

Electronic Supplementary Information

Mechanofluorochromism, polymorphism and thermochromism of novel D- π -A piperidin-1-yl-substituted isoquinoline derivatives

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Contents:

1. Experimental

Measurements and materials

^1H , ^{13}C , and ^{19}F NMR spectra were tested on a Bruker DRX 500 NMR or DRX 400 NMR spectrometer. Melting points were tested on WRS-1B digital melting point meter (uncorrected). High-resolution electrospray ionization (HRMS-ESI) mass spectra were performed using a Hitachi Nano Frontier LD spectrometer. Elemental analyses (C, H, and N) were obtained using an Elementar Vario MICRO analyzer. X-Ray diffraction (XRD) patterns were performed using an Empyrean X-ray diffraction instrument. Fluorescence spectra were obtained using a Cary Eclipse fluorescence spectrophotometer. The absolute fluorescence quantum yields and fluorescence lifetime decays were performed using Jobin Yvon Horiba FluoroMax-4 fluorometer. UV-vis absorption spectra were conducted on a UV-3600 Shimadzu spectrophotometer. Differential scanning calorimetry (DSC) experiments were conducted on a TA-DSC Q2000 at a heating rate of 10 °C/min. Fluorescence microscopic images were obtained using a Leica DMI3000B inverted optical microscope. Single-crystal X-ray data were collected with graphite-monochromated $\text{MoK}\alpha$ radiation on a Bruker-Nonius Smart Apex CCD diffractometer. 2,6-Dimethyl-4-pyranone (**2**), cyanoacetic acid, trifluoromethanesulfonic anhydride (Tf_2O), 4-bromo-*N,N*-diphenylaniline (**4**), 9-(4-bromophenyl)-9*H*-carbazole (**5**), trimethylsilyl acetylene, and tetrabutyl ammonium fluoride (TBAF) were commercially available and used directly. 4-Ethynyl-*N,N*-diphenylaniline (**8**)¹ and 9-(4-ethynylphenyl)-9*H*-carbazole (**9**)² were synthesized using compound **4** and compound **5** as the starting material based on the previous literatures, respectively.

Synthesis of 2-(2,6-dimethyl-4*H*-pyran-4-ylidene)-3-oxopentanedinitrile (**1**)

Compound **2** (1.24 g, 10.0 mmol) and cyanoacetic acid (4.25 g, 60.0 mmol) were dissolved in

acetic anhydride (10 mL) with stirring at 140°C for 3 h. After the reaction was completed, the reaction mixture was allowed to cool to room temperature and then poured into water (500 mL). After 30 min of stirring, the mixture was extracted three times with dichloromethane. Anhydrous sodium sulfate was added to dry the organic phase and then the organic solvent was evaporated by decompression. The residue was passed through a silica gel column chromatography (ethyl acetate-petroleum ether = 1:2) to afford a yellow solid (727.8 mg, 34.0% yield). M. p. 175.3-176.1°C. ¹H NMR (CDCl₃, 500 MHz): δ 8.31 (s, 1H), 6.70 (s, 1H), 3.88 (s, 2H), 2.41 (s, 3H), 2.40 (s, 3H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ 182.0, 165.74, 165.69, 155.6, 119.5, 114.0, 109.4, 108.2, 85.4, 31.8, 20.3, 20.1 ppm. HRMS (ESI) m/z: [M+Na]⁺ calculated for C₁₂H₁₀N₂O₂Na, 237.0640; found, 237.0644.

Synthesis of 8-hydroxy-3,6-dimethyl-1-(piperidin-1-yl)isoquinoline-7-carbonitrile (PIQ)

A mixture of compound **1** (642.2 mg, 3.0 mmol) and piperidine (510.5 mg, 6.0 mmol) in acetonitrile (10 mL) was stirred at 90°C for 4 h. After the reaction was completed, the reaction mixture was allowed to cool to room temperature and the organic solvent was evaporated by decompression. The residue was passed through a silica gel column chromatography (ethyl acetate-petroleum ether = 1:5) to afford a white solid (716.9 mg, 85.0% yield). M. p. 169.7-170.1°C. ¹H NMR (CDCl₃, 400 MHz): δ 16.63 (s, 1H), 7.19 (s, 1H), 6.88 (s, 1H), 3.26-3.14 (m, 4H), 2.58 (s, 3H), 2.55 (s, 3H) 1.90-1.82 (m, 5H), 1.54-1.42 (m, 1H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ 164.4, 160.3, 154.0, 142.7, 141.9, 117.6, 116.3, 114.9, 109.4, 95.2, 52.8, 25.6, 24.0, 23.1, 21.2 ppm. HRMS (ESI) m/z: [M+H]⁺ calculated for C₁₇H₂₀N₃O, 282.1601; found, 282.1603.

Synthesis of 7-cyano-3,6-dimethyl-1-(piperidin-1-yl)isoquinolin-8-yl trifluoromethanesulfonate (**3**)

Pyridine (592.8 mg, 7.5 mmol) was added to the mixture of **PIQ** (702.9 mg, 2.5 mmol) and dichloromethane (10 mL) at 0°C. After being stirring for 5 min at 0°C, trifluoromethane sulfonic anhydride (1.41 g, 5.0 mmol) was added to the reaction mixture drop by drop. The reaction mixture was allowed to warm to the room temperature and further stirred for 3 h. Then 1 mL ether and 2 mL 10% hydrochloric acid solution were added to quench the reaction. The mixture was extracted with dichloromethane, and the organic phase was washed with saturated sodium bicarbonate solution and then dried with anhydrous sodium sulfate. The organic solvent was evaporated by decompression and the residue was passed through a silica gel column chromatography (ethyl acetate-petroleum ether = 1:10) to afford a green solid (831.4 mg, 80.5% yield). M. p. 186.8-187.1 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.47 (s, 1H), 6.88 (s, 1H), 3.45-3.25 (m, 4H), 2.64 (s, 3H), 2.53 (s, 3H) 1.83-1.52 (m, 6H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ 158.5, 154.4, 148.7, 142.8, 140.3, 126.4, 118.7 (q, J_{C-F} = 319.5 Hz), 113.6, 110.6, 110.0, 103.9, 24.7, 24.5, 24.3, 20.7 ppm. ¹⁹F NMR (CDCl₃, 470 MHz): δ -73.1 ppm. HRMS (ESI) m/z:

[M+Na]⁺ calculated for C₁₈H₁₈F₃N₃O₃SNa, 436.0919; found, 436.0919.

Synthesis of compounds 6 and 7

The general procedure is as follows: a mixture of compound **4/5** (10.0 mmol), CuI (95.5 mg, 0.5 mmol), Pd(PPh₃)₂Cl₂ (175.3 mg, 0.25 mmol), and trimethylsilyl acetylene (2.95 g, 30.0 mmol) in 20 mL triethylamine and 20 mL THF was stirred for 12 h at 80°C in N₂ atmosphere. The organic solvent was evaporated by decompression and the residue was passed through a silica gel column chromatography (petroleum ether) to afford pure compound **6/7**.

N,N-Diphenyl-4-((trimethylsilyl)ethynyl)aniline (6). White solids (2.69 g), 78.7% yield. ¹H NMR (DMSO-*d*₆, 500 MHz): 7.36-7.30 (m, 6H), 7.13-7.05 (m, 6H), 6.83 (d, *J* = 8.5 Hz, 2H), 0.20 (s, 9H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ 147.7, 146.3, 132.7, 129.6, 124.9, 123.9, 120.9, 114.6, 105.5, 92.7, -0.12 ppm. HRMS (ESI) *m/z*: [M+Na]⁺ calculated for C₂₃H₂₃NSiNa, 364.1498; found, 364.1493.

9-(4-((Trimethylsilyl)ethynyl)phenyl)-9H-carbazole (7). White solids (2.79 g), 82.1% yield. ¹H NMR (CDCl₃, 500 MHz): 8.14 (d, *J* = 7.5 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.44-7.40 (m, 4H), 7.33-7.28 (m, 2H), 0.31 (s, 9H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ 140.6, 137.8, 133.5, 126.7, 126.0, 123.6, 122.2, 120.3, 120.2, 109.7, 104.3, 95.4, -0.04 ppm. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₃H₂₂NSi, 340.1516, found, 340.1510.

Synthesis of compounds 8 and 9

The general procedure is as follows: a mixture of compound **6/7** (5.0 mmol) and tetrabutylammonium fluoride (10.0 mmol) in THF (20 mL) was stirred for 12 h at 0°C in a N₂ atmosphere. The organic solvent was evaporated by decompression and the residue was passed through a silica gel column chromatography (petroleum ether) to afford pure compound **8/9**.

4-Ethynyl-N,N-diphenylaniline (8). White solids (1.02 g), 75.8% yield. ¹H NMR (DMSO-*d*₆, 500 MHz): 7.35-7.32 (m, 6H), 7.12-7.05 (m, 6H), 6.86 (d, *J* = 8.5 Hz, 2H), 4.06 (s, 1H) ppm. ¹³C NMR (DMSO-*d*₆, 125 MHz): 147.7, 146.4, 132.8, 129.6, 124.8, 123.9, 121.2, 114.2, 83.6, 79.5 ppm. HRMS (ESI) *m/z*: [M+Na]⁺ calculated for C₂₀H₁₅NNa, 292.1102; found, 292.1104.

9-(4-Ethynylphenyl)-9H-carbazole (9). White solids (1.04 g), 78.1% yield. ¹H NMR (DMSO-*d*₆, 500 MHz): 8.25 (d, *J* = 7.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.46-7.41 (m, 4H), 7.32-7.29 (m, 2H), 4.34 (s, 1H) ppm. ¹³C NMR (DMSO-*d*₆, 125 MHz): δ 139.7, 137.2, 133.5, 126.7, 126.3, 122.9, 120.6, 120.5, 120.3, 109.6, 82.8, 81.5 ppm. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₀H₁₄N, 268.1121; found, 268.1124.

Synthesis of 8-((4-(diphenylamino)phenyl)ethynyl)-3,6-dimethyl-1-(piperidin-1-yl)isoquinoline-7-carbonitrile (IQ-TPA)

A mixture of compound **8** (807.4 mg, 3.0 mmol), compound **3** (826.8 mg, 2.0 mmol), CuI (22.9 mg, 0.12 mmol), and Pd(PPh₃)₂Cl₂ (84.0 mg, 0.12 mmol) in triethylamine (8 mL) and *N*, *N*-

dimethylformamide (8 mL) was stirred for 12 h at 100°C in a N₂ atmosphere. The mixture was allowed to cool to room temperature and then water (75 mL) was added. The reaction mixture was extracted with dichloromethane and the organic solvent was evaporated by decompression. The residue was passed through a silica gel column chromatography (dichloromethane-petroleum ether = 1:4) to afford a yellow-green solid (505.6 mg, 47.5% yield). M. p. 224.2-225.0 °C. ¹H NMR (CDCl₃, 500 MHz): 7.58 (d, *J* = 8.5 Hz, 2H), 7.33-7.29 (m, 5H), 7.16 (d, *J* = 8.0 Hz, 4H), 7.10 (t, *J* = 14.5 Hz, 2H), 7.05 (d, *J* = 9.0 Hz, 2H), 6.84 (s, 1H), 3.64 (br, 2H), 3.17 (br, 2H), 2.61 (s, 3H), 2.50 (s, 3H), 1.88-1.49 (m, 6H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ 160.6, 152.8, 148.8, 146.9, 141.7, 139.4, 133.0, 129.4, 127.3, 125.8, 125.4, 123.9, 121.5, 117.9, 115.9, 115.2, 115.0, 111.6, 102.4, 87.8, 53.0, 25.4, 24.6, 24.2, 20.9 ppm. HRMS (ESI) *m/z*: [M+H]⁺ calculated for C₃₇H₃₃N₄, 533.2700; found, 533.2698. Anal. calcd. for C₃₇H₃₂N₄: C, 83.43; H, 6.06; N, 10.52. Found: C, 83.98; H, 6.03; N, 10.47.

