Electronic Supplementary Information

Highly Selective Fluorescent Detection for $Pd^{2+/4+}$ Species Based on the Catalyzed Aromatic Claisen Rearrangement

Xuejing Li[a], Huanhuan Huang[a], Yuqing Zhu[a], Hong Zhao[a,] and Zhifei Wang[a,b,]**

[a] School of Chemistry and Chemical Engineering, Southeast University, Nanjing, 211189, China.

[b] Jiangsu key laboratory of advanced metallic materials, Nanjing, 211189.

* Corresponding author: Dr. Zhifei Wang, Email: zfwang@seu.edu.cn； Dr.. Hong Zhao, Email: zhaohong@seu.edu.cn;

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1. Experimental Section

1.1 Materials and instruments

All general reagents and solvents were purchased from commercial sources and used without further purification. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on an AVANCE AV-300 spectrometer and an AVANCE AV-500 spectrometer. High resolution mass spectra (HRMS) were recorded with a Micromass Q-TOF Mass spectrometer. UV-visible absorption spectra were determined on a Shimadu UV-3600 spectrophotometer. Fluorescence spectra were measured on a HORIBA FL-4 Max spectrometer. Fluorescence quantum yield and fluorescence lifetime were measured on a Horiba Jobin Yvon Inc. Fluorolog 3-TSCPC.

1.2 Synthesis

1.2.1. Synthesis of 4-bromo-*N*-butyl-1,8-naphthalimide (**2**)

4-bromo-1,8-naphthalic anhydride (**1**) (5 g, 18 mmol) and *N*-butylamine (1.05 mL, 36 mmol) were dissolved in 50 mL acetic acid, and the solution was refluxed for 8 h. After cooling down to room temperature, 300 mL water was added to the reaction mixture. Then yellowish sediment was collected by filtration. The crude product was purified by column chromatography on silica gel with ethyl acetate and petroleum (1:15, V:V) to give **2**. [1] Yield: 74% (4.43 g). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.66 (d, J = 8.0 Hz, 1H), 8.57(d, J = 12.0 Hz, 1H), 8.41(d, J = 8.0 Hz, 1H), 8.04(d, J = 8.0 Hz, 1H), 7.84 (t, J = 8.0 Hz, 1H), 4.18 (t, J = 8.0 Hz, 2H), 1.68-1.76 (m, 2H), 1.40-1.50 (m, 2H), 0.98 (t, J = 8.0 Hz, 3H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 13.8, 20.3, 30.1, 40.3, 114.6, 122.3, 123.1, 128.0, 129.0, 130.1, 130.6, 131.0, 131.1, 131.9, 133.1, 163.5. HRMS (ESI-Q-TOF): (M^+, $C_{16}H_{14}BrNO_2$), calcd: 332.0286; found: 332.0292.

1.2.2. Synthesis of *N*- butyl -4-methoxy-1,8-naphthalimide (**3**)

Sodium (0.46 g, 20 mmol) was added into methanol, and sodium methylate (30 mL) was obtained when all sodium was dissolved. Then, compound **2** (2 g, 6.2 mmol) was added into the reaction solution and refluxed overnight. After cooling to room temperature, the precipitate was filtered and washed three times with distilled water.

Compound **3** was obtained as yellow needles. [1] Yield: 88% (1.56 g). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.60 (d, *J* = 8.0 Hz, 1H), 8.56 (d, *J* = 12.0 Hz, 2H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 4.17 (t, *J* = 8.0 Hz, 2H), 4.13 (s, 3H), 1.68-1.75 (m, 2H), 1.40-1.50 (m, 2H), 0.98 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 13.8, 20.4, 30.3, 40.1, 56.1, 105.1, 114.6, 115.2, 122.5, 123.4, 125.9, 128.5, 131.4, 133.3, 160.7, 163.9, 164.5. HRMS (ESI-Q-TOF): (M^+, $C_{17}H_{17}NO_3$), calcd: 284.1287; found: 284.1281.

1.2.3. Synthesis of *N*-butyl-4-hydroxy-1,8-naphthalimide (**4**)

A mixture of compound **3** (1.5 g, 5.3 mmol) and 50 ml of concentrated HI (57%) was refluxed for 6 h. After cooling to room temperature, and adjusting pH to neutral with sodium hydroxide solution, the precipitate was filtered to give compound **4** as yellow needles. [1] Yield: 88% (1.25 g). ^{1}H NMR (400 MHz, d_6-DMSO, ppm): 11.86 (s, 1H), 8.55 (d, *J* = 8.0 Hz, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 7.78 (t, *J* = 6.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 4.03 (t, *J* = 8.0 Hz, 2H), 1.56-1.64 (m, 2H), 1.30-1.39 (m, 2H), 0.92 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (300 MHz, d_6-DMSO): δ 13.5, 19.7, 29.6, 39.0, 109.8, 112.5, 121.7, 122.3, 125.3, 128.6, 129.0, 130.9, 133.3, 160.1, 162.8, 163.5. HRMS (ESI-Q-TOF): (M^+, $C_{16}H_{15}NO_3$), calcd: 270.1130; found: 270.1122.

1.2.4. Synthesis of probe **1**

Compound **4** (1 g, 3.7 mmol) was dissolved in 20 mL DMF, and the resulting solution was stirred at 0 °C. When K_2CO_3 (1 g, 7.2 mmol) was added, the color of reaction solution changed from yellow to orange immediately. Then allyl bromide (0.53 g, 4.4 mmol) was added. After reacting 24 h, 150 mL of water was added and the product was extracted into dichloromethane (3×50 mL). The aqueous layer was discarded. The crude product was purified by column chromatography on silica gel with ethyl acetate and hexane (1:10, V:V) as eluent and crystallized from the eluent mixture of solvents to give probe **1** as crystals. **[1]** Yield: 78% (0.89 g); m.p. 128.6-130.2. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 8.61 (d, *J* = 6.0 Hz, 2H), 8.55 (d, *J* = 9.0Hz, 1H), 7.71 (t, *J* = 9.0 Hz, 1H), 7.04 (d, *J* = 6.0 Hz, 1H), 6.12-6.24 (m, 1H), 5.55 (d, *J* = 18.0 Hz, 1H), 5.42 (d, *J* = 12.0 Hz ,1H), 4.86 (d, *J* = 3.0 Hz, 2H), 4.17 (t, *J* = 6.0 Hz,

2H), 1.67-1.77 (m, 2H), 1.39-1.49 (m, 2H), 0.98 (t, J = 7.5 Hz, 3H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 13.8, 20.4, 30.3, 40.1, 69.5, 106.2, 115.3, 118.7, 122.5, 123.6, 125.9, 128.6, 129.4, 131.5, 131.9, 133.2, 159.6, 163.9, 164.5. HRMS (ESI-Q-TOF): (M^+, $C_{19}H_{19}NO_3$), calcd: 310.1443; found: 310.1441. Anal Calcd for $C_{19}H_{19}NO_3$: C 73.77, H 6.19, N 4.43 %; found C 73.79, H 6.21, N 4.46 %.

