

## COMMUNICATION

# Hollow and mesoporous aluminosilica encapsulated Pt-CoO<sub>x</sub> for selective hydrogenation of substituted nitroaromatics

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### Experimental

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## Materials

$K_2PtCl_4$  (98%),  $CoCl_2 \cdot 6H_2O$ , Brij® L4, 1-octane, Tetraethyl silicate (TEOS),  $Na_2CO_3$ ,  $NaAlO_2$ , Hexadecyl trimethyl ammonium bromide (CTAB),  $NaBH_4$ , *o*-chloronitrobenzene (*o*-CNB), *m*-chloronitrobenzene (*m*-CNB), *p*-chloronitrobenzene (*p*-CNB), *p*-bromonitrobenzene (*p*-BNB), *m*-nitroacetophenone (*m*-NAP), *p*-nitrobenzaldehyde (*p*-NBA), *p*-nitrotoluene (*p*-NT), and *o*-nitrophenol (*o*-NP) were obtained from Aladdin Reagents Co., Ltd. (China). Anhydrous ethanol, acetone, and ammonium hydroxide ( $NH_3 \cdot H_2O$ , 25-28%) were purchased from Sinopharm Chemical Reagents Co., Ltd. (China). Deionized water was used throughout. All reagents were used directly without further purification.

## Synthesis of Pt-CoO<sub>x</sub>@HMANS and Pt@HMANS.

In a typical procedure, 5.66 g of Brij® L4 was fully dissolved in 45 ml of 1-octane in a 250 mL three-necked round-bottomed flask at 50 °C under magnetic stirring (300 r/min). Then, 1.5 ml of aqueous solution containing 0.048 mmol  $K_2PtCl_4$  and 0.048 mmol  $CoCl_2 \cdot 6H_2O$  were added in the above transparent microemulsion. The resultant mixture was stirred for 30 min, followed by injecting 0.5 ml of ammonia aqueous solution containing 0.05 g  $NaBH_4$ . After 60 min, 0.6 ml of ammonia aqueous solution and 2 ml of TEOS were successively added dropwise to the flask. After that, the system was maintained at 50 °C for 2 h. The PtCo@SiO<sub>2</sub> core-shell NPs were collected by centrifugation and washed with acetone twice.

Pt-based yolk-shell nanoreactors were synthesized by a modified selective etching method.<sup>1</sup> 50 mg of the as-synthesized PtCo@SiO<sub>2</sub> core-shell NPs were dispersed in 10 ml of deionized water by ultrasonication in 50 ml single neck flask. Then 0.0125 g of CTAB, 0.0265 g of  $NaAlO_2$ , and 0.205 g of  $Na_2CO_3$  were added to the flask in sequence. The system was heated to 95 °C with stirring for 3h. Upon cooling to room temperature, the resultant mixture was collected by centrifugation and washed with deionized water and ethanol. The products were further calcined at 550 °C for 6 h with at a rate of 1.5 °C/min in air to obtain the Pt-CoO<sub>x</sub>@HMANS.

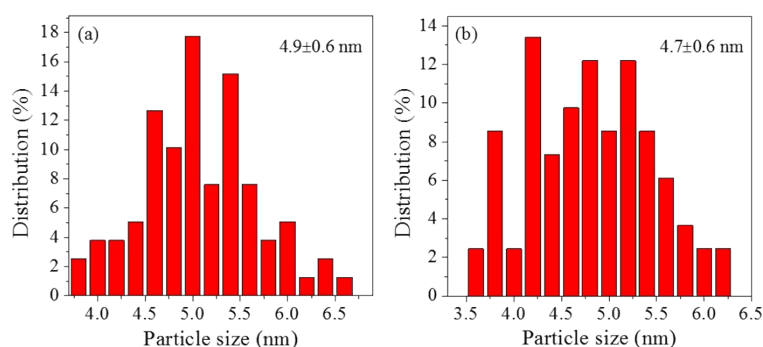
The Pt@HMANS was prepared by the same procedure except that without the addition of Co precursor.

