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One-pot catalytic hydrocracking of raw woody biomass into chemicals over supported carbide catalysts: simultaneous conversion of cellulose, hemicellulose and lignin

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1. Materials and analysis methods

Birch wood, poplar, pine, basswood, ashtree, beech, and xylosma, as well as yate, these lignocellulosic materials were obtained from Dalian Hongda Wood Co., Ltd, China. They were milled, screened into powders in size of < 40 meshes and dried under vacuum at 100 ^{o}C for 3 days before use. The standard samples ethylene glycol, 1,2- propylene glycol, 1,2-hexanediol, were purchased from Kemio Chemistry Co. Ltd., Tianjin, China. The standard samples 1,2-pentadiol, glyceraldehyde, (tetrahydrofuran-2-yl)methanol, 2-methoxyphenol, 4-methoxyphenol were obtained from Aladdin Chemistry Co. Ltd., Shanghai, China. 1,2-Butylene glycol, 2-ethylphenol, 2,6-dimethoxyphenol, hydroxyacetone, 4-ethyl-2-methoxyphenol, 4-ethylphenol, were obtained from Acros. Guaiacylpropane, 4-(2-hydroxyethyl)-2-methoxyphenol were purchased from Sigma. 4-allyl-2,6-dimethoxyphenol was purchased from ABCR Gmbh & Co. (Karlsruhe, Germany). Guaiacylpropanol was obtained from Tokyo Chemical Industry Co. Ltd. All other chemicals were supplied by local suppliers and used without further purification.

All the FT-IR spectra were collected on an FTIR spectrometer (Bruker Equinox 55 spectrometer) with a resolution of 4 cm^{-1} and 64 scans in the region of 4000–400 cm^{-1}. IR spectra of the biomass samples were recorded as KBr pellets. Elemental analysis (C, H, N, S) of biomass was done on a Vario MICRO elemental analyzer. Elemental analysis of the leached (or dissolved) catalyst was accomplished using a Thermo iCAP Model 6300 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP). X-ray diffraction (XRD) patterns of the catalysts were recorded on a PW3040/60 X' Pert PRO (PANalytical) diffractometer equipped with a Cu Kα radiation source (λ = 0.15432 nm), operating at 40 kV and 40 mA.

2. Supporting tables

Table S1 Element analysis of C, H, N, S contents in raw biomass (0.01%).

Entry	Analyze time	N (%)	H (%)	C (%)	S (%)
Birch	1	0	6.469	47.65	0.009
	2	0.064	6.392	47.66	
	Average	**0.032**	**6.431**	**47.66**	
Poplar	1	0.009	6.324	46.61	0.022
	2	0.007	6.312	46.55	
	Average	**0.008**	**6.318**	**46.58**	
Basswood	1	0.036	6.247	47.07	0.014
	2	0.042	6.234	47.03	
	Average	**0.039**	**6.241**	**47.05**	
Ashtree	1	0.025	6.197	47.26	0.021
	2	0.012	6.226	47.24	
	Average	**0.019**	**6.212**	**47.25**	
Beech	1	0.053	6.208	46.70	0.019
	2	0.043	6.180	46.74	
	Average	**0.048**	**6.194**	**46.72**	
Xylosma	1	0.058	6.153	47.52	0.012
	2	0.111	6.112	47.5	
	Average	**0.084**	**6.133**	**47.51**	
Pine	1	0.063	6.312	47.23	0.019
	2	0.057	6.367	47.23	
	Average	**0.06**	**6.34**	**47.23**	
Yate	1	3.17	5.955	45.17	0.030
	2	3.225	5.929	45.02	
	Average	**3.20**	**5.942**	**45.10**	
Corn stalk	1	**0.75**	**6.01**	**44.73**	0.146

The mass of C, H and N in feedstocks were determined by CHNS analyzer, (Vario EL III, Element, Germany). Surfur content was determined by EMIA-V2 series Carbon/Sulfur Combustion Analyzer.

Table S2. Carbon balance for the lignocellulose transformation over 4%metal-30%W_2C/AC catalysts. In this table, one can find that the carbon balances obtained over Ni-W_2C/AC are better than those of other catalysts.

