

## SUPPORTING INFORMATION

### **Water-based synthesis of gold and silver nanoparticles with cuboidal and spherical shapes using luteolin tetraphosphate at room temperature**

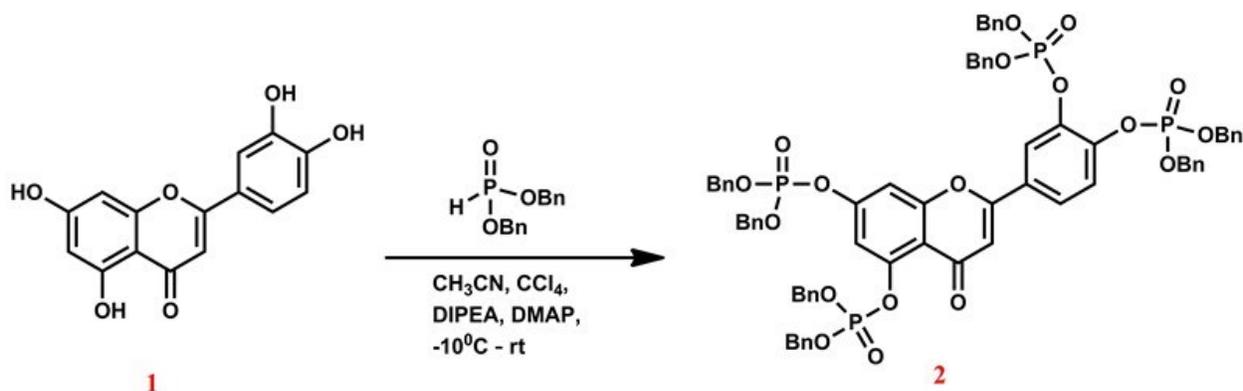
*Francis J. Osonga, Phuong Le, David Luther, Laura Sakhaee and Omowunmi A. Sadik\**

Department of Chemistry

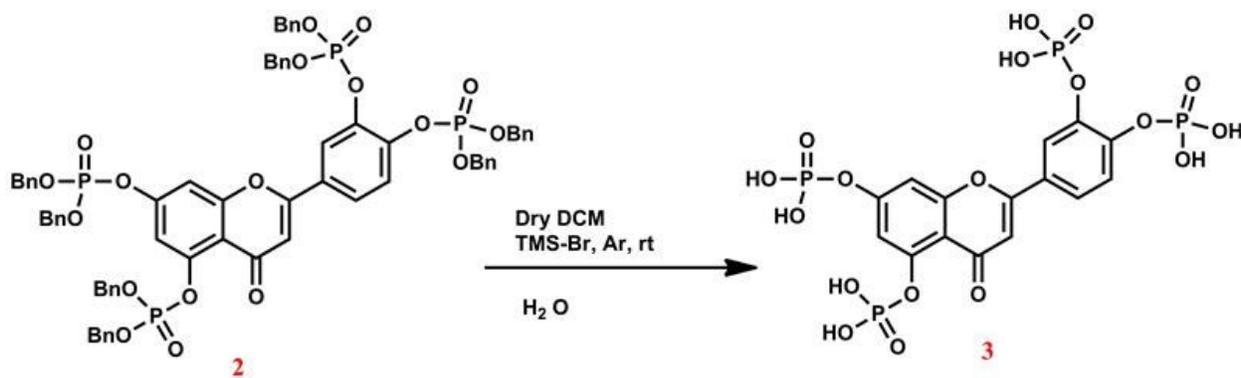
Center for Research in Advanced Sensing Technologies & Environmental Sustainability  
(CREATES), State University of New York at Binghamton, P.O. Box 6000, Binghamton, NY,  
13902

### **Synthesis of 4', 5', 5, 7 Tetraphosphoflavone Intermediate (LTPI)**

The flasks and a stir bar were purged with N<sub>2</sub>. Luteolin (250mg) and anhydrous acetonitrile (10mL) was mixed to form yellow suspension. This mixture was cooled to -10°C (achieved by NaCl in ice) while stirring. As the yellow suspension was formed, CCl<sub>4</sub> (1.4mL, 14.34mmol, 15.5eq.) was added. Followed by the addition of N, N-Diisopropylethylamine (1.0mL, 5.83mmol, 6.3eq.), then N, N-Dimethylaminopyridine (34mg, 0.278mmol, 0.3eq.) were added, and allowed to stir for 5 minutes. For the next 6 minutes, dibenzyl phosphite solution (1.53mL, 6.94mmol, 7.5eq.) was added drop by drop and the solution was allowed to form a uniform yellow color. The reaction was stopped after 45 min. 0.5M aqueous potassium phosphate monobasic (KH<sub>2</sub>PO<sub>4</sub>) (16ml/50 ml CH<sub>3</sub>CN) was added before the mixture was allowed to warm to room temperature. After three hours, the mixture was transferred into a 250mL separatory funnel and diluted with 50mL Ethyl acetate (EtOAc). The mixture was washed with 3 x 50 mL of DI water, followed by addition of 50mL brine and the organic fraction was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, before being finally concentrated under reduced pressure. The resulting thick amber oil was purified by flash chromatography (ethyl acetate: hexane, 1: 2) to provide 226mg of luteolin teraphosphate intermediate (LTPI)<sub>2</sub> in 48% yield as a clear yellow oil.



