

SUPPORTING INFORMATION

An efficient one-pot synthesis of industrially valuable primary organic carbamates and N-substituted ureas by reusable Merrifield anchored iron(II)-anthra catalyst [Fe^{II}(Anthra-Merf)] using urea as a sustainable carbonylation source

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Effect of amount of urea and alcohol on benzyl carbamate formation

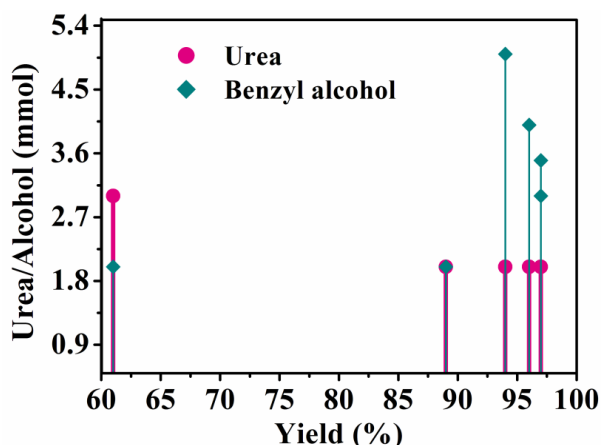


Fig. S1 Effect of reactant amount (mmol) for benzyl carbamate synthesis. Reaction conditions: urea, benzyl alcohol, 1,4-dioxane (3.5 mL), Fe^{II}(Anthra-Merf) catalyst (0.02 g, 0.0188 mmol based on Fe active centre), temperature (120 °C), time (6.5 h).

The concentration of urea (mmol) and benzyl alcohol (mmol) was varied for benzyl carbamate synthesis and to explore the scope of this reaction in a broader sense. The result of these experiments is represented in Fig. S1. After the study of using several amounts of substrate, it revealed that maximum yield was found when urea and alcohol were used in 2:3 mmol ratio. When the alcohol amount was greater than the previous one by keeping the amount of urea constant, the yield of the respective product decreased in a regular pattern. Decreasing the amount of alcohol with respect to urea, the carbamate yield decreases. During carbamate synthesis, the maximum amount of product yield was acquired by taking the urea and alcohol in 2:3 millimolar ratio. In this regard, it is significant to point out that despite the using of excess alcohol no disubstitution occurred in urea, *i.e.* only mono-substituted product was isolated. Hence the mono-substitution is more advantageous than any other reported systems.¹

Effect of amount of urea and benzylamine on benzylurea formation

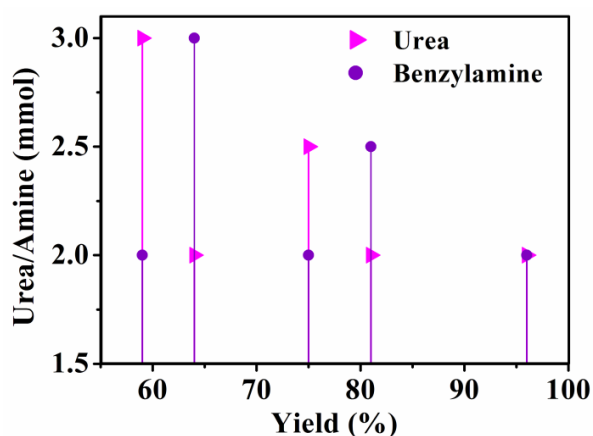


Fig. S2 Amount of urea and benzylamine for benzylurea synthesis under the usage of 25 mg of Fe^{II}(Anthra-Merf) catalyst. Reaction conditions: urea, benzylamine, 1,4-dioxane (3 mL), temperature (100 °C), time (8 h), Fe^{II}(Anthra-Merf) catalyst (0.025 g, 0.0235 mmol based on Fe active centre).

For monosubstituted urea synthesis, the various amount of urea and benzylamine were reacted with the Fe^{II}(Anthra-Merf) catalyst represented in Fig. S2. In the presence of 0.025 g of catalyst, 2:2 mmol ratio of urea to benzylamine exhibited the maximum yield for unsymmetrical urea (benzylurea) production. Increase in the concentration (mmol) of benzylamine without altering urea's concentration and vice-versa leading to a rapid fall in benzylurea yield. Under the application of ambient condition, various concentration of reactants provided different percentage of yield of benzylurea, from which we get the maximum one with respect to 2 mmol of urea and 2 mmol of benzylamine.

¹HNMR data of carbamates

Decyl carbamate

¹HNMR (400 MHz, CDCl₃): δ0.837-0.894 (m, 3H), 1.123-1.420 (m, 14H), 1.524-1.626 (m, 2H), 3.580-3.639 (m, 2H), 4.849 (s, 1H) ppm.

Pentyl carbamate

¹HNMR (400 MHz, CDCl₃): δ0.840-0.873 (m, 3H), 1.420-1.472 (m, 2H), 1.586-1.624 (t, *J*=8.4 Hz, 4H), 4.007-4.041 (m, 2H), 4.551 (s, 2H) ppm.

Butyl carbamate

¹HNMR (400 MHz, CDCl₃): δ0.897-0.964 (m, 3H), 1.341-1.429 (m, 2H), 1.570-1.657 (m, 2H), 4.030-4.078 (m, 2H), 4.738 (s, 2H) ppm.

Isopropyl carbamate

¹HNMR (400 MHz, CDCl₃): δ1.183-1.262 (m, 6H), 4.886-4.948 (m, 1H) ppm.

1-naphthyl carbamate

¹HNMR (400 MHz, CDCl₃): δ5.487 (s, 1H), 6.782-6.801 (d, *J*=7.6 Hz, 1H), 7.234-7.309 (m, 1H), 7.421-7.517 (m, 3H), 7.787-7.824 (m, 1H), 8.160-8.184 (t, *J*=4.4 Hz, 1H) ppm.

2-(diethylamino)ethyl carbamate

¹HNMR (400 MHz, CDCl₃): δ0.943-0.979 (t, *J*=7.2 Hz, 6H), 2.482-2.536 (m, 4H), 2.584-2.681 (m, 2H), 4.043-4.072 (t, *J*=6 Hz, 2H), 5.106 (s, 2H) ppm.

Octan-3-yl carbamate

¹HNMR (400 MHz, CDCl₃): δ0.874-0.911 (t, *J*=7.6 Hz, 6H), 1.285-1.396 (m, 8H), 1.528-1.573 (m, 2H), 3.938-3.998 (m, 1H), 4.798 (s, 2H) ppm.

3-bromopropyl carbamate

¹HNMR (400 MHz, CDCl₃): δ2.150-2.213 (m, 2H), 3.454-3.503 (m, 2H), 4.194-4.225 (t, *J*=6.8 Hz, 2H), 4.711 (s, 2H) ppm.

Benzyl carbamate

¹HNMR (400 MHz, CDCl₃): δ5.190 (s, 2H), 7.263 (s, 1H), 7.374-7.392 (t, *J*=4.8 Hz, 4H) ppm.

4-chlorobenzyl carbamate

¹HNMR (400 MHz, CDCl₃): δ4.639 (s, 2H), 5.037 (s, 1H) 7.259-7.328 (m, 4H) ppm.

4-fluorobenzyl carbamate

¹HNMR (400 MHz, CDCl₃): δ4.771 (s, 1H), 5.053 (s, 2H), 7.017-7.061 (m, 2H), 7.312-7.355 (m, 2H) ppm.

4-nitrobenzyl carbamate

¹HNMR (400 MHz, CDCl₃): δ4.841 (s, 2H), 5.201 (s, 2H), 7.505-7.548 (t, *J*=8.8 Hz, 2H), 8.206-8.228 (d, *J*=8.8 Hz, 2H) ppm.

2-methoxyphenyl carbamate

¹HNMR (400 MHz, CDCl₃): δ3.805 (s, 3H), 4.614 (s, 1H), 6.879-6.901 (d, *J*=8.8 Hz, 2H), 7.279-7.311 (m, 2H) ppm.

Phenethyl carbamate

¹HNMR (400 MHz, CDCl₃): δ2.848-2.881 (t, *J*=6.4 Hz, 2H), 4.261-4.296 (t, *J*=7.2 Hz, 2H), 4.665 (s, 1H), 7.215-7.246 (m, 3H), 7.284-7.333 (m, 2H) ppm.

Cyclohexyl carbamate

¹HNMR (400 MHz, CDCl₃): δ1.148-1.367 (m, 6H), 1.450-1.489 (m, 1H), 1.639-1.669 (m, 2H), 1.775-1.833 (m, 2H), 4.650 (m, 2H) ppm.

Pyridin-4-yl carbamate

¹HNMR (400 MHz, CDCl₃): δ5.336 (s, 2H), 7.497-7.523 (d, *J*=10.4 Hz, 2H), 7.708-7.716 (d, *J*=3.2 Hz, 2H) ppm.

Pyridin-2-yl carbamate

¹HNMR (400 MHz, CDCl₃): δ5.031 (s, 2H), 6.242 (s, 1H), 6.532-6.555 (d, *J*=9.2 Hz, 1H), 7.324-7.440 (m, 2H) ppm.

Tert-butyl carbamate

¹HNMR (400 MHz, CDCl₃): δ1.454 (s, 9H), 4.583 (s, 2H) ppm.

¹HNMR data of N-substituted ureas

N-phenylurea

¹HNMR (400 MHz, CDCl₃): δ6.642 (s, 1H), 7.118-7.153 (m, 1H), 7.305-7.364 (m, 4H) ppm.

Butylurea

¹HNMR (400 MHz, CDCl₃): δ0.904-0.941 (t, *J*=7.2 Hz, 3H), 1.324-1.399 (m, 2H), 1.448-1.520 (m, 2H), 3.123-3.172 (m, 2H), 4.605 (s, 2H), 4.945 (s, 1H) ppm.

Cyclohexylurea

¹HNMR (400 MHz, CDCl₃): δ1.136-1.199 (m, 3H), 1.305-1.407 (m, 2H), 1.584-1.736 (m, 5H), 3.438-3.484 (m, 1H), 4.333 (s, 1H), 4.455 (s, 1H) ppm.

Hexylurea

¹HNMR (400 MHz, CDCl₃): δ0.869-0.898 (t, *J*=7.2 Hz, 3H), 1.295-1.330 (d, *J*=14 Hz, 6H), 1.468-1.518 (m, 2H), 3.126-3.176 (m, 2H), 4.214 (s, 1H), 4.322 (s, 1H), 4.477 (s, 1H) ppm.

Benzylurea

¹HNMR (400 MHz, CDCl₃): δ4.173-4.262 (m, 2H), 5.081 (s, 1H), 5.314 (s, 1H), 7.127-7.276 (m, 5H) ppm.

4-methoxyphenylurea

¹HNMR (400 MHz, CDCl₃): δ3.781 (s, 3H), 6.822-6.845 (m, 2H), 7.328-7.354 (m, 2H), 7.759 (s, 1H) ppm.

Morpholine-4-carboxamide

¹HNMR (400 MHz, CDCl₃): δ3.639 (s, 4H), 3.722 (s, 4H) ppm.

1-methyl-1-phenylurea

¹HNMR (400 MHz, CDCl₃): δ3.259 (s, 3H), 6.168 (s, 2H), 7.143-7.327 (m, 4H), 7.399-7.437 (t, *J*=7.6 Hz, 1H) ppm.

