# Suplementary Data

## Gold nanoparticle decorated with a cinchonine organocatalyst: application in the asymmetric α-amination of β-ketoesteres

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**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 Cientificotècnics of the Universitat de Barcelona using a multichanel Perkin Elmer instrument, model Optima 3200 RL. HR-MS measurements were performed at the Servei Anàlisi Química of the Uiversitat 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.

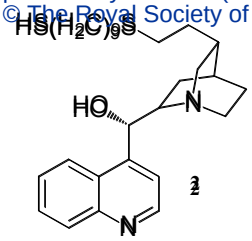
Alugram® SIL G/$UV_{254}$ sheets (Macherey-Nagel) were used for thin-layer chromatography. Column chromatography was carried out using SDS brand silica gel with a grain size of 35-70 μm and a pore size of 60 Å.

Transmission electron microscopy (TEM) analyses were performed in the *Servei de Microscòpia of the 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.

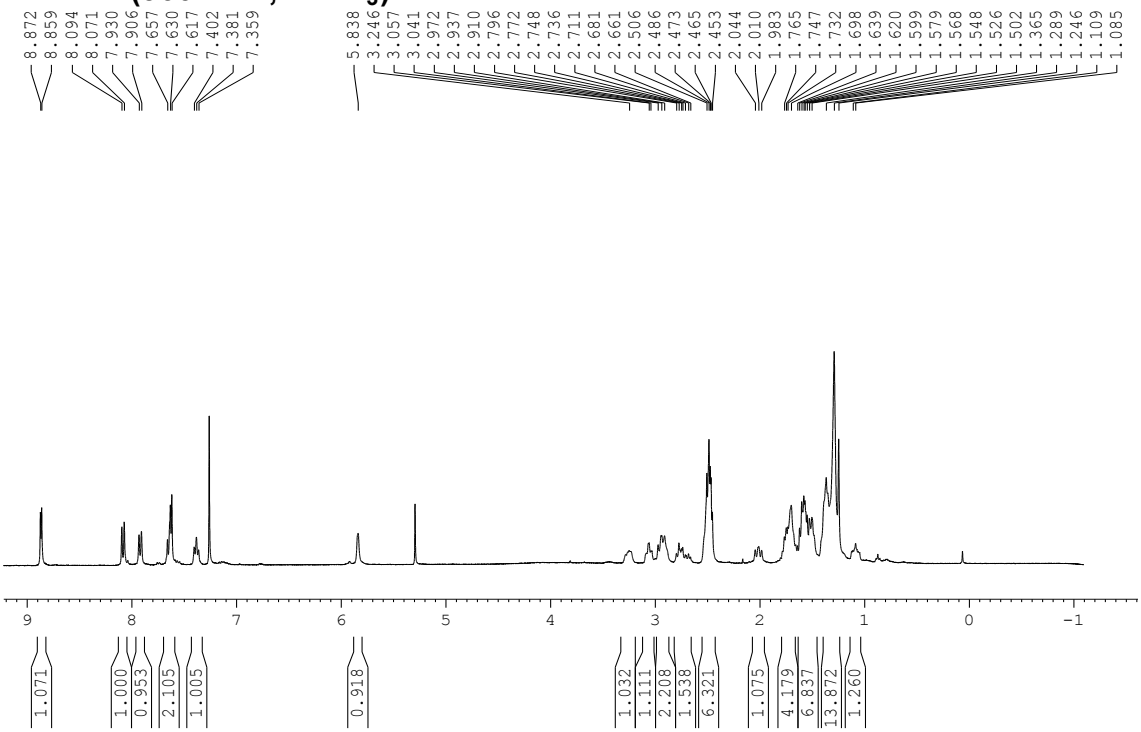
Enantiomeric excesses were determined, unless otherwise stated, by HPLC using a chiral column Chirapak IC.

Elemental analyses are the average of two determinations.

