# Supporting information

## Sequential Hydrogenation of Nitroaromatics to Alicyclic Amines via Highly-dispersed Ru-Pd Nanoparticles Anchored on Air-exfoliated $C_3N_4$ Nanosheets

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## 1 Catalyst characterization

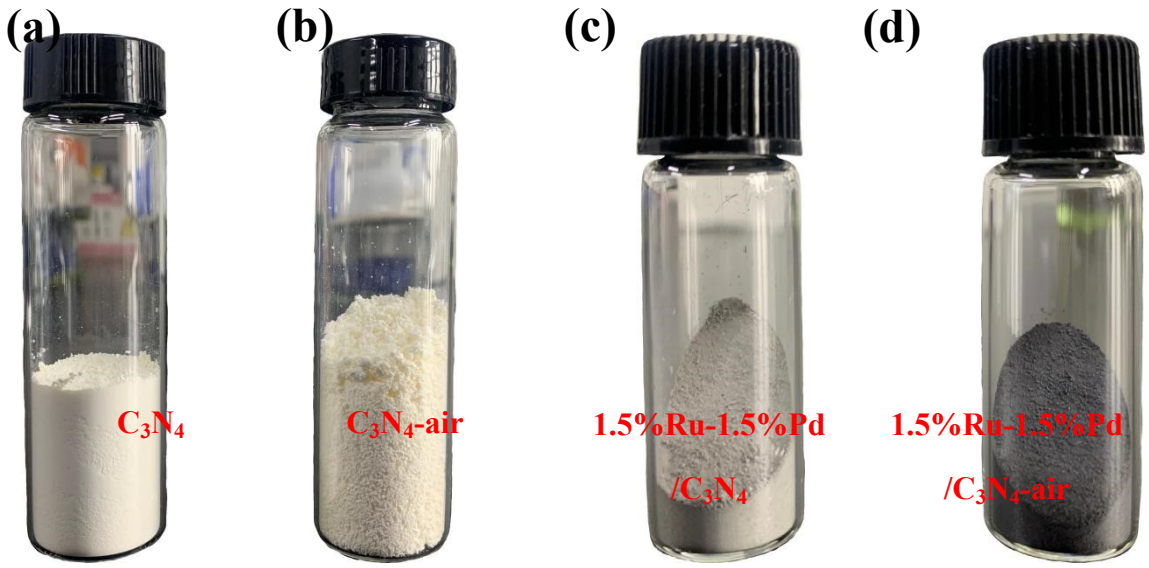



**Fig. S1.** Pictures of (a) $C_3N_4$, (b) $C_3N_4$-air, (c) 1.5%Ru-1.5%Pd/$C_3N_4$, (d) 1.5%Ru-1.5%Pd/ $C_3N_4$-air.

**Table S1** Structural properties of Ru-Pd cascade catalysts and support, as well as corresponding performance of catalysts

| Catalyst | Ru[a] | Pd[a] | $S_{BET}$[b] | $d_{pore}$[b] | $V_{pore}$[b] | Conv.[c] | Sel.[c] |
|---|---|---|---|---|---|---|---|
| 1.5%Ru-1.5%Pd/$C_3N_4$-air | 1.42 | 1.44 | 96.24 | 9.68 | 0.23 | 100.0% | 96.8% |
| 1.5%Ru-1.5%Pd/$C_3N_4$ | 1.54 | 1.57 | 83.50 | 22.38 | 0.23 | 100.0% | 34.6% |
| $C_3N_4$-air | - | - | 137.22 | 13.65 | 0.47 | - | - |
| $C_3N_4$ | - | - | 85.48 | 22.24 | 0.48 | - | - |
| 1.5%Ru-1.5%Pd/C | 1.34 | 1.38 | 35.61 | 4.36 | 0.04 | 100.0% | 7.5% |

[a] Ru/Pd loading (wt.%). Determined by ICP-OES.

[b] $S_{BET}$ ($m^2 \cdot g^{-1}$) was BET surface area; $d_{pore}$ (nm) and $V_{pore}$ ($cm^3 \cdot g^{-1}$) were average pore diameter and total pore volume. Determined by $N_2$ adsorption-desorption.

[c] Conversion of nitrobenzene; Selectivity of cyclohexylamine; Determined by GC.

