Supporting information for:

Activity Enhancement in Cyanation of Aryl Halides through Confinement of Ionic Liquid in the Nanospaces of SBA-15-supported Pd Complex

Babak Karimi,* [a] Asghar Zamani [a] and Fariborz Mansouri [a]

[a] Department of Chemistry, Institute for Advanced Studies in Basic
Sciences (IASBS), PO. Box 45195–1159, Gava Zang, Zanjan, Iran.
E-mail: karimi@iasbs.ac.ir; Fax: +98-241-4214949;
Tel: +98-241-4153225

Contents:

General information:

All chemicals were purchased from commercial suppliers and all solvents were purified and dried using standard procedures. Liquid NMR was obtained on a 400 MHz Bruker Avance instrument using $CDCl_3$ as solvent and TMS as internal standard. Nitrogen sorption experiments were recorded using a Belsorp-BEL, Inc. analyzer at 77 K. Prior to the measurement, the materials was degassed at 373 K for 12 h. The surface areas were calculated by BET method and the pore size distributions were calculated from the adsorption branch of the isotherms using BJH method. TEM image was taken on a FEI Tecnai 12 BioTWIN microscope operated at 120 kV. DRIFT spectrum was determined using a Brucker-Vector 22. Thermogravimetric analysis was conducted from room temperature to 800 °C in an air flow using a Pheometric Scientific analyzer.

Preparation of SBA-15

The synthesis of SBA-15 has been achieved using known procedure described by Stucky and his co-workers.[1] In a typical preparation procedure, 4.0 g of Pluronic P123 (Aldrich, average Mw $\cong$5800) was dissolved in 30 g of water and 120 g of 2 M HCl solution with stirring at 35 ºC. Then 8.50 g of tetraethoxysilane (TEOS) was added into that solution with stirring at 35 ºC for 20 h. The mixture was aged at 80 ºC overnight without stirring. The solid was filtered off and washed thoroughly with hot ethanol/water using a Soxhelet apparatus for 18 h to remove the surfactant molecules. It was dried in air at 110 ºC overnight.

Preparation of aminopropyl functionalized SBA-15

Refluxing the SBA-15 (10 g) with 3-aminopropyltrimethoxysilane (10 mmol) in dry toluene for 18 h. The solid materials were filtered off and washed with hot toluene for 12 h in a continuous extraction apparatus (Soxhelet) and then dried in oven at 90 ºC overnight to give aminopropyl functionalized SBA-15.

Preparation of iminopyridine functionalized SBA-15

2-acetylpyridine (0.97 g, 8 mmol) was added to a mixture of the oven dried aminopropyl functionalized SBA-15 (5 g) in super dry ethanol (150 mL) in a 250 mL round bottomed flask. The reaction mixture was stirred at 60 ºC for 24 h. The ligand-grafted silica was filtered at the reaction temperature and the resulting solid was washed thoroughly with hot toluene and ethanol to remove unreacted ketone. It was dried in air at 90 ºC overnight to furnish the corresponding iminopyridine functionalized SBA-15.

Preparation of SBA-15-Pd

iminopyridine functionalized SBA-15 (3 gr) was added to a solution of palladium acetate (0.035 gr Merck) in dry acetone (100 mL). The reaction mixture was stirred at room temperature for 24 h. After stirring, the solid was filtered, washed with acetone, ethanol and ether in order to remove any adsorbed palladium on the surface. It was then dried in an oven at 90 ºC overnight to furnish the corresponding SBA-15 supported complex (**SBA-15-Pd**).

Preparation of catalyst 1

SBA-15-Pd (3 gr) was added to a solution of 1-butyl-3-methylimidazolium hexafluorophosphate (1.5 cc) in dry acetone (100 mL). The reaction mixture was stirred at room temperature for 24 h. After stirring, acetone was slowly removed under reduced pressure. The resulting powder was then dried in an oven at 90 ºC overnight to give final catalyst **1** at a loading *ca.*0.032 ± 0.001 mmol g^{-1} (atomic absorption spectroscopy (AA)).

General procedure for the cyanation reaction using catalyst 1:

a mixture of 1.0 mmol aryl halide, 0.7 mmol $K_4[Fe(CN)_6]$ ($K_4[Fe(CN)_6]x3H_2O$ is ground to a fine powder and dried in vacuum (ca. 2 mbar) at 80 ºC over night), 2 mmol K_2CO_3, 2-4 mol% phosphine ligand and 1-2 mol% catalyst **1** in 2 mL DMF at 120 ºC was stirred vigorously under argon atmosphere. The reaction progress was monitored by

GC analysis after completion of the reaction; the mixture was allowed to cool to room temperature and was then filtered and washed with H_2O and ethyl acetate. The organic phase was separated and dried over $MgSO_4$ and the solvent was then removed under reduced pressure. Pure products were obtained after recrystallization or by isolation of the residue by column chromatography on silica.

The recovery of the catalyst 1:

The cyanation reaction over the catalyst **1** was carried out under an argon flow by treatment 1 mol% of the catalyst with $K_4[Fe(CN)_6]$ (3.5 mmol), phenyl iodide (5 mmol), 2 mol% triphenyl phosphine and K_2CO_3 (10 mmol) in DMF at 120 °C. The reaction progress was monitored by GC using dodecane as internal standard. After completion of the reaction, the resulting mixture was filtered and washed with H_2O and ethylacetate thoroughly. The recovered catalyst was then successfully reused 3 times under the same reaction conditions.

In other method, we added phenyl iodide, $K_4[Fe(CN)_6]$, and K_2CO_3 to catalyst without separation of previous reaction runs. In this method we can recover the catalyst 4 times.

Procedure for the hot filtration test:

This experiment was conducted in a water solution containing 1 mmol phenyl iodide, 0.7 mmol $K_4[Fe(CN)_6]$, 1 mol% catalyst, 2 mmol K_2CO_3 and triphenyl phosphine (2 mol%) at 120 °C. After 35% of the coupling reaction was completed, the solution was filtered and then filtrate was allowed to progress at 120 °C for 24h. The reaction progress was monitored by GC.

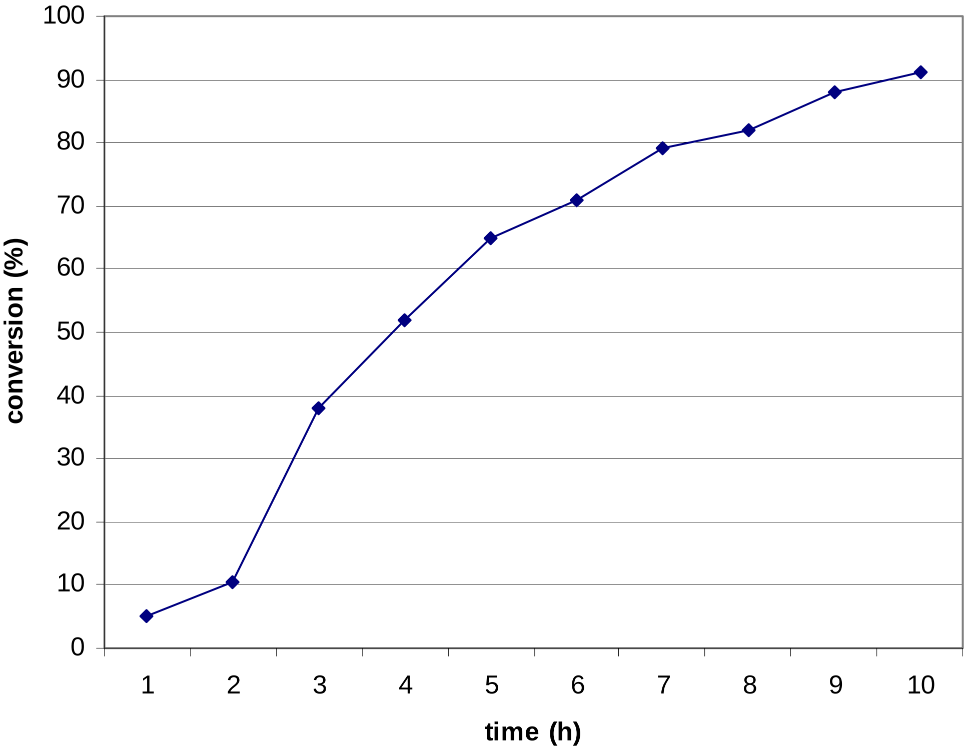


Figure S1. Kinetic of cyanation reaction using **IL@SBA-15-Pd**

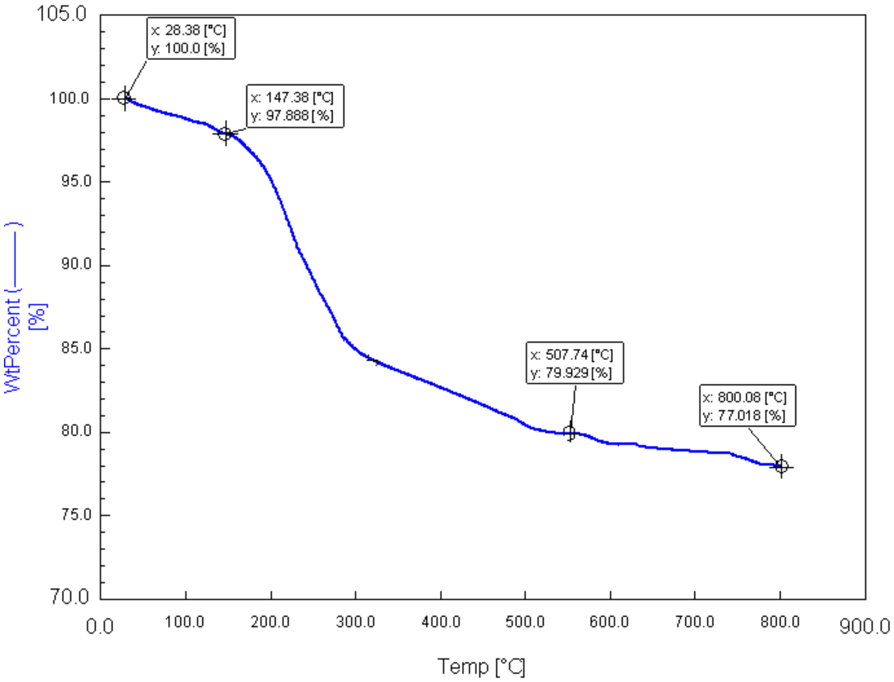


Figure S2. Thermal gravimetric analysis (TGA) of SBA-15-Pd

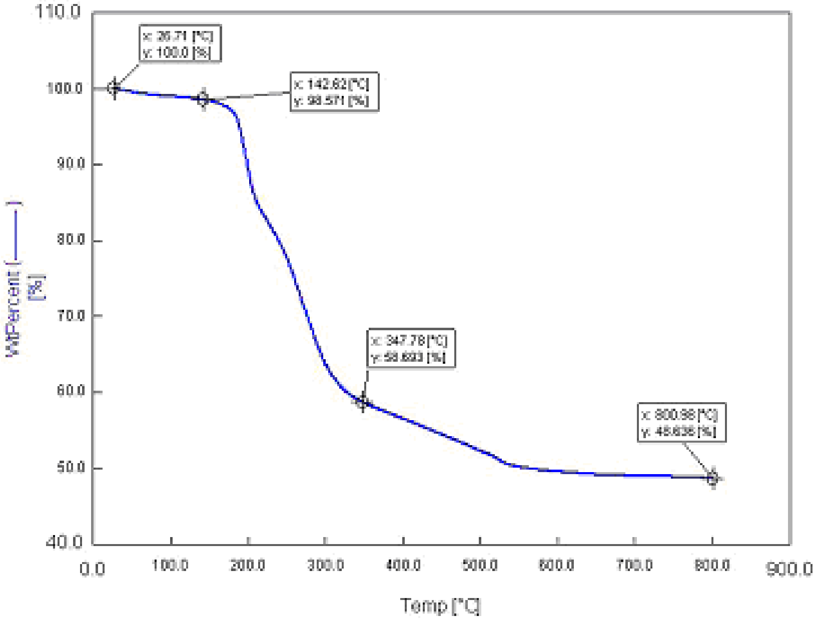


Figure S3. Thermal gravimetric analysis (TGA) of **IL@SBA-15-Pd**.

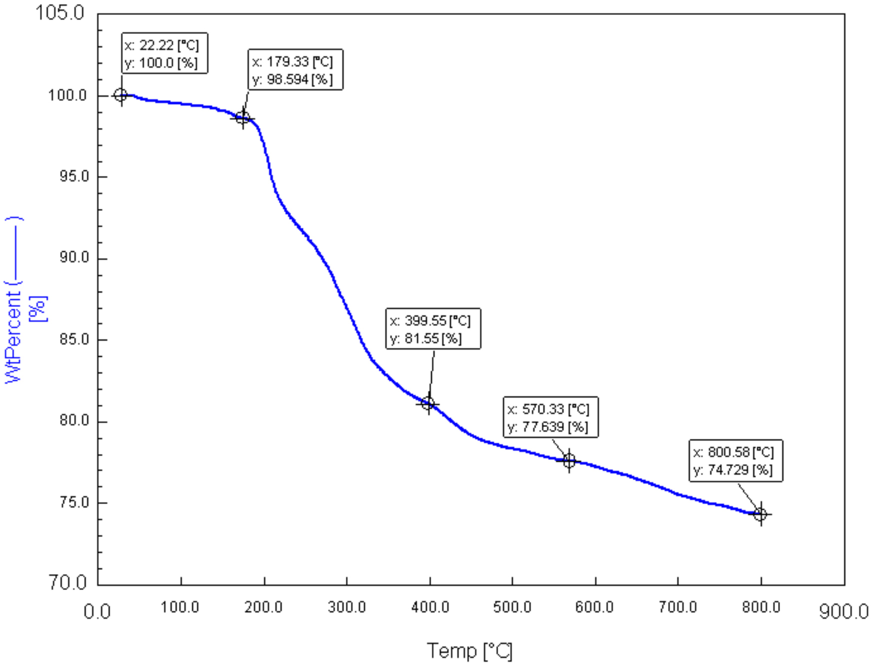


Figure S4. Thermal gravimetric analysis (TGA) of recovered **IL@SBA-15-Pd**.

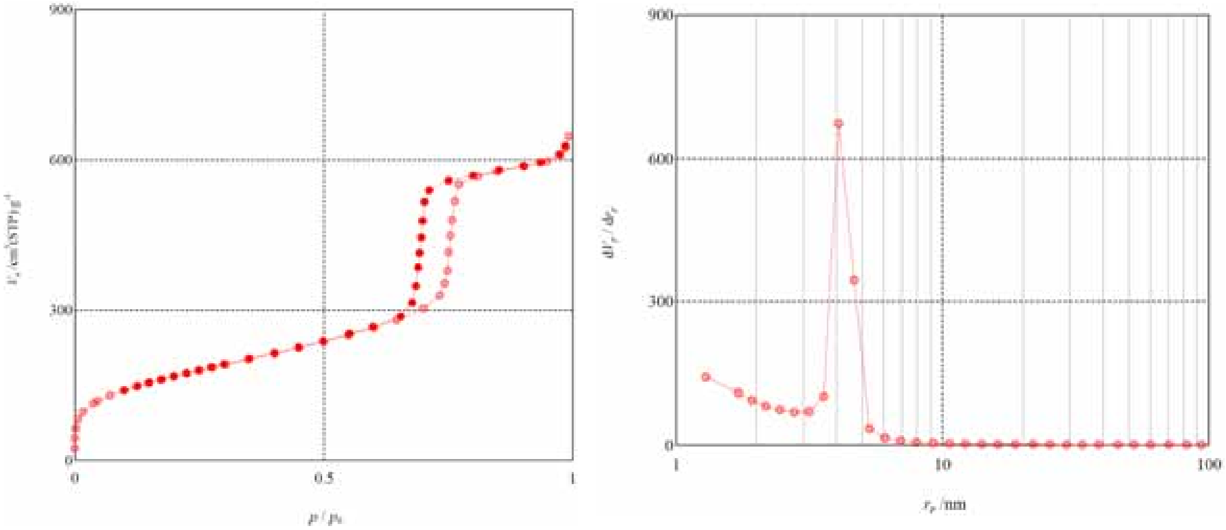


Figure S5. Nitrogen adsorption-desorption isotherm (a) and pore size distribution (b) of the **SBA-15-Pd** material indicating very high uniformity and narrow size distribution of mesochannels.

