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Supporting Information

Long-range hydrogen-bond relay catalysing excited-state proton transfer reaction

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[†] These authors contributed equally

Contents

1. Synthesis method, NMR, MASS, mid-IR, and X-ray of Materials

7-nitro-1,2,3,4-tetrahydroquinoline (compound 2) and **7-amino-1,2,3,4-tetrahydroquinoline (compound 3)** are reported in Reference section.[S1,S2]

Ethyl-7-((ethoxycarbonyl)amino)-3,4-dihydroquinoline-1(2*H*)-carboxylate (compound 4): In a 100mL two-neck round-bottom flask, compound **3** (4.23 g, 28.54 mmol) was dissolved in CH_2Cl_2 (45.0 mL). Subsequently, pyridine (5.75 mL, 71.36 mmol) was added to the solution and the mixture was stirred at 0℃. After stirring for 30 minutes, ethyl chloroformate (5.98 mL, 62.79 mmol) was added dropwise in the mixture, stirred at room temperature for 12 hours. The result was wash with 10% $HCl_{(aq)}$ two times (30 mL x 2) and H_2O three times. The organic layer was dried with $MgSO_4$, concentrated under reduced pressure to give the compound **4** as brown oil without any purification. Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (s, 1 H), 7.15 (s, 1 H), 6.99 (d, *J* = 8.0, 2.5 Hz, 1 H), 6.48 (s, 1 H), 4.23 (dq, *J* = 11.8, 7.1 Hz,4 H), 3.78 – 3.64 (m, 2 H), 2.68 (t, *J* = 6.5 Hz, 2 H), 1.89 (dt, *J* = 12.7, 6.4 Hz, 2 H), 1.30 (tt, *J* = 22.5, 11.3 Hz, 6 H) ppm.

Ethyl-6-bromo-7-((ethoxycarbonyl)amino)-3,4-dihydroquinoline-1(2*H*)-carboxylate (compound 5): The compound **4** (6.74 g, 23.06 mmol) was dissolved in THF under nitrogen and stirred at 0℃. Then the solution of N-bromosuccinimide (NBS, 4.92 g, 27.67 mmol) in THF was added into the reaction, stirred at room temperature for 12 hours. The result was concentrated under reduced pressure. The crude product was washed with H_2O (20 mL x 3) three times. The organic layer was dried with $MgSO_4$, concentrated under reduced pressure to give compound **5** as yellow solid without any purification. Yield: 78%. ^{1}H NMR (400 MHz, Acetone): δ = 8.37 (s, 1 H), 7.59 (s, 1 H), 7.31 (s, 1 H), 4.23 (dq, *J* = 11.8, 7.1 Hz,4 H), 3.78 – 3.64 (m, 2 H), 2.68 (t, *J* = 6.5 Hz, 2 H), 1.89 (dt, *J* = 12.7, 6.4 Hz, 2 H), 1.30 (tt, *J* = 22.5, 11.3 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, CD_3OCD_3) δ = 154.88 (s), 154.31 (s), 139.2 (s), 134.69 (s), 132.39 (s), 128.32 (s), 119.38 (s), 109.48 (s), 62.39 (s), 61.63 (s), 45.37 (s), 27.28 (s), 23.63 (s), 14.80 (s), 14.71 (s)ppm.

Ethyl-7-((ethoxycarbonyl)amino)-6-((trimethylsilyl)ethynyl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (compound 6): In a two-neck round round-bottom flask, the mixture of compound **5** (6.32 g, 17.02 mmol), copper(I) iodide (3.24 g, 17.02 mmol) and bis(triphenylphosphine)palladium(II) dichloride (5.97 g, 8.51 mmol) was dissolved in 40mL Et_3N / Toluene (3:1). The ethynyltrimethylsilane (3.63 mL, 25.53 mmol) was added to the mixture, stirred at 90℃ for 18 hours. The result was filtered through celite and then concentrated under reduced pressure. The crude was purified by silica column chromatography (EA/Hex 1:10) to afford the compound **6** as yellow oil with yield of 68%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (s, 1 H), 7.25 (s, 1 H), 7.09 (s, 1 H), 4.23 (dq, *J* = 14.0, 7.1 Hz, 4 H), 3.75 – 3.69 (m, 2 H), 2.64 (t, *J* = 6.5 Hz, 2 H), 1.91 – 1.82 (m, 2 H), 1.30 (q, *J* = 7.4 Hz, 6 H), 0.25 (s, 9 H) ppm.

Ethyl-6,7-dihydro-1*H*-pyrrolo[3,2-*g*]quinoline-8(5*H*)-carboxylate (compound 7): The 60mL ethanol (99.5%, extra dry) was stirred in the two-neck round-bottom flask under nitrogen. Subsequently, the sodium metal (2.66 g, 115.7 mmol) was added into the solution at room temperature, stirred until all of sodium metal was dissolved. The compound **6** (4.30 g, 11.57 mmol) in the ethanol (99.5%, extra dry) was added into the reaction and then stirred at 80℃ for 10 hours. The crude product was concentrated under reduced pressure and purified by silica column chromatography (EA/Hex 1:6) to afford the

compound **7** as yellow solid with yield of 49%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (s, 1 H), 7.72 (s, 1 H), 7.31 (s, 1 H), 7.18 – 7.04 (m, 1 H), 6.41 (s, 1 H), 4.24 (q, *J* = 7.1 Hz, 2 H), 3.76 (t, *J* = 6.5 Hz, 2 H), 2.81 (t, *J* = 6.5 Hz, 2 H), 2.01 – 1.86 (m, 2 H), 1.31 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.4 (s), 24.2 (s), 25.5 (s), 43.1 (s), 46.1 (s), 102.7 (s), 103.5 (s), 103.7 (s), 119.2 (s), 121.3 (s), 123.2 (s), 125.3 (s), 128.1 (s), 130.4 (s) ppm.

5,6,7,8-tetrahydro-1*H*-pyrrolo[3,2-*g*]quinoline (compound 8): The compound **7** (1.2 g, 4.91 mmol) was dissolved in 40mL ethanol, stirred at room temperature. The 10M $NaOH_{(aq)}$ (10 mL) was added dropwise in the reaction and then the mixture was stirred at 90℃ for 3 hours. The crude product was concentrated under reduced pressure and purified by silica column chromatography (EA/Hex 1:3) to afford the compound **8** as dark yellow solid with yield of 48%. Compound **8** is not stable, which must do the next step, immediately. ^{1}H NMR (400 MHz, CDCl3): δ = 7.69 (s, 1 H), 7.18 (s, 1 H), 6.92 (dd, *J* = 3.2, 2.3 Hz, 1 H), 6.45 (s, 1 H), 6.32 (ddd, *J* = 3.1, 2.0, 0.9 Hz, 1 H), 6.10 (s, 1 H), 3.35 – 3.25 (m, 2 H), 2.88 (t, *J* = 6.4 Hz, 2 H), 1.95 (m, Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.14 (s), 28.75 (s), 40.34 (s), 94.70 (s), 104.70 (s), 117.07 (s), 118.26 (s), 120.05 (s), 124.83 (s), 136.34 (s), 137.30 (s) ppm.

1*H*-pyrrolo[3,2-*g*]quinoline (PyrQ): The *o*-xylene was added into the mixture of compound **8** (832.1 mg, 4.83 mmol) and activated carbon (832.1 mg), stirred under oxygen. After stirring for 10 minutes, the reaction was heated to 120℃ and stirred for 24 hours. The crude product was filtered through celite and then concentrated under reduced pressure. The crude product was purified by silica column chromatography (EA/Hex 1:2) to obtain **PyrQ** as yellow solid. Yield: 26%. m.p. 167.0-167.5 °C (decomp.) ^{1}H NMR (500 MHz, Acetone) δ 10.48 (s, 1H), 8.76 (dd, *J* = 4.0, 1.7 Hz, 1H), 8.35 – 8.30 (m, 1H), 8.13 (s, 1H), 8.08 (s, 1H), 7.68 (dd, *J* = 3.2, 2.3 Hz, 1H), 7.27 (dd, *J* = 8.4, 4.0 Hz, 1H), 6.72 – 6.66 (m, 1H); ^{13}C NMR (500 MHz, Acetone): δ= 149.32 (s), 145.62 (s), 140.03 (s), 136.68 (s), 131.19 (s), 131.13 (s), 123.77 (s), 118.56 (s), 118.03 (s), 108.67 (s), 101.35 (s) ppm; HRMS (ESI): *m/z* calcd for $C_{11}H_8N_2$ [M^+]: 168.0687; Found: 168.0686.

Ethyl 3-cyano-6,7-dihydro-1*H*-pyrrolo[3,2-*g*]quinoline-8(5*H*)-carboxylate (compound 9): Compound **7** (1.4 g, 5.37 mmol) was dissolved in DMF (8 mL) and then added to a flask containing $POCl_3$ (0.53 mL) and DMF (2 mL) which had been stirred for 30 minutes at 0°C. After stirring at 40°C for 3 hours, I_2 (3.64 g, 28.65 mmol) and $NH_{3(aq)}$ (10 mL) were added to the reaction mixture. The obtained mixture was stirred for 3 hours at room temperature. After the reaction, the mixture was poured into saturated Na_2SO_3 solution and extracted with $CHCl_3$ (15 mL x 4). The organic layer was dried over Na_2SO_4, filtered, and purified by silica column chromatography (EA/Hex 1:4) to provide compound **9** in 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.71 (s, 1H), 7.14 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 1H), 3.88 – 3.51 (m, 1H), 2.95 – 2.73 (m, 1H), 2.01 – 1.87 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, DMSO): δ = 13.29 (s), 21.71 (s), 30.99 (s), 43.12 (s), 47.36 (s), 101.24 (s), 102.35 (s), 104.04 (s), 119.84 (s), 122.11 (s), 123.22 (s) , 124.38 (s) , 128.88 (s), 133.43 (s), 152.61 (s) ppm.

5,6,7,8-tetrahydro-1*H*-pyrrolo[3,2-*g*]quinoline-3-carbonitrile (compound 10): The compound **9** (1 g, 3.71 mmol) was dissolved in 40 mL ethanol, stirred at room temperature. The 10M $NaOH_{(aq)}$ (10 mL) was added dropwise in the reaction and then the mixture was stirred at 90°C for 3 hours. The resulted solution was concentrated under reduced pressure and purified by silica column chromatography (EA/Hex 1:4) to afford compound **10** as white solid with yield of 49%. Compound **10** is not stable, which

must proceed with the next-step synthesis immediately.

1*H*-pyrrolo[3,2-*g*]quinoline-3-carbaldehyde (PyrQ-al): **PyrQ** (65.1 mg, 0.39 mmol) was dissolved in DMF (2 mL) and then added to a flask containing $POCl_3$ (0.039 mL) and DMF (3 mL) which was stirred for 30 minutes at 0℃. After stirring at 40℃ for 3 hours, the reaction mixture was treated with iced water, followed by removing DMF under reduced pressure. The crude product was purified by silica column chromatography (EA/Hex 1:1) to obtain **PyrQ-al** as yellow solid. Yield: 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.42 (s, 1 H), 9.97 (s, 1 H), 8.23 (q, 1 H), 8.00 (s, 1 H), 7.89 (s, 1 H), 7.75 (d, 1 H), 7.49 (s, 1 H), 7.03 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.1 (s), 159.1 (s), 156.4 (s), 150.6 (s), 145.0 (s), 143.5 (s), 140.6 (s), 135.5 (s), 133.8 (s), 128.3 (s), 124.1 (s), 117.52 (s) ppm. HRMS (ESI): *m/z* calcd for $C_{12}H_8N_2O$ [M^+]: 196.0637; Found: 196.0634.

1*H*-pyrrolo[3,2-*g*]quinoline-3-carbonitrile (PyrQ-CN): The *o*-xylene was added into the mixture of compound **10** (340.1 mg, 1.72 mmol) and activated carbon (340.1 mg), stirred under oxygen. After stirring for 10 minutes, the reaction was heated to 120^{o}C and stirred for 24 hours. The resulted solution was filtered through celite and then concentrated under reduced pressure. The crude product was purified by silica column chromatography (EA/Hex 1:1) to obtain **PyrQ-CN** as yellow solid. Yield: 29%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.62 (s, 1 H), 8.77 (q, 1 H), 8.49 (d, 1 H), 8.23 (s, 1 H), 7.94 (s, 1 H), 7.77 (dd, *J* = 8.4, 4.0 Hz, 1 H), 7.58 (d, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.1 (s), 159.1 (s), 156.4 (s), 150.6 (s), 145.0 (s), 143.5 (s), 140.6 (s), 135.5 (s), 133.8 (s), 128.3 (s), 124.1 (s), 117.52 (s) ppm. HRMS (ESI): *m/z* calcd for $C_{12}H_7N_3$ [M^+]: 193.0640; Found: 193.0641.

