Supplementary Information (SI) for Green Chemistry.
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Supplementary information

Production of High-Carbon-Number Hydrocarbon Bio-Aviation Fuels via Catalytic Hydrogenation of Vanillin and Non-Catalytic Condensation: A Mechanistic Study with DFT and Experimental Insights

Table of contents

Fig. S1 Hydrogenation results using different carbon-supported metal catalysts (Ru, Pd, Pt, Ni, Co) exhibiting products of VANOL (1), CRSOL (2), dimer **1** (4). (Reaction conditions: 2 mmol of VAN, a mixed solvent of 30 mL of DI water and 15 mL of n-octane, 150 °C of reaction temperature, 1 h of reaction time, 0.05 g of 1 wt% Ru/C, catalyst/substrate = 0.17 w/w, 5 MPa of H_2 pressure measured at room temperature)

Fig. S2 HAADF-STEM images of (A) 1 wt% Ru/C, (B) 3 wt% Ru/C, and (C) 5 wt% Ru/C.

Fig. S3 GC-MS results for condensation of VAN, VANOL, and CRSOL depicted in Table 1. Reaction conditions: 2 mmol of reactant (VAN, VANOL, or CRSOL) each or a mixture 1 mmol VANOL and 1 mmol CRSOL, a mixed solvent of DI water (30 mL) and n-octane (15 mL), 0 or 0.05 g of 1 wt% Ru/C, 50 bar H_2 measured at room temperature, 200 °C of reaction temperature, 1 h of reaction time.

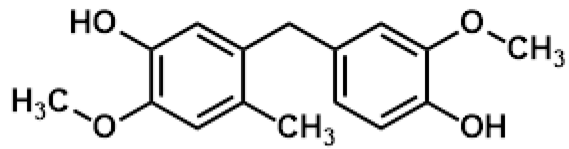
Fig. S4 Reusability of Ru/C catalyst over multiple reaction cycles exhibiting products of VANOL (1), CRSOL (2), dimer **1** (4). (Reaction conditions: 2 mmol of VAN, a mixed solvent of 30 mL of DI water and 15 mL of n-octane, 150 °C of reaction temperature, 1 h of reaction time, 0.05 g of 1 wt% Ru/C, catalyst/substrate = 0.17 w/w, 50 bar of H_2 pressure measured at room temperature)

Fig. S5 DFT-calculated structures of reactants and intermediates on Ru surface depicted in Fig. 7.

Fig. S6 GC-MS results for the second reaction for hydrodeoxygenation of a mixture containing dimer **1**. The first reaction (R1) is hydrogenation and condensation of VAN. (Reaction conditions: 2 mmol of VAN, a mixed solvent of 30 mL of DI water and 15 mL of n-octane, 0.05 g of 1 wt% Ru/C catalyst, 30 bar of H_2 pressure (measured at room temperature), 150 °C of reaction temperature, 3 h of reaction time.) The second reaction (R2) is hydrodeoxygenation of the product of R1. (Reaction conditions: a product mixture of R1 as a reactant, 0.3 g of 3 wt% Ru/HZSM-5 catalyst, 50 bar of H_2 pressure (measured at room temperature), 200 °C of reaction temperature, 3 h of reaction time.)

Fig. S7 XRD results of 3 wt% Ru/HZSM-5.

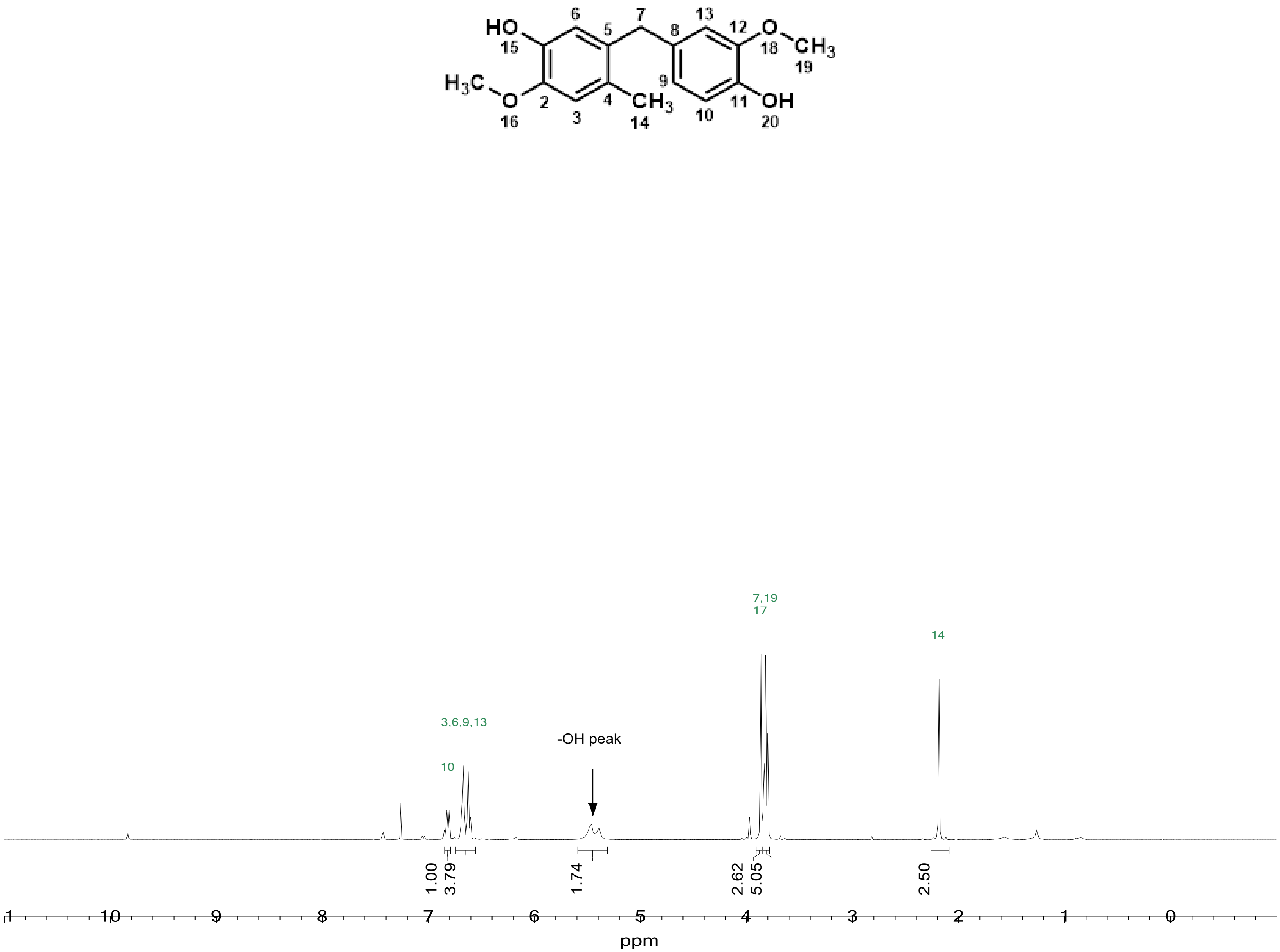
NMR spectra (^{1}H, ^{13}C, COSY, HSQC, HMBC) of compound 1



