

Supporting Information

Amide exchange reaction: A simple and efficient CuO catalyst for diacetamide synthesis

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1 General experiment information

All solvents and chemicals used in this work were obtained commercially without further purification.

1.1 Catalyst preparation

The clubbed CuO catalyst was prepared by the hydrothermal method. At ambient temperature, 50 mmol CuCl₂·2H₂O, 50 mmol Na₂CO₃ and 50 ml deionized water, under vigorous stirring, were added into a 100 ml hydrothermal synthesis reactor. Then, 15 ml glycol was dropwise added into the above solution, reacting at 200 °C for 12 h. The resulting precipitate was separated and washed by deionized water until the pH value of the supernatant was nearly ~ 7, dried at 80 °C in air for 1 h and calcined at 400 °C for 4 hours in air.

1.2 Catalyst characterization

1.2.1 X-ray diffraction (XRD)

The XRD of the freshly prepared CuO and used CuO were measured on a Siemens D/max-RB powder X-ray diffract meter. Diffraction patterns were recorded with Cu K α radiation (40 mA, 40 kV) over a 2 θ range of 10° to 80° and a positionsensitive detector using a step size of 0.01° and a step time of 0.15 s.

1.2.2 Scanning electron microscope (SEM)

The SEM of the freshly prepared CuO catalyst was recorded on a JSM-6701F field emission scanning electron microscope with magnification times of 1×10⁵.

1.2.3 Temperature Programmed Reduction (TPR)

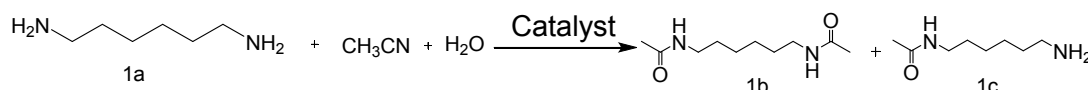
Temperature-programmed reduction (TPR) of H₂ was carried out on TPR/TPD flow system equipped with a TCD-MS detector. TPR analysis was conducted with 10 % H₂/Ar (50 ml min⁻¹). In a typical experiment, the solid sample (100 mg with particle size 160–200 nm) was pretreated at 400 °C for 1 h under Ar flow (50 ml min⁻¹) and then cooled to room temperature under argon gas flow (50 ml min⁻¹). The profile was recorded at a heating rate of 10°C min⁻¹ from ambient temperature to 600 °C and maintained at this temperature until the TCD signal of H₂ returned to the baseline.

1.3 Catalyst screening

The results of the catalyst screening of the model reaction of HDA, CH₃CN and H₂O at 180 °C for 2 h are shown in Table 1. Obviously, no HMBA was formed and the primary product was 1c if no catalyst was used in this reaction (entry 1). Next, the catalytic performance of different metallic oxide catalysts was studied. Apparently, the prepared CuO catalyst shows the excellent catalytic performance than other metallic oxides in this reaction, and 100% HDA conversion and > 99% HMBA selectivity were obtained (entry 11). When other catalysts including Fe₂O₃, MgO, CeO₂, Nb₂O₅, SiO₂, TiO₂, Y₂O₃, Al₂O₃ and ZnO were employed, much lower HDA conversions and HMBA selectivity were obtained (entry 2-10). To sum up, the prepared CuO catalyst might be more suitable for the AER of HDA, CH₃CN and H₂O.

Table 1 Catalyst screening for the synthesis of HMBA^a

Entry	Ratio HDA: CH ₃ CN: H ₂ O	Catalyst/mg	Conv.(%) ^b	Sel.(%) ^c	
				1b	1c
1	1:3:6	None	8	-	trace