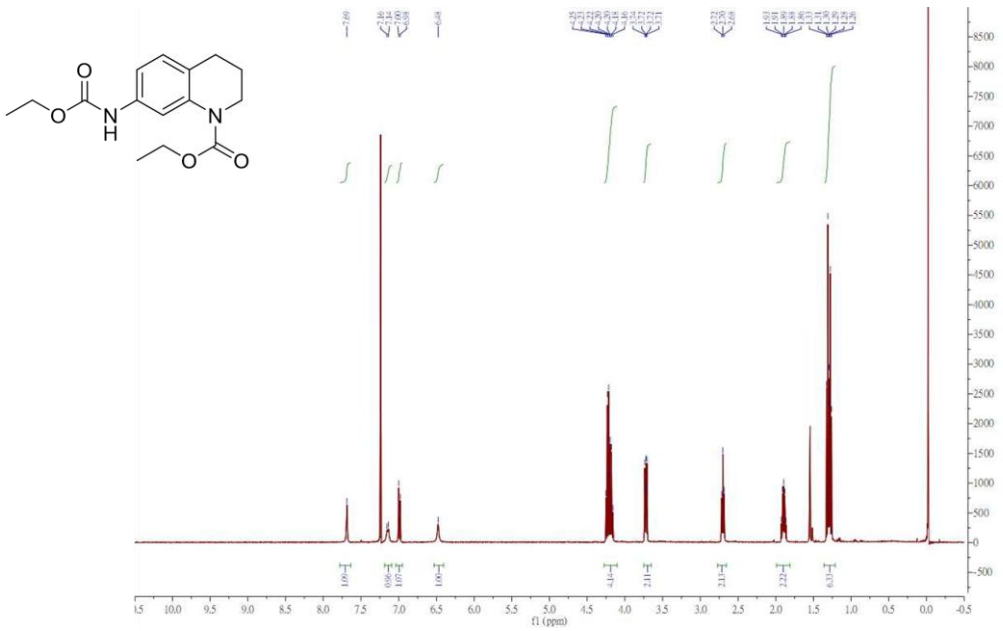

Figure S1. The ^{1}H-NMR spectrum of **Ethyl-7-((ethoxycarbonyl)amino)-3,4-dihydroquinoline-1(2H)-carboxylate** (**compound 4**).

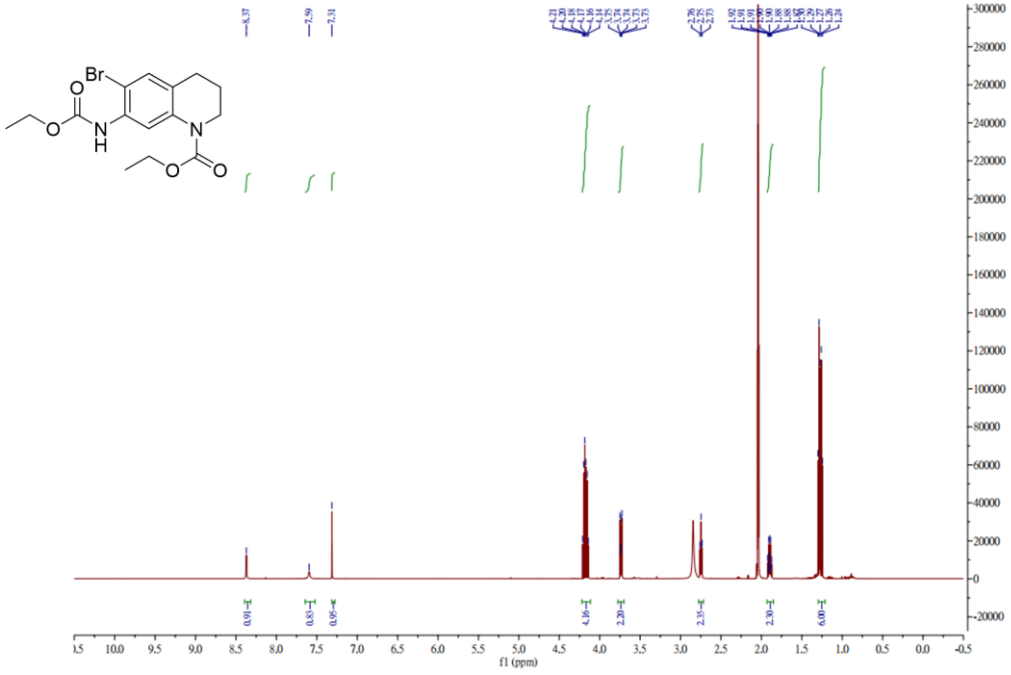

Figure S2. The ^{1}H-NMR spectrum of **Ethyl-6-bromo-7-((ethoxycarbonyl)amino)-3,4-dihydroquinoline-1(2H)-carboxylate** (**compound 5**).

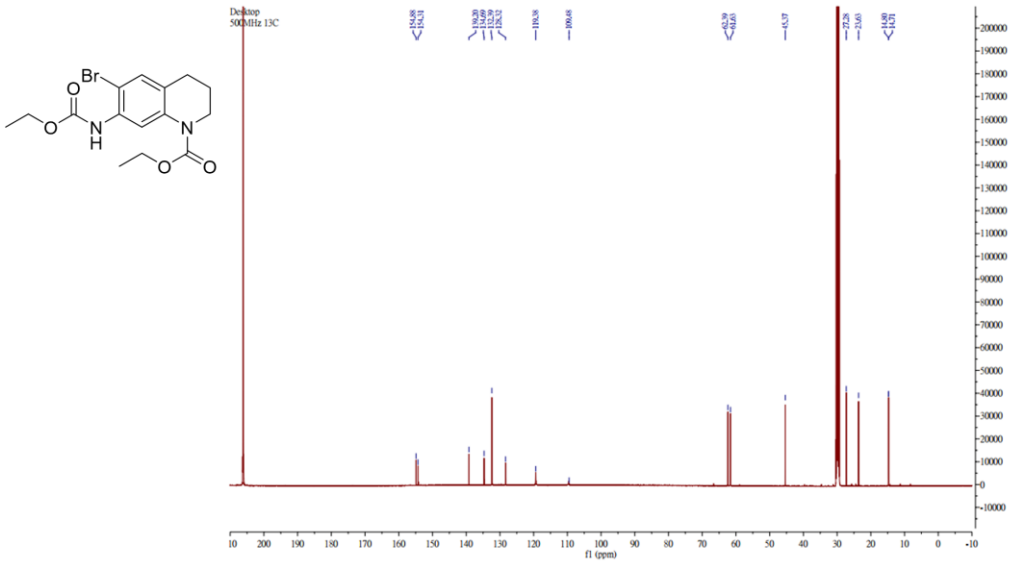

Figure S3. The ^{13}C-NMR spectrum of **Ethyl-6-bromo-7-((ethoxycarbonyl)amino)-3,4-dihydroquinoline-1(2H)-carboxylate** (**compound 5**).

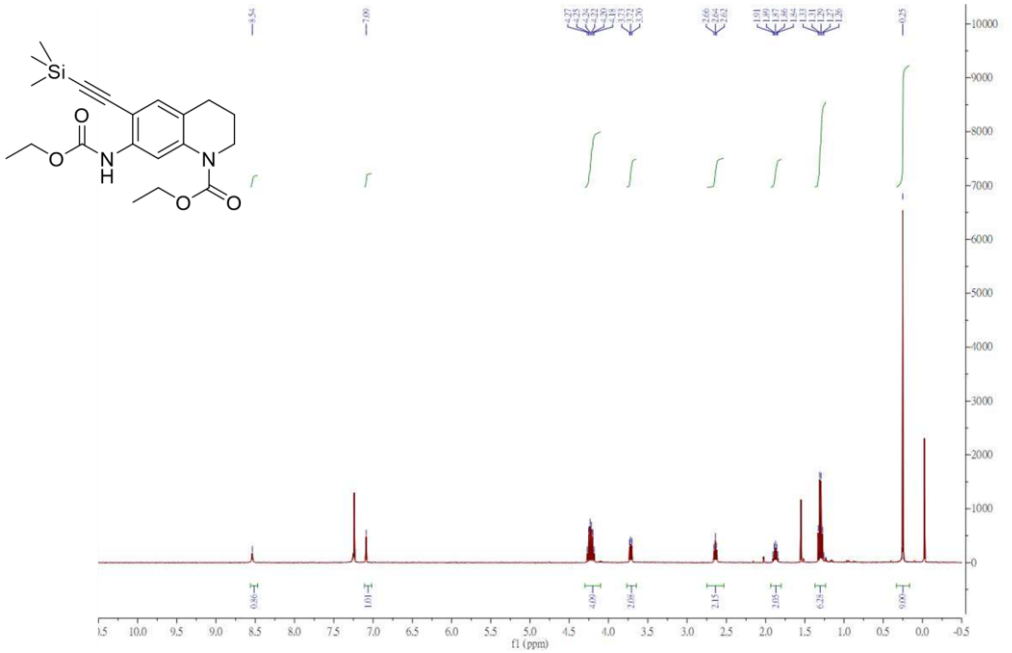

Figure S4. The ^{1}H-NMR spectrum of **Ethyl-7-((ethoxycarbonyl)amino)-6-((trimethylsilyl)ethynyl)-3,4-dihy droquinoline-1(2H)-carboxylate** (**compound 6**).

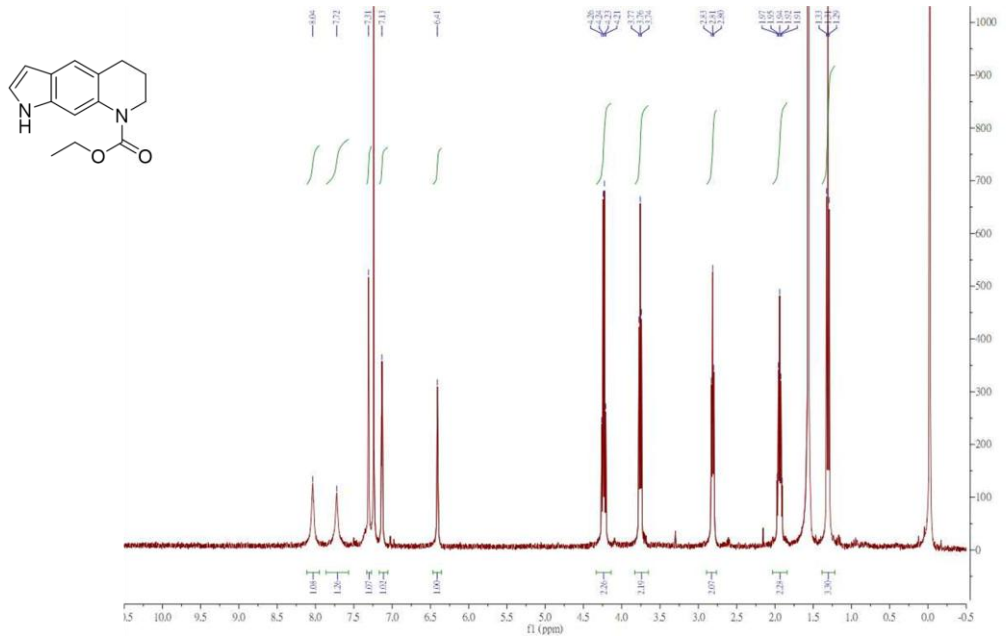

Figure S5. The ^{1}H-NMR spectrum of **Ethyl-6,7-dihydro-1H-pyrrolo[3,2-g]quinoline-8(5H)-carboxylate** (**compound 7**).

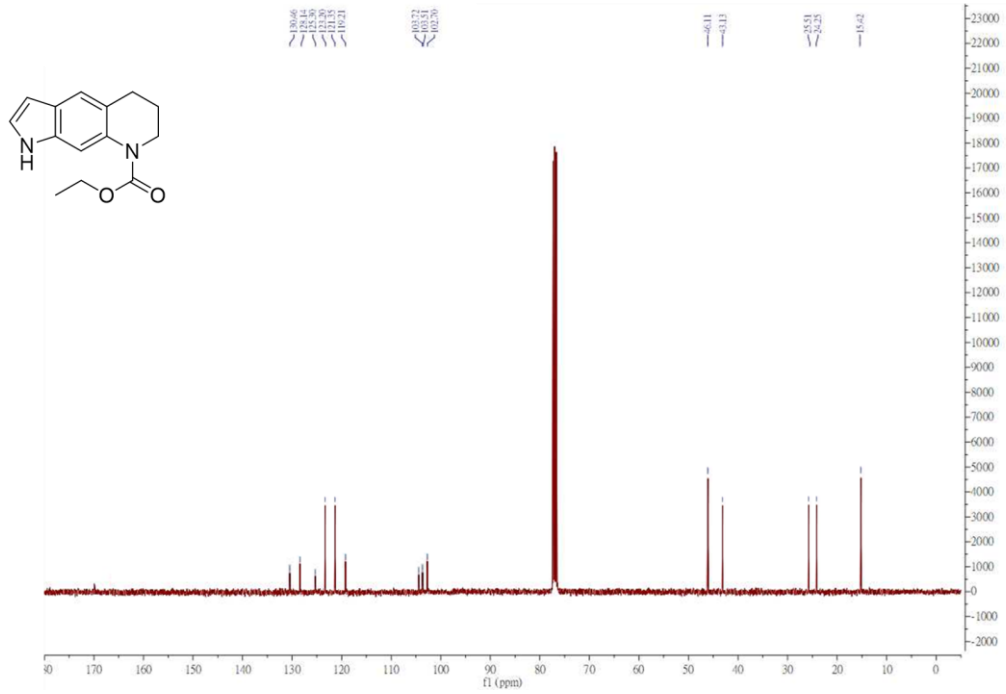

Figure S6. The ^{13}C-NMR spectrum of **Ethyl-6,7-dihydro-1H-pyrrolo[3,2-g]quinoline-8(5H)-carboxylate** (**compound 7**).

