Supporting Information

A reaction-based scenario for fluorescent probing of Au(III) ions in human cells and plants

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1. EXPERIMENTAL

All chemicals were purchased from commercial suppliers. NMR spectra were measured on Varian VNMRJ 400 Nuclear Magnetic Resonance Spectrometer. All spectroscopic were collected on a Horiba-Duetta, the two-in-one

fluorescence and absorbance spectrometer. The samples were measured in a quartz cuvette with a path length of 10.0 mm and a volume of 2.0 mL. Fluorescence imaging was performed with Zeiss Axio Observer inverted fluorescence microscope. pH was recorded by HI-8014 instrument (HANNA). Mass spectra were recorded on Agilent 6530 Accurate-Mass QTOF LC/MS. All measurements were conducted at least in triplicate. All experiments were performed under argon atmosphere.

Synthesis of KEREM-1

To a mixture of BOD-AC (140 mg, 0.4 mmol) and 2-iodoprop-2-en-1-ol (147 mg, 0.8 mmol) in THF (20 mL) were added $PdCl_2(PPh_3)_2$ (29 mg, 0.1 equiv.), CuI (15 mg, 0.2 equiv.) and diisopropylamine (11.6 mL). The reaction mixture was stirred overnight at 50 ℃. After completion of the reaction as monitored by TLC, the solvent was evaporated and the resulting residue was extracted with water and CH_2Cl_2 (3 x 30 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. The resultant residue was purified by column chromatography with hexane: ethyl acetate (2:1) to afford **KEREM-1** as red solid (98 mg, 70 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ= 7.51 – 7.48 (m, 3H), 7.28 – 7.25 (m, 2H), 6.03 (s, 1H), 5.52 (dd, J=2.7, 1.3 Hz, 1H), 5.48 (dd, J = 2.7, 1.3 Hz, 1H), 4.19 (s, 2H), 2.63 (s, 3H), 2.57 (s, 3H), 1.43 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ= 158.1, 156.39, 145.07, 142.87, 142.3, 134.74, 132.70, 131.51, 130.28, 129.4, 129.35, 127.97, 122.36, 119.45, 114.70, 93.51, 83.83, 65.64, 32.08, 29.85, 14.70, 13.27. HRMS: m/z: Calcd. for $(C_{24}H_{23}BF_2N_2O)$ [M+H]$^+$: 405.1950; found 405.1951.

Synthesis of BOD-FUR

$AuCl_3$ (30 mg, 0.1 mmol) was added to **KEREM-1** (40 mg, 0.1 mmol) in PBS/EtOH (10 mL, (7/3 (v/v)). The reaction mixture was stirred for 2 hours at room temperature. The resulting solution was extracted with CH_2Cl_2 (3x10mL) and dried over $MgSO_4$. After evaporation of solvent, the resultant residue was purified by column chromatography. (20 mg, 50% yield). ^1H NMR (400 MHz, $CDCl_3$) δ= 7.50 – 7.48 (m, 3H), 7.31 – 7.29 (m, 2H), 7.21 – 7.19 (m, 1H), 6.09 (s, 1H), 6.01 (s, 1H), 2.68 (s, 3H), 2.57 (s, 3H), 2.05 (d, J = 1.1 Hz, 3H), 1.43 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ= 156.50, 154.36, 148.25, 143.92, 142.19, 139.02, 138.58, 135.17, 132.08, 130.95, 129.33, 129.19, 128.16, 123.4, 121.85, 121.22, 111.60, 29.85, 14.65, 14.03, 13,02, 9.95. HRMS: m/z: Calcd. for $(C_{24}H_{23}BF_2N_2O)$ [M+H]$^+$: 405.1950; found 405.1962.

2. ANALYTICAL STUDIES

Fluorescence quantum yield was calculated with the following equation;

$$\Phi_{F(X)} = \Phi_{F(S)} (A_S F_X / A_X F_S) (n_X/n_S)^2$$

Rhodamine 6G, Φ_F=0.95 in ethanol, was used as the standard.[1]

A: absorbance at the excitation wavelength,

Φ_F: fluorescence quantum yield,

F: area under the corrected emission curve

n: refractive index of the solvents.

S and X refer to the standard and the unknown, respectively. ($\Phi_{F(KEREM-1)}$ = 0.122, $\Phi_{F(BOD-FUR)}$ =0.703)
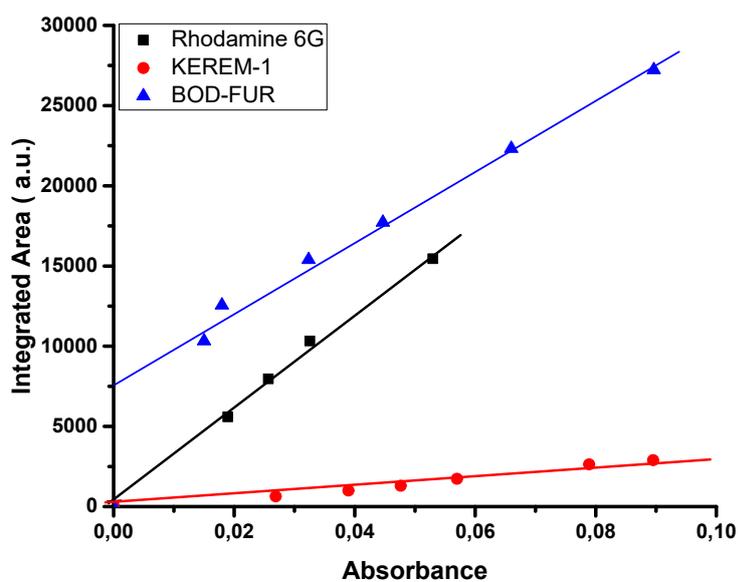
Fig. S1 Quantum yield plot, Relative fluorescence intensities using Rhodamine 6G as the standard.

