

Supporting Information

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A General and Efficient Heterogeneous Gold-Catalyzed Hydration of Nitriles in Neat Water under Mild Atmospheric Conditions

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1. Preparation

A. Catalytic materials

Gold catalysts including 1.5 wt % Au/TiO₂ (reference catalyst, type A, lot no. 02-1) and 4.5 wt % Au/Fe₂O₃ (reference catalyst, type C, lot no. 02-5) were supplied by the World Gold Council (WGC). 0.9 wt % Au/Al₂O₃ was purchased from Mintek. HAuCl₄, Au(PPh₃)₃Cl, Au₂O₃ and Au powder were provided by Aldrich.

B. Preparation of Au/TiO₂-VS catalysts

A modified deposition-precipitation (DP) procedure as our previously report^[S1] has been employed to prepare the 0.5 wt % Au/TiO₂-VS sample. An appropriate amount of TiO₂ (Evonik P25, specific surface area: 45 m²/g nonporous, 70% anatase and 30% rutile) was added to 100 mL of aqueous HAuCl₄ solution at a fixed pH = 8 adjusting with 0.2 M NaOH. The mixture was aged for 2 h at 80 °C under vigorous stirring, after which the suspension was cooled to room temperature. Extensive washing with 0.2 M NH₄NO₃ and then deionized water was followed to remove Na⁺ and Cl⁻. The samples were dried under vacuum at room temperature for 12 h, and then reduced in 5% H₂/Ar at 300 °C for 2 h. The as-prepared Au/TiO₂ with very small Au nanoparticles (*ca.* 1.9 nm, see TEM data in Figure S1) was denoted as Au/TiO₂-VS.

C. Preparation of Pd/TiO₂ and Pt/TiO₂ catalysts

0.5 wt % Pd/TiO₂ and 0.5 wt % Pt/TiO₂ catalysts were prepared by incipient-wetness impregnation of the support (P25, Evonik), with aqueous solution of H₂PtCl₆·6H₂O (Aldrich), Pd(NO₃)₂·6H₂O precursors of appropriate concentrations (typically 1.0 mL/g support). After a perfect mixing of the corresponding slurries, samples were dried under vacuum at room temperature for 12 h and then reduced in 5% H₂/Ar at 450 °C for 3 h.

D. Preparation of Ag/HAP catalysts

Hydroxyapatite (HAP) was prepared through a liquid-precipitation method.^[S2] 3 wt % Ag/HAP was prepared by the procedure following the literature.^[S3] An appropriate amount of HAP was soaked in aqueous solution of AgNO₃ and stirred at 25 °C for 6 h. The obtained slurry was filtered, washed, and dried at room temperature *in vacuo*. Reduction with an aqueous solution of KBH₄ yielded HAP-supported Ag/HAP.

E. Preparation of Ru(OH)_x/Al₂O₃ catalysts

The 1 wt % Ru(OH)_x/Al₂O₃ catalyst was prepared by the procedure following the literature.^[S4] An appropriate amount of γ-Al₂O₃ (JRC-ALO-4) was vigorously stirred with aqueous solution of RuCl₃ for 15 min at room

temperature. The initially brown aqueous phase became clear, and the powder turned to dark gray. The powder was filtered, washed with a large amount of water, and then dried in *vacuo*. The obtained powder was added into 30 mL of deionized water and the pH of the solution was slowly adjusted to 13.2 by addition of an aqueous solution of NaOH (1.0 M) and the resulting slurry was stirred for 24 h. The powder color was changed from dark gray to dark green. The solid was filtered off, washed with a large amount of water, and dried in *vacuo* to afford Ru(OH)_x/Al₂O₃.

F. Preparation of Au/SiO₂ catalysts

1.0 wt % Au/SiO₂ catalysts were prepared by DP with NH₃ solution method.^[S5] An appropriate amount of SiO₂ (Aldrich, Davisil) was introduced into the HAuCl₄ solution. The slurry was stirred at 75 °C for 1 h in order to let the precursor to diffuse into the pores of silica. After stirring, the solution was cooled down to room temperature and 4 M NH₄OH was added to the solution under stirring. Adding the ammonia solution yielded a colorless liquid over the suspended silica support. After 1 h stirring the support was yellow and the liquid phase remained colorless. The catalyst was washed three times with de-ionized water at room temperature and separated by centrifugation. After washing the catalysts were dried overnight in an oven at 60 °C. Prior to their use the catalysts were reduced in 5% H₂/Ar at 300 °C. The gold content was analyzed by ICP-AES. *Safety note:* The mixing of gold chloride and ammonia solutions may lead to the formation of explosive gold compounds (fulminating gold).^[S6] However, gold catalysts have been prepared by similar way using ammonia solution as a washing agent, but the explosive character of the prepared samples was not experienced. Based on our experimental observations, mixing of ammonia solution (not concentrated, 4 M) with gold chloride solution with very low concentration (0.5 mM) at room temperature does not result in explosive and friction-sensitive gold compounds.

G. Preparation of Au/HAP catalysts

Homogeneous DP method using urea as the precipitation agent has been employed to prepare the 3.0 wt % Au/HAP sample.^[S7] Typically, an appropriate amount of HAP was added to an aqueous solution with aqueous solution of HAuCl₄ and urea (urea/Au = 100, molar ratio). The suspension was heated to 90 °C and stirred for 4 h, followed by filtering and washing for several times with distilled water. The resulting solid product was dried overnight and finally the purple catalyst was obtained by calcination at 300 °C for 4 h.

H. Preparation of Au/CeO₂ catalysts

0.5 wt % Au/CeO₂ catalysts were prepared by a routine DP method.^[S8] An appropriate amount of aqueous solutions of HAuCl₄ was heated to 80 °C under vigorous stirring. The pH was adjusted to 10 by dropwise addition of NaOH (0.2 M), and then suitable amount of CeO₂ (Evonik, Adnano 90, specific surface area: 90 m²/g) was dispersed in the solution. The mixture was aged for 2 h at 80 °C, after which the suspension was cooled to room temperature. Extensive washing with deionized water was then followed until it was free of chloride ions. The samples were dried under vacuum at room temperature for 12 h, and reduced in 5% H₂/Ar at 300 °C.

I. Preparation of Au colloid catalysts

Citrate-stabilized Au colloid was also prepared according to the literature method.^[S9] 20 mL aqueous solution containing 2.5×10^{-4} M HAuCl₄ and 2.5×10^{-4} M trisodium citrate was prepared in a conical flask. Next, 0.6 mL of

ice-cold, freshly prepared 0.1M NaBH₄ solution was added to the solution while stirring. The solution turned pink immediately after adding NaBH₄, indicating particle formation.

J. Preparation of 1.0 wt% Au/C catalysts

Au/C catalyst was prepared by the procedure as described elsewhere.^[S10] Typically, the poly vinyl alcohol (PVA) was added (Au/PVA = 1.5:1, wt/wt) to a aqueous solution containing 5.0×10^{-4} M HAuCl₄ at 25 °C under vigorous stirring. The obtained solution was then left under stirring for 10 min. A following rapid injection of an aqueous solution of 0.1 M NaBH₄ (Au/ NaBH₄ = 1:5, mol/mol), led to formation of a dark orange-brown solution, indicating the formation of the gold sol. Activated carbon (refluxed with 2.5 wt % HNO₃ solution for 6 h) was then added to the colloidal gold solution under stirring and kept in contact until total adsorption (1 wt % of gold on the support) occurred. After 2 h, the slurry was filtered and the total absorption of gold was checked by ICP analysis of the filtrate. The average Au particle size based on TEM was ca. 3.2 nm (Figure S1).

2. Catalytic activity measurements

A. General procedure for Hydration of Nitriles

A typical procedure for the hydration of nitriles is as follows. Metal catalysts (metal: 1 mol %) was added to the mixture of nitriles (1.0 mmol) in H₂O (3 mL) in a reaction vessel equipped with a condenser under air. The resulting mixture was vigorously stirred at desired temperature. After the reaction, the reaction mixture was extracted with a mixture of CHCl₃ and methanol (10:1) three times. Conversion and yield of the hydrated products were determined by HPLC [STR ODSII (150×4 mm), detection at 254 nm, flow rate 1.0 mL/min eluent: a mixture of methanol and water (3:7)]. HPLC retention times were in agreement with those of authentic samples and also with the reported data.

B. Procedure for 100-mmol scale hydration of pyrazinecarbonitrile and reuse of Au/TiO₂-VS

A mixture of nitrile (100 mmol), Au/TiO₂-VS (Au: 0.001 mol %), H₂O (35 mL) was charged into autoclave (100 mL). The reaction mixture was stirred (1000 rpm with a magnetic stir bar) at 140 °C under air. After the hydration, the spent Au/TiO₂-VS could be easily separated from the reaction mixture at 90 °C by a filtration and the isolated Au/TiO₂-VS were washed with ethanol and deionized water prior to reuse. These recycling procedures were repeated ten times in the same manner. Time profile of 10th reuse experiment is shown in Figure S3. For isolation, after the reaction mixture cooled down to room temperature, the water was evaporated under reduced pressure and the product was purified by flash chromatography using a gradient of pentane/ethyl acetate (7:3 →0:1).