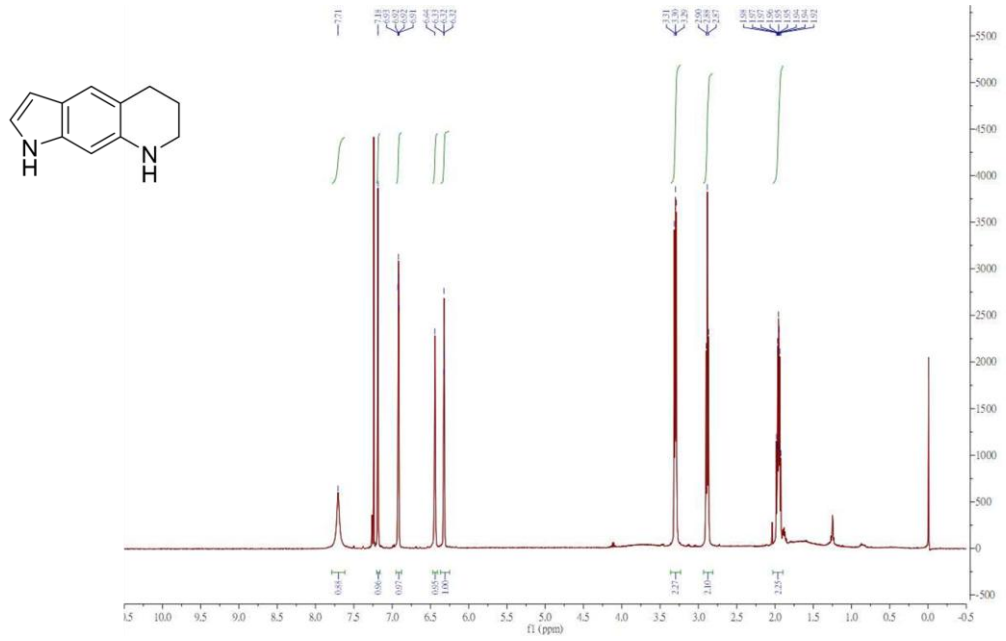

Figure S7. The ^{1}H-NMR spectrum of **5,6,7,8-tetrahydro-1H-pyrrolo[3,2-g]quinoline** (**compound 8**).

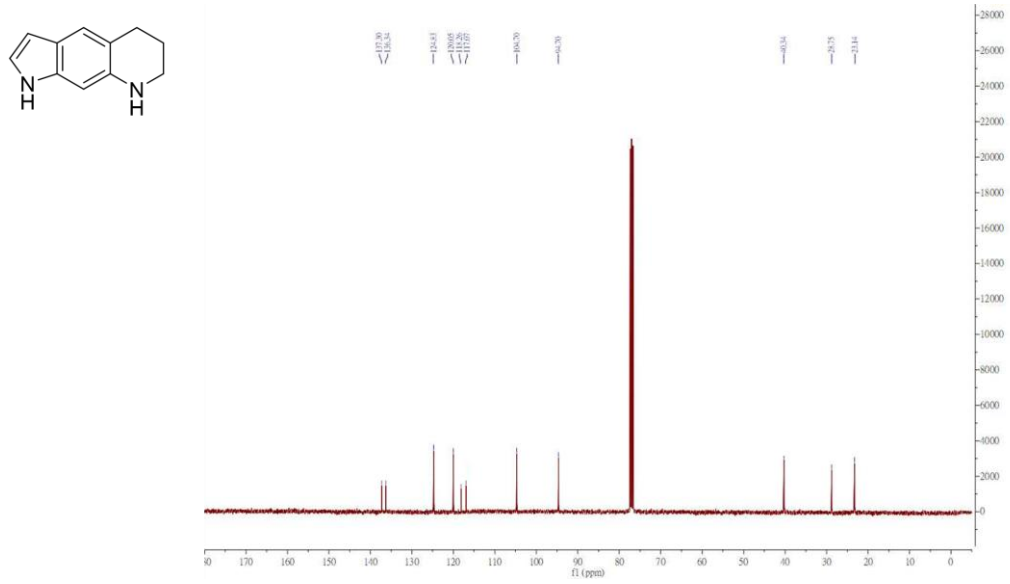

Figure S8. The ^{13}C-NMR spectrum of **5,6,7,8-tetrahydro-1H-pyrrolo[3,2-g]quinoline** (**compound 8**).

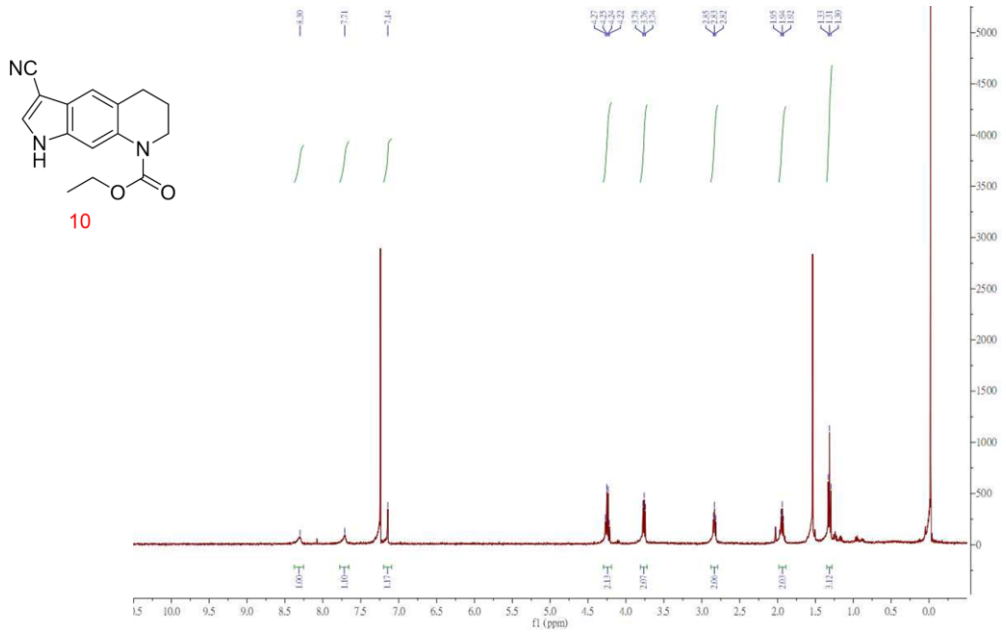

Figure S9. The ^{1}H-NMR spectrum of **Ethyl 3-cyano-6,7-dihydro-1H-pyrrolo[3,2-g]quinoline-8(5H)-carboxylate** (**compound 9**).

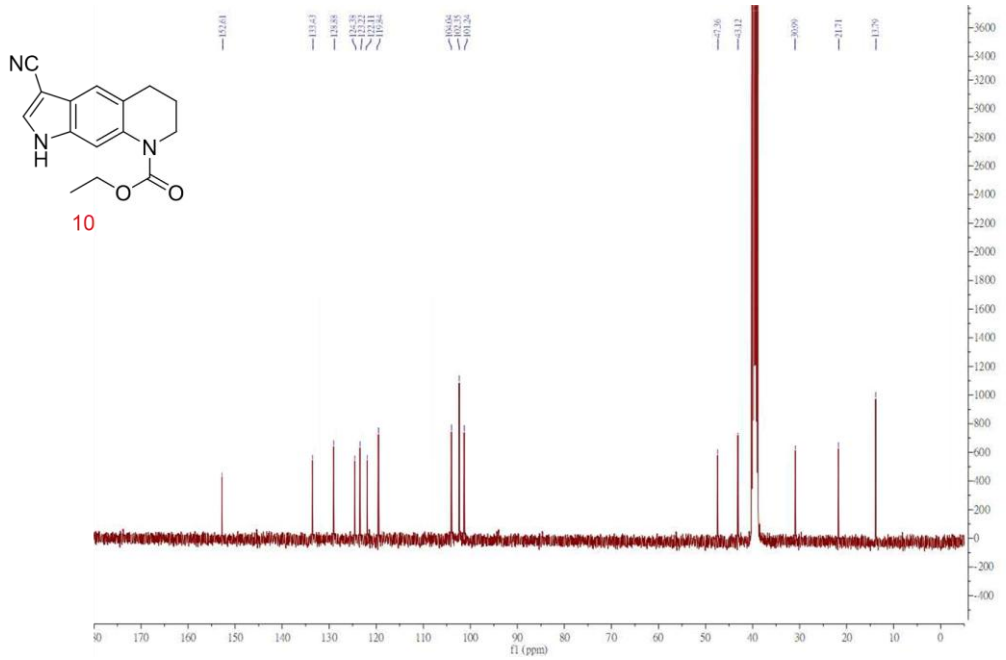

Figure S10. The ^{13}C-NMR spectrum of **Ethyl 3-cyano-6,7-dihydro-1H-pyrrolo[3,2-g]quinoline-8(5H)-carboxylate** (**compound 9**).

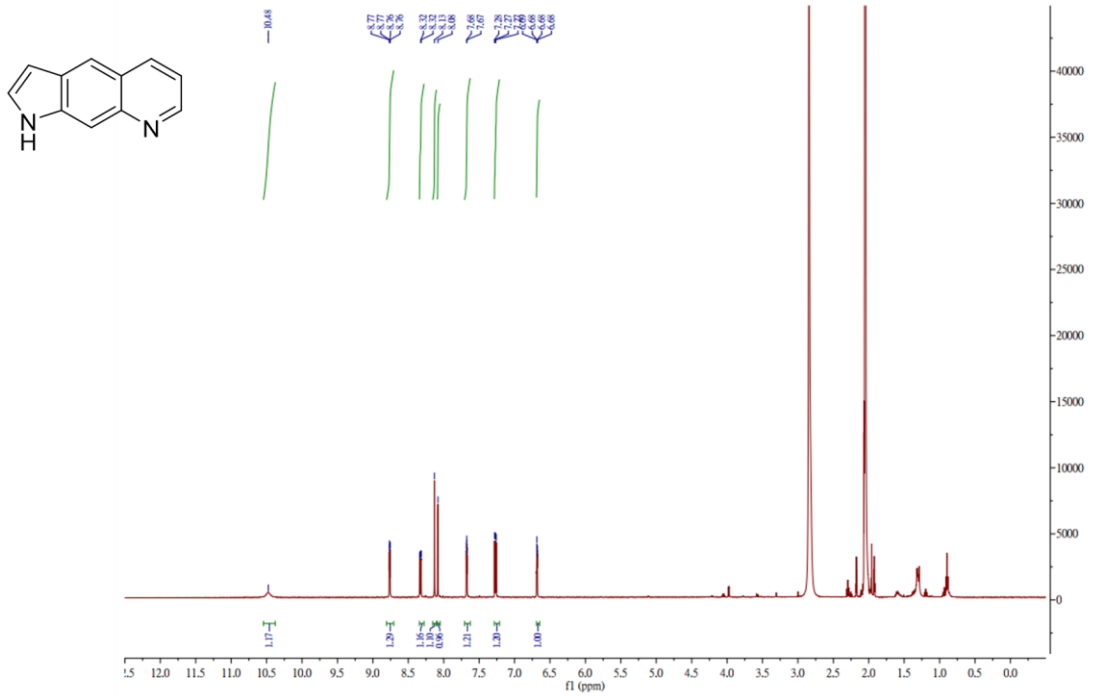

Figure S11. The ^{1}H-NMR spectrum of **1H-pyrrolo[3,2-g]quinoline (PyrQ)**.

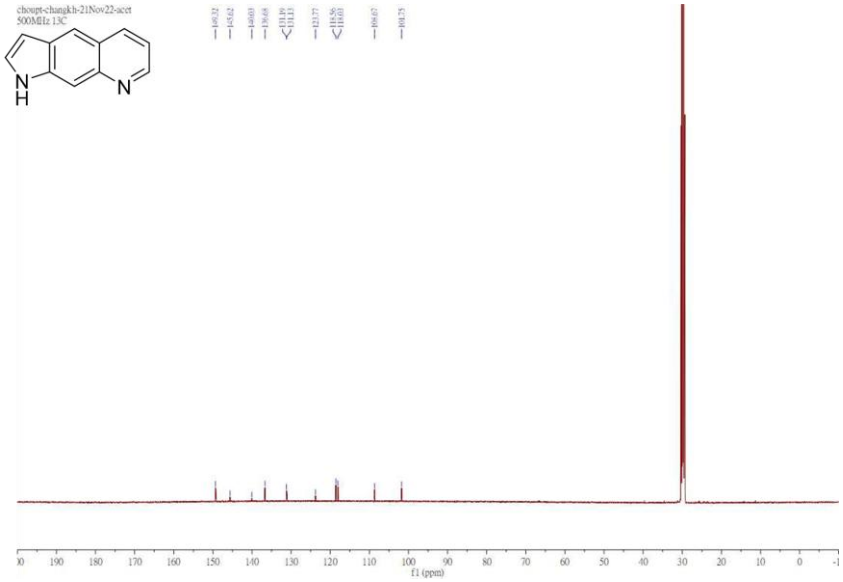

Figure S12. The ^{13}C-NMR spectrum of **1H-pyrrolo[3,2-g]quinoline (PyrQ)**.

