

SUPPORTING INFORMATION

Ligand effect in the Rh-NPs catalysed partial hydrogenation of substituted arenes.

Jessica Llop Castelbou, Aitor Gual, Elisabet Mercadé, Carmen Claver* and Cyril Godard*

Table of contents :

S1. General, materials and characterization techniques.

S2. Synthesis of the diphosphite 4 derived from 4-4'-dihydroxydiphenyl

S3. Synthesis of Rhodium $[\text{Rh}(\eta^3\text{-(C}_3\text{H}_5)_3]$ precursor from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$

S4. Synthesis of rhodium nanoparticles stabilized by P-ligands

S5. Synthesis of rhodium nanoparticles stabilized by mixture of solvents

S6. General procedure for the synthesis of the Rh-NPs using the seeded-growth method.

S7. Characterization of the rhodium nanoparticles Rh1-Rh5

S8. Catalytic experiments

S9. References

S1. General, materials and characterization techniques.

General methods. All syntheses were performed using standard Schlenk techniques under N₂ or Ar atmosphere. Chemicals were purchased from Aldrich Chemical Co, Fluka and Strem. All solvents were distilled over drying reagents and were deoxygenated before use. The precursor Rh(η^3 -(C₃H₅)₃), was prepared following previously described methods.^{[1][2]} The synthesis of Rh-nanoparticles were performed using 200ml Fisher Porter and pressurized on a high pressure line.

The deuterated solvents for NMR measurements were dried over molecular sieves. ¹H, ¹³C {1H}, and ³¹P {1H} NMR spectra were obtained on a Varian Mercury 400 MHz spectrometer. Chemical shifts were calibrate relative to SiMe₄ (¹H and ¹³C NMR) as internal standard or 85% H₃PO₄ as external standard (³¹P NMR).

The TEM experiments were performed at the “Unitat de Microscopia dels Serveis Científicotècnics de la Universitat Rovira I Virgili” (TEM-SCAN) in Tarragona with a Zeiss 10 CA electron microscope operating at 100 kV with resolution of 3 Å. The particles size distributions were determined by a manual analysis of enlarged images. At least 300 particles on a given grid were measured in order to obtain a statistical size distribution and a mean diameter.

XRD measurements were made using a Siemens D5000 diffractometer (Bragg- Brentano parafocusing geometry and vertical θ - θ goniometer) fitted with a curved graphite diffracted- beam monochromator, incident and diffracted- beam Soller slits, a 0.06° receiving slit and scintillation counter as a detector. The angular 2 θ diffraction range was between 26 and 95°. The data were collected with an angular step of 0.05° at 16s per step and sample rotation. A low background Si(510) wafer was used as sample holder. Cu_{K α} radiation was obtained from a copper X- ray tube operated at 40kV and 30mA.

GS-MS spectroscopy was carried out on a HP 6890A spectrometer, with an achiral HP-5 column (0.25mm x 30m x 0.25um), T^a= 250°C injector, flow 1.5ml/min.

XPS experiments were performed in a PHI 5500 Multitechnique System (from Physical Electronics) with a monochromatic X-ray source (Aluminium Kalfa line of 1486.6 eV energy and 350 W), placed perpendicular to the analyzer axis and calibrated using the 3d5/2 line of Ag with a full width at half maximum (FWHM) of 0.8 eV. The analized area was a circle of 0.8 mm diameter, and the selected resolution for the spectra was 187.5eV of Pass Energy and 0.8 eV/ step for the general spectra and 23.5 eV of Pass Energy and 0.1 eV/step for the spectra of the different elements in the depth profile spectra. A low energy electron gun (<10 eV) was used in order to discharge the surface when necessary. All measurements were performed in a ultra high vacuum (UHV) chamber pressure between 5x10⁻⁹ and 2x10⁻⁸ torr.

S2. Synthesis of the diphosphite **4** derived from 4-4'-dihydroxydiphenyl

4,4',6,6'-Tetra-*tert*-butyl-2,2'-bisphenol (0.9g, 2.2mmol) was dissolved in 30ml of dry and degassed toluene. Degassed pyridine (2.13ml, 27mmol) was added carefully to 0.46 mL of distilled PCl₃ at 0°C. The bisphenol solution was slowly added to the PCl₃/pyridine solution. The reaction was stirred during 16h at 60°C to form the 4,4',6,6'-tetra-*tert*-butyl-2,2'- biphenylphosphochloridrite. The pyridine salts formed were removed by filtration under argon atmosphere. The reaction mixture was concentrated under reduced pressure and the product was used without purification in the following reaction (estimated yield 90%).

4-4'-dihydroxydiphenyl (0.149g, 0.8mmol, 1eq) was dissolved in 4mL of dry and degassed toluene. 4,4',6,6'-tetra- *tert*- butyl- 2,2'- biphenylphosphochloridrite (0.94g, 1.97mmol, 2.1eq) was dissolved in 3.12 mL of degassed pyridine (38.7 mmol). The 4-4'- dihydroxydiphenyl solution was added to the phosphochloridrite/pyridine solution and the mixture stirred overnight at room temperature. Purification was carried out by column chromatography under nitrogen with dry and degassed toluene as eluent, yielding **4** as a white solid (yield 400mg, 85%).

¹H NMR (400MHz, toluene d₈, δ in ppm): δ =7.62 (d, *J*=2.4Hz, 4H), 7.38 (d, *J*=2.4Hz, 4H), 7.13 (d, *J*= 8Hz, 4H), 7.08 (d, *J*= 8Hz, 4H), 1.61 (s, 36H, ^tBu- *ortho*), 1.28 (s, 36H, ^tBu-*para*).

¹³C NMR (400MHz, toluene d₈, δ in ppm): δ =151.9 (d, *J*_{PC}= 6 Hz, -C-), 147.1 (-C- Ar), 146.3 (d, *J*_{PC}= 6Hz, -C-), 140.7 (-C- Ar), 136.45 (-C- Ar), 133.8 (d, *J*_{PC}= 3Hz, -C-), 128.3 (CH-), 127.15 (CH-), 124.6 (d, *J*_{PC}= 6Hz, -CH), 122.0 (d, *J*_{PC}= 8Hz, -CH), 35.7 (-C^{IV}-, ^tBu), 34.7 (-C^{IV}-, ^tBu), 31.5 (CH₃-, ^tBu), 31.4 (CH₃-, ^tBu).

³¹P NMR (400MHz, toluene d₈, δ in ppm): δ =145.19

S3. Synthesis of Rhodium [Rh(η³-(C₃H₅)₃)] precursor from RhCl₃ 3H₂O

The synthesis was carried out according to the procedure described in the literature.^{[1],[2]}

Allylmagnesium bromide (35mmol) was added to a cold suspension (-10°C) of RhCl₃ 3H₂O (1.1g, 5.3 mmol) in THF (93 ml). The solution slowly lost its red-brown color to become yellow. The solution was then allowed to warm to room temperature and stirred for an additional 16 hours. The solvent was removed under reduced pressure and the residue extracted with pentane (previously distilled and deoxygenated) (3x20mL). The sublimation was carried out in a water bath at 40 °C and the formation of yellow crystals was observed onto the cold finger. (Yield= 520mg, 55%)

S4. Synthesis of rhodium nanoparticles stabilized by P-ligands

The synthesis of the Rh nanoparticles was carried out following the method reported by Chaudret and co-workers.^[3] In a typical procedure, the [Rh(η³-(C₃H₅)₃)] (64 mg, 0.28 mmol) was placed into a Fischer- Porter reactor and dissolved at -110°C (acetone/ N₂ bath) in 64 mL of dry and deoxygenated THF (using freeze-pump-thaw techniques) in the presence of the appropriate ligand (0.2 equivalents for bidentate ligands and 0.4 equivalents for monodentate ligands). The Fischer-Porter reactor was then pressurized under 6 bar of H₂ and stirred for 30 minutes at

room temperature. The solution was then heated to 40°C and stirred at this temperature during 24 h. The initial colorless solution became black after 1h. A small amount (5 drops approx.) of the solution was deposited under an argon atmosphere on a carbon-covered copper grid for transmission electron microscopy analysis. The rest of the solution was concentrated under reduced pressure. Precipitation and washing with pentane (3 x 15ml) was then carried out, obtaining a black precipitate. (Yield= *ca.* 25-30 mg, 30-35%)

S5. Synthesis of rhodium nanoparticles stabilized by a THF/MeOH mixture of solvents

The synthesis of the Rh nanoparticles was carried out following the method reported by Chaudret and co-workers.^[4] In a typical procedure, the $[\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_3]$ (64 mg, 0,28 mmol) was placed into a Fischer- Porter reactor, a mixture of solvents THF/MeOH in a 97.5:2.5 ratio was added. The Fischer-Porter reactor was then pressurized under 4 bar of H_2 and stirred at room temperature during 16h. The solution became black immediately. A small amount (5 drops approx.) of the solution was deposited under an argon atmosphere onto a carbon-covered copper grid for transmission electron microscopy analysis. The rest of the solution was concentrated under reduced pressure. Precipitation and washing with pentane (3 x 15ml) was then carried out, obtaining a black precipitate. (Yield= *ca.* 10-15 mg, 35-40%)

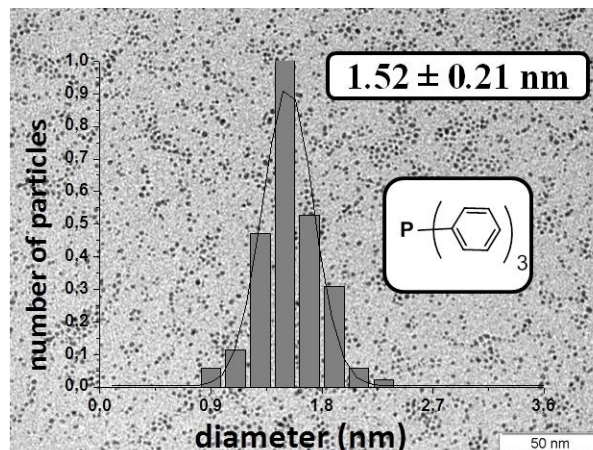
S6. General procedure for the synthesis of the Rh-NPs using the seeded-growth method.

In a typical procedure, the corresponding mixture of solvents (THF/MeOH 97.5:2.5) of 32 mL containing $[\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_3]$ (32 mg, 0.14 mmol) was added to a half THF/MeOH solution of previously prepared Rh-NPs (0.14 mmol of Rh).^[5] The reaction mixture was placed in a Fischer-Porter reactor, which was then pressurized under 4 bar of H_2 and stirred at room temperature during 16h. A small amount (5 drops approx.) of the solution was deposited under an argon atmosphere onto a carbon-covered copper grid for transmission electron microscopy analysis (TEM). The rest of the solution was concentrated under reduced pressure. Precipitation and washing with pentane (3 x 15ml) was then carried out, obtaining a black precipitate.

