Supplementary Information

Zn(0)-Catalyzed Mild and Chemoselective Hydrogenation of Nitroarenes

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1. Generals

All chemicals are purchased from Aladdin (Shanghai, China) and used as receipt without any further purification. All chemicals used are of the analytical grade. ^{1} H NMR recorded on the instrument Bruker Avance 400 ^{13}C NMR spectrum, ^{1}H NMR to 400 MHz, ^{13}C NMR recorded as 100 MHz, in all cases, $CDCl_3$ or DMSO-d_6 as solvent. All chemical shifts (δ) were quoted in parts per million and reported relative to an internal tetramethylsilane (TMS, δ 0.00) standard. Yields of some products were measured by HPLC analysis using a SHIMADZU instrument equipped with a Wonda Sil C18-WR column (5 μm).

The Transmission Electron Microscope (TEM) measurements were performed using a JEM 2100F microscope. The samples were dispersed in ethanol with ultrasonic for 5min and then dropped onto a carbon film on copper grid. And the instrument was operated at 200 kV. Inductively coupled plasma-optical emission spectrometer (ICP-OES) from Perkin Elmer Nexion 300 was used to identify the Zn content of the nanoparticles. Samples were prepared by digesting 10 mg of nanoparticles in 2.0 mL of H_2O_2 and 8ml aqua regia using constant temperature drying oven for 3 hours. The solutions was made up to 50 mL in standard flask and start to detect Zn.

X-ray diffraction (XRD) patterns was collected from 5^{o} to 90^{o} with a step of 0.02 on a Bruker D 8 Advance diffractometer with Cu Kα radiation (λ = 1.5418 Å) and a Lynxeye one-dimensional detector. Elemental analysis (EA) measurement was performed using the Flash 2000. X-Ray photoelectron spectroscopy (XPS) measurements were obtained in ultra-high vacuum (base pressure of 1×10^{-10} mbar) equipped with an Al source (Kα radiation of 1486.6 eV) and an Escalab 250Xi analyser at 53^{o} detection angle. The number of active atoms were determined by chemisorption analysis of hydrogen under 50^{o}C using an AutoChem II 2920 instrument.

2. General procedure for the preparation of Zn-ligands

To a round bottle, the ligand (0.1 mmol) dissolved in HBF_4 (40%, 800μl) was added, and then sodium nitrate (13.8mg, 0.2mmol) dissolved in ultrapure water (1ml) was dropwise introduced. The solution was stirred at 0^{o}C for 1 h, subsequently, which was introduced to another reaction kit containing toluene (2.5ml), ultrapure water(2ml) and zinc chloride ($ZnCl_2$, 0.2mmol, 27.2mg)，the resulted mixture was stirred for another 1h. $NaBH_4$ (30mg, 0.8mmol) dissolved in ultrapure water(1ml) was dropped slowly at room temperature to the previous solution and incubated at room temperature for 2 h. The mixture was transferred to a separatory funnel, washed three times with water, and the aqueous phase was separated, and centrifuged in a 10 ml centrifuge tube to separate the solution. The solid was washed with ethanol, and sonicated for 20 minutes, and centrifuged, the resulted solid was dried to provide Zn-ligands.

3. Schematic profile of catalytic behavior with pH

The selectivity of Zn-L_4 toward the nitrobenzene of the model substrate for the desired product aniline at different pH conditions was evaluated by employing Zn-L_4 at the loading of 20 mol%. The results are shown in **Figure S1**. Results indicated that the yield increased firstly and then decreased with pH. When at pH = 7.0, the yield reached the highest one. We did not observe any obvious vibration in the selectivity of Zn-L_4 when processed at varying pHs (**Figure S1**), which almost kept constant at about 99.9%. The above results demonstrated that the

selectivity of the catalyst Zn-L_4 was pH-tolerant, though obvious decline in its activity from its highest point when at pH=7.0 was observed.

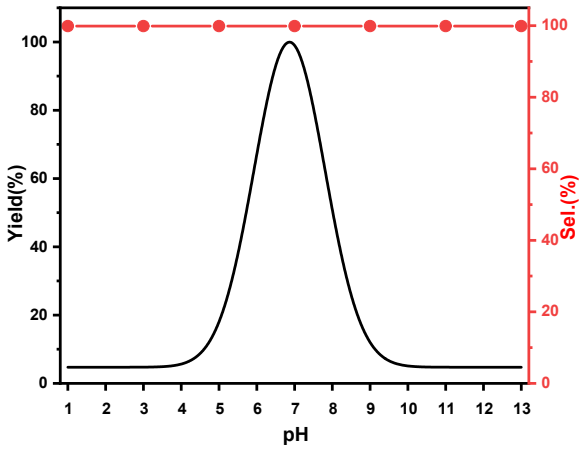

Figure S1. Profile of selectivity and yields with pH

4. Experimental Procedures

4.1 General procedure for the hydrogenation of nitroarenes

The nitroarene (0.05 mmol) and Zn-L_4 (2.5 mg, 20 mmol%) were introduced to a dry reaction flask (25 ml) filed H_2O (pH, 7.0) od 10mL equipped with a magnetic bar, the mixture was stirred with bottle mouth sealed with a balloon full of H_2 at 35°C. The process was monitored by TLC. Substrate conversions or product yields were determined by HPLC equipped with a reverse-phase C18 column. When reaction was completed, the solution was extracted with ethyl acetate, and then was washed with saturated brine (3 ×10 ml). The organic phase was combined, and dried over Na_2SO_4. Which was treated under vacuum to remove organic solvents, the resulted crude products were purified by chromatography using a silica-gel column to provide pure products. (since the reaction scale is small, the products were combined several times to obtain a higher concentration of the sample.)

4.2 General procedure for the selective hydrogenation of nitroarene mixed with equal equivalent of aryl ketones

To a dry flask (25 ml) equipped with a magnetic bar, 10 mL H_2O was added, and a mixture containing equal equivalents of nitroarene (0.05 mmol) and aryl ketone (0.05 mmol) was introduced, the pH of the resulted mixture was made at 7.0, which was stirred with a balloon full of H_2 at 35°C. The reaction mixture was monitored by TLC. Conversions of substrates or product yields were determined by HPLC equipped with a reverse-phase C18 column. When reactions were completed, the solution were extracted with ethyl acetate, and then washed with saturated brine (3×10 ml). The organic solvents were removed under vacuum to provide crude oil and was dried by over anhydrate Na_2SO_4 to afford crude products, which were purified by chromatography to provide pure products (since the reaction scale is small, the products can be combined several times to obtain a higher concentration of the sample.)

4.3 General procedure for the selective hydrogenation of nitroarene mixed with equal equivalent of aryl olefins

To a dry flask (25 ml) equipped with a magnetic bar, 10 mL H_2O was added, and a mixture containing equal equivalents of nitroarene (0.05 mmol) and aryl olefins (0.05 mmol) was introduced, the pH of the resulted mixture was made at 7.0, which was stirred with a balloon full of H_2 at 35°C. The reaction mixture was monitored by TLC. Conversions of substrates or product yields were determined by HPLC equipped with a reverse-phase C18 column. When reactions were completed, the solution were extracted with ethyl acetate, and then washed with saturated brine (3×10 ml). The organic solvents were removed under vacuum to provide crude oil and was dried by over anhydrate Na_2SO_4 to afford crude products, which were purified by chromatography to provide pure products (since the reaction scale is small, the products can be combined several times to obtain a higher concentration of the sample.)

5. Elemental analysis and ICP-OES of Zn-NPs (Zn-L_4)

The Elemental analysis showed that an average of one metal atom of zinc was found for each ligand, indicating that the ratio between nitrogen and zinc elements (mol) is N: Zn = 2 :1.

Table S1 Elemental analysis（EA）and inductively coupled plasma-optical emission spectrometer (ICP-OES) of Zn-NPs

Content (wt%)			
C[a]	H[a]	N[a]	Zn[b]
48.11	3.86	11.23	28.68

[a] Measured by elemental analysis (EA). [b] Measured by inductively coupled plasma-optical emission spectrometer (ICP-OES).

6. H-H COSY spectrum and ^{13}C NMR analysis of the catalyst

In order to demonstrate that these signals originate from Zn-bound 1,8-diaminonaphthalene while not from desorbed ligand molecules, a certain amount of 1,8-diaminonaphthalene was mixed at an unequal equivalent (**Figure S2**). This leads to the appearance of a second set of ^{1}H signals which can be assigned to

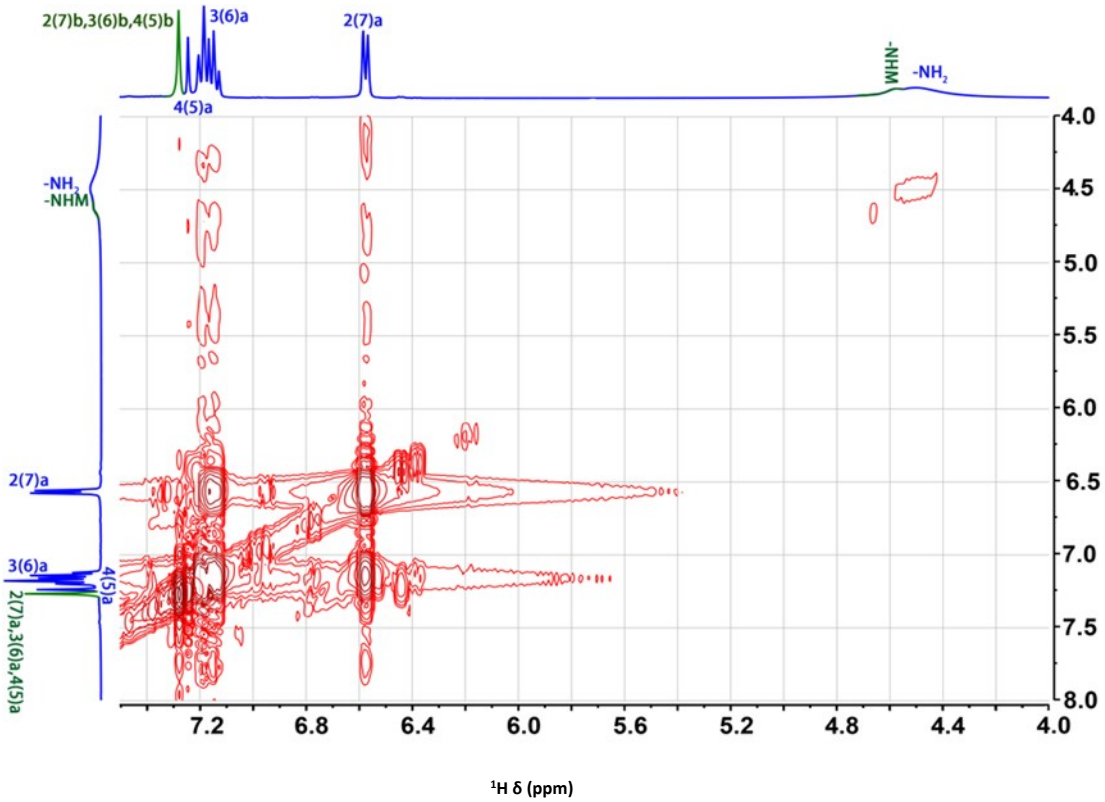

Fig. S2 ^{1}H and HH-COSY spectrum (360 MHz, 8.4 T, DMSO) of a mixture of free 1,8-diaminonaphthalene (blue) and Zn bound 1,8-diaminonaphthalene (green).

free 1,8-diaminonaphthalene in alkaline D_2O. Identification of the signals that belong to the same molecule can be verified by correlations in the HH-COSY spectrum (**Figure S2**), confirming the Zn-bound ligand is 1,8-diaminonaphthalene. It can thus be distinguished between unbound- (in **blue, Figure S3**) and Zn-bound 1,8-diaminonaphthalene (in **green, Figure S3**). The ^{1}H signals of the two inequivalent protons are labelled with 2a and 2b in **Figure S2**. Comparison of the same protons in free- and Zn-bound-1,8-diaminonaphthalene shows that the signals of 2(7) are considerably more shifted than the 3(6), and 4(5) protons (numbering according to **Figure S2**). This effect may be related to the fact that these protons are in closer proximity to the carbon atom which is chemically altered due to the binding to Zn. Besides, the ^{1}H signals of -NH_2 at 4.46ppm in free 1,8-diaminonaphthalene was chemically shifted to 4.52 after bound to Zn and the fact that ^{13}C signals of Zn-bound 1,8- diaminonaphthalene were chemically shifted confirmed the chemically binding state of Zn-bound 1,8-diaminonaphthalene as well (**Figure S4**).

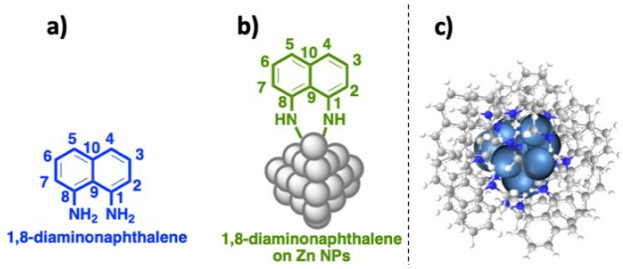

Fig. S3 Structures of: a) unbound 1,8-diaminonaphthalene (blue) and b) Zn-bound 1,8-diaminonaphthalene (green) under alkaline conditions, and c) the proposed possible structure of Zn-NPs

A comparison of ^{13}C NMR spectra of pure ligand and Zn bound 1,8-diaminonaphthalene was made, as shown in **Figure S4**, the fact that the ^{13}C signals of the Zn-bound 1,8-diaminonaphthalene undergoes an obvious shift proved the chemical binding state as well (**Figure S4**).