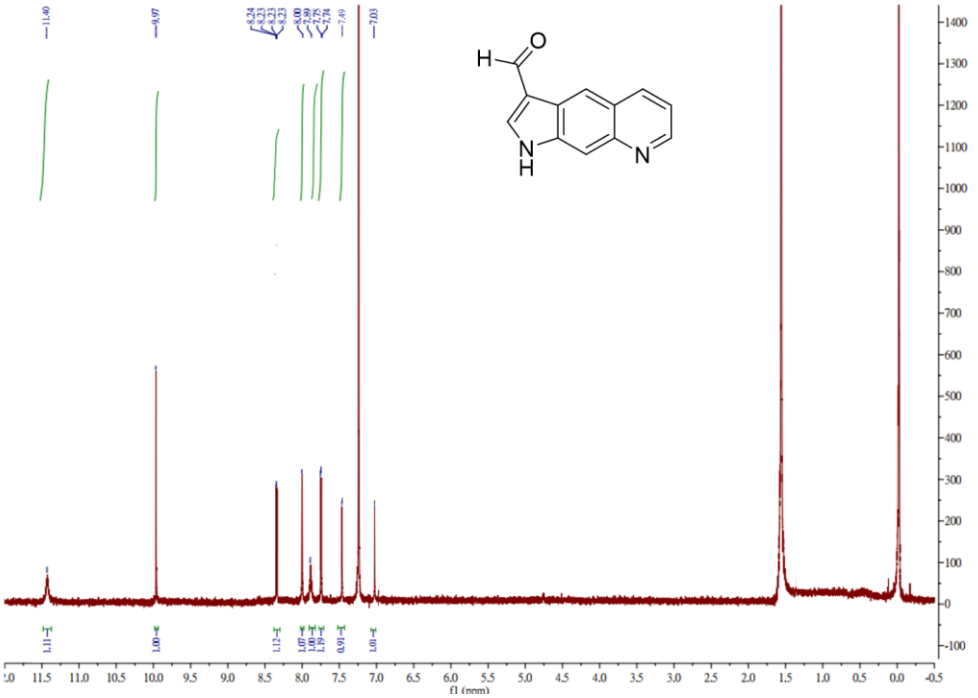

Figure S13. The ^{1}H-NMR spectrum of **1H-pyrrolo[3,2-g]quinoline-3-carbaldehyde (PyrQ-al)**.

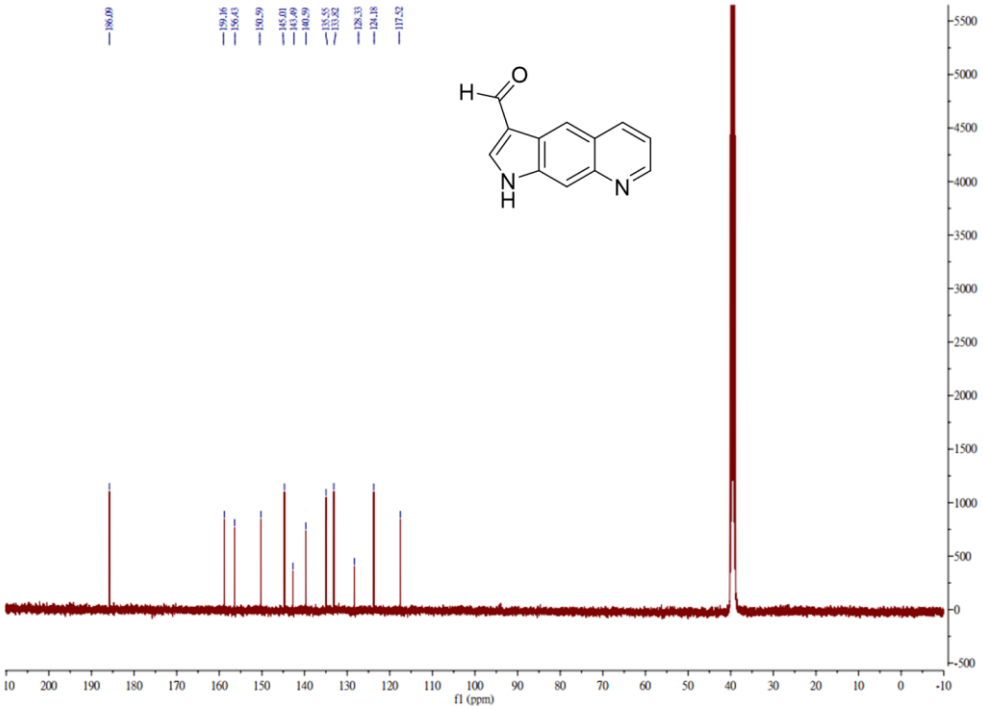

Figure S14. The ^{13}C-NMR spectrum of **1H-pyrrolo[3,2-g]quinoline-3-carbaldehyde (PyrQ-al)**.

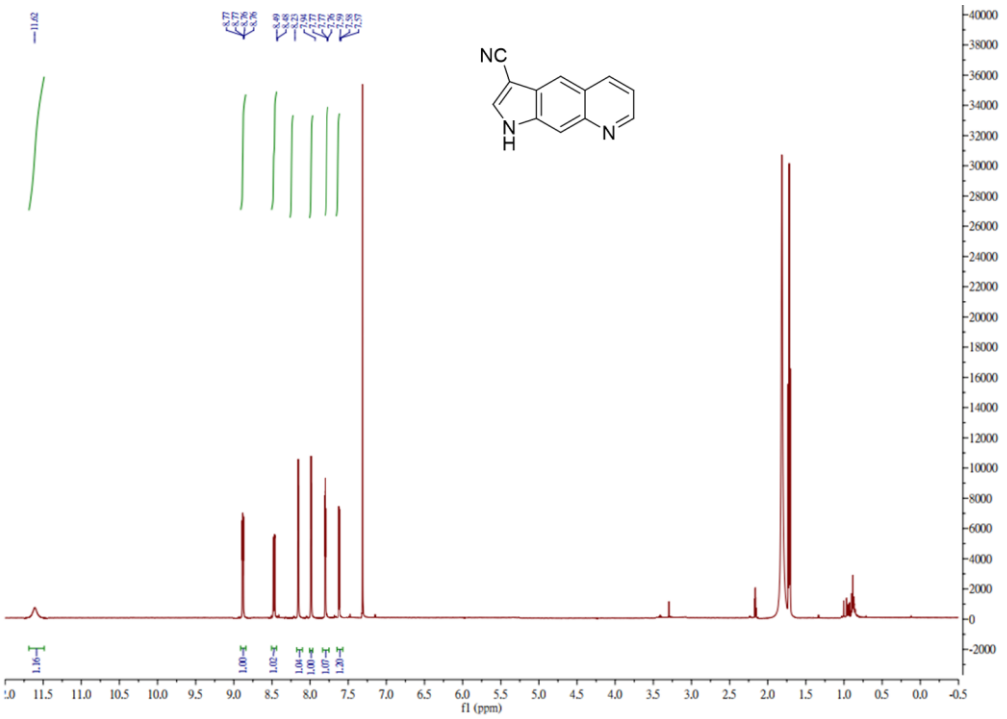

Figure S15. The ^{1}H-NMR spectrum of **1H-pyrrolo[3,2-g]quinoline-3-carbonitrile (PyrQ-CN)**.

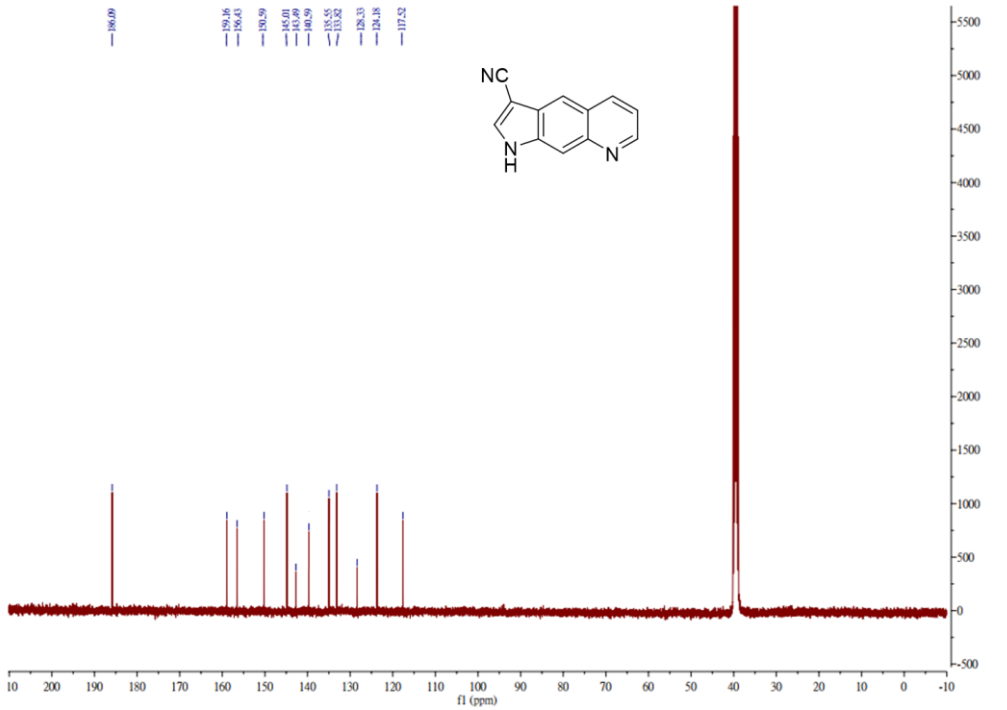

Figure S16. The ^{13}C-NMR spectrum of **1H-pyrrolo[3,2-g]quinoline-3-carbonitrile (PyrQ-CN)**.

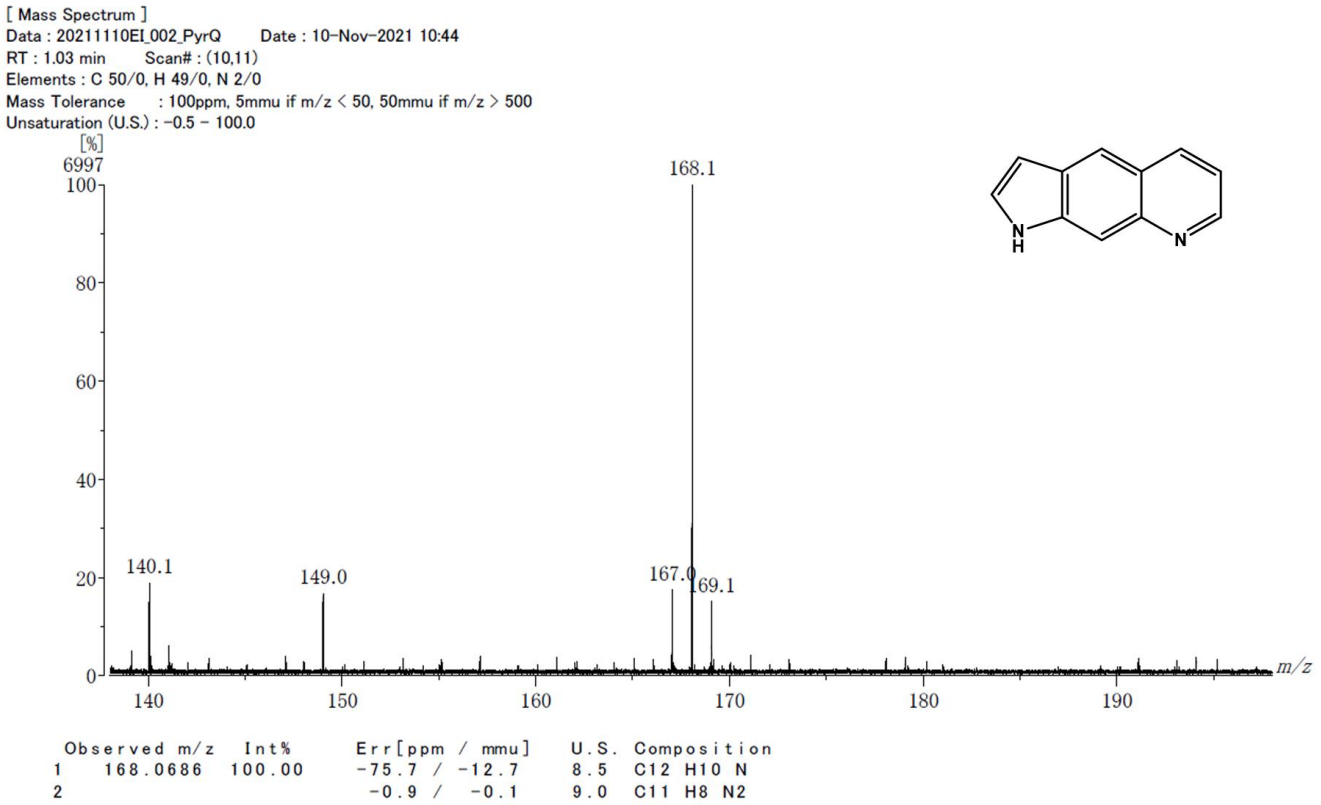

Figure S17. The MS spectrum of 1H-pyrrolo[3,2-g]quinoline (**PyrQ**), which measured by Electrospray Ionization (ESI).