1.2.5. Synthesis of **5**

Probe **1** was refluxed in *N*-methylpyrrolidone overnight to give **5**. [2] Yield: 38 %; m.p. 181.2-182.7. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 8.58 (d, J = 6.0 Hz, 1H), 8.52 (d, J = 9.0 Hz, 1H), 8.40 (s, 1H), 7.70 (t, J = 7.5 Hz, 1H), 6.39 (s, 1H), 6.04-6.15 (m, 1H), 5.38 (s, 1H), 5.34 (d, J = 3.0 Hz ,1H), 4.17 (t, J = 6.0 Hz, 2H), 3.69 (d, J = 6.0 Hz, 2H), 1.66-1.76 (m, 2H), 1.38-1.48 (m, 2H), 0.98 (t, J = 7.5 Hz, 3H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 13.7, 20.3, 30.2, 35.3, 40.1, 115.1, 118.2, 119.9, 122.5, 122.8, 125.87, 128.2, 128.7, 131.1, 134.8, 134.9, 156.1, 164.0, 164.5. HRMS (ESI-Q-TOF): (M^+, $C_{19}H_{19}NO_3$), calcd: 310.1443; found: 310.1439. Anal Calcd for $C_{19}H_{19}NO_3$: C 73.77, H 6.19, N 4.43 %; found C 73.80 H, 6.21, N 4.44 %.

1.3 Fluorescence study

Preparation of parent stock solutions used for fluorescence study in aqueous solvent

solution	Reagent	Solvent	Conc.
A	Probe 1	DMSO	10.0 mM
B	Na_2PdCl_4	H_2O	2 mM
C	K_2PdCl_6	H_2O	2 mM
D	Pd-Cube	H_2O	2 mM
E	Pt-CTAB	H_2O	2 mM
F	K_2PtCl_4	H_2O	2 mM
G	H_2PtCl_6	H_2O	2 mM
H	NaCl	H_2O	2 mM
I	$CaCl_2$	H_2O	2 mM
J	$MnCl_2$	H_2O	2 mM

K	$CoCl_2$	H_2O	2 mM
L	$CuCl_2$	H_2O	2 mM
M	$ZnCl_2$	H_2O	2 mM
N	$CdCl_2$	H_2O	2 mM
O	$NiCl_2$	H_2O	2 mM
P	$AuCl_3$	H_2O	2 mM
Q	AgCl	H_2O	2 mM
R	$FeCl_3$	H_2O	2 mM

In all experiments, various metal solutions were added to 4 mL $Na_2CO_3/NaHCO_3$ buffer (pH=10) solution. Solution A (5.0 μL, [Probe **1**]$_{final}$=12.5 μM) was added to the mixture, and the samples were incubated in a water bath before fluorescence measurement.

2. ^{1}H NMR and ^{13}C NMR Data

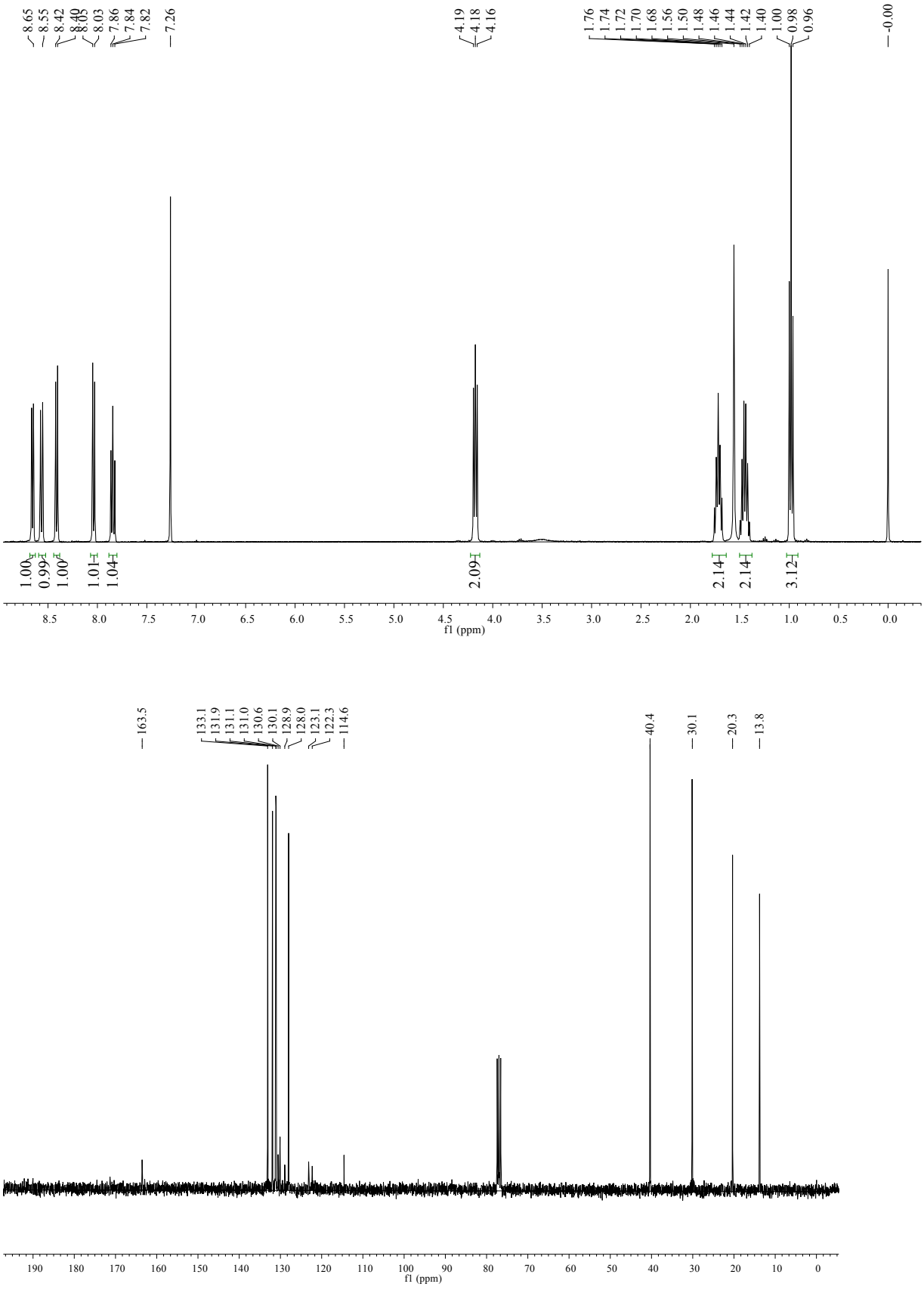


Fig. S1 ^{1}H NMR and ^{13}C NMR spectra of compound **2** ($CDCl_3$)