Entry	Substrate	Catalyst	Conversion by weight %	C in liquid phase %	C in gas %				
					Total	CO	CH_4	CO_2	C_2H_6
1	Birch	Ni-W_2C/AC	89.7	89.7	1.11	0.06	0.13	0.92	0.00
2	Birch	Pd-W_2C/AC	90.0	79.6	1.94	0.06	0.30	1.38	0.20
3	Birch	Pt-W_2C/AC	90.1	73.2	2.83	0.15	0.24	1.89	0.55
4	Birch	Ir-W_2C/AC	85.8	79.8	2.72	0.00	1.53	0.70	0.49
5	Birch	Ru-W_2C/AC	91.5	10.0	72.08	3.77	59.93	0.00	8.39
6	Poplar	Ni-W_2C/AC	88.1	85.1	3.78	0.07	0.28	3.43	0.00
7	Basswood	Ni-W_2C/AC	86.4	83.2	2.87	0.16	0.26	1.90	0.55
8	Ashtree	Ni-W_2C/AC	91.7	86.7	1.15	0.06	0.11	0.98	0.00
9	Beech	Ni-W_2C/AC	88.0	87.7	1.74	0.13	0.19	1.42	0.00
10	Xylosma	Ni-W_2C/AC	88.0	81.8	1.82	0.12	0.15	1.55	0.00
11	Bagasse	Ni-W_2C/AC	91.8	76.2	4.14	0.16	0.36	3.62	0.00
12	Pine	Ni-W_2C/AC	77.5	67.8	1.52	0.05	0.16	1.31	0.00
13	Yate	Ni-W_2C/AC	76.2	62.0	4.14	0.16	0.36	3.62	0.00

The mass of carbon in liquid phase was determined by elemental liqui TOC, Germany. Carbon in gas was detected using a gas chromatograph (Agilent 6890N, TCD detector, Paropak Q column) and was calculated by the method described in our previous study. (M. Zheng, A. Wang, N. Ji, J. Pang, X. Wang and T. Zhang, *ChemSusChem*, 2010, 3, 63.)
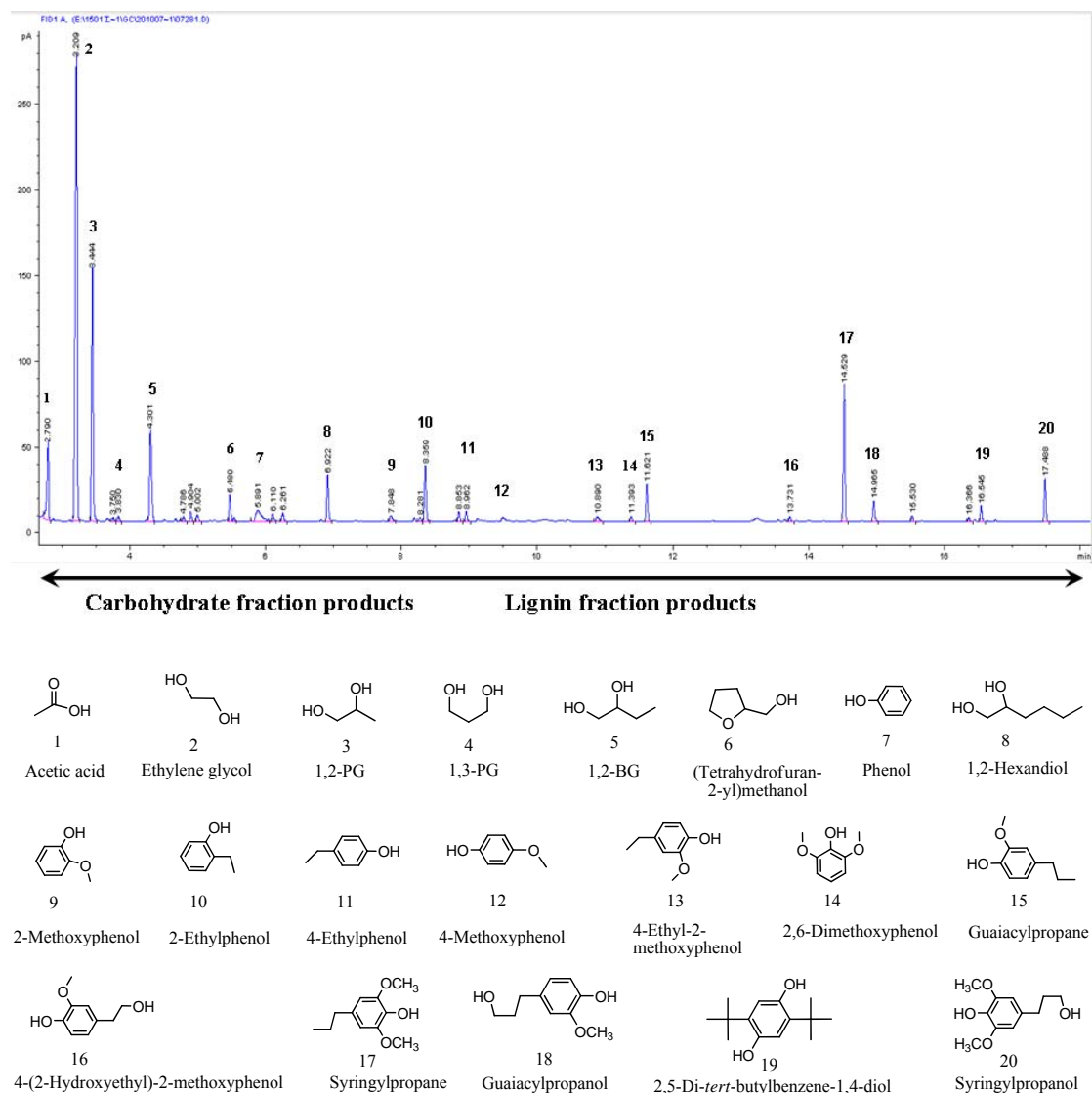
3. Supporting Figures