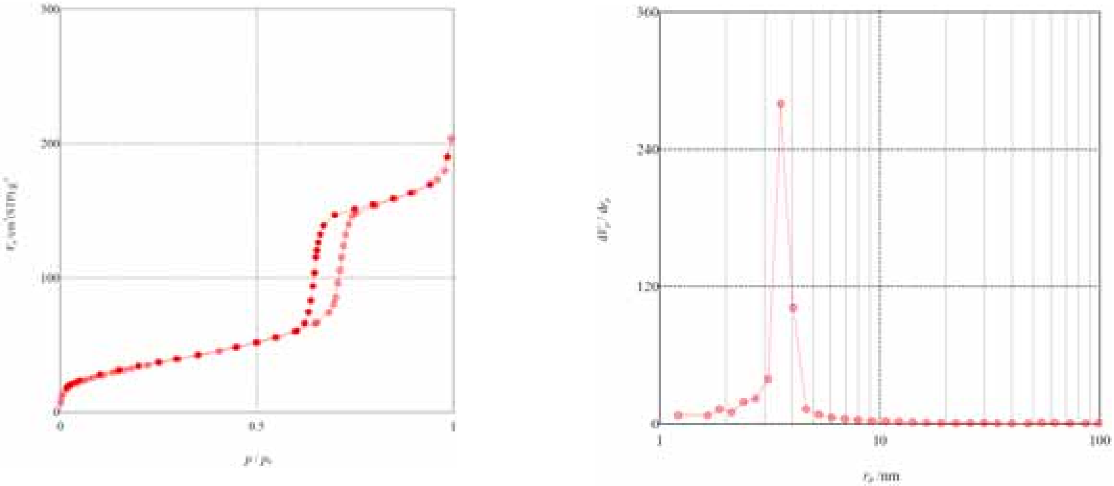


Figure S6. Nitrogen adsorption-desorption isotherm (a) and pore size distribution (b) of the **IL@SBA-15-Pd** material indicating very high uniformity and narrow size distribution of mesochannels.

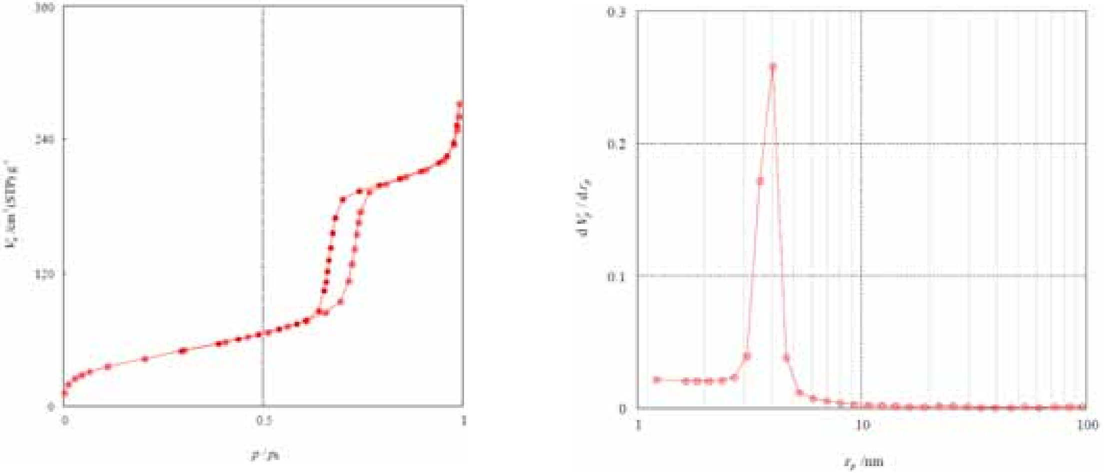


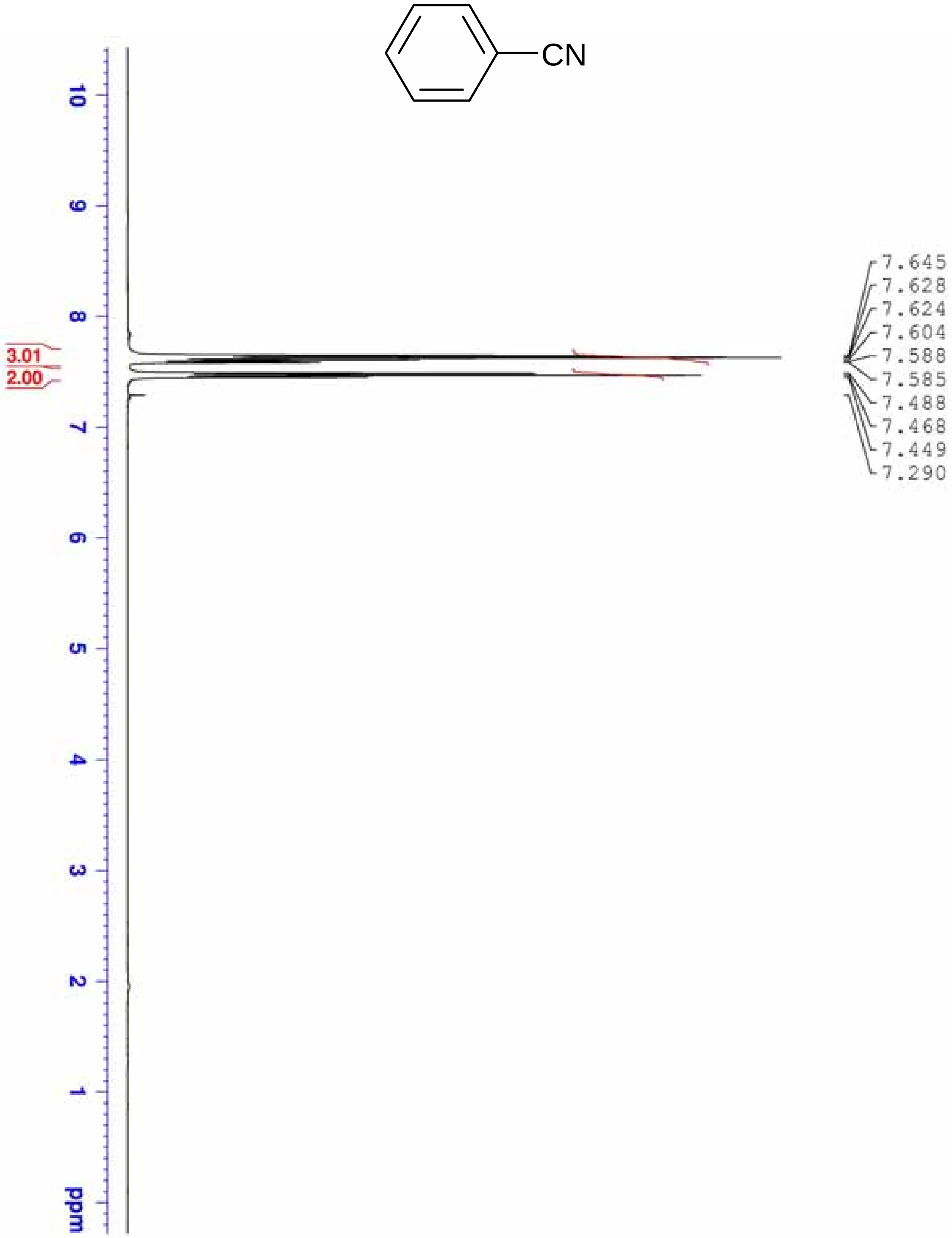
Figure S7. Nitrogen adsorption-desorption isotherm (a) and pore size distribution (b) of the recovered **IL@SBA-15-Pd** material indicating very high uniformity and narrow size distribution of mesochannels.

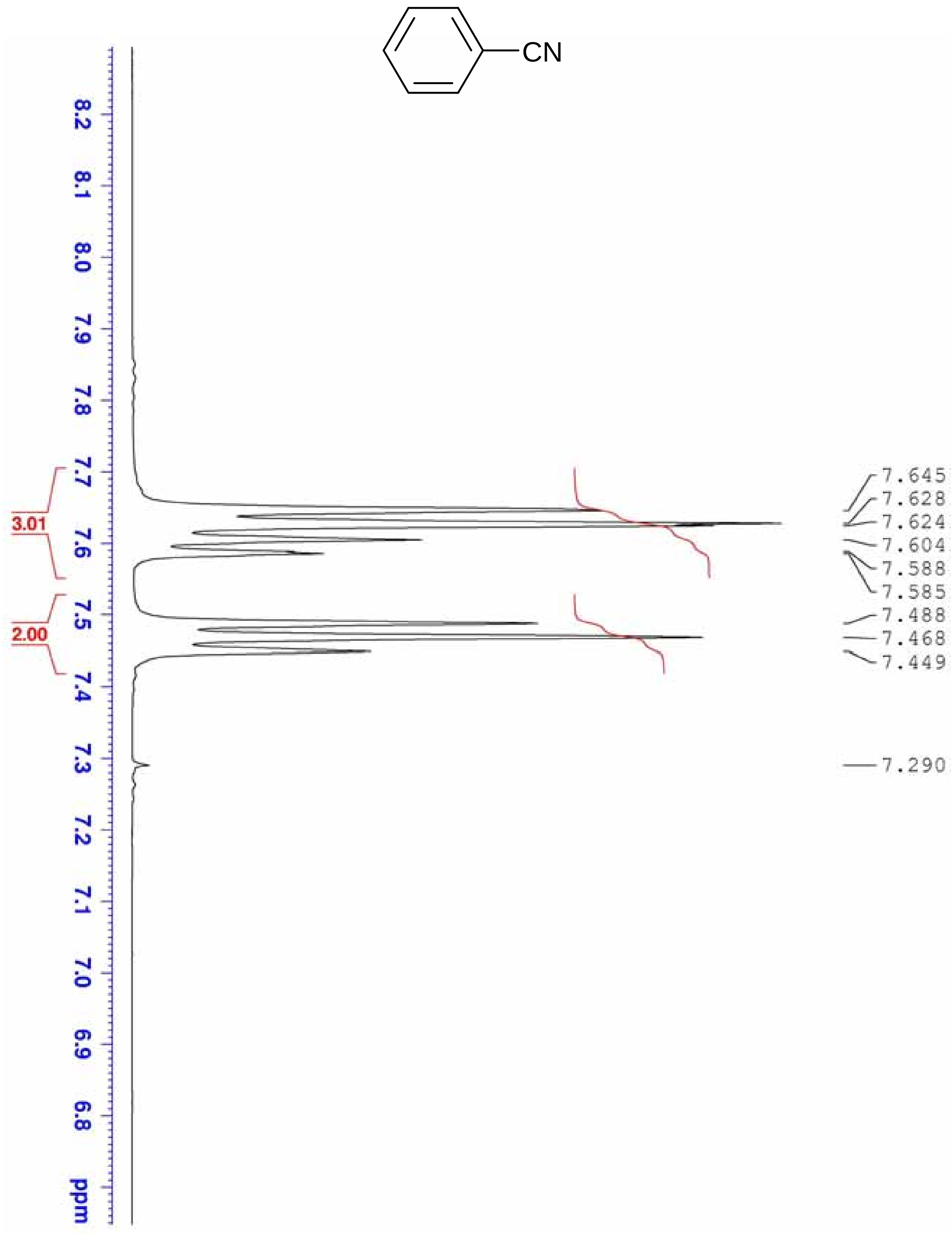
Table S1. Structural parameters of **SBA-15-Pd**, **IL@SBA-15-Pd** and recovered **IL@SBA-15-Pd** determined from nitrogen sorption experiments:

Sample	BET surface area (m^2/g)	BJH pore diameter (nm)	Pore volume (cm^3/g)
SBA-15-Pd	599	5.4	0.99
IL@SBA-15-Pd	119	4.1	0.30
Recovered catalyst	158	4.6	0.40

^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC, TMS) and ^{13}C NMR (63 MHz, CDCl$_3$, 25 ºC, TMS) spectra of the coupling products

Benzonitrile

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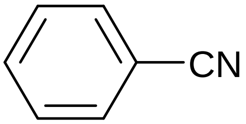
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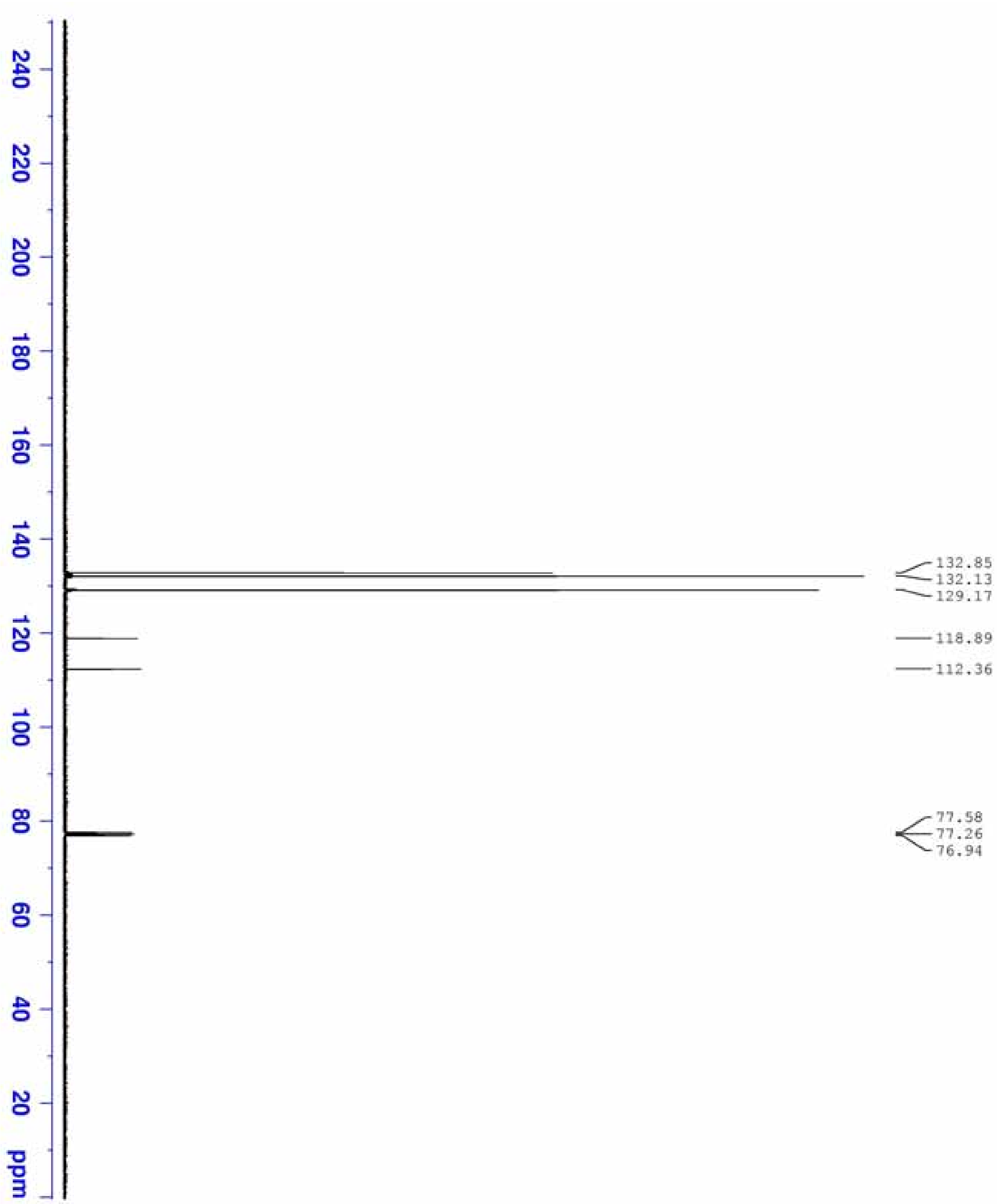
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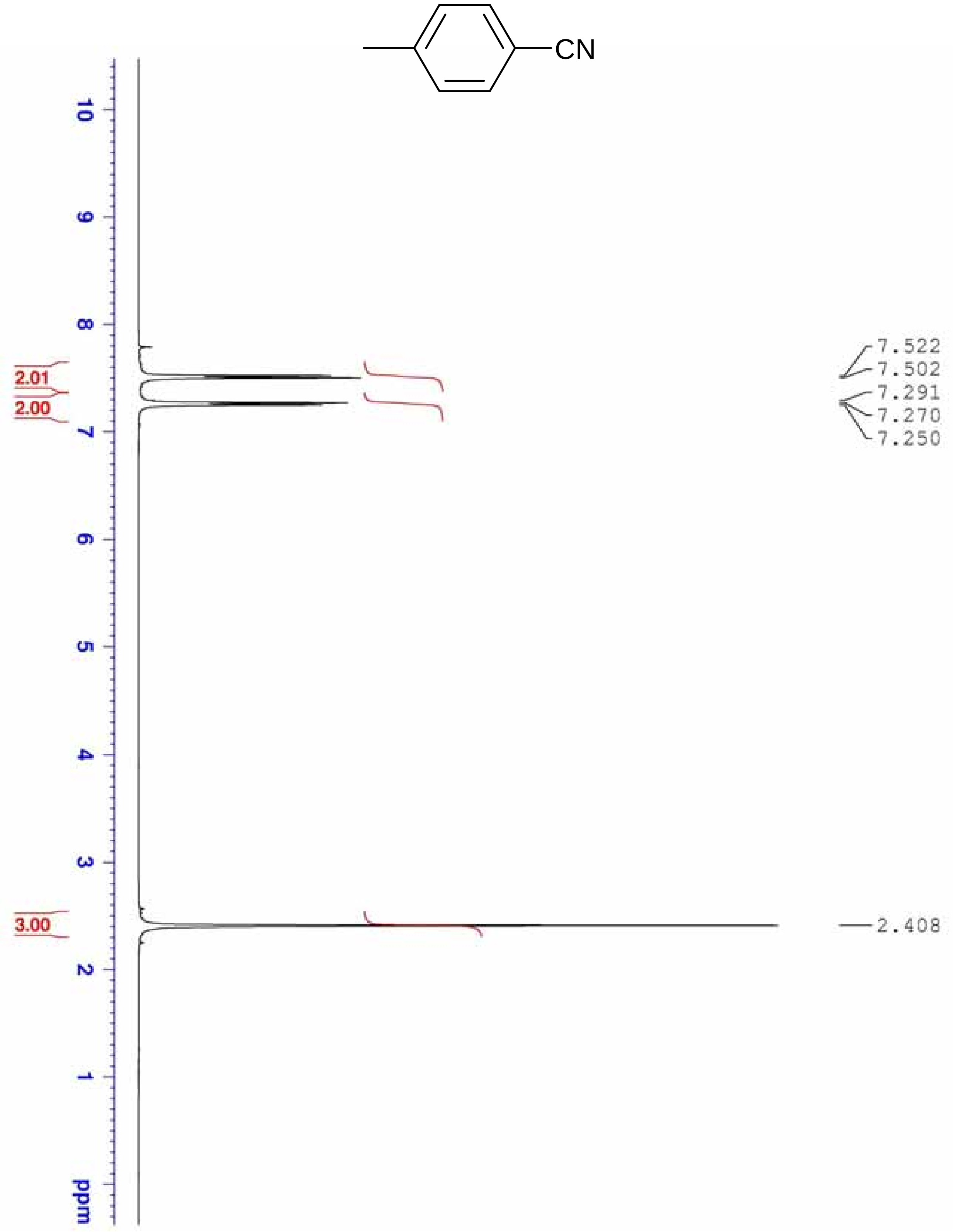

