Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

SUPPORTING INFORMATION

Selective catalytic hydrogenation of polycyclic aromatic hydrocarbons promoted by ruthenium nanoparticles.

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Table of contents:

S1. General, materials and characterization techniques.

General methods. All syntheses were performed using standard Schlenk techniques under N_2 or Ar atmosphere. Chemicals were purchased from Aldrich Chemical Co, Alfa Aesar, Fluka and Strem. All solvents were distilled over drying reagents and were deoxygenated before use. The precursor [Ru(COD)(COT)] was purchased from Nanomeps.

The TEM experiments were performed at the "Unitat de Microscopia dels Serveis Cientificotècnics 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.

The HRTEM experiments were performed at the Unitat de Microscopia dels Serveis Científics i Tecnològics de la Universitat de Barcelona with a JEOL 1010 electron microscope working at 200kV with a resolution of 2.5 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.

The elemental analysis was performed at the Centres Científics i Tecnològics of the Universitat de Barcelona (UB) using the Inductive Coupled Plasma / Optical Emission Spectroscopy technique (ICP-OES) with a Perkin Elmer Optima 3200RL instrument using standard conditions.

XRD measurements were made using a Siemens D5000 difractometer (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 2θ 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. $Cu_{k\alpha}$ radiation was obtained from a copper X- ray tube operated at 40kV and 30mA.

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.

WAXS analysis were performed at CEMES-CNRS. Samples were sealed in 1 mm diameter Lindemann glass capillaries. The samples were irradiated with graphite-monochromatized Mokα (0.071069 nm) radiation and the X-ray intensity scattered measurements were performed using a dedicated two-axis diffractometer. Radial distribution functions (RDF) were obtained after Fourier transform of the reduced intensity functions.

The TGA experiments were carried out in the furnace of a Mettler Toledo TGA/SDTA851 instrument.

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= 250ºC injector, flow 1.5ml/min.

S2. Synthesis of ruthenium nanoparticles stabilized by P-ligands[1]

The synthesis of the Ru nanoparticles was carried out following the previously reported procedure[1]. In a typical procedure, the [Ru(COD)(COT)] (400 mg, 1.268 mmol) was placed into a Fischer- Porter reactor and dissolved in 400 mL of dry and deoxygenated THF (using freeze-pump-thaw techniques) in the presence of 0.4 equivalents of PPh_3). The Fischer-Porter reactor was then pressurized under 3 bar of H_2 and stirred for 24 h at room temperature. The initial yellow solution became black after 20 minutes. 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 to 40 mL under reduced pressure. Precipitation and washing with pentane (3 x 15ml) was then carried out, obtaining a black precipitate (Yield= *ca*. 140 mg, 80%).

TEM: mean size 1.32±0.28 nm

XRD: hcp crystalline ruthenium nanoparticles, coherence length 1.01±0.02 nm

XPS: 3d5/2(280.68 eV) and 3d3/2(285.38 eV), 100% Ru(0) on the nanoparticles surface

TGA: 69% Ru, 29% PPh_3, 2% THF.

S3. Catalytic experiments. General procedures

In a typical experiment, a 5 entries autoclave or an autoclave Par 477 equipped with PID control temperature and reservoir for kinetic measurements were charged in the glove-box with 3 mg of Ru nanoparticles (the catalyst concentration was calculated based on the total number of metallic atoms in the NPs) and the substrate in 10 mL of solvent. Molecular hydrogen was then introduced until the desired pressure was reached. The reaction was stirred during the corresponding time at the desired temperature. The autoclave was then depressurised. The solution was filtered over silica and analysed by gas chromatography.

Conversion and selectivity was determined by GC-MS and *cis*/*trans* selectivity was confirmed by NOE experiments in NMR. GC-MS spectroscopy was carried out on a HP 6890A spectrometer, with an HP-5 column (0.25mm x 30m x 0.25µm). The method used for the polyaromatic systems consist in an initial isotherm period at 130°C for 10 min followed by a 10°C min^{-1} temperature ramp to 180°C and a hold time of 35 min, flow 3.5 ml/min.

The method used for the substituted naphthalenes consist in an initial isotherm period at 40°C for 3 min followed by a 3°C min^{-1} temperature ramp to 120°C and a hold time of 12 min, flow 1.3 ml/min.

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

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

- Substrate **1**: tr_{1}=2.03 min, tr_{1a}=1.83 min, tr_{1b}=1.58 min, tr_{1c}=1.41 min.
- Substrate **2**: tr_{2}=14.91min, tr_{2a}=14.22 min, tr_{2b}=13.15 min, tr_{2c}=10.73 min, tr_{2d}=12.76 min, tr_{2e}=8.37 min.
- Substrate **3**: tr_{3}=14.72 min, tr_{3a}=13.04 min, tr_{3b}=14.31 min, tr_{3c}=13.71 min.
- Substrate **4**: tr_{4}= 46.46 min, tr_{4a}= 44.62 min, tr_{4b}= 41.16 min, tr_{4c}= 36.74 min, tr_{4d}= 20.58 min, tr_{4e}= 21.90 min.
- Substrate **5**: tr_{5}= 22.80 min, tr_{5a}= 20.80 min, tr_{5b}= 18.27 min.
- Substrate **6**: tr_{6}=5.56 min, tr_{6a}=4.91 min, tr_{6b}= 3.68 min, tr_{6c}= 3.02 min.
- Substrate **7**: tr_{7}=27.39 min, tr_{7a}=25.96 min, tr_{7b}=23.70 min, tr_{7c}=20.51 min.
- Substrate **9**: tr_{9}=5.46 min, tr_{9a}=4.55 min, tr_{9b}=3.39 min, tr_{9c}= 2.90 min.
- Substrate **10**: tr_{10}=2.11 min, tr_{10a}=2.04 min, tr_{10b}= 1.96 min, tr_{10c}=1.86 min.
- Substrate **11**: tr_{11}=7.94 min, tr_{11a}=6.41 min.
- Substrate **12**: tr_{12a}=11.56min, tr_{12b}=10.79 min, tr_{12c}=9.21 min.
- Substrate **13**: tr_{13}=14.06 min, tr_{13a}=12.55 min, tr_{13b}=13.61 min.

S4. Gas Chromatography-Mass Spectrometry

- Hydrogenation of Naphthalene **1**

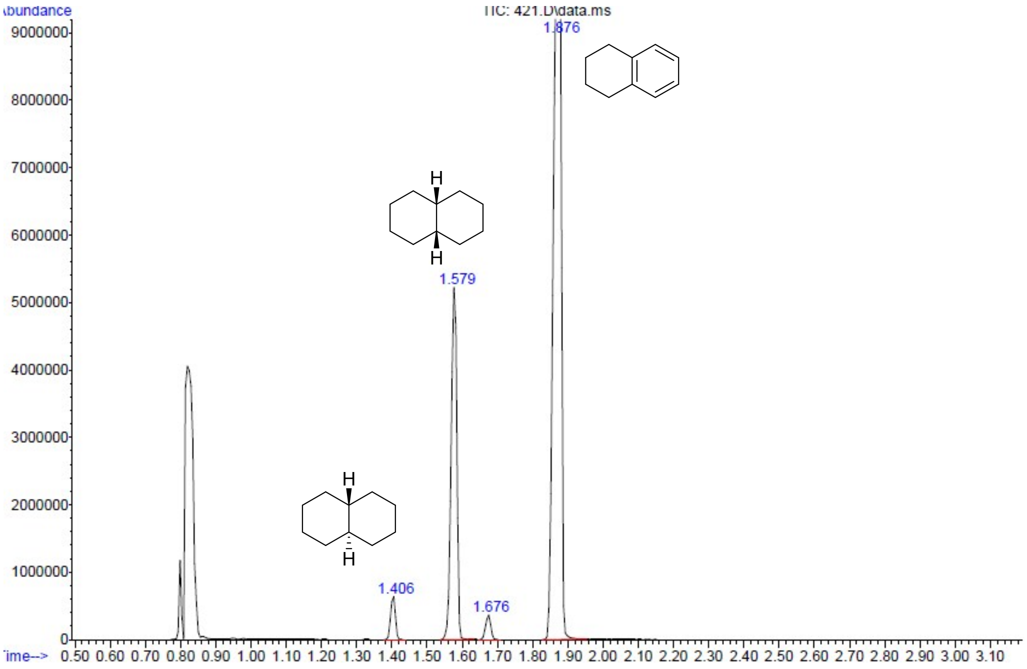

Figure 1. GC of the products formed in the hydrogenation of Naphthalene **1**.

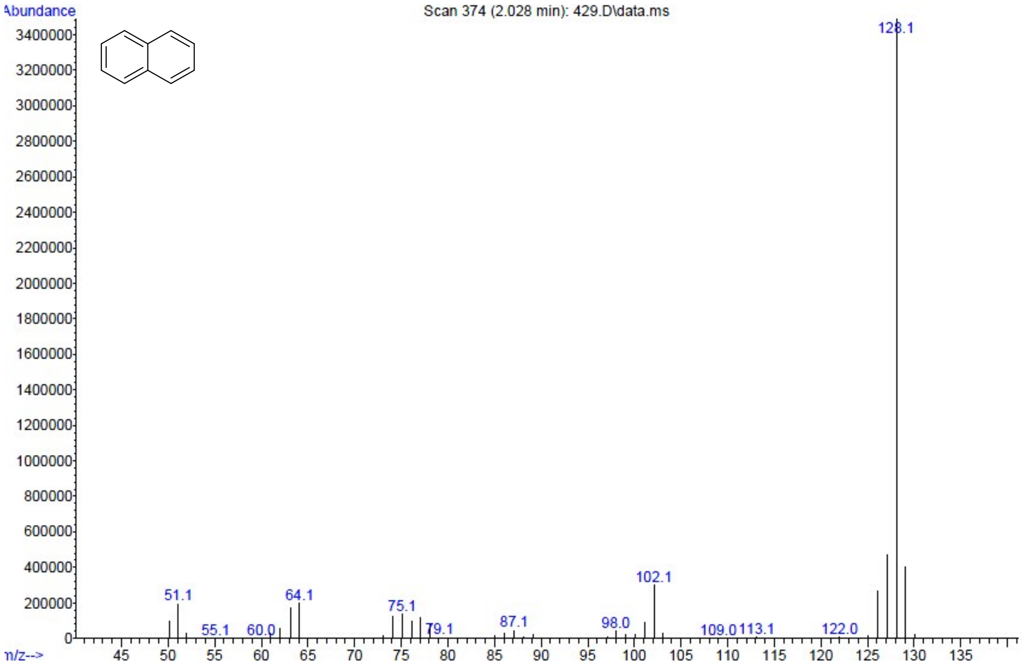

Figure 2. MS of **1**.

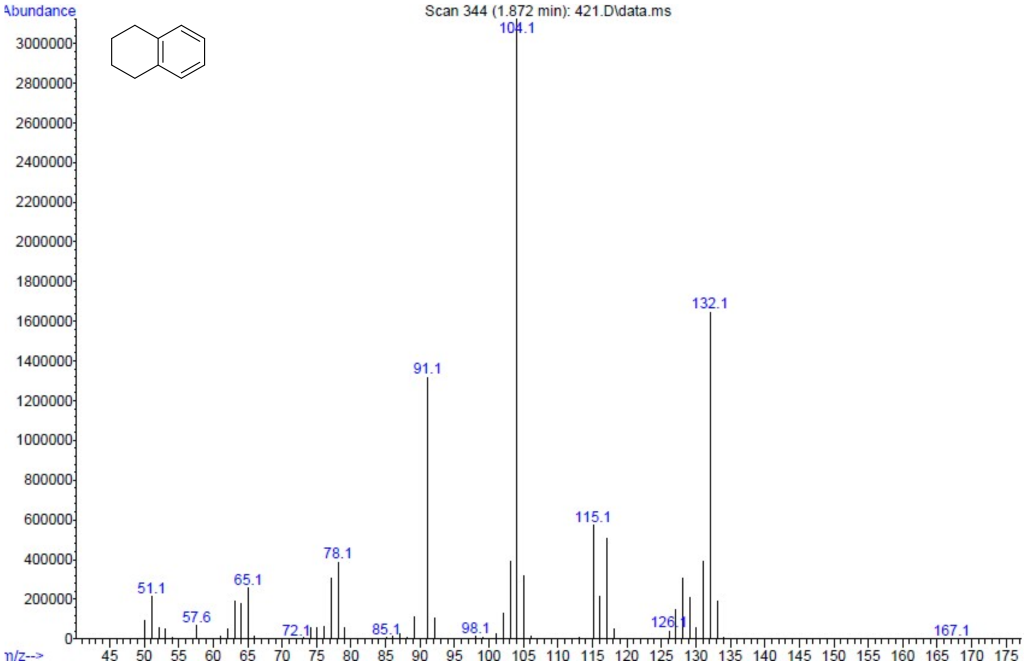

Figure 3. MS of **1a**.

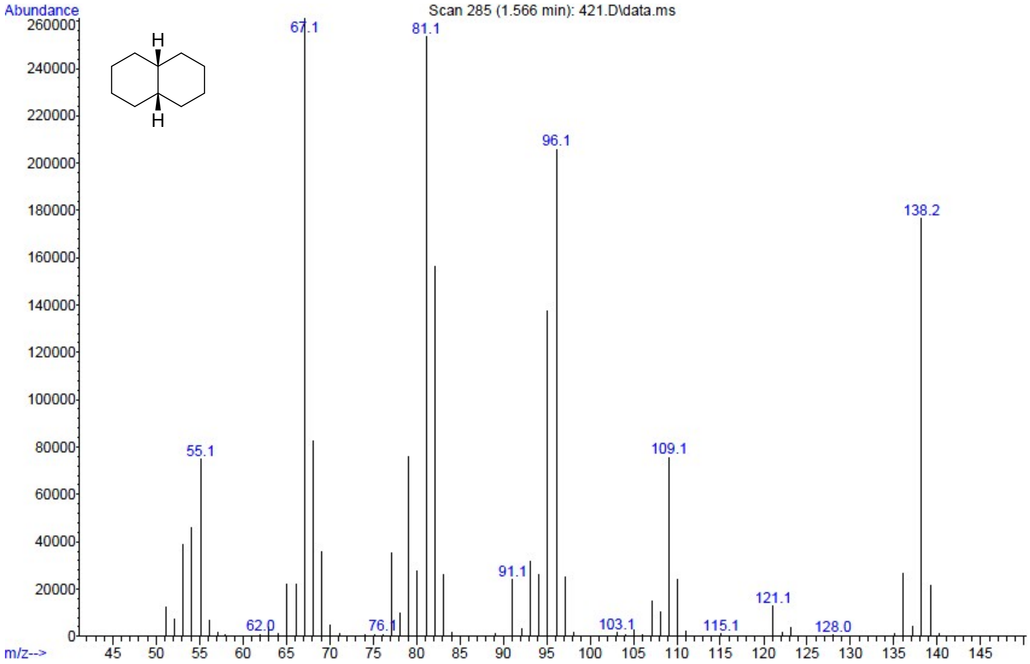

Figure 4. MS of **1b**.

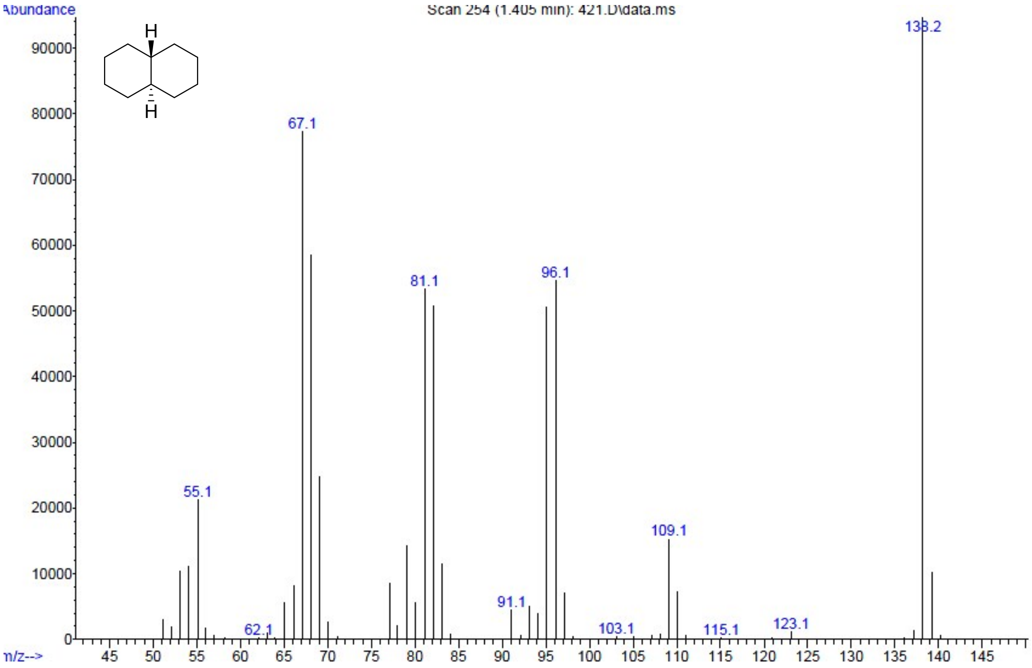

Figure 5. MS of **1c**.