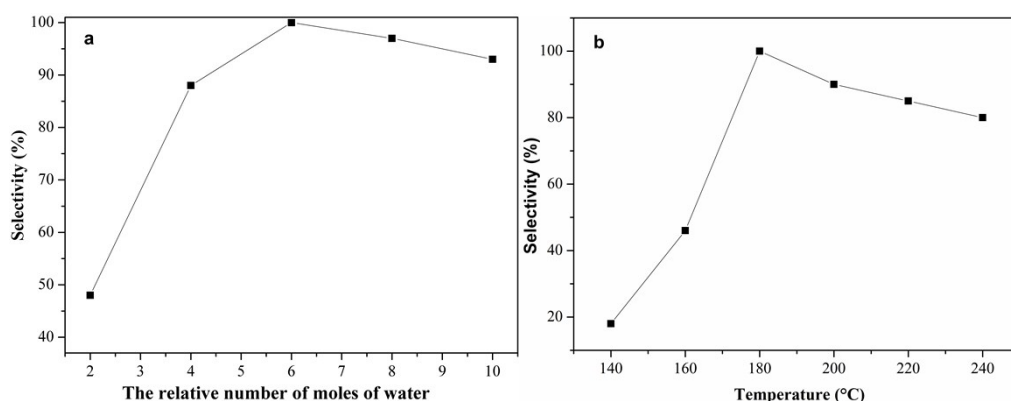
2	1:3:6	Fe ₂ O ₃ /50	12	81	19
3	1:3:6	MgO/50	22	11	89
4	1:3:6	CeO ₂ /50	22	15	85
5	1:3:6	Nb ₂ O ₅ /50	23	13	87
6	1:3:6	SiO ₂ /50	25	21	79
7	1:3:6	TiO ₂ /50	33	19	81
8	1:3:6	Y ₂ O ₃ /50	39	18	82
9	1:3:6	Al ₂ O ₃ /50	44	14	86
10	1:3:6	ZnO/50	73	34	66
11	1:3:6	CuO/50	100	>99	trace

^aReaction conditions: 0.01mol 1a, 0.03 mol CH₃CN, 0.06 mol H₂O, 0.00625 mol catalyst, 180 °C, 2 h. ^bConversion of HDA was determined by GC. ^cSelectivity by GC analysis was based on the consumed HDA.

1.4 Reaction conditions optimization

Then, we have optimized the reaction conditions of the model reaction of HDA, CH₃CN and H₂O. Primarily, the influence of the ratio of HDA, CH₃CN and H₂O was investigated. As shown in Figure S1a, when the HDA: CH₃CN was 1:3 (molar ratio), with the increasing of the amount of H₂O, the HDA conversion was not influenced by the change. But, the HMBA selectivity firstly increased and then decreased. The former phenomenon might be explained by the reason that when the amount of CH₃CN was a constant value, the more H₂O added in the reaction system the more CH₃CONH₂ was formed to react with HDA to conduct subsequent reaction. The latter indicated that the catalytic activity of the catalyst in AER was decreased since the H₂O might have a negative effect on the CuO catalyst.

Soon afterwards, the reaction temperature, reaction time and the amount of the catalyst were further studied. Figure S1b indicates that with the increasing of the reaction temperature from 140 °C to 180 °C, the HMBA selectivity was dramatically increased. But, it was slowly decreased from 180 °C to 240 °C. It might be the AER of HDA, CH₃CN and H₂O which is an exothermic reaction that causes the phenomenon. Then, different reaction times were also discussed in this work. From Figure S1c we can know that increased reaction times ought to be good for the AER of HDA, CH₃CN and H₂O (molar ratio, 1:3:6) under 180 °C using freshly prepared CuO as the catalyst. Because of limited HDA, the HMBA selectivity was reached a constant 100 % when the reaction time was from 2 to 3 h even more times in this situation. What is more, we have screened the optimal amount of the catalyst. Just as Figure S1d indicates that the 50 mg CuO to catalyze the reaction is the proper amount under our reaction conditions.



