

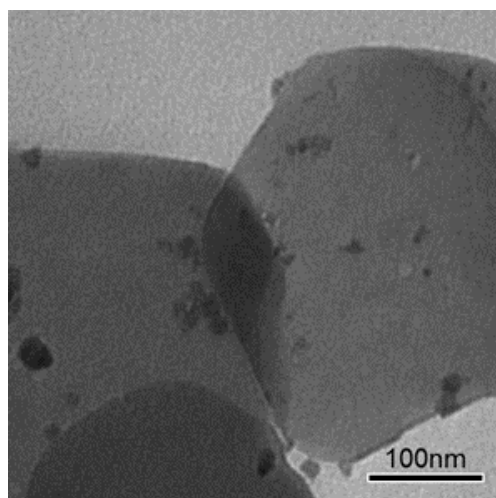
# Supplementary Materials: Electron-Enriched Pd Nanoparticles for Selective Hydrogenation of Halonitrobenzenes to Haloanilines

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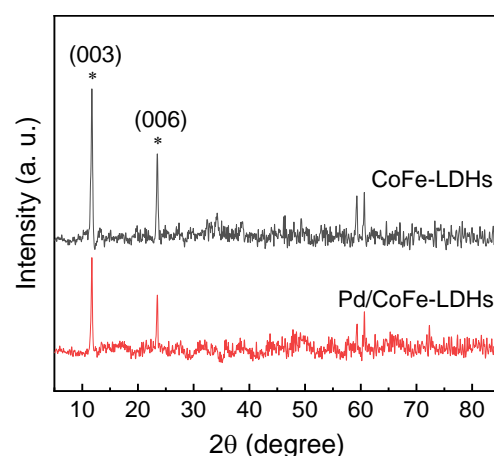
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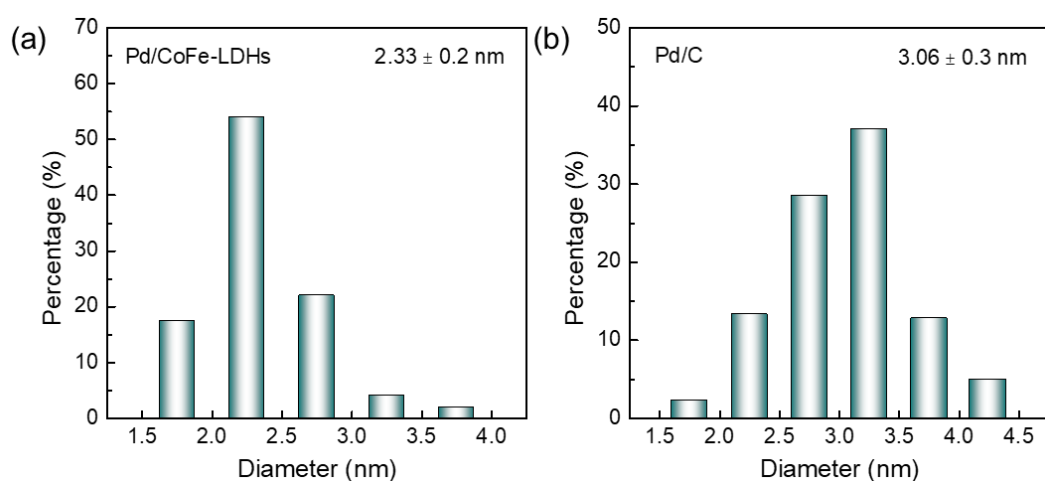
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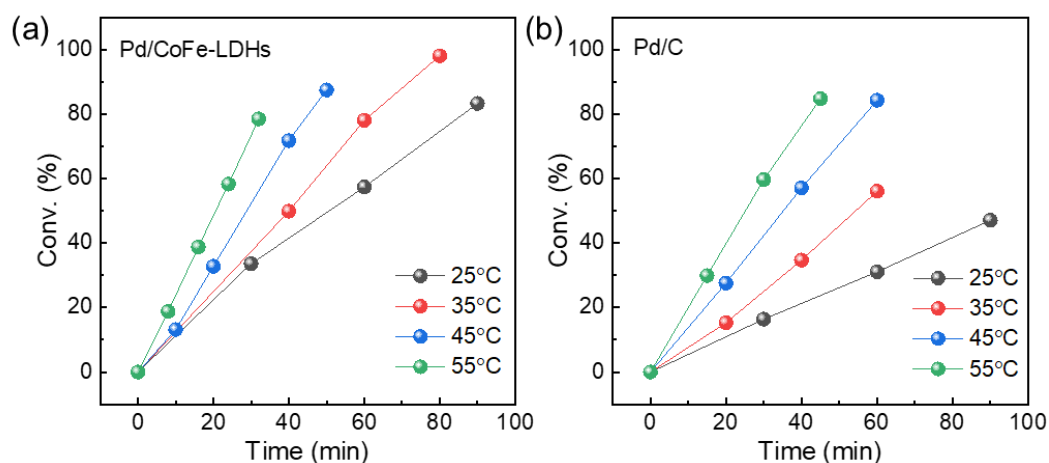
**Figure S1.** TEM image of CoFe-LDHs supports.



