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Nickel-catalyzed intelligent reductive transformation of aldehyde group with hydrogen

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Table S1 Crystallographic data and structure refinement summary for 2D Ni-based MOF

Identification code	$[Ni(tia)(H_2O)_2]_{\infty}$
Empirical formula	$C_{40}H_{36}N_{12}Ni_4O2_4$
Formula weight	1303.57
Temperature/K	289.15
Crystal system	monoclinic
Space group	P21/c
a/Å, b/Å, c/Å	10.4214(18), 16.803(3), 7.336(2)
α/°, β/°, γ/°	90, 96.12(2), 90
Volume/Å^3	1277.3(5)
Z	1
ρ calcg/cm^3	1.6945
μ/mm^{-1}	1.548
F(000)	665.8
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.62 to 65.92
Reflections collected	6313
Independent reflections	4032 [R_{int} = 0.0804, R_{sigma} = 0.1710]
Data/restraints/parameters	4032/0/183
Goodness-of-fit on F^2	0.986
Final R indexes [I>=2σ (I)]	*R1* = 0.1245, *wR2* = 0.2924
Final R indexes [all data]	*R1* = 0.2218, *wR2* = 0.3781
Largest diff. peak/hole / e Å^{-3}	5.14/-2.45

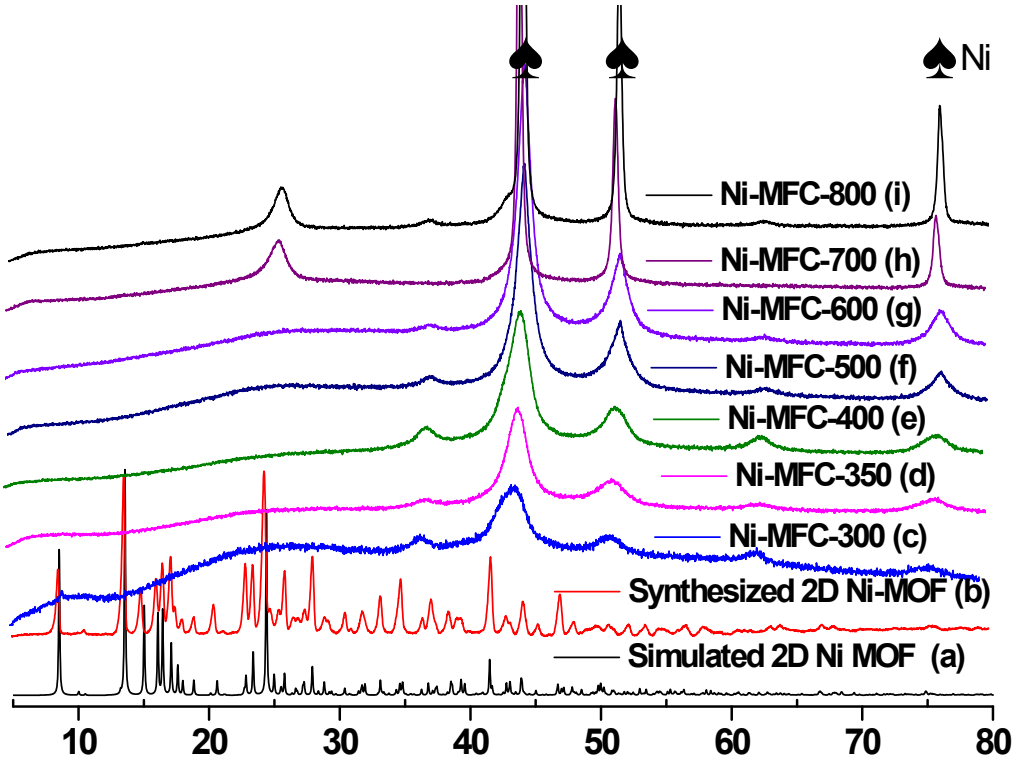


Fig. S1 The PXRD patterns of the as-synthesized MOFs and the derived Ni-MFC catalysts

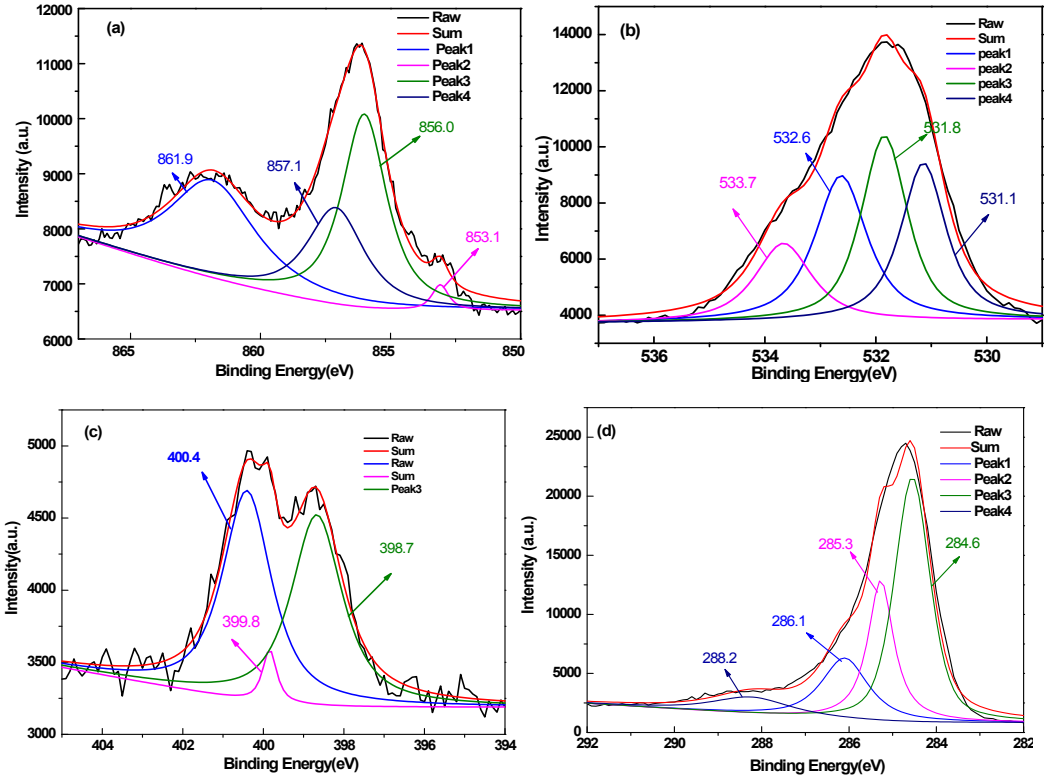


Fig. S2. XPS analysis for the fresh Ni-MFC-500: (a) Ni2p3/2; (b) O1s; (c) N1s; (d) C1s

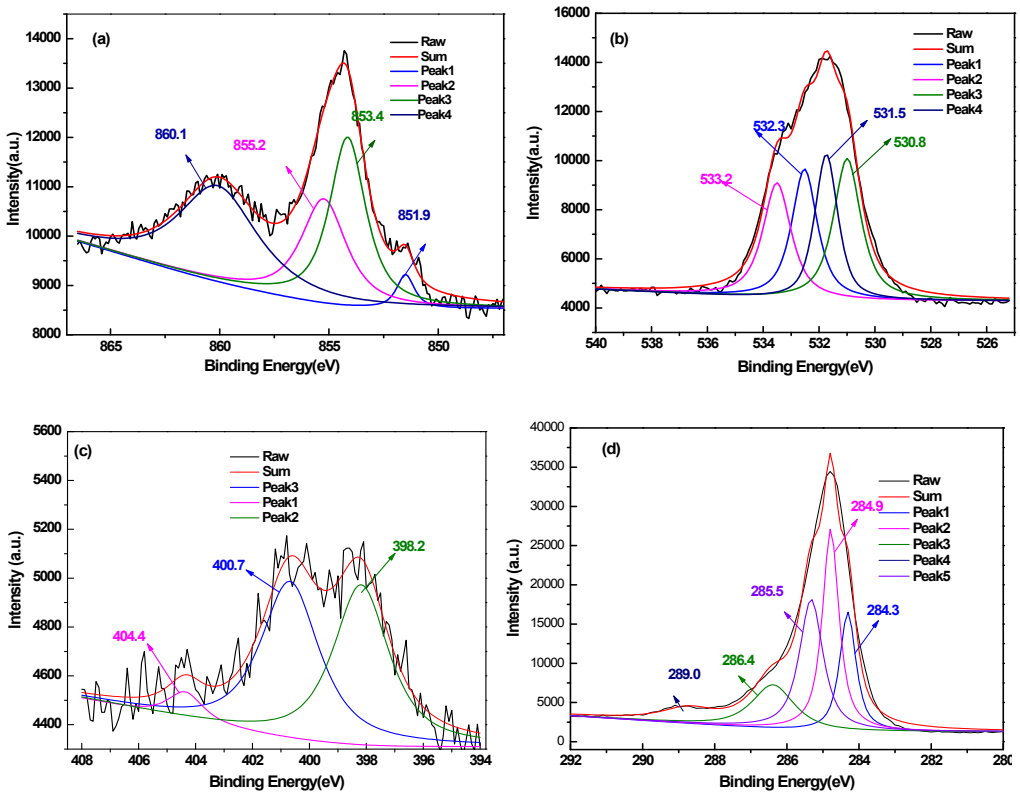


Fig. S3. XPS analysis for the used Ni-MFC-700: (a) Ni2p3/2; (b) O1s; (c) N1s; (d) C1s

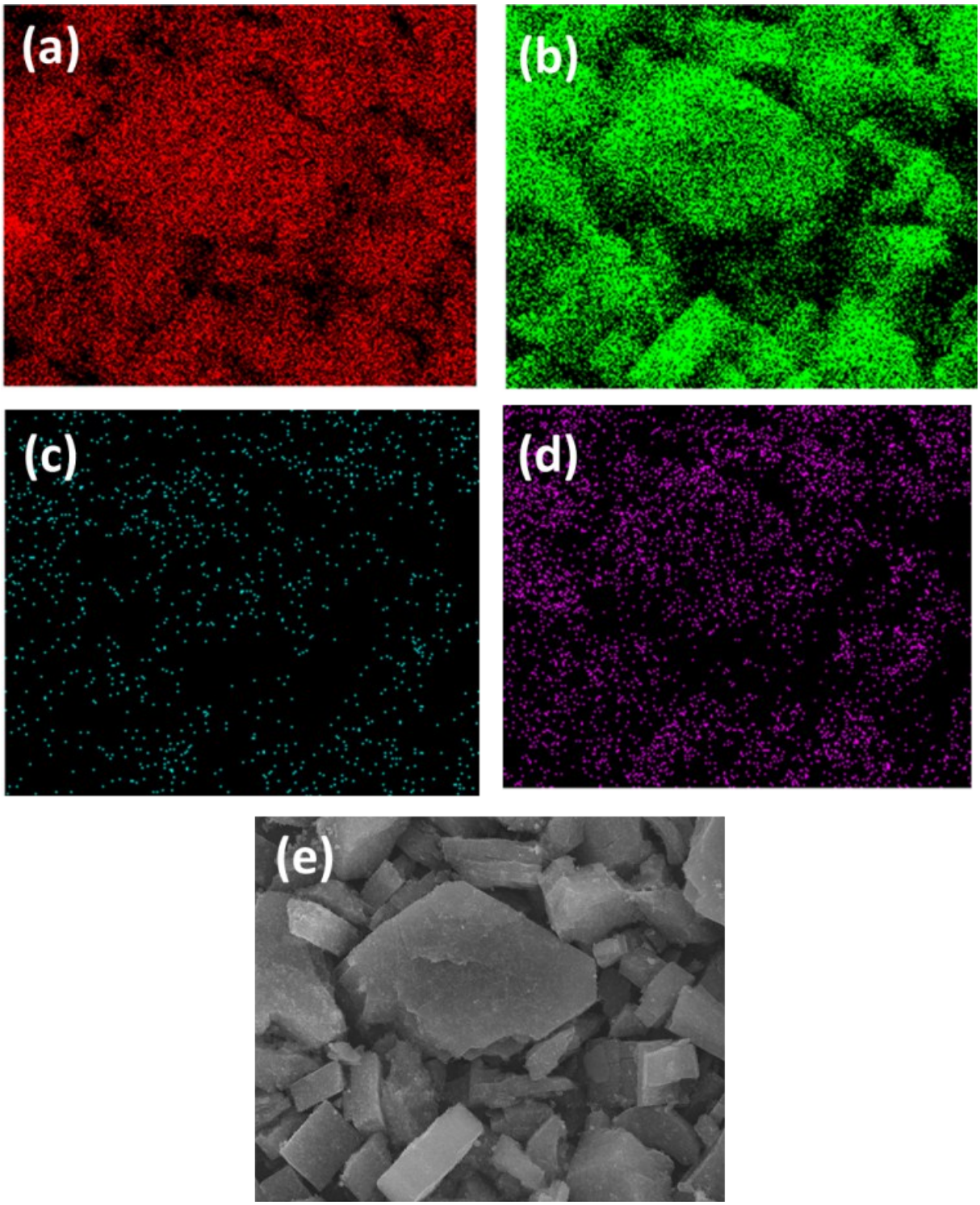


Fig. S4 Element mapping from HRSEM images of fresh Ni-MFC-700: (a) Ni; (b) C; (c) N; (d) O; (e) SEM image