Pyridyl urea

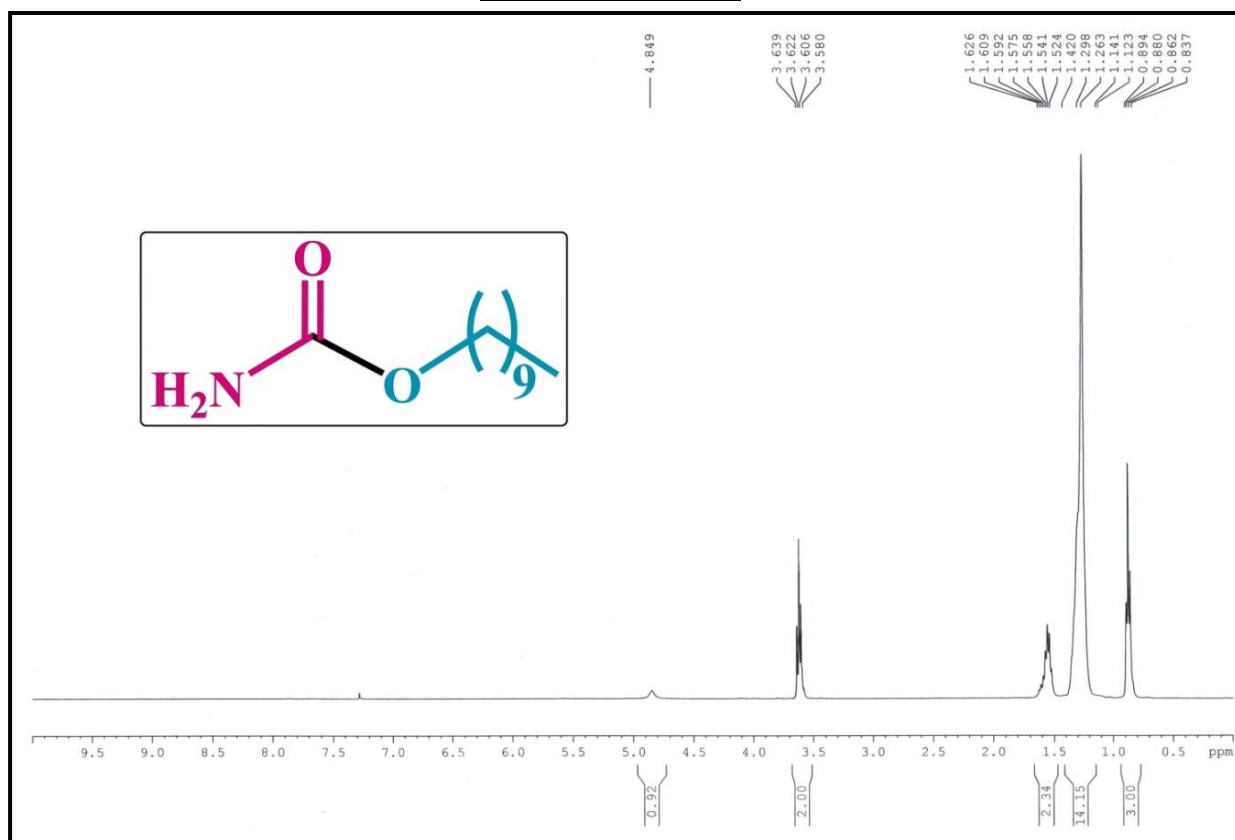
¹HNMR (400 MHz, CDCl₃): δ4.532 (s, 1H), 6.976-7.009 (m, 2H), 7.671-7.714 (m, 1H), 8.355-8.371 (m, 1H) ppm.

(3-pyridyl)urea

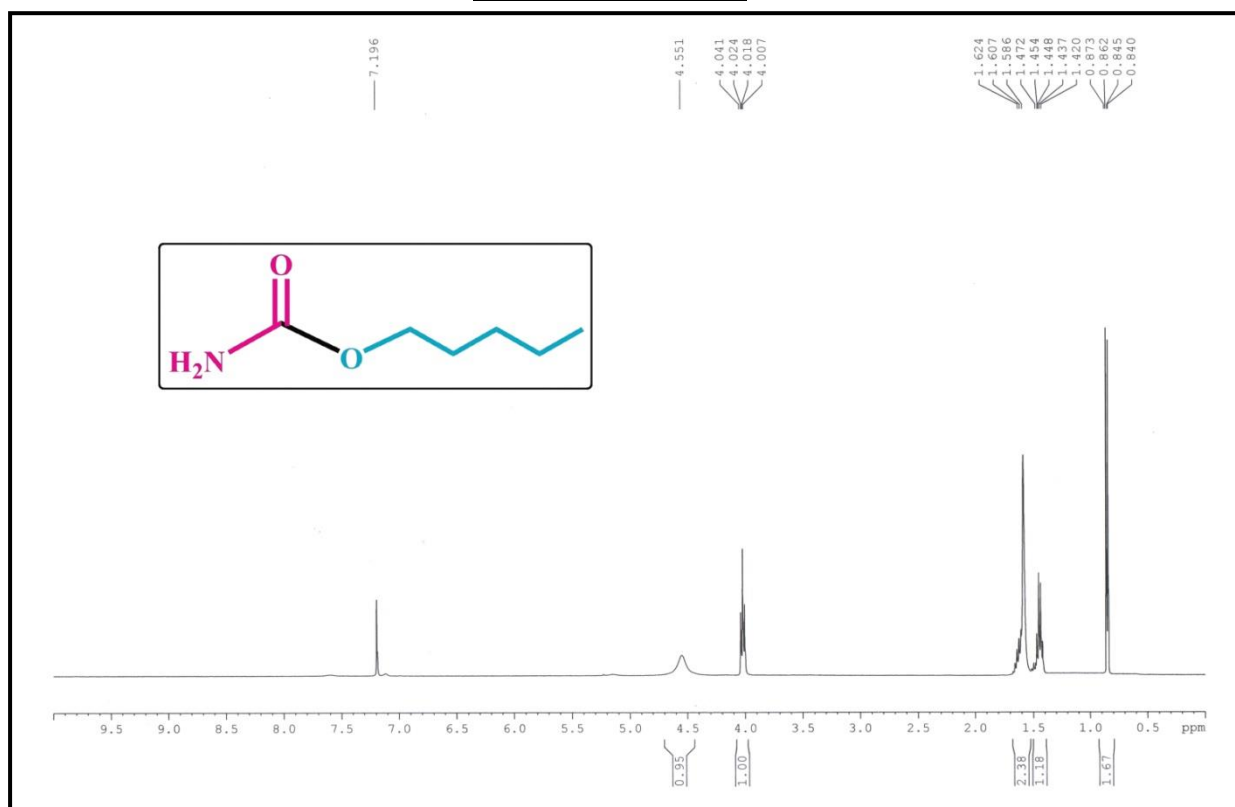
¹HNMR (400 MHz, CDCl₃): δ6.723 (s, 2H), 7.523-7.544 (t, *J*=5.2 Hz, 1H), 8.306-8.317 (d, *J*=4.4 Hz, 2H), 8.482-8.488 (d, *J*=2.4 Hz, 2H) ppm.