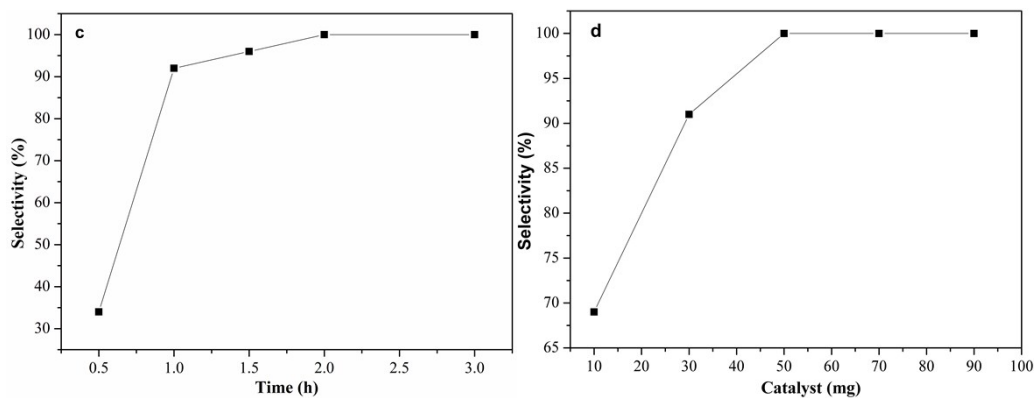


Figure S1 Results of the reaction conditions optimization

2.1 Copies of IR spectra

Fourier transform infrared spectroscopy (FT-IR) transmission data was collected from a pressed catalyst disk made with KBr in the range of 4000–400 cm^{-1} with a Nicolet 5700 FT-IR.

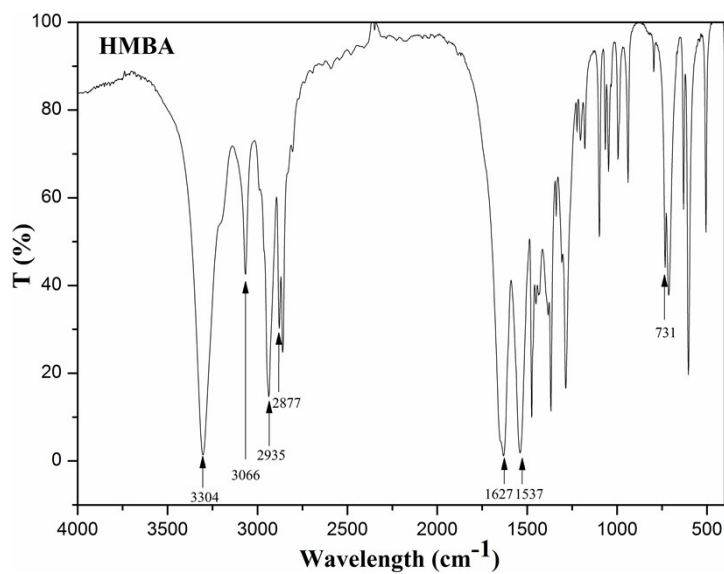


Figure S2 IR (KBr) cm^{-1} : 3304, 3066 (NH); 2935, 2877 (CH); 1627 (C=O); 1537; 731.