Synthesis of 8-((4-(9*H*-carbazol-9-yl)phenyl)ethynyl)-3,6-dimethyl-1-(piperidin-1-yl)isoquinoline-7-carbonitrile (IQ-PC)

A mixture of compound **9** (801.3 mg, 3.0 mmol), compound **3** (826.8 mg, 2.0 mmol), CuI (22.9 mg, 0.12 mmol), and Pd(PPh₃)₂Cl₂ (84.0 mg, 0.12 mmol) in triethylamine (8 mL) and *N,N*-dimethylformamide (8 mL) was stirred for 12 h at 100°C in a N₂ atmosphere. After the mixture was cooled to room temperature, a large number of solids were precipitated. The precipitate was filtrated under vacuum and was passed through a silica gel column chromatography (dichloromethane-petroleum ether = 1:3) to afford a yellow-green solid (719.0 mg, 67.8% yield). M. p. 281.0-282.0°C. ¹H NMR (CDCl₃, 500 MHz): 8.16 (d, *J* = 8.0 Hz, 2H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.46-7.42 (m, 3H), 7.34-7.31 (m, 2H), 6.89 (s, 1H), 3.70 (br, 2H), 3.24 (br, 2H), 2.66 (s, 3H), 2.54 (s, 3H), 1.94-1.55 (m, 6H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ 160.6, 153.0, 141.8, 140.5, 139.5, 138.6, 133.5, 126.9, 126.63, 126.59, 126.1, 123.7, 120.4, 117.8, 116.2, 115.7, 111.8, 109.8, 100.6, 89.0, 53.2, 25.5, 24.6, 24.2, 21.0 ppm. HRMS (ESI) *m/z*: [M+H]⁺ calculated for C₃₇H₃₁N₄, 531.2543; found, 531.2565. Anal. calcd. for C₃₇H₃₀N₄: C, 83.74; H, 5.70; N, 10.56. Found: C, 83.27; H, 5.74; N, 10.61.

Notes and references

1. C. Teng, X. Yang, C. Yang, S. Li, M. Cheng, A. Hagfeldt and L. Sun, *J. Phys. Chem. C*, 2010, **114**, 9101–9110.
2. A. Aguilar-Granda, S. Pérez-Estrada, A. E. Roa, J. Rodríguez-Hernández, S. Hernández-Ortega, M. Rodríguez and B. Rodríguez-Molina, *Cryst. Growth Des.*, 2016, **16**, 3435–3442.

2. Figures, schemes, and tables

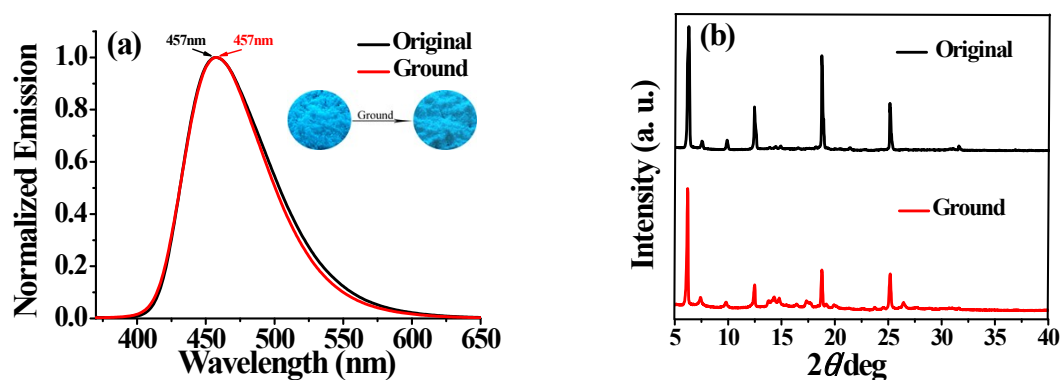
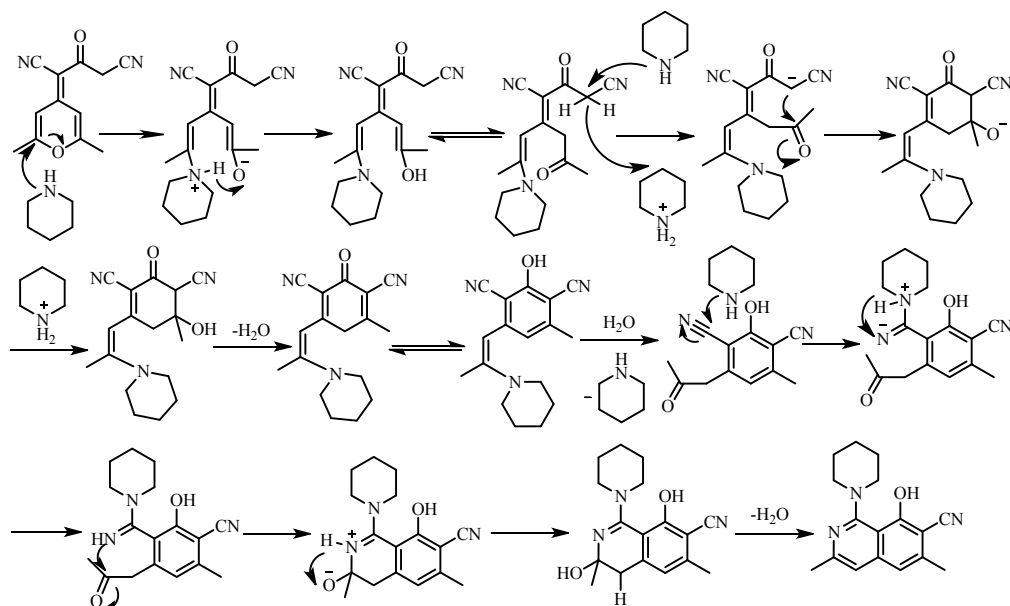


Fig. S1 Normalized fluorescence spectra (a) and XRD curves (b) of the **PIQ** solid samples before and after grinding. Inset: Emission pictures of the **PIQ** solid samples before and after grinding under the UV light ($\lambda_{\text{ex}} = 365 \text{ nm}$).



Scheme S1 Possible mechanism of **PIQ** prepared from compound **1** and piperidine.

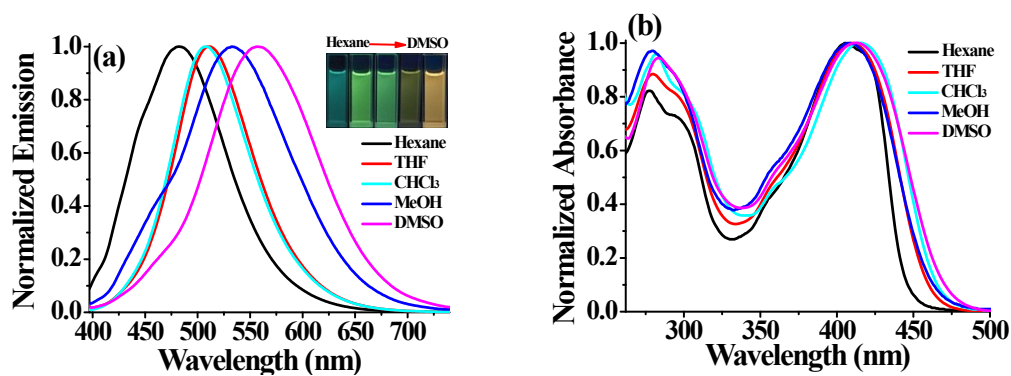


Fig. S2 Normalized emission (a) and absorption (b) spectra of **IQ-TPA** in different solvents. Concentration: $1 \times 10^{-5} \text{ M}$.

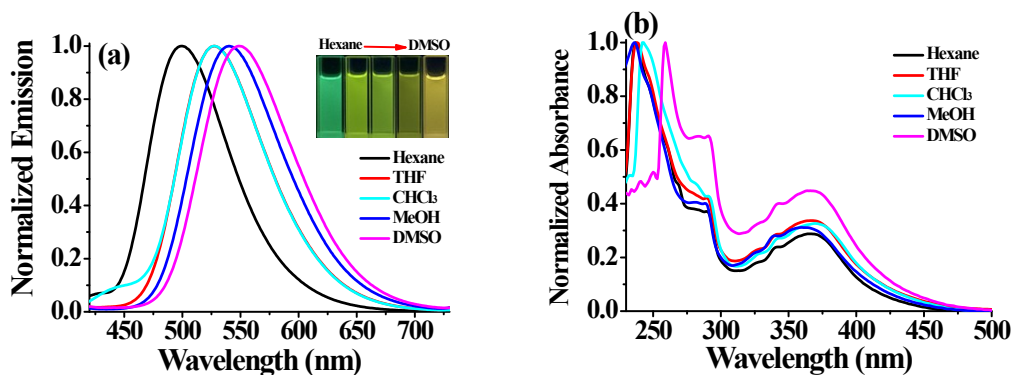


Fig. S3 Normalized emission (a) and absorption (b) spectra of **IQ-PC** in different solvents. Concentration: 1×10^{-5} M.

Table S1 Crystal data and details of collection and refinement for the polymorphs of **IQ-TPA** and **IQ-PC**.

	IQ-TPA-<i>g</i>	IQ-TPA-<i>γ</i>	IQ-PC-<i>g</i>	IQ-PC-<i>γ</i>
CCDC (no.)	1940020	1940022	1940021	1940023
Empirical formula	$C_{37}H_{32}N_4$	$C_{37}H_{32}N_4$	$C_{37}H_{30}N_4$	$C_{37}H_{30}N_4$
Formula weight	532.66	532.66	530.65	530.65
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P 2_1/c$	$P 2_1/c$	$P n a 2_1$	$P n a 2_1$
<i>Z</i>	4	4	4	4
D_{calcd} [Mg/m ³]	1.212	1.214	1.242	1.240
$F(000)$	1128	1128	1120	1120
θ range [°]	2.535-24.996	2.629-25.998	2.567-25.495	2.566-25.992
R_1 [$I > 2\sigma(I)$]	0.0831	0.0447	0.0441	0.0445
wR_2 [$I > 2\sigma(I)$]	0.2060	0.1050	0.0845	0.0967
<i>a</i> [Å]	10.951(2)	10.9558(3)	8.1615(2)	8.1632(4)
<i>b</i> [Å]	10.159(2)	10.1374(3)	33.9887(12)	33.999(2)
<i>c</i> [Å]	26.604(5)	26.5962(7)	10.2333(3)	10.2383(5)
α [deg]	90	90	90	90
β [deg]	99.365(7)	99.3760(10)	90	90
γ [deg]	90	90	90	90
V [Å ³]	2920.3(10)	2914.40(14)	2838.71(15)	2841.5(3)
GOF	1.036	1.034	1.062	1.056
R(int)	0.0832	0.0531	0.0392	0.0563
No. of reflns collected	12707	41504	12972	23645
No. of unique reflns	5102	5723	5168	5532
R_1 (all data)	0.1392	0.0685	0.0674	0.0704
wR_2 (all data)	0.2602	0.1221	0.0965	0.1109

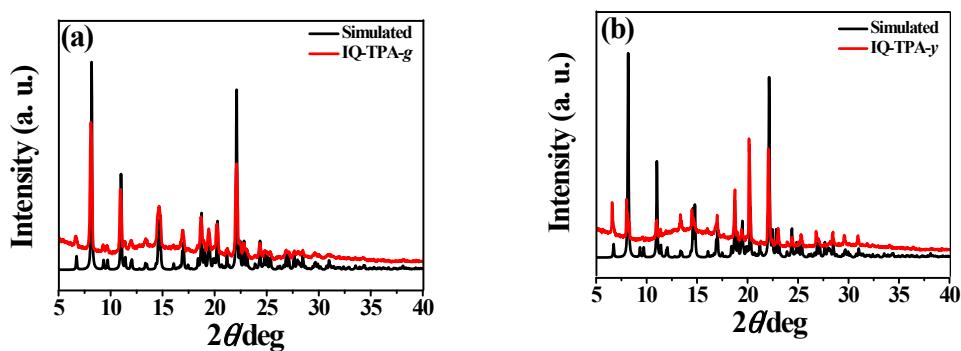


Fig. S4 Comparison of experimental XRD curves and the simulated XRD curves obtained from the corresponding single crystals of IQ-TPA: IQ-TPA-*g* (a) and IQ-TPA-*y* (b).

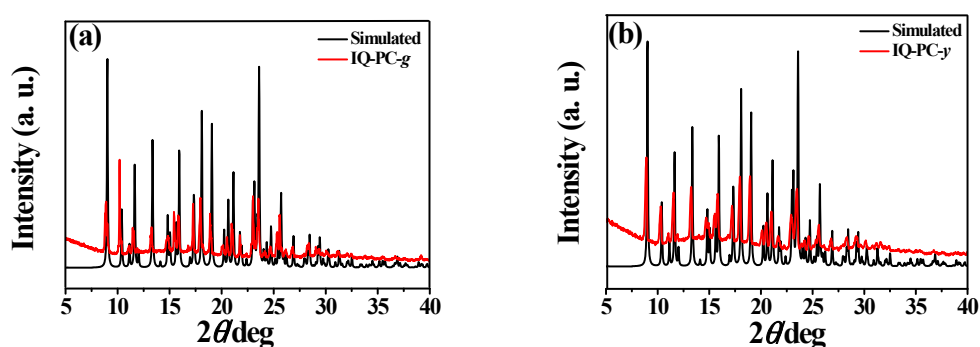


Fig. S5 Comparison of experimental XRD curves and the simulated XRD curves obtained from the corresponding single crystals of IQ-PC: IQ-PC-*g* (a) and IQ-PC-*y* (b).

