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Electronic Supplementary Information

1,7/8-Substituted isoquinoline derivatives: position isomerism caused by HIO_3-induced dehydrogenation and solid-state fluorescent stimulus-responsive properties

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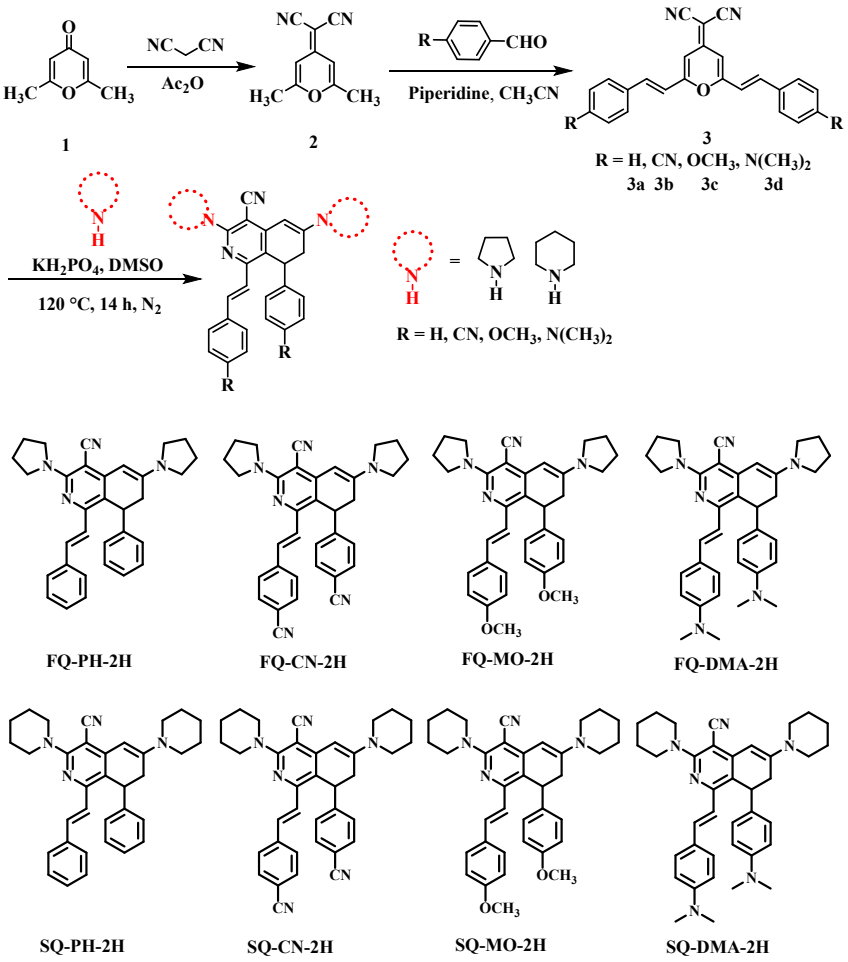

Scheme S1 Synthesis of various 7,8-dihydroisoquinoline derivatives.

1. Experimental

1.1 Measurements and materials

^{1}H and ^{13}C NMR spectra were performed with a Bruker DRX 500/400 NMR spectrometer or a Bruker DRX 400 NMR spectrometer. HRMS-ESI mass spectra were performed with a Hitachi Nano Frontier LD spectrometer. Absorption spectra were performed with a UV-3600 Shimadzu spectrophotometer. Fluorescence spectra were conducted on a HITACHI F-7000 fluorometer. Fluorescence quantum yields (Φ_F) in solid state were conducted on a FluoroMax-4 (Horiba Jobin Yvon) fluorometer. Single-crystal X-ray diffraction measurements were obtained on a Bruker-Nonius Smart Apex CCD diffractometer with graphite monochromated Mo Kα radiation. 2-(2,6-Dimethyl-4*H*-pyran-4-ylidene)malononitrile (**2**) was synthesized by the reaction of 2,6-dimethyl-4*H*-pyran-4-one (**1**) and malononitrile in the presence of acetic anhydride according to the previous report (Scheme S1).[1] 2-(2,6-di((*E*)-Styryl)-4*H*-pyran-4-ylidene)malononitrile (**3a**), 2-(2,6-bis((*E*)-4-cyanostyryl)-4*H*-pyran-4-ylidene)malononitrile (**3b**), 2-(2,6-bis((*E*)-4-methoxystyryl)-4*H*-pyran-4-ylidene)malononitrile (**3c**), and 2-(2,6-bis((*E*)-4-(dimethylamino)-styryl)-4*H*-pyran-4-ylidene)malononitrile (**3d**) were synthesized using compound **2** and the corresponding aromatic aldehydes as the materials according to the previous literature.[2] (*E*)-8-Phenyl-3,6-di(pyrrolidin-1-yl)-1-styryl-7,8-dihydroisoquinoline-4-carbonitrile (**FQ-Ph-2H**), (*E*)-8-phenyl-3,6-di(piperidin-1-yl)-1-styryl-7,8-dihydroisoquinoline-4-carbonitrile (**SQ-Ph-2H**), (*E*)-8-(4-methoxyphenyl)-1-(4-methoxystyryl)-3,6-di(piperidin-1-yl)-7,8-dihydroisoquinoline-4 -carbonitrile (**SQ-MO-2H**), and (*E*)-8-(4-(dimethylamino)phenyl)-1-(4-(dimethylamino)styryl)-3,6-di(piperidin-1-yl)-7,8-dihydroisoquinoline-4-carbonitrile (**SQ-DMA-2H**) were synthesized according to the previous literature,[2] using compound **3** and as pyrrolidine/piperidine the materials.

1.2 General procedure for 7,8-dihydroisoquinoline derivatives FQ-CN-2H, FQ-MO-2H, FQ-DMA-2H, and SQ-CN-2H.

A mixture of compound **3b/3c/3d** (5.0 mmol), pyrrolidine/piperidine (20.0 mmol), KH_2PO_4 (15.0 mmol), and DMSO (15.0 mL) was stirred at 120 °C for 14 h under N_2 atmosphere. After being cooled to the room temperature, the reaction mixture was poured into CH_2Cl_2 (100 mL), and the organic layer was washed with water (50 mL) for three times, and then dried over Na_2SO_4. After removal of solvent under reduced pressure, the residue was purified by flash chromatography on silica gel to afford the corresponding product.

(*E*)-8-(4-Cyanophenyl)-1-(4-cyanostyryl)-3,6-di(pyrrolidin-1-yl)-7,8-dihydroisoquinoline-4-carbonitrile (FQ-CN-2H). Following the general procedure, using petroleum ether/ethyl acetate (4:1, v/v) as the eluent to afford a red solid (1.23 g, 46% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.70 (d, J = 15.5 Hz, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 7.5 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 6.93-6.88 (m, 3H), 5.13 (s, 1H), 4.07 (s, 1H), 3.80-3.77 (m, 5H), 3.38-3.35 (m, 2H), 3.12-3.08 (m, 1H), 2.13-2.03 (m, 9H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): 163.8, 163.5, 155.8, 144.8, 141.9, 141.3, 132.4, 131.7, 131.5, 130.0, 127.6, 127.5, 121.1, 119.9, 118.8, 118.6, 111.2, 110.6, 96.0, 78.1, 49.5, 48.6, 47.2, 37.1, 25.5 ppm.

(*E*)-8-(4-Methoxyphenyl)-1-(4-methoxystyryl)-3,6-di(pyrrolidin-1-yl)-7,8-dihydroisoquinoline-4-carbonitrile (FQ-MO-2H). Following the general procedure, using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford a yellow solid (0.92 g, 32% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.69 (d, J = 14.5 Hz, 1H), 7.36 (d, J = 7.5 Hz, 2H), 7.07 (d, J = 6.5 Hz, 2H), 6.93 (d, J = 15.0 Hz, 1H), 6.84 (d, J = 7.5 Hz, 2H), 6.75 (d, J = 7.5 Hz, 2H), 5.46 (s, 1H), 4.42 (d, J = 6.5 Hz, 1H), 3.85 (br, 4H), 3.80 (s, 3H), 3.73 (s, 3H), 3.30 (br, 4H), 2.98-2.84 (m, 2H), 1.97-1.85 (m, 8H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): 159.6, 157.9, 156.7, 152.3, 151.1, 150.9, 135.8, 134.2, 129.9, 128.5, 128.3, 1219., 120.6, 113.9, 113.7, 113.1, 90.6, 81.2, 55.2, 55.0, 48.8, 47.6, 36.4, 34.7, 25.6, 24.9 ppm.

(*E*)-8-(4-(Dimethylamino)phenyl)-1-(4-(dimethylamino)styryl)-3,6-di(pyrrolidin-1-yl)-7,8-dihydroisoquinoline-4-carbonitrile (FQ-DMA-2H). Following the general procedure, using petroleum ether/ethyl acetate (10:1, v/v) as the eluent to afford a yellow solid (1.51 g, 52% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.68 (d, J = 15.5 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 15.0 Hz, 1H), 6.64 (d, J = 8.5 Hz, 2H), 6.59 (d, J = 8.0 Hz, 2H), 5.45 (s, 1H), 4.39 (d, J = 7.0 Hz, 1H), 3.85 (br, 4H), 3.32 (br, 4H), 2.96 (s, 6H), 2.93-2.89 (m, 2H), 2.87 (s, 6H), 1.96-1.85 (m, 8H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): 156.7, 152.2, 151.3, 150.3, 149.0, 134.8, 131.9, 130.4, 128.5, 128.0, 125.6, 120.9, 119.8, 113.3, 112.6, 112.0, 90.7, 80.9, 48.9, 47.6, 40.62, 40.58, 40.32, 40.28, 36.3, 34.7, 25.7, 25.0 ppm.

(*E*)-8-(4-Cyanophenyl)-1-(4-cyanostyryl)-3,6-di(piperidin-1-yl)-7,8-dihydroisoquinoline-4-carbonitrile (SQ-CN-2H). Following the general procedure, using petroleum ether/ethyl acetate (10:1, v/v) as the eluent to afford a yellow solid (2.28 g, 80% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.74 (d, J = 15.0 Hz, 1H), 7.64 (d, J = 7.5 Hz, 2H), 7.56 (d, J = 7.5 Hz, 2H), 7.34 (d, J = 7.5 Hz, 2H), 6.95 (d, J = 8.5 Hz, 3H), 5.37 (s, 1H), 4.11 (s, 1H), 3.57 (br, 4H), 3.56 (br, 5H), 3.01-2.98 (m, 1H), 1.73-1.66 (m, 12H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): 165.9, 165.2, 160.6, 144.6, 141.4, 141.0, 132.3, 132.1, 131.3, 130.2, 127.5, 127.1, 123.7, 118.8, 118.6, 118.5, 111.2, 110.5, 97.90, 97.86, 82.8, 49.8, 45.6, 38.1, 29.6, 25.8, 25.5, 24.6, 23.9 ppm.

1.3 General procedure for the target isoquinoline derivatives

A mixture of various 7,8-dihydroisoquinoline derivatives (1.0 mmol), hydroiodic acid (1.2 mmol), acetonitrile (10.0 mL) was stirred at 80 °C for 45 min. After being cooled to the room temperature, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the corresponding product.

(*E*)-8-Phenyl-3,6-di(pyrrolidin-1-yl)-1-styrylisoquinoline-4-carbonitrile (FQ-Ph-8). Following the general procedure, using petroleum ether/ethyl acetate (10:1, v/v) as the eluent to afford a yellow solid (409.5 mg, 84% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.54 (d, J = 15.5 Hz, 1H), 7.45-7.37 (m, 5H), 7.19-7.18 (m, 3H), 6.93-6.91 (m, 2H), 6.79 (d, J = 2.0 Hz, 1H), 6.67 (d, J = 15.0 Hz, 1H), 6.62 (d, J = 2.0 Hz, 1H), 3.94 (br, 4H), 3.50 (t, J = 6.5 Hz, 4H), 2.08-2.04 (m, 8H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): 155.3, 154.6, 148.5, 144.2, 143.7, 142.9, 136.5, 133.9, 129.2,

128.5, 128.2, 127.4, 127.3, 120.7, 116.3, 112.6, 98.9, 76.2, 48.9, 47.6, 25.5, 25.3 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{32}H_{31}N_4$, 471.2543; found, 471.2537.

(*E*)-8-(4-Cyanophenyl)-1-(4-cyanostyryl)-3,6-di(pyrrolidin-1-yl)isoquinoline-4-carbonitrile (FQ-CN-8). Following the general procedure, using petroleum ether/ethyl acetate (10:1, v/v) as the eluent to afford a red solid (200.1 mg, 37% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.71 (d, J = 8.0 Hz, 2H), 7.53 (t, J = 6.5 Hz, 4H), 7.48 (d, J = 14.5 Hz, 1H), 6.95 (d, J = 8.0 Hz, 2H), 6.81 (d, J = 2.0 Hz, 1H), 6.56 (d, J = 2.0 Hz, 1H), 6.52 (d, J = 15.0 Hz, 1H), 3.94 (br, 4H), 3.49 (t, J = 6.0 Hz, 4H), 2.10-2.04 (m, 8H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): 155.0, 154.3, 148.5, 144.5, 140.7, 140.5, 132.4, 132.3, 132.2, 131.6, 130.1, 127.3, 120.3, 118.7, 118.4, 116.5, 116.4, 112.3, 111.7, 111.4, 99.6, 49.1, 47.8, 25.6, 25.5 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{34}H_{29}N_6$, 521.2448; found, 521.2452.

(*E*)-8-(4-Methoxyphenyl)-1-(4-methoxystyryl)-3,6-di(pyrrolidin-1-yl)isoquinoline-4-carbonitrile (FQ-MO-8). Following the general procedure, using petroleum ether/ethyl acetate (15:1, v/v) as the eluent to afford a yellow solid (182.2 mg, 33% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.92 (d, J = 15.5 Hz, 1H), 7.82 (s, 1H), 7.62 (d, J = 15.0 Hz, 1H), 7.39 (d, J = 7.5 Hz, 2H), 7.02 (s, 1H), 6.96 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 7.5 Hz, 2H), 3.99 (br, 4H), 3.88 (s, 3H), 3.84 (s, 3H), 3.09 (br, 4H), 2.04 (br, 4H), 1.81 (br, 4H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): 160.2, 158.5, 155.3, 155.1, 151.0, 141.4, 137.0, 134.9, 130.2, 129.4, 129.1, 128.7, 120.8, 119.9, 114.1, 113.8, 113.5, 102.9, 76.2, 55.3, 55.2, 51.1, 49.0, 25.58, 25.56 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{34}H_{35}N_4O_2$, 531.2755; found, 531.2749.

(*E*)-7-(4-(Dimethylamino)phenyl)-1-(4-(dimethylamino)styryl)-3,6-di(pyrrolidin-1-yl)isoquinoline-4-carbonitrile (FQ-DMA-7). Following the general procedure, using petroleum ether/ethyl acetate (15:1, v/v) as the eluent to afford an orange solid (333.3 mg, 56% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, J = 15.2 Hz, 1H), 7.85 (s, 1H), 7.58-7.52 (m, 3H), 7.36 (d, J = 8.0 Hz, 2H), 7.26 (s, 1H), 7.02 (s, 1H), 6.83 (br, 1H), 6.71 (d, J = 8.8 Hz, 2H), 3.98 (t, J = 5.6 Hz, 4H), 3.12 (t, J = 5.2 Hz, 4H), 3.03 (s, 6H), 3.02 (s, 6H), 2.03 (t, J = 6.8 Hz, 4H), 1.81 (t, J = 7.6 Hz, 4H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): 155.6, 155.5, 151.1, 150.7, 149.2, 141.2, 137.6, 130.7, 129.8, 129.1, 129.0, 124.8, 121.1, 117.5, 113.9, 112.0, 111.9, 102.8, 75.6, 51.1, 48.9, 40.6, 40.5, 40.19, 40.15, 25.59, 25.56 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{36}H_{41}N_6$, 557.3387; found, 557.3380.