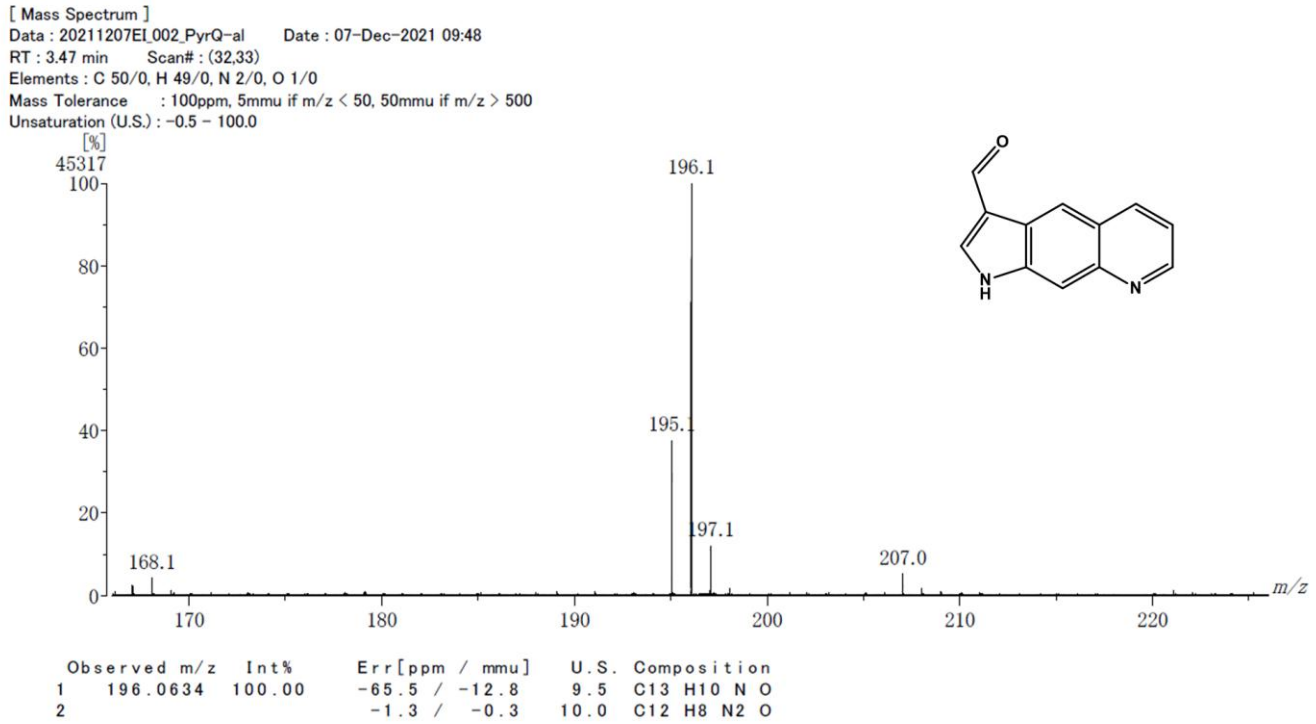

Figure S18. The MS spectrum of 1H-pyrrolo[3,2-g]quinoline-3-carbaldehyde (**PyrQ-al**), which measured by Electrospray Ionization (ESI).

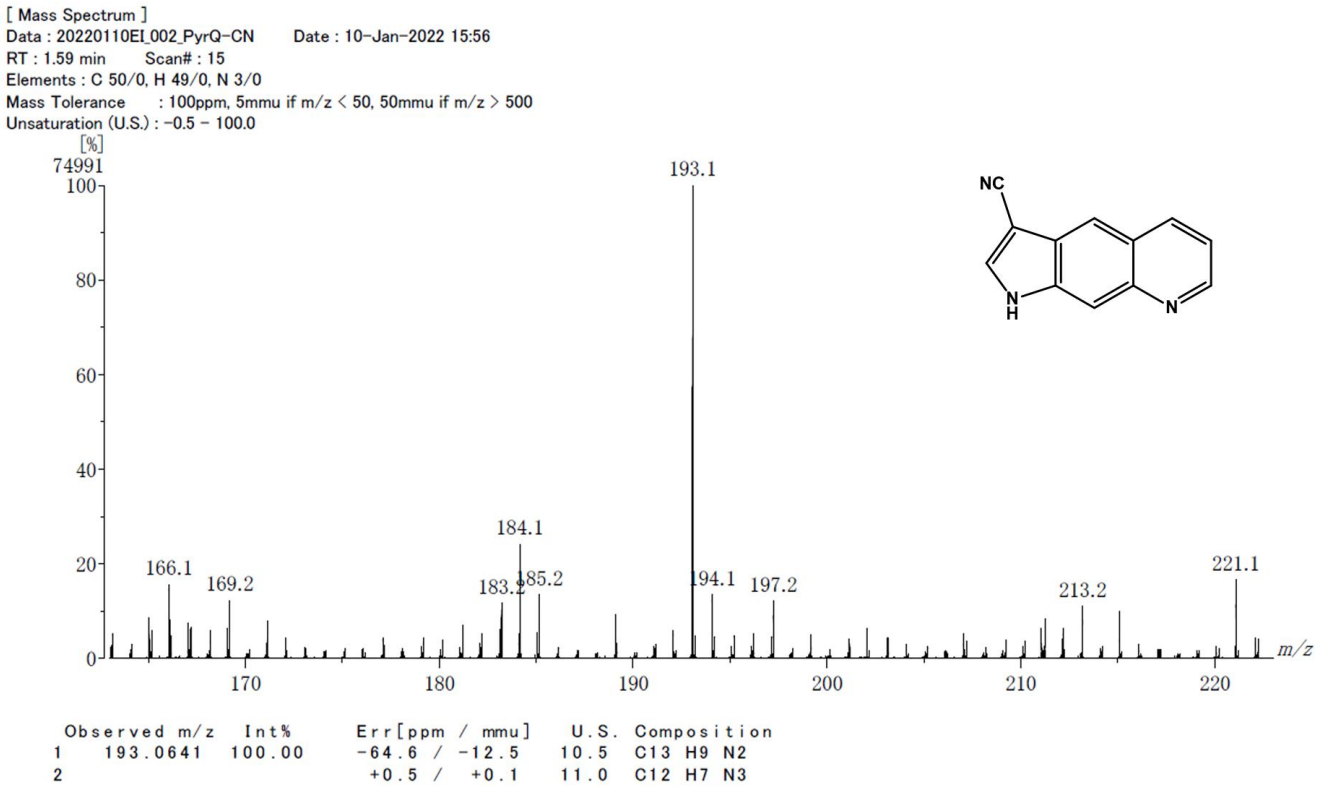

Figure S19. The MS spectrum of 1H-pyrrolo[3,2-g]quinoline-3-carbonitrile (**PyrQ-CN**), which measured by Electrospray Ionization (ESI).

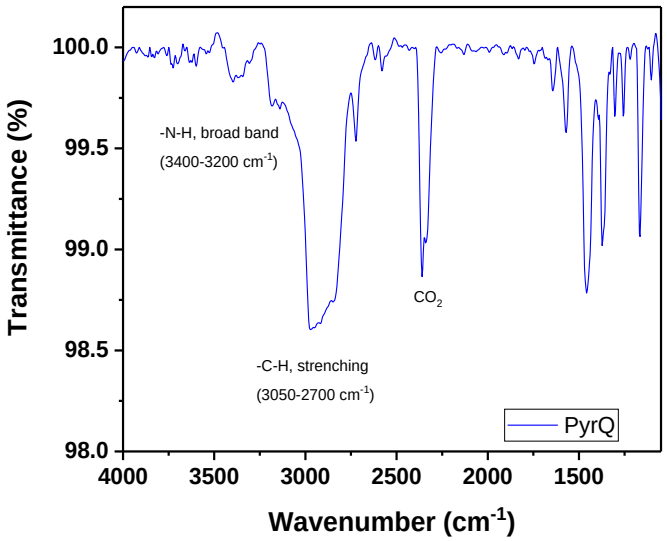

Figure S20. The mid-IR spectrum of 1*H*-pyrrolo[*3*,*2*-*g*]quinoline (**PyrQ**). The -NH absorption peak is found around 3400-3200 cm^{-1}.

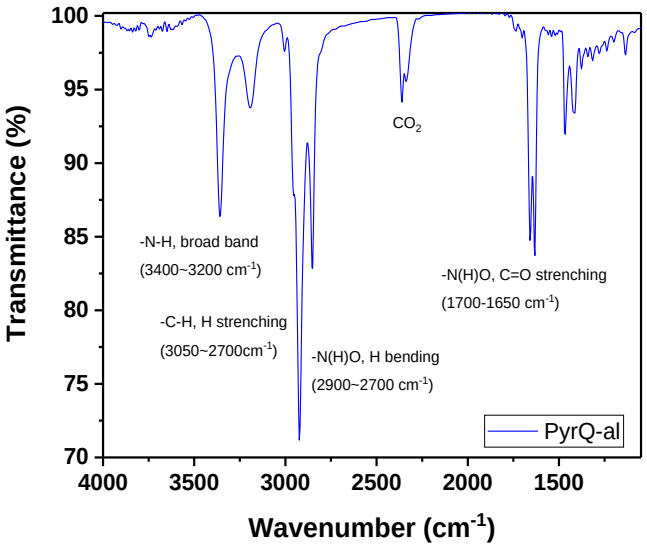

Figure S21. The mid-IR spectrum of 1*H*-pyrrolo[*3*,*2*-*g*]quinoline-3-carbaldehyde (**PyrQ-al**). The -NH absorption peak is found around 3400-3200 cm^{-1}. There is an obvious carbonyl group (C=O) characteristic peak at 1700-1650 cm^{-1} and C-H of the aldehyde absorption peak at 2900-2700 cm^{-1}.

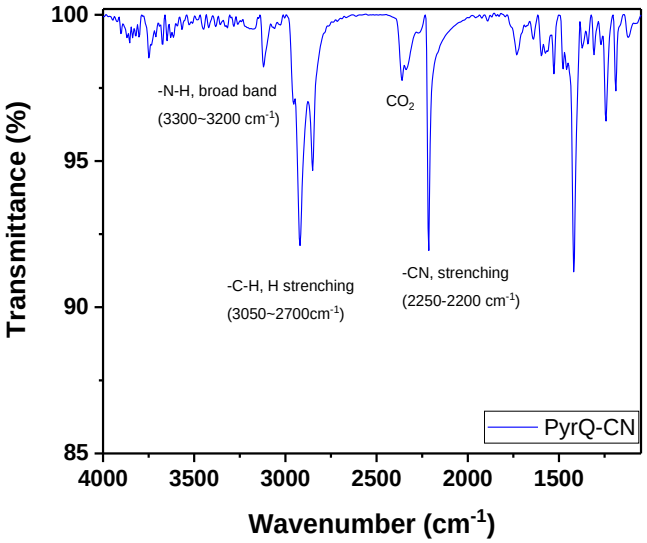

Figure S22. The mid-IR spectrum of 1*H*-pyrrolo[*3*,*2*-*g*]quinoline-3-carbonitrile (**PyrQ-CN**). The -NH absorption peak is found around 3300-3200 cm^{-1}.Also, **PyrQ-CN** has a significant nitrile group (-CN) stretch peak at 2250-2200 cm^{-1}.

Table 1. Crystal data and structure refinement for ic20904**.**

Identification code	ic20904	
Empirical formula	C11 H8 N2	
Formula weight	168.19	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.7781(2) Å	α= 90°.
	b = 10.1450(4) Å	β= 90°.
	c = 14.0978(4) Å	γ = 90°.
Volume	826.40(5) $Å^3$	
Z	4	
Density (calculated)	1.352 Mg/m^3	
Absorption coefficient	0.083 mm^{-1}	
F(000)	352	
Crystal size	0.185 x 0.166 x 0.079 mm^3	
Theta range for data collection	2.473 to 30.000°.	
Index ranges	-8<=h<=7, -14<=k<=14, -19<=l<=19	
Reflections collected	15065	
Independent reflections	2423 [R(int) = 0.0401]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9602 and 0.8198	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2423 / 0 / 122	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0393, wR2 = 0.1069	
R indices (all data)	R1 = 0.0434, wR2 = 0.1111	
Absolute structure parameter	-0.4(10)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.212 and -0.168 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ic20904. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	2372(3)	9447(2)	2934(1)	34(1)
C(2)	4168(3)	10271(2)	3180(1)	37(1)
C(3)	5779(3)	9621(2)	3707(1)	38(1)
C(4)	5861(3)	7141(2)	4194(1)	34(1)
C(5)	5472(4)	4741(2)	4477(1)	39(1)
C(6)	4239(4)	3618(2)	4348(1)	42(1)
C(7)	2125(4)	3678(2)	3855(1)	40(1)
N(8)	1232(3)	4762(2)	3504(1)	34(1)
C(9)	1559(3)	7065(2)	3204(1)	30(1)
C(10)	2827(3)	8211(2)	3283(1)	30(1)
C(11)	4996(3)	8274(2)	3782(1)	31(1)
C(12)	4632(3)	5948(2)	4112(1)	32(1)
C(13)	2451(3)	5916(2)	3614(1)	29(1)

Table 3. Bond lengths [Å] and angles [°] for ic20904.

N(1)-C(10)	1.372(2)
N(1)-C(2)	1.377(3)
C(2)-C(3)	1.361(3)
C(3)-C(11)	1.444(3)
C(4)-C(11)	1.381(3)
C(4)-C(12)	1.409(3)
C(5)-C(6)	1.356(3)
C(5)-C(12)	1.415(3)
C(6)-C(7)	1.406(3)
C(7)-N(8)	1.312(3)
N(8)-C(13)	1.375(2)
C(9)-C(10)	1.379(2)
C(9)-C(13)	1.400(2)
C(10)-C(11)	1.439(2)
C(12)-C(13)	1.442(2)

C(10)-N(1)-C(2)	108.62(16)
C(3)-C(2)-N(1)	111.09(18)
C(2)-C(3)-C(11)	106.47(17)
C(11)-C(4)-C(12)	119.86(16)
C(6)-C(5)-C(12)	119.87(18)
C(5)-C(6)-C(7)	119.12(19)
N(8)-C(7)-C(6)	124.34(19)
C(7)-N(8)-C(13)	118.01(16)
C(10)-C(9)-C(13)	118.28(15)
N(1)-C(10)-C(9)	129.78(16)
N(1)-C(10)-C(11)	107.57(16)
C(9)-C(10)-C(11)	122.65(16)
C(4)-C(11)-C(10)	118.94(17)
C(4)-C(11)-C(3)	134.84(17)
C(10)-C(11)-C(3)	106.22(17)
C(4)-C(12)-C(5)	122.75(16)
C(4)-C(12)-C(13)	120.02(16)
C(5)-C(12)-C(13)	117.21(17)
N(8)-C(13)-C(9)	118.28(15)
N(8)-C(13)-C(12)	121.46(16)
C(9)-C(13)-C(12)	120.23(16)

Symmetry transformations used to generate equivalent atoms:

2. Photophysical measurements

Method and measurement:

The absorption and emission spectra were recorded by Hitachi U-3310 and U-5700 spectrophotometer and Edinburgh FS980 fluorometer at National Taiwan University. The spectrum of all titled compounds was measured in methanol, cyclohexane and dichloromethane.