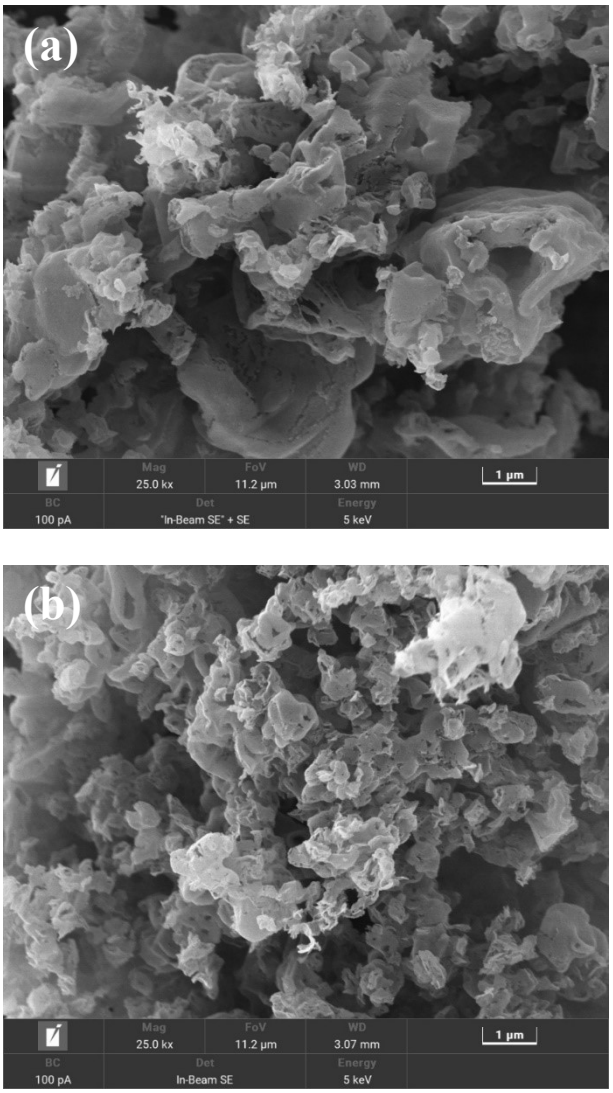



**Fig. S2.** SEM images. (a) 1.5%Ru-1.5%Pd/$C_3N_4$, (b)1.5%Ru-1.5%Pd/$C_3N_4$-air

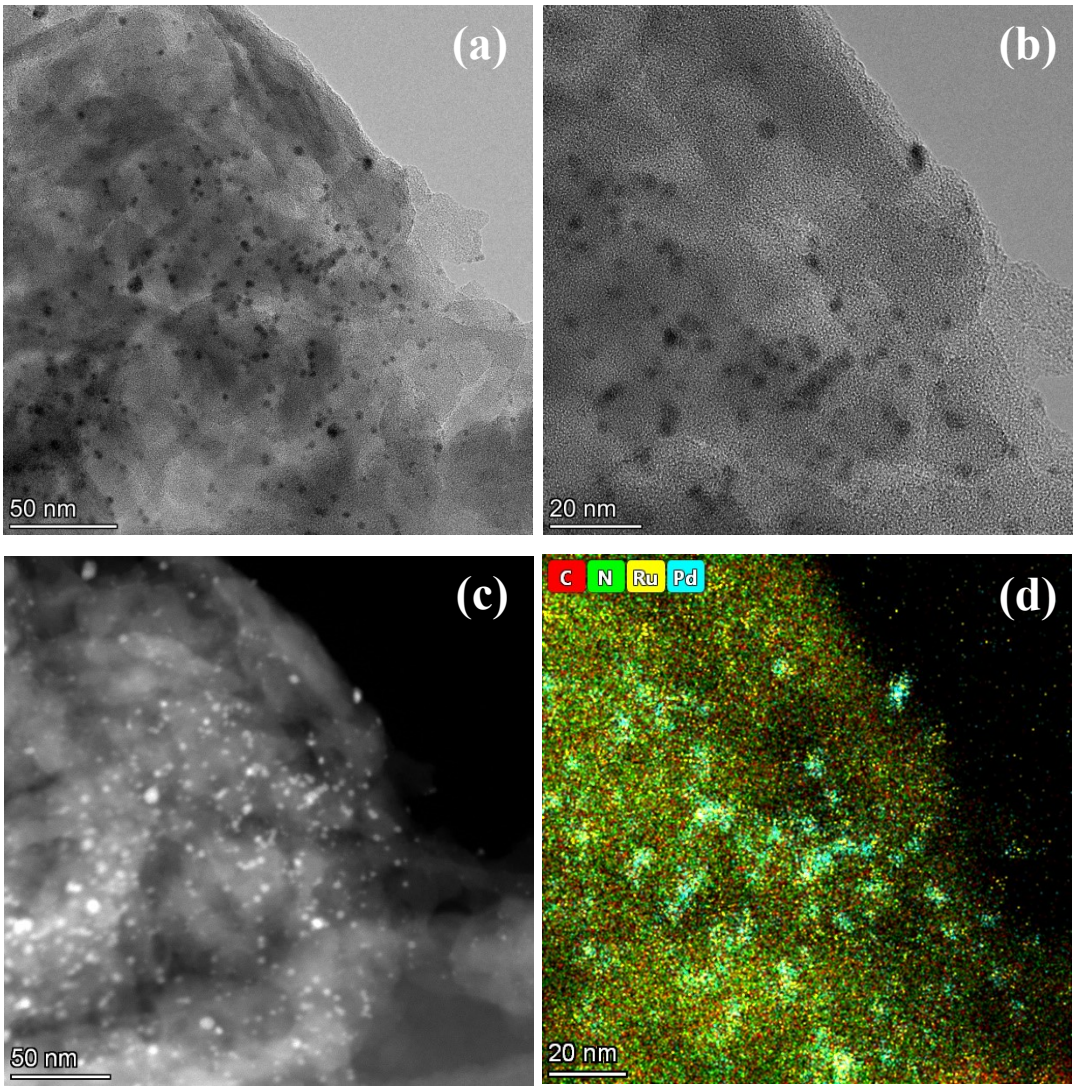



**Fig. S3.** Microstructure of 1.5%Ru-1.5%Pd/$C_3N_4$-air. (a) TEM (50 nm), (b) TEM (20 nm), (c) HAADF-STEM (50nm), (d) overall EDS element mapping.

**Table S2** XPS Fitting data of N 1s

| Catalyst | C=N-C | N-$(C)_3$ | -$NH_2$ | charge effect |
|---|---|---|---|---|
| $C_3N_4$-air | 398.5[a] | 399.9 | 401.1 | 404.2 |
| | 0.64[b] | 0.25 | 0.04 | 0.07 |
| 3%Ru/$C_3N_4$-air | 398.2 | 399.9 | 401.1 | 403.4 |
| | 0.67 | 0.24 | 0.03 | 0.07 |
| 3%Pd/$C_3N_4$-air | 398.2 | 399.7 | 400.9 | 404.2 |
| | 0.67 | 0.21 | 0.05 | 0.07 |
| 1.5%Ru-1.5%Pd/$C_3N_4$-air | 398.2 | 399.7 | 401.0 | 404.2 |
| | 0.63 | 0.24 | 0.05 | 0.08 |

[a] For each catalyst, the data of first line is Binding energy (eV), BE for short.

[b] The data in second line is proportion of corresponding specie.

**Table S3** XPS Fitting data of Ru 3p

| Catalyst | Ru $3p_{3/2}$ | | Ru $3p_{1/2}$ | | $Ru^0/Ru^{\sigma+}$ |
|---|---|---|---|---|---|
| | $Ru^0$ | $Ru^{\sigma+}$ | $Ru^0$ | $Ru^{\sigma+}$ | |
| 3%Ru/$C_3N_4$-air | 462.3 | 465.8 | 484.5 | 487.5 | 1.96 |
| 1.5%Ru-1.5%Pd/$C_3N_4$-air | 462.3 | 465.8 | 483.5 | 487.5 | 1.96 |

**Table S4** XPS Fitting data of Pd 3d

| Catalyst | Pd $3d_{5/2}$ | | Pd $3d_{3/2}$ | | $Pd^0/Pd^{2+}$ |
|---|---|---|---|---|---|
| | $Pd^0$ | $Pd^{2+}$ | $Pd^0$ | $Pd^{2+}$ | |
| 3%Pd/$C_3N_4$-air | 335.4 | 337.3 | 340.6 | 342.5 | 1.32 |
| 1.5%Ru-1.5%Pd/$C_3N_4$-air | 335.4 | 337.3 | 340.6 | 342.6 | 1.37 |

## 2 Catalyst evaluation

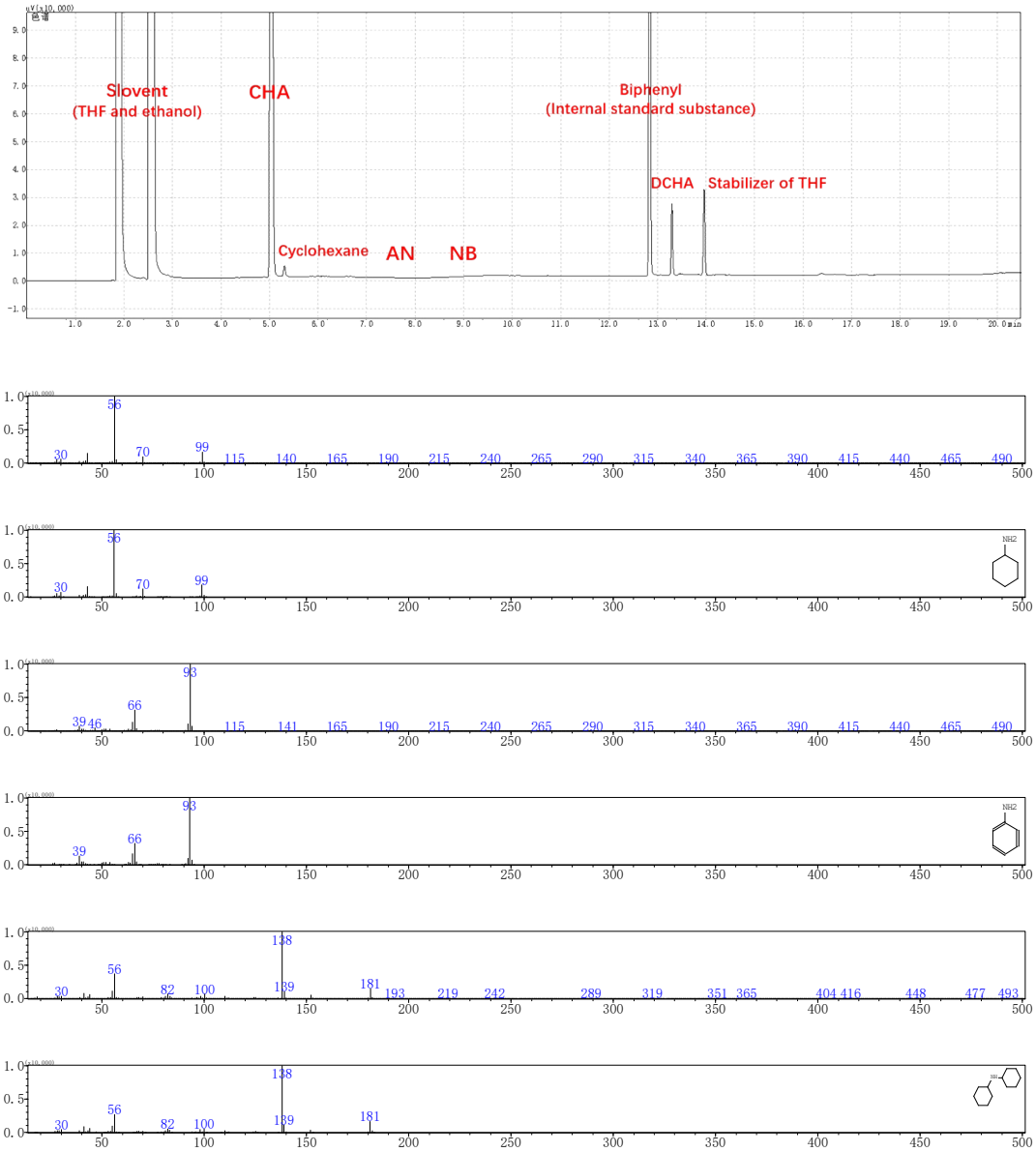



**Fig. S4.** GC-MS results and standard spectrum of NB complete hydrogenation. Reaction conditions: 1 mmol NB, 25wt.% catalysts (based on substrate), 10 mL THF, 80℃, 3 MPa $H_2$, 3 h

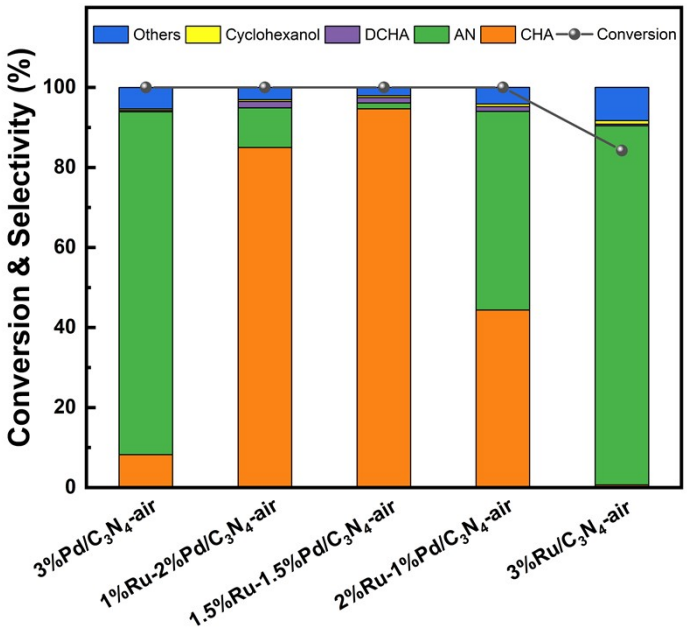



**Fig. S5.** Effect of Ru/Pd loading on NB conversion and CHA selectivity. Reaction conditions: 1 mmol NB, 25wt.% catalysts, 10 mL THF, 80 °C, 5 MPa $H_2$, 4 h.

