Supporting Information

Nanoparticle-supported and magnetically recoverable palladium (Pd) catalyst: A selective and sustainable oxidation protocol with high turn over number

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Contents:

General Experimental:

The phase of the as-synthesized nanoparticles was determined by XRD in a MMS X-ray diffractometer with a Cu Kα source in the 2θ range 10 to 70. The data were collected with a step of 0.5 deg/min. TEM micrographs were recorded on a JEOL JSM-1200 II microscope at an operating voltage of 120 kV. The particles were dispersed in ethanol by ultrasonication, loaded on a carbon coated copper grid, and then allowed to dry at room temperature before recording the micrographs. Elemental analyses of the catalyst before as well as after the reactions were performed on a Perkin Elmer Optima 3300 DV ICP-AES. Five mg of each sample was dissolved in 2.5 mL of concentrated aqua regia and the volume was adjusted to 50 mL in a volumetric flask. This solution was then used for the elemental analysis. Gas chromatographic mass spectroscopy (GCMS) spectra were collected on a HP 6890 series GC system coupled with a 5973 Mass Selective Detector. Thin layer chromatography (TLC) (silica gel; 10 % ethyl acetate: hexane) and gas chromatography (GC) were used to monitor the reactions. The substrate conversions and product selectivities were determined by GC-MS. The crude products were identified by GC-MS qualitative analysis using a GC system with a Mass selective detector. The identities were further confirmed for representative compounds by ^{1}H and ^{13}C NMR spectra that were recorded in deuterated chloroform-*d* ($CDCl_3$) with tetramethylsilane (TMS) as internal reference using a 300 MHz NMR spectrometer.

Synthesis of magnetic nano-ferrites:

$FeSO_4 \cdot 7H_2O$ (13.9 g) and $Fe_2(SO_4)_3$ (20 g) were dissolved in 500 mL water in a 1000 mL beaker. Ammonium hydroxide (25 %) was added slowly to adjust the pH of the solution to 10. The reaction mixture was then continually stirred for 1 h at 60 ^{0}C. The precipitated nanoparticles were separated magnetically, washed with water until the pH reached 7, and then dried under a vacuum at 60 °C for 2 h. Ferrite was characterized by X-ray diffraction (XRD) (Fig 1b) and transmission electron microscopy (TEM) (Fig 1a) This magnetic nano-ferrite (Fe_3O_4) was then used for further chemical modification.

Surface modification of nano-ferrites:

Nano-Fe_3O_4 (2 gm) was dispersed in 25 mL water by sonication for 30 min. Dopamine hydrochloride (2 gm) dissolved in 5 mL of water was added to this solution and again sonicated for 2 h. The amine-functionalized nanomaterial was then precipitated using acetone, isolated by centrifugation, and dried under vacuum at 60 ^{0}C for 2 h.

FT-IR evidently confirms the anchoring of dopamine on ferrite surfaces.

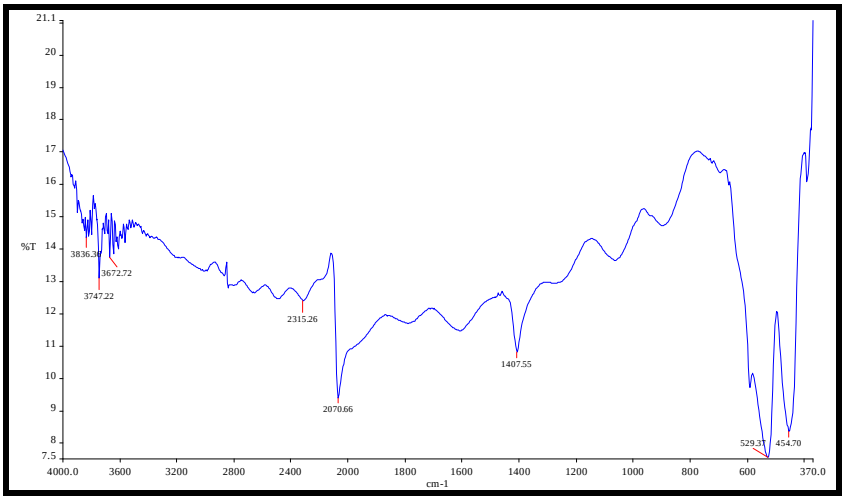


Fig. FT-IR of dopa-amine functionalized catalyst

Synthesis of nano-ferrite-Pd catalyst:

Amine-functionalized Nano-Fe_3O_4 (1 gm) was dispersed in water and sodium palladium chloride solution in water was added to the mixture to get 10 wt % of Pd. Hydrazine monohydrate solution in water was added dropwise to bring the pH of this mixture to 9, followed by addition of 0.1 gm of $NaBH_4$. The reaction mixture was then stirred for 24 h at room temperature. The product was allowed to settle, washed several times with water and acetone, and dried under vacuum at 60 ^{0}C for 2 h. Catalyst characterization by X-ray diffraction (XRD) (Fig 1d) and transmission electron microscopy (TEM) (Fig 1c) confirm the anchoring of Pd nanoparticles ferrite surfaces. The weight percentage of Pd in the catalyst was found to be 7.91 % by ICP-AES analysis.

Oxidation of alcohols using nano-ferrite-Pd catalyst:

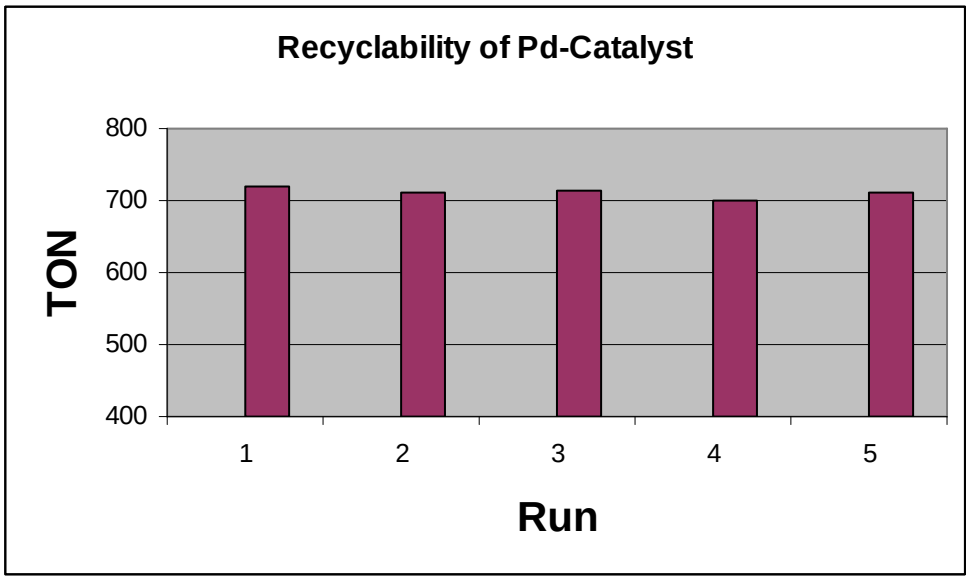
10 mmol of alcohol and 0.025 mole % of nano-ferrite-Pd catalyst were placed in a 10 mL glass tube with a magnetic stirrer bar. H_2O_2 (1 equiv) was then added dropwise to the reaction mixture under stirring at room temperature. The reaction was continuously stirred at 75-80 ^{0}C for 6 h. After completion of the reaction, stirring was stopped. Within 30-45 s, the reaction mixture turned clear and catalyst was deposited on the magnetic bar, which was easily removed from reaction mixture using an external magnet. Conversion and selectivity were periodically determined by GC analysis. All products are known in the literature and were identified by comparison of their ^{1}H and ^{13}CNMR with literature data and comparing their GC-MS spectra with standard Wiley mass spectral library.

Oxidation of olefins using nano-ferrite-Pd catalyst:

10 mmol of olefins and 0.025 mole % of nano-ferrite-Pd catalyst were placed in a 10 mL glass tube with a magnetic stirrer bar. H_2O_2 (2 equiv) was then added to the reaction mixture dropwise under stirring at room temperature and the same procedure described above was followed

Recyclability and Pd-leaching study:

For practical applications of heterogeneous systems, the lifetime of the catalyst and its level of reusability are very important factors. To clarify this issue, we established a set of experiments for the oxidation of benzyl alcohol using the recycled nano-Fe_3O_4-Pd catalyst. After the completion of the first reaction to afford the corresponding aldehyde, the catalyst was recovered magnetically, washed with methanol, and finally dried at 60 ^{0}C for 10 min. A new reaction was then performed with fresh reactants and H_2O_2, under the same conditions. The nanoferrite-supported Pd catalyst could be used at least 5 times without any change in activity.



Metal leaching was studied by ICP-AES analysis of the catalyst before and after the five reaction cycles. The Pd concentration was found to be 7.91 % before reaction and 7.86 % after the reaction, which confirmed negligible Pd leaching; this is due to dopamine anchor on nano-ferrite surface (Scheme 1), which is acting as a chelating agent and preventing Pd-leaching. Also, no Pd metal was detected in the final oxidation product.

In fact, to date there is no 100% leach proof Pd catalyst; hence, the most important criteria in choosing the catalyst is Pd metal recovery. It would be preferable to use a more accessible, lower cost Pd catalyst provided that the process works at high TONs, and that the catalyst leaves no remnants of metal within the end product, since metal contamination is highly regulated by the pharmaceutical industry. All above conditions were well satisfied by our recyclable nano-ferrite-supported Pd catalyst, which works at high TON with excellent selectivity and yields negligible Pd concentration in the end product after completion of the reaction.

