

# **SUPPORTING INFORMATION – Covalently anchored homogeneous gold complex on carbon nanotubes: a reusable catalyst.**

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## 1. Instrumental

**X-ray photoelectron spectroscopy.** XPS analyses were carried out at room temperature with a SSI-X-probe (SSX 100/206) photoelectron spectrometer from Surface Science Instruments (USA) equipped with a monochromatized microfocus Al X ray source. Samples were stuck onto small sample holders with double-face adhesive tape and then placed on an insulating home-made ceramic carousel (Macor®, Switzerland). Charge effects were avoided by placing a nickel grid above the samples and using a flood gun set at 8 eV. The energy scale was calibrated with reference to the Au<sub>4f7/2</sub> peak at 84 eV and the binding energies were calculated with respect to the C-(C,H) component of the C<sub>1s</sub> peak fixed at 284.8 eV. Data treatment was performed with the CasaXPS program (Casa Software Ltd., UK). The peaks were decomposed into a sum of Gaussian/Lorentzian (85/15) after subtraction of a Shirley type baseline.

**ICP Analysis.** ICP AES were recorded on an ICAP 6500 from THERMO SCIENTIFIC. These analysis proceeded first by a mineralization of the solid (solution of H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub>) followed by dissolution of gold using aqua regia. Determination of the gold contained in a solution followed these steps: x grams of the solution were first evaporated before destruction of the organic matrix thanks to 3 ml of concentrated HNO<sub>3</sub> (65 wt%). The resulting solution was dried and then dissolution of gold was obtained using 2 ml of aqua regia and followed by dilution with water (20 ml).

**Thermogravimetric analysis.** Thermograms were recorded on a TGA/SDTA 851<sup>e</sup> simultaneous DSC-TGA instrument from METTLER TOLEDO. These analyses were carried out with a heating ramp of 10 °C/min and under N<sub>2</sub> flow (100 ml/min) with the samples (3 – 5 mg) placed into alumina containers.

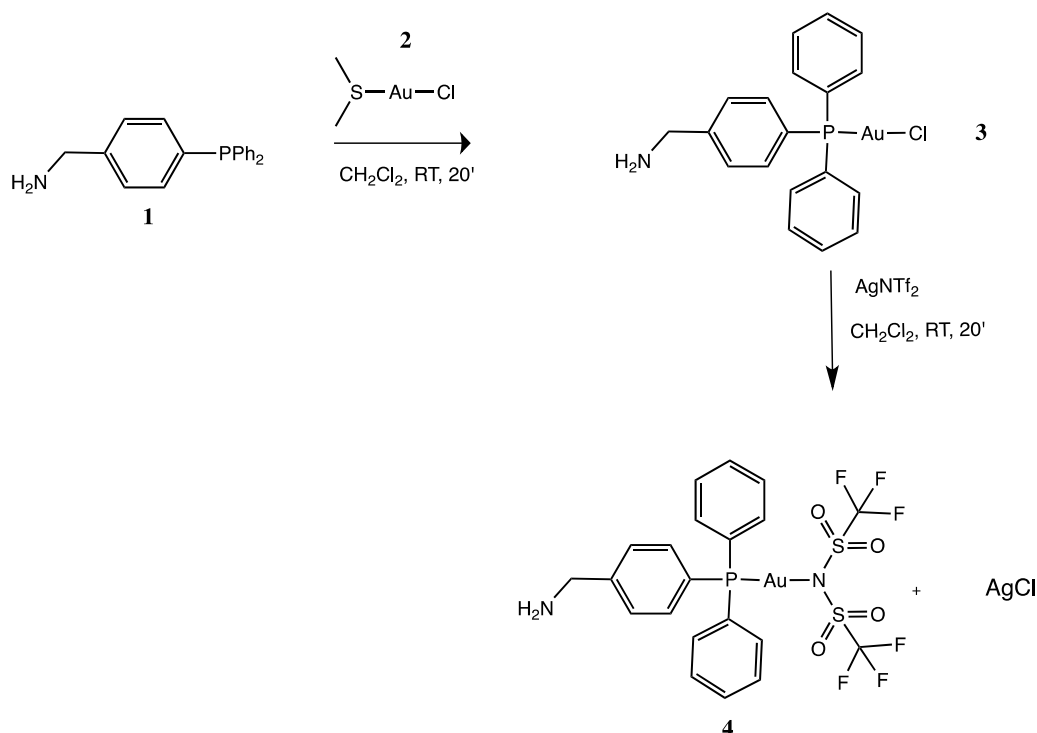
**Nuclear magnetic resonance.** NMR spectra were recorded on BRUKER spectrometers (300 MHz or 500 MHz for <sup>1</sup>H, 123 MHz for <sup>13</sup>C, 121 MHz for <sup>31</sup>P, 282 MHz for <sup>19</sup>F). Chemical shifts are reported in  $\delta$  (ppm) from CDCl<sub>3</sub>/tetramethylsilane or D<sub>6</sub>-Acetone with the solvent resonance as the internal standard for <sup>1</sup>H NMR and <sup>13</sup>C NMR.

**Mass spectrometry.** HRMS were recorded on a Q-Extractive orbitrap from ThermoFisher. Samples were ionized by ESI (capillary temperature: 250 °C, vaporizer temperature: 250 °C, sheath gas flow rate: 20).

**General methods:** Unless otherwise stated, all the manipulations were carried out under an atmosphere of Ar using standard Schlenk techniques and with anhydrous solvents. Hexane was distilled from sodium benzophenone under Ar. Dichloromethane was distilled from CaH<sub>2</sub>. MWNTs were obtained from Nanocyl (Thin MWCNT, 95+% C purity). The following compounds were obtained according to literature procedures: **6**<sup>[1]</sup>, **10**<sup>[1]</sup> and **12**<sup>[2]</sup>.

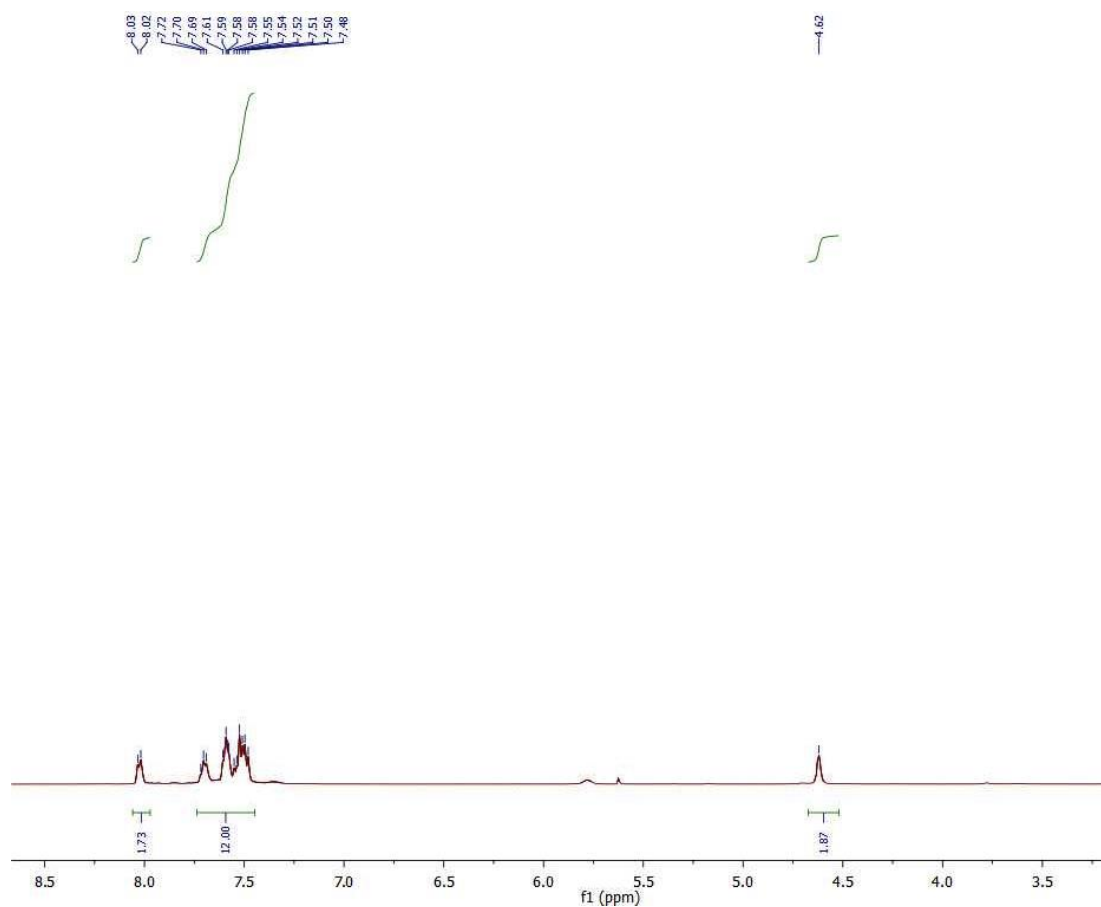
## 2. Synthesis and spectral data of gold complex **4**

