Supporting Information

High Graphite N Content in Nitrogen-Doped Graphene as an Efficient Metal-free Catalyst for Reduction of Nitroarenes in Water

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1. General Information

^{1}H NMR spectra are recorded on JNM-LA300FT-NMR (300 MHz, 400 MHz) spectrometers. ^{1}H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shifts of $CDCl_3$ at 7.26 ppm and CD_3OD at 3.33 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broadened), and coupling constants (Hz). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F254 (Merck).

2. Mechanism study for the reduction of nitroarenes

0.5 mmol p-nitrchlorobenzene (40 mg) was moved into a reactor together with 2 mg NG-1 and 1 ml water at room temperature. The mixture was stirred for 1-2 min for thoroughly mixing. 5 equiv. of $NaBH_4$ (1.25 mmol/mL) 2mL was added dropwise into the above solution under magnetic stirring at room temperature. After reacting for 0.5 hour, the sample was dissolved in ethyl acetate and analyzed by GC-MS. The initial temperature of the column was 70 °C held for 1 min and was programmed to 300 °C at 15 °C/min, then held for 15 min at 300 °C, the sample injection volume was 2 μL. Helium was used as carrier gas at a flow rate of 1.1 mL/min on split mode (1:50).

3. Computational details

All the electronic structure and energy calculations were carried out by the spin-polarized density functional theory (DFT) using the Vienna ab initio simulation package (VASP).[1-4] PAW potentials were used to describe ion cores and valence electrons interactions.[5,6] The adopted exchange-correlation functional is the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof.[7] A kinetic energy cut off of 350 eV was used with a plane-wave basis set. The integration of the Brillouin zone was conducted using a 5×5×1 Monkhorst-Pack grid.[8] All atoms were fully relaxed and optimized until the force was converged to 0.05 eV/Å and the total energy was converged to 1.0×10^{-5} eV/atom.

Four kinds of nitrogen doped graphene (NG), graphitic N, pyridinic N, pyrrolic N, and pyridinic N oxidized, were established based on the 4 × 4 single layer graphene, armchair and zigzag ribbons. The structures were designed according to previous reference.[9] The periodical graphene slab 9.86 Å × 8.60 Å in size was used. The edge graphene ribbon was prepared with the size of 20 Å × 8.60 Å. To avoid the image

interactions sufficiently large vacuum of 15.0 Å has been taken along the z-axis.

The adsorption energy (E_{ads}) of nitrobenzene was defined as follows:

$$E_{ads} = E_{substrate+nitrobenzene} - E_{nitrobenzene} - E_{substrate} \quad (1)$$

where $E_{substrate+nitrobenzene}$, $E_{nitrobenzene}$, and $E_{substrate}$ are corresponding to the total energies of a nitrobenzene molecule and four NG substrates, a gas phase nitrobenzene, and an isolated substrate, respectively. A negative value indicates an exothermic chemisorption.