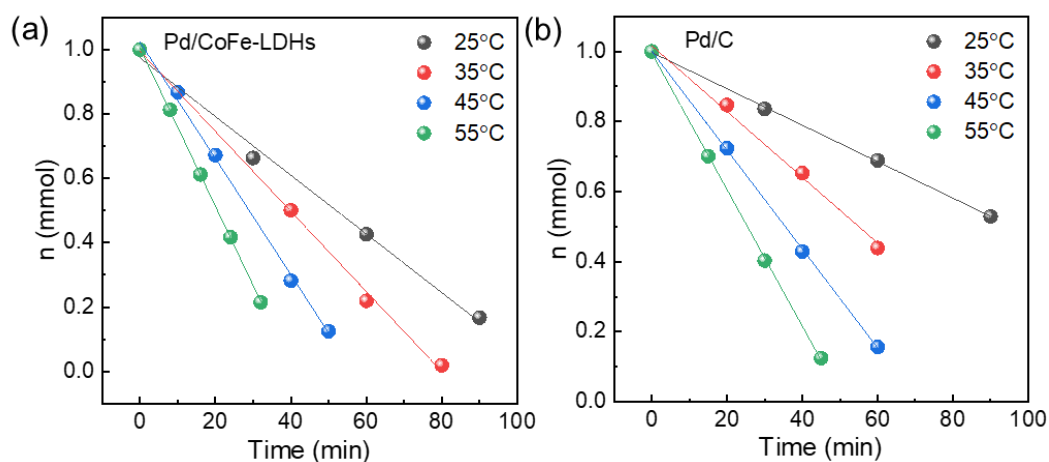
**Figure S2.** XRD patterns of the CoFe-LDHs supports and Pd/CoFe-LDHs catalyst.