### 2.1 Experimental: synthesis of **4**

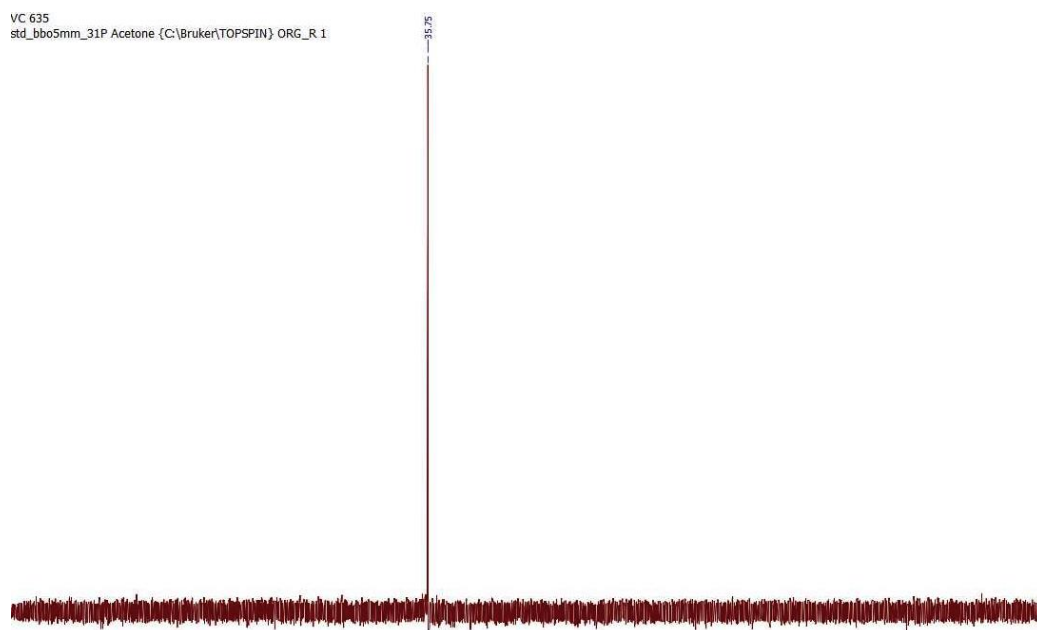


The bifunctional ligand **1**<sup>[3]</sup> (58 mg, 0.2 mmol) was added to a solution of ClAuSMe<sub>2</sub> **2** (59 mg, 0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8 ml). The resulting mixture was stirred at room temperature for 20 minutes and was finally vacuum dried to obtain gold complex **3** as a white solid. **3** was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (8 ml) and AgNTf<sub>2</sub> (78 mg, 0.2 mmol) was added. The mixture was stirred at room temperature for 20 minutes, then filtered through a millipore membrane in a disposable plastic syringe and the solution was concentrated by removing most of the solvent on the Schlenk line. Hexane was added (20 ml) to induce precipitation of **4** (121 mg, 79%) as a white solid: <sup>1</sup>H NMR (500 MHz, D<sub>6</sub>-Acetone) δ 8.03-7.48 (m, 14H), 4.62 (s, 2H). <sup>13</sup>C NMR (126 MHz, D<sub>6</sub>-Acetone) δ 145.10, 135.67, 135.56, 135.11, 135.00, 133.72, 131.63, 131.53, 130.73, 130.63, 129.42, 128.92, 128.44, 127.93, 122.34, 119.79, 117.23, 48.79, 48.68; <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>) δ 35.75; <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ -81.24. HRMS-ESI: m/z calcd for C<sub>19</sub>H<sub>18</sub>N<sub>1</sub><sup>197</sup>Au<sub>1</sub>P<sub>1</sub>: 488.08390; found 488.08369. HRMS-ESI m/z calcd for C<sub>2</sub>O<sub>4</sub>N<sub>1</sub>F<sub>6</sub><sup>32</sup>S<sub>2</sub><sup>-</sup>: 279.91674; found 279.91788

## 2.2 $^1\text{H}$ NMR, $^{31}\text{P}$ NMR, $^{13}\text{C}$ NMR, $^{19}\text{F}$ NMR, HR-MS and TGA of **4** (Fig S1 to S7)