S7. Characterization of the rhodium nanoparticles Rh1-Rh5

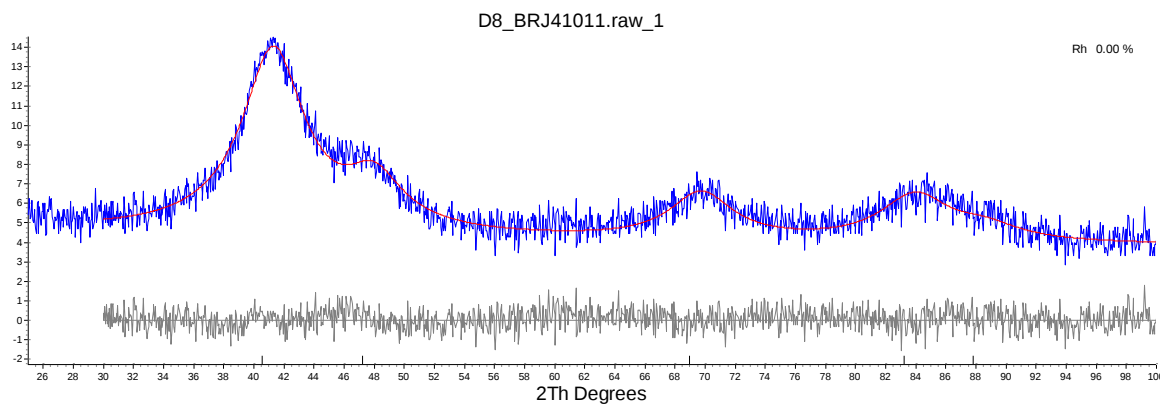
Rh1: Nanoparticles stabilized by PPh_3

TEM:

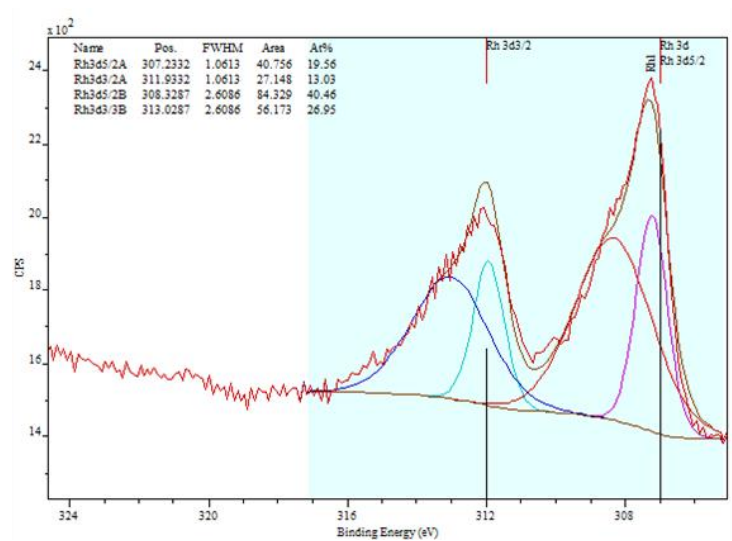


Elemental analysis: 4.57 % P, 36.49 % Rh

XRD: hcp crystalline Rh nanoparticles, coherence length 1.49 ± 0.034 nm

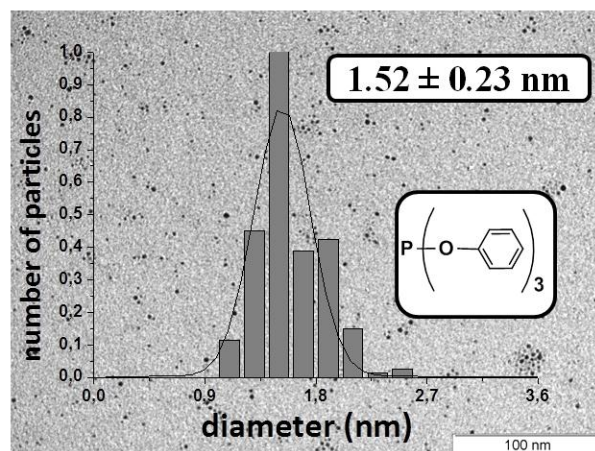


XPS: 0-30% of $\text{Rh}^{\delta+}$ at the surface of the NPs.



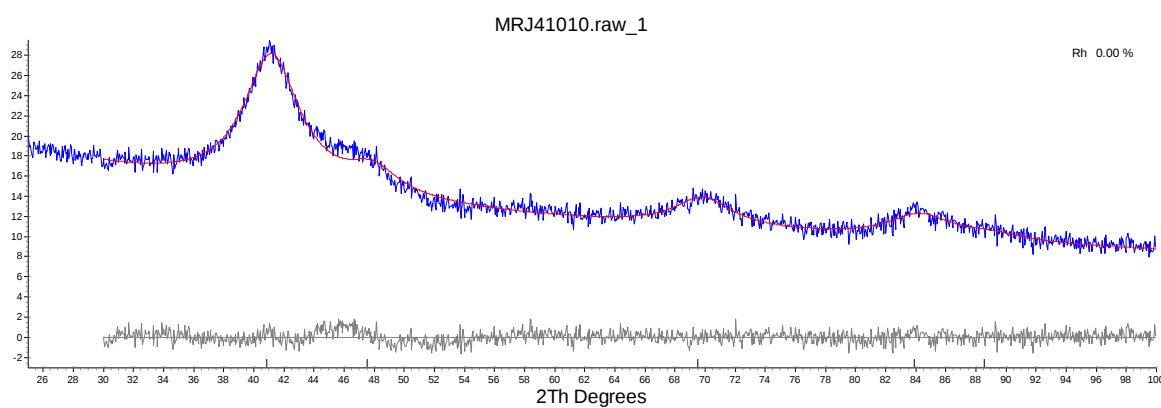
Rh2: Nanoparticles stabilized by $\text{P}(\text{OPh})_3$

TEM

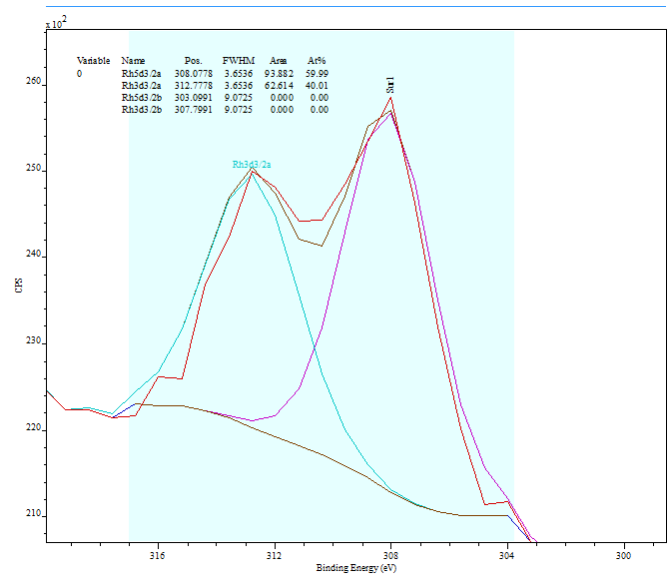


Elemental analysis : 4.59% P, 14.12% Rh.

XRD: hcp crystalline Rh nanoparticles, coherence length $1.53 \pm 0.023 \text{ nm}$

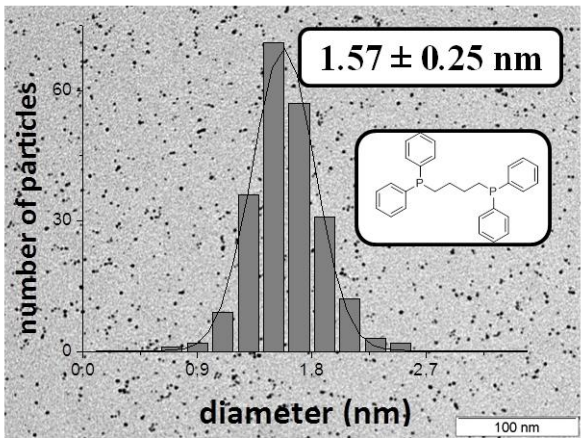


XPS: 100% of Rh(0) at the surface of the NPs.



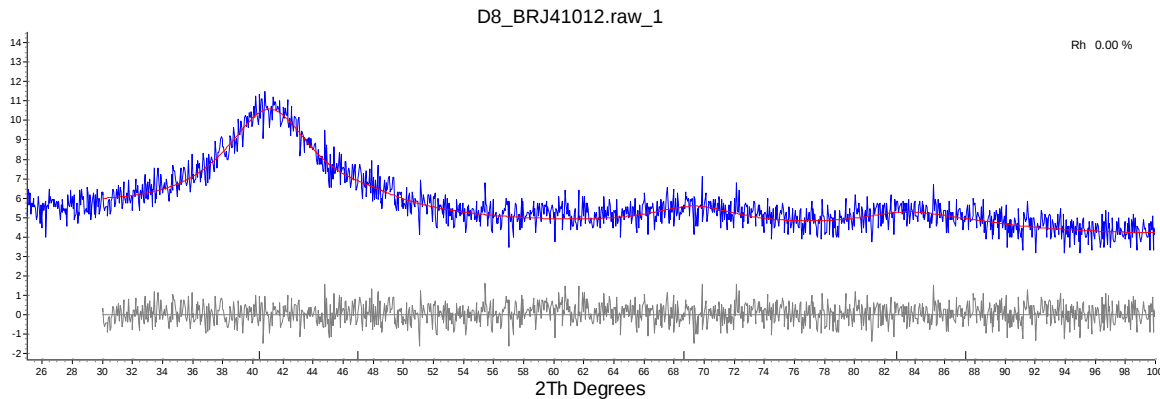
Rh3: Nanoparticles stabilized by dppb

TEM:

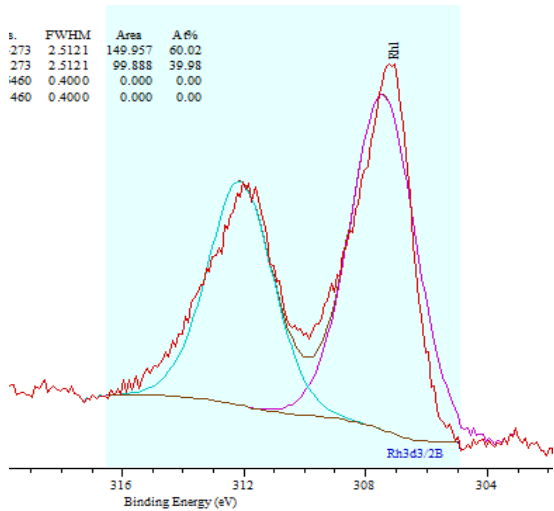


Elemental analysis: 4.41 % P, 41.83 % Rh

XRD: hcp crystalline Rh nanoparticles, coherence length 1.49 ± 0.07 nm

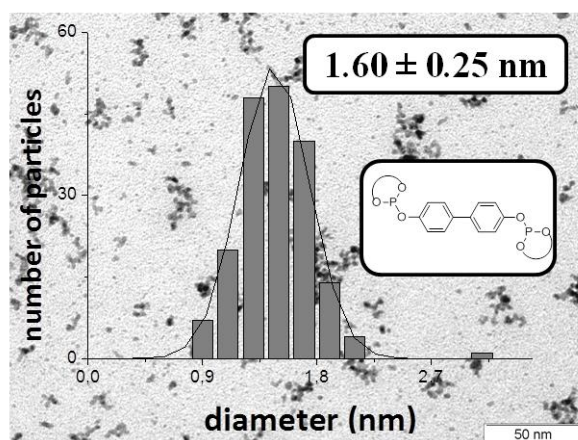


XPS: 100% of Rh(0) at the surface of the NPs.



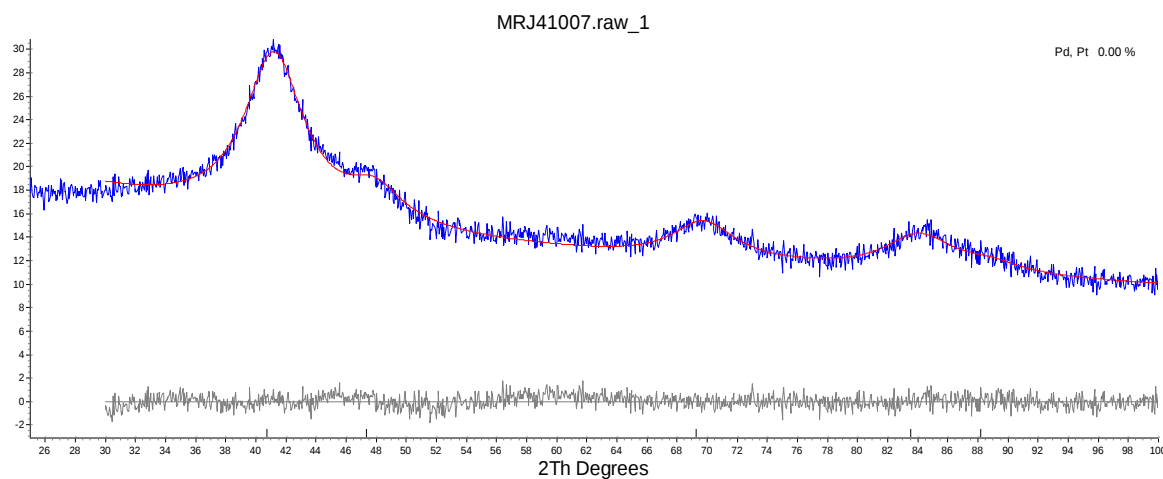
Rh4: Nanoparticles stabilized by the diphosphite **4**

TEM:

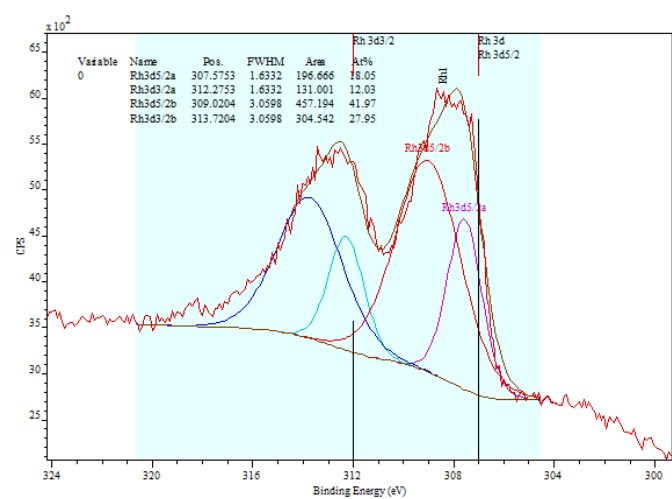


Elemental analysis: 2.09 % P, 15.56 % Rh

XRD: hcp crystalline Rh nanoparticles, coherence length 1.43 ± 0.02 nm

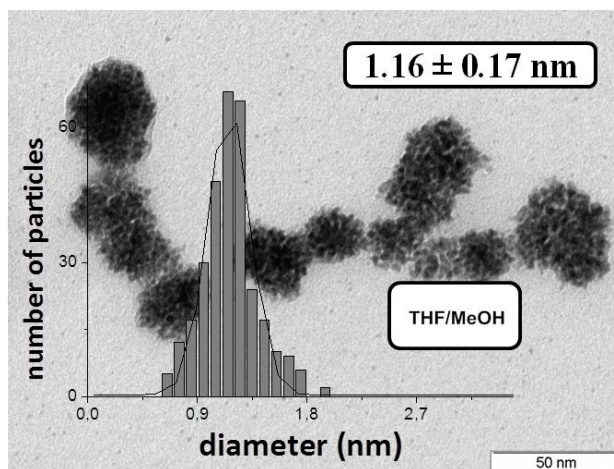


XPS: 0-30% of $\text{Rh}^{\delta+}$ at the surface of the NPs.



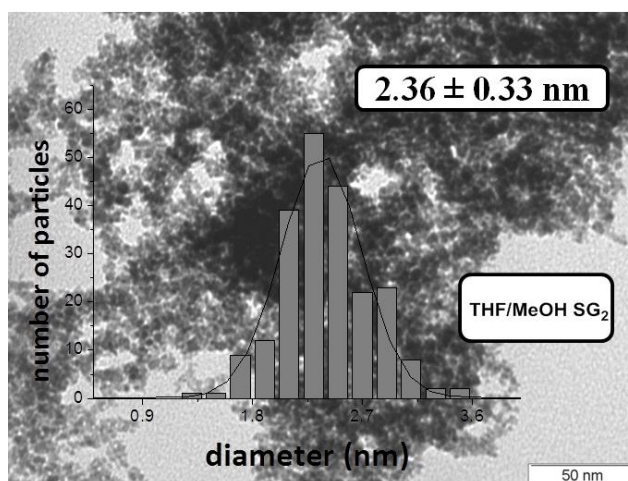
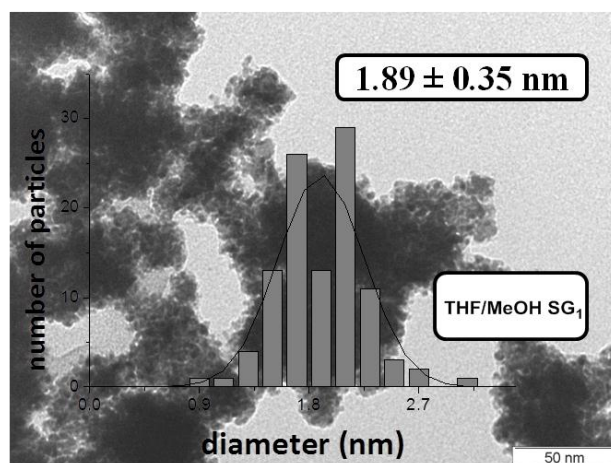
Rh5: Nanoparticles stabilized by THF/ MeOH

TEM:



Elemental analysis: 47.46 % Rh

TEM pictures of THF/MeOH nanoparticles synthesised by seeded growth method



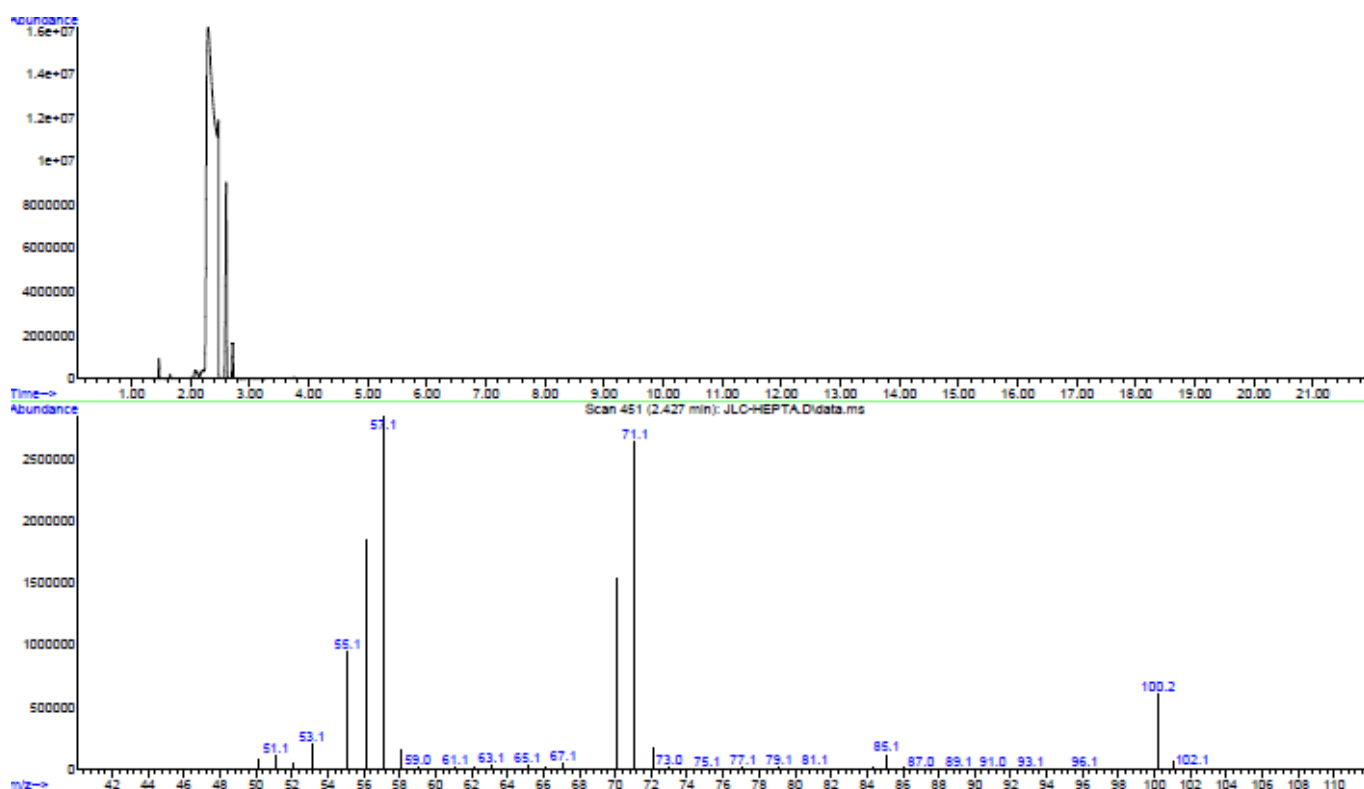
S8. Catalytic experiments

In a typical experiment, a 5 entries autoclave was charged in the glove-box with 3.5 mg of Rh nanoparticles and 1.24 mmol of the substrate in 10 ml of heptane. Molecular hydrogen was then introduced until the desired pressure was reached. At the end of the reaction, the autoclave was depressurized and the solution was filtered over celite and analyzed by Gas Chromatography. The identification of the reaction products were performed by GC-MS and the quantification by GC-FID on a HP 6890A spectrometer with an HP-5 column (0.25mm x 30m x 0.25um), $T^a = 205^\circ\text{C}$ injector, flow 1.5ml/min.

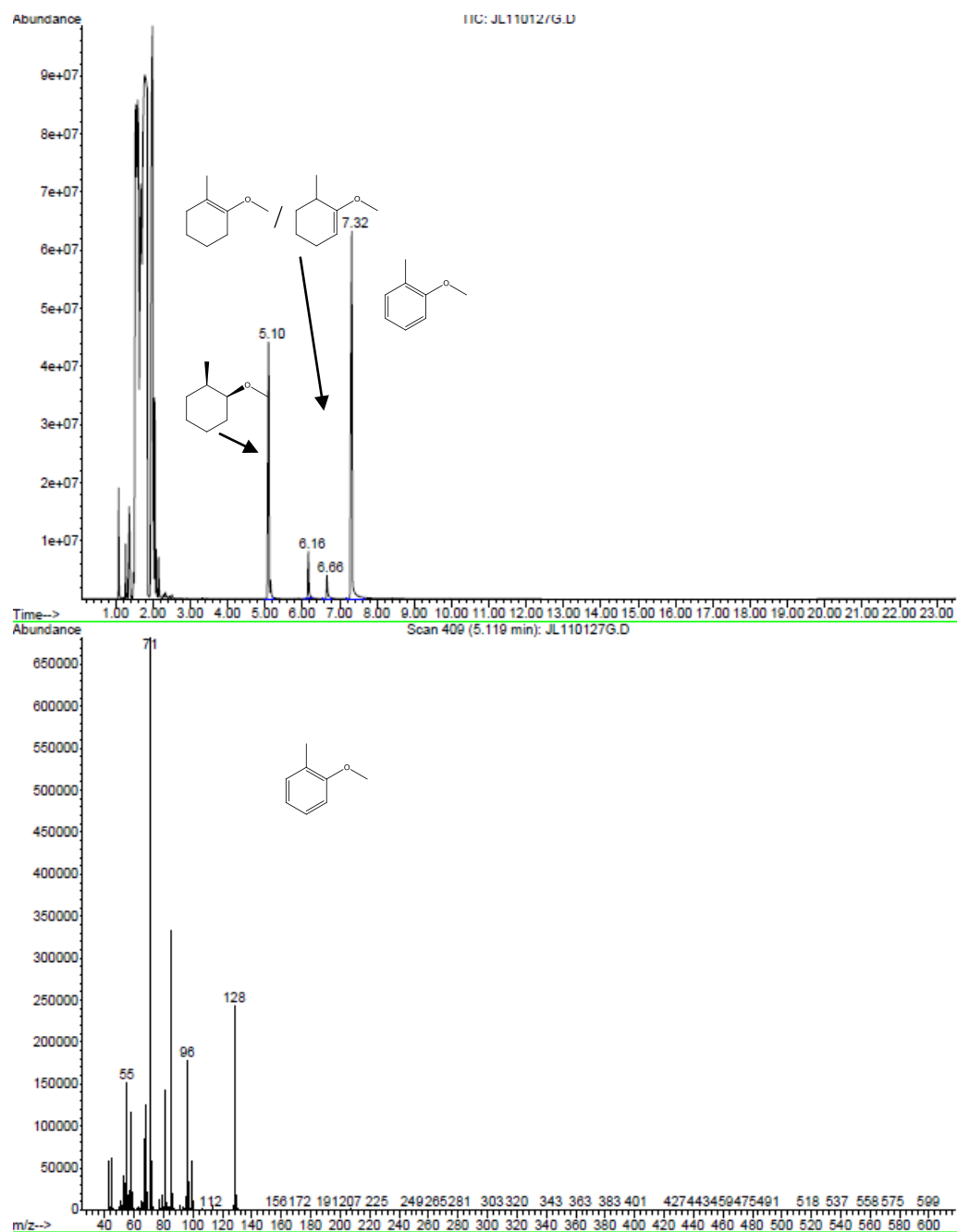
In the following sections, the GC-MS chromatograms of the hydrogenation reactions are displayed:

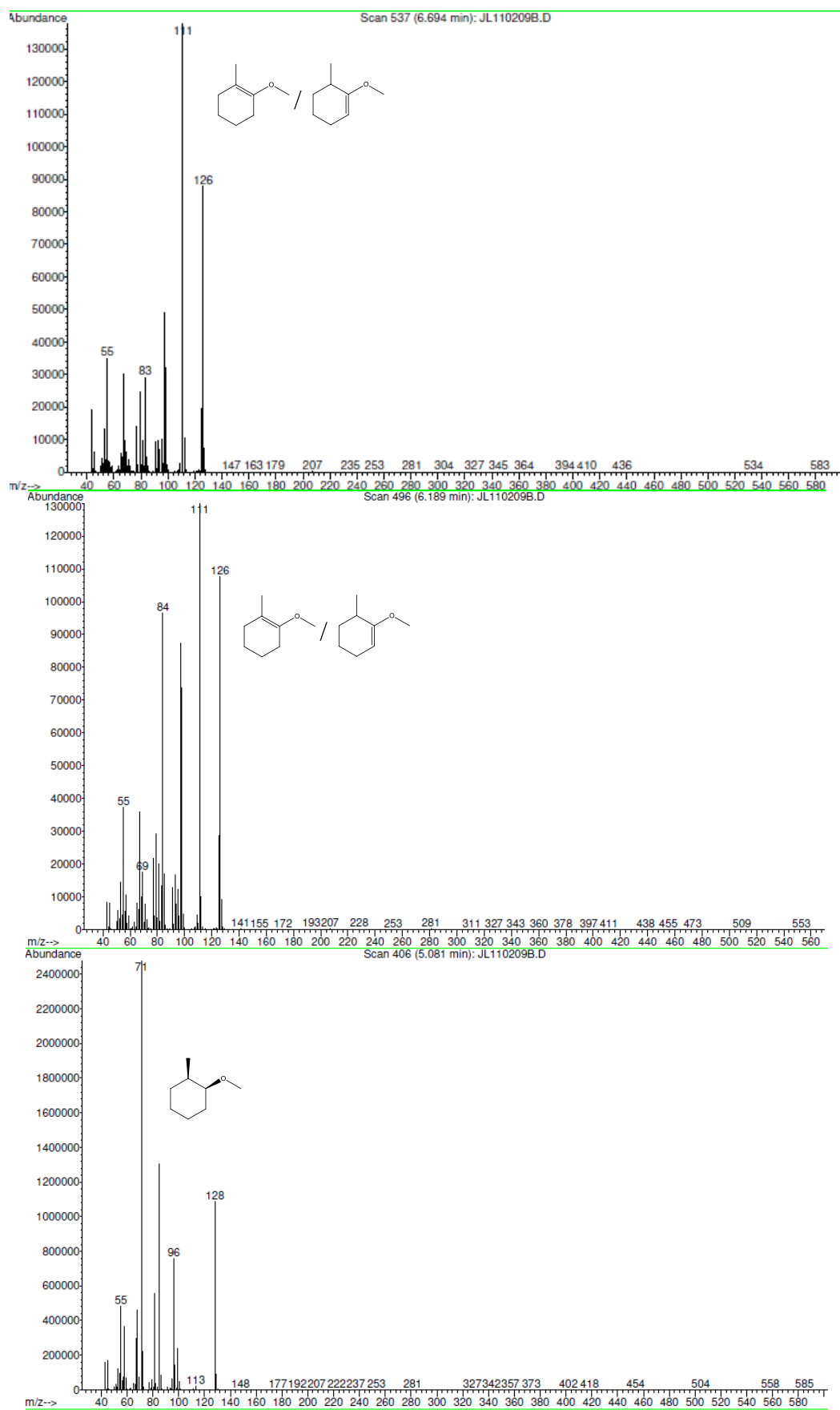
(Note: the drawing do not represent the absolute configuration of the products)

