

Electronic Supplementary Information for  
**Radical intermediates in chloroform reactions over  
triphenylphosphine-protected Au nanoparticles**

Marco Conte, Karen Wilson and Victor Chechik\*

Department of Chemistry, University of York at Heslington, York, United Kingdom, YO10 5DD

\* To whom correspondence may be addressed. E-mail: vc4@york.ac.uk, Fax: (+)-44-1904-432516.

**Contents:**

Figure S1. EPR spectra of DMPO spin adducts formed during reaction of $\text{CHCl}_3$ (a) and $\text{CDCl}_3$ (b) over Au/CeO <sub>2</sub> .	S3
Figure S2a. TEM image of triphenylphosphine protected gold nanoparticles purified via gel permeation chromatography: first fraction set containing bigger particles	S4
Figure S2b. TEM images of triphenylphosphine protected gold nanoparticles purified via gel permeation chromatography: second fraction set containing smaller particles.	S5
Figure S3. TEM image of gold triphenylphosphine protected gold nanoparticles after treatment with PbO <sub>2</sub> in $\text{CH}_2\text{Cl}_2$ solution (1 min).	S6
Figure S4. EPR spectra of DMPO spin adducts formed during reaction of $\text{CDCl}_3$ with triphenylphosphine protected gold nanoparticles: as prepared (a), PbO <sub>2</sub> treated (b), and treated with PbO <sub>2</sub> and purified by gel permeation chromatography (c).	S7

Figure S5. Effect of air treatment ( $20 \text{ mL min}^{-1}$ ) on the ratio of DMPO spin adducts formed in a reaction of  $\text{CDCl}_3$  with triphenylphosphine protected gold nanoparticles: sample as prepared (a), and treated for 1 min (b), 10 min (c), and 30 min (d). S8

Figure S6. Effect of  $\text{Ce}(\text{SO}_4)_2$  on the ratio of DMPO spin adducts formed in a reaction of  $\text{CDCl}_3$  with triphenylphosphine protected gold nanoparticles: sample as prepared (a), treated with emulsion containing  $10^{-2} \text{ M}$ .  $\text{Ce}(\text{SO}_4)_2$  (b). S9

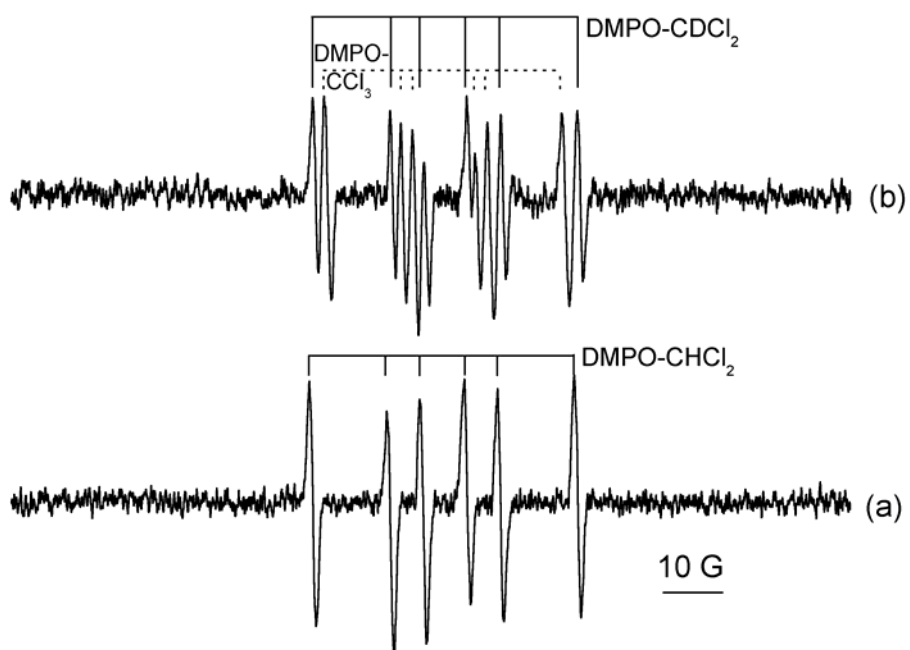
Figure S7. Effect of purification conditions on the activity of gold nanoparticles. EPR spectra of DMPO spin adducts formed from  $\text{CDCl}_3$  are shown for the following samples of triphenylphosphine protected gold nanoparticles: crude material (a), particles purified using gel permeation chromatography using  $\text{CH}_2\text{Cl}_2$  as eluent (b); particles purified using gel permeation chromatography using  $\text{CH}_2\text{Cl}_2$  containing  $\text{NaBH}_4$  as eluent (c). S10