**Figure S1.**  $^1\text{H}$  NMR spectrum of gold complex **4** (recorded in  $\text{D}_6$ -Acetone).



**Figure S2.**  $^{31}\text{P}$  NMR spectrum of gold complex **4** (recorded in  $\text{D}_6$ -Acetone).

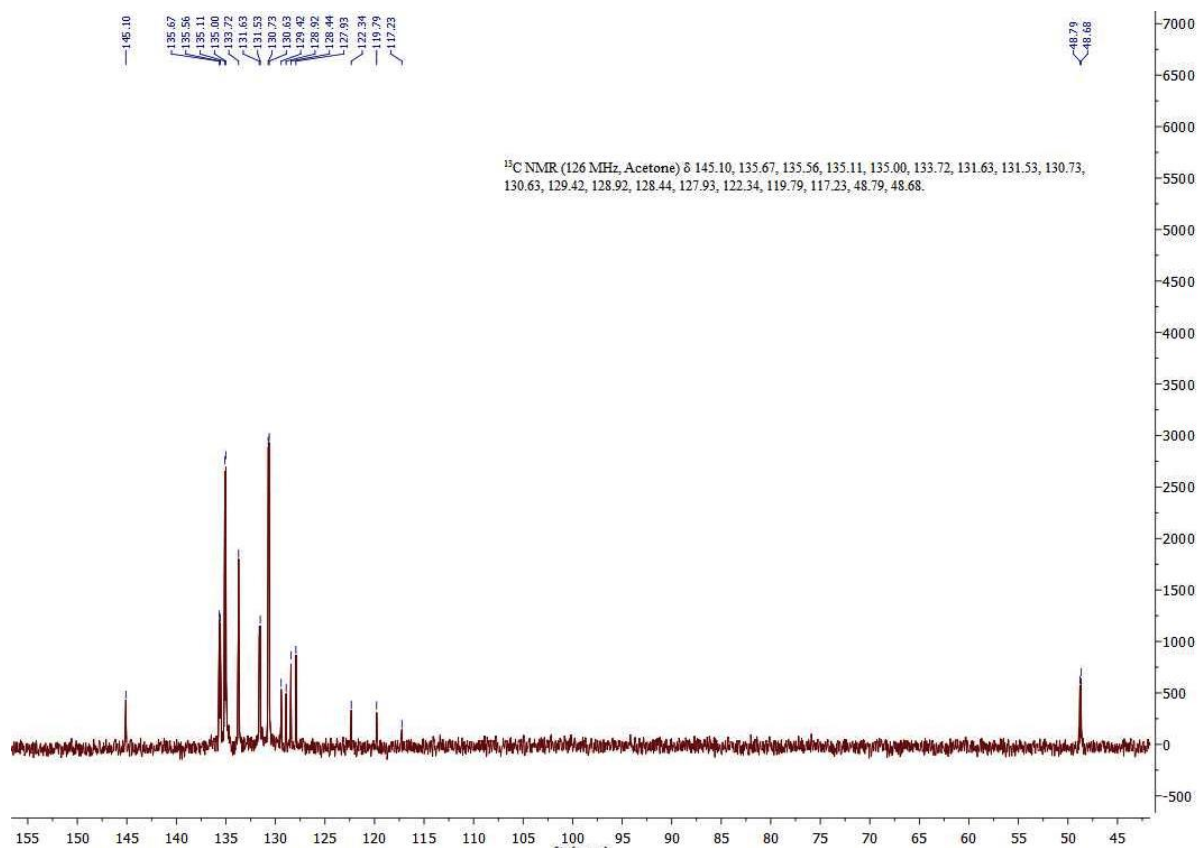


Figure S3.  $^{13}\text{C}$  NMR spectrum of gold complex **4** (recorded in  $\text{D}_6$ -Acetone).

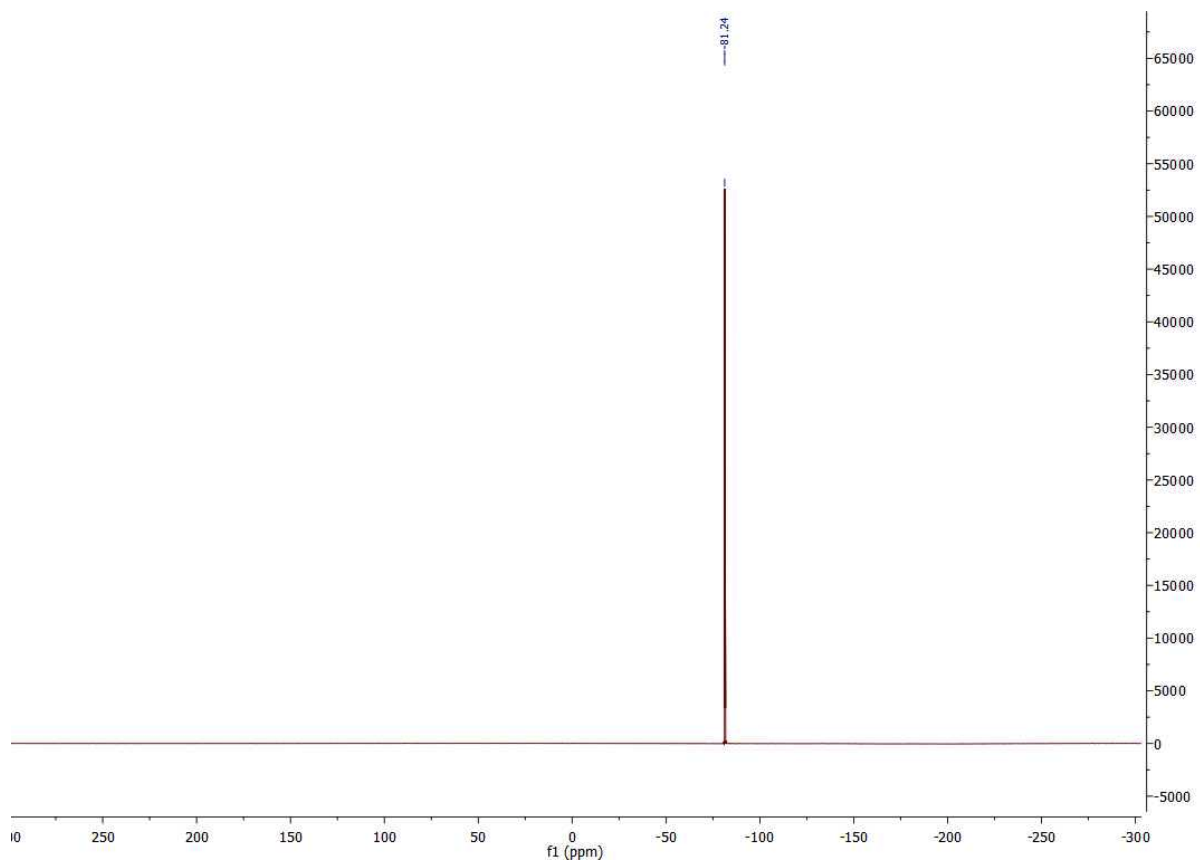
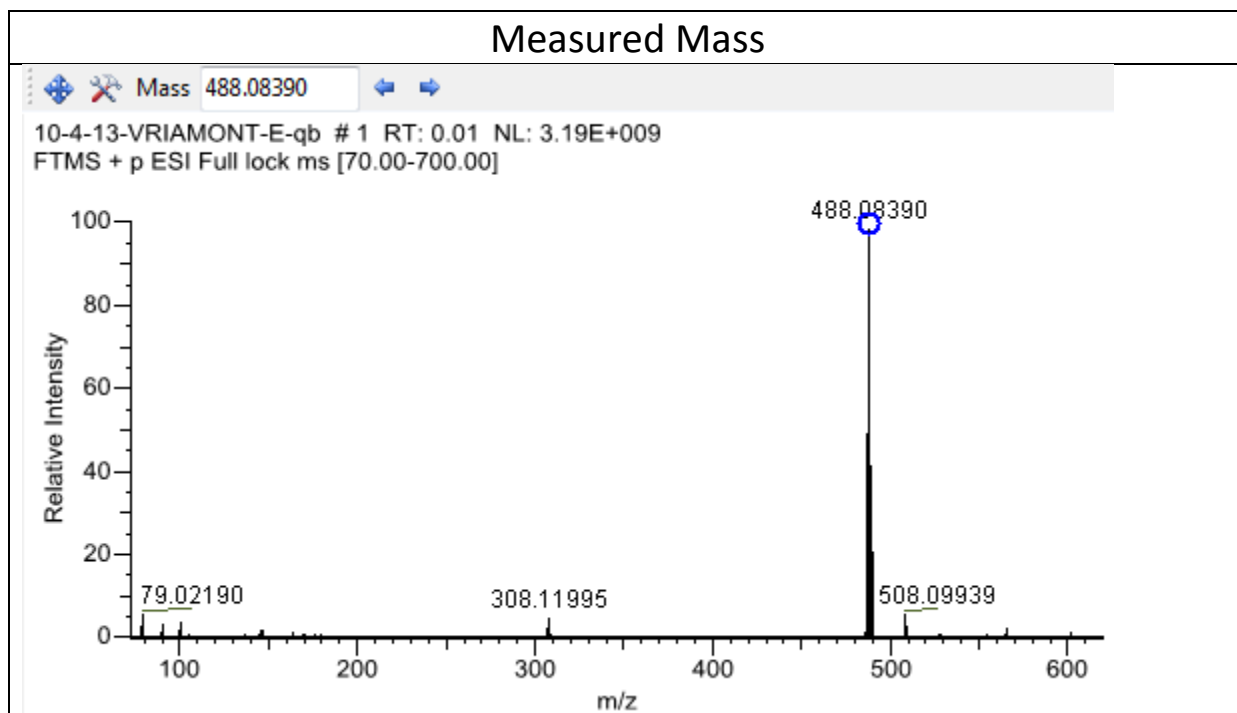


Figure S4.  $^{19}\text{F}$  NMR spectrum of gold complex **4** (recorded in  $\text{D}_6$ -Acetone).