C. Comparison of the procedure for hydration in D₂O and H₂O

A mixture of nitrile (1 mmol), Au/TiO₂-VS (Au: 0.2 mol %), H₂O or D₂O (5 mL) was charged into a reaction vessel equipped with a condenser under air (10 mL). The reaction mixture was stirred (1000 rpm with a magnetic stir bar) at 60 °C. A significant kinetic isotope effect ($k_H/k_D = 1.43 \pm 0.02$) was observed for the Au/TiO₂-VS-catalyzed hydration of **1**, suggesting that O-H bond cleavage could be involved in the rate-determining step.

D. Procedure for competitive hydration of benzonitrile and *p*-substituted benzonitriles

Competitive hydration of benzonitrile and *p*-substituted benzonitriles was carried out as follows. A mixture of 0.5 mmol benzonitrile, 0.5 mmol *p*-substituted benzonitriles, Au/TiO₂-VS (Au: 0.1 mol %) and 5 mL H₂O was charged into a reaction vessel equipped with a condenser under air. The reaction mixture was stirred at 80 °C for 30 min and stopped the reaction by filtrated the catalysts at this temperature. The results were determined by HPLC as above described. It should be noted that under this reaction condition, the raw material and products were dispersed very well in water. The order of reactivity was *p*-OCH₃ < *p*-CH₃ < *p*-H < *p*-Cl < *p*-NO₂. The good linearity of Hammett plots suggests that the present hydration proceeds with a single mechanism. The slope of the linear line gave a Hammett ρ value of 0.79. The positive Hammett value might be due to the formation of a negatively charged transition state which is also consistent with the proposed mechanism.

E. Procedure for conversion of 6-aminocapronitrile to ε-caprolactam

A mixture of 6-aminocapronitrile (1 mmol), metal catalysts (Au: 1 mol %), and H₂O (5 mL) was charged into an autoclave (50 mL). The reaction mixture was magnetically stirred (1000 rpm) at 120 °C under air for 12 h. The isolated yield achieved to 91%, this result shows that it is possible to achieve high conversion of 6-aminocapronitrile with excellent selectivity to ε-caprolactam through this clean one-pot procedure.

3. Results

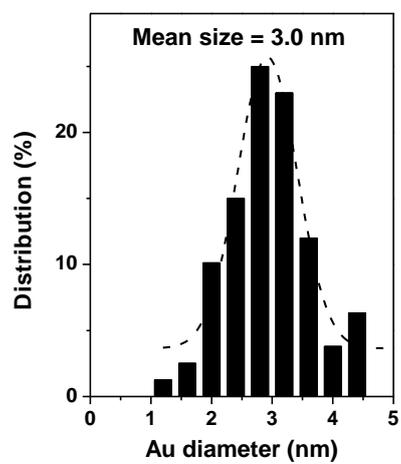
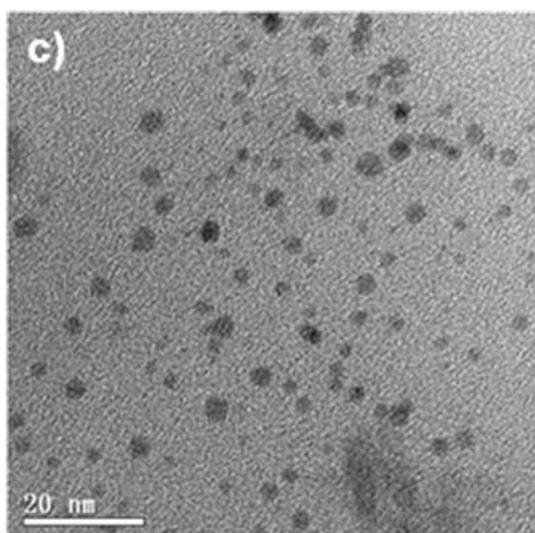
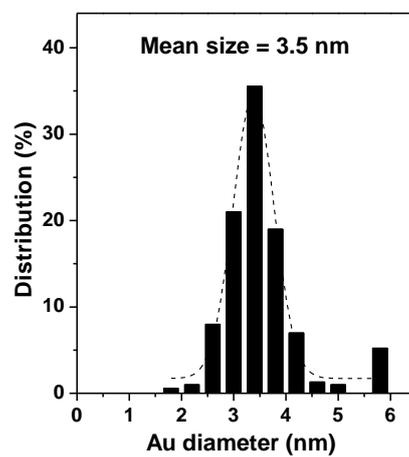
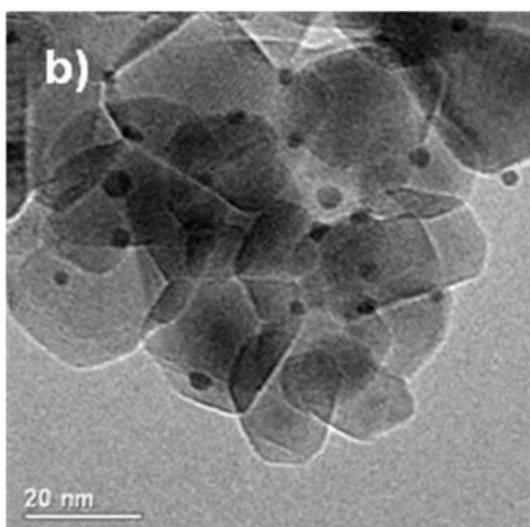
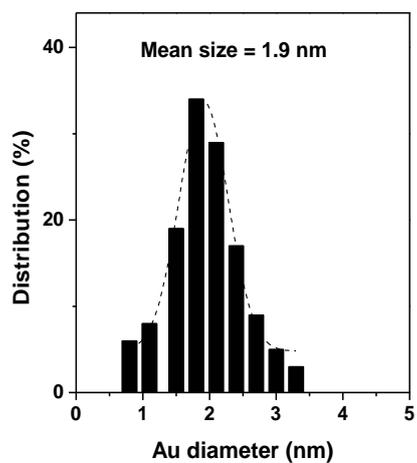
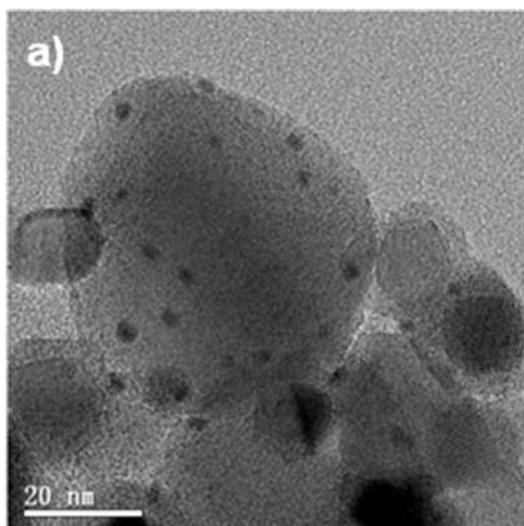
A. Hydration of benzonitrile using different catalyst

Table S1 Hydration of benzonitrile (**1**) to benzamide (**2**) with various catalysts^[a]

Entry	catalysts	Atmosphere	Conversion (%)	Selectivity (%)	Yield (%) ^[b]
1	HAuCl ₄	air	n.r.	/	/
2	Au(PPh ₃) ₃ Cl	air	n.r.	/	/
3	Au ₂ O ₃	air	n.r.	/	/
4	Au colloid	air	n.r.	/	/
5	Au powder	air	n.r.	/	/
6	no	air	n.r.	/	/
7 ^[c]	TiO ₂ (P25)	air	n.r.	/	/
8	Au/TiO ₂ -VS	air	>99	99	99
9	Au/TiO ₂ -VS	Ar	>99	99	99
10	Au/TiO ₂ -VS	O ₂	>99	99	99

[a] Reaction conditions: benzonitrile (1 mmol), catalyst (Au: 1 mol %), H₂O (3 mL), 60 °C, 4 h. [b] Conversion and selectivity determined by HPLC analysis. [c] 200 mg pure TiO₂.

