

Supporting information

Photo-Induced C-H Bond Activation of *N,N'*-Dialkylethylenediamine upon Aza-Michael Addition to 1,8-Pyrenedione: Facile Synthesis of Fluorescent Pyrene Derivatives

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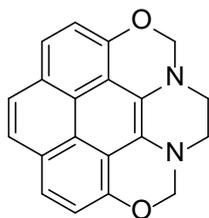
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Experimental Section

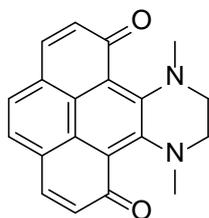
Experiments involving air sensitive components were performed under a positive pressure of nitrogen in glove bag. Silicone gel was degassed in vacuum for 1h. Methanol and dichloromethane were degassed by nitrogen for 1 h. ^1H and ^{13}C NMR spectra were recorded in deuterated solvents with a Bruker spectrometer (Karlsruhe, Germany). High resolution ESI-MS spectra were obtained from the microTOF-Q II 1026 mass spectrometer with an ESI source. All solvent used were of reagent grade unless otherwise specified. Sodium bicarbonate was purchased from Sino Chemical Co. Pte Ltd. All chemicals unless indicated were obtained from Sigma Aldrich and used as received.

Synthesis of **1**



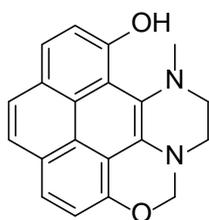
Pyrene-1,8-dione (0.15 g, 0.65 mmol) was dissolved in CH_3CN (100 mL), then 2.0 equiv. N, N'-dimethylethylenediamine (142 μL , 1.30 mmol) was added and then the solution was exposed to air at r. t. 2 h to get a brown solution. The crude product was purified with silica gel column chromatography (EA: hexane = 1:2, v/v) and gave pure compound **1** as a bright yellow powder (0.09 g, 46 %). ^1H NMR (300 MHz, $(\text{CD}_3)_2\text{CO}$, 293K) δ 7.91 (d, J = 8.3 Hz, 2H, Ar-H), 7.86 (s, 2H, Ar-H), 7.46 (d, J = 8.3 Hz, 2H, Ar-H), 5.00 (s, 4H, NCH_2O), 3.61 (s, 4H, $\text{NCH}_2\text{CH}_2\text{N}$). ^{13}C NMR (125 MHz, $(\text{CD}_3)_2\text{CO}$, 293K) δ 149.3, 127.0, 125.8, 123.1, 121.5, 119.3, 113.9, 112.6, 81.4, 44.2. HRMS(ESI-MS) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{15}\text{N}_2\text{O}_2$ 314.1050; Found 314.1054.

Synthesis of **2**



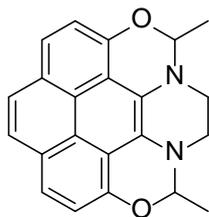
Pyrene-1,8-dione (0.10 g, 0.43 mmol) was dissolved in CH₃CN (100 mL), then 2.0 equiv. N, N'-dimethylethylenediamine (94 μL, 0.86 mmol) was added and the reaction mixture was stirred in the dark at r. t. for 30 min to get a red solution. The crude product was purified with silica gel column chromatography (CH₂Cl₂: MeOH = 2:1, v/v) and gave pure product **2** as red powder (0.06 g, 46%). ¹H NMR (300 MHz, CD₃OD, 293K) δ 7.76 (d, *J* = 9.4 Hz, 2H, Ar-*H*), 7.51 (s, 2H, Ar-*H*), 6.68 (d, *J* = 9.4 Hz, 2H, Ar-*H*), 3.99 (s, 4H, NCH₂CH₂N), 3.06 (s, 3H, NCH₃). ¹³C NMR (75 MHz, CD₃OD, 293K) δ 182.2, 151.6, 141.2, 128.8, 127.3, 126.0, 115.8, 108.1, 51.7, 45.2. HRMS(ESI-MS) *m/z*: [M+H]⁺ Calcd for C₂₀H₁₇N₂O₂ 317.1214; Found 317.1210.

Synthesis of **3**



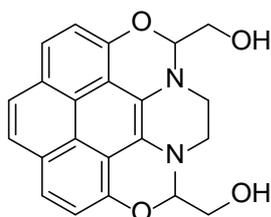
Pyrene-1,8-dione (0.15 g, 0.65mmol) was dissolved in CH₃CN (100 mL), then 2.0 equiv. N, N'-dimethylethylenediamine (142 μL, 1.30 mmol) was added. The reaction mixture was stirred in the dark at r. t. for 30 min and then placed under the 254 nm UV lamp for 0.5 h. The crude product was purified with silica gel column chromatography (EA: hexane = 1:2, v/v) and gave product **3** as yellow powder (0.09 g, 42%). ¹H NMR (400 MHz, CD₃CN, 293K) δ 12.38 (s, 1H, OH), 7.96 (d, *J* = 8.2 Hz, 1H, Ar-*H*), 7.84 (d, *J* = 8.2 Hz, 1H, Ar-*H*), 7.79 (d, *J* = 9.2 Hz, 1H, Ar-*H*), 7.74 (d, *J* = 9.2 Hz, 1H, Ar-*H*), 7.43 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.34 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 5.18 (d, *J* = 6.2 Hz, 1H, NCH₂O), 5.00 (d, *J* = 6.8 Hz, 1H, NCH₂O), 3.69 (m, 2H, NCH₂CH₂N), 3.47 (m, 2H, NCH₂CH₂N), 2.83 (s, 3H, NCH₃). ¹³C NMR (75 MHz, CD₃CN, 293K) δ 153.6, 149.6, 129.5, 127.5, 126.7, 125.9, 125.6, 125.5, 124.5, 124.4, 124.3, 124.2, 124.2, 123.3, 120.7, 115.8, 114.6, 114.2, 80.3, 48.8, 46.0, 37.5. EI-MS *m/z*: [M]⁺ Calcd for C₂₀H₁₆N₂O₂ 316.3; Found 316.3.

Synthesis of **4**



Pyrene-1,8-dione (0.15 g, 0.65 mmol) was dissolved in CH₃CN (100 mL), then 2.0 equiv. N, N'-diethylethylenediamine (186 μL, 1.30 mmol) was added and the reaction mixture was stirred at r.t. for 12 h to get a brown solution. The crude product was purified with silica gel column chromatography (EA: hexane = 1:10, v/v) and gave compound **4** as yellow powder (0.14 g, 62%). ¹H NMR (300 MHz, (CD₃)₂CO, 293K) δ 7.89 (dd, *J* = 8.3, 2.0 Hz, 2H, Ar-*H*), 7.83 (d, *J* = 1.5 Hz, 2H, Ar-*H*), 7.41 (dd, *J* = 8.3, 0.9 Hz, 2H, Ar-*H*), 5.09 (q, *J* = 5.6 Hz, 1H, CHCH₃), 4.74 (q, *J* = 5.5 Hz, 1H, CHCH₃), 3.81–3.64 (m, 2H, NCH₂CH₂N), 3.58–3.39 (m, 2H, NCH₂CH₂N), 1.72 (d, *J* = 5.5 Hz, 3H, CH₃), 1.57 (d, *J* = 5.6 Hz, 3H, CH₃). ¹³C NMR (75 MHz, (CD₃)₂CO, 293K) δ 148.0, 126.8, 125.7, 123.2, 123.1, 114.1, 113.7, 87.2, 86.3, 44.6, 44.4, 19.4, 17.3. HRMS(ESI-MS) *m/z*: [M+H]⁺ Calcd for C₂₂H₁₉N₂O₂ 343.1361; Found 343.1422.

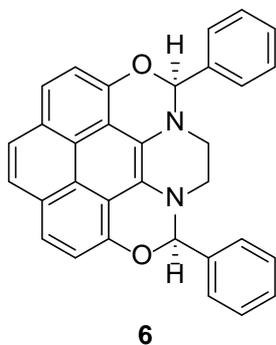
Synthesis of **5**



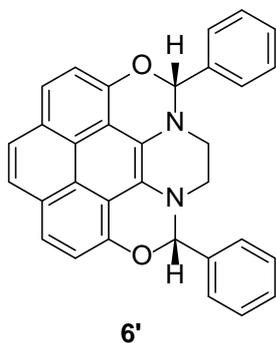
Pyrene-1,8-dione (0.15 g, 0.65 mmol) was dissolved in CH₃CN (100 mL), then 2.0 equiv. [2-(Hydroxymethyl-amino)-ethylamino]-methanol (190 μL, 1.30 mmol) was added and the reaction mixture was stirred at r.t. for 12 h to get a brown solution. The crude product was purified with silica gel column chromatography (EA) and gave compound **5** as yellow powder (0.16 g, 68%). ¹H NMR (400 MHz, (CD₃)₂CO, 293K) δ 7.90 (dd, *J* = 8.2, 7.6 Hz, 2H, Ar-*H*), 7.84 (d, *J* = 4.9 Hz, 2H, Ar-*H*), 7.45 (d, *J* = 2.6 Hz, 1H, Ar-*H*), 7.43 (d, *J* = 2.6 Hz, 1H, Ar-*H*), 5.01 (dd, *J* = 4.9, 3.9 Hz, 1H, CHCH₂OH), 4.76 (t, *J* = 3.4 Hz, 1H, CHCH₂OH), 4.23–4.11 (m, 4H, CHCH₂OH), 4.07–3.87 (m, 4H, NCH₂CH₂N). ¹³C NMR (75 MHz, (CD₃)₂SO, 293K) δ 147.6, 146.4,

125.3, 124.7, 122.2, 121.9, 119.6, 119.2, 118.4, 117.0, 113.2, 112.9, 111.1, 89.0, 88.4, 60.8, 60.0, 43.2, 42.9. HRMS(ESI-MS) m/z : $[M+H]^+$ Calcd for $C_{22}H_{19}N_2O_4$ 375.1272; Found 375.1278.

Synthesis of **6** and **6'**



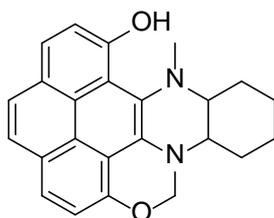
Pyrene-1,8-dione (0.10 g, 0.43mmol) was dissolved in CH_3CN (50 mL), then 2.0 equiv. *N,N'*-dibenzylethylenediamine (0.21 g, 0.86 mmol) was added and the reaction mixture was stirred at r.t. for 24 h to get a yellow solution. The crude product was purified with silica gel column chromatography (EA: hexane = 1:10, v/v) and gave yellow compound **6** as yellow powder (0.07 g, 35 %). 1H NMR (300 MHz, $(CD_3)_2CO$, 293K) δ 7.95 (d, $J = 8.3$ Hz, 2H, Ar-*H*), 7.90 (s, 2H, Ar-*H*), 7.63–7.55 (m, 4H, Ar-*H*), 7.45 (m, 8H, Ar-*H*), 5.85 (s, 2H, OCHAr), 3.26 (s, 4H, NCH_2). ^{13}C NMR (75 MHz, $(CD_3)_2CO$, 293K) δ 150.0, 137.6, 130.8, 129.6, 129.4, 127.1, 125.9, 123.6, 121.7, 120.8, 114.1, 112.6, 92.3, 45.3. HRMS(ESI-MS) m/z : $[M+H]^+$ Calcd for $C_{32}H_{23}N_2O_2$ 467.1754; Found 467.1756.



The crude product was purified with silica gel column chromatography (EA/hexane = 1/5) and gave yellow compound **6'** as yellow powder (0.06 g, 30 %). 1H NMR (300 MHz, $(CD_3)_2CO$, 293K) δ 7.88 (d, $J = 8.3$ Hz, 2H, Ar-*H*), 7.81 (s, 2H, Ar-*H*), 7.61 (m, 4H, Ar-*H*), 7.42 (m, 6H, Ar-*H*), 7.38 (d, $J = 8.3$ Hz, 2H, Ar-*H*), 5.48 (s, 2H, OCHAr),

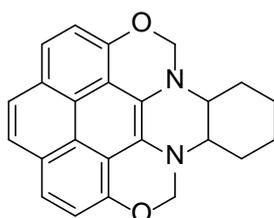
3.19 (t, $J = 7.5$ Hz, 2H, NCH₂), 2.84 (t, $J = 7.5$ Hz, 2H, NCH₂). ¹³C NMR (75 MHz, (CD₃)₂CO, 293K) δ 150.0, 148.7, 138.2, 137.6, 130.8, 130.4, 129.6, 129.6, 129.4, 129.1, 127.1, 125.9, 123.6, 123.4, 114.2, 114.1, 112.6, 92.3, 91.2, 45.3, 45.0. HRMS(ESI-MS) m/z : [M+H]⁺ Calcd for C₃₂H₂₃N₂O₂ 467.1754; Found 467.1756.