¹HNMR Copies of Carbamates

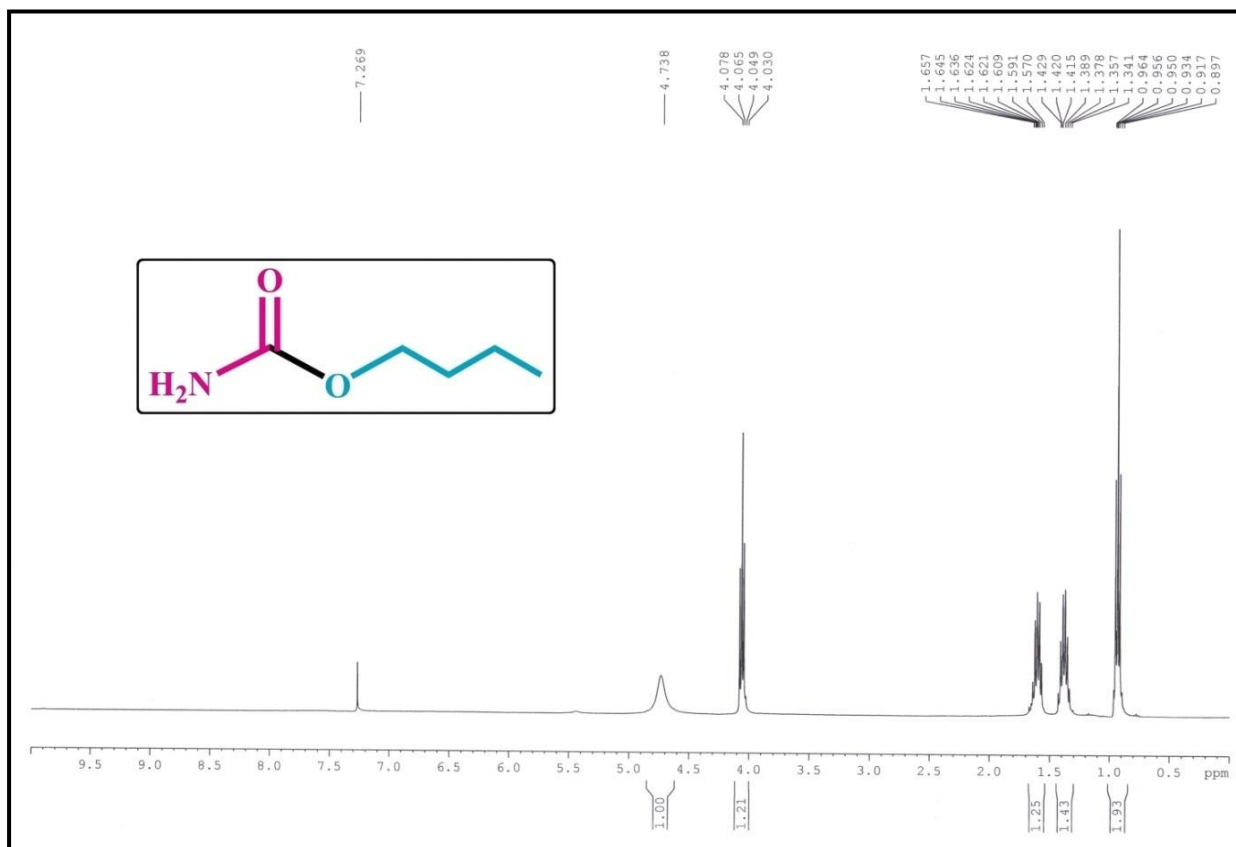
Decyl carbamate



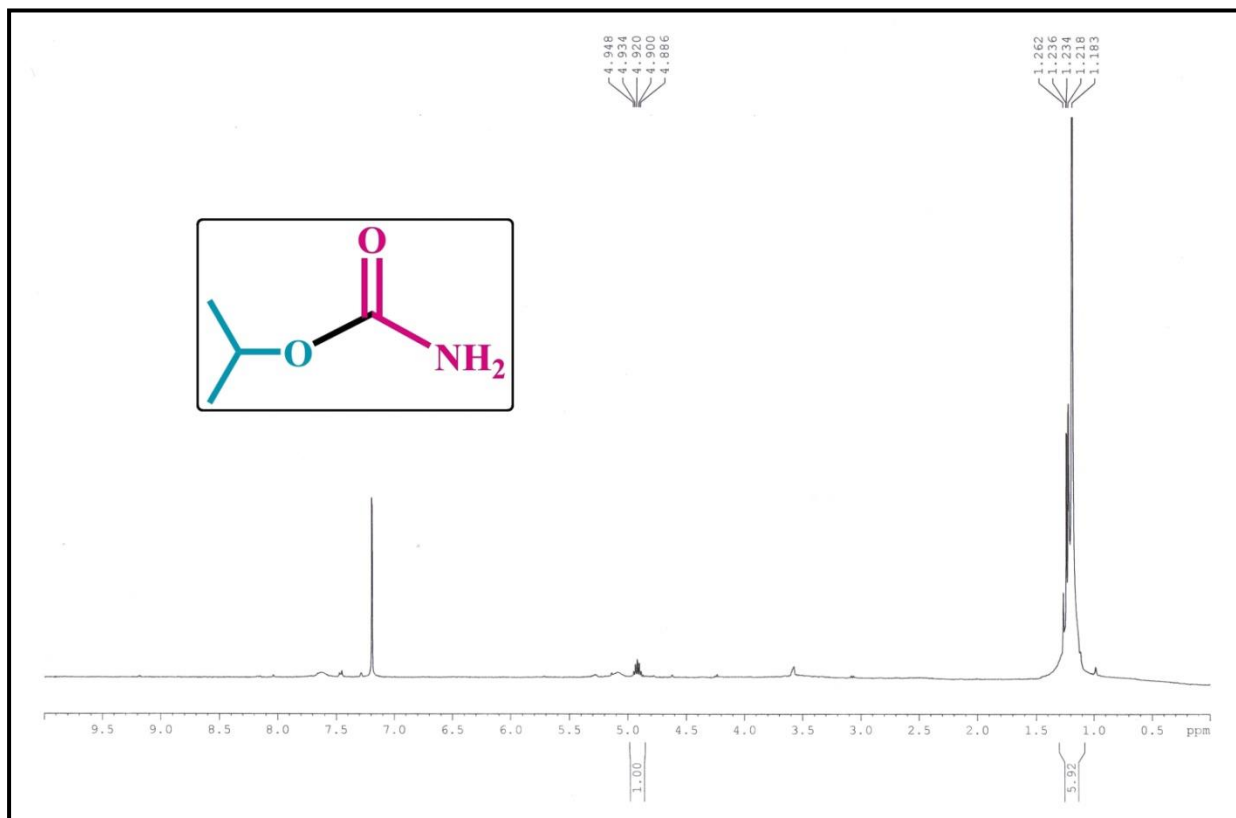
Pentyl carbamate



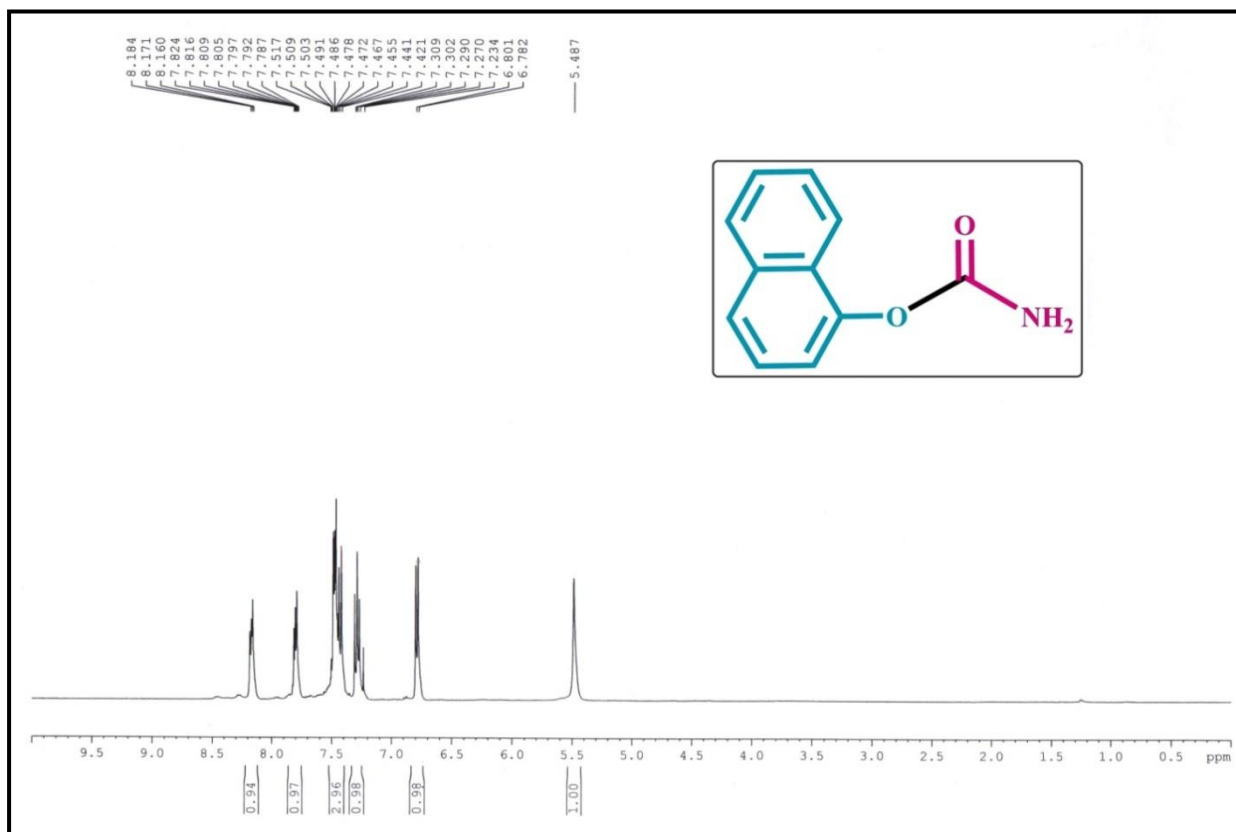
Butyl carbamate



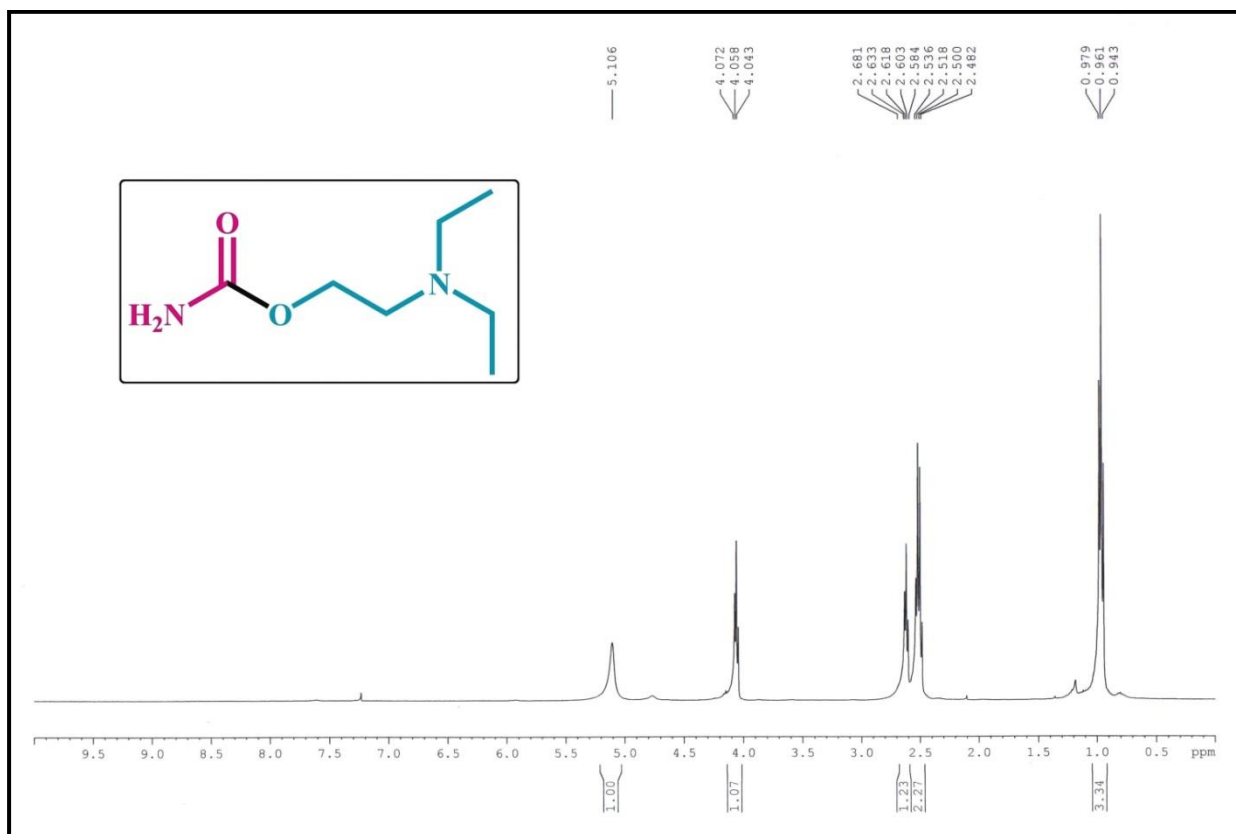