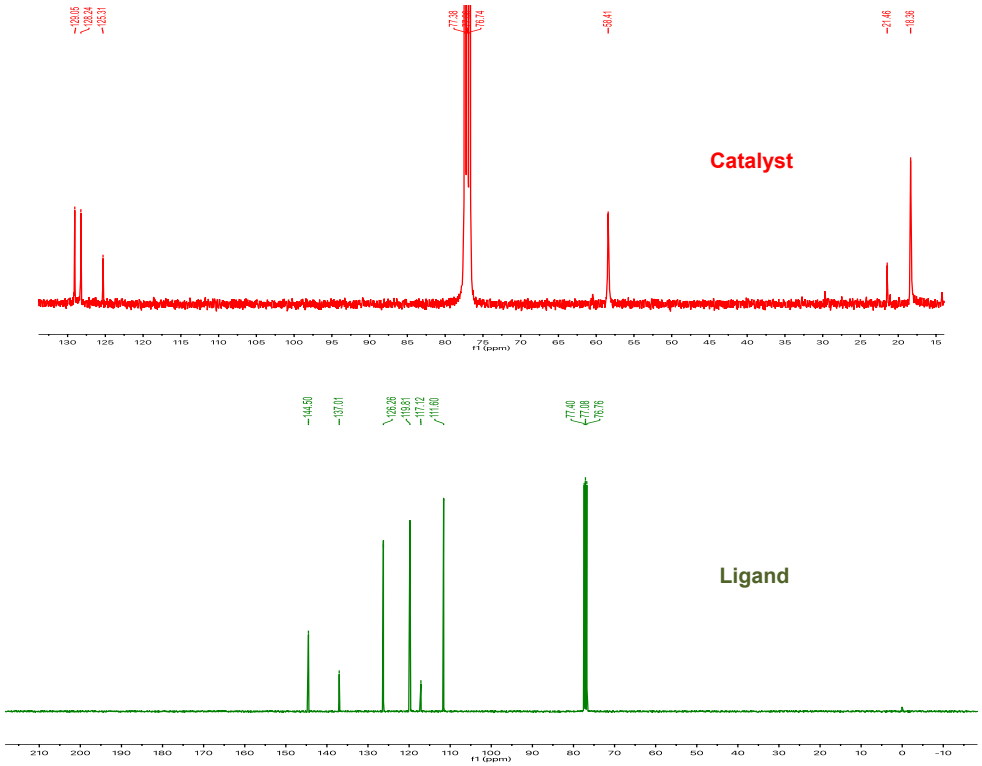

Figure S4. ^{13}C NMR spectra of pure 1,8-diaminonaphthalene (green) and Zn bound 1,8-diaminonaphthalene (red)

7. Recycling of Zn-NPs

The recyclability of the Zn-NPs were tested using nitrobenzene. When reaction was completed, the reaction mixture was placed stationary for one hour, and remove the organic phase. The resulting solid was washed using ethanol and dried under vacuum. Followed is the employment of the recycled Zn-NPs to catalyze a second round of reactions, and then a third, and the results were summarized in **Figure S5**,which indicated that the Zn-NPs could be repeated at least four times without any obvious loss in its catalytic activity, nor in its selectivity.

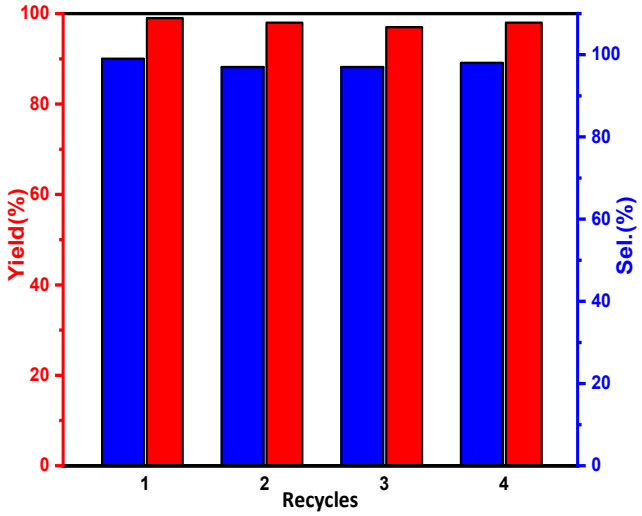

Figure S5 Catalytic recycles of Zn-NPs

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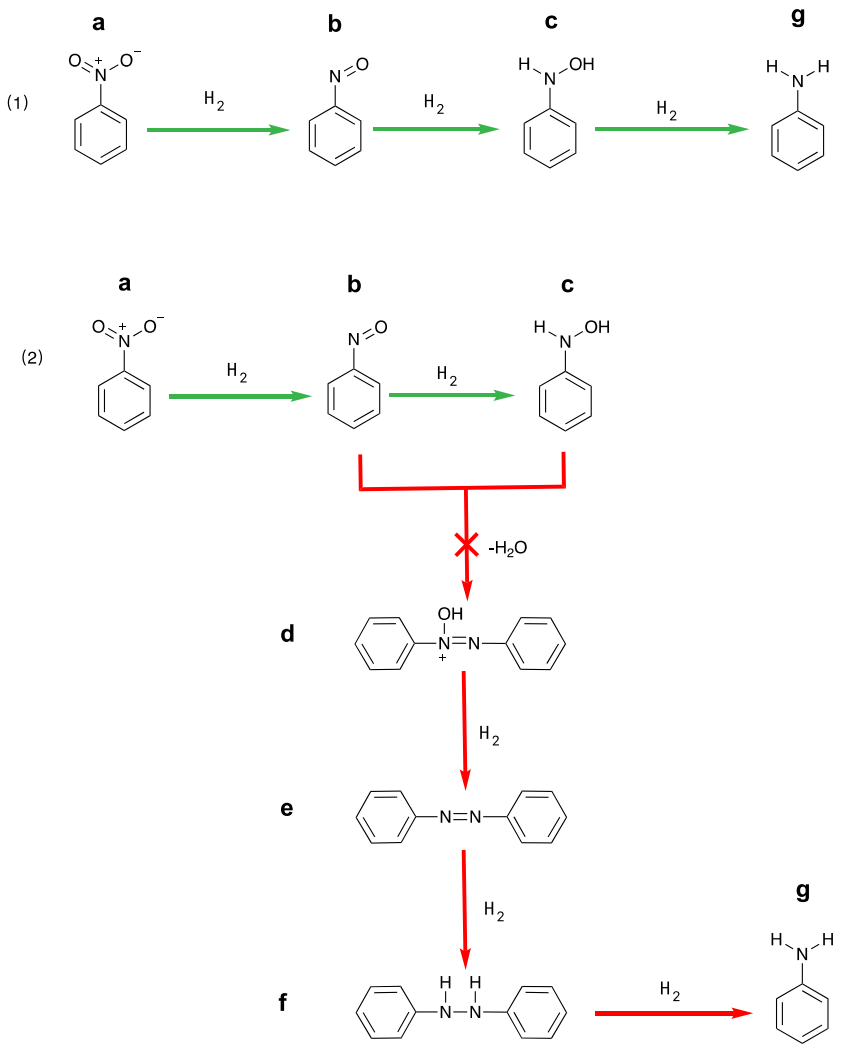
8. *Exploration of the reaction mechanism*

By referencing some publications,[1] there might be two possible synthetic routes towards the hydrogenation of the nitrobenzene (**Figure S6**). Based on the reaction facts that during reaction, the formation of some intermediates, for instance, nitrosobenzene (**b**) was detected by HPLC analysis by comparing with standard samples (**Figure S7a**), confirming the formation of **b** from **a** with H_2. However, the formation of stable intermediates azobenzene (**e)** was not detected (**Figure S7b**). Consequently, it confirmed that **b** continued to form **c** and then to **g** under H_2, which didn't react with **c** to form an unstable compound **d**, and further to generate **e**. Therefore, in summary, route (1) seems more plausible, and the proposed reaction mechanism was presented in **Figure 4** in the maintext.



. **Figure S6.** Probable mechanism for nitro compounds reduction.

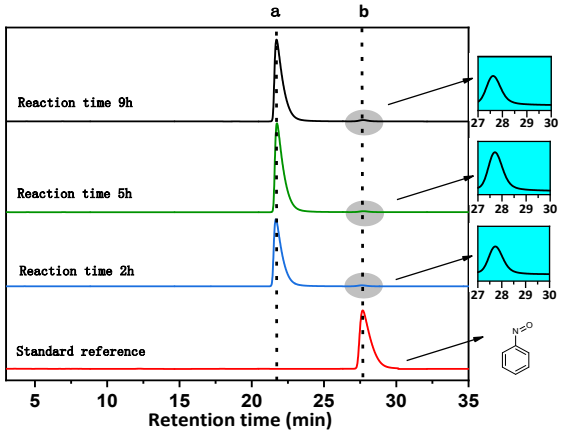


Figure S7a

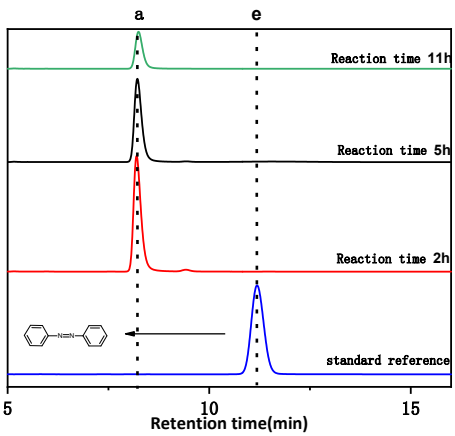
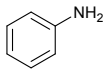


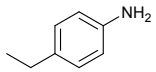
Figure S7b

Figure S7. HPLC analysis for exploring possible mechanism

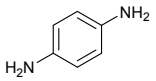
9.Characterization data for all products



aniline **^{1}H NMR (400MHz, $CDCl_3$)**: δ (ppm) 7.31-7.27 (m 2H), 6.92-6.88 (m 1H), 6.78-6.76 (m 2H), 3.71 (brs 2H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ (ppm) 146.64, 129.43, 118.60, 115.25.

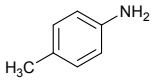


4-ethylaniline **^{1}H NMR (400MHz, $CDCl_3$)**: δ (ppm) 7.08-7.06 (m 2H), 6.72-6.68 (m 2H), 3.60 (brs 2H), 2.64-2.59 (m 2H), 1.28-1.24 (m 3H).**^{13}C NMR (100MHz, $CDCl_3$)**: δ (ppm) 144.09, 134.49, 128.63, 115.32, 28.03, 16.00.

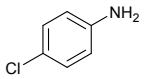


benzene-1,4-diamine **^{1}H NMR (400MHz, $CDCl_3$)**: δ (ppm) 6.37 (s 4H), 4.18 (brs 4H). **^{13}C NMR (100MHz, $CDCl_3$)**:

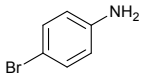
δ (ppm) 139.39, 115.92.



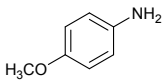
p-toluidine **^{1}H NMR (400MHz, $CDCl_3$)**: δ (ppm) 6.95 (d *J* = 8.0Hz 2H), 6.58 (d *J* = 8.0Hz 2H), 3.49 (brs 2H), 2.23 (s 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ (ppm) 143.90, 129.81, 127.80, 115.32, 20.50.



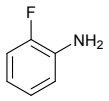
4-chloroaniline **^{1}H NMR (400MHz, $CDCl_3$):** δ (ppm) 7.16-7.12 (m 2H), 6.67-6.63 (m 2H), 3.68 (brs 2H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ (ppm) 144.97, 129.13, 123.16, 116.25.



p-bromo Aniline **^{1}H NMR (400MHz, $CDCl_3$)**: δ (ppm) 7.31-7.26 (m 2H), 6.63-6.59(m 2H), 3.71(brs 2H).**^{13}C NMR (100MHz, $CDCl_3$)**: δ (ppm) 145.44, 132.03, 116.73, 110.21.

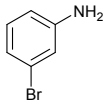


4-methoxyaniline **^{1}H NMR (400MHz, $CDCl_3$)**: δ (ppm) 6.74-6.70 (m 2H), 6.63-6.59 (m 2H), 3.71 (s 3H), 3.42 (brs 2H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ (ppm) 152.78, 140.12, 116.44, 114.86, 55.75.

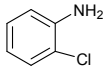


2-fluoroaniline **^{1}H NMR (400MHz, $CDCl_3$)**: δ (ppm) 7.07-6.97 (m 2H), 6.85-6.73(m 2H), 3.77 (brs 2H).

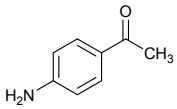
^{13}C NMR (100MHz, $CDCl_3$): δ (ppm) 151.76 (d *J* = 237.0 Hz), 134.52 (d *J* = 13.0 Hz), 124.47 (d *J* = 4.0 Hz), 118.66 (d *J* = 7.0 Hz), 115.25 (d *J* = 19.0 Hz).



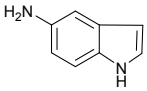
3-bromoanilines **^{1}H NMR (400MHz, $CDCl_3$)**: δ (ppm) 7.07-7.03 (m 1H), 6.93-6.87 (m 2H), 6.64-6.61 (m 1H), 3.75 (brs 2H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ (ppm) 147.84, 130.64, 123.05, 121.36, 117.83, 113.67.



