Electronic Supplementary Information

Ketone-enol tautomerism, polymorphism, mechanofluorochromism, and solid-state acidochromism of isoquinolinone-arylidenehydrazine derivatives

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Contents:

1. Experimental

1.1 Measurements and materials

NMR spectra were obtained on a Bruker DRX 500 NMR spectrometer. High-resolution electrospray ionization (HRMS-ESI) mass spectra were conducted on a Hitachi Nano Frontier LD spectrometer. Melting points were performed with a WRS-1B digital melting point meter (uncorrected). Fluorescence spectra were performed with a HITACHI F-7000 fluorometer. Absolute fluorescence quantum yields (Φ_F) in solid state and time-resolved emission decay parameters were conducted on a FluoroMax-4 (Horiba Jobin Yvon) fluorometer. Absorption spectra were conducted on a UV-3600 Shimadzu spectrophotometer. X-Ray powder diffraction (XRD) patterns were conducted on an Empyrean X-ray diffraction instrument. Single-crystal X-ray diffraction measurements were obtained on a Bruker-Nonius Smart Apex CCD diffractometer with graphite monochromated Mo Kα radiation. Methyl piperidine-4-carboxylate, hydrazine hydrate, and various aromatic aldehydes were purchased from commercial suppliers and used directly.

Synthesis of methyl 1-(7-cyano-8-hydroxy-3,6-dimethylisoquinolin-1-yl)piperidine-4-carboxylate (2)

The mixture of compound **1** (2.0 g, 9.3 mmol), methyl piperidine-4-carboxylate (18 mmol), and CH_3CN (15 mL) was stirred at 90 °C for 5 h. After being cooled to the room temperature, the reaction mixture was filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the corresponding product. White solid (2.9 g, 92% yield). M. p. 224.3-224.6 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 15.65 (s, 1H), 7.21 (s, 1H), 6.93 (s, 1H), 3.73 (s, 3H), 3.26-3.24 (m, 4H), 2.58 (s, 3H), 2.56 (s, 3H), 2.23-2.20 (m, 2H), 2.07-1.99 (m, 3H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.3, 163.3, 160.0, 154.0, 142.6, 141.9, 117.7, 116.0, 115.6, 109.3, 95.5, 51.9, 51.8, 40.4, 28.2, 23.9, 21.2 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{19}H_{21}N_3O_3$, 340.1656; found, 340.1653.

Synthesis of 1-hydrazinyl-3,6-dimethyl-8-oxo-2,8-dihydroisoquinoline-7-carbonitrile (3)

The mixture of compound **2** (2.5 g, 7.5 mmol), hydrazine hydrate (15 mL), and EtOH (15 mL) was stirred at 80 °C for 8 h. After being cooled to the room temperature, the mixture was poured in methanol (100 mL) to precipitate out the crude product. The crude product was washed with methanol five times and then dried to afford the pure target compound. Pale yellow solid (1.6 g, 96% yield). M. p. 344.5-344.9 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 13.27 (s, 1H), 6.28 (d, J = 0.5 Hz, 1H), 6.13 (s, 1H), 2.29 (d, J = 1.0 Hz, 3H), 2.72 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.6, 155.8, 148.0, 141.3, 138.9, 119.4, 107.6, 106.7, 104.7, 98.3, 21.0, 18.8 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{12}H_{12}N_4O$, 229.1084; found, 229.1080.

Synthesis of the target compounds

General procedure: The mixture of compound **3** (1.5 g, 6.5 mmol), aromatic aldehyde (12 mmol), and DMF (15 mL) was stirred at 120 °C for 12 h. After being cooled to the room temperature, the mixture was poured into methanol (200 mL) and then stirred for 2 h to separate out the crude product. The crude product was washed by methanol three times and then dried to afford the pure target compound. Characterization data of the target compounds are listed as follows.

(*Z*)-1-((*E*)-Benzylidenehydrazono)-8-hydroxy-3,6-dimethyl-1,2-dihydroisoquinoline-7-carbonitrile (BHIQ). Yellow-green solid (1.9 g, 93% yield). M. p. 231.3-231.6 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 16.35 (s, 1H), 11.26 (s, 1H), 8.46 (s, 1H), 8.00-7.98 (m, 2H), 7.48-7.47 (m, 3H)，6.46 (s, 1H)，6.34 (s, 1H)，2.37 (s, 1H)，2.35 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.3, 153.0, 151.7, 147.1, 141.1, 140.9, 134.2, 130.4, 128.6, 128.1, 117.3, 111.2, 107.0, 105.0, 97.0, 20.8, 19.2 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{19}H_{16}N_4O$, 317.1397; found, 317.1399.

(*Z*)-8-Hydroxy-3,6-dimethyl-1-((*E*)-(naphthalen-2-ylmethylene)hydrazono)-1,2-dihydroisoquinoline-7-carbonitrile (NHIQ). Yellow-green solid (2.3 g, 96% yield). M. p. 277.5-278.1 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 16.42 (s, 1H), 11.36 (s, 1H), 8.62 (s, 1H), 8.39 (dd, J = 9.0 Hz, 1.5 Hz, 2H), 8.25 (s, 1H)，8.00 (d, J = 9.0 Hz, 1H)，7.97 (dd, J = 9.0 Hz, 6.5 Hz, 2H), 7.60-7.56 (m, 2H)，6.52 (s, 1H)，6.39 (s, 1H)，2.41 (s, 3H)，2.38 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.4, 153.0, 151.6, 147.1, 141.2, 141.0, 134.0, 132.8, 132.1, 129.8, 128.4, 128.1, 127.8, 127.3, 126.8, 123.8, 117.5, 111.3, 107.1, 105.1, 97.0, 20.9, 19.3 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{23}H_{18}N_4O$, 367.1554; found, 367.1549.

(*Z*)-1-((*E*)-(Anthracen-9-ylmethylene)hydrazono)-8-hydroxy-3,6-dimethyl-1,2-dihydroisoquinoline-7-carbonitrile (AHIQ). Orange solid (2.4 g, 90% yield). M. p. 288.3-288.7 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 16.55 (s, 1H), 11.54 (s, 1H), 9.63 (s, 1H), 8.74 (s, 1H), 8.63 (d, J = 8.5 Hz, 2H), 8.16 (d, J = 7.5 Hz, 2H), 7.64-7.58 (m, 4H)，6.53 (s, 1H)，6.40 (s, 1H)，2.40 (s, 3H)，2.28 (s, 3H) ppm. ^{13}C NMR (DMSO-d_6，125 MHz): δ 169.6, 153.1, 150.8, 147.1, 141.3, 141.1, 130.8, 129.8, 129.3, 128.7, 127.0, 126.1, 125.6, 125.4, 117.6, 111.2, 107.2, 105.0, 97.0, 20.9, 19.1. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{27}H_{20}N_4O$, 417.1710; found, 417.1713.

(*E*)-1-(2-(4-(Diphenylamino)benzylidene)hydrazineyl)-3,6-dimethyl-8-oxo-2,8-dihydroisoquinoline-7-carbonitrile (TPHIQ). Yellow-green solid (2.9 g, 94% yield). M. p. 275.1-275.6 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 15.37 (s, 1H), 9.24 (s, 1H), 8.20 (s, 1H), 7.57 (d, J = 8.8 Hz, 2H), 7.32-7.28 (m, 4H)，7.15-7.08 (m, 6H), 7.04 (d, J = 8.4 Hz, 1H), 6.44 (s, 1H), 5.99 (s, 1H), 2.45 (s, 3H), 2.29 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.3, 153.5, 152.8, 150.2, 146.9, 146.7, 140.6, 138.5, 129.5, 128.9, 127.1, 125.4, 124.1, 121.7, 116.4, 114.1, 106.2, 105.1, 98.0, 21.2, 19.6 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{31}H_{25}N_5O$, 484.2132; found, 484.2134.

2. Figures and tables

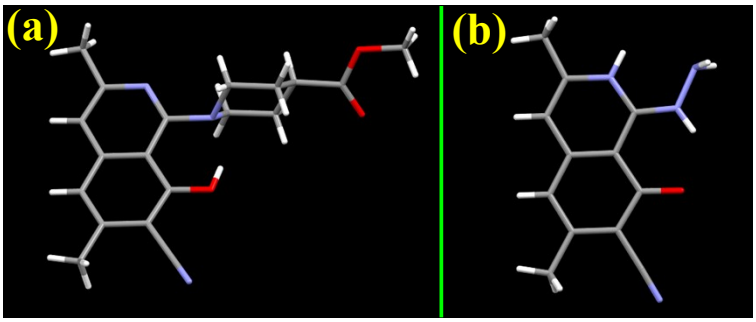


Fig. S1 Crystal structures of compound **2** (a) and compound **3** (b).

Table S1 Crystal data and details of collection and refinement for intermediates **2** and **3**.

Compound	**2**	**3**
CCDC (no.)	2091622	2091623
Empirical formula	$C_{19}H_{21}N_3O_3$	$C_{14}H_{18}N_4O_2S$
Formula weight	339.39	306.38
Temperature (K)	293(2)	294(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	P 2(1)/c
Z	2	4
D_{calcd} [Mg/m^3]	1.280	1.358
F (000)	1.023	648
θ range [°]	2.305-25.992	2.113 -25.998
R_1 [I>2σ(I)]	0.0530	0.0484
wR_2 [I>2σ(I)]	0.1313	0.1185
a [Å]	9.084(6)	13.6700(7)
b [Å]	9.380(5)	13.8069(5)
c [Å]	11.255(6)	8.0610(3)
α [deg]	77.947(17)	90
β [deg]	76.979(19)	99.975(2)
γ [deg]	72.387(18)	90
V [Å^3]	880.3(8)	1498.44(11)
GOF	1.023	1.026
R (int)	0.0603	0.0227
No. of reflcns collected	12556	7292
No. of unique reflcns	3452	2900
R_1 (all data)	0.0861	0.0620
wR_2 (all data)	0.1568	0.1314

