

## **Electronic supplementary information (ESI)**

### **Synergistic Catalysis: Cobalt-catalyzed Cascade Reaction for the Oxidative Cleavage of Olefins to Access Esters**

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## **Experimental**

### **Preparation of the catalysts**

Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (1.5 mmol, 374 mg) and 1,10-phenanthroline (3 mmol, 595 mg) were dissolved in distilled water. At the same time, colloidal silica was dispersed in 40 mL distilled water. The mixture is then added to the silicon dioxide. The reaction was carried out at 60°C for 4 h, then heated to 110 °C to evaporate to remove water. After grinding, the powder was put into a porcelain boat and pyrolyzed at constant temperature for 2 hours under the protection of nitrogen at 600-900 °C. The silica template was removed with sodium hydroxide solution and the metal impurities were removed with hydrochloric acid solution. The heterogeneous mesoporous catalyst was obtained by washing and drying the distilled water.

### **The reaction process of oxidative cleavage of olefins to esters**

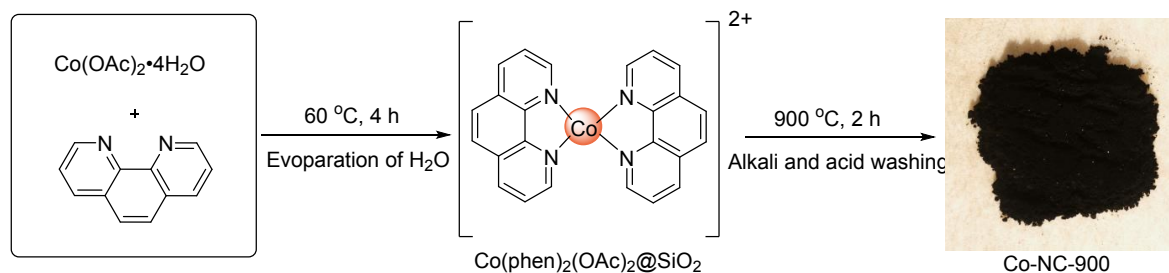
Magneton, catalysts, K<sub>2</sub>CO<sub>3</sub>, reaction substrates and anhydrous methanol were added in the reaction bottle. Place the reaction bottle at the bottom of the autoclave and leave a lid with a small opening of 1 mm in diameter on the cap of the reaction bottle. The autoclave was filled with oxygen of 0.6 MPa and reacted for 24 hours. After the reaction is completed, the reaction kettle is cooled to room temperature, the kettle is deflated, biphenyl and anhydrous methanol are added, and the biphenyl is stirred at room temperature until the biphenyl is completely dissolved. The reaction solution was centrifuged and tested by GC and GC-MS.

### **characterization**

The X-ray power diffraction (XRD) spectrum was obtained by Cu-K $\alpha$  radiation on Bruker D2 Phaser powder diffractometer. The Raman spectrum was collected by a 532 nm diode pumped solid state laser on a commercial Raman spectrometer (Invia, Renishaw plc.). The content of Co was measured by inductively coupled plasma emission spectrometer (ICP-OES Optima 7300V). The nitrogen adsorption isotherm curve was obtained by AUTOSORB-1MP automatic specific surface area and micropore analyzer. The X-ray photoelectron spectroscopy (XPS) were recorded by Thermo Scientific ESCALAB 250Xi instrument using Al K $\alpha$  radiation anode ( $h\nu = 1486.6$  eV) and the C1s peak (284.6 eV) was used as the internal standard to correct the binding energies (BE). It is noted that C1s peak at 284.6 eV is due the NC material itself rather than adventitious carbon. JEM-2100 transmission electron microscope (TEM) operated at an accelerating voltage of 120.0 kV. The morphology and elemental analysis of the samples were characterized by scanning electron microscopy (SEM) JEOL JEM-F200 equipped with an energy dispersive

spectroscopy (EDS). The H<sub>2</sub> and CO<sub>2</sub> generated from oxidation of styrene were qualitatively analyzed by mass spectrometry (Balzers omnistar) and Ar is used as carrier gas, and the H<sub>2</sub> was further confirmed using gas chromatography (Agilent technologies 7890A, TCD detector).