4. The GC-MS spectra of reduction reaction intermediate products

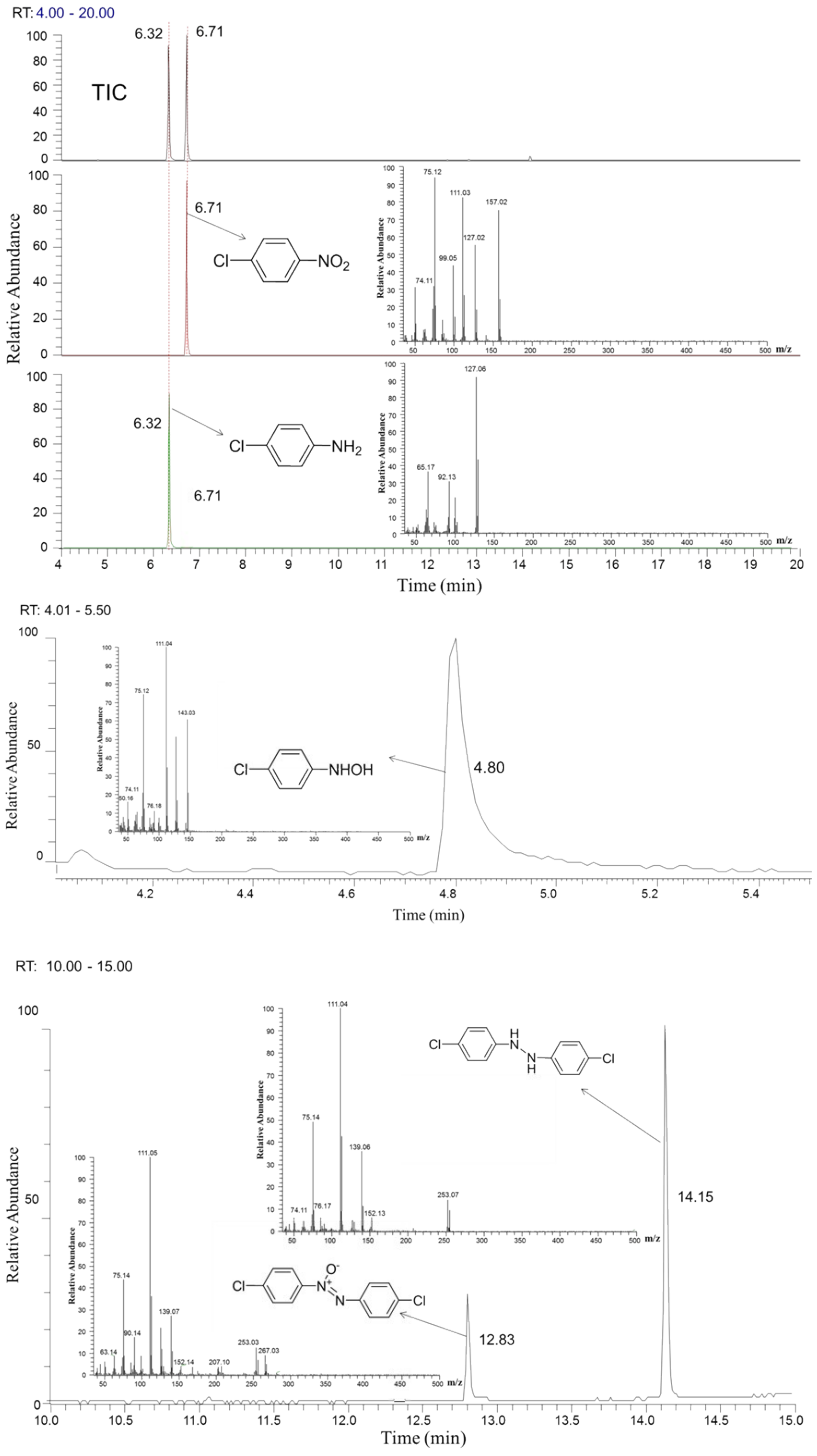


Fig. S1 The GC-MS spectra of reduction reaction intermediate products.

5. A proposed reaction mechanism for NG catalyze reduction of nitroarene

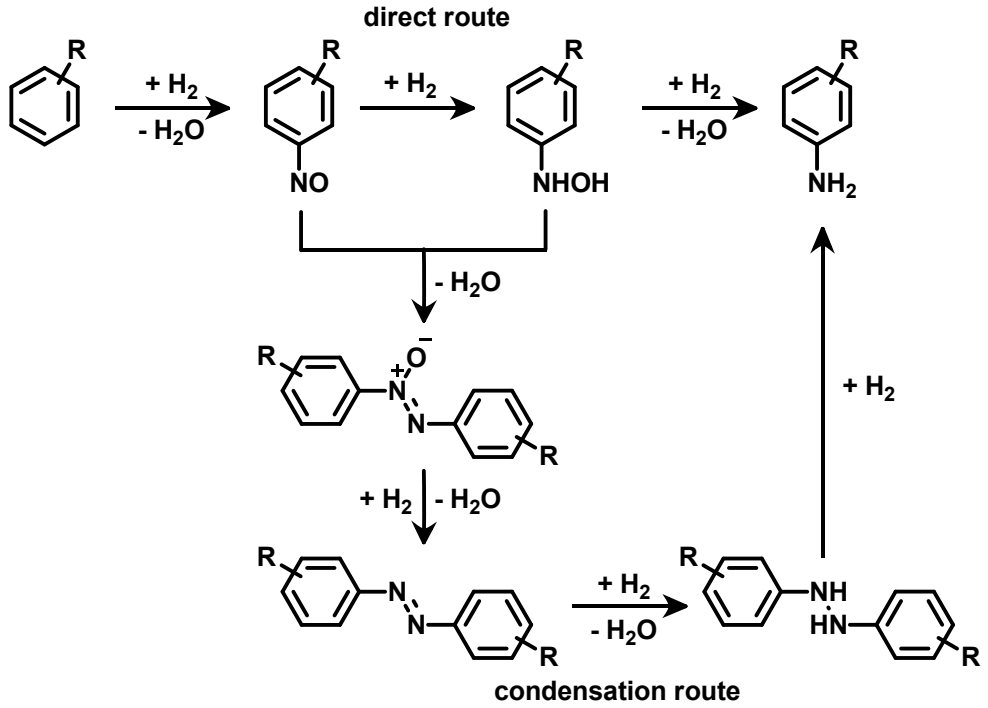
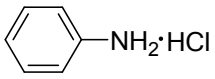


Fig. S2 Schematic of the proposed reaction pathway for nitroarenes reduction

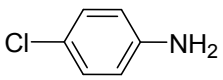
6. Spectroscopic data of the products:

Aniline hydrochloride (Table 3, entry 1)[10]



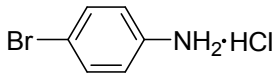
^{1}H NMR (400 MHz, CD_3OD) δ 7.57-7.52 (m, 3H), 7.44 (d, J = 8.8 Hz, 2H).

4-Chloroaniline (Table 3, entry 2)[11]



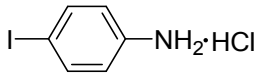
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, J = 8.4 Hz, 2H), 6.33 (d, J = 8.4 Hz, 2H), 3.66 (s, 2H).

4-Bromoaniline hydrochloride (Table 3, entry 3)[10]



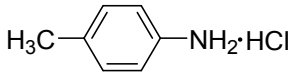
^{1}H NMR (300 MHz, CD_3OD) δ 7.74 (d, J = 8.7 Hz, 2H), 7.36 (d, J = 8.7 Hz, 2H).