Synthesis of 7 and 7'



7'

Pyrene-1,8-dione (0.15 g, 0.65 mmol) was dissolved in CH₃CN (100 mL), then 2.0 equiv. N, N'-dimethylcyclohexyldiamine (86 μ L, 1.30 mmol) was added and the reaction mixture was stirred at r.t. for 12 h to get a brown solution. The crude product was purified with silica gel column chromatography (EA : hexane = 1:10, v/v) and gave compound 7' as yellow powder (0.15 g, 63%). ¹H NMR (400 MHz, CD₃CN, 293K) δ = 12.64 (s, 1H, OH), 7.96 (d, $J = 8.4$ Hz, 1H, Ar-H), 7.84 (d, $J = 8.3$ Hz, 1H, Ar-H), 7.79 (d, $J = 8.9$ Hz, 1H, Ar-H), 7.73 (d, $J = 8.9$ Hz, 1H, Ar-H), 7.42 (d, $J = 8.4$ Hz, 1H, Ar-H), 7.33 (d, $J = 8.3$ Hz, 1H, Ar-H), 5.41 (d, $J = 7.3$ Hz, 1H, NCH₂O), 4.93 (d, $J = 7.3$ Hz, 1H, NCH₂O), 3.40–3.28 (m, 2H, NCHCHN), 2.69 (s, 3H, CH₃), 2.60 (d, $J = 9.2$ Hz, 1H, NCH₂CH₂), 1.85 (d, $J = 8.6$ Hz, 1H, NCH₂CH₂), 1.79–1.66 (m, 2H, NCH₂CH₂), 1.54–1.33 (m, 4H, CH₂CH₂). ¹³C NMR (75 MHz, (CD₃)₂SO, 293K) δ 152.3, 148.5, 129.0, 126.0, 125.5, 124.6, 124.0, 123.2, 123.1, 122.4, 121.6, 114.7, 113.1, 112.9, 111.7, 75.5, 60.1, 47.4, 29.3, 24.8, 23.5. HRMS(ESI-MS) m/z : [M+H]⁺ Calcd for C₂₄H₂₃N₂O₂ 371.1516; Found 371.1516.

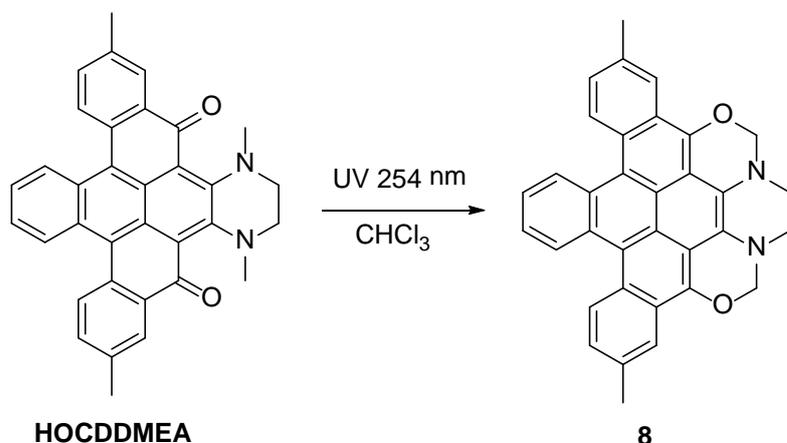


7

Compound 7' (0.010 g, 0.027 mmol) was dissolved in CD₃CN (0.6 mL), then exposed

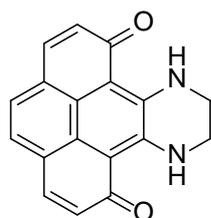
to room light for 20 hours at r. t. to get a bright yellow solution. The pure compound **7** was obtained (0.009 g, 90%). $^1\text{H NMR}$ (300 MHz, $(\text{CD}_3)_2\text{CO}$, 293K) δ 7.86 (d, $J = 8.1$ Hz, 2H, Ar- H), 7.82 (s, 2H, Ar- H), 7.45 (d, $J = 8.3$ Hz, 2H, Ar- H), 5.45 (d, $J = 6.3$ Hz, 2H, NCH_2O), 4.56 (d, $J = 4.6$ Hz, 2H, NCH_2O), 3.11 (s, 2H, NCHCHN), 2.47 – 2.37 (m, 2H, NCH_2CH_2), 1.98–1.87 (m, 2H, CH_2CH_2), 1.47 (d, $J = 4.8$ Hz, 2H, CH_2CH_2). HRMS(ESI-MS) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}_2$ 369.1514; Found 369.1564.

Synthesis of **8**



The HOCDDEA (0.01 g, 0.02 mmol) was dissolved in CDCl_3 (0.5 mL) and then placed under the 254 nm UV lamp for 20 h to give clean transformation to product **8** as orange powder (0.01 g, 100%). $^1\text{H NMR}$ (400 MHz, CDCl_3 , 293K) δ 9.10 (d, $J = 8.8$ Hz, 2H, Ar- H), 9.06 (dd, $J = 6.3, 3.5$ Hz, 2H, Ar- H), 8.31 (s, 2H, Ar- H), 7.63 (dd, $J = 6.3, 3.4$ Hz, 2H, Ar- H), 7.55 (d, $J = 8.0$ Hz, 2H, Ar- H), 5.08 (s, 4H, OCH_2N), 3.62 (s, 2H, $\text{NCH}_2\text{CH}_2\text{N}$), 2.69 (s, 6H, PhCH_3). HRMS(ESI-MS) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{34}\text{H}_{25}\text{N}_2\text{O}_2$ 492.1832; Found 492.1835.

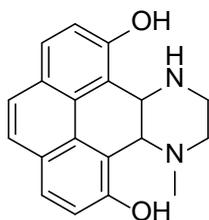
Synthesis of compound **9**



Pyrene-1,8-dione (0.15 g, 0.65 mmol) was dissolved in CH_3CN (100 mL), then 2.0 equiv. ethylenediamine (86 μL , 1.30 mmol) was added and the reaction mixture was

stirred at r.t. for 12 h to get a red solution. The crude product was purified with silica gel column chromatography (EA) and gave red compound **9** as red powder (0.10 g, 67%). ¹H NMR (300 MHz, CDCl₃, 293K) δ 12.56 (s, 2H, NH), 7.77 (d, *J* = 9.5 Hz, 2H, Ar-*H*), 7.56 (s, 2H, Ar-*H*), 6.84 (d, *J* = 9.5 Hz, 2H, Ar-*H*), 3.90 (s, 4H, CH₂). ¹³C NMR (75 MHz, CDCl₃, 293K) δ 185.7, 146.2, 140.5, 128.0, 126.1, 125.5, 121.2, 108.0, 38.3. HRMS(ESI-MS) *m/z*: [M+Na]⁺ Calcd for C₁₈H₁₂N₂O₂Na 311.0804; Found 311.0791.

Synthesis of compound 10



The reaction of Pyrene-1,8-dione (8 mg, 0.034 mmol) and N-methylethylenediamin (6 μL, 0.068 mmol) was monitored by ¹H NMR spectrum in CD₃CN. The reaction mixture was stirred at r. t. for 30 min to get a brown solution. ¹H NMR (300 MHz, CD₃CN, 293K) δ 7.63 (dd, *J* = 13.6, 4.7 Hz, 2H, Ar-*H*), 7.43 (s, 2H, Ar-*H*), 7.10 (d, *J* = 8.6 Hz, 1H, Ar-*H*), 7.03 (d, *J* = 8.6 Hz, 1H, Ar-*H*), 4.73 (d, *J* = 3.9 Hz, 1H, ArCHNCH₃), 3.98 (d, *J* = 3.9 Hz, 1H, ArCHNH), 3.27 (s, 3H NCH₂CH₂NCH₃), 2.92 (t, *J* = 1.8 Hz, 2 H, NCH₂CH₂NCH₃), 2.90 (t, *J* = 1.8 Hz, 2H, NCH₂CH₂NCH₃). HRMS(ESI-MS) *m/z*: [M+H]⁺ Calcd for C₁₉H₁₉N₂O₂ 307.1441; Found 307.1448. The brown solution was placed under the 254 nm UV lamp for 20 h to give clean transformation to product **9** as red solution.

Determination of fluorescence quantum yield of synthesized compounds.

Fluorescence quantum yields of compounds **1**, **4**, **5**, **6**, **7**, and **9** were calculated using the following equation.

$$\Phi_{F_{sample}} = \Phi_{F_{standard}} \frac{Abs_{standard}}{Abs_{sample}} \frac{\Sigma F_{sample}}{\Sigma F_{standard}} \frac{\eta_{sample}^2}{\eta_{standard}^2}$$

So,

$$\Phi_{F_{sample}} = \Phi_{F_{standard}} \frac{Slope_{sample}}{Slope_{standard}} \frac{\eta_{sample}^2}{\eta_{standard}^2}$$

Where Φ_F stands for fluorescence quantum yields; Abs and ΣF denote the absorbance

at the excitation wavelength and the measured integrated fluorescence intensity, and η is the refractive index of the solvent used. Fluorescein ($\Phi_F = 0.95$) in 0.1 M NaOH solution was selected as standards.

Figures and Tables

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brown

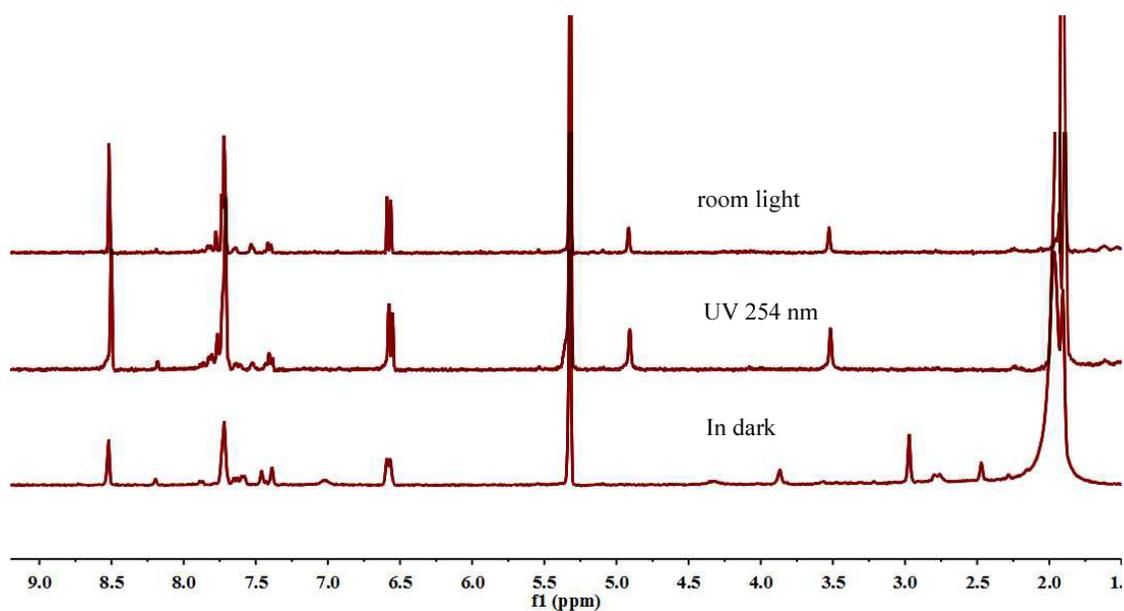


Figure S1. NMR spectra of the reaction of Pyrene-1,8-dione with N,N'-dimethylethylenediamine in the different conditions (solvent: CD₃CN).

