Supporting Information

Facile reduction of aromatic nitro compounds to aromatic amines catalysed by support-free nanoporous silver

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Preparation of Catalyst. $Al_{75}Ag_{25}$ (at.%) alloy was prepared by melting pure Al (99.9 wt.%) and pure Ag (99.95 wt.%) in a quartz crucible using a high frequency induction furnace in argon atmosphere. Using a single roller melt-spinning apparatus, the alloy ingots were remelted in a quartz tube by high-frequency induction heating and then rapidly solidified onto a copper roller at a circumferential speed of 18 m s^{-1}. The ribbons obtained were normally 20-50 mm in thickness, 2-5 mm in width and several centimeters in length. Sodium hydroxide solution (10 wt %) was used to etch the aluminum in the Al-Ag alloy at room temperature for 24 h.

Experimental Section. The reduction of 4-NP was given as a representative example. Reactions were performed using catalyst 0.05 mmol, 4-NP 20 mM and $NaBH_4$ 500 mM in 10 mL aqueous solution at room temperature. Ultraviolet and visible (UV/Vis) spectrophotometer was used to analyze the reaction process. When the reaction was finished, the reaction mixture was concentrated by rotary evaporation. And the residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (60~90 ^{o}C) (1:1) as eluent to give 4-AP. The recovered catalyst was washed with ethanol and water and reused without further purification.

Scanning electron microscope (SEM) observation was carried out using a JEOL JSM-6700F instrument operated at an accelerating voltage of 3.0 kV.

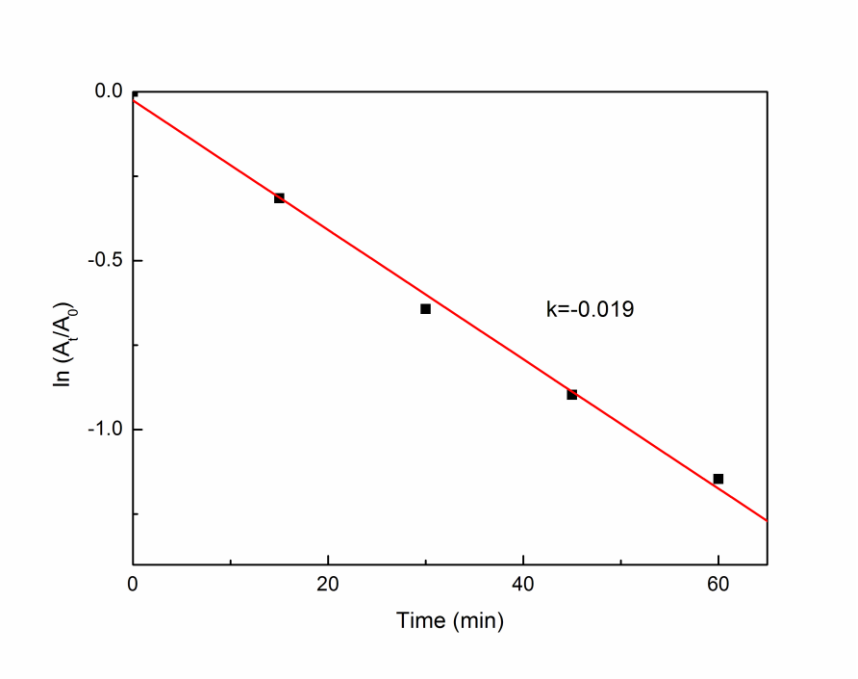


Figure. S1 Plot of $\ln(A_t/A_0)$ versus time for the reduction of 4-nitrophenol over np-Ag-Mg

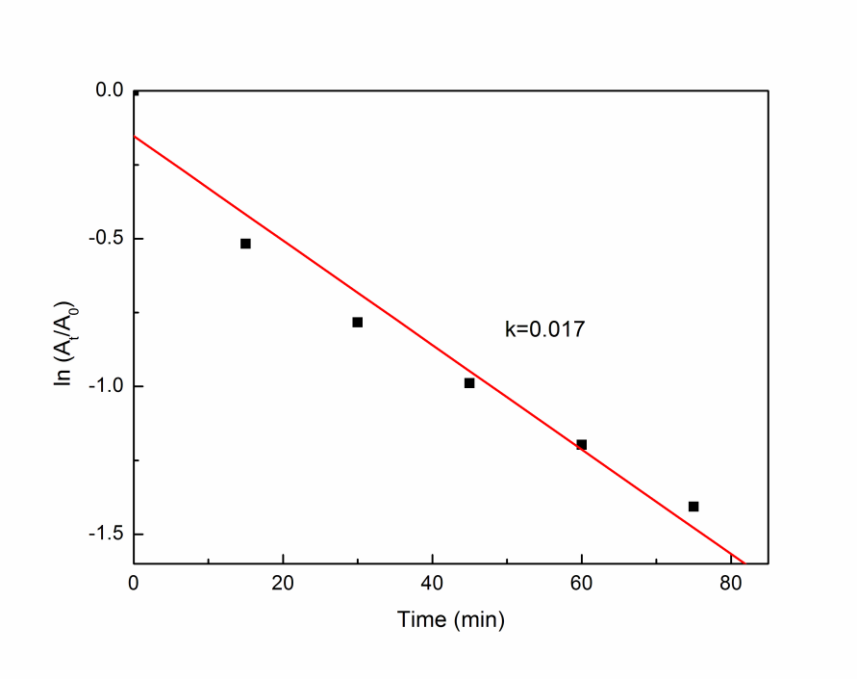


Figure. S2 Plot of $\ln(A_t/A_0)$ versus time for the reduction of 4-nitrophenol over np-Cu