### Supporting results

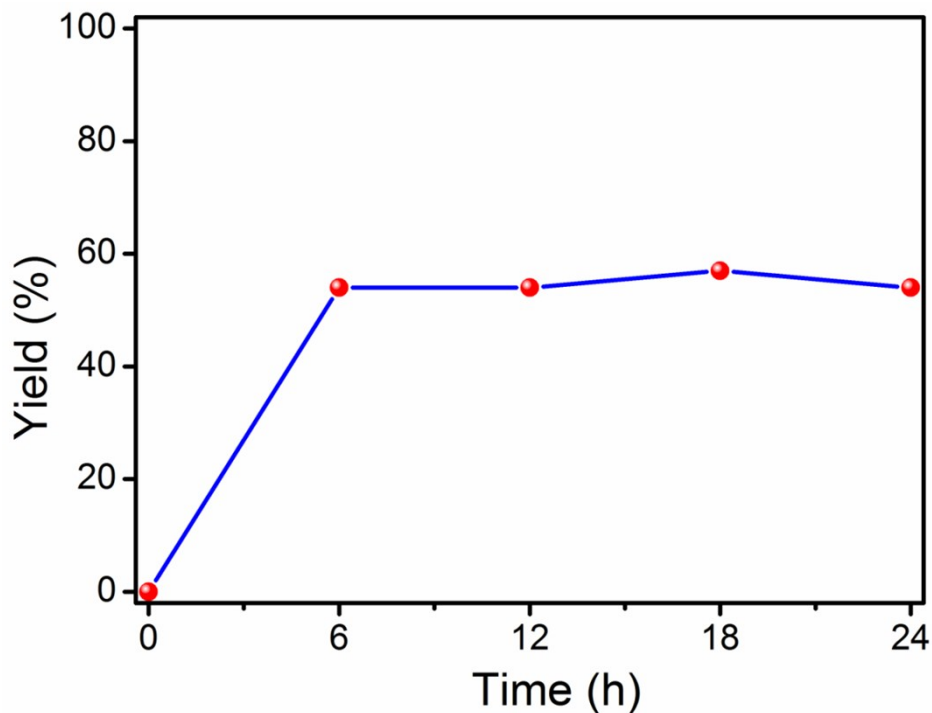


**Fig. S1** Preparation of the catalysts.

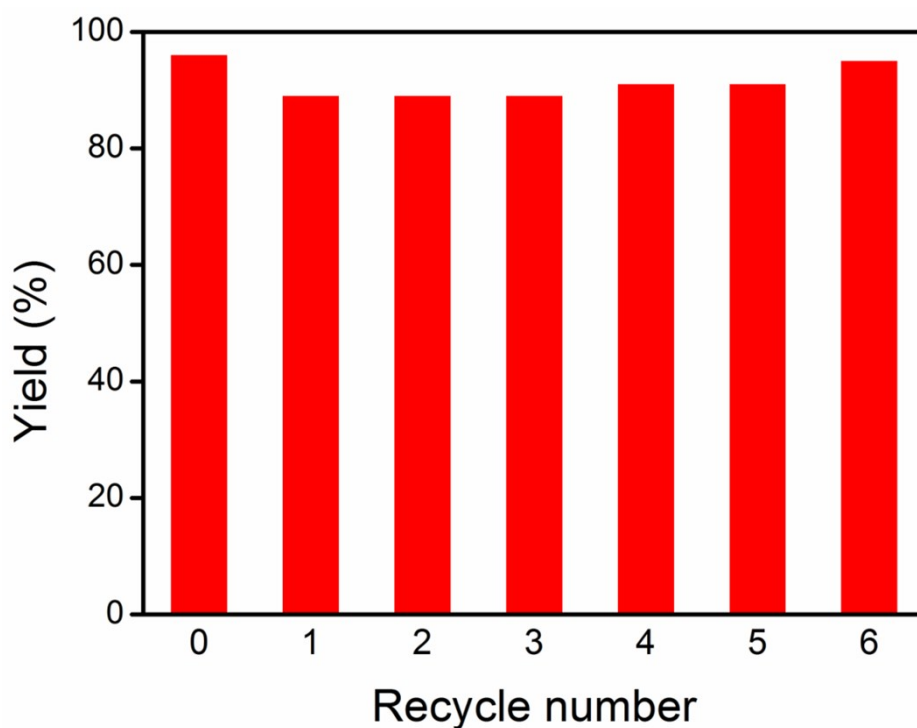
**Table S1.** Screening of base types. <sup>[a]</sup>

Entry	alkali	Conv.[%]	Yield[%]
1	K <sub>2</sub> CO <sub>3</sub>	98	89
2	Cs <sub>2</sub> CO <sub>3</sub>	99	92
3	Na <sub>2</sub> CO <sub>3</sub>	97	82
4	NaOH	77	42
5	KOH	97	54

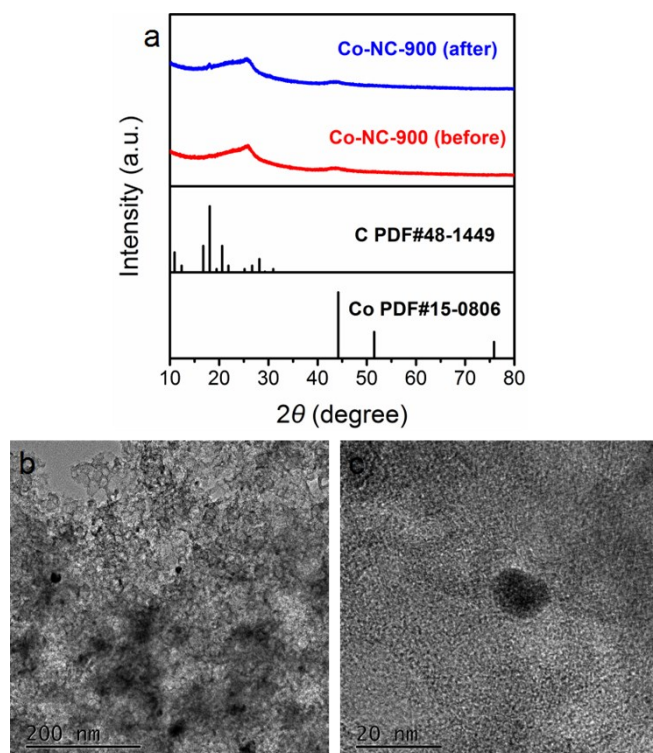
[a] Reaction conditions: styrene (0.25 mmol), Co-NC-900 (7.5 mol%), MeOH (4 mL), 0.6 MPa O<sub>2</sub>, 150 °C. Conversion and yield are measured by GC.