2. Spectral data of 1-10

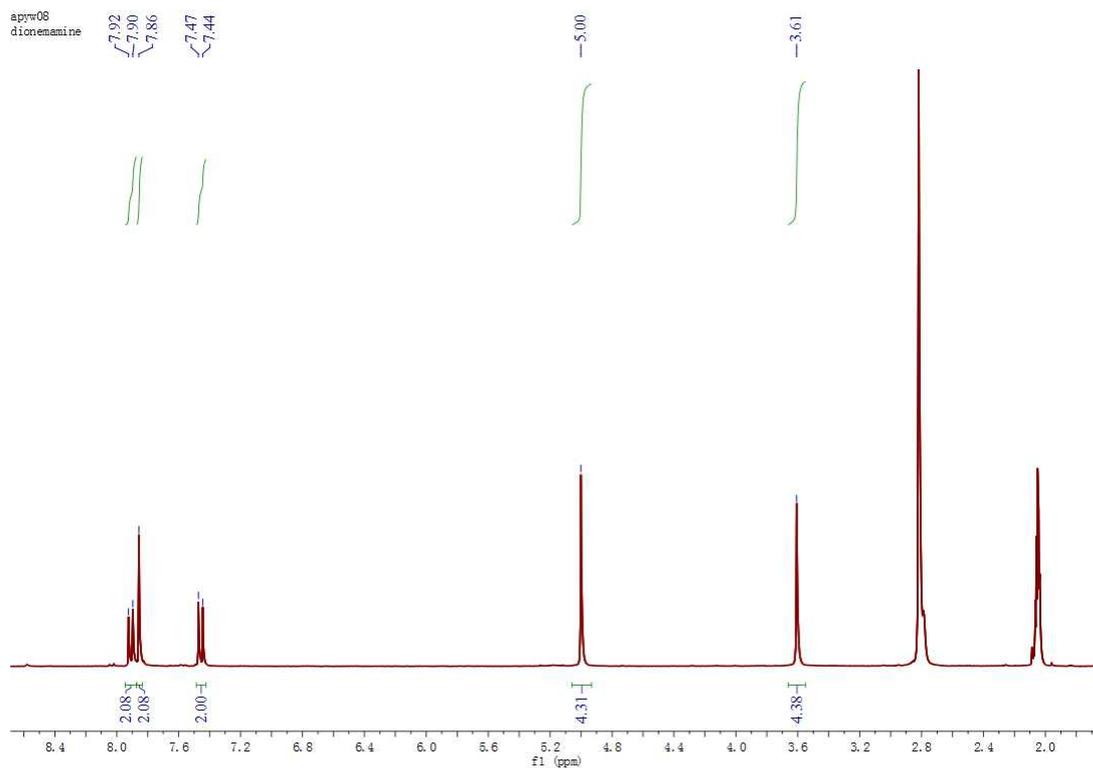


Figure S2. ^1H NMR spectrum of compound **1**

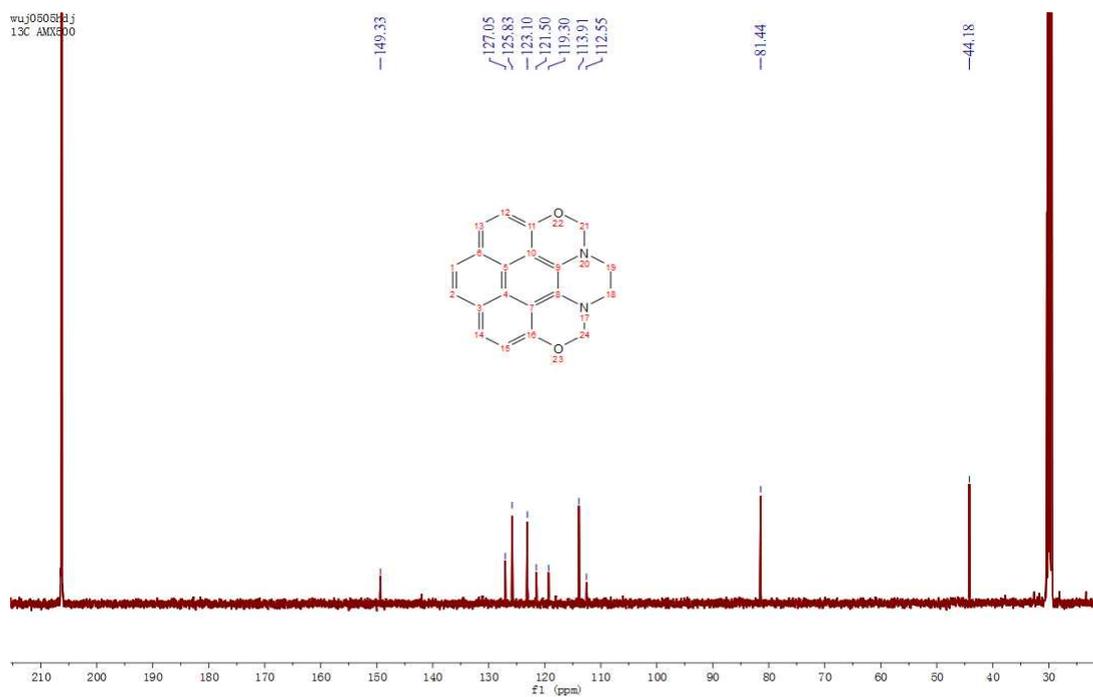


Figure S3. ^{13}C NMR spectrum of compound **1**

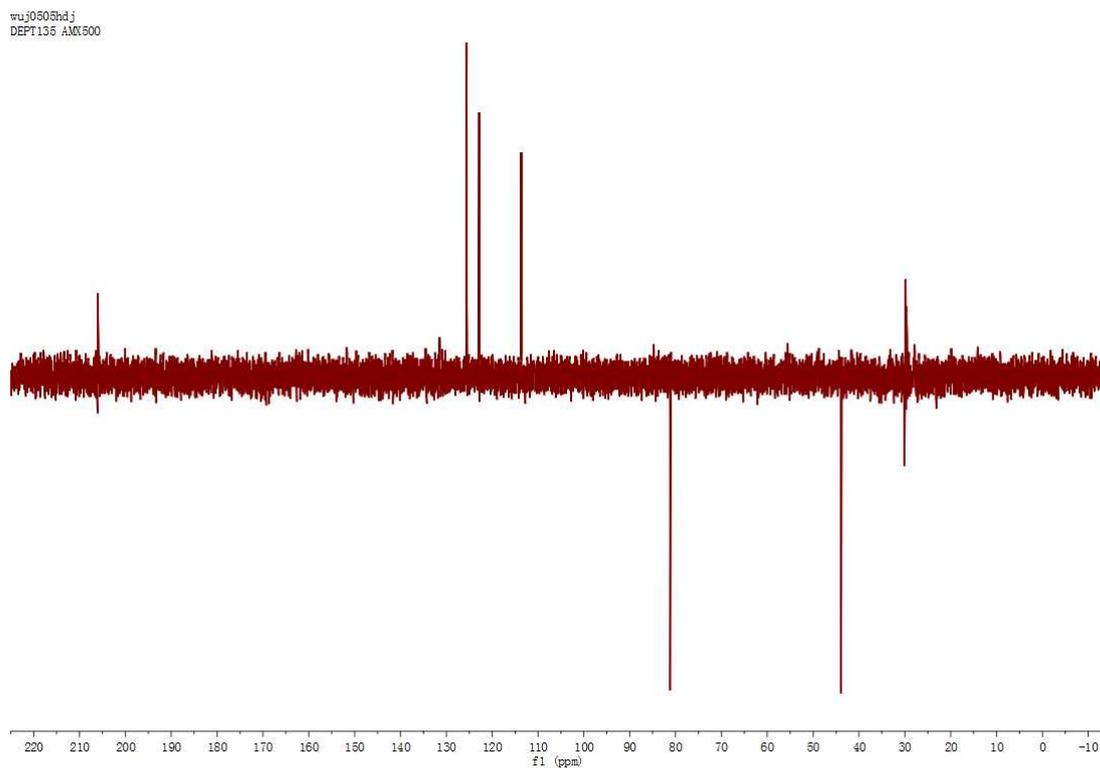


Figure S4. DEPT spectrum of compound **1**

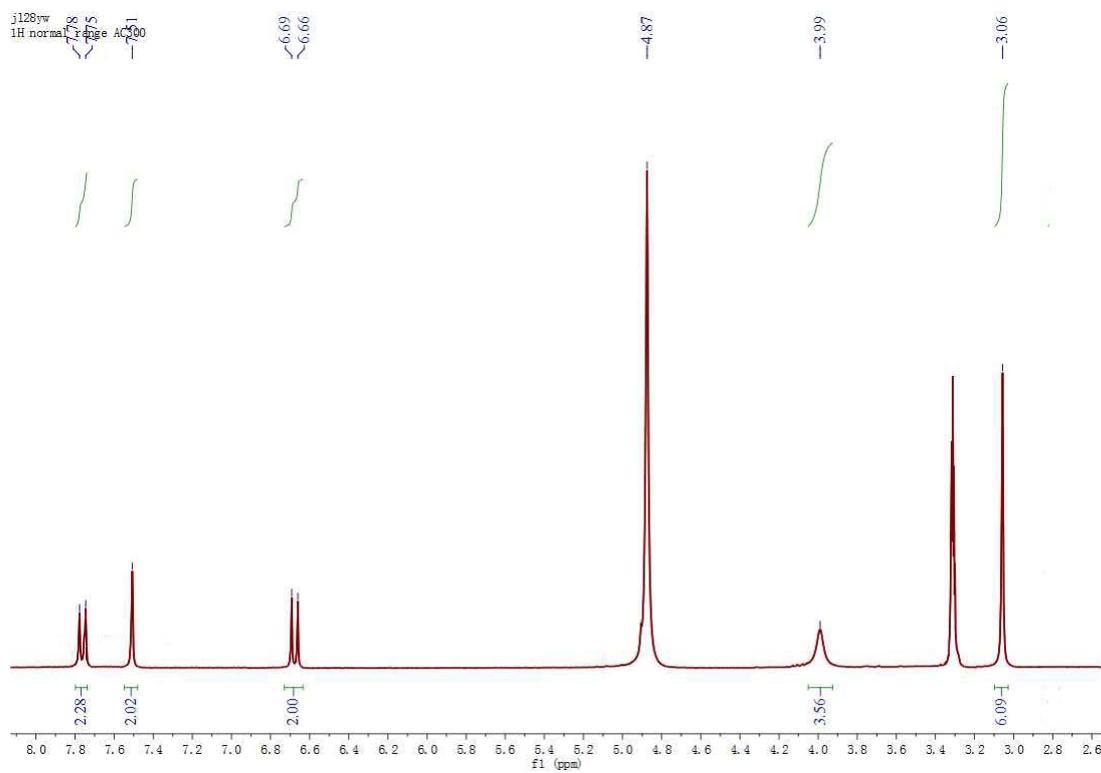


Figure S5. ^1H NMR spectrum of compound **2**

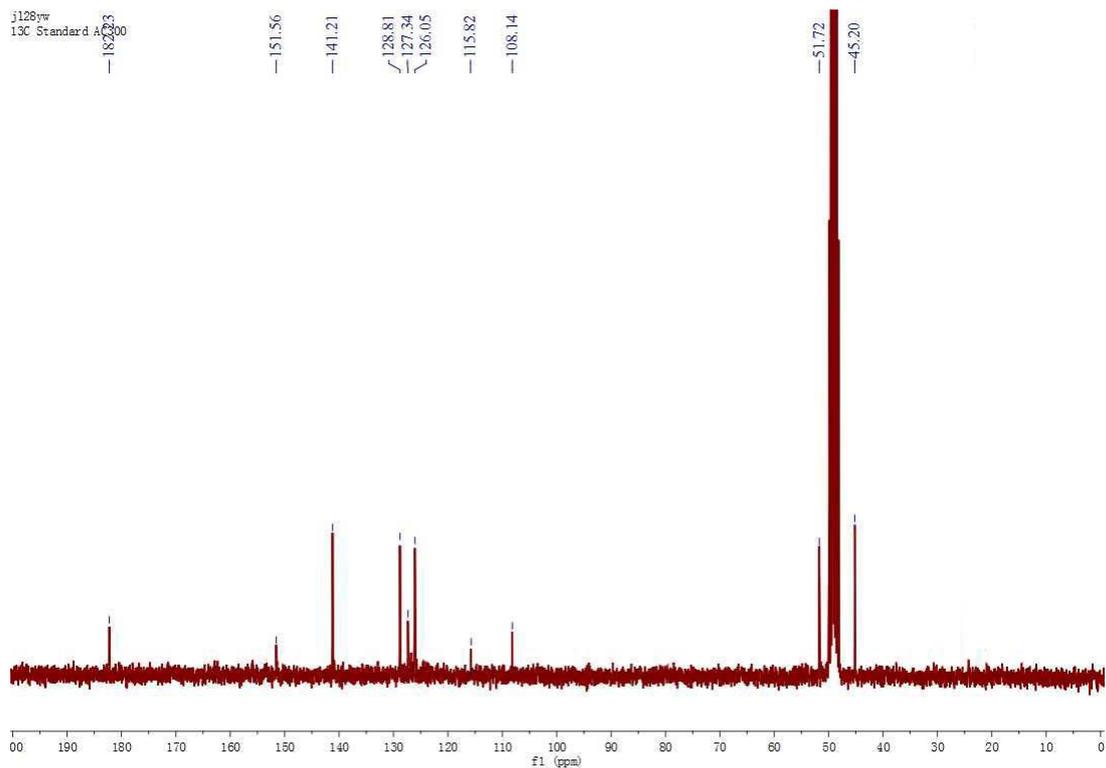


Figure S6. ¹³C NMR spectrum of compound 2.

