)nicotinamide (P24M).

A mixture of 6-(9*H*-carbazol-9-yl)nicotinonitrile (0.4 g, 1.50 mmol), 30 % H_2O_2 (1.25 g, 37.5 mmol), KOH (0.74 g, 18.5 mmol), and DMSO (30 mL) was stirred for 3 h at 40 ℃. After cooling to room temperature, the mixture was extracted with dichloromethane. The combined organic layer was dried with anhydrous $MgSO_4$, and filtered and concentrated in vacuo. The crude product was purified by silica-gel column chromatography using dichloromethane as the eluent to give the compound as a white solid (0.4 g, yield 90 %). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.16 (d, *J* = 2.4 Hz, 1H), 8.56–8.45 (m, 1H), 8.32–8.16 (m, 3H), 7.89 (dd, *J* = 9.8, 8.4 Hz, 3H), 7.68 (s, 1H), 7.46 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 2H), 7.37–7.21 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 165.74, 152.63, 148.83, 138.61, 138.49, 127.18, 126.50, 123.76, 121.36, 120.39, 117.93, 111.63. Anal. Calcd. For $C_{18}H_{11}N_3O$: C, 75.25; H, 4.56; N, 14.63. Found: C, 75.32; H, 4.49; N, 14.61.

Scheme 4. The synthetic route of P25N and P25M.



2-(9*H*-carbazol-9-yl)nicotinonitrile (P25N).

A mixture of K_2CO_3 (0.75 g, 5.46 mmol), 9*H*-carbazole (0.91 g, 5.45 mmol), 2-bromo-4-fluoropyridine (1.0 g, 5.46 mmol) and 1,10-phenanthroline monohydrate (0.06 g, 0.55 mmol) in DMF (30 mL) was stirred at room temperature. CuI (0.4 g, 1.10 mmol) was added to the mixture and stirred at 128 ℃ for 48 h. After cooling to room temperature, the reaction mixture was extracted with dichloromethane. The combined organic layer was dried with anhydrous $MgSO_4$, and filtered and concentrated in vacuo. The crude product was purified by silica-gel column chromatography using petroleum ether/dichloromethane (1:1, v/v), yielding a white solid (0.4 g, yield 25.2 %). ^{1}H NMR (500 MHz, Chloroform-d): δ 8.89 (d, *J* = 5.0 Hz, 1H), 8.12 (d, *J* = 7.7 Hz, 2H), 7.93–7.87 (m, 3H), 7.52–7.45 (m, 3H), 7.37 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.84, 150.69, 138.86, 126.62, 124.84, 122.58, 121.99, 121.61, 120.39, 119.94, 116.12, 111.19. Anal. Calcd. For $C_{18}H_{11}N_3$: C, 80.28; H, 4.12; N, 15.60. Found: C, 80.19; H, 4.02; N, 15.79.

2-(9*H*-carbazol-9-yl)isonicotinamide (P25M).

A mixture of 2-(9*H*-carbazol-9-yl)nicotinonitrile (0.4 g, 1.50 mmol), 30 % H_2O_2 (1.25 g, 37.5 mmol), KOH (0.74 g, 18.5 mmol), and DMSO (30 mL) was stirred for 3 h at 40 ℃. After cooling to room temperature, the mixture was extracted with dichloromethane. The combined organic layer was dried with anhydrous $MgSO_4$, and filtered and concentrated in vacuo. The crude product was purified by silica-gel column chromatography using dichloromethane as the eluent to give the compound as a white solid (0.4 g, yield 90 %). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.84 (d, *J* = 5.1 Hz, 1H), 8.41 (s, 1H), 8.23 (d, *J* = 7.7 Hz, 2H), 8.12 (d, *J* = 1.3 Hz, 1H), 7.89 (s, 1H), 7.86–7.76 (m, 3H), 7.46 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 165.67, 151.41, 150.21, 144.68, 138.78, 126.45, 123.51, 121.12, 120.40, 119.55, 116.57, 111.27. Anal. Calcd. For $C_{18}H_{11}N_3O$: C, 75.25; H, 4.56; N, 14.63. Found: C, 75.32; H, 4.49; N, 14.61.

Supplementary Figures and Tables

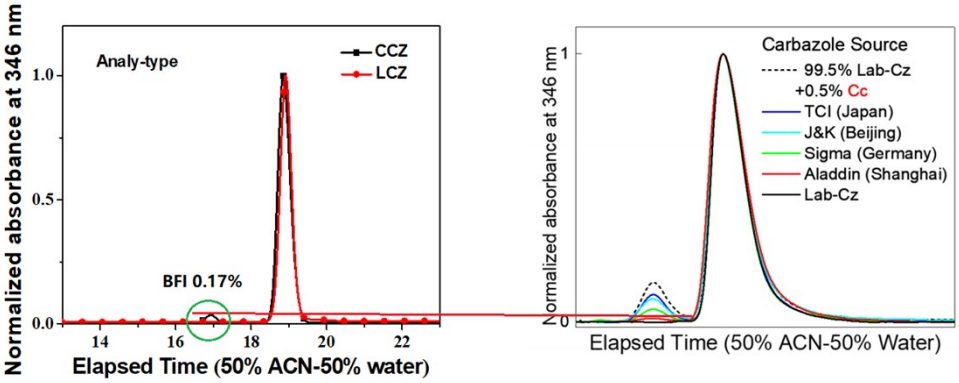


Figure S1. HPLC spectra of **CCZ** and **LCZ** monitored at the onset absorption of 346 nm with 50/50 acetonitrile (ACN)-water ratio (v/v). By comparing with Liu (right), the content of 1H-benzo[f]indole (BFI) in CCZ we used is about 0.17%.