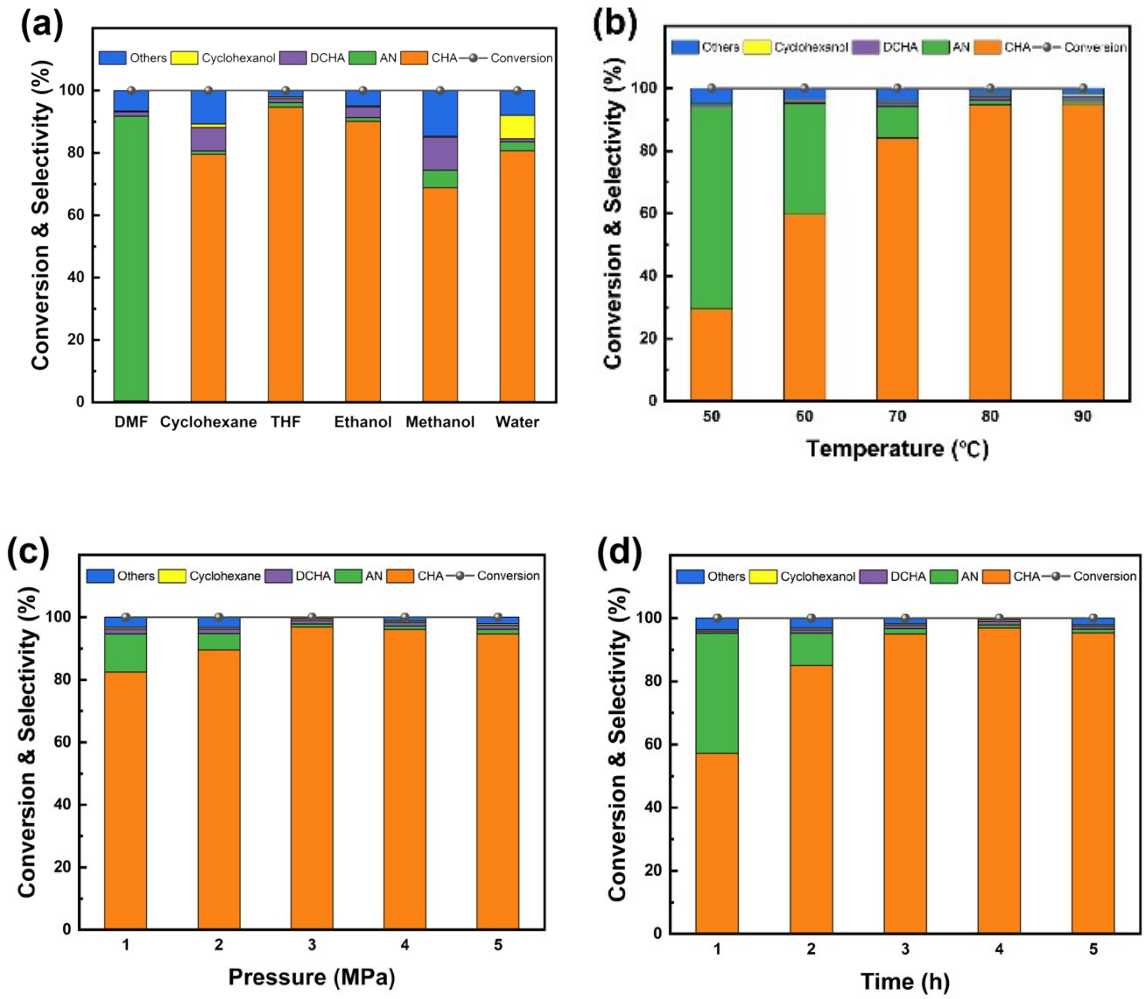



**Fig. S6.** Effects of reaction parameters on conversion and selectivity. (a) solvents (fixed reaction conditions: 10 mL solvents, 80 °C, 5 MPa $H_2$, 4 h), (b) temperature (10 mL THF, 5 MPa $H_2$, 4 h), (c) pressure (10 mL THF, 80 °C, 4 h), (d) time (10 mL THF, 80 °C, 3 MPa $H_2$).

## 3 Hydrogenation mechanism

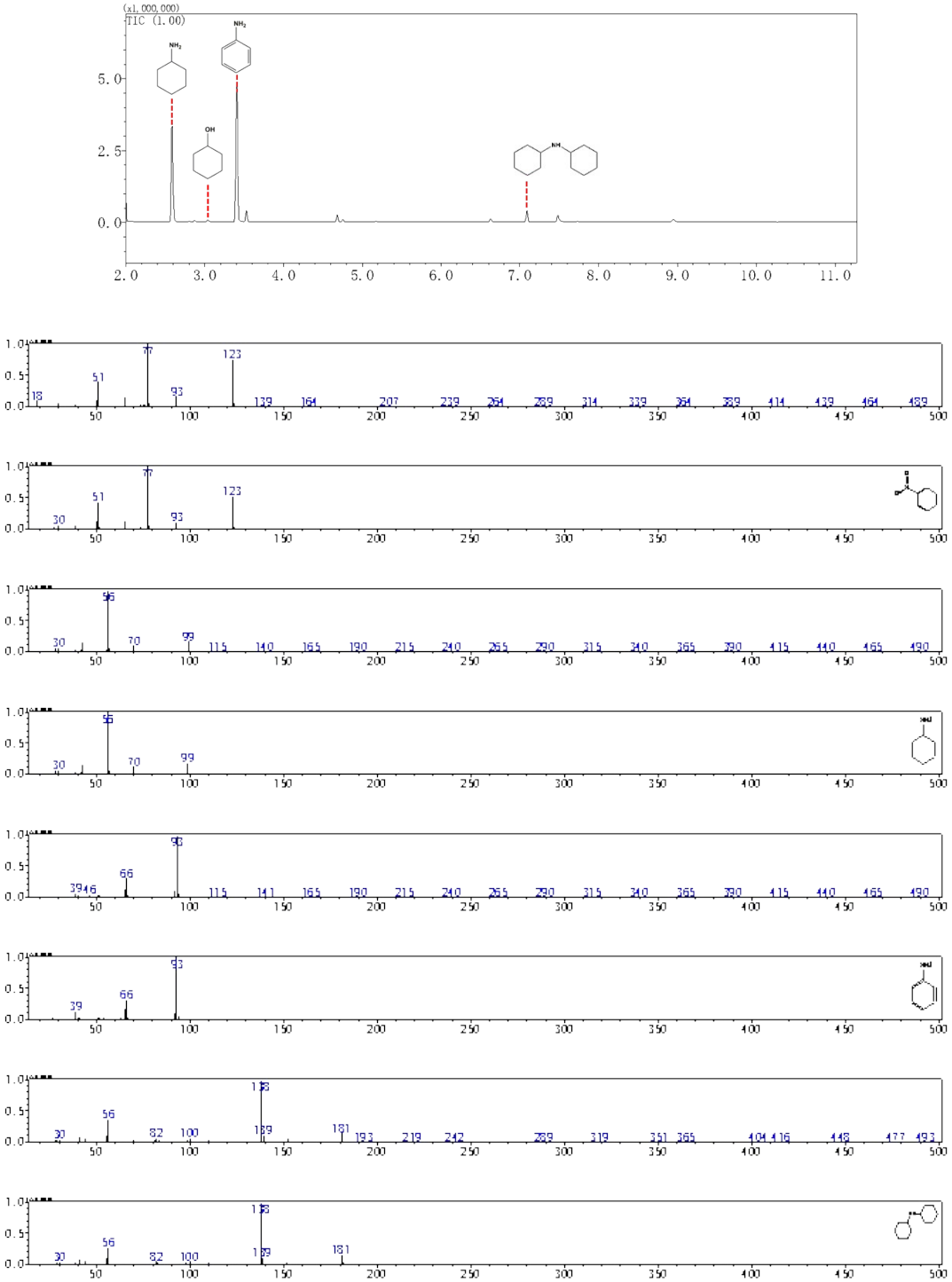



**Fig. S7.** GC-MS result and standard spectrum of incomplete hydrogenation. Reaction conditions: 1 mmol NB, 25wt.% 1.5%Ru-1.5%Pd/$C_3N_4$-air, 10 mL THF, 80℃, 3 MPa $H_2$, 1 h.