TEM and XRD images of pine structured α-Fe_2O_3

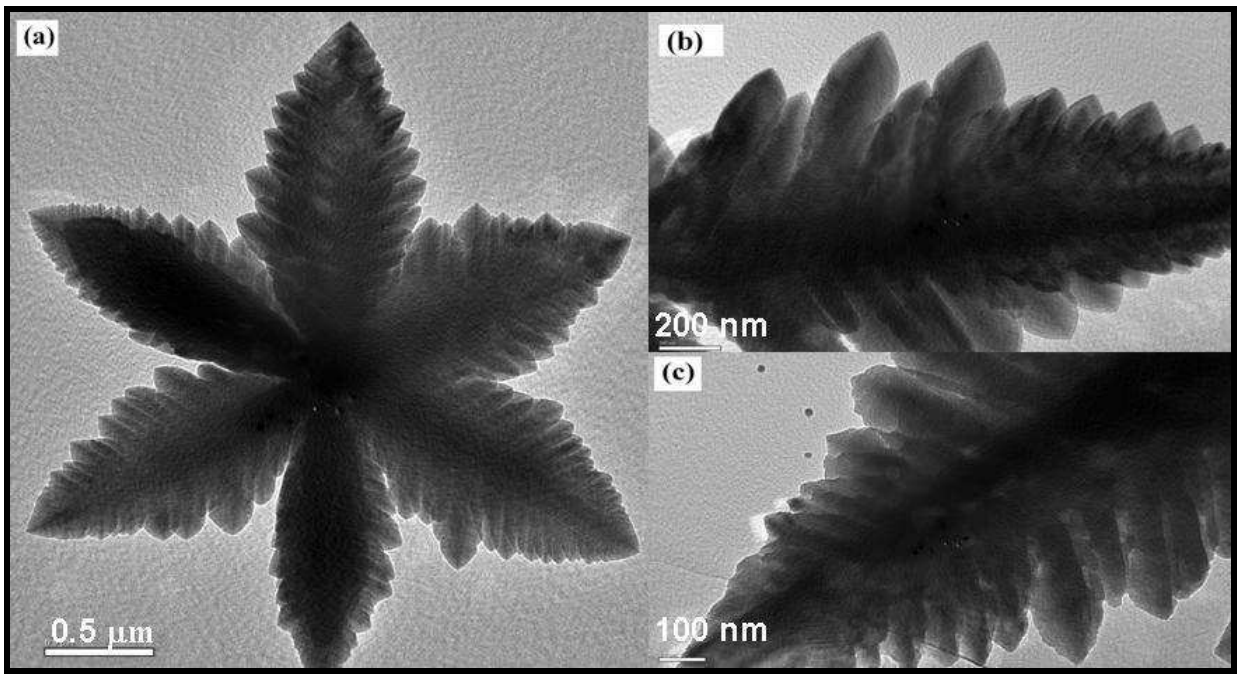


Figure 1 TEM of single-crystal α-Fe_2O_3

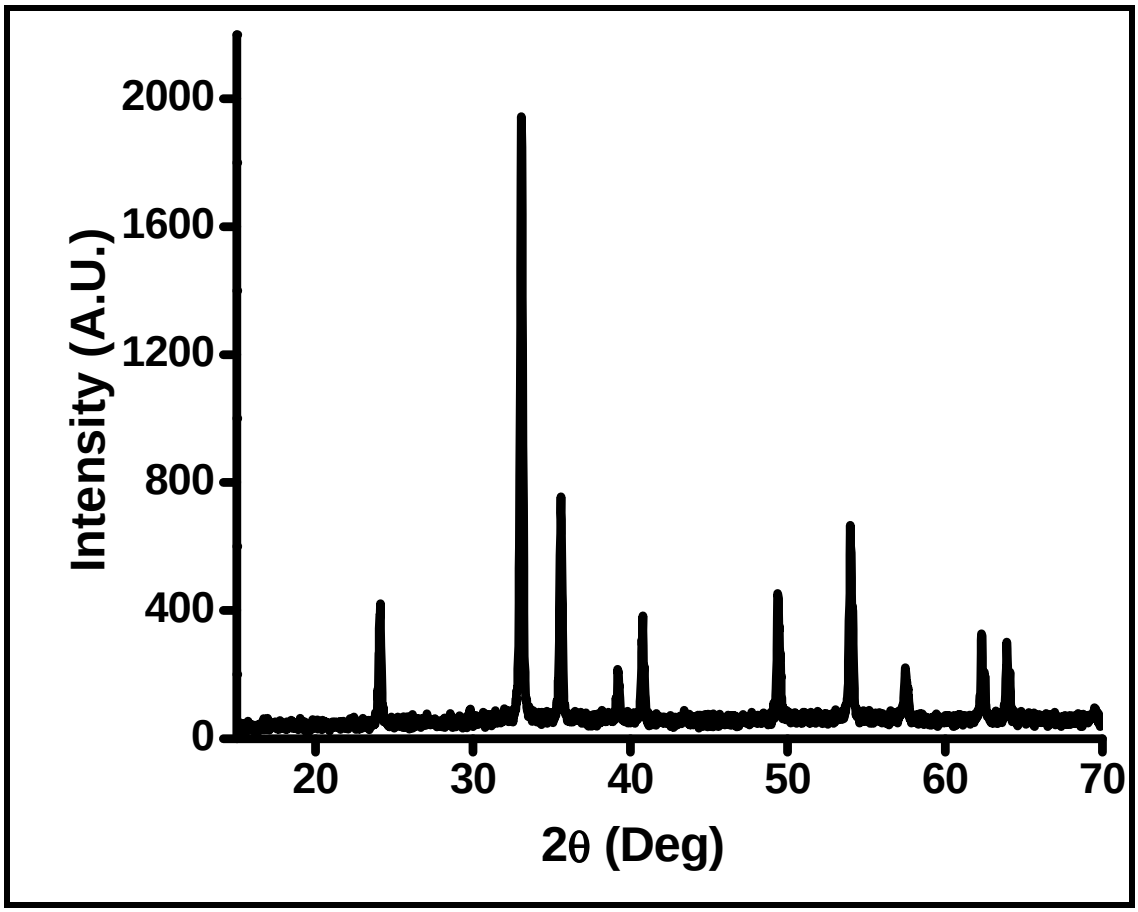


Figure 2 XRD of single-crystal α-Fe_2O_3

MS Spectrum of Benzaldehyde

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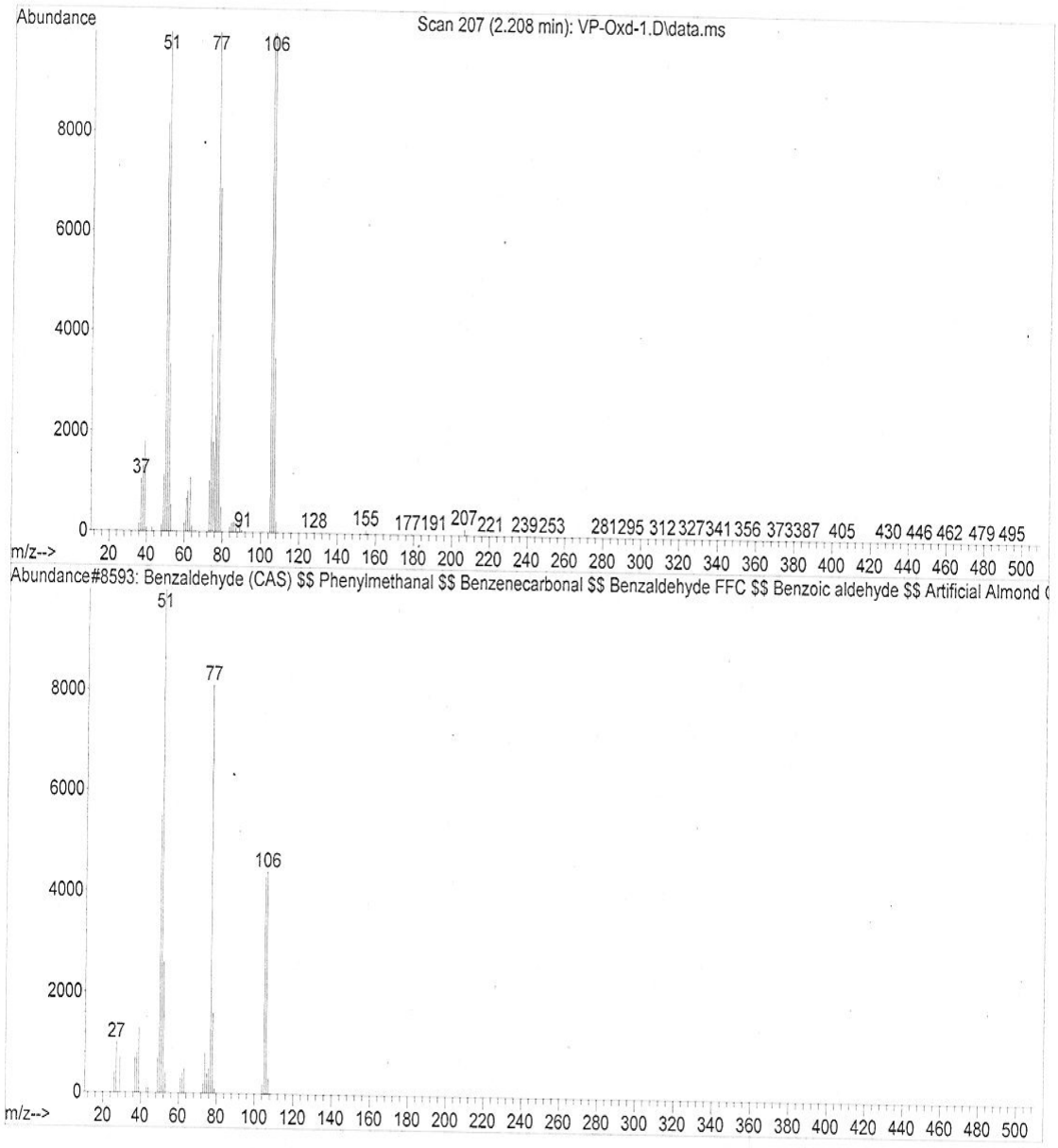
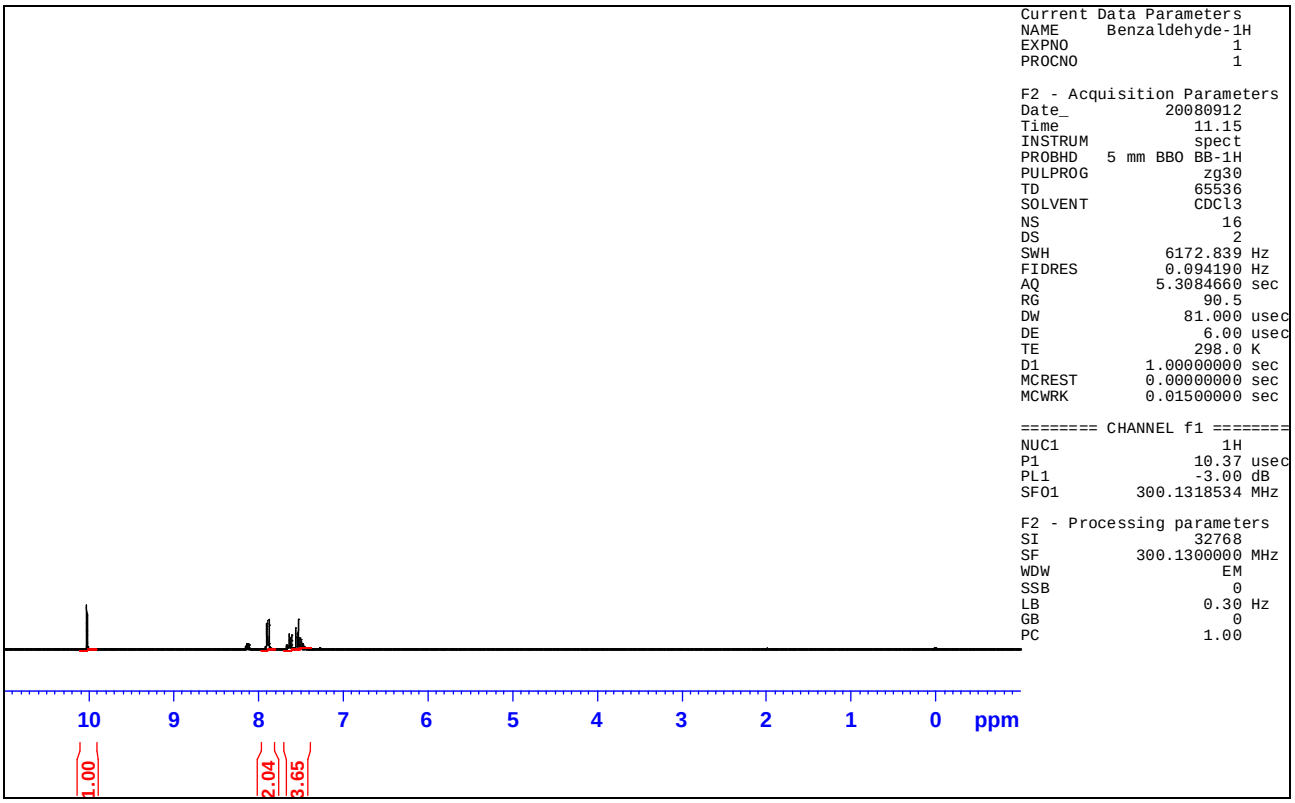


^{1}H-NMR spectrum of benzaldehyde

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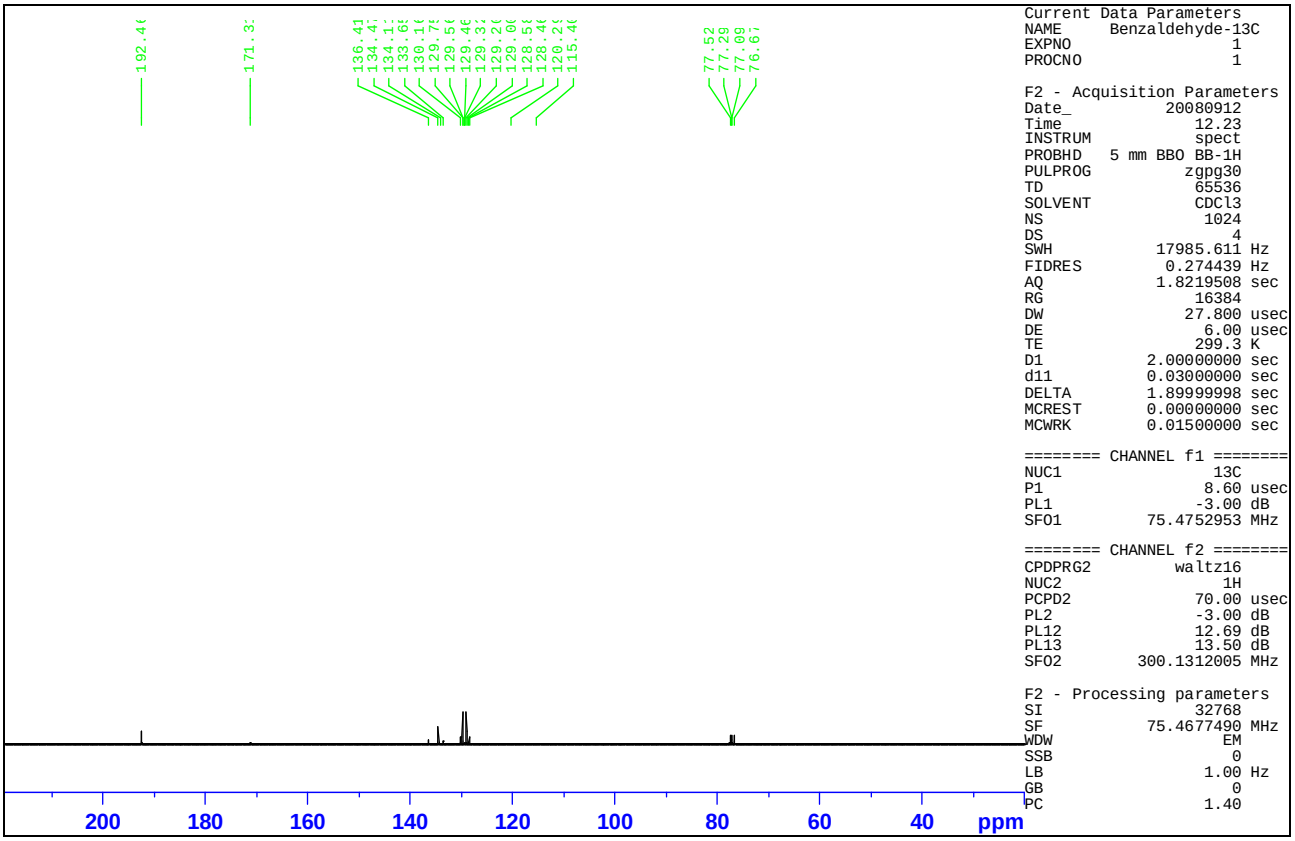


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MS spectrum of 4-chloro-benzaldehyde

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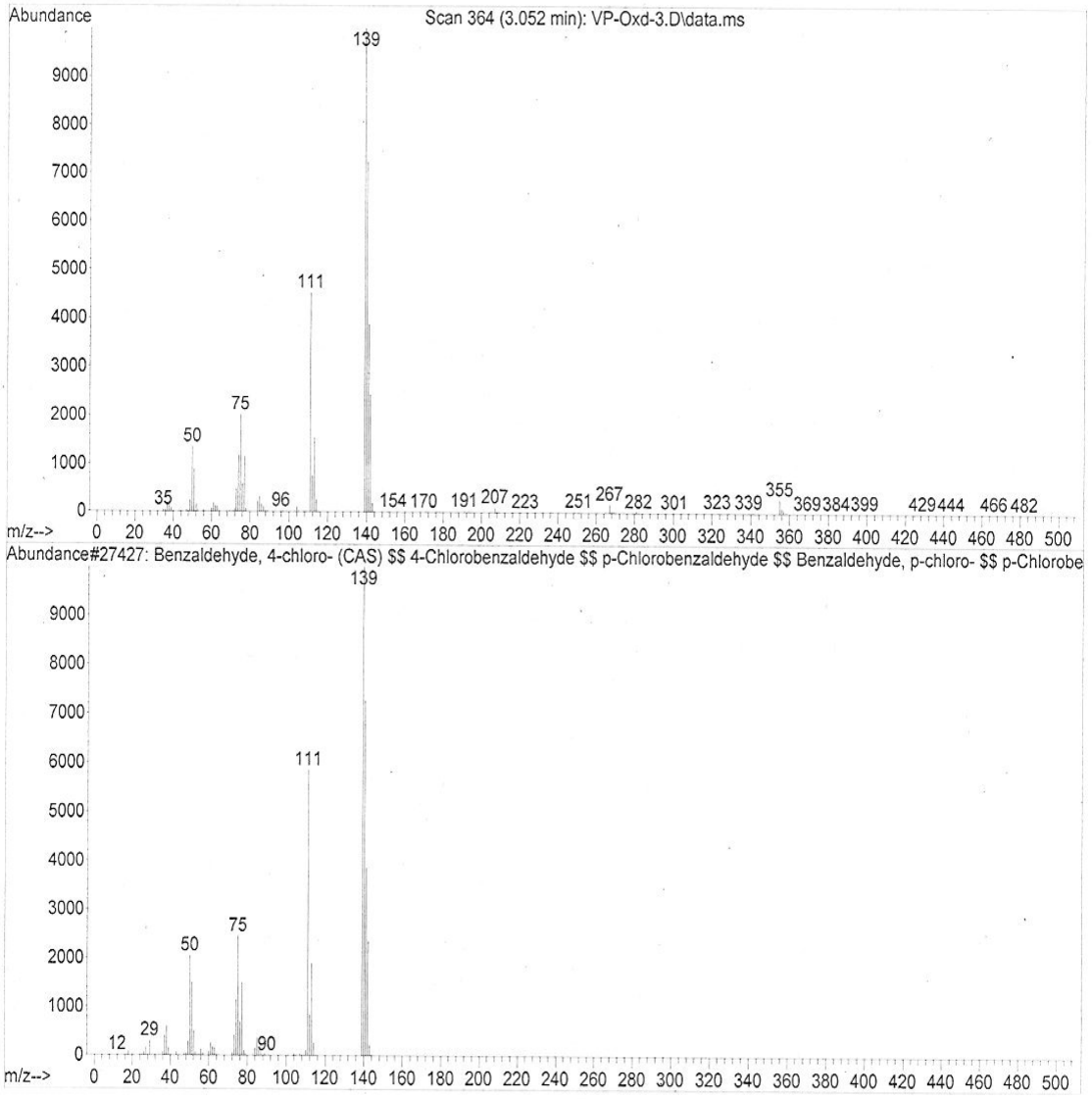

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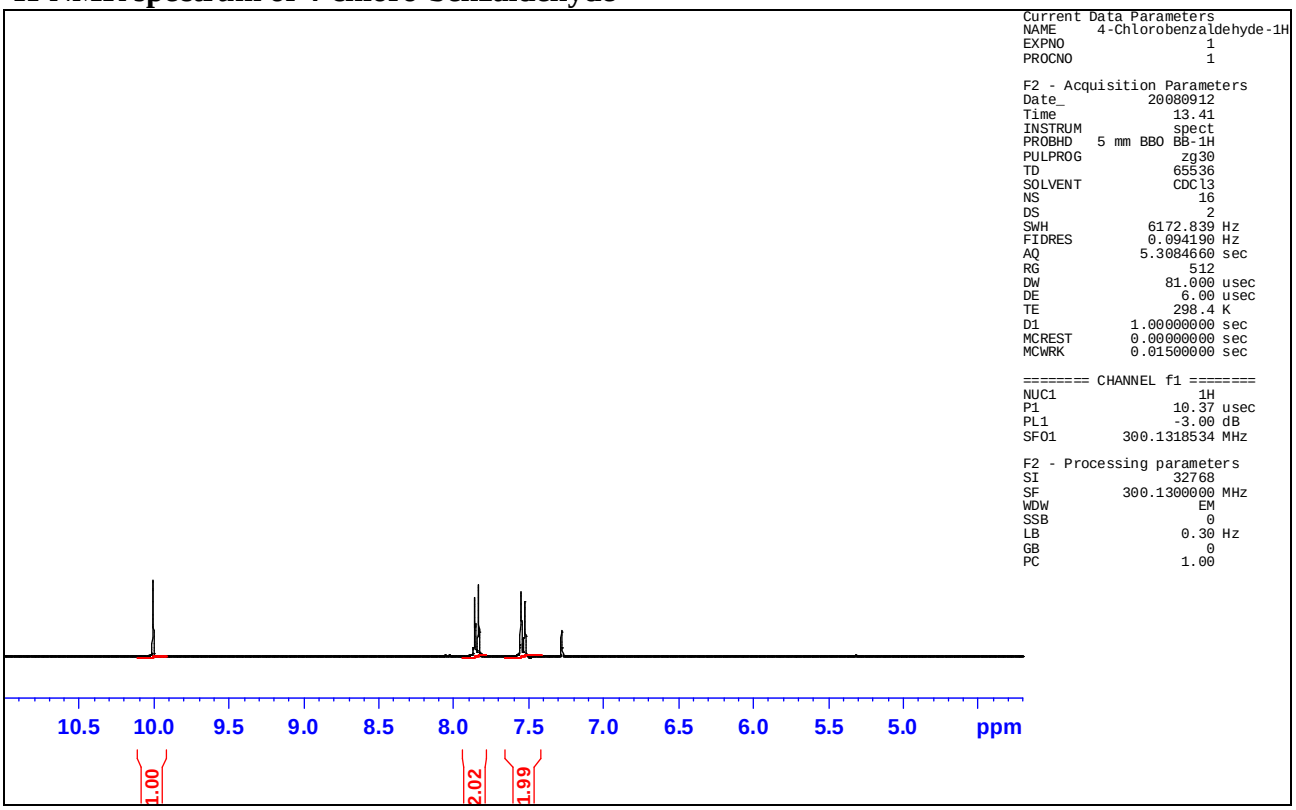