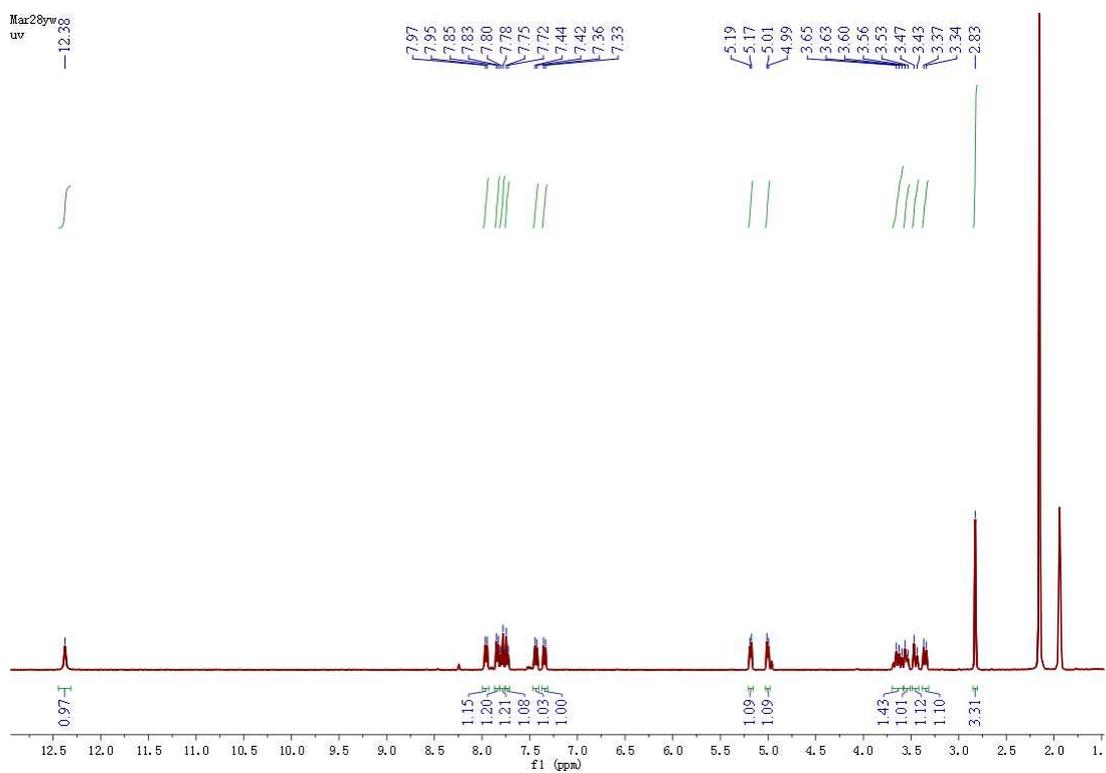


Figure S7. ¹H NMR spectrum of compound 3

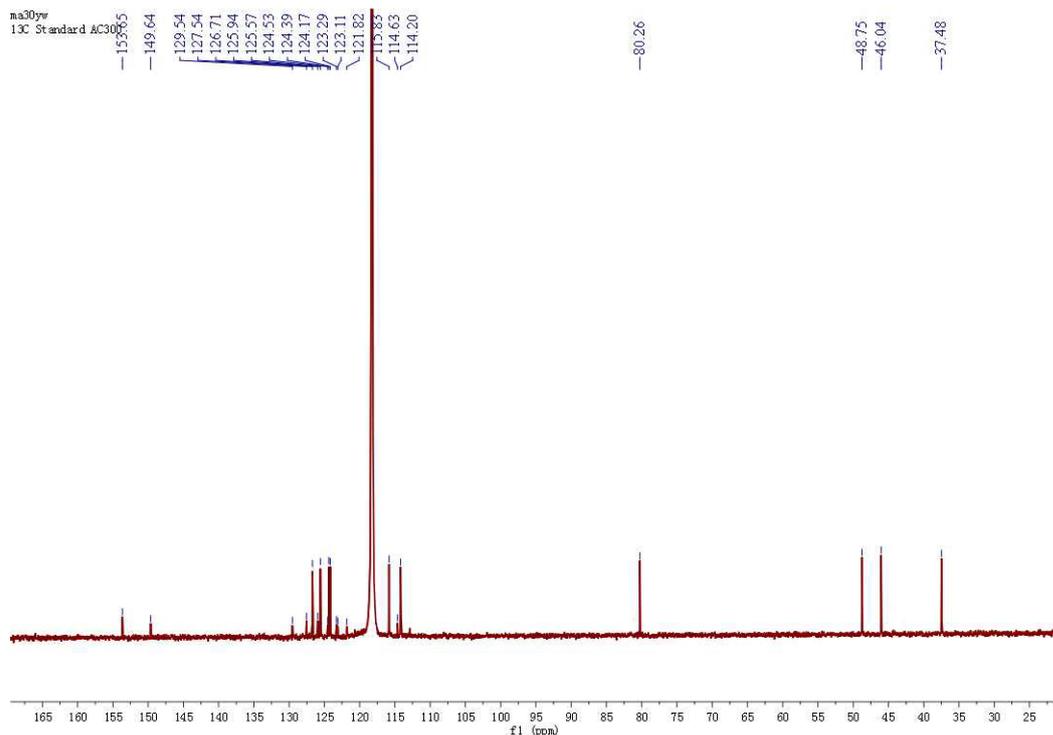


Figure S8. ^{13}C NMR spectrum of compound **3**

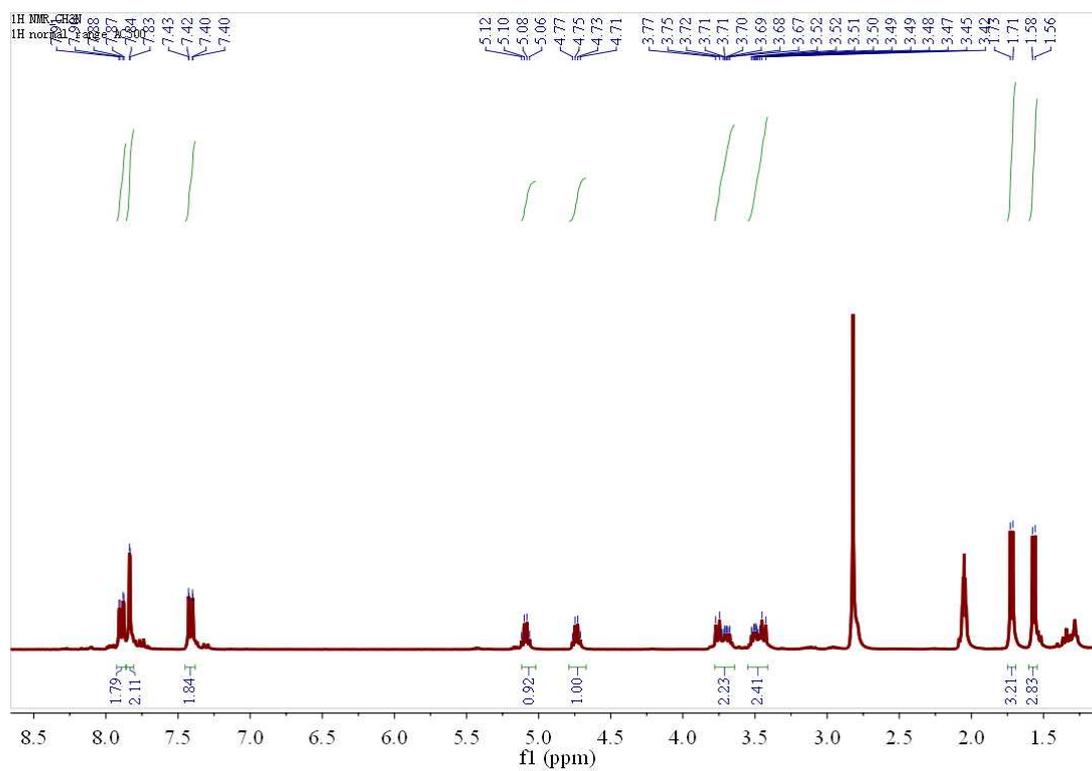


Figure S9. ^1H NMR spectrum of compound **4**

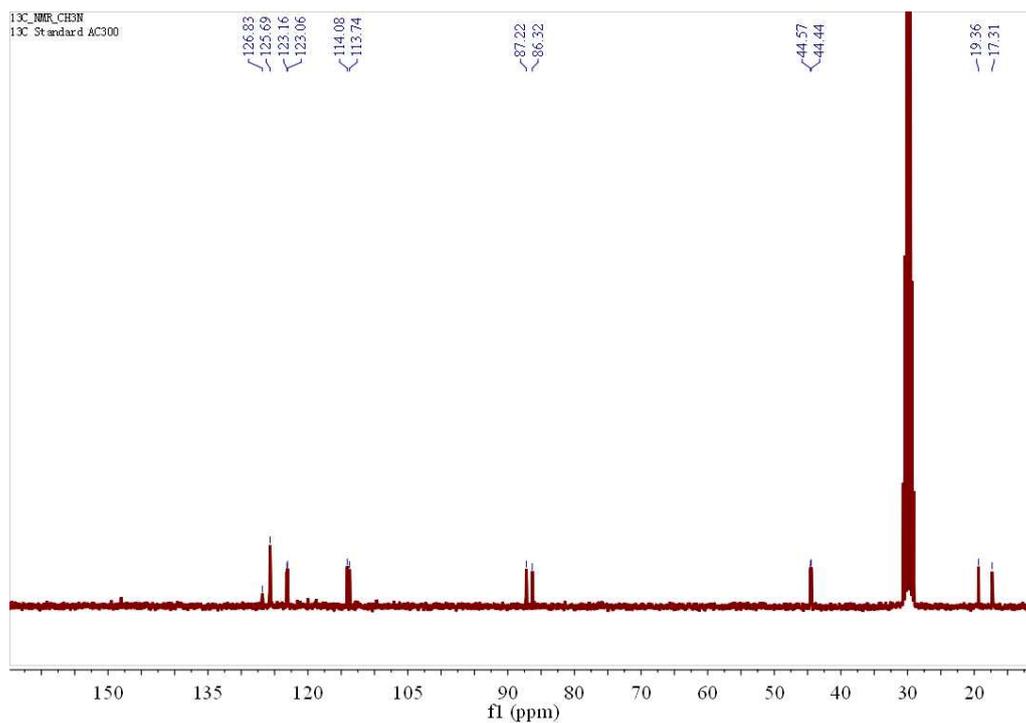


Figure S10. ^{13}C NMR spectrum of compound **4**

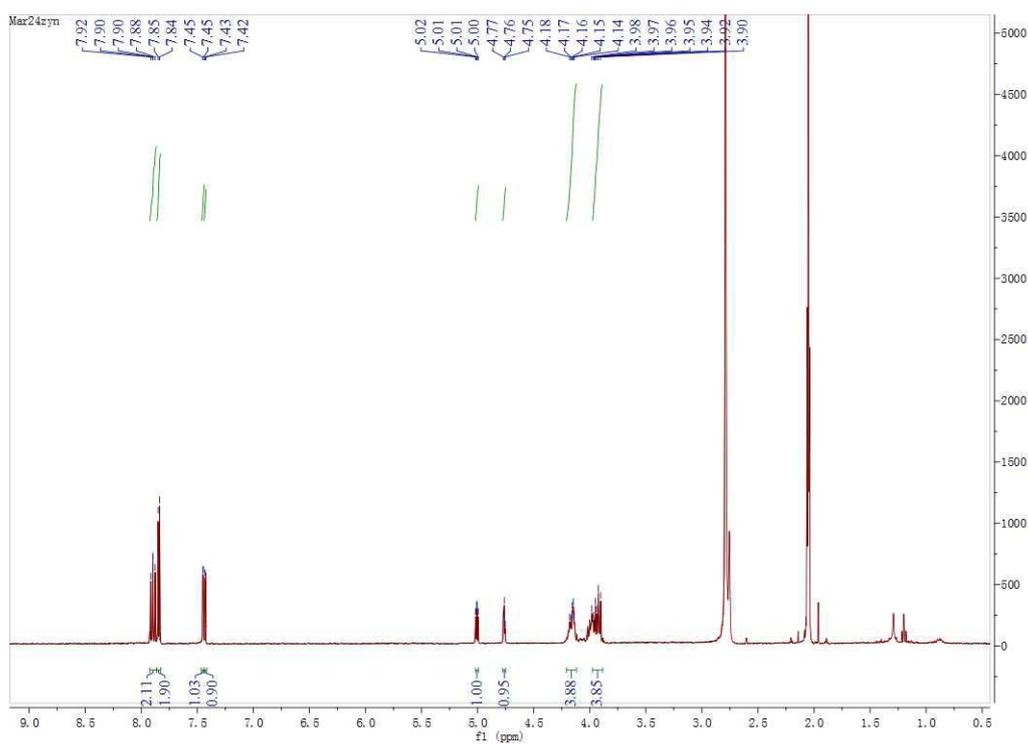


Figure S11. ^1H NMR spectrum of compound **5**