(*E*)-8-Phenyl-3,6-di(piperidin-1-yl)-1-styrylisoquinoline-4-carbonitrile (SQ-Ph-8). Following the general procedure, using petroleum ether/ethyl acetate (15:1, v/v) as the eluent to afford a yellow solid (222.2 mg, 40% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.59 (d, J = 15.0 Hz, 1H), 7.44-7.41 (m, 5H), 7.20-7.16 (m, 4H), 6.96-6.92 (m, 3H), 6.64 (d, J = 15.5 Hz, 1H), 3.90 (br, 4H), 3.47 (br, 4H), 1.79-1.69 (m, 12H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): 158.6, 155.0, 151.8, 144.3, 143.5, 142.4, 136.6, 134.0, 129.2, 128.6, 128.2, 128.1, 127.5, 127.3, 119.7, 118.7, 114.5, 102.3, 80.1, 49.3, 48.6, 26.2, 25.4, 24.8, 24.3 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{34}H_{35}N_4$, 499.2856; found, 499.2850.

(*E*)-8-(4-Cyanophenyl)-1-(4-cyanostyryl)-3,6-di(piperidin-1-yl)isoquinoline-4-carbonitrile (SQ-CN-8). Following the general procedure, using petroleum ether/ethyl acetate (10:1, v/v) as the eluent to afford a yellow solid (171.1 mg, 31% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.72 (d, J = 8.0 Hz, 2H), 7.56-7.48 (m, 5H), 7.17 (s, 1H), 6.96 (d, J = 8.0 Hz, 3H), 6.51 (d, J = 15.5 Hz, 1H), 3.89 (br, 4H), 3.48 (br, 4H), 1.76-1.70 (m, 12H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): 158.5, 153.5, 151.8, 148.1, 144.7, 140.6, 140.1, 132.4, 132.3, 131.2, 130.1, 129.4, 119.3, 119.0, 118.6, 118.3, 114.0, 111.8, 111.5, 103.0, 100.0, 80.4, 49.3, 48.7, 29.7, 26.2, 25.5, 24.8, 24.3 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{36}H_{33}N_6$, 549.2761; found, 549.2758.

(*E*)-7-(4-Methoxyphenyl)-1-(4-methoxystyryl)-3,6-di(piperidin-1-yl)isoquinoline-4-carbonitrile (SQ-MO-7). Following the general procedure, using petroleum ether/ethyl acetate (10:1, v/v) as the eluent to afford a yellow solid (329.2 mg, 59% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.96 (d, J = 15.0 Hz, 1H), 7.89 (s, 1H), 7.68-7.60 (m, 5H), 7.30 (s, 1H), 7.00 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 7.5 Hz, 2H), 3.88 (s, 6H), 3.85 (br, 4H), 2.96 (br, 4H), 1.79-1.74 (m, 6H), 1.50 (br, 6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): 160.5, 159.0, 158.8, 155.7, 115.2, 141.3, 137.7, 133.4, 133.2, 129.5, 129.3, 127.8, 119.7, 119.2, 116.9, 114.2, 113.9, 109.3, 81.8, 55.3, 52.0, 49.8, 26.2, 25.6, 24.8, 24.0 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{36}H_{39}N_4O_2$, 559.3068; found, 559.3062.

(*E*)-7-(4-(Dimethylamino)phenyl)-1-(4-(dimethylamino)styryl)-3,6-di(piperidin-1-yl)isoquinoline-4-carbonitrile (FQ-DMA-7). Following the general procedure, using petroleum ether/ethyl acetate (15:1, v/v) as the eluent to afford an orange solid (316.5 mg, 54% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.96 (d, J = 15.0 Hz, 1H), 7.91 (s, 1H), 7.63-7.54 (m, 5H), 7.29 (s, 1H), 6.85 (br, 2H), 6.71 (d, J = 7.5 Hz, 2H), 3.85 (br, 4H), 3.03 (s, 12H), 2.97 (br, 4H), 1.79-1.73 (m, 6H), 1.52 (br, 6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): 159.3, 155.7, 155.6, 150.8, 149.5, 140.7, 138.3, 133.4, 129.2, 129.0, 127.5, 124.6, 119.5, 117.2, 116.9, 112.4, 111.9, 109.1, 81.3, 51.9, 49.8, 40.58, 40.56, 40.18, 40.16, 26.3, 25.7, 24.8, 24.1 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{38}H_{45}N_6$, 585.3700; found, 585.3695.

References

1. H. Li, Y. Guo, G. Li, H. Xiao, Y. Lei, X. Huang, J. Chen, H. Wu, J. Ding and Y. Cheng, *J. Phys. Chem. C*, 2015, **119**, 6737–6748.
2. X. Zhang, D. Wang, H. Shen, S. Wang, Y. Zhou, Y. Lei, W. Gao, M. Liu, X. Huang and H. Wu, *Org. Chem. Front.*, 2021, **8**, 856–867.

2. Schemes, figures, and tables

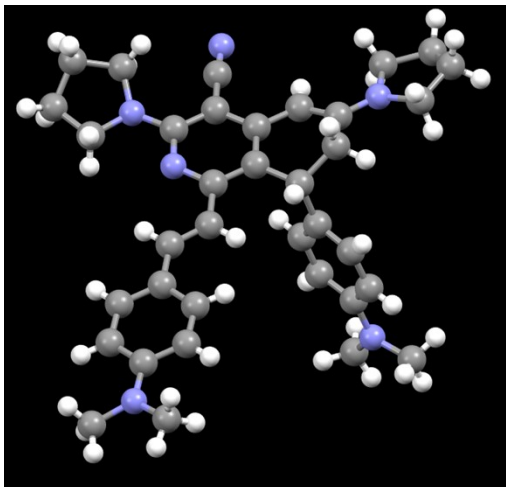

Fig. S1 Crystal structure of **FQ-DMA-2H**. Single crystal of **FQ-DMA-2H** is obtained from a slow diffusion of a petroleum ether/$CHCl_3$ mixture (1:2, v:v).

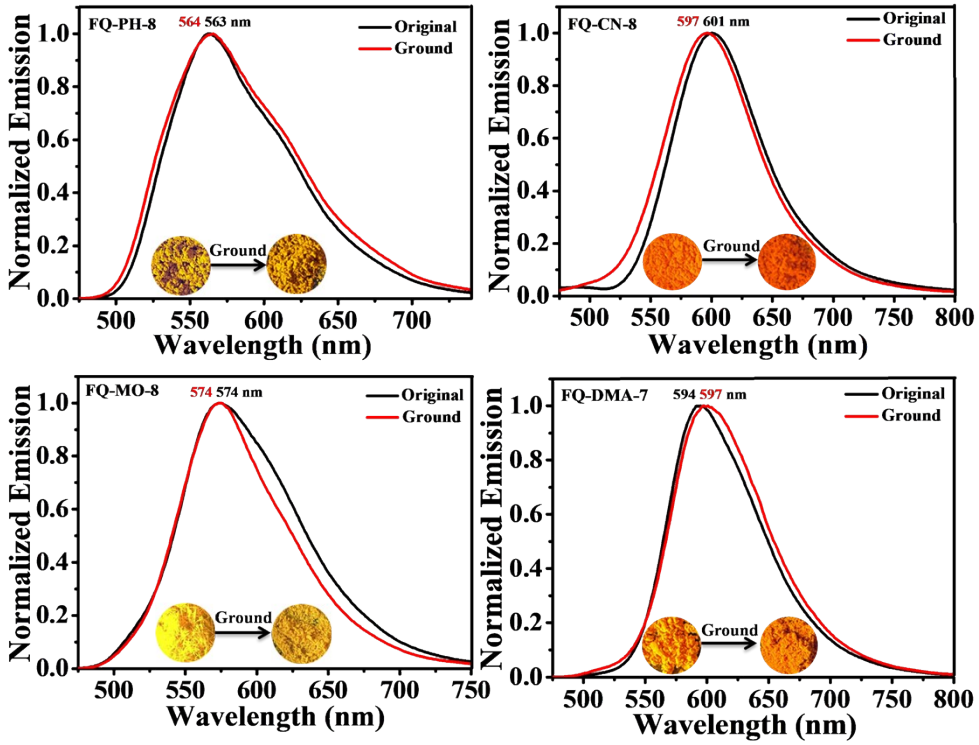

Fig. S2 Fluorescence spectra of the original samples of pyrrolidin-1-yl-substituted isoquinolines before and after grinding.

Table S1 Emission wavelengths and quantum efficiencies of the target compounds under different conditions.

Compound	Type	λ_{em} (nm)	Φ_F (%)
FQ-PH-8	Original	563	7.3
	Ground	564	5.4
	Acid-fumed	618	0.5
FQ-CN-8	Original	601	0.7
	Ground	597	0.5
	Acid-fumed	630	0.2
FQ-MO-8	Original	574	4.7
	Ground	574	1.3
	Acid-fumed	627	0.3
FQ-DMA-7	Original	597	1.5
	Ground	594	0.6
	Acid-fumed	534	0.2
SQ-PH-8	Original	582	6.1
	Ground	576	4.0
	Acid-fumed	629	0.6
SQ-CN-8	Original	587	14.1
	Ground	583	3.5
	Acid-fumed	535	0.05
SQ-MO-7	Original	587	23.2
	Ground	579	5.4
	Acid-fumed	650	3.3
SQ-DMA-7	Original	612	3.7
	Ground	602	1.3
	Acid-fumed	594	0.4

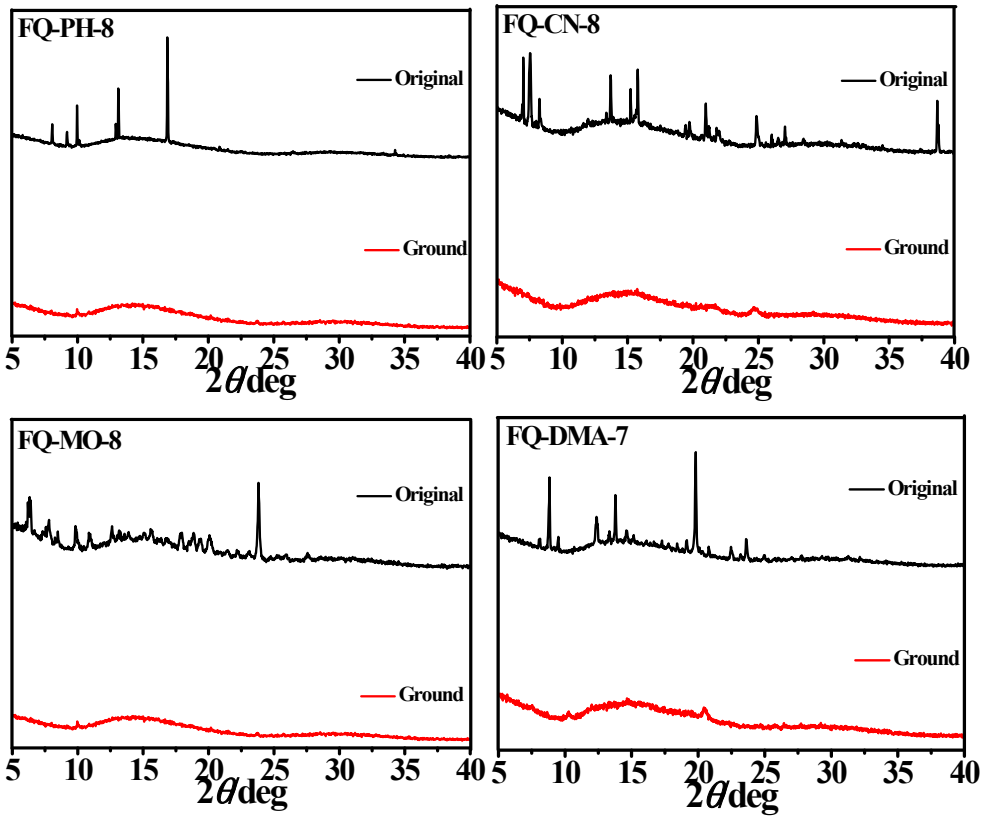

Fig. S3 XRD curves of pyrrolidin-1-yl-substituted isoquinolines before and after grinding.

Table S2 Crystal data and details of collection and refinement for the pyrrolidin-1-yl-substituted compounds.

	FQ-DMA-2H	**FQ-PH-8**	**FQ-CN-8**	**FQ-MO-8**	**FQ-MO-7**	**FQ-DMA-7**
CCDC (no.)	2161234	2161235	2161236	2161238	2161237	2161239
Empirical formula	$C_{36}H_{42}N_6$	$C_{32}H_{30}N_4$	$C_{34}H_{28}N_6$	$C_{34}H_{34}N_4O_2$	$C_{34}H_{34}N_4O_2$	$C_{36}H_{40}N_6$
Formula weight	558.75	470.60	520.62	530.65	530.65	556.74
Temperature (K)	293.01	293(2)	293(2)	293(2)	213(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	*P* 1 2(1)/n1	*P* 2(1)/n	*P*$\bar{1}$	*P*$\bar{1}$	*P*$\bar{1}$	*P* 2(1)/c
Z	4	4	4	2	2	4
D_{calcd} [Mg/m^3]	1.059	1.211	1.279	1.264	1.231	1.086
F (000)	1200	1000	1096	564	564	1192
θ range [°]	2.423-25.499	2.074-24.994	2.079-26.000	2.294-25.499	2.432-25.499	2.459-24.999
R_1 [I>2σ(I)]	0.0673	0.0808	0.0552	0.0511	0.0521	0.0914
wR_2 [I>2σ(I)]	0.1733	0.1833	0.1274	0.1101	0.1119	0.2639
a [Å]	13.3509(10)	6.3523(18)	8.6436(4)	9.4015(4)	8.4322(15)	17.1607(13)
b [Å]	10.8299(8)	19.643(6)	13.9559(6)	11.3355(5)	12.189(2)	8.3021(7)
c [Å]	24.274(2)	20.707(8)	23.8230(10)	13.9846(5)	14.487(3)	24.754(2)
α [deg]	90	90	100.8030(10)	82.1270(10)	104.542(6)	90
β [deg]	93.508(2)	92.809(10)	93.3960(10)	70.8020(10)	96.455(7)	105.113(2)
γ [deg]	90	90	105.4040(10)	87.3020(10)	90.161(6)	90
V [Å^3]	3503.2(5)	2580.7(14)	2703.3(2)	1394.20(10)	1431.4(5)	3404.8(5)

GOF	1.063	1.034	1.004	1.036	1.048	0.926
R(int)	0.0940	0.0912	0.0570	0.0507	0.0400	0.0608
No. of reflcns collected	35897	11437	54303	33329	17362	27781
No. of unique reflcns	6505	4529	10617	5181	5309	5977
R_1 (all data)	0.1394	0.1867	0.0999	0.0810	0.0827	0.1994
wR_2 (all data)	0.2212	0.2429	0.1576	0.1287	0.1318	0.3211

Table S3 Crystal data and details of collection and refinement for the piperidin-1-yl-substituted compounds.

