

## Supporting Information for Publication

### **$\alpha$ -Alkylation of Ketones with Primary Alcohols by Active non-Noble Metal Cu/CuO<sub>x</sub> Catalyst**

Dongyuan Yang,<sup>a,b</sup> Hongli Wang<sup>\*c</sup> and Chun-Ran Chang<sup>\*a</sup>

<sup>a</sup> Shaanxi Key Laboratory of Energy Chemical Process Intensification, School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an 710049, China

E-mail: changcr@mail.xjtu.edu.cn

<sup>b</sup> Shaanxi yanchang Petroleum (Group) Corp. Ltd., Xi'an, 710069, China.

<sup>c</sup> State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

E-mail: hlwang@licp.cas.cn

## Table of Contents

<b>I.</b>	<b>General information and experimental section .....</b>	<b>S3</b>
<b>II.</b>	<b>Characterization results of catalysts .....</b>	<b>S5</b>
<b>III.</b>	<b>NMR spectra of the products.....</b>	<b>S9</b>
<b>IV.</b>	<b>References.....</b>	<b>S21</b>

## 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 CuK $\alpha$ 1 radiation and current of 40 kV and 150 mA, respectively. The XRD patterns were scanned in the 2 Theta range of 10-80 °. 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<sup>-7</sup> 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<sub>2</sub> 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 100 °C for 12 h, at a rate of 10 °C•min<sup>-1</sup>. 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 (<sup>1</sup>H).

## Experimental Section:

All solvents and chemicals were used without any further purification. The characterisation data for products **3a**,<sup>1</sup> **3b**,<sup>2</sup> **3c**,<sup>3</sup> **3d**,<sup>3</sup> **3e**,<sup>4</sup> **3f**,<sup>1</sup> **3g**,<sup>1</sup> **3h**,<sup>1</sup> **3i**,<sup>1</sup> **3j**,<sup>5</sup> **3k**,<sup>1</sup> **3l**,<sup>2</sup> **3m**,<sup>1</sup> **3n**,<sup>6</sup> **3o**,<sup>7</sup> **3p**,<sup>7</sup> **3q**,<sup>3</sup> **3r**,<sup>8</sup> **3s**,<sup>7</sup> **3t**,<sup>3</sup> **3u**,<sup>2</sup> **3v**,<sup>1</sup> **3w**,<sup>1</sup> **3x**<sup>9</sup> have been reported in literature.

### Preparation of Cu/CuOx catalyst <sup>10</sup>

Firstly, the commercially available CuO was heated in air with 5 °C/min to 450 °C and kept for 4 h. Then, the obtained materials were reduced in hydrogen flow at different temperatures (200 °C -350 °C) for 3 hours in a home-made tube furnace, resulting in series of Cu/CuOx-T catalysts, where T denote the reduction temperature.

### General procedure for the $\alpha$ -alkylation of ketones with primary alcohols

A mixture of ketone **1** (1.0 mmol), alcohols **2** (1.5 mmol), K<sub>3</sub>PO<sub>4</sub> (106 mg, 0.50 mmol), Cu/CuOx-250 (50 mg), and n-hexane (4 mL) were added to a 15 mL thick-walled pressure glass tube which is purchased from synthware company and exchanged with Ar. The press tube was sealed by a screw cap. The reaction mixture was stirred at 170 °C for 6 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<sub>3</sub> and subjected for NMR analysis.

For each catalyst recycling, the Cu/CuOx-250 catalyst was separated by centrifugation, washed with ethyl acetate (8 mL x 2), water (8 mL x 2), acetone (8 mL x 2), dried under air at room temperature and then reused for the next run.

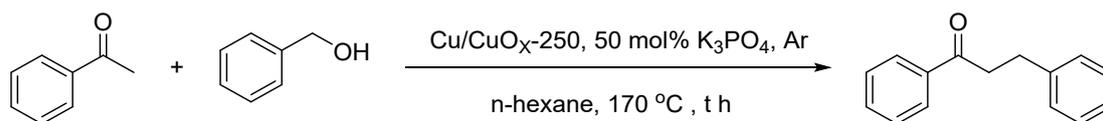
## II. Characterization results of catalysts

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

Entry	Catalyst	Cu (wt%) <sup>[a]</sup>	SA (m <sup>2</sup> g <sup>-1</sup> ) <sup>[b]</sup>	APR (nm) <sup>[b]</sup>	PV (cm <sup>3</sup> g <sup>-1</sup> ) <sup>[b]</sup>
1	CuO	78.7	12.22	24.2	0.148
2	Cu/CuO <sub>x</sub> -200	83.7	7.14	3.6	0.013
3	Cu/CuO <sub>x</sub> -250	90.2	4.74	5.2	0.012
4	Cu/CuO <sub>x</sub> -300	90.5	8.09	3.5	0.014
5	Cu/CuO <sub>x</sub> -350	94.5	12.52	1.9	0.012

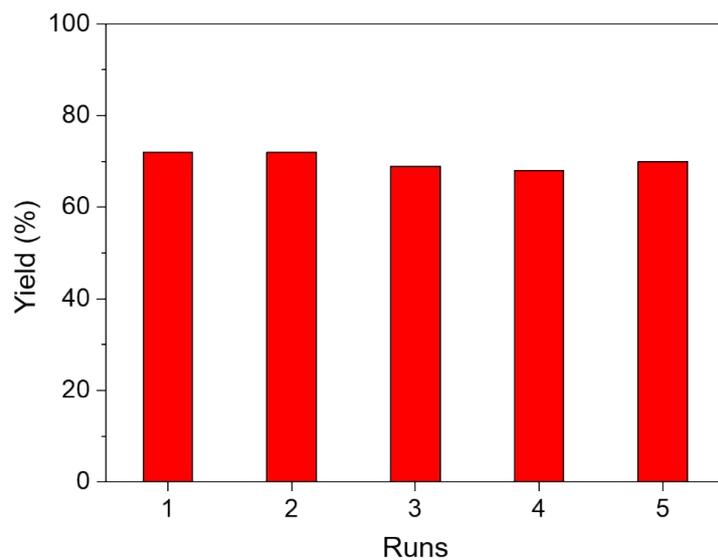
[a] Determined by ICP-AES. [b] Determined by an IQ<sub>2</sub> automated gas sorption analyzer. SA: BET surface area; APS: average pore radius; PV: pore volume.

**Table S2** The hot filtration test for Cu/CuO<sub>x</sub>-250 catalyzed  $\alpha$ -alkylation of acetophenone and benzyl alcohol <sup>a</sup>

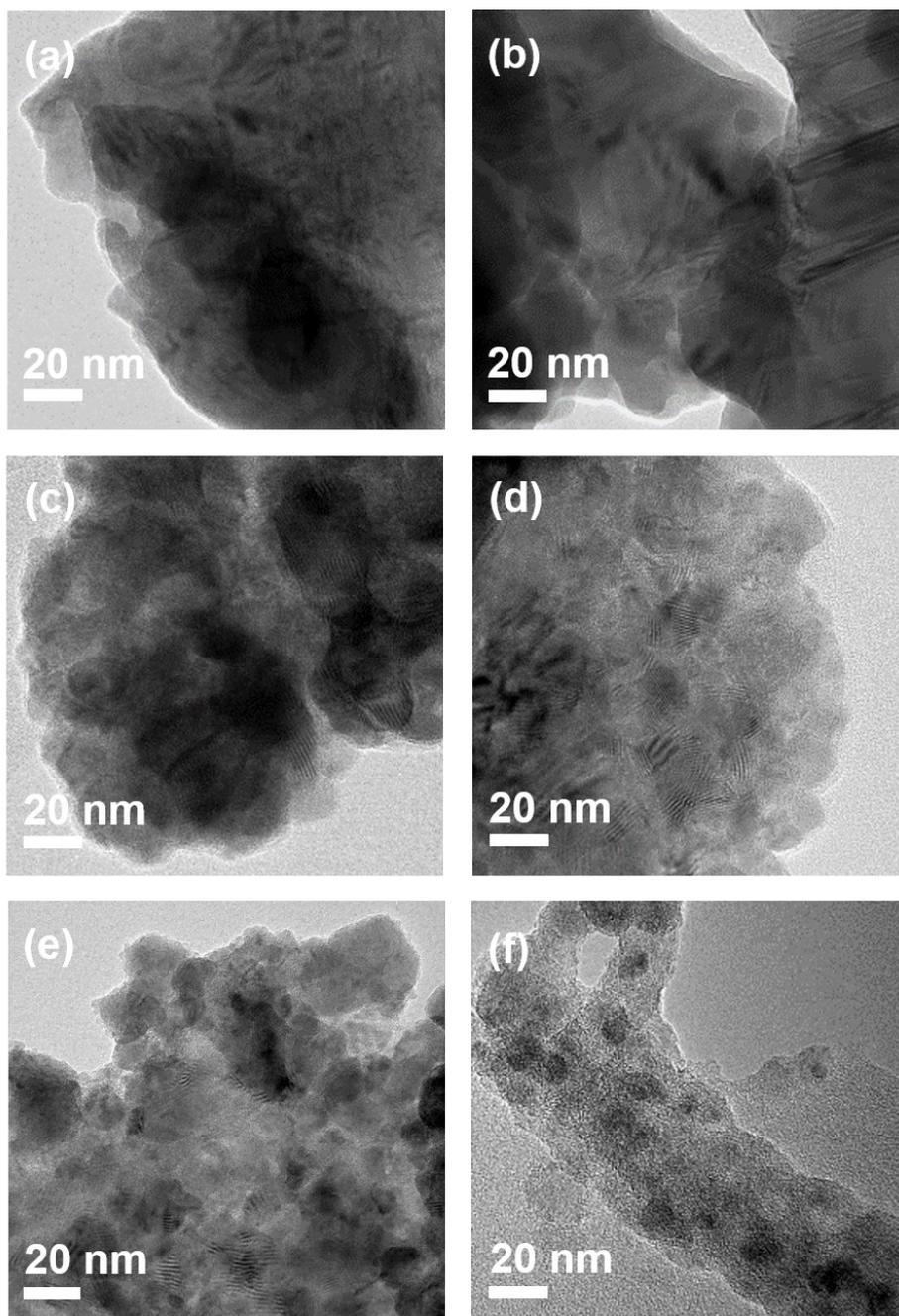


Entry	t (h)	Yield <sup>b</sup> (%)
1	0.25	5.5
2	0.25	8.5
3	average	7.0
4	0.25+5.75	6.0
5	0.25+5.75	8.5
6	average	7.3