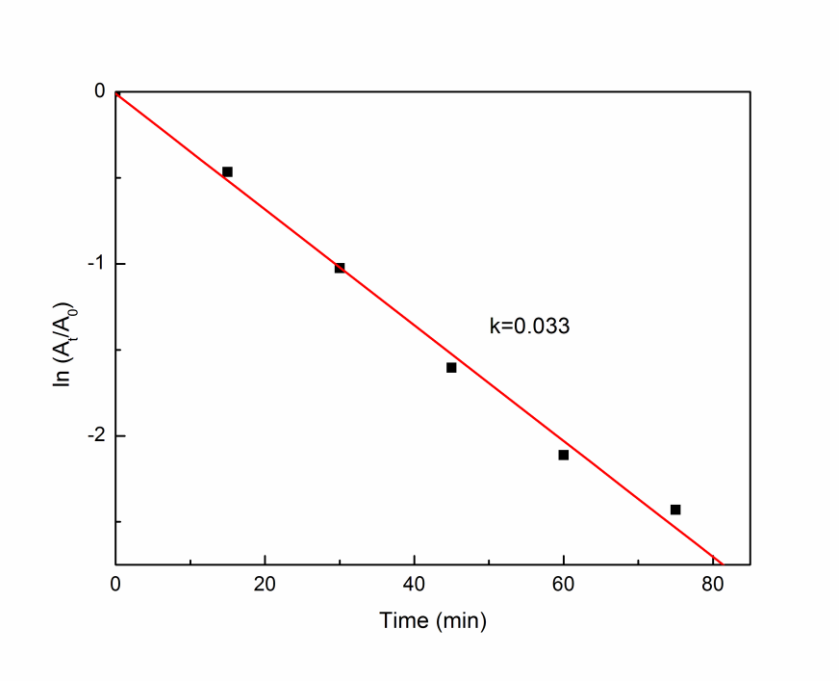


Figure. S3 Plot of ln(A_t/A_0) versus time for the reduction of 4-nitrophenol over np-Pd

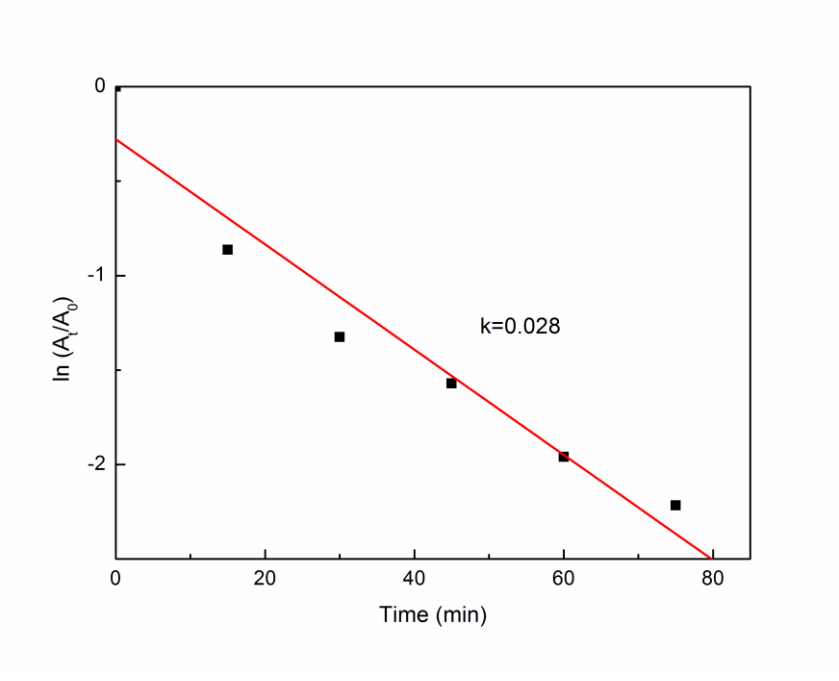


Figure. S4 Plot of ln(A_t/A_0) versus time for the reduction of 4-nitrophenol over np-Au

The calculation of the TOF:

The BET result of np-Ag-Mg was 14 m^2/g,

$$\text{TON} = \frac{Product\ Molecules}{Active\ Sites} = \frac{0.2 \times 10^{-3}\ mol\ \times\ 6.022\ \times\ 10^{23}\ mol^{-1}}{14\ m^2/g\ \times\ 5\ \times\ 10^{-3} g \times\ 1.4\ \times\ 10^{19}\ atom/m^2}$$

$$= 123$$

$$\text{TOF} = \frac{TON}{Reaction\ time} = \frac{123}{120\ min} = 1.02\ min^{-1}$$

The BET result of np-Pd was 40 m^2/g

$$\text{TON} = \frac{Product\ Molecules}{Active\ Sites} = \frac{0.2 \times 10^{-3}\ mol\ \times\ 6.022\ \times\ 10^{23}\ mol^{-1}}{40\ m^2/g\ \times\ 5\ \times\ 10^{-3} g \times\ 1.4\ \times\ 10^{19}\ atom/m^2}$$

$$= 43$$

$$\text{TOF} = \frac{TON}{Reaction\ time} = \frac{43}{90\ min} = 0.48\ min^{-1}$$

The BET result of np-Au was 8 m^2/g

$$\text{TON} = \frac{Product\ Molecules}{Active\ Sites} = \frac{0.2 \times 10^{-3}\ mol\ \times\ 6.022\ \times\ 10^{23}\ mol^{-1}}{8\ m^2/g\ \times\ 0.01\ g \times\ 1.4\ \times\ 10^{19}\ atom/m^2}$$

$$= 108$$

$$\text{TOF} = \frac{TON}{Reaction\ time} = \frac{108}{105\ min} = 1.03\ min^{-1}$$

The BET result of np-Cu was 10 m^2/g,

$$\text{TON} = \frac{Product\ Molecules}{Active\ Sites}$$

$$= \frac{0.2 \times 10^{-3}\ mol\ \times\ 6.022\ \times\ 10^{23}\ mol^{-1}}{15\ m^2/g\ \times\ 3.2\ \times\ 10^{-3} g \times\ 1.4\ \times\ 10^{19}\ atom/m^2} = 178$$

$$\text{TOF} = \frac{TON}{Reaction\ time} = \frac{178}{150\ min} = 1.19\ min^{-1}$$