	SQ-PH-8	**SQ-CN-8**	**SQ-MO-7**	**SQ-DMA-7**
CCDC (no.)	2161240	2161241	2161242	2161243
Empirical formula	$C_{34}H_{34}N_4$	$C_{36}H_{32}N_6$	$C_{36}H_{38}N_4O_2$	$C_{38}H_{44}N_6$
Formula weight	498.65	548.67	558.70	584.79
Temperature (K)	293(2)	293(2)	293.15	293(2)
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	2	2	2	2
D_{calcd} [Mg/m^3]	1.198	1.229	1.117	1.159
F (000)	532	580	596	628
θ range [°]	2.533-25.499	2.632-25.500	2.458-25.499	2.129-24.999
R_1 [I>2σ(I)]	0.0499	0.0657	0.0679	0.0734
wR_2 [I>2σ(I)]	0.1210	0.1427	0.1751	0.1441
a [Å]	10.1544(7)	8.7218(11)	10.0144(19)	11.5660(18)
b [Å]	11.9375(9)	12.9533(15)	13.195(3)	11.9295(19)
c [Å]	13.0772(10)	14.4264(17)	13.519(3)	13.2606(19)
α [deg]	71.511(2)	69.115(3)	109.990(6)	71.789(5)
β [deg]	70.377(2)	79.040(3)	92.980(6)	75.051(4)
γ [deg]	72.567(2)	79.308(3)	96.345(6)	88.530(5)
V [Å^3]	1382.59(18)	1482.6(3)	1660.7(6)	1676.2(4)
GOF	1.031	1.048	1.098	1.013
R(int)	0.0396	0.0845	0.0701	0.1173
No. of reflcns collected	33681	34528	31358	30313
No. of unique reflcns	5117	5518	6166	5900
R_1 (all data)	0.0686	0.1443	0.1191	0.1972
wR_2 (all data)	0.1376	0.1850	0.2100	0.2044

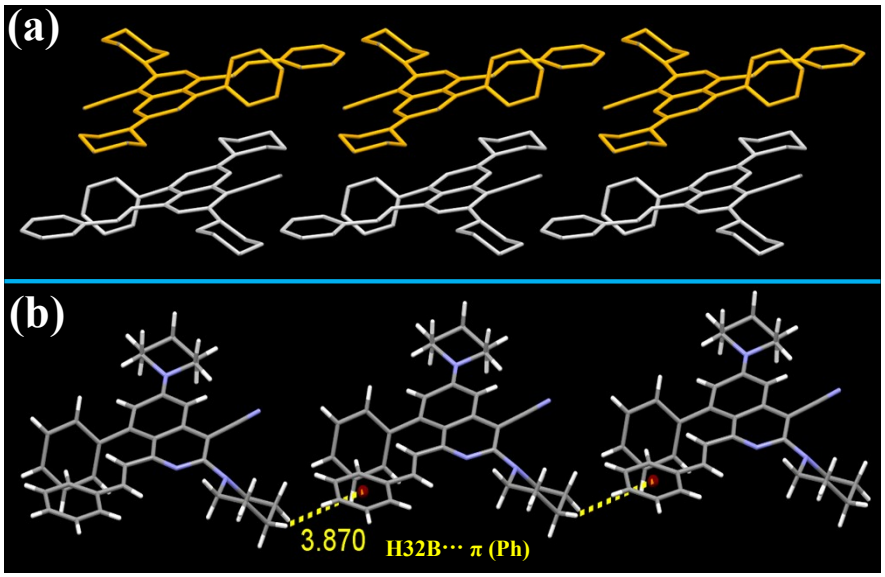

Fig. S4 Stacking arrangements (a) and intramolecular interactions (b) of single crystal **SQ-PH-8**.

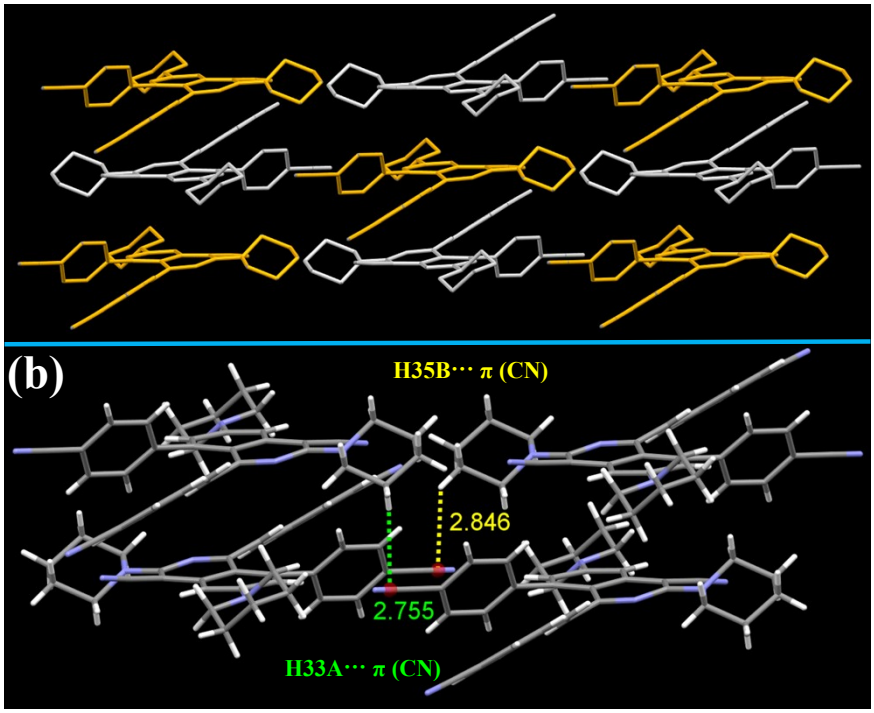

Fig. S5 Stacking arrangements (a) and intramolecular interactions (b) of single crystal **SQ-CN-8**.

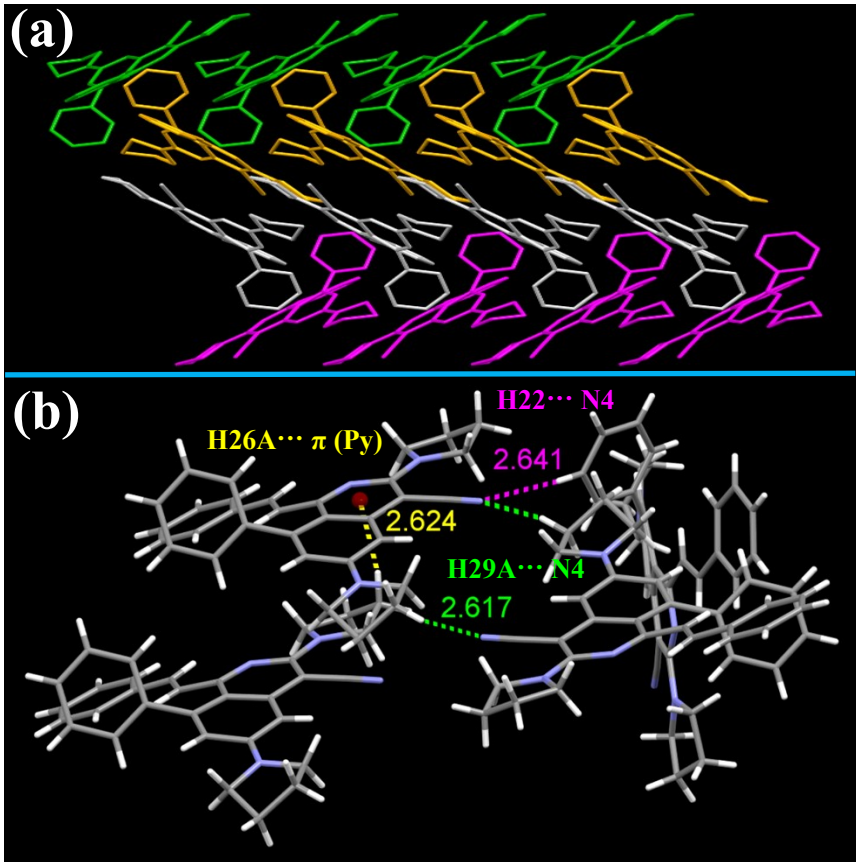

Fig. S6 Stacking arrangements (a) and intramolecular interactions (b) of single crystal **FQ-PH-8**.

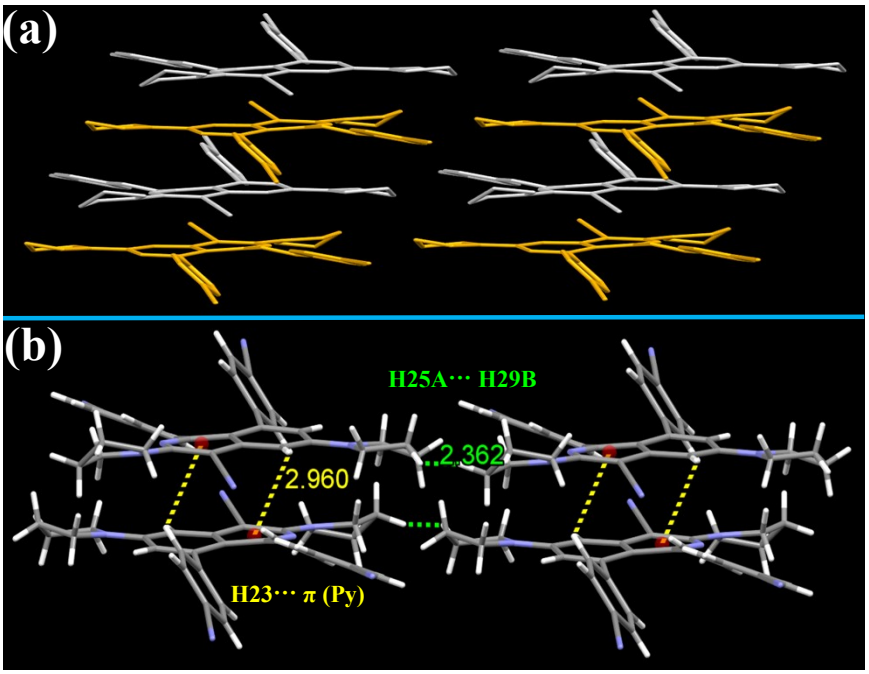

Fig. S7 Stacking arrangements (a) and intramolecular interactions (b) of single crystal **FQ-CN-8**.

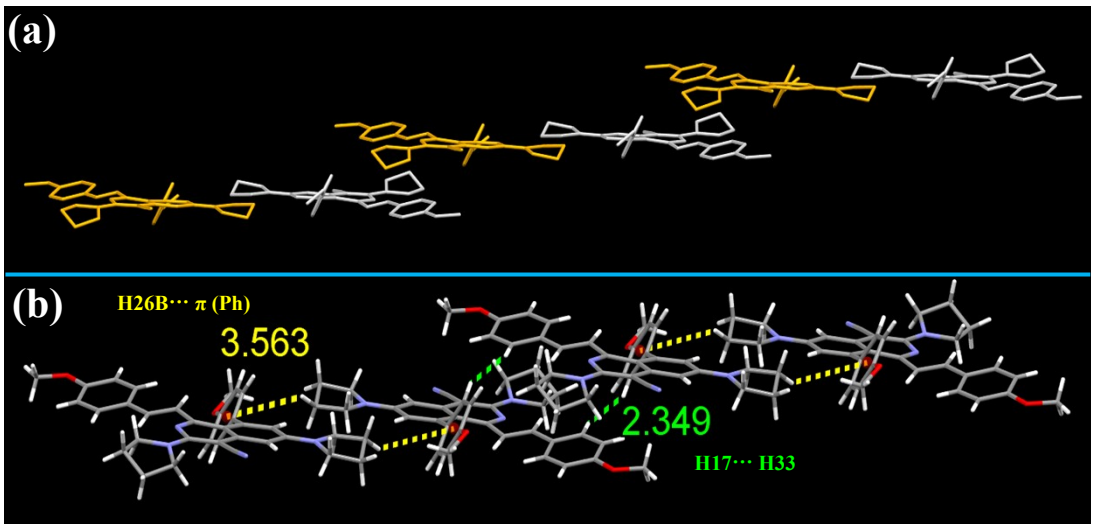

Fig. S8 Stacking arrangements (a) and intramolecular interactions (b) of single crystal **FQ-MO-8**.

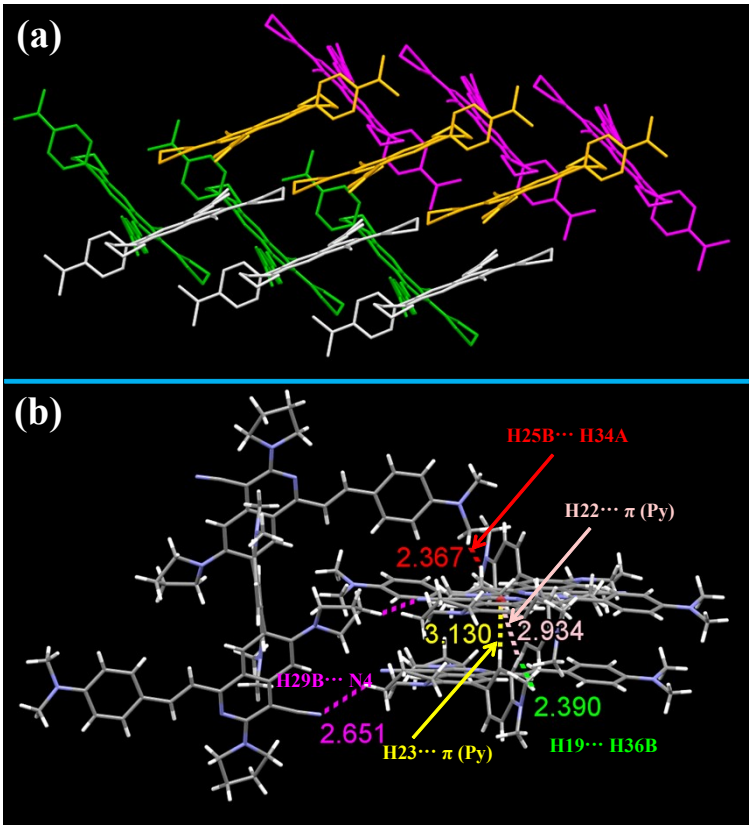

Fig. S9 Stacking arrangements (a) and intramolecular interactions (b) of single crystal **FQ-DMA-7**.