Detection limit was calculated from the following formula;

$$Detection\ limit = 3\sigma bi/m,$$

σbi: standard deviation of blank measurements,

m: slope between intensity versus sample concentration.

The fluorescence changes of 10 examples of **KEREM-1** (10.0 µM) were measured to determine the standart deviation of the blanks.[2] A good linear relationship between the fluorescence intensity and Au^{3+} concentration was obtained over the range of 0.1 − 0.9 µM (R^2= 0.9964). The detection limit was calculated as 358 nM. All measurements were performed in triplicates.
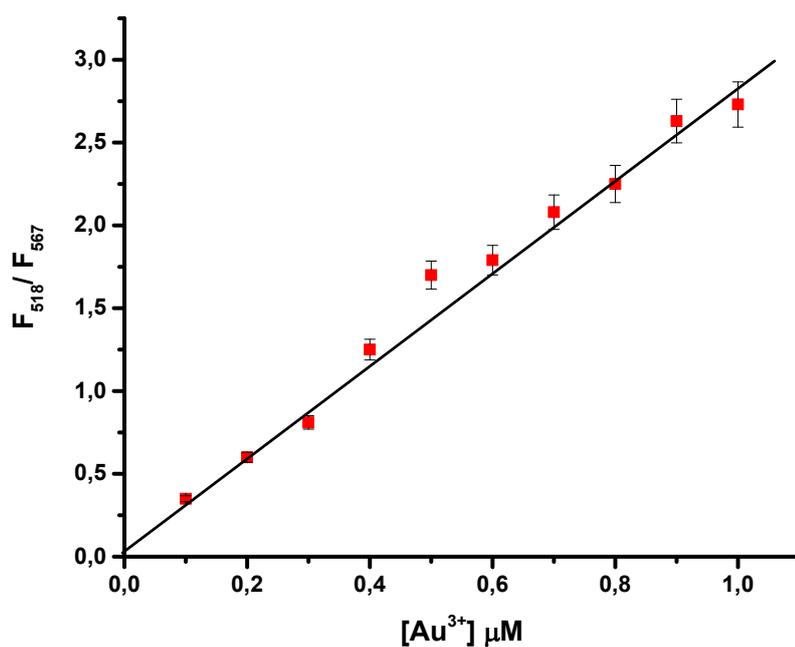
Fig. S2 Fluorescence titration of **KEREM-1** (10.0 μM) with Au^{3+} (0.1- 0.9 μM,) in PBS (0.01 M) /EtOH (pH 7.0, v/v,7:3). (λ_{ex}:460 nm, emission wavelengths: F_{518}/ F_{567} at 25 ℃).
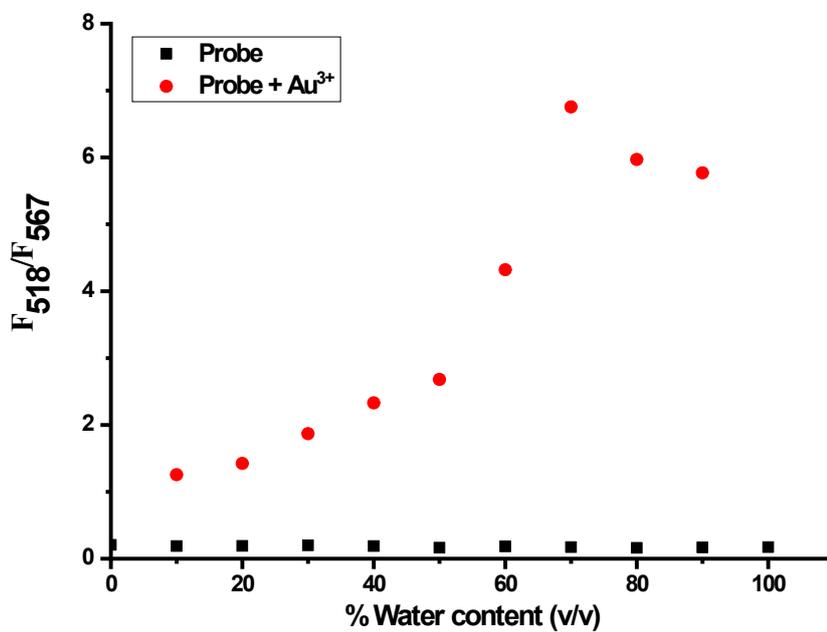
Fig. S3 The effect of water content on the response of **KEREM-1** (10 μM) toward Au^{3+} (100μM, 10 Equiv.) in PBS (0.01 M) /EtOH (pH 7.0, v/v,7:3). (λ_{ex}: 460 nm, emission: F_{518}/ F_{567} at 25 ℃).