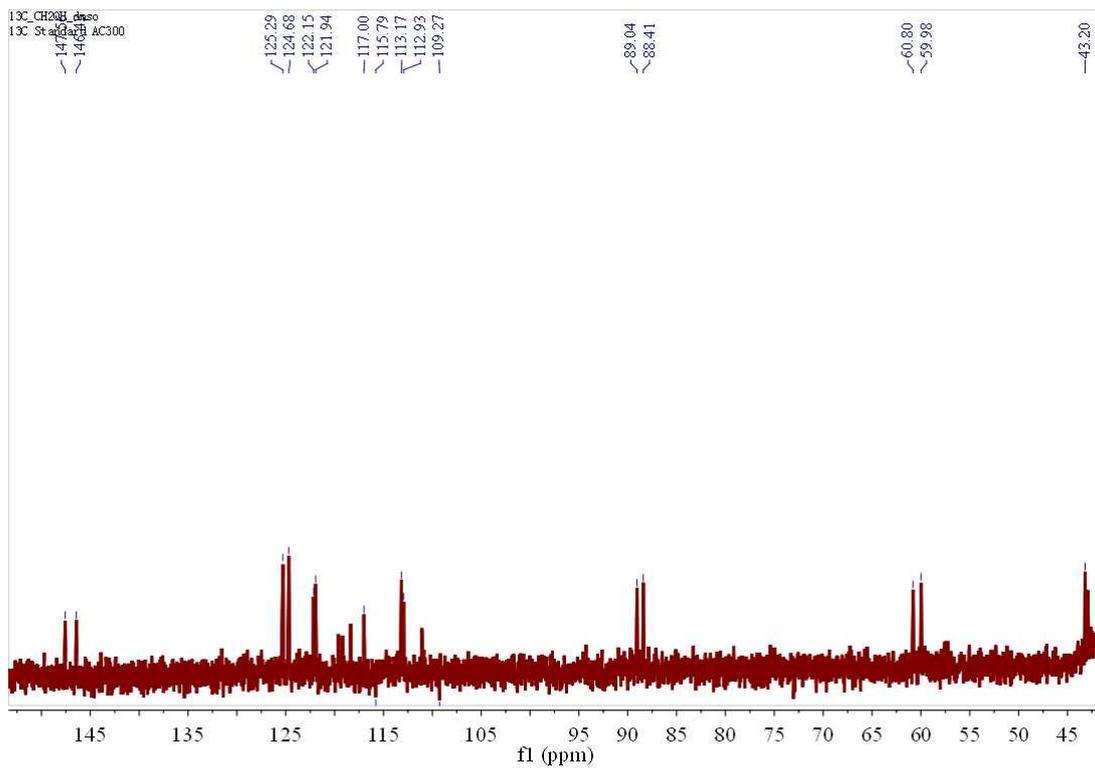


Figure S12. ^{13}C NMR spectrum of compound 5

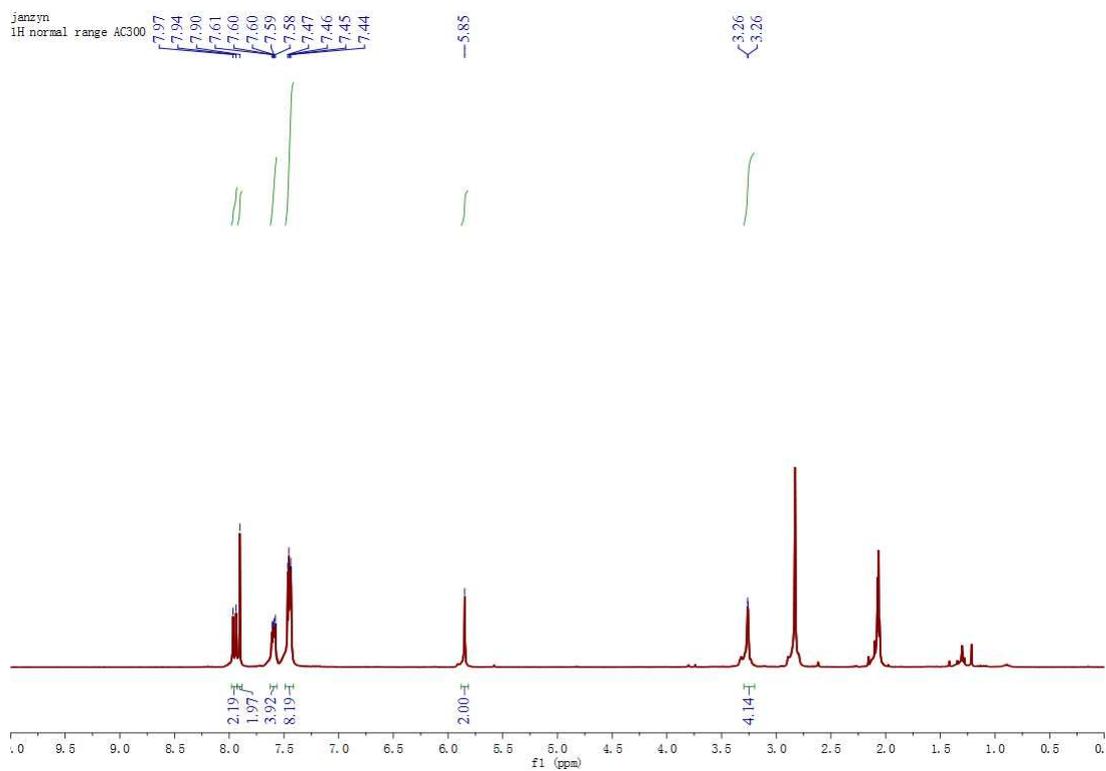


Figure S13. ^1H NMR spectrum of compound 6

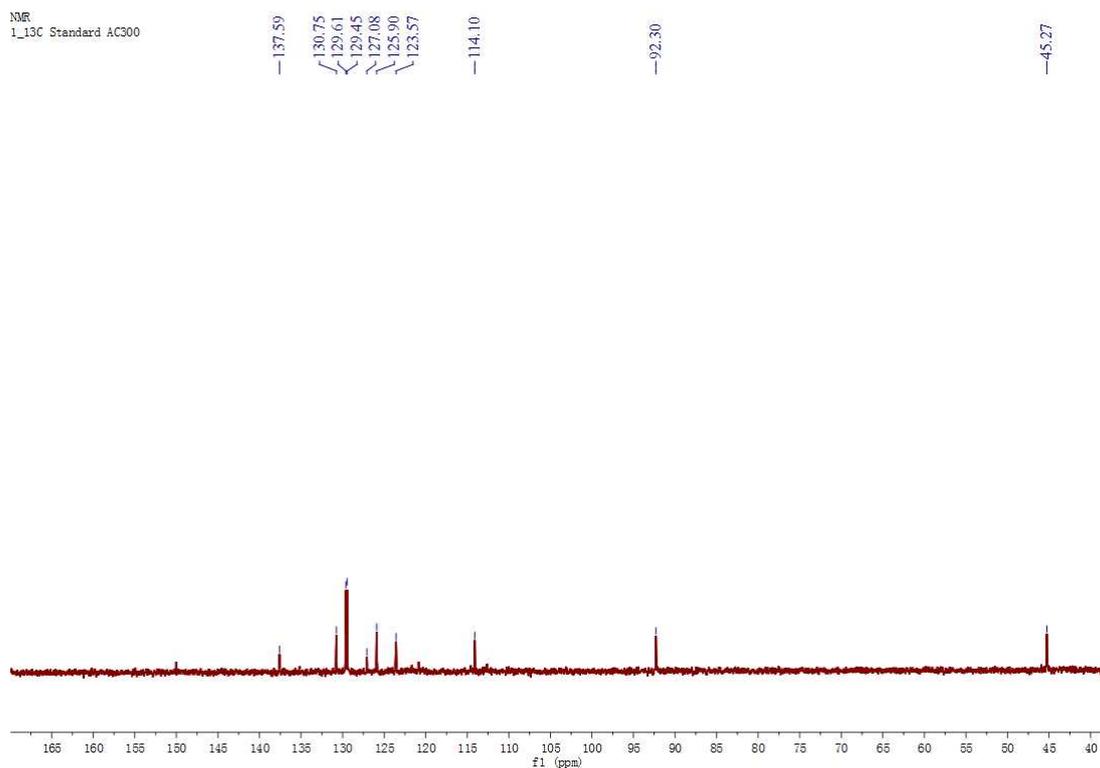


Figure S14. ^{13}C NMR spectrum of compound **6**

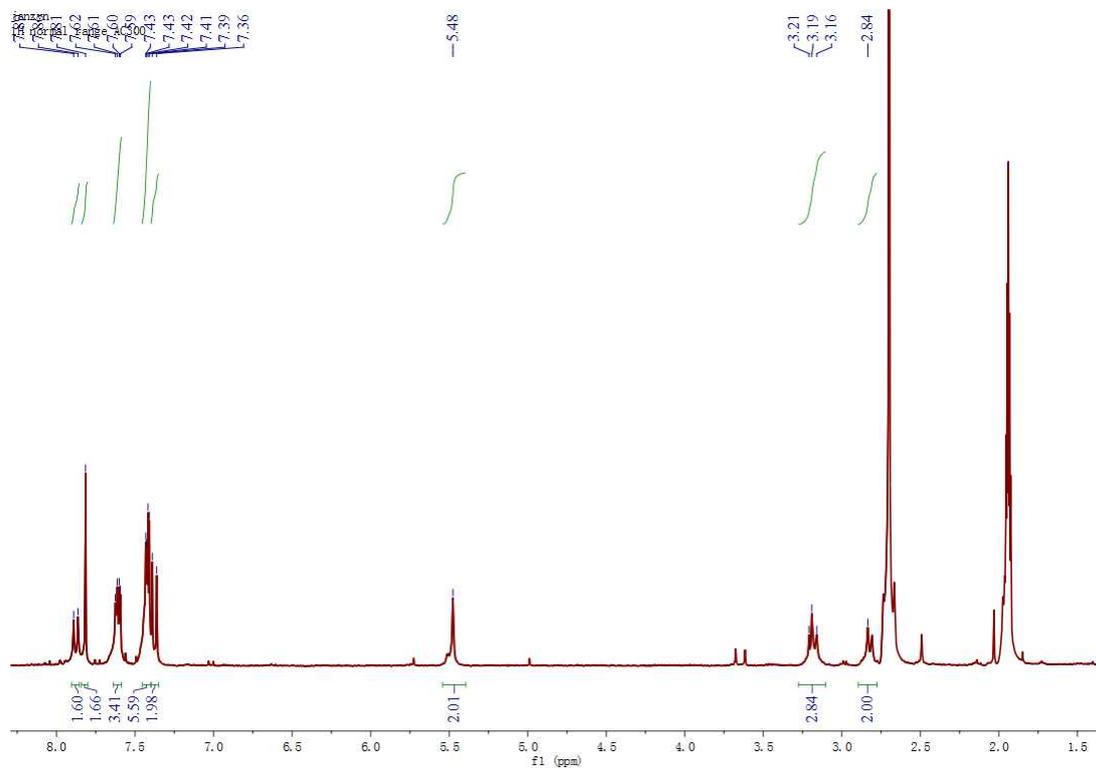


Figure S15. ^1H NMR spectrum of compound **6'**

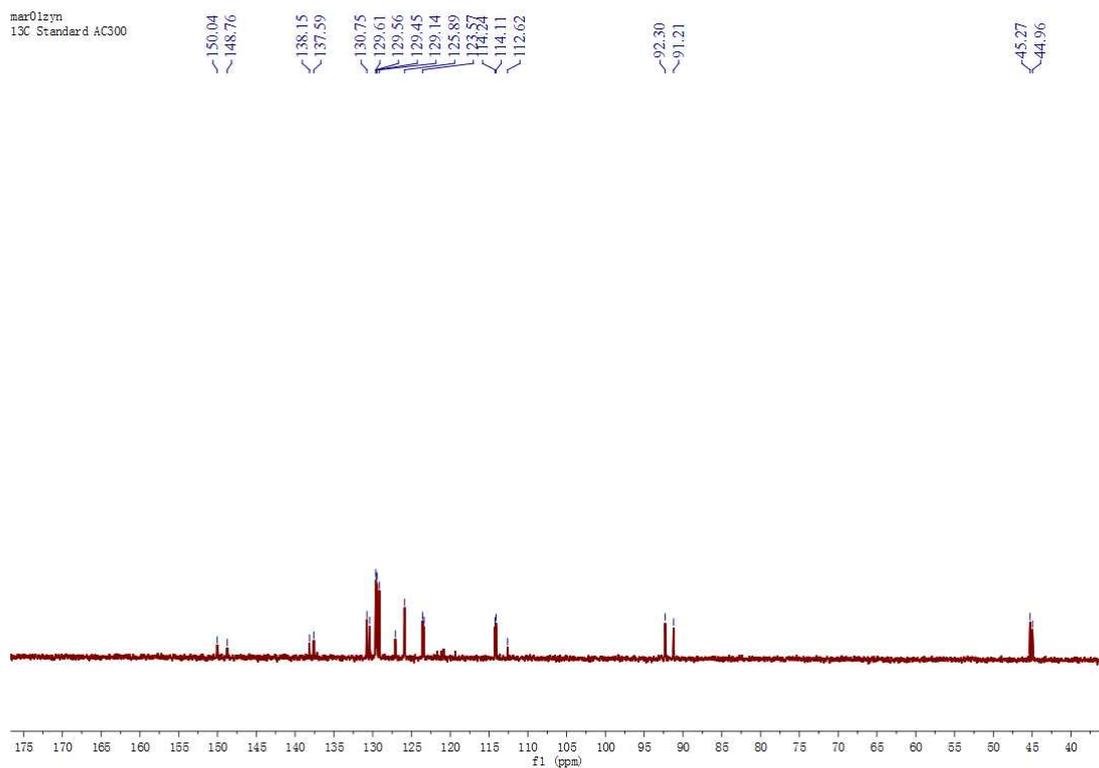


