

Supporting information

Chemo-selective reduction of nitro and nitrile compounds with magnetic carbon nanotubes-supported Pt(II) catalyst under mild conditions

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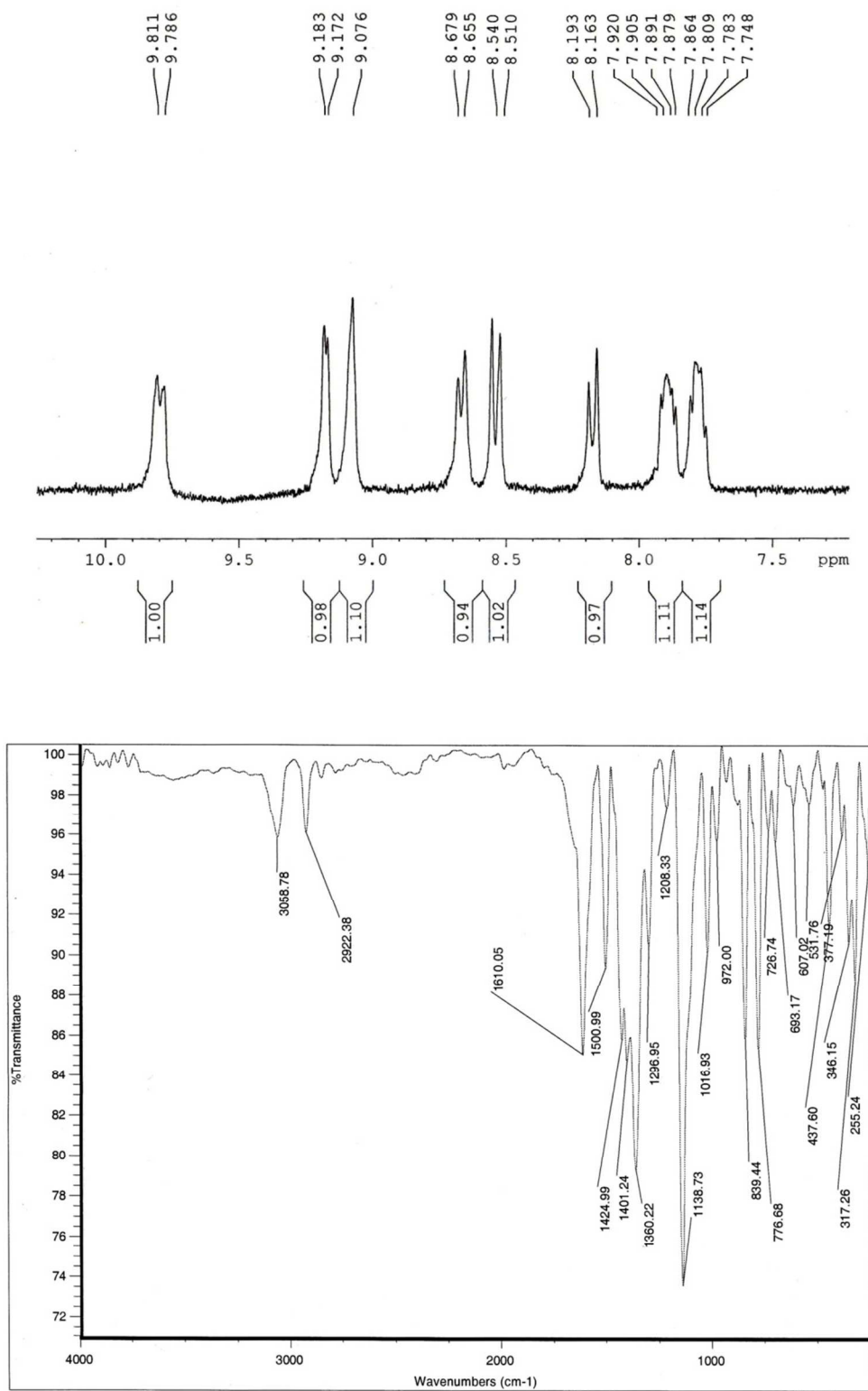
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^1H -NMR and FT-IR spectra of *cis*-[Pt(1,7-phenanthroline)(DMSO)Cl₂] complex:



X-ray structure analysis

The X-ray diffraction measurements for *cis*-[Pt(1,7-Phen)(DMSO)Cl₂] was made on a Bruker APEX II CCD area detector diffractometer with graphite monochromated Mo K α radiation (λ = 0.71073 Å) at 298 K. The structure of the title complex was solved by SHELX-97 and absorption correction was done using the SADABS program.^{1,2} Data collection, cell refinement, and data reduction were performed by APEX II, SAINT, SHELXTL and PLATON.²⁻⁶ The molecular graphic were generated by using Mercury 2.4 program.⁷

Spectroscopic characterization of *cis*-[Pt(1,7-Phen)(DMSO)Cl₂]

IR absorptions of *cis*-[Pt(1,7-Phen)(DMSO)Cl₂] are listed in the experimental section. The infrared spectrum for this compound show several weak absorption bands in the region of 3059–2922 cm⁻¹, which are assigned to the C-H stretching vibrations of the pyridine and phenyl rings and the dimethyl sulfoxide methyl groups. The weak to strong vibrational bands in the region of 1610-531 cm⁻¹ are assigned to C-H, C=C, C=N, C-C, and C-N stretching and deformation vibrational bands of the pyridine and phenyl rings and the dimethyl sulfoxide methyl groups.⁸⁻¹¹ In addition, the strong absorption band at 1139 cm⁻¹ is assigned to ν (S=O) for DMSO ligand, showing Pt-S coordination.¹² Far infrared spectrum for *cis*-[Pt(1,7-Phen)(DMSO)Cl₂] was observed between 438 and 255 cm⁻¹. The medium absorption bands observed at 438 and 255 cm⁻¹ are assigned to Pt-N and Pt-S frequencies, respectively. Also, two medium absorption bands observed at 346 and 317 cm⁻¹ are assigned to Pt-Cl frequencies.¹²⁻¹⁵

Description of the molecular structure of [cis-[Pt(1,7-Phen)(DMSO)Cl₂]

Crystallographic data for *cis*-[Pt(1,7-Phen)(DMSO)Cl₂] are given in Table 1 and selected bond lengths and angles are presented in Table 2. This complex *cis*-[Pt(1,7-Phen)(DMSO)Cl₂] crystallizes in the triclinic crystal system with *P* $\bar{1}$ space group. The molecular structure of the title complex together with the atomic labeling scheme is shown in Figure S1. As shown in this Figure, the platinum(II) cation is four-coordinated in a square-planar configuration by one S atom from one dimethyl sulfoxide ligand, one N atom from one 1,7-phenanthroline ligand and two chloride anions. In this complex, the Pt–N and Pt–S bond lengths, 2.016(9) and 2.205(3) Å, are similar to that found in [Pt(py)(DMSO)Cl₂], 2.023(7) and 2.209(2) Å (py is pyridine),¹⁶ but are slightly smaller than that found in [Pt(metpy)(DMSO)Cl₂], 2.033(8) and 2.220(3) Å (metpy is

methoxypyridine).¹⁷ The bond lengths of Pt-Cl are slightly different, because of the different *trans* effects of the S and N atoms.¹⁸ The bond length of Pt1-Cl1 *trans* to the N atom is 2.293(3)Å. This bond length is slightly smaller than the bond Pt1-Cl2, 2.321(3)Å, *trans* to the S atom. The Pt-S bond lengths are also similar to that found in [Pt(metpy)(DMSO)Cl₂], 2.293(3) and 2.311(3)Å.¹⁷ Furthermore, the S=O bond length, 1.462(9)Å, is significantly shorter than that in the free dimethyl sulfoxide molecule, 1.531(5)Å,¹⁹ but is similar to that found in [Pt(metpy)(DMSO)Cl₂], 1.461(7).¹⁷ The pyridine and phenyl rings are slightly distorted from planarity. The mean planes of rings A (N1/C1-C4/C12), B (C4/C5/C9-C12) and C (N2/C5-C9) make the following dihedral angles with each other: A/B = 2.93, A/C = 3.20 and B/C = 1.00°.

In the crystal structure of *cis*-[Pt(1,7-Phen)(DMSO)Cl₂], Figure S2, there are $\pi \cdots \pi$ interactions between the pyridine and phenyl rings, Cg2 \cdots Cg3ⁱ [distance is 3.557(7), symmetry code: i = 1-x,-y,1-z, and Cg2 and Cg3 are centroids of the rings (C4/C5/C9-C12) and (N2/C5-C9), respectively] and intermolecular C-H \cdots Cl and C-H \cdots O hydrogen bonds (Table 3) in the crystal packing. These $\pi \cdots \pi$ interactions and intermolecular C-H \cdots Cl and C-H \cdots O hydrogen bonds are effective in the stabilization of the crystal structure and the formation of the 3D supramolecular complex.

Crystallographic data for the structural analyses of *cis*-[Pt(1,7-Phen)(DMSO)Cl₂] have been deposited with the Cambridge Crystallographic Data Centre bearing the CCDC No. **1536141**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK.