Chromatogram of heptane used as solvent

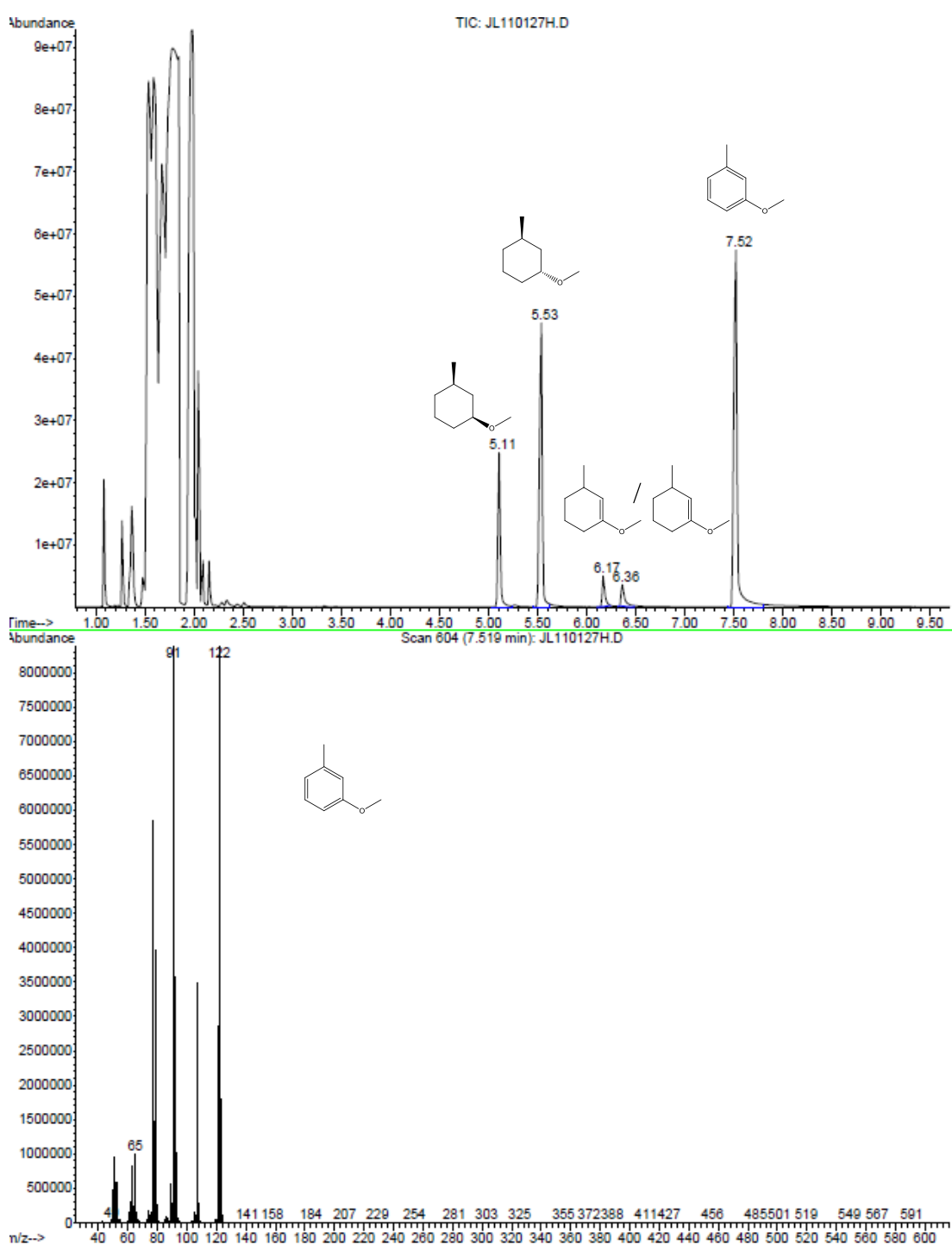


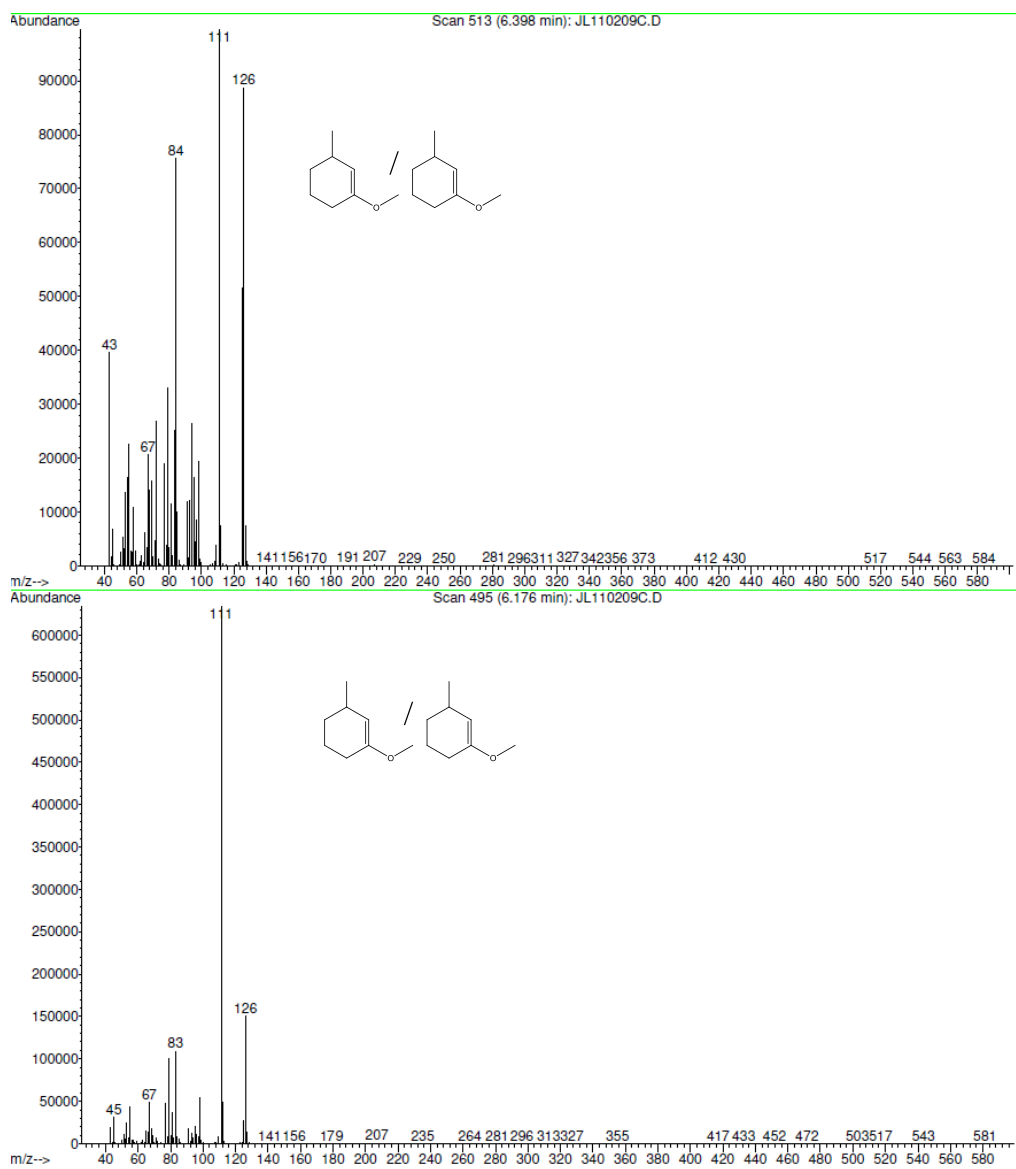
Hydrogenation of *o*-methylanisole

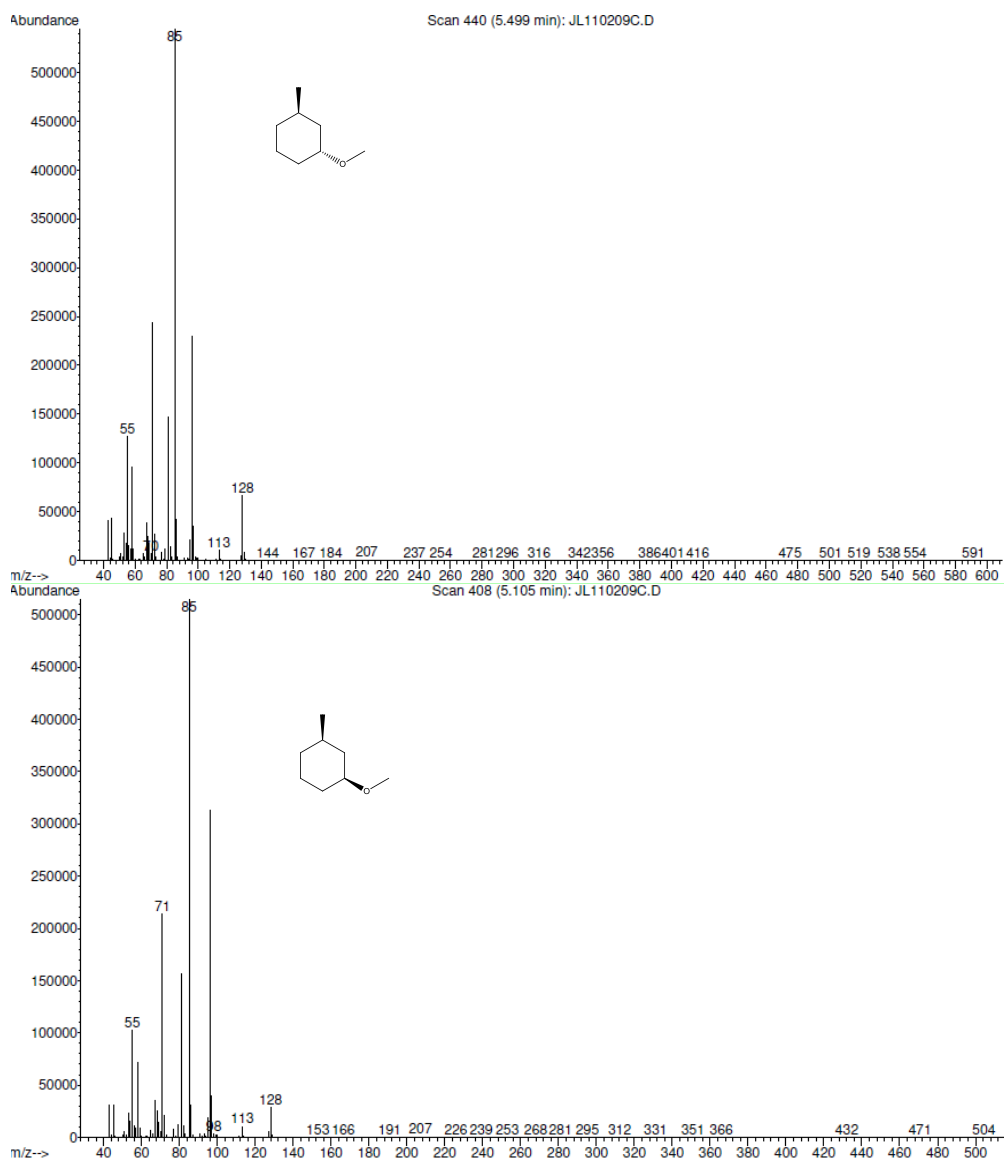




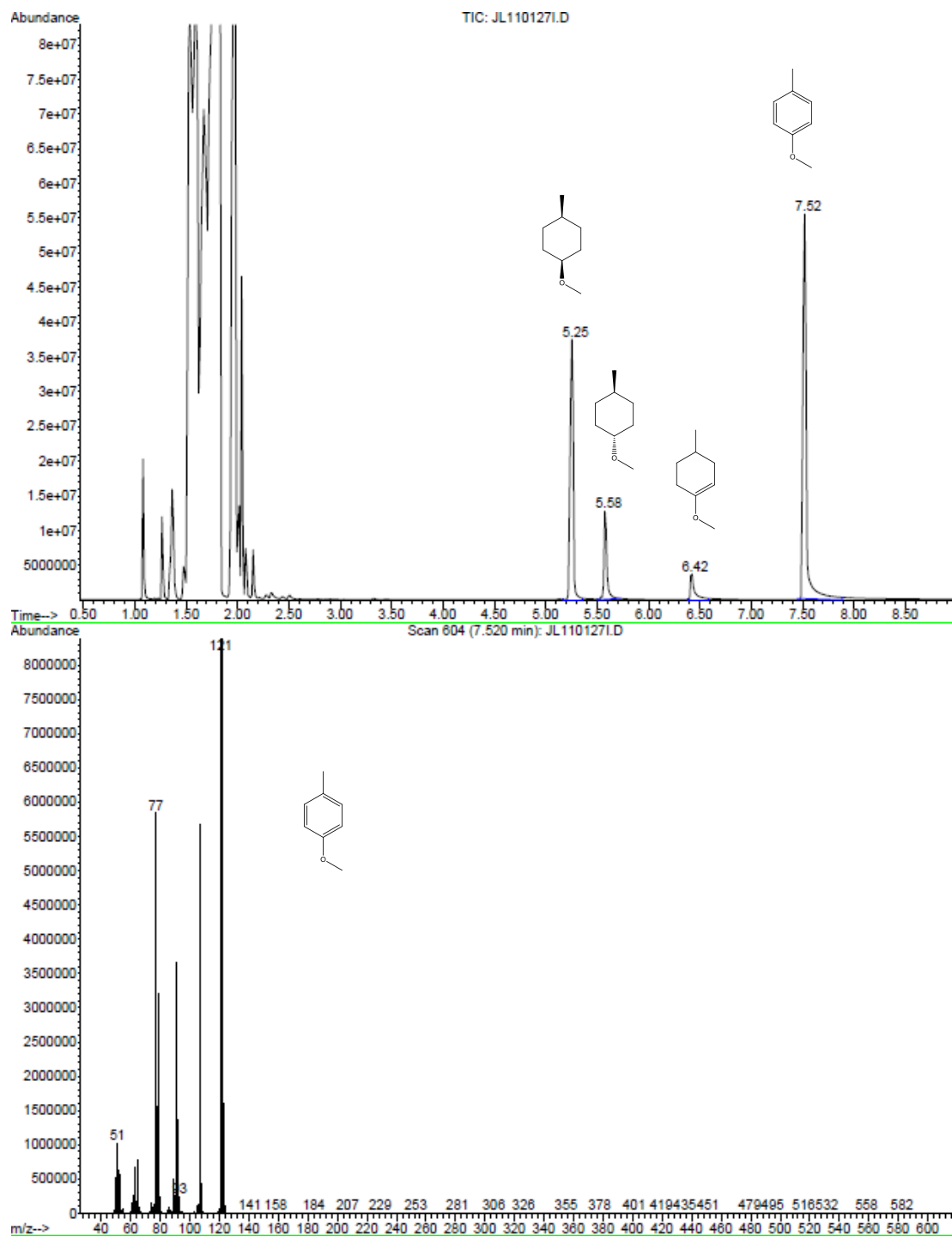
