Supporting Information for Publication

Palladium Single-Atom Catalysts Supported on Ceria for α-Alkylation of Ketones with Primary Alcohols

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I. General information and experimental section

General Information:

XRD measurements were conducted by using a Smartlab-SE automated transmission diffractometer (STOE) equipped with an incident beam curved germanium monochromator with CuKa1 radiation and current of 40 kV and 150 mA, respectively. The XRD patterns were scanned in the 2 Theta range of 10-90 °. XPS were obtained using a Escalab 250Xi instrument equipped with monochromatic Al target and dual anode Al/Mg target X-ray sources, including large-area XPS, micro-area XPS and XPS parallel imaging. The electron binding energy was referenced to the C1s peak at 284.8 eV. The background pressure in the chamber was less than 10^{-7} Pa. The peaks were fitted by Gaussian–Lorentzian curves after a Shirley background subtraction. For quantitative analysis, the peak area was divided by the element-specific Scofield factor and the transmission function of the analyzer. The BET surface area measurements were performed on a Quantachrome IQ_2 at the temperature of 77 K. The pore size distribution was calculated from the desorption isotherm by using the Barrett, Joyner, and Halenda (BJH) method. Prior to measurements, the samples were degassed at 300 ^{o}C for 3 h, at a rate of 10 ^{o}C•min^{-1}. Transmission electron microscope (TEM) was carried out on a FEI Tecnai G2 F20S-Twin using an accelerating voltage of 200 kV. For sample preparation, the powders were dispersed in ethanol with the assistance of sonication, and one drop of the solution was dropped onto a micro grid. NMR spectra were measured by using a Bruker ARX 400 spectrometer at 400 MHz (^{1}H).

Experimental Section:

All solvents and chemicals were used without any further purification.

Preparation of CeO_2 nanorods (CeO_2-C)[1, 2]

The typical process for the preparation of CeO_2 rods is as follows: 1.96 g $Ce(NO_3)_3 \cdot 6H_2O$ was dissolved in 40 mL deionized water, 16.88 g NaOH was dissolved in 30 mL deionized water and added dropwise after cooling to room temperature. Then, the mixed solution was stirred quickly for 30 min with a magnetic stirrer. The obtained suspension was then transferred into a 100 mL hydrothermal reactor, which was sealed and maintained at 180 °C for 24 h and then cooled to ambient temperature. The resulting precipitates were separated by centrifuging and washing with distilled water (until pH = 7) several times. Finally, the CeO_2-C samples were obtained by drying at 80 °C for 16 h and calcining in air at 500 °C for 4 h at a ramping rate of 5 °C min^{-1}.

Preparation of CeO_2 nanorods (CeO_2-R)[1, 2]

The typical process for the preparation of CeO_2 rods is as follows: 1.96 g $Ce(NO_3)_3 \cdot 6H_2O$ was dissolved in 40 mL deionized water, 16.88 g NaOH was dissolved in 30 mL deionized water and added dropwise after cooling to room temperature. Then, the mixed solution was stirred quickly for 30 min with a magnetic stirrer. The obtained suspension was then transferred into a 100 mL hydrothermal reactor, which was sealed and maintained at 100 °C for 24 h and then cooled to ambient temperature. The resulting precipitates were separated by centrifuging and washing with distilled water (until pH = 7) several times. Finally, the CeO_2-NR samples were obtained by drying at 80 °C for 16 h and calcining in air at 500 °C for 4 h at a ramping rate of 5 °C min^{-1}.

Preparation of CeO_2 octahedrons (CeO_2-O)[3]

The typical process for the preparation of CeO_2 octahedrons is as follows: 1.96 g $Ce(NO_3)_3 \cdot 6H_2O$ was dissolved in 40 mL deionized water, 36 mg NaOH was dissolved in 30 mL deionized water and added dropwise after cooling to room temperature. Then, the mixed solution was stirred quickly for 30 min with a magnetic stirrer. The obtained suspension was then transferred into a 100 mL hydrothermal reactor, which was sealed and maintained at 180 °C for 24 h and then cooled to ambient temperature. The resulting precipitates were separated by centrifuging and washing with distilled water (until pH = 7) several times. Finally, the CeO_2-O samples were obtained by drying at 80 °C for 16 h and calcining in air at 500 °C for 4 h at a ramping rate of 5 °C min^{-1}.

Preparation of CeO_2 polyhedrons (CeO_2-P)[4]

In a standard preparation process of CeO_2-P, 5.208 g of $Ce(NO_3)_3\cdot 6H_2O$ and 60 mL of deionized water were mixed under magnetic stirring, followed by adding 1.5 g of poly(vinyl pyrrolidone) under stirring for an additional 30 min. After a clear solution was formed, 13 mL of $N_2H_4\cdot H_2O$ (80%) was added slowly under stirring for 15 min. The resulting solution was then moved into the 100 mL reactor and treated at 180 °C for 12 h. Finally, the precipitation was then purified by centrifugation. After it was rinsed using deionized water (until pH = 7) and pure ethanol for an additional three times, the CeO_2-P samples were obtained by drying at 80 °C for 16 h and calcining in air at 500 °C for 4 h at a ramping rate of 5 °C min^{-1}.

Preparation of different Pd/CeO_2 catalysts

$Pd(OAc)_2$ (10.6 mg) was added to 5.0 mL acetone and agitated at room temperature until complete dissolution. Then 500 mg CeO_2-C/CeO_2-R/CeO_2-O/CeO_2-P powder was added and the mixture was stirred at room temperature overnight resulting in a dry powder. The obtained dry power was calcined in air with a heating ramp of 5 °C/min to 400 °C and held at that temperature for 4 h to obtain the final catalyst sample, which is denoted as Pd/CeO_2-C, Pd/CeO_2-R, Pd/CeO_2-O and Pd /CeO_2-P.

General procedure for the α-alkylation of ketones with primary alcohols

A mixture of ketone 1 (1.0 mmol), alcohols 2 (1.2 mmol), K_3PO_4 (53 mg, 0.25 mmol), Pd/CeO_2-C (40 mg), and n-hexane (4 mL) were added to a 15 mL press tube and exchanged with Ar. The press tube was sealed by a screw cap. The reaction mixture was stirred at 130 ^{o}C for 12 h. After the reaction finished, 1,3,5-trimethoxybenzene (56.0 mg, 0.33 mmol) was added to mixture. Then the crude reaction mixture was diluted with ethyl acetate, stirred, and filtered. Next, filtrate was concentrated by rotary evaporator under vacuum. The obtained residue was dissolved in $CDCl_3$ and subjected for NMR analysis.

For each catalyst recycling, the Pd/CeO_2-C catalyst was separated by centrifugation, washed with water (8 mL x 2), acetone (8 mL x 3), dried under air at room temperature and then reused for the next run.

II. Characterization results of catalysts

1. **Table S1** The physical properties of catalysts

Entry	Catalyst	Pd (wt%) [a]	SA ($m^2\ g^{-1}$) [b]	APR (nm) [b]	PV ($cm^3\ g^{-1}$) [b]
1	CeO_2-C	--	50.2	9.8	0.246
2	CeO_2-R	--	125.1	6.2	0.388
3	CeO_2-P	--	49.0	10.8	0.265
4	CeO_2-O	--	51.1	7.6	0.194
5	Pd/CeO_2-C	1.2	45.5	9.2	0.209
6	Pd/CeO_2-R	1.2	107.1	7.2	0.387
7	Pd/CeO_2-P	1.1	45.9	9.6	0.221
8	Pd/CeO_2-O	0.9	31.8	12.1	0.193

[a] Determined by ICP-AES. [b] Determined by an IQ_2 automated gas sorption analyzer. SA: BET surface area; APS: average pore radius; PV: pore volume.

Table S2 Best-fit parameters extracted from the Pd K-edge FT EXAFS ppectra of Pd/CeO_2-C and Pd/CeO_2-C-used catalyst

Sample	**Edge**	**Path**	**CN**	**R(Å)**	**σ^2(10^{-3} Å)**	**ΔE_0(eV)**	**R-factor**
Pd/CeO_2-C	Pd-K	Pd-O	2.89	2.05	1.00	4.35	0.010
		Pd-Ce	0.74	2.66	2.11	-7.72	
Pd/CeO_2-C-used	Pd-K	Pd-O	3.33	2.07	4.26	5.29	0.013
		Pd-Ce	0.75	2.60	2.44	-17.82	

Notes: CN, coordination number; R, distance between absorber and backscatter atoms. σ2, Debye-Waller factor; ΔE_0, the inner potential difference between the reference compound and the experimental sample. R-factor, the goodness of fit.

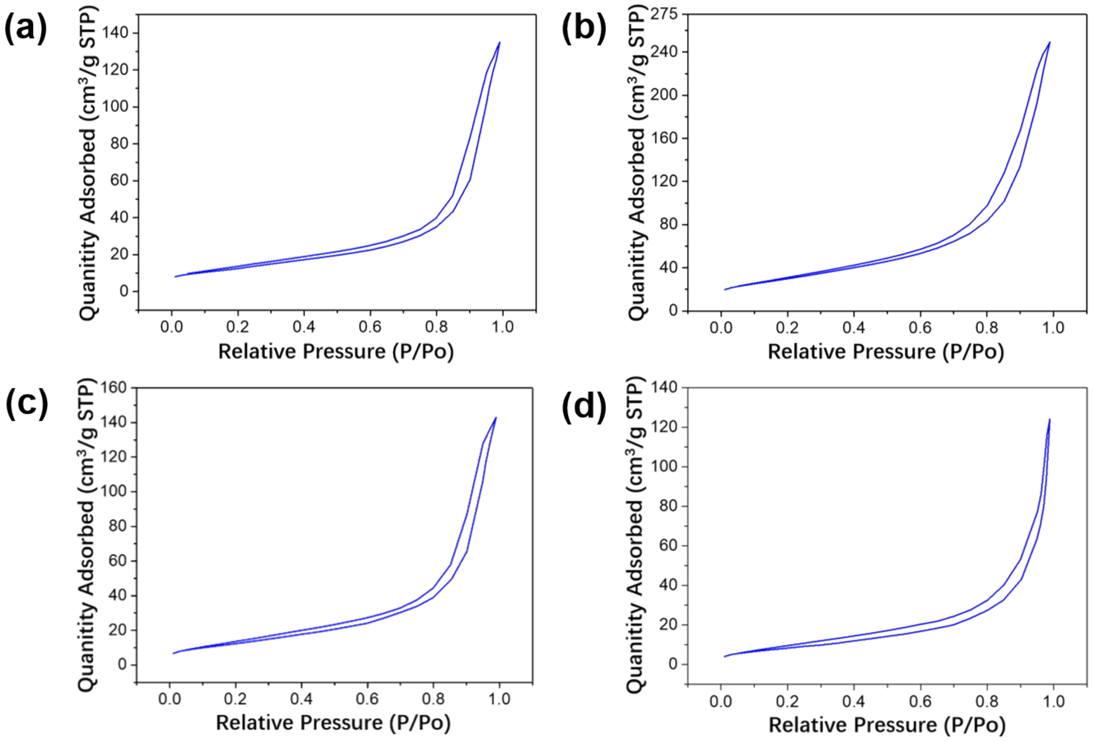


Fig. S1 N_2 adsorption-desorption isotherm of Pd/CeO_2 samples. (a) Pd/CeO_2-C, (b) Pd/CeO_2-R, (c) Pd/CeO_2-P, (d) Pd/CeO_2-O.

