Supporting Information

Oxidative Cleavage of β-O-4 Bonds in Lignin Model Compounds with a Single-atom Co Catalyst

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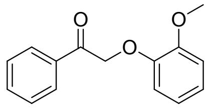
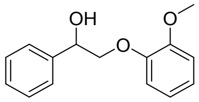
7. References

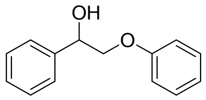
1. Synthesis of the model compounds



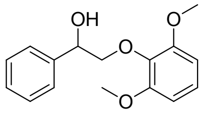
2-(2-methoxyphenoxy)-1-phenylethanone (MPP-one) was obtained by the reaction of 2-bromoacetophenone (7.36 g) and guaiacol (5.74 g) in aceton (150 ml) solution which contains K_2CO_3 (9.2 g). After reflux at 60°C overnight, K_2CO_3 was removed by filtration and the solvent was removed under reduced pressure. MPP-one was obtained after the remained solid was washed by ether for few times to remove the unreacted reactants.



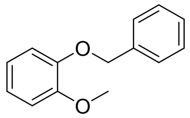
2-(2-methoxyphenoxy)-1-phenylethanol (MPP-ol) was synthesized from the reduction of MPP-one. Firstly, MPP-one (3.5 g) was dissolved in THF (60 ml), $NaBH_4$ (1.09 g) was dissolved in water (10ml). Then, the $NaBH_4$ solution was added in the THF dropwise under stirring at room temperature. After stirring for 3h, HCl (3 ml, 2 M) was added in the reaction system. H_2O (32 ml) was used to accelerate the phase separation and the aqueous phase was extracted by ether (3×10 ml) and combined the organic phase. Then, saturated $NaHCO_3$ solution was used to neutralize the HCl, and anhydrous Na_2SO_4 was used to remove the residual water in the organic phase. Finally, the 2-(2-methoxyphenoxy)-1-phenylethanol was obtained after and the solvents were removed under reduced pressure.



2-phenoxy-1-phenylethanol (PP-ol) was obtained from the reduction of 2-phenoxy-1-phenylethanone (PP-one) in a similar method as described above. Firstly, PP-one was synthesized by the reaction of 2-bromoacetophenone (7.36 g) and phenol (3.6 g) in aceton (150 ml) solution which contains K_2CO_3 (5.47 g). After reflux at 60°C overnight, K_2CO_3 was separated by filtration and the solvent was removed under reduced pressure. After that, the solid was dissolved in ethyl acetate and washed with water (3×10 ml). Anhydrous Na_2SO_4 was used to remove the residual water in the organic phase. The crude product of PP-one was recrystallized from ethanol. As described above, PP-ol was obtained from the reduction of PP-one with a similar method to obtain MPP-ol from MPP-one.



2-(2,6-dimethoxyphenoxy)-1-phenylethanol (DMP-ol) was synthesized from the reaction of 2-bromoacetophenone (7.36 g) and 2,6-dimethoxyphenoxy (7.13 g) in aceton (150 ml) solution which contains K_2CO_3 (9.2 g). After reflux at 60°C overnight, K_2CO_3 was separated by filtration and then rotary evaporation was used to remove the solvent. 2-(2,6-dimethoxyphenoxy)-1-phenylethanone (DMP-one) was obtained from recrystallizztion in ethanol. Then, DMP-one was reduced in a mixture solution of THF and water (4:1) which contains $NaBH_4$, and crude DMP-ol can be obtained using a similar purification method as above. The pure DMP-ol was obtained by flash column chromatography (pentane : ethyl acetate, 3:2).



1-(benzyloxy)-2-methoxybenzene (BMB) was synthesized according to the following method: benzyl bromide (5.7 g), guaiacol (4.1 g), K_2CO_3 (8.3 g) and KI (0.83 g) were combined together in acetone (45 mL) and refluxed at 60°C under stirring overnight. The mixture was filtered and the solvent was removed under reduced pressure. Then, deionized water (50 mL) was added in the solid and the reaction mixture was extracted with ethyl acetate (3×10 mL). The organic phase was washed with a saturated $NaHCO_3$ solution, dried over $MgSO_4$ and filtered. The solution was concentrated under reduced pressure and BMB was crystallized from a cold ethanol solution.

2. Preparation of Co nanoparticles

Co nanoparticles were prepared from a metal organic framework (MOF) precursor according to literature methods.[1] In brief, $Co(NO_3)_2 \cdot 6H_2O$ (549 mg, 3 mmol) in MeOH (15 ml) was slowly added to 2-methylimidazole (MeIM) (615 mg, 7.5 mmol) in MeOH (15 ml) and the resulting mixture was ultrasonicated for 10 min. at room temperature. The mixture was transferred into a stainless-steel autoclave (50 ml) and heated at 120°C for 4 h. After the reaction, the precipitates was obtained by centrifugation and the solid was washed by ethanol (3×15 ml) and by dried in vacuum at 60°C overnight. The resulting solid material was ground into a powder using a ceramic mortar and pyrolysed at 800°C under N_2 atmosphere for 3 h with a heating rate of 5°C/min. The resulting Co nanoparticles were used directly.