2.2 Copies of ^1H NMR

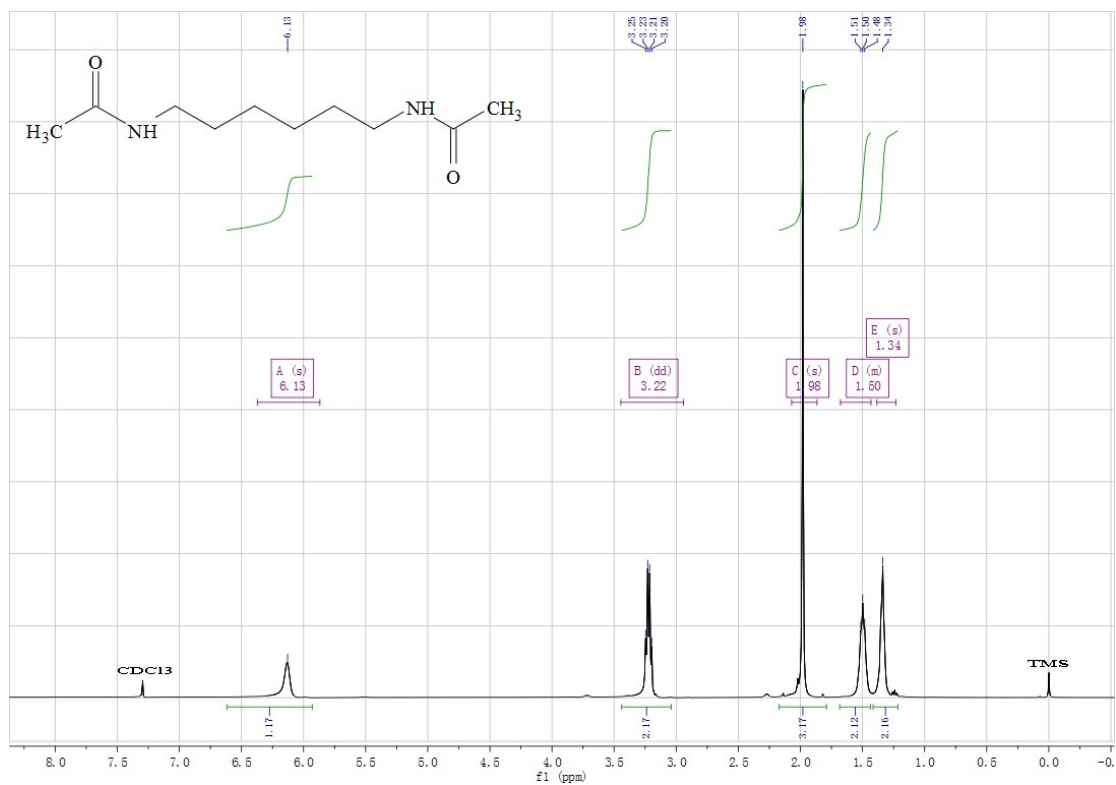
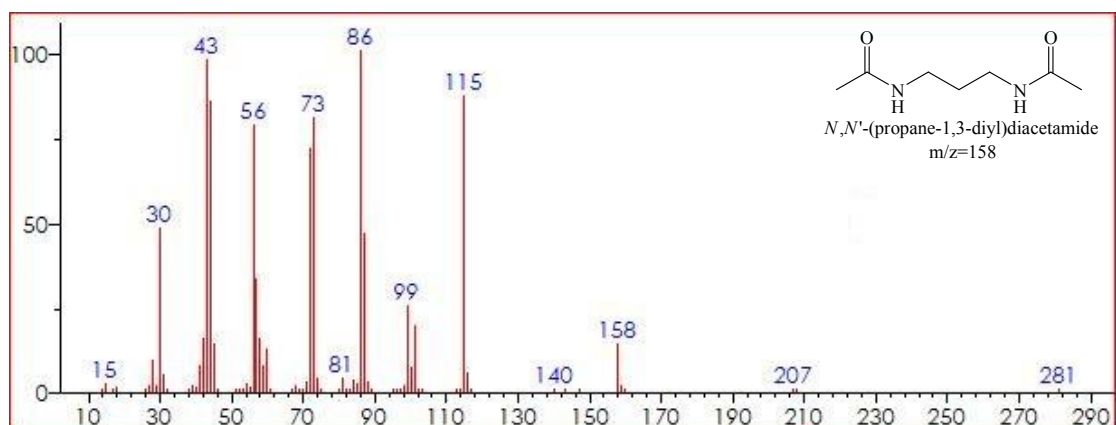
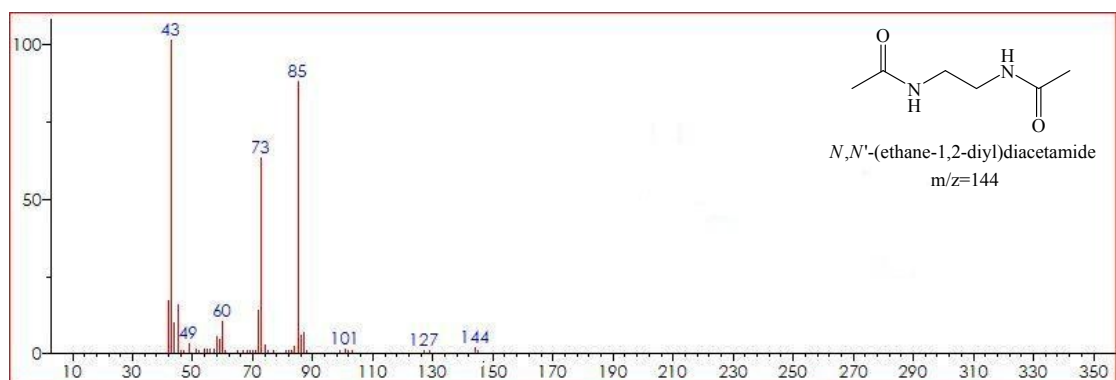
