

# Supporting Information

## for

### Reaction-Based Fluorescent Sensing of Au(I)/Au(III) Species: Mechanistic Implications on Vinylgold Intermediates

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#### CONTENT

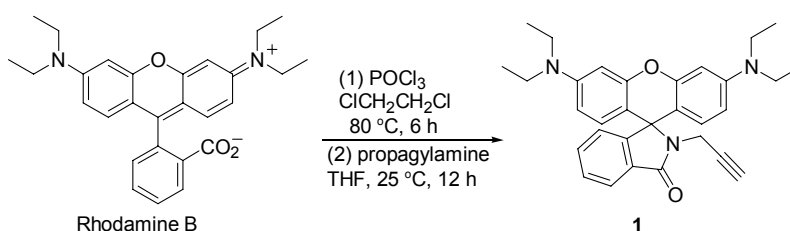
1. Synthesis of probe **1** and characterization data for compounds **2b** and **3**.
2. **Figure S1**. Color change (left) and fluorescence change (right, in the black box) of probe **1** (10  $\mu$ M) upon addition of 3 equiv of AuCl in the 1:1 CH<sub>3</sub>CN/PBS buffer (pH = 7.2).
3. **Figure S2**. Time-dependent fluorescence change of probe **1** (10  $\mu$ M) in the presence of an equimolar amount of (a) AuCl and (b) AuCl<sub>3</sub>, measured in 1:1 CH<sub>3</sub>CN/PBS buffer (pH = 7.2).  $\lambda_{\text{ex}}$  = 530 nm.
4. **Figure S3**. (a) Time-dependent fluorescence change acquired for an equimolar mixture of probe **1** (10  $\mu$ M) and AuCl<sub>3</sub>, measured in 1:1 CH<sub>3</sub>CN/PBS buffer (pH = 7.2). (b) Change in the fluorescence intensity depending on the equivalent of AuCl<sub>3</sub> added to probe **1**, measured after 1 h for each sample.  $\lambda_{\text{ex}}$  = 530 nm.
5. **Figure 4**. Comparison of fluorescence response of probe **1** toward Au(I) and Au(III) in the presence of all the other metal species [1.0 equiv of Mg(II), Ba(II), Cr(II), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Pd(II), Cu(II), Ag(I), Zn(II), Cd(II), Hg(II), and Pb(II); as chloride salts except for AgNO<sub>3</sub>] in the 1:1 CH<sub>3</sub>CN/PBS buffer (pH = 7.2), taken after 3 h of mixing.  $\lambda_{\text{ex}}$  = 530 nm.
6. **Figure S5**. Plot of fluorescence intensity for a mixture of probe **1** (10  $\mu$ M) and AuCl in 1:1 CH<sub>3</sub>CN/PBS buffer (pH 7.2) in the range 2–50  $\mu$ M of AuCl, taken after 20 min of mixing.  $\lambda_{\text{ex}}$  = 530 nm.
7. **Figure S6**. Fluorescence spectrum of probe **1** (10  $\mu$ M) upon addition of AuCl (1.5  $\mu$ M/0.4 ppm) in 1:1 CH<sub>3</sub>CN/PBS buffer (pH 7.2), taken after 20 min of mixing, which shows the signal-to-background ratio is more than three.

8. **Figure S7.** Time-dependent fluorescence change of probe **1** (10  $\mu\text{M}$ ) in the presence of an equimolar amount of (a) AuCl and (b) AuCl<sub>3</sub>, measured in CH<sub>3</sub>CN.  $\lambda_{\text{ex}}$  = 530 nm.
9. NMR spectra and Mass data for compounds **1**, **2b** and **3**.

## 1. General Methods

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker DPX-300 and DRX-500. Coupling constants ( $J$  value) are reported in hertz. The chemical shifts are shown in ppm. UV absorption spectra were obtained using a HP 8453 UV/Vis spectrophotometer. Fluorescence spectra were recorded on a Photon Technical International Fluorescence system. High-resolution MALDI-TOF mass spectrometry was performed on an Applied Biosystem Voyager 4394 (ionization method,  $\text{N}_2$  laser (337 nm, 3 ns pulse): analyzer 2.0 m linear mode; 3.0 reflector mode).

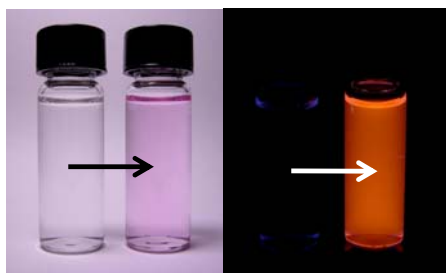
### Synthesis of probe 1:



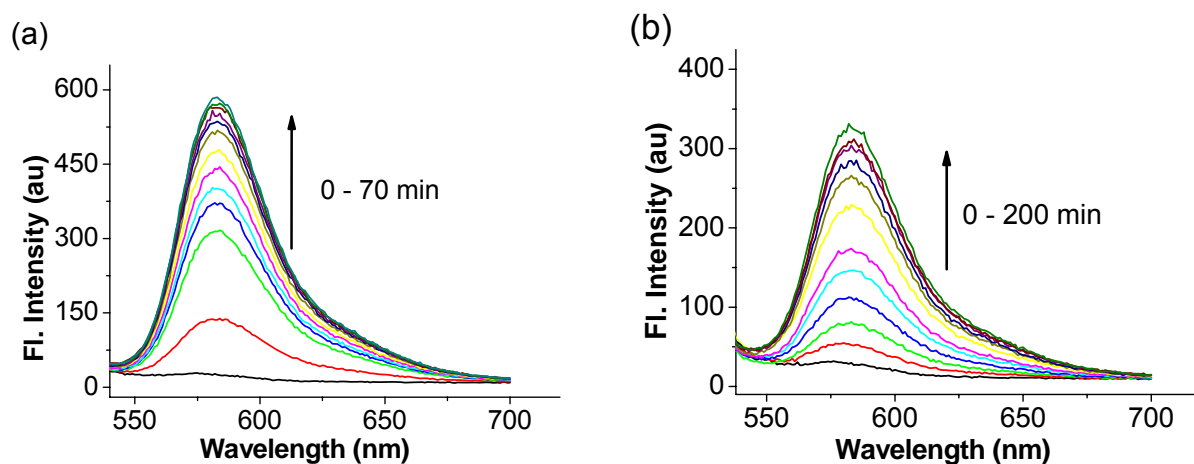
Rhodamine B (1.0 g, 2.09 mmol) was dissolved in 1,2-dichloroethane and  $\text{POCl}_3$  was added dropwise via syringe (1.26 mL, 13.52 mmol) with vigorous stirring. The mixture was stirred under reflux for 6 h at  $80\text{ }^\circ\text{C}$ . The reaction mixture was cooled to room temperature and the solvent was carefully evaporated in vacuo. The residue obtained was dissolved in THF and then treated with triethylamine (1.66 mL, 12 mmol) followed by propargylamine (0.12 mg, 2.2 mmol), and the resulting solution was stirred overnight  $25\text{ }^\circ\text{C}$ . The resulting dark-red mixture was subjected to column chromatography ( $\text{Al}_2\text{O}_3$ , eluent: 80% EtOAc in Hexane). Probe 1 can be purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ -Hexane as a pale pink crystal substance (701 mg, 70%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, 293K):  $\delta$  7.92 (m, 1H), 7.42 (m, 2H), 7.10 (m, 1H), 6.47 (d,  $J = 8.9$  Hz, 2H), 6.39 (d,  $J = 2.5$  Hz, 2H), 6.27 (dd,  $J = 2.6, 8.9$  Hz, 2H), 3.95 (d,  $J = 2.5$  Hz, 2H), 3.33 (q,  $J = 7.0$  Hz, 8H), 1.76 (t,  $J = 2.5$  Hz, 1H), 1.20 (m, 12H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  167.4, 153.8, 153.5, 148.9, 132.7, 130.5, 129.2, 128.1, 123.8, 123.1, 108.1, 105.1, 97.8, 78.3, 70.1, 64.8, 44.4, 14.3, 12.6. FAB:  $m/z$  calcd. for  $\text{C}_{31}\text{H}_{33}\text{N}_3\text{O}_2$  ( $\text{M} + \text{H}$ ) $^+$  479.60; found 480.24.

Compound **2b**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  8.25 (d,  $J = 8.1$  Hz, 1H), 7.68 (m, 2H), 7.35 (s, 1H), 7.13 (d,  $J = 9.3$  Hz, 1H), 6.87 (m, 4H), 6.52 (s, 1H), 3.65 (q, 8H), 2.18 (s, 3H), 1.36 (t,  $J = 12.3$  Hz, 12H). EI:  $m/z$  calcd. for  $\text{C}_{31}\text{H}_{34}\text{N}_3\text{O}_2$  ( $\text{M}$ ) $^+$  480.6; found 480.2.

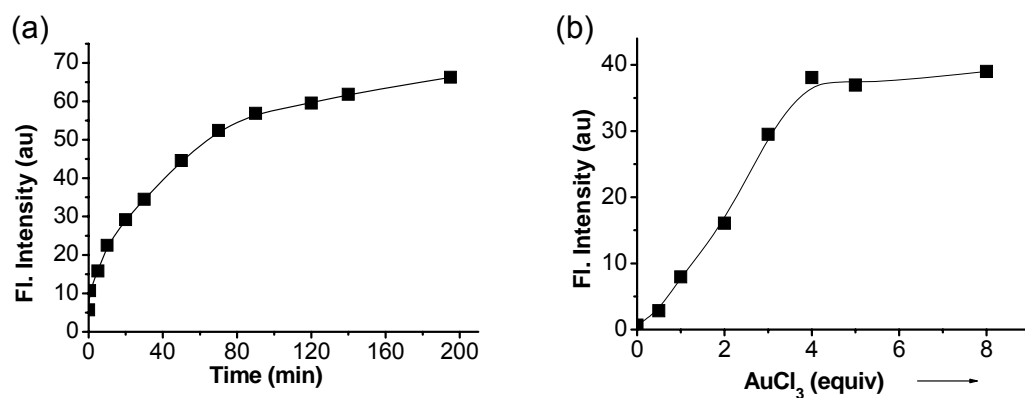
Compound **3**: A dark red powder.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, 293 K):  $\delta$  9.64 (s, 1H), 8.45 (m, 1H), 7.80 (m, 2H), 7.62 (s, 1H), 7.41 (m, 1H), 7.1 (d,  $J = 9.6$  Hz, 2H), 6.92 (d,  $J = 2.4$  Hz, 2H), 6.77 (dd,  $J = 2.4, 9.6$  Hz, 2H), 3.60 (q,  $J = 7.2$  Hz, 8H), 1.31 (m, 12H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz, 293 K):  $\delta$  176.5, 162.5, 158.2, 155.7, 149.4, 138.8, 132.3, 132.1, 131.1, 131.0, 130.8, 129.9, 125.2, 117.9, 114.2, 114.0, 96.9, 46.2, 12.7. EI MS:  $m/z$  calcd. for  $\text{C}_{31}\text{H}_{32}\text{N}_3\text{O}_4$  494.6; found 494.1.