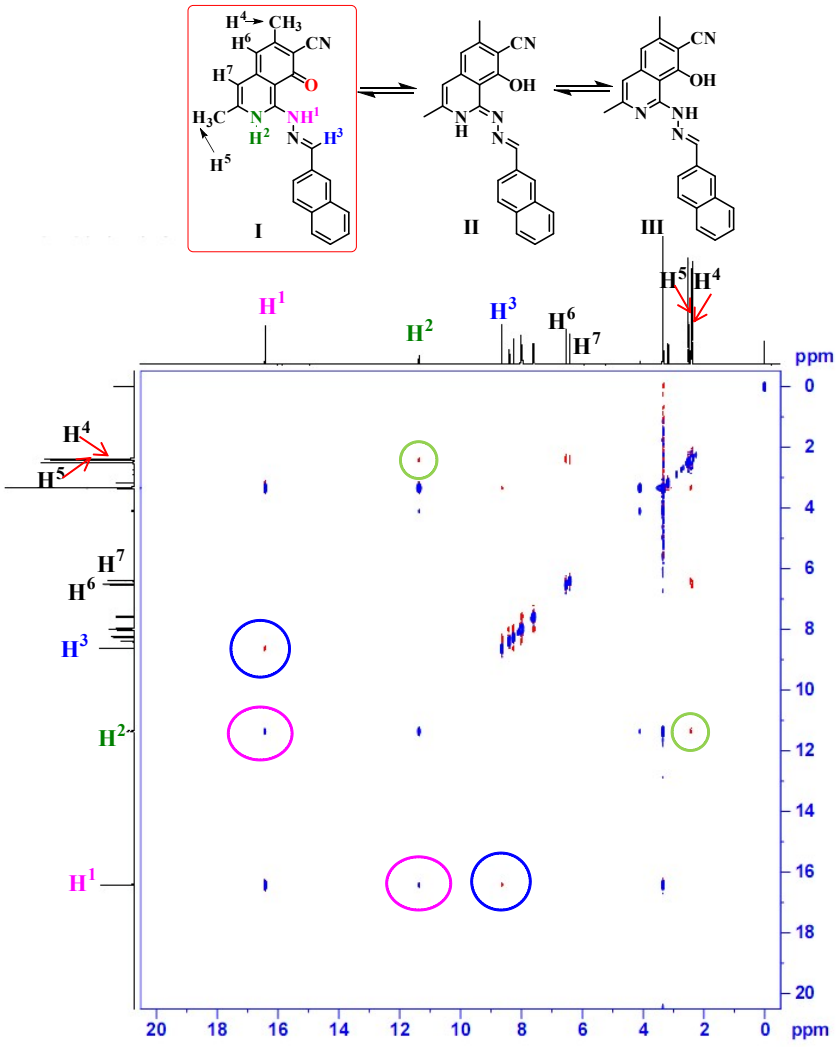


Fig. S2 NOESY spectrum of **NHIQ** in DMSO-d_6.

Table S2 Absolute Energy (Hartree) of different structural forms of the target compounds under the environment of chloroform.

Compound	Absolute Energy (Hartree)		
	Form-**I**	Form-**II**	Form-**III**
AHIQ	-1335.540875	-1335.540143	-1335.475019
BHIQ	-1028.193731	-1028.192836	-1028.137098
NHIQ	-1181.877371	-1181.876459	-1181.815842
TPHIQ	-1545.783189	-1545.781810	-1545.712879

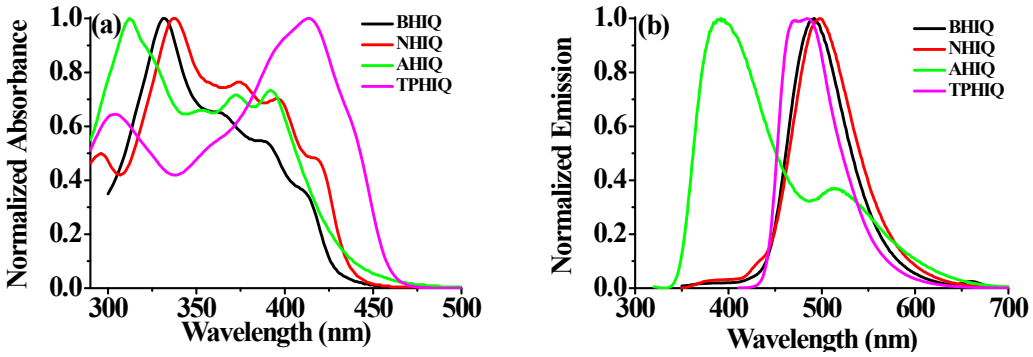


Fig. S3 Normalized absorption (a) and fluorescence (b) spectra of the isoquinolinone-arylidenehydrazine derivatives in $CHCl_3$ at a concentration of 1×10^{-5} mol/L.

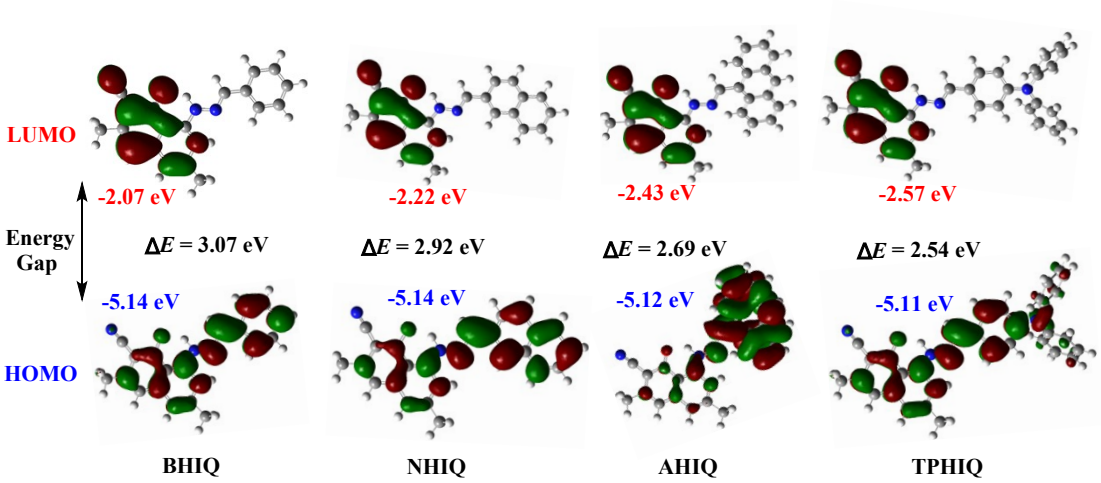
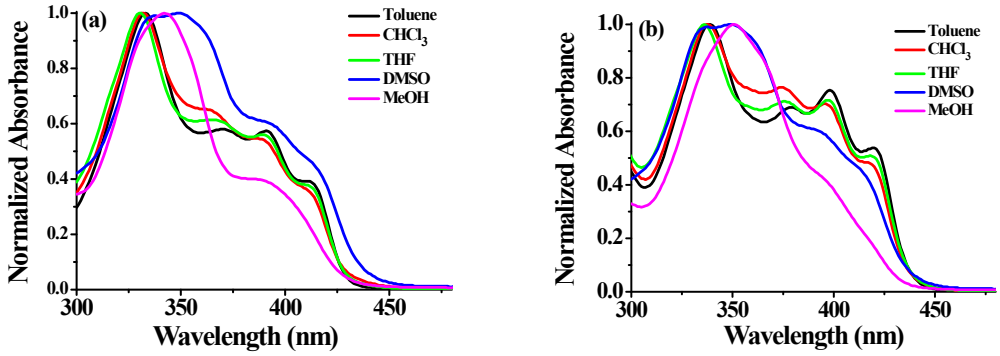


Fig. S4 HOMO and LUMO distributions and energy gaps (ΔE) of isoquinolinone-arylidenehydrazine derivatives obtained from DFT calculations.



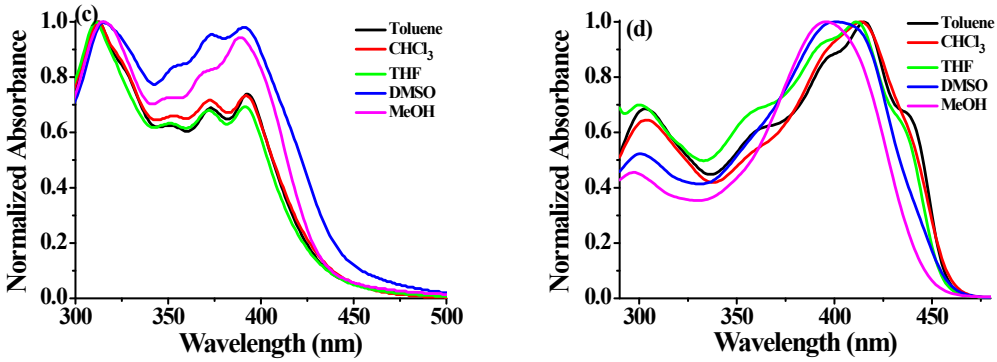


Fig. S5 Normalized absorption spectra of **BHIQ** (a), **NHIQ** (b), **AHIQ** (c), and **TPHIQ** (d) in various solvents. Concentration: 1×10^{-5} mol/L.

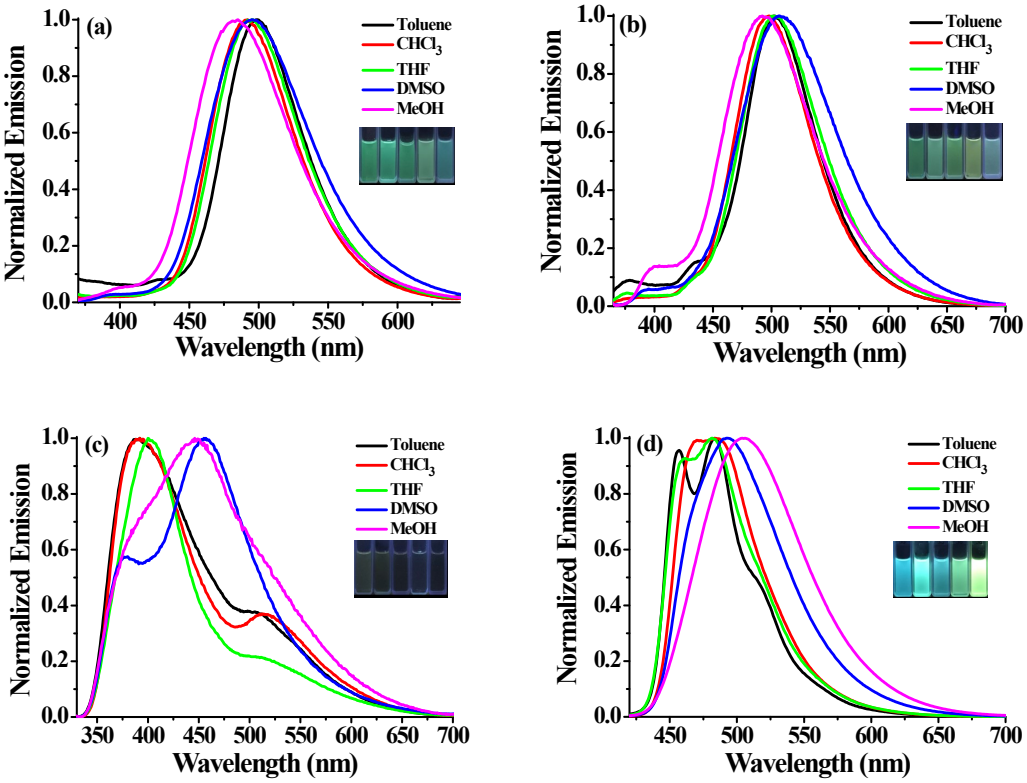


Fig. S6 Normalized fluorescence spectra of **BHIQ** (a), **NHIQ** (b), **AHIQ** (c), and **TPHIQ** (d) in various solvents. Inset: Fluorescence photos in different solvents and the solvent from left to right is toluene, $CHCl_3$, THF, DMSO, and CH_3OH. Concentration: 1×10^{-5} mol/L.