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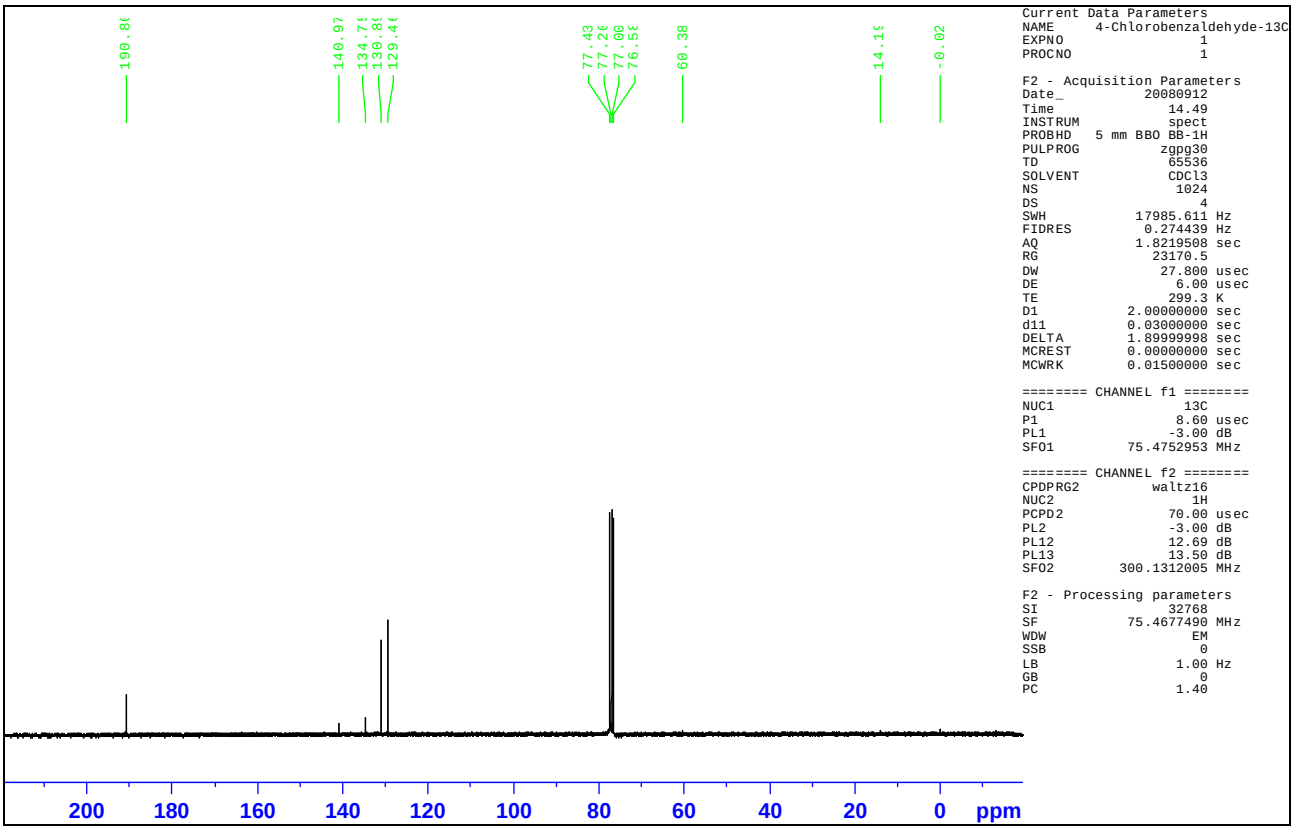

MS spectrum of 2-chloro-benzaldehyde

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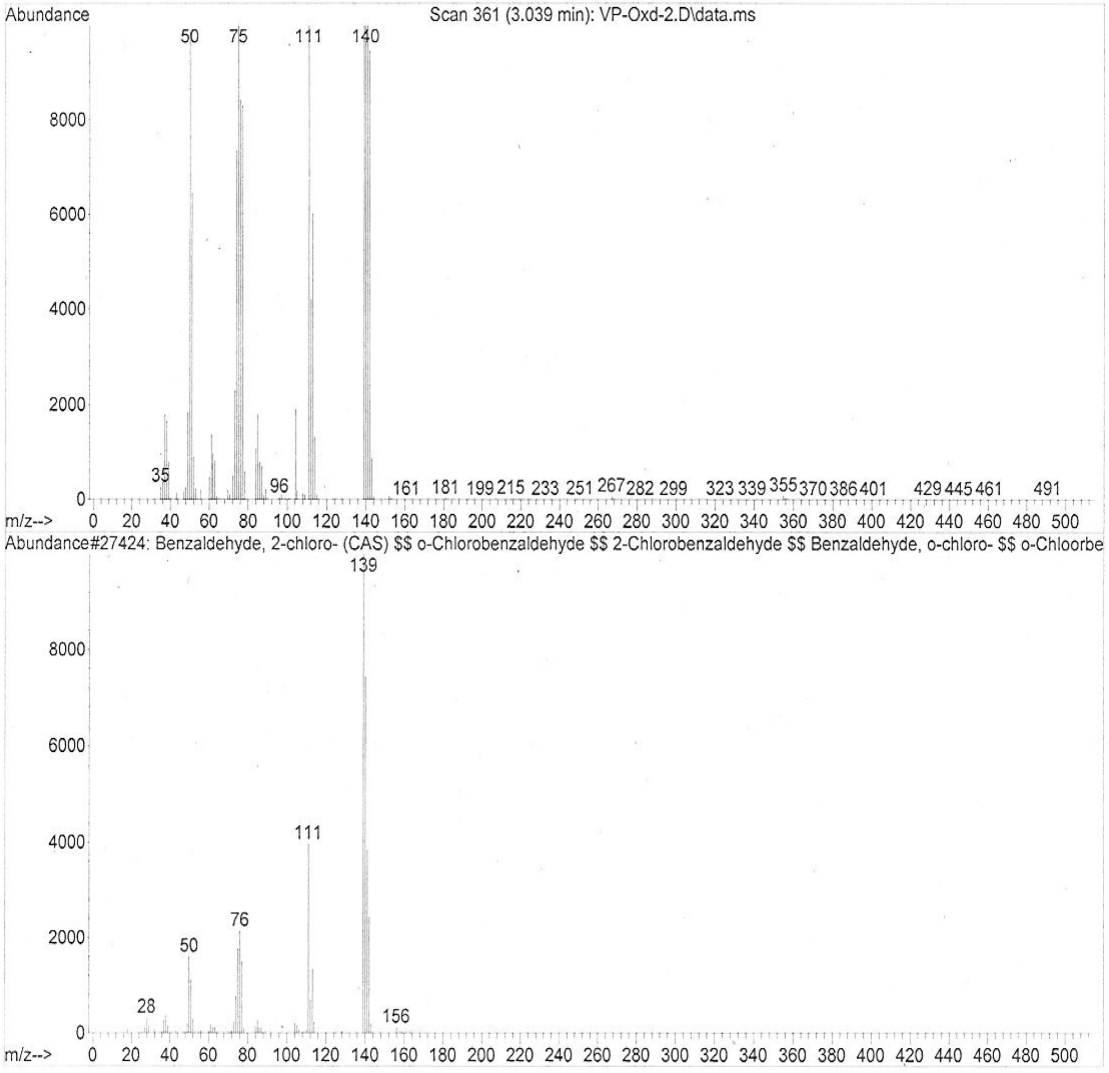

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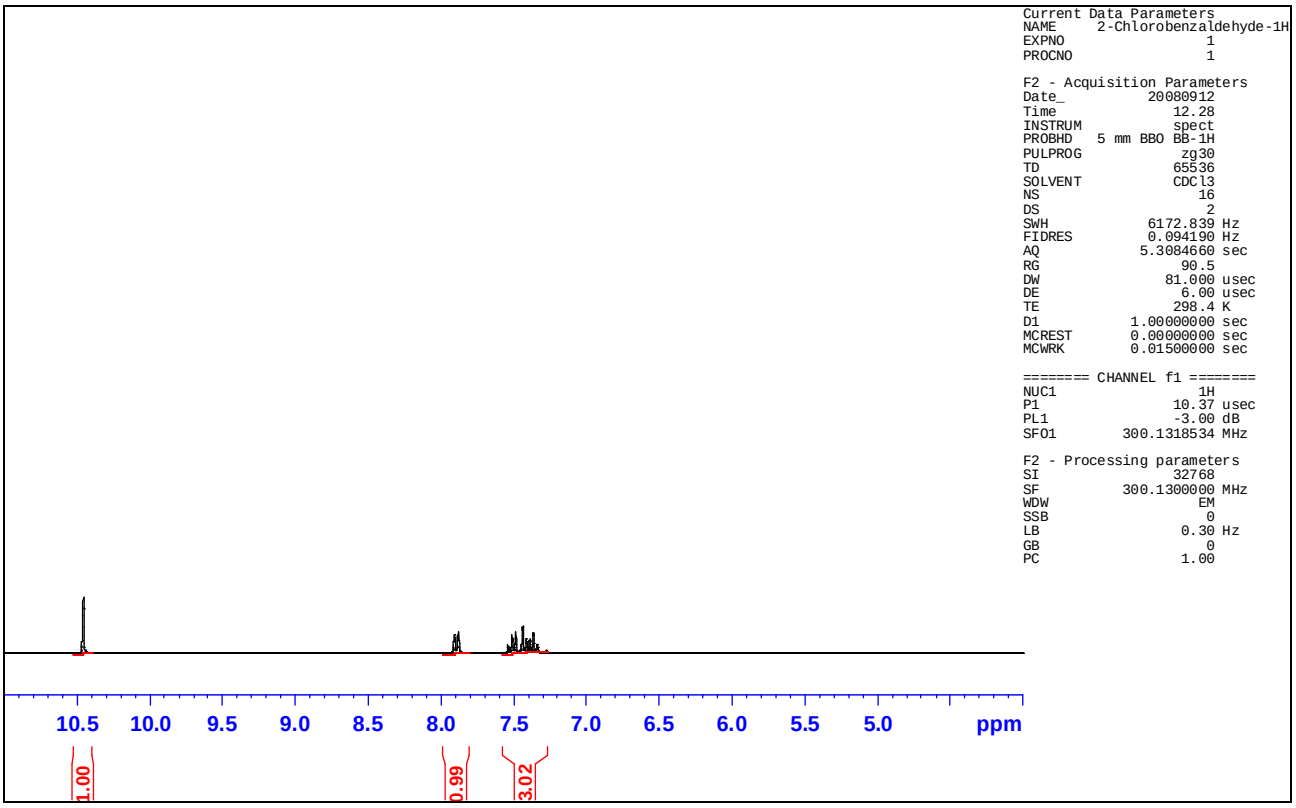

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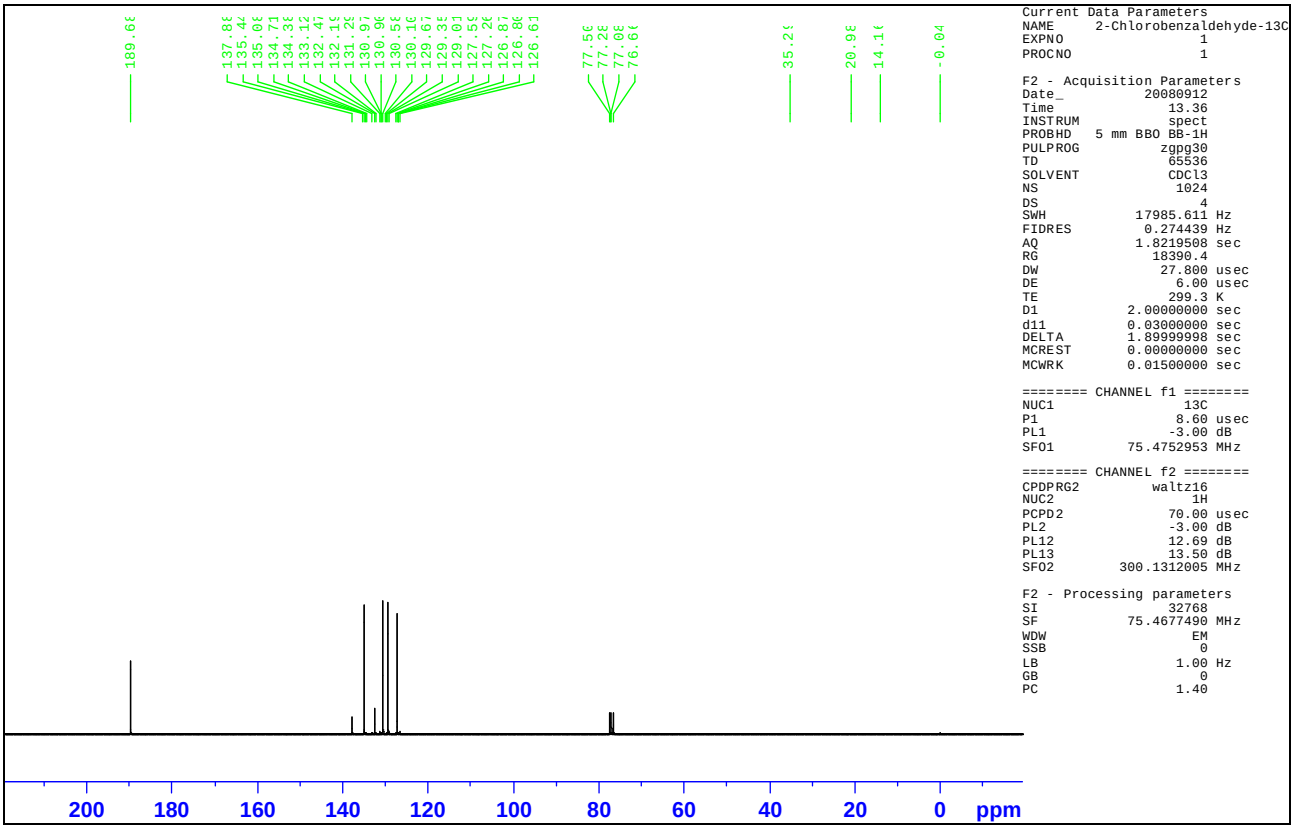
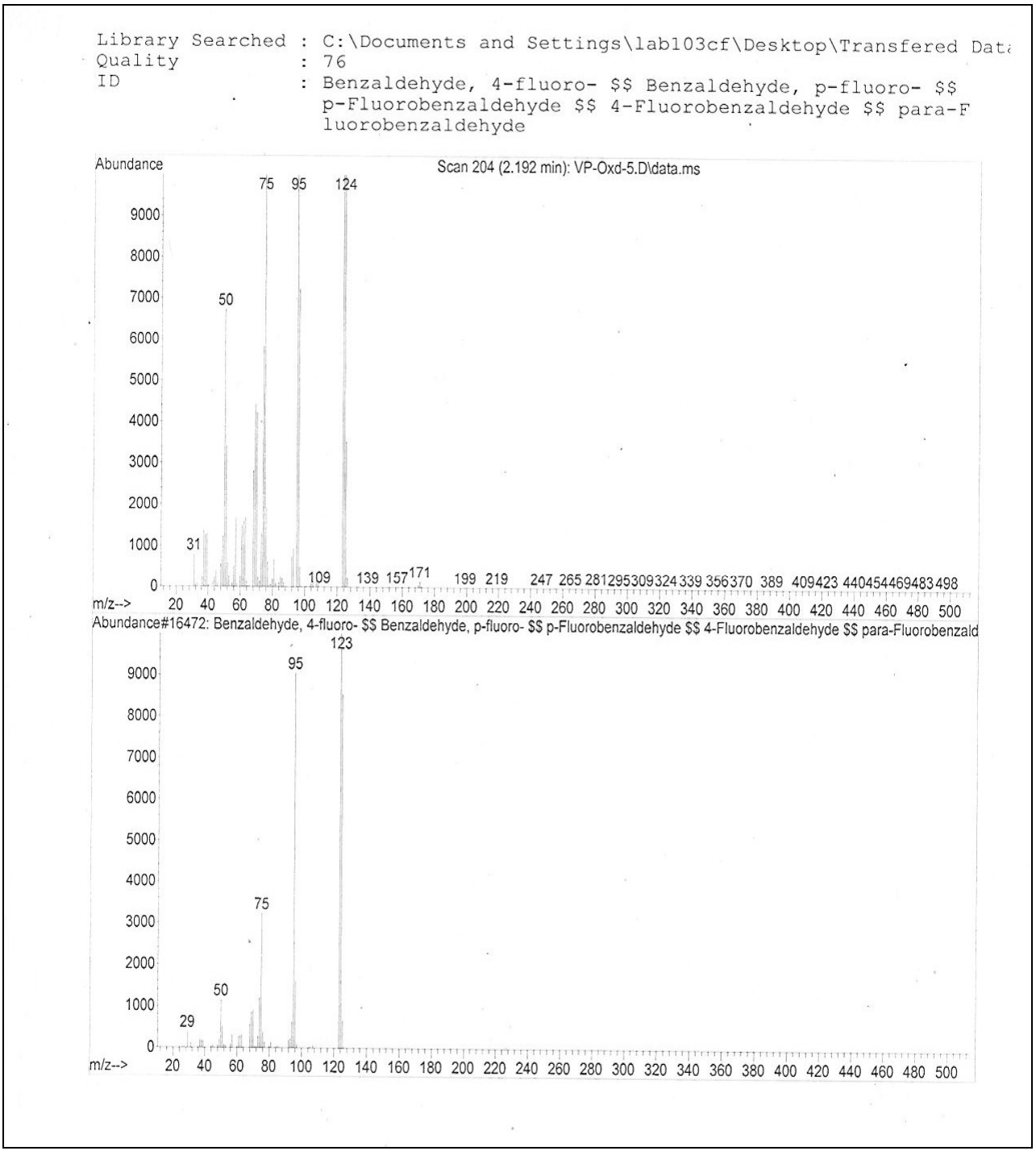


