# Electronic Supplementary Information

## 3,6-Diamino-7,8-dihydroisoquinoline-4-carbonitrile derivatives: unexpectedly facile synthesis, full-color-tunable solid-state emissions and mechanofluorochromic activities

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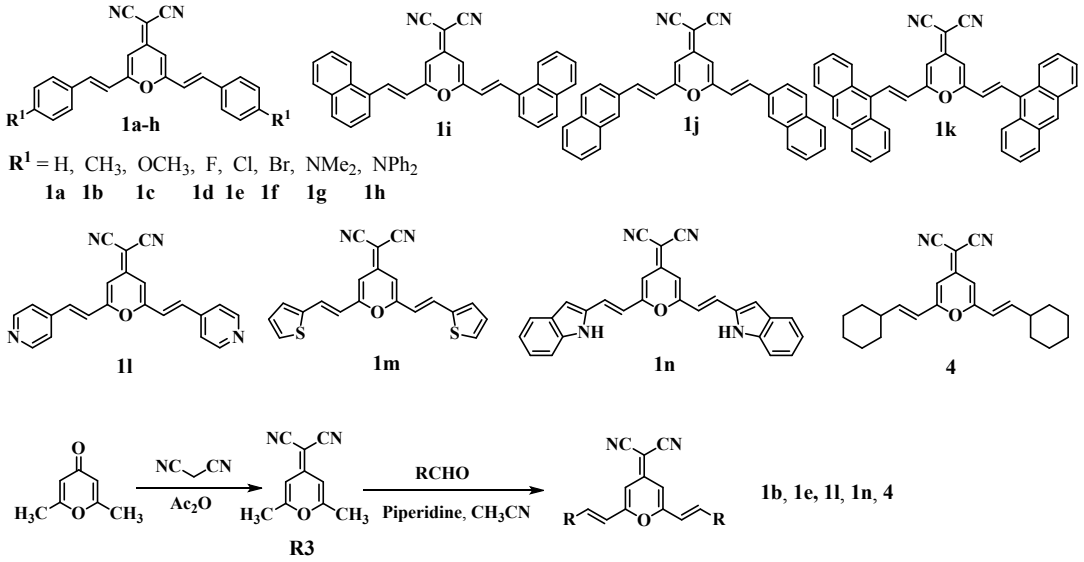
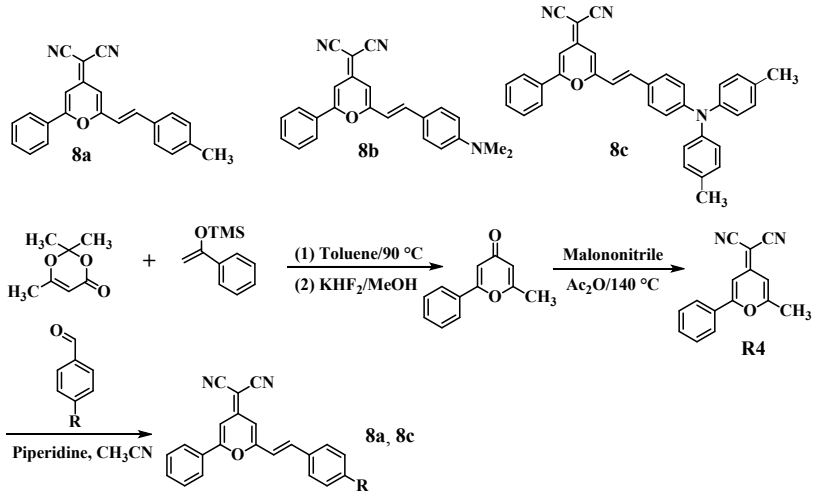
## Contents:




**Scheme S1** Chemical structures of symmetrical DCMP derivatives and synthetic routes of **1b**, **1e**, **1l**, **1n**, and **4**.




**Scheme S2** Chemical structures non-asymmetric DCMP derivatives and synthetic routes of **8a** and **8c**.

## 1. Experimental

### 1.1 Measurements and materials

$^{1}H$ and $^{13}C$ NMR spectra were performed with a Bruker DRX 500 NMR spectrometer or a Bruker DRX 400 NMR spectrometer. High-resolution electrospray ionization (HRMS-ESI) mass spectra were conducted on a Hitachi Nano Frontier LD spectrometer. The mass spectra were conducted on a Finnigan DCMDX-30000 LCQ DCMD mass spectrometer. Melting points were conducted on a WRS-1B digital melting point meter (uncorrected). Absorption spectra were performed with a UV-3600 Shimadzu spectrophotometer. Fluorescence spectra were conducted on a HITACHI F-

7000 fluorometer. Absolute fluorescence quantum yields ($\Phi_F$) in solid state and time-resolved emission decay parameters 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. The symmetrical DCMP derivatives 2-(2,6-di((*E*)-styryl)-4*H*-pyran-4-ylidene)malononitrile (**1a**)[1], 2-(2,6-bis((*E*)-4-methoxystyryl)-4*H*-pyran-4-ylidene)malononitrile (**1c**)[2], 2-(2,6-bis((*E*)-4-fluorostyryl)-4*H*-pyran-4-ylidene) malononitrile (**1d**)[3], 2-(2,6-bis((*E*)-4-bromostyryl)-4*H*-pyran-4-ylidene)malononitrile (**1f**)[4], 2-(2,6-bis((*E*)-4-(dimethylamino)styryl)-4*H*-pyran-4-ylidene)malononitrile (**1g**)[5], 2-(2,6-bis((*E*)-4-(diphenylamino)styryl)-4*H*-pyran-4-ylidene)malononitrile (**1h**) [6], 2-(2,6-bis((*E*)- 2-(naphthalen-1-yl)vinyl)-4*H*-pyran-4-ylidene) malononitrile (**1i**) [7], 2-(2,6-bis((*E*)-2-(naphthalen- 2-yl)vinyl)-4*H*-pyran-4-ylidene)malononitrile (**1j**) [7], 2-(2,6-bis((*E*)-2-(anthracen-9-yl)vinyl)-4*H*-pyran-4-ylidene)malononitrile (**1k**)[2], 2-(2,6-bis((*E*)-2-(thiophen-2-yl)vinyl)-4*H*-pyran-4-ylidene) malononitrile (**1m**)[8] were synthesized according to the previous literatures. 2-(2,6-Bis((*E*)-4-methylstyryl)-4*H*-pyran-4-ylidene)malononitrile (**1b**), 2-(2,6-bis((*E*)-4-chlorostyryl)-4*H*-pyran- 4-ylidene)malononitrile (**1e**), 2-(2,6-bis((*E*)-2-(pyridin-4-yl)vinyl)-4*H*-pyran-4-ylidene)malononitrile (**1l**), 2-(2,6-bis((*E*)-2-(1*H*-indol-2-yl)vinyl)-4*H*-pyran-4-ylidene)malononitrile (**1n**), and 2-(2,6-bis((*E*)-2-cyclohexylvinyl)-4*H*-pyran-4-ylidene)malononitrile (**4**) were synthesized by a method similar to that in the literature, using 2-(2,6-dimethyl-4*H*-pyran-4-ylidene)malononitrile (**R3**) and the corresponding aldehydes as the starting materials (Scheme S1).[7] The non-symmetrical DCMP derivative (*E*)-2-(2-(4-(dimethylamino)styryl)-6-phenyl-4*H*-pyran-4-ylidene)malononitrile (**8b**) was synthesized according to the previous literature.[9] (*E*)-2-(2-(4-Methylstyryl)-6-phenyl-4*H*-pyran-4-ylidene)malononitrile (**8a**) and (*E*)-2-(2-(4-(di-*p*-tolylamino)styryl)-6-phenyl-4*H*-pyran-4-ylidene)malononitrile (**8c**) were synthesized by a method similar to that in the literature, using 2-(2-methyl-6-phenyl-4*H*-pyran-4-ylidene)malononitrile (**R4**) and the corresponding aromatic aldehydes as the starting materials (Scheme S2).[10] Ethyl 2-cyano-2-(2,6-di((*E*)-styryl)-4*H*-pyran-4-ylidene)acetate (**6**) was synthesized using ethyl 2,6-dimethyl-4-pyrone, 2-cyanoacetate, and benzaldehyde as the raw materials according to the previous literature.[11]

**1.2 General procedure for the symmetrical DCMP derivatives 1b, 1e, 1l, 1n, and 4.**

A mixture of compound **R3** (1.0 mmol), various aldehydes (6.0 mmol), piperidine (1.0 mL), and acetonitrile (10 mL) was refluxed under $N_2$ atmosphere for 24 h. The reaction mixture was poured into in methanol (50 mL) to precipitate out the crude product after being cooled to the room temperature. The crude product was washed with acetone and methanol three times, respectively, and then dried to afford the corresponding pure product. Characterization data of the DCMP derivatives are listed as follows.

**2-(2,6-Bis((*E*)-4-methylstyryl)-4*H*-pyran-4-ylidene)malononitrile (1b).** Yellowish-brown solid (252 mg, 67% yield). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.54-7.49 (m, 6H), 7.28-7.26 (m, 4H),

6.73 (d, $J$ = 16.0 Hz, 2H), 6.67 (s, 2H), 2.43 (s, 6H) ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{26}H_{21}N_2O$, 377.1654; found, 377.1652.

**2-(2,6-Bis((*E*)-4-chlorostyryl)-4*H*-pyran-4-ylidene)malononitrile (1e).** Yellow-green solid (312 mg, 75% yield). $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.53 (d, $J$ = 8.5 Hz, 4H), 7.47 (d, $J$ = 16.0 Hz, 4H), 7.43 (d, $J$ = 8.5 Hz, 4H), 6.75 (d, $J$ = 16.0 Hz, 2H), 6.72 (s, 2H) ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{24}H_{15}Cl_2N_2O$, 417.0561; found, 417.0550.

**2-(2,6-Bis((*E*)-2-(pyridin-4-yl)vinyl)-4*H*-pyran-4-ylidene)malononitrile (1l).** Deep yellow solid (196 mg, 56% yield). NMR spectra of compound **1l** cannot be obtained because of very poor solubility in common organic solvents. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{22}H_{15}N_4O$, 351.1246; found, 351.1242.

**2-(2,6-Bis((*E*)-2-(1*H*-indol-2-yl)vinyl)-4*H*-pyran-4-ylidene)malononitrile (1n).** Red solid (349 mg, 82% yield). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 11.87 (s, 2H), 8.25 (d, $J$ = 8.0 Hz, 2H), 8.00 (d, $J$ = 16.0 Hz, 2H), 7.51 (d, $J$ = 8.0 Hz, 2H), 7.28-7.19 (m, 6H), 6.92 (s, 2H) ppm. $^{13}$C NMR (DMSO-$d_6$, 125 MHz): $\delta$ 160.4, 156.3, 137.6, 132.6, 132.5, 124.6, 122.7, 120.9, 120.8, 116.7, 113.3, 112.8, 112.4, 104.4, 52.6 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{28}H_{19}N_4O$, 427.1559; found, 427.1553.

**2-(2,6-Bis((*E*)-2-cyclohexylvinyl)-4*H*-pyran-4-ylidene)malononitrile (4).** Greyish-green solid (202 mg, 56% yield). NMR spectra of compound **4** cannot be obtained because of very poor solubility in common organic solvents. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{24}H_{29}N_2O$, 361.2280; found, 361.2270.

**1.3 General procedure for the non-symmetric DCMP derivatives 8a and 8c.**

A mixture of compound **R4** (1.0 mmol), various aldehydes (1.5 mmol), piperidine (0.4 mL), and acetonitrile (10 mL) was refluxed under $N_2$ atmosphere for 10 h. The reaction mixture was poured into in methanol (50 mL) to precipitate out the crude product after being cooled to the room temperature. The crude product was washed with methanol three times and then dried to afford the corresponding pure product. Characterization data of the DCMP derivatives are listed as follows.

**(*E*)-2-(2-(4-Methylstyryl)-6-phenyl-4*H*-pyran-4-ylidene)malononitrile (8a).** Yellow solid (248 mg, 74% yield). $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 8.13-8.12 (m, 1H), 7.70-7.59 (m, 6H), 7.39 (d, $J$ = 16.0 Hz, 1H), 7.28 (d, $J$ = 8.0 Hz, 2H), 7.15 (d, $J$ = 2.0 Hz, 1H), 6.98 (d, $J$ = 1.6 Hz, 1H), 2.35 (s, 3H) ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{23}H_{17}N_2O$, 337.1341; found, 337.1344.

**(*E*)-2-(2-(4-(Di-*p*-tolylamino)styryl)-6-phenyl-4*H*-pyran-4-ylidene)malononitrile (8c).** Dark red solid (357 mg, 69% yield). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.88-7.86 (m, 2H), 7.61-7.53 (m, 3H), 7.47 (d, $J$ = 15.6 Hz, 1H), 7.38 (d, $J$ = 8.4 Hz, 1H), 7.13 (d, $J$ = 8.0 Hz, 1H), 7.09-7.05 (m, 5H), 6.97 (d, $J$ = 8.4 Hz, 1H), 6.71 (d, $J$ = 2.0 Hz, 1H), 6.60 (d, $J$ = 16.0 Hz, 1H), 2.35 (s, 6H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 159.6, 159.5, 156.1, 150.6, 144.1, 138.2, 134.3, 132.2, 130.6,

130.2, 129.4, 129.1, 126.4, 126.2, 125.8, 120.2, 115.48, 115.45, 114.7, 106.5, 104.2, 59.1, 20.9 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{36}H_{28}N_3O$, 518.2232; found, 518.2219.

**1.4 General procedure for the DDIC derivatives**

A mixture of compound **1a-n/8a-c** (0.3 mmol), various secondary amines (1.2 mmol), $KH_2PO_4$ (0.9 mmol), and DMSO (2.5 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 $CH_2Cl_2$ (20 mL), and the organic layer was washed with water (10 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. Characterization data of the DDIC derivatives are listed as follows.

**(*E*)-8-Phenyl-3,6-di(piperidin-1-yl)-1-styryl-7,8-dihydroisoquinoline-4-carbonitrile (3aa).** Following the general procedure, using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford a yellow-green solid (135.1 mg, 90% yield). M. p. 171.8-172.3°C. $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 7.65 (d, $J$ = 15.0 Hz, 1H), 7.54 (d, $J$ = 7.5 Hz, 2H), 7.35 (t, $J$ = 7.5 Hz, 2H), 7.30-7.21 (m, 4H), 7.16-7.11 (m, 3H), 5.61 (s, 1H), 4.77-4.75 (m, 1H), 3.47-3.46 (m, 4H), 3.32-3.27 (m, 2H), 3.26-3.21 (m, 2H), 2.88-2.87 (m, 2H), 1.66-1.65 (m, 4H), 1.63-1.61(m, 2H), 1.56-1.51 (m, 2H), 1.45-1.39 (m, 4H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 161.6, 153.1, 151.8, 150.5, 143.2, 137.0, 135.2, 128.53, 128.50, 128.2, 127.3, 127.2, 126.6, 123.8, 119.0, 116.3, 93.8, 87.5, 50.2, 47.7, 37.8, 33.4, 26.0, 25.2, 24.8, 24.4 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{34}H_{37}N_4$, 501.3013; found, 501.2997.

**(*E*)-3,6-Bis(4-methylpiperidin-1-yl)-8-phenyl-1-styryl-7,8-dihydroisoquinoline-4-carbonitrile (3ab).** Following the general procedure, using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford a yellow-green solid (130.0 mg, 82% yield). M. p. 193.0-193.4°C. $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 7.65 (d, $J$ = 15.2 Hz, 1H), 7.53 (d, $J$ = 7.6 Hz, 2H), 7.35 (t, $J$ = 7.6 Hz, 2H), 7.30-7.20 (m, 4H), 7.17-7.11 (m, 3H) , 5.63 (s, 1H) , 4.77-4.74 (m, 1H), 4.08 (d, $J$ = 12.0 Hz, 2H), 3.79-3.70 (m, 2H), 2.95-2.85 (m, 4H) , 2.82-2.74 (m, 2H), 1.73 (d, $J$ = 12.8 Hz, 2H), 1.62-1.53 (m, 4H), 1.35-1.23 (m, 3H), 0.96 (d, $J$ = 6.4 Hz, 3H), 0.90 (d, $J$ = 11.2 Hz, 1H), 0.82 (d, $J$ = 5.6 Hz, 3H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 161.5, 153.1, 151.8, 150.5, 143.2, 137.0, 135.2, 128.54, 128.52, 128.2, 127.30, 127.25, 126.6, 123.8, 119.0, 116.3, 93.9, 87.5, 49.6, 49.4, 47.2, 47.0, 37.9, 34.31, 34.29, 33.7, 33.4, 33.2, 31.2, 30.9, 22.0, 21.6 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{36}H_{41}N_4$, 529.3326; found, 529.3330.

**(*E*)-3,6-Bis(3-methylpiperidin-1-yl)-8-phenyl-1-styryl-7,8-dihydroisoquinoline-4-carbonitrile (3ac).** Following the general procedure, using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford a yellow-green solid (107.8 mg, 68% yield). M. p. 181.2-183.6 °C. $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 7.64 (d, $J$ = 15.2 Hz, 1H), 7.52 (d, $J$ = 7.2 Hz, 2H), 7.35 (t, $J$ = 7.2 Hz, 2H), 7.30-7.20 (m, 4H), 7.16-7.10 (m, 3H) , 5.61 (s, 1H) , 4.75-4.74 (m, 1H), 4.05-3.97 (m, 2H), 3.71-3.59 (m, 2H), 2.94-2.73 (m, 4H), 2.67-2.53 (m, 2H), 1.82-1.53 (m, 6H), 1.47-1.39 (m, 1H),

1.34-1.28 (m, 1H), 1.17-1.04 (m, 2H), 0.93 (d, $J$ = 6.4 Hz, 3H), 0.81 (t, $J$ = 5.6 Hz, 3H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 161.3, 153.0, 151.9, 150.5, 143.2, 137.0, 135.2, 128.54, 128.50, 128.2, 127.27, 127.25, 126.6, 123.8, 119.1, 116.1, 93.7, 87.3, 56.9, 54.2, 49.7, 47.3, 33.4, 32.9, 31.1, 30.2, 25.5, 24.8, 24.4, 19.3, 19.1, 19.0 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{36}H_{41}N_4$, 529.3326; found, 529.3328.

**(*E*)-3,6-Bis(3,5-dimethylpiperidin-1-yl)-8-phenyl-1-styryl-7,8-dihydroisoquinoline-4-carbonitrile (3ae).** Following the general procedure, using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford a yellow-green solid (83.5 mg, 50% yield). M. p. 213.2-215.0°C. $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 7.63 (d, $J$ = 15.2 Hz, 1H), 7.50 (d, $J$ = 7.6 Hz, 2H), 7.35 (t, $J$ = 7.6 Hz, 2H), 7.29-7.20 (m, 4H), 7.16-7.10 (m, 3H) , 5.61 (s, 1H) , 4.73-4.72 (m, 1H), 4.13 (d, $J$ = 13.2 Hz, 2H), 3.68 (t, $J$ = 13.2 Hz, 2H), 2.92-2.83 (m, 2H) , 2.47-2.40 (m, 2H), 2.37-2.25 (m, 2H), 1.82-1.66 (m, 4H), 1.45-1.38 (m, 2H), 0.90 (d, $J$ = 6.4 Hz, 6H), 0.82 (t, $J$ = 6.8 Hz, 6H), 0.76-0.68 (m, 2H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 160.9, 152.8, 151.9, 150.5, 143.2, 137.0, 135.2, 128.6, 128.5, 128.2, 127.27, 127.26, 126.6, 123.8, 119.1, 116.0, 93.8, 87.1, 56.4, 56.3, 54.00, 53.95, 42.7, 42.2, 37.8, 33.5, 31.20, 31.15, 31.1, 30.2, 19.3, 19.2, 19.0 ppm. HRMS (ESI) m/z: $[M+H]^+$calculated for $C_{38}H_{45}N_4$, 557.3639; found, 557.3653.

**(*E*)-3,6-Bis(4-hydroxypiperidin-1-yl)-8-phenyl-1-styryl-7,8-dihydroisoquinoline-4-carbonitrile (3af).** Following the general procedure, using petroleum ether/ethyl acetate (1:10, v/v) as the eluent to afford a yellow-green solid (146.9 mg, 92% yield). M. p. 172.7-173.6°C. $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 7.65 (d, $J$ = 15.5 Hz, 1H), 7.54 (d, $J$ = 7.5 Hz, 2H), 7.35 (t, $J$ = 7.5 Hz, 2H), 7.30-7.21 (m, 4H) , 7.16-7.11 (m, 3H) , 5.64 (s, 1H) , 4.78-4.72 (m, 3H), 3.90-3.88 (m, 2H), 3.70-3.64 (m, 2H) , 3.61-3.53 (m, 2H), 3.17-3.11 (m, 2H), 3.06-2.96 (m, 2H), 2.89-2.88 (m, 2H), 1.89-1.87 (m, 2H),1.72-1.66 (m, 2H), 1.57-1.50 (m, 2H), 1.32-1.25 (m, 2H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 161.1, 152.9, 151.7, 150.7, 142.9, 136.8, 135.6, 128.60, 128.58, 128.4, 127.3, 127.2, 126.8, 123.5, 118.8, 116.7, 94.3, 87.7, 68.3, 67.0, 46.7, 44.1, 44.0, 37.8, 34.47, 34.45, 33.5, 33.4, 33.3 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{34}H_{37}N_4O_2$, 533.2911; found, 533.2923.

**(*E*)-1,1'-(4-Cyano-8-phenyl-1-styryl-7,8-dihydroisoquinoline-3,6-diyl)bis(piperidine-4-carboxamide) (3ah).** Following the general procedure, using ethyl acetate/methyl alcohol (10:1, v/v) as the eluent to afford a yellow-green solid (140.7 mg, 80% yield). M. p. 156.7-157.3 °C. $^1$H NMR (DMSO-$d_6$, 400 MHz):$\delta$ 7.66 (d, $J$ = 14.8 Hz, 1H), 7.54 (d, $J$ = 7.2 Hz, 2H), 7.37-7.28 (m, 6H), 7.22 (t, $J$ = 7.6 Hz, 3H), 7.17-7.13 (m, 2H) , 6.79 (s, 2H) , 5.64 (s, 1H), 4.78-4.76 (m, 1H), 4.11 (d, $J$ = 14.0 Hz, 2H), 3.78 (t, $J$ = 15.2 Hz, 2H) , 2.99-2.80 (m, 6H), 2.37-2.30 (m, 2H), 1.84-1.67 (m, 6H), 1.53-1.36 (m, 2H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 177.4, 176.5, 161.2, 153.0, 151.5, 150.9, 142.8, 136.8, 135.7, 128.7, 128.6, 128.4, 127.3, 127.2, 126.8, 123.4, 118.7, 116.9, 94.6, 88.1, 48.9, 48.8, 46.3, 46.0, 43.7, 42.2, 37.8, 33.4, 28.9, 28.8, 28.1, 27.7 ppm. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{36}H_{38}N_6NaO_2$, 609.2954; found, 609.2945.

**(*E*)-Dimethyl 1,1'-(4-cyano-8-phenyl-1-styryl-7,8-dihydroisoquinoline-3,6-diyl)bis(piperi-**

**dine-4-carboxylate) (3ai).** Following the general procedure, using petroleum ether/ethyl acetate (4:1, v/v) as the eluent to afford a yellow-green solid (147.9 mg, 80% yield). M. p. 189.0-189.6°C. $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 7.66 (d, $J$ = 15.5 Hz, 1H), 7.55 (d, $J$ = 7.5 Hz, 2H), 7.35 (t, $J$ = 7.5 Hz, 2H), 7.30-7.20 (m, 4H), 7.16-7.11 (m, 3H) , 5.63 (s, 1H) , 4.79-4.77 (m, 1H), 4.02 (d, $J$ = 13.0 Hz, 2H), 3.76-3.68 (m, 2H), 3.63 (s, 3H) , 3.59 (s, 3H), 3.09-3.01 (m, 2H), 2.98-2.87 (m, 4H), 2.66-2.58 (m, 2H), 1.98-1.95 (m, 2H), 1.85-1.68 (m, 4H), 1.47-1.38 (m, 2H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 175.3, 174.5, 161.2, 152.9, 151.5, 150.8, 142.8, 136.9, 135.6, 128.61, 128.57, 128.4, 127.3, 127.2, 126.8, 123.5, 118.6, 116.9, 94.6, 88.2, 51.8, 51.7, 48.7, 48.6, 46.1, 45.9, 41.3, 40.6, 37.8, 33.4, 28.2, 28.1, 27.4, 27.2 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{38}H_{41}N_4O_4$, 617.3123; found, 617.3119.

**(*E*)-8-Phenyl-3,6-bis(4-phenylpiperidin-1-yl)-1-styryl-7,8-dihydroisoquinoline-4-carbonitrile (3aj).** Following the general procedure, using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford an orange-yellow solid (184.0 mg, 94% yield). M. p. 202.4-202.9 °C. $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 7.70 (d, $J$ = 15.2 Hz, 1H), 7.55 (d, $J$ = 7.6 Hz, 2H), 7.37-7.24 (m, 13H), 7.21-7.17 (m, 4H), 7.12 (d, $J$ = 7.6 Hz, 2H) , 5.72 (s, 1H) , 4.83-4.81 (m, 1H), 4.26 (d, $J$ = 10.4 Hz, 2H), 3.97-3.85 (m, 2H), 3.07-2.92 (m, 2H), 2.96-2.88 (m, 4H) , 2.81-2.72 (m, 2H), 1.94-1.91 (m, 2H), 1.86-1.70 (m, 4H), 1.48-1.32 (m, 2H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 161.4, 153.0, 151.8, 150.7, 146.2, 145.1, 143.0, 136.9, 135.4, 128.62, 128.57, 128.5, 128.4, 128.3, 127.4, 127.3, 126.9, 126.74, 126.71, 126.4, 126.2, 123.6, 118.9, 116.6, 94.3, 87.9, 50.1, 49.9, 47.6, 47.4, 43.1, 42.6, 37.9, 33.48, 33.47, 33.43, 32.9, 32.3 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{46}H_{45}N_4$, 653.3639; found, 653.3645.

**(*E*)-8-Phenyl-3,6-di(pyrrolidin-1-yl)-1-styryl-7,8-dihydroisoquinoline-4-carbonitrile (3ak).** Following the general procedure, using petroleum ether/ethyl acetate (2:1, v/v) as the eluent to afford a yellow-green solid (137.4 mg, 97% yield). M. p. 186.1-187.5 °C. $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 7.62 (d, $J$ = 15.2 Hz, 1H), 7.52 (d, $J$ = 7.6 Hz, 2H), 7.34 (t, $J$ = 7.6 Hz, 2H), 7.28-7.19 (m, 4H), 7.17-7.09 (m, 3H) , 5.32 (s, 1H) , 4.73 (d, $J$ = 7.2 Hz, 1H) , 3.72 (d, $J$ = 5.6 Hz, 4H), 3.24 (br, 4H), 3.07-2.89 (m, 2H), 1.92-1.79 (m, 8H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz):$\delta$156.8, 152.6, 151.1, 150.7, 143.8, 137.2, 134.7, 128.50, 128.46, 128.0, 127.4, 127.2, 126.4, 124.1, 120.6, 113.3, 90.8, 81.7, 48.9, 47.7, 37.4, 34.6, 25.7, 25.0 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{32}H_{33}N_4$, 473.2700; found, 473.2707.

**(*E*)-3,6-Di(azepan-1-yl)-8-phenyl-1-styryl-7,8-dihydroisoquinoline-4-carbonitrile (3al).** Following the general procedure, using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford a yellow-green solid (112.5 mg, 71% yield). M. p. 170.7-171.2 °C. $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 7.60 (d, $J$ = 15.5 Hz, 1H), 7.50 (d, $J$ = 7.5 Hz, 2H), 7.35 (t, $J$ = 7.5 Hz, 2H), 7.27 (t, $J$ = 7.5 Hz, 1H), 7.23-7.16 (m, 5H) , 7.12 (t, $J$ = 7.0 Hz, 1H) , 5.53 (s,1H) , 4.71 (t, $J$ = 4.0 Hz, 1H), 3.85-3.77 (m, 4H), 3.47-3.37 (m, 4H), 2.92 (d, $J$ = 4.0 Hz, 2H) , 1.84 (br, 4H), 1.60-1.54 (m, 6H), 1.37-1.32 (m, 3H) 1.23-1.19 (m, 3H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 158.4, 153.1, 152.0, 150.2, 143.2, 137.2, 134.7, 128.5, 128.4, 128.0, 127.4, 127.2, 126.5, 124.1, 120.4, 113.6, 90.9,

81.7, 50.11, 50.06, 37.8, 33.2, 29.0, 27.4, 26.2 ppm. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{36}H_{40}N_4Na$, 551.3145; found, 551.3135.

**(*E*)-3,6-Dimorpholino-8-phenyl-1-styryl-7,8-dihydroisoquinoline-4-carbonitrile (3am).** Following the general procedure, using petroleum ether/ethyl acetate (2:1, v/v) as the eluent to afford a yellow-green solid (93.8 mg, 62% yield). M. p. 213.2-213.5°C. $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 7.69 (d, $J$ = 15.0 Hz, 1H), 7.56 (d, $J$ = 7.0 Hz, 2H), 7.35 (t, $J$ = 7.0 Hz, 2H), 7.31-7.22 (m, 4H), 7.17-7.12 (m, 3H) , 5.65 (s,1H) , 4.83-4.82 (m, 1H), 3.76 (t, $J$ = 4.0 Hz, 4H), 3.61-3.54 (m, 4H), 3.50 (t, $J$ = 5.0 Hz, 4H) , 3.32-3.27 (m, 2H), 3.17-3.13 (m, 2H), 2.97-2.87 (m, 2H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 160.8, 153.4, 151.2, 151.1, 142.8, 136.7, 136.0, 128.7, 128.6, 128.5, 127.3, 127.2, 126.9, 123.2, 118.4, 117.4, 95.0, 88.5, 66.9, 66.1, 49.3, 46.6, 37.7, 33.1 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{32}H_{33}N_4O_2$, 505.2598; found, 505.2602.

**(*E*)-3,6-Bis(benzyl(methyl)amino)-8-phenyl-1-styryl-7,8-dihydroisoquinoline-4-carbonitrile (3an).** Following the general procedure, using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford a yellow-green solid (103.0 mg, 60% yield). M. p. 159.6-160.3 °C. $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$7 .55 (d, $J$ = 15.5 Hz, 1H), 7.48 (d, $J$ = 7.5 Hz, 2H), 7.36-7.31 (m, 6H), 7.28-7.20 (m, 5H), 7.19-7.15 (m, 6H) , 6.83 (d, $J$ = 7.0 Hz, 2H), 5.54 (s, 1H), 4.92 (d, $J$ = 15.5 Hz, 1H), 4.81-4.76 (m, 2H), 4.63 (d, $J$ = 16.5 Hz, 1H), 4.44 (d, $J$ = 16.5 Hz, 1H), 3.16 (s, 3H), 3.00 (d, $J$ = 4.5 Hz, 2H), 2.89 (s, 3H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 159.7, 152.8, 152.7, 150.6, 142.7, 139.0, 137.0, 136.9, 135.4, 128.7, 128.6, 128.5, 128.4, 128.2, 127.8, 127.5, 127.22, 127.19, 126.9, 126.7, 126.2, 123.6, 119.6, 115.0, 92.0, 84.2, 55.5, 54.5, 38.8, 38.2, 37.9, 33.5 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{40}H_{37}N_4$, 573.3013; found, 573.3002.

**(*E*)-1-(4-Methylstyryl)-3,6-di(piperidin-1-yl)-8-(*p*-tolyl)-7,8-dihydroisoquinoline-4-carbonitrile (3ba).** Following the general procedure, using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford a yellow-green solid (118.9 mg, 75% yield). M. p. 156.8-157.8°C. $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 7.61 (d, $J$ = 15.5 Hz, 1H), 7.43 (d, $J$ = 8.0 Hz, 2H), 7.18-7.15 (m, 3H), 7.04-7.00 (m, 4H), 5.60 (s, 1H), 4.70-4.68 (m, 1H) , 3.46 (br, 4H), 3.31-3.27 (m, 2H), 3.25-3.20 (m, 2H), 2.84 (d, $J$ = 4.0 Hz, 2H), 2.29 (s, 3H) , 2.18 (s, 3H), 1.66-1.61 (m, 6H), 1.56-1.52 (m, 2H), 1.45-1.41 (m, 4H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 161.6, 153.3, 151.7, 150.7, 140.3, 138.2, 136.0, 135.1, 134.3, 129.3, 129.2, 127.3, 127.1, 122.9, 119.1, 116.4, 93.8, 87.5, 50.3, 47.7, 37.4, 33.3, 26.0, 25.2, 24.8, 24.4, 21.3, 21.0 ppm. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{36}H_{40}N_4$, 551.3145; found, 551.3163.

**(*E*)-8-(4-Methoxyphenyl)-1-(4-methoxystyryl)-3,6-di(piperidin-1-yl)-7,8-dihydroisoquinoline-4-carbonitrile (3ca).** Following the general procedure, using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford a yellow-green solid (110.9 mg, 66% yield). M. p. 174.9-176.2 °C. $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 7.61 (d, $J$ = 15.0 Hz, 1H), 7.49 (d, $J$ = 8.5 Hz, 2H), 7.10-7.05 (m, 3H), 6.92 (d, $J$ = 8.5 Hz, 2H), 6.77 (d, $J$ = 8.5 Hz, 2H) , 5.60 (s, 1H) , 4.67 (br,1H) , 3.76 (s, 3H), 3.65 (s, 3H), 3.45 (br, 4H), 3.29-3.27 (m, 2H) , 3.24-3.22 (m, 2H), 2.83-2.82 (m, 2H), 1.66-1.61 (m, 6H), 1.56-1.54 (m, 2H), 1.45-1.43 (m, 4H) ppm. $^{13}$C NMR ($CDCl_3$,

125 MHz): $\delta$ 161.7, 160.0, 158.2, 153.2, 151.6, 150.9, 135.4, 134.8, 129.9, 128.7, 128.4, 121.7, 119.2, 116.3, 114.1, 113.9, 93.8, 87.4, 55.3, 55.2, 50.3, 47.7, 37.1, 33.6, 26.1, 25.3, 24.9, 24.4 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{36}H_{41}N_4O_2$, 561.3224; found, 561.3205.

**(*E*)-8-(4-Fluorophenyl)-1-(4-fluorostyryl)-3,6-di(piperidin-1-yl)-7,8-dihydroisoquinoline-4-carbonitrile (3da).** Following the general procedure, using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford a yellow-green solid (57.9 mg, 36% yield). M. p. 134.8-135.6 °C. $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 7.66-7.61 (m, 3H), 7.22-7.16 (m, 4H), 7.04 (t, $J$ = 8.5 Hz, 2H), 5.61 (s, 1H), 4.81-4.80 (m, 1H), 3.47-3.46 (m, 4H), 3.30-3.19 (m, 4H), 2.90-2.82 (m, 2H), 1.66-1.61 (m, 6H), 1.56-1.53 (m, 2H), 1.48-1.39 (m, 4H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 162.7 (d, $J$ = 246.3 Hz), 161.6, 161.59 (d, $J$ = 242.5 Hz), 152.9, 151.8, 150.3, 138.8, 134.1, 133.2, 128.81 (d, $J$ = 7.5 Hz), 128.79 (d, $J$ = 7.5 Hz), 123.2, 118.9, 115.9, 115.6 (d, $J$ = 21.3 Hz), 115.3 (d, $J$ = 21.3 Hz), 93.7, 87.5, 50.2, 47.7, 37.1, 33.5, 26.0, 25.3, 24.8, 24.3 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{34}H_{35}F_2N_4$, 537.2824; found, 537.2810.

**(*E*)-8-(4-Chlorophenyl)-1-(4-chlorostyryl)-3,6-di(piperidin-1-yl)-7,8-dihydroisoquinoline-4-carbonitrile (3ea).** Following the general procedure, using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford a yellow-green solid (76.7 mg, 45% yield). M. p. 187.2-188.5°C. $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 7.65-7.60 (m, 3H), 7.41 (d, $J$ = 8.5 Hz, 2H), 7.29-7.25 (m, 3H), 7.16 (d, $J$ = 8.5 Hz, 2H), 5.60 (s, 1H), 4.82-4.81 (m, 1H), 3.48-3.47 (m, 4H), 3.30-3.22 (m, 4H), 2.91-2.83 (m, 2H), 1.66-1.61 (m, 6H), 1.56-1.53 (m, 2H), 1.44-1.41 (m, 4H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 161.6, 152.9, 151.8, 150.2, 141.6, 135.4, 134.1, 134.0, 132.5, 128.8, 128.72, 128.69, 128.4, 123.9, 118.8, 115.7, 93.7, 87.6, 50.2, 47.7, 37.3, 33.3, 26.0, 25.3, 24.8, 24.3 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{34}H_{35}Cl_2N_4$, 569.2233; found, 569.2244.