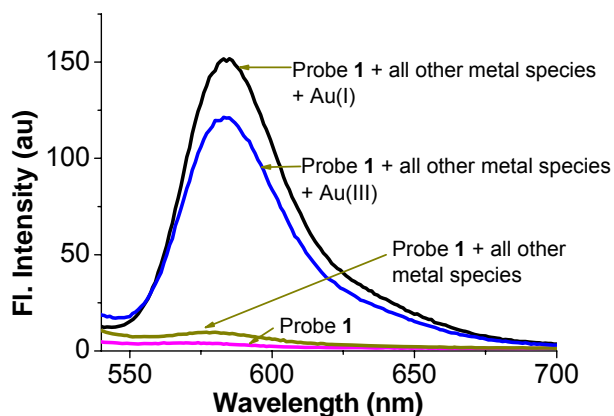
**Figure S1.** Color change (left) and fluorescence change (right, in the black box) of probe **1** ( $10\ \mu\text{M}$ ) upon addition of 3 equiv of  $\text{AuCl}_3$  in the 1:1  $\text{CH}_3\text{CN}/\text{PBS}$  buffer ( $\text{pH} = 7.2$ ).



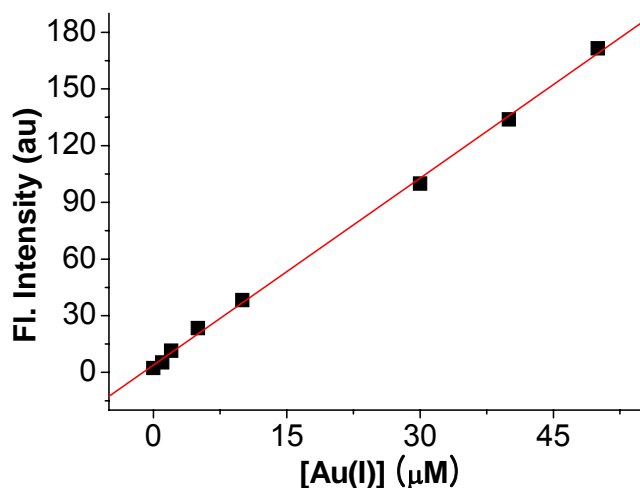
**Figure S2.** Time-dependent fluorescence change of probe **1** ( $10\ \mu\text{M}$ ) in the presence of an equimolar amount of (a)  $\text{AuCl}$  and (b)  $\text{AuCl}_3$ , measured in 1:1  $\text{CH}_3\text{CN}/\text{PBS}$  buffer ( $\text{pH} = 7.2$ ).  $\lambda_{\text{ex}} = 530\ \text{nm}$ .



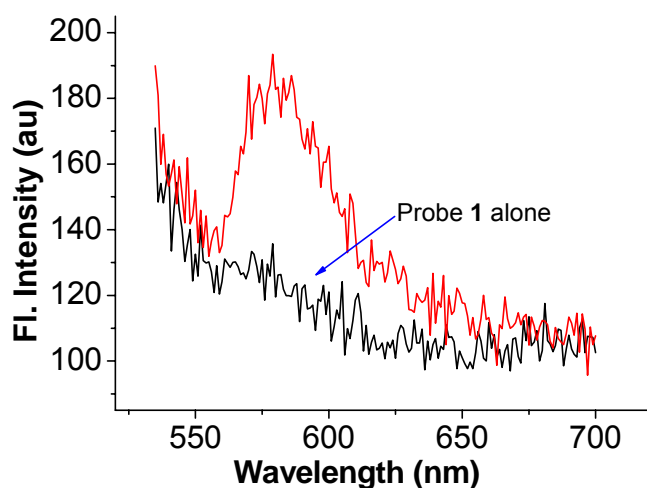
**Figure S3.** (a) Time-dependent fluorescence change acquired for an equimolar mixture of probe **1** ( $10\ \mu\text{M}$ ) and  $\text{AuCl}_3$ , measured in 1:1  $\text{CH}_3\text{CN}/\text{PBS}$  buffer ( $\text{pH} = 7.2$ ). (b) Change in the fluorescence intensity depending on the equivalent of  $\text{AuCl}_3$  added to probe **1**, measured after 1 h for each sample.  $\lambda_{\text{ex}} = 530\ \text{nm}$ .