Figure S8. EPR spectra of DMPO spin adducts formed in a reaction of  $\text{CDCl}_3$  with triphenylphosphine protected gold nanoparticles: sample was exposed to air for 3 days (a), and treated with  $\text{CH}_2\text{Cl}_2$  containing  $\text{NaBH}_4$  (b). S11

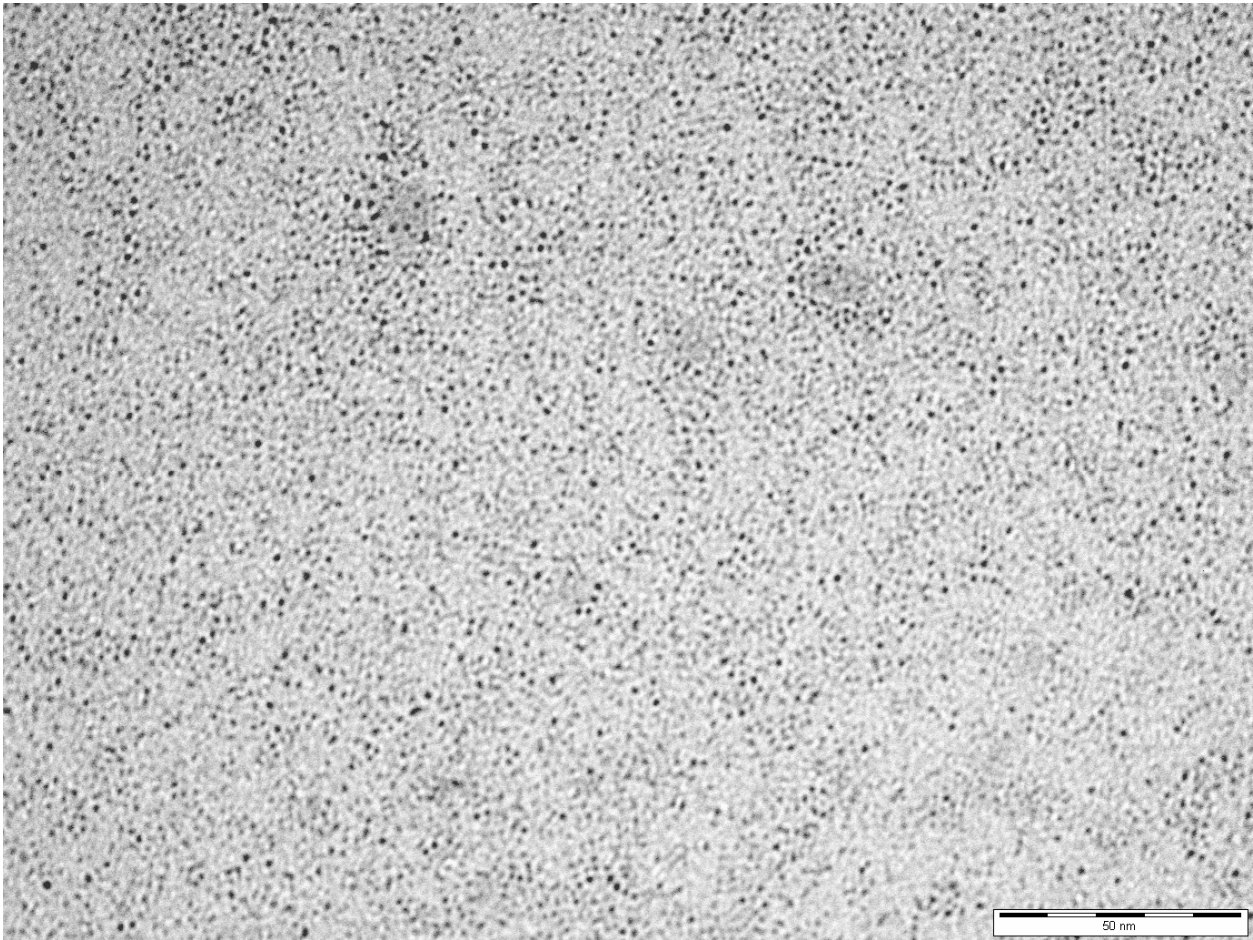
Figure S9. X-ray photoelectron spectroscopy in the  $\text{P}_{2p}$  region for triphenylphosphine protected gold nanoparticles: as prepared, exposed to air, treated with  $\text{Ce}(\text{SO}_4)_2$  and  $\text{PbO}_2$ . S11