Table S1. Crystallographic and structural refinement data for *cis*-[Pt(1,7-Phen)(DMSO)Cl₂].

Formula	C ₁₄ H ₁₄ Cl ₂ N ₂ OPtS
Formula weight	524.32
Temperature /K	298(2)
Wavelength λ /Å	0.71073
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
Crystal size /mm	0.39×0.30×0.25
<i>a</i> /Å	8.0582(16)
<i>b</i> /Å	9.782(2)
<i>c</i> /Å	11.229(2)
α /°	77.923(16)
β /°	81.716(16)
γ /°	67.235(15)
Volume /Å ³	796.2(3)
Z	2
Density (calc.)/g.cm ⁻¹	2.187
θ ranges for data collection	2.29-27.00
F(000)	496
Absorption coefficient	9.276
Index ranges	-10 ≤ <i>h</i> ≤ 10 -12 ≤ <i>k</i> ≤ 10 -13 ≤ <i>l</i> ≤ 14
Data collected	7372
Unique data (<i>R</i> _{int})	3472, 0.0981
Parameters, restraints	192, 0
Final <i>R</i> ₁ , <i>wR</i> ₂ (Obs. data)	0.0613, 0.1562
Final <i>R</i> ₁ , <i>wR</i> ₂ (All data)	0.0691, 0.1638
Goodness of fit on <i>F</i> ² (S)	1.113
Largest diff peak and hole/e.Å ⁻³	1.251, -1.301

Table S2. Selected bond lengths (Å) and angles (°) for *cis*-[Pt(1,7-Phen)(DMSO)Cl₂].

Pt1-N1	2.016(9)	N1-Pt1-Cl1	178.9(2)
Pt1-S1	2.205(3)	S1-Pt1-Cl1	90.63(11)
Pt1-Cl1	2.293(3)	N1-Pt1-Cl2	87.9(3)
Pt1-Cl2	2.321(3)	S1-Pt1-Cl2	177.10(10)
O-S	1.462(9)	Cl1-Pt1-Cl2	91.58(12)
N1-Pt1-S1	89.9(3)		

Table S3. Hydrogen bond geometry for *cis*-[Pt(1,7-Phen)(DMSO)Cl₂] in crystal packing.

D-H...A	D-H/Å	H...A/Å	D...A/Å	D-H...A/°	Symmetry code
C1-H1...Cl2	0.93	2.810	3.701(13)	161	-x,1-y,2-z
C6-H6...Cl1	0.93	2.927	3.75(1)	148	-
C8-H13A...Cl1	0.96	2.936	3.88(2)	167	-
C7-H7...O1	0.93	2.560	3.46(2)	118	1-x,-y,1-z

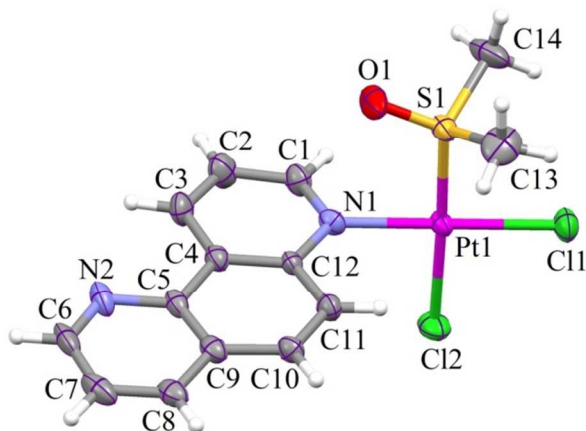


Figure S1. Fragment of the crystal structure of *cis*-[Pt(1,7-Phen)(DMSO)Cl₂]. Thermal ellipsoids are at the 40% probability level.