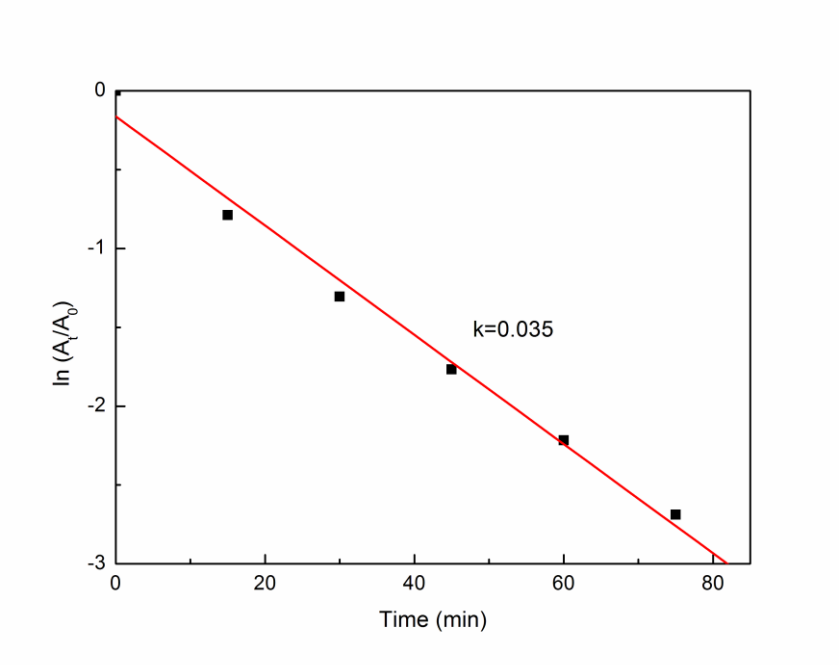


Figure. S5 Plot of $\ln(A_t/A_0)$ versus time for the reduction of 4-nitrophenol over np-Ag with C_{NaBH4}=200 mM.

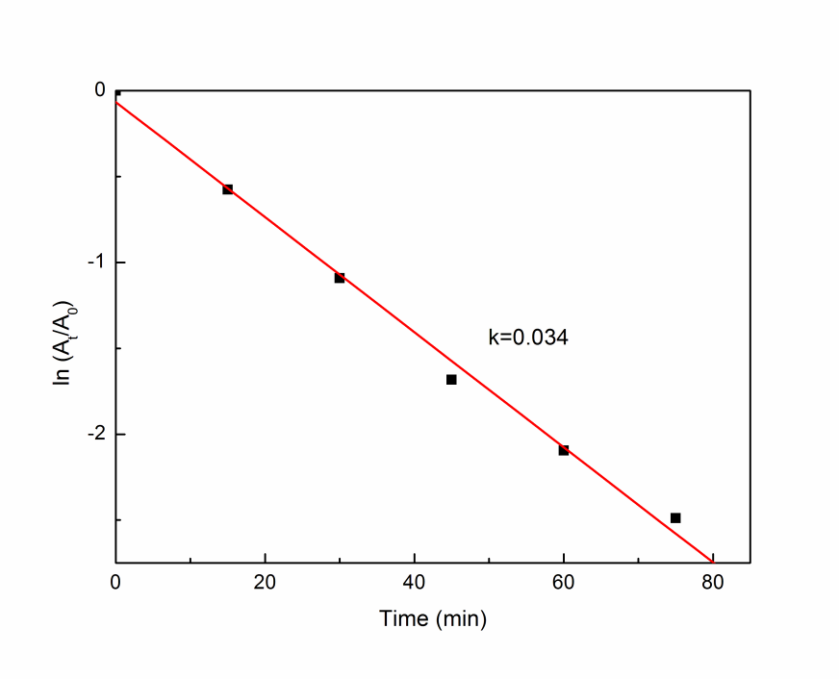


Figure. S6 Plot of $\ln(A_t/A_0)$ versus time for the reduction of 4-nitrophenol over np-Ag with C_{NaBH4}=1000 mM.

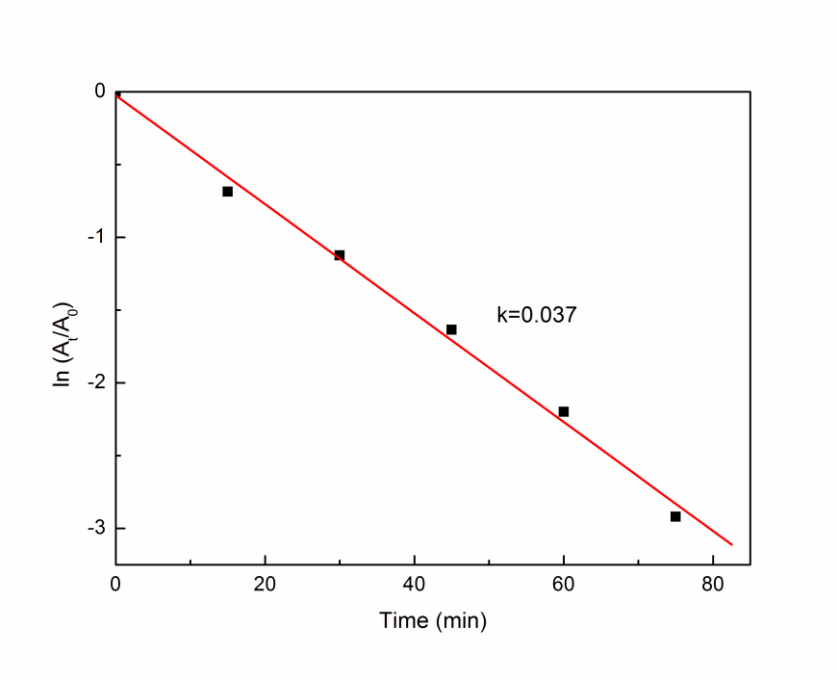


Figure. S7 Plot of $\ln(A_t/A_0)$ versus time for the reduction of 4-nitrophenol over np-Ag with C_{NaBH4}=2000 mM.