Table S3 Crystal data and details of collection and refinement for the target compounds.

Compound	**BHIQ-*g***	**BHIQ-*ms***	**BHIQ-*ms*'**[a]	**NHIQ-*sb***	**NHIQ-*g***
CCDC (no.)	2091614	2091615	-	2091617	2091616
Empirical formula	$C_{39}H_{34}Cl_2N_8O_2$	$C_{19}H_{18}N_4O_2$	$C_{19}H_{18}N_4O_2$	$C_{23}H_{22}N_4O_3$	$C_{23}H_{18}N_4O$
Formula weight	717.64	334.37	334.37	402.44	366.41
Temperature (K)	293(2)	190(2)	293(2)	193(2)	190(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	*P* 2(1)/c	*P* 2(1)/c	*P* 2(1)/c	*P*$\bar{1}$	*P* 2(1)/c
Z	4	4	4	4	8
D_{calcd} [Mg/m^3]	1.303	1.338	1.309	1.286	1.255
F (000)	1496	704	704	848	1536
θ range [°]	2.551-25.500	5.44-53.83	2.847-25.997	1.962-24.999	2.315-54.106
R_1 [I>2σ(I)]	0.0678	0.0370	0.0426	0.0909	0.0677
wR_2 [I>2σ(I)]	0.1327	0.1023	0.1061	0.2588	0.1346
a [Å]	7.1128(8)	9.2319(3)	9.2933(3)	6.8893(10)	9.3230(5)
b [Å]	24.249(3)	7.4023(2)	7.4829(3)	10.2811(14)	33.211(2)
c [Å]	21.338(2)	24.3921(8)	24.4887(9)	31.330(4)	12.8183(7)
α [deg]	90	90	90	89.906(4)	90
β [deg]	96.157(4)	95.2650(10)	95.1110(10)	84.037(4)	102.176(3)
γ [deg]	90	90	90	70.494(4)	90
V [Å^3]	3659.2(7)	1659.86(9)	1696.19(11)	2079.1(5)	3879.6(4)
GOF	1.049	0.950	1.038	1.063	0.934
R (int)	0.0964	0.0474	0.0334	0.0685	0.0553
No. of reflcns collected	52601	3021	16722	33258	6830
No. of unique reflcns	6817	2588	3335	7302	2863
R_1 (all data)	0.1541	0.0483	0.0632	0.1408	0.1538
wR_2 (all data)	0.1766	0.1085	0.1227	0.3223	0.1622

Compound	**AHIQ-*o***	**AHIQ-*r***	**TPHIQ**	**TPHIQ-TFA**
CCDC (no.)	2091619	2091618	2091620	2091621
Empirical formula	$C_{27}H_{20}N_4O$	$C_{27}H_{20}N_4O$	$C_{31}H_{31}N_5O_4$	$C_{35}H_{27}F_6N_5O_5$
Formula weight	416.47	416.47	537.61	711.61
Temperature (K)	293(2)	293(2)	193(2)	293(2)
Crystal system	Triclinic	Monoclinic	Orthorhombic	Triclinic
Space group	*P*$\bar{1}$	*P* 2(1)/c	*P* c a 21	*P*$\bar{1}$
Z	2	4	4	2
D_{calcd} [Mg/m^3]	1.328	1.356	1.294	1.395
F (000)	436	872	1136	732
θ range [°]	2.596 -26.000	2.525-25.498	2.375-25.496	2.225-25.500
R_1 [I>2σ(I)]	0.0450	0.0611	0.0581	0.0598
wR_2 [I>2σ(I)]	0.1125	0.1356	0.1155	0.1454
a [Å]	9.8422(4)	10.4452(13)	21.928(2)	11.2227(8)
b [Å]	9.9010(3)	14.5388(17)	18.6382(14)	11.5198(9)
c [Å]	12.4255(4)	14.352(2)	6.7530(5)	13.9598(12)
α [deg]	74.2740(10)	90	90	95.662(3)

β [deg]	78.7650(10)	110.632(4)	90	96.684(2)
γ [deg]	63.7490(10)	90	90	107.307(2)
V [Å^3]	1041.36(6)	2039.8(5)	2760.0(4)	1694.4(2)
GOF	1.022	1.053	1.078	1.010
R (int)	0.0342	0.0592	0.0477	0.0745
No. of reflcns collected	17859	9391	12704	29491
No. of unique reflcns	4066	3775	4819	6273
R_1 (all data)	0.0647	0.1213	0.0881	0.0975
wR_2 (all data)	0.1289	0.1758	0.1319	0.1732

[a] **BHIQ-*ms***' was obtained from **BHIQ-*ms*** a week later in natural environment.

Table S4 The fluorescence properties and lifetime decays parameters of the target compounds under different conditions.

Compound	Type	λ_{em} (nm)	Φ_F (%)	τ_1 [a] (ns)	A_1 [b] (%)	τ_2 [a] (ns)	A_2 [b] (%)	$<\tau>$ [c] (ns)	k_f [d] (s^{-1})	k_{nr} [e] (s^{-1})
BHIQ-*g*	Original	504	15	1.51	73	5.86	27	2.70	5.6×10^7	3.1×10^8
	Ground	502	7	0.53	49	18.9	51	9.88	7.1×10^6	9.4×10^7
	Fumed	479	14	0.04	74	14.3	26	3.75	3.7×10^7	2.3×10^8
BHIQ-*ms*	Original	485	12	0.13	57	8.64	43	3.79	3.1×10^7	2.3×10^8
	Gently ground	480	21	0.49	77	5.45	23	1.64	1.3×10^8	4.8×10^8
	Strongly ground	491	10	0.11	59	8.48	41	3.54	2.8×10^7	2.5×10^8
	Fumed	480	12	0.63	76	8.31	24	2.46	4.8×10^7	3.6×10^8
BHIQ[f]	TFA	437, 455	18	0.43	87	2.57	13	0.71	2.5×10^8	1.2×10^9
	TEA	487	11	0.24	75	3.79	25	1.13	9.7×10^7	7.8×10^8
NHIQ-*sb*	Original	481	9	0.60	79	4.27	21	1.37	6.6×10^7	6.6×10^8
	Ground	515	4	0.55	44	9.75	56	5.71	7.0×10^6	1.7×10^8
	Fumed	482	9	0.34	71	4.34	29	1.52	6.0×10^7	6.0×10^8
NHIQ-*g*	Original	503	15	1.13	75	4.65	25	2.02	7.4×10^7	4.2×10^8
	Ground	512	5	0.69	49	9.23	51	5.07	1.0×10^7	1.9×10^8
	Fumed	504	11	0.34	70	4.79	30	1.66	6.6×10^7	5.4×10^8
NHIQ[g]	TFA	459, 528	24	4.73	66	1.70	34	3.69	6.5×10^7	2.1×10^8
	TEA	492	9	4.36	21	0.19	79	1.06	8.5×10^7	8.6×10^8
AHIQ-*r*	Original	578, 625	6	0.3	56	8.02	44	3.69	1.6×10^7	2.5×10^8
	Ground	580, 624	8	0.12	73	11.2	27	3.13	2.6×10^7	2.9×10^8
AHIQ-*o*	Original	567	10	8.89	15	0.83	85	2.04	5.0×10^7	4.4×10^8
	Ground	559	8	26.4	13	1.06	87	1.01	7.9×10^7	9.1×10^8

	Fumed	566	13	15.7	16	0.74	84	3.13	4.2×10^7	2.8×10^8
AHIQ[h]	TFA	543, 577	10	0.33	86	9.18	14	1.57	6.4×10^7	5.7×10^8
	TEA	583	9	8.07	6	0.04	94	0.52	1.7×10^8	1.8×10^9
TPHIQ	Original	519	8	15.3	39	0.39	61	6.20	1.3×10^7	1.5×10^8
	Ground	513	6	5.23	21	0.33	79	1.36	4.4×10^7	6.9×10^8
	TFA	542, 620	7	12.9	14	0.49	86	3.16	2.2×10^7	2.9×10^8
	TEA	519	6	0.12	64	4.8	36	1.80	3.3×10^7	5.2×10^8

[a] τ_1 and τ_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: $k_{nr} = (1-\Phi_F)/<\tau>$. [f] **BHIQ-*g*** or **BHIQ-*ms***. [g] **NHIQ-*sb*** or **NHIQ-*g***. [h] **AHIQ-*r*** or **AHIQ-*o***.

Table S5 Summarization of the interactions in the single crystals of the target compounds.

Crystal	Interactions	d/Å	Crystal	Interactions	d/Å
BHIQ-*g*	H11···π (Ph)	3.638	**BHIQ-*ms***	π (Ph)···π (C=N)	3.386
	π (Ph)···π (C=N)	3.413		π (C=N)···π (C=O)	3.494
	π (Ph)···π (C=N)	3.553		N2-H2A···O1	1.839
	O2-H2A···N7	1.762		H2···O1	2.473
	O1-H1A···N3	1.807			
	N5-H5···N2	2.303			
	H38···N2	2.695			
	H37···O1	2.641			
NHIQ-*g*	H18A···π (C≡N)	2.895	**NHIQ-*sb***	π (Ph)···π (Ph)	3.789
	H45C···π (Ph)	2.619		π (Ph)···π (Ph)	3.646
	π (Ph)···π (Pyridine)	3.581		π (Ph)···π (Pyridine)	3.742
	π (Ph)···π (Pyridine)	3.725		H13···N2	2.705
	N6-H6A···O2	1.881		H3···O1	1.712
	N2-H2A···O1	1.861		H20···H10A	2.647
	H7···O2	2.544			
	H26···O1	2.668			
	H9···N8	2.648			
	H28···N8	2.577			
AHIQ-*r*	H11···π (Ph)	3.446	**AHIQ-*o***	H4···π (Ph)	3.359
	H21···π (Ph)	3.709		π (Ph)···π (Ph)	4.193
	O1-H1···N3	1.720		O1-H1···N3	1.727
	H11B···O1	2.474		H18··· H26	2.392
	H2···N2	2.745		H10B···N2	2.722
TPHIQ	π (C=N)···π (C=N)	3.421		H16···N2	2.671
	π (Pyridine)···π (Ph)	3.595			
	H10A···π (C≡N)	2.771			
	N3-H3···O1	1.782			
	H10C···N2	2.968			
	H18···N2	2.633			