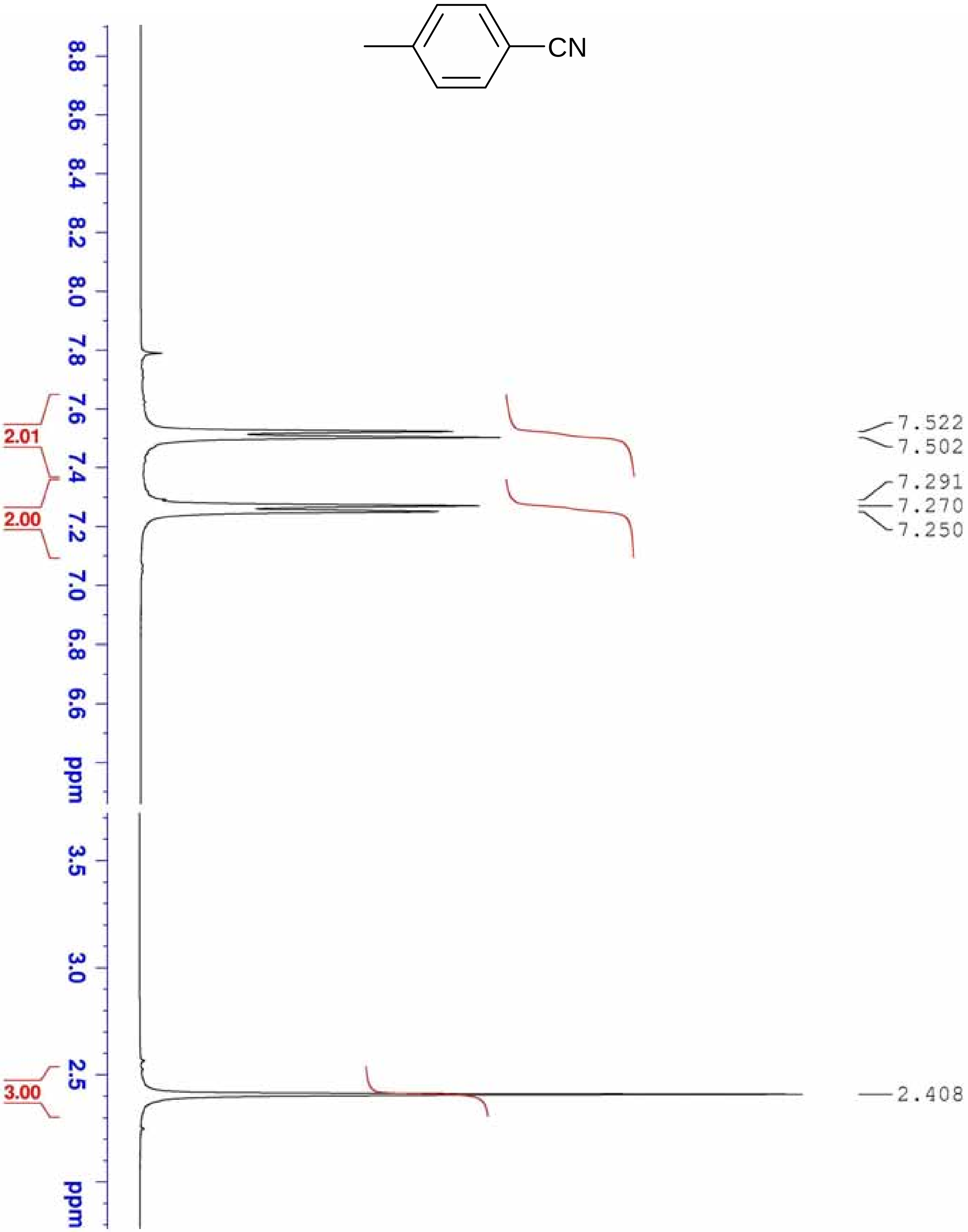
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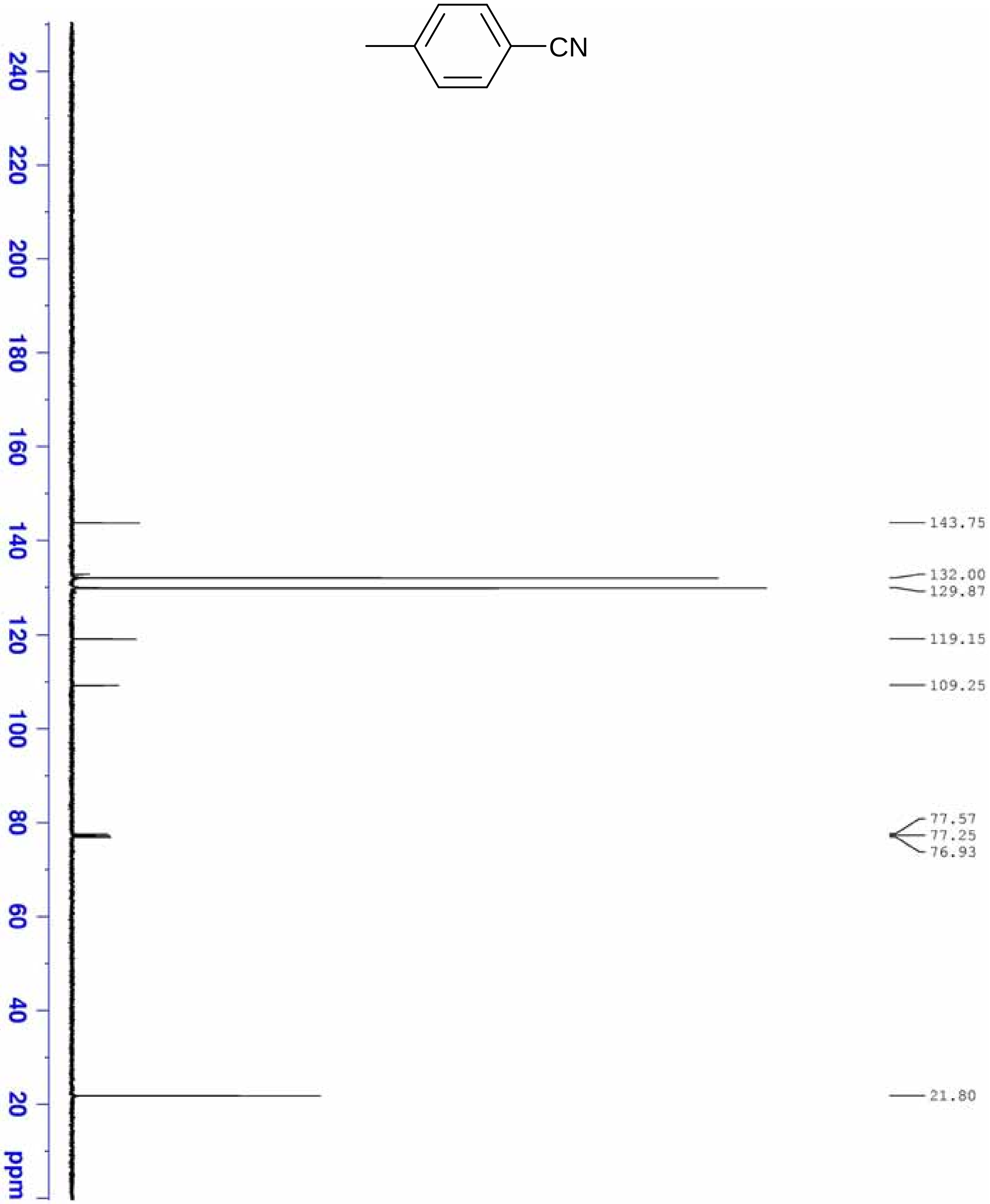
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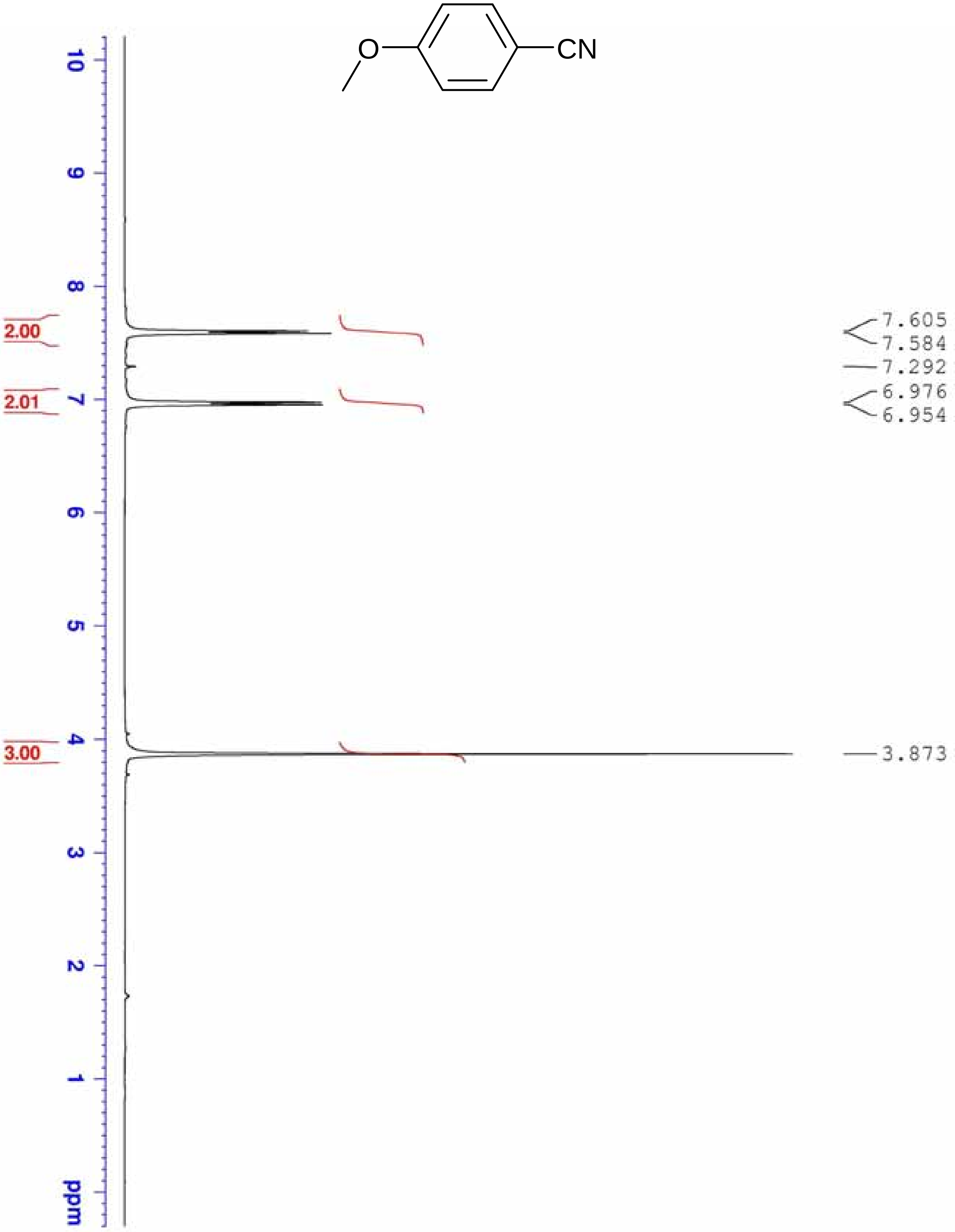
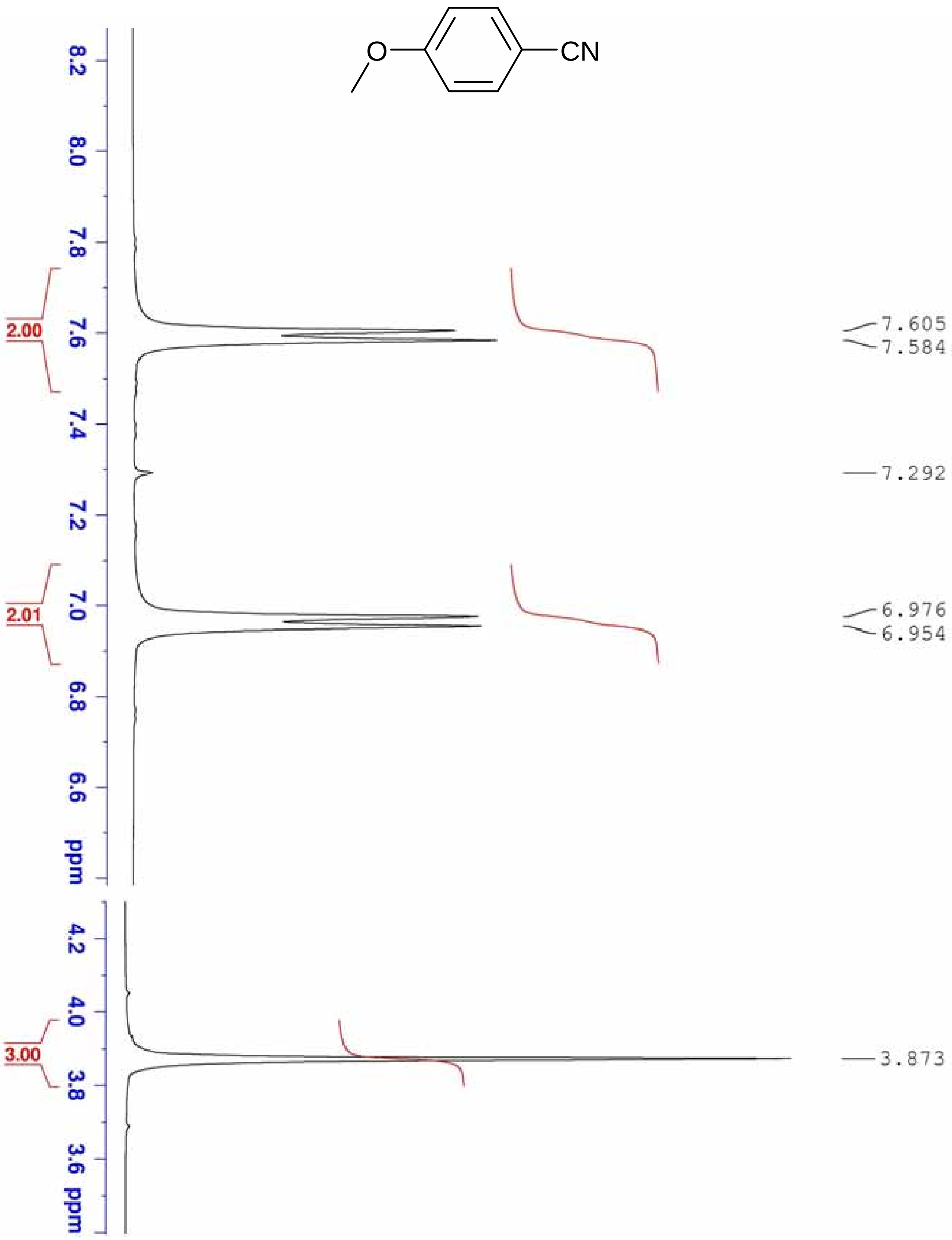
4-Methoxybenzonitrile