4-Iodoaniline hydrochloride (Table 3, entry 4)[10]



^{1}H NMR (300 MHz, CD_3OD) δ 7.91 (d, J = 8.7 Hz, 2H), 7.20 (d, J = 8.7 Hz, 2H).

4-Methylaniline hydrochloride (Table 3, entry 5)

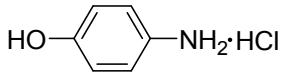


^{1}H NMR (300 MHz, CD_3OD) δ 7.38 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 2.41 (s, 3H).

4-Nitroaniline (Table 3, entry 6)[11]

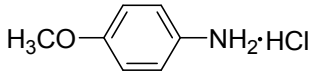
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (s, 4H), 3.31 (s, 4H).

4-Aminophenol hydrochloride (Table 3, entry 7)



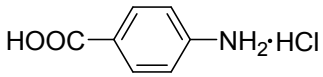
^{1}H NMR (300 MHz, CD_3OD) δ 7.24 (d, 2H), 6.92 (d, J = 8.7 Hz, 2H).

4-Methoxyaniline hydrochloride (Table 3, entry 8)



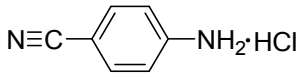
^{1}H NMR (300 MHz, CD_3OD) δ 7.38 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 3.79 (s, 3H).

4-Amino-benzoic acid hydrochloride (Table 3, entry 9)



^{1}H NMR (300 MHz, CD_3OD) δ 8.16 (d, J = 8.7 Hz, 2H), 7.48 (m, J = 8.7 Hz, 2H).

4-Aminobenzonitrile (Table 3, entry 10)



^{1}H NMR (400 MHz, CD_3OD) δ 7.76 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.8 Hz, 2H).

References

(1) G. Kresse and J. Furthmuller, *Comp. Mater. Sci.*, 1996, **6**, 15–50.
(2) G. Kresse and J. Hafner, *Phys. Rev. B*, 1993, **47**, 558–561.
(3) G. Kresse and J. Hafner, *Phys. Rev. B*, 1994, **49**, 14251–14269.
(4) G. Kresse and J. Furthmuller, *Phys. Rev. B*, 1996, **54**, 11169–11186.
(5) P. E. Blochl, *Phys. Rev. B*, 1994, **50**, 17953–17979.
(6) G. Kresse, D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758–1775.
(7) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
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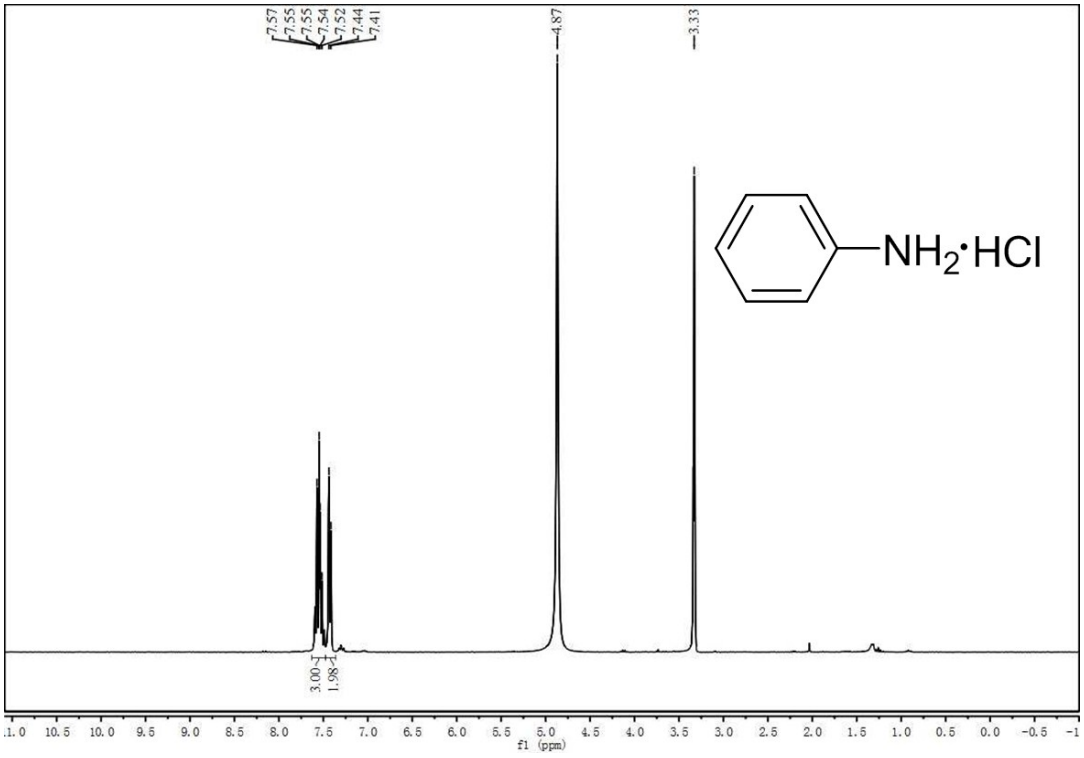
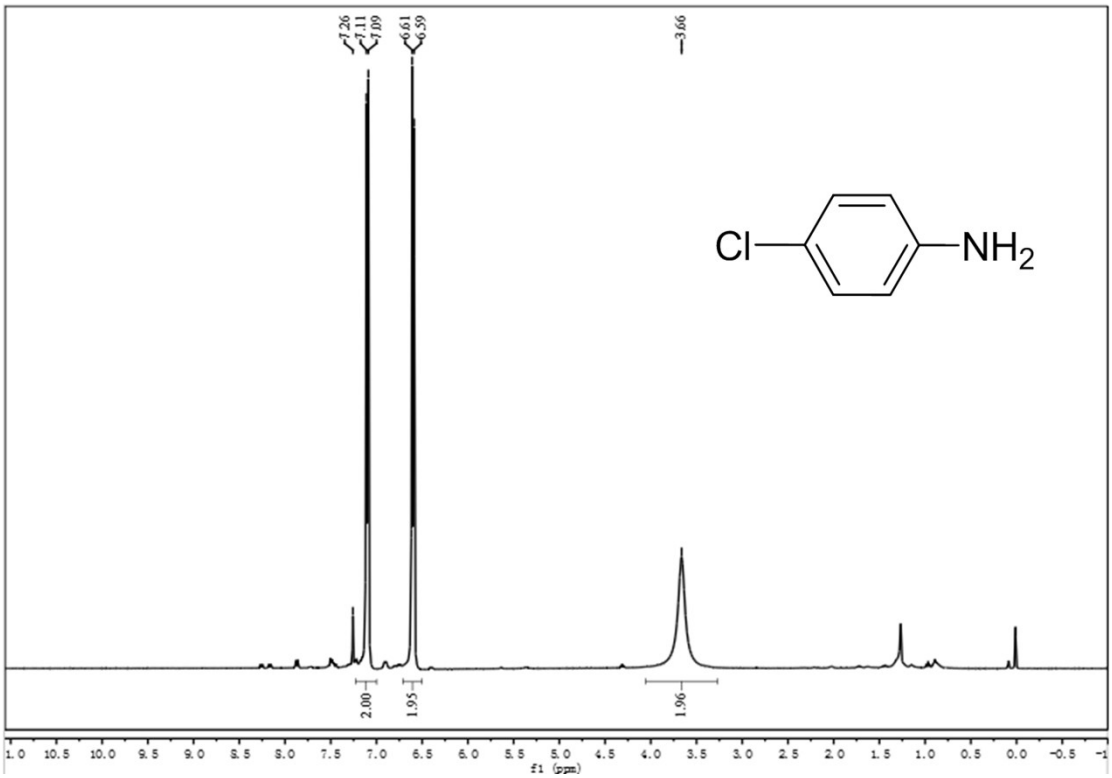
(9) W. Liang, J. Chen, Y. Liu and S.Chen, *ACS Catalysis*, 2014, **4**, 4170-4177.
(10) R. G. de Noronha, C. C. Romão and A. C. Fernandes, *J. Org. Chem*., 2009, **74**, 960-6964.
(11) D. Cantillo, M. M. Moghaddam and C. O. Kappe, *J. Org. Chem*., 2013, **78**, 4530-4542.

