Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Highly-efficient and magnetically-separable ZnO/Co@N-CNTs catalyst for hydrodeoxygenation of lignin and its derived species under mild conditions

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Table S1 Summary of the reported HDO of vanillin over various types of heterogeneous catalysts.

	Catalysts	Solvent	P_{H2} (MPa)	T (°C)	t (h)	Conv. (%)	Creosol selectivity (%)	Reference
Noble metal-based catalyst	Au/CNTs	H_2O	1.0	200	6	100	75	[1]Yang *et al*. RSC Adv. 2014
	Ru/CNTs	H_2O	1.0	150	3	100	96	[2]Yang *et al*. Catal. Comm. 2014
	Ru_1/mpg-C_3N_4^{a}	H_2O	4.0	140	4	100	100	[3]Tian *et al*. J. Am. Chem. Soc. 2018
	Pd/CM180^b	H_2O	1.0	100	1	>99	94	[4]Zhu *et al*. Green Chem. 2014
	Pd/SO_3H-MIL-101(Cr)	H_2O	1.0	90	1	100	98.4	[5]Zhang *et al*. J. Mater. Chem. A. 2015
	Pd/CN^c	H_2O	1.0	150	6	100	100	[6]Xu *et al.* J. Am. Chem. Soc. 2012
	Pd/SWNT^c-SiO_2	H_2O	0.34	100	6	100	45	[7]Crossley *et al.* Science 2010
	Pd/TiO_2@NC^c	H_2O	1.0	150	6	95.5	>99.5	[8]Wang *et al.* ChemSusChem 2014
	Pd/C	AcOH	1.0	55	24	>99	99	[9]Wang *et al*. Tetrahedron, 2006
	Pd/POP^d	IPA	1.0	140	18	96.5	98.2	[10]Singuru *et al*. ChemCatChem 2017
	Pd/PRGO^e/Ce-MOF	H_2O	1.0	100	5	100	>99	[11]Ibrahim *et al*. ChemCatChem. 2017
Non-noble-metal based-catalyst	$CoMoS_x/Al_2O_3$	Dodecane	5.0	300	6	53	23	[12]Jongerius *et al.* J. Catal.,2012
	Co/NC-600^c	Isopropanol	1.0	150	4	98.2	85.1	[13]Jiang *et al*. ChemSusChem. 2018
	Co/NC-700^c	H_2O	FA^f	180	4	100	95.7	[14]Yang *et al*. Green Chem. 2017
	Ni/N-doped CB^g	H_2O	0.5	150	2	74.4	64.6	[15]Nie *et al*. Green Chem. 2017
	Cu/AC-600	H_2O	4.0	120	3	100	70.0	[16]Fan et al. Small 2018
	Cu/PMO^h	MeOH	4.0	180	18	100	90	[17]Petitjean *et al*. Green Chem. 2016
	Ga-Cu/HNZY^i	MeOH	1.0	180	2	100	100	[18]Verma *et al.* Green Chem. 2018
	ZnO/Co@N-CNT	H_2O	0.7	130	2	100	100^j	This work
			0.7	150	2	100	100^k	

[a]mpg = mesoporous graphitic; [b]CM180 = carbonaceous microspheres-180 (hydrothermal temperature); [c]NC = nitrogen-doped carbon; [d]POP = porous organic polymer; [e]PRGO = partially reduced graphene oxide; [f]FA= formic acid; [g]CB = carbon black; [h]PMO = porous metal oxide; [i]HNZY = H-nanozeolite-Y; [j]catalyst-to-feed ratio of 0.28; [k]catalyst-to-feed ratio of 0.20.

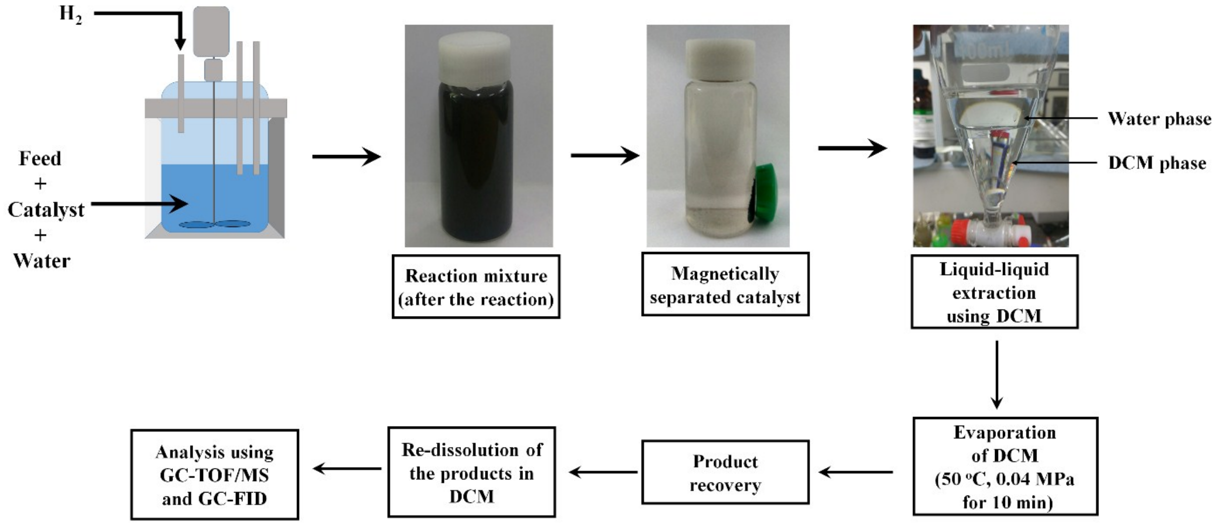
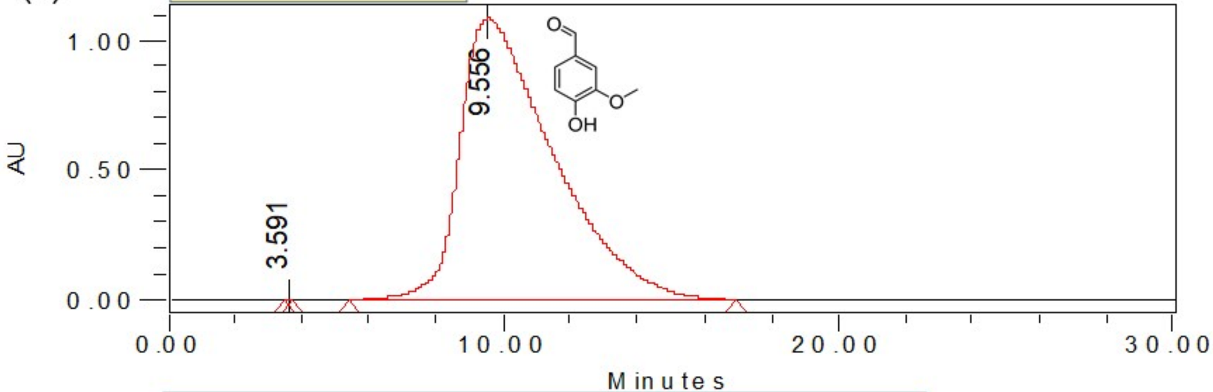


Fig. S1 Flow diagram of product separation after the HDO and HD reactions.

(a) Before the reaction



(b) After the reaction & liquid-liquid extraction using DCM

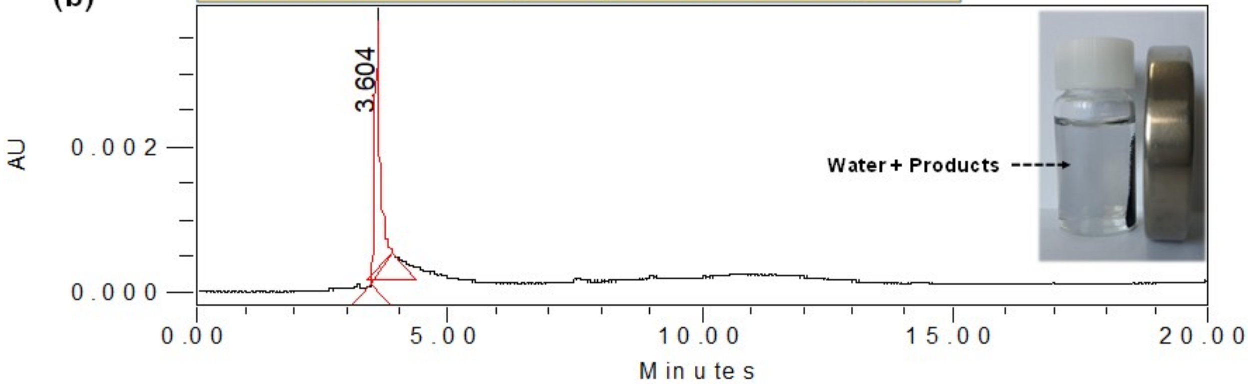


Fig. S2 HPLC chromatograms of the water phase (a) before the reaction (water + vanillin); and (b) after the reaction and liquid-liquid extraction, which was performed three times using 30 mL DCM. Inset of figure (b): after the reaction, the catalysts were separated from the liquid product (creosol) in water using a magnetic bar. Reaction conditions: 250 mg vanillin, 50 mg ZCI1-700 catalyst, 30 mL H_2O, 150 °C, 0.7 MPa initial H_2 pressure, reaction time of 2 h.

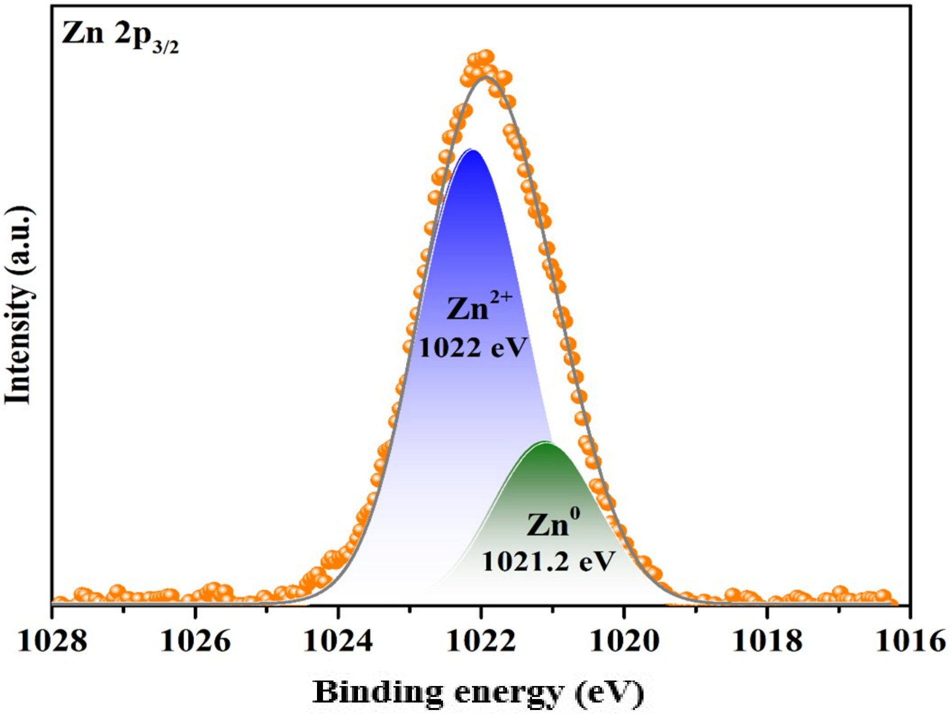

Zn 2p3/2
Zn2+
1022 eV
Zn0
1021.2 eV
Intensity (a.u.)
1028
1026
1024
1022
1020
1018
1016
Binding energy (eV)

Fig. S3 Deconvoluted Zn 2p core level XPS spectra of ZCI1-700.