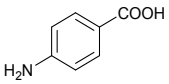
o-chloroaniline **^{1}H NMR (400MHz, $CDCl_3$)**: δ (ppm) 7.31-7.29 (m 1H), 7.14-7.10 (m 1H), 6.82-6.73 (m 2H), 4.09 (brs 2H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ (ppm) 142.95, 129.44, 127.67, 119.31, 119.05, 115.91.



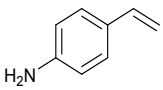
p-aminoacetophenone **^{1}H NMR (400MHz, $CDCl_3$)**: δ (ppm) 7.84-7.82(m 2H), 6.69-6.66(m 2H), 4.23(brs 2H), 2.53(s 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ (ppm) 196.57, 151.23, 130.82, 127.79, 113.72, 26.10.



5-Aminoindole **^{1}H NMR (400MHz, $CDCl_3$)**: δ (ppm) 10.58(s, 1H), 7.13-7.08(m,2H), 6.70(d,*J*=4.0Hz,1H), 6.51 -6.48(m,1H), 6.14-6.13(m,1H), 4.41(s,2H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ (ppm) 141.47, 130.22, 129.00, 12 5.19, 112.28, 111.84, 103.67, 100.08.

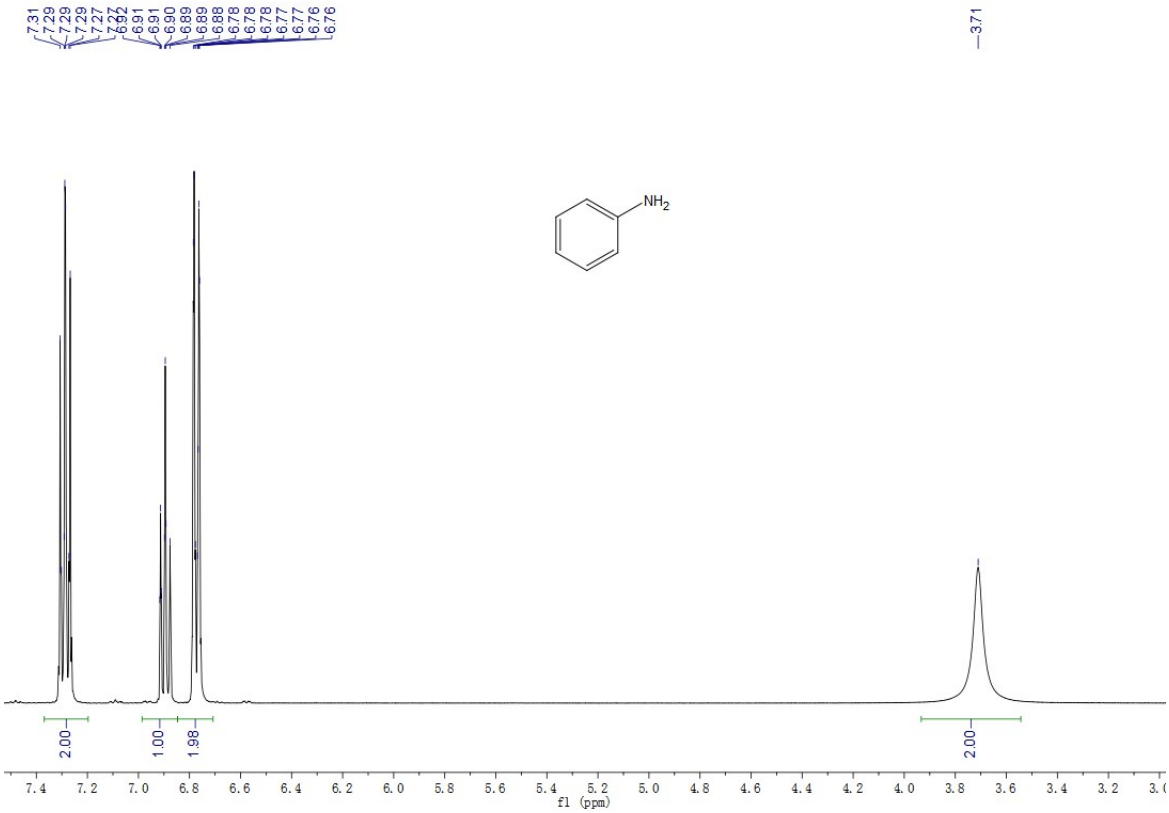


p-Aminobenzoic acid **^{1}H NMR (400MHz, $CDCl_3$)**: δ (ppm) 11.97(s,1H), 7.64-7.61(m,2H), 6.57-6.54(m,2H), 5.87(s,2H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ (ppm) 168.00, 153.61, 131.70, 117.34, 113.04.

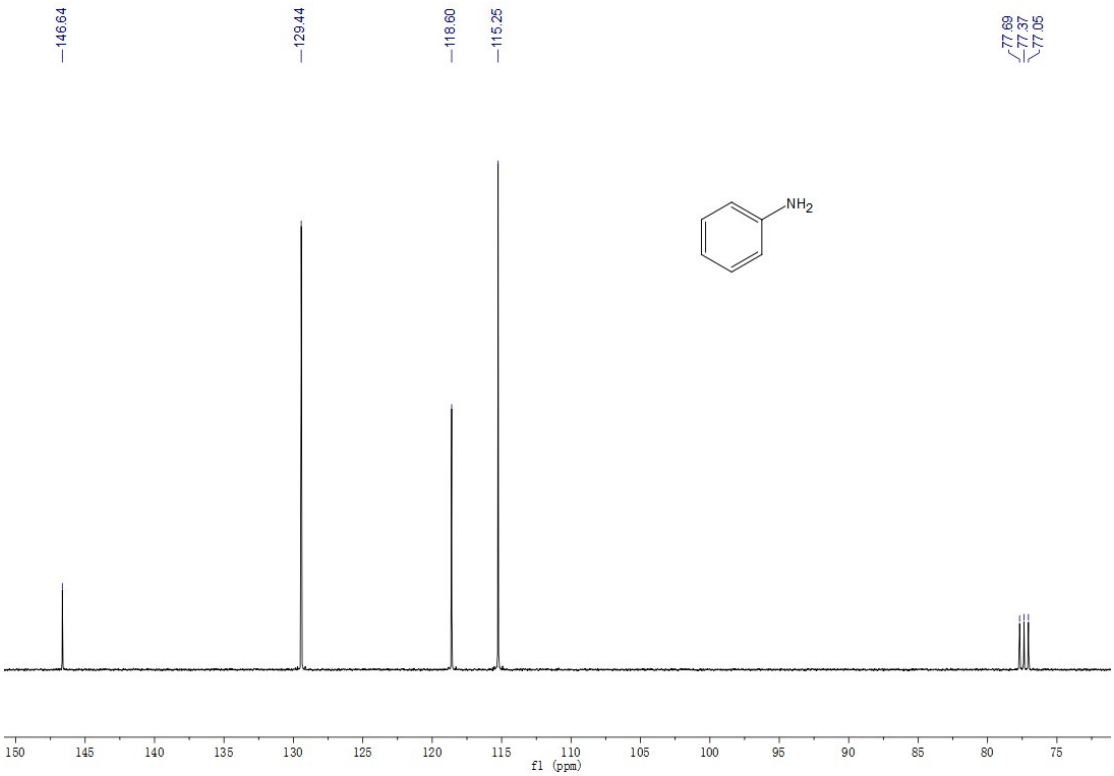


4-vinylaniline **^{1}H NMR (400MHz, $CDCl_3$)**: δ (ppm) 7.22-7.06(m, 2H), 6.64-6.46(m,3H), 5.50-5.44(m,1H), 5.23(s,2H),4.93-4.86(m,1H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ (ppm) 149.23, 137.39, 127.29, 125.53, 114.20, 108.69.

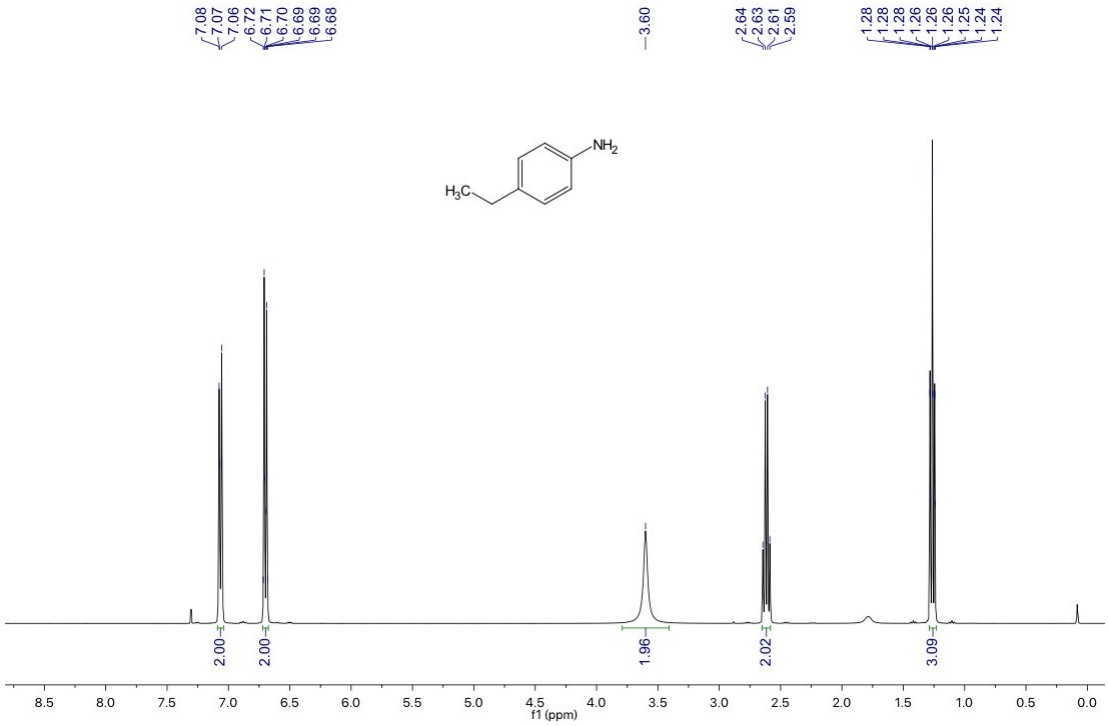
10. ^{1}H NMR and ^{13}C NMR spectra of products