- Hydrogenation of Anthracene **2**

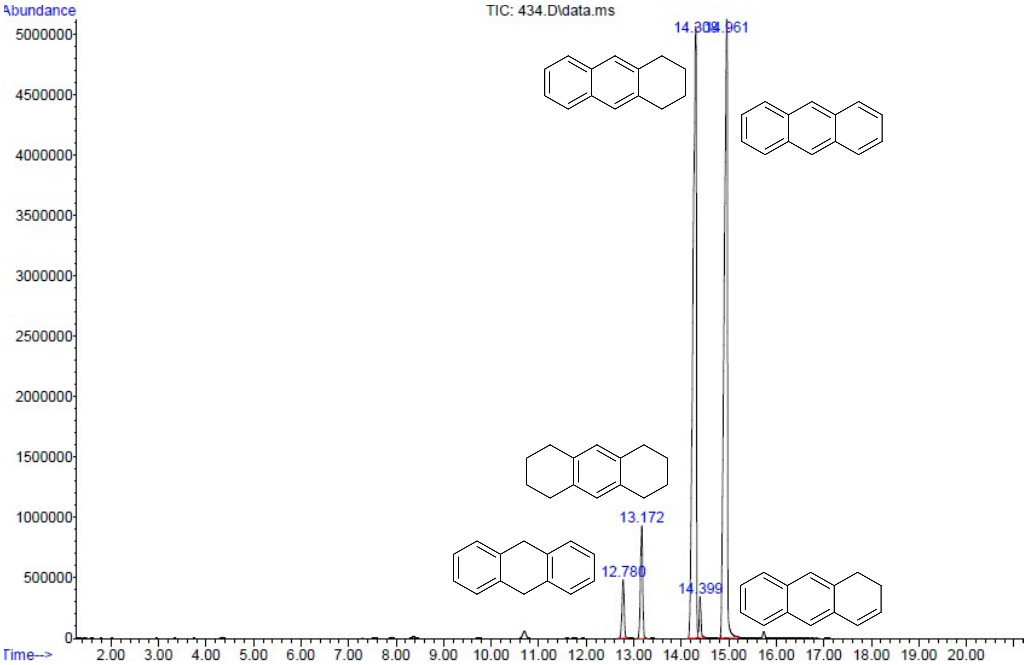

Figure 6. GC of the products formed in the hydrogenation of Anthracene **2**.

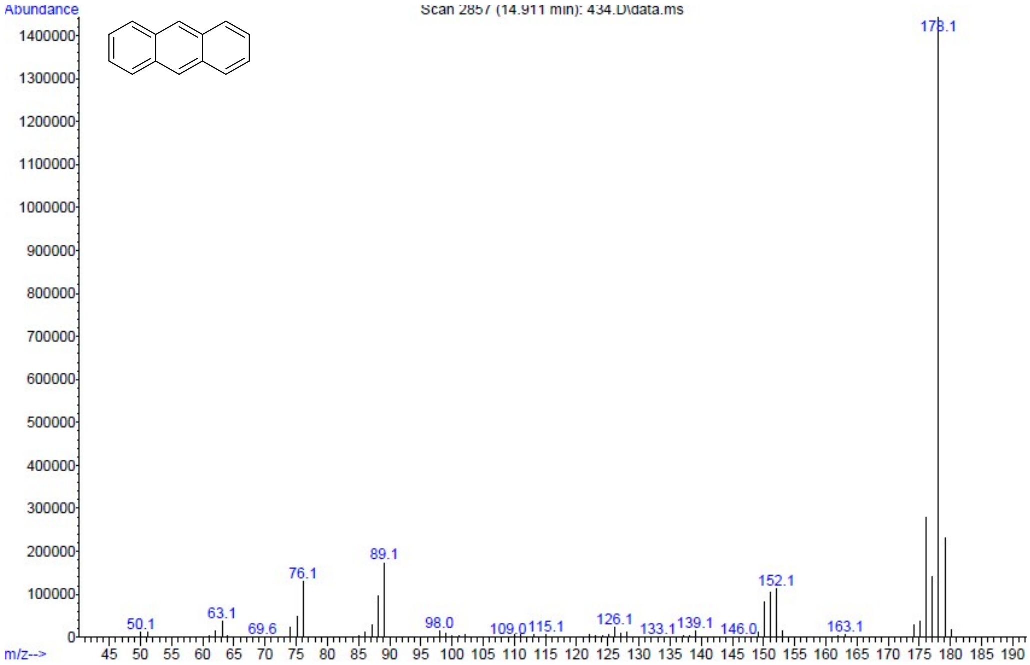

Figure 7. MS of **2**.

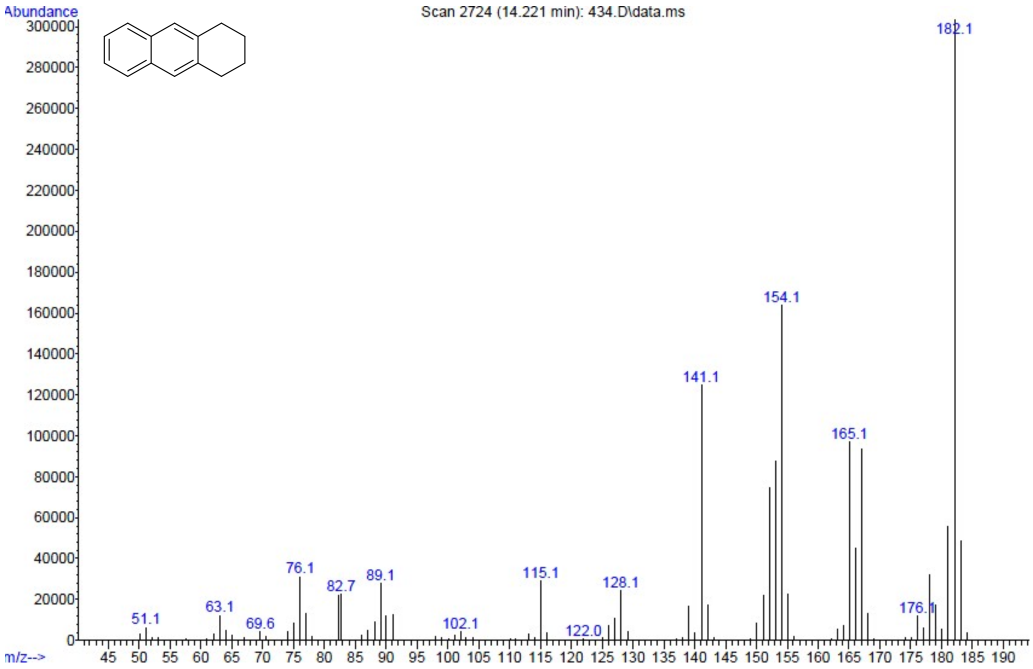

Figure 8. MS of **2a**.

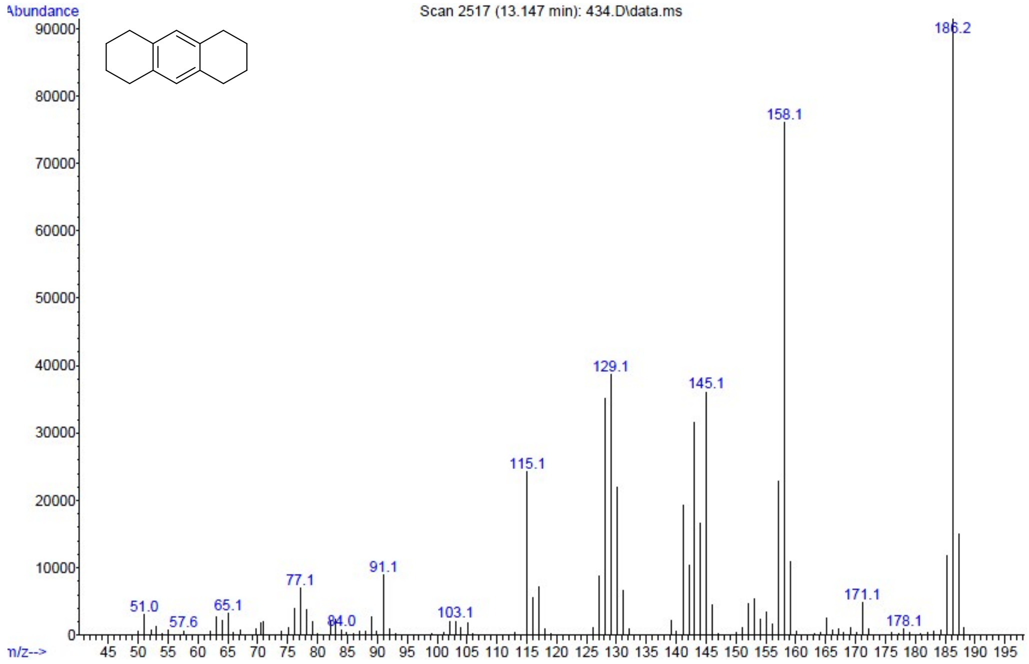

Figure 9. MS of **2b**.

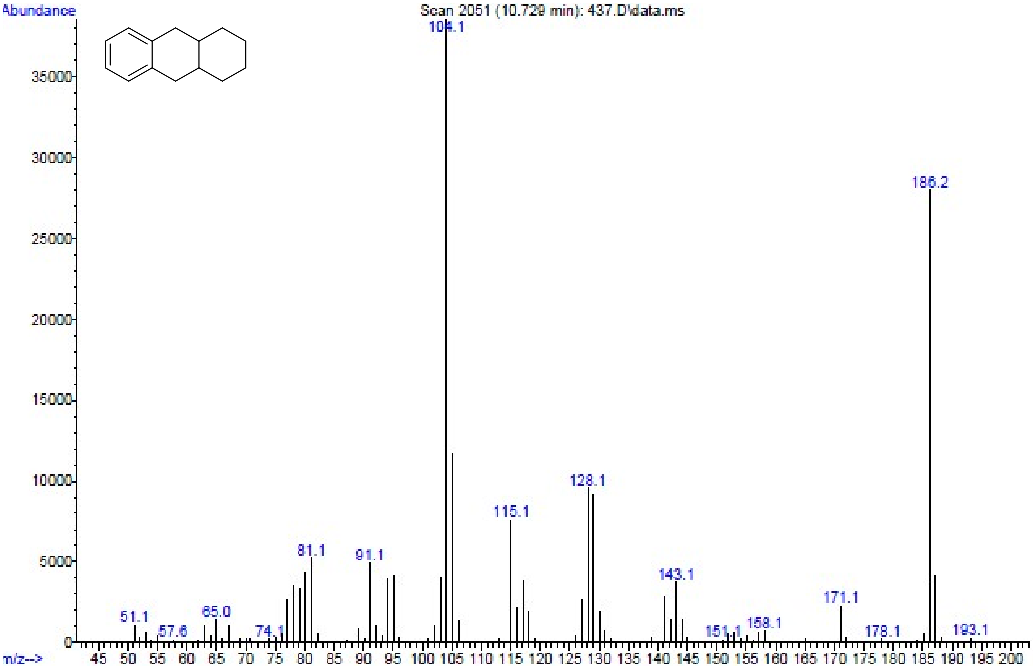

Figure 10. MS of **2c**.

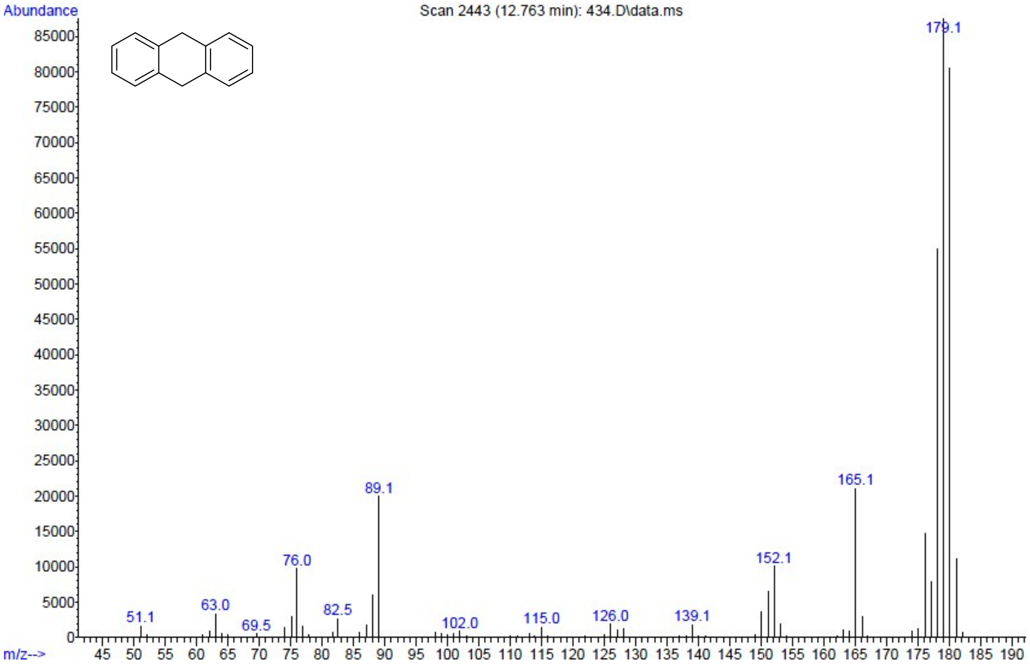

Figure 11. MS of **2d**.

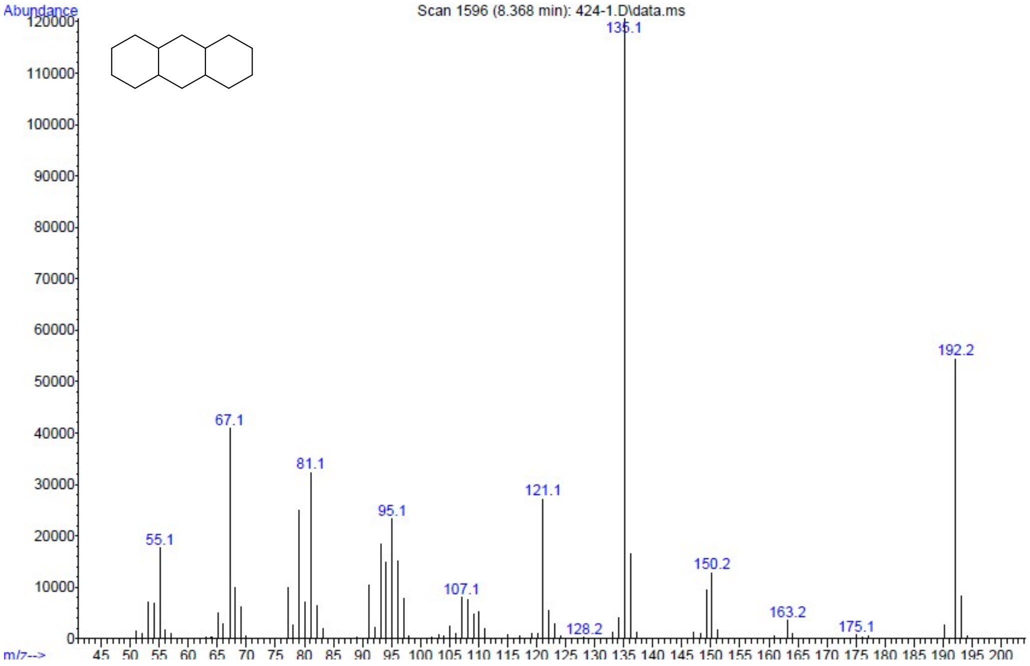

Figure 12. MS of **2e**.

- Hydrogenation of Phenanthrene **3**

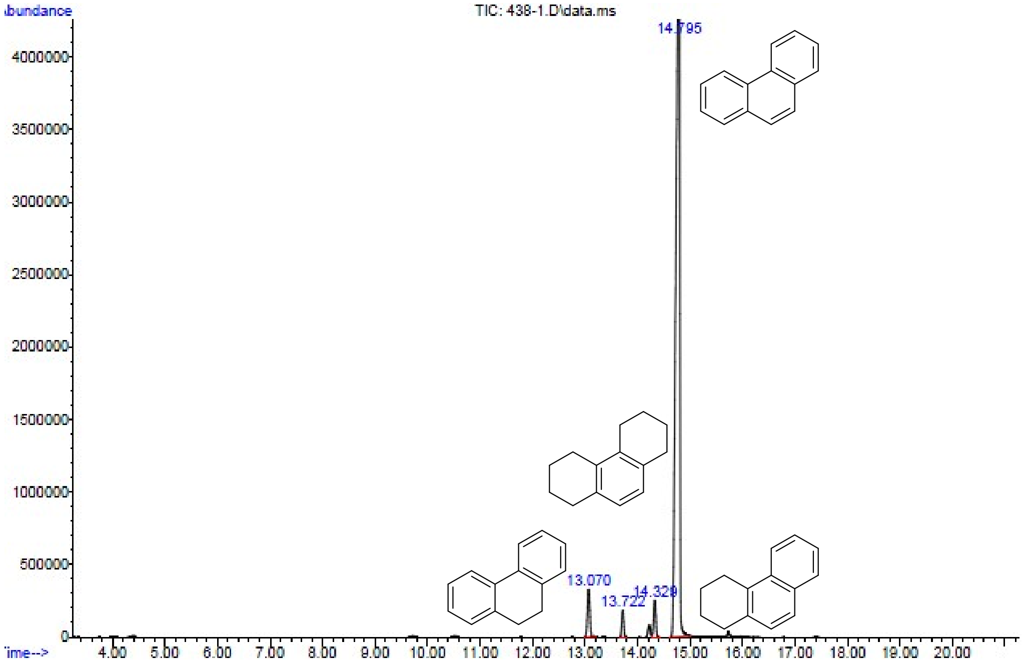

Figure 13. GC of the products formed in the hydrogenation of Phenanthrene **3**.