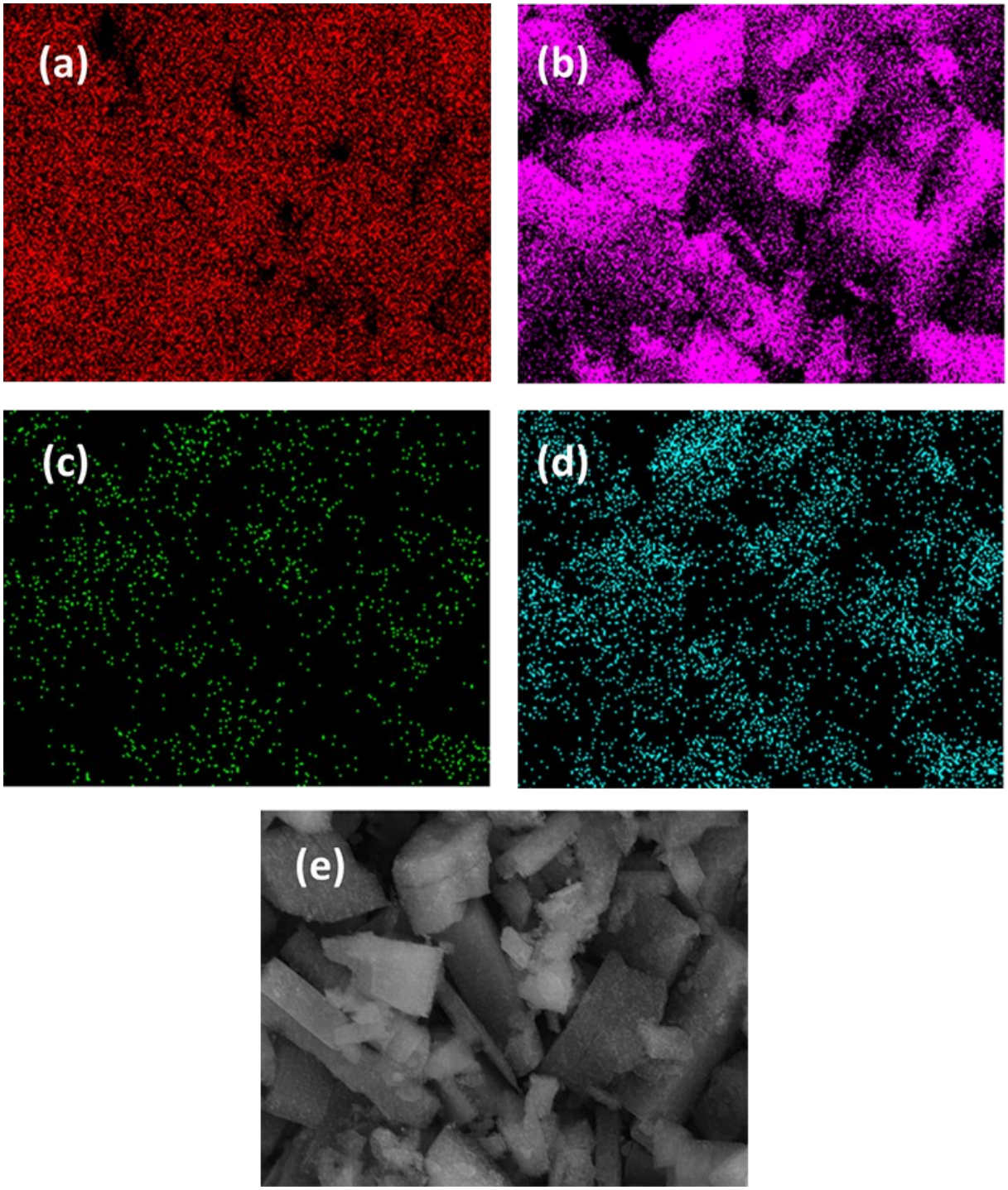


Fig. S5 Element mapping from HRSEM images of used Ni-MFC-700: (a) Ni; (b) C; (c) N; (d) O; (e) SEM Image

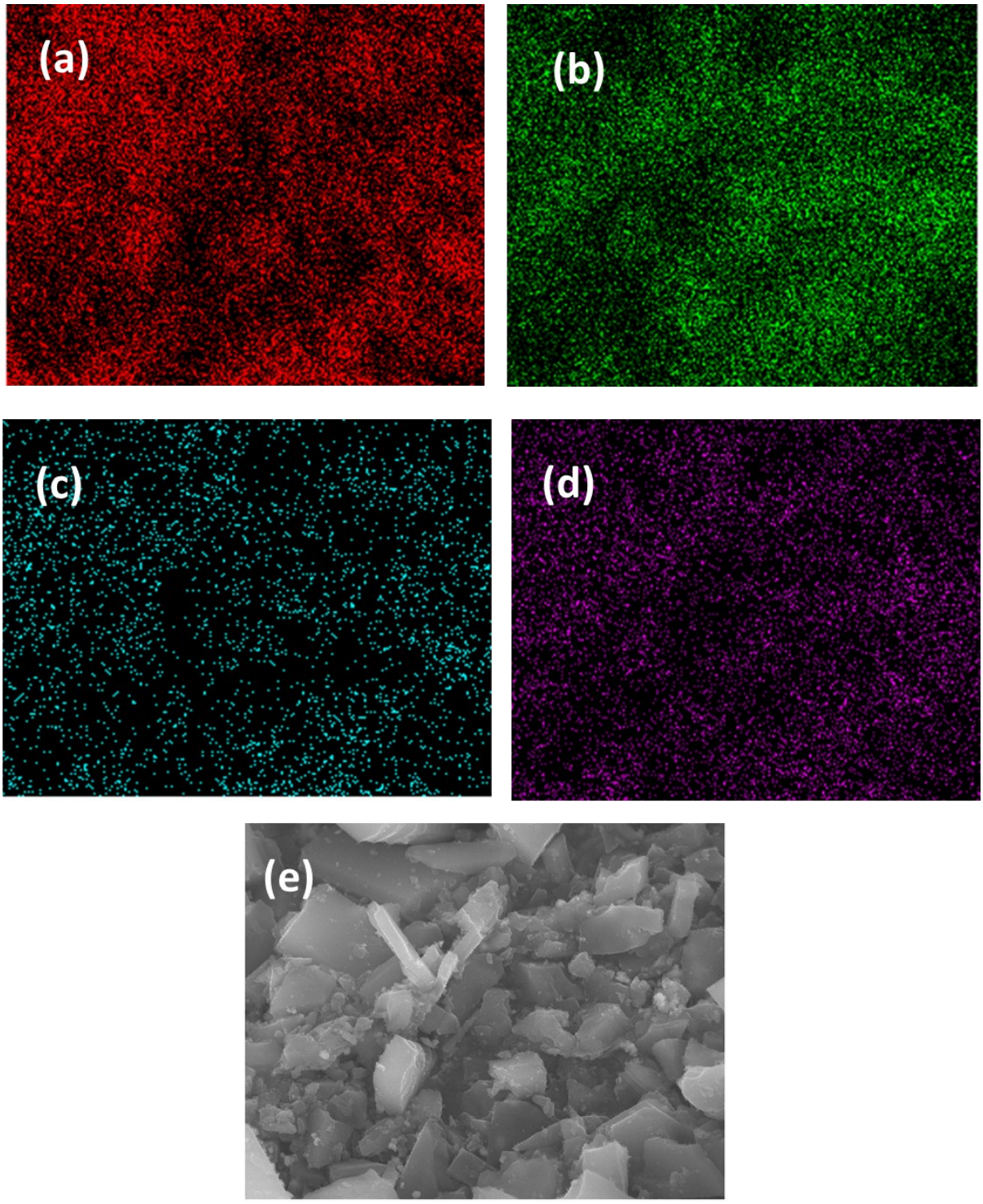


Fig. S6 Element mapping from HRSEM images of fresh Ni-MFC-500: (a) Ni; (b) C; (c) N; (d) O; (e) SEM image

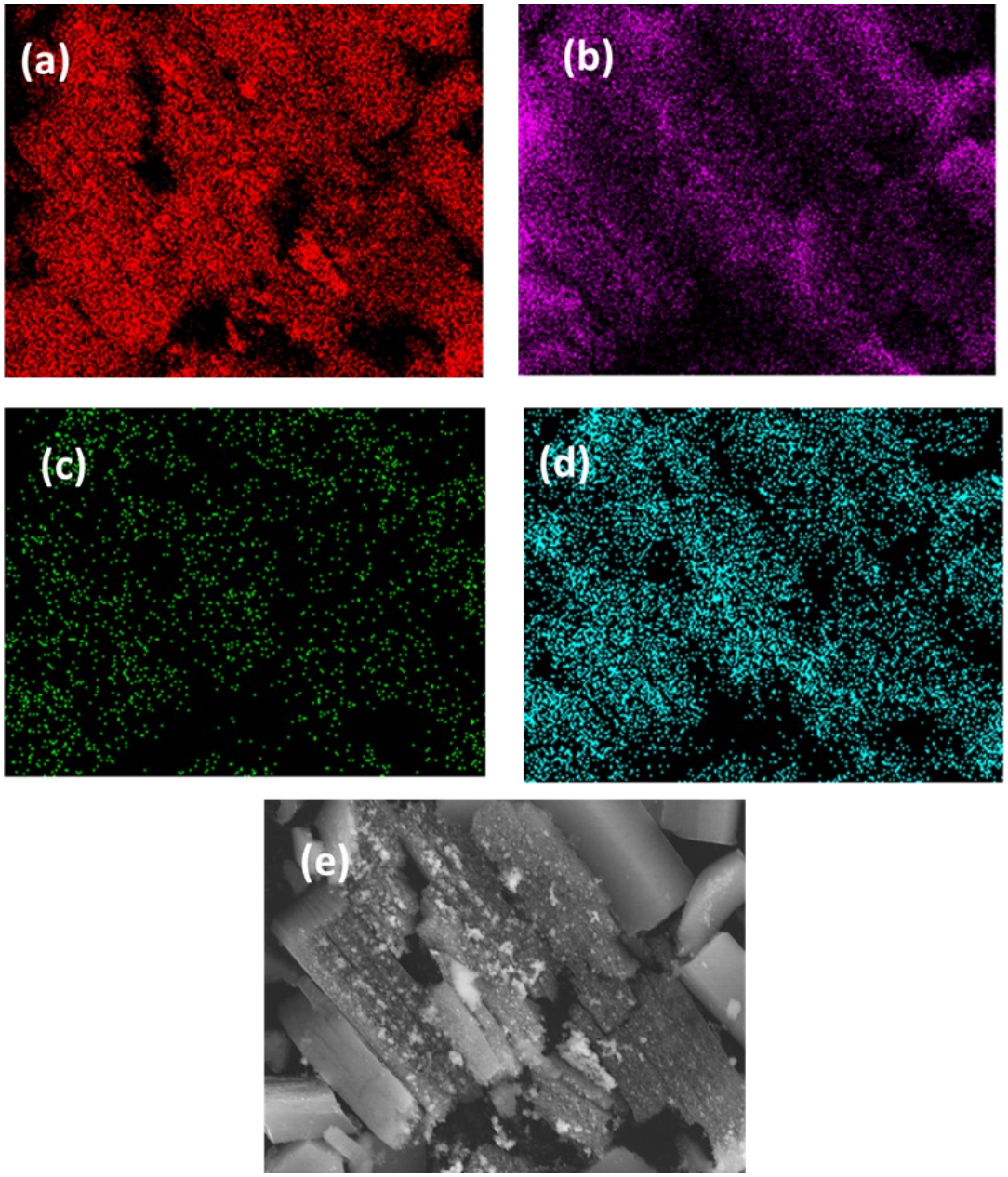


Fig. S7 Element mapping from HRSEM images of used Ni-MFC-500: (a) Ni; (b) C; (c) N; (d) O; (e) SEM image

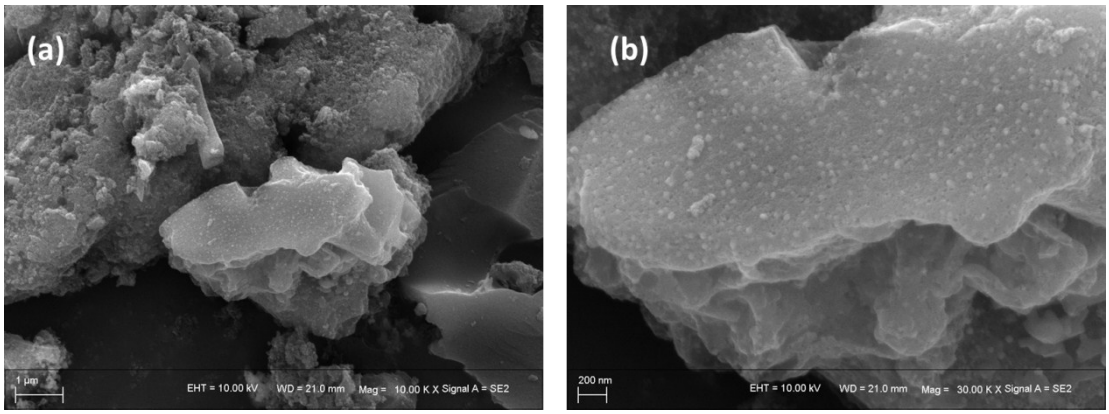


Fig. S8 FESEM images of the as-obtained Ni/activated carbon catalyst at different magnification

Table S2 Textural parameters for the derived Ni-MFC catalysts

Catalysts	BET ($m^2 g^{-1}$)	Pore size(Å)	Pore volume($cm^3 \cdot g^{-1}$)
Ni-MFC-500	119.4	46.1	0.14
Ni-MFC-700	103.6	56.5	0.15
Ni-MFC-800	103.10	50.5	0.13
Ni-MFC-500 [a]	184.1	27.6	0.13
Ni-MFC-700 [a]	117.5	52.4	0.15

[a] The catalysts were recycled for 5 times.

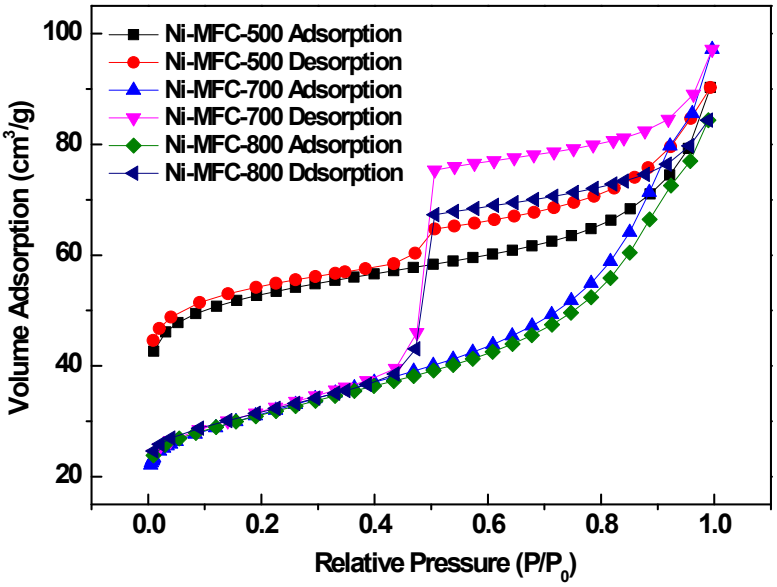


Fig. S9 Nitrogen adsorption-desorption isotherm of the fresh Ni-MFC catalysts.

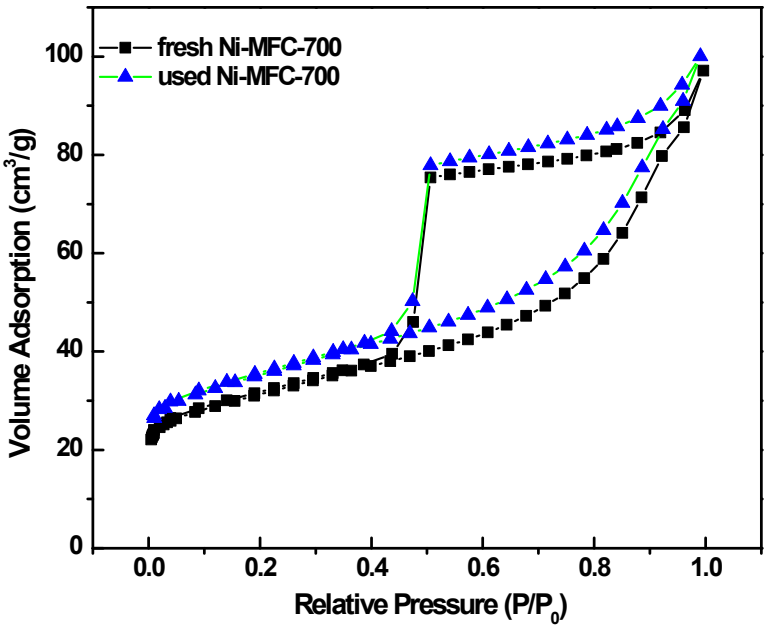


Fig. S10 Nitrogen adsorption-desorption isotherm of the fresh and used catalysts.