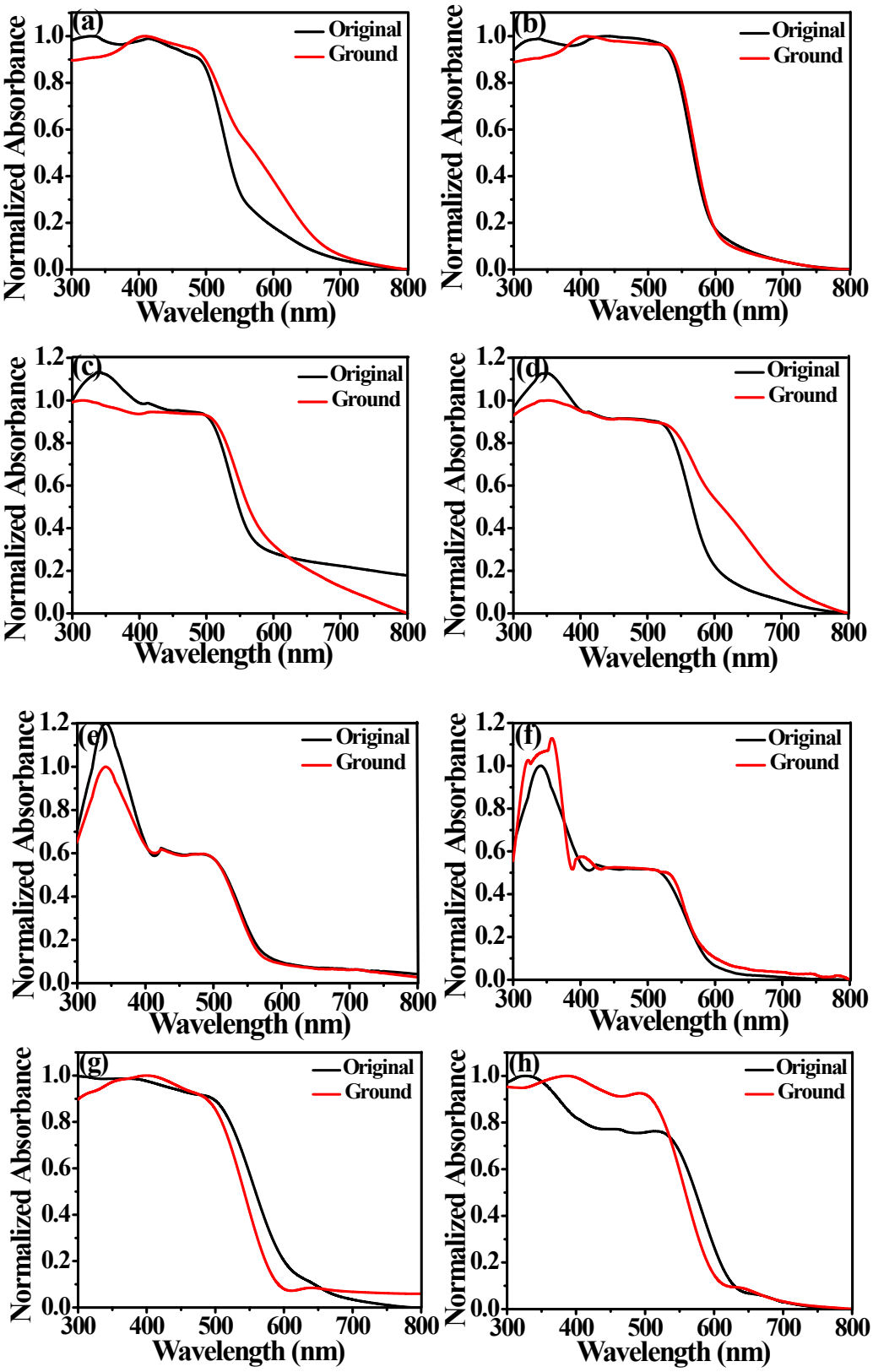

Fig. S10 Solid-state absorption spectra of the original samples of **FQ-PH-8** (a), **FQ-CN-8** (b), **FQ-MO-8** (c), **FQ-DMA-7** (d), **SQ-PH-8** (e), **SQ-CN-8** (f), **SQ-MO-7** (g), and **SQ-DMA-7** (h) before and after grinding.

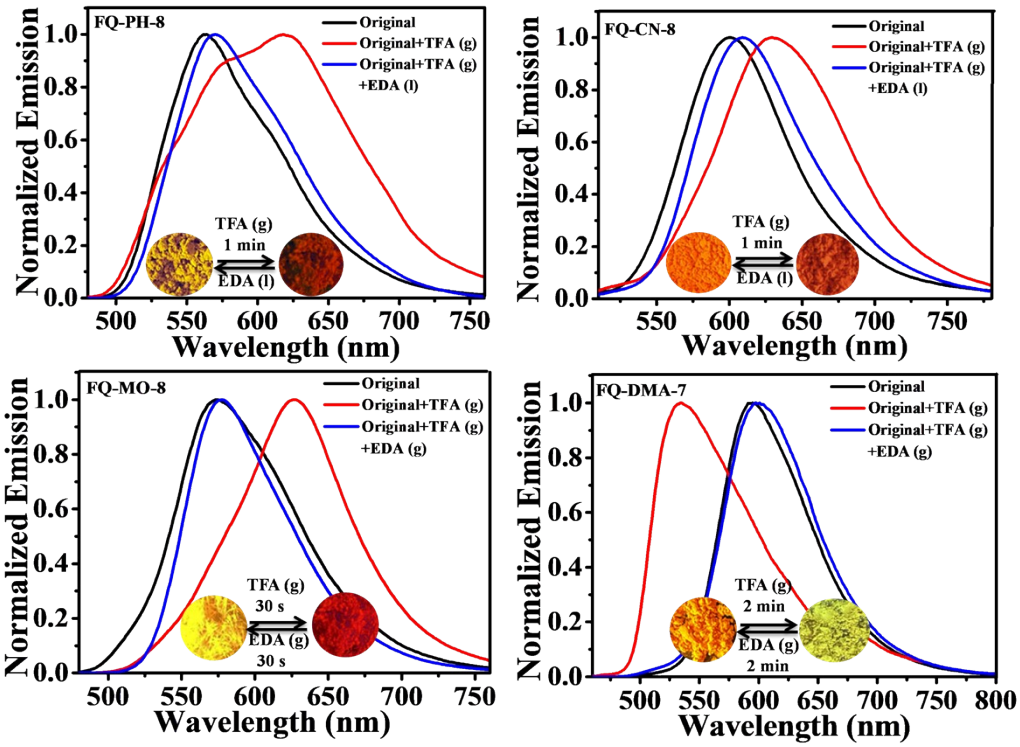

Fig. S11 Emission spectra of the original samples of pyrrolidin-1-yl-substituted isoquinolines upon TFA (g) and then EDA (l)/(g). Inset: fluorescence color pictures under different conditions.

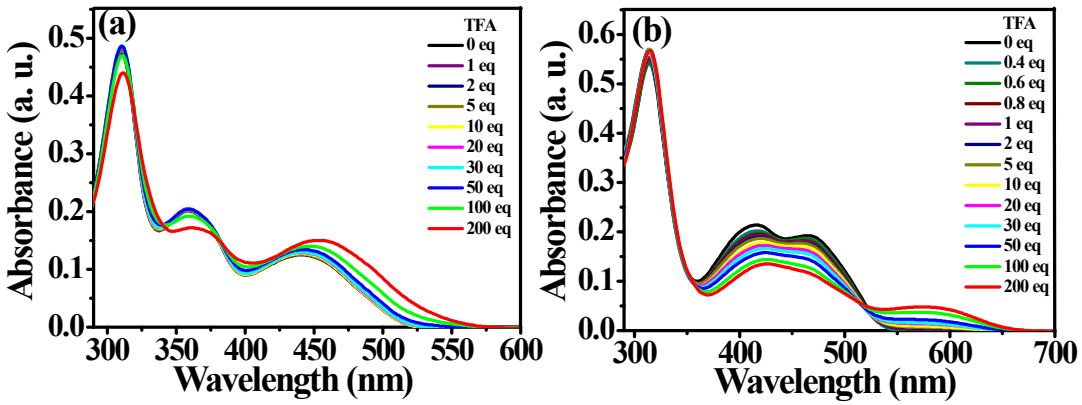

Fig. S12 Absorption spectra of **SQ-MO-7** (a) and **SQ-DMA-7** (b) in $CHCl_3$ solvent at 1×10^{-5} mol/L with the gradual addition of TFA.

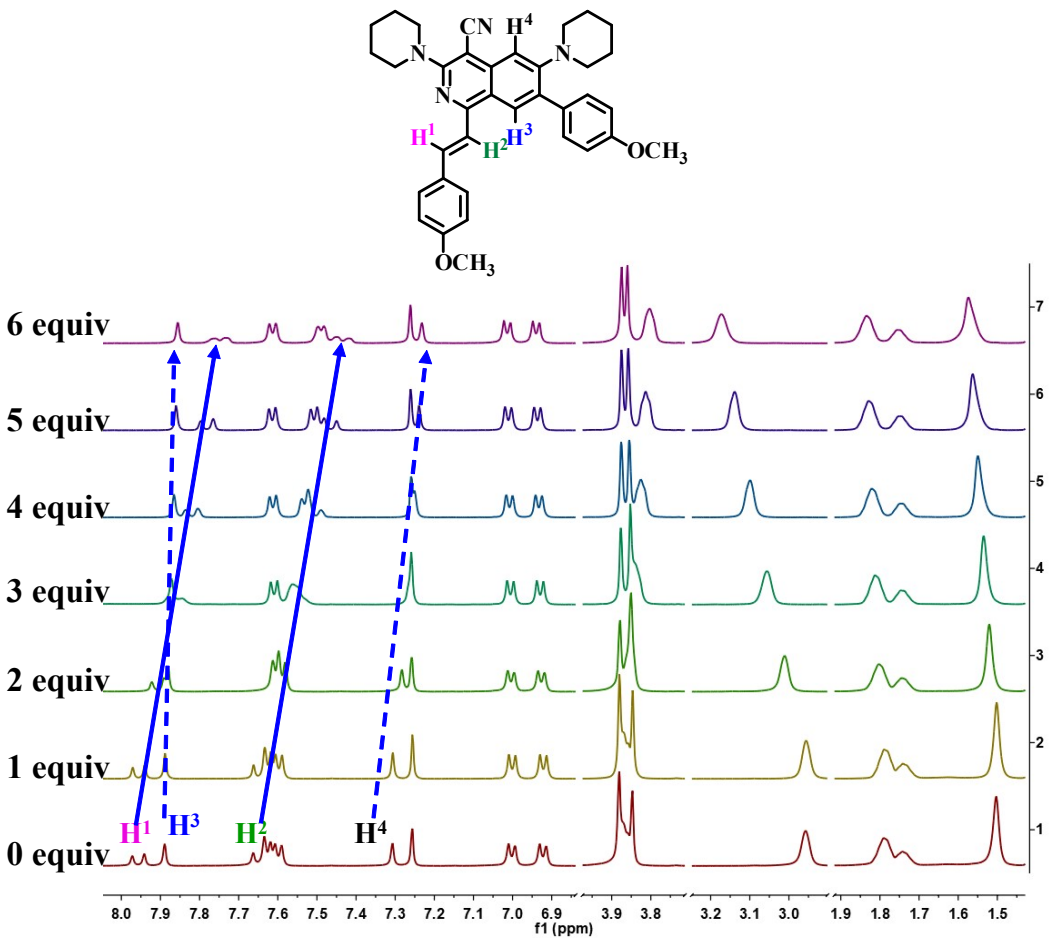

Fig. S13 Titration experiment of ^{1}H NMR spectra of **SQ-MO-7** in $CDCl_3$ with the gradual addition of TFA.

4. NMR spectra

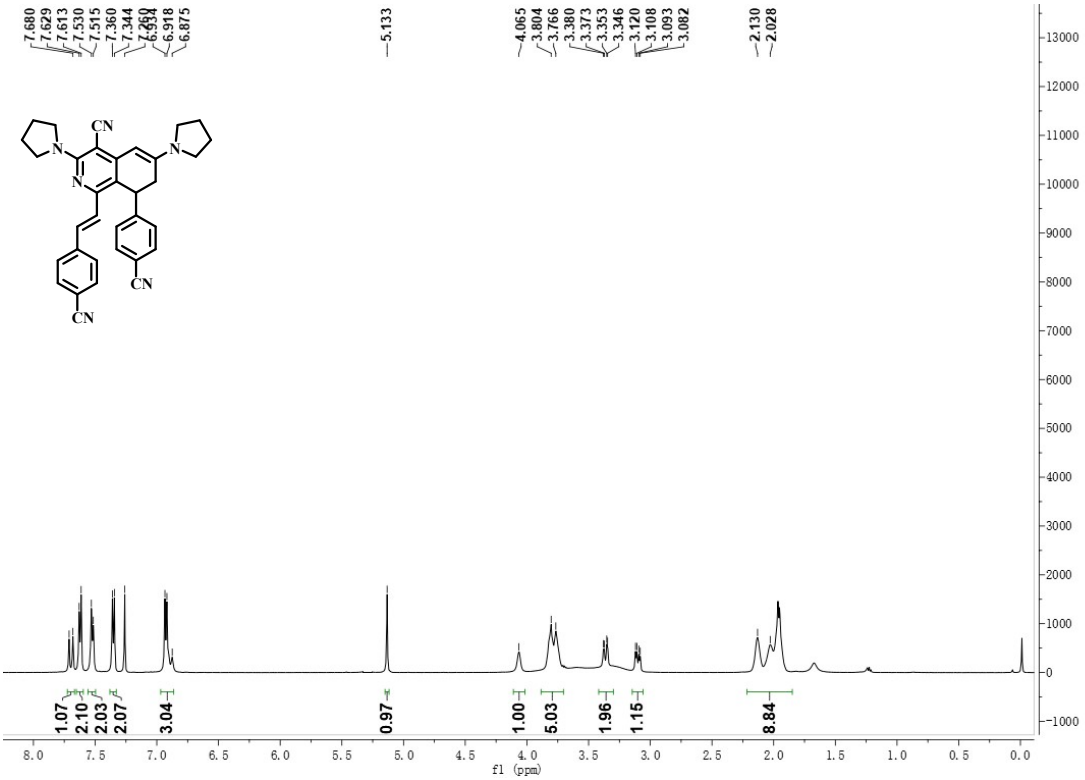

Fig. S14 ^{1}H NMR of **FQ-CN-2H** ($CDCl_3$, 500 MHz).

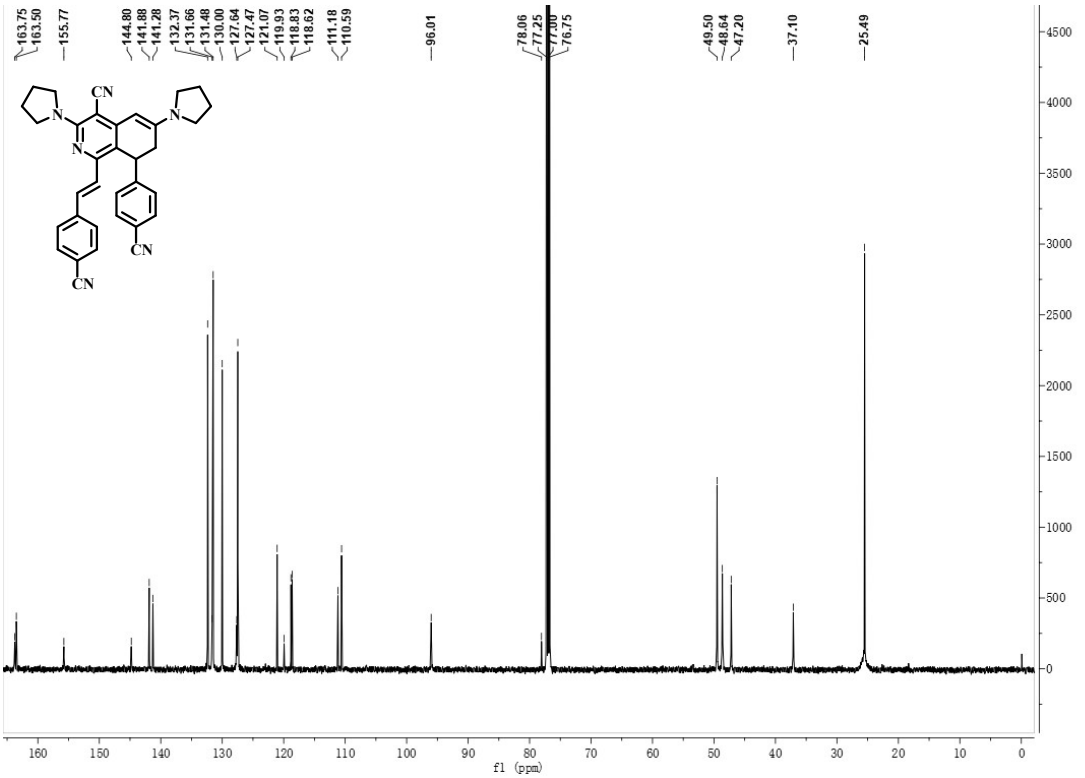

Fig. S15 ^{13}C NMR of **FQ-CN-2H** ($CDCl_3$, 125 MHz).