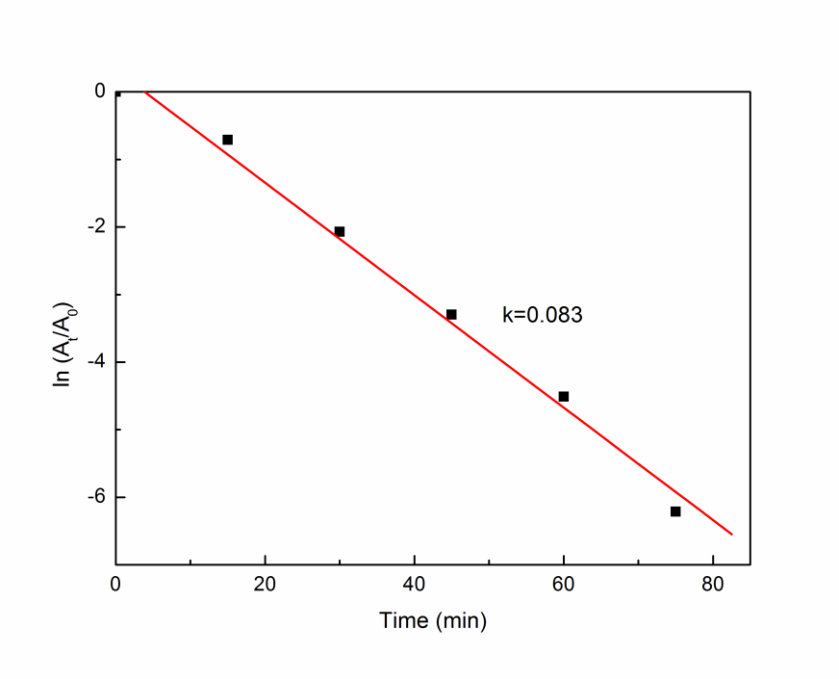


Figure. S8 Plot of $\ln(A_t/A_0)$ versus time for the reduction of 4-nitrophenol over np-Ag with $C_{4\text{-NP}}$=10 mM.

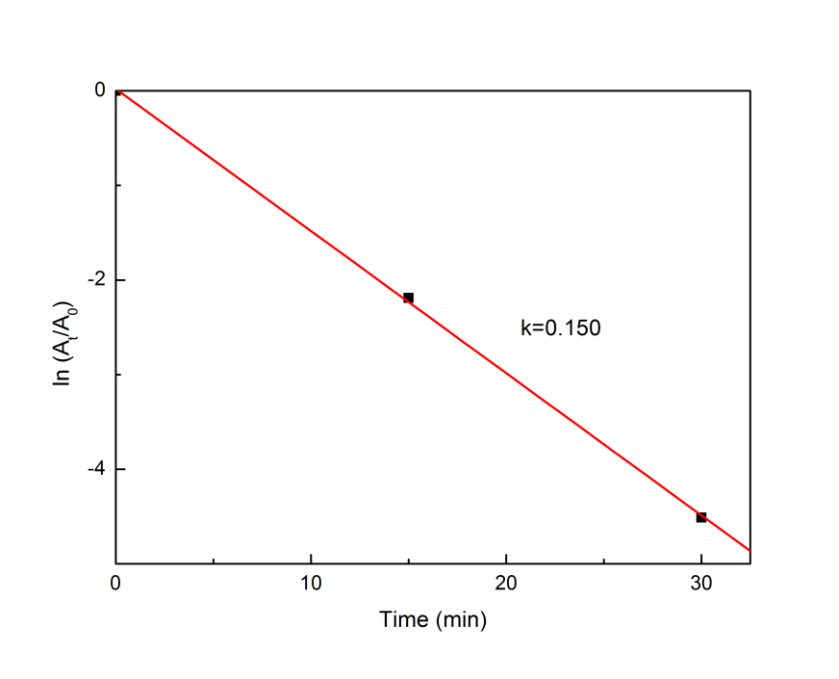


Figure. S9 Plot of $\ln(A_t/A_0)$ versus time for the reduction of 4-nitrophenol over np-Ag with $C_{4\text{-NP}}$=5 mM.

NMR signals:

Aniline: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17-7.10 (m, 2H), 6.76-6.71 (m, 1H), 6.65-6.61 (m, 2H), 3.54 (s, 2H).

2-Aminophenol: ^{1}H NMR (300 MHz, d_6-DMSO) δ 8.90 (bs, 1H), 6.64-6.50 (m, 3H), 6.40-6.34 (m,1H), 4.45 (bs, 1H).

3-Aminophenol: ^{1}H NMR (300 MHz, d_6-DMSO) δ 8.80 (bs, 1H), 6.76 (t, J= 8.4 Hz, 1H), 6.00-5.97 (m, 2H), 5.925-5.90 (b, J=7.5 Hz, 1H), 4.87 (bs, 2H).

4-Aminophenol: ^{1}H NMR (300 MHz, d_6-DMSO) δ 8.33 (bs, 1H), 6.49-6.38 (m, 4H), 4.37 (bs, 1H).

o-Toluidine: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05-7.00 (m, 2H), 6.72-6.65 (m, 2H), 3.58 (bs, 2H), 2.16 (s, 3H).

m-Toluidine: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.02 (t, d, *J*=12 Hz, 1H), 6.56 (d, *J*=7.2 Hz, 1H), 6.45 (d, *J*=7.2 Hz, 2H), 3.50 (bs, 2H), 2.24 (s, 3H).