Fig. S1 Typical GC-FID trace of the liquids products of birch wood hydrogenation sample. GC condition: Aglient 6890 GC, HP-5 column (30 m × 0.32 mm × 0.25 μm), inject. 280 °C, oven: 10 °C/min, from 70 °C to 280 °C, retain 5 min, FID detec. 300 °C. 2-Ethylphenol (compound 10) is the internal standard. All the MS spectra are omitted, they have been conformed by standard samples.
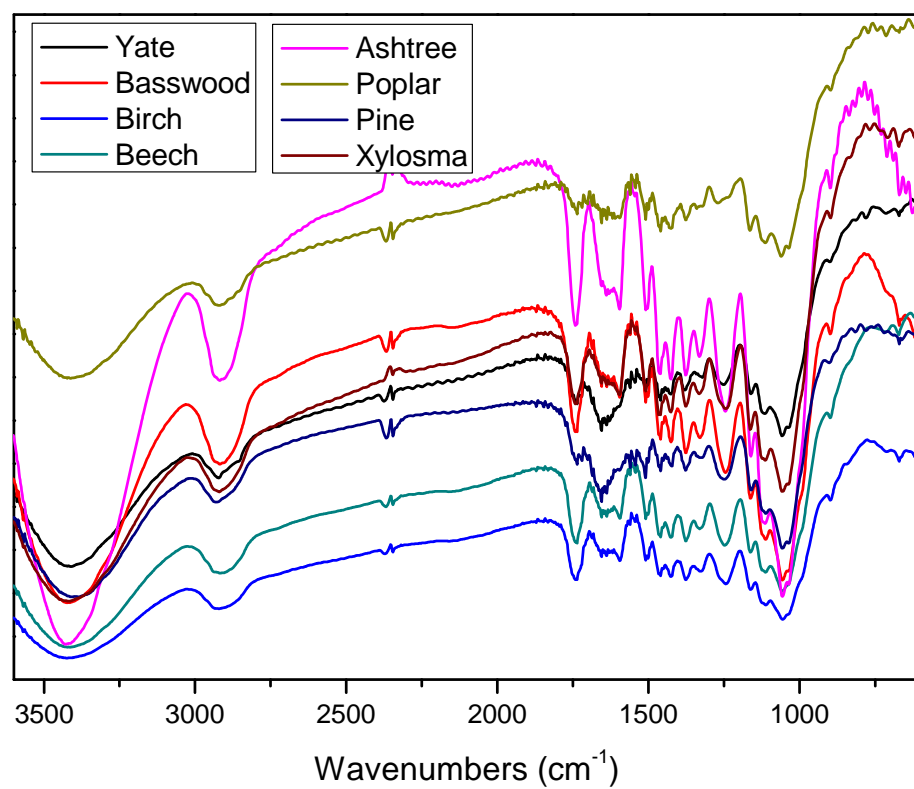
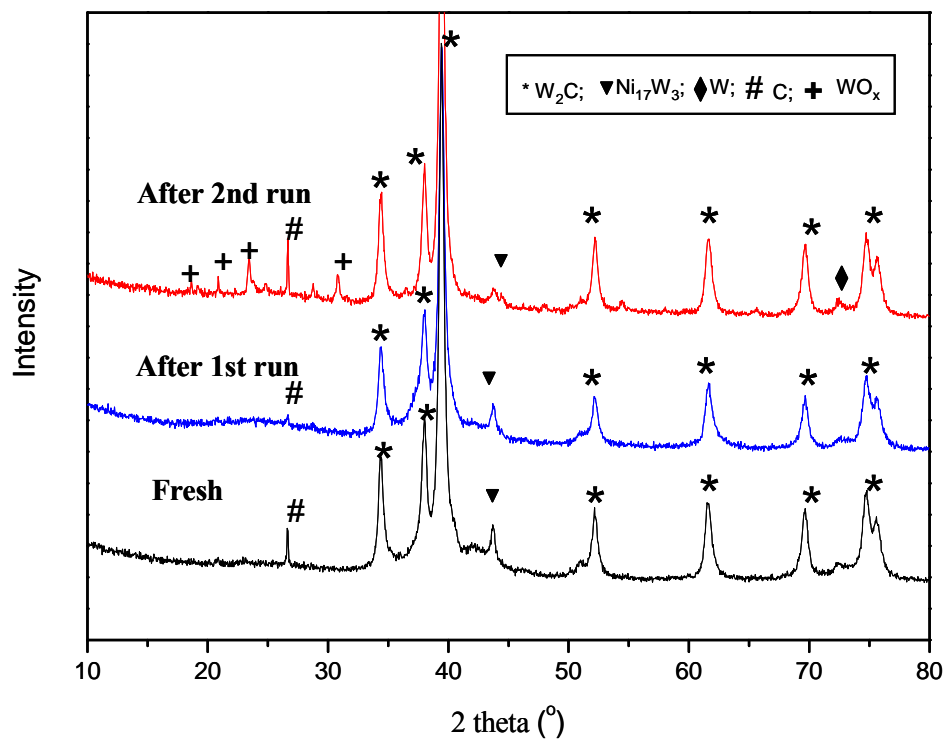**Fig. S2** The FT-IR spectra of various raw woody biomass samples.