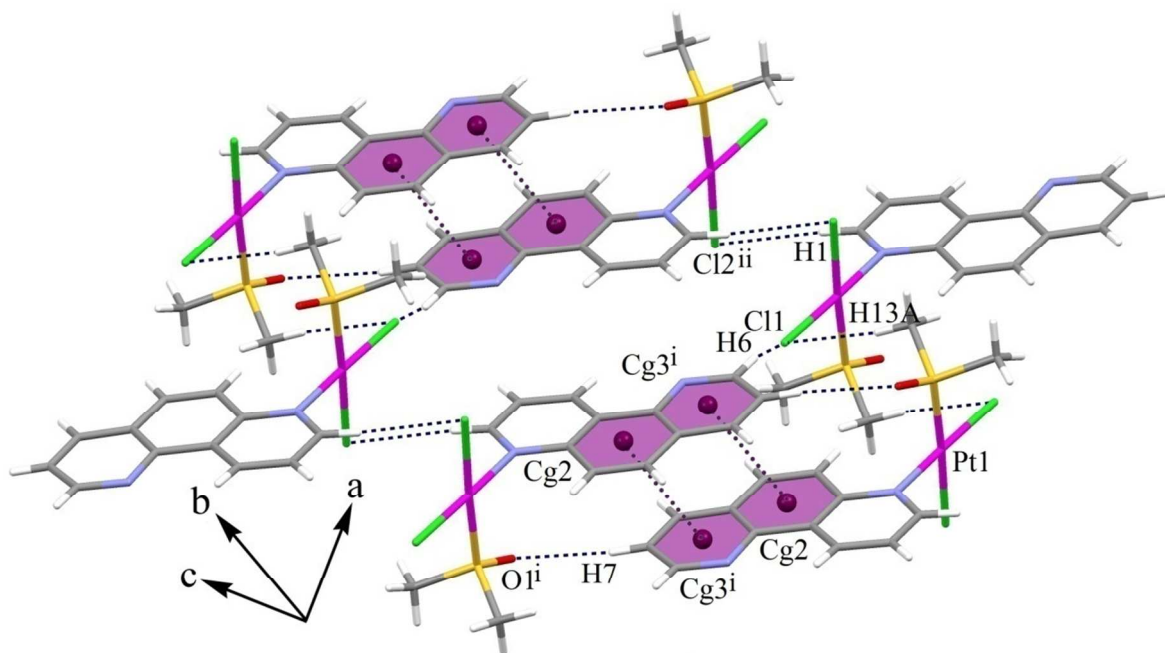
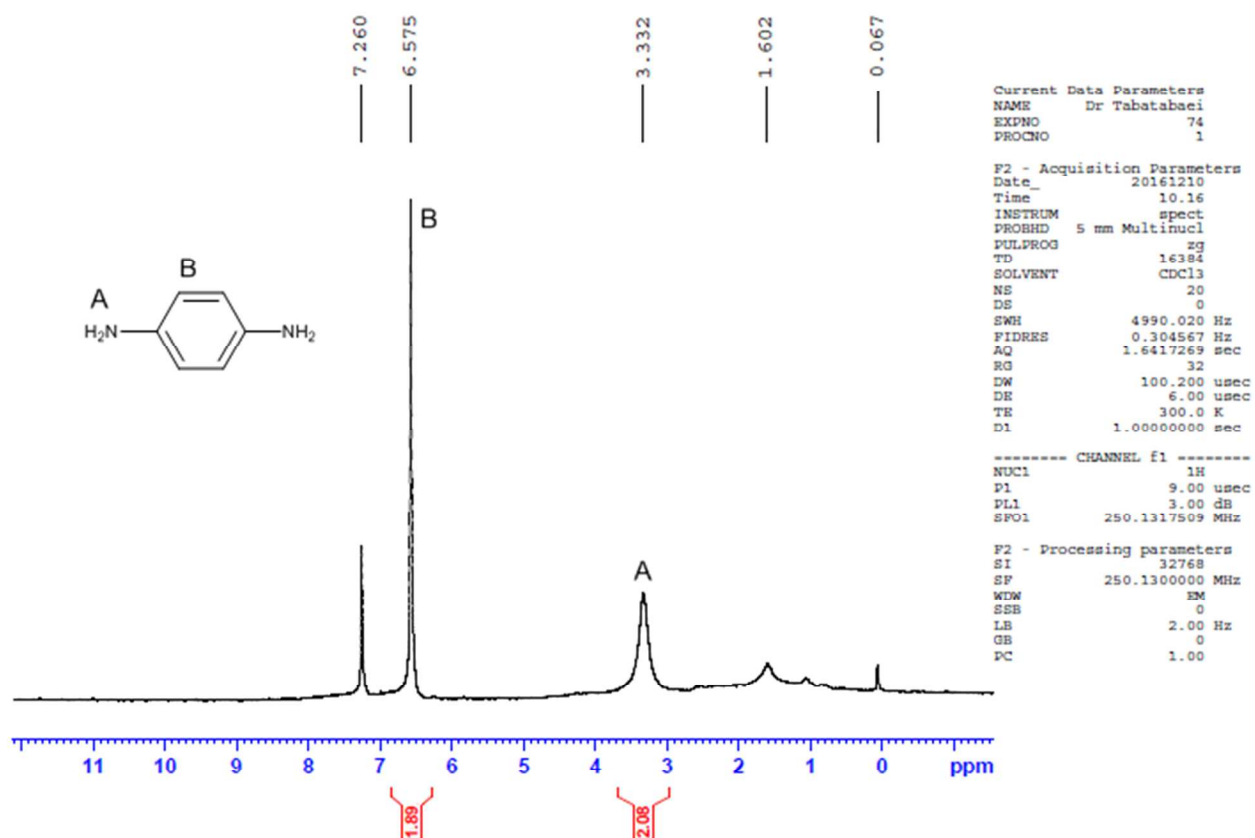
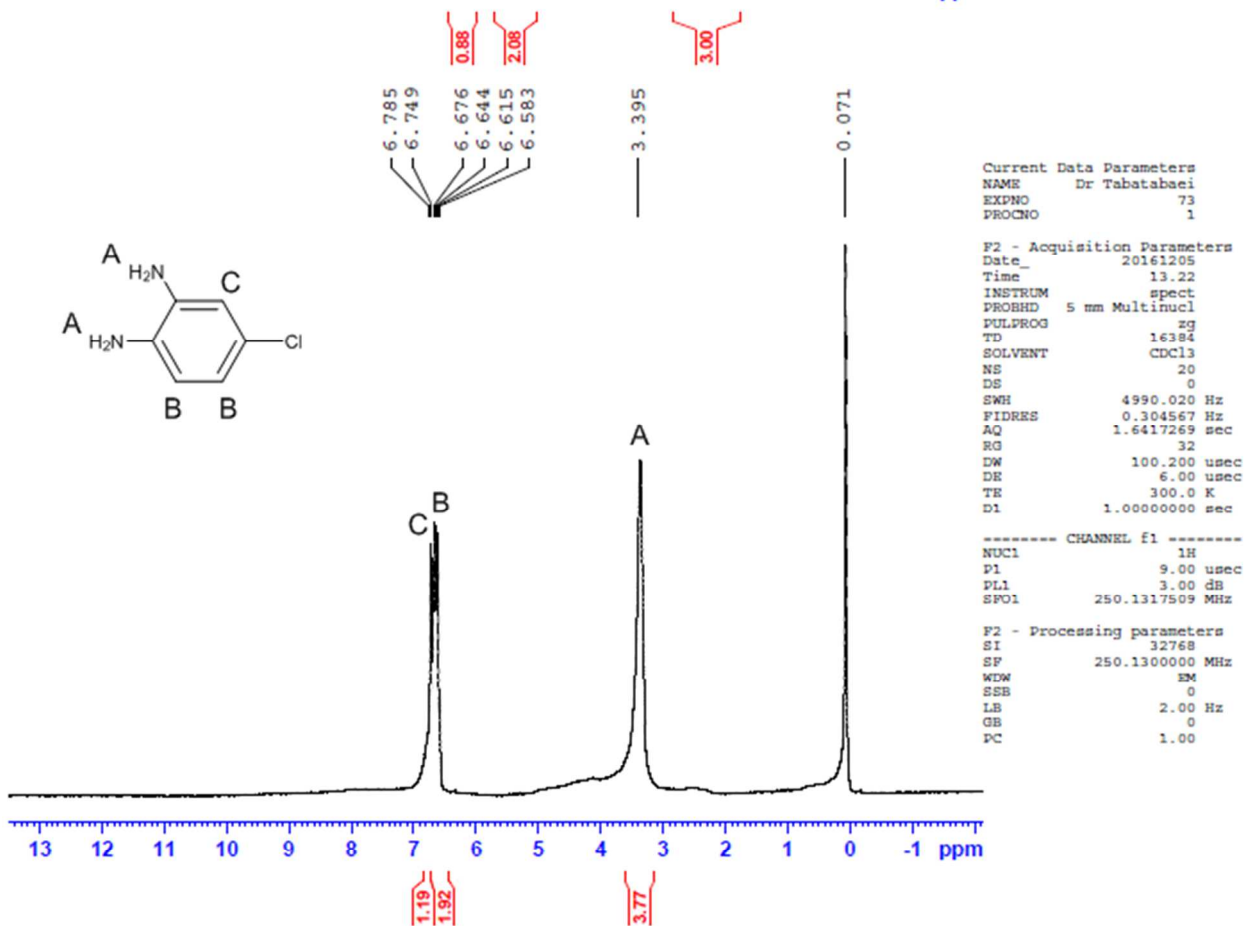
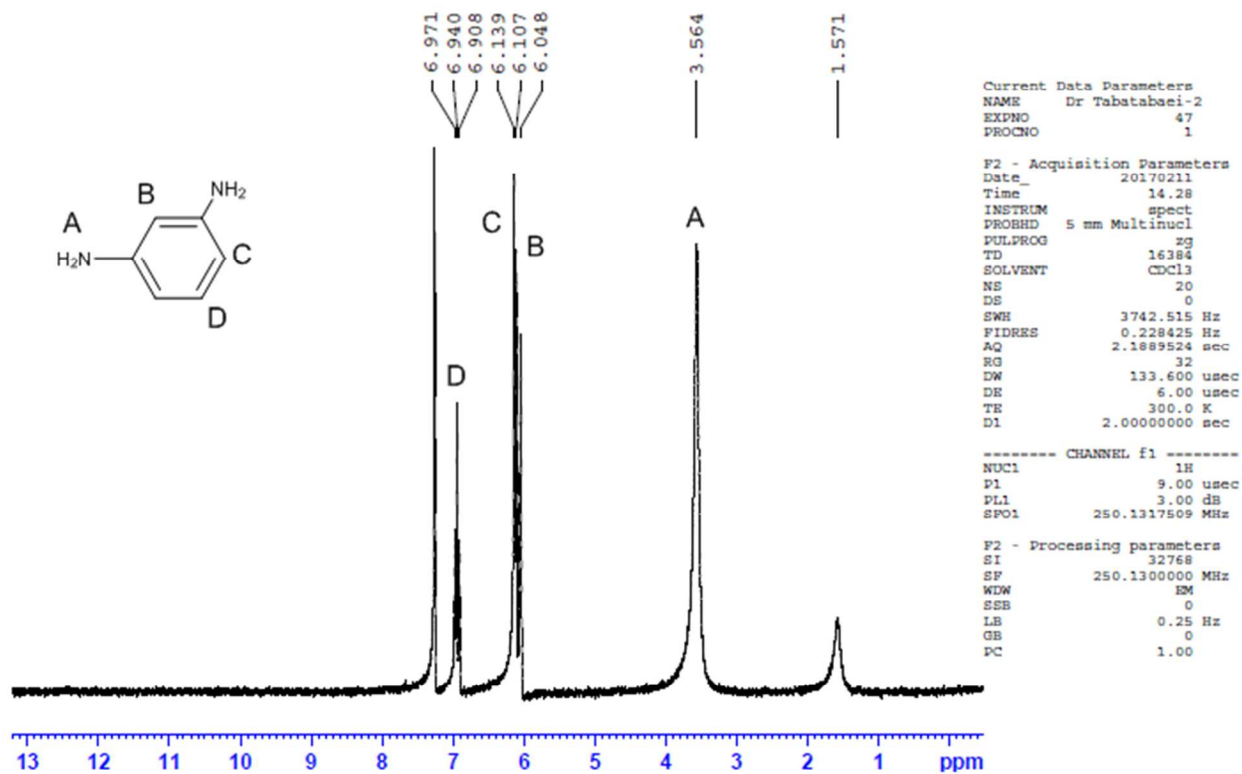
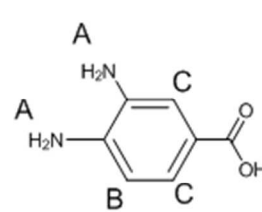
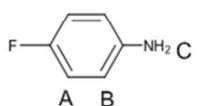