Isopropyl carbamate



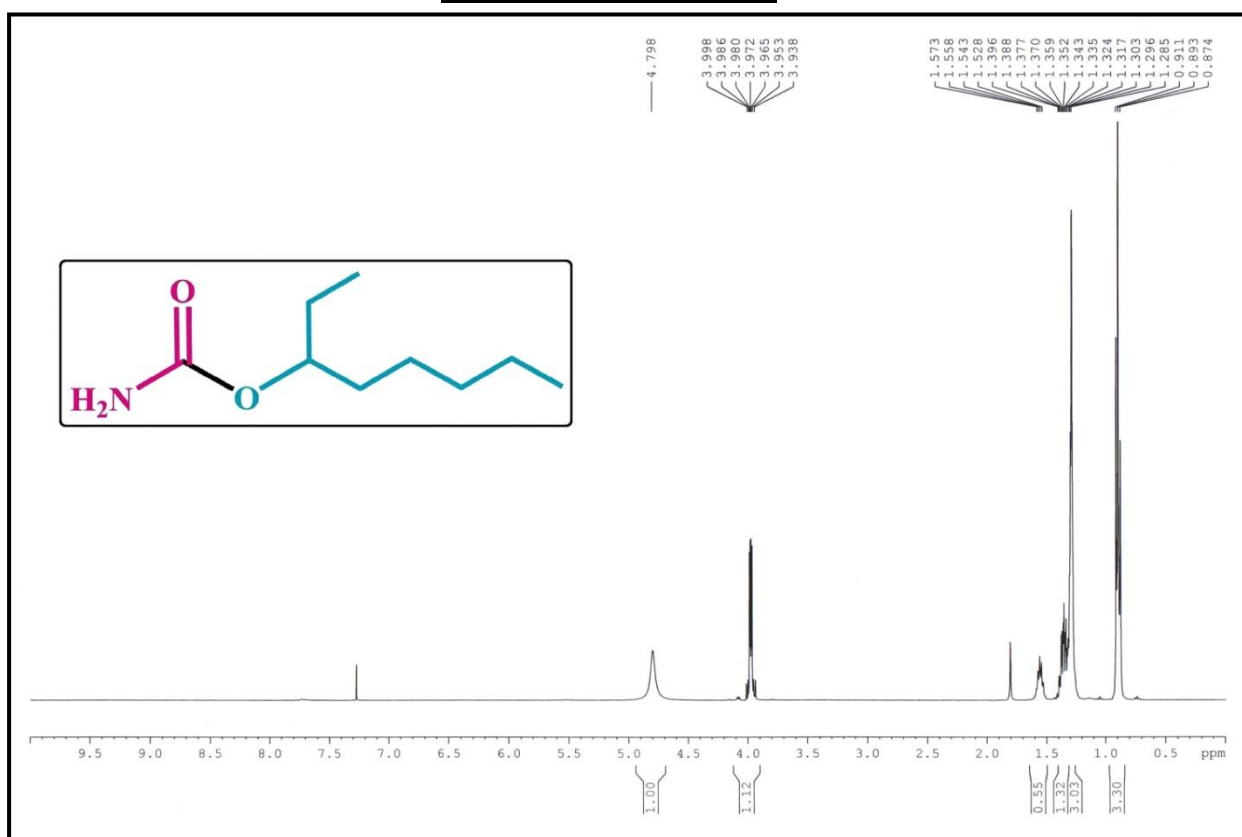
1-naphthyl carbamate



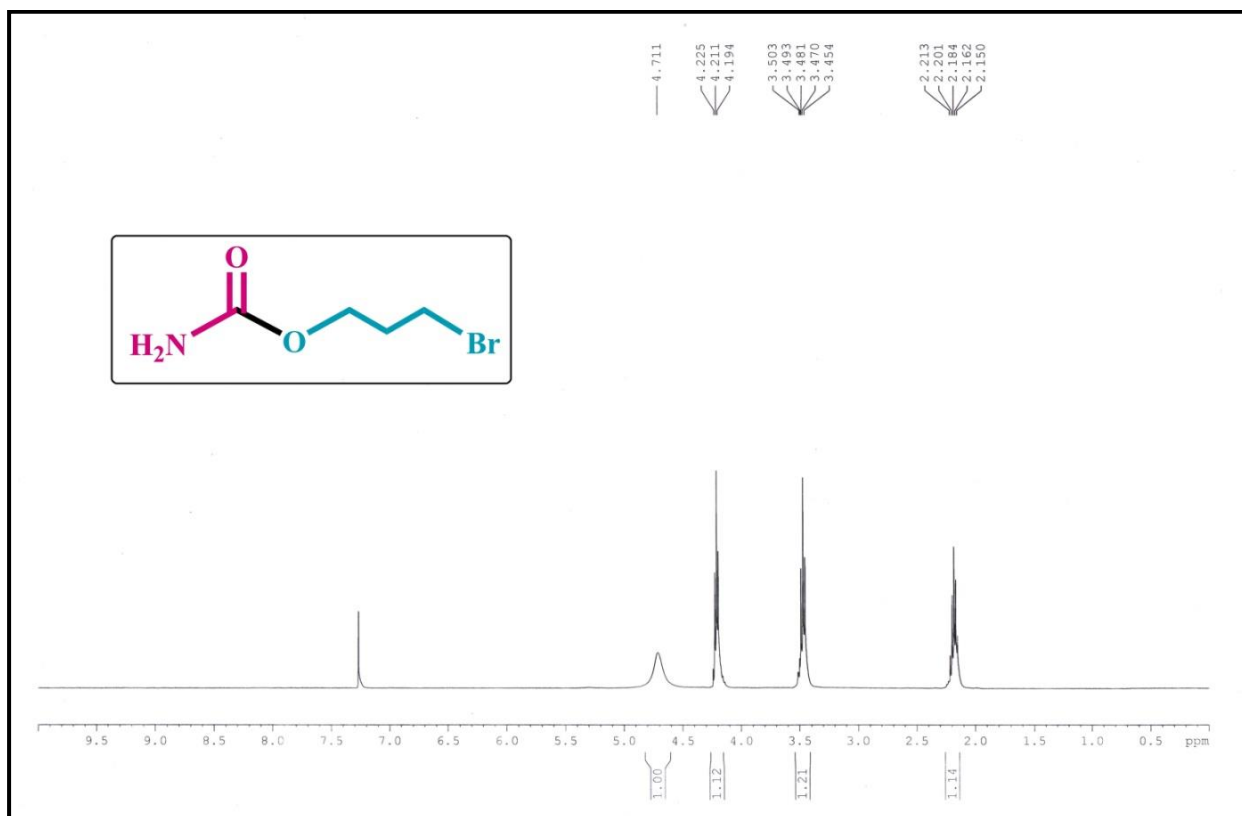
2-(diethylamino)ethyl carbamate



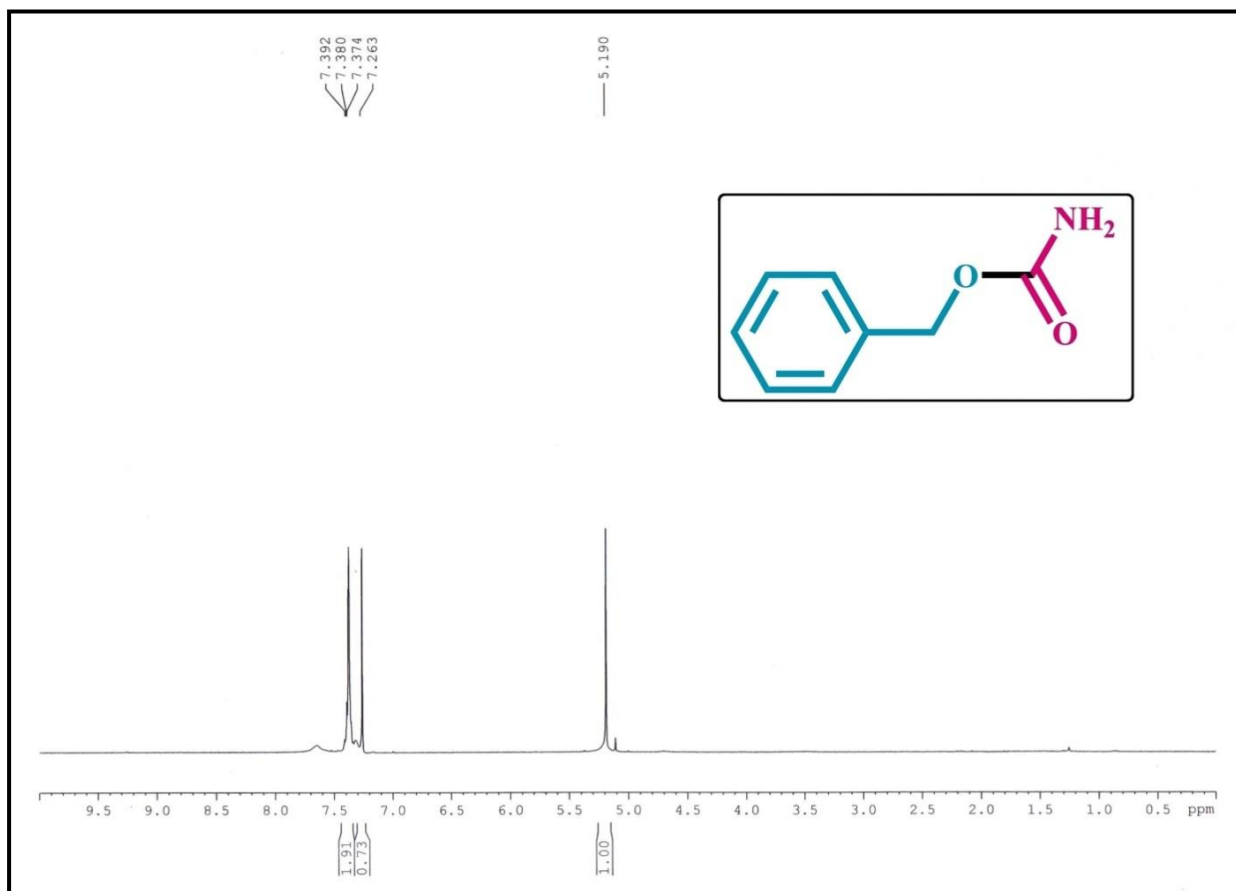
Octan-3-yl carbamate



