Electronic Supporting Information

Indole and indazole derivatives containing salicylaldimine as fluorescence materials for multi-stimuli responsive though assembling AIEgen in multistate

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Experimental section

Materials and methods

All used chemical reagents (analytical purity) were bought from reagent companies without further purification. The reactions were monitored by thin-layer chromatography (TLC) by silica gel GF_{254}. Column chromatography was using the silica gel as stationary phase (200–300 mesh), ethyl acetate and petroleum ether were used as mobile phases. ^{1}H and ^{13}C NMR spectra were recorded on a 500 MHz (Bruker AVANCE III 500) and used DMSO–d_6 as solvents. UV/Vis absorption spectra were recorded by Thermo Scientific Evolution 350. Edinburgh Instruments FLS 1000 spectrometer was used to measure the fluorescent properties of title compounds and other complexes. TGA curves were obtained by a simultaneous thermal analyzer (Netzsch STA 449F5) and the dynamic light scattering (DLS) research was tested on a Malvern ZS90 instrument.

Fluorescence properties of the title compounds

The compounds **3NC**–**7NC** were dissolved in dimethylsulfoxide (DMSO) and acetonitrile (CH_3CN) respectively to prepare as stock solutions (1000 μM). These solutions were diluted by twentieth to obtain standard solution (50 μM), which were used to study the characteristics of the fluorescence emission and UV/Vis absorption spectra of the compounds in solvents. The Commission Internationale del'Eclairage (CIE) chromaticity coordinates were directly generated by the software Fluoracle Setup V2.12.1 with integrating sphere (slit widths: 1 nm/1 nm), besides the quantum yields (Φ_f) were directly calculated by the same software with integrating sphere.

Fluorescence and UV/Vis spectra analytical procedure of Cu^{2+} ion recognition.

UV/Vis and fluorescence measurements were performed in a H_2O/CH_3CN (v/v, 95/5) solution containing the **4NC-3** (50 μM). The standard stock solutions (1 mM) were prepared by dissolving the appropriate amount metal salts of LiCl, NaCl, $AgNO_3$, $CoCl_2$, $CuCl_2$, $NiCl_2$, $FeCl_2$, $BaCl_2$, $SnCl_2$, $ZnCl_2$, $CrCl_3$, $Cd(NO_3)_3$, $Fe(NO_3)_3$, $Al_2(SO_4^{2-})_3$ in deionized water, and then these solutions were diluted by twentieth to obtain standard solution (50 μM) to use for titration.

Preparation of the fluorescence PDMS (4NC-3-PDMS) films.

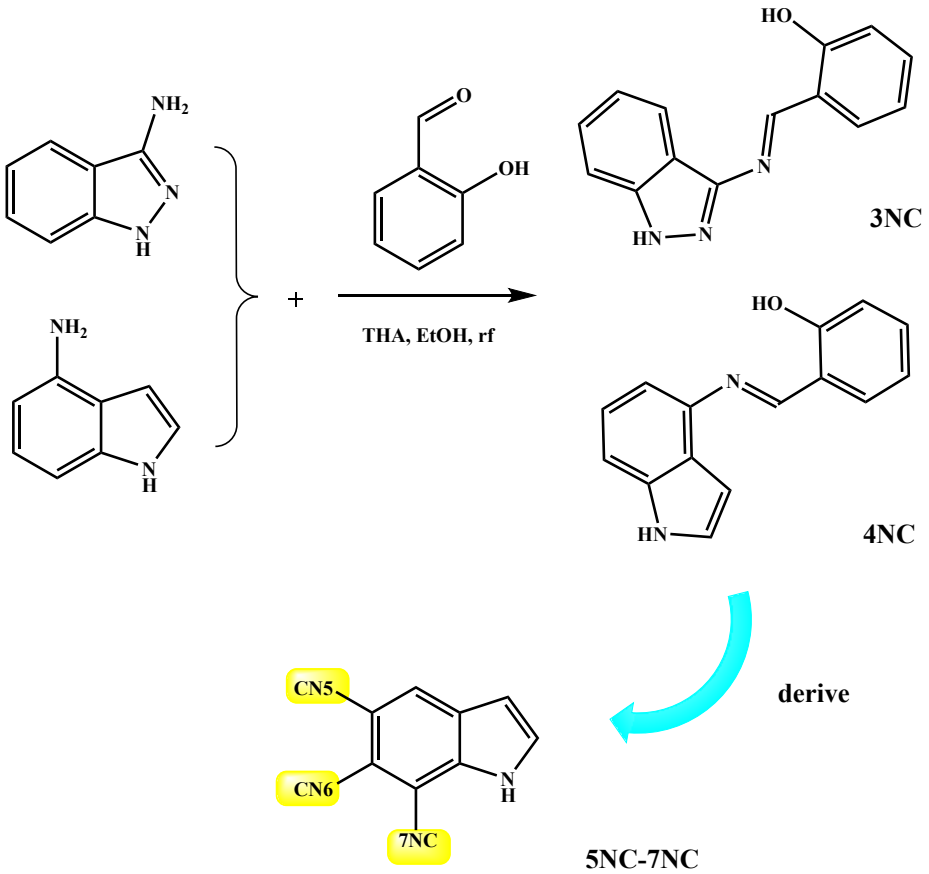
Preparation of the fluorescence molecule incorporated PDMS films (**4NC-3**-PDMS) was carried out using the commercially available Sylgard 184 silicone elastomer kit from Dow Inc. 10 mg **4NC-3** was dissolved in 1 mL acetone by ultrasound, which was mixed with Sylgard 184 silicone elastomer (10 g) evenly. Next, 1 mL curing agent (1 g) was poured into the PDMS and evenly spread on cleaned glass panels after uniform mixing, the resulting coated glass slides are then heated on a hot plate at 100 ℃ for 4 h, normal concentration resulting film was **4NC-3**-PDMS film with uniform composition. Aggregated state **4NC-3**-PDMS film was similar to the method, only increased the amount of added compounds to 50 mg with the other quantities remain unchanged.

Theoretical calculations

The calculations were based on polarization function by Gaussian 09 suite of programs using b3lyp functional with 6–311G (d,p) with 20 states, Software Multiwfn and VMD were used for further analysis of calculation results and the visualization of highest occupied molecular orbital

(HOMO) and lowest unoccupied molecular orbital (LUMO).

Synthesis



Scheme S1. Synthesis route and structure of title compounds **3NC**-**7NC**.

Synthesis of (*E*)-2-(((1H-indazol-3-yl)imino)methyl)phenol (3NC)

A solution of 1*H*-indol-3-amine (0.40 g, 3 mmol), salicylaldehyde (0.73 g, 6 mmol), and trifluoroacetic acid (TFA) with catalyst amount in anhydrous ethanol (50 mL) was stirred under reflux for 6 h. crude product was purified by silica column chromatography using ethyl acetate/petroleum ether (1/3, V/V) as mobile phase to give blackish green powder **3NC** (0.54 g, 76%); ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.17 (s, 1H), 13.14 – 12.73 (s, 1H), 9.45 (s, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 8.2 Hz, 1H), 7.44 (t, J = 7.4 Hz, 2H), 7.24 (t, J = 7.3 Hz, 1H), 7.05 – 6.96 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.70, 160.69, 148.51, 142.01, 133.86, 132.94, 127.40, 121.87, 120.00, 119.84, 117.11, 116.78, 111.24; HRMS (ESI) m/z calcd for $C_{14}H_{11}N_3O$ $[M + H]^+$ 238.0975, found 238.0977.

Synthesis of (*E*)-2-(((1H-indol-4-yl)imino)methyl)phenol (4NC)

A solution of 1*H*-indole-4-amine (0.39 g, 3 mmol), salicylaldehyde (0.73 g, 6 mmol), and trifluoroacetic acid (TFA) with catalyst amount in anhydrous ethanol (50 mL) was stirred under reflux for 6 h. crude product was purified by silica column chromatography using ethyl acetate/petroleum ether (1/3, V/V) as mobile phase to give bright yellow powder **4NC** (0.56 g, 79%); ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.80 (s, 1H), 11.35 (s, 1H), 9.16 – 9.06 (m, 1H), 7.70 (d,

J = 7.7 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.38 (d, J = 8.0 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 7.11 – 7.05 (m, 1H), 7.00 (dd, J = 7.6, 4.2 Hz, 2H), 6.57 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.90, 161.09, 133.43, 132.96, 126.58, 123.30, 122.07, 119.99, 119.49, 117.09, 111.08, 109.04, 98.97; HRMS (ESI) m/z calcd for $C_{15}H_{12}N_2O$ $[M + H]^+$ 237.1023, found 237.1021.

Synthesis of (*E*)-2-(((1H-indol-5-yl)imino)methyl)phenol (5NC)

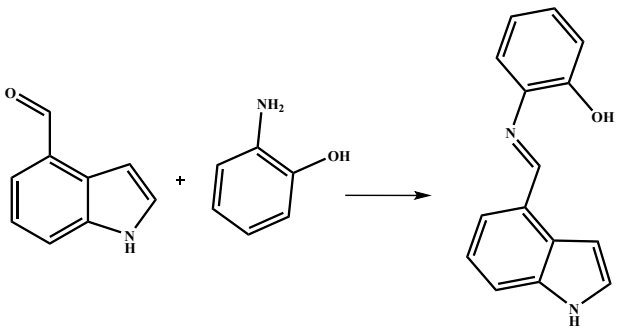
The synthetic route and purification method of **5NC** was the same as that for **4NC**, the ingredient 1*H*-indol-4-amine was replaced by 1*H*-indol-5-amin, and the consumptions was also the same. Orange powder; yield: 0.57 g, 81%; ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.73 (s, 1H), 11.24 (s, 1H), 9.02 (s, 1H), 7.63 (d, J = 11.5 Hz, 2H), 7.48 (d, J = 8.6 Hz, 1H), 7.41 (t, J = 2.6 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.27 (dd, J = 8.6, 1.8 Hz, 1H), 6.97 (t, J = 8.0 Hz, 2H), 6.50 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 160.77, 160.74, 140.22, 135.73, 132.86, 132.67, 128.65, 127.23, 120.05, 119.39, 116.94, 115.76, 113.08, 112.57, 102.27; HRMS (ESI) m/z calcd for $C_{15}H_{12}N_2O$ $[M + H]^+$ 237.1023, found 237.1023.

Synthesis of (*E*)-2-(((1H-indol-6-yl)imino)methyl)phenol (6NC)

The synthetic route and purification method of **6NC** was the same as that for **4NC**, the ingredient 1*H*-indol-4-amine was replaced by 1*H*-indol-6-amin, and the consumptions was also the same. Bright yellow powder; yield: 0.6 g, 85%; ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.64 (s, 1H), 11.25 (s, 1H), 10.24 – 10.18 (m, 1H), 9.04 (s, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.47 (s, 1H), 7.42 – 7.41 (m, 1H), 7.41 – 7.37 (m, 1H), 7.19 (dd, J = 8.4, 1.5 Hz, 1H), 6.98 (t, J = 7.9 Hz, 2H), 6.48 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 161.29, 160.76, 142.11, 136.74, 133.04, 132.78, 127.66, 127.27, 121.14, 120.03, 119.44, 116.96, 113.57, 104.93, 101.83; HRMS (ESI) m/z calcd for $C_{15}H_{12}N_2O$ $[M + H]^+$ 237.1023, found 237.1027.

Synthesis of (*E*)-2-(((1H-indol-7-yl)imino)methyl)phenol (7NC)

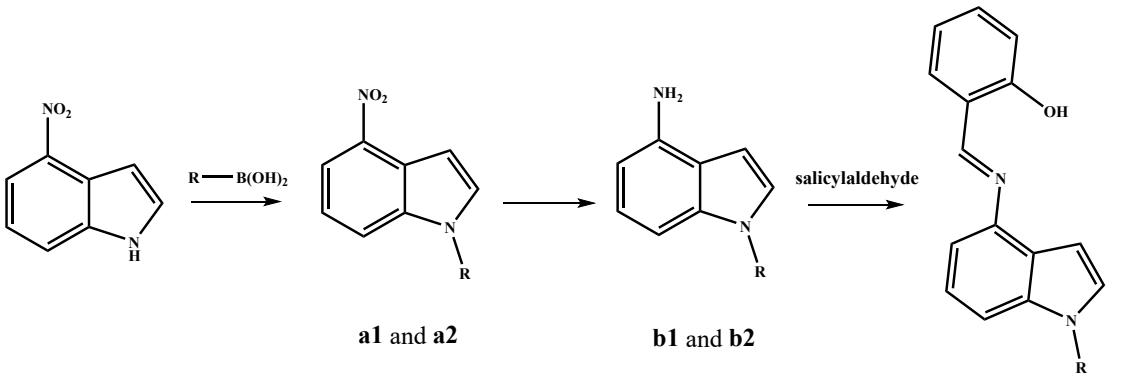
The synthetic route and purification method of **7NC** was the same as that for **4NC**, the ingredient 1*H*-indol-4-amine was replaced by 1*H*-indol-7-amin, and the consumptions was also the same. Orange powder; yield: 0.52 g, 73%; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.74 (s, 1H), 11.41 (s, 1H), 9.06 (s, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 6.9 Hz, 1H), 7.45 (t, J = 7.7 Hz, 1H), 7.36 (s, 1H), 7.11 – 7.05 (m, 2H), 7.01 (t, J = 7.1 Hz, 2H), 6.52 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.75, 160.93, 133.89, 133.28, 132.45, 130.87, 129.37, 124.85, 120.44, 119.91, 119.52, 119.43, 117.19, 109.87, 103.13; HRMS (ESI) m/z calcd for $C_{15}H_{12}N_2O$ $[M + H]^+$ 237.1023, found 237.1026.



Scheme S2. The synthetic route of compound **4CN**.

Synthesis of (*E*)-2-(((1H-indol-4-yl)methylene)amino)phenol (4CN).

A solution of 1*H*-indole-4-carbaldehyde (0.44 g, 3 mmol), 2-aminophenol (0.65 g, 6 mmol), and trifluoroacetic acid (TFA) with catalyst amount in anhydrous ethanol (50 mL) was stirred under reflux for 6 h. crude product was purified by silica column chromatography using ethyl acetate/petroleum ether (1/3, V/V) as mobile phase to give orange powder **4CN** (0.47 g, 67%); ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.39 (s, 1H), 8.93 (s, 1H), 8.91 (s, 1H), 7.63 (d, J = 7.3 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.52 (t, J = 2.5 Hz, 1H), 7.29 (s, 1H), 7.23 (t, J = 7.3 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.07 (t, J = 7.4 Hz, 1H), 6.93 (d, J = 7.9 Hz, 1H), 6.86 (t, J = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 160.76, 151.13, 139.91, 136.99, 127.99, 127.58, 127.07, 126.52, 123.21, 121.10, 120.04, 119.92, 116.34, 115.20, 102.26, 100.00; ; HRMS (ESI) m/z calcd for $C_{15}H_{12}N_2O$ $[M + H]^+$ 237.1023, found 237.1021.



a1 and **a2** **b1** and **b2** **4NC-1** and **4NC-3**

a1: R = phenyl; **a2**: R = TPA; **b1**: R = phenyl; **b2**: R = TPA

Scheme S3. The synthetic route of compound **4NC-1** and **4NC-3**.

Synthesis of (*E*)-2-(((1-phenyl-1H-indol-4-yl)imino)methyl)phenol (4NC-1).

A mixture of 4-nitro-1*H*-indole (0.81 g, 5 mmol), cupric acetate hydrate (1.38 g, 7 mmol), and phenylboronic acid (1.22 g, 10 mmol) were add to 100 mL dichloromethane, and then 2 mL triethylamine was added dropwise to the solution, the reaction mixture was stirred for 24 h, filtration, concentrate the reaction solution, recrystallization of petroleum ether to obtain crude intermediate nitro substituted indole **a1**.

Subsequently, stirred intermediate **a1** in 30 mL ethanol, ammonium chloride (0.27 g, 5 mmol) in 10 mL distilled water was dropped in the system, the reaction mixture was heated to reflux and powered zinc (0.97 g, 15 mmol) was added at reflux temperature. After 6 h the reaction monitored by TLC detection, the residue was extracted with ethyl acetate, and the combined extracts were washed with saturated brine, light yellow solid substituted indoleamine **b1** was obtained by removal of solvent. The comprehensive yield: 0.32 g, 31%.

The specific synthesis method of the compound **4NC-1** was the same as that of **4NC**, except that 1*H*-indol-4-amine was replaced with 1-phenyl-1*H*-indol-4-amine.

4NC-1: yellow powder; yield: 0.42 g, 91%; ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.58 (s, 1H), 9.16 (s, 1H), 7.74 (dd, J = 11.2, 4.9 Hz, 2H), 7.65 – 7.59 (m, 4H), 7.51 (d, J = 8.2 Hz, 1H), 7.45

(dd, J = 9.0, 4.9 Hz, 2H), 7.30 (t, J = 7.9 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.04 – 6.98 (m, 2H), 6.81 (d, J = 3.1 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.72, 161.04, 141.19, 139.39, 136.72, 133.72, 133.07, 130.36, 129.77, 127.25, 124.70, 124.54, 123.60, 119.98, 119.62, 117.13, 110.16, 109.80, 101.24; HRMS (ESI) m/z calcd for $C_{21}H_{16}N_2O$ [M + H]$^+$ 313.1336, found 313.1339.

Synthesis of (*E*)-2-(((1-(4-(diphenylamino)phenyl)-1H-indol-4-yl)imino)methyl)phenol (4NC-3).

The synthetic route was similar to that of 4NC-1, except phenylboronic acid was replaced by triphenylamine boronic acid. Comprehensive yield of the first two steps: 0.56 g, 29%.