3. Characterization of the catalysts

Table S1 Cobalt content of the Co-N-C catalyst.

Entry	Cobalt content (ppm)	Cobalt content (wt%)
1	7.88	3.15
2	7.79	3.11
3	8.38	3.35

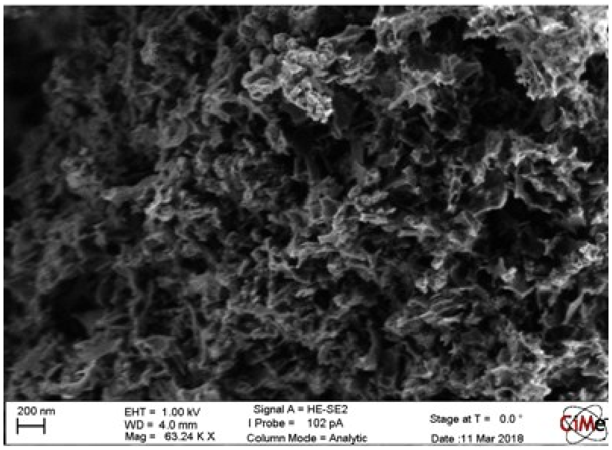


Figure S1 Representative SEM image of Co-N-C catalyst.

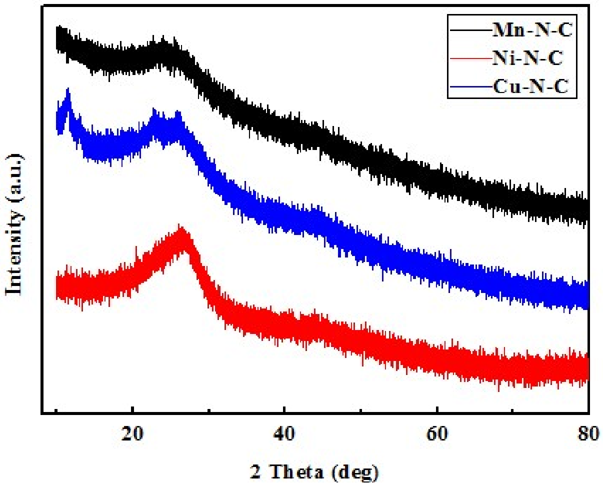


Figure S2 XRD patterns of the Mn-N-C, Ni-N-C and Cu-N-C catalysts.

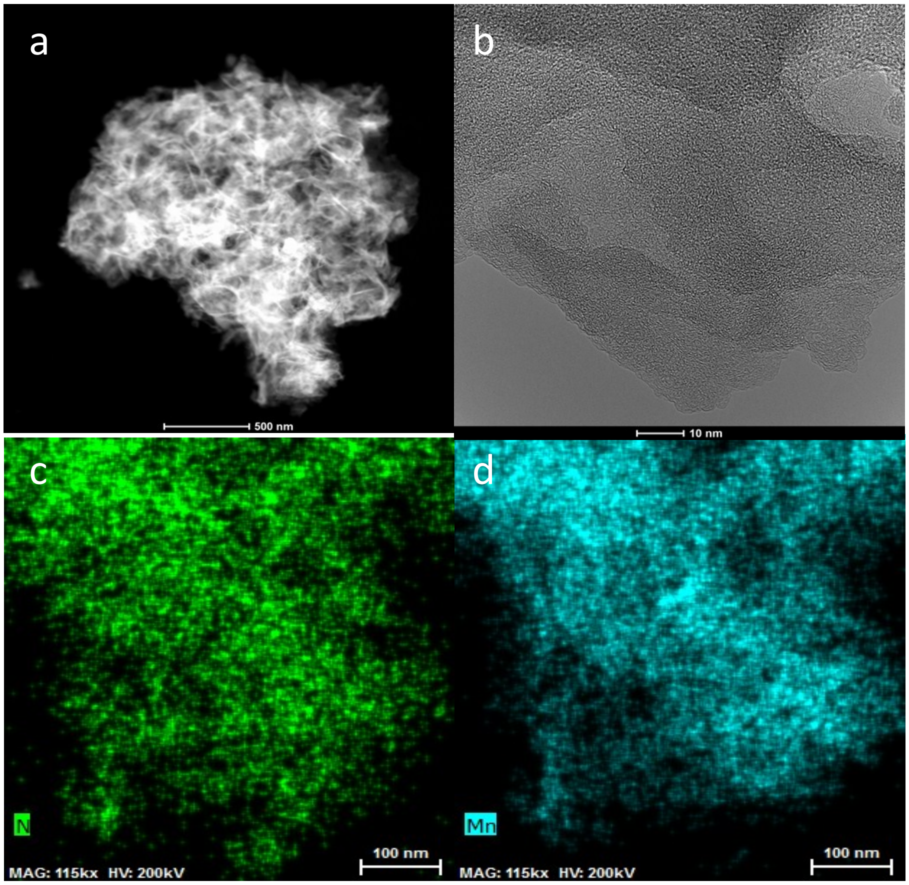


Figure S3 Representative TEM dark filed image (a) and bright filed image (b) of the Mn-N-C catalyst, and corresponding EDX mapping image of N (c) and Mn (d) of the Mn-N-C catalyst.