B. TEM images of supported gold catalysts



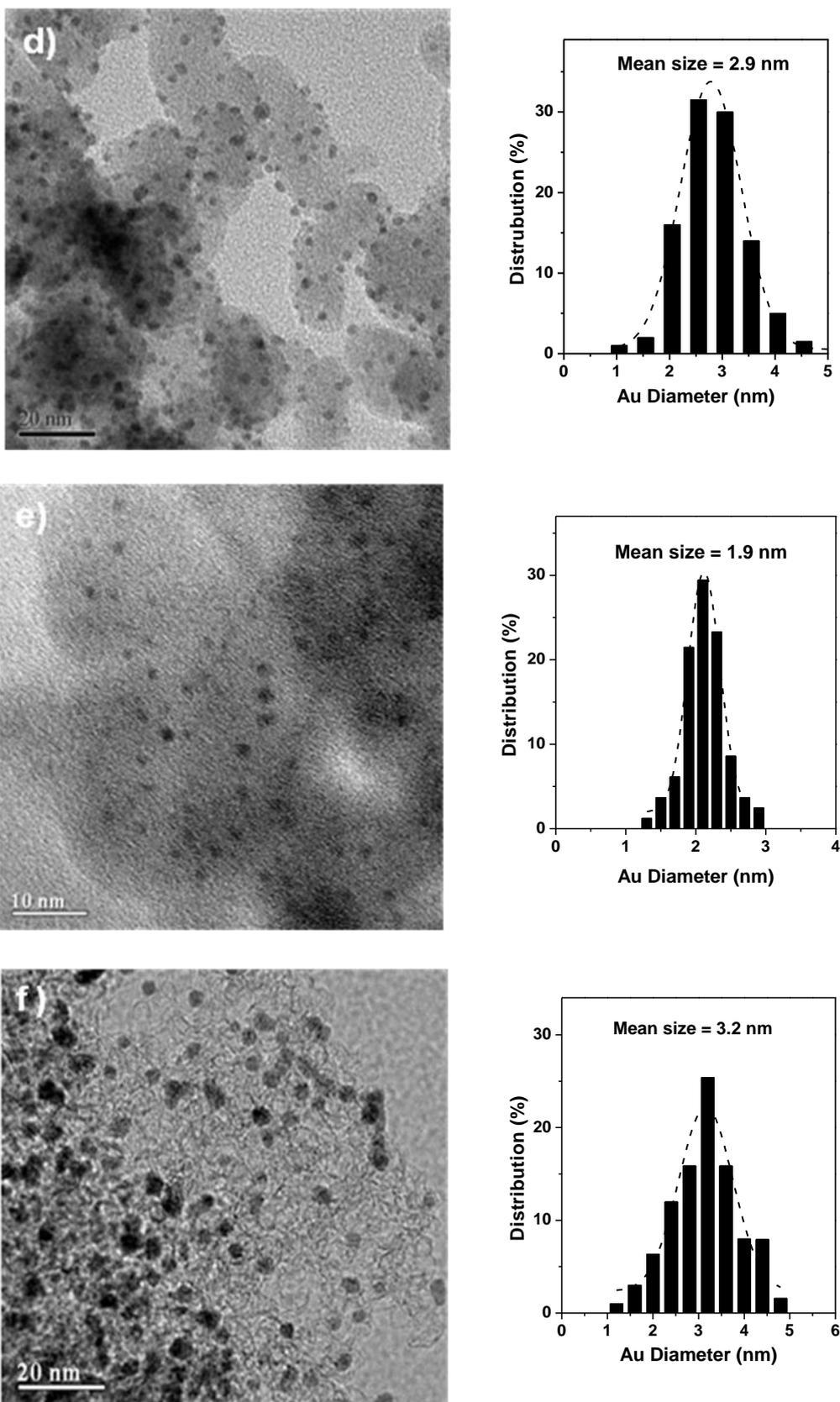


Figure S1. TEM image and gold particle size distribution of a) Au/TiO₂-VS; b) Au/TiO₂; c) Au *colloid*; d) Au/HAP; e) Au/SiO₂; f) Au/C.

C. XANES spectra

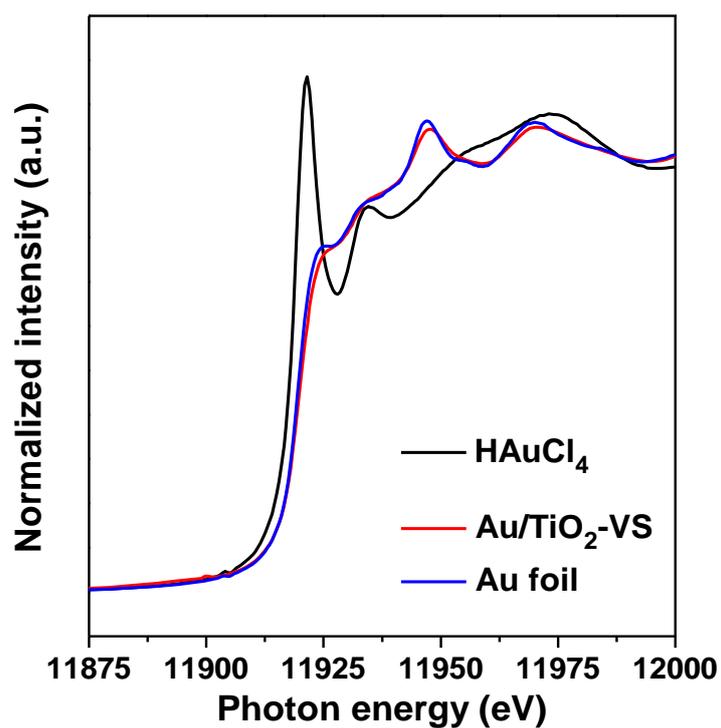


Figure S2. Au L₃-edge XANES spectra of the HAuCl₄, Au foil and Au/TiO₂-VS

D. Recycle result of Au/TiO₂-VS

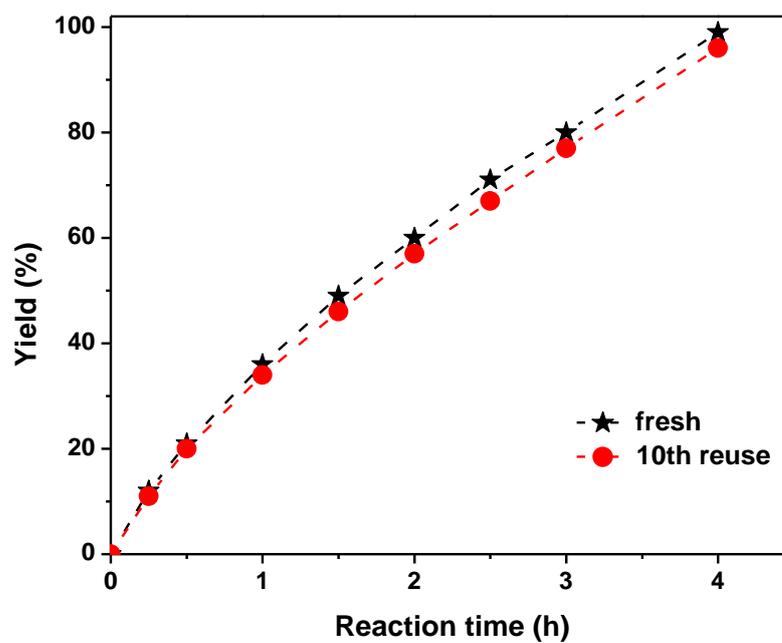


Figure S3. The profile of hydration of pyrazinecarbonitrile over Au/TiO₂-VS.

E. FTIR study of the interaction between the Au/TiO₂-VS and nitriles

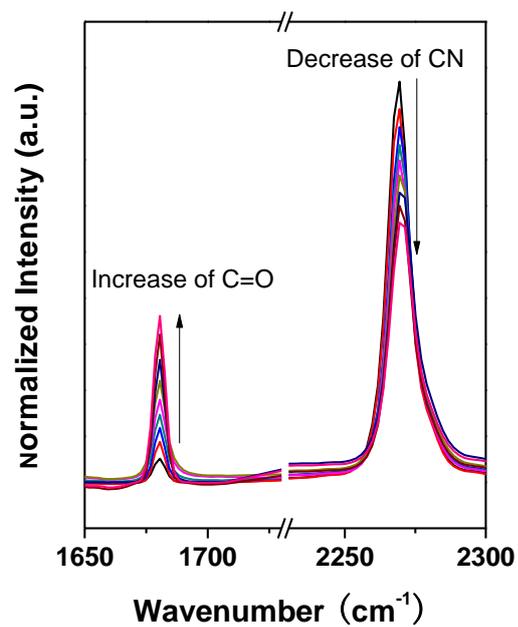


Figure S4. Time-resolved FTIR spectra of 1 adsorbed on Au/TiO₂-VS.

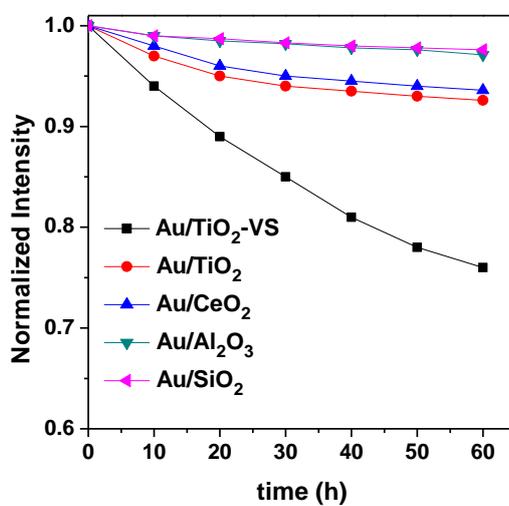


Figure S5. Decrease of 1 adsorbed on various gold catalysts (the bands were normalized using the corresponding intensities based on the in situ FTIR data).