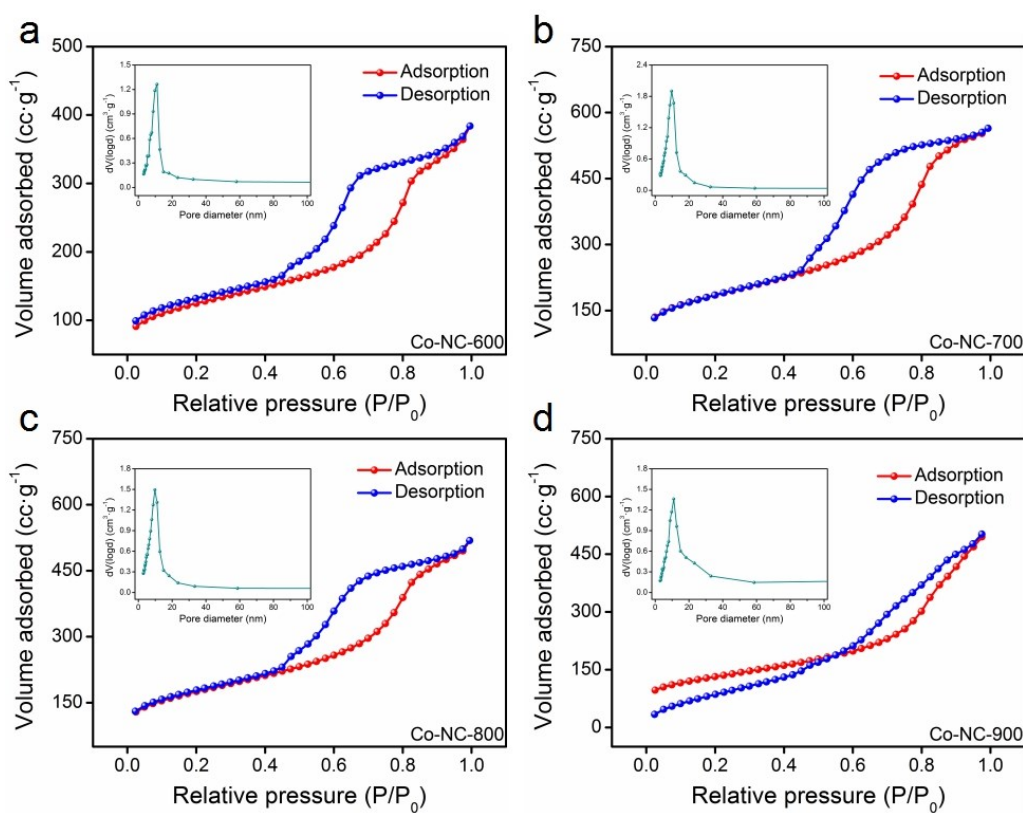
**Fig. S2** Hot filtration test for the oxidative cleavage of styrene. Reaction conditions: styrene (0.25 mmol), Co-NC-900 (7.5 mol%),  $\text{K}_2\text{CO}_3$  (20 mol%), MeOH (4 mL), 0.6 MPa  $\text{O}_2$ , 150 °C. Yields were determined by GC.



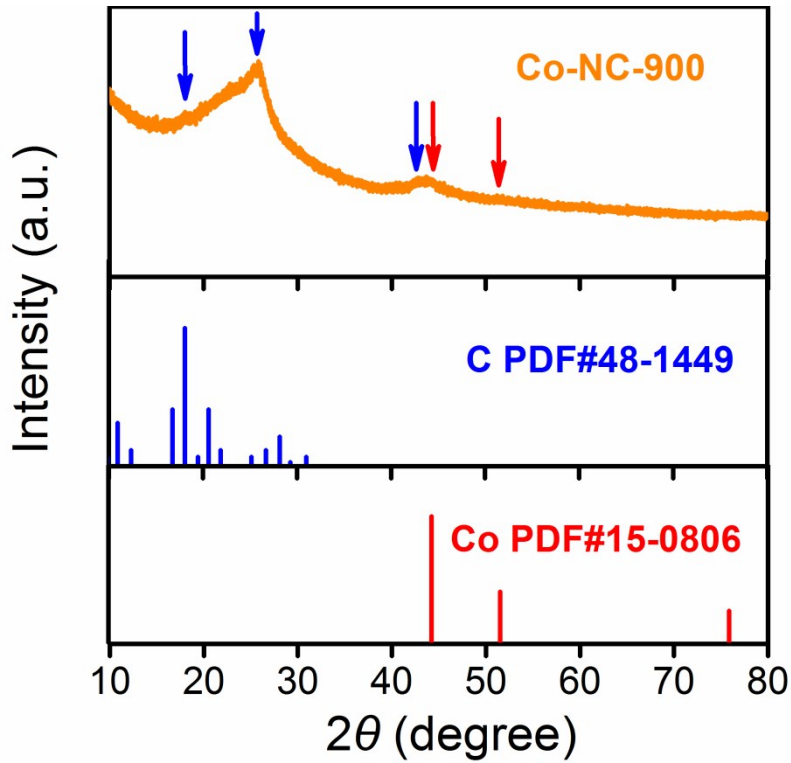
**Fig. S3** Recycling of Co-NC-900 for aerobic oxidative cleavage of styrene. Reaction conditions: styrene (0.25 mmol), Co-NC-900 (10 mol%),  $\text{K}_2\text{CO}_3$  (20 mol%), MeOH (4 mL), 0.6 MPa  $\text{O}_2$ , 150 °C, 24 h. Yields were determined by GC.



**Fig. S4** (a) The XRD spectra of the Co-NC-900 catalyst before and after cycles of reaction. (b) TEM image and (c) HRTEM image of the Co-NC-900 catalyst after cycles of reaction.