MS spectrum of 4-fluoro-benzaldehyde



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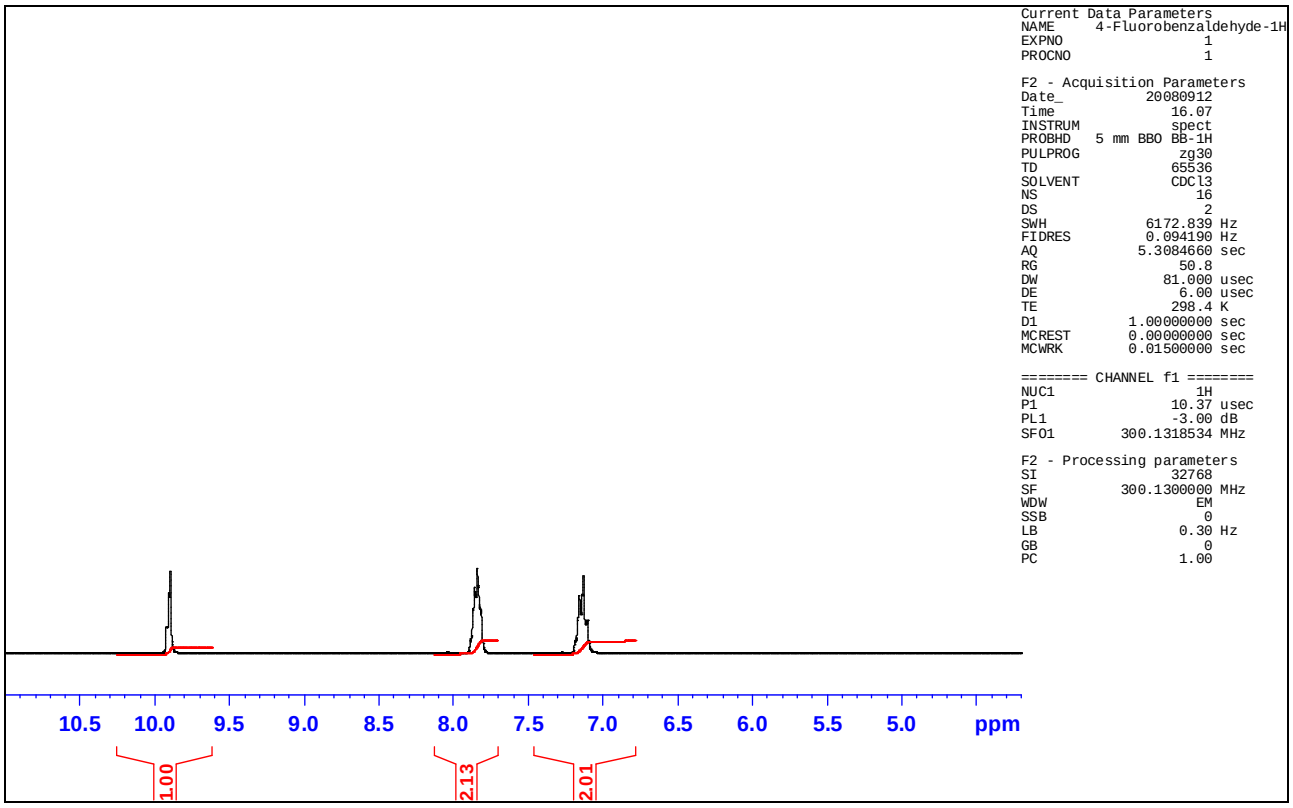

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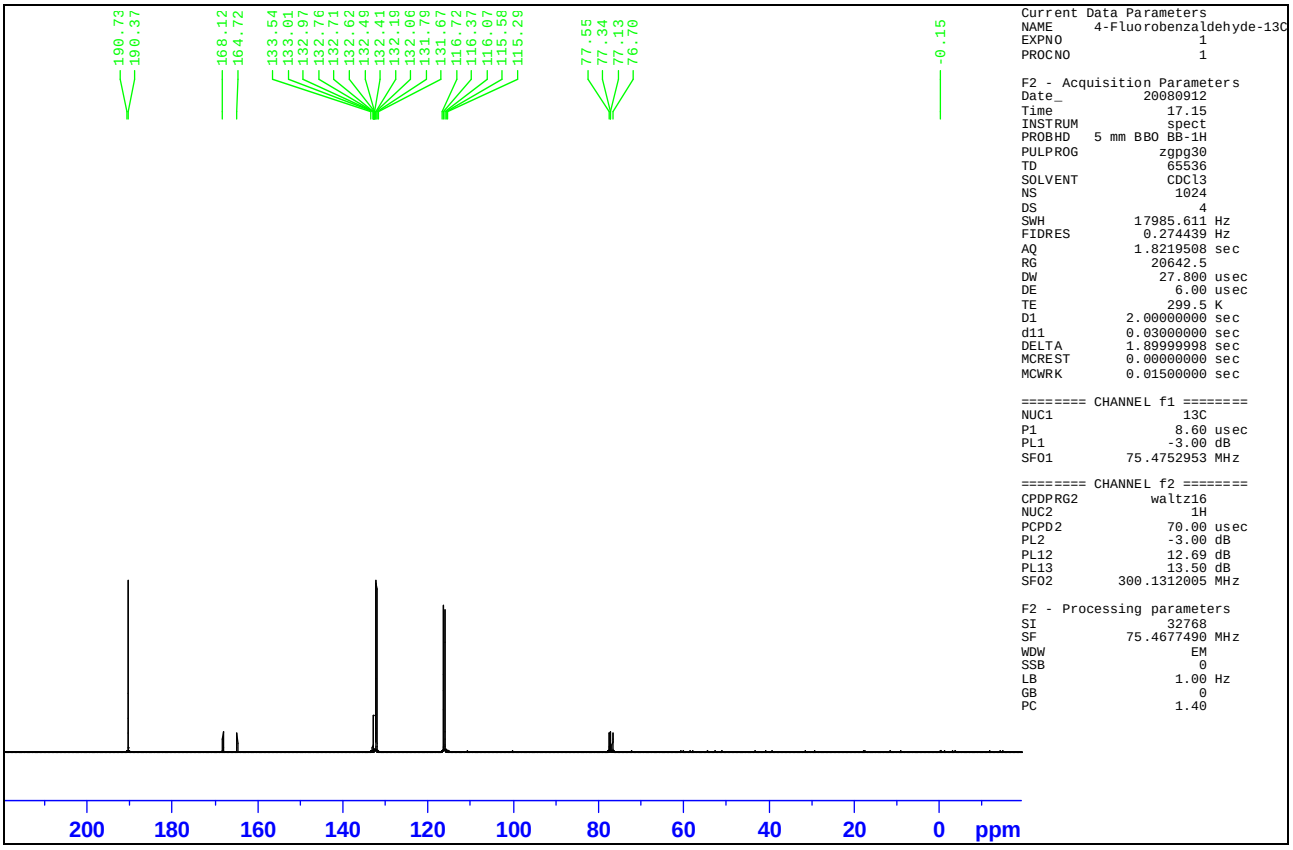

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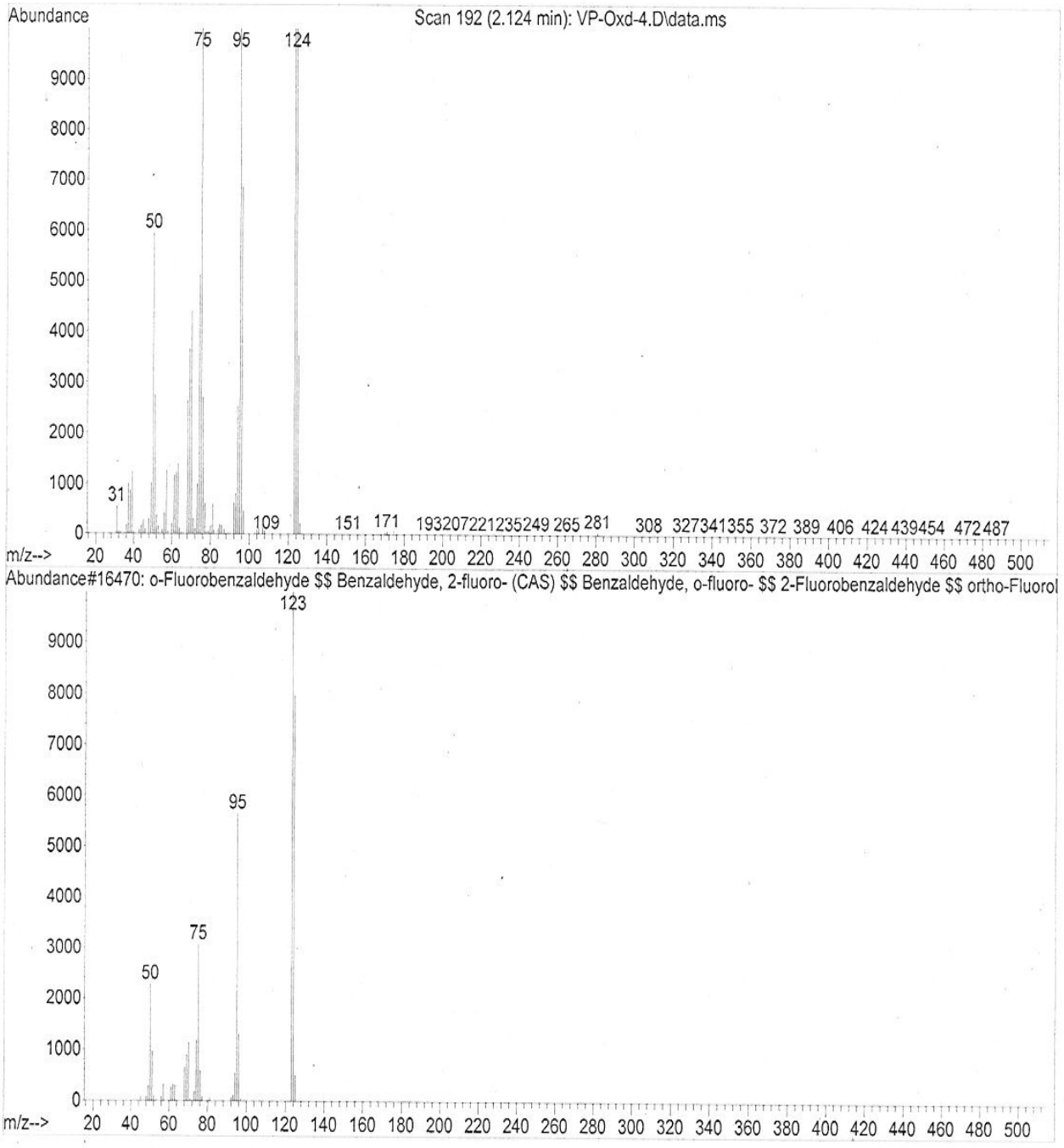

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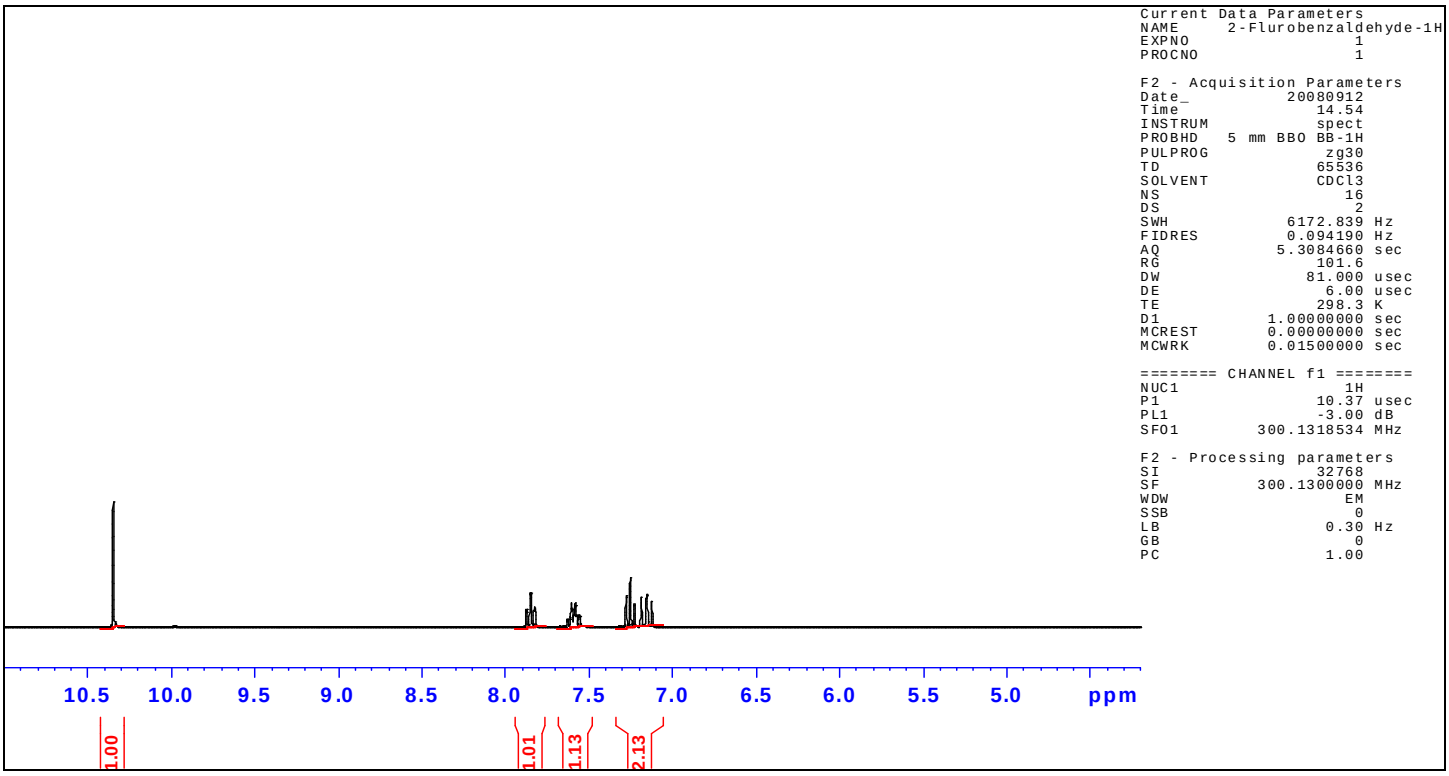

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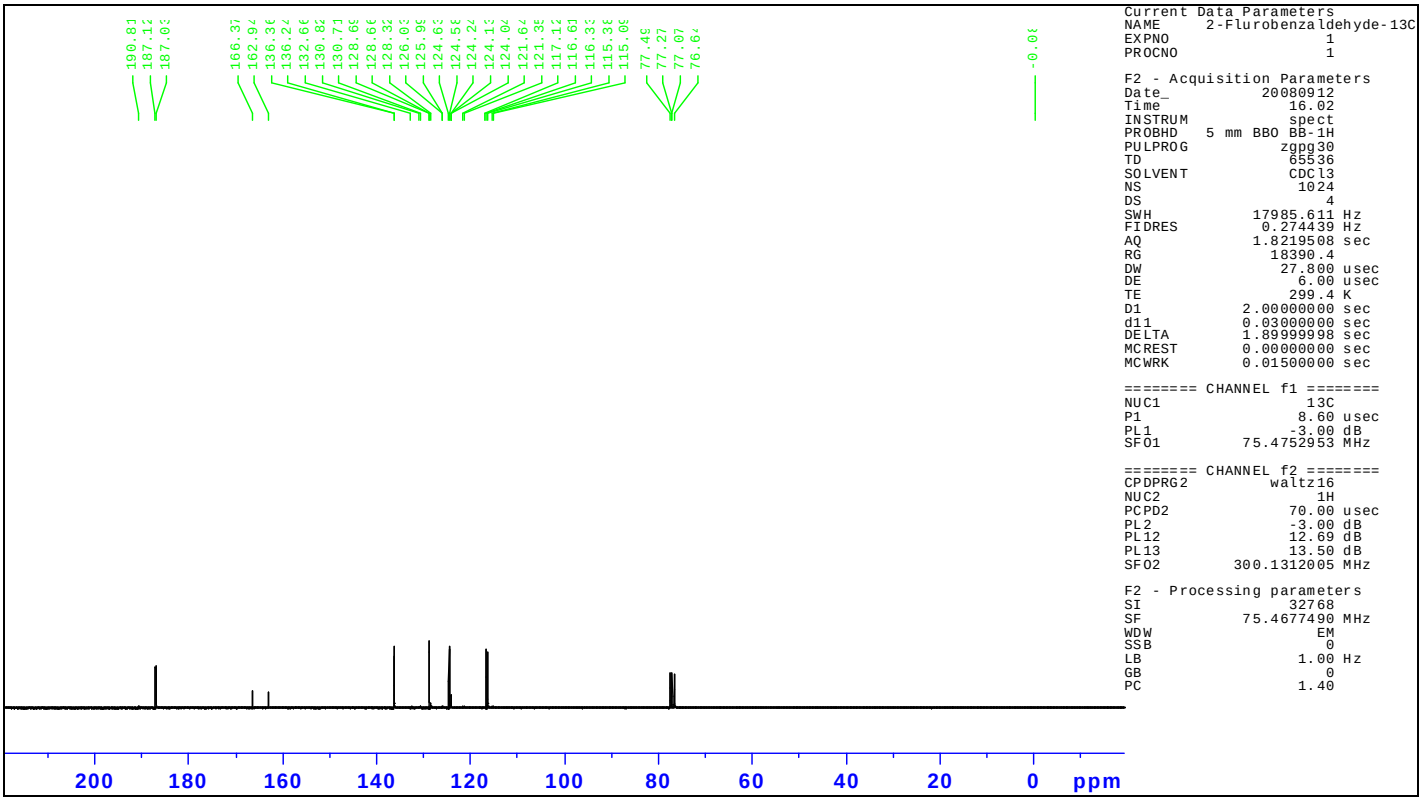