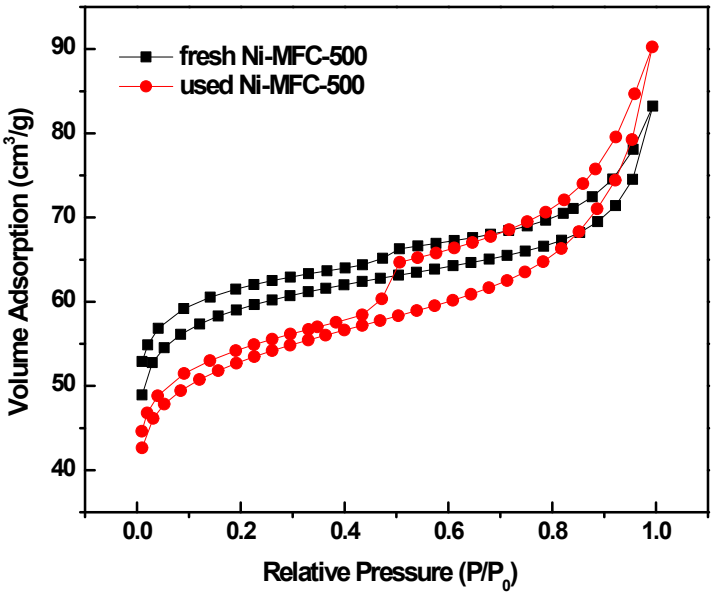


Fig. S11 Nitrogen adsorption-desorption isotherm of the fresh and used catalysts.

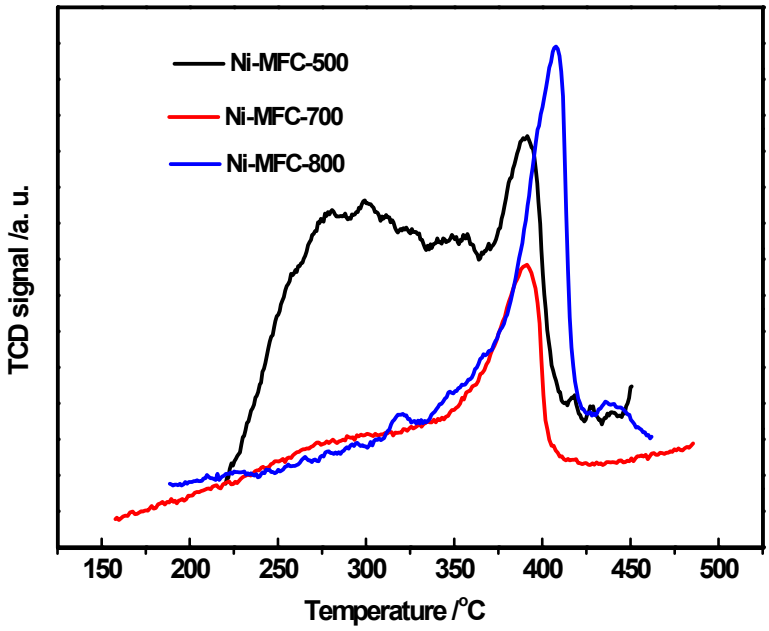


Fig. S12 NH_3-TPD profiles of the fresh Ni-MFC catalysts.

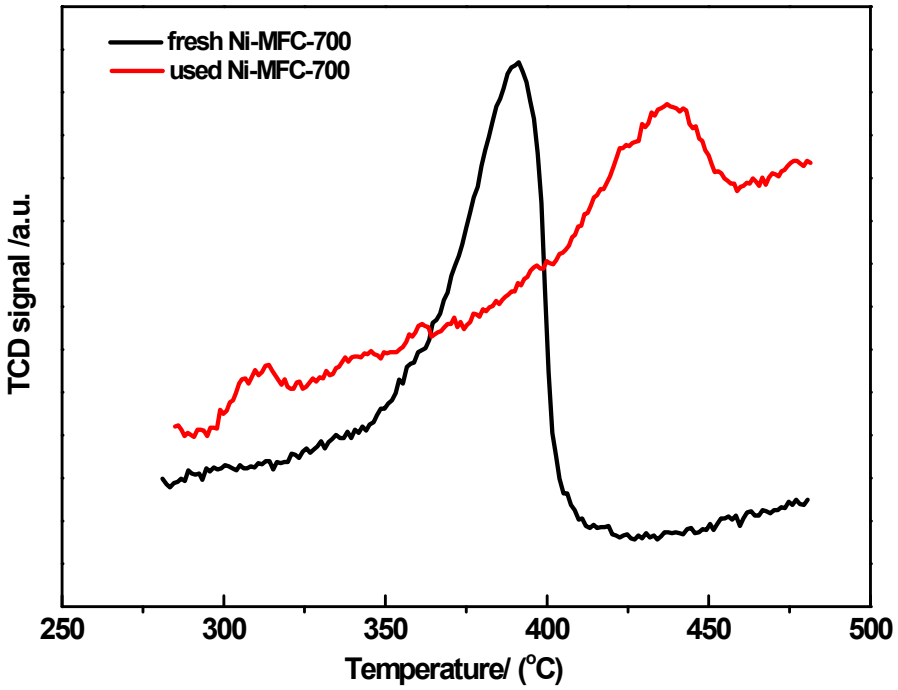


Fig. S13 NH_3-TPD profiles of the fresh and used Ni-MFC-700 catalysts.

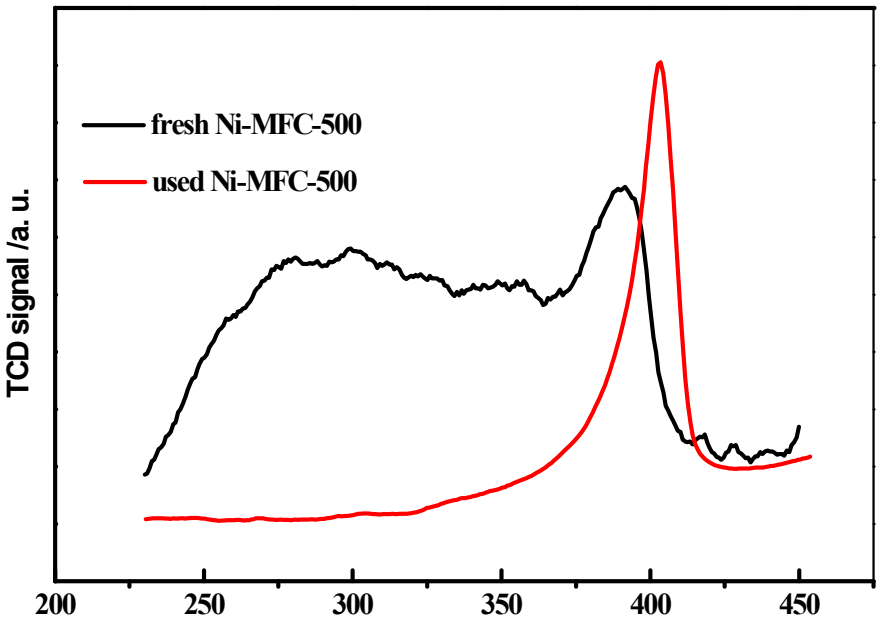


Fig. S14 NH_3-TPD profiles of the fresh and used Ni-MFC-500 catalysts.

Table S3 The Ni content of the as-obtained catalysts

Entry	Catalyst	Calculation (mol/g)	Found (mol/g) [a]
1	Ni-MFC	0.0031 [b]	0.0029
2	Ni-MFC-300	0.0034 [c]	0.0032
3	Ni-MFC-350	0.0040 [c]	0.0039
4	Ni-MFC-400	0.0044 [c]	0.0045
5	Ni-MFC-500	0.0046 [c]	0.0043
6	Ni-MFC-600	0.0047 [c]	0.0048
7	Ni-MFC-700	0.0049 [c]	0.0044
8	Ni-MFC-800	0.0049 [c]	0.0049
9	Ni/Activated Carbone	0.0013 [d]	0.0014
10	Ni/γ-Al_2O_3-700	0.0013 [d]	0.0012
11	Ni/nano graphite-700	0.0013 [d]	0.0015
12	Ni/TiO_2-700	0.0013 [d]	0.0012
13	Ni/ZrO_2-700	0.0013 [d]	0.0013
14	Ni/nano MgO-700	0.0013 [d]	0.0012

[a] The Ni content was determined by inductively coupled plasma spectroscopy (ICP).

[b] The theoretical Ni content was calculated based on the formula of Ni-MFC ($C_{40}H_{36}N_{12}Ni_4O_{24}$: 1303.57).

[c] $$Ni\ content\left(^{mol}/_{g}\right) = \frac{\frac{m_{(Ni\text{–}MFC)}}{M_{(Ni\text{–}MFC)}}}{m_{(Ni\text{–}MFC-A)}}$$ (A = 300-700)

[d] $$Ni\ content\left(^{mol}/_{g}\right) = \frac{\frac{m_{Ni(NO_3).6H_2O}}{M_{Ni(NO_3).6H_2O}}}{\frac{m_{Ni(NO_3).6H_2O}}{M_{Ni(NO_3).6H_2O}} \times M_{Ni} + m_{Support}}$$

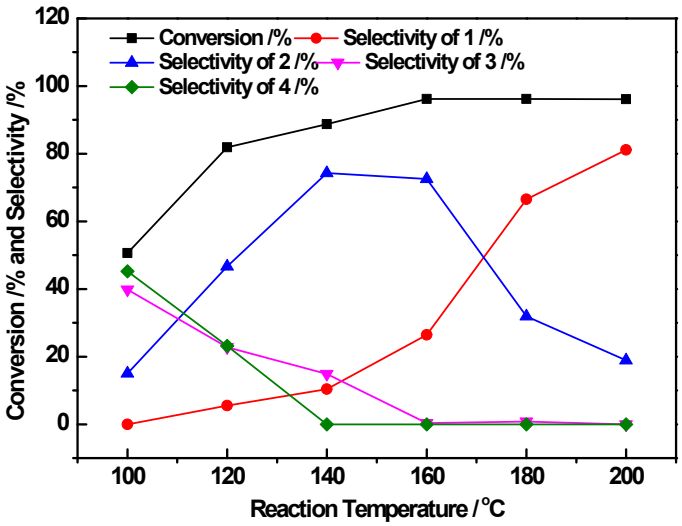


Fig. S15 Influence of reaction temperature on the products distribution (Reaction conditions: 0.1 g vanillin, 0.025 g catalyst, in 15 mL methanol, under 2 MPa of H_2, for 4 h).

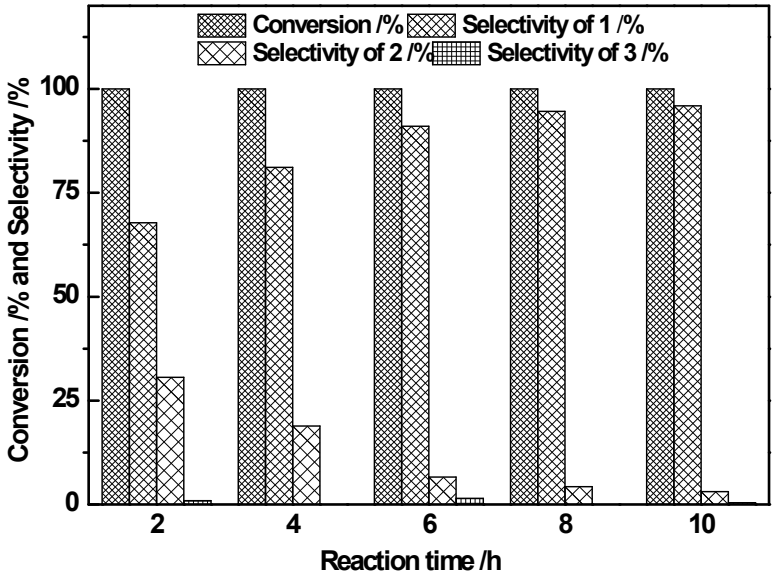


Fig. S16 Influence of reaction time on the products distribution (Reaction conditions: 0.1 g vanillin, 0.025 g catalyst, in 15 mL methanol, under 2 MPa of H_2, at 200 °C).

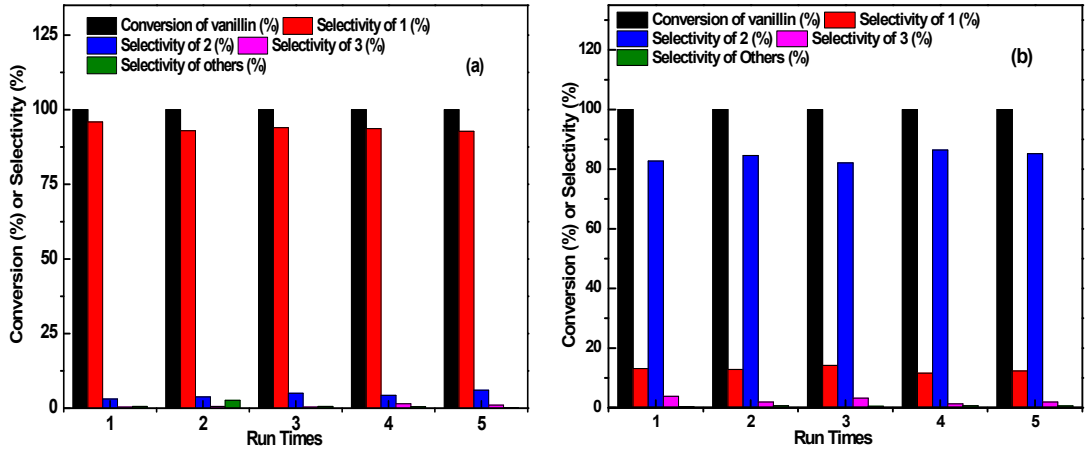


Fig. S17 The recyclability of Ni-MFC-700 and Ni-MFC-500 catalysts (Reaction conditions: 0.1 g vanillin,

0.025 g catalyst, in 15 mL methanol, under 2 MPa of H_2, at 200 ^oC for 10 h).