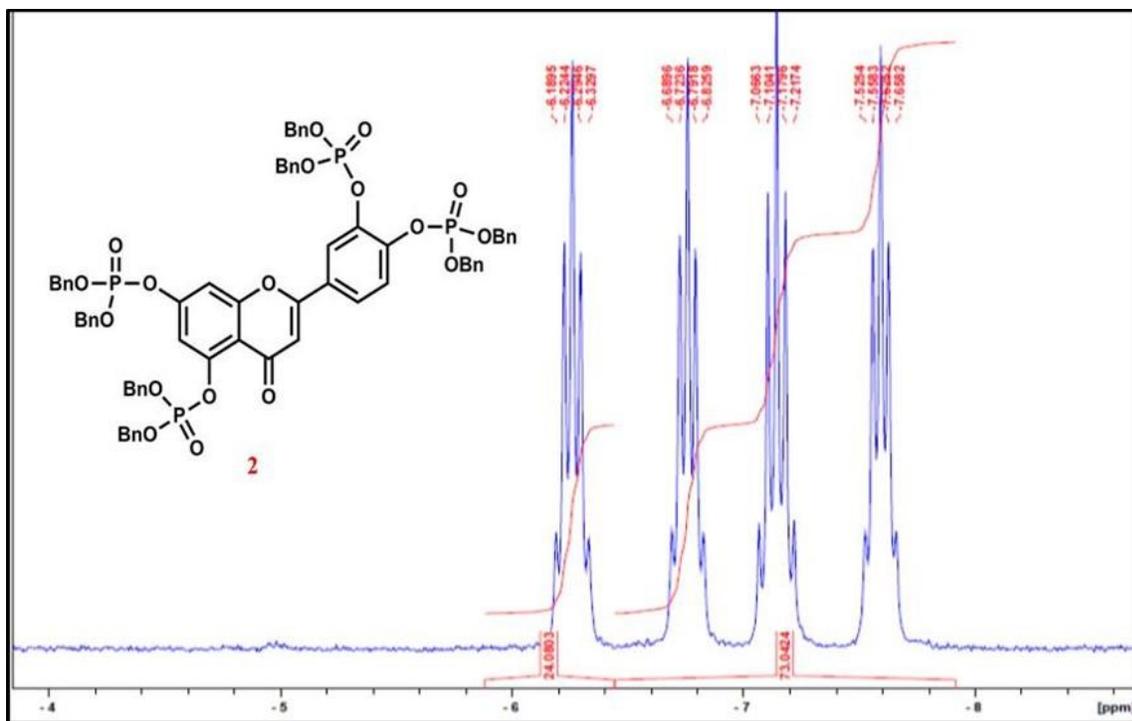
**Figure S1A:** Synthesis of LTP Intermediate, using N,N-Diisopropylethylamine (DIPEA), 4-Dimethylaminopyridine (DMAP), Acetonitrile (CH<sub>3</sub>CN), and Carbon tetrachloride (CCl<sub>4</sub>).



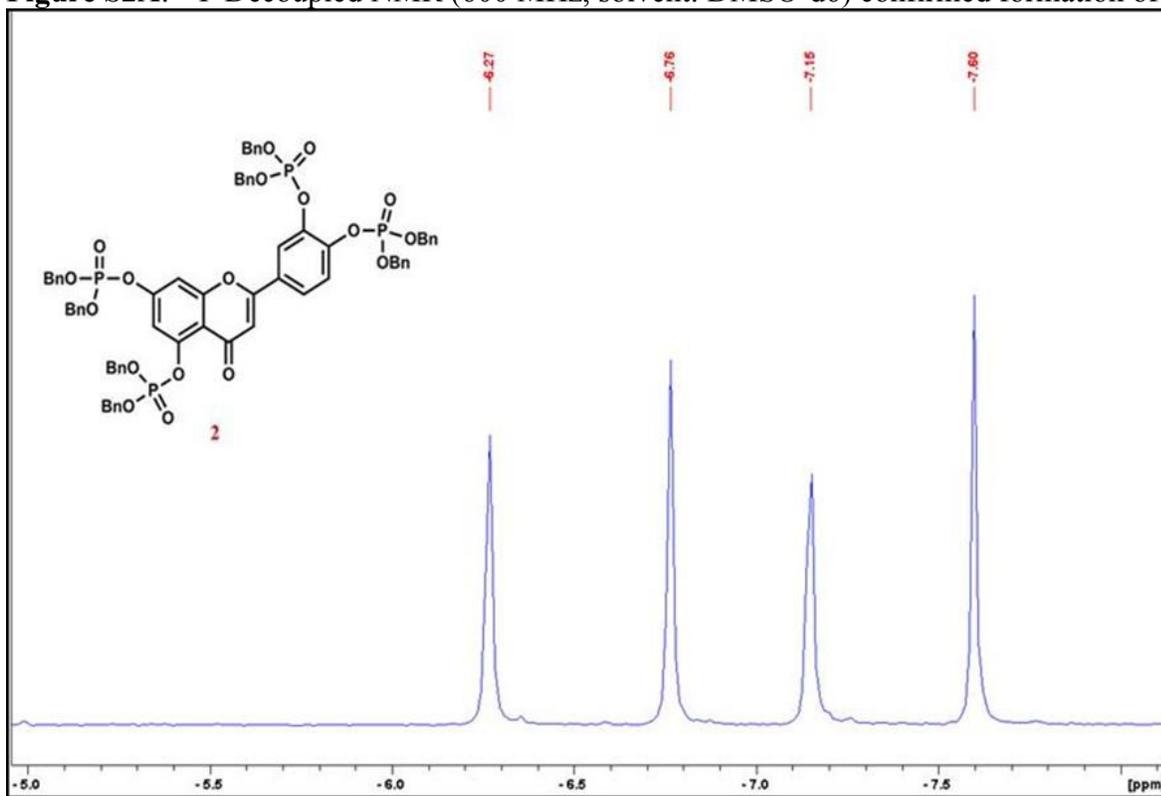
**Figure S1B:** Debenzylation of LTPI to form LTP using anhydrous dichloromethane (DCM), Bromotrimethylsilane (TMS-Br), Argon (Ar), room temperature (rt), and water.