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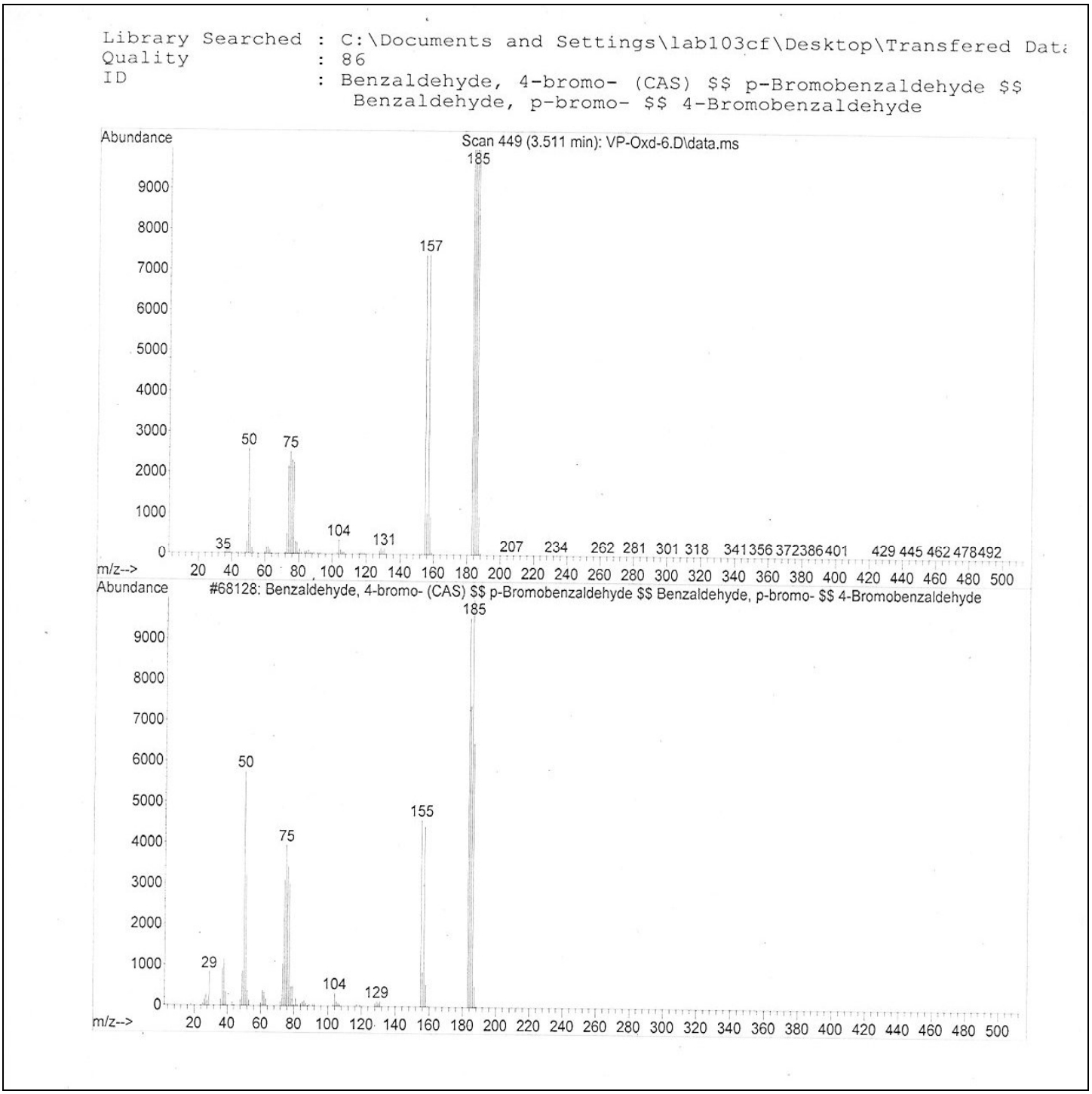

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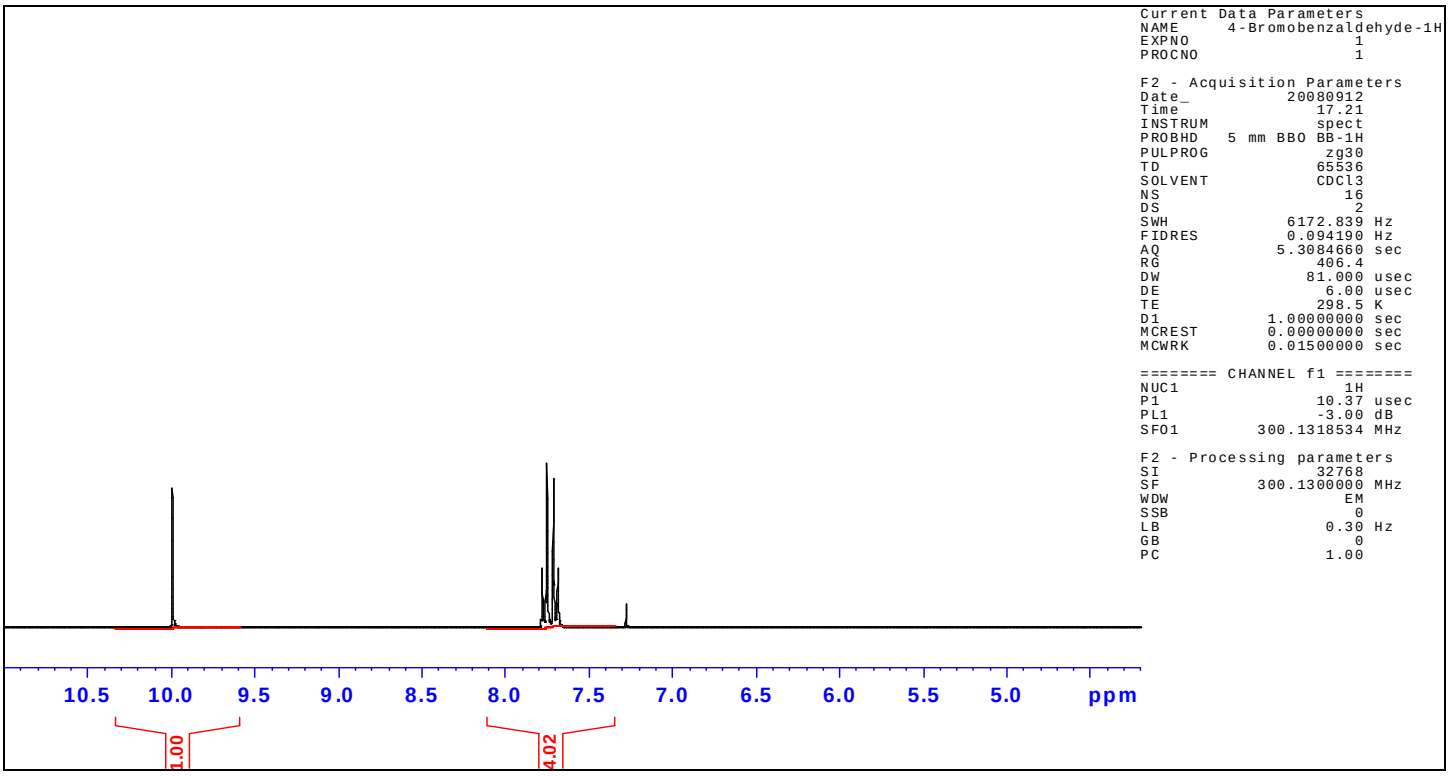

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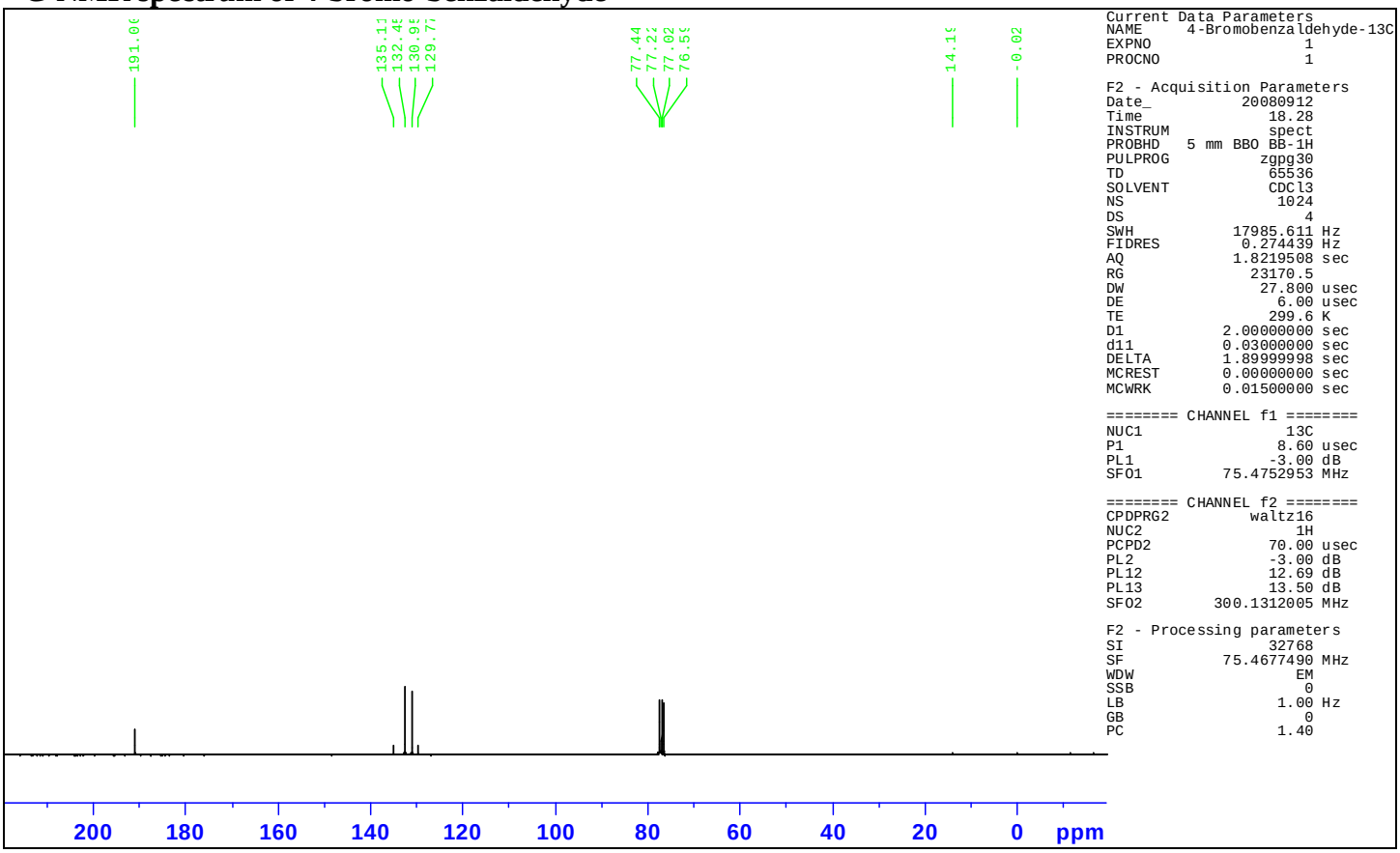

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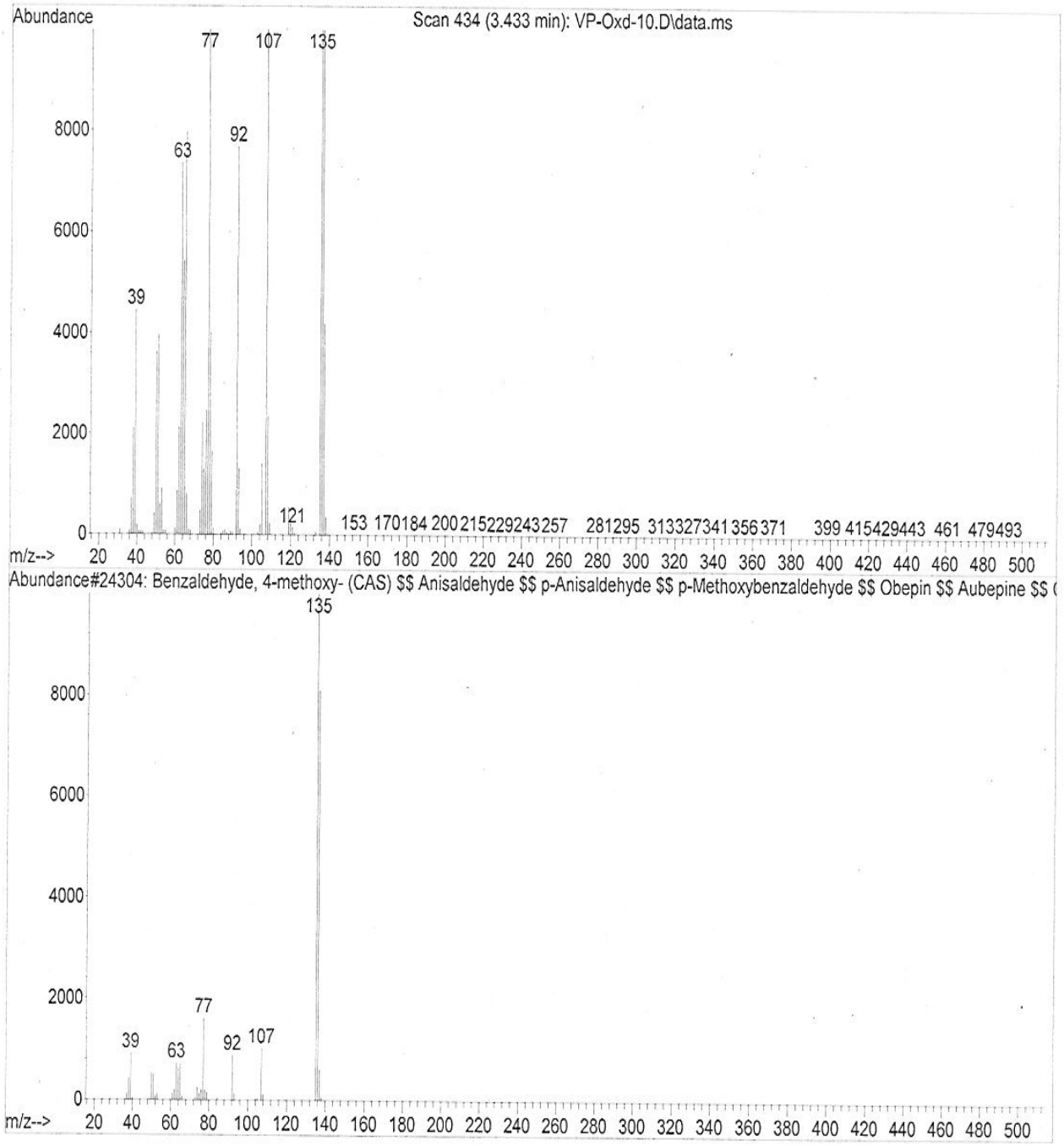

