

Highly Selective Fluorescent Probe for Au³⁺ Based on Cyclization of Propargylamide

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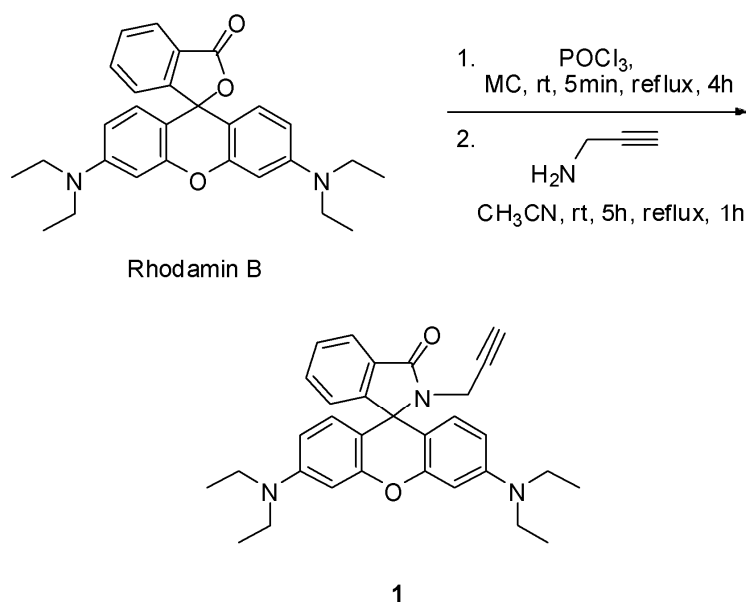
Experimental Section	S2 page
Figure. S1. ¹ H NMR (CDCl ₃ , 250 MHz) spectrum of 1	S4 page
Figure. S2 ¹³ C NMR (CDCl ₃ , 62.5 MHz) spectrum of 1	S4 page
Figure. S3 Naked eye detection.....	S5 page
Figure. S4 Absorbance spectra of 1	S5 page
Figure. S5 Fluorescence response of 1 with Au ³⁺ in the presence of various metal ions.....	S6 page
Figure S6 Fluorescence response of 1 with Au ³⁺ in the presence of various metal ions.....	S6 page
Figure S7 Fluorescence spectra of 1	S7 page
Figure. S8 ¹ H NMR (CDCl ₃ , 500 MHz) spectrum of 2	S7 page
Figure. S9 ¹³ C NMR (CDCl ₃ , 500 MHz) spectrum of 2	S8 page
Figure. S10 FAB MS of 2	S8 page
Figure. S11 Kinetic analysis of 1 in the presence of Au ³⁺	S9 page

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Experimental Section

General methods. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Chromatography was carried out on silica gel 60 (230-400 mesh ASTM; Merck). Thin layer chromatography (TLC) was carried out using Merck 60 F₂₅₄ plates with a thickness of 0.25 mm. Preparative TLC was performed using Merck 60 F₂₅₄ plates with a thickness of 1 mm. Reverse-phase chromatography was carried out using YMC*GEL polymerC18. ¹H NMR and ¹³C NMR spectra were recorded using Bruker 250 or Varian 500. Mass spectra were obtained using a JMS-HX 110A/110A Tandem Mass Spectrometer (JEOL). UV absorption spectra were obtained on UVIKON 933 Double Beam UV/VIS Spectrometer. Fluorescence emission spectra were obtained using RF-5301/PC Spectrofluorophotometer (Shimadzu).