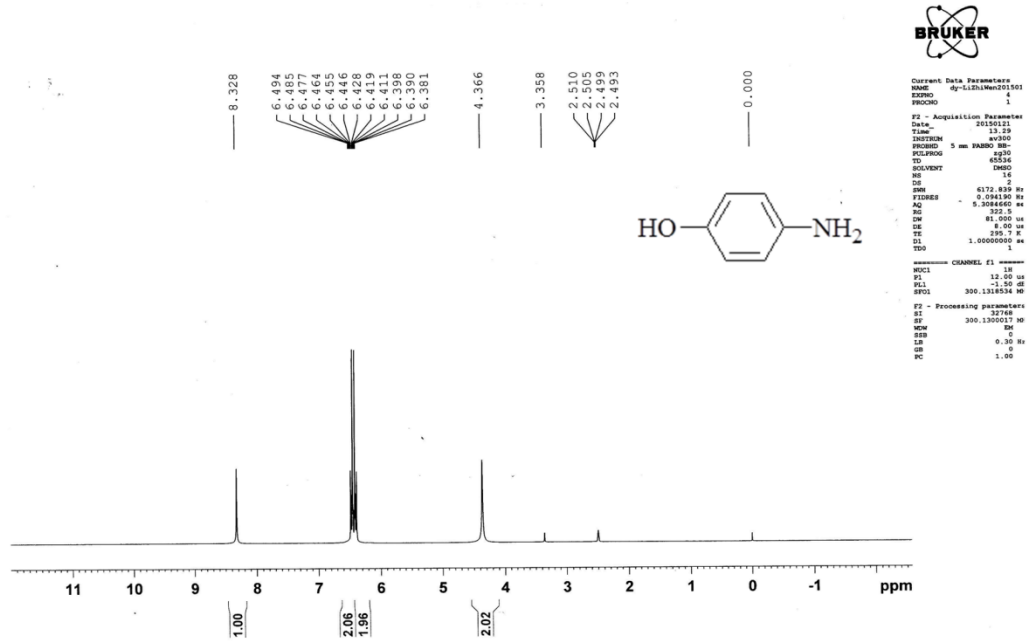
p-Toluidine: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97 (d, *J*=8.1 Hz, 2H), 6.61 (d, *J*=8.4 Hz, 2H), 3.45 (bs, 2H), 2.24 (s, 3H).

p-Phenylenediamine: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.57 (s, 4H), 3.31 (bs, 4H).

4-Iodoaniline: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, *J*=8.7 Hz, 2H), 6.47 (d, *J*=8.7 Hz, 2H), 3.53 (bs, 2H).

Methyl-4-aminobenzoate: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J*=6 Hz, 2H), 6.64 (d, *J*=6 Hz, 2H), 4.14 (bs, 2H), 2.51 (s, 3H).

4-Aminobenzonitrile: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J*=8.7 Hz, 2H), 6.65 (d, *J*=8.7 Hz, 2H), 4.15 (bs, 2H).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4.366
3.358
2.510
2.505
2.499
2.493
0.000
HO
NH2
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10
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8
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6
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4
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1
0
-1
ppm
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2.06
1.96
2.02

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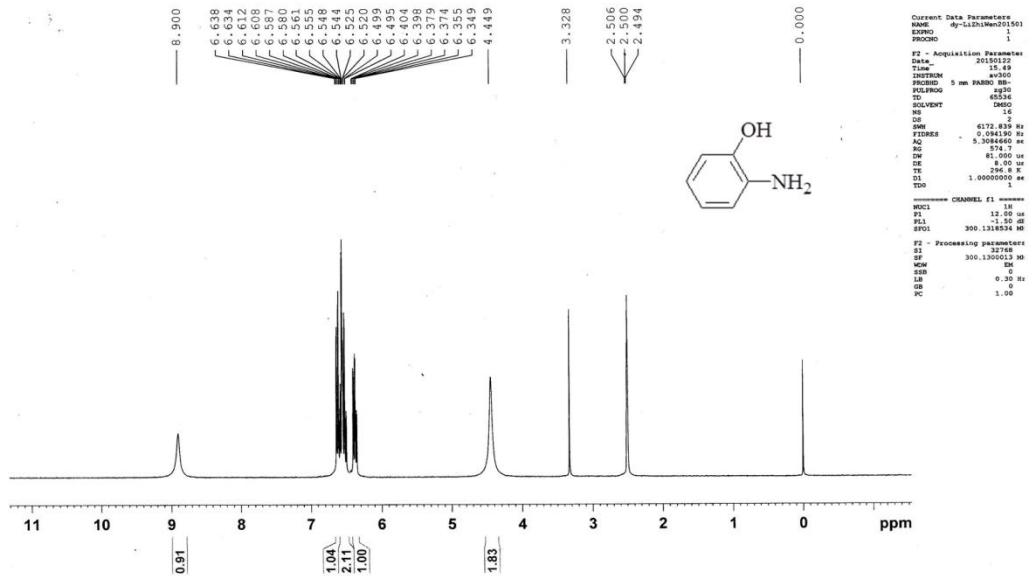
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6.495
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TE 296.8 K
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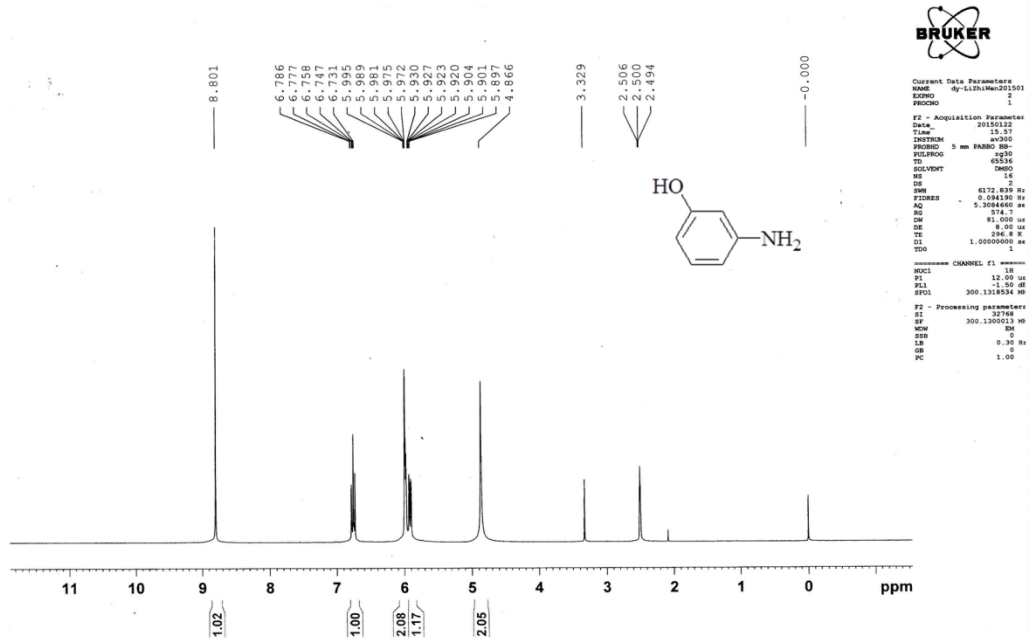