5-(4-hydroxy-3-methoxybenzyl)-2-methoxy-4-methylphenol (**1**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (d, J = 8.5 Hz, 1H), 6.72 – 6.59 (m, 4H), 5.51 – 5.37 (m, 2H), 3.86 (s, 3H), 3.84 – 3.79 (m, 5H), 2.18 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 144.8, 143.9, 143.5, 132.6, 132.2, 127.9, 121.5, 116.2, 114.3, 113.1, 111.4, 56.2, 56.0, 38.6, 19.4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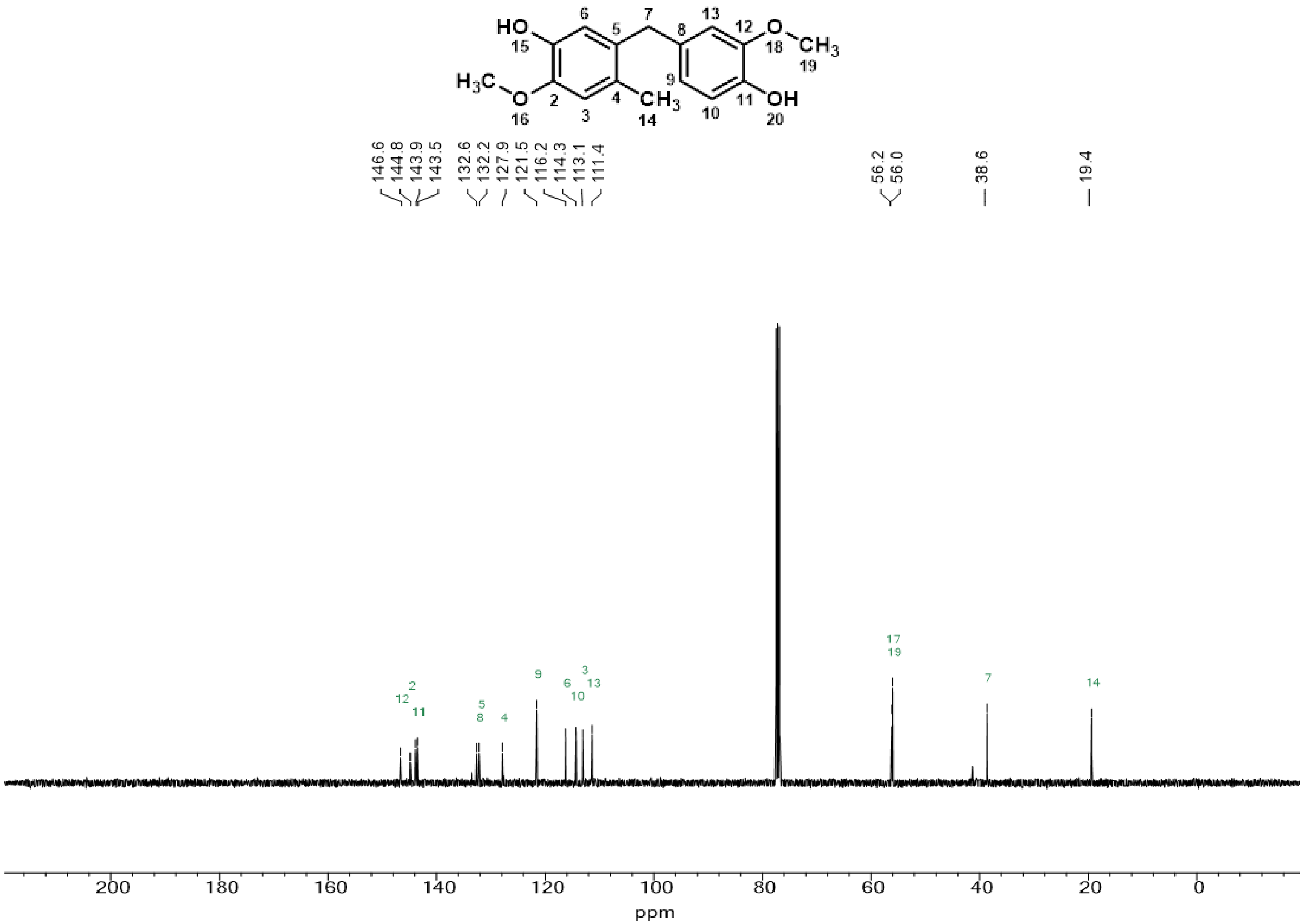
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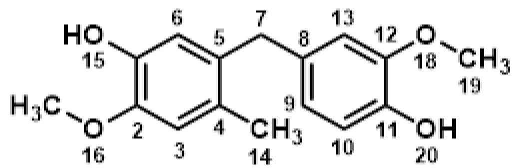