Synthesis



Compound 1. A solution of rhodamine B base (1.0 g, 2.3 mmol) in 1,2 dichloroethane (12mL) was stirred, and phosphorus oxychloride (0.6 mL) was added dropwise over 5 min. the solution was refluxed for 4 h. The reaction mixture was cooled and evaporated in vacuo to give rhodamine B acid chloride, which was not purified but confirmed with the reported ¹H NMR. The crude acid chloride was dissolved in acetonitrile (125mL) and added dropwise over 5 h to a solution of propargyl amine (0.65 g, 9.03 mmol) in acetonitrile (50mL) at room temperature. The reaction mixture was then refluxed for 1h. After the solvent was evaporated under reduced pressure, the crude product was purified by silica-gel column chromatography (Hexane:EtOAc = 7:3, v/v) to give the 1.1 g of product (yield; 92%): mp 191-193 °C; ¹H NMR (CDCl₃, 250 MHz) δ (ppm): 7.94 (m, 1H), 7.45 (m, 1H), 7.12 (m, 1H), 6.49 (d, 2H, *J* = 8.9 Hz), 6.39 (d, 2H, *J* = 2.5 Hz), 6.28 (dd, 2H, *J* = 2.6 Hz), 3.95 (d, 2H, *J* = 2.5 Hz), 3.38

(d, 2H, $J = 2.5$ Hz), 1.77 (t, 1H, $J = 2.5$ Hz), 1.25 (t, 12H, $J = 7.0$ Hz); ^{13}C NMR (CDCl_3 , 62.5 MHz) δ (ppm): 167.4, 153.8, 153.5, 148.8, 132.6, 130.4, 129.1, 128.0, 123.8, 123.0, 108.0, 105.0, 97.7, 78.3, 70.0, 64.8, 44.4, 28.5, 12.6. FAB MS $m/z = 479.2577$ $[\text{M} + \text{H}]^+$, calc. for $\text{C}_{31}\text{H}_{33}\text{N}_3\text{O}_2 = 479.2573$.

Compound 2 AuCl_3 (126 mg, 0.42 mmol) was dissolved in 20 mL ethanol and was then added dropwise to a solution of **1** (200 mg, 0.42 mmol) in 150 mL aqueous ethanol. After stirred for 6 h in air atmosphere at room temperature, the reaction solution was filtered. After evaporation of the solvent, the residue was purified by reverse-phase column chromatography ($\text{CH}_3\text{OH} : \text{H}_2\text{O} = 50:50$, v/v) to afford 17 mg of product (yield, 8.2%). ^1H NMR (CDCl_3 , 500 MHz) δ (ppm): 9.62 (s, 1H), 8.40 (br, 1H), 7.79-7.68 (m, 3H), 7.35 (br, 1H), 7.03 (d, 2H, $J = 9.5$ Hz), 6.84 (s, 2H), 6.78 (d, 2H, $J = 9.5$ Hz), 3.57 (q, 8H, $J = 6.5$ Hz), 1.25 (t, 12H, $J = 6.5$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ (ppm): 176.8, 158.2, 157.1, 155.9, 132.4, 132.2, 131.3, 131.0, 130.9, 130.2, 125.4, 114.6, 114.1, 97.0, 46.4, 12.9. FAB MS $m/z = 494.2448$ $[\text{M} + \text{H}]^+$, calc. for $\text{C}_{31}\text{H}_{32}\text{N}_3\text{O}_3 = 494.2444$.

Preparation of metal ion solutions for fluorescent study

Stock solutions (10 mM) of the perchlorate salts of Ag^+ , Al^{3+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Hg^{2+} , K^+ , Li^+ , Mg^{2+} , Mn^{2+} , Na^+ , Ni^{2+} , Pb^{2+} and Zn^{2+} ions in distilled water and stock solutions (10 mM) of the chloride salts of Cu^+ , Pd^{2+} , Pt^{2+} and Au^+ ions in DMSO were prepared. Stock solutions (10 mM) of chloride salts of Au^{3+} ions in ethanol were prepared. Stock solutions of host (300 μM) were also prepared in ethanol. In a typical experiment, test solutions were prepared by placing 50 μL of the probe stock solution into a test tube, adding an appropriate aliquot of each metal stock, and diluting the solution to 3 mL with 0.01 M HEPES (pH 7.4) and ethanol. Normally, excitation was at 558 nm. Both the excitation and emission slit widths were 3nm/5 nm. Fluorescence spectra were measured after addition of Au^{3+} for 10min. For low concentration titration of Au^{3+} , fluorescence spectra were measured after addition of Au^{3+} for 30min, and both the excitation and emission slit widths were either 5nm/5nm or 5 nm/10nm.