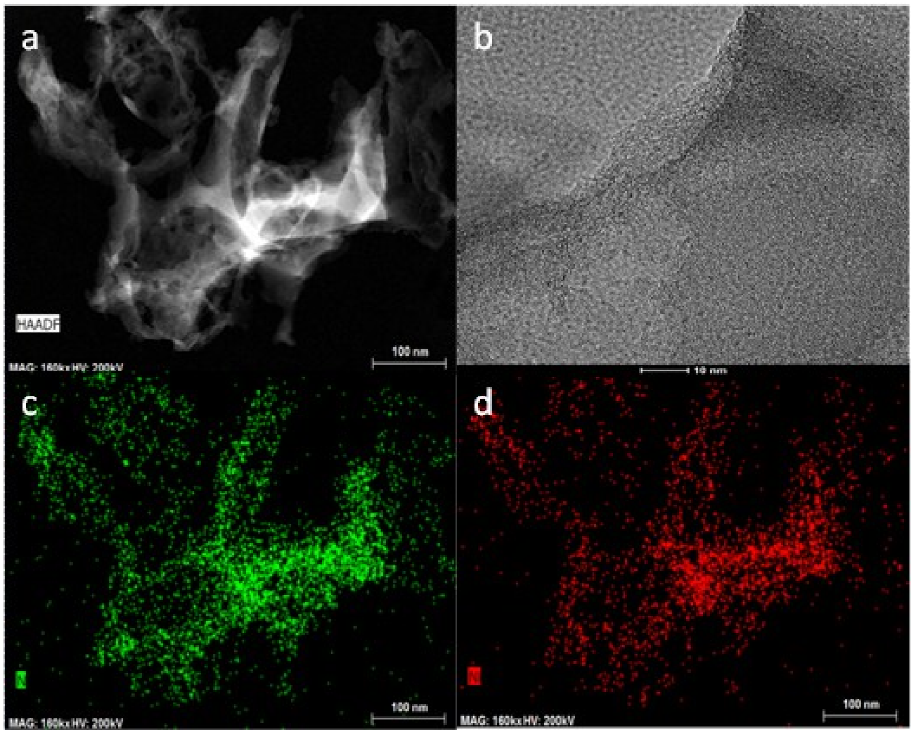


Figure S4 Representative TEM dark filed image (a) and bright filed image (b) of the Ni-N-C catalyst, and corresponding EDX mapping image of N (c) and Ni (d) of the Ni-N-C catalyst.

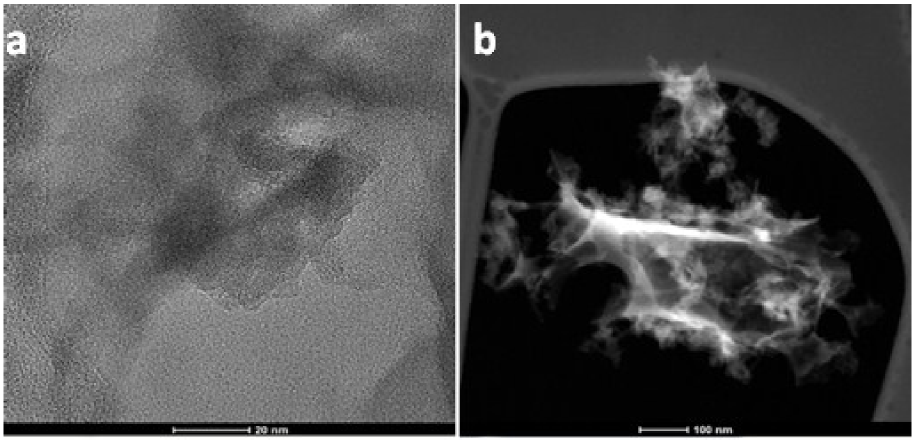


Figure S5 Representative TEM bright filed (a) and dark filed (b) image of the Cu-N-C.

