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Supporting Information

Ceria promoted Co@NC catalyst for biofuel upgrade: synergy between ceria and cobalt species

Bowei Wang[abc], Ruixiao Gao[a], Dan Zhang[a], Yuyao Zeng[a], Fangying Zhang[a], Xilong Yan[abc], Yang Li[abc*], Ligong Chen[abc*]

[a] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, P. R. China.

[b] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, P. R. China.

[c] Tianjin Engineering Research Center of Functional Fine Chemicals, Tianjin, P. R. China.

* Corresponding authors. E-mail: lgchen@tju.edu.cn (L. Chen); liyang777@tju.edu.cn (Y. Li)

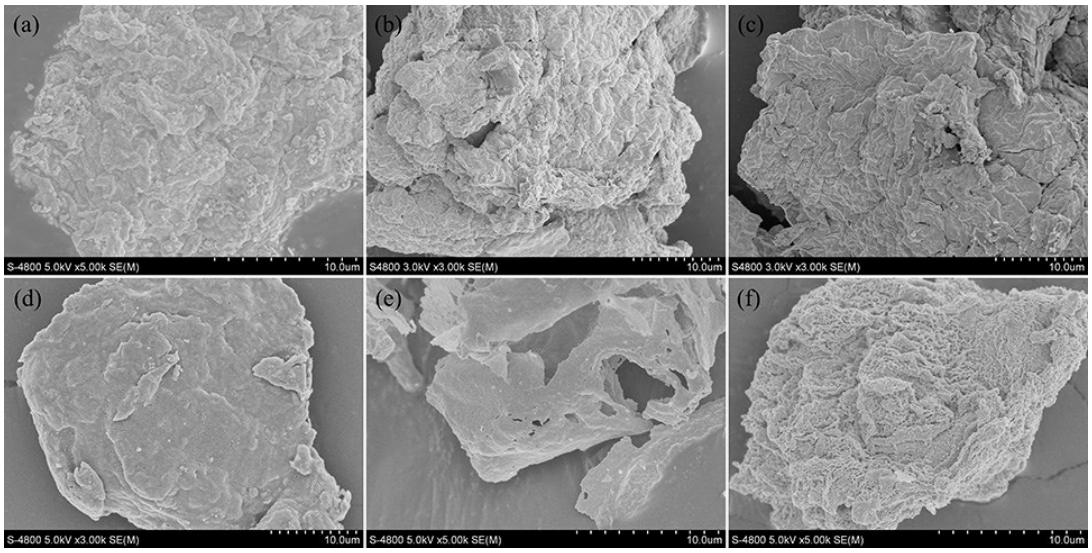


Fig. S1. SEM images of (a) Co/Ce@NC-700, (b) Co/Ce@NC, (c) Co/Ce@NC-1000, (d) Co@NC, (e) Co/Ce, and (f) Ce@NC.

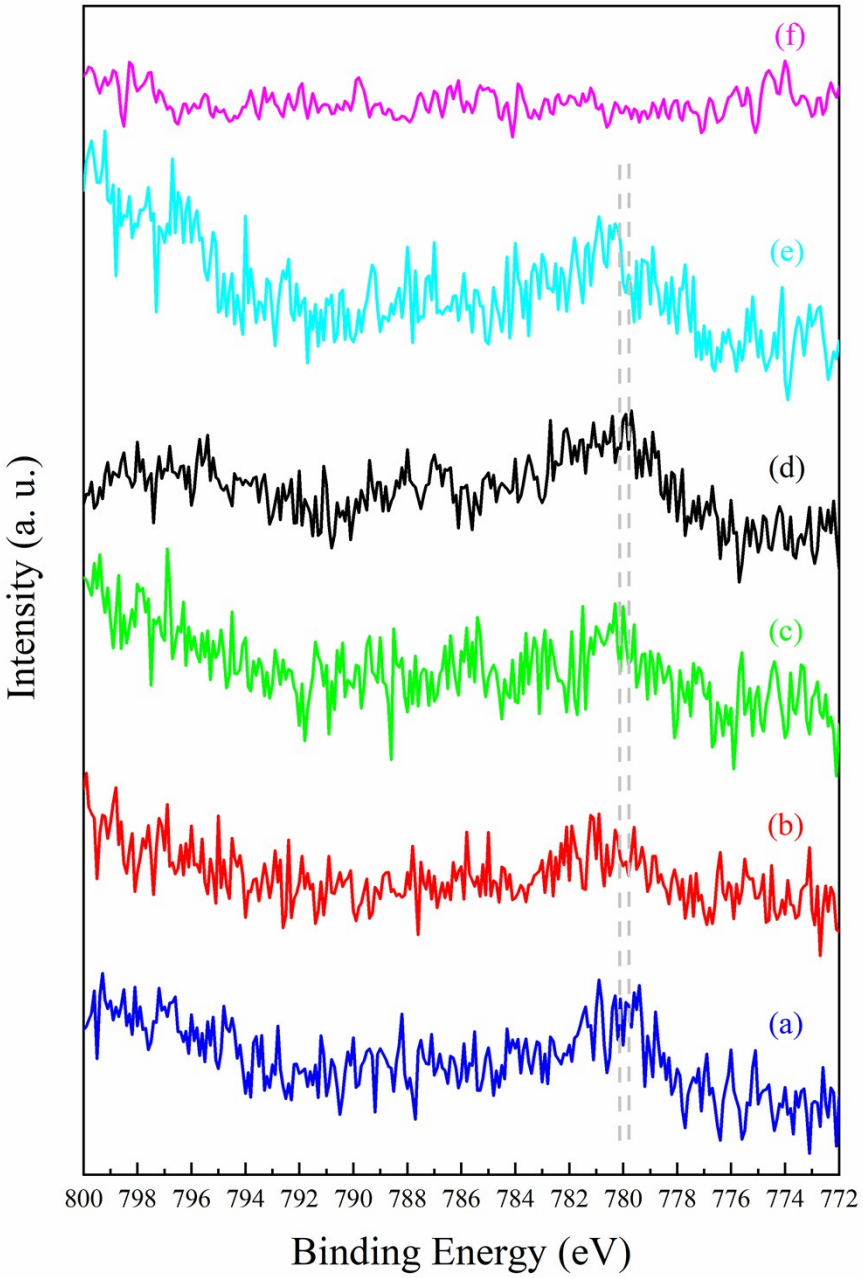


Fig. S2. High-resolution XPS spectra of Co 2p region for (a) Co/Ce@NC-700, (b) Co/Ce@NC, (c) Co/Ce@NC-1000, (d) Co@NC, (e) Co/Ce, and (f) Ce@NC.

