# *Supplementary Material*

## Easy Recycling of Nanoscale $Fe_2O_3$-Based Catalysts for Nitroarene Reduction to Anilines by Pyrolysis of Metallogel

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## 1. General

### Materials and Instruments

All reagents were commercially available and used without further purification Except triethylamine and dichloromethane were removed water. $^1H$ spectra were collected on 400 MHz Bruker AVANCE 400 spectrometers. Chemical shifts were reported in ppm. Deuterium reagents was $d^6$-DMSO. SEM images were collected on FEI quanta 450 instrument. GC-MS were obtained with Shimadzu GCMS-QP 2010SE.

## 2. Synthesis and characterization

### 2.1 The synthesis of gelator 2B-N3.

As shown in Scheme **S1**, 3-aminopyridine (1.88 g, 20 mmol) and triethylamine (3 mL, 21.55 mmol) were mixed in dichloromethane (50 mL), then slowly added 50 mL dichloromethane solution with (2, 2'-bipyridine)-4, 4'-dicarbonyl dichloride (2.80 g, 10 mmol) to it at 0 °C. After dropping, added triethylamine into it, and gradually stir to raise the temperature to room temperature. After reaction for 7 hours, filtered and washed with dichloromethane, crude product dissolved with hot DMSO, recrystallized with water obtained white solid powder (0.52 g, 14.0 %) - N, N '- di (3-pyridyl) - 2, 2-bipyridine-4, 4-diformamide (Abbreviated as **2B-N3**) $^1$H-NMR (400 MHz, DMSO) 10.91 (d, $J$ = 6.6 Hz, 2H), 8.98 (dd, $J$ = 13.8, 2.7 Hz, 6H), 8.38 (dd, $J$ = 4.7, 1.4 Hz, 2H), 8.29 - 8.20 (m, 2H), 8.05 - 7.96 (m, 2H), 7.46 (dd, $J$ = 8.2, 4.7 Hz, 2H) (Figure **S1**). LC-MS $[M+H]^+$ calculated for $C_{22}H_{16}N_4O_2$ : m/z 396.13; found: 397.14.

**Scheme S1.** Synthesis of **2B-N3**

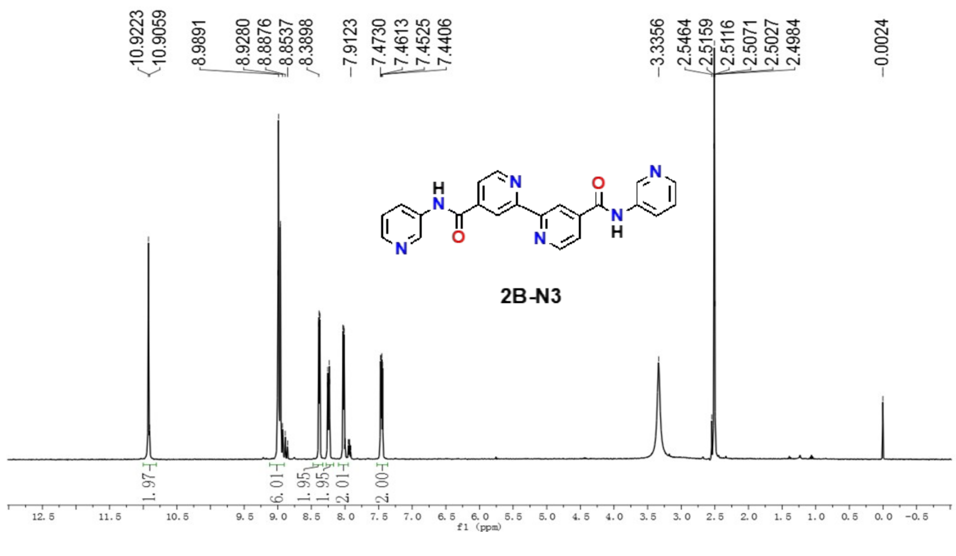
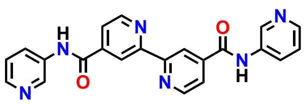




**Figure S1.** $^1$H-NMR spectrum (400 MHz, DMSO) of compound **2B-N3**

### 2.2 The synthesis of metallogel Fe-2B-N3.

**Table S1**. Determination of gelling property of gelator in different metal ions.

| Gelator | Metal Ion | State | Metal Ion | State |
|---|---|---|---|---|
| | $AlCl_3$ | S | $Mg(NO_3)_2$ | I |
| | $Al(NO_3)_3$ | S | $MgSO_4$ | I |
| | $Al_2(SO_4)_3$ | S | $ZnCl_2$ | I |
| | $FeCl_3$ | P | $Zn(NO_3)_2$ | I |
| | ***$Fe(NO_3)_3$*** | ***G*** | $ZnSO_4$ | I |
| | $Fe_2(SO_4)_3$ | P | $CaCl_2$ | I |
| | $FeCl_2$ | S | $Ca(NO_3)_2$ | I |
| | $FeSO_4$ | I | $SnCl_2$ | P |
| | $Fe(NO_3)_2$ | S | $SnCl_4$ | P |
| | $CuCl_2$ | I | $Pb(NO_3)_2$ | I |
| | $Cu(NO_3)_2$ | I | $NiCl_2$ | I |
| | $CuSO_4$ | I | $Ni(NO_3)_2$ | I |
| | $Cu(CH_3COO)_2$ | I | $NiSO_4$ | I |
| | $CrCl_3$ | S | $La(NO_3)_3$ | P |
| | $Cr(NO_3)_3$ | P | $CeCl_3$ | P |
| | $Cr_2(SO_4)_3$ | S | $Ce(NO_3)_3$ | P |
|  | $CdCl_2$ | I | $SrCl_2$ | I |
| | $Cd(NO_3)_2$ | I | $Sr(NO_3)_2$ | I |
| **2B-N3** | $CdSO_4$ | I | LiCl | I |
| | $CoCl_2$ | P | $LiNO_3$ | I |
| | $Co(NO_3)_2$ | P | NaCl | I |
| | $CoSO_4$ | P | $NaNO_3$ | I |
| | $MnCl_2$ | I | $Na_2SO_4$ | I |
| | $Mn(NO_3)_2$ | I | KCl | I |
| | $MnSO_4$ | I | $KNO_3$ | I |
| | $MgCl_2$ | I | $K_2SO_4$ | I |
| | $BaCl_2$ | I | RbCl | I |
| | $Ba(NO_3)_2$ | I | $AgNO_3$ | I |

G = gel; S = solution; P = precipitate; I = insoluble. **2B-N3**: 0.1 mmol; metal ions: 0.1 mol/L

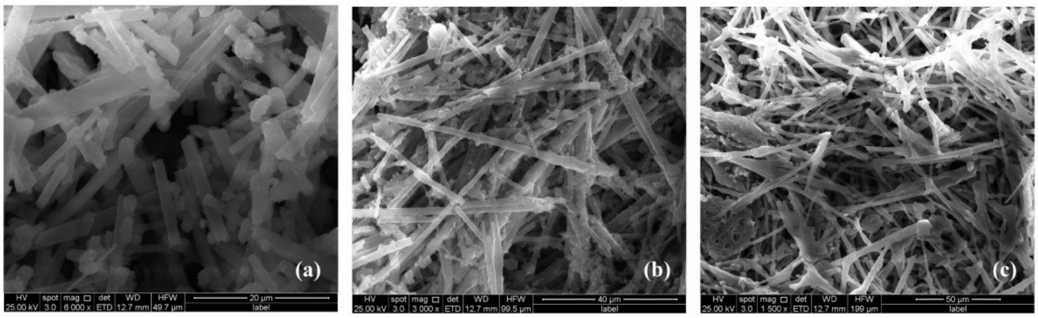
## 2.3 Determination of minimum gel concentration (MGCs) and microstructure.

