

# Supporting Information

## A supramolecular photocatalyst for the reduction of Au(III) to Au(I) and high-turnover generation of gold nanocrystals

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### Table of contents

1. Extraction of AuCl<sub>3</sub> by **1** in toluene and dichloromethane and characterization of the complexes.
2. Transmission electron microscopy of AuNP
3. XPS analysis of AuNP
4. UV-Vis mass spectrometry of photolyzed solutions
5. FRET calculation
6. VT-NMR of **1**•2AuCl<sub>3</sub>.
7. Dismutation of Au<sup>I</sup> in solution
8. Synthesis of **1**
9. Procedure for preparing AuNP
10. Protocol for gold catalysis
11. Spectral characterization of synthetic intermediates.

## 1. Extraction of AuCl<sub>3</sub> by **1** in toluene and dichloromethane and characterization of the complexes.

The binding of AuCl<sub>3</sub> by **1** was followed spectroscopically by monitoring the absorption of Au(III) at 330 nm, and the complexes were characterized using mass spectroscopy (field desorption ionization). Both dissolution of solid HAuCl<sub>4</sub> into a solution of **1** (toluene or dichloromethane) or extraction of AuCl<sub>3</sub> from an aqueous solution of HAuCl<sub>4</sub> by a solution of **1** in toluene or dichloromethane gave the same results.

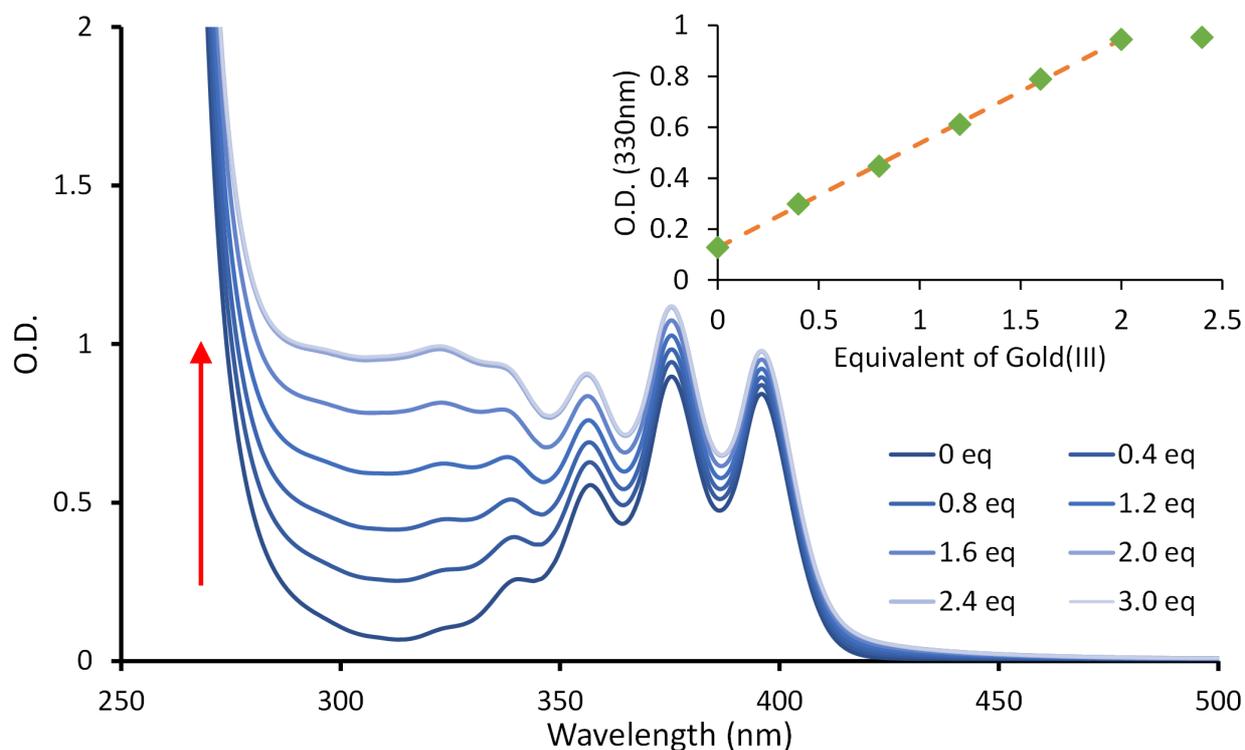


Figure S1. Variation of the absorbance of a solution of **1** (60.5 μM, CH<sub>2</sub>Cl<sub>2</sub>) upon addition of solid HAuCl<sub>4</sub>. Inset shows variation of the OD at 330 nm. No further variation is observed beyond the addition of 2 equivalents of HAuCl<sub>4</sub>.

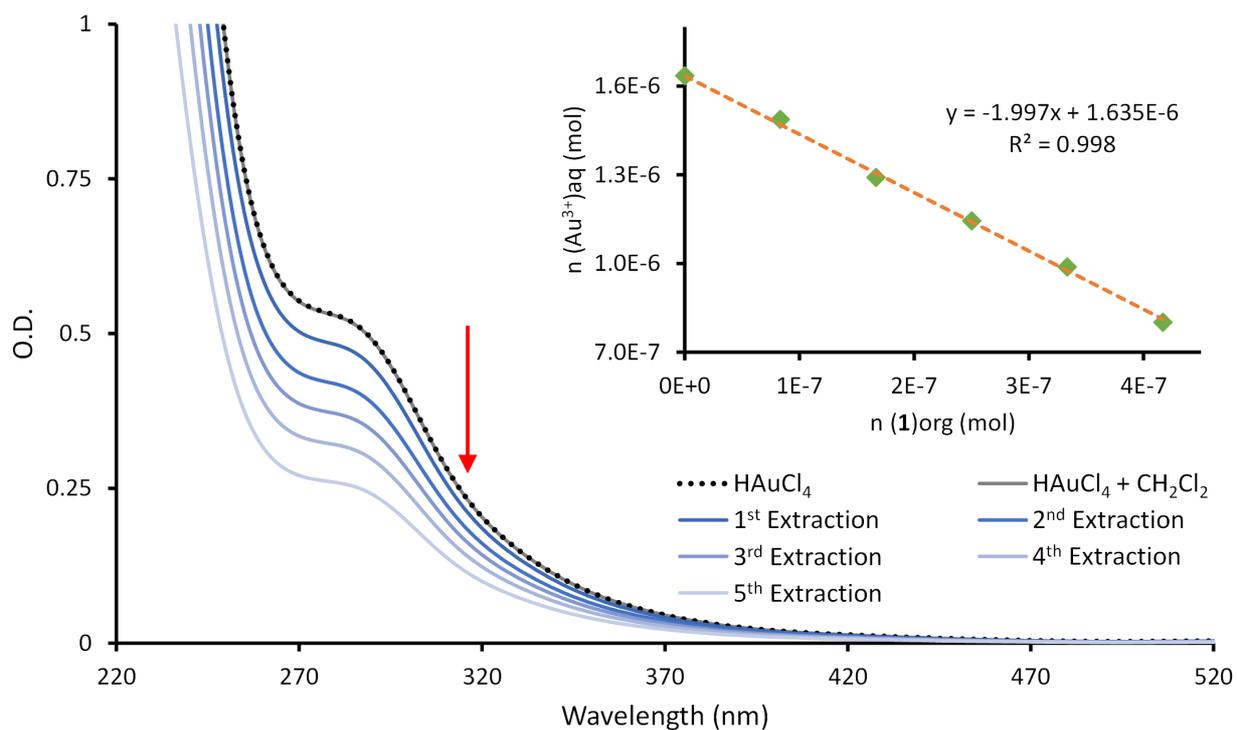


Figure S2. Absorbance of an aqueous solution of  $\text{HAuCl}_4$  (0.16 mM, 10 mL) upon addition (2 mL) of a solution of **1** ( $\text{CH}_2\text{Cl}_2$ , 40  $\mu\text{M}$ ).

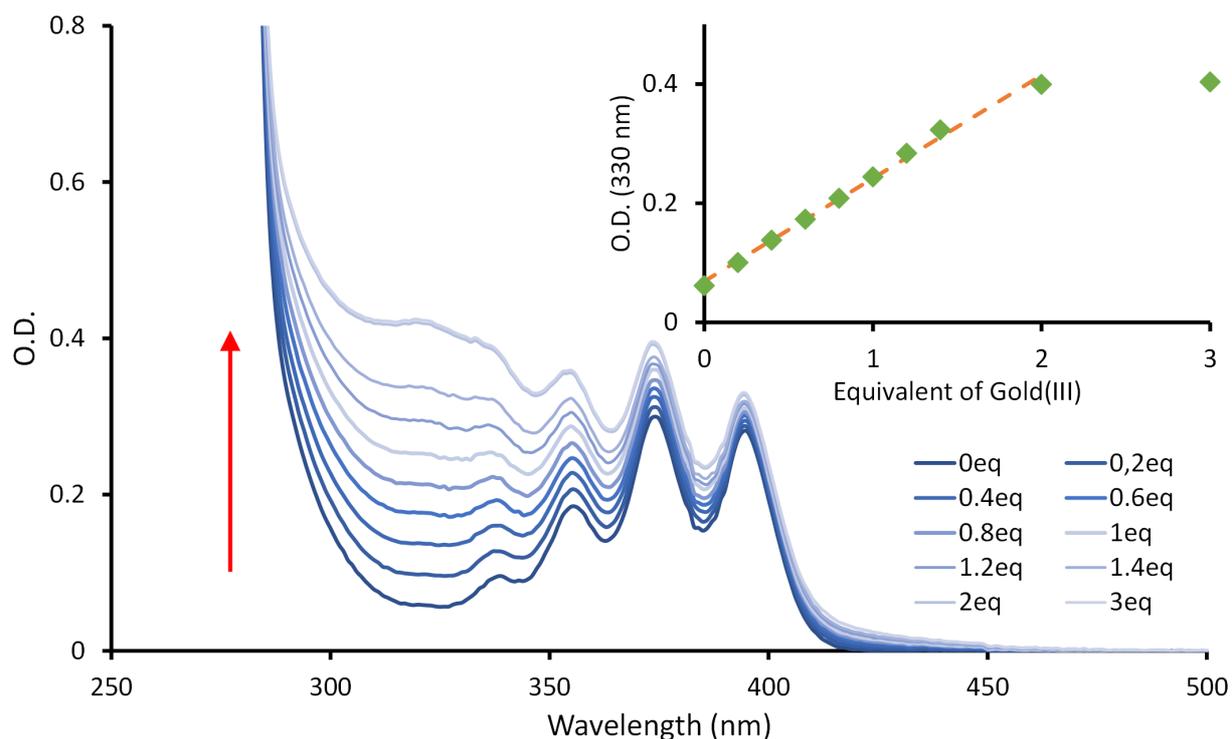


Figure S3. Variation of the absorbance of a solution of **1** (20  $\mu\text{M}$ , toluene) upon addition of solid  $\text{HAuCl}_4$ . Inset shows variation of the OD at 330 nm. No further variation is observed beyond the addition of 2 equivalents of  $\text{HAuCl}_4$ .

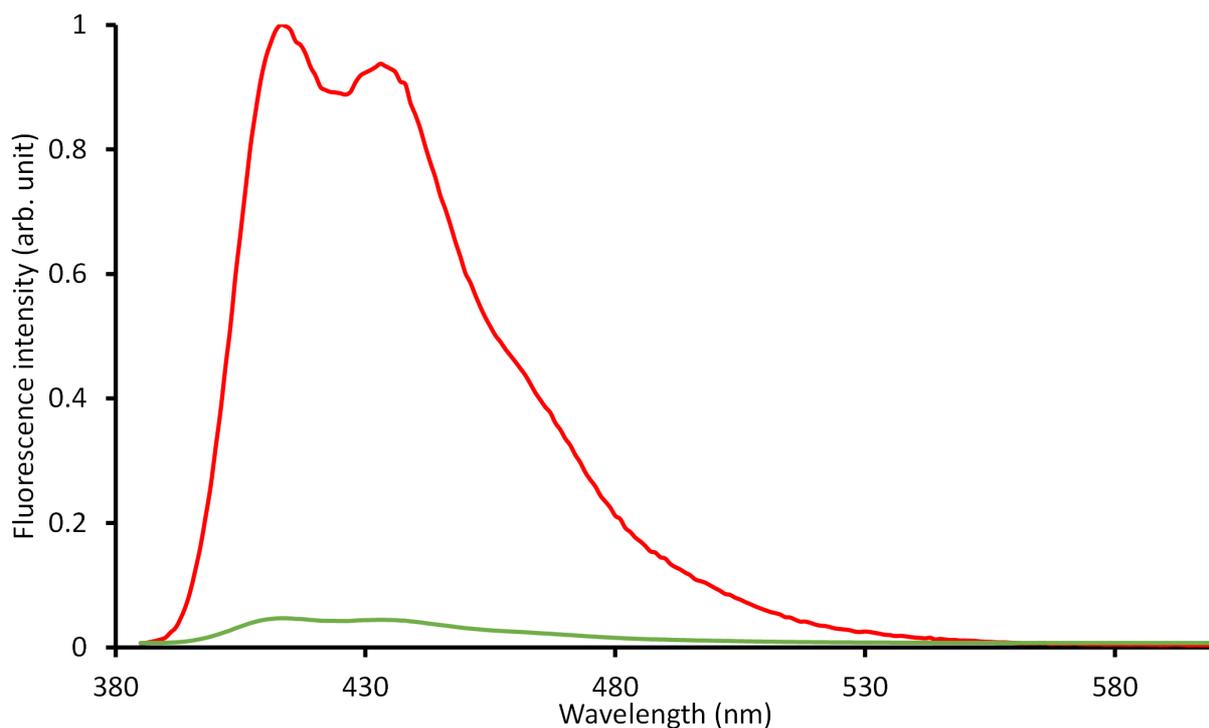


Figure S4. Fluorescence emission spectra of **1** (red line) **1**•2AuCl<sub>3</sub> (green line) in dichloromethane solution ( $\lambda_{\text{exc}} = 365 \text{ nm}$ ,  $1 \mu\text{M}$ ).

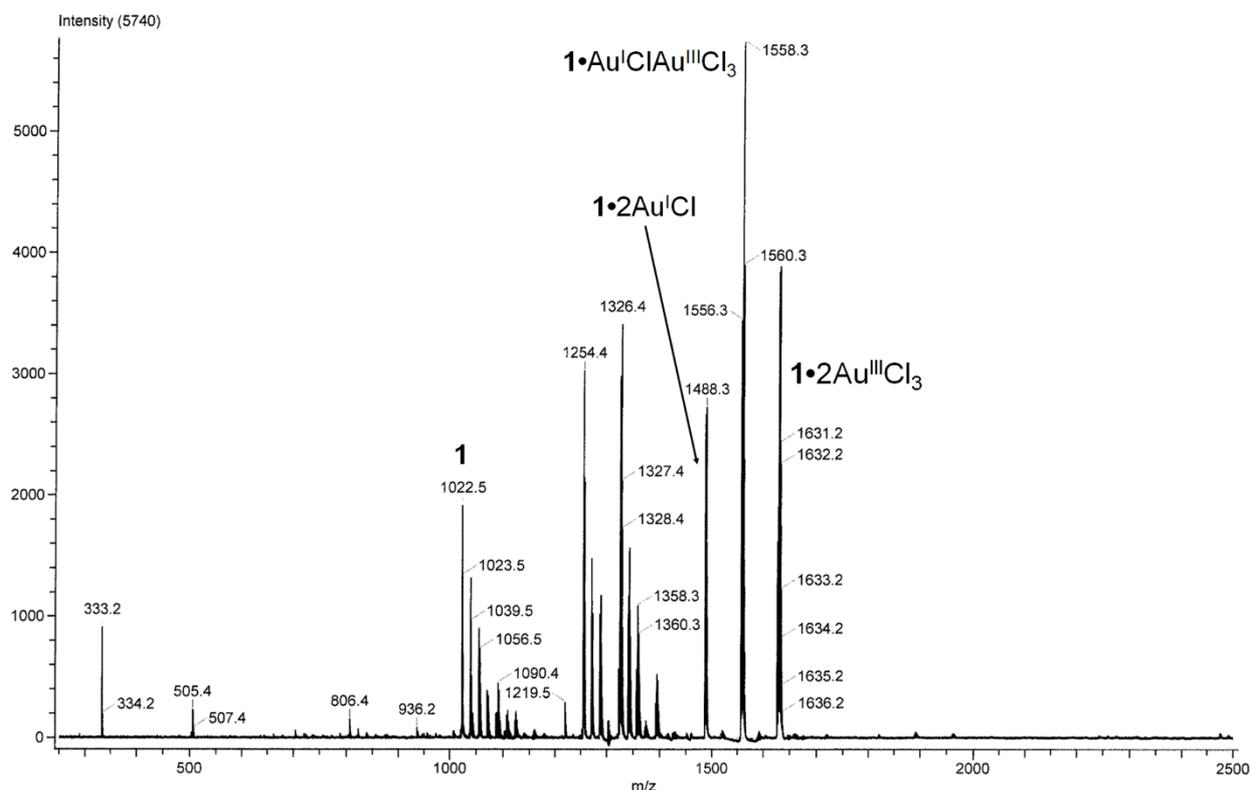


Figure S5. Mass spectra (FD<sup>+</sup>) of **1**•2AuCl<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> obtained by extraction of an aqueous solution of HAuCl<sub>4</sub>. Partial reduction of the bound Au(III) is assigned to either exposure to ambient light during sample preparation or during ionization.