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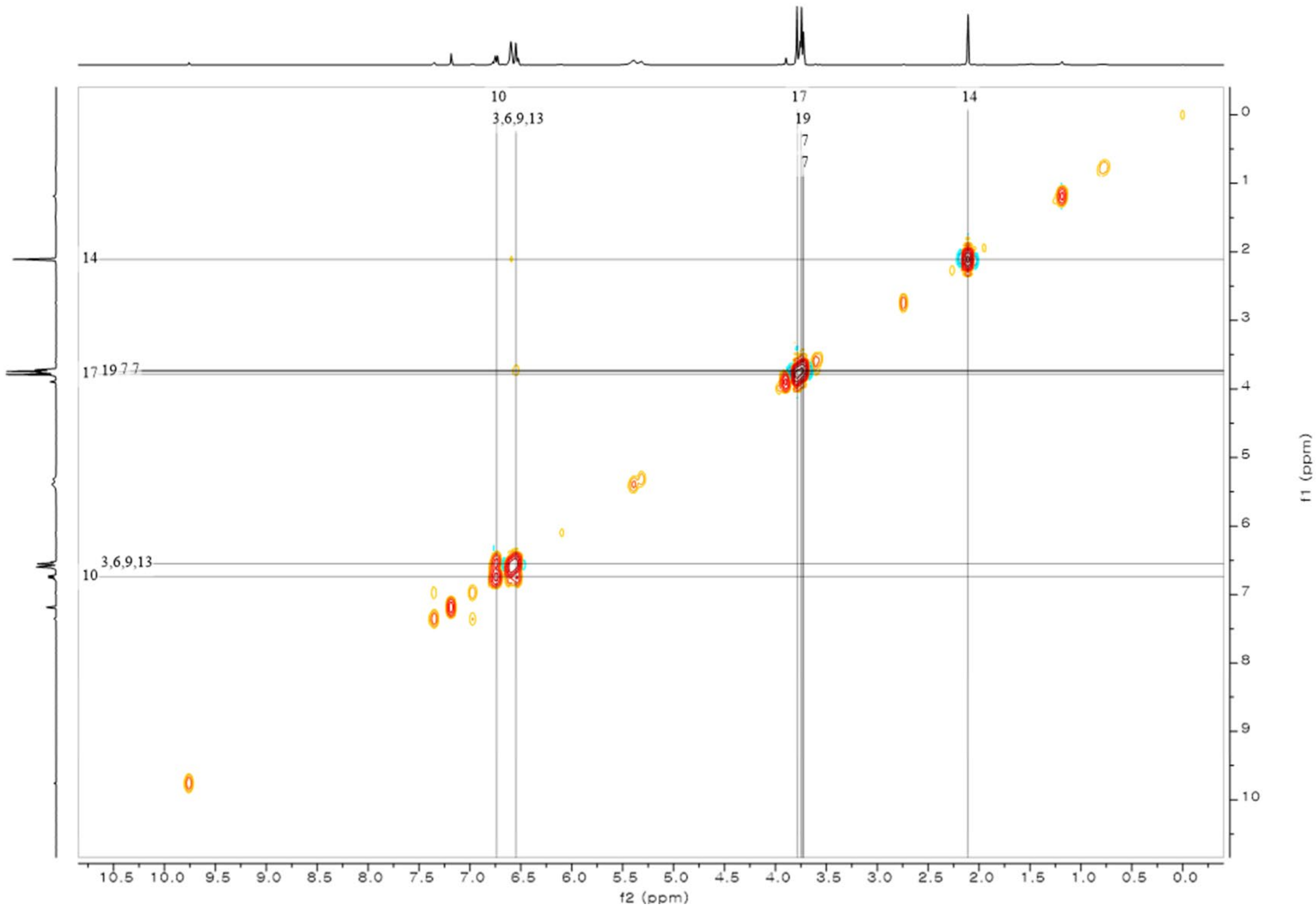
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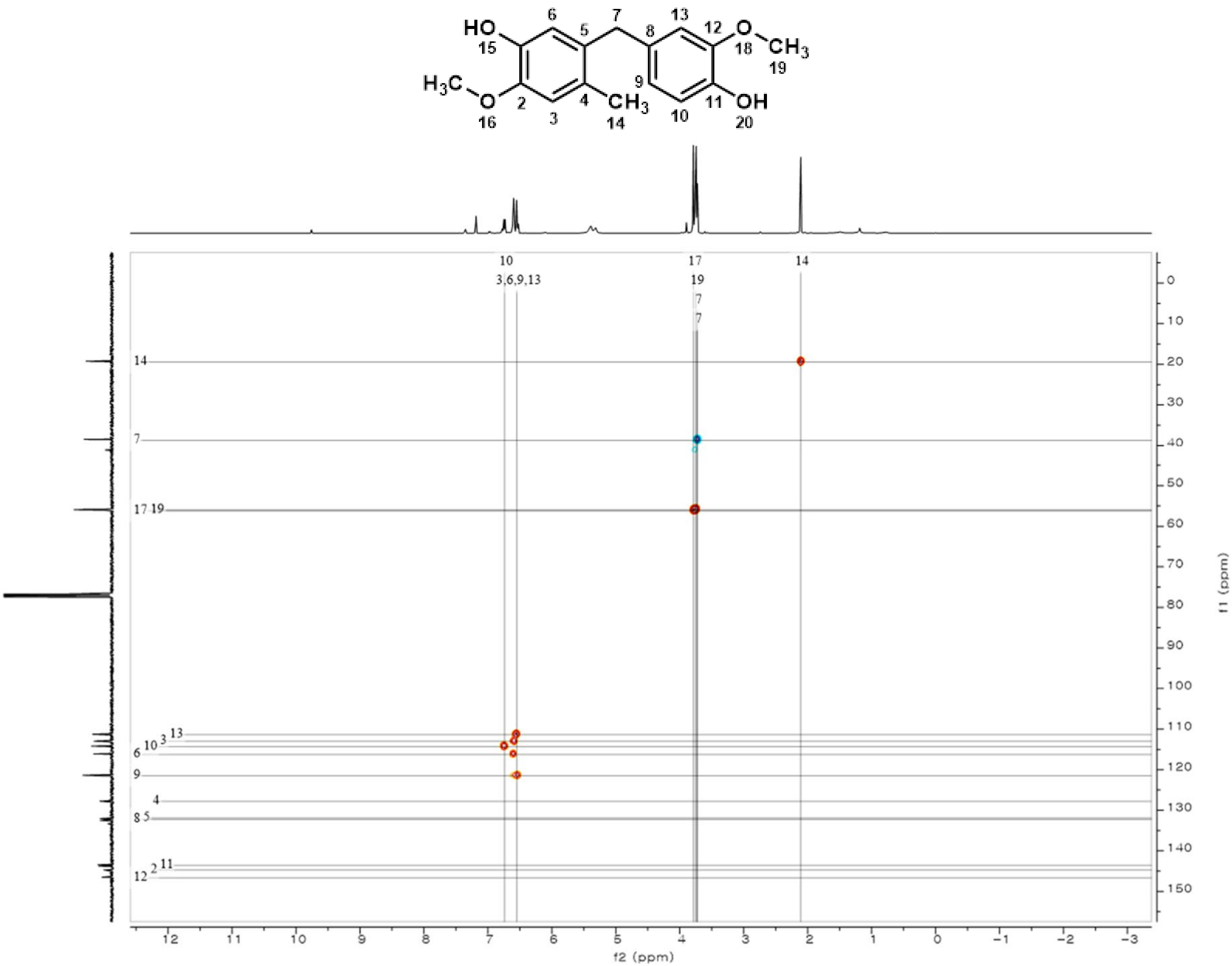
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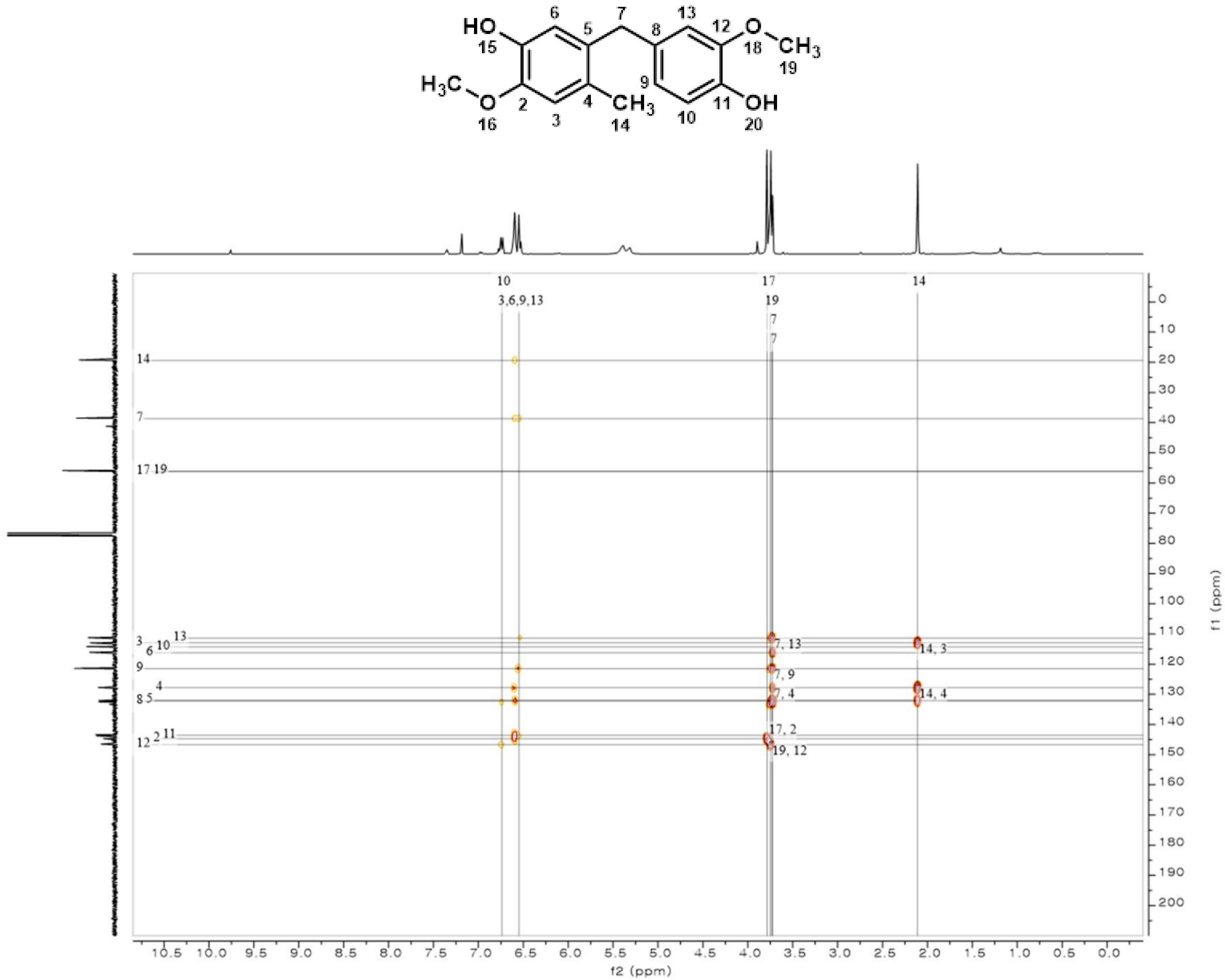