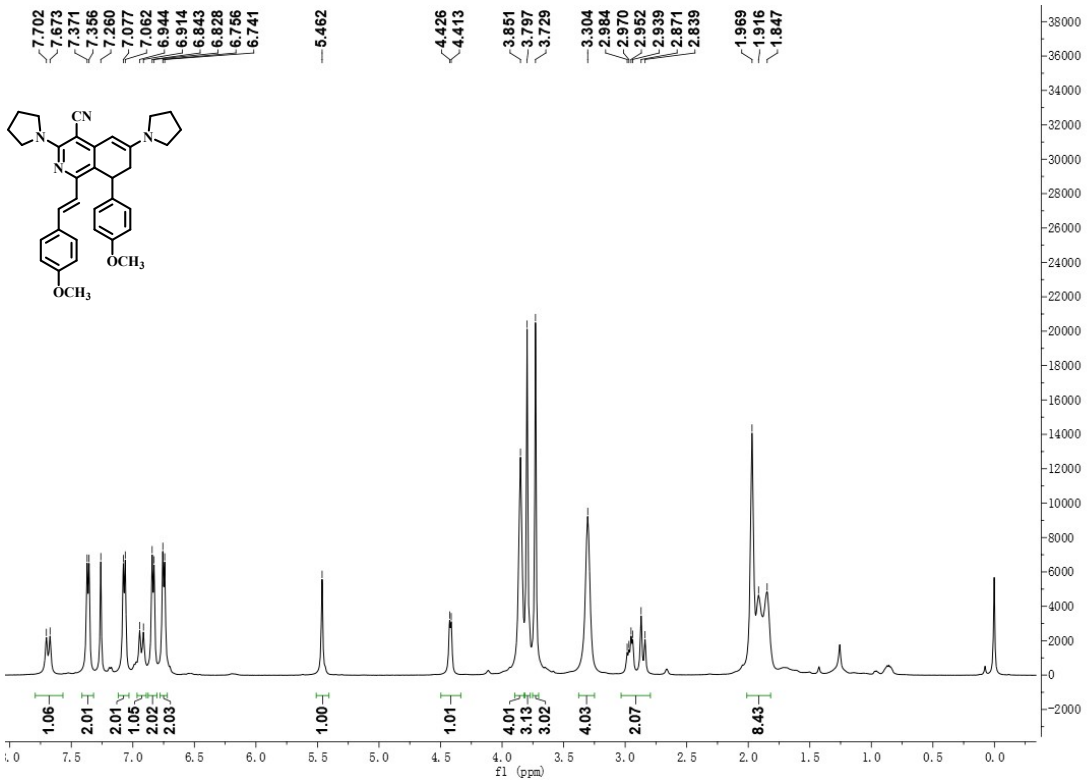

Fig. S16 ^{1}H NMR of **FQ-MO-2H** ($CDCl_3$, 500 MHz).

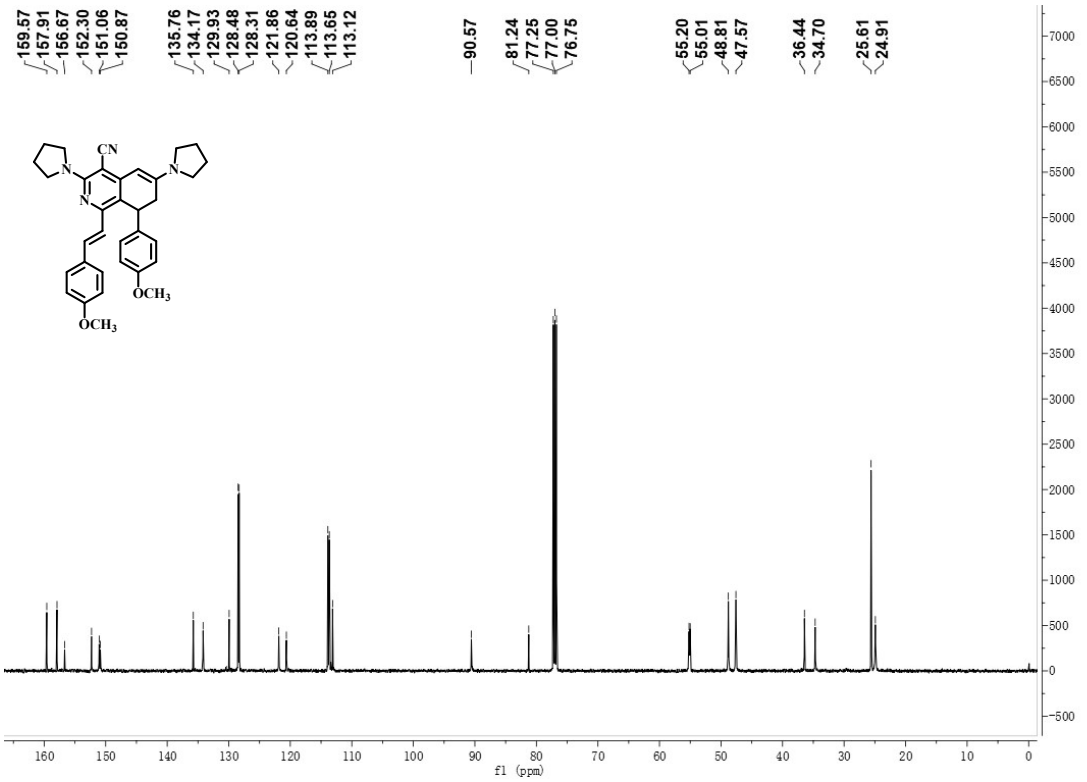

Fig. S17 ^{13}C NMR of **FQ-MO-2H** ($CDCl_3$, 125 MHz).

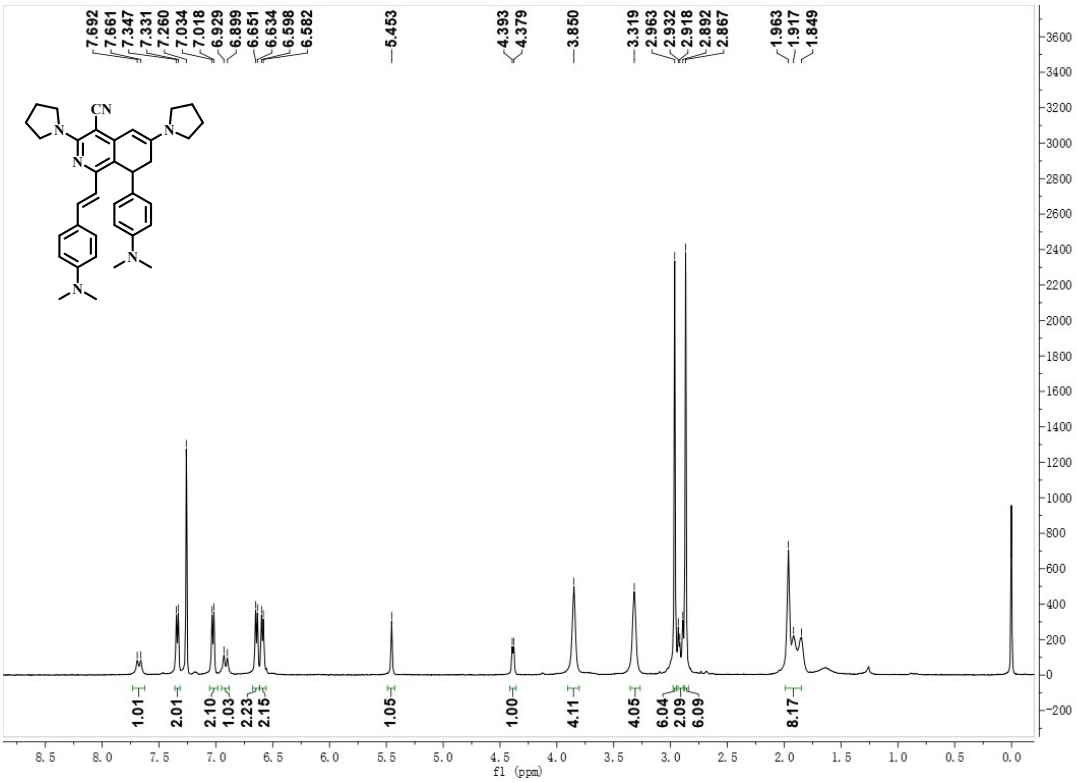

Fig. S18 ^{1}H NMR of **FQ-DMA-2H** ($CDCl_3$, 500 MHz).

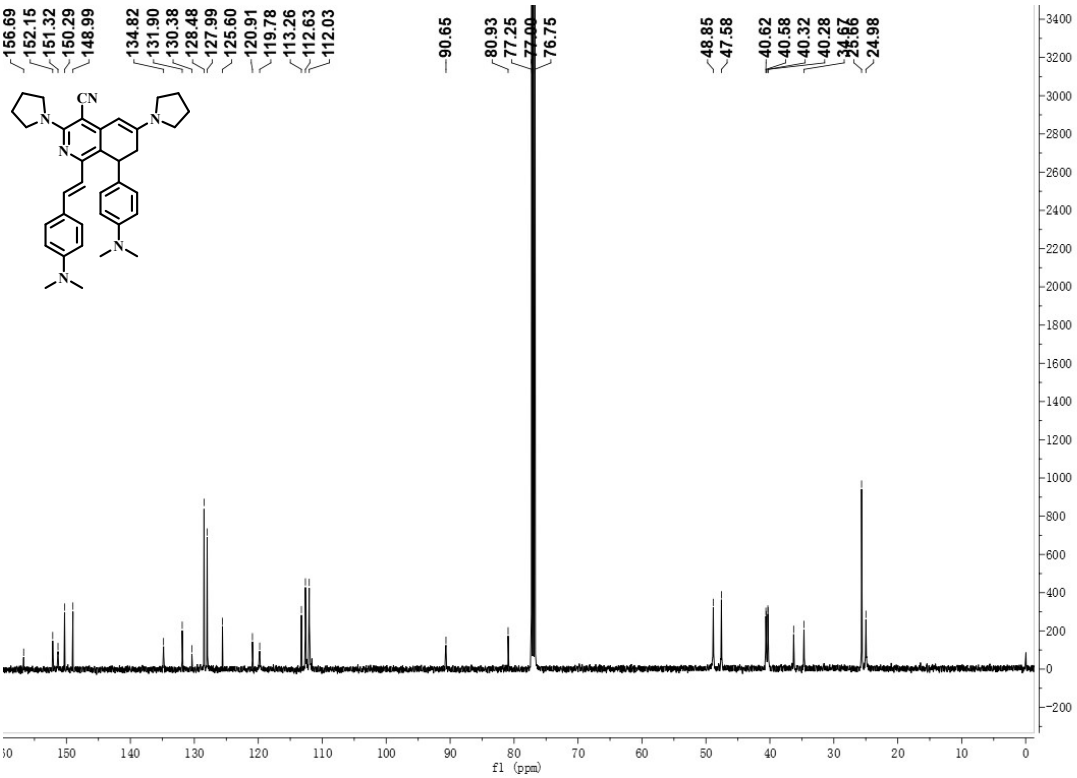

Fig. S19 ^{13}C NMR of **FQ-DMA-2H** ($CDCl_3$, 125 MHz).

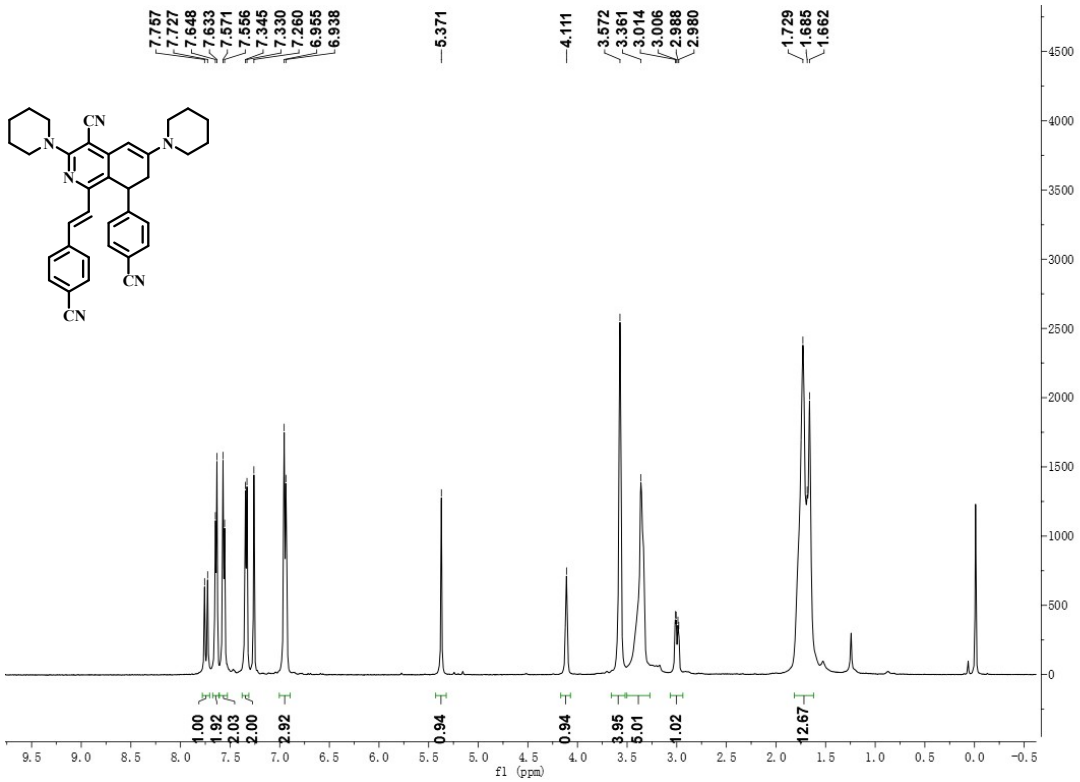

Fig. S20 ^{1}H NMR of **SQ-CN-2H** ($CDCl_3$, 500 MHz).