**(*E*)-8-(4-Bromophenyl)-1-(4-bromostyryl)-3,6-di(piperidin-1-yl)-7,8-dihydroisoquinoline-4-carbonitrile (3fa).** Following the general procedure, using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford a yellow-green solid (90.5 mg, 46% yield). M. p. 189.6-190.9 °C. $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 7.62 (d, $J$ = 15.5 Hz, 1H), 7.54 (s, 4H), 7.41 (d, $J$ = 8.0 Hz, 2H), 7.28 (d, $J$ = 15.0 Hz, 1H), 7.10 (d, $J$ = 8.5 Hz, 2H), 5.60 (s, 1H), 4.80-4.79(m, 1H), 3.47-3.46 (m, 4H), 3.30-3.22 (m, 4H), 2.91-2.82 (m, 2H), 1.66-1.62 (m, 6H), 1.56-1.53 (m, 2H), 1.45-1.40 (m, 4H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 161.6, 152.9, 151.8, 150.1, 142.1, 135.9, 134.2, 131.8, 131.7, 129.1, 128.7, 124.0, 122.2, 120.6, 118.8, 115.7, 93.7, 87.6, 50.2, 47.7, 37.3, 33.2, 26.0, 25.3, 24.8, 24.3 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{34}H_{35}Br_2N_4$, 657.1223; found, 657.1226.

**(*E*)-8-(4-(Dimethylamino)phenyl)-1-(4-(dimethylamino)styryl)-3,6-di(piperidin-1-yl)-7,8-dihydroisoquinoline-4-carbonitrile (3ga).** Following the general procedure, using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford an orange-yellow solid (100.3 mg, 57% yield). M. p. 156.3-157.6°C. $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 7.57 (d, $J$ = 15.5 Hz, 1H), 7.36 (d, $J$ = 8.5 Hz, 2H), 6.97-6.94 (m, 3H), 6.68 (d, $J$ = 8.5 Hz, 2H), 6.56 (d, $J$ = 9.0 Hz, 2H), 5.59 (s, 1H), 4.54-4.52 (m, 1H), 3.44-3.43 (m, 4H), 3.30-3.26 (m, 2H), 3.23-3.19 (m, 2H), 2.93 (s, 6H), 2.78 (s, 6H),

1.66-1.60 (m, 7H), 1.56-1.41 (m, 7H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 161.6, 153.4, 151.4, 151.2, 150.4, 149.2, 135.3, 131.5, 128.6, 127.9, 125.5, 119.6, 119.3, 116.4, 112.7, 112.1, 94.0, 87.0, 50.3, 47.6, 40.6, 40.3, 36.8, 33.5, 26.0, 25.2, 24.8, 24.4 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{38}H_{47}N_6$, 587.3857; found, 587.3850.

**(*E*)-8-(4-(Diphenylamino)phenyl)-1-(4-(diphenylamino)styryl)-3,6-di(piperidin-1-yl)-7,8-dihydroisoquinoline-4-carbonitrile (3ha).** Following the general procedure, using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford an orange-red solid (167.2 mg, 67% yield). M. p. 156.3-157.6 °C. $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 7.60 (d, $J$ = 15.0 Hz, 1H), 7.42 (d, $J$ = 8.5 Hz, 2H), 7.31 (t, $J$ = 7.5 Hz, 4H), 7.19 (t, $J$ = 8.0 Hz, 4H), 7.13-7.02 (m, 9H), 6.96 (t, $J$ = 7.5 Hz, 2H), 6.88-6.86 (m, 6H), 6.83 (d, $J$ = 8.5 Hz, 2H), 5.58 (s, 1H), 4.62 (d, $J$ = 7.0 Hz, 1H), 3.44 (br, 4H), 3.31-3.23 (m, 4H), 2.89-2.78 (m, 2H), 1.64-1.63 (m, 4H), 1.60-1.55 (m, 4H), 1.42-1.41 (m, 4H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 161.6, 153.1, 151.6, 150.8, 148.0, 147.8, 147.3, 146.2, 137.6, 134.6, 131.0, 129.3, 129.1, 128.2, 128.1, 124.8, 124.1, 123.9, 123.3, 122.8, 122.6, 122.2, 119.1, 116.3, 93.8, 87.2, 50.2, 47.8, 37.4, 33.3, 26.0, 25.4, 24.8, 24.5 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{58}H_{55}N_6$, 835.4483; found, 835.4479.

**(*E*)-8-(Naphthalen-1-yl)-1-(2-(naphthalen-1-yl)vinyl)-3,6-di(piperidin-1-yl)-7,8-dihydroisoquinoline-4-carbonitrile (3ia).** Following the general procedure, using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford a yellow-green solid (140.5 mg, 78% yield). M. p. 212.3-213.4 °C. $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 8.46 (d, $J$ = 15.0 Hz, 1H), 8.29 (d, $J$ = 8.5 Hz, 1H), 7.98 (d, $J$ = 8.5 Hz, 1H), 7.93 (d, $J$ = 8.0 Hz, 1H), 7.75 (d, $J$ = 8.0 Hz, 1H), 7.75 (d, $J$ = 8.0 Hz, 1H), 7.72 (d, $J$ = 8.0 Hz, 1H), 7.66 (d, $J$ = 8.0 Hz, 1H), 7.63-7.60 (m, 1H), 7.56-7.53 (m, 1H), 7.42-7.39 (m, 1H), 7.33-7.28 (m, 2H), 7.18 (t, $J$ = 7.5 Hz, 1H), 7.10 (d, $J$ = 7.0 Hz, 1H), 7.02 (d, $J$ = 7.5 Hz, 1H), 6.90 (d, $J$ = 15.0 Hz, 1H), 5.85 (s, 1H), 5.37 (d, $J$ = 8.0 Hz, 1H), 3.70-3.67 (m, 4H), 3.19-3.15 (m, 2H), 3.13-3.08 (m, 2H), 3.03-2.98 (m, 1H), 2.88 (d, $J$ = 15.5 Hz, 1H), 1.86-1.77 (m, 4H), 1.73-1.69 (m, 2H), 1.59 (br, 3H), 1.52-1.49 (m, 2H),1.43-1.37 (m, 4H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 161.8, 153.4, 152.6, 150.9, 138.0, 134.4, 134.3, 133.6, 132.3, 131.3, 130.2, 129.5, 128.39, 128.38, 127.4, 126.5, 126.4, 126.0, 125.8, 125.7, 125.4, 125.3, 124.1, 123.7, 122.2, 119.1, 116.8, 93.4, 87.5, 50.3, 47.7, 33.1, 32.4, 26.1, 25.1, 24.9, 24.3 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{42}H_{41}N_4$, 601.3326; found, 601.3313.

**(*E*)-8-(Naphthalen-2-yl)-1-(2-(naphthalen-2-yl)vinyl)-3,6-di(piperidin-1-yl)-7,8-dihydroisoquinoline-4-carbonitrile (3ja).** Following the general procedure, using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford an orange solid (158.5 mg, 88% yield). M. p. 155.2-155.4 °C. $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 7.98 (s, 1H), 7.89-7.85 (m, 3H), 7.82-7.77 (m, 5H), 7.62 (s, 1H), 7.50-7.47 (m, 2H), 7.46-7.44 (m, 2H), 7.42-7.38 (m, 2H), 5.68 (s, 1H), 5.00 (d, $J$ = 6.5 Hz, 1H), 3.53 (br, 4H), 3.30-3.28 (m, 2H), 3.26-3.22 (m, 2H), 3.01-2.94 (m, 2H), 1.70-1.69 (m, 4H), 1.65-1.64 (m, 2H), 1.52-1.49 (m, 2H), 1.45-1.39 (m, 4H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 161.7, 153.2, 152.0, 150.7, 140.7, 135.4, 134.5, 133.51, 133.47, 133.3, 132.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.6, 127.5, 126.3, 126.0, 125.92, 125.90, 125.5, 124.1, 123.7, 119.1,

116.2, 93.9, 87.6, 50.3, 47.6, 38.1, 33.4, 26.1, 25.2, 24.8, 24.3 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{42}H_{41}N_4$, 601.3326; found, 601.3327.

**(*E*)-8-(Anthracen-9-yl)-1-(2-(anthracen-9-yl)vinyl)-3,6-di(piperidin-1-yl)-7,8-dihydroisoquinoline-4-carbonitrile (3ka).** Following the general procedure, using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford an orange-red solid (105.1 mg, 50% yield). M. p. 244.0-245.1 °C. $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 8.51 (t, $J$ = 3.5 Hz, 1H), 8.32 (s, 1H), 8.25 (d, $J$ = 15.5 Hz, 1H), 8.14 (d, $J$ = 8.5 Hz, 1H), 8.06 (d, $J$ = 9.5 Hz, 1H) , 7.90-7.86 (m, 3H) , 7.45 (t, $J$ = 7.0 Hz, 1H), 7.40-7.36 (m, 3H), 7.27 (t, $J$ = 7.0 Hz, 1H), 7.21 (t, $J$ = 8.0 Hz, 1H), 7.19-7.14 (m, 4H), 6.26 (d, $J$ = 15.5 Hz, 1H), 6.07 (t, $J$ = 10.0 Hz, 1H), 5.91 (s, 1H), 3.57-3.55 (m, 4H), 3.27-3.19 (m, 5H), 2.81 (q, $J$ = 9.0 Hz, 1H), 1.74-1.66 (m, 4H), 1.63-1.60 (m, 2H), 1.53-1.41 (m, 6H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 161.0, 153.5, 151.8, 150.4, 137.8, 132.7, 132.4, 131.9, 131.6, 131.2, 130.9, 129.7, 129.6, 129.0, 128.9, 128.7, 128.1, 127.7, 126.9, 126.3, 126.2, 125.5, 125.3, 125.2, 124.72, 124.67, 124.5, 122.1, 119.3, 118.2, 93.3, 87.7, 50.2, 47.4, 34.7, 33.9, 26.0, 25.3, 24.9, 24.2 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{50}H_{45}N_4$, 701.3639; found, 701.3631.

**(*E*)-3,6-Di(piperidin-1-yl)-8-(thiophen-2-yl)-1-(2-(thiophen-2-yl)vinyl)-7,8-dihydroisoquinoline-4-carbonitrile (3la).** Following the general procedure, using petroleum ether/ethyl acetate (3:1, v/v) as the eluent to afford a yellow-green solid (86.1 mg, 56% yield).M. p. 174.8-175.6 °C. $^1$H NMR ($CDCl_3$, 500 MHz):$\delta$ 7.91 (d, $J$ = 15.0 Hz, 1H), 7.23 (d, $J$ = 5.0 Hz, 1H), 7.15 (d, $J$ = 3.5 Hz, 1H), 7.09 (d, $J$ = 15.0 Hz, 1H), 7.04 (dd, $^3J$ = 5.0 Hz, $^4J$ = 1.0 Hz, 1H), 7.00 (dd, $J$ = 5.0 Hz, $J$ = 3.5 Hz, 1H), 6.82 (dd, $^3J$ = 5.0 Hz, $^4J$ = 3.5 Hz, 1H), 6.75 (d, $J$ = 3.5 Hz, 1H), 5.76 (s, 1H), 4.71 (d, $J$ = 6.0 Hz, 1H), 3.56 (t, $J$ = 5.0 Hz, 4H), 3.37-3.32 (m, 2H), 3.28-3.24 (m, 2H), 2.94 (d, $J$ = 15.5 Hz, 1H), 2.82-2.77 (m, 1H), 1.76-1.72 (m, 4H), 1.67-1.63 (m, 6H), 1.59-1.56 (m, 2H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 161.6, 153.3, 150.8, 149.7, 146.6, 142.7, 128.2, 127.9, 127.8, 126.4, 125.6, 124.2, 123.5, 123.0, 118.9, 116.5, 93.4, 87.7, 77.3, 77.0, 76.8, 50.2, 47.7, 33.8, 33.1, 26.0, 25.4, 24.8, 24.4 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{30}H_{33}N_4S_2$, 513.2141; found, 513.2139.

**(*E*)-3,6-Di(piperidin-1-yl)-8-(pyridin-4-yl)-1-(2-(pyridin-4-yl)vinyl)-7,8-dihydroisoquinoline-4-carbonitrile (3ma).** Following the general procedure, using petroleum ether/ethyl acetate (1:1, v/v) as the eluent to afford a yellow-green solid (63.3 mg, 42% yield). M. p. 245.6-245.9 °C. $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 8.58 (d, $J$ = 6.0 Hz, 2H), 8.24 (d, $J$ = 6.0 Hz, 2H), 7.62-7.57 (m, 3H), 7.47 (d, $J$ = 15.5 Hz, 1H), 6.77 (d, $J$ = 6.0 Hz, 2H), 5.25 (s, 1H) , 4.64 (t, $J$ = 5.0Hz, 1H), 3.43 (br, 8H), 3.31-3.27 (m, 1H), 2.95-2.91 (m, 1H), 1.67-1.63 (m, 8H), 1.593 (br, 4H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 165.8, 162.7, 160.7, 150.2, 149.1, 144.7, 144.5, 144.0, 131.6, 128.0, 124.7, 123.9, 121.4, 118.4, 98.3, 83.2, 50.0, 49.8, 45.3, 37.4, 25.9, 25.5, 24.7, 24.0 ppm. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{32}H_{34}N_6Na$, 525.2737; found, 525.2757.

**(*E*)-1-(2-(1*H*-Indol-2-yl)vinyl)-8-(1*H*-indol-2-yl)-3,6-di(piperidin-1-yl)-7,8-dihydroisoquinoline-4-carbonitrile (3na).** Following the general procedure, using petroleum ether/ethyl acetate (2:1, v/v) as the eluent to afford a yellow-green solid (116.2 mg, 67% yield).M.

p.253.5-254.4°C. $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 11.39 (d, $J$ = 2.0 Hz, 1H), 10.72 (d, $J$ = 2.0 Hz, 1H), 7.91-7.89 (m, 1H), 7.84 (d, $J$ = 15.0 Hz, 1H), 7.62 (d, $J$ = 3.0 Hz, 1H) , 7.34-7.31 (m, 2H) , 7.22 (d, $J$ = 8.0 Hz, 1H), 7.14-7.11 (m, 2H), 7.05 (t, $J$ = 7.5 Hz, 1H), 7.00 (d, $J$ = 15.0 Hz, 1H), 6.71 (t, $J$ = 7.5 Hz, 1H), 6.62 (d, $J$ = 2.0 Hz, 1H), 5.66 (s, 1H), 4.93 (d, $J$ = 6.0 Hz, 1H), 3.51-3.43 (m, 4H), 3.25-3.21 (m, 2H), 3.18-3.13 (m, 2H), 2.92-2.84 (m, 2H), 1.73-1.61 (m, 6H), 1.52-1.39 (m, 6H) ppm. $^{13}$C NMR (DMSO-$d_6$, 125 MHz): $\delta$ 161.1, 154.4, 151.1, 150.3, 137.2, 136.1, 129.0, 125.7, 124.6, 123.0, 121.8, 121.0, 119.9, 118.8, 118.61, 118.57, 118.1, 116.7, 116.4, 113.6, 111.9, 111.7, 91.8, 85.6, 50.0, 47.1, 32.4, 29.1, 25.6, 24.7, 24.3, 23.8 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{38}H_{39}N_6$, 579.3231; found, 579.3217.

**1-Phenyl-3,6-di(piperidin-1-yl)-8-(*p*-tolyl)-7,8-dihydroisoquinoline-4-carbonitrile (9aa).** Following the general procedure, using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford a white solid (105.5 mg, 72% yield). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 7.33-7.28 (m, 3H), 7.22-7.20 (m, 2H), 7.01 (d, $J$ = 8.0 Hz, 2H), 6.83 (d, $J$ = 8.5 Hz, 2H), 5.62 (s, 1H) , 4.16 (d, $J$ = 5.0 Hz, 1H) , 3.45-3.43 (m, 4H) , 3.28-3.23 (m, 2H), 3.22-3.17 (m, 2H), 2.85-2.75 (m, 2H), 2.21 (s, 3H), 1.64-1.60 (m, 6H), 1.55-1.51 (m, 2H), 1.44-1.35 (m, 4H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 161.8, 156.2, 153.7, 152.1, 140.7, 140.3, 135.7, 129.0, 128.7, 127.9, 127.7, 127.4, 118.9, 115.6, 93.9, 87.8, 50.2, 47.6, 38.3, 33.7, 26.0, 25.2, 24.8, 24.4, 21.0 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{33}H_{37}N_4$, 489.3018; found, 489.3004.

**8-(4-(Dimethylamino)phenyl)-1-phenyl-3,6-di(piperidin-1-yl)-7,8-dihydroisoquinoline-4-carbonitrile (9ba).** Following the general procedure, using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford a white solid (57.4 mg, 37% yield). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 7.35-7.29 (m, 3H), 7.26-7.25 (m, 2H), 6.74 (d, $J$ = 8.5 Hz, 2H), 6.55 (d, $J$ = 9.0 Hz, 2H), 5.61 (s, 1H) , 4.11 (d, $J$ = 5.0 Hz, 1H) , 3.43-3.42 (m, 4H) , 3.29-3.24 (m, 2H), 3.22-3.18 (m, 2H), 2.81 (s, 6H), 2.79 (br, 1H), 2.75-2.71 (m, 1H), 1.64-1.59 (m, 6H), 1.55-1.52 (m, 2H), 1.47-1.37 (m, 4H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 161.8, 156.1, 153.9, 152.0, 149.0, 140.4, 131.8, 128.8, 128.1, 127.8, 127.6, 118.9, 116.1, 112.5, 93.9, 87.8, 50.2, 47.6, 40.6, 37.8, 33.8, 26.0, 25.2, 24.8, 24.4 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{34}H_{40}N_5$, 518.3284; found, 518.3286.

**8-(4-(Di-*p*-tolylamino)phenyl)-1-phenyl-3,6-di(piperidin-1-yl)-7,8-dihydroisoquinoline-4-carbonitrile (9ca).** Following the general procedure, using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford a white solid (132.5 mg, 66% yield). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 7.34-7.31 (m, 3H), 7.26-7.25 (m, 2H), 7.04 (d, $J$ = 8.0 Hz, 4H), 6.81-6.78 (m, 6H), 6.73 (d, $J$ = 8.5 Hz, 2H) , 5.61 (s, 1H) , 4.14 (d, $J$ = 5.0 Hz, 1H), 3.42 (br, 4H), 3.30-3.23 (m, 4H), 2.85-2.73 (m, 2H), 2.22 (s, 6H), 1.58 (br, 8H), 1.38 (br, 4H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 161.8, 156.2, 153.6, 152.0, 146.4, 145.4, 140.4, 137.1, 132.1, 129.7, 128.8, 128.1, 127.9, 127.7, 124.2, 122.7, 118.9, 115.8, 93.8, 87.7, 50.2, 47.8, 38.1, 33.5, 26.0, 25.4, 24.8, 24.5, 20.7 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{46}H_{48}N_5$, 670.3910; found, 670.3907.

**1.5 Synthesis of (*E*)-3-oxo-8-phenyl-6-(piperidin-1-yl)-1-styryl-7,8-dihydro-3*H*-isochromene-4-carbonitrile (7).**

A mixture of compound **6** (0.3 mmol), piperidine (1.2 mmol), and DMSO (3 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 $CH_2Cl_2$ (20 mL), and the organic layer was washed with water (10 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 orange solid **7** (45.7 mg, 35% yield). $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.48-7.44 (m, 1H), 7.35-7.33 (m, 2H), 7.30-7.27 (m, 5H), 7.23-7.21 (m, 1H), 7.18-7.16 (m, 2H), 6.69 (d, $J$ = 15.5 Hz, 1H), 5.80 (s, 1H), 4.45 (d, $J$ = 6 Hz, 1H), 3.47 (br, 4H), 3.05-2.93 (m, 2H), 1.66-1.63 (m, 4H), 1.53 (br, 2H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 160.9, 159.5, 156.6, 153.7, 142.4, 137.2, 135.3, 129.4, 128.9, 128.7, 127.5, 127.3, 126.6, 117.4, 115.2, 110.4, 93.2, 78.6, 48.8, 36.7, 33.5, 23.9 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{29}H_{27}N_2O_2$, 435.2073; found, 435.2071.

**1.6 Synthesis of 2-((*E*)-2-((*E*)-1-hydroxy-3-phenylallylidene)-5-(piperidin-1-yl)-1,6- dihydro-[1,1'-biphenyl]-3(2*H*)-ylidene)malononitrile (11A).**

The mixture of compound **1a** (0.3 mmol), **2a** (1.2 mmol), $KH_2PO_4$ (0.6 mmol), and DMSO (3 mL) was stirred at 120 °C for 2 h under $N_2$ atmosphere. After being cooled to the room temperature, the reaction mixture was poured into $CH_2Cl_2$ (20 mL), and the organic layer was washed with water (10 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 using ethyl acetate/methanol (1:1, v/v) as the eluent to afford the red solid **11A** (41.1 mg, 31% yield). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.46 (d, $J$ = 15.2 Hz, 1H), 7.38 (d, $J$ = 7.2 Hz, 2H), 7.33-7.28 (m, 5H), 7.22 (d, $J$ = 6.4 Hz, 1H), 7.17 (d, $J$ = 7.6 Hz, 2H), 6.68 (d, $J$ = 15.6 Hz, 1H), 5.72 (s, 1H), 4.39 (t, $J$ = 4.0 Hz, 1H), 3.72 (br, 1H), 3.39 (br, 4H), 2.88 (d, $J$ = 4.0 Hz, 2H), 1.64-1.60 (m, 2H), 1.52-1.49 (m, 4H) ppm. $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 160.8, 157.2, 152.1, 151.9, 147.0, 142.8, 136.4, 135.7, 129.3, 128.9, 128.8, 127.4, 127.2, 126.8, 115.4, 109.4, 93.2, 48.5, 37.2, 33.5, 25.8, 24.1 ppm. MS (ESI, m/z): 434.15 $[M+H]^+$.

The mixture of **11A** (86.7 mg, 0.2 mmol), **2a** (0.8 mmol), $KH_2PO_4$ (0.4 mmol), and DMSO (3 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 $CH_2Cl_2$ (20 mL), and the organic layer was washed with water (10 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 using ethyl acetate/methanol (5:1, v/v) as the eluent to afford **3aa** in 92% yield.

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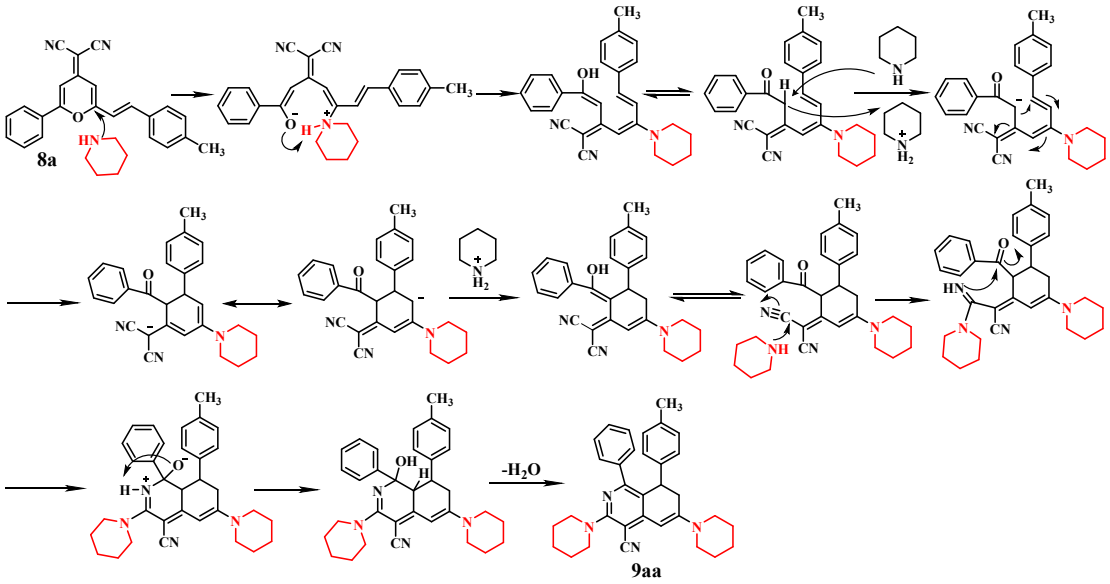
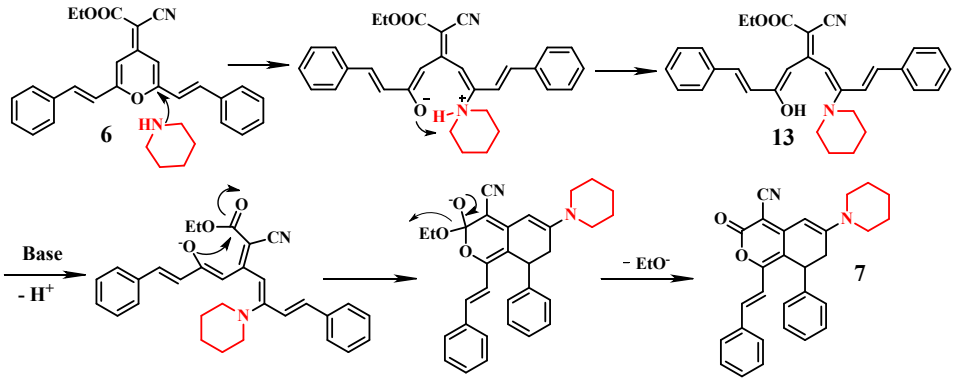
## 2. Schemes, figures, and tables




**Scheme S3** Possible reaction mechanism of compound **9aa** prepared from compound **8a** and piperidine.




**Scheme S4** Possible reaction mechanism of compound **7** prepared from compound **6** and piperidine.

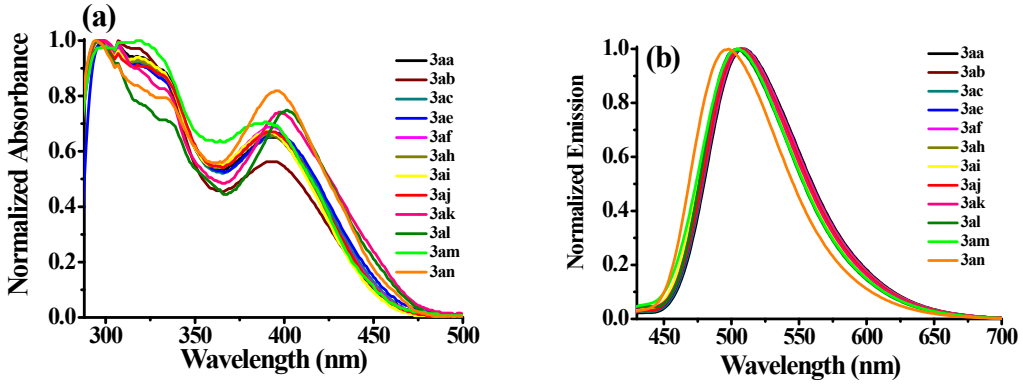



**Fig. S1** Normalized absorption (a) and fluorescence (b) spectra of **3aa-an** (except **3ad** and **3ag**) in THF solvent. Concentration: $1\times10^{-5}$ mol/L.

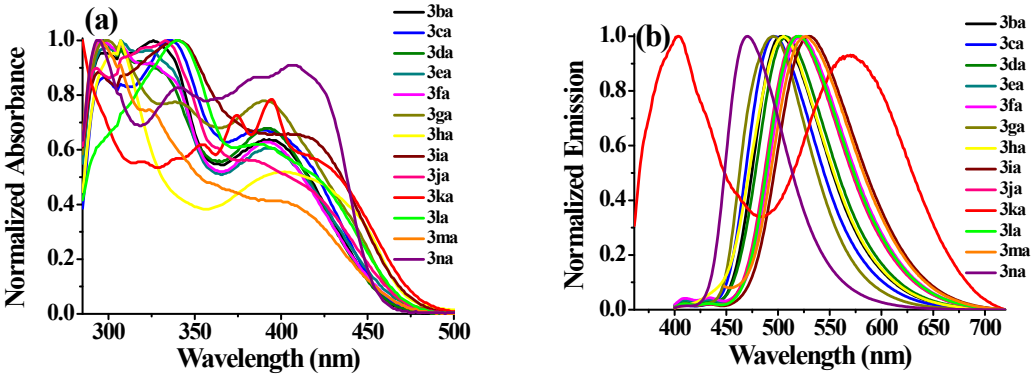



**Fig. S2** Normalized absorption (a) and fluorescence (b) spectra of **3ba-na** in THF solvent. Concentration: $1\times10^{-5}$ mol/L.

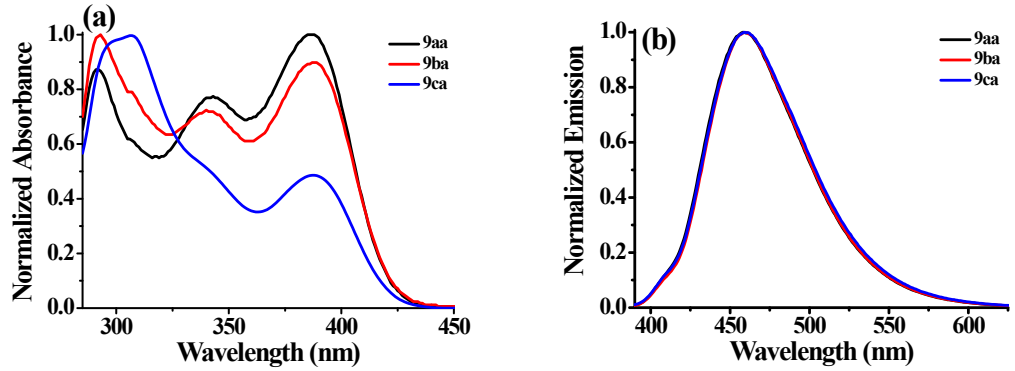



**Fig. S3** Normalized absorption (a) and fluorescence (b) spectra of **9aa-ca** in THF solvent. Concentration: $1\times10^{-5}$ mol/L.

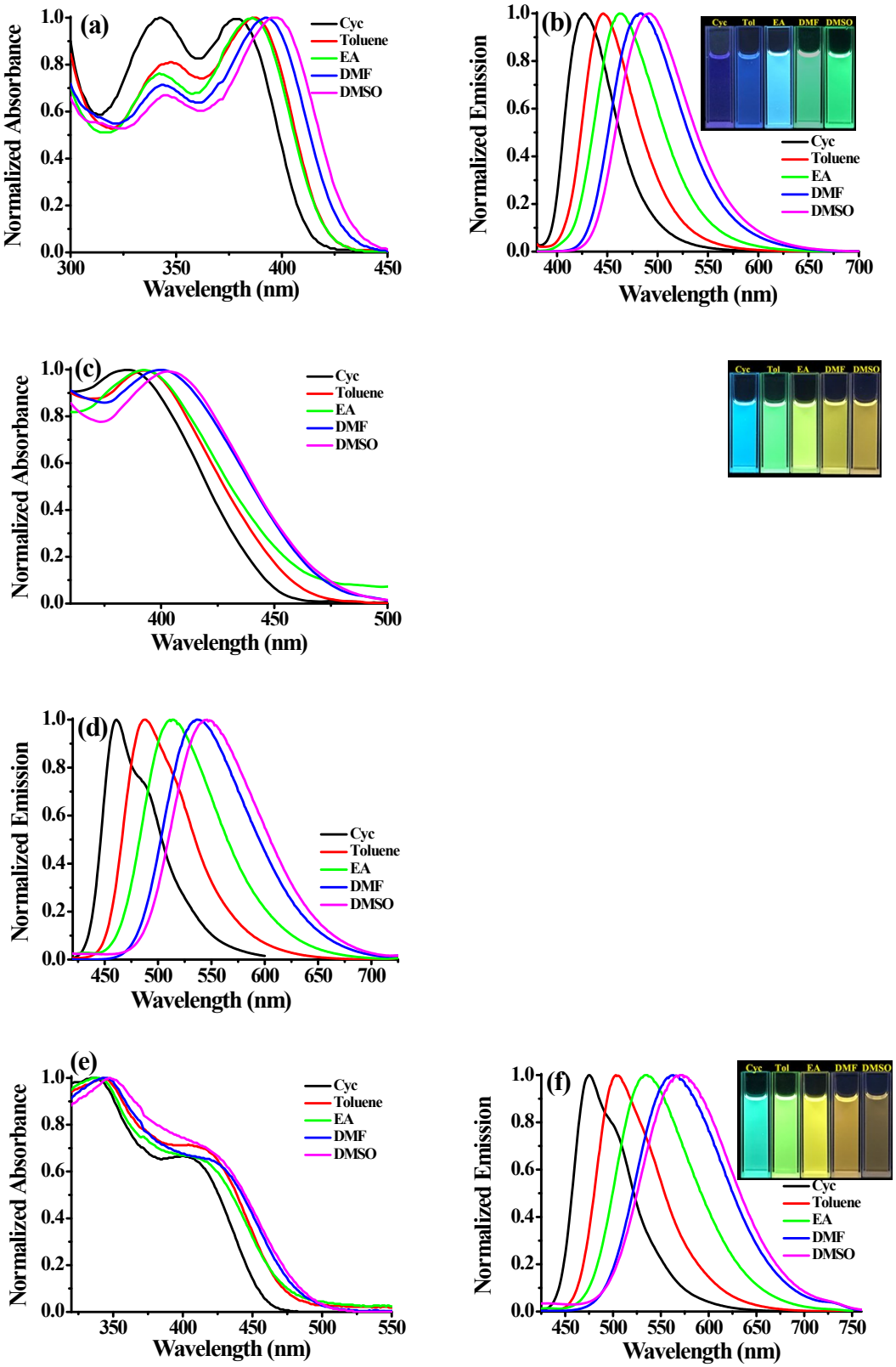



**Fig. S4** Absorption and fluorescence spectra of **9aa** (a,b), **3aa** (c,d), and **3ia** (e,f) in different solvents ($1 \times 10^{-5}$ mol/L). Inset: Fluorescence photos in different solvents at a concentration of $1 \times 10^{-5}$ mol/L under UV irradiation (365 nm).

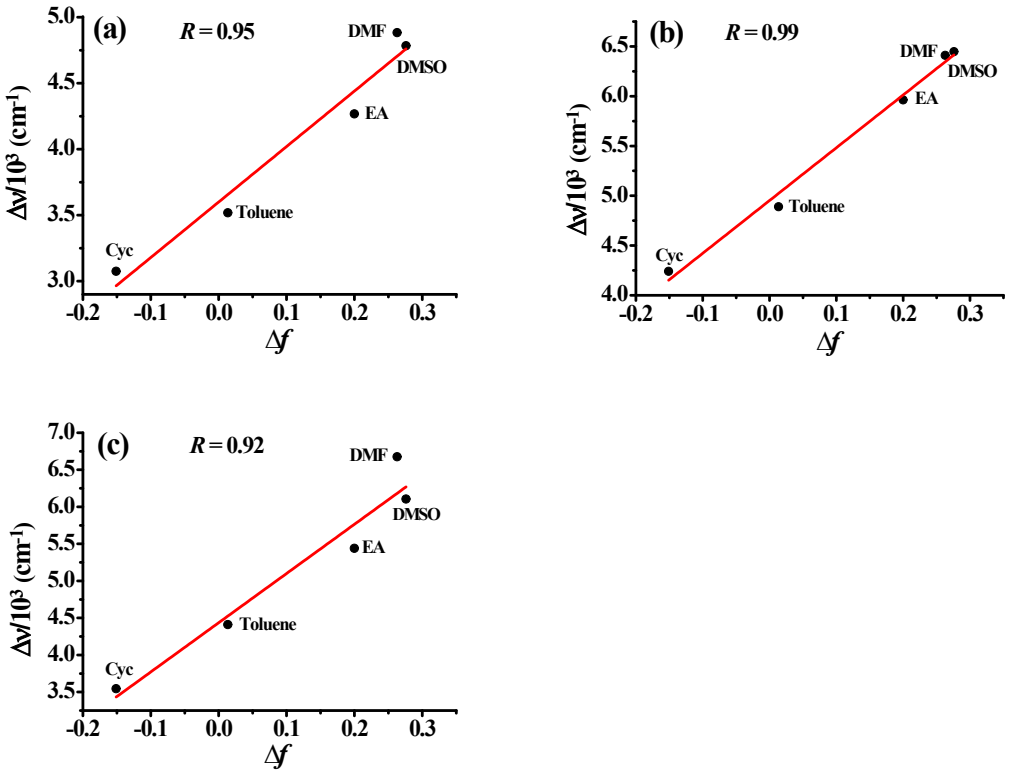



**Fig. S5** Linear fitting of Stokes shifts ($\Delta\nu$) of **9aa** (a), **3aa** (b), and **3ia** (c) with orientation polarizability ($\Delta f$) in various solvents.