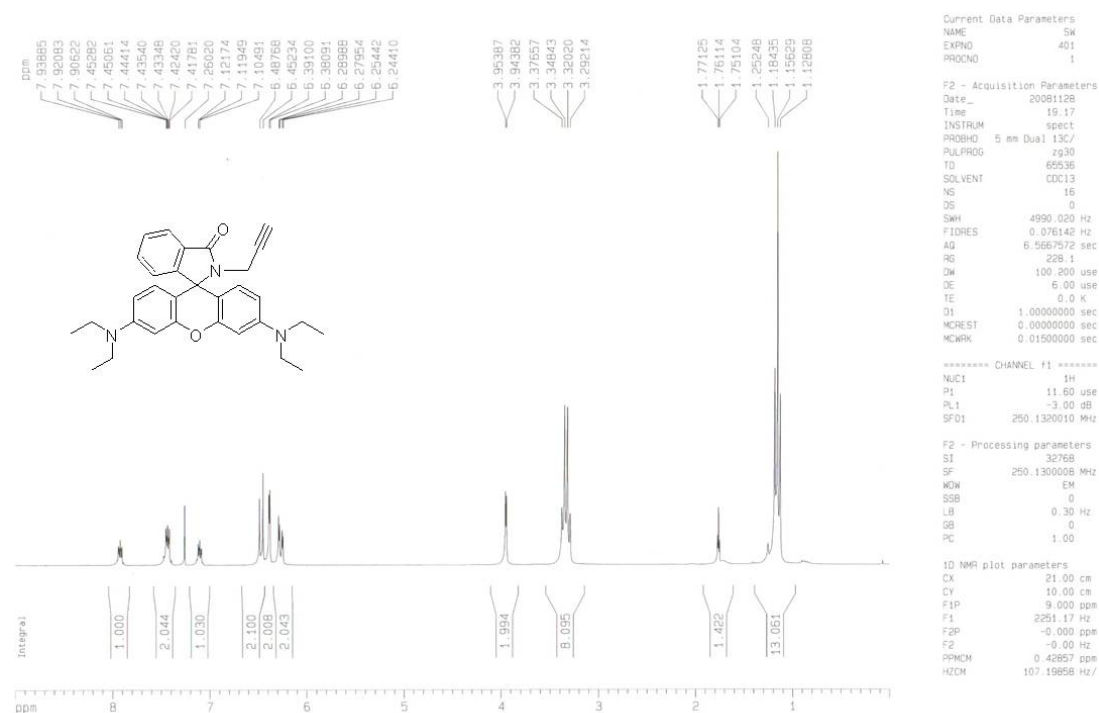


Fig. S1. ¹H NMR (250 MHz) of compound **1** in CDCl₃.