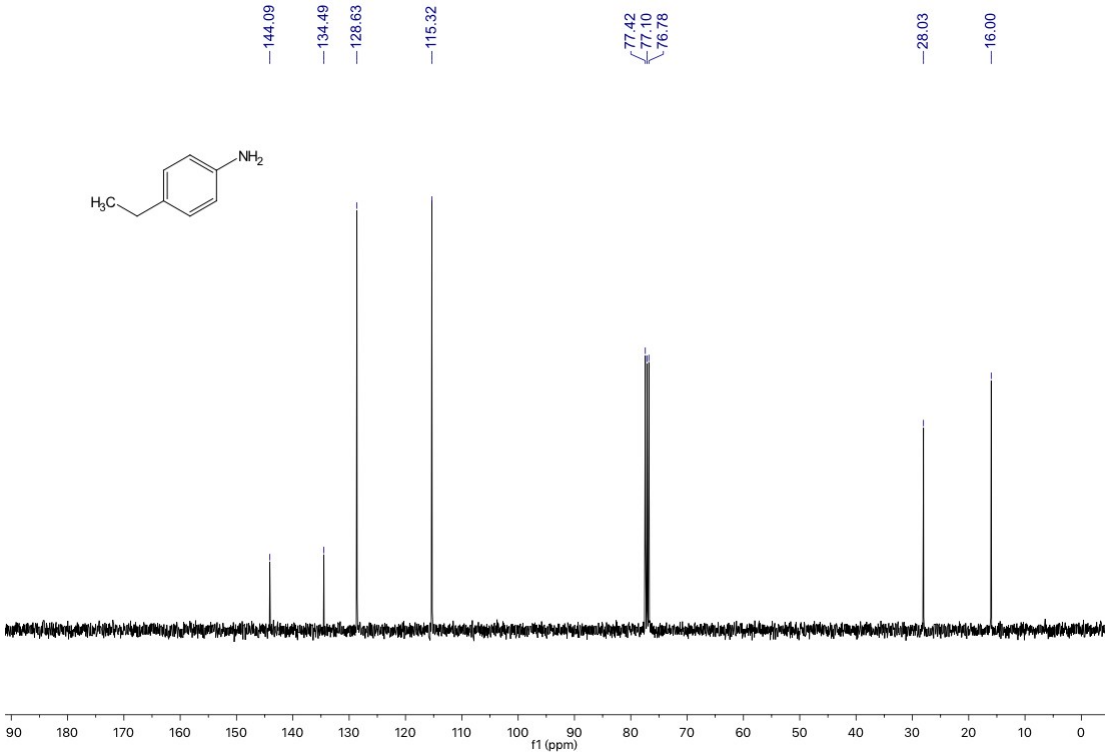
^{1}H NMR of aniline



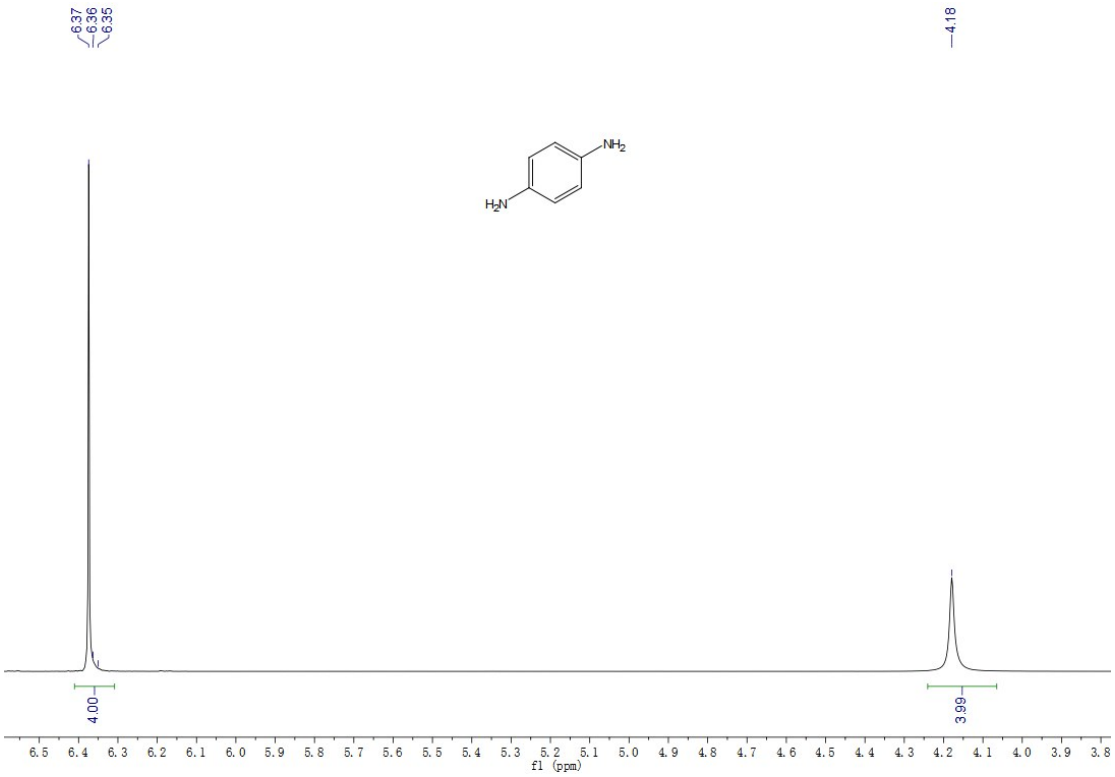
^{13}C NMR of aniline



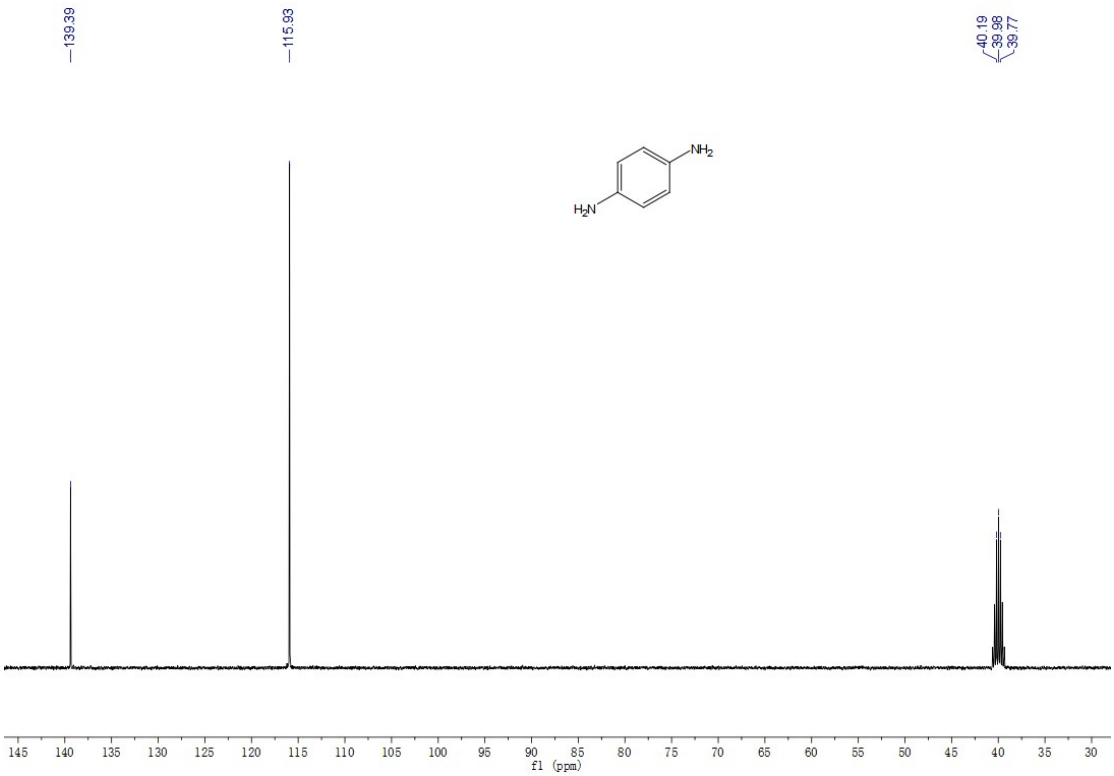
^{1}H NMR of 4-ethylaniline



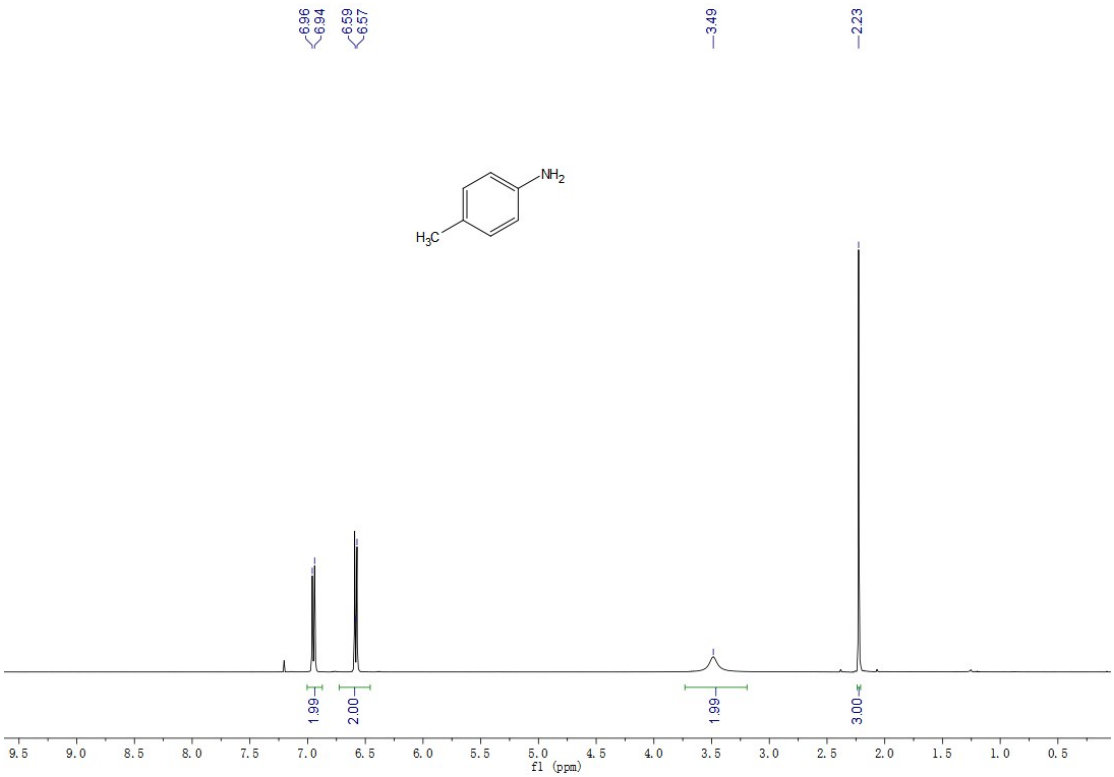
^{13}C NMR of 4-ethylaniline



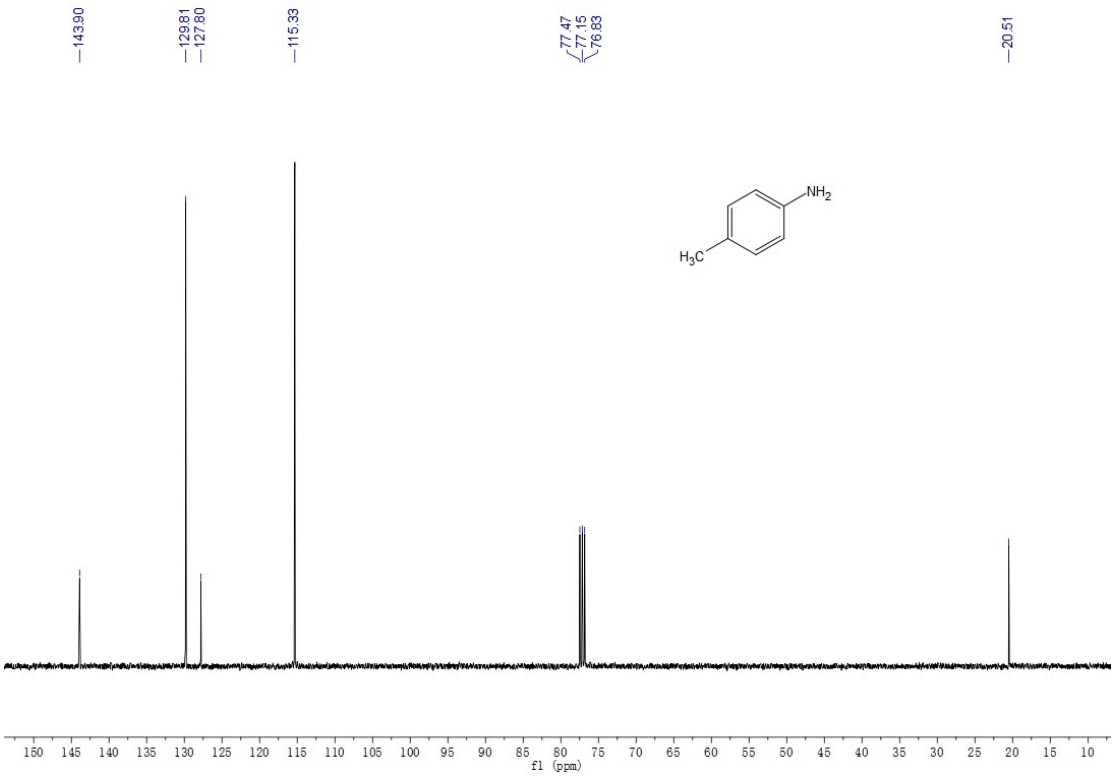
^{1}H NMR of benzene-1,4-diamine



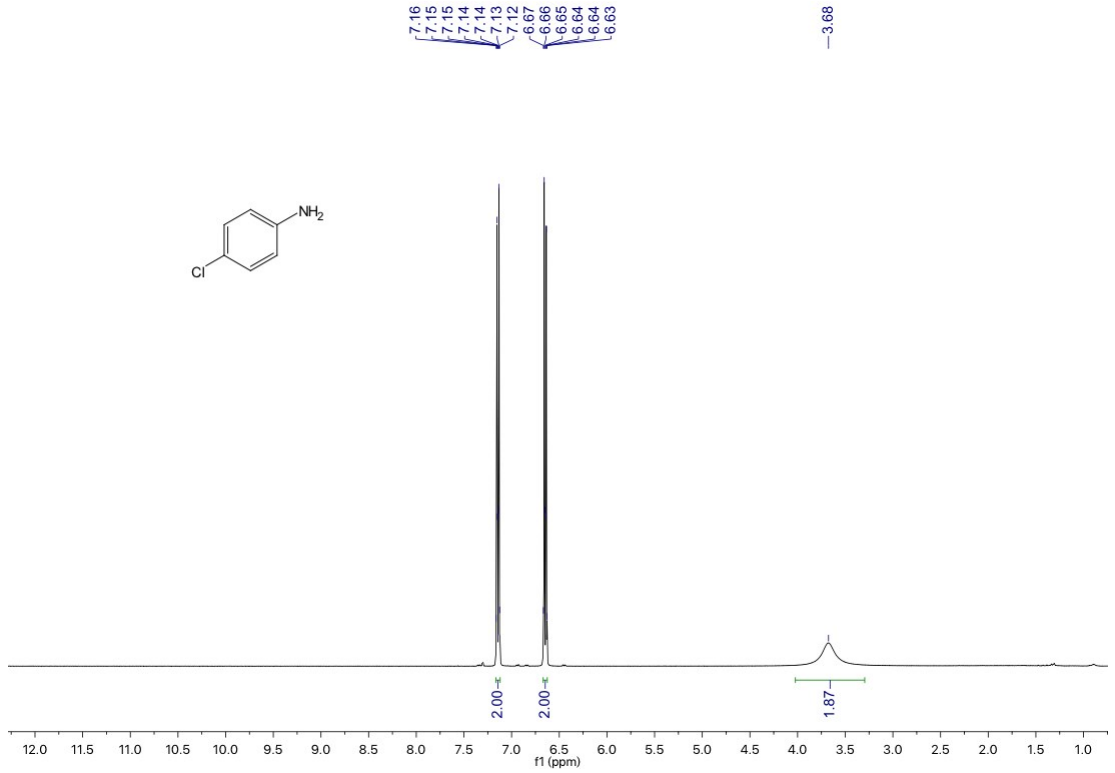
^{13}C NMR of benzene-1,4-diamine