Weigh amounts of gelator (**2B-N3**) into a small bottle, added 1.0 mL 0.1 mol/L Fe $(NO_3)_3$, heated and ultrasonic them to dissolved, cooled to room temperature. If stable supramolecular metallogel was formed, then added Fe $(NO_3)_3$ solution until the stable metallogel cannot be formed. Use the mass ratio of gelator to the volume of $Fe^{3+}$ to obtain the minimum gelling concentration of metallogel. The minimum amounts of **2B-N3** dissolved in 1mL Fe $(NO_3)_3$ aqueous solution of different concentration necessary for gelatinizing aqueous solution efficiently was assigned to minimum gel concentration (MGCs) of **2B-N3**. As the concentration of Fe $(NO_3)_3$ solution increased, the minimum gelling concentration of metallogel also increased, and its microstructure will change due to different concentrations (**Table S2**).

**Table S2**. MGCs at different Fe $(NO_3)_3$ concentrations

| Fe $(NO_3)_3$ | MGCs |
|---|---|
| 0.010 M | 12.6 mg/mL |
| 0.020 M | 15.3 mg/mL |
| 0.030 M | 16.6 mg/mL |
| 0.040 M | 18.2 mg/mL |
| 0.050 M | 20.1 mg/mL |
| 0.100 M | 39.5 mg/mL |
| 0.150 M | 53.0 mg/mL |
| 0.200 M | 70.1 mg/mL |

**Figure S2.** (a, b, c = 6000x, 3000x, 1500x) Microstructure of areogel of Fe $(NO_3)_3$ = 0.1 M




## 2.4 Characterization of catalyst.

**Table S3**. Comparison of catalytic activity of different catalytic materials

| Number | Catalyst | Temperature (℃) | Time (min) | Con. (%) | Sel. (%) |
|---|---|---|---|---|---|
| 1 | 600-2h-1 | 80 | 20 | >99.9 | >99.9 |
| 2 | 700-2h-1 | 80 | 13 | >99.9 | >99.9 |
| 3 | 800-1h-1 | 80 | 13 | >99.9 | >99.9 |
| 4 | 800-3h-1 | 80 | 14 | >99.9 | >99.9 |
| 5 | 900-2h-1 | 80 | 15 | >99.9 | >99.9 |

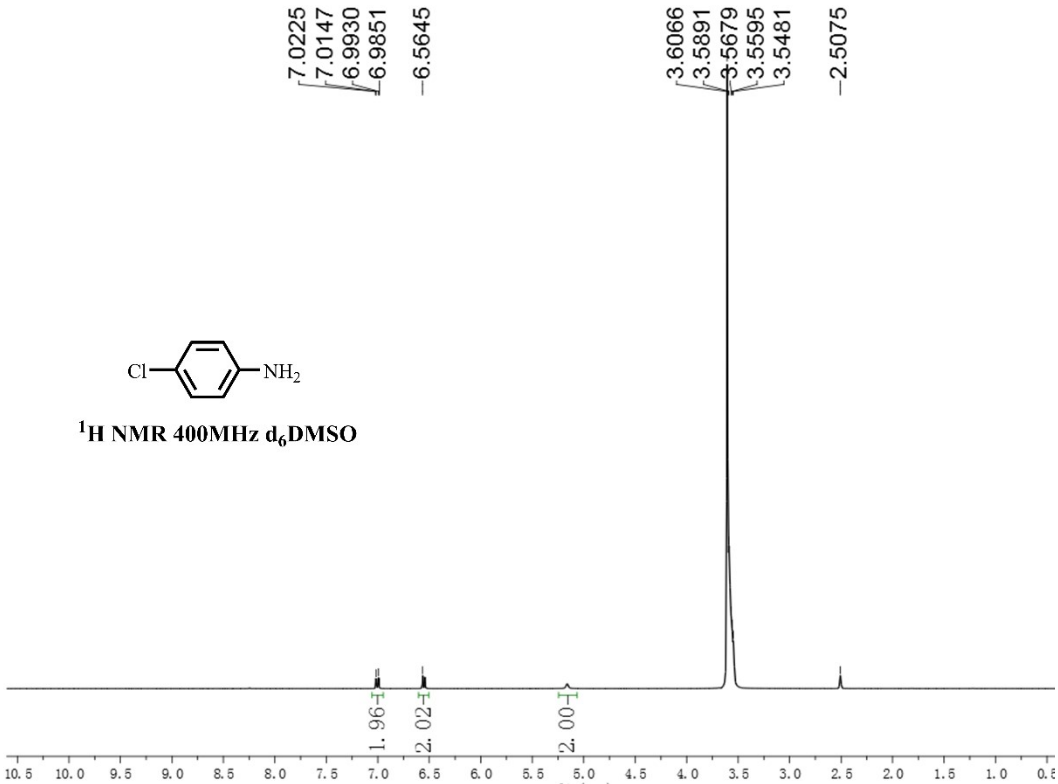
**Table S4**. Iron content in different catalytic materials

| Catalytic material | Iron content (total Fe, wt %) |
|---|---|
| 600-2h-1 | 18.31 |
| 700-2h-1 | 20.92 |
| **L** (800-2h-1) | 21.74 |
| 900-2h-1 | 21.89 |
| 800-1h-1 | 21.19 |
| 800-2h-0 | 23.37 |
| 800-2h-2 | 22.44 |
| 800-2h-3 | 22.50 |
| 800-3h-1 | 26.77 |

## 2.5 TOF calculation method [1].

$$\text{Turnover frequency (TOF)} = \frac{moles\ of\ converted\ substrate}{moles\ of\ Fe\ \times\ reaction\ time\ (h)}$$