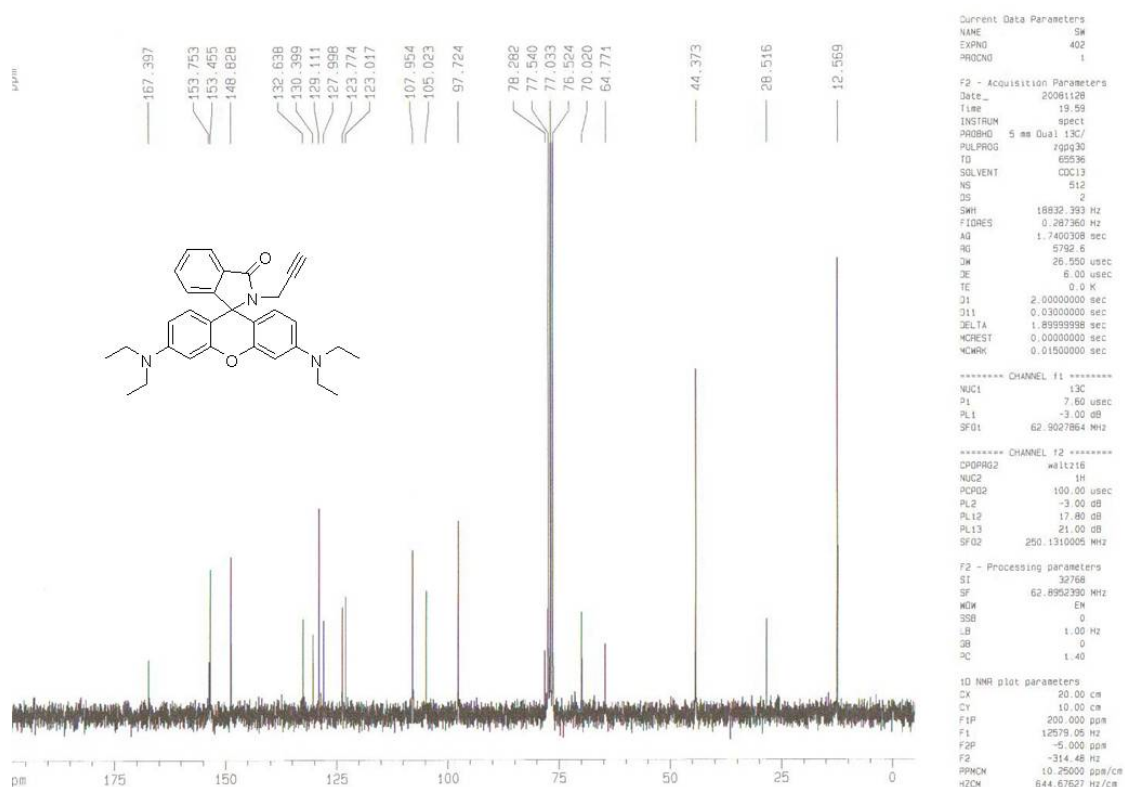


Fig. S2. ¹³C NMR (62.5 MHz) of compound **1** in CDCl₃.

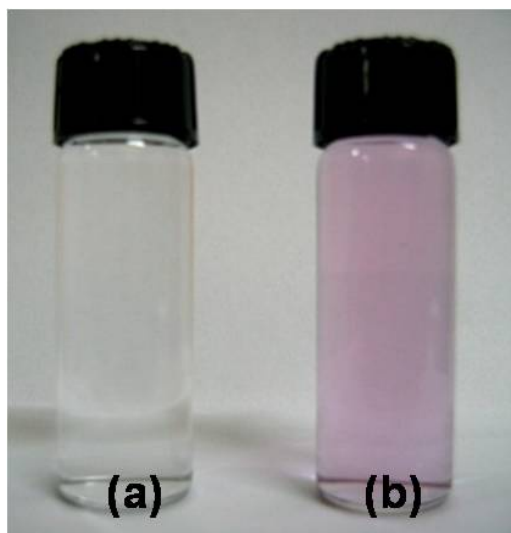


Fig. S3. Naked eye detection of (a) and (b): Color change of only probe **1** (50 μM) and in the presence of Au^{3+} (10 equiv.), respectively.