## Characterization

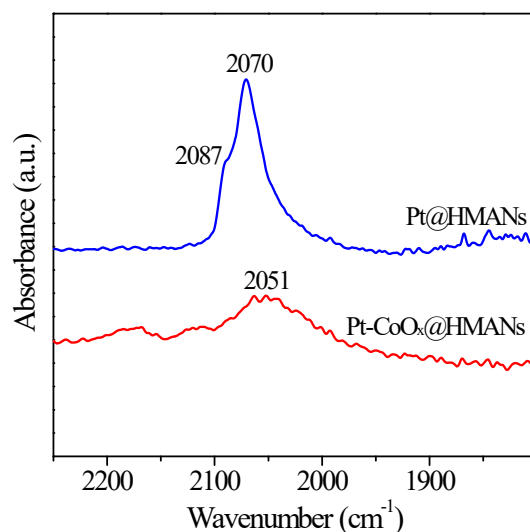
X-ray diffractions (XRD) patterns were obtained using Bruker D8 Advance X-ray diffractometer with Cu K $\alpha$  radiation. Transmission electron microscopy (TEM) images with energy-dispersive spectroscopy (EDS) were tested by the Talos F200x instrument. The BET surface area and pore size distributions of the nanoreactors were obtained on the Micromeritics ASAP-2020 Mautomatic specific surface area and porous physical adsorption analyzer. X-ray photoelectron spectroscopy (XPS) spectra of the samples were conducted on an AXIS ULTRADLD multifunctional X-ray photoelectron spectroscope with an Al source. The results were corrected by C 1s (284.8 eV), and its curve fitting was performed using the Casa XPS software. The diffuse reflectance Fourier transform infrared spectra (DRIFT-IR) with CO probes of Pt-CoO<sub>x</sub>@HMANS and Pt@HMANS were obtained using a Nicolet-6700 Fourier transform infrared spectrometer. The samples were firstly pretreated by Ar purging at 100 °C for 1 h and then cooled down to room temperature. After that, the sample was exposed to pure CO at a gas flow rate of 20 mL/min for 30 min. Finally, the free CO was removed by Ar purging and the spectra were recorded.

## Activity test

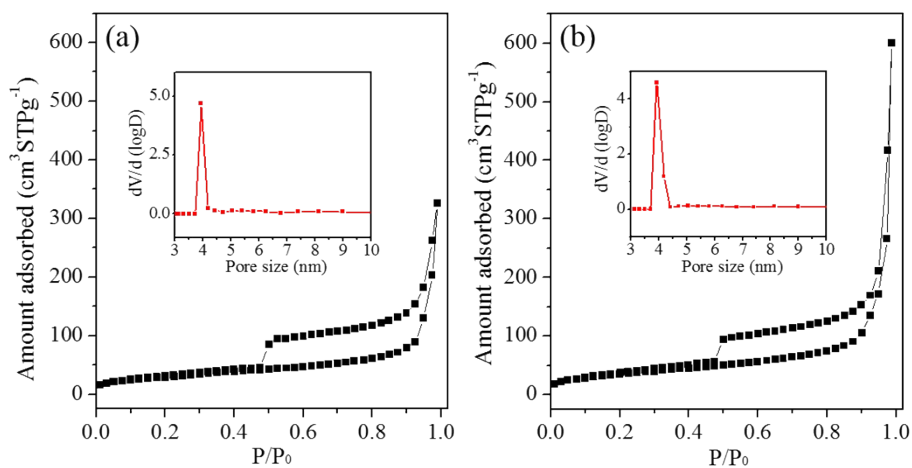
The catalytic reduction of *o*-CNB, *m*-CNB, *p*-CNB, *p*-BNB, *m*-NAP, *p*-NBA, *p*-NT, and *o*-NP with H<sub>2</sub> were performed in a 100 ml of three-necked round-bottomed flask under mild reaction conditions (45 °C, 0.1 MPa H<sub>2</sub>). Briefly, 25 mg of nanocatalyst, 10 ml of absolute ethanol, and 0.5 mmol of various substituted nitroaromatics were mixed in the flask under a magnetic stirring (700 r/min). Then the system was heated to 45 °C under 0.1 MPa H<sub>2</sub> flow. After reaction, the hydrogenation products were analyzed by a gas chromatograph GC 2060 equipped with a flame ionization detector.