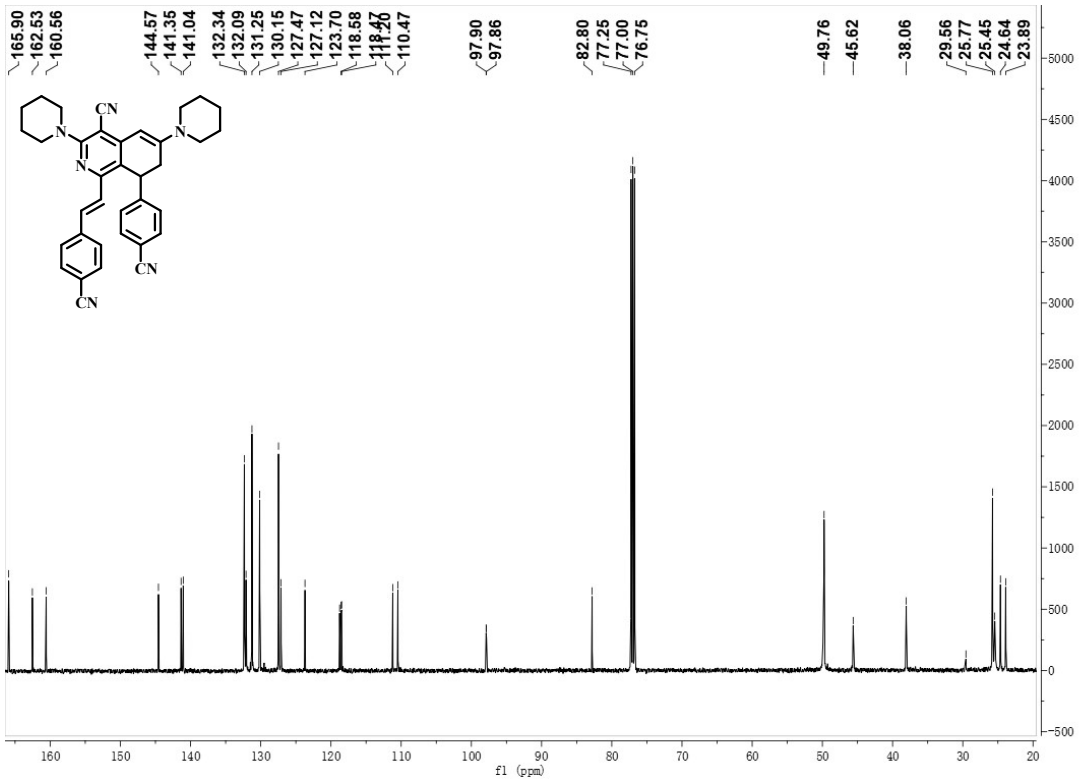

Fig. S21 ^{13}C NMR of **SQ-CN-2H** ($CDCl_3$, 125 MHz).

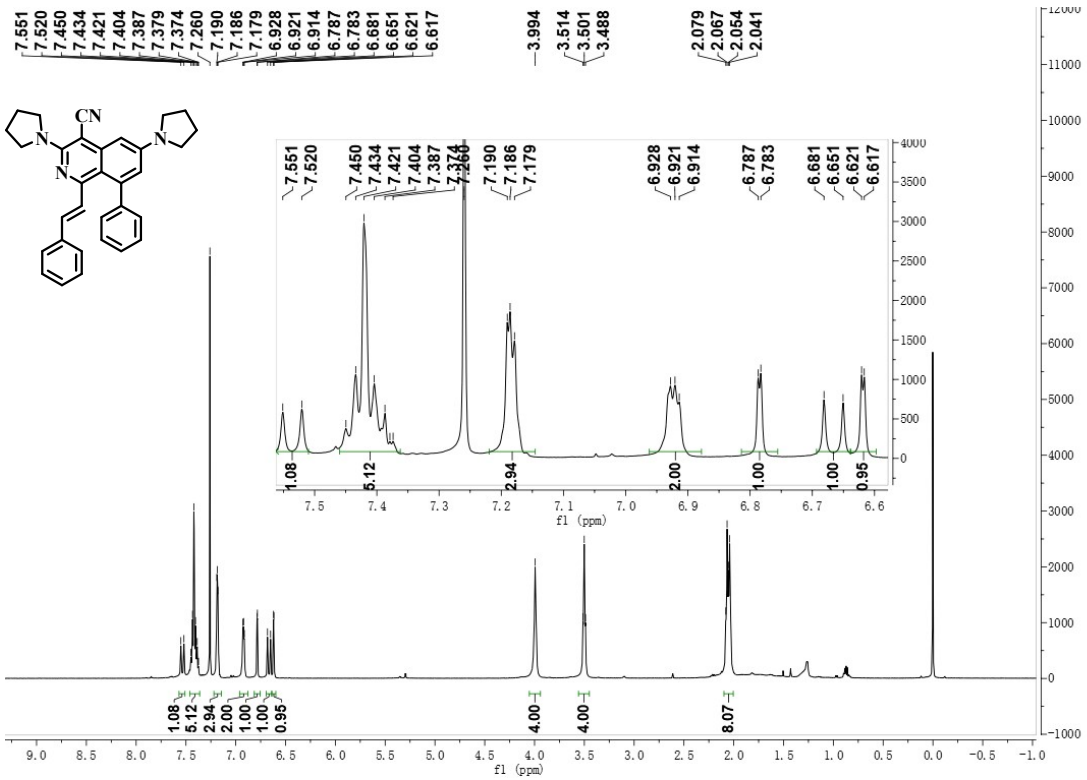

Fig. S22 ^{1}H NMR of **FQ-PH-8** ($CDCl_3$, 500 MHz).

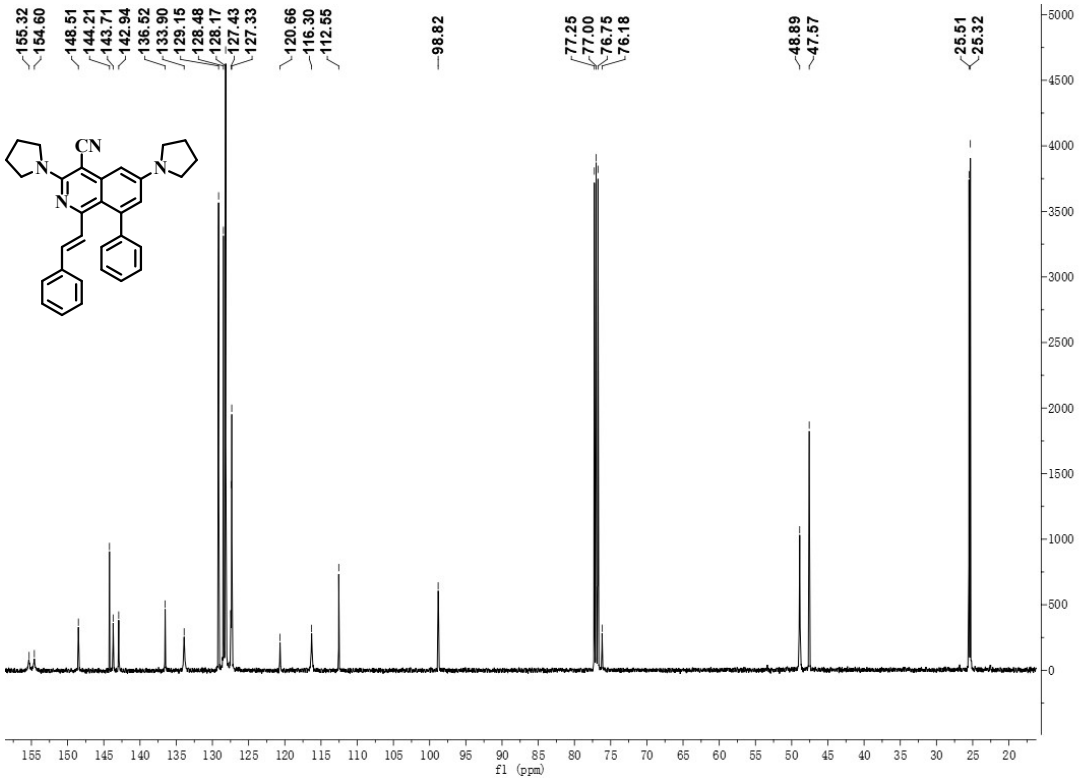

Fig. S23 ^{13}C NMR of **FQ-PH-8** ($CDCl_3$, 125 MHz).

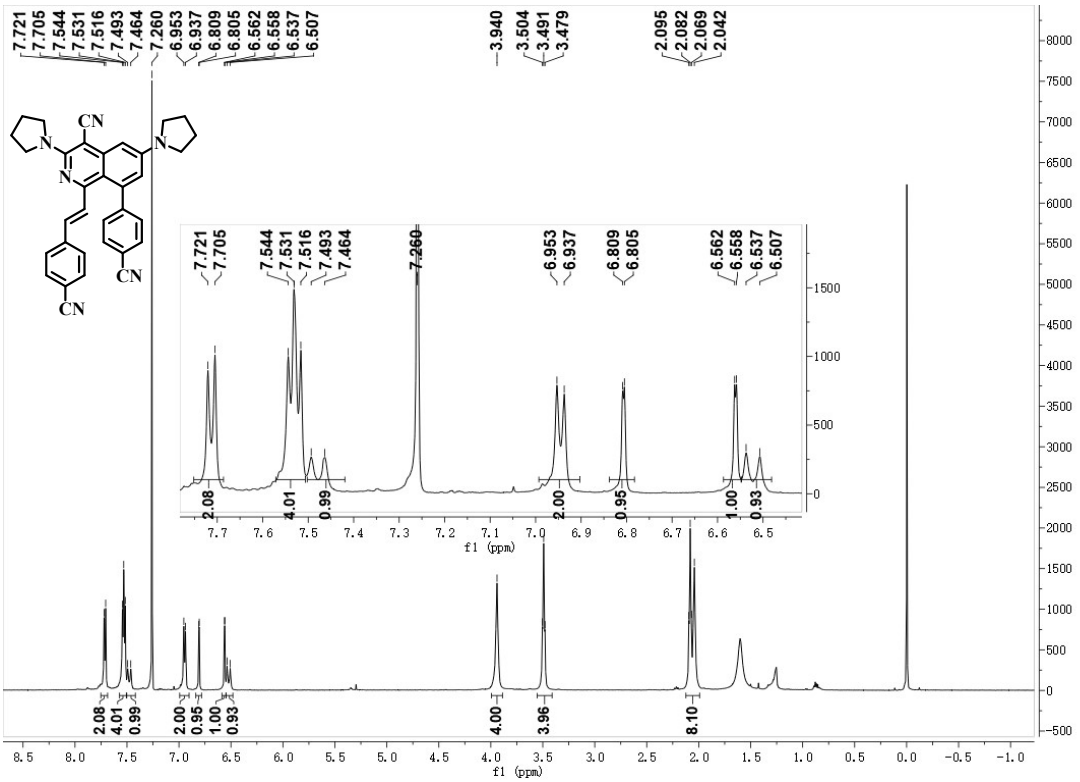

Fig. S24 ^{1}H NMR of **FQ-CN-8** ($CDCl_3$, 500 MHz).

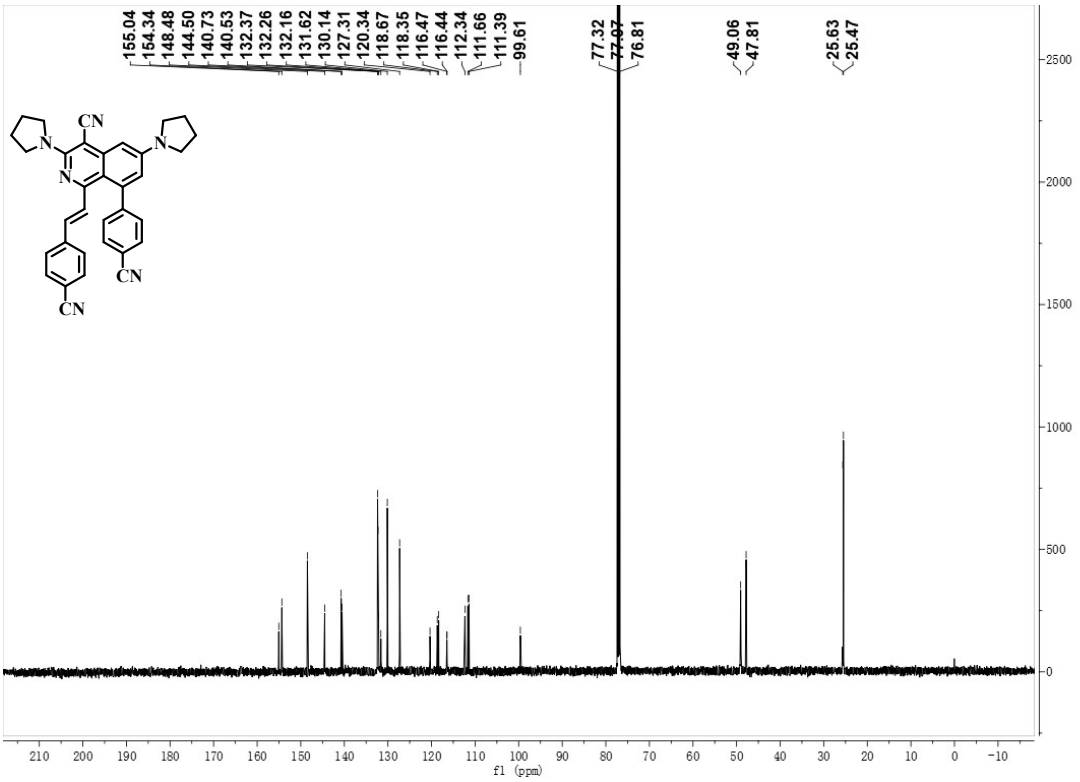

Fig. S25 ^{13}C NMR of **FQ-CN-8** ($CDCl_3$, 125 MHz).

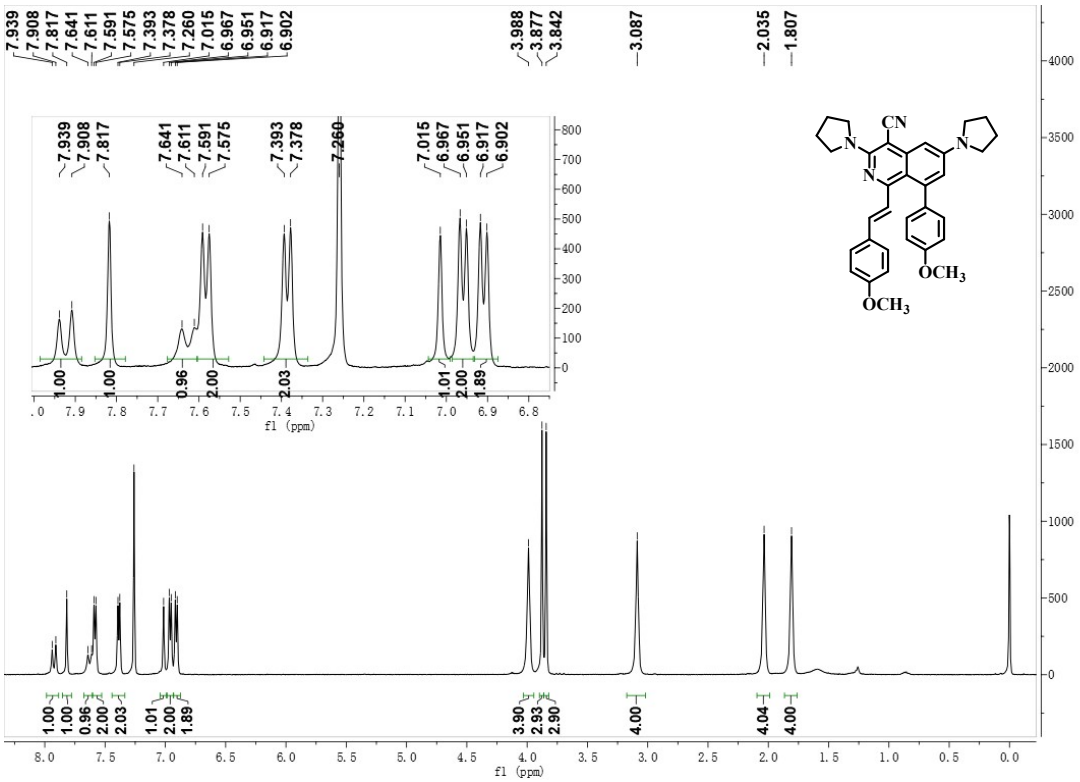

Fig. S26 ^{1}H NMR of **FQ-MO-8** ($CDCl_3$, 500 MHz).