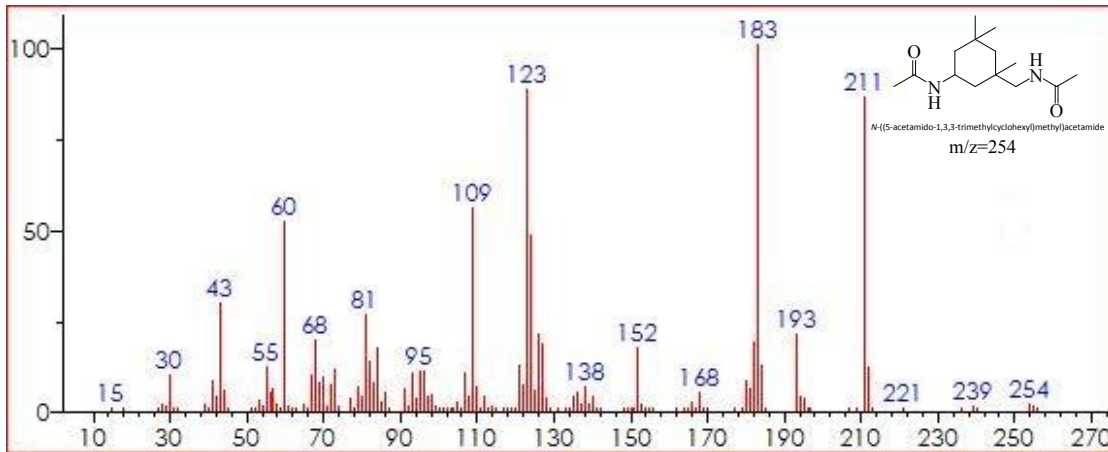
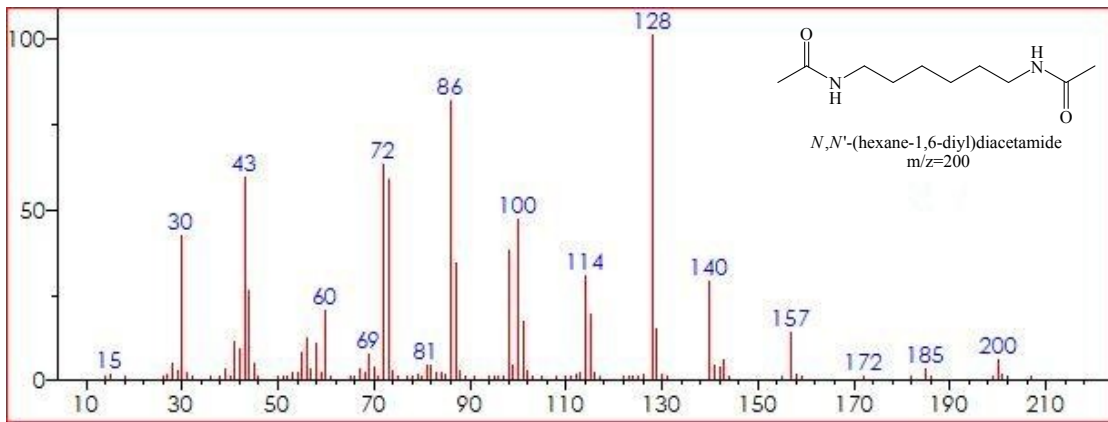
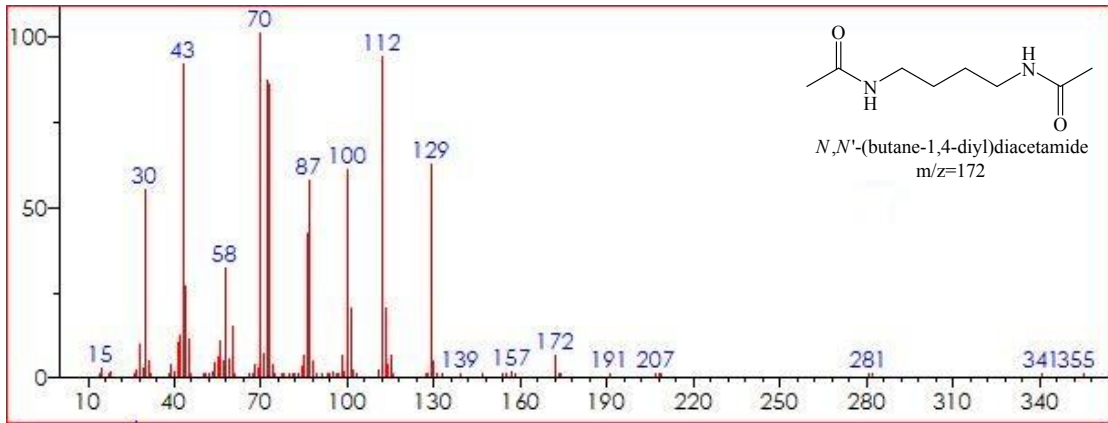
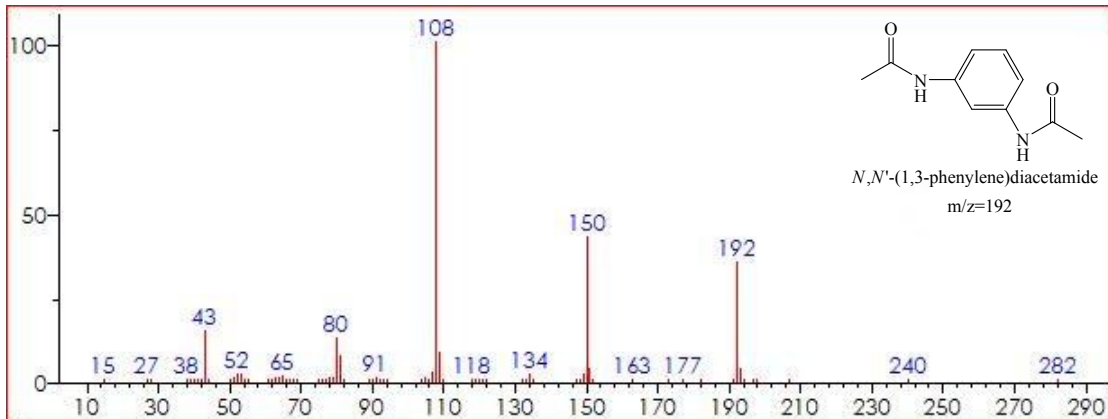
