

Supporting Information

Efficient, Solvent-free Aminolysis of Esters Catalyzed by Sodium

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Experimental

General Remarks

N-propylamine, sodium methoxide, sodium, sodium amide and all the ester reagents were commercial products from Aladdin[®] with the highest purity available ($\geq 97\%$) and were used without further purification. *N,N*-dimethylformamide and all the inorganic reagents were commercial products from Sinopharm Chemical Reagent Co., Ltd. with a purity of over 99% and were used as received.

GC analyses were performed on GC Agilent 1790F series. Quantitative analysis of the products were carried out by external standard method using GC analyses. Gas Chromatography-Mass Spectrometer (GC-MS) analyses were performed on GC-MS Agilent 5973-6890 series (FID detector, weakly polar capillary column SE-30, nitrogen as carrier gas). ¹H NMR spectra were recorded using Bruker DRX-400 spectrometer using solvent peaks as CDCl₃ solutions after purification by recrystallization using ethanol. Melting points were determined in open capillaries using an Electrothermal 9100 without further corrections.

Acetamide:

A mixture of ethyl acetate (26.4 g, 0.3 mol), sodium (0.5 g, 0.02 mol) were added to a 100 mL high pressure reaction kettle equipped with stirrer and a temperature measuring device. The kettle was purged with nitrogen gas until the pressure was 3.0 mPa and kept steady for 30 minutes in order to prove it was sealed well. And then the nitrogen gas was running out by opening the outlet vale. It was repeated three times to replace all

the air in the kettle. After this, liquid ammonia (20.4 g, 1.2 mol) was added to the kettle from the inlet valve. The reaction mixture was heated slowly to 90 °C and kept for 7 h with stirring. After completion of the reaction, the mixture was cooled to room temperature (20 °C), and the rest ammonia was released into recycle system by opening outlet valve. Then the mixture was dissolved in 50 ml *N, N*-dimethylformamide before GC detection. Melting point was determined after the solvent removed under reduced pressure.

Propionamide:

A mixture of methyl propionate (26.4 g, 0.3 mol), sodium (0.5 g, 0.02 mol) were added to a 100 mL high pressure reaction kettle equipped with stirrer and a temperature measuring device. The kettle was purged with nitrogen gas until the pressure was 3.0 mPa and kept steady for 30 minutes in order to prove it was sealed well. And then the nitrogen gas was running out by opening the outlet valve. It was repeated three times to replace all the air in the kettle. After this, liquid ammonia (15.3 g, 0.9 mol) was added to the kettle from the inlet valve. The reaction mixture was heated slowly to 90 °C and kept for 6 h with stirring. After completion of the reaction, the mixture was cooled to room temperature (20 °C), and the rest ammonia was released into recycle system by opening outlet valve. Then the mixture was dissolved in 50 ml *N, N*-dimethylformamide before GC detection. Melting point was determined after the solvent removed under reduced pressure.

Butyramide:

A mixture of methyl butyrate (30.6 g, 0.3 mol), sodium (0.5 g, 0.02 mol) were added to a 100 mL high pressure reaction kettle equipped with stirrer and a temperature measuring device. The kettle was purged with nitrogen gas until the pressure was 3.0 mPa and kept steady for 30 minutes in order to prove it was sealed well. And then the nitrogen gas was running out by opening the outlet vale. It was repeated three times to replace all the air in the kettle. After this, liquid ammonia (20.4 g ,1.2 mol) was added to the kettle from the inlet vale. The reaction mixture was heated slowly to 120 °C and kept for 6 h with stirring. After completion of the reaction, the mixture was cooled to room temperature (20 °C), and the rest ammonia was released into recycle system by opening outlet vale. Then the mixture was dissolved in 50 ml *N, N*-dimethylformamide before GC detection. Melting point was determined after the solvent removed under reduced pressure.