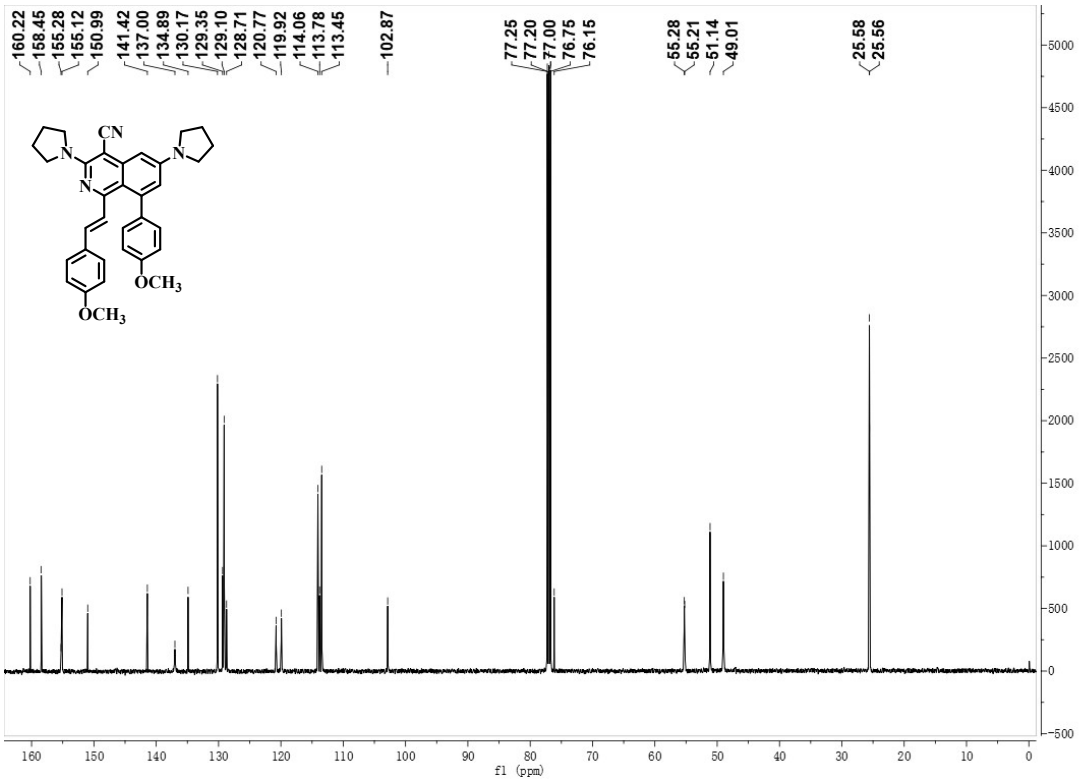

Fig. S27 ^{13}C NMR of **FQ-MO-8** ($CDCl_3$, 125 MHz).

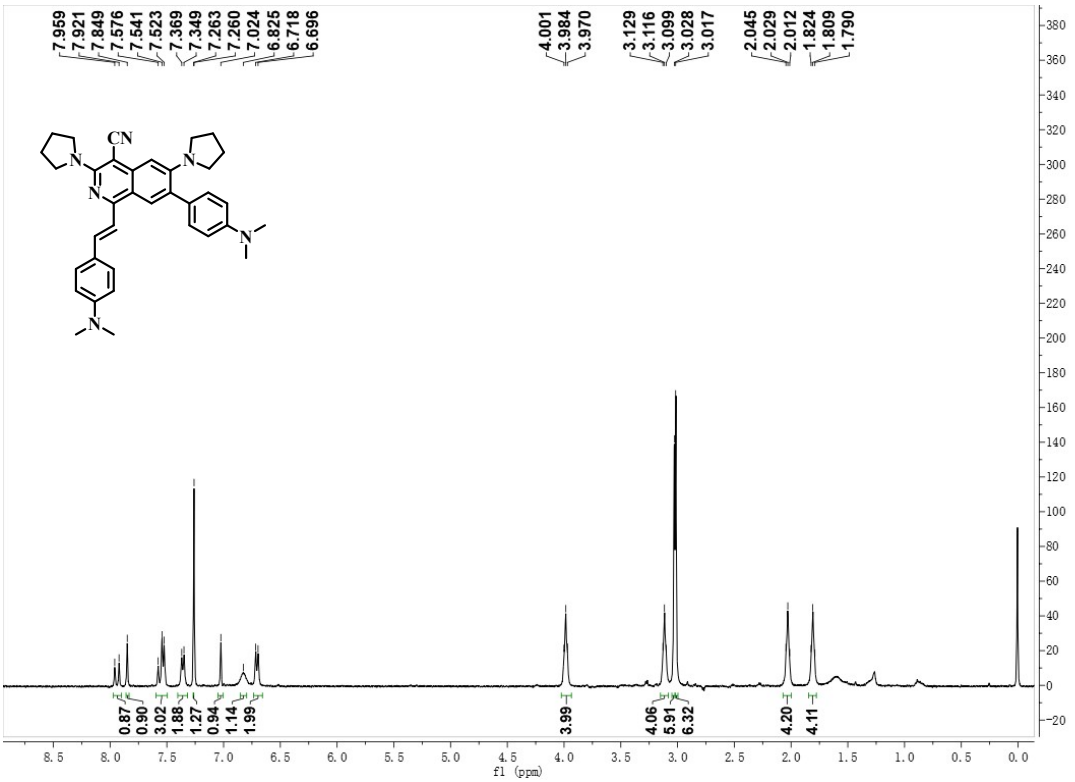

Fig. S28 ^{1}H NMR of **FQ-DMA-7** ($CDCl_3$, 400 MHz).

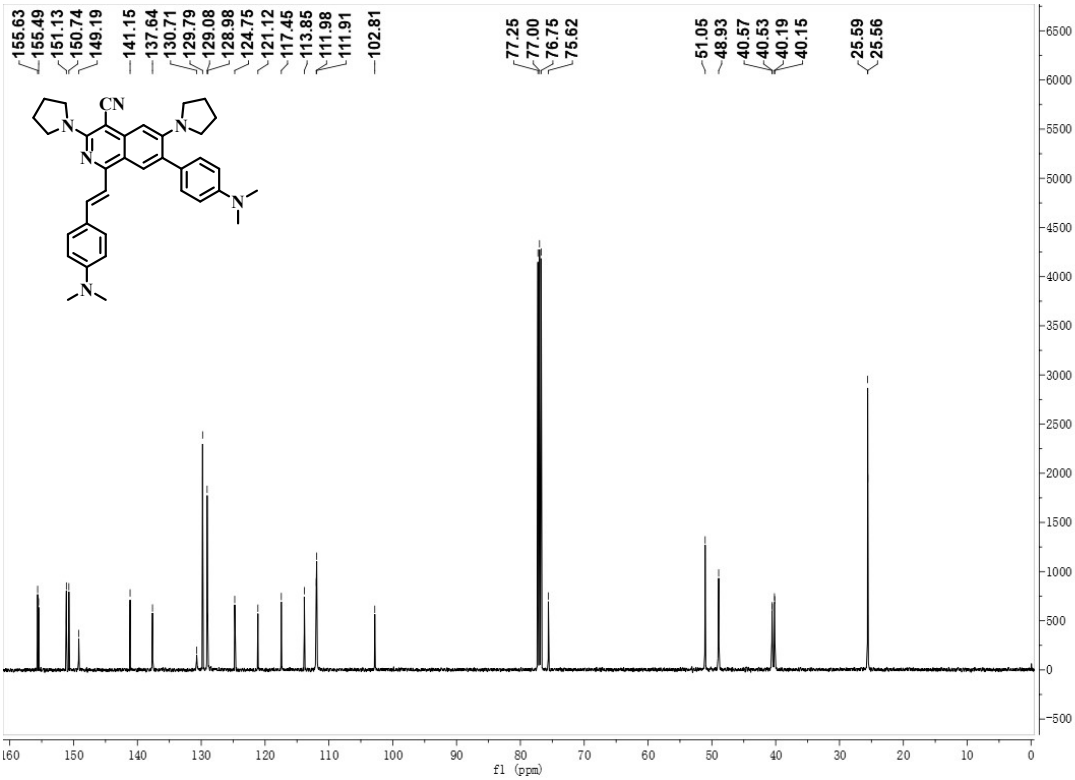

Fig. S29 ^{13}C NMR of **FQ-DMA-7** ($CDCl_3$, 125 MHz).

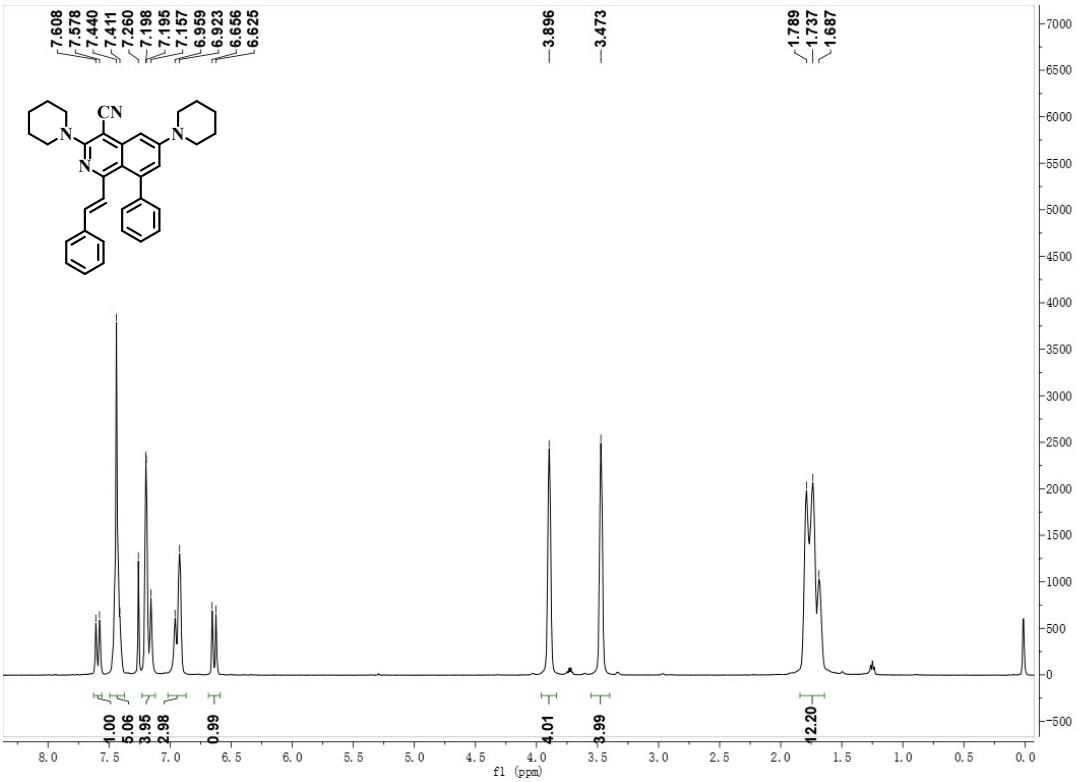

Fig. S30 ^{1}H NMR of **SQ-PH-8** ($CDCl_3$, 500 MHz).

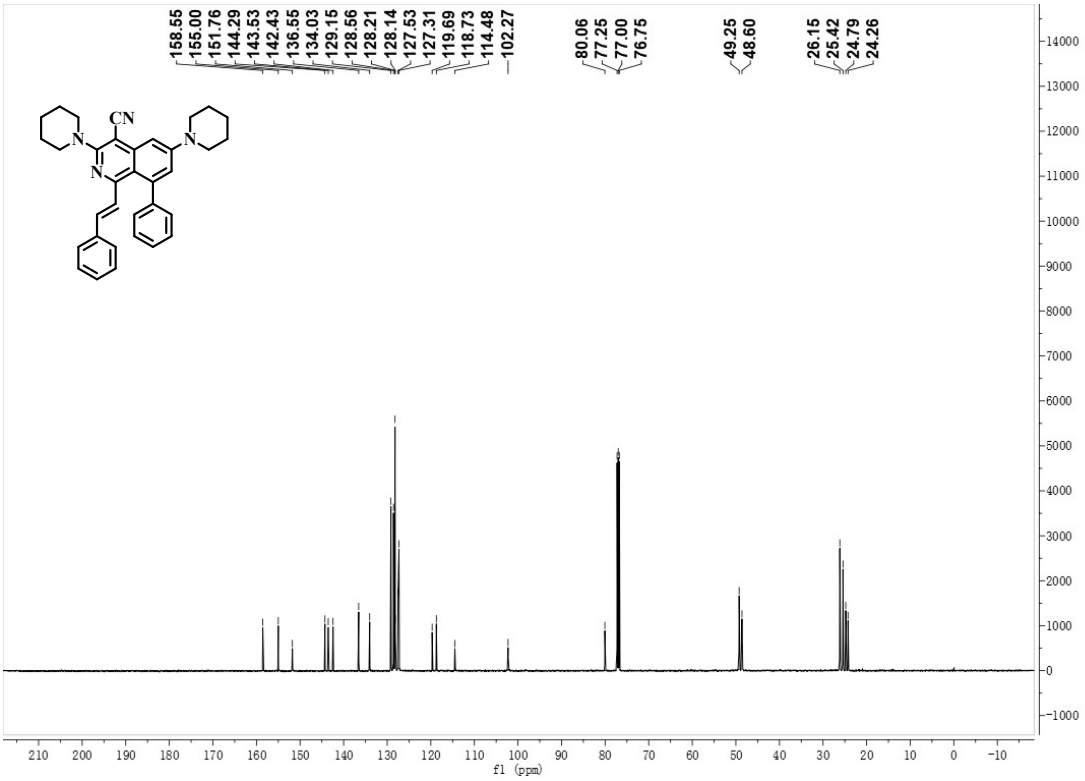

Fig. S31 ^{13}C NMR of **SQ-PH-8** ($CDCl_3$, 125 MHz).