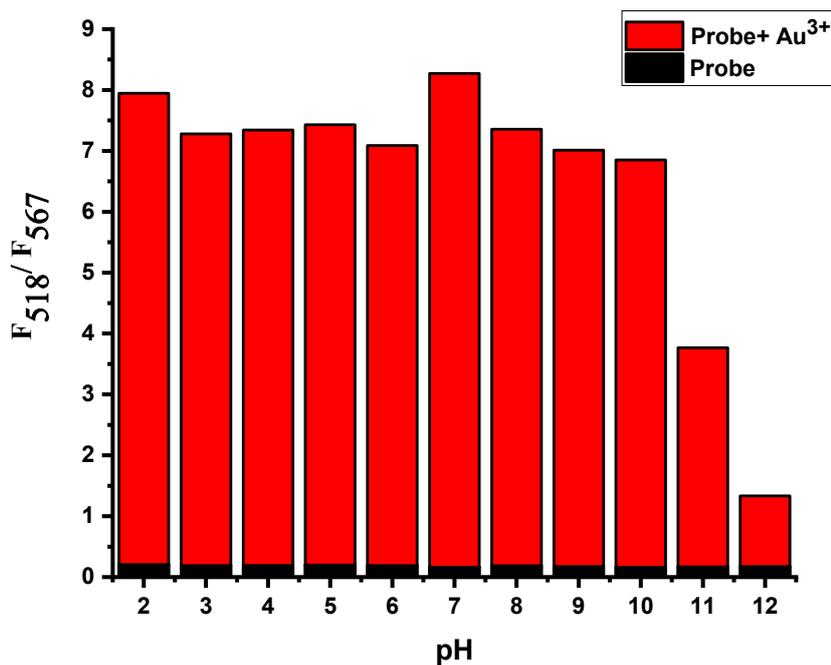
Fig. S4 pH effect on the response of **KEREM-1** (10 μM) toward Au^{3+} (100 μM, 10 Equiv.) in PBS (0.01 M) /EtOH) (pH 7.0, v/v,7:3). (λ_{ex}: 460 nm, emission: F_{518}/ F_{567} at 25 ℃).
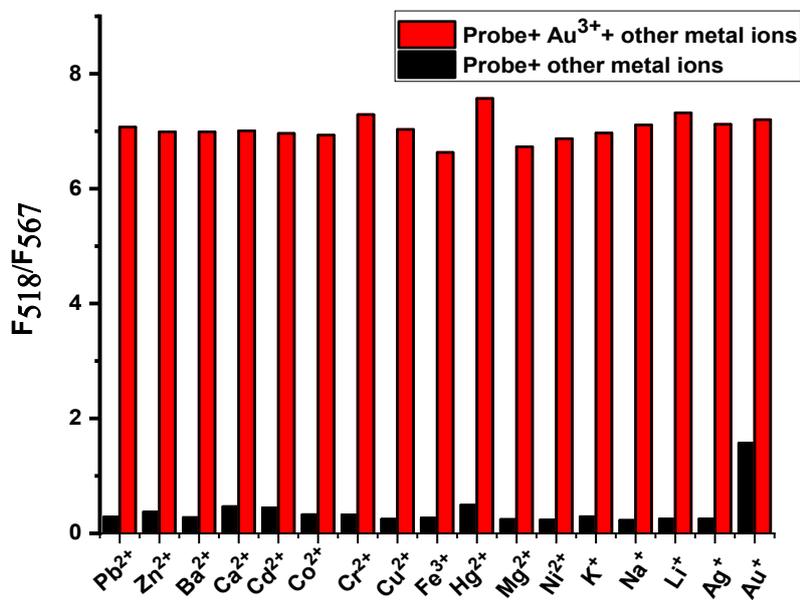
Fig. S5 Bar graph notation of fluorescence intensities of **KEREM-1** (10 μM) with Au^{3+} (100 μM, 10 Equiv.) and 20 equiv. of other metal ions in PBS (0.01 M) /EtOH) (pH 7.0, v/v, 7:3) (λ_{ex}: 460 nm, emission: F_{518}/ F_{567} at 25 ℃).
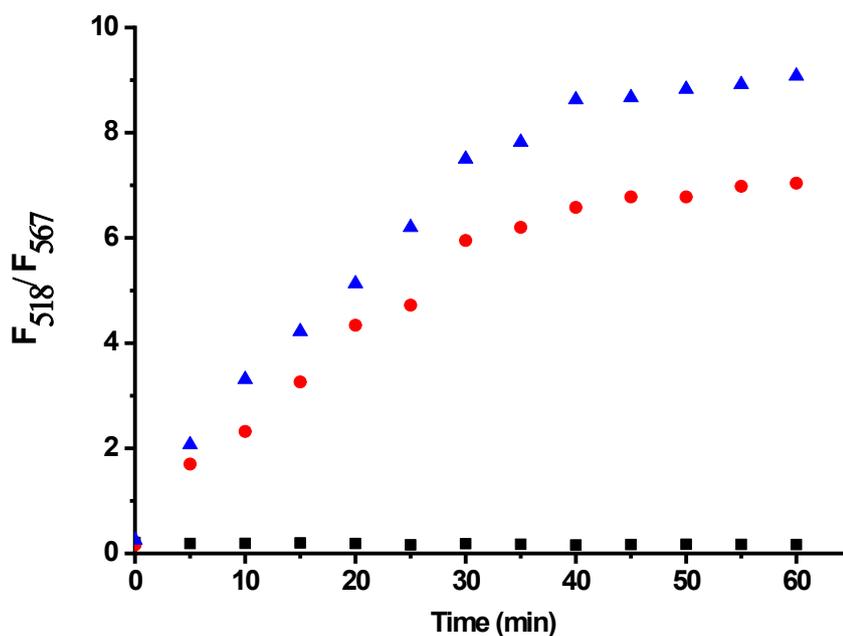
Fig. S6 Reaction time profiles of **KEREM-1** (10 μM) in the absence (■) and presence of Au^{3+} [10 (●), 30(▲) μM.]. The fluorescence intensities at 518 nm and 567 nm were continuously monitored at time intervals in 0.01 M PBS buffer/ EtOH (pH 7.0, v/v, 7:3) (λ_{ex}: 460 nm, emission wavelengths: F_{518}/ F_{567} at 25 °C).