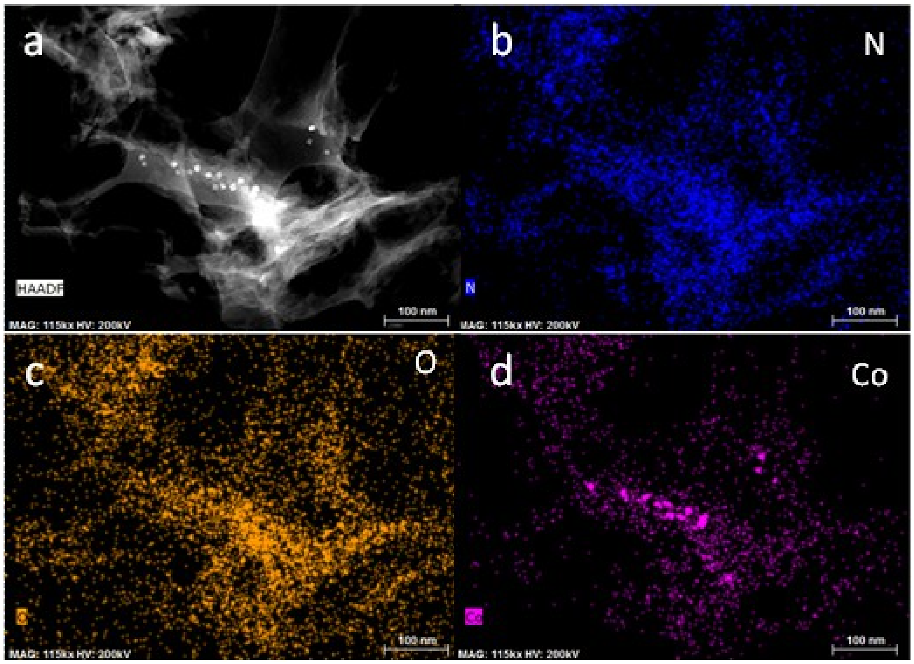


Figure S6 Representative TEM dark filed image (a) of the Co-N-C catalyst with nanoparticles and corresponding EDX mapping image of N (b), O (c) and Co (d) of the Co-N-C catalyst with nanoparticles.

4. Effect of reaction time and the control experiments

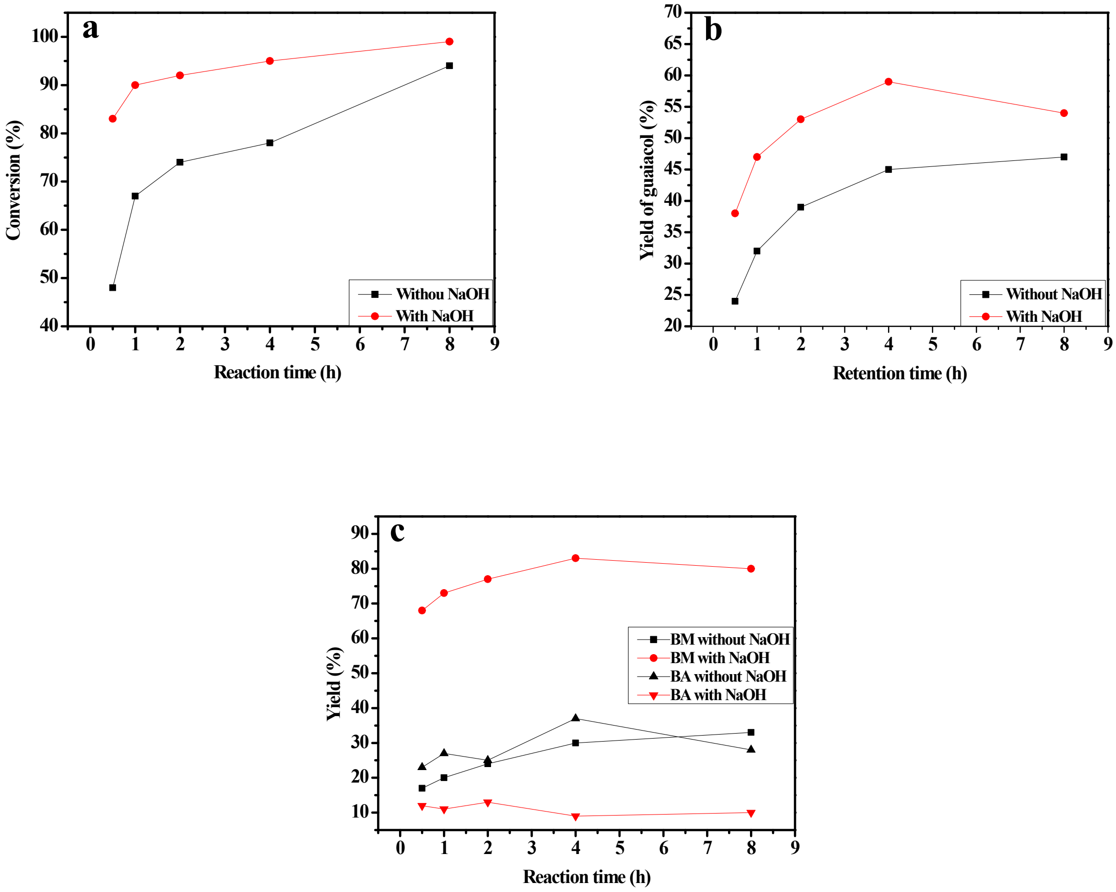


Figure S7 Effect of reaction time on (a) 2-(2-methoxyphenoxy)-1-phenylethanol (MPP-ol) conversion, (b) guaiacol (G) yield, (c) methyl benzoate (MB) yield and benzoic acid (BA) yield. Reaction conditions: Co-N-C (20 mg), MPP-ol (0.2 mmol), methanol (5 ml), air (1 MPa), 150°C.