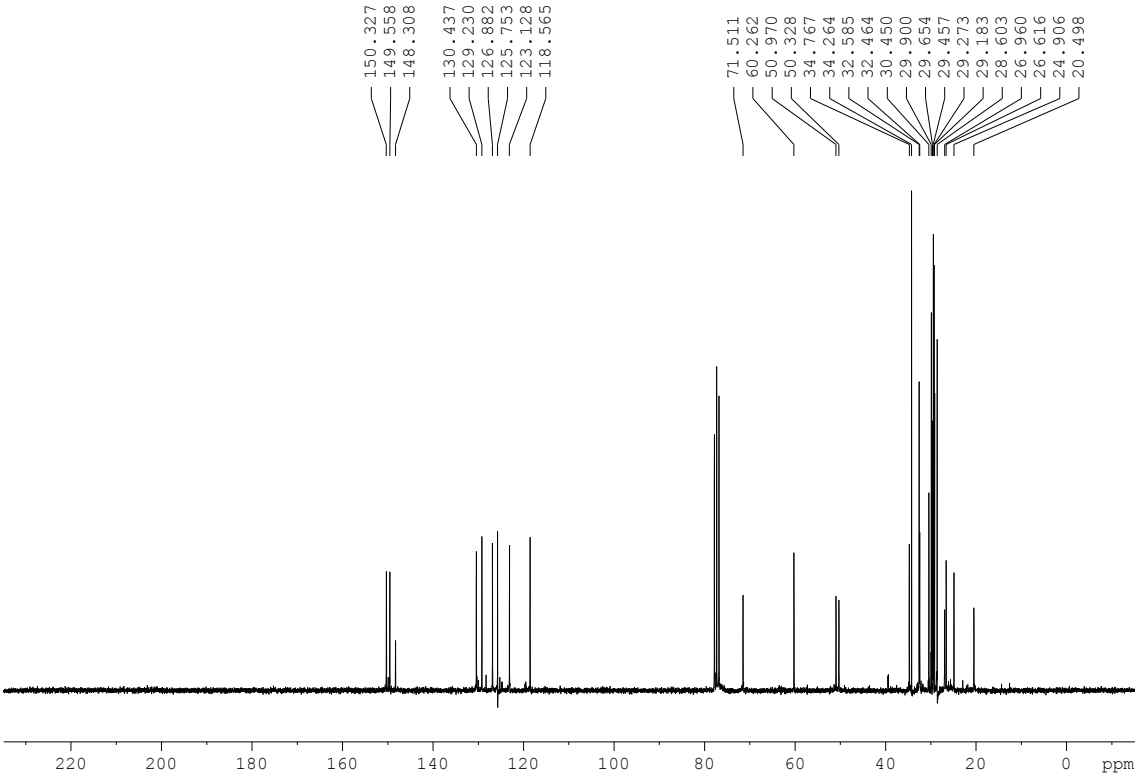
Experiments requiring argon atmosphere were carried out using standard Schlenk techniques.