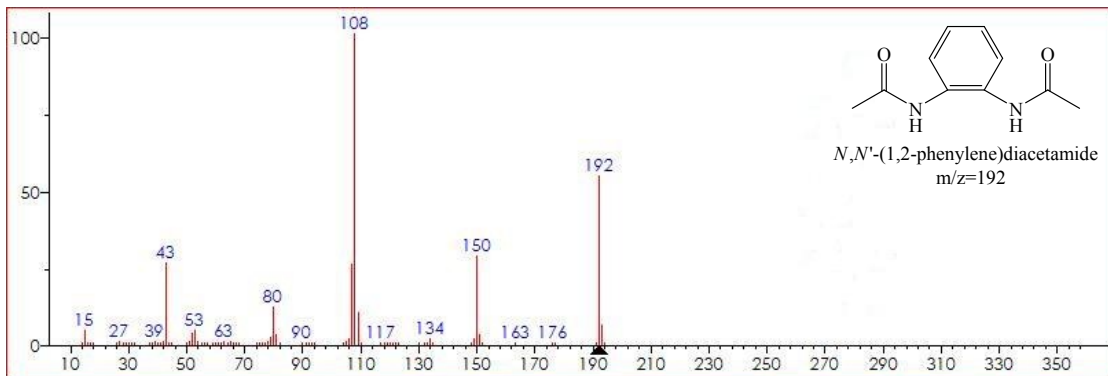
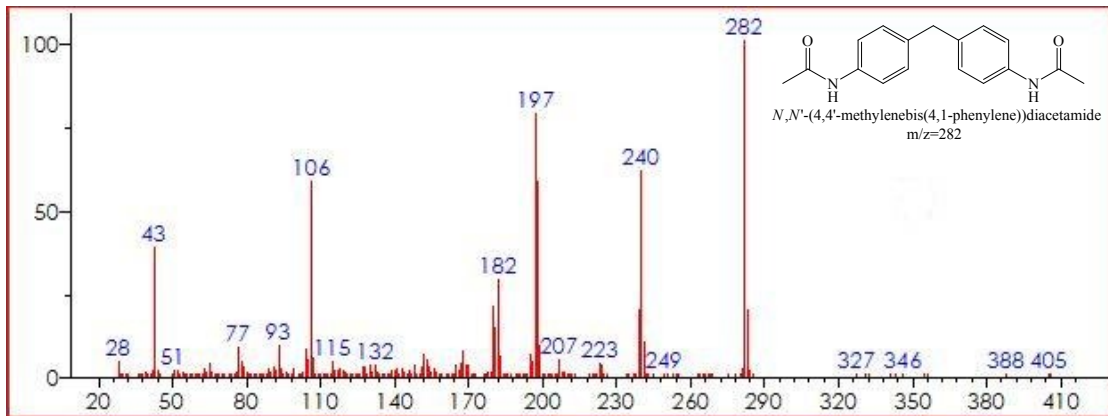
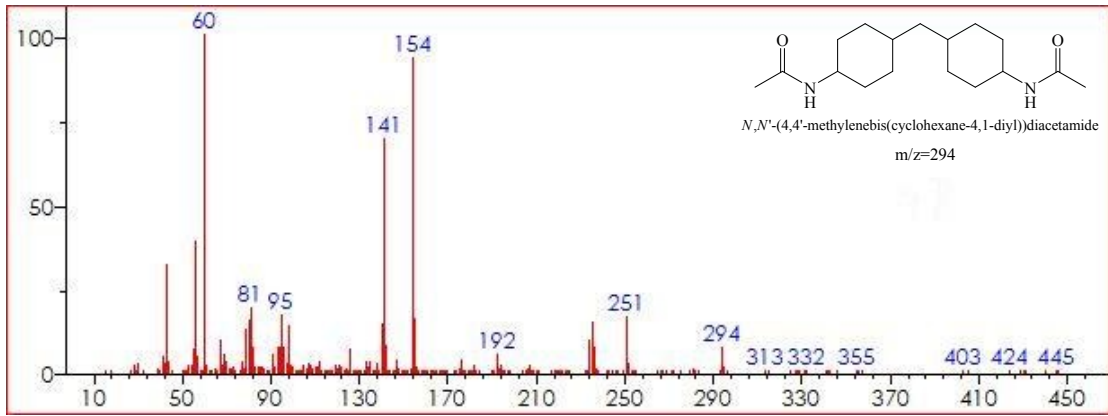