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19, 12

Supplementary Tables

Table S1. Effects of catalyst-to-substrate ratio on yield in vanillin hydrogenation at 150 °C depicted in Fig. 1(a).[a, c]

Catalyst/substrate (w/w)	Product yield (%)						Vanillin conversion (%)
	Vanillyl alcohol	Creosol	**1**[b]	2-Methoy-4-methyl cyclohexanol	4-Methyl cyclohexanol	Methyl cyclohexane	
0.00	16 ± 2.3						23 ± 1.3
0.10	28 ± 1.3	28 ± 1.0	3 ± 0.3		0		91 ± 0.8
0.17	21 ±0.5	45 ± 0.5	13 ± 0.8		0		100
0.25	10 ± 0.5	65 ± 2.9	2 ± 0.3		0		100
0.29	0	62 ± 2.2	0	6 ± 0.8	3 ± 0.4	2 ± 0.1	100
0.33	0	55 ± 2.4	0	6 ± 0.6	4 ± 0.6	3 ± 0.2	100
0.50	0	55 ± 4.8	0	11 ± 2.5	10 ± 3.1	4 ± 0.1	100

[a] Reaction conditions: 2 mmol of vanillin, 30 mL of DI water 30 mL, 15 mL of n-octane 15 mL, 0.03-0.15 g of 1 wt% Ru/C catalyst, 50 bar of H_2 pressure (measured at room temperature), 150 °C of reaction temperature, 1 h of reaction time.

[b] **1**: 5-(4-hydroxy-3-methoxybenzyl)-2-methoxy-4-methylphenol.

[c] Data are presented as mean ± standard deviation from three independent experiments.

Table S2 Effects of catalyst-to-substrate ratio on yield in vanillin hydrogenation at 200 °C depicted in Fig. 1(b).[a, c]

Catalyst/substrate (w/w)	Product yield (%)						Vanillin conversion (%)
	Creosol	Guaiacol	**1**[b]	2-Methoy-4-methyl cyclohexanol	4-Methyl cyclohexanol	Methyl cyclohexane	
0.00	16 ± 1.3						29 ± 0.8
0.10	58 ± 3.7	2	7 ± 0.1	0	0		100
0.17	72 ± 0.3	2	5 ± 0.1	0	0		100
0.25	73 ± 0.2	1	3 ± 0.1	0	0		100
0.29	0	0	0	48 ± 1.0	28 ± 0.2	2	100
0.33	0	0	0	49 ± 0.3	29 ± 0.2	3 ± 0.1	100
0.50	0	0	0	51 ± 0.1	31 ± 0.1	4 ± 0.3	100

[a] Reaction conditions: 2 mmol of vanillin, 30 mL of DI water 30 mL, 15 mL of n-octane 15 mL, 0.03-0.15 g of 1 wt% Ru/C catalyst, 50 bar of H_2 pressure (measured at room temperature), 200 °C of reaction temperature, 1 h of reaction time.

[b] **1**: 5-(4-hydroxy-3-methoxybenzyl)-2-methoxy-4-methylphenol.

[c] Data are presented as mean ± standard deviation from three independent experiments.

Table S3 Effects of Ru metal loading on yield in vanillin hydrogenation at 150 °C depicted in Fig. 3(a).[a, c]

Metal loading (wt%)	Product yield (%)						Vanillin conversion (%)
	Vanillyl alcohol	Creosol	**1**[b]	2-Methoy-4-methyl cyclohexanol	4-Methyl cyclohexanol	Methyl cyclohexane	
1	21 ± 1.0	45 ± 1.0	13 ± 1.5	0	0	0	100
3	0	80 ± 2.3	3 ± 0.5	0	0	0	100
5	0	64 ± 1.8	2	7 ± 0.5	5 ± 1.0	2 ± 2.0	100

[a] Reaction conditions: 2 mmol of vanillin, 30 mL of DI water 30 mL, 15 mL of n-octane 15 mL, 0.05 g of Ru/C catalyst, 50 bar of H_2 pressure (measured at room temperature), 150 °C of reaction temperature, 1 h of reaction time.

[b] **1**: 5-(4-hydroxy-3-methoxybenzyl)-2-methoxy-4-methylphenol.

[c] Data are presented as mean ± standard deviation from three independent experiments.

Table S4 Effect of catalyst-to-substrate ratio on yield in vanillin hydrogenation at 200 °C depicted in Fig. 3(b).[a, c]

Metal loading (wt%)	Product yield (%)						Vanillin conversion (%)
	Creosol	Guaiacol	**1**[b]	2-Methoy-4-methyl cyclohexanol	4-Methyl cyclohexanol	Methyl cyclohexane	
1	72 ± 0.5	2	5 ± 0.3	0	0	0	100
3	0	0	0	35 ± 2.0	33 ± 2.5	2 ± 0.4	100
5	0	0	0	37 ± 1.5	35 ± 1.0	2 ± 0.3	100

[a] Reaction conditions: 2 mmol of vanillin, 30 mL of DI water 30 mL, 15 mL of n-octane 15 mL, 0.05 g of Ru/C catalyst, 50 bar of H_2 pressure (measured at room temperature), 200 °C of reaction temperature, 1 h of reaction time.

[b] **1**: 5-(4-hydroxy-3-methoxybenzyl)-2-methoxy-4-methylphenol.

[c] Data are presented as mean ± standard deviation from three independent experiments.

Table S5 Texture and physicochemical properties of Ru catalysts.

Catalyst	S_{BET} (m^2/g)	S_{micro} (m^2/g)[a]	$S_{external}$ (m^2/g)[b]	Particle size (nm)[c]
1 wt% Ru/C	1029	823	206	0.93 ± 0.35
3 wt% Ru/C	805	631	174	0.98 ± 0.37
5 wt% Ru/C	724	561	163	0.99 ± 0.46
3 wt% Ru/HZSM-5	374	350	24	n.a.

[a] $S_{micro} = S_{BET} - S_{external}$.