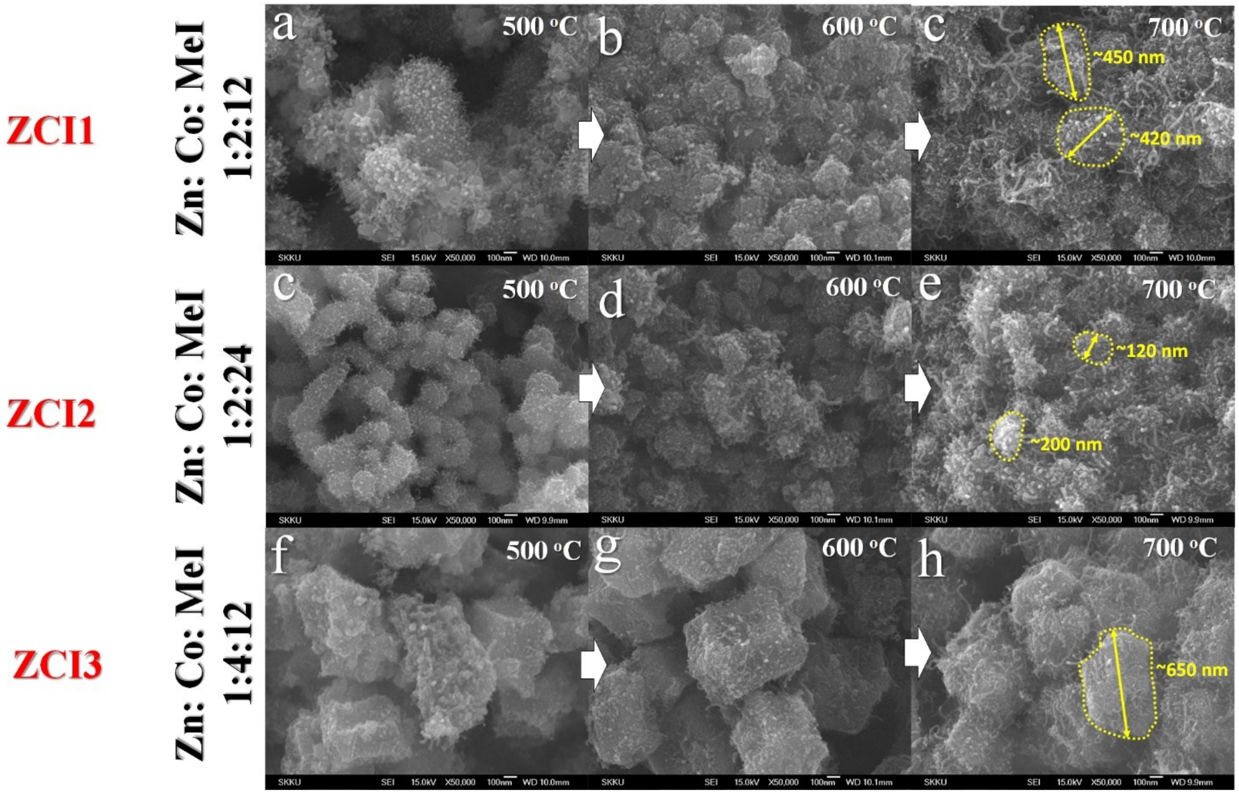


Fig. S4 SEM images of calcined ZCI1, ZCI2, and ZCI3 that were prepared at different ratios of Zn:Co:MeI at various temperatures of 500–700 ℃. See Table 1 for the preparation conditions used for synthesizing ZCI1, ZCI2, and ZCI3.

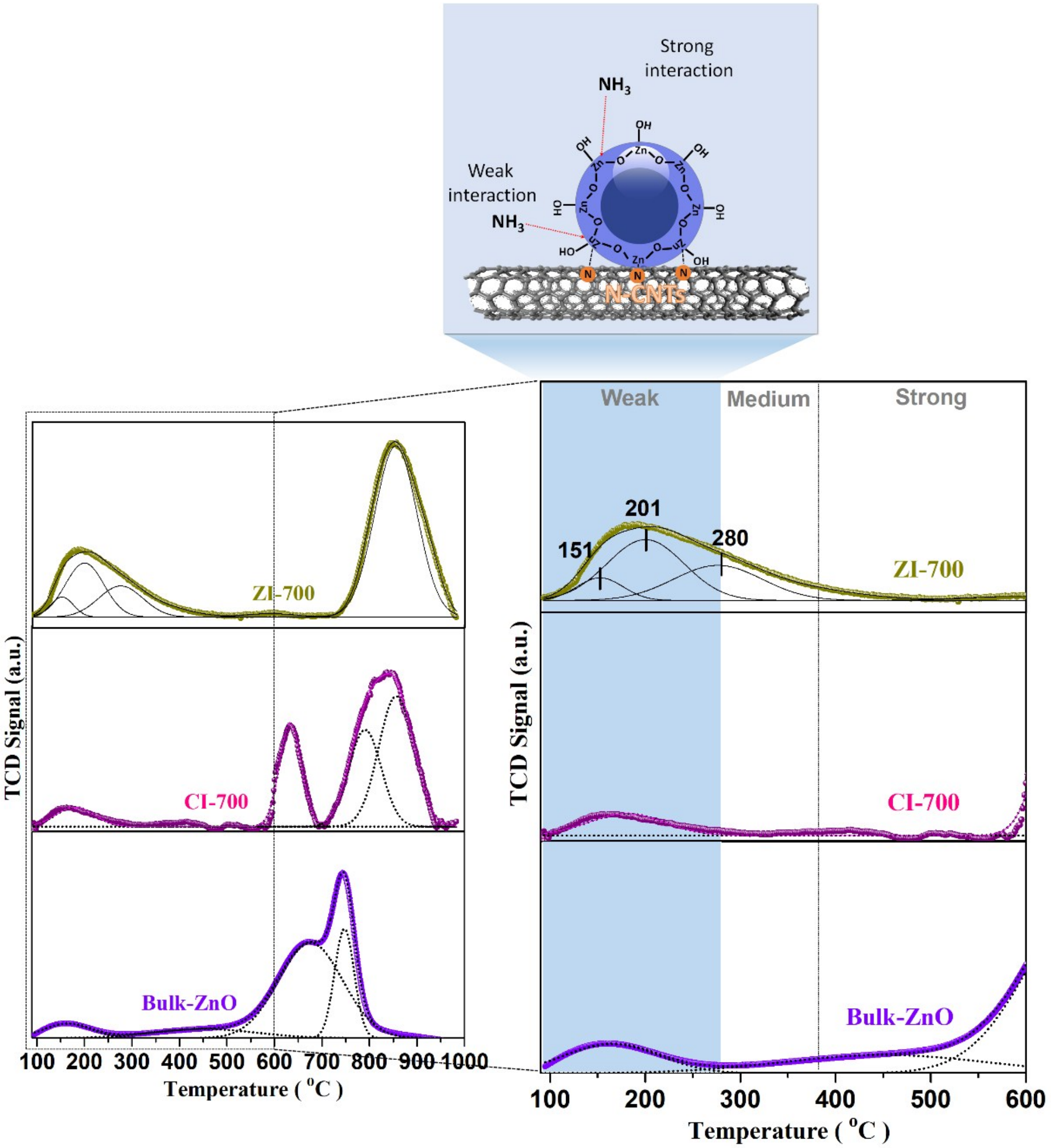


Fig. S5 NH$_3$-TPD profiles of crystalline ZnO bulk particles, ZI-700 and CI-700.

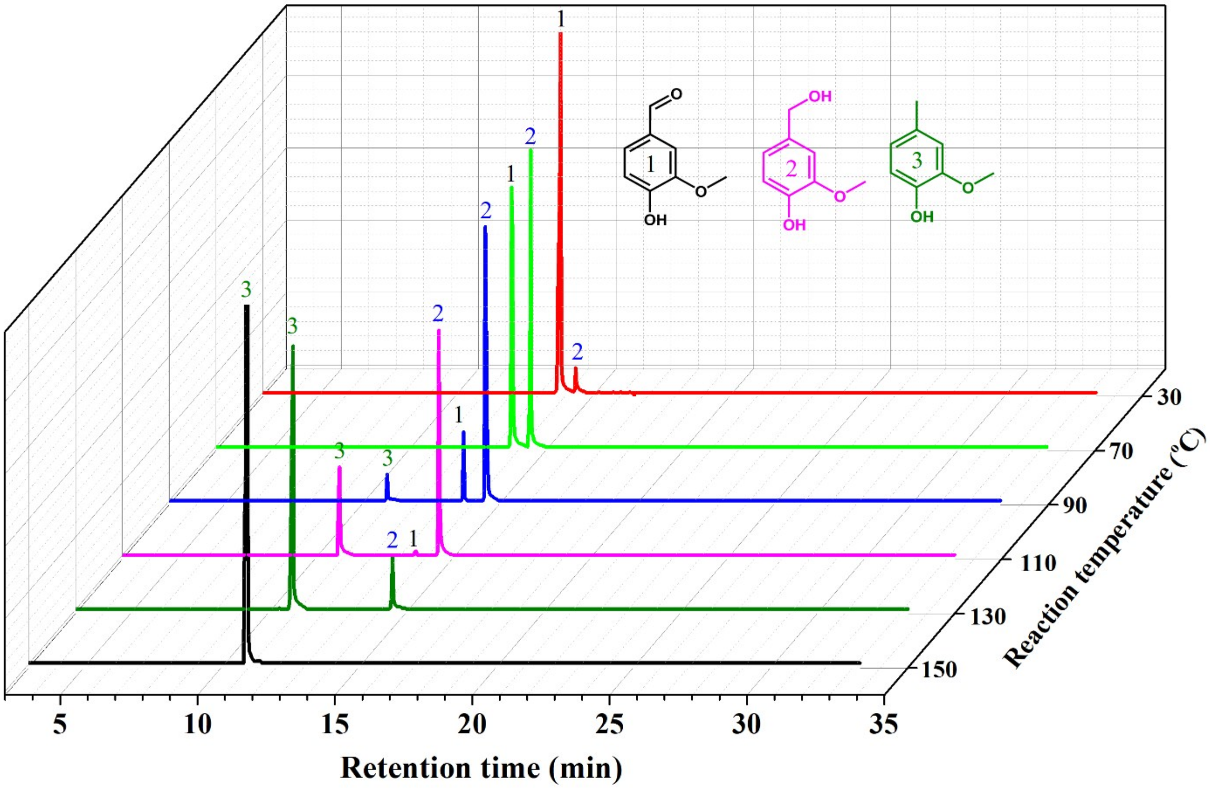


Fig. S6 GC-TOF/MS chromatograms of the products obtained at different reaction temperatures over ZCI1-700 catalyst. Reaction conditions: 250 mg vanillin, 50 mg catalyst, 30 mL H_2O, 0.7 MPa initial H_2 pressure, reaction time of 2 h.

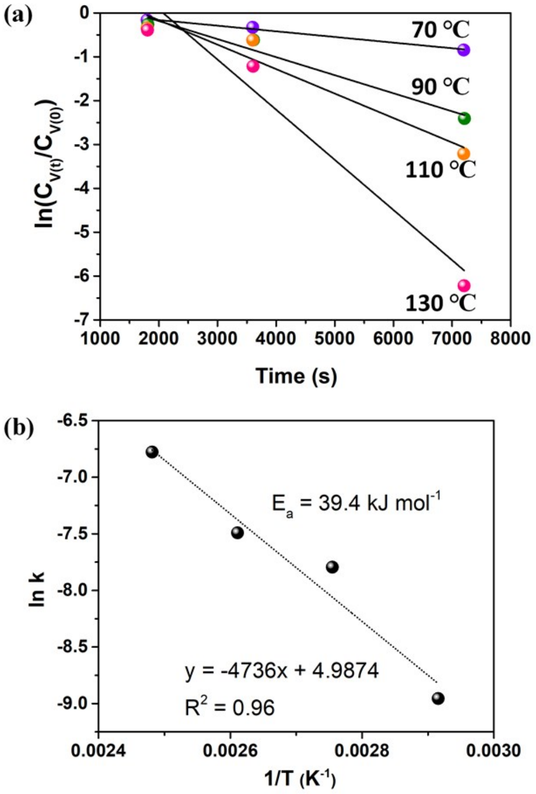


Fig. S7 (a) Plot of time vs ln(C/C_0, vanillin) over ZnO/Co@N-CNTs catalyst at different temperatures (catalyst to feed ratio = 0.20, feed = 250 mg; H_2O = 30 mL); (b) Arrhenius plots of ln*k vs* (1/T), where, $C_{V,0}$ is the initial concentration of vanillin, $C_{V,t}$ is the concentration of vanillin after reaction in certain time.

Simple kinetic study follows a first-order reaction based on the feed conversion.

$$\frac{dC_V}{dt} = -kC_V \Rightarrow C_{V(t)} = C_{V(0)}e^{-kt} \Rightarrow \frac{C_{V(t)}}{C_{V(0)}} = e^{-kt}$$

$$\frac{C_{V(t)}}{C_{V(0)}} = 1 - X_V \Rightarrow 1 - X_V = e^{-kt} \Rightarrow -\ln(1 - X_V) = kt$$

$$k = A\exp\left(-\frac{E_a}{R.T}\right) \Rightarrow \qquad \ln k = -\frac{E_a}{RT} + \ln A$$

Synthetic procedure of ZnO/Co@AC

The ZnO/Co@AC catalyst was prepared by an incipient wetness impregnation method. The Zn/Co metal ratio on the activated carbon support was maintained at 1:2, which is identical to the Zn/Co metal molar ratio in the ZCI1 sample. In typical synthesis of ZnO/Co@AC, $Co(NO_3)_2{\cdot}6H_2O$ (1.82 g, 2 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (0.42 g, 1 mmol) salts were dissolved in 10 mL of ethanol under stirring to achieve a clear solution. Then 1 g of activated carbon (–20+40 mesh, Alfa Aesar, USA) was transferred into the solution, and the final mixture was stirred at 80 °C until the solvent used for the impregnation evaporated. Finally, the ZnO/Co@AC catalyst was synthesized by activating the dried powder at 700 °C under a 5% H_2/Ar flow at a rate of 10 mL min^{-1} for 5 h with a ramping rate of 2 °C min^{-1}.