## 2.6 $^1$H-NMR of the reduced product.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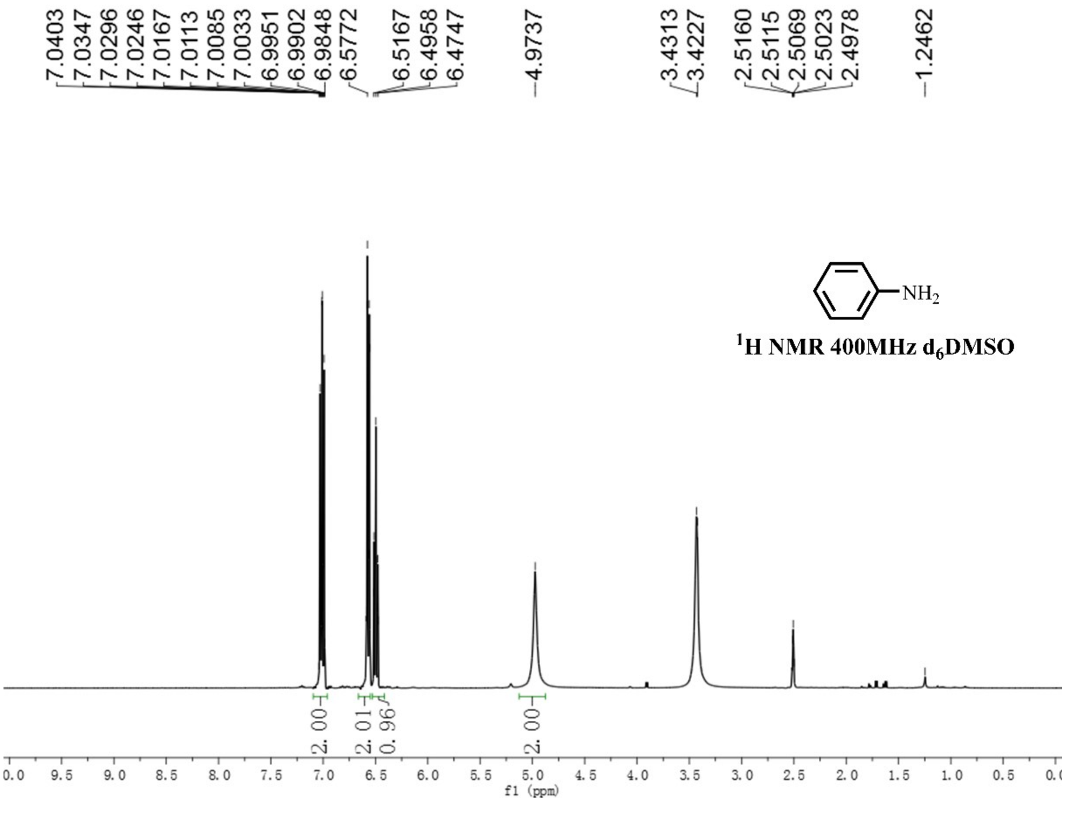
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2.00
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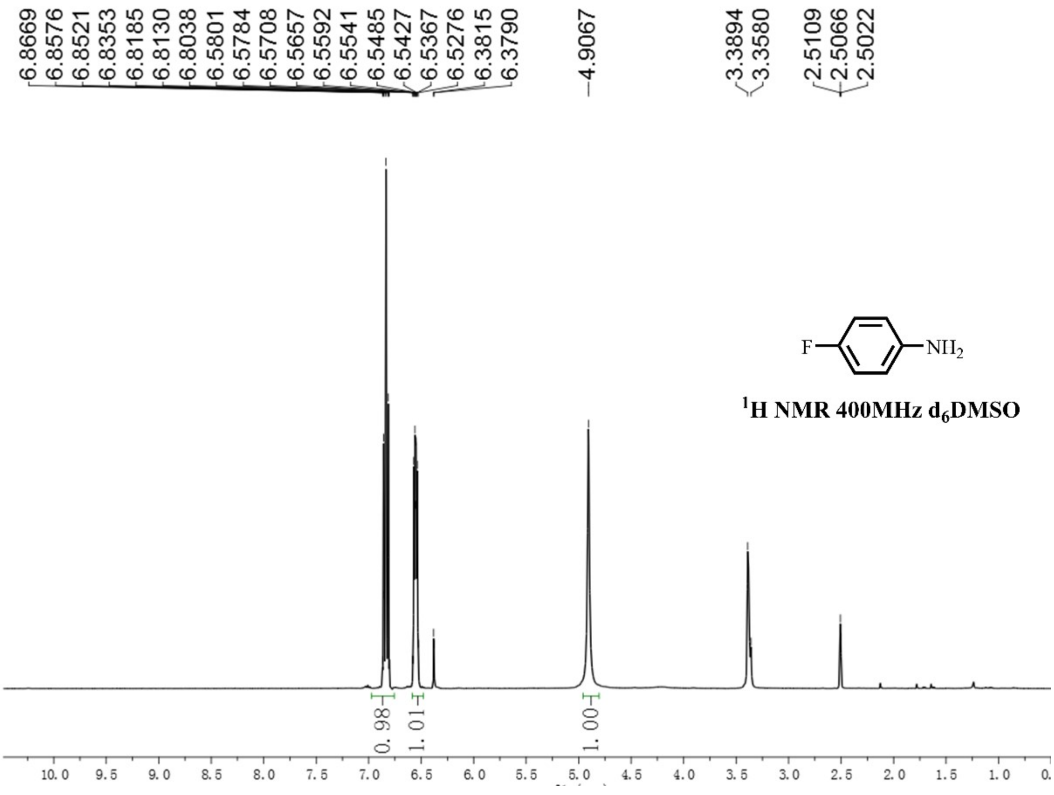
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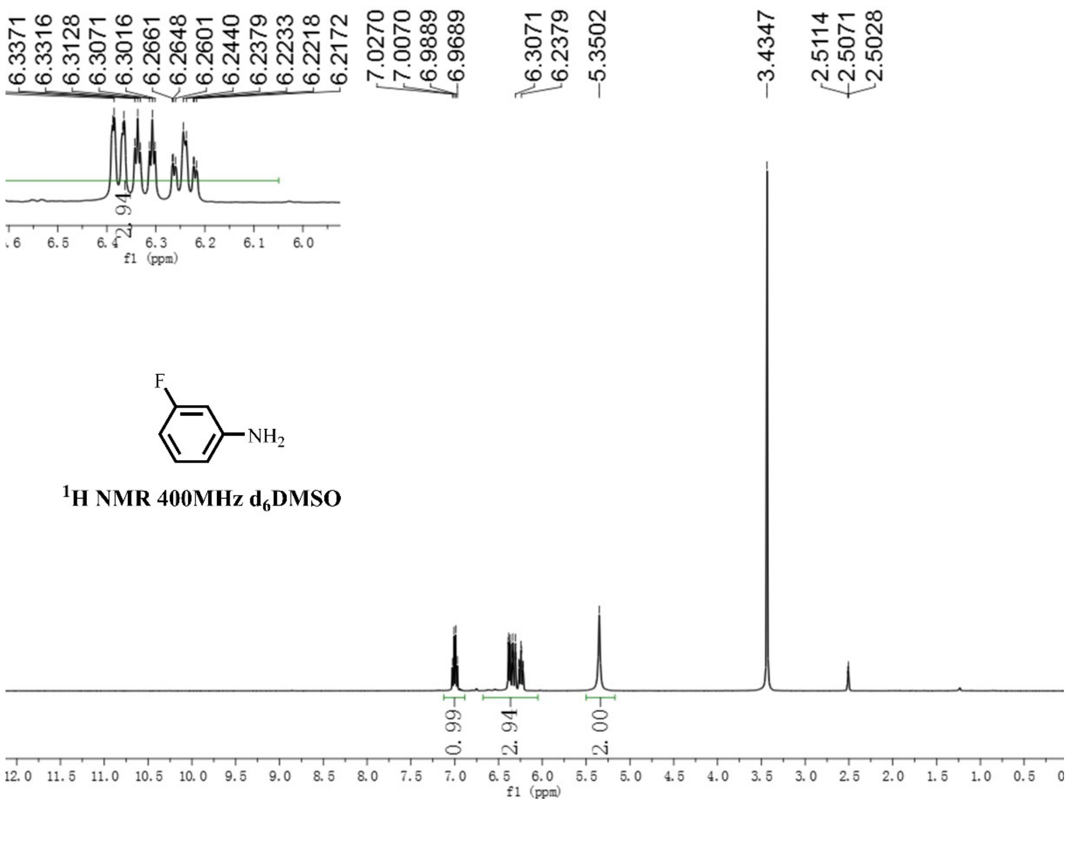