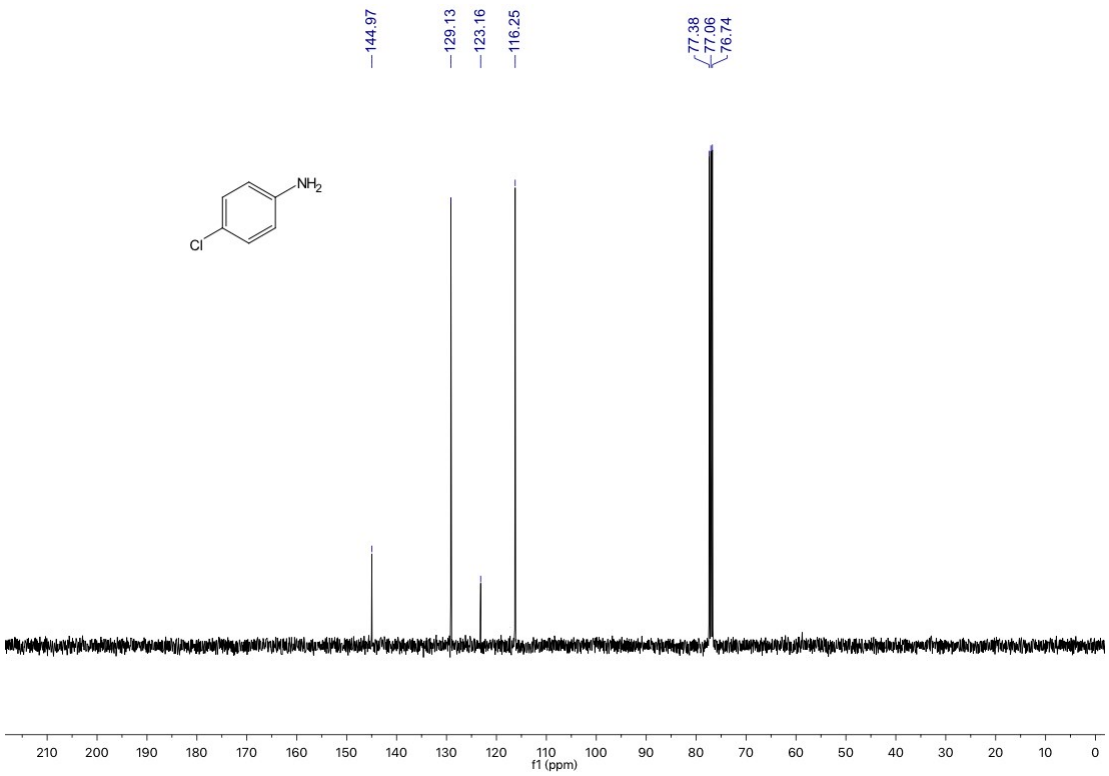
^{1}H NMR of *p*-toluidine



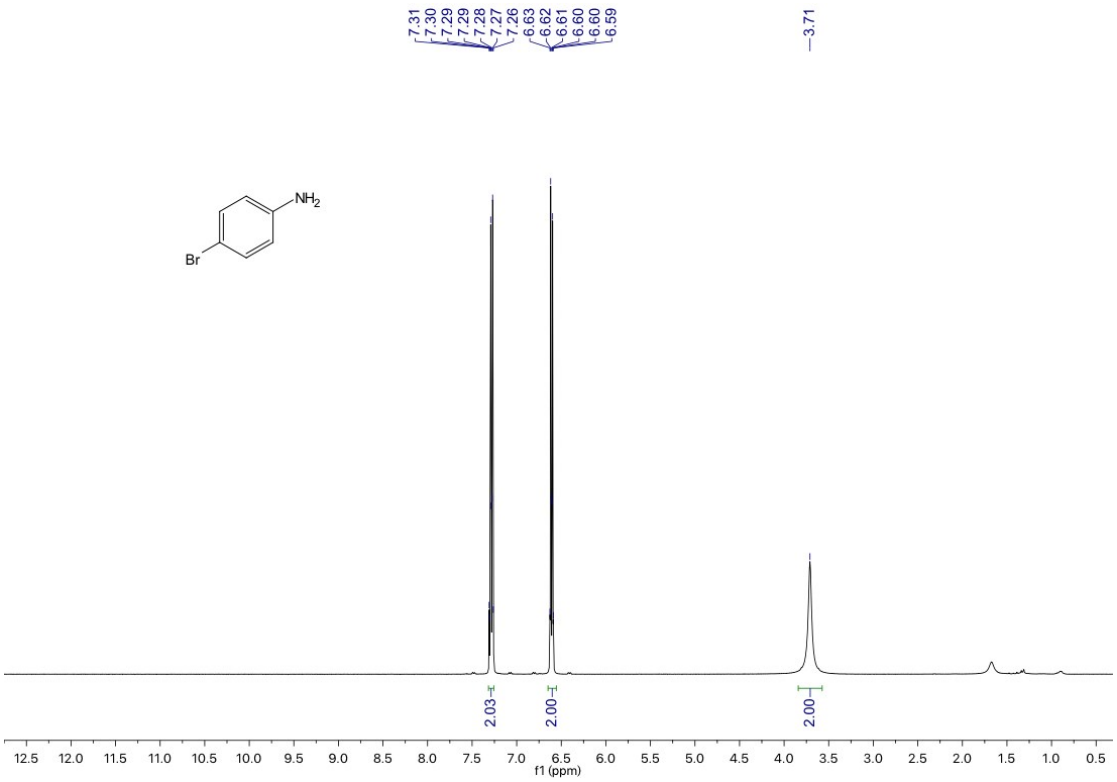
^{13}C NMR of *p*-toluidine



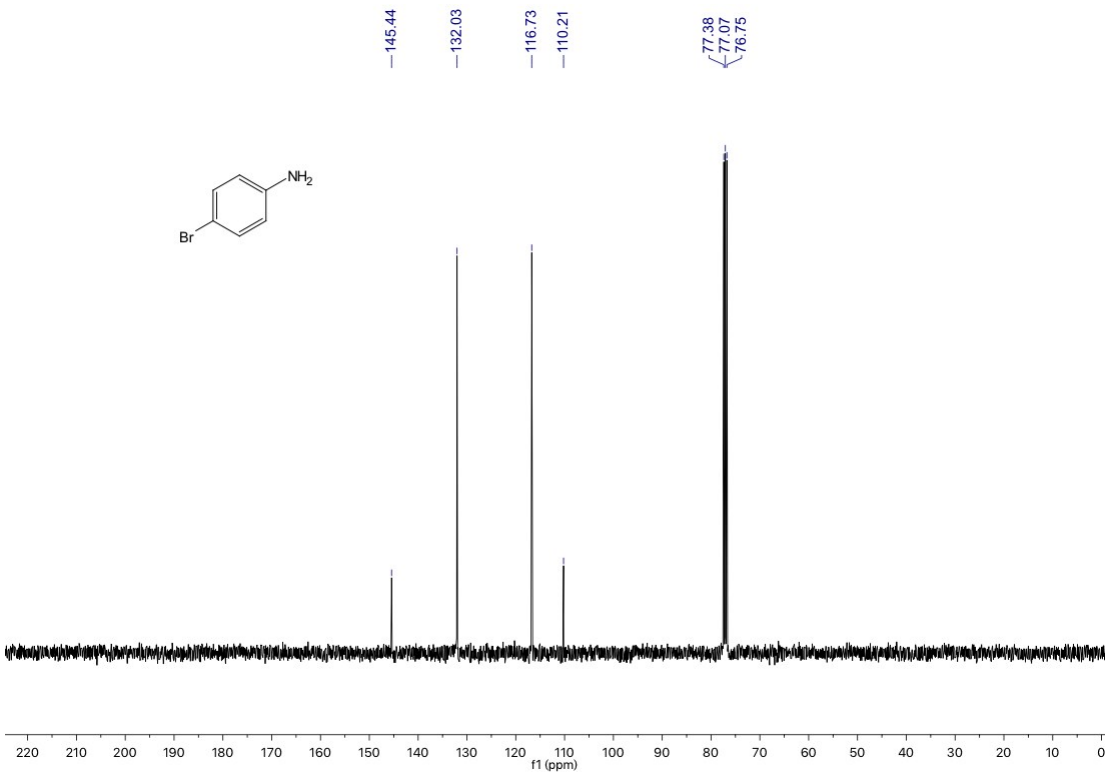
^{1}H NMR of 4-chloroaniline



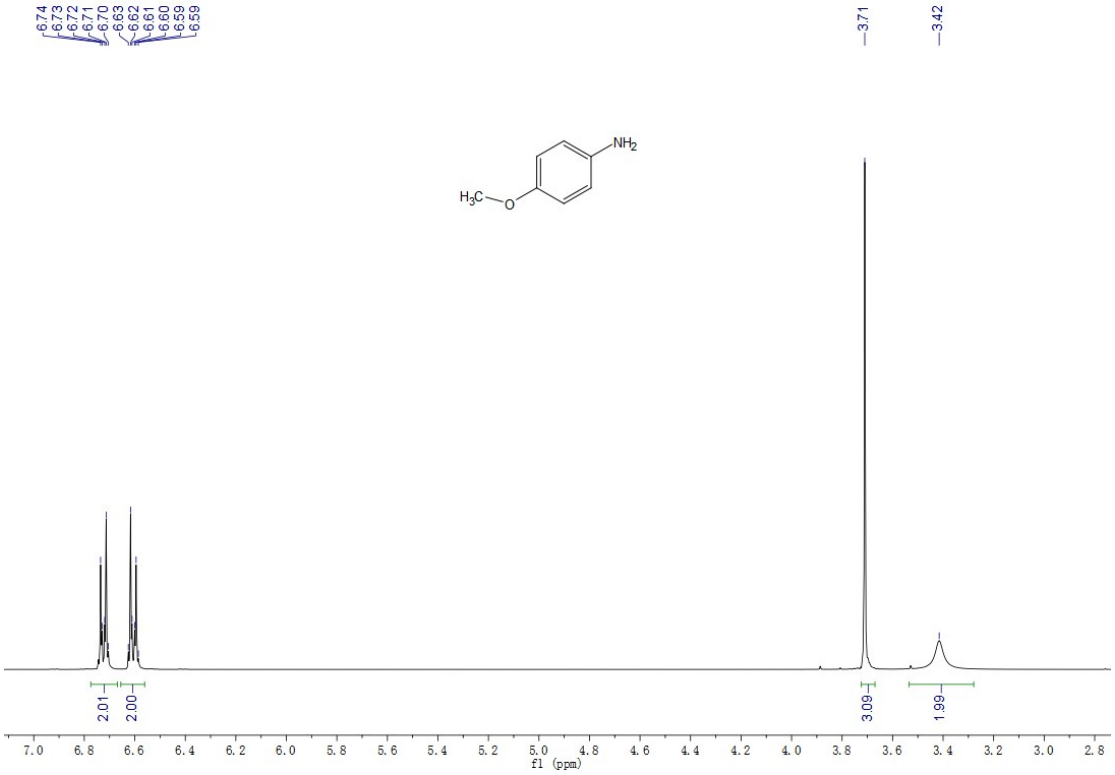
^{13}C NMR of 4-chloroaniline



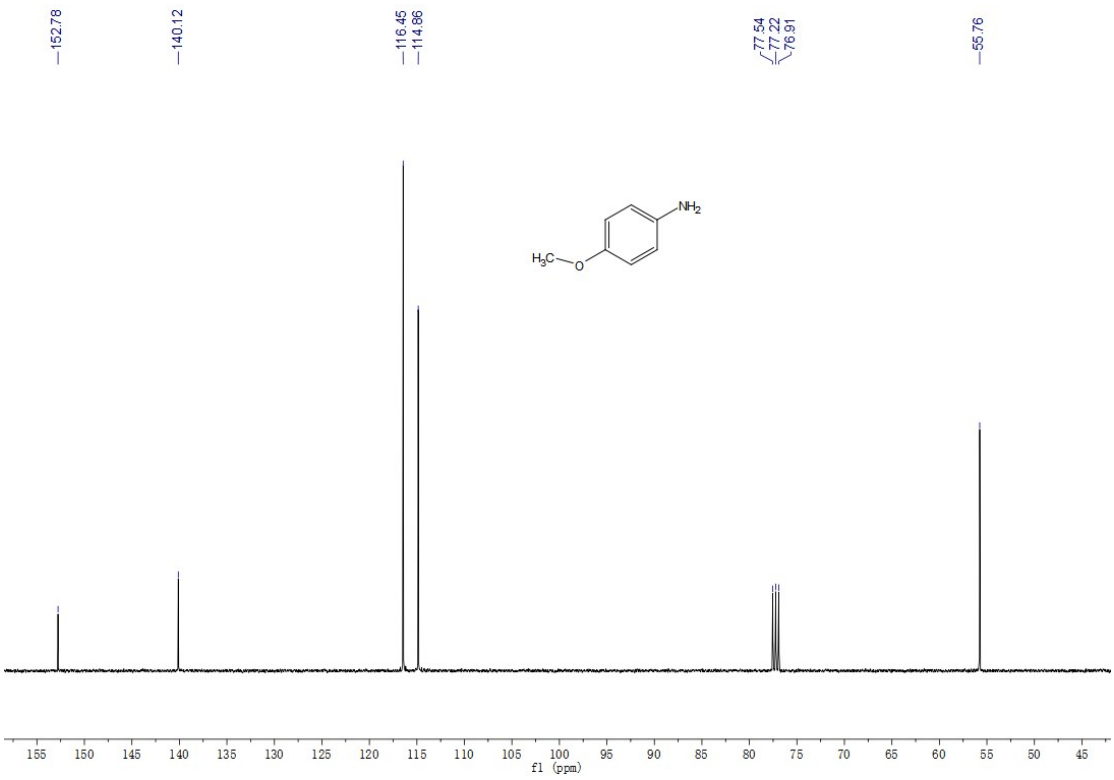
^{1}H NMR of *p*-bromo Aniline



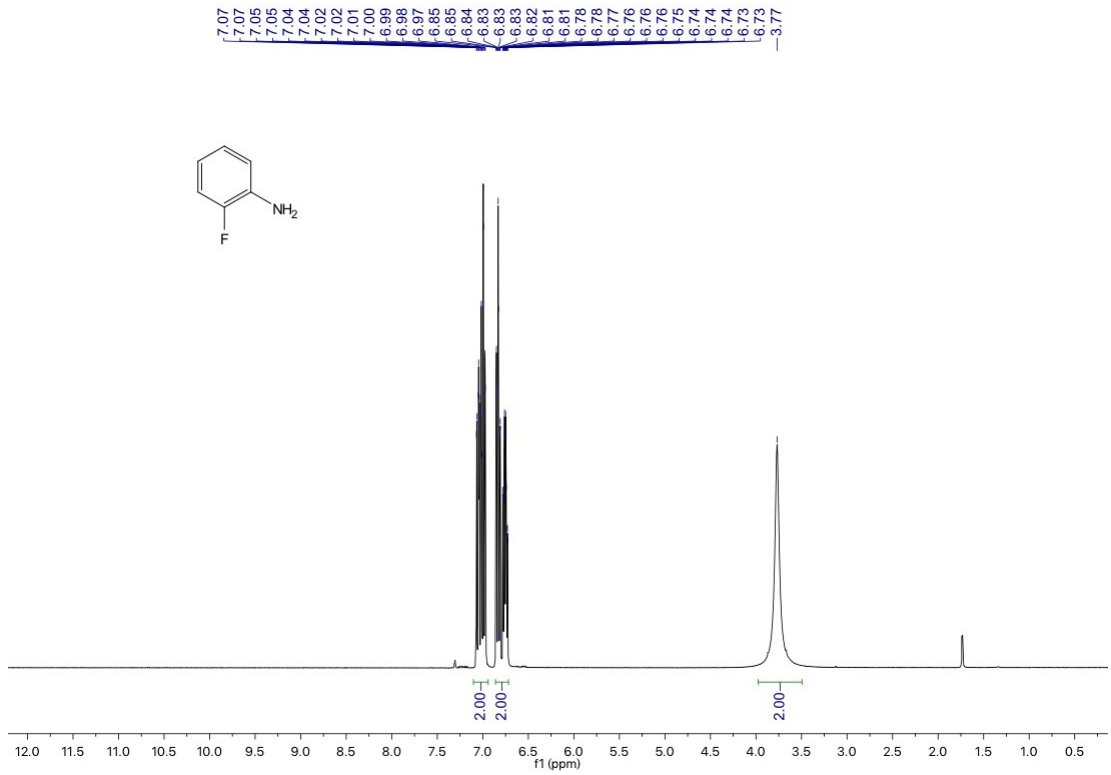
^{13}C NMR of *p*-bromo Aniline