4NC-1: yellow powder; yield: 0.58 g, 81%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.59 (s, 1H), 9.16 (s, 1H), 7.72 (dd, J = 8.4, 5.6 Hz, 2H), 7.53 (d, J = 8.6 Hz, 2H), 7.50 (d, J = 8.2 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 7.37 (t, J = 7.8 Hz, 4H), 7.29 (t, J = 7.9 Hz, 1H), 7.21 (d, J = 7.5 Hz, 1H), 7.16 (d, J = 8.6 Hz, 2H), 7.11 (t, J = 8.3 Hz, 6H), 7.04 – 7.00 (m, 2H), 6.79 (d, J = 3.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.67, 161.68, 147.31, 147.20, 137.06, 136.75, 133.79, 129.45, 129.41, 128.57, 125.48, 125.19, 123.85, 123.62, 121.67, 121.03, 120.98, 120.72, 119.91, 117.94, 117.84, 117.67, 103.47; HRMS (ESI) m/z calcd for $C_{33}H_{25}N_3O$ [M + H]$^+$ 480.2071, found 480.2073.

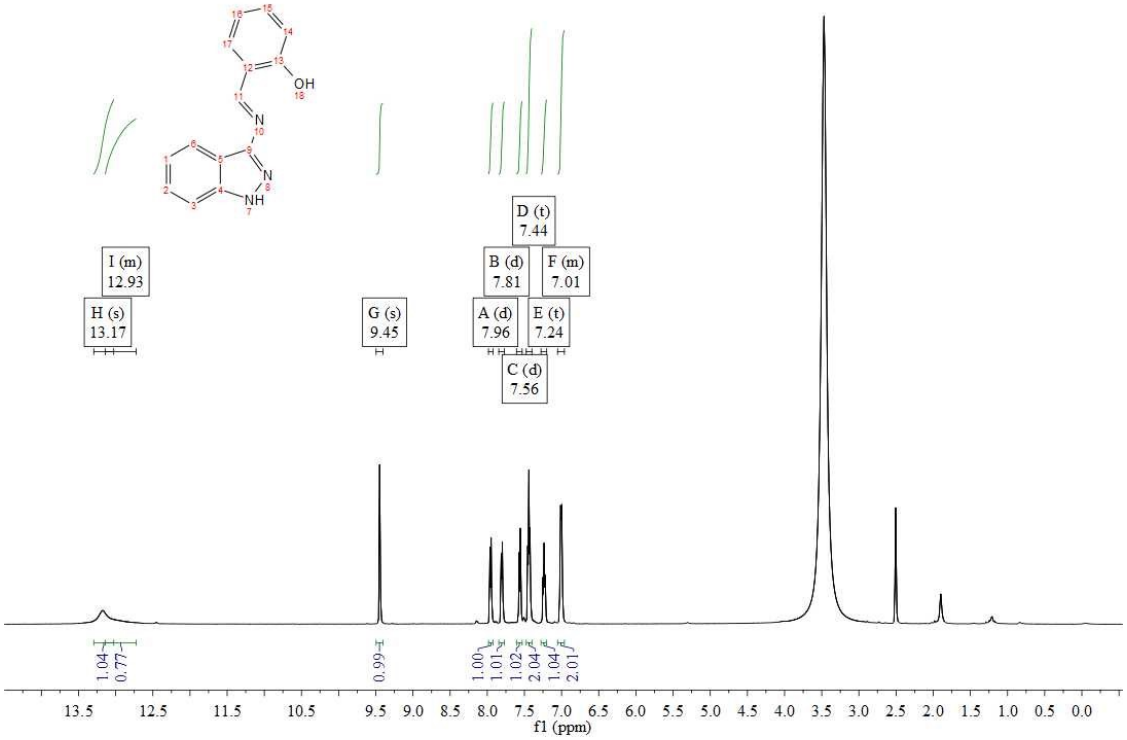


Figure S1. ^{1}H NMR spectrum of compound **3NC**.

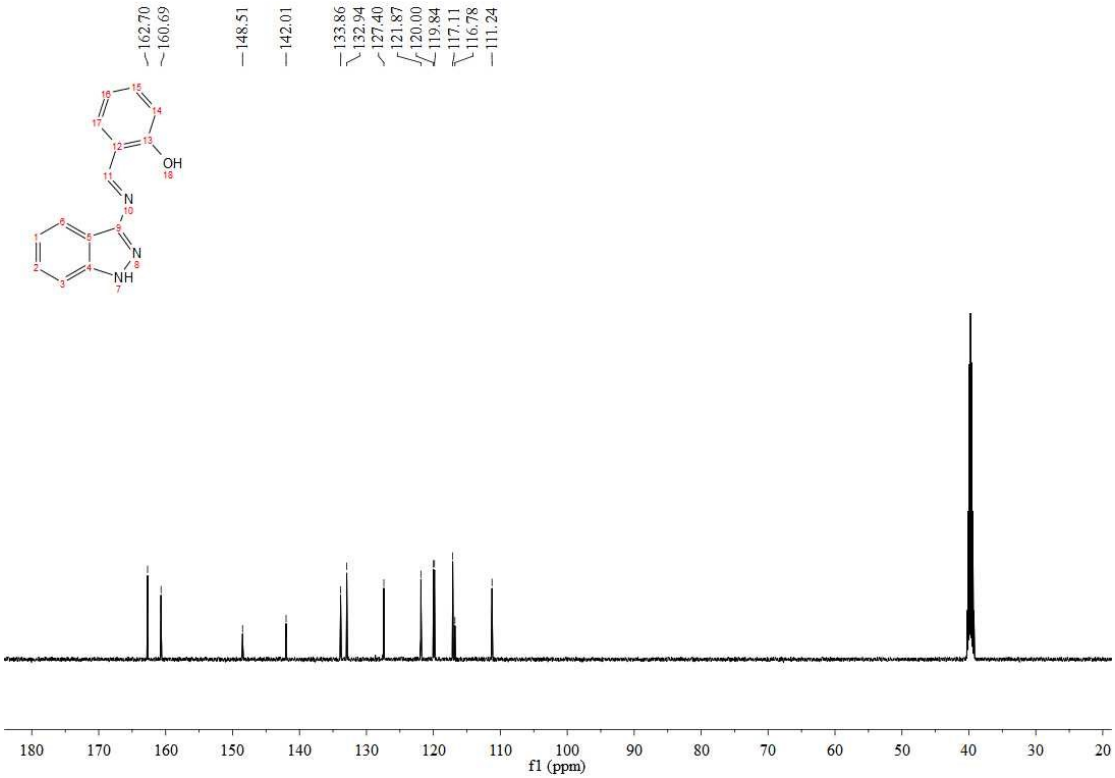


Figure S2. ^{13}C NMR spectrum of compound **3NC**.

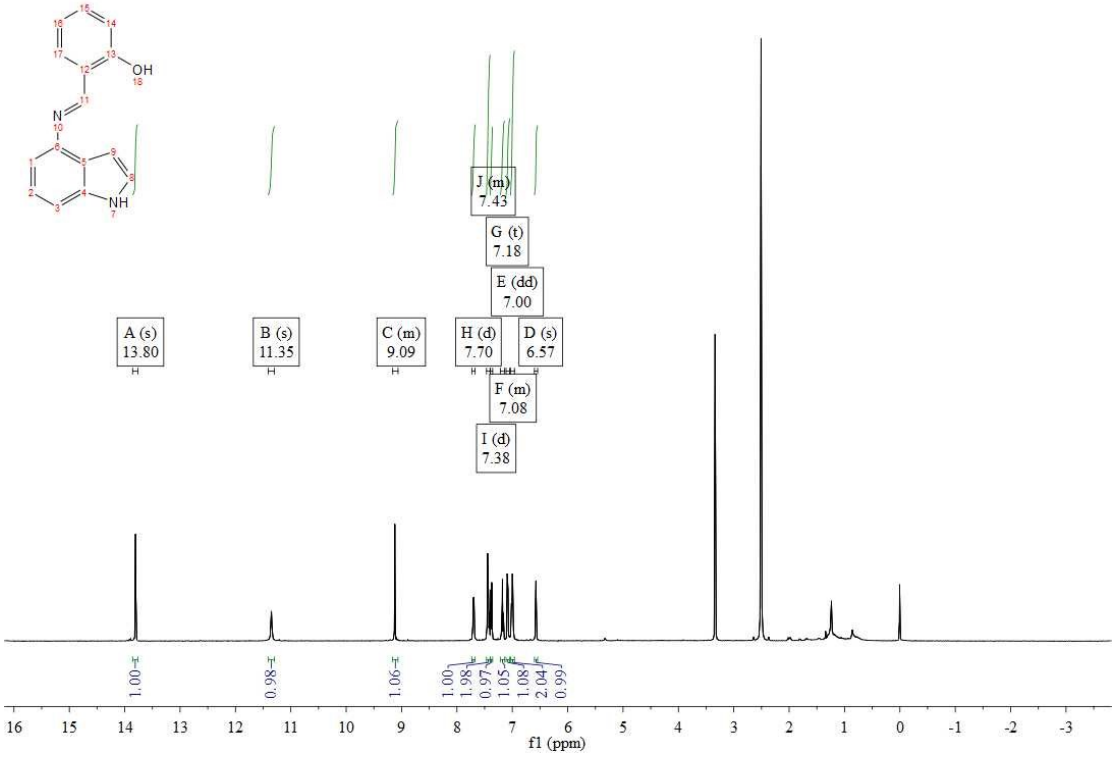


Figure S3. ^{1}H NMR spectrum of compound **4NC**.

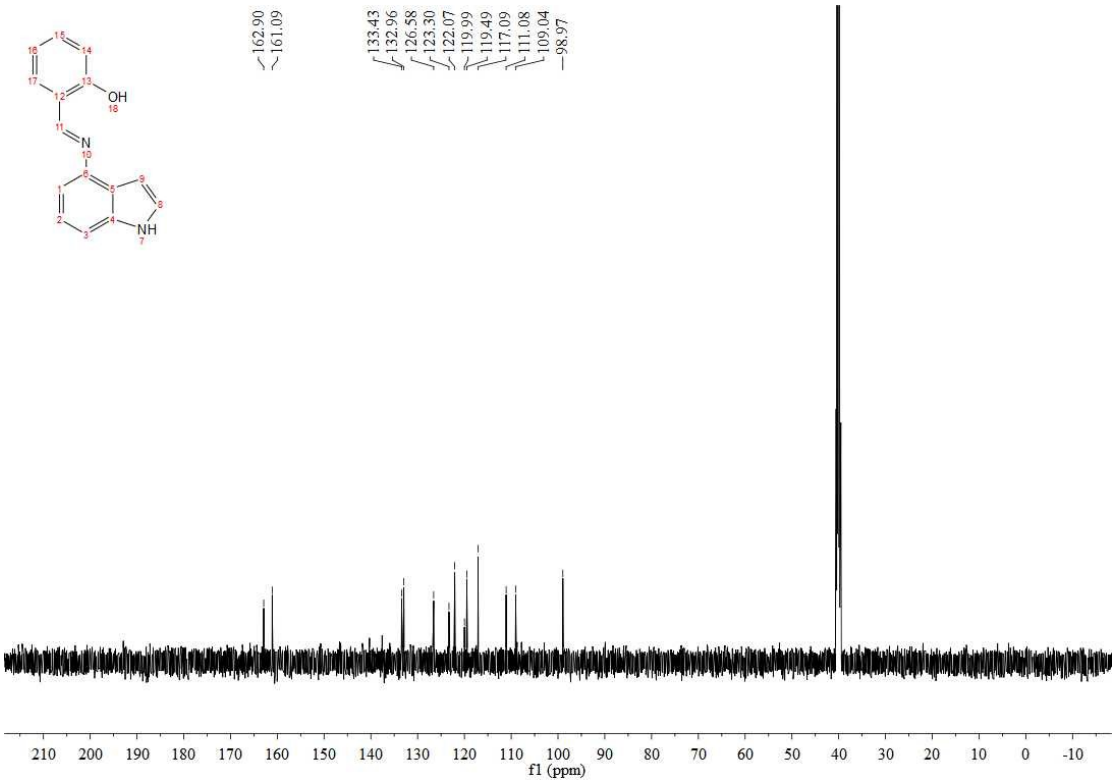


Figure S4. ^{13}C NMR spectrum of compound **4NC**.

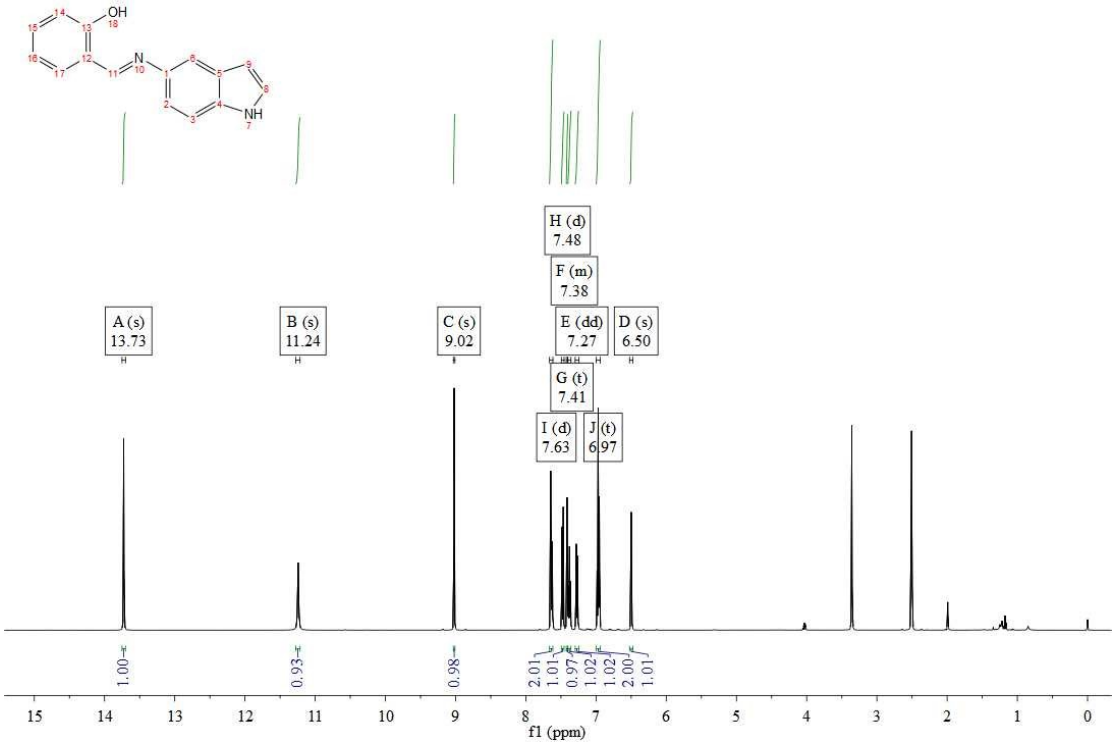


Figure S5. ^{1}H NMR spectrum of compound **5NC**.

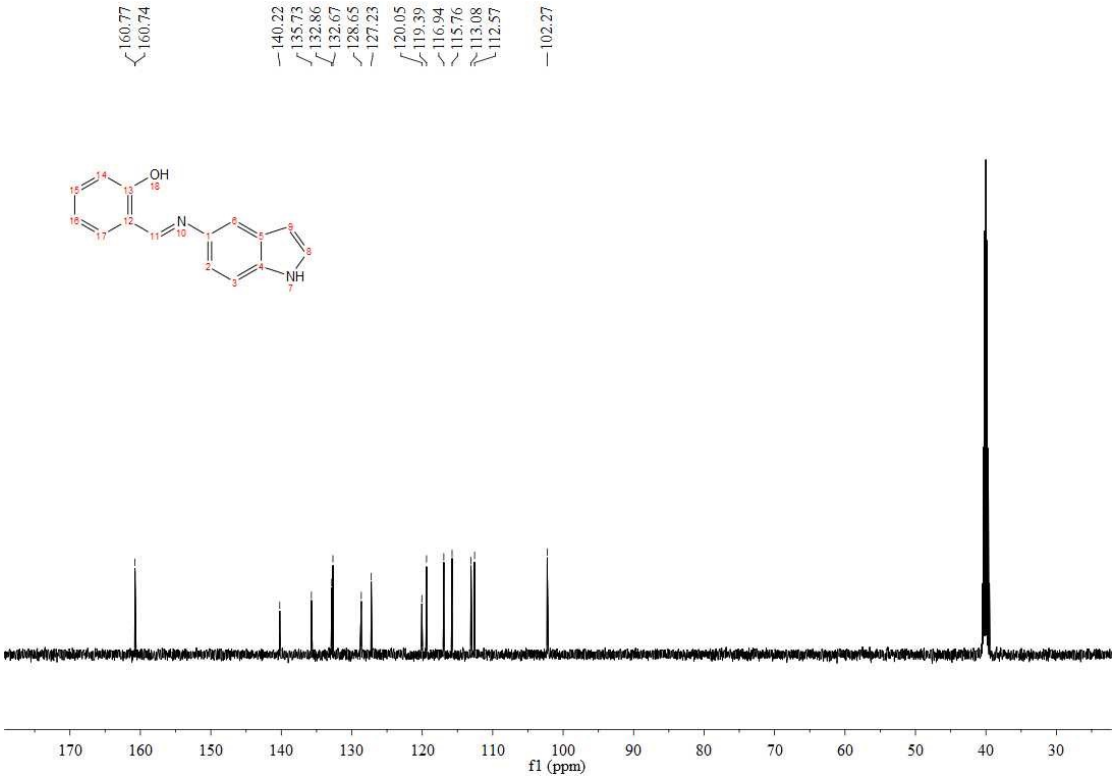


Figure S6. ^{13}C NMR spectrum of compound **5NC**.