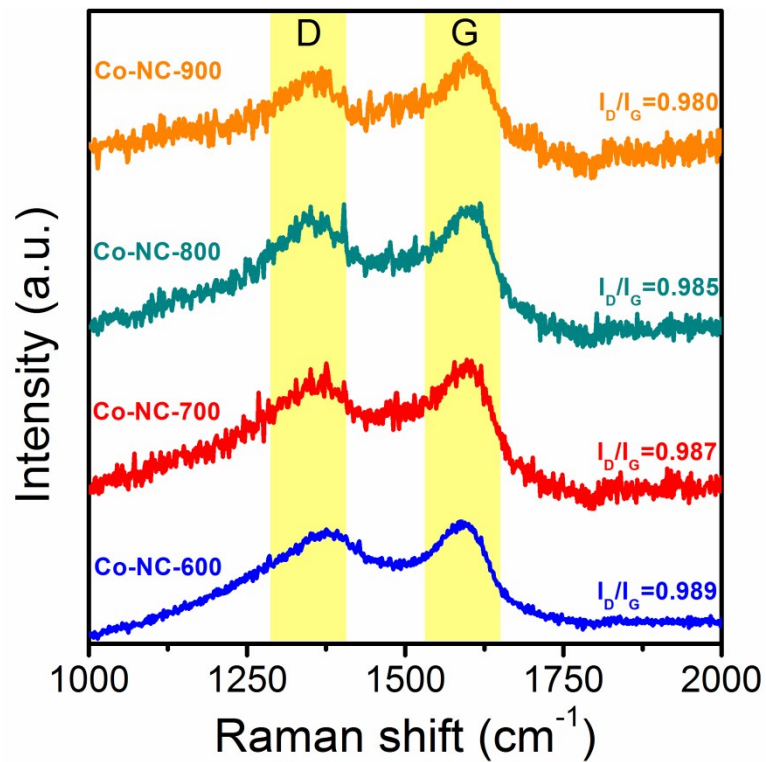


**Fig. S5**  $N_2$  adsorption/desorption isotherms at 77K and mesopore size distribution plot for Co-NC-600 (a), Co-NC-700 (b), Co-NC-800 (c), Co-NC-900 (d).

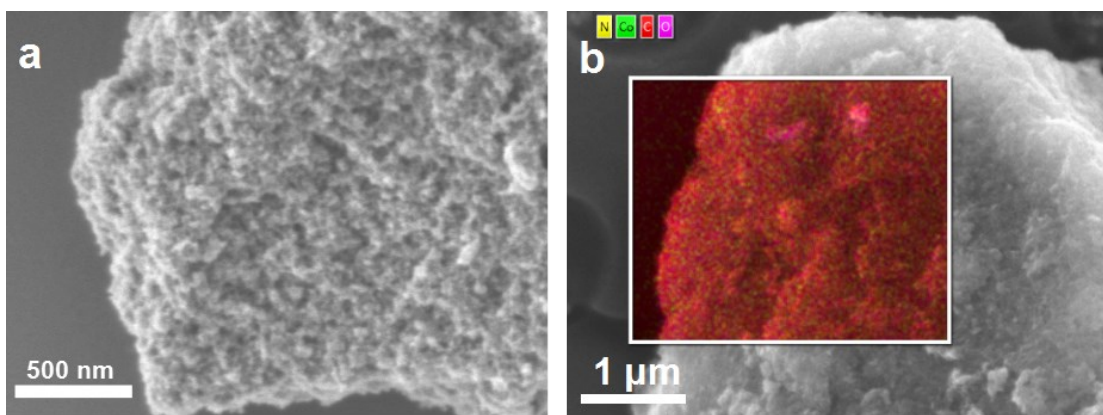


**Fig. S6** XRD patterns of Co-NC-900.

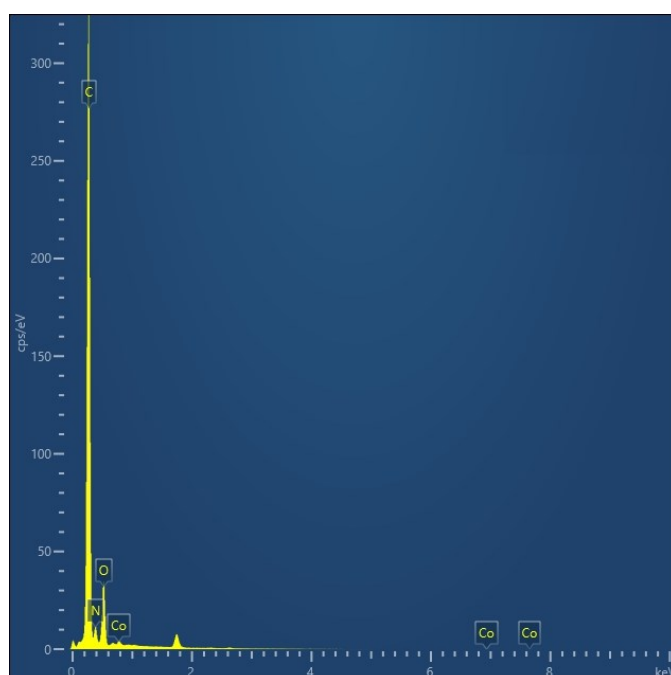
The appearance of the wide peaks of 25° and 43° was attributed to the graphite carbon formed by the pyrolysis. The diffraction peak at 18.0° belongs to the nitrogen-doped carbon.<sup>1</sup>