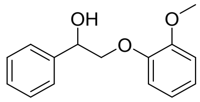
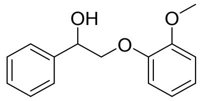
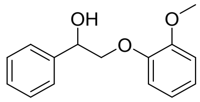
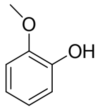
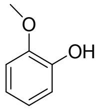
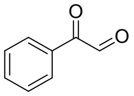
Table S2 Conversion of benzoic acid (BA) to methyl benzoate (BM) under different conditions. [a]

Entry	Catalyst		Solvent	Conv. (%)	Yield (%)[b]
	Co-N-C	NaOH			
1	/	/	MeOH	32	18
2	20 mg	/	MeOH	37	21
3	/	/	MeCN	<5	/
4	20 mg	/	MeCN	<5	/
5	/	0.2 mmol	MeOH	46	24
6	20 mg	0.2 mmol	MeOH	78	63

[a] Reaction conditions, benzoic acid (0.2 mmol), solvent (5 ml), air (1 MPa), 150°C, 4 h.

[b] Yields were determined by GC-FID.

Table S3 Control experiments. [a]

Entry	Substance	Conv. (%)	Yield (%)		
			G	BM	BA
1[b]		71	53	38	14
2[c]		81	46	51	9
3[d]		84	52	53	12
4		0		n.d.	
5[e]		0		n.d.	
6		96		93	

n.d. = not detected.

[a] Reaction conditions: catalyst (20 mg), NaOH (0.2 mmol), substrate (0.2 mmol), methanol (5 ml), air (1 MPa), 150°C, 4 h.

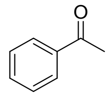
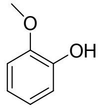
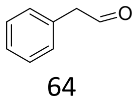
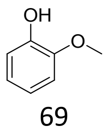
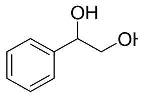
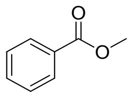
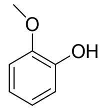
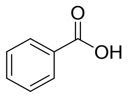
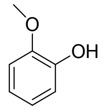
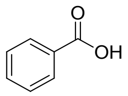
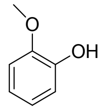
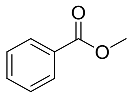
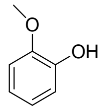
[b] The Co-N-C catalyst used in this run was unsuccessful synthesized and contains nanoparticles.

[c] NaOH was replaced by MgO (0.2 mmol).

[d] NaOH was replaced by CaO (0.2 mmol).

[e] Without NaOH.

Table S4 Catalytic systems for the oxidation of 2-(2-methoxyphenoxy)-1-phenylethanol ((MPP-ol).

Entry	Solvent	Catalyst	Oxidant	Condition		Conv. (%)	Yield (%)	Ref.
				Temp. (°C)	Time (h)			
1	Toluene	$RuHCl(CO)(PPh_3)_3$	/	125	48	93	 80  75	[2]
2[a]	[Bmim] NTf_2	CH_3ReO_3	/	180	14	98	 64  69	[3]
3	MeOH/ H_2O	Co-deuteroporphyrin	oxone	RT	8	100	 85 /	[4]
4	MeOH	Pd/CeO_2	1 bar O_2	185	24	90	 25  68	[5]
5	MeCN/ MeOH	$VOSO_4$ Cu	4 bar O_2	100	12	93	 93  26	[6]
6[b]	H_2O	[OMIm] [OAc]	15 bar O_2	110	2	99	 80  94	[7]
7	MeOH	Co-N-C	10 bar Air	150	4	95	 83  59	This work

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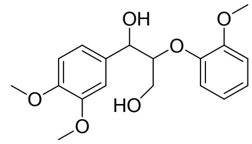
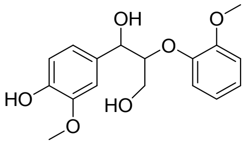
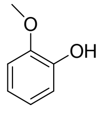
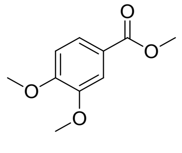
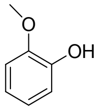
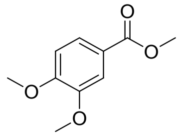
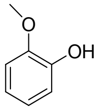
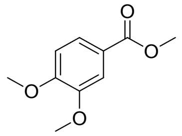
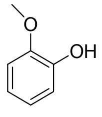
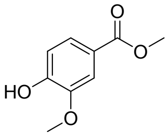
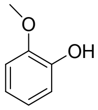
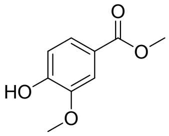
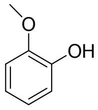
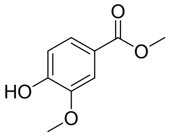
[a] Microwave heating. $[Bmim]NTf_2$ = 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide.
[b] [OMIm][OAc] = 1-octyl-3-methylimidazolium acetate.