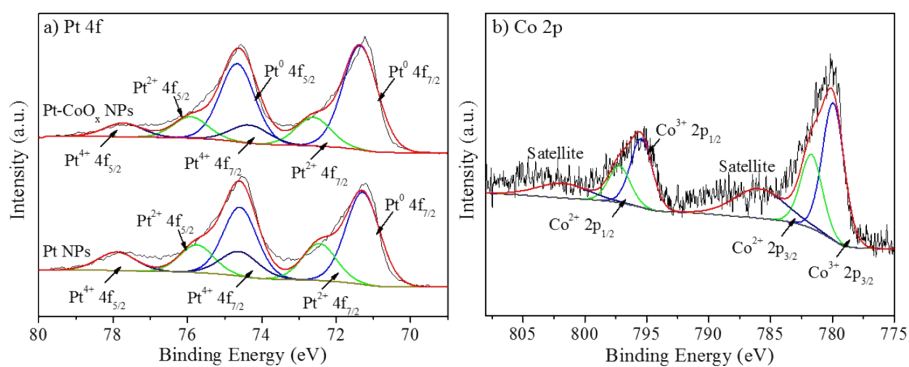
**Figure S1.** Size distributions of Pt NPs showing: (a) Pt@HMANS, (b) Pt-CoO<sub>x</sub>@HMANS.



**Figure S2.** DRIFT-IR spectra with CO probes of Pt-CoO<sub>x</sub>@HMANS and Pt@HMANS.



**Figure S3.** N<sub>2</sub> adsorption-desorption isotherms and pore size distribution curves (inset) showing: (a) Pt-CoO<sub>x</sub>@HMANS and (b) Pt@HMANS.



**Figure S4.** XPS spectra of a) Pt 4f and b) Co 2p.

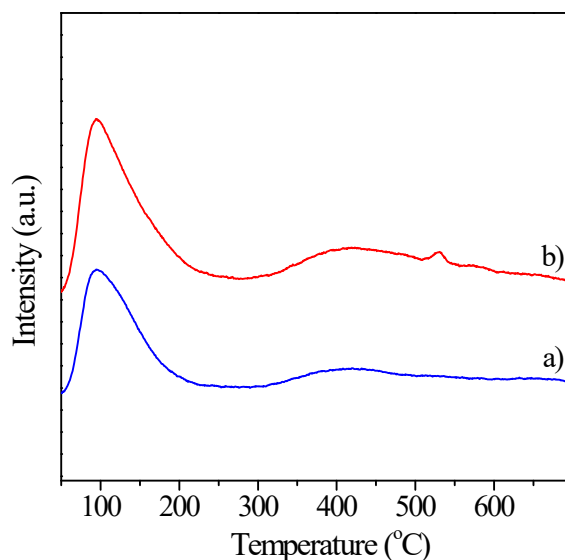


Figure S5.  $\text{NH}_3$ -TPD patterns of the a)  $\text{Pt-CoO}_x/\text{SiO}_2$  and b)  $\text{Pt-CoO}_x/\text{HMANs}$ .

Table S1. XPS Results of Pt NPs and  $\text{Pt-CoO}_x$  NPs.