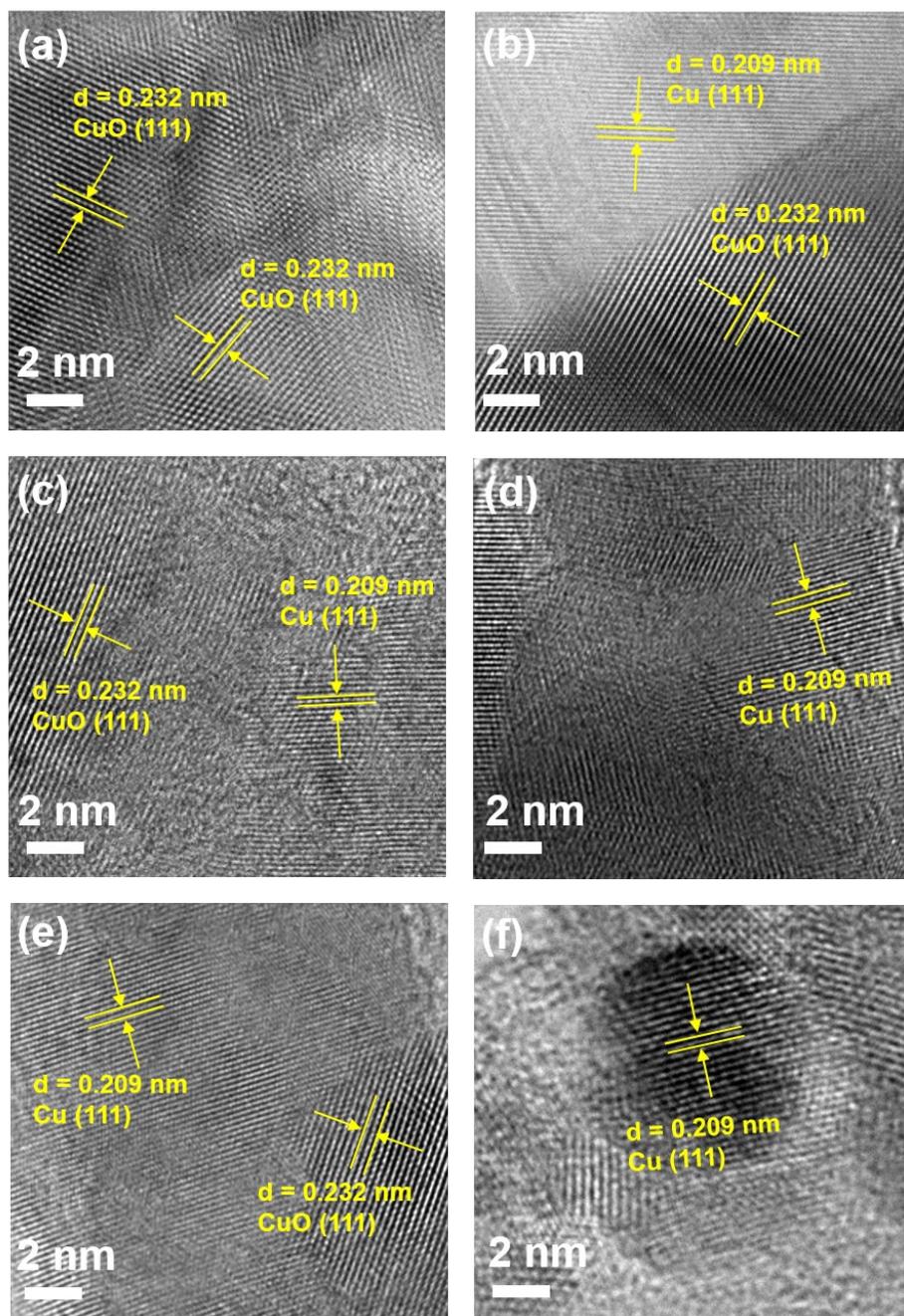
a. Reaction conditions: acetophenone (1.0 mmol), benzyl alcohol (1.5 mmol), CuO<sub>x</sub>-250 (50 mg), K<sub>3</sub>PO<sub>4</sub> (50 mol%), n-hexane (4.0 mL), 170 °C, t h; b. Determined by <sup>1</sup>H NMR.



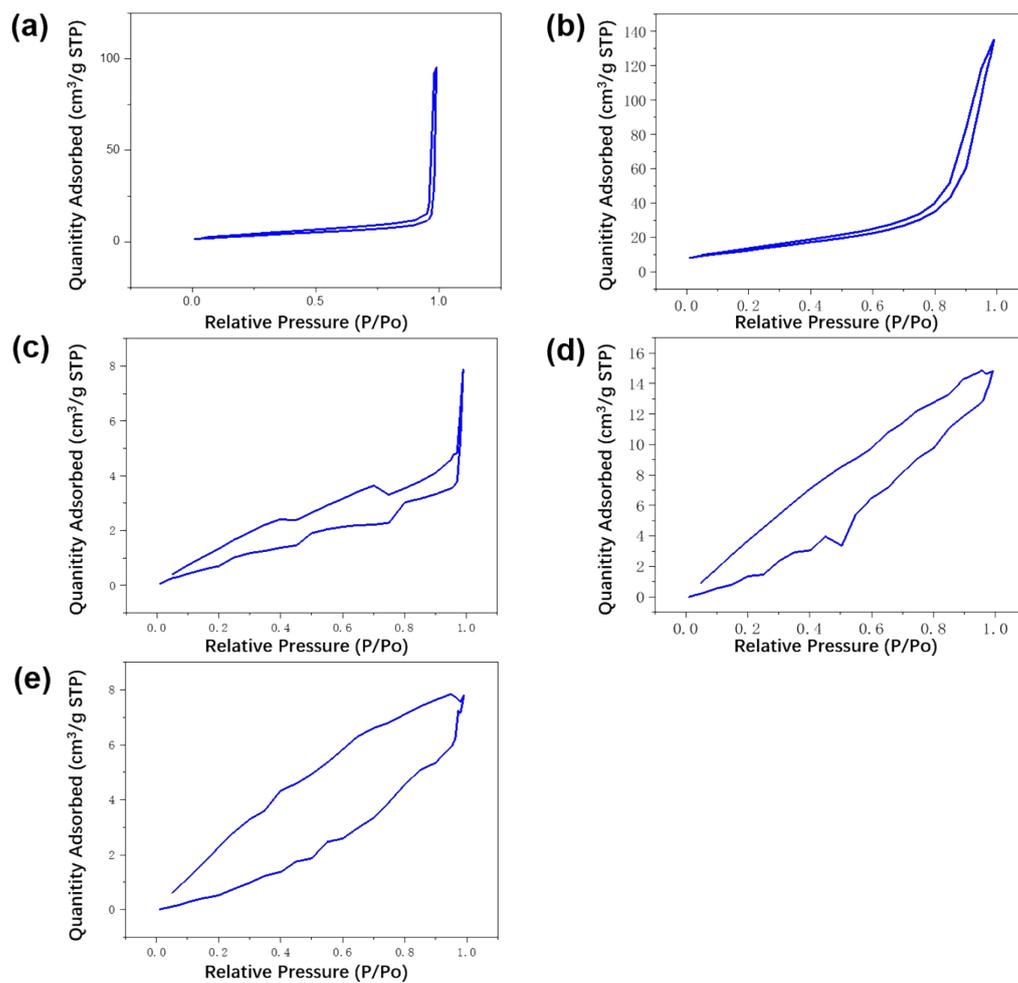
**Fig. S1** Recycling test of the Cu/CuOx-250 catalyst with 1 hour reaction time. Reaction conditions: ketone (1.0 mmol), alcohol (1.5 mmol), Cu/CuOx-250 (50 mg),  $K_3PO_4$  (0.5 mmol), n-hexane (4.0 mL), 170 °C, 1 h.



**Fig. S2** TEM images of the Cu/CuOx samples. (a) CuO, (b) Cu/CuOx-200, (c) Cu/CuOx-250, (d) Cu/CuOx-300, (e) Cu/CuOx-350, (f) used Cu/CuOx-250.



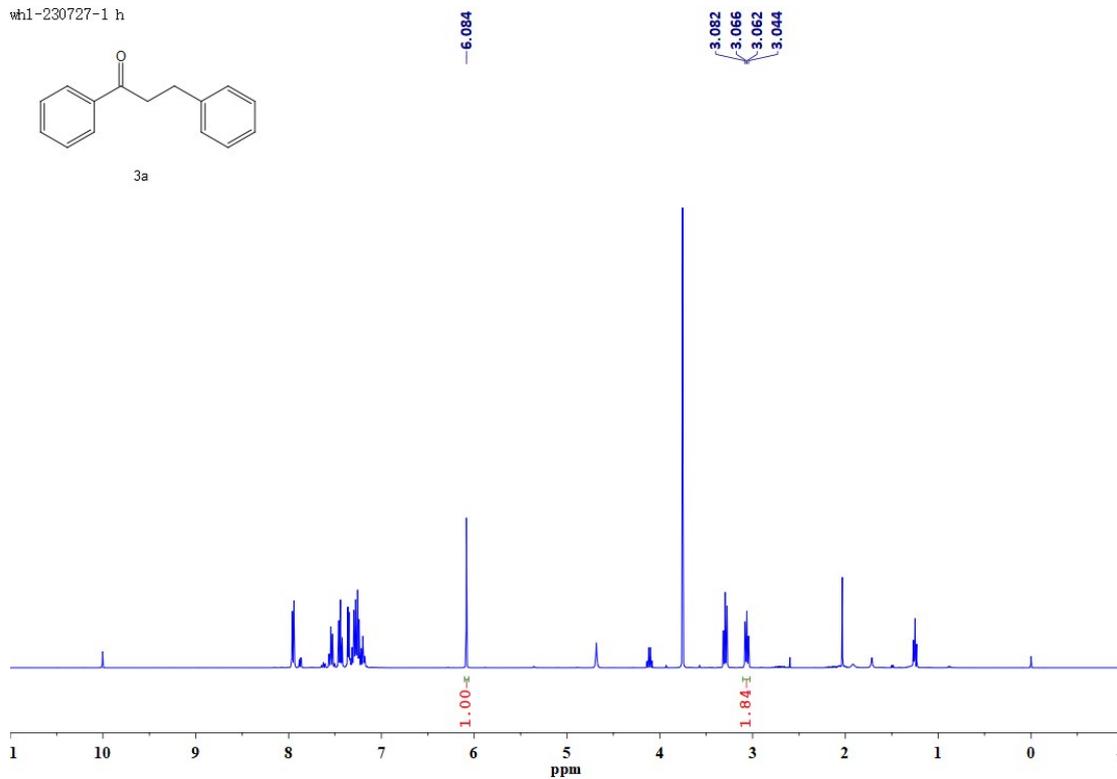
**Fig. S3** HR-TEM images of the Cu/CuOx samples. (a) CuO, (b) Cu/CuOx-200, (c) Cu/CuOx-250, (d) Cu/CuOx-300, (e) Cu/CuOx-350, (f) used Cu/CuOx-250.