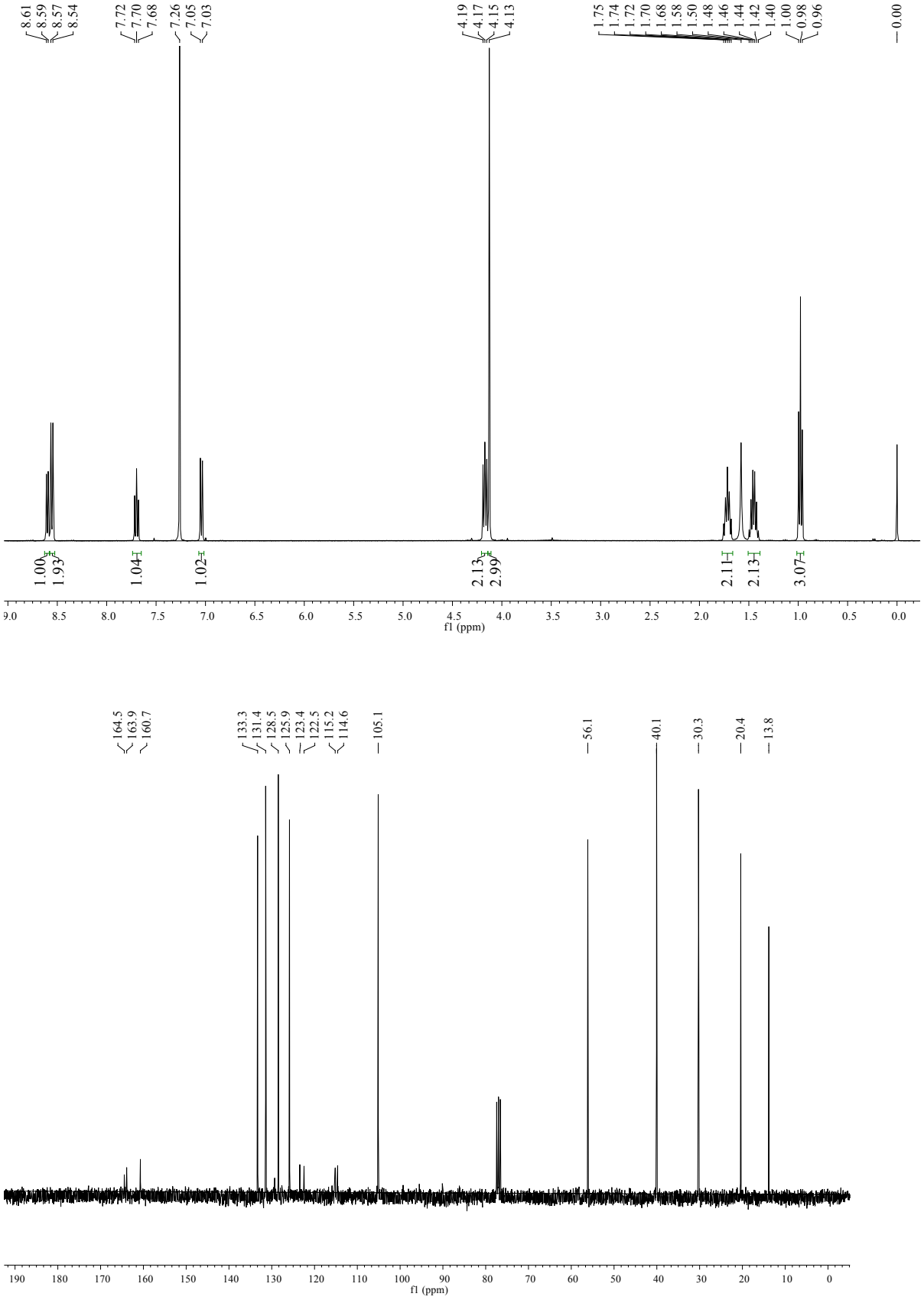


Fig. S2 ^{1}H NMR and ^{13}C NMR spectra of compound **3** ($CDCl_3$)

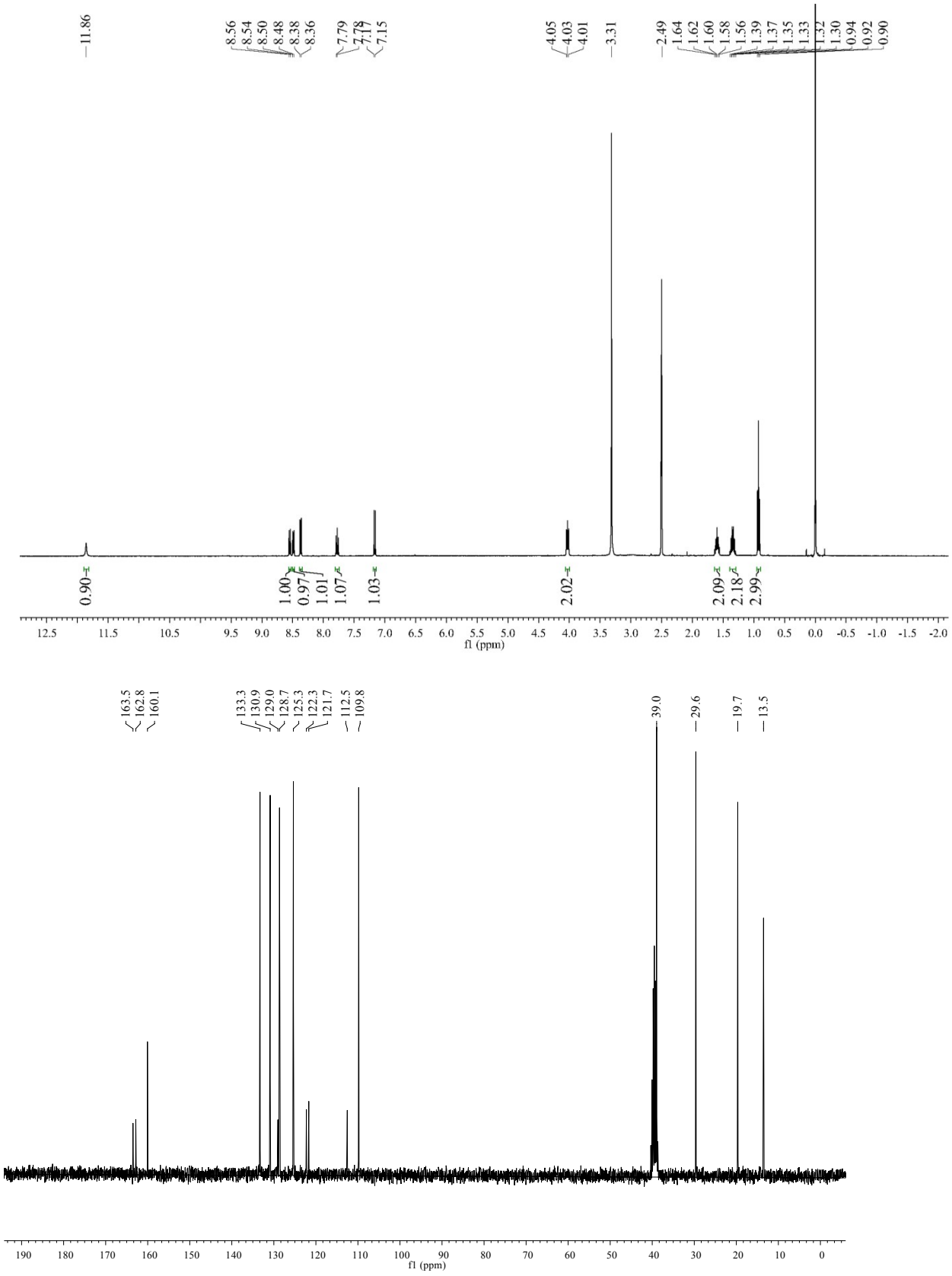


Fig. S3 ^{1}H NMR and ^{13}C NMR spectra of compound **4** (d_6-DMSO)