Isobutyramide:

A mixture of methyl isobutyrate (30.6 g, 0.3 mol), sodium (0.5 g, 0.02 mol) were added to a 100 mL high pressure reaction kettle equipped with stirrer and a temperature measuring device. The kettle was purged with nitrogen gas until the pressure was 3.0 mPa and kept steady for 30 minutes in order to prove it was sealed well. And then the nitrogen gas was running out by opening the outlet vale. It was repeated three times to replace all the air in the kettle. After this, liquid ammonia (20.4 g ,1.2 mol) was added to the kettle from the inlet vale. The reaction mixture was heated slowly to 120 °C and

kept for 8h with stirring. After completion of the reaction, the mixture was cooled to room temperature (20 °C), and the rest ammonia was released into recycle system by opening outlet valve. Then the mixture was dissolved in 50 ml *N, N*-dimethylformamide before GC detection. Melting point was determined after the solvent removed under reduced pressure.

Hexanamide:

A mixture of methyl caproate (39.0 g, 0.3 mol), sodium (0.5 g, 0.02 mol) were added to a 100 mL high pressure reaction kettle equipped with stirrer and a temperature measuring device. The kettle was purged with nitrogen gas until the pressure was 3.0 mPa and kept steady for 30 minutes in order to prove it was sealed well. And then the nitrogen gas was running out by opening the outlet valve. It was repeated three times to replace all the air in the kettle. After this, liquid ammonia (20.4 g, 1.2 mol) was added to the kettle from the inlet valve. The reaction mixture was heated slowly to 145 °C and kept for 6h with stirring. After completion of the reaction, the mixture was cooled to room temperature (20 °C), and the rest ammonia was released into recycle system by opening outlet valve. Then the mixture was dissolved in 50 ml *N, N*-dimethylformamide before GC detection. Melting point was determined after the solvent removed under reduced pressure.

Benzamide:

A mixture of methyl benzoate (40.8 g, 0.3 mol), sodium (0.5 g, 0.02 mol) were added to a 100 mL high pressure reaction kettle equipped with stirrer and a temperature measuring device. The kettle was purged with nitrogen gas until the pressure was 3.0 mPa and kept steady for 30 minutes in order to prove it was sealed well. And then the nitrogen gas was running out by opening the outlet vale. It was repeated three times to replace all the air in the kettle. After this, liquid ammonia (25.5 g ,1.5 mol) was added to the kettle from the inlet vale. The reaction mixture was heated slowly to 140 °C and kept for 5 h with stirring. After completion of the reaction, the mixture was cooled to room temperature (20 °C), and the rest ammonia was released into recycle system by opening outlet vale. Then the mixture was dissolved in 50 ml *N, N*-dimethylformamide before GC detection. Melting point was determined after the solvent removed under reduced pressure.

Benzeneacetamide:

A mixture of methyl phenylacetate (30.0 g, 0.2 mol), sodium (0.3 g, 0.012 mol) were added to a 100 mL high pressure reaction kettle equipped with stirrer and a temperature measuring device. The kettle was purged with nitrogen gas until the pressure was 3.0 mPa and kept steady for 30 minutes in order to prove it was sealed well. And then the nitrogen gas was running out by opening the outlet vale. It was repeated three times to replace all the air in the kettle. After this, liquid ammonia (18.7 g ,1.1 mol) was added to the kettle from the inlet vale. The reaction mixture was heated slowly to 140 °C and kept for 5.5 h with stirring. After completion of the reaction, the mixture was cooled to

room temperature (20 °C), and the rest ammonia was released into recycle system by opening outlet valve. Then the mixture was dissolved in 50 ml *N, N*-dimethylformamide before GC detection. Melting point was determined after the solvent removed under reduced pressure.

Acetamide (aminolysis of phenyl acetate)