Samples	Pt/Oxidized Pt	Pt/M (XPS)	Pt/M (ICP)
$\text{Pt-CoO}_x$ NPs	58.8/41.2	44.7/55.3	46.7/53.3
Pt NPs	68.3/31.7	-	

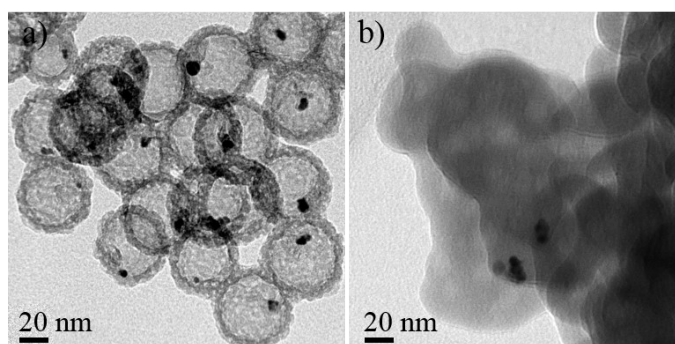


Figure S6. TEM images of a)  $\text{Pt-CoO}_x/\text{SiO}_2$  and b)  $\text{Pt-CoO}_x/\text{HMANs}$ .

The  $\text{Pt-CoO}_x/\text{SiO}_2$  was synthesized by the same procedure as the  $\text{Pt-CoO}_x/\text{HMANs}$  except that without the addition of  $\text{NaAlO}_2$  during the selective etching process.

Table S2. The catalytic hydrogenation performance of *p*-CNB over various catalysts.

Catalysts <sup>a</sup>	Conversion (%)	Selectivity (%)	
		<i>p</i> -CAN	Others
$\text{Pt-CoO}_x/\text{HMANs}$	96.9	98.5	1.5
$\text{Pt-CoO}_x/\text{SiO}_2$	89.6	98.8	1.2
$\text{Pt-CoO}_x/\text{HMANs}$	78.1	68.6	31.4

<sup>a</sup>Reaction conditions: reactants-0.5 mmol; EtOH-10.0 mL;  $\text{H}_2$ -0.10 MPa; reaction temperature-45 °C; reaction time-1.5 h; speed of agitation-700 rpm. Catalysts-0.025 g.

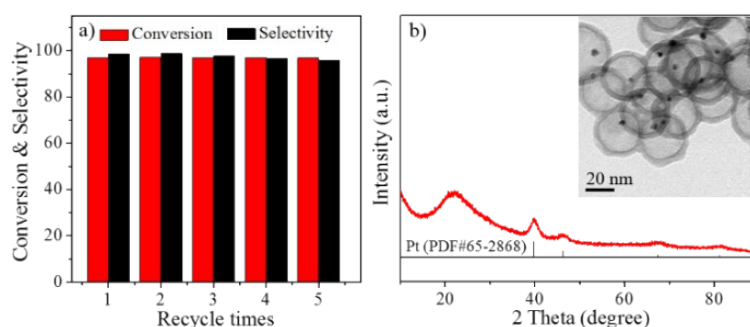
**Table S3.** Comparison of catalytic performance of Pt-CoO<sub>x</sub>@HMANs and previously reported heterogeneous catalysts for the selective hydrogenation of *m*-CNB.

Catalysts	Conditions			Conv. (%)	Sel. (%)	TON <sup>a</sup> /h	Ref.
	T (°C)	P (MPa)	t (h)				
Pt-CoO <sub>x</sub> @HMANs	45	0.1	1.5	94.7	99.4	105	This work
Pt/CMK-3-HQ	80	2.0	1	100	100	12	1
PtZn/SiO <sub>2</sub>	40	0.1	1	100	99	26	2
Ir-FeO <sub>x</sub> /SBA-15	45	0.1	2	97.8	100	49	3
IrNi/Al <sub>2</sub> O <sub>3</sub>	45	0.1	2	100	92	31	4
Ir-CoO <sub>x</sub> @SiO <sub>2</sub>	45	0.1	2	96.7	95.5	25	5
Ir/CNT	25	2.0	5	100	100	31	6
Ir nanowires	40	0.3	0.6	93.3	99	15	7

<sup>a</sup> Turnover number (TON) is measured as moles of products per total molar metal atoms.