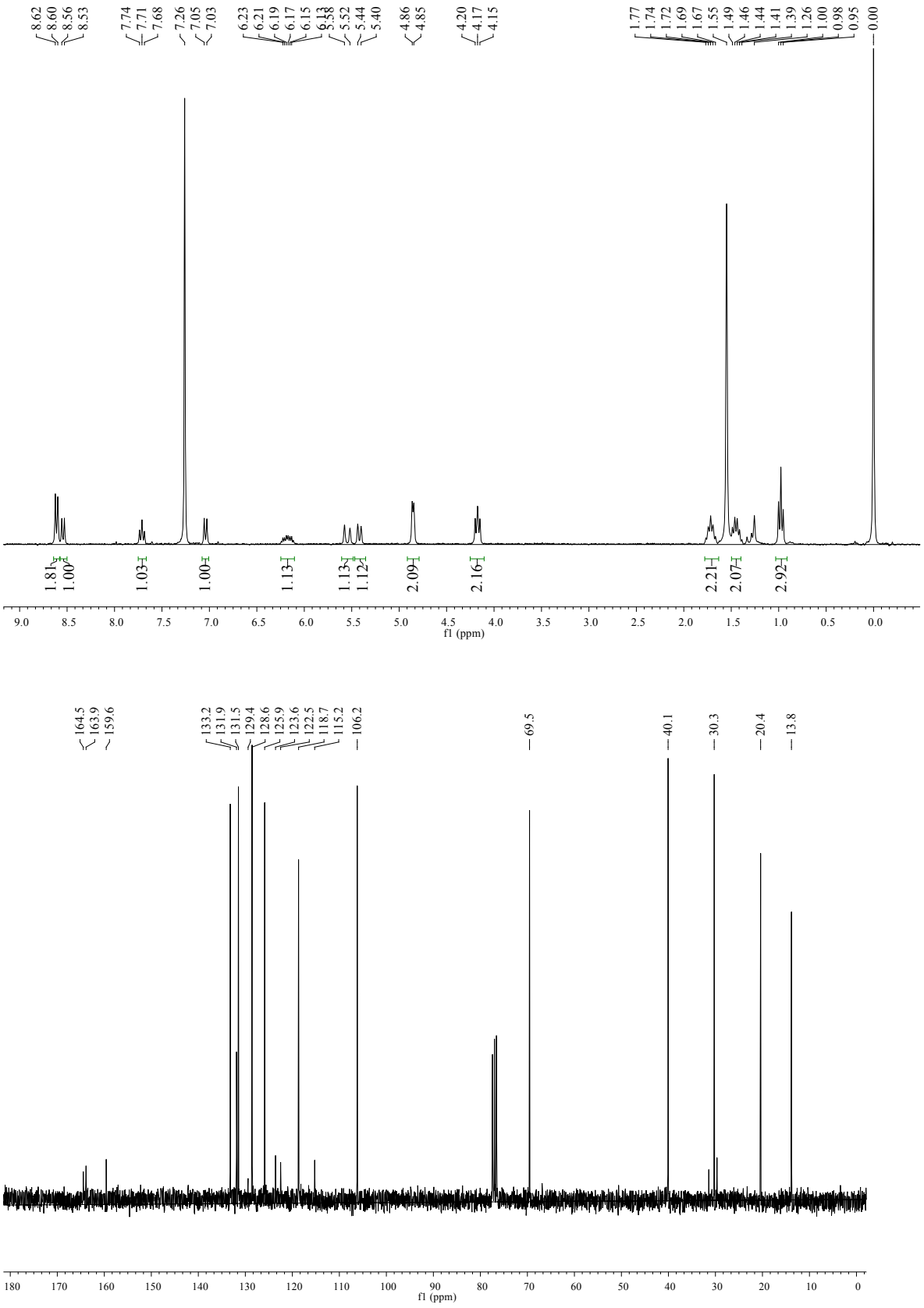


Fig. S4 ^{1}H NMR and ^{13}C NMR spectra of probe 1 ($CDCl_3$)

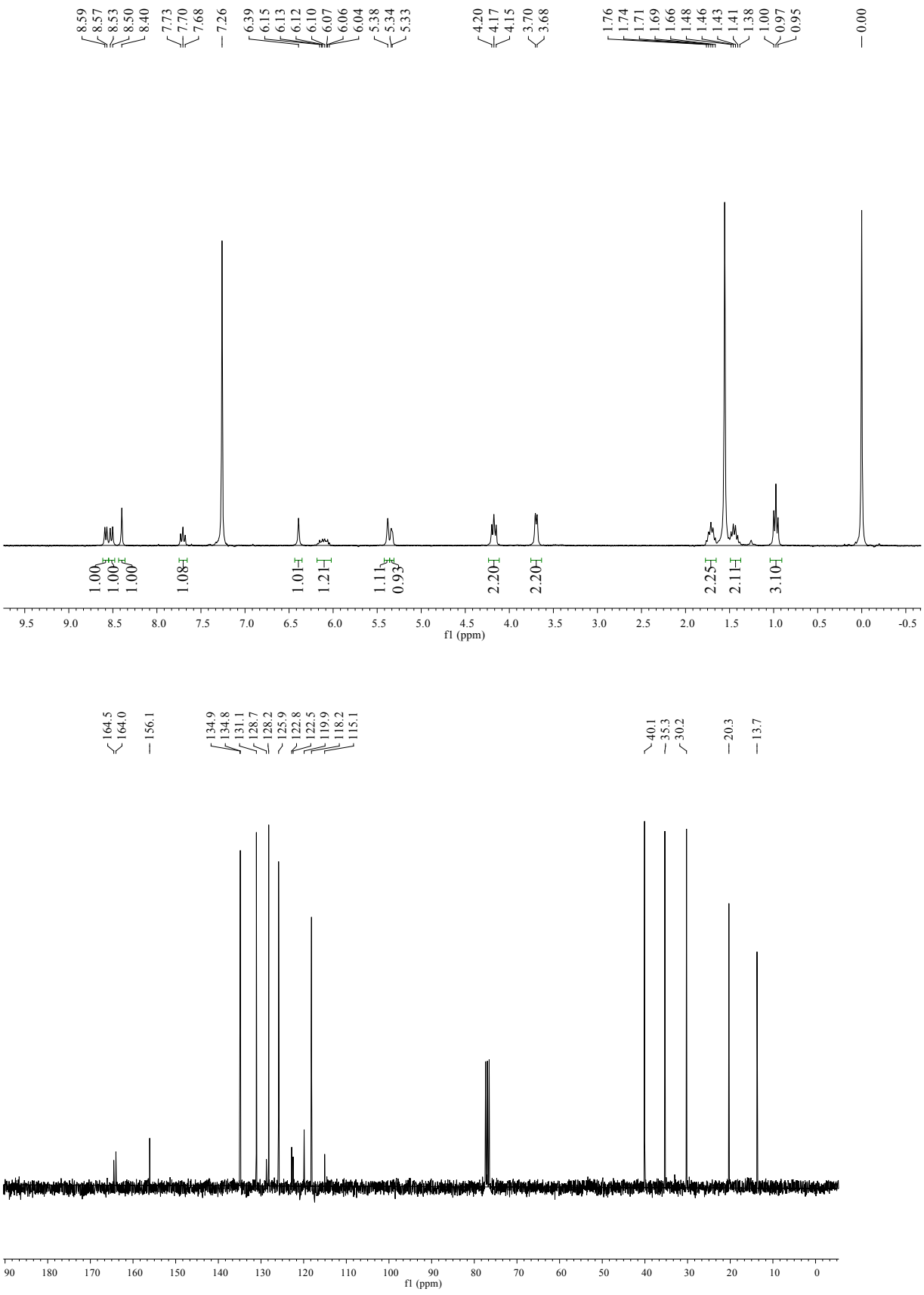
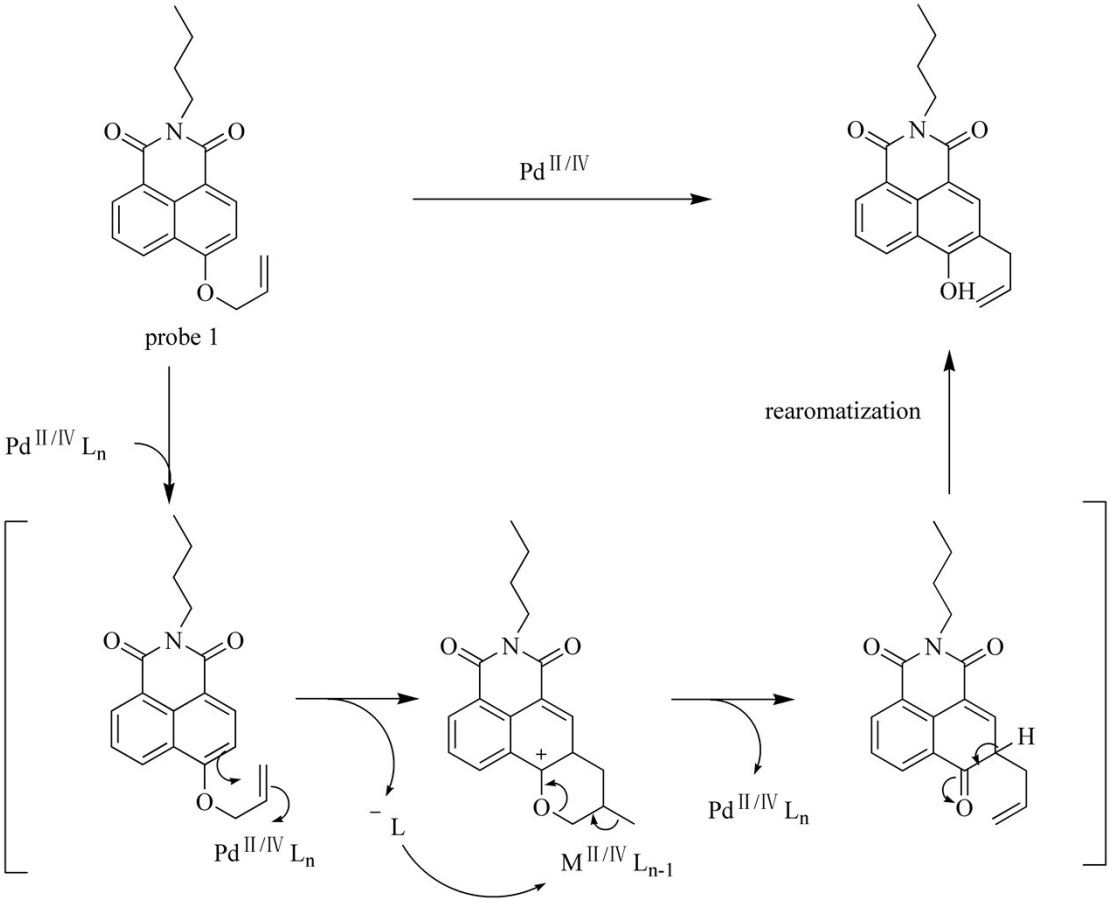