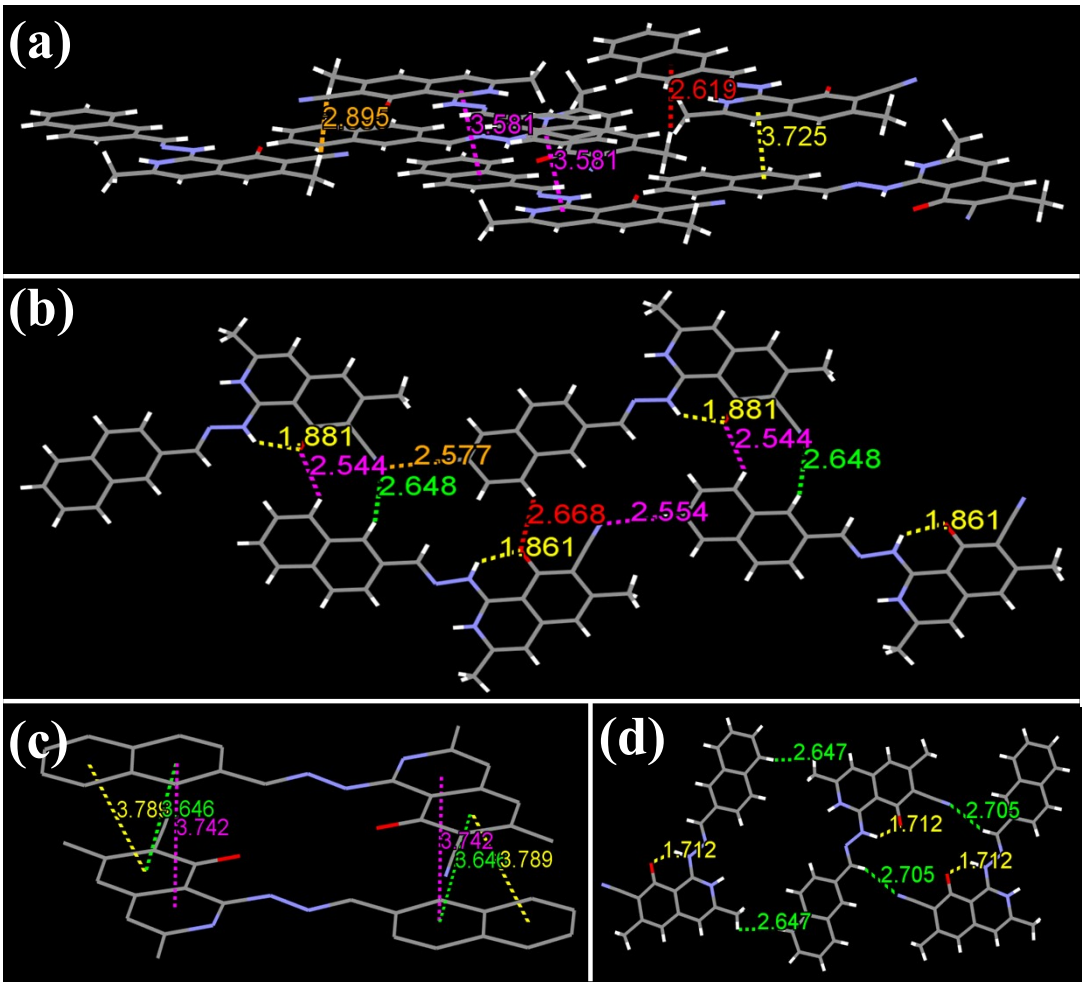


Fig. S7 Intermolecular interactions in columns and interactions in horizontal direction in the single crystals of **NHIQ-*g*** (a,b) and **NHIQ-*sb*** (c,d).

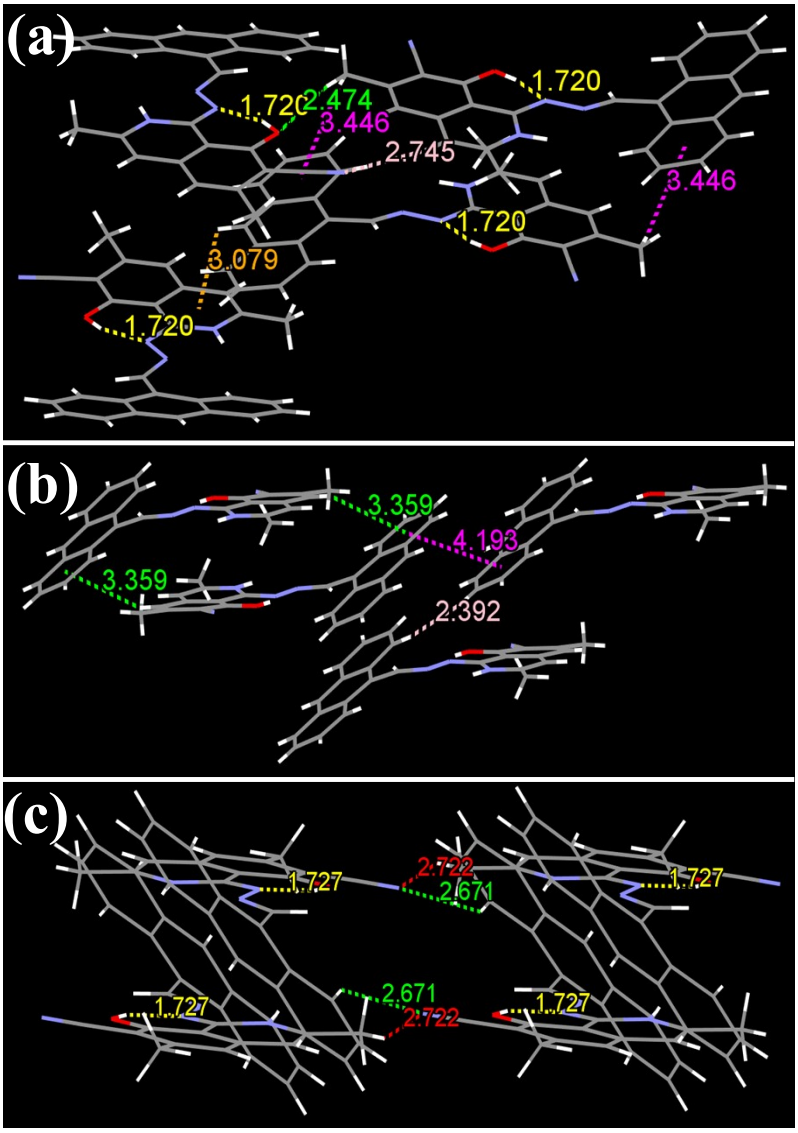


Fig. S8 Intramolecular and intermolecular interactions in the single crystals of crystal **AHIQ-*r*** (a) and **AHIQ-*o*** (b,c).

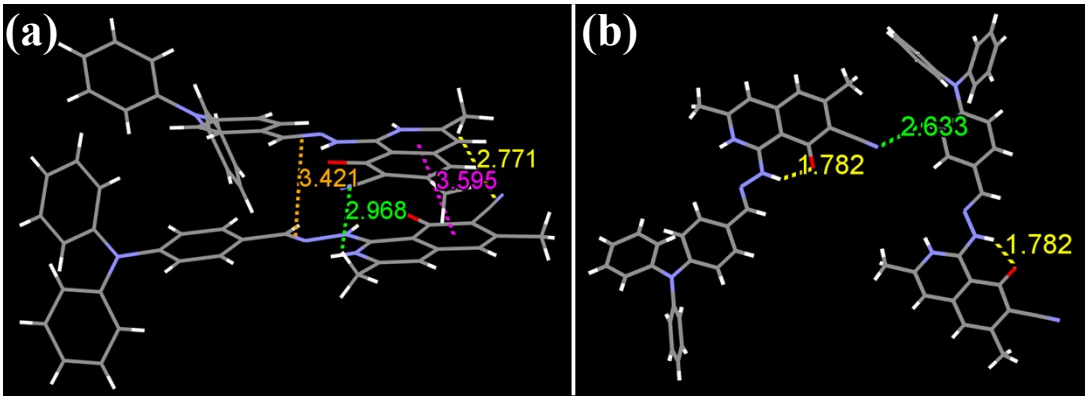


Fig. S9 Single crystal **TPHIQ**: intramolecular and intermolecular interactions.

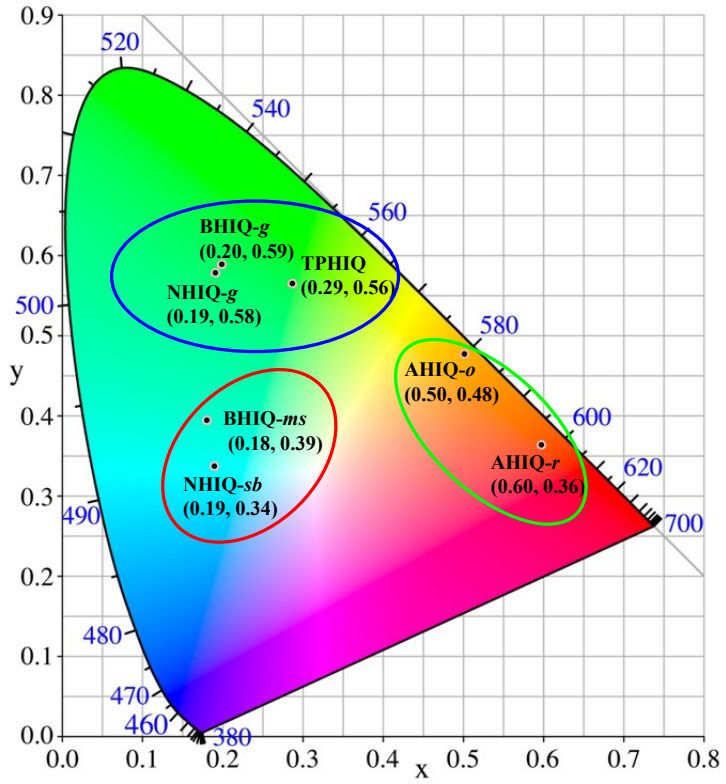


Fig. S10 CIE coordinates of the isoquinolinone-arylidenehydrazine derivatives in the crystalline state.