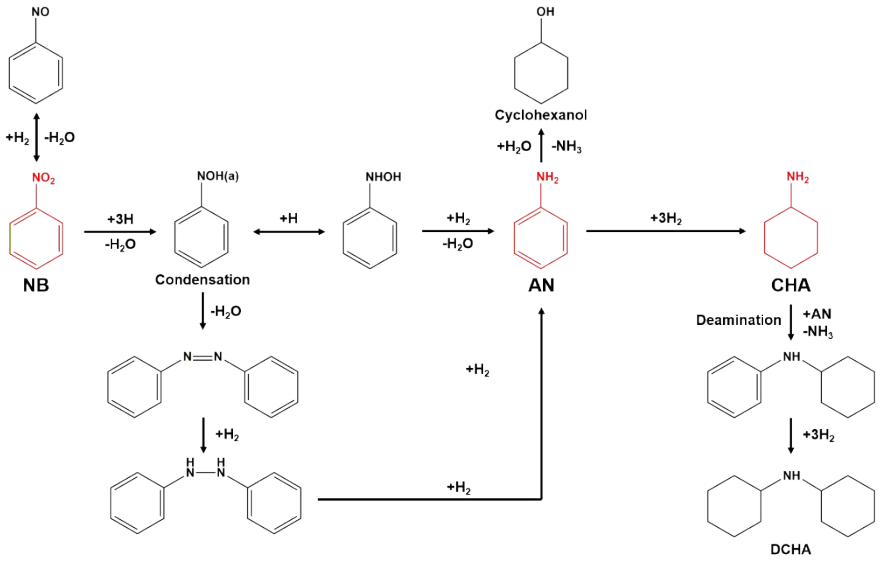



**Fig. S8.** Proposed reaction pathway of hydrogenation of NB[1-3]

## 4 Hydrogenation Kinetics

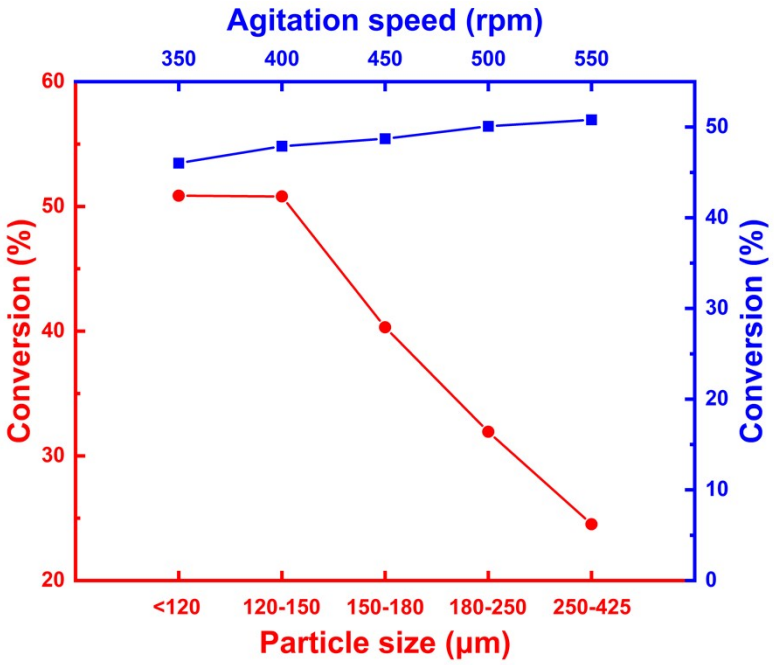



**Fig. S9.** Effect of internal (red) and external (blue) diffusion. Reaction condition: 10 mmol NB, 1wt.% catalyst, 15 mL THF, 50 ℃, 1 MPa $H_2$, 0.5 h.

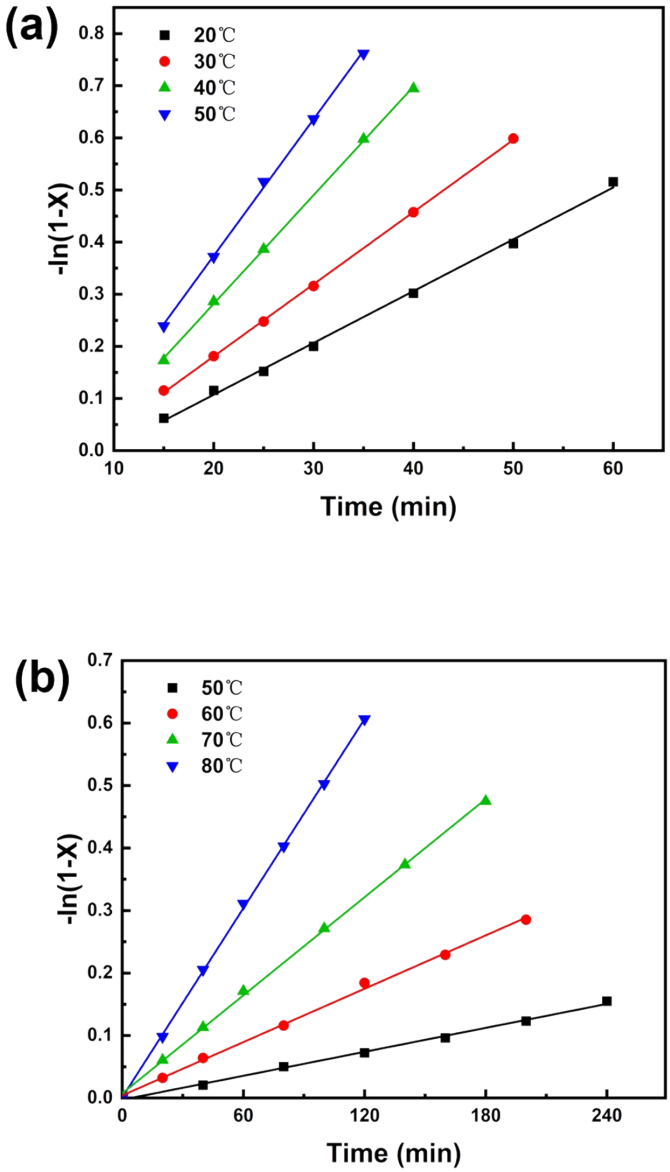



**Fig. S10.** Plots of -ln(1-X) versus time over 1.5%Ru-1.5%Pd/$C_3N_4$-air. (a) nitrobenzene hydrogenation, (b) aniline hydrogenation.

**Table S5.** Kinetics linear fit of hydrogenation of nitrobenzene over 1.5%Ru-1.5%Pd/$C_3N_4$-air.

| Temperature ℃ | Linear fit equation | K ($min^{-1}$) | $R^2$ |
|---|---|---|---|
| 20 | y=0.0099x-0.0914 | 0.0099 | 0.9978 |
| 30 | y=0.0138x-0.0961 | 0.0138 | 0.9998 |
| 40 | y=0.0208x-0.1349 | 0.0208 | 0.9996 |
| 50 | y=0.0262x-0.1502 | 0.0262 | 0.9990 |

**Table S6.** Relevant kinetic data of hydrogenation of nitrobenzene

| Catalyst | Solvent | Temperature (°C) | Pressure (MPa) | Activation energy (kJ/mol) | References |
|---|---|---|---|---|---|
| Ru-Pd/$C_3N_4$-air | THF | 20-50 | 1.0 | 26.26[this work] | - |
| Ru/NC | Methanol | 20-50 | 2.0 | 43.70 | Yang et al.[4] |
| Pd/$Al_2O_3$ | Methanol | 31-46 | 1.3 | 40.90 | Duan et al.[5] |
| Pd/P123 | Water | 30-75 | 3.0 | 40.18 | Huang et al.[6] |
| Ni/$SiO_2$ | Water | 50-250 | 0.5-5.0 | 35.10 | Relvas et al [7] |
| CuNiCr/kieselguhr | None | 230-290 | 0.1 | 43.39 | Petrov et al.[8] |
| Au/$ZrO_2$ | Ethanol | 25-50 | 4.0 | 67.20 | Gomez et al.[9] |

**Table S7.** Kinetics linear fit of hydrogenation of aniline over 1.5%Ru-1.5%Pd/$C_3N_4$-air

| Temperature ℃ | Linear fit equation | k ($min^{-1}$) | $R^2$ |
|---|---|---|---|
| 50 | y=0.0006x-0.0028 | 0.0006 | 0.9971 |
| 60 | y=0.0014x+0.0040 | 0.0014 | 0.9980 |
| 70 | y=0.0026x+0.0073 | 0.0026 | 0.9993 |
| 80 | y=0.0050x+0.0011 | 0.0050 | 0.9997 |