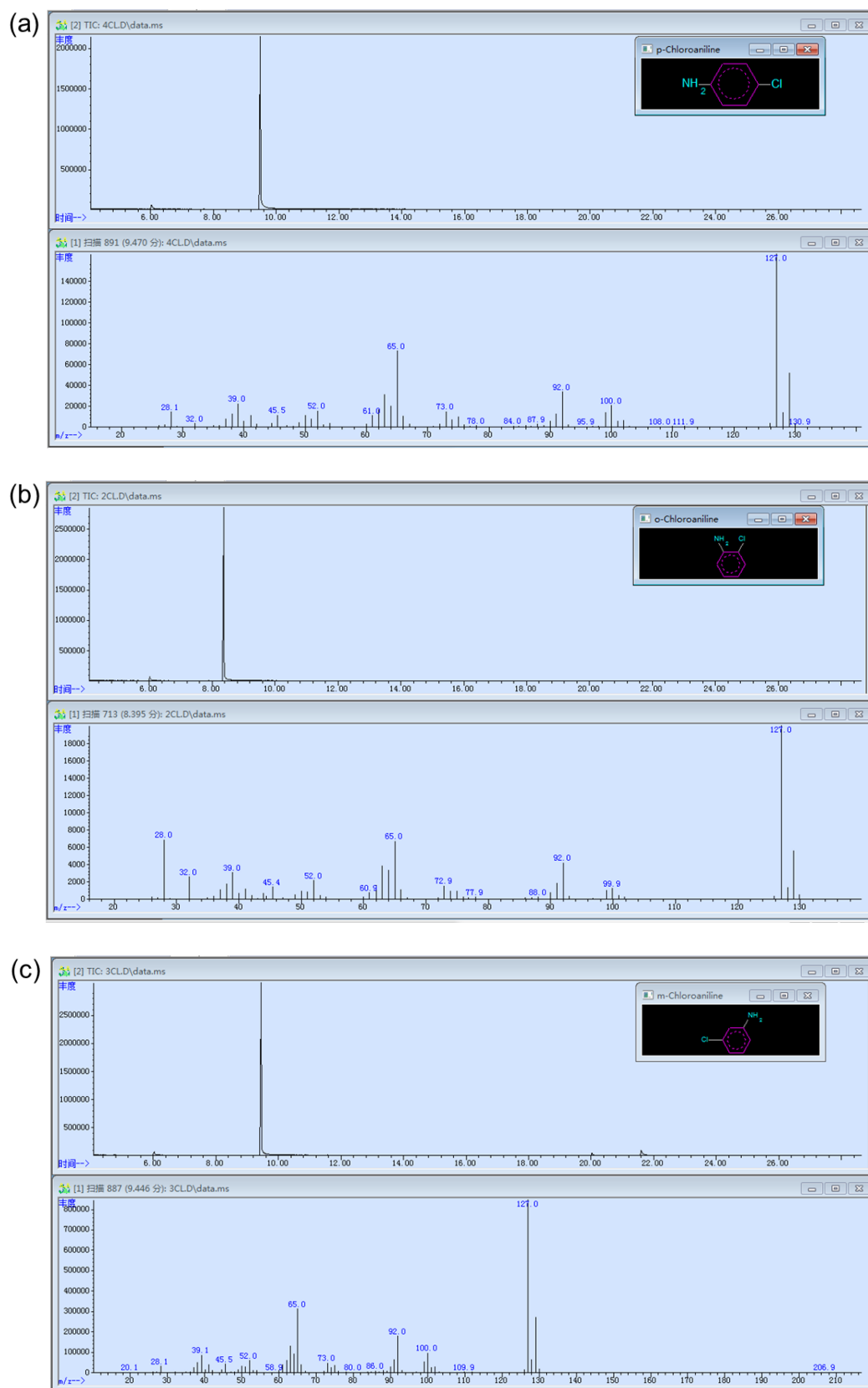
**Figure S3.** (a) Size distribution of Pd nanoparticles in Pd/CoFe-LDHs catalyst; (b) Size distribution of Pd nanoparticles in Pd/C catalyst.