**Table S1** UV-vis absorption maxima and fluorescence emission maxima of **9aa** and solvent polarity parameter in different solvents.

| | Cyc | Toluene | EA | DMF | DMSO |
|---|---|---|---|---|---|
| $\lambda_{abs}^{max}$/nm | 379 | 387 | 388 | 393 | 398 |
| $\nu_{abs}^{max}$/cm$^{-1}$ | 2639 | 2584 | 2577 | 2545 | 2513 |
| $\lambda_{em}^{max}$/nm | 429 | 448 | 465 | 484 | 494 |
| $\lambda_{em}^{max}$/cm$^{-1}$ | 2331 | 2232 | 2151 | 2066 | 2024 |
| $\Delta\nu$/cm$^{-1}$ | 3075 | 3518 | 4268 | 4784 | 4883 |
| $\Delta f$ | -0.151 | 0.0135 | 0.2 | 0.263 | 0.276 |

**Table S2** UV-vis absorption maxima and fluorescence emission maxima of **3aa** and solvent polarity parameter in different solvents.

| | Cyc | Toluene | EA | DMF | DMSO |
|---|---|---|---|---|---|
| $\lambda_{abs}^{max}$/nm | 387 | 394 | 394 | 400 | 405 |
| $\nu_{abs}^{max}$/cm$^{-1}$ | 2584 | 2538 | 2538 | 2500 | 2469 |
| $\lambda_{em}^{max}$/nm | 463 | 488 | 515 | 539 | 547 |
| $\lambda_{em}^{max}$/cm$^{-1}$ | 2160 | 2049 | 1942 | 1855 | 1828 |

| | | | | | |
|---|---|---|---|---|---|
| $\Delta\nu$/cm$^{-1}$ | 4242 | 4889 | 5963 | 6447 | 6410 |
| $\Delta f$ | -0.151 | 0.0135 | 0.2 | 0.263 | 0.276 |

**Table S3** UV-vis absorption maxima and fluorescence emission maxima of **3ia** and solvent polarity parameter in different solvents.

| | Cyc | Toluene | EA | DMF | DMSO |
|---|---|---|---|---|---|
| $\lambda_{abs}^{max}$/nm | 408 | 413 | 415 | 419 | 415 |
| $\nu_{abs}^{max}$/cm$^{-1}$ | 2451 | 2421 | 2410 | 2387 | 2410 |
| $\lambda_{em}^{max}$/nm | 477 | 505 | 536 | 563 | 574 |
| $\lambda_{em}^{max}$/cm$^{-1}$ | 2096 | 1980 | 1866 | 1776 | 1742 |
| $\Delta\nu$/cm$^{-1}$ | 3545 | 4411 | 5440 | 6104 | 6674 |
| $\Delta f$ | -0.151 | 0.0135 | 0.2 | 0.263 | 0.276 |

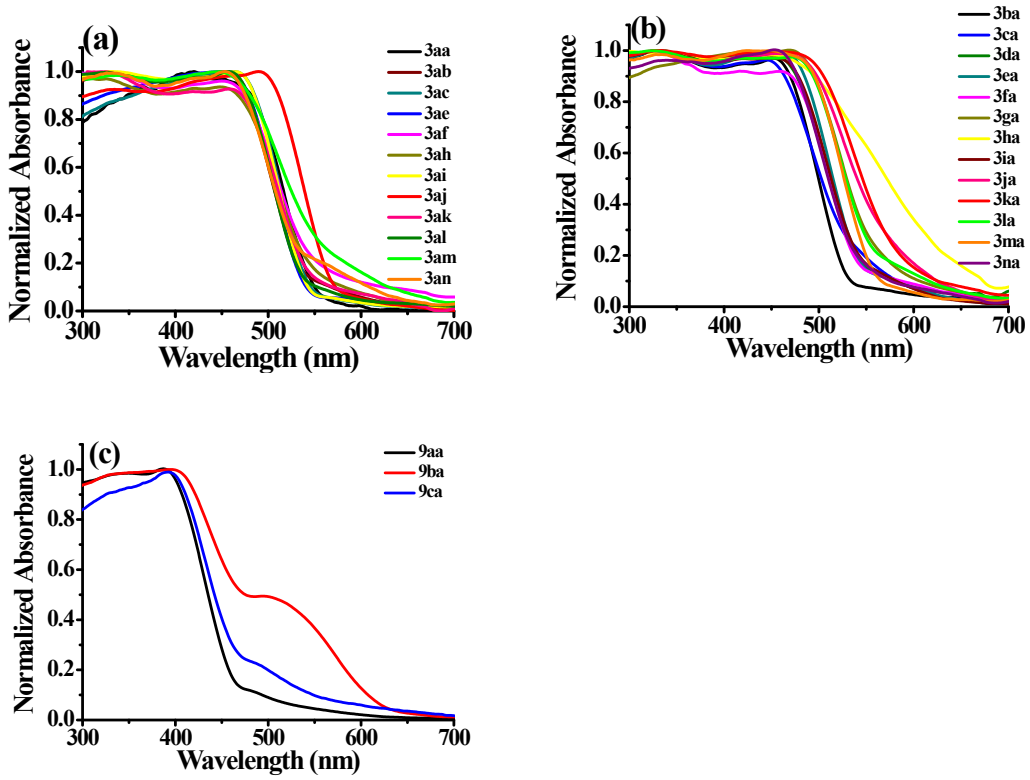



**Fig. S6** Normalized absorption spectra of the DDIC derivatives in solid state: (a) **3aa-an** (except **3ad** and **3ag**); (b) **3ba-na**; (c) **9aa-ca**.

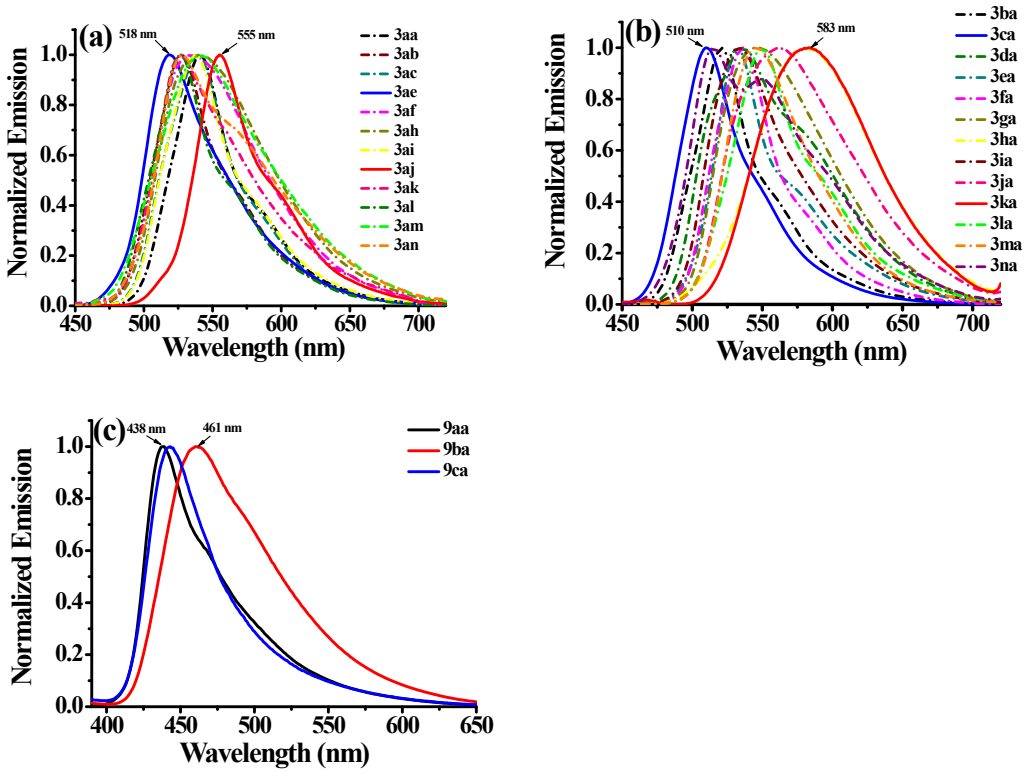



**Fig. S7** Normalized fluorescence spectra of the DDIC derivatives in solid state: (a) **3aa-an** (except **3ad** and **3ag**); (b) **3ba-na**; (c) **9aa-ca**.

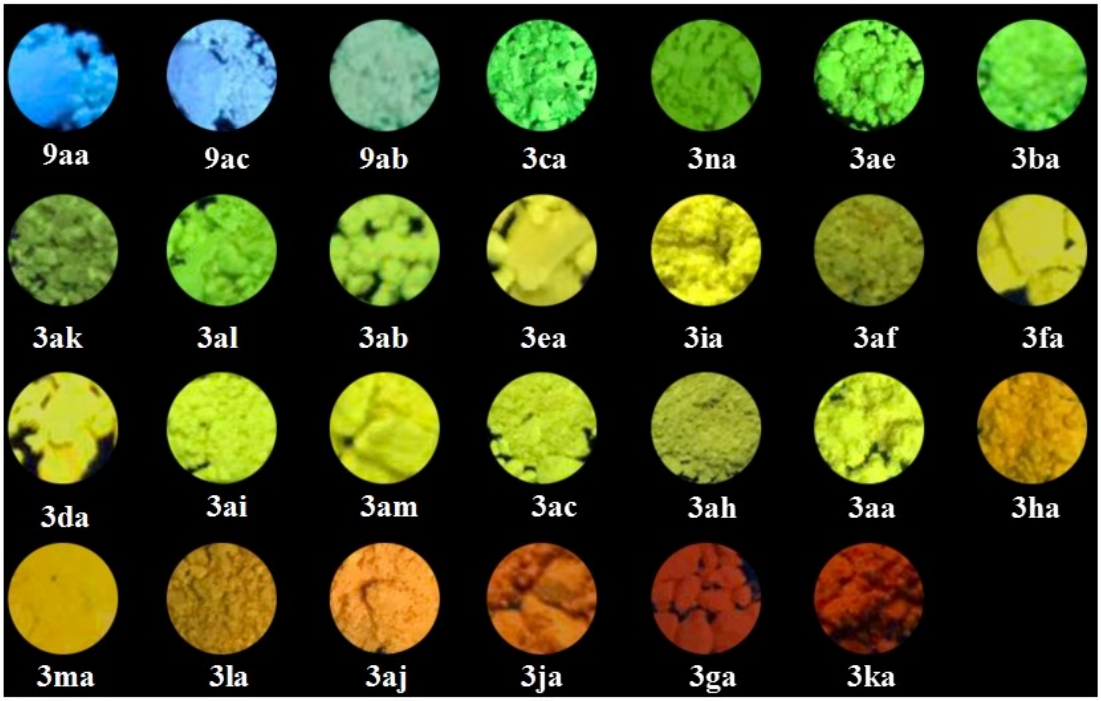



**Fig. S8** Full-color fluorescence images of the DDIC derivatives in solid state under the irradiation of 365 nm light.

**Table S4** Photophysical properties of some DDIC derivatives (**3aa**, **3aj**, **3am**, **3ca**, **3ia**, **3ka**, and **9aa**) in THF solvent and solid state.

| Compound | $\lambda_{abs}$ (THF, nm) | $\lambda_{em}$ (THF, nm) | $\lambda_{abs}$ (Solid, nm) | $\lambda_{em}$ (Solid, nm) | $\Phi_F$ (Solid, %) |
|---|---|---|---|---|---|
| **3aa** | 297, 394 | 509 | 420 | 541 | 36 |
| **3aj** | 296, 393 | 507 | 333, 491 | 555 | 7 |
| **3am** | 307, 389 | 504 | 333, 446 | 542 | 17 |
| **3ca** | 297, 335, 390 | 496 | 328, 448 | 510 | 28 |
| **3ia** | 294, 340, 410 | 530 | 333, 454 | 534 | 18 |
| **3ka** | 354, 374, 395, 435 | 403, 570 | 330, 455 | 583 | 7 |
| **9aa** | 307, 387 | 459 | 388 | 438 | 18 |

## 3. Culture methods, crystal data, intermolecular interactions, and stacking arrangements of single crystals of some target compounds

CCDC 2045529-2045536 contains supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Single crystals of **3aa**, **3ca**, and **3ia** were all obtained from a slow diffusion of a petroleum ether/$CHCl_3$ mixture (1:1, v:v). Single crystals of **3ka** and **3am** were both cultured from a slow diffusion of a $CHCl_3$/$CH_3OH$ mixture (1:1, v:v). Single crystals of **3aj**, **9aa**, and **7** were all obtained from a slow evaporation of ethyl acetate/petroleum ether (2:1 = v:v) mixture.

**Table S5** Crystal data and details of collection and refinement for **3aa**, **3aj**, **3am**, and **3ca**.

| | **3aa** | **3aj** | **3am** | **3ca** |
|---|---|---|---|---|
| CCDC (no.) | 2045529 | 2045530 | 2045531 | 2045532 |
| Empirical formula | $C_{34}H_{36}N_4$ | $C_{46}H_{44}N_4$ | $C_{32}H_{32}N_4O_2$ | $C_{36}H_{40}N_4O_2$ |
| Formula weight | 500.67 | 652.85 | 504.61 | 560.72 |
| Temperature (K) | 293(2) | 293(2) | 294(2) | 293(2) |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | *P* 2(1)/c | *P* 2(1)/c | *P* 2(1)/c | *P* 2(1)/c |
| *Z* | 4 | 4 | 8 | 4 |
| $D_{calcd}$ [Mg/m$^3$] | 1.160 | 1.180 | 1.235 | 1.196 |
| *F* (000) | 1072 | 1392 | 2144 | 1200 |

| | | | | |
|---|---|---|---|---|
| $\theta$ range [°] | 2.537-24.999 | 2.435-24.999 | 1.876-24.999 | 2.371-25.498 |
| $R_1$ [I>2σ(I)] | 0.0745 | 0.0882 | 0.0943 | 0.0597 |
| $wR_2$ [I>2σ(I)] | 0.1736 | 0.1929 | 0.1996 | 0.1447 |
| $a$ [Å] | 10.9183(18) | 10.5749(6) | 22.889(3) | 12.1453(5) |
| $b$ [Å] | 10.4266(16) | 10.5365(5) | 14.6221(14) | 10.1503(5) |
| $c$ [Å] | 25.338(6) | 33.2701(17) | 17.1874(17) | 25.2750(13) |
| $\alpha$ [deg] | 90 | 90 | 90 | 90 |
| $\beta$ [deg] | 96.505(7) | 97.521(2) | 109.396(3) | 92.166(2) |
| $\gamma$ [deg] | 90 | 90 | 90 | 90 |
| $V$ [Å$^3$] | 2865.9(9) | 3675.1(3) | 5426.0(10) | 3113.6(3) |
| GOF | 1.096 | 1.068 | 1.037 | 1.040 |
| $R$(int) | 0.0886 | 0.0778 | 0.2247 | 0.0486 |
| No. of reflcns collected | 12517 | 9178 | 49754 | 29737 |
| No. of unique reflcns | 5007 | 5228 | 9544 | 5790 |
| $R_1$ (all data) | 0.1734 | 0.1679 | 0.2194 | 0.0877 |
| $wR_2$ (all data) | 0.2398 | 0.2258 | 0.2849 | 0.1671 |

**Table S6** Crystal data and details of collection and refinement for **3ia**, **3ka**, **9aa**, and **7**.

| | **3ia** | **3ka** | **9aa** | **7** |
|---|---|---|---|---|
| CCDC (no.) | 2045533 | 2045534 | 2045536 | 2045535 |
| Empirical formula | $C_{42}H_{40}N_4$ | $C_{50}H_{44}N_4$ | $C_{33}H_{36}N_4$ | $C_{29}H_{26}N_2O_2$ |
| Formula weight | 600.78 | 700.89 | 488.66 | 434.52 |
| Temperature (K) | 293(2) | 293(2) | 293(2) | 293(2) |
| Crystal system | Monoclinic | Triclinic | Monoclinic | Triclinic |
| Space group | *P* 2(1)/c | *P*$\bar{1}$ | *P* 2(1)/c | *P* -1 |
| $Z$ | 4 | 2 | 4 | 2 |
| $D_{calcd}$ [Mg/m$^3$] | 1.208 | 1.218 | 1.179 | 1.258 |
| $F$ (000) | 1280 | 744 | 1048 | 460 |
| $\theta$ range [°] | 1.707-25.000 | 2.486-24.999 | 2.364-25.495 | 2.473-25.999 |
| $R_1$ [I>2σ(I)] | 0.0582 | 0.0886 | 0.0484 | 0.0496 |
| $wR_2$ [I>2σ(I)] | 0.1260 | 0.1697 | 0.1152 | 0.1160 |
| $a$ [Å] | 12.499(2) | 10.1185(11) | 12.2487(8) | 9.3166(3) |
| $b$ [Å] | 13.196(2) | 13.2506(15) | 22.7619(12) | 9.3518(3) |
| $c$ [Å] | 20.980(4) | 16.4503(18) | 10.5788(7) | 13.4041(4) |
| $\alpha$ [deg] | 90 | 109.397(3) | 90 | 99.6900(10) |
| $\beta$ [deg] | 107.331(3) | 94.543(3) | 111.074(2) | 92.9490(10) |
| $\gamma$ [deg] | 90 | 109.846(3) | 90 | 93.0970(10) |
| $V$ [Å$^3$] | 3303.2(10) | 1910.5(4) | 2752.1(3) | 1147.34(6) |
| GOF | 0.991 | 1.049 | 1.040 | 1.046 |

| | | | | |
|---|---|---|---|---|
| $R$(int) | 0.0641 | 0.1032 | 0.0414 | 0.0470 |
| No. of reflcns collected | 17960 | 32049 | 13132 | 20872 |
| No. of unique reflcns | 5825 | 6708 | 5086 | 4502 |
| $R_1$ (all data) | 0.1151 | 0.1969 | 0.0800 | 0.0728 |
| $wR_2$ (all data) | 0.1504 | 0.2223 | 0.1378 | 0.1329 |

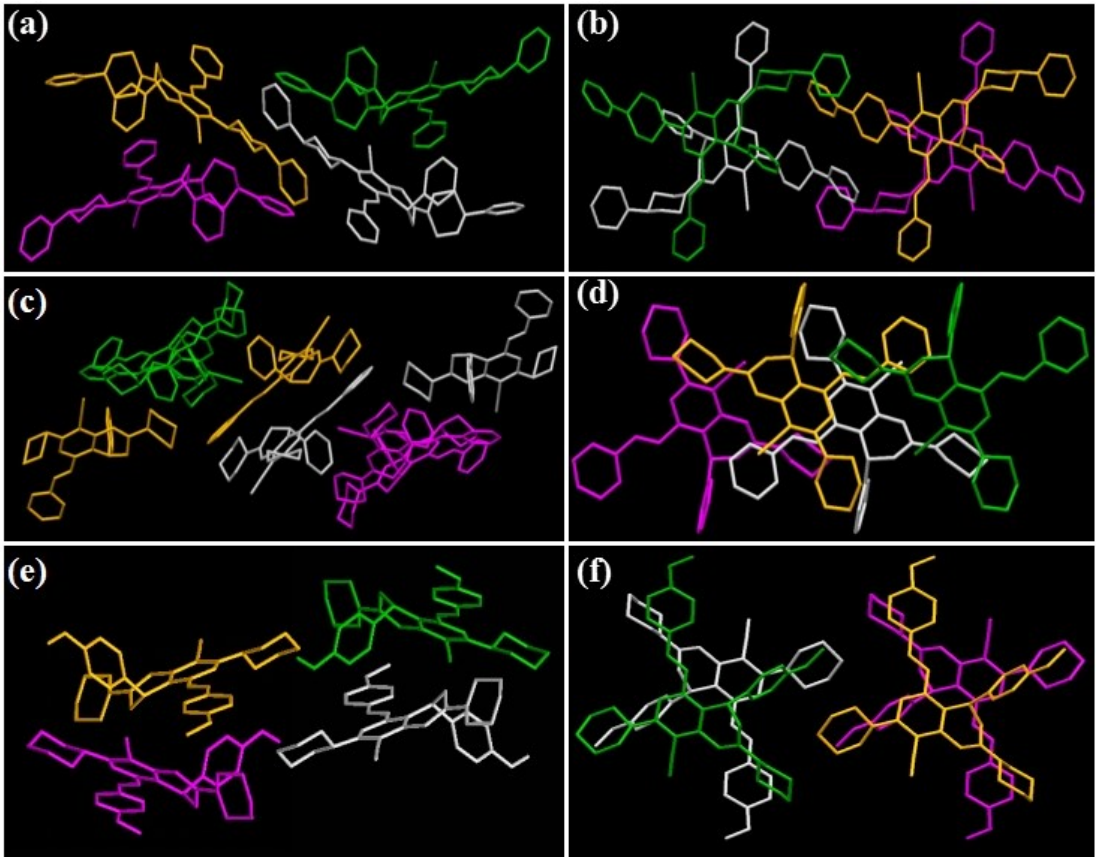



**Fig. S9** Stacking arrangements in the crystals of some DDIC derivatives: **3aj** in a lattice cell (a) and viewed along the *b*-axis (b); **3am** in a lattice cell (c) and viewed along the *b*-axis (d); **3ca** in a lattice cell (e) and viewed along the *b*-axis (f).

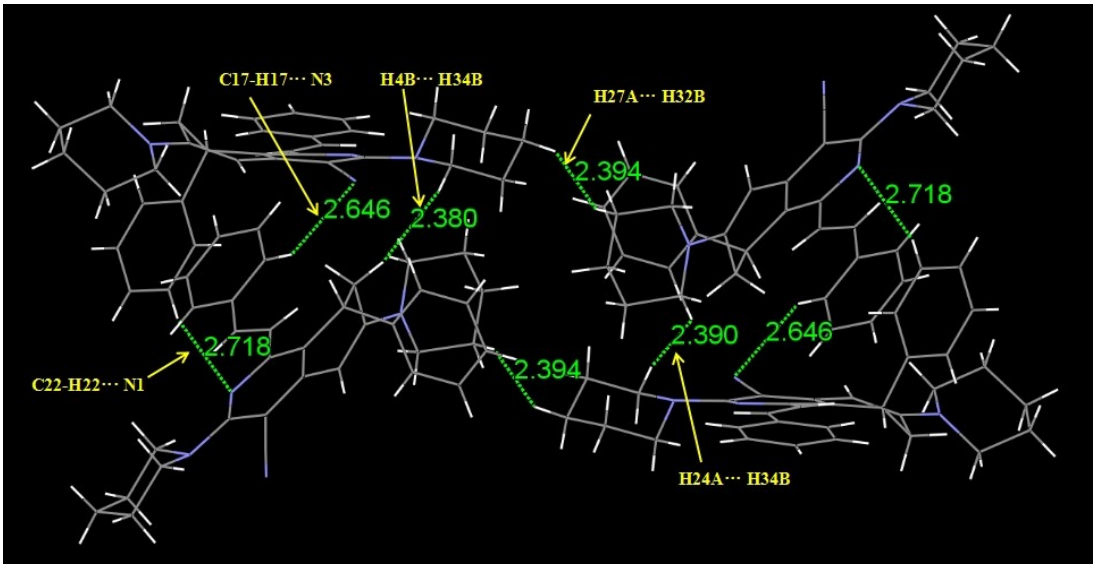



**Fig. S10** The intramolecular interactions of single crystal **3aa** containing C–H···N bonds and C–H···H interactions.

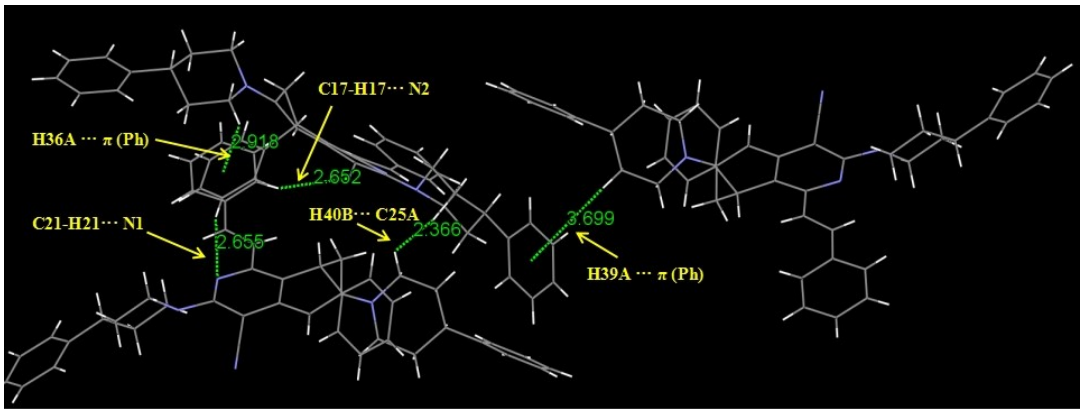



**Fig. S11** The intramolecular interactions of single crystal **3aj** containing C–H···N bonds, and C–H···π and C–H···H interactions.

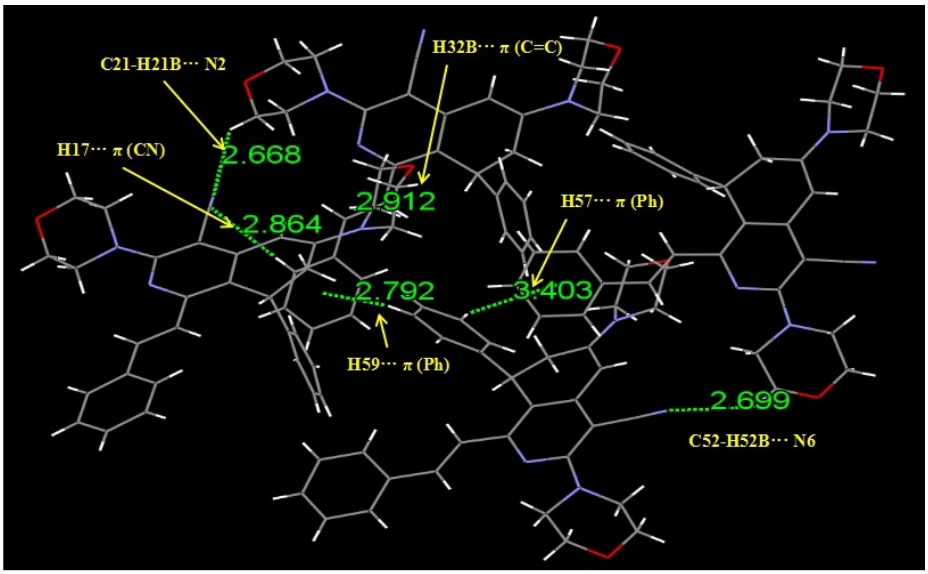


**Fig. S12** The intramolecular interactions of single crystal **3am** containing C–H···N bonds and C–H···π interactions.

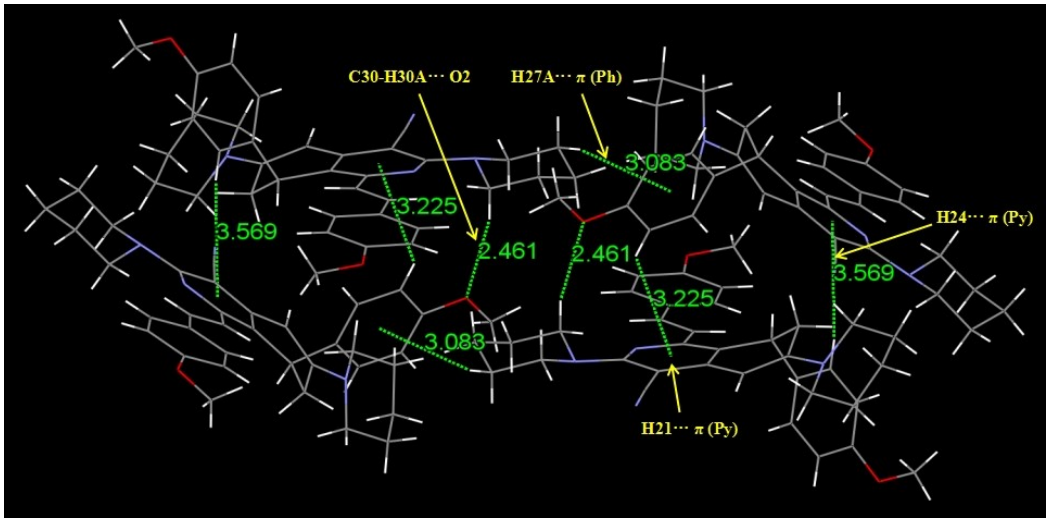



**Fig. S13** The intramolecular interactions of single crystal **3ca** containing C–H···O bond and C–H···π interactions.

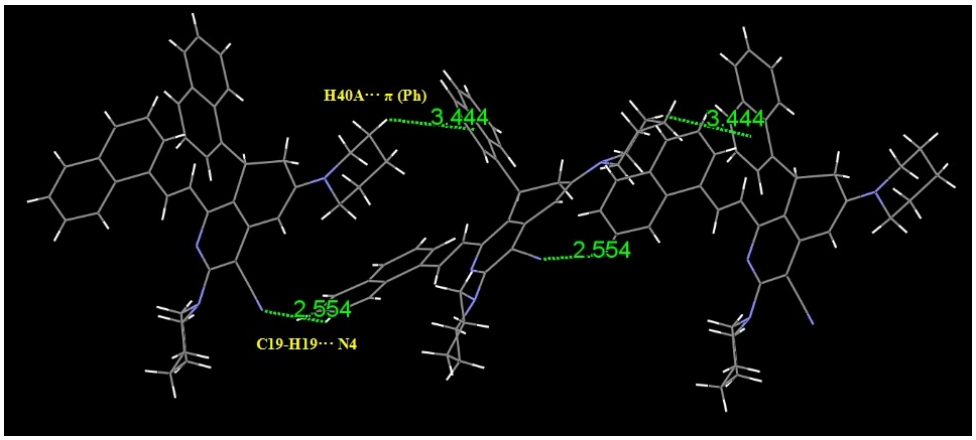



**Fig. S14** The intramolecular interactions of single crystal **3ia** containing C–H···N bonds and C–H···π interactions.

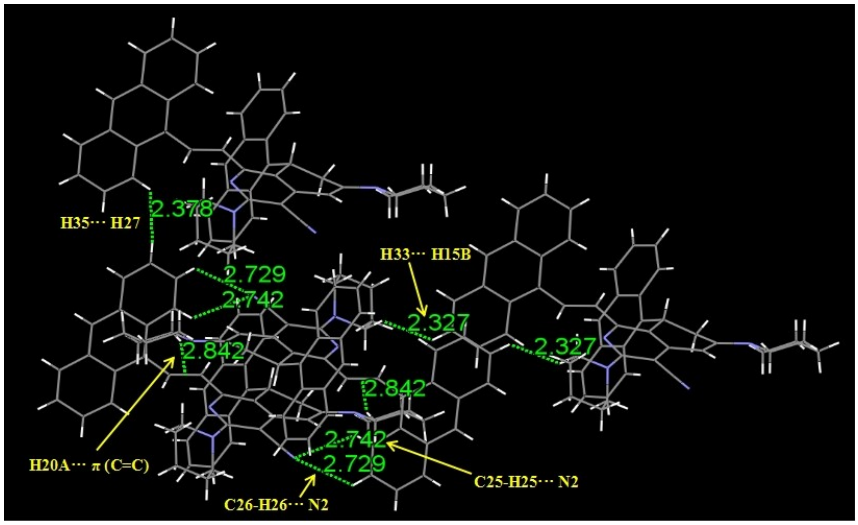


**Fig. S15** The intramolecular interactions of single crystal **3ka** containing C–H···N bonds, and C–H···π and C–H···H interactions.

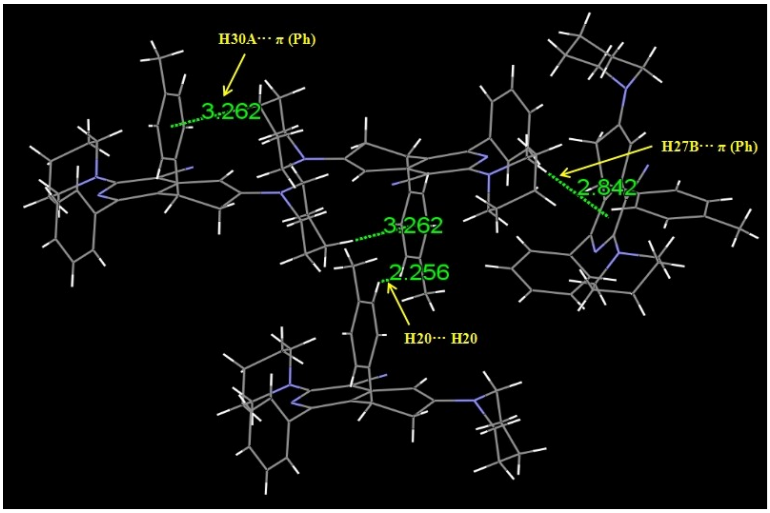



**Fig. S16** The intramolecular interactions of single crystal **9aa** containing C–H···π and C–H···H interactions.

**Table S7** The fluorescence properties and lifetime decays parameters of **9aa**, **3aj**, and **3ka** under different conditions.

| Compound | Type | $\lambda_{em}$ (nm) | $\Phi_F$ (%) | $\tau_1$ [a] (ns) | $A_1$ [b] (%) | $\tau_2$ [a] (ns) | $A_2$ [b] (%) | $<\tau>$ [c] (ns) | $k_f$ [d] ($s^{-1}$) | $k_{nr}$ [e] ($s^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| **9aa** | Original | 441 | 18 | 0.35 | 91 | 1.93 | 9 | 0.49 | $3.7\times10^8$ | $1.7\times10^9$ |
| | Ground | 471 | 8 | 0.36 | 84 | 3.89 | 16 | 0.92 | $8.7\times10^7$ | $9.9\times10^8$ |
| | Fumed | 441 | 14 | 0.28 | 93 | 3.00 | 7 | 0.47 | $3.0\times10^8$ | $1.8\times10^9$ |
| **3aj** | Original | 555 | 7 | 0.42 | 59 | 8.80 | 41 | 3.86 | $1.8\times10^7$ | $2.4\times10^8$ |
| | Ground | 538 | 23 | 0.55 | 82 | 10.2 | 48 | 5.35 | $4.3\times10^7$ | $1.4\times10^8$ |
| | Fumed | 555 | 8 | 0.41 | 56 | 8.00 | 44 | 3.75 | $2.1\times10^7$ | $2.5\times10^8$ |
| **3ka** | Original | 583 | 7 | 0.23 | 55 | 7.74 | 45 | 3.58 | $2.0\times10^7$ | $2.6\times10^8$ |
| | Ground | 568 | 13 | 0.41 | 56 | 7.06 | 44 | 3.32 | $3.9\times10^7$ | $2.6\times10^8$ |
| | Recrystallized | 583 | 9 | 0.35 | 51 | 6.80 | 49 | 3.49 | $2.6\times10^7$ | $2.6\times10^8$ |

[a] $\tau_1$ and $\tau_2$ are the lifetimes of the shorter-lived and longer-lived species, respectively. [b] $A_1$ and $A_2$ are the amplitudes of the shorter-lived and longer-lived species, respectively. [c] Weighted mean lifetime $<\tau>$ obtained from the equation: $<\tau> = (A_1\tau_1+A_2\tau_2)/(A_1+A_2)$. [d] Radiative rate constant $k_f$ obtained from the equation: $k_f = \Phi_F/<\tau>$. [e] Non-radiative rate constant $k_{nr}$ obtained from the equation: $k_{nr} = (1-\Phi_F)/<\tau>$.

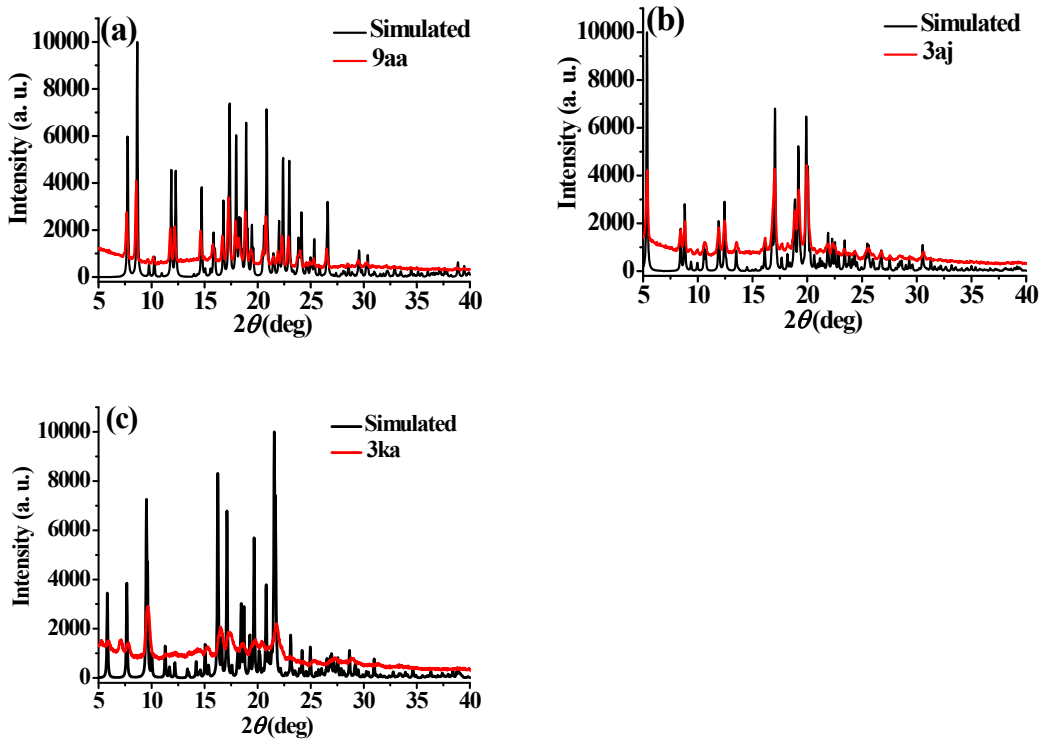



**Fig. S17** Comparison of experimental XRD curves of the original samples of **9aa** (a), **3aj** (b), and **3ka** (c) and the simulated XRD curves obtained from the corresponding single crystals.