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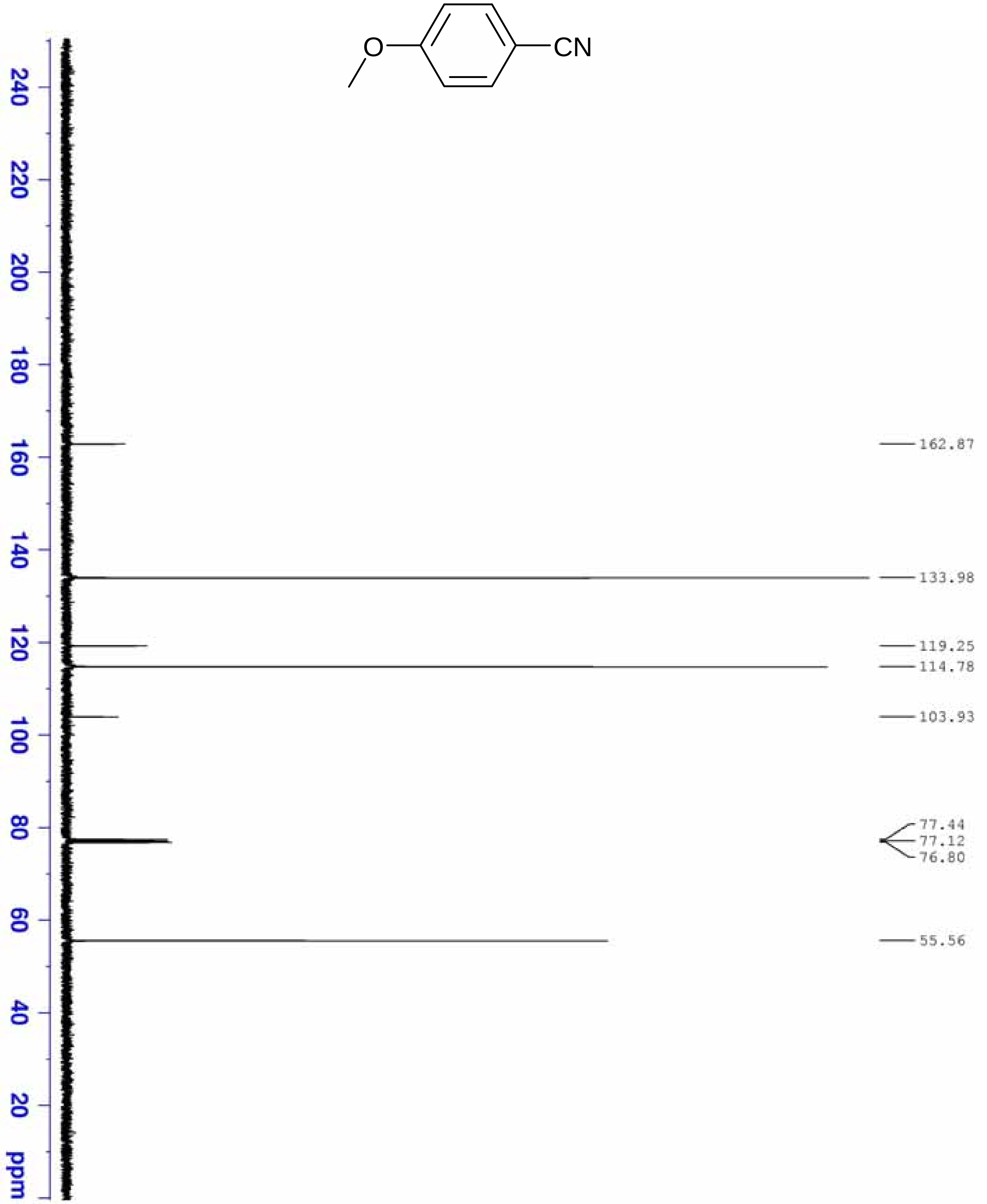
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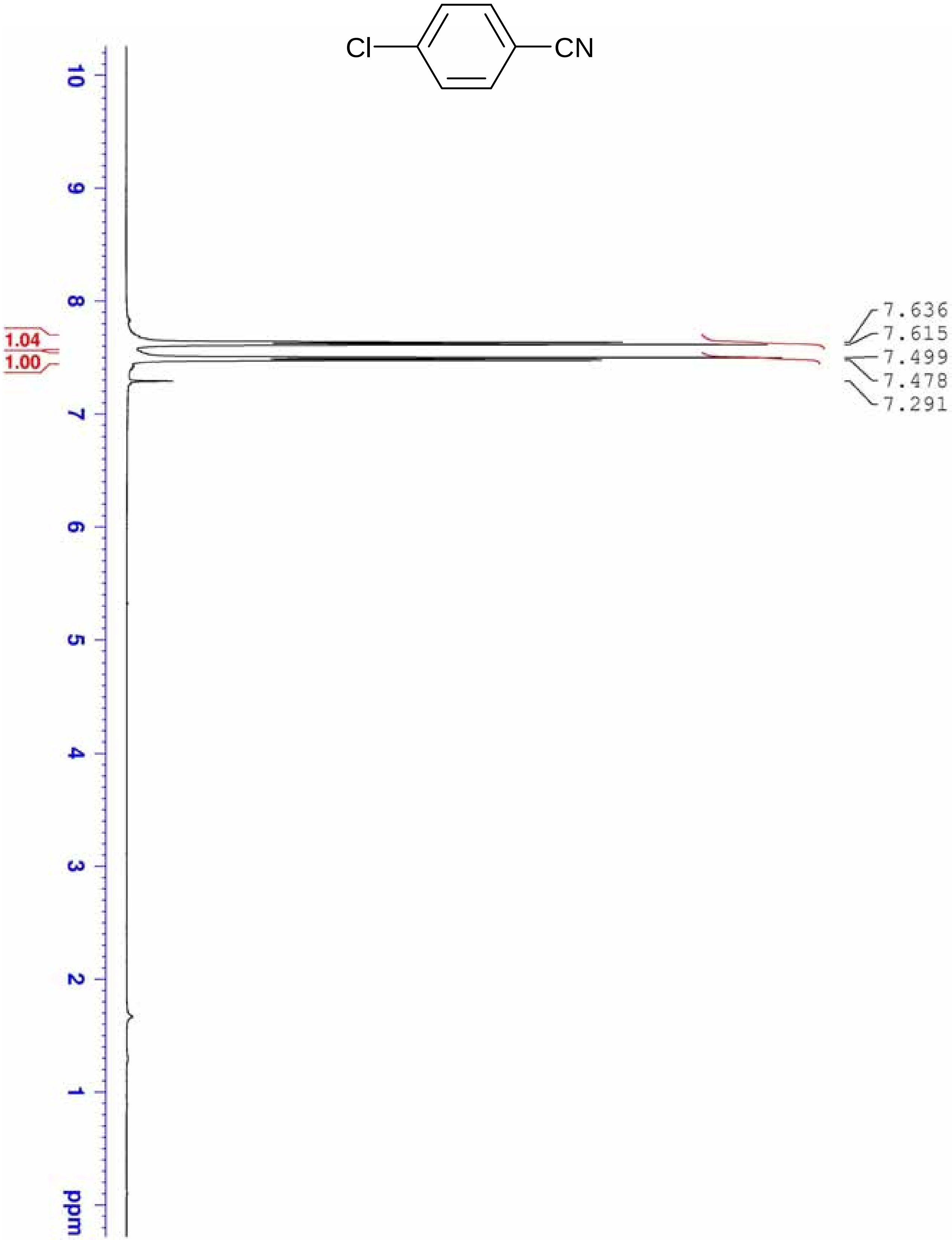

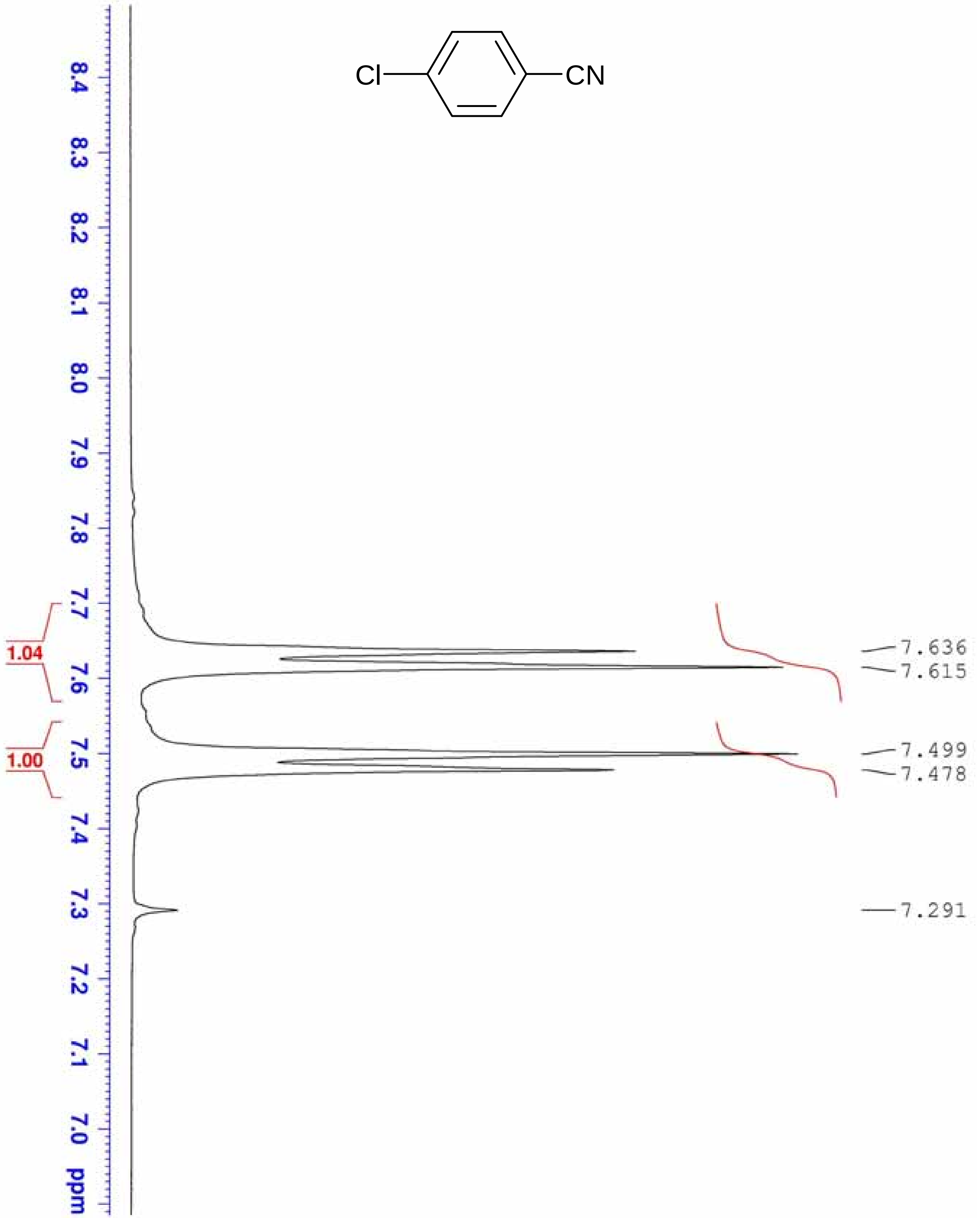
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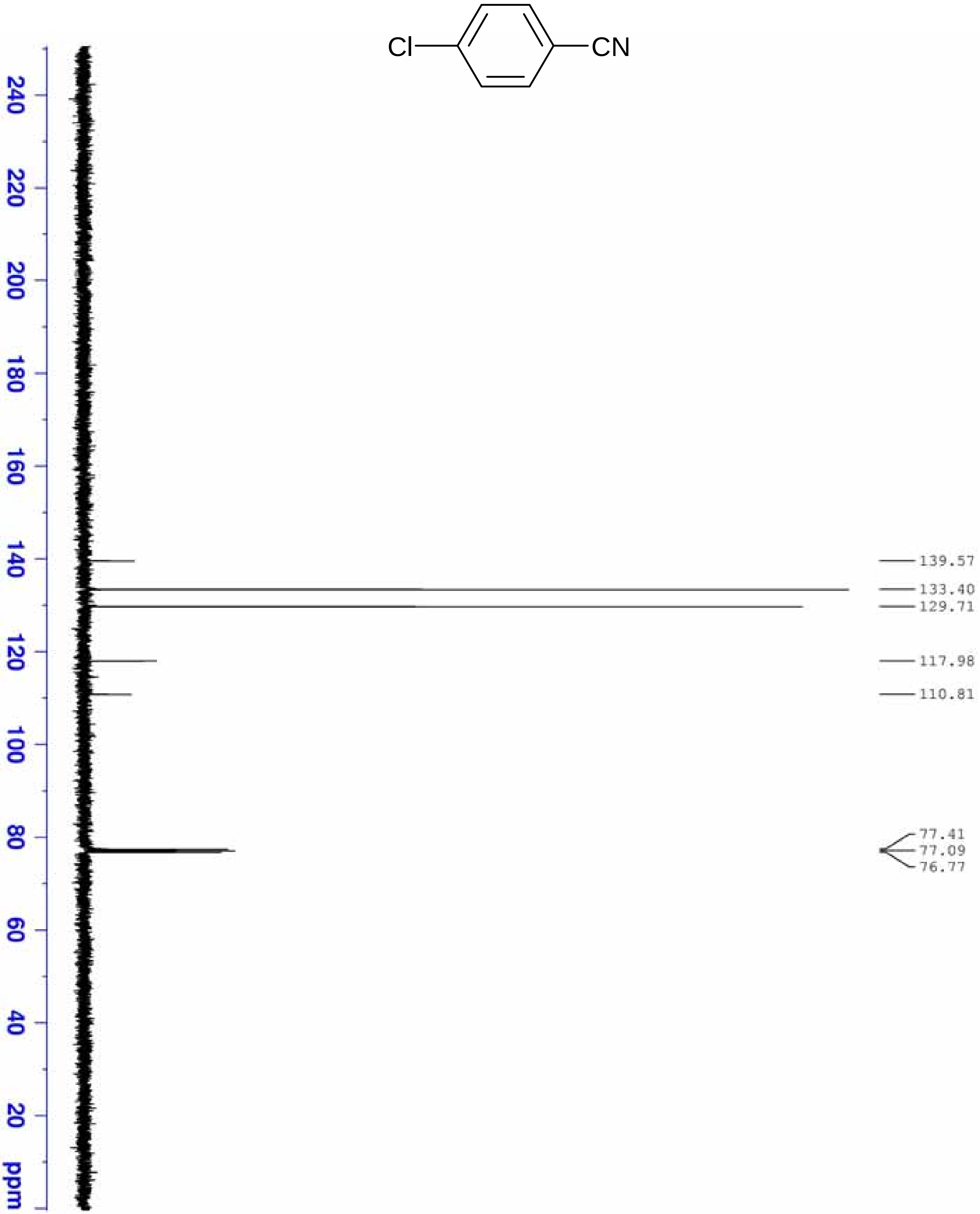
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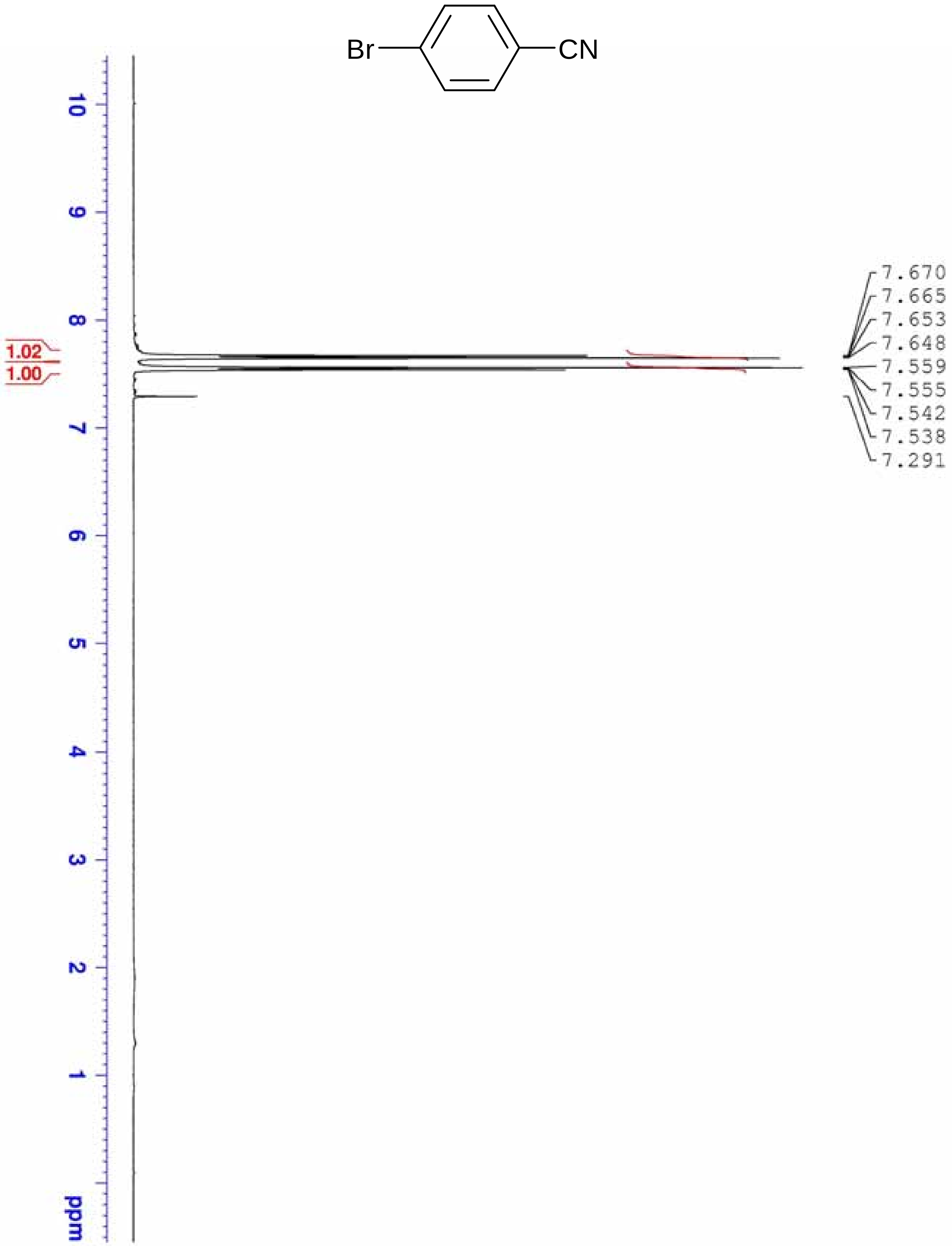