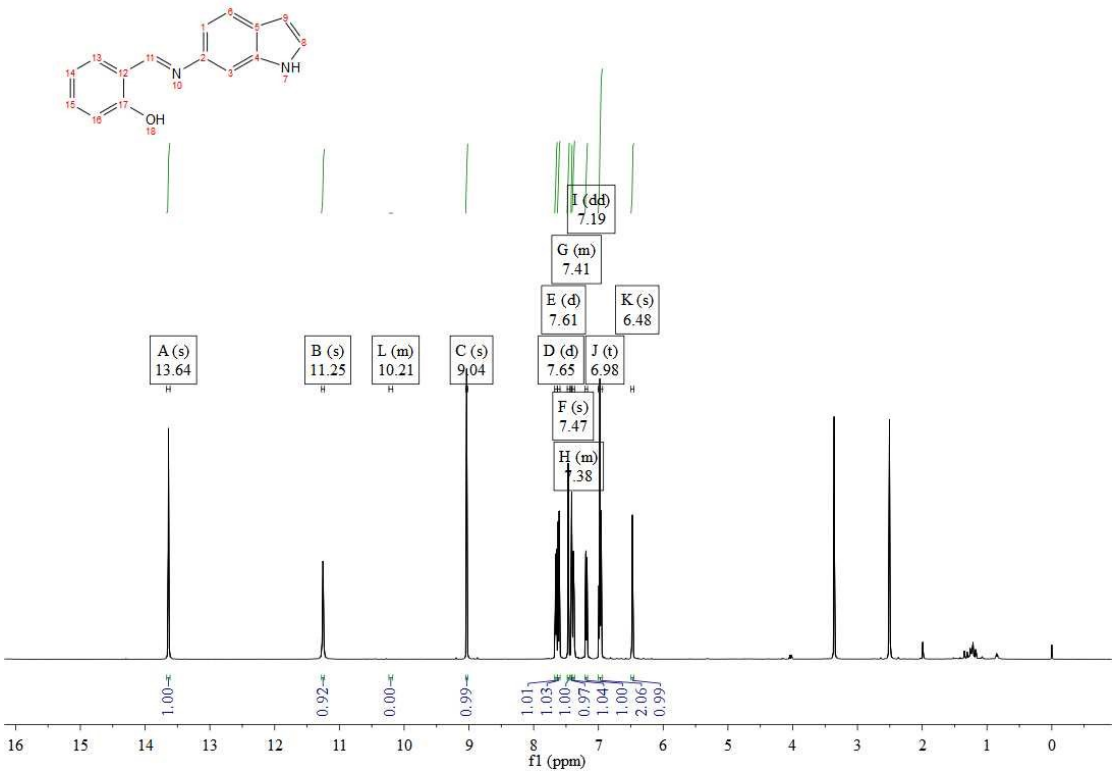


Figure S7. ^{1}H NMR spectrum of compound **6NC**.

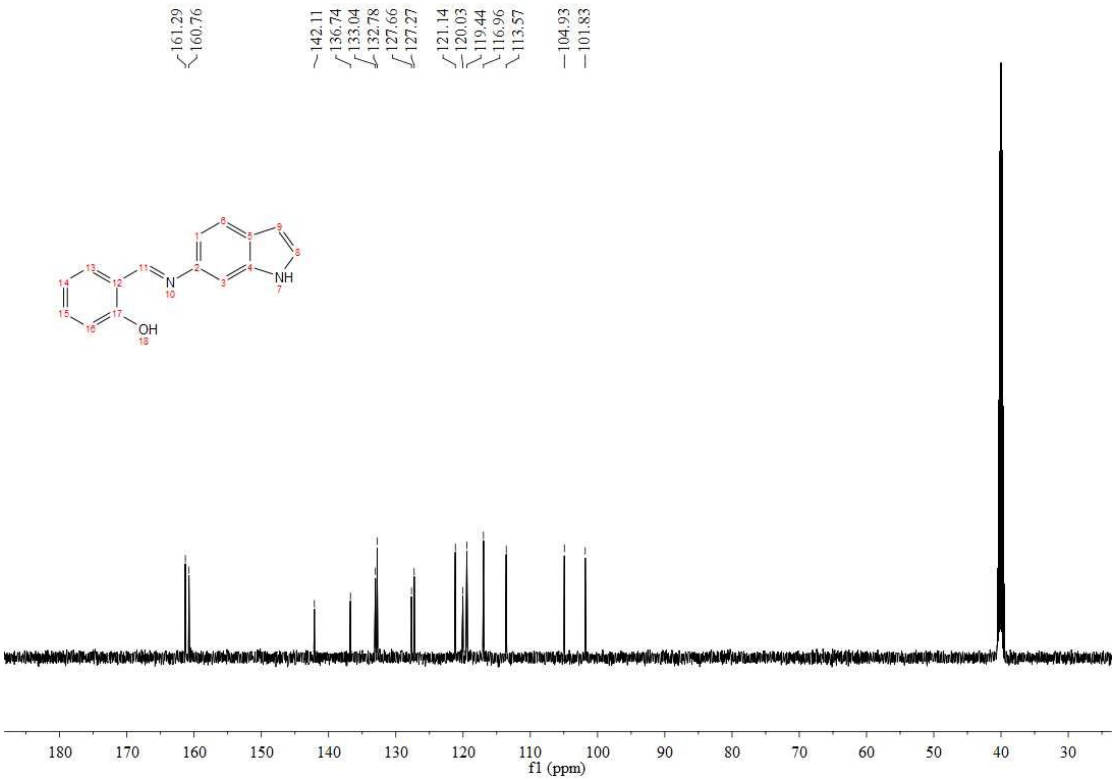


Figure S8. ^{13}C NMR spectrum of compound **6NC**.

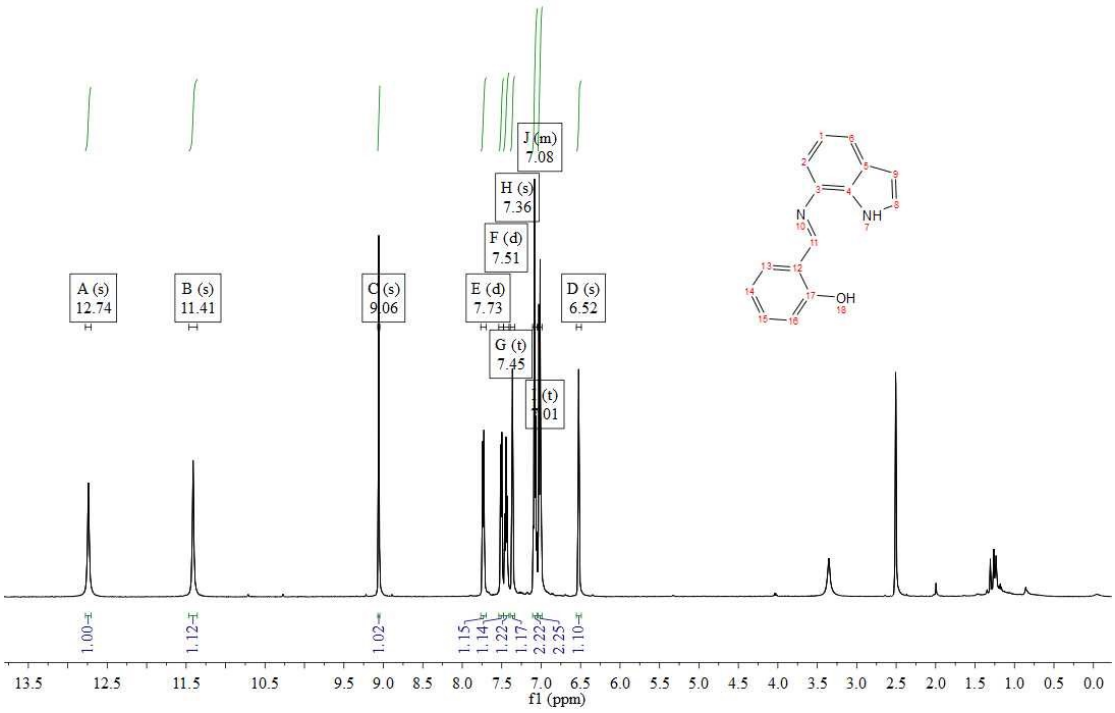


Figure S9. ^{1}H NMR spectrum of compound **7NC**.

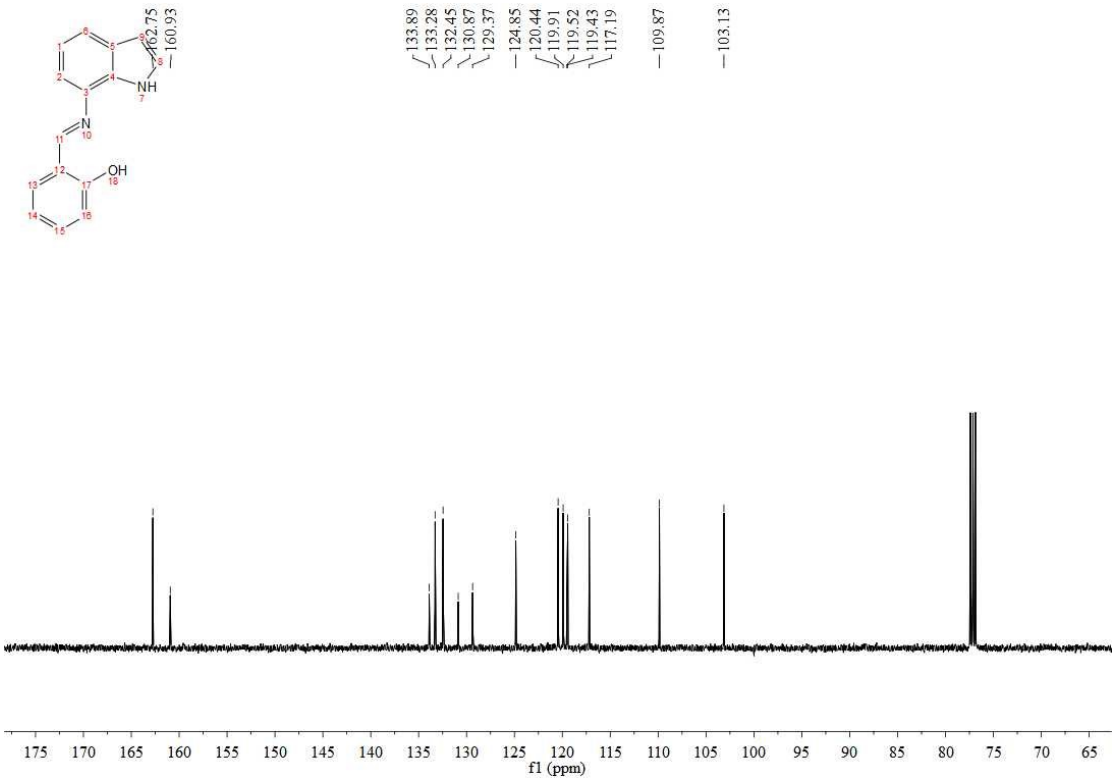


Figure S10. ^{13}C NMR spectrum of compound **7NC**.

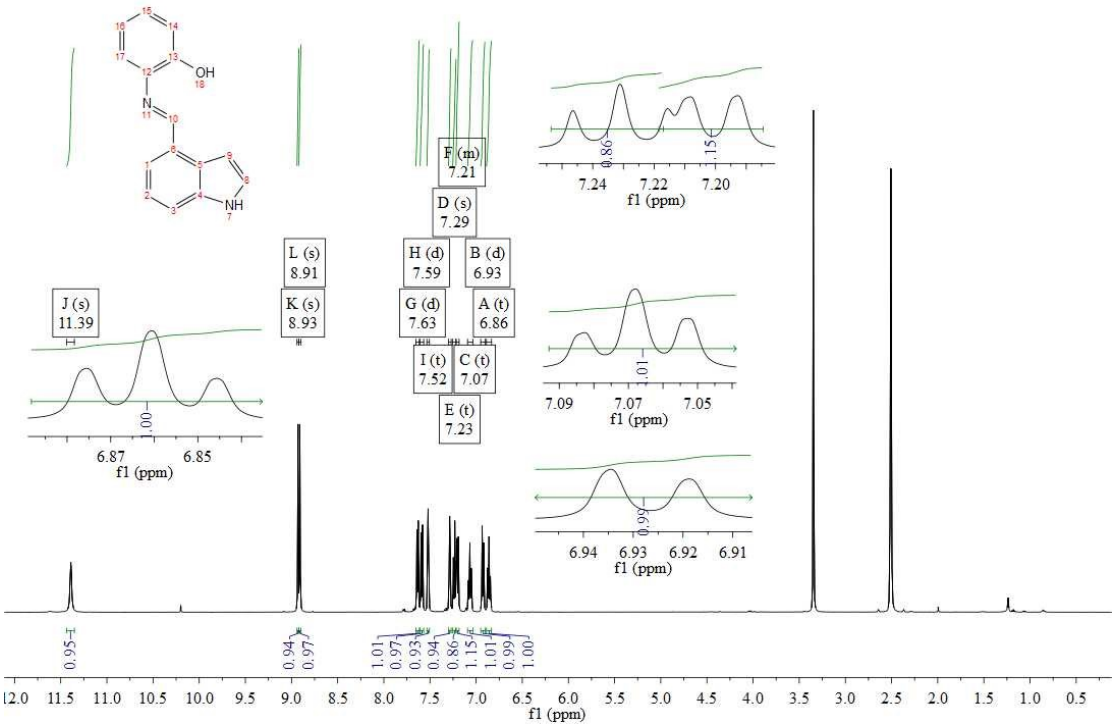


Figure S11. ^{1}H NMR spectrum of compound **4CN**.

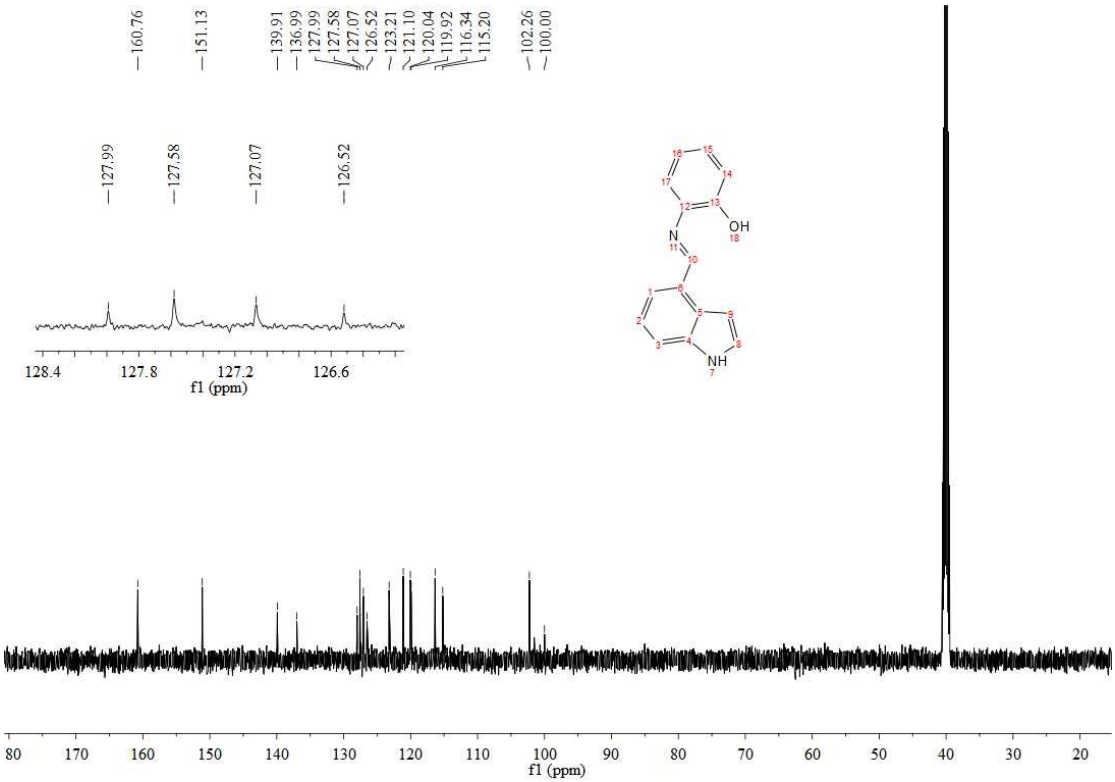


Figure S12. ^{13}C NMR spectrum of compound **4CN**.

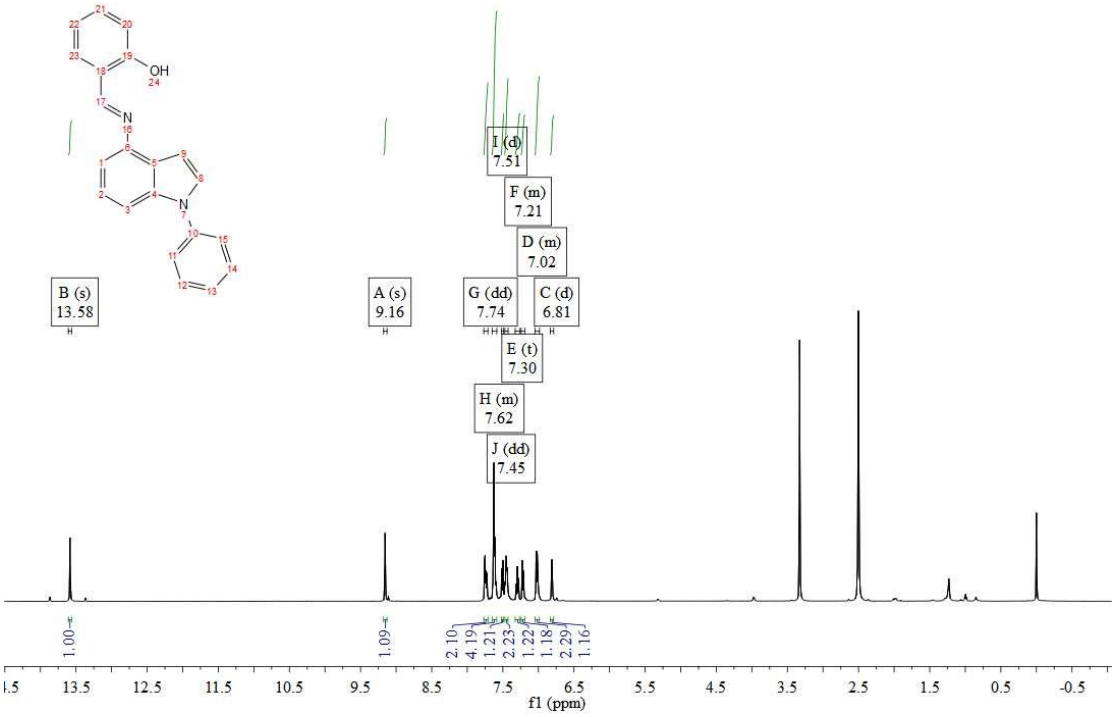


Figure S13. ^{1}H NMR spectrum of compound **4NC-1**.