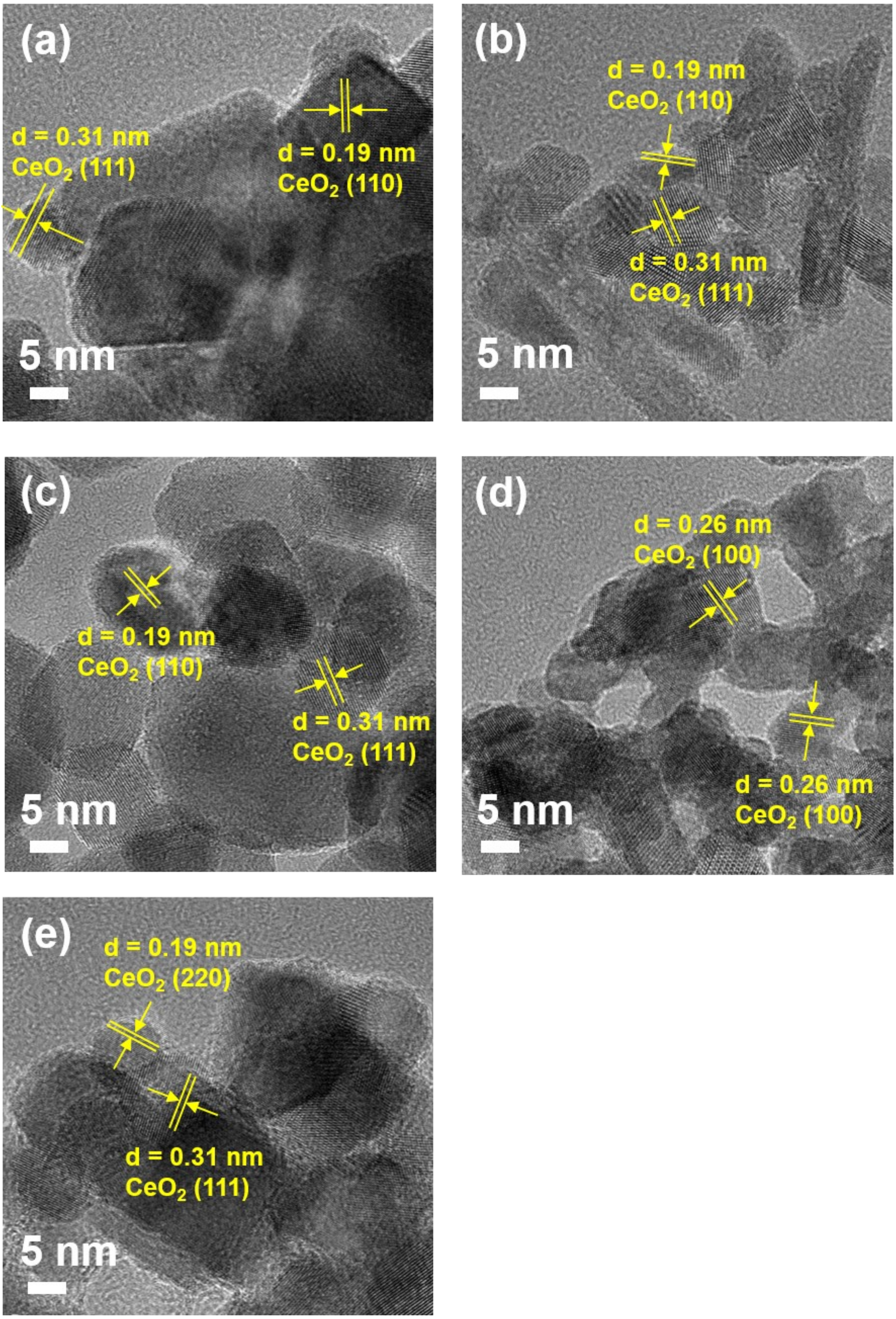


Fig. S2 HR-TEM images of the Pd/CeO$_2$ samples. (a) Pd/CeO$_2$-C, (b) Pd/CeO$_2$-R, (c) Pd/CeO$_2$-P, (d) Pd/CeO$_2$-O, (e) Pd/CeO$_2$-C-used.

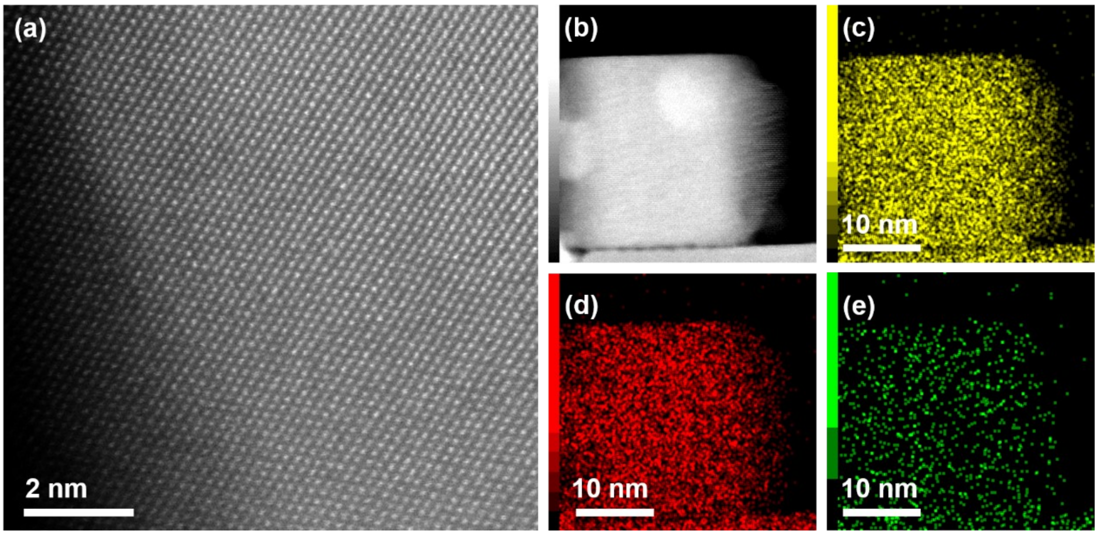


Fig. S3 AC HAADF-STEM image (a) and EDX mappings (b-e) of Pd/CeO_2-C-used catalyst.