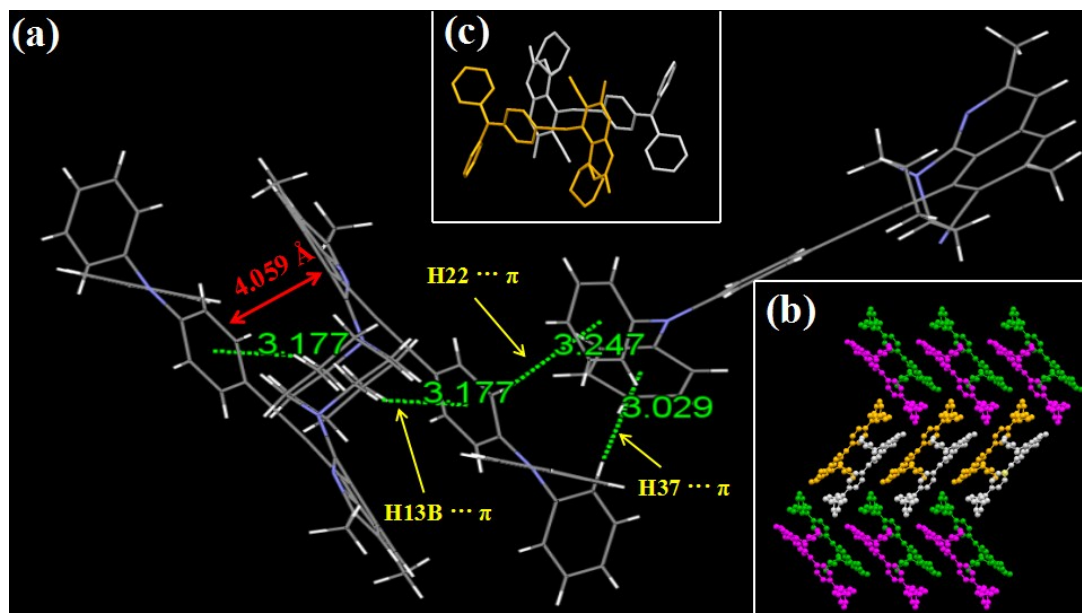


Fig. S6 Single crystal IQ-TPA-*y*: (a) Intermolecular interactions; (b) Zigzag stacking arrangement viewed along the *a*-axis; (c) Stacking arrangement along the *b*-axis.

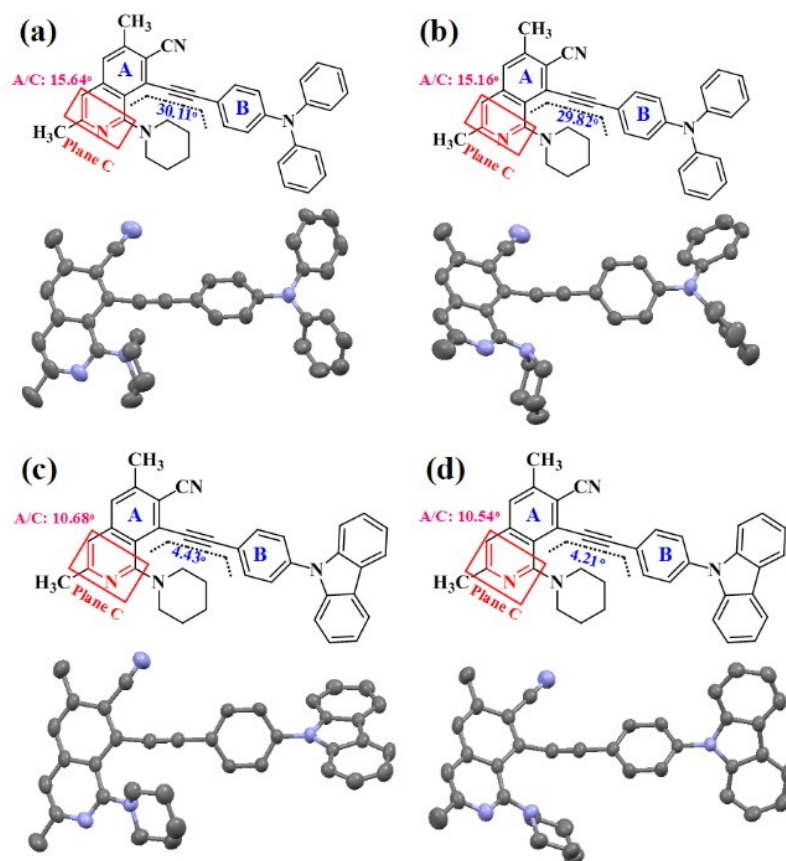


Fig. S7 Selected dihedral angles and torsion angles along with π -plane of **IQ-TPA-g** (a), **IQ-TPA-y** (b), **IQ-PC-g** (c), and **IQ-PC-y** (d).

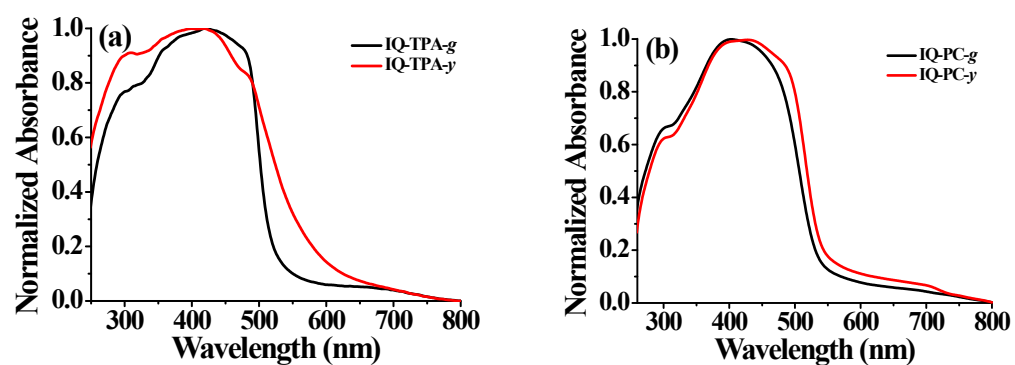


Fig. S8 Normalized solid-state absorption spectra of the polymorphs of **IQ-TPA** (a) and **IQ-PC** (b).

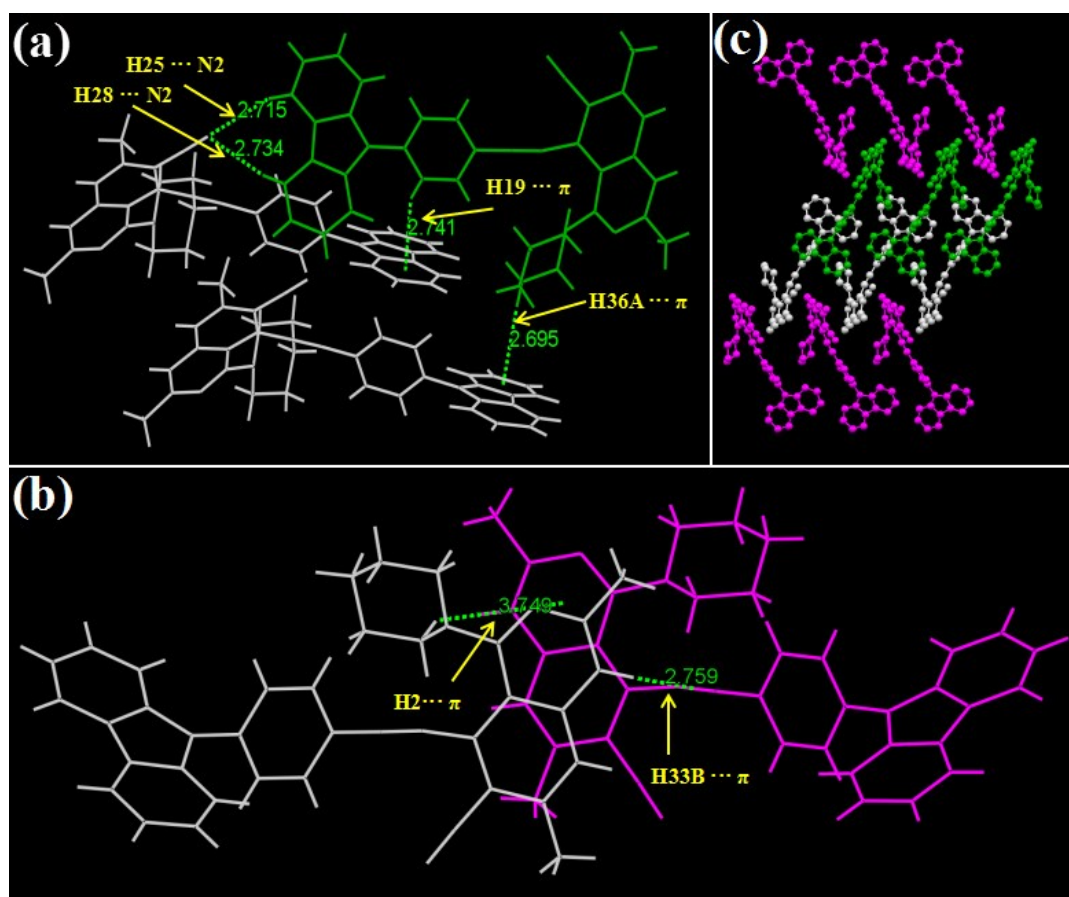


Fig. S9 Single crystal IQ-PC-y: (a) (b) Intermolecular interactions; (c) Zigzag stacking arrangement viewed along the *c*-axis.

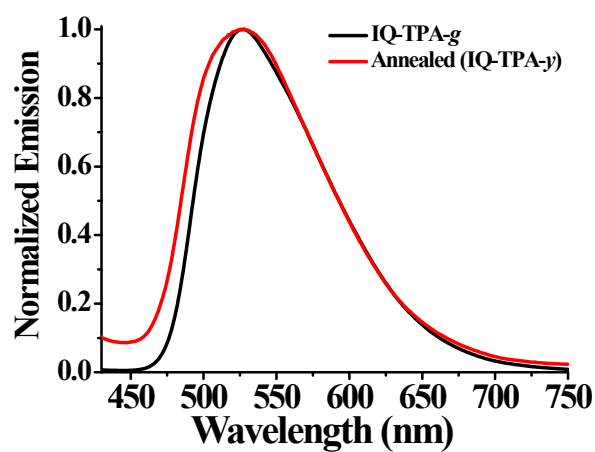


Fig. S10 Comparison of the fluorescence spectra of IQ-TPA-g and the annealed sample of IQ-TPA-y.

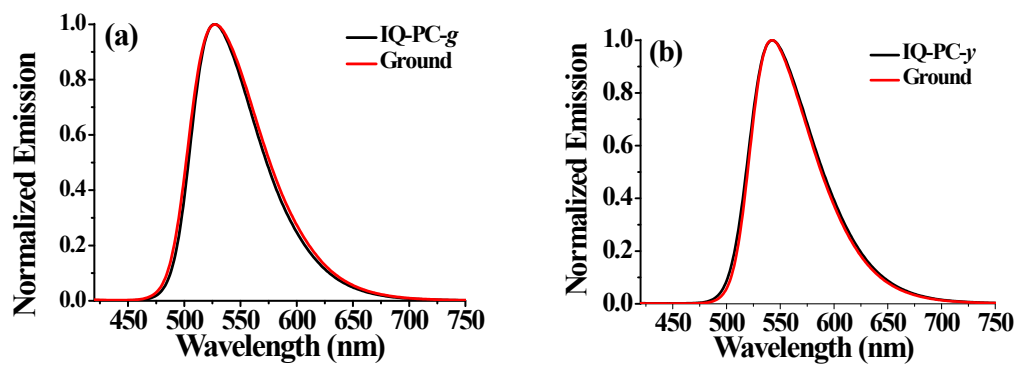


Fig. S11 Fluorescence spectra of IQ-PC-g (a) and IQ-PC-y (b) before and after grinding.