Figure S16. ^{13}C NMR spectrum of compound **6'**

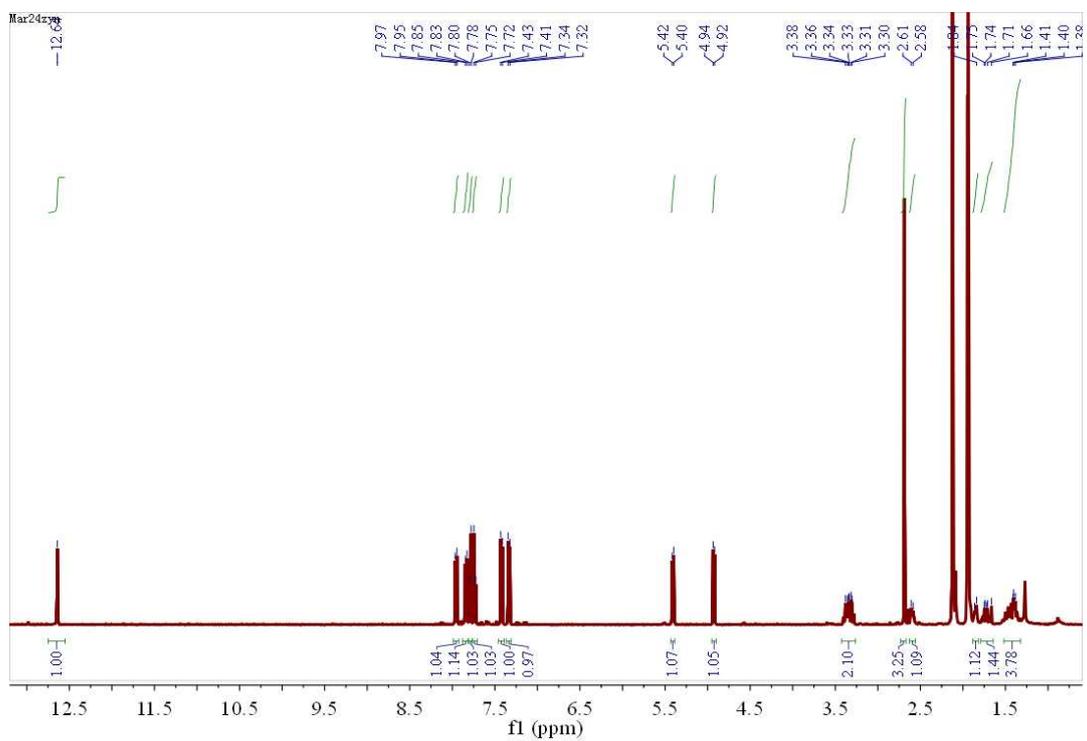


Figure S17. ^1H NMR spectrum of compound **7'** (solvent: CD_3CN).

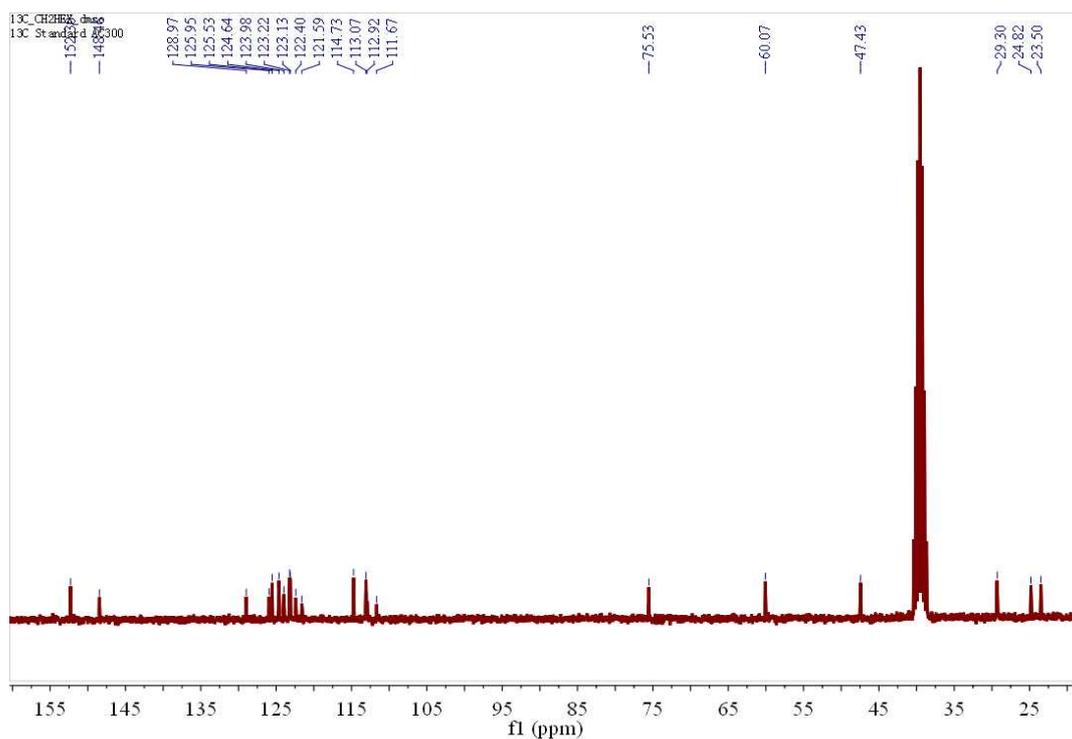


Figure S18. ^{13}C NMR spectrum of compound 7'

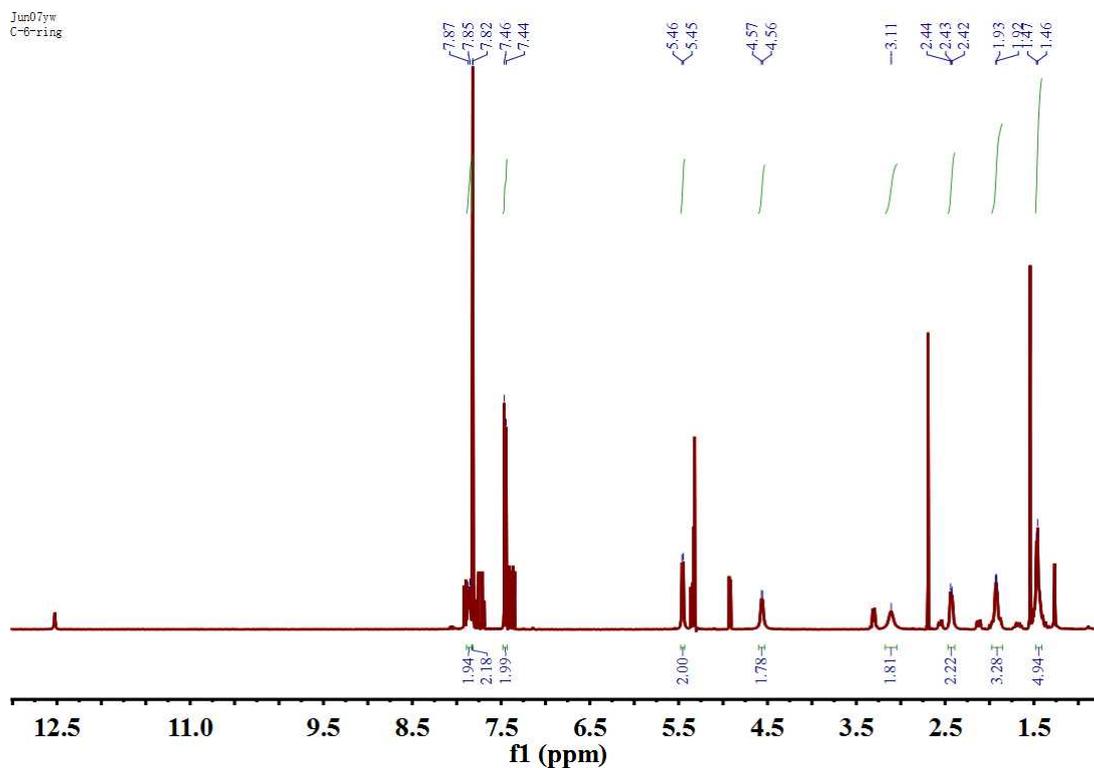


Figure S19. ^1H NMR spectrum of compound 7 (solvent: CD_3CN).

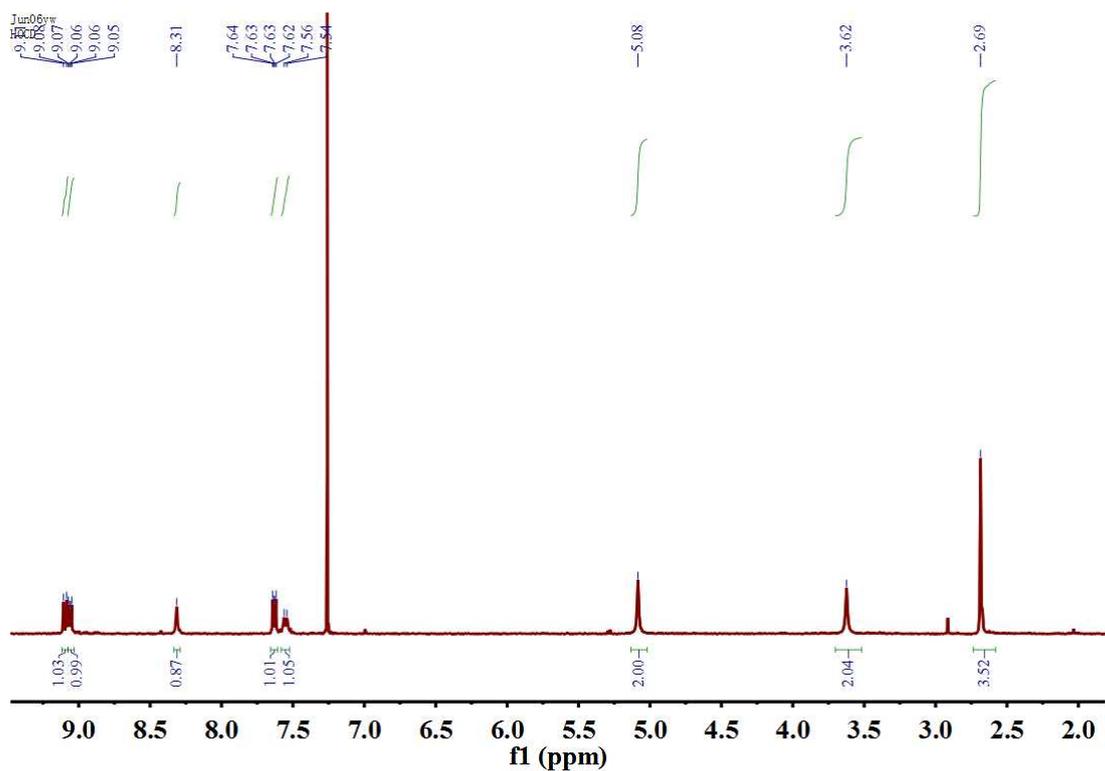


Figure S20. ^1H NMR spectrum of compound **8** (CDCl_3).