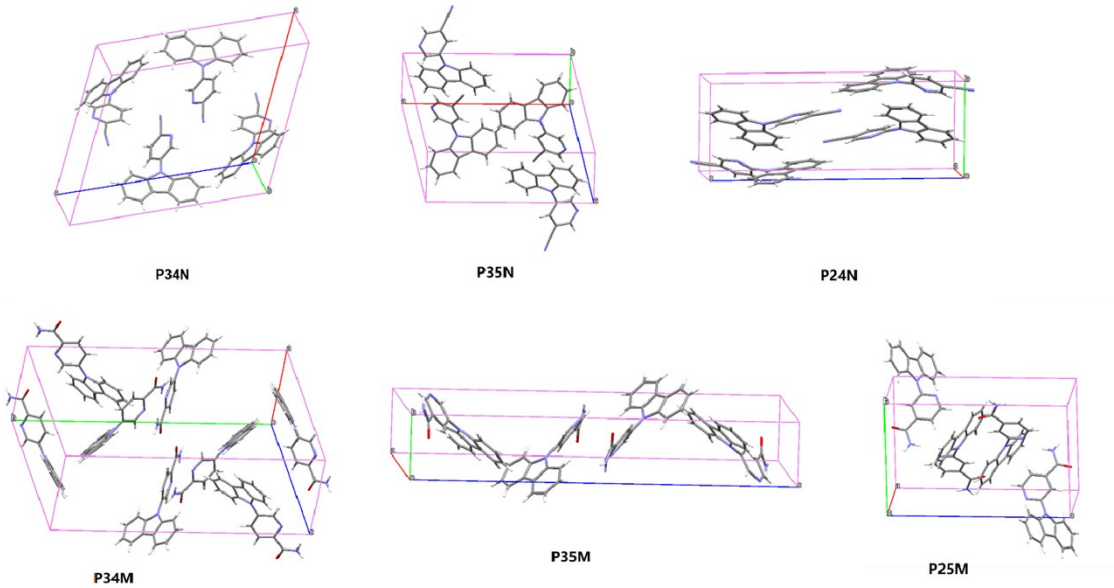
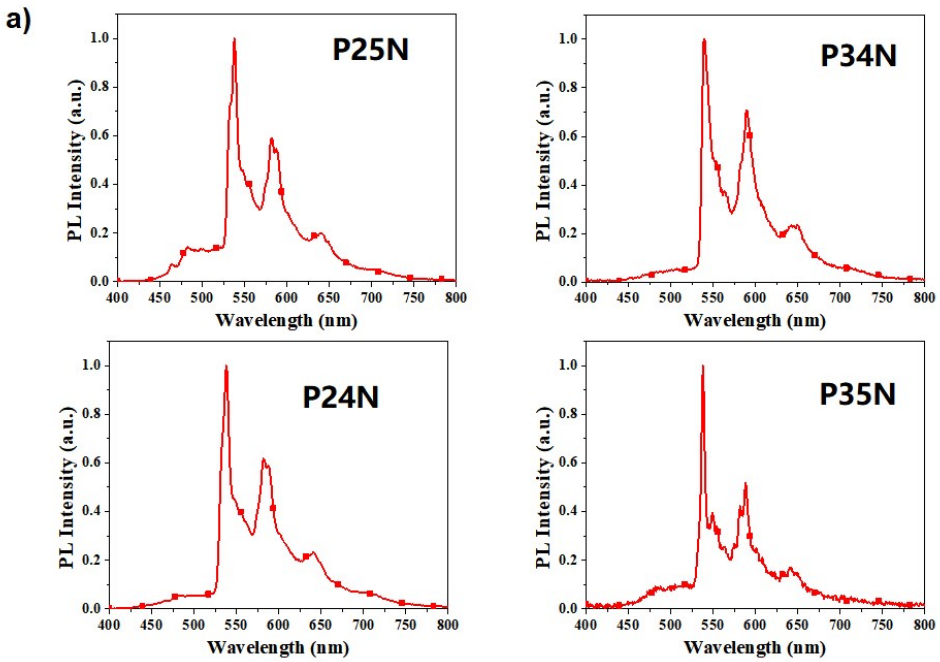


Figure S2. The RTP unit cell structures of **P35N**, **P34N**, **P24N**, **P35M**, **P34M** and **P25M** measured at room temperature under 365 nm excitation.



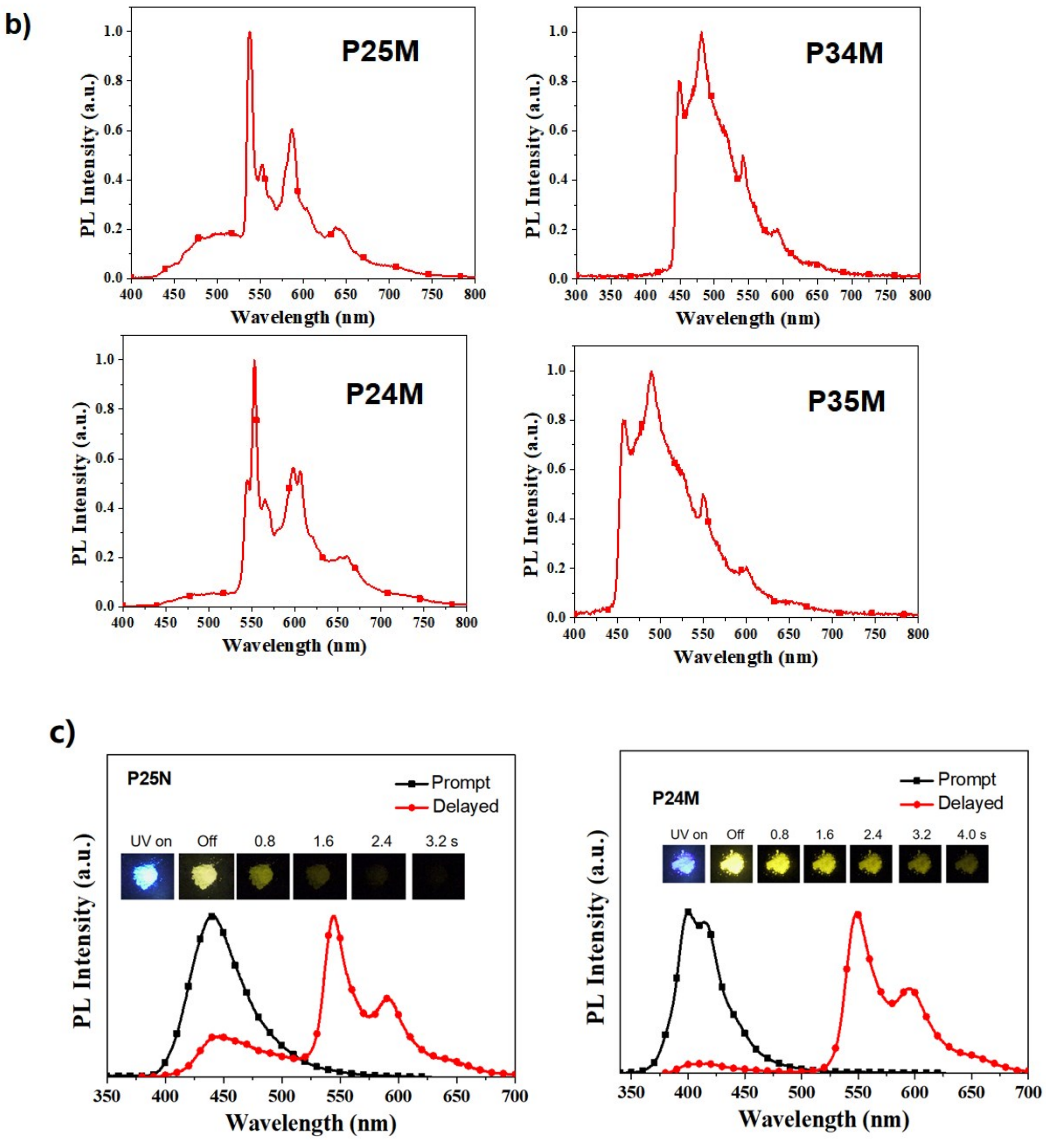


Figure S3. The prompt spectra of a) **P25N, P34N, P24N, P35N;** b) **P25M, P34M, P24M, P35M** at 78 K (in liquid nitrogen) under 365 nm excitation. c) The prompt and delayed spectra and photographs of **P25N** and **P24M** measured at room temperature under 365 nm excitation.