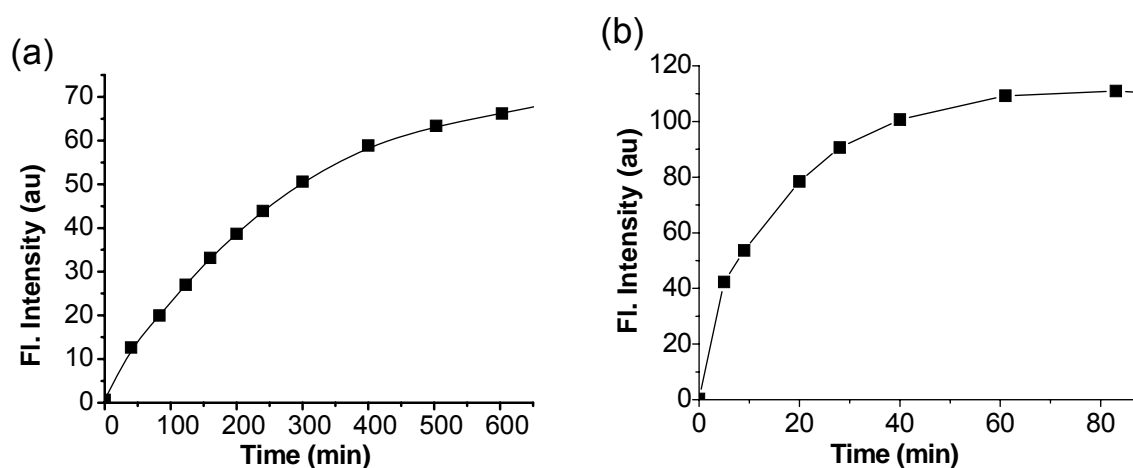
**Figure S4.** Comparison of fluorescence response of probe **1** toward Au(I) and Au(III) in the presence of all the other metal species [1 equiv of Mg(II), Ba(II), Cr(II), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Pd(II), Cu(II), Ag(I), Zn(II), Cd(II), Hg(II), and Pb(II); as chloride salts except for AgNO<sub>3</sub>] in the 1:1 CH<sub>3</sub>CN/PBS buffer (pH = 7.2), taken after 3 h of mixing.  $\lambda_{\text{ex}} = 530$  nm.



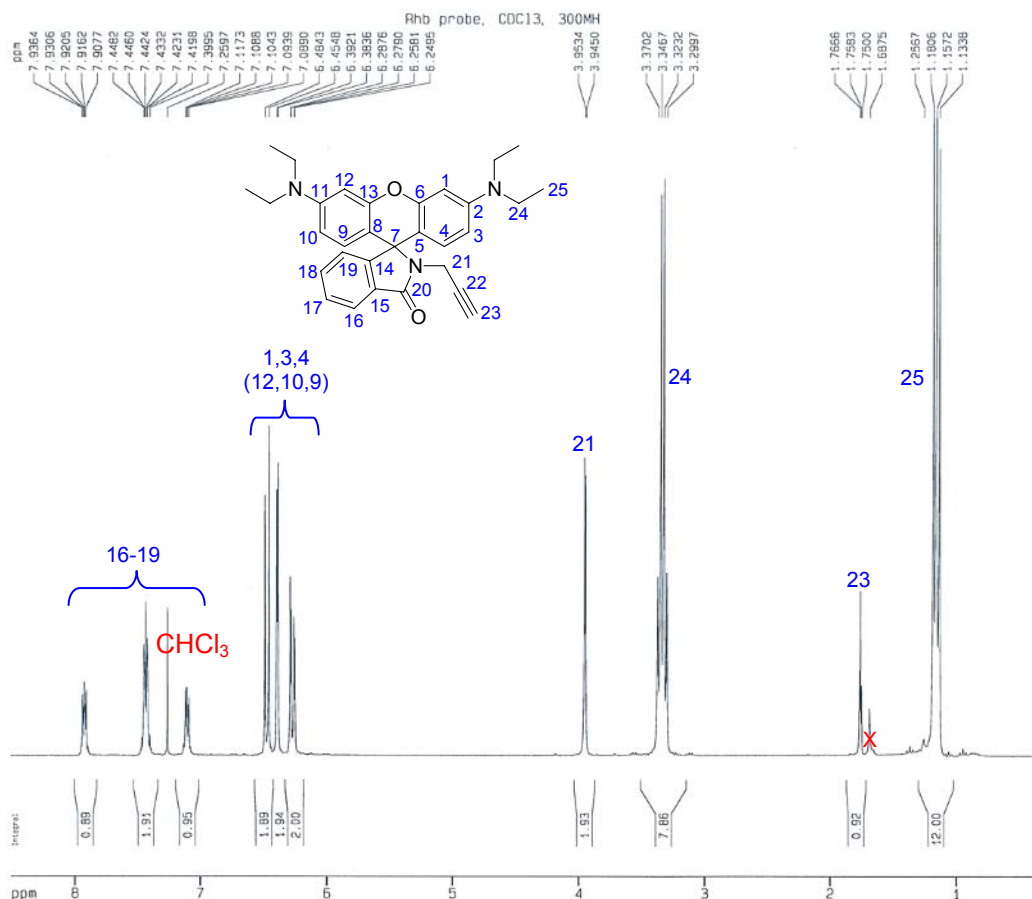
**Figure S5.** Plot of fluorescence intensity for a mixture of probe **1** (10  $\mu\text{M}$ ) and AuCl in 1:1 CH<sub>3</sub>CN/PBS buffer (pH 7.2) in the range 2–50  $\mu\text{M}$  of AuCl, taken after 20 min of mixing.  $\lambda_{\text{ex}} = 530$  nm.



**Figure S6.** Fluorescence spectrum of probe **1** (10  $\mu\text{M}$ ) upon addition of AuCl (1.5  $\mu\text{M}$ /0.4 ppm) in 1:1  $\text{CH}_3\text{CN}$ /PBS buffer (pH 7.2), taken after 20 min of mixing, which shows the signal-to-background ratio is more than three.