Synthesis procedure of ZnO/Co@CNT

ZIF synthesis was conducted according to a previously reported method with some modifications.[19] Essentially, $Co(NO_3)_2{\cdot}6H_2O$ (582 mg, 2 mmol), $Zn(NO_3)_2{\cdot}6H_2O$ (297 mg, 1 mmol), and 1,3,5-benzenetricarboxylic acid (BTC, 2.5 g, 12 mmol) were dissolved in 70 mL N,N'-dimethyl formamide (DMF, Alfa Aesar, USA) with stirring to form a clear solution. The final solution was transferred in to a Teflon lined autoclave and kept in an oven at 120 °C for 24 h. The as-synthesized precipitate was centrifuged and washed with ethanol four times and then dried at 80 °C for 12 h. The produced Zn/Co-BTC was designated as ZCB. The ZCB sample was carbonized at 700 °C under a 5% H_2/Ar flow at a rate of 10 mL min^{-1} for 5 h with a ramping rate of 2 °C min^{-1}. The synthesized catalyst was designated as ZCB-700.

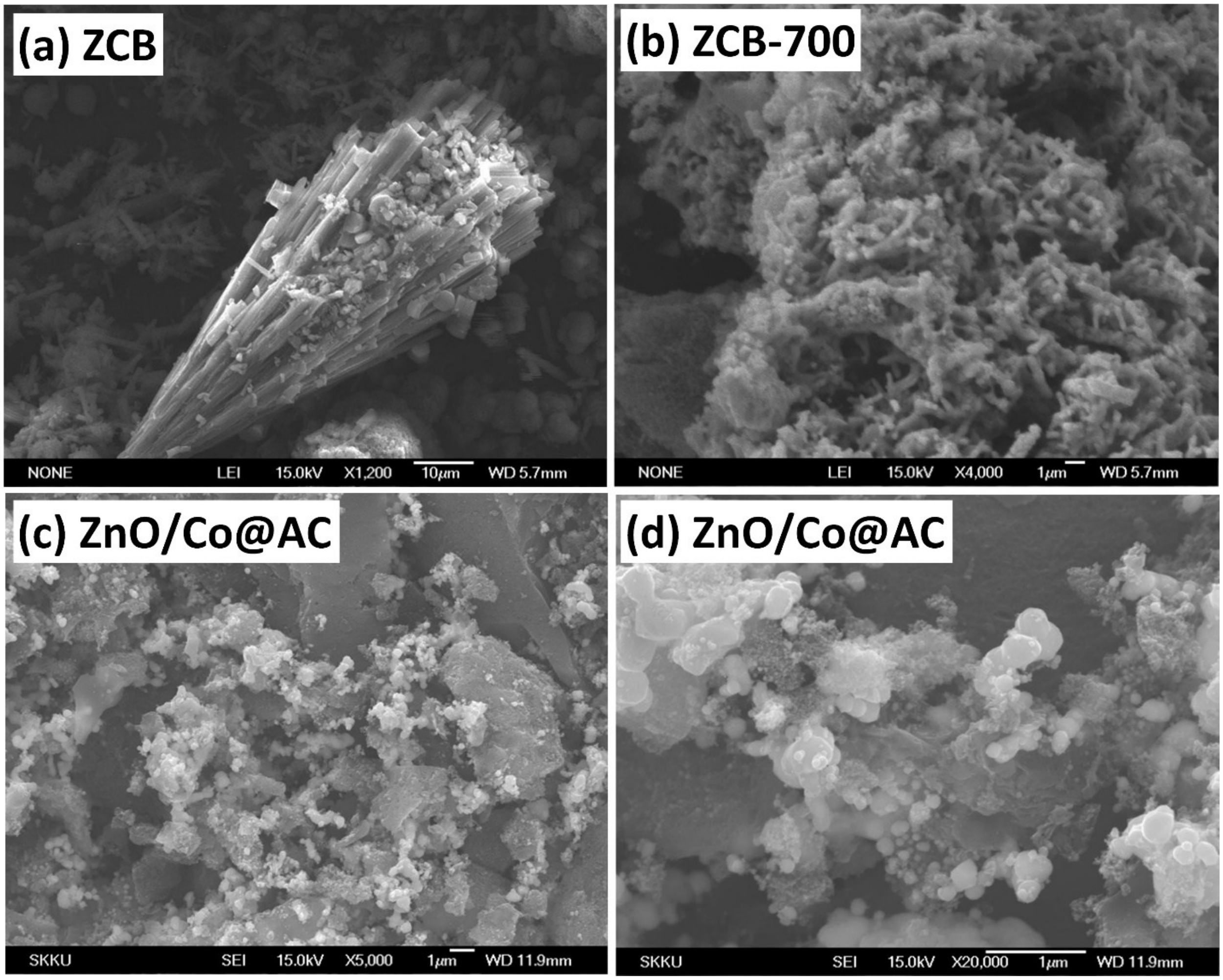


Fig. S8 SEM image of (a) ZCIB, (b) ZCB-700, and (c-d) ZnO/Co@AC.

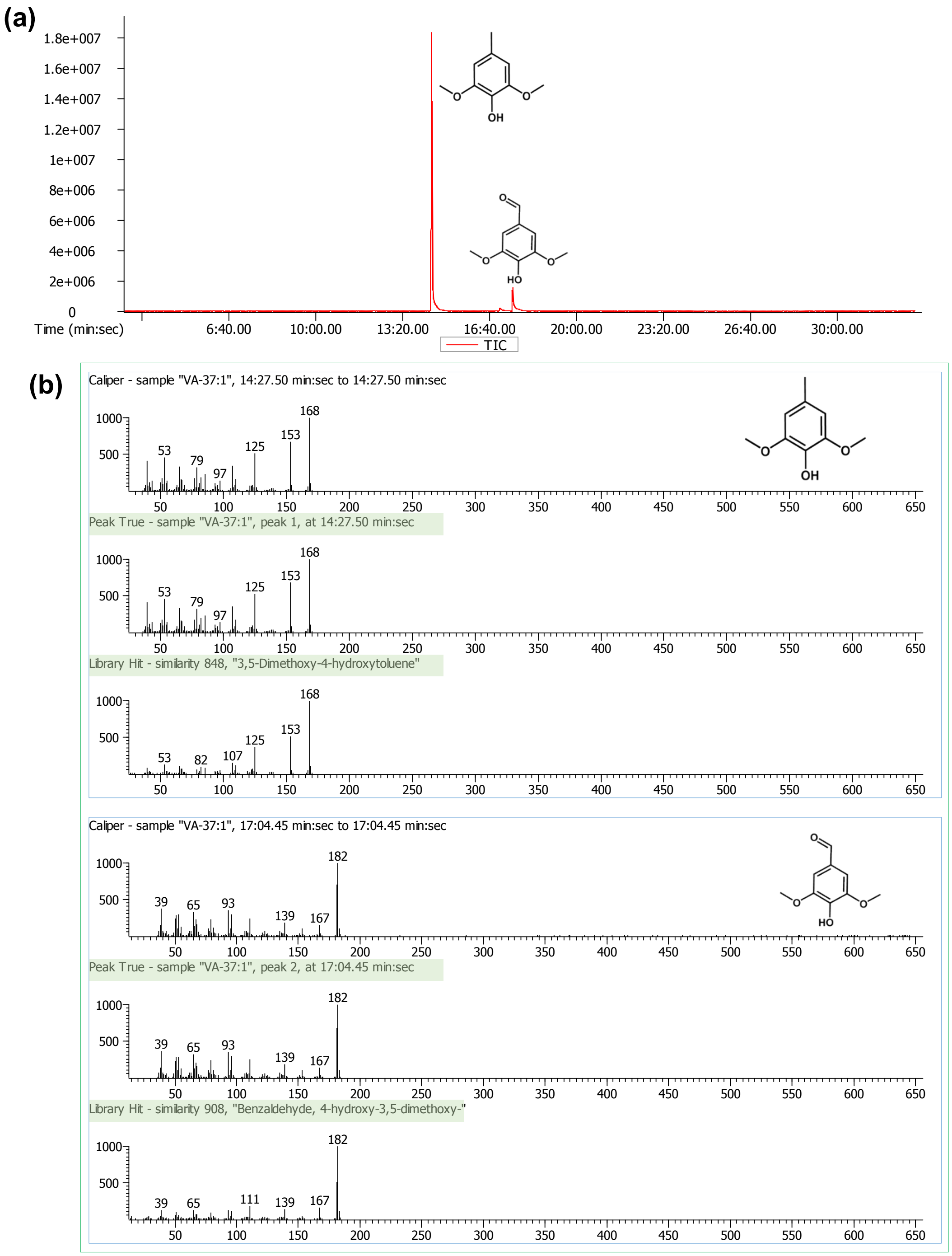


Fig. S9 (a) GC-TOF/MS chromatogram and (b) representative mass-spectrometer spectra of the observed compounds produced in the syringaldehyde reaction over the ZCI1-700 catalyst. Reaction conditions: 250 mg syringaldehyde, 50 mg catalyst, 30 mL H_2O, 130 °C, 0.7 MPa initial H_2 pressure, reaction time of 2 h.

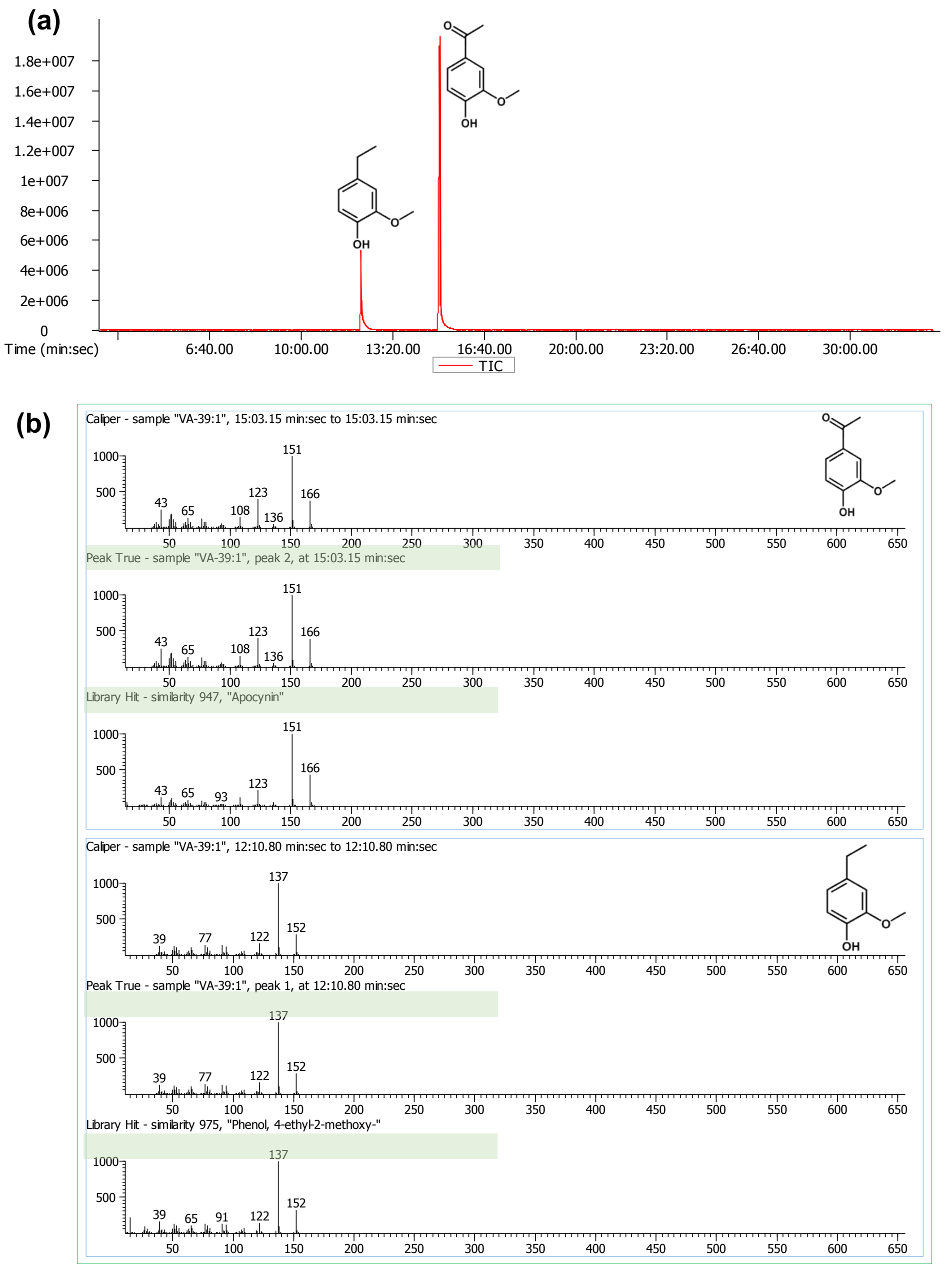


Fig. S10 (a) GC-TOF/MS chromatogram and (b) representative mass-spectrometer spectra of the observed compounds produced in the acetovanillone reaction over the ZCI1-700 catalyst. Reaction conditions: 250 mg acetovanillone, 50 mg catalyst, 30 mL H_2O, 130 °C, 0.7 MPa initial H_2 pressure, reaction time of 2 h.