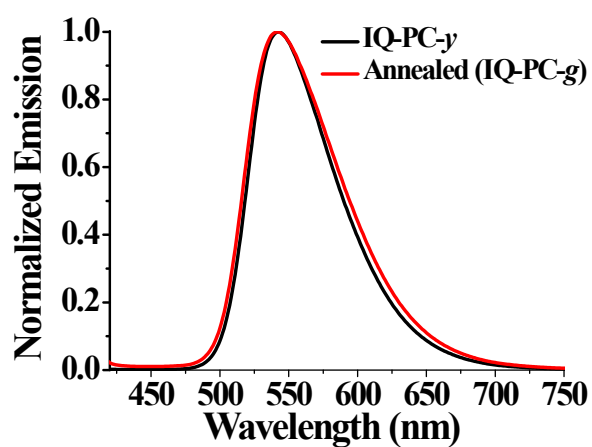


Fig. S12 Comparison of the fluorescence spectra of IQ-PC-y and the annealed sample of IQ-PC-g.

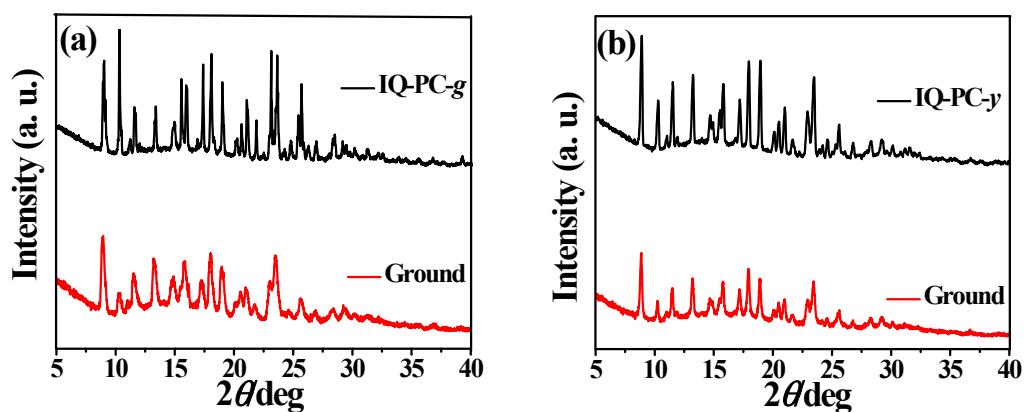


Fig. S13 XRD curves of the polymorphs of IQ-PC before and after grinding.

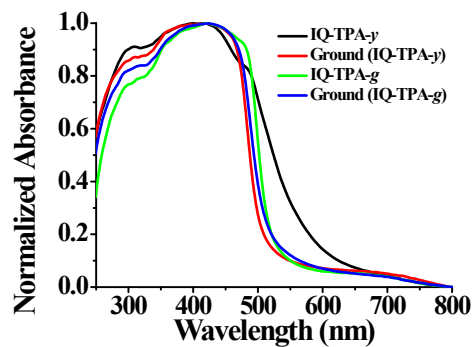


Fig. S14 Normalized solid-state absorption spectra of **IQ-TPA-y**, the ground sample of **IQ-TPA-y**, and **IQ-TPA-g**.

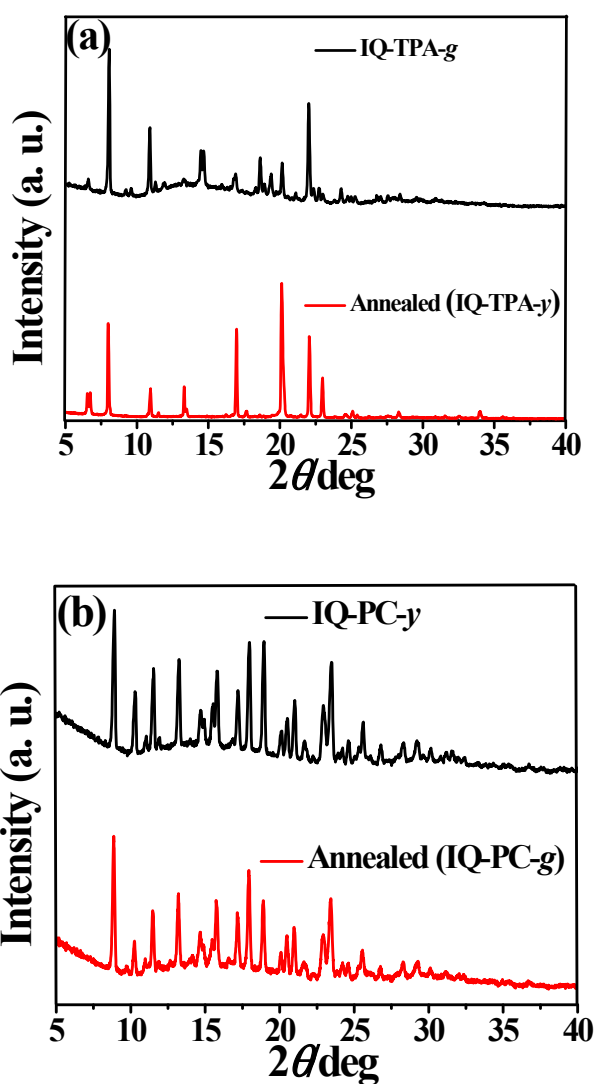


Fig. S15 (a) Comparison of the XRD curves of **IQ-TPA-g** and the annealed sample of **IQ-TPA-y**. (b) Comparison of the XRD curves of **IQ-PC-y** and the annealed sample of **IQ-PC-g**.

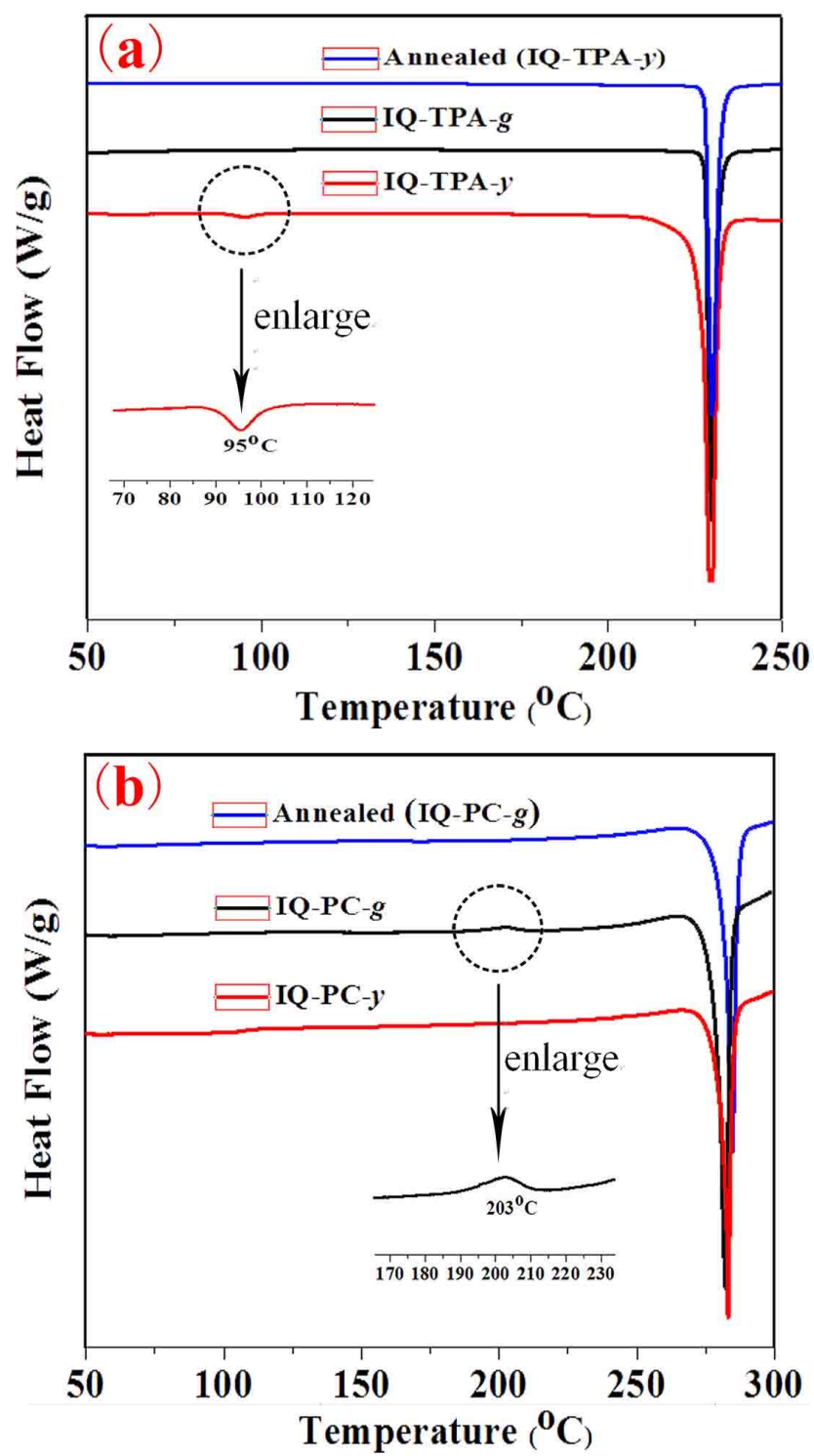


Fig. S16 DSC curves of IQ-TPA (a) and IQ-PC (b) solid samples under various conditions.

3. Spectra of NMR

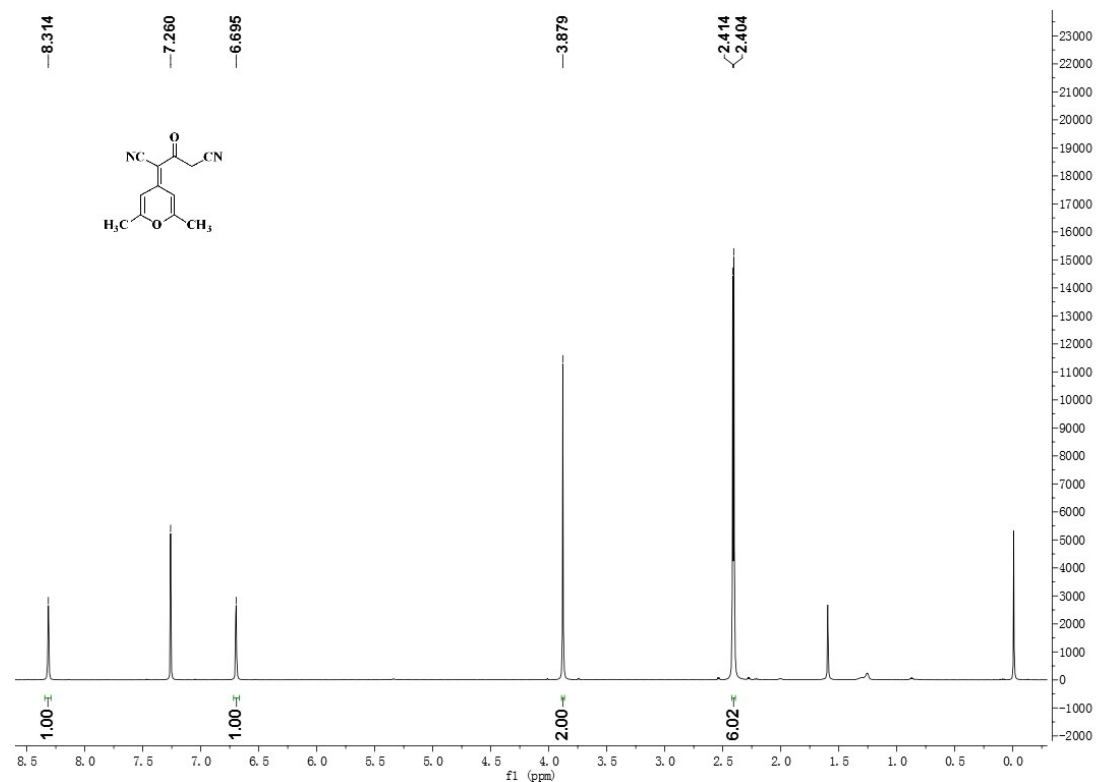


Fig. S17 ^1H NMR of compound 1 (CDCl_3 , 500 MHz).