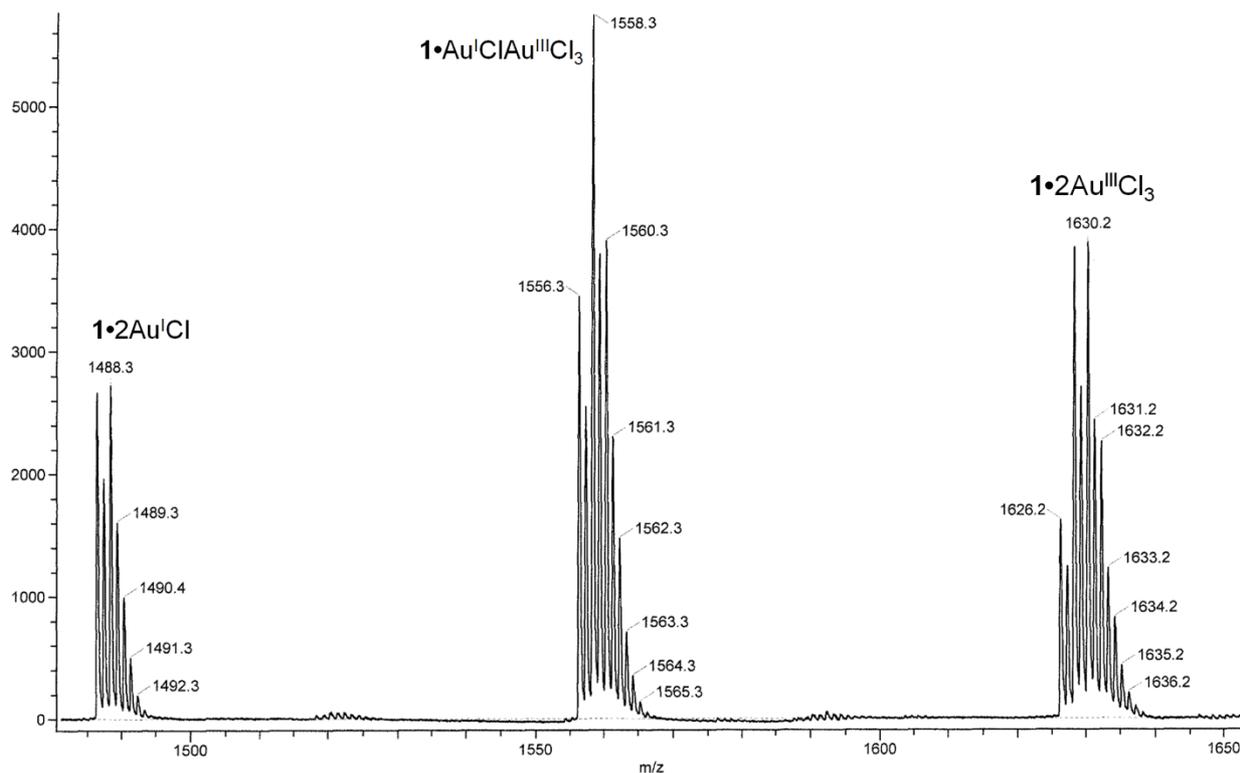


Figure S6. Zoom of the region between 1480 and 1650 Da from Figure S5.

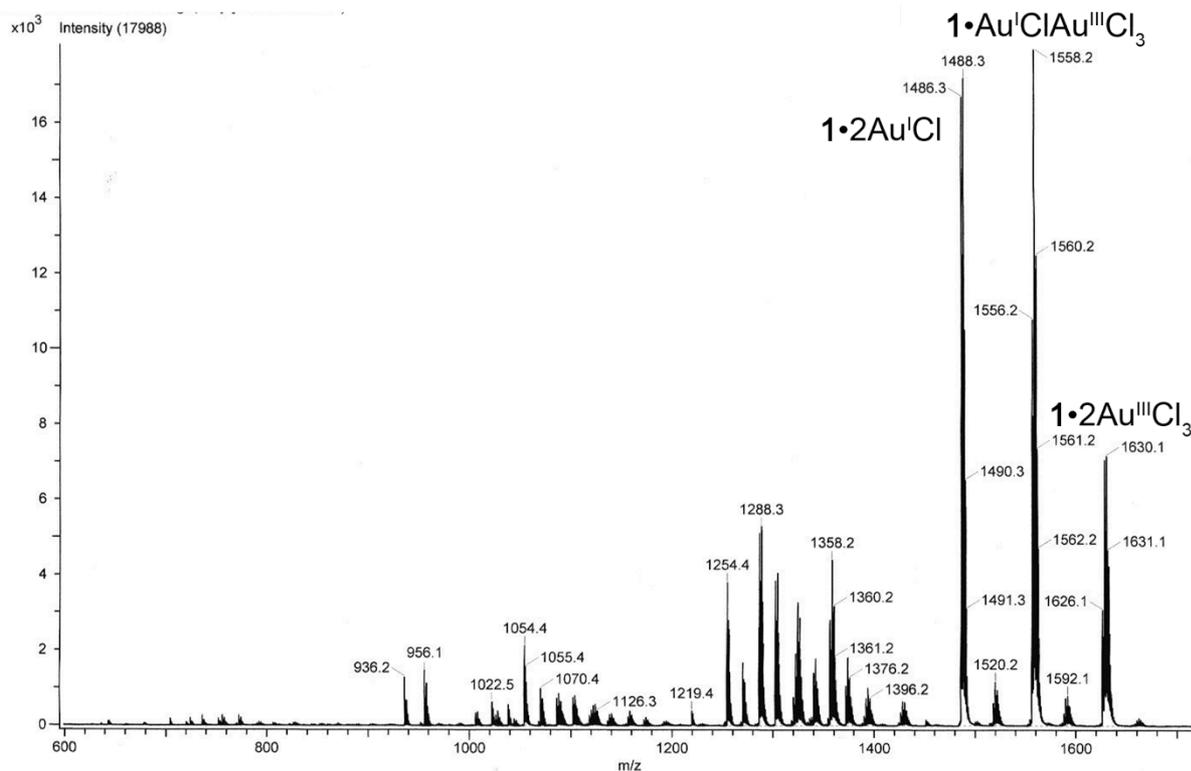


Figure S7. Mass spectra (FD<sup>+</sup>) of **1•2AuCl<sub>3</sub>** in toluene obtained by extraction of an aqueous solution of HAuCl<sub>4</sub>. Partial reduction of the bound Au(III) is assigned to either exposure to ambient light during sample preparation or during ionization.

## 2. Transmission electron microscopy of AuNP.

AuNP were prepared by irradiation of a dichloromethane or toluene solution of  $1 \cdot 2\text{AuCl}_3$  (0.25 mM) as described below. The aqueous dispersion of AuNP thus obtained was placed in contact with a collodion-covered TEM grid.

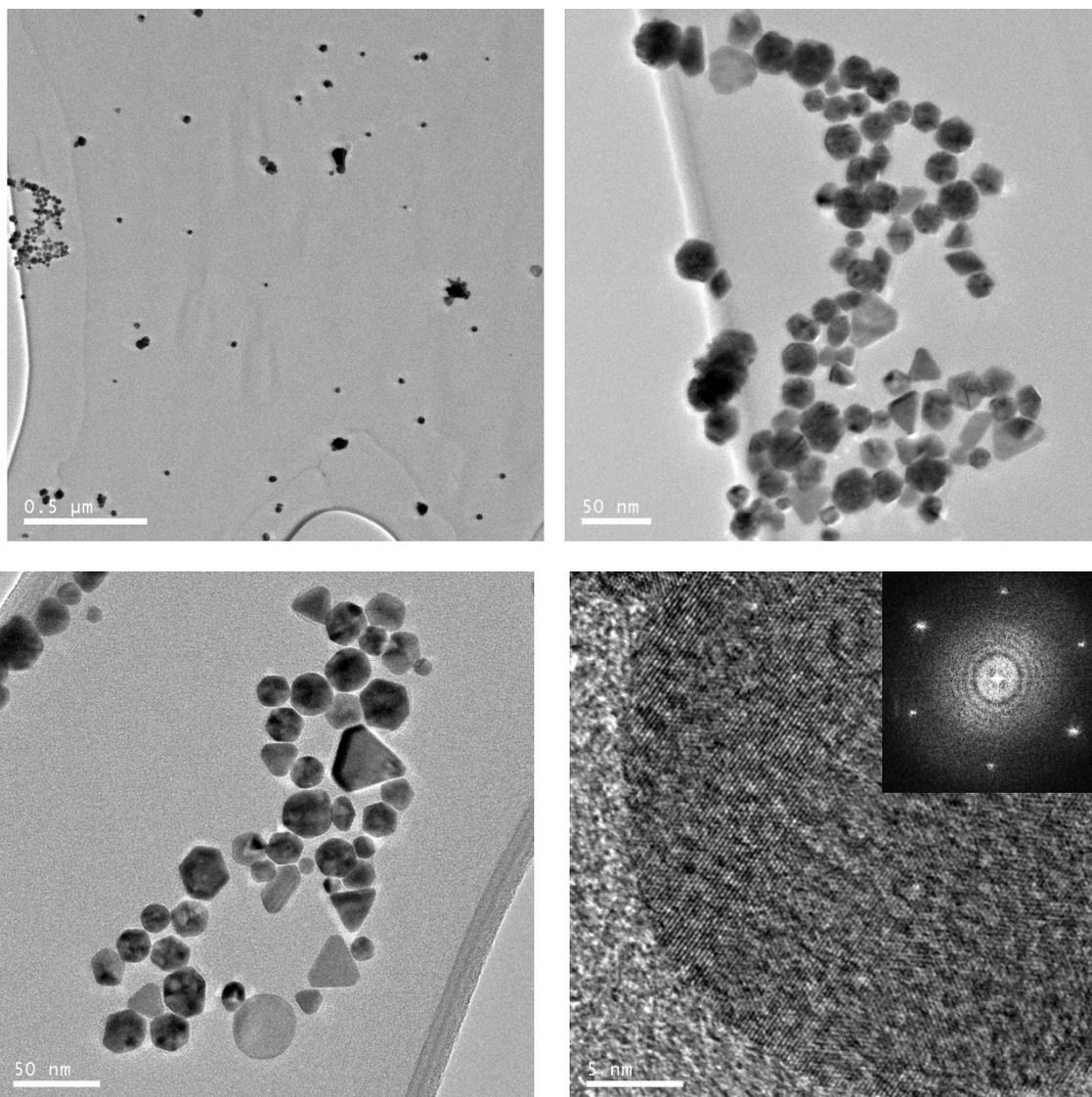


Figure S8. Wide-field and close up TEM images of AuNP obtained from irradiation of a dichloromethane solution of  $1 \cdot 2\text{AuCl}_3$ . All particles appear crystalline, including small spherical AuNP (bottom right, FT in inset).

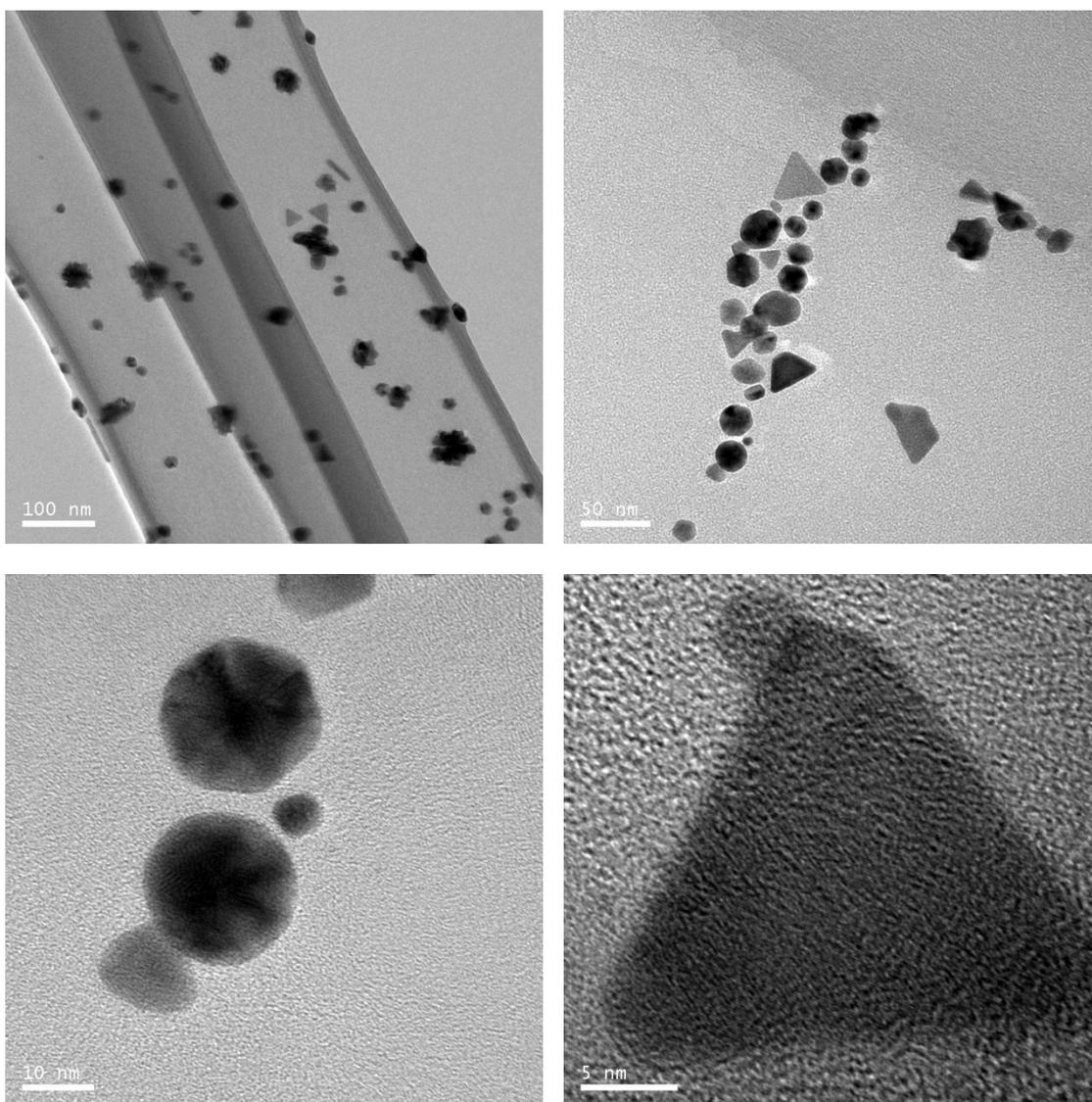


Figure S9. Wide-field and close up TEM images of AuNP obtained from irradiation of a toluene solution of  $\mathbf{1} \cdot 2\text{AuCl}_3$ .

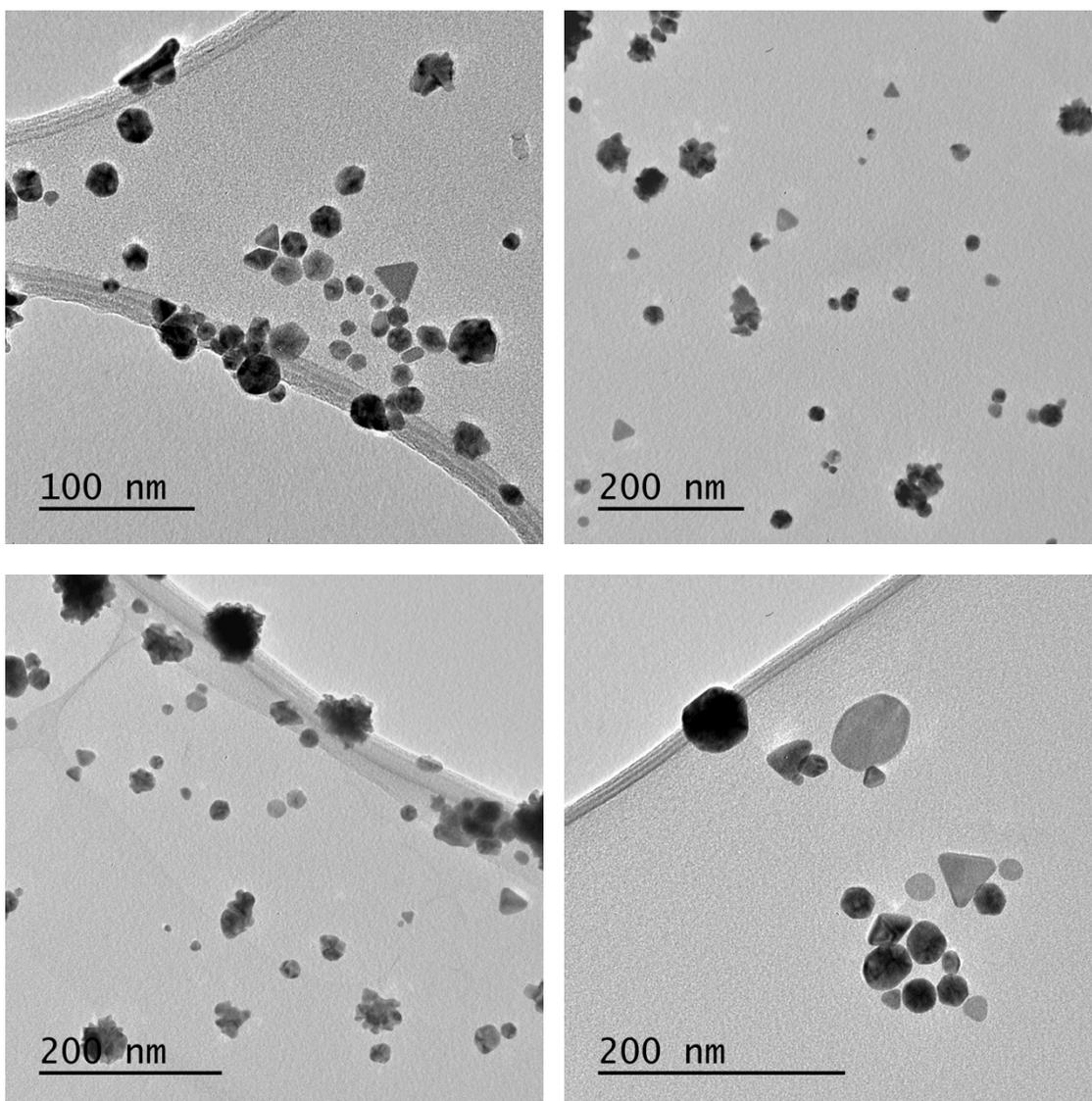
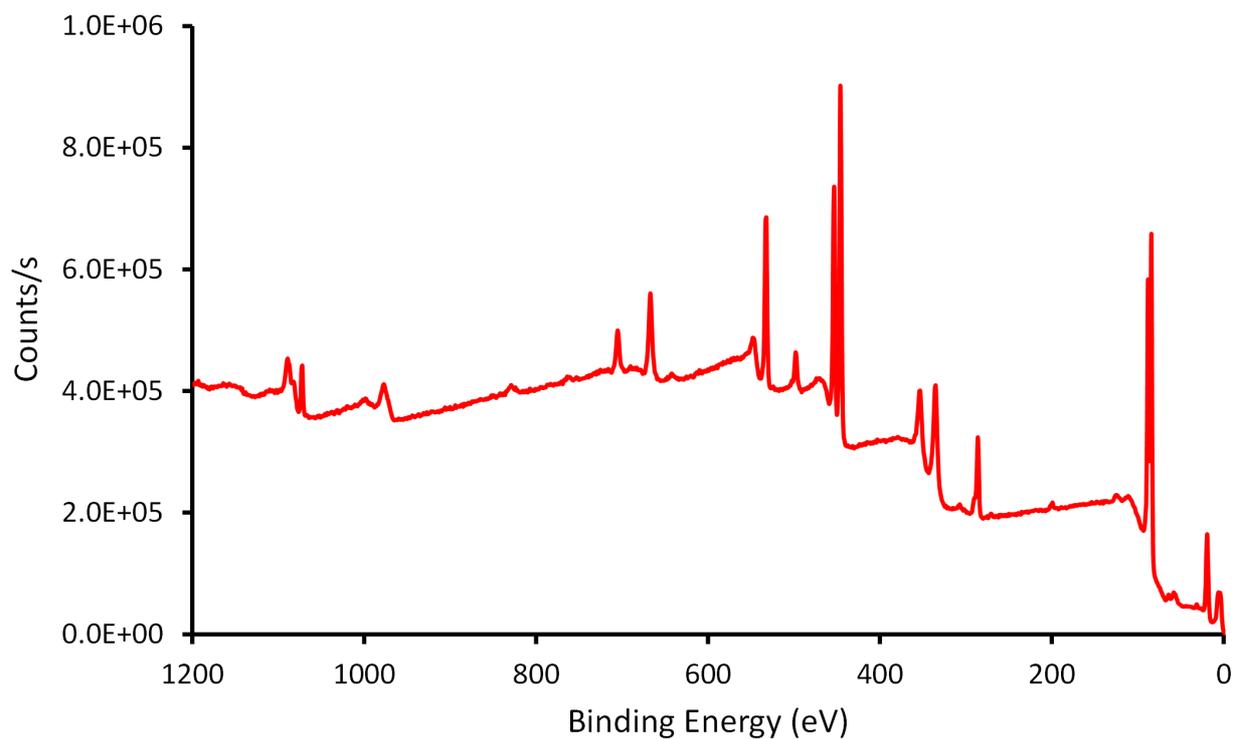


Figure S10. TEM images of AuNP obtained from irradiation of a dichloromethane (top) or toluene (bottom) solution of  $\mathbf{1} \cdot 2\text{AuCl}_3$  after standing 24h. Some aggregation and maturation is observed.