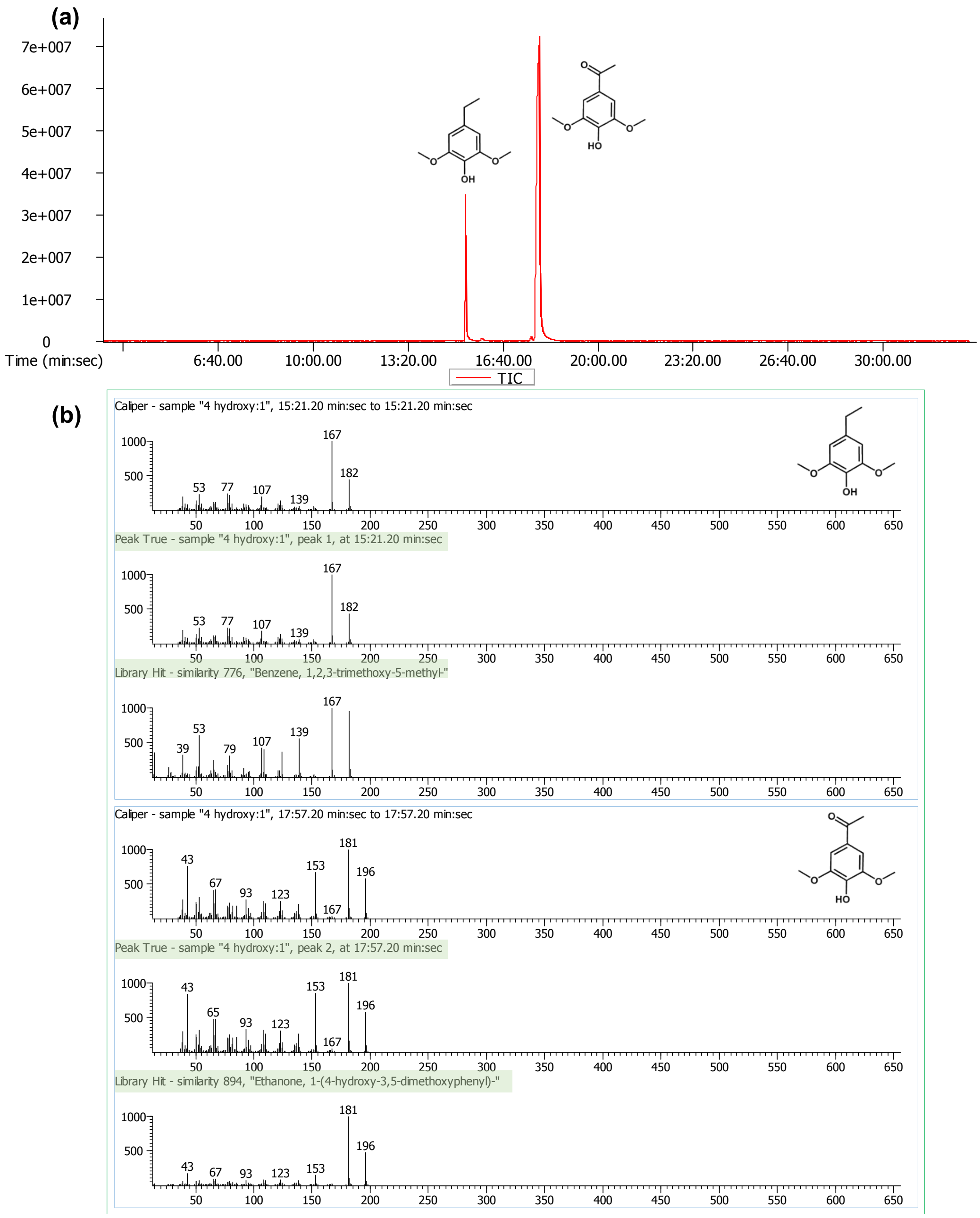


Fig. S11 (a) GC-TOF/MS chromatogram and (b) representative mass-spectrometer spectra of the observed compounds produced in the acetosyringone reaction over the ZCI1-700 catalyst. Reaction conditions: 250 mg acetovanillone, 50 mg catalyst, 30 mL H_2O, 130 °C, 0.7 MPa initial H_2 pressure, reaction time of 2 h.

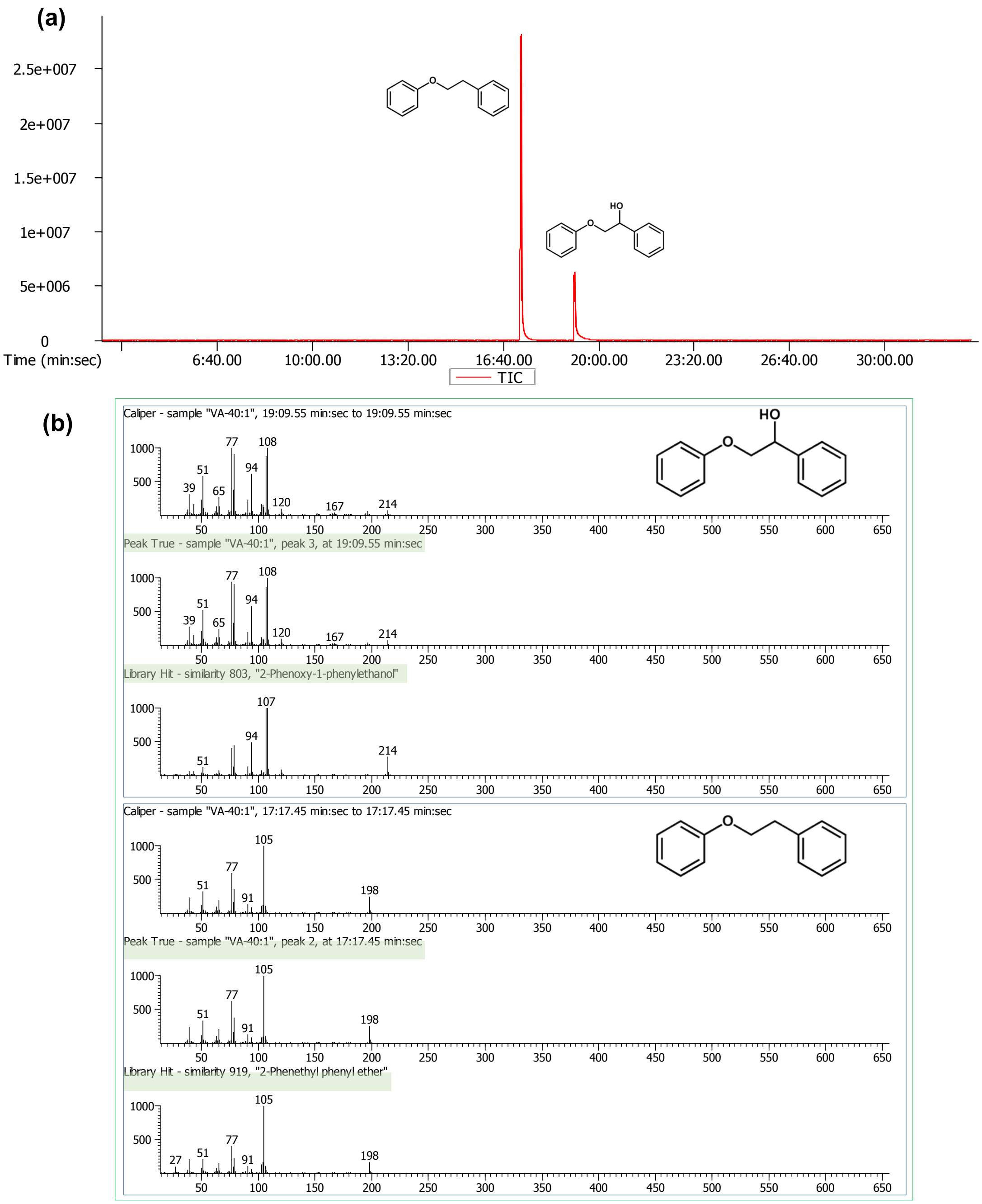
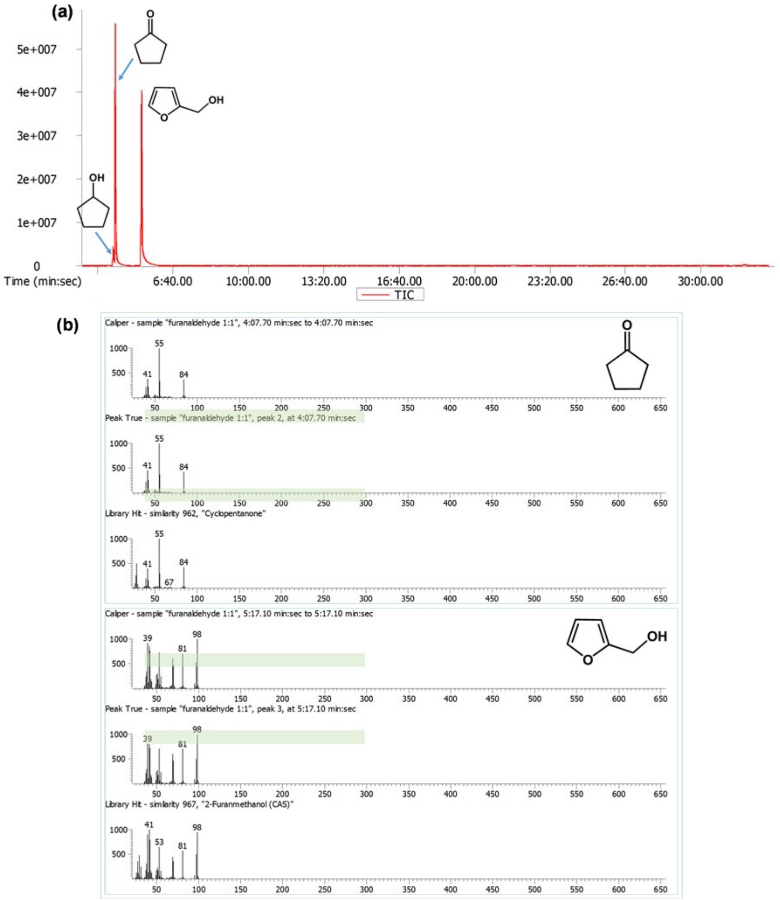


Fig. S12 (a) GC-TOF/MS chromatogram and (b) representative mass-spectrometer spectra of the observed compounds produced in the 2-phenoxy-1-phenylethanol reaction over the ZCI1-700 catalyst. Reaction conditions: 250 mg 2-phenoxy-1-phenylethanol, 50 mg catalyst, 30 mL H_2O, 130 °C, 0.7 MPa initial H_2 pressure, reaction time of 2 h.



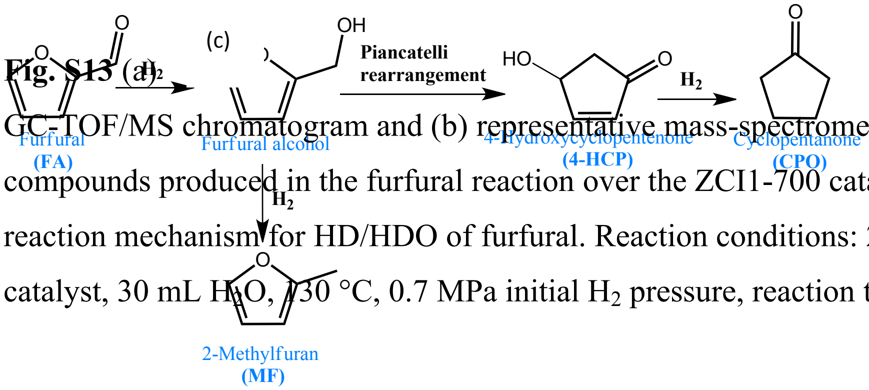


Fig. S13 (a) GC-TOF/MS chromatogram and (b) representative mass-spectrometer spectra of the observed compounds produced in the furfural reaction over the ZCI1-700 catalyst, and (c) plausible reaction mechanism for HD/HDO of furfural. Reaction conditions: 250 mg furfural, 50 mg catalyst, 30 mL H_2O, 130 °C, 0.7 MPa initial H_2 pressure, reaction time of 2 h.