- Hydrogenation of *m*-methylanisole

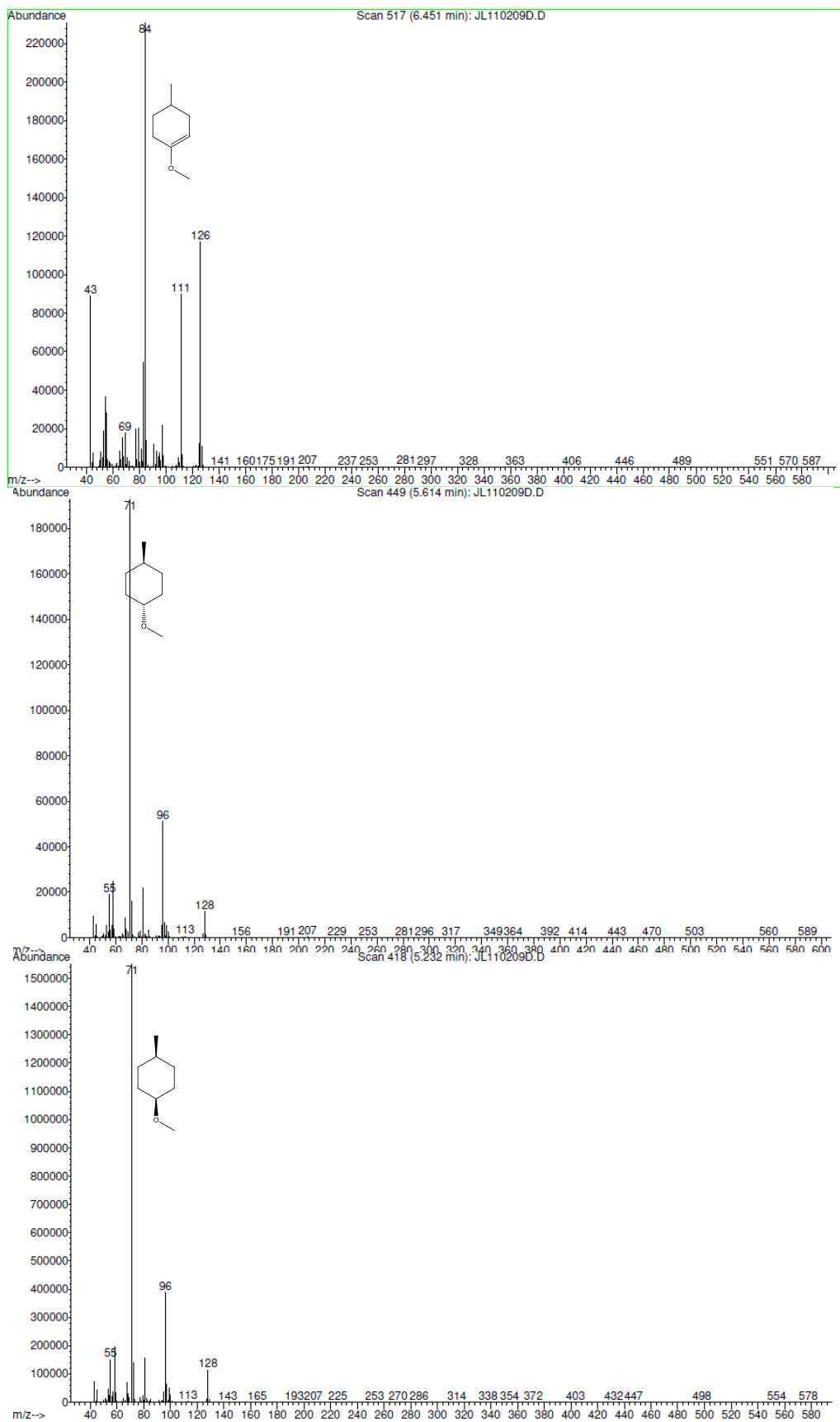




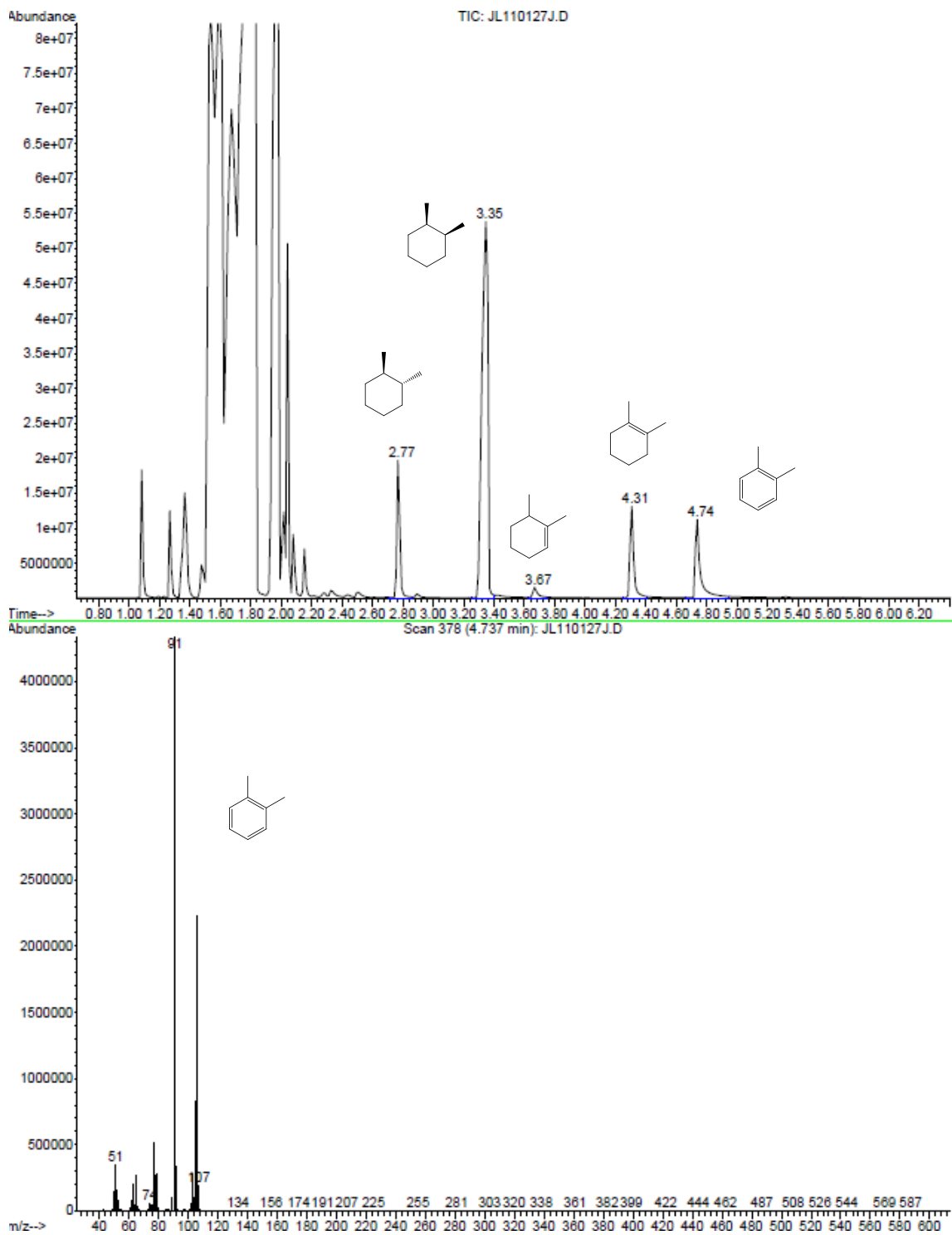


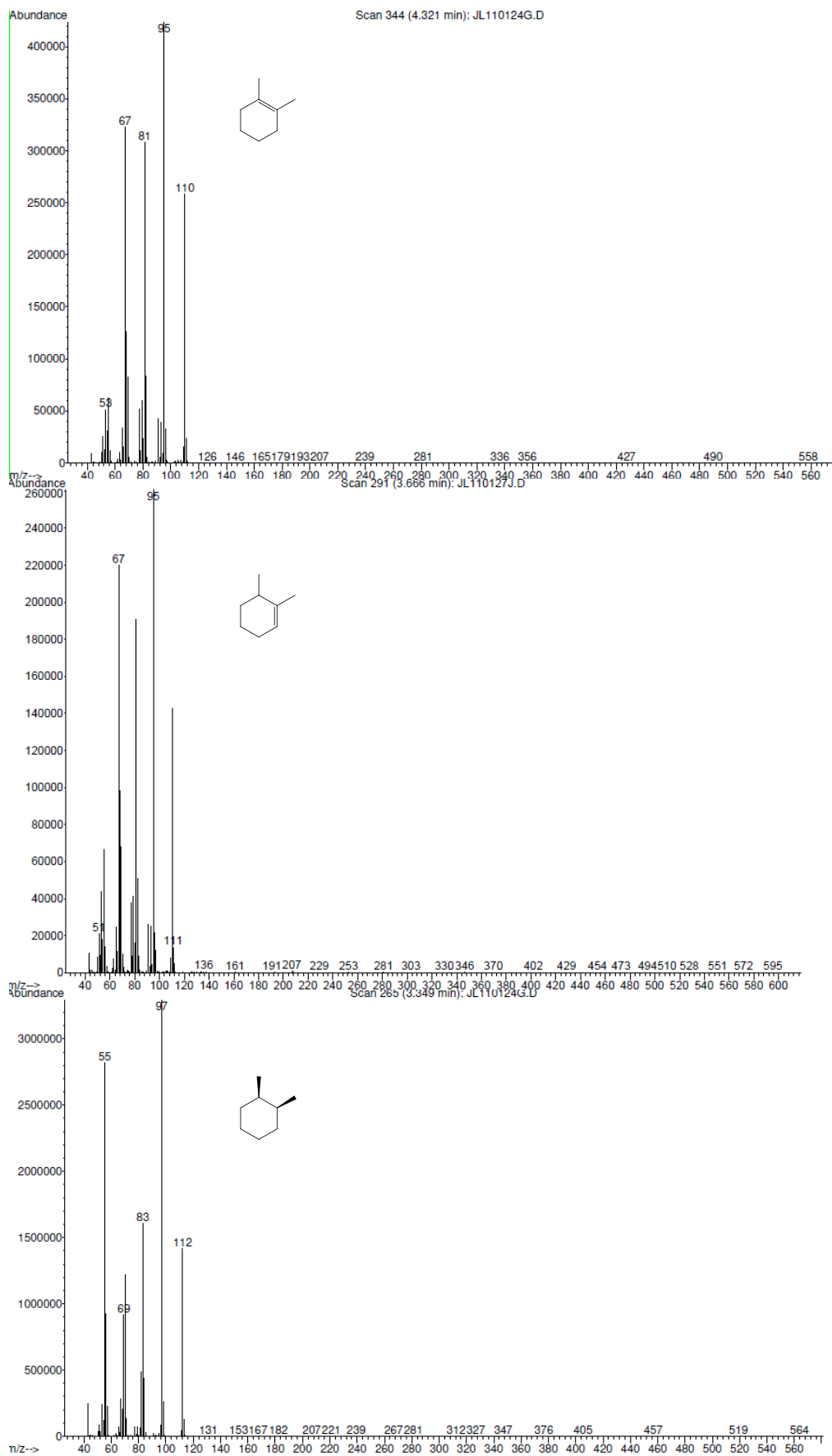
- Hydrogenation of *p*-methylanisole