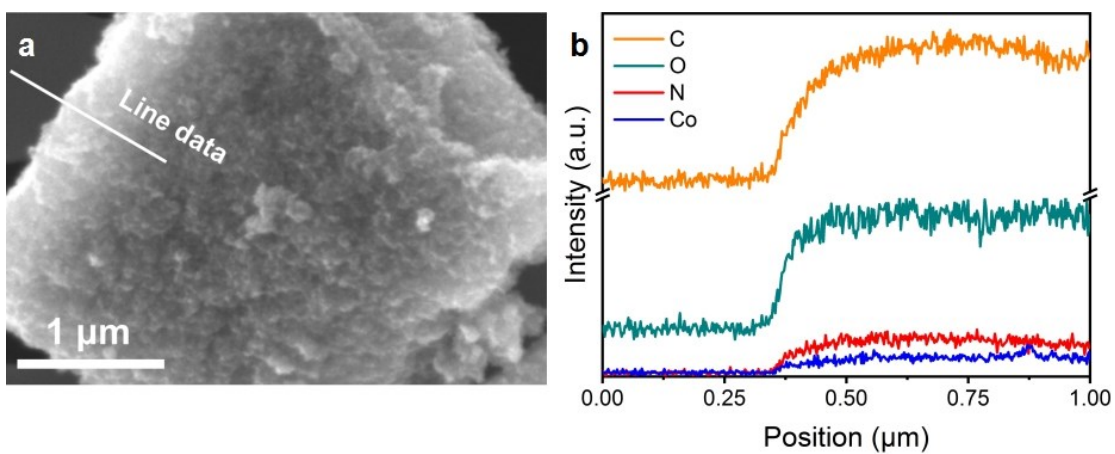
**Fig. S7** Raman spectra of Co-NC-900 catalyst.