#### Reference

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**Figure S7.** a) Recycle performance of Pt-CoO<sub>x</sub>@HMANs for the selective hydrogenation of *p*-CNB; b) XRD pattern and TEM image (inset) of Pt-CoO<sub>x</sub>@HMANs after five successive reactions.

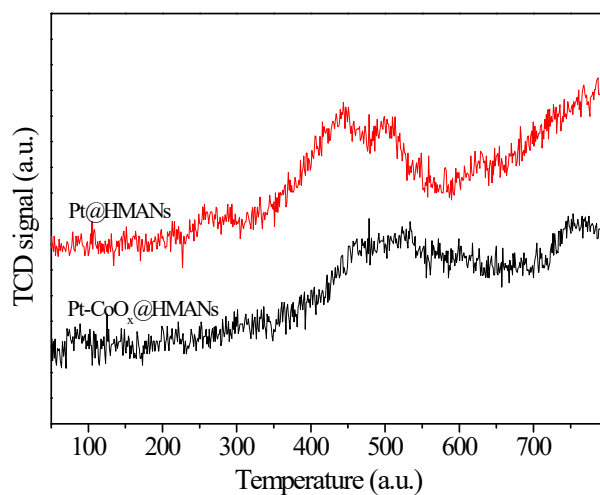
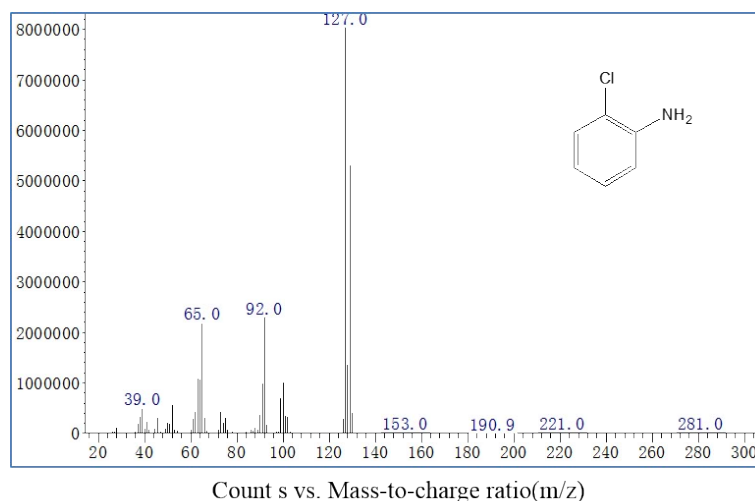


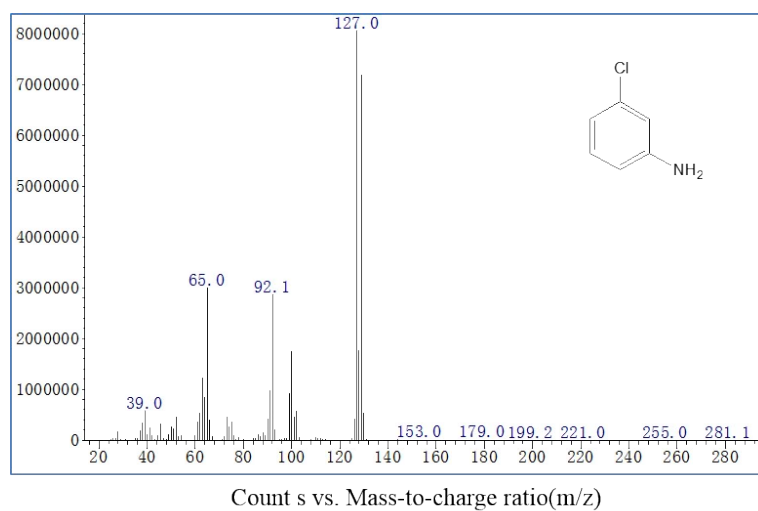
Figure S8. H<sub>2</sub>-TPD profiles of Pt@HMANS and Pt-CoO<sub>x</sub>@HMANS.