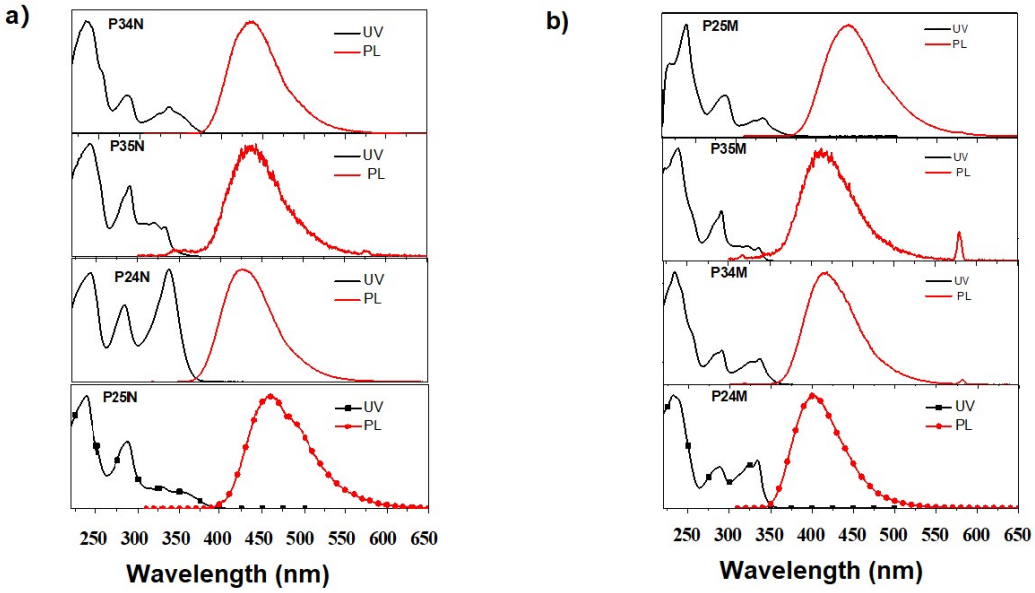
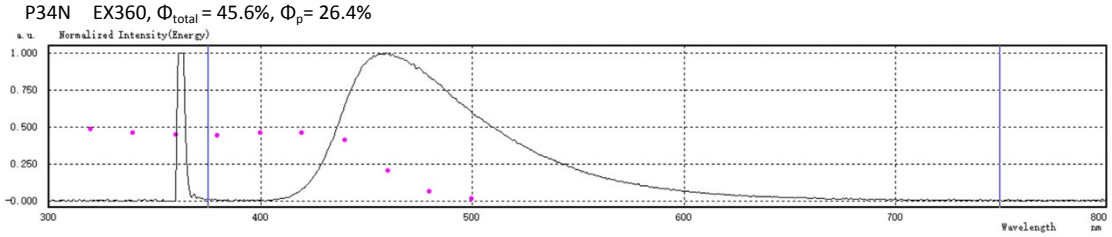


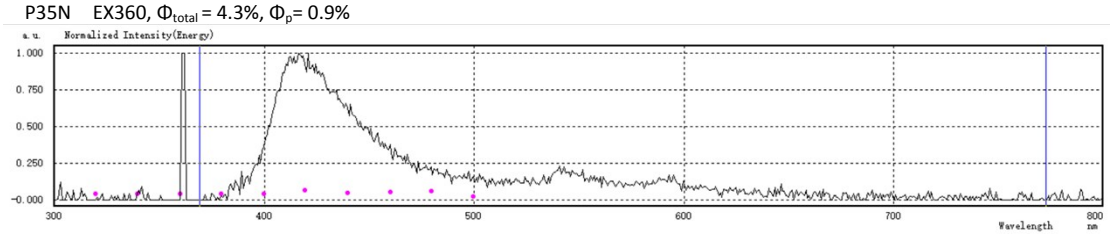
Figure S4. The absorption and photoluminescence spectra of a) **P35N**, **P34N**, **P24N**, **P25N**; b) **P35M**, **P34M**, **P25M**, **P24M** in THF solution.

Compound	λex/nm	Emission (nm)	τ_1 (ms)	τ_2 (ms)	τ_3 (ms)	τ_4 (ms)	τ_a (ms)
P35N	365	545	16.41 (2.56%)	195.0 (23.98%)	528.3 (73.46%)		435.27
P34N		501	2.973 (55.65%)	10.57 (24.80%)	41.13 (14.00%)	445.8 (5.55%)	34.78
P24N		547	10.17 (2.27%)	706.8 (97.73%)			690.99
P25N		545	12.17 (5.92%)	330.2 (94.08%)			311.37
P35M		548	18.53 (0.74%)	861.2 (99.26%)			854.96
P34M		549	5.998 (2.78%)	274.4 (10.53%)	685.0 (86.69%)		622.89
P24M		549	185.8 (30.91%)	871.8 (69.09%)			659.76
P25M		547	1.66 (43.96%)	27.7 (20.95%)	467.4 (35.09%)		170.54

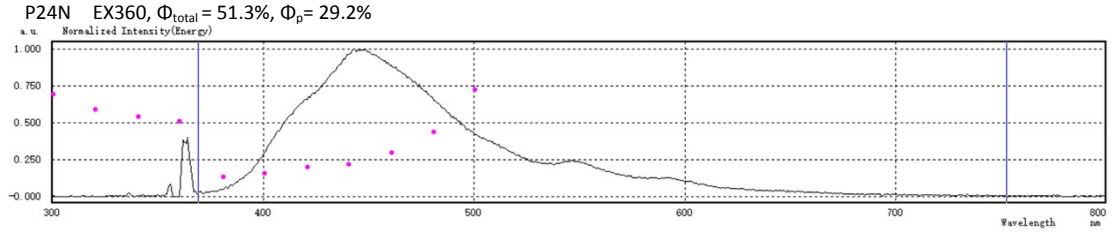
P34N EX360, Φ_{total} = 45.6%, Φ_p= 26.4%



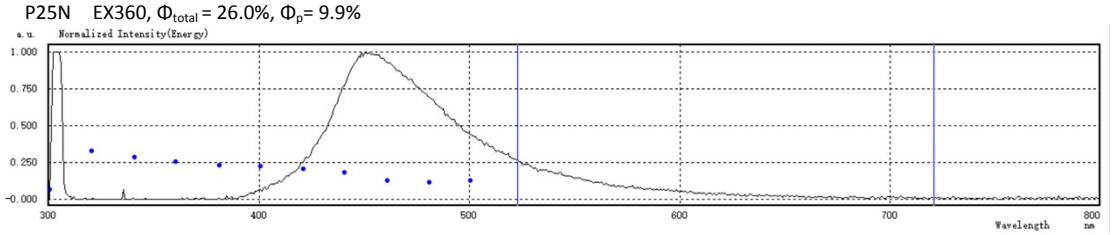
P35N EX360, Φ_{total} = 4.3%, Φ_p= 0.9%



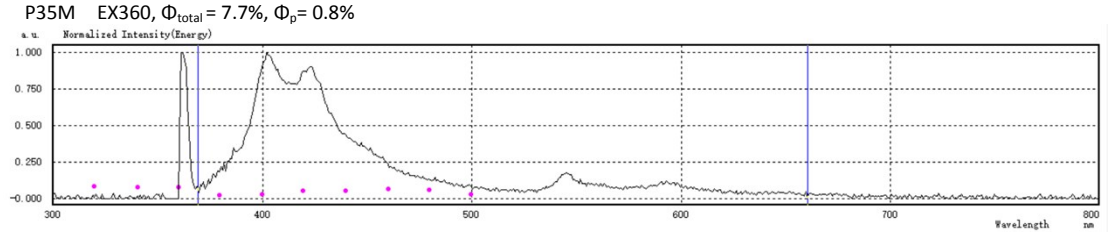
P24N EX360, Φ_{total} = 51.3%, Φ_p= 29.2%