[b] Obtained by t-plot analysis with BET surface area.

[c] Measured using the HAADF-STEM images.

Table S6 Effect of reaction pressure and time on yield in vanillin hydrogenation and condensation depicted in Fig. 4(a).[a]

H_2 pressure (bar)[b]	Reaction time (h)	Product yield (%)						Vanillin conversion (%)
		Vanillyl alcohol	Creosol	2-methoxy-4-methyl cyclohexanol	4-methyl cyclohexanol	methyl cyclohexane	**1**[c]	
10	1	10	30				0	50
	2	14	28				6	66
	3	13	33				11	73
	6	20	39				16	95
30	1	23	31				7	86
	2	22	45				9	99
	3	10	43				19	99
	6		50	7	6		10	99
50	1	22	44				14	99
	2	10	55	4			9	99
	3	0	60	6	8		8	99
	6	0	0	46	24	4	0	99

[a] Reaction conditions: 2 mmol of vanillin, 30 mL of DI water, 15 mL of n-octane, 0.05 g of 1 wt% Ru/C catalyst, 150° C of reaction temperature, 1–6 h of reaction time.

[b] Measured at room temperature.

[c] **1**: 5-(4-hydroxy-3-methoxybenzyl)-2-methoxy-4-methylphenol.

Table S7 Effect of reaction temperature on yield in vanillin hydrogenation and condensation depicted in Fig. 4(b).[a]

Temperature (°C)	Product yield (%)				Vanillin conversion (%)
	Vanillyl alcohol	Creosol	Guaiacol	**1**[b]	
50	26				42 ± 1.9
75	83 ± 1.9	2 ± 1.5			86 ± 2.0
100	56 ± 3.7	9 ± 4.0			83 ± 4.9
150	21 ± 1.0	45 ± 1.0		13 ± 1.5	100
200		73	2 ± 0.5	4 ± 1.0	100

[a] Reaction conditions: 2 mmol of vanillin, 30 mL of DI water, 15 mL of n-octane, 0.05 g of 1 wt% Ru/C catalyst, 50 bar of H_2 pressure (measured at room temperature), 1 h of reaction time.

[b] **1**: 5-(4-hydroxy-3-methoxybenzyl)-2-methoxy-4-methylphenol.

Table S8 Effect of reaction pressure and temperature on yield in vanillin hydrogenation and condensation depicted in Fig. 5.[a]

Temperature (°C)	H_2 pressure (bar)	Product yield (%)				Vanillin conversion (%)
		Vanillyl alcohol	Creosol	Guaiacol	**1**[b]	
50	10	18				25
	30	18				30
	50	26				40
75	10	70				74
	30	90				93
	50	85				88
100	10	22	3			42
	30	32	4			53
	50	60	5			77
150	10	10	30			50
	30	23	31		7	86
	50	22	44		14	99
200	10		70		7	85
	30		80		8	99
	50		73	1	3	99

[a] Reaction conditions: 2 mmol of vanillin, 30 mL of DI water, 15 mL of n-octane, 0.05 g of 1 wt% Ru/C catalyst, 10–50 bar of H_2 pressure (measured at room temperature), 50–200 °C of reaction temperature, 1 h of reaction time.

[b] **1**: 5-(4-hydroxy-3-methoxybenzyl)-2-methoxy-4-methylphenol

Table S9 Non-catalytic condensation of vanillyl alcohol and creosol on yield depicted in Fig. 7.[a]

Temperature (°C)	Product yield (%)		
	Vanillyl alcohol	Creosol	**1**[b]
25	50	50	
50	53	43	
100	53	43	
150	22	47	
200		33	34

[a] Reaction conditions: 1 mmol of vanillyl alcohol and creosol each, 30 mL of DI water, 15 mL of n-octane, 50 bar of N_2 pressure (measured at room temperature), 3 h of reaction time.

[b] **1**: 5-(4-hydroxy-3-methoxybenzyl)-2-methoxy-4-methylphenol.

Table S10 Py-FTIR-measured acidity of catalysts.

Catalyst	Brønsted acid (mmol/g)	Lewis acid (mmol/g)	(Brønsted acid) /(Lewis acid)
HZSM-5	0.12	0.79	0.15
3 wt% Ru/HZSM-5	0.05	0.35	0.14

Supplementary Figures

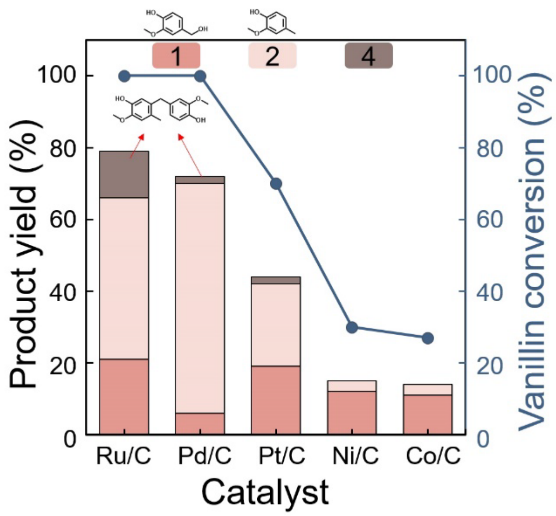


Fig. S1 Hydrogenation results using different carbon-supported metal catalysts (Ru, Pd, Pt, Ni, Co) exhibiting products of VANOL (1), CRSOL (2), dimer **1** (4). (Reaction conditions: 2 mmol of VAN, a mixed solvent of 30 mL of DI water and 15 mL of n-octane, 150 °C of reaction temperature, 1 h of reaction time, 0.05 g of 1 wt% Ru/C, catalyst/substrate = 0.17 w/w, 5 MPa of H_2 pressure measured at room temperature)