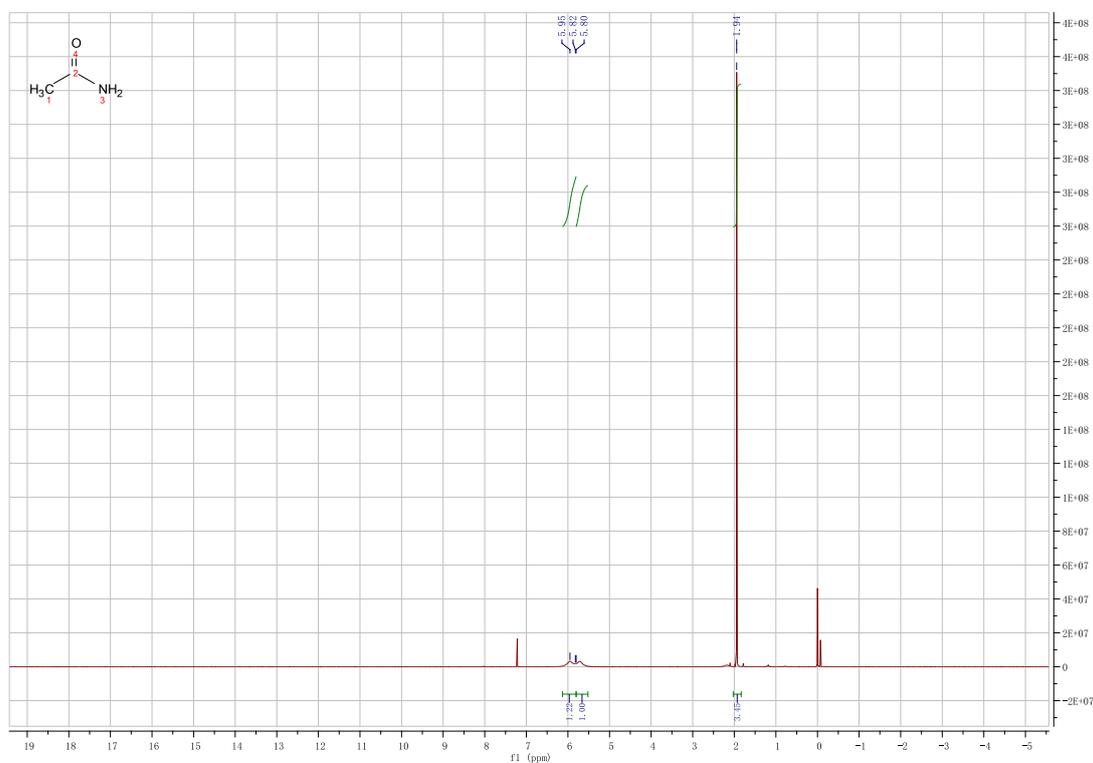
A mixture of phenyl acetate (27.2 g, 0.2 mol), sodium (0.3 g, 0.012 mol) were added to a 100 mL high pressure reaction kettle equipped with stirrer and a temperature measuring device. The kettle was purged with nitrogen gas until the pressure was 3.0 mPa and kept steady for 30 minutes in order to prove it was sealed well. And then the nitrogen gas was running out by opening the outlet valve. It was repeated three times to replace all the air in the kettle. After this, liquid ammonia (17.0 g, 1.0 mol) was added to the kettle from the inlet valve. The reaction mixture was heated slowly to 140 °C and kept for 4 h with stirring. After completion of the reaction, the mixture was cooled to room temperature (20 °C), and the rest ammonia was released into recycle system by opening outlet valve. Then the mixture was dissolved in 50 ml *N, N*-dimethylformamide before GC detection. Melting point was determined after the solvent removed under reduced pressure.

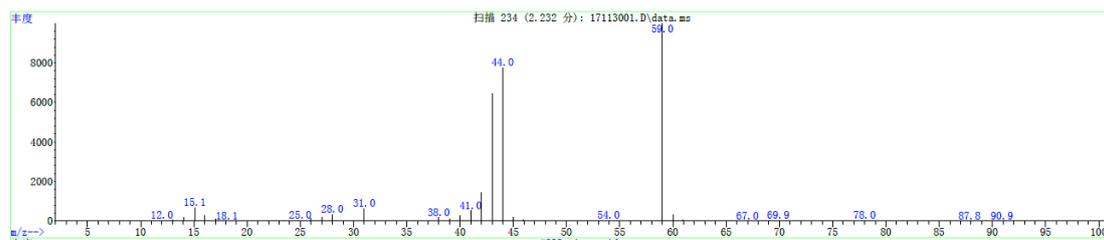
Acetamide (aminolysis of benzyl acetate)