Figure S10.  $^1\text{H-NMR}$  spectra of triphenylphosphine protected gold nanoparticles purified by gel permeation chromatography. Only trace amount of tetraoctylammonium bromide ( $\delta$  1-4 ppm) was detected (peaks at 5.7 ppm and 7.8 ppm are from residual solvent protons,  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ ). S12

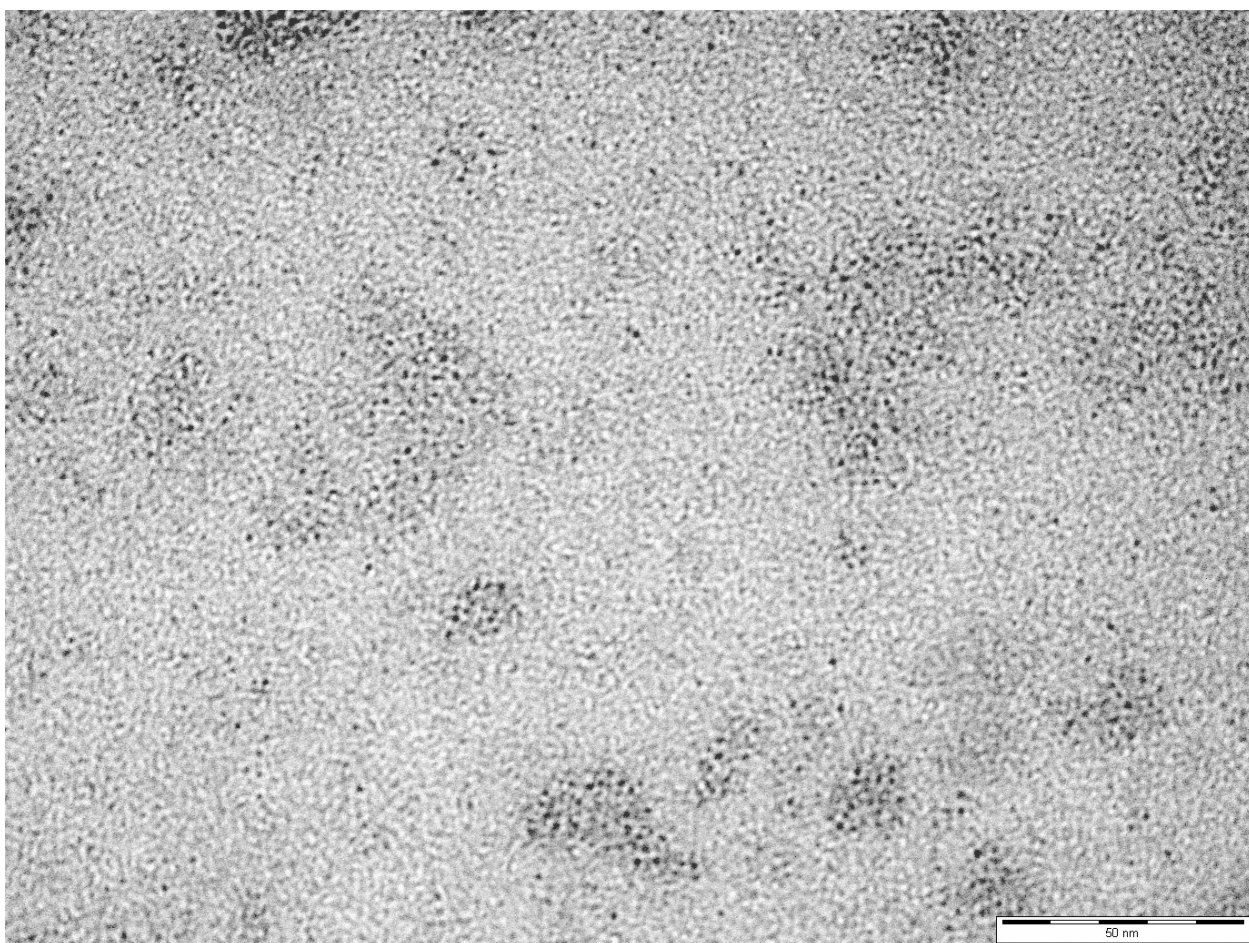
Figure S11. Thermal gravimetric analysis (TGA) of triphenylphosphine protected gold nanoparticles. S12