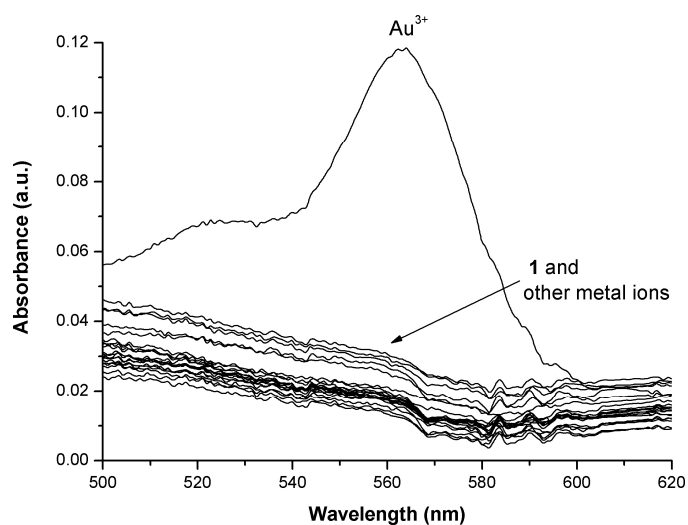


Fig. S4. Absorbance spectra of **1** (50 μM) with Ag^+ , Al^{3+} , Au^+ , Au^{3+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Hg^{2+} , K^+ , Li^+ , Mg^{2+} , Mn^{2+} , Na^+ , Ni^{2+} , Pb^{2+} , Pd^{2+} , Pt^{2+} and Zn^{2+} ions (100 μM) in EtOH-HEPES buffer (0.01 M, pH 7.4) (1:1, v/v). For Cu^+ , Pd^{2+} , Pt^{2+} and Au^+ , due to the solubility problem, DMSO-HEPES buffer (0.01 M, pH 7.4) (1:1, v/v) was used. All the fluorescence data were observed after 30 min.

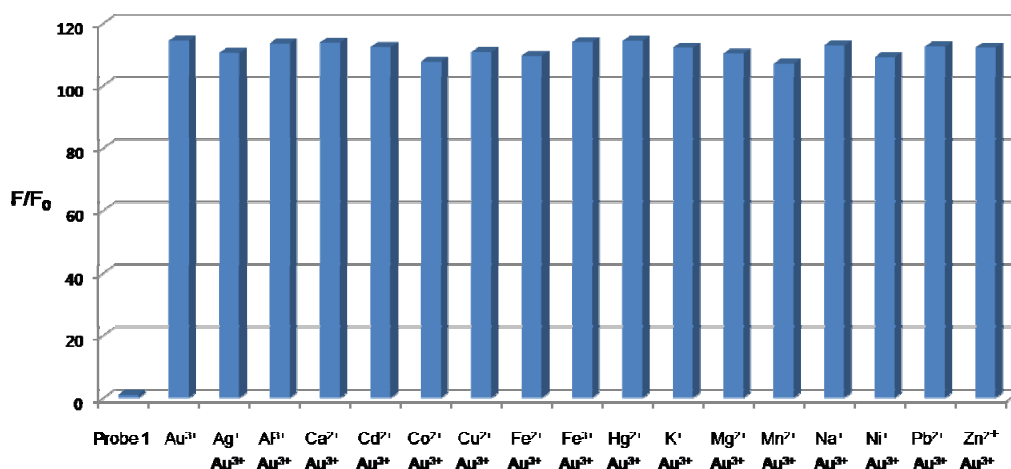


Fig. S5 Fluorescence responses of **1** (5 μ M) with Au^{3+} (50 μ M) in the presence of various metal ions (50 μ M) in EtOH-HEPES buffer (0.01 M, pH 7.4) (1:1, v/v). All the fluorescence data were observed after 10 min. (λ_{ex} = 558 nm, λ_{em} = 579 nm, slit: 3 nm/5 nm).