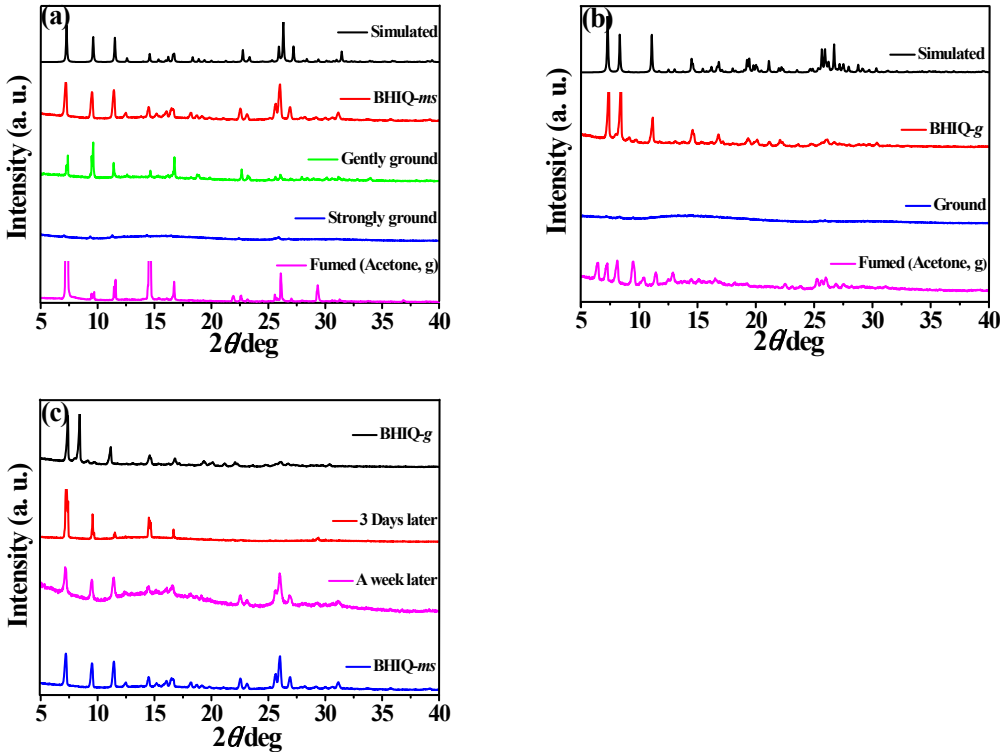


Fig. S11 XRD curves of **BHIQ-*ms*** (a) and **BHIQ-*g*** (b) under different conditions. (c) Change of XRD curves of **BHIQ-*g*** in natural environment.

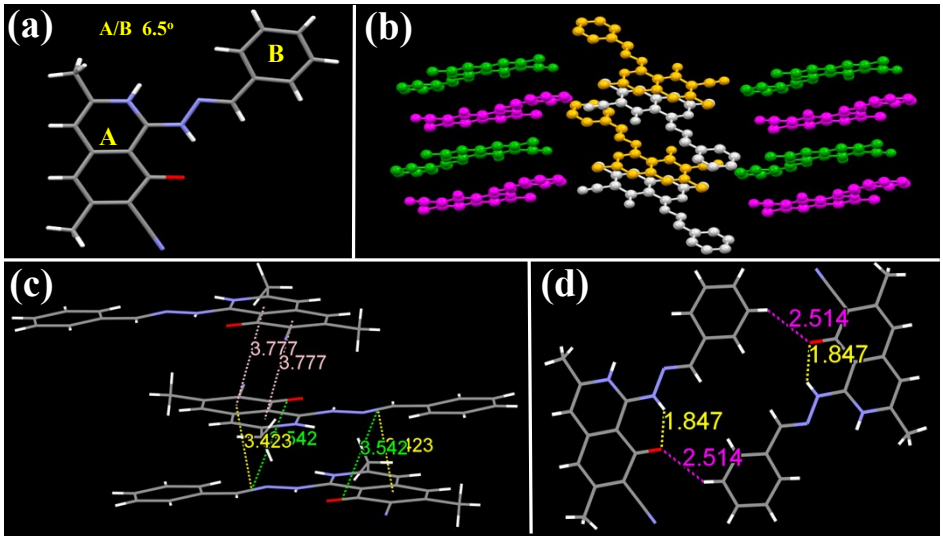


Fig. S12 The single crystal **BHIQ-*ms*'** obtained from **BHIQ-*g*** a week later in natural environment: (a) single crystal structure; (b) stacking arrangement; (c) intermolecular interactions in a column; (d) interactions in horizontal direction.

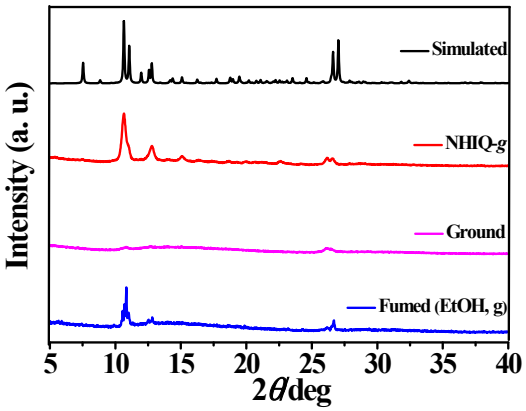


Fig. S13 XRD curves of **NHIQ-*g*** under different conditions.

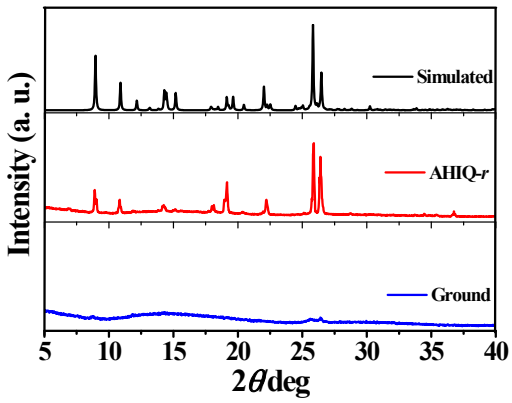


Fig. S14 XRD curves of **AHIQ-*r*** under different conditions.

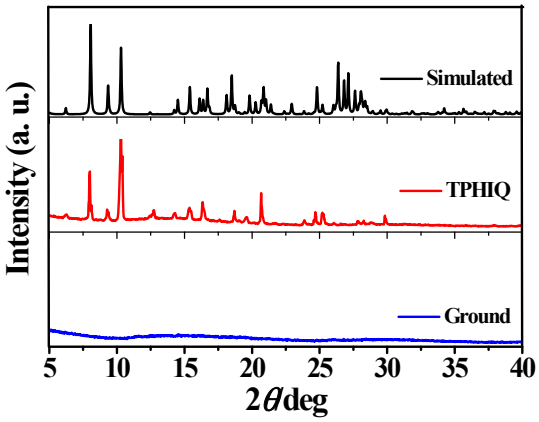


Fig. S15 XRD curves of **TPHIQ** under different conditions.

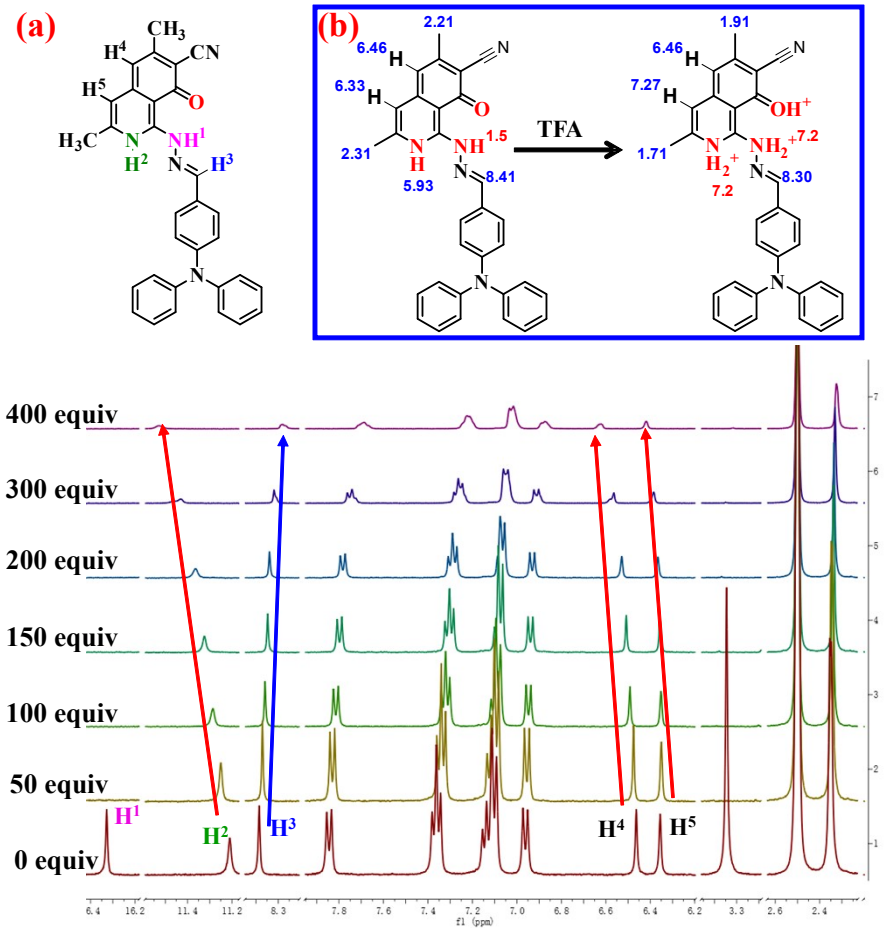


Fig. S16 (a) ^{1}H NMR spectra of **TPHIQ** in DMSO-d_6 with the addition of TFA. (b) Chemical shifts of protons of **TPHIQ** obtained from the simulation of ChemDraw software.