1.00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7.0070
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6.9689
6.3071
6.2379
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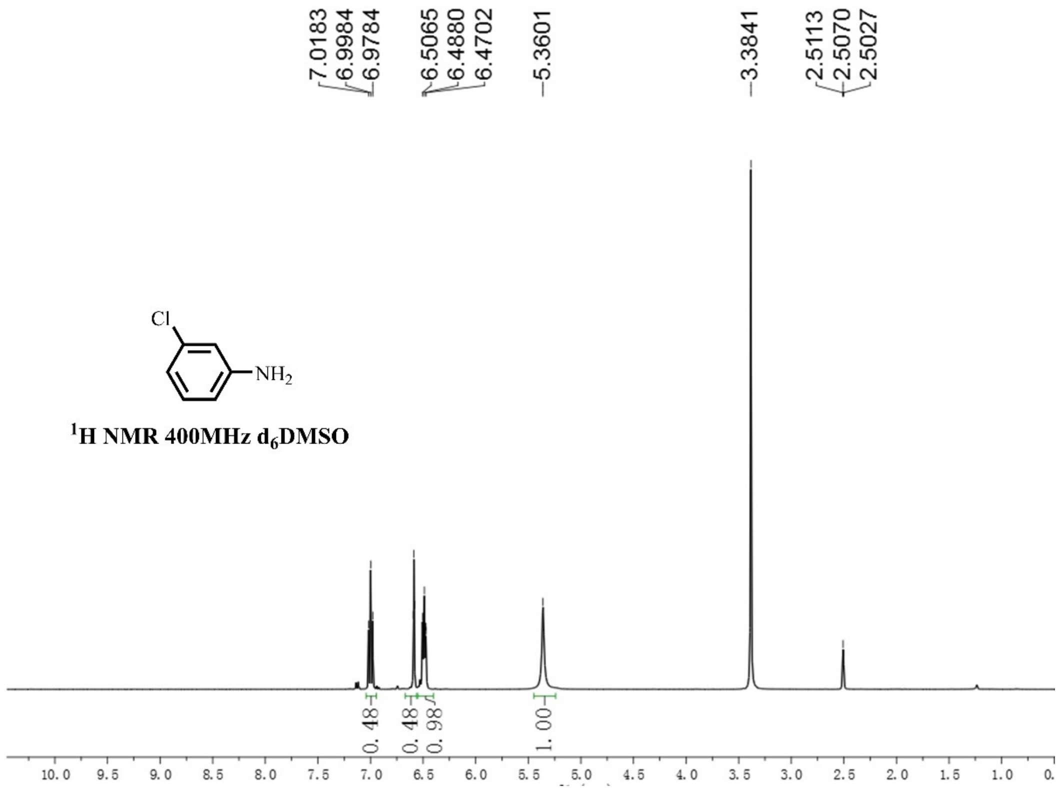
2.00
f1 (ppm)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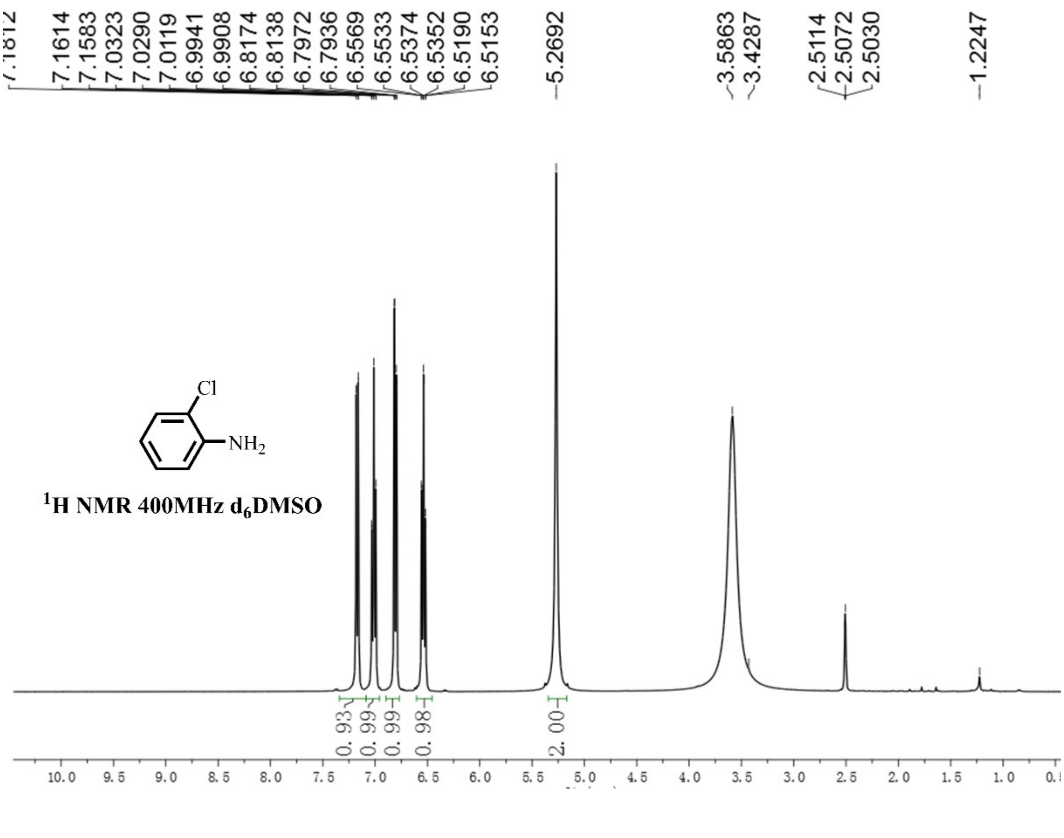
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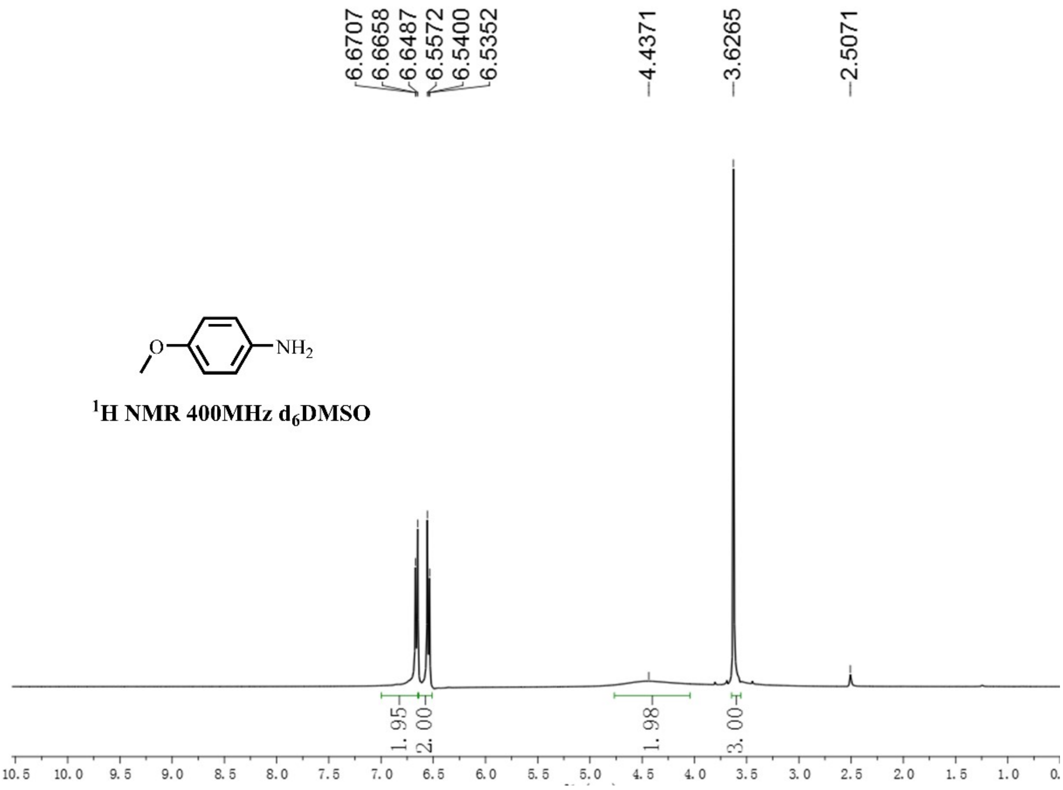