**Fig. S8** SEM images under LED mode.

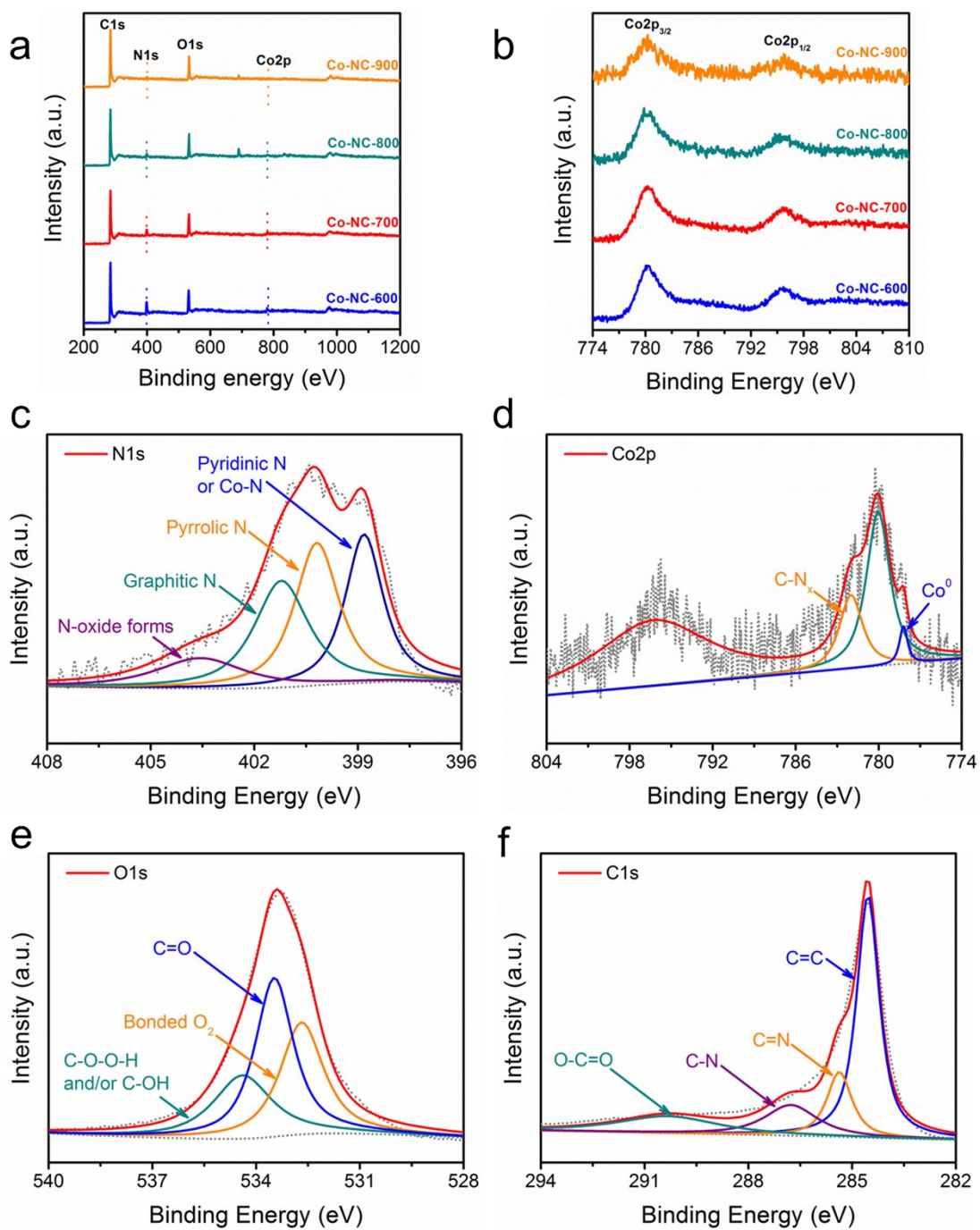


**Fig. S9** EDX spectrum of Co-NC-900 catalyst.



**Fig. S10** EDX line scan mode of Co-NC-900.



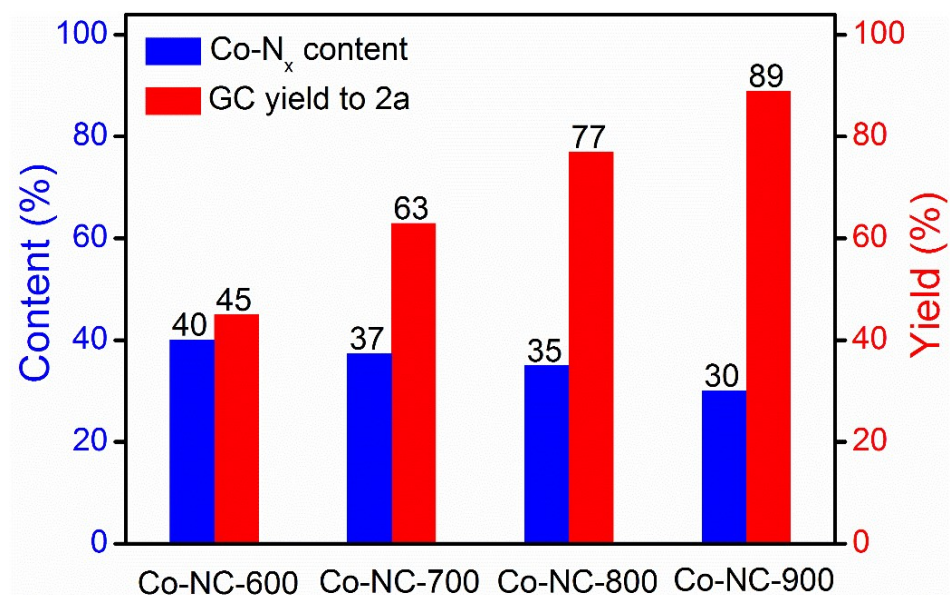
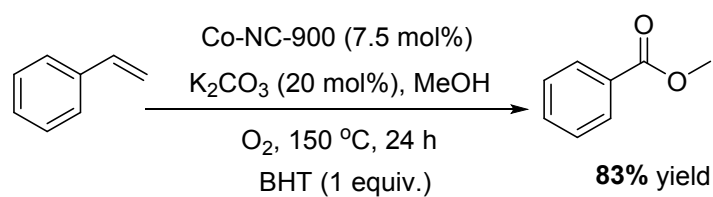


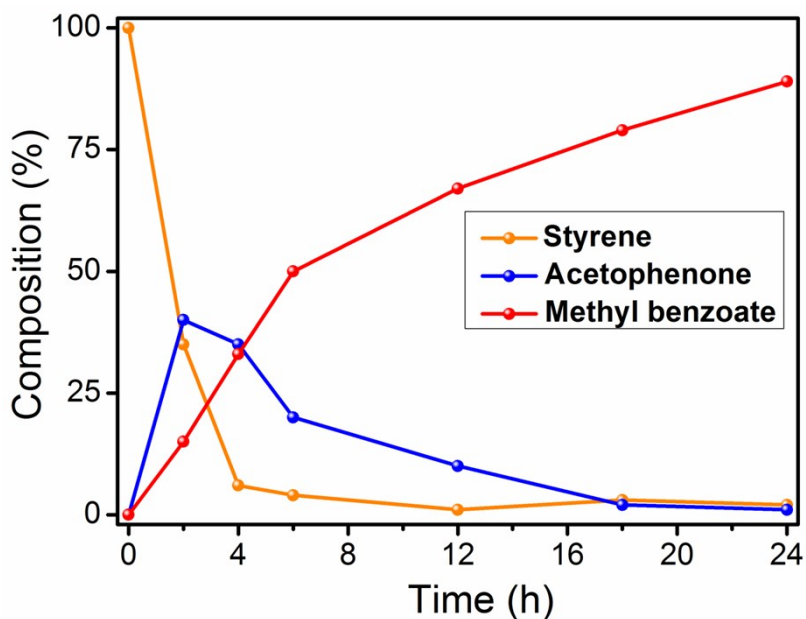
**Fig. S11** (a) XPS spectrum of Co-NC-900. (b) XPS spectrum of Co amplified by Co-NC-900. (c) XPS Spectrum of N 1s. (d) XPS spectrum of Co 2p. (e) XPS Spectrum of O 1s in Co-NC-900. (f) XPS spectrum of C 1s in Co-NC-900.