3. ^{1}H NMR charts of the products:

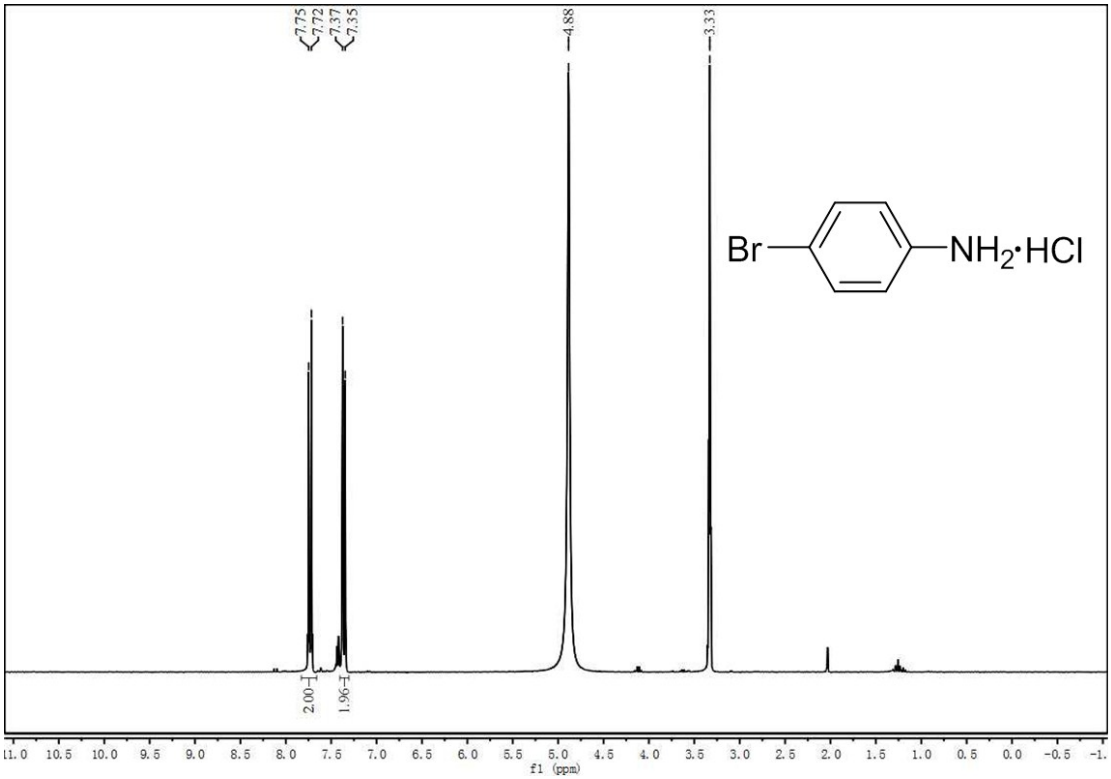
Aniline hydrochloride (Table 3, entry 1):