135mg of LTPI (Compound 2) was dissolved in 5mL anhydrous dichloromethane (DCM). Then bromotrimethylsilane (TMSBr) (2 equivalents for each hydroxyl in the parent molecule) was added before the mixture was stirred at room temperature under argon for another three hours. The reaction was terminated by adding 10mL of ultrapure water. The organic layer was extracted using hexane. The aqueous phase was then concentrated under reduced pressure giving a yellow powder (compound 3) in 86 % yield.

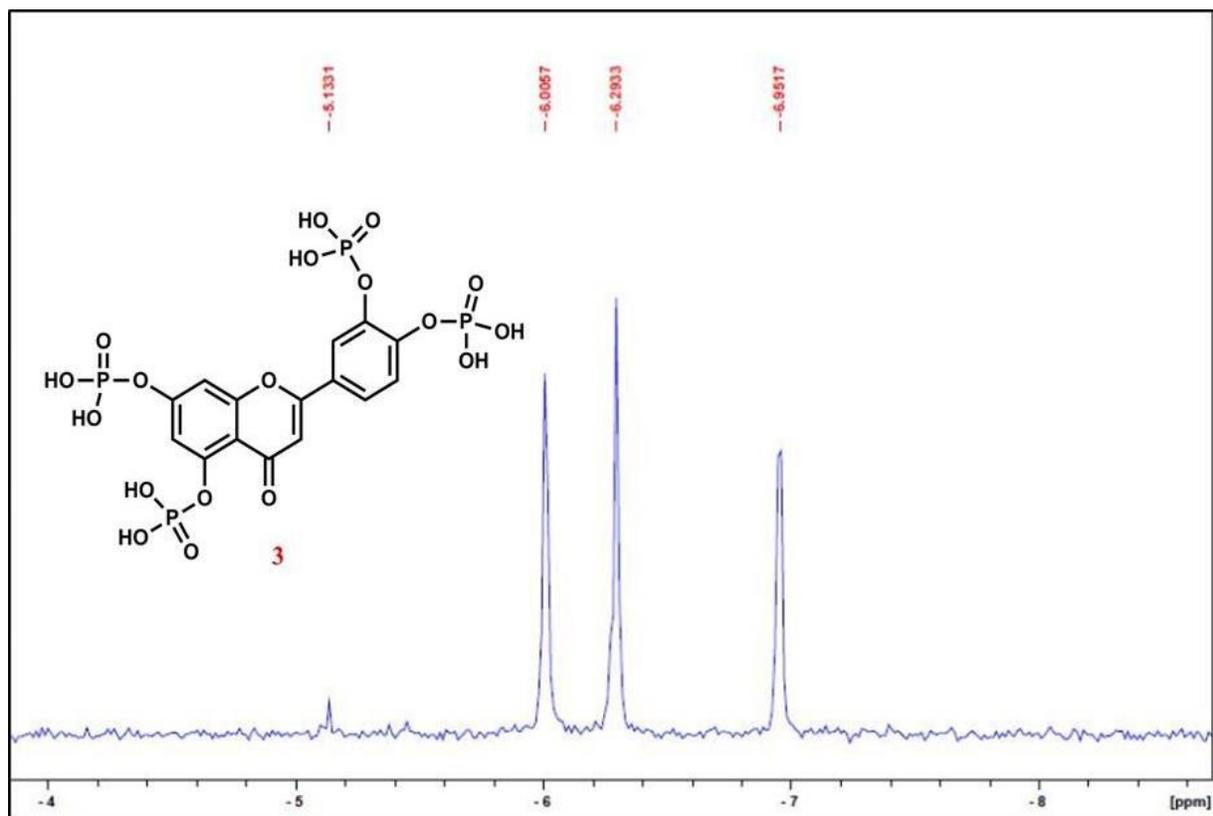
### NMR Characterization.