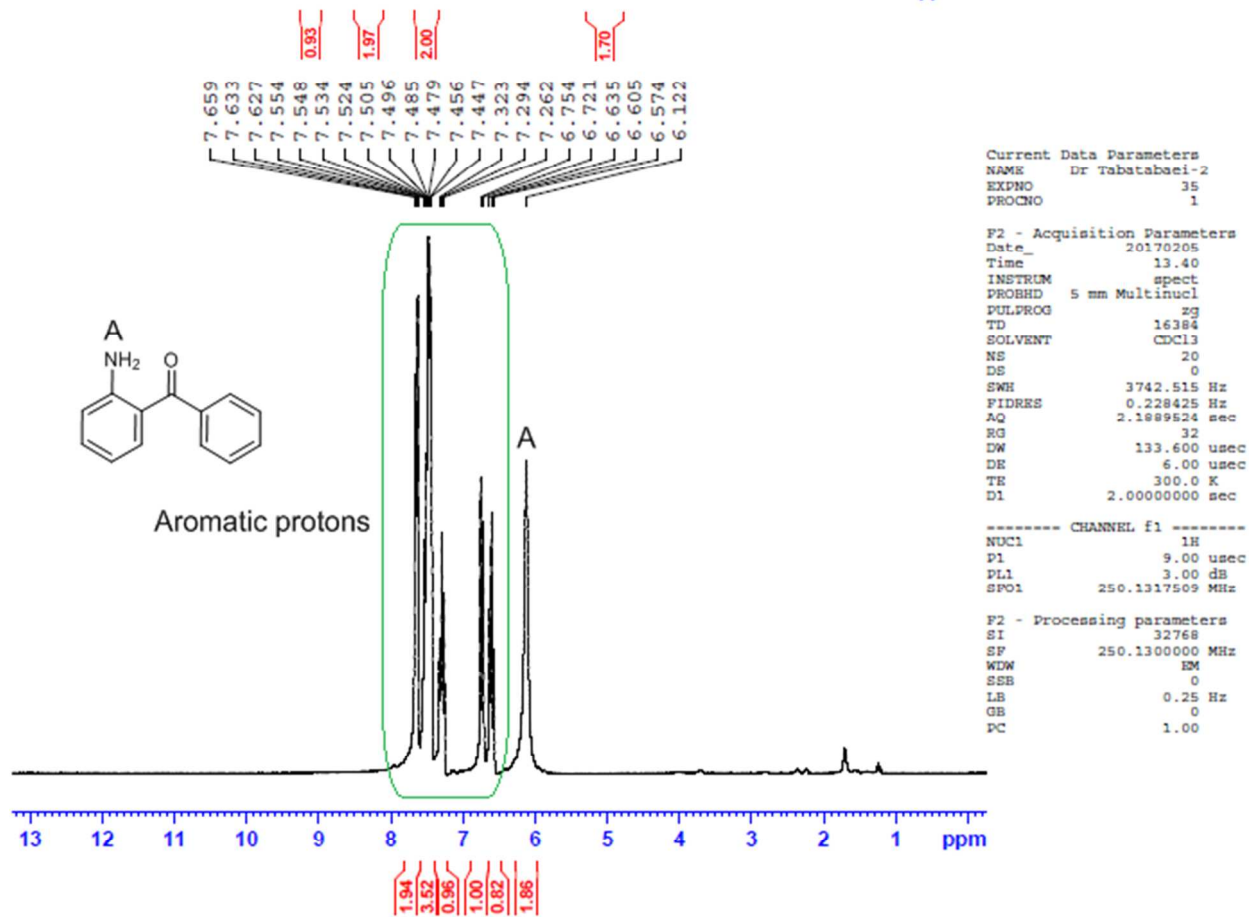
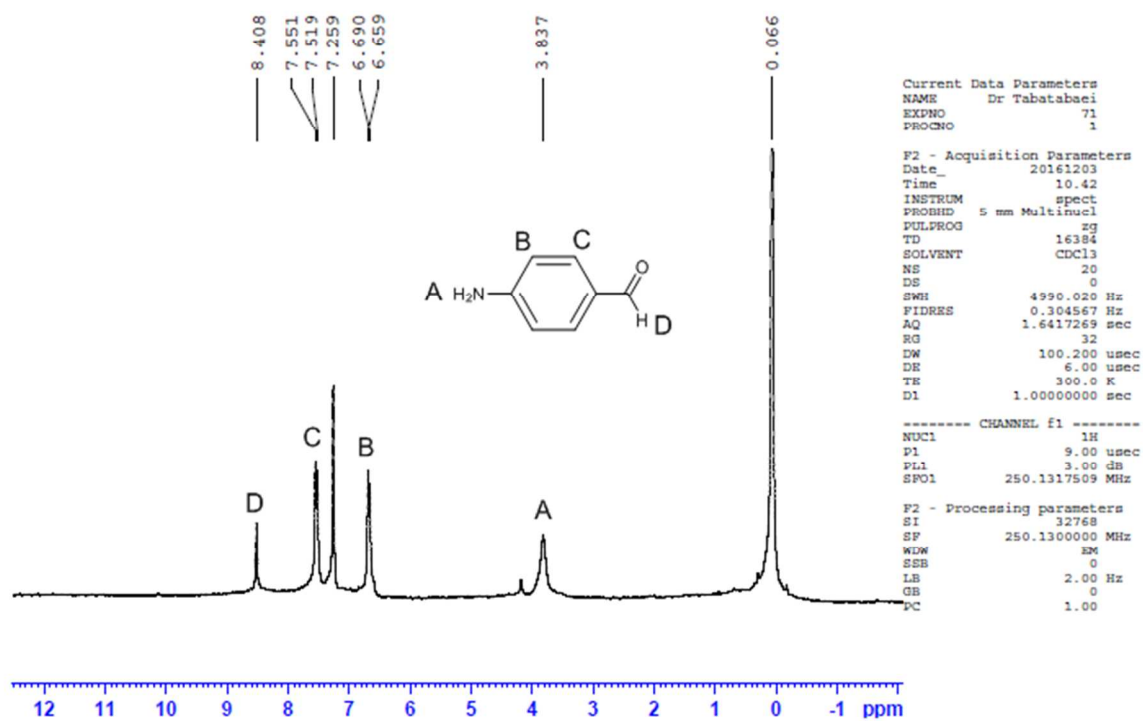
Figure S2. Crystal packing diagram for *cis*-[Pt(1,7-Phen)(DMSO)Cl₂]. Intermolecular C-H...Cl and C-H...O hydrogen bonds and $\pi \dots \pi$ contacts are shown as dashed lines. Symmetry codes: (i) 1-x, -y, 1-z; (ii) -x, 1-y, 2-z.

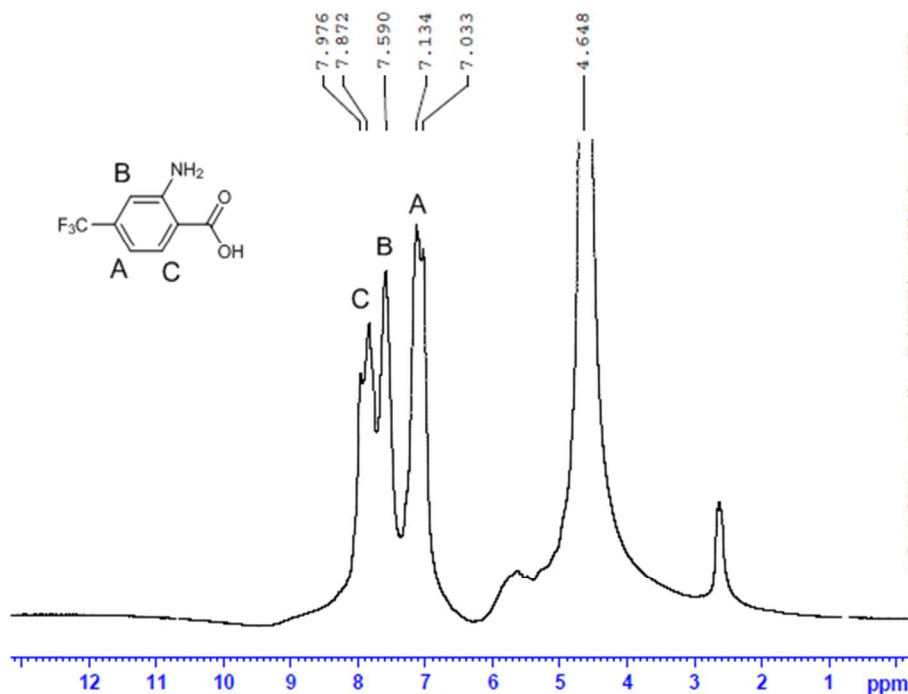
^1H -NMR spectra of the amine products obtained from the catalytic reduction of nitro- and nitrile-substrates: (The catalytic process performance was directed by GC (Agilent 7890A series) equipped with a FID detector and a HP-5 column (30 mm×0.32 mm×0.25 μm).