A mixture of benzyl acetate (30.0 g, 0.2 mol), sodium (0.3 g, 0.012 mol) were added to a 100 mL high pressure reaction kettle equipped with stirrer and a temperature measuring device. The kettle was purged with nitrogen gas until the pressure was 3.0

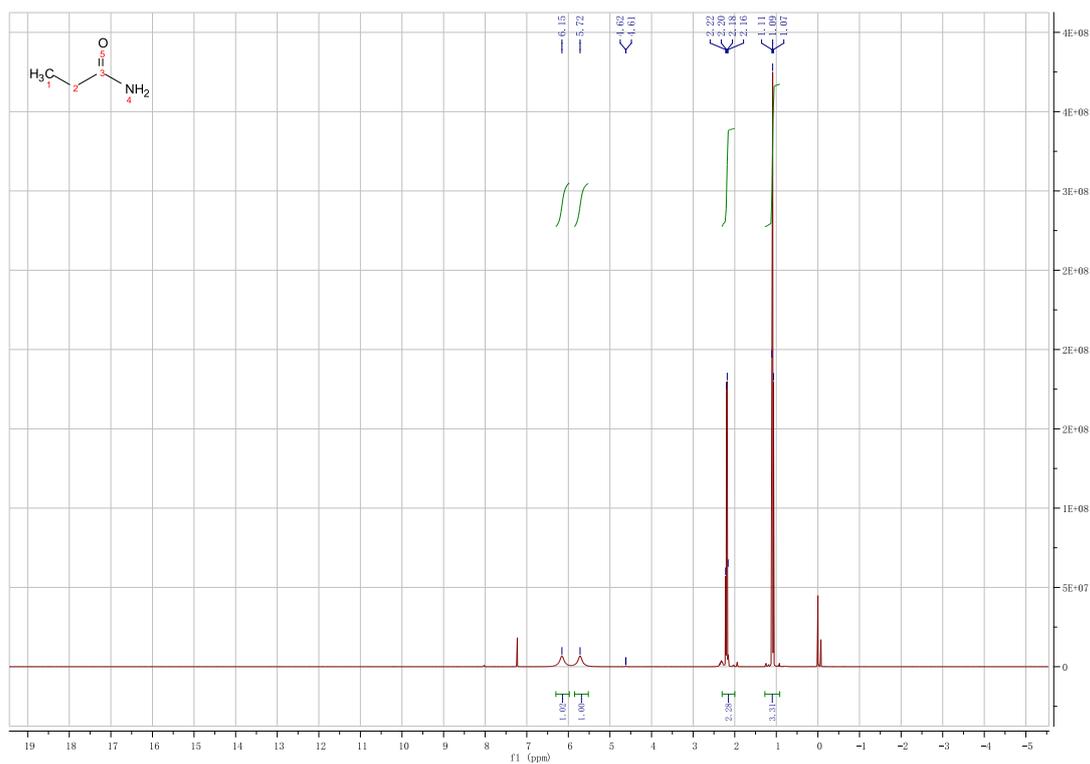
mPa and kept steady for 30 minutes in order to prove it was sealed well. And then the nitrogen gas was running out by opening the outlet vane. It was repeated three times to replace all the air in the kettle. After this, liquid ammonia (17.0 g ,1.0 mol) was added to the kettle from the inlet vane. The reaction mixture was heated slowly to 140 °C and kept for 5 h with stirring. After completion of the reaction, the mixture was cooled to room temperature (20 °C), and the rest ammonia was released into recycle system by opening outlet vane. Then the mixture was dissolved in 50 ml *N,N*-dimethylformamide before GC detection. Melting point was determined after the solvent removed under reduced pressure.