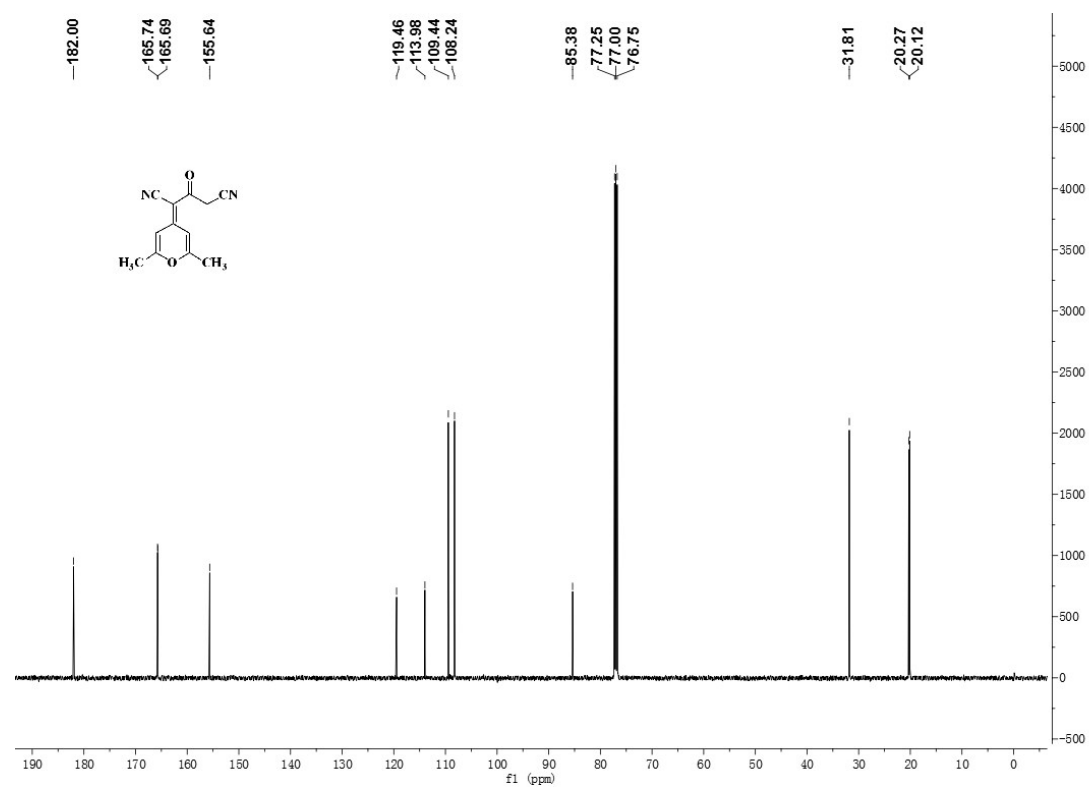


Fig. S18 ^{13}C NMR of compound 1 (CDCl_3 , 125 MHz).

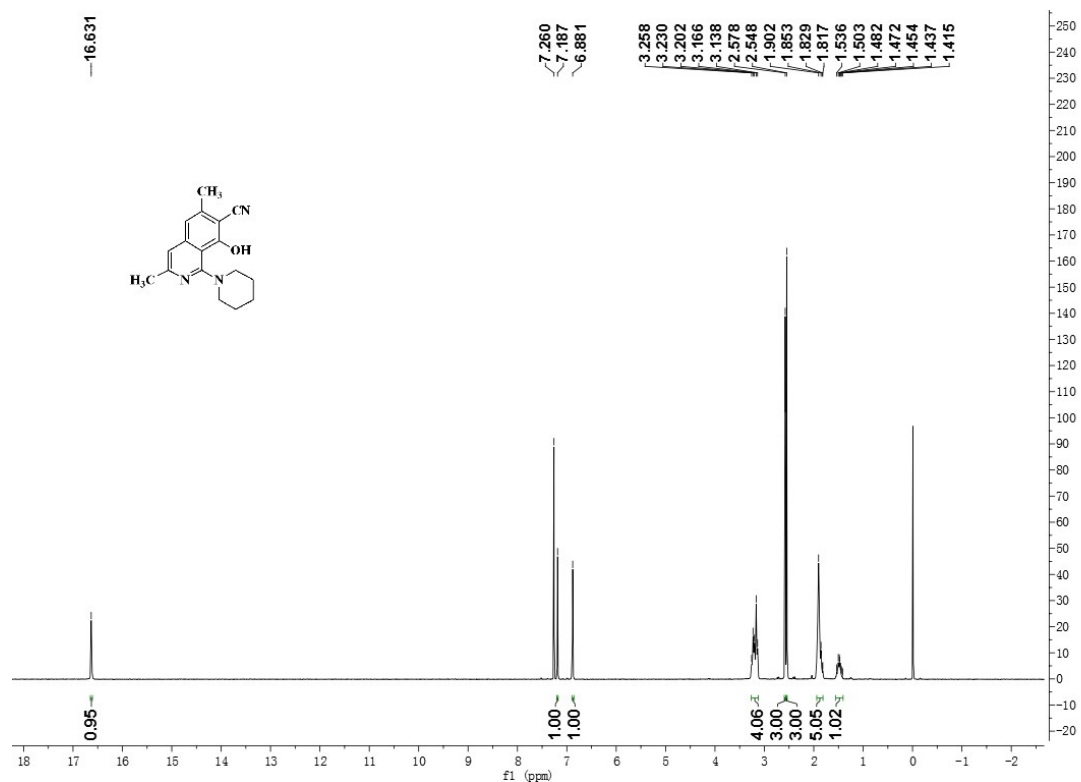


Fig. S19 ¹H NMR of PIQ (CDCl₃, 400 MHz).

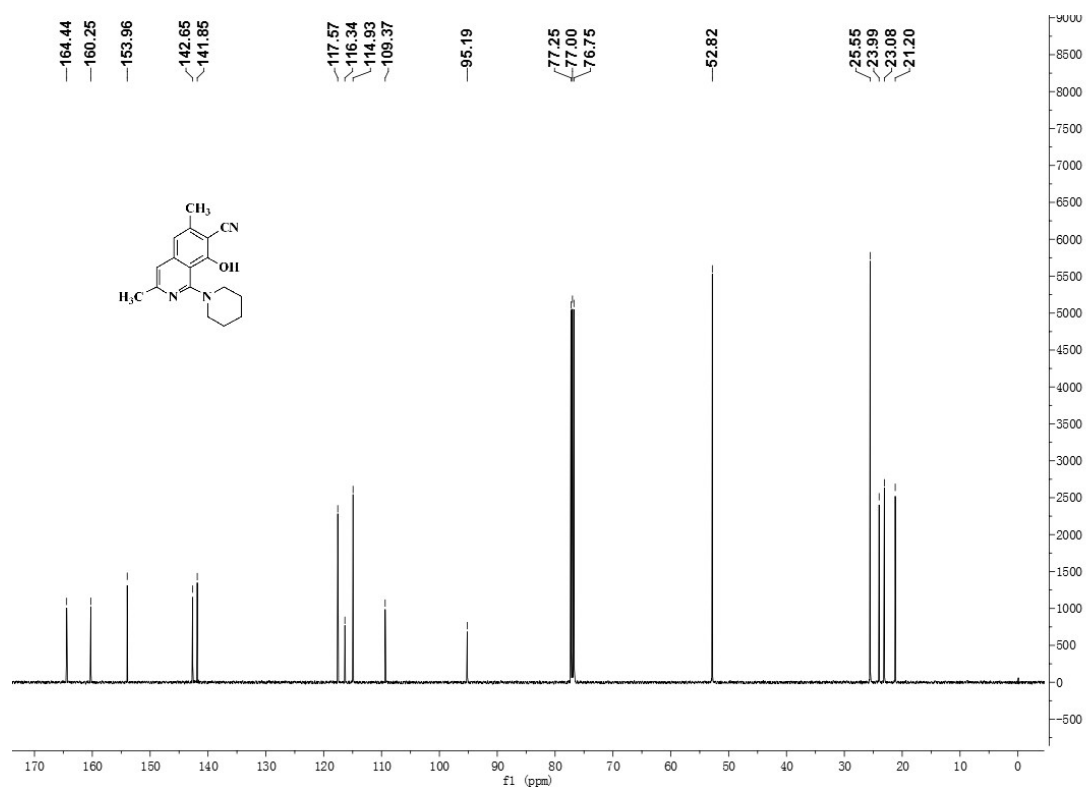


Fig. S20 ¹³C NMR of PIQ (CDCl₃, 125 MHz).

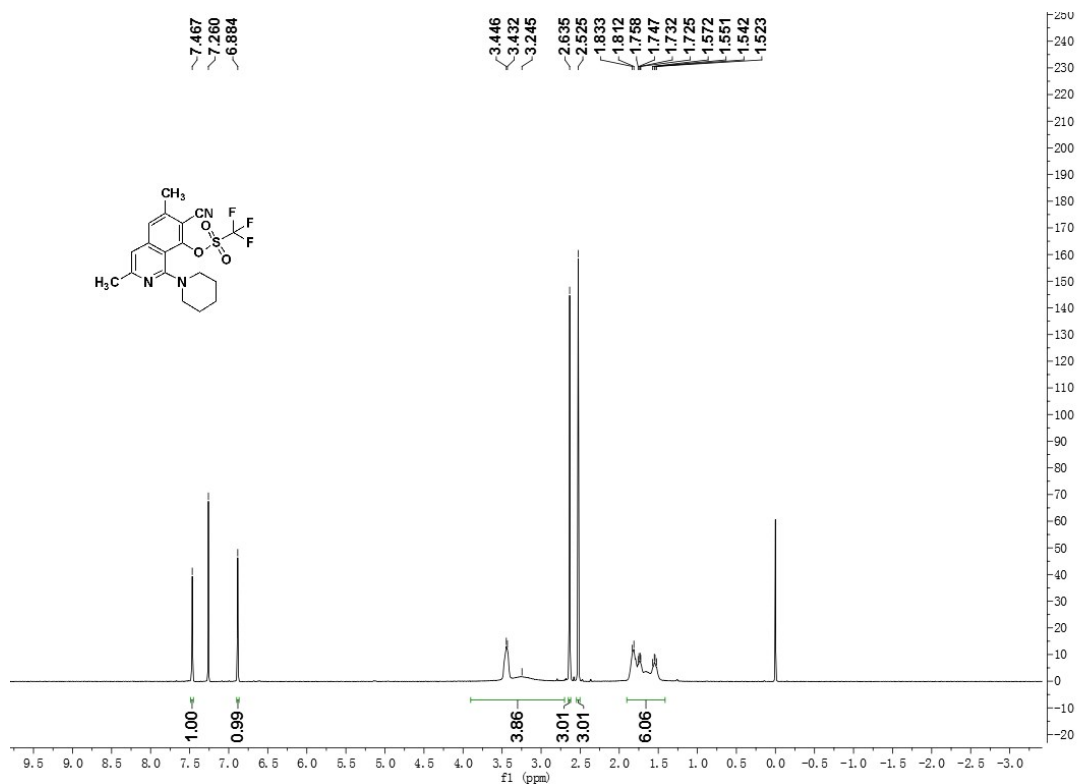


Fig. S21 ¹H NMR of compound **3** (CDCl₃, 400 MHz).

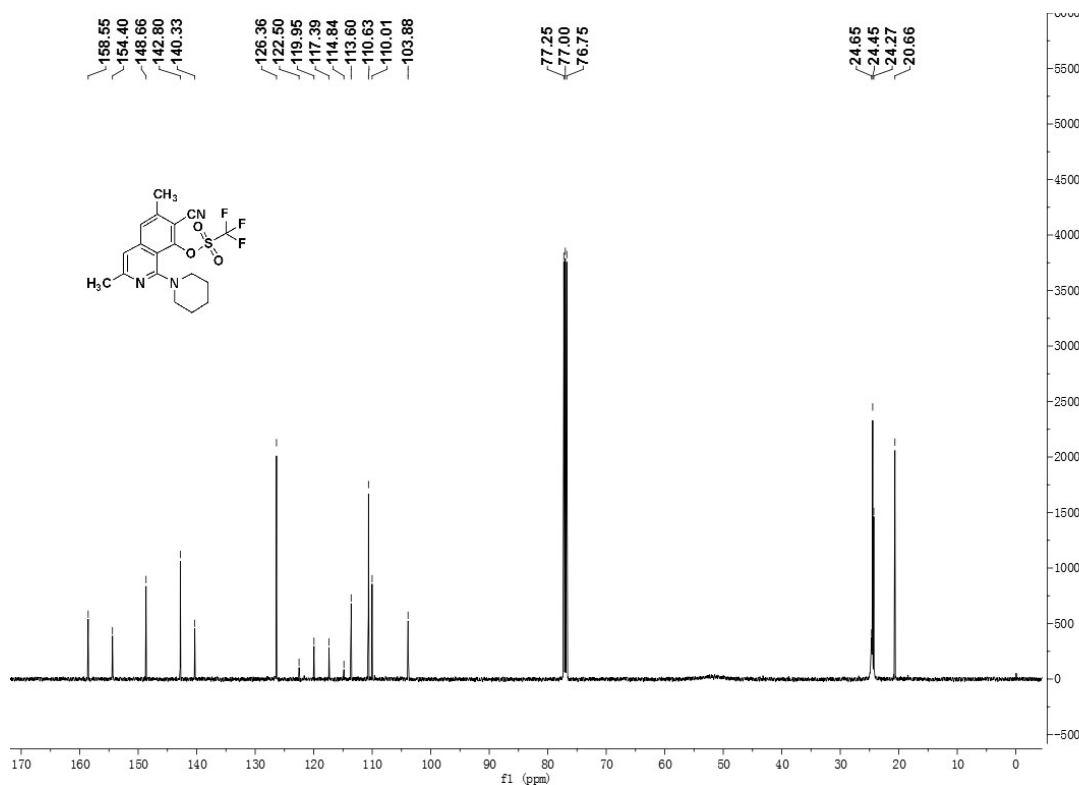


Fig. S22 ¹³C NMR of compound **3** (CDCl₃, 125 MHz).