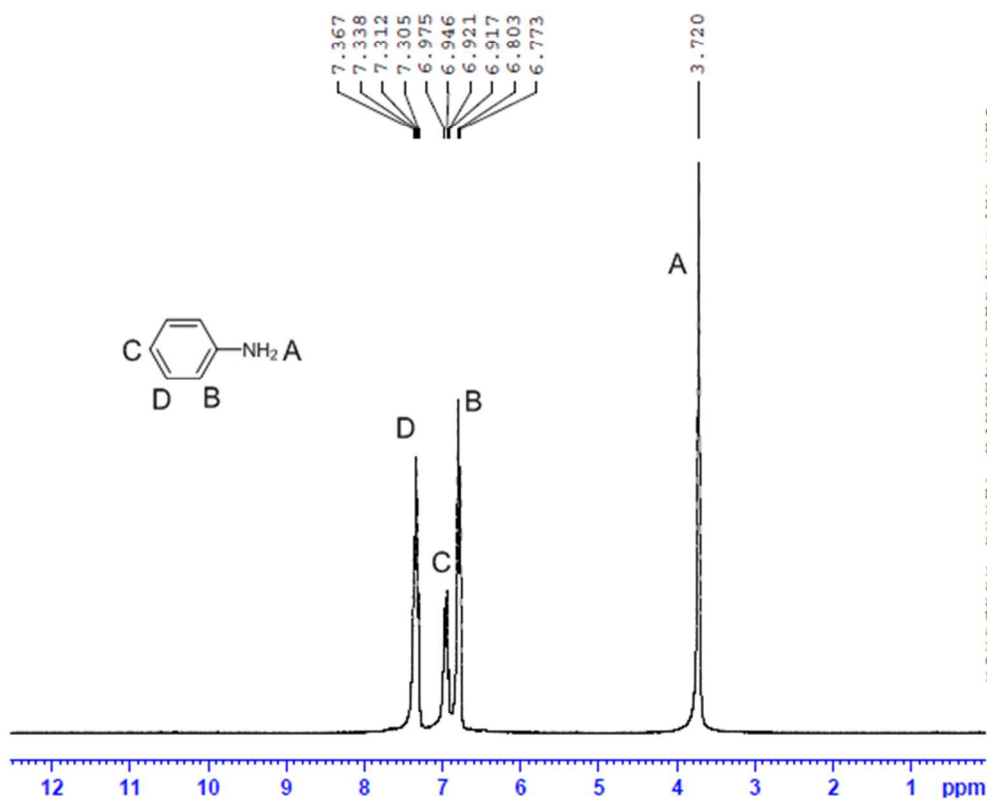


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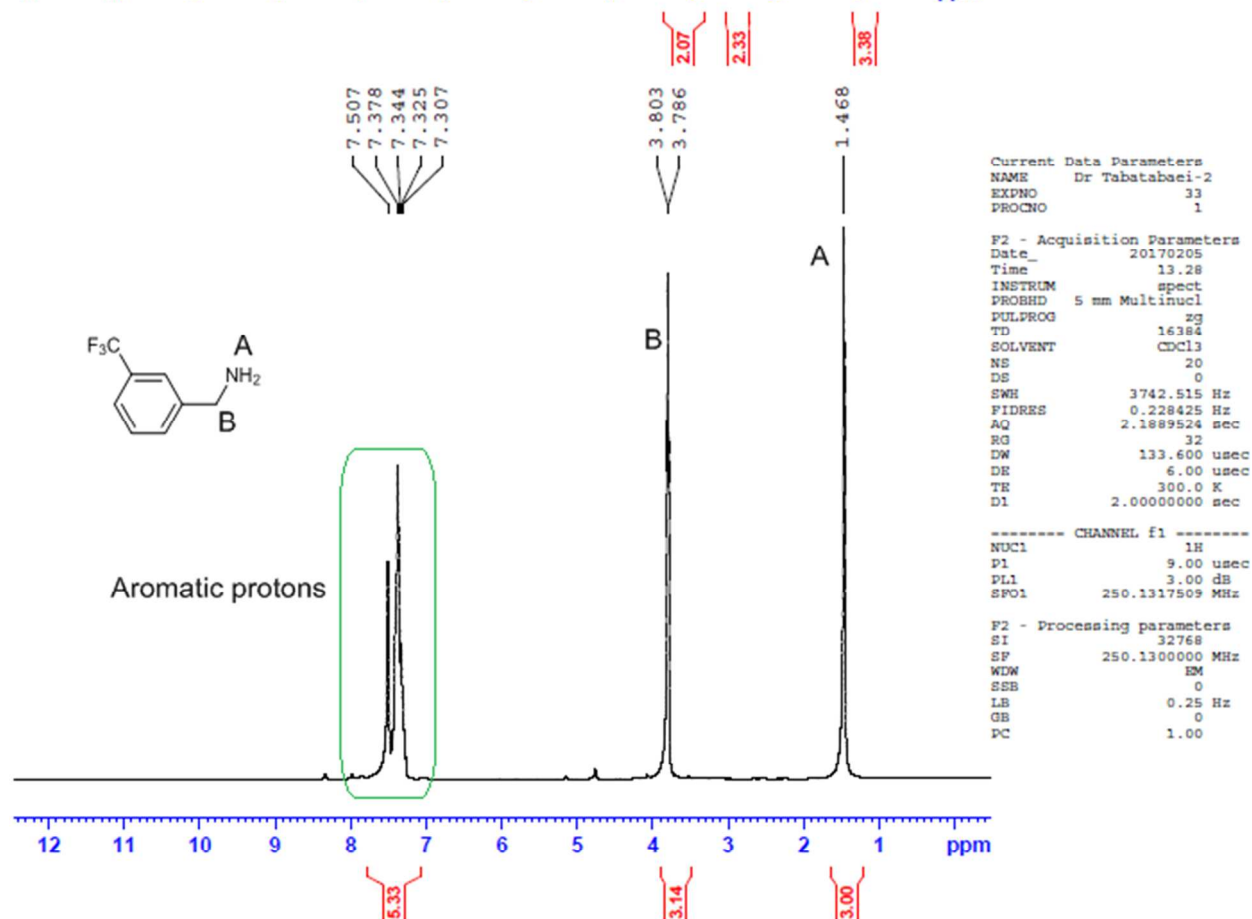
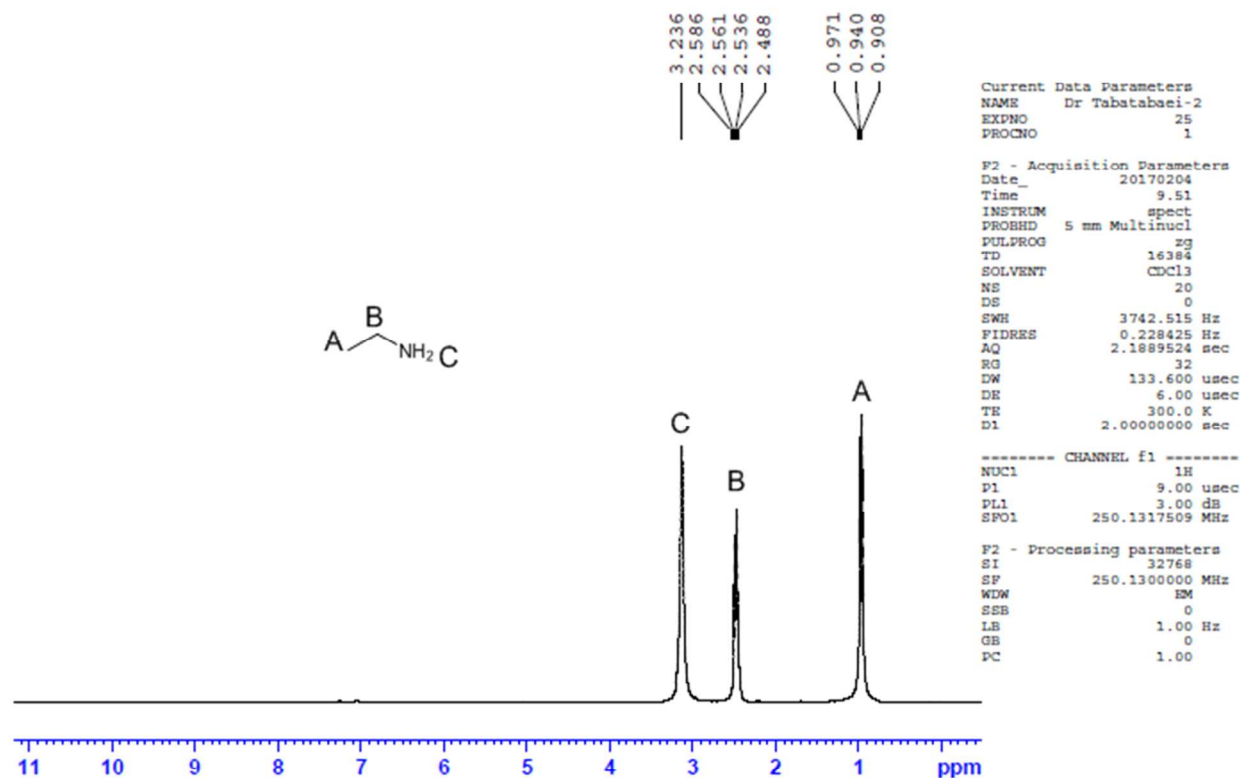