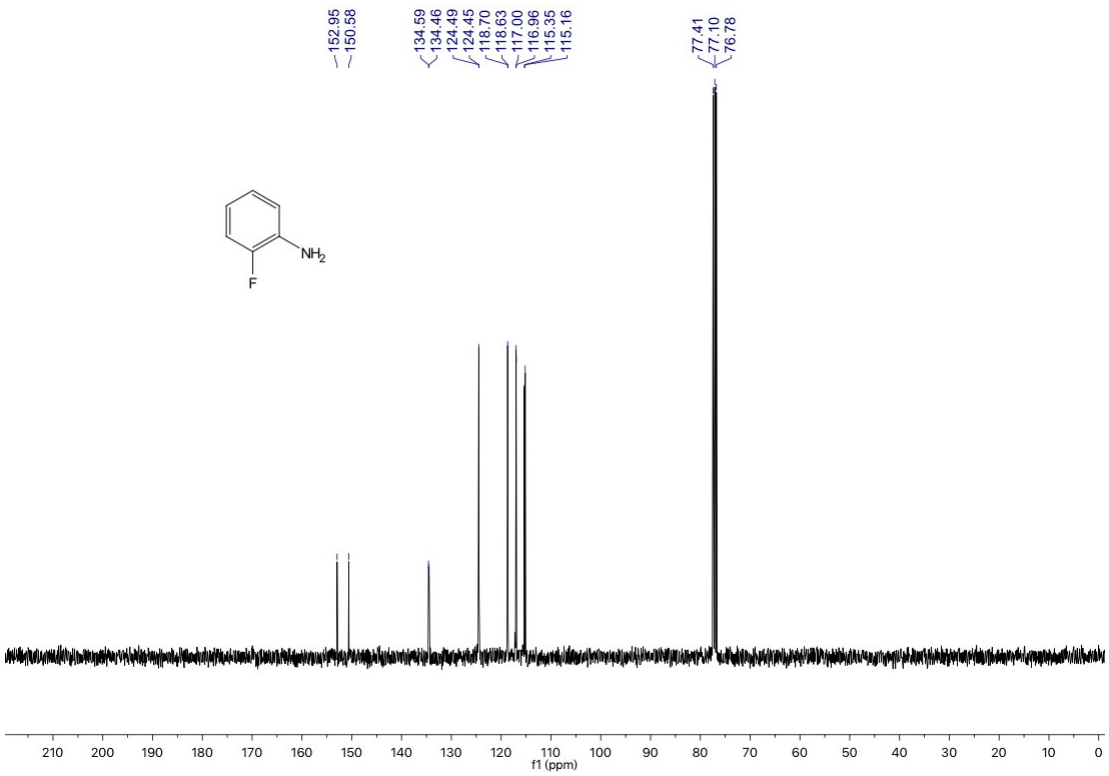
^{1}H NMR of 4-methoxyaniline



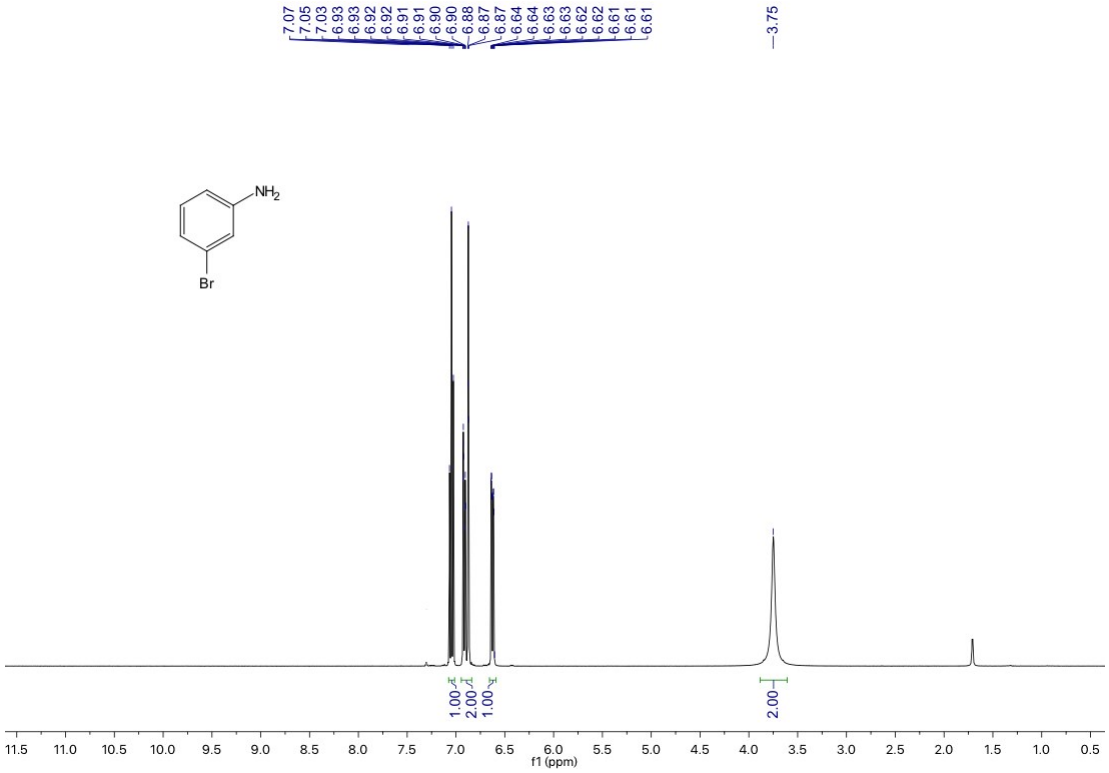
^{13}C NMR of 4-methoxyaniline



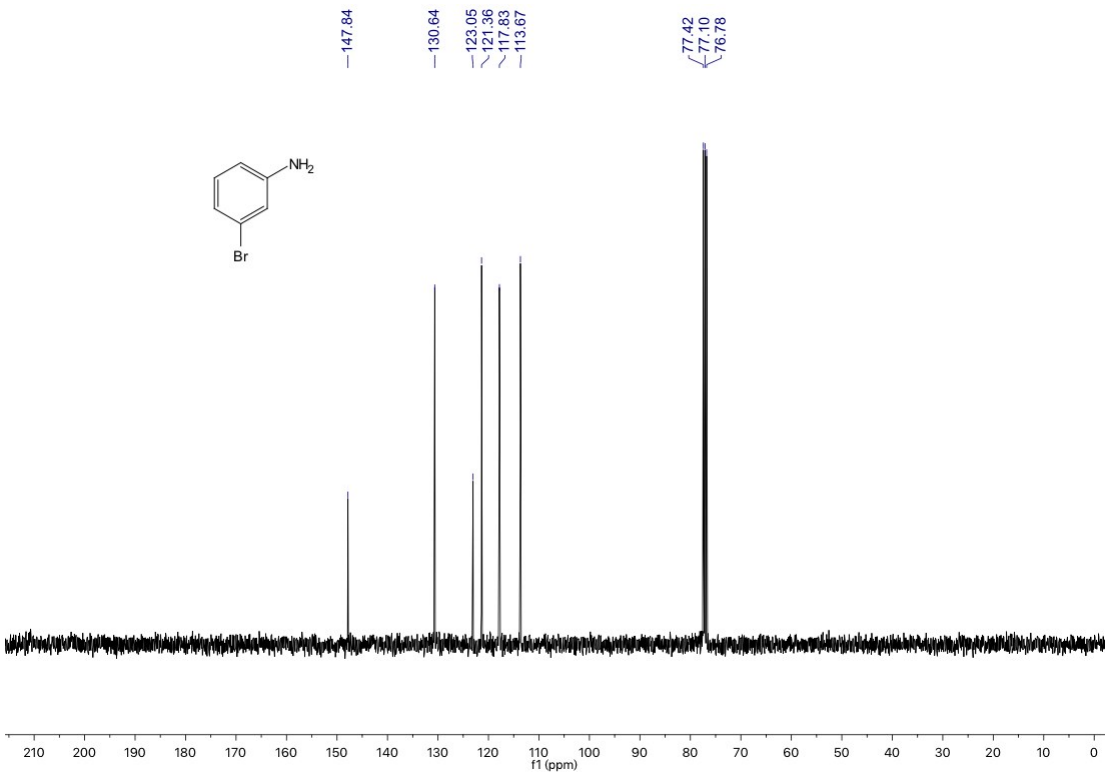
^{1}H NMR of 2-fluoroaniline



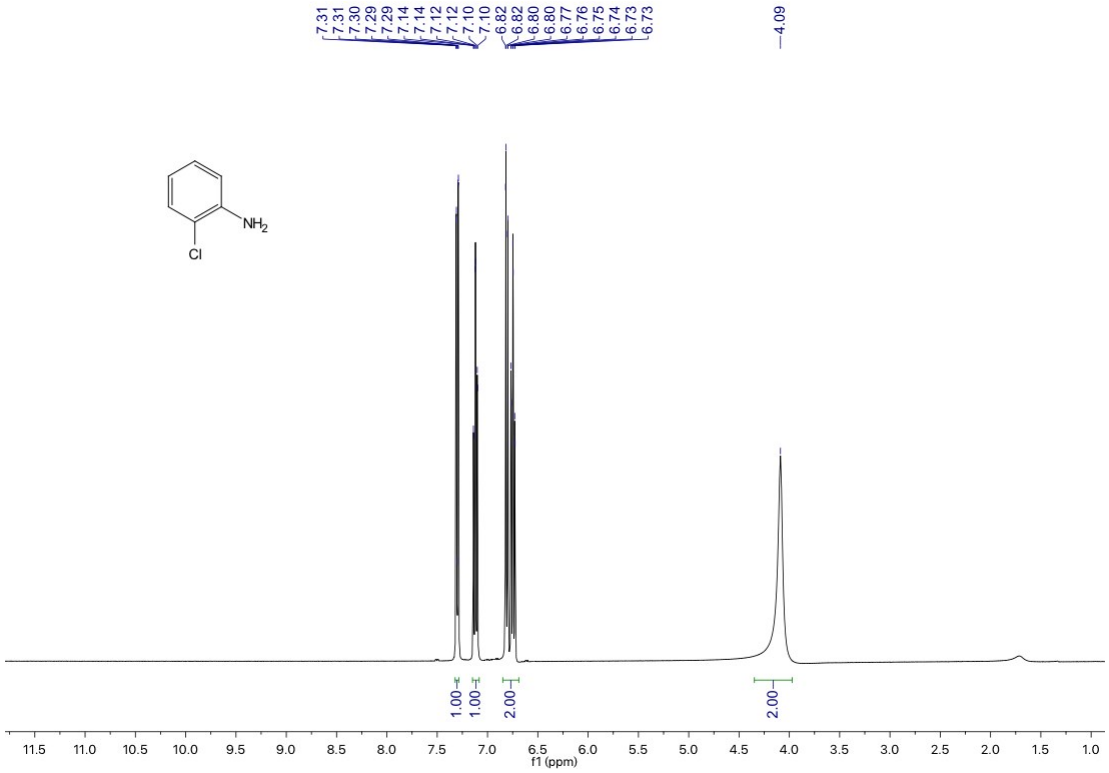
^{13}C NMR of 2-fluoroaniline



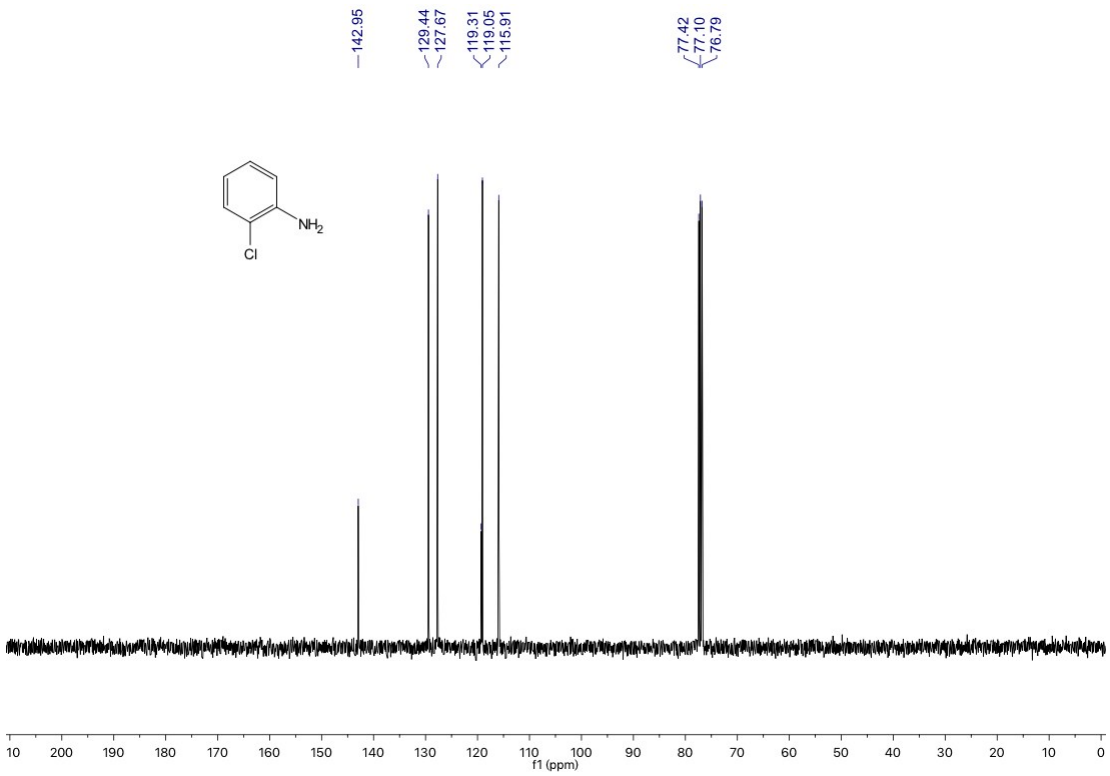
^{1}H NMR of 3-bromoanilines



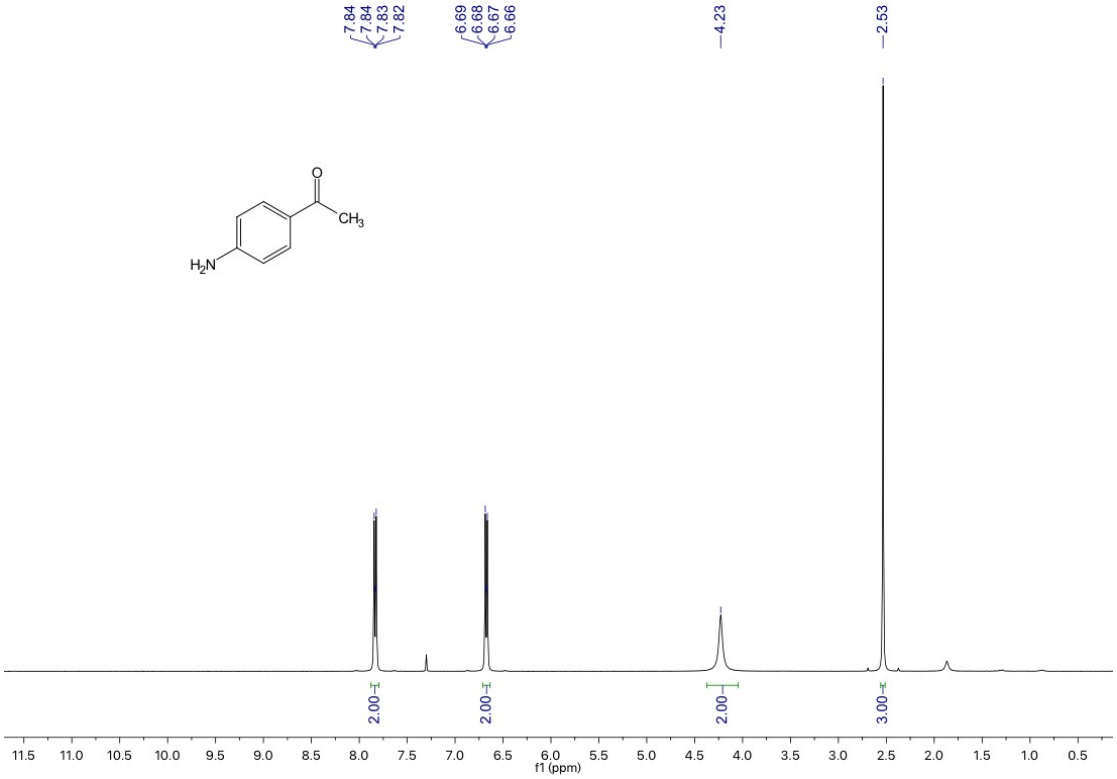
^{13}C NMR of 3-bromoanilines