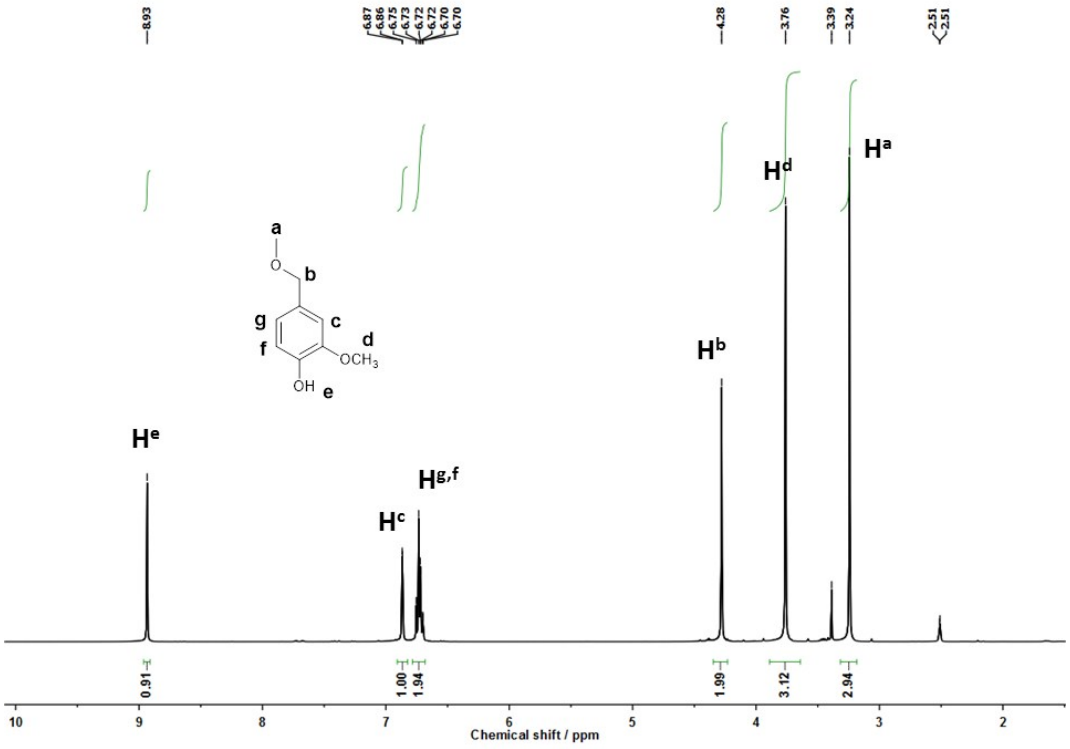
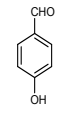
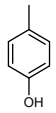
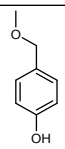
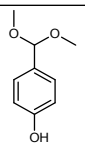
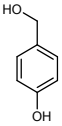
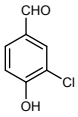
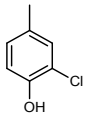
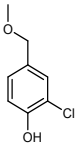
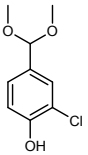
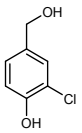
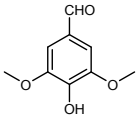
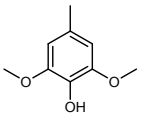
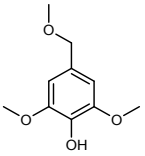
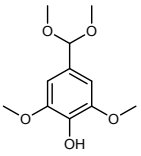
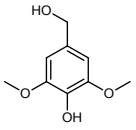
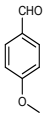
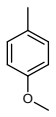
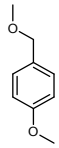
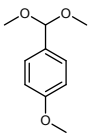
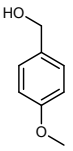
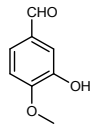
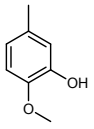
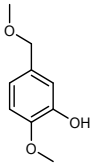
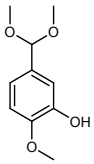
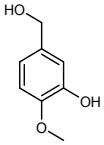
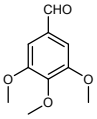
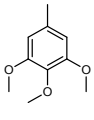
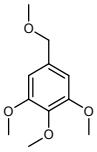
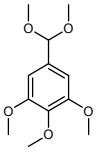
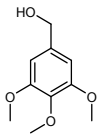
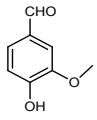
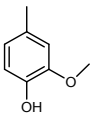
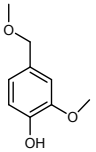
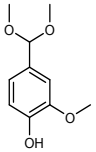
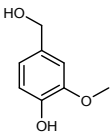


Fig. S18 ^{1}HNMR spectrum (400 MHz, 300 K) of compound **2** in DMSO-d_6

Table S4. Hydrogenolysis of other lignin models using Ni-MFC-700 as catalyst [a]

Substrates	Conv. (%)[b]	Product distribution (%) [b]				
 (**5**)	100	 6.1	 82.2	 0	 0	Others 11.7
 (**6**)	100	 10.3	 84.8	 0	 0	Others 4.9
 (**7**)	100	 51.5	 48.5	 0	 0	Others 0
 (**8**)	97.0	 0	 7.5	 24.9	 67.6	Others 0
 (**9**)	100	 4.0	 2.9	 0	 93.1	Others 0
 (**10**)	98.4	 1.1	 2.5	 0	 90.4	Others 6.0
						Others
Vanillin	100	26.4	72.5	0.4	0	0.7

[a] Reaction conditions: 0.1 g substrate, 0.025 g catalyst, in 15 mL methanol, at160 °C for 4 h.

[b] The results were obtained by GC analysis with the internal standard technique, 1,3-dichlorobenzene as internal standard.

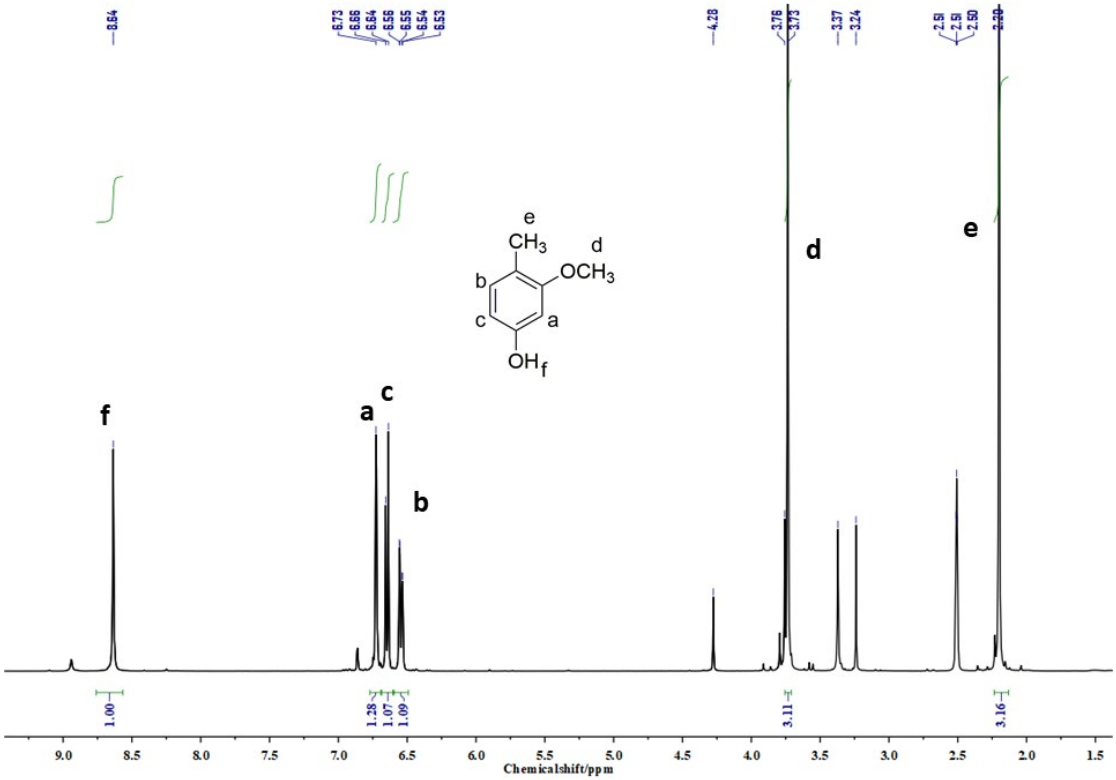


Fig. S19[1]HNMR spectrum (400 MHz, 300 K) of the products of vanillin hydrogenolysis in DMSO-d_6 (After reaction finished, the solvents were evaporated).

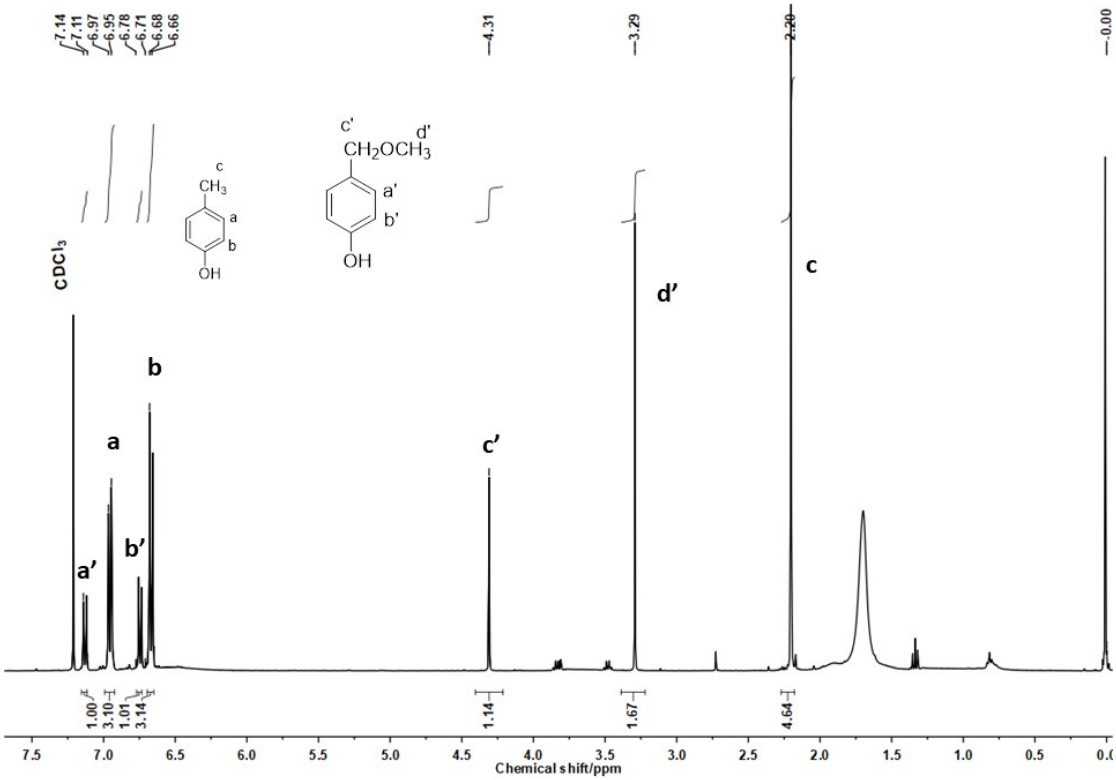


Fig. S20 [1]HNMR spectrum (400 MHz, 300 K) of the products of 4-hydroxybenzaldehyde (**5**) hydrogenolysis in $CDCl_3$ (After reaction finished, the solvents were evaporated).

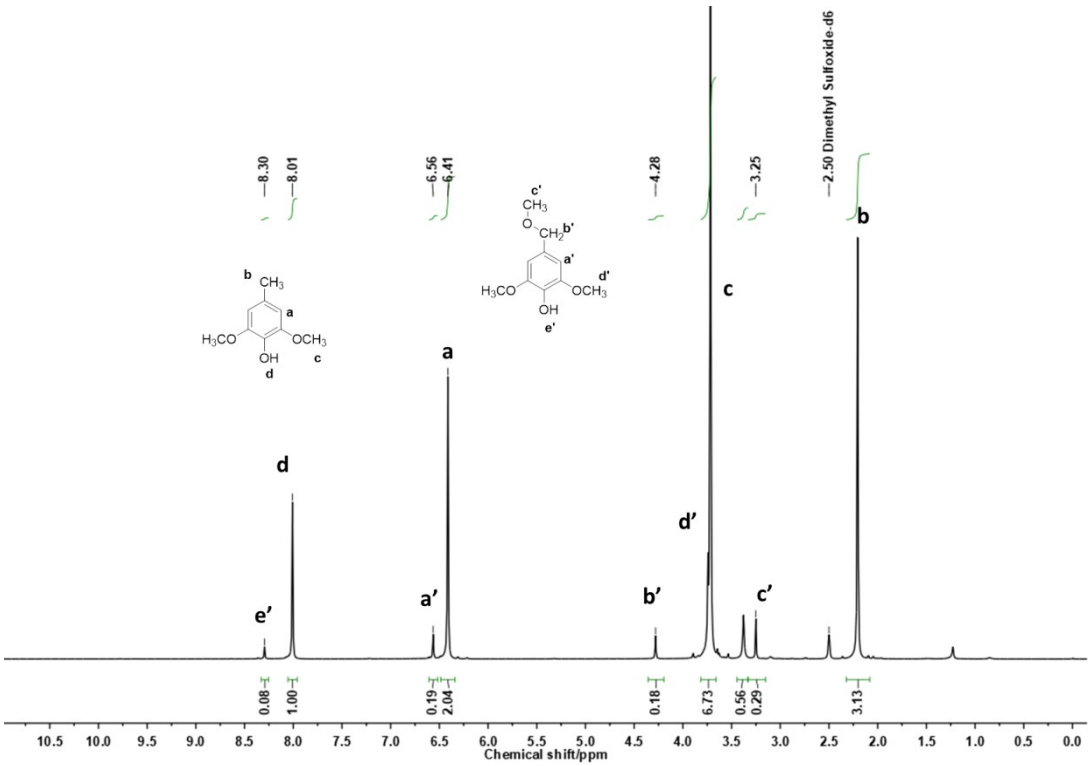


Fig. S21 ^{1}HNMR spectrum (400 MHz, 300 K) of the 3,5-dimethoxy-4-hydroxybenzaldehyde (**7**) hydrogenolysis in DMSO-d_6 (After reaction finished, the solvents were evaporated).