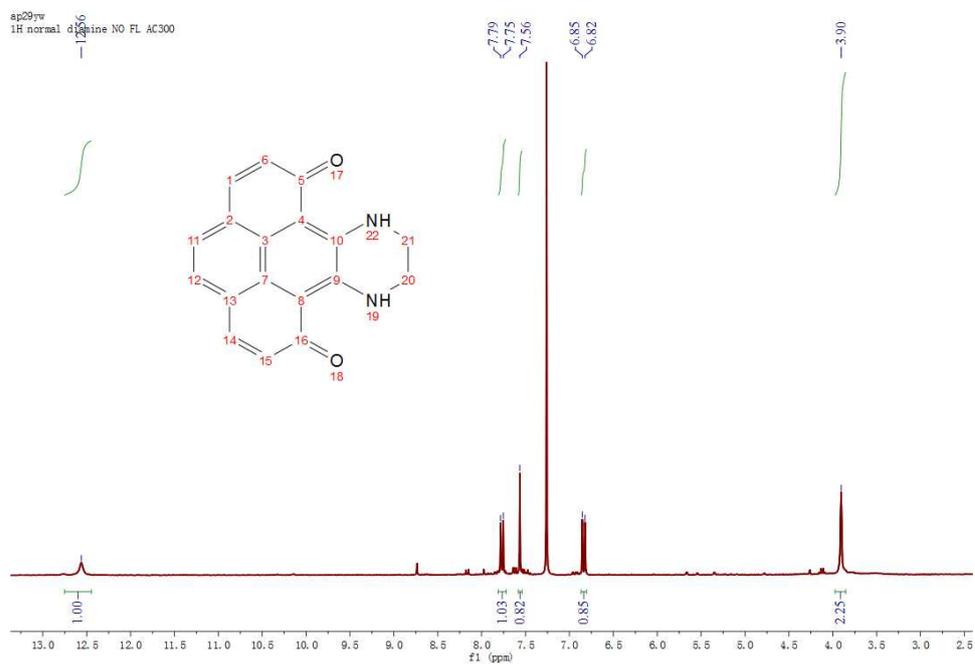


Figure S21. ^1H NMR spectrum of compound **9** (Solvent CDCl_3).

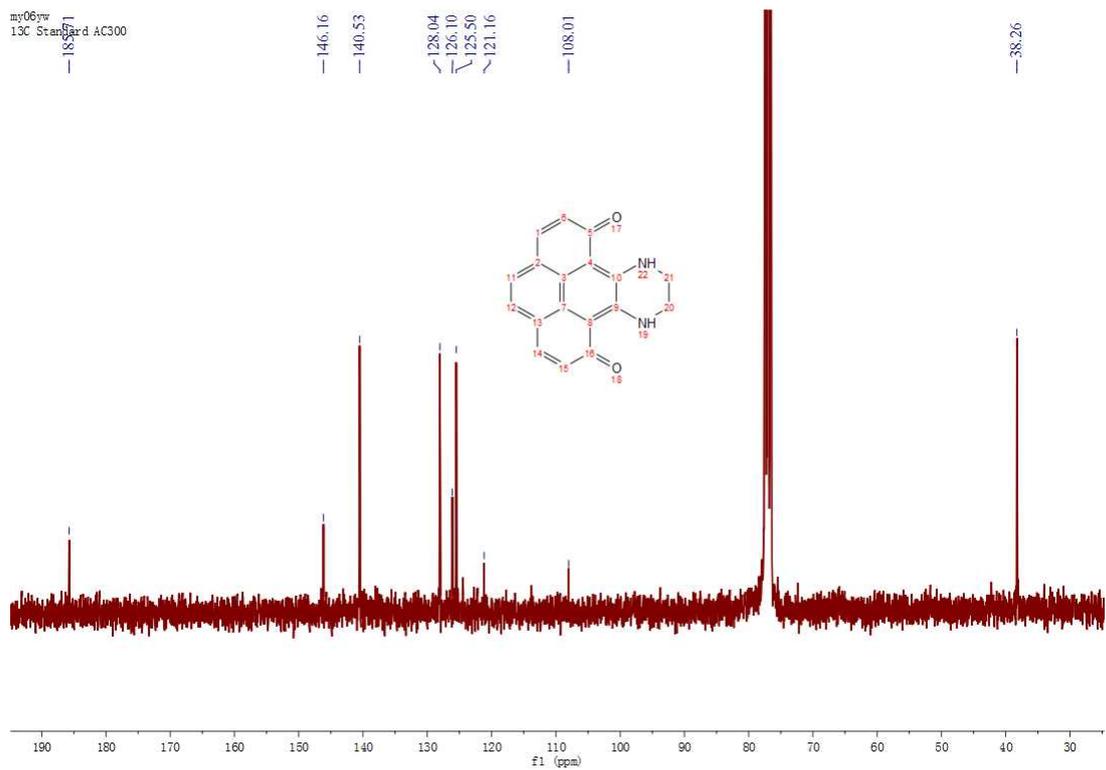


Figure S22. ^{13}C NMR spectrum of compound **9**

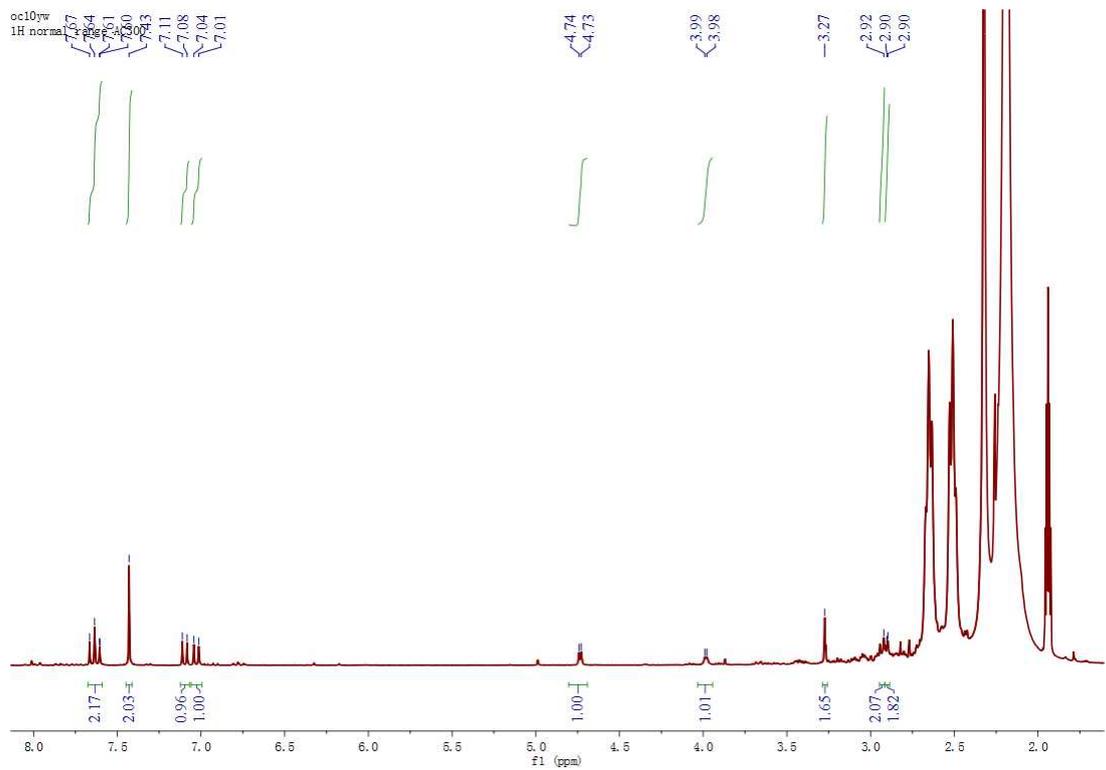


Figure S23. ^1H NMR spectrum of compound **10**

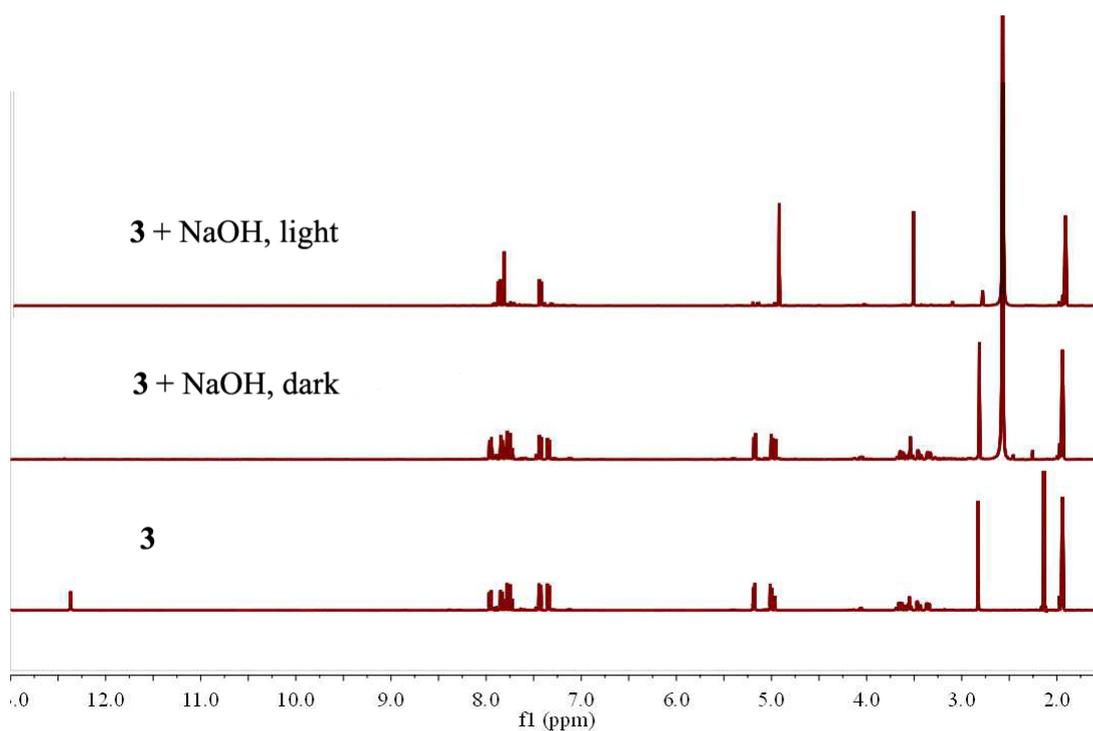


Figure S24. NMR spectra of reaction mixture of compound **3** and NaOH in the different conditions. (NaOH was dissolved in D₂O, Solvent: CD₃CN).

Ju127yw
UV

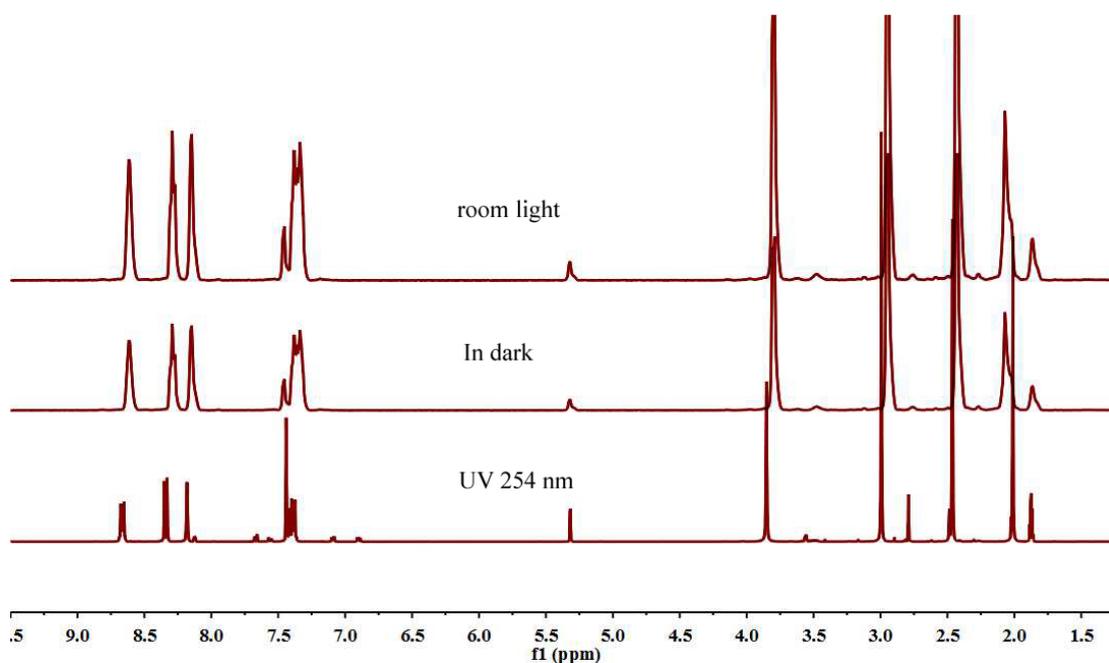


Figure S25. NMR spectra of compound **HOCD**, which was exposed to the different conditions.