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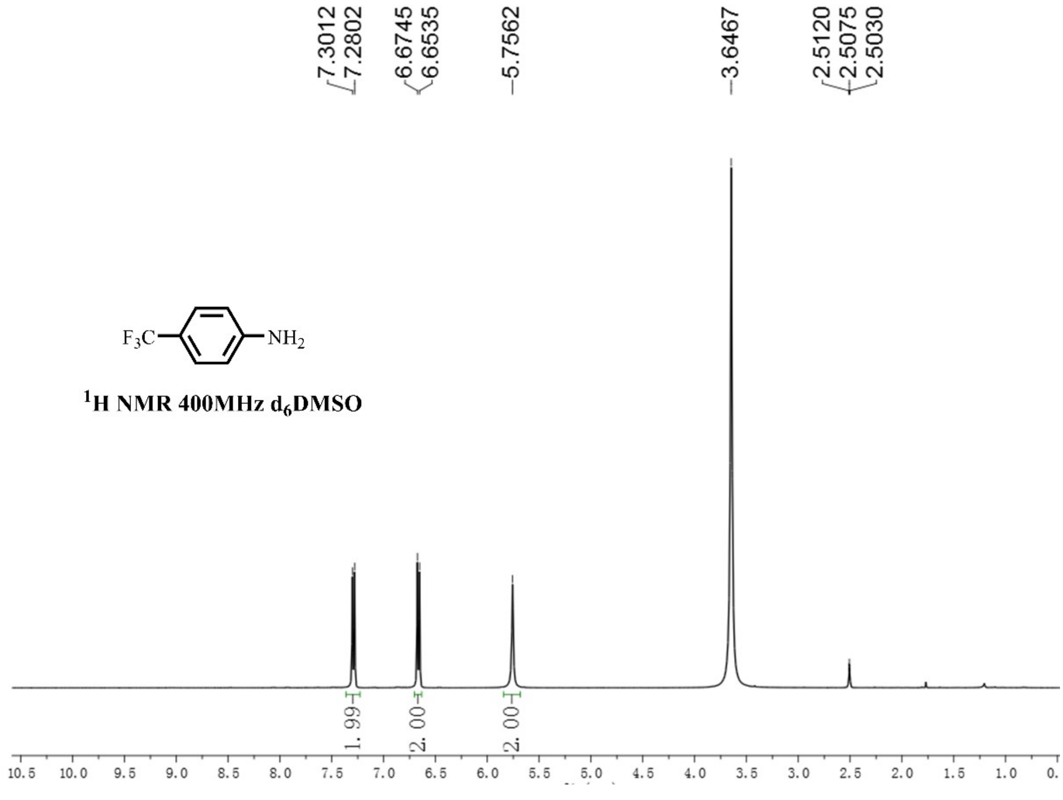
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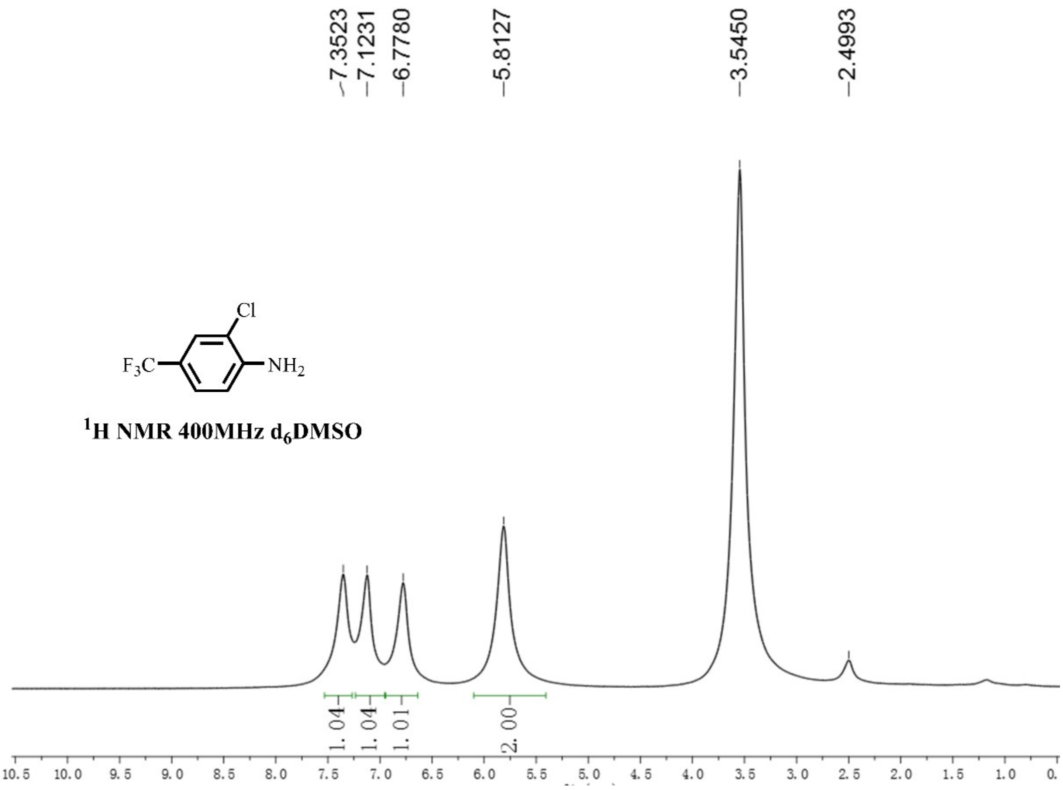
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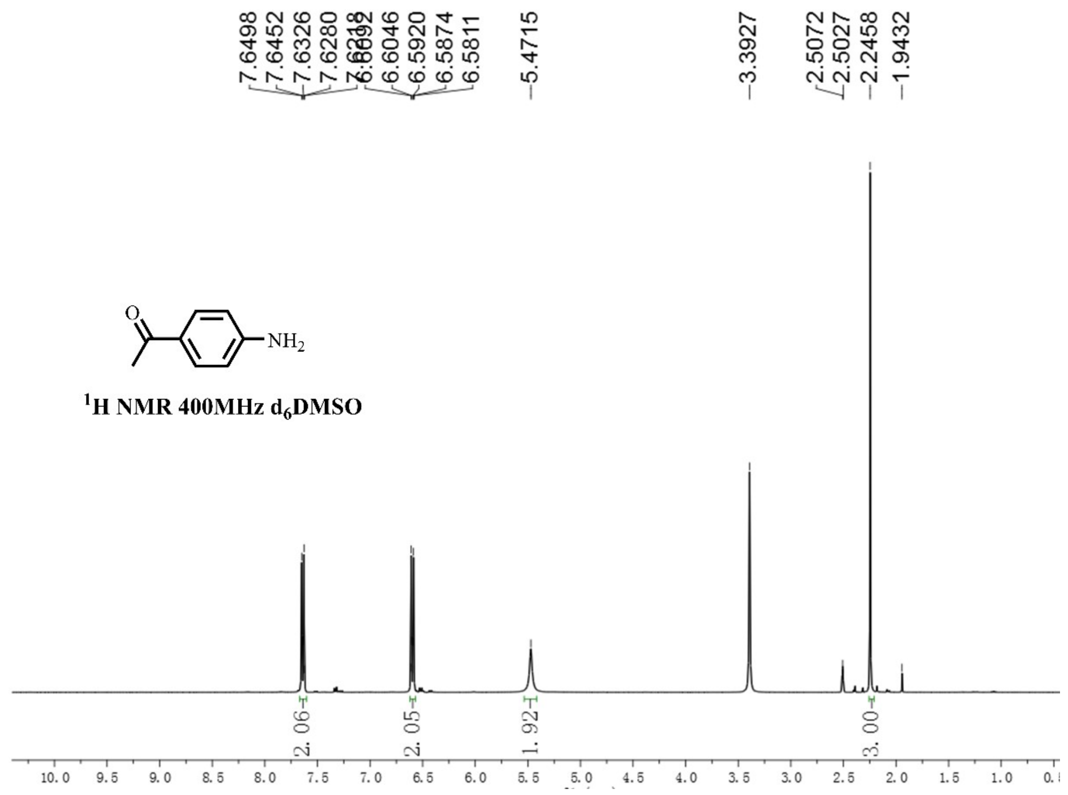
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3.00
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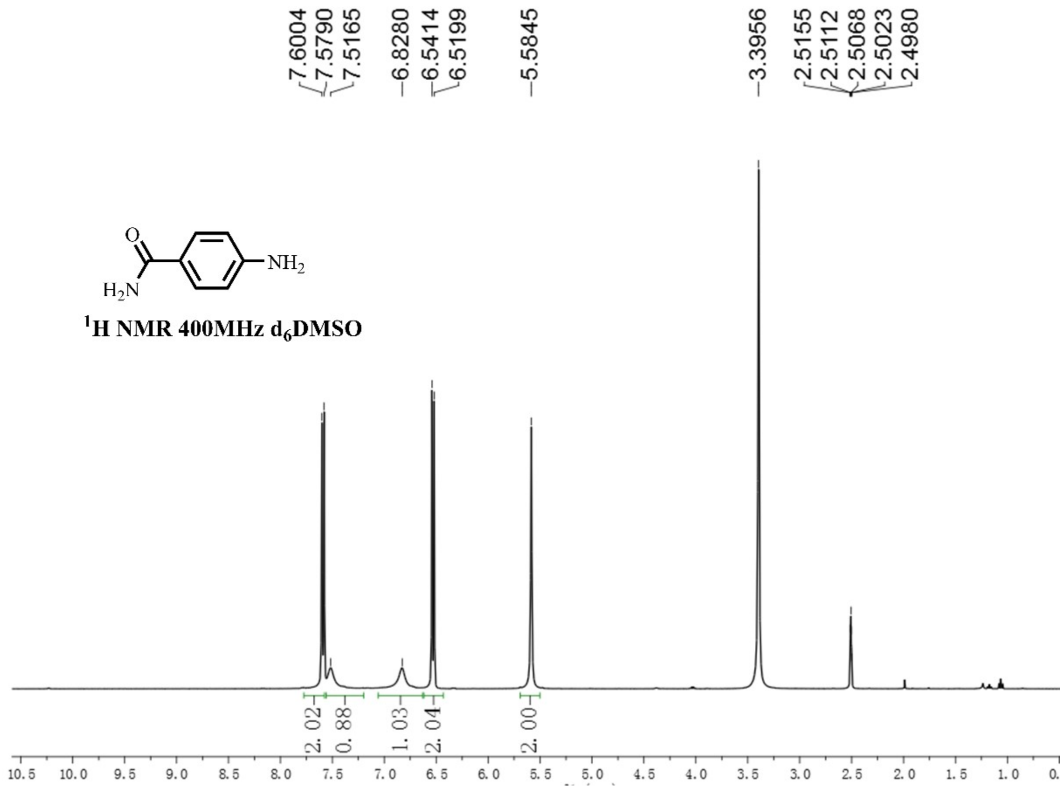