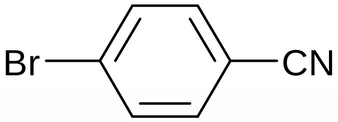
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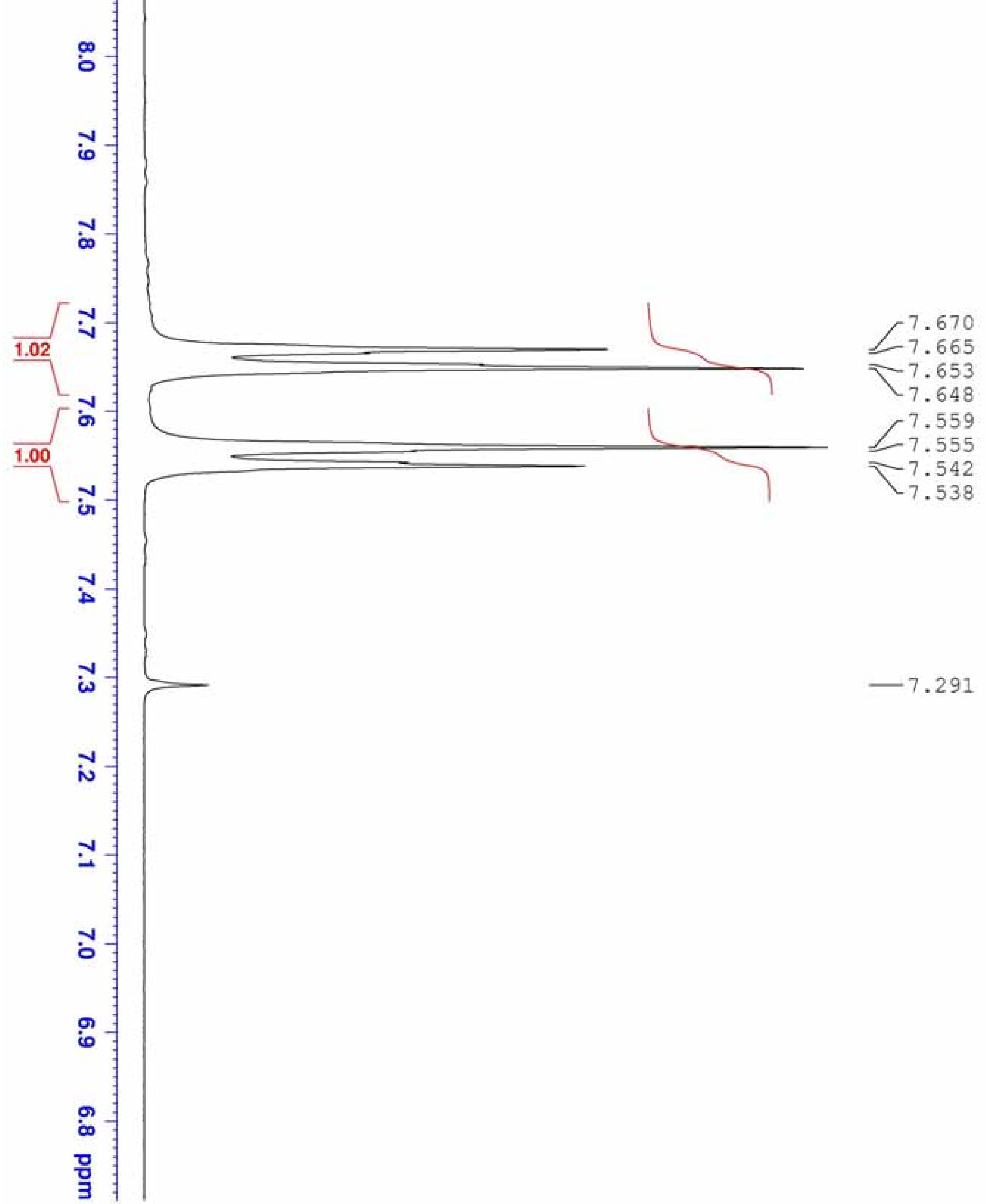
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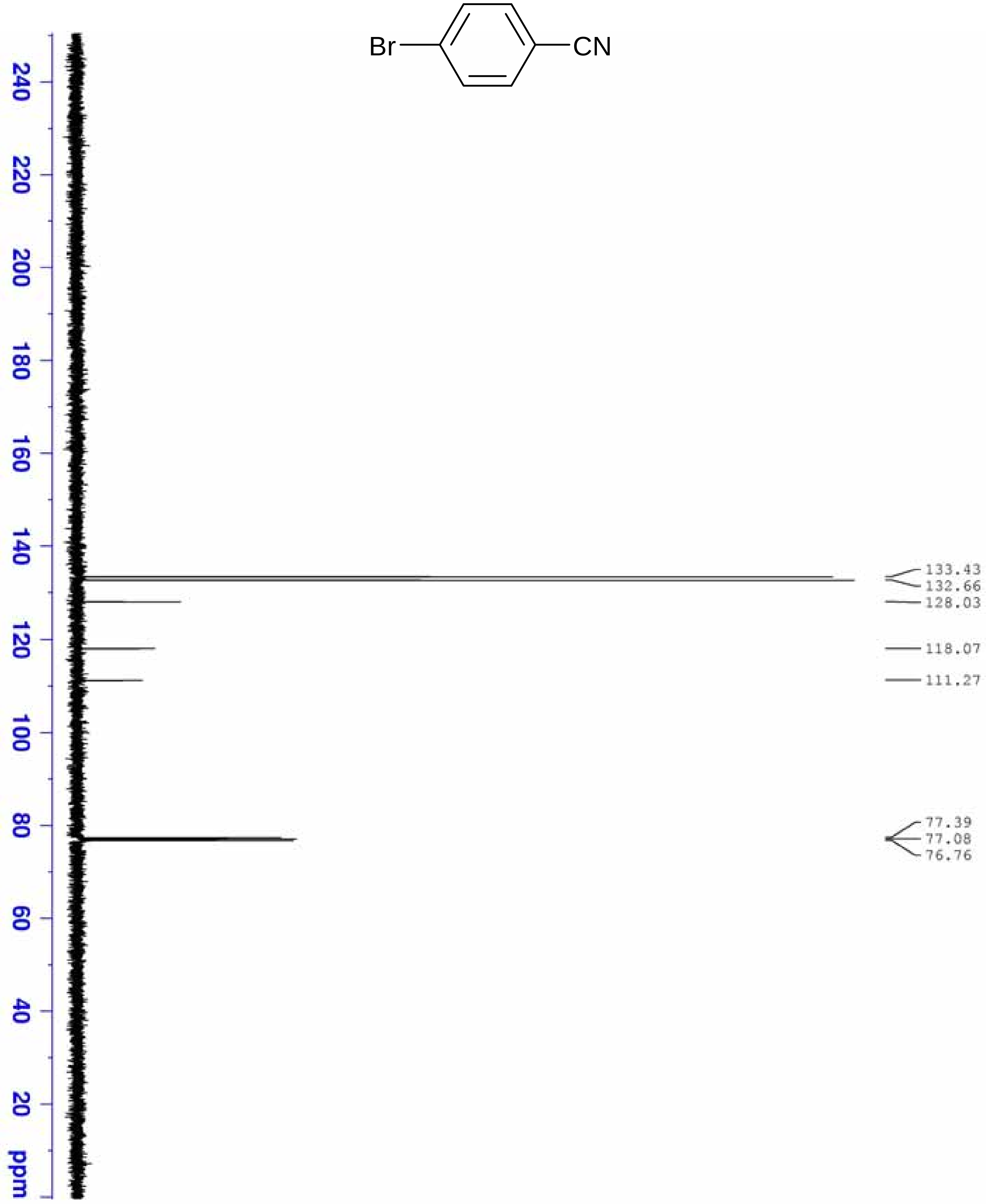
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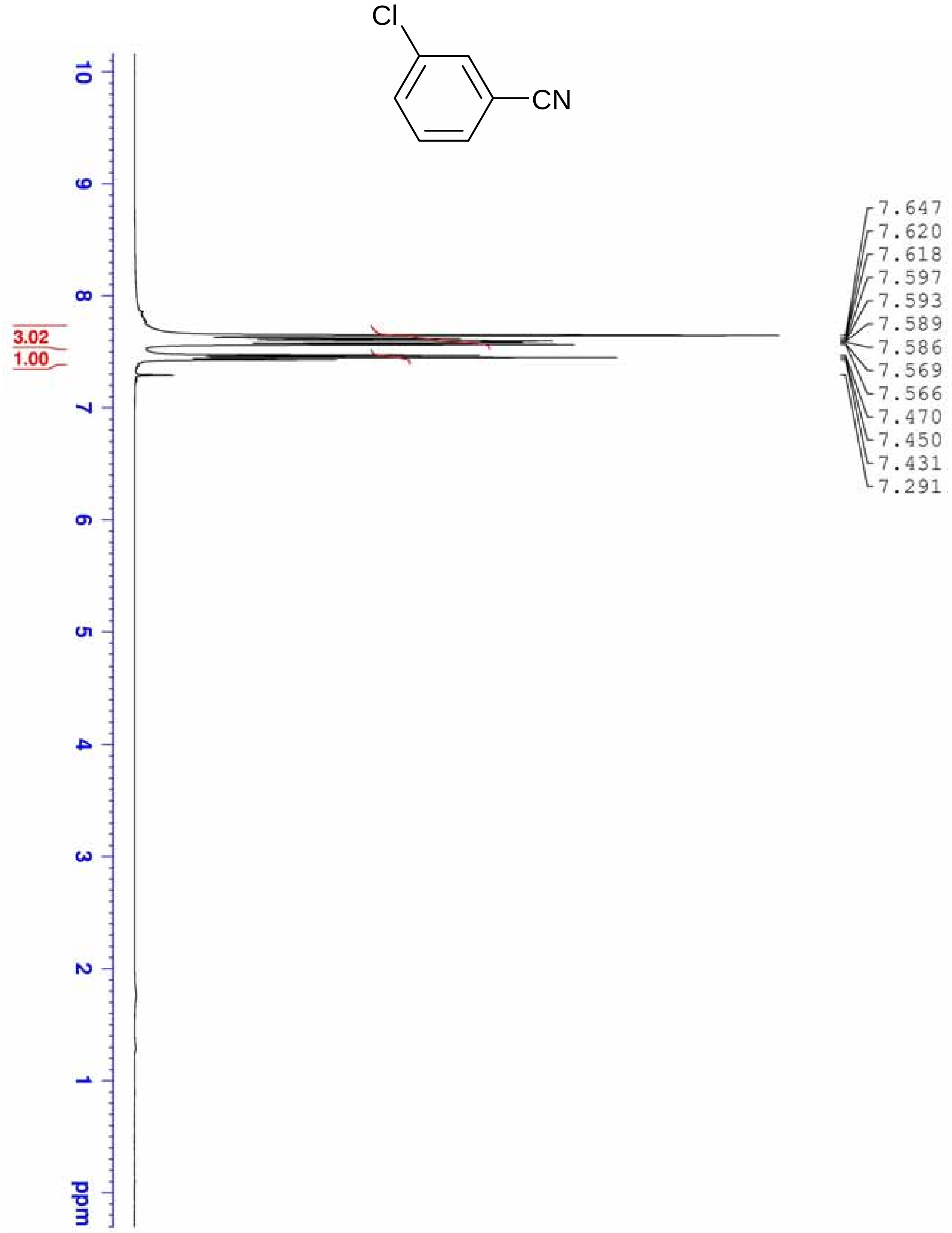