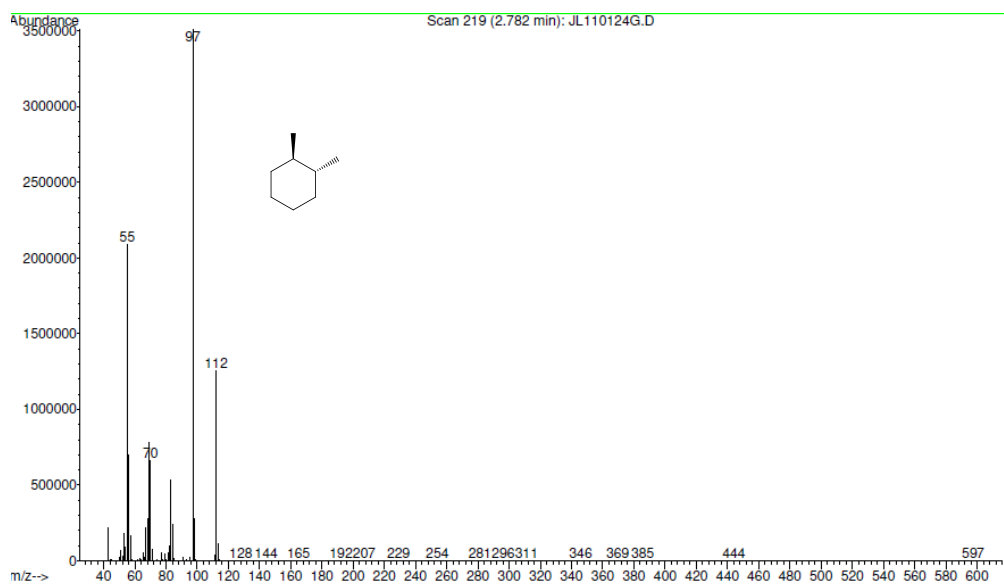




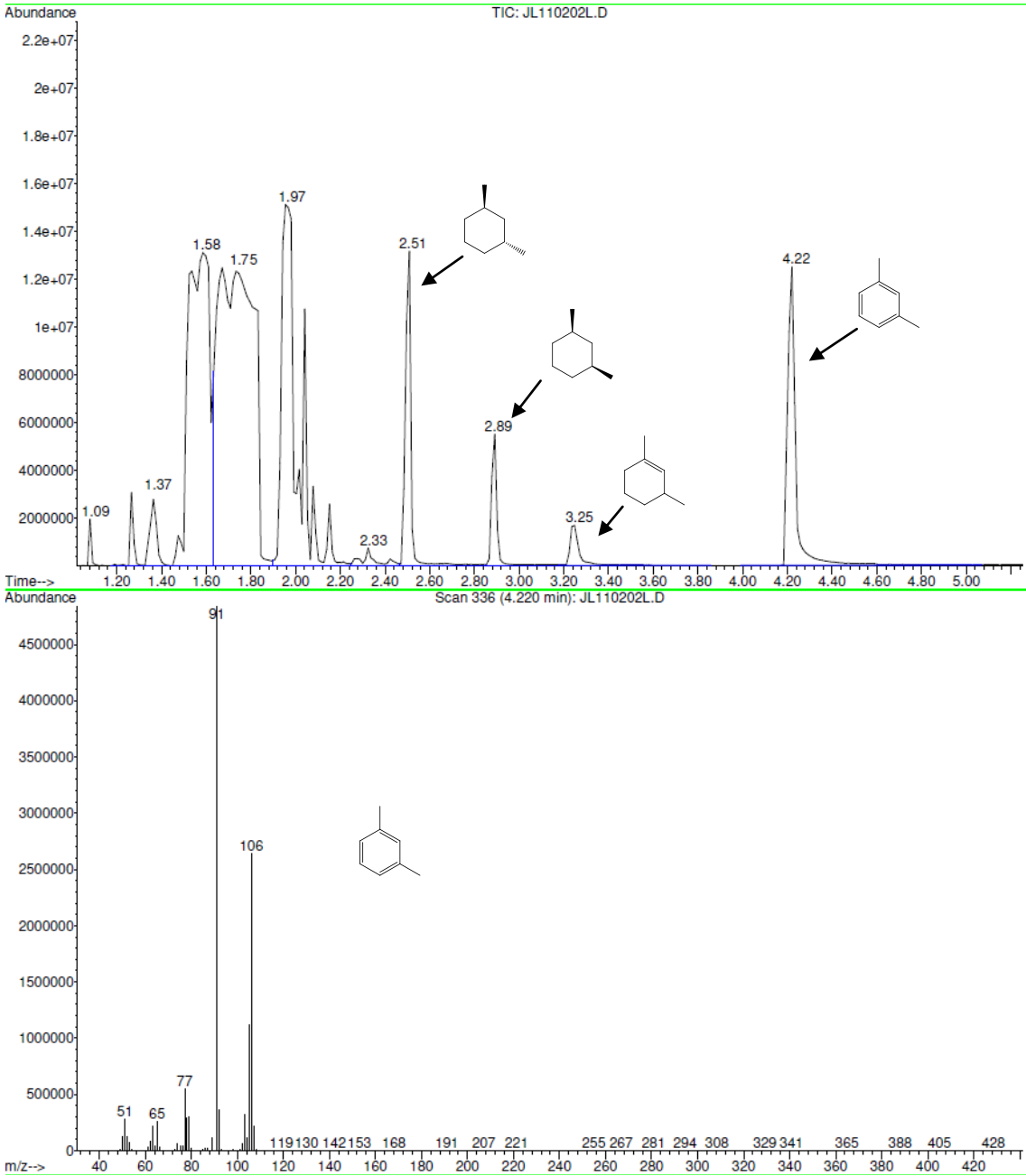
- Hydrogenation of *o*-xylene

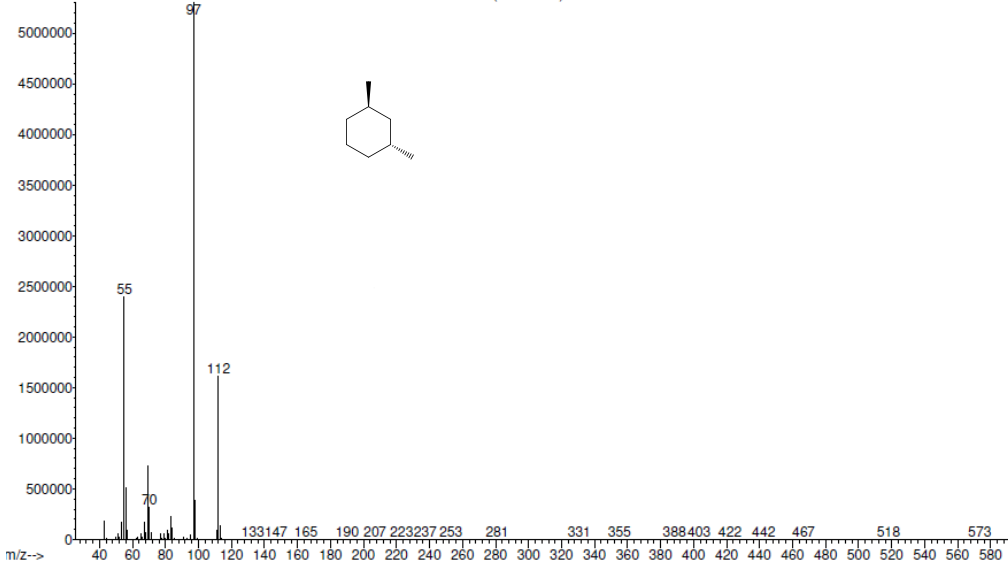
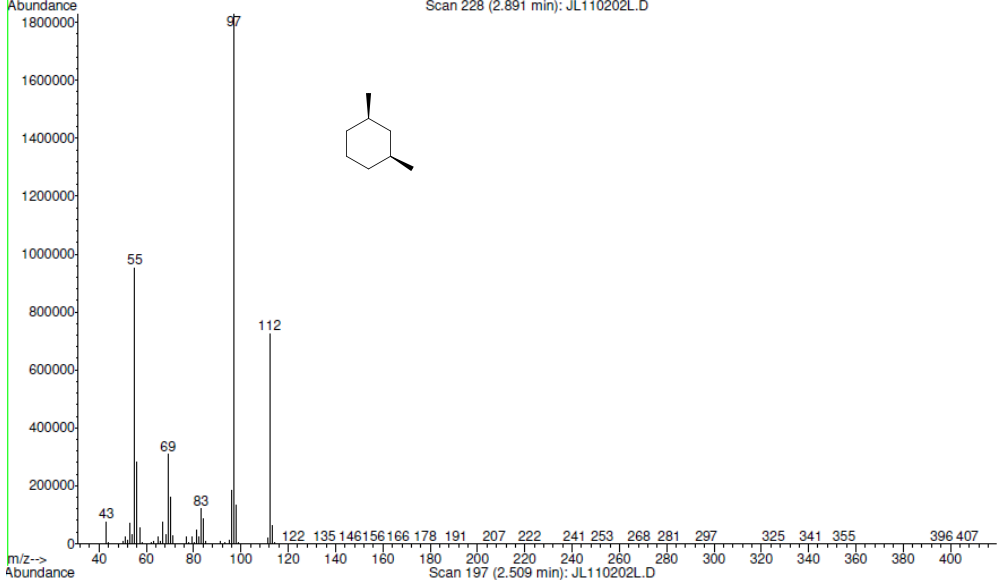
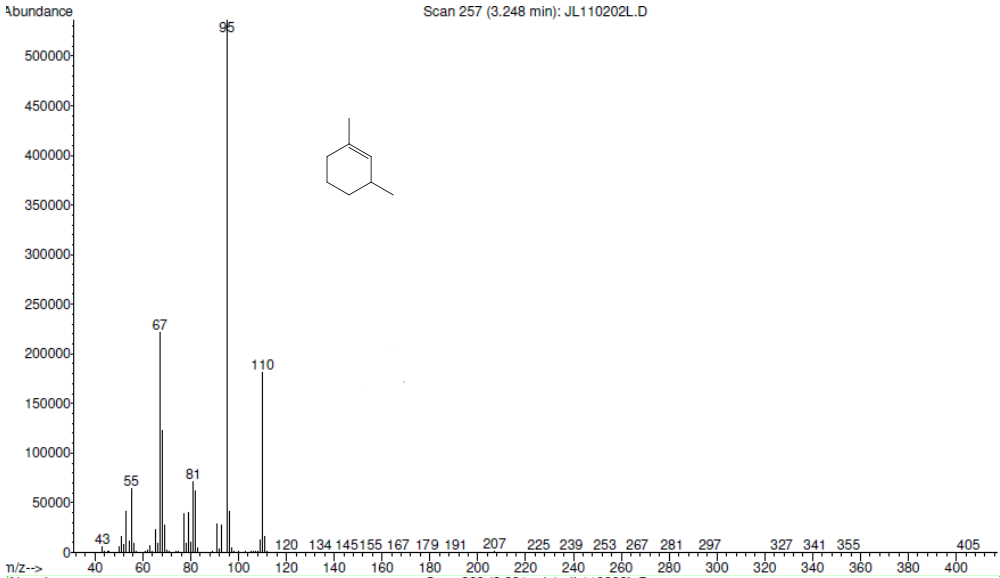