Fig. S5 ^{1}H NMR and ^{13}C NMR spectra of compound **5** ($CDCl_3$)

3. Scheme



Scheme S1 Claisen rearrangement of probe **1**

4. Absorption spectrum

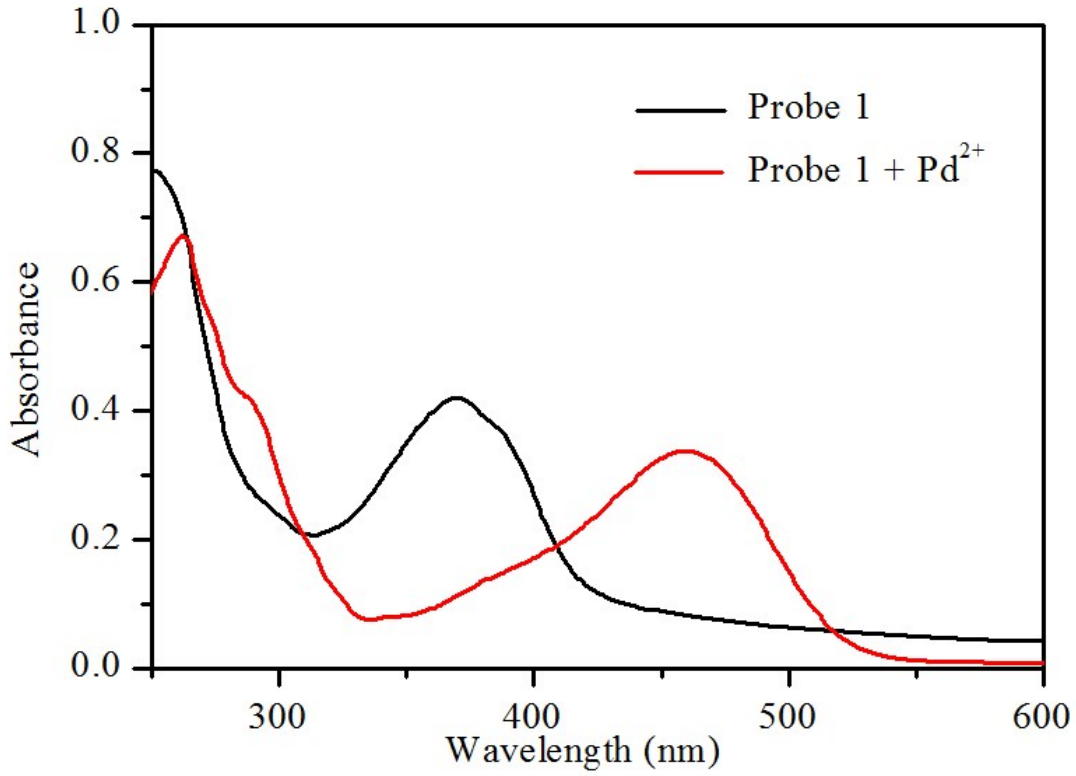


Fig. S6 UV-visible absorption spectra changes of probe **1** upon treatment with Pd^{2+} in $Na_2CO_3/NaHCO_3$ buffer (pH=10) solution.