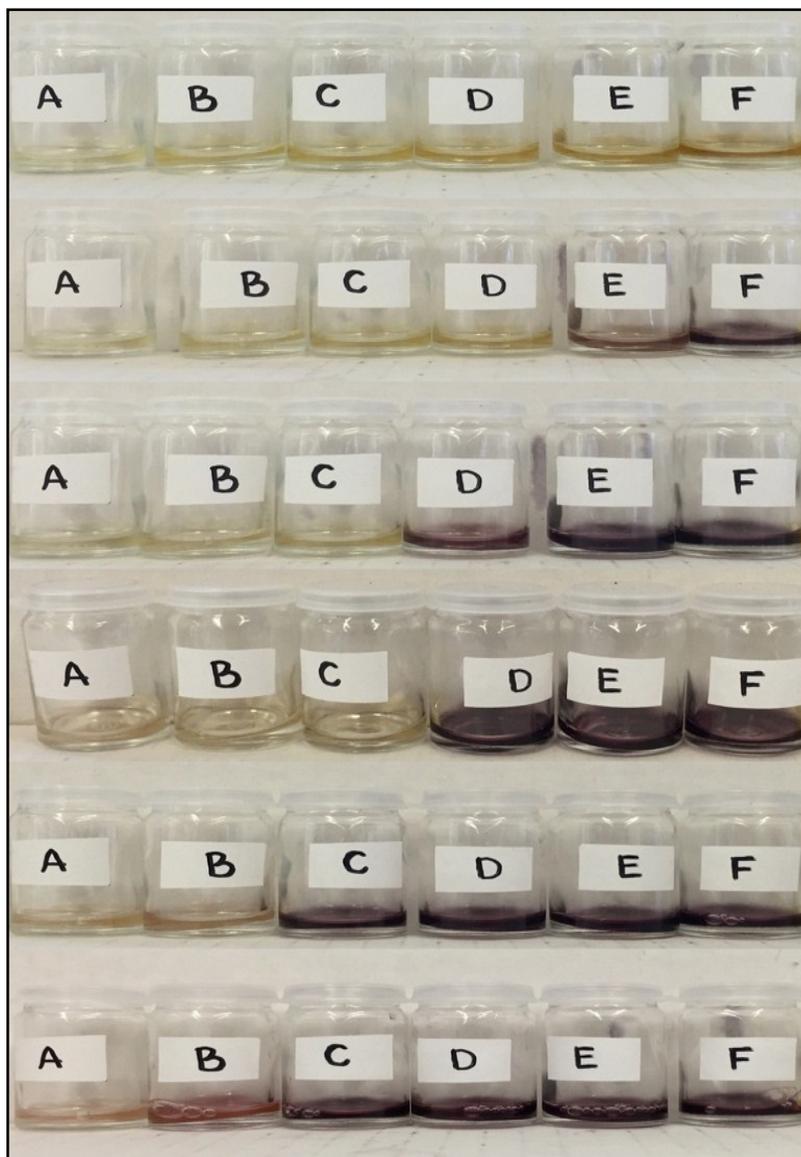
**Figure S2A:**  $^{31}\text{P}$  Decoupled NMR (600 MHz, solvent: DMSO- $d_6$ ) confirmed formation of LTPI



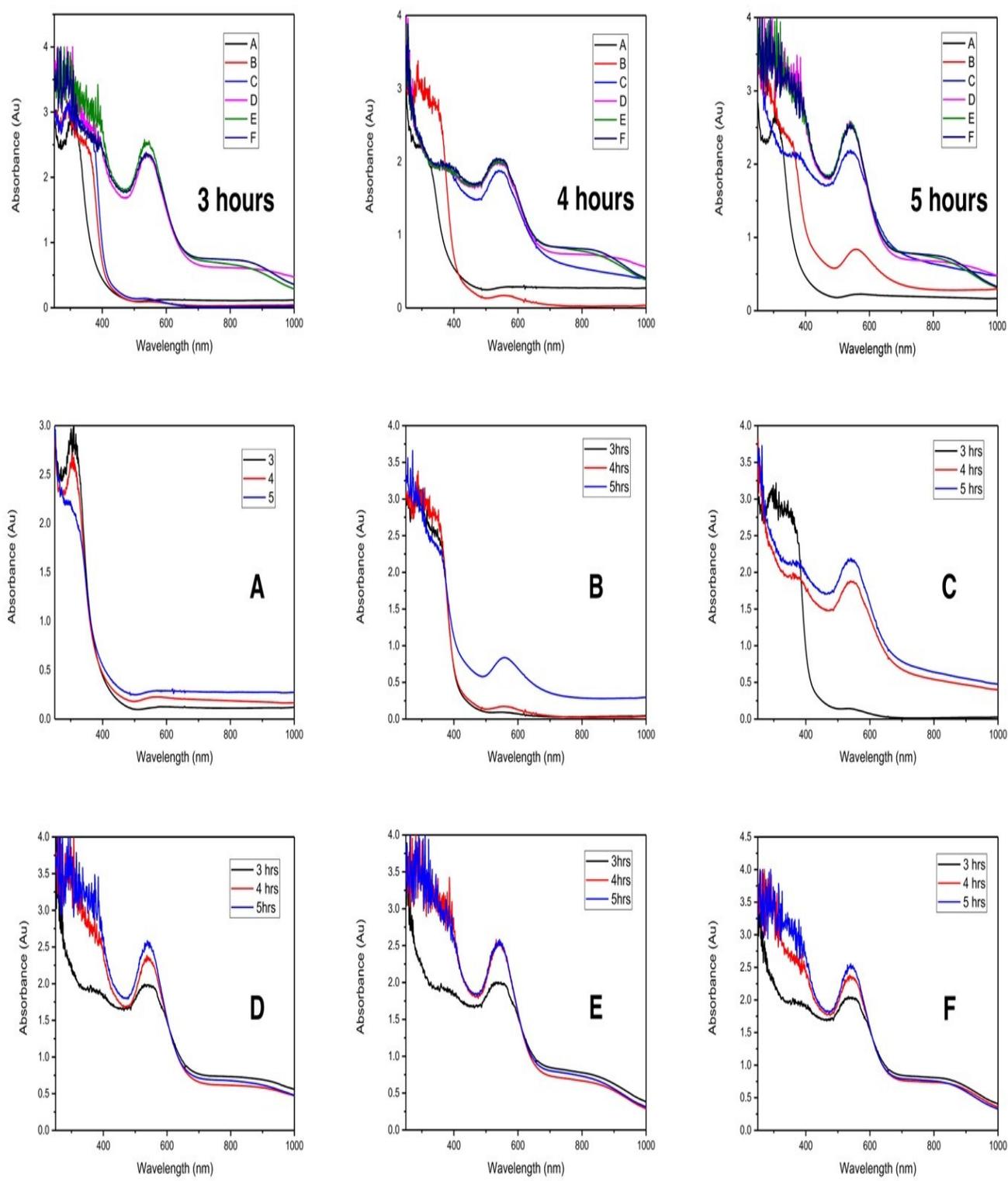
**Figure S2B:**  $^{31}\text{P}$  Decoupled NMR (600 MHz, solvent: DMSO- $d_6$ ) confirmed formation of LTPI.