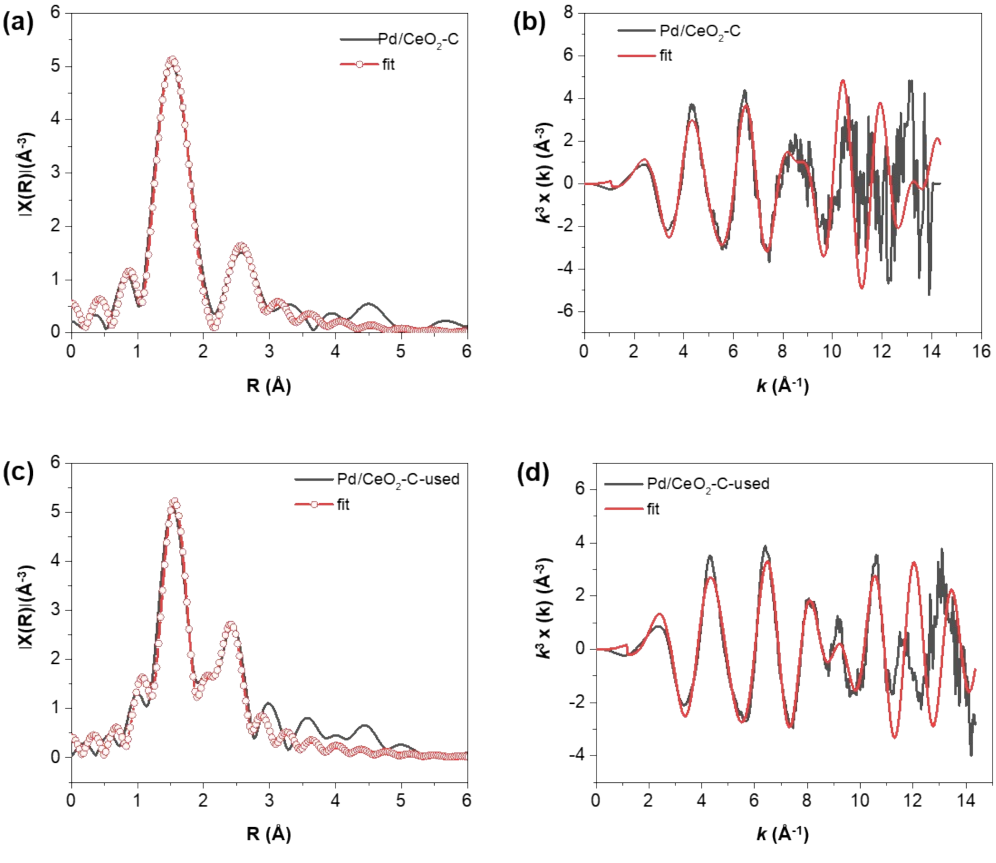
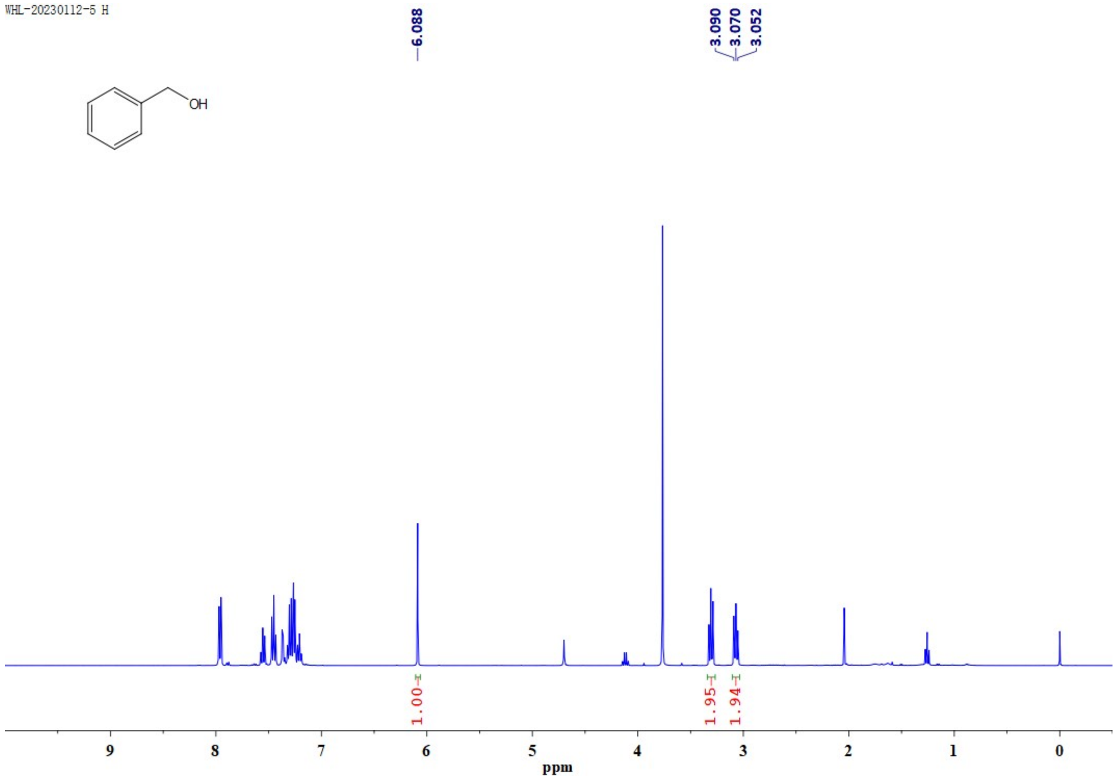
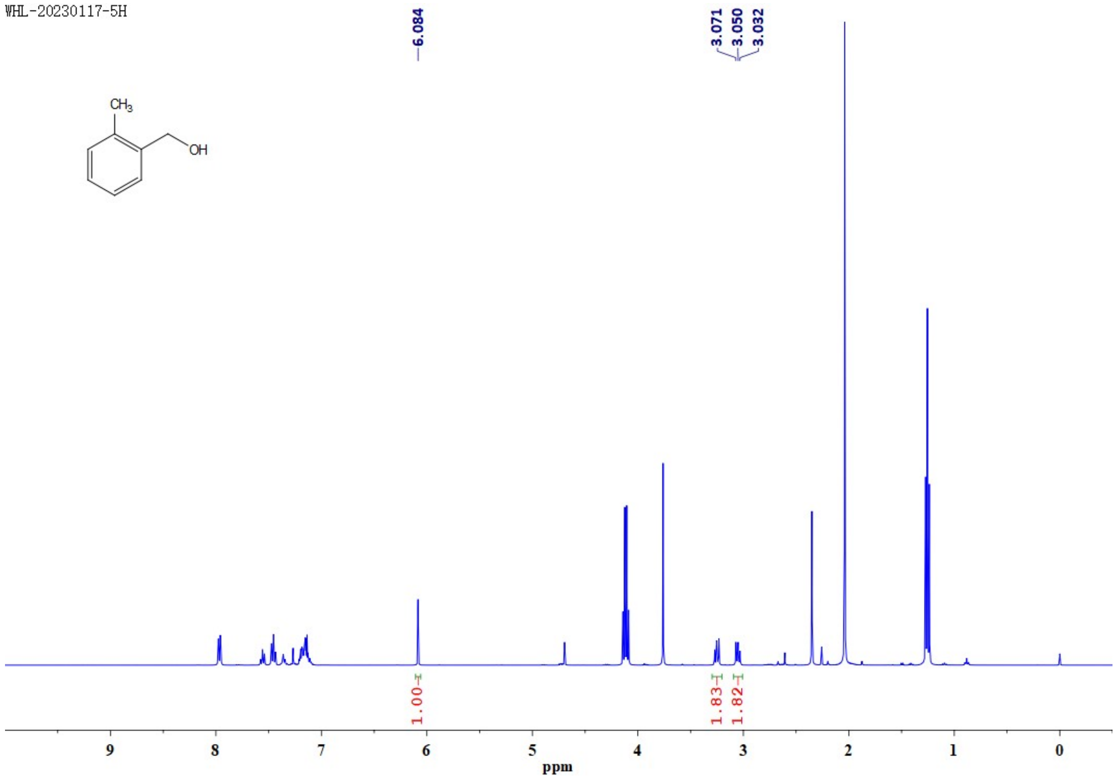
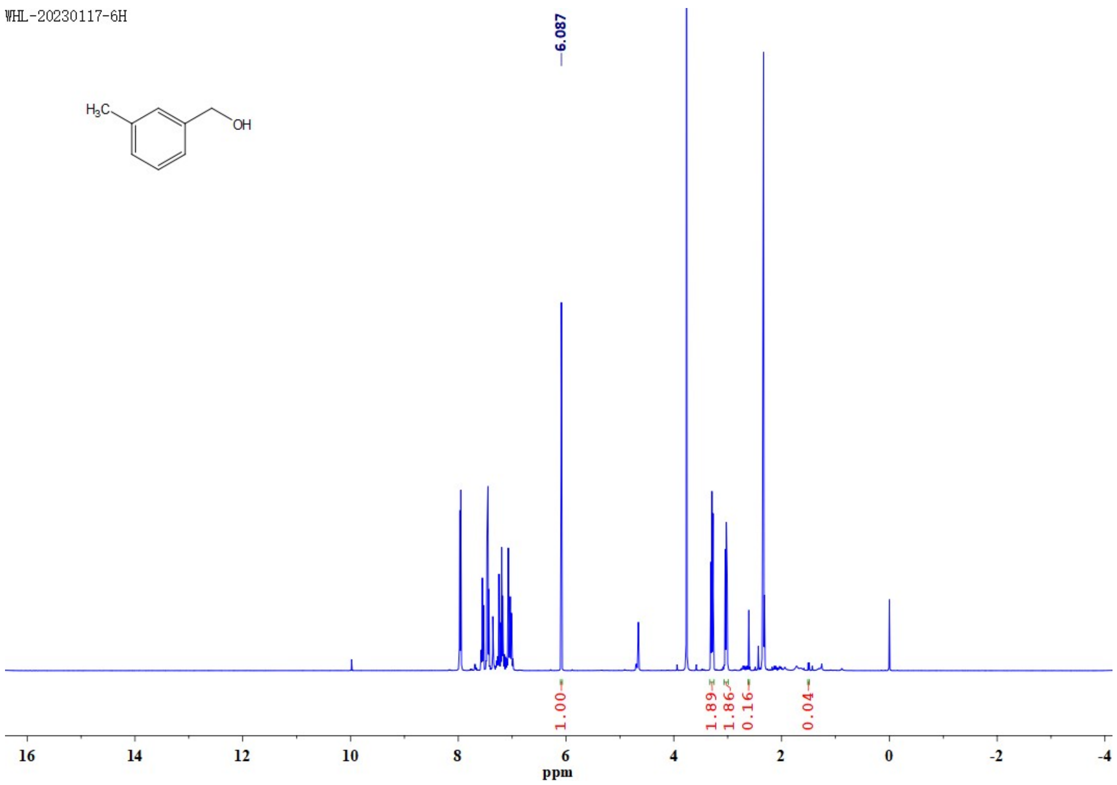


Fig. S4 Fitting results (a, c) for Pd/CeO_2-C and Pd/CeO_2-C-used catalyst and *k*-space spectra (b, d) of Pd/CeO_2-C and Pd/CeO_2-C-used catalyst.