### 3. XPS analysis of AuNP

(i)



(ii)

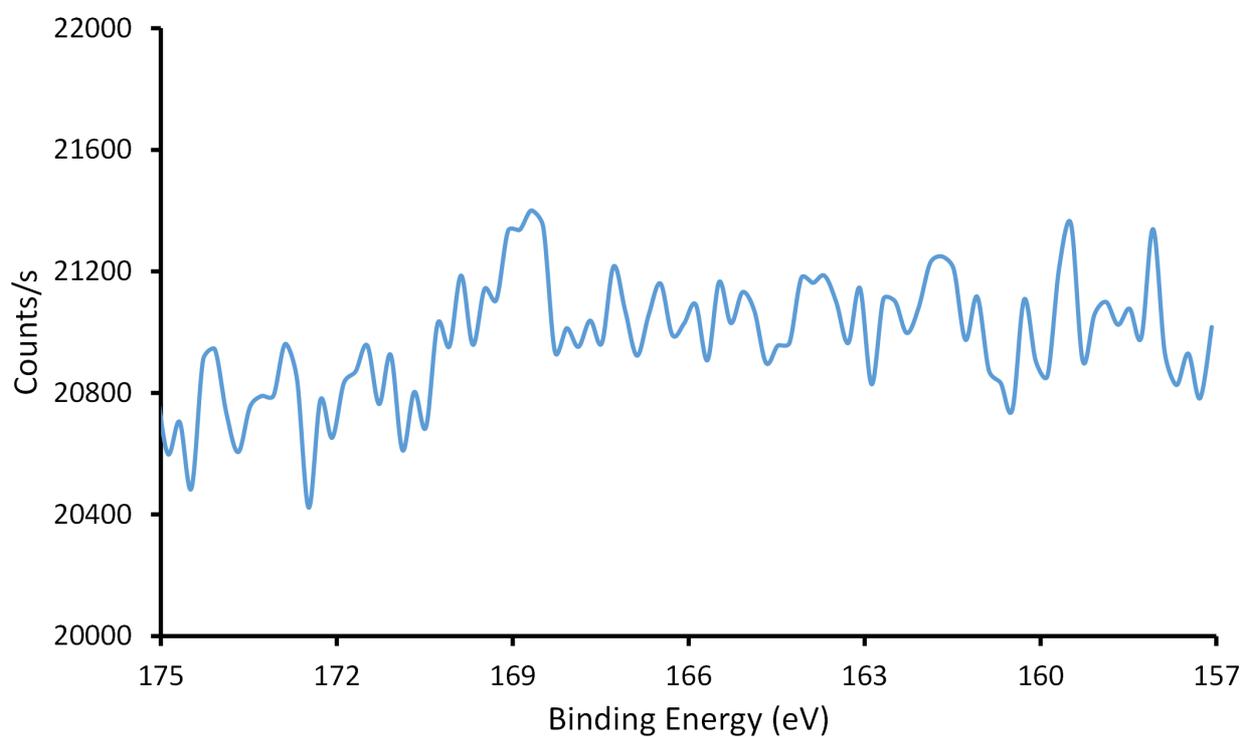
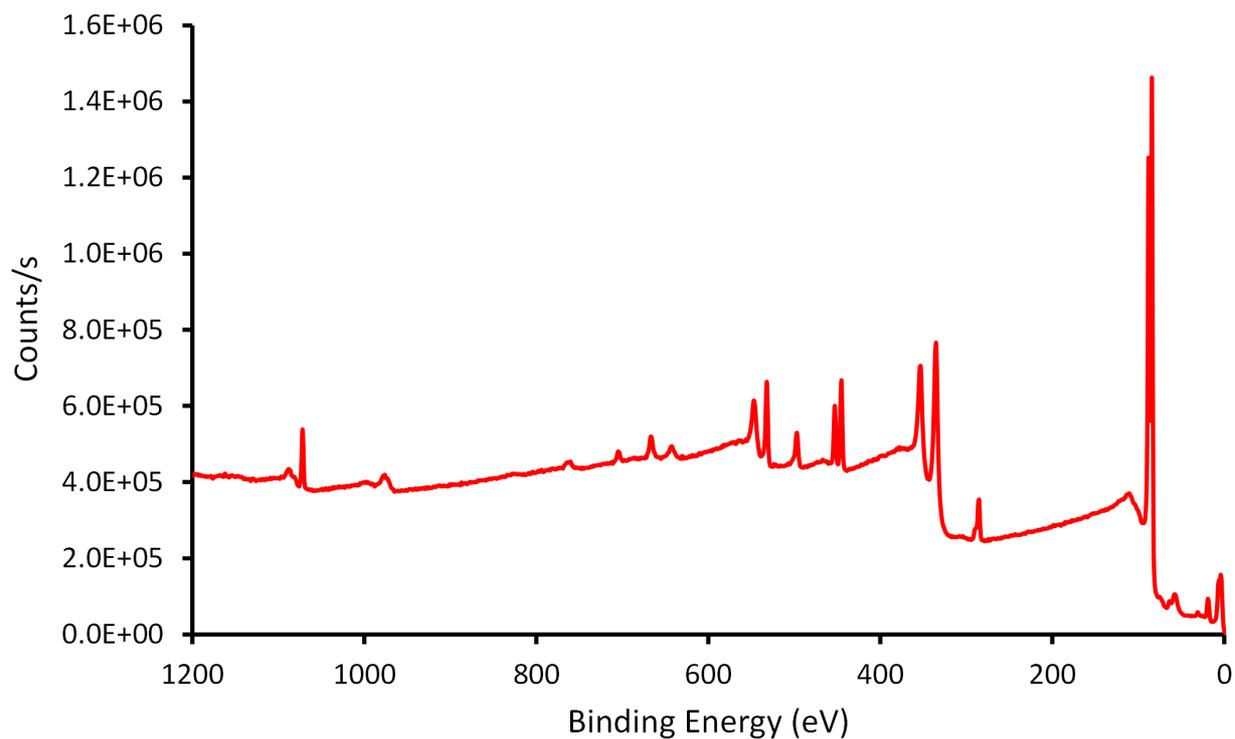


Figure S11. X-ray photoelectron spectroscopy of AuNP obtained from irradiation of a dichloromethane solution of  $\mathbf{1} \cdot 2\text{AuCl}_3$  deposited on In substrate: (i) Global spectrum, (ii) No signal is observed for the S(2p) signal at 168.91 eV.

Table S1. Analysis of XPS data from Figure S11

Name	Peak BE	Height Counts	FWHM eV	Area (P) CPS.eV	At. %	
Au4f7	83.97	113463.68	0.9	120166.42	11.89	
Au4f7	86.12	3566.76	1.58	5862.25	0.58	
	87.7	87.66	87964.97	0.9	91481.55	0
	89.8	89.82	2782.07	1.63	4711.94	0
Cl2p	199.13	1418.94	1.19	3984.91	1.64	
Csp2	284.92	4137.67	1.54	6636.17	6.21	
Csp3	285.52	15297.71	1.54	24574.12	23	
	287.1	287.1	3135.22	1.4	4571.94	4.28
	288.9	288.94	1511.14	1.63	2560.65	2.4
	290.3	290.25	2502.04	1.63	4251.97	3.98
N1s	398.15	242.09	0.34	1306	0.68	
In3d5	443.96	6014.33	1.05	6603.87	0.46	
In3d5	445.54	119462.08	1.62	202562.51	14.17	
O1s	530.48	7786.04	1.33	10829.94	3.44	
O1s	532.27	39748.32	2.02	83682.38	26.62	
Na1s	1072.28	8138.78	1.79	15441.75	0.66	

(i)



(ii)

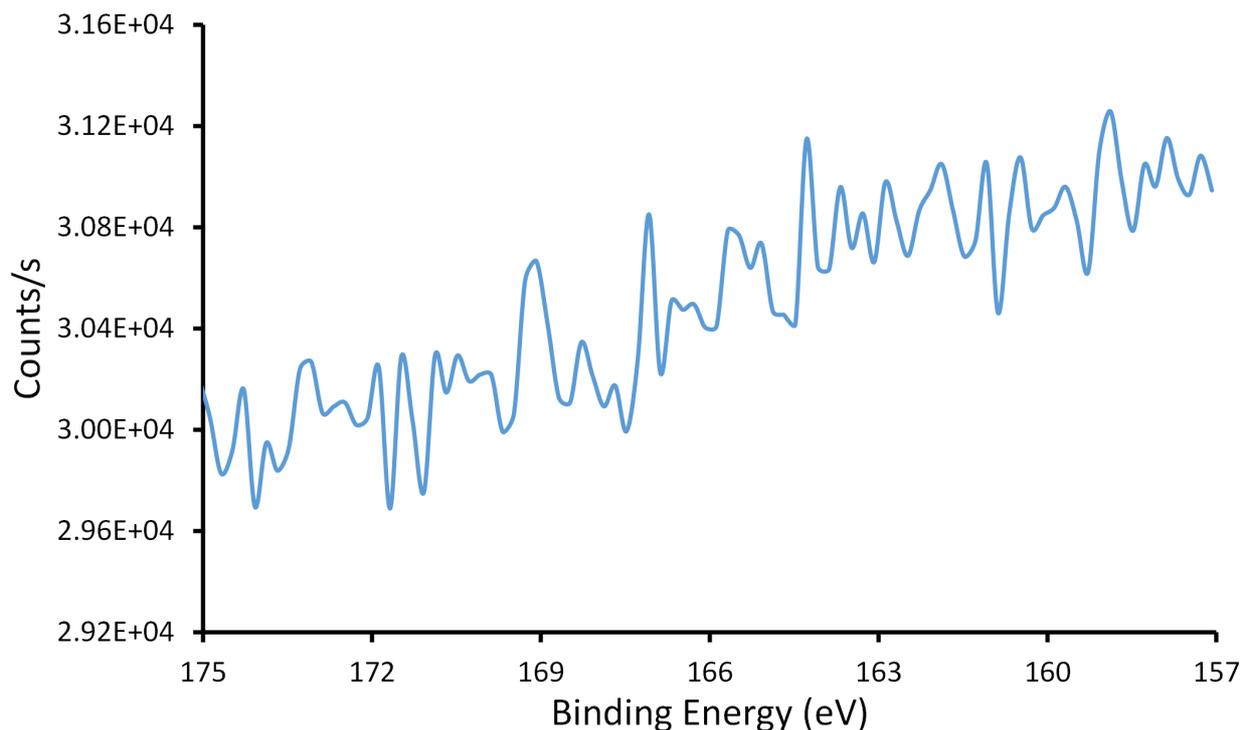


Figure S12. X-ray photoelectron spectroscopy of AuNP obtained from irradiation of a toluene solution of  $1 \cdot 2\text{AuCl}_3$  deposited on In substrate: (i) Global spectrum, (ii) No signal is observed for the S(2p) signal at 168.91 eV.

Table S2. Analysis of XPS data from Figure S12.

Name	Peak BE	Height Counts	FWHM eV	Area (P) CPS.eV	At. %
<b>Au4f7</b>	84.02	102780.54	0.85	102926.76	13.42
<b>Au4f7</b>	86.08	3195.34	1.7	5688.77	0.74
<b>87.7</b>	87.7	78821.4	0.85	77840.88	0
<b>89.8</b>	89.78	2492.36	1.7	4406.83	0
<b>Cl2p</b>	199.31	622.99	1.48	1972.41	1.07
<b>Csp2</b>	285.05	2045.2	1.64	3506.69	4.33
<b>Csp3</b>	285.65	12468.43	1.64	21390.01	26.39
<b>287.4</b>	287.39	1507.82	1.3	2043.26	2.52
<b>288.9</b>	288.94	1238.99	1.57	2031.45	2.51
<b>290.2</b>	290.24	2310.09	1.57	3781.3	4.66
<b>N1s</b>	399.56	510.56	0.32	1445.64	0.99
<b>In3d5</b>	443.89	7112.53	1.04	7746.51	0.71
<b>In3d5</b>	445.54	82320.38	1.65	141829.19	13.08
<b>O1s</b>	530.59	6808.52	1.46	10372.82	4.35
<b>O1s</b>	532.3	29429.83	1.89	58112.82	24.36
<b>Na1s</b>	1072.21	8055.43	1.72	15621.64	0.87

#### 4. UV-Vis mass spectrometry of photolyzed solutions

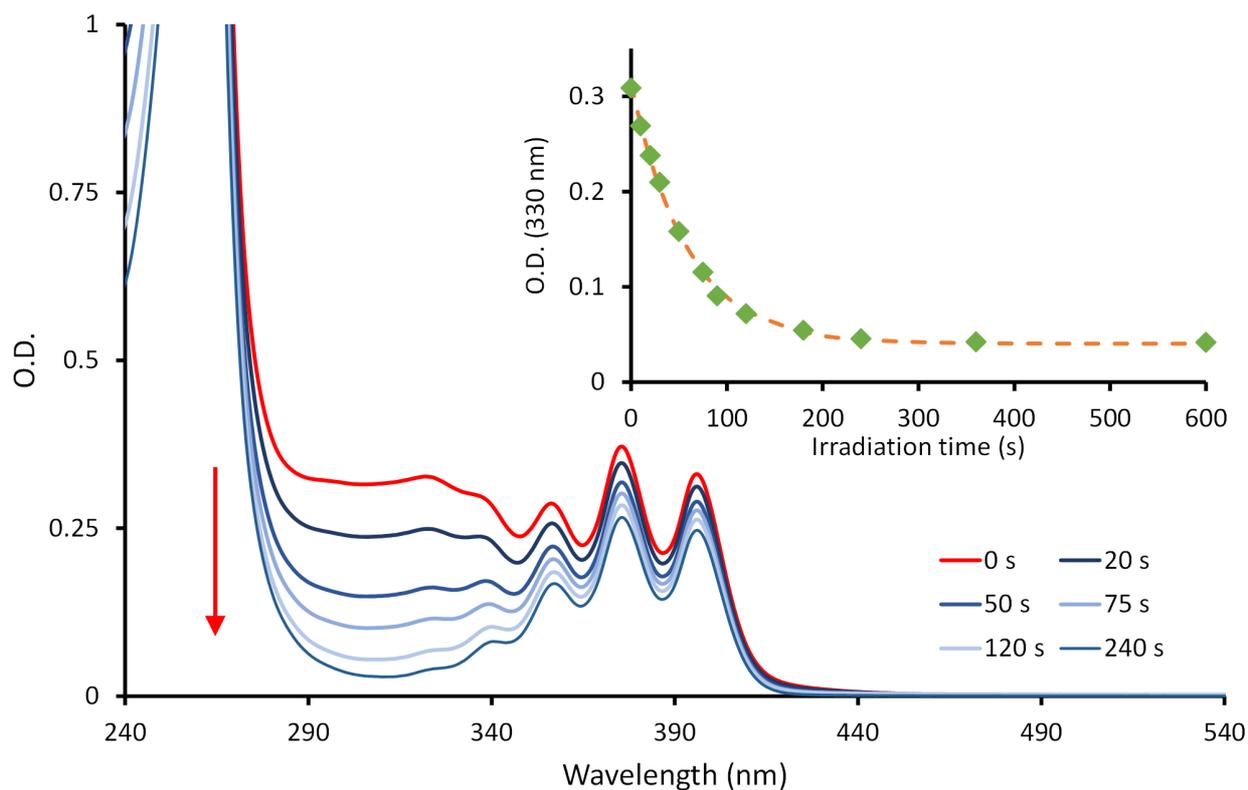


Figure S13. Changes in the UV-Vis absorption and fluorescence emission spectra of  $1 \cdot 2\text{AuCl}_3$  in dichloromethane solution upon irradiation ( $\lambda_{\text{exc}} = 365 \text{ nm}$ ,  $20 \mu\text{M}$ ).

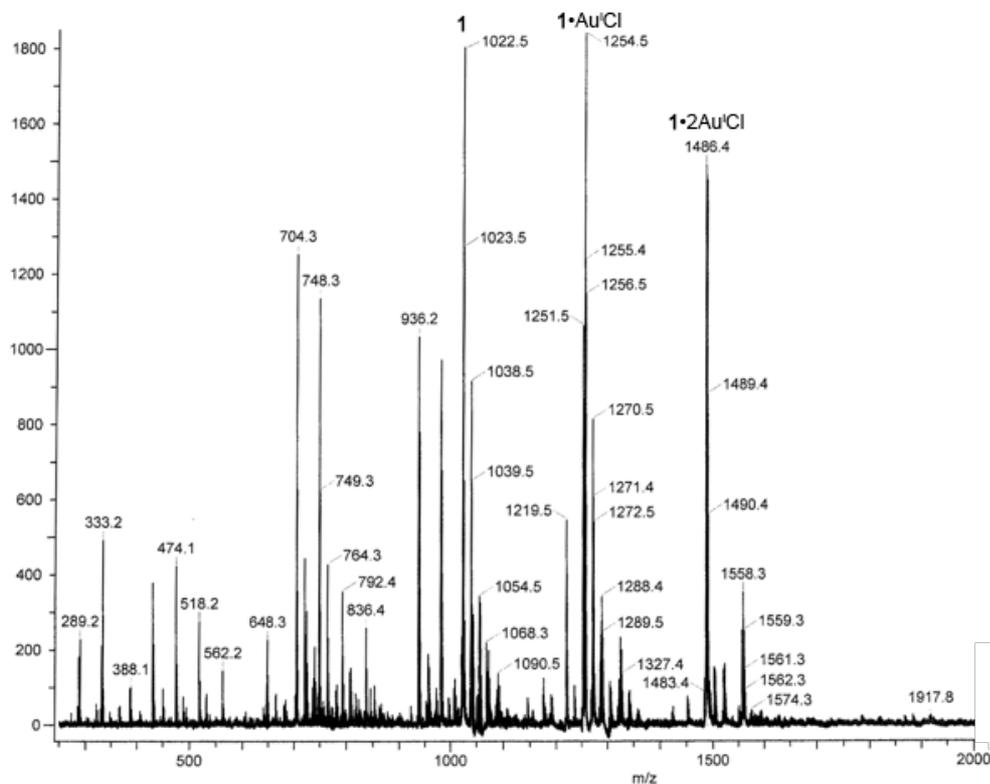


Figure S14. Mass spectra (FD+) of  $1 \cdot 2\text{AuCl}_3$  in dichloromethane after irradiation.