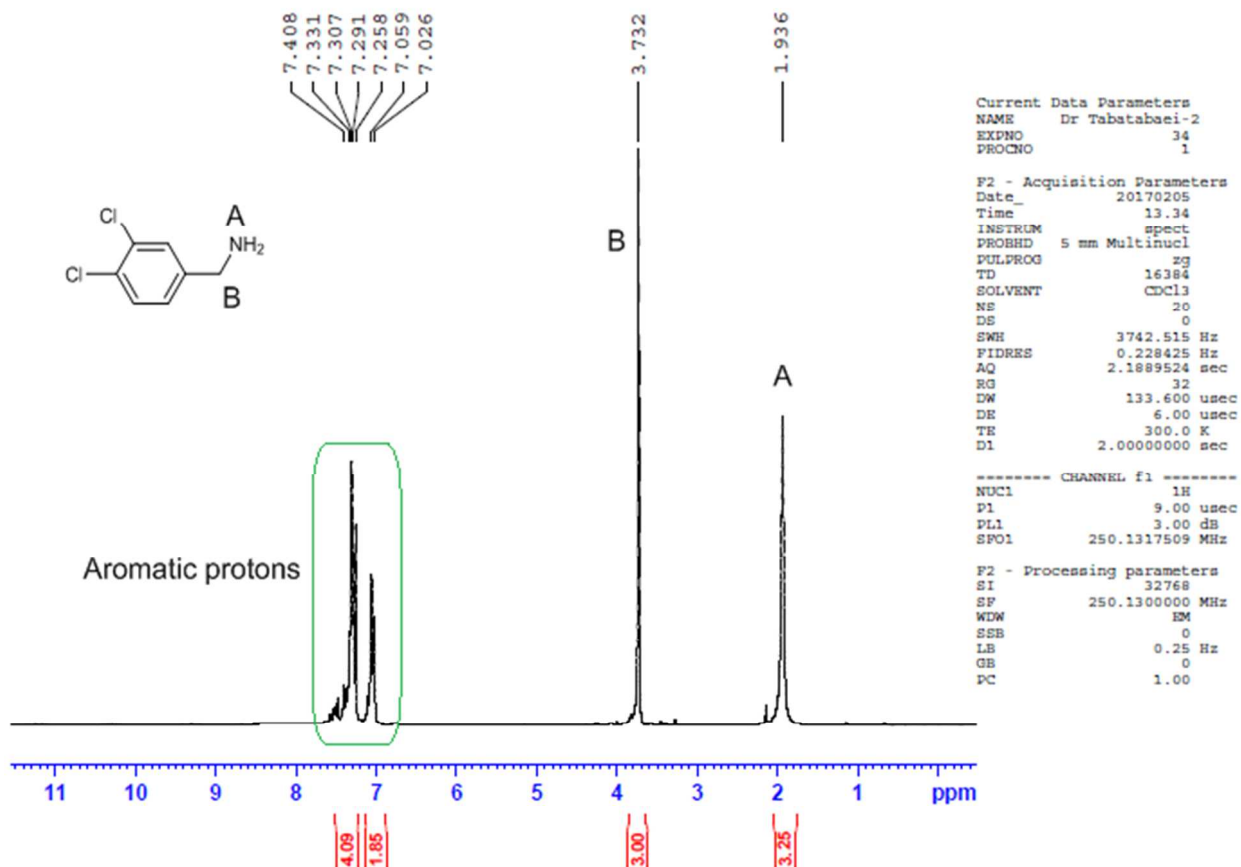
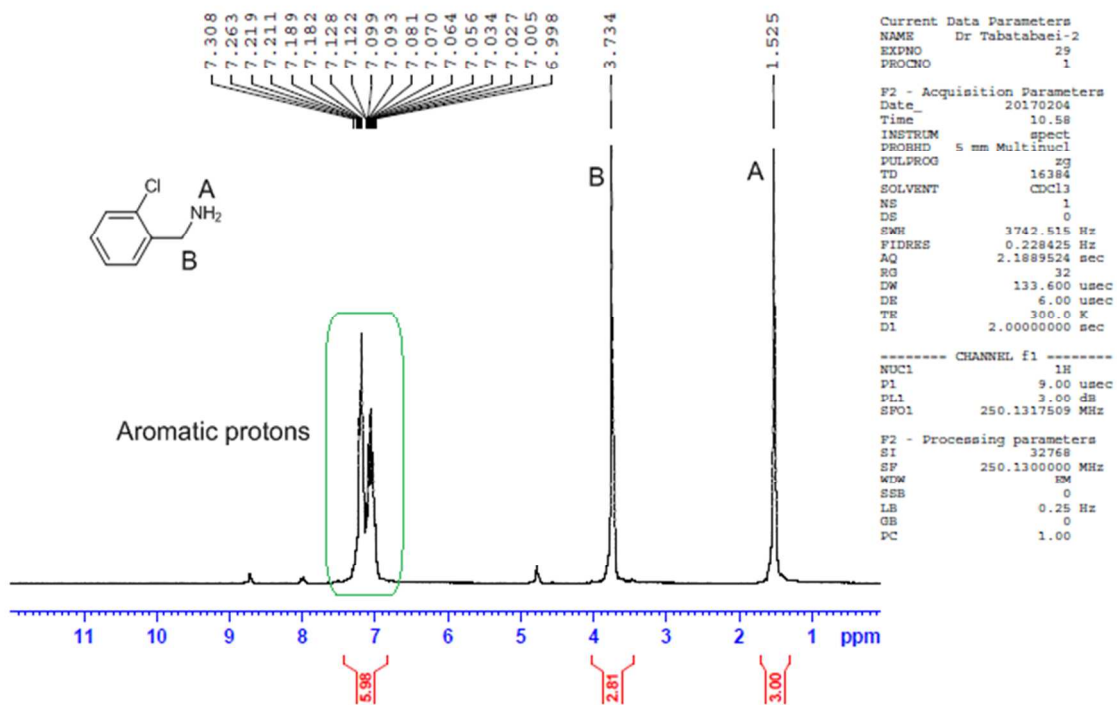
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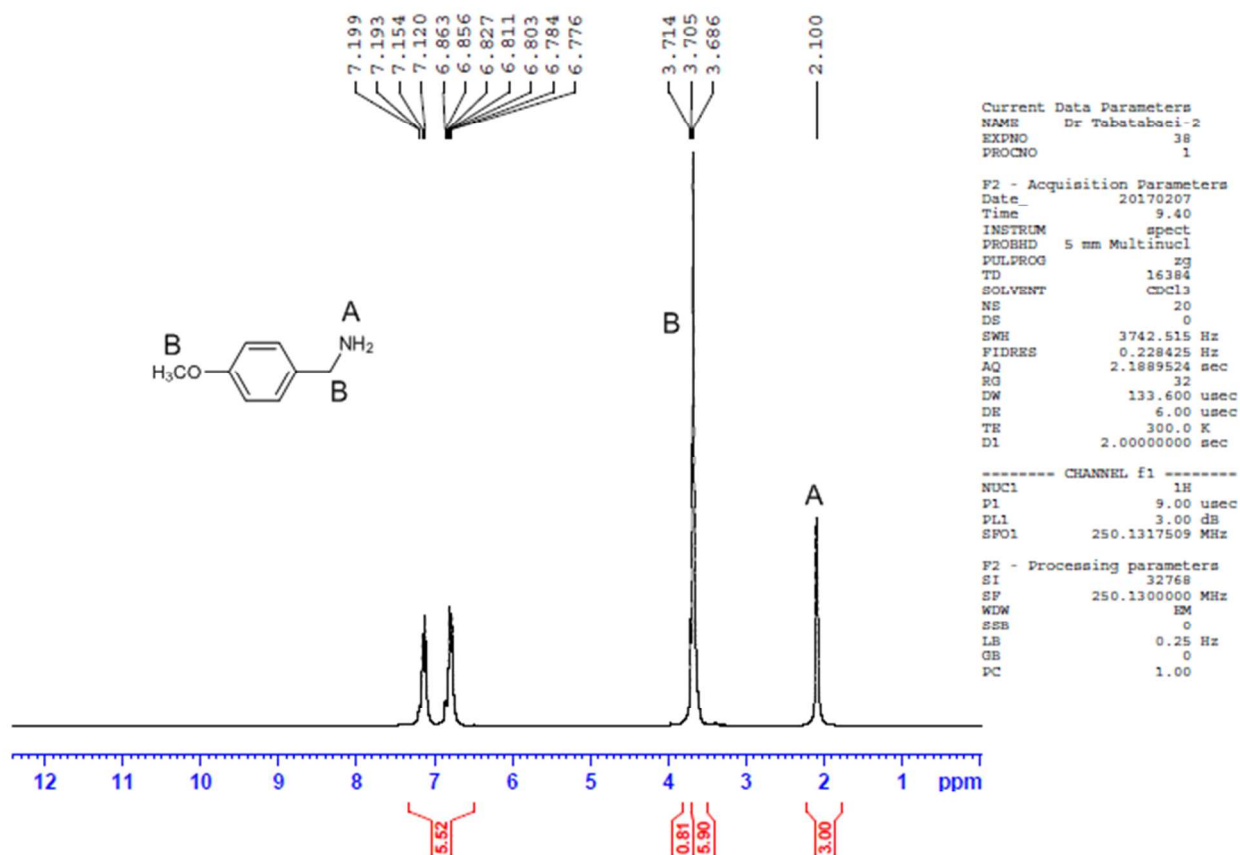
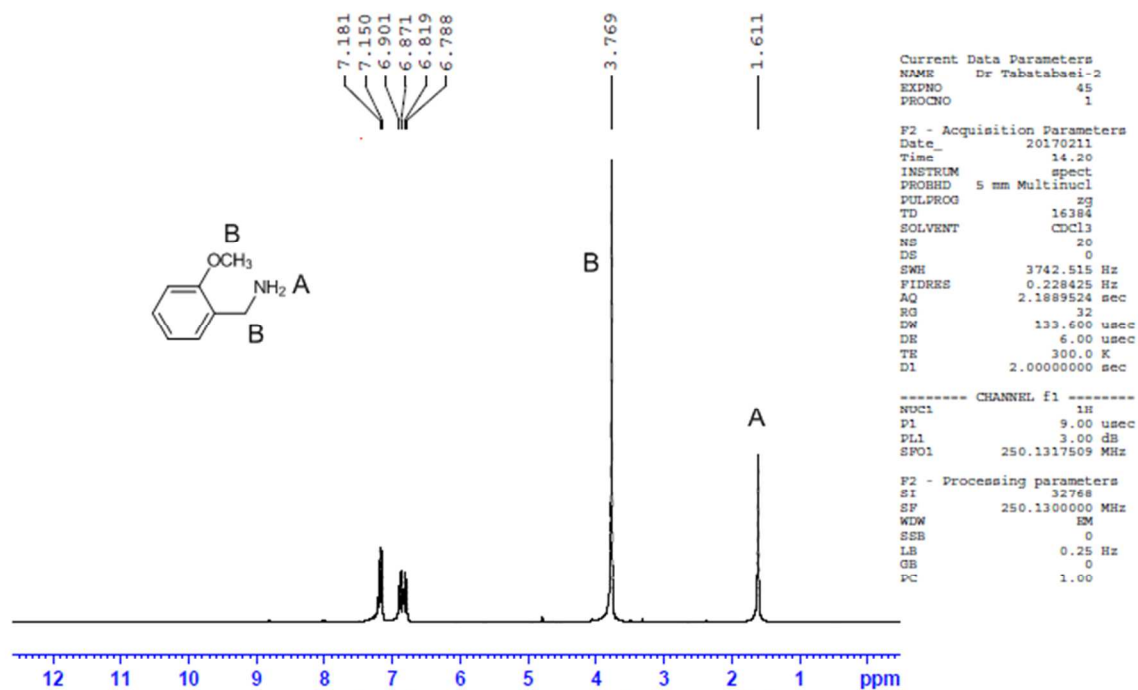