## Characterization of the main product for hydrogenation of various substituted nitroaromatics by GC-MS (Agilent 7890B-5977A).

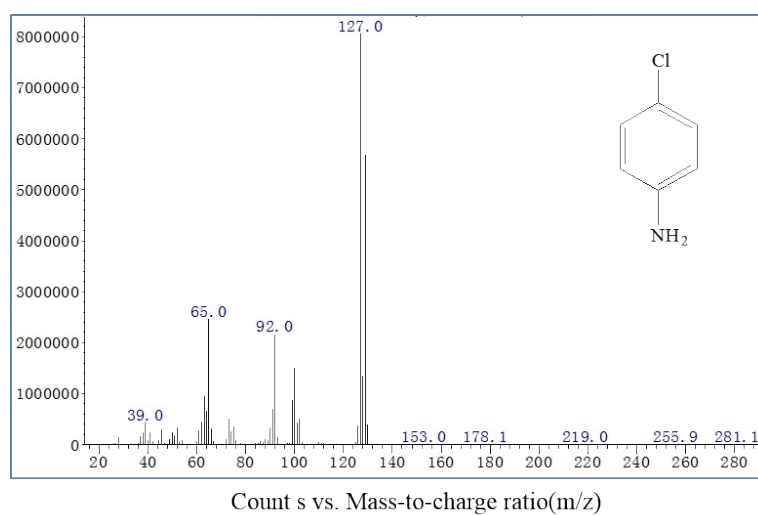
1, identification of the desired product for hydrogenation of *o*-CNB



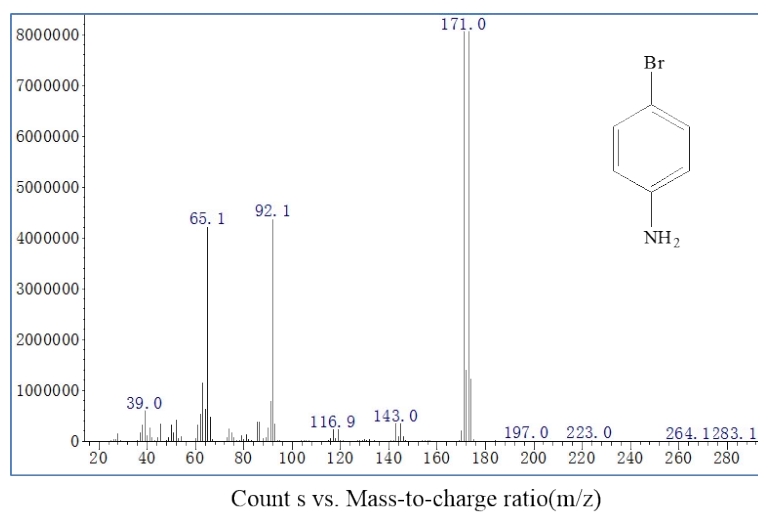
2, identification of the desired product for hydrogenation of *m*-CNB