3. PHOTOSTABILITY STUDIES

The photostability of the **KEREM-1** was investigated in 0.01 M PBS buffer-ethanol (7:3) system. Sample was placed in 10x10 mm quartz cuvette and it was positioned 15 cm away from the light source (green led, 500-570 nm). Incident radiation intensity was calculated as 3.3 mV/cm^2. Absorbance measurements were performed for a period of 9 hours at 1 hour time intervals and degradation rate was calculated from the equation below:

$\ln(A_t/A_0)=k_{deg} \times t$

where; A_t is absorbance at the irradiation time, A_0 is absorbance at t=0, t is time.
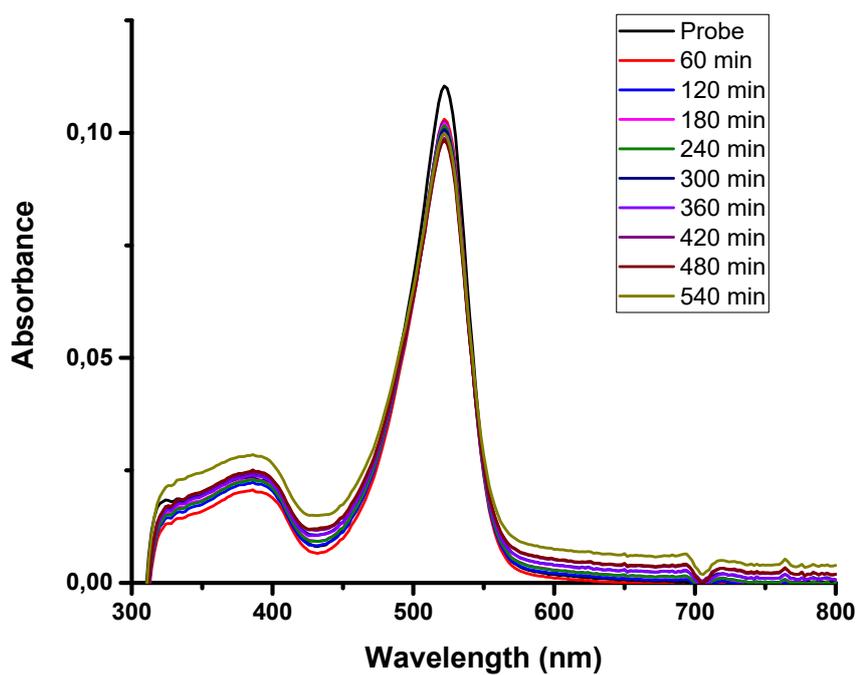
Fig. S7 Absorbance changes of **KEREM-1** by irradiation with green led.

$y= 9E\text{-}05X + 0{,}0616$
$R^2 = 0, 8688$
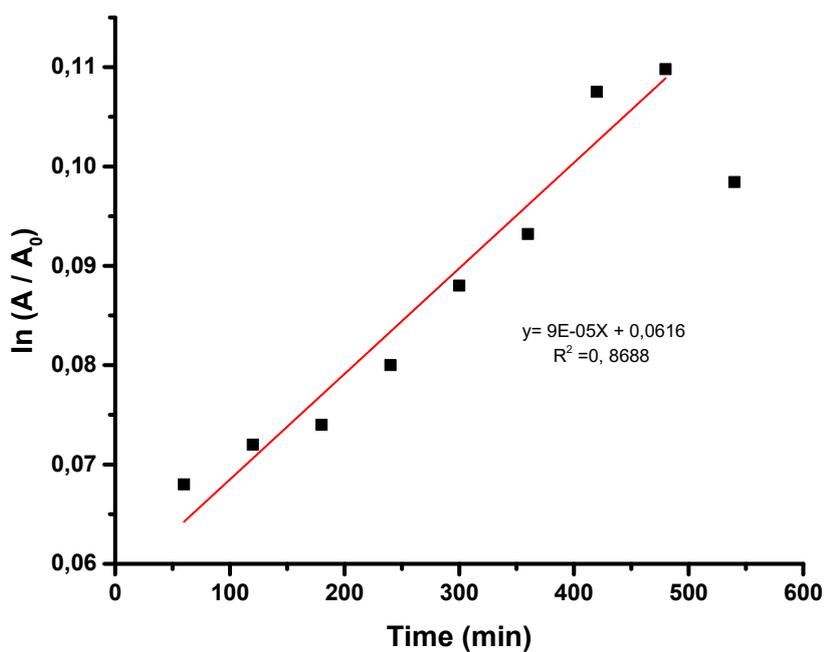
Fig. S8 ln (A_t/A_0)/time graphic of **KEREM-1.**

4. ELECTROCHEMICAL STUDIES

Electrochemical studies of **KEREM-1** and **BOD-FUR** were carried out by using a CH Potentiostat and glassy carbon as working electrode, platinum wire as counter electrode, Ag wire as reference electrode and ferrocene as internal standard in 0.1 M acetonitrile solution of tetrabutylammoniumhexafluorophosphate (TBAPF$_6$) electrolyte system. Scan rate of 200 mV/s was applied, and all the solutions were deoxygenated with nitrogen gas bubbling. Highest occupied molecular orbital (HOMO) energy level and lowest unoccupied molecular orbital (LUMO) energy level of **KEREM-1** and **BOD-FUR** were calculated by using the following equations:[3,4]

$$E_{LUMO} = -e(E_{1/2(red., dye)} - E_{1/2(Fc/Fc+)} + 4.8)$$

$$E_{HOMO} = -e(E_{1/2(ox., dye)} - E_{1/2(Fc/Fc+)} + 4.8)$$

where, $E_{1/2(Fc/Fc+)}$ is 0.41V.
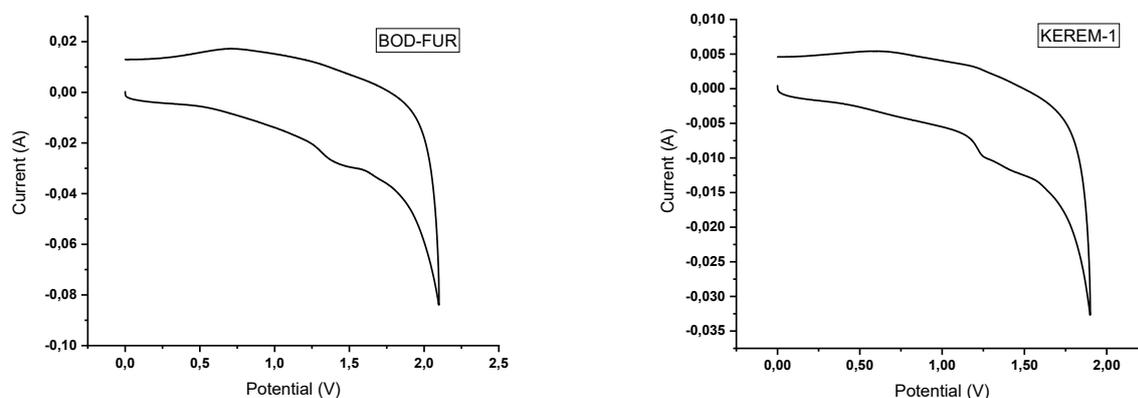
Fig. S9 Cyclic Voltammograms for **KEREM-1** and **BOD-FUR**. (Reported redox potentials of the compounds were the arithmetic mean of the forward and reverse redox onset potentials.)