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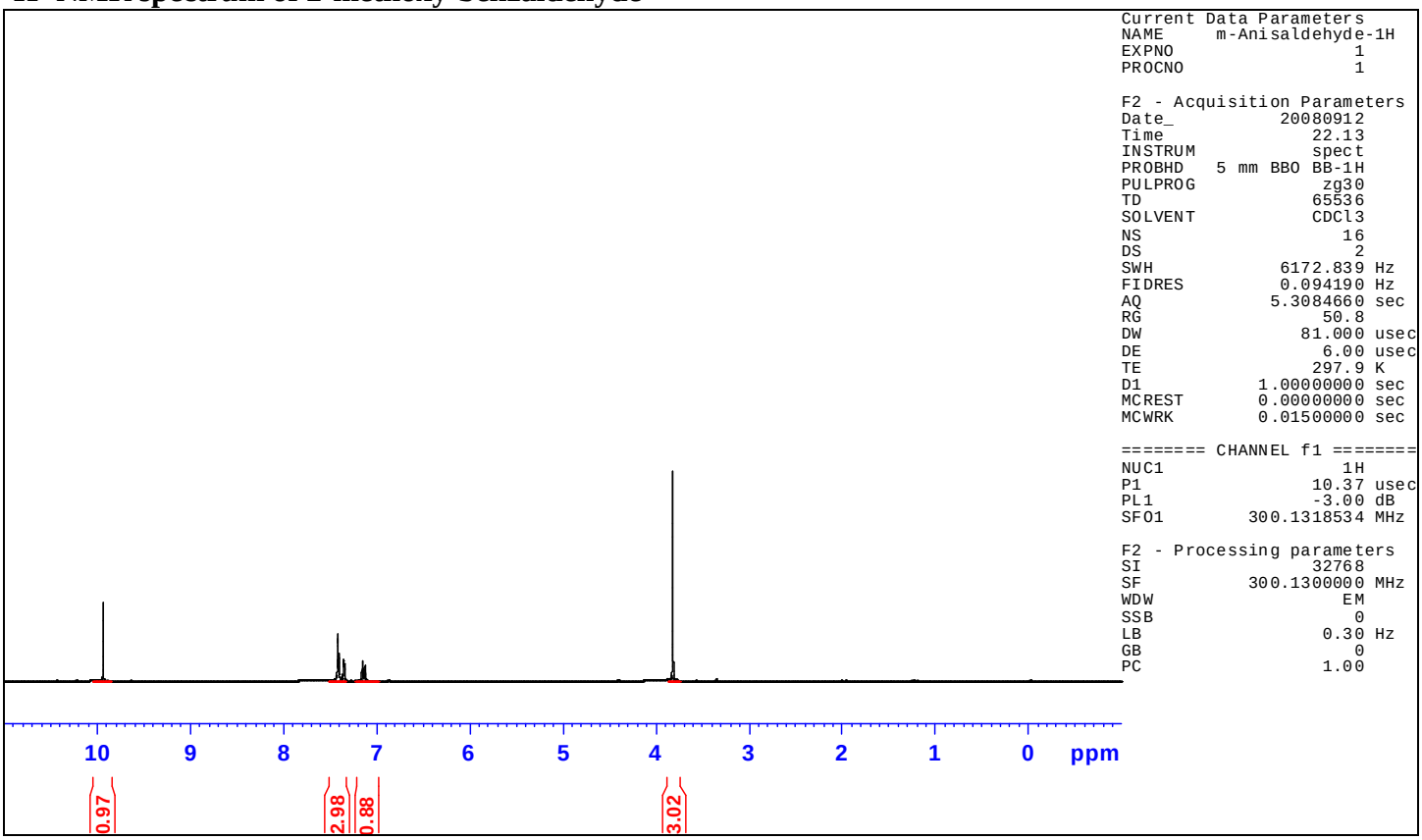
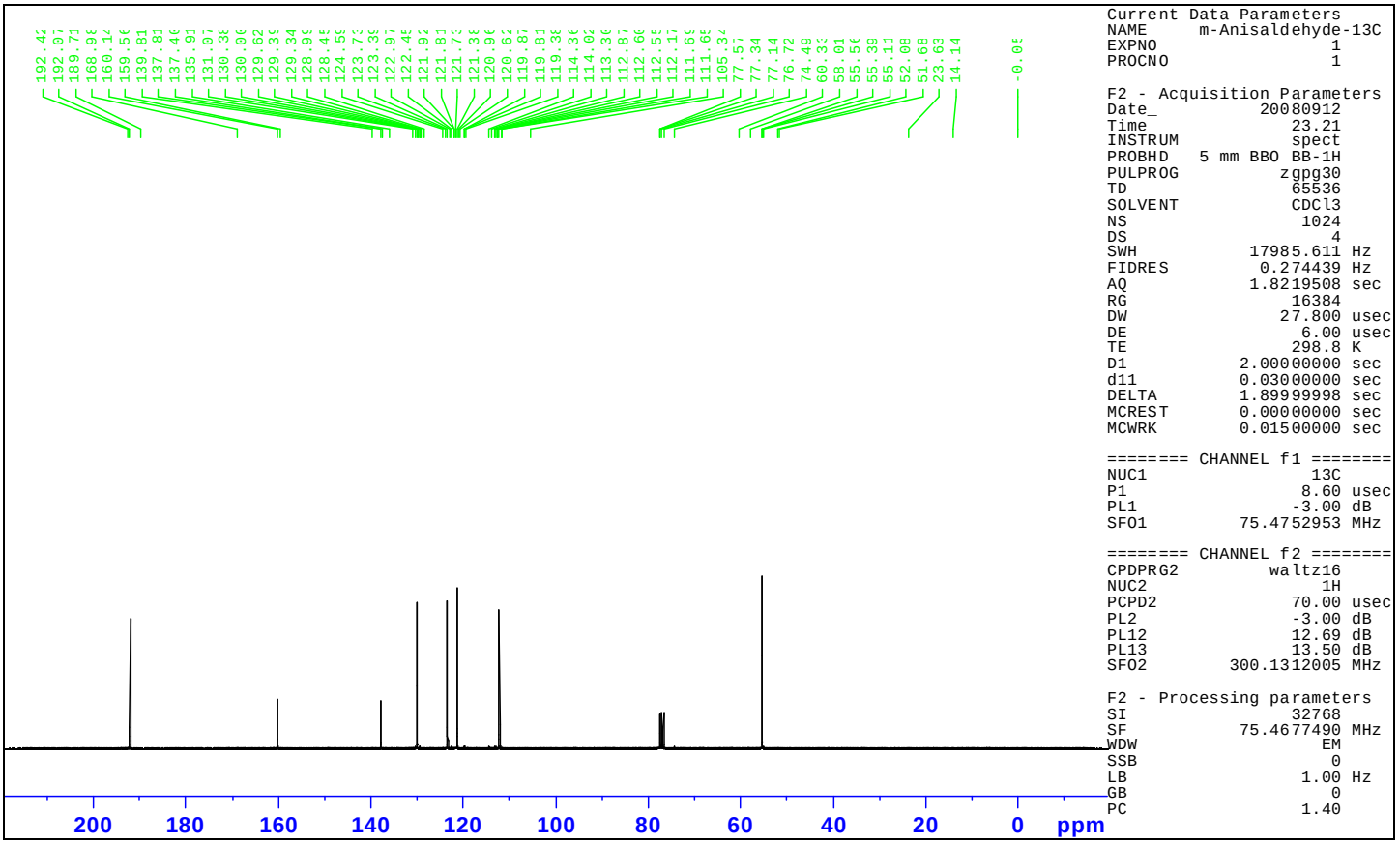


^{13}C-NMR spectrum of 2-methoxy-benzaldehyde



MS spectrum of phenyl butryaldehyde

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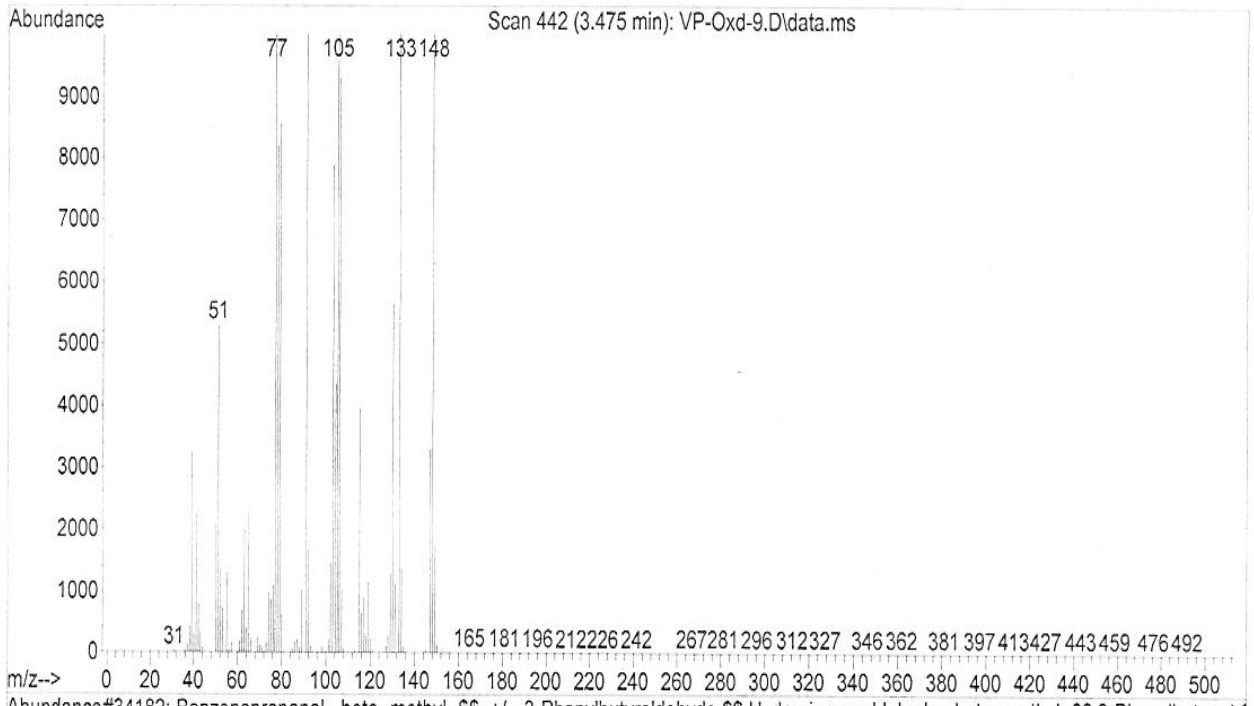
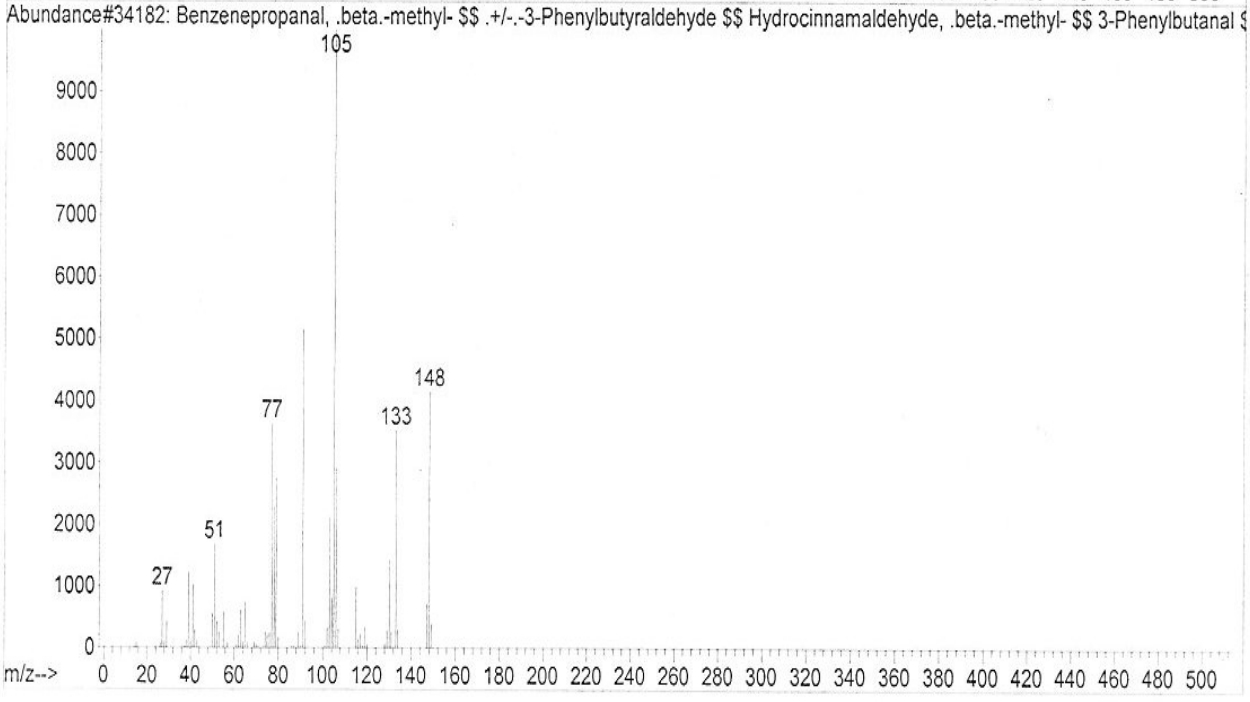
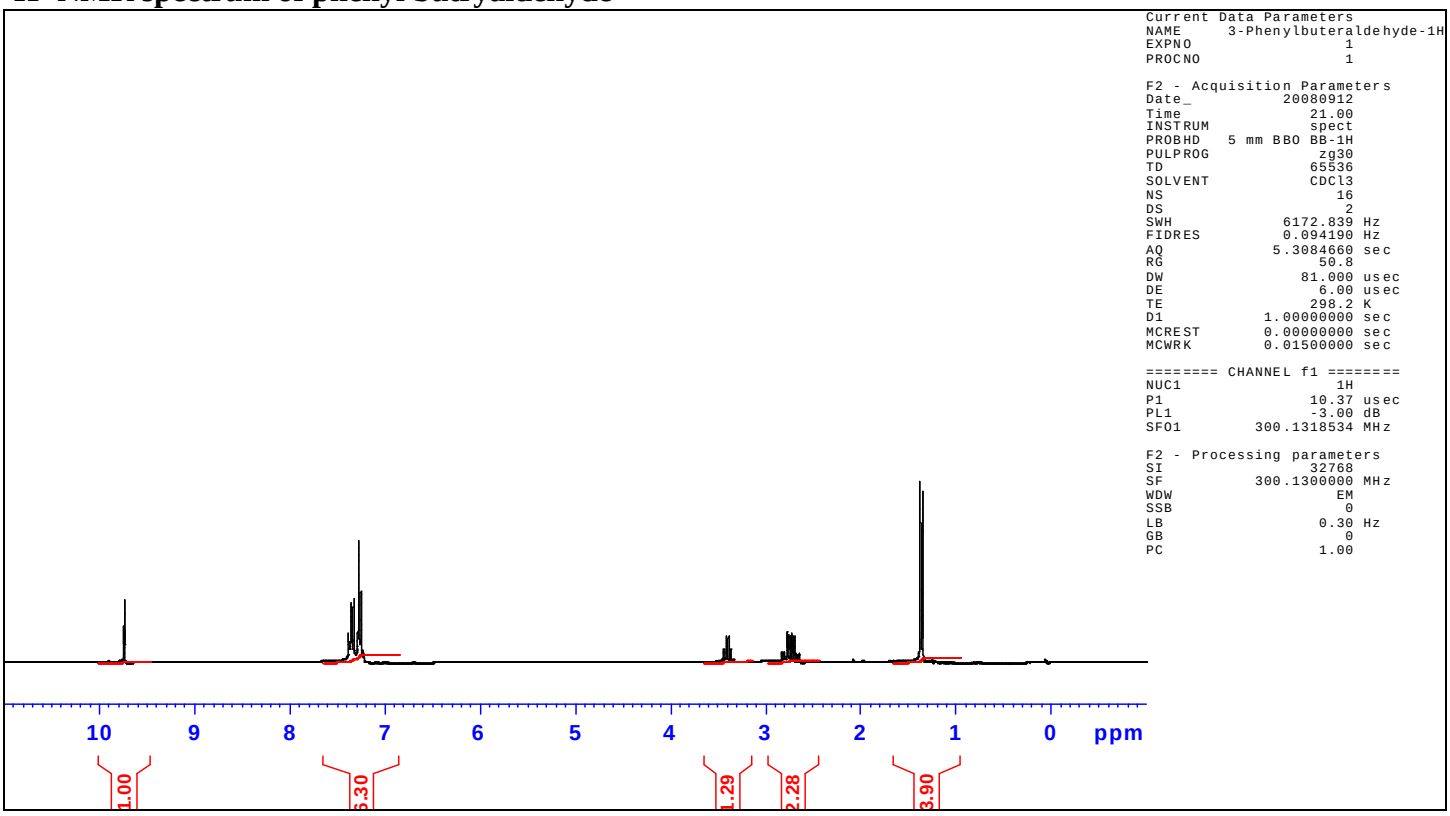