**Figure S2C:**  $^{31}\text{P}$  Decoupled NMR (600 MHz, solvent: DMSO- $d_6$ ) LTP confirmed formation of LTP.



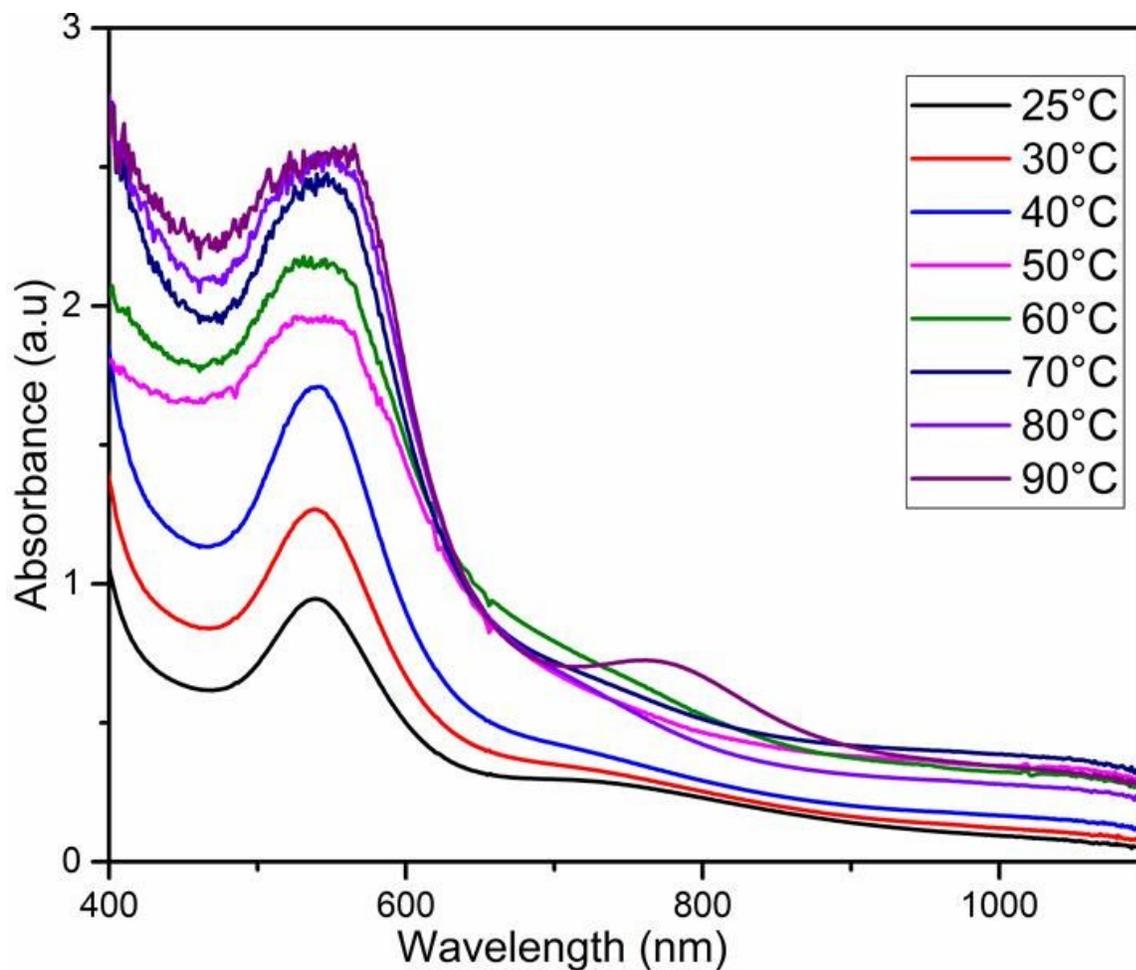
**Figure S3A:** Concentration of LTP dependence, from top to bottom: right after preparation, 1hr, 2hrs, 3hrs, 4hrs, and 5hrs. The amount of LTP and pure water were varied: 0.3mg + 1mL (A), 0.6mg + 0.8mL (B), 0.9mg + 0.6mL (C), 1.2mg + 0.4mL(D), 1.5mg + 0.2mL (E), and 1.8mg + 0mL (F); and each of them were reacted with 0.3mL of 5mM H<sub>Au</sub>Cl<sub>4</sub>.