Acetamide

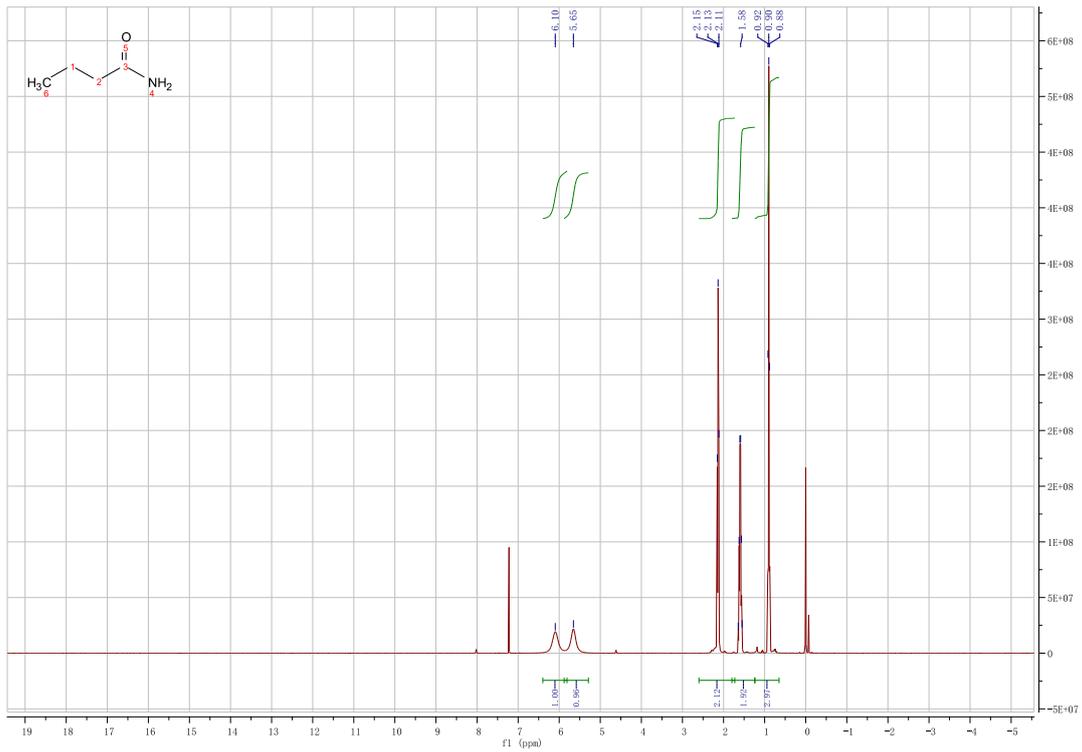




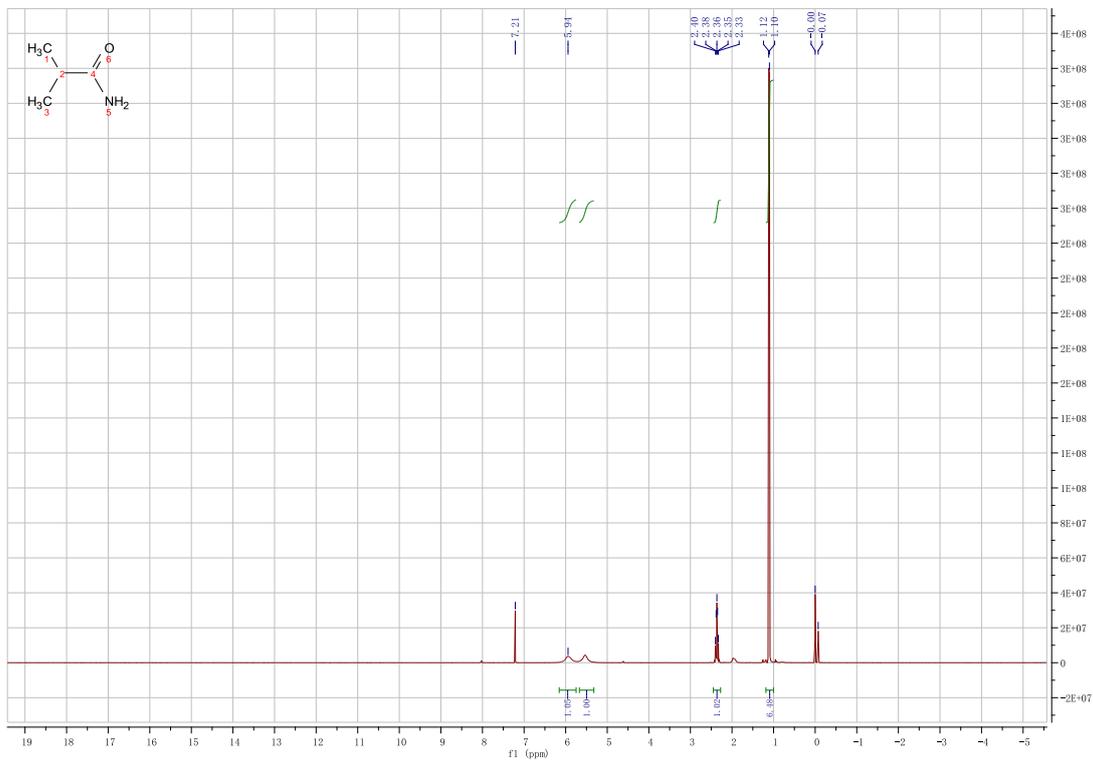