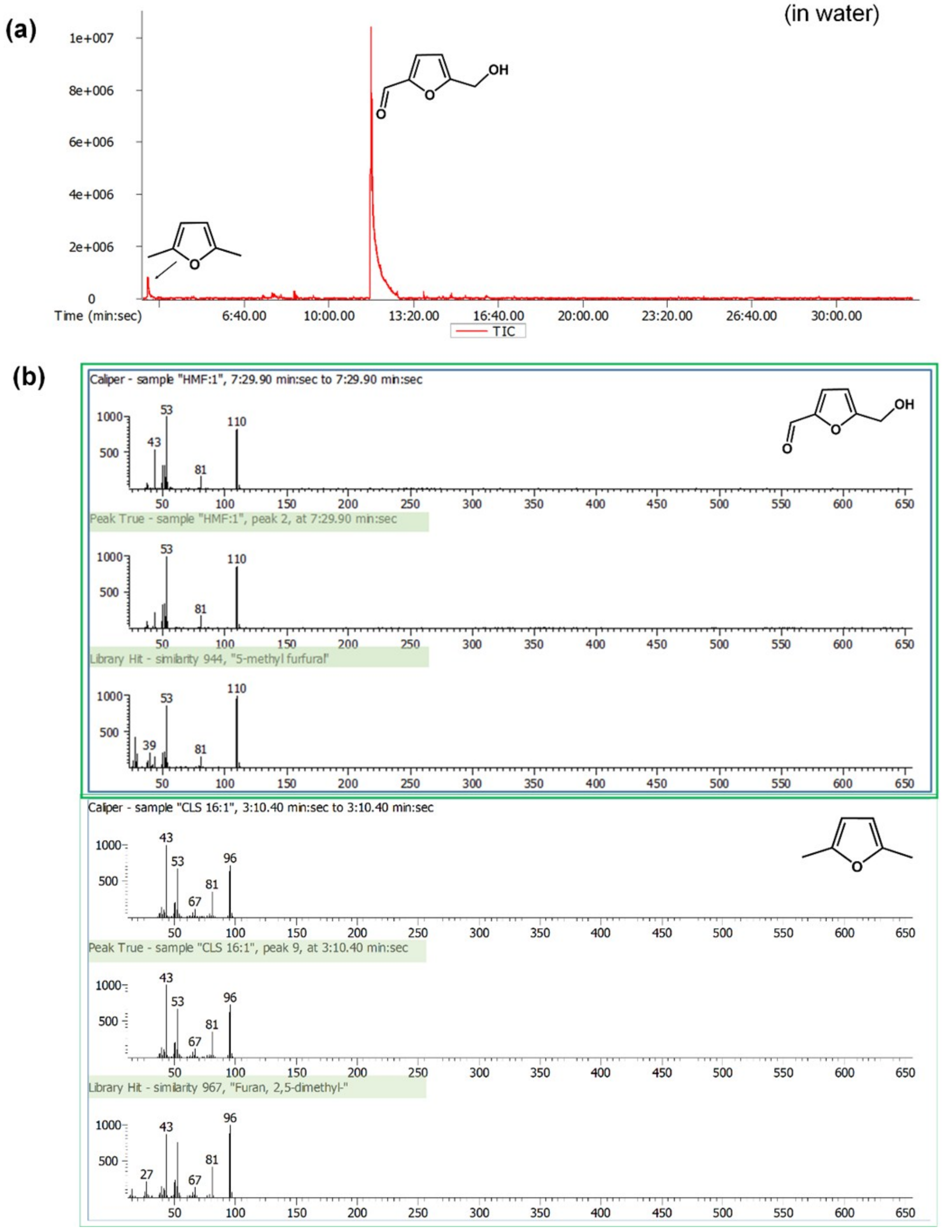


Fig. S14 (a) GC-TOF/MS chromatogram and (b) representative mass-spectrometer spectra of the observed compounds produced in the 5-HMF reaction over ZCI1-700 catalyst in water media. Reaction conditions: 250 mg 5-HMF, 50 mg catalyst, 30 mL H_2O, 130 °C, 0.7 MPa initial H_2 pressure, reaction time of 2 h.

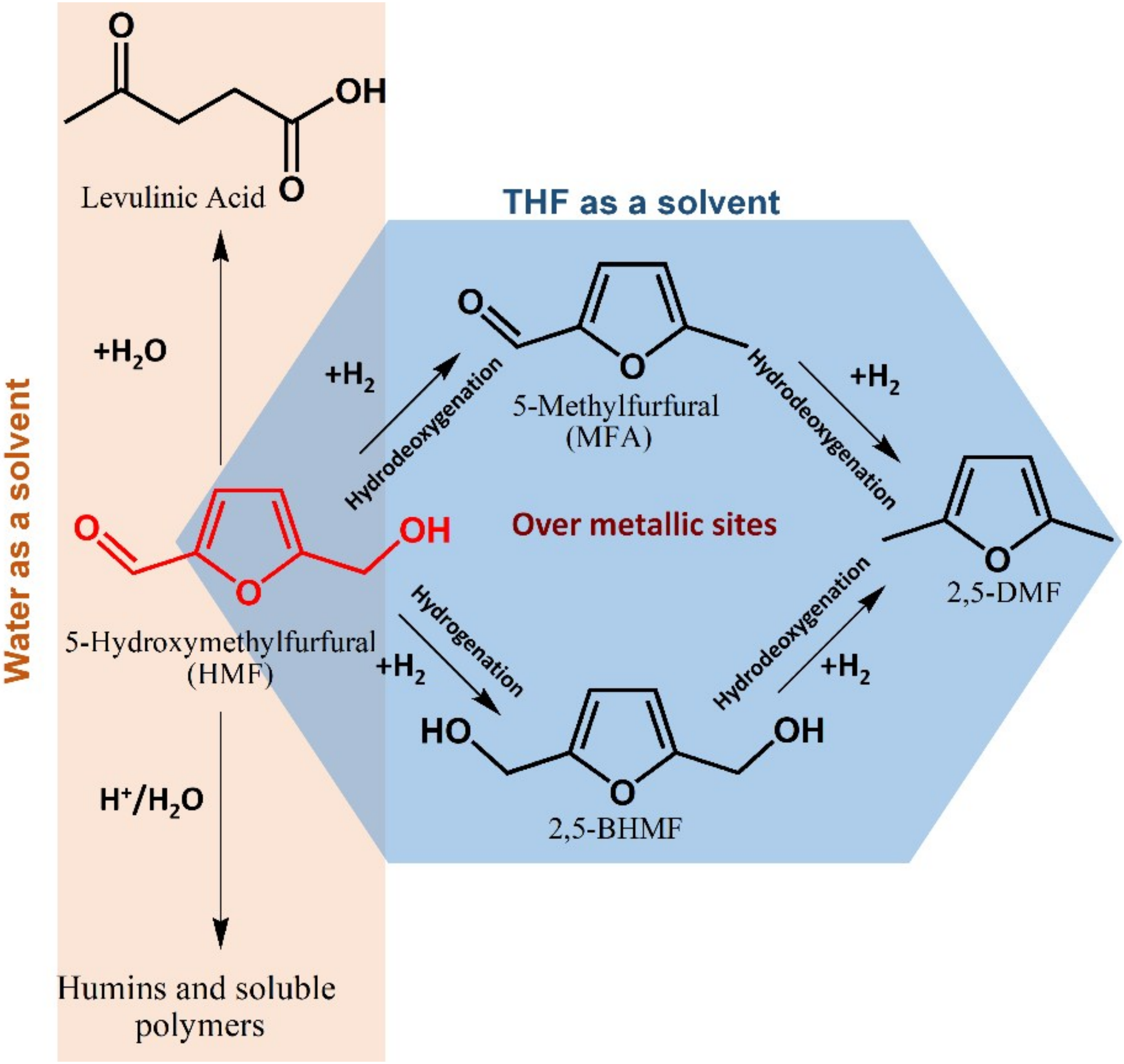


Fig. S15 Reaction pathway for the hydrodeoxygenation study of 5-HMF in water and THF solvent.

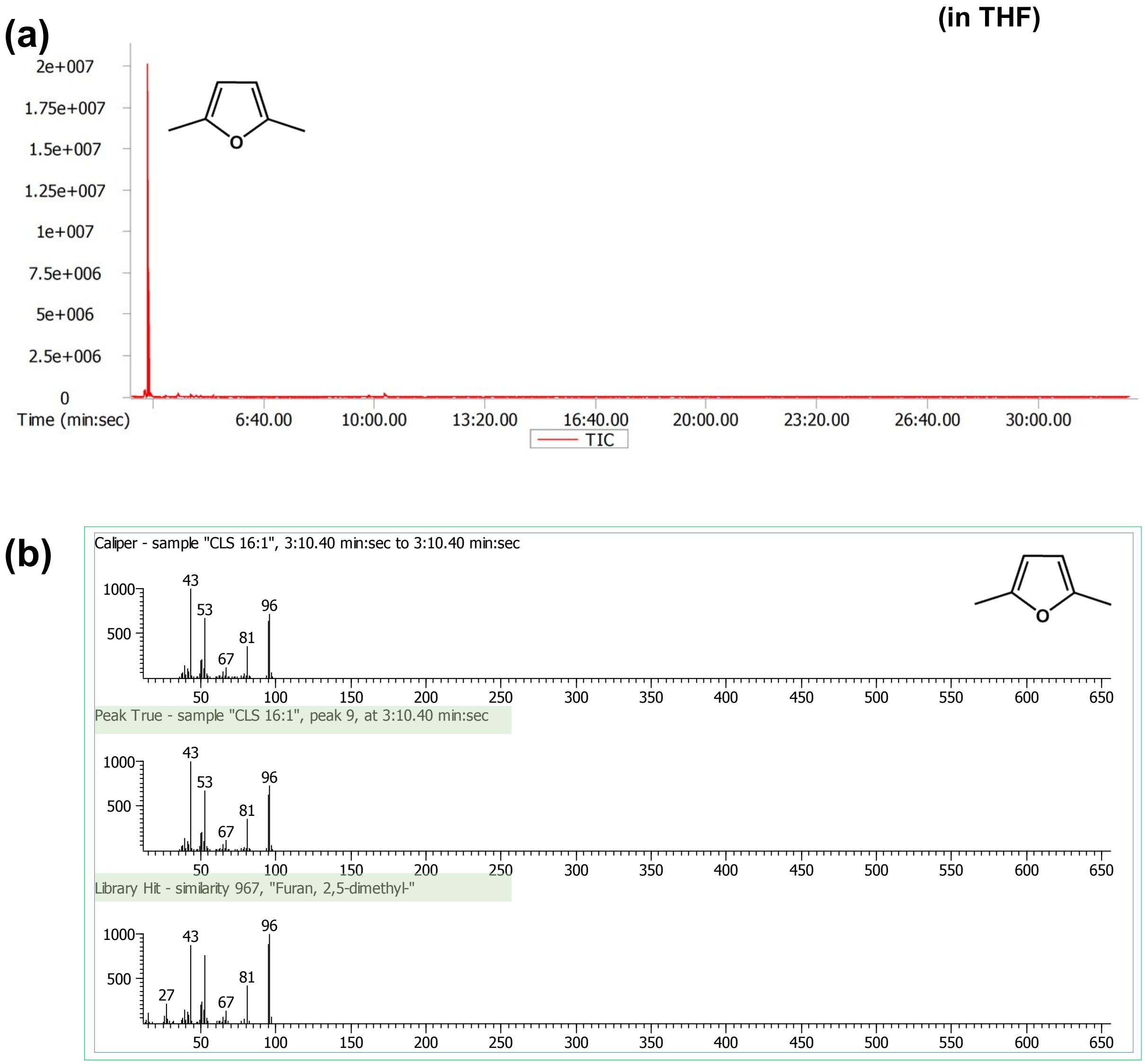


Fig. S16 (a) GC-TOF/MS chromatogram and (b) representative mass-spectrometer spectra of the observed compounds produced in the 5-HMF reaction over the ZCI1-700 catalyst in a THF medium. Reaction conditions: 250 mg 5-HMF, 50 mg catalyst, 30 ml THF, 130 °C, 0.7 MPa initial H_2 pressure, reaction time of 2 h.