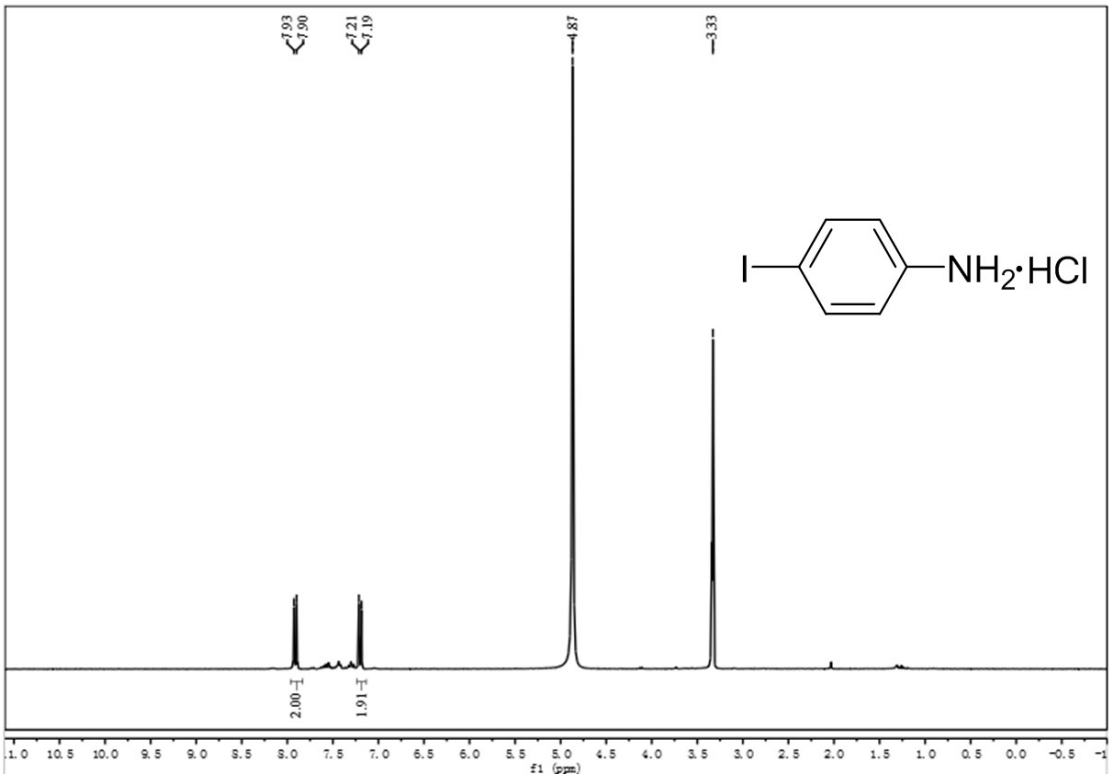
4-Chloroaniline (Table 3, entry 2):



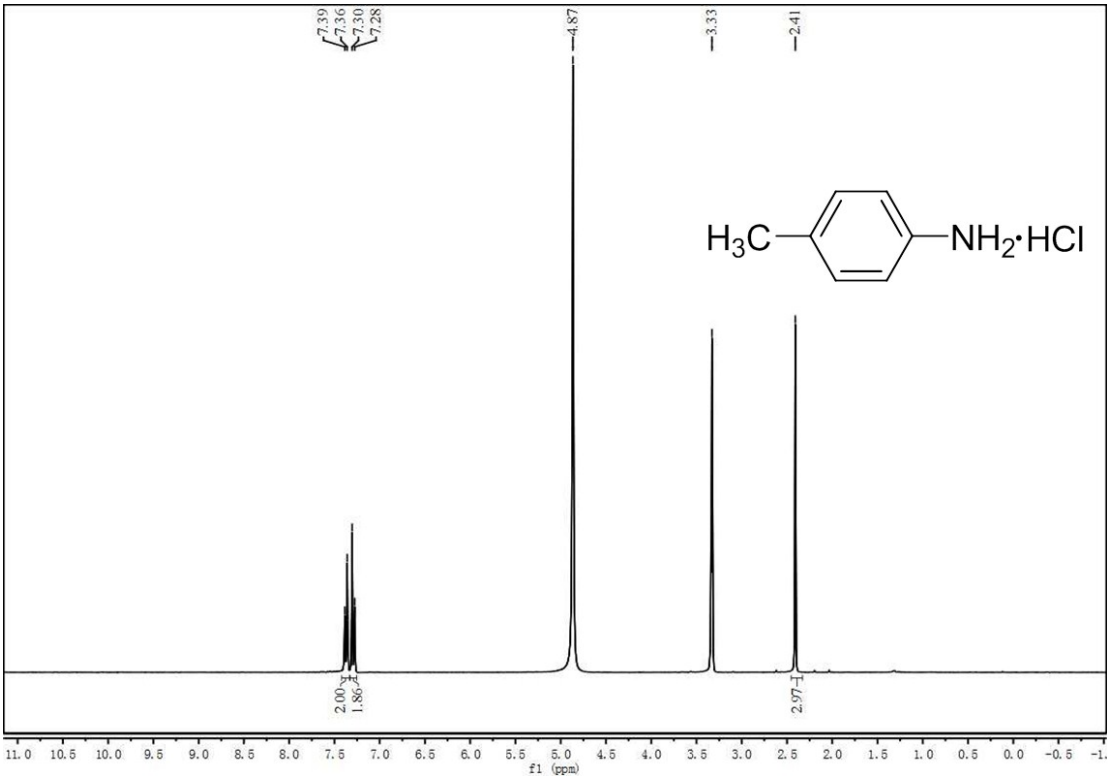
4-Bromoaniline hydrochloride (Table 3, entry 3):