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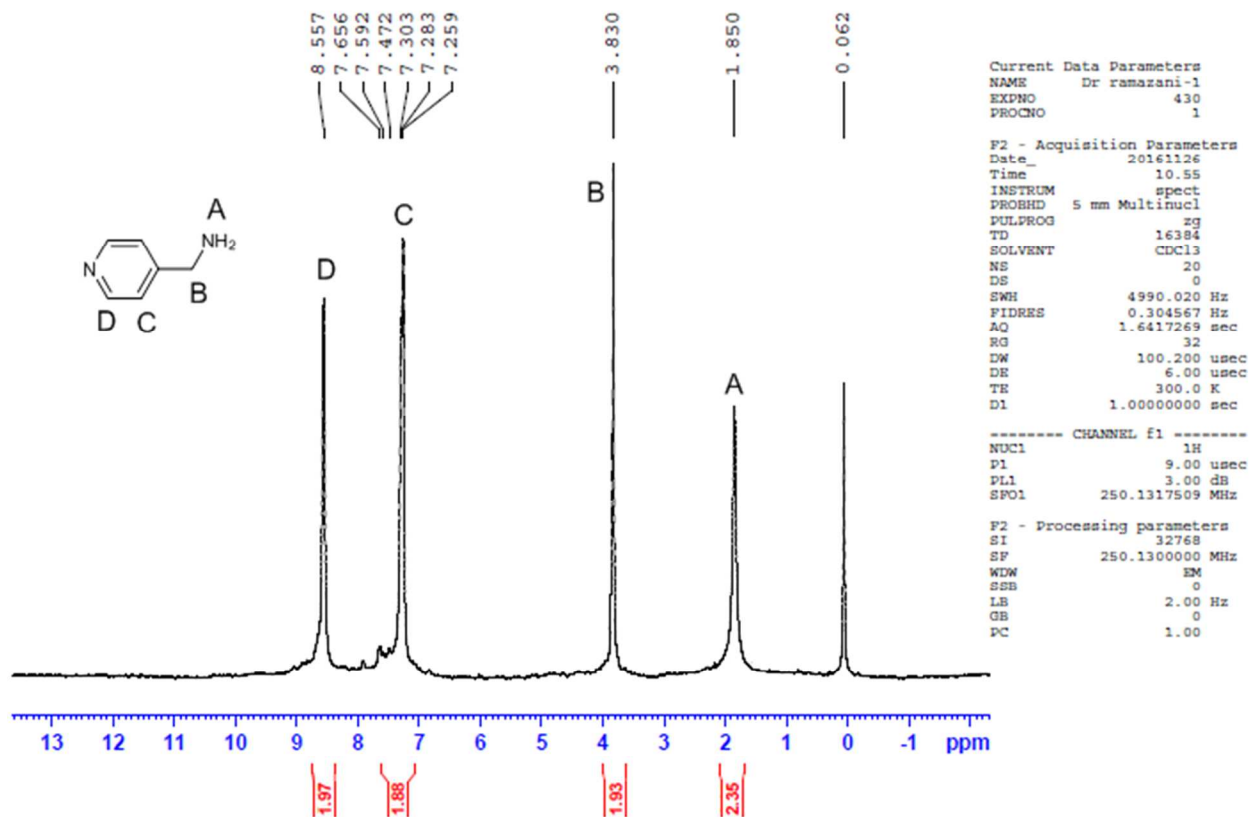
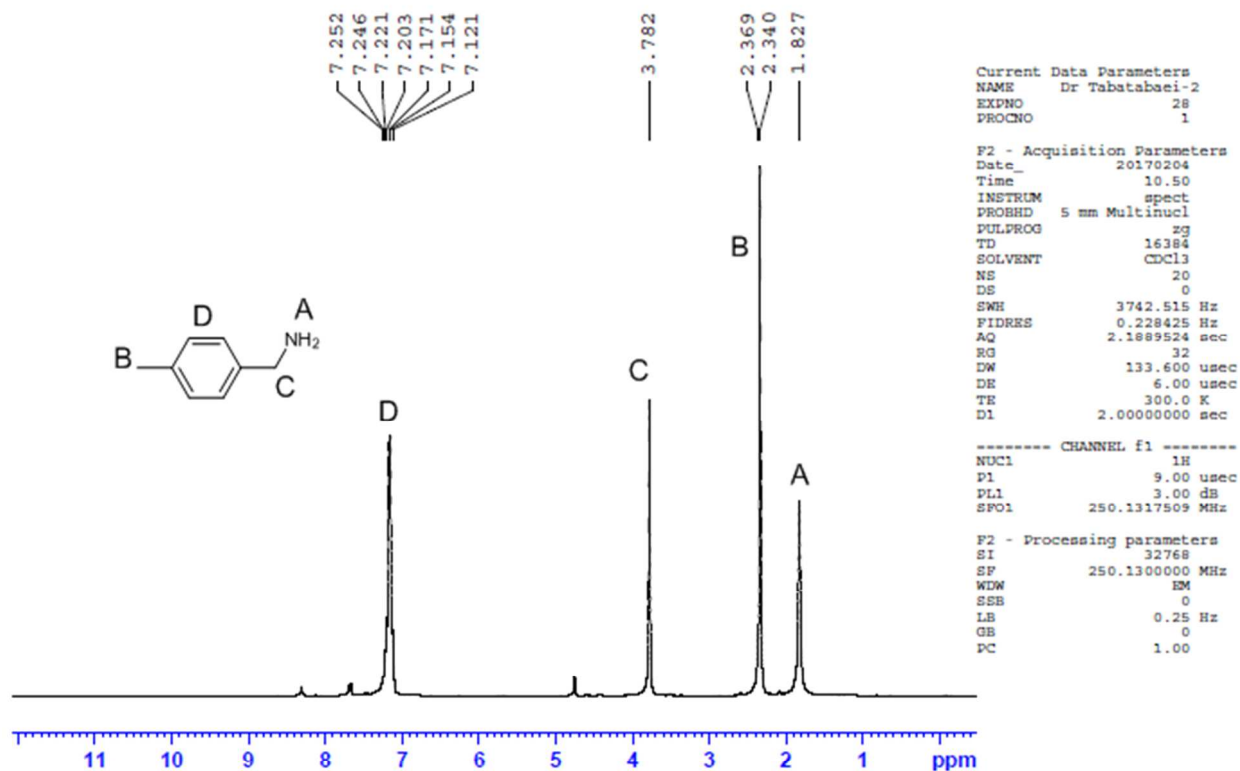
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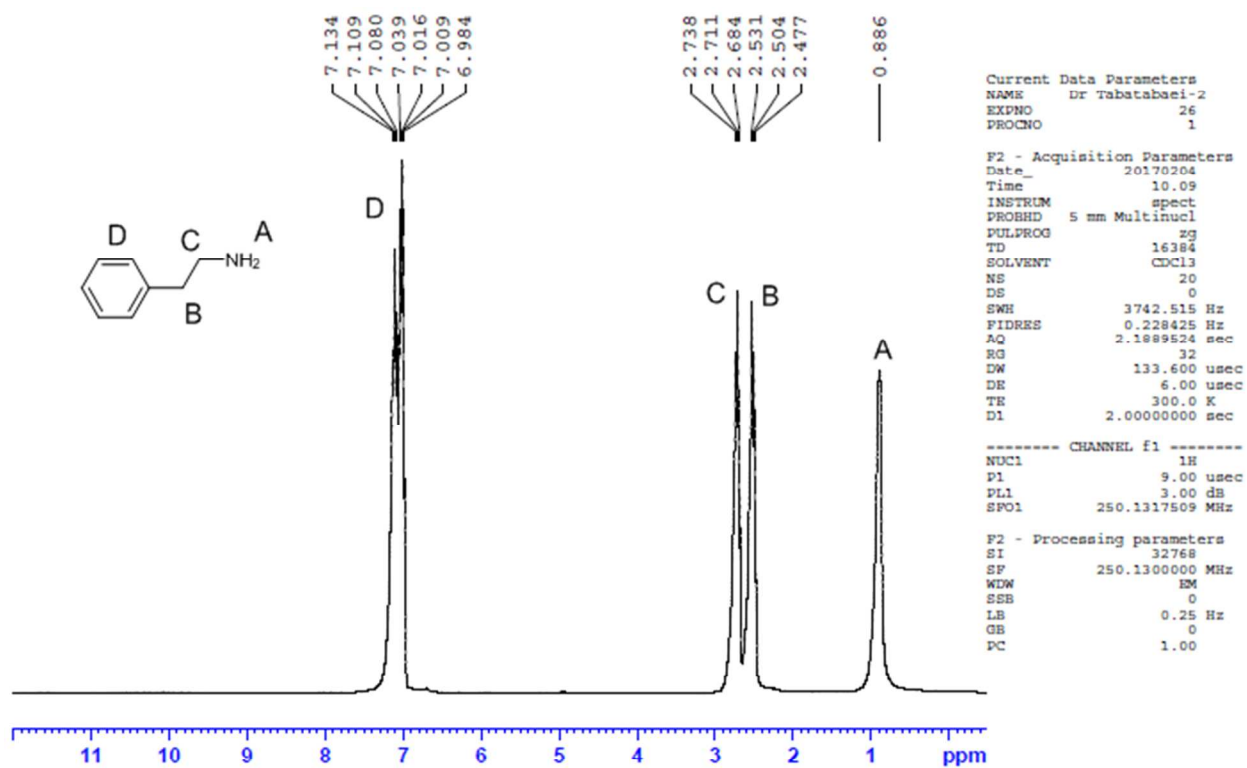