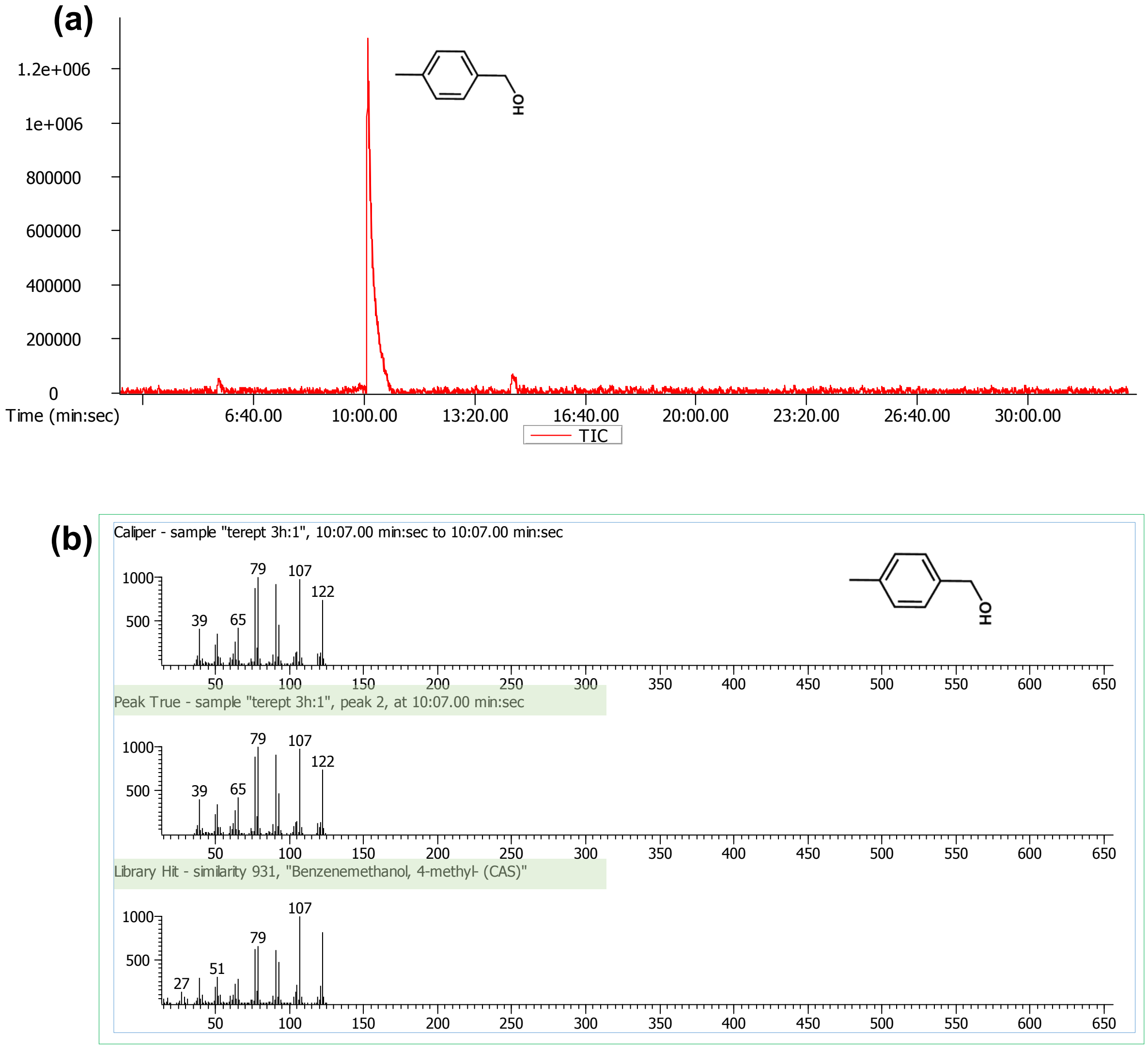


Fig. S17 (a) GC-TOF/MS chromatogram and (b) representative mass-spectrometer spectra of the observed compounds produced in the terephthaldehyde reaction over the ZCI1-700 catalyst. Reaction conditions: 250 mg terephthaldehyde, 50 mg catalyst, 30 mL H_2O, 130 °C, 0.7 MPa initial H_2 pressure, reaction time of 2 h.

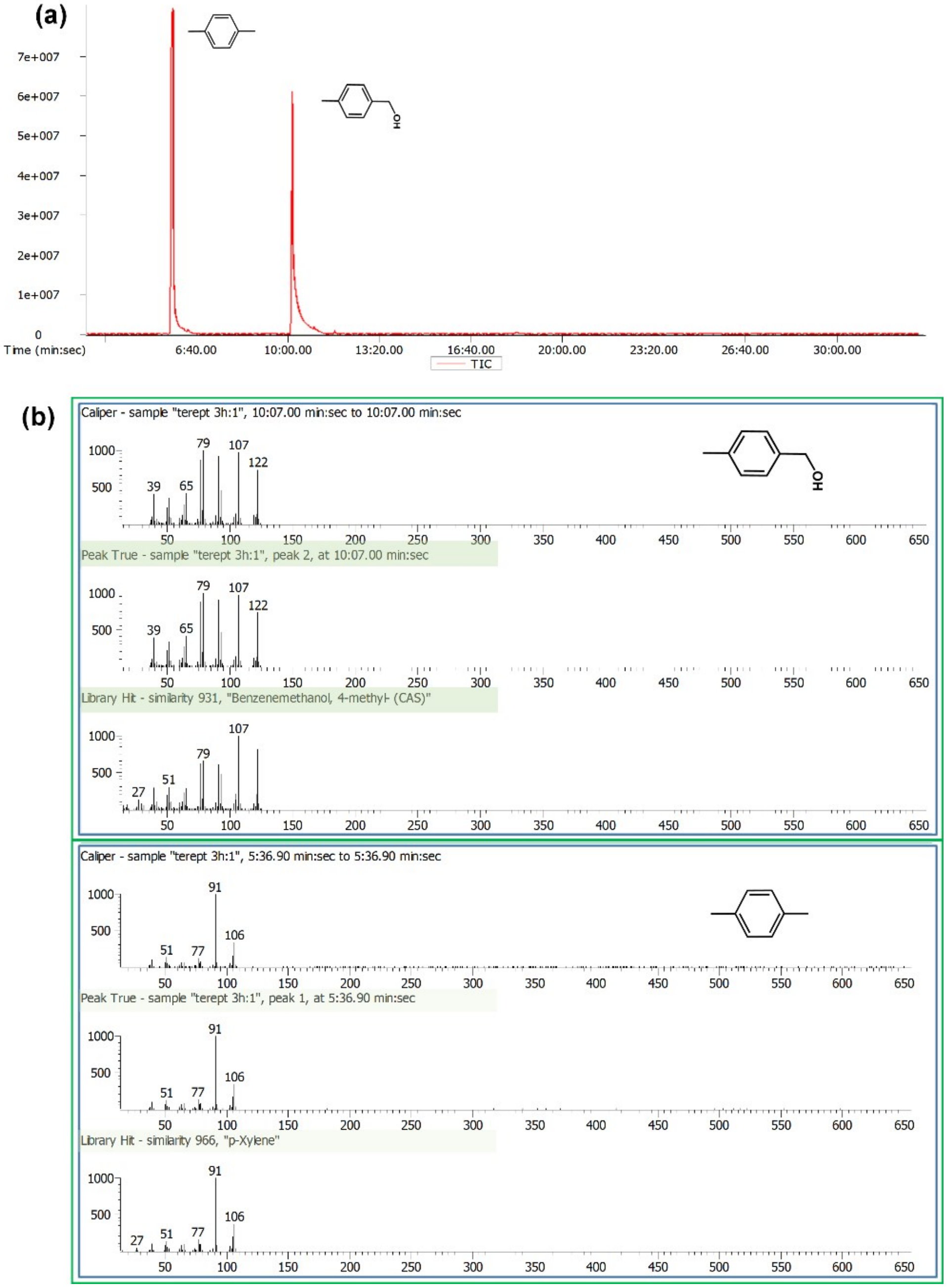


Fig. S18 (a) GC-TOF/MS chromatogram and (b) representative mass-spectrometer spectra of the observed compounds produced in the terephthaldehyde reaction over the ZCI1-700 catalyst. Reaction conditions: 250 mg terephthaldehyde, 50 mg catalyst, 30 mL H_2O, 130 °C, 0.7 MPa initial H_2 pressure, reaction time of 240 min.

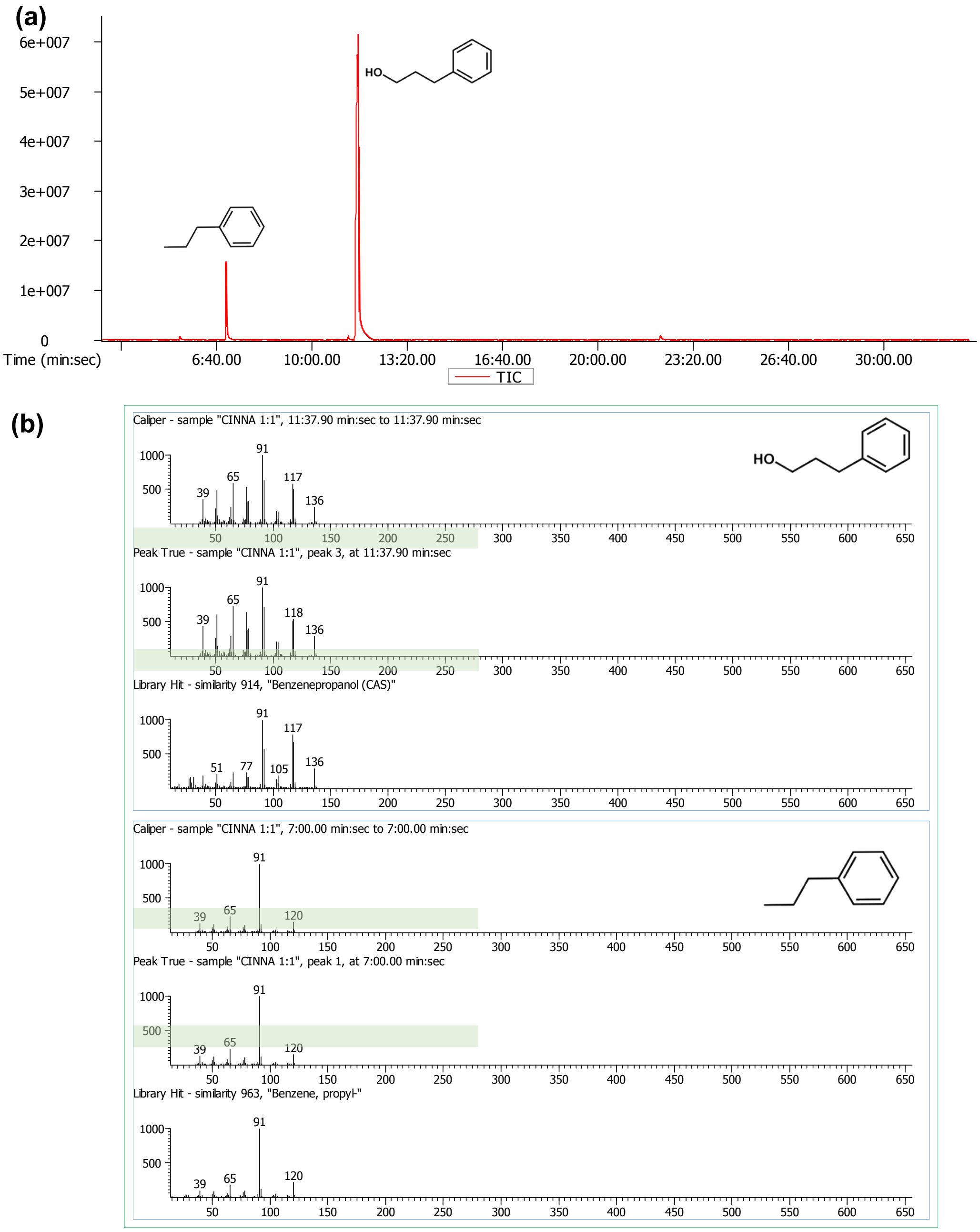


Fig. S19 (a) GC-TOF/MS chromatogram and (b) representative mass-spectrometer spectra of the observed compounds produced in the cinnamaldehyde reaction over the ZCI1-700 catalyst. Reaction conditions: 250 mg cinnamaldehyde, 50 mg catalyst, 30 mL H_2O, 130 °C, 0.7 MPa initial H_2 pressure, reaction time of 2 h.