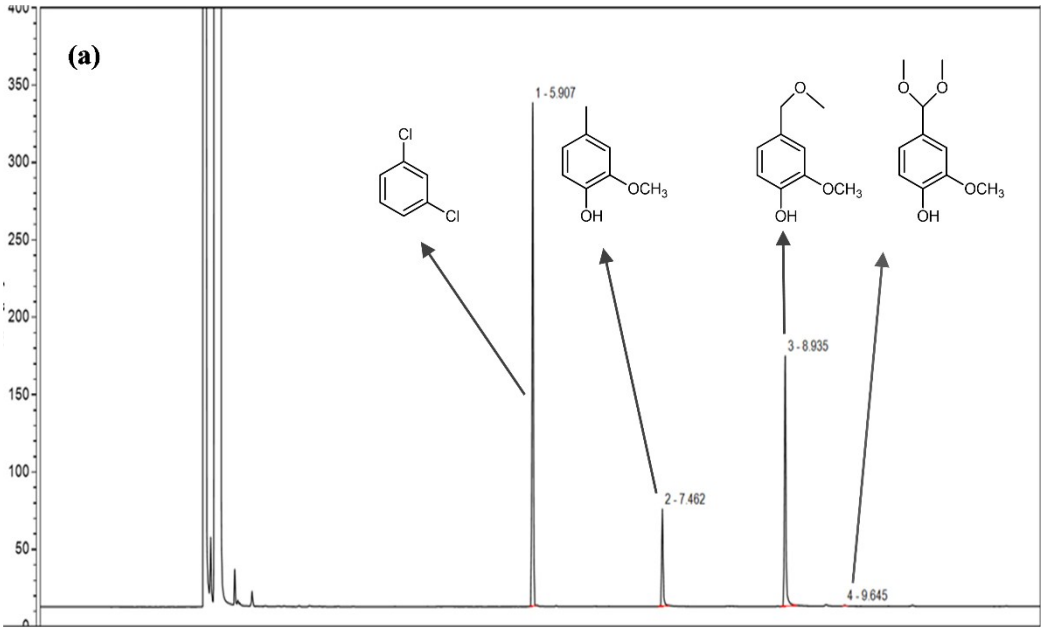


Fig. S22 GC analysis for products of vanillin hydrogenolysis in methanol with Ni-MFC-700 catalyst [a. Reaction condition: vanillin (0.1 g), methanol (15 mL), under 2 MPa of H_2, at 160 ^oC for 4 h; b. Reaction condition: vanillin (0.1 g), methanol (15 mL), under 2 MPa of H_2, at 200 ^oC for10 h]

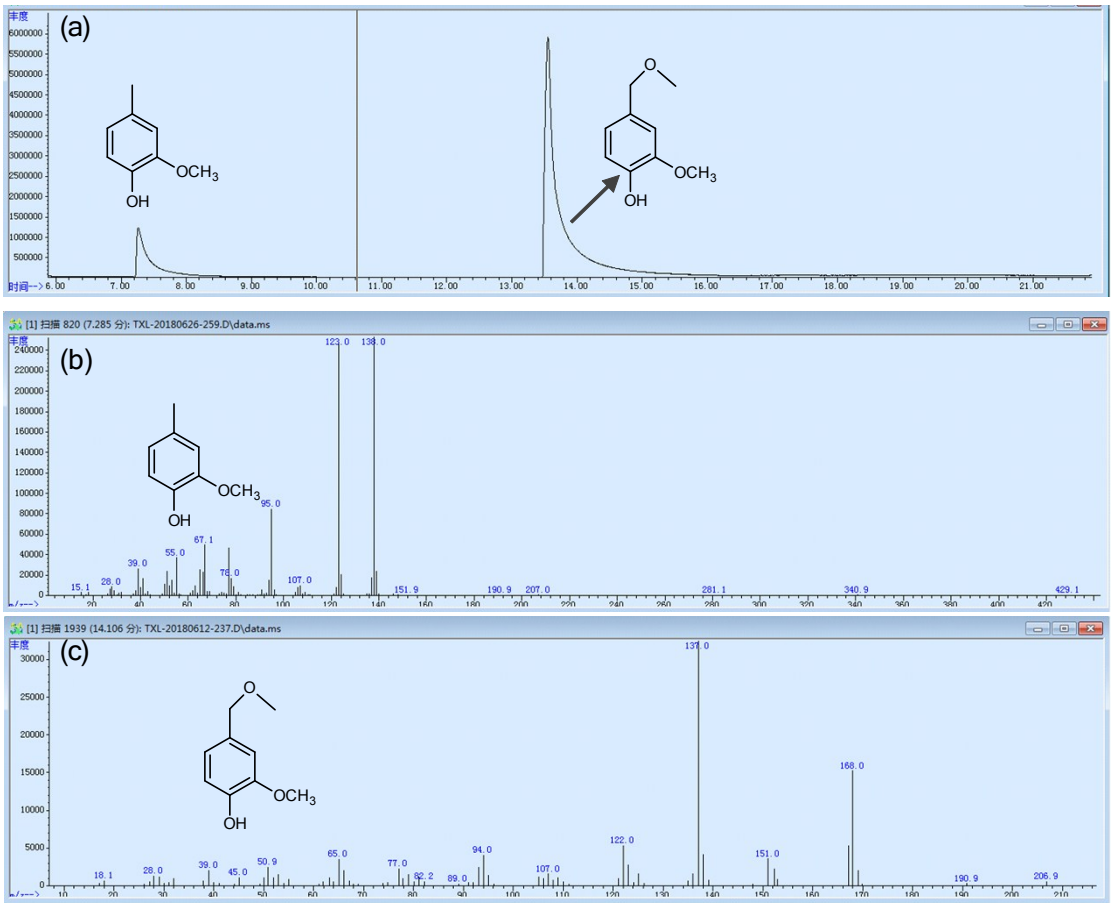


Fig. S23 GC-MS analysis for products of vanillin hydrogenolysis in methanol with Ni-MFC-700 catalyst: [a. GC spectrum of the reaction mixtures; b. MS analysis for **1**; c. MS analysis for **2**; The GC-MS spectrum of **3** was shown in **Fig. S23(e**)].

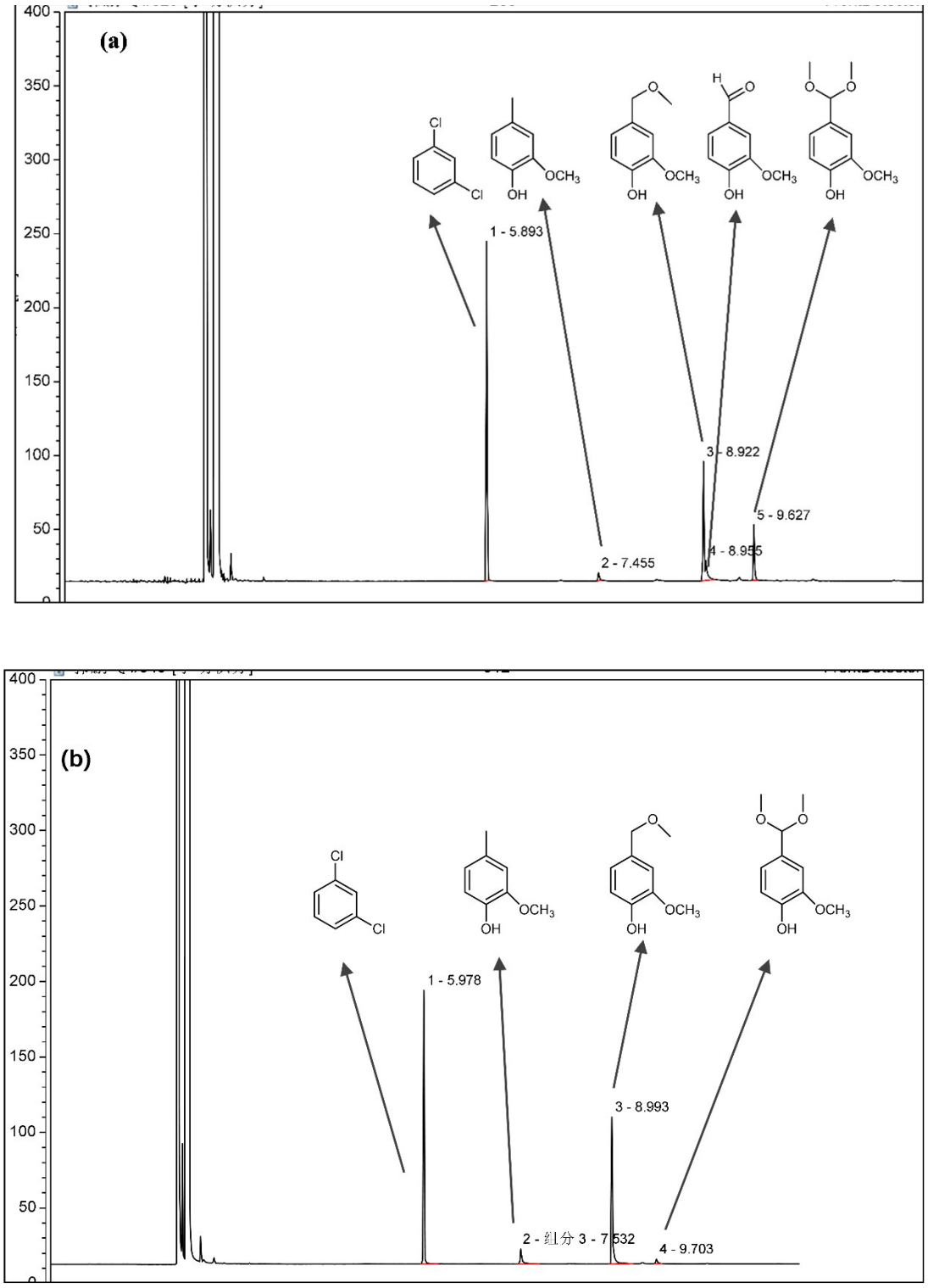


Fig. S24 GC analysis for the products of vanillin hydrogenolysis in methanol with (a) Ni-MFC-350 and (b) Ni-MFC-500 catalyst (Reaction condition: vanillin (0.1g), methanol (15 mL), under 2 MPa of H_2, at 160 ^oC for 4 h).

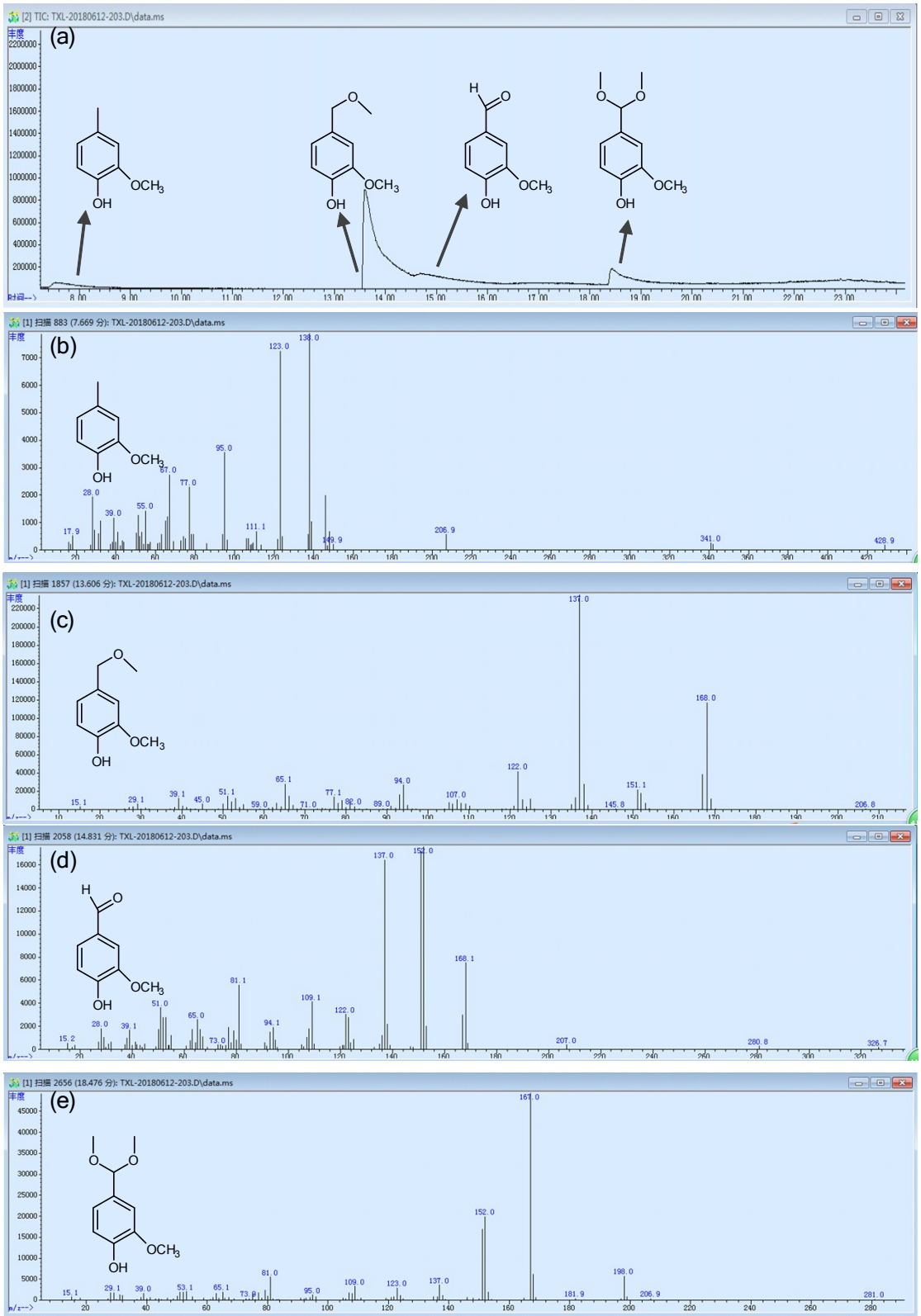


Fig. S25 GC-MS analysis for products of vanillin hydrogenolysis in methanol with Ni-MFC-350 catalyst [a. GC spectrum of the reaction mixtures ; b. MS analysis for **1** ; c. MS analysis for **2** ; d. MS analysis for vanillin; and (e) MS analysis for **3** during reaction.

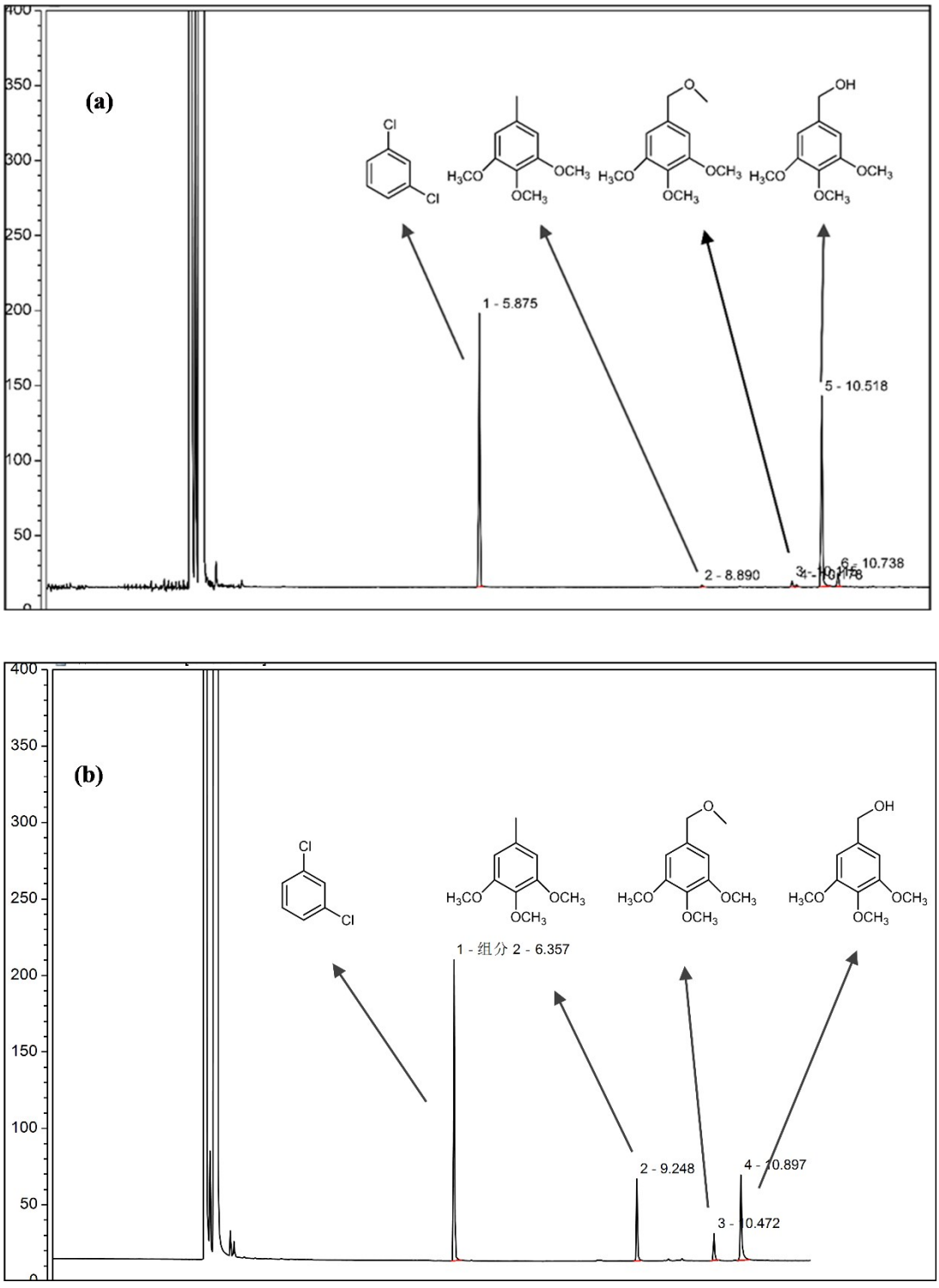


Fig. S26 GC analysis for products of 3, 4, 5-trimethoxybenzaldehyde hydrogenation with Ni-MFC-700 [a. Reaction condition: 0.1 g substrate, methanol (15 mL), 2 MPa of H_2, at 160 ^oC for 4 h; b. Reaction condition: 0.1 g substrate, methanol (15 mL), 2 MPa of H_2, at 200 ^oC for10 h]