P25N EX360, Φ_{total} = 26.0%, Φ_p= 9.9%



P35M EX360, Φ_{total} = 7.7%, Φ_p= 0.8%



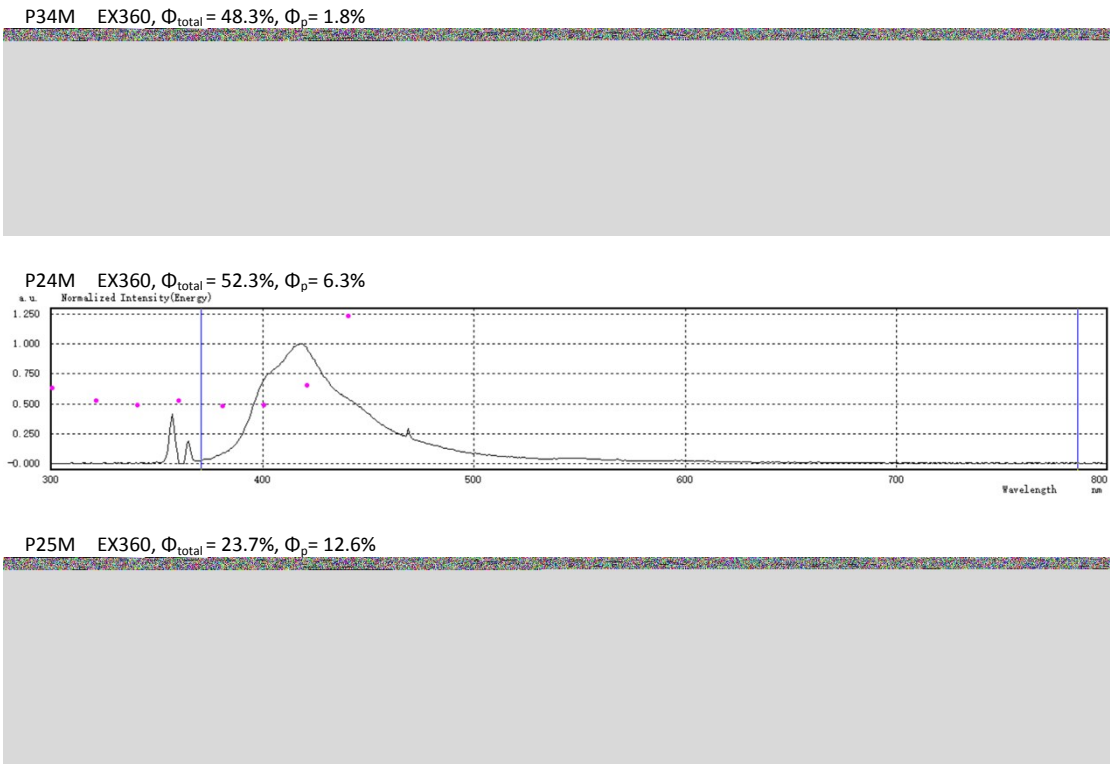


Figure S5. The RTP lifetimes, unit cell structures and quantum yield of **P35N, P34N, P24N, P25N, P35M, P34M, P24M** and **P25M** measured at room temperature under 365 nm excitation.

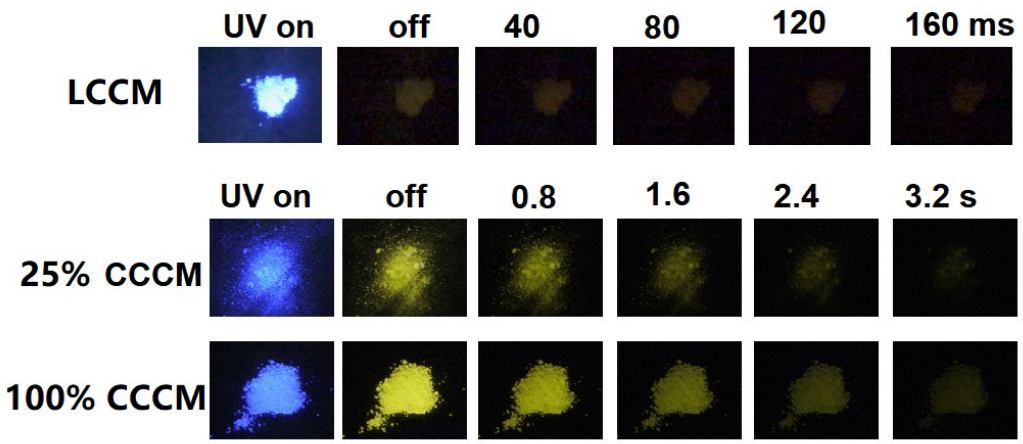


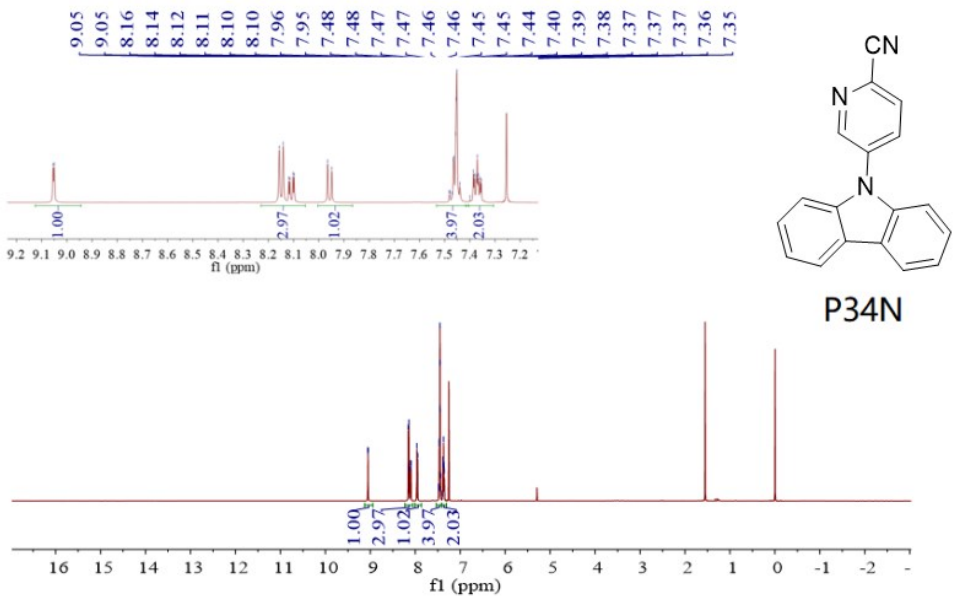
Figure S6. The low temperature phosphorescence photographs of CCZ and LCZ derivatives at 78 K (in liquid nitrogen) under 365 nm excitation.

Table S1. The crystal structual data of P34N, P24N, P35N, P25M, P34M and P35M.

Compound reference	Colorless **P34N** crystal	Colorless **P24N** crystal	Colorless **P35N** crystal	Colorless **P25M** crystal	Colorless **P34M** crystal	Colorless **P35M** crystal
Chemical formula	$C_{18}H_{11}N_3$	$C_{18}H_{11}N_3$	$C_{18}H_{11}N_3$	$C_{18}H_{13}N_3O$	$C_{18}H_{13}N_3O$	$C_{18}H_{13}N_3O$
Formula weight	269.30	269.30	269.30	287.31	287.31	287.31
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P 21/c	P 21/n	P 21/c	P 21/n	P 21/c	P 21/n
a/ Å	18.140(14)	9.034(3)	15.379(9)	8.543(8)	7.8374(11)	9.4696(11)
b/ Å	3.914(3)	7.442(2)	7.516(4)	10.702(9)	25.281(3)	5.0807(6)
c/ Å	18.577(14)	20.076(6)	11.563(6)	16.886(15)	14.813(2)	29.630(4)
α/°	90	90	90	90	90	90
β/°	95.169(16)	99.057(6)	100.885(9)	91.104(17)	102.932(3)	96.439(2)
γ/°	90	90	90	90	90	90