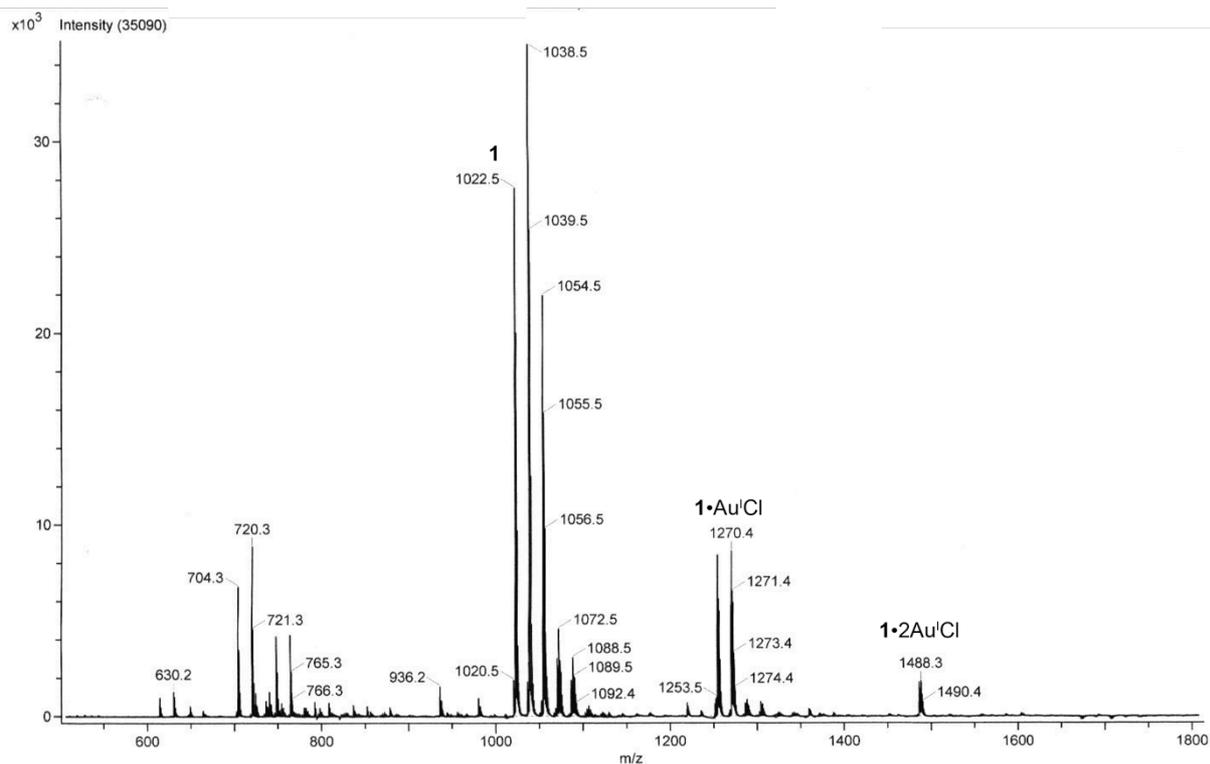


Figure S15. Mass spectra (FD+) of  $1 \cdot 2\text{AuCl}_3$  in toluene after irradiation.

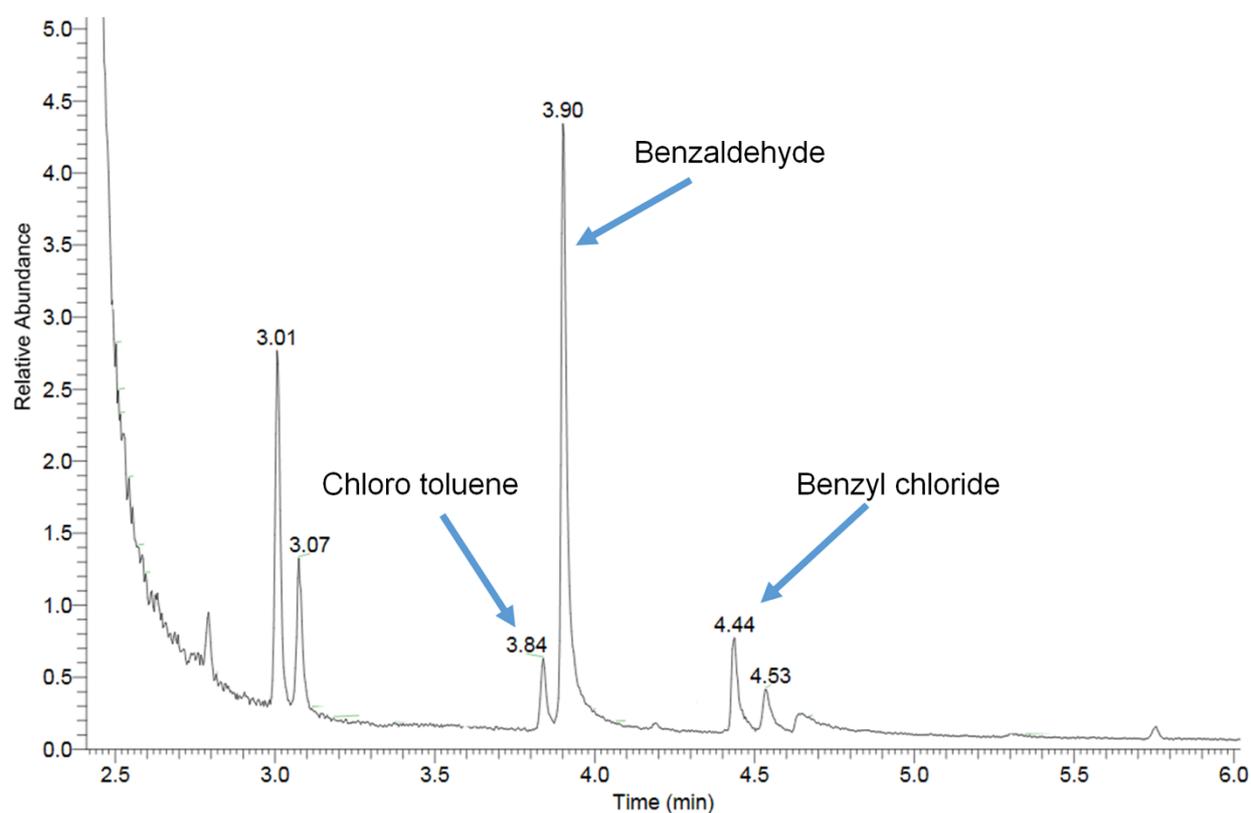
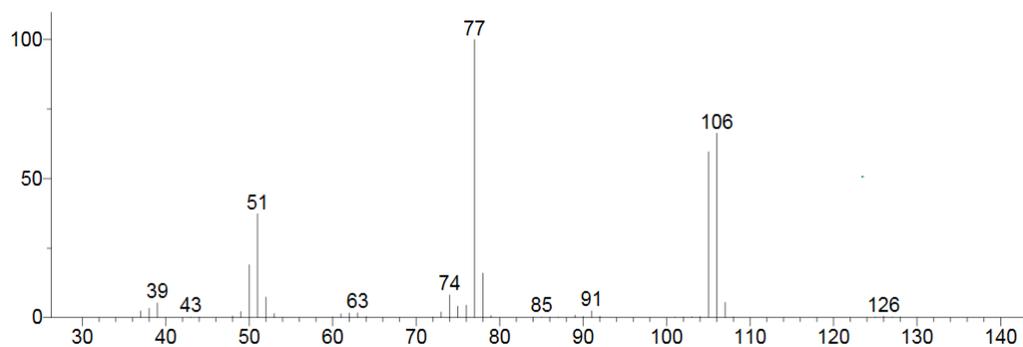


Figure S16. GC-MS analysis of toluene solution after irradiation of  $1 \cdot 2\text{AuCl}_3$  and formation of AuNP (Conditions: Ultralloy-5 column, 30m, low temperature pyrolysis).



Hit 1 : Benzaldehyde  
 C<sub>7</sub>H<sub>6</sub>O; MF: 909; RMF: 919; Prob 63.1%; CAS: 100-52-7; Lib: mainlib; ID: 40379.

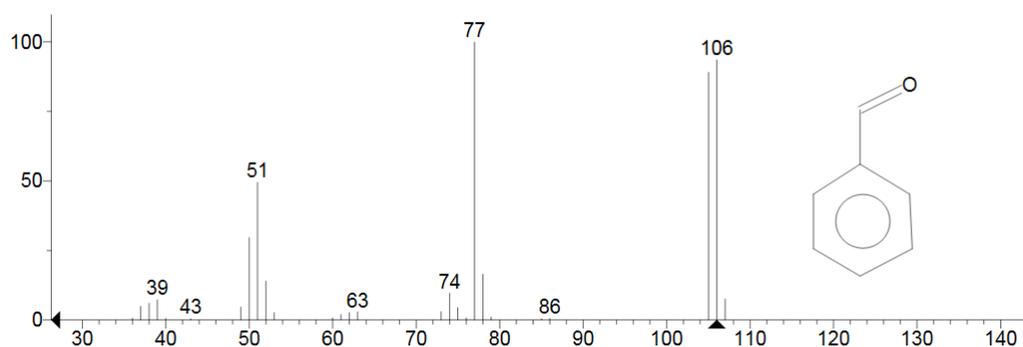
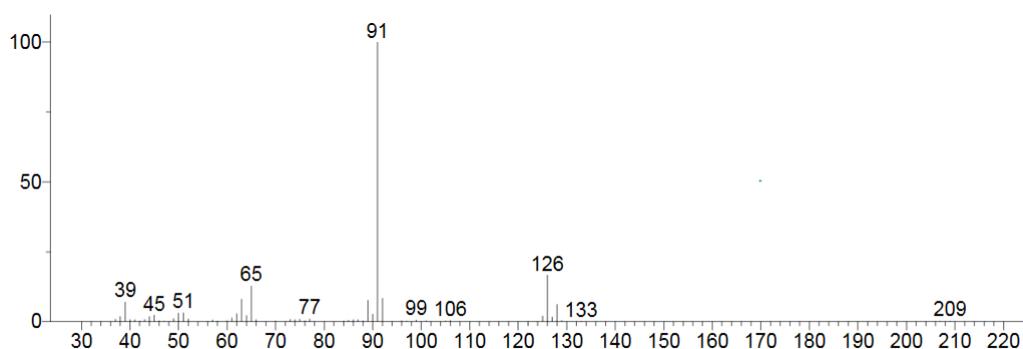


Figure S17. Mass spectrum of peak with RT = 3.90 min in Figure S16 (top) and comparison with reference spectrum for benzaldehyde (bottom).



Hit 1 : Benzyl chloride  
 C<sub>7</sub>H<sub>7</sub>Cl; MF: 918; RMF: 924; Prob 67.0%; CAS: 100-44-7; Lib: mainlib; ID: 52879.

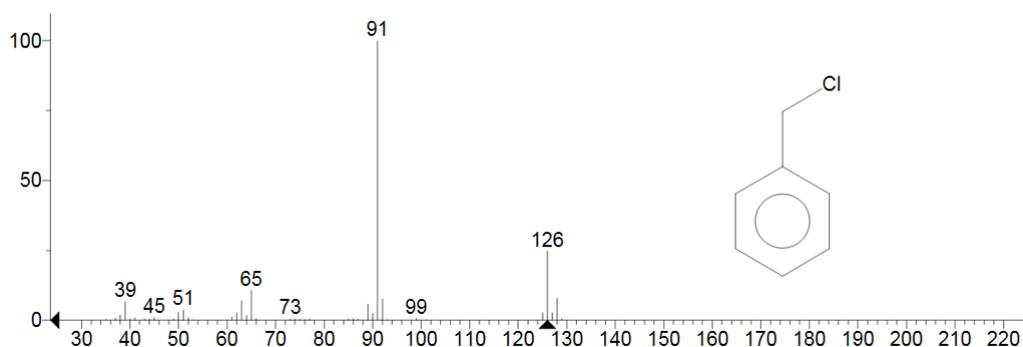
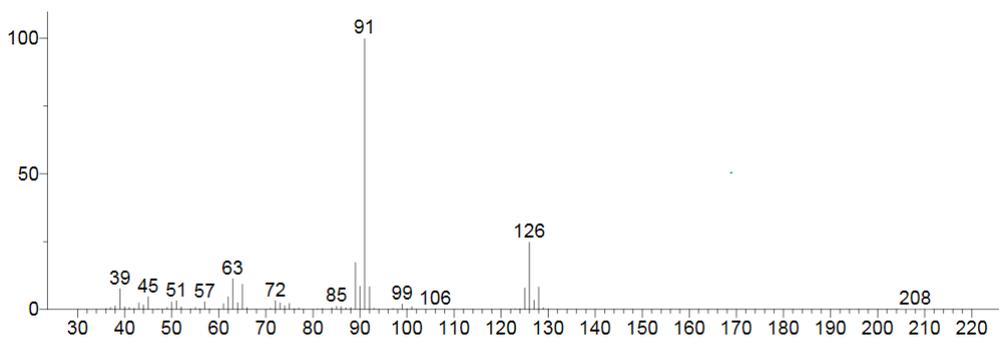


Figure S18. Mass spectrum of peak with RT = 4.440 min in Figure S16 (top) and comparison with reference spectrum for benzyl chloride (bottom).



Hit 1 : Benzene, 1-chloro-2-methyl-  
 C7H7Cl; MF: 879; RMF: 881; Prob 30.8%; CAS: 95-49-8; Lib: mainlib; ID: 52876.

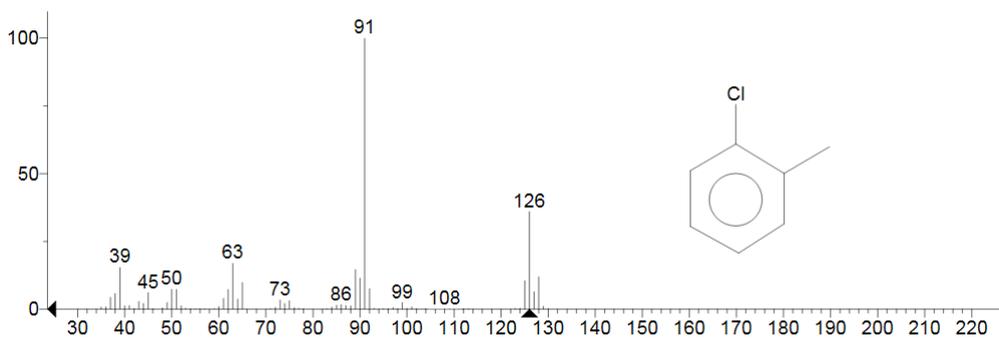


Figure S19. Mass spectrum of peak with RT = 3.84 min in Figure S16 (top) and comparison with reference spectrum for *o*-chlorotoluene (bottom).

## 5. FRET Calculation

To calculate the rate of intramolecular resonance energy transfer between the excited diphenylanthracene chromophore and one of the two AuCl<sub>3</sub> moieties, we subtracted the absorption spectra of **1** from that of the **1**•(AuCl<sub>3</sub>)<sub>2</sub> complex (in dichloromethane) to extract the absorption by the AuCl<sub>3</sub> moiety. The latter is similar, albeit slightly shifted, to previously reported AuCl<sub>3</sub> complexes in organic solvents and possesses significant absorption ( $\epsilon = 950 \text{ cm.L}^{-1}.\text{mol}^{-1}$ ) at 405 nm where the emission maximum of **1** is located (see Figure S19). From the overlap integral between the emission spectrum of the donor and the absorption spectrum of the acceptor, one can calculate the expected rate for a Förster energy transfer process according to eq. 1:

$$k_{EnT} = \frac{1}{\tau_D} \left(\frac{R_0}{r}\right)^6 \text{ where } R_0 = Cste * \left(\frac{\kappa^2 \Phi_D^0 J}{n^4}\right)^{1/6} \quad (\text{eq 1})$$

, where  $J$  is the calculated overlap integral ( $9.84 \times 10^{12} \text{ M}^{-1}\text{cm}^{-1}\text{nm}^4$ ),  $\Phi_D^0$  is the emission quantum yield of the donor (0.96),  $n$  is the refraction index of the solvent (1.494 for dichloromethane), and  $\kappa^2$  is a constant that reflects the relative orientation of the transition dipole moments of the donor and acceptor. Taking  $\kappa^2 = 2/3$  (isotropic orientation of donor and acceptors), one finds the Förster radius,  $R_0$ , to be 2.3 nm. From this, and the experimentally-determined quenching rate ( $5.0 \times 10^{10} \text{ s}^{-1}$ ), one can calculate the separation between the donor and acceptor to be 0.85 nm.