3. NMR spectra

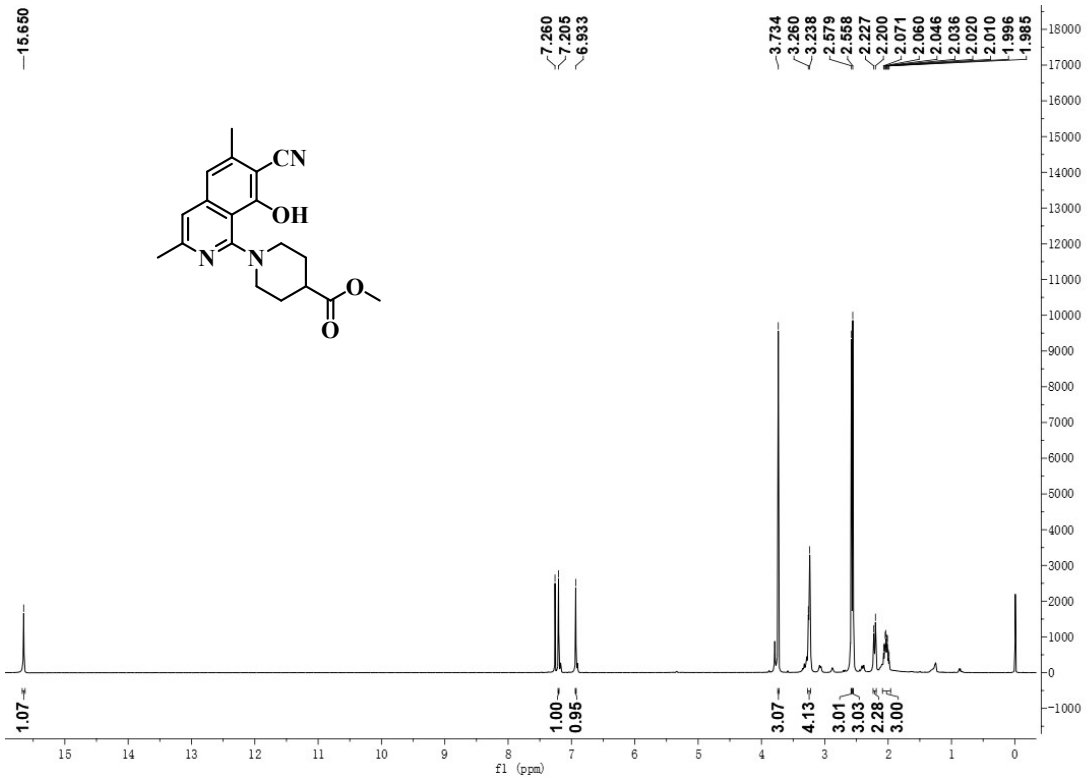


Fig. S17 ^{1}H NMR of compound **2** ($CDCl_3$, 500 MHz).

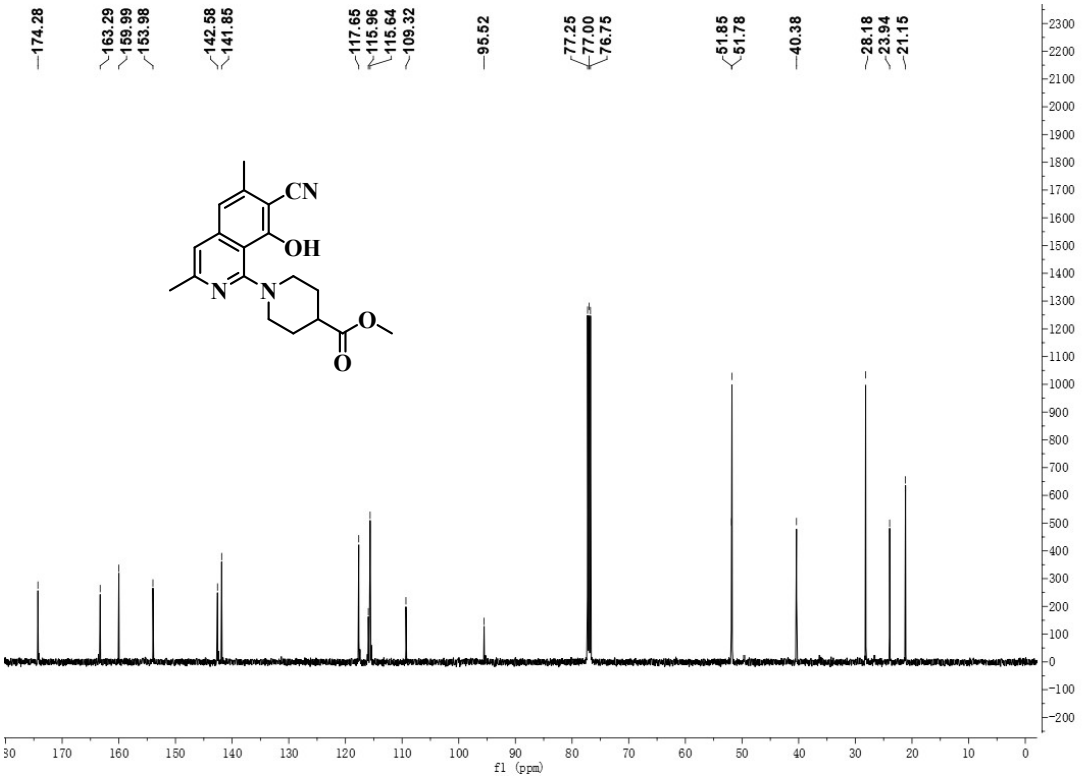


Fig. S18 ^{13}C NMR of compound **2** ($CDCl_3$, 125 MHz).

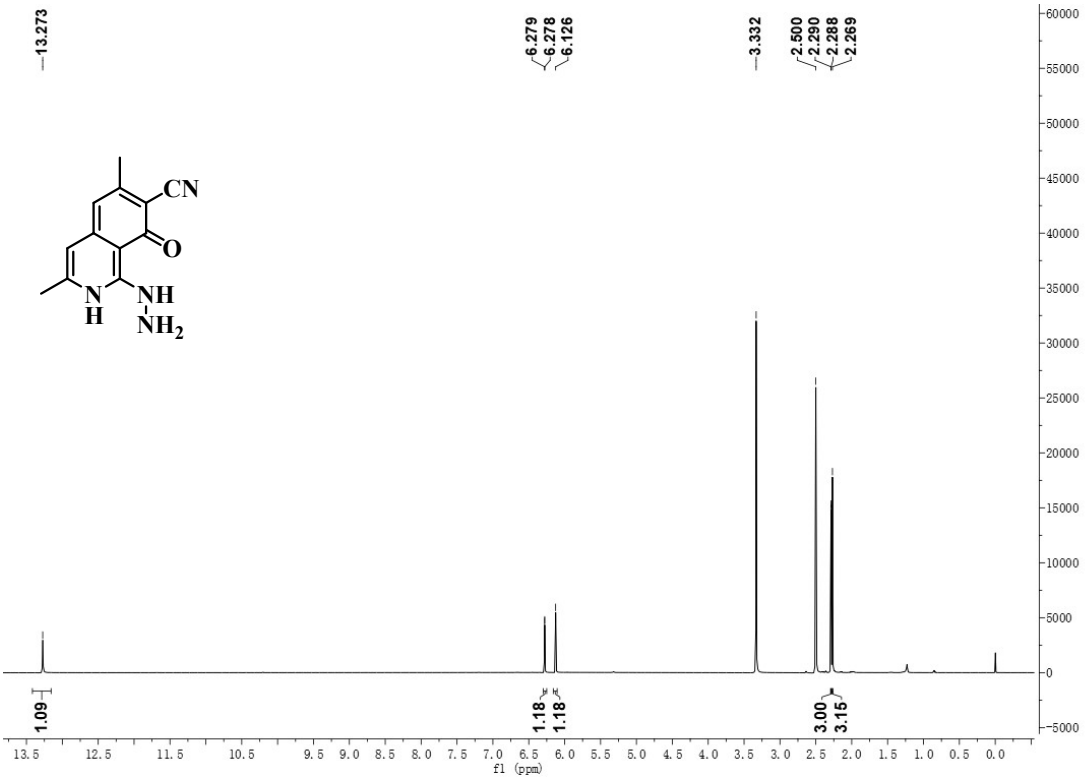


Fig. S19 ^{1}H NMR of compound **3** (DMSO-d_6, 500 MHz).

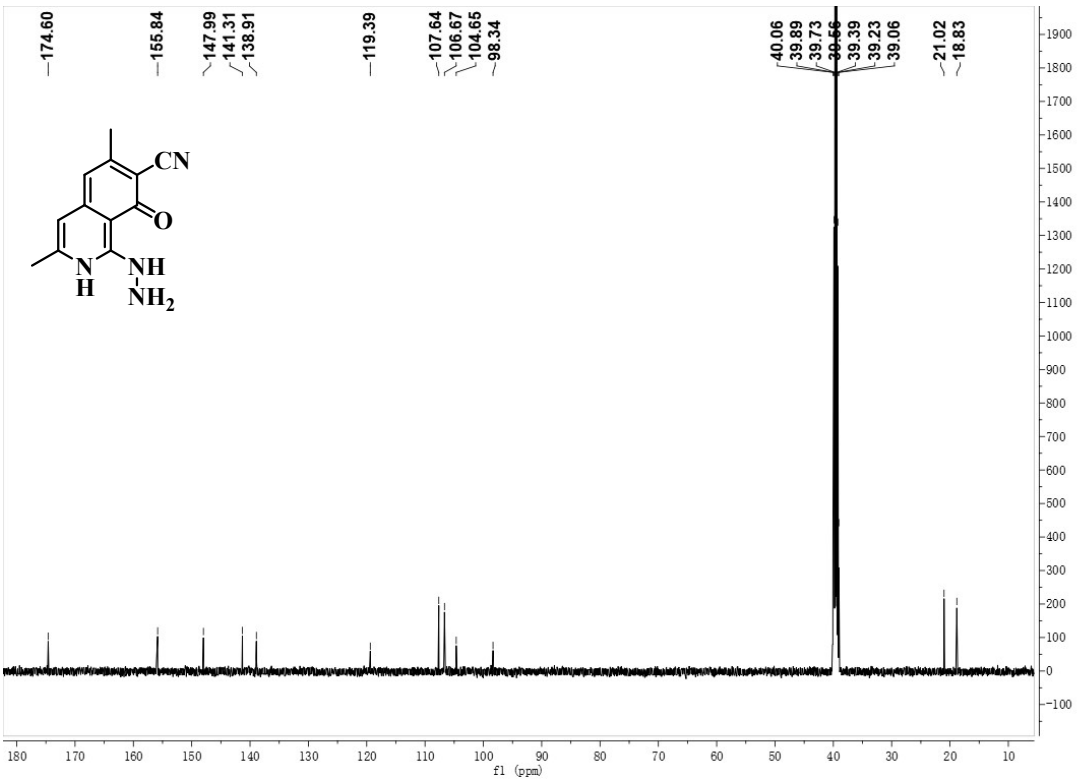


Fig. S20 ^{13}C NMR of compound **3** (DMSO-d_6, 125 MHz).