Unit cell volume/ Å^3	1313.6(17)	1332.9(7)	1312.5(12)	1544(2)	2860.6(7)	1416.6(3)
Temperature/K	100	100	100	100	100	100
Z	4	4	4	4	4	4
Density (calculated) /g cm^{-3}	1.362	1.342	1.363	1.236	1.334	1.347
F(000)	560	560	560	600	1200	600
Theta range for data collection	2.562 to 24.997 deg.	2.647 to 24.992 deg.	3.028 to 24.994 deg.	2.652 to 27.561 deg.	2.666 to 24.998 deg.	2.767 to 24.996 deg.
Index ranges	-21<=h<=20, -4<=k<=4, -15<=l<=22	-10<=h<=10, -8<=k<=7, -23<=l<=22	-16<=h<=18, -8<=k<=8, -13<=l<=7	-10<=h<=9, -12<=k<=13, -21<=l<=21	-9<=h<=9, -30<=k<=16, -17<=l<=17	-10<=h<=11, -6<=k<=6, -27<=l<=35
Completeness to theta	25.242 99.8%	24.992 99.9%	24.994 99.4%	25.242 95.3%	24.988 99.7%	24.996 99.4%
Absorption coefficient	None	None	None	None	None	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2302 / 24 / 201	2342 / 0 / 191	2298 / 0 / 198	3394 / 0 / 200	5035 / 0 / 397	2489 / 0 / 199
Goodness-of-fit on F^2	1.112	0.991	1.017	0.971	0.782	0.993
CCDC number	2046606	2056175	2046603	2056176	2046605	2053954

NMR Spectra



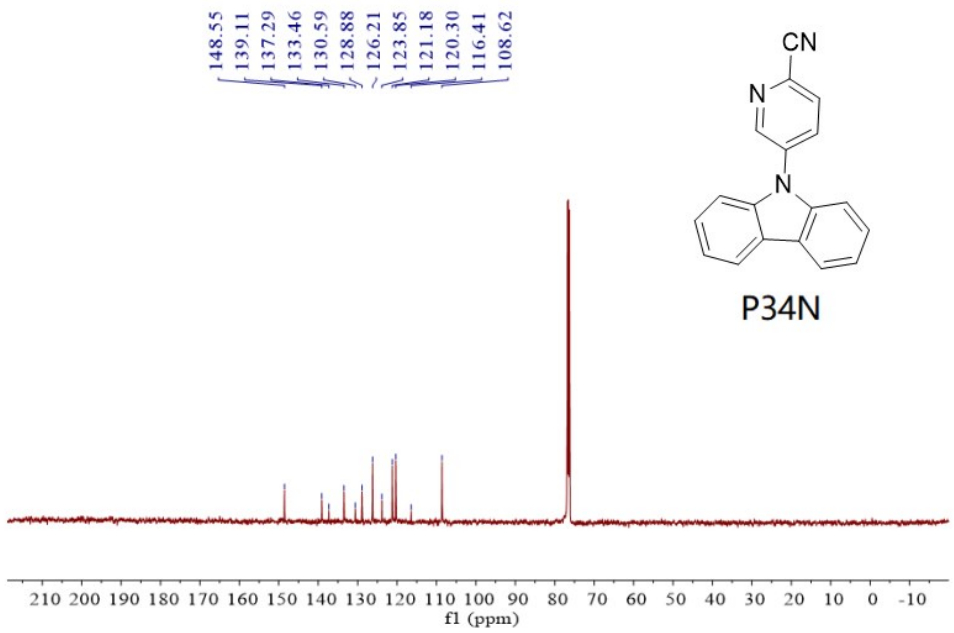
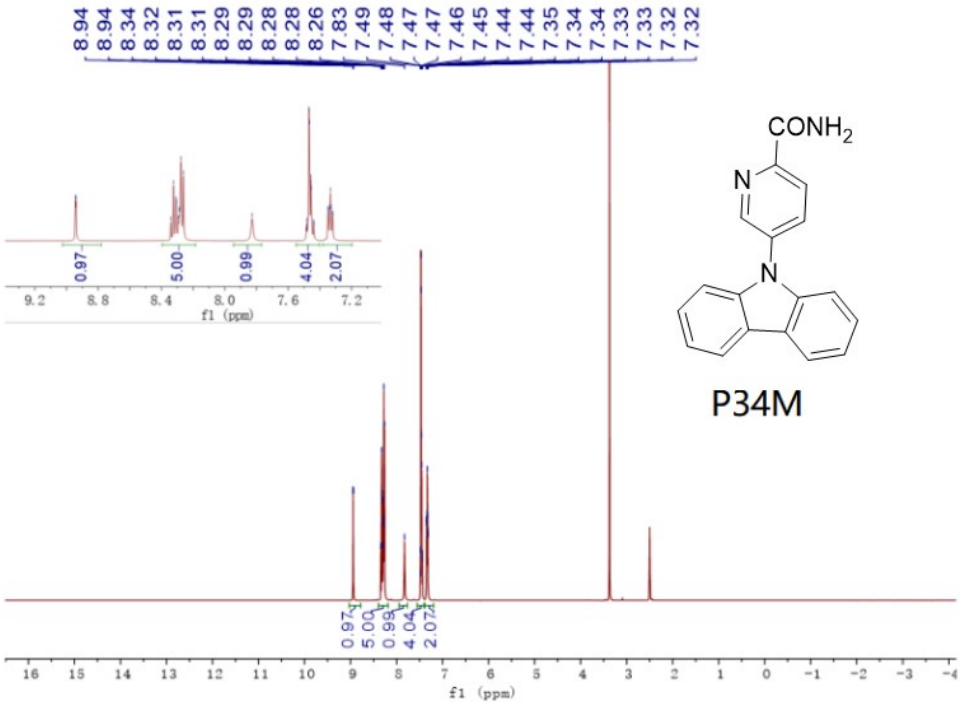


Figure S7. ^{1}H NMR and ^{13}C NMR spectra of **P34N** in $CDCl_3$.



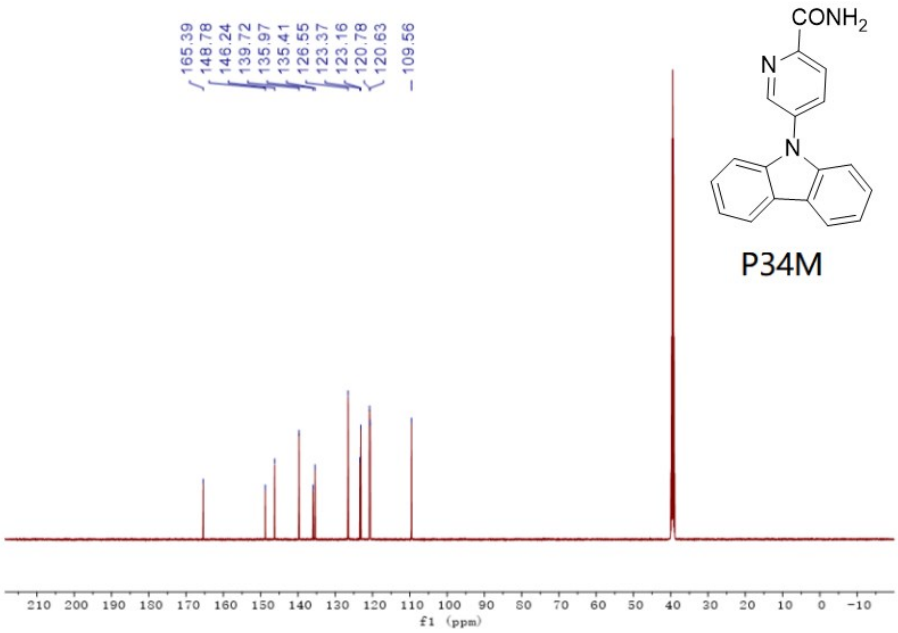
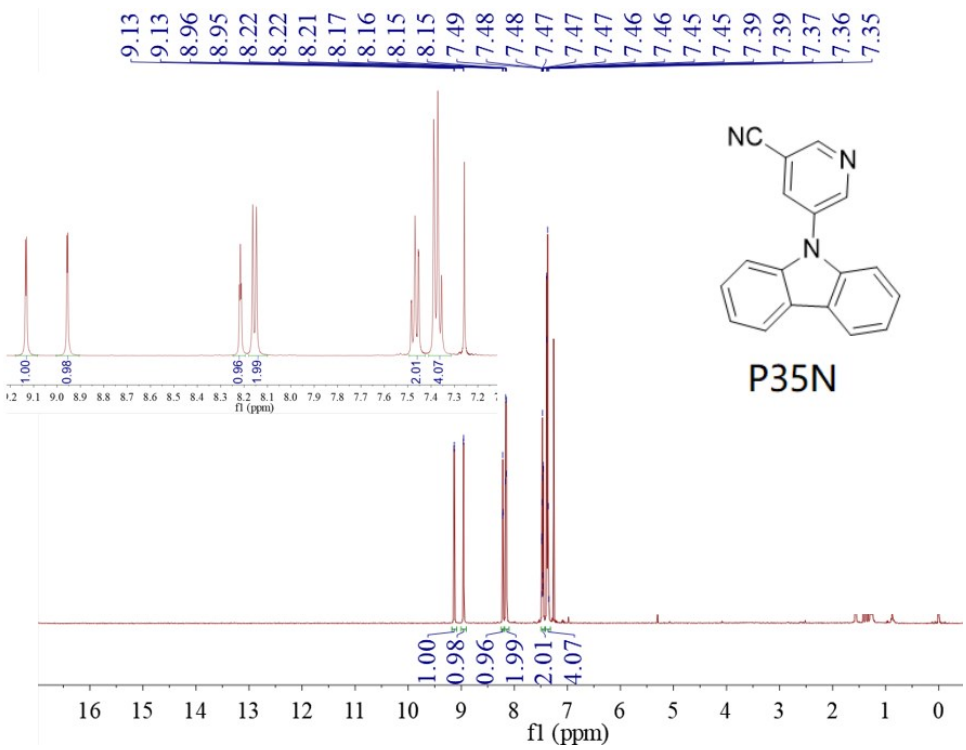