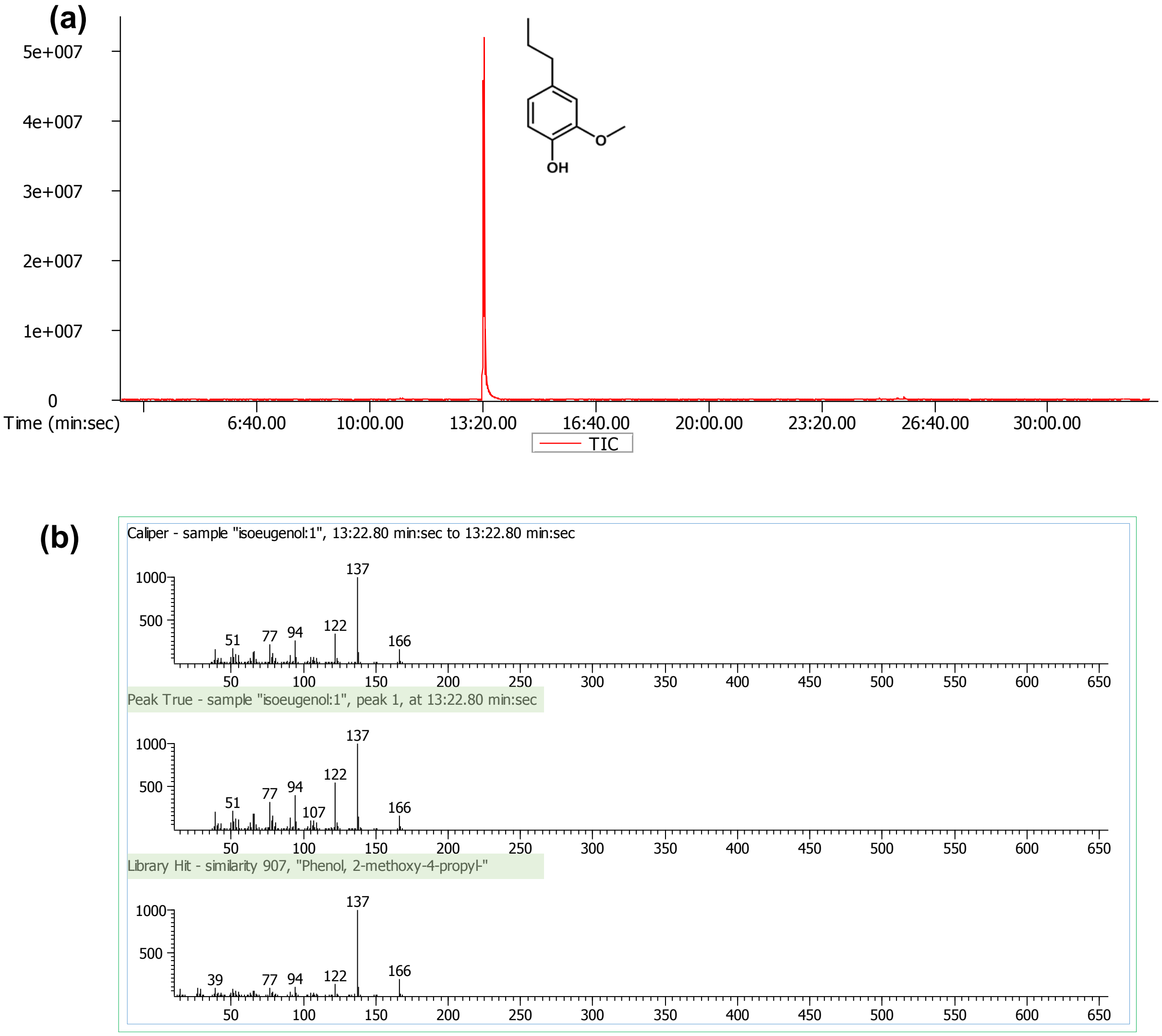


Fig. S20 (a) GC-TOF/MS chromatogram and (b) representative mass-spectrometer spectra of the observed compounds produced in the isoeugenol reaction over the ZCI1-700 catalyst. Reaction conditions: 250 mg isoeugenol, 50 mg catalyst, 30 mL H_2O, 130 °C, 0.7 MPa initial H_2 pressure, reaction time of 2 h.

Lignin bio-oil (LBO) production from concentrated strong acid hydrolysis lignin (CSAHL)

The LBO from concentrated strong acid hydrolysis lignin (CSAHL) was produced according to the procedure mentioned in our previous study[20] with slight variation, and the schematic representation is shown in Fig. S21. Briefly, the desired amounts of CSAHL, formic acid (CSAHL-to-formic acid weight ratio of 1.0:1.2), and ethanol (CSAHL-to-ethanol weight ratio was fixed at 1.0:5.8) were loaded in a stainless batch reactor (SUS316) equipped with a magnetic stirrer (JM-3200, Hanwoul Engineering Inc., South Korea). The reactor was purged with nitrogen and pressurized to 1.0 MPa at room temperature. The reaction was then allowed to occur at 350 °C for 1 h. During the reaction, the reactor pressure increased from 29.7 to 45.0 MPa. After the reaction, the reactor was quenched with cold water, and it was then further cooled to room temperature using an electric fan. The gases produced during the liquefaction were released, and the solid material stuck on the stirrer was recovered by washing with acetone. The final reaction mixture was filtered using a Hyundai Micro filter paper to separate the liquid product from the solid material. The filtrate (bio-oil + unreacted ethanol + acetone) was kept for rotary-evaporation at 60 °C under reduced vacuum (0.08 MPa) for 0.5 h to collect the LBO. After rotary evaporation, the recovered LBO was further dried in an oven at 70 °C for 24 h to remove the remaining solvents.

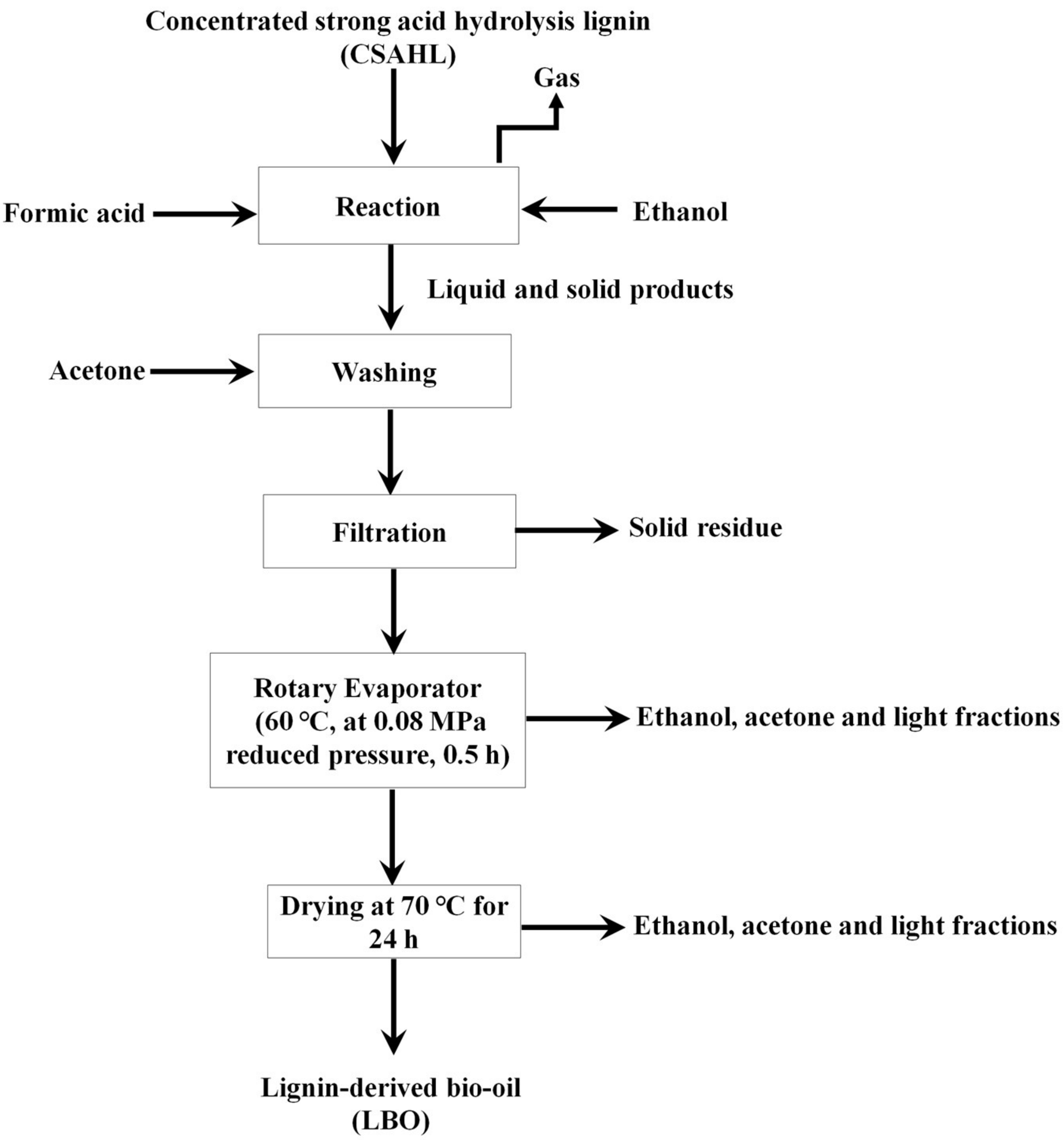


Fig. S21 Scheme of the procedure for producing lignin-derived bio-oil (LBO).

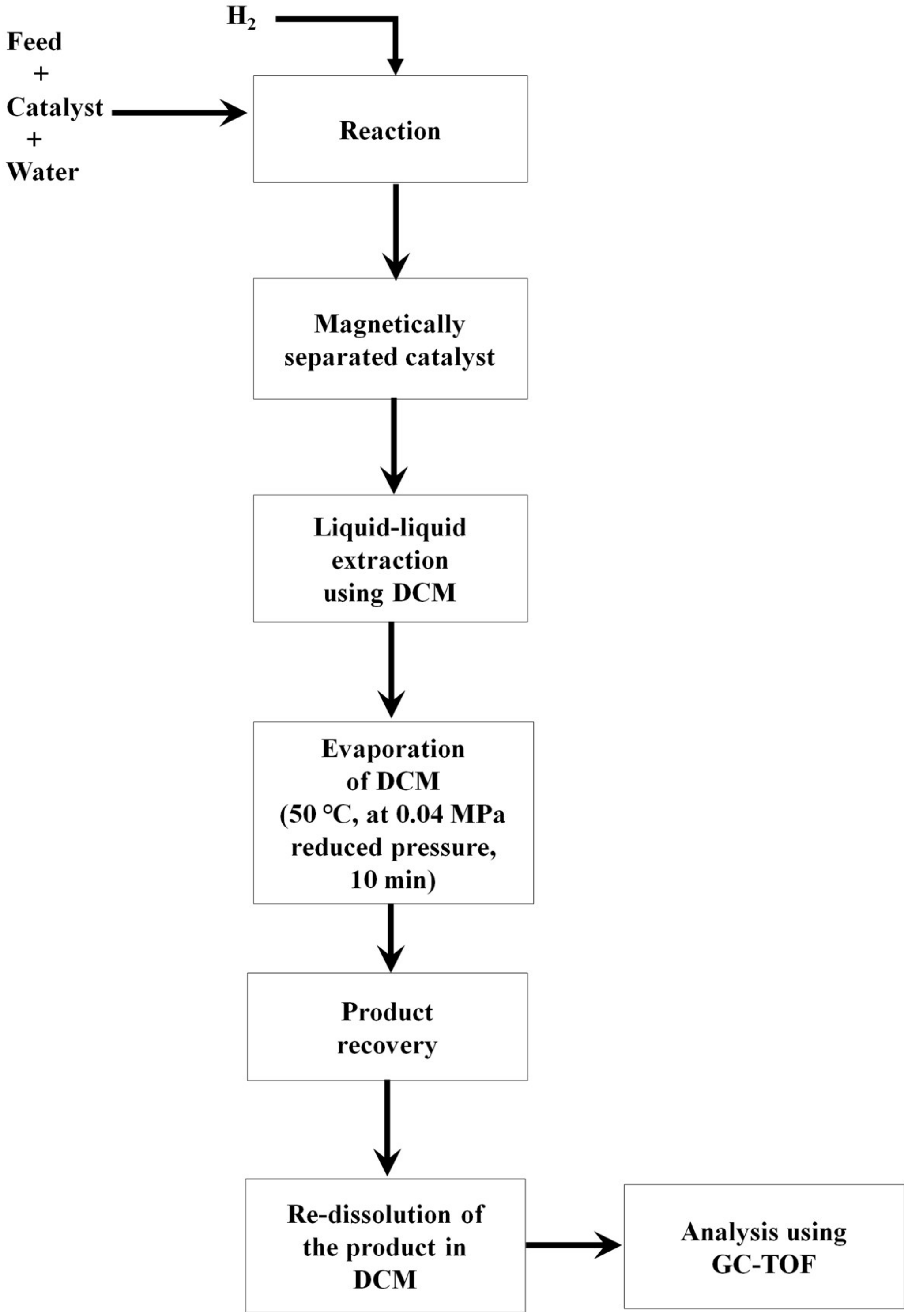


Fig. S22 Product separation procedure after the kraft lignin and LBO conversion over ZCI1-700.

Table S2 Chemical compounds in the liquid products from the depolymerization and hydrodeoxygenation of kraft lignin over the ZCI1-700 catalyst at 350 °C, 5 MPa initial H_2, a catalyst-to-feed ratio of 0.33 for 6 h as measured using GC-TOF/MS.