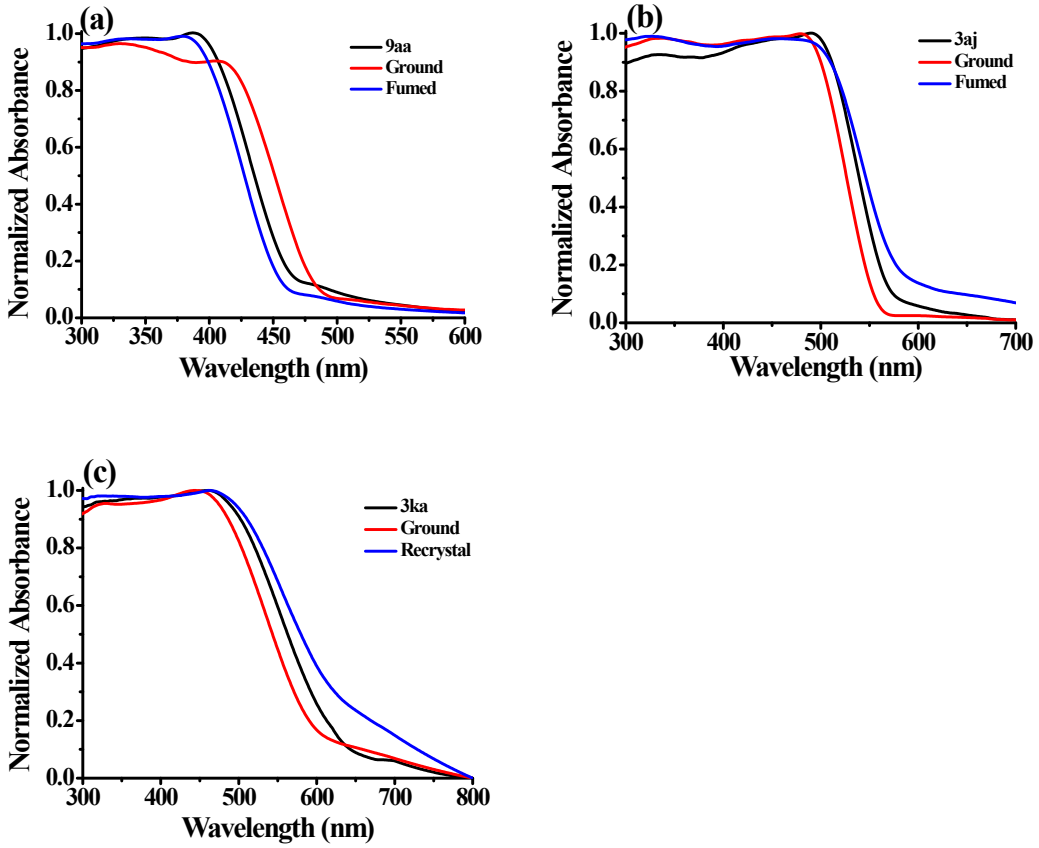



**Fig. S18** Normalized absorption spectra of **9aa** (a), **3aj** (b), and **3ka** (a) under different conditions.

## 4. NMR spectra

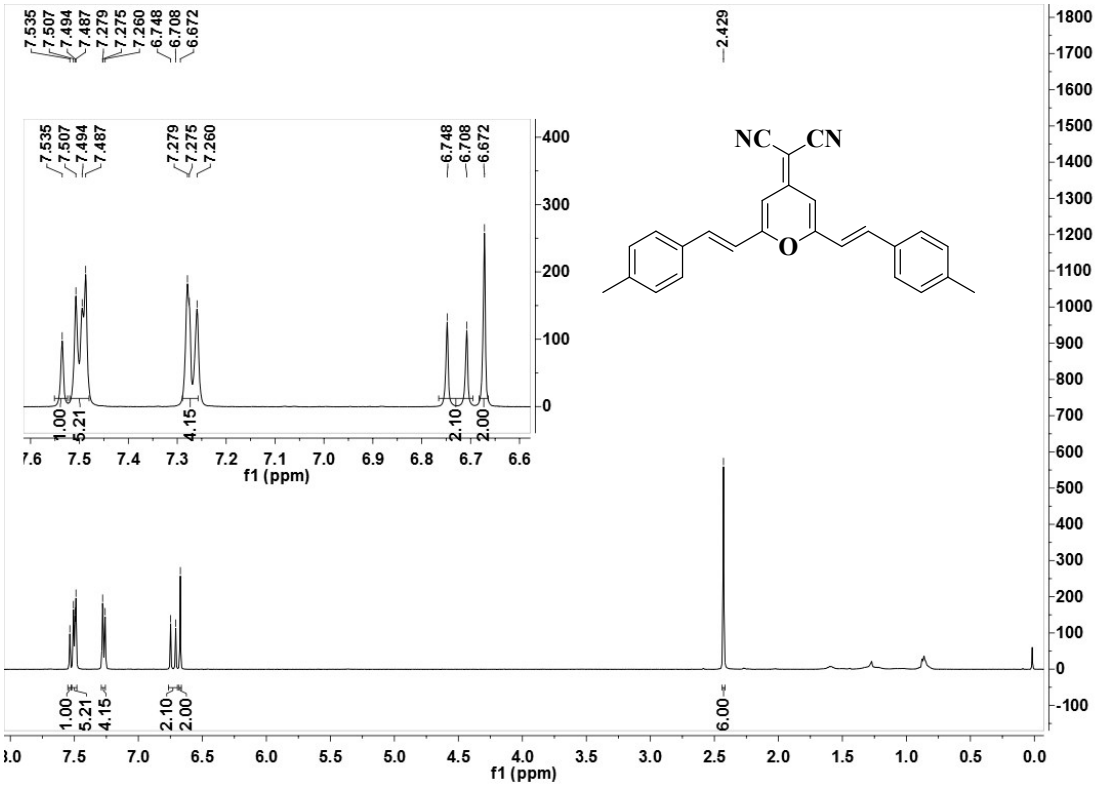



**Fig. S19** $^{1}$H NMR of **1b** ($CDCl_3$, 400 MHz).

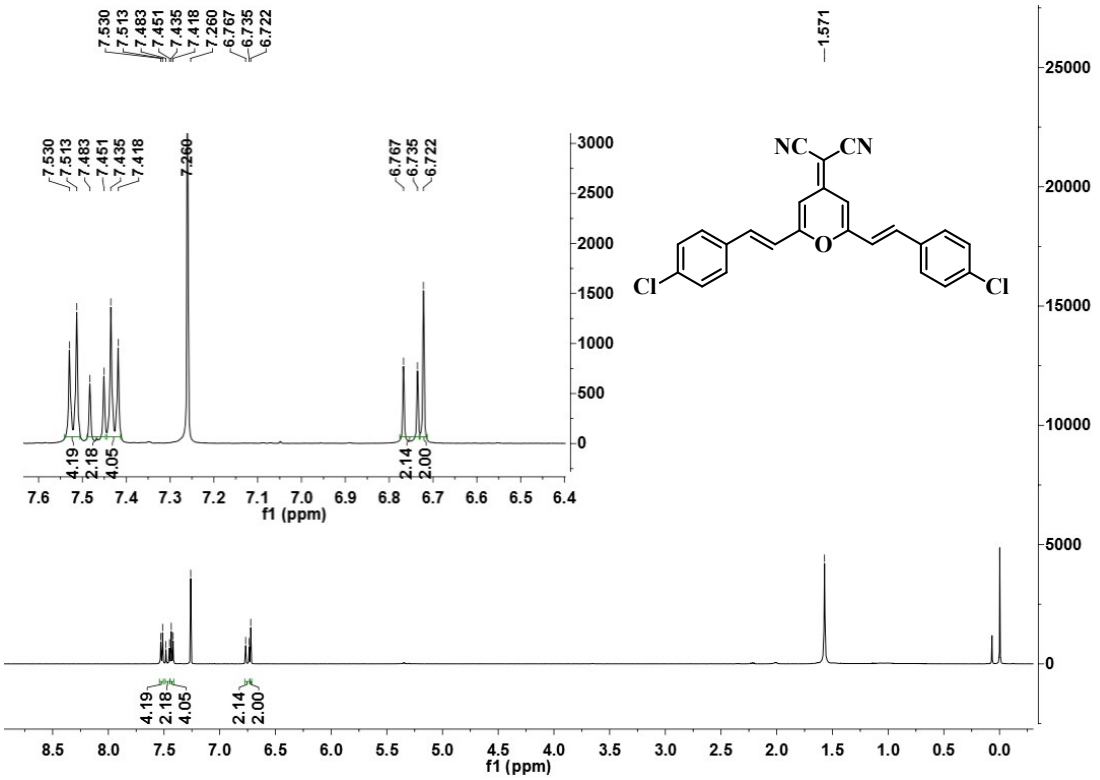



**Fig. S20** $^1$H NMR of **1e** ($CDCl_3$, 500 MHz).

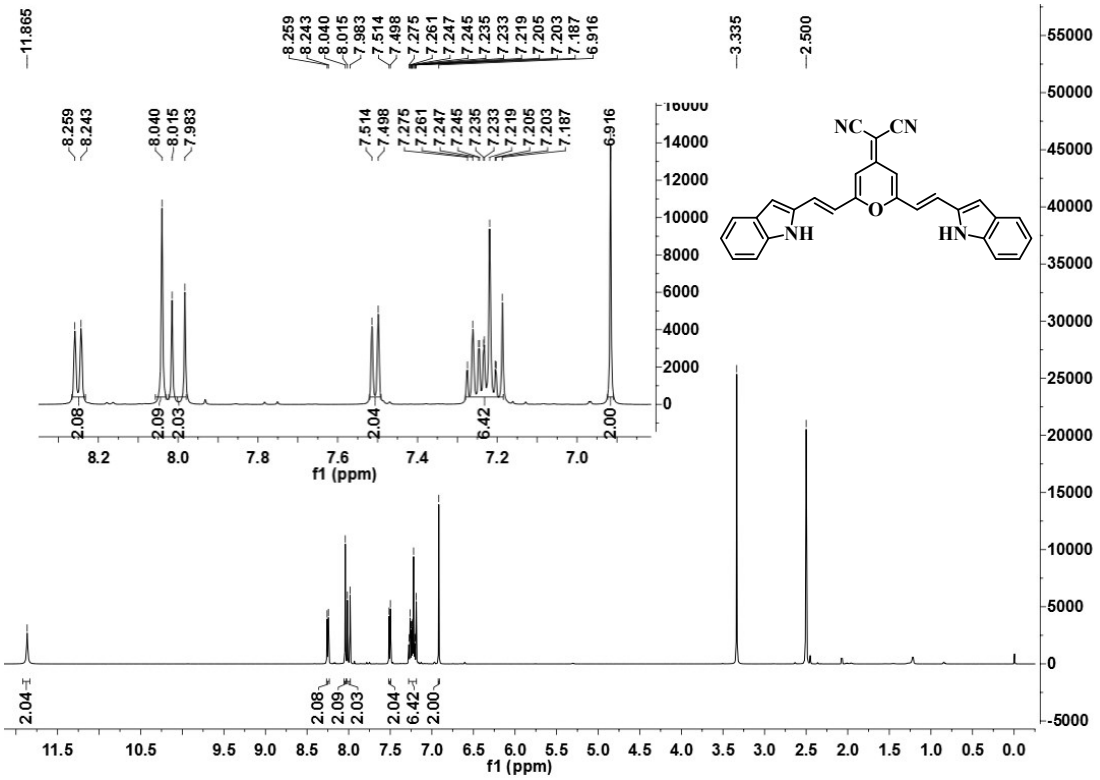



**Fig. S21** $^1$H NMR of **1n** (DMSO-$d_6$, 500 MHz).

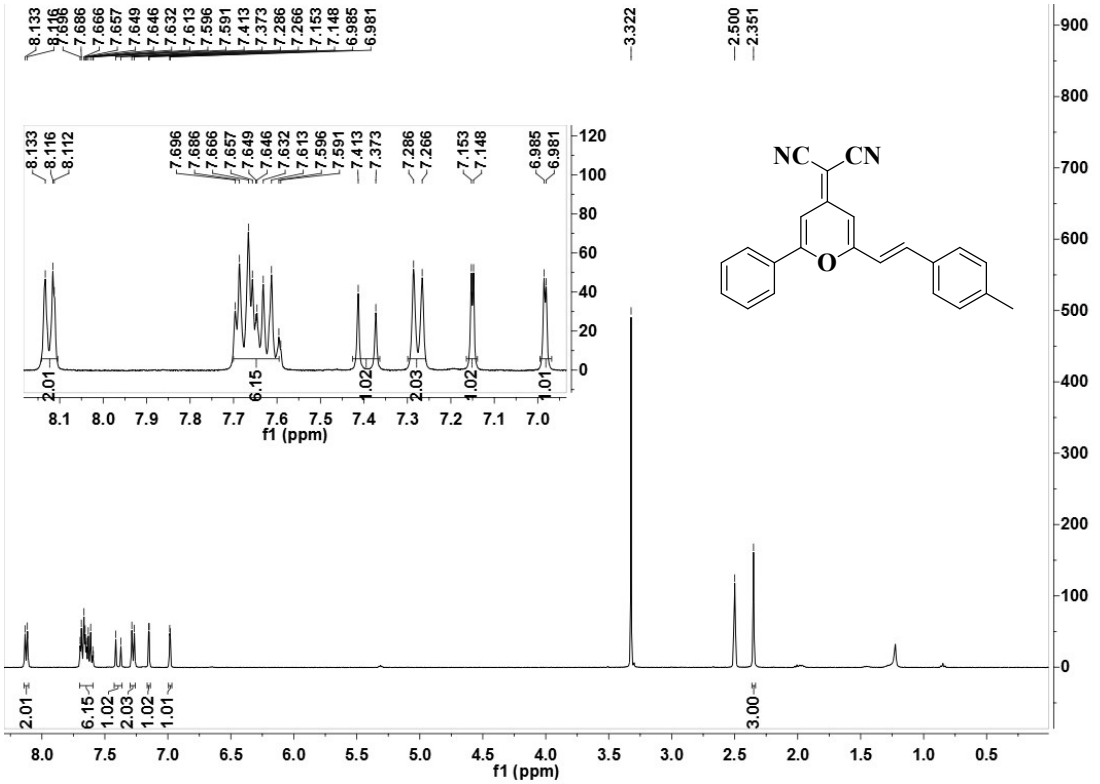



**Fig. S22** $^1$H NMR of **8a** (DMSO-$d_6$, 400 MHz).

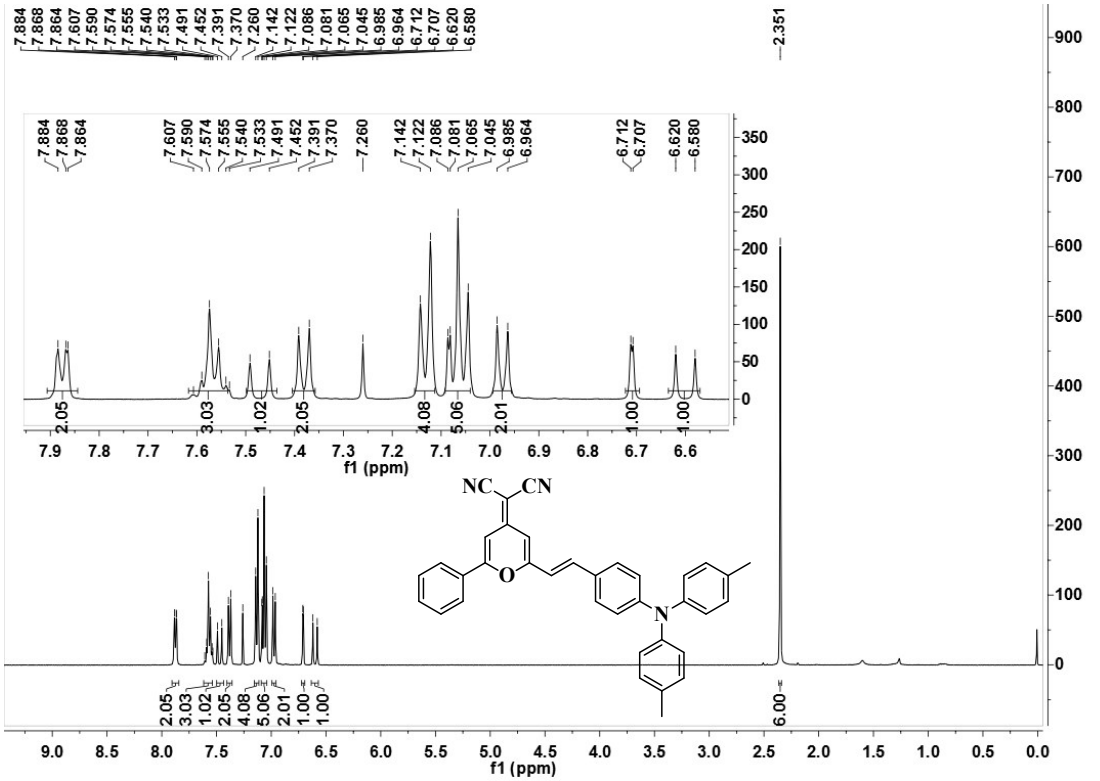



**Fig. S23** $^1$H NMR of **8c** ($CDCl_3$, 400 MHz).

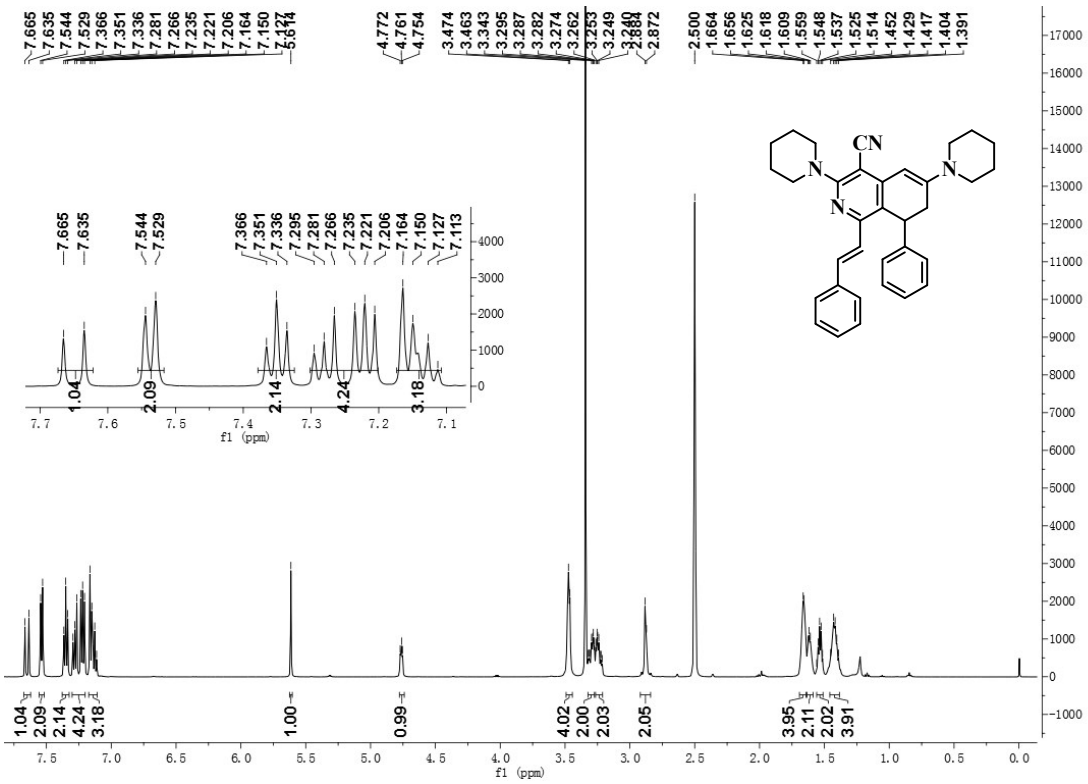


**Fig. S24** $^{1}$H NMR of **3aa** (DMSO-$d_6$, 500 MHz).

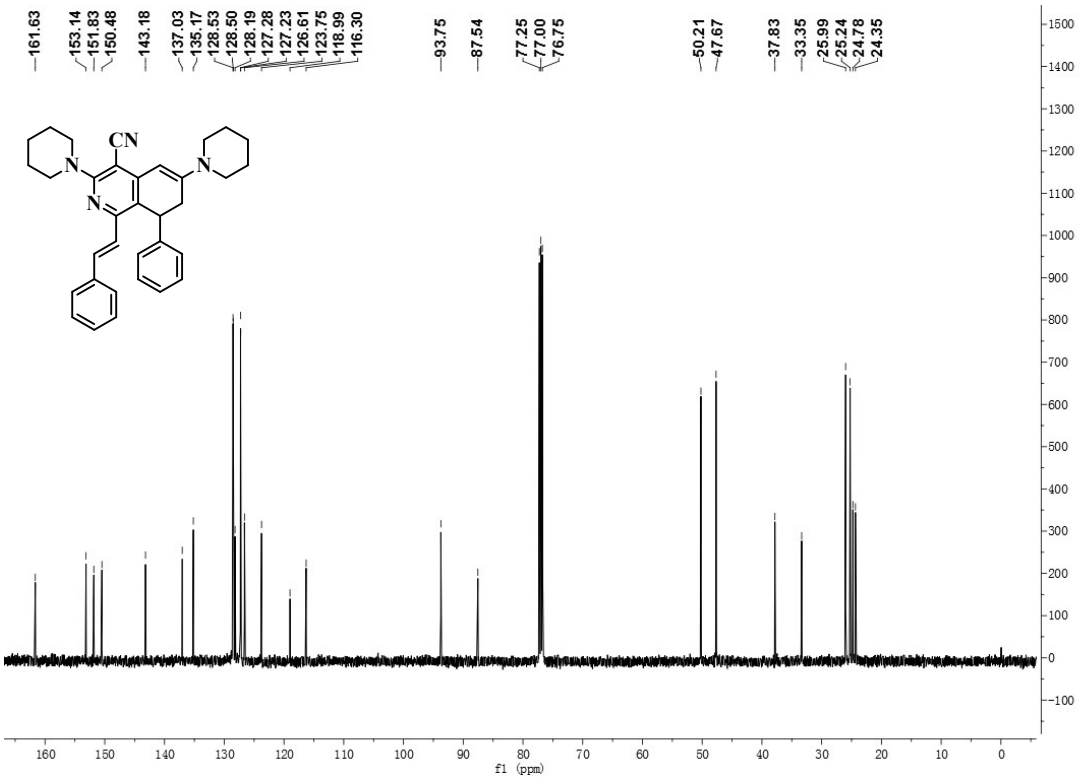


**Fig. S25** $^{13}$C NMR of **3aa** ($CDCl_3$, 125 MHz).

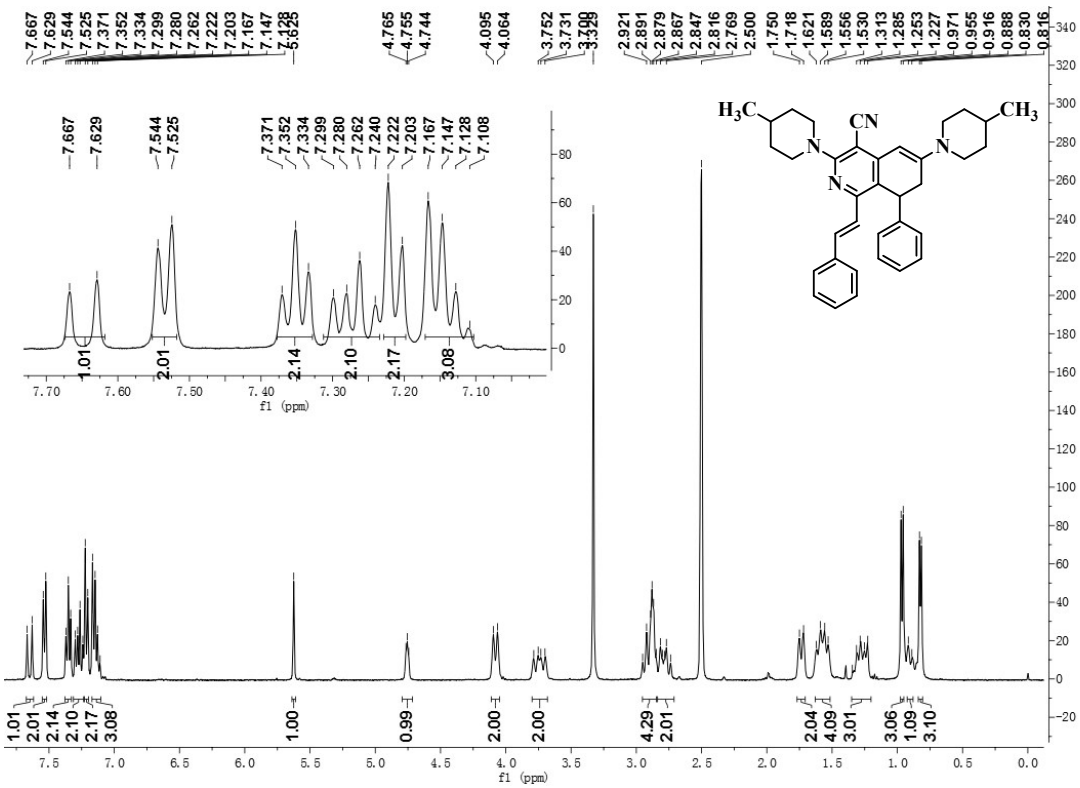


**Fig. S26** $^{1}$H NMR of **3ab** (DMSO-$d_6$, 400 MHz).

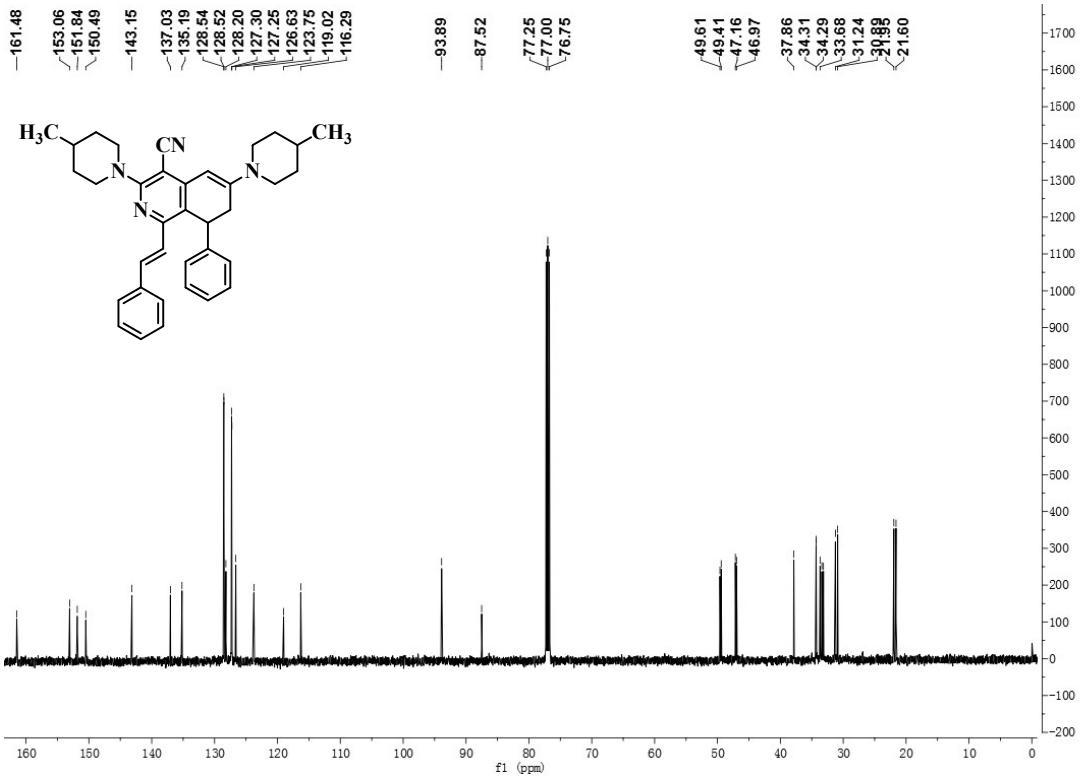


**Fig. S27** $^{13}$C NMR of **3ab** ($CDCl_3$, 125 MHz).

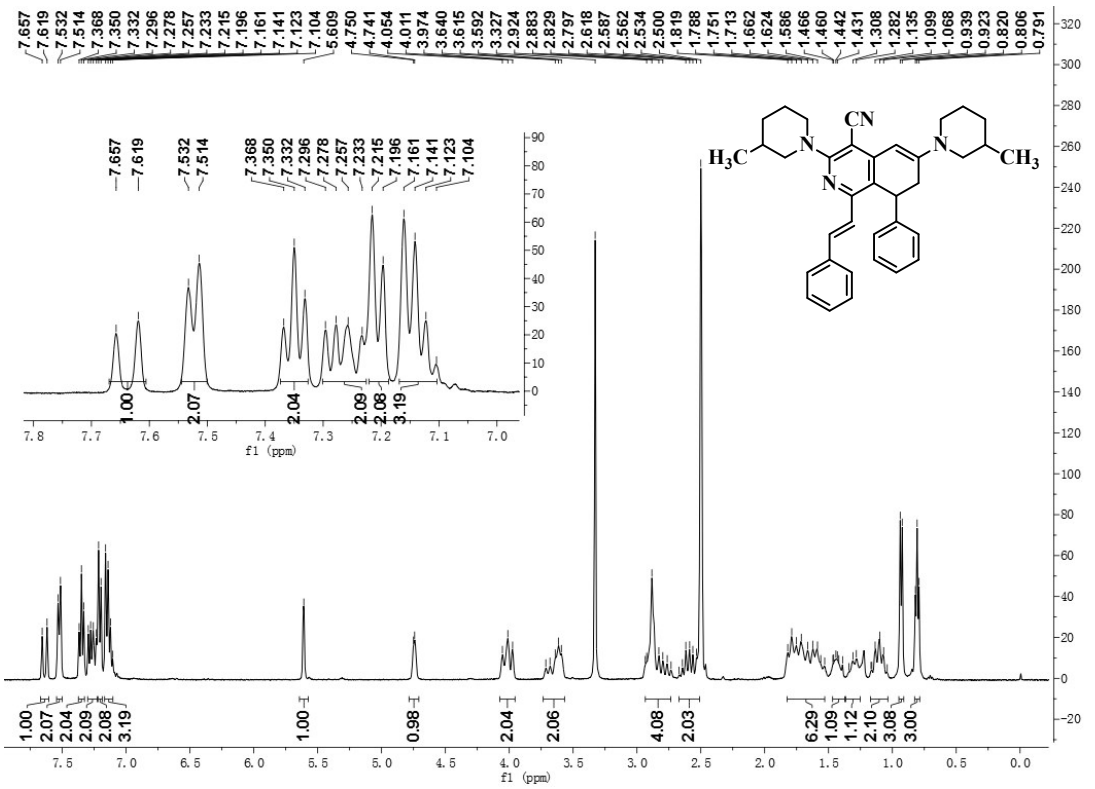


**Fig. S28** $^{1}$H NMR of **3ac** (DMSO-$d_6$, 400 MHz).

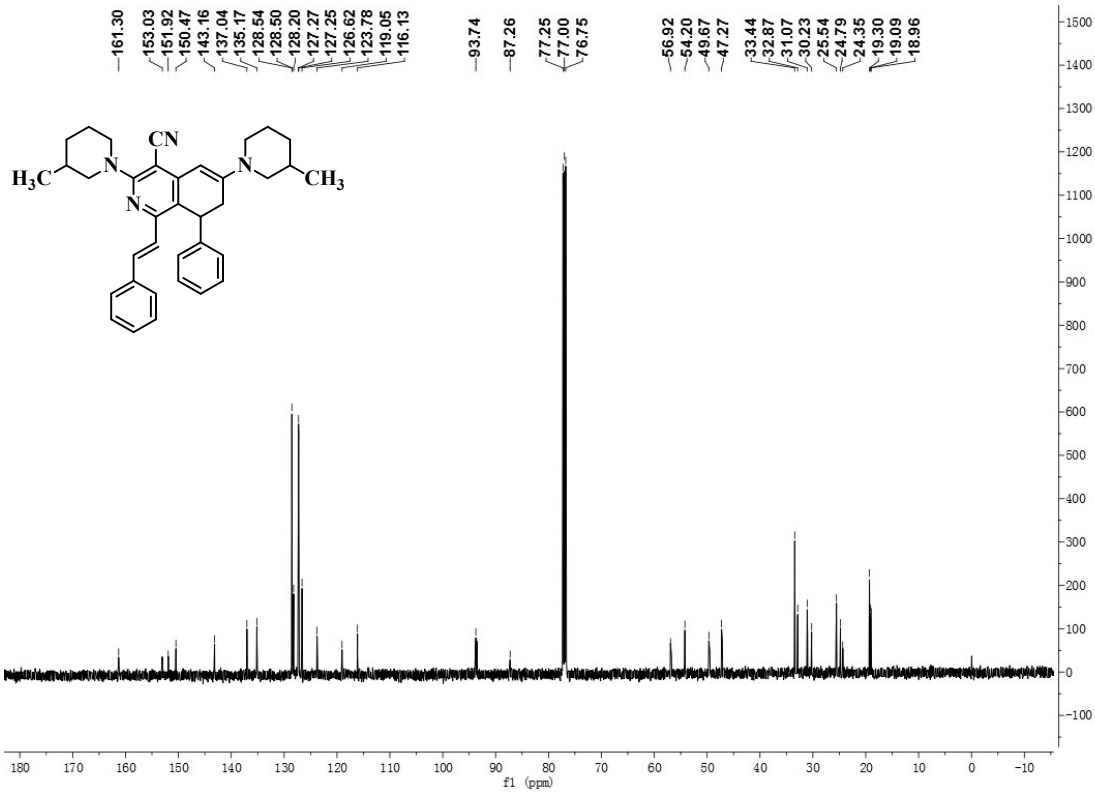
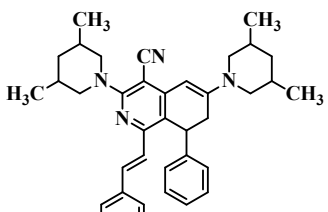