F. H₂O and D₂O effect to the catalytic activity

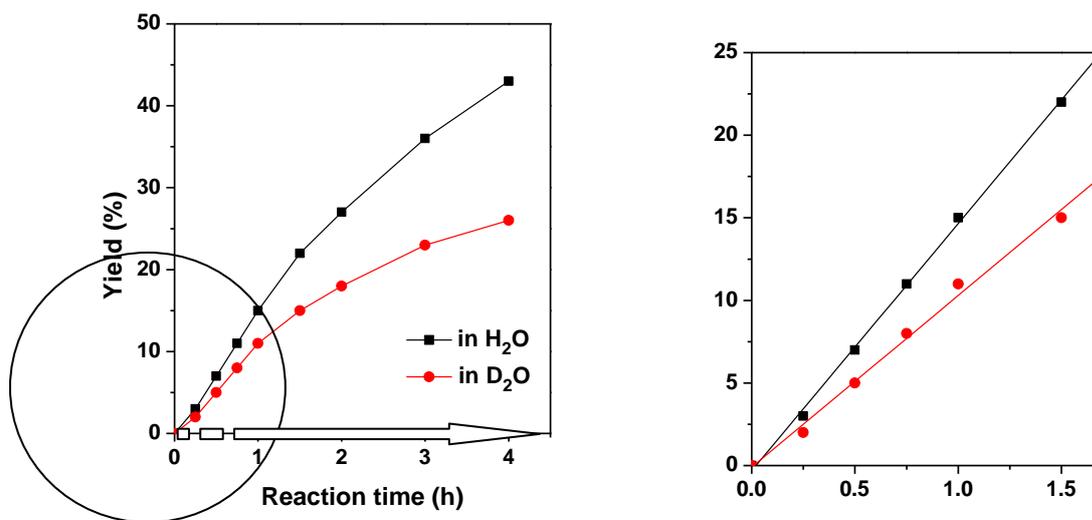


Figure S6. The profile of hydration of benzonitrile with Au/TiO₂-VS in H₂O and D₂O.

G. Hammett plots for the competitive reaction of benzonitrile and *p*-substituted benzonitrile using Au/TiO₂-VS

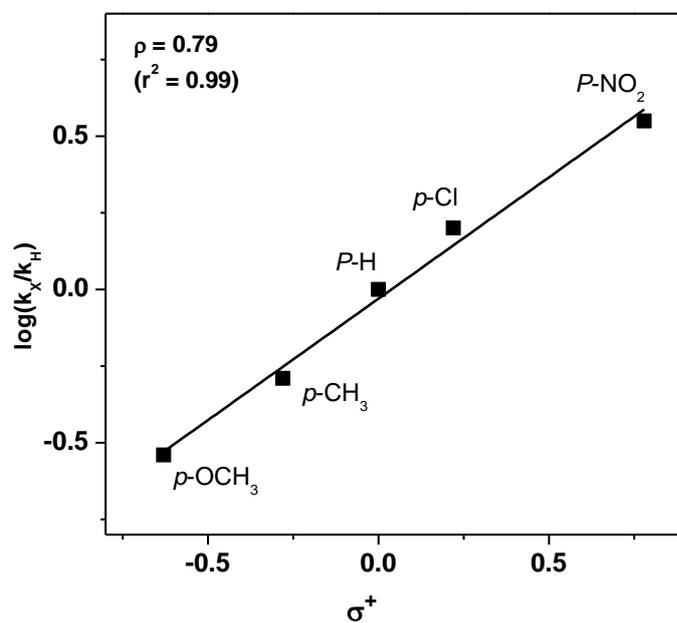
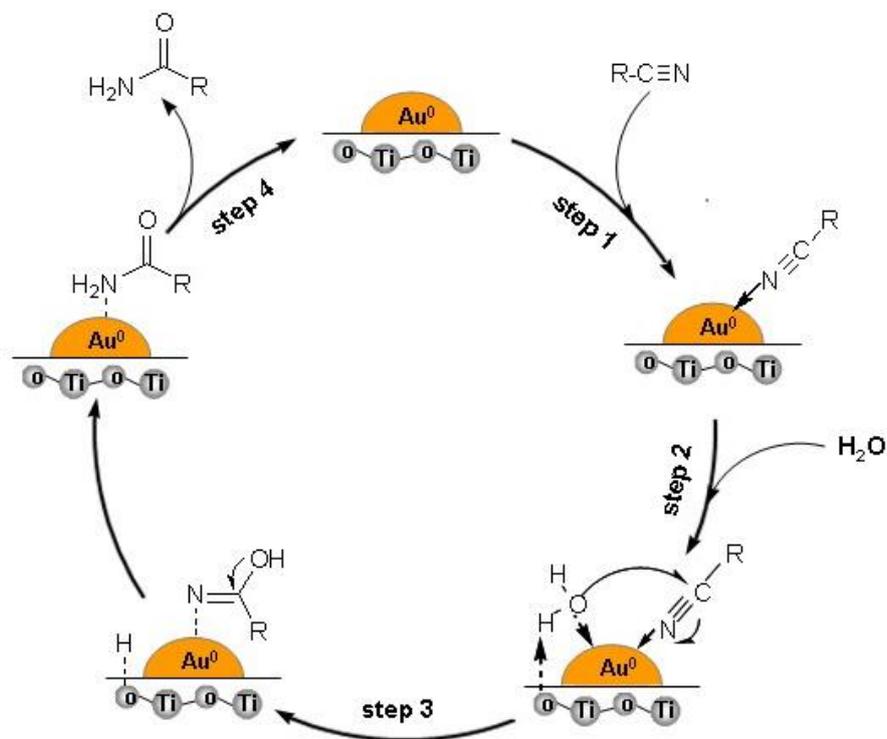


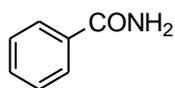
Figure S7. Brown-Okamoto plot for the competitive reaction of hydration of benzonitrile and *p*-substituted benzonitrile.

H. Proposed reaction mechanism

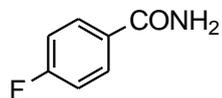


Scheme S1. A proposed reaction mechanism for the Au/TiO₂-VS catalyzed hydration of nitriles

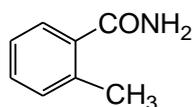
I. Characterization of amides



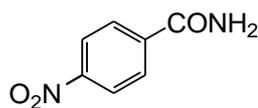
(Table 1, entry 1). $^1\text{H-NMR}$ (CH_3OD , 400 MHz) δ 7.87 (d, $J = 4.8$ Hz, 2H), 7.53 (t, $J = 7.3$ Hz, 1H), 7.45 (t, $J = 7.5$ Hz, 2H).



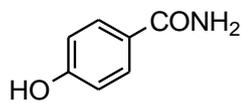
(Table 1, entry 2). $^1\text{H-NMR}$ (CH_3OD , 400 MHz) δ 7.93 (q, $J = 4.8$ Hz, 2H), 7.18 (t, $J = 8.8$ Hz, 2H).



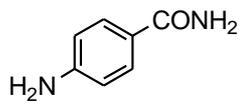
(Table 1, entry 8). $^1\text{H-NMR}$ (CH_3OD , 400 MHz) δ 7.40 (d, $J = 3.8$ Hz, 1H), 7.34 (d, 1H), 7.23 (q, 2H), 2.43 (s, 3H).



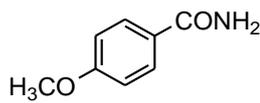
(Table 1, entry 10). $^1\text{H-NMR}$ (CH_3OD , 400 MHz) δ 8.31 (d, $J = 4.2$ Hz, 2H), 8.07 (d, $J = 3.6$ Hz, 2H).



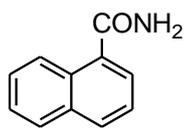
(Table 1, entry 11). $^1\text{H-NMR}$ (CH_3OD , 400 MHz) δ 7.50 (d, $J = 4.2$ Hz, 2H), 6.87 (d, $J = 4.2$ Hz, 2H).



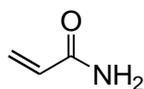
(Table 1, entry 12). $^1\text{H-NMR}$ (CH_3OD , 400 MHz) δ 7.64 (d, $J = 3.8$ Hz, 2H), 6.66 (d, $J = 3.8$ Hz, 2H).



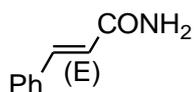
(Table 1, entry 13). $^1\text{H-NMR}$ (CH_3OD , 400 MHz) δ 7.85 (d, $J = 5.8$ Hz, 2H), 6.98 (d, $J = 4.4$ Hz, 2H), 3.85 (s, 3H).



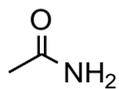
(Table 1, entry 20). ¹H-NMR (CH₃OD, 400 MHz) δ 8.29 (d, *J* = 3.8 Hz, 1H), 7.98 (d, *J* = 4.2 Hz, 1H), 7.92 (d, *J* = 3.8 Hz, 1H), 7.67 (d, *J* = 3.6 Hz, 1H), 7.54 (m, 3H).



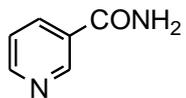
(Table 1, entry 23). ¹H-NMR (CH₃OD, 400 MHz) δ 6.25 (t, *J* = 5.6 Hz, 2H), 5.70 (q, *J* = 4.8 Hz, 1H).