Compounds	Retention time	%area
Alcohols		
2-Hexen-1-ol	05:50.0	0.61
Cyclopentanemethanol	06:16.1	0.15
Phenol	07:37.7	3.03
Phenol, 2-methyl-	09:09.8	3.00
Phenol, 4-methyl-	09:09.2	14.40
Phenol, 2,3-dimethyl-	10:18.7	0.58
Phenol, 4-ethyl-	10:33.1	4.40
Phenol, 4-propyl-	11:54.2	9.66
1H-Inden-5-ol, 2,3-dihydro-	13:06.5	6.26
1-Ethyl-2-methyl-1,2-dihydrocyclobutabenzen-1-ol	13:44.8	0.57
Anisole, o-(1-ethylvinyl)-	15:33.2	0.31
Ketones		
Cyclopentanone	04:09.4	0.89
Cyclopentanone, 3-methyl-	05:11.0	0.41
Cyclohexanone	05:55.9	23.71
Cyclohexanone, 2-methyl-	06:54.4	5.20
Cyclohexanone, 3-methyl-	07:01.0	3.34
Cyclohexanone, 2-ethyl-	08:29.2	1.04
Cyclohexanone, 3-ethyl-	08:57.6	0.65
Cyclohexanone, 4-ethyl-	09:03.7	0.67
Cyclohexanone, 2-propyl-	10:01.2	0.61
4,4-Dimethylcyclohexadienone	10:35.3	1.80
4-Propylcyclohexanone	10:36.7	0.42
Spiro[4.4]nonan-1-one	11:16.8	0.77
5H-Inden-5-one, octahydro-, cis-	11:33.1	0.74
2,5-Cyclohexadien-1-one, 3,4,4-trimethyl-	11:55.5	3.76
Alkane		
Heptane, 2,4-dimethyl-	04:34.3	0.74
Hexane, 3-ethyl-	05:19.5	0.26
Decane	07:45.1	0.59
Decane, 4-methyl-	08:06.6	0.30
DODECANE	08:38.9	0.75
Pentadecane	13:43.0	2.35
Tridecane	14:49.4	0.52
Others		
Benzoic acid, 2-hydroxy-, methyl ester	10:58.1	0.50
Benzene, 1,3-bis(1,1-dimethylethyl)-	11:39.8	0.84
Naphthalene, 1,2,3,4-tetrahydro-5-methyl-	12:00.2	0.73
2-Naphthalenol, 5,6,7,8-tetrahydro-	14:49.2	0.80
Anthracene, 1,2,3,4,5,6,7,8-octahydro-	17:43.9	1.01
Total area%		**96.37**

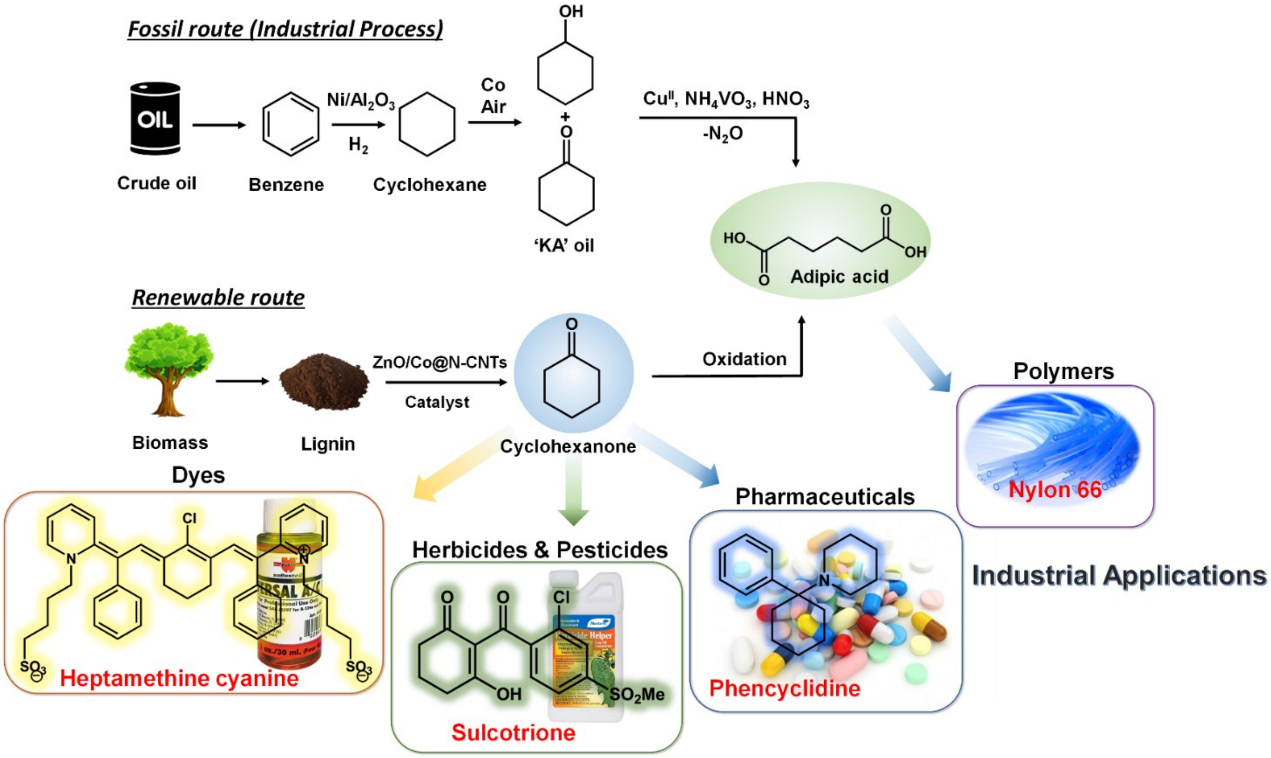


Fig. S23 Schematic representation of the fossil fuel route for the commercial production of cyclohexanone *vs.* the plausible renewable lignin route for the production of cyclohexanone and a wide range potential industrial applications of cyclohexanone.

Table S3 Chemical compounds of LBO as measured using GC-TOF/MS.

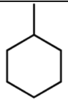
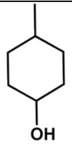
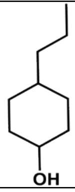
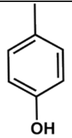
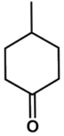
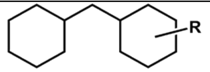
Compounds	Retention time	%area
Ether/ alcohol		
Phenol, 2-methoxy-	09:23.5	4.01
Phenol, 2-ethoxy-	10:22.6	0.29
2-Methoxy-6-methylphenol	10:44.6	0.26
Creosol	10:54.3	12.82
3,4-Dimethoxytoluene	11:35.8	0.34
2-Ethoxy-4-methylphenol	11:48.5	0.24
Phenol, 4-ethyl-2-methoxy-	12:07.3	17.35
2-Methoxy-4-ethyl-6-methylphenol	12:49.3	0.57
Phenol, 2,6-dimethoxy-	13:13.6	1.75
p-Cymene-2,5-diol	13:13.8	2.57
Phenol, 2-methoxy-4-propyl-	13:20.1	13.3
Benzaldehyde, 2-hydroxy-5-methoxy-	14:03.0	1.18
Phenol, (1,1-dimethylethyl)-4-methoxy-	14:08.1	0.47
3,5-Dimethoxy-4-hydroxytoluene	14:24.0	1.81
Phenol, 2-methoxy-4-(1-propenyl)-	14:29.7	1.89
Phenol, 2-methoxy-4-(1-propenyl)-	14:44.5	0.47
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	15:03.9	0.92
Benzene, 1,2,3-trimethoxy-5-methyl-	15:20.5	1.75
Homovanillyl alcohol	15:35.2	3.75
Benzeneacetic acid, 4-hydroxy-3-methoxy-	15:41.6	1.68
Benzoic acid, 4-hydroxy-3-methoxy-, ethyl ester	16:09.5	0.79
Ethyl homovanillate	16:44.8	1.70
Benzenepropanol, 4-hydroxy-3-methoxy-	16:55.9	5.00
2-Propanone, 1-hydroxy-3-(4-hydroxy-3-methoxyphenyl)-	23:31.8	3.37
Phenol, 2-methoxy-4-propyl-	23:41.3	0.56
(E)-9-Octadecenoic acid ethyl ester	21:58.6	3.89
9-Octadecenoic acid, ethyl ester	22:02.1	2.60
Total area%		**85.33**

Table S4 Chemical compounds in the liquid products from hydrodeoxygenation of LBO over the ZCI1-700 catalyst at 350 °C, 5 MPa initial H_2, a catalyst-to-feed ratio of 0.33 for 6 h as measured using GC-TOF/MS

Compounds	Retention time	%area
Phenol and Alcohol		
Phenol	07:40.7	3.20
Phenol, 2-methyl-	08:50.7	0.80
Phenol, 3-methyl-	09:10.5	11.34
Phenol, 2-ethyl-	10:06.7	1.60
Phenol, 2,3-dimethyl-	10:18.8	0.52
Phenol, 4-ethyl-	10:33.9	1.83
Phenol, 3-ethyl-	10:35.9	8.35
Phenol, 3,4-dimethyl-	11:01.4	1.15
Phenol, 2-ethyl-5-methyl-	11:36.3	1.32
Phenol, 4-propyl-	11:54.2	7.63
Phenol, 2-ethyl-6-methyl-	11:55.0	2.27
Phenol, 2-ethyl-4-methyl-	12:12.7	1.20
2,5-Diethylphenol	12:36.4	0.64
2,5-Diethylphenol	12:46.5	0.61
1H-Inden-5-ol, 2,3-dihydro-	12:47.1	2.66
Phenol, 2-ethyl-4,5-dimethyl-	13:05.4	1.04
1H-Inden-5-ol, 2,3-dihydro-	13:06.2	3.46
Phenol, 2-(2-methylpropyl)-	13:18.9	1.20
2-(But-2'-enyl) phenol	13:40.1	2.15
Tetradecane	13:42.6	0.95
4-Ethylcatechol	13:45.0	3.69
1-Naphthalenol, 5,6,7,8-tetrahydro-	14:47.0	0.88
2-Naphthalenol, 5,6,7,8-tetrahydro-	14:47.0	0.95
2-Naphthalenol	15:33.8	1.52
1-Naphthalenol, 3-methyl-	16:58.3	1.51
Ketone		
2-Pentanone	02:43.1	0.87
Cyclopentanone	04:09.2	2.21
Cyclopentanone, 2-methyl-	05:00.1	2.15
Cyclopentanone, 3-methyl-	05:10.1	1.77
Cyclohexanone	05:56.6	7.53
Cyclopentanone, 2,3-dimethyl-	05:59.0	0.90
Cyclopentanone, 2-ethyl-	06:46.6	0.80
Cyclohexanone, 2-methyl-	06:55.3	2.07
Cyclohexanone, 3-methyl-, (R)-	07:02.1	0.64
3-Ethylcyclopentanone	07:10.6	0.83
Cyclohexanone, 2-ethyl-	08:29.3	1.55
Cyclohexanone, 4-ethyl-	09:03.7	0.80
4-Propylcyclohexanone	10:36.8	0.51
1,2,3,5,6,7-Hexahydro-inden-4-one	11:54.7	2.42
Others		
Heptane, 2,4-dimethyl- (CAS)	04:34.1	0.69
Benzene, 1,3-bis(1,1-dimethylethyl)-	11:39.5	0.72

Benzene, 1,2,4-trimethyl-5-(1-methylethyl)- (CAS)	14:40.6	0.73
1,2-Dihydroxy-4-(1-propyl)benzene	14:53.6	2.03
Anisole, o-(1-ethylvinyl)-	15:31.3	1.21
4b,8-Dimethyl-2-isopropylphenanthrene, 4b,5,6,7,8,8a,9,10-octahydro-	19:27.7	2.80
Total area%		**87.35**

Table S5 Summary of the reported HDO reactions of vanillin over different types of heterogeneous catalysts.

Catalyst	Solvent	H_2 (MPa)	T (°C)	T (h)	Conv. (%)	0Os	1Os (-OH)			1Os (>O)	Oligomers	Others	Ref.
													
Ru/MWCNT[a,c]	H_2O	4.0	270	1	100	10.0	32.7	27.9	-	-	12.7	16.7	Dwiatmoko et al.[21]
Ru@Al[b]	H_2O	4.0	270	2	100	12.8	-	-	-	-	26.1	48.5	Yati et al.[22]
ZnO/Co@N-CNT[c]	H_2O	5.0	350	6	100	-	-	-	52.0	47.9	-	-	This work

[a] MWCNT = multiwalled carbon nanotube.

[b] Products in yield (mol%).

[c] Products in selectivity (%).

Table S6 Chemical compounds of the liquid products produced from vanillin detected using GC-TOF/MS over the ZCI1-700 catalyst.[a]

Compounds	Retention time	%area
Reaction at 250 °C		
1,2-Benzenediol, 4-methyl-	12:25.6	98.40
Reaction at 300 °C		
p-Cresol	09:08.0	72.02
Cyclohexanone, 4-methyl-	06:57.2	20.16
Reaction at 350 °C		
p-Cresol	09:10.8	51.91
Cyclohexanone, 4-methyl-	06:57.2	48.07

[a] 250 mg feed, 50 mg ZCI1-700, 5 MPa initial H_2, reaction time of 6 h

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