### Calculated Mass

Spectral Fit: 100.00  
Max dM: 2.00[Ppm] max dI 2.00% Threshold 0.00

Mass	Intensity[%]	dM[Ppm]	dI[%]	Fit[%]	Contrib[%]
488.08369	100.0	0.44	0.00	100.00	100.00
489.08705	20.6	8.00	8.00	100.00	100.00
490.09042	2.0	-1.39	-1.91	100.00	100.00
491.09379	0.1	8.00	8.00	100.00	100.00
492.09716	0.0	8.00	8.00	100.00	100.00

### Formula

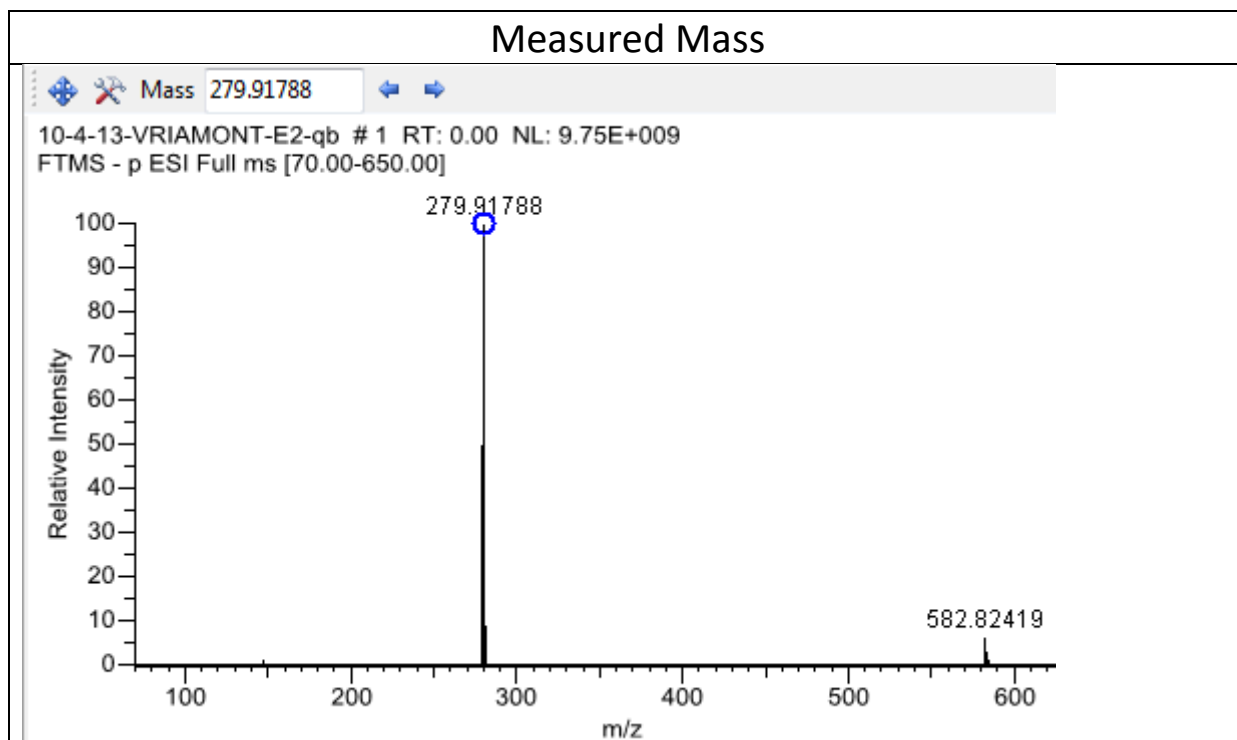
Mass	Intensity	Intensity[%]	Resolution
488.08390	3189588736	100	93380

Mass	Composition	Fit
488.08369	C <sub>19</sub> H <sub>18</sub> N <sub>1</sub> <sup>197</sup> Au <sub>1</sub> P <sub>1</sub>	100.00

Ref : VC 635

Figure S5 HR-MS of gold complex 4 (C<sub>19</sub>H<sub>18</sub>N<sub>1</sub><sup>197</sup>Au<sub>1</sub>P<sub>1</sub>)



### Calculated Mass

Spectral Fit: 100.00  
Max dM: 5.00[Ppm] max dI 2.00% Threshold 0.00

Mass	Intensity[%]	dM[Ppm]	dI[%]	Fit[%]	Contrib[%]
279.91674	100.0	4.05	0.00	100.00	100.00
280.91974	2.5	-5.22	0.26	100.00	100.00
281.91254	9.0	-0.16	-0.36	100.00	100.00
281.92095	0.9	-4.82	-0.23	100.00	100.00
282.91582	0.2	0.08	-0.07	100.00	100.00
282.92391	0.0	-0.19	-0.02	100.00	100.00
283.90849	0.2	0.30	-0.03	100.00	100.00
283.91668	0.1	1.64	-0.02	100.00	100.00
283.92509	0.0	20.00	8.00	100.00	100.00
284.91194	0.0	20.00	8.00	100.00	100.00
284.91984	0.0	20.00	8.00	100.00	100.00
285.90771	0.0	20.00	8.00	100.00	100.00
285.91256	0.0	20.00	8.00	100.00	100.00

### Formula

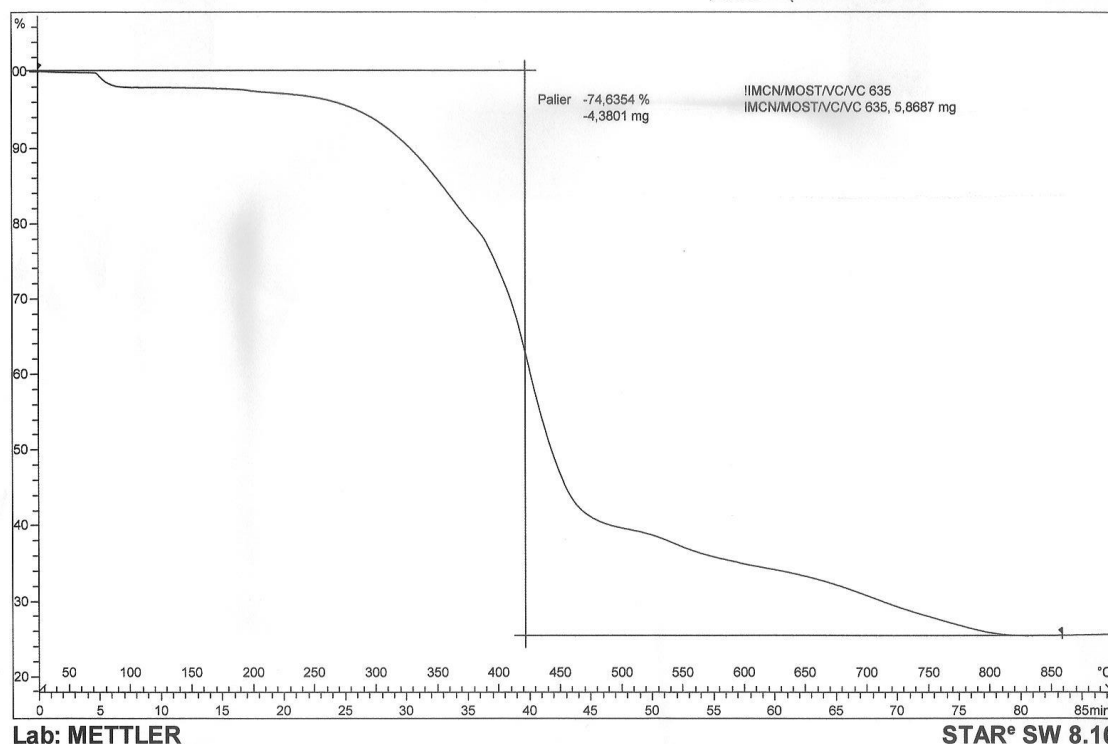
Mass	Intensity	Intensity[%]	Resolution
279.91788	9753416704	100	64867