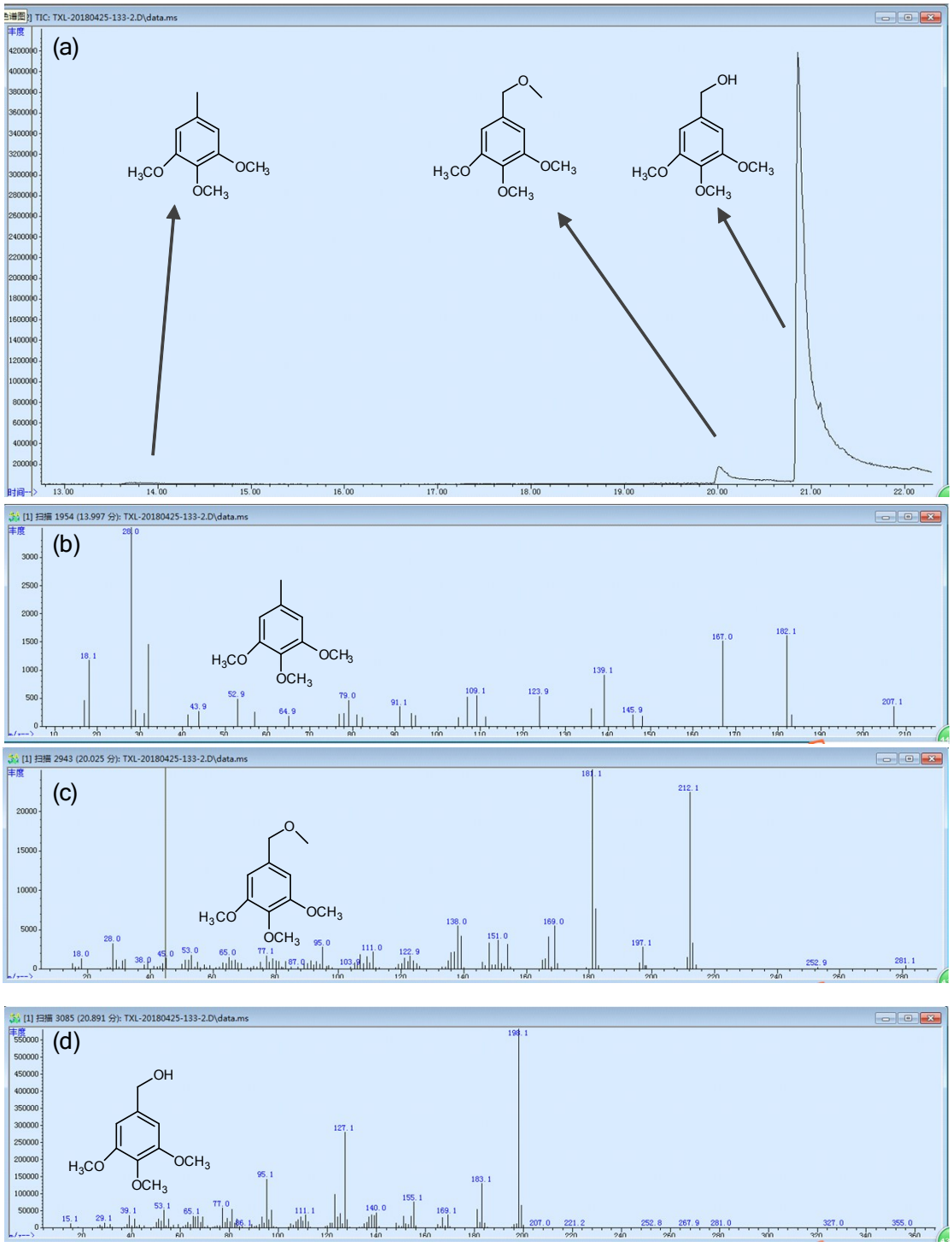


Fig. S27 GC-MS analysis for products of 3,4,5-trimethoxybenzaldehyde hydrogenation with Ni-MFC-700 [a. GC spectrum; b. MS analysis for 1,2,3-trimethoxy-5- methylbenzene; c. MS for 1,2,3-trimethoxy-5-(methoxymethyl)benzene; d. MS for (3,4,5-trimethoxyphenyl)methanol]

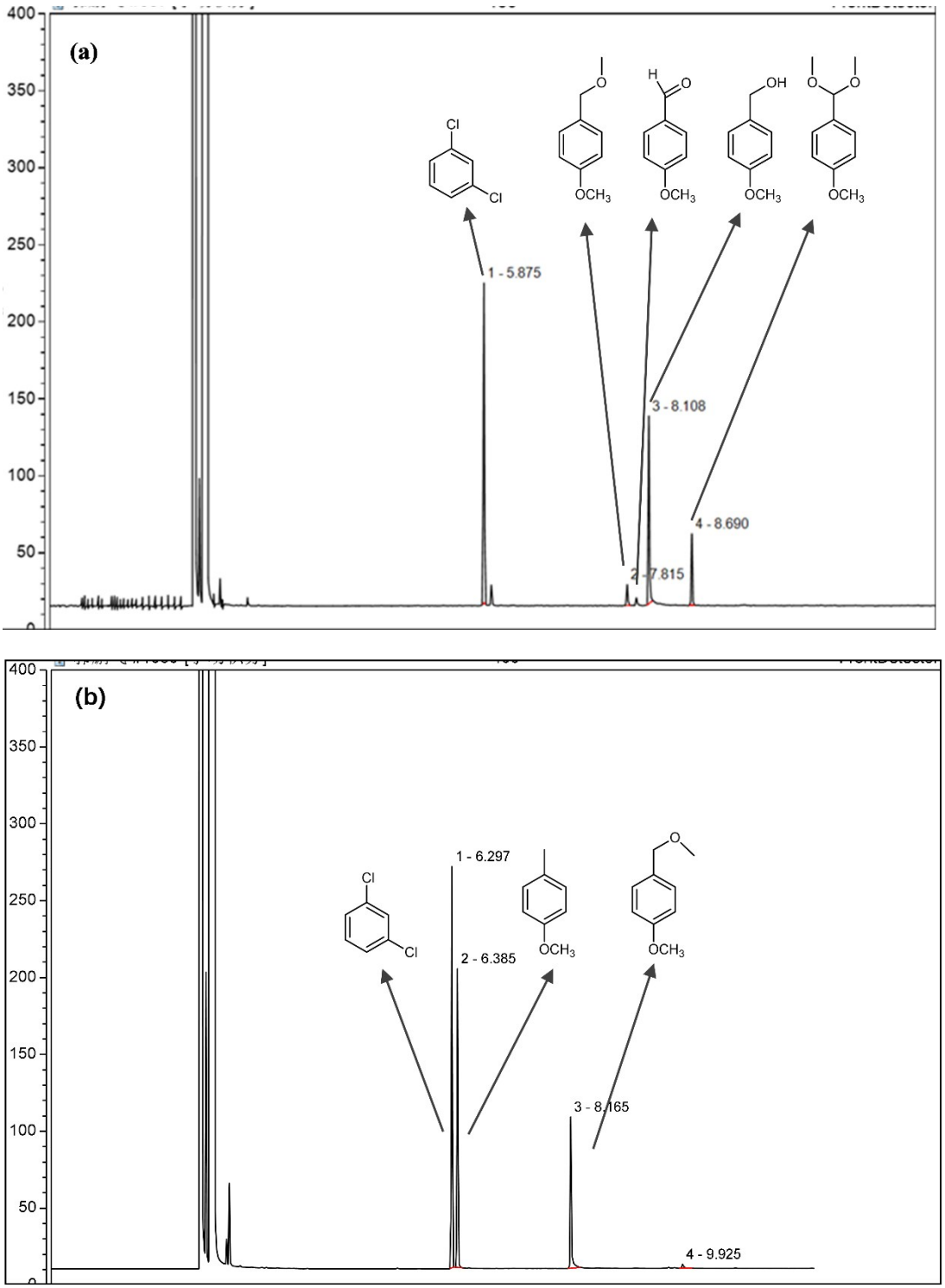


Fig. S28 GC analysis for products of 4-methoxybenzaldehyde hydrogenolysis with Ni-MFC-700 [a. Reaction condition: 0.1 g substrate, methanol (15 mL), under 2 MPa of H_2, at 160 ^oC for 4 h; b. Reaction condition: 0.1 g substrate, methanol (15 mL), under 2 MPa of H_2, at 200 ^oC for 10 h]

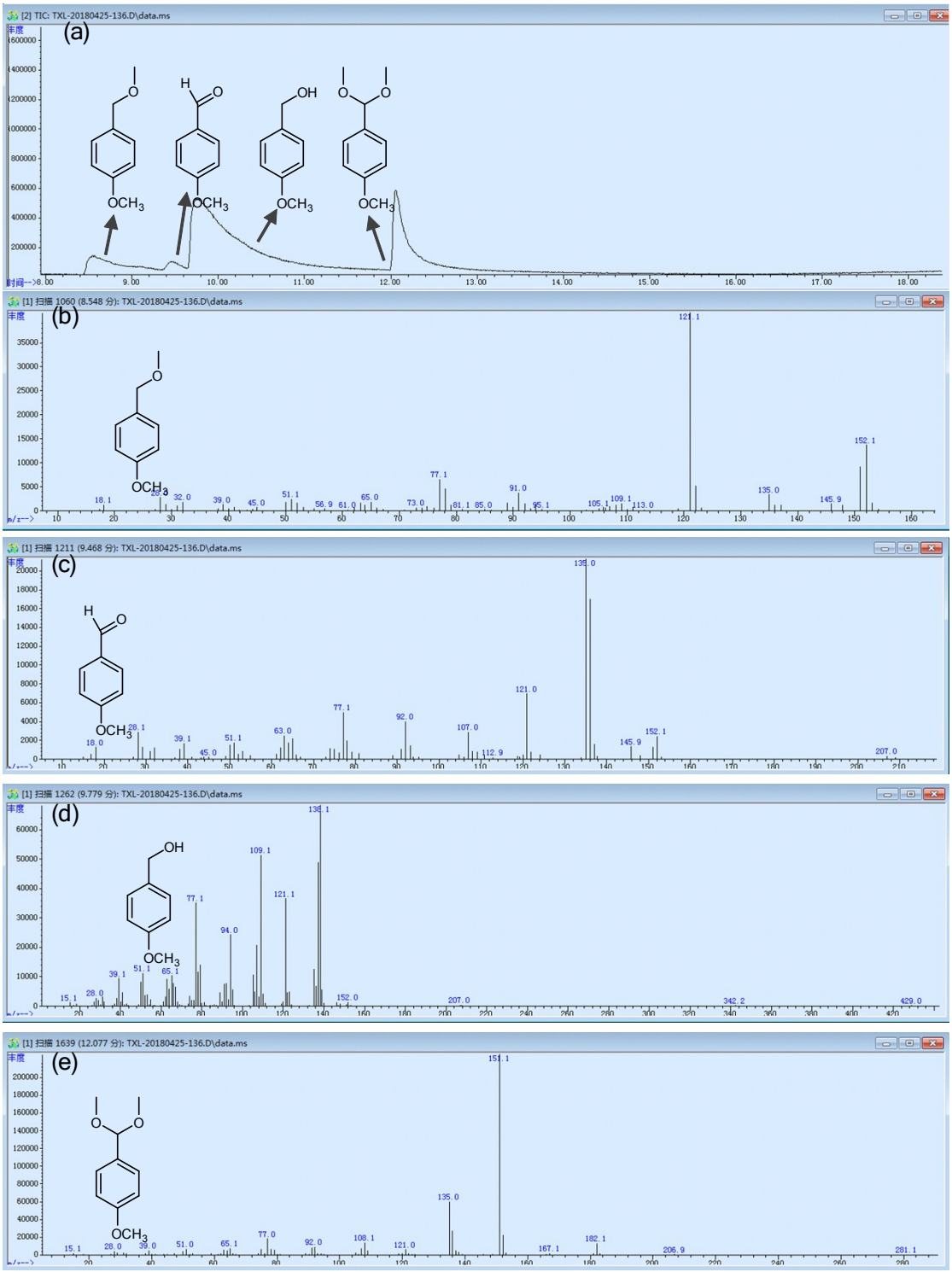


Fig. S29 GC-MS analysis the hydrogention of 4-methoxybenzaldehyde with Ni-MFC-700 [a. GC spectrum; b. MS for 1-methoxy-4-(methoxymethyl)benzene; c. MS for 4-methoxy benzaldehyde; d.MS for (4-methoxyphenyl)methanol;e.MS for 1-(dimethoxymethyl)-4-methoxybenzene]