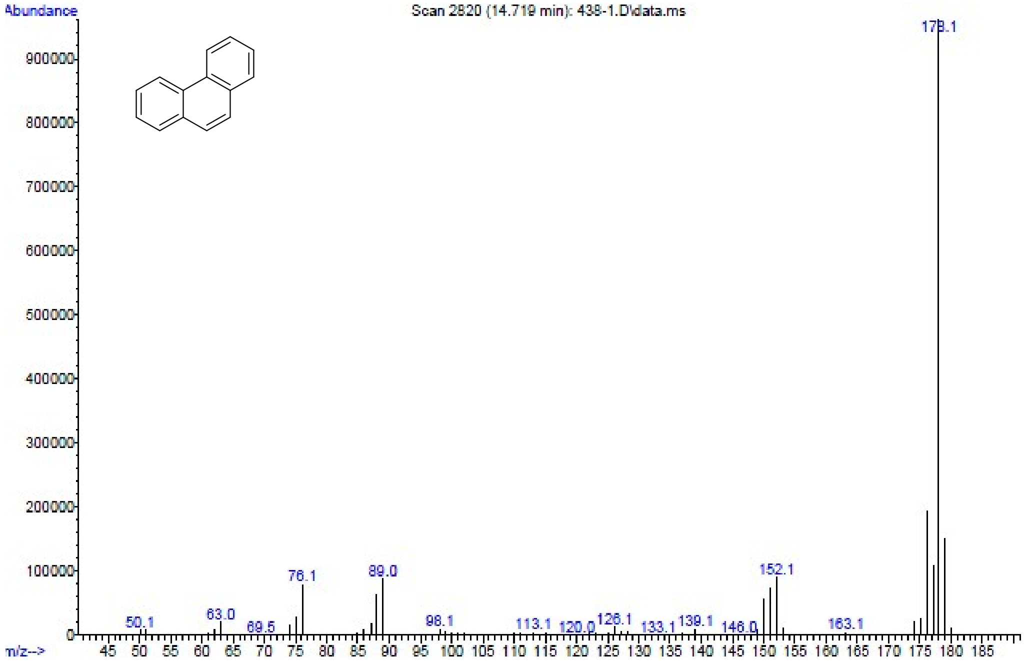

Figure 14. MS of **3**.

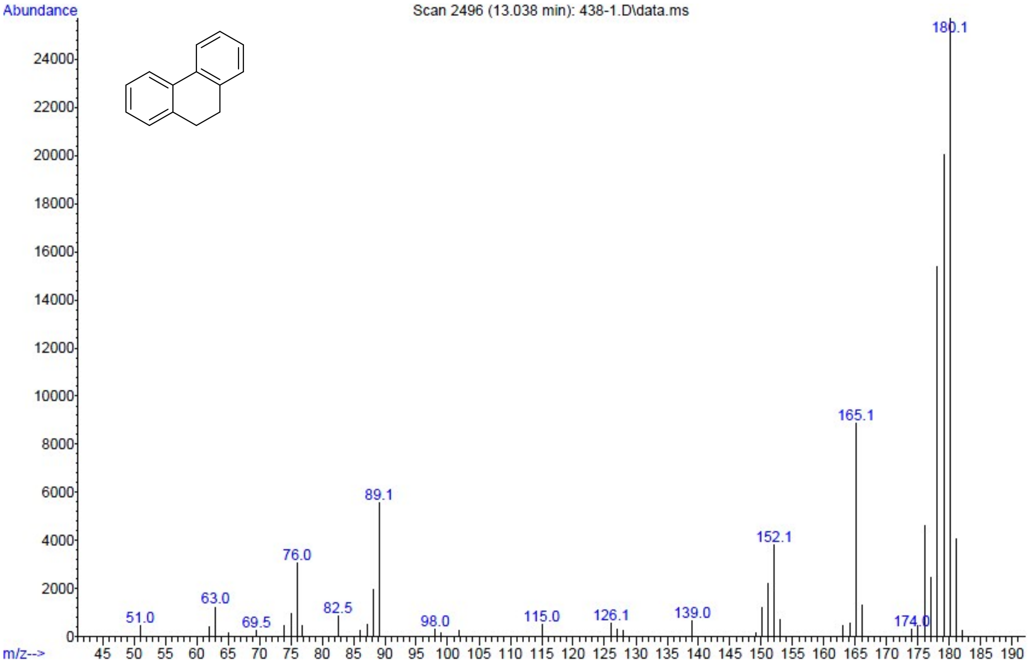

Figure 15. MS of **3a**.

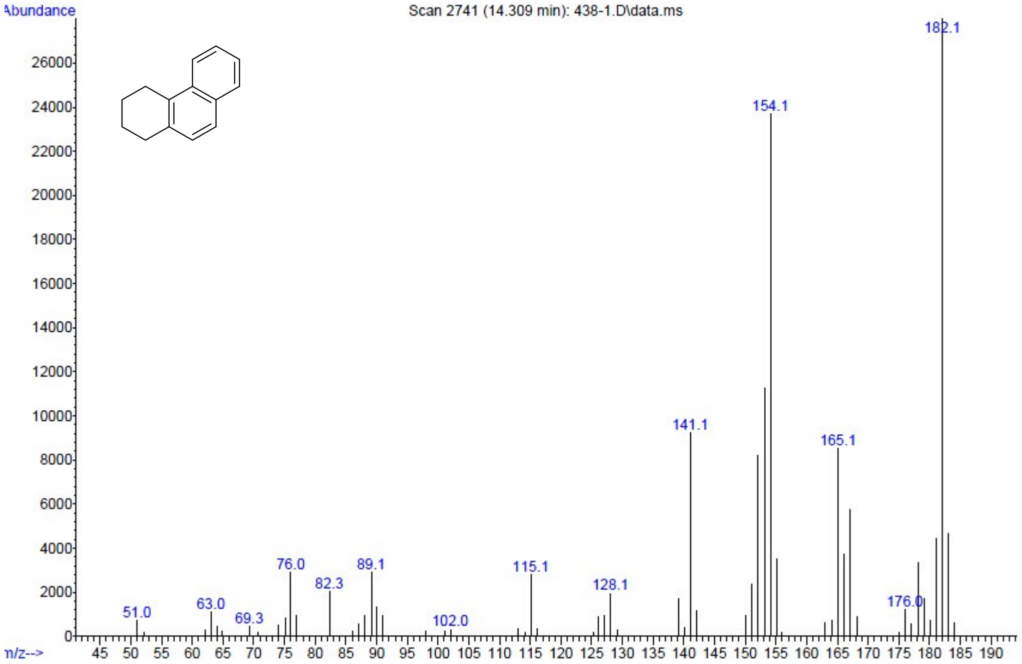

Figure 16. MS of **3b**.

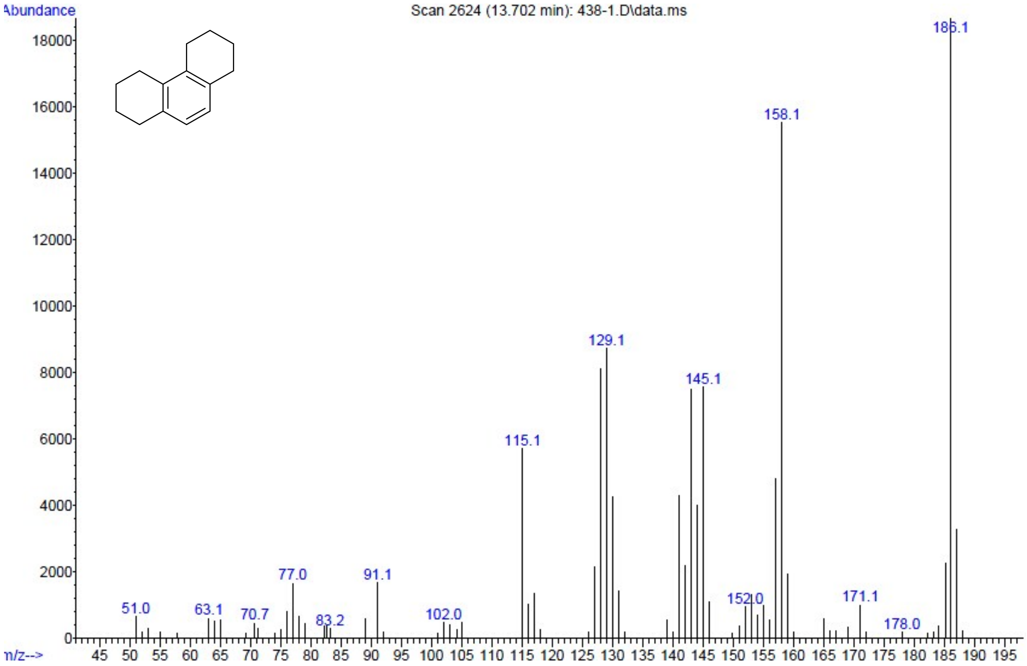

Figure 17. MS of **3c**.

- Hydrogenation of Triphenylene **4**

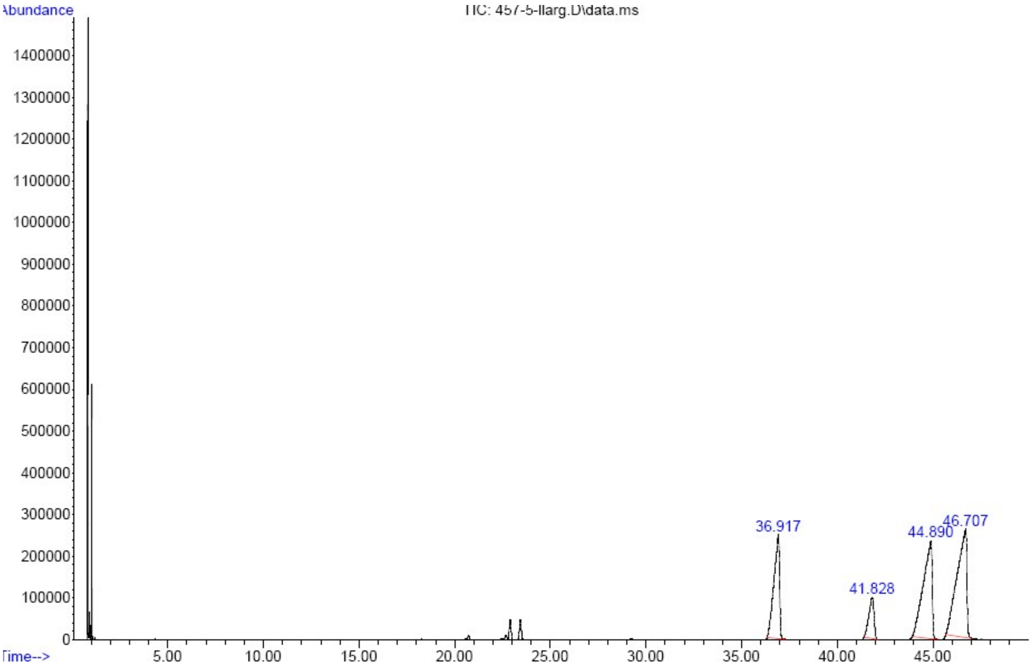

Figure 18. GC of the products formed in the hydrogenation of Phenanthrene **4**.

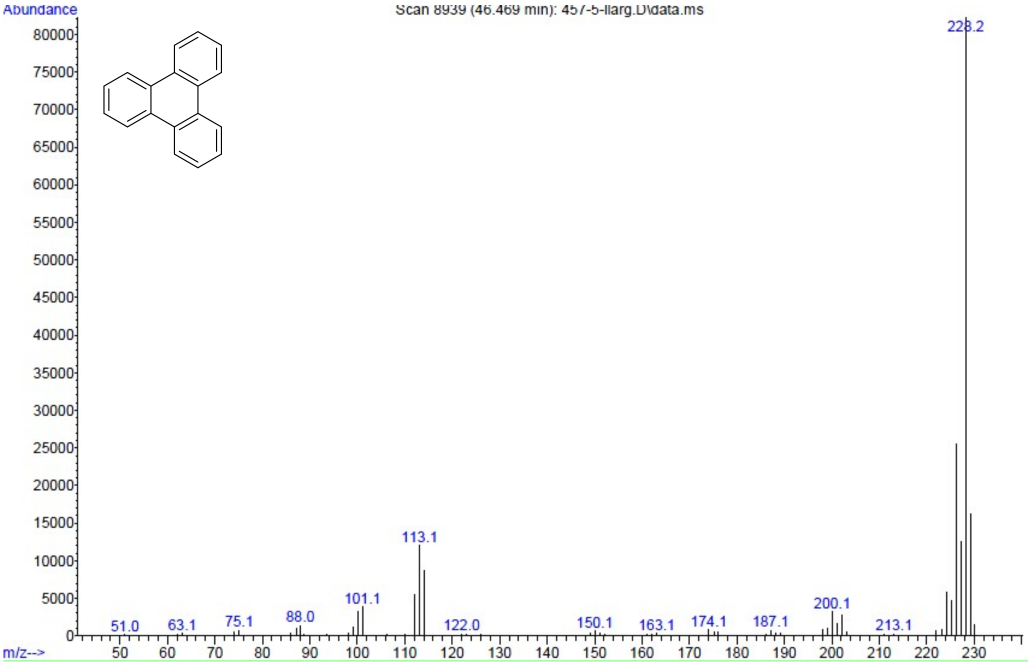

Figure 19. MS of **4a**.

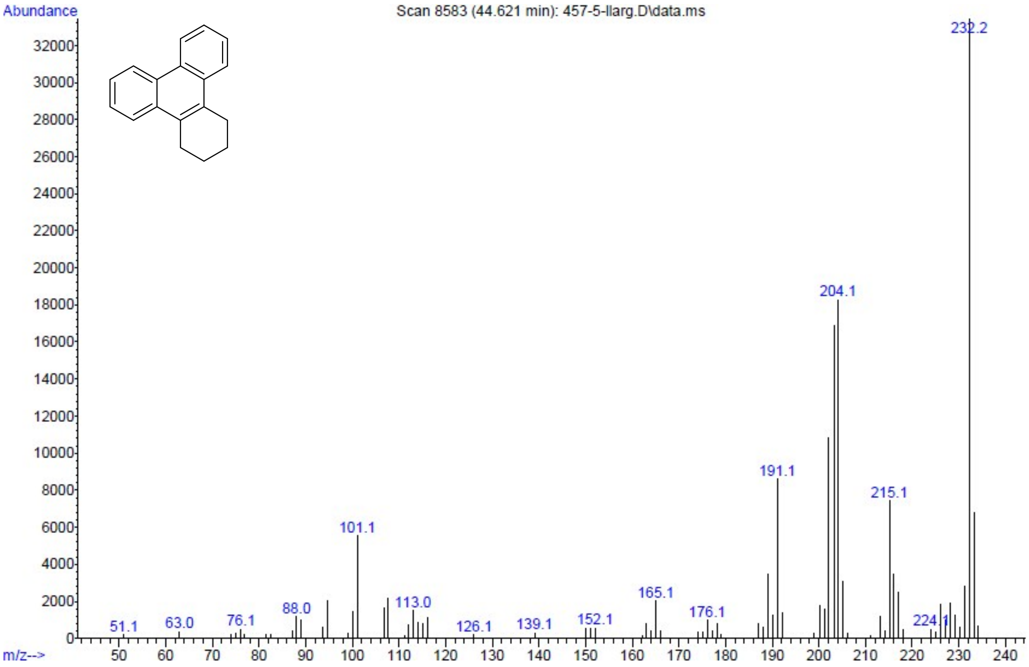

Figure 20. MS of **4a**.

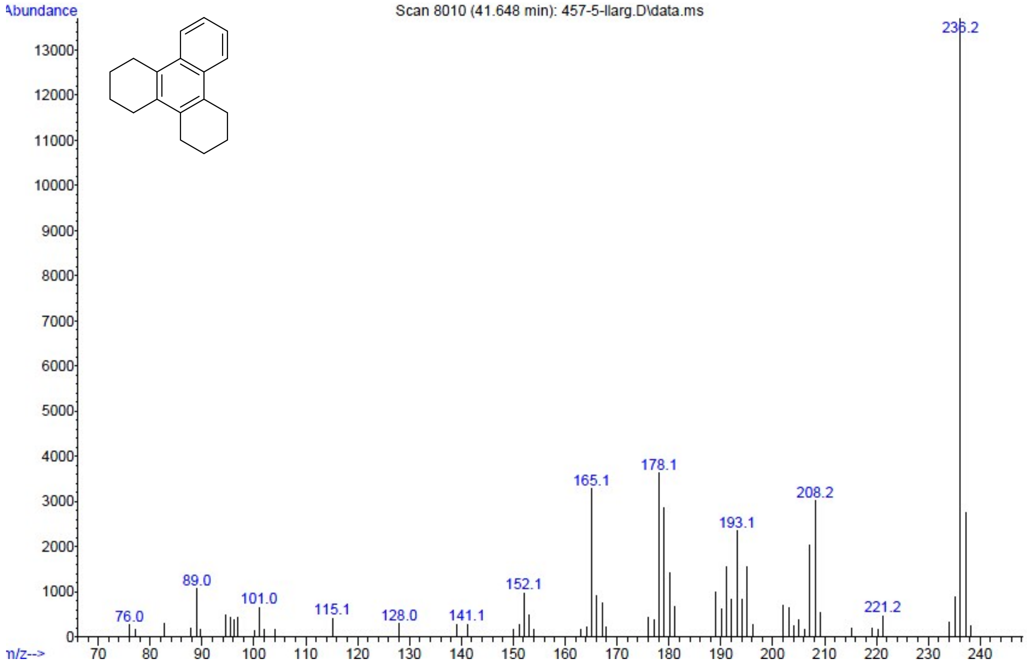

Figure 21. MS of **4b**.