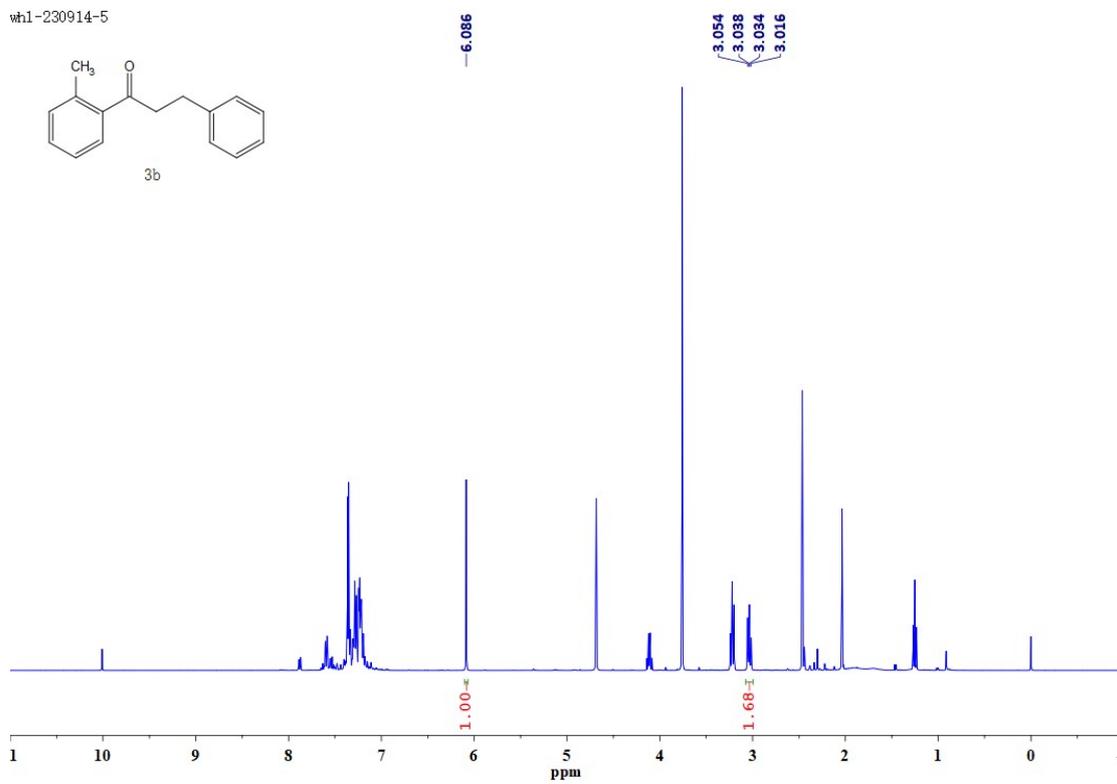
**Fig. S4**  $N_2$  adsorption-desorption isotherm of Cu/CuOx samples. (a) CuO, (b) Cu/CuOx-200, (c) Cu/CuOx-250, (d) Cu/CuOx-300, (e) Cu/CuOx-350, (f) used Cu/CuOx-250.

### III NMR spectra of the products

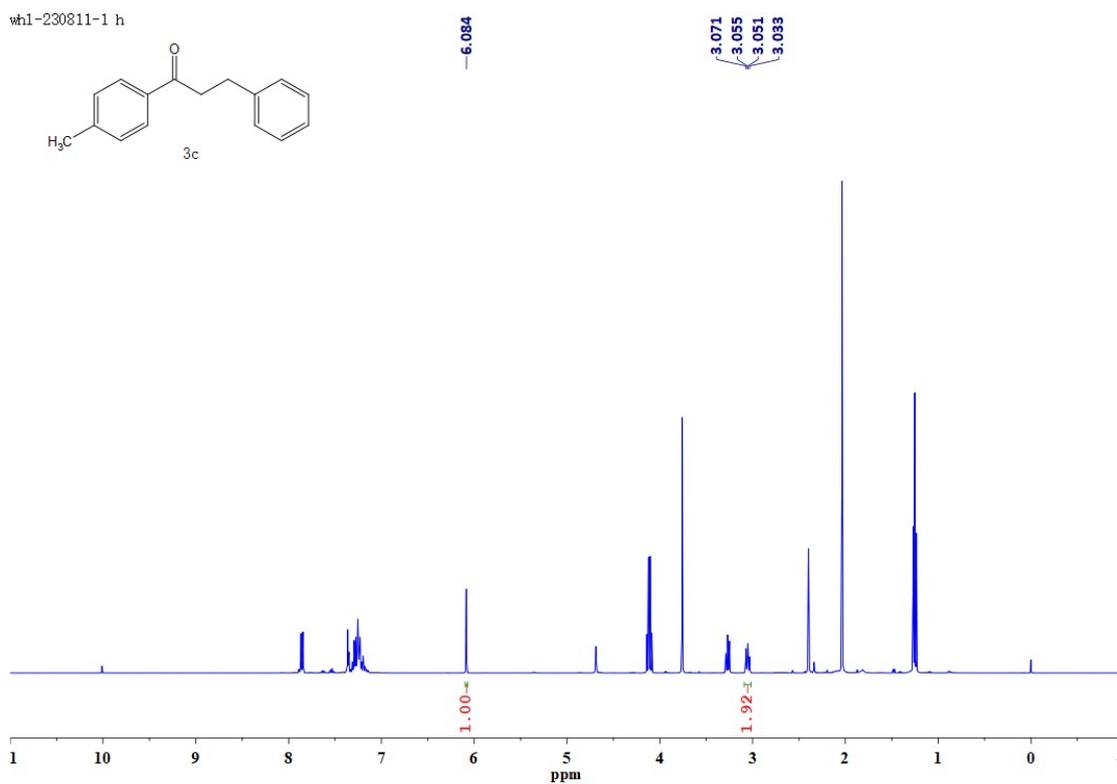
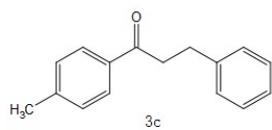
wh1-230727-1 h



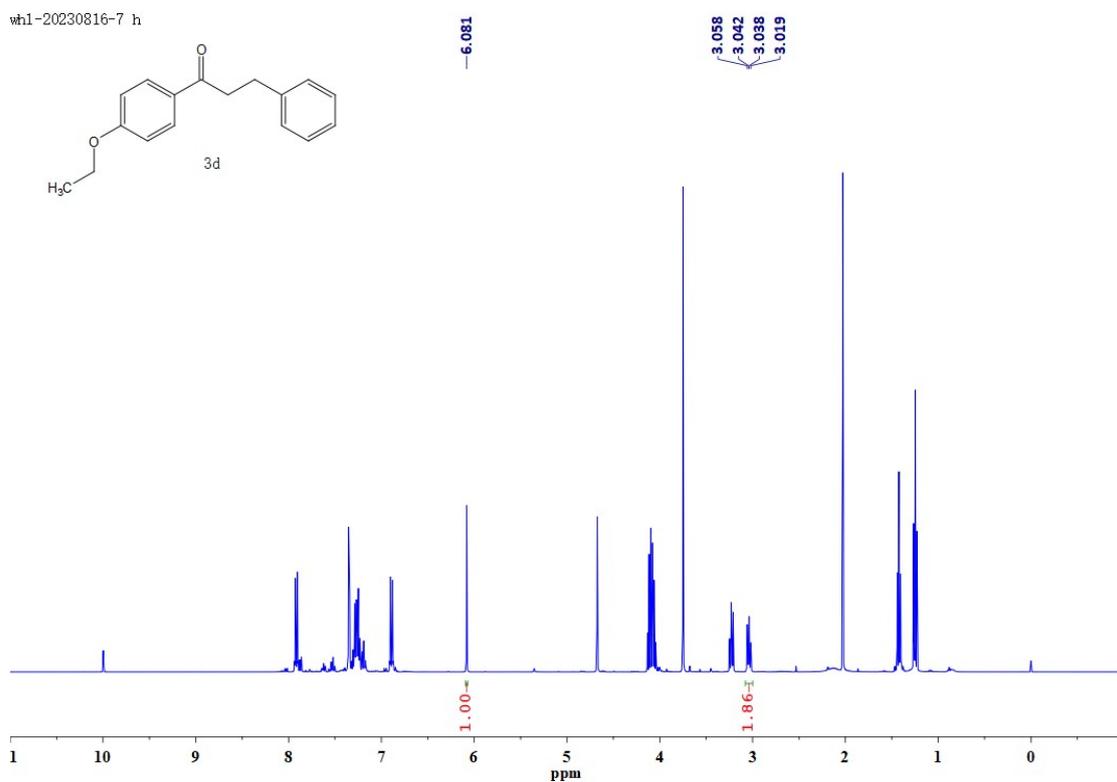
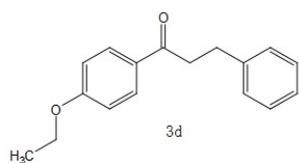
wh1-230914-5