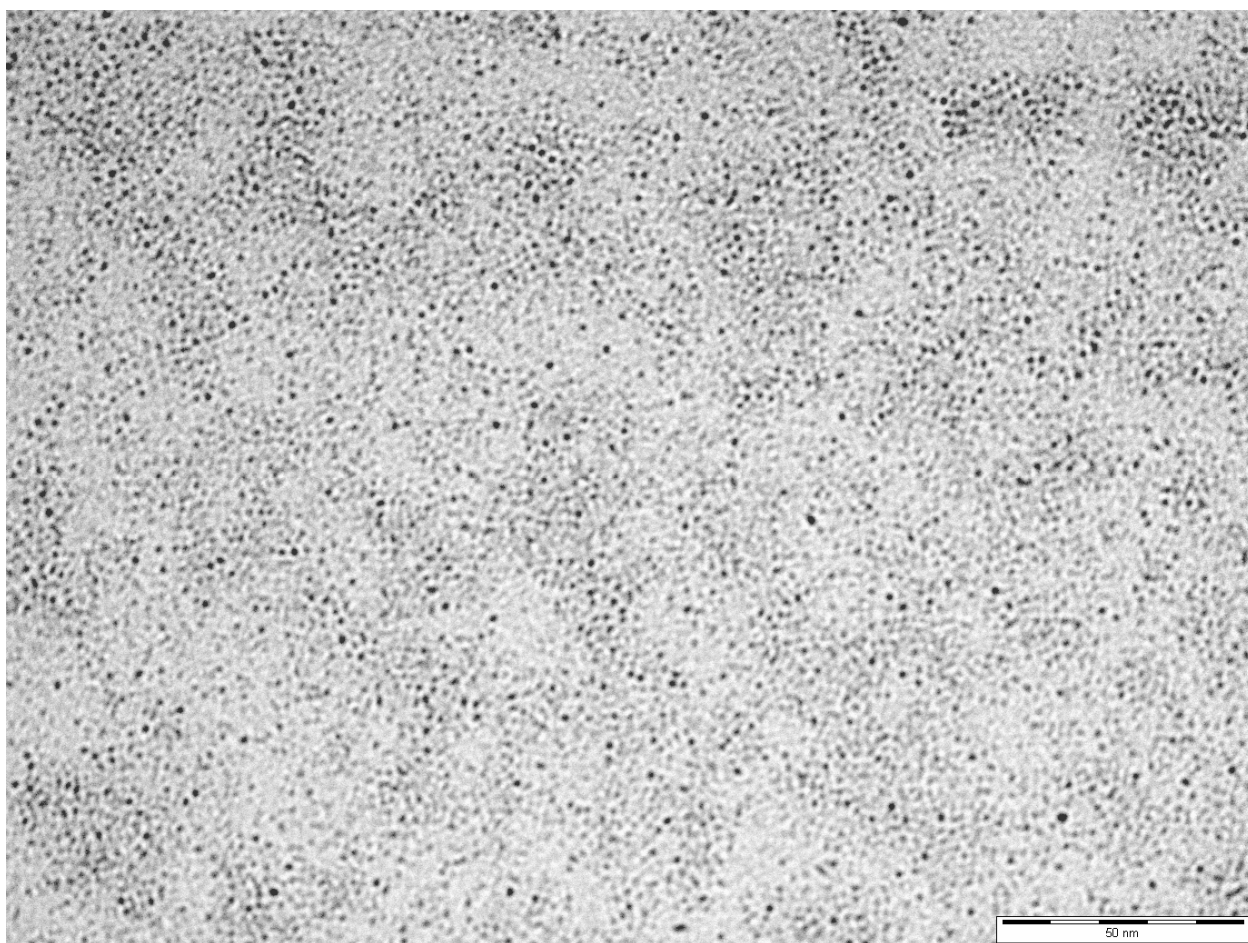
**Figure S1.** EPR spectra of DMPO spin adducts formed during reaction of CHCl<sub>3</sub> (a) and CCl<sub>3</sub> (b) over Au/CeO<sub>2</sub>.