Fig. S3 XRD patterns of Ni-W$_2$C/AC catalyst before and after reaction
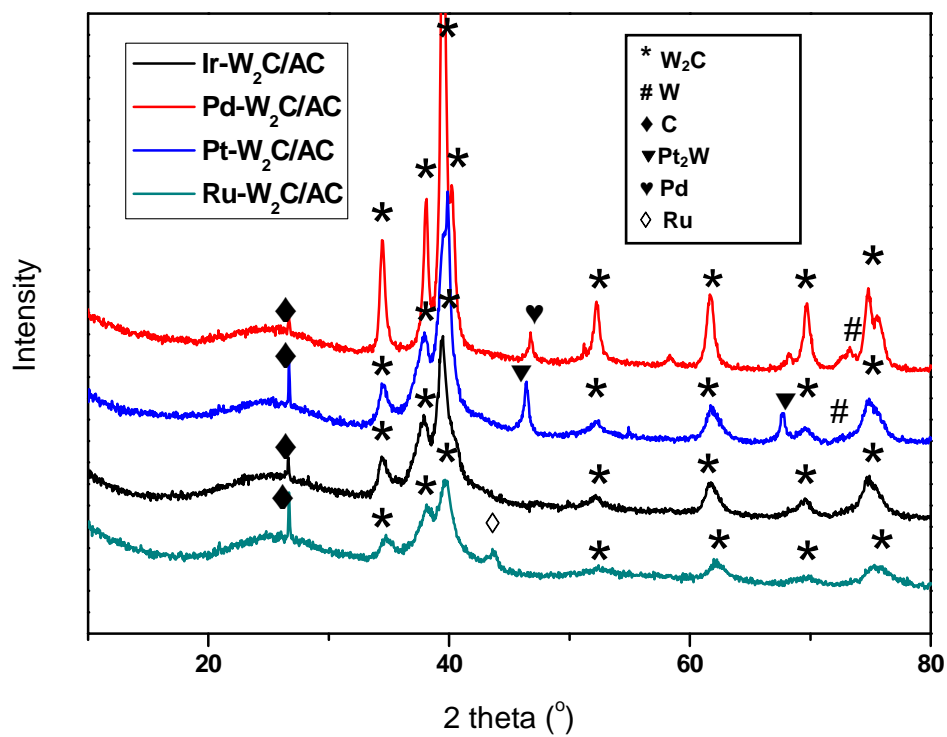