**Fig. S29** $^{13}$C NMR of **3ac** ($CDCl_3$, 125 MHz).





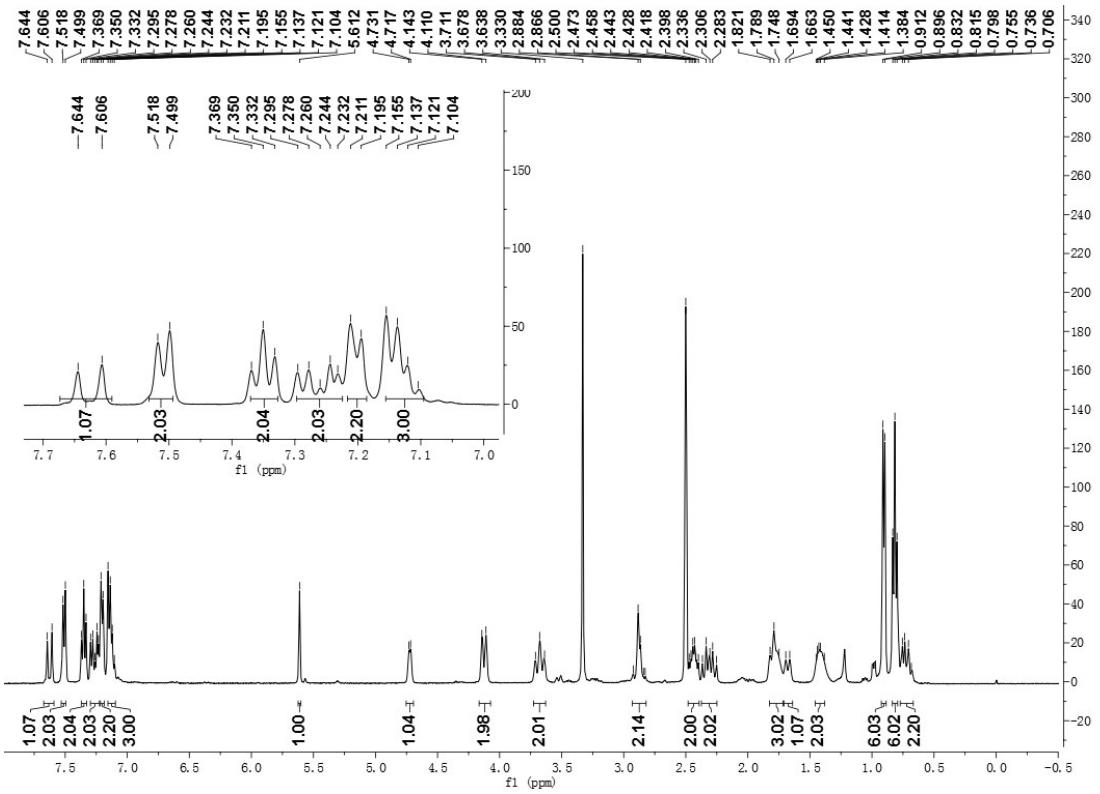


**Fig. S30** $^{1}$H NMR of **3ae** (DMSO-$d_6$, 400 MHz).

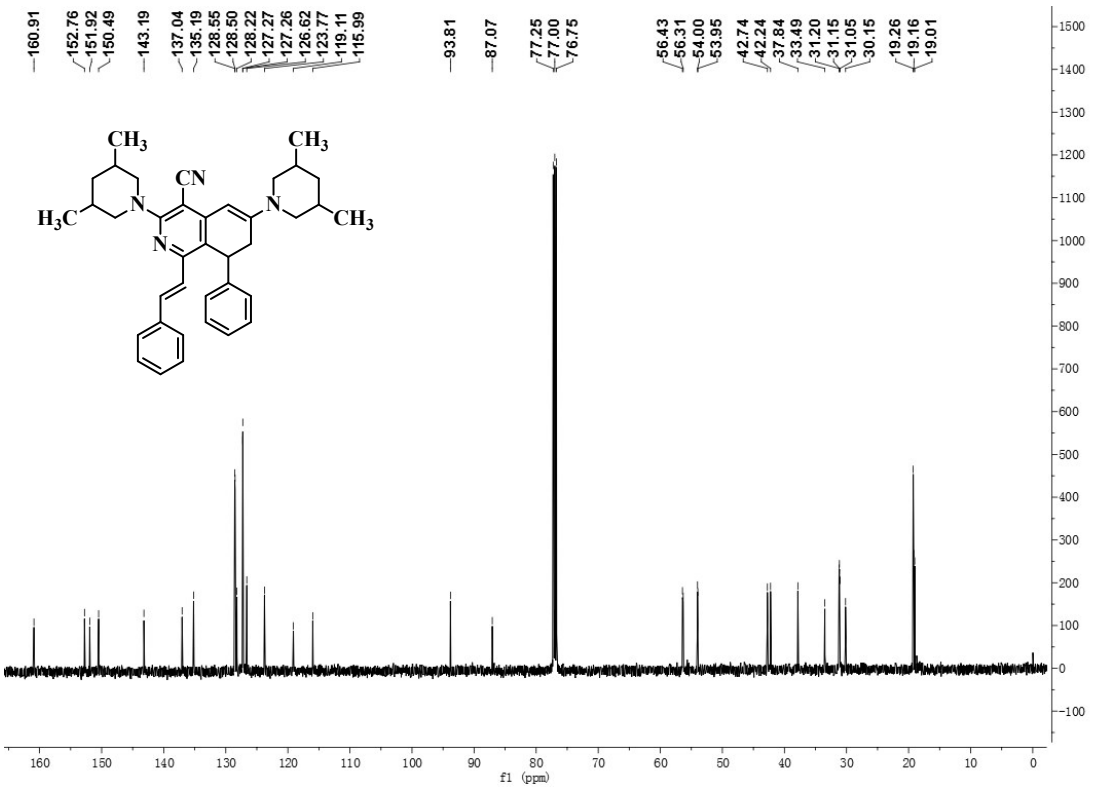


**Fig. S31** $^{13}$C NMR of **3ae** ($CDCl_3$, 125 MHz).

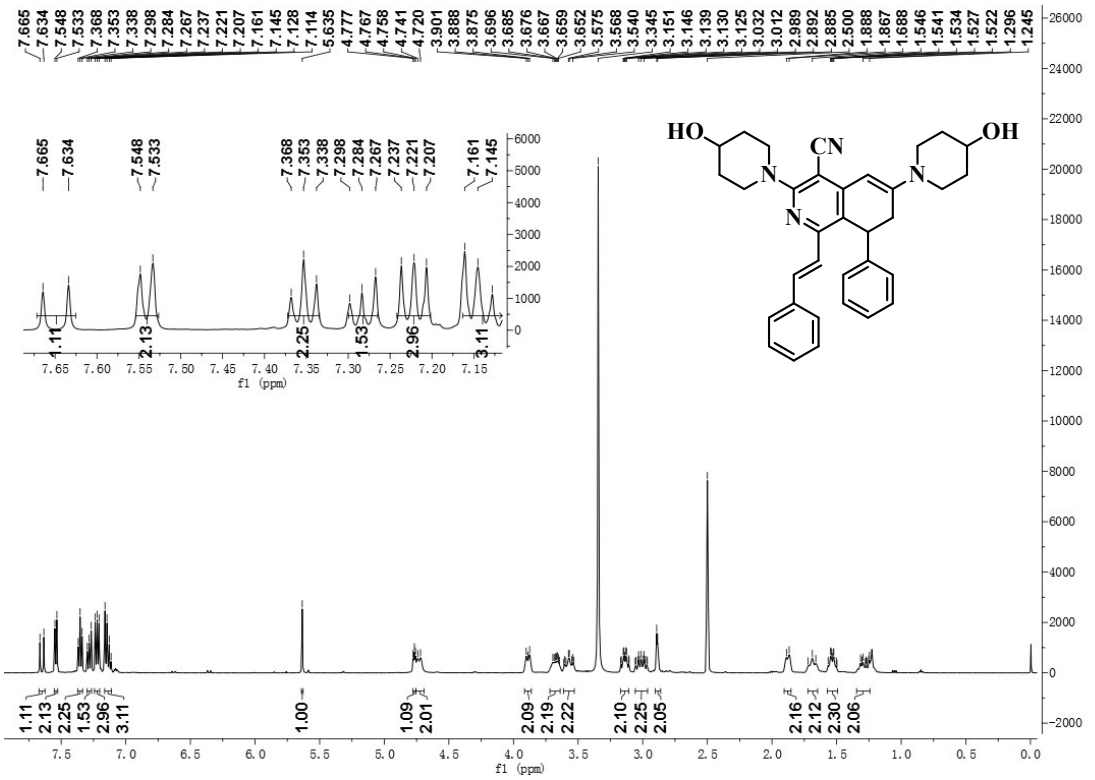



**Fig. S32** $^{1}$H NMR of **3af** (DMSO-$d_6$, 500 MHz).

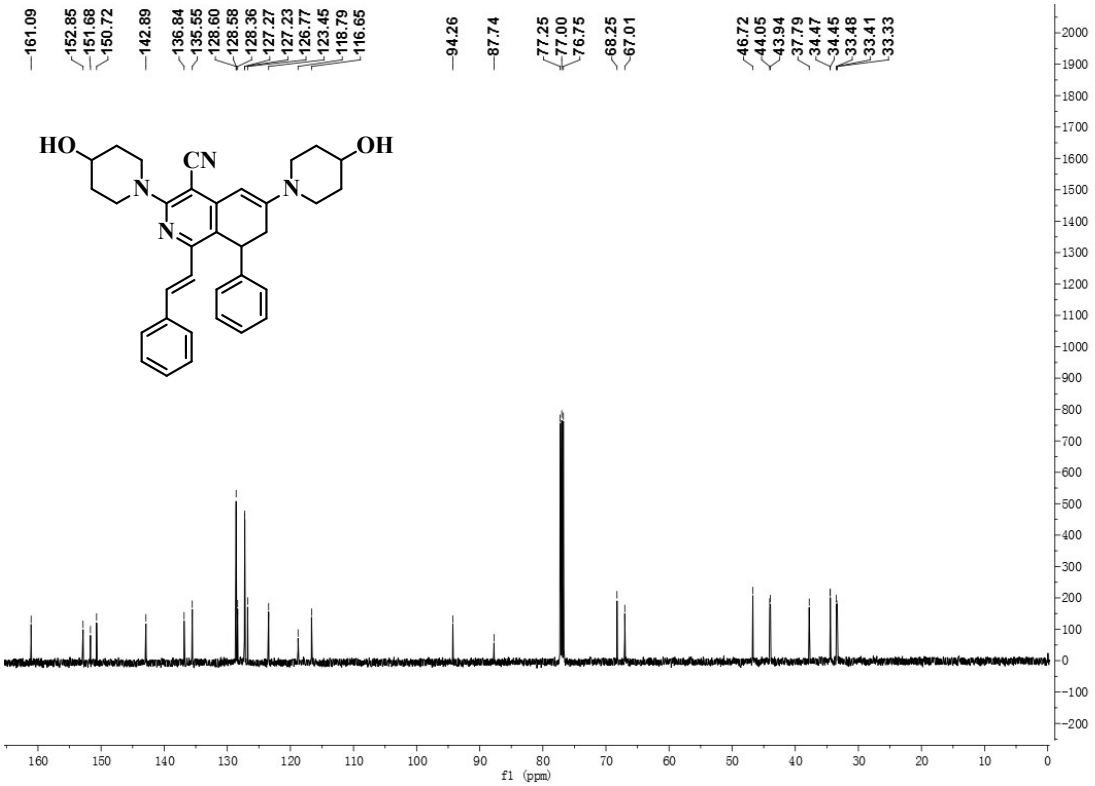



**Fig. S33** $^{13}$C NMR of **3af** ($CDCl_3$, 125 MHz).

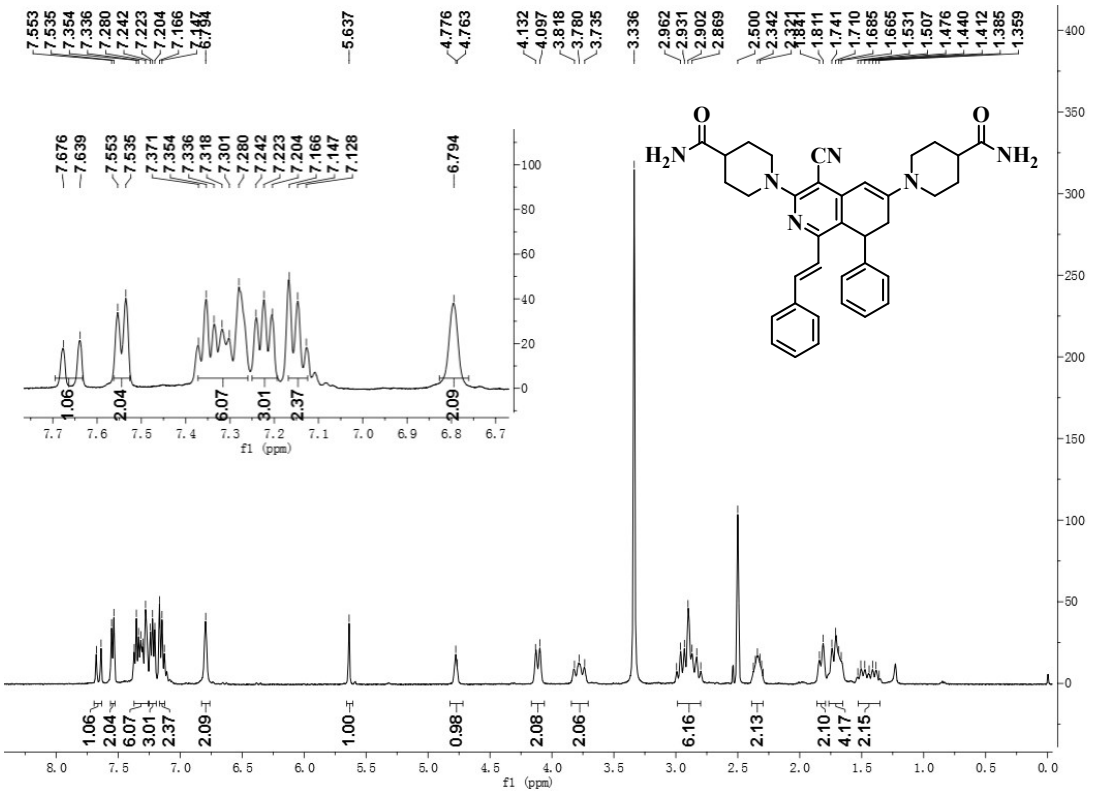


**Fig. S34** $^{1}$H NMR of **3ah** (DMSO-$d_6$, 400 MHz).

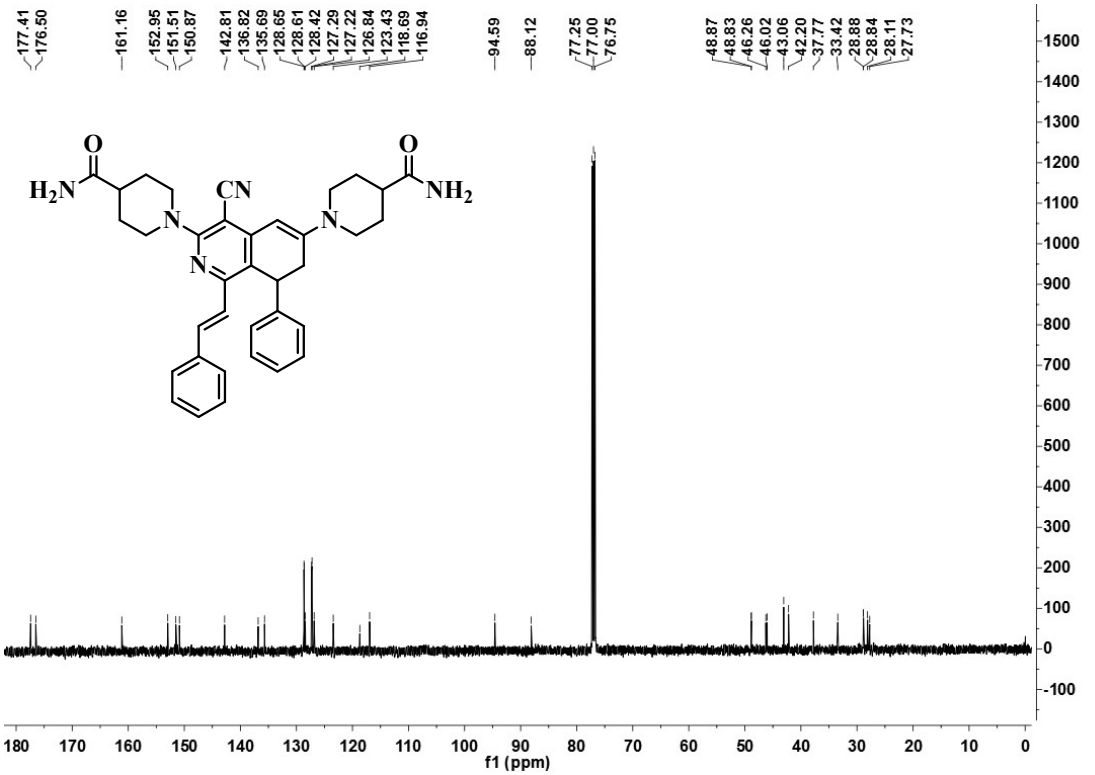


**Fig. S35** $^{13}$C NMR of **3ah** ($CDCl_3$, 125 MHz).

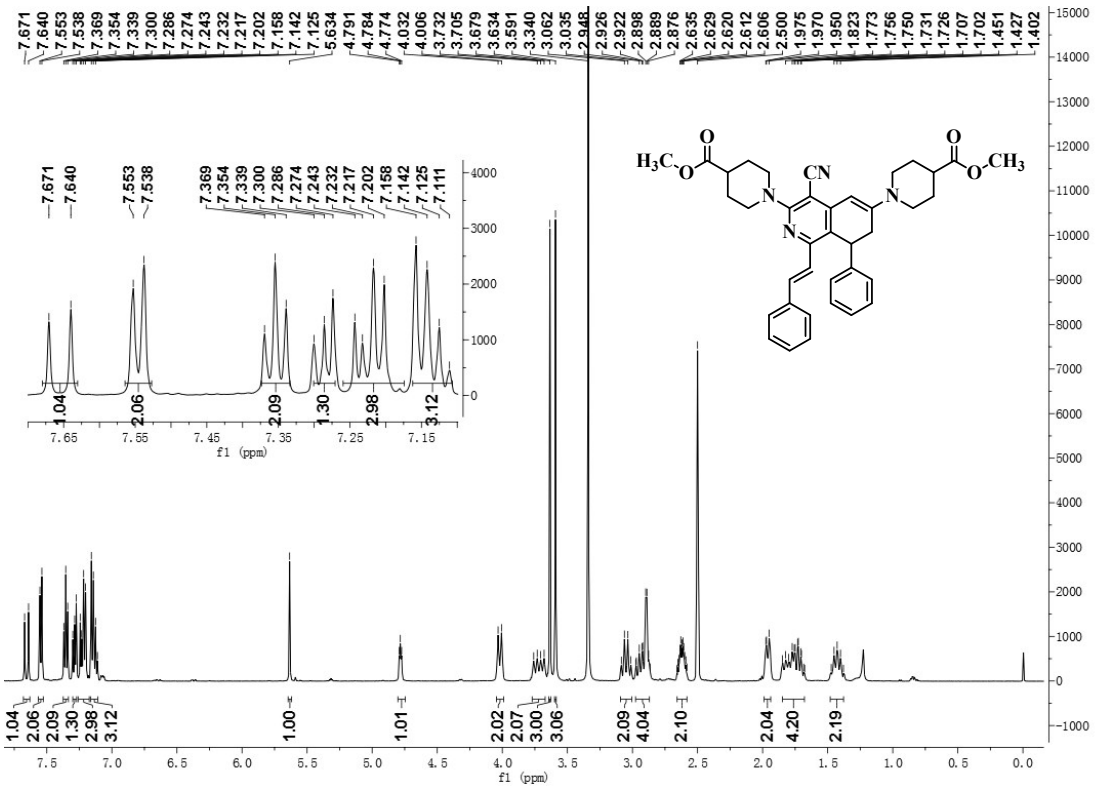


**Fig. S36** $^{1}$H NMR of **3ai** (DMSO-$d_6$, 500 MHz).

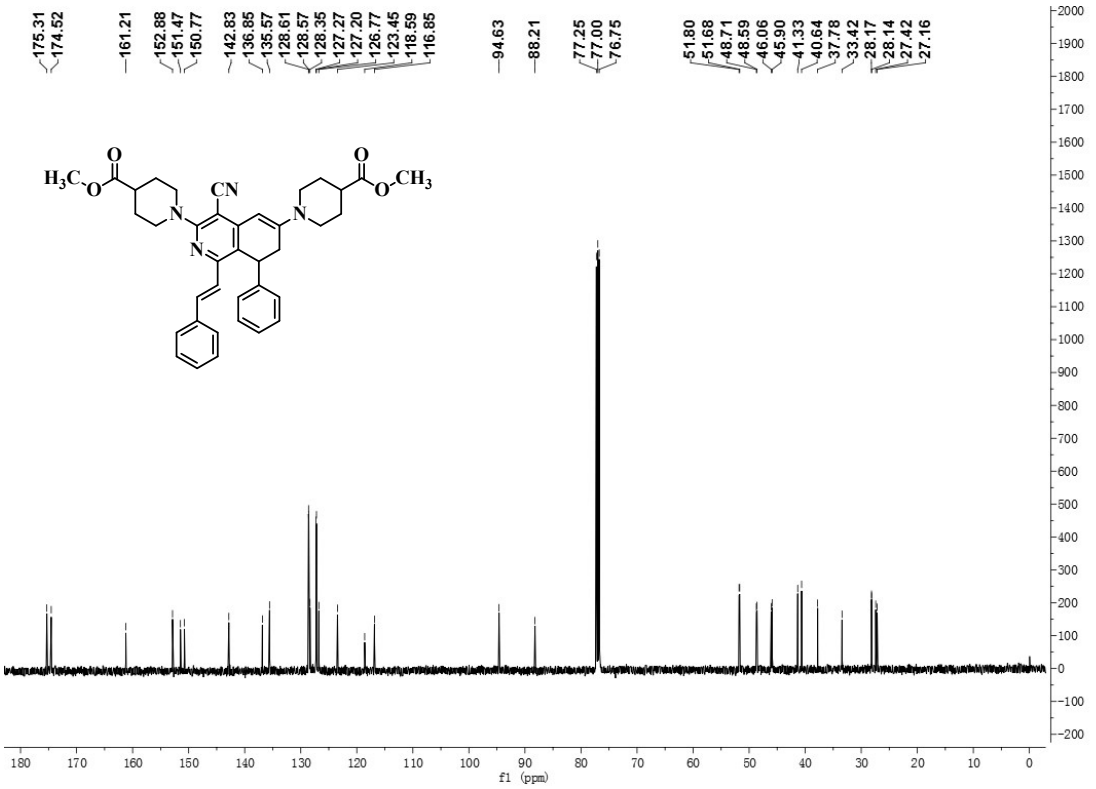


**Fig. S37** $^{13}$C NMR of **3ai** ($CDCl_3$, 125 MHz).

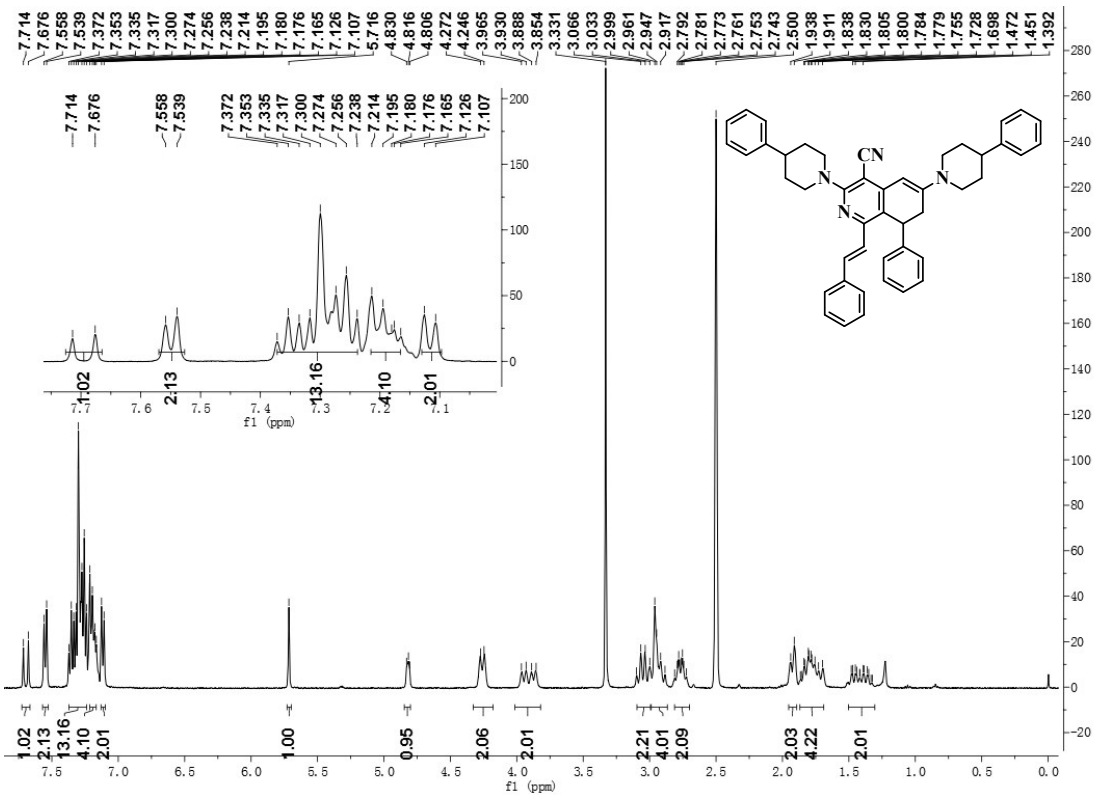



**Fig. S38** $^{1}$H NMR of **3aj** (DMSO-$d_6$, 400 MHz).

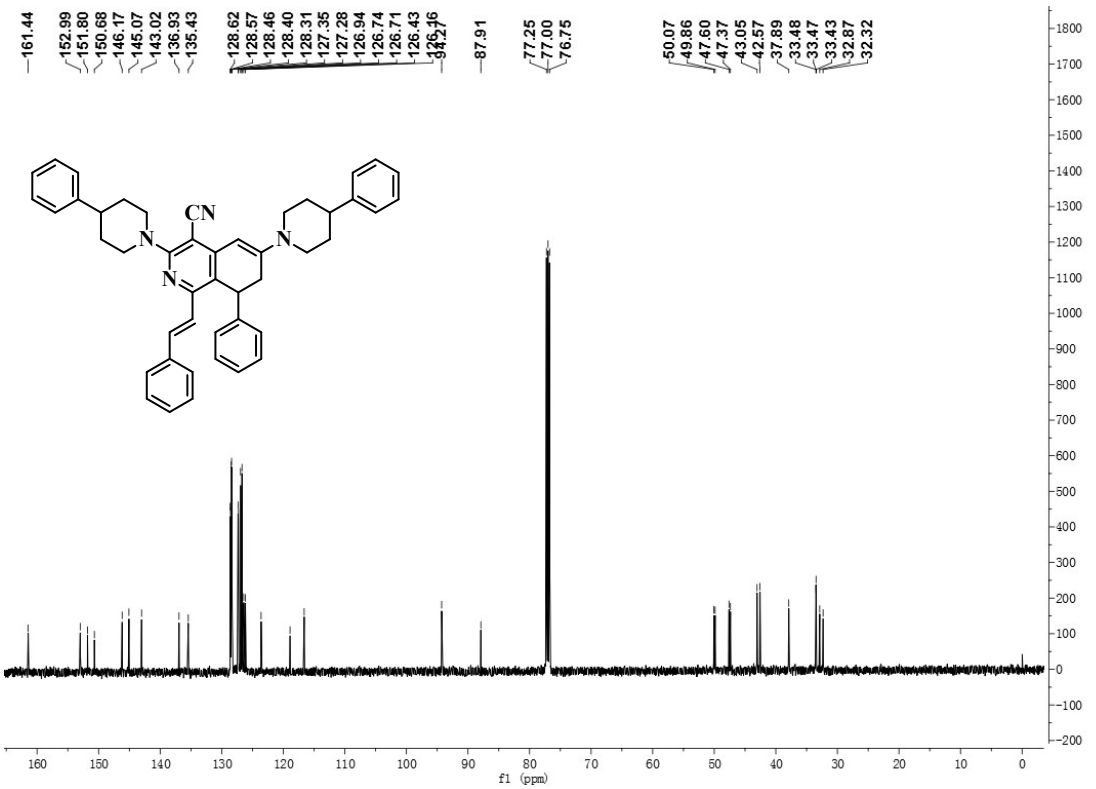



**Fig. S39** $^{13}$C NMR of **3aj** ($CDCl_3$, 125 MHz).

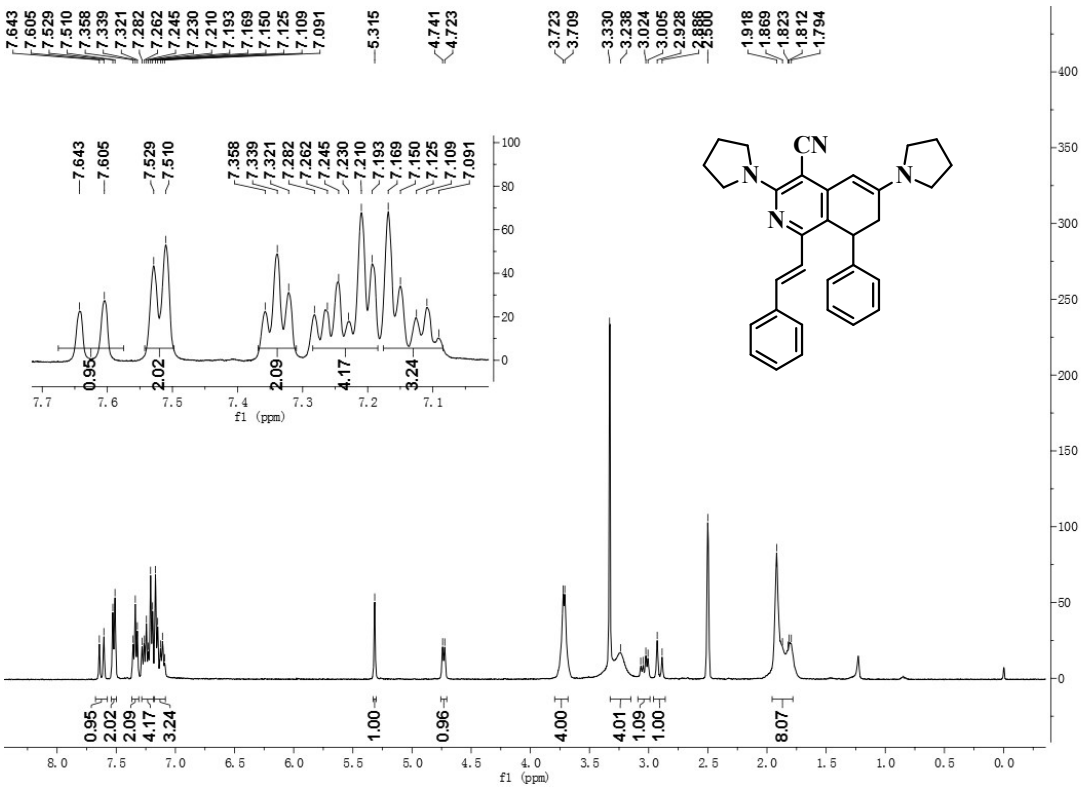


**Fig. S40** $^{1}$H NMR of **3ak** (DMSO-$d_6$, 400 MHz).

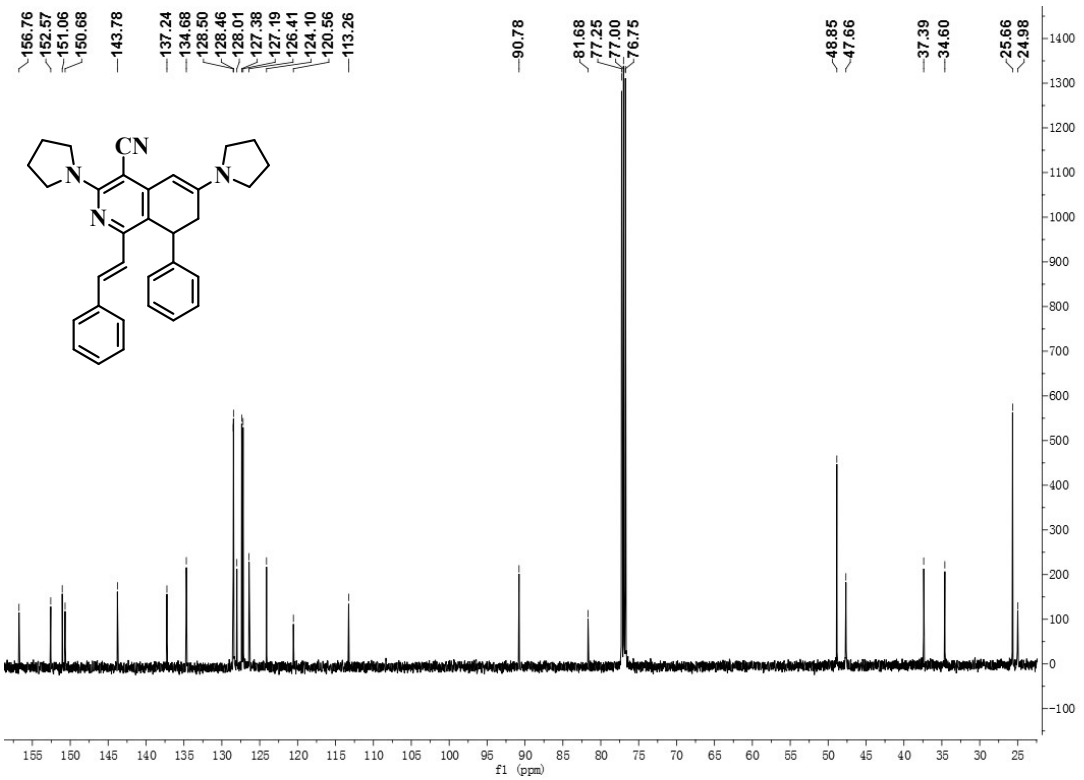


**Fig. S41** $^{13}$C NMR of **3ak** ($CDCl_3$, 125 MHz).

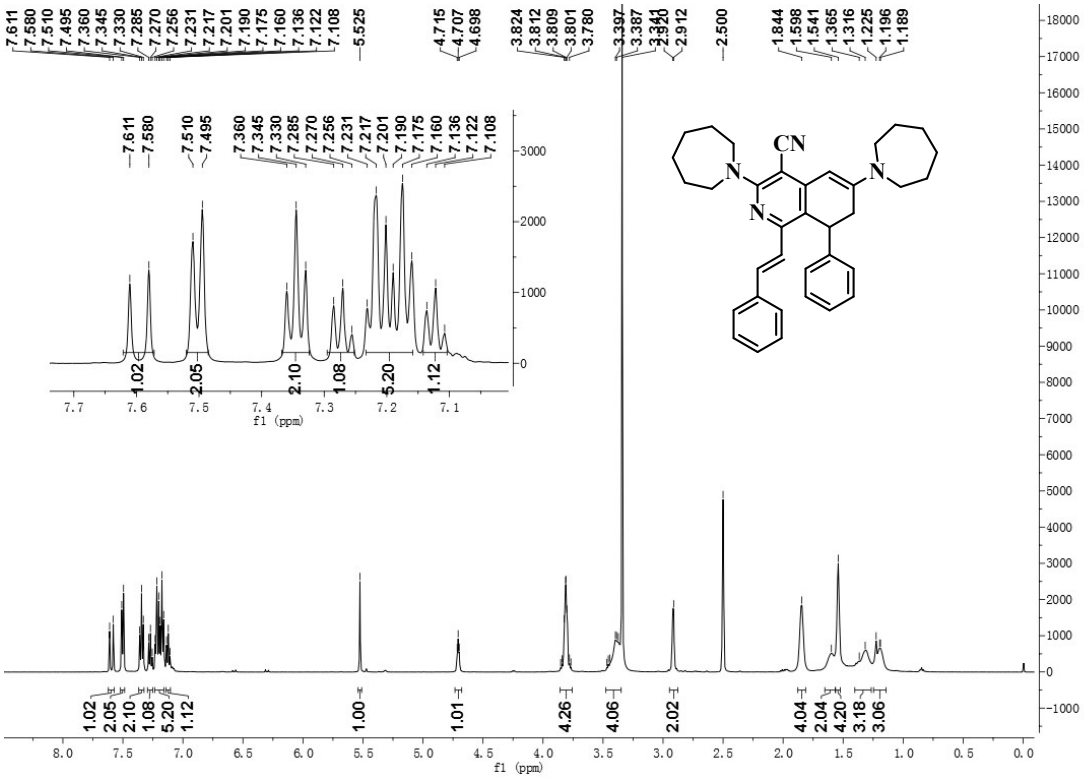



**Fig. S42** $^{1}$H NMR of **3al** (DMSO-$d_6$, 500 MHz).

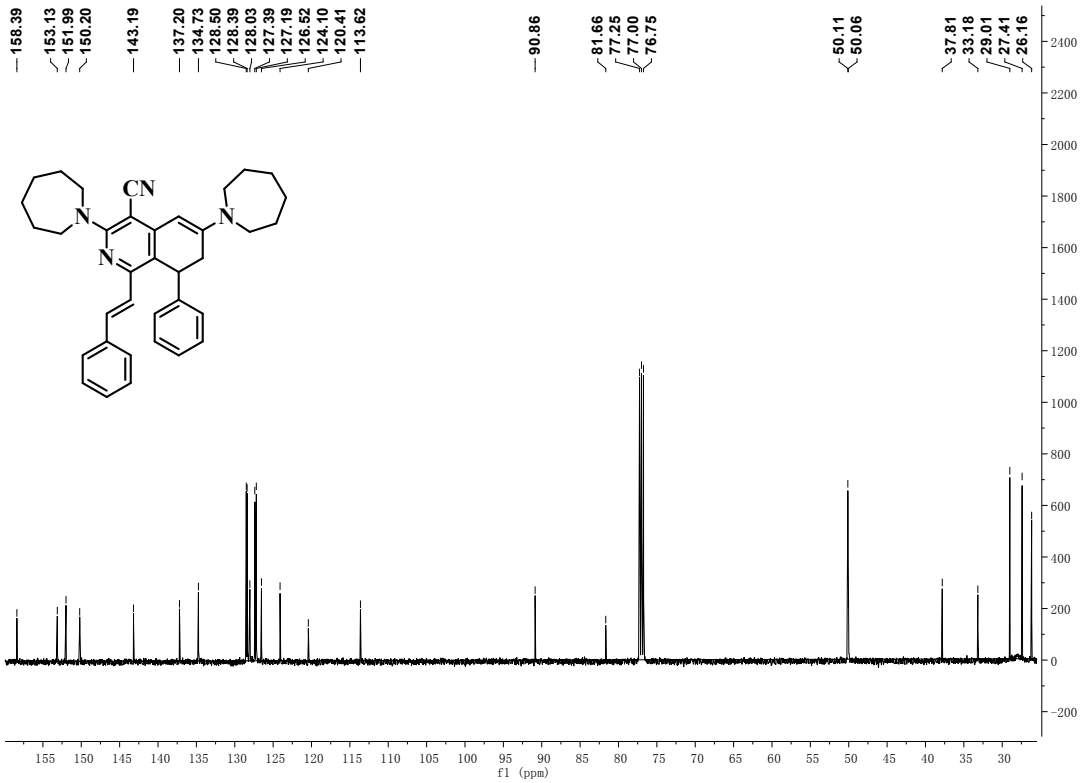