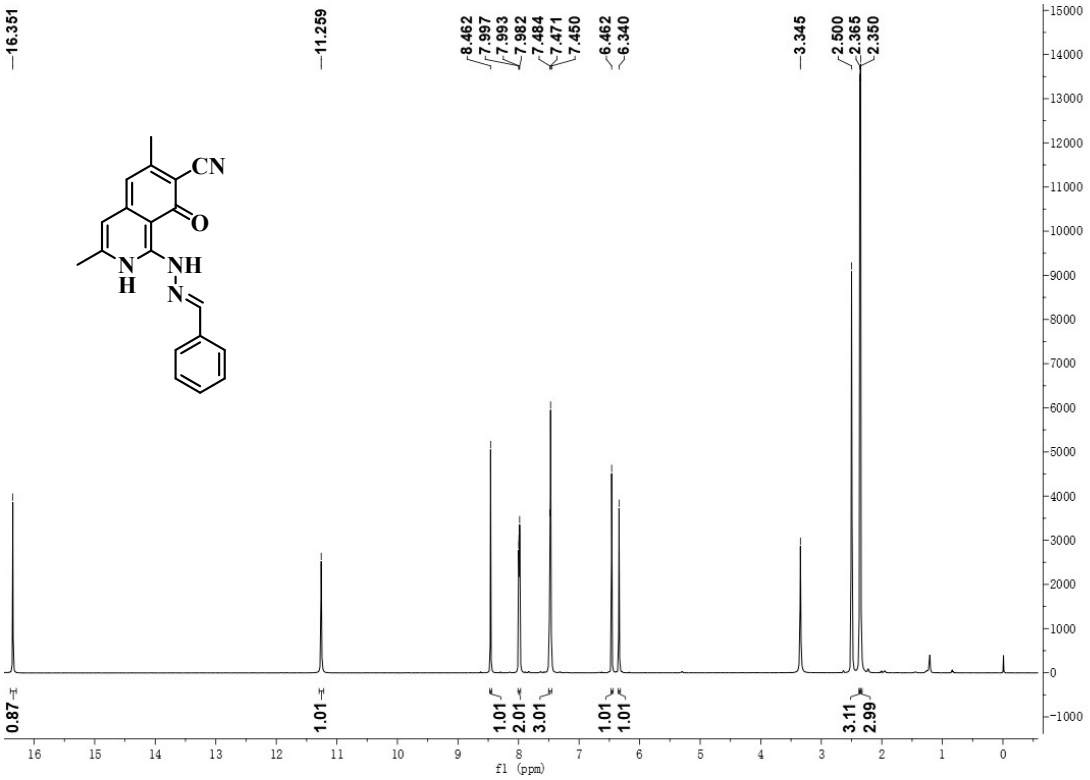


Fig. S21 ^{1}H NMR of **BHIQ** (DMSO-d_6, 500 MHz).

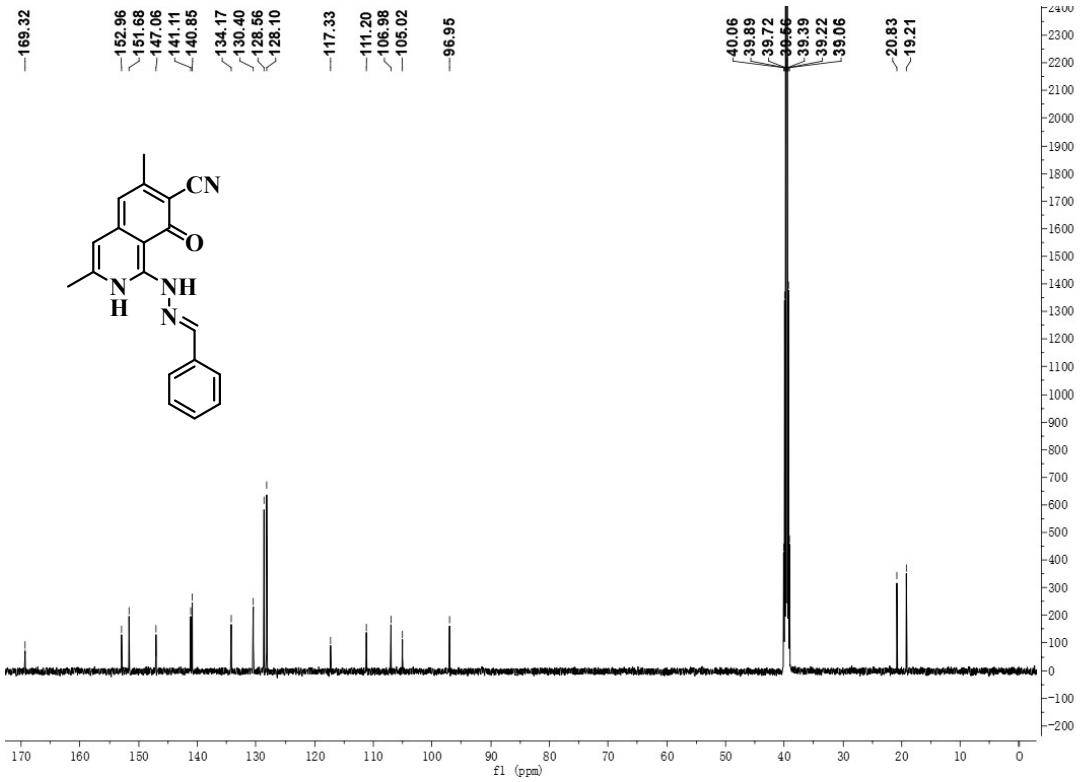


Fig. S22 ^{13}C NMR of **BHIQ** (DMSO-d_6, 125 MHz).

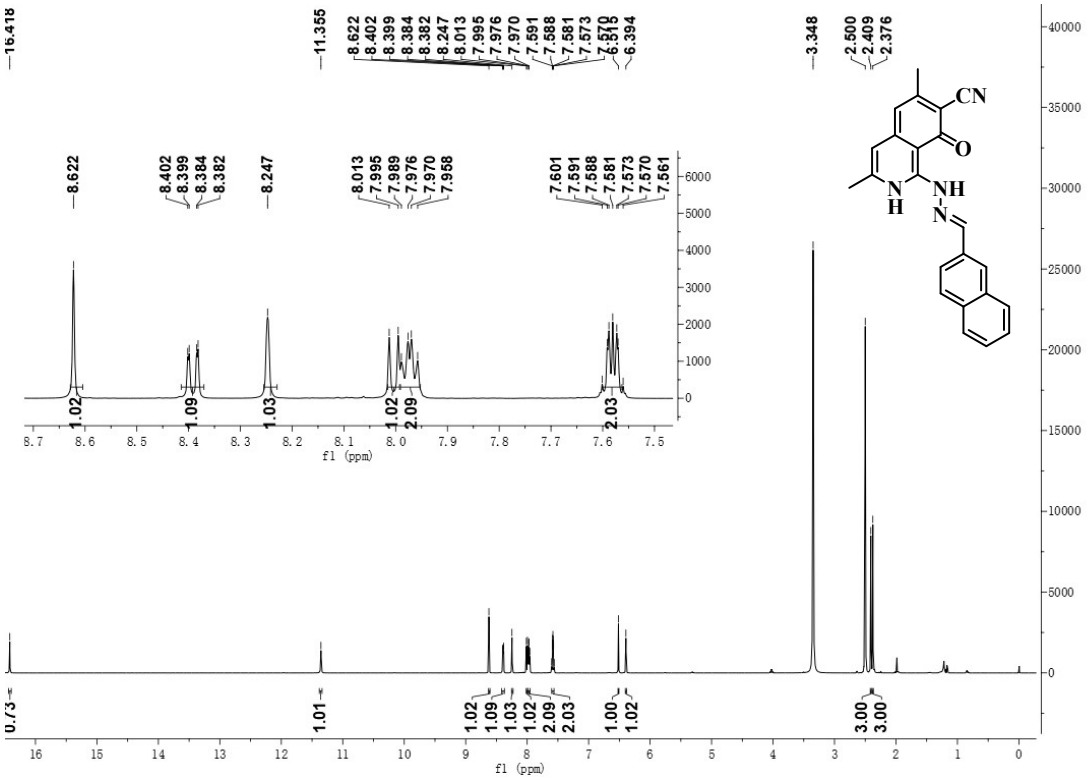


Fig. S23 ^{1}H NMR of **NHIQ** (DMSO-d_6, 500 MHz).

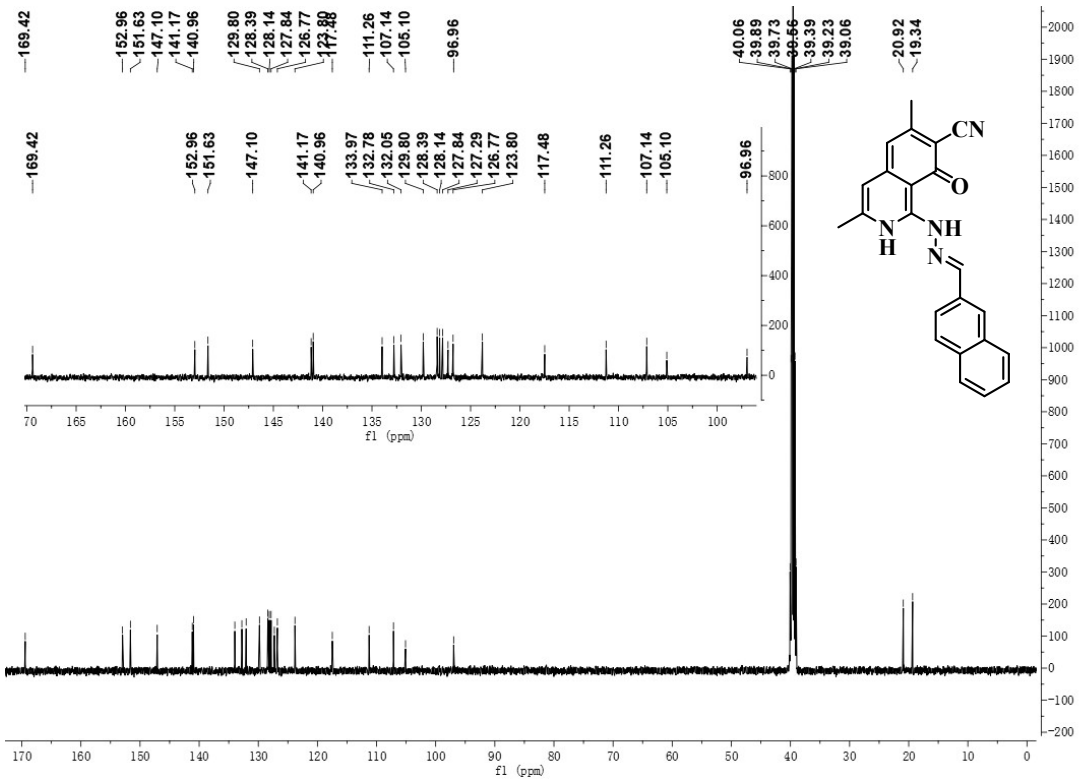


Fig. S24 ^{13}C NMR of **NHIQ** (DMSO-d_6, 125 MHz).