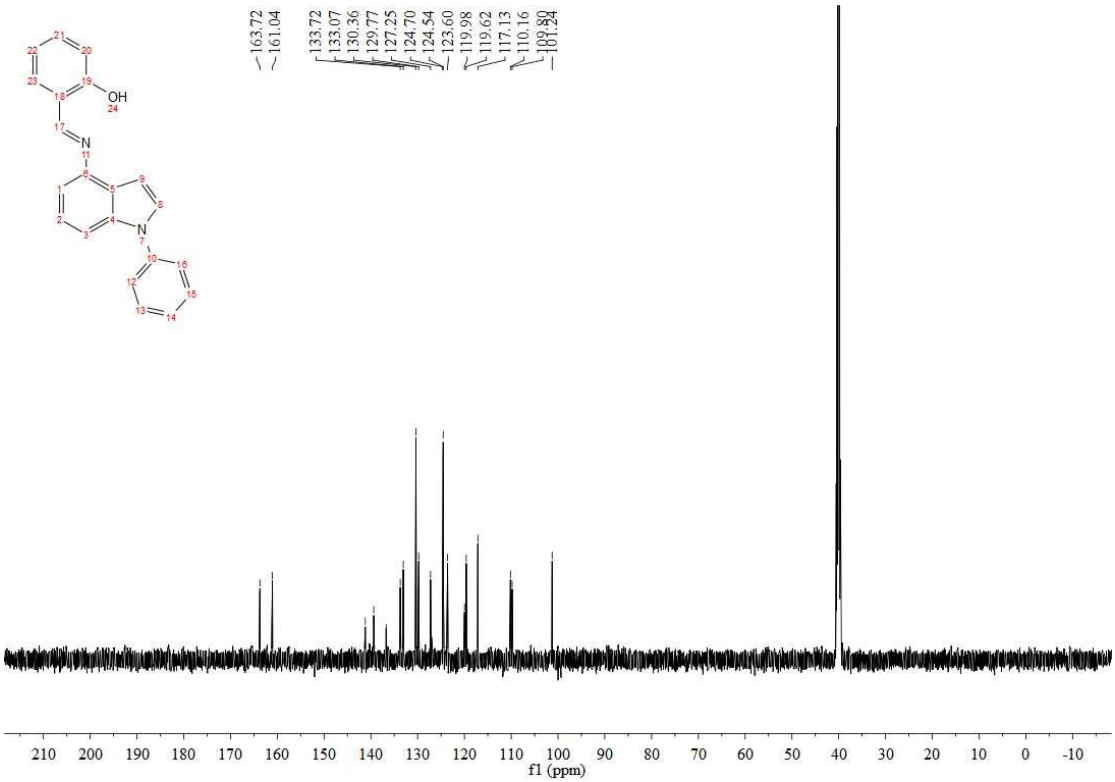


Figure S14. ^{13}C NMR spectrum of compound **4NC-1**.

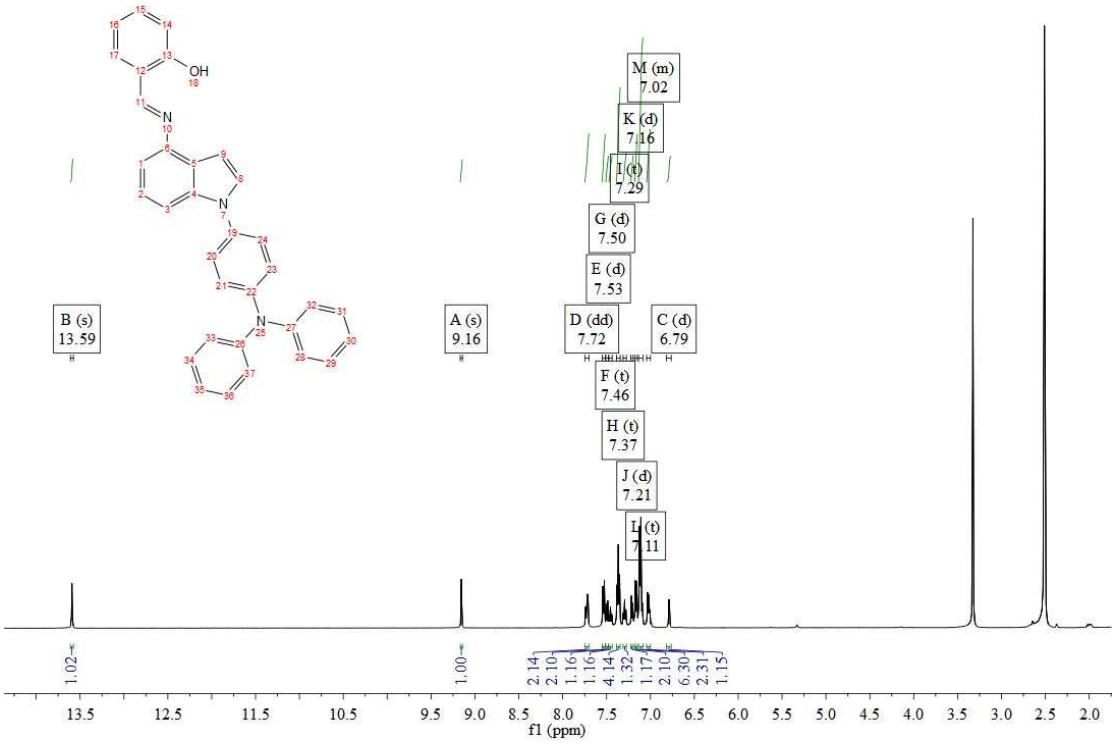


Figure S15. ^{1}H NMR spectrum of compound **4NC-3**.

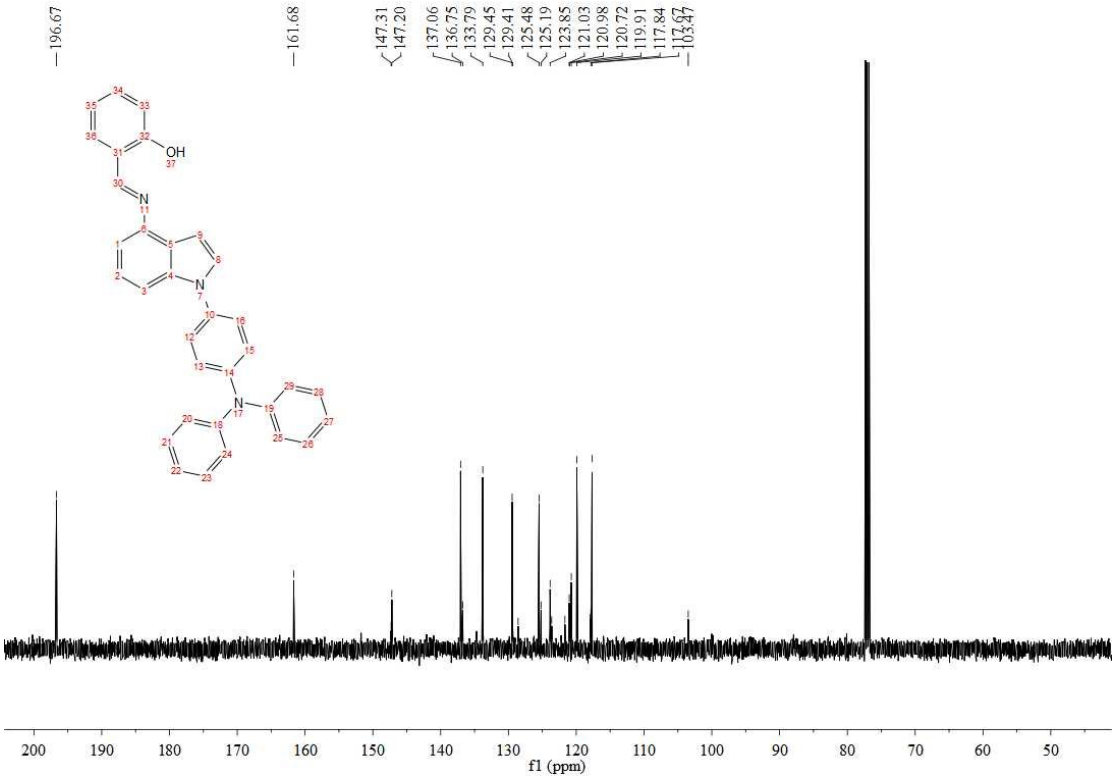


Figure S16. ^{13}C NMR spectrum of compound **4NC-3**.

Table S1. Crystal data and structure refinement for compound **3NC** (CCDC number: 2308721).

Identification code	cu_20230922_YS_NLG_HHR_3_0m
Empirical formula	$C_{14}H_{11}N_3O$
Formula weight	237.26
Temperature/K	193.00
Crystal system	trigonal
Space group	$P3_2$
a/Å	13.6284(3)
b/Å	13.6284(3)
c/Å	5.4093(2)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	870.08(5)
Z	3
ρ_{calc}g/cm^3	1.358
μ/mm^{-1}	0.720
F(000)	372.0
Crystal size/mm^3	0.15 × 0.07 × 0.06

Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.49 to 136.376
Index ranges	$-15 \leq h \leq 16$, $-16 \leq k \leq 16$, $-6 \leq l \leq 5$
Reflections collected	7186
Independent reflections	1906 [R_{int} = 0.0647, R_{sigma} = 0.0471]
Data/restraints/parameters	1906/1/164
Goodness-of-fit on F^2	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0333, wR_2 = 0.0723
Final R indexes [all data]	R_1 = 0.0447, wR_2 = 0.0762
Largest diff. peak/hole / e $Å^{-3}$	0.12/-0.15
Flack parameter	-0.1(3)

Table S2. Crystal data and structure refinement for compound **6NC** (CCDC number: 2308722).

Identification code	mo_20230922_YS_NLG_HHR_6_0m
Empirical formula	$C_{15}H_{12}N_2O$
Formula weight	236.27
Temperature/K	193.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.3901(6)
b/Å	5.6092(3)
c/Å	15.9163(6)
α/°	90
β/°	115.169(2)
γ/°	90
Volume/$Å^3$	1162.74(9)
Z	4
ρ_{calc}g/cm^3	1.350
μ/mm^{-1}	0.087
F(000)	496.0
Crystal size/mm^3	0.13 × 0.11 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.656 to 55.002
Index ranges	$-18 \leq h \leq 17$, $-7 \leq k \leq 7$, $-20 \leq l \leq 18$
Reflections collected	12070
Independent reflections	2645 [R_{int} = 0.0602, R_{sigma} = 0.0444]
Data/restraints/parameters	2645/0/164
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0451, wR_2 = 0.1090
Final R indexes [all data]	R_1 = 0.0639, wR_2 = 0.1232

Largest diff. peak/hole / e $Å^{-3}$	0.23/-0.16

Table S3. Crystal data and structure refinement for compound **7NC** (CCDC number: 2308723).

Identification code	mo_20230922_YS_NLG_HHR_7_0m
Empirical formula	$C_{15}H_{12}N_2O$
Formula weight	236.27
Temperature/K	193.00
Crystal system	monoclinic
Space group	Cc
a/Å	8.3409(5)
b/Å	21.7821(13)
c/Å	7.6787(5)
α/°	90
β/°	120.072(2)
γ/°	90
Volume/$Å^3$	1207.30(13)
Z	4
$\rho_{calc}g/cm^3$	1.300
μ/mm^{-1}	0.083
F(000)	496.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.484 to 50.706
Index ranges	$-10 \le h \le 10$, $-26 \le k \le 26$, $-9 \le l \le 9$
Reflections collected	8497
Independent reflections	1999 [R_{int} = 0.0489, R_{sigma} = 0.0420]
Data/restraints/parameters	1999/2/164
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0343, wR_2 = 0.0797
Final R indexes [all data]	R_1 = 0.0362, wR_2 = 0.0814
Largest diff. peak/hole / e $Å^{-3}$	0.13/-0.14
Flack parameter	-1.0(7)

Table S4. Quantum yields of synthesized compounds in solid. [a]

Comp.	**4CN**	**3NC**	**4NC**	**5NC**	**6NC**	**7NC**	**4NC-1**	**4NC-3**
QY(Φ_f)	–[b]	0.17	0.19	0.31	0.20	–[b]	0.21	0.37

[a] The quantum yields (Φ_f) were directly calculated by the same software with integrating sphere.

[b] Basically, compounds **4CN** and **7NC** without fluorescence emission properties.

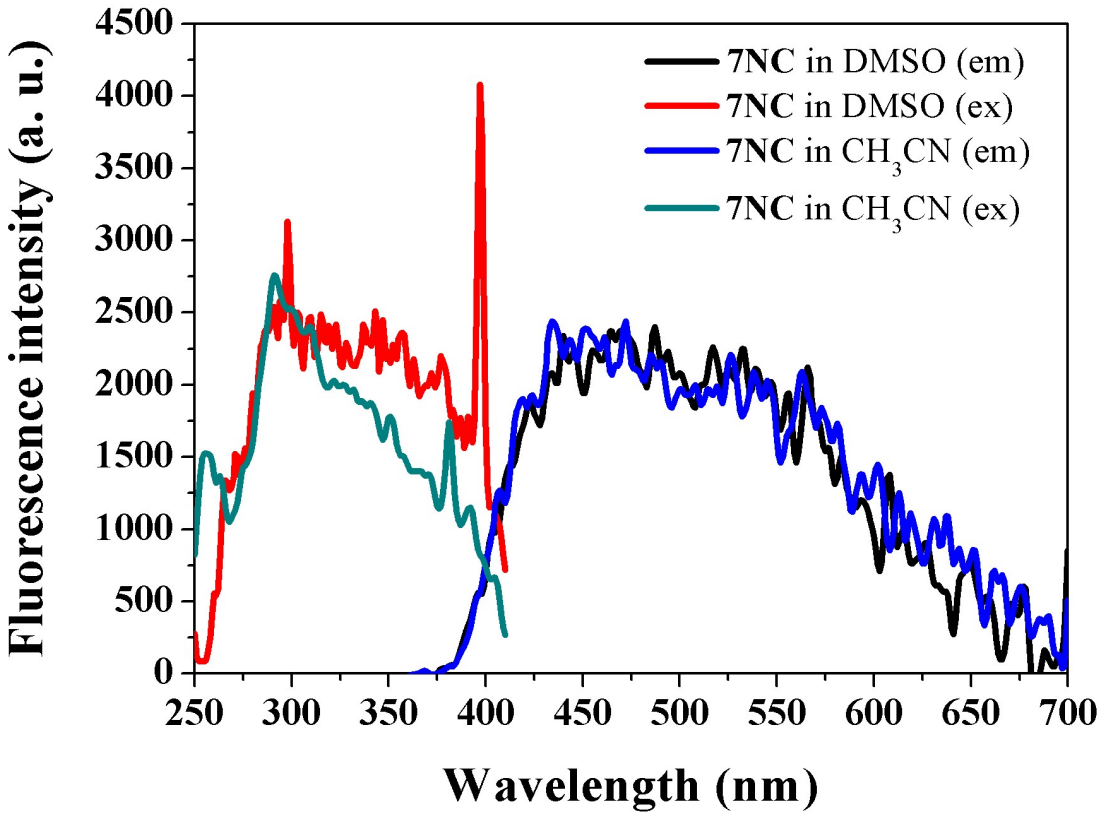


Figure S17. Fluorescence spectra of compound **7NC** in solutions (50 μM).

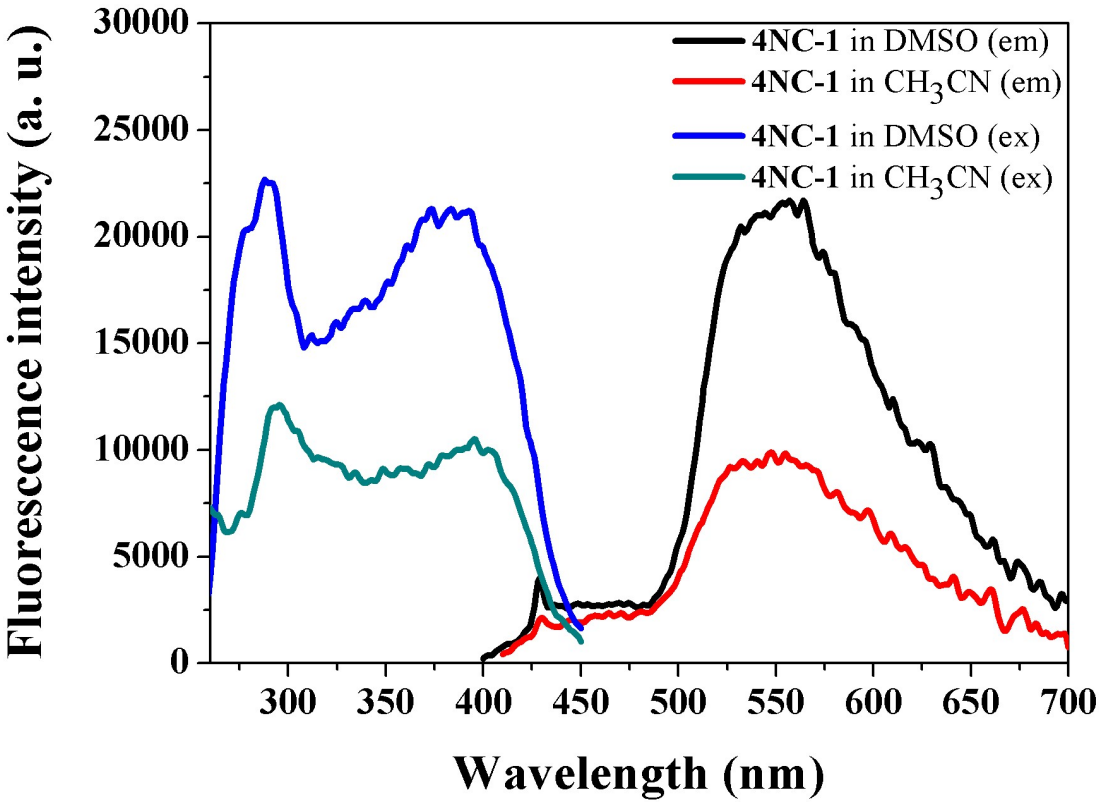


Figure S18. Fluorescence spectra of compound **4NC-1** in solutions (50 μM).