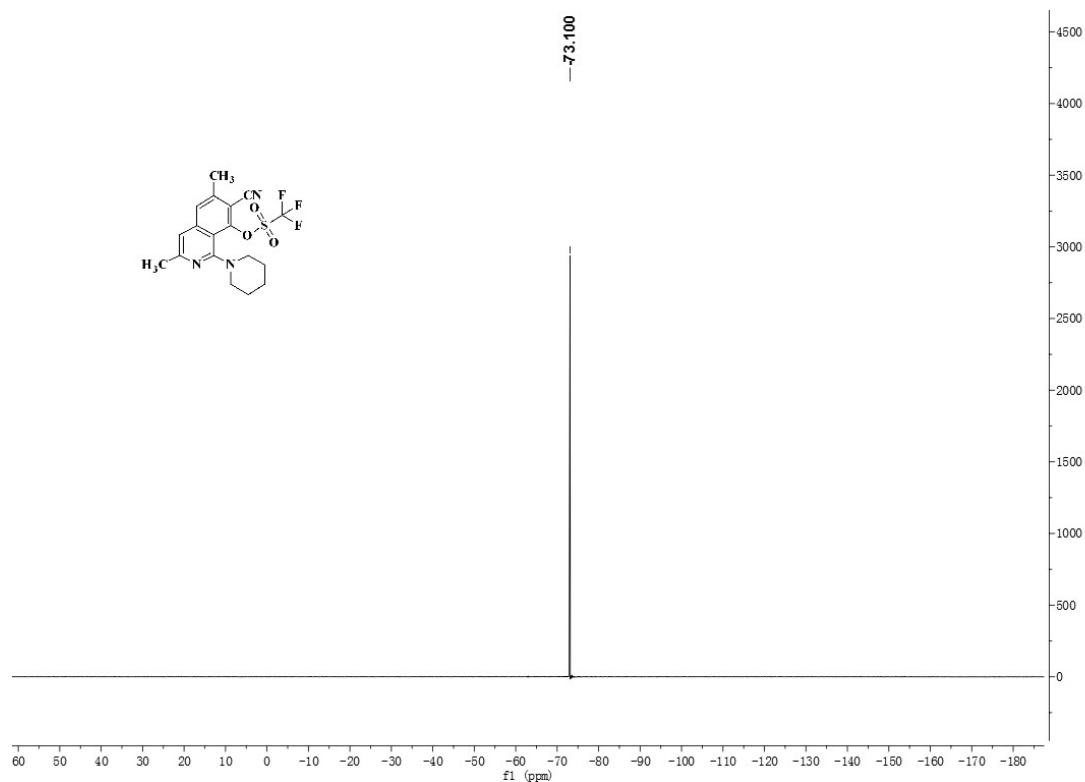


Fig. S23 ^{19}F NMR of compound 3 (CDCl₃, 470 MHz).

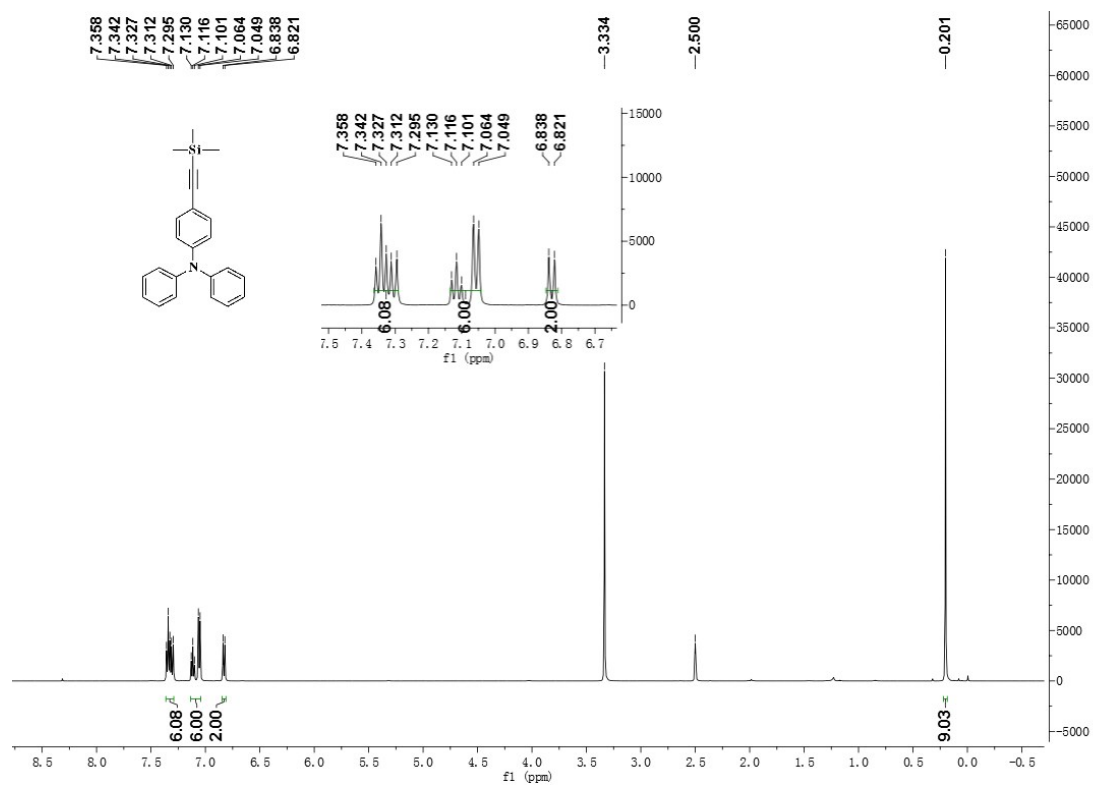


Fig. S24 ^1H NMR of compound 6 (DMSO-*d*₆, 500 MHz).

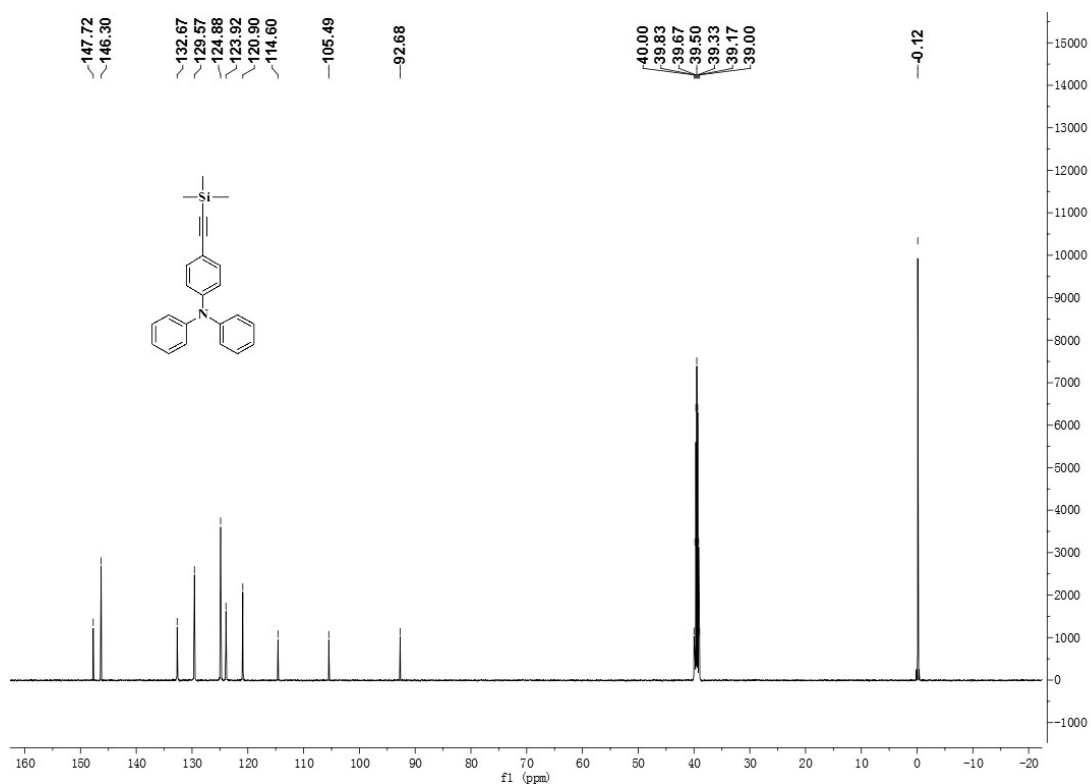


Fig. S25 ¹³C NMR of compound 6 (DMSO-*d*₆, 125 MHz).

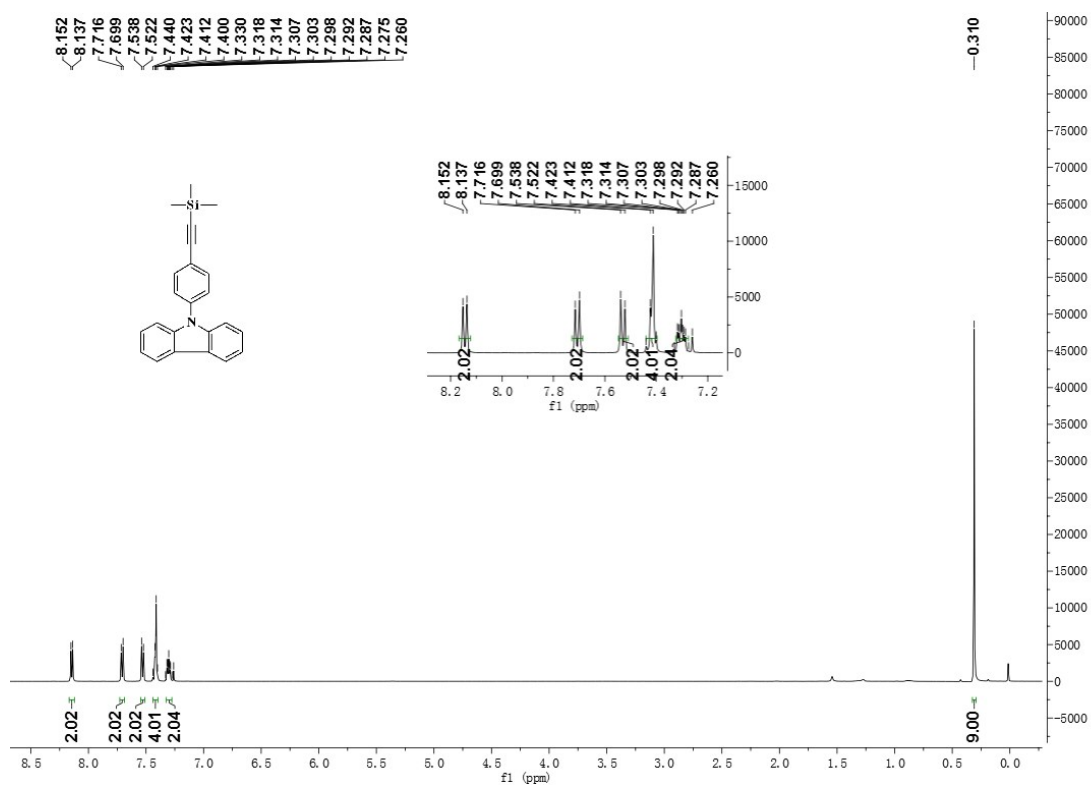


Fig. S26 ¹H NMR of compound 7 (CDCl₃, 500 MHz).