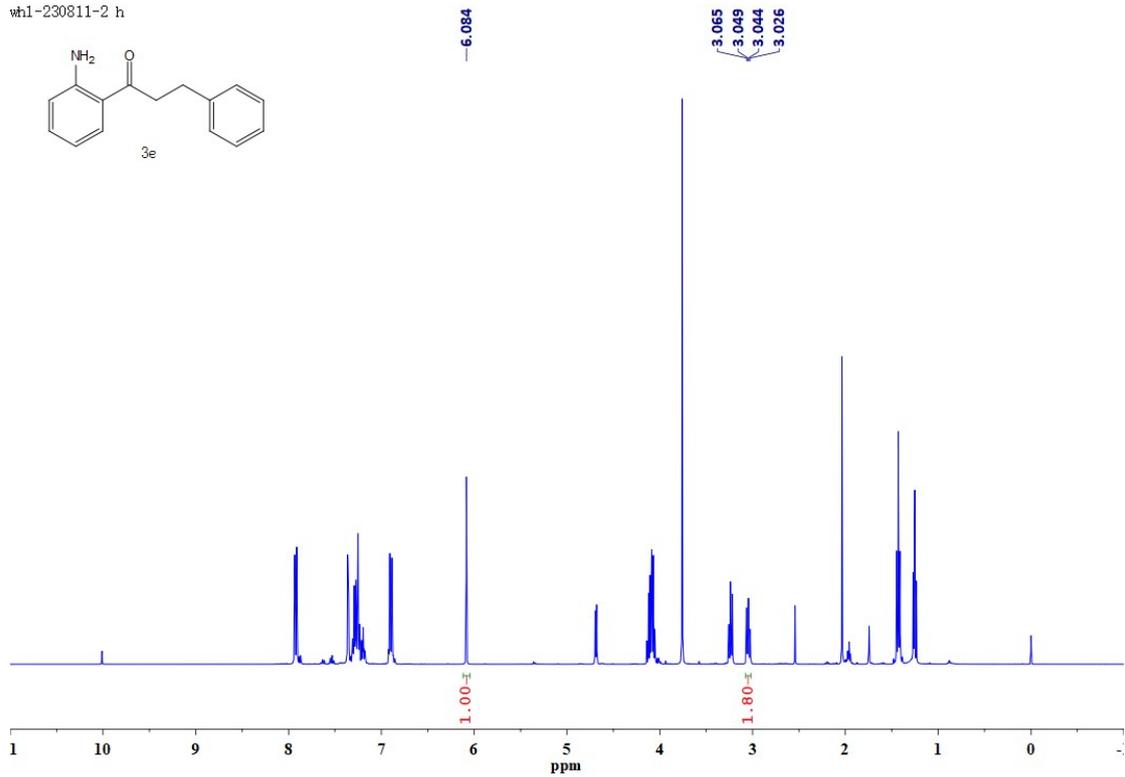
wh1-230811-1 h



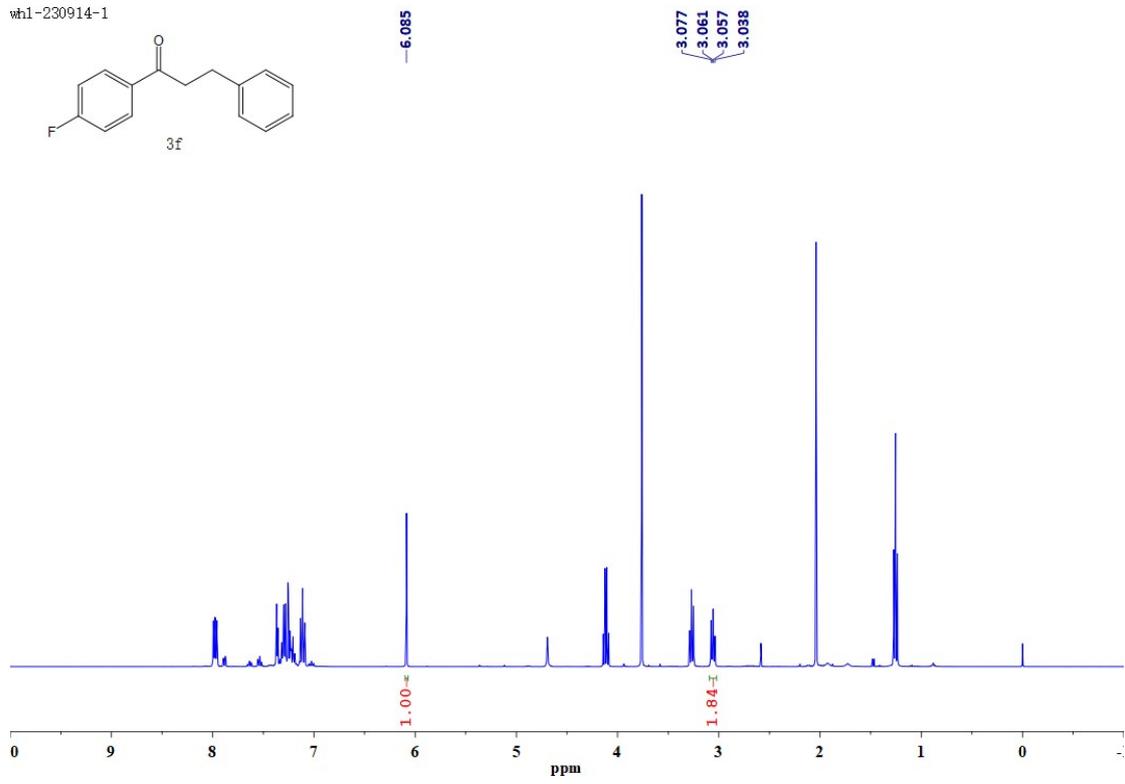
wh1-20230816-7 h



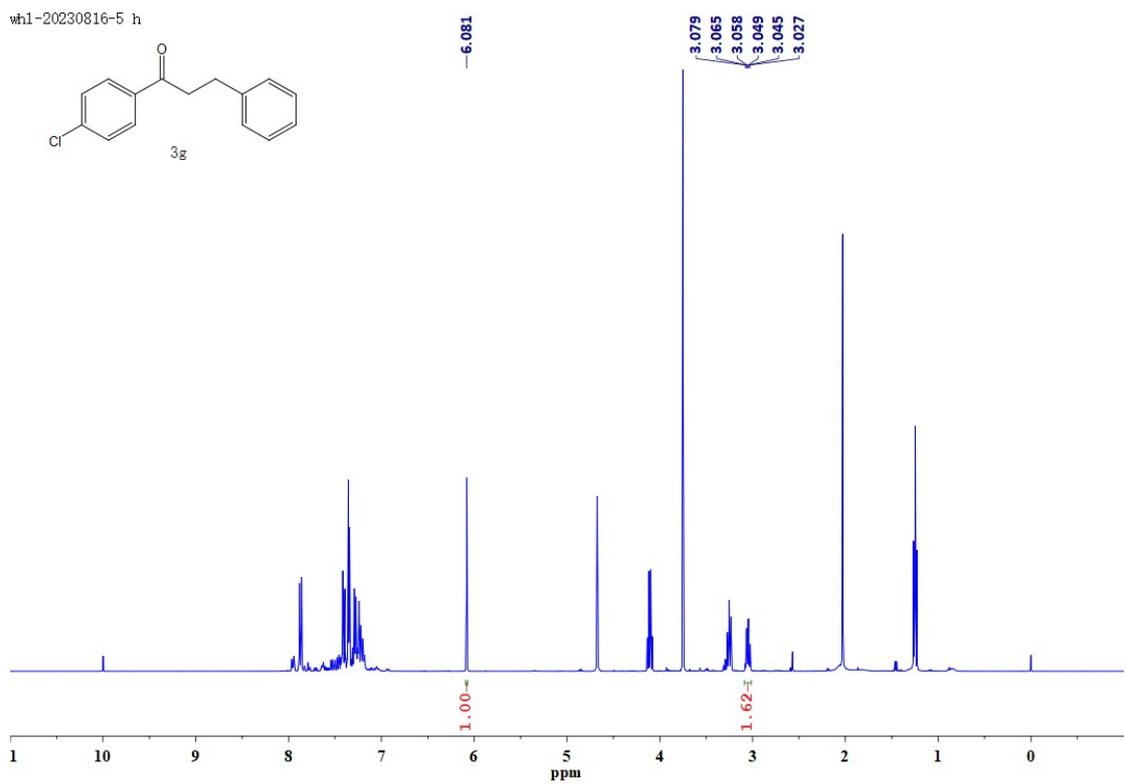
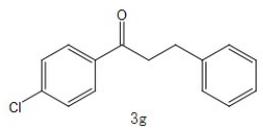
wh1-230811-2 h



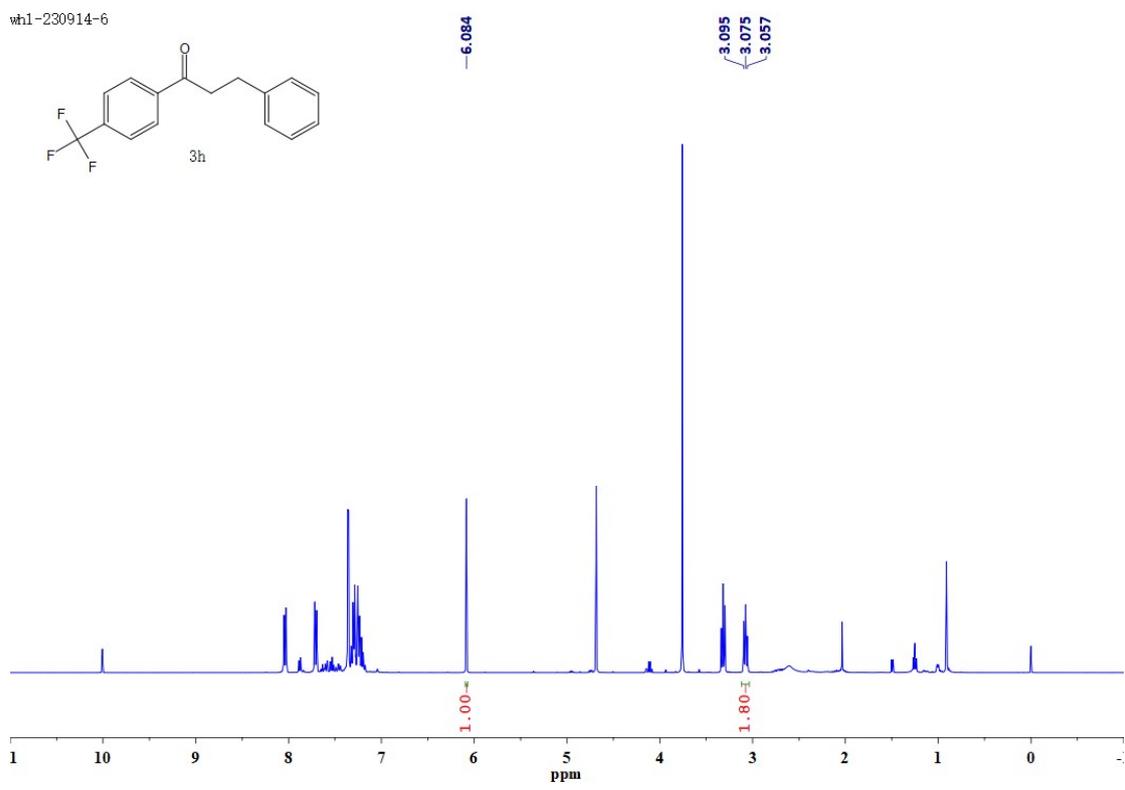
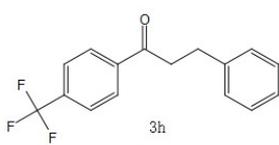
wh1-230914-1