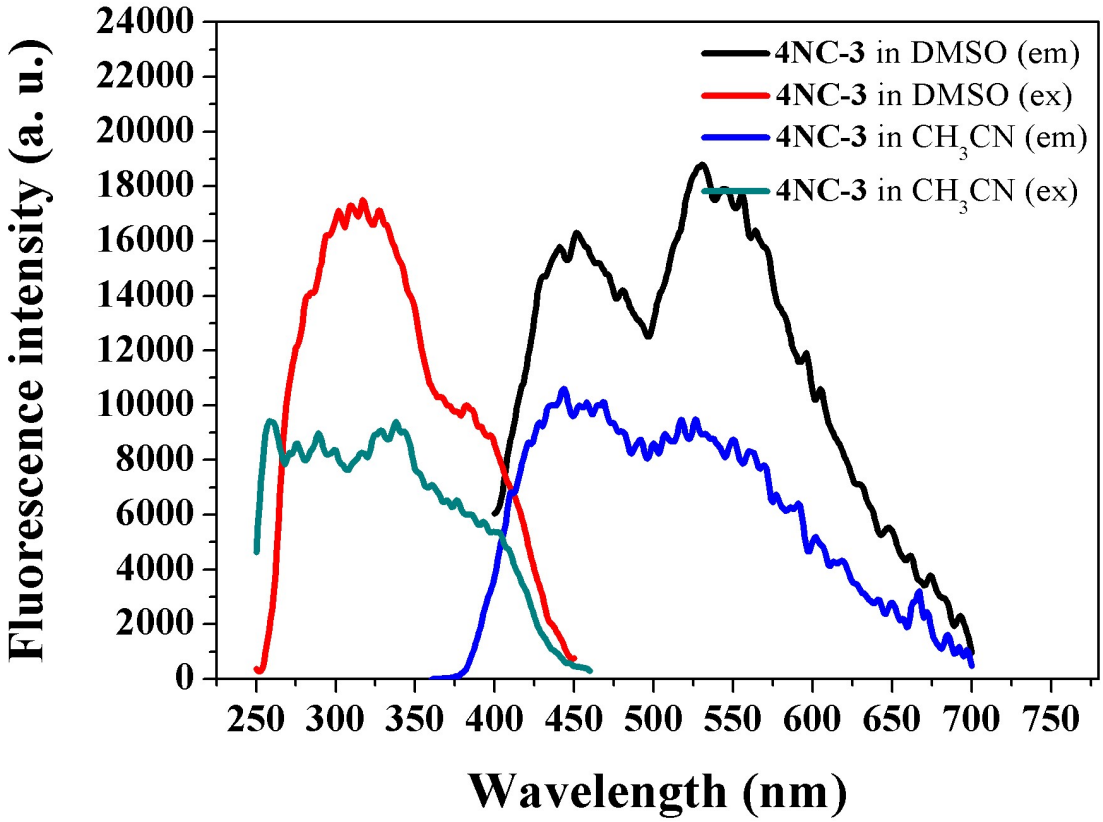


Figure S18. Fluorescence spectra of compound **4NC-3** in solutions (50 μM).

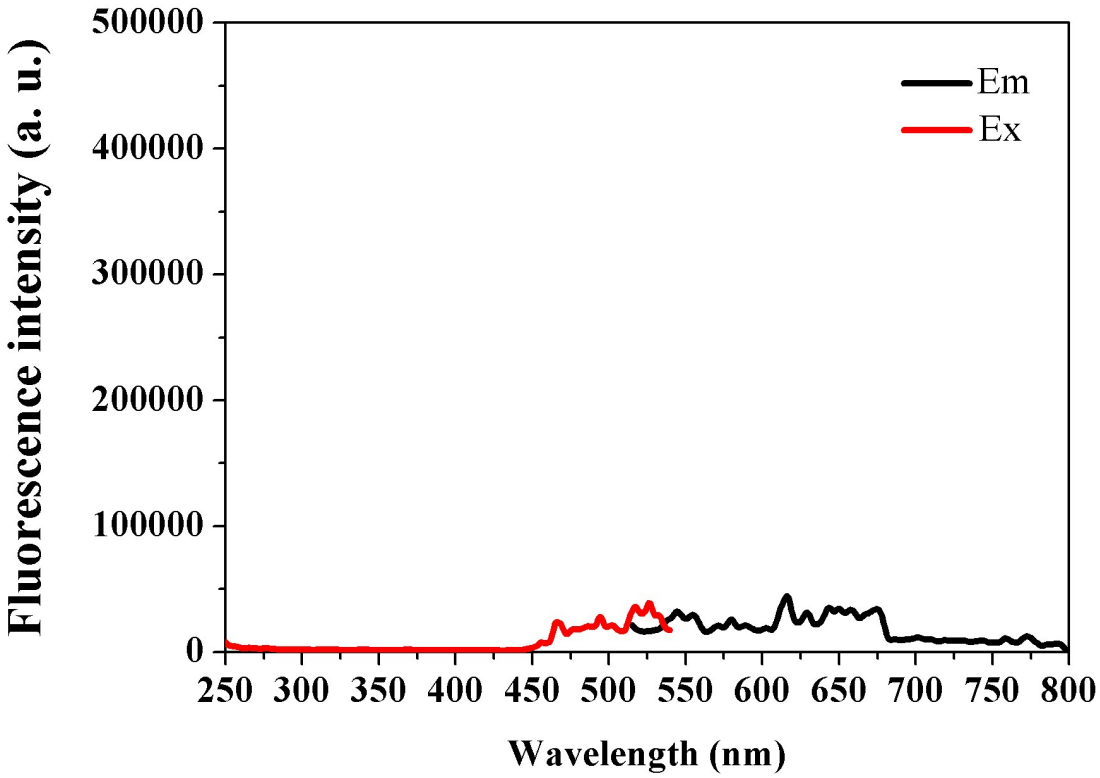


Figure S19. Fluorescence spectra of compound **4CN** in solid.

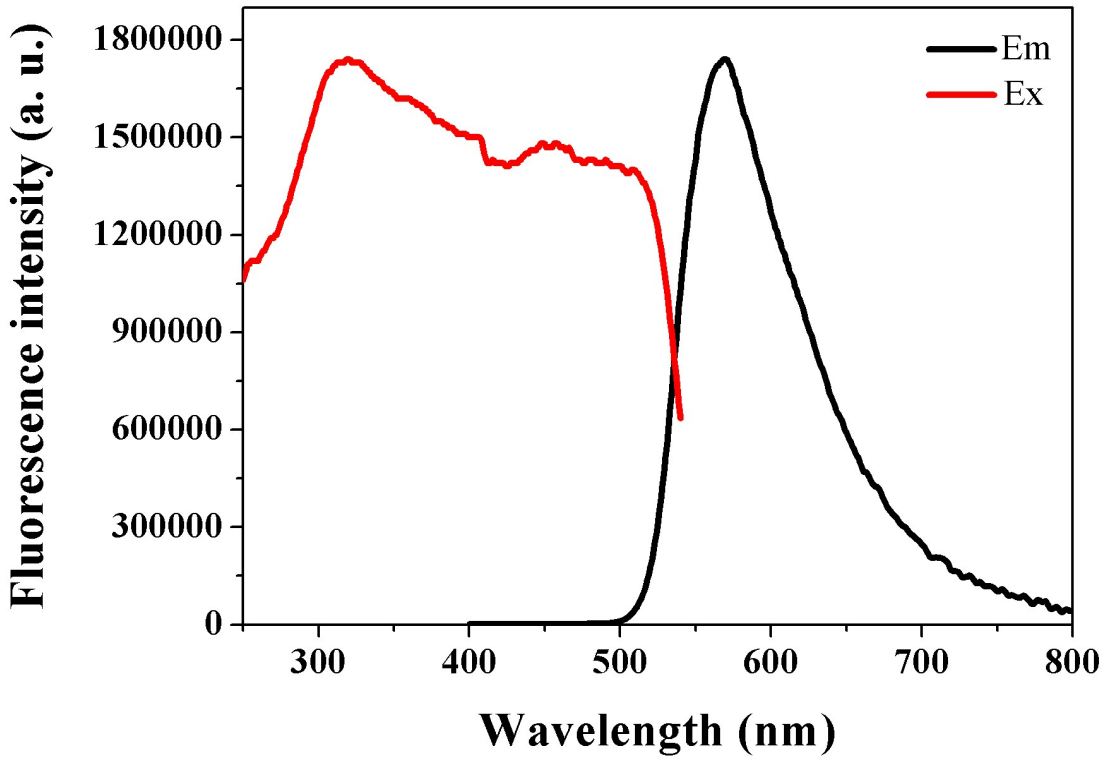


Figure S20. Fluorescence spectra of compound **4NC** in solid.

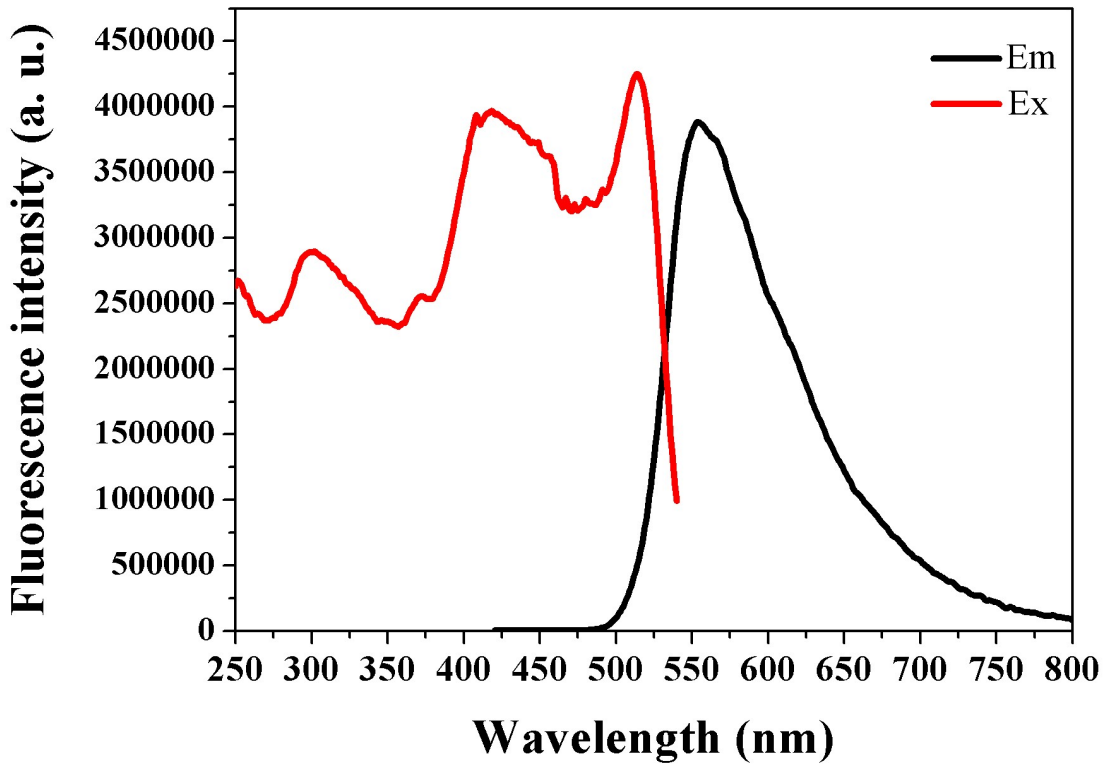


Figure S21. Fluorescence spectra of compound **5NC** in solid.

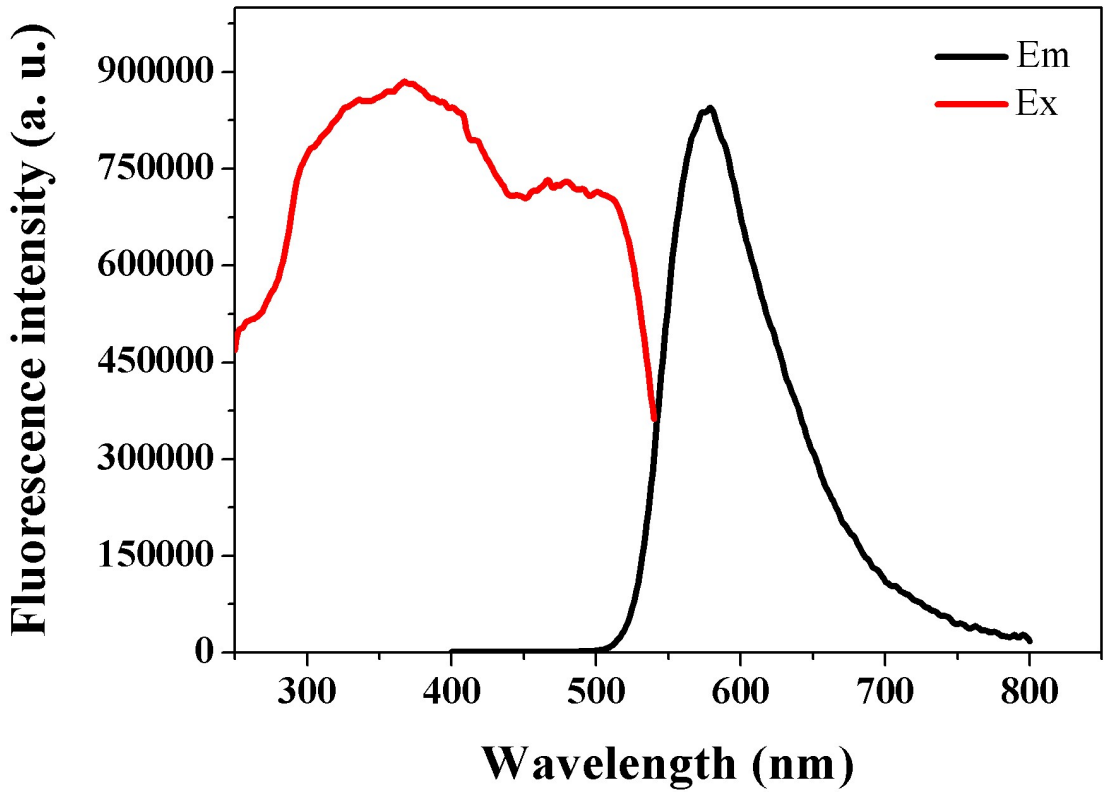


Figure S21. Fluorescence spectra of compound **6NC** in solid.

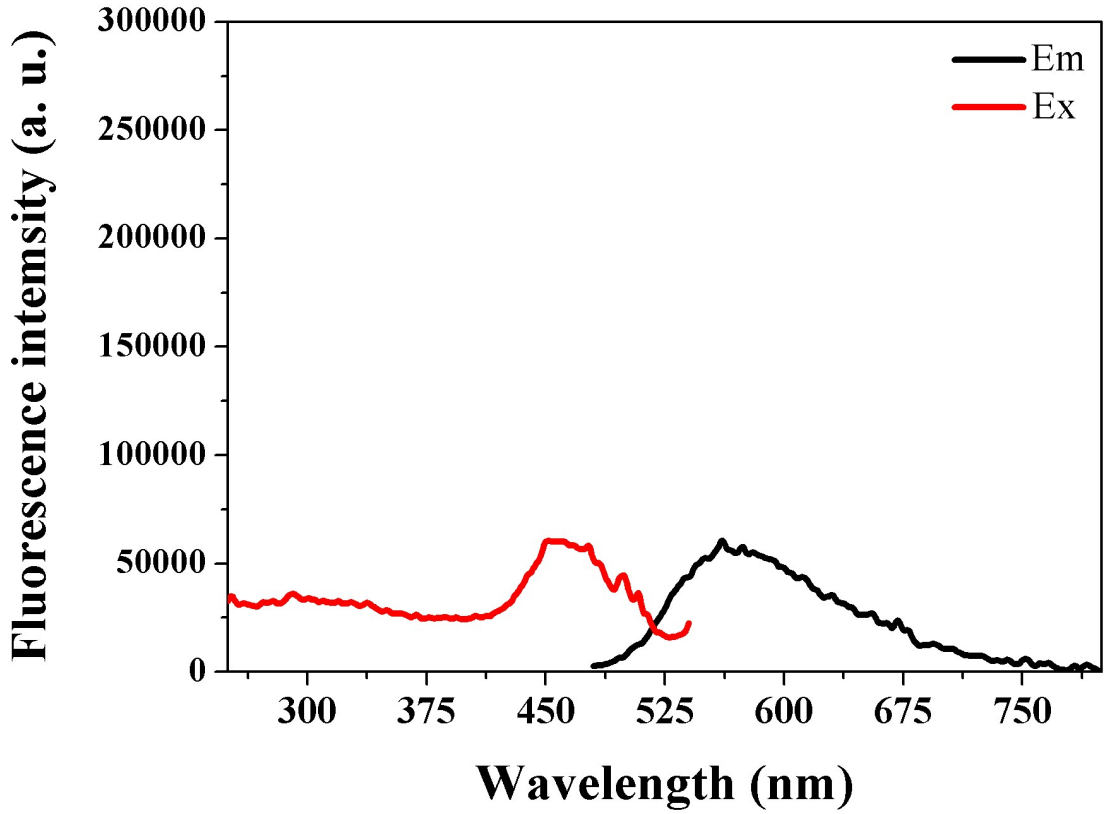


Figure S22. Fluorescence spectra of compound **7NC** in solid.