5. REFERENCES

(1) A. M. Brouwer, *Pure Appl. Chem.*, 2011, **83**, 2213-2228.
(2) M. Üçüncü, E. Karakuş, M. Emrullahoğlu, *Chem. Commun.*, 2016, **52**, 8247-8250.
(3) D. O. Cowan, R. L. E. Drisko, *J. Am. Chem. Soc.* 1970, **92**, 21, 6281–6285.
(4) M. Kus, Ö. Hakli, C. Zafer, C. Varlikli, S. Demic, S. Özçelik, S. Icli, *Organic Electronics,* 2008, **9**, 757-766.

6. PROPOSED MECHANISM
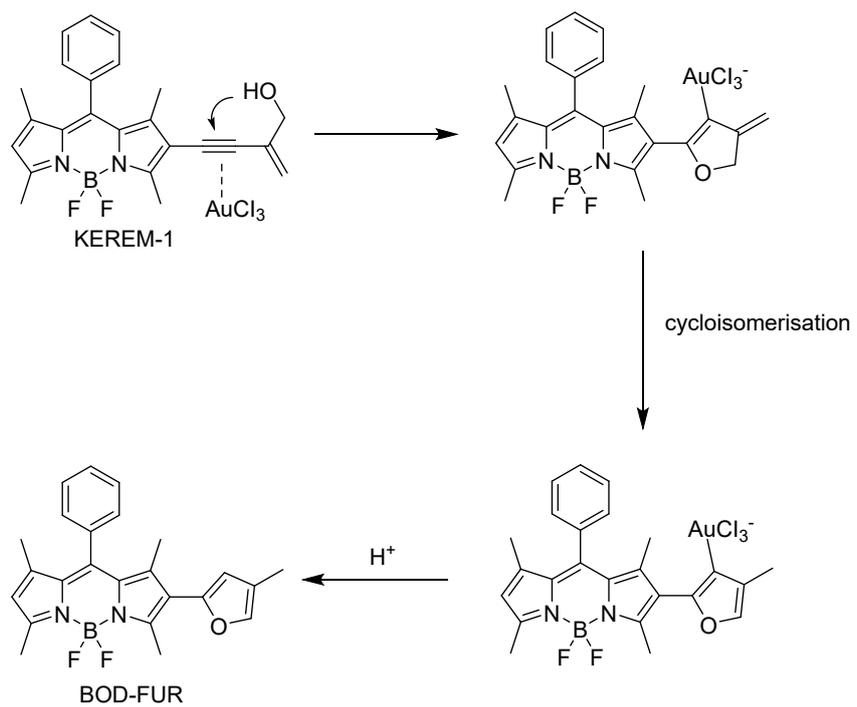
Fig. S7 Mechanism for gold ion catalyzed intramolecular cyclisation.