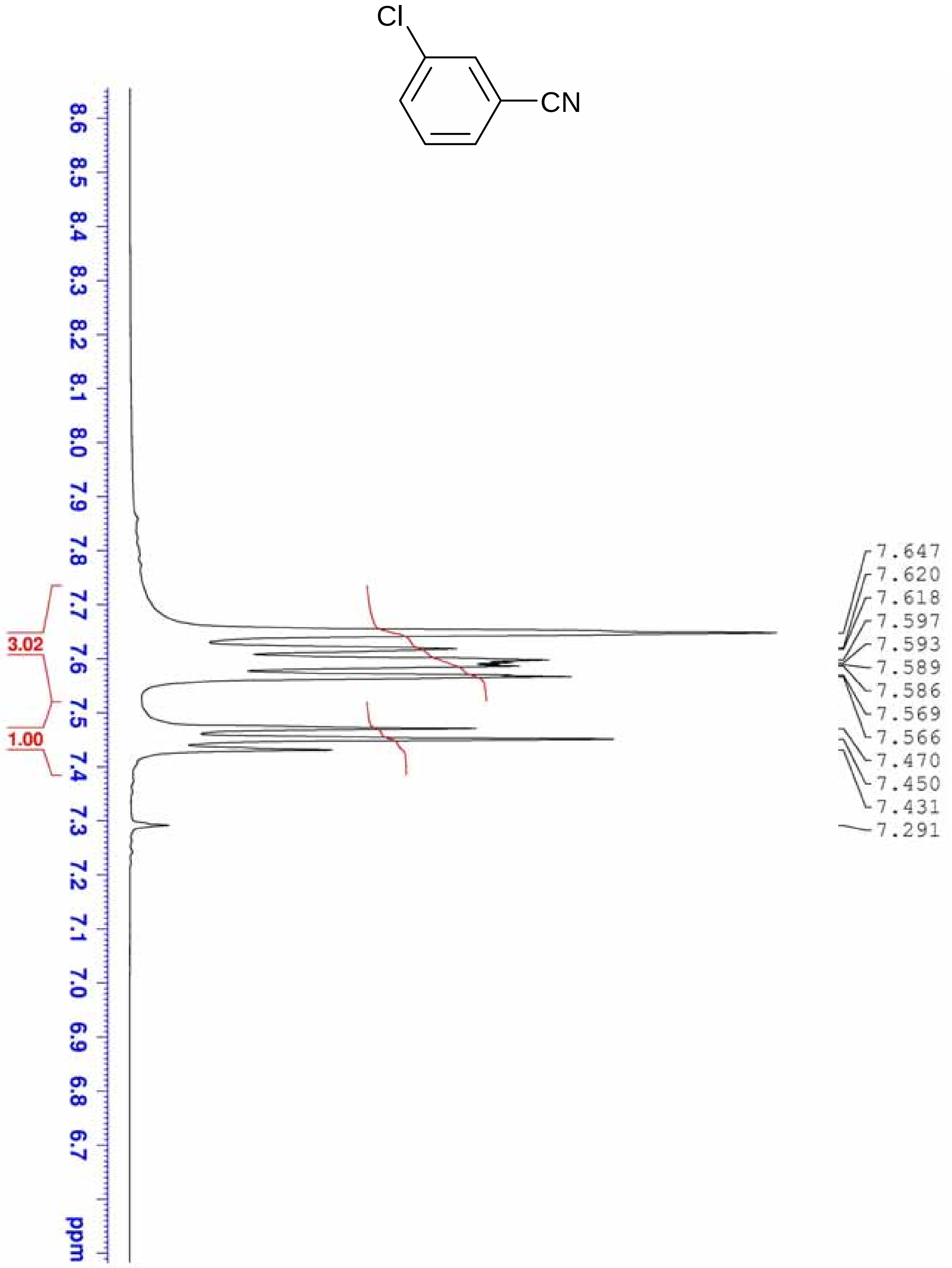
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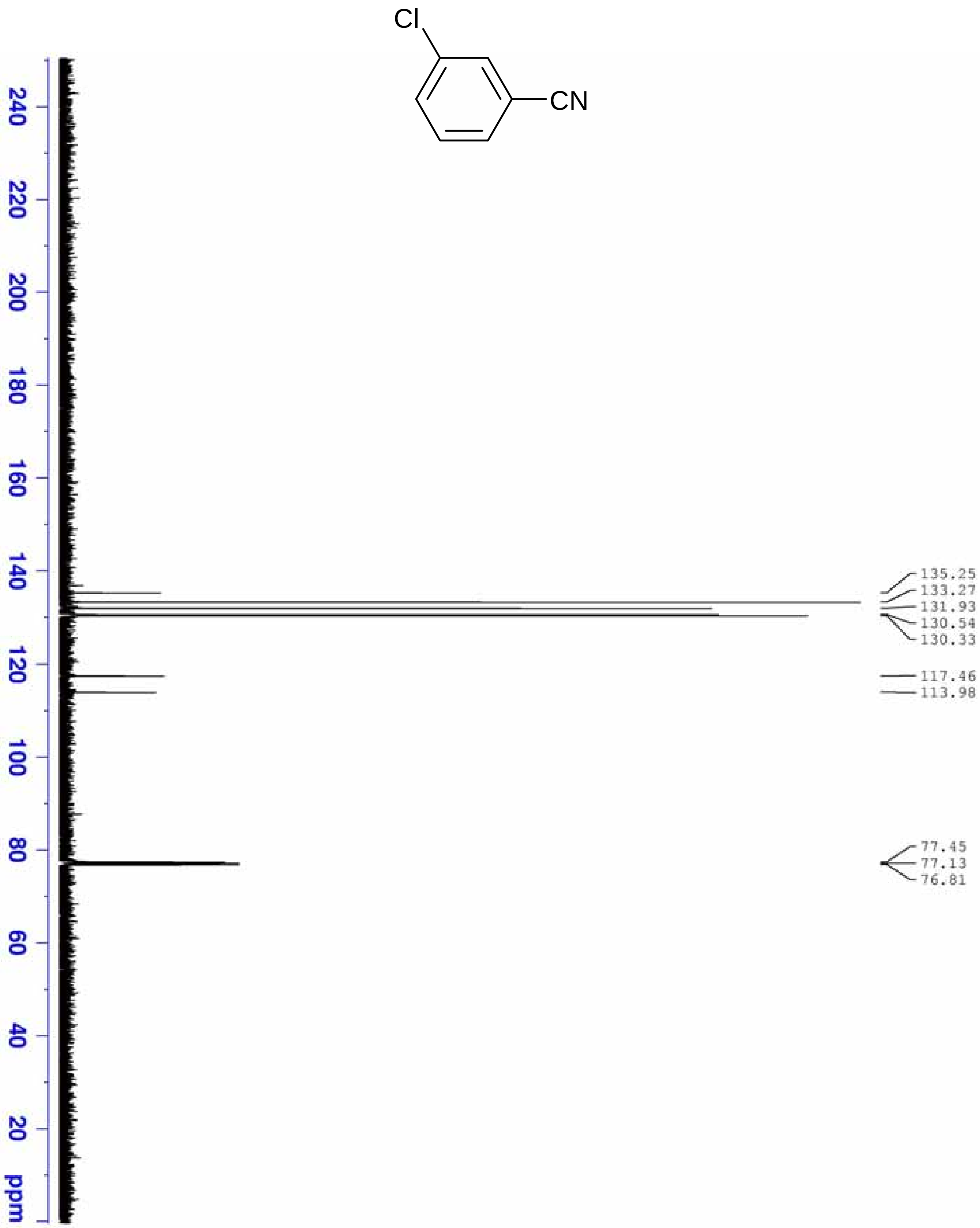
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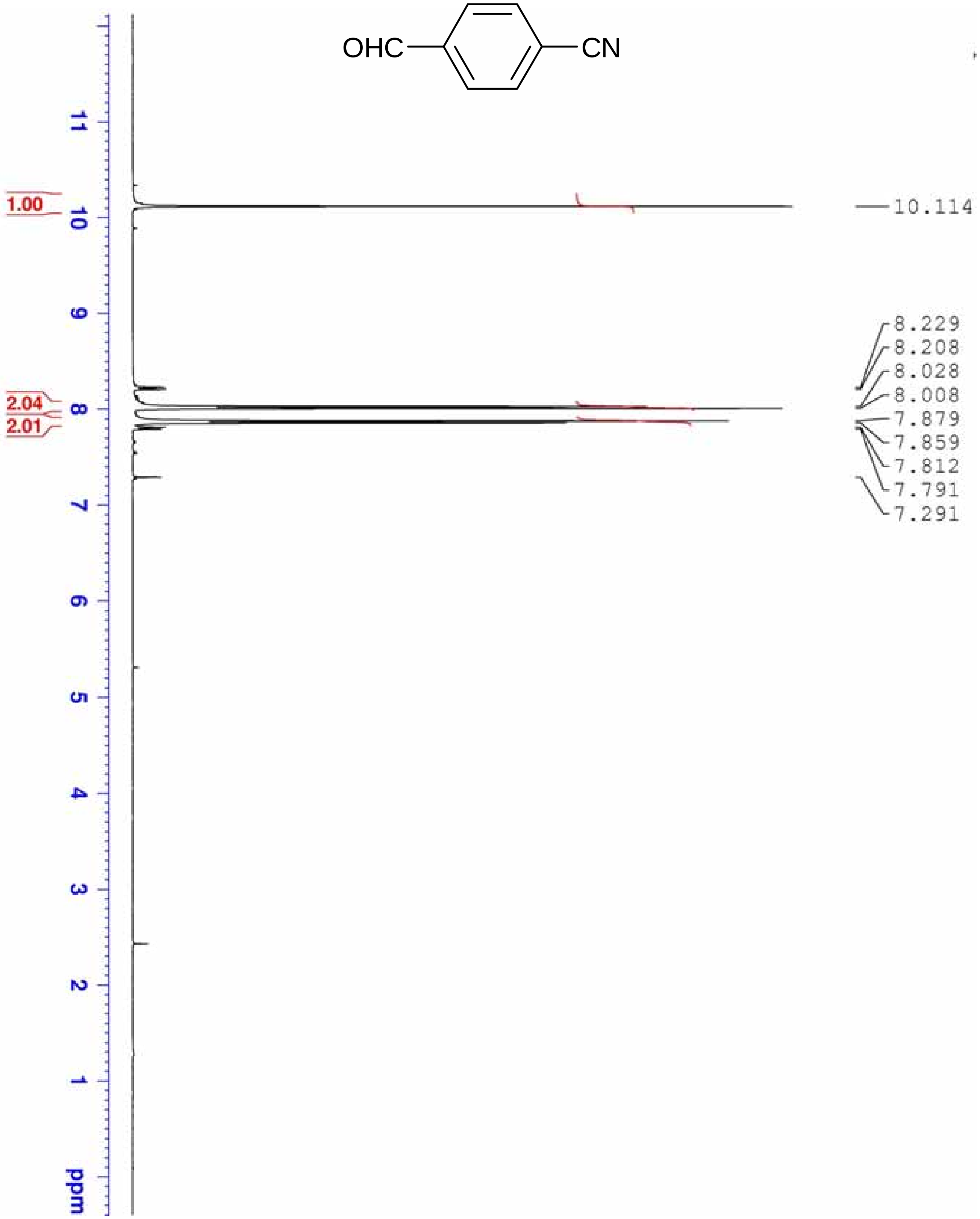

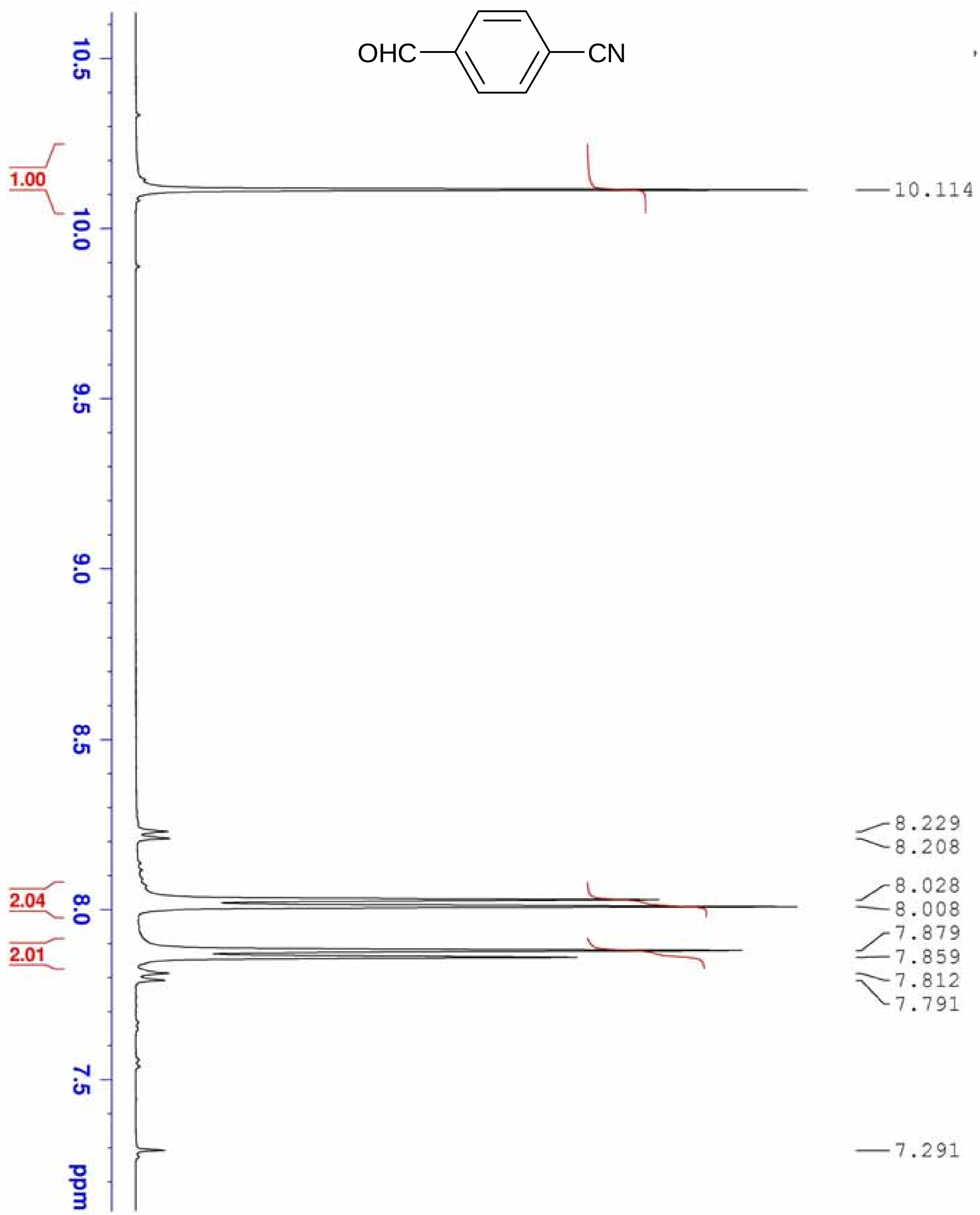
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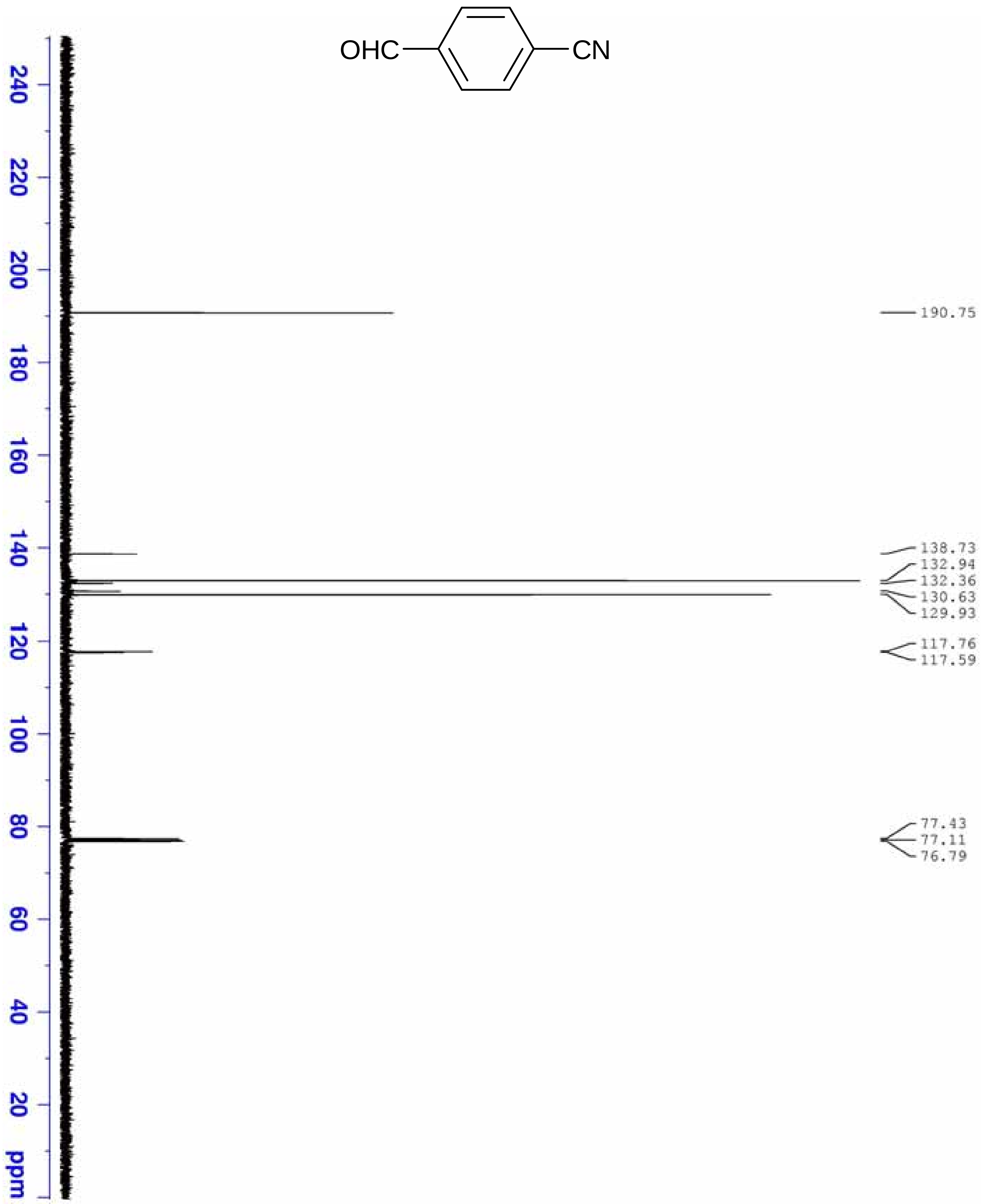
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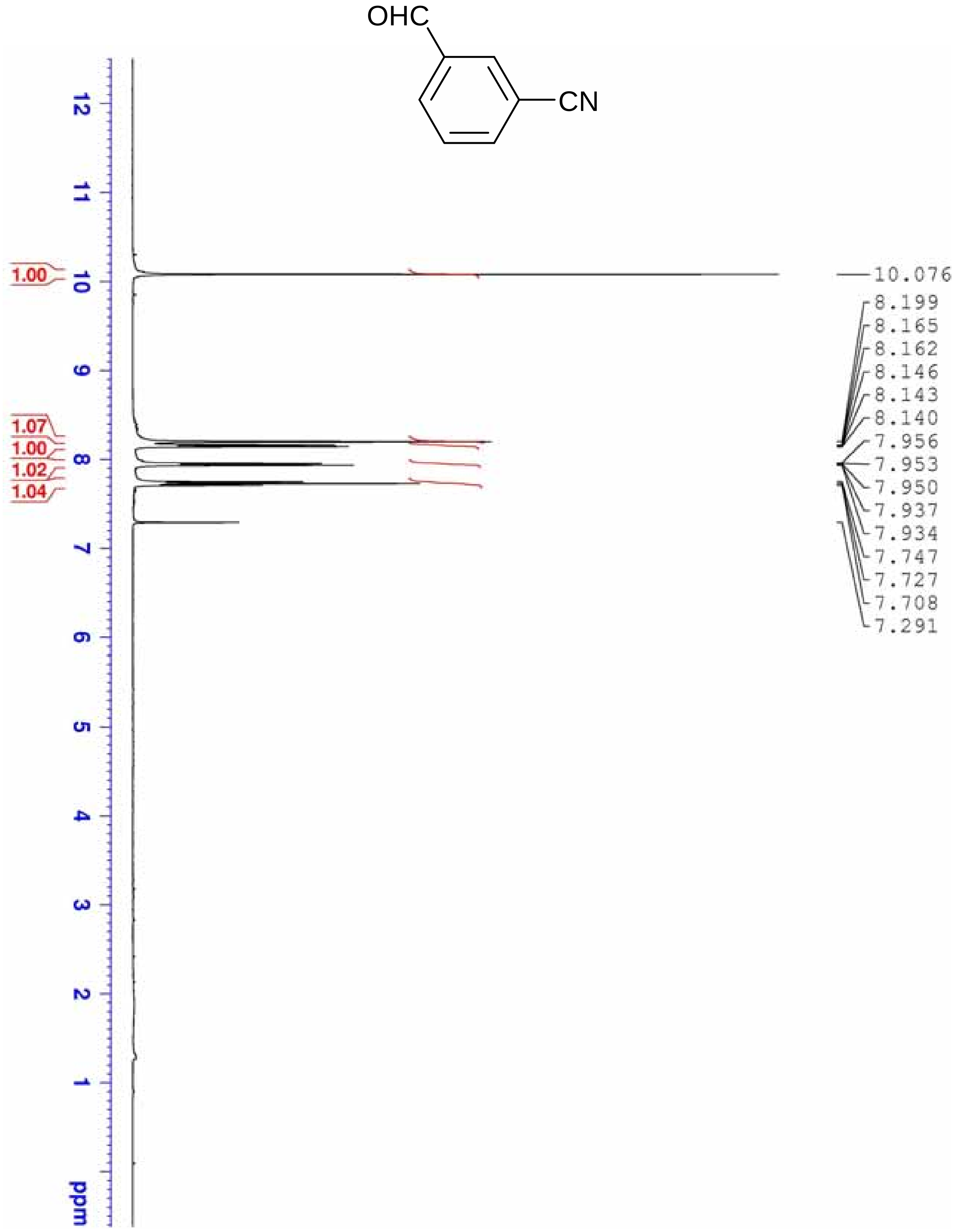