**Figure S7.** Time-dependent fluorescence change of probe **1** (10  $\mu\text{M}$ ) in the presence of an equimolar amount of (a) AuCl and (b) AuCl<sub>3</sub>, measured in  $\text{CH}_3\text{CN}$ .  $\lambda_{\text{ex}} = 530 \text{ nm}$ . (Because of difficulty in excluding a trace of water molecules in the solvent, the data is dependent on each measurement.)



Current Data Parameters

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EXPNO	1
PROCNO	1

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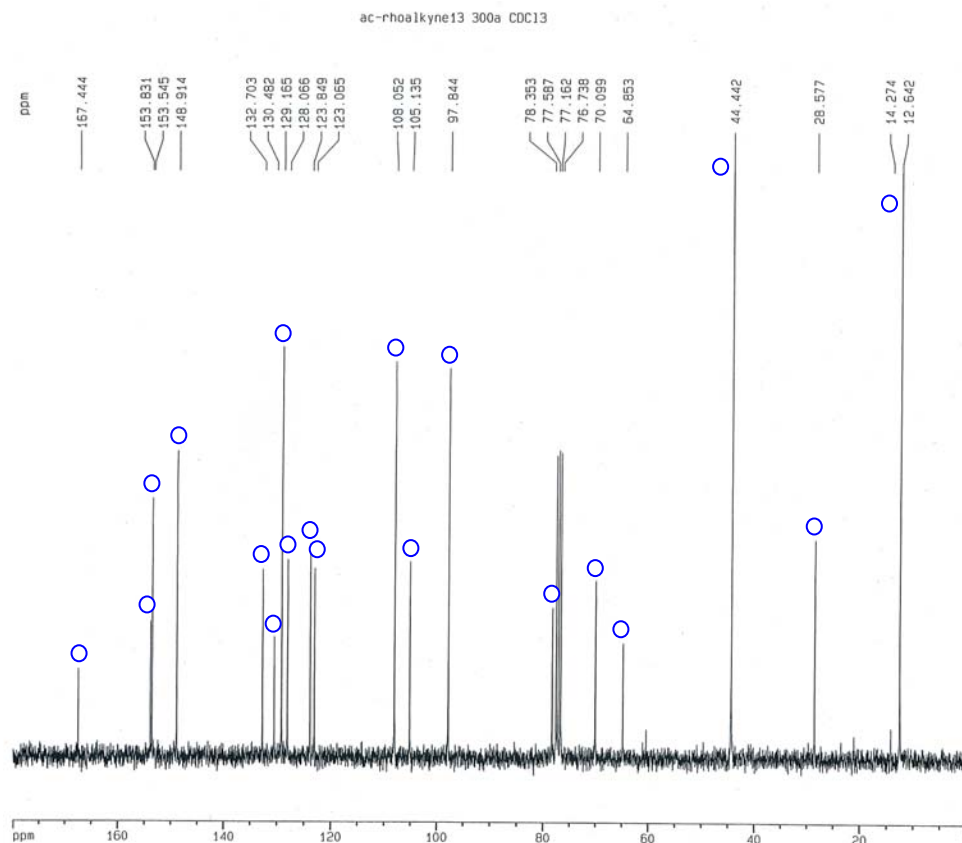
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FIDRES	0.188380 Hz
AQ	2.6542580 sec
RG	362
DM	81.000 usec
DE	4.50 usec
TE	300.0 K
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P1	9.50 usec
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SFO1	300.1318034 MHz
NUC1	1H
PL1	1.00 dB

F2 - Processing parameters

SI	16384
SF	300.1300064 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	21.00 cm
F1P	8.503 ppm
F1	2552.01 Hz
F2P	0.328 ppm
F2	98.42 Hz
PPMCM	0.38929 ppm/cm
HZCM	115.83775 Hz/cm