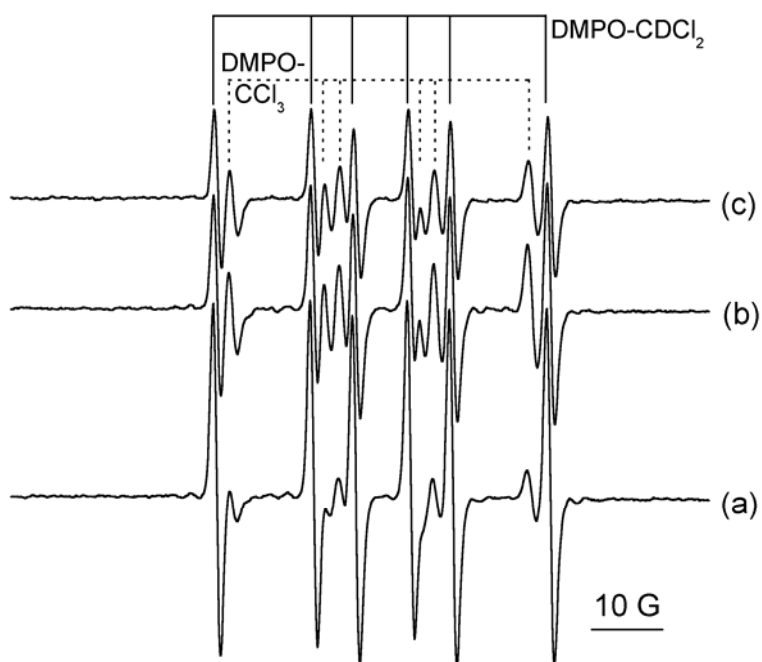
**Figure S2a:** TEM image of triphenylphosphine protected gold nanoparticles purified *via* gel permeation chromatography: first fraction set containing bigger particles



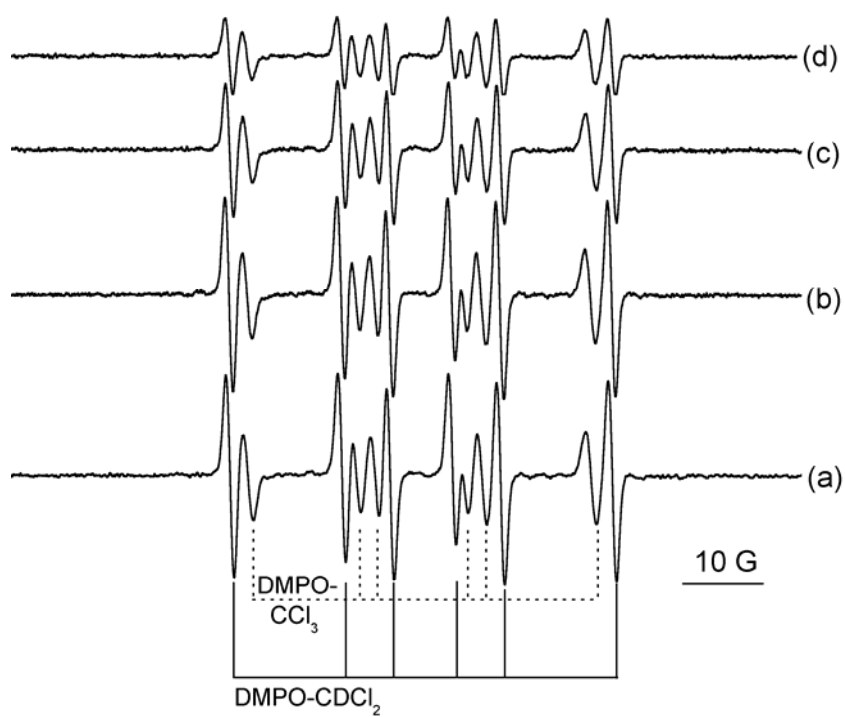
**Figure S2b:** TEM images of triphenylphosphine protected gold nanoparticles purified via gel permeation chromatography: second fraction set containing smaller particles.



**Figure S3:** TEM image of gold triphenylphosphine protected gold nanoparticles after treatment with  $\text{PbO}_2$  in  $\text{CH}_2\text{Cl}_2$  solution (1 min).