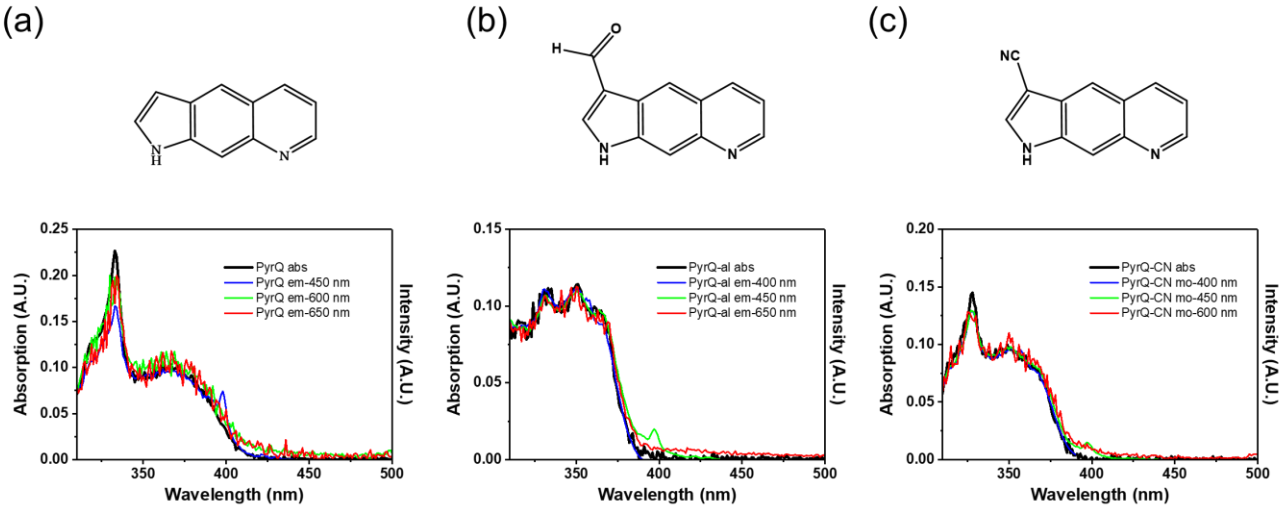

Figure S23. The excitation spectrum of (a) **PyrQ**, (b) **PyrQ-al**, and (c) **PyrQ-CN** in MeOH.

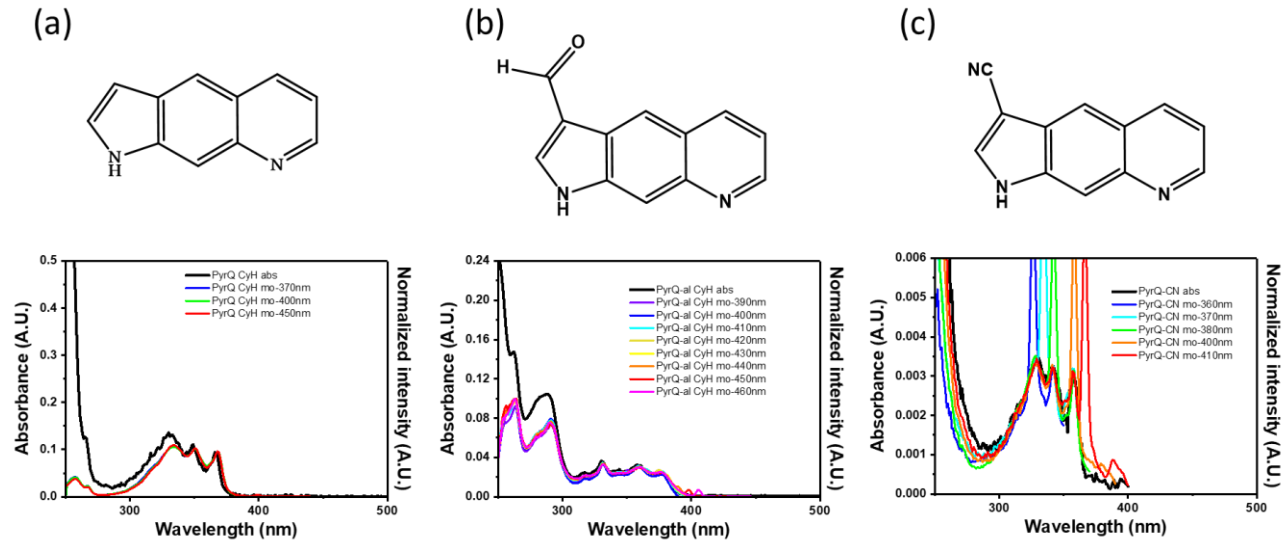

Figure S24. The excitation spectrum of (a) **PyrQ**, (b) **PyrQ-CN** in cyclohexane.

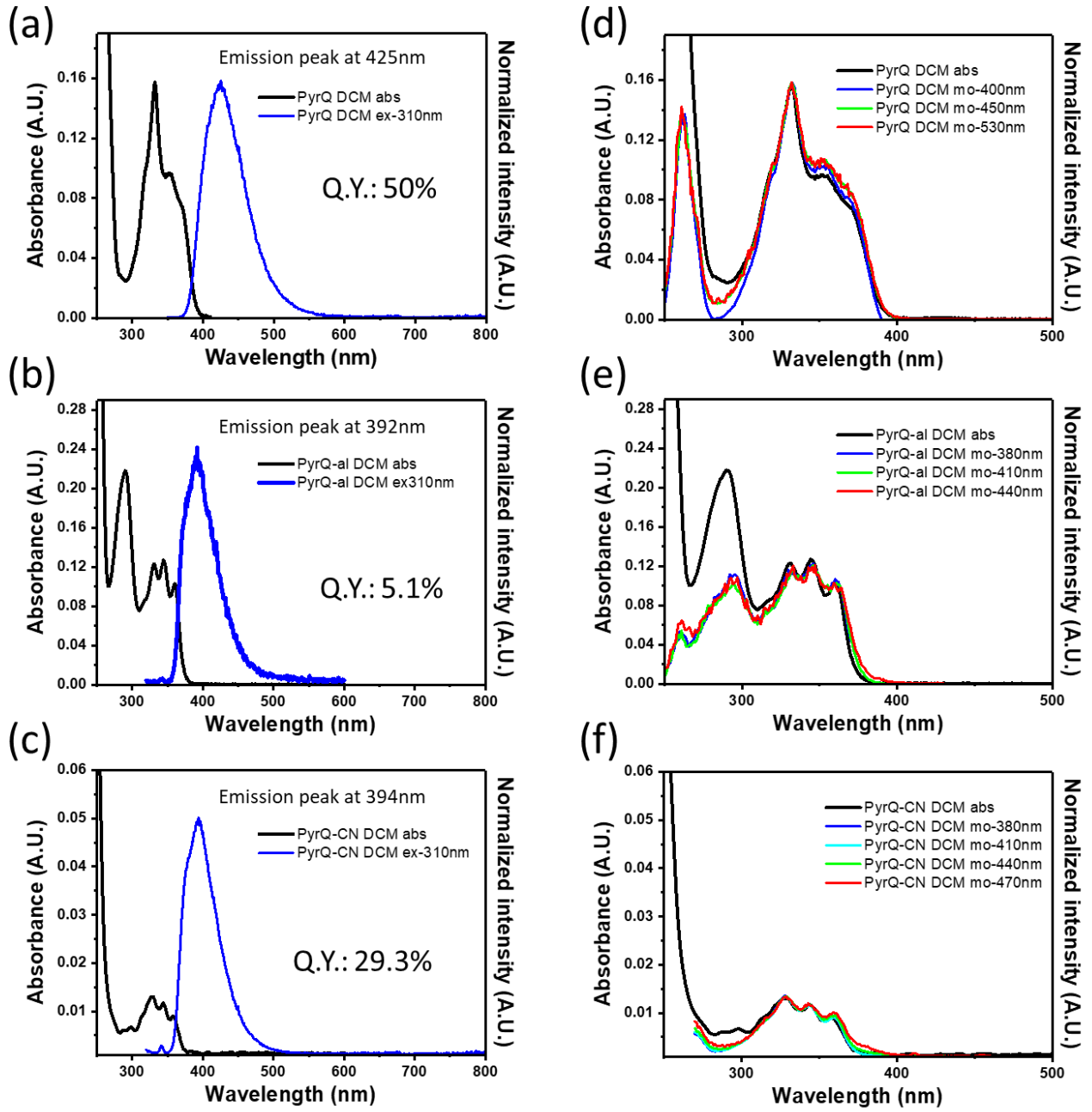

Figure S25. The emission spectrum of (a) **PyrQ**, (b) **PyrQ-al**, and (c) **PyrQ-CN** in dichloromethane, these spectra all reveal solely normal Stokes shifted emission. The excitation spectrum of (d) **PyrQ**, (e) **PyrQ-al**, and (f) **PyrQ-CN** are also measured, and these are similar to their absorption spectrum. It implies that these emissions originate from themselves. (**PyrQ-CN** is difficult to dissolve in dichloromethane.)

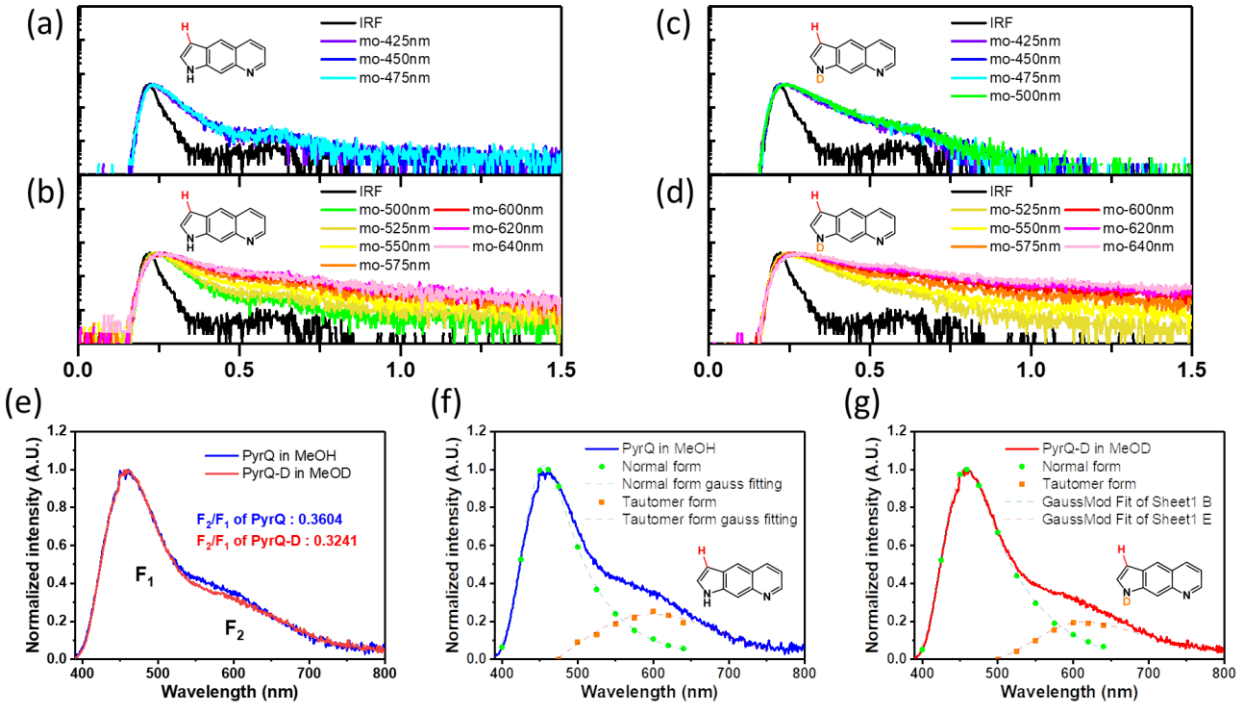

Figure S26 PyrQ in MeOH, (a) monitored at ≤ 475nm, has one decay kinetics, (b) when it is >475nm, has two decay kinetics. This is due to the tautomer contribution being at > 475nm. In comparison, the proton transfer rate of **PyrQ-D** in MeOD is slower, so its fluorescence intensity will be weaker, (c) ≤ 500nm, has one decay kinetics, (d) when it >500nm, has two decay kinetics. (e) Normalized fluorescence intensity of **PyrQ** and **PyrQ-D** in MeOH and MeOD, and the F_2(461nm)/F_1(600nm) ratio are 0.3604 and 0.3241 for **PyrQ** (in MeOH) and **PyrQ-D** (in MeOD), respectively. Besides, calculate integral values for kinetic decay curve of two species (normal form and tautomeric form), and drawing the deconvolution plots of (f) **PyrQ** and (g) **PyrQ-D** are depicted (The green ball is F_1 intensity, the orange square is F_2 intensity, and all dash line is defined by the gauss fitting of their intensity point).

Table S4. The radiative and non-radiative rates (k_r and k_{nr}) of **PyrQ** (in MeOH) and **PyrQ-D** (in MeOD) are roughly estimated by deconvolution.

Compound	Solvent	Total PLQY[a]	intensity fraction of F_1[b]	intensity fraction of F_2[b]	F_1 PLQY[c]	F_2 PLQY[c]	τ_{decay} (s)[d]	τ_{decay2} (s)[d]	F_2 band k_r[e]	F_2 band k_{nr}[e]
PyrQ	CH_3OH	0.2%	0.7904	0.2096	0.1581%	0.0419%	4.4×10^{-11}	4.27×10^{-10}	9.82×10^{5}	2.34×10^{9}
PyrQ-D	CH_3OD	0.4%	0.8449	0.1551	0.3380%	0.0620%	7.4×10^{-11}	8.34×10^{-10}	7.44×10^{5}	1.20×10^{9}

[a] The total PLQY refers to Table 1 in TEXT.