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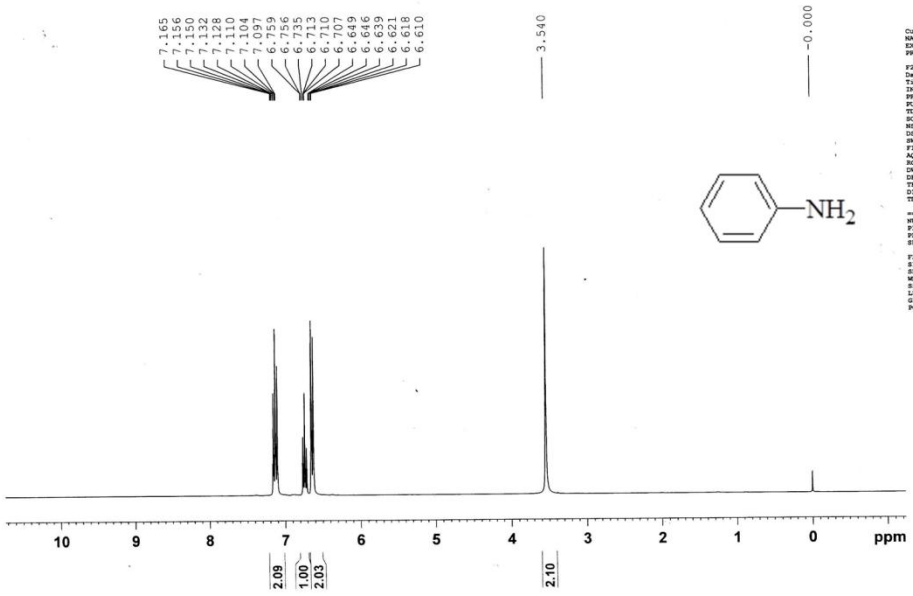