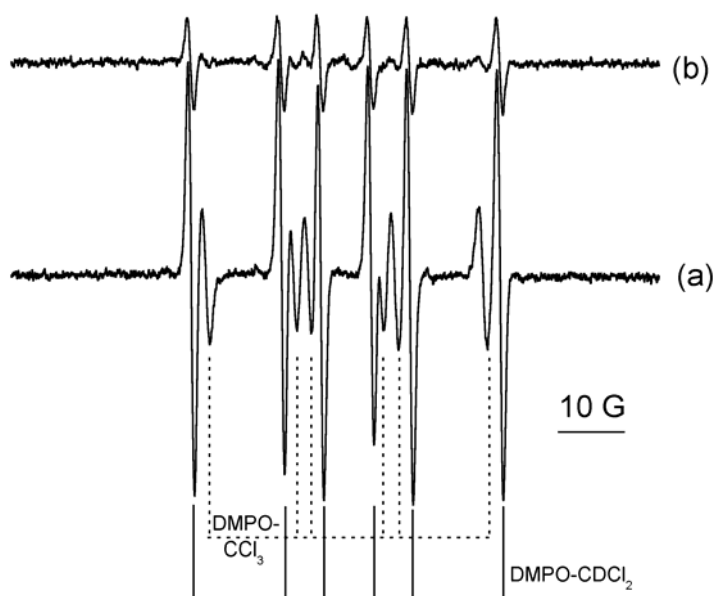


**Figure S4:** EPR spectra of DMPO spin adducts formed during reaction of  $\text{CDCl}_3$  with triphenylphosphine protected gold nanoparticles: as prepared (a),  $\text{PbO}_2$  treated (b), and treated with  $\text{PbO}_2$  and purified by gel permeation chromatography (c).

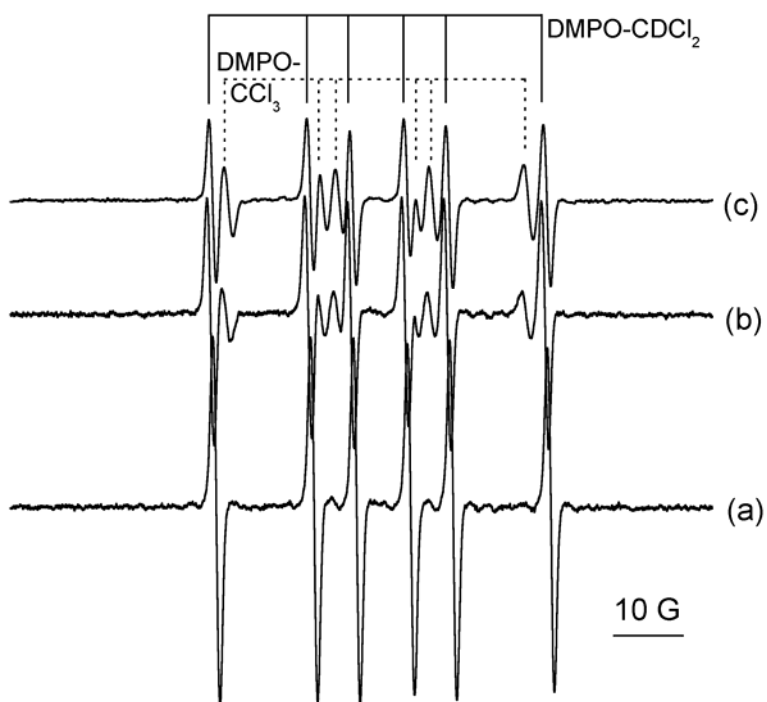


**Figure S5:** Effect of air treatment ( $20 \text{ mL min}^{-1}$ ) on the ratio of DMPO spin adducts formed in a reaction of  $\text{CDCl}_3$  with triphenylphosphine protected gold nanoparticles: sample as prepared (a), and treated for 1 min (b), 10 min (c), and 30 min (d).