III NMR spectra of the products



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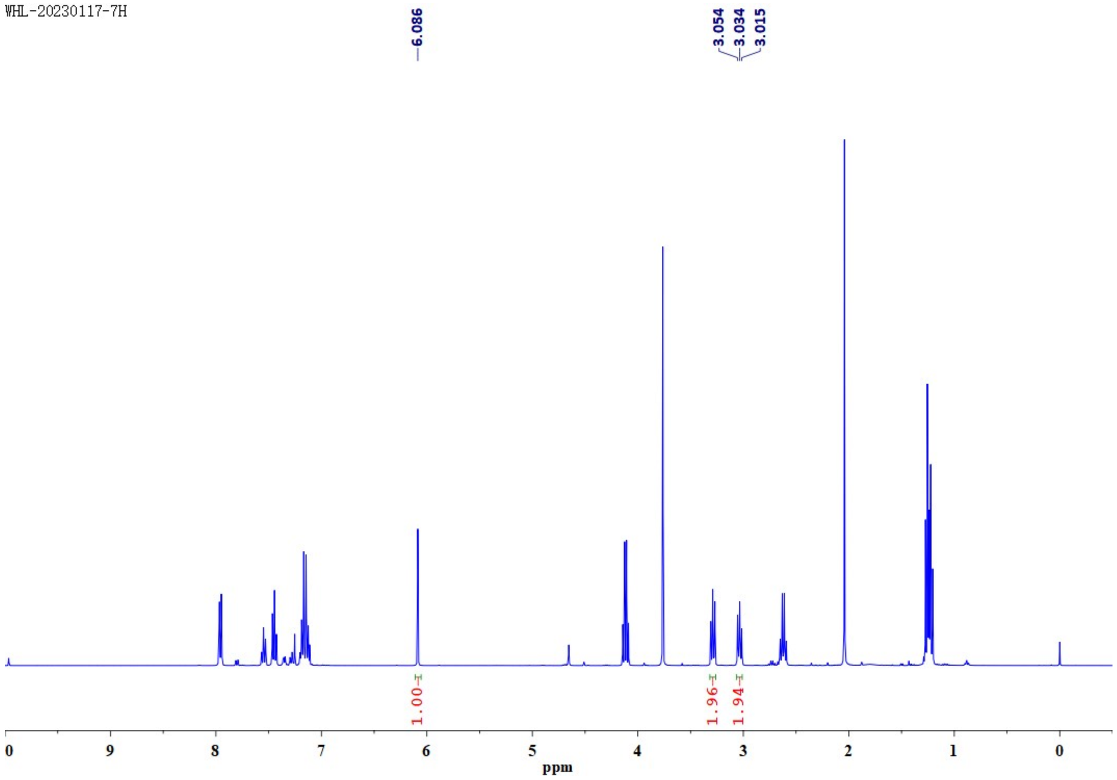
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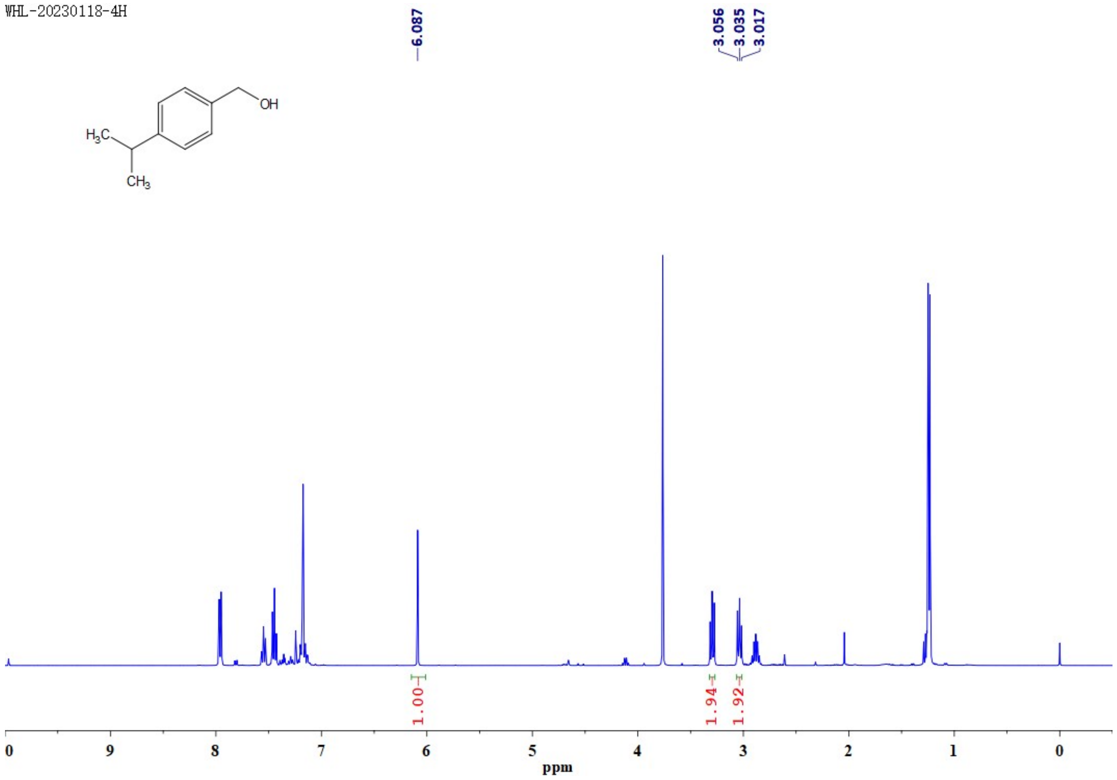
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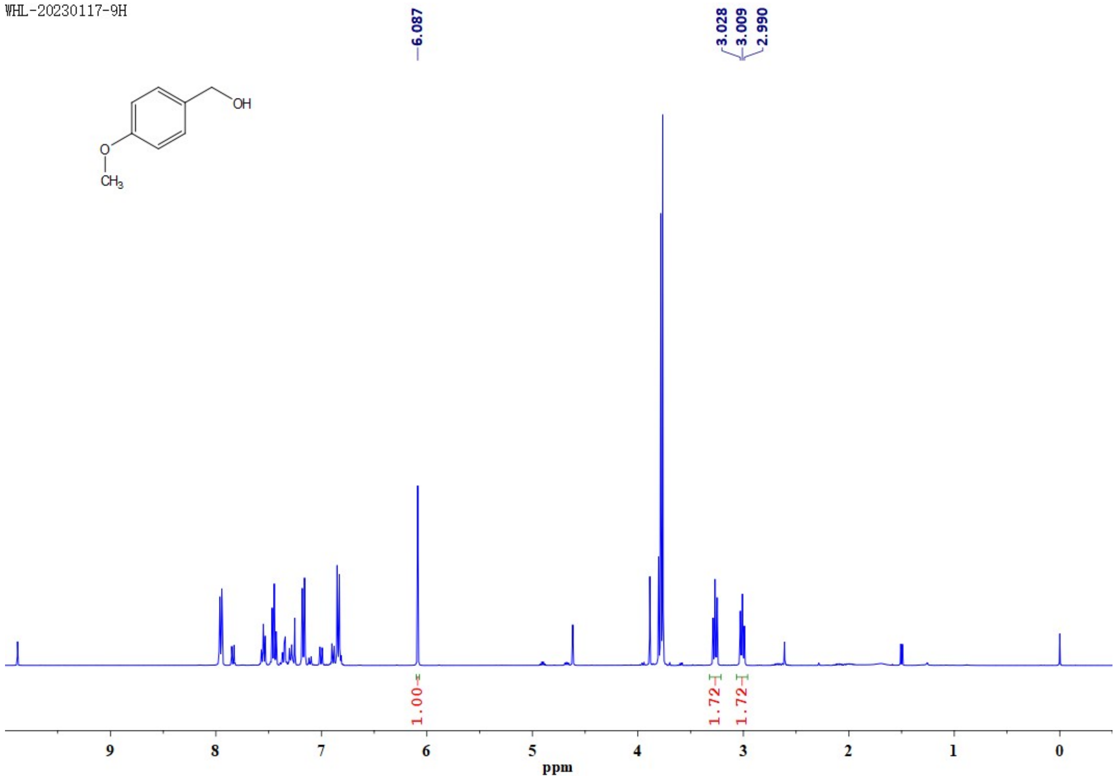
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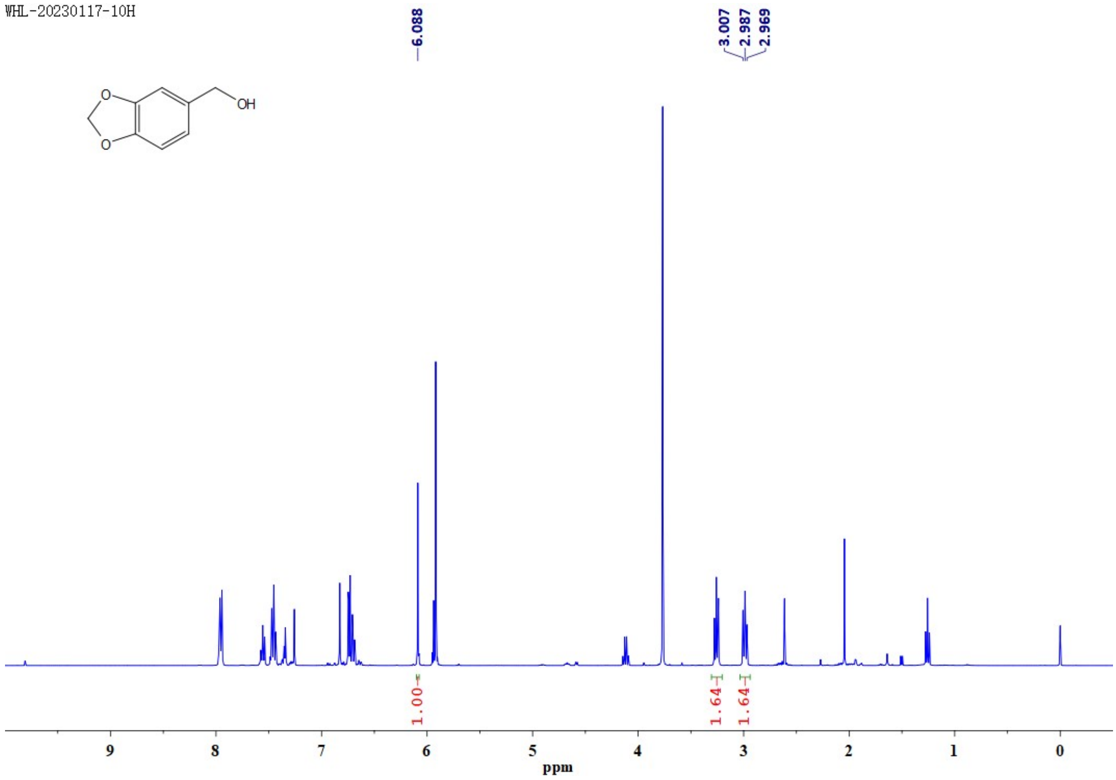