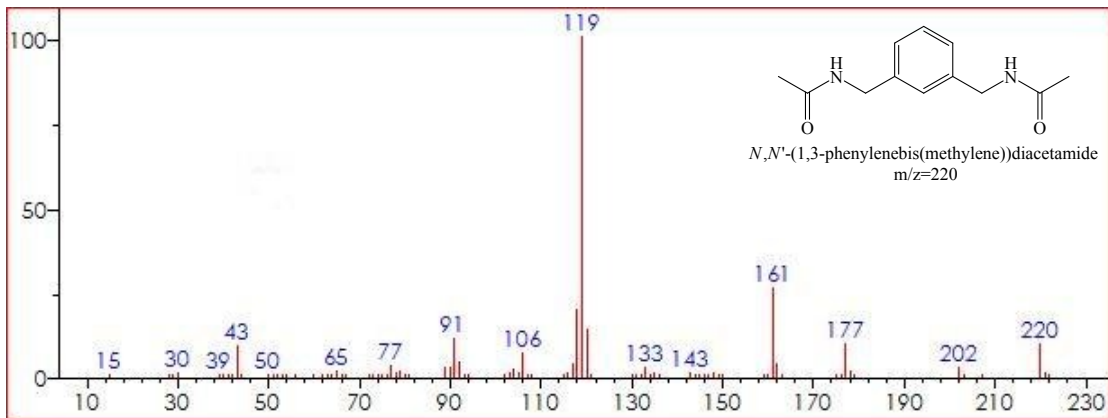
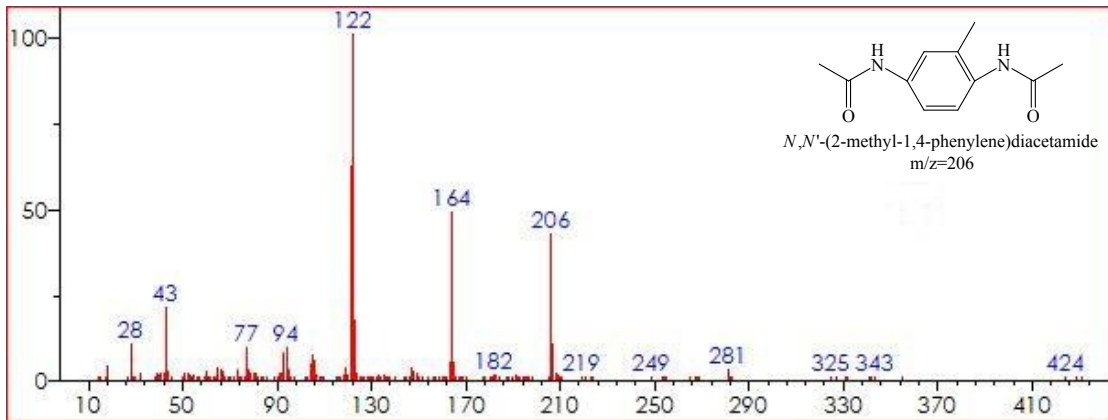
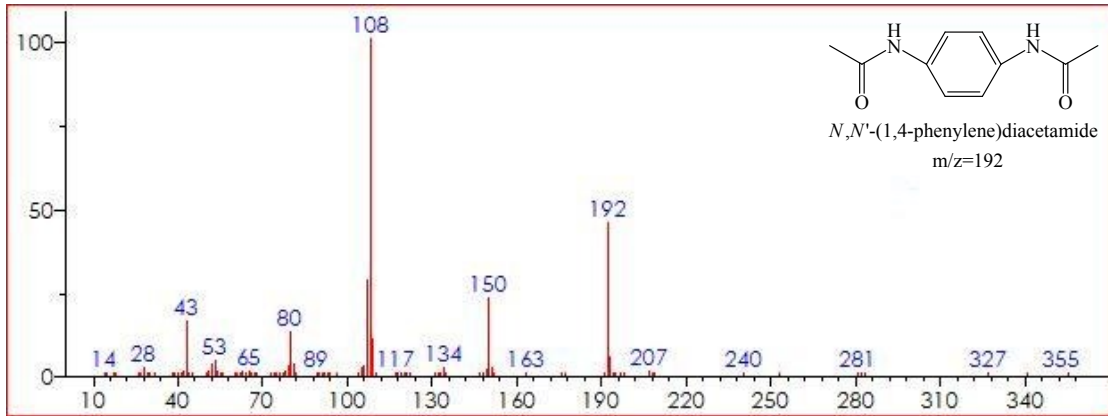
Figure S3 ¹H NMR (400 MHz, CDCl₃): δ 6.13 (s, 1H), 3.22 (dd, J = 13.1, 6.6 Hz, 2H), 1.98 (s, 3H), 1.68 – 1.43 (m, 2H), 1.34 (s, 2H)