[b] This value is the integral of the emission intensity (F_1 or F_2) divided by the integral of total emission intensity (F_1+F_2), which is estimated by deconvolution (Figs. S26f and S26g).

[c] The PLQY of F_1 and F_2.

[d] The τ_{decay} and τ_{decay2} refer to Table 2 in TEXT.

[e] The k_r and k_{nr} of F_2 emission band are estimated by F_2 band PLQY and τ_{decay2}.

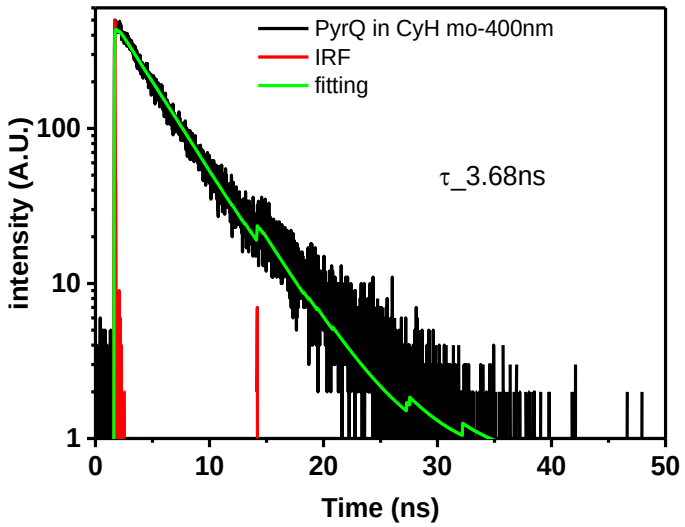

Figure S27 PyrQ has only one dynamic decay lifetime of 3.68ns, measured by a TCSPC technique with a repetition rate of 8.2MHz Ti: Sapphire laser generated by an AOM system.

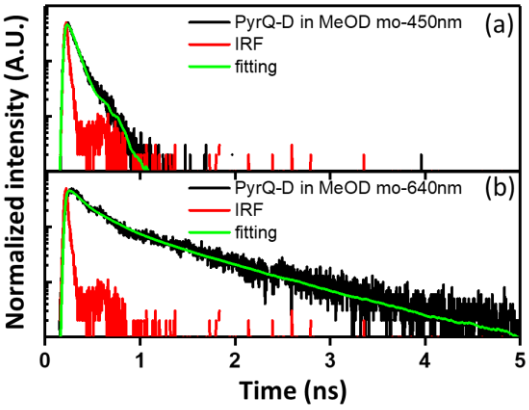

Figure S28. Time-resolved fluorescence of **PyrQ-D** in CH_3OD monitored at (a) F_1 and (b) F_2 regions.

3. pH titration

Method and measurement:

The absorption and emission spectra were recorded by Hitachi U-3310 spectrophotometer and Edinburgh FS980 fluorometer at National Taiwan University. The titration experiments of all titled compounds were measured in water. p*H* meter is PH500 pH/mV/Temp Meter (Clean Corp.) with an electrode of Polilyte HT (Hamilton). Sodium hydroxide is First Grade (Shimakyu).

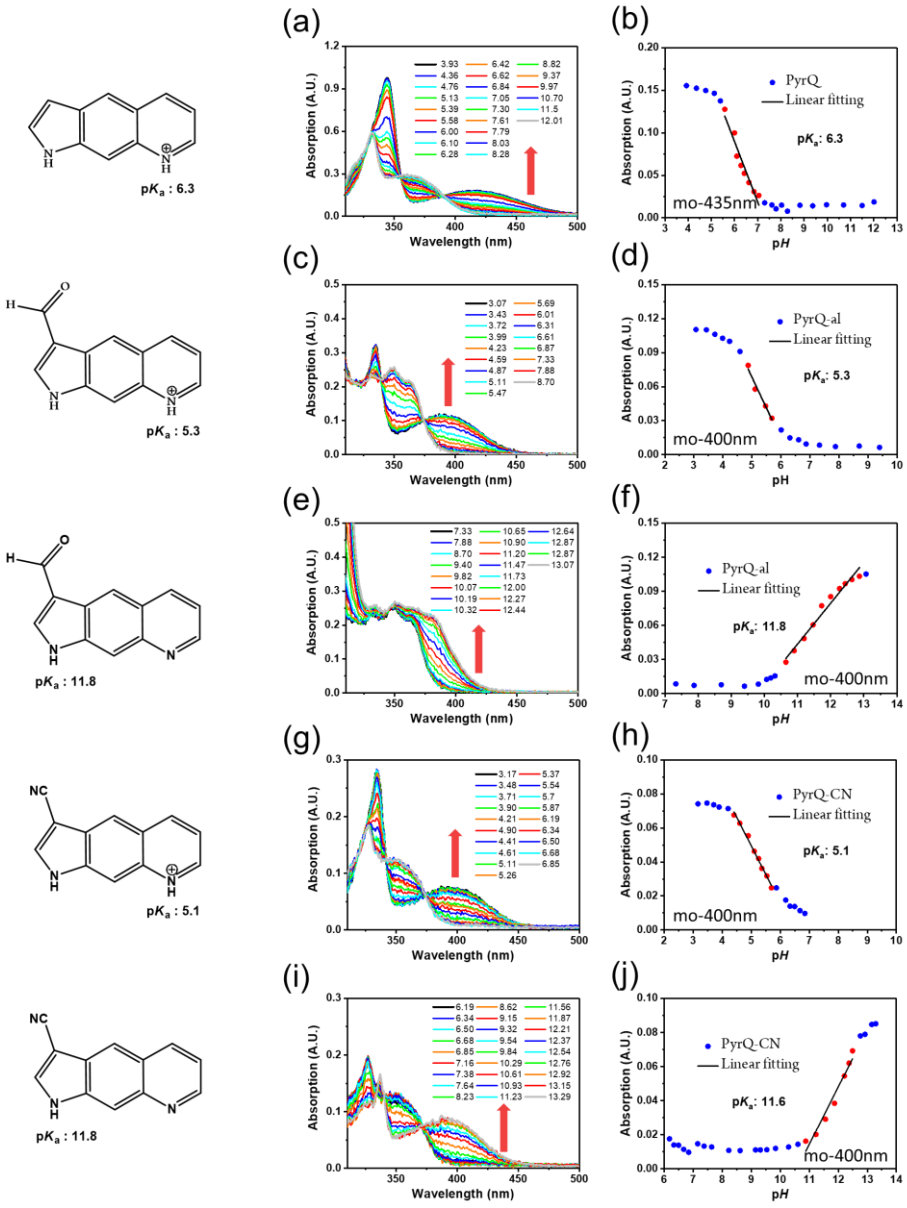

Figure S29. According to the absorption variation of (**a**) **PyrQ**, (**c**)(**e**) **PyrQ-al**, and (**g**)(**i**) **PyrQ-CN** in p*H* titration experiment, the pK_a of (**b**) **PyrQ**, (**d**)(**f**) **PyrQ-al**, and (**h**)(**j**) **PyrQ-CN** proton acceptor sites are calculated. All measurements are carried out in the water.

4. Theoretical computation (1) – Gaussian program

Table S5. Calculated optical properties of **PyrQ**, **PyrQ-al**, and **PyrQ-CN** based on B3LYP/6–31+G(d,p) level in methanol.

Name	Normal form absorption [a]		Normal form emission [b]		Tautomer emission [c]	
	Absorption (nm)	f	Emission (nm)	f	Emission (nm)	f
PyrQ	373.01	0.0574	433.39	0.1351	819.41	0.0142
PyrQ-al	362.03	0.1061	409.49	0.1655	662.00	0.0194
PyrQ-CN	355.59	0.0815	406.52	0.1561	672.80	0.0190

[a] The structure was optimized in the ground state.

[b] The normal form structure was optimized in S_1 state.

[c] The tautomer structure was optimized in S_1 state.

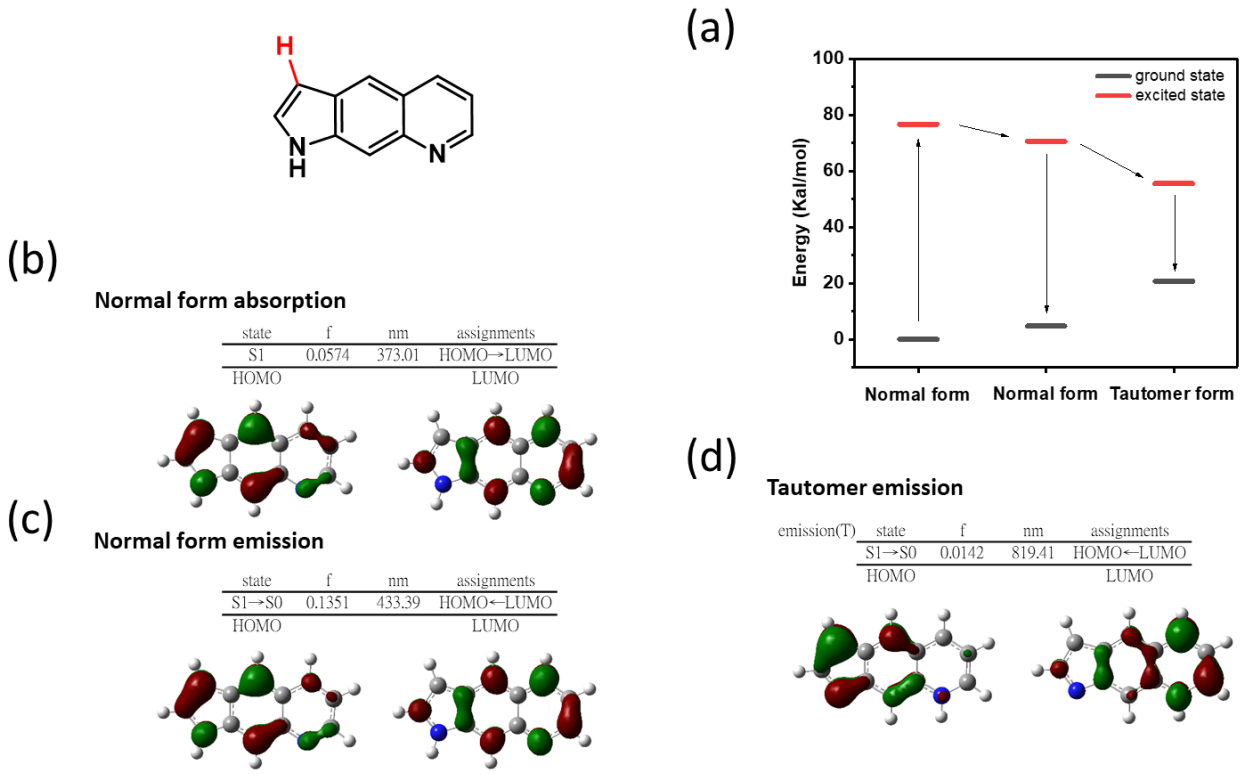

Figure S30. We performed thermodynamic calculations of SCPT based on B3LYP/6–31+G(d,p) level in methanol. (**a**) plot of SCPT process of **PyrQ**, the calculated result of **PyrQ** for (**b**) normal form absorption process, (**c**) normal form emission process, and (**d**) tautomer emission process. (The molecular orbital isovalue is set at 0.05.)

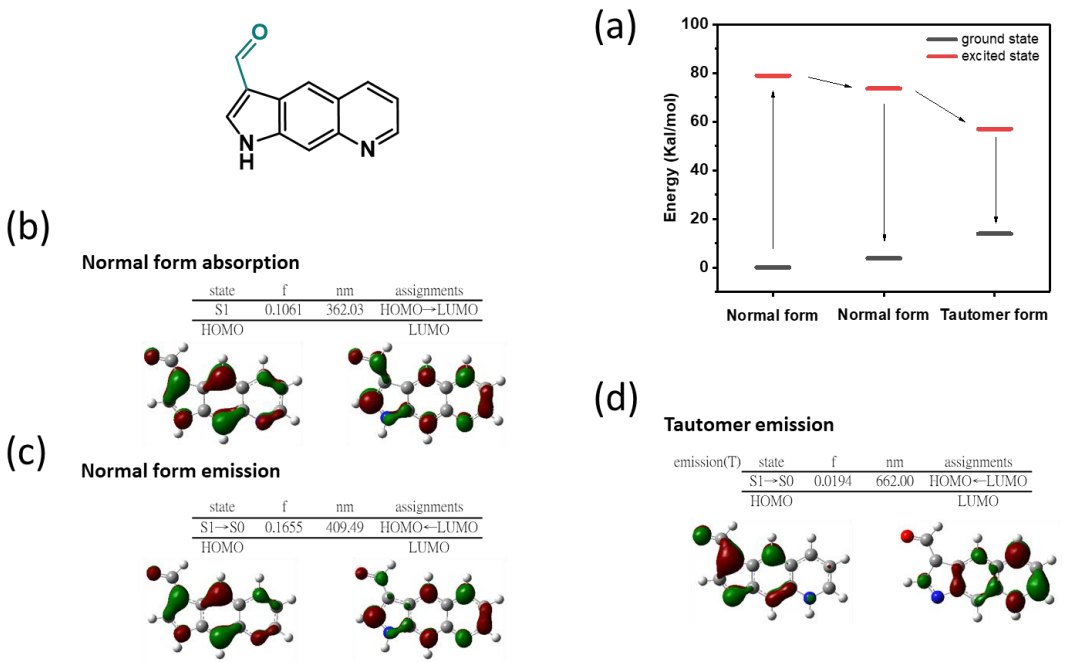

Figure S31. We performed thermodynamic calculations of SCPT based on B3LYP/6–31+G(d,p) level in methanol. (**a**) plot of SCPT process of **PyrQ-al**, the calculated result of **PyrQ-al** for (**b**) normal form absorption process, (**c**) normal form emission process, and (**d**) tautomer emission process. (The molecular orbital isovalue is set at 0.05.)