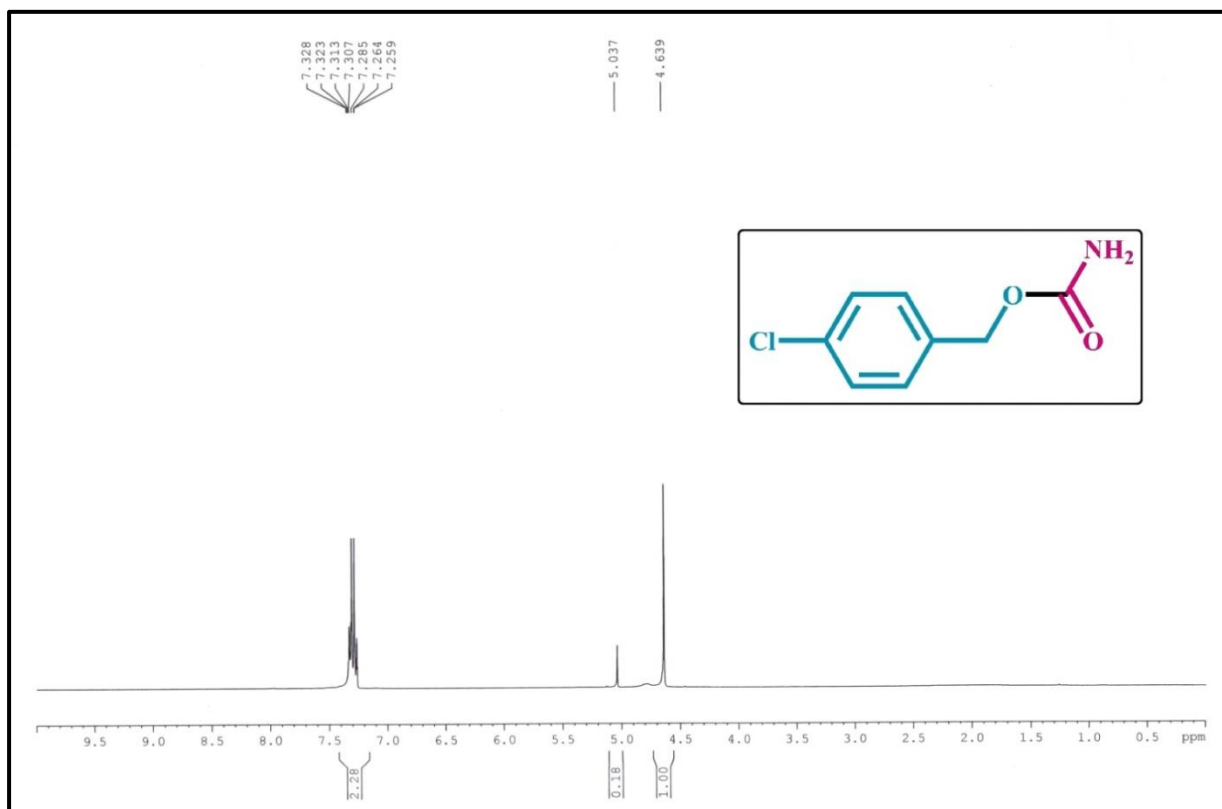
3-bromopropyl carbamate



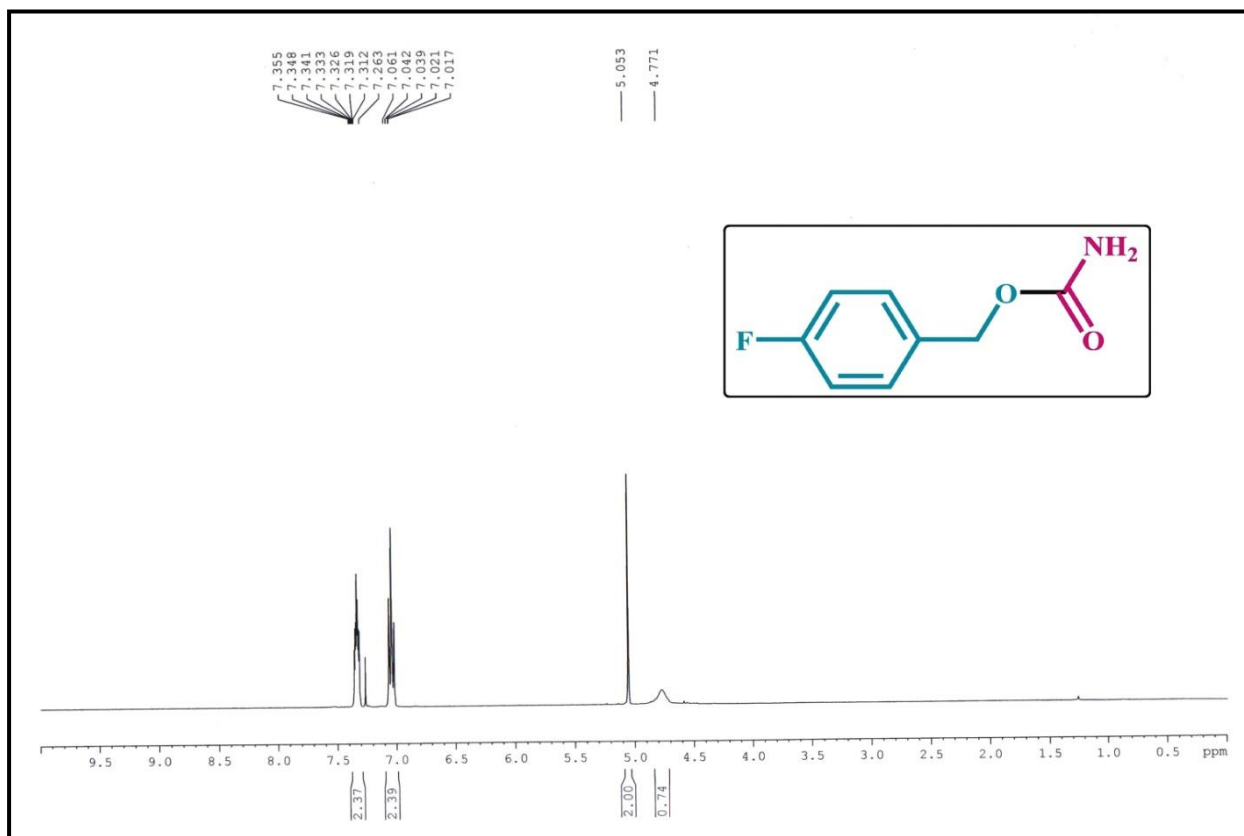
Benzyl carbamate



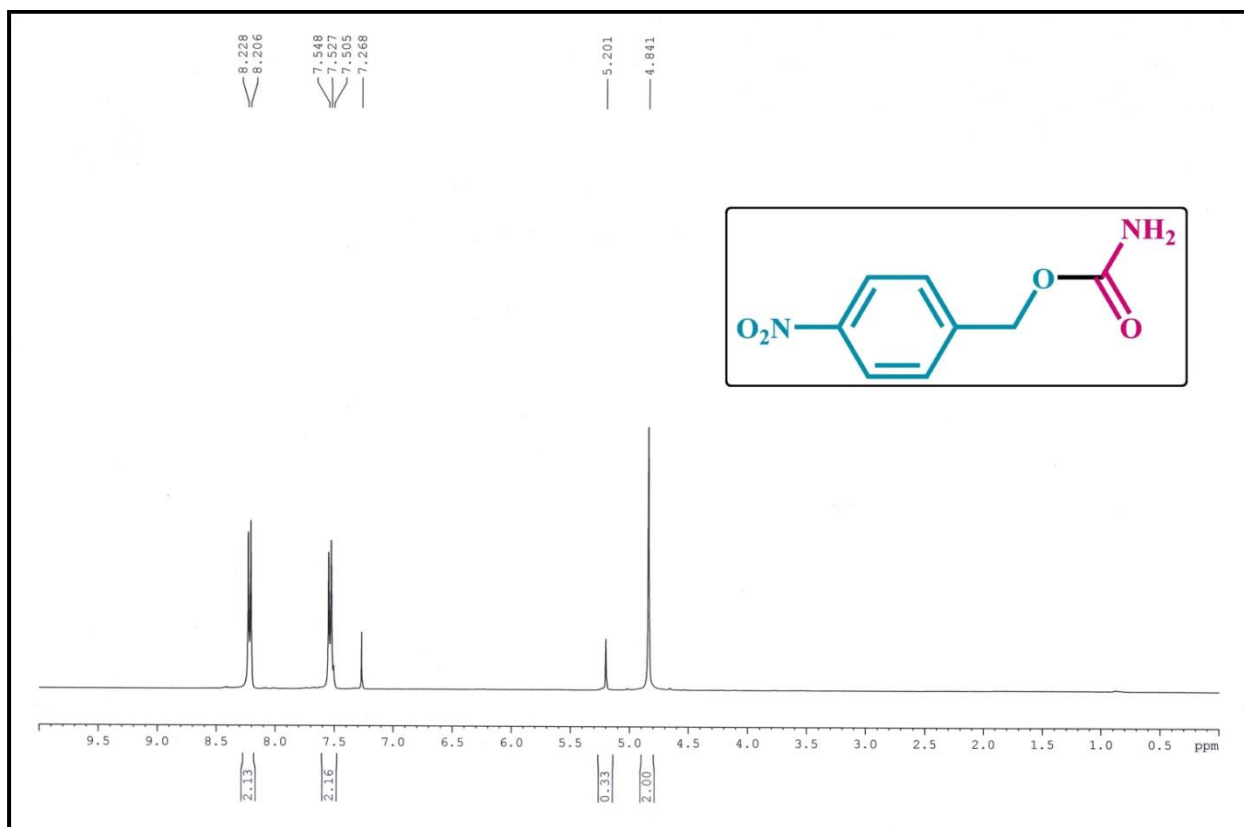
4-chlorobenzyl carbamate



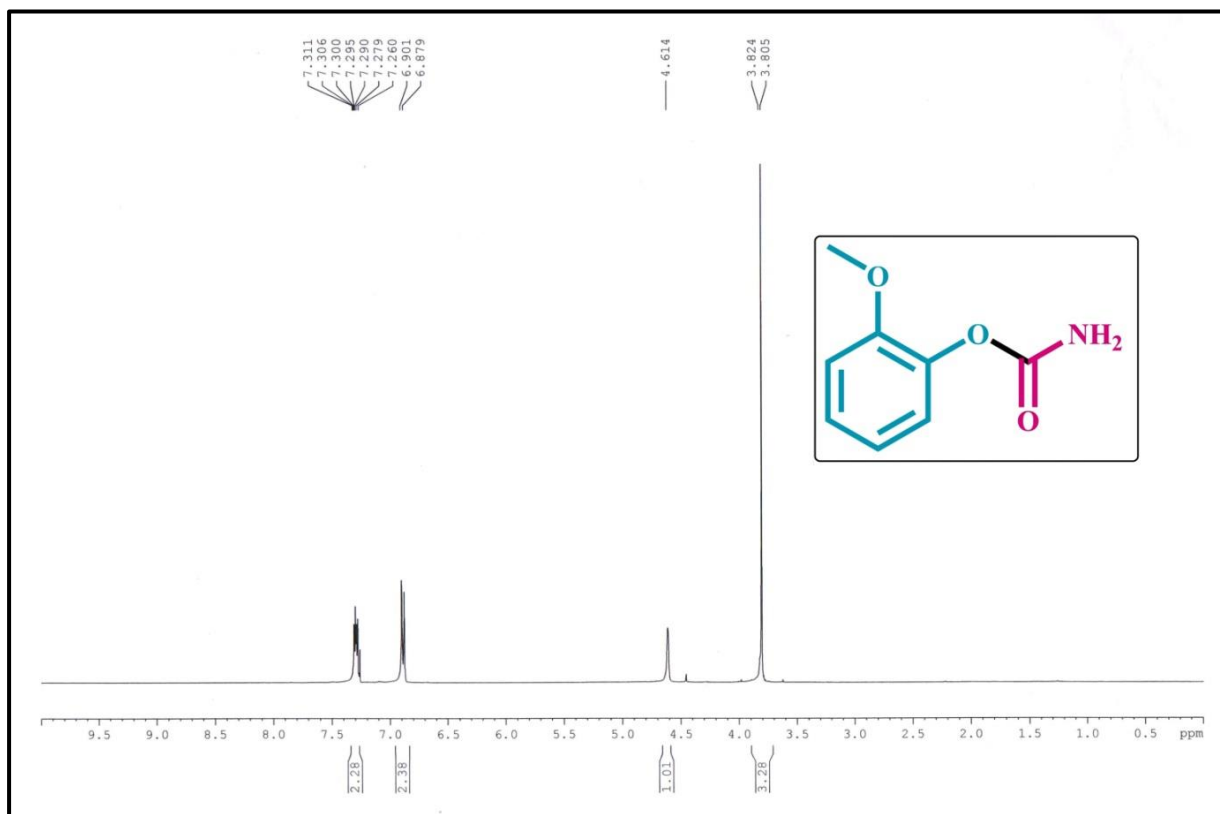
4-fluorobenzyl carbamate