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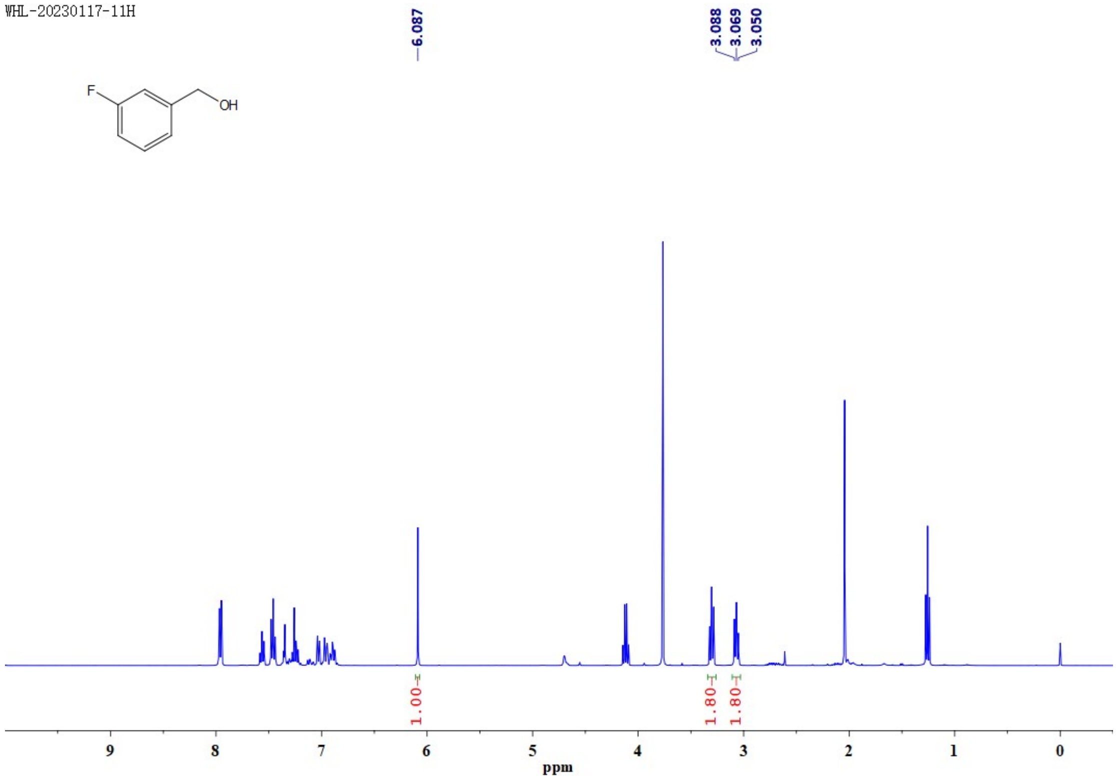
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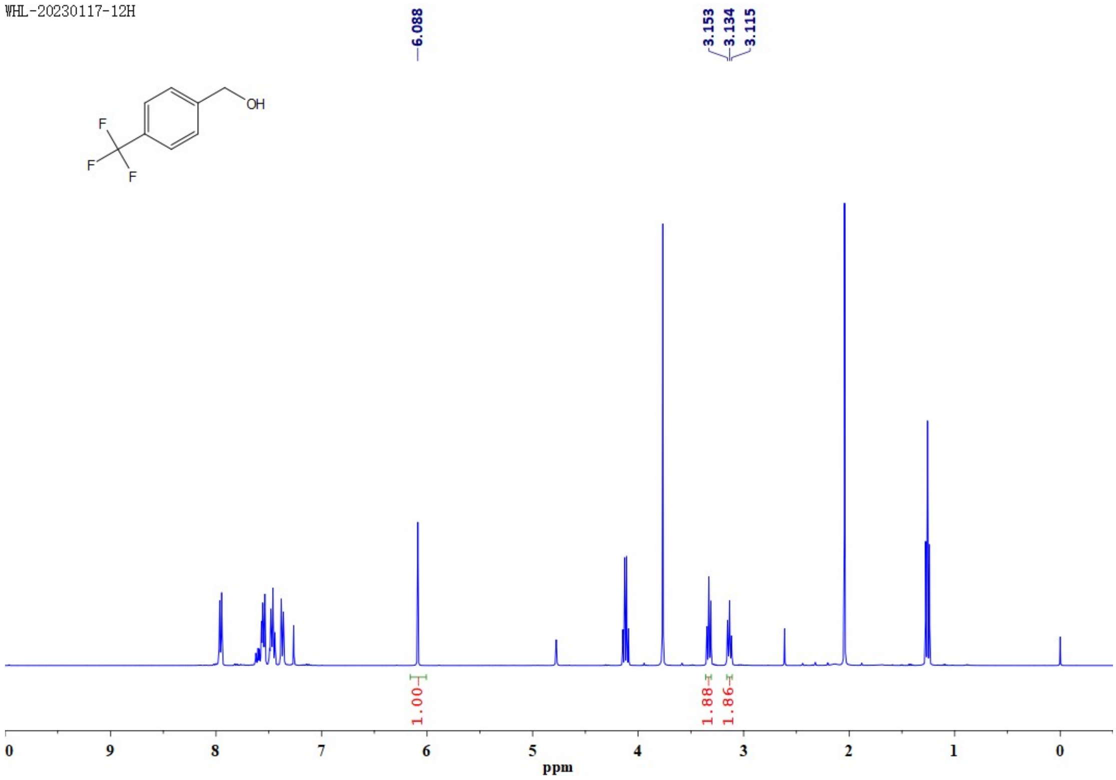
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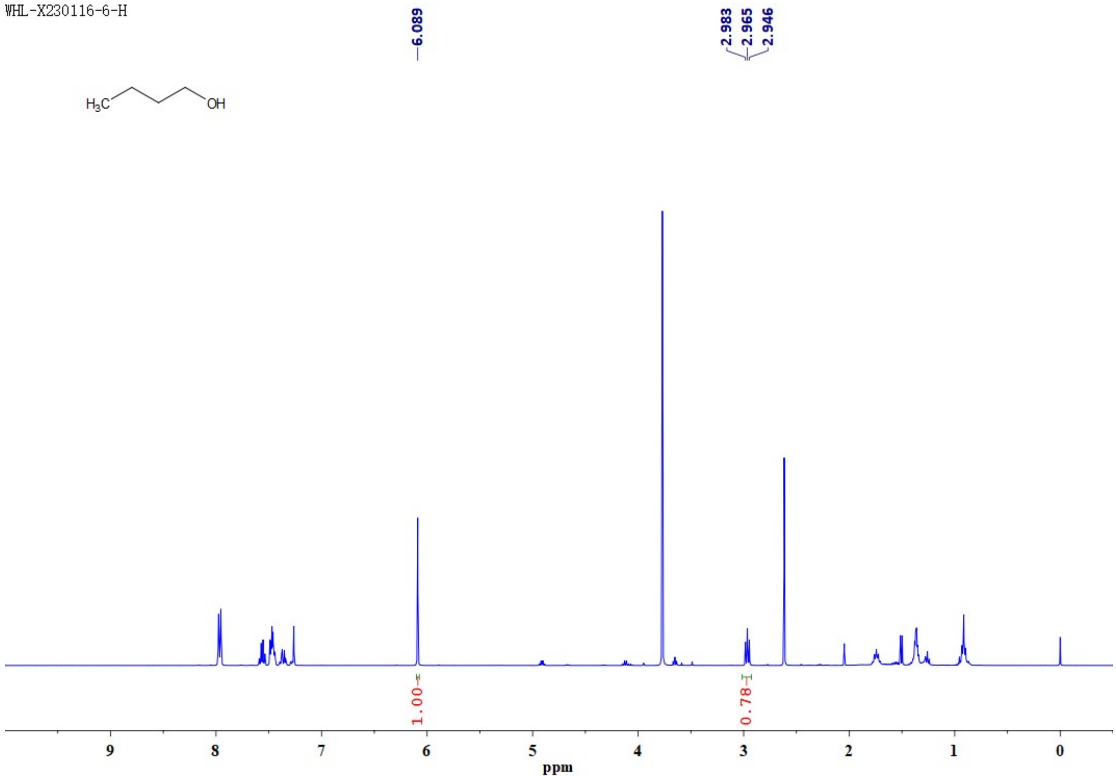
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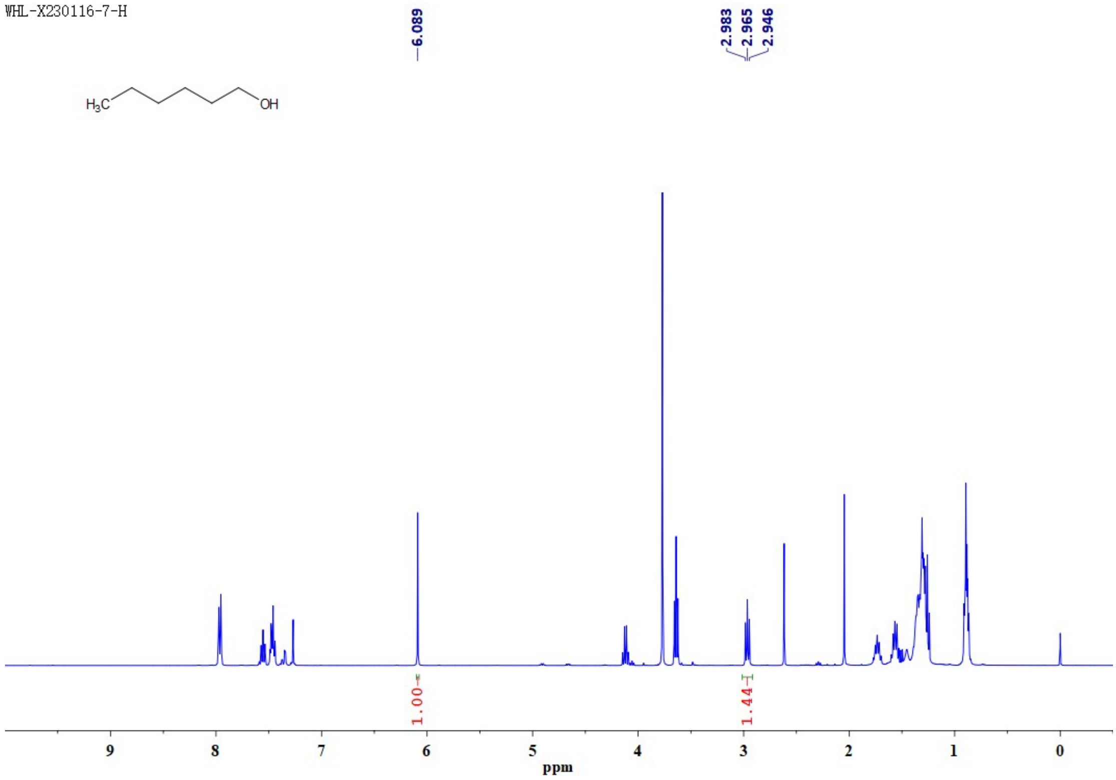
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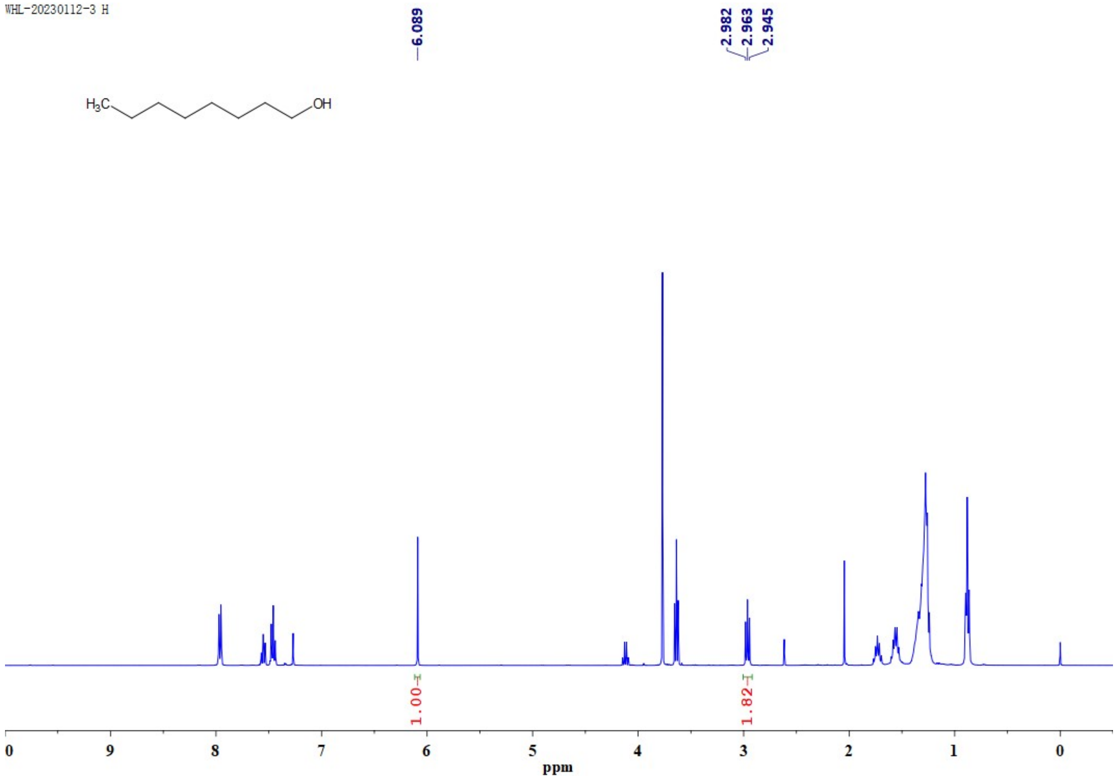