Mass	Composition	Fit
279.91674	C <sub>2</sub> O <sub>4</sub> N <sub>1</sub> F <sub>6</sub> <sup>32</sup> S <sub>2</sub>	100.00

Ref : VC 635

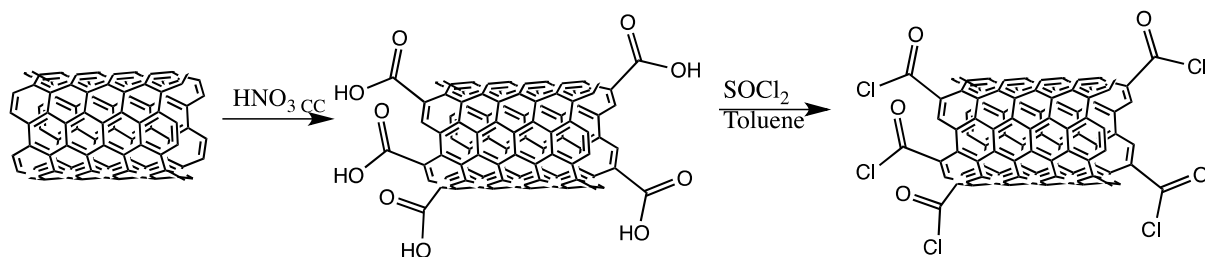
Figure S6 HR-MS of gold complex 4 (C<sub>2</sub>O<sub>4</sub>N<sub>1</sub>F<sub>6</sub><sup>32</sup>S<sub>2</sub>) – NTf<sub>2</sub> counter ion



**Figure S7** TGA under air of gold complex **4**. Calculated weight loss if only gold left after thermolysis: 74.36%; found 74.63%.

### 3 Prefunctionalization of the MWNTs

#### 3.1 Oxidation and Chlorination steps: experimental procedure.



#### Experimental procedure <sup>[4]</sup>:

A solution of concentrated  $\text{HNO}_3$  (240 ml) was added to pristine MWNTs (Thin MWNTs, 95+ % C purity, Nanocyl, 2 g, 166 mol) and heated under reflux for 2h ( $120^\circ\text{C}$ ). The solution was allowed to cool to room temperature, filtrated under filtration unit using Millipore membrane filters (DURAPORE MEMBRANE FILTERS, FILTER TYPE 0.22 microns GV) and extensively washed until neutral pH. Oxidized MWNTs were dried overnight at  $80^\circ\text{C}$ . Toluene (100 ml) was added to oxidized MWNTs as well as 6 ml of  $\text{SOCl}_2$  and the solution was heated under reflux for 5h ( $120^\circ\text{C}$ ). The solution was allowed to cool to room temperature, filtrated on filtration unit using Millipores membrane filters (0.22 microns) and



extensively washed with toluene. The powder was dried overnight and stored under argon atmosphere in a glove box.

#### 4 Anchoring of the gold complex **4** onto MWNTs to obtain **5** in dichloromethane: time effect

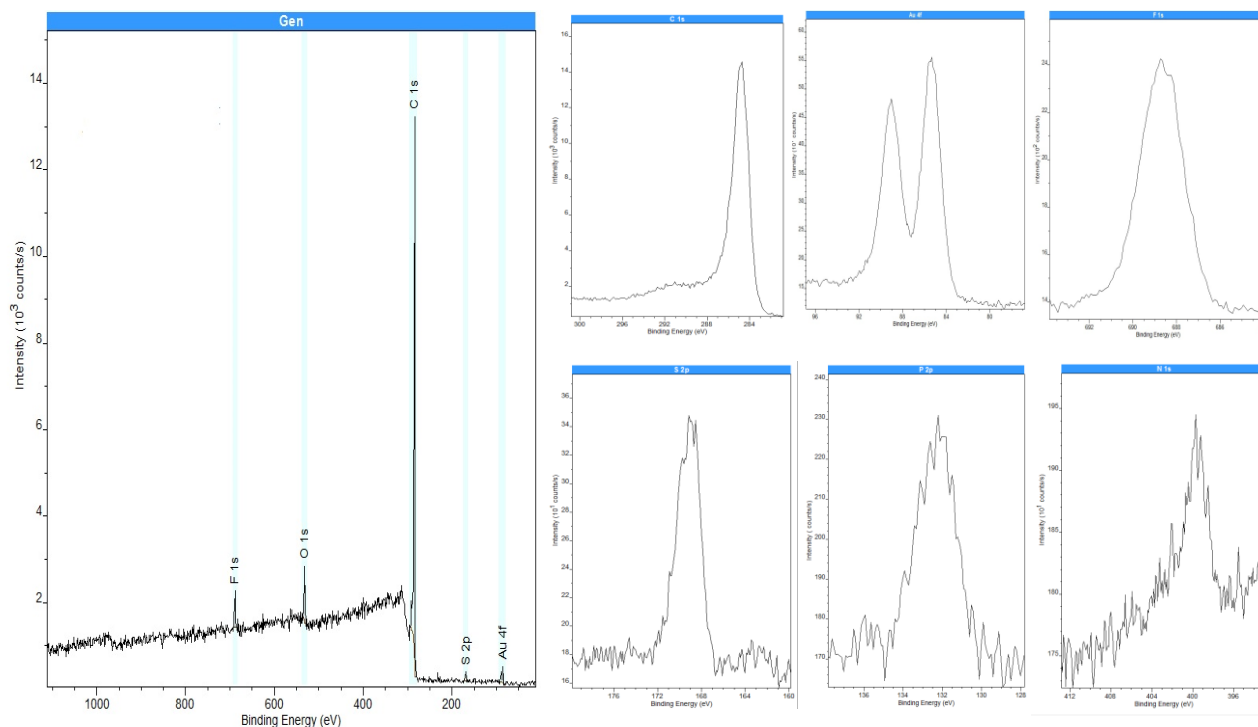
##### 4.1 Experimental: anchoring of the gold complex **4** onto MWNTs to obtain **5**

The prefunctionalized MWNTs (200 mg, 16.66 mmol) were submitted to ultrasound for 1 hour in dichloromethane (20 ml). The gold(I) complex **4** was then added (200 mg, 0.26 mmol) and the resulting mixture was stirred at room temperature during variable durations (from 2 hours to 1 day). The solution was filtrated on a filtration unit (Millipores membrane filters, 0.22 microns) to separate the gold supported homogeneous catalyst **5** from the unreacted gold catalyst contained in the solution and washed twice with dichloromethane. The resulting supported homogeneous catalyst was vacuum dried.