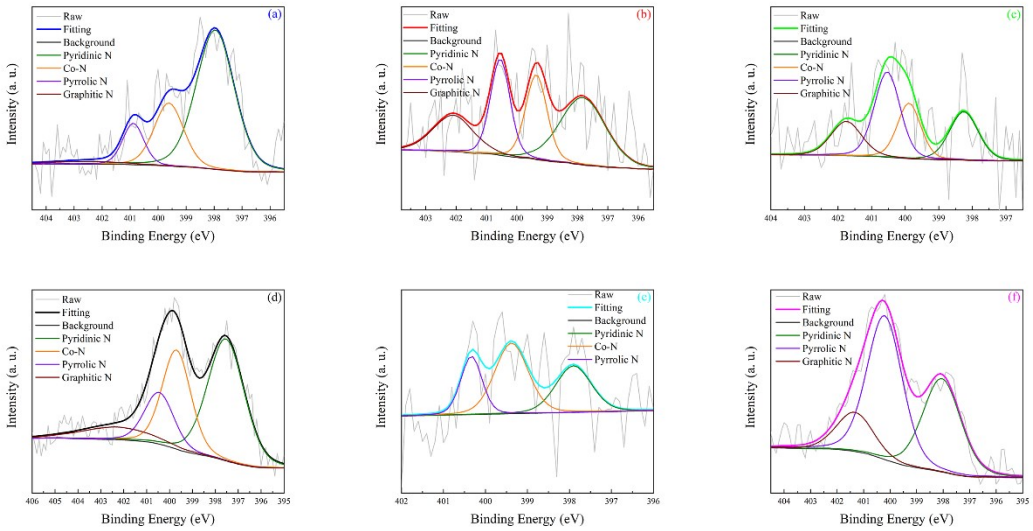


Fig. S3. High-resolution XPS spectra of N 1s region for (a) Co/Ce@NC-700, (b) Co/Ce@NC, (c) Co/Ce@NC-1000, (d) Co@NC, (e) Co/Ce, and (f) Ce@NC.

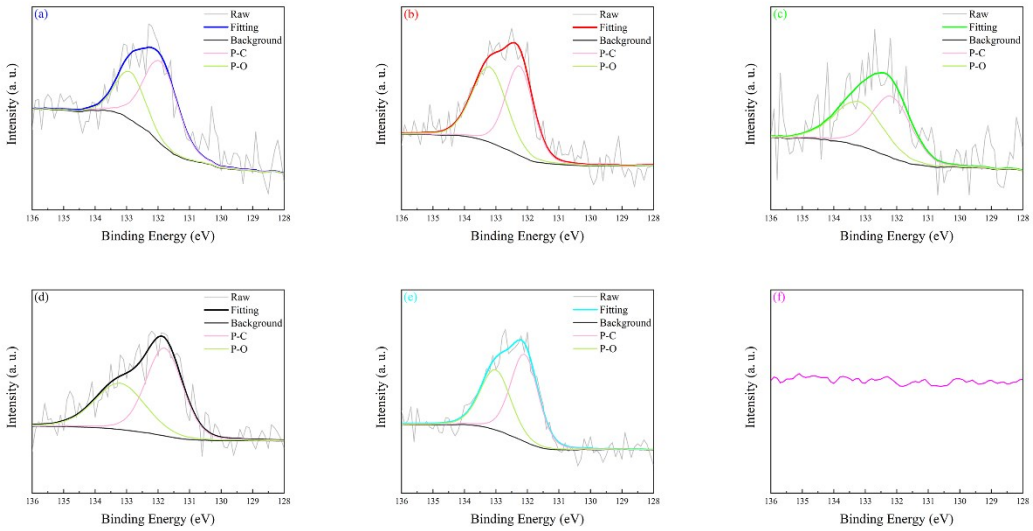


Fig. S4. High-resolution XPS spectra of P 2p region for (a) Co/Ce@NC-700, (b) Co/Ce@NC, (c) Co/Ce@NC-1000, (d) Co@NC, (e) Co/Ce, and (f) Ce@NC.

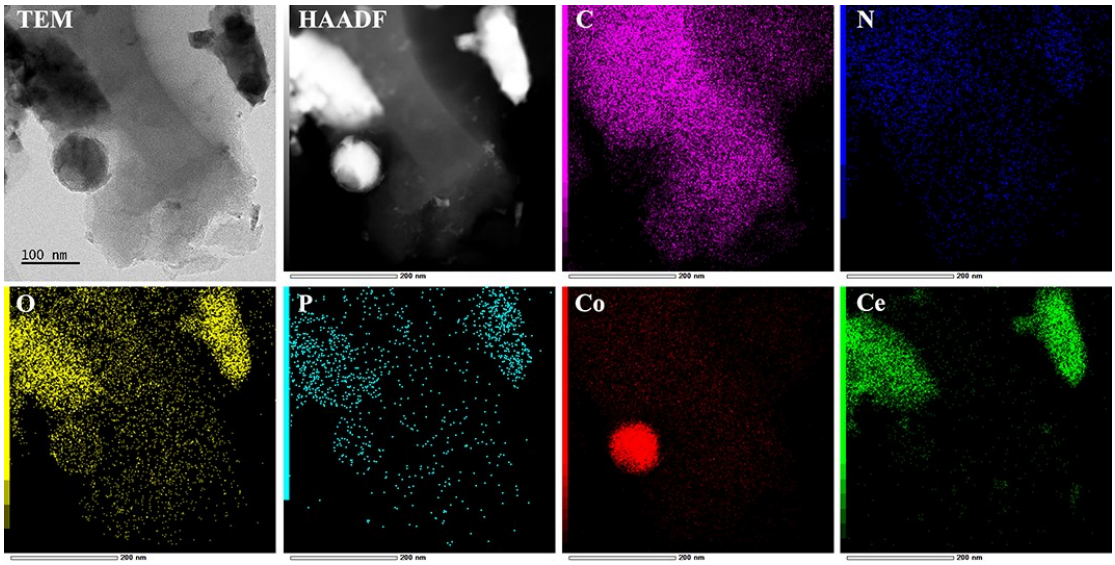


Fig. S5. TEM, HAADF, and EDS mapping images of Co-CeO_2@NC.

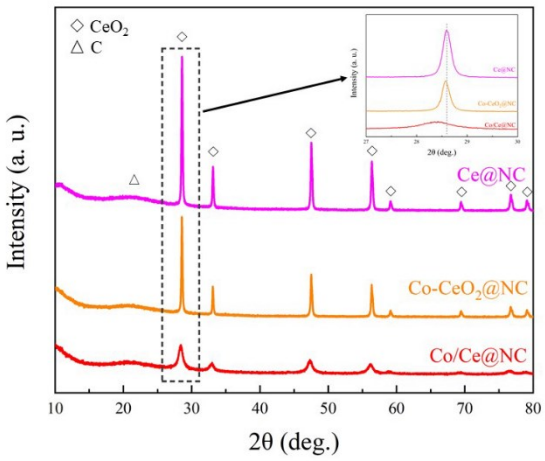


Fig. S6. XRD patterns of Co/Ce@NC, Co-CeO_2@NC, and Ce@NC.