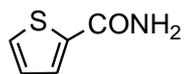
(Table 1, entry 26). ¹H-NMR (CH₃OD, 400 MHz) δ 7.57 (s, 3H), 7.38 (s, 3H), 6.66 (d, *J* = 7.6 Hz, 1H).



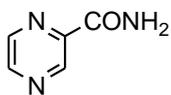
(Table 1, entry 28). ¹H-NMR (CH₃OD, 400 MHz) δ 1.94 (s, 3H).



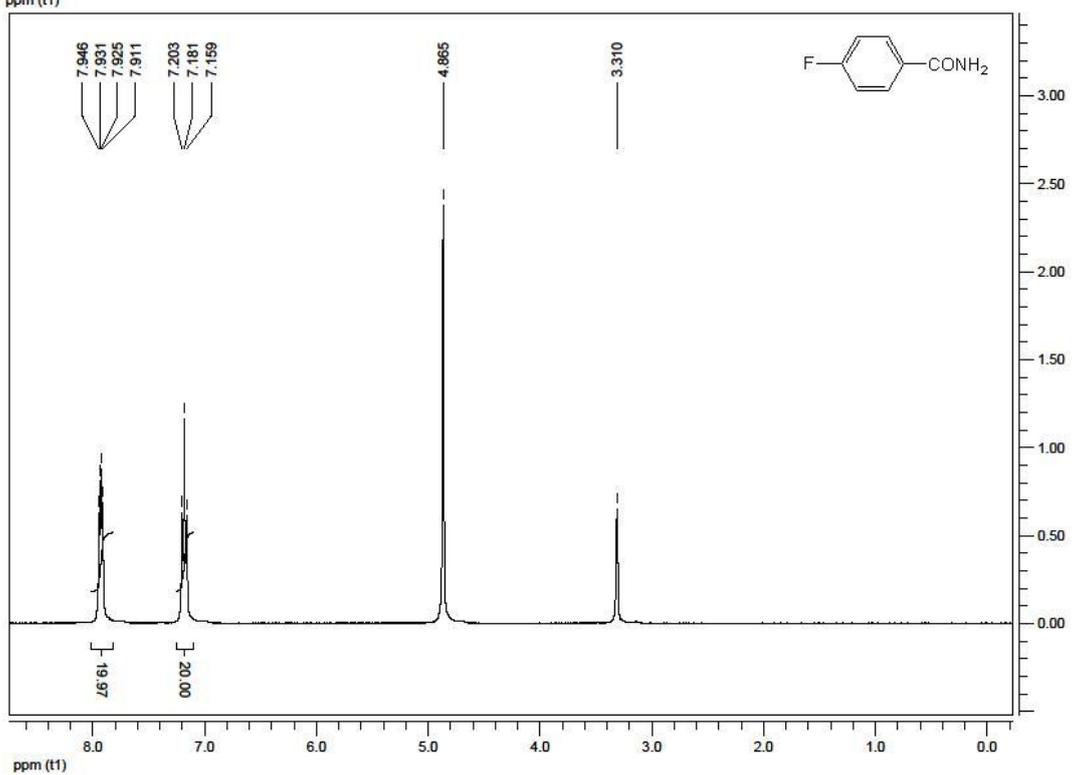
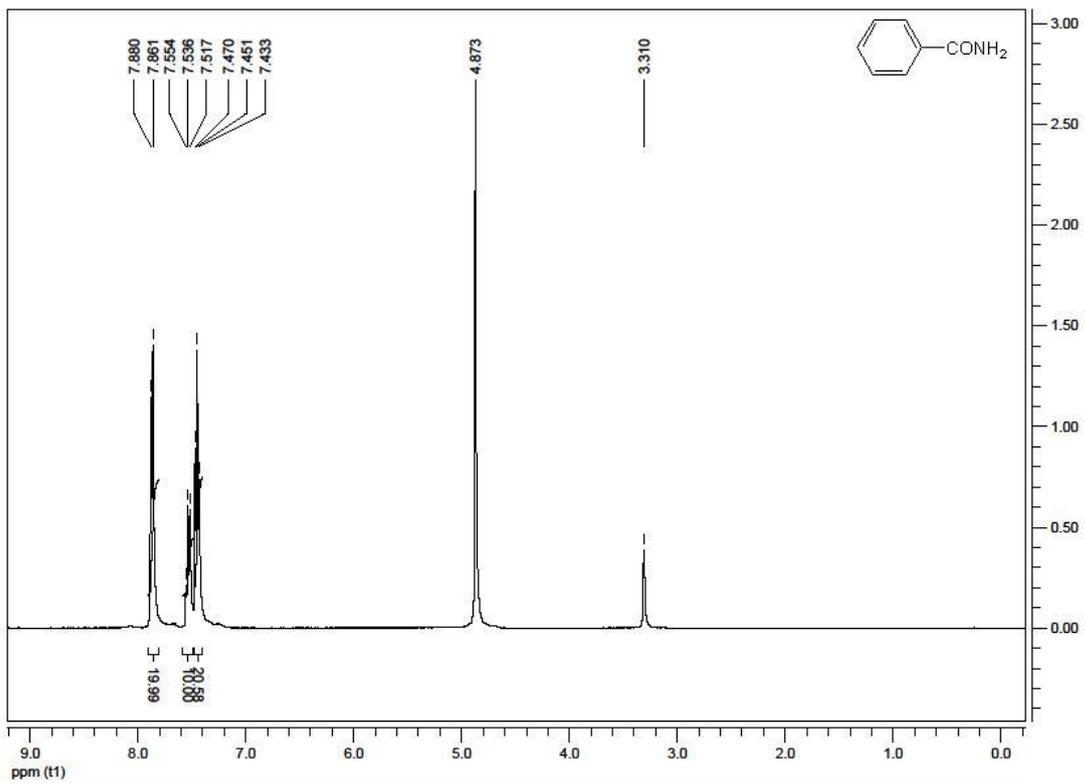
(Table 1, entry 29). ¹H-NMR (CH₃OD, 400 MHz) δ 9.02 (s, 1H), 8.69 (d, *J* = 2.2 Hz, 1H), 8.29 (m, 1H), 7.54 (m, 1H).

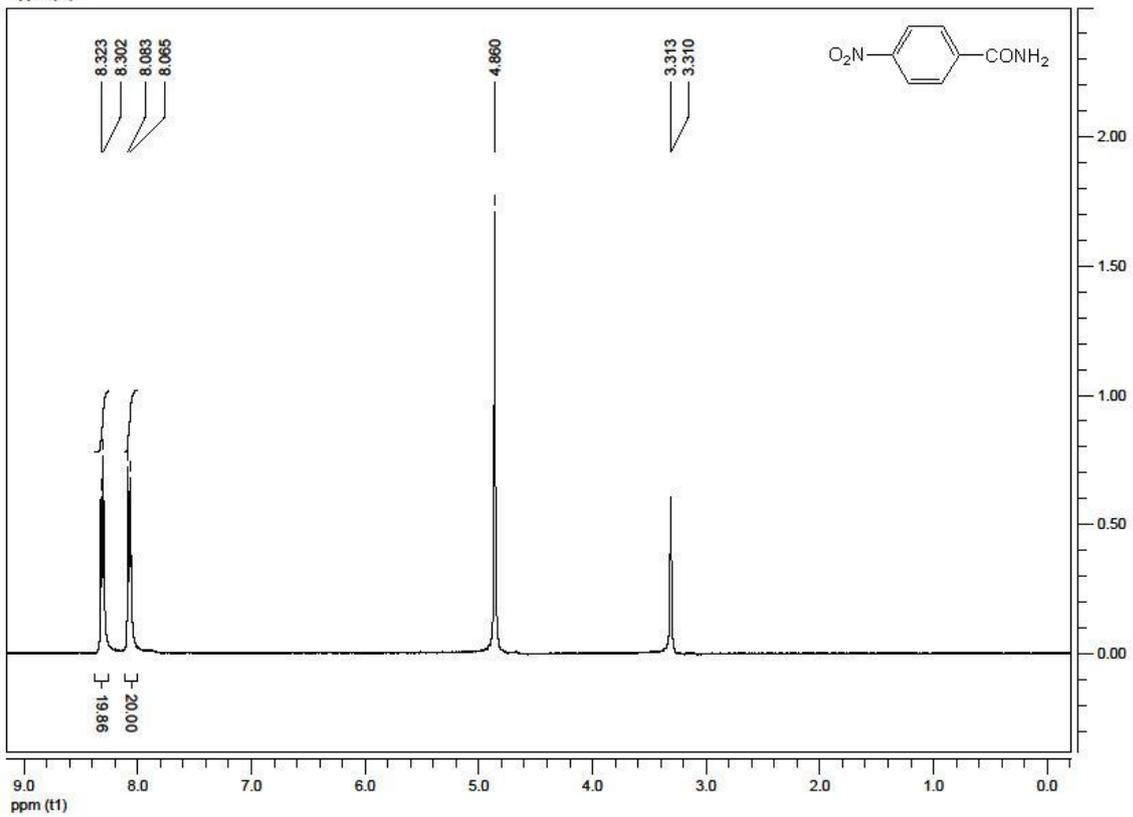
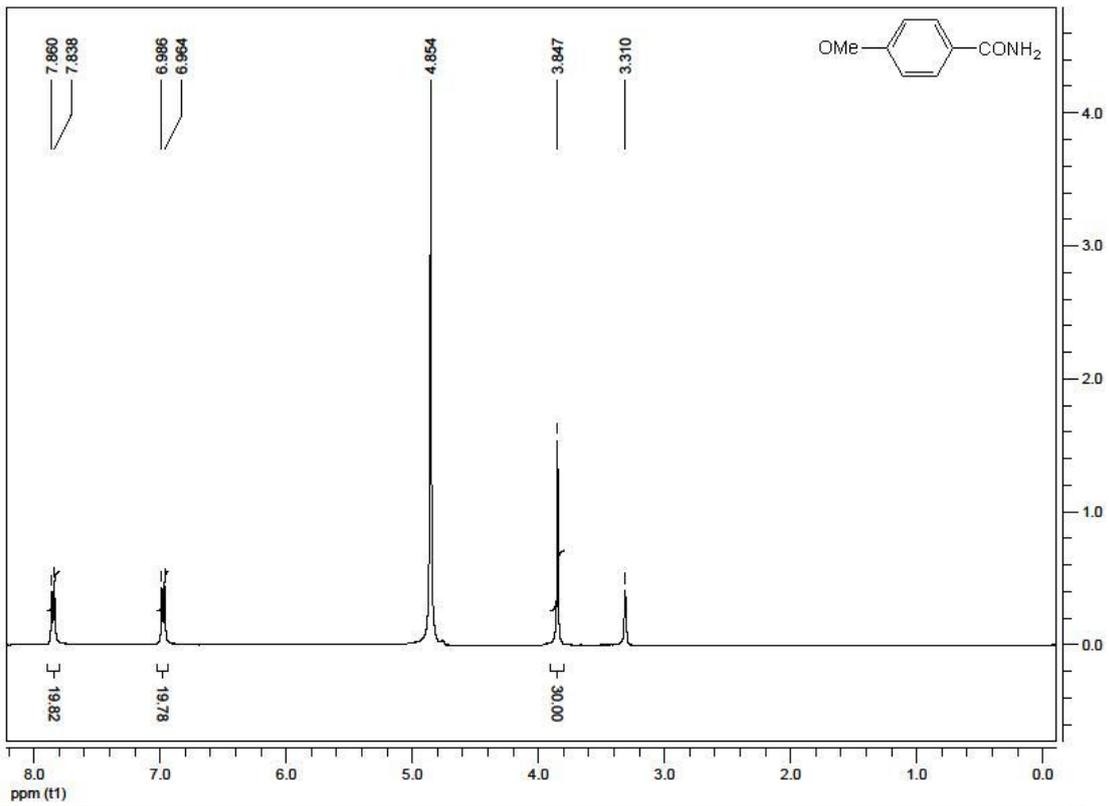