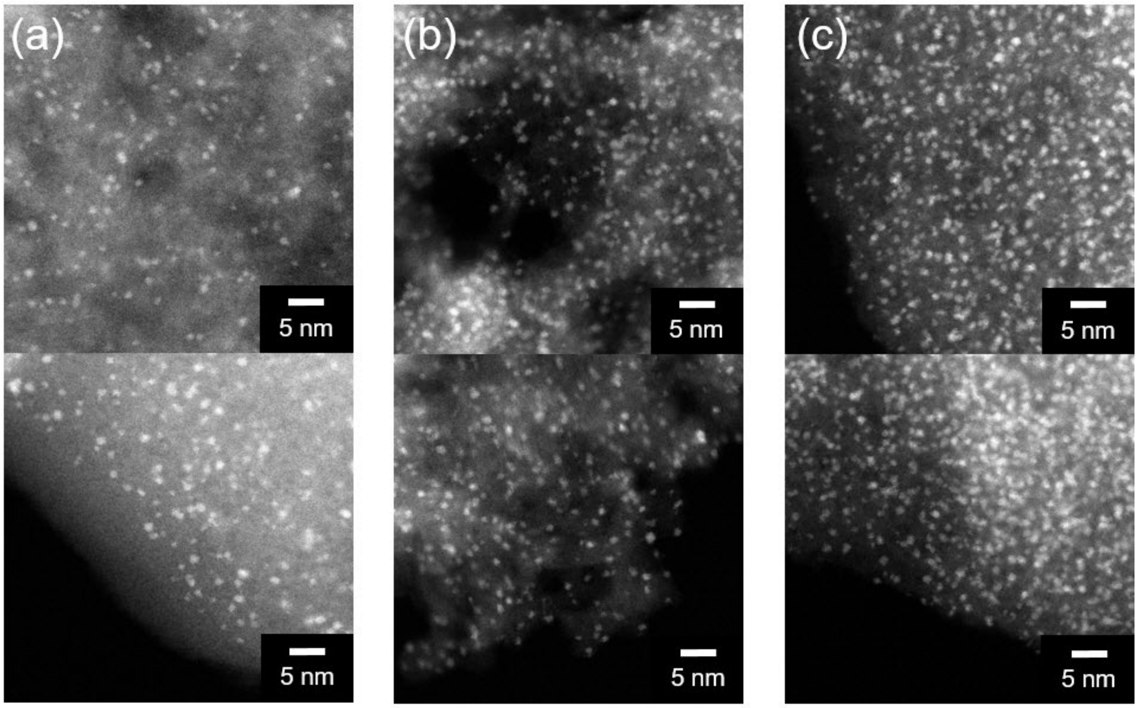
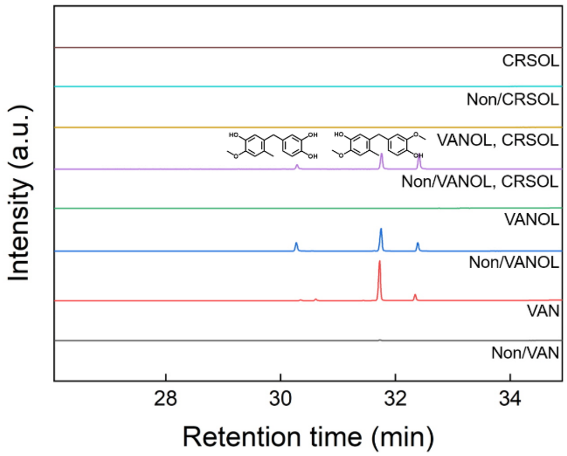


Fig. S2 HAADF-STEM images of (A) 1 wt% Ru/C, (B) 3 wt% Ru/C, and (C) 5 wt% Ru/C.



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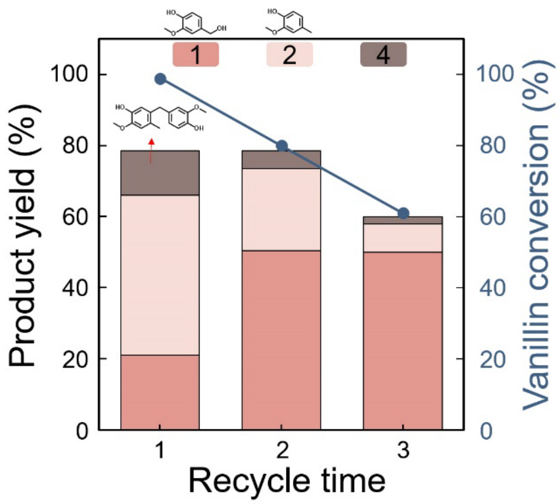

Fig. S4 Reusability of Ru/C catalyst over multiple reaction cycles exhibiting products of VANOL (1), CRSOL (2), dimer **1** (4). (Reaction conditions: 2 mmol of VAN, a mixed solvent of 30 mL of DI water and 15 mL of n-octane, 150 °C of reaction temperature, 1 h of reaction time, 0.05 g of 1 wt% Ru/C, catalyst/substrate = 0.17 w/w, 50 bar of H_2 pressure measured at room temperature)