##### 4.2 Table S1: XPS (variable durations)

Anchoring Time (h)	Au%	F/Au	N/Au	P/Au	S/Au	Au 4f <sub>7/2</sub> binding energy (eV)
(calculated ratio)	-	6	2	1	2	85.5 (Au <sup>I</sup> )
<b>2</b>	0.21	9.3	1.8	0.9	3.0	84.9
<b>4</b>	0.26	8.1	1.9	0.9	2.7	85.1
<b>7</b>	0.27	8.0	2	1.0	2.7	85.4
<b>24</b>	0.26	9.0	1.9	0.8	2.5	85.3
<b>Repeatability</b>						
<b>7</b>	0.21	8.1	2.4	0.8	2.9	85.2
<b>24</b>	0.27	8.8	1.8	0.9	2.9	85.1

### 4.3 XPS spectra of **5** after an anchoring time of 7h (general spectrum and each element considered)



4.4 Table S2: ICP values for an anchoring time of 7h (3 different samples)

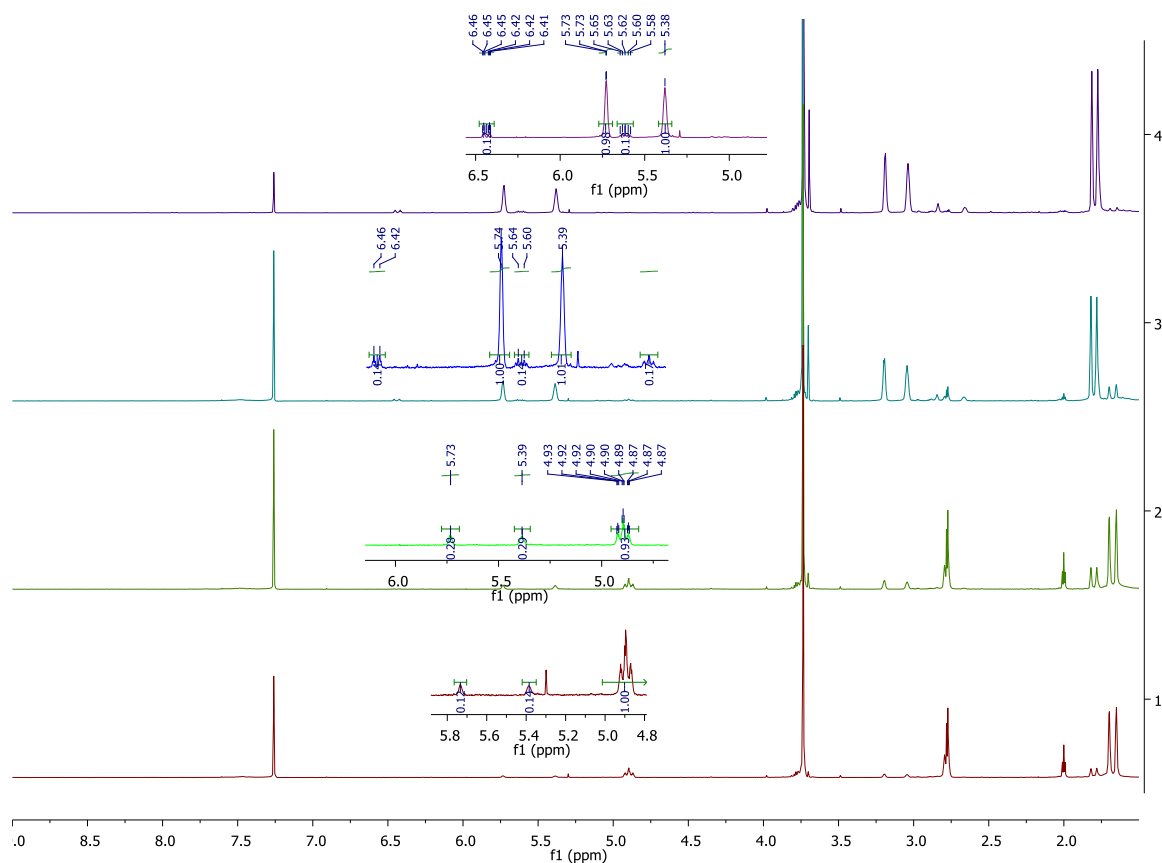
Entry	Gold Percentage (ICP) (weight %)	Gold complexes onto MWNTS (mmol.g <sup>-1</sup> MWNTs)
1	3.38	0.17
2	3.49	0.18
3	4.12	0.21

## 5. Homogeneous gold catalysis

### 5.1 Experimental section: cyclization of **6** into **7** and **8**

The enyne **6** (49.8 mg, 0.21 mmol) in dichloromethane (2 ml) was added to gold catalyst **4** (4.2.10<sup>-3</sup> mmol, 3.2 mg, 2 mol%) in dichloromethane (3 ml). The reaction mixture was controlled by <sup>1</sup>H NMR after variable duration time (3, 6, 23 and 28 hours) in order to follow and record the evolution of the conversion rate. After these durations, the solutions were filtered through SiO<sub>2</sub> and vacuum dried before analysis. The conversion to products **7** and **8** reaches 87% after 23 hours and 100% after 28 hours and gives predominantly the 5-exo dig

product **7** compared to the 6-endo-dig product **8** in a ratio 88/12. These two products were referenced in the literature [1], [5].



**Figure S8**  $^1\text{H}$  NMR of the cyclization reaction of enyne **6** after 3h (red), 6h (green), 23h (blue) and 28h (violet). The insets show the appearance of the major cyclized products (**7**) in the two first cases and the presence of the products **7** and **8** after 23h in a ratio 88/12.

## 6. Supported homogeneous catalysis

### 6.1 General procedure for $\text{Au}^{\text{I}}$ system **5** catalyzed cyclization of enyne **6**, **9** and **12**.

*f*-MWNTs **5** ( $8.4 \cdot 10^{-3}$  mmol, 2 mol% (**6**) or 5 mol% (**9** and **12**) of supported gold complex based on ICP values, typically 40 mg) were submitted to ultrasound in  $\text{CH}_2\text{Cl}_2$  (7 ml) for 10 minutes. The enyne (0.42 mmol for **6**, 0.17 mmol for **9** and **12**) in  $\text{CH}_2\text{Cl}_2$  (3 ml) was then added and the mixture was stirred for 6h (**6**) or 18 hours (**9** and **12**). Agitation was then stopped and the solvent was removed on the Schlenk line. 3 aliquots of 3 ml of dichloromethane were successively added to the dried nanotubes in order to solubilize the cyclized enynes and successively removed using a syringe with a needle surrounded by cotton and wrapped with Teflon to insure separation between soluble cyclized enynes and insoluble supported homogeneous catalyst **5**. The obtained solutions were filtered through celite and analyzed by  $^1\text{H}$  NMR. The solid was vacuum dried. The obtained yield was respectively of 85% (84.7 mg) for products **7** and **8** in a ratio 88/12, 87% (35.8 mg) for products **10** and **11** in

a ratio 55/45 and 90% (32.8 mg) for product **13**. The cyclized compounds **10**, **11** and **13** have been reported in the literature previously [2].