### 3, identification of the desired product for hydrogenation of *p*-CNB

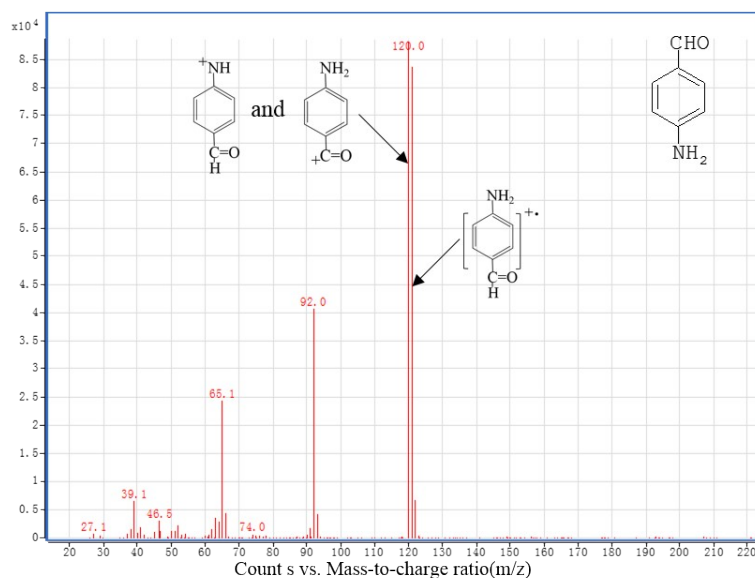
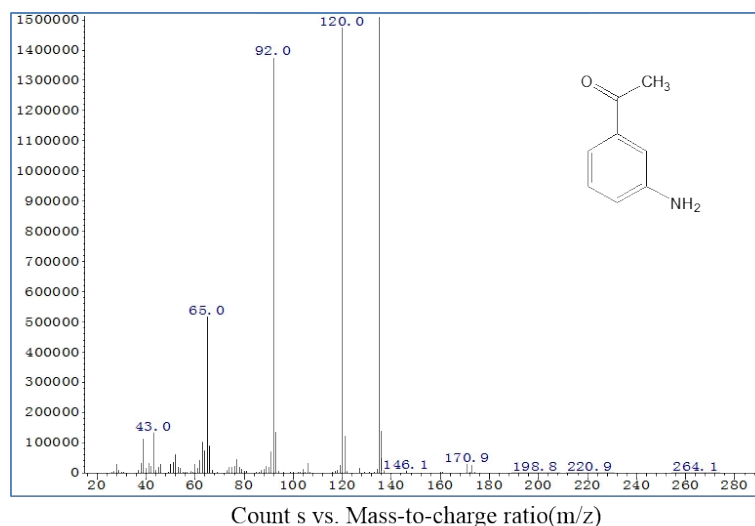


### 4, identification of the desired product for hydrogenation of *p*-BNB

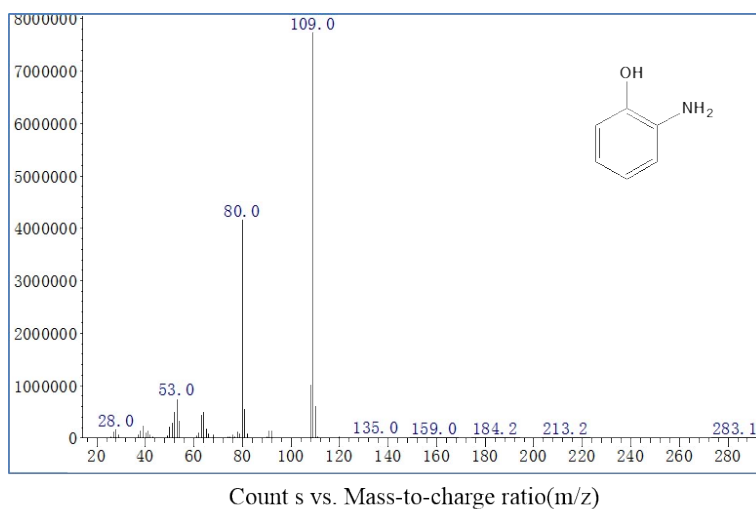


5, identification of the desired product for hydrogenation of *p*-NBA

a) Characterization of the main product for hydrogenation of *p*-nitrobenzaldehyde by GC-MS. Note: there is no MS reference data in GC-MS for this product (*p*-aminobenzaldehyde), and we ascribe the signals at 121 and 120 to the species shown in the following Figure.

6, identification of the desired product for hydrogenation of *m*-NAP7, identification of the desired product for hydrogenation of *o*-NP





8, identification of the desired product for hydrogenation of *p*-NT