Table S5 Conversion of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-propane-1,2-diol (DMPD) and guaiacylglycerol-guaiacyl ether (GGE).[a]

DMPD:		GGE:	

		Condition					
Entry	Substance	Temp. (°C)	Time (h)	Pressure (MPa)	Conv. (%)[b]	Products (% Yield)[c]	
1	DMPD	150	5~10	Air 1MPa	<5%	 n.d.	 n.d.
2	DMPD	180	10	Air 1MPa	43	 22	 29
3	DMPD	200	10	Air 1.5MPa	61	 38	 47
4	GGE	150	5~10	Air 1MPa	<5%	 n.d.	 n.d.
5	GGE	180	10	Air 1MPa	24	 19	 11
6	GGE	200	10	Air 1.5MPa	42	 26	 19

n.d. = not detected.

[a] Reaction conditions: catalyst (20 mg), NaOH (0.2 mmol), substrate (0.2 mmol), methanol (5 ml).
[b] Conversion was determined by HPLC.
[c] Yields were obtained by GC-FID.

5. The recycle experiment and the characterization of the recycled catalyst

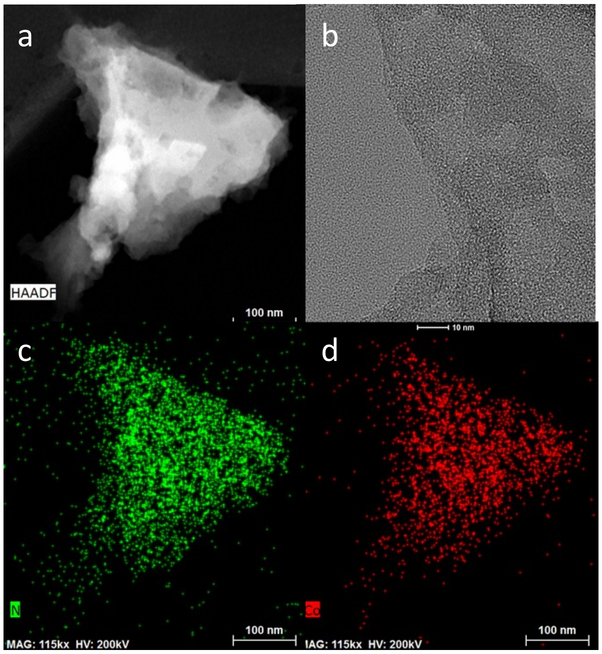


Figure S8 Representative TEM dark field (a) and bright field (b) image of Co-N-C catalyst after eight catalytic cycles and the corresponding EDX mapping image (c, d) of the catalyst.

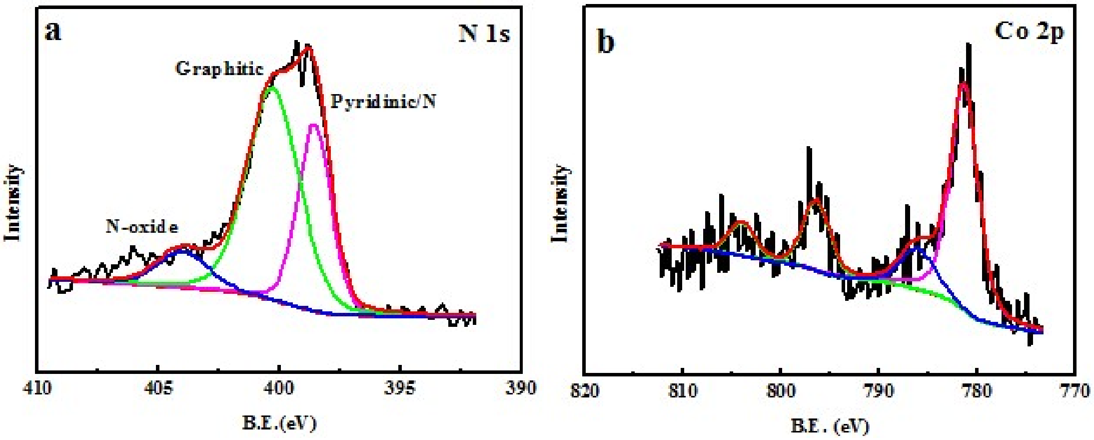


Figure S9 N 1s (a) and Co 2p (b) XPS spectrum of Co-N-C catalyst after eight catalytic cycles.