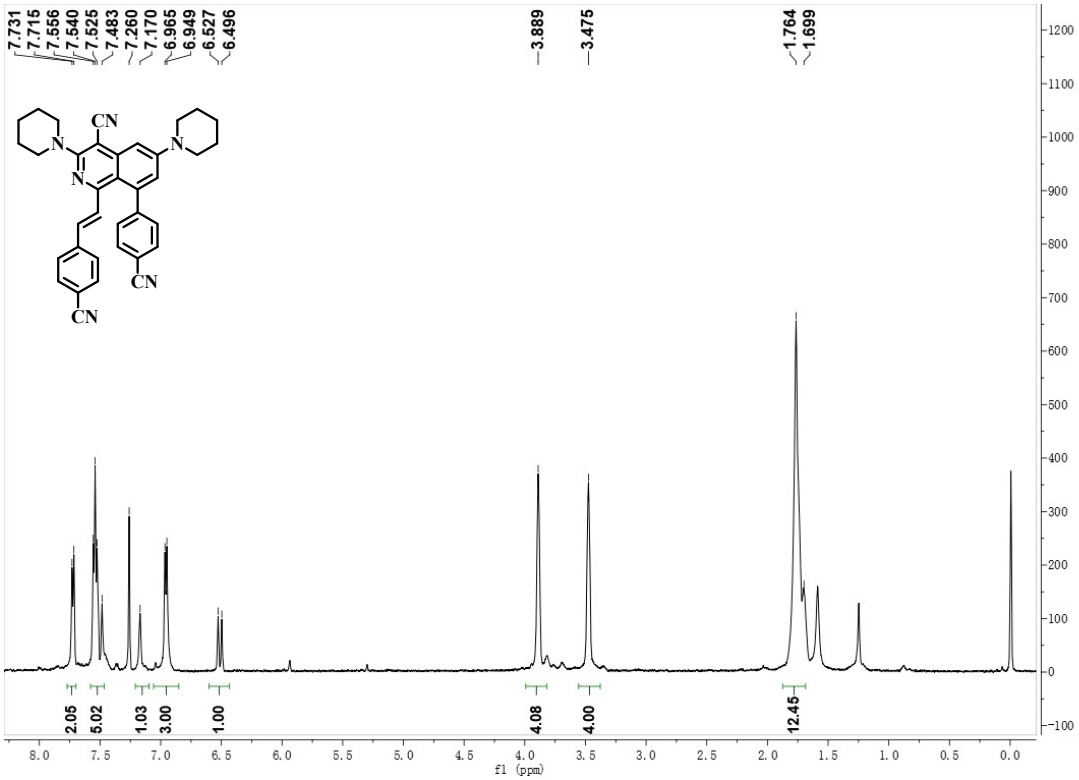

Fig. S32 ^{1}H NMR of **SQ-CN-8** ($CDCl_3$, 500 MHz).

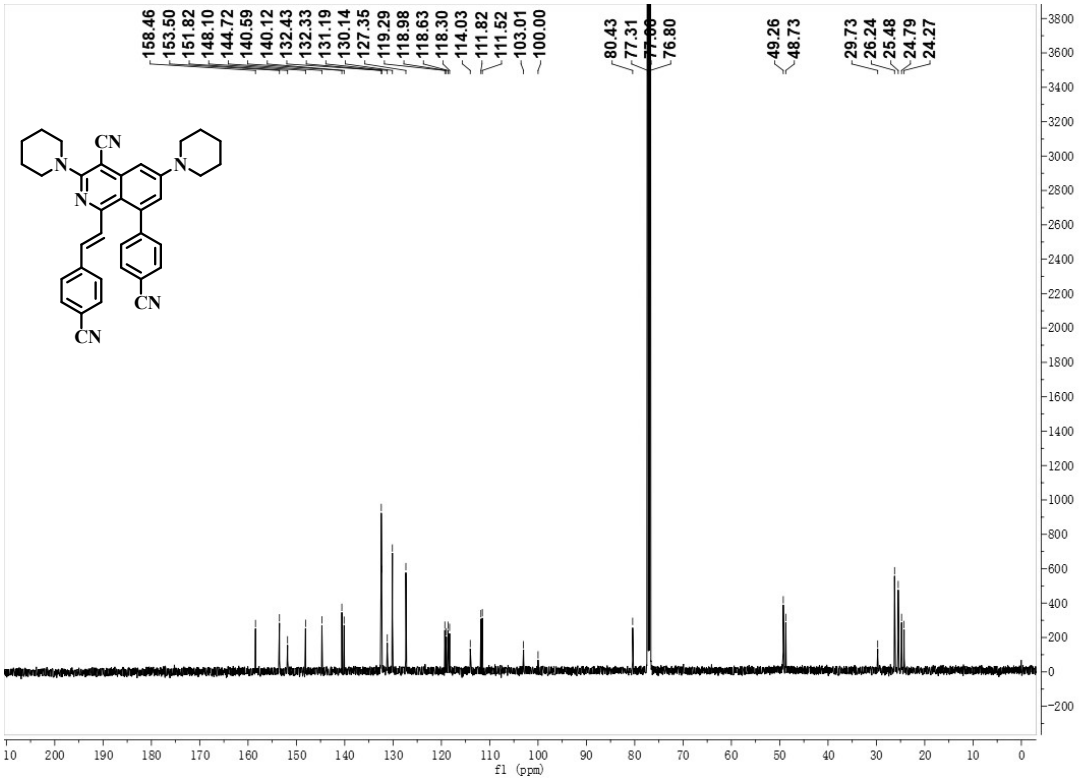

Fig. S33 ^{13}C NMR of **SQ-CN-8** ($CDCl_3$, 125 MHz).

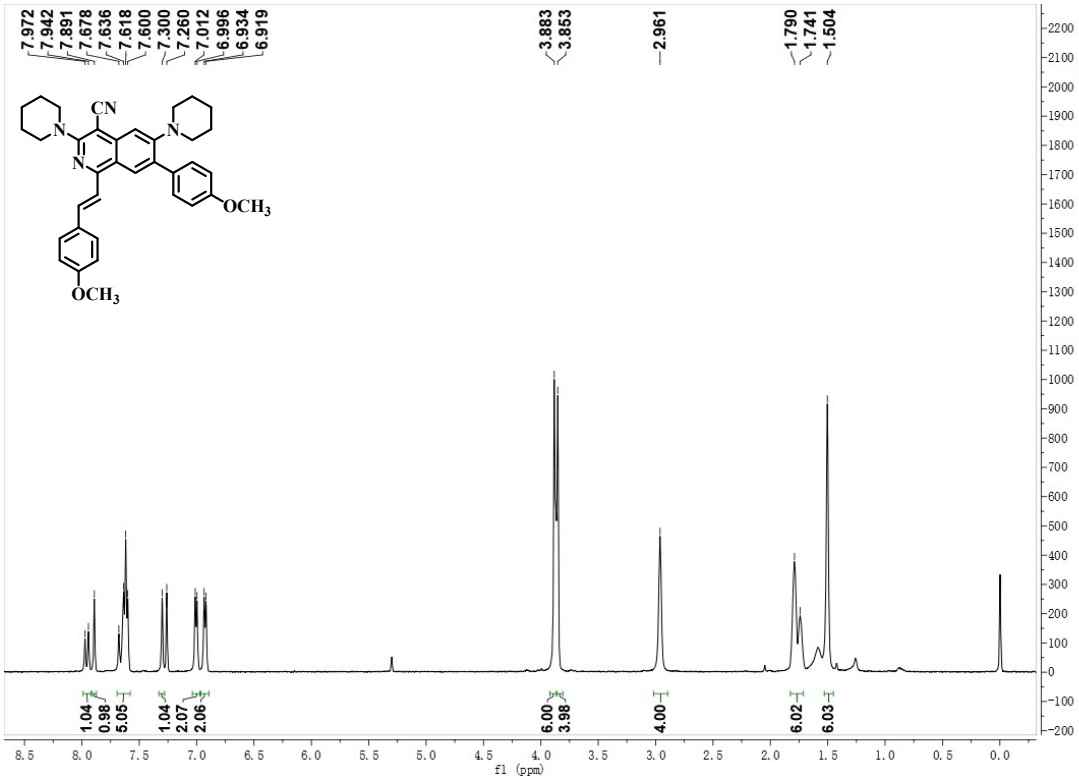

Fig. S34 ^{1}H NMR of **SQ-MO-7** ($CDCl_3$, 500 MHz).

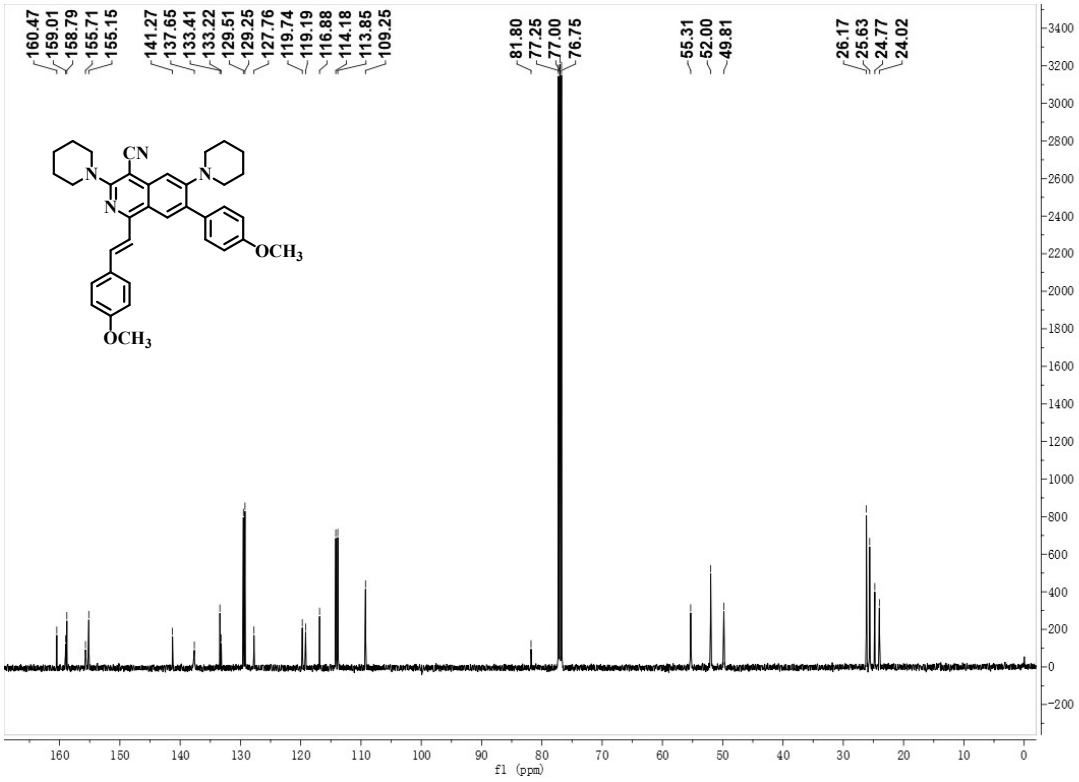

Fig. S35 ^{13}C NMR of **SQ-MO-7** ($CDCl_3$, 125 MHz).

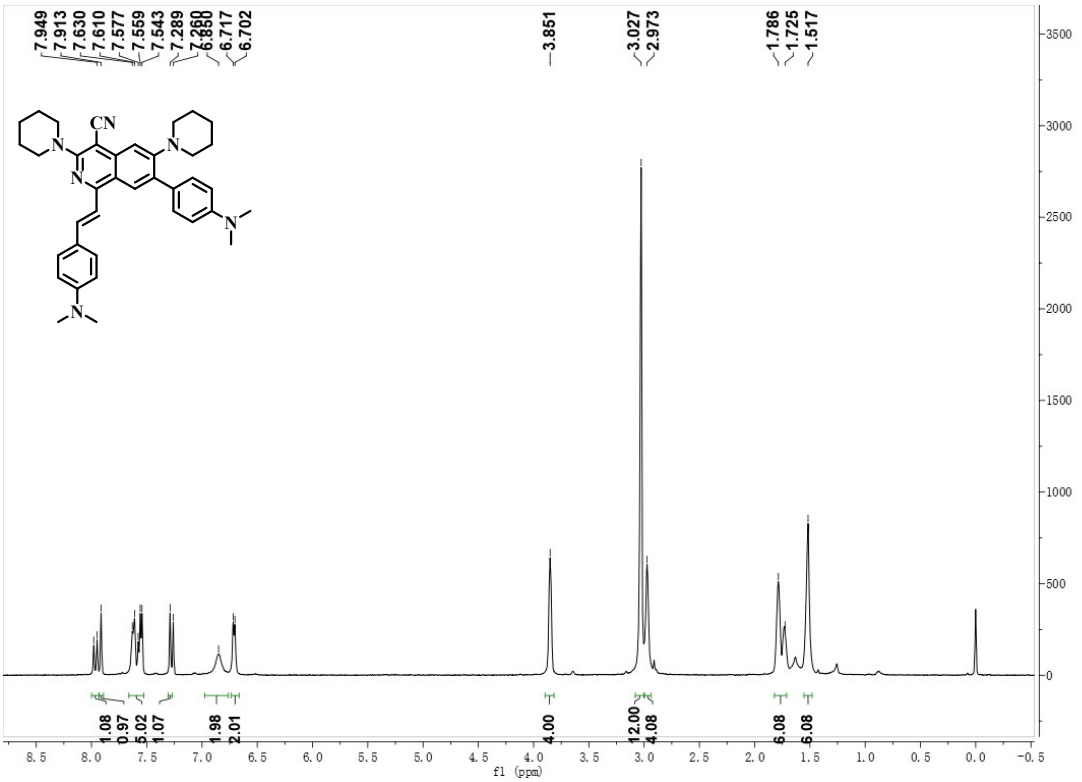

Fig. S36 ^{1}H NMR of **SQ-DMA-7** ($CDCl_3$, 500 MHz).

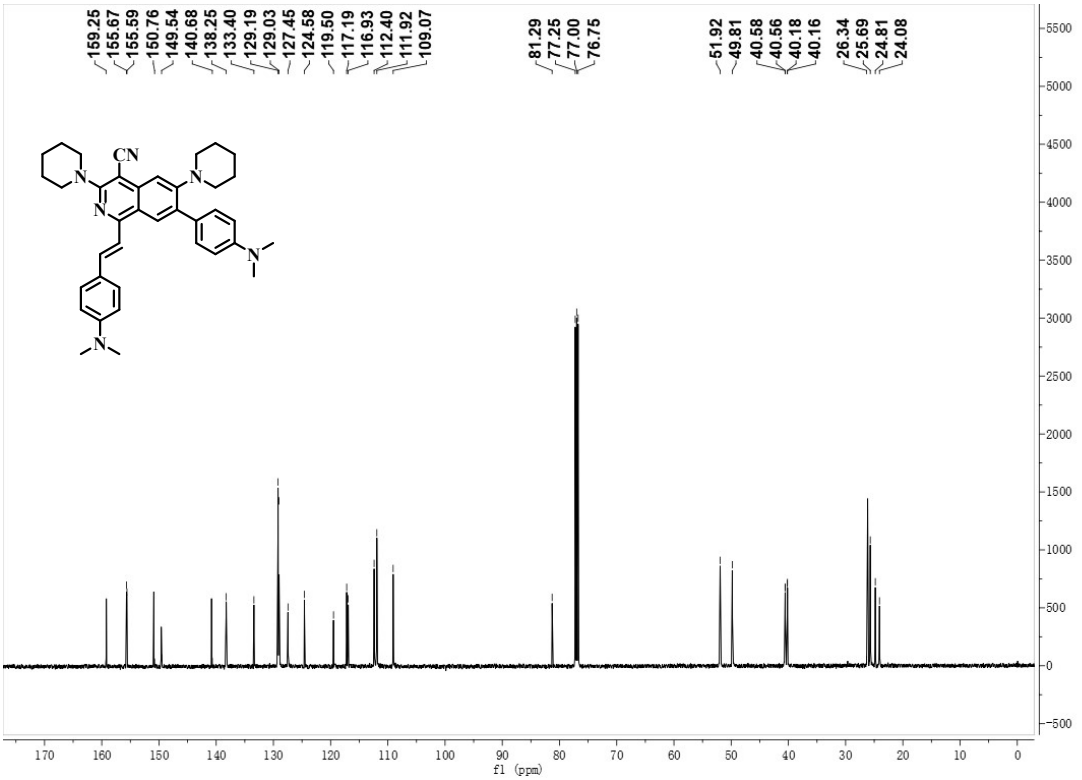

Fig. S37 ^{13}C NMR of **SQ-DMA-7** ($CDCl_3$, 125 MHz).