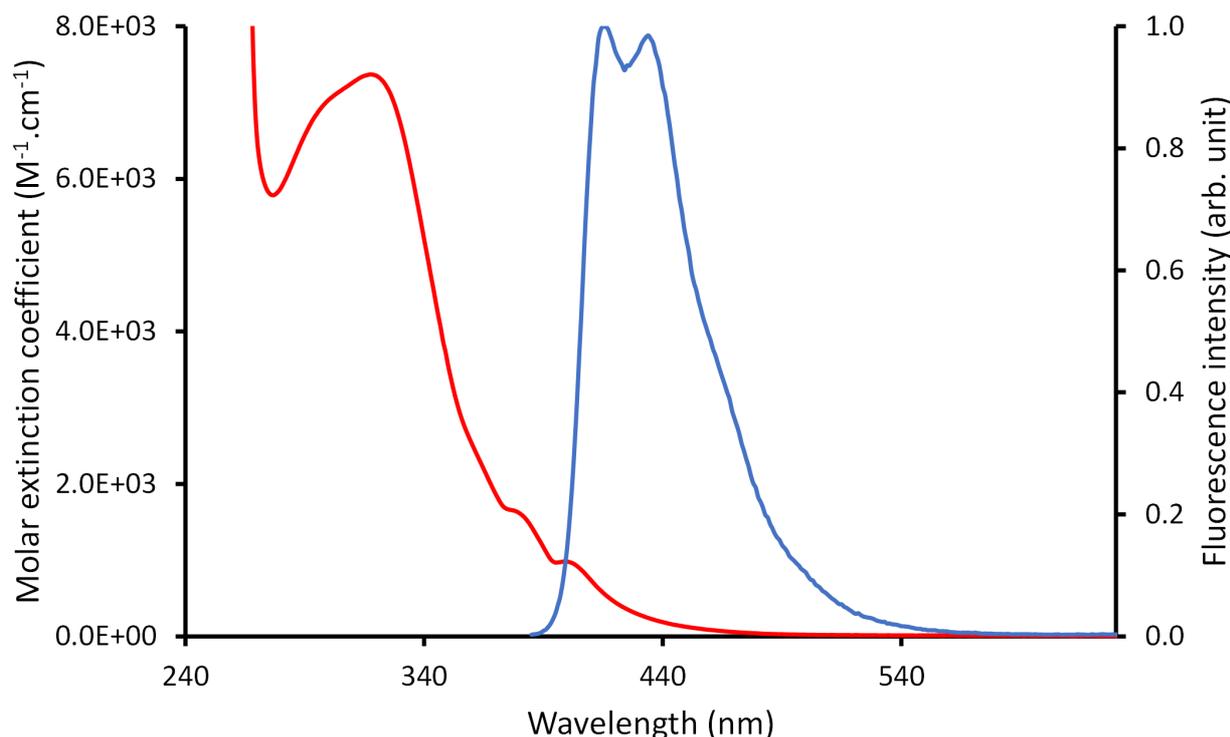


Figure S20. Calculated absorption spectrum of AuCl<sub>3</sub> bound to **1** in dichloromethane obtained by subtracting the absorption of **1** from that of the complex (red line) and emission spectrum of **1** in dichloromethane ( $\lambda_{\text{exc}} = 365 \text{ nm}$ , blue line).

## 6. VT-NMR of $1 \cdot 2\text{AuCl}_3$ .

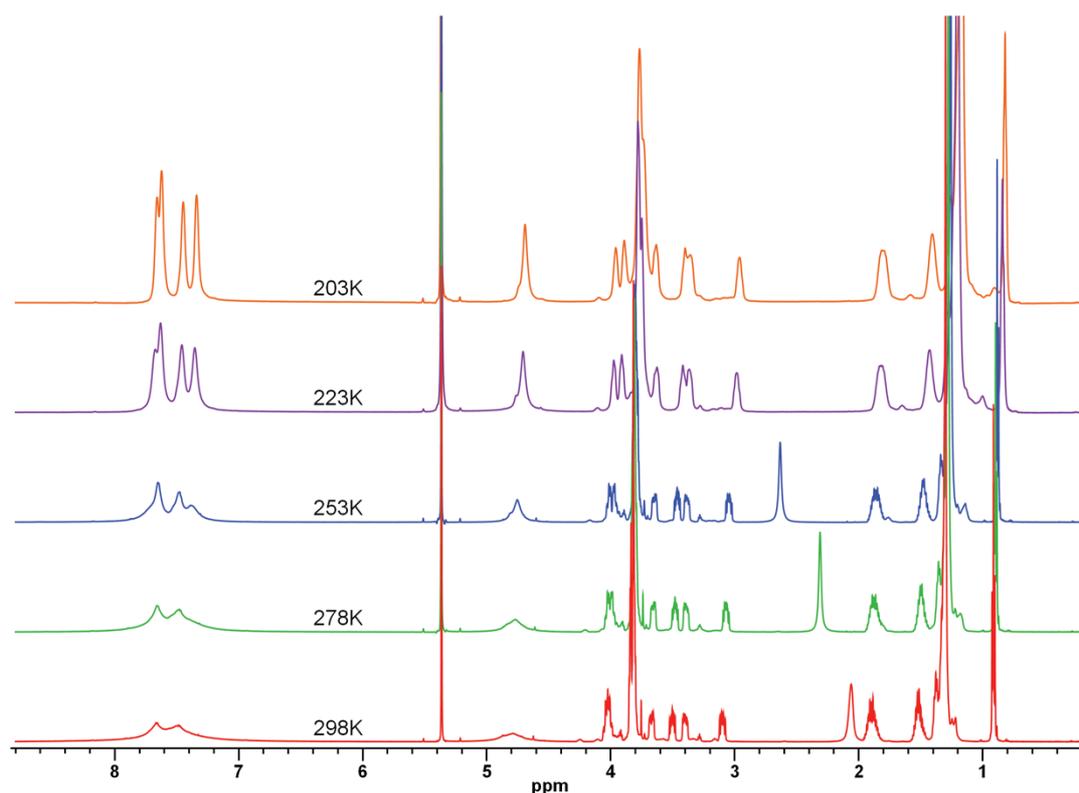


Figure S21. Variable-temperature NMR spectrum of  $1 \cdot 2\text{AuCl}_3$  in  $\text{CD}_2\text{Cl}_2$  at 600 MHz.

## 7. Dismutation of Au in solution.

The recovery of the absorption of Au(III) at 330 nm was monitored upon allowing an irradiated solution of  $1 \cdot 2\text{AuCl}_3$  in dichloromethane to stand in the dark after a short period of irradiation to produce Au(I) and Au(II).

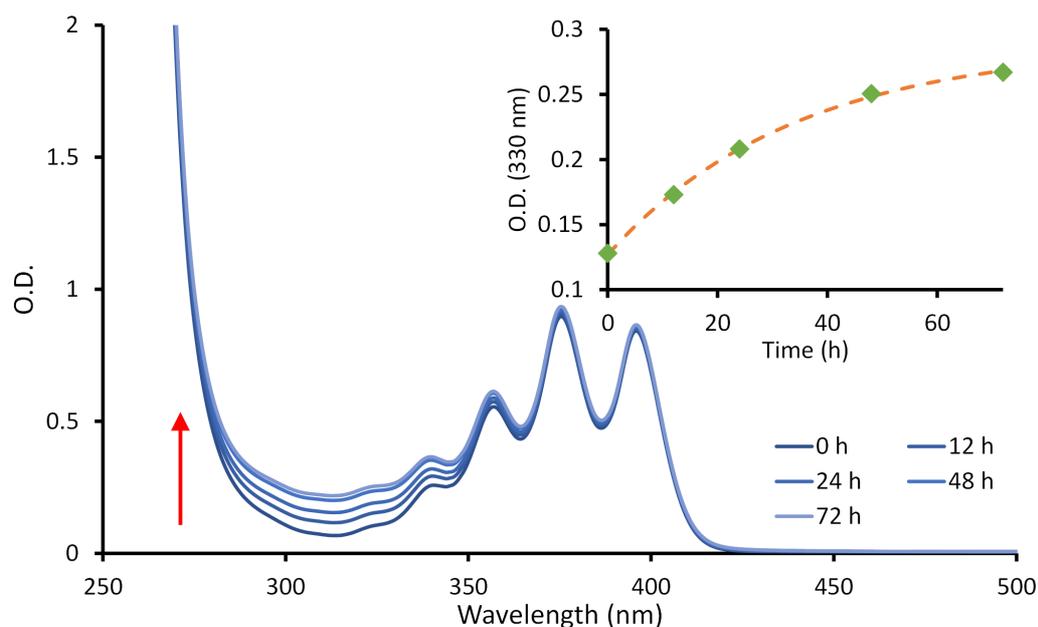
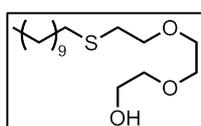
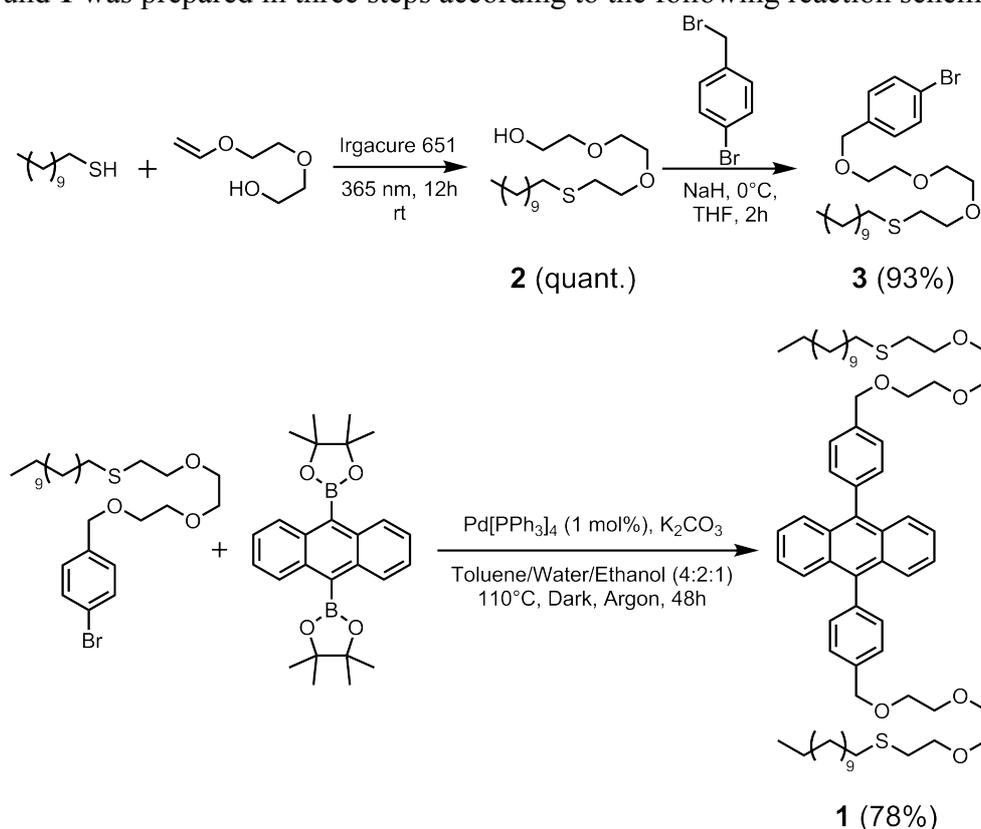


Figure S22. UV-vis spectrum of a solution of  $1 \cdot 2\text{AuCl}_3$  in dichloromethane ( $60 \mu\text{M}$ ) upon standing in the dark after a short period of irradiation (10 min, 365 nm, 6W). Inset shows recovery of the absorbance at 330 nm assigned to the recovery of Au(III) from the dismutation of Au(I) and Au(II).

## 8. Synthesis of 1.

Compound **1** was prepared in three steps according to the following reaction scheme:

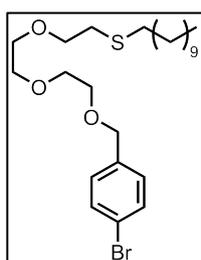


**2-(2-(2-(dodecylthio)ethoxy)ethoxy)ethanol (2).** To a degassed mixture of 1-dodecanethiol (10 g, 50 mmol) and diethylene glycol monovinyl ether (6.6 g, 50 mmol) was added Irgacure 651 (1 mol%, 128 mg, 0.5 mmol). The reaction mixture was irradiated at 365 nm for 2 h and stirred for 12 hours. The product was used without further purification as a white crystalline solid (16.6 g, 100%).

**<sup>1</sup>H NMR (200MHz, CDCl<sub>3</sub>):** δ (ppm) = 3.80-3.50 (m, CH<sub>2</sub>O, 10H), 2.70 (t, J = 7.2 Hz, CH<sub>2</sub>S, 2H), 2.53 (t, J = 7.2 Hz, CH<sub>2</sub>S, 2H), 2.4 (t, J = 5.6 Hz, OH, 1H), 1.56 (m, SCH<sub>2</sub>CH<sub>2</sub>, 2H), 1.45-1.15 (m, CH<sub>2</sub>, 18H), 0.86 (t, J = 6.8 Hz, CH<sub>3</sub>, 3H).

**<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):** δ (ppm) = 72.5 (CH<sub>2</sub>), 71.0 (CH<sub>2</sub>), 70.4 (CH<sub>2</sub>), 70.3 (CH<sub>2</sub>), 61.8 (CH<sub>2</sub>), 32.6 (CH<sub>2</sub>), 31.9 (CH<sub>2</sub>), 31.4 (CH<sub>2</sub>), 29.8 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 29.4 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>).

**HRMS (ESI):** calcd for C<sub>18</sub>H<sub>38</sub>O<sub>3</sub>S m/z = 334.2542; found m/z = 334.2498 [M]<sup>+</sup>.

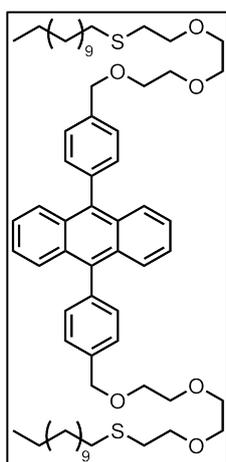


**1-(4-bromophenyl)-2,5,8-trioxa-11-thiatricosane (3).** To a cold suspension of sodium hydride (60 % in mineral oil, 600 mg, 15 mmol) in dry THF (50 mL) was added a solution of **2** (4 g, 12 mmol) in dry THF (15 mL). The reaction mixture was stirred for 30 min. at 0°C, then a solution of 4-bromobenzyl bromide (2.6 g, 10 mmol) in THF (10 mL) was added and the reaction mixture was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated ammonium chloride solution (10 mL) and the solvent was removed under reduced pressure. The residue was poured in water (50 mL) and extracted with diethyl ether (4x25 mL). The organic phases were collected, dried and evaporated

under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/ethyl acetate, 80:20) and a colorless oil (4.68 g, 93 %) was obtained.

**<sup>1</sup>H NMR (200MHz, CDCl<sub>3</sub>):** δ (ppm) = 7.47 (d, J = 8.0 Hz, CH, 2H), 7.23 (d, J = 8.0 Hz, CH, 2H), 4.53 (s, PhCH<sub>2</sub>O, 2H), 3.80-3.50 (m, CH<sub>2</sub>O, 10H), 2.70 (t, J = 7.2 Hz, CH<sub>2</sub>S, 2H), 2.53 (t, J = 7.2 Hz, CH<sub>2</sub>S, 2H), 1.56 (m, SCH<sub>2</sub>CH<sub>2</sub>, 2H), 1.45-1.15 (m, CH<sub>2</sub>, 18H), 0.86 (t, J = 6.8 Hz, CH<sub>3</sub>, 3H).

**HRMS (FD):** calcd for C<sub>25</sub>H<sub>43</sub>BrO<sub>3</sub>S *m/z* = 502.2116; found *m/z* = 502.2086 [M]<sup>+</sup>.



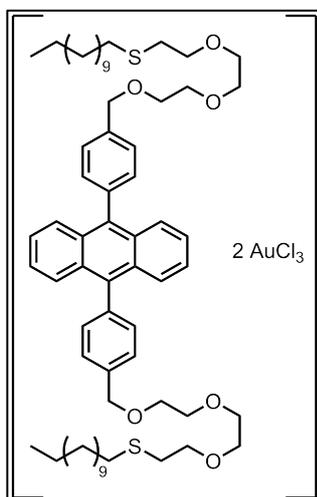
**9,10-bis(4-(2,5,8-trioxa-11-thiatricosyl)phenyl)anthracene (1):** To a solution of **3** (3.5 g, 7 mmol) in a mixture of toluene (20 mL), water (10 mL) and ethanol (5 mL) in the dark under argon atmosphere was added 9,10-anthracenediboronic acid bis(pinacol) ester (1 g, 2.3 mmol) and potassium carbonate (6 g, 45 mmol). The reaction mixture was degassed by argon bubbling for 1 hour. Then solid tetrakis(triphenylphosphine) palladium (0) (1 mol%, 27 mg, 23 μmol) was added and the reaction mixture was heated to reflux for 48 hours. The reaction mixture was allowed to cool to room temperature, the solvent was removed under reduced pressure and the residue was poured in water (100 mL) and extracted with diethyl ether (4x30 mL). The organic phases were collected, dried and evaporated, the residue was purified on chromatography column (silica gel, dark, hexane/ethyl acetate, 80:20) and a yellow fluorescent oil (1.85 g, 78 %) was obtained. The product is highly sensitive to light and oxygen.

**<sup>1</sup>H NMR (800MHz, CD<sub>2</sub>Cl<sub>2</sub>):** δ (ppm) = 7.73 (m, CH, 4H), 7.64 (d, J = 8.1 Hz, CH, 4H), 7.49 (d, J = 8.1 Hz, CH, 4H), 7.37 (m, CH, 4H), 4.77 (s, PhCH<sub>2</sub>O, 4H), 3.81 (m, CH<sub>2</sub>O, 4H), 3.77 (m, CH<sub>2</sub>O, 4H), 3.73 - 3.63 (m, CH<sub>2</sub>O, 12H), 2.74 (t, J = 7.2 Hz, CH<sub>2</sub>S, 4H), 2.57 (t, J = 7.2 Hz, CH<sub>2</sub>S, 4H), 1.60 (m, SCH<sub>2</sub>CH<sub>2</sub>, 4H), 1.45-1.25 (m, CH<sub>2</sub>, 36H), 0.91 (t, J = 6.8 Hz, CH<sub>3</sub>, 6H).

**<sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):** δ (ppm) = 138.4 (Cq), 138.1 (Cq), 137.1 (Cq), 131.5 (CH), 130.1 (Cq), 127.9 (CH), 127.1 (CH), 125.2 (CH), 73.3 (CH<sub>2</sub>), 71.2 (CH<sub>2</sub>), 71.0 (CH<sub>2</sub>), 70.9 (CH<sub>2</sub>), 70.5 (CH<sub>2</sub>), 70.2 (CH<sub>2</sub>), 32.8 (CH<sub>2</sub>), 32.1 (CH<sub>2</sub>), 31.7 (CH<sub>2</sub>), 30.0 (CH<sub>2</sub>), 29.8 (CH<sub>2</sub>), 29.7 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 29.4 (CH<sub>2</sub>), 29.0 (CH<sub>2</sub>), 22.8 (CH<sub>2</sub>), 14.0 (CH<sub>3</sub>).

**UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):** λ<sub>max</sub> (nm), ε (M<sup>-1</sup>.cm<sup>-1</sup>) = 262 (108000), 341 (4110), 357 (9000), 375 (14560), 397 (13680).

**HRMS (FD):** calcd for C<sub>64</sub>H<sub>94</sub>O<sub>6</sub>S<sub>2</sub> *m/z* = 1022.6492; found *m/z* = 1022.6525 [M]<sup>+</sup>.



**9,10-bis(4-(2,5,8-trioxa-11-thiatricosyl)phenyl)anthracene gold(III) chloride complex (1•2AuCl<sub>3</sub>):**

**Method A :** To a solution of **1** (10 mg, 10 μmol) in dichloromethane or toluene (10 mL) was added solid potassium tetrachloroaurate (15 mg, 40 μmol). The solution was sonicated in the dark for 1 hour. The organic phase was collected and used without further purification.