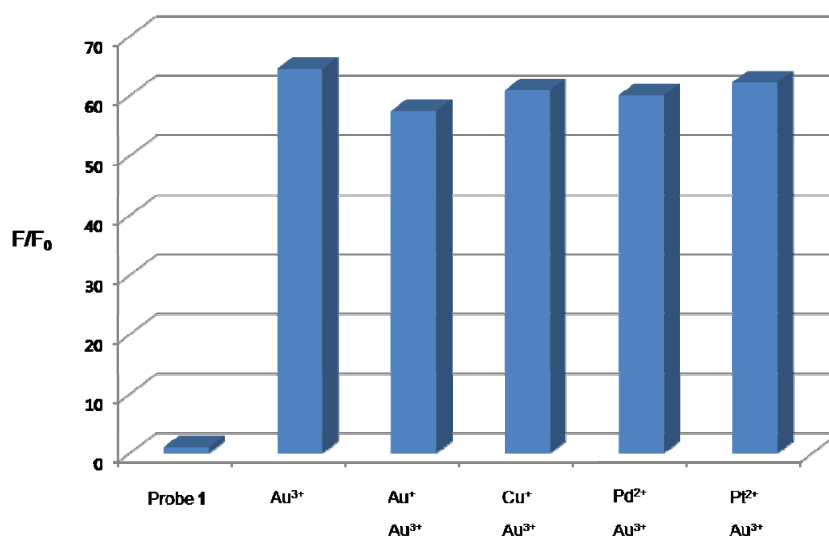


Fig. S6 Fluorescence responses of **1** (5 μ M) with Au^{3+} (50 μ M) in the presence of various metal ions (50 μ M) in DMSO-HEPES buffer (0.01 M, pH 7.4) (1:1, v/v). All the fluorescence data were observed after 10 min. (λ_{ex} = 558 nm, λ_{em} = 579 nm, slit: 3 nm/5 nm).

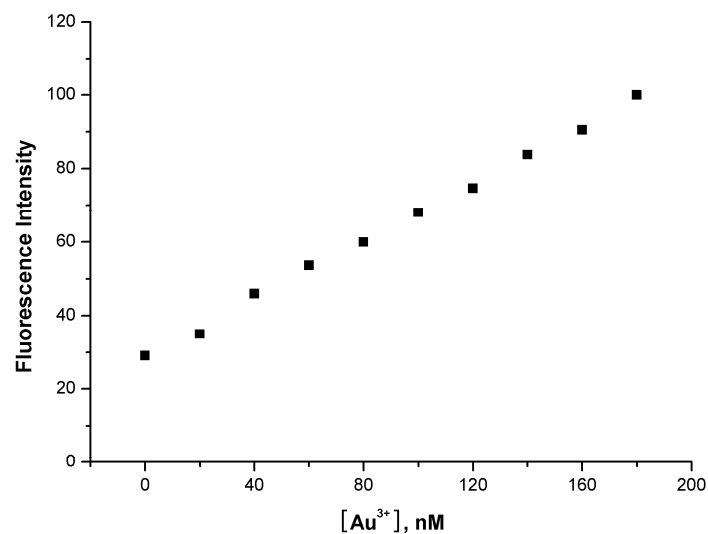


Fig. S7. Fluorescence responses of **1** (1 μ M) in EtOH-water (1:1, v/v) toward various amounts of Au³⁺. All the fluorescence data were observed after 30 min. (λ_{ex} = 558 nm, λ_{em} = 579 nm, slit: 5 nm/10 nm)