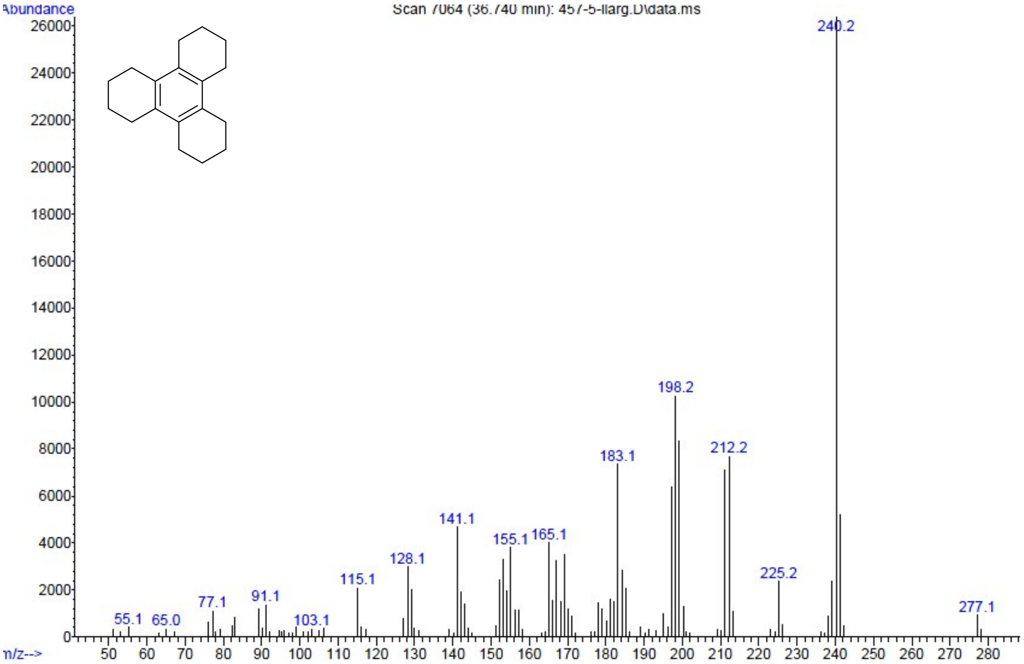

Figure 22. MS of **4c**.

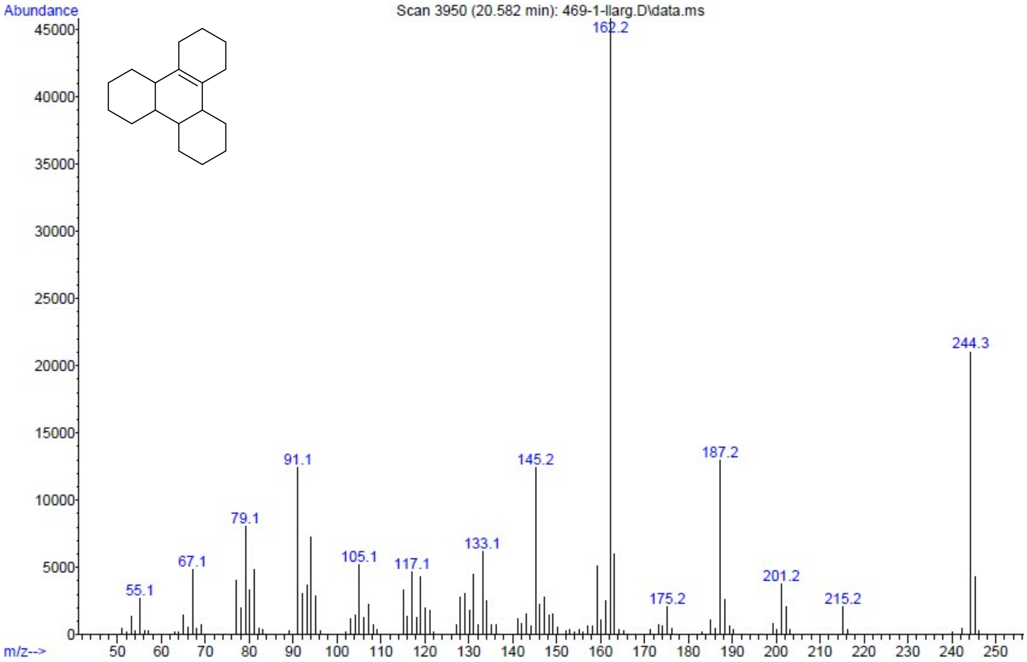

Figure 23. MS of **4d**.

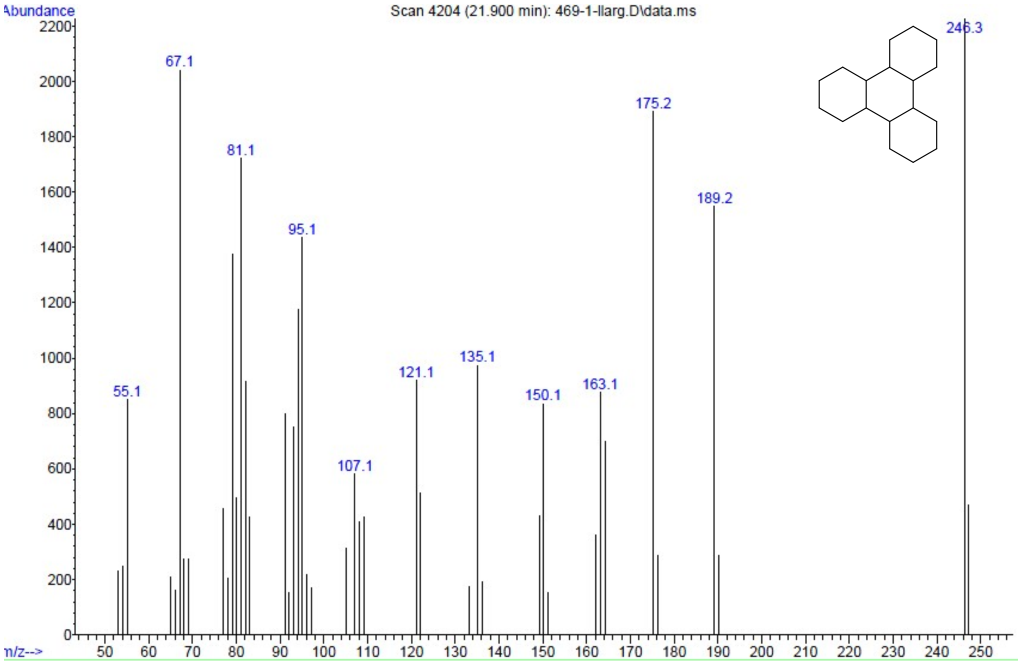

Figure 24. MS of **4e**.

- Hydrogenation of Pyrene **5**

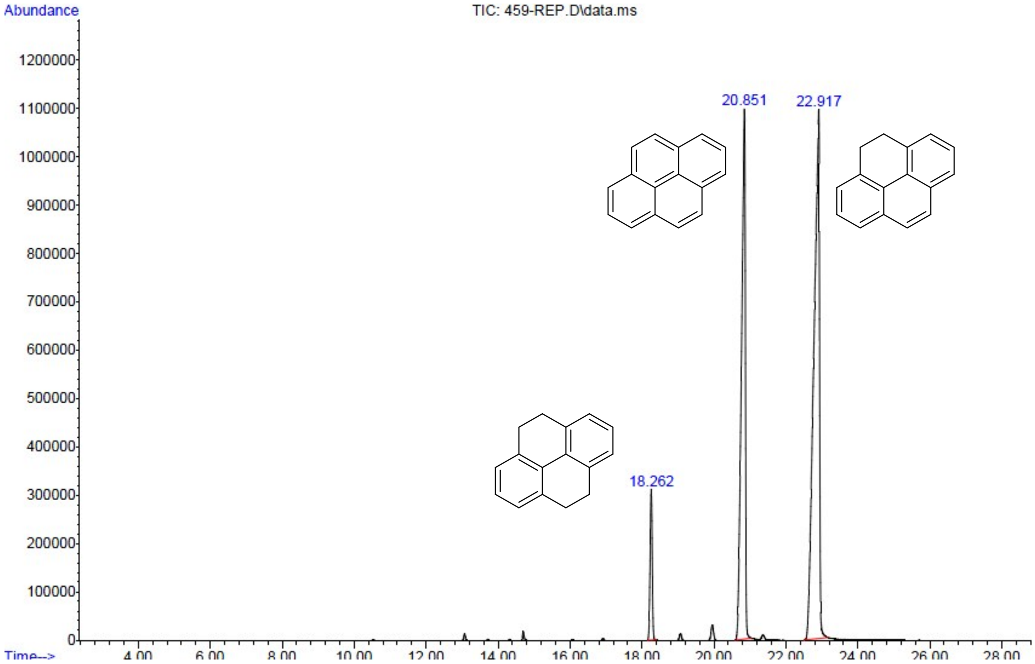

Figure 25. GC of the products formed in the hydrogenation of Pyrene **5**.

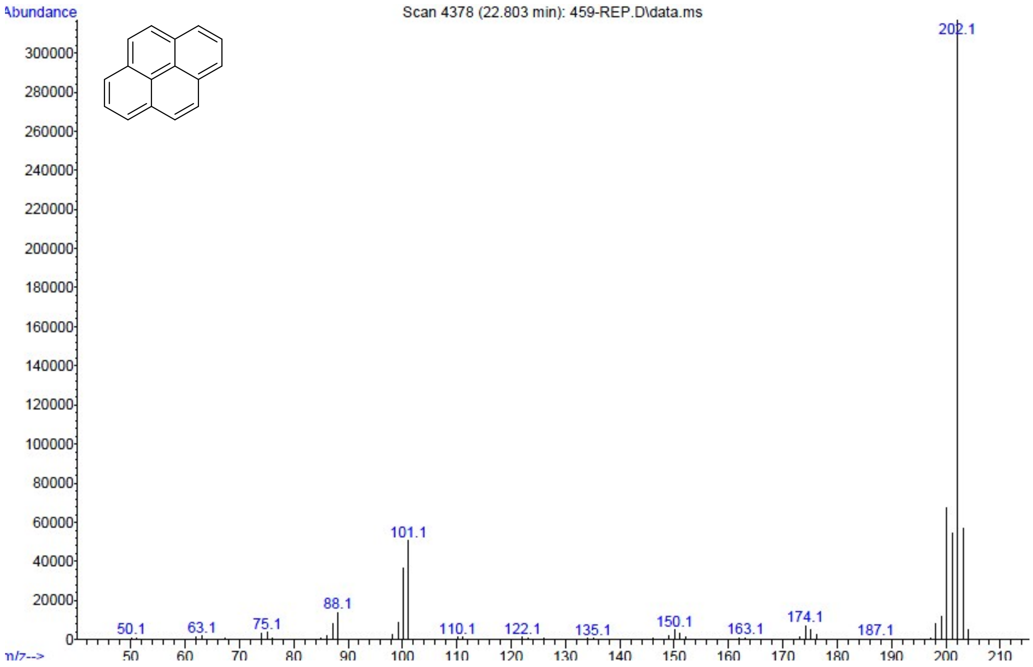

Figure 26. MS of **5**.

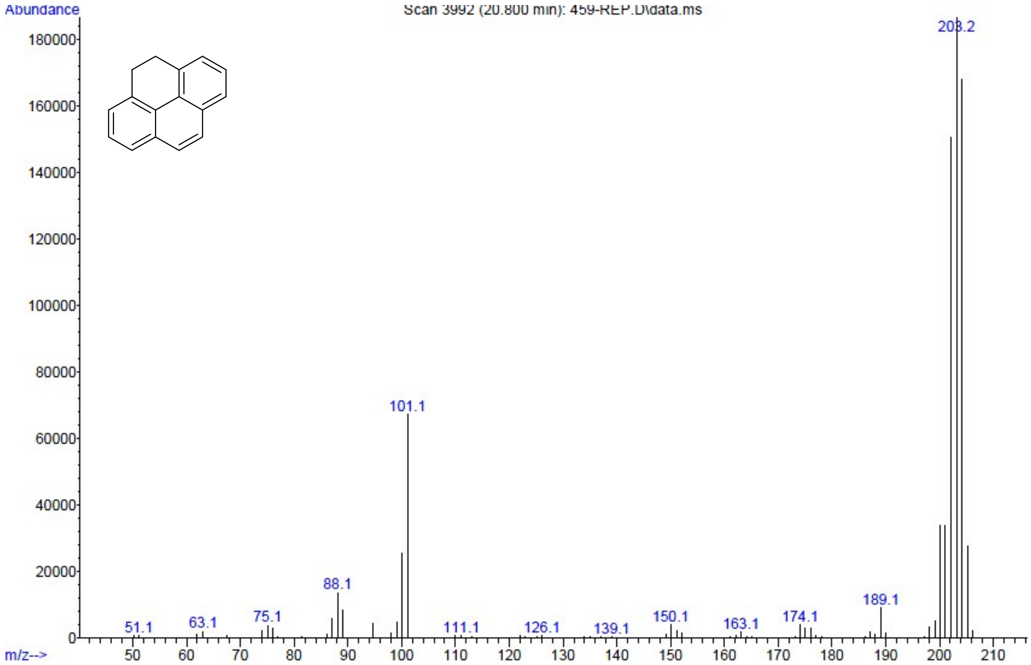

Figure 27. MS of **5a**.

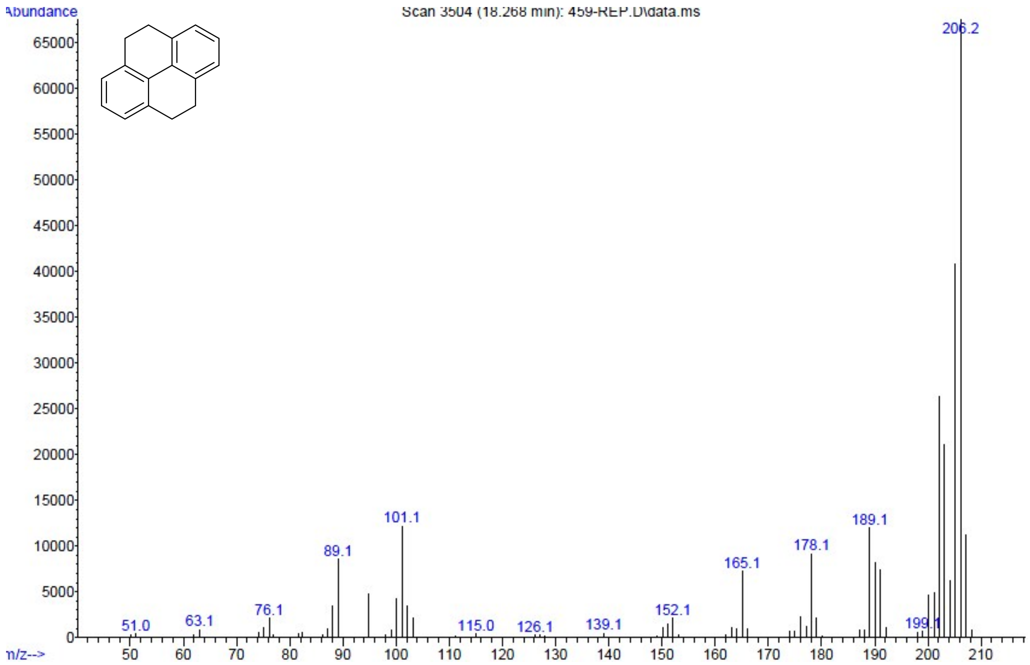

Figure 28. MS of **5b**.

- Hydrogenation of 1-methylnaphthalene **6**

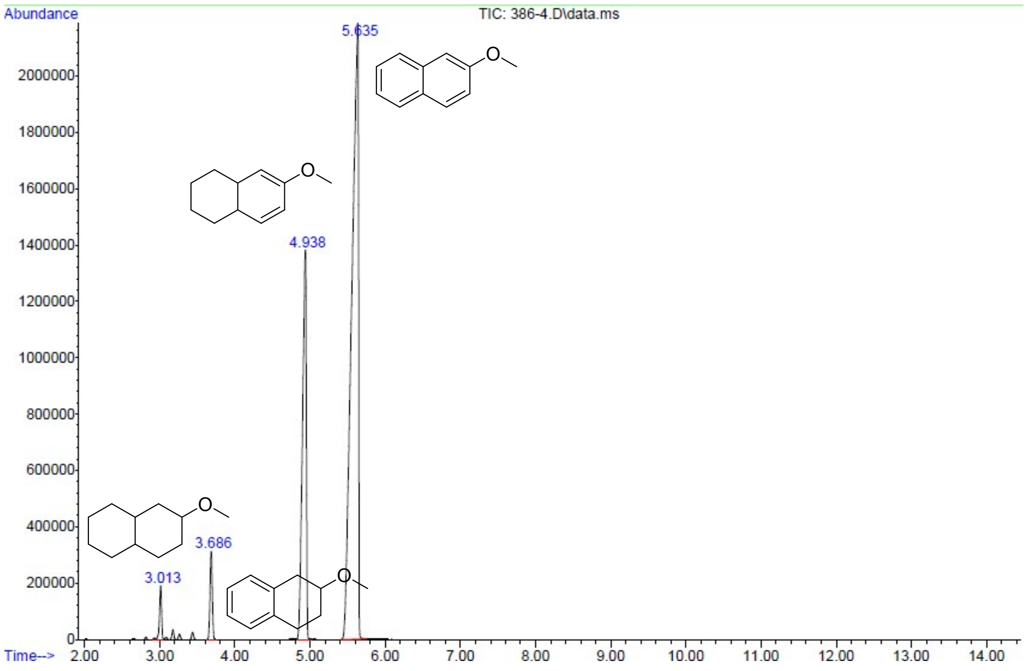

Figure 29. GC of the products formed in the hydrogenation of 1-methylnaphthalene **6**.