**Method B :** To a solution of **1** (10 mg, 10 μmol) in dichloromethane or toluene (10 mL) was added a solution of potassium tetrachloroaurate (15 mg, 40 μmol) in water (10 mL). The reaction mixture was shaken vigorously in the dark for 15 minutes and then

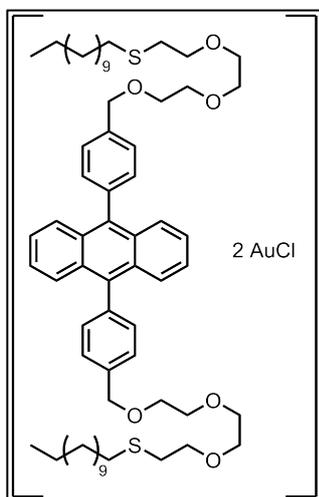
centrifuged for 10 minutes at 3000 rpm. The organic phase was collected and used without further purification.

**<sup>1</sup>H NMR (800MHz, CD<sub>2</sub>Cl<sub>2</sub>):** δ (ppm) = 7.95 - 7.15 (br, CH, 16H), 4.77 (s, PhCH<sub>2</sub>O, 4H), 4.01 (m, OCH<sub>2</sub>CH<sub>2</sub>S, 4H), 3.85 - 3.75 (m, CH<sub>2</sub>O, 16H), 3.66 (m, OCH<sub>2</sub>CH<sub>2</sub>S, 2H), 3.49 (m, CH<sub>2</sub>CH<sub>2</sub>S, 2H), 3.39 (m, OCH<sub>2</sub>CH<sub>2</sub>S, 2H), 3.09 (m, CH<sub>2</sub>CH<sub>2</sub>S, 2H), 1.88 (m, CH<sub>2</sub>CH<sub>2</sub>S, 4H), 1.50 (m, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, 4H), 1.40-1.20 (m, CH<sub>2</sub>, 32H), 0.91 (t, J = 6.8 Hz, CH<sub>3</sub>, 6H).

**<sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):** δ (ppm) = 138.4 (Cq), 138.1 (Cq), 137.1 (Cq), 131.5 (CH), 130.1 (Cq), 127.9 (CH), 127.1 (CH), 125.2 (CH), 73.3 (CH<sub>2</sub>), 71.4 (CH<sub>2</sub>), 70.9 (CH<sub>2</sub>), 70.7 (CH<sub>2</sub>), 70.2 (CH<sub>2</sub>), 66.7 (CH<sub>2</sub>), 40.9 (CH<sub>2</sub>), 40.4 (CH<sub>2</sub>), 32.1 (CH<sub>2</sub>), 29.8 (CH<sub>2</sub>), 29.7 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 29.4 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 28.7 (CH<sub>2</sub>), 27.9 (CH<sub>2</sub>), 22.8 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>).

**UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):** λ<sub>max</sub> (nm), ε (M<sup>-1</sup>.cm<sup>-1</sup>) = 323 (15670), 357 (14440), 375 (17820), 397 (15540).

**MS (FD+):** m/z = 1630.2; calc. 1630.21 (C<sub>64</sub>H<sub>94</sub>O<sub>6</sub>S<sub>2</sub>Au<sub>2</sub>Cl<sub>6</sub>).



**9,10-bis(4-(2,5,8-trioxa-11-thiatricosyl)phenyl)anthracene gold(I) chloride complex (1·2AuCl):** A solution of 1·2AuCl<sub>3</sub> in dichloromethane or toluene (0.5 mM, 2 mL) was prepared according to the previous method (A or B) and was irradiated with a TLC lamp (365 nm, 6 W) or with a LED (400 nm, 10 W) until the solution turns colorless. The solution was used without further purification

**UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):** λ<sub>max</sub> (nm), ε (M<sup>-1</sup>.cm<sup>-1</sup>) = 262 (107100), 323 (2200), 357 (9100), 375 (14530), 397 (13340).

**MS (FD+):** m/z = 1488.4; calc. 1488.40 (C<sub>64</sub>H<sub>94</sub>O<sub>6</sub>S<sub>2</sub>Au<sub>2</sub>Cl<sub>2</sub>).

## 8. Procedure for preparing AuNP.

All gold nanoparticles solutions were prepared according to the following procedure. A solution of **1** in dichloromethane (0.1 to 1 mM, 10 mL) or toluene (0.1 to 1 mM, 10 mL) was prepared in a centrifugation tube (50 mL). An appropriate volume of a solution of tetrachloroauric acid or potassium tetrachloroaurate in milliQ water (4 mM, 50 mL) was added to provide 4 equivalents of gold(III) per **1**. MilliQ water was added to fulfill the total volume to 10mL. The biphasic system was agitated on an orbital stirring table at 300rpm for 15 minutes. The emulsion was centrifuged at 3000rpm for 15 minutes, then the aqueous phase was removed and replaced by milliQ water (10 mL). The reaction mixture was agitated and irradiated (TLC lamp 365 nm (6W) or LED 400 nm (10W)) in the same time on an orbital stirring table at 300rpm for 15 minutes. The aqueous phase become red and the organic phase colorless. The reaction mixture was centrifuged at 1500rpm for 15 minutes and the aqueous phase, containing gold nanoparticles was collected and used without further purification.

## 12. Protocol for gold catalysis

A solution of  $1 \cdot 2\text{AuCl}_3$  (1.5 mM, 2 mL) in toluene- $d_8$  was prepared according to the procedure to form the nanoparticles: A solution of tetrachloroauric acid trihydrate in  $\text{D}_2\text{O}$  (5 mM, 2 mL) was extracted with a solution of **1** in toluene- $d_8$  (1.5 mM, 2 mL). Then the phases were separated by centrifugation (4000 rpm, 10 min) and the organic phase was collected and stored in the dark. 2,2-dimethyl-*N*-2-propynyl-propanamide (**4**) was prepared according to the known procedure described in literature.<sup>1</sup>

### Gold(III) catalysis :

A solution of  $1 \cdot 2\text{AuCl}_3$  in toluene- $d_8$  (1.5 mM, 0.5 mL) was placed in a NMR tube. The solvent was removed under reduced pressure at room temperature in the dark and replaced by a solution of 2,2-dimethyl-*N*-2-propynyl-propanamide (**4**) in dichloromethane- $d_2$  (0.15 M, 0.5 mL). The final concentrations were 1.5 mM in **1** and 0.15 M for the substrate (catalyst loading = 1 mol%). The reaction was followed by  $^1\text{H}$  NMR (Figure S24).

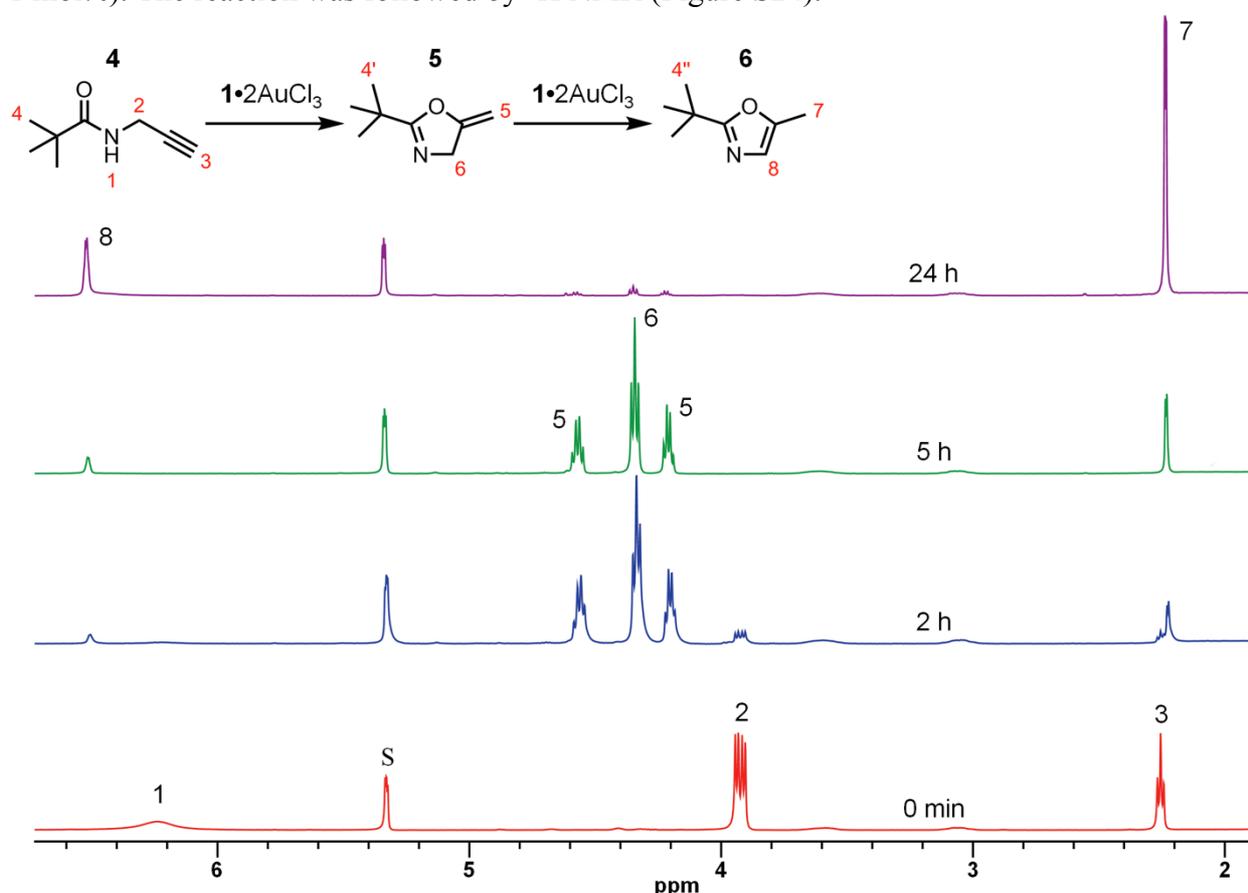


Figure S23:  $^1\text{H}$  NMR spectra (200 MHz,  $\text{CD}_2\text{Cl}_2/\text{toluene-}d_8$ ) of the cyclization reaction in the presence of  $1 \cdot 2\text{AuCl}_3$ .

### Gold(I) catalysis :

A solution of  $1 \cdot 2\text{AuCl}_3$  in toluene- $d_8$  (1.5 mM, 0.5 mL) was placed in a NMR tube and irradiated (TLC lamp, 365 nm) until the solution was colorless. The solvent was removed under reduced pressure at room temperature in the dark and replaced by a solution of 2,2-dimethyl-*N*-2-propynyl-propanamide (**4**) in dichloromethane- $d_2$  (0.15 M, 0.5 mL). The final concentrations were 1.5 mM for the catalyst and 0.15 M for the substrate (catalyst loading = 1 mol%). The reaction was followed by  $^1\text{H}$  NMR (Figure S25).

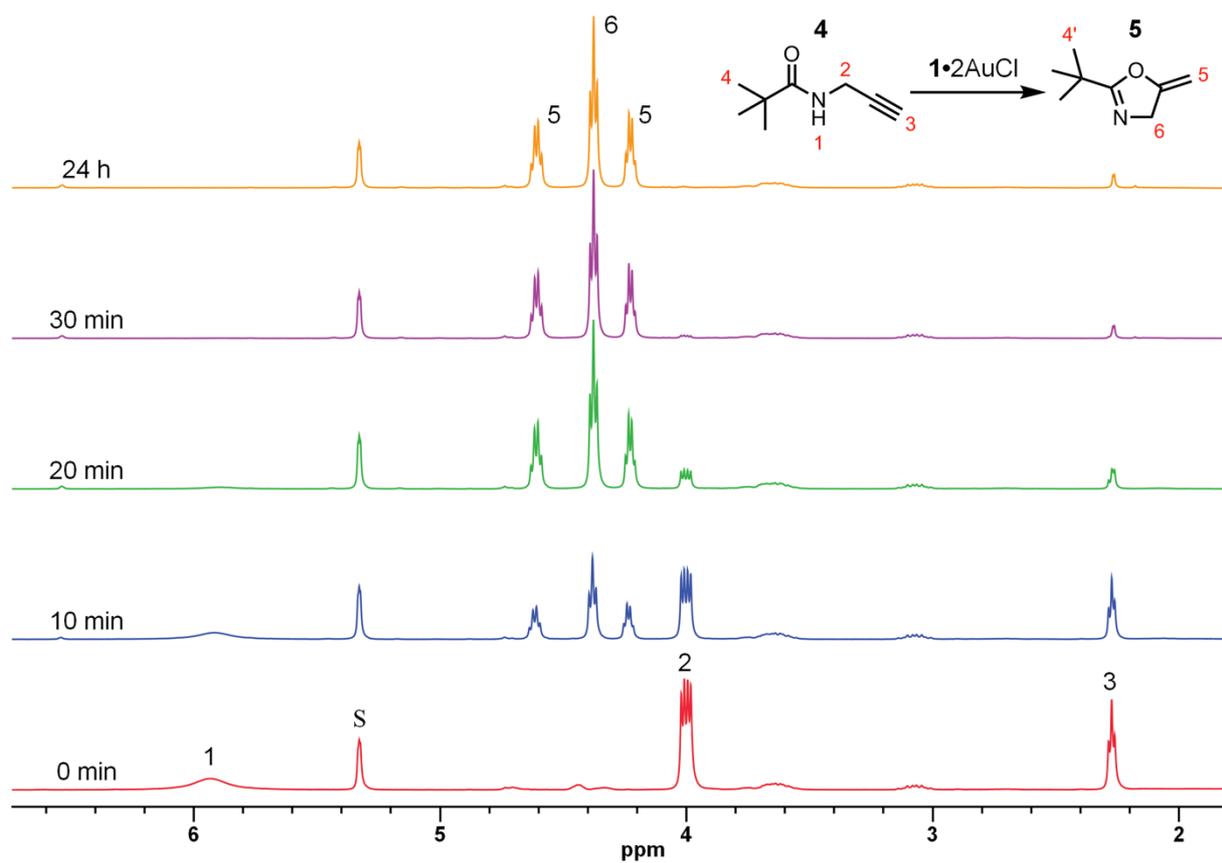


Figure S24: <sup>1</sup>H NMR spectra (200 MHz, CD<sub>2</sub>Cl<sub>2</sub>/toluene-d<sub>8</sub>) of the cyclization reaction in the presence of 1·2AuCl prepared by irradiation of 1·2AuCl<sub>3</sub> in toluene.