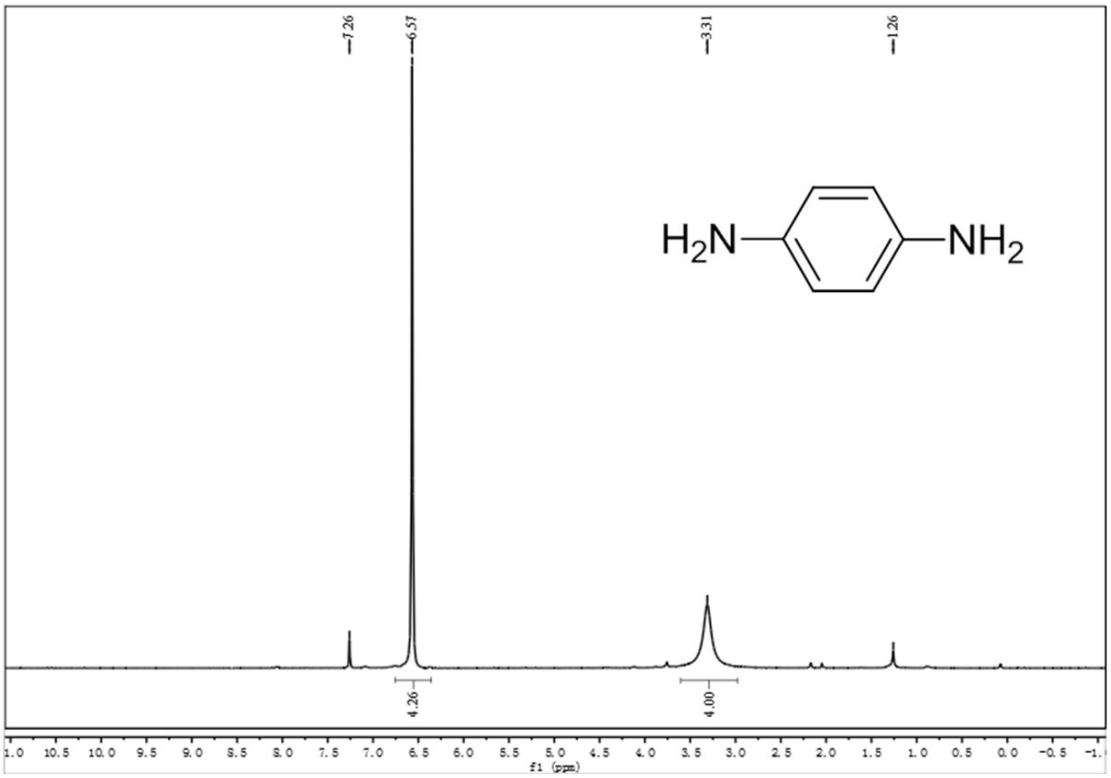
4-Iodoaniline hydrochloride (Table 3, entry 4)