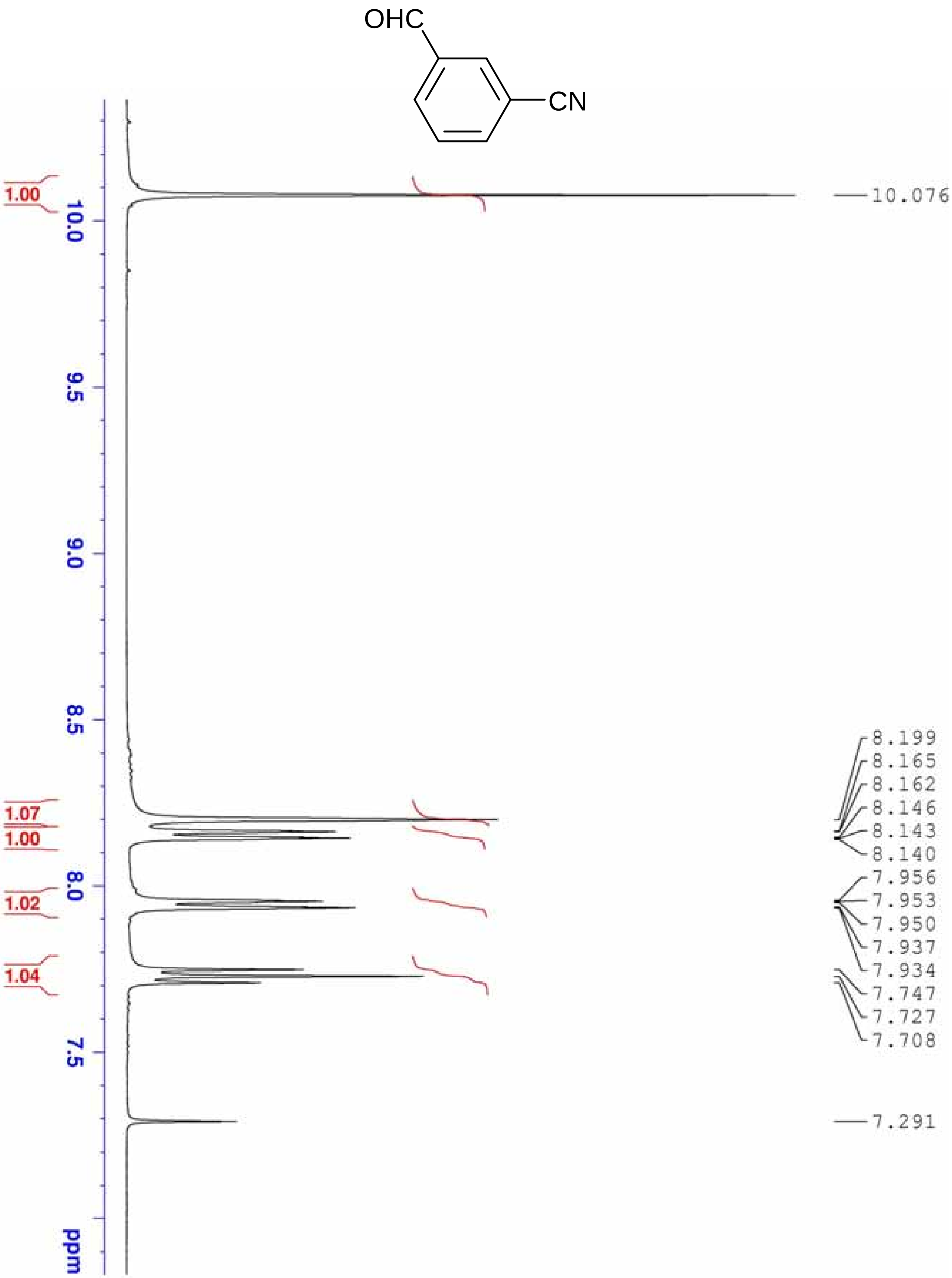
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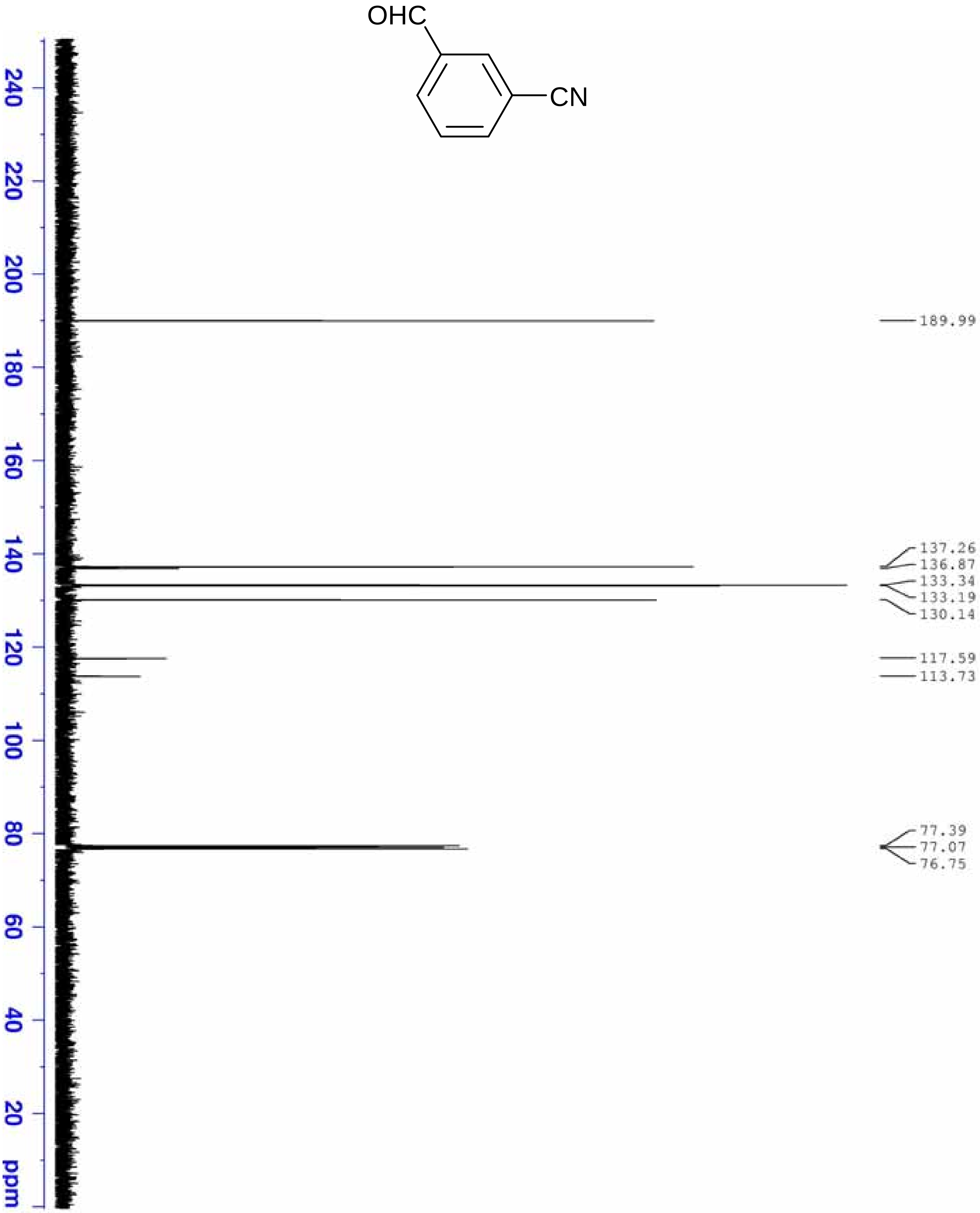
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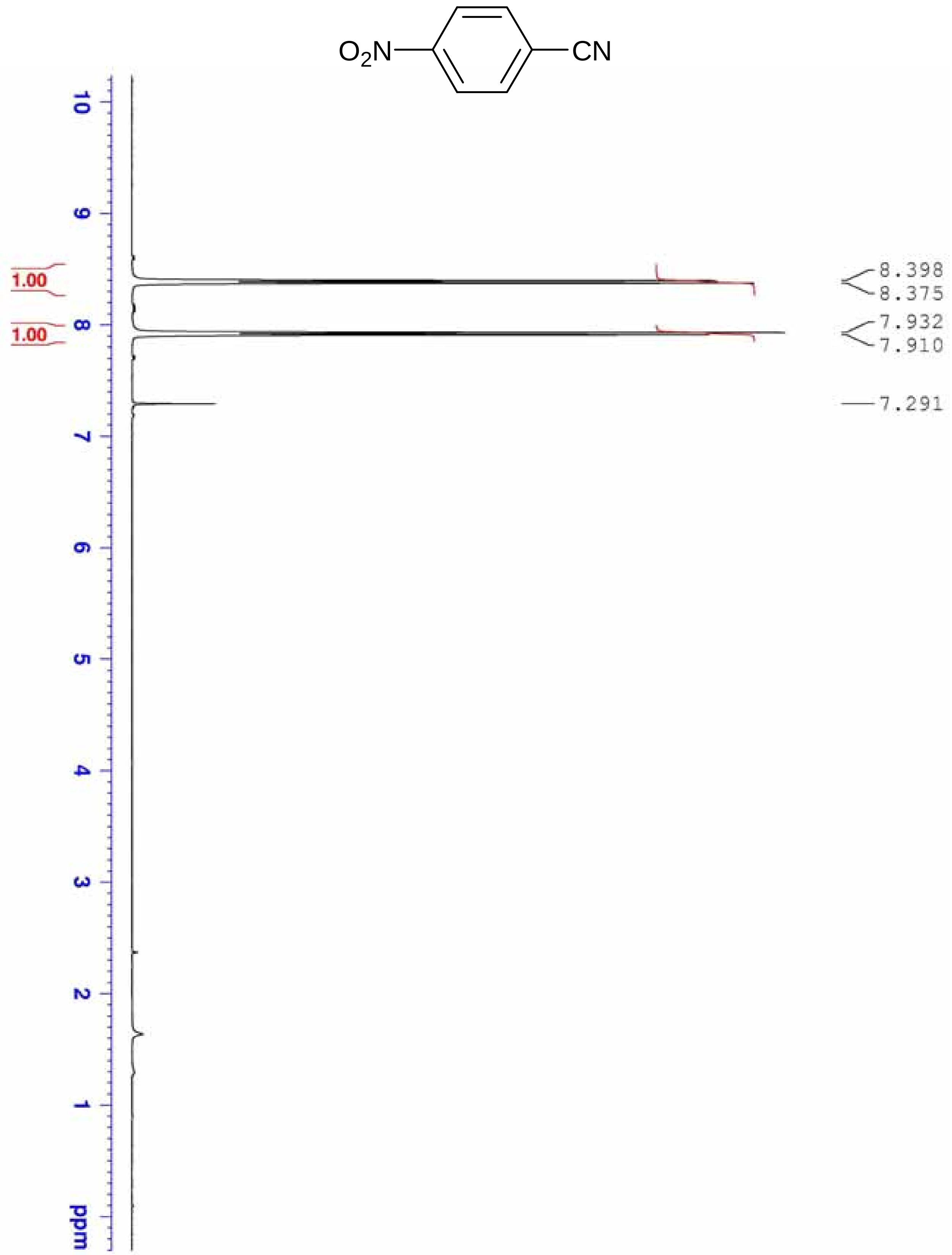