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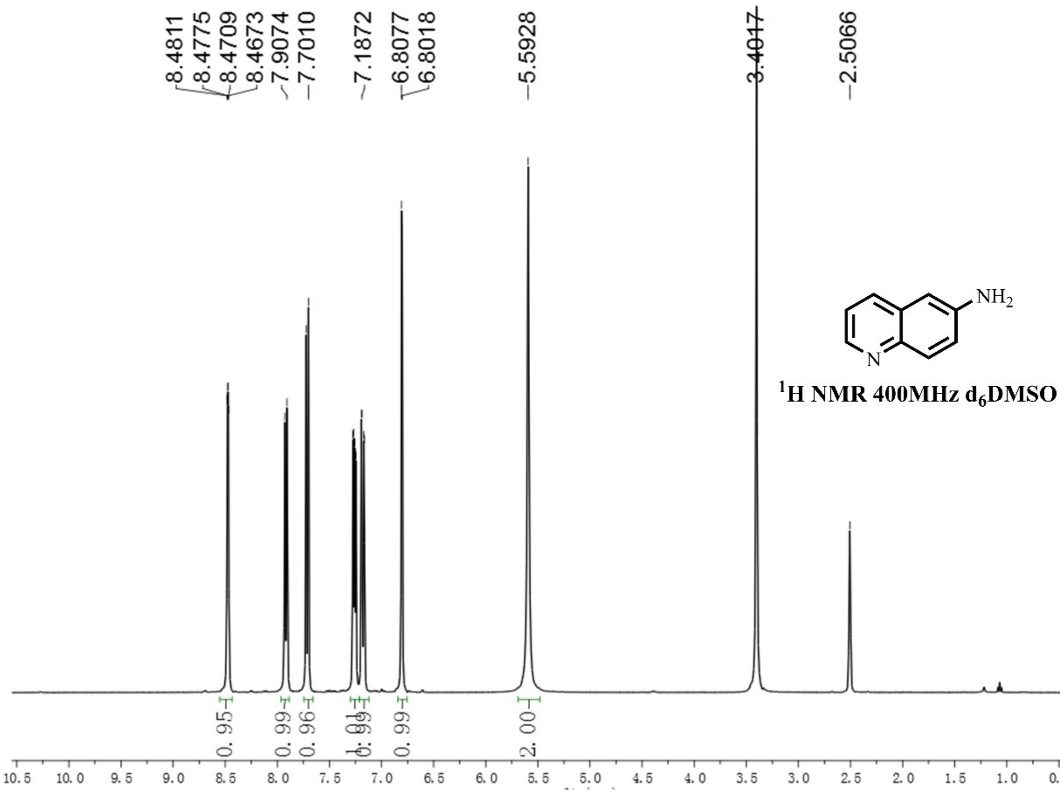
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N
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0.96
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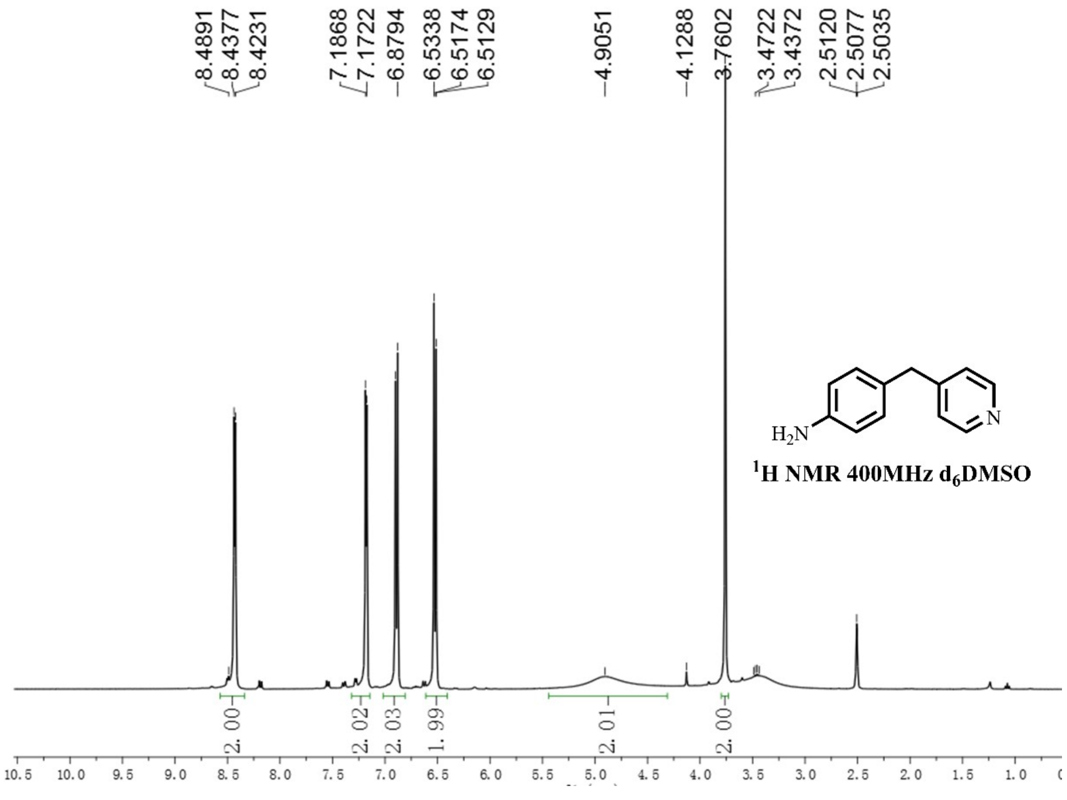
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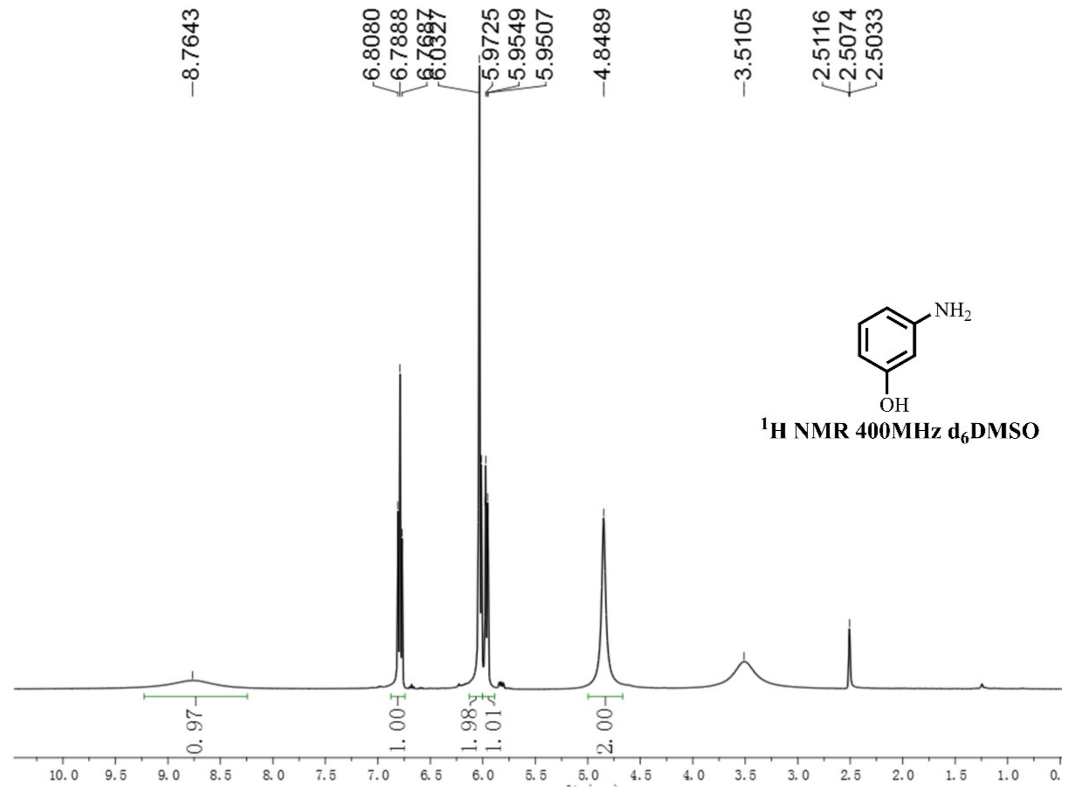