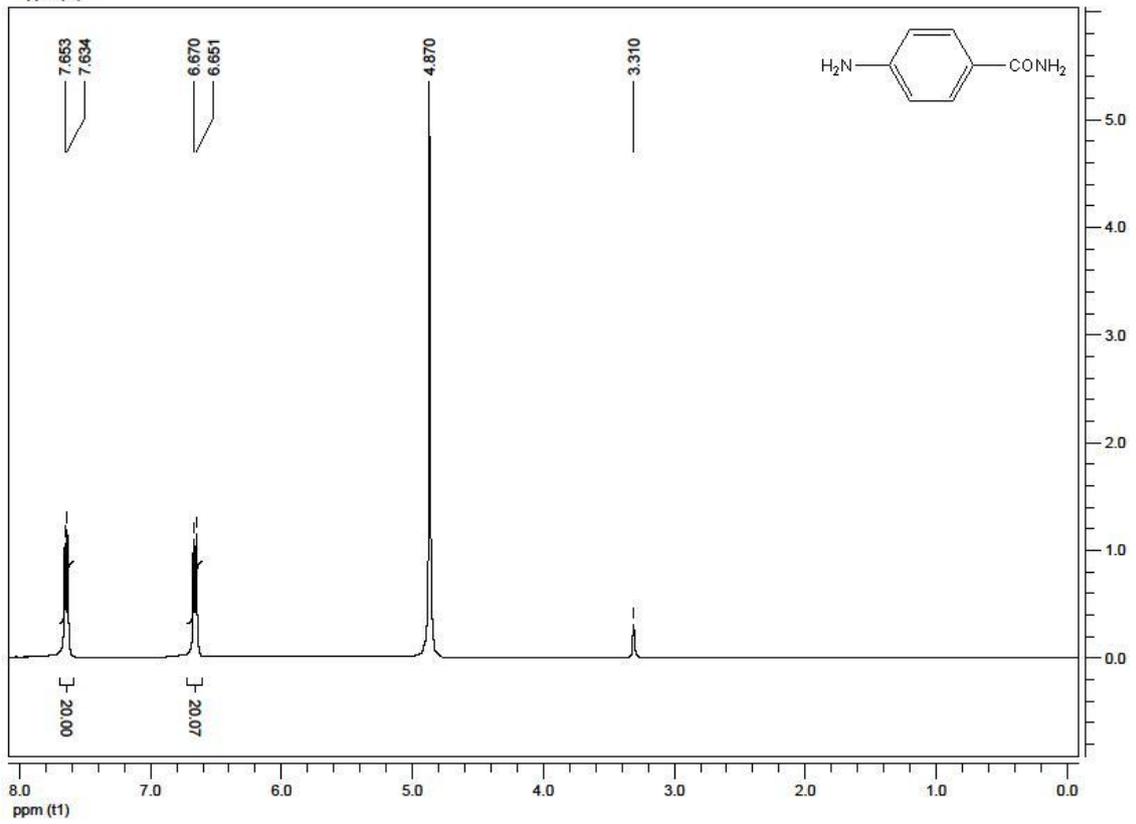
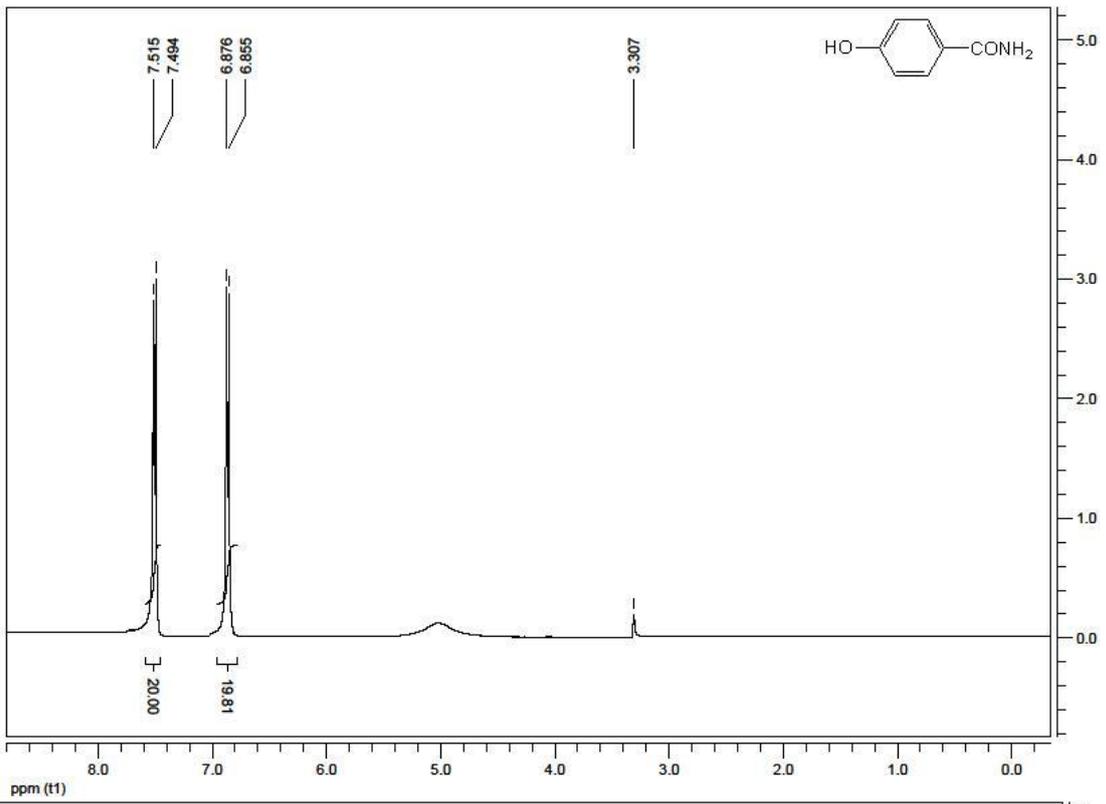
(Table 1, entry 31). ¹H-NMR (CH₃OD, 400 MHz) δ 7.71 (d, *J* = 1.6 Hz, 1H), 7.66 (d, *J* = 2.4 Hz, 1H), 7.12 (t, *J* = 4.1 Hz, 1H).