**Table S2.** XPS spectroscopic analysis composition of Co-NC-X catalyst.

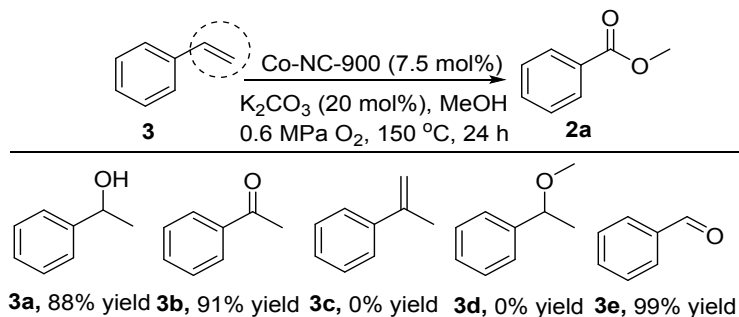
Sample	C(at.%)	N(at.%)					O(at.%)	Co(at.%)		
		Total	Pyridinic-N or Co-N	Pyrrolic-N	Graphitic-N	Oxide-N		Total	Co <sup>0</sup>	Co-N <sub>x</sub>
Co-NC-900	82.8	2.2	27.2	31.1	28.4	13.3	14.9	0.1	5.4	30.1
Co-NC-800	80.7	4.4	39.4	30.4	23.6	6.7	14.7	0.2	4.2	35.0
Co-NC-700	77.6	7.1	41.4	28.5	20.6	9.4	14.9	0.4	3.5	37.4
Co-NC-600	76.2	9.5	55.1	26.5	17.4	0.9	13.7	0.5	1.9	40.1

**Fig. S12** Effect of the content of Co-N<sub>x</sub> sites in the catalysts Co-NC-X for the benchmark reaction under standard condition.**Scheme S1.** Radical trapping experiment.

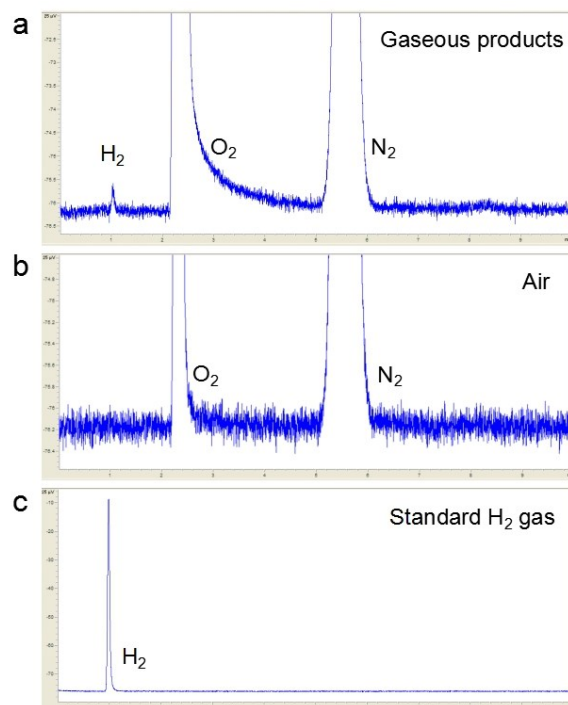


**Fig. S13** Time course experiment catalyzed by Co-NC-900 for the transformation of styrene. Reaction conditions: styrene (0.25 mmol), Co-NC-900 (7.5 mol%),  $K_2CO_3$  (20 mol%), MeOH (4 mL), 0.6 MPa  $O_2$ , 150 °C, 24 h. Yields are measured by GC.

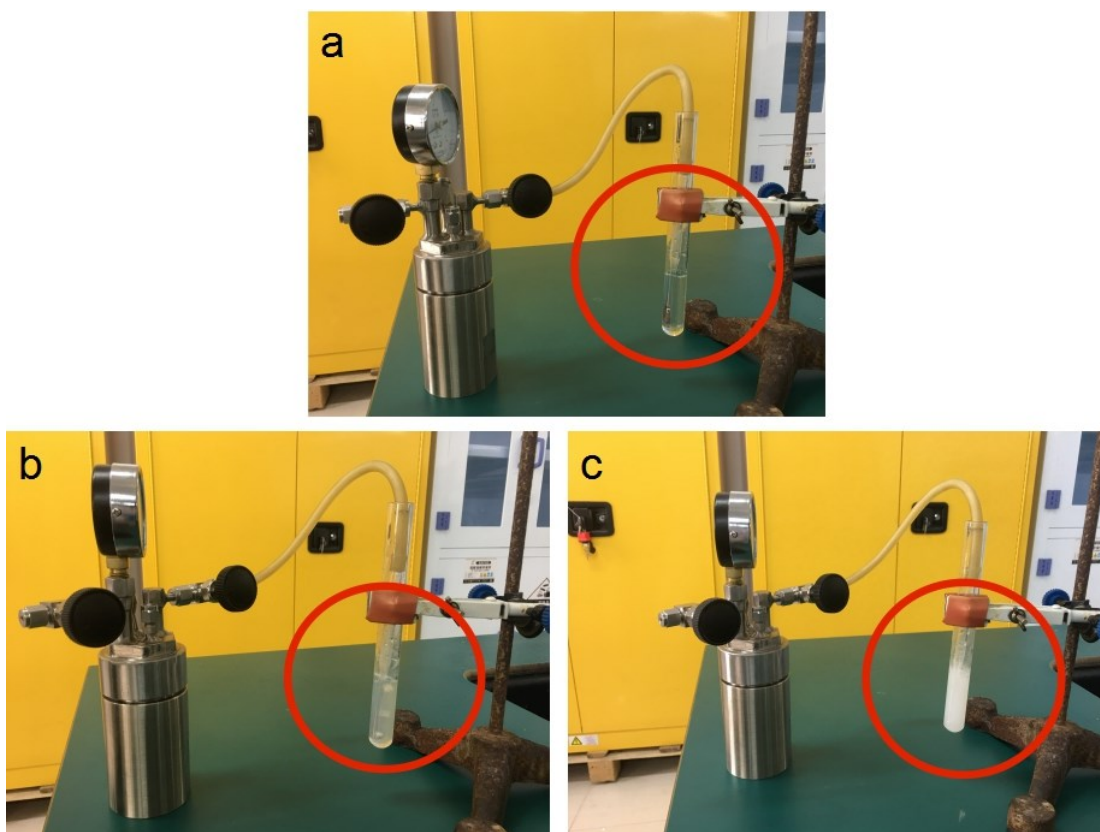
**Table S3.** Control experiments<sup>a</sup>