7. NMR SPECTRA OF COMPOUNDS
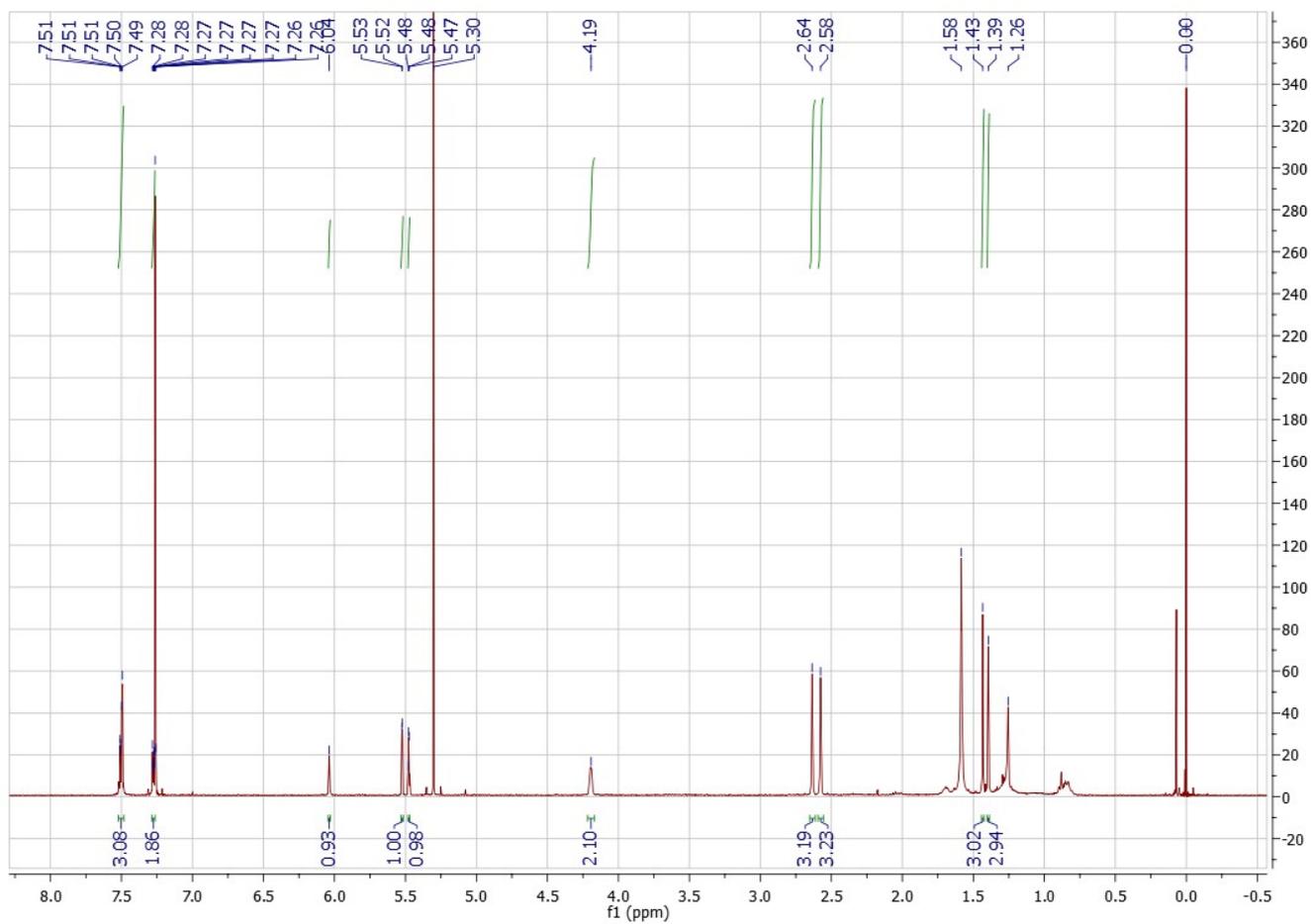
Fig. S8 ^{1}H NMR of KEREM-1
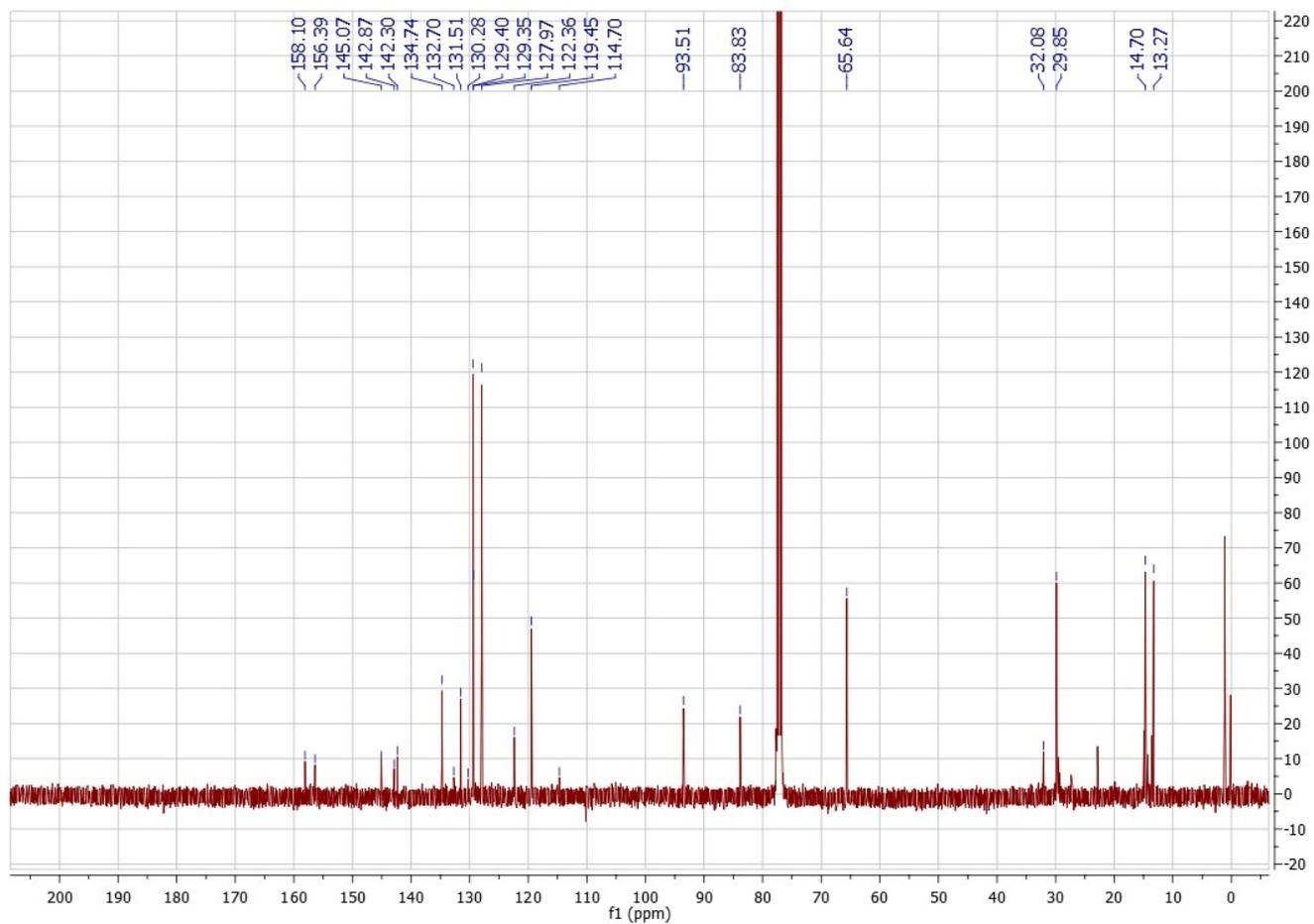
Fig. S9 ^{13}C NMR of KEREM-1