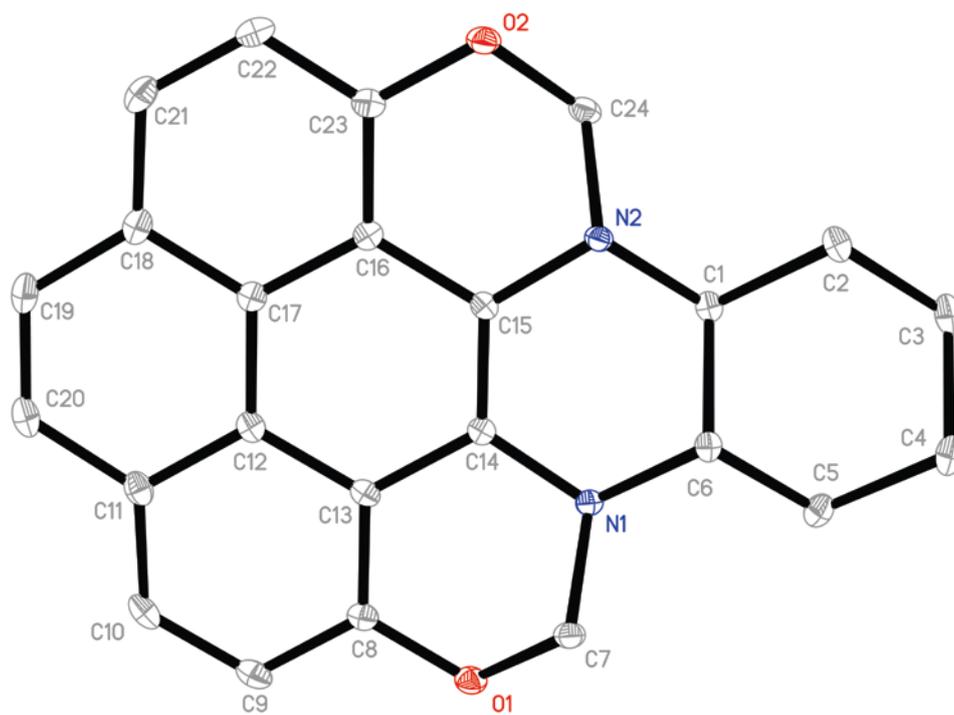


Figure S26. The molecular structure of compound **7**. Thermal ellipsoids are shown at the 30% probability level.

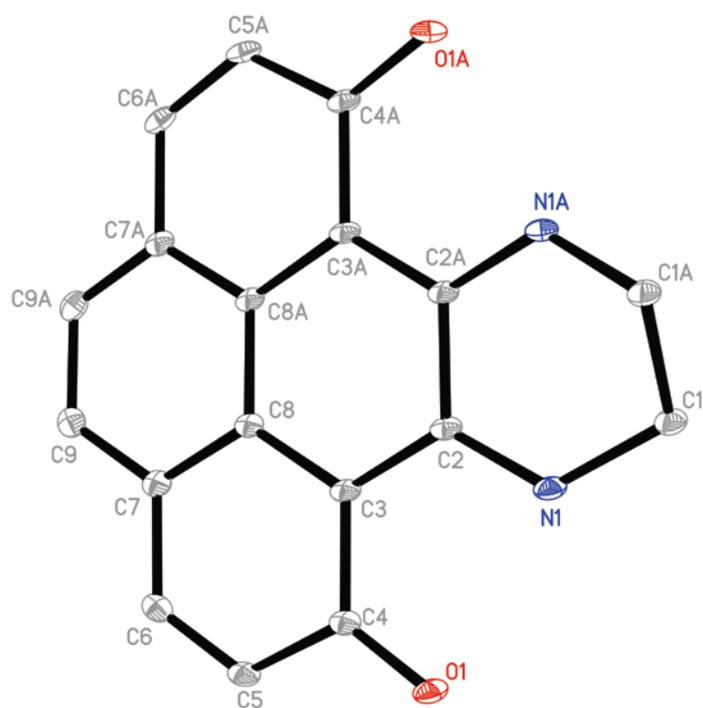


Figure S27. The molecular structure of complex **9**. Thermal ellipsoids are shown at the 30% probability level.

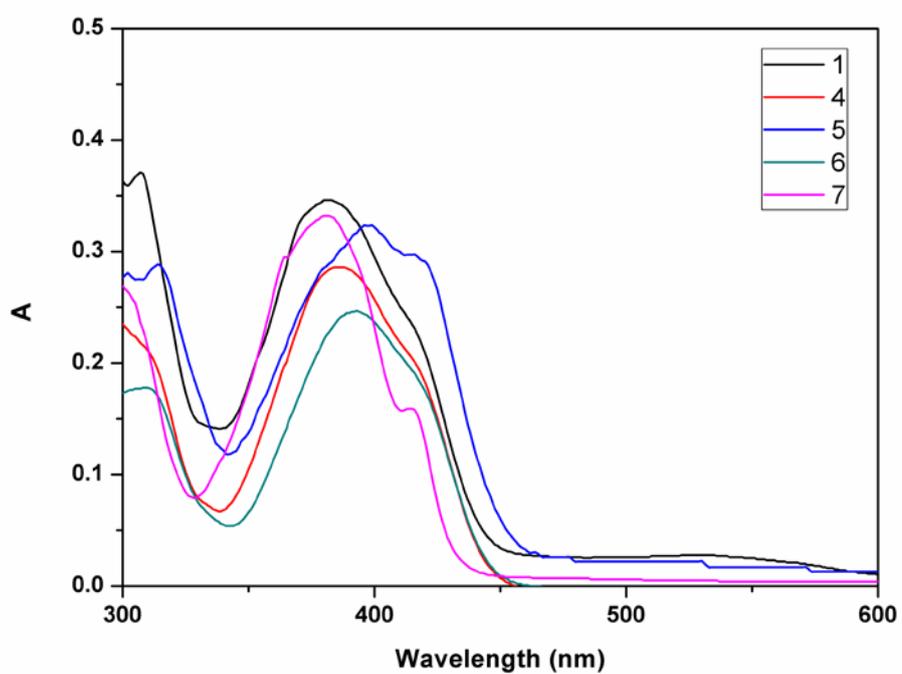


Figure S28. UV-Vis spectra of **1**, **4**, **5**, **6**, **7** in methanol. (100 $\mu\text{mol/L}$)

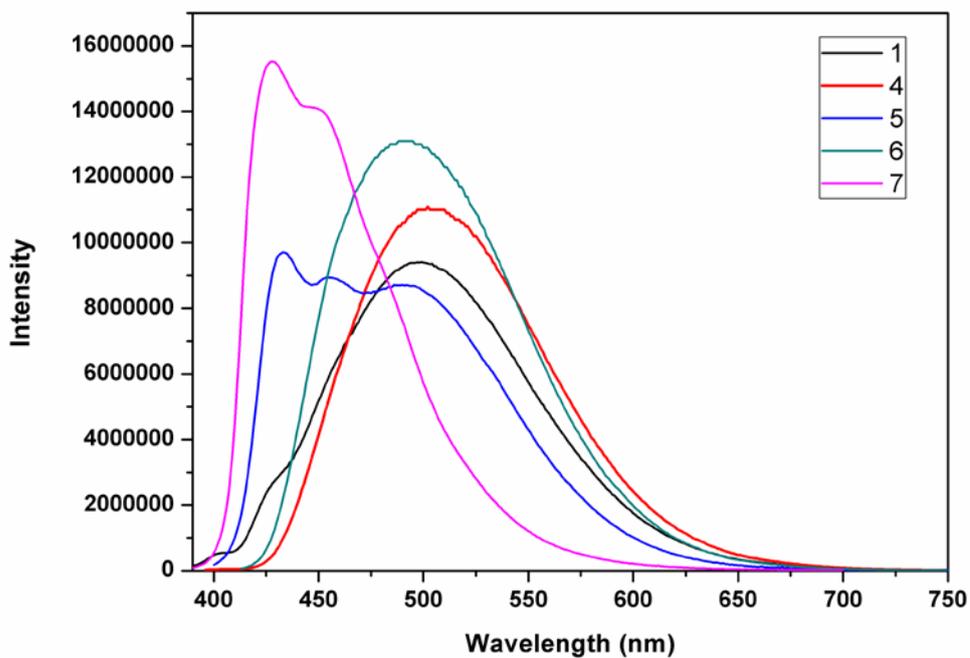


Figure S29. Fluorescence spectra of **1**, **4**, **5**, **6**, **7** in methanol. ($10 \mu\text{mol/L}$, $\lambda_{\text{ex}} = 380 \text{ nm}$).

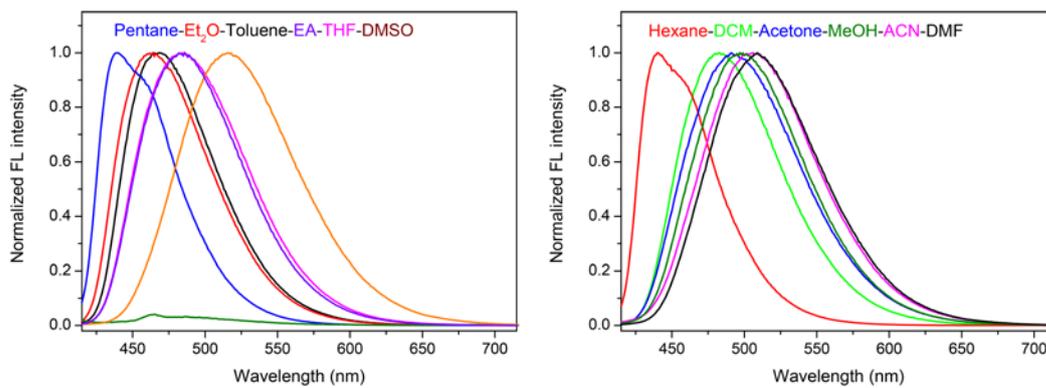


Figure S30. Fluorescence emission spectra of compound **6** ($5 \mu\text{M}$) in different solvents. Excitation wavelength was 400 nm .

Table S-1. The absorbance and fluorescence spectra data of compound **6** at 5×10^{-6} M in Different Solvents

Solvent	Dielectric constant (ϵ)	Absorption λ_{abs} (nm)	Emission λ_{em} (nm)	Stokes shift (nm)
Pentane	1.84	393	440	47
Hexane	1.89	393	441	48
Et ₂ O	4.33	395	464	69
Toluene	2.38	396	468	68
DCM	8.93	397	483	86
EA	6.02	396	484	88
THF	7.58	396	484	88
Acetone	20.7	397	491	94
MeOH	32.7	392	497	105
ACN	37.5	396	506	100
DMF	36.7	400	509	109
DMSO	46.7	402	516	114

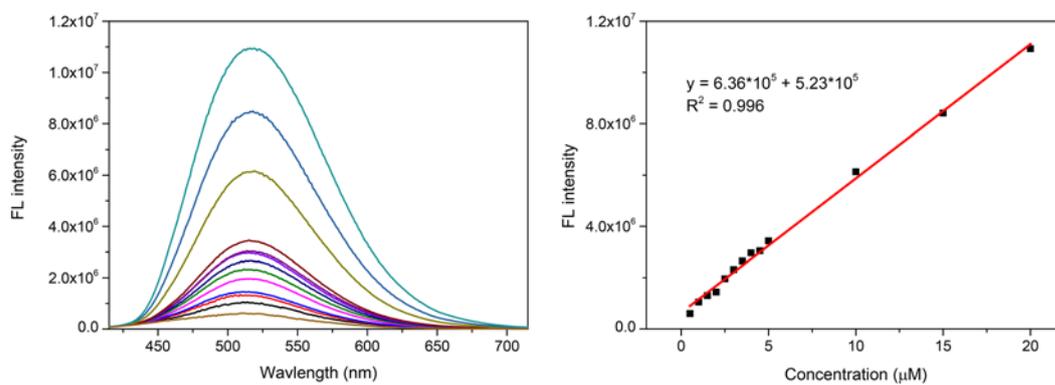


Figure S31. Fluorescence emission spectra of compound **6** at different concentrations (0.5 μM-20 μM) in acetonitrile.

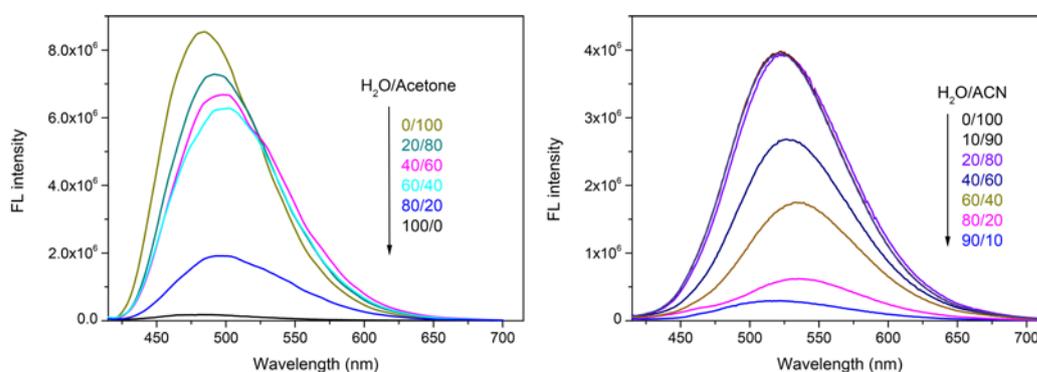


Figure S32. Fluorescence emission spectra of compound **4** (left, 5 μM) and compound **6** (right, 5 μM) in mixed solvents containing different amounts of water.