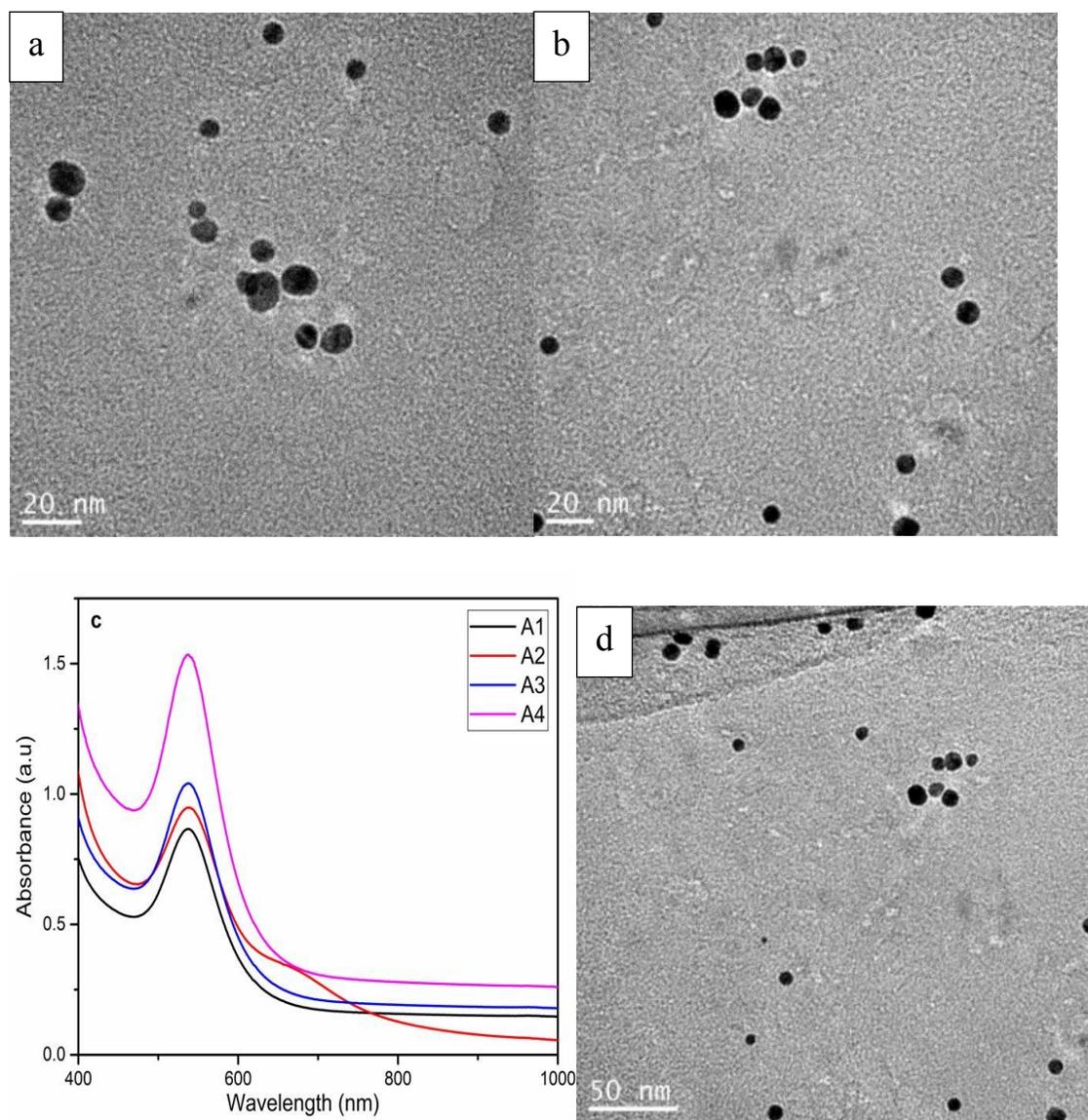
**Figure S3B:** UV-Vis Spectra of the effect of concentration LTP on the formation of AuNPs, (a) after 3 hours, (b) after 4 hours, (c) after 5 hours, (d) A, (e) B, (f) C, (g) D, (h) E, (i) F.