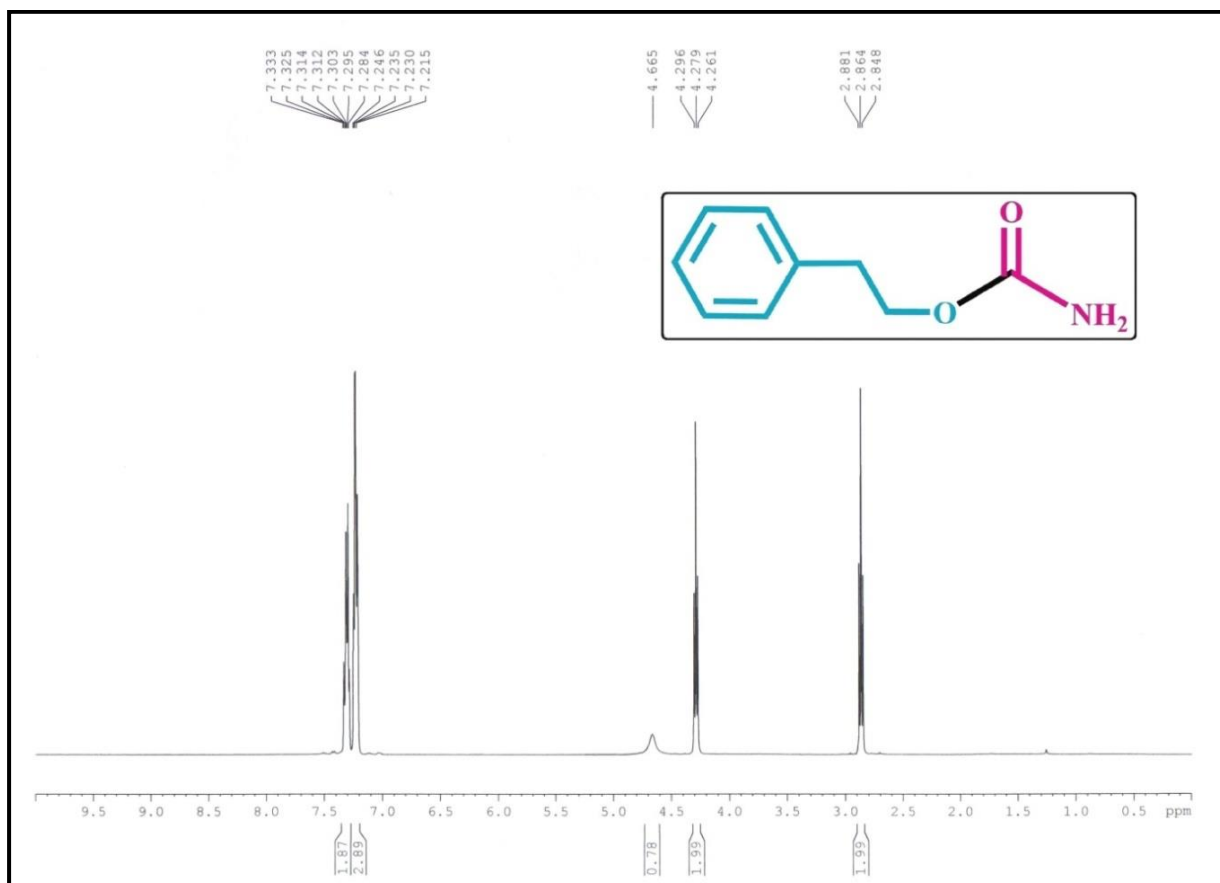
4-nitrobenzyl carbamate



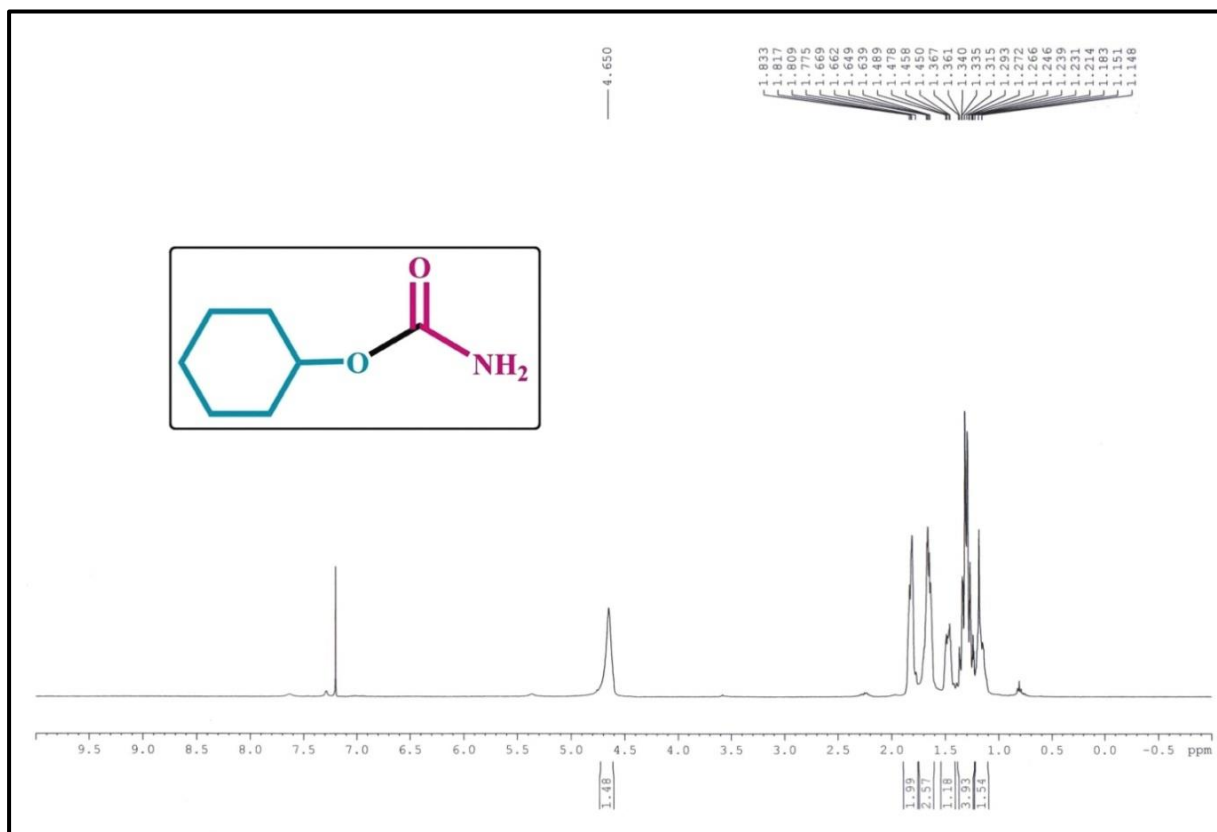
2-methoxyphenyl carbamate



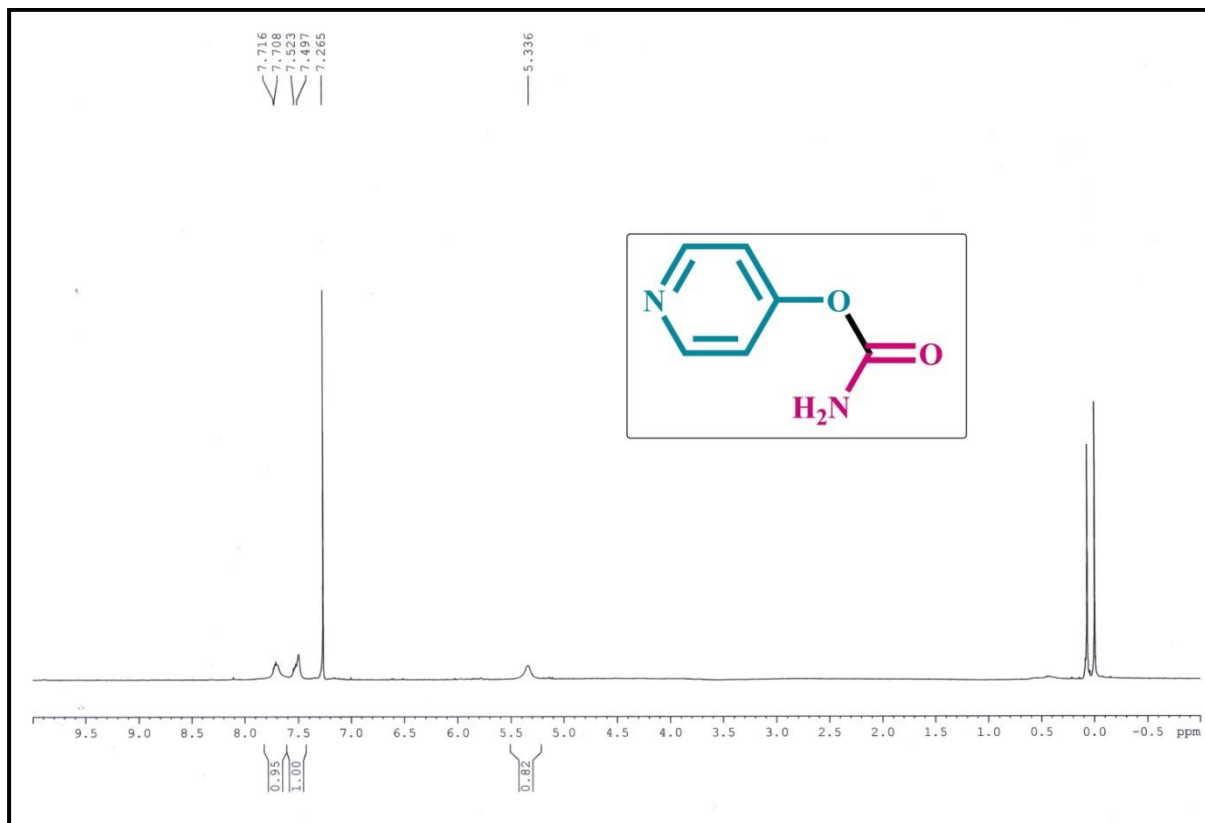
Phenethyl carbamate



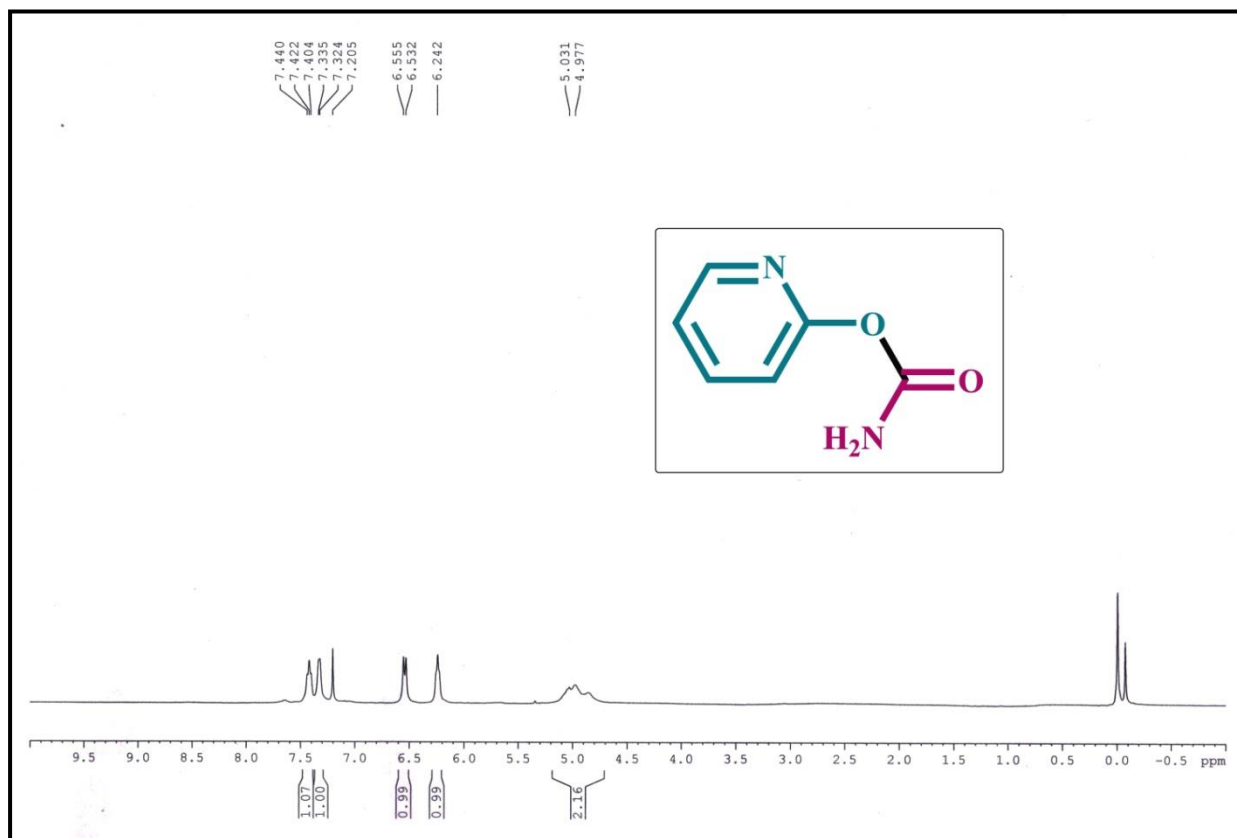