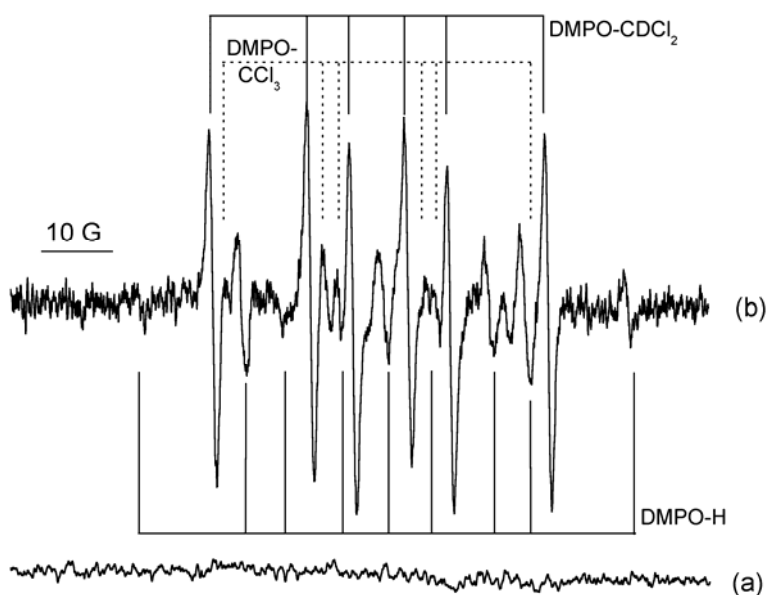




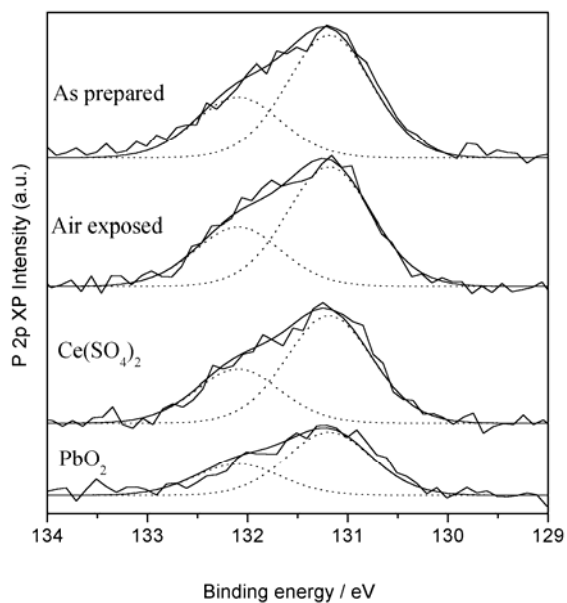
**Figure S6:** Effect of  $\text{Ce}(\text{SO}_4)_2$  on the ratio of DMPO spin adducts formed in a reaction of  $\text{CDCl}_3$  with triphenylphosphine protected gold nanoparticles: sample as prepared (a), treated with emulsion containing  $10^{-2}$  M.  $\text{Ce}(\text{SO}_4)_2$  (b).



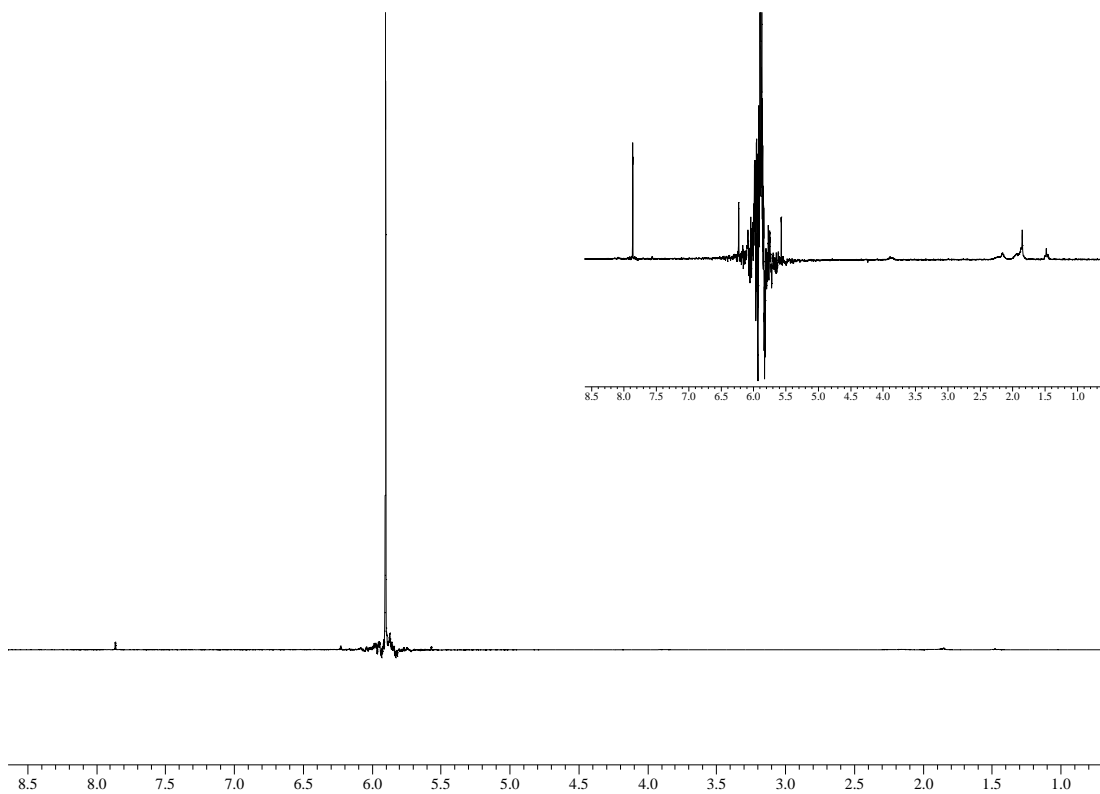
**Figure S7:** Effect of purification conditions on the activity of gold nanoparticles. EPR spectra of DMPO spin adducts formed from  $\text{CDCl}_3$  are shown for the following samples of triphenylphosphine protected gold nanoparticles: crude material (a), particles purified using gel permeation chromatography using  $\text{CH}_2\text{Cl}_2$  as eluent (b); particles purified using gel permeation chromatography using  $\text{CH}_2\text{Cl}_2$  containing  $\text{NaBH}_4$  as eluent (c).