**Table S8.** Relevant kinetic data of hydrogenation of aniline

| Catalyst | Solvent | Temperature (℃) | Pressure (MPa) | Activation energy (kJ/mol) | References |
|---|---|---|---|---|---|
| Ru-Pd/$C_3N_4$-air | THF | 20-50 | 3.0 | 66.3[this work] | - |
| Ni powder | None | 160-200 | 1.0-10.0 | 72.0 | Mink et al.[10] |
| Ni/Si/Al | None | 150-200 | 6.0-10.0 | 62.0 | Mink et al.[10] |
| Ru/$Al_2O_3$ | Cyclohexane and water two-phase | 105-145 | 4.8 | 50.4 | Roy et al.[11] |

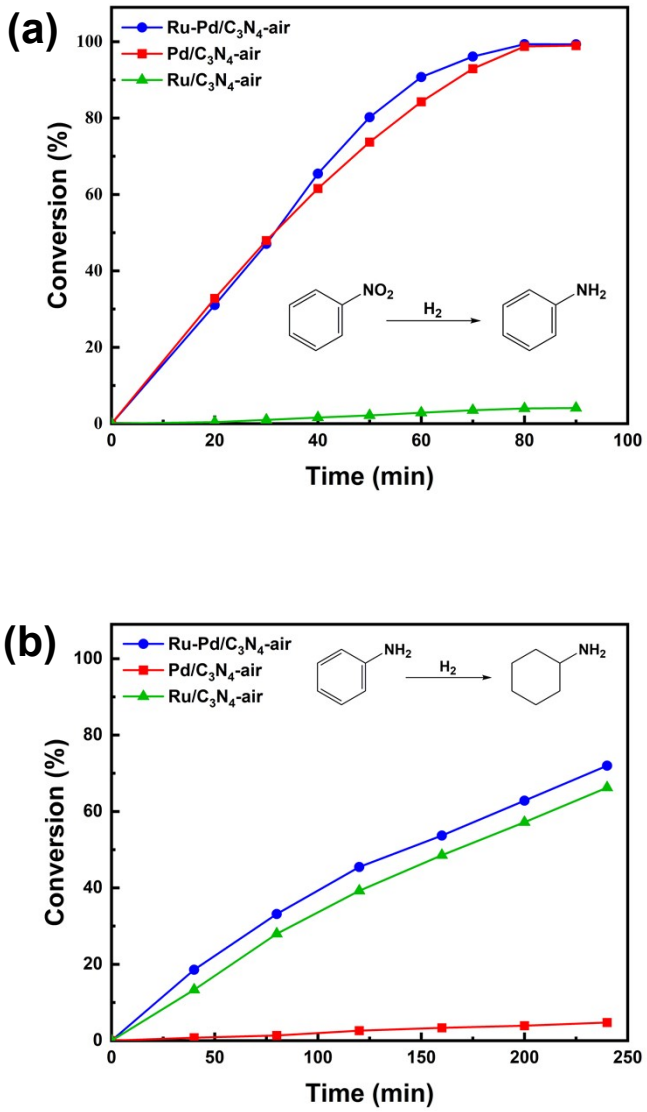



**Fig. S11.** (a) NB conversion vs. Time over 1.5%Ru-1.5%Pd/$C_3N_4$-air, 3%Ru/$C_3N_4$-air, and 3%Pd/$C_3N_4$-air. Reaction conditions: 70 mmol NB, 1wt.% catalyst, 105 mL THF, 50 ℃, 1 MPa $H_2$. (b) NB conversion vs. Time over 1.5%Ru-1.5%Pd/$C_3N_4$-air, 3%Ru/$C_3N_4$-air, and 3%Pd/$C_3N_4$-air. Reaction condition: 10 mmol AN, 25wt.% catalyst, 100 mL THF, 80 ℃, 3 MPa $H_2$.

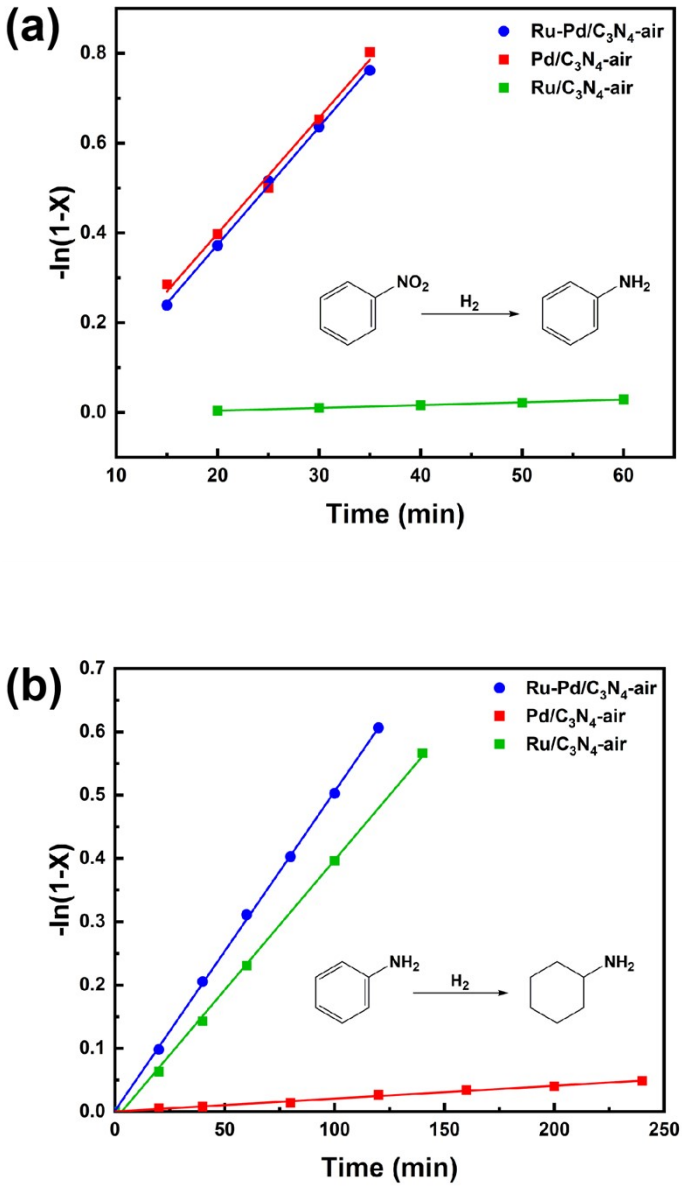



**Fig. S12.** Plots of -ln(1-X) versus time over different catalysts. (a) nitrobenzene hydrogenation, (b) aniline hydrogenation.

**Table S9.** Kinetics linear fit of hydrogenation of nitrobenzene over different catalysts

| Catalyst | Linear fit equation | k ($min^{-1}$) | $R^2$ |
|---|---|---|---|
| 1.5%Ru-1.5%Pd/$C_3N_4$-air | y=0.0262x-0.1502 | 0.0262 | 0.9990 |
| 3%Pd/$C_3N_4$-air | y=0.0258x-0.1176 | 0.0258 | 0.9922 |
| 3%Ru /$C_3N_4$-air | y=0.0006x-0.0087 | 0.0006 | 0.9979 |

**Table S10.** Kinetics linear fit of hydrogenation of aniline over different catalysts

| Catalyst | Linear fit equation | k ($min^{-1}$) | $R^2$ |
|---|---|---|---|
| 1.5%Ru-1.5%Pd/$C_3N_4$-air | y=0.0050x+0.0011 | 0.0050 | 0.9997 |
| 3%Pd/$C_3N_4$-air | y=0.0002x+0.0001 | 0.0002 | 0.9934 |
| 3%Ru/$C_3N_4$-air | y=0.0041x-0.0128 | 0.0041 | 0.9987 |