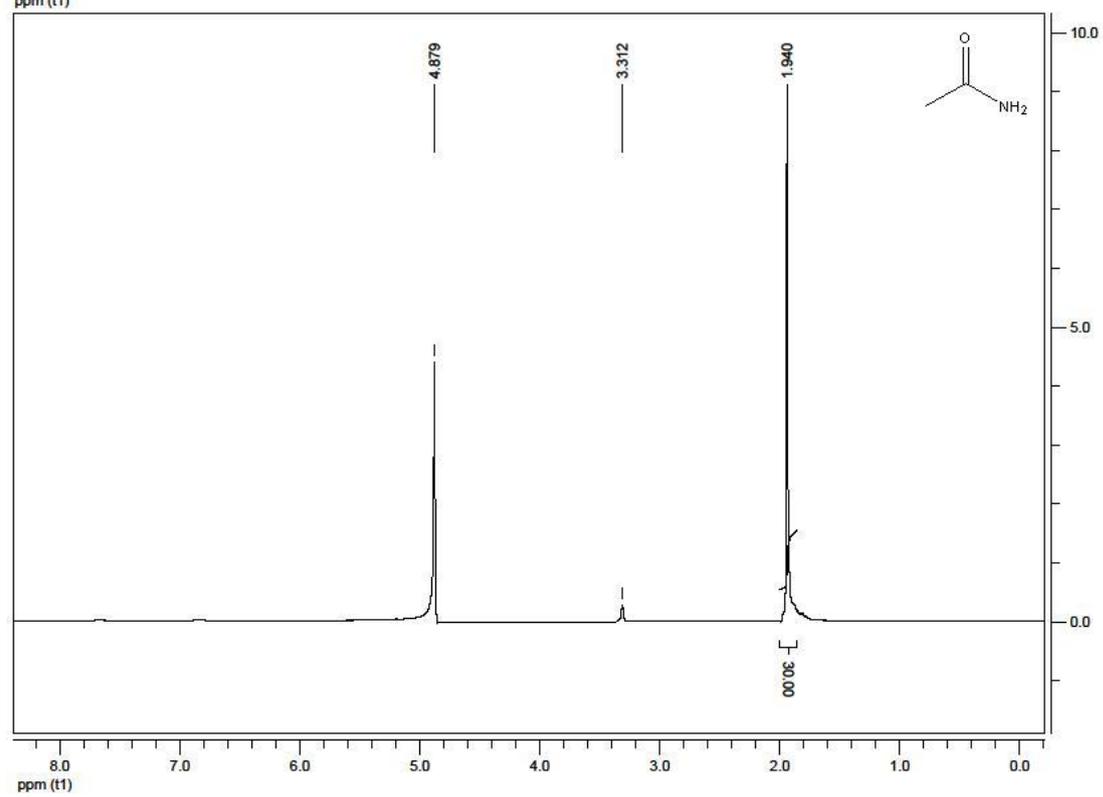
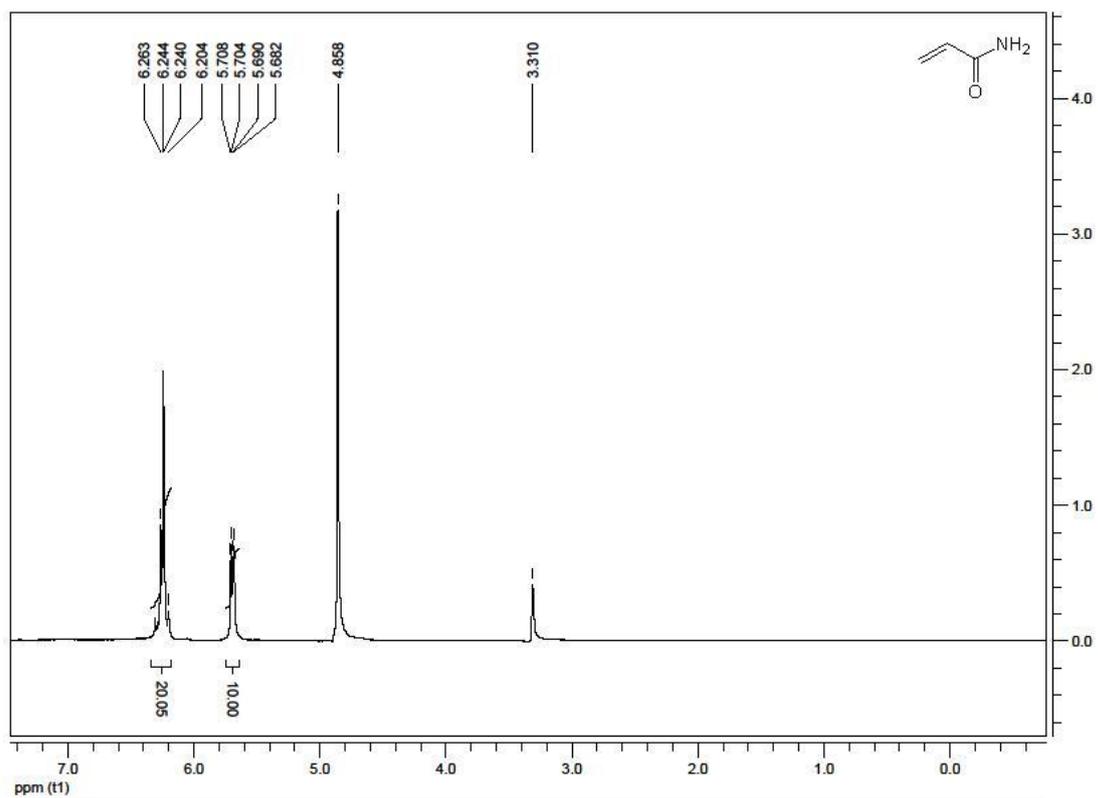


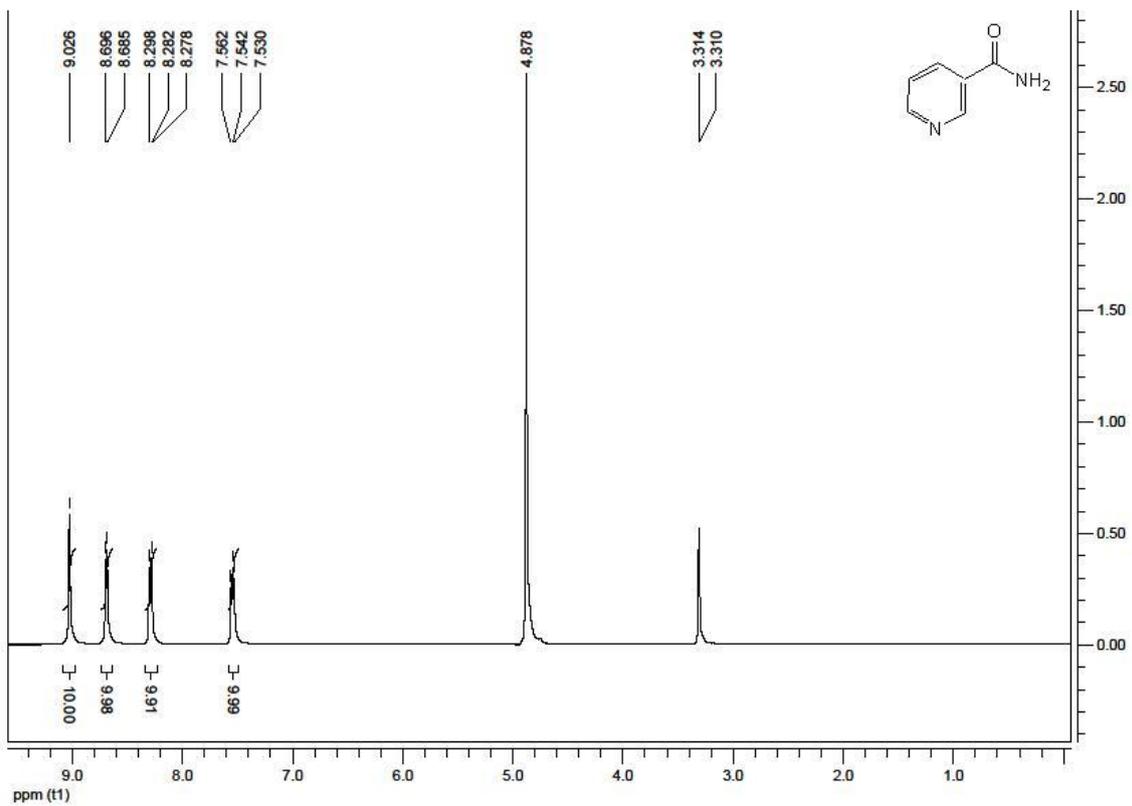
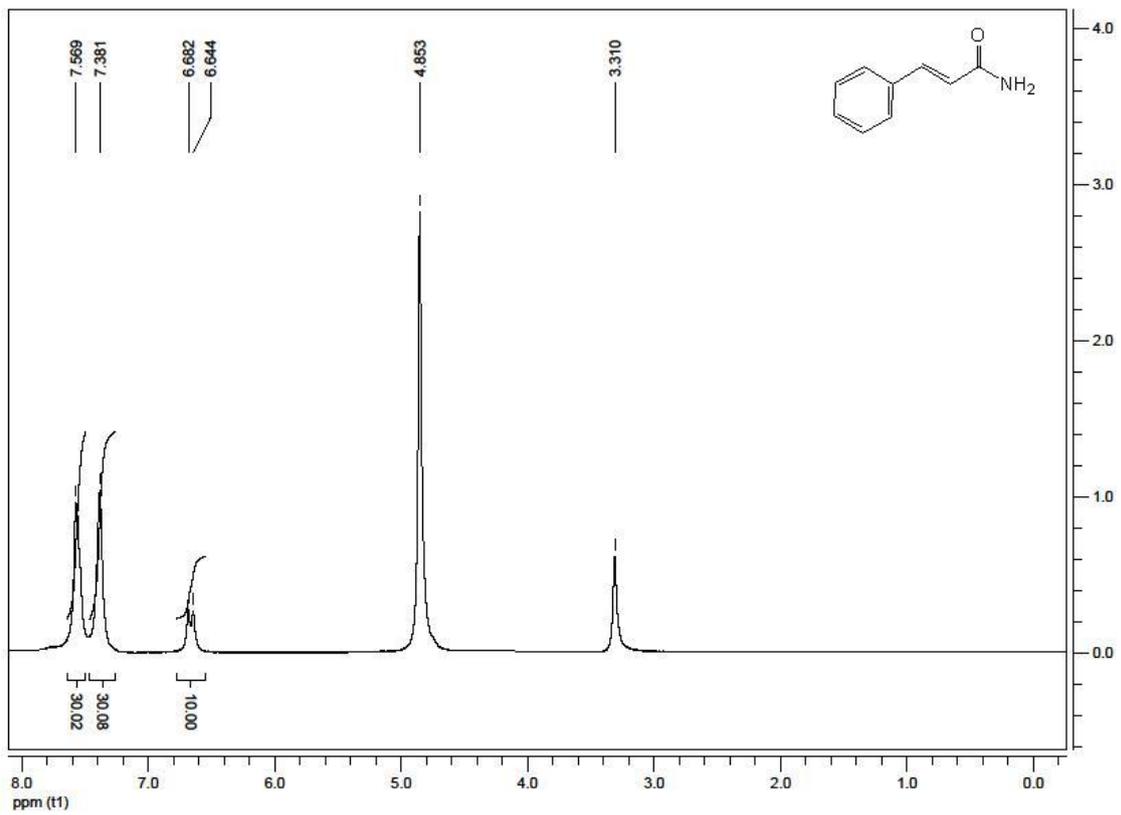
(Table 1, entry 32,33). ¹H-NMR (CH₃OD, 400 MHz) δ 9.25 (s, 1H), 9.78 (s, 1H), 9.68 (s, 1H).