Cyclohexyl carbamate



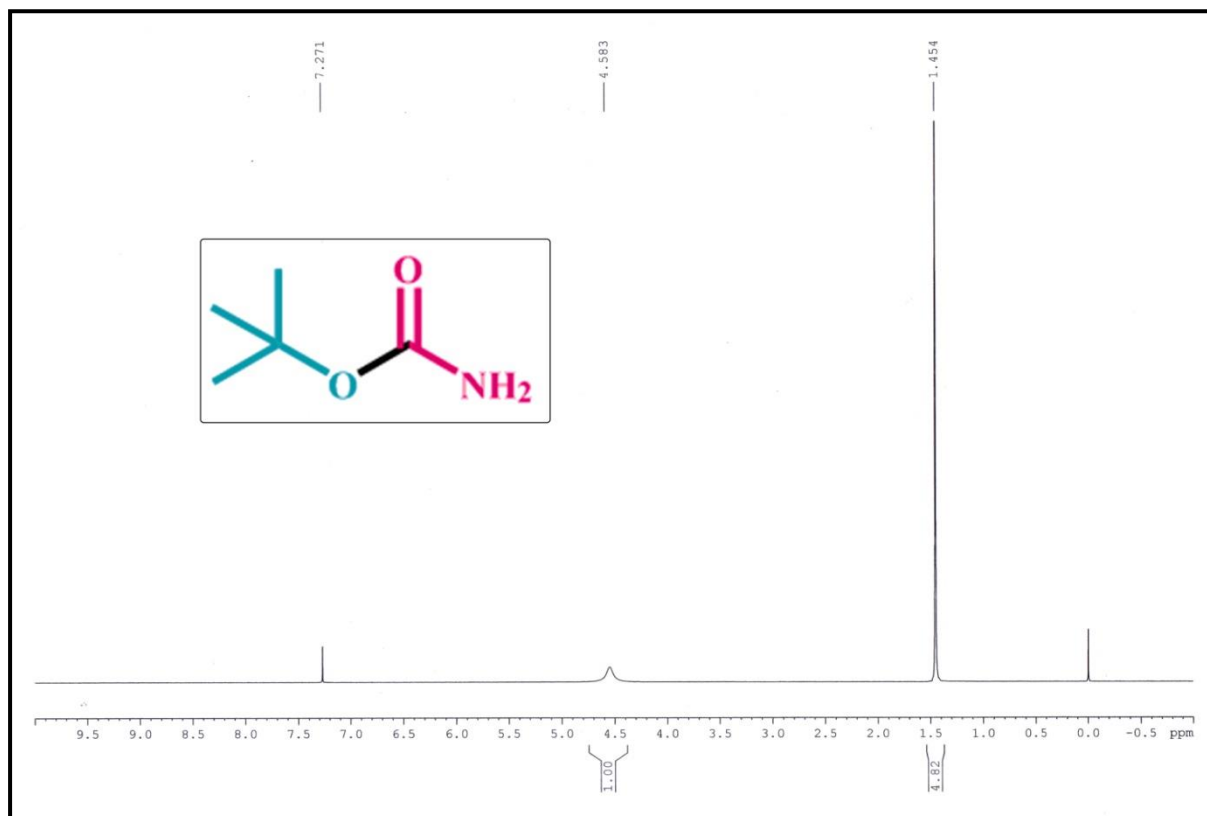
Pyridin-4-yl carbamate



Pyridin-2-yl carbamate

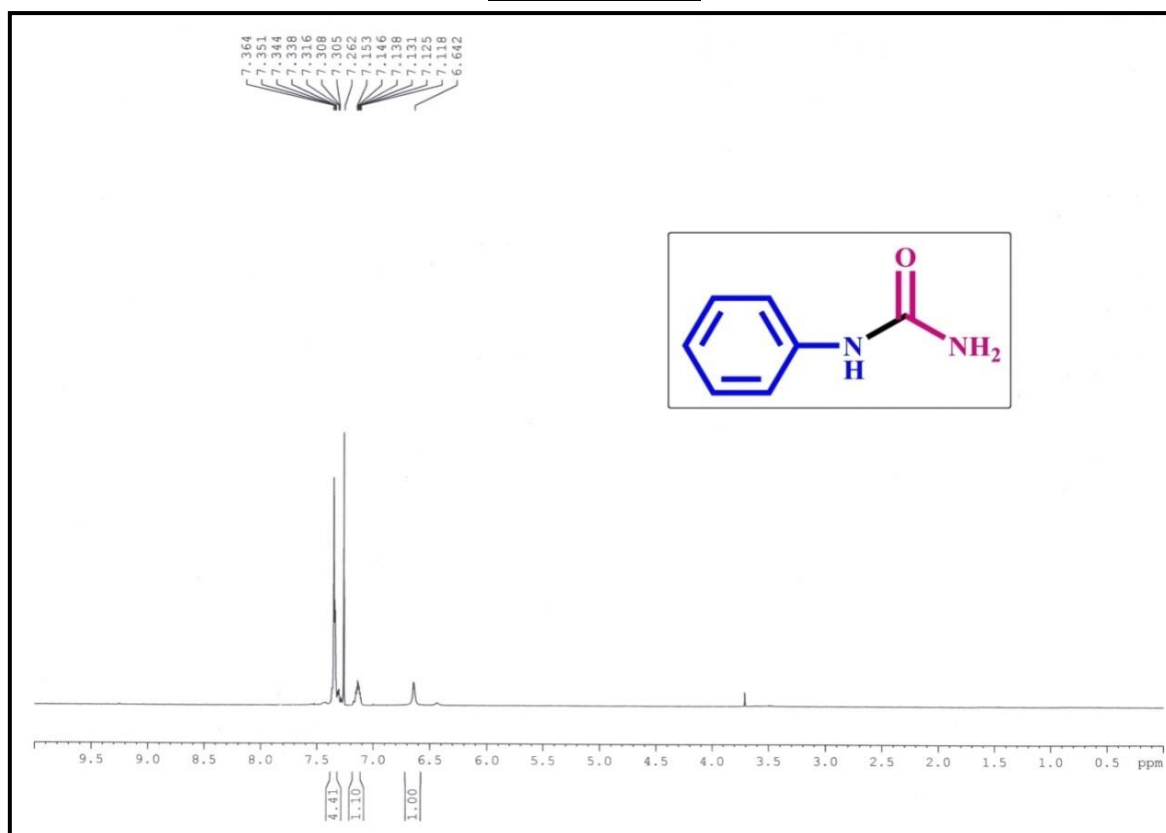


Tert-butyl carbamate

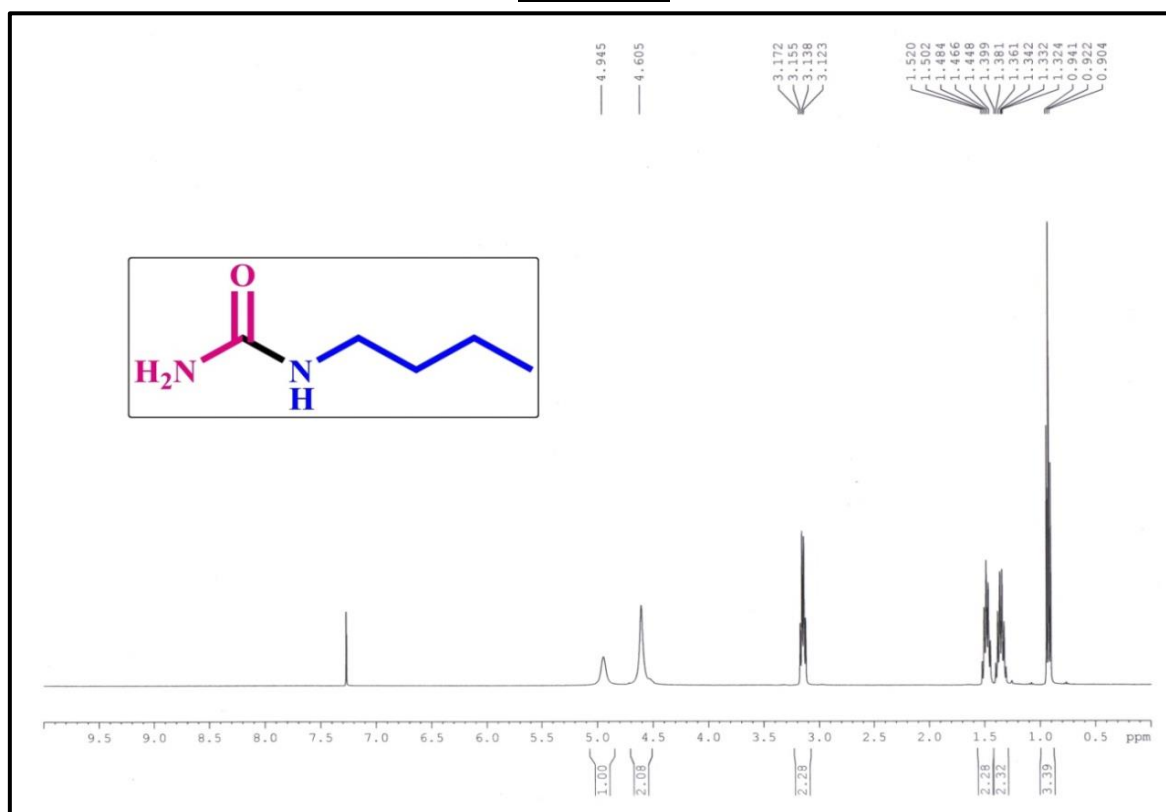