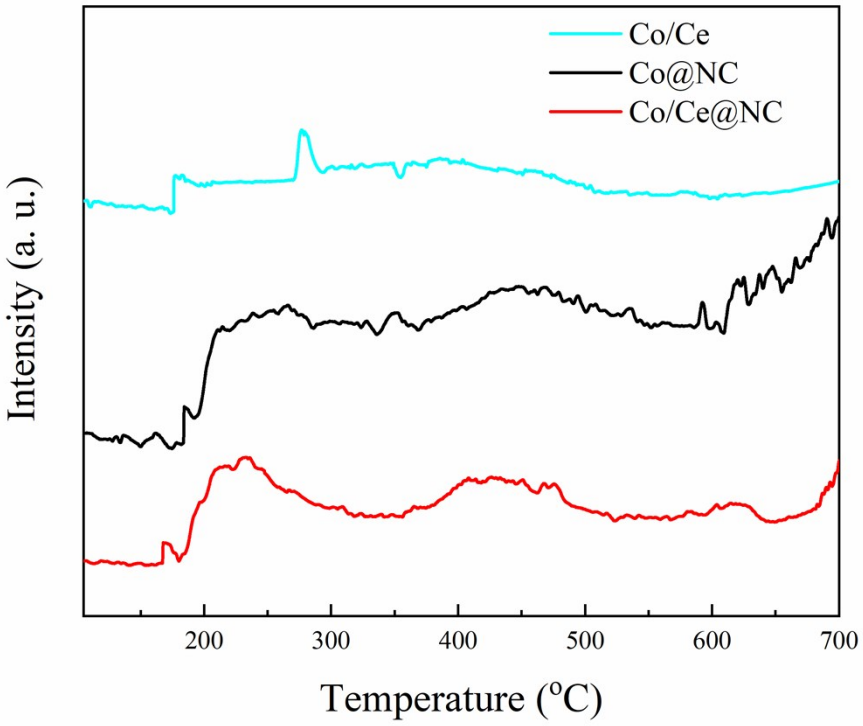


Fig. S7. NH_3-TPD profiles of Co/Ce@NC, Co@NC, and Co/Ce.

Computational methods [S13-15]

All static calculations were carried out using spin-polarized density functional theory (DFT) with generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) as implemented in VASP 5.4.4. The cutoff energy of plane-wave basis set is 400 eV and 3 3 1 K-points grid sampling was used for Brillouin zone integration. Atomic positions were optimized by conjugate gradient algorithm until the forces were less than 0.03 eV/Å. Transition states were searched by climbing image nudged elastic-band method (CI-NEB) and further confirmed by vibrational frequency analysis.

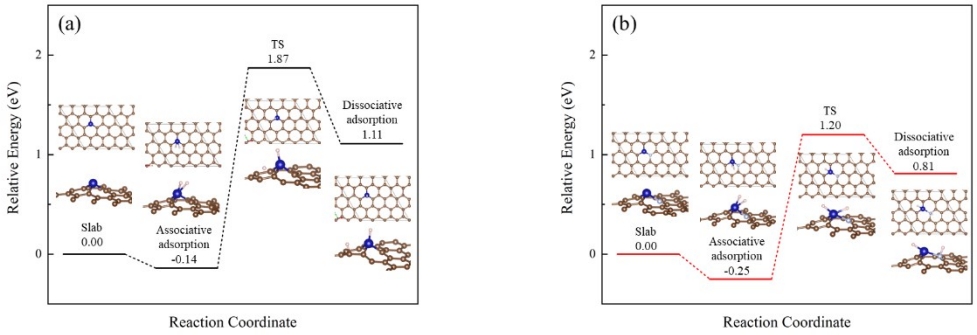


Fig. S8. Relative energy diagram of catalytic H_2 dissociation over Co-loaded graphene without nitrogen species (a) and with pyridine nitrogen species (b).

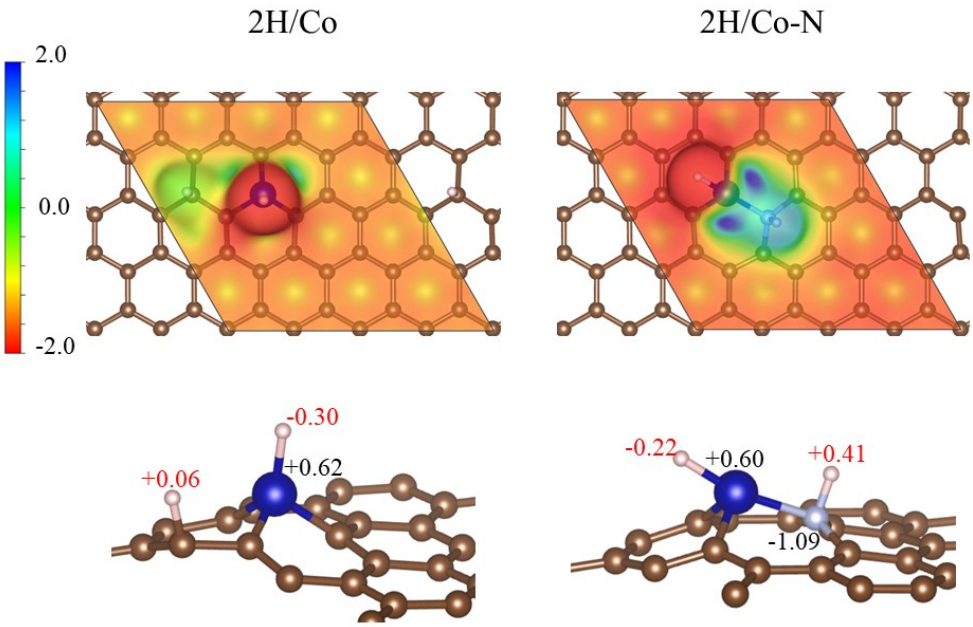


Fig. S9. Electron-density isosurfaces of 2H/Co and 2H/Co-N. The electron-density isosurfaces are plotted at 0.005 e*bohr^{-1}. The color bar represents the electrostatic potential scale.

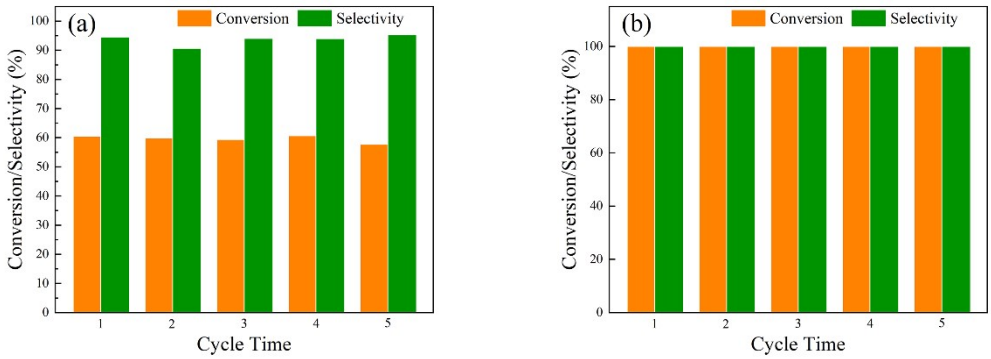


Fig. S10. Stability of Co/Ce@NC. Reaction conditions: vanillin (0.13 mmol); 2 mL ethanol; 5 mol% catalyst; 170 ^{o}C; 1 MPa H_2; 3 h (a) or 6 h (b).

Table S1. Summarization for preparation details of catalysts in this work.