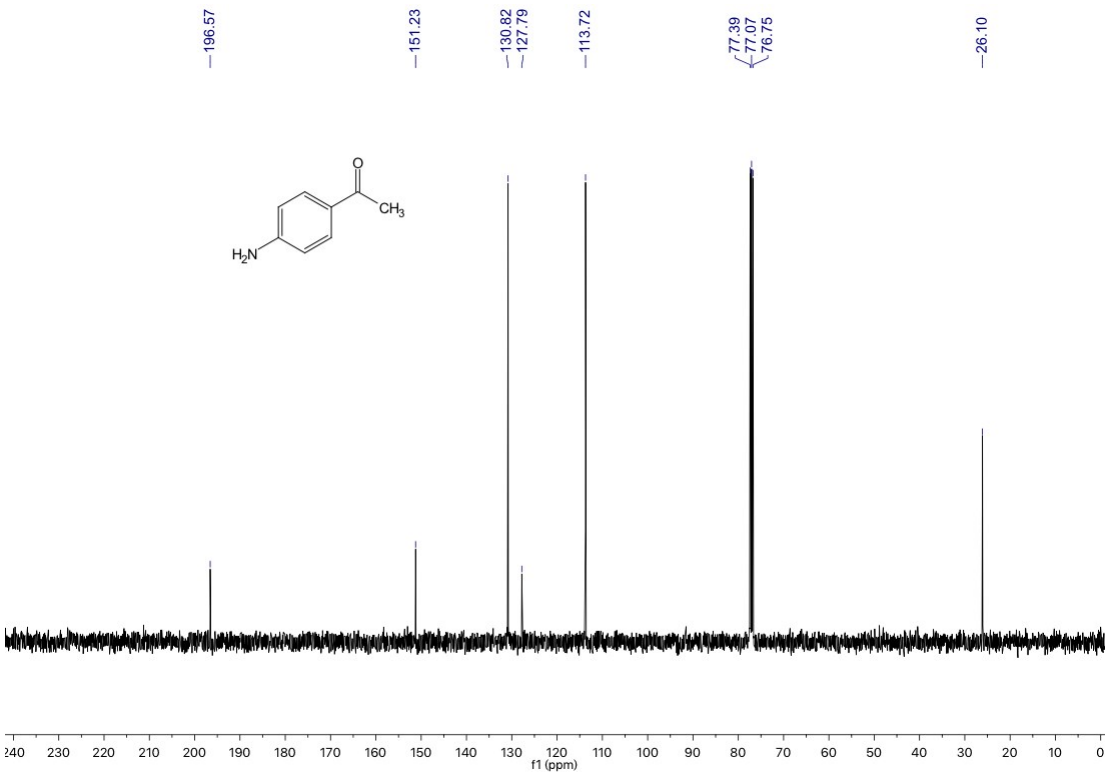
^{1}H NMR of *o*-chloroaniline



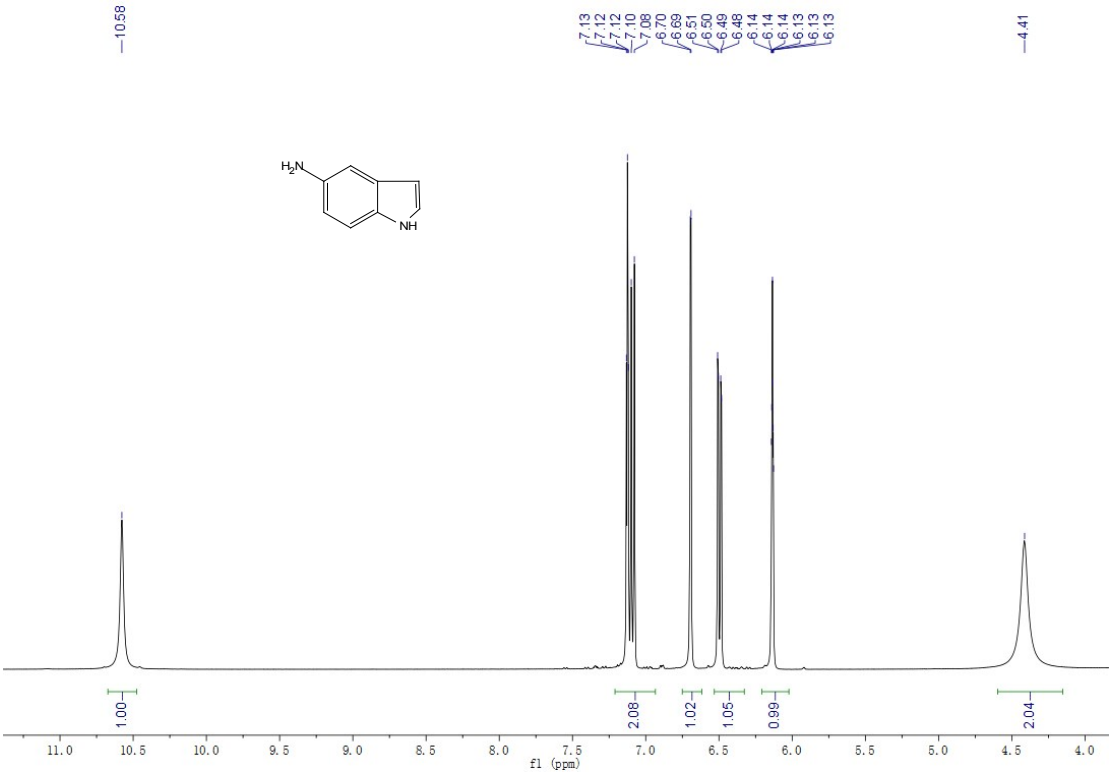
^{13}C NMR of *o*-chloroaniline



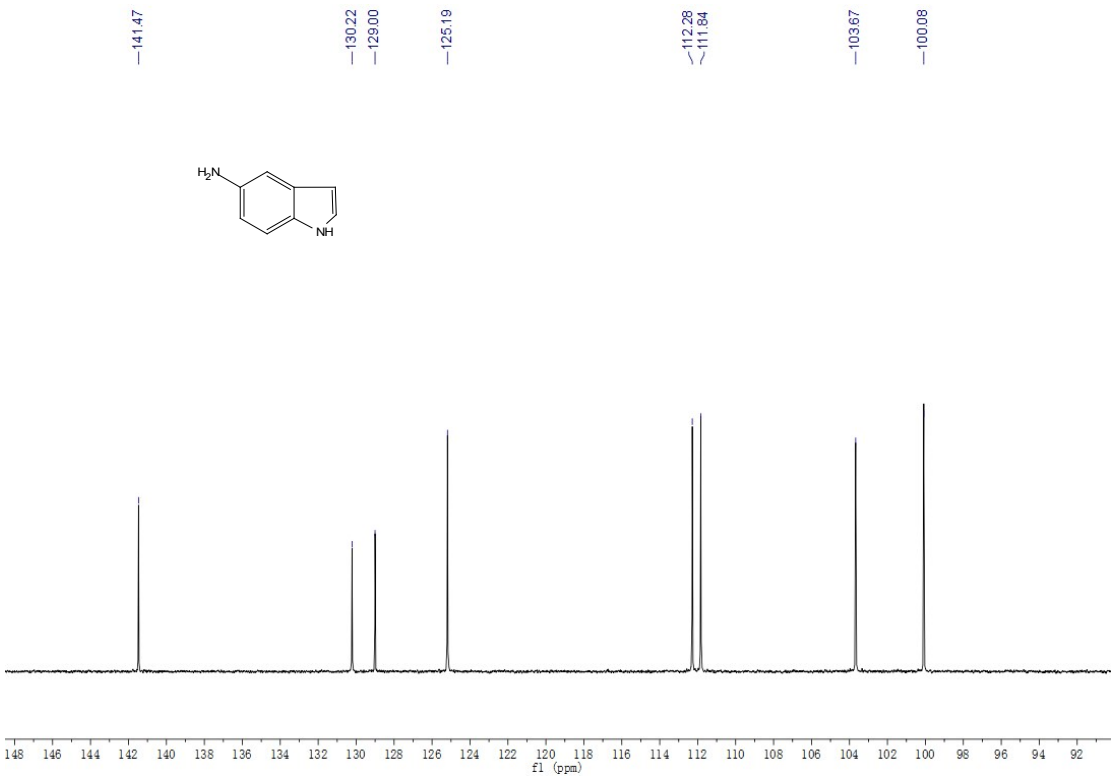
^{1}H NMR of *p*-aminoacetophenone



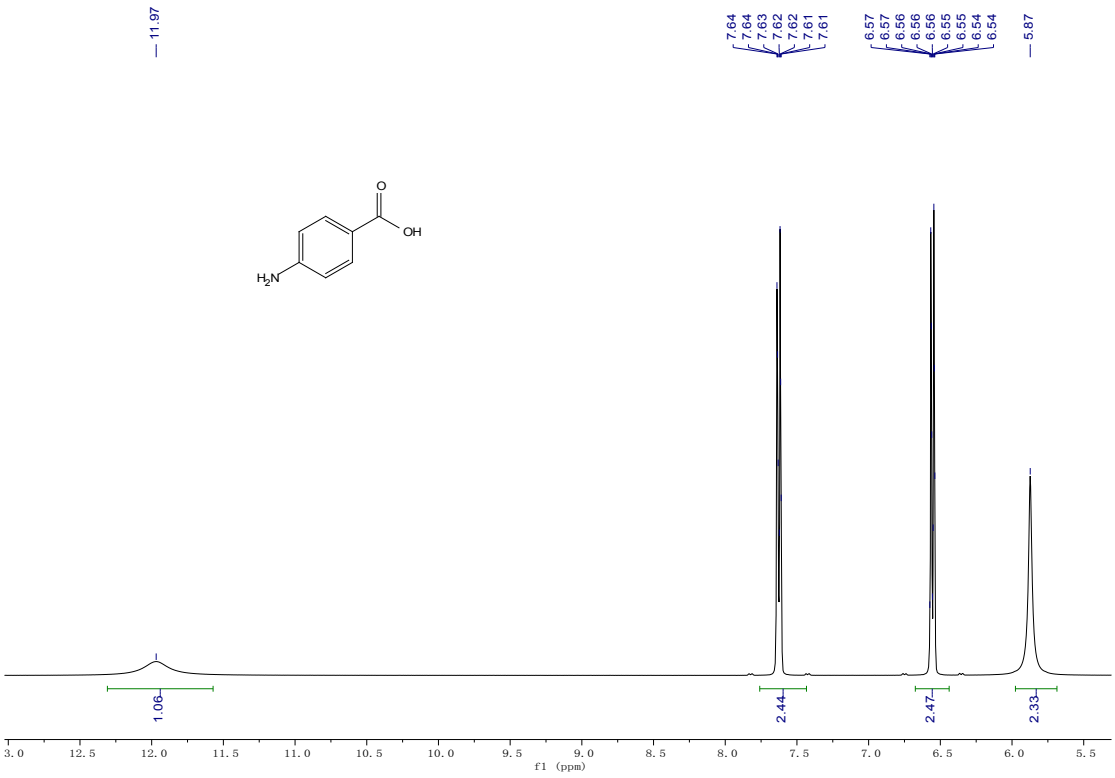
^{13}C NMR *p*-aminoacetophenone



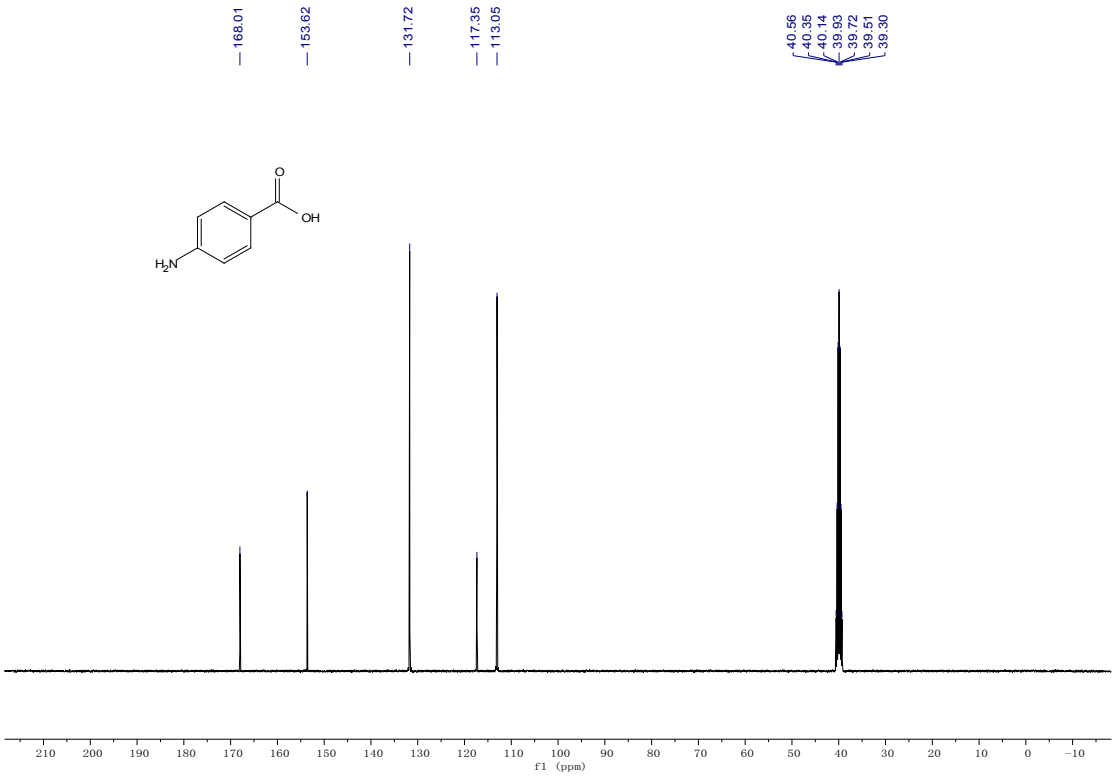
^{1}H NMR of 5-Aminoindole



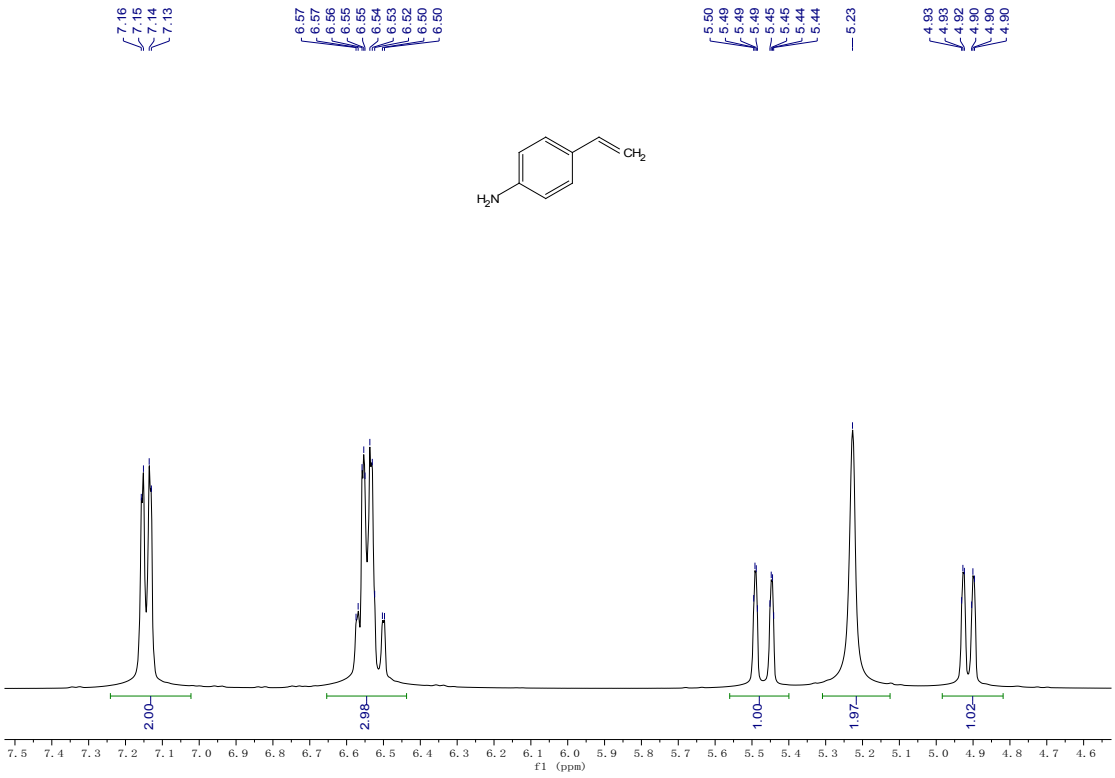
^{13}C NMR of 5-Aminoindole