Figure S8. ^{1}H NMR and ^{13}C NMR spectra of P34M in DMSO-d_6.



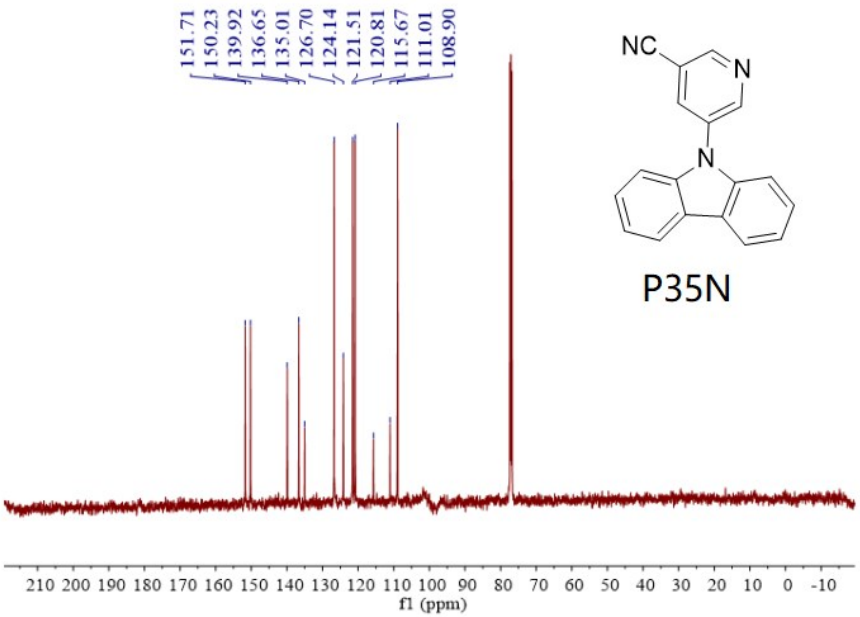
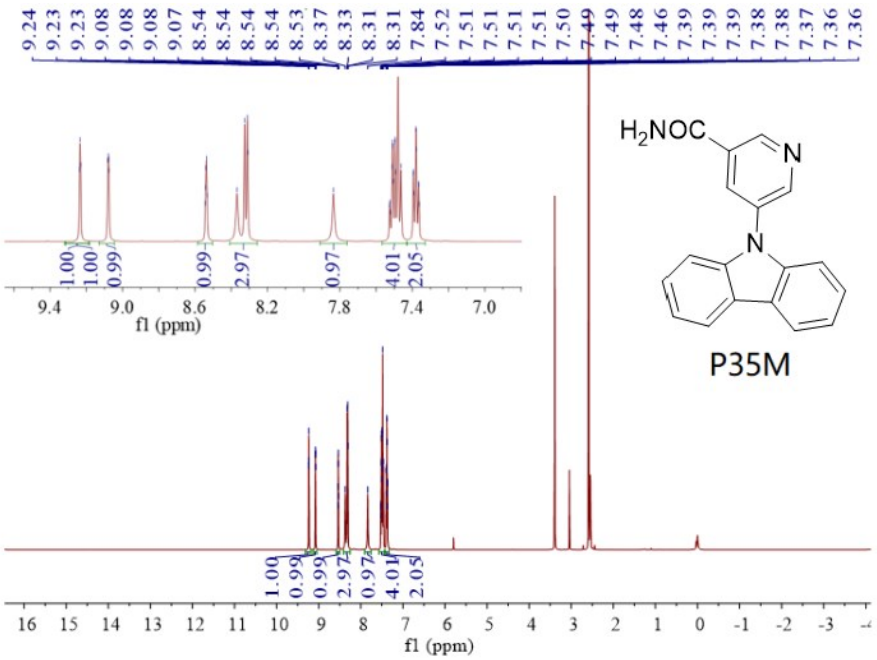


Figure S9. ^{1}H NMR and ^{13}C NMR spectra of P35N in $CDCl_3$.



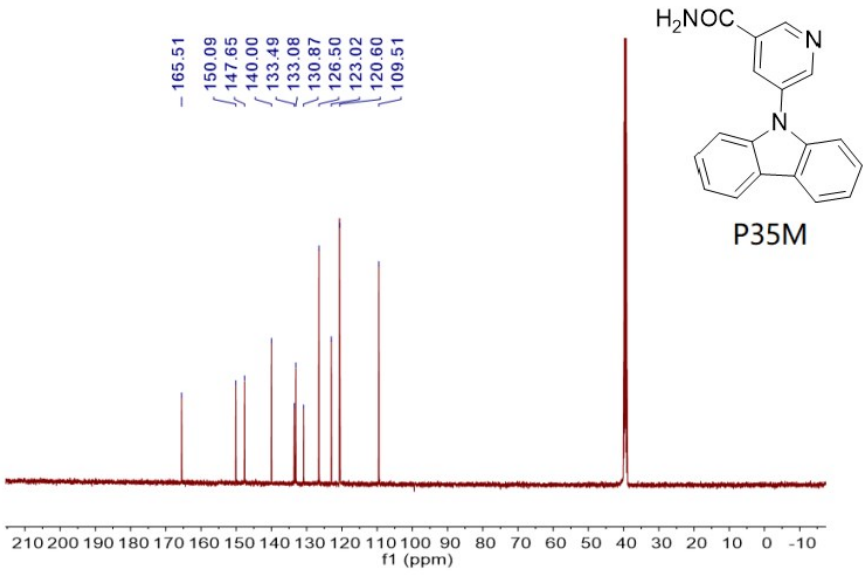
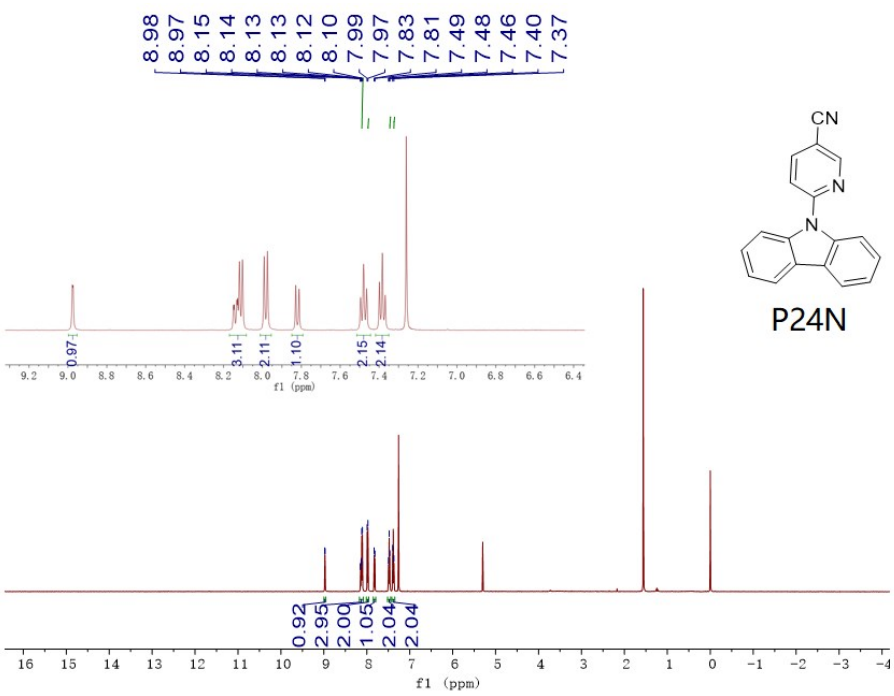