Sample [a]	Active metal source	Carbon source	Additive (Source)	Pyrolysis temperature
Co/Ce@NC	vitamin B_{12}	chitosan	CeO_2 ($Ce(NO_3)_3·6H_2O$, 0.63 g)	850 °C
Co/Ce@NC-700	vitamin B_{12}	chitosan	CeO_2 ($Ce(NO_3)_3·6H_2O$, 0.63 g)	700 °C
Co/Ce@NC-1000	vitamin B_{12}	chitosan	CeO_2 ($Ce(NO_3)_3·6H_2O$, 0.63 g)	1000 °C
Co/Ce@C	vitamin B_{12}	glucose	CeO_2 ($Ce(NO_3)_3·6H_2O$, 0.63 g)	850 °C
Co/Ce@NC (WP)	$Co(CH_3COO)_2·4H_2O$	chitosan	CeO_2 ($Ce(NO_3)_3·6H_2O$, 0.63 g)	850 °C
Co/Ce	vitamin B_{12}	-	CeO_2 ($Ce(NO_3)_3·6H_2O$, 1.26 g)	850 °C
Co-CeO_2@NC	vitamin B_{12}	chitosan	CeO_2 (CeO_2)	850 °C
Ce@NC	-	chitosan	CeO_2 ($Ce(NO_3)_3·6H_2O$, 0.63 g)	850 °C
Co@NC	vitamin B_{12}	chitosan (2.5 g)	-	850 °C
Co@C	vitamin B_{12}	glucose (2.5 g)	-	850 °C
Fe/Ce@NC	$Fe(CH_3COO)_2·4H_2O$	chitosan	CeO_2 ($Ce(NO_3)_3·6H_2O$, 0.63 g)	850 °C
Cu/Ce@NC	$Cu(CH_3COO)_2·H_2O$	chitosan	CeO_2 ($Ce(NO_3)_3·6H_2O$, 0.63 g)	850 °C
Ni/Ce@NC	$Ni(CH_3COO)_2·4H_2O$	chitosan	CeO_2 ($Ce(NO_3)_3·6H_2O$, 0.63 g)	850 °C
Co/Al@NC	vitamin B_{12}	chitosan	Al_2O_3 ($Al(NO_3)_3·9H_2O$, 1.84 g)	850 °C
Co/Si@NC	vitamin B_{12}	chitosan	SiO_2 (nano-SiO_2, 20 nm)	850 °C
Co/Ti@NC	vitamin B_{12}	chitosan	TiO_2 (nano-TiO_2, 20 nm)	850 °C

[a] General preparation procedure: Initially, the suspension of active metal source (active metal 0.13 mmol), additive (0.25 g), and carbon source (1.25 g) in 80 vol% ethanol (60 mL) was stirred under refluxing for 4 h. Subsequently, the solvent was slowly removed under vacuum. The obtained solid was dried in vacuum at 60 °C and then grounded into a fine powder. Finally, the powder was pyrolyzed at 850 °C for 2 h under argon atmosphere to yield the catalyst.

Table S2. Surface N content, peak positions and relative amount of nitrogen species for Co/Ce@NC-700, Co/Ce@NC, Co/Ce@NC-1000, Co@NC, Co/Ce, and Ce@NC based on XPS analysis

Sample	Surface N Content (wt%)	Pyridinic N		Co-N		Pyrrolic N		Graphitic N	
		BE (eV)	Ratio (%)	BE (eV)	Ratio (%)	BE (eV)	Ratio (%)	BE (eV)	Ratio (%)
Co/Ce@NC-700	4.18	398.0	64.49	399.6	22.50	400.9	10.62	402.5	2.39
Co/Ce@NC	2.50	397.8	37.19	399.4	22.08	400.5	22.97	402.1	17.76
Co/Ce@NC-1000	1.51	398.3	23.32	399.9	21.92	400.5	36.97	401.8	17.79
Co@NC	3.56	397.5	46.02	399.7	29.18	400.5	15.56	402.3	9.24
Co/Ce	1.31	397.9	31.55	399.4	44.91	400.3	23.54	-	-
Ce@NC	3.71	398.1	35.18	-	-	400.2	50.50	401.3	14.32

Table S3. Catalytic hydrogenation of nitrobenzene or styrene

Entry	Catalyst	Substrate	Conversion (%)	Selectivity (%)
1 [a]	Co@NC	nitrobenzene	6.18±0.8	>99 [c]
2 [a]	Co/Ce@NC	nitrobenzene	85.78±1.3	>99 [c]
3 [b]	Co@NC	styrene	62.66±1.0	>99 [d]
4 [b]	Co/Ce@NC	styrene	96.14±1.7	>99 [d]

[a] Reaction Conditions: nitrobenzene (0.25 mmol); solvent: methanol (2.50 mL); 0.60 mol% catalyst; 140 ^{o}C; 2 MPa H_2; 1 h.

[b] Reaction Conditions: styrene (0.13 mmol); solvent: methanol (2.50 mL); 1.20 mol% catalyst; 140 ^{o}C; 2 MPa H_2; 4 h.

[c] Selectivity of aniline.

[d] Selectivity of ethylbenzene.

Table S4. Summary of catalyst consumption among reported non-noble metal-based catalysts for the HDO of vanillin.

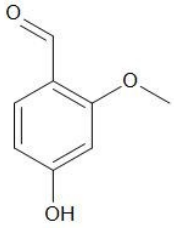
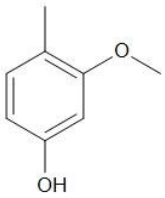
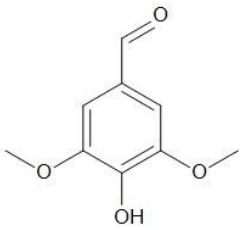
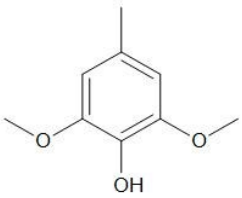
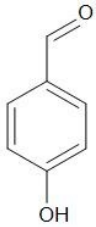
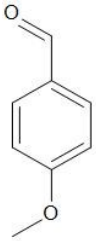
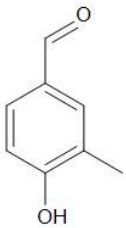
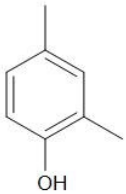
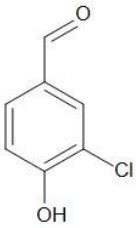
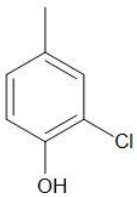
	Catalyst	Catalyst dosage [a]	Hydrogen Source	Solvent	Conv. (%) [b]	Selec. (%) [c]	Ref.
M@NC catalysts	Co/N-C-600	11.82 mol%	H_2	isopropanol	98.2	85.1	S1
	ZnO/Co-N-CNT	21.48 mol%	H_2	water	100	89.1	S2
	$Co/NG_8/CF$	19.42 mol%	H_2	water	95	>99	S3
	Co@NC-700	7.90 mol%	HCOOH	water	95.7	100	S4
	Co@NG-6	4.60 mol%	HCOOH	water	98.5	100	S5
	Co/Ce@NC	5.00 mol%	H_2	water or ethanol	>99	>99	This
		10.00 mol%	ethanol	ethanol	>99	>99	work
Other non-noble metal-based catalysts	sulfided $CoMo/Al_2O_3$	not given	H_2	dodecane	53	23	S6
	Co_xP@POP	8.26 mol%	H_2	isopropanol	99.3	83.4	S7
	Ni/NCB-900	2.18 mol%	H_2	water	74.4	64.6	S8
	SS-Ni/SiO_2	25.92 mol%	H_2	decalin	99.8	89.0	S9
	Cu-PMO	11.41 mol%	H_2	methanol	100	90	S10
	Ga-doped Cu/HNZY	5.10 mol%	H_2	methanol	100	99	S11
	Cu/AC-600	13.61 mol%	H_2	water	99.9	93.2	S12
			isopropanol	isopropanol	99.8	99.1	