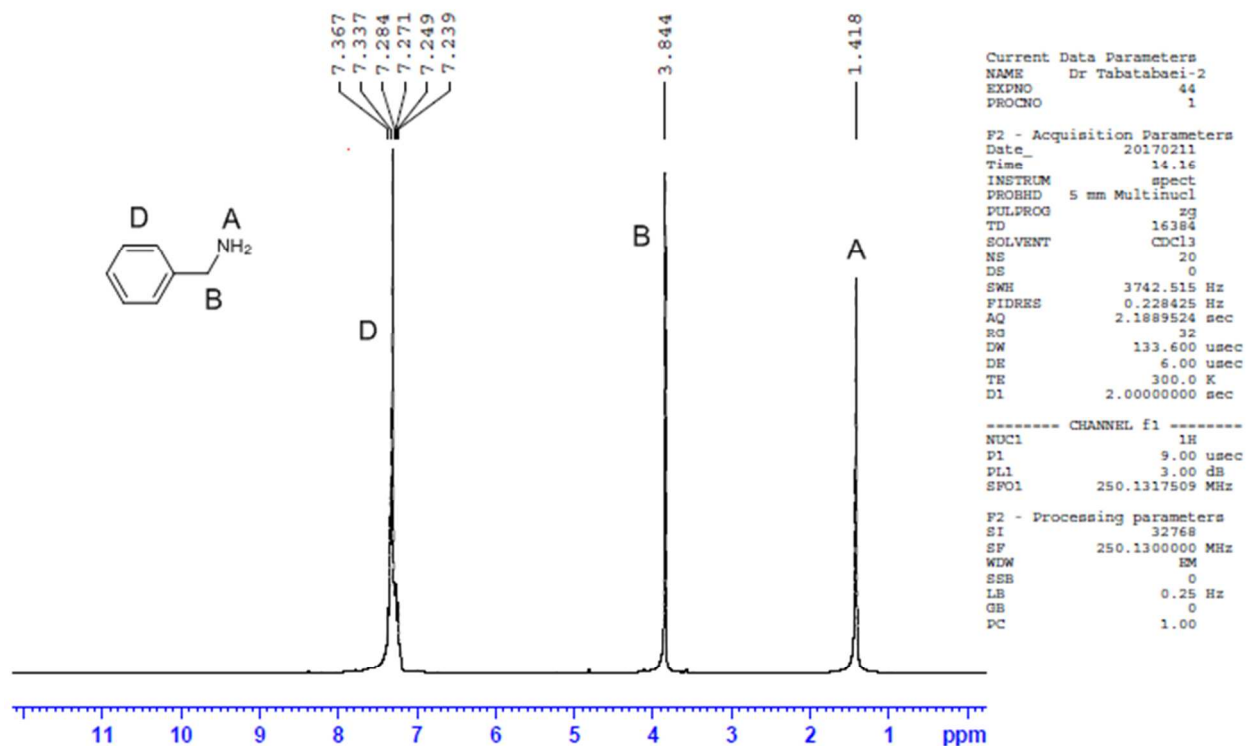
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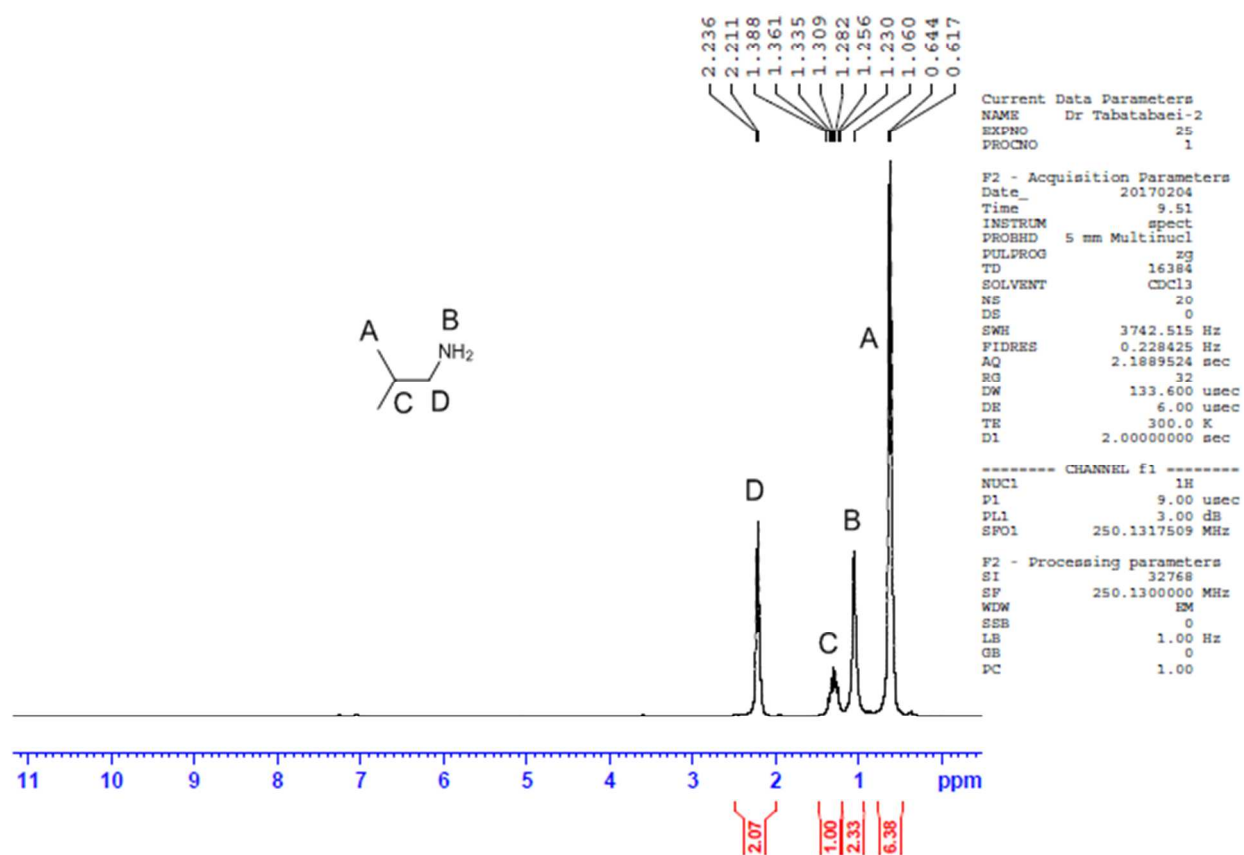












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