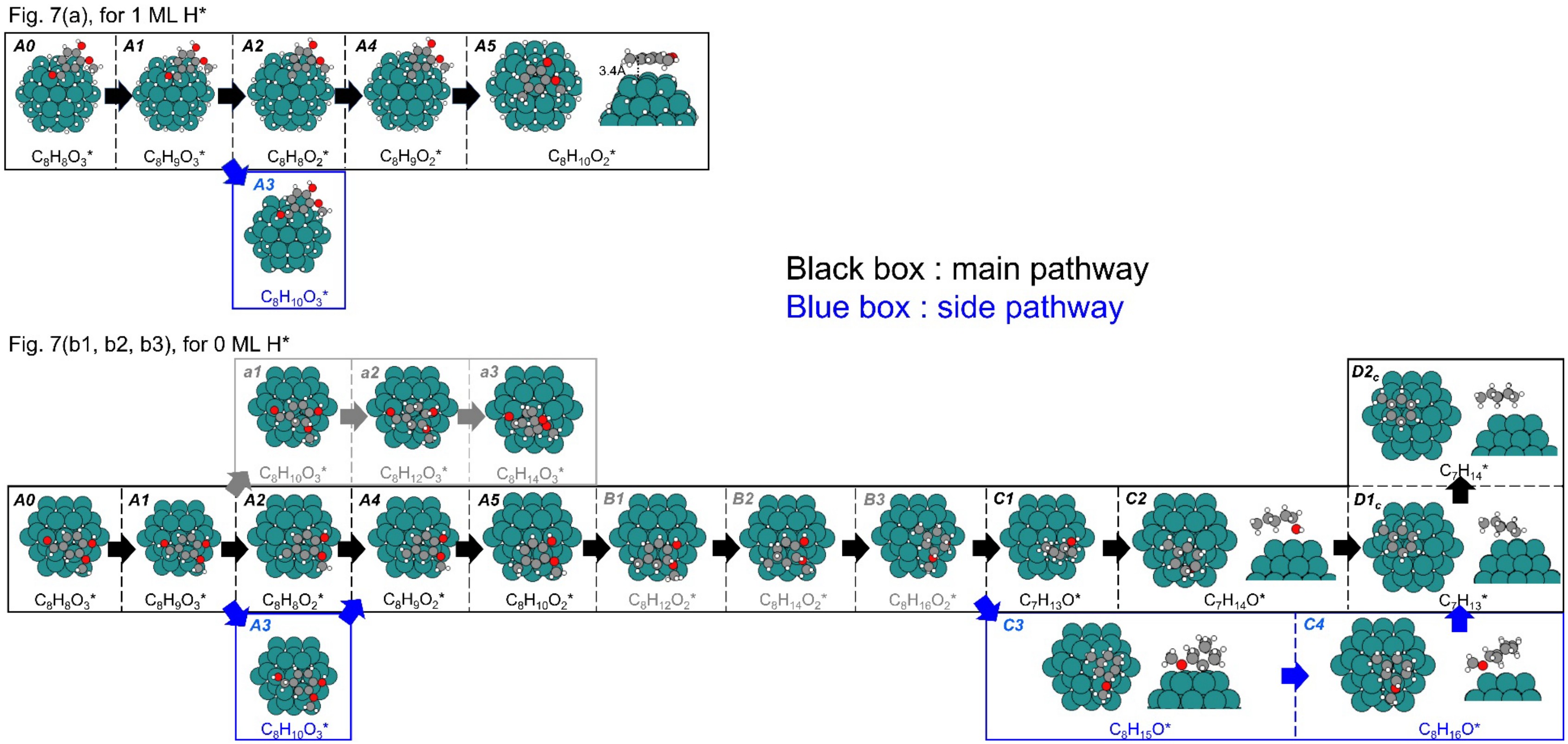

Fig. S5 DFT-calculated structures of reactants and intermediates on Ru surface depicted in Fig. 7.

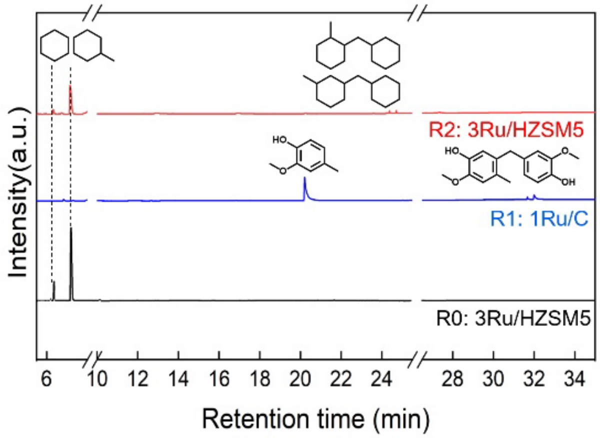

Fig. S6 GC-MS results for the second reaction for hydrodeoxygenation of a mixture containing dimer **1**. The first reaction (R1) is hydrogenation and condensation of VAN. (Reaction conditions: 2 mmol of VAN, a mixed solvent of 30 mL of DI water and 15 mL of n-octane, 0.05 g of 1 wt% Ru/C catalyst, 30 bar of H_2 pressure (measured at room temperature), 150 °C of reaction temperature, 3 h of reaction time.) The second reaction (R2) is hydrodeoxygenation of the product of R1. (Reaction conditions: a product mixture of R1 as a reactant, 0.3 g of 3 wt% Ru/HZSM-5 catalyst, 50 bar of H_2 pressure (measured at room temperature), 200 °C of reaction temperature, 3 h of reaction time.)

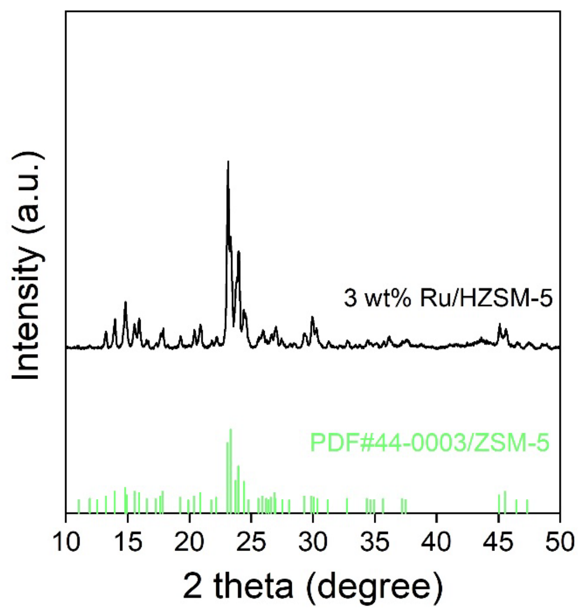

Fig. S7 XRD results of 3 wt% Ru/HZSM-5.