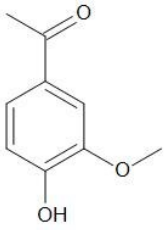
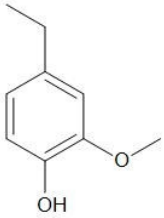
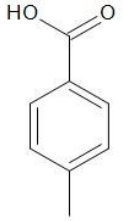
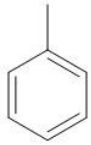
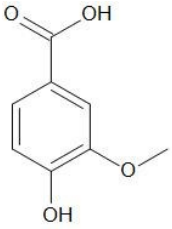
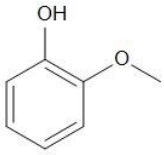
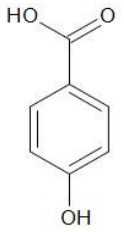
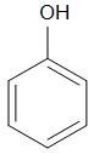
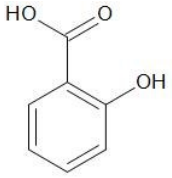
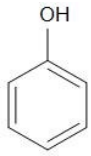
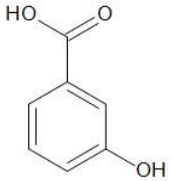
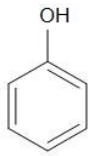
[a] based on active metal component.

[b] Conversion of vanillin.

[c] Selectivity of creosol.

Table S5. General applicability of Co/Ce@NC for hydrodeoxygenation. [a]

Entry	Substrate	Conversion (%)	Product	Selectivity (%)
1 [b]		>99		>99
2 [c]		>99		>99
3 [d]		98.07		>99
4 [d]		98.40		>99
5 [e]		95.74		88.87
6 [f]		97.43		92.00

7 [g]		>99		>99
8 [h]		>99		>99
9 [i]		>99		>99
10 [i]		>99		>99
11 [i]		>99		>99
12 [i]		>99		>99

[a] Reaction conditions: substrate (0.13 mmol); 2 mL water; 5 mol% catalyst; 170 °C; 1 MPa H_2. [b] 8 h. [c] 10 h. [d] 12 h. [e] 2 mL ethanol; 22 h. [f] 2 mL ethanol; 18 h. [g] 2 mL ethanol; 24 h. [h] 6 h. [i] 4 h.

Table S6. Selection of catalysts [a]

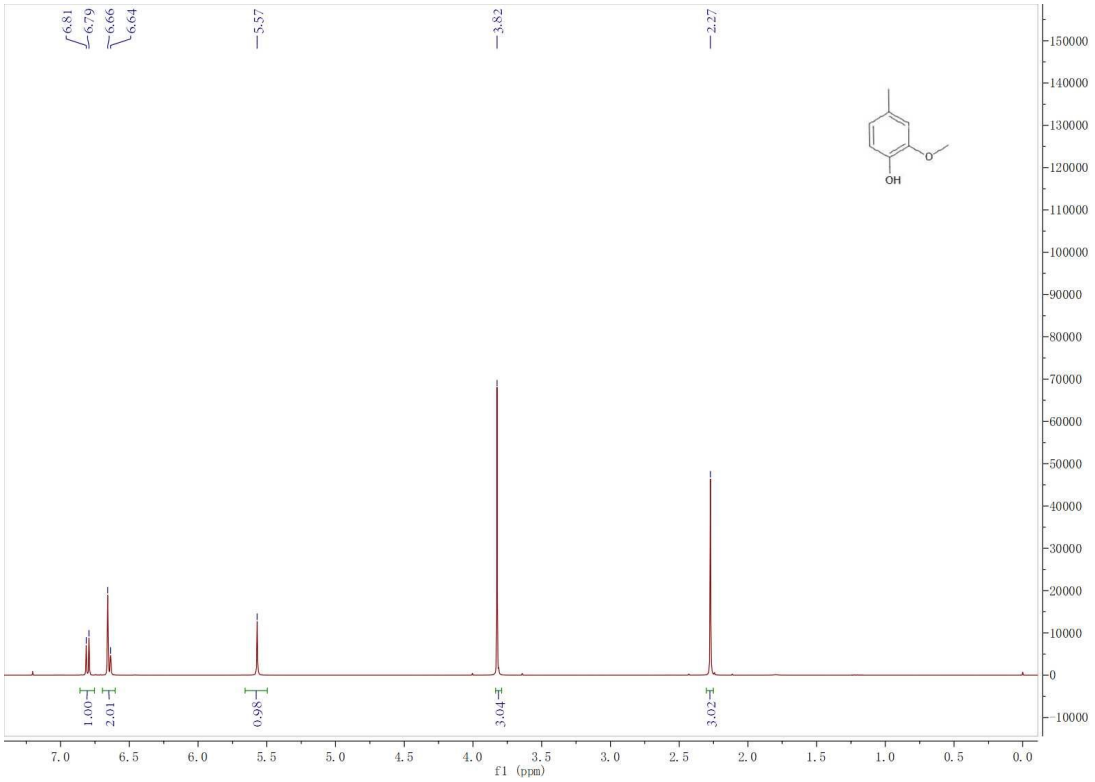
Entry	Catalyst	Conversion (%) [b]	Selectivity (%) [c]
1	Cu/Ce@NC	6.93±0.5	>99
2	Co/Ce@NC	85.78±1.3	>99
3	Ni/Ce@NC	17.8±1.0	>99
4	Fe/Ce@NC	3.38±0.6	>99
5	Co/Al@NC	4.11±0.8	>99
6	Co/Si@NC	29.87±1.0	>99
7	Co/Ti@NC	12.76±1.1	>99

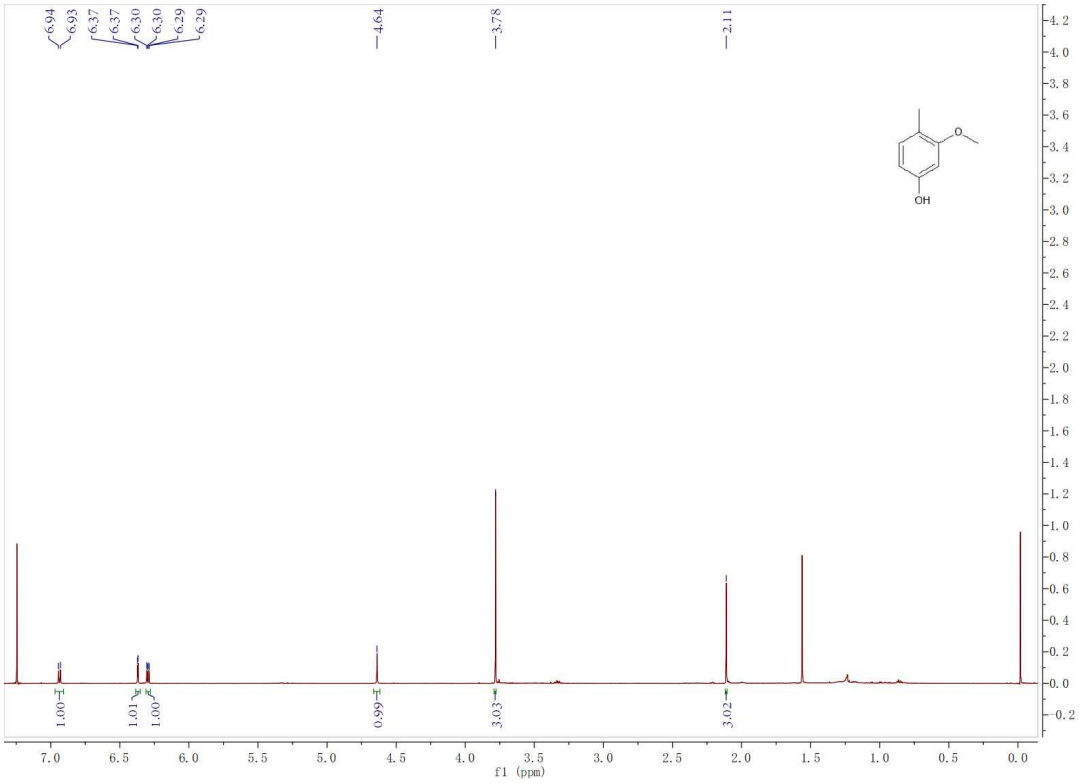
[a] Reaction Conditions: nitrobenzene (0.25 mmol); solvent: methanol (2.50 mL); 10 mg catalyst; 140 ^{o}C; 2 MPa H_2; 1 h.