**Fig. S43** $^{13}$C NMR of **3al** ($CDCl_3$, 125 MHz).

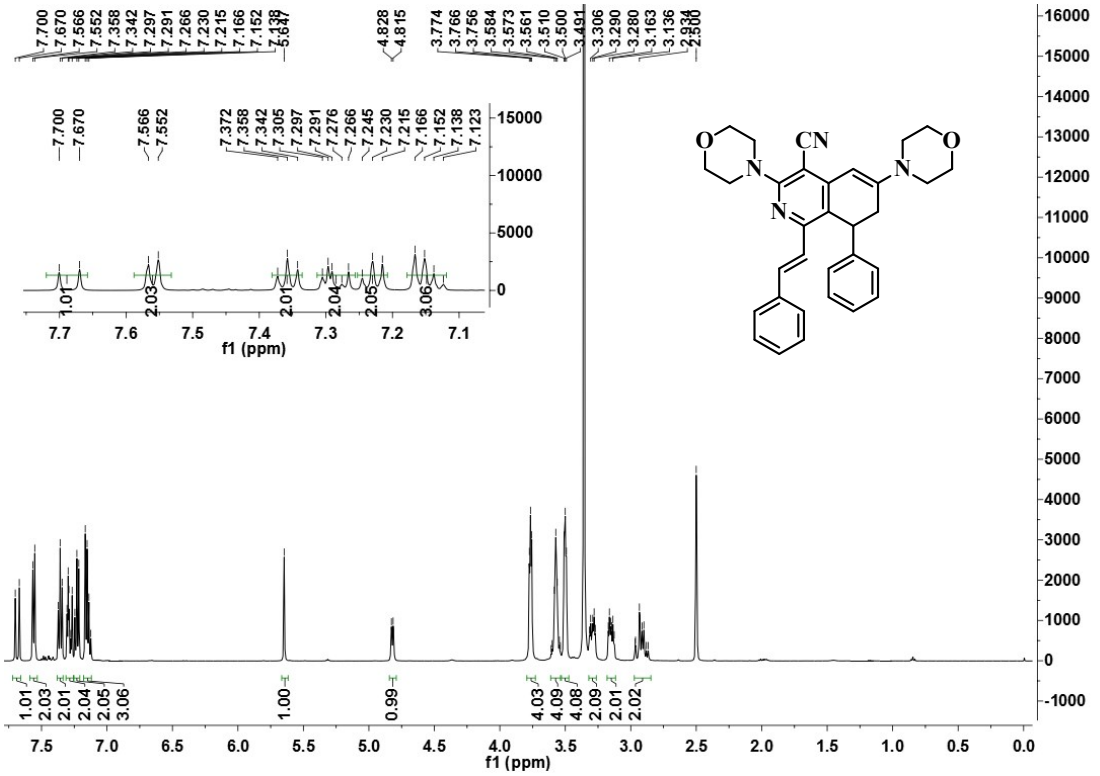



**Fig. S44** $^{1}$H NMR of **3am** (DMSO-$d_6$, 500 MHz).

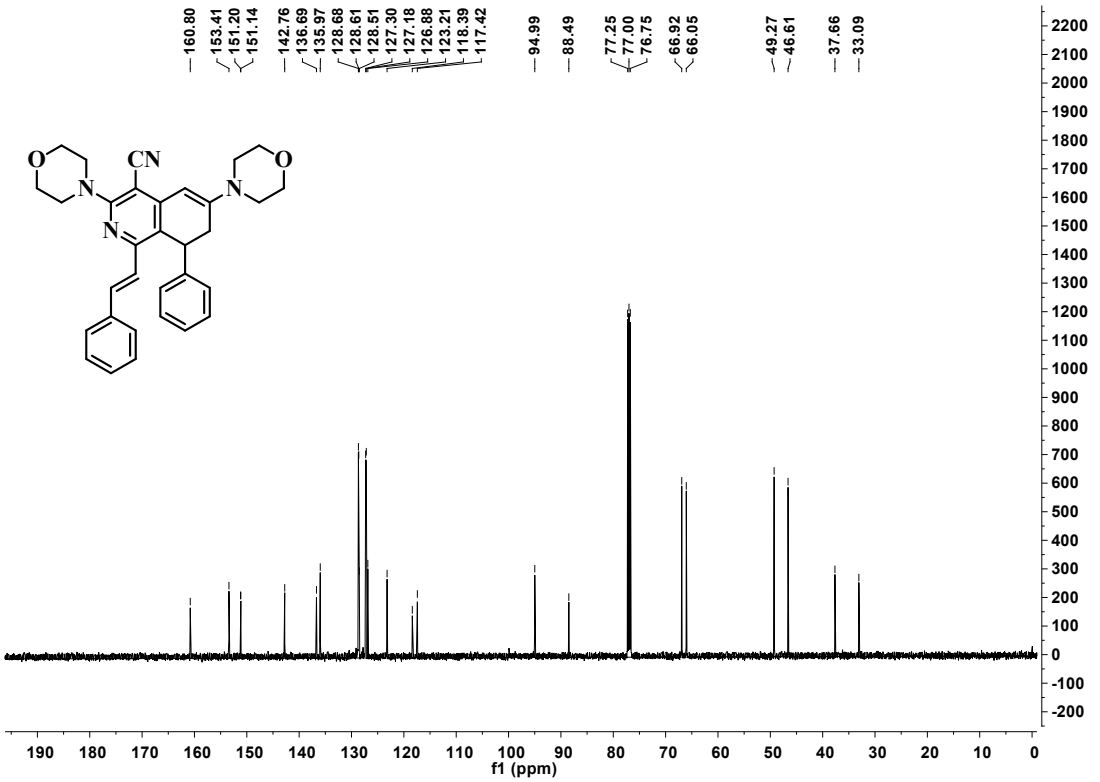



**Fig. S45** $^{13}$C NMR of **3am** ($CDCl_3$, 125 MHz).

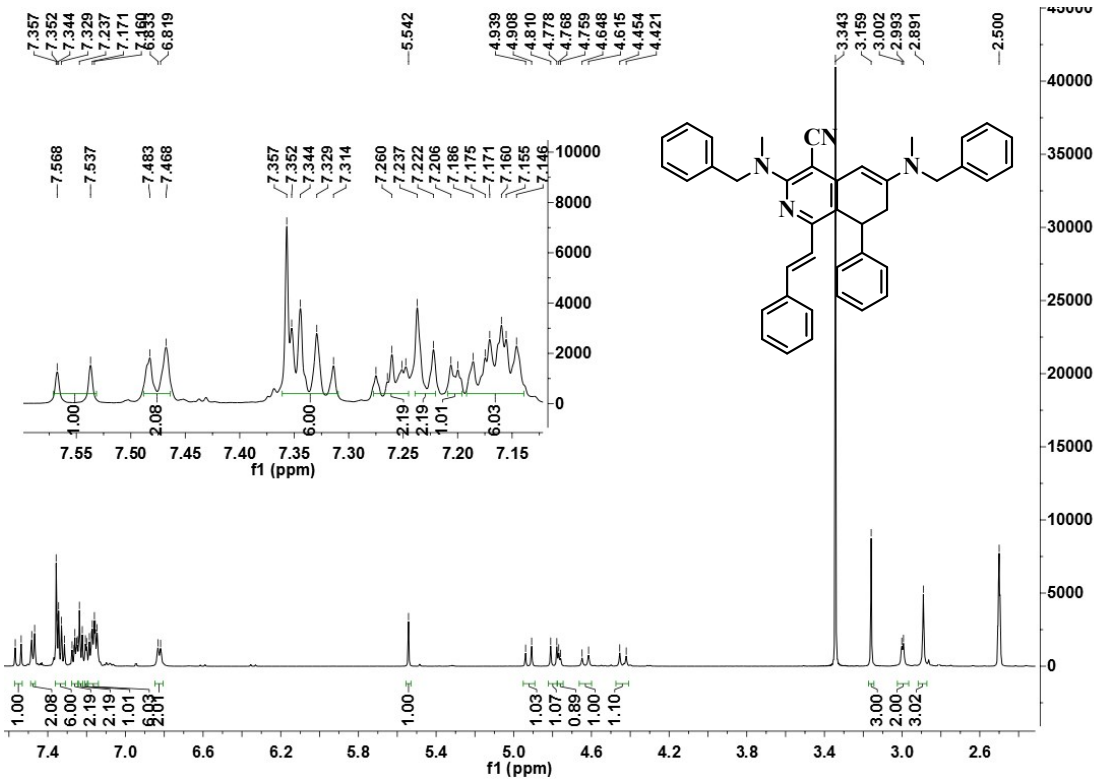



**Fig. S46** $^{1}$H NMR of **3an** (DMSO-$d_6$, 500 MHz).

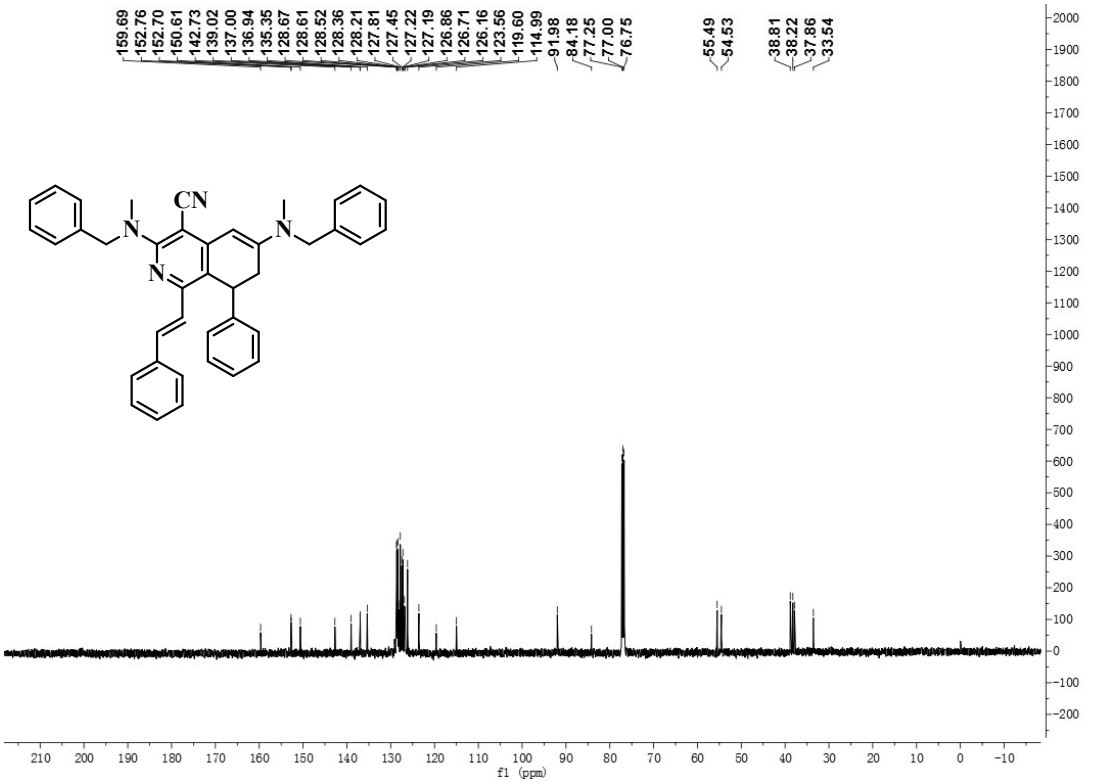



**Fig. S47** $^{13}$C NMR of **3an** ($CDCl_3$, 125 MHz).

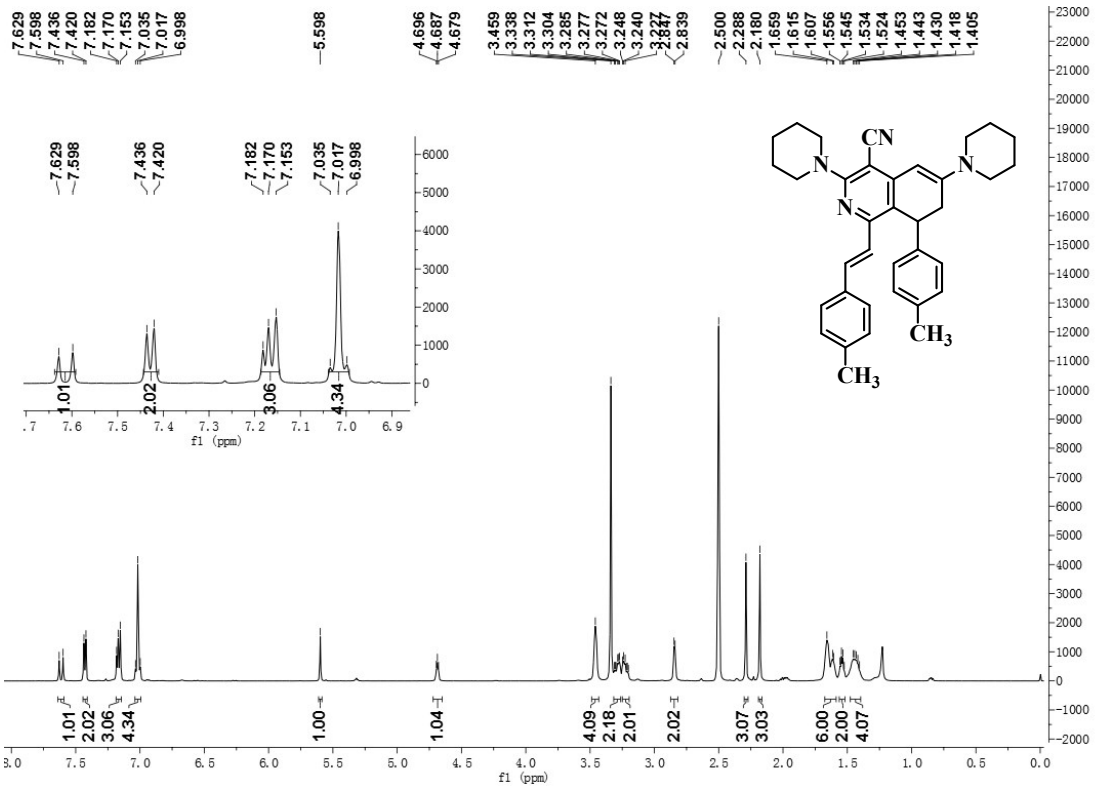



**Fig. S48** $^{1}$H NMR of **3ba** (DMSO-$d_6$, 500 MHz).

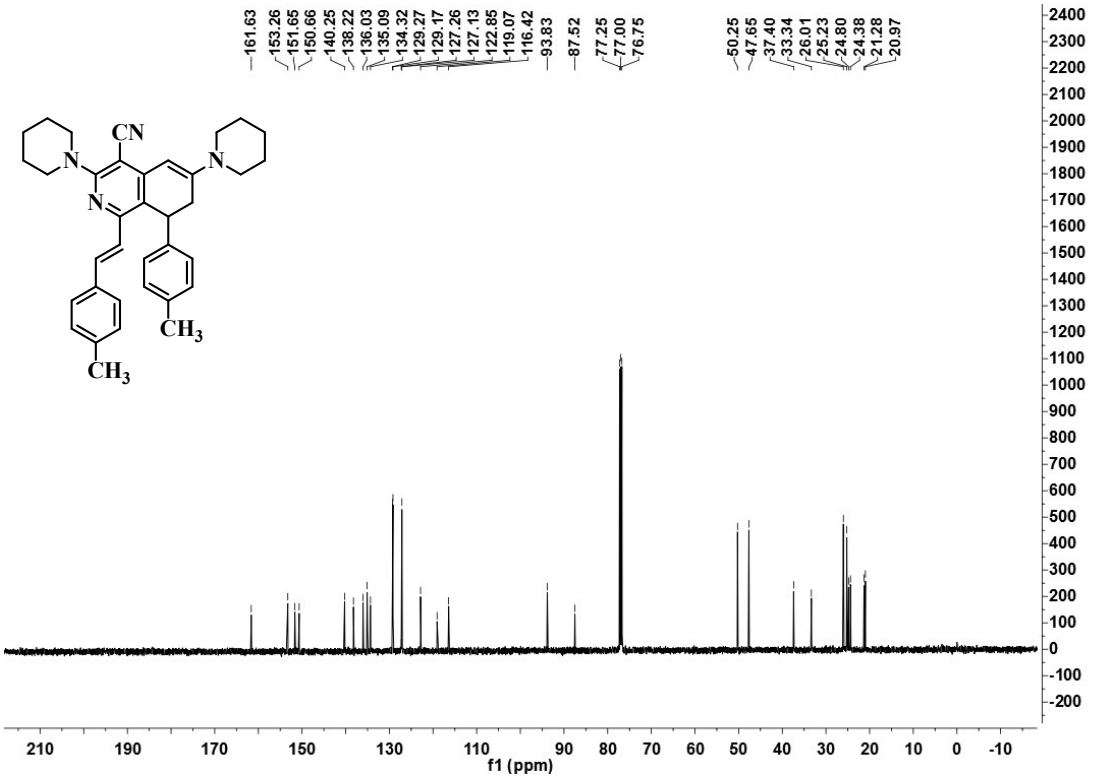



**Fig. S49** $^{13}$C NMR of **3ba** ($CDCl_3$, 125 MHz).

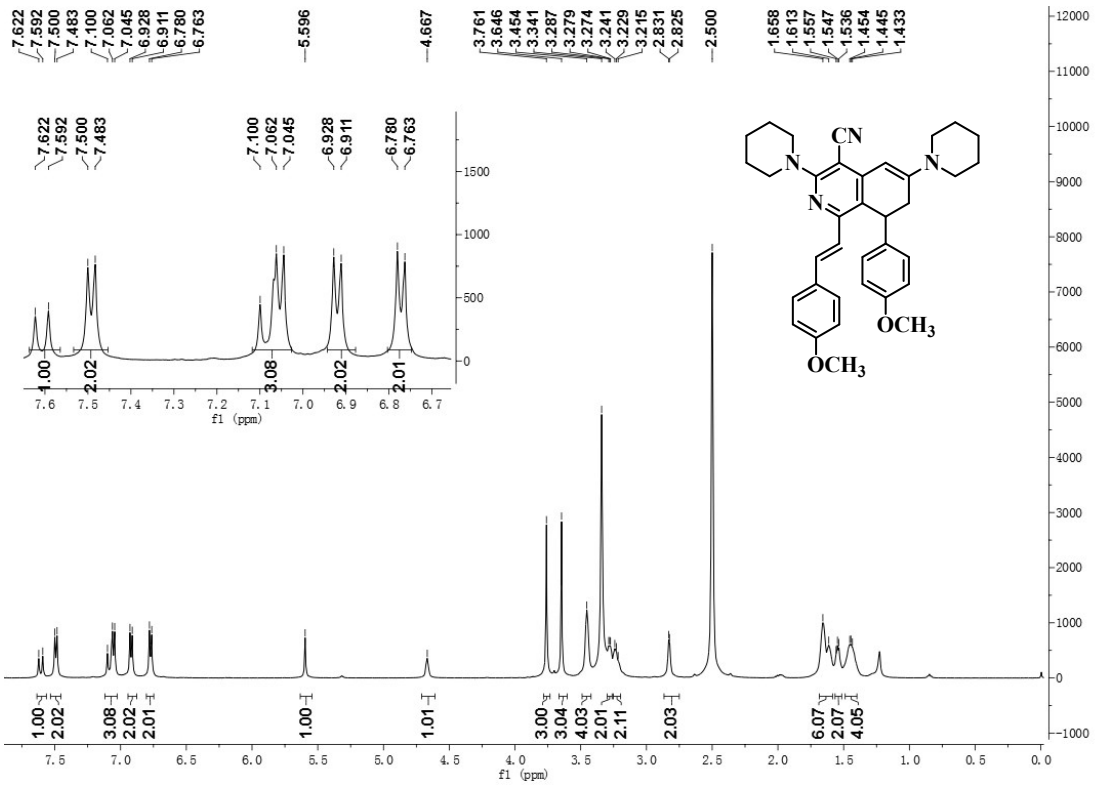



**Fig. S50** $^{1}$H NMR of **3ca** (DMSO-$d_6$, 500 MHz).

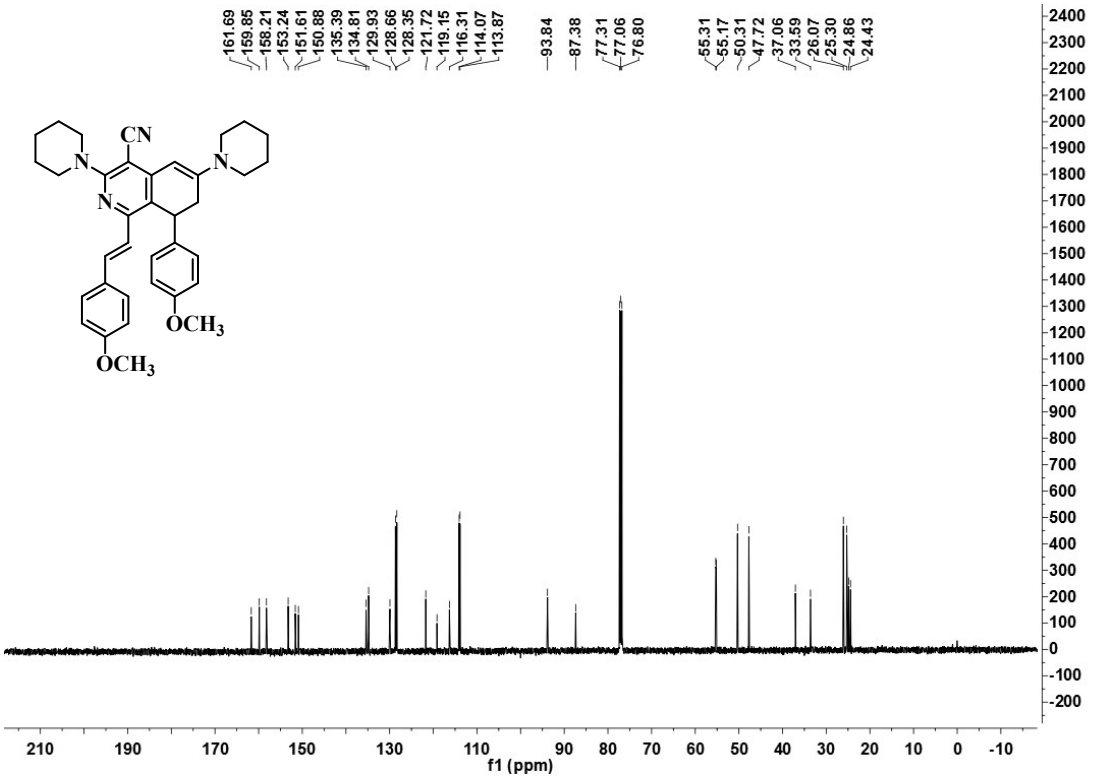



**Fig. S51** $^{13}$C NMR of **3ca** ($CDCl_3$, 125 MHz).

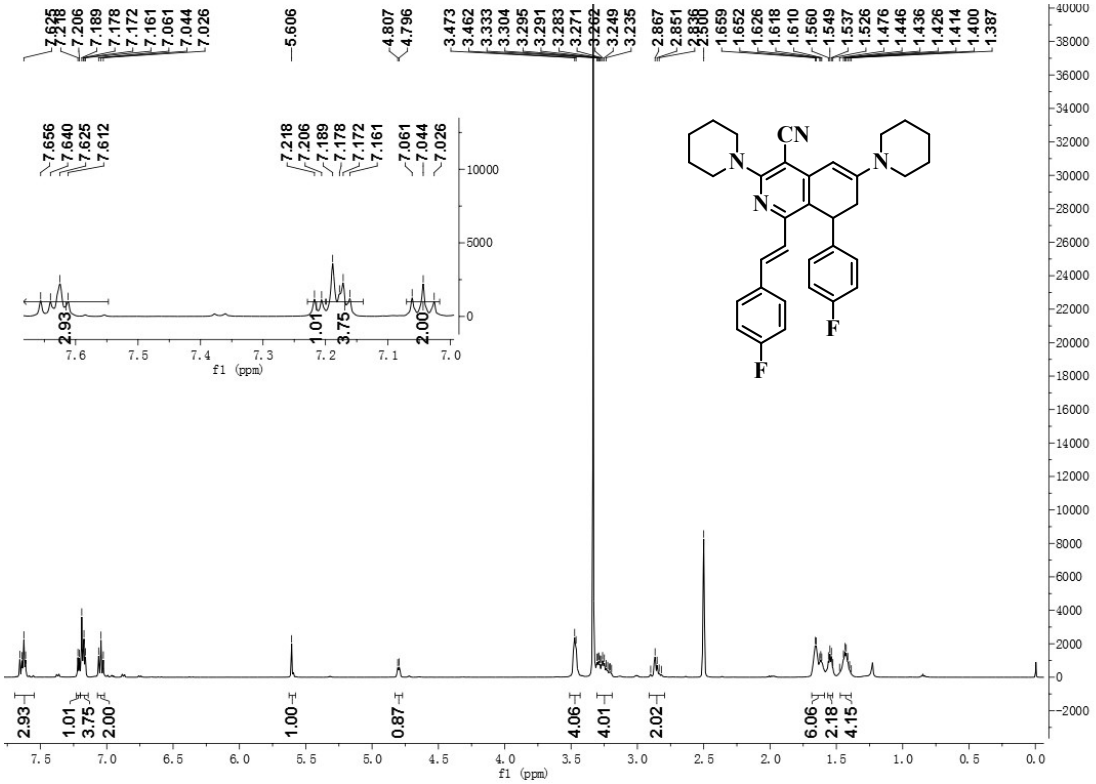


**Fig. S52** $^{1}$H NMR of **3da** (DMSO-$d_6$, 500 MHz).

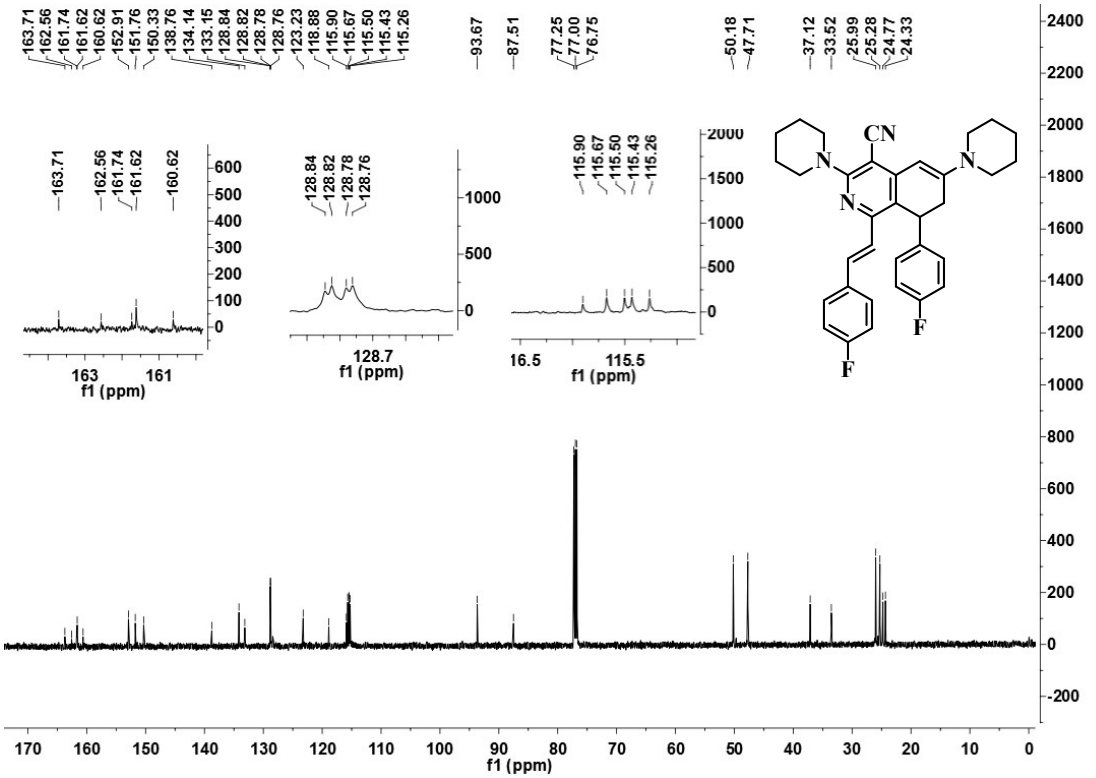


**Fig. S53** $^{13}$C NMR of **3da** ($CDCl_3$, 125 MHz).

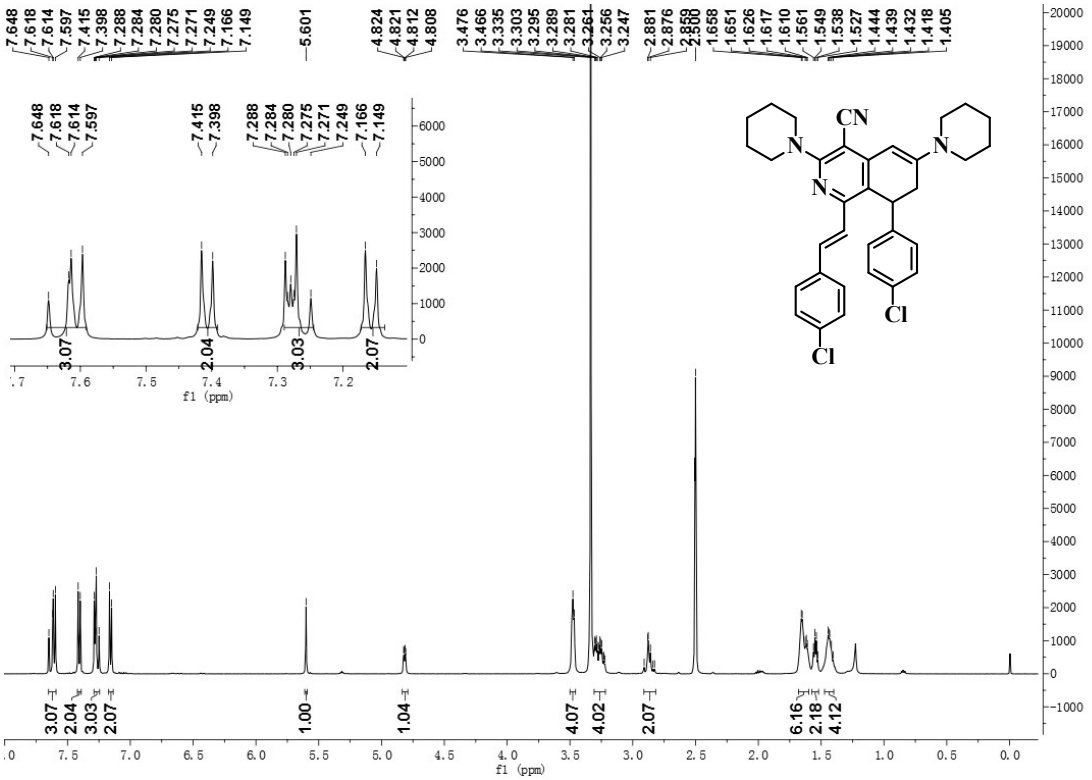



**Fig. S54** $^{1}$H NMR of **3ea** (DMSO-$d_6$, 500 MHz).

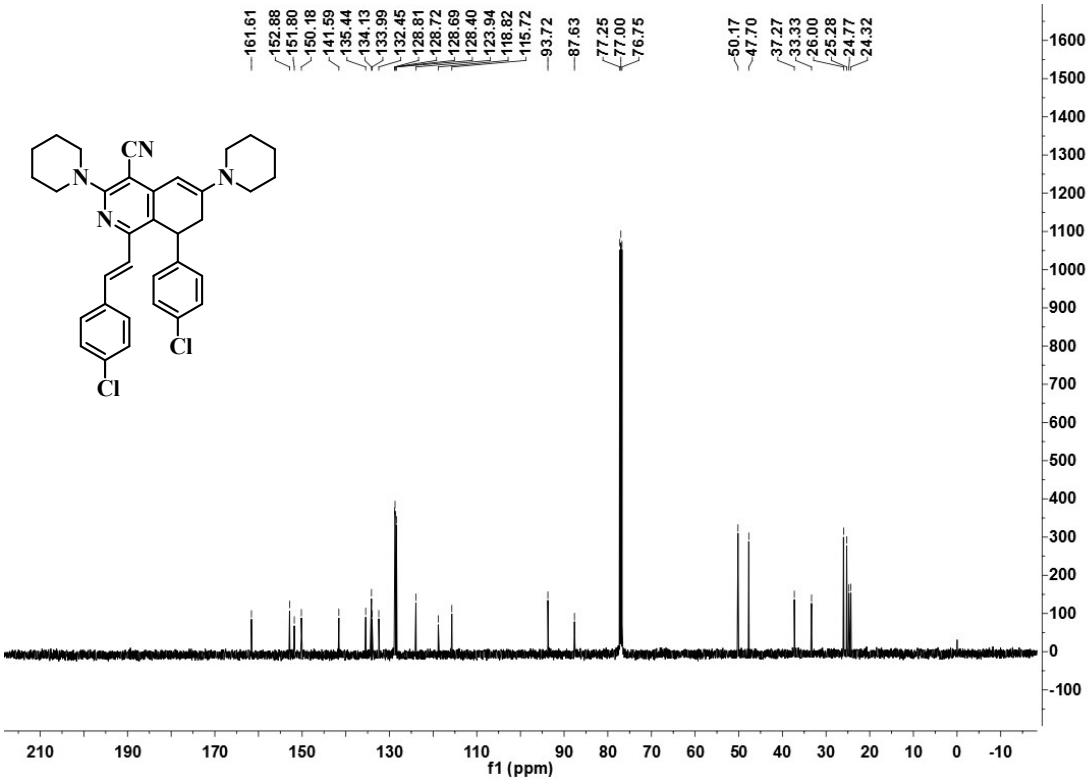



**Fig. S55** $^{13}$C NMR of **3ea** ($CDCl_3$, 125 MHz).

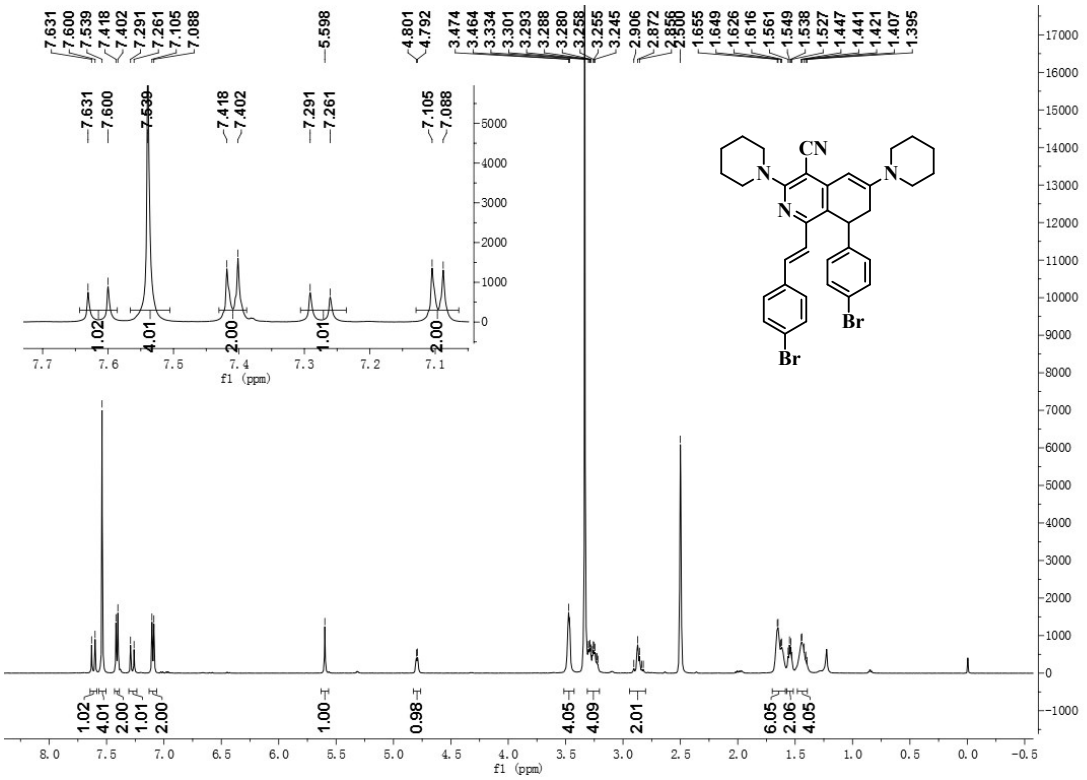


**Fig. S56** $^{1}$H NMR of **3fa** (DMSO-$d_6$, 500 MHz).

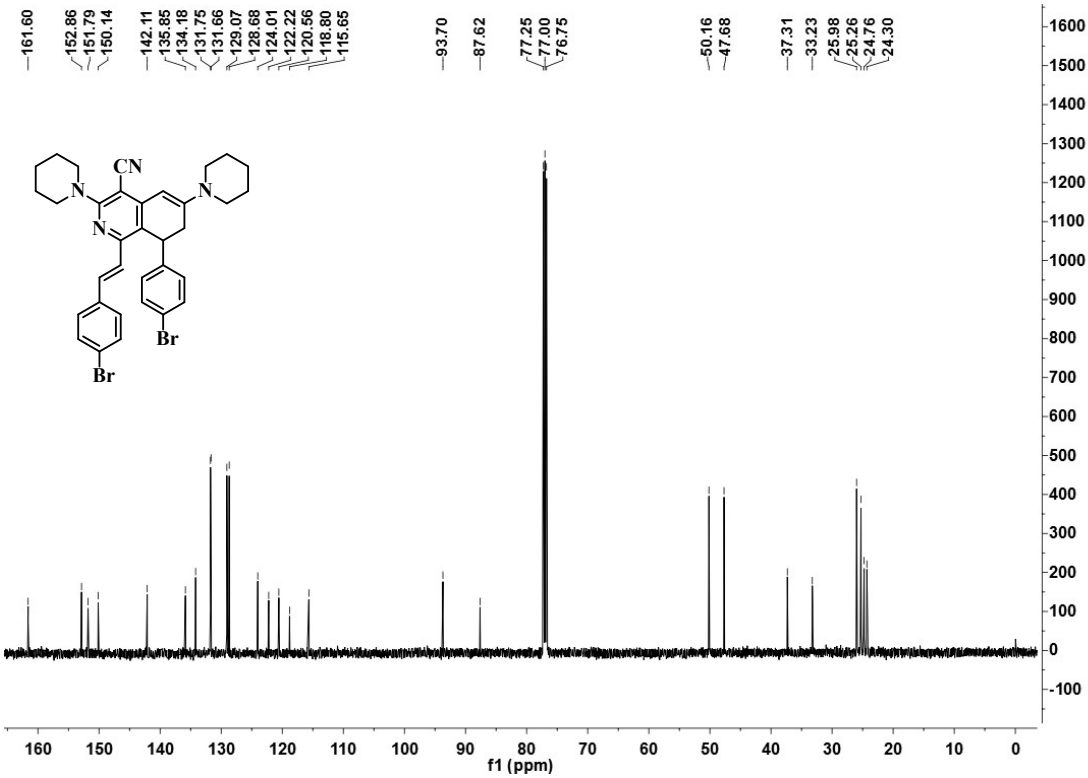