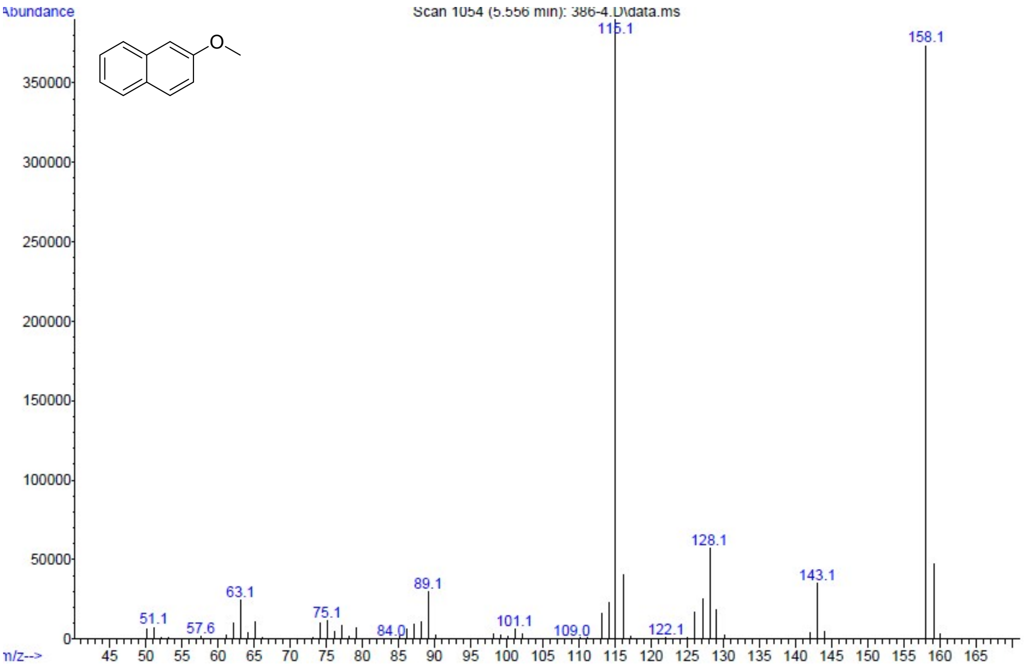

Figure 30. MS of **6**.

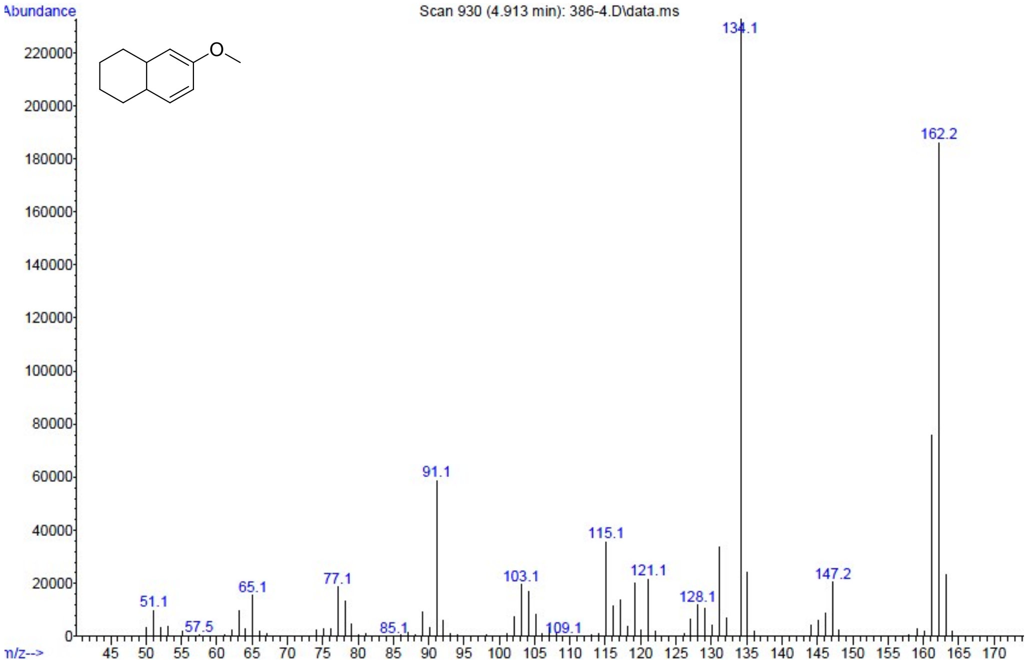

Figure 31. MS of **6a**.

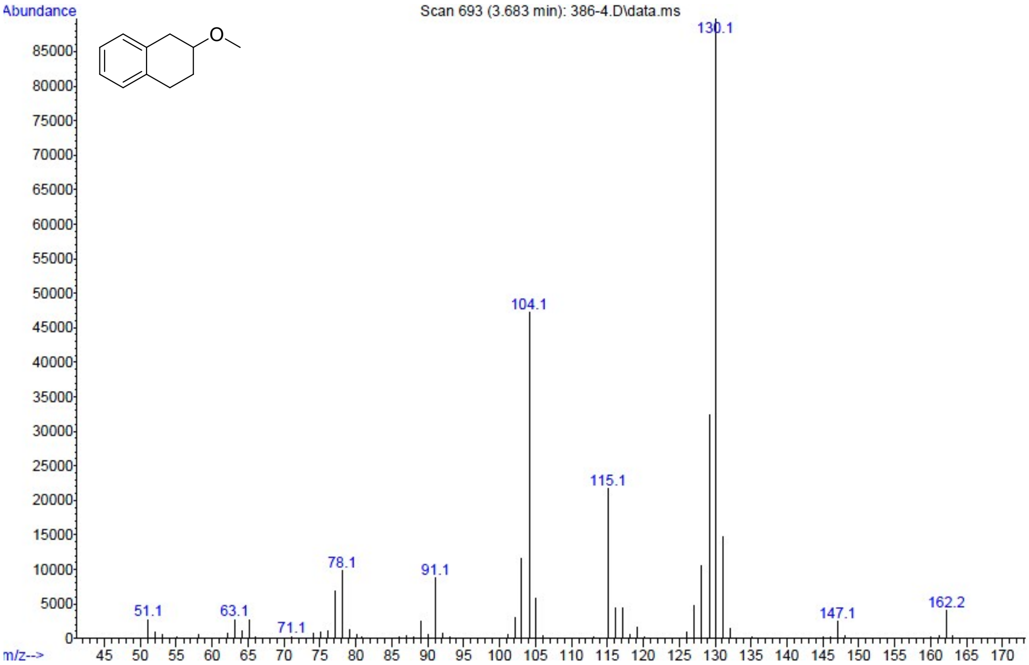

Figure 32. MS of **6b**.

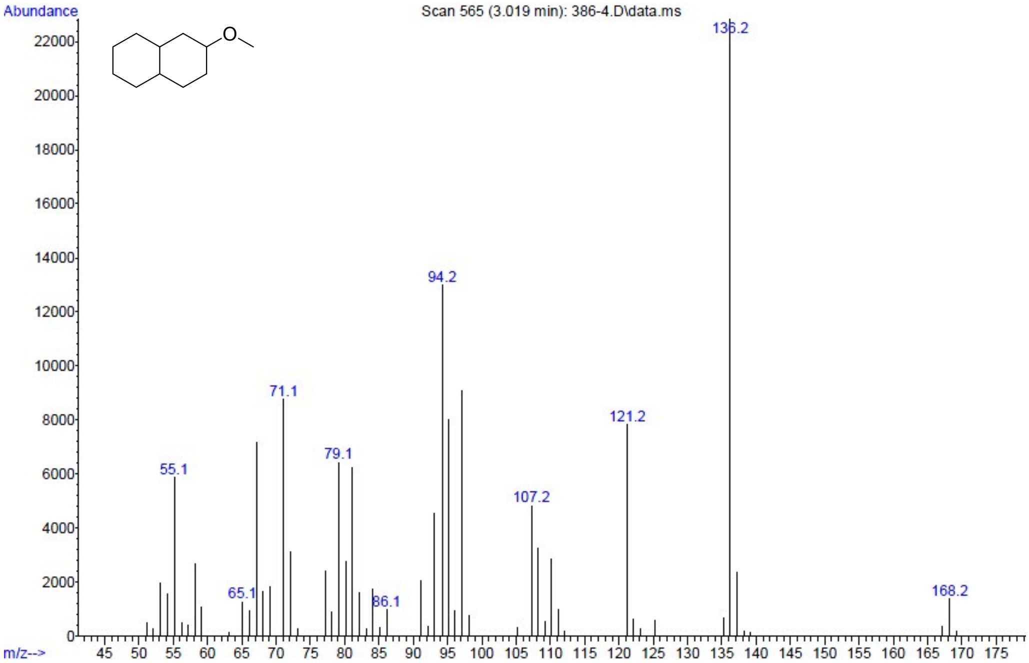

Figure 33. MS of **6c**.

- Hydrogenation of 2-methylnaphthalene **7**

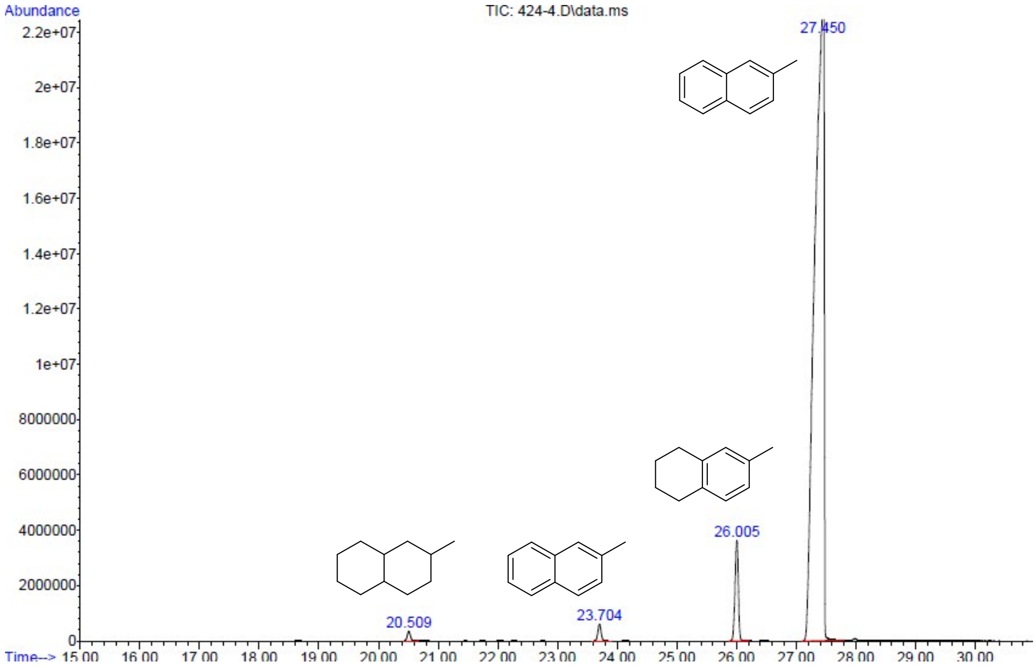

Figure 34. GC of the products formed in the hydrogenation of 2-methylnaphthalene **7**.

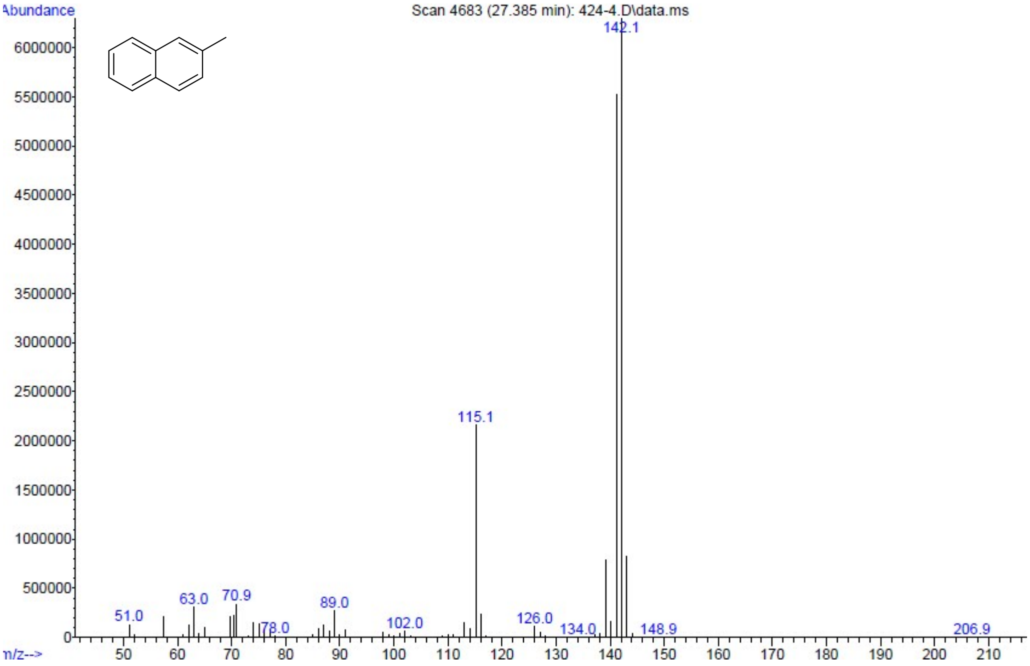

Figure 35. MS of **7**.

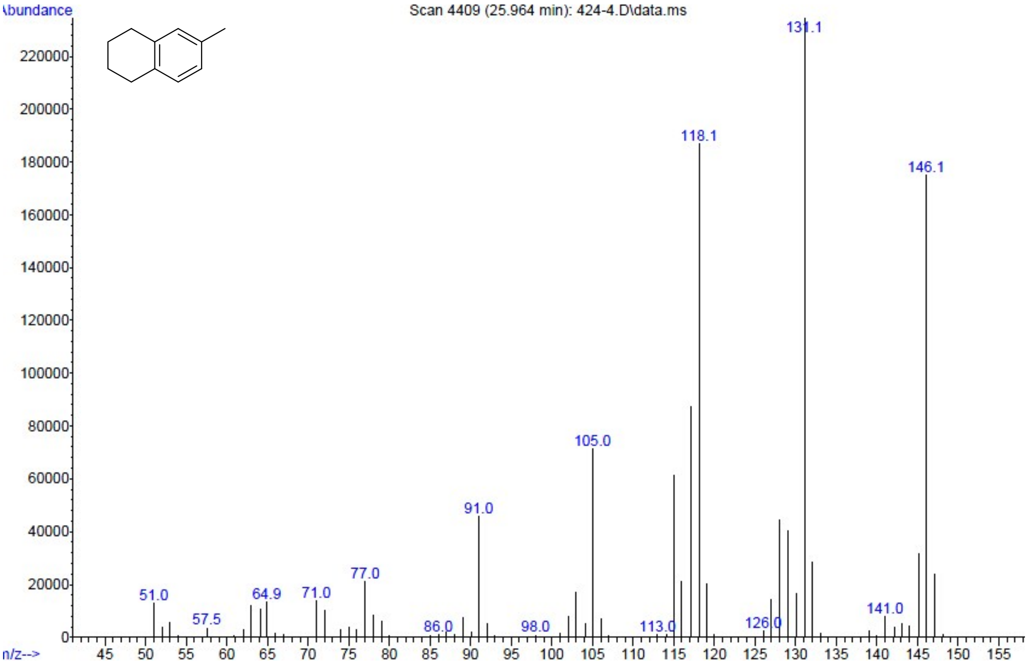

Figure 36. MS of **7a**.

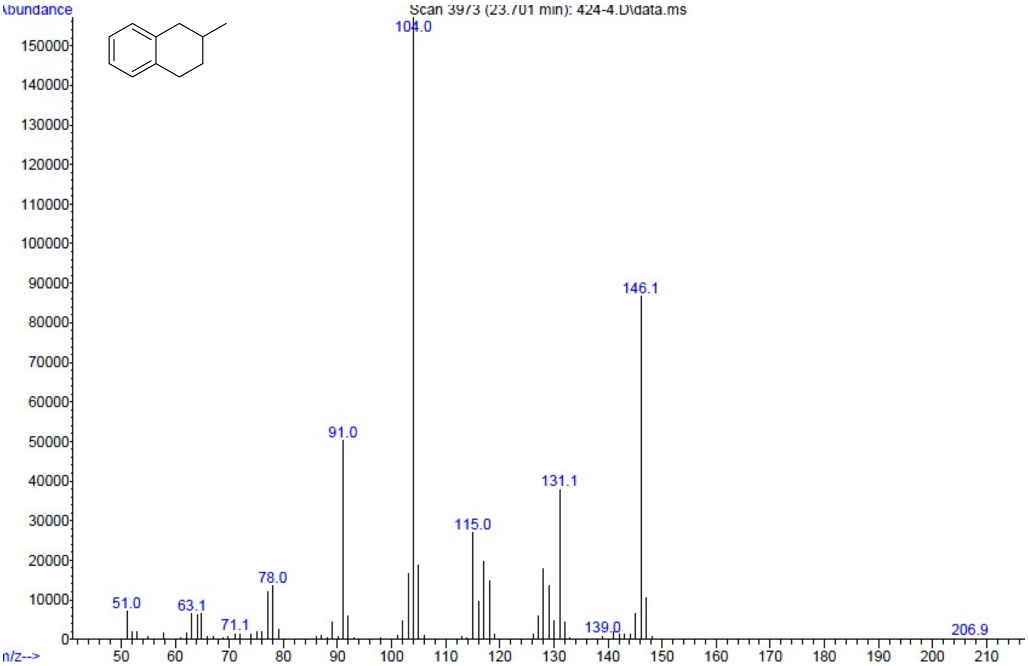

Figure 37. MS of **7b**.