### 13. Spectral characterization of synthetic intermediates.

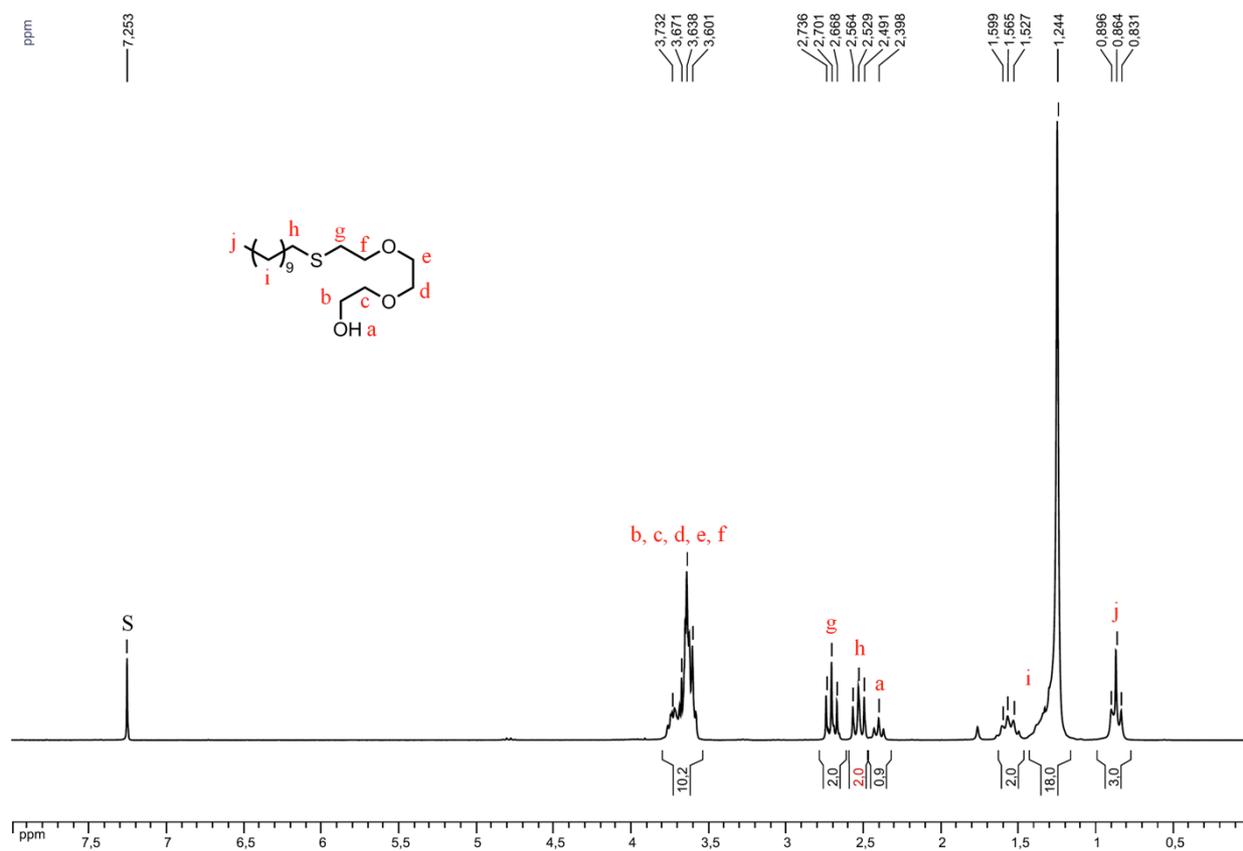


Figure S25. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) of 2

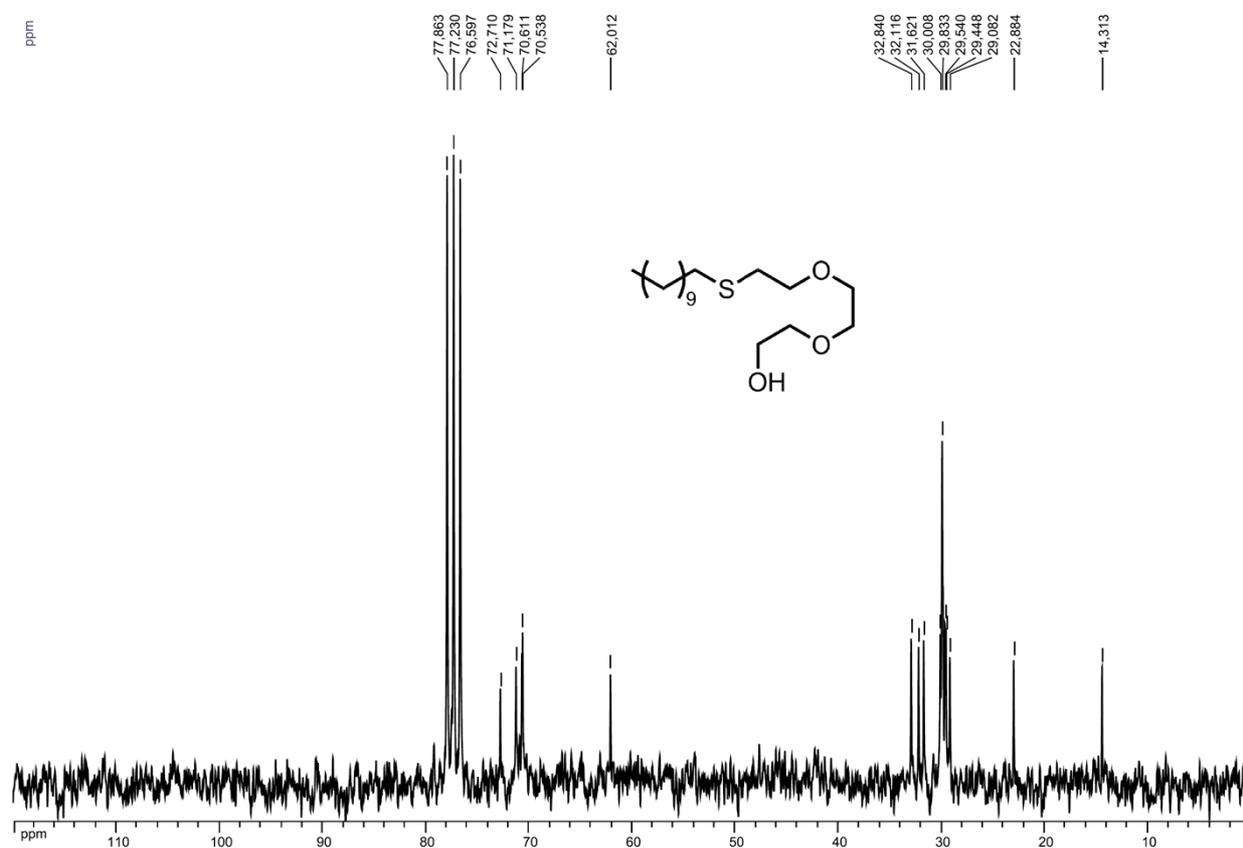
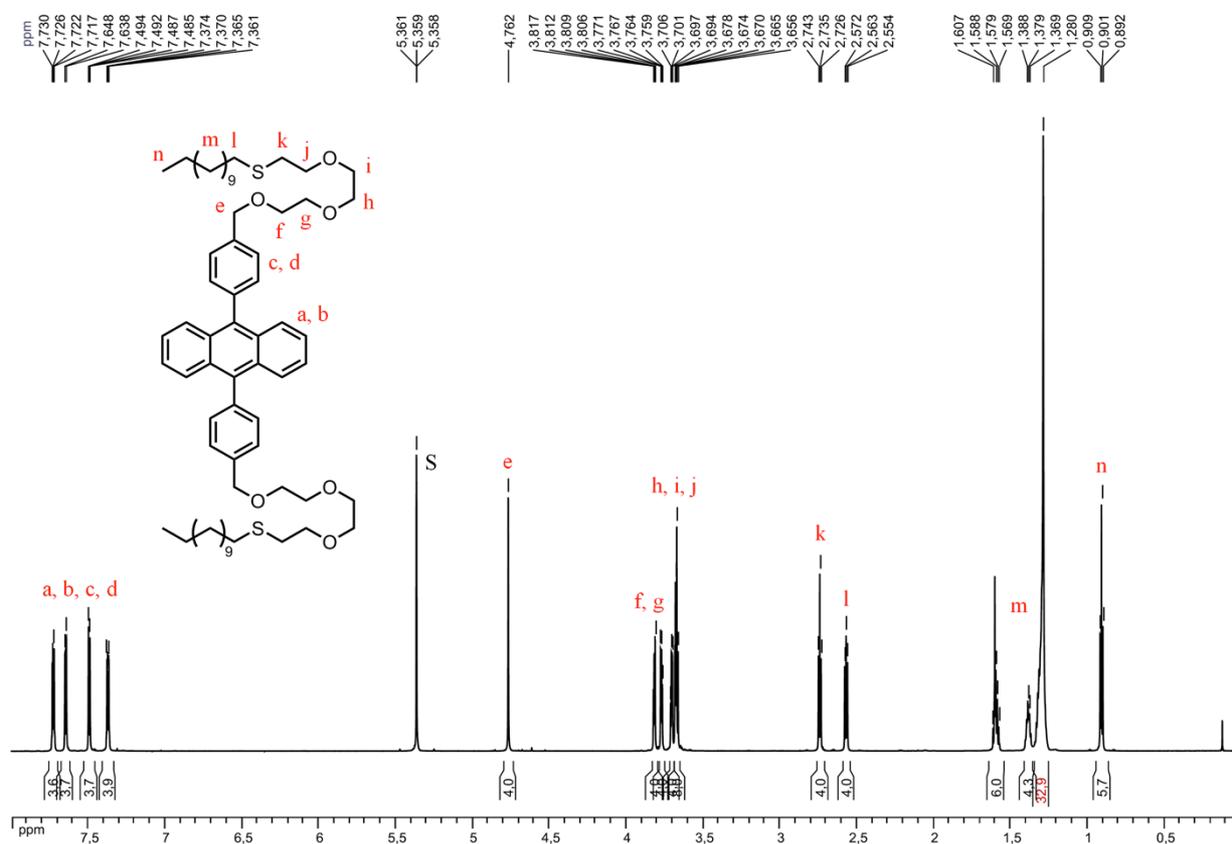
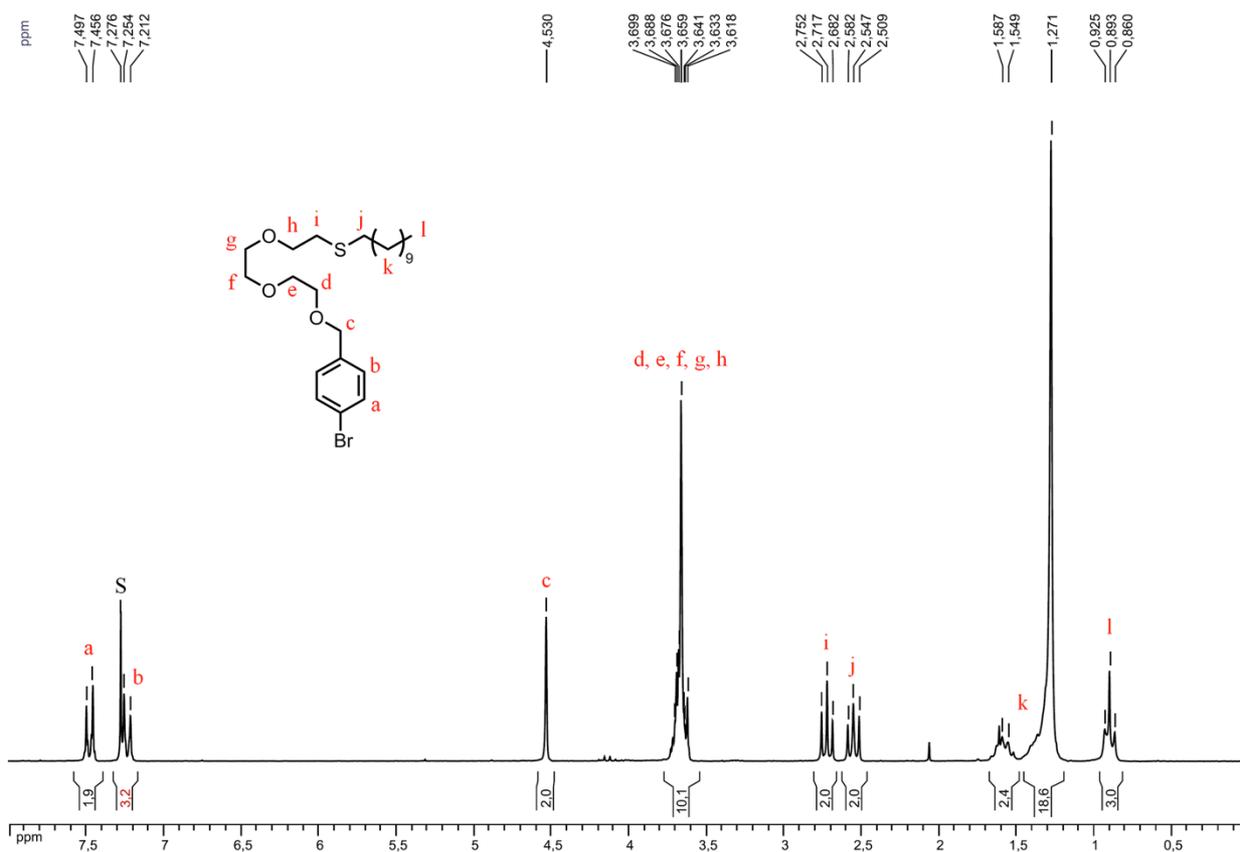