## 5 Catalyst recyclability and versatility

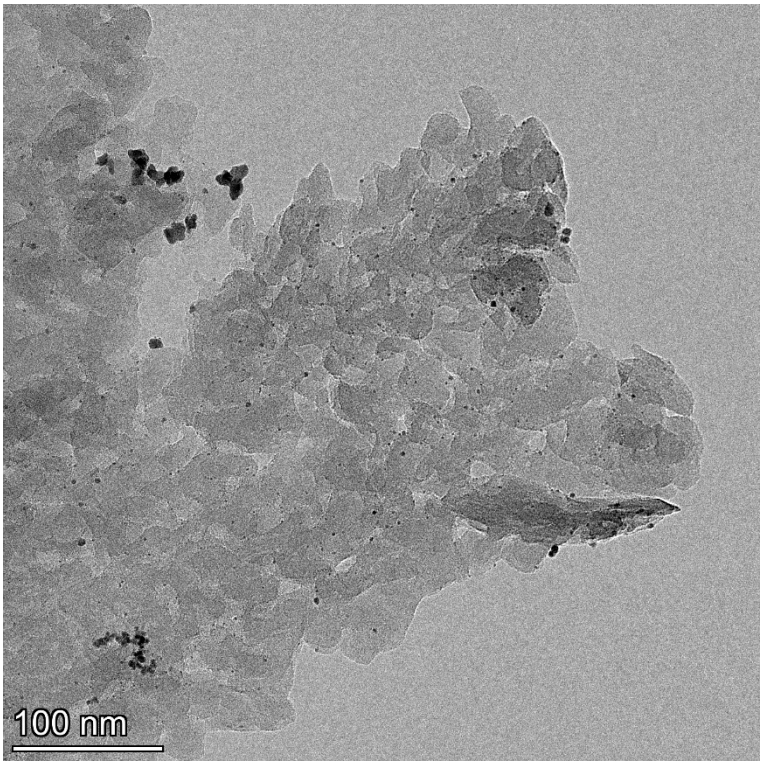
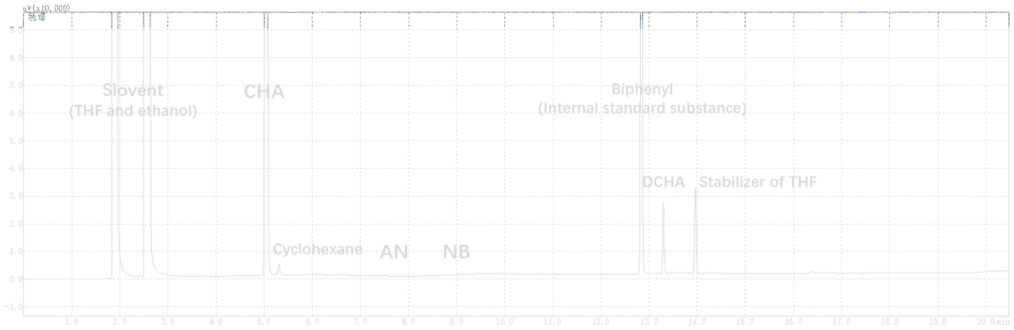



**Fig. S13.** TEM images of recycled 1.5%Ru-1.5%Pd/$C_3N_4$-air

**Nitrobenzene (GC characteristic peaks):**




**o-nitrotoluene:**

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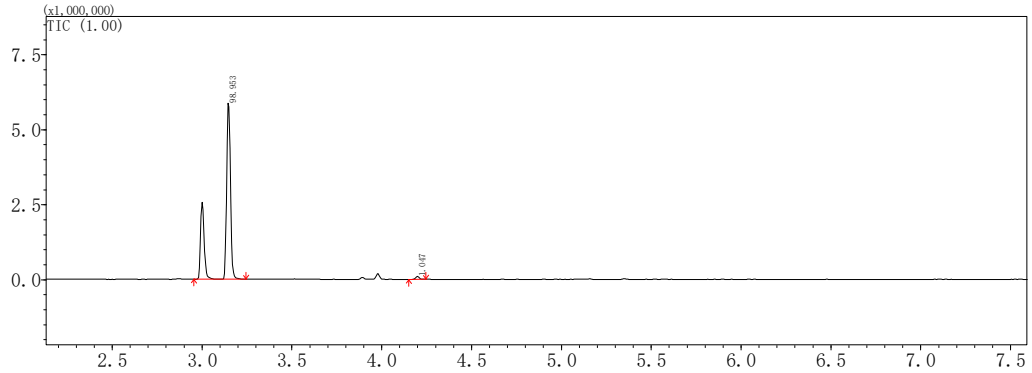


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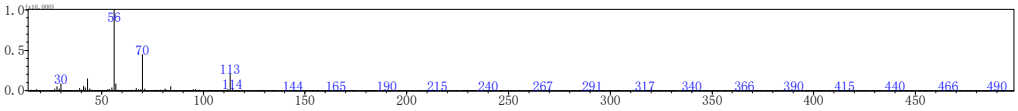
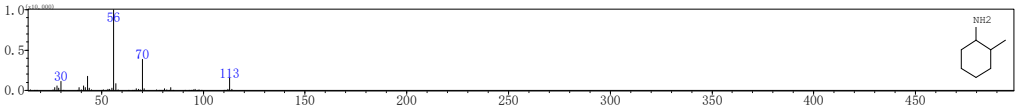
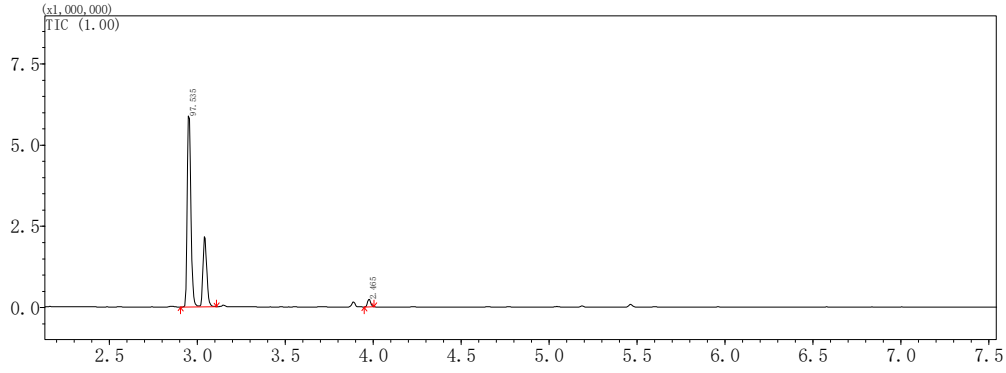



**(c)**




**m-nitrotoluene:**

**(a)**



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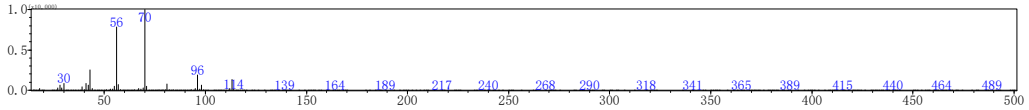


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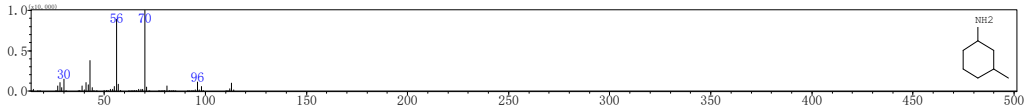


**p-nitrotoluene:**

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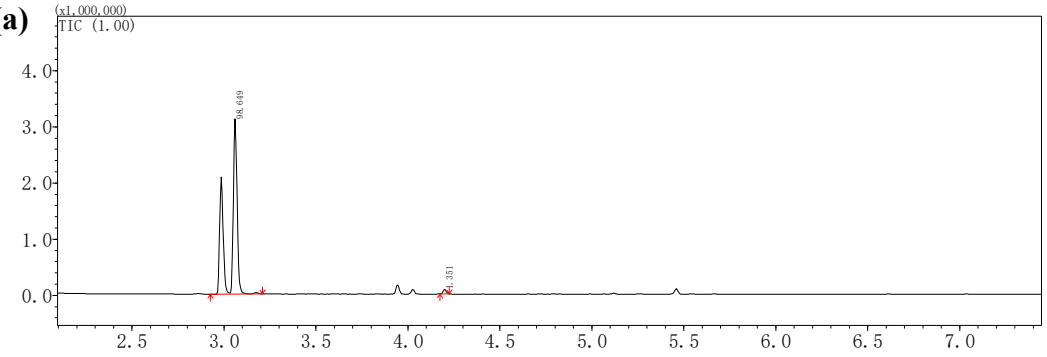


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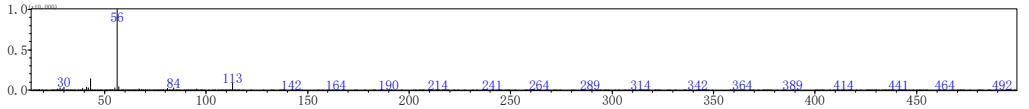


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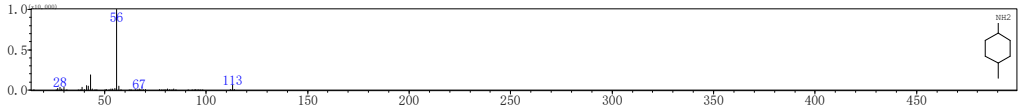