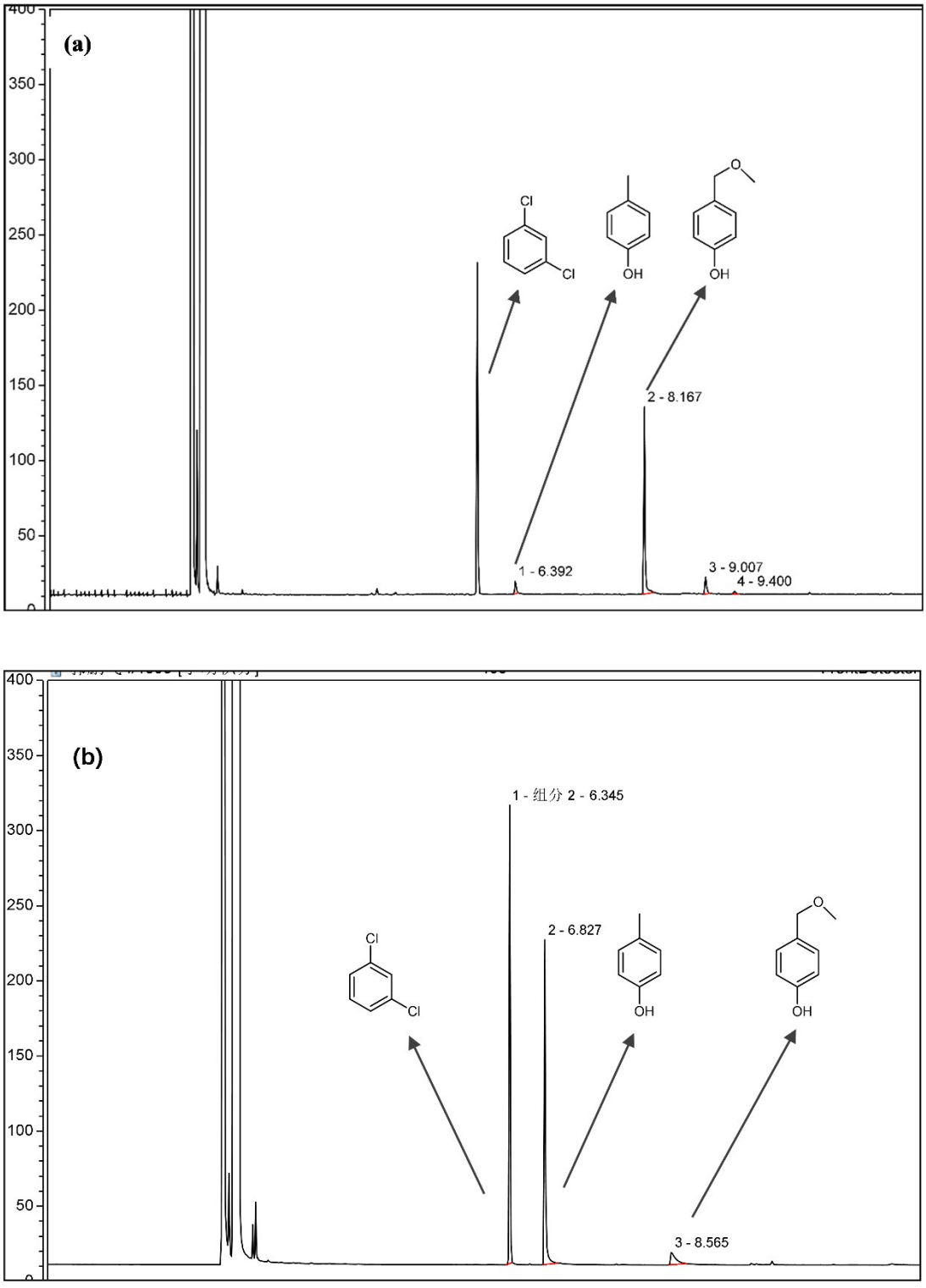


Fig. S30 GC analysis for products of p-hydroxybenzaldehyde hydrogenolysis with Ni-MFC-700 [a. Reaction condition: 0.1 g substrate, methanol (15 mL), under 2 MPa of H_2, at 160 ^oC for 4 h; b. Reaction condition: 0.1 g substrate, methanol (15 mL), under 2 MPa of H_2, at 200 ^oC for 10 h]

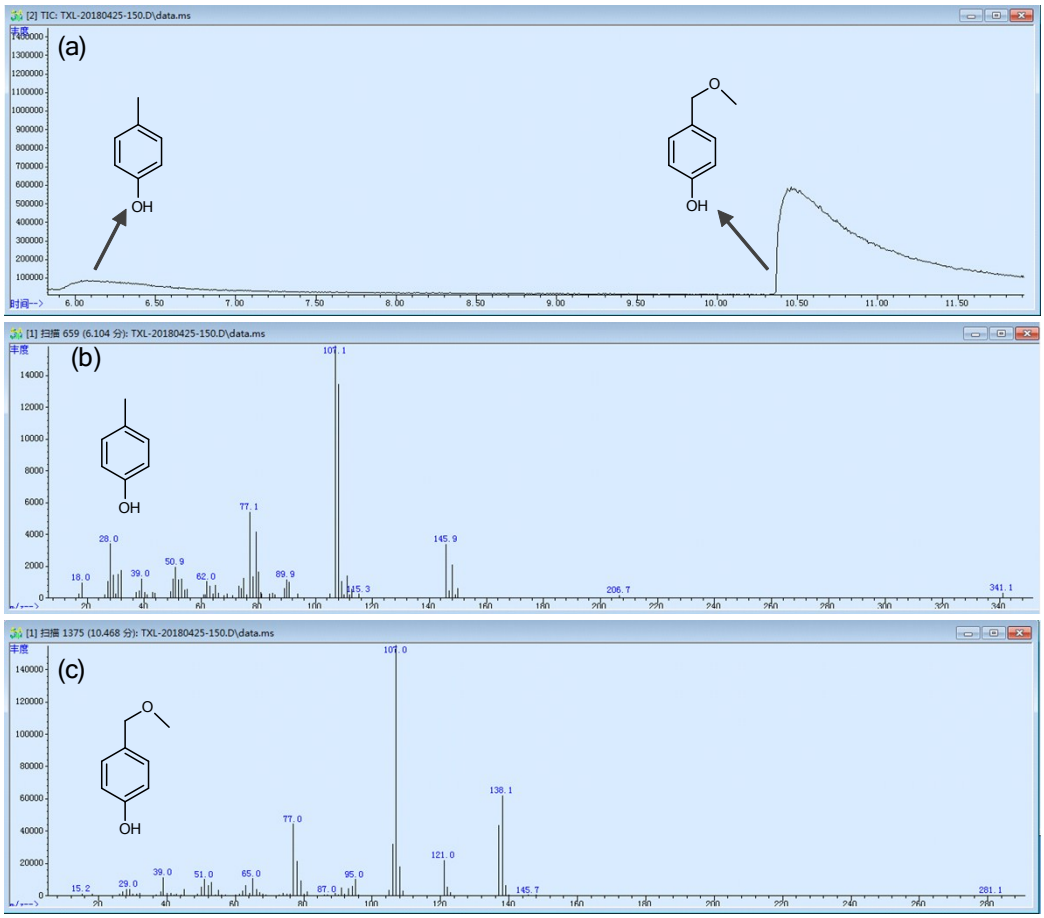


Fig. S31 GC-MS analysis for products of p-hydroxybenzaldehyde hydrogenolysis with Ni-MFC-700 [a. GC spectrum of the reaction mixtures; b. MS analysis for p-cresol; c. MS analysis for 4-(methoxymethyl)phenol]

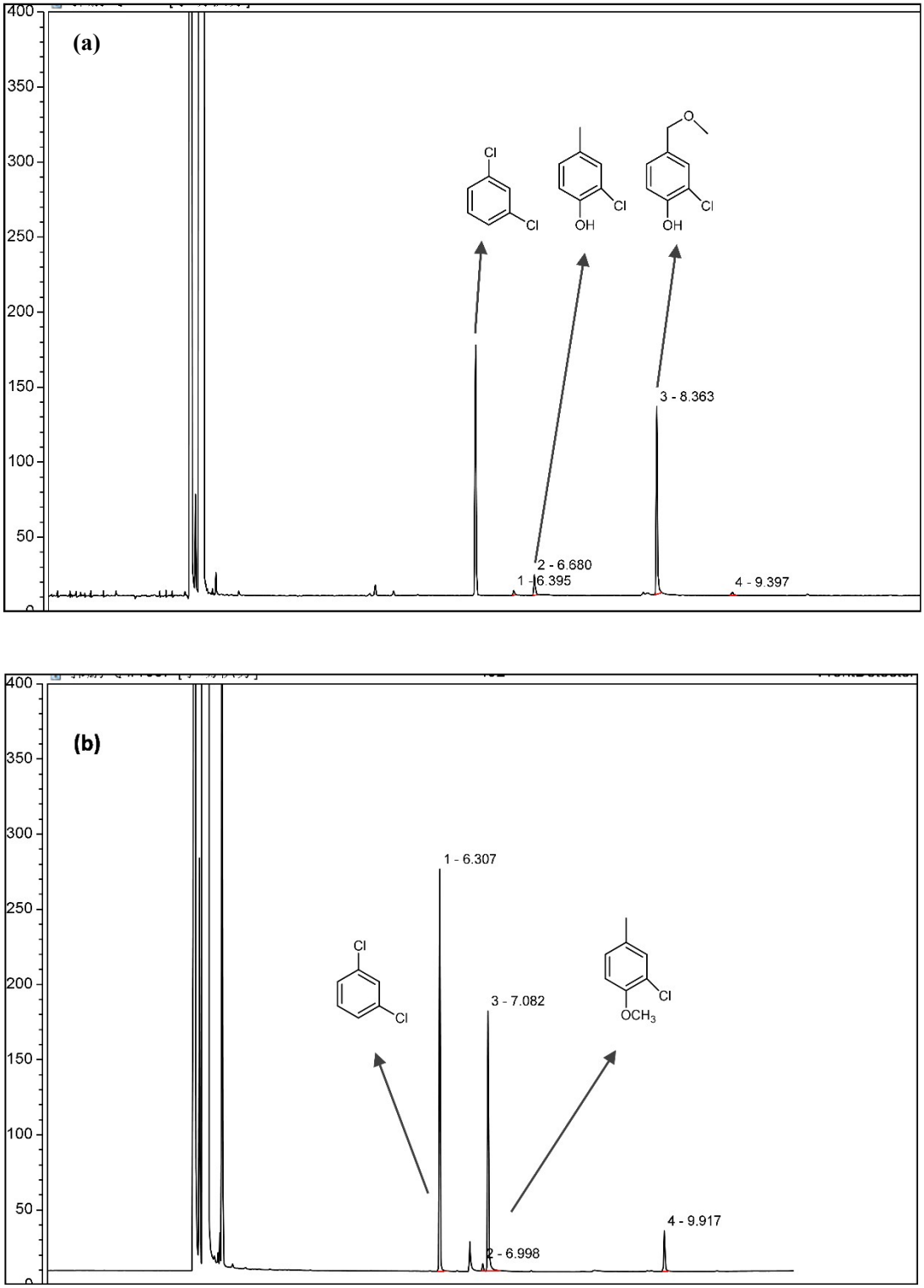


Fig. S32 GC analysis for products of 3-chloro-4-hydroxybenzaldehyde hydrogenolysis with Ni-MFC-700 [a. Reaction condition: 0.1 g substrate, methanol (15 mL), 2 MPa of H_2, at 160 ^oC for 4 h; b. Reaction condition: 0.1 g substrate, methanol (15 mL), 2 MPa of H_2, at 200 ^oC for 10 h]

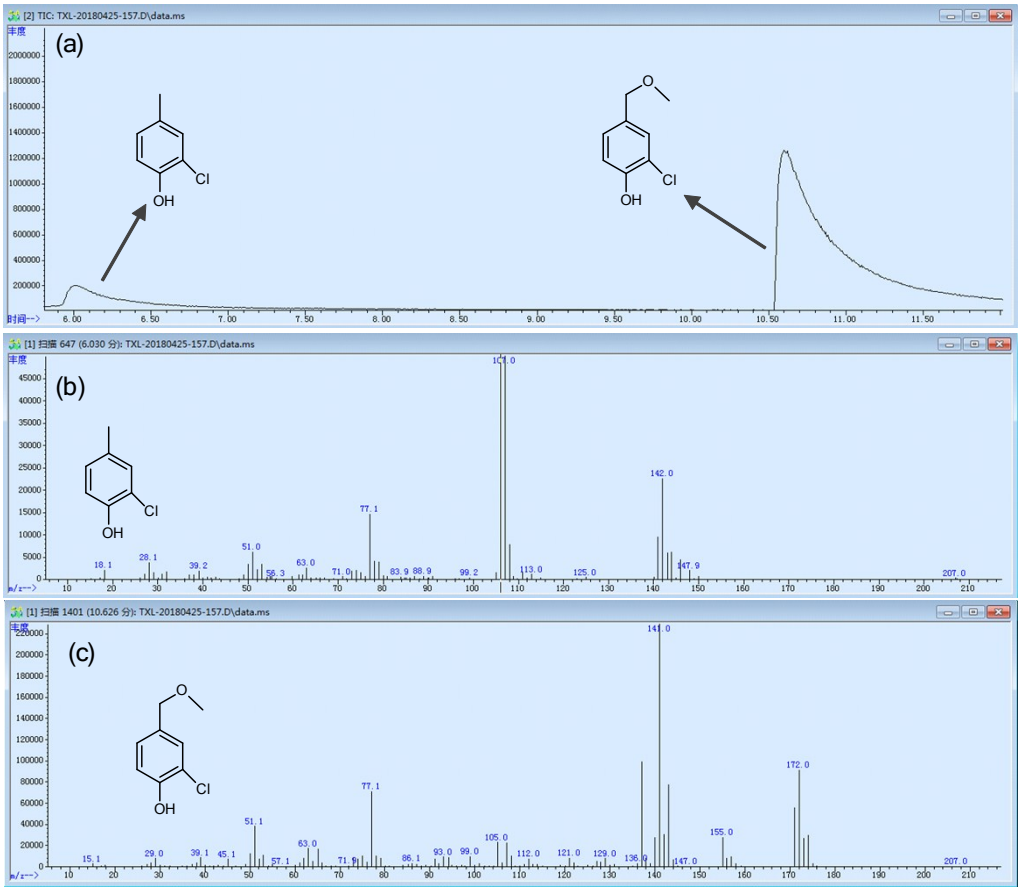


Fig. S33. GC-MS analysis for products of 3-chloro-4-hydroxybenzaldehyde hydrogenolysis with Ni-MFC-700 catalyst [a. GC spectrum of the reaction mixtures; b. MS analysis for 2-chloro-4-methylphenol; c. MS analysis for 2-chloro-4-(methoxymethyl)phenol.]