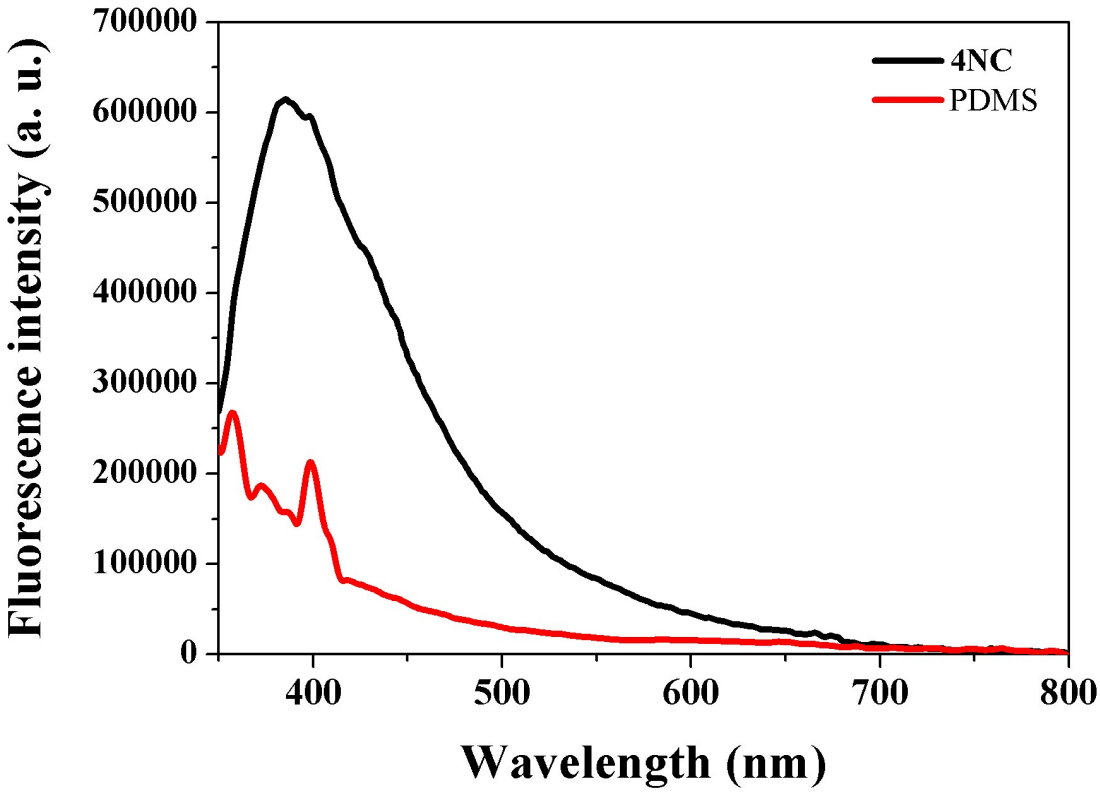


Figure S23. Fluorescence spectra of compound **4NC**-PDMS and pure PDMS films.

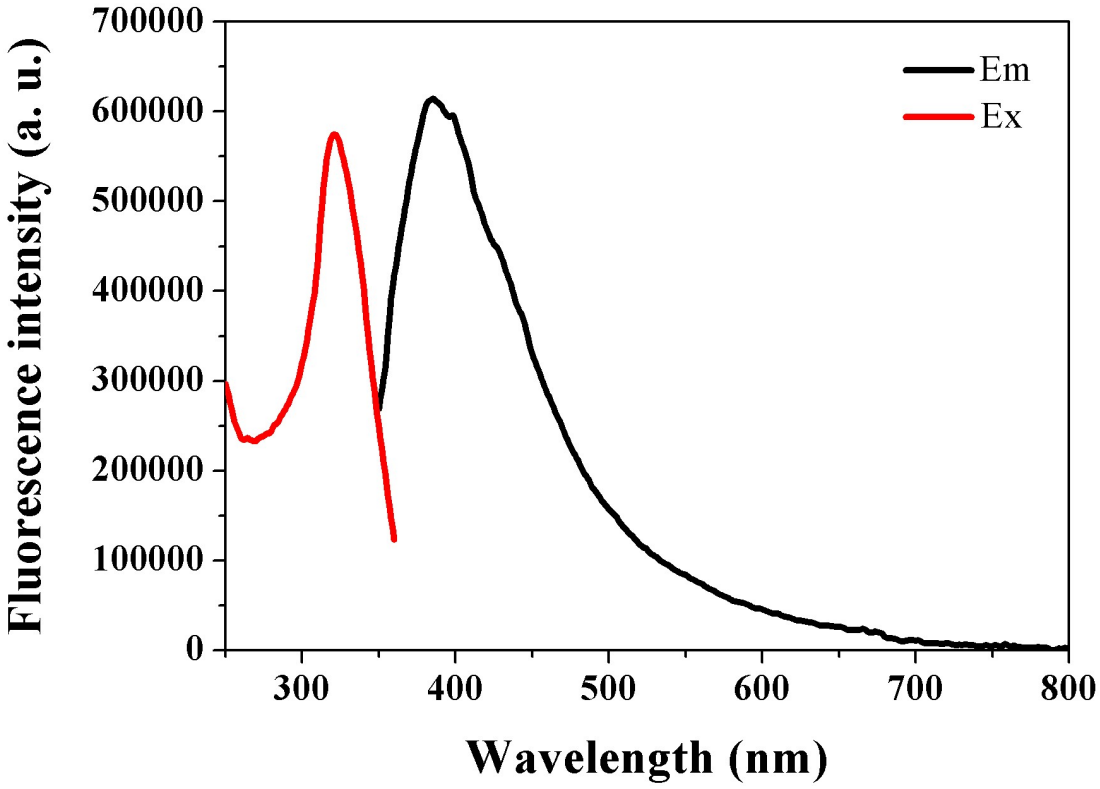


Figure S24. Ex and Em fluorescence spectra of **4NC**-PDMS film.

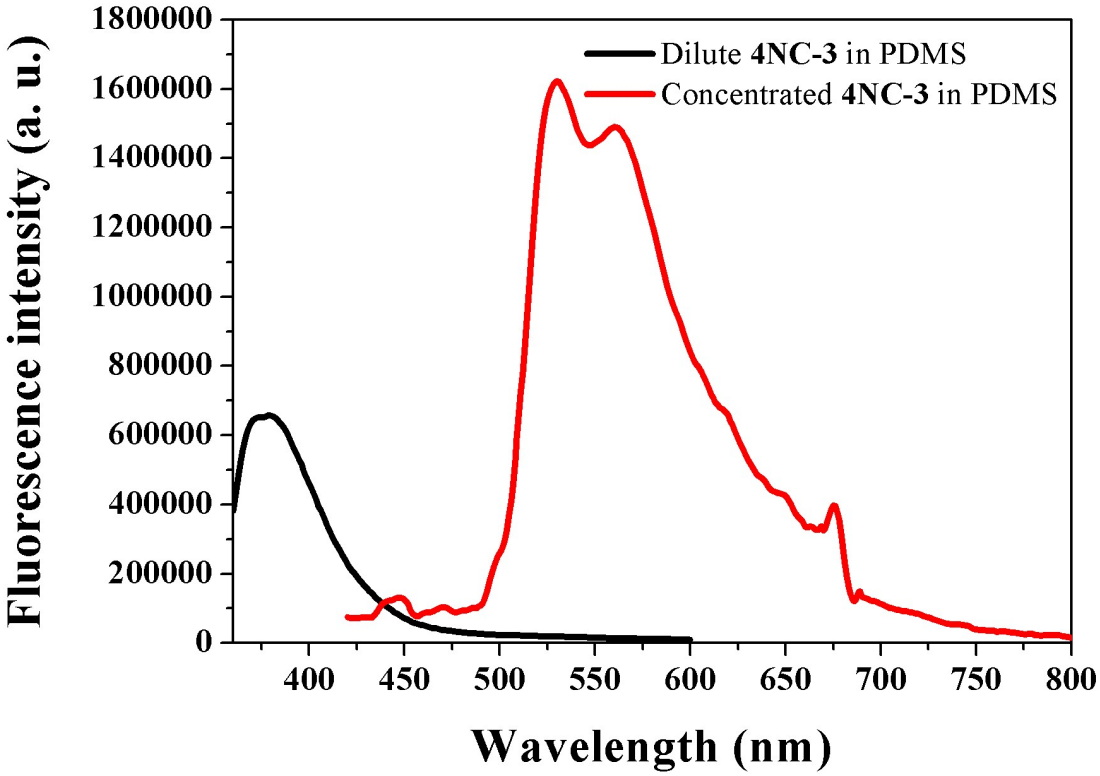


Figure S25. Fluorescence spectra of dilute and concentrate **4NC-3**-PDMS films.

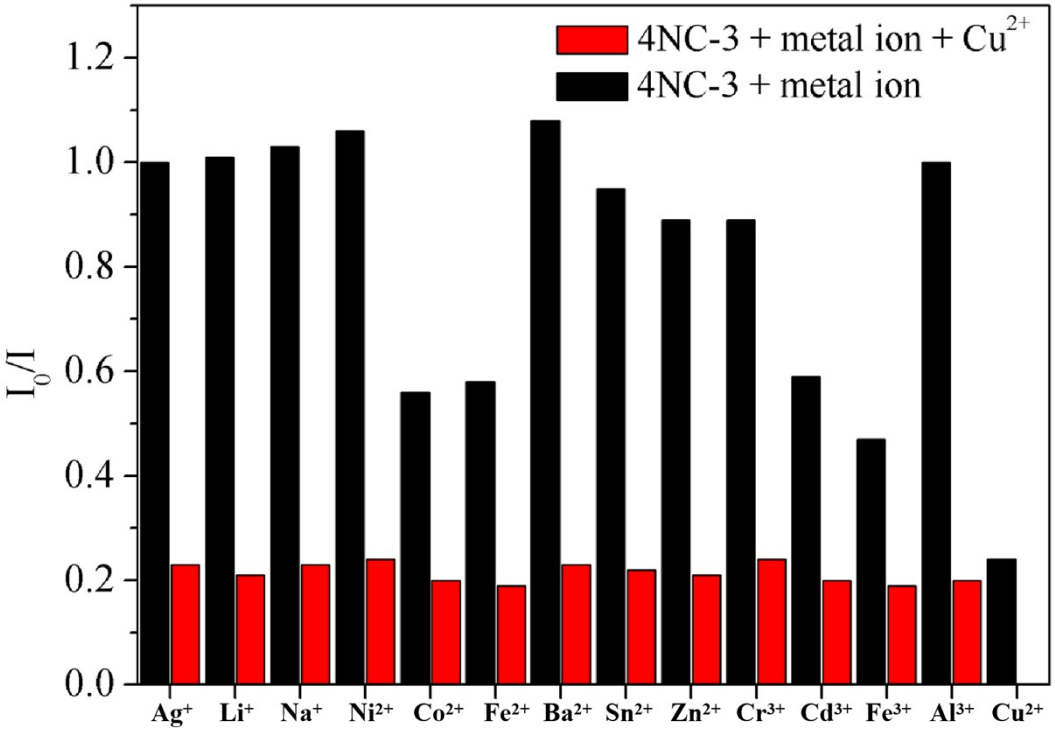


Figure S26. Fluorescence intensity changes of 4NC-3 (50 μM) upon addition of metal ions (250 μM) and Cu^{2+} (50 μM).

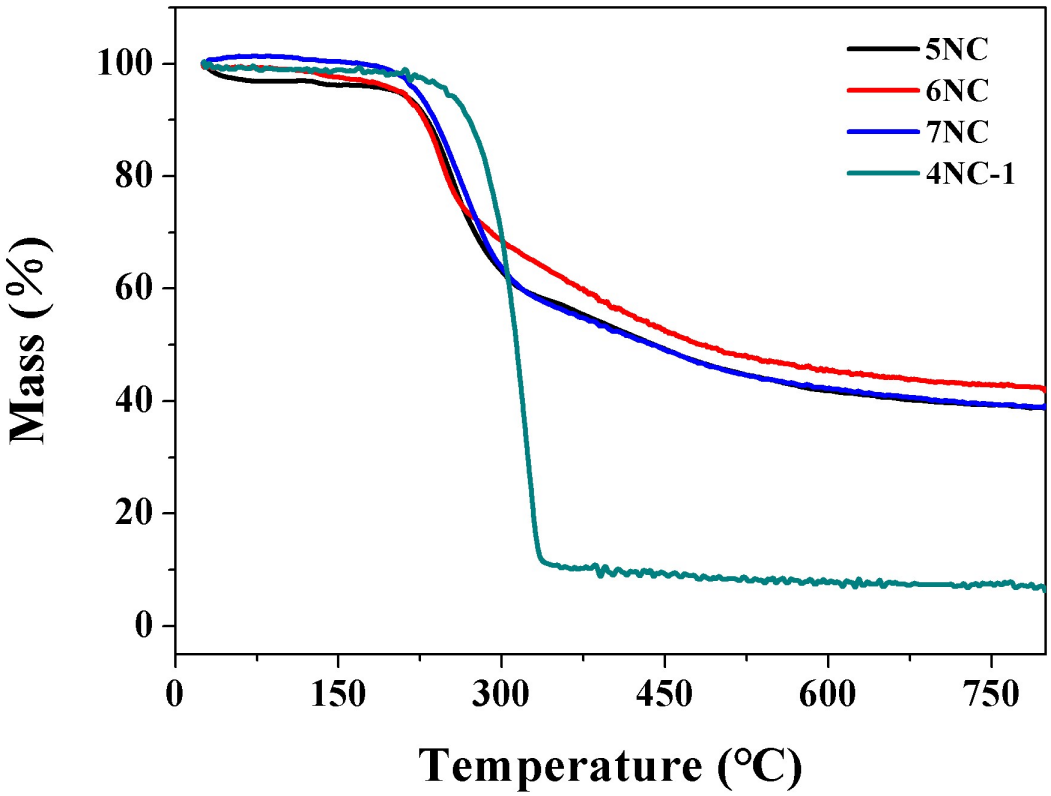


Figure S27. The TGA curves of title compounds **5NC**, **6NC**, **7NC**, and **4NC-1**.