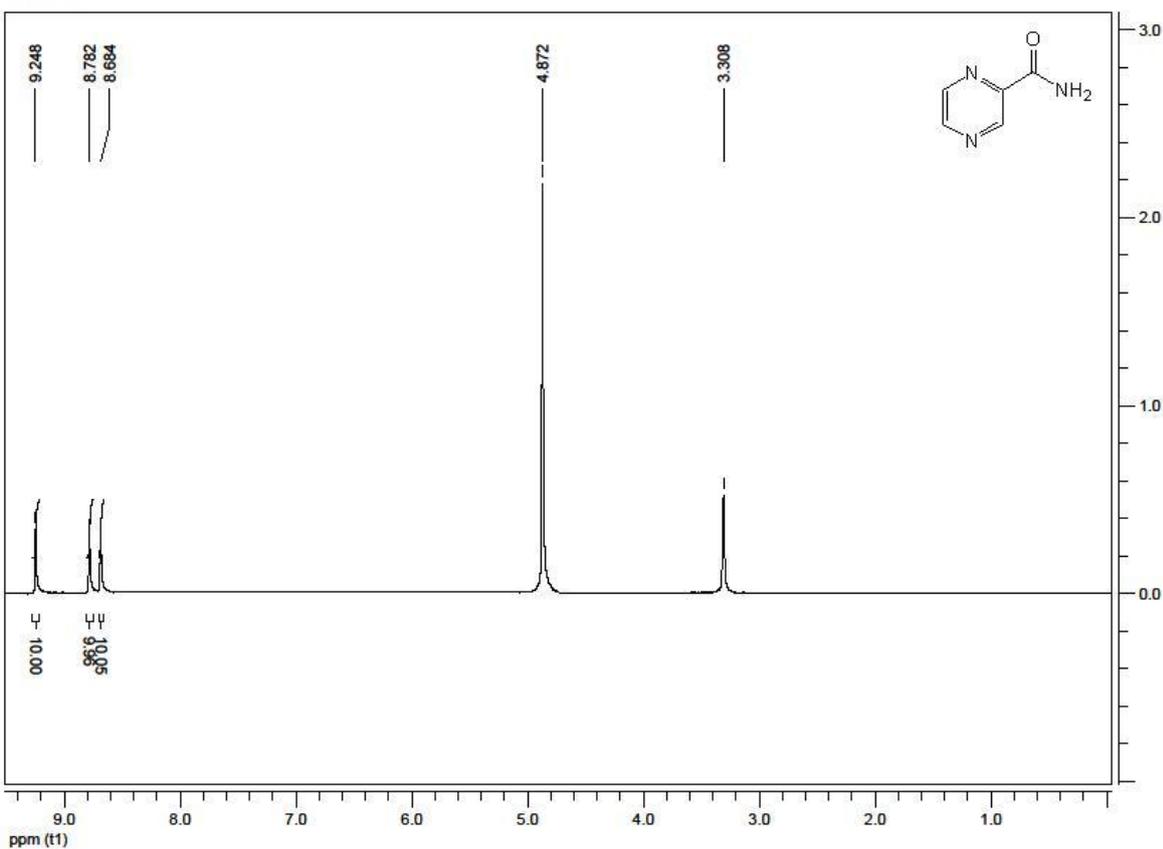
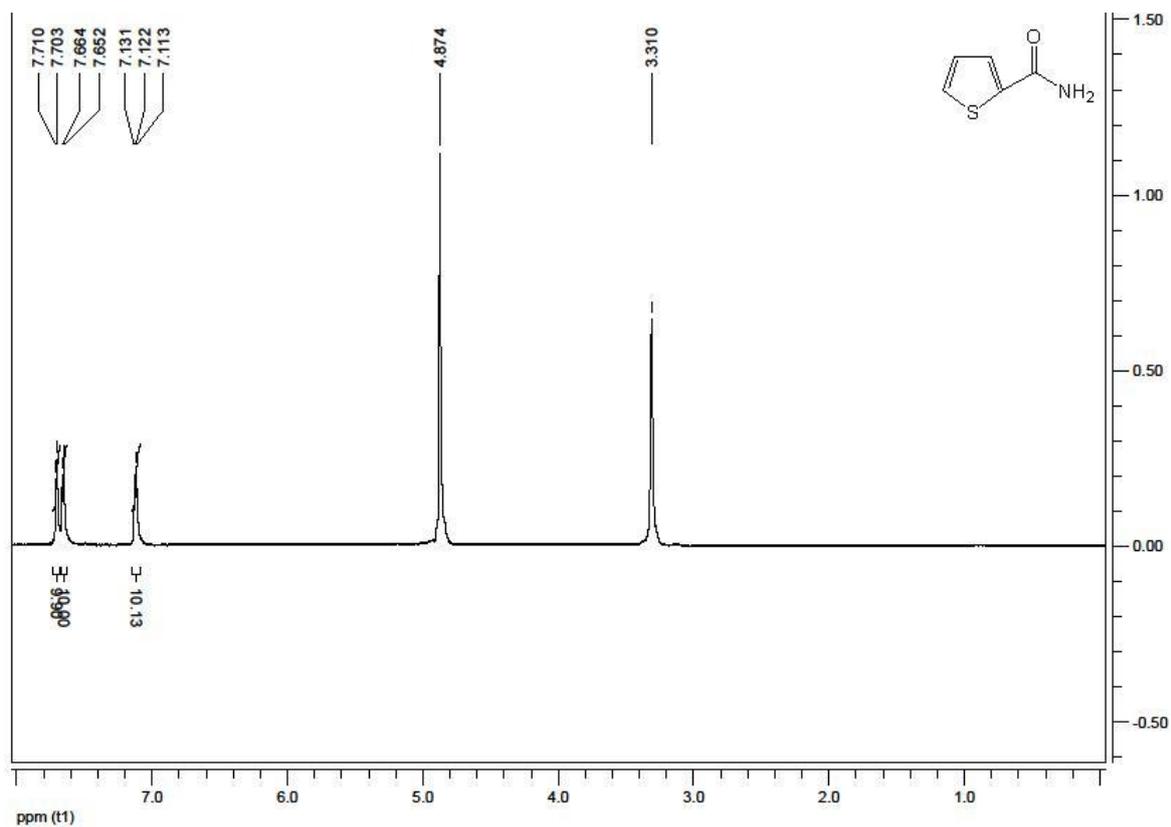












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