Propionamide



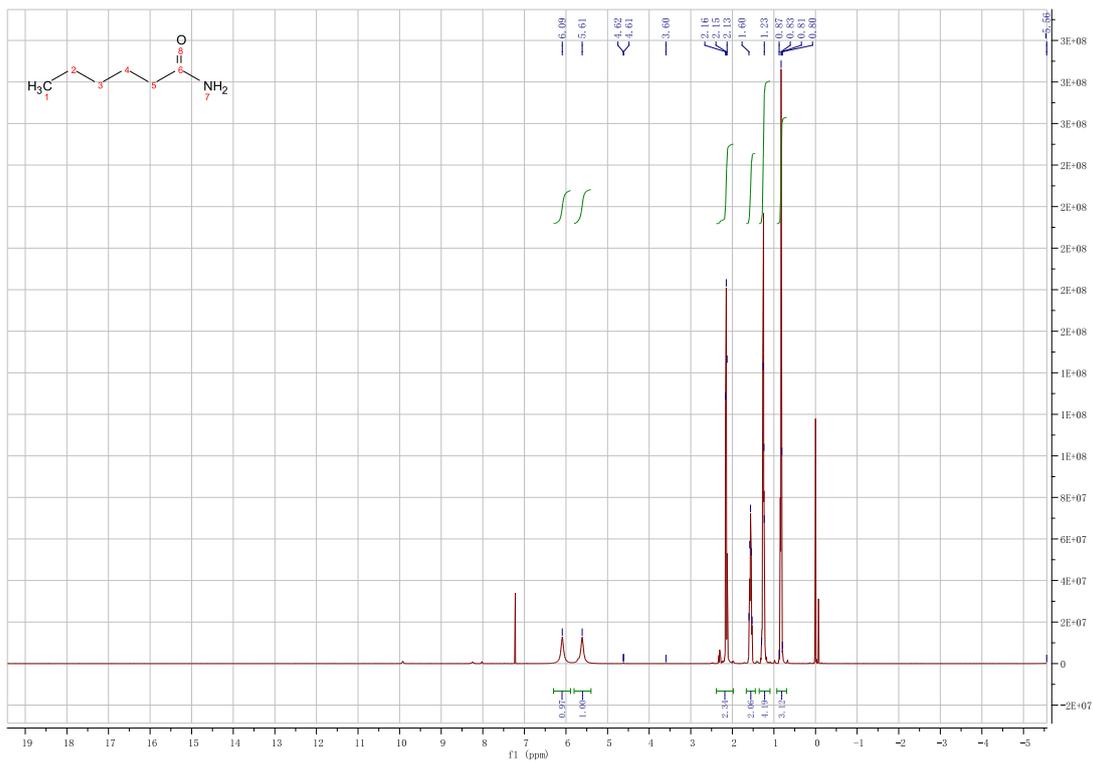
Butyramide



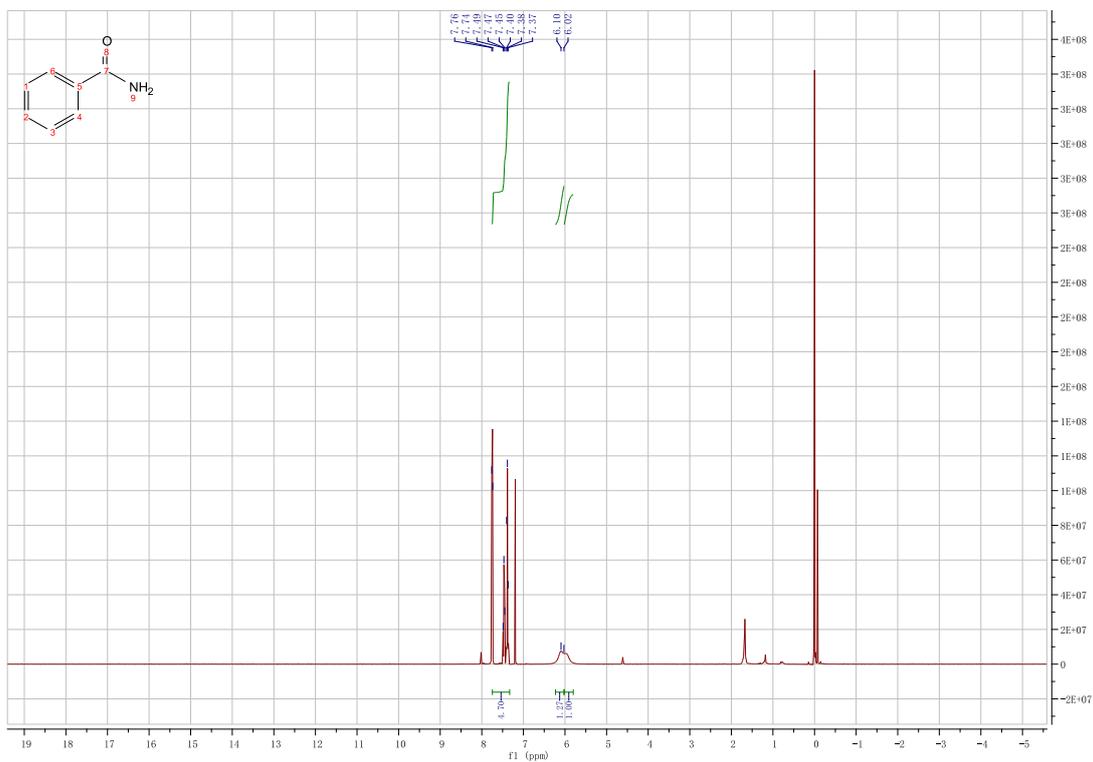