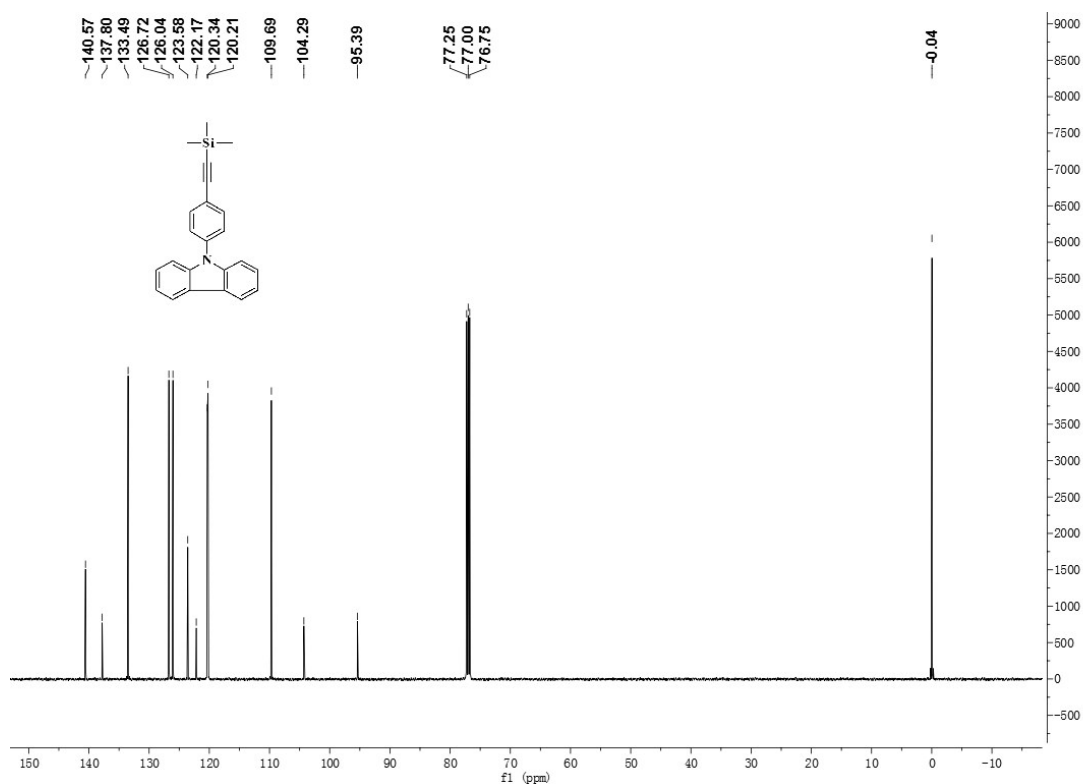


Fig. S27 ¹³C NMR of compound 7 (CDCl₃, 125 MHz).

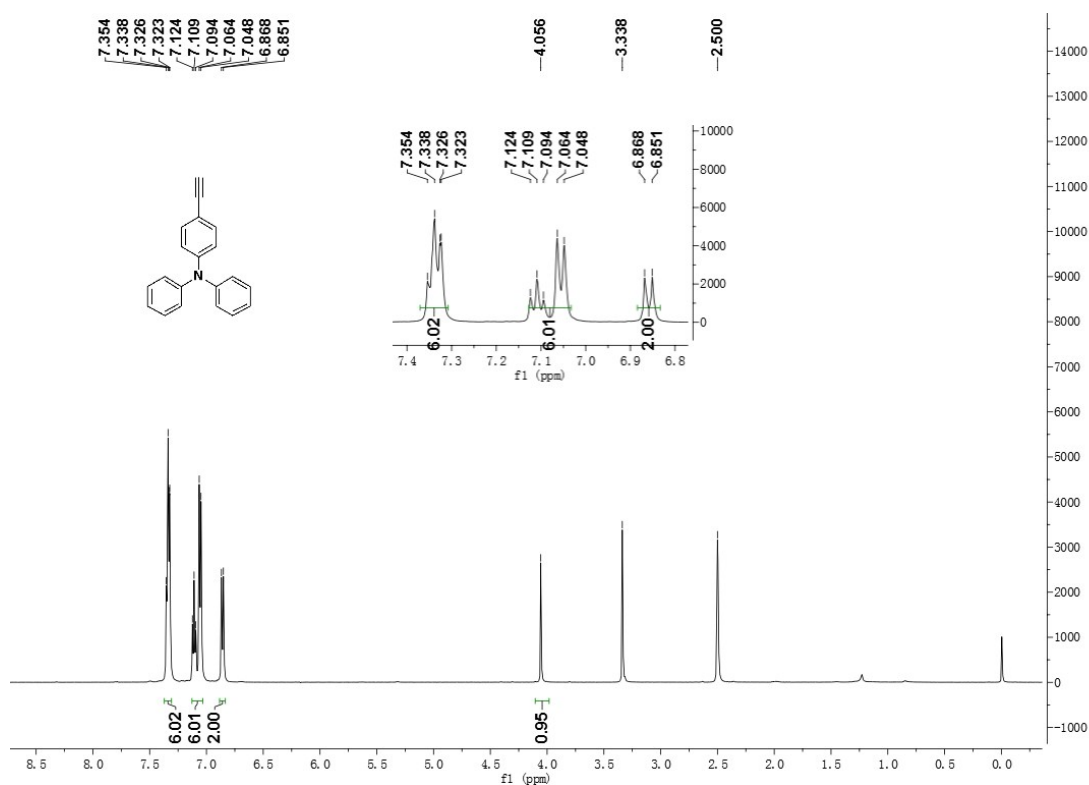


Fig. S28 ¹H NMR of compound 8 (DMSO-*d*₆, 500 MHz).

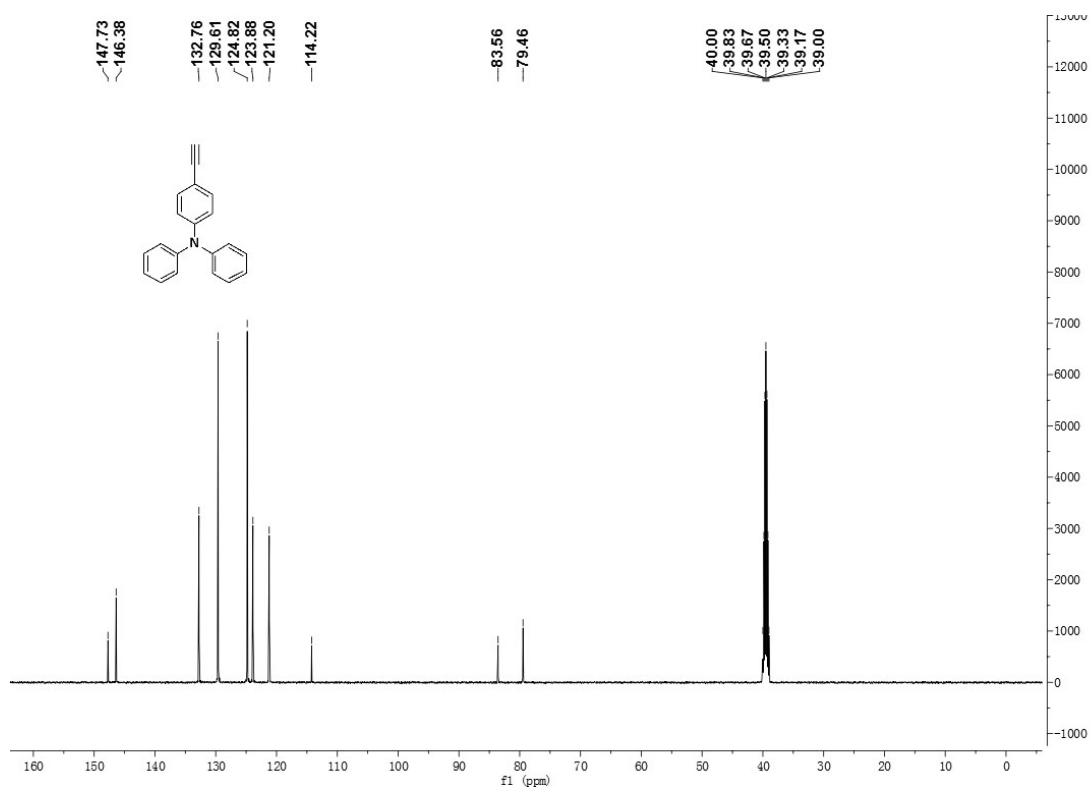


Fig. S29 ¹³C NMR of compound 8 (DMSO-*d*₆, 125 MHz).

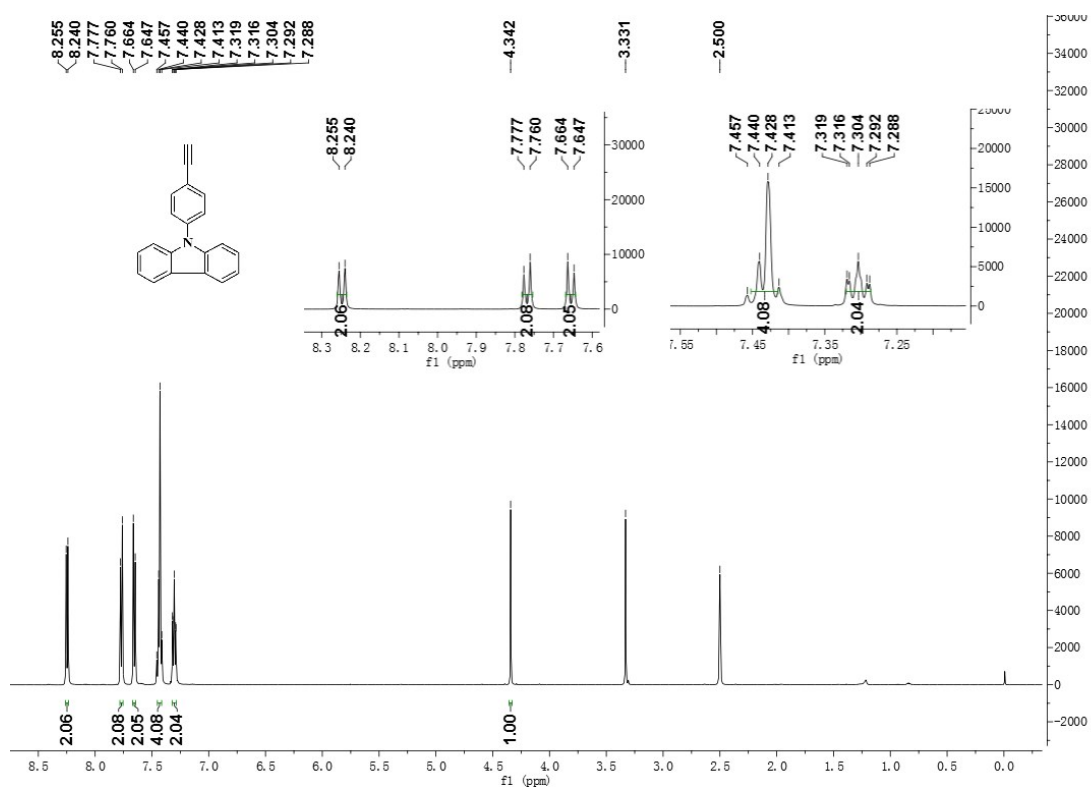


Fig. S30 ¹H NMR of compound 9 (DMSO-*d*₆, 500 MHz).

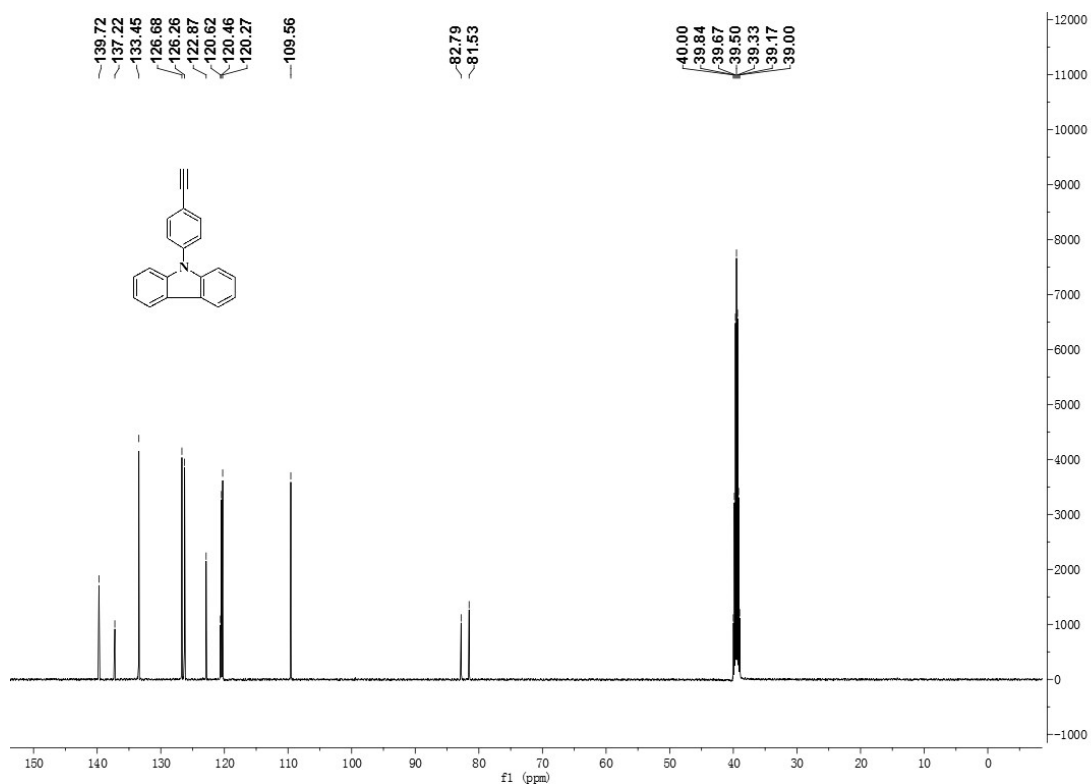


Fig. S31 ¹³C NMR of compound **9** (DMSO-*d*₆, 125 MHz).

