Supplementary Data

Gold nanoparticle decorated with a cinchonine organocatalyst: application in the asymmetric $\alpha$-amination of $\beta$-ketoesters

Lynay Santacruz,$^{a,b}$ Sandra Niembro,$^a$ Anna Santillana,$^a$ Alexandr Shafir$^{a,*}$ and Adelina Vallribera$^{a,*}$

$^a$ Departament de Química, Universitat Autònoma de Barcelona, 08193, Cerdanyola del Vallès, Barcelona, Spain. Fax: 34 935812477; Tel: 34 935813045; E-mail: adelina.vallribera@uab.es

$^b$ Departamento de Química, Universidad de Nariño, sede Torobajo, calle 18 carrera 30, Pasto, Colombia.

Table of contents

General Information........................................................................................................S2
$^1$H and $^{13}$CNMR of compound 2..................................................................................S3
IR of compound 2............................................................................................................S4
$^1$HNMR of compound 3..................................................................................................S4
$^{13}$CNMR and IR of compound 3.....................................................................................S5
Comparison $^1$HNMR of dodecanthiol 4 and 4@$\text{Au}$.......................................................S6
TEM images and particle size distribution of 4@$\text{Au}$......................................................S6
Comparison $^1$HNMR of cinchonine derivative 2 and 2@$\text{Au}$..........................................S7
TEM images and particle size distribution of 2@$\text{Au}$......................................................S7
General procedure for the $\alpha$-amination reaction.............................................................S8
HPLC analysis of 7..........................................................................................................S8
General Information.

All NMR measurements were carried out at the Servei de Ressonància Magnètica Nucler at the Universitat Autònoma de Barcelona. Routine $^1$H, $^{13}$C and $^{19}$F NMR spectra were recorded on Bruker AC250 (250 MHz for $^1$H) and Avance360 (360 MHz for $^1$H) instruments. $^1$H NMR chemical shifts are given relative to the residual protic solvent in CDCl$_3$ (7.26 ppm). $^{13}$C{$_^1$H} NMR spectra are given relative to CDCl$_3$ (77.36 ppm).

Infrared spectra were recorded using a Bruker Tensor 27 instrument equipped with an ATR Golden Gate cell and a diamond window. Routine CHN elemental analyses were performed at the Servei de Microanàlisi del CSIC de Barcelona. ICP measurements of gold contents were done at the Serveis Científico-tècnics of the Universitat de Barcelona using a multichannel Perkin Elmer instrument, model Optima 3200 RL. HR-MS measurements were performed at the Servei Anàlisi Química of the Universitat Autònoma de Barcelona.

Gas chromatography analysis was accomplished using Hewlett-Packard 5890A chromatograph with a capillary HP Ultra 1 column (12 m x 0.2 mm x 0.33 µm). The integrated areas and peak positions in the chromatograms were referenced internally to undecane.

Melting points were determined using a Reichert brand melting point apparatus and are uncorrected.

Alugram® SIL G/UV$_{254}$ sheets (Macherey-Nagel) were used for thin-layer chromatography. Column chromatography was carried out using SDS brand silica gel with a grain size of 35-70 µm and a pore size of 60 Å.

Transmission electron microscopy (TEM) analyses were performed in the Servei de Microscòpia de la Universitat Autònoma de Barcelona, using a JEOL JEM-2010 model at 200 kV. The TEM measurements were made by sonication of the nanoparticulate material in perfluorooctyl bromide for several minutes; then, one drop of the finely divided suspension was placed on a specially produced structureless carbon support film having a thickness of 4-6 nm and dried before observation.

Enantiomeric excesses were determined, unless otherwise stated, by HPLC using a chiral column Chirapak IC.

Elemental analyses are the average of two determinations.

Experiments requiring argon atmosphere were carried out using standard Schlenk techniques.
IR (ATR)

Wavenumber cm⁻¹

Transmittance [%]

1H-RMN (360 MHz, CDCl₃)

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Comparison 1HNMR of dodecanthiol, 4, and dodecanthiolate-gold nanoparticles $4@Au$

TEM images and particle size distribution of $4@Au$
Comparison 1HNMR of cinchonine derivative 2 and 2@Au

![HNMR spectrum]

R-SH = HS-(CH$_2$)$_{11}$CH$_3$
Q-SH = cinchonine derivative 2

TEM images and particle size distribution of 2@Au

![TEM images]

Electronic Supplementary Material (ESI) for New Journal of Chemistry
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General experimental procedure for asymmetric α-amination reaction: to a solution of the dibenzyl azodicarboxylate (0.066 g, 0.21 mmol), in 2 mL of CH₂Cl₂ at -0°C was added the β-ketoester 5 (29 µL, 0.2 mmol) and the catalyst 2@Au (0.010 g, 5% mol). The resulting solution was stirred at 0°C for one hour. The reaction mixture was filtered through celite and then the residue was purified by chromatography through silica-gel using hexanes/AcOEt (5:1) as eluent to give 87 mg (92% rdt) of \( N,N' \)-bis(benzyloxycarbonyl)-1-hydrazino-2-oxo-cyclohexanecarboxylic acid ethyl ester, 7, with a 76 ee.

![HPLC chromatogram of racemic mixture of 7:](image)

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HPLC chromatogram 79% ee of 7:

![HPLC chromatogram 79% ee of 7:](image)

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