Isobutyramide:



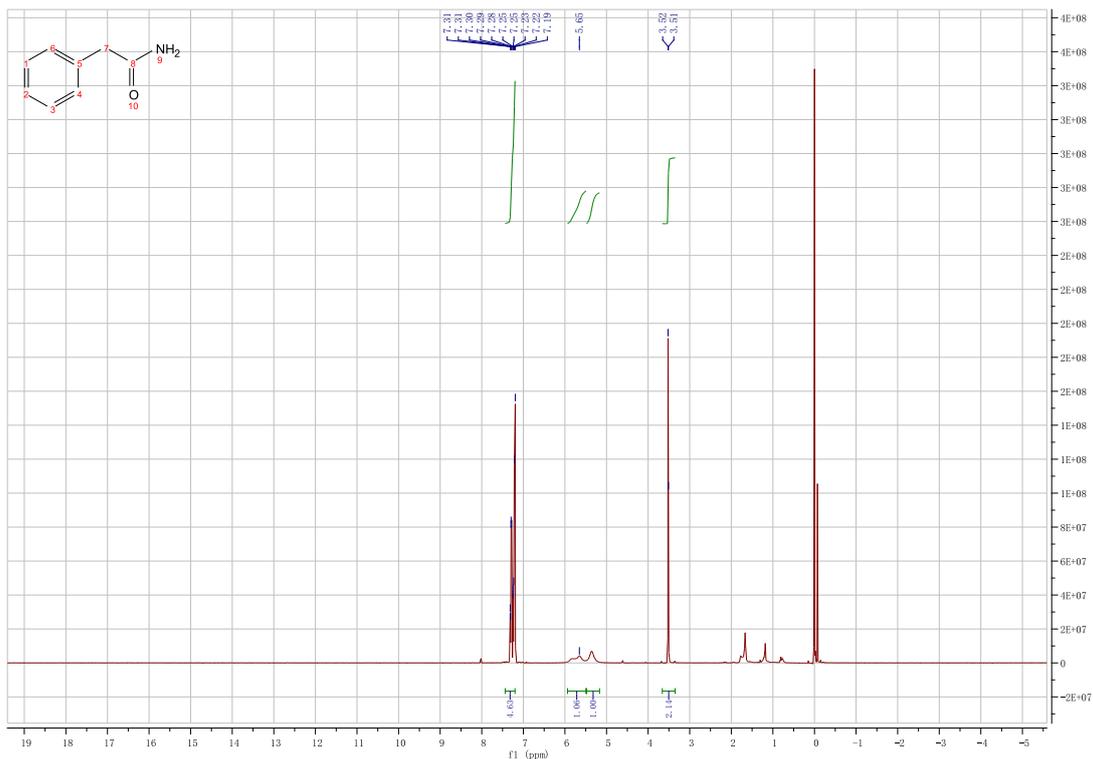
Hexanamide:



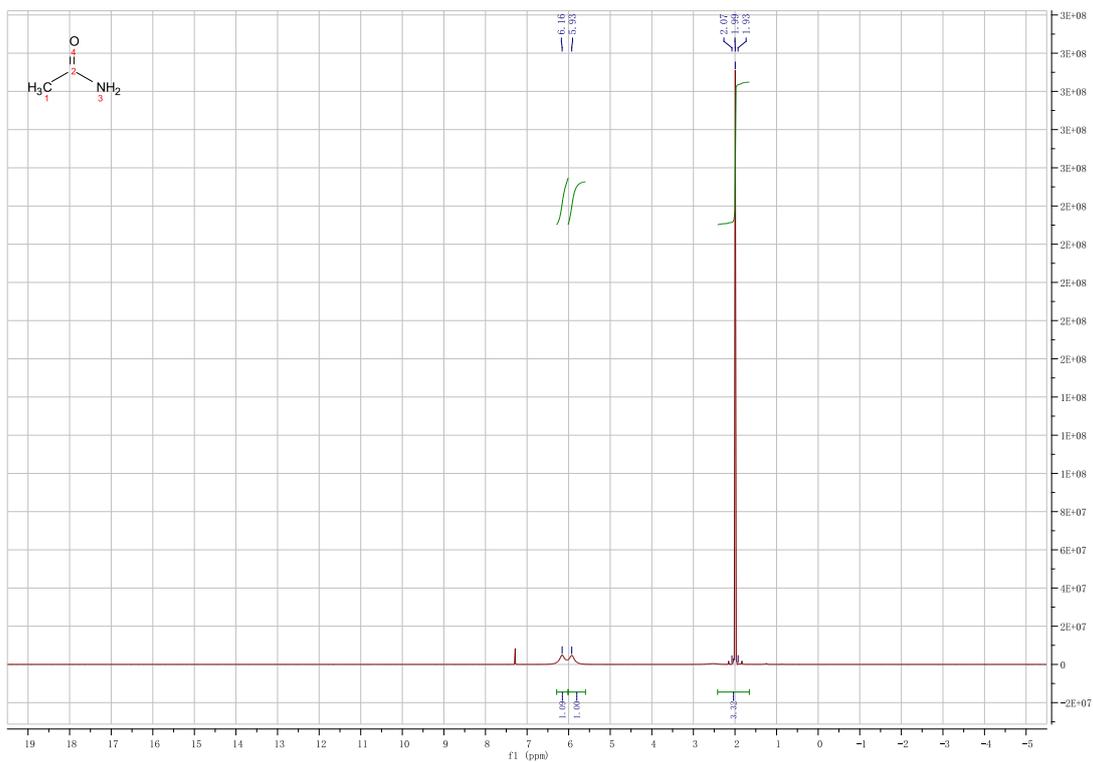
Benzamide:



Benzeneacetamide:



Acetamide (aminolysis of phenyl acetate):



Acetamide (aminolysis of benzyl acetate):