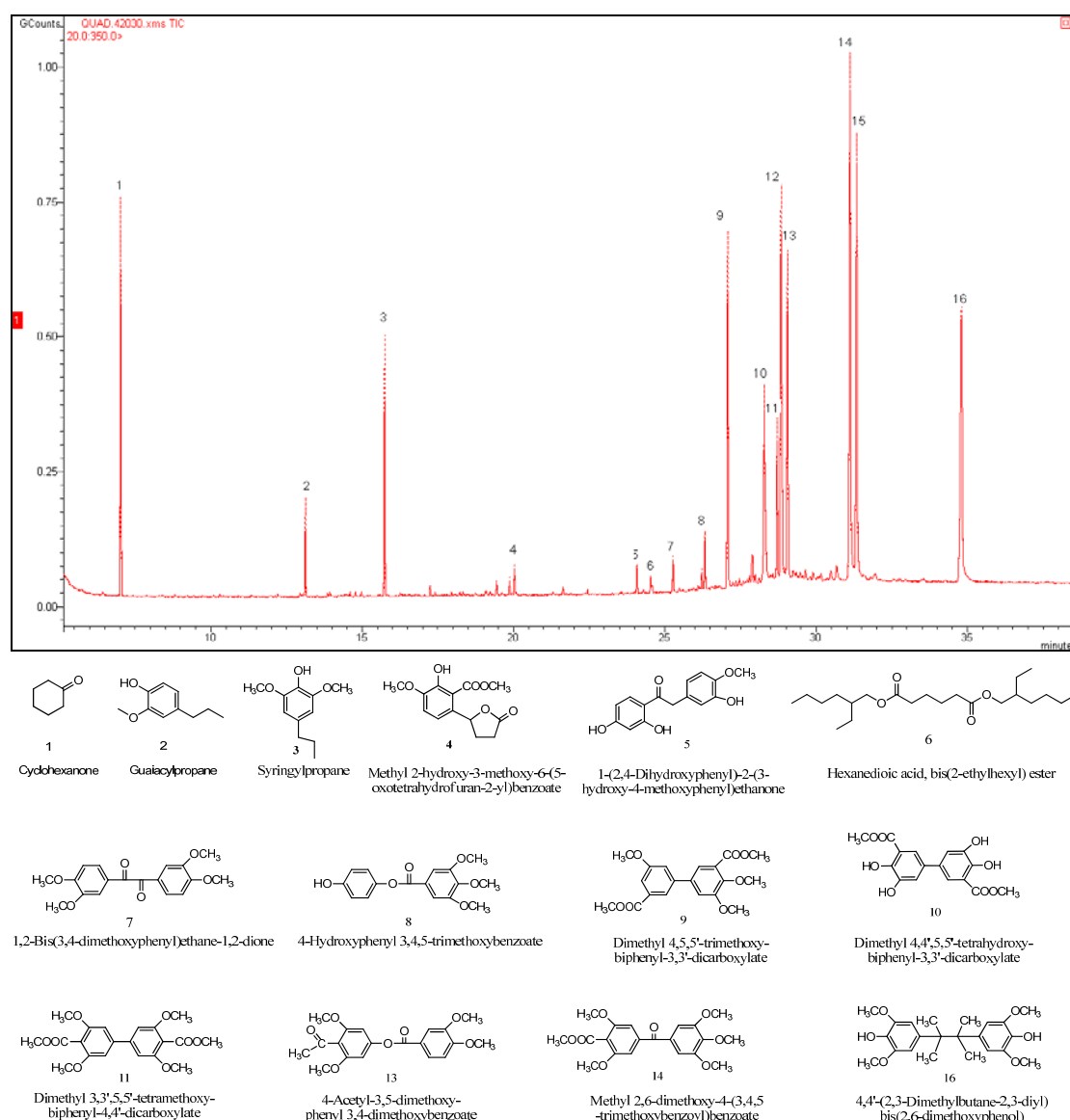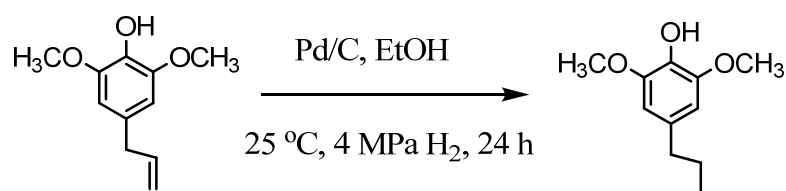**Fig. S4** XRD patterns of noble metals promoted W_2C/AC catalysts