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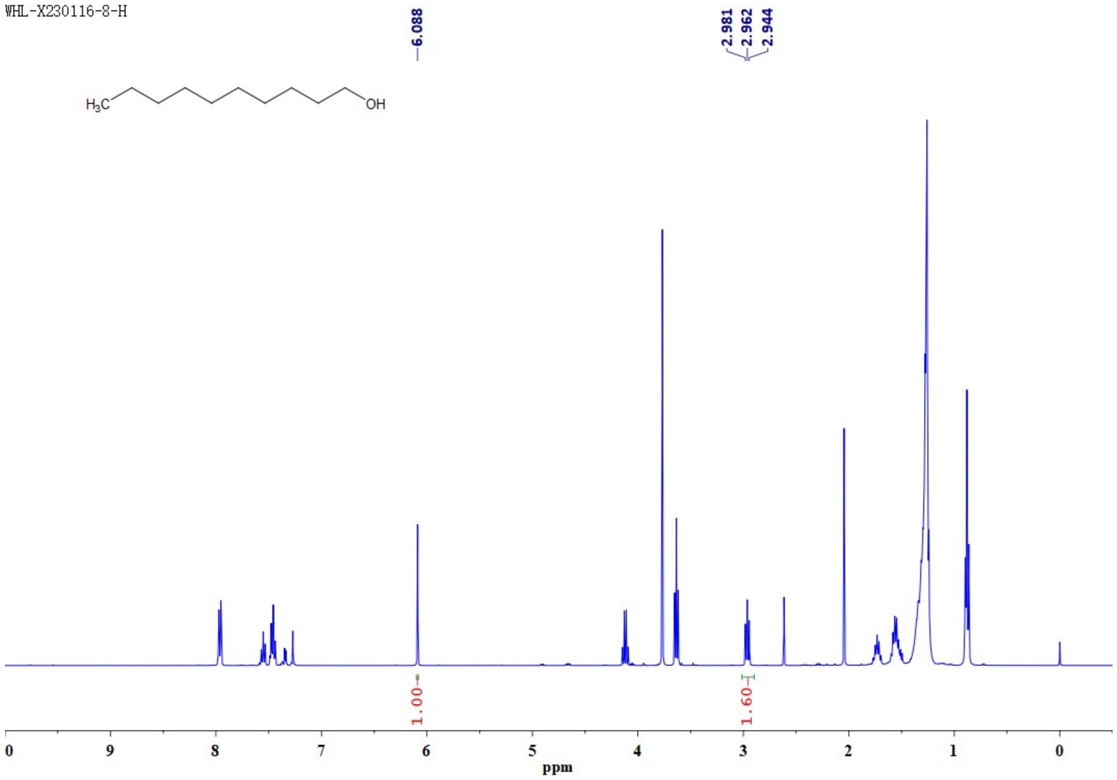
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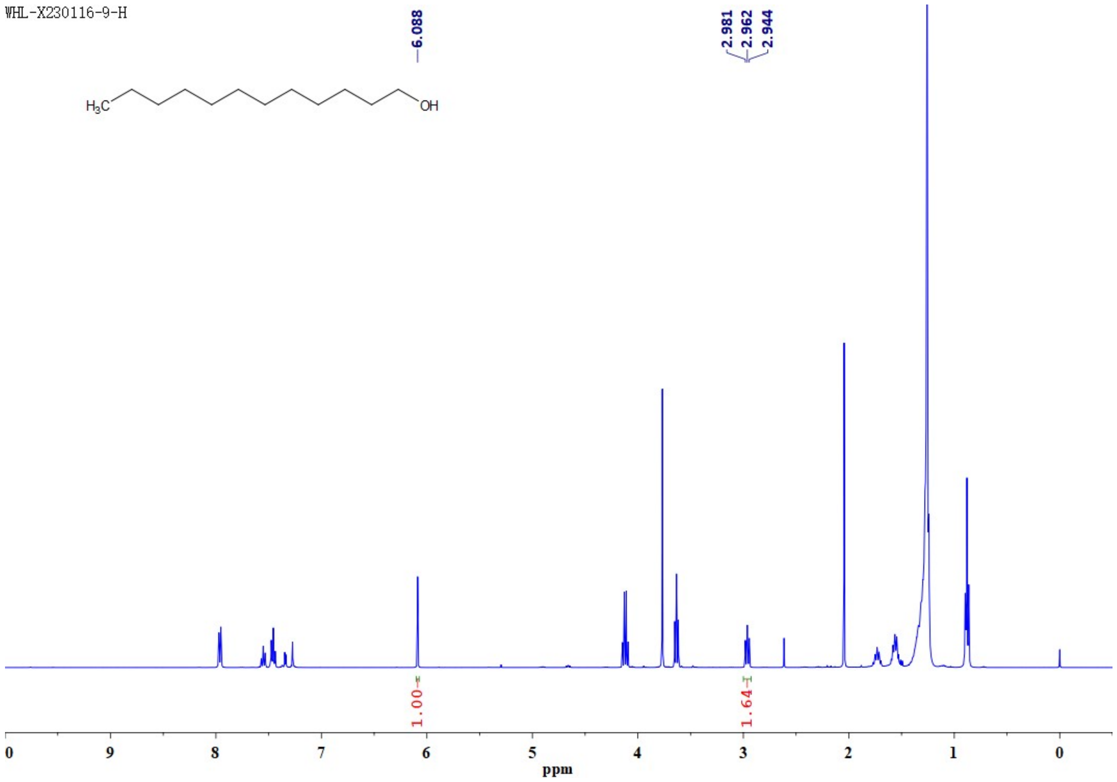
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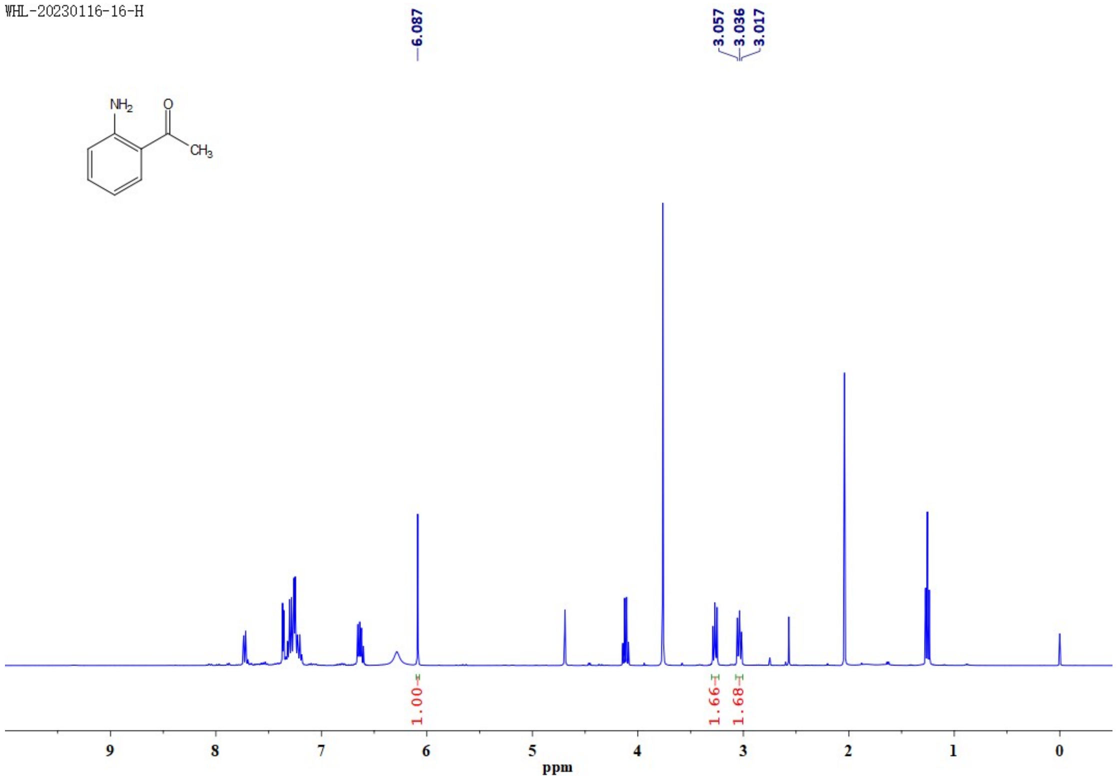
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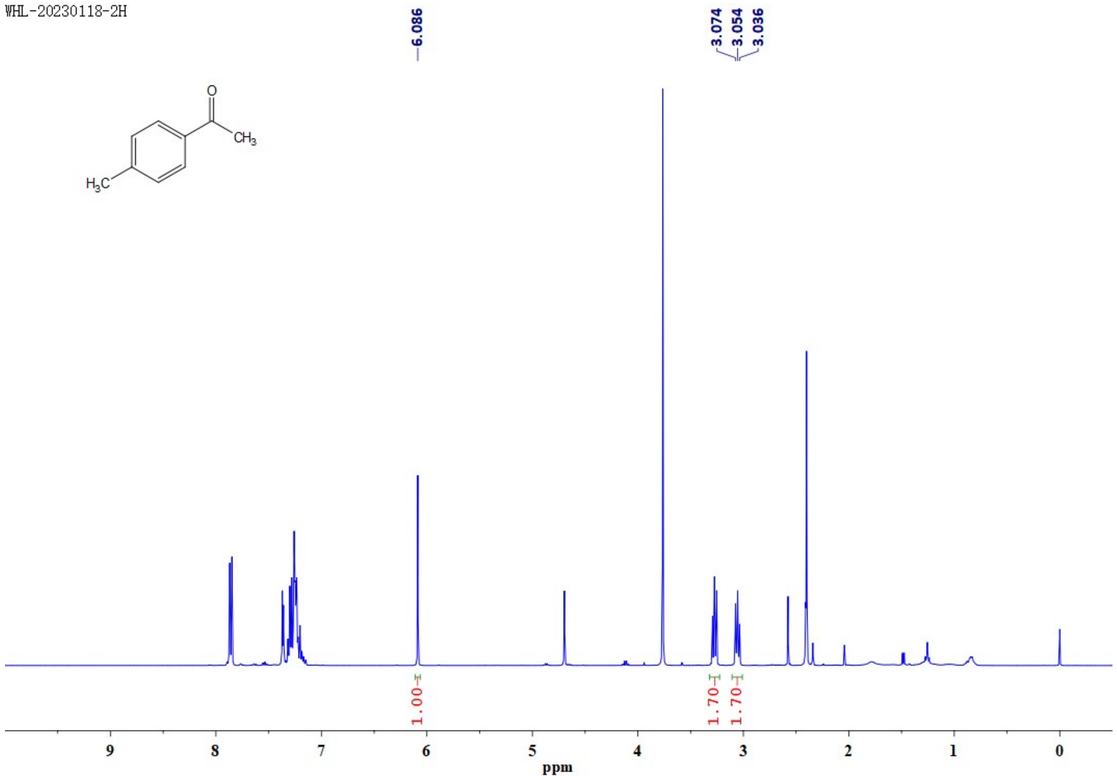
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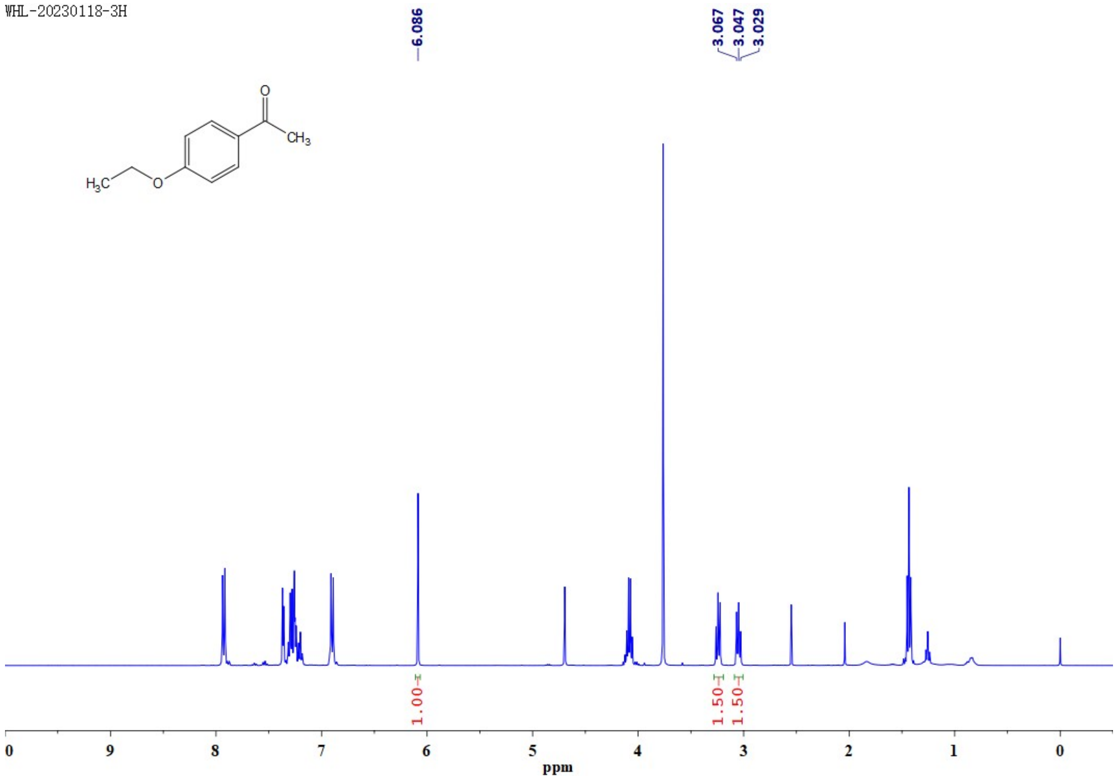