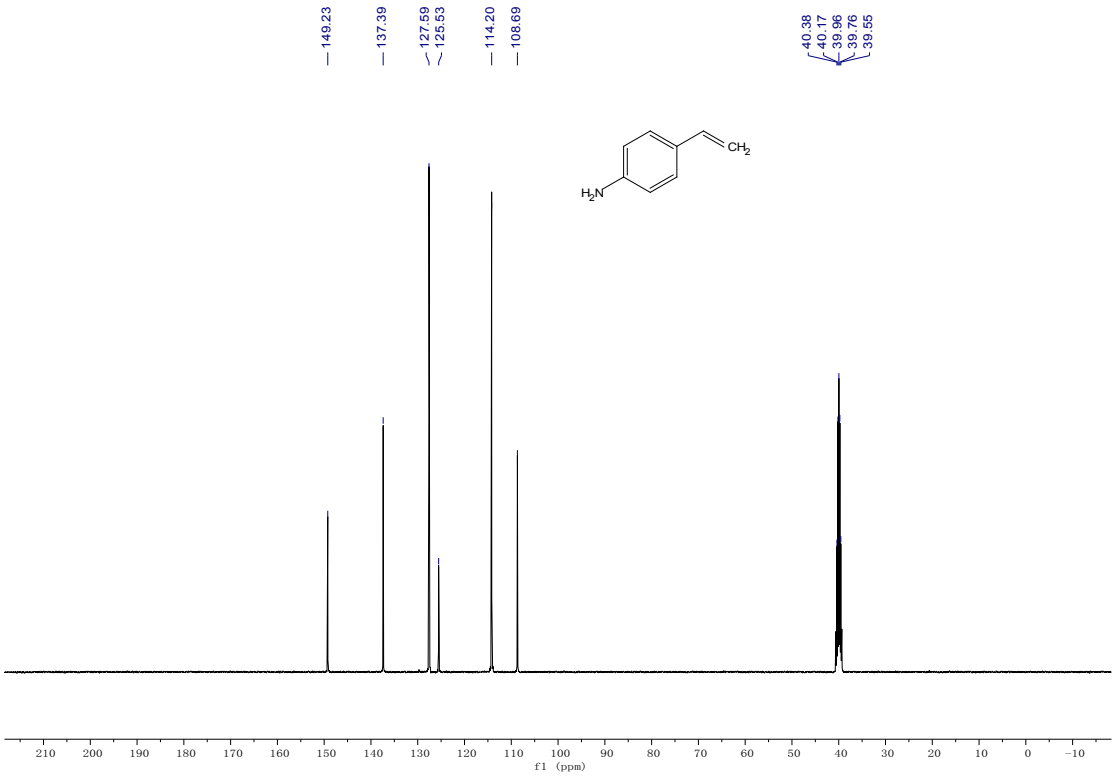
^{1}H NMR of *p*-Aminobenzoic acid



^{13}C NMR of *p*-Aminobenzoic acid



^{1}H NMR of 4-vinylaniline



^{13}C NMR of 4-vinylaniline

11. Reference

1 (*a*) X. Sheng, B. Wouters, T. Breugelmans, A. Hubin, I. F. J. Vankelecom, P. P. Pescarmona, *Appl. Catal. B Environ.*, 2014, **147**, 330-339; (*b*) U. Sharma, P. Kumar, N. Kumar, V. Kumar, B. Singh, *Adv. Synth. Catal.*, 2010, **352**, 1834–1840.