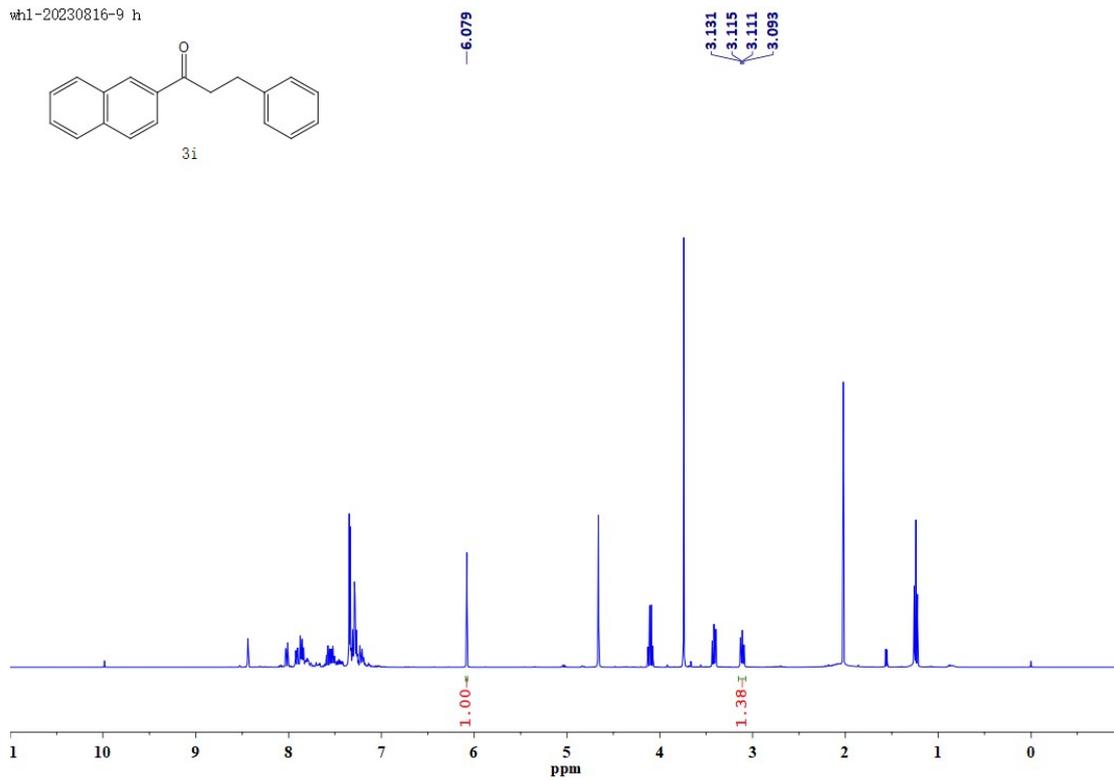
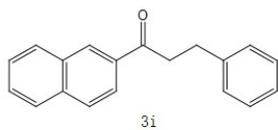
wh1-20230816-5 h



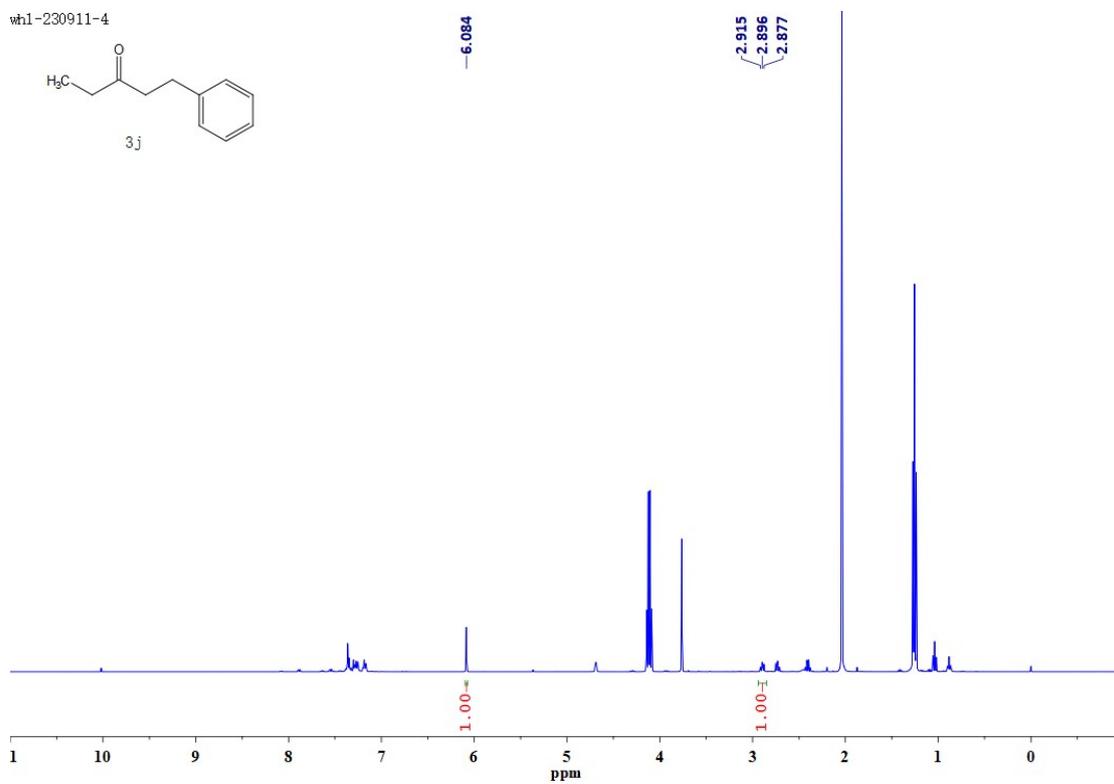
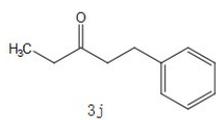
wh1-230914-6



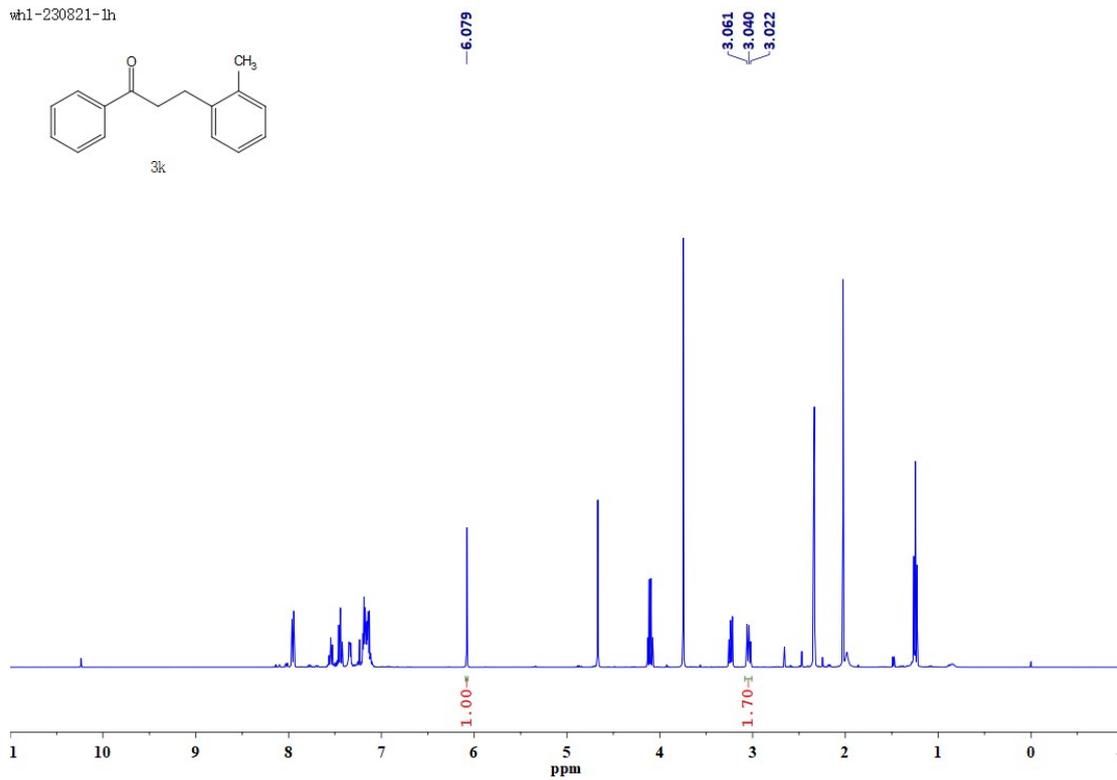
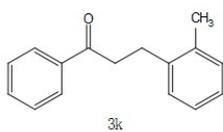
wh1-20230816-9 h



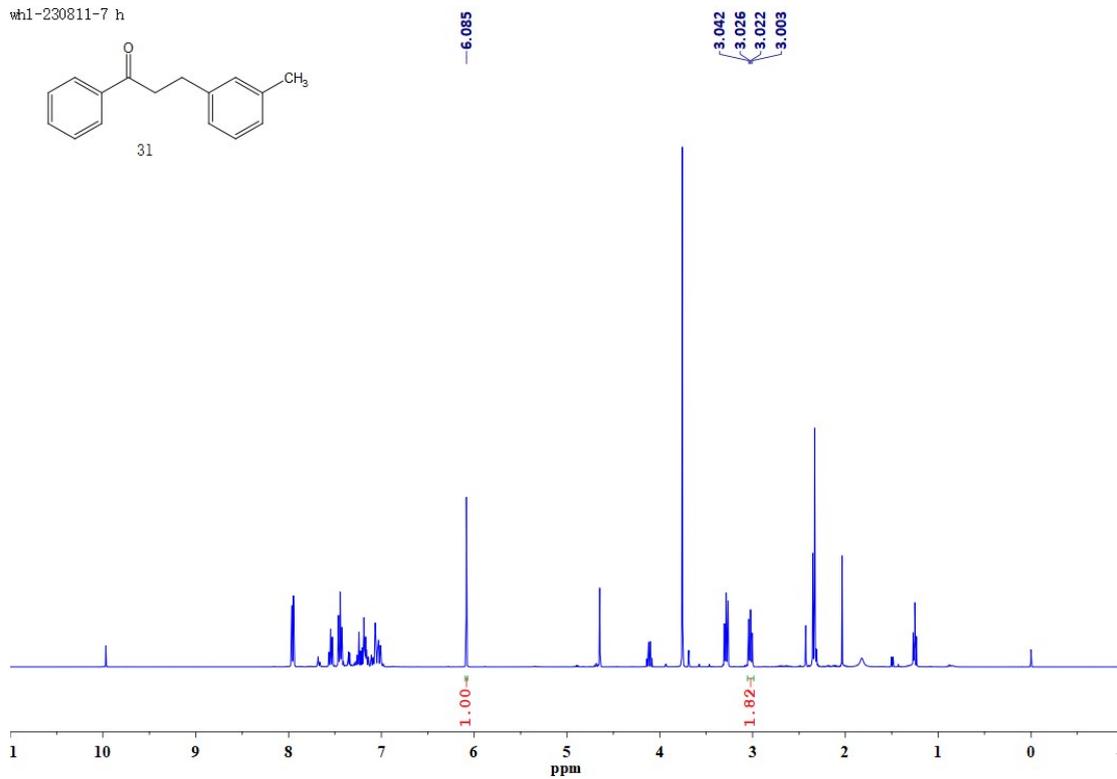
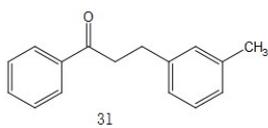
wh1-230911-4