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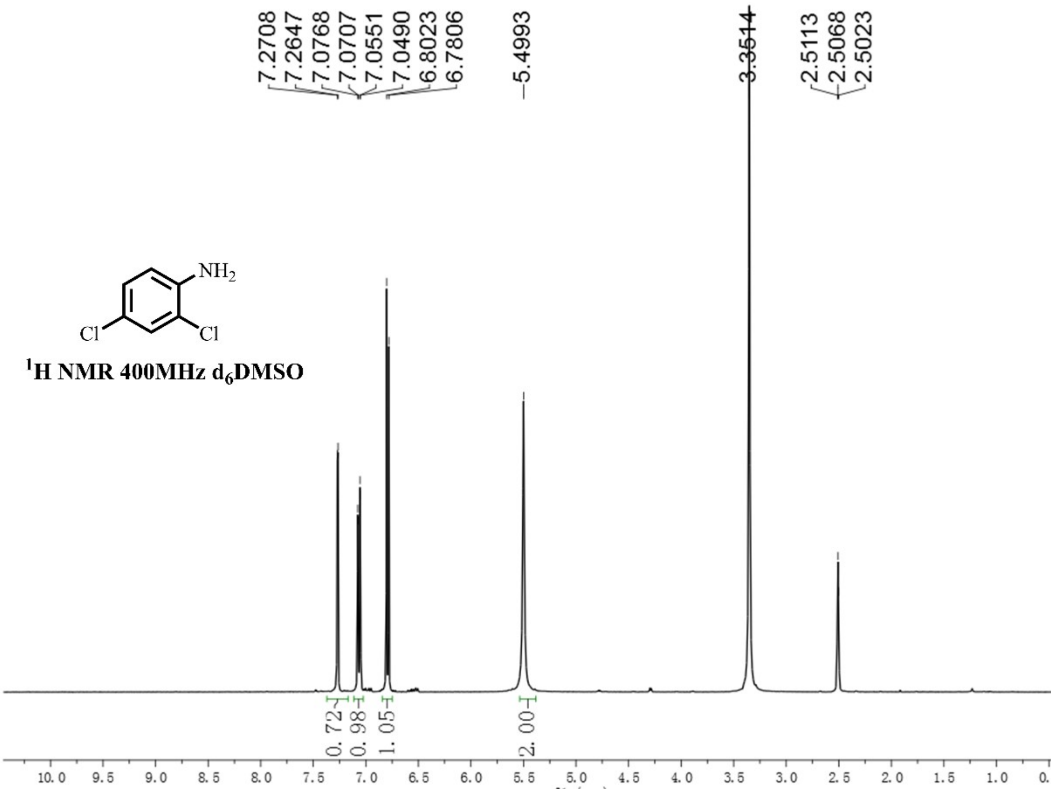
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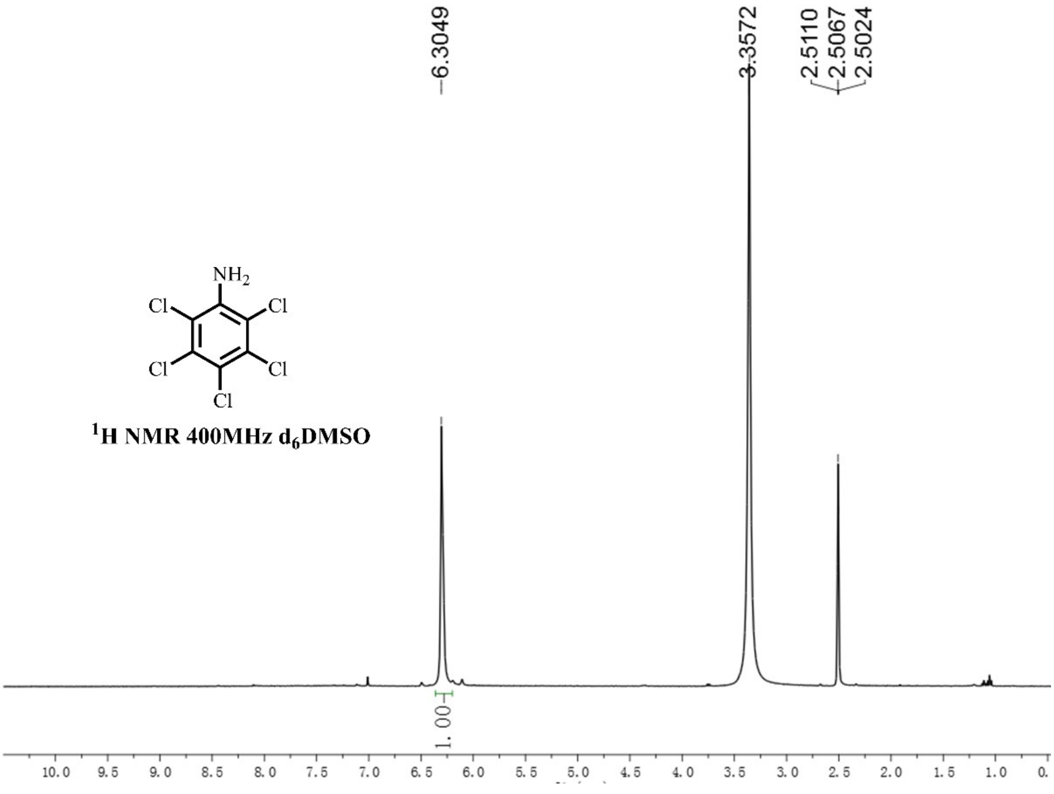
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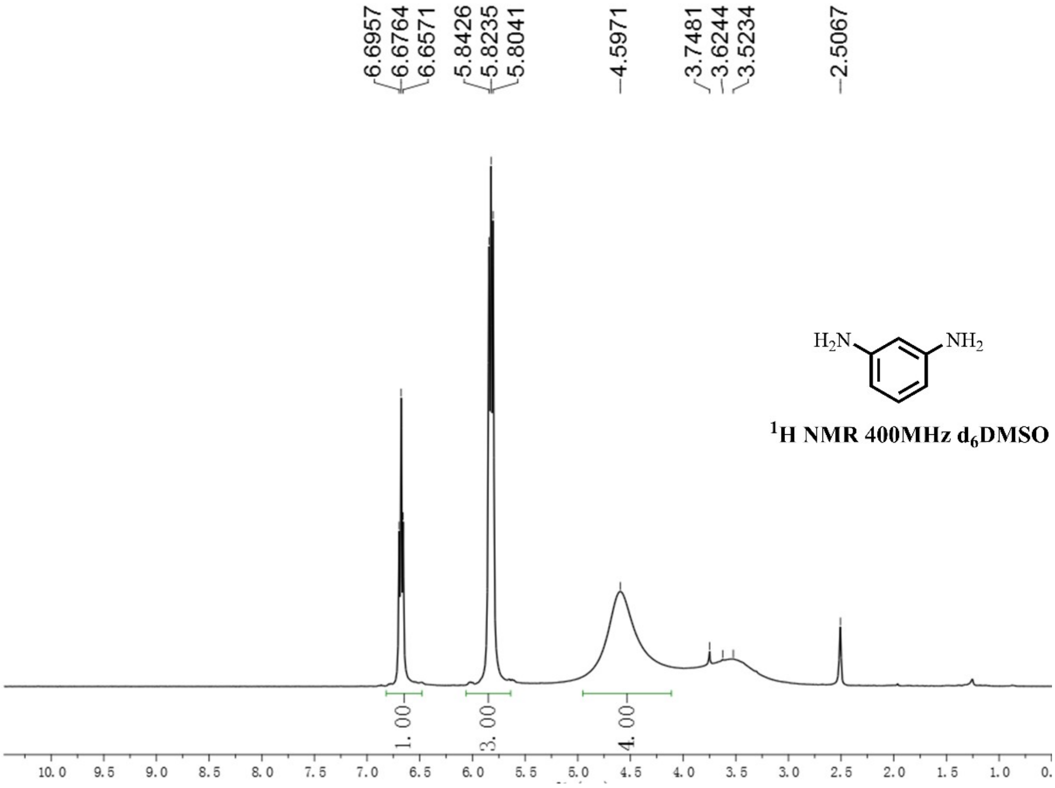


**Figure S3.** $^{1}$H-NMR (400 MHz, $d^6$-DMSO) reaction products.

## 2.7 Possible reaction mechanisms.

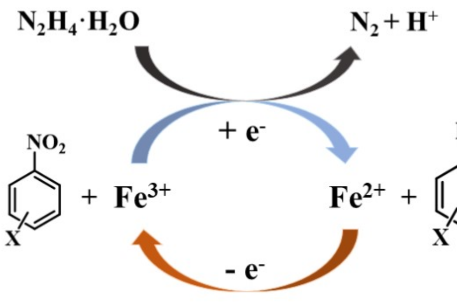


**Figure S4.** Possible mechanism of catalyst **L** for reducing nitrobenzene to aniline.

## 2.8 Reference


[1] X. -L. Cui, Q. -L. Zhang, M. Tian, Z. -P. Dong. Facile fabrication of γ-$Fe_2O_3$-nanoparticle modified N-doped porous carbon materials for the efficient hydrogenation of nitroaromatic compounds. *N. J. Chem*, 2017, **41** (18), 10165-10173.