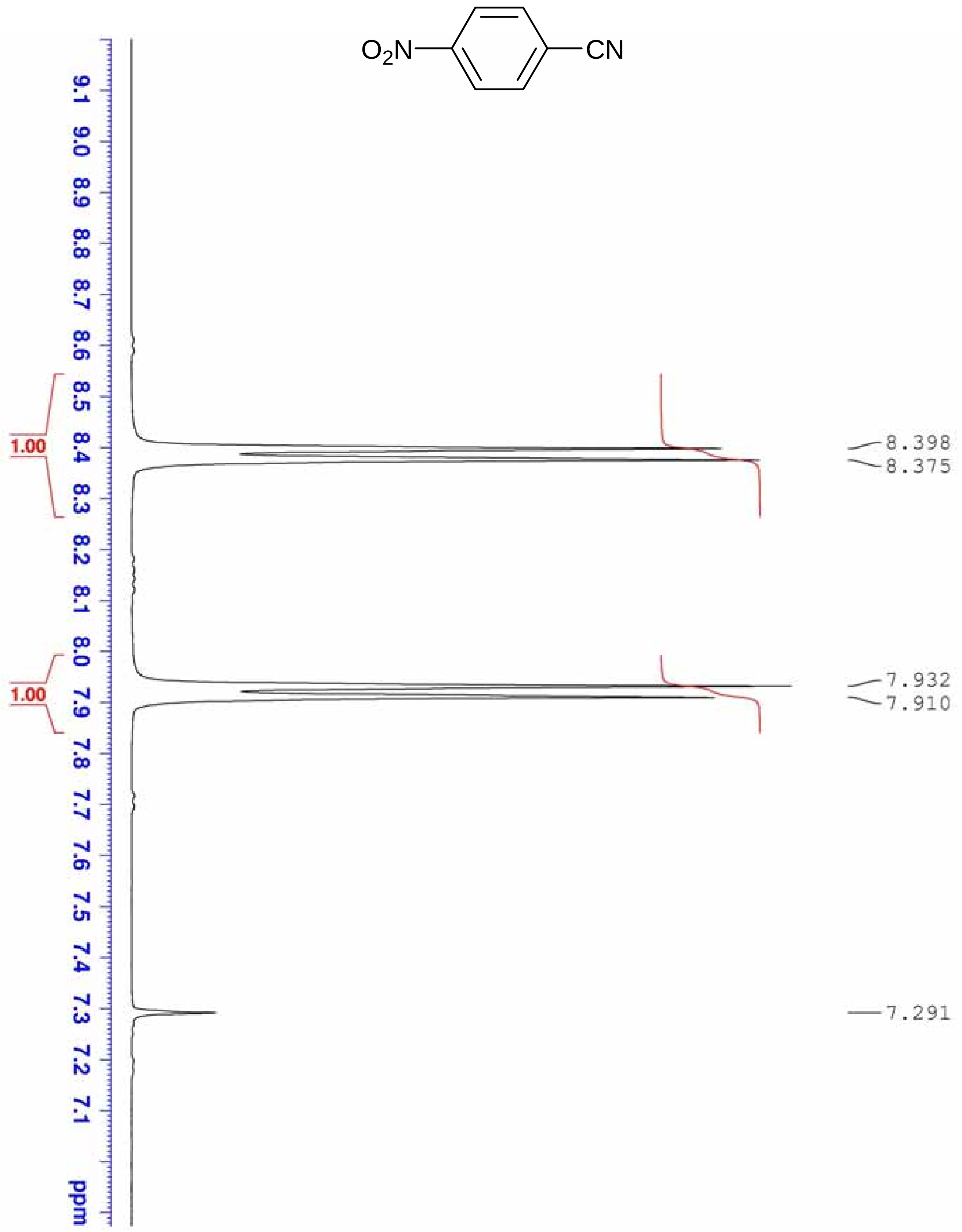
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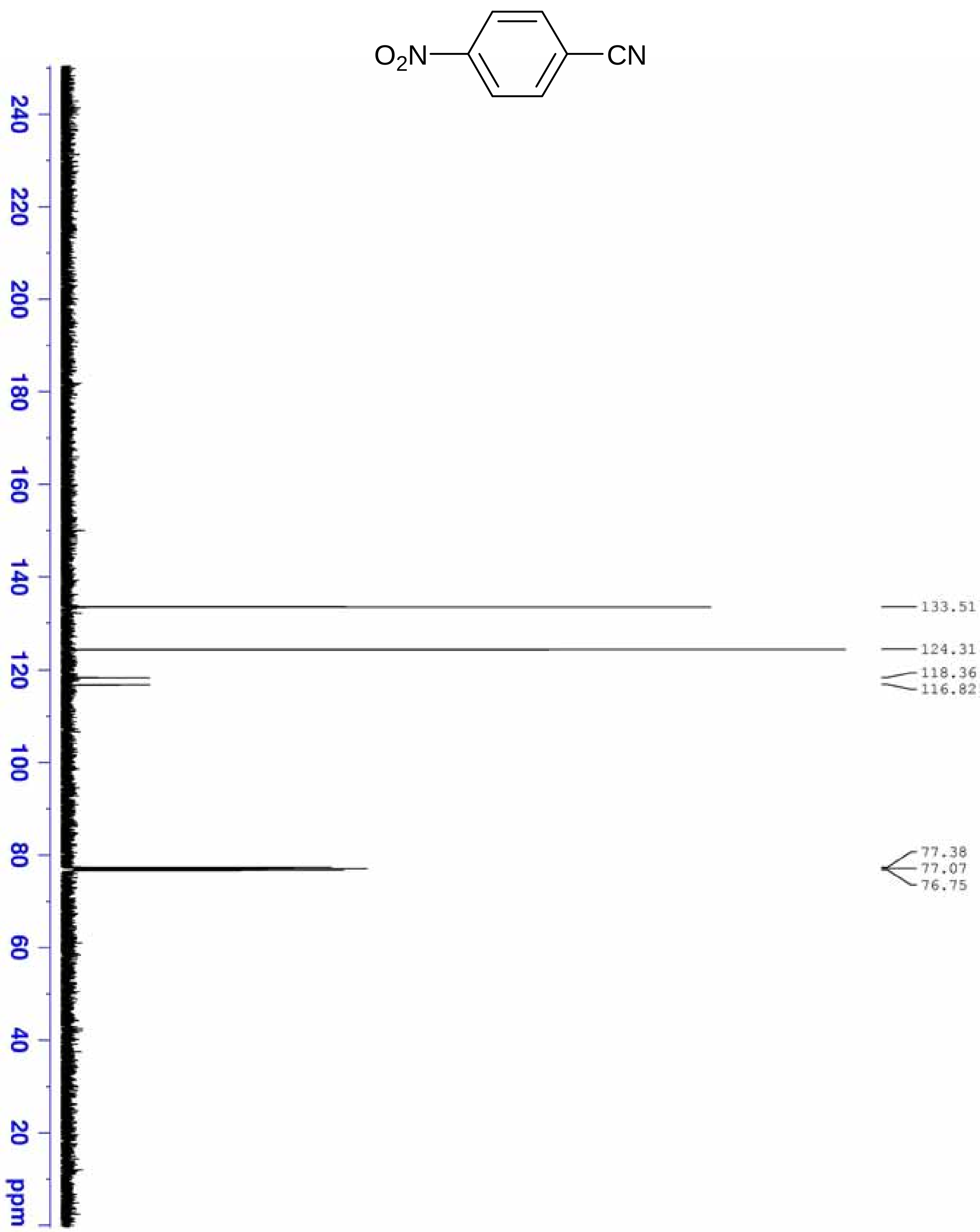
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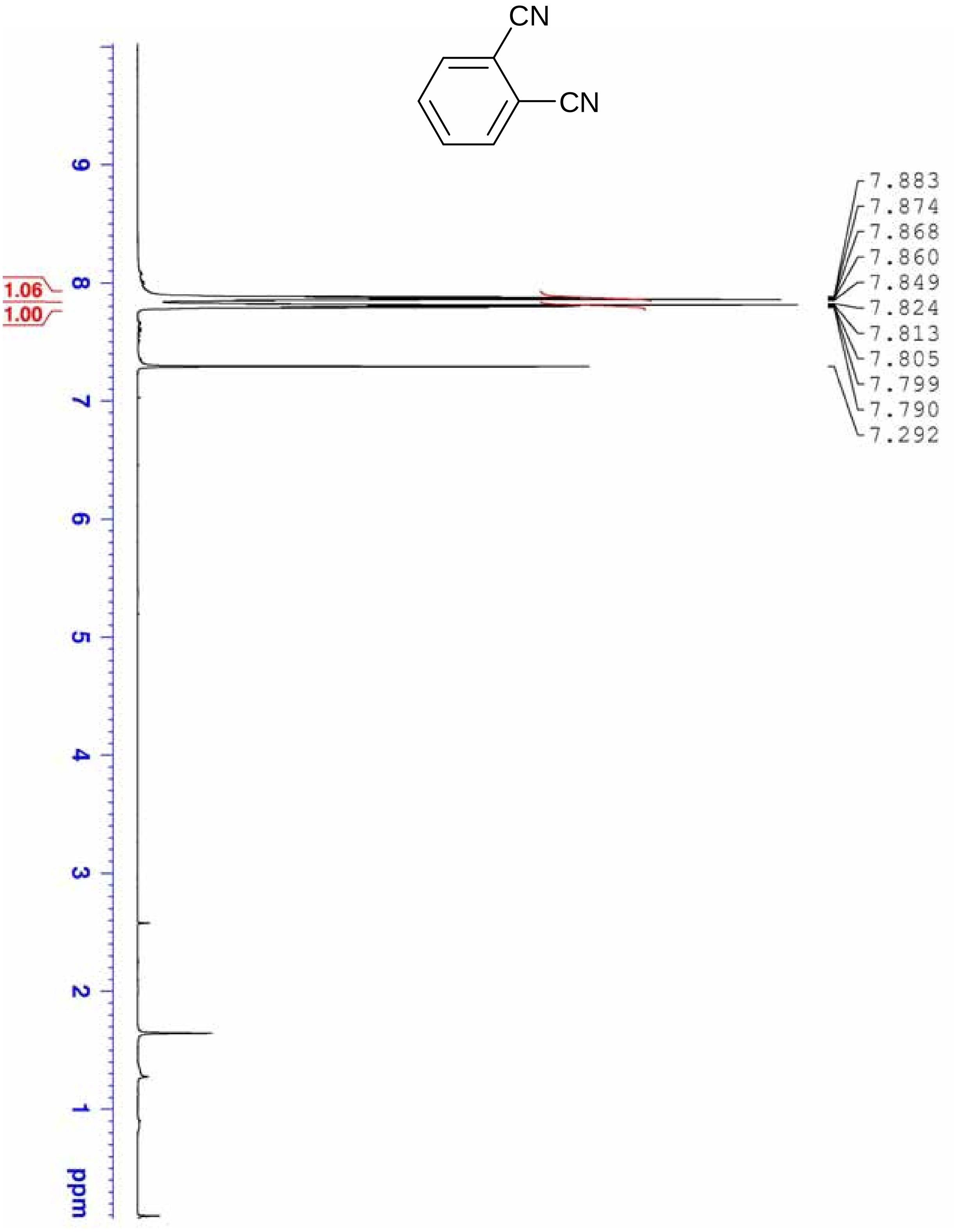
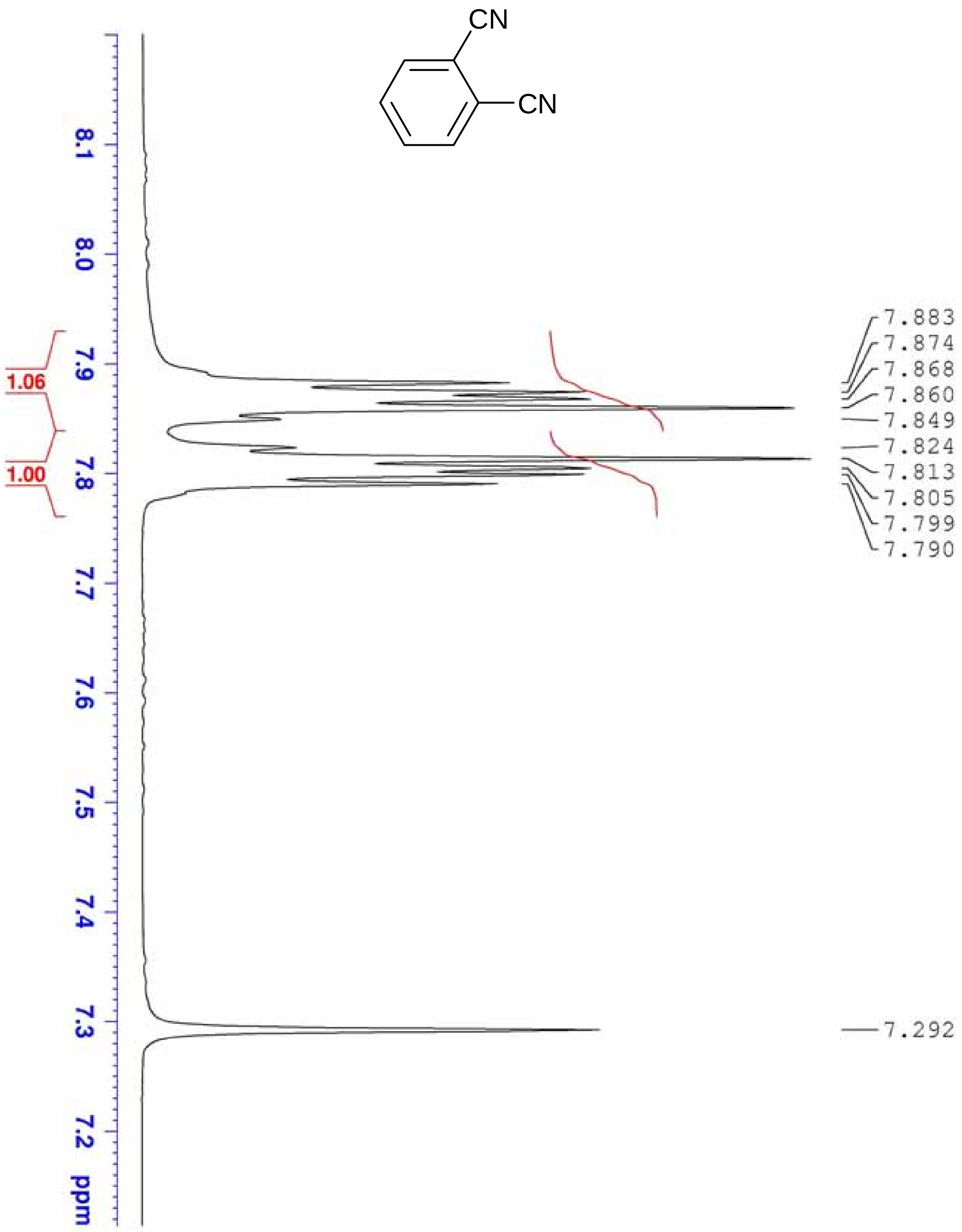
***o*-Phthalonitrile**

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1.00
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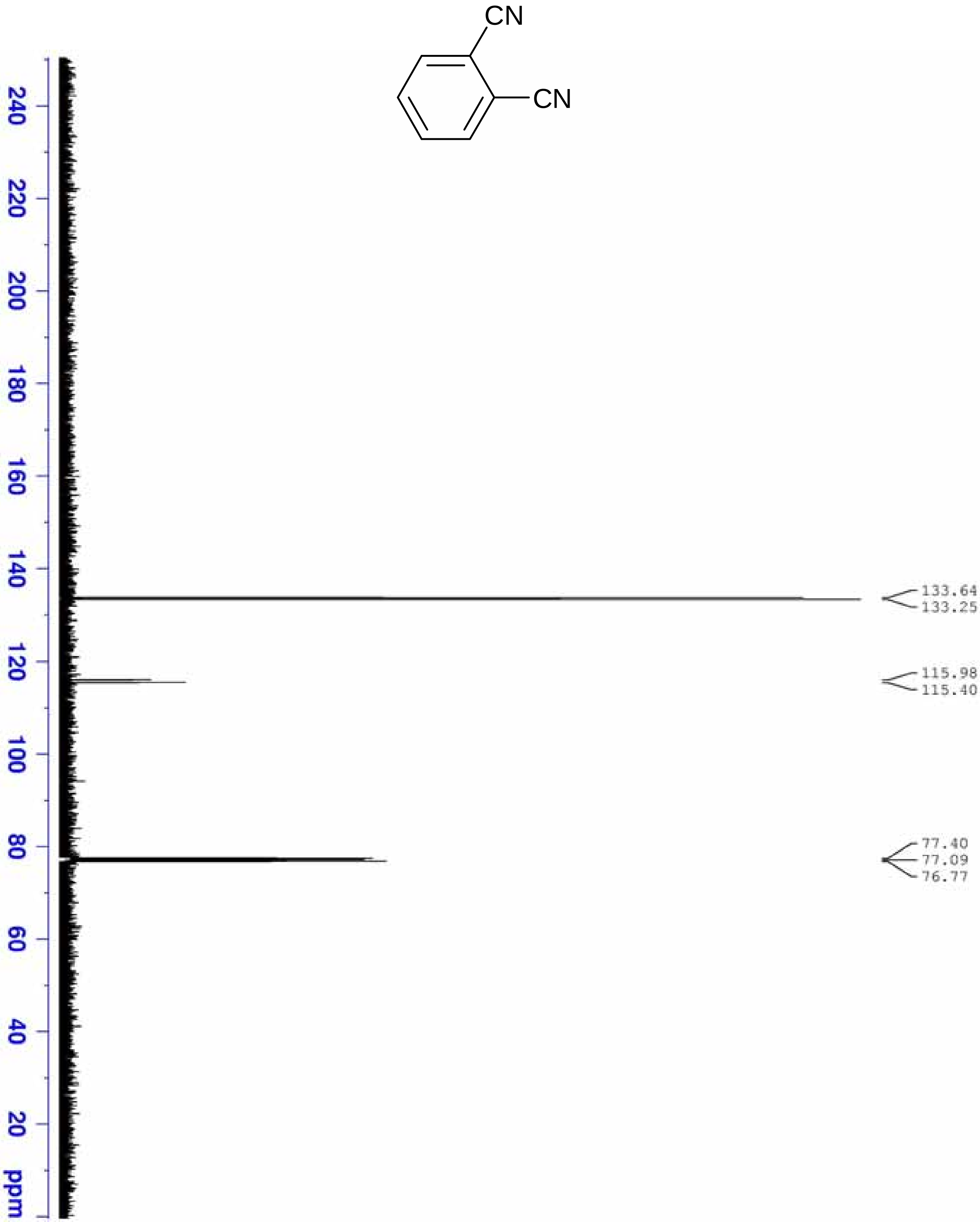
7.868
7.860
7.849
7.824
7.813
7.805
7.799
7.790
7.292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77.40
77.09
76.77

References:

[1] D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.*1998, **120**, 6024.