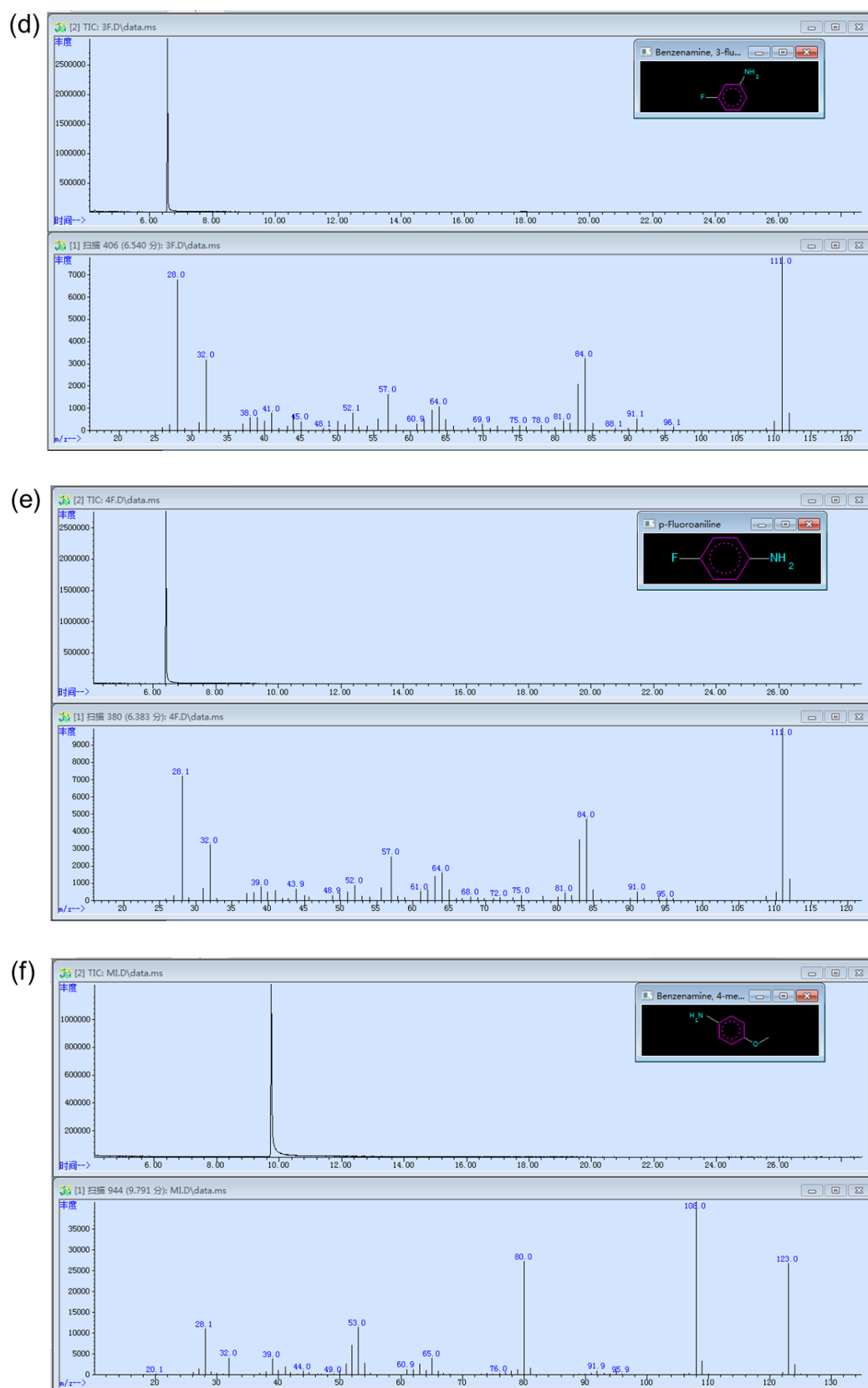


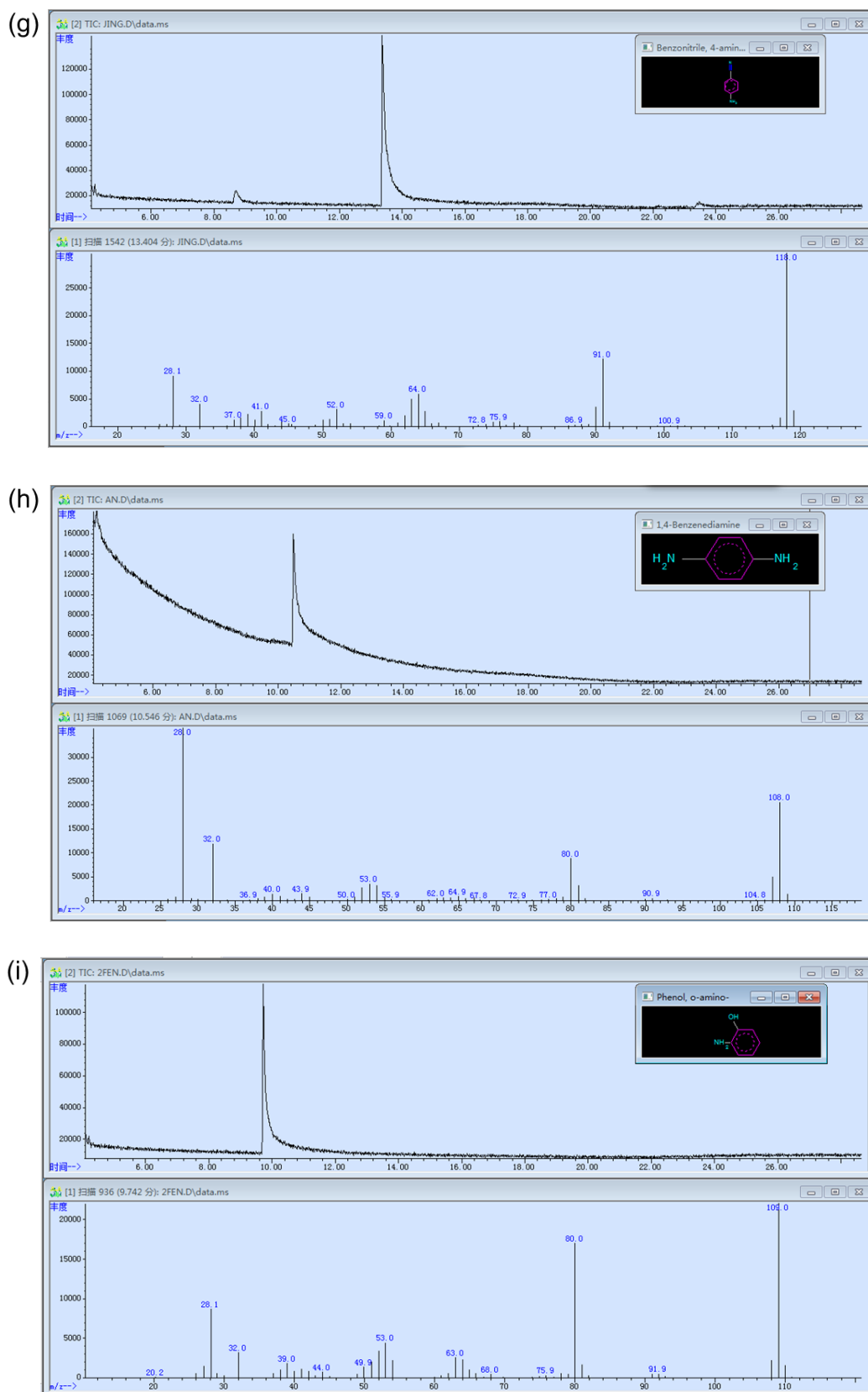
**Figure S4.** (a) The conversion of *p*-CNB at various reaction temperature catalyzed by Pd/CoFe-LDHs; (b) The conversion of *p*-CNB at various reaction temperature catalyzed by Pd/C. Reaction conditions: *p*-CNB (1.0 mmol), catalysts (10.0 mg), isopropanol (2.0 mL), and 0.5 MPa of H<sub>2</sub>.