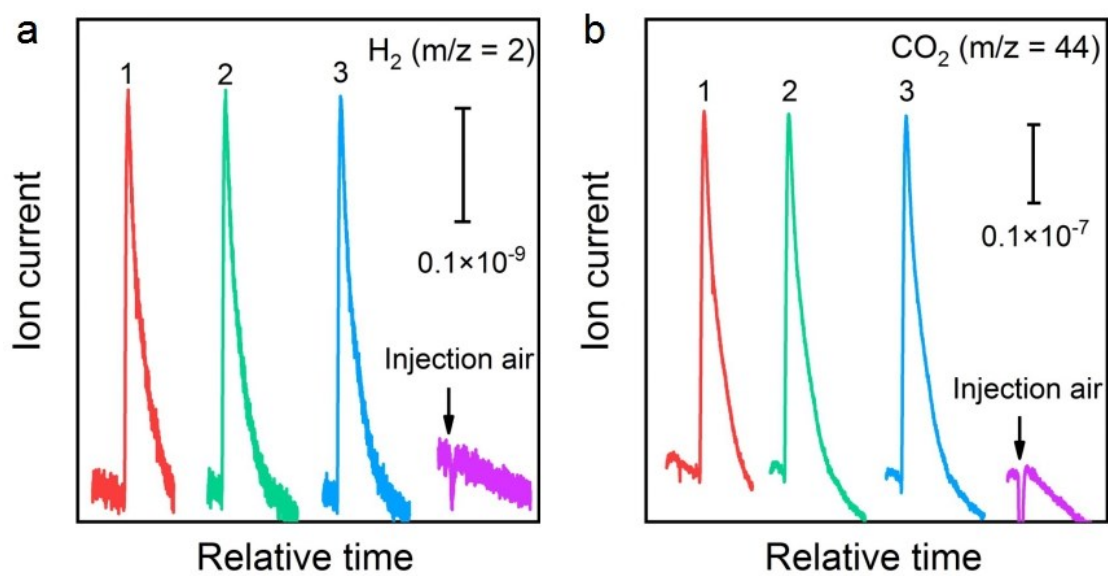
<sup>a</sup> Reaction conditions: **3** (0.25 mmol),  $K_2CO_3$  (20 mol%), catalyst (7.5 mol%), MeOH (4 mL), 0.6 MPa  $O_2$ , 150 °C. Yield was determined by GC using biphenyl as the internal standard.



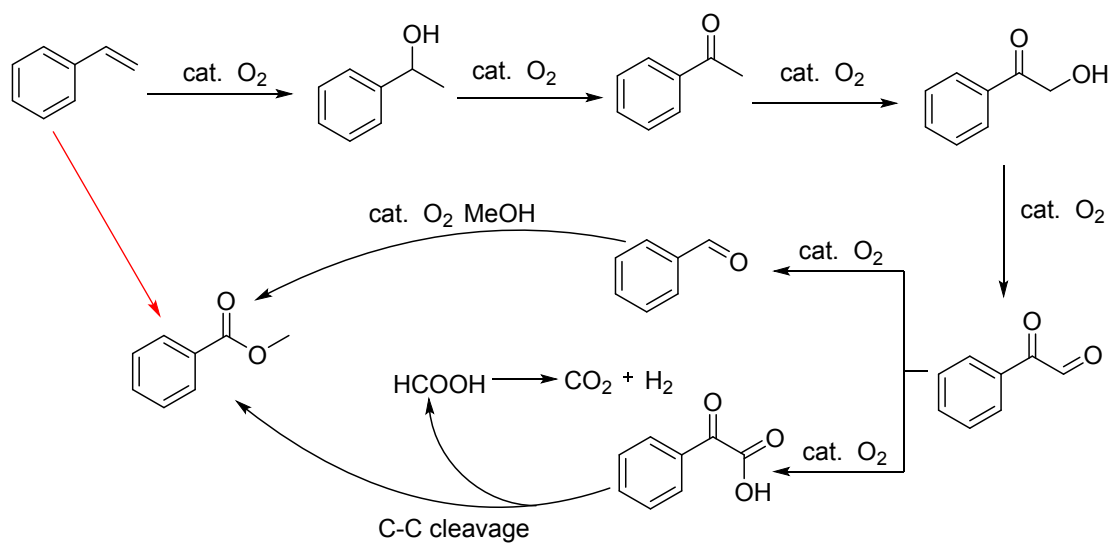
**Fig. S14** GC analysis of a) the gaseous products released during oxidative cleavage of styrene b) air and c) standard hydrogen.



**Fig. S15** Lime-water-test for the oxidative cleavage of styrene.



**Fig. S16** Mass spectrometry of  $\text{H}_2$  and  $\text{CO}_2$  generated from oxidative cleavage of styrene (1, 2, and 3 represent three parallel injections), and air was injected as the blank.



**Scheme S2.** Proposed mechanism of the oxidative cleavage C=C bonds of styrene to ester over the Co-NC-900 catalyst.

## Reference

- 1 H. Luo, L. Wang, S. Shang, G. Li, Y. Lv, S. Gao and W. Dai, *Angew. Chem., Int. Ed.*, 2020, **59**, 19268.