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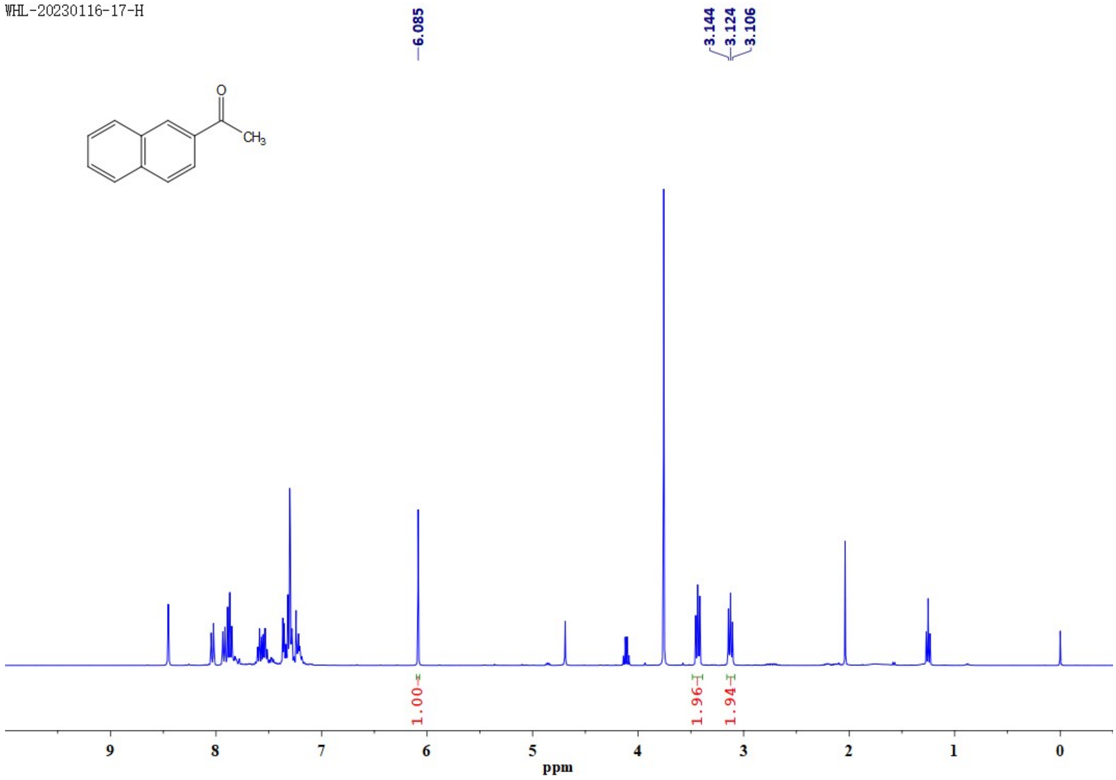
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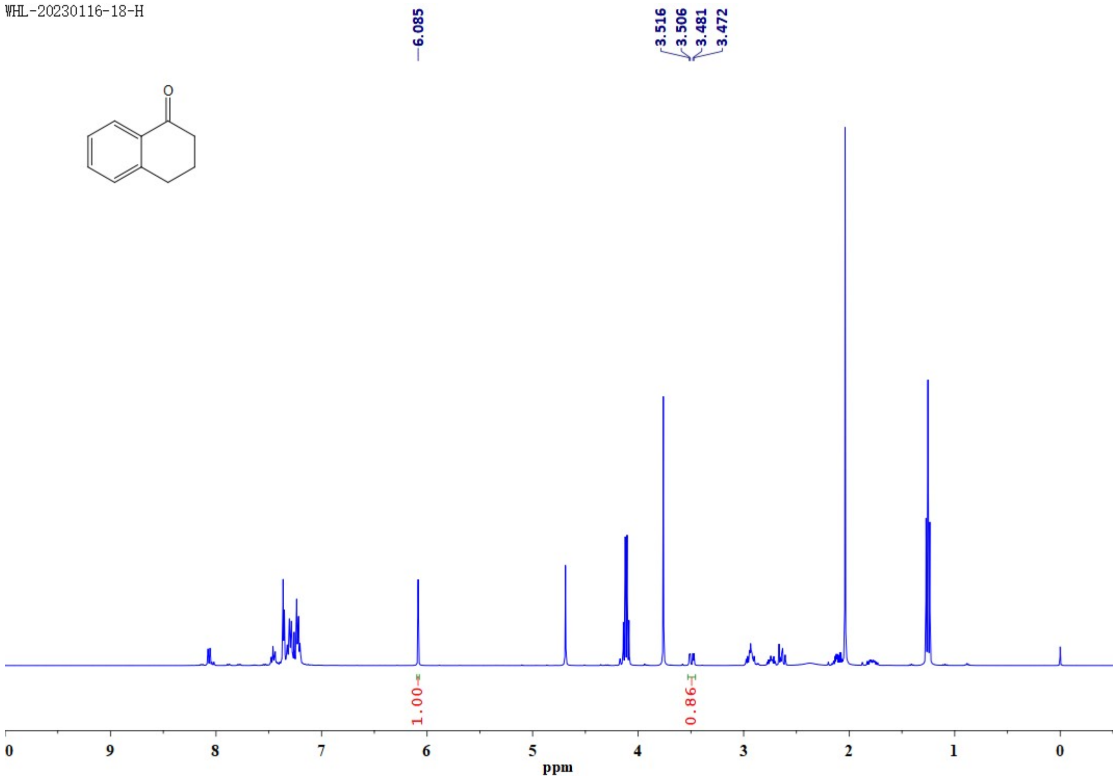
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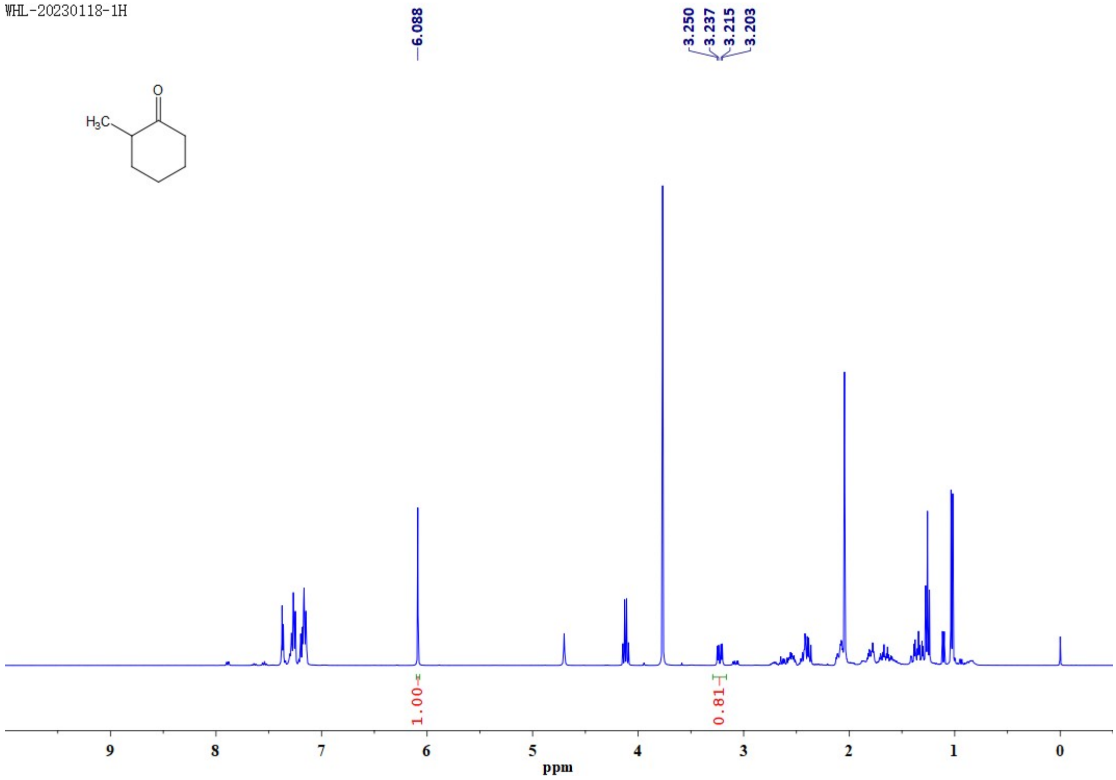
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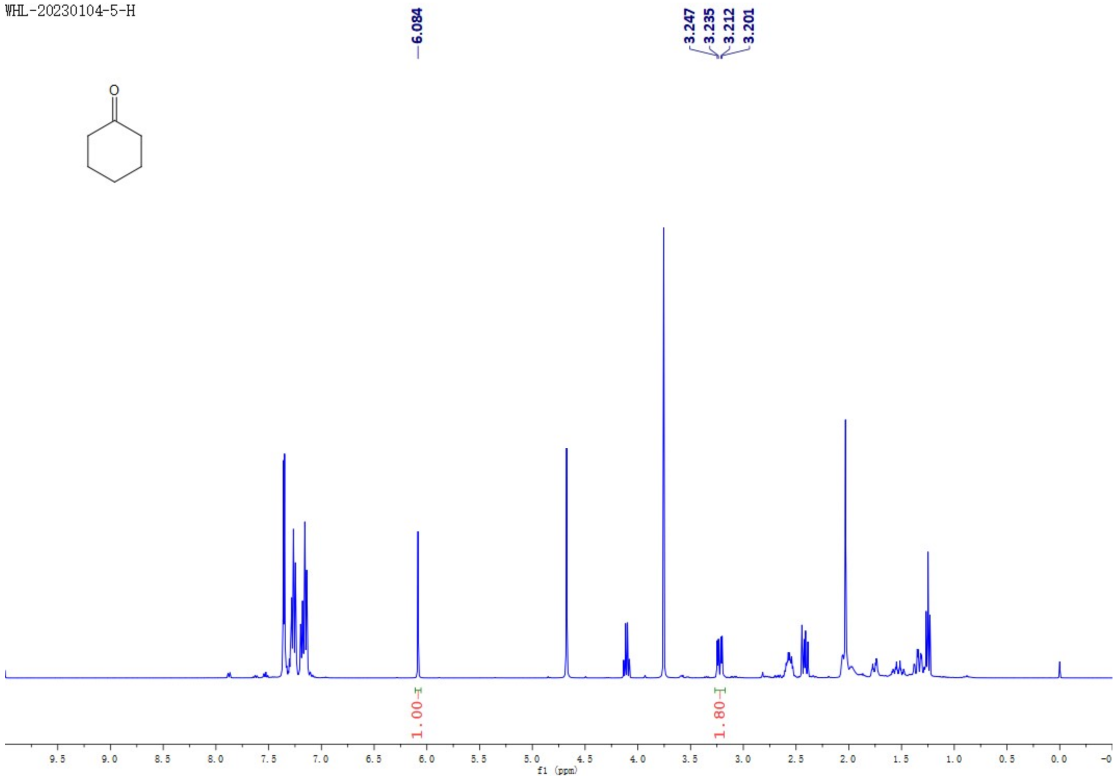
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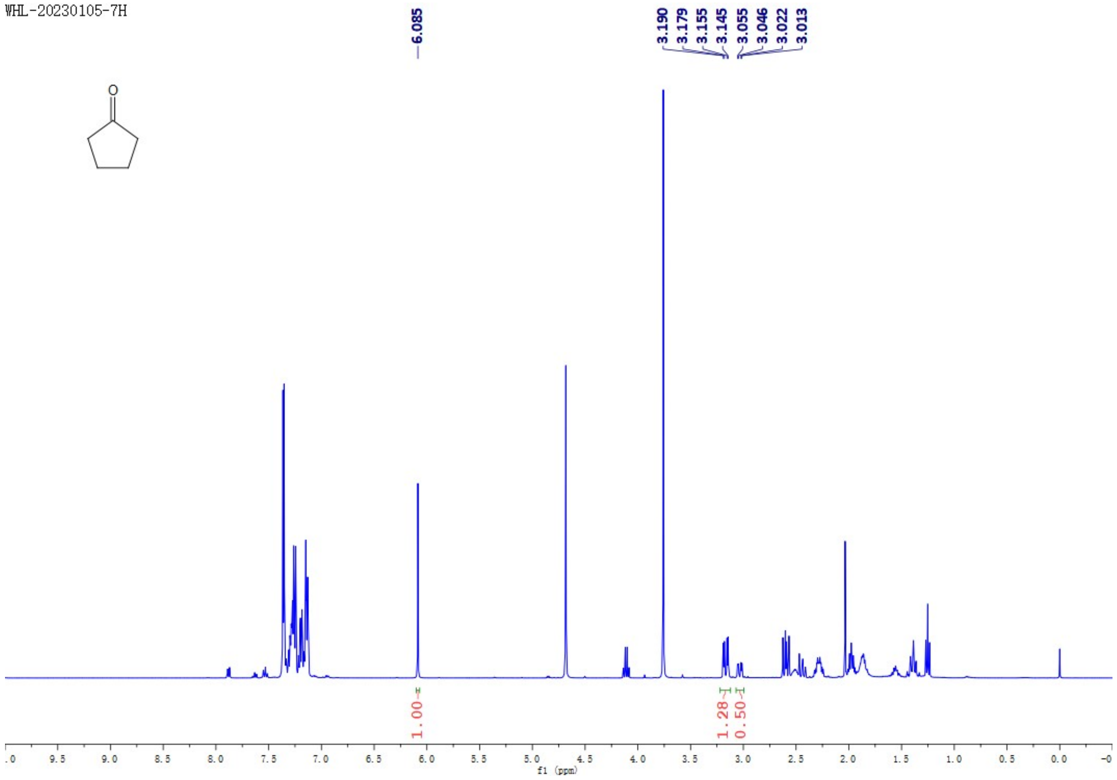