**2-ethylnitrobenzene:**

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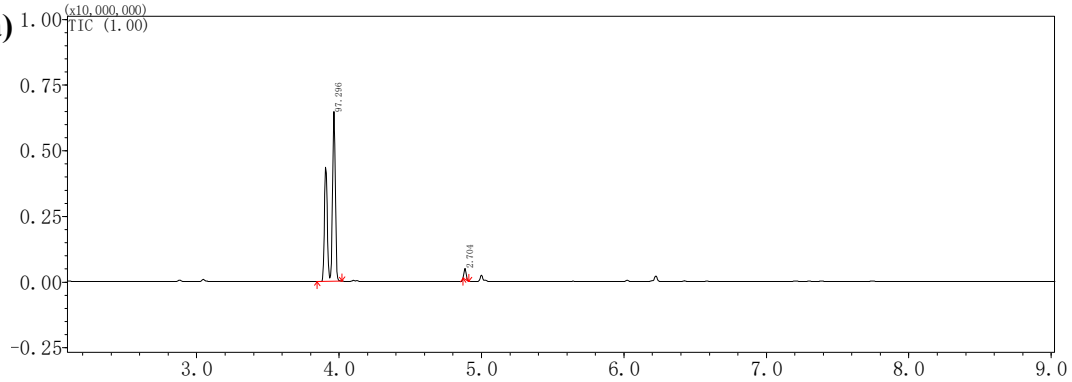


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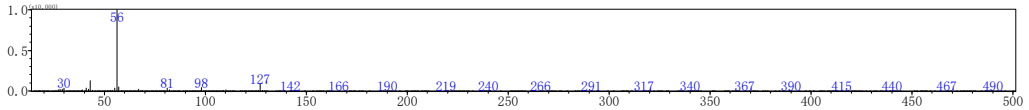

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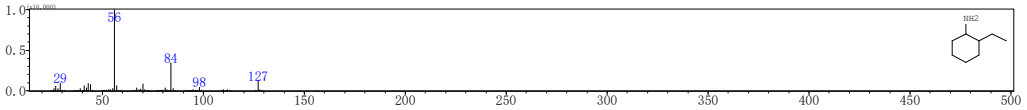


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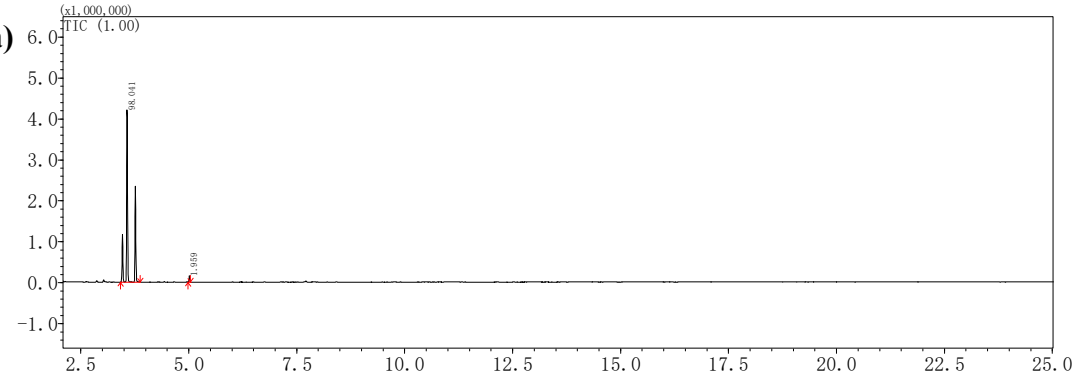
**(a)**

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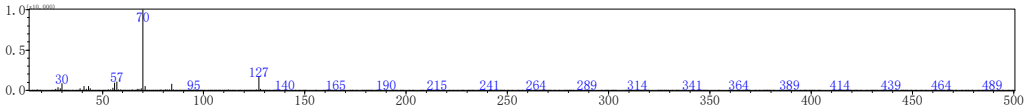


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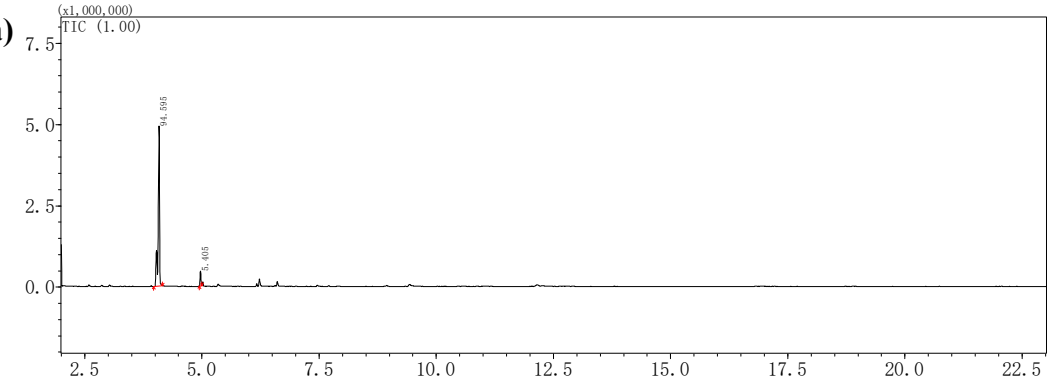


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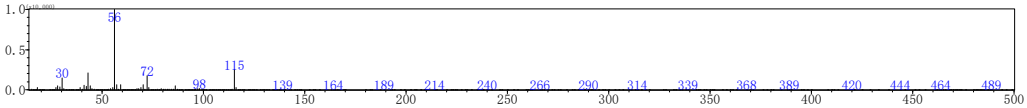


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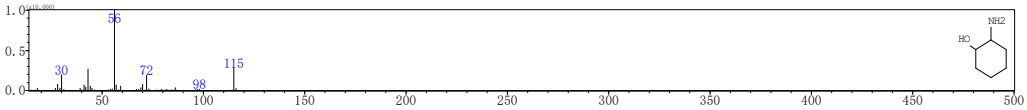


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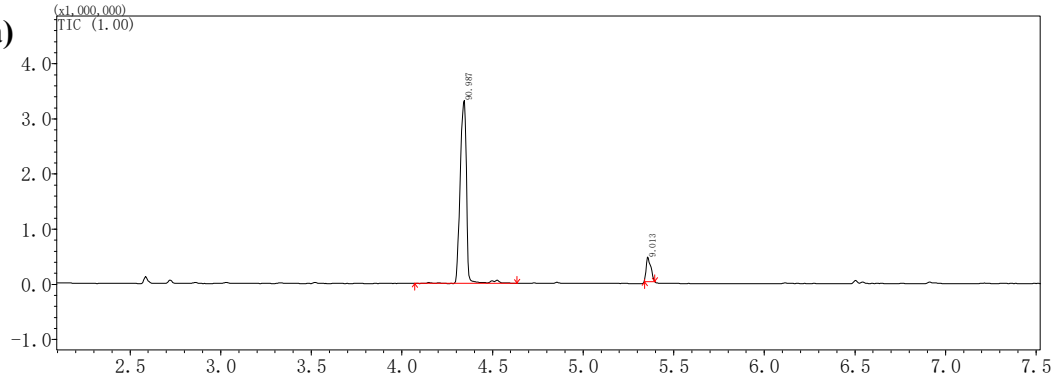


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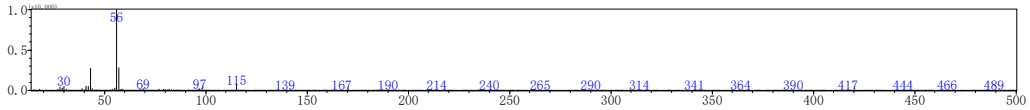


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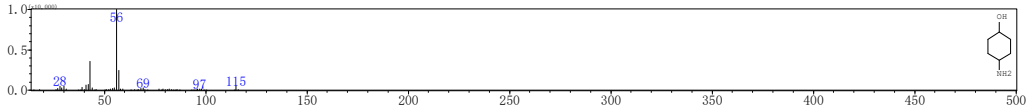
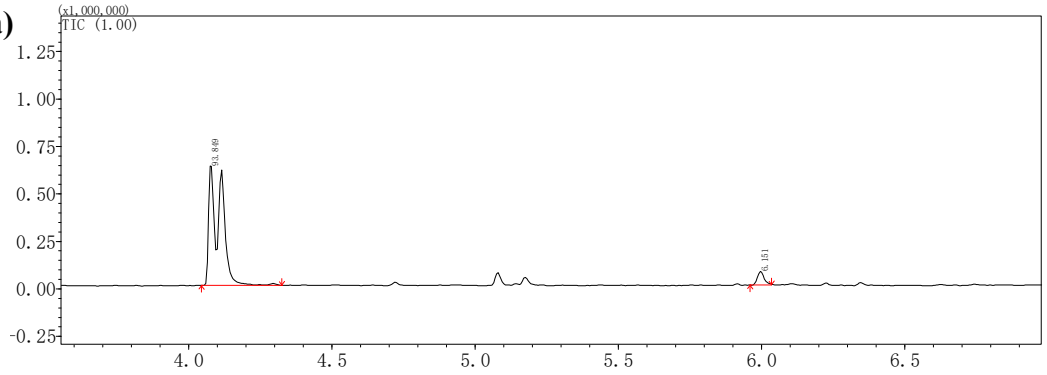
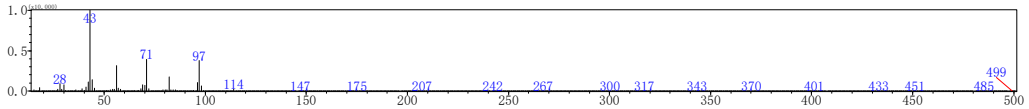