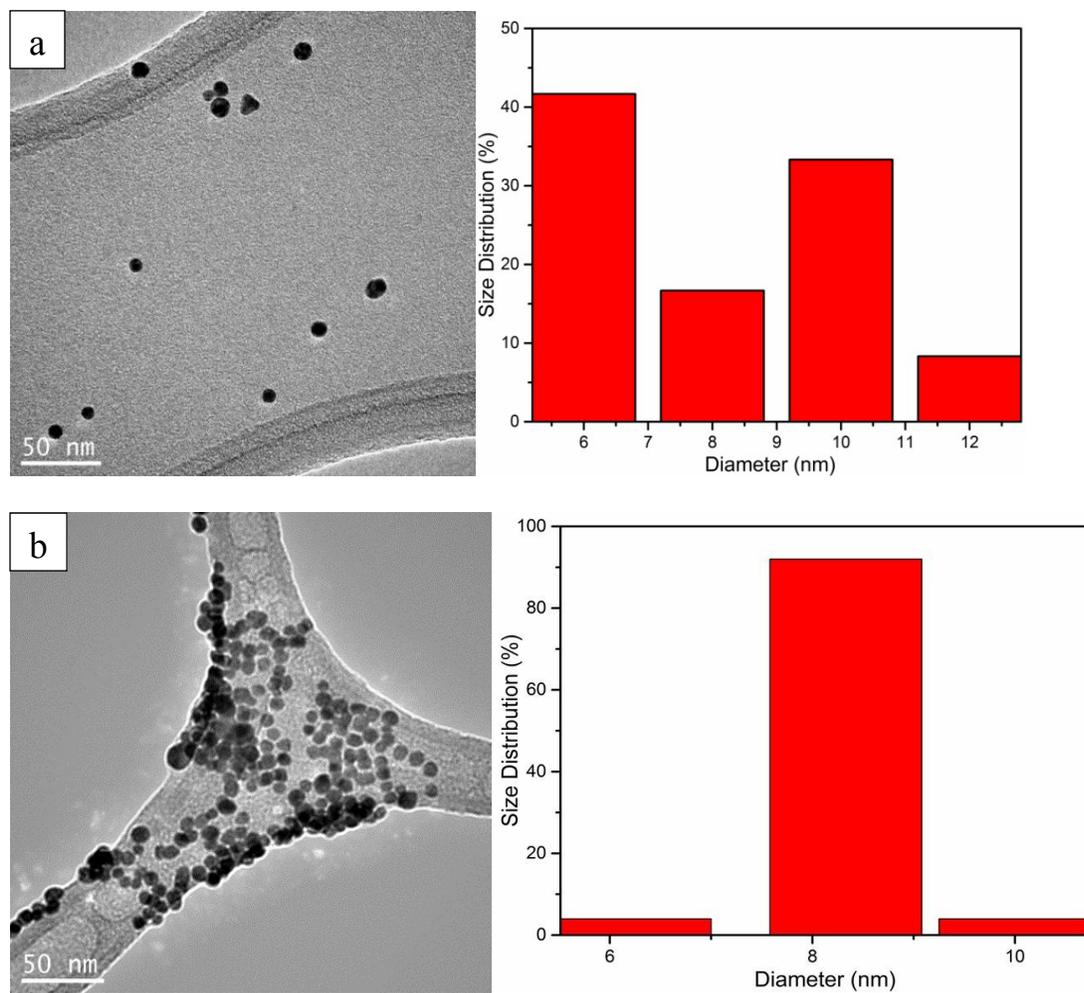
**Figure S4:** Effect of temperature on the formation of AuNPs derived from LTP. Eight samples were prepared at room temperature by reacting  $300\mu\text{L}$  of  $5\text{mM}$   $\text{HAuCl}_4$ ,  $1.5\text{mg}$  of LTP, and  $200\text{mL}$  of pure water and reaction carried out at  $25^\circ\text{C}$ ,  $30^\circ\text{C}$ ,  $40^\circ\text{C}$ ,  $50^\circ\text{C}$ ,  $60^\circ\text{C}$ ,  $70^\circ\text{C}$ ,  $80^\circ\text{C}$ , and  $90^\circ\text{C}$ . The formation of red –wine color signified the formation of AuNPs.



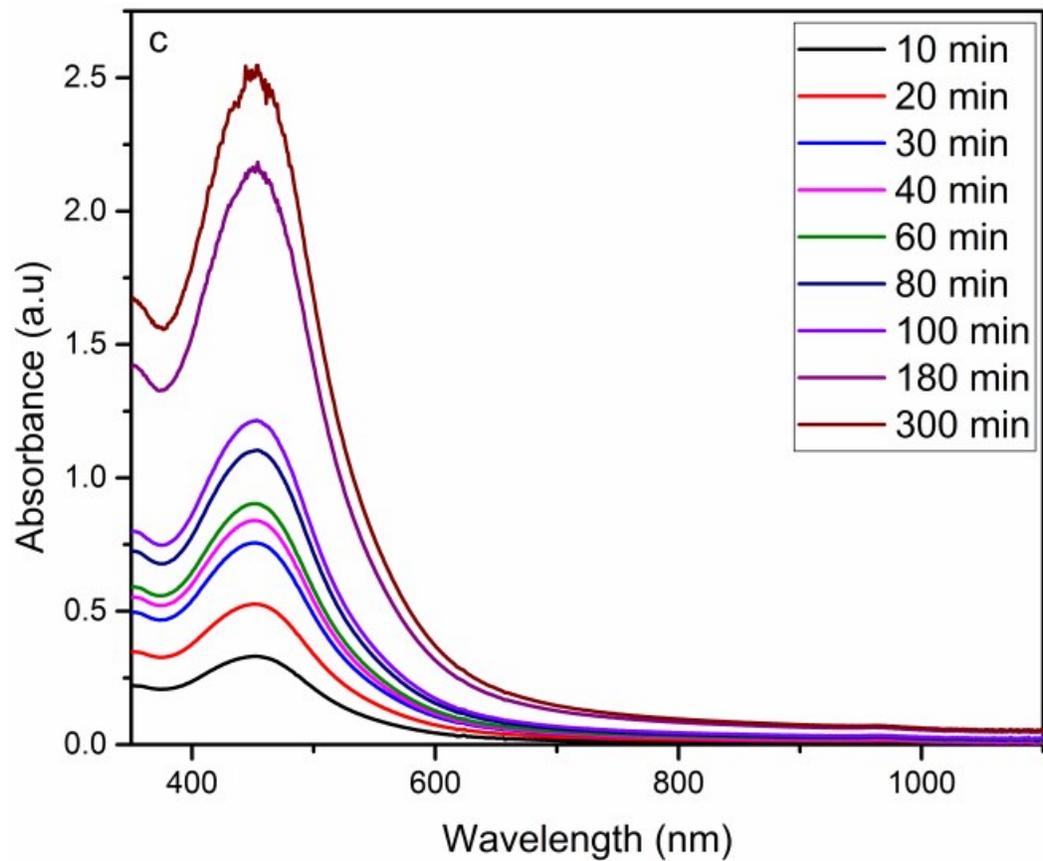
**Figure S5:** UV-Vis -NIR showing the effect of temperature on the formation of AuNPs derived from LTP. The reaction was done by reacting 300 $\mu$ L of 5mM HAuCl<sub>4</sub>, 1.5mg of LTP, and 200mL of nanopure deionized water at 25°C, 30°C, 40°C, 50°C, 60°C, 70°C, 80°C, and 90°C. A second SPR peak was formed at 90°C implying that anisotropic AuNPs were formed.