3 Copies of GC-MS spectra of diacetamides









4 Copy of GC-MS spectra of 2-methyl-1H-benzo[d]imidazole

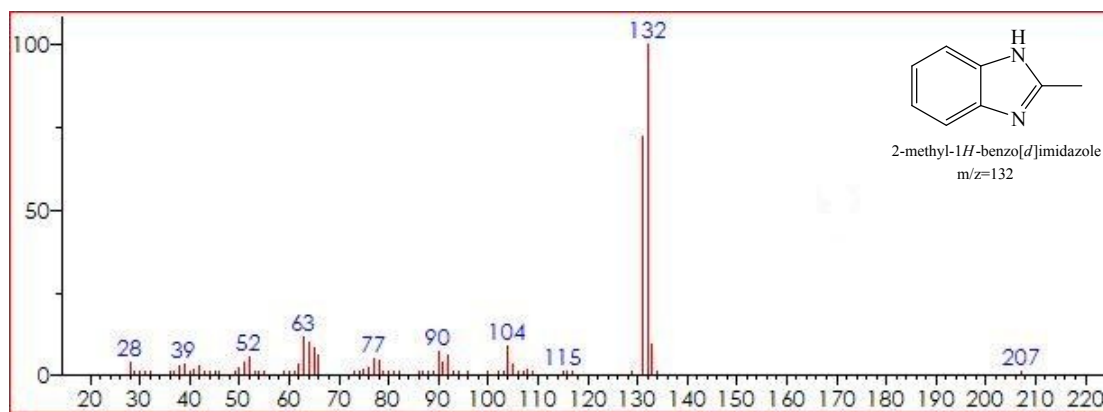


Figure S4 The GC-MS of 2-methyl-1H-benzo[d]imidazole