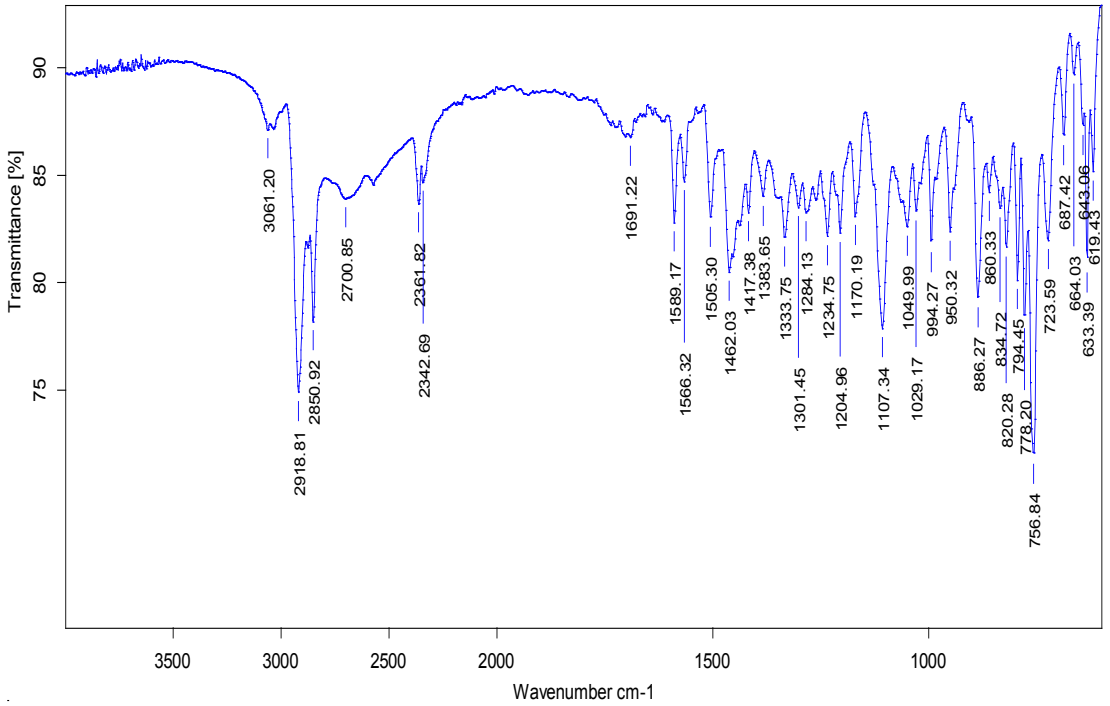

## $^{1}$H-RMN (360 MHz, $CDCl_3$)

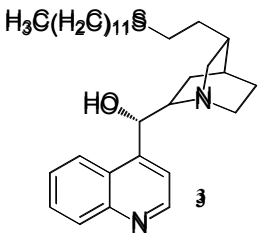



## $^{13}$C-RMN (62.5 MHz, $CDCl_3$)

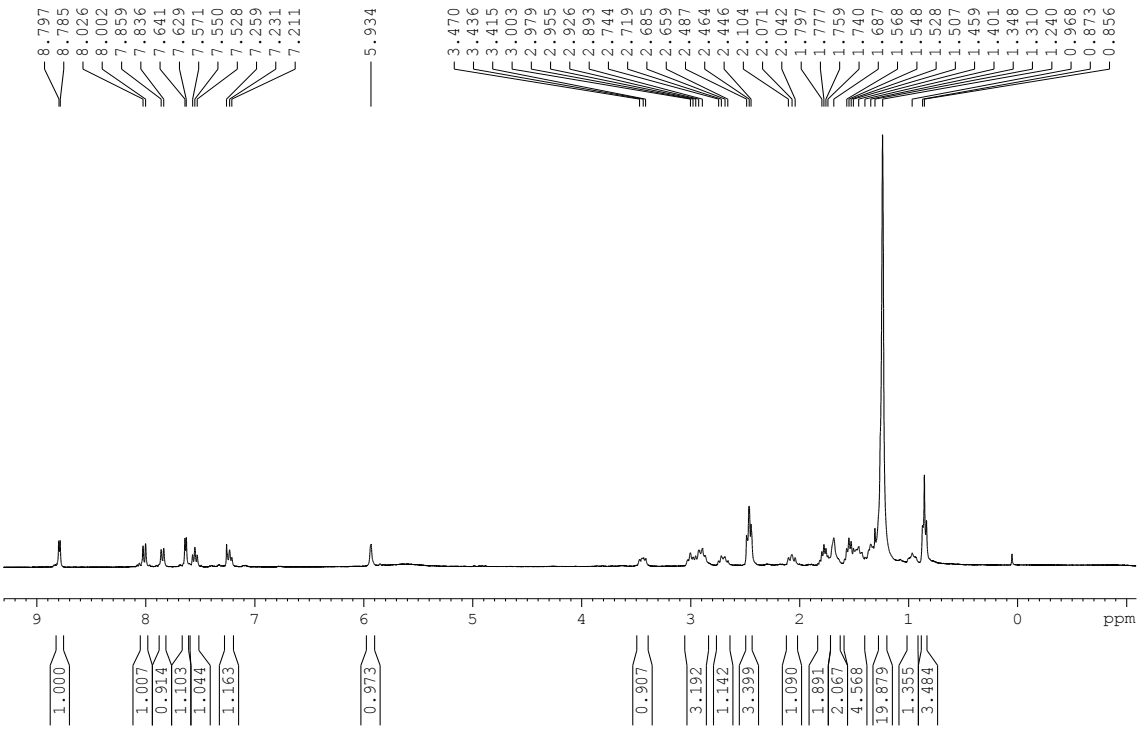