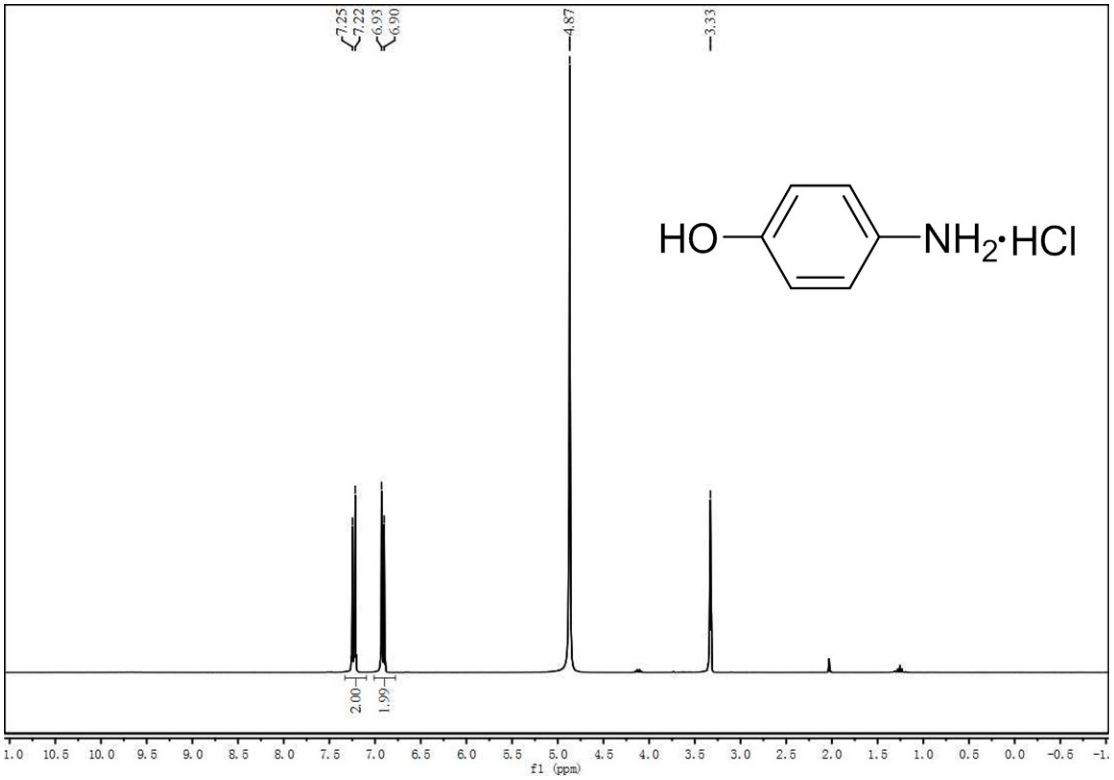
4-Methylaniline hydrochloride (Table 3, entry 5)



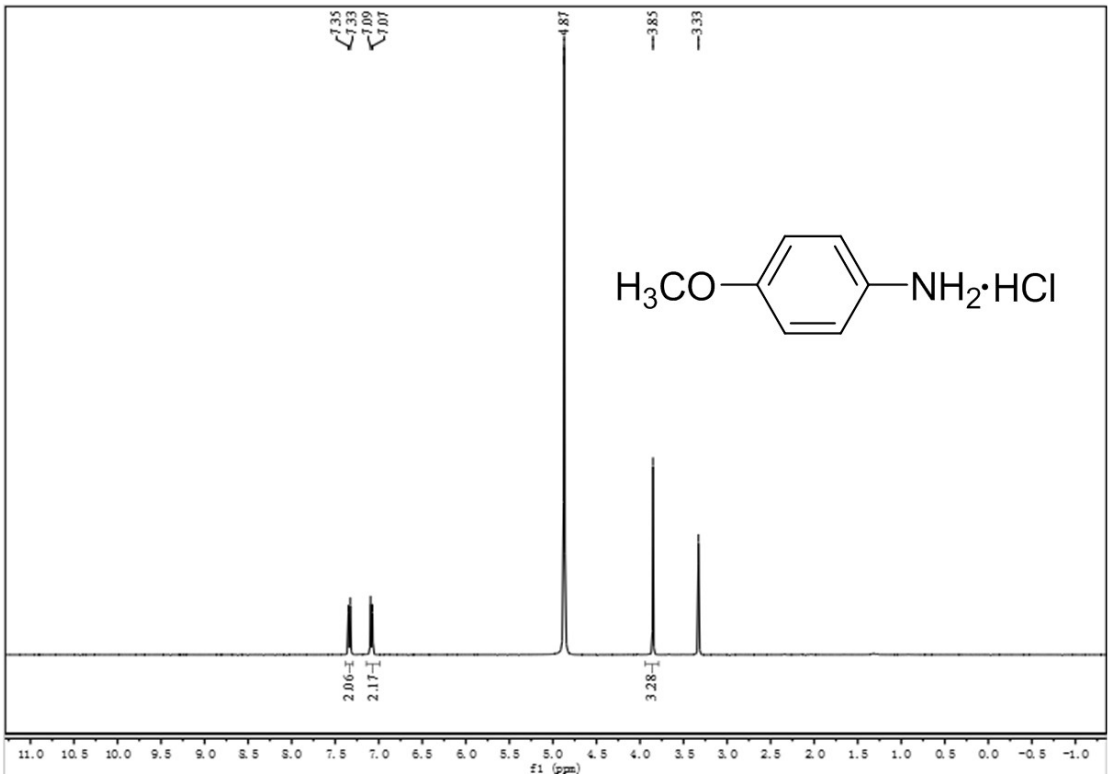
4-Nitroaniline (Table 3, entry 6)