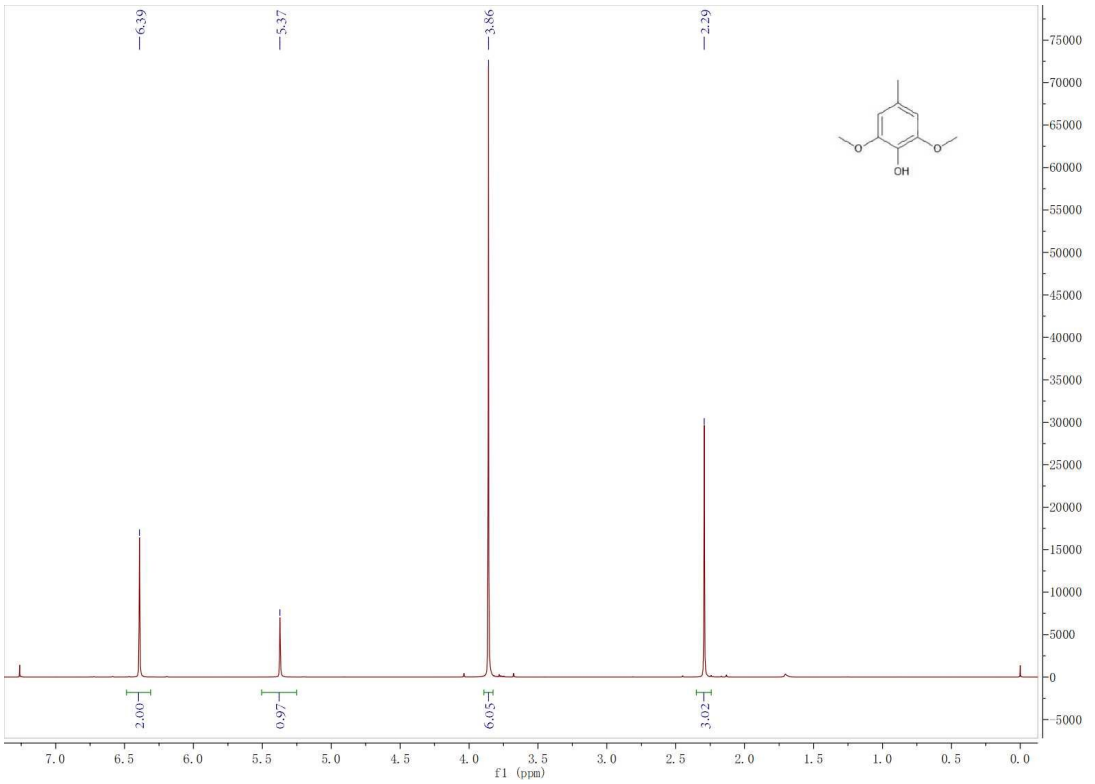
[b] Conversion of nitrobenzene.

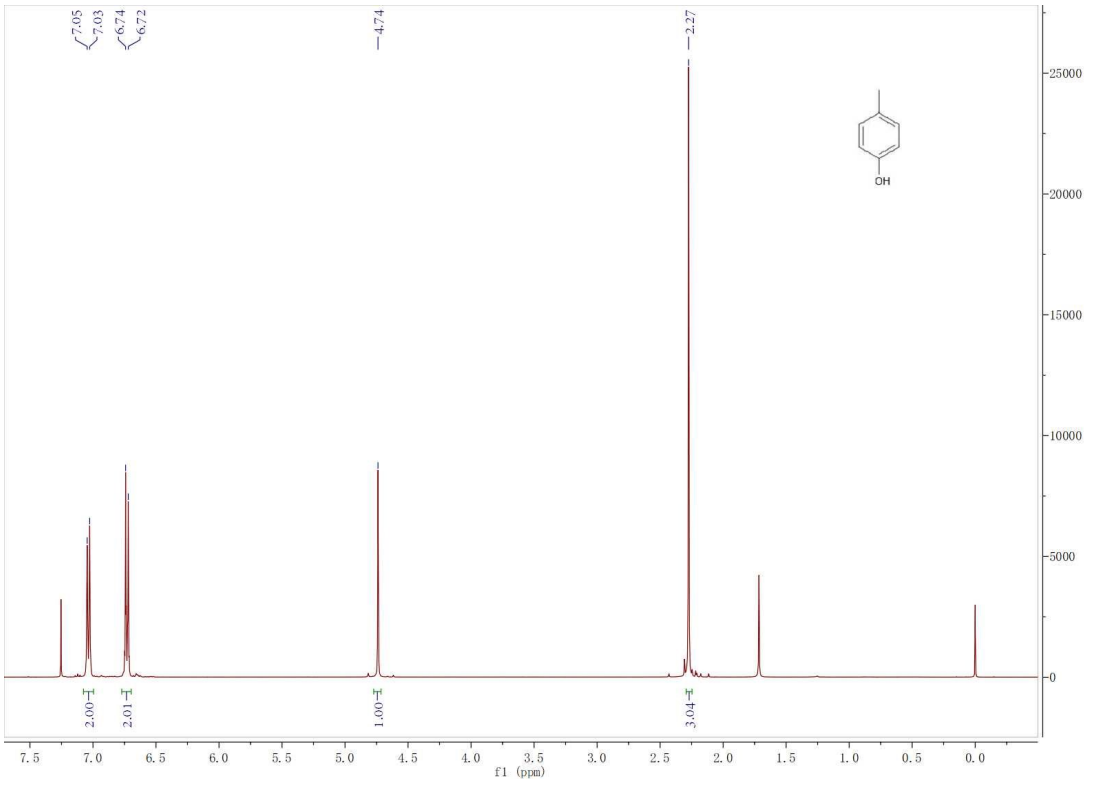
[c] Selectivity of aniline.