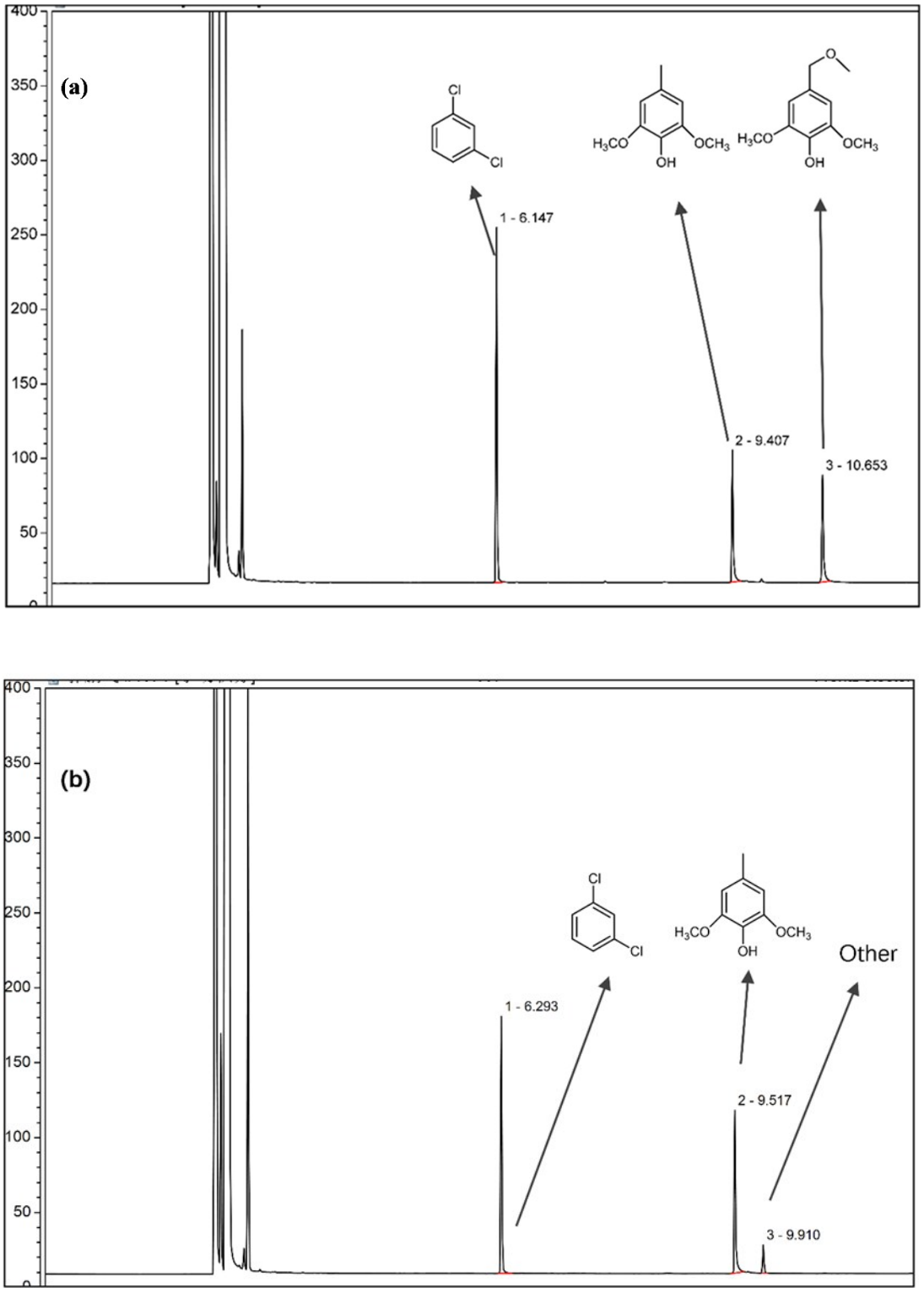


Fig. S34. GC analysis for products of 3,5-dimethoxy-4-hydroxybenzaldehyde hydrogenolysis with Ni-MFC-700 [a. Reaction condition: 0.1 g substrate, methanol (15 mL), 2 MPa of H_2 at 160 ^oC for 4 h; b. Reaction condition: 0.1 g substrate, methanol (15 mL), under 2 MPa of H_2 at 200 ^oC for 10 h]

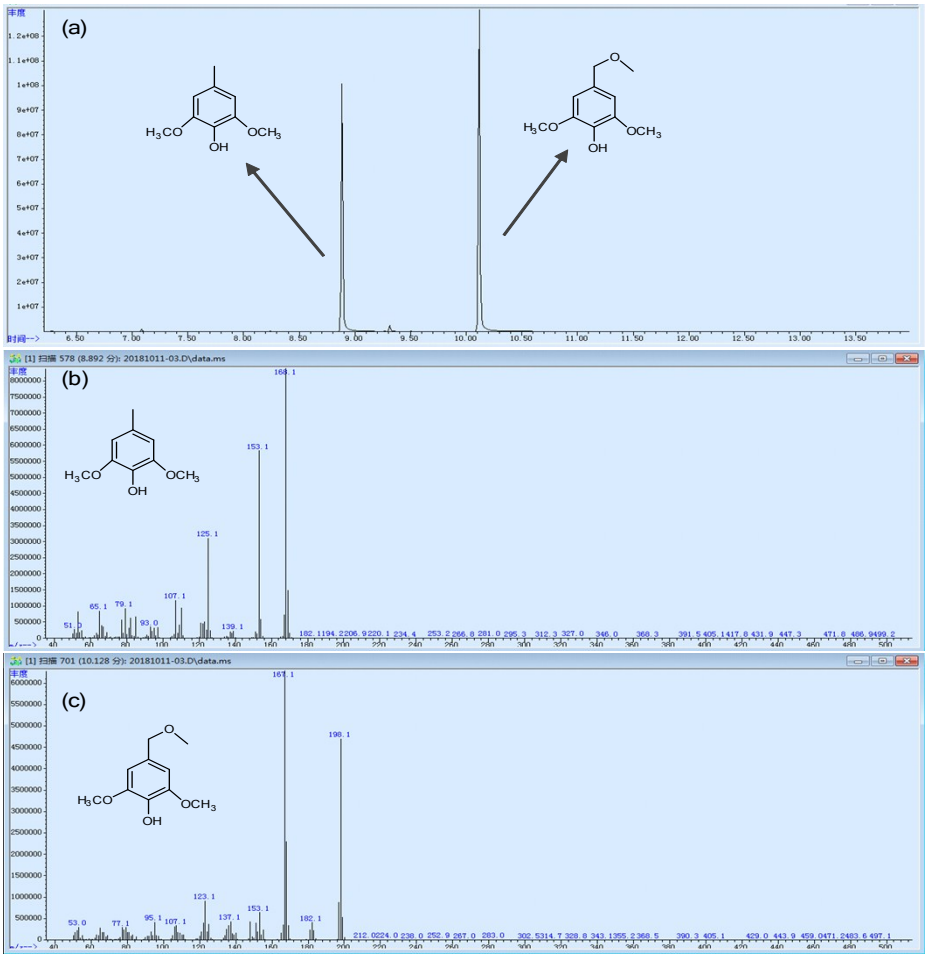


Fig. S35. GC-MS analysis for products of 3,5-dimethoxy-4-hydroxybenzaldehyde hydrogenolysis with Ni-MFC-700 [a. GC spectrum of the reaction mixtures; b. MS analysis for 2,6-dimethoxy-4-methylphenol; c. MS analysis for 2,6-dimethoxy-4-(methoxymethyl)phenol]

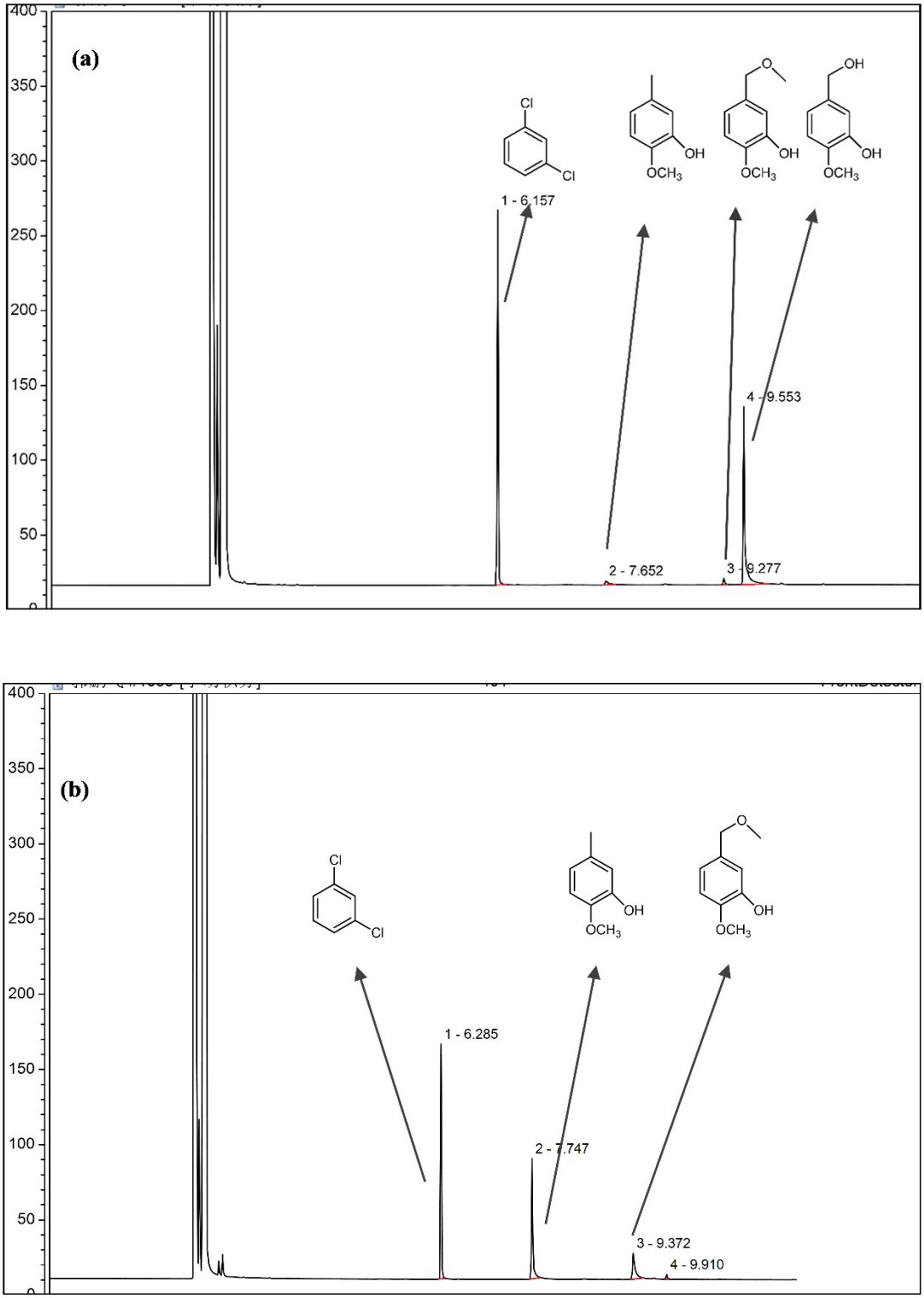


Fig. S36. GC analysis for products of 3-hydroxy-4-methoxybenzaldehyde hydrogenolysis with Ni-MFC-700 [a. Reaction condition: 0.1 g substrate, methanol (15 mL), 2 MPa of H_2, at 160 ^oC for 4 h; b. Reaction condition: 0.1 g substrate, methanol (15 mL), 2 MPa of H_2, at 200 ^oC for 10 h]

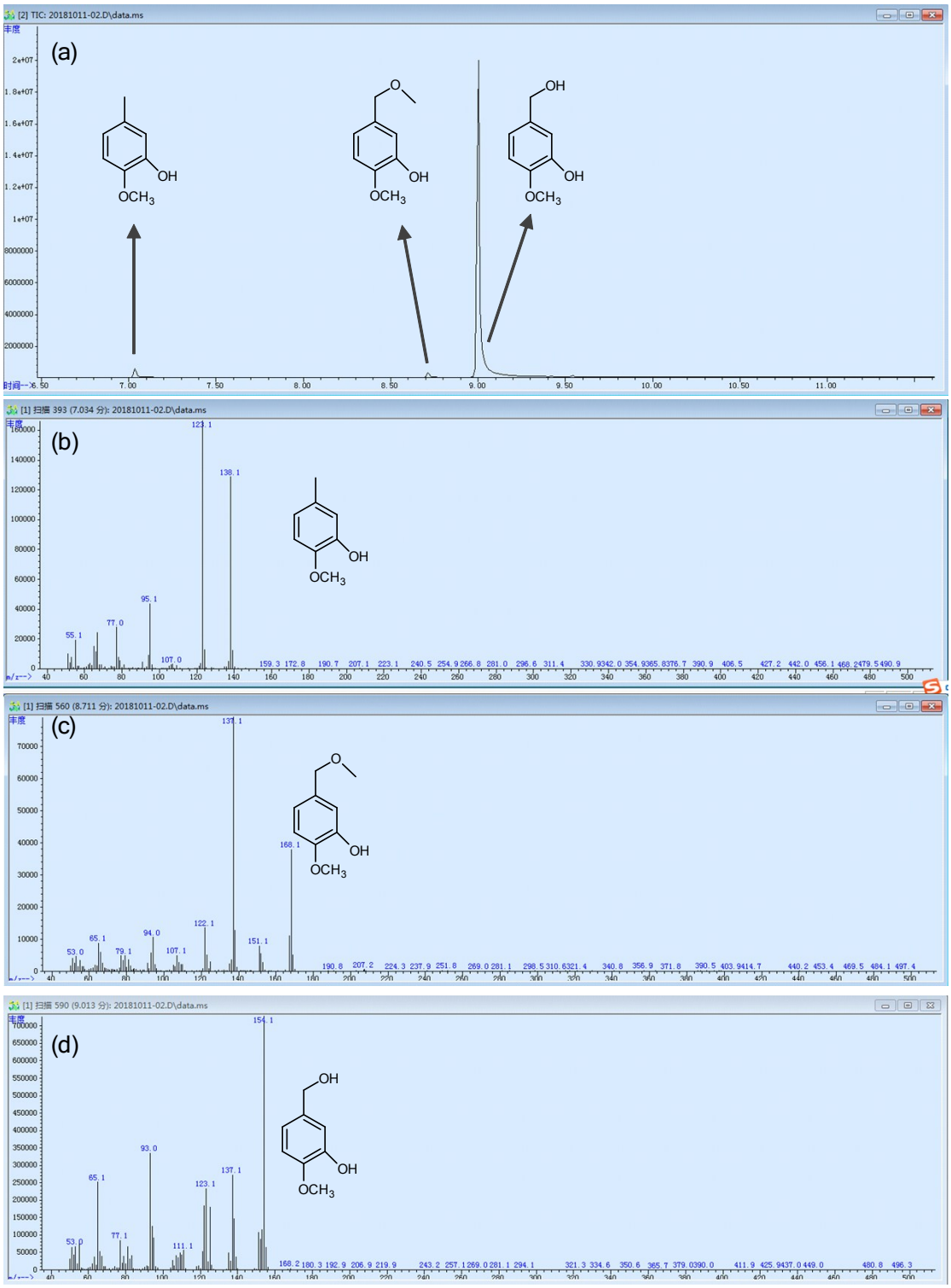


Fig. S37. GC-MS analysis for products of 3-hydroxy-4-methoxybenzaldehyde hydrogenolysis with Ni-MFC-700 [a. GC spectrum; b. MS analysis for 2-methoxy-5-methylphenol; c. MS analysis for 2-methoxy-5-(methoxymethyl)phenol; d. MS analysis for 5-(hydroxymethyl)-2-methoxyphenol].