## IR (ATR)

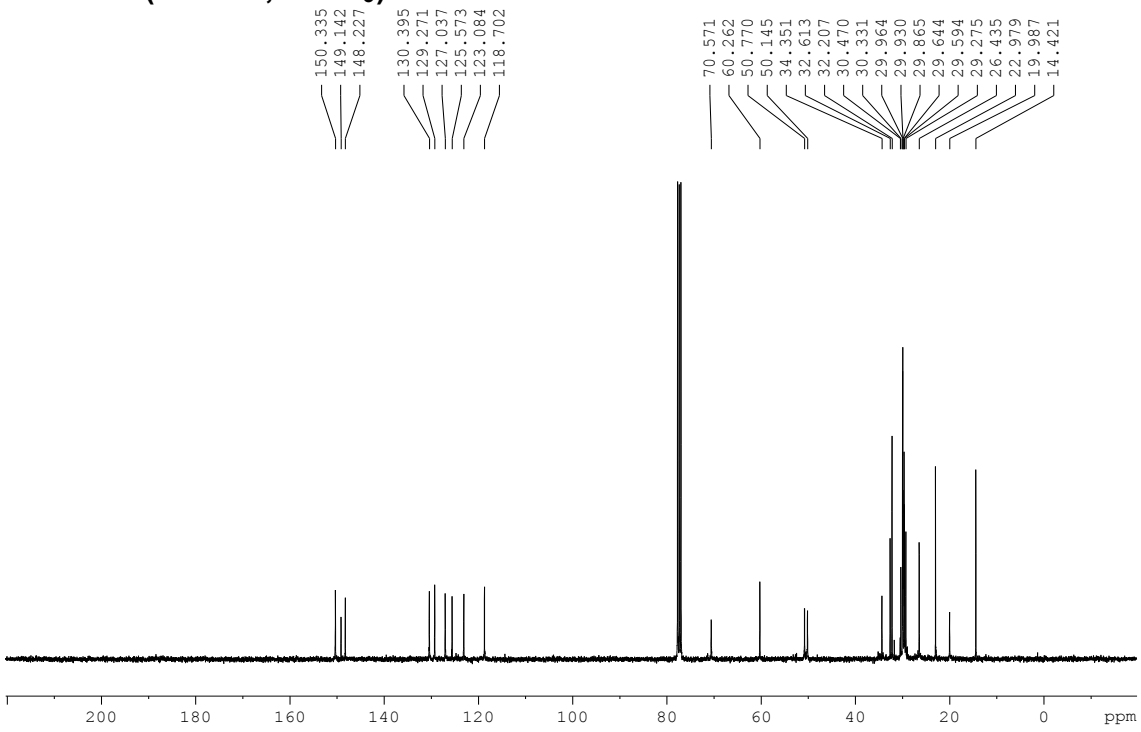


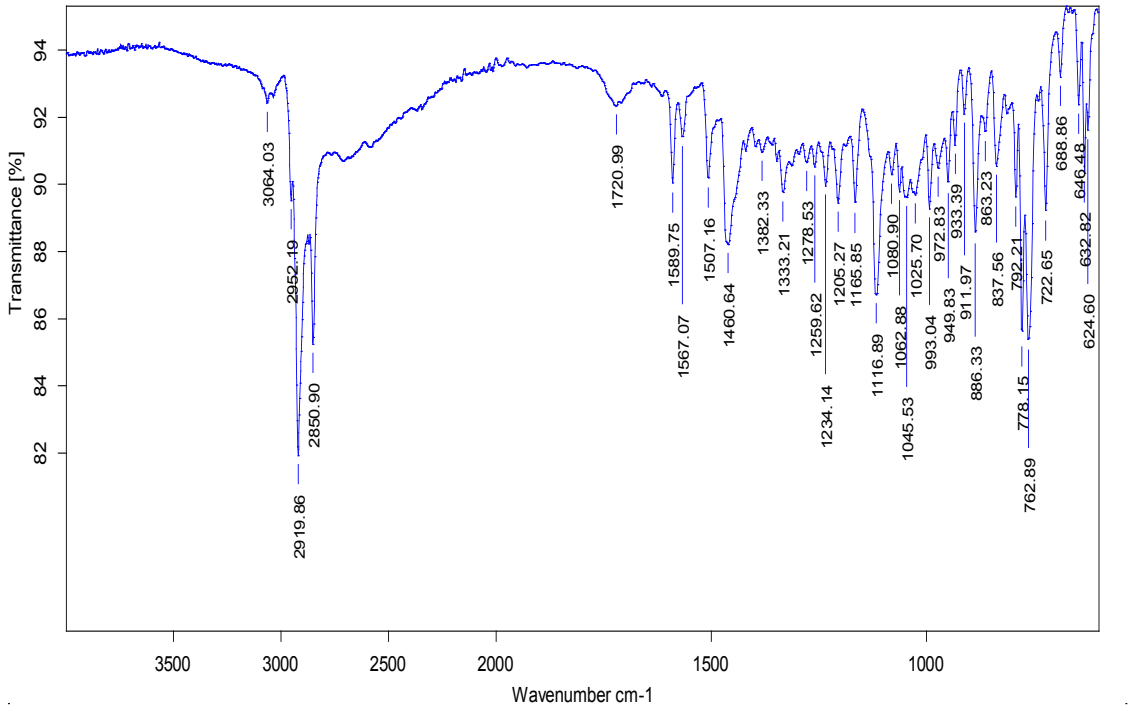

## $^1$H-RMN (360 MHz, $CDCl_3$)



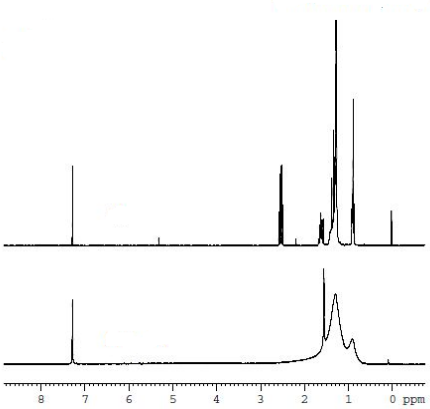
## $^{13}$C-RMN (90 MHz, $CDCl_3$)

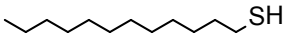



## IR (ATR)

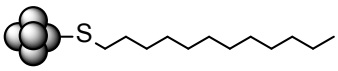


Comparison 1HNMR of dodecanthiol, **4**, and dodecanthiolate-gold nanoparticles **4@Au**