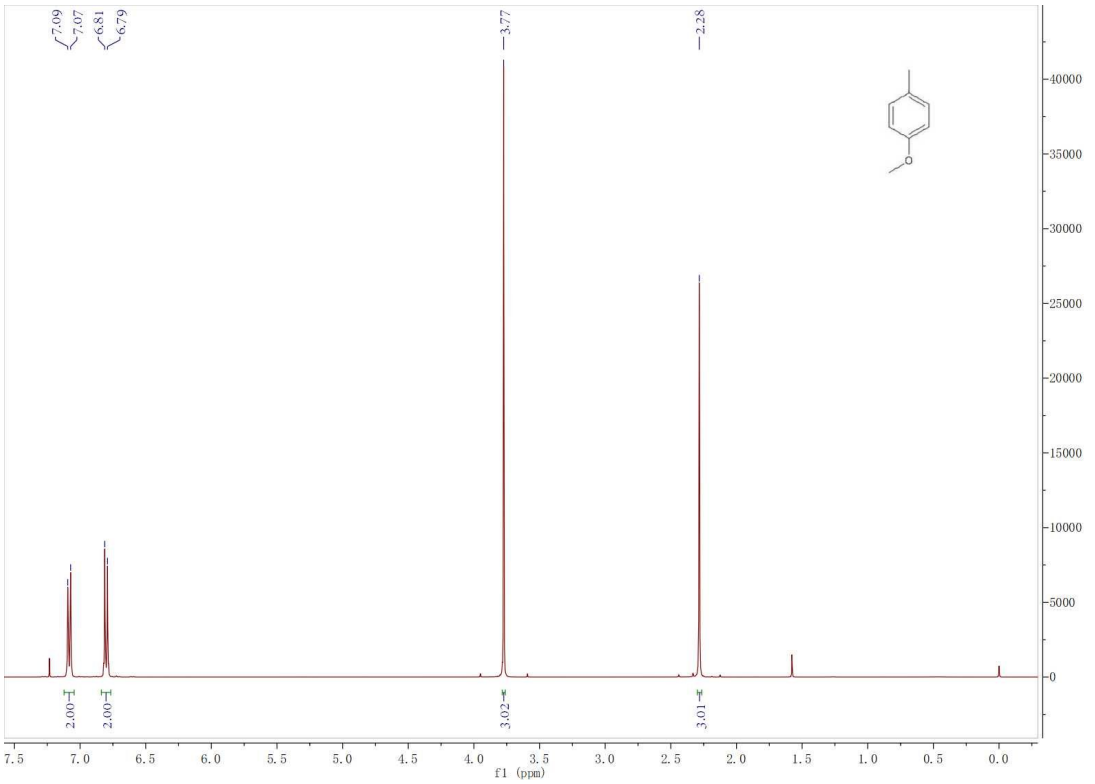
^{1}H NMR spectra of the products:

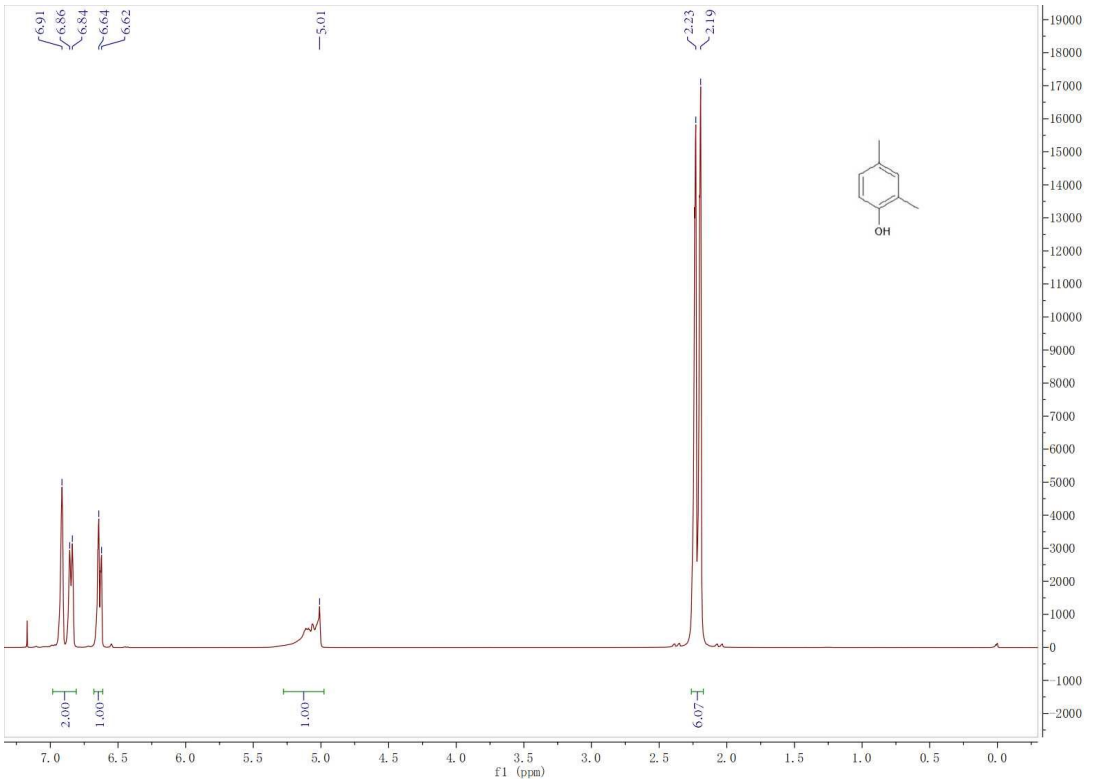


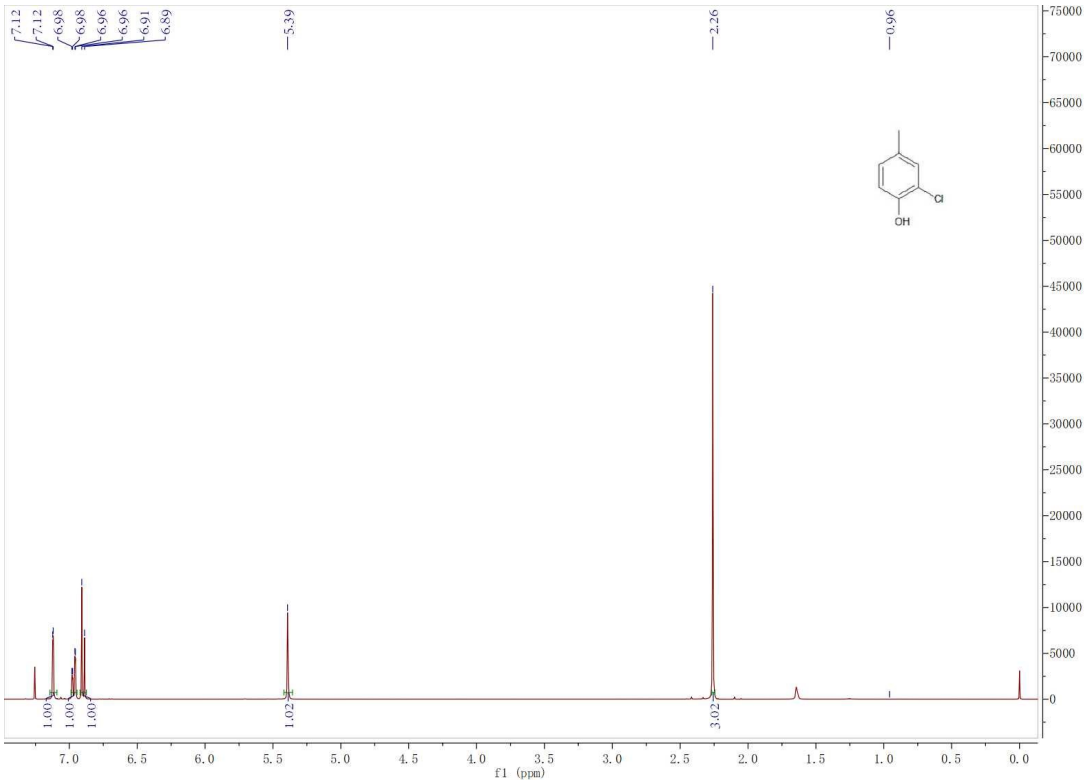


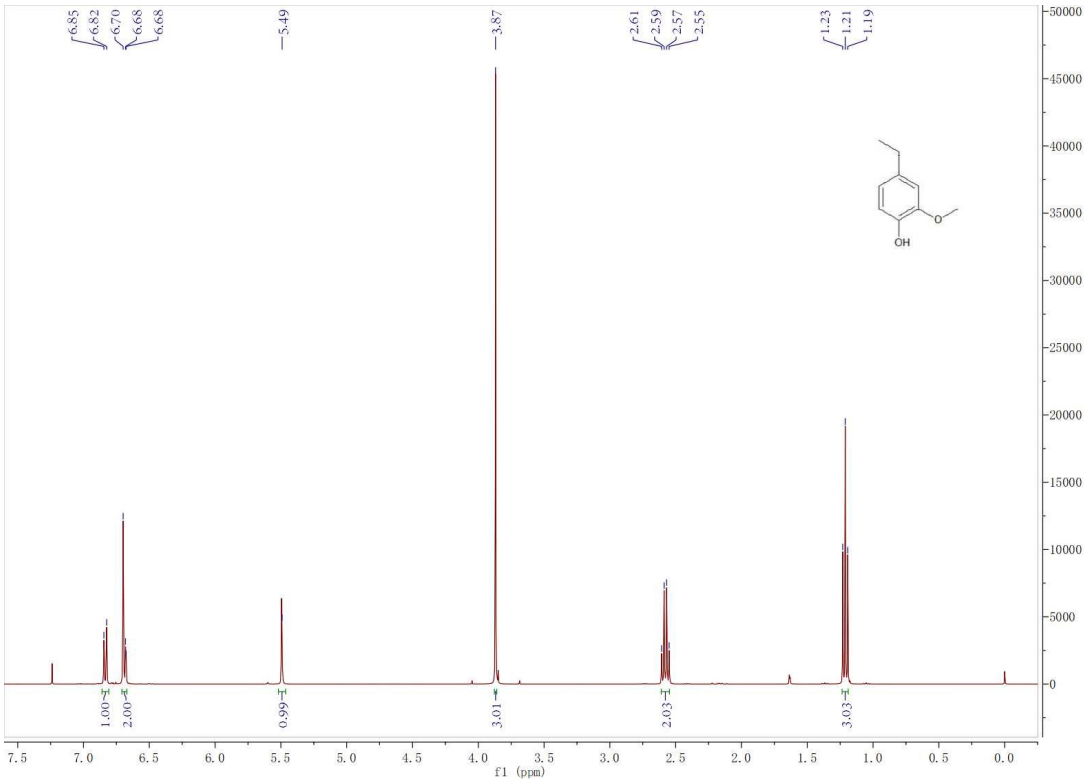

6.39
5.37
3.86
2.29
OH
2.00
0.97
6.05
3.02
f1 (ppm)

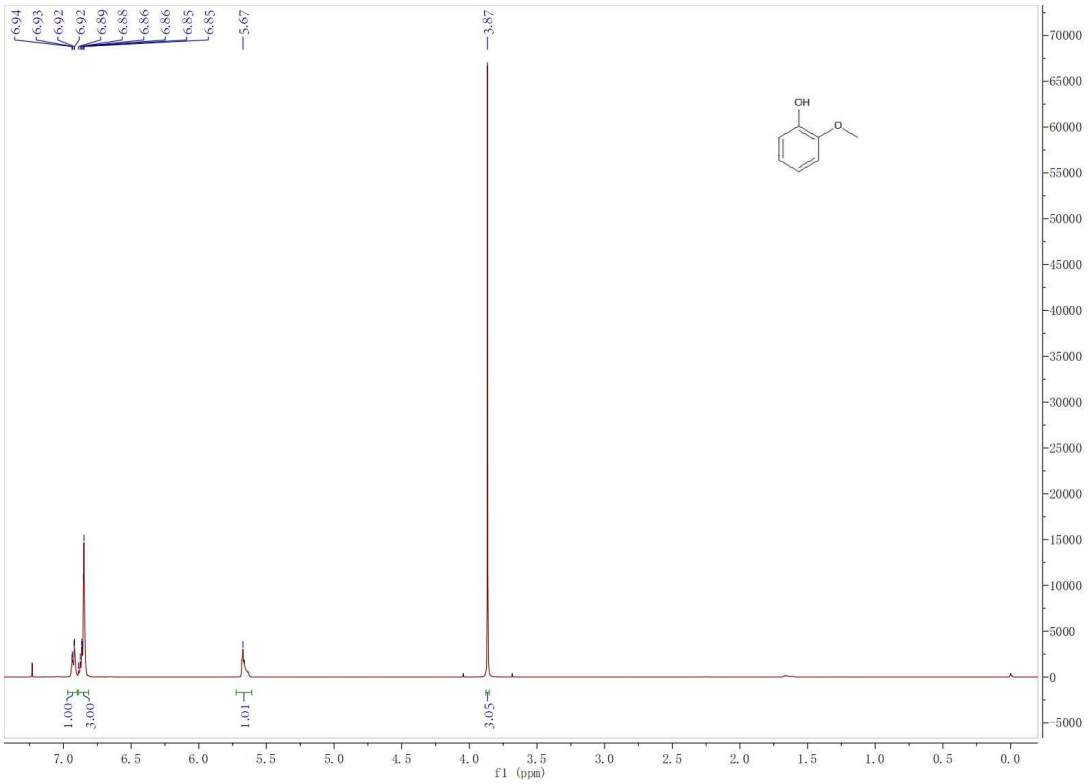

7.05
7.03
6.74
6.72
4.74
2.27
OH
2.00
2.01
1.00
3.04
f1 (ppm)


7.09
7.07
6.81
6.79
3.77
2.28
2.00
2.00
3.02
3.01
f1 (ppm)


6.91
6.86
6.84
6.64
6.62
5.01
2.23
2.19
OH
2.00
1.00
1.00
6.07
f1 (ppm)


7.12
7.12
6.98
6.98
6.96
6.96
6.91
6.89
5.39
2.26
0.96
Cl
OH
1.00
1.00
1.00
1.02
3.02
f1 (ppm)


6.85
6.82
6.70
6.68
6.68
5.49
3.87
2.61
2.59
2.57
2.55
1.23
1.21
1.19
O
OH
1.00
2.00
0.99
3.01
2.03
3.03
f1 (ppm)


6.94
6.93
6.92
6.92
6.89
6.88
6.86
6.86
6.85
6.85
5.67
3.87
OH
O
1.00
3.00
1.01
3.05
f1 (ppm)

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