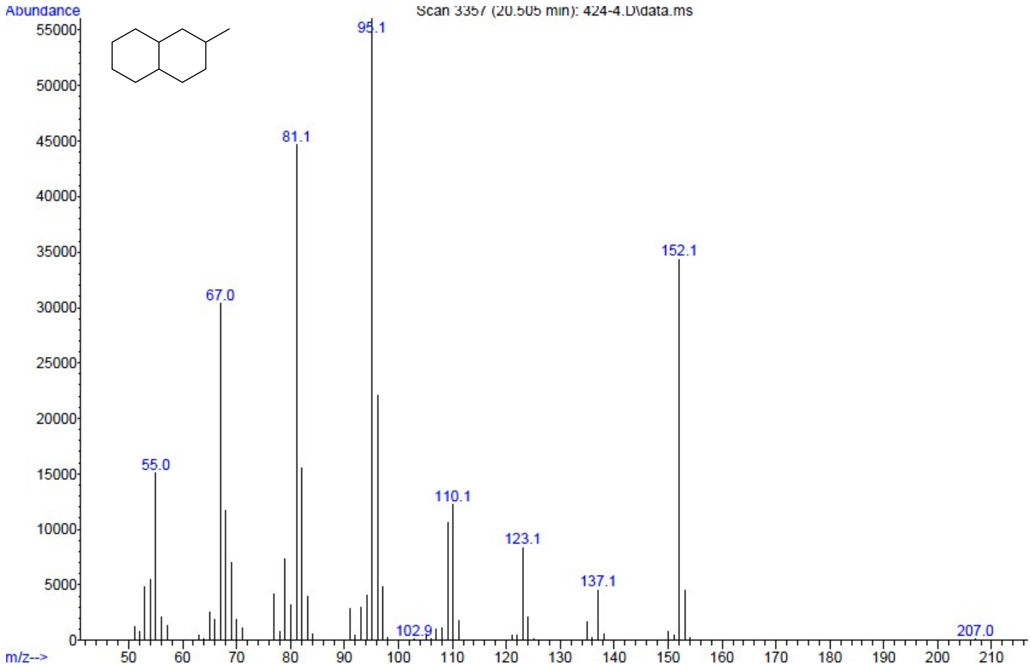

Figure 38. MS of **7c**.

- Hydrogenation of 1-methylnaphthalene **9**

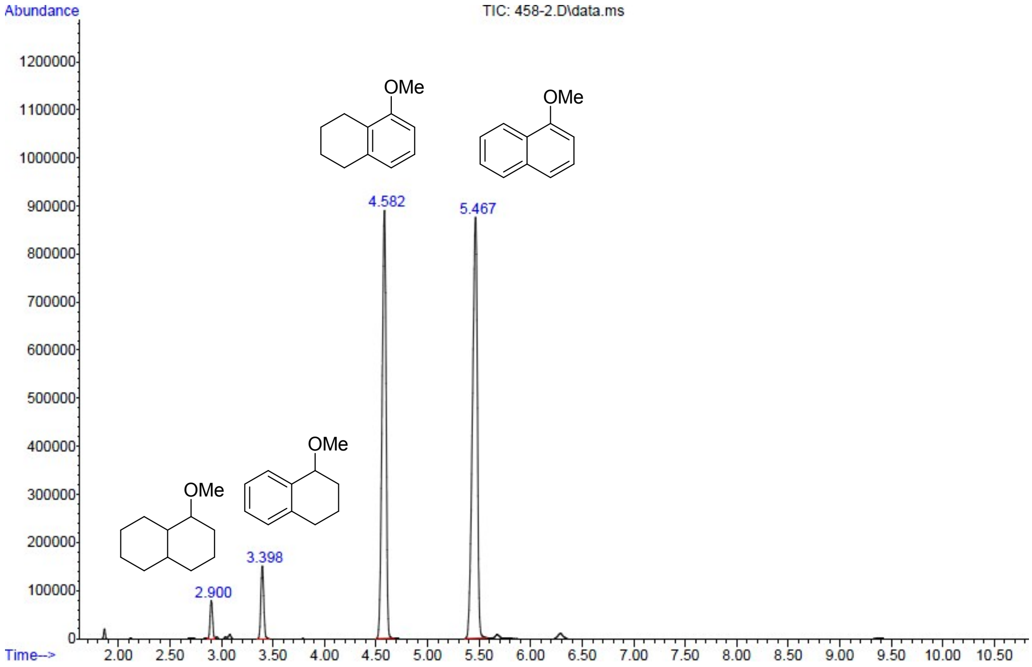

Figure 39. GC of the products formed in the hydrogenation of 1-methylnaphthalene **9**.

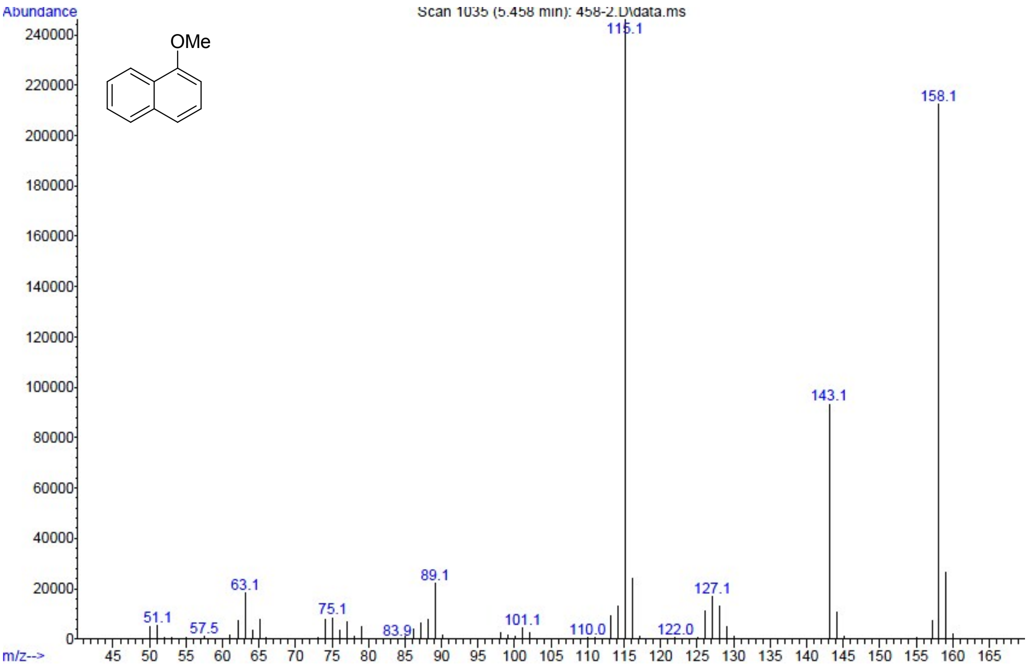

Figure 40. MS of **9**.

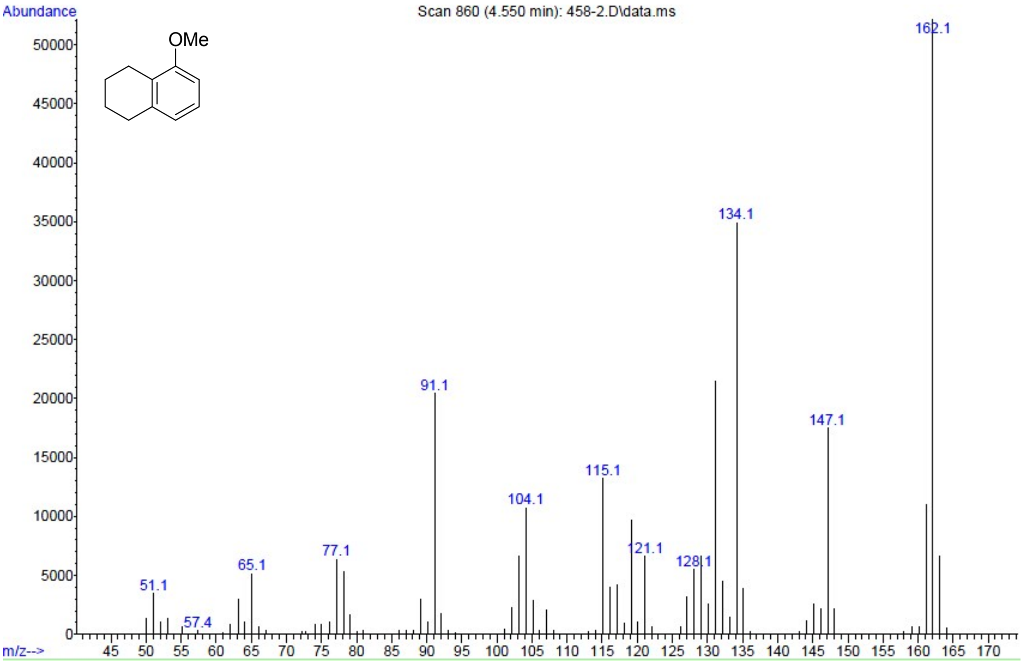

Figure 41. MS of **9a**.

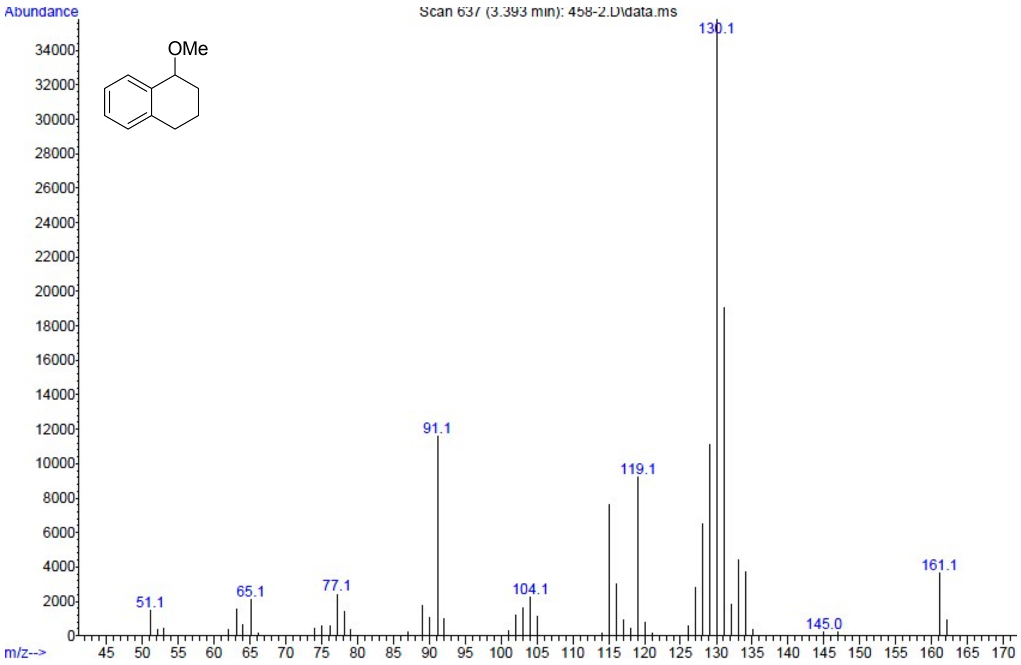

Figure 42. MS of **9b**.

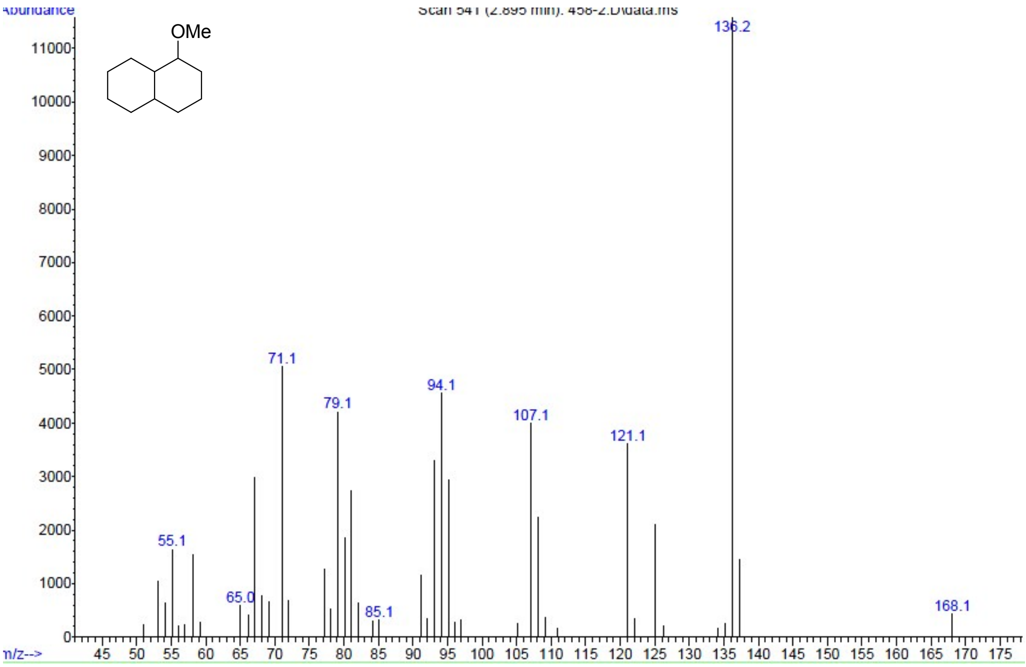

Figure 43. MS of **9c**.

- Hydrogenation of 1-(trifluoromethyl)naphthalene **10**

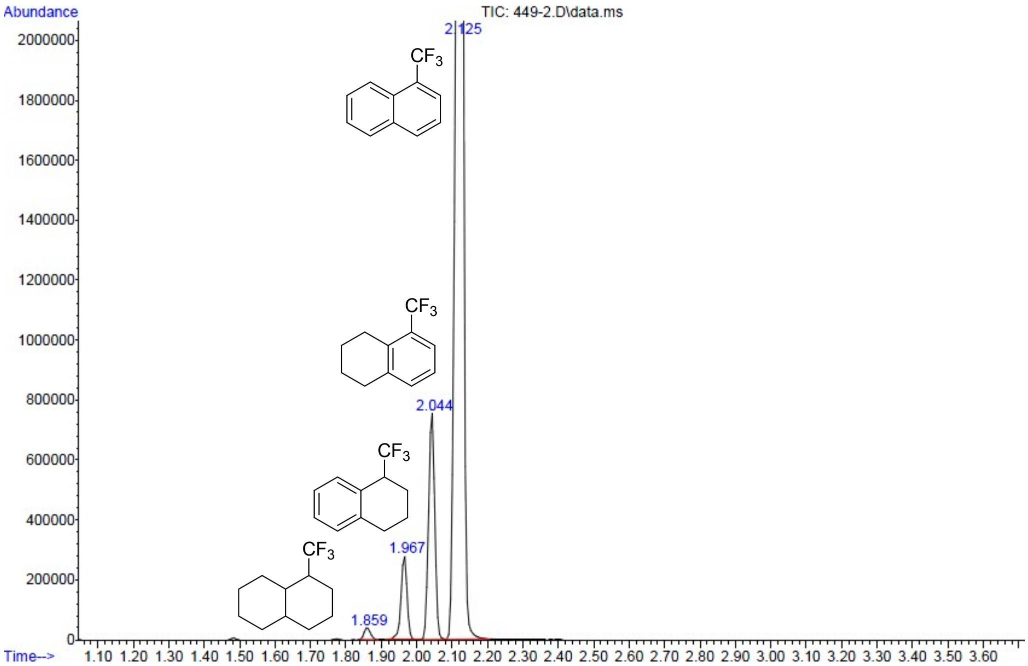

Figure 44. GC of the products formed in the hydrogenation of 1-(trifluoromethyl)naphthalene **10**.

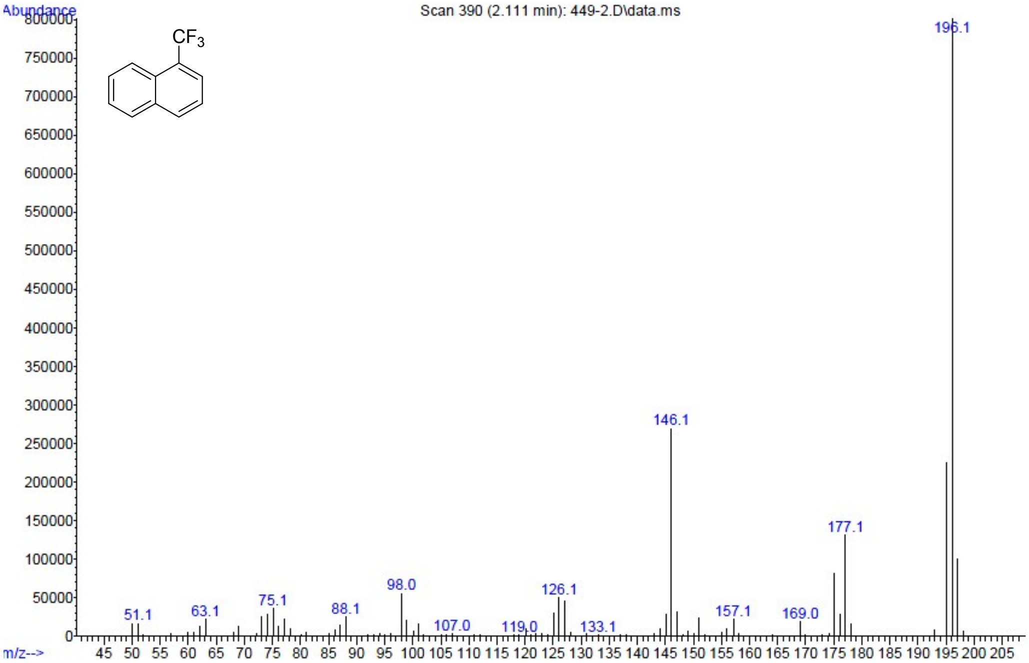

Figure 45. MS of **10**.