Figure S10. ^{1}H NMR and ^{13}C NMR spectra of **P35M** in DMSO-d_6.



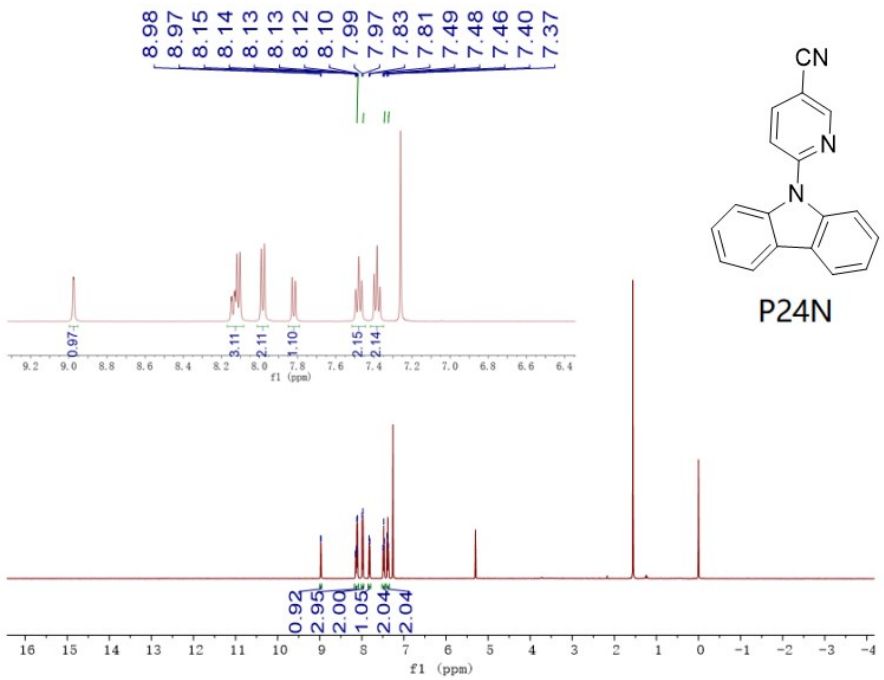
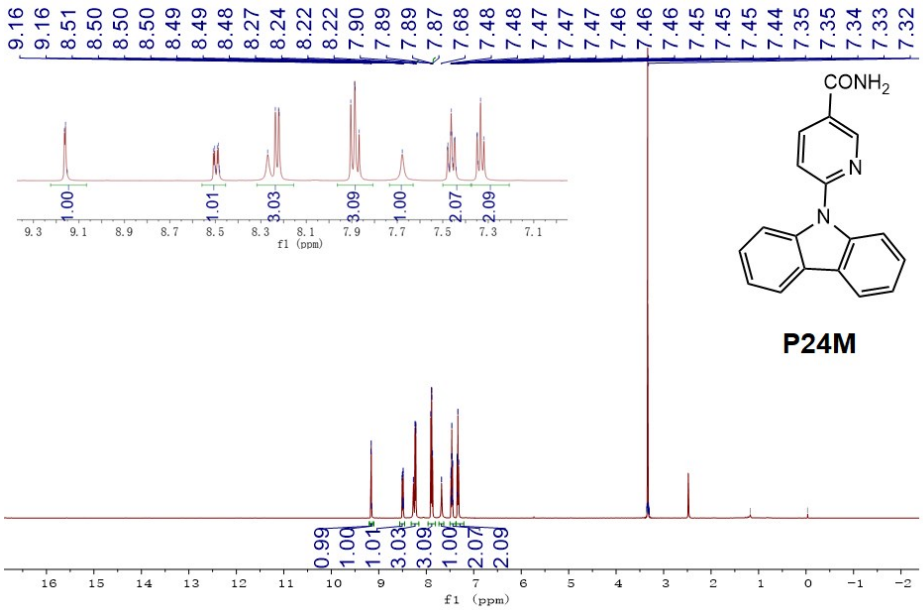


Figure S11. ^{1}H NMR and ^{13}C NMR spectra of **P24N** in $CDCl_3$.



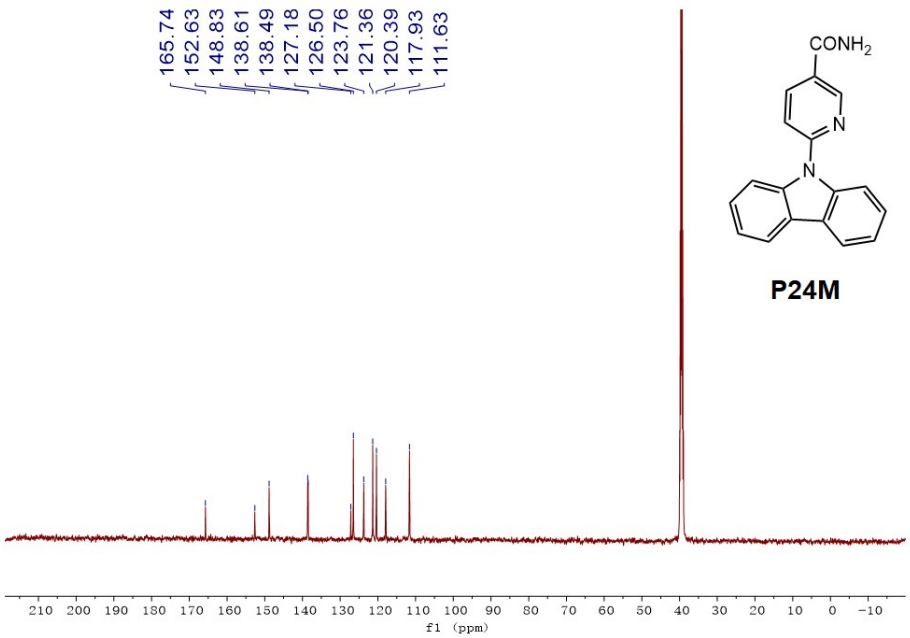
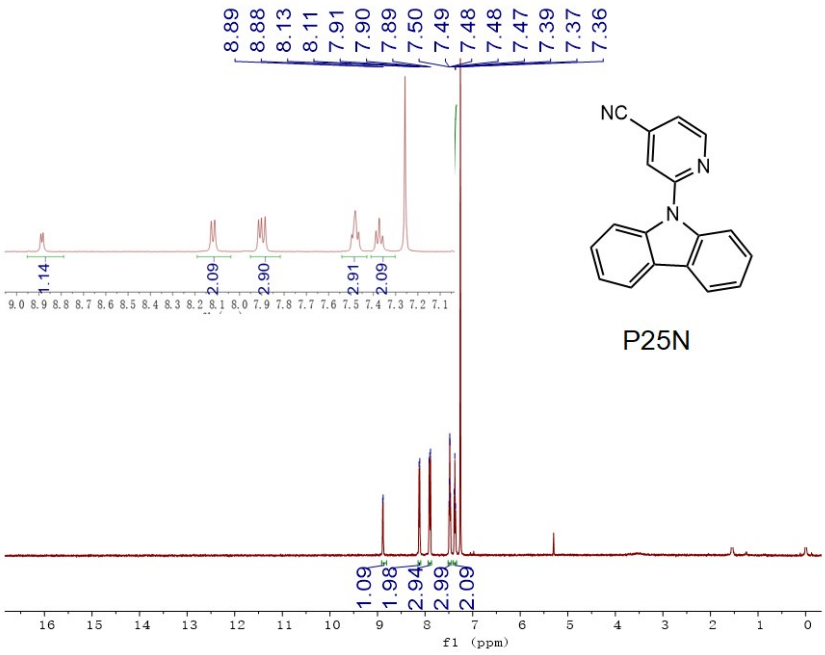