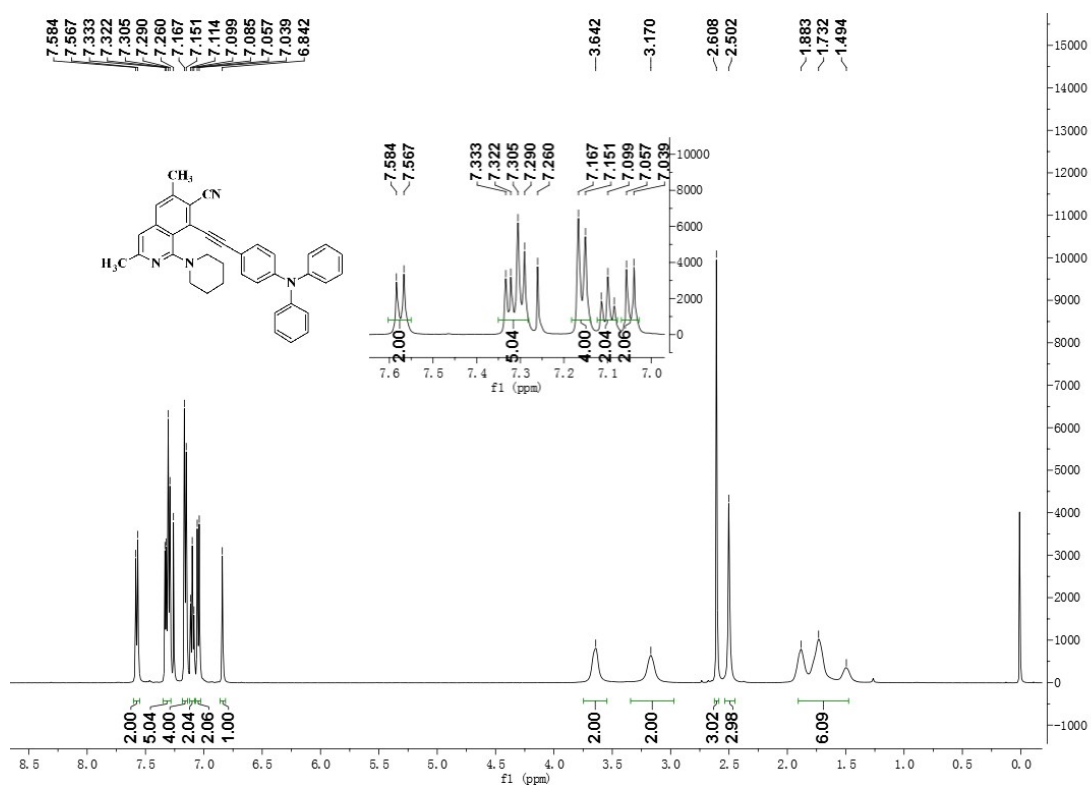


Fig. S32 ¹H NMR of IQ-TPA (CDCl₃, 500 MHz).

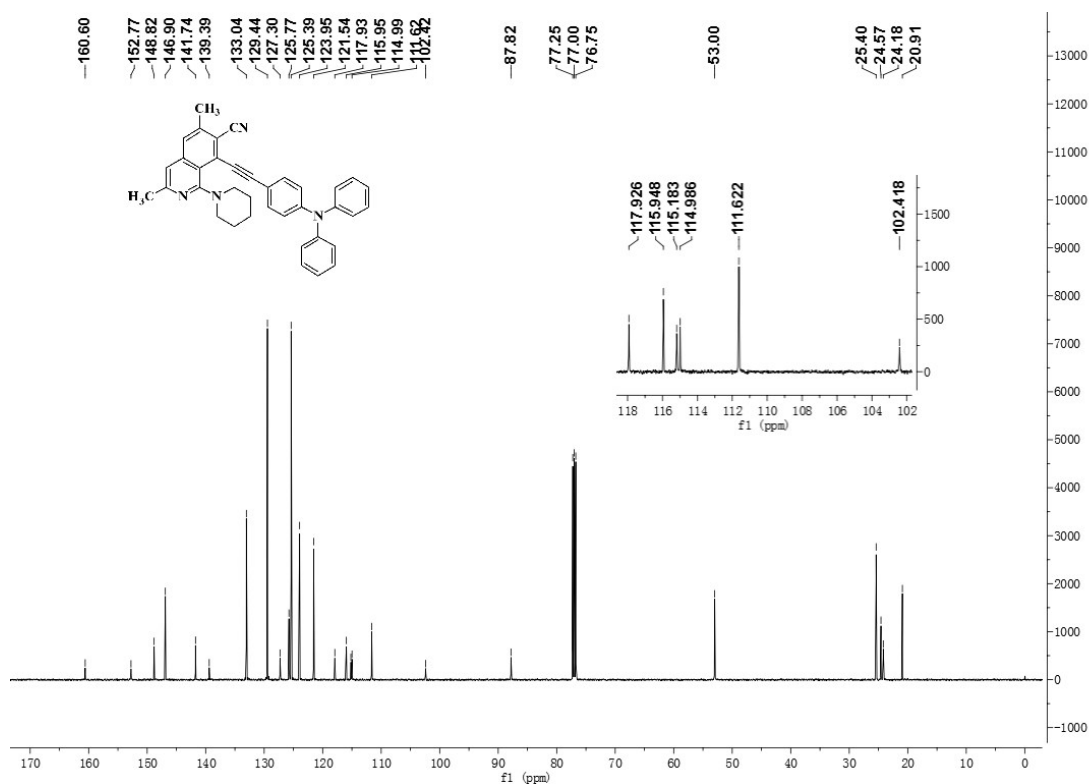


Fig. S33 ¹³C NMR of compound IQ-TPA (CDCl₃, 125 MHz).

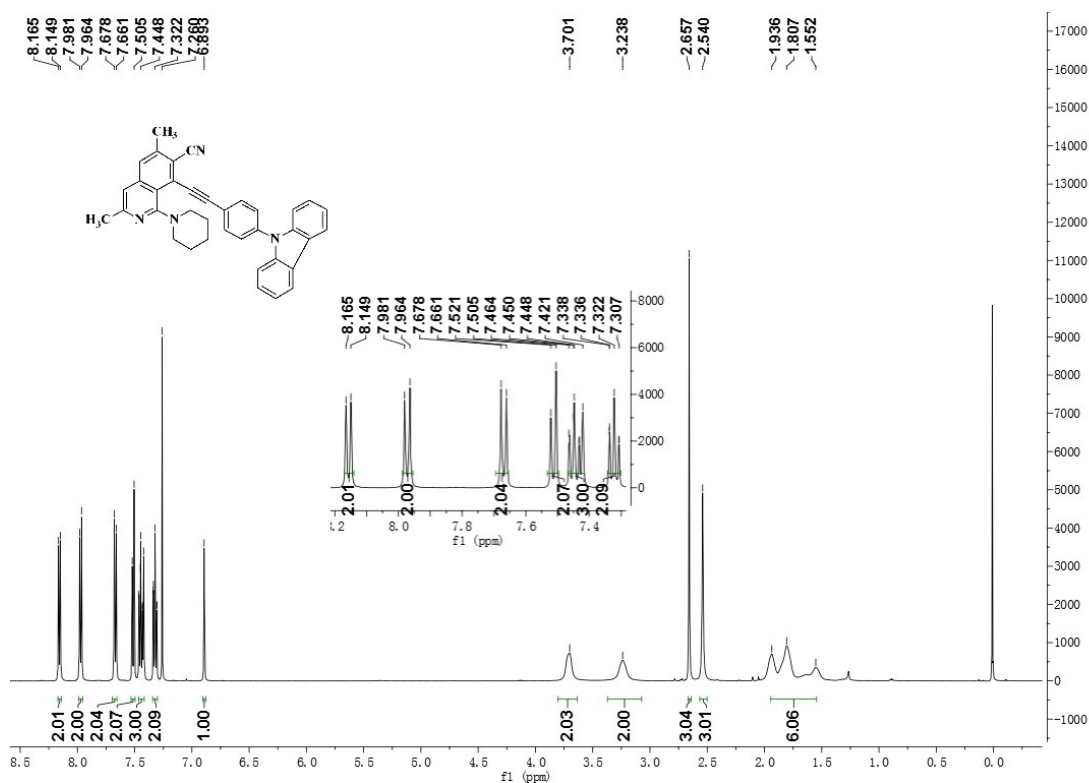


Fig. S34 ¹H NMR of IQ-PC (CDCl₃, 500 MHz).

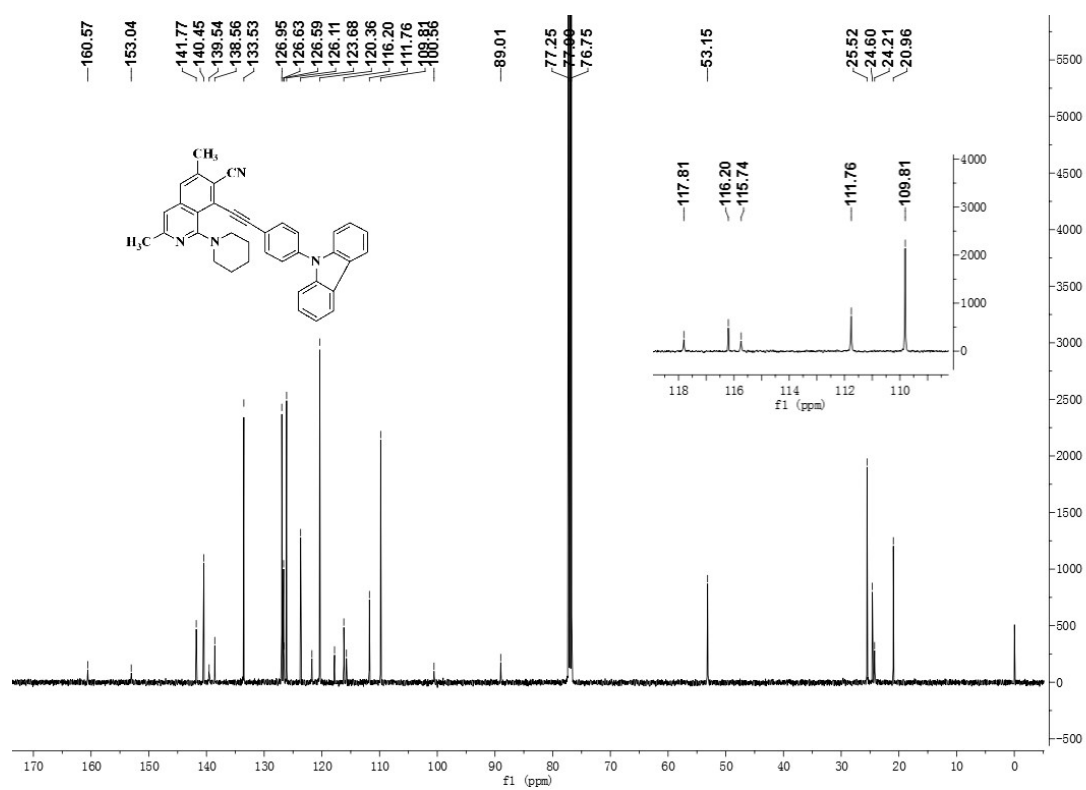


Fig. S35 ¹³C NMR of IQ-PC (CDCl₃, 125 MHz).