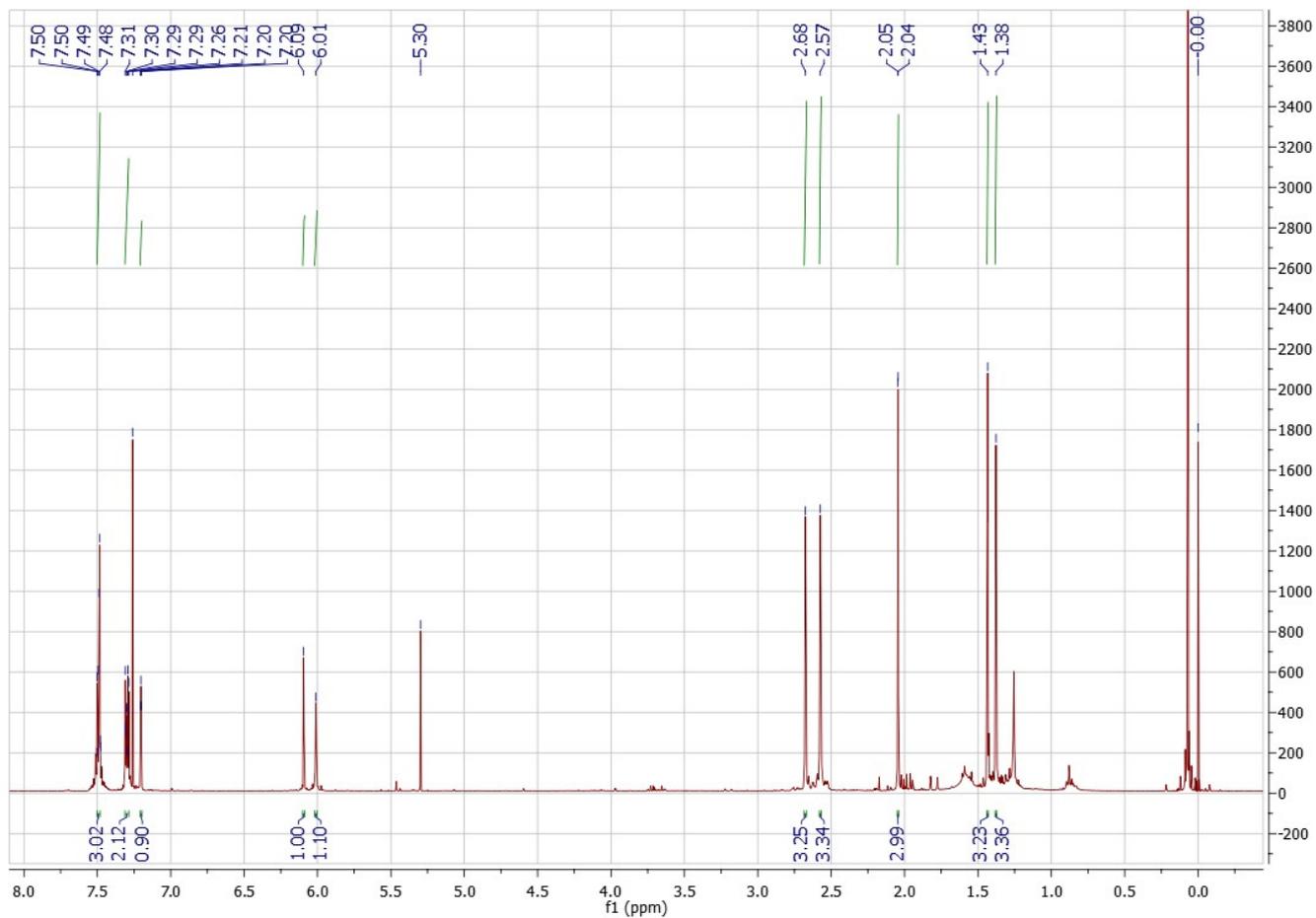
Fig. S10 ^{1}H NMR of BOD-FUR
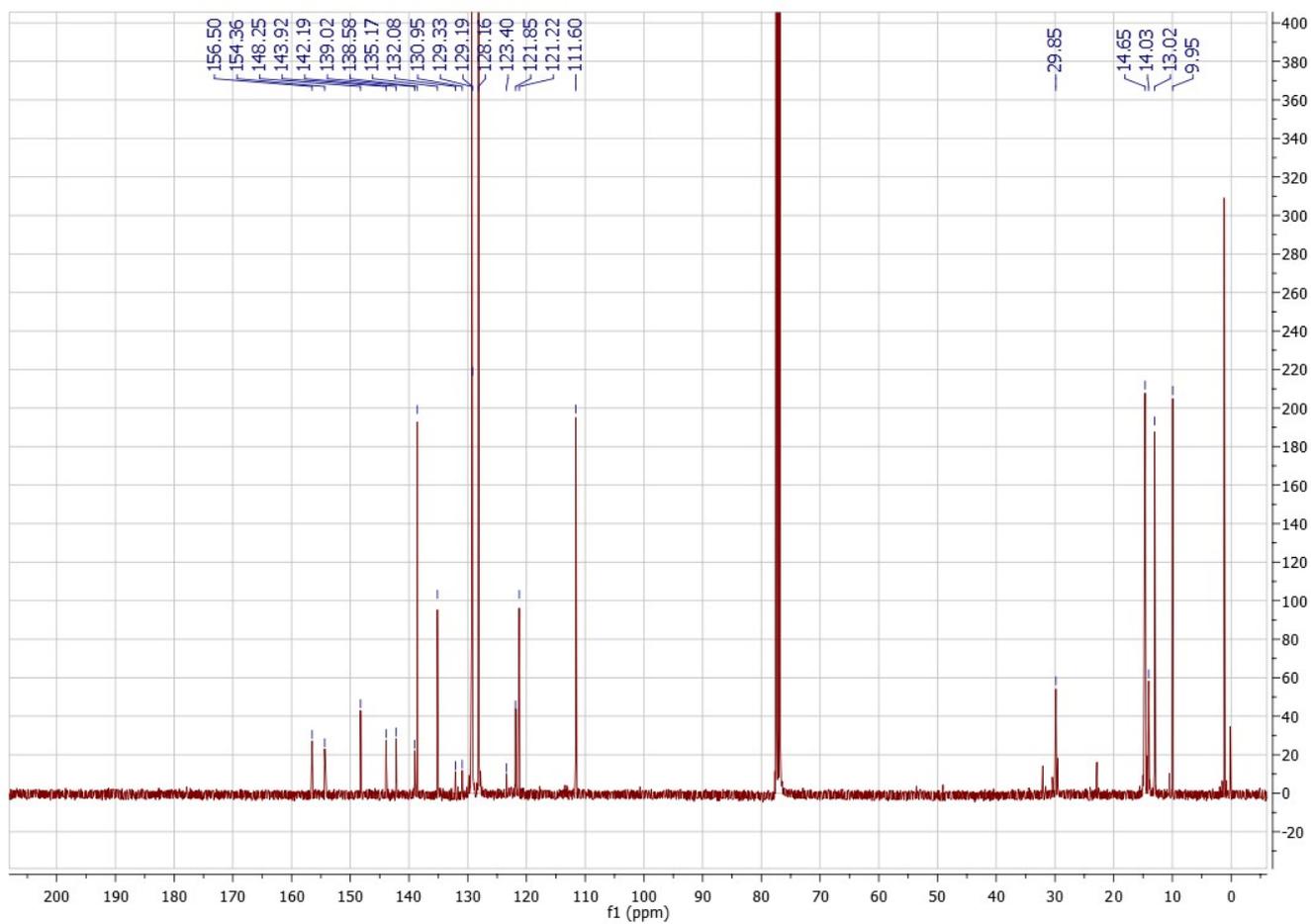
Fig. S11 ^{13}C NMR of BOD-FUR