5. Fluorescence properties

Fluorescence quantum yield and fluorescence lifetime were recorded on a Horiba Jobin Yvon Inc. Fluorolog 3-TSCPC in Na_2CO_3/$NaHCO_3$ buffer (pH=10) solution with an excitation wavelength of 379 nm. Probe **1** has a high fluorescence quantum yield (Φ) of 66.72 %(Fig. S7) compared with other 1,8-naphthalimide derivatives.[3-5]

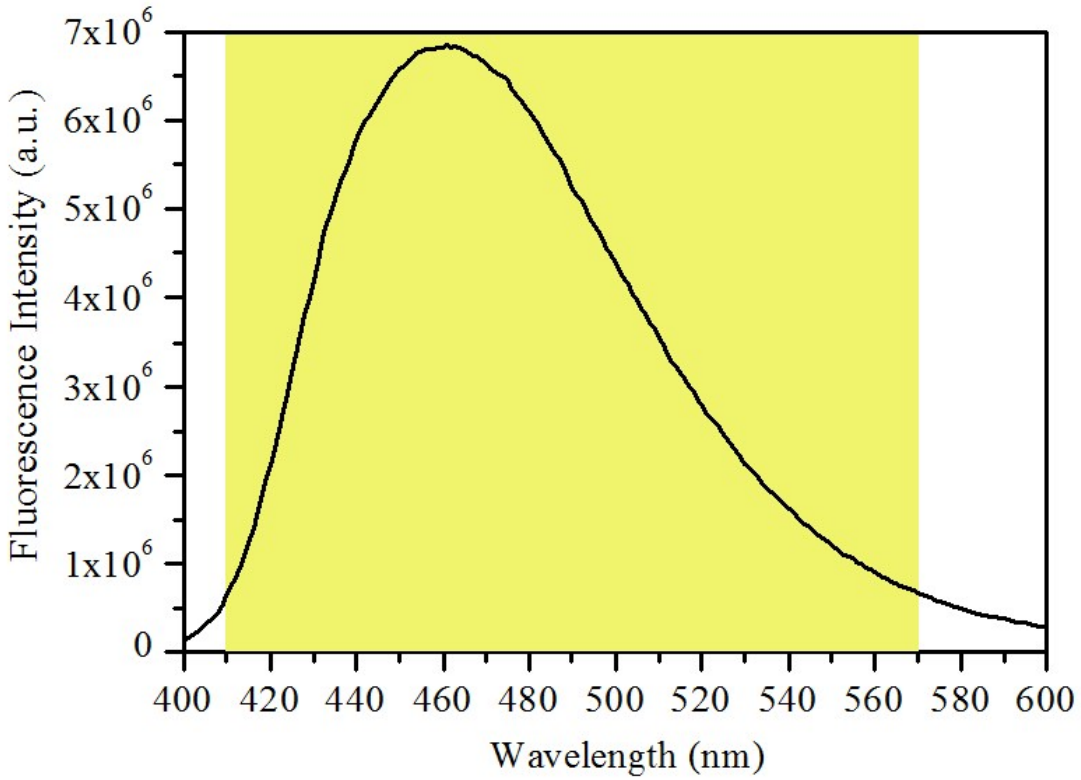


Fig. S7 Fluorescence quantum yield (Φ) values of probe **1** (10μM) in Na_2CO_3/$NaHCO_3$ buffer (pH=10) solution determined within 410-570 nm (yellow area).

Table S1 Fitting parameters of the corresponding probe 1 fluorescence decay curve.

Ex(nm)	Em(nm)	[a]τ_1(ns)	[a]τ_2(ns)	τ_{avg}(ns)	CHI-SQ
379	461	2.80(38.95)	8.69(61.05)	4.78	1.09

[a] Abundances shown in brackets.

The fluorescence lifetimes (τ) of probe **1** were determined by using a time correlated single photon counting (TCSPC).[6-8] Two fluorescence lifetimes were

observed, and the average fluorescence lifetime of probe **1** was given in Table S1. The

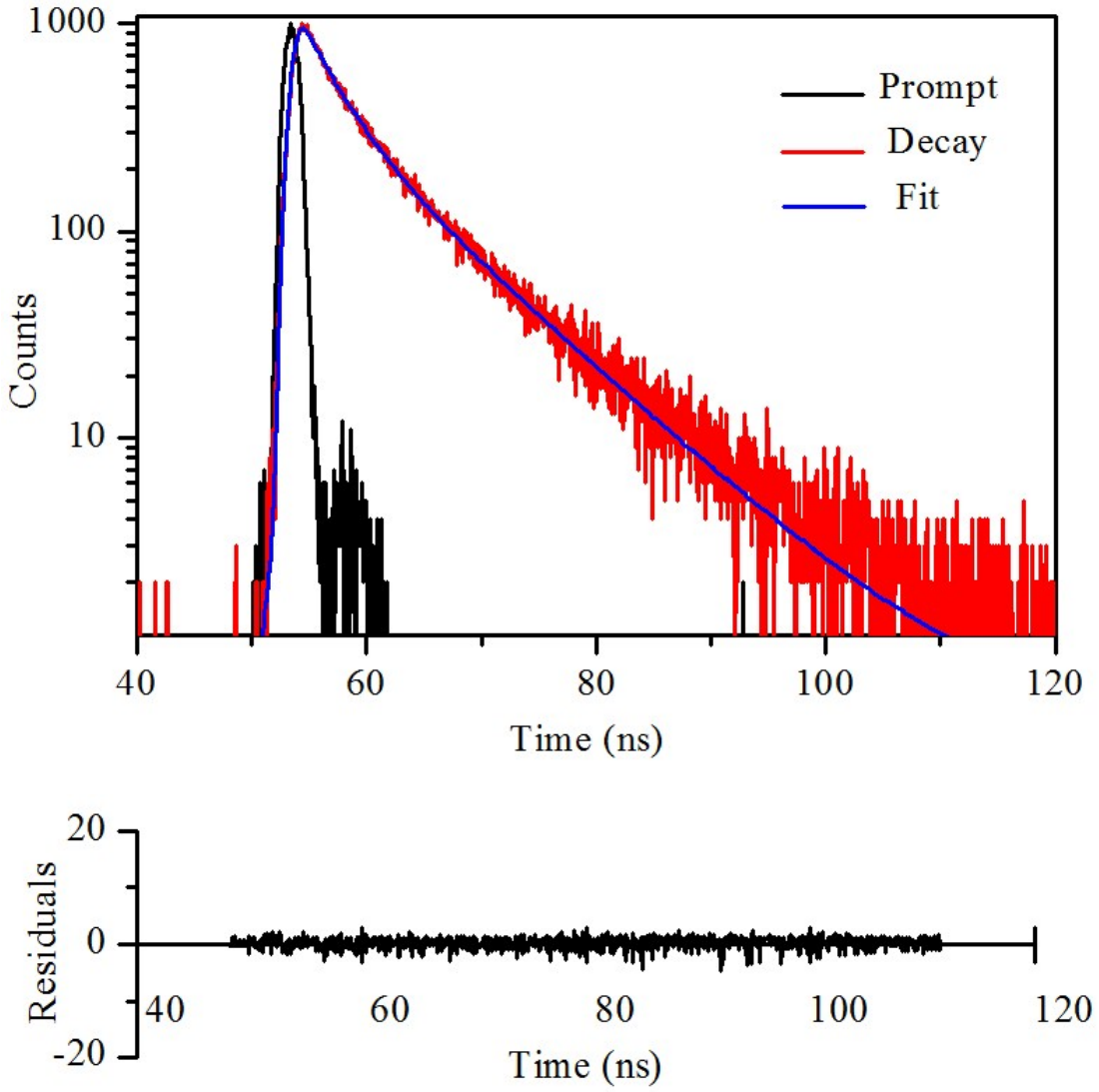


Fig. S8 Fluorescence decay and fitting curves of probe **1** with residuals. Ex=379 nm.

bi-exponential decay (Fig. S8) could be attributed to a small amount of aggregation of probe **1** (shorter) and free probe **1** (longer) in Na_2CO_3/$NaHCO_3$ buffer (pH=10) solution.[6,9,10]