6.2 Enynes tested and  $^1\text{H}$  NMR of the obtained products (**10**, **11** and **13**) ( $^1\text{H}$  NMR spectra of products **7** and **8** are given in section 7: Recyclability)

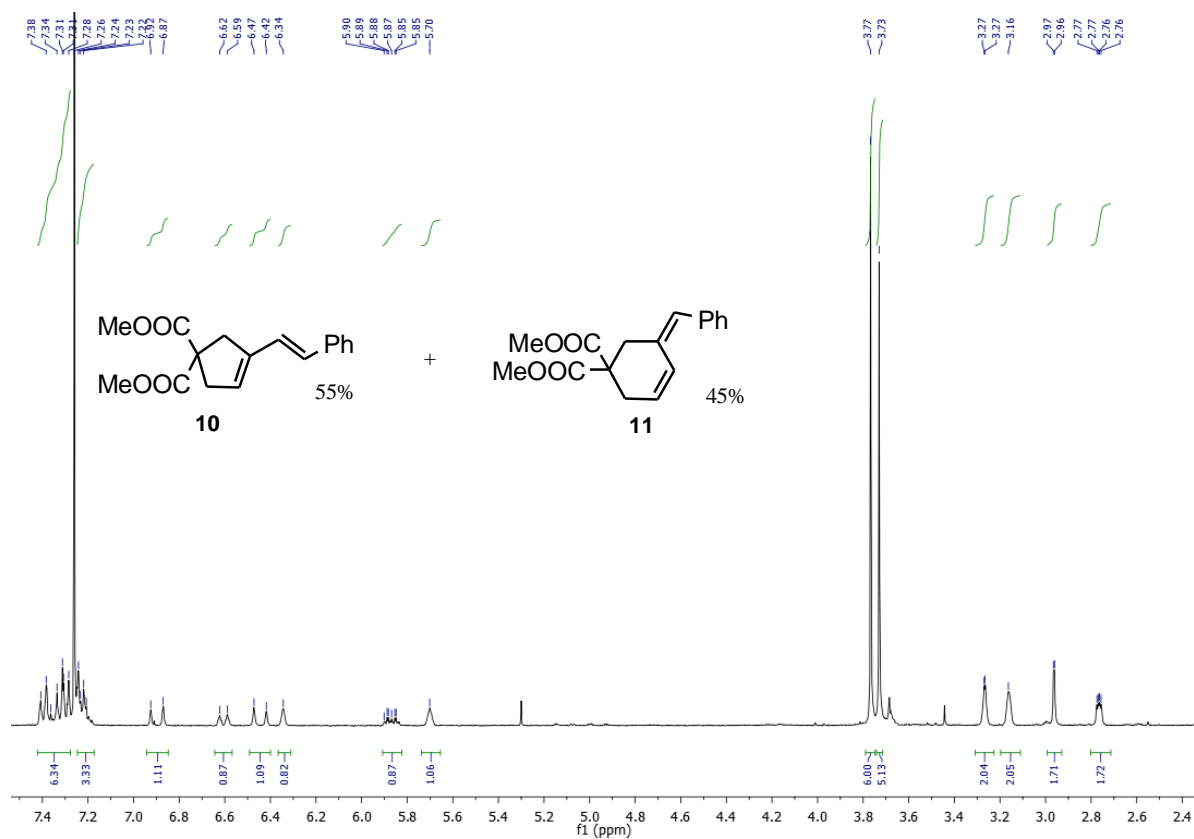


Figure S9  $^1\text{H}$  NMR spectrum of products **10** and **11**.