^{1}H -NMR spectrum of phenyl butryaldehyde



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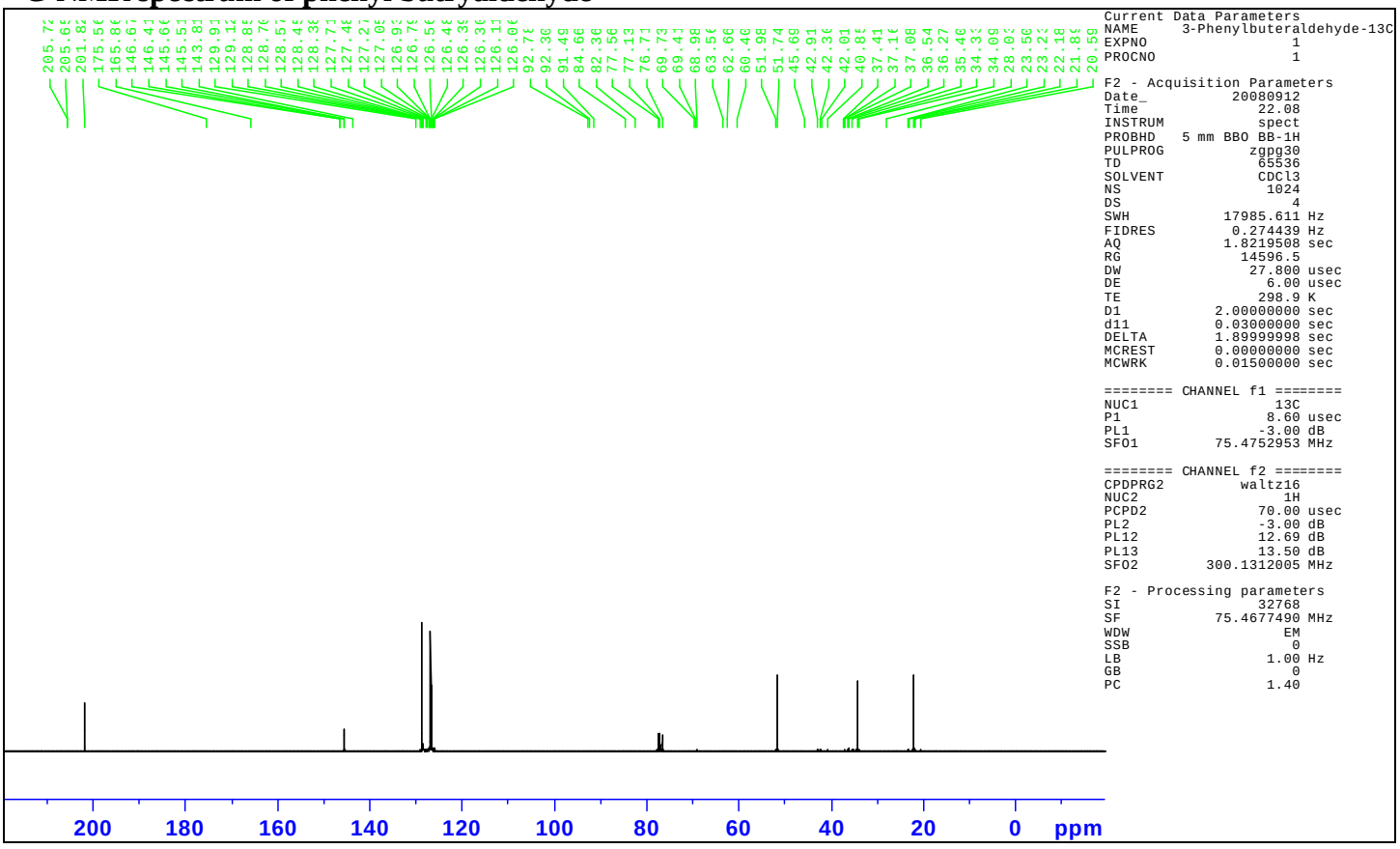

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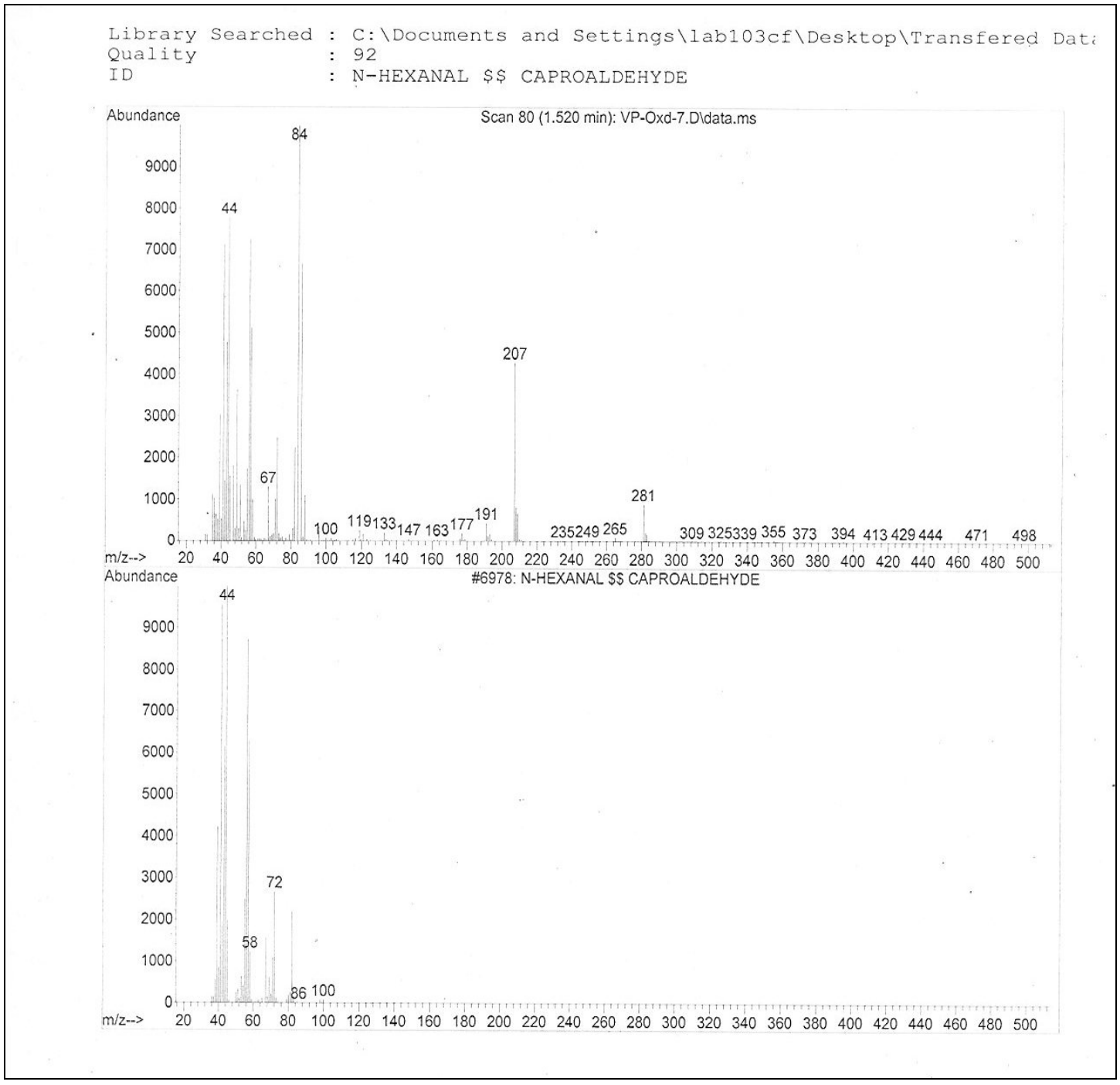

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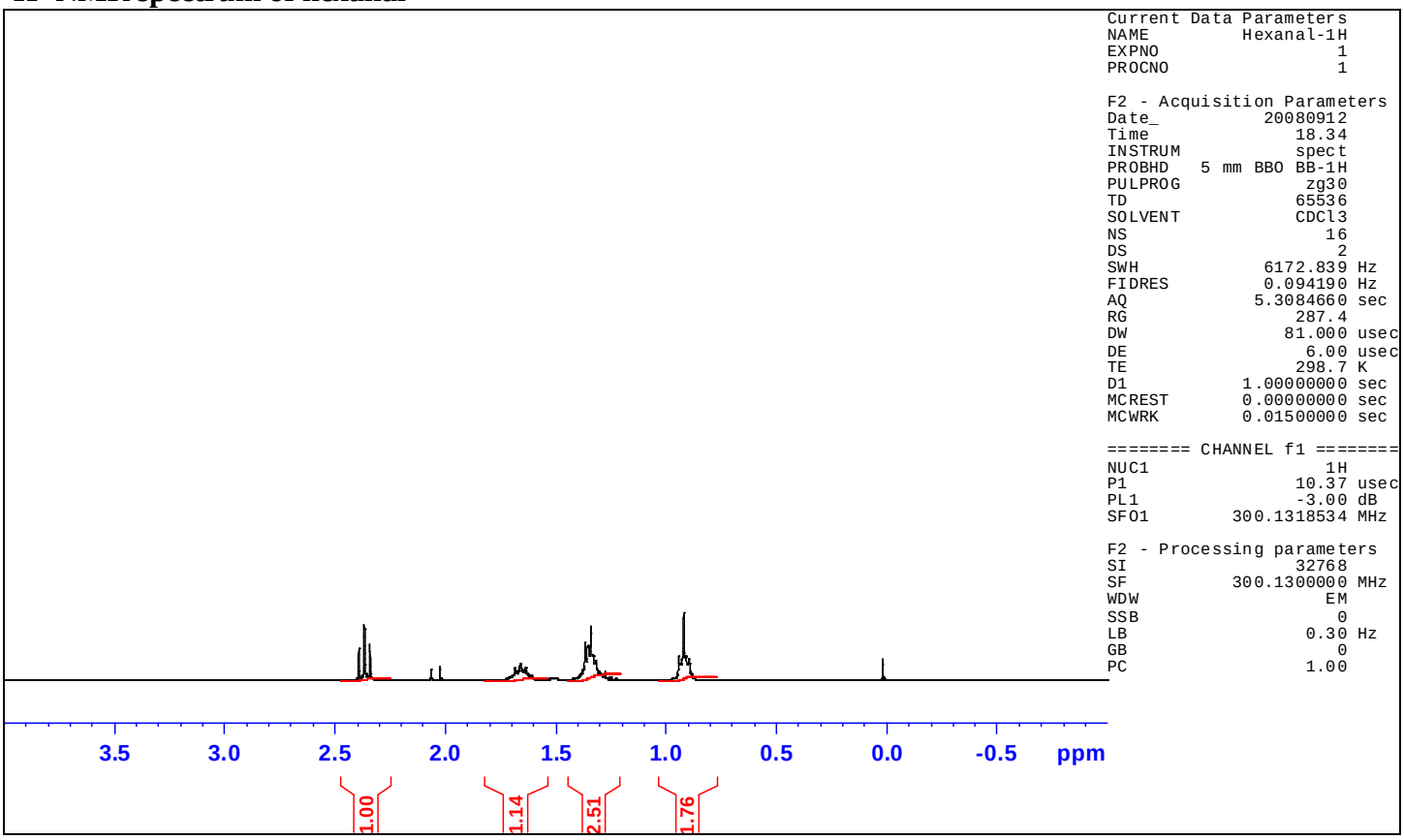

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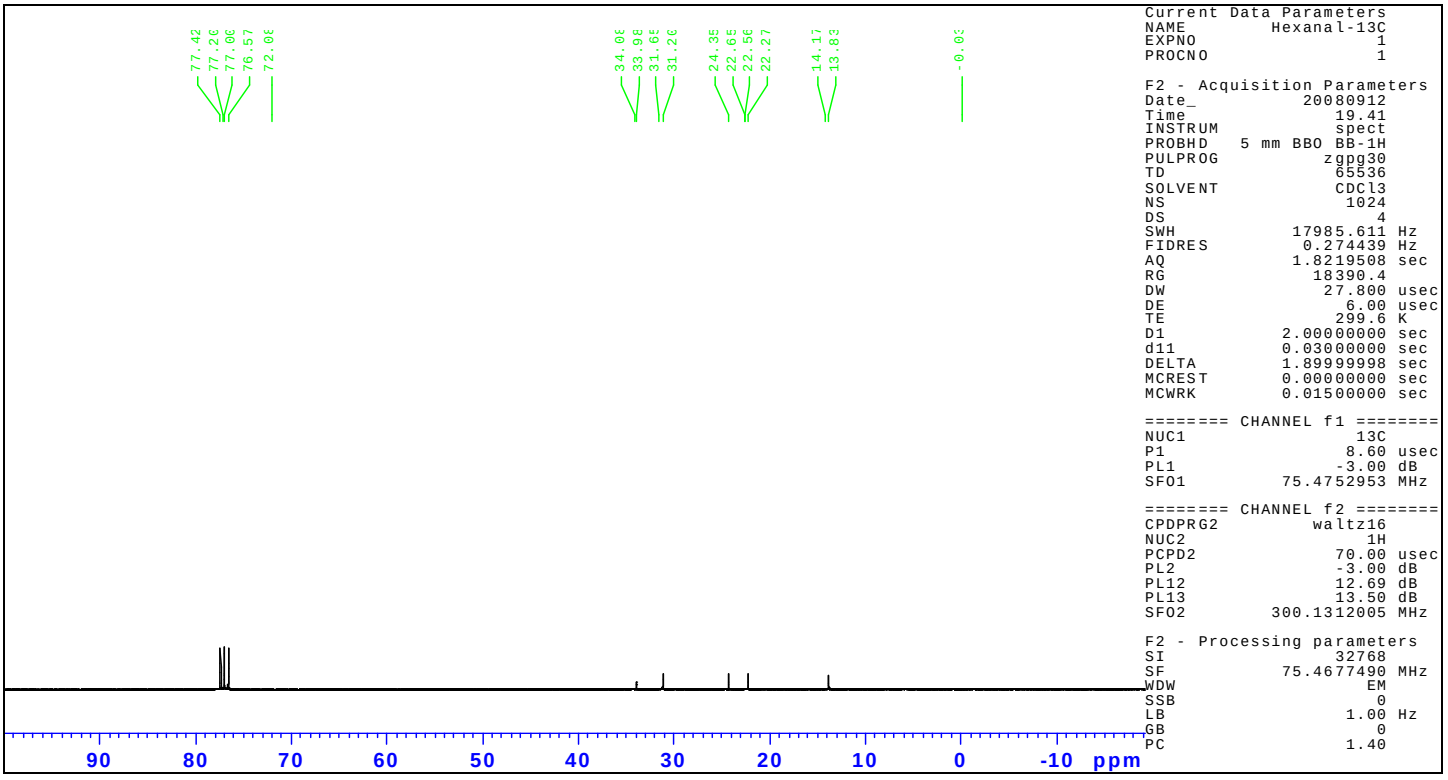