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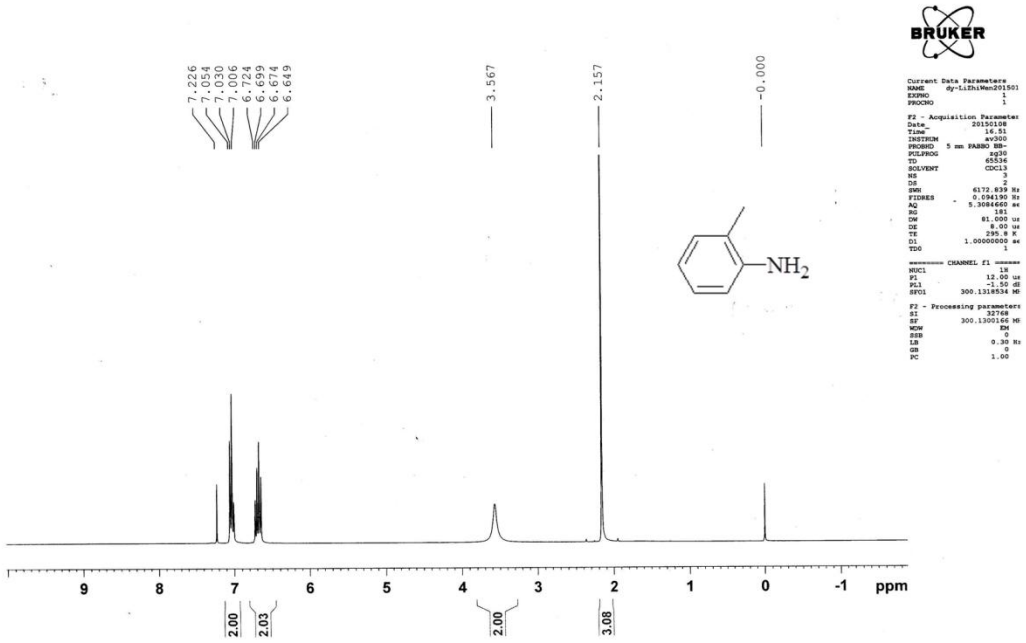
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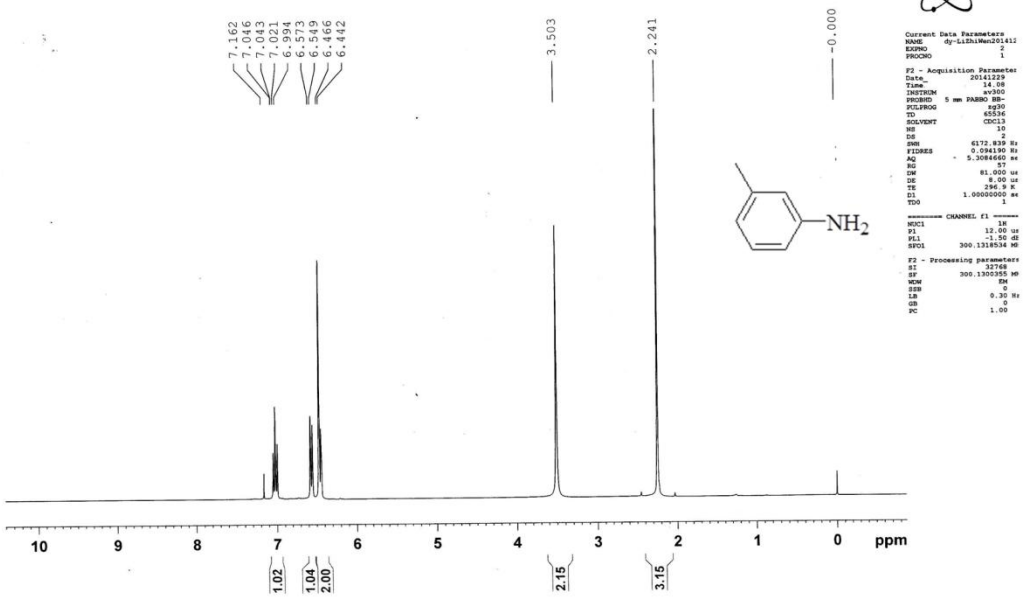
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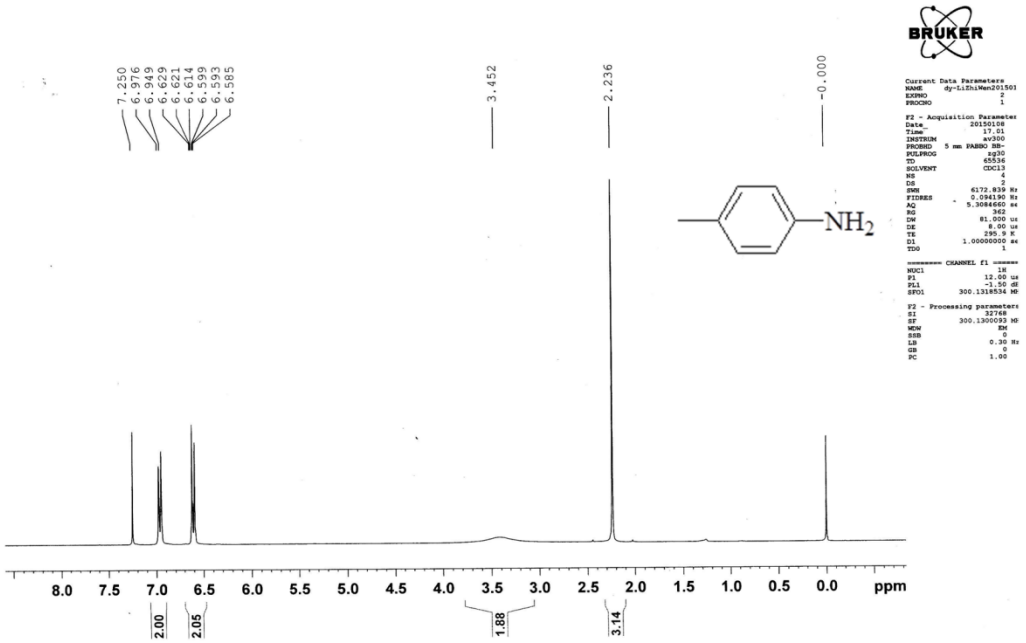
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3.14

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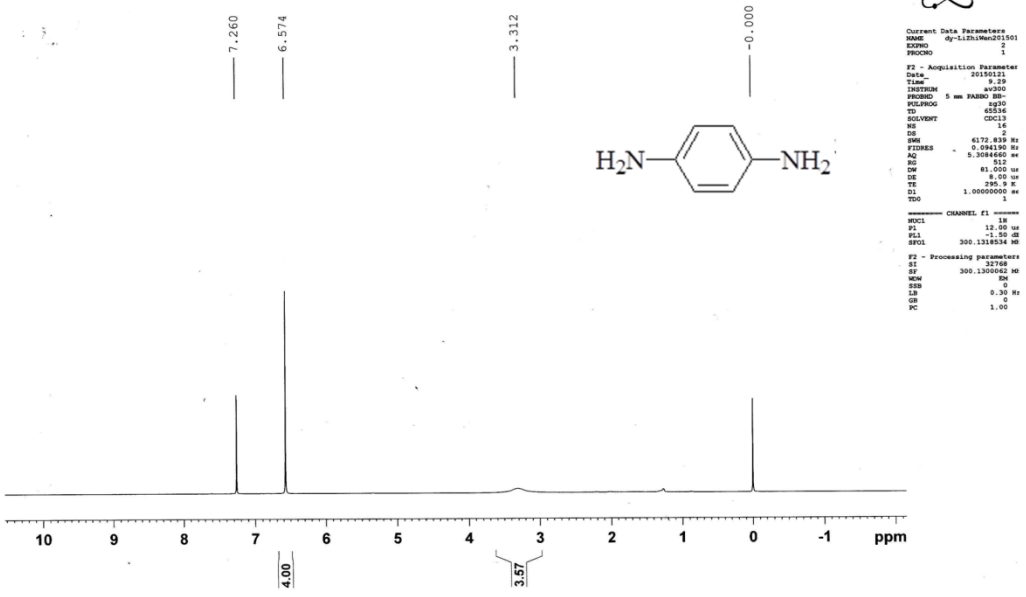
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TE 295.9 K
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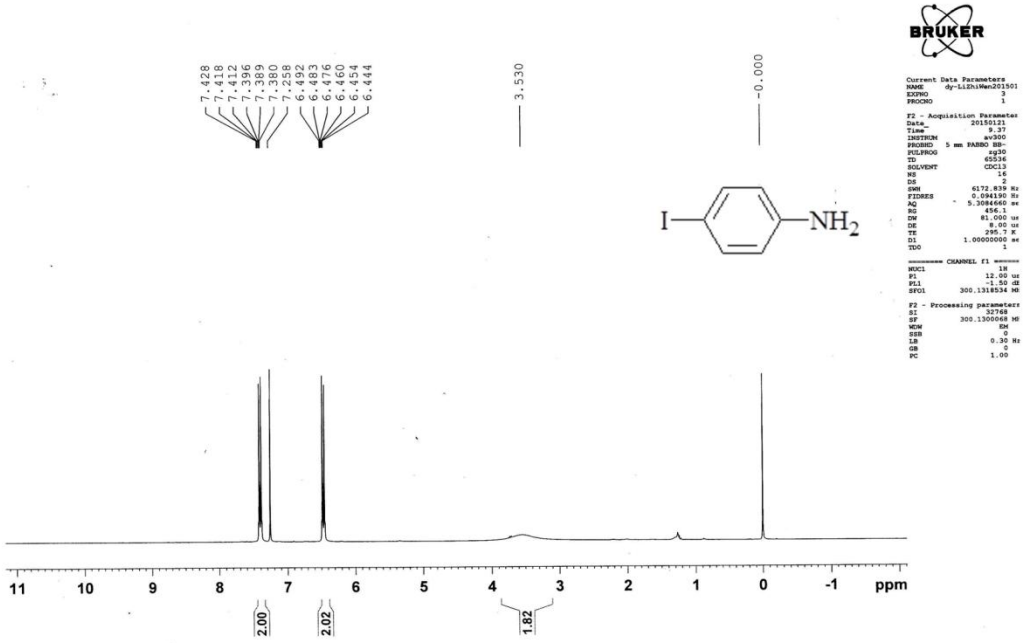