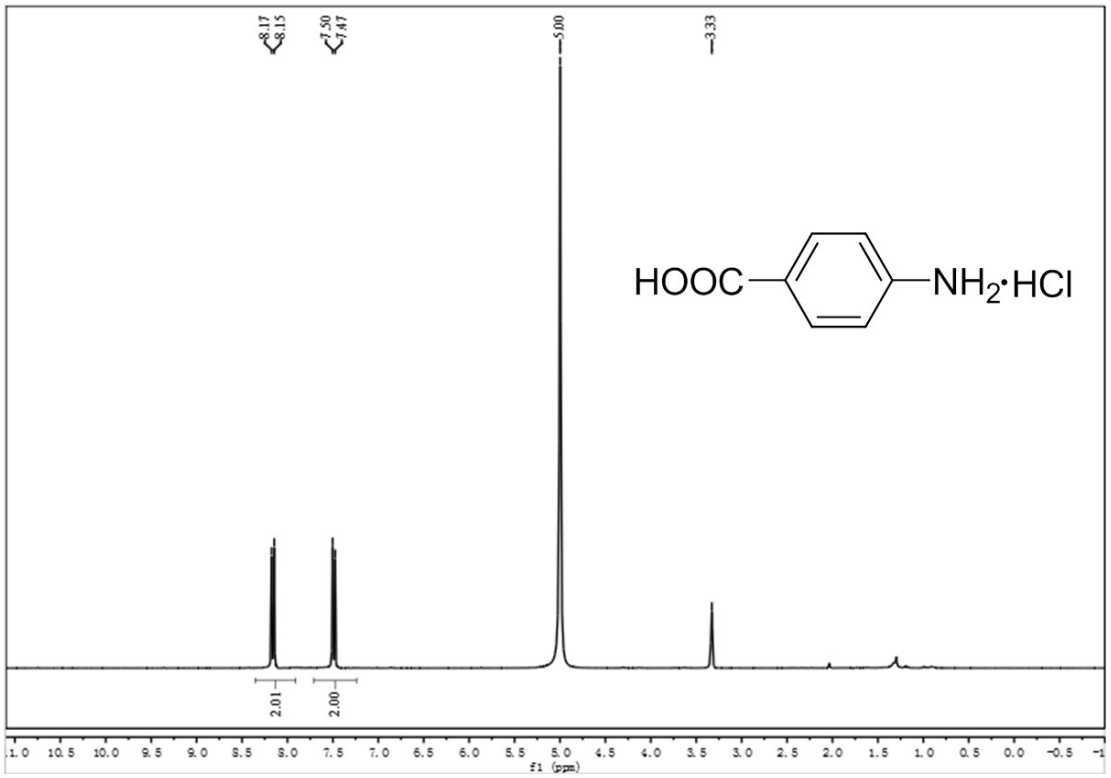
4-Aminophenol hydrochloride (Table 3, entry 7)



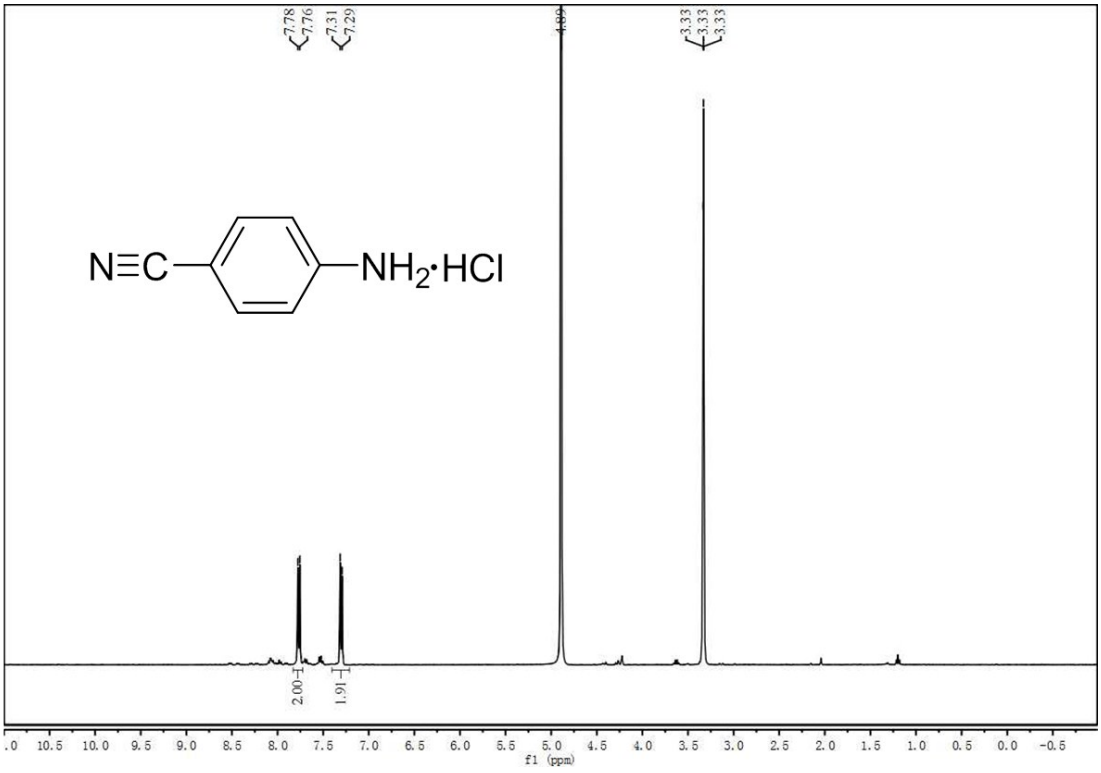
4-Methoxyaniline hydrochloride (Table 3, entry 8)



4-Amino-benzoic acid hydrochloride (Table 3, entry 9)



4-Aminobenzonitrile (Table 3, entry 10)


7.78
7.76
7.31
7.29
4.89
3.33
3.33
3.33
N≡C
NH2·HCl
2.00
1.91
f1 (ppm)