**Figure S6A:** TEM images of AuNPs in which (a) was for sample A1 and (b) and (d) for sample A2. A1. Uv-Vis spectra of AuNPs formed 3mM  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  were reacted with 3mM LTP in a ratio of 1:1, 1:1.5, 1:2 and 1:3 for A1, A2, A3 and A4 respectively at pH 9. The SPR peak and absorbance were as follows: A1 (538 nm and absorbance 0.86593 a.u), A2 (539 nm and absorbance (0.9483 a.u), A3 (537 nm, 1.04117 a.u) and A4 (535 nm; 1.5328 a.u).



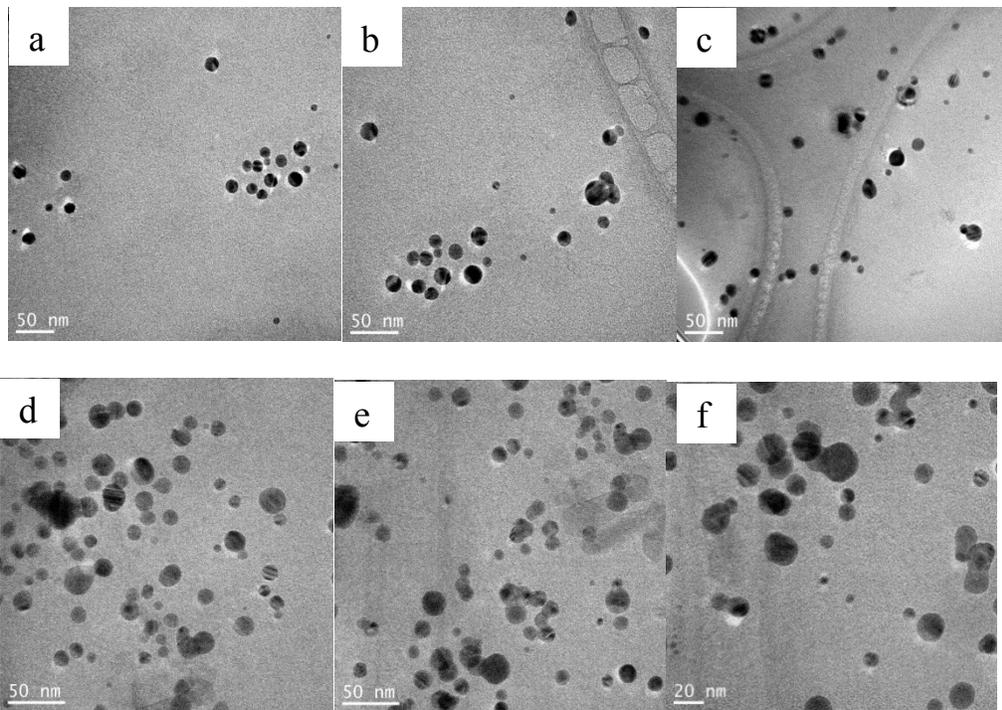
**Figure S6B:** UV-Vis spectra showing the formation of AuNPs whereby concentration of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  was varied while concentration of LTP remained constant at pH (a) 6 and (b) 9.



**Figure S7:** UV-Vis spectra showing the time dependence reaction for the formation of AgNPs when  $\text{AgNO}_3$  and LTP were reacted at ratio of 1:1.



**Figure S8:** Digital images showing the formation of LTP derived silver nanoparticles at varied concentrations of  $\text{AgNO}_3$  while concentration of LTP remained constant and the reaction was conducted in the ratio 1:1, 1:2, 1:3, 2:1.5 and 2:3 ( $\text{AgNO}_3$ : LTP) S1, S2, S3, S4 and S5 respectively heated to  $60^\circ\text{C}$  at pH9.



**Figure S9:** Representative TEM images of synthesized AgNPs a, b, c for samples F while d, e and f were images for sample G.