Figure S12. ^{1}H NMR and ^{13}C NMR spectra of **P24M** in DMSO-d_6.



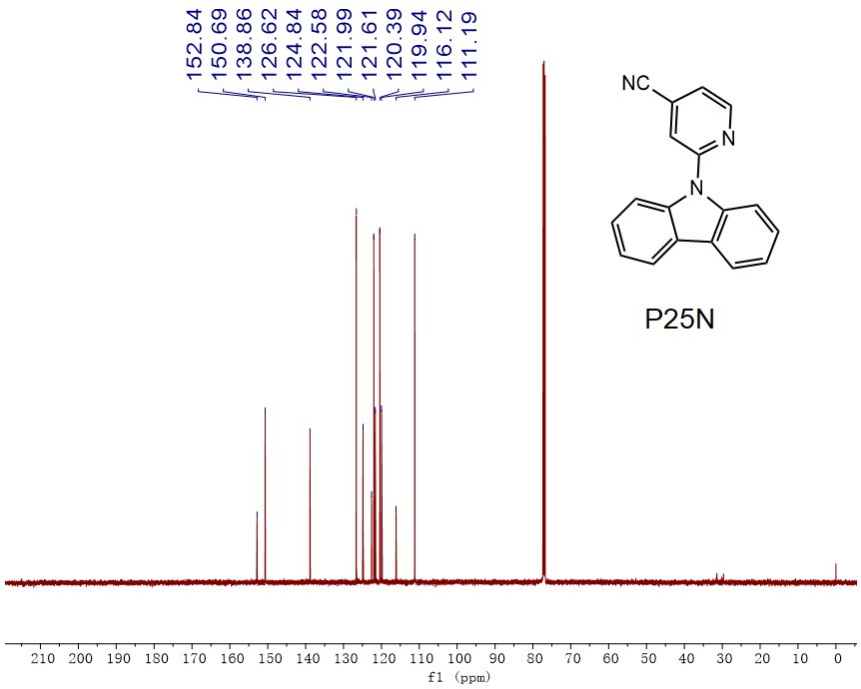
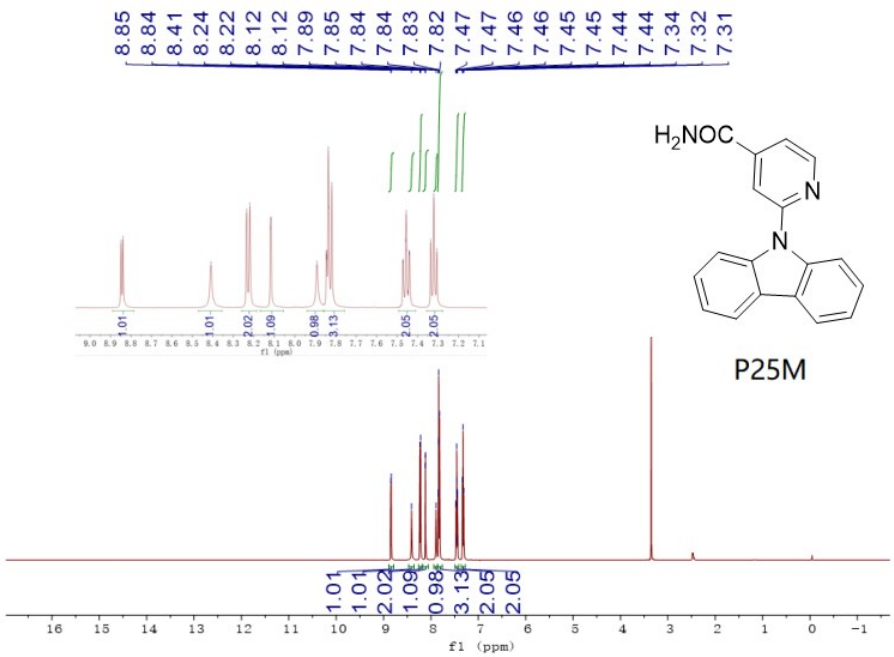


Figure S13. ^{1}H NMR and ^{13}C NMR spectra of **P25N** in $CDCl_3$.



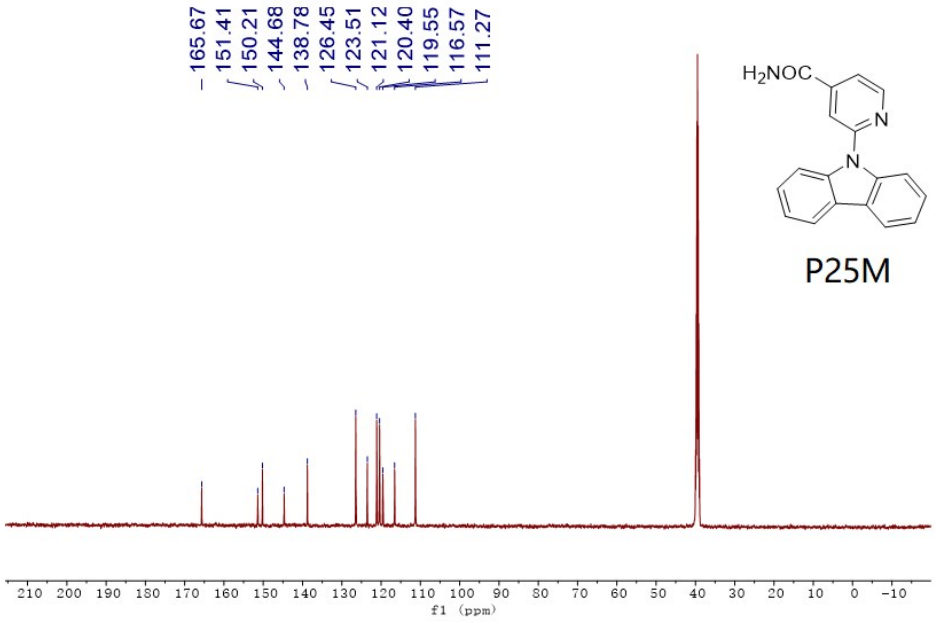


Figure S14. ^{1}H NMR and ^{13}C NMR spectra of **P25M** in DMSO-d_6.