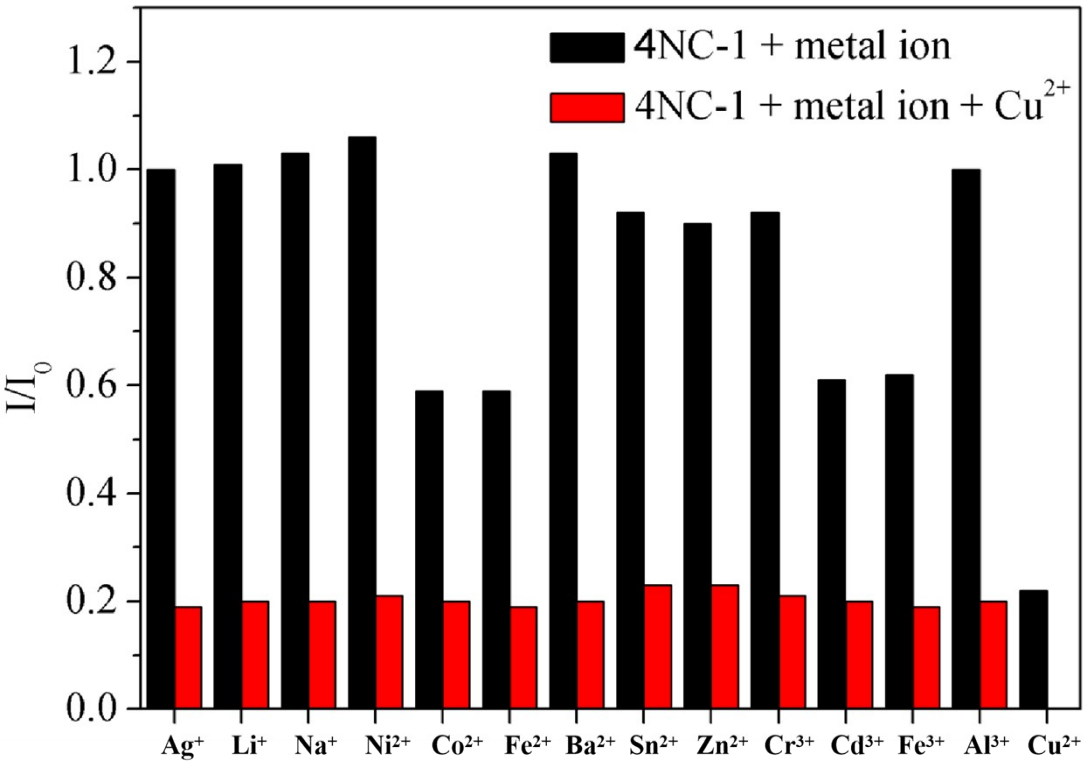


Figure S28. Fluorescence spectra of anti-interference effect of **4NC-1**

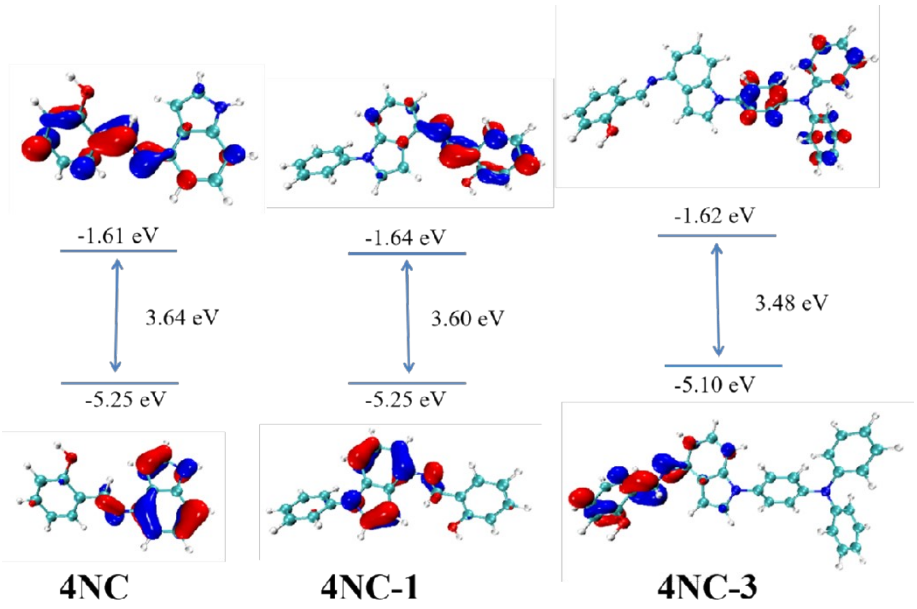
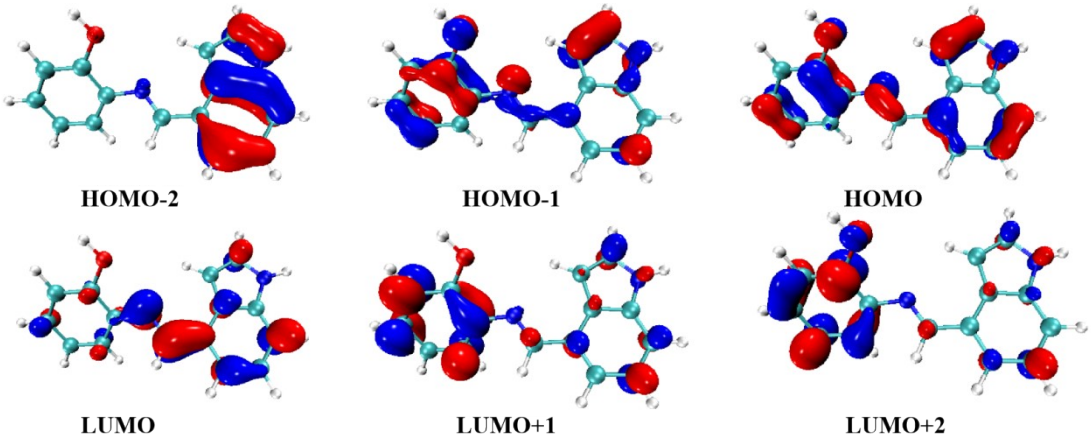
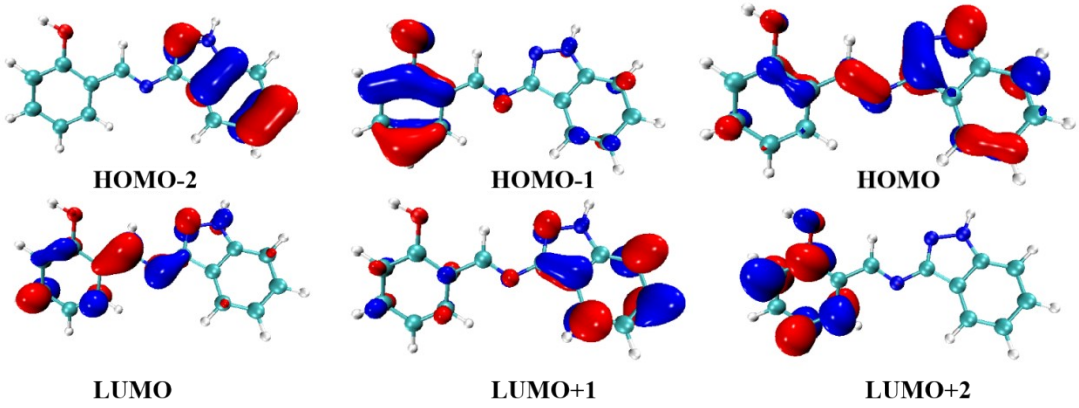


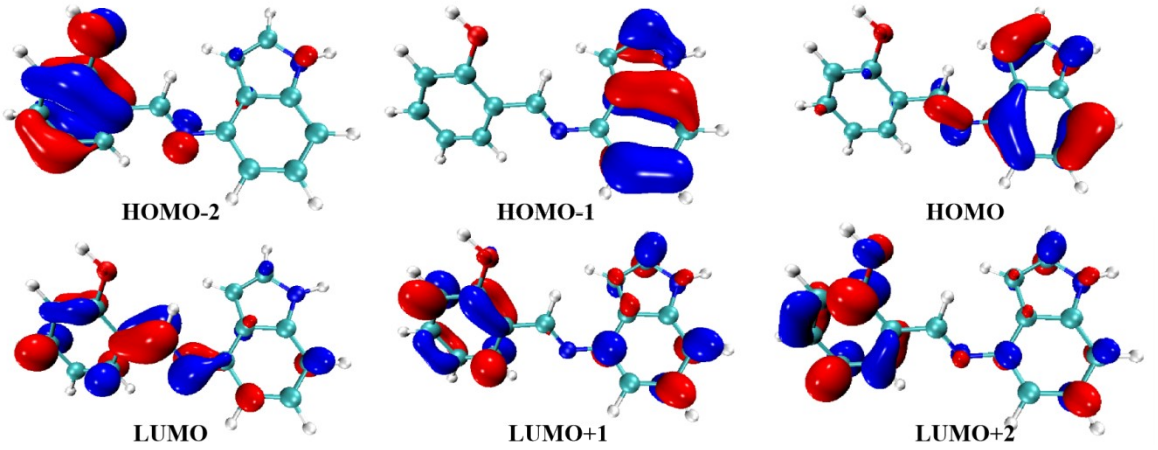
Figure S29. The HOMO and LUMO orbitals of **4NC, 4NC-1**, and **4NC-3**.



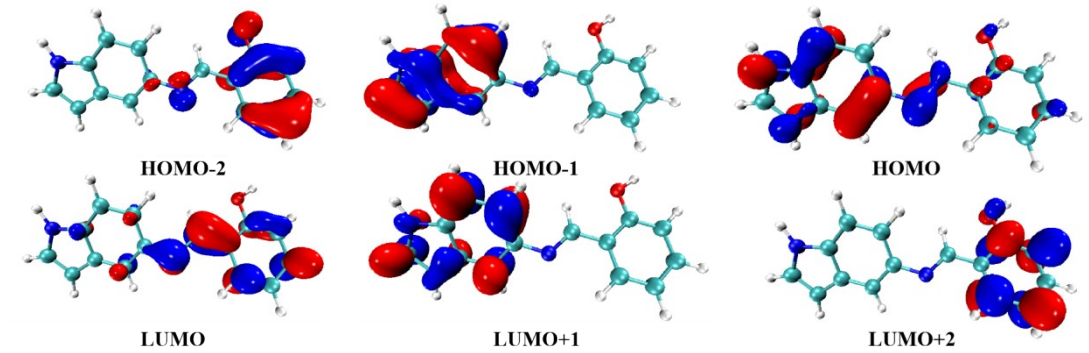
Frontier MOs of **4CN**.



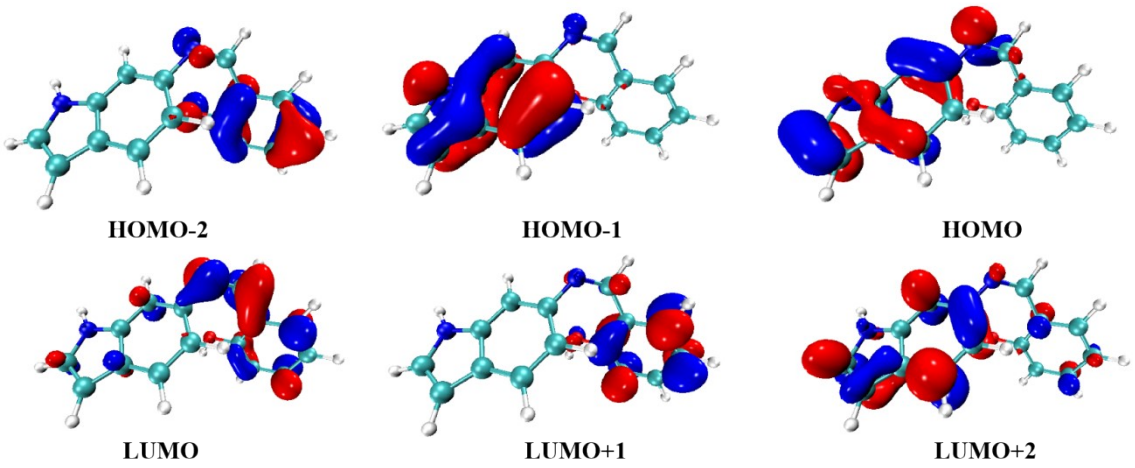
Frontier MOs of **3NC**.



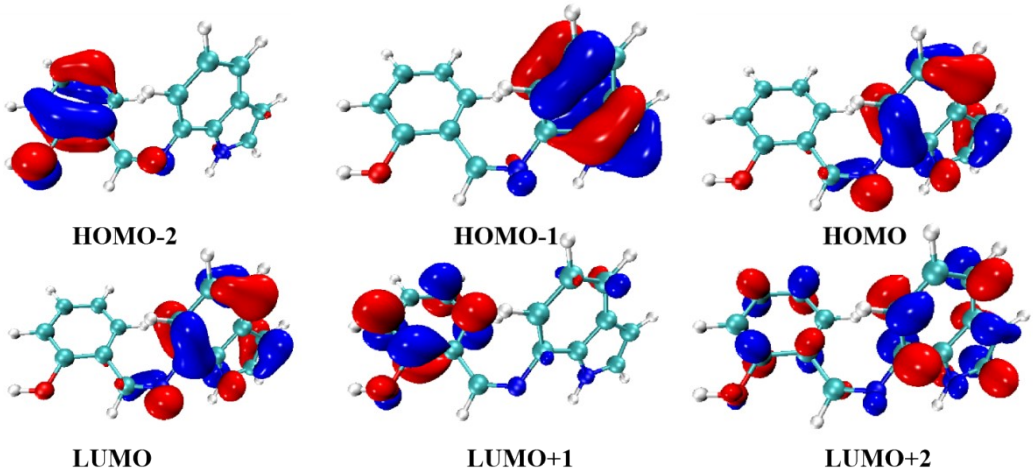
Frontier MOs of **4NC**.



Frontier MOs of **5NC**.



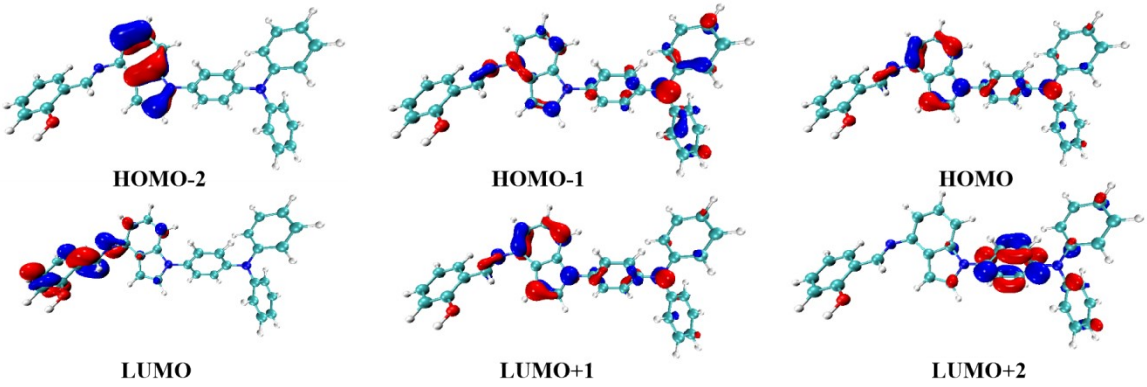
Frontier MOs of **6NC**.



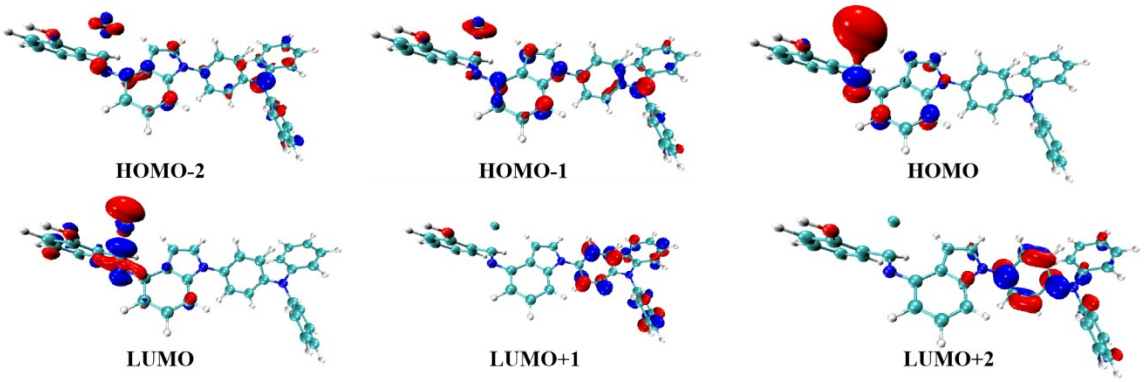
Frontier MOs of **7NC**.

Table S5. Orbital energy of **4CN** and **3NC-7NC** (eV)

Comp.	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2
4CN	-6.27	-5.93	-5.46	-1.59	-0.06	0.21
3NC	-6.38	-5.76	-5.41	-1.48	-0.37	0.02
4NC	-6.35	-6.04	-5.25	-1.61	-0.16	0.07
5NC	-6.36	-5.87	-5.21	-1.33	-0.24	-0.12
6NC	-6.65	-6.47	-5.63	-1.78	-0.69	-0.05
7NC	-6.51	-5.90	-5.25	-1.63	-0.27	-0.13



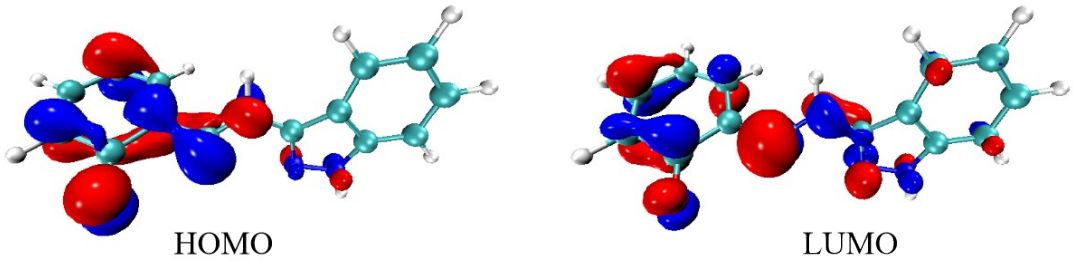
Frontier MOs of **4NC-3**.



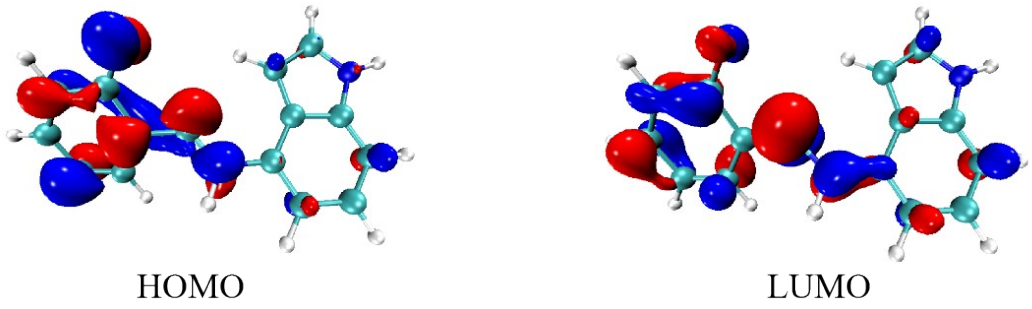
Frontier MOs of **4NC-3**-Cu^{2+}.

Table S6. Orbital energy of **4NC-3** and **4NC-3**-Cu^{2+} (eV).

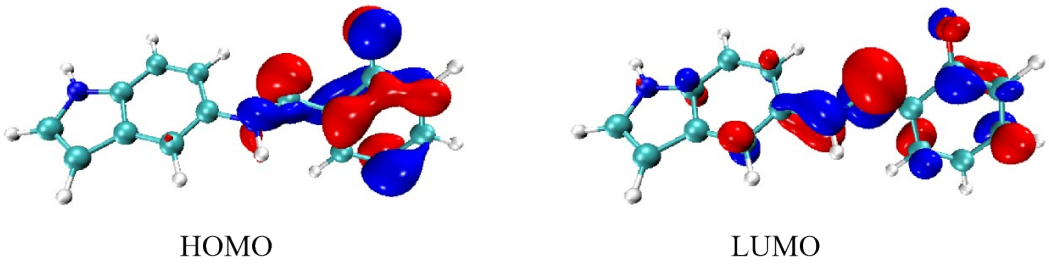
Comp.	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2
4NC-3	-6.05	-5.45	-5.09	-1.62	-0.88	-0.84
4NC-3-Cu^{2+}	-5.41	-5.20	-3.89	-1.44	-0.88	-0.84



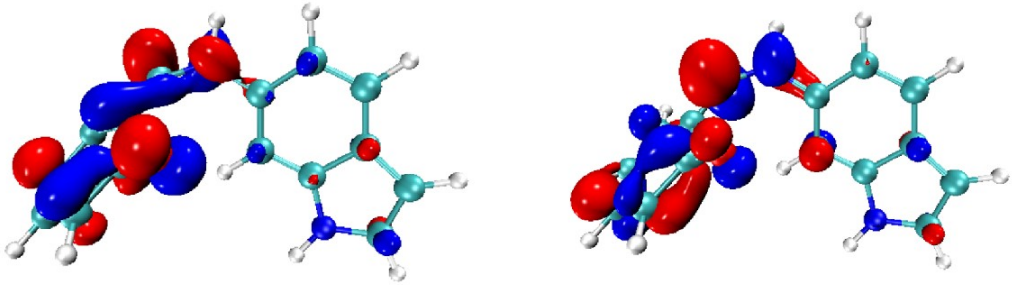
HOMO and LUMO orbitals of **3NC**.