Table S6 XPS surface content of fresh and the recycled Co-N-C catalyst.

Catalyst	C (%)	O (%)	Co (%)	N (%)
Co-N-C	50.2	26.7	4.5	9.9
Recycled Co-N-C	80.5	9.7	1.0	8.5

6. Characterization of β-O-4 lignin model compounds

^{1}H NMR spectrum of the substrates

^{1}H NMR spectrum of the prepared substrates 2-(2-methoxyphenoxy)-1-phenylethanol (Fig. S10), 2-(2-methoxyphenoxy)-1-phenylethanone (Fig. S11), 2-phenoxy-1-phenylethanol (Fig. S12), 2-(2,6-dimethoxyphenoxy)-1-phenylethanol (Fig. S13), 1-(benzyloxy)-2-methoxybenzene (Fig. S14). Spectra were recorded on a Bruker DMX 400 instrument using a $CDCl_3$ as solvent.

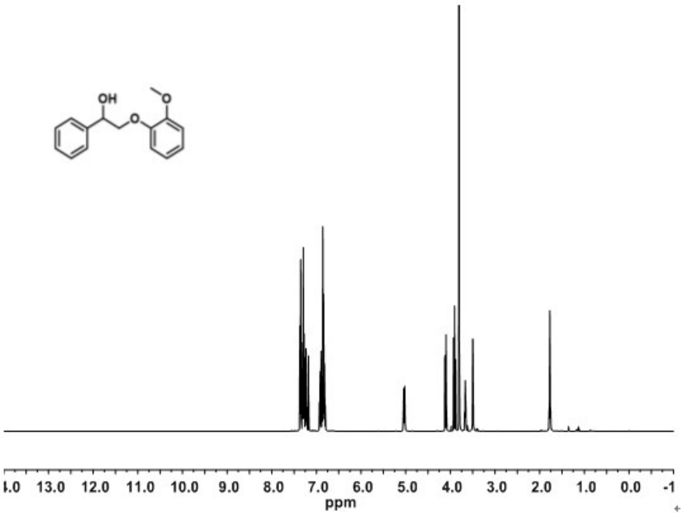


Figure S10 ^{1}H NMR spectrum of 2-(2-methoxyphenoxy)-1-phenylethanol.

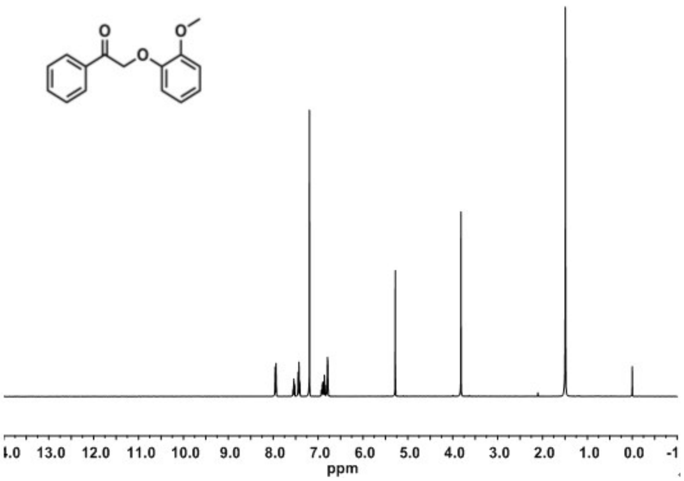


Figure S11 ^{1}H NMR spectrum of 2-(2-methoxyphenoxy)-1-phenylethanone.

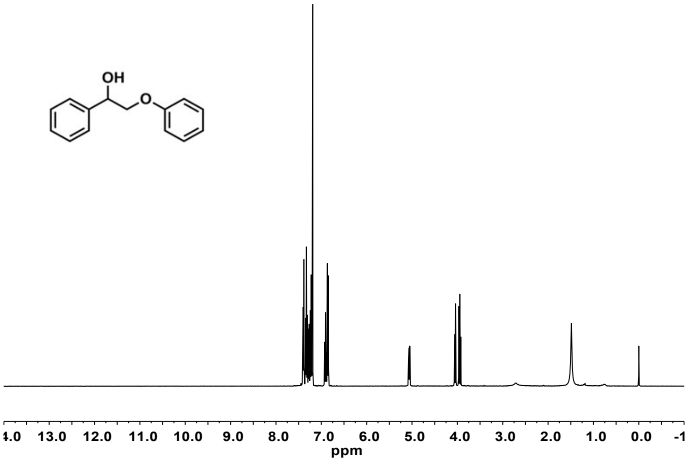


Figure S12 ^{1}H NMR spectrum of 2-phenoxy-1-phenylethanol.