Fig. S5 GC-MS total ion current trace of the tar that generated in the fourth run over Ni-W$_2$C/AC catalyst. After the fourth run, the tar mixed with the catalyst was cautiously collected with scoop and was subsequently dissolved in CH$_2$Cl$_2$, the solid residue was separated by filtration, and the filtrate was sent for GC-MS analysis. It was found that many kinds of phenol derivatives were detected. The following tabulated products are some of the phenol derivatives that we have confirmed.

NO	Name	Formula	MW:
1	Cyclohexanone	C$_6$H$_{10}$O	98
2	Guaiacylpropane	C$_{10}$H$_{14}$O$_2$	166
3	Syringylpropane	C$_{11}$H$_{16}$O$_3$	196
4	Methyl 2-hydroxy-3-methoxy-6-(5-oxotetrahydrofuran-2-yl)benzoate	C$_{12}$H$_{12}$O$_5$	236
5	1-(2,4-Dihydroxyphenyl)-2-(3-hydroxy-4-methoxyphenyl)ethanone	C$_{15}$H$_{14}$O$_5$	274
6	Hexanedioic acid, bis(2-ethylhexyl) ester	C$_{22}$H$_{42}$O$_4$	370
7	1,2-Bis(3,4-dimethoxyphenyl)ethane-1,2-dione	C$_{18}$H$_{18}$O$_6$	330

8	4-Hydroxyphenyl 3,4,5-trimethoxybenzoate	$C_{16}H_{16}O_6$	304
9	Dimethyl 4,5,5'-trimethoxy-biphenyl-3,3'-dicarboxylate	$C_{19}H_{38}O_4$	330
10	Dimethyl 4,4',5,5'-tetrahydroxy-biphenyl-3,3'-dicarboxylate	$C_{16}H_{14}O_8$	334
11	Dimethyl 3,3',5,5'-tetramethoxy-biphenyl-4,4'-dicarboxylate	$C_{20}H_{22}O_8$	390
12	Unknown	$C_{20}H_{24}O_6$	360
13	4-Acetyl-3,5-dimethoxy-phenyl 3,4-dimethoxybenzoate	$C_{19}H_{20}O_7$	360
14	Methyl 2,6-dimethoxy-4-(3,4,5-trimethoxybenzoyl)benzoate	$C_{20}H_{22}O_8$	390
15	Unknown	$C_{21}H_{26}O_7$	390
16	4,4'-(2,3-Dimethylbutane-2,3-diyl)bis(2,6-dimethoxyphenol)	$C_{20}H_{22}O_8$	390

4. Preparation of standard compound 2,6-dimethoxyl-4-propylphenol

0.99 g 4-allyl-2,6-dimethoxyphenol and 0.1 g 5 wt% Pd/C was placed in 10 ml ethanol and transferred in 100 ml autoclave. The mixture was treated with 4 MPa H_2 at room temperature for 24 h. Then, the solution was filtered and the solvent was removed under vacuum to provide a colorless oil, this oil was purified by column chromatography on silica gel (petroleum ether: dichloromethane = 20 : 1 to 5 : 1), affording 0.91 g 2,6-dimethoxy-4-propylphenol with the yield of 92%. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.39 (s, 2H), 5.51 (s, 1H), 3.82 (s, 6H), 2.51-2.47 (t, 6H), 1.65-1.56 (m, 2H), 0.95-0.91 (t, 3H). ^{13}C NMR (100MHz, CDCl$_3$) δ = 146.79, 133.64, 132.65, 104.97, 56.07, 38.14.

13C NMR (LCZ in CDCl3)