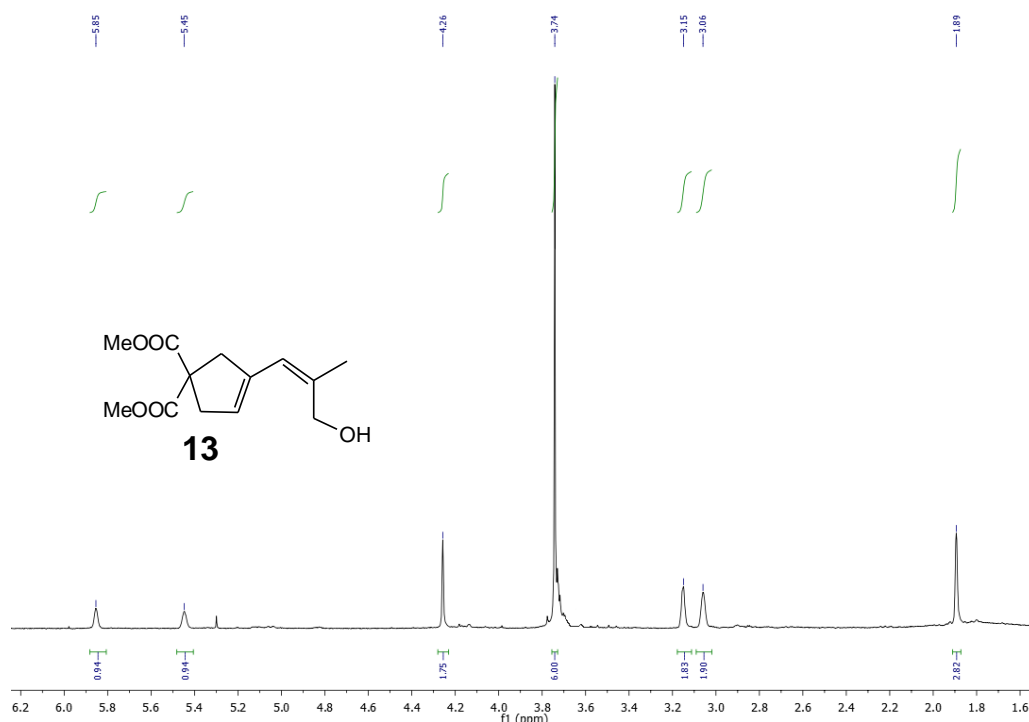


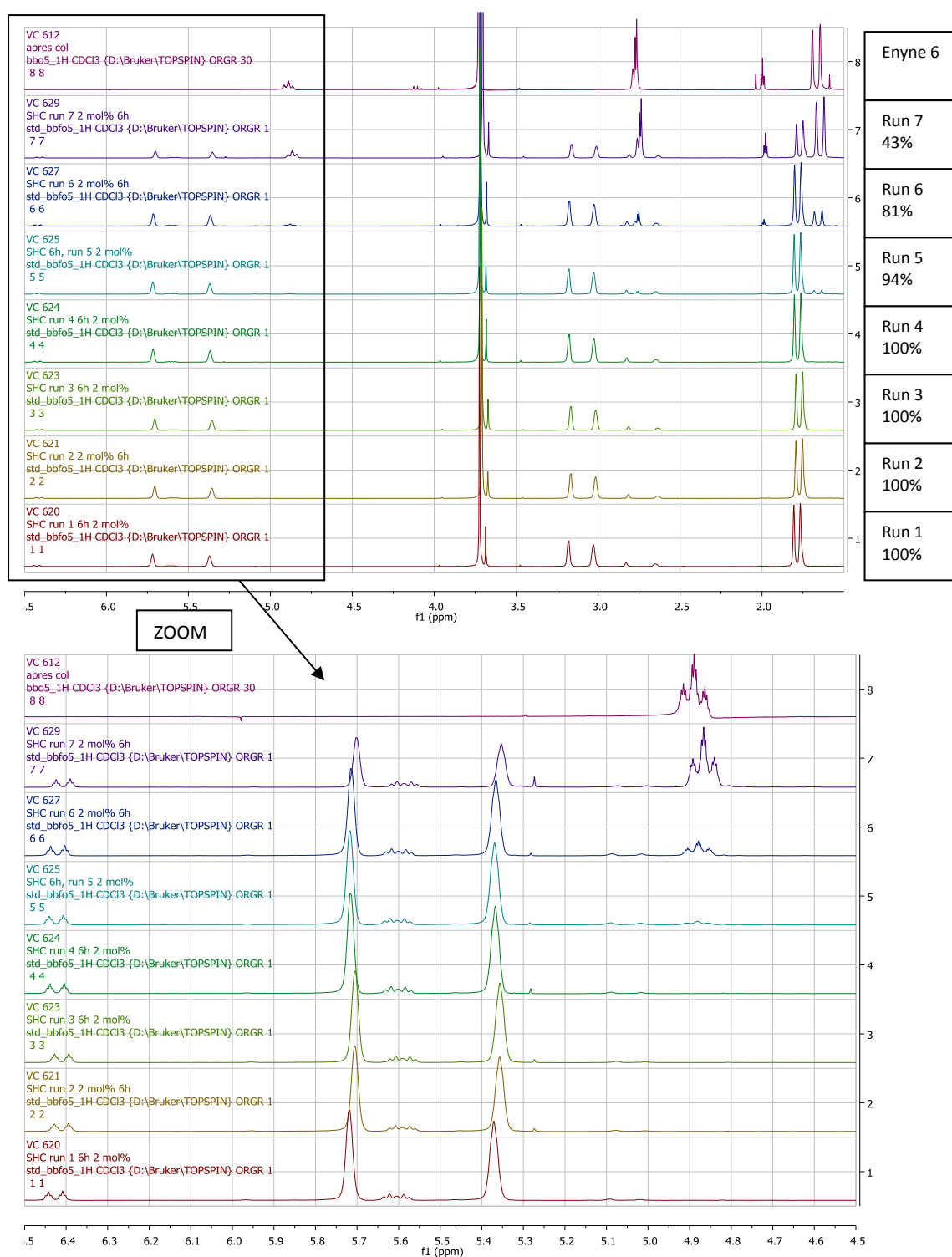
Figure S10 <sup>1</sup>H NMR spectrum of product **13**.

## 7. Recyclability of the catalyst **5** in cyclization of enyne **6**

### 7.1 General procedure for recycling of system **5**: cyclization of enyne **6**

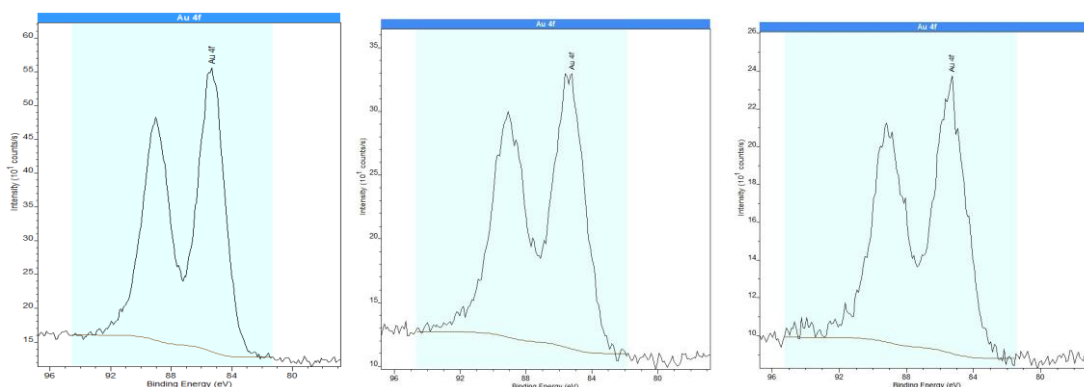
*f*-MWNTs **5** ( $8.4 \cdot 10^{-3}$  mmol, 2 mol% of supported gold complex based on ICP values, typically 40 mg) were submitted to ultrasound in CH<sub>2</sub>Cl<sub>2</sub> (7 ml) for 10 minutes. The enyne **6** (0.42 mmol, 99.6 mg) in CH<sub>2</sub>Cl<sub>2</sub> (3 ml) was then added and the mixture was stirred for 6h. Agitation was then stopped and the solvent was removed on the Schlenk line. 3 aliquots of 3 ml of dichloromethane were successively added to the dried nanotubes in order to solubilize the cyclized enynes and successively removed using a syringe with a needle surrounded by cotton and wrapped with Teflon to ensure a separation between soluble cyclized enynes and insoluble supported homogeneous catalyst **5**. The solid was vacuum dried and the obtained solutions were filtered through celite (except when the solutions were analyzed by ICP) and analyzed by <sup>1</sup>H NMR. The following runs proceeded similarly to the protocol described above using the *f*-MWNTs previously used. The obtained yields for the first four runs (quantitative conversion) were of 85% (84.7 mg) in a constant ratio 88/12 for products **7** and **8** respectively.

## 7.2 $^1\text{H}$ NMR of the successive catalytic runs of cyclization of enyne **6**



**Figure S11**  $^1\text{H}$  NMR along the runs and comparison with the starting material, *i.e.* enyne **6** as well as a zoom between 6.5 and 4.5 ppm to observe peaks of the major and minor products **7** and **8**.

7.3 Figure S12: Gold oxidation state of system **5** before catalysis and after run 3 and run 7 (XPS)



**Figure S12** XPS of gold a) after anchoring of the gold catalyst (left side), b) after 3 catalytic runs (middle), c) after 7 catalytic runs (right).

NB: the average tabulated values of Au 4f<sub>7/2</sub> for an oxidation state of Au(0), Au(I) and Au(III) are the following: 84 eV, 85.5 eV and 87 eV respectively <sup>[6]</sup>.

7.4 Table S3: XPS results of the supported homogeneous gold catalyst before catalysis and after run 3 and run 7.

Entry	Number of run(s)	Elements (at. %)							Ratio				
		C	O	N	F	S	P	Au	Au/C	P/Au	N/Au	S/Au	F/Au
<b>1</b>	0	91.32	5.00	0.50	1.99	0.68	0.27	0.25	0.0027	1.1	2.0	2.7	8.0
<b>2</b>	3	90.48	6.56	0.35	1.67	0.60	0.18	0.17	0.0019	1.1	2.1	3.5	9.8
<b>3</b>	7	90.27	7.82	0.36	0.93	0.39	0.12	0.14	0.0016	0.9	2.6	2.8	6.6

**References:**

- [1] J. W. Faller, P. P. Fontaine, *J. Org. Chem.*, 2006, **71**, 1912
- [2] C. Nieto-Oberhuber, M. Paz Muñoz, S. Lopez, E. Jiménez-Nuñez, C. Nevado, E. Herrero Gomez, M. Raducan, A. M. Echavarren, *Chem. Eur. J.*, 2006, **12**, 1677-1693
- [3] M. Nishimura, M. Ueda, N. Miyaura, *Tetrahedron*, 2002, **58**, 5779
- [4] S. Hermans, V. Bruyr, M. Devillers, *J. Mater. Chem.*, 2012, **22**, 14479
- [5] S. Gaillard, J. Bosson, R. S. Ramon, P. Nun, A. M. Z. Slawin, S. P. Nolan, *Chem. Eur. J.*, 2010, **16**, 13729 - 13740
- [6] Handbook of X-ray Photoelectron Spectroscopy C. D. Wanger, W. M. Riggs, L. E. Davis, J. F. Moulder and G. E. Muilenberg Perkin-Elmer Corp., Physical Electronics Division, Eden Prairie, Minnesota, USA, 1979