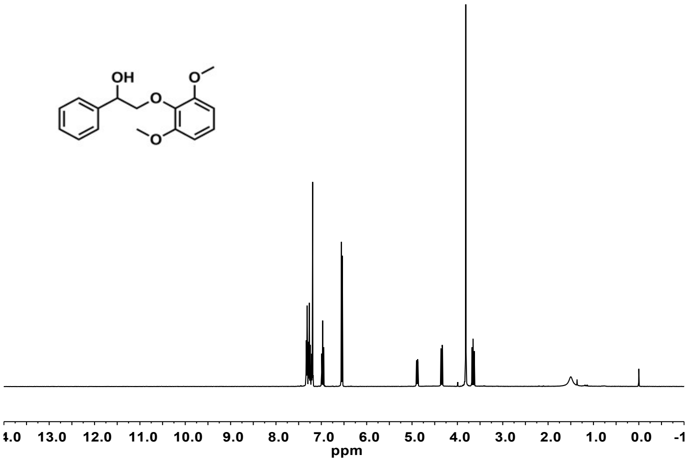


Figure S13 ^{1}H NMR spectrum of 2-(2,6-dimethoxyphenoxy)-1-phenylethanol.

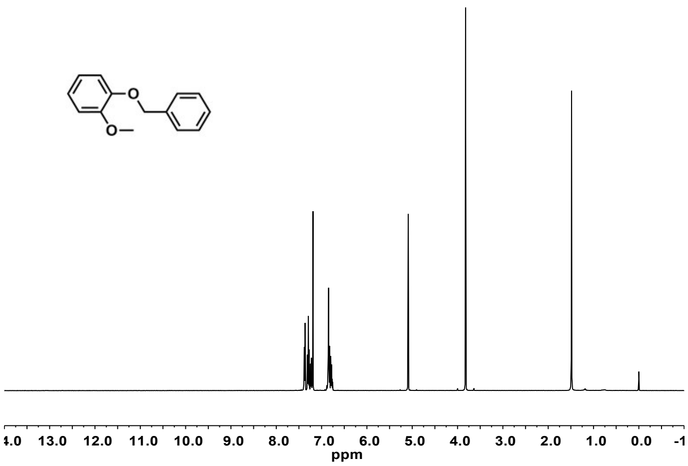


Figure S14 ^{1}H NMR spectrum of 1-(benzyloxy)-2-methoxybenzene.

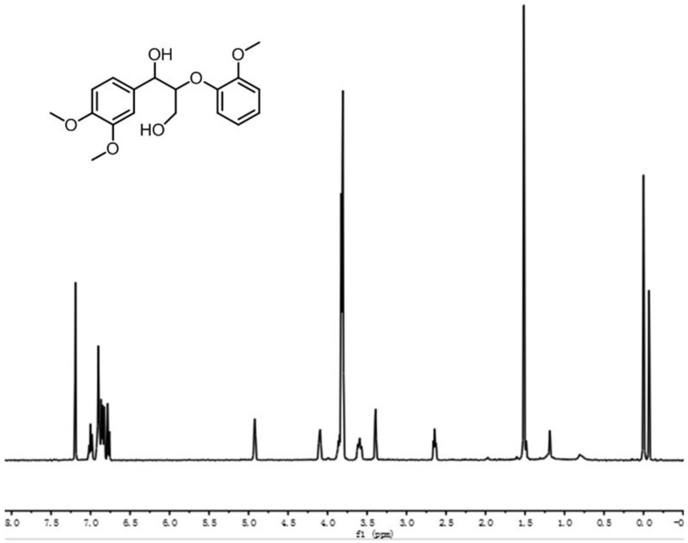


Figure S15 ^{1}H NMR spectrum of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-propane-1,2-diol (DMPD).

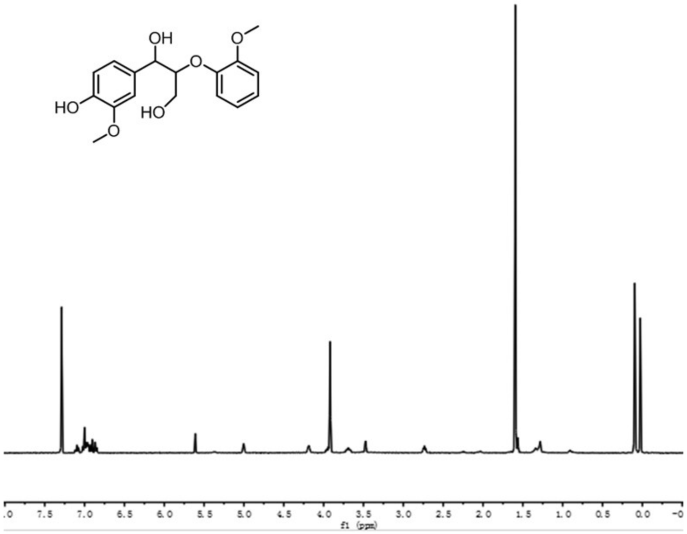


Figure S16 ^{1}H NMR spectrum of guaiacylglycerol-guaiacyl ether (GGE).

7. References

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