

Supporting Information for:

A Rationally Designed Fluorescence Turn-On Probe for the Gold(III) Ion

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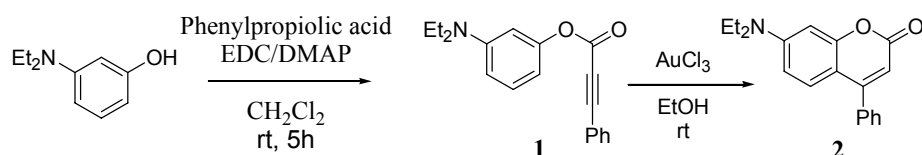
1. Instruments and reagents

All fluorescence and UV-vis absorption spectra were recorded in FP 6500 fluorescence spectrometer and HP 8453 absorption spectrometer, respectively. The ^1H and ^{13}C NMR spectra were recorded at 300 MHz NMR spectroscopy. Mass spectra were recorded on G6401A MS-spectrometer. All experiments were carried out with commercially available reagents and solvents, and used without further purification, unless otherwise noted.

Fluorescence cell imaging of HaCaT cell line

Human keratinocyte cell line, HaCaT were cultured in RPMI 1640 medium supplemented with 10% heat-inactivated fetal bovine serum, 100 units/ml penicillin, and 100 $\mu\text{g}/\text{ml}$ streptomycin. Cells were seeded at a density of 5×10^4 cells per well in a 6 well size cover glass bottom dish in culture medium overnight. HaCaT cells were treated with 10 μM of HAuCl_4 for 30 min at 37°C and washed 3 times with PBS. These cells were then fixed with 3.7% PFA (paraformaldehyde) solution at 4°C for 15 min. After 3 times' washing with PBS, the cells were exposed to 50 μM of sensor for 10 min at room temperature and the images were obtained by using confocal laser microscope ($\times 600$, $\times 100$). For the cell imaging study, HAuCl_4 and sensor stock were prepared in DMSO and diluted with culture medium or PBS.

2. Synthesis of 1, 2, 3 and 4



Probe 1. 3-(Diethylamino)phenol (760 mg, 4.60 mmol), phenylpropionic acid (672 mg, 4.60 mmol), EDC (900 mg, 4.69 mmol) and DMAP (224 mg, 2.68 mmol) were dissolved in 5 mL CH_2Cl_2 in a flask. The clear black reaction mixture was stirred at 0°C for 1 hr and then kept at room temperature for another 5 hr. After evaporating all the volatiles under reduced pressure, purification by flash column chromatography on silicagel ($\text{EtOAc} : n\text{-hexane}=1:4$, $R_f = 0.57$) afforded the desired probe 1 as light yellowish oil (673.6 mg, yield 50 %).

^1H NMR (CDCl_3 , 300 MHz): δ 7.65 (d, $^3J = 6.8$ Hz, $^4J = 1.2$ Hz, 2H), 7.50 (t, $J = 7.3$ Hz, 1H), 7.44 (dd, $^3J = 7.4$ Hz, $^4J = 1.2$ Hz, 2H), 7.25 (t, $^3J = 8.1$ Hz, 1H), 6.59 (dd, $^3J = 6.0$ Hz, $^4J = 2.4$ Hz, 1H), 6.48 (dd, $^3J = 8.4$ Hz, $^4J = 2.1$ Hz, 2H), 3.40 (q, $^3J = 7.0$ Hz, 4H), 1.20 (t, $^3J = 7.0$ Hz, 6H).

^{13}C NMR (CDCl_3 , 75 MHz): δ 152.69, 151.59, 149.12, 133.26, 131.01, 130.06, 128.75, 119.58, 109.75, 107.90, 104.50, 88.44, 80.759, 44.780, 12.90 (15 carbon peaks).

HRMS (FAB $^+$, m-NBA): m/z obs'd 293.1415 ($[\text{M}]^+$, cal'd 293.1416 for $\text{C}_{19}\text{H}_{19}\text{O}_2\text{N}$).

2. To a solution of 1 (586 mg, 2.00 mmol) in 5 mL $\text{CH}_2\text{Cl}_2/\text{EtOH}$ (4:1, v/v) was added $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (79 mg, 0.20 mmol) and the yellow reaction mixture was further stirred overnight at rt. After evaporating all the volatiles under reduced pressure, purification by flash column chromatography on silicagel ($\text{EtOAc} : n\text{-hexane}=1:5$, $R_f = 0.23$) afforded the desired product 2 as clear orange oil (410 mg, yield 70 %).

^1H NMR (CDCl_3 , 300 MHz): δ 7.46-7.44 (m, 5H), 7.24 (d, $^3J = 8.9$ Hz, 1H), 6.54 (d, $^4J = 2.4$ Hz, 1H), 6.51 (dd, $^3J = 8.9$ Hz, $^4J = 2.4$ Hz, 1H), 5.97 (s, 1H), 3.39 (q, $^3J = 6.9$ Hz, 4H), 1.20 (t, $^3J = 6.9$ Hz, 6H).

^{13}C NMR (CDCl_3 , 75 MHz): δ 162.12, 156.79, 156.16, 150.63, 136.19, 129.25, 128.62, 128.32, 127.92, 108.56, 108.15, 107.83, 97.75; 44.74, 12.43 (15 carbon peaks).

HRMS (FAB $^+$, m-NBA): m/z obs'd 294.1495 ($[\text{M}+\text{H}]^+$, cal'd 294.1494 for $\text{C}_{19}\text{H}_{20}\text{O}_2\text{N}$).

3. To phenol (94 mg, 1.0 mmol), phenylpropionic acid (146 mg, 1.00 mmol), EDC (191.7 mg, 1.00 mmol) and DMAP (50 mg, 0.40 mmol) were dissolved in 4 mL CH_2Cl_2 in a flask. The clear reaction mixture was stirred at 0°C for 1 hr and then kept at room temperature for another 5 hr. After evaporating all the volatiles under reduced pressure, purification by flash column chromatography on silicagel ($\text{EtOAc} : n\text{-hexane}=1:4$, $R_f = 0.58$) afforded the desired probe 3 as light yellowish oil (126.9 mg, yield 57 %).

^1H NMR (CDCl_3 , 300 MHz): δ 7.64 – 7.62 (m, 2H), 7.50 – 7.38 (m, 5H), 7.31 – 7.18 (m, 3H).

4. To 3-(Diethylamino)phenol (165 mg, 1.0 mmol), cinnamic acid (148 mg, 1.00 mmol), EDC (191.7 mg, 1.00 mmol) and DMAP (50 mg, 0.40 mmol) were dissolved in 4 mL CH₂Cl₂ in a flask. The clear black reaction mixture was stirred at 0 °C for 1 hr and then kept at room temperature for another 5 hr. After evaporating all the volatiles under reduced pressure, purification by flash column chromatography on silicagel (EtOAc : *n*-hexane=1:4, R_f= 0.56) afforded the desired probe **4** as a white solid (228.5 mg, yield 77 %).

¹H NMR (CDCl₃, 300 MHz): δ 7.88 (d, ³J = 15.9 Hz, 1H), 7.60 (m, 2H), 7.50 (m, 3H), 7.23 (t, ³J = 8.4 Hz, 1H), 6.66 (d, ³J = 15.9 Hz, 1H), 6.56 (m, 1H), 6.44 (m, 2H), 3.38 (q, ³J = 7.2 Hz, 4H), 1.18 (t, ³J = 7.2 Hz, 6H).

¹³C NMR (CDCl₃, 75 MHz): δ 165.58, 152.19, 149.08, 146.19, 134.40, 130.64, 129.94, 129.06, 128.34, 117.85, 109.29, 108.20, 104.82, 44.74, 12.94. (15 carbon peaks).

3. NMR spectra of compounds **1**, **2**, **3** and **4**

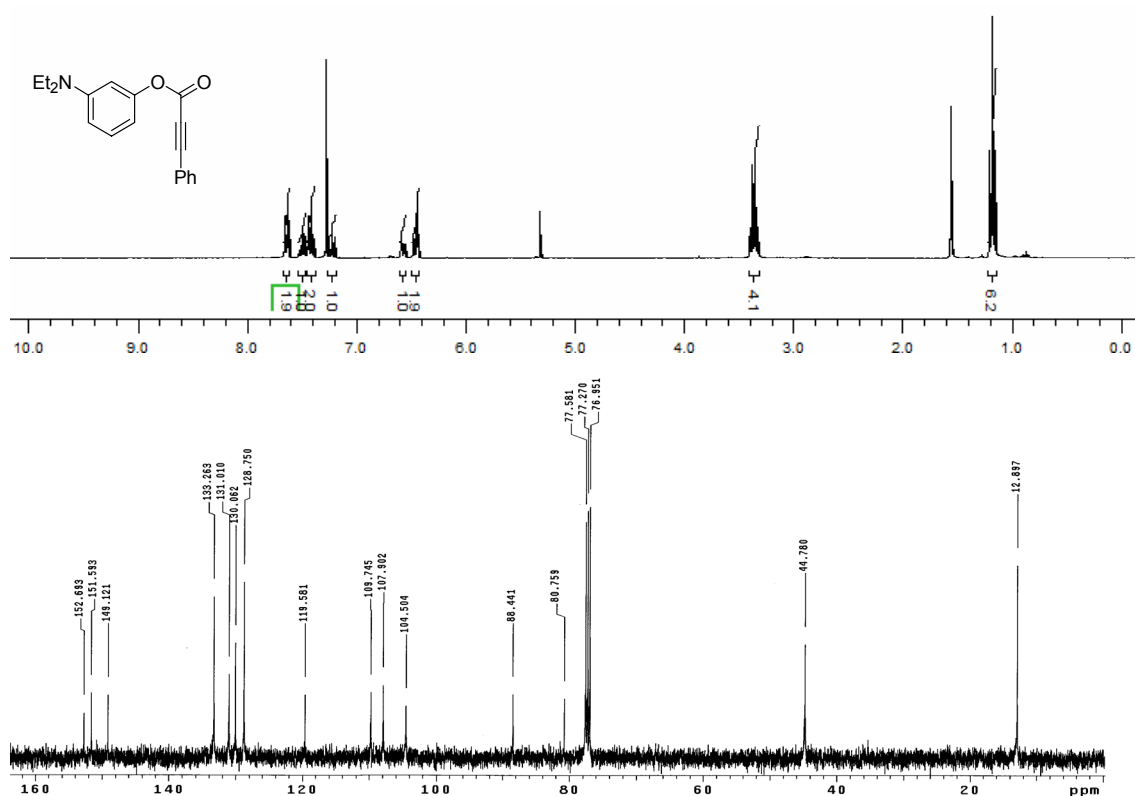


Figure S1. ¹H and ¹³C NMR spectra of **1**.

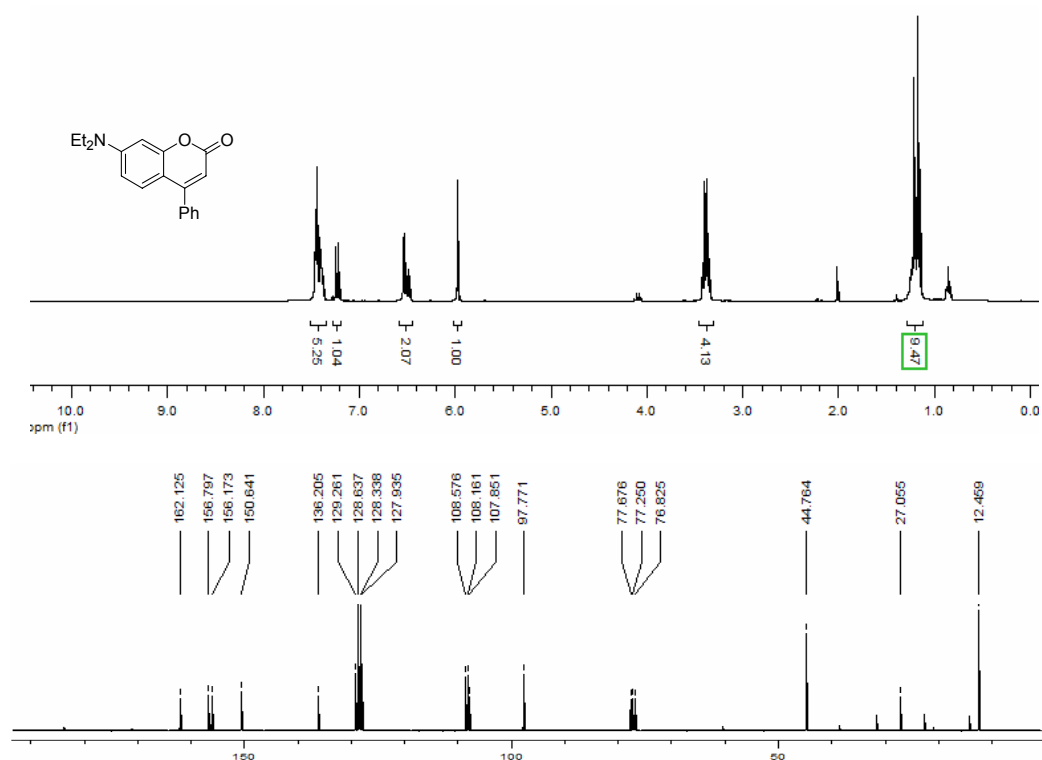


Figure S2. ¹H and ¹³C NMR of **2**.

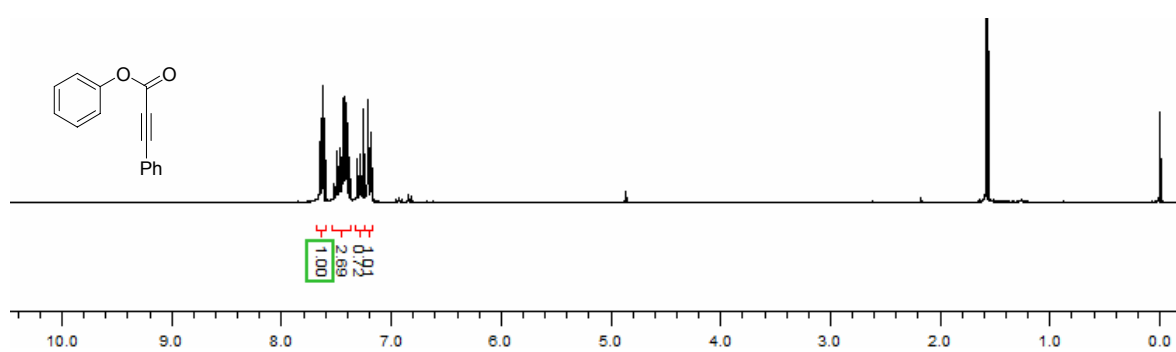


Figure S3. ¹H NMR spectrum of **3**.

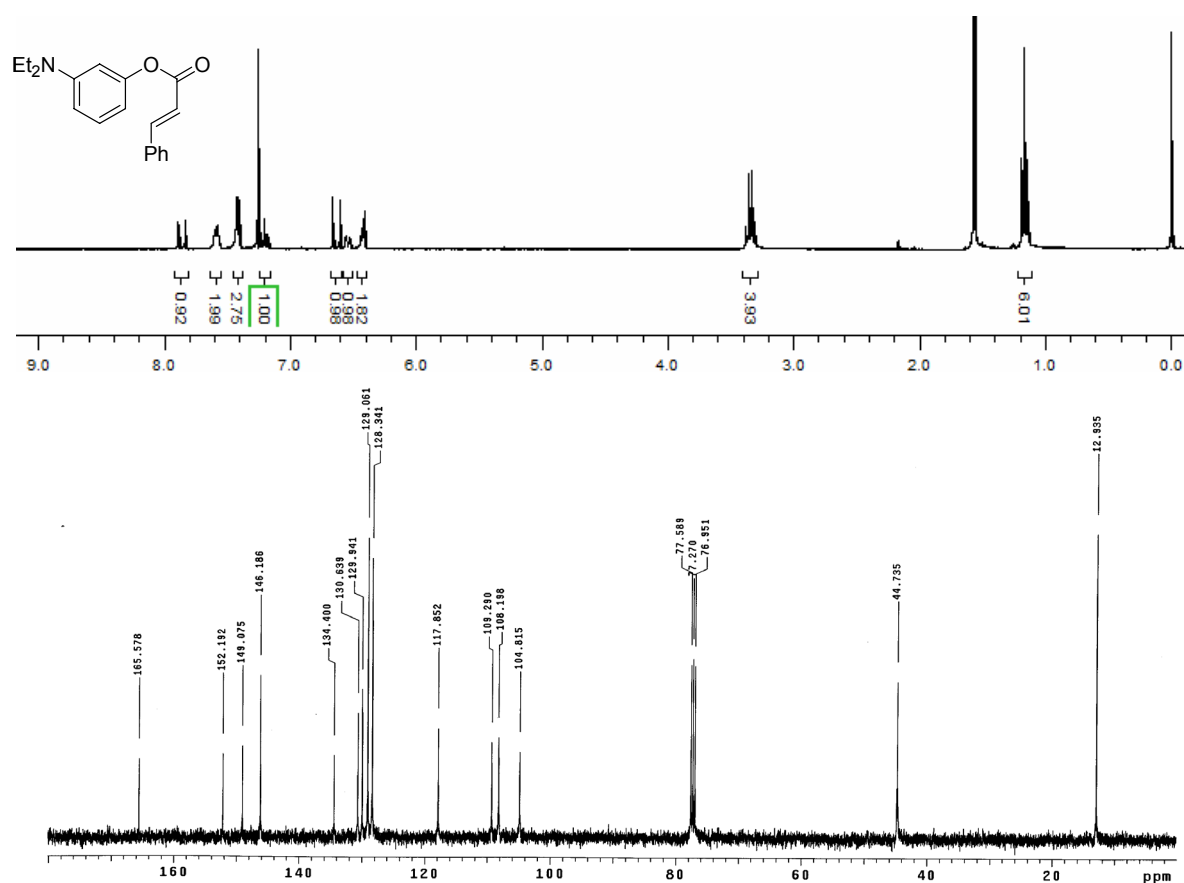


Figure S4. ¹H NMR and ¹³C NMR spectra of 4.

4. Comparison of hydroarylation reactions of **1** and its control compounds

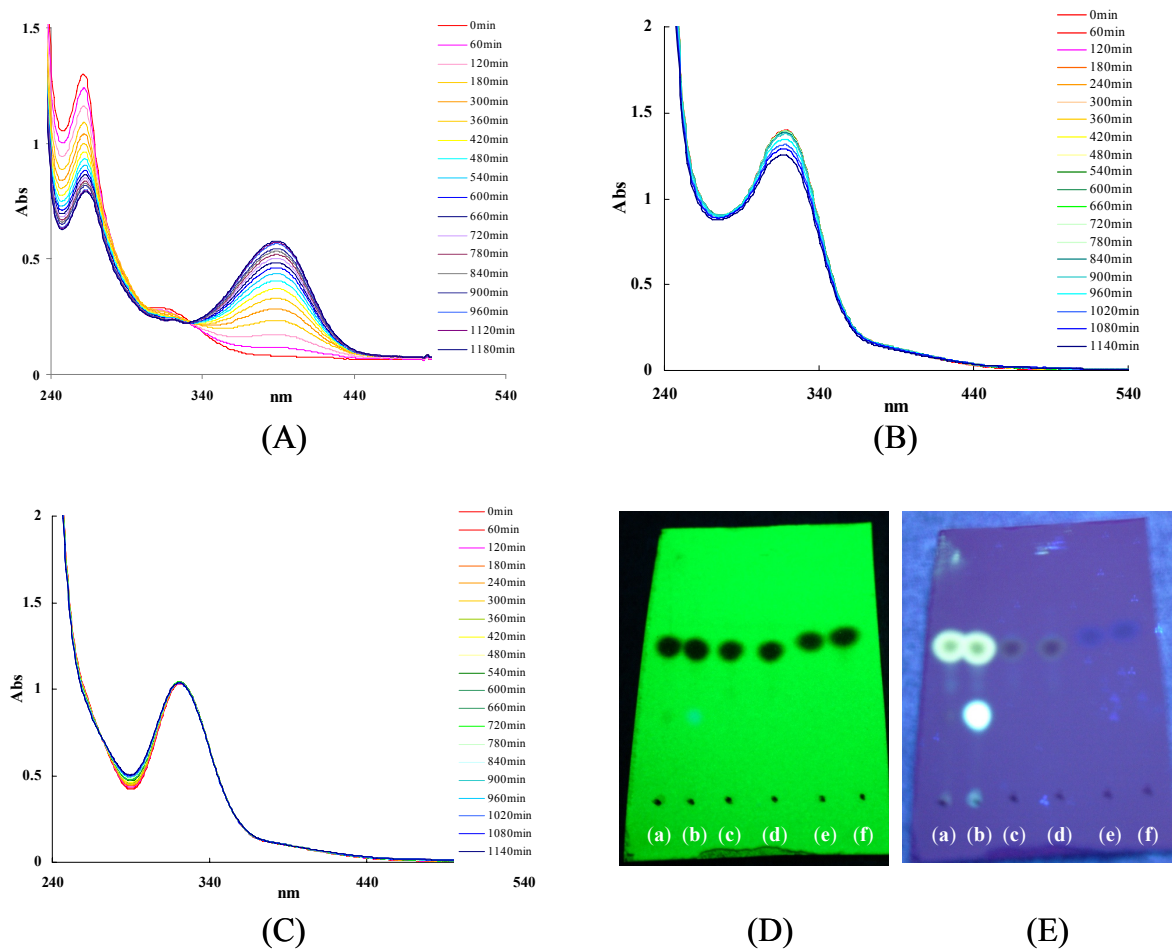


Figure S5. Time-dependent spectral changes upon addition of 10 equiv Au(III) to 30 μ M of **1** (A), **3** (B), **4** (C) in EtOH. UV-vis (D) and fluorescence (E) chromatograms of **1**, **3** and **4** (0.2 M) for the catalytic hydroarylation reaction in ethanol with 10 mol % AuCl₃ (a) **1**, (b) **1** + Au(III) after 30 min, (c) **3**, (d) **3** + Au(III) after 30 min, (e) **4**, (f) **4** + Au(III) after 30 min.

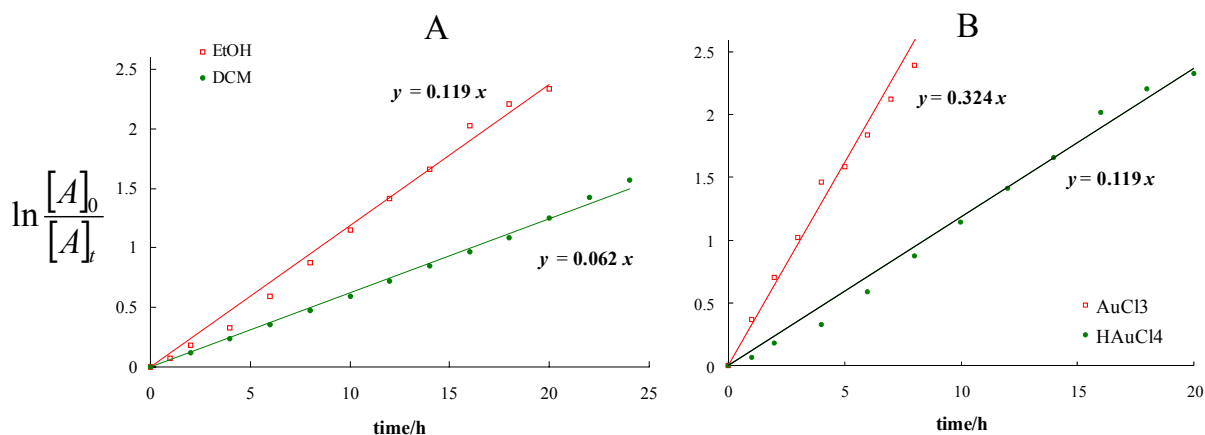


Figure S6. Kinetic analysis for the hydroarylation reaction of **1**, [1] = 30 μ M and Au(III) (10 equiv). (A) EtOH vs DCM, (B) AuCl₃ vs HAuCl₄.

5. Fluorescence intensities of **1** in the presence of various competitive metals

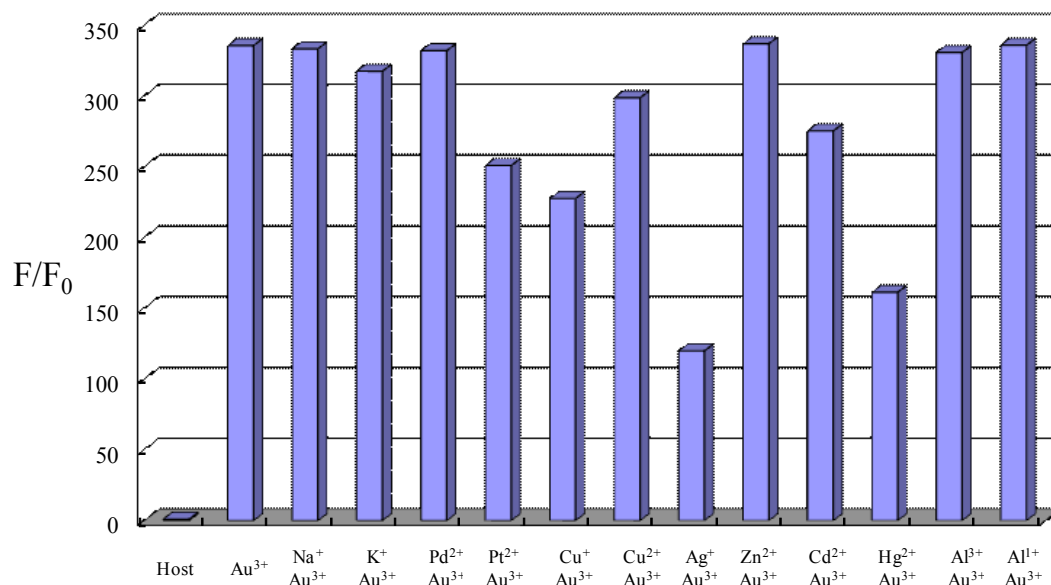


Figure S7. Competitive metal ion selectivity measurement. Fluorescence spectra of **1** (30 μ M) were measured after stepwise additions of various metal ions (1.0 equiv, 1 day) and Au³⁺ ion (1.0 equiv, 1 day) in EtOH. F_0 is the fluorescence intensity of **1** alone at 488 nm.

6. Fluorescence emission images

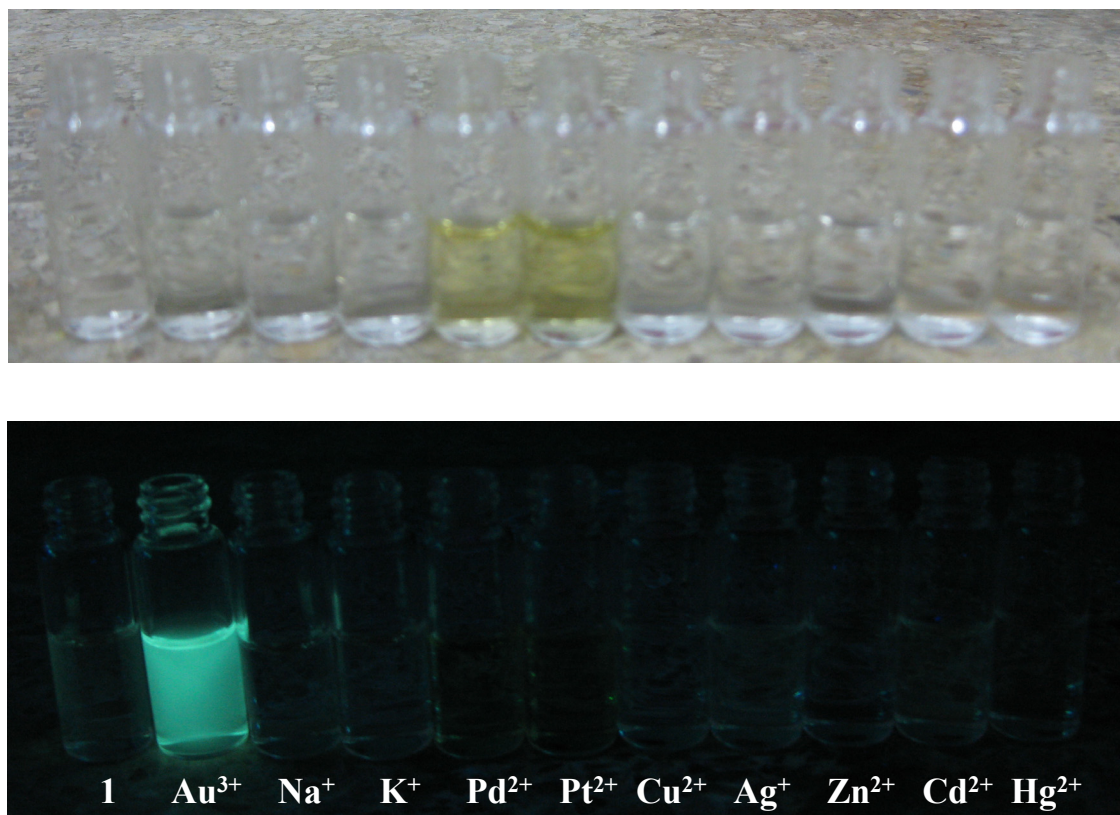


Figure S8. Naked eye detection of metal ions of **1** (30 μ M), where 10 equiv of Au(III) ions were added whereas 100 equiv of other ions were added. All the counteranions were chlorides except Ag(I) ion where triflate anion was used.

7. Fluorometric determination of limit of gold(III) detection

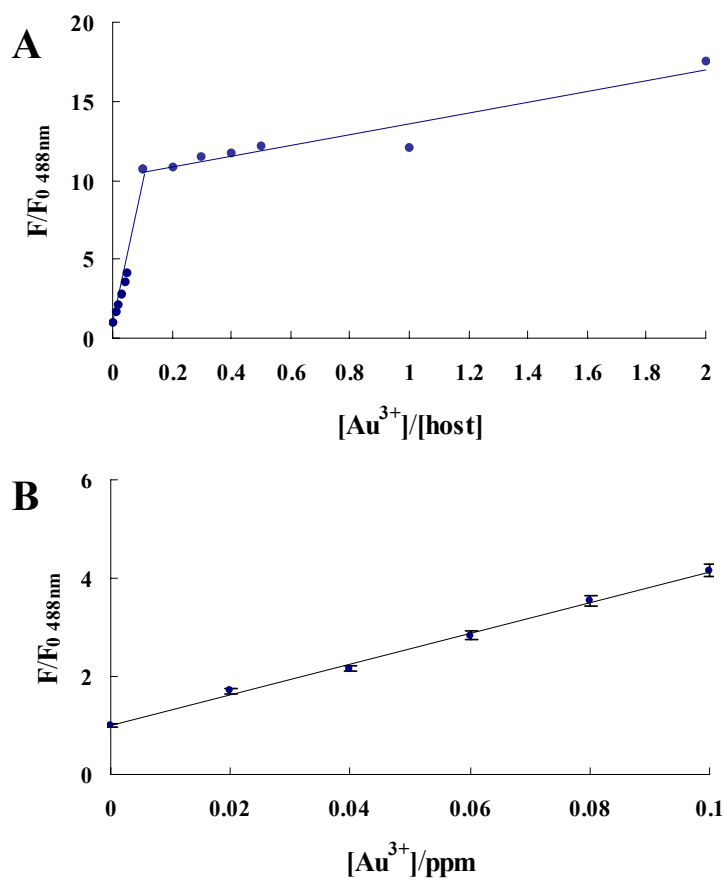


Figure S9. (A) Fluorescence responses of **1** (10 μM) in EtOH toward various amounts of Au(III) ions. (B) Linear plot of fluorescence intensity of **1** against sub-ppm level of Au(III) ion.

8. Mass spectra of compound **1** and **2**

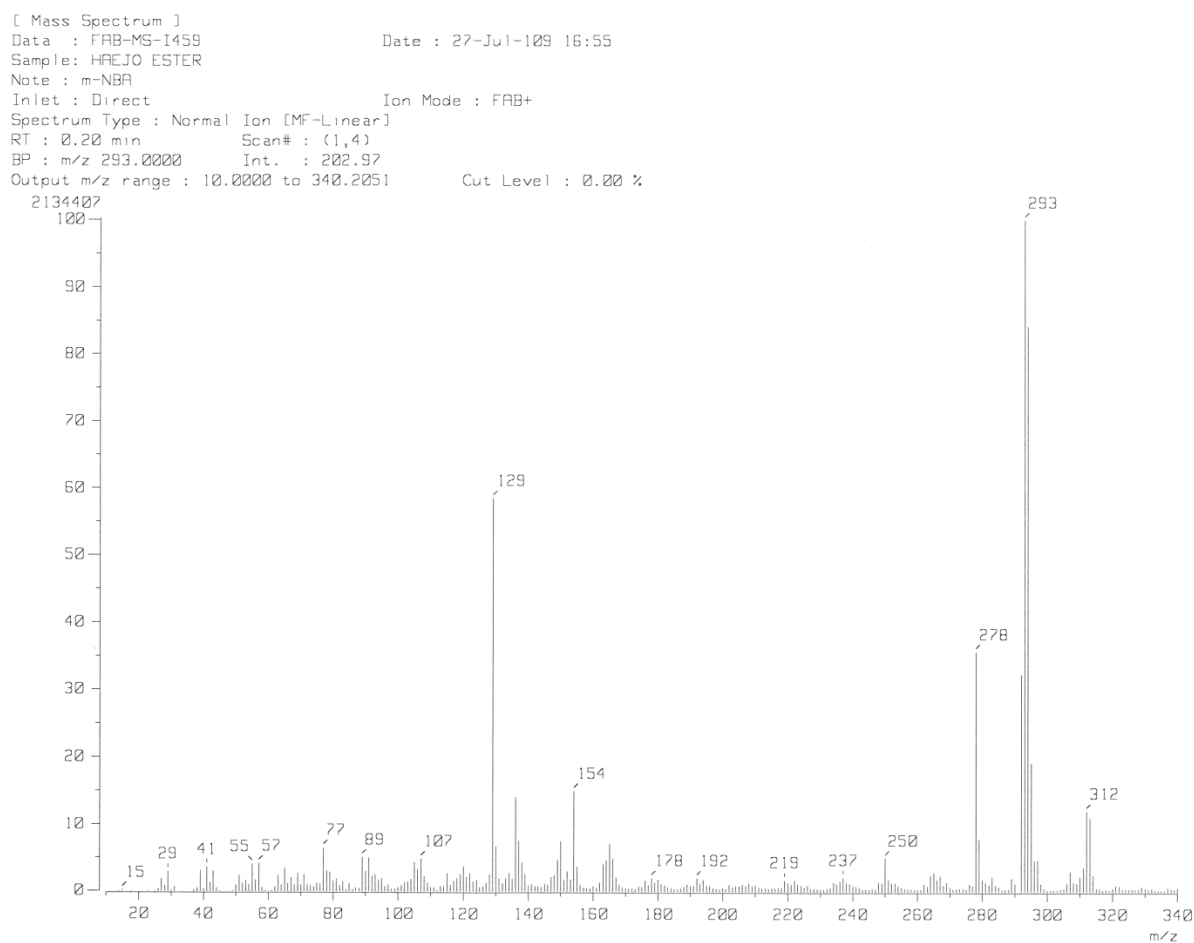


Figure S10. Mass spectrum of **1**.

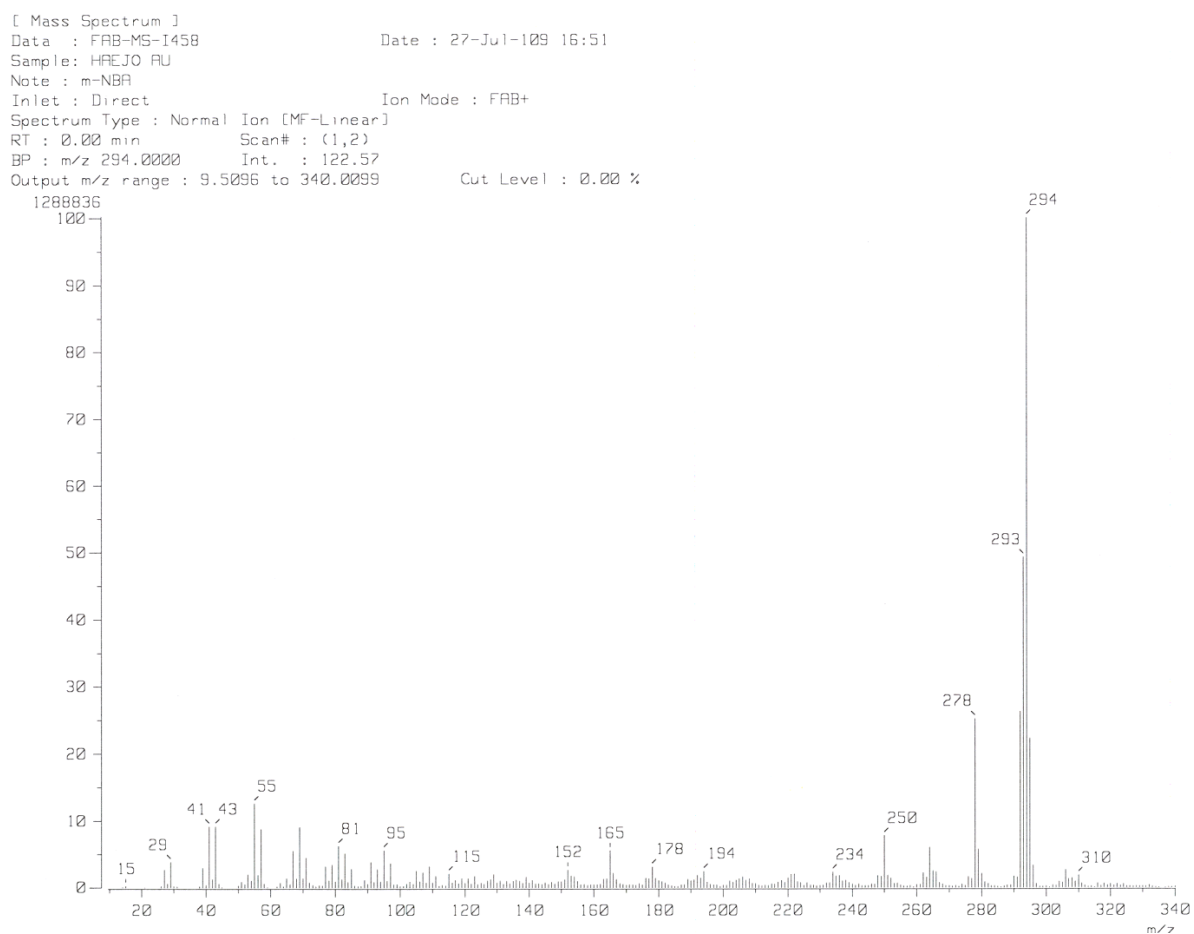


Figure S11. Mass spectrum of **2**.