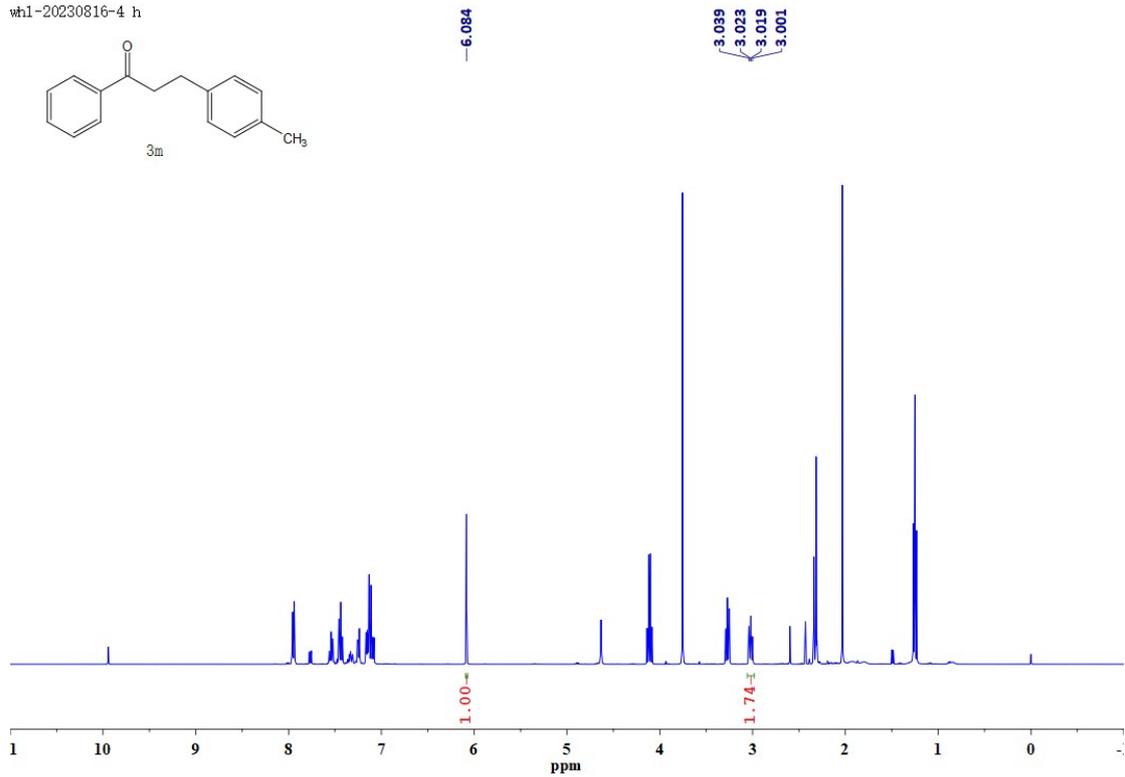
wh1-230821-1h



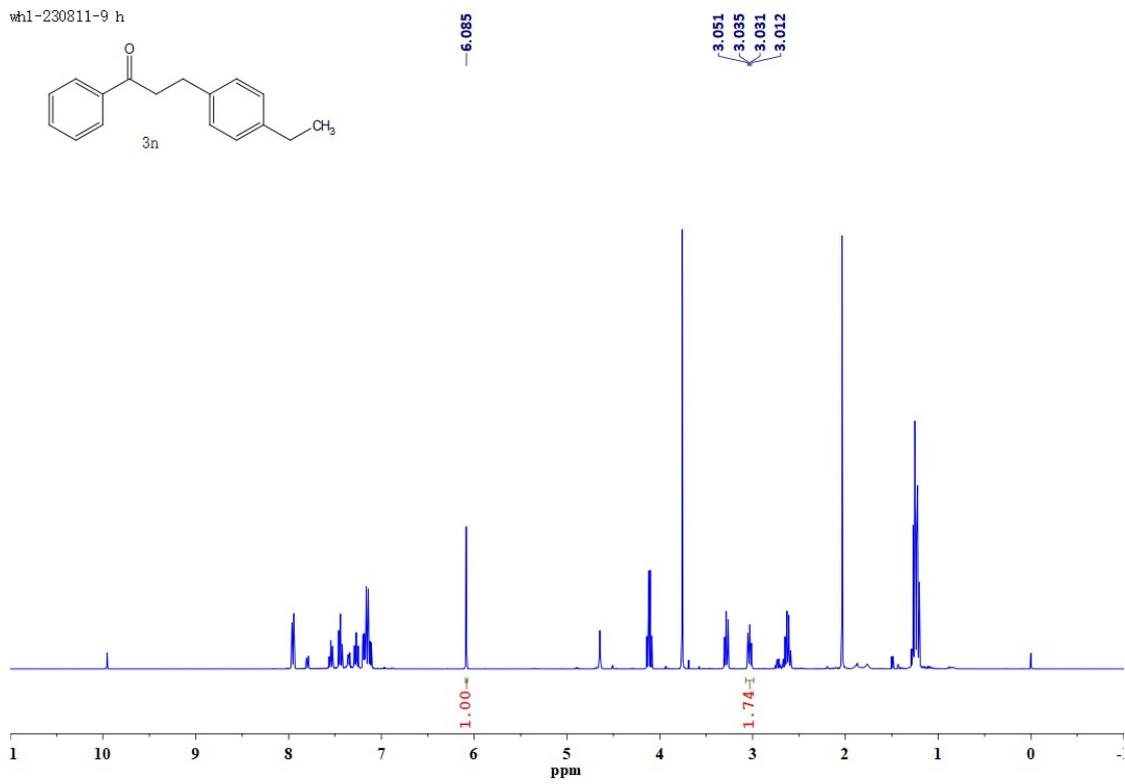
wh1-230811-7 h



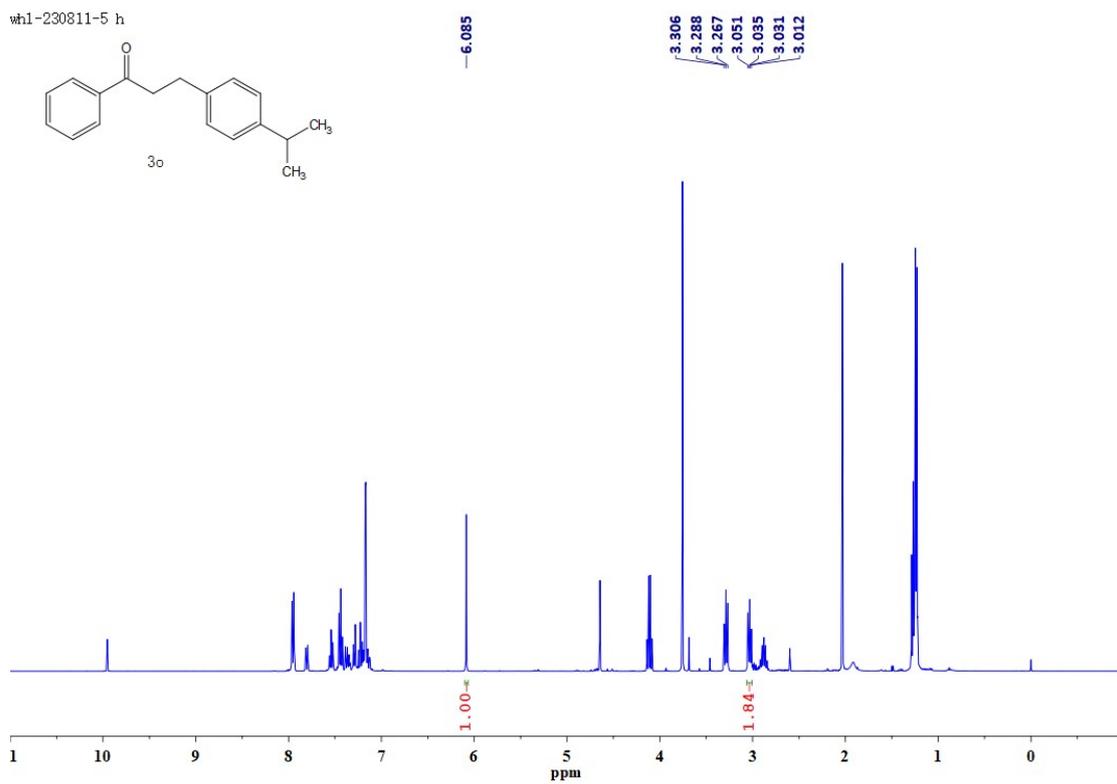
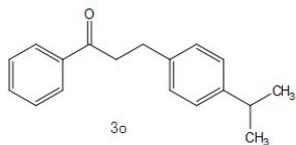
wh1-20230816-4 h



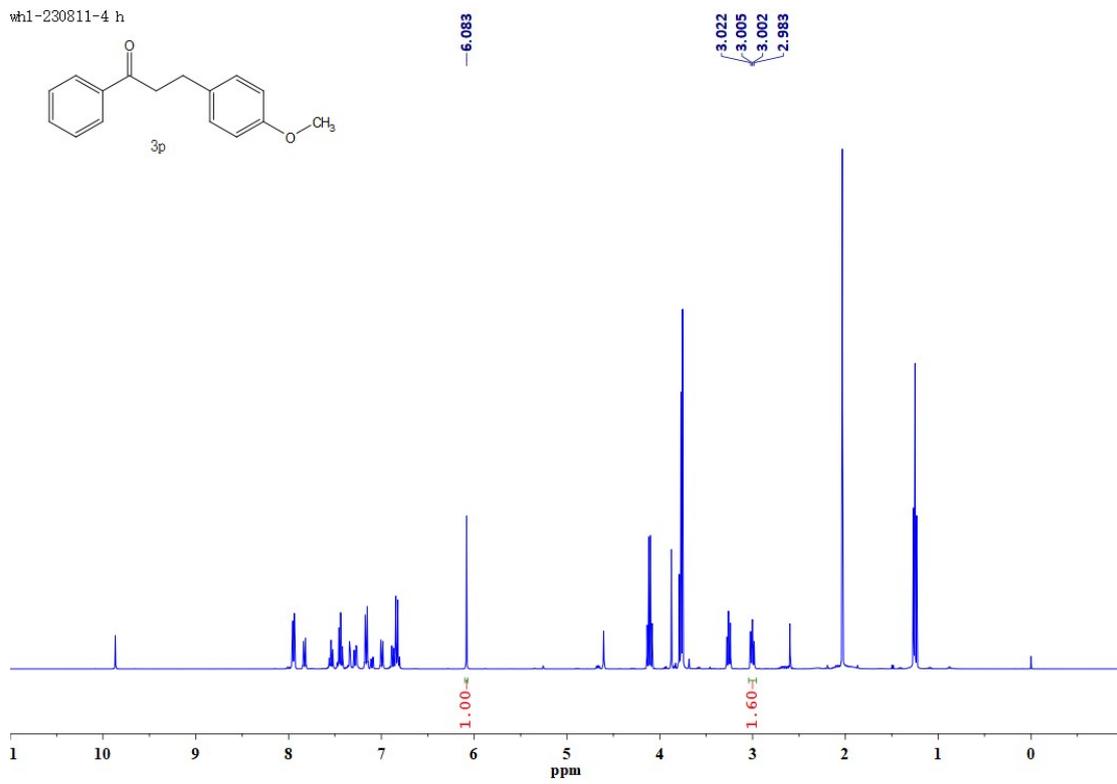
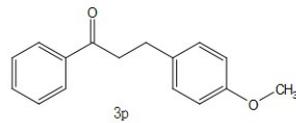
wh1-230811-9 h