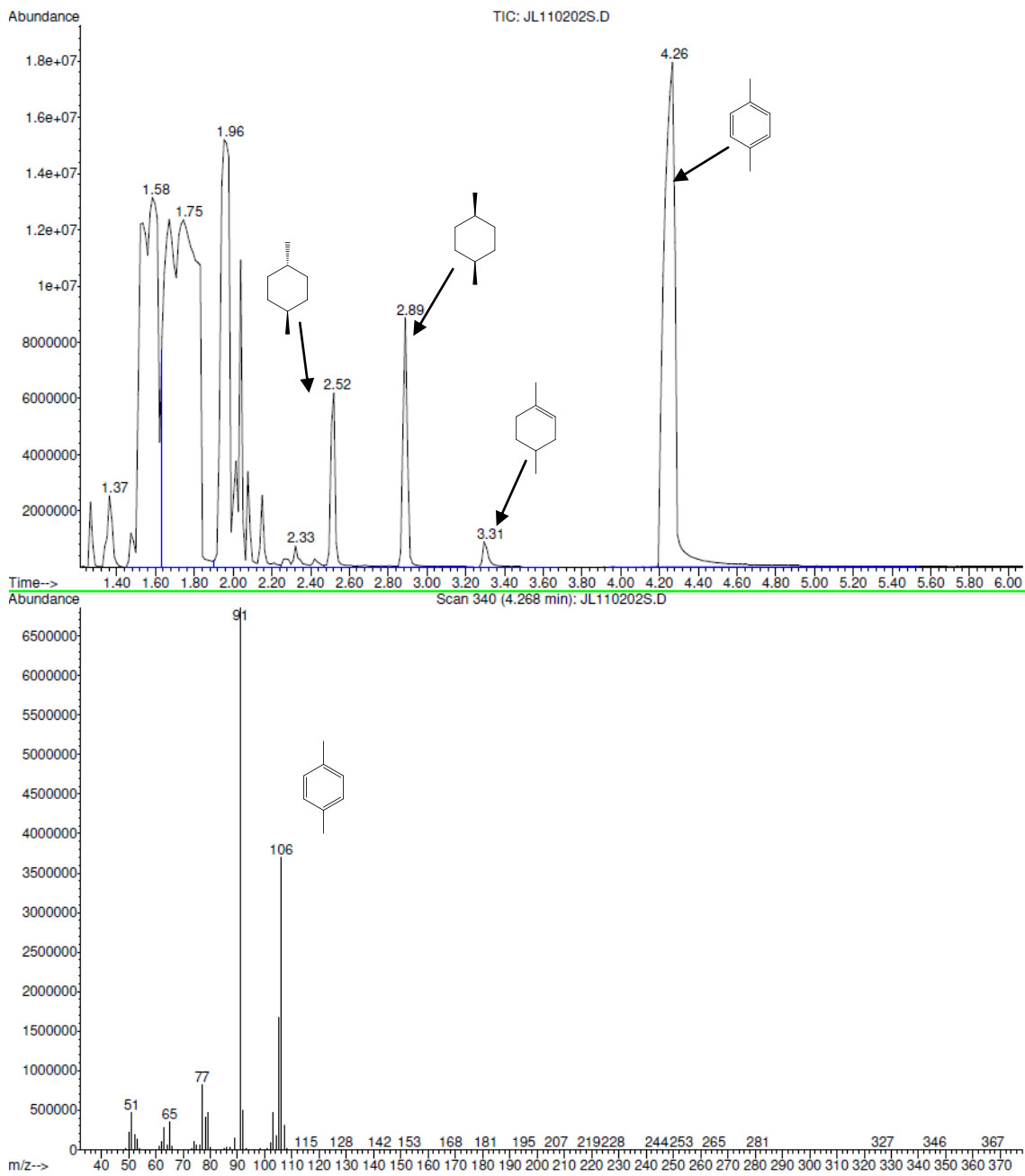


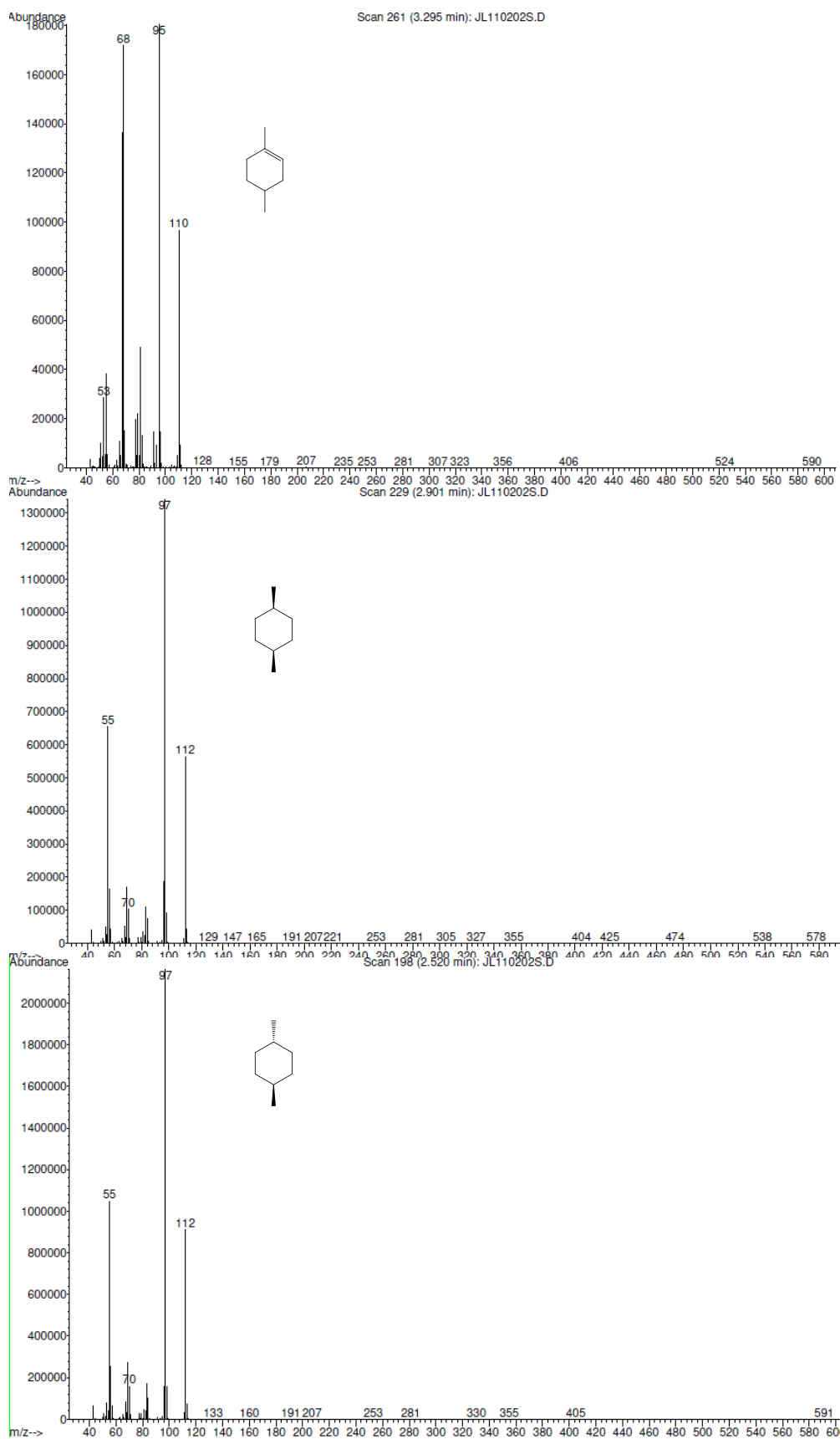
-Hydrogenation of *m*- xylene



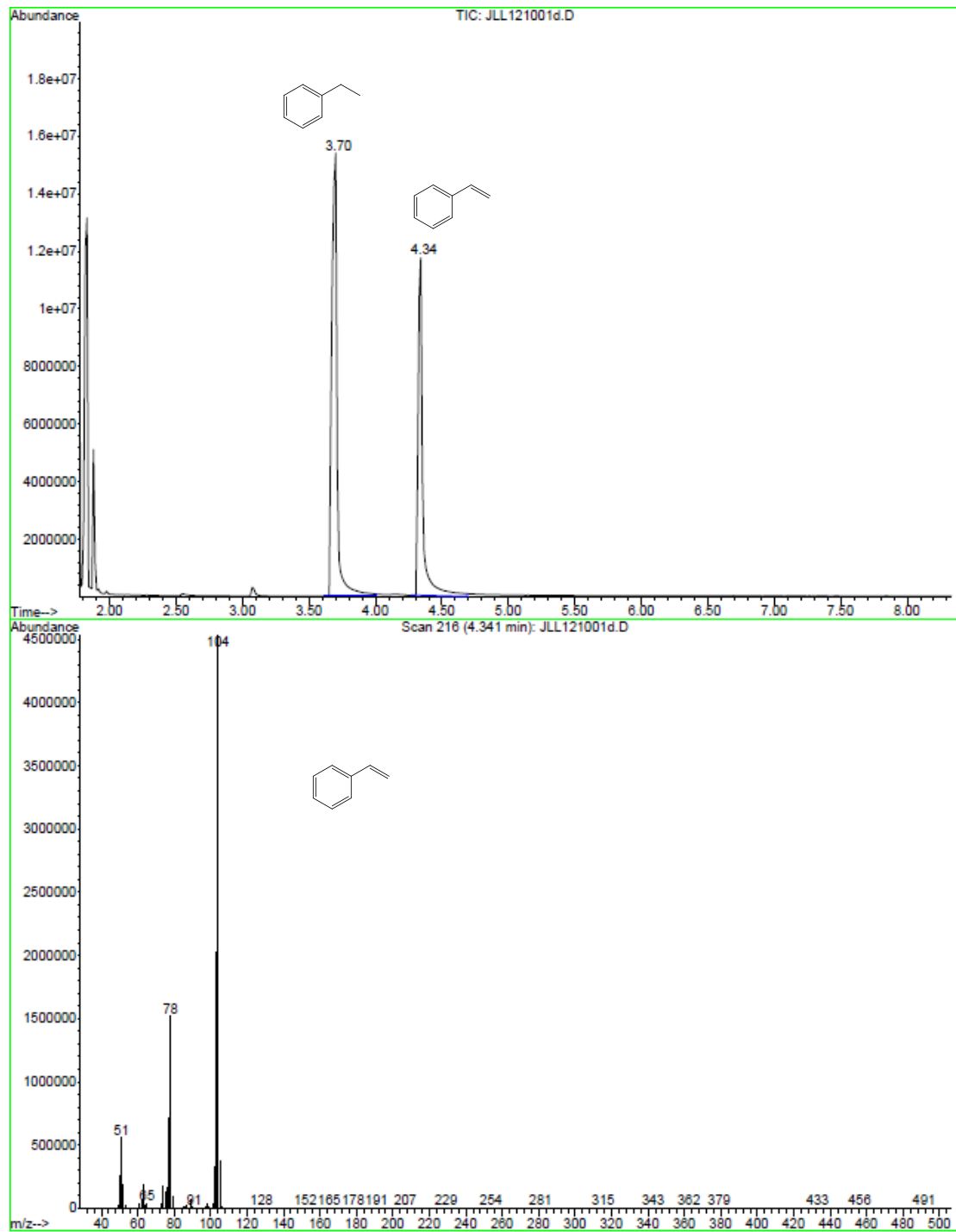


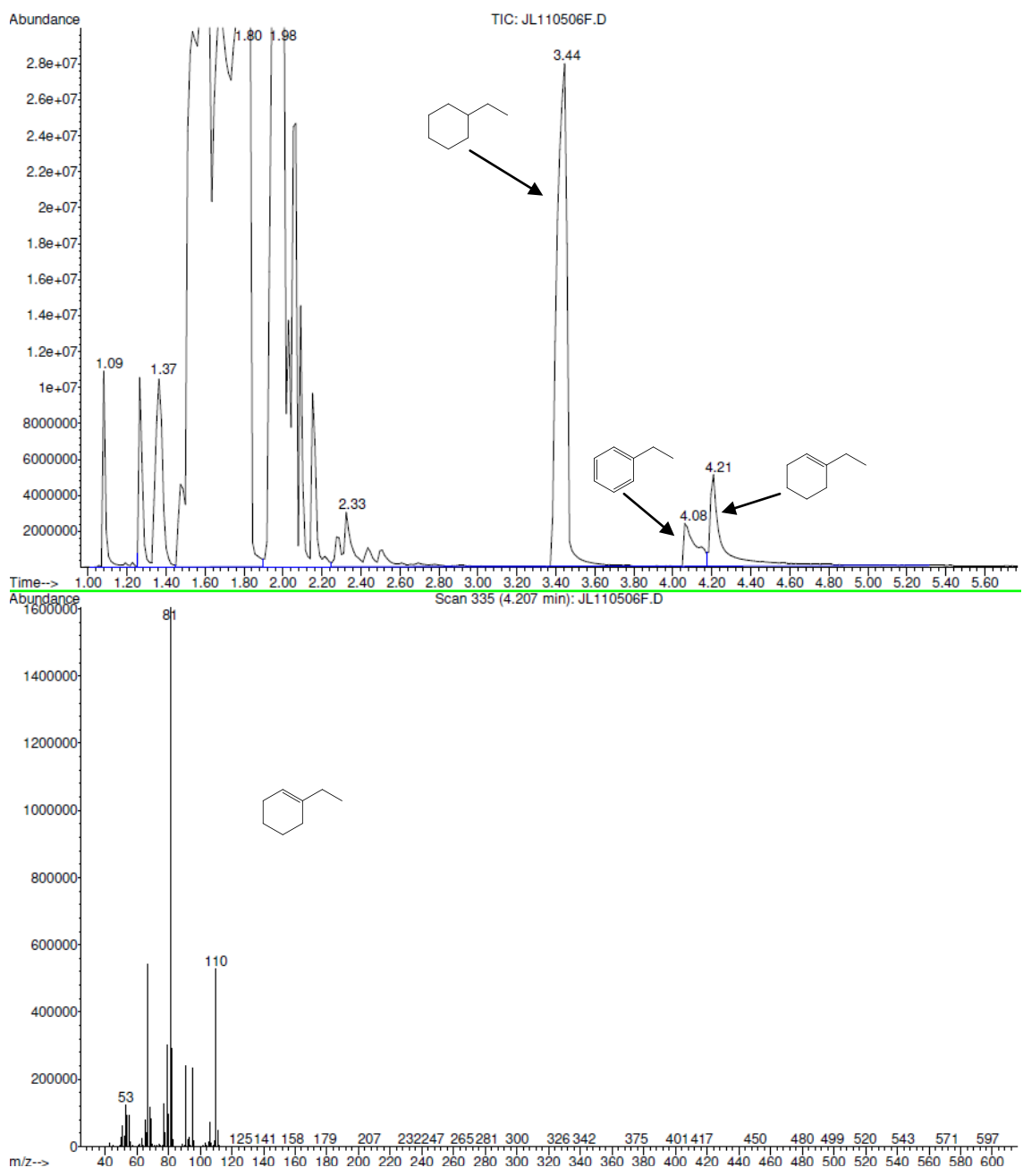
- Hydrogenation of *p*-xylene

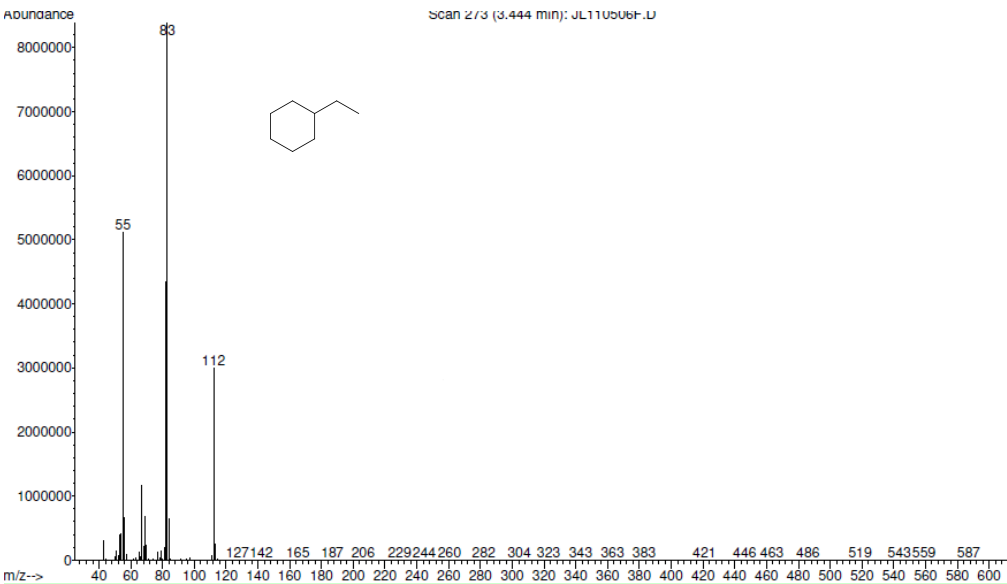
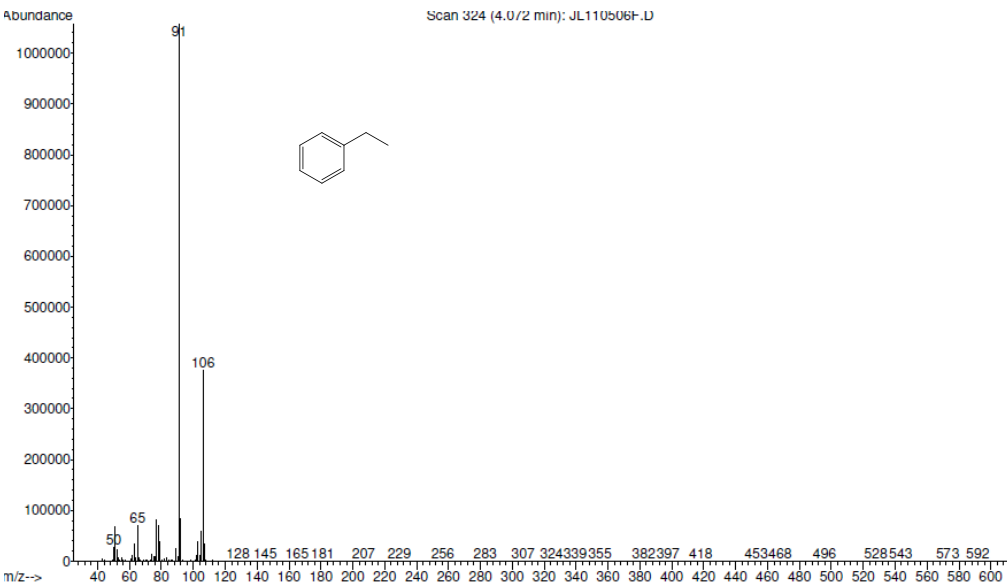




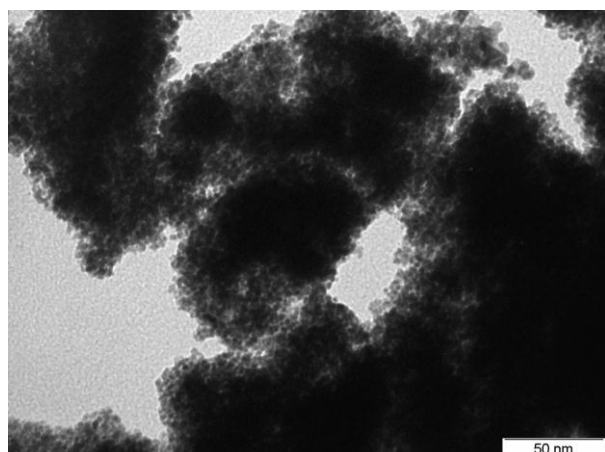
- Hydrogenation of styrene







Example of a TEM micrograph of the nanoparticles after catalytic experiments.



S9.References

- [1] M. D. Fryzuk, W. E. Piers in *Organometallic Syntheses* (Eds.:R. B. King, J. J. Eisch), Elsevier, Amsterdam, **1986**, vol. 3, p.128.
- [2] W. A. Herrmann in *Synthetic Methods of Organometallic and Inorganic Chemistry* (Ed.: W. A. Herrmann), Thieme, Stuttgart, **1996**, p. 38.
- [3] B. Chaudret, *C. R. Physique*, **2005**, 6, 117-131.
- [4] K. Pelzer, O. Vidoni, K. Philippot, B. Chaudret and V. Collière, *Adv. Funct. Mater*, **2003**, 13, 118-126.
- [5] C.X. Xiao, Z.P. Cai, T. Wang, Y. Kou, N. Yan, *Angew. Chem. Int. Ed.*, **2008**, 47, 746- 749.