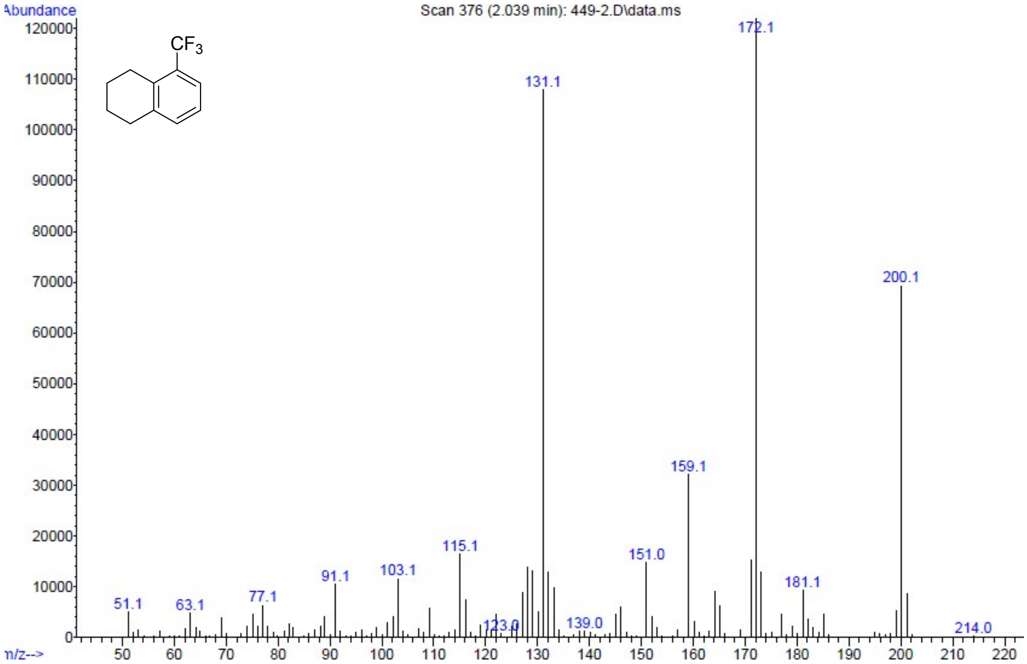

Figure 46. MS of **10a**.

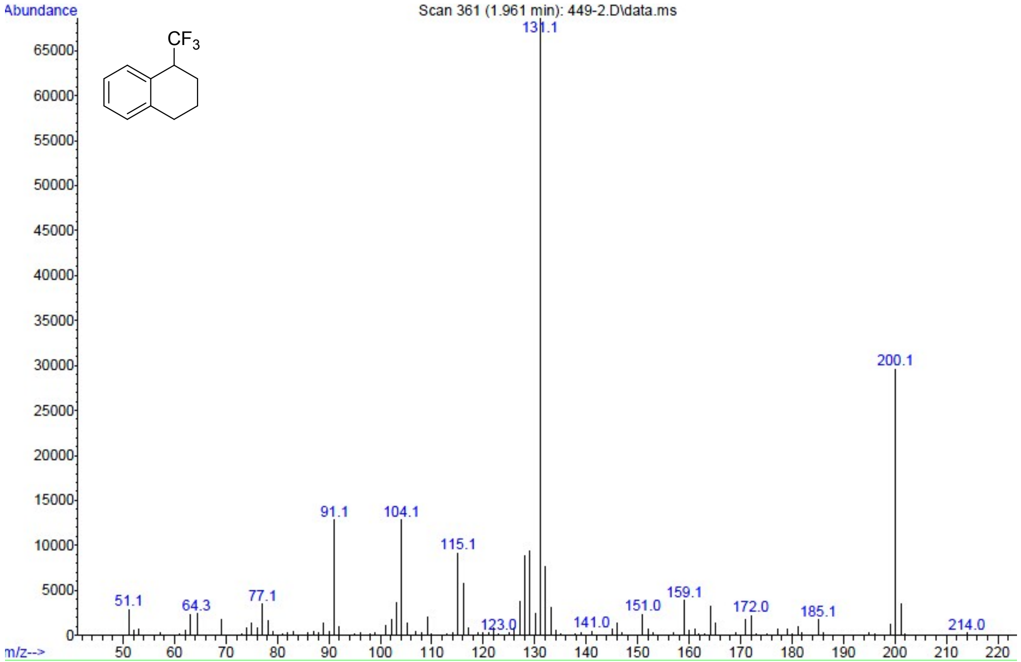

Figure 47. MS of **10b**.

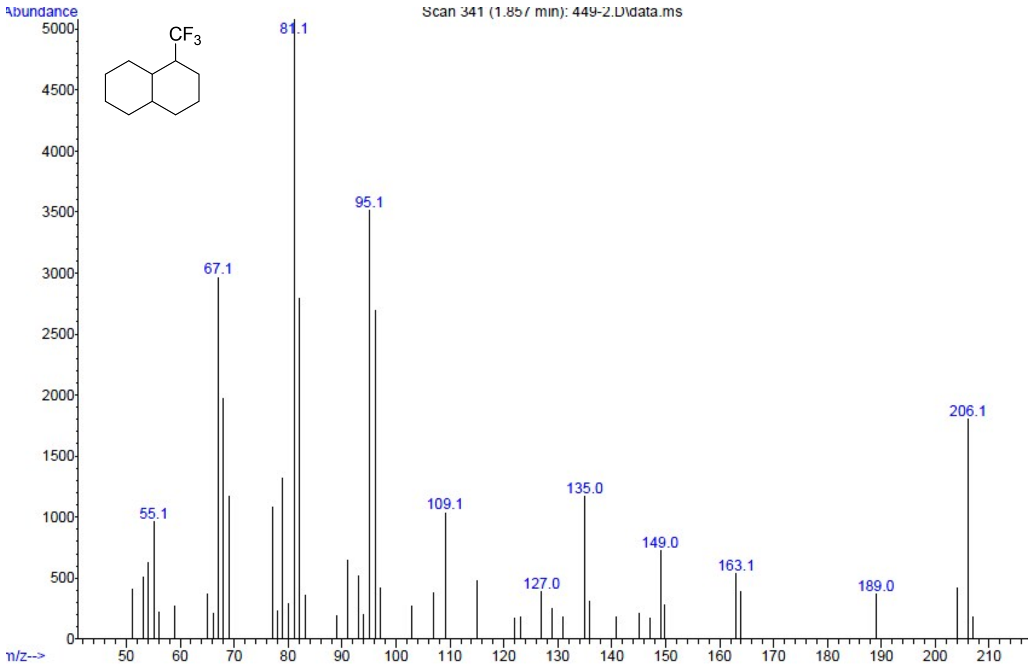

Figure 48. MS of **10c**.

- Hydrogenation of naphthalen-1-amine **11**

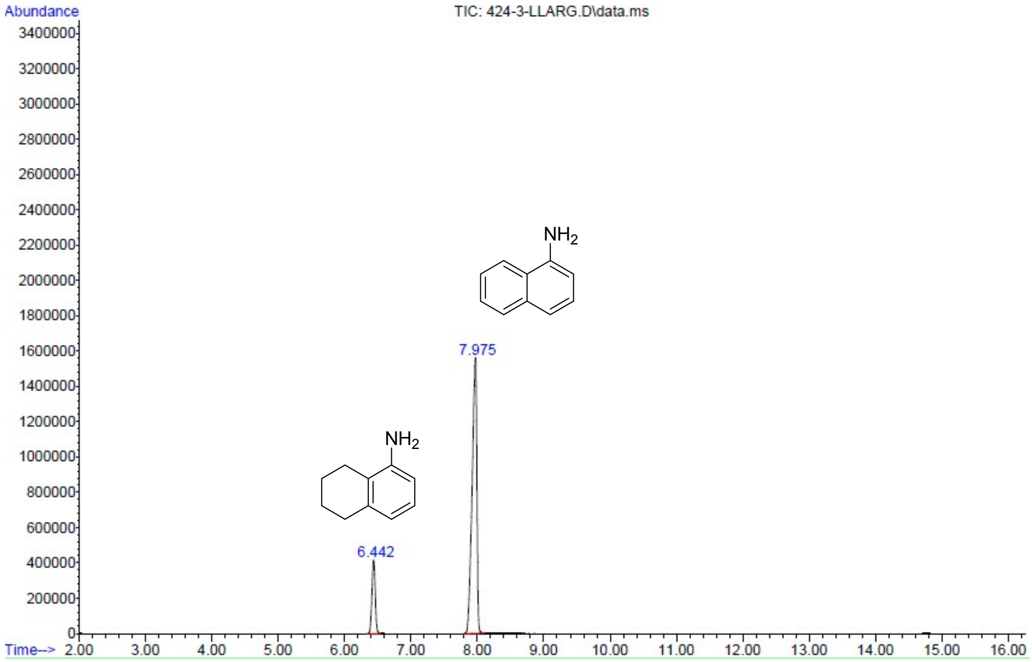

Figure 49. GC of the products formed in the hydrogenation of naphthalen-1-amine **11**.

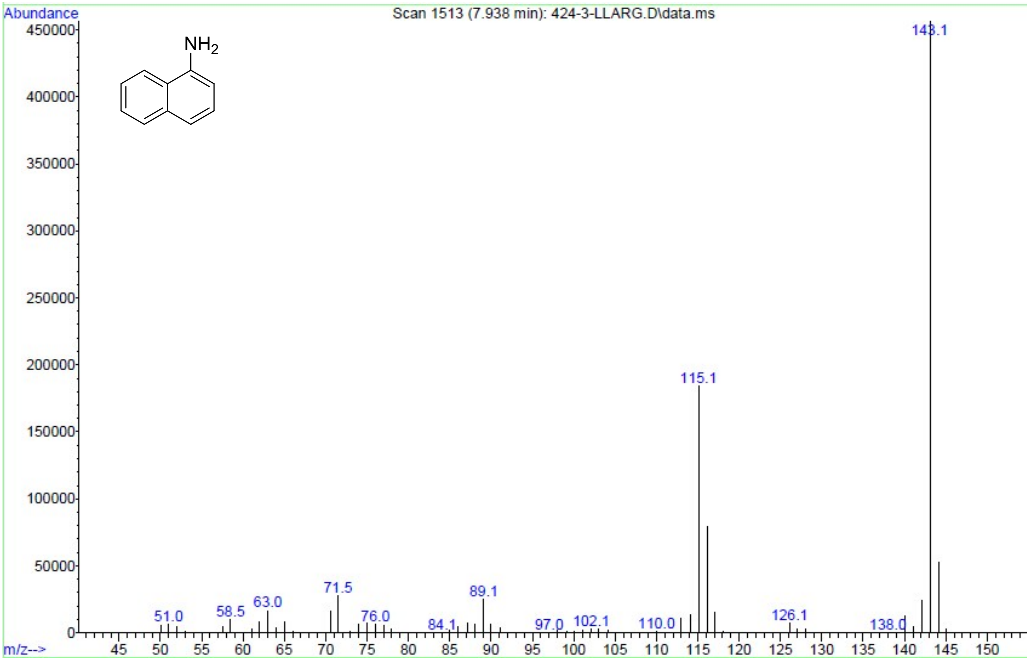

Figure 50. MS of **11**.

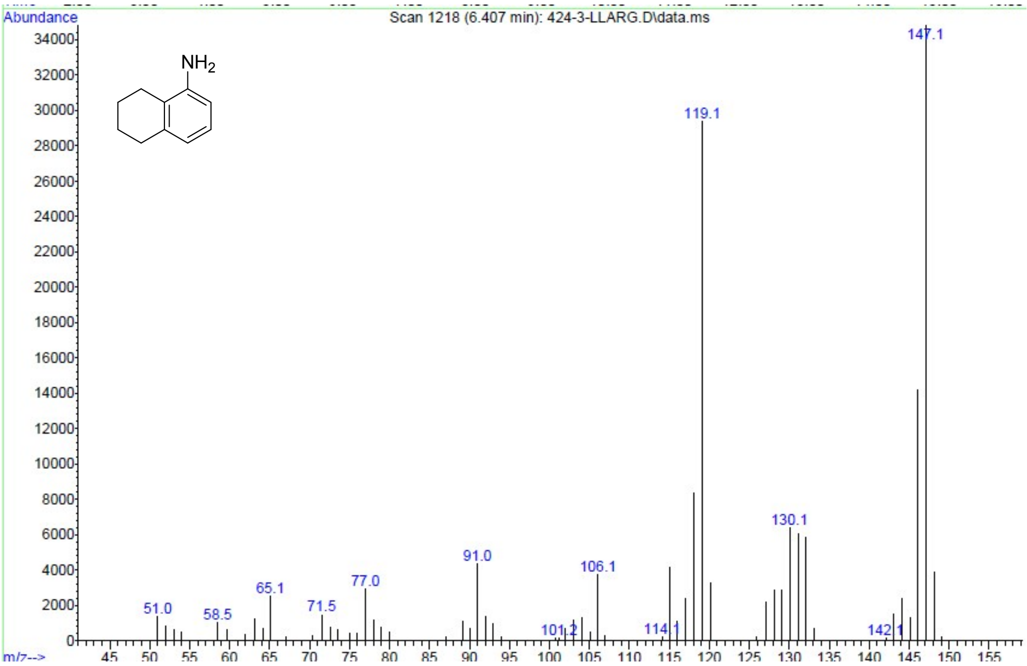

Figure 51. MS of **11a**.

- Hydrogenation of 1-(naphthalen-2-yl)ethanone **12**

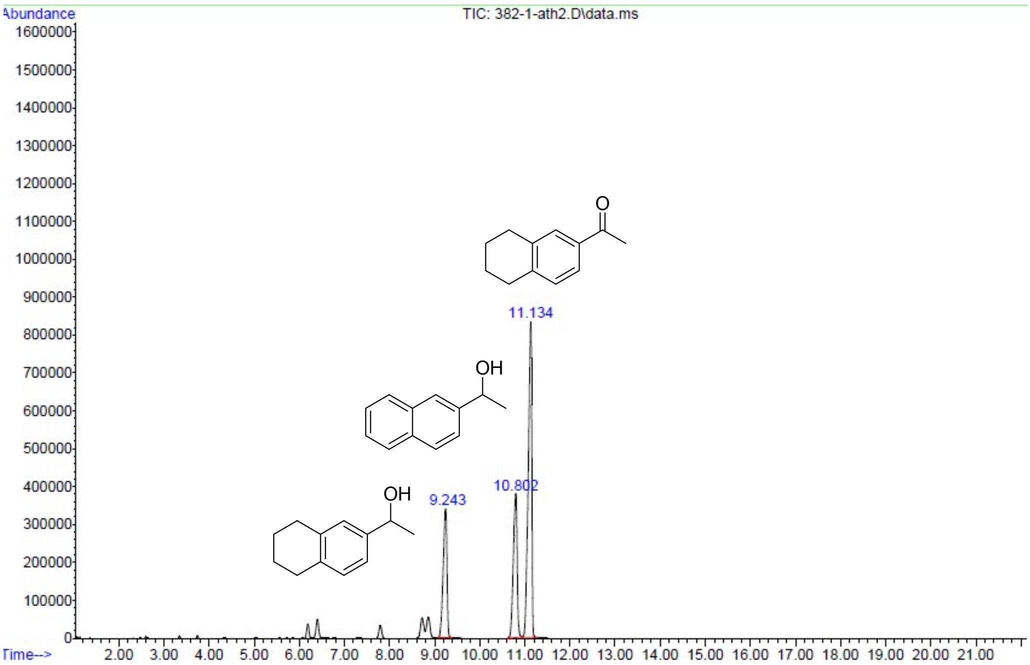

Figure 52. GC of the products formed in the hydrogenation of 1-(naphthalen-2-yl)ethanone **12**.

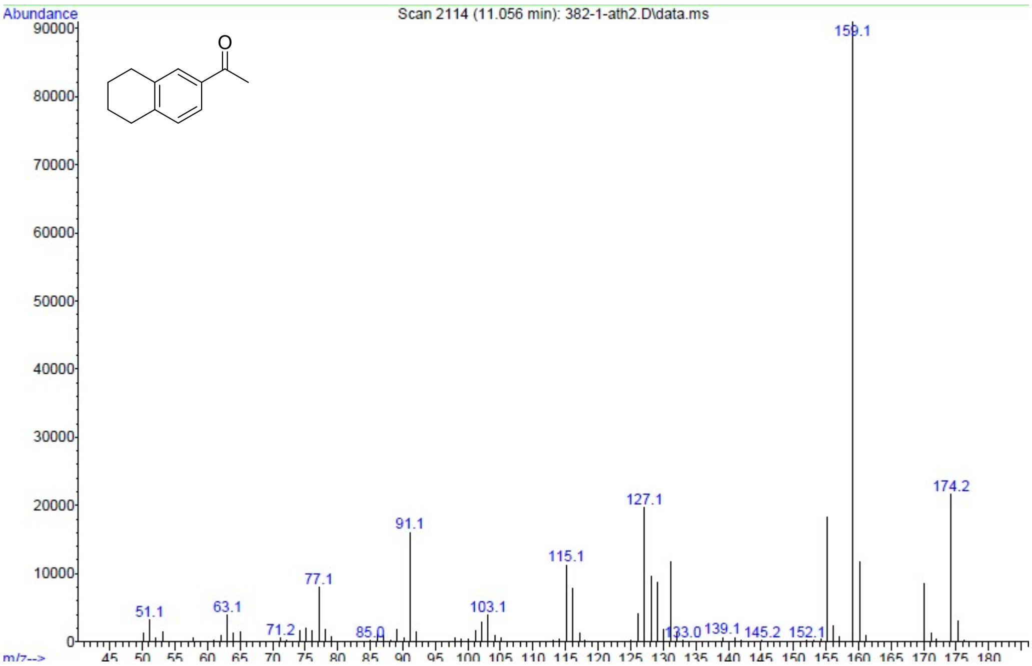

Figure 53. MS of **12a**.