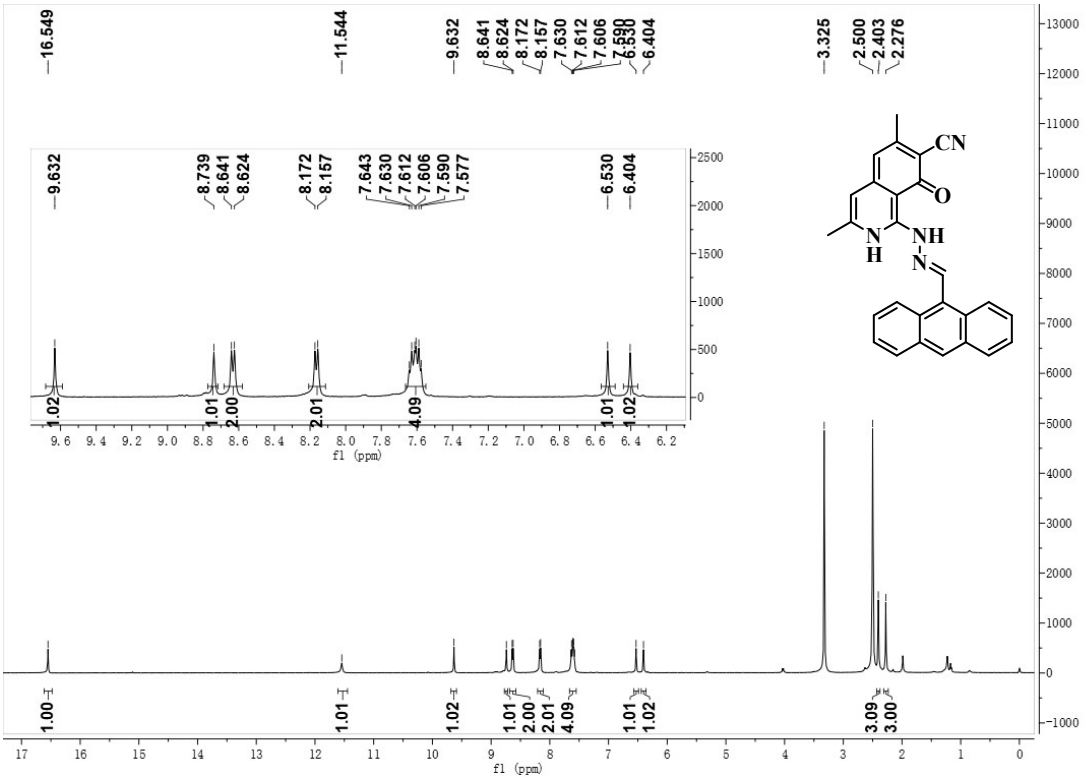


Fig. S25 ^{1}H NMR of **AHIQ** (DMSO-d_6, 500 MHz).

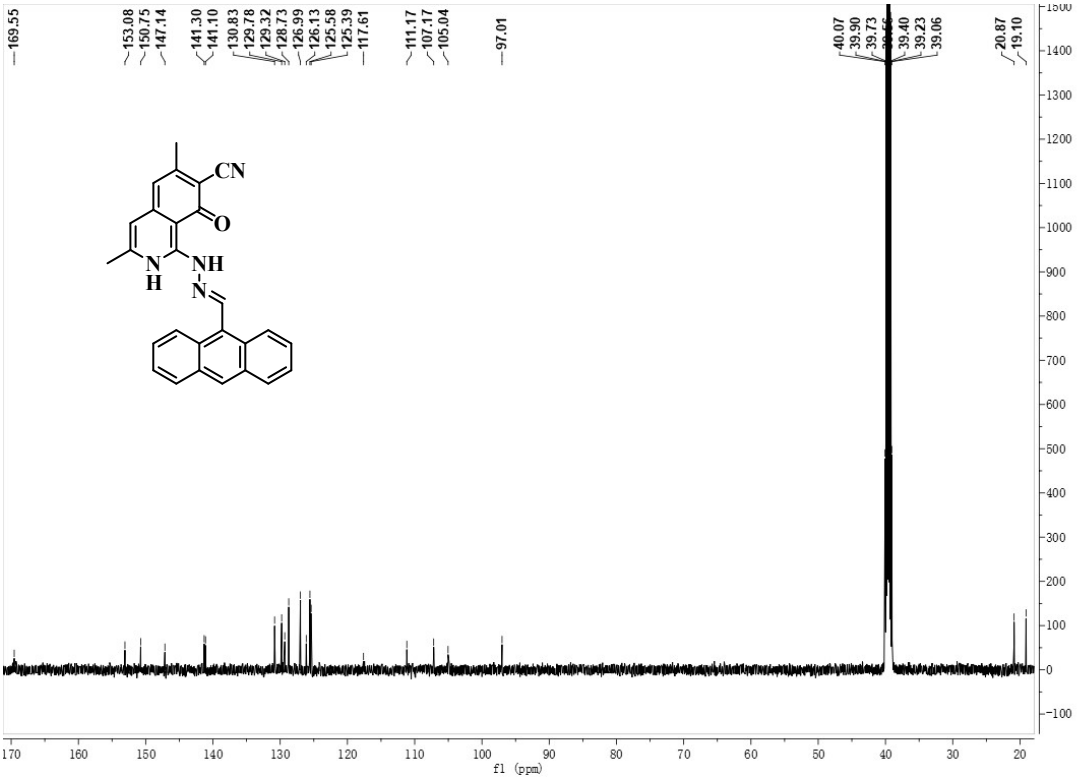


Fig. S26 ^{13}C NMR of **AHIQ** (DMSO-d_6, 125 MHz).

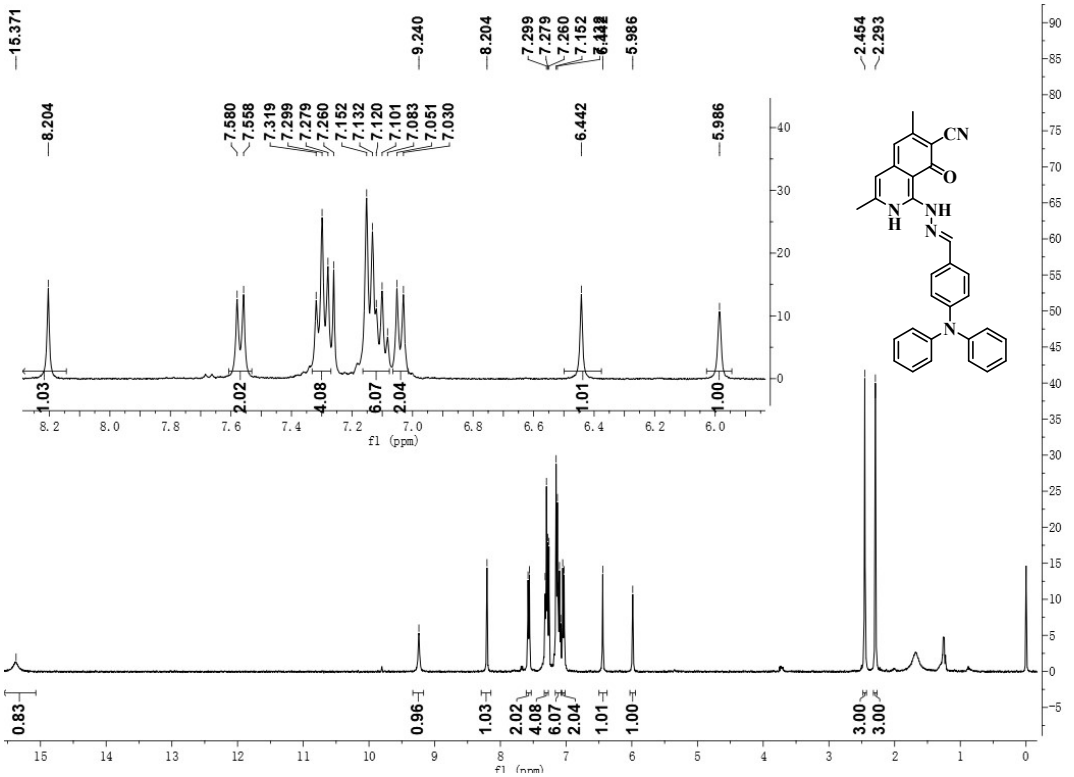


Fig. S27 ^{1}H NMR of **TPHIQ** ($CDCl_3$, 500 MHz).

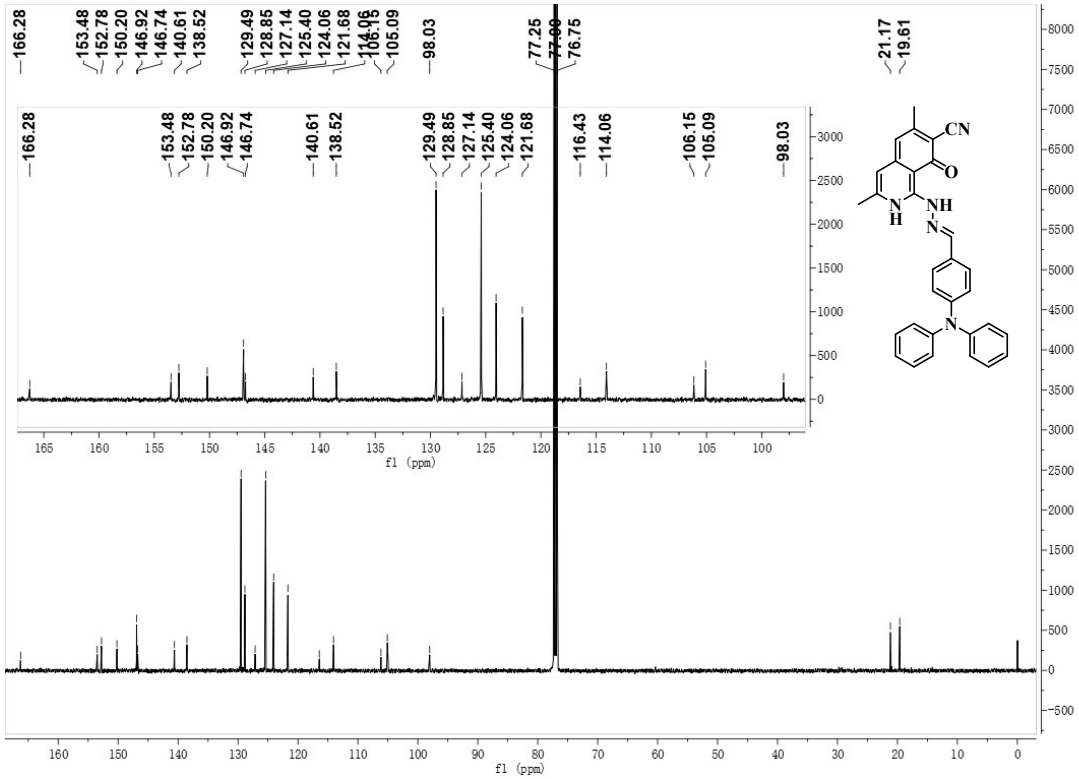


Fig. S28 ^{1}H NMR of **TPHIQ** ($CDCl_3$, 125 MHz).