8. HRMS of COMPOUNDS
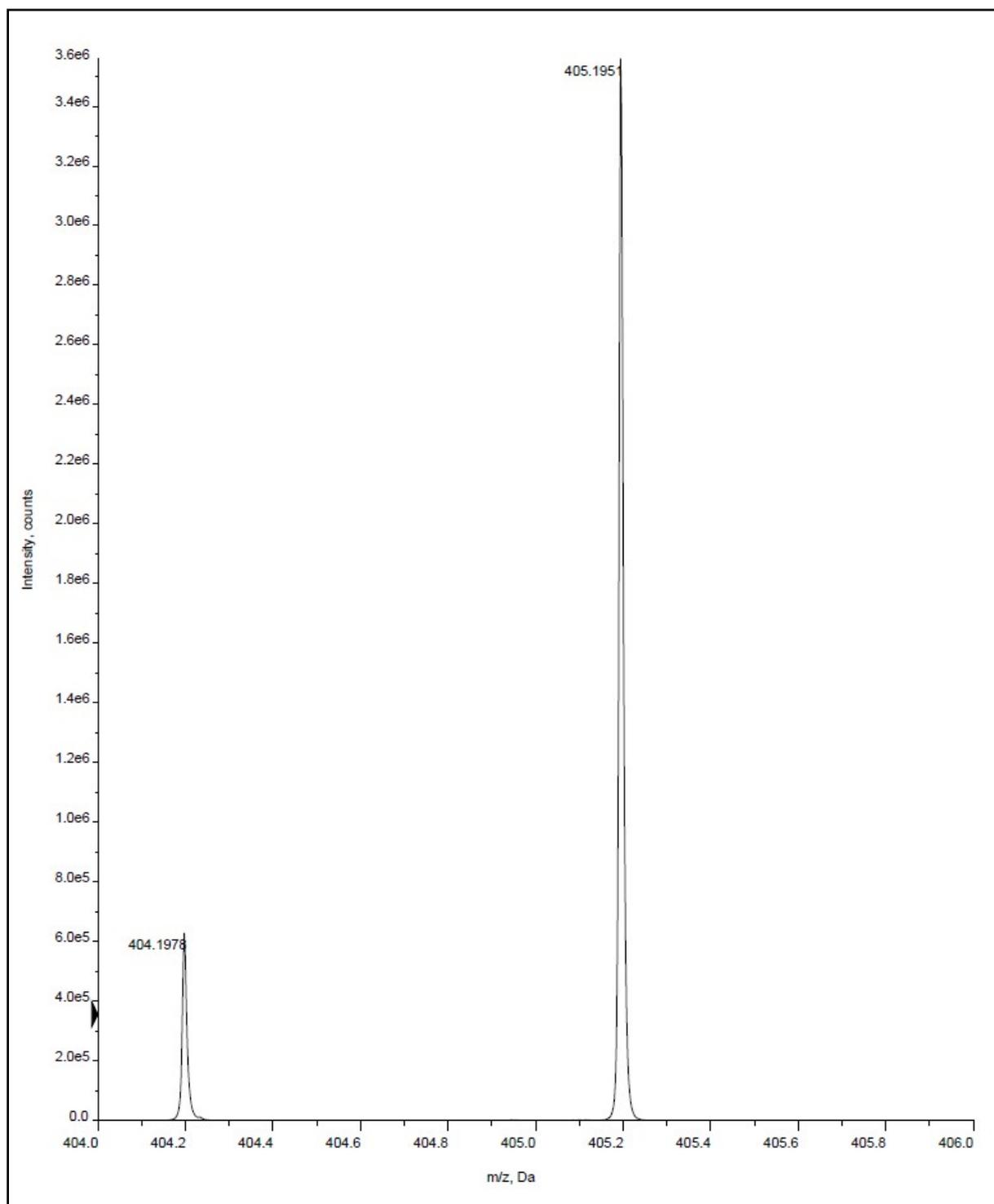
Fig. S12 HRMS of KEREM-1

Fig. S13 HRMS of BOD-FUR