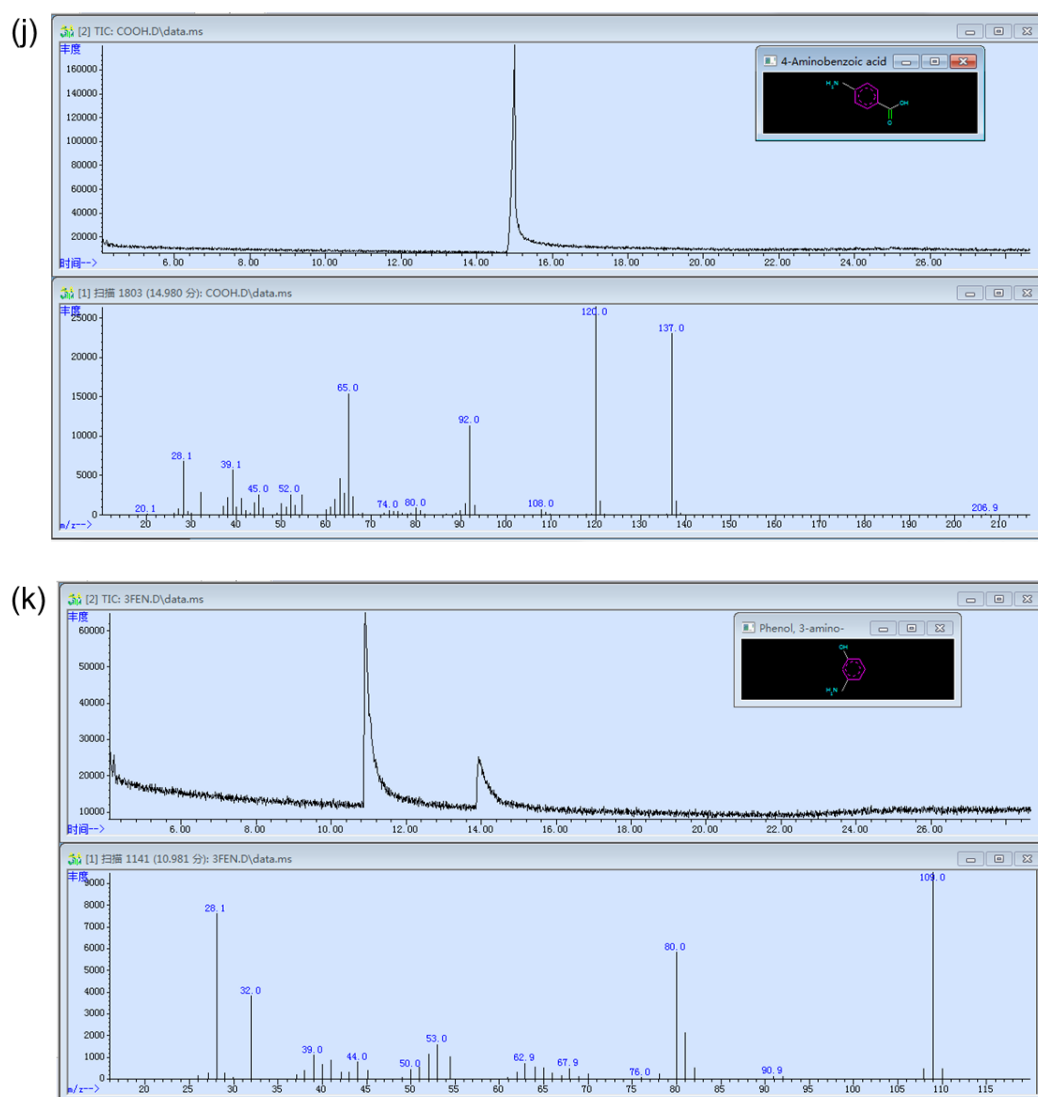


**Figure S5.** (a) The amount of *p*-CNB as a function of reaction time at various temperatures catalyzed by Pd/CoFe-LDHs; (b) The amount of *p*-CNB as a function of reaction time at various temperatures catalyzed by Pd/C.









**Figure S6.** The GC-MS spectra of hydrogenation of (a) *para*-chloronitrobenzene (*p*-CNB), (b) *ortho*-chloronitrobenzene, (c) *meta*-chloronitrobenzene, (d) 3-fluoro-nitrobenzene, (e) 4-fluoro-nitrobenzene, (f) 4-nitroanisole, (g) 4-nitrobenzonitrile, (h) 4-nitroaniline, (i) 2-nitrophenol, (j) 4-nitrobenzoic acid, (k) 3-nitrophenol.

**Table S1.** Hydrogenation of *p*-CNB under different conditions.

Entry	Solvents	T (°C)	P (Mpa)	Time (min)	Conv. (%)	Sel. (%)
1	Toluene	25	0.5	120	11.9	78.7
2	Cyclohexane	25	0.5	120	18.9	81.8
3	Methanol	25	0.5	120	99.9	62.7
4	Ethanol	25	0.5	120	99.9	85.5
5	Isopropanol	25	0.5	120	97.4	93.5
6	Isopropanol	35	0.5	80	98.1	89.4
7	Isopropanol	45	0.5	60	99.9	90.1
8	Isopropanol	55	0.5	40	98.5	90.6
9	Isopropanol	25	1	60	70.8	90.7
10	Isopropanol	25	1.5	60	99.9	91.5

Reaction conditions: *p*-CNB (1.0 mmol), catalysts (10.0 mg), solvents (2.0 mL).

**Equation S1:** The Pd dispersion (D) was calculated according to:

$$D = \frac{1.11}{d}$$

Where d is the mean diameter of Pd nanoparticles (nm).

**Equation S2:** The TOF value was calculated according to:

$$\text{TOF} = \frac{n_0 \times \text{Conv.}}{\frac{m_{\text{cat.}} \times \text{wt\%Pd} \times D}{M_{\text{Pd}}} \times t}$$

Where  $n_0$  is the mole of initial substrate, Conv. is the conversion of substrates,  $m_{\text{cat.}}$  is the weight of catalyst, wt%Pd is the actual loading content of Pd, D is the dispersion of Pd,  $M_{\text{Pd}}$  is the atomic weight of Pd, and t is the reaction time (h).