MS spectrum of piperonyl aldehyde

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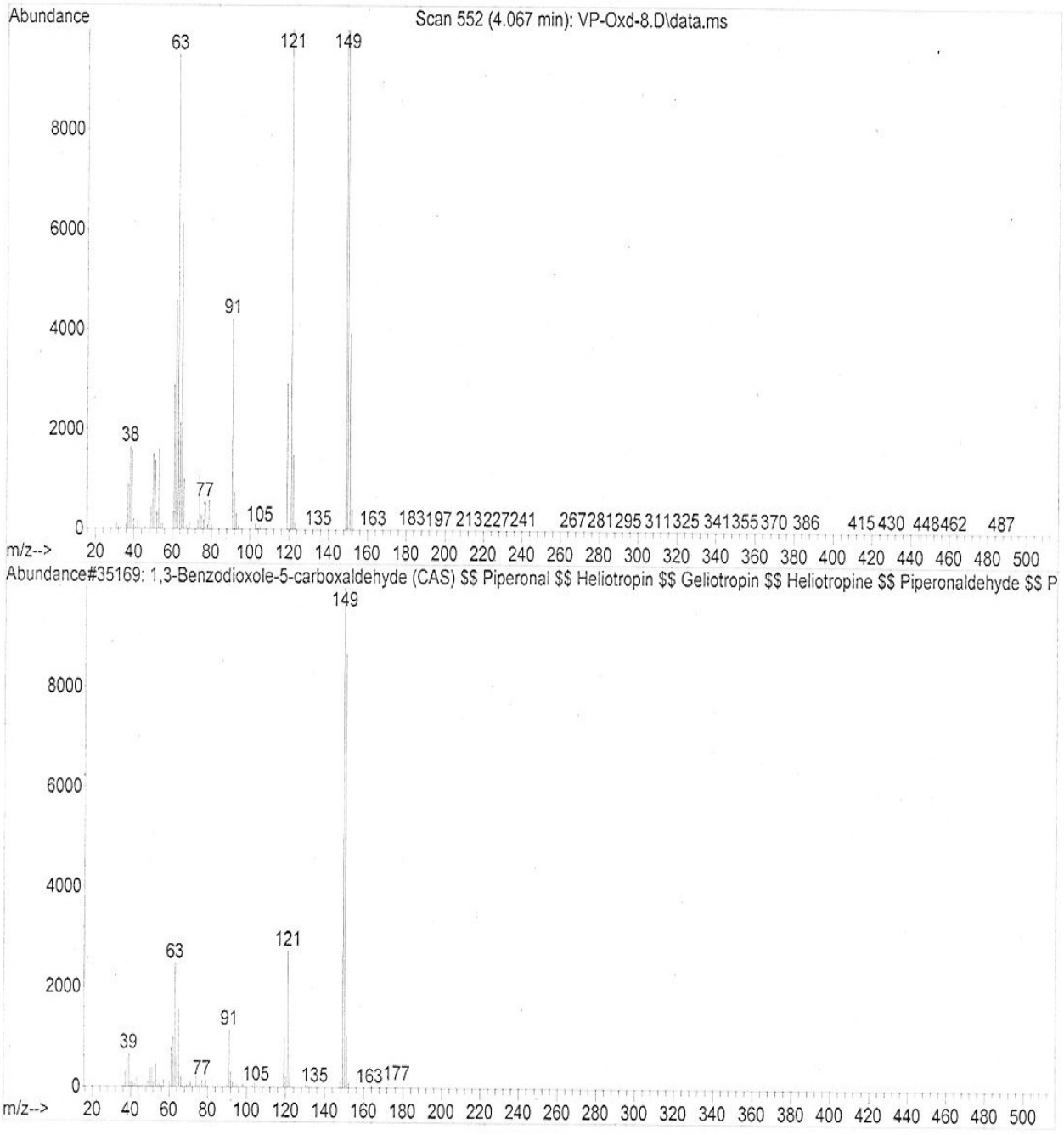
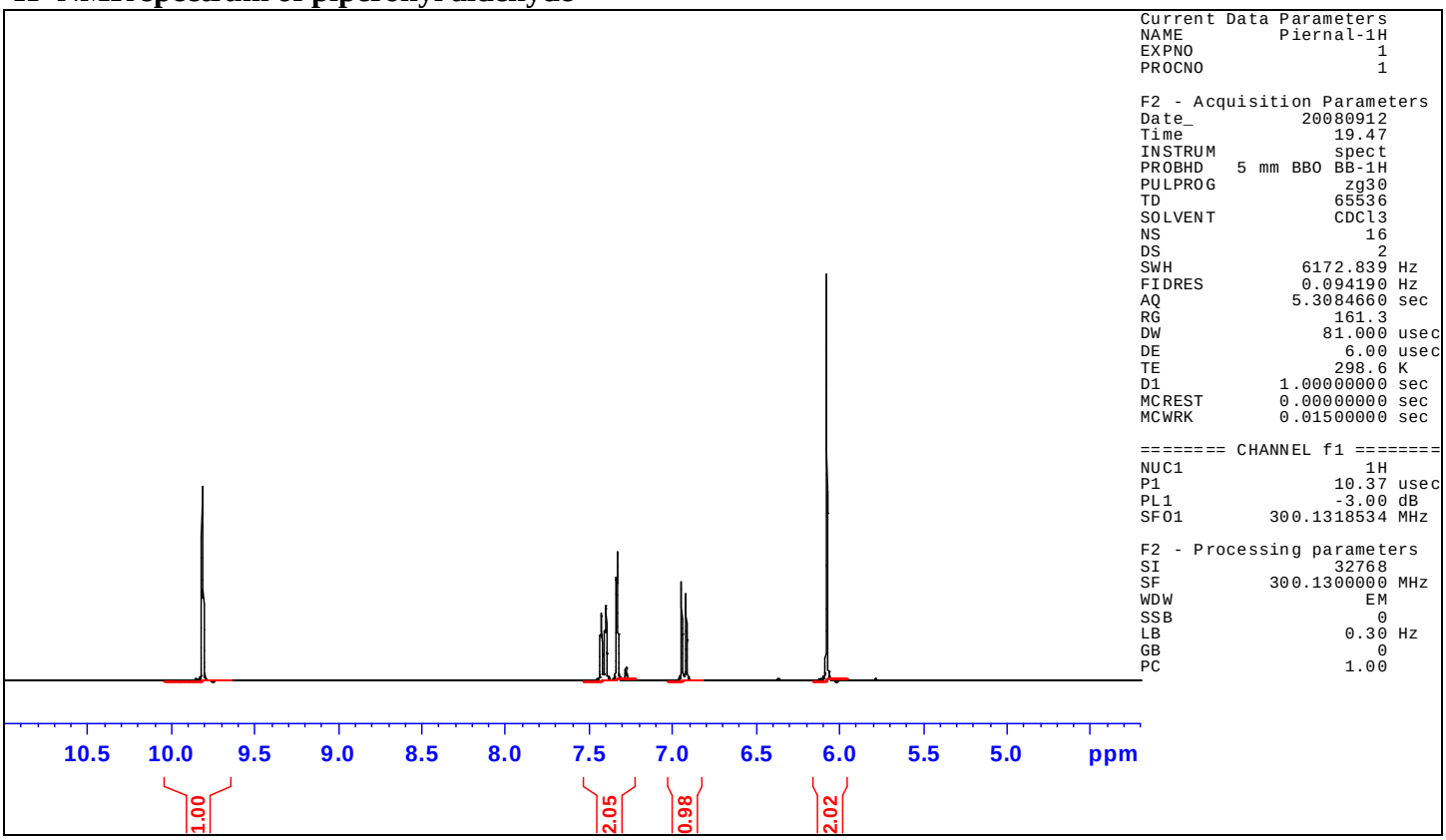
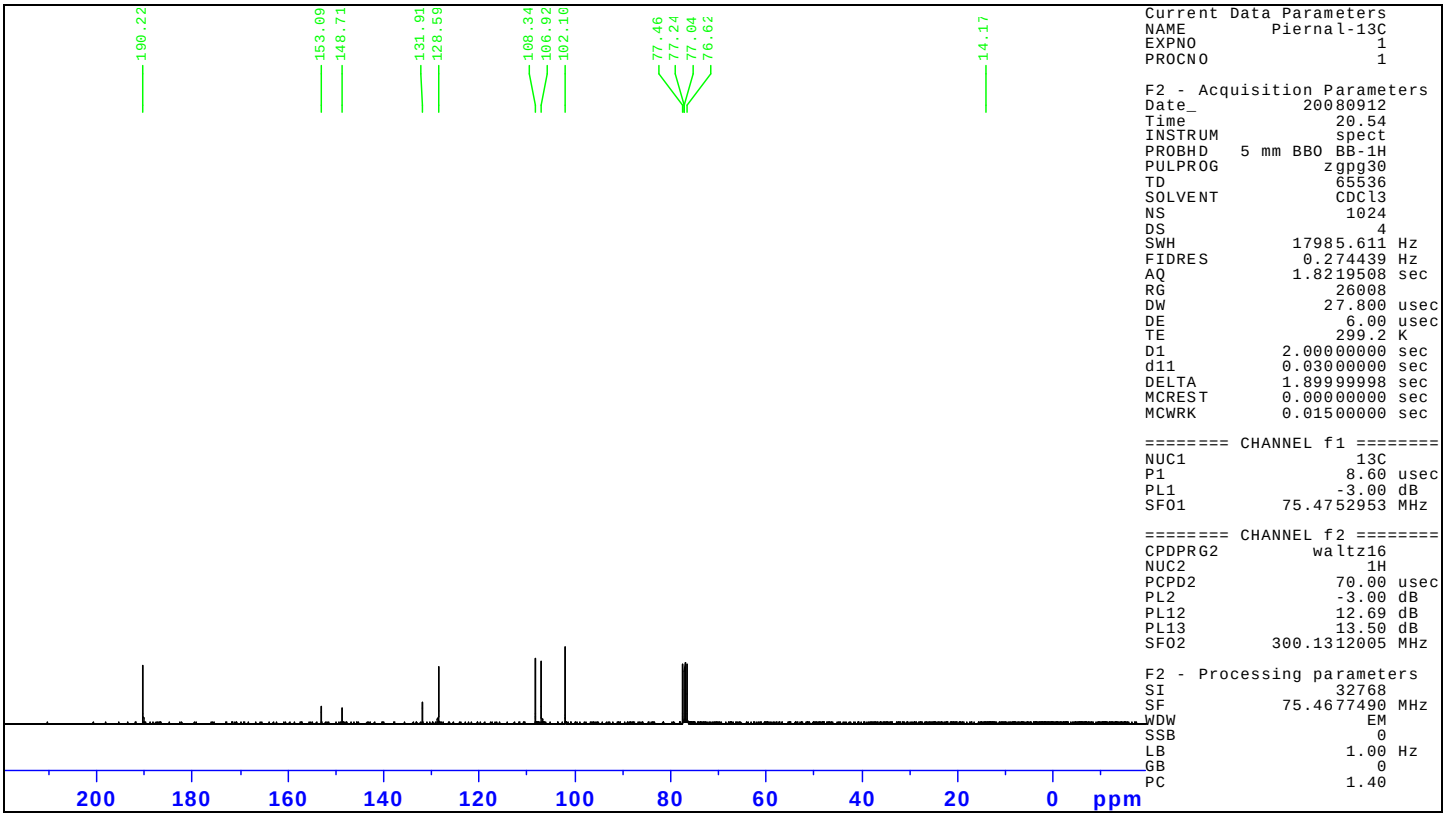


^{1}H -NMR spectrum of piperonyl aldehyde



^{13}C-NMR spectrum of piperonyl aldehyde



MS spectrum of 2-furyl aldehyde

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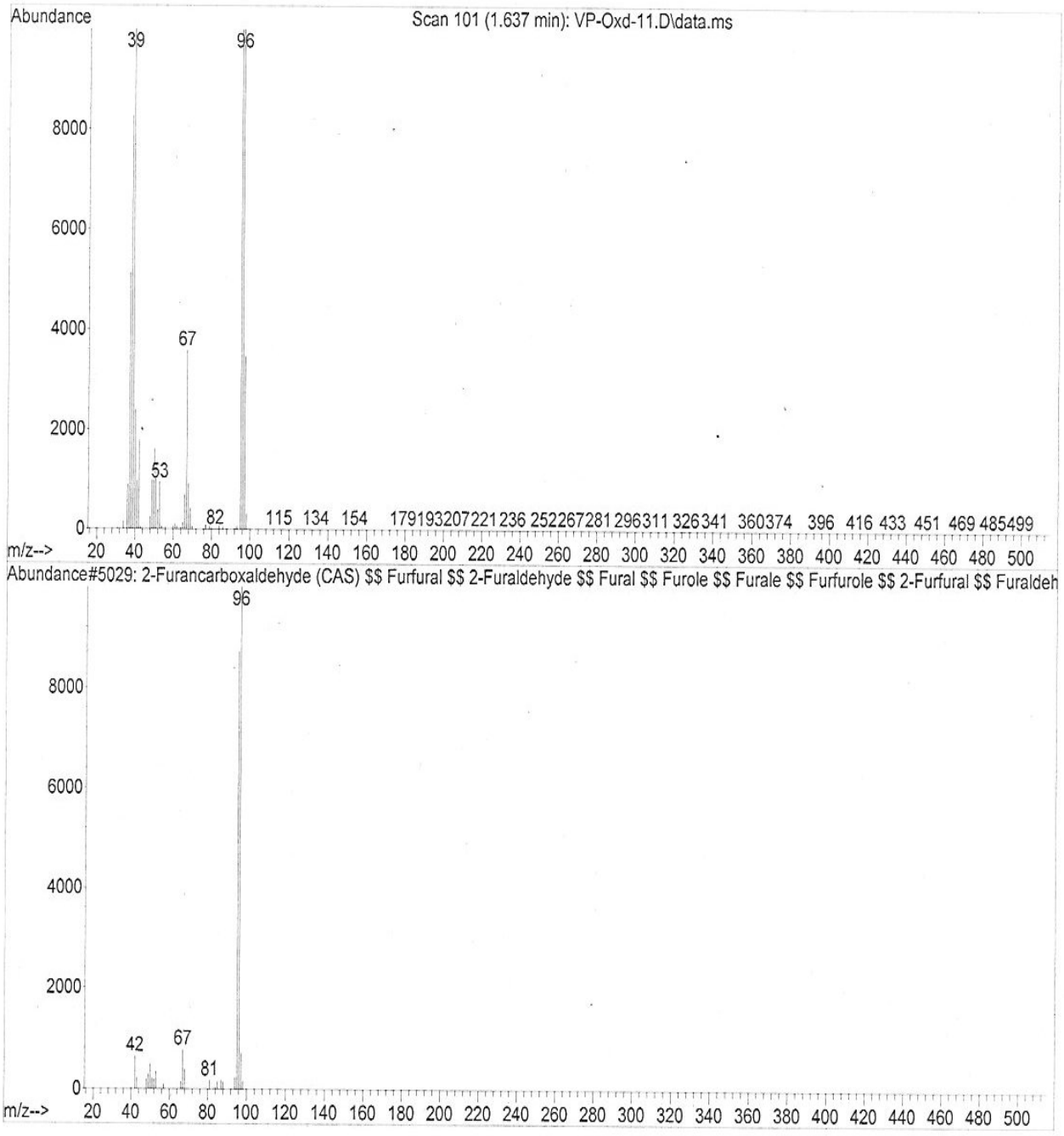
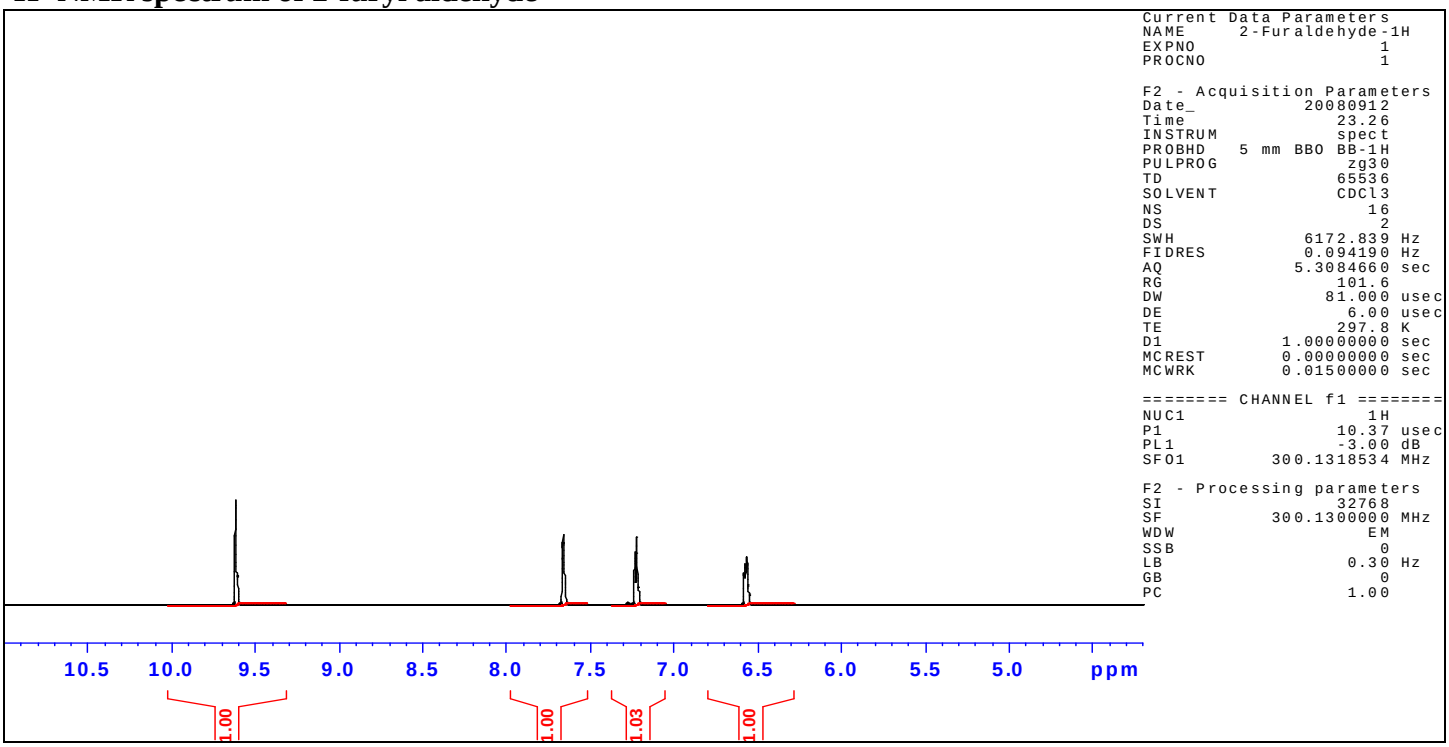


^{1}H -NMR spectrum of 2-furyl aldehyde



^{13}C-NMR spectrum of 2-furyl aldehyde