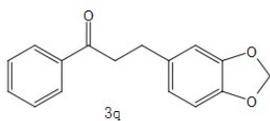
wh1-230811-5 h



wh1-230811-4 h

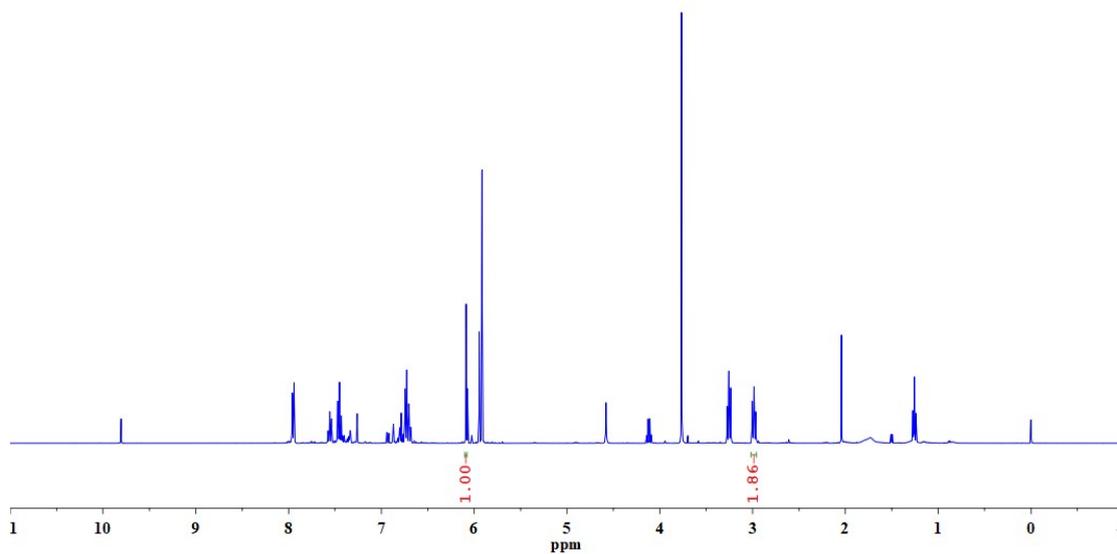


wh1-230811-8 h

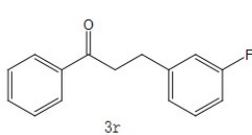


6.087

3.004  
2.987  
2.984  
2.966

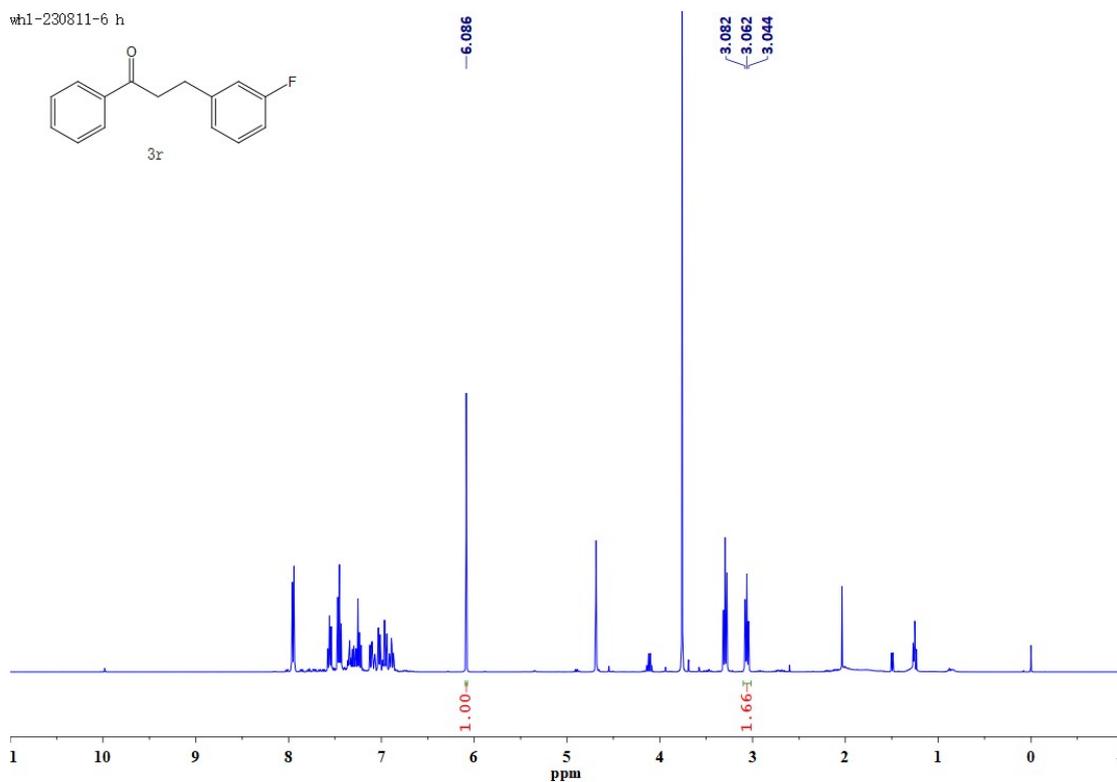


wh1-230811-6 h

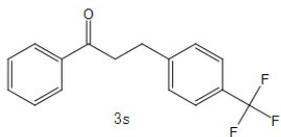


6.086

3.082  
3.062  
3.044

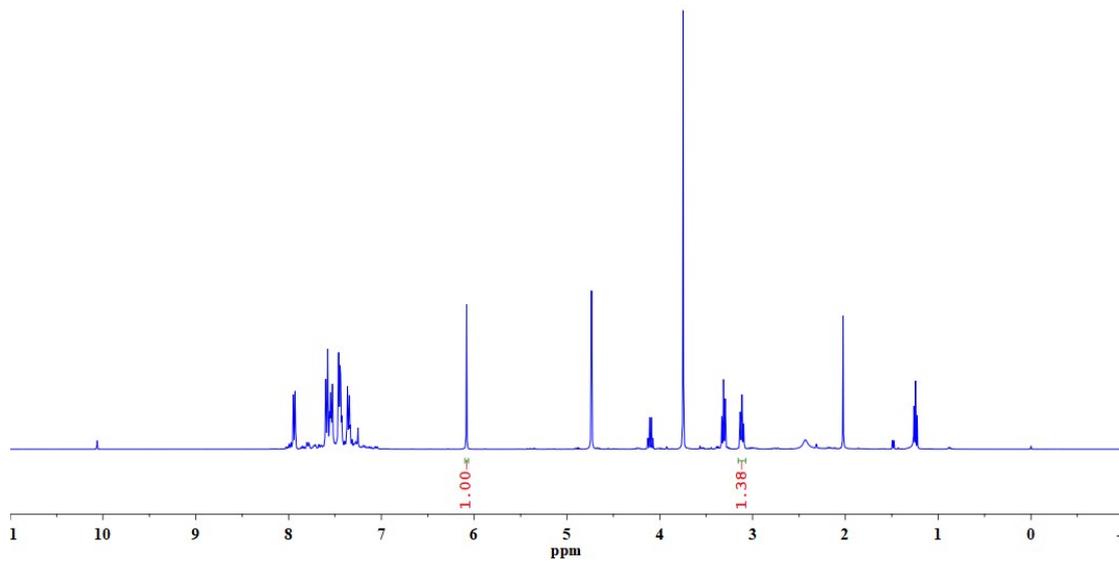


wh1-230904-3

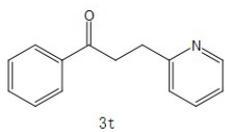


6.082

3.133  
3.115  
3.096

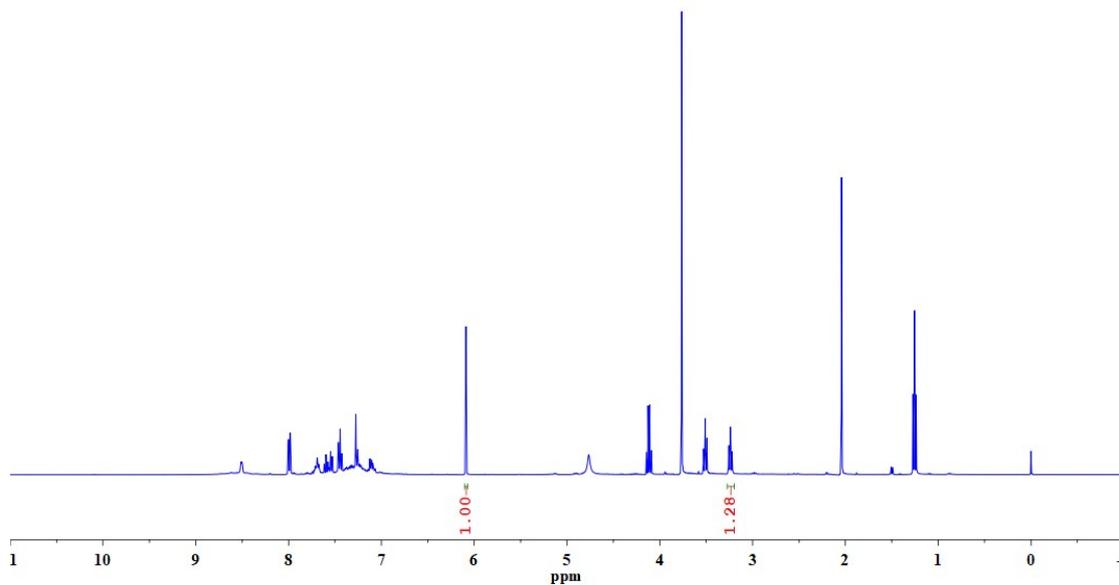


wh1-230907-1

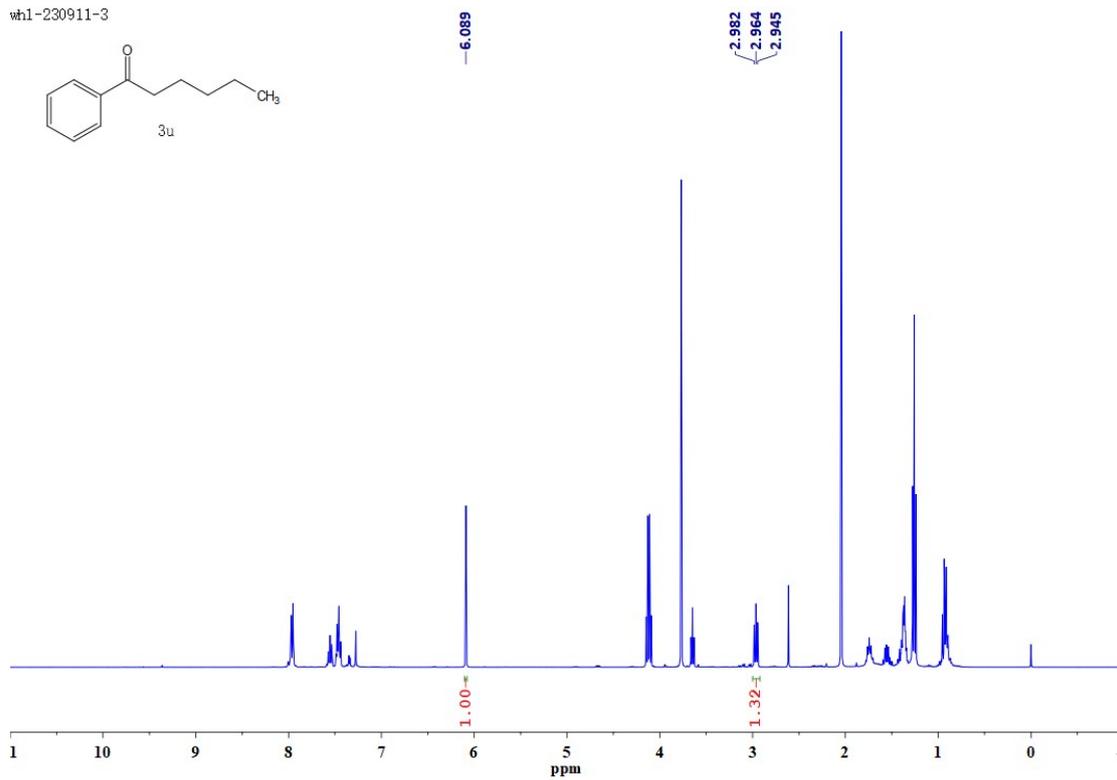
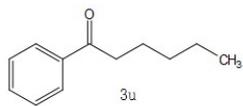


6.089

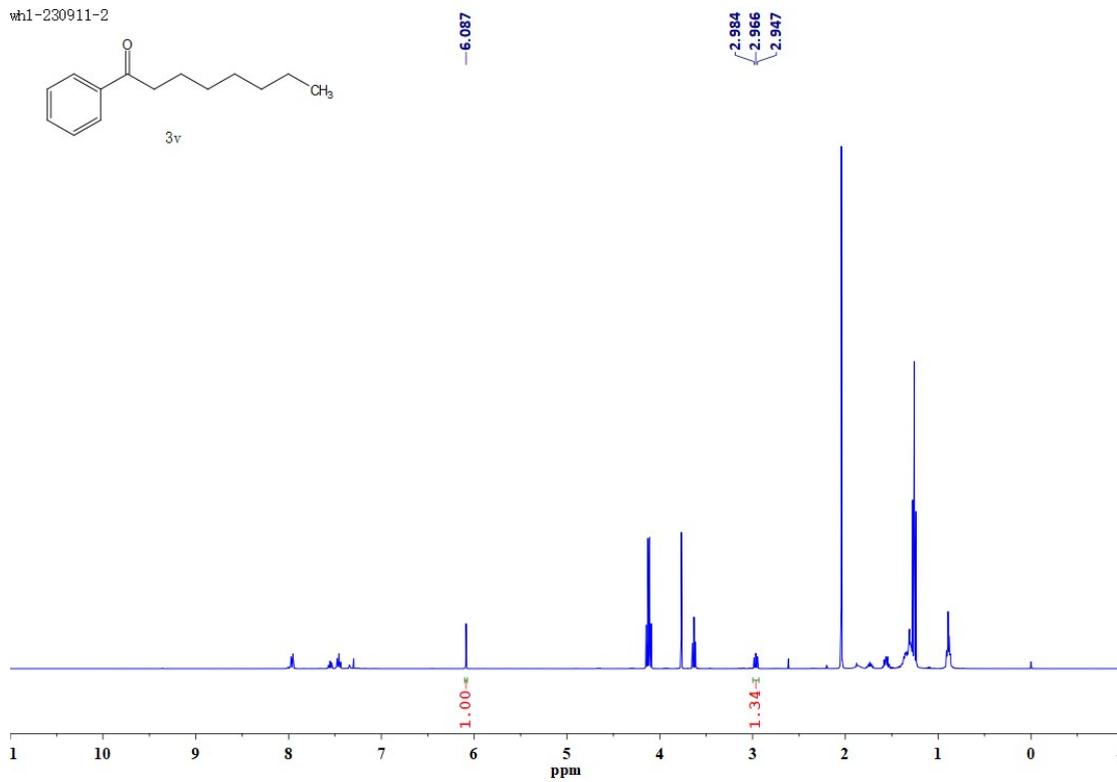
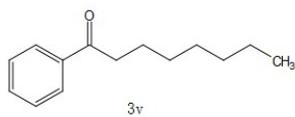
3.257  
3.239  
3.221



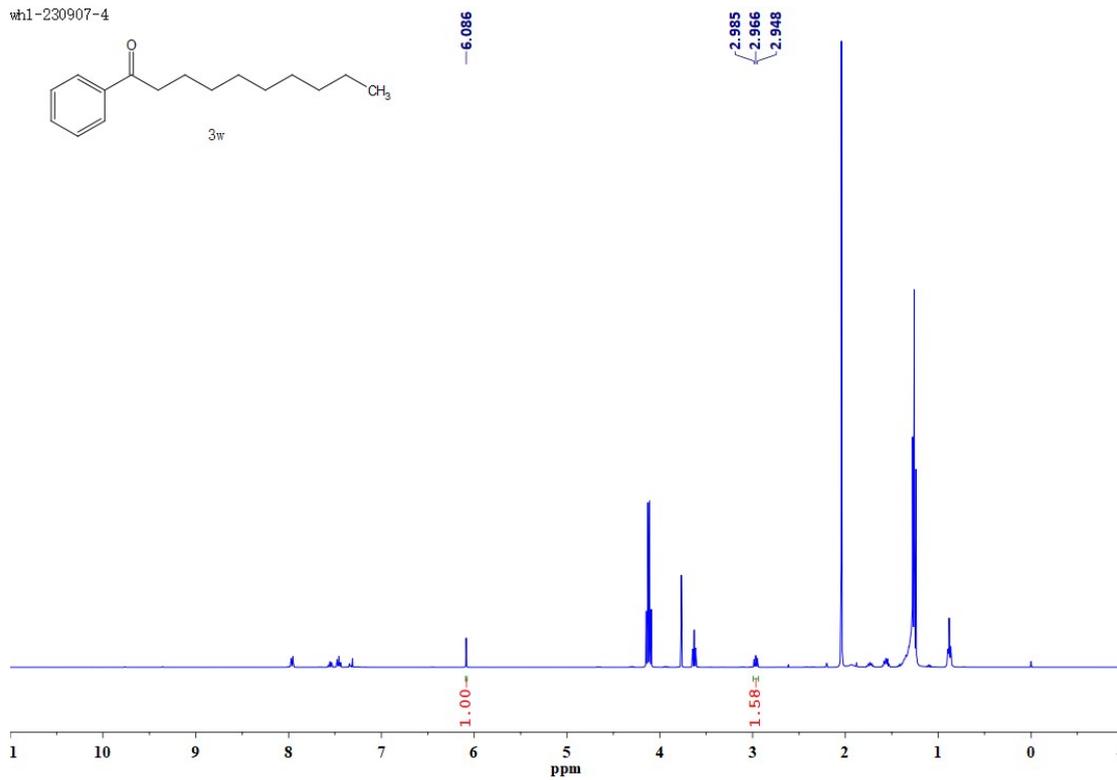
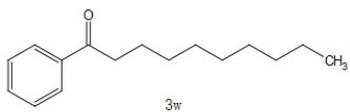
wh1-230911-3



wh1-230911-2



wh1-230907-4



## IV References

1. G. Zhang, J. Wu, H. Zeng, S. Zhang, Z. Yin and S. Zheng, *Org. Lett.*, 2017, **19**, 1080-1083.