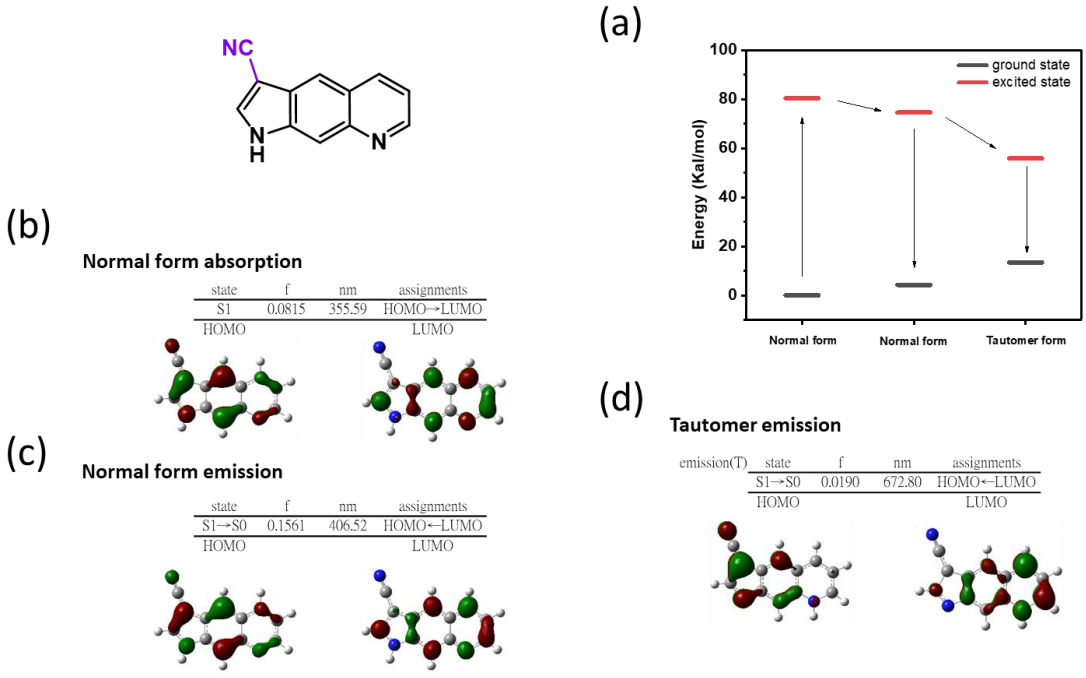

Figure S32. We performed thermodynamic calculations of SCPT based on B3LYP/6–31+G(d,p) level in methanol. (**a**) plot of SCPT process of **PyrQ-CN**, the calculated result of **PyrQ-CN** for (**b**) normal form absorption process, (**c**) normal form emission process, and (**d**) tautomer emission process. (The molecular orbital isovalue is set at 0.05.)

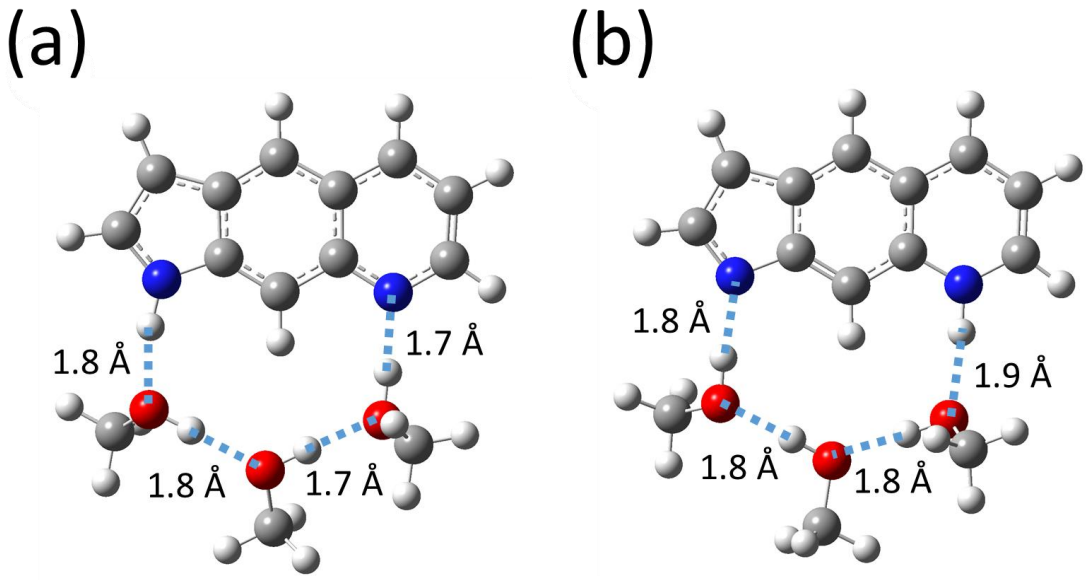

Figure S33. We performed optimization of **PyrQ** structure with two or three methanol molecules, which calculated based on B3LYP/6–31+G(d,p) level. (**a**) normal form in S_1 state, and (**b**) tautomer form in S_1 state.

Table S6. Calculated optical properties of **PyrQ**, **PyrQ-al**, and **PyrQ-CN** based on CAM-B3LYP/6–31+G(d,p) level in methanol.

Name	Normal form absorption [a]		Normal form emission [b]		Tautomer emission [c]	
	Absorption (nm)	f	Emission (nm)	f	Emission (nm)	f
PyrQ	328.32	0.0913	392.09	0.2211	622.23	0.0350
PyrQ-al	319.67	0.1627	372.95	0.2432	525.41	0.0538
PyrQ-CN	315.52	0.1319	371.57	0.2412	527.84	0.0535

[a] The structure was optimized in the ground state.

[b] The normal form structure was optimized in S_1 state.

[c] The tautomer structure was optimized in S_1 state.

Table S7. Calculated optical properties of **PyrQ**, **PyrQ-al**, and **PyrQ-CN** based on B3LYP/6–31+G(d,p) level in cyclohexane.

Name	Normal form absorption [a]		Normal form emission [b]	
	Absorption (nm)	f	Emission (nm)	f
PyrQ	366.76	0.0673	414.11	0.0847
PyrQ-al	360.53	0.1066	398.37	0.0990
PyrQ-CN	354.36	0.0911	395.05	0.0974

[a] The structure was optimized in the ground state.

[b] The normal form structure was optimized in S_1 state.

[c] The tautomer structure was optimized in S_1 state.

Table S8. Calculated optical properties of **PyrQ**, **PyrQ-al**, and **PyrQ-CN** based on CAM-B3LYP /6–31+G(d,p) level in cyclohexane.

Name	Normal form absorption [a]		Normal form emission [b]	
	Absorption (nm)	f	Emission (nm)	f
PyrQ	324.62	0.1043	372.78	0.1413
PyrQ-al	318.93	0.1634	360.33	0.1533
PyrQ-CN	314.63	0.1444	357.94	0.1549

[a] The structure was optimized in the ground state.

[b] The normal form structure was optimized in S_1 state.

[c] The tautomer structure was optimized in S_1 state.

5. Theoretical computation (2) – MD

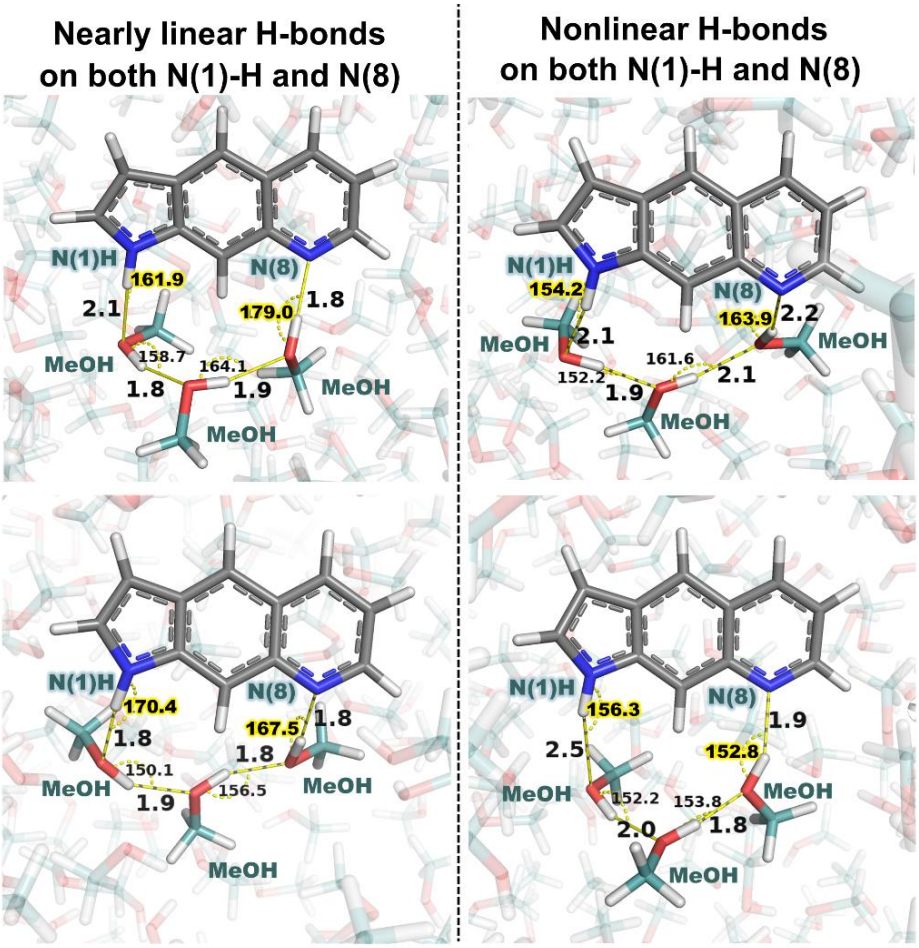

Figure S34. The MD snapshot of **PyrQ**:$(MeOH)_3$ complex are shown the geometry requires, which are more nearly linear hydrogen bonds or nonlinear hydrogen bonds on both N(1)-H and N(8) sites.

Table S9. Simulation obtained the existence time of bulk state and relay state (τ_1 and τ_{-1}). This table only considers n= 3~5 for **PyrQ**s:$(MeOH)_n$. The durations of the bulk state and relay state were measured 10 times within a timeframe of 1 ns using MD trajectory data.

Compound	Relay state time (fs)	Bulk state time (fs)	K_{eq}
PyrQ	23139	976861	0.023687
	31543	968457	0.03257
	17469	982531	0.01778
	7141	992859	0.007192
	30266	969734	0.031211
	38110	961890	0.03962
	23826	976174	0.024408
	43048	956952	0.044984
	41389	958611	0.043176
	10902	989098	0.011022
PyrQ-D	8961	991039	0.009042
	24827	975173	0.025459
	54386	945614	0.057514
	63360	936640	0.067646
	1135	998865	0.001136
	31849	968151	0.032897
	48015	951985	0.050437
	23783	976217	0.024362
	16495	983505	0.016772
	13085	986915	0.013258
PyrQ-al	25451	974549	0.026116
	15407	984593	0.015648
	867	999133	0.000868
	6247	993753	0.006286
	48541	951459	0.051017
	23195	976805	0.023746
	17912	982088	0.018239
	25179	974821	0.025829
	43970	956030	0.045992
	8502	991498	0.008575
PyrQ-CN	37219	962781	0.038658
	2302	997698	0.002307
	27586	972414	0.028369
	12125	987875	0.012274
	28948	971052	0.029811
	10646	989354	0.010761
	5819	994181	0.005853
	18271	981729	0.018611
	11102	988898	0.011227
	15179	984821	0.015413

Table S10. The k_{PT} was calculated by experimental k_{SCPT} and computational K_{eq}.

Compound	Solvent	τ_{decay} (ps)[a]	$k_{SCPT}(s^{-1})$ [b]	K_{eq} [c]	$k_{PT}(s^{-1})$ [d]
PyrQ	CH_3OH	44	2.27×10^{10}	2.8%	8.11×10^{11}
PyrQ-D	CH_3OD	74	1.35×10^{10}	2.9%	4.66×10^{11}
PyrQ-al	CH_3OH	100	1.00×10^{10}	2.2%	4.55×10^{11}
PyrQ-CN	CH_3OH	155	0.65×10^{10}	1.7%	3.82×10^{11}

[a] The fluorescence decay lifetime of normal form measured by time-resolved fluorescence spectroscope.

[b] k_{SCPT} is $1/\tau_{decay}$.

[c] Equilibrium constant (average) of bulk state and relay state in the methanol, which calculated by MD (see Table S9).

[d] Rate constant of proton transfer, which was calculated by eq. 1 in the TEXT.

6. Reference

S1. S. M. Westaway, Y. K. Chung, J. B. Davis, V. Holland, J. C. Jerman, S. J. Medhurst, H. K. Rami, G. Stemp, A. J. Stevens, M. Thompson, K. Y. Winbornb, J. Wright, *Bioorg. Med. Chem. Lett.*, 2006, **16**, 4533–4536.

S2. v. Braun, *Chem. Ber.*, 1913, **46**, 3182.