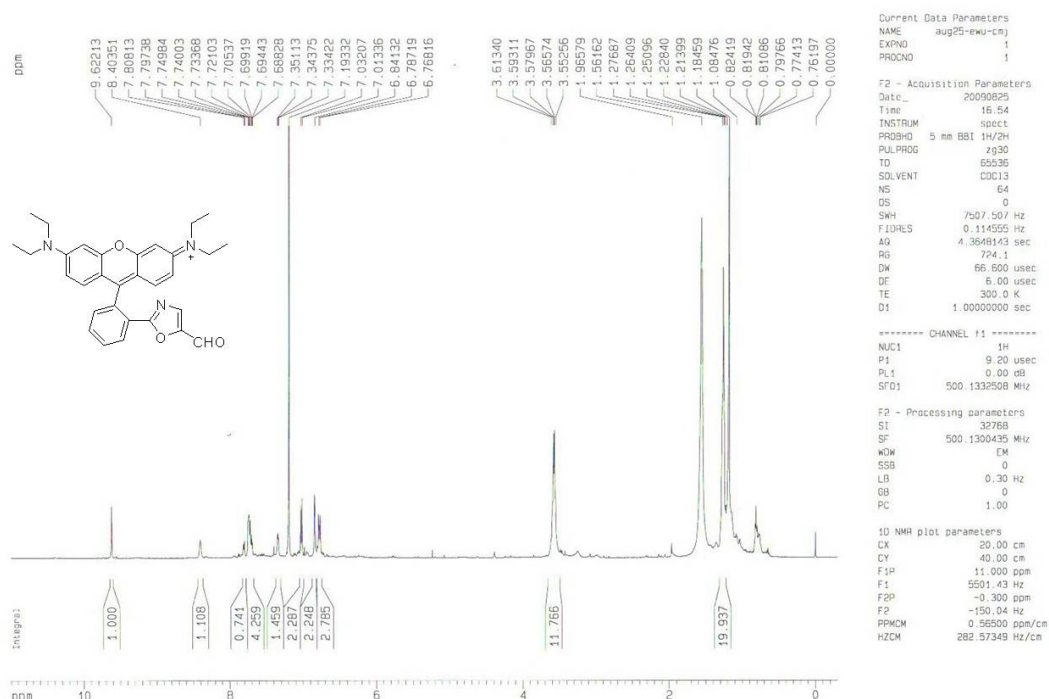


Fig. S8. ¹H NMR (500 MHz) of compound **2** in CDCl₃.

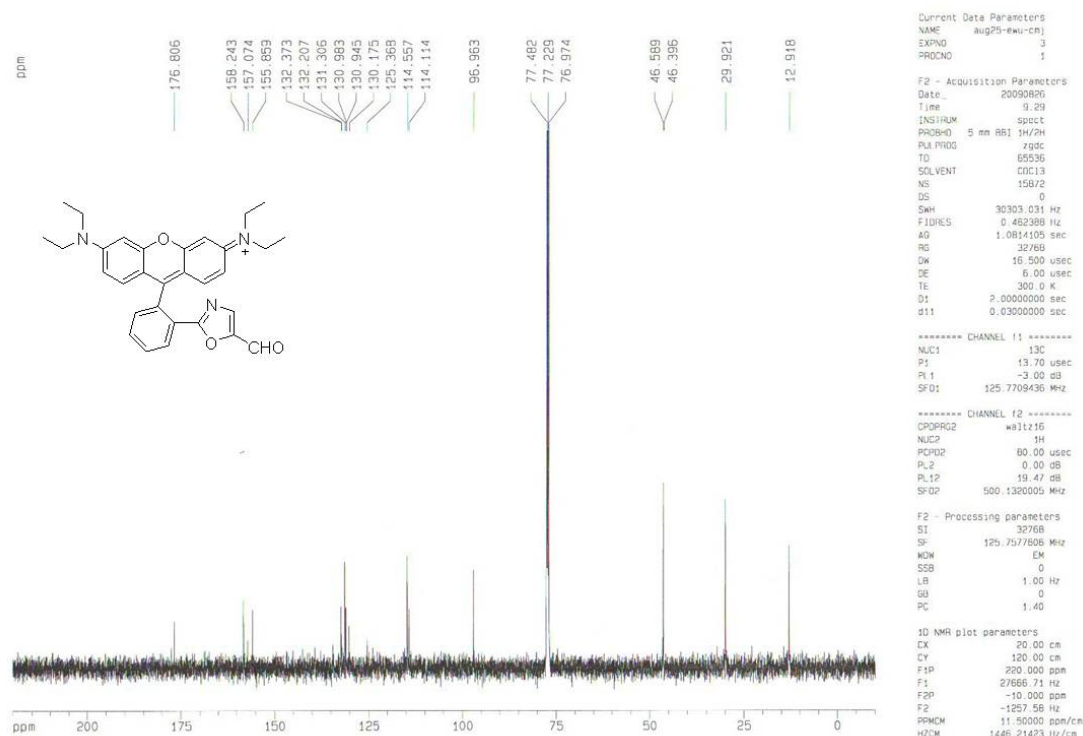


Fig. S9. ^{13}C NMR (500 MHz) of compound **2** in CDCl_3 .