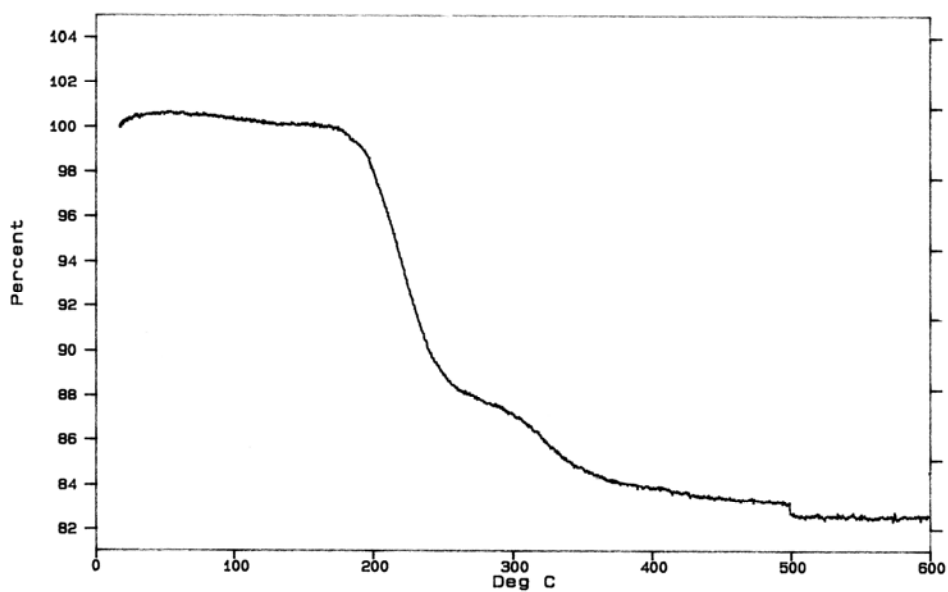
**Figure S8:** EPR spectra of DMPO spin adducts formed in a reaction of  $\text{CDCl}_3$  with triphenylphosphine protected gold nanoparticles: sample was exposed to air for 3 days (a), and treated with  $\text{CH}_2\text{Cl}_2$  containing  $\text{NaBH}_4$  (b).



**Figure S9:** X-ray photoelectron spectroscopy in the  $\text{P}_{2p}$  region for triphenylphosphine protected gold nanoparticles: as prepared, exposed to air, treated with  $\text{Ce}(\text{SO}_4)_2$  and  $\text{PbO}_2$ .



**Figure S10:**  $^1\text{H-NMR}$  spectra of triphenylphosphine protected gold nanoparticles purified by gel permeation chromatography. Only trace amount of tetraoctylammonium bromide ( $\delta$  1-4 ppm) was detected (peaks at 5.7 ppm and 7.8 ppm are from residual solvent protons,  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ ).



**Figure S11:** Thermal gravimetric analysis (TGA) of triphenylphosphine protected gold nanoparticles.