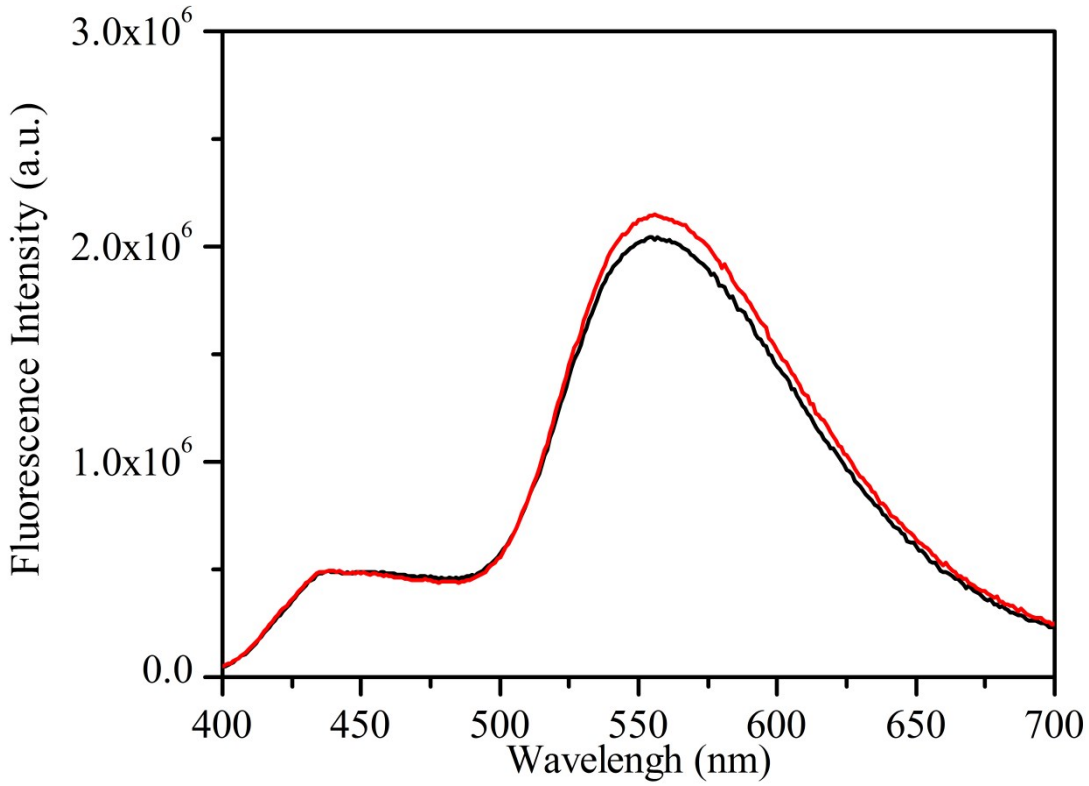


Fig. S9 The characteristic fluorescence spectrum of a standard pure compound **5** (red) and the product (black) of probe **1**. Ex=379 nm. Slit: 5.0 nm/5.0 nm.

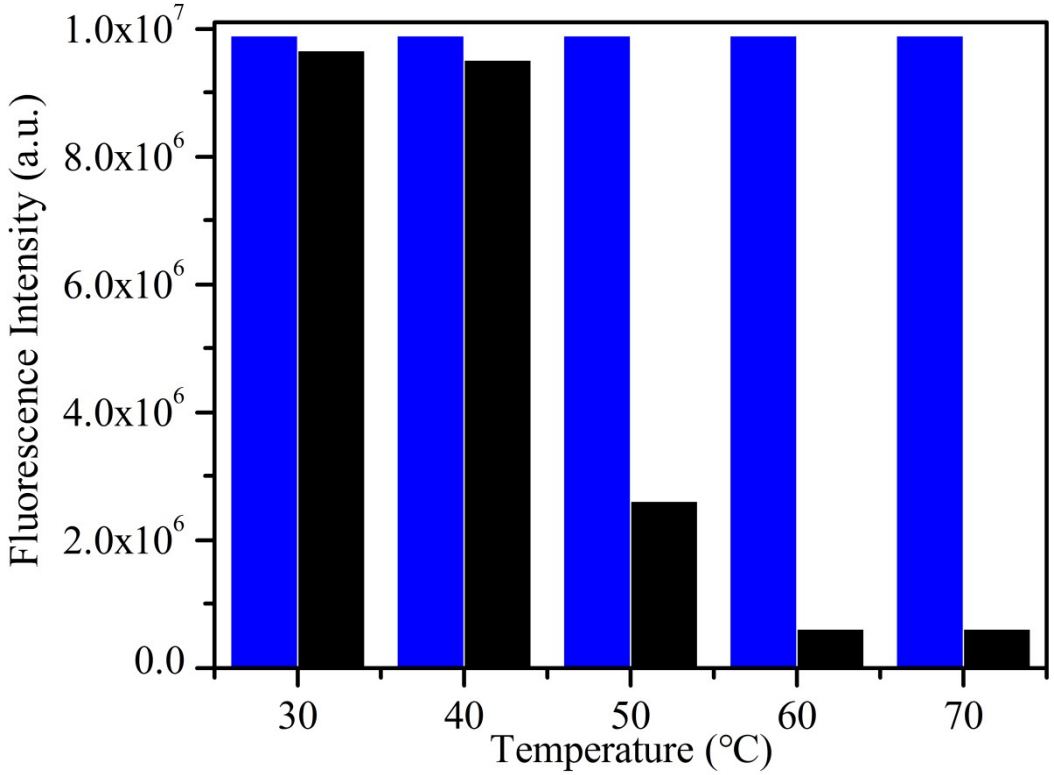


Fig. S10 Temperature-dependent fluorescent intensities at 461 nm of probe **1** (12.5 μM) in Na_2CO_3/$NaHCO_3$ buffer (pH=10) solution in the presence of Na_2PdCl_4 (25 μM). And the assays were performed for 4 h at each temperature. Blue: in the absence of Pd^{2+}, black: in the presence of Pd^{2+}. Ex=379 nm. Slit: 5.0 nm/5.0 nm.