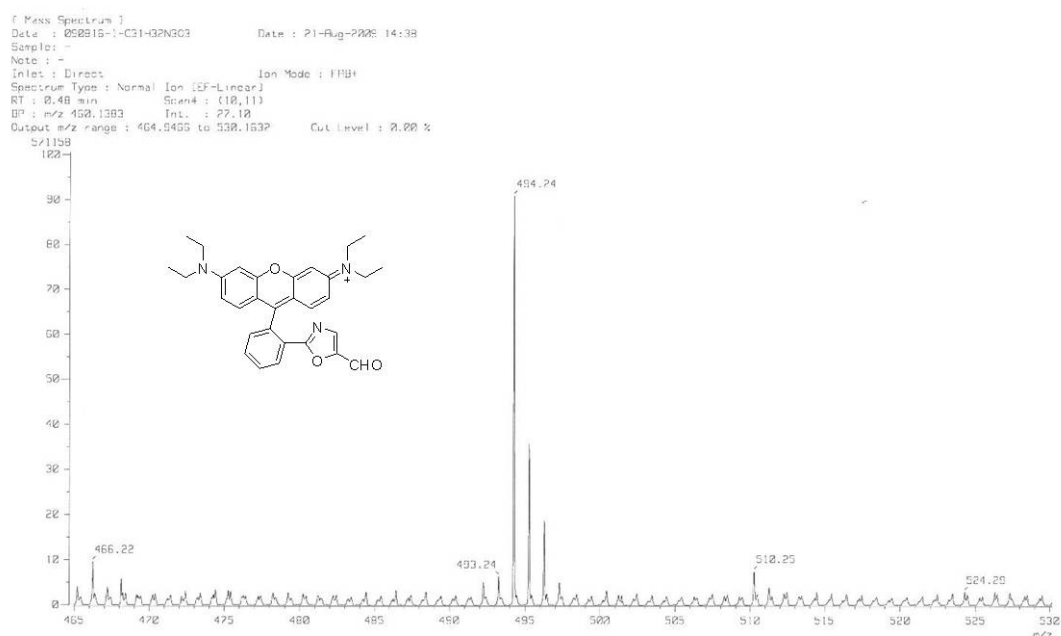


Fig. S10. FAB MS of **2** in CHCl_3 .

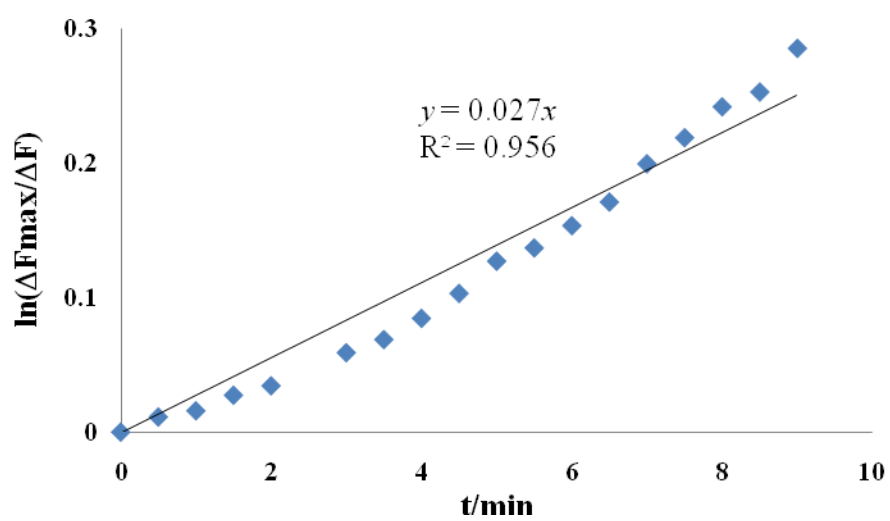


Fig. S11. Kinetic analysis of **1** (5 μM) with 10 equiv. of Au^{3+} in EtOH-HEPES buffer (0.01 M, pH 7.4) (1:1, v/v).