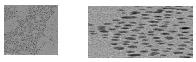


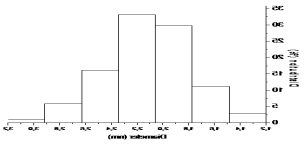




**$Au_{np}$, 4**

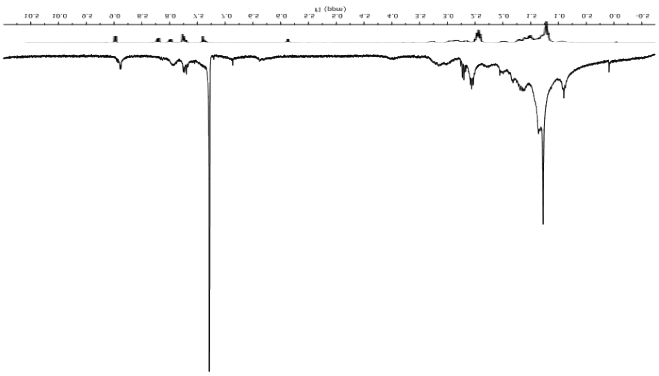


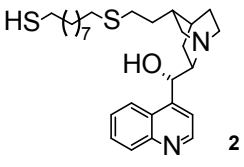

TEM images and particle size distribution of **4@Au**

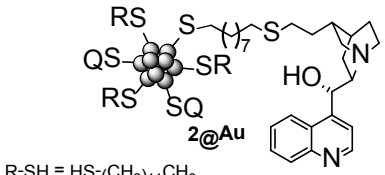




Comparison 1HNMR of cinchonine derivative **2** and **2@Au$_{np}$**

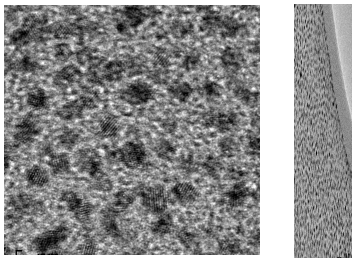


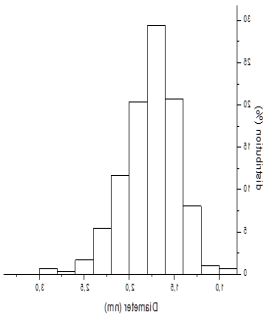


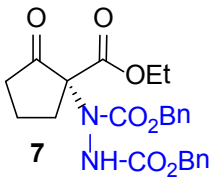

R-SH = HS-$(CH_2)_{11}CH_3$
Q-SH = cinchonine derivative **2**

TEM images and particle size distribution of **2@Au$_{np}$**



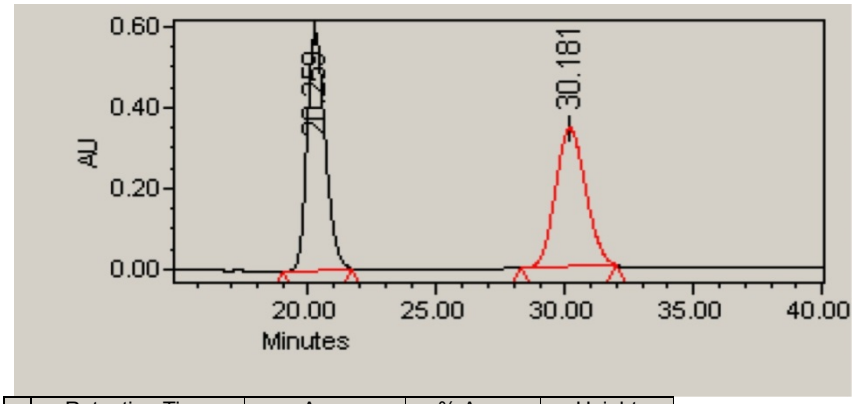


**General experimental procedure for asymmetric α-amination reaction**: to a solution of the dibenzyl azodicarboxylate (0.066 g, 0.21 mmol), in 2 mL of $CH_2Cl_2$ at -0°C was added the β-ketoester **5** (29 μL, 0.2 mmol) and the catalyst **2@Au** (0.010 g, 5 % mol). The resulting solution was stirred at 0°C for one hour. The reaction mixture was filtered through celite and then the residue was purified by chormatography 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*.



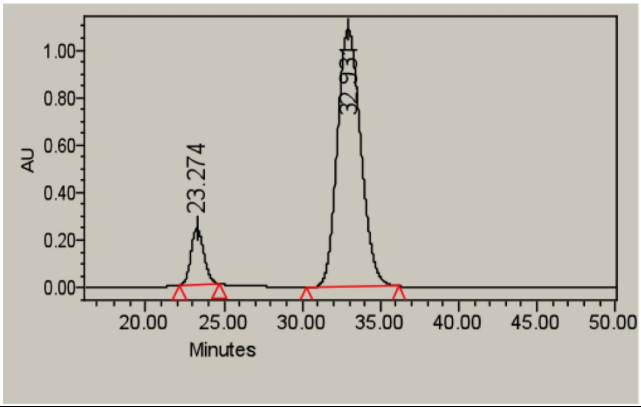

**7**

HPLC chromatogram of racemic mixture of **7:**




| | Retention Time | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 20.259 | 28943255 | 50.41 | 587292 |
| 2 | 30.181 | 28473404 | 49.59 | 344156 |

HPLC chromatogram 79% *ee* of **7:**




| | Retention Time | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 23.274 | 13699345 | 10.82 | 239235 |
| 2 | 32.931 | 112869336 | 89.18 | 1083043 |