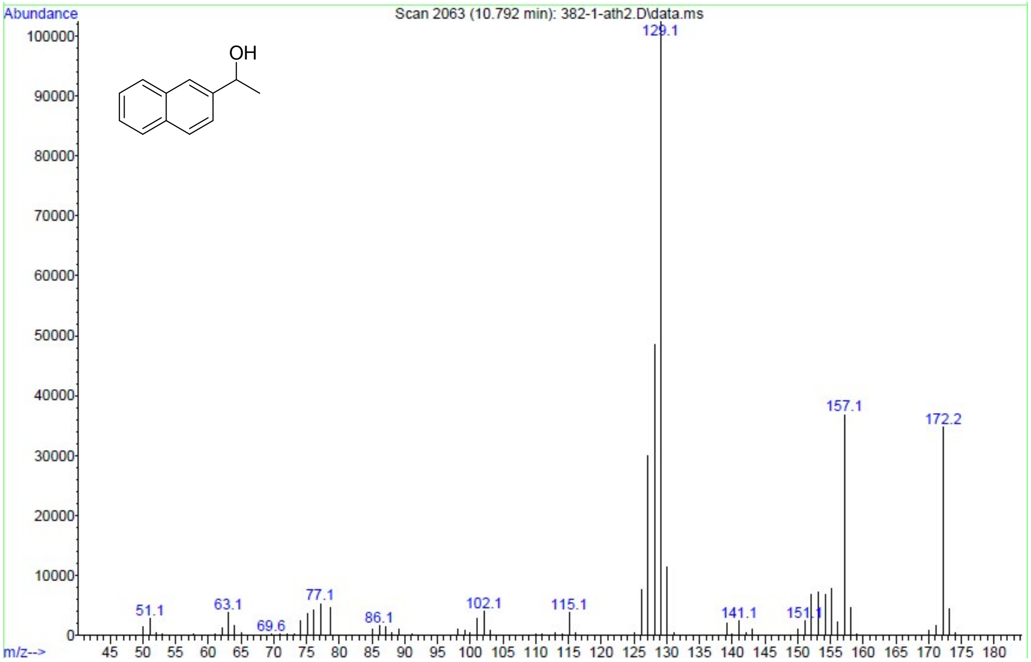

Figure 54. MS of **12b**.

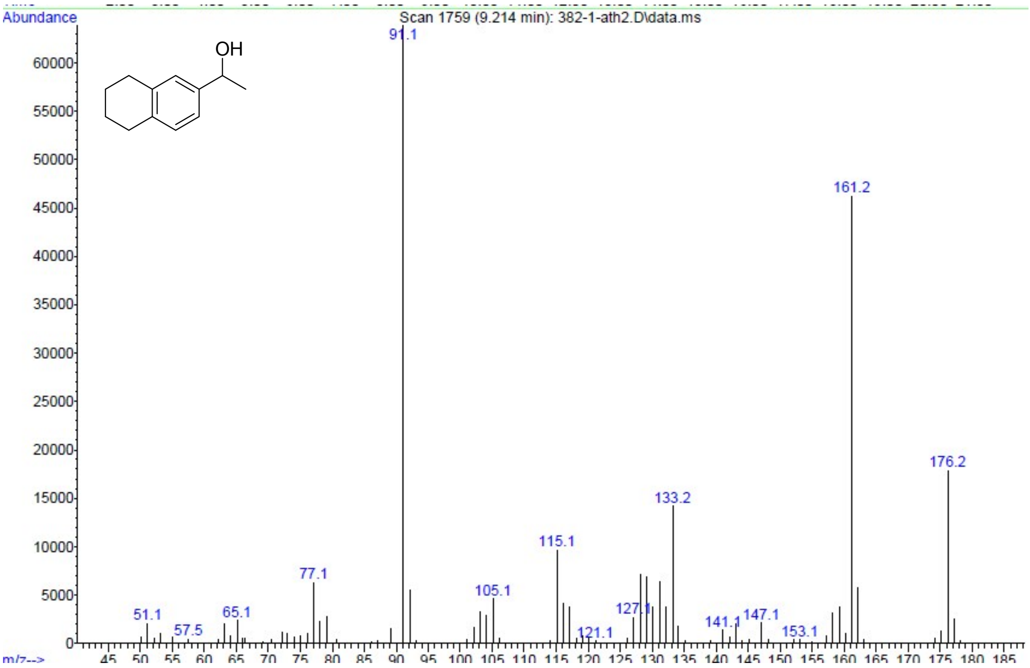

Figure 55. MS of **12c**.

- Hydrogenation of 1-(6-methylnaphthalen-2-yl)ethanone **13**

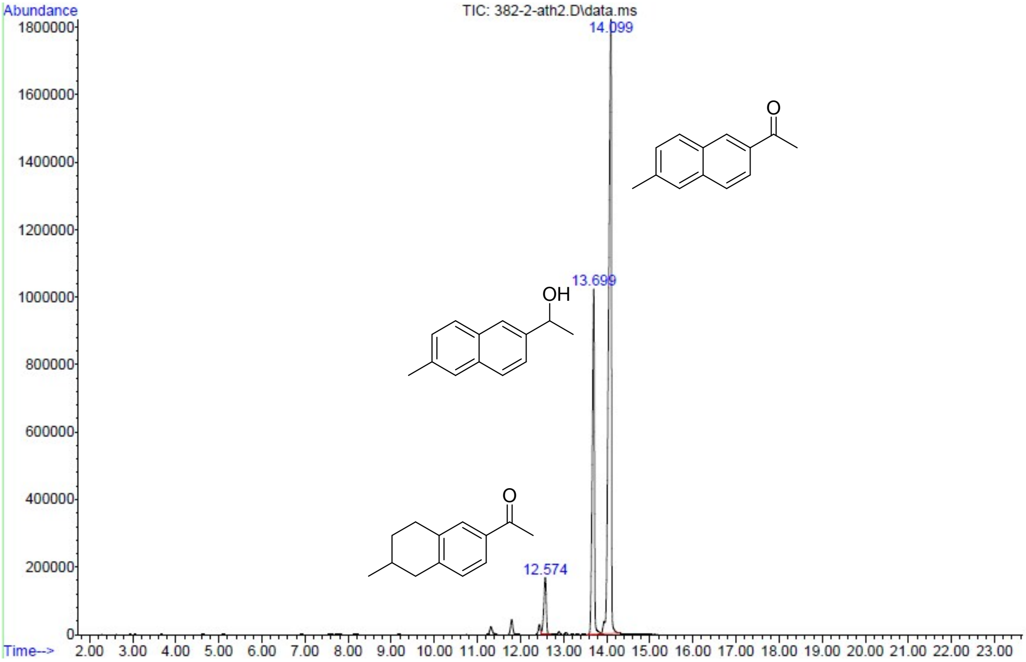

Figure 56. GC of the products formed in the hydrogenation of 1-(6-methylnaphthalen-2-yl)ethanone **13**.

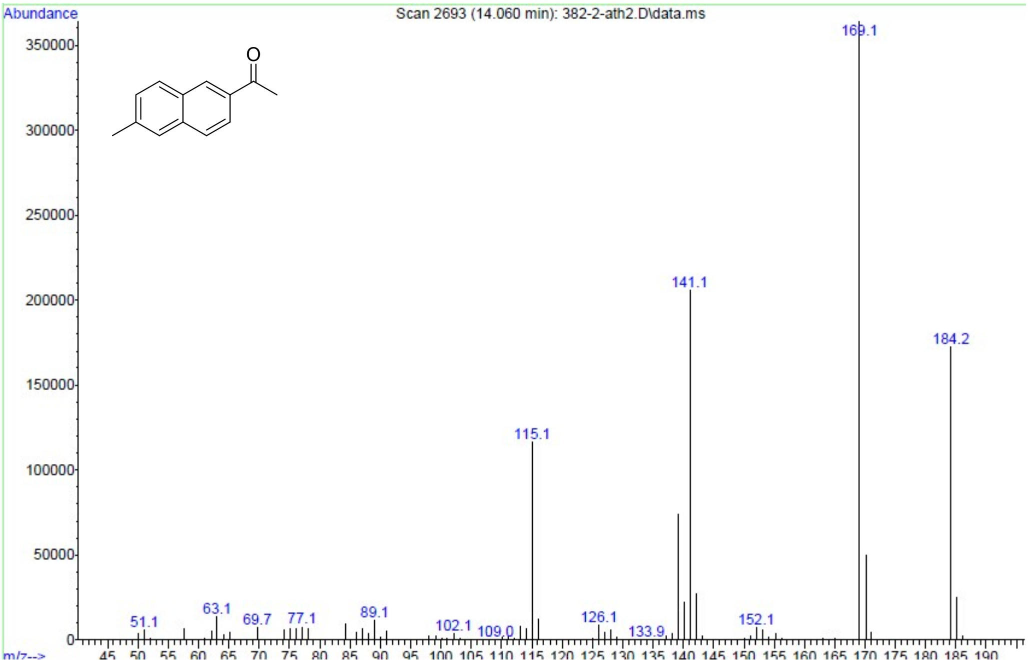

Figure 57. MS of **13**.

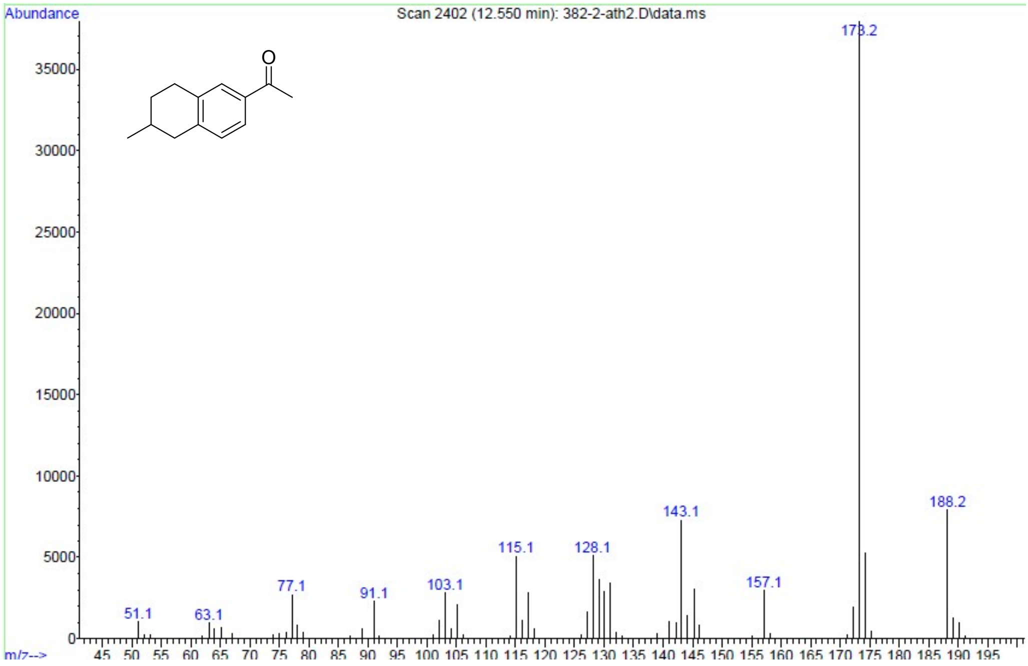

Figure 58. MS of **13a**.

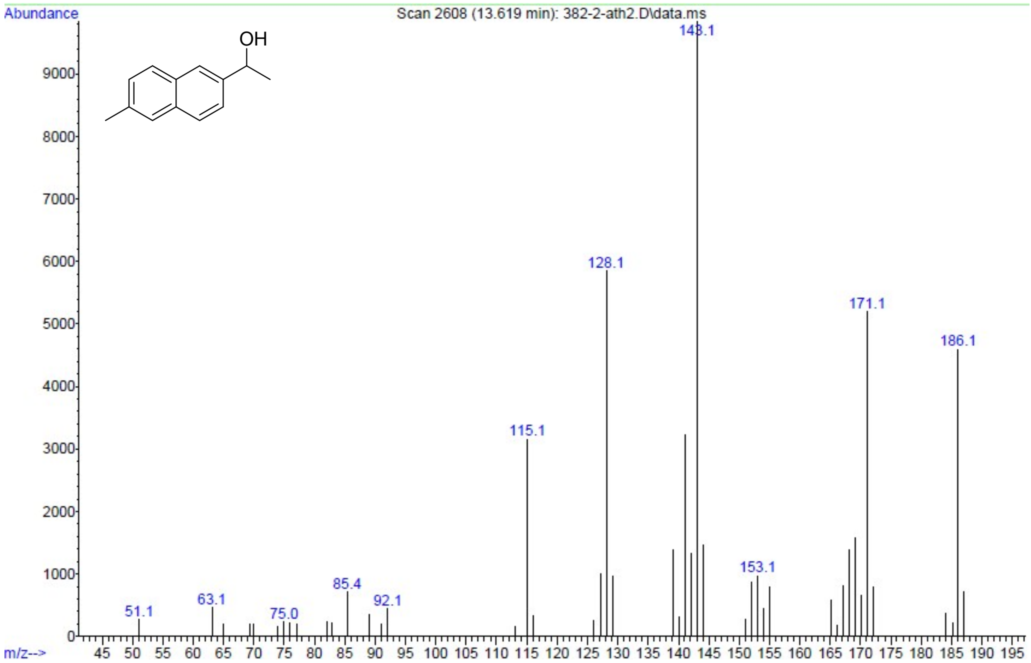

Figure 59. MS of **13b**.

- Hydrogenation of 1-(naphthalen-1-yl)ethanone **14**

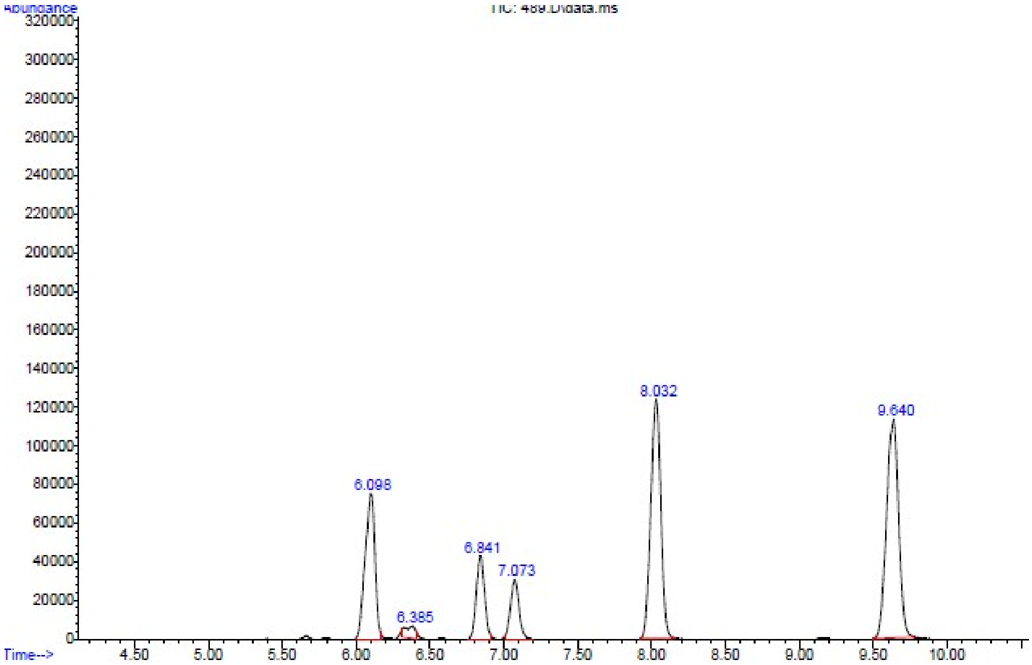

Figure 60. GC of the products formed in the hydrogenation of 1-(naphthalen-1-yl)ethanone **14**.

The different molecular peaks were not observed in the GC-MS of compound **14**, for this reason, the proportion of each product formed was determined by NMR.

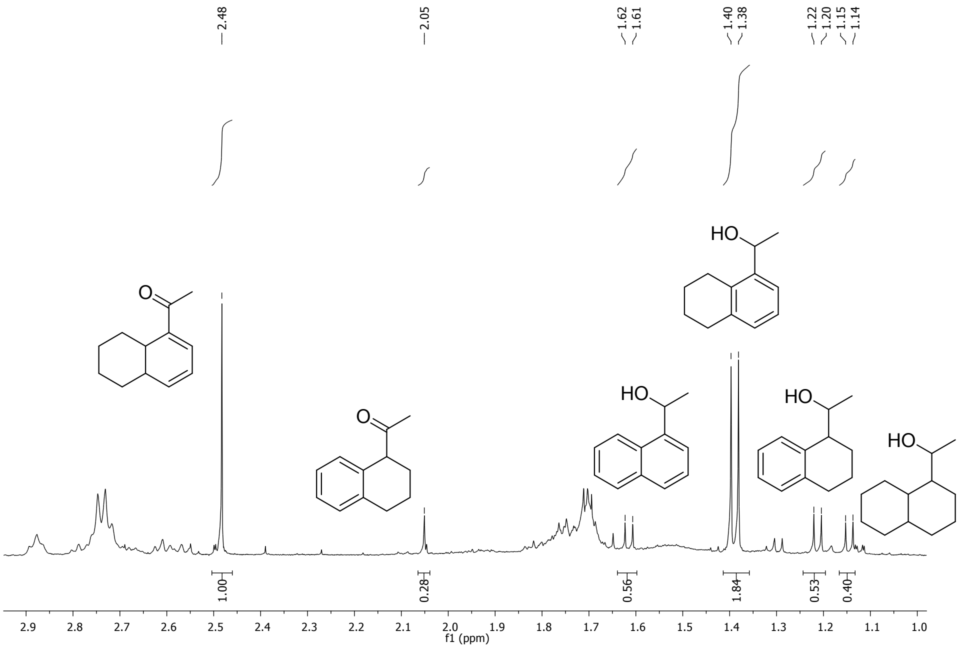

Figure 61. NMR (aliphatic zone) of the products formed in the hydrogenation of 1-(naphthalen-1-yl)ethanone **14**.

S5. References

[1] Llop-Castelbou, J.; Bresó-Femenia, E.; Blondeau, P.; Chaudret, B.; Castillón, S.; Claver, C.; Godard, C. *ChemCatChem.* **2014**, *6*, 3160–3168.