2. L. Rakers, F. Schäfers and Frank Glorius, *Chem. Eur. J.*, 2018, **24**, 15529-15532.
3. X. Cui, Y. Zhang, F. Shi and Y. Deng, *Chem. Eur. J.*, 2011, **17**, 1021-1028.
4. S. Bhat and V. Sridharan, *Chem. Commun.*, 2012, **48**, 4701-4703.
5. L. Zhang, X. Xie, L. Fu and Z. Zhang, *J. Org. Chem.*, 2013, **78**, 3434-3437.
6. A. Stroba, F. Schaeffer, V. Hindie, L. Lopez-Garcia, I. Adrian, W. Fröhner, R. W. Hartmann, R. M. Biondi and M. Engel, *J. Med. Chem.*, 2009, **52**, 4683-4693.
7. R. Wang, J. Ma and F. Li. *J. Org. Chem.*, 2015, **80**, 10769-10776.
8. B. Pandey, S. Xu and K. Ding, *Org. Lett.*, 2019, **21**, 7420-7423.
9. Y. Yu and L. S. Liebeskind, *J. Org. Chem.*, 2004, **69**, 3554-3557.
10. X. Dai, T. Li, B. Wang, C. Kreyenschulte, S. Bartling, S. Liu, D. He, H. Yuan, A. Brückner, F. Shi, J. Rabeah and X. Cui, *Angew. Chem. Int. Ed.*, 2023, **62**, e202217380 (1 of 8).