Figure S26. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz) of 2



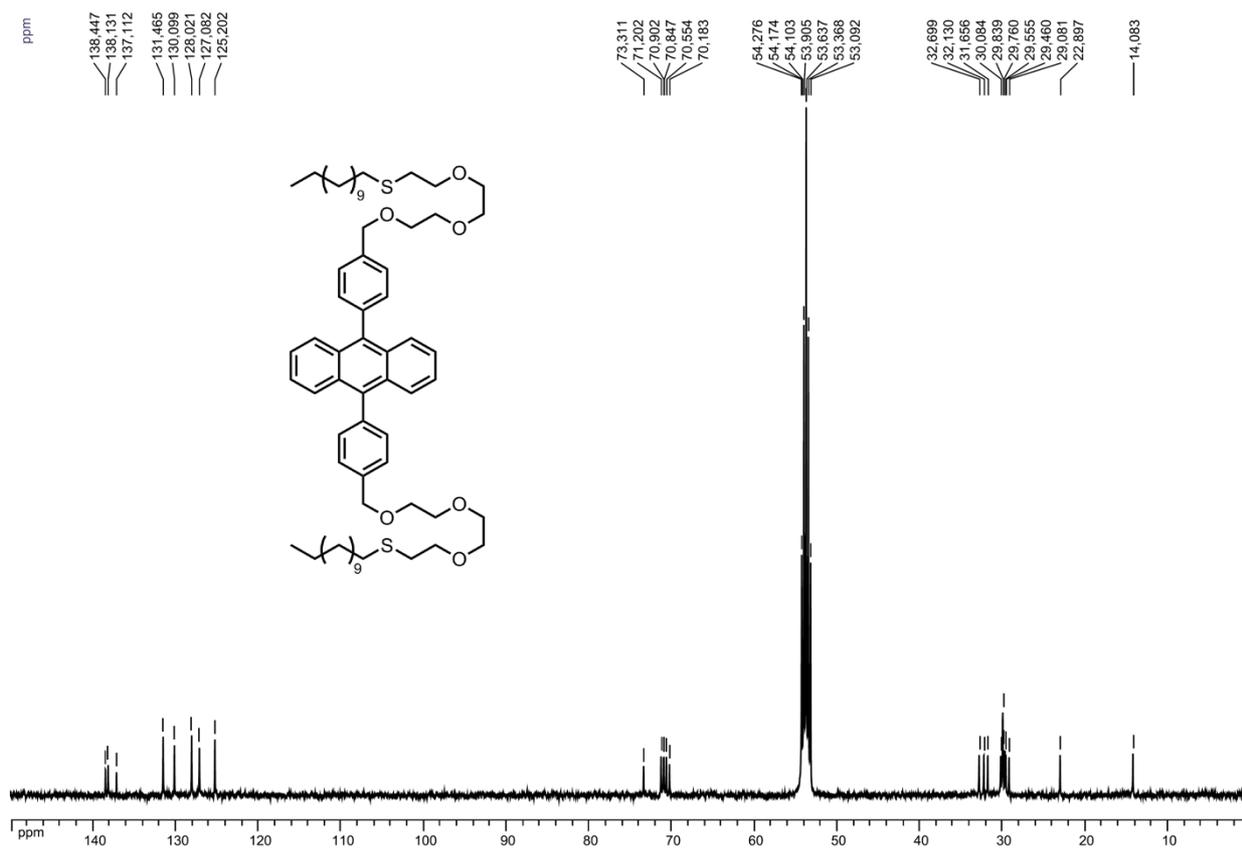


Figure S29. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz) of **1**

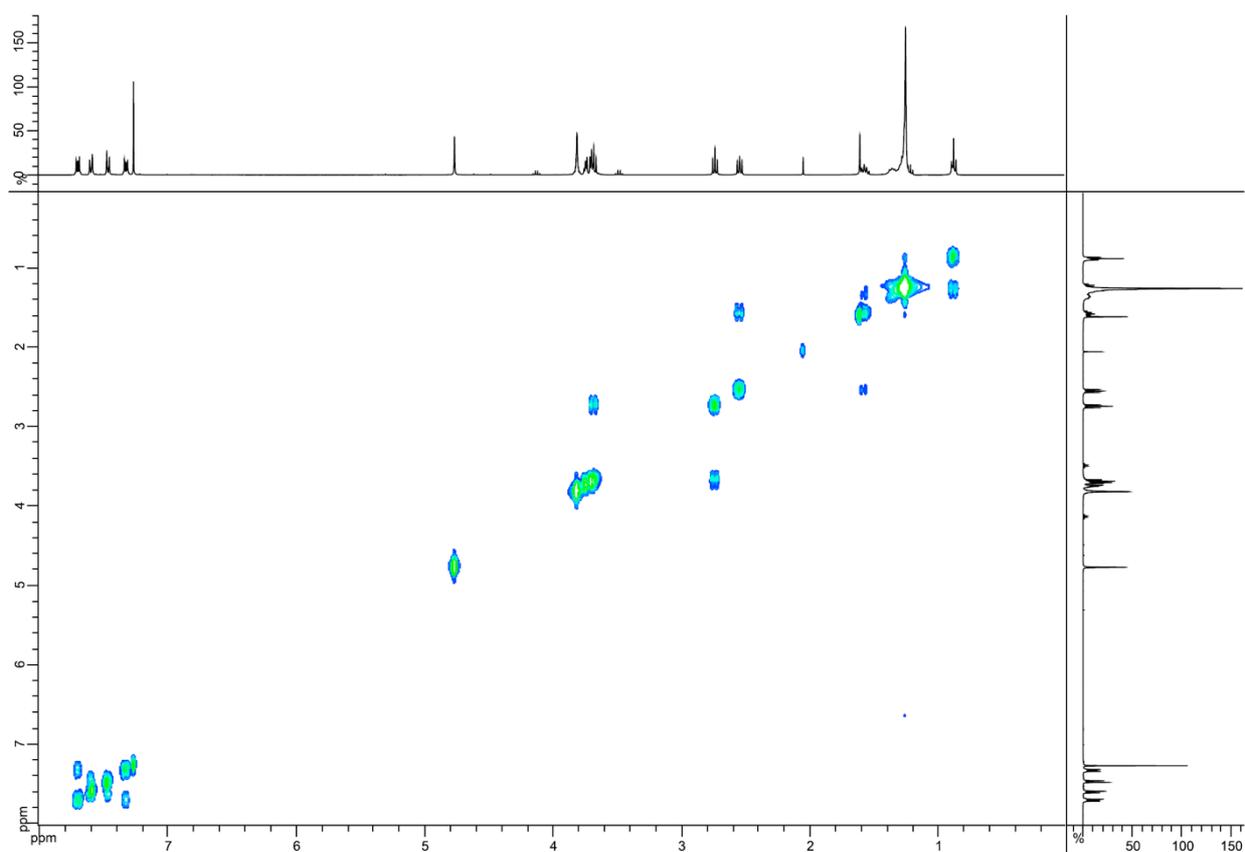


Figure S30: COSY NMR (CDCl<sub>3</sub>, 400 MHz) of **1**

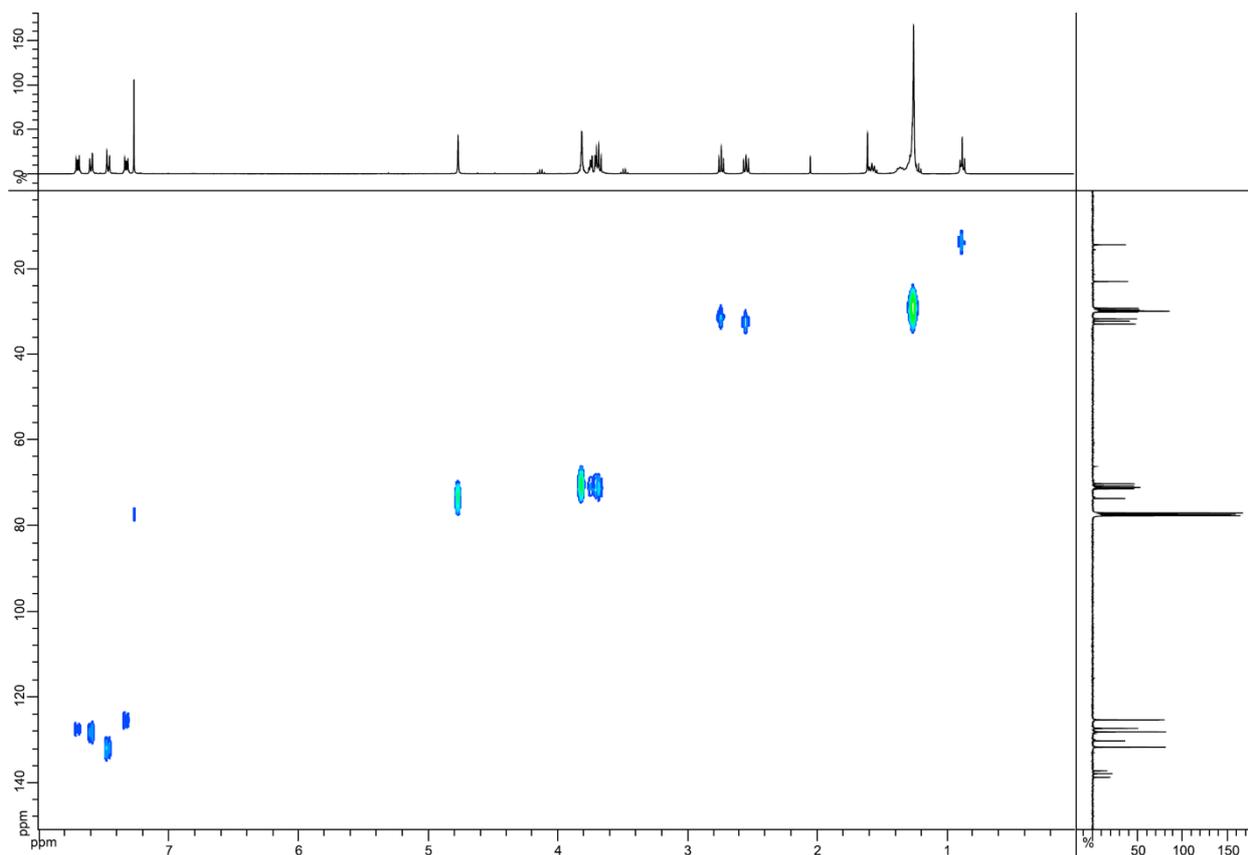


Figure S31 : HSQC NMR ( $\text{CDCl}_3$ , 400 MHz) of **1**

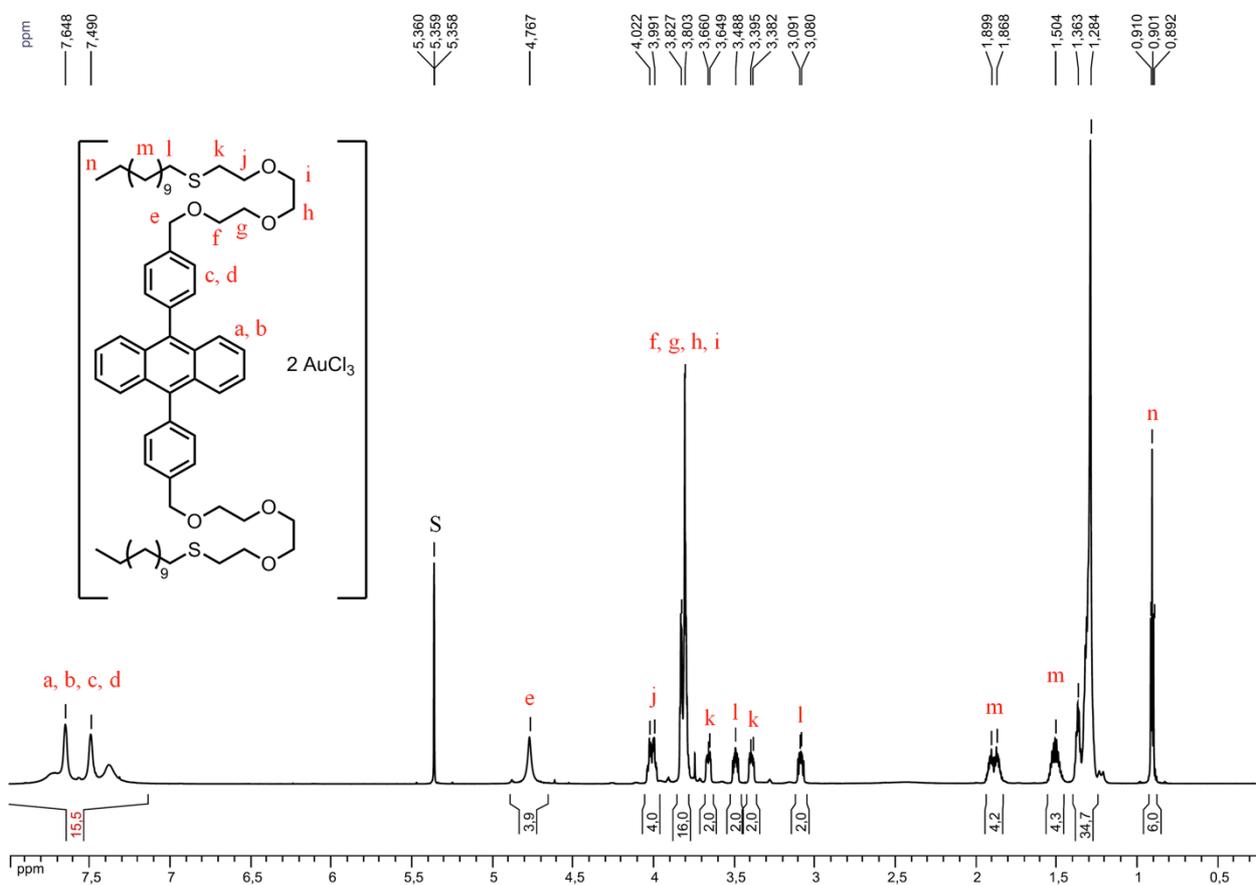


Figure S32.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 800 MHz) of **1**· $2\text{AuCl}_3$ .

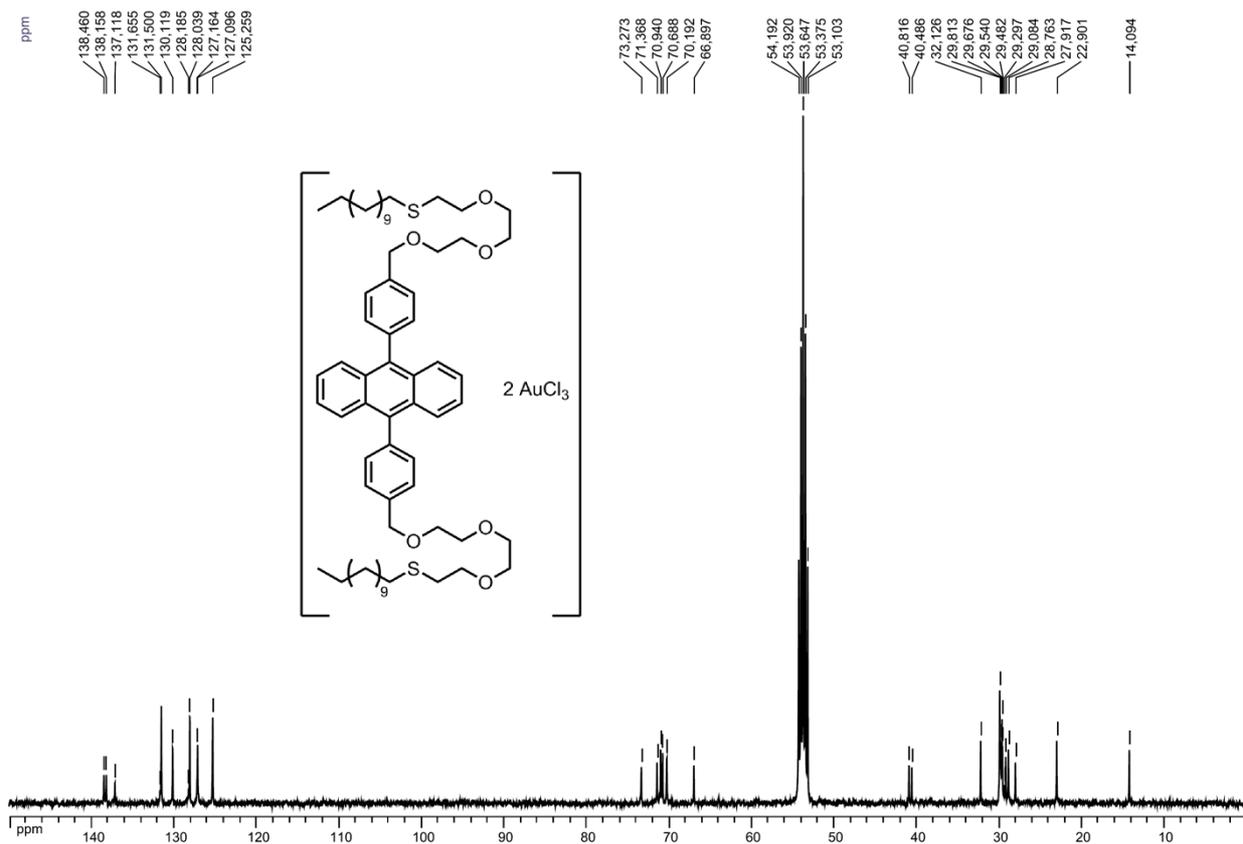


Figure S33.  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz) of  $\mathbf{1}\cdot 2\text{AuCl}_3$ .

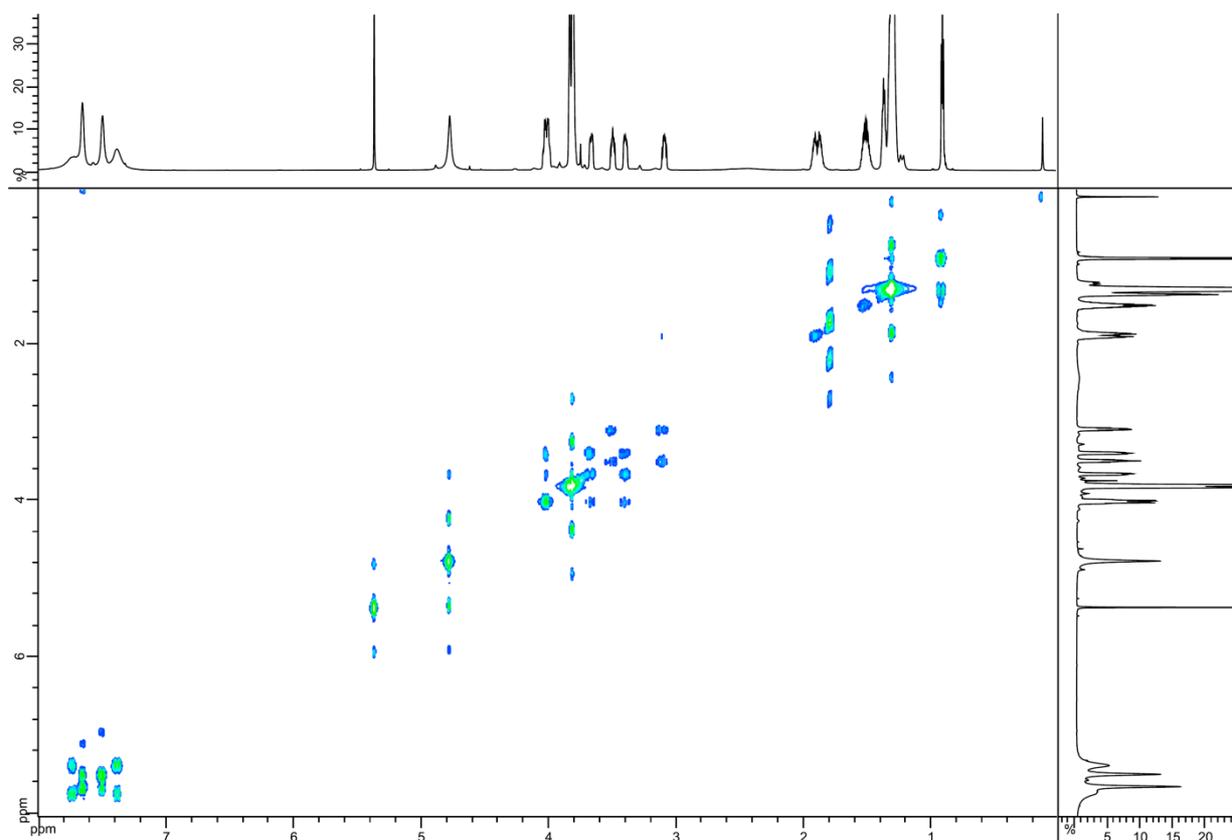


Figure S34. COSY NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz) of  $\mathbf{1}\cdot 2\text{AuCl}_3$ .

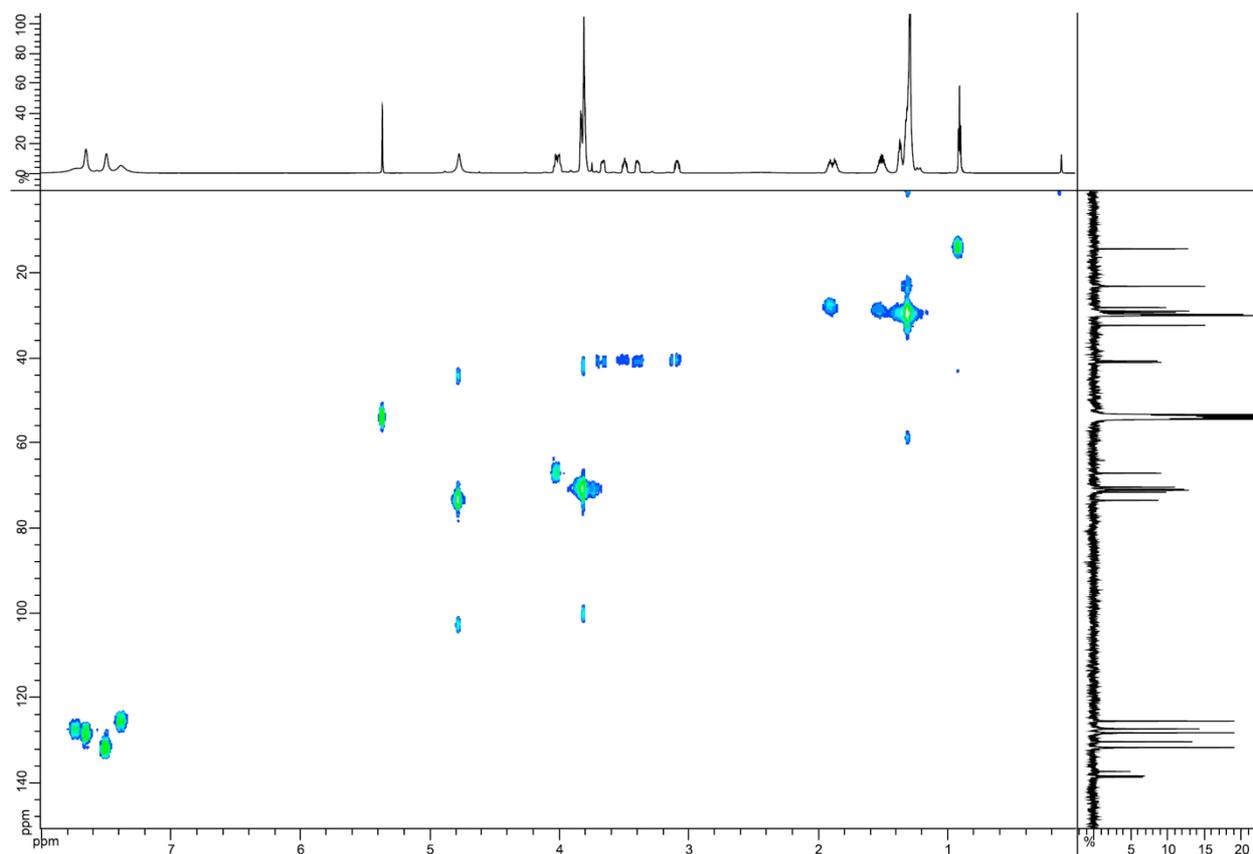


Figure S35. HSQC NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz) of  $\mathbf{1}\cdot\mathbf{2AuCl}_3$ .

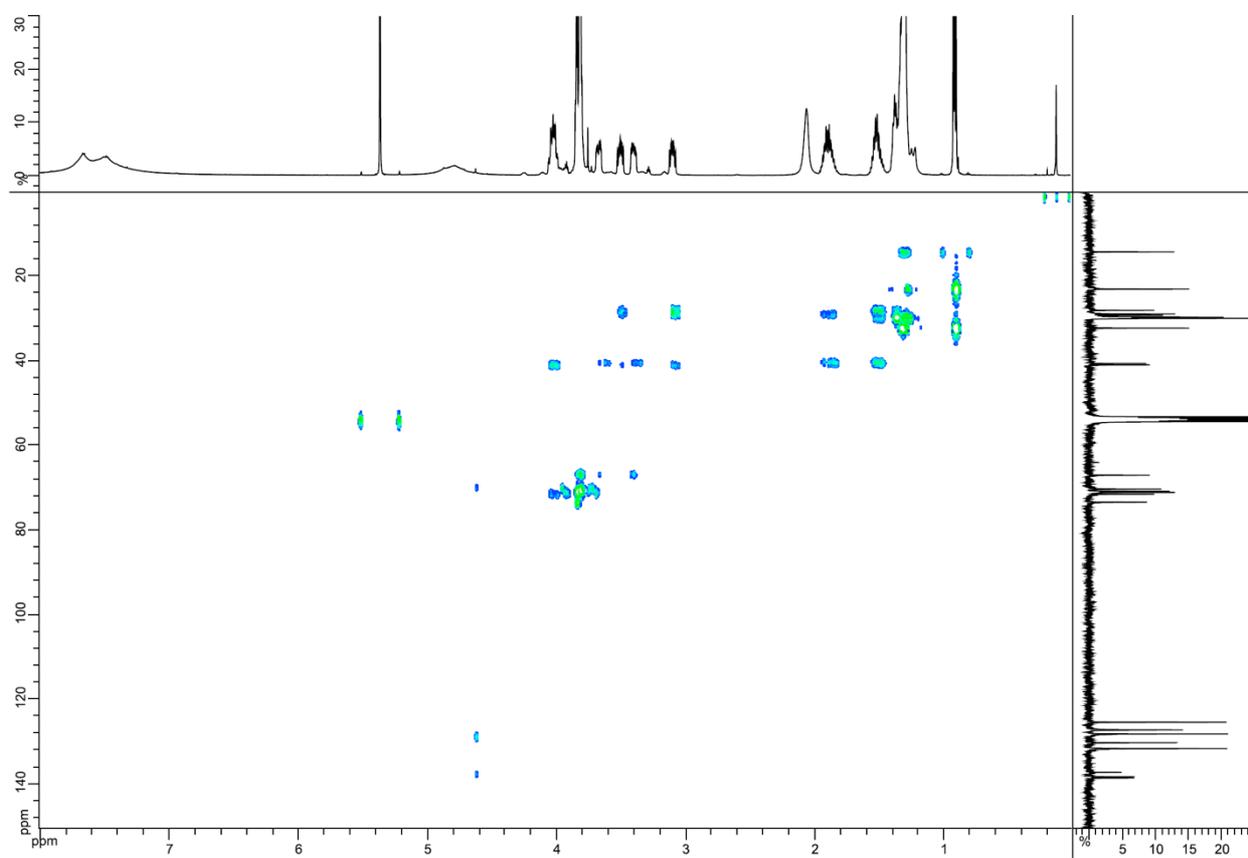


Figure S36. HMBC NMR ( $\text{CD}_2\text{Cl}_2$ , 600 MHz) of  $\mathbf{1}\cdot\mathbf{2AuCl}_3$ .

## References

- (1) Weyrauch, J. P.; Hashmi, A. S. K.; Schuster, A.; Hengst, T.; Schetter, S.; Littmann, A.; Rudolph, M.; Hamzic, M.; Visus, J.; Rominger, F.; Frey, W.; Bats, J. W. *Chem. Eur. J.* **2010**, *16*, 956-963.