¹HNMR Copies of N-substituted ureas

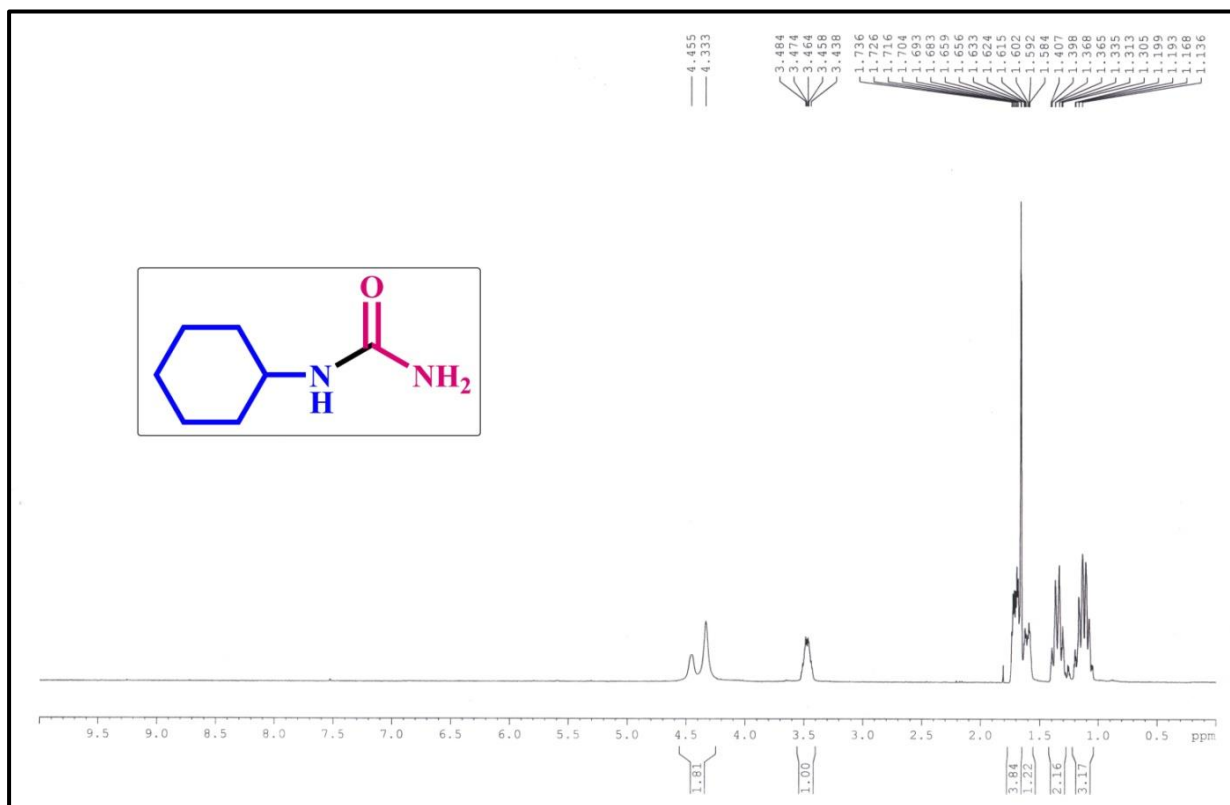
N-phenylurea



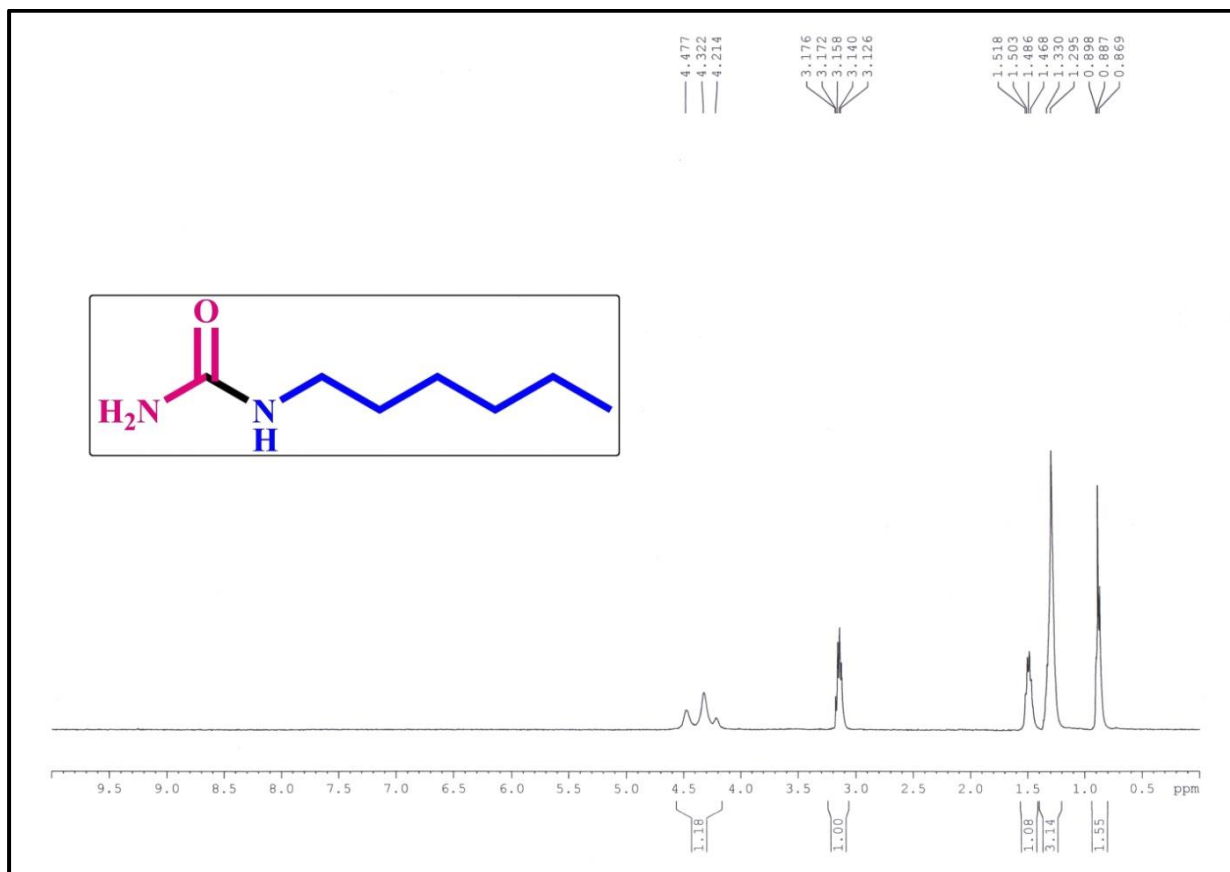
Butylurea



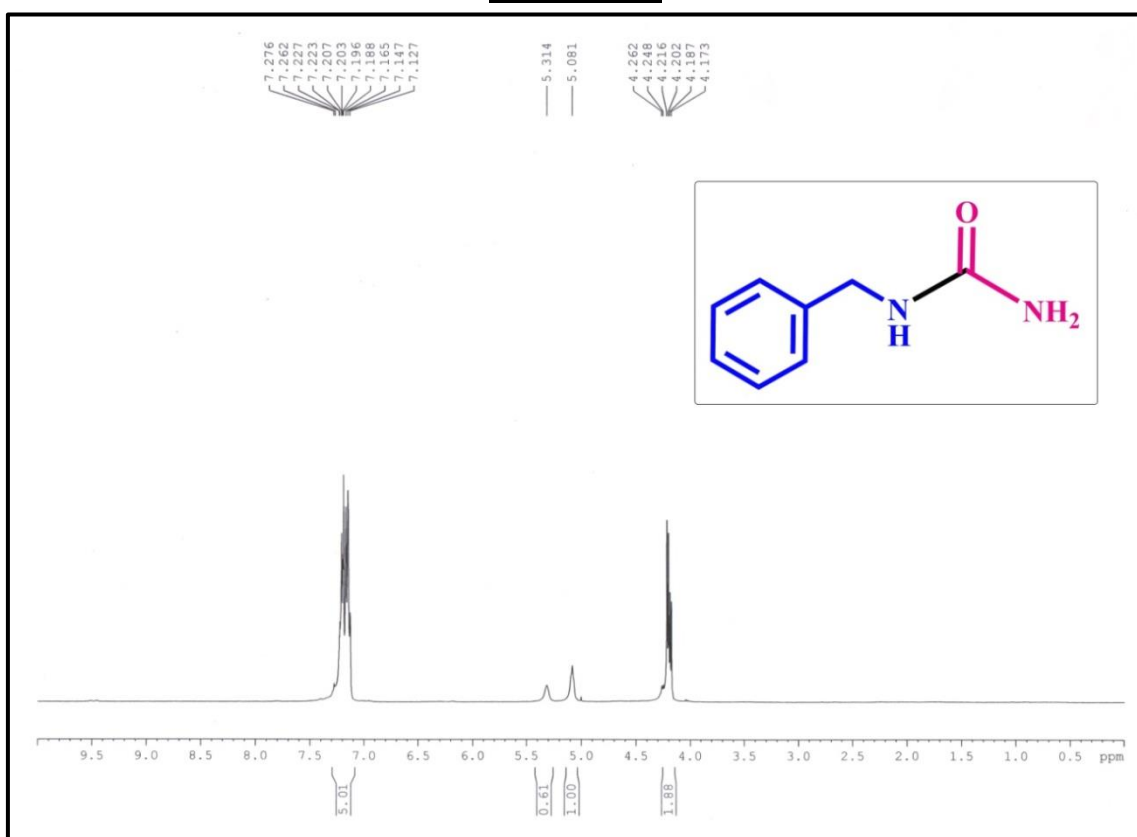
Cyclohexylurea



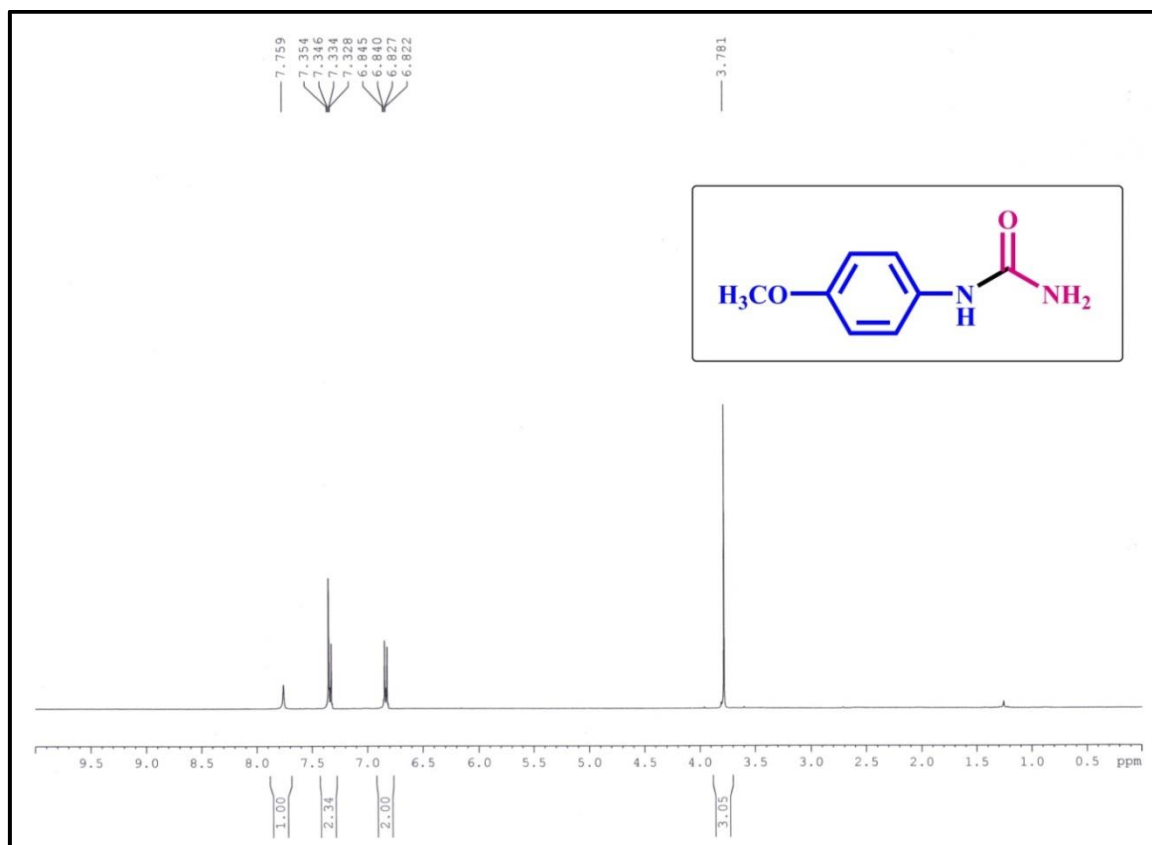
Hexylurea