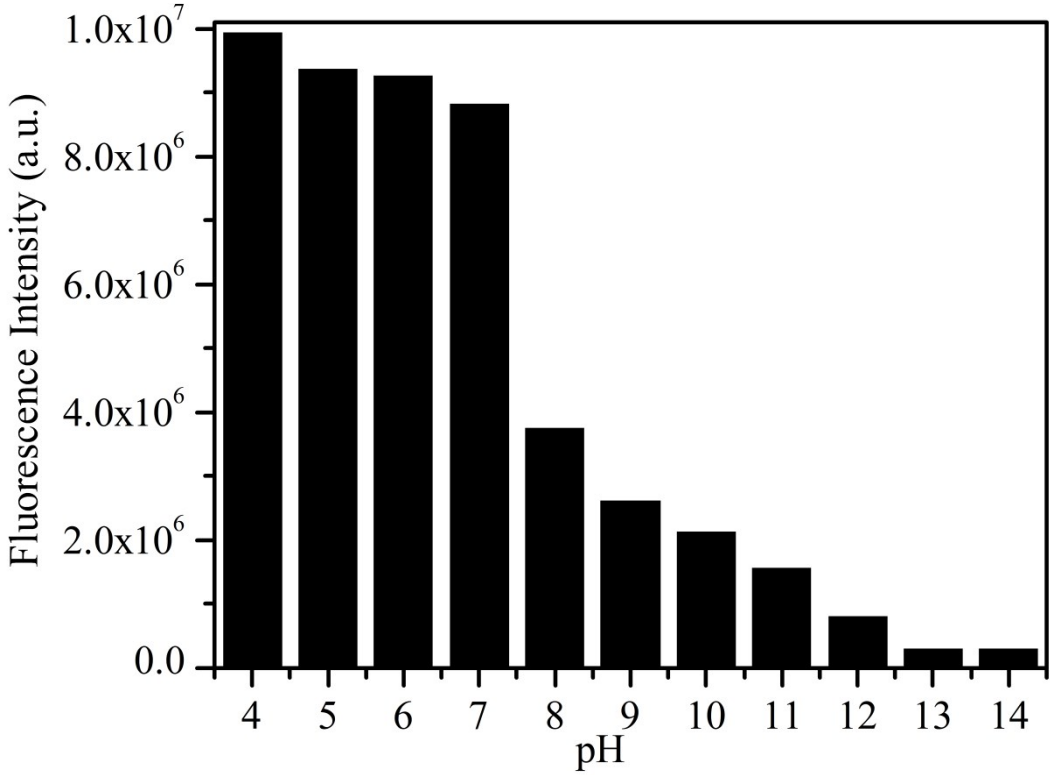


Fig. S11 Effects of pH on the fluorescence intensity at 461 nm of probe **1** (12.5 μM) in the presence of Na_2PdCl_4 (25 μM) in aqueous solution at 50 ^oC. And the assays were performed for 4 h at each pH value. Ex=379 nm. Slit: 5.0 nm /5.0 nm.

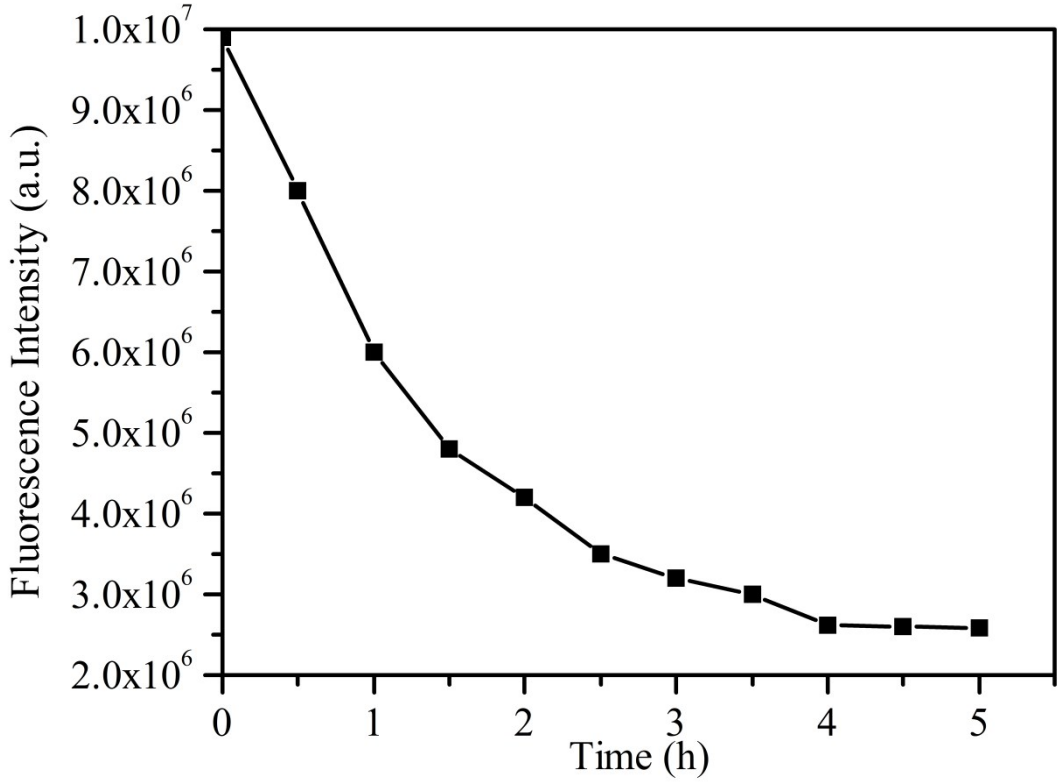


Fig. S12 Time-dependent fluorescent intensities of probe **1** (12.5 μM) in the presence of Na_2PdCl_4 (25 μM) in Na_2CO_3/$NaHCO_3$ buffer (pH=10) at 50 ^oC. Ex=379 nm. Slit: 5.0 nm/5.0 nm.

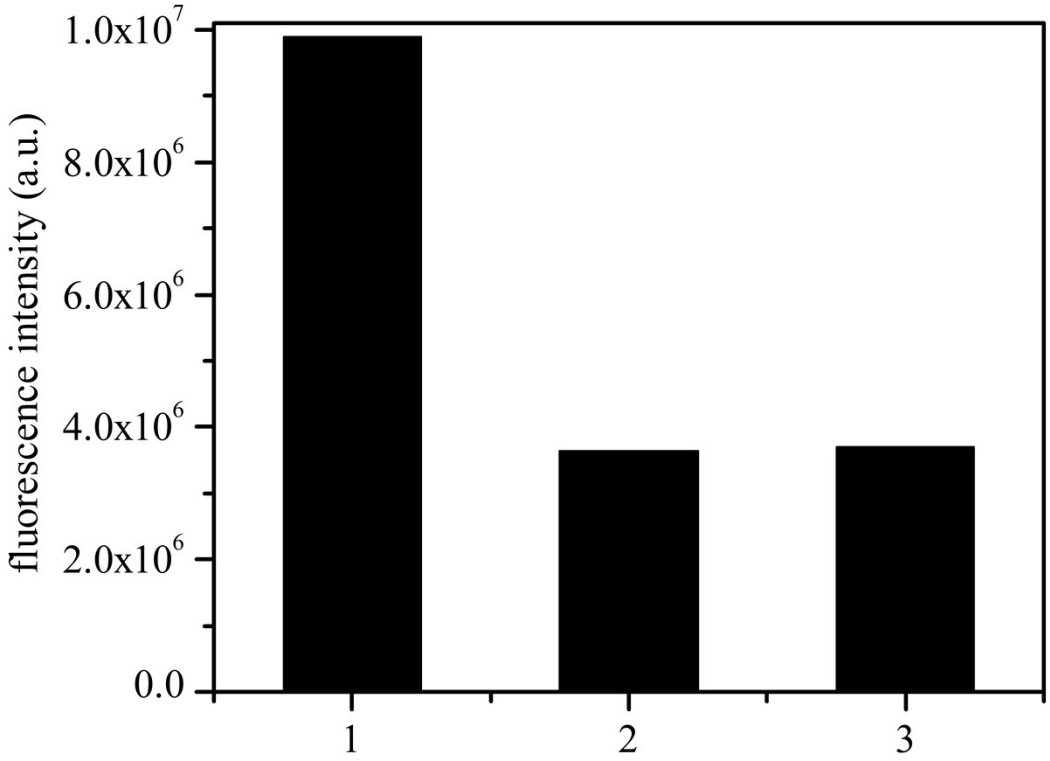


Fig. S13 Fluorescence intensity changes at 461 nm of probe **1** (12.5 μM) in $Na_2CO_3/NaHCO_3$ buffer (pH=10) solution in the presence of water (used as the control) (1), 15 μM Pd^{2+} (2), TWC (15 μM Pd^{n+} and 25 μM Pt^{n+}) (3), respectively. And the assays were performed for 4 h at 50 ^{o}C (pH=10). Ex=379 nm. Slit: 5.0 nm/5.0 nm.

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