HOMO and LUMO orbitals of **4NC**.

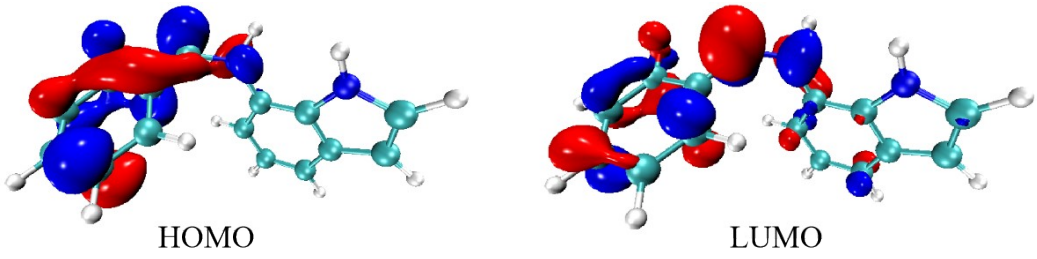


HOMO and LUMO orbitals of **5NC**.



HOMO LUMO

HOMO and LUMO orbitals of **6NC**.



HOMO LUMO

HOMO and LUMO orbitals of **7NC**.

Table S7. Energy gap differences of **3NC**-**7NC** (enolate forms) between HOMO and LUMO.

Comp.	**3NC**	**4NC**	**5NC**	**6NC**	**7NC**
Energy gap	3.16	3.15	3.42	3.10	3.25

XYZ coordinates optimized molecular geometry of **4CN**.

C	3.53721812	0.22468122	-0.09219250
C	2.11585534	0.27566931	-0.09083215
C	1.39556368	-0.91322066	0.18667155
C	2.12501963	-2.07600943	0.45209756
C	3.52651810	-2.09634537	0.44165167
C	4.25294497	-0.94491532	0.16798083
C	1.74403615	1.62633042	-0.38614938
H	1.58584519	-2.99218869	0.66976715
H	4.04888567	-3.02252724	0.65049497
H	5.33750997	-0.95676640	0.15985888
H	0.73822288	2.00240529	-0.44928798
N	3.98922414	1.49381444	-0.38061183
H	4.95433204	1.76761157	-0.44877975
C	2.90579539	2.33185916	-0.55410791
H	3.05422245	3.37520821	-0.78500038
C	-2.21225300	-0.15861522	-0.10043466
C	-3.02031594	0.88963656	0.39441946
C	-2.84689269	-1.26984839	-0.67135779

C	-4.40863918	0.78868260	0.33580698
C	-4.23499081	-1.36189089	-0.73837596
H	-2.23123221	-2.05053615	-1.10330212
C	-5.01759679	-0.33126693	-0.22830440
H	-5.01634239	1.59755372	0.73258030
H	-4.69825887	-2.22675166	-1.19851112
H	-6.09901090	-0.38650788	-0.27503234
O	-2.38831276	1.96789341	0.94031371
H	-3.05356331	2.60688591	1.21614200
N	-0.82323113	0.00697378	-0.06425197
C	-0.06222632	-0.98443331	0.20633421
H	-0.47627941	-1.96493406	0.48336220\

XYZ coordinates optimized molecular geometry of **3NC**.

C	3.40815009	0.73169451	-0.10494737
C	2.41487865	-0.26727010	-0.00215195
C	4.12985450	-1.89660723	0.34437738
C	5.11130344	-0.88556102	0.23793057
C	4.77375699	0.43800737	0.01356576
C	1.17353670	0.43429174	-0.17477605
N	2.73096471	1.90119480	-0.32163146
H	3.10911133	2.81358621	-0.51327874
C	2.78337689	-1.60010814	0.22790764
H	2.02465699	-2.36899725	0.30794704
H	4.44468540	-2.91878964	0.51950295
H	6.15706148	-1.15515035	0.33476169
H	5.53262942	1.20781421	-0.06559563
N	1.38739839	1.72795323	-0.37675296
N	-0.07430594	-0.17302370	-0.16099573
C	-1.12587991	0.54250819	0.01085745
H	-1.06315706	1.61740249	0.18721192
C	-2.46498315	-0.04561343	-0.02153780
C	-3.59875095	0.75603383	0.22037157
C	-2.66139184	-1.40884489	-0.29153532
C	-4.87825832	0.19738004	0.18883909
C	-3.93051932	-1.96602329	-0.32155226
H	-1.77992590	-2.00974933	-0.47751543
C	-5.04255592	-1.15642257	-0.08028673
H	-5.74267612	0.82779886	0.37730450
H	-4.05912677	-3.02083463	-0.53257460
H	-6.04108536	-1.57812709	-0.10210667
O	-3.39941401	2.08032619	0.48451999
H	-4.25036857	2.50877662	0.62147224

XYZ coordinates optimized molecular geometry of **4NC**.

C	3.53639722	0.21978832	-0.01175363
C	2.12510092	0.26765251	-0.18310871
C	1.37922354	-0.92369074	0.01895644
C	2.07885167	-2.08738415	0.34384615
C	3.46802452	-2.09235380	0.53046725
C	4.22137598	-0.94023687	0.35717009
C	1.80631420	1.60707308	-0.59825347
H	1.50682023	-2.99905215	0.46548485
H	3.96127751	-3.01763624	0.80550261
H	5.29782136	-0.94478689	0.48673037
H	0.83516204	2.00822219	-0.83501022
N	4.02480415	1.47836473	-0.29335200
H	4.99487601	1.74202929	-0.27161078
C	2.98119263	2.30530666	-0.65386661
H	3.16205097	3.33434699	-0.92174440
C	-2.24338879	-0.17375003	0.03728093
C	-3.07969942	0.88436633	0.44290815
C	-2.83720647	-1.30163032	-0.54809403
C	-4.46213708	0.80089908	0.26651449
C	-4.21021147	-1.38788513	-0.72441252
H	-2.17893566	-2.10487753	-0.85535099
C	-5.02429367	-0.33054748	-0.31398312
H	-5.09387804	1.62552620	0.58464850
H	-4.64781965	-2.26936331	-1.17749014
H	-6.09906641	-0.38418829	-0.44571129
O	-2.49167837	1.98354097	1.00475594
H	-3.17320382	2.61933131	1.24494541
N	-0.00983366	-1.03185036	-0.13250770
C	-0.79136887	-0.08498355	0.22763712
H	-0.42552045	0.82077669	0.71472517

XYZ coordinates optimized molecular geometry of **5NC**.

C	-3.72981944	0.59126554	0.17632889
C	-3.34298838	-0.72253185	-0.20287647
C	-1.03788592	-0.11071690	0.19199247
C	-1.45826180	1.18819642	0.58189882
C	-2.79507687	1.54708386	0.58262541
C	-4.54816464	-1.43166138	-0.53378676
H	-0.71932370	1.90325444	0.92242879
H	-3.10172786	2.53713053	0.90282567
H	-4.62877271	-2.45507322	-0.86452695
N	-5.10320489	0.65751379	0.07762222
H	-5.66522166	1.46605949	0.28109075

C	-5.58891647	-0.56350472	-0.35218525
H	-6.64803648	-0.71102312	-0.49416450
C	-1.98612347	-1.06615654	-0.17187729
H	-1.64551638	-2.05979779	-0.43747714
N	0.30876094	-0.51836914	0.18997897
C	1.24894936	0.31799183	-0.03760795
H	1.05558003	1.36469101	-0.28788768
C	2.66051224	-0.08024275	0.00409204
C	3.04132636	-1.39115469	0.32633064
C	3.67374079	0.85491440	-0.28305747
C	4.37503027	-1.77060901	0.36272421
H	2.24965787	-2.09704748	0.54506767
C	5.01717869	0.47676263	-0.24555619
C	5.36603257	-0.83034597	0.07540799
H	4.64560174	-2.78928668	0.61366807
H	5.78662450	1.21044266	-0.46941013
H	6.41258006	-1.11221398	0.10112519
O	3.29567871	2.13173894	-0.59507527
H	4.08103300	2.65919490	-0.77206443

XYZ coordinates optimized molecular geometry of **6NC**.

C	-2.77718434	0.37241901	-0.24958331
C	-2.67294880	-0.67322517	0.70759691
C	-0.48102397	0.15380632	1.26771379
C	-0.59665694	1.18191428	0.29774855
C	-1.76898470	1.31377275	-0.44485184
C	-3.89852059	-1.41871261	0.64853221
H	-1.85998082	2.12740101	-1.15443399
H	-4.16432001	-2.28049537	1.24055727
N	-4.01153832	0.24781413	-0.85335269
H	-4.37542245	0.85771410	-1.56507885
C	-4.68221225	-0.83114148	-0.30633667
H	-5.67180727	-1.09061778	-0.64834565
C	-1.50225231	-0.75465024	1.47918375
H	-1.39828306	-1.52174686	2.23917191
H	0.41875861	0.10303028	1.86781538
N	0.39169253	2.16628659	0.12540614
C	1.64139582	1.93485425	0.03427766
H	2.27793134	2.82493417	0.02583010
C	2.41120794	0.66390074	-0.04175135
C	2.05860161	-0.42032244	-0.86731935
C	3.59843784	0.56983516	0.69635610
C	2.84469852	-1.57477956	-0.88224622
C	4.38112595	-0.57895636	0.68823871

H	3.89425079	1.41844714	1.30513675
C	3.99334728	-1.65828243	-0.10283762
H	2.55680974	-2.40491546	-1.52104730
H	5.28321311	-0.63038807	1.28568637
H	4.59073010	-2.56254999	-0.12717627
O	0.96440341	-0.28704282	-1.66295700
H	0.77762687	-1.12576896	-2.09716179

XYZ coordinates optimized molecular geometry of **7NC**.

C	2.24906837	-0.44257244	-0.01606573
C	3.20218346	0.60287312	0.06746471
C	1.70672509	1.74742107	1.55743238
C	0.76515675	0.70817023	1.44730225
C	1.00798007	-0.40462338	0.64148423
C	4.32045912	0.19819666	-0.73918022
H	5.23098607	0.75086026	-0.90998071
N	2.76326224	-1.41715588	-0.83825661
H	2.32291682	-2.30804804	-0.99644634
C	4.02030537	-1.03257112	-1.25929681
H	4.60200869	-1.67279745	-1.90384582
C	2.91172753	1.71884988	0.87147346
H	3.62279286	2.53144955	0.96845057
H	1.47692257	2.58958676	2.20081822
H	-0.16013747	0.75803622	2.00836430
N	0.18554534	-1.54084643	0.55515076
C	-1.06953117	-1.52265293	0.31400476
H	-1.57240963	-2.48605928	0.40346243
C	-1.96518494	-0.42410420	-0.11477136
C	-3.33680995	-0.51582412	0.19501490
C	-1.54321071	0.64588020	-0.91759189
C	-4.23879381	0.44312069	-0.26878285
C	-2.43898825	1.59634628	-1.38911867
H	-0.49622239	0.72068235	-1.17906959
C	-3.78989728	1.49593256	-1.05741545
H	-5.29023373	0.36098232	-0.00836377
H	-2.08749146	2.40970921	-2.01204553
H	-4.49742353	2.23558549	-1.41442016
O	-3.73812283	-1.56609918	0.97055077
H	-4.69551690	-1.54183279	1.06868887

XYZ coordinates optimized molecular geometry of **4NC-3**.

C	-1.63729310	0.97594583	-0.25172089
C	-2.97672736	0.50140301	-0.30311794
C	-4.03341167	1.44399621	-0.39755809

C	-3.69895470	2.79654367	-0.48014252
C	-2.36960854	3.23329421	-0.42079771
C	-1.31723903	2.33521332	-0.30777026
C	-2.90751122	-0.93358150	-0.31346409
H	-4.50758977	3.50971141	-0.58355260
H	-2.15876125	4.29515133	-0.47732374
H	-0.29029087	2.67588767	-0.29017226
H	-3.72723356	-1.63136888	-0.35078998
N	-0.79803400	-0.13458077	-0.20882697
C	-1.58735610	-1.27519517	-0.25970475
H	-1.12467855	-2.24827604	-0.21927729
C	-7.28709606	-0.23669859	0.12330284
C	-7.78881287	-1.30274537	0.89492791
C	-8.17203573	0.43889335	-0.72984800
C	-9.13397112	-1.66656543	0.80857459
C	-9.50894760	0.08028251	-0.81758604
H	-7.76870736	1.25485202	-1.31676703
C	-9.98969656	-0.97745793	-0.04346166
H	-9.50591763	-2.49117539	1.41021710
H	-10.17534146	0.61696373	-1.48215922
H	-11.03229507	-1.26886530	-0.10202548
O	-6.91728043	-1.96091627	1.71741764
H	-7.38973110	-2.65278909	2.19124423
N	-5.39291276	1.11079214	-0.46978941
C	-5.87406072	0.14603510	0.21920204
H	-5.26947974	-0.42240469	0.92863177
C	0.62033159	-0.13488372	-0.15333684
C	1.30030367	0.63435226	0.79512007
C	1.35810382	-0.92836201	-1.03596976
C	2.68738102	0.61209211	0.85708723
H	0.73782760	1.22699907	1.50587462
C	2.74527425	-0.95310328	-0.97320462
H	0.84158204	-1.50533887	-1.79399533
C	3.43334603	-0.18164601	-0.02615799
H	3.20028744	1.20289524	1.60571444
H	3.30381416	-1.56295860	-1.67221494
N	4.84919501	-0.20313745	0.03760247
C	5.57073431	1.00144817	0.26574368
C	6.65177204	1.02385647	1.15721545
C	5.21354764	2.18284367	-0.39824977
C	7.36088892	2.20137377	1.37107300
H	6.93155351	0.11580986	1.67722471
C	5.91751940	3.35974656	-0.16479130
H	4.38436717	2.17235743	-1.09516210

C	6.99697262	3.37698222	0.71676329
H	8.19465345	2.20122027	2.06441401
H	5.62798404	4.26483532	-0.68714157
H	7.54736681	4.29404805	0.89106323
C	5.55252215	-1.42802875	-0.12844097
C	6.71134195	-1.48119205	-0.91489015
C	5.10021066	-2.59988485	0.49342880
C	7.40225942	-2.67892434	-1.06706381
H	7.06562924	-0.58099815	-1.40202831
C	5.78798909	-3.79672519	0.32135450
H	4.21008412	-2.56620066	1.10976034
C	6.94431620	-3.84455505	-0.45536662
H	8.29697649	-2.70209385	-1.67930063
H	5.42437648	-4.69376371	0.81028595
H	7.48147514	-4.77720468	-0.58166123

XYZ coordinates optimized molecular geometry of **4NC-3**-Cu^{2+}.

C	-1.02581411	0.90608314	-0.10096371
C	-2.35799519	0.41286698	-0.03987409
C	-3.44633901	1.32538607	-0.21934905
C	-3.10954689	2.66612574	-0.49793055
C	-1.79092745	3.11510836	-0.54924924
C	-0.72119369	2.24739379	-0.35002256
C	-2.25702978	-1.01230189	0.10908673
H	-3.93300159	3.35084221	-0.65879561
H	-1.59460402	4.16117784	-0.75607085
H	0.30186283	2.59267392	-0.41800820
H	-3.06542392	-1.71915035	0.19209235
N	-0.16312646	-0.17962283	0.04231861
C	-0.92742511	-1.32929932	0.15626247
H	-0.44671175	-2.28341234	0.29994037
C	-6.72446925	-0.14225300	0.69784835
C	-7.68011753	0.02168364	-0.32422077
C	-7.19631517	-0.37825209	1.99304002
C	-9.04225861	-0.00949344	-0.03687581
C	-8.55655465	-0.41671784	2.28776419
H	-6.47009221	-0.51464345	2.78788970
C	-9.48280328	-0.22077617	1.26809974
H	-9.76173250	0.12004403	-0.84094797
H	-8.88818204	-0.58770421	3.30510890
H	-10.54596900	-0.23834773	1.47850891
O	-7.21638162	0.14704644	-1.60817039
H	-7.96495227	0.26864139	-2.20247783
N	-4.78694531	1.04347988	-0.16998704

C	-5.25528832	-0.06010451	0.44757463
H	-4.66239651	-0.50376048	1.25853294
C	1.25583086	-0.15090479	0.04605056
C	1.95265910	0.74186917	0.86545951
C	1.97842055	-1.03899528	-0.75537117
C	3.34108311	0.74779592	0.87968828
H	1.40318104	1.41136428	1.51546942
C	3.36710217	-1.03468189	-0.74062178
H	1.44762285	-1.71485485	-1.41546902
C	4.07185882	-0.13957714	0.07636667
H	3.86774758	1.43576971	1.52923478
H	3.91324904	-1.71952975	-1.37719278
N	5.48920180	-0.13091553	0.09051031
C	6.19374379	1.10416483	0.13186971
C	7.30740911	1.25894742	0.96838818
C	5.78695740	2.18376742	-0.66383512
C	7.99959015	2.46516151	0.99954427
H	7.62564757	0.43060114	1.58950305
C	6.47484814	3.39184375	-0.61298635
H	4.93201506	2.07020328	-1.31920742
C	7.58664150	3.54015820	0.21434246
H	8.85901919	2.56798985	1.65275532
H	6.14670268	4.21690863	-1.23544100
H	8.12412228	4.48058233	0.24643982
C	6.21029941	-1.35620589	0.05599839
C	7.34048671	-1.49342584	-0.76131164
C	5.80392150	-2.44442156	0.84035895
C	8.04873129	-2.69048900	-0.78484077
H	7.65911777	-0.65852920	-1.37334363
C	6.50831135	-3.64317466	0.79716883
H	4.93651040	-2.34422011	1.48136847
C	7.63629166	-3.77391028	-0.01109921
H	8.92088938	-2.77938493	-1.42306299
H	6.18054346	-4.47470467	1.41122501
H	8.18677771	-4.70698398	-0.03694845
Cu	-5.06742938	-1.30788837	-1.06495842