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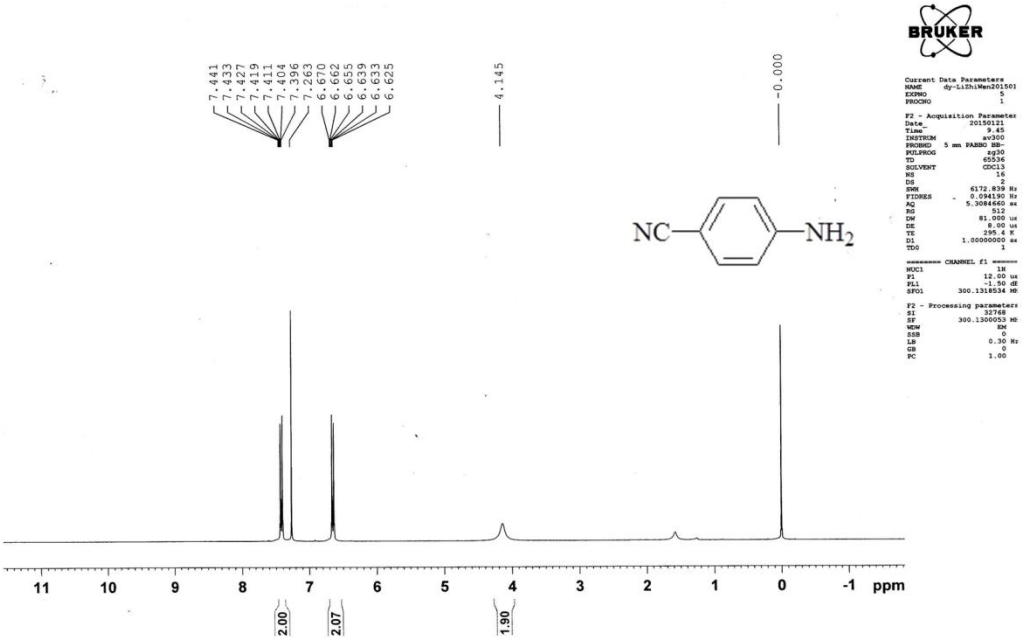

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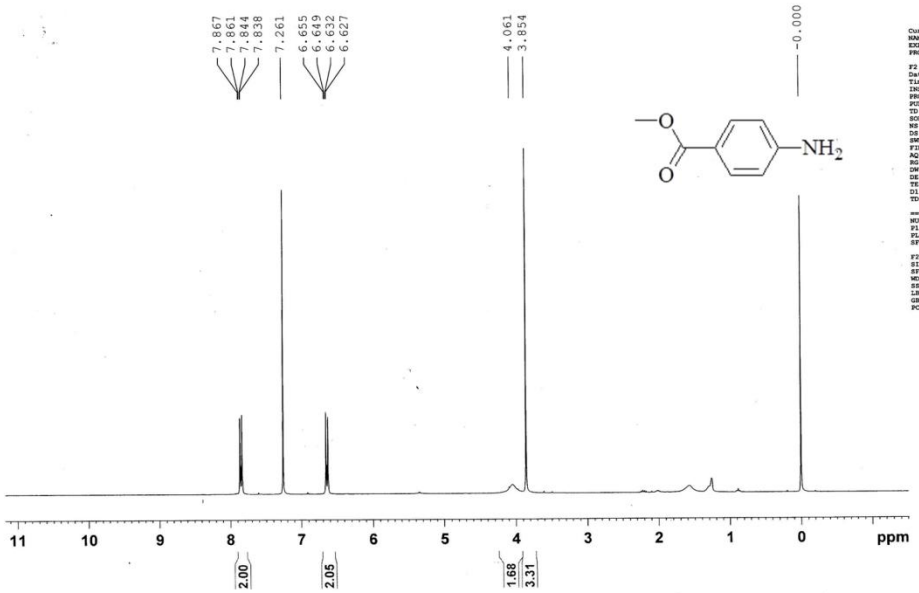

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AQ 5.3084660 se
RG 574.7
DW 81.000 us
DE 8.00 us
TE 296.0 K
D1 1.00000000 se
TD0 1

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