**3-nitroaniline:**

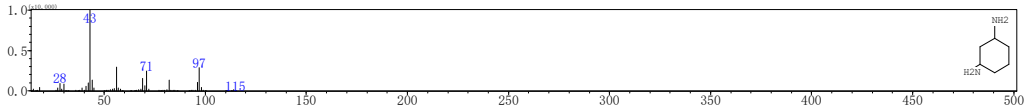
**(a)**



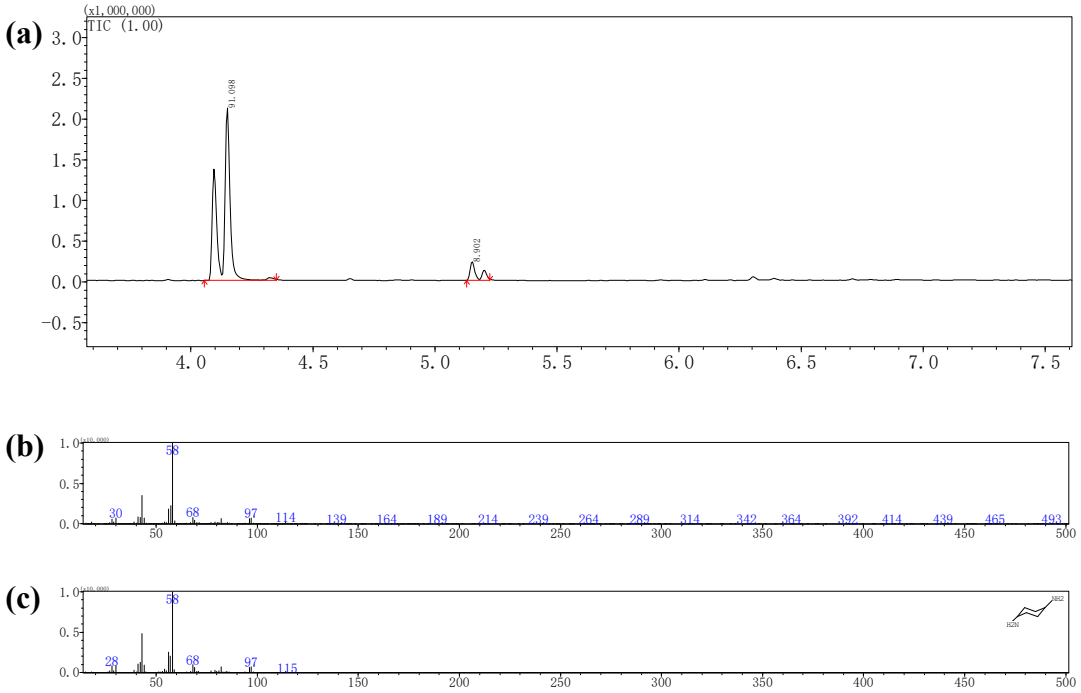

**(b)**



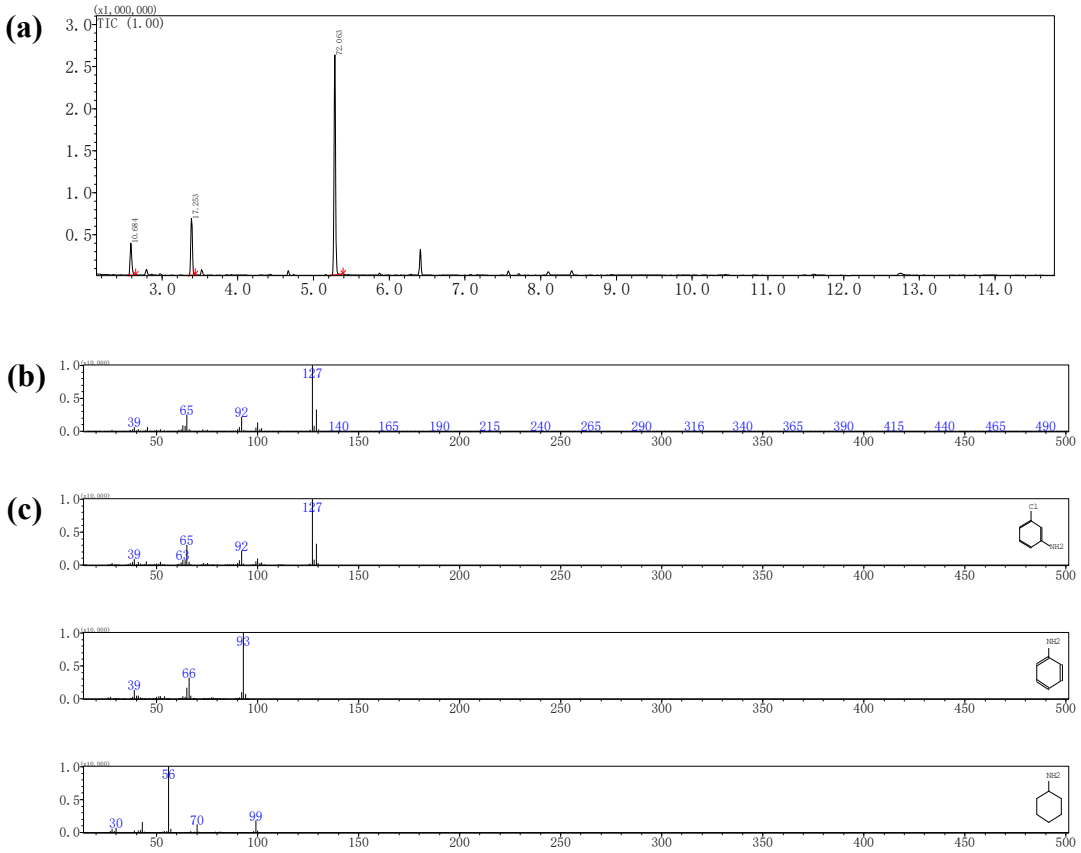

**(c)**




**4-nitroaniline:**




**3-nitrochlorobenzene:**



**4-nitrobenzoic acid:**

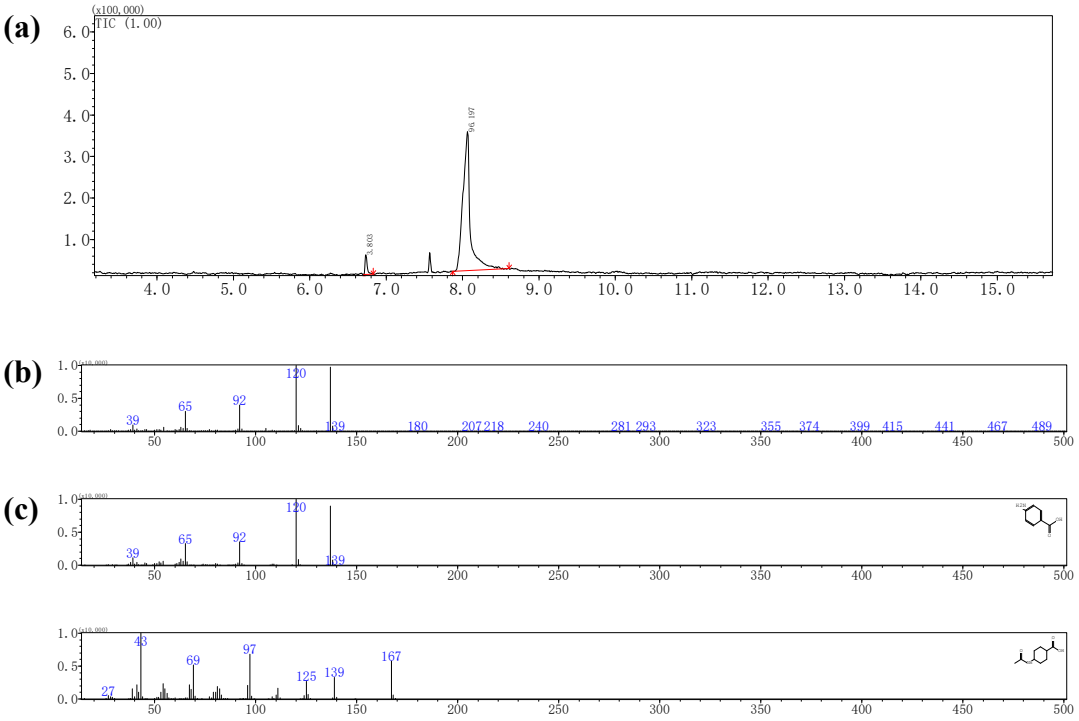



**Fig. S14.** Original results of GC-MS. (a) GC-MS characteristic peaks, (b) detected fragment peaks, (c) fragment peak in database.

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