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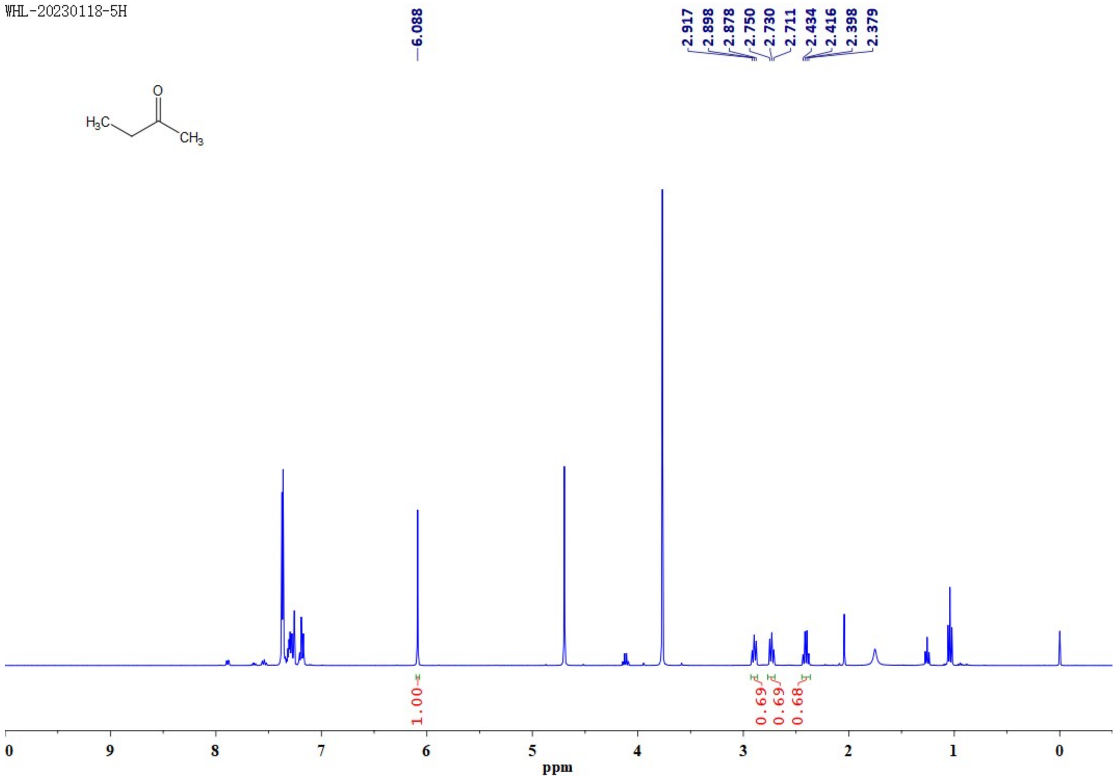

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IV References

1. Z. Hu, X. Liu, D. Meng, Y. Guo, Y. Guo, G. Lu, Effect of Ceria Crystal Plane on the Physicochemical and Catalytic Properties of Pd/Ceria for CO and Propane Oxidation, ACS Catal. 2013, 6, 2265-2279.

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