**Fig. S57** $^{13}$C NMR of **3fa** ($CDCl_3$, 125 MHz).

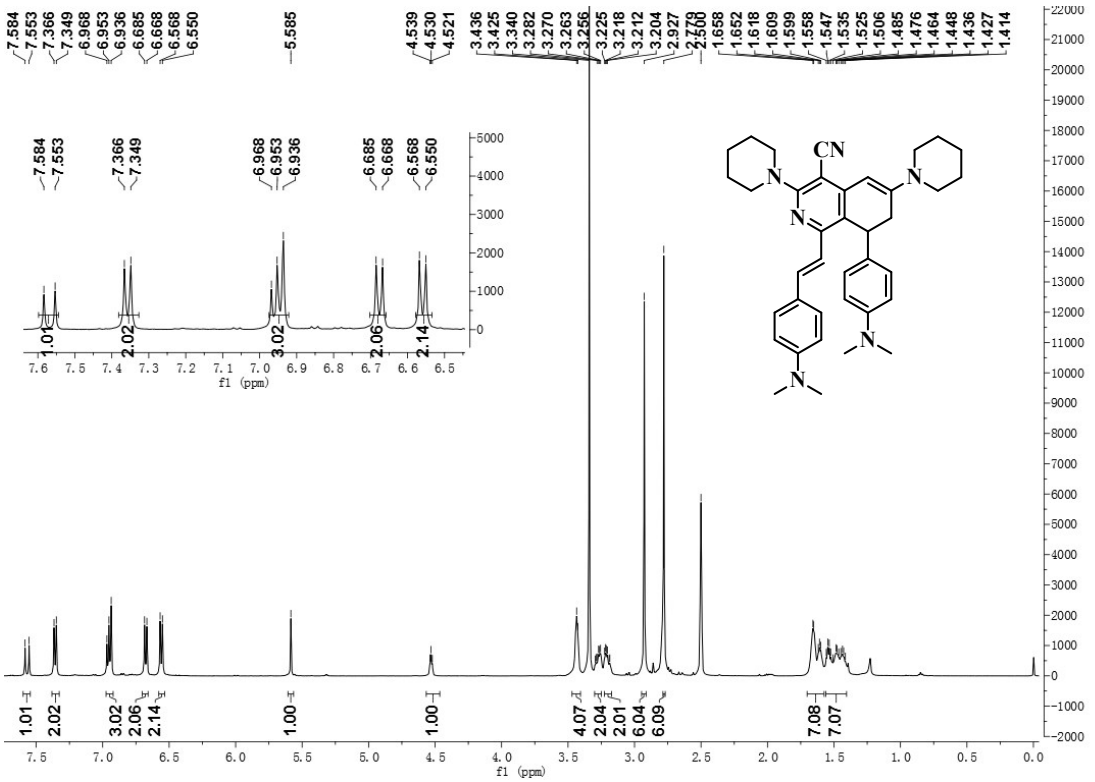


**Fig. S58** $^{1}$H NMR of **3ga** (DMSO-$d_6$, 500 MHz).

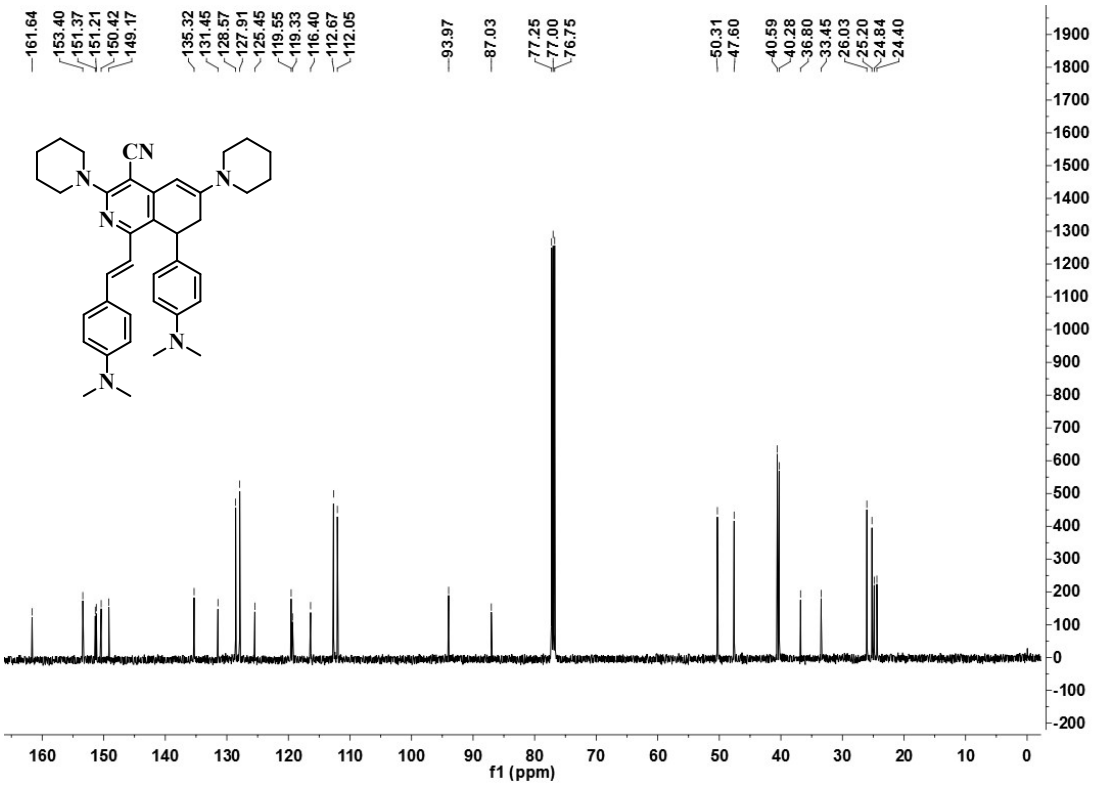


**Fig. S59** $^{13}$C NMR of **3ga** ($CDCl_3$, 125 MHz).

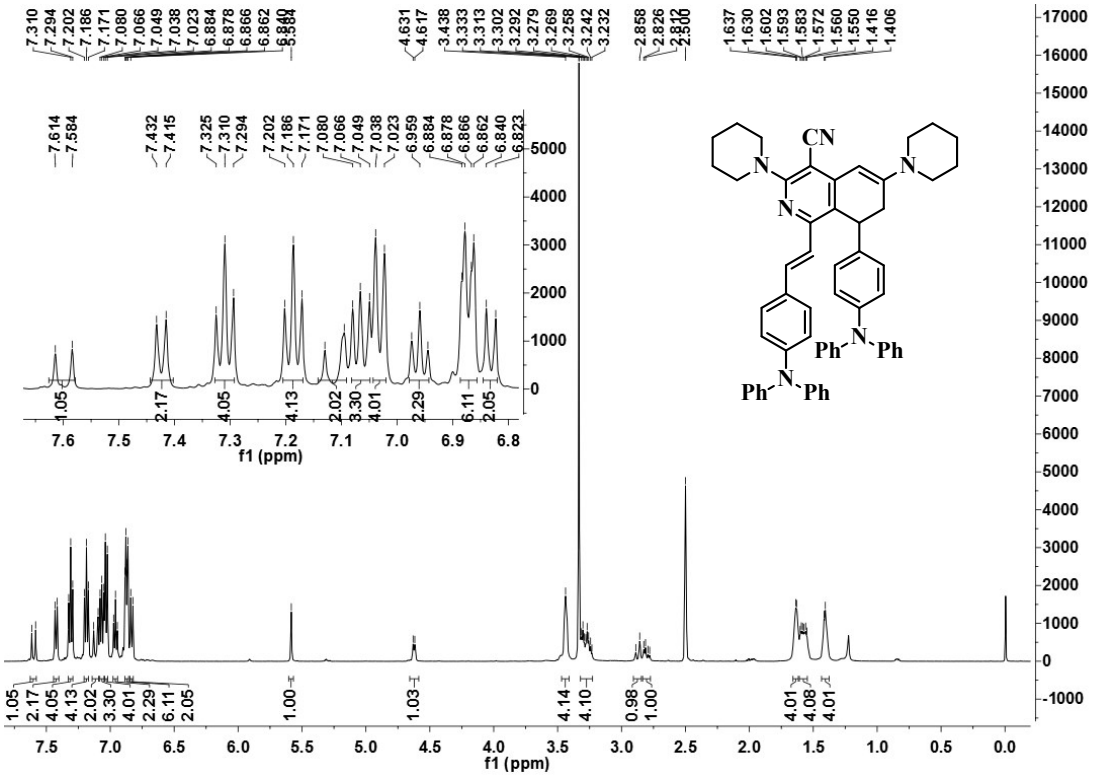


**Fig. S60** $^{1}$H NMR of **3ha** (DMSO-$d_6$, 500 MHz).

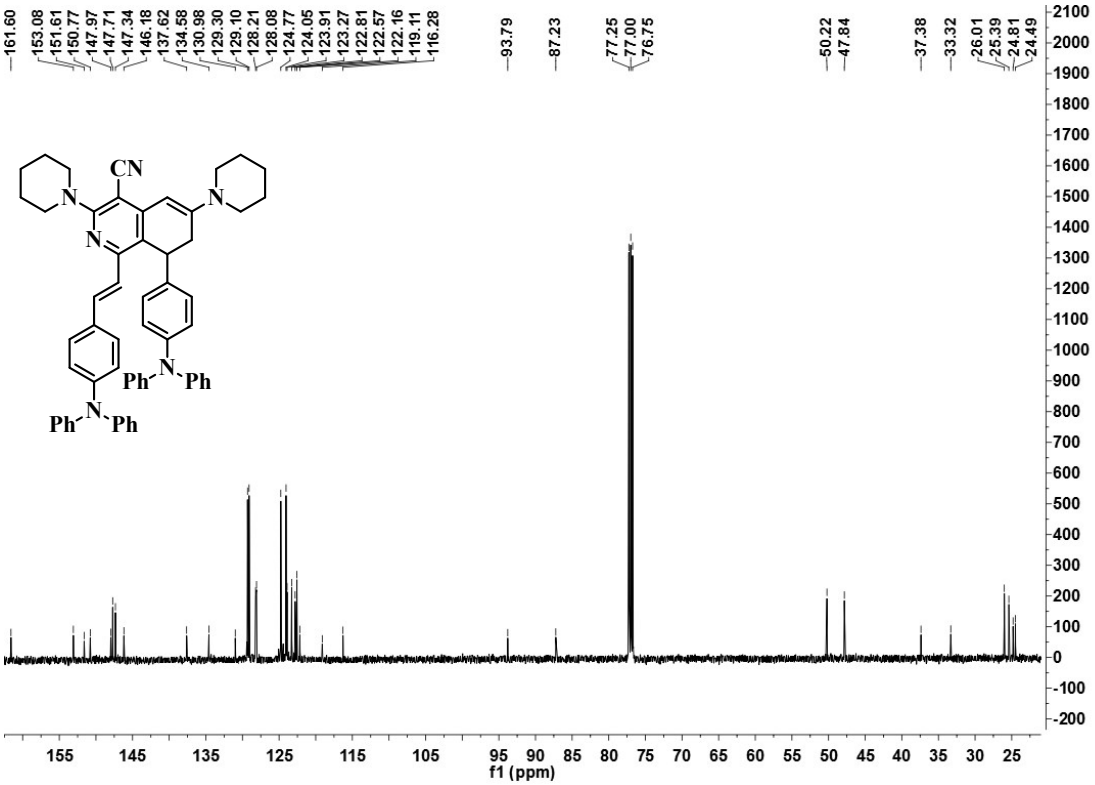


**Fig. S61** $^{13}$C NMR of **3ha** ($CDCl_3$, 125 MHz).

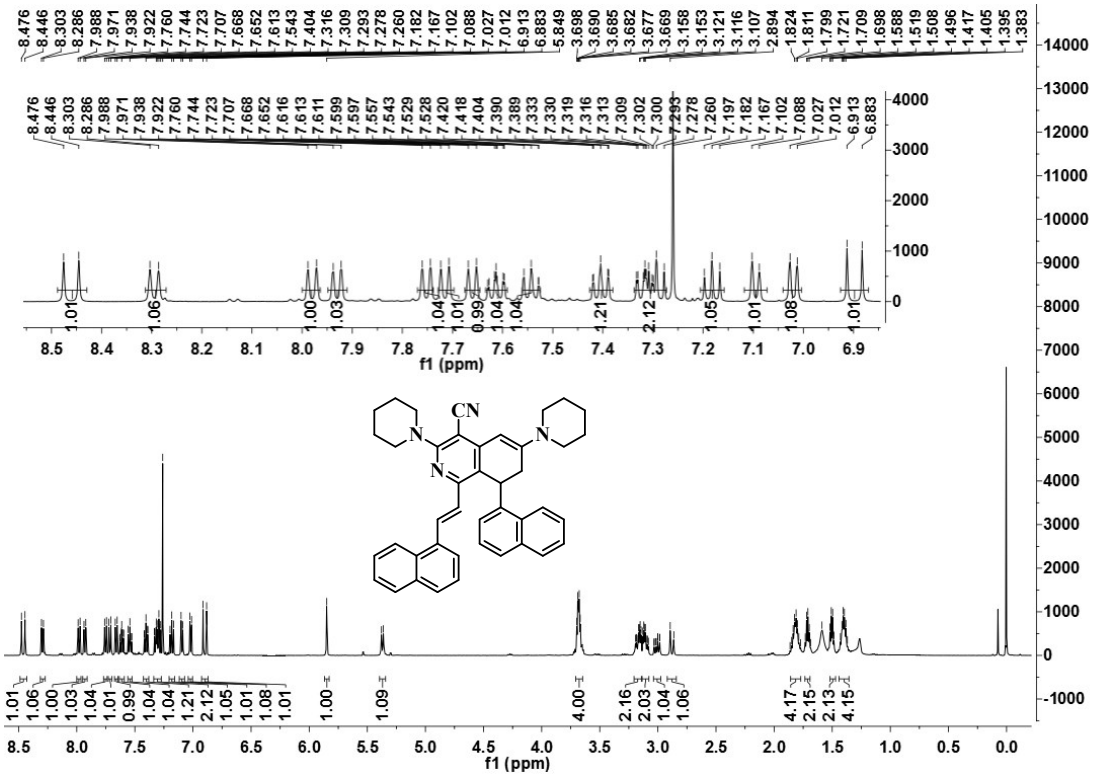


**Fig. S62** $^{1}$H NMR of **3ia** ($CDCl_3$, 500 MHz).

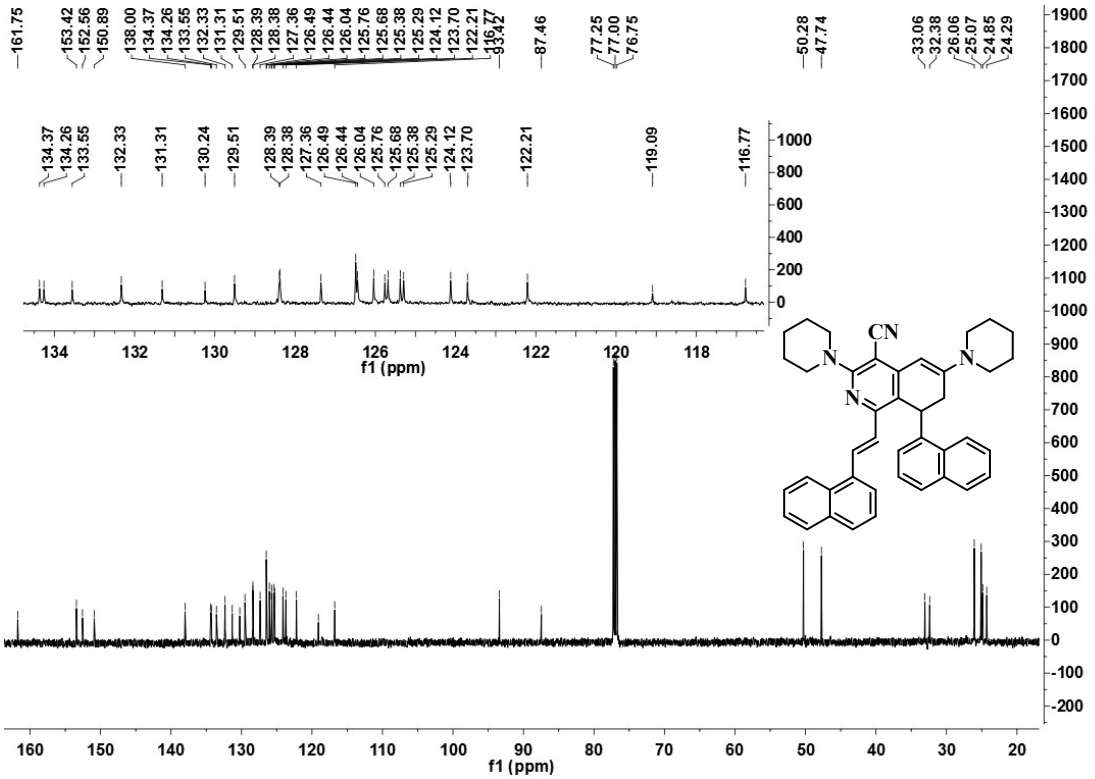


**Fig. S63** $^{13}$C NMR of **3ia** ($CDCl_3$, 125 MHz).

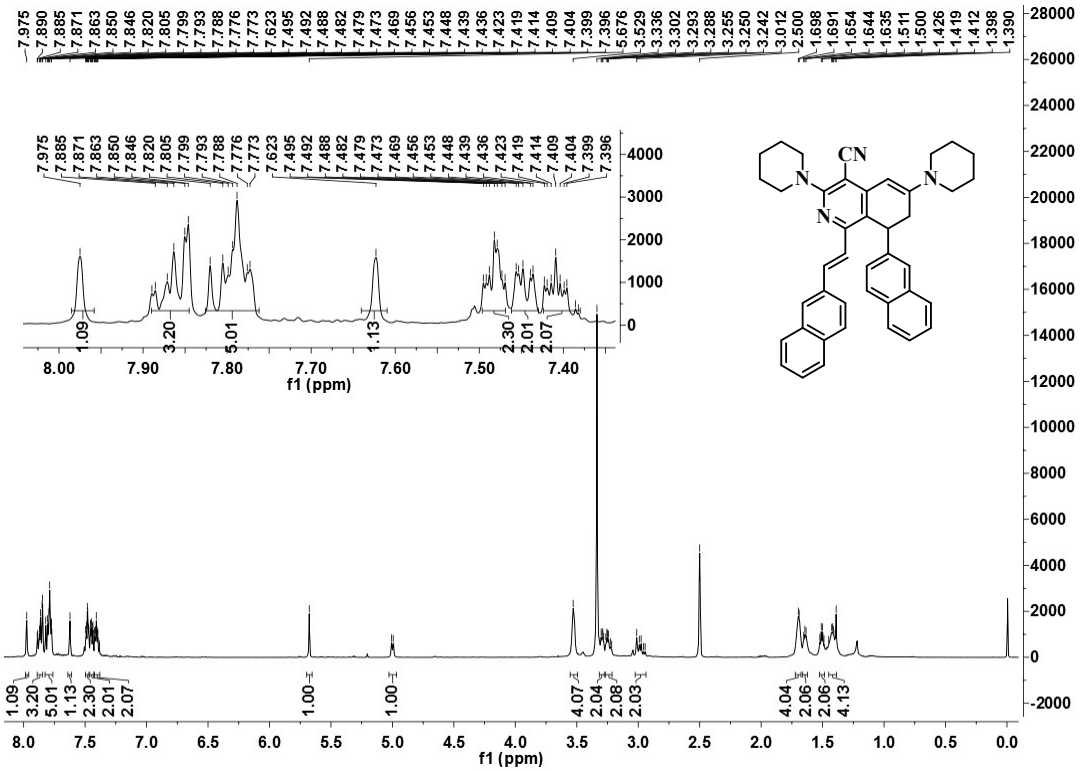


**Fig. S64** $^{1}$H NMR of **3ja** (DMSO-$d_6$, 500 MHz).

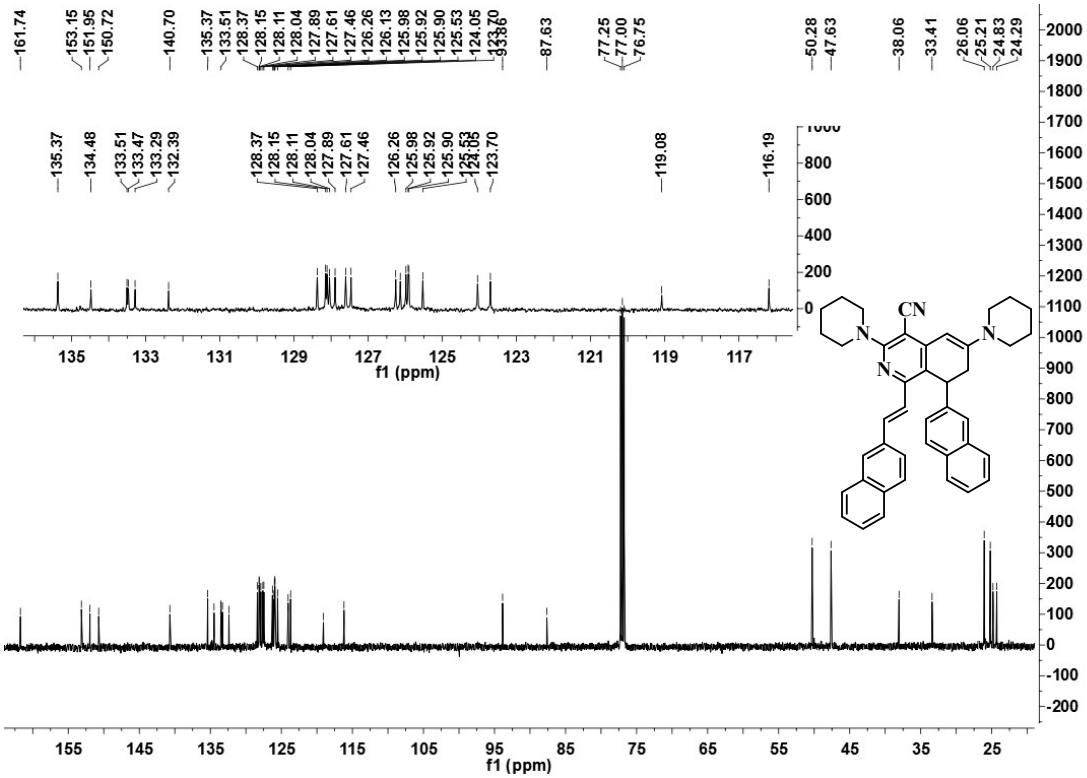


**Fig. S65** $^{13}$C NMR of **3ja** ($CDCl_3$, 125 MHz).

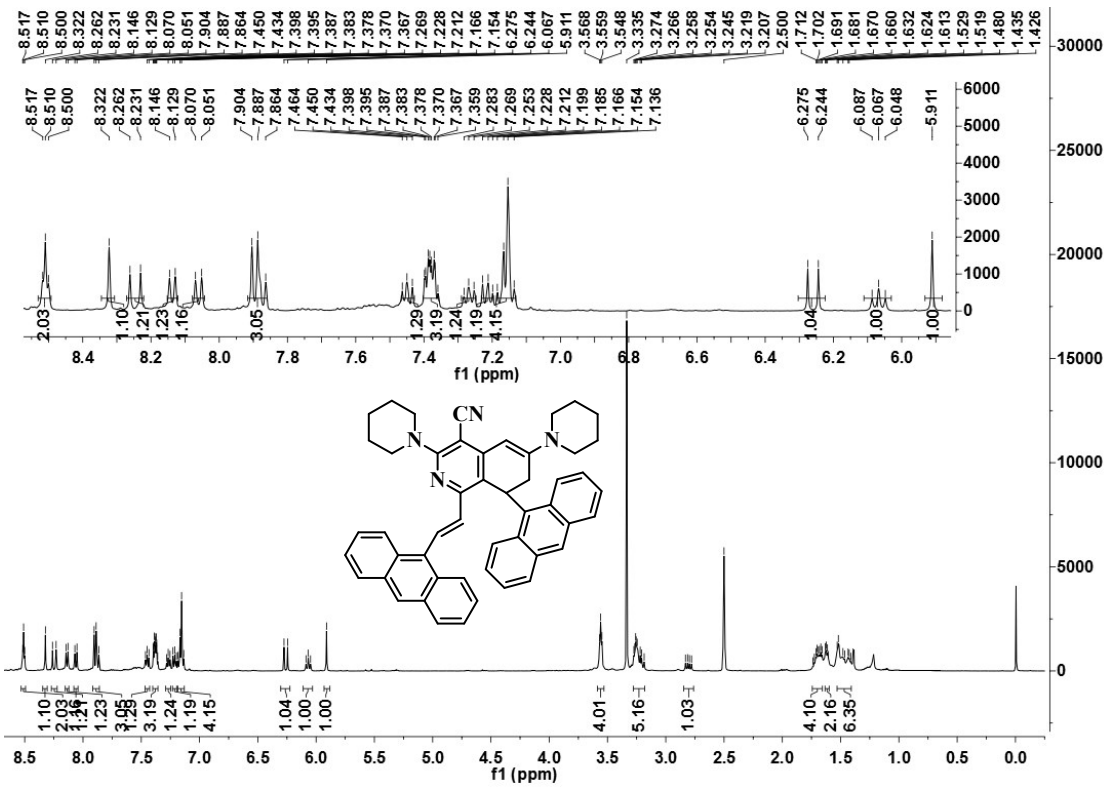



**Fig. S66** $^{1}$H NMR of **3ka** (DMSO-$d_6$, 500 MHz).

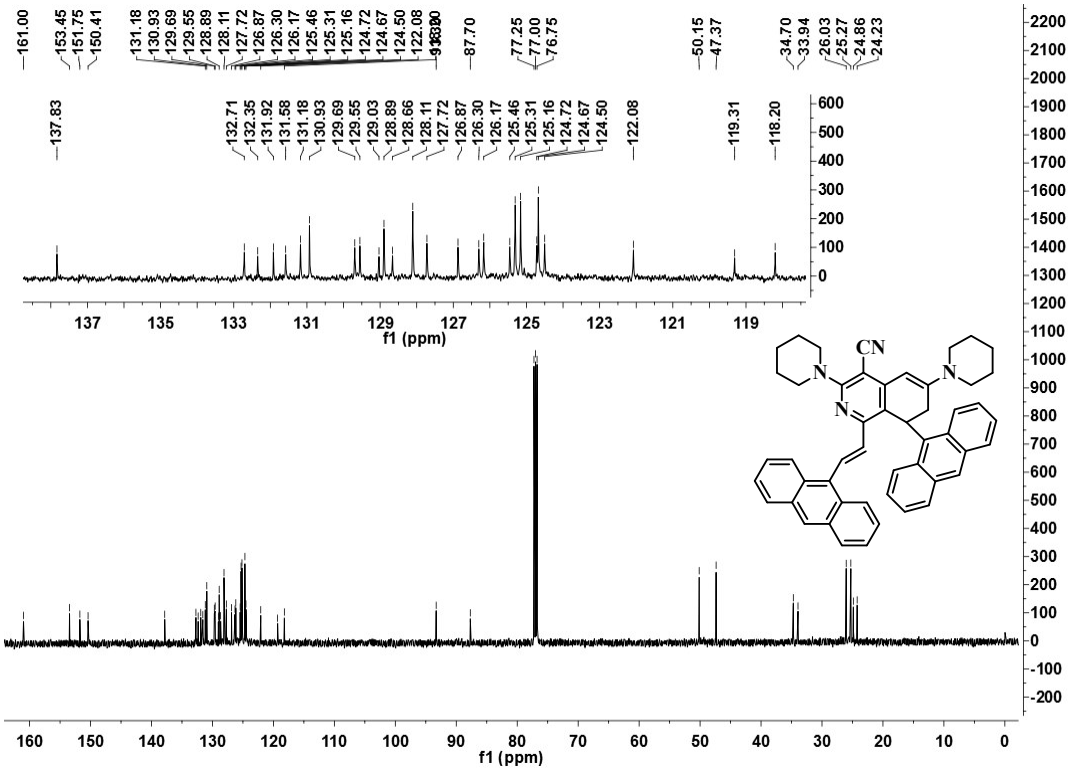



**Fig. S67** $^{13}$C NMR of **3ka** ($CDCl_3$, 125 MHz).

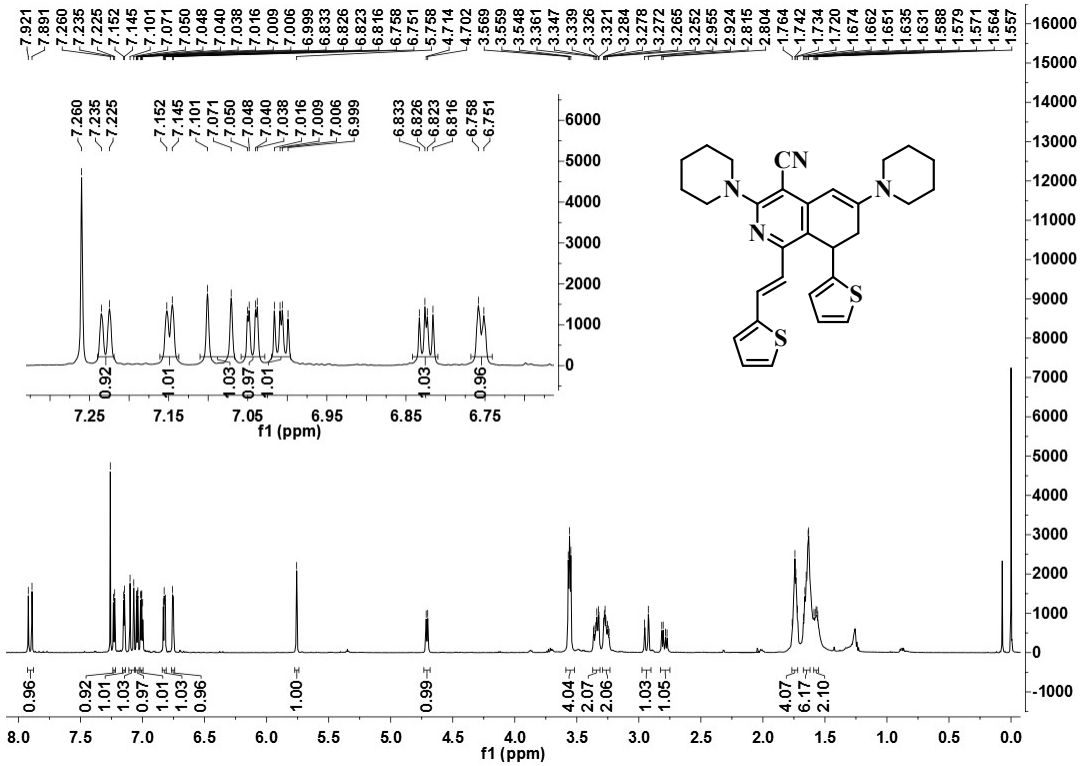



**Fig. S68** $^{1}$H NMR of **3la** ($CDCl_3$, 500 MHz).

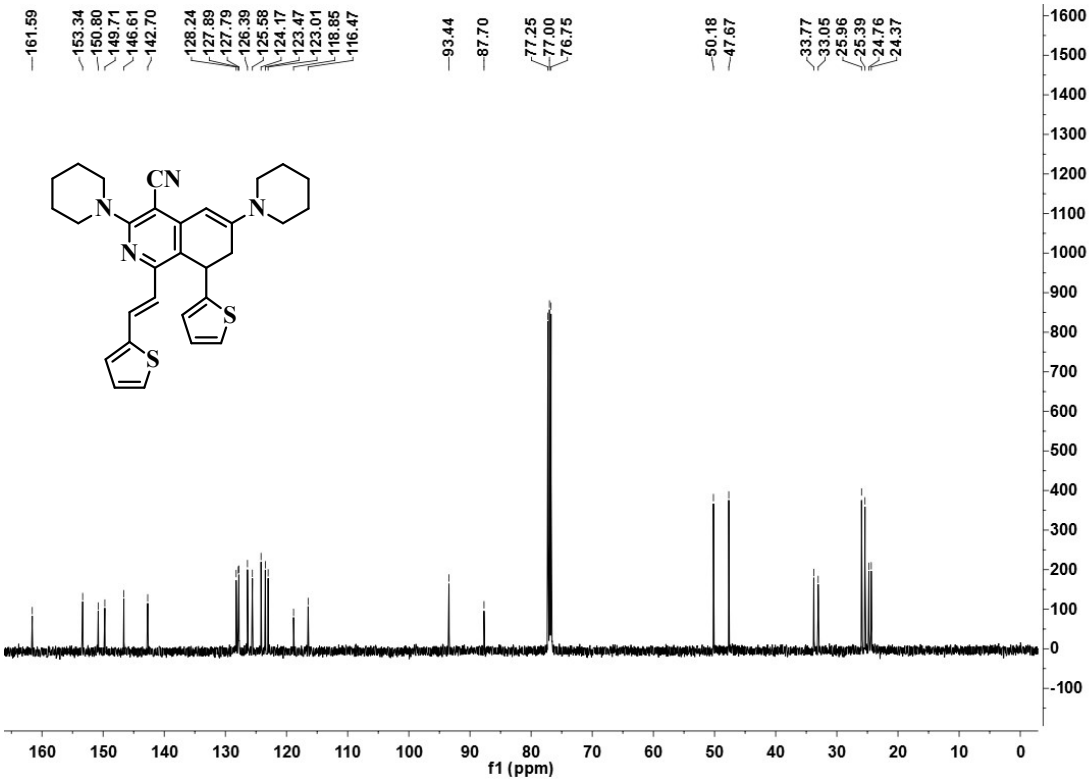



**Fig. S69** $^{13}$C NMR of **3la** ($CDCl_3$, 125 MHz).

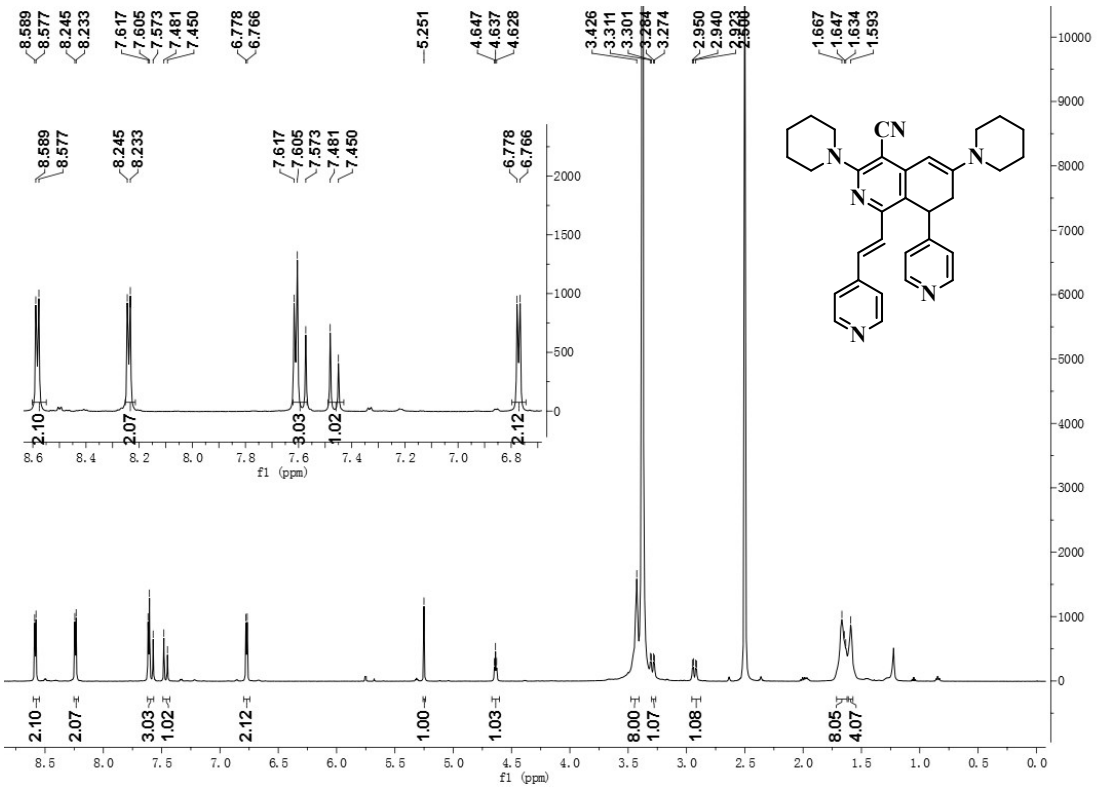


**Fig. S70** $^{1}$H NMR of **3ma** (DMSO-$d_6$, 500 MHz).

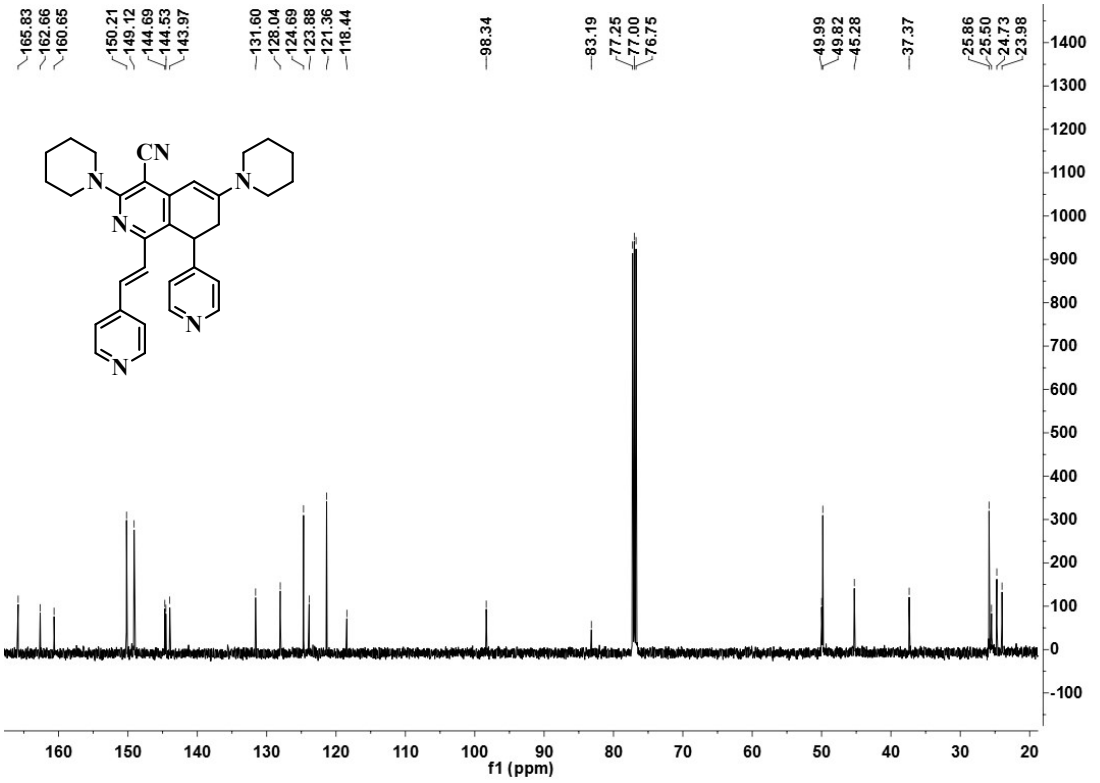


**Fig. S71** $^{13}$C NMR of **3ma** ($CDCl_3$, 125 MHz).

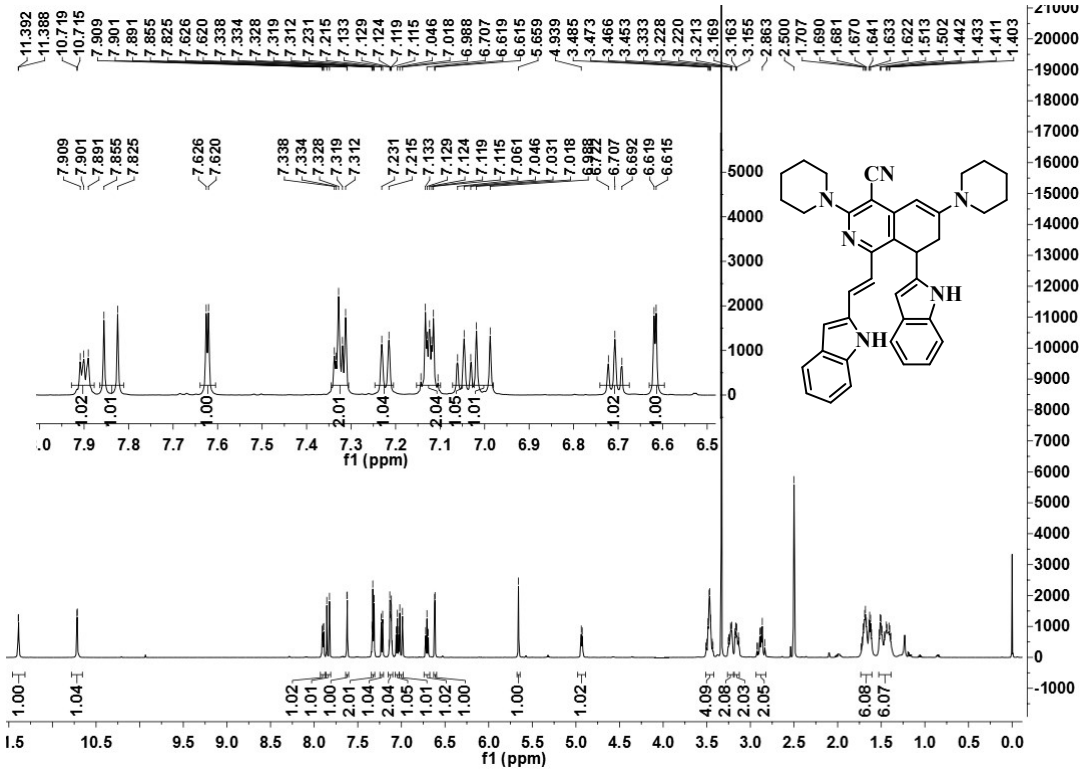



**Fig. S72** $^{1}$H NMR of **3na** (DMSO-$d_6$, 500 MHz).

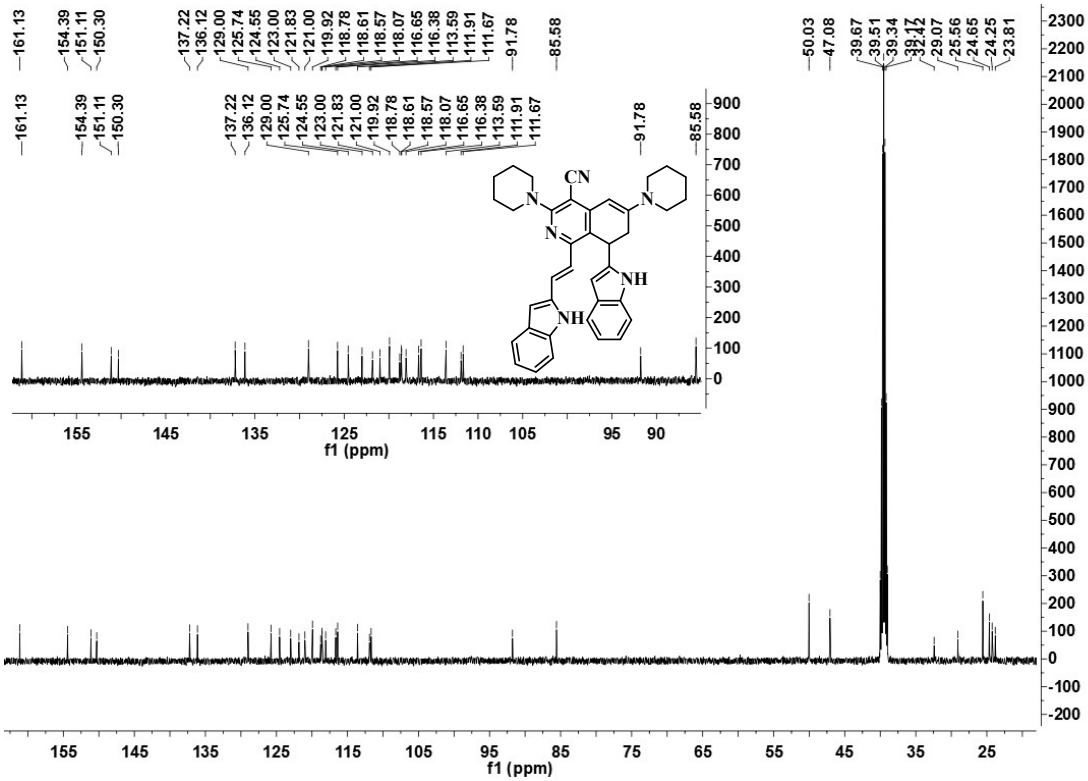



**Fig. S73** $^{13}$C NMR of **3na** (DMSO-$d_6$, 125 MHz).

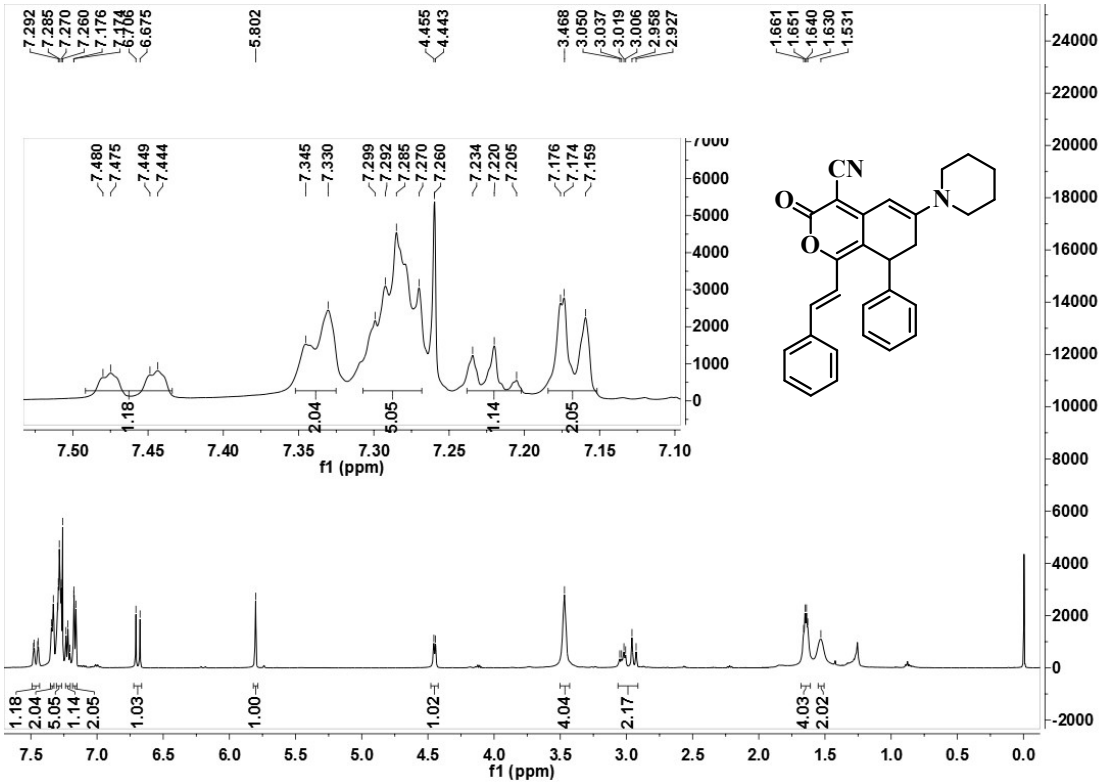



**Fig. S74** $^{1}$H NMR of **7** ($CDCl_3$, 500 MHz).

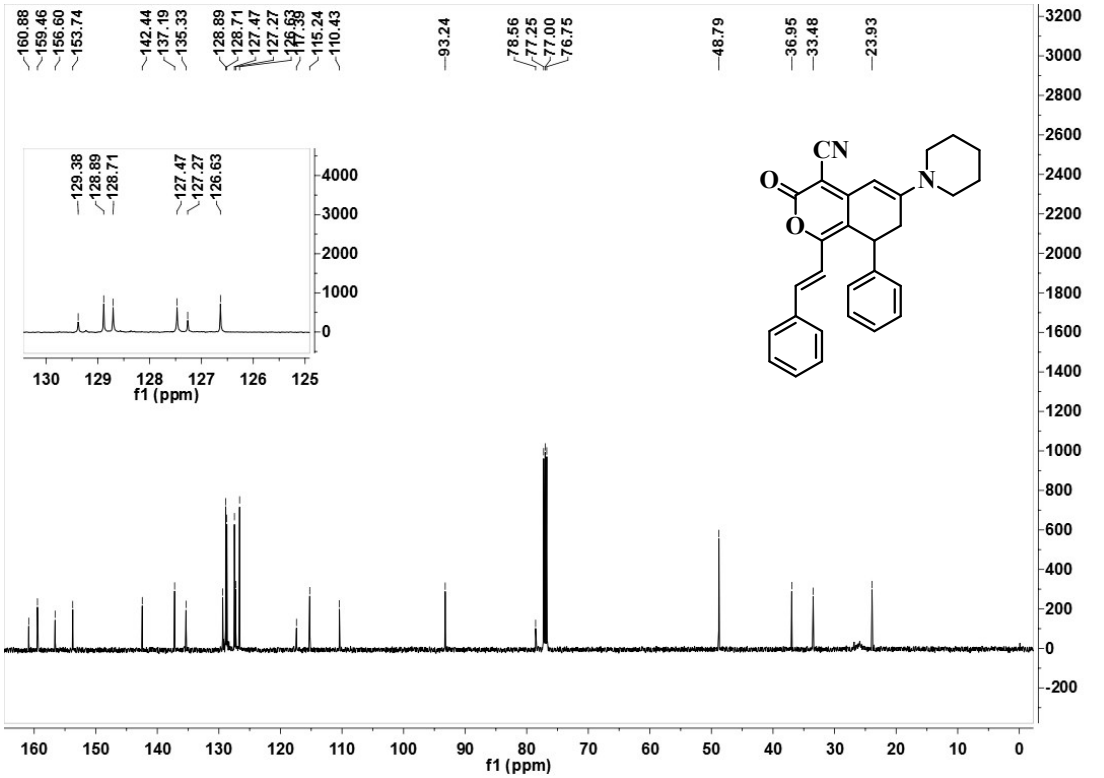



**Fig. S75** $^{13}$C NMR of **7** ($CDCl_3$, 125 MHz).

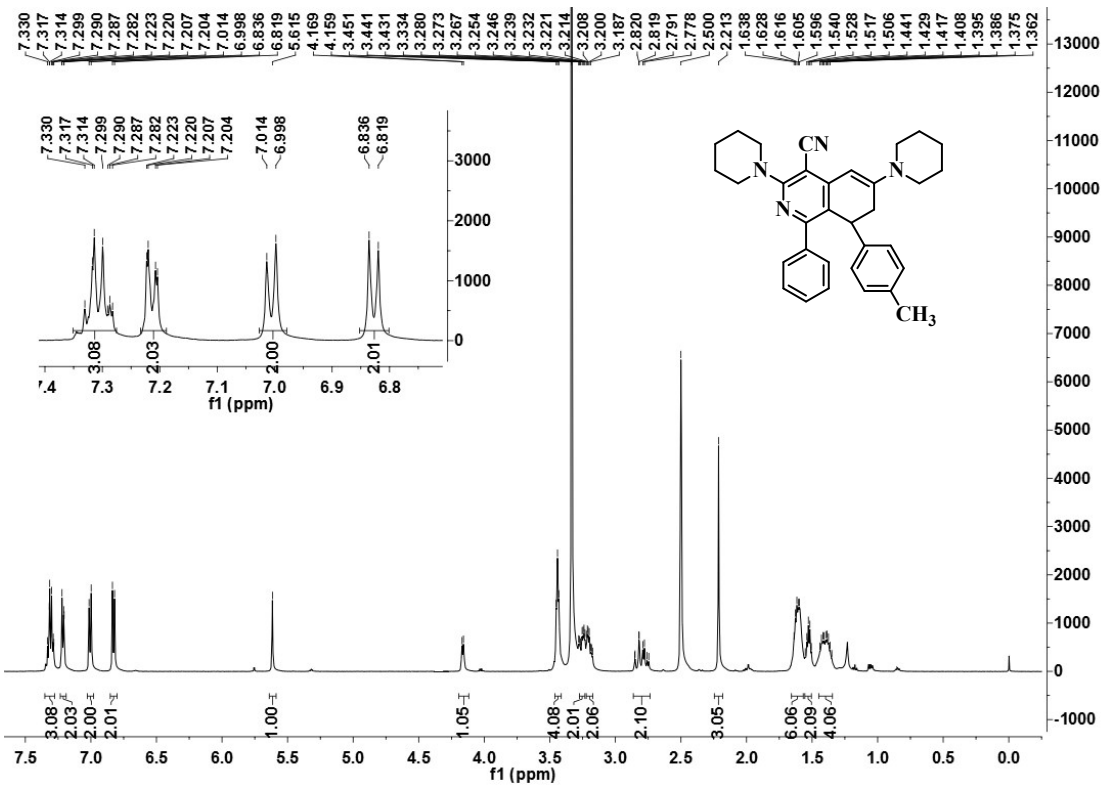



**Fig. S76** $^{1}$H NMR of **9aa** (DMSO-$d_6$, 500 MHz).

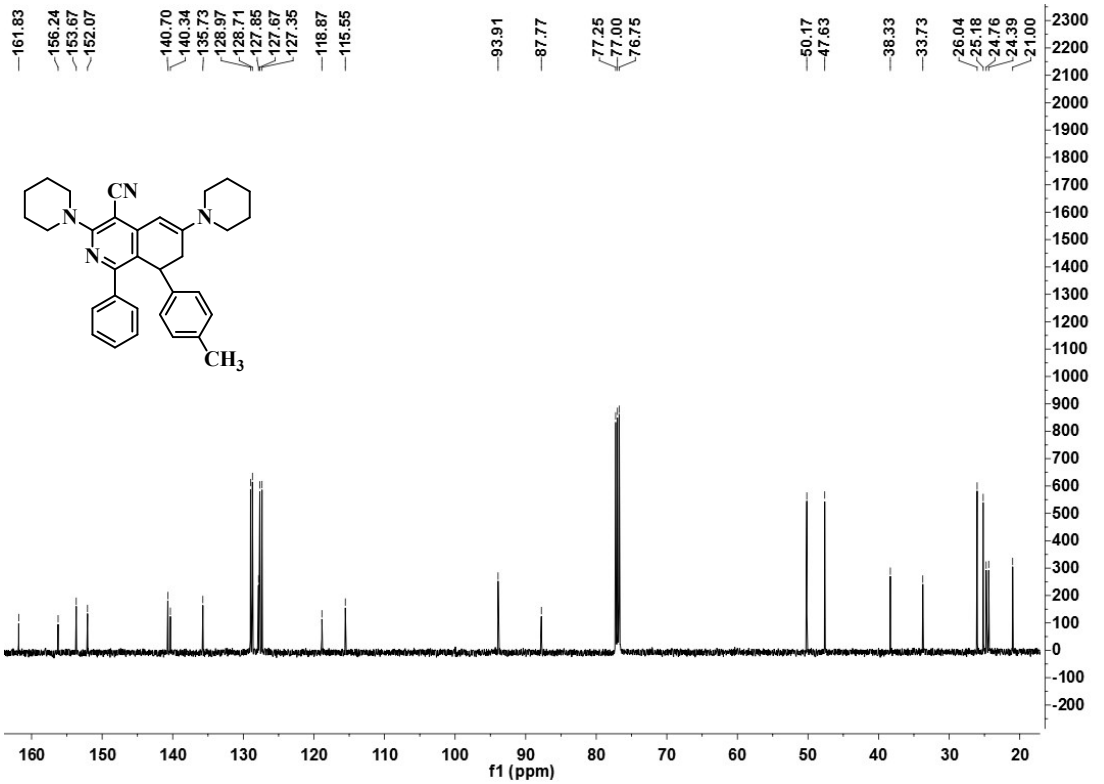



**Fig. S77** $^{13}$C NMR of **9aa** ($CDCl_3$, 125 MHz).

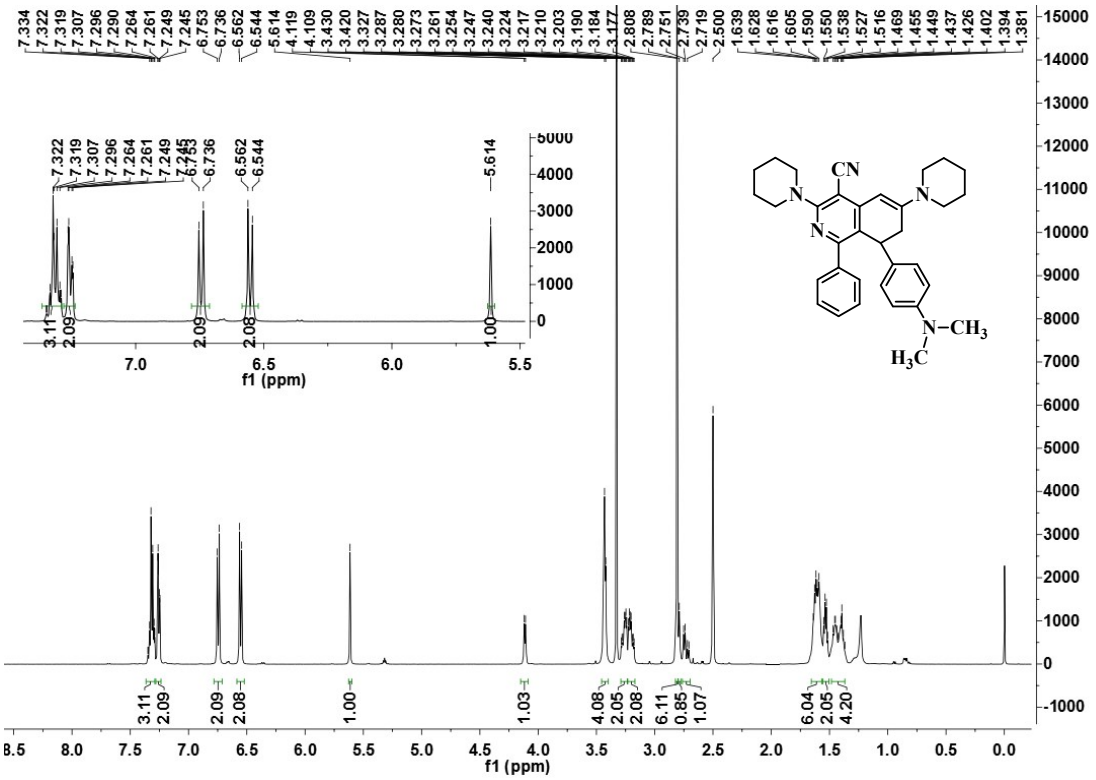



**Fig. S78** $^{1}$H NMR of **9ba** (DMSO-$d_6$, 500 MHz).

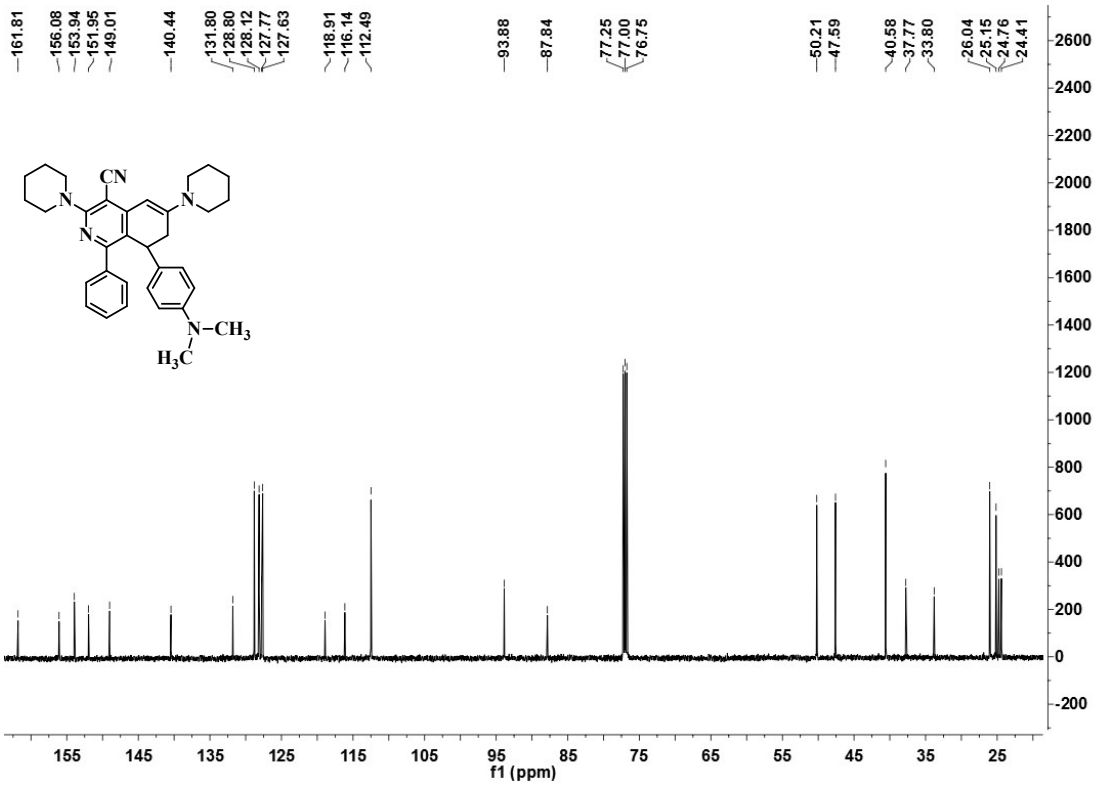



**Fig. S79** $^{13}$C NMR of **9ba** ($CDCl_3$, 125 MHz).

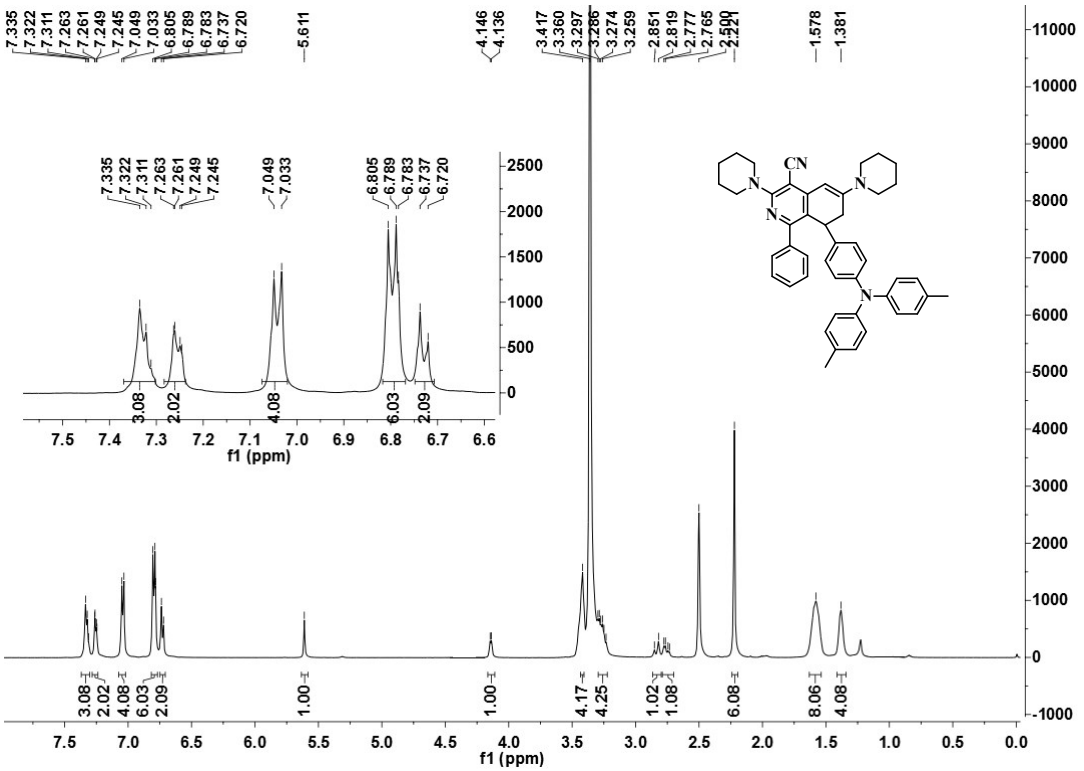


**Fig. S80** $^{1}$H NMR of **9ca** (DMSO-$d_6$, 500 MHz).

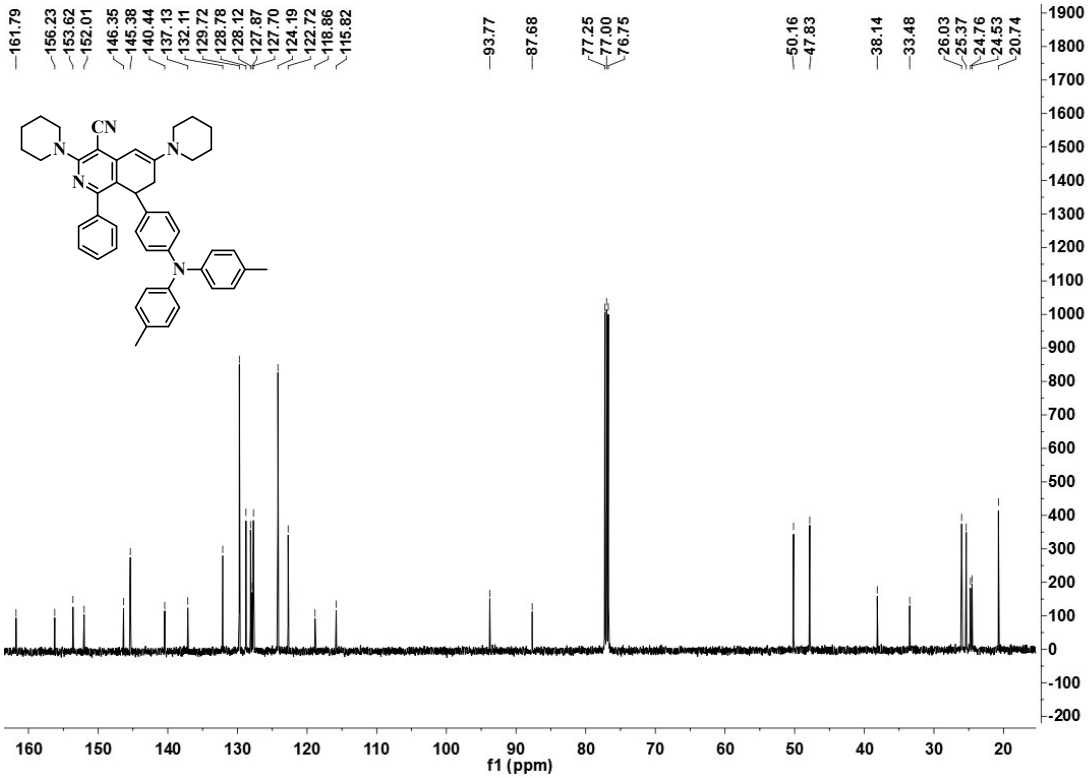


**Fig. S81** $^{13}$C NMR of **9ca** ($CDCl_3$, 125 MHz).

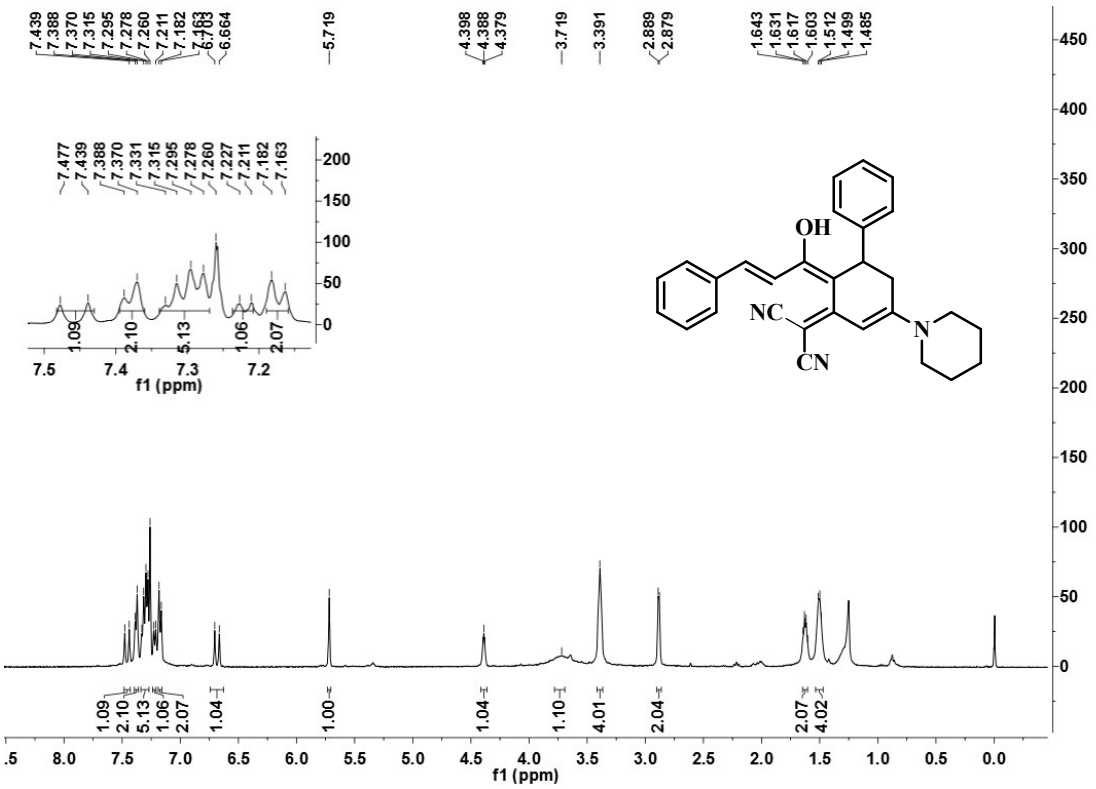



**Fig. S82** $^{1}$H NMR of **11A** ($CDCl_3$, 400 MHz).

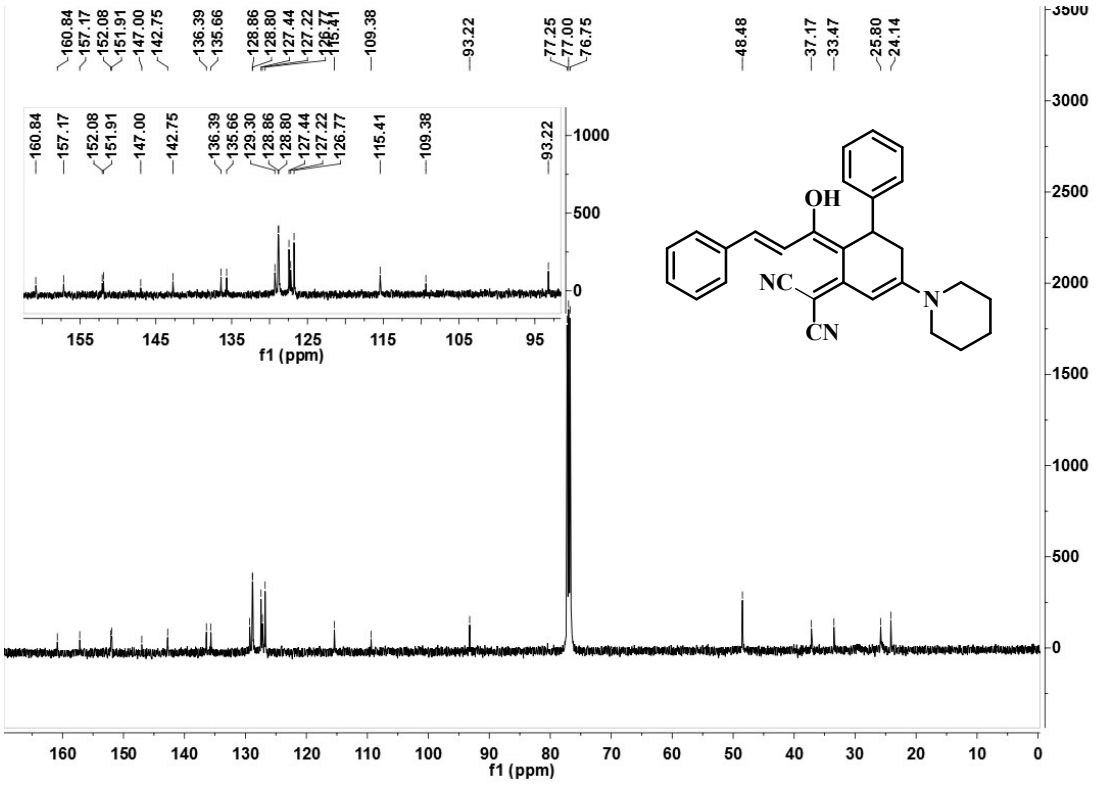



**Fig. S83** $^{13}$C NMR of **11A** ($CDCl_3$, 125 MHz).

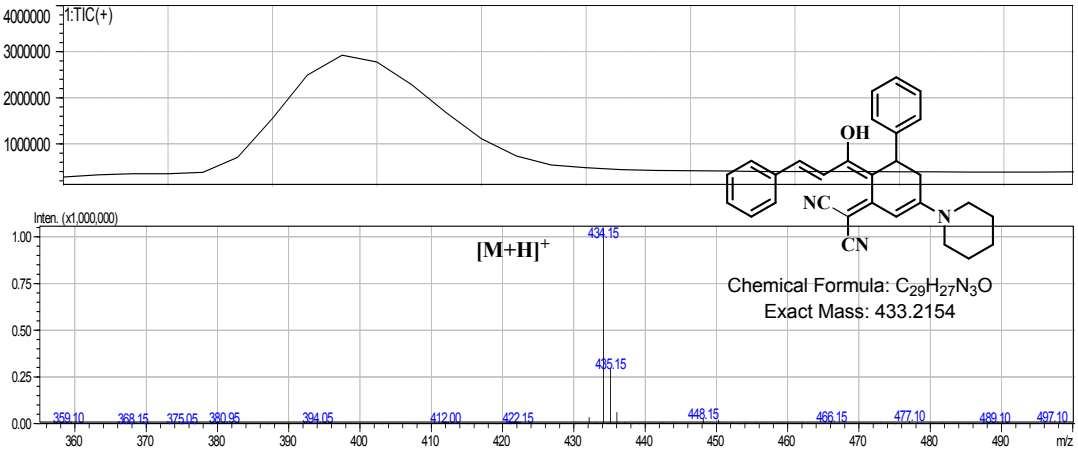



**Fig. S84** ESI-MS of **11A**.