Current Data Parameters

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EXPNO	13
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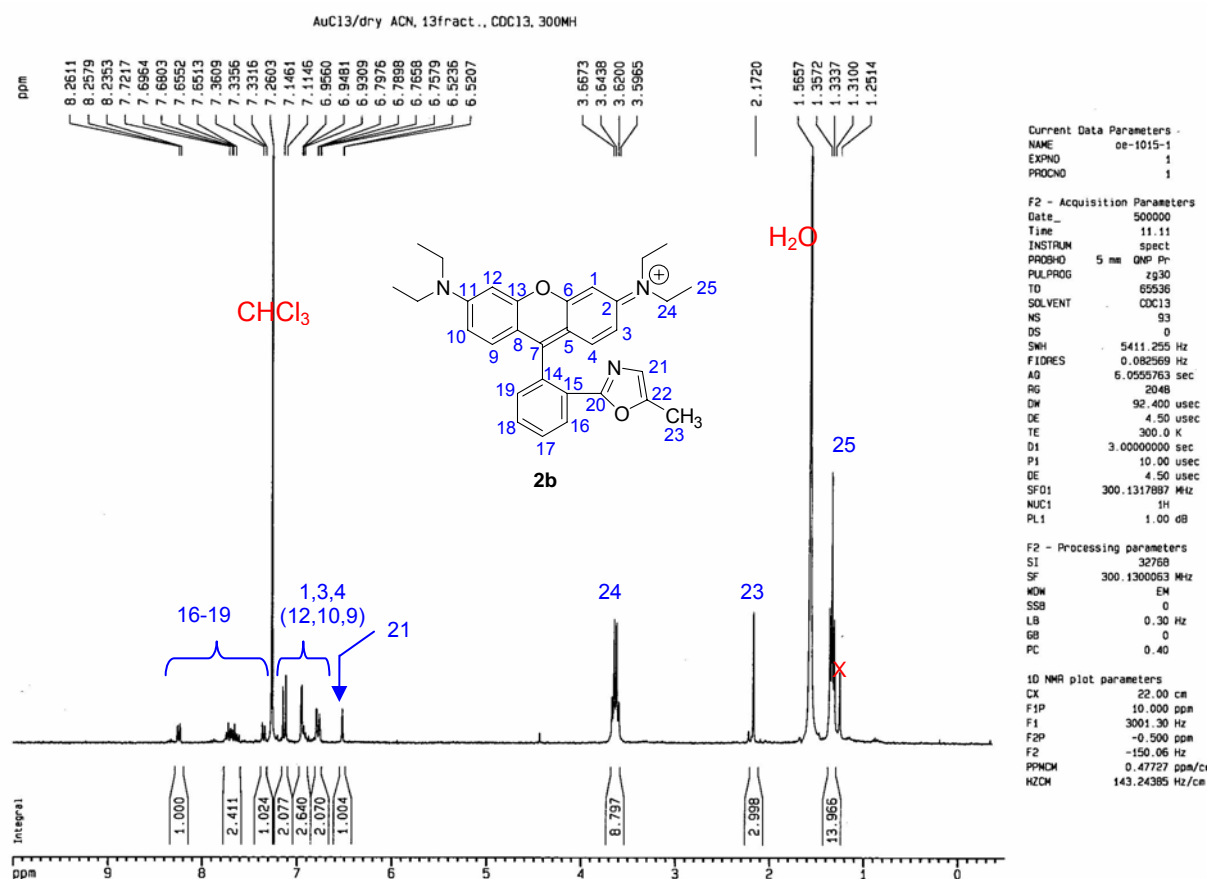
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RG	3251
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TE	300.0 K
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D12	0.0000200 sec
PL13	25.00 dB
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PCPD2	100.00 usec
SFO2	300.1312005 MHz
NUC2	13C
PL2	1.00 dB
PL12	23.00 dB
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F2 - Processing parameters

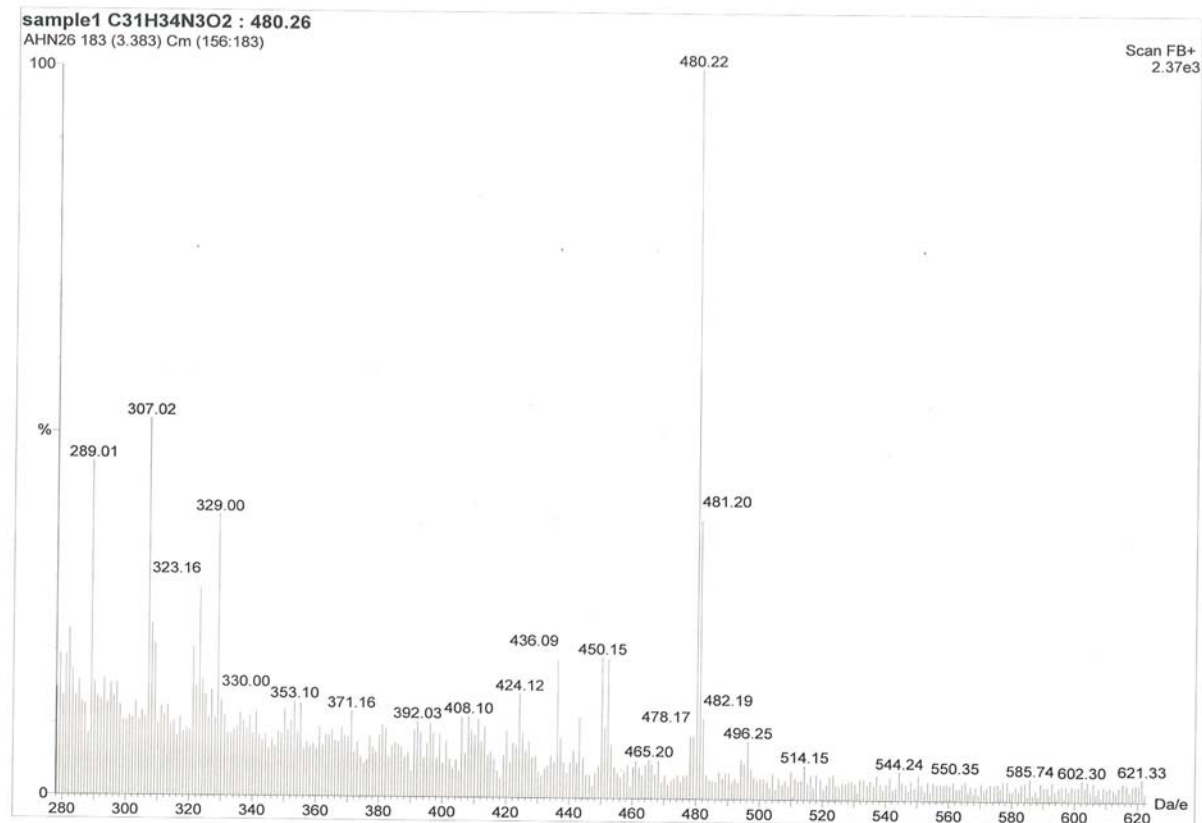
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1D NMR plot parameters

CX	22.00 cm
F1P	189.000 ppm
F1	13584.19 Hz
F2P	-0.500 ppm
F2	-37.73 Hz
PPMCM	8.20455 ppm/cm
HZCM	619.17653 Hz/cm

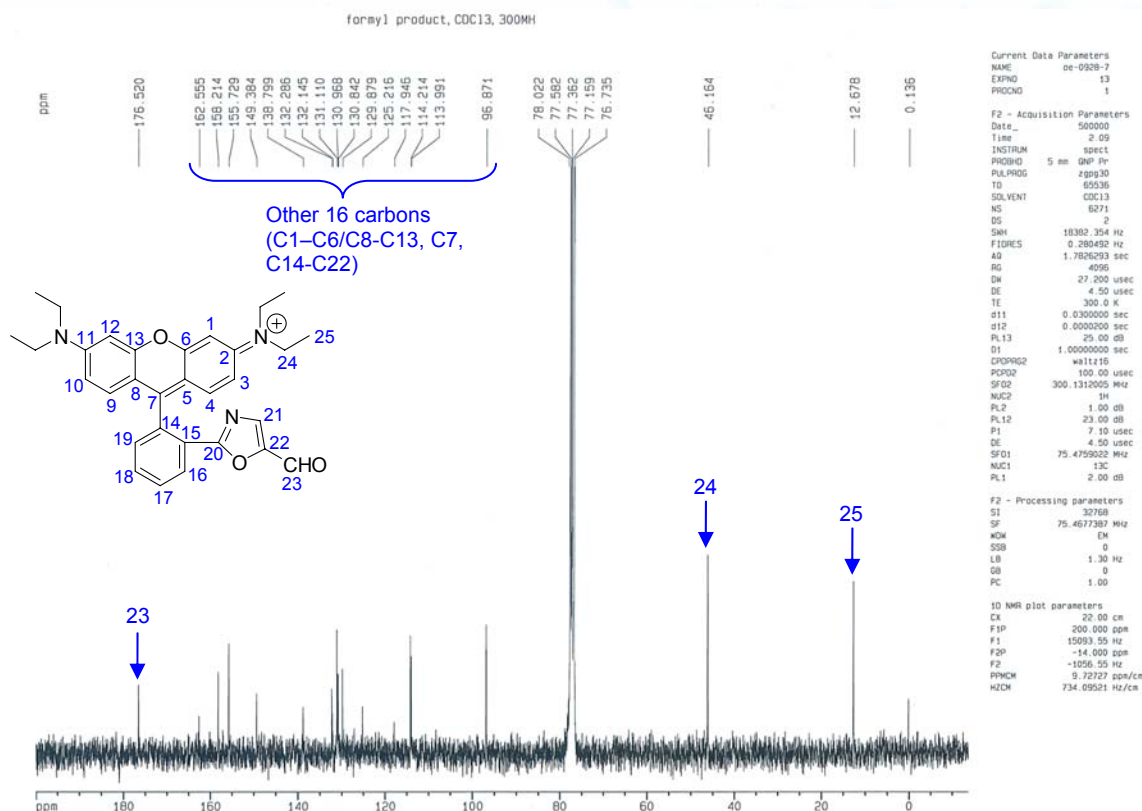
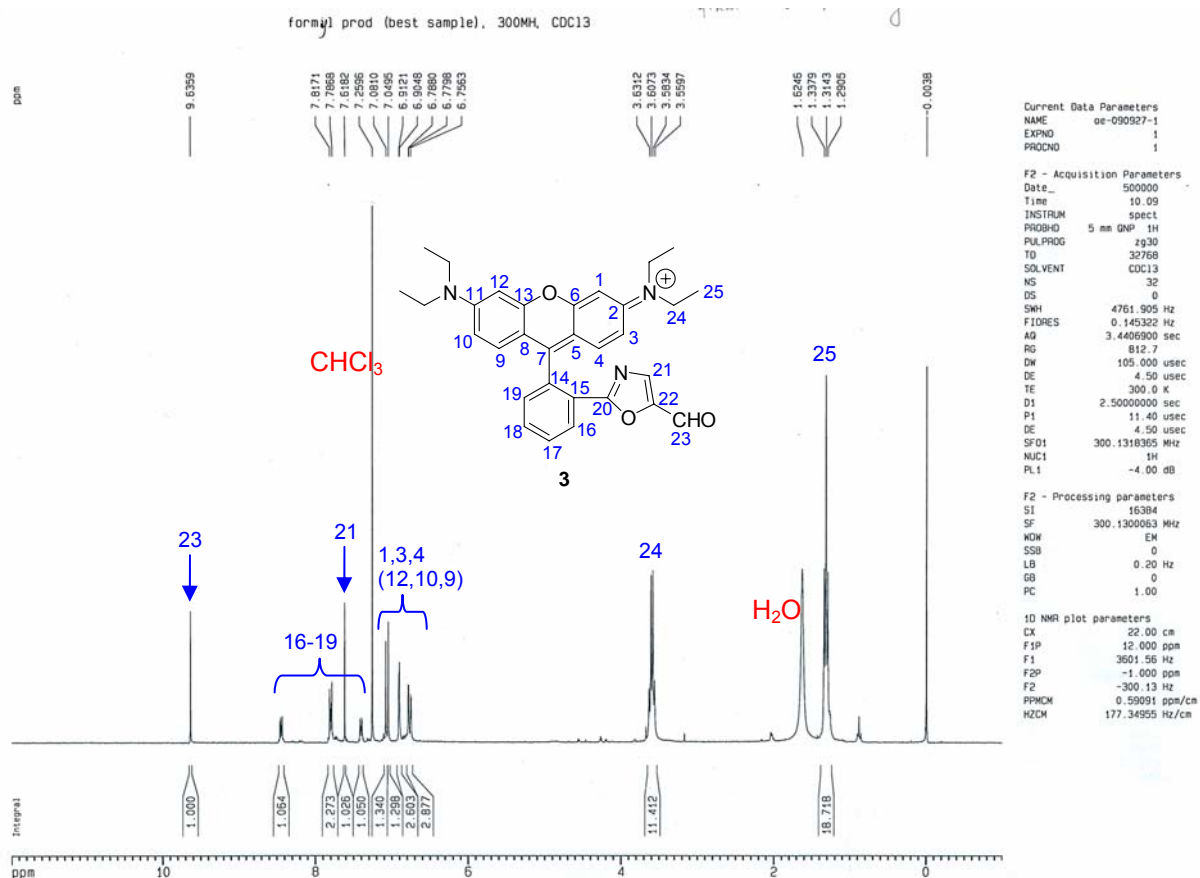


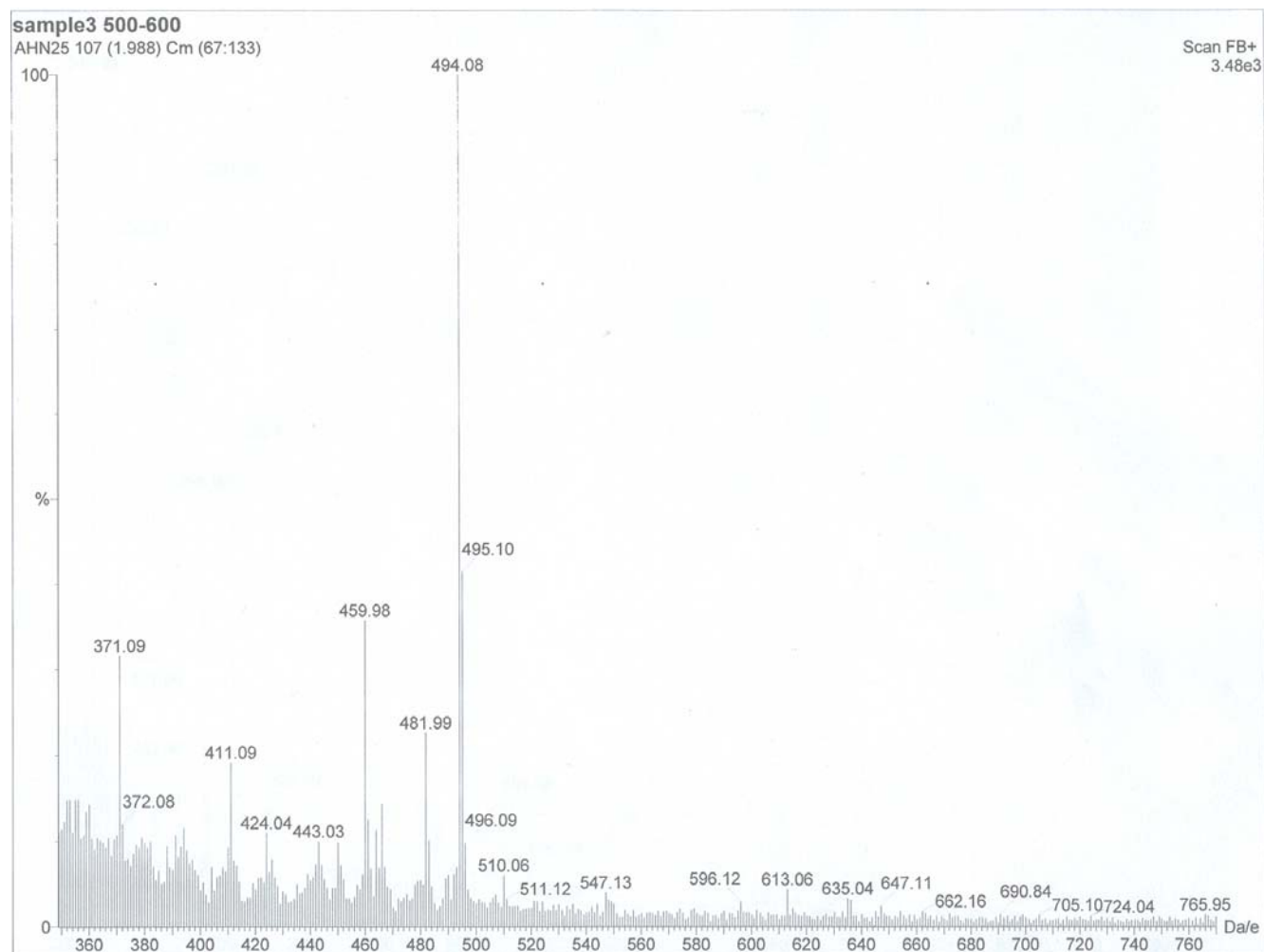
X: Impurities such as high-molecular-weight hydrocarbons (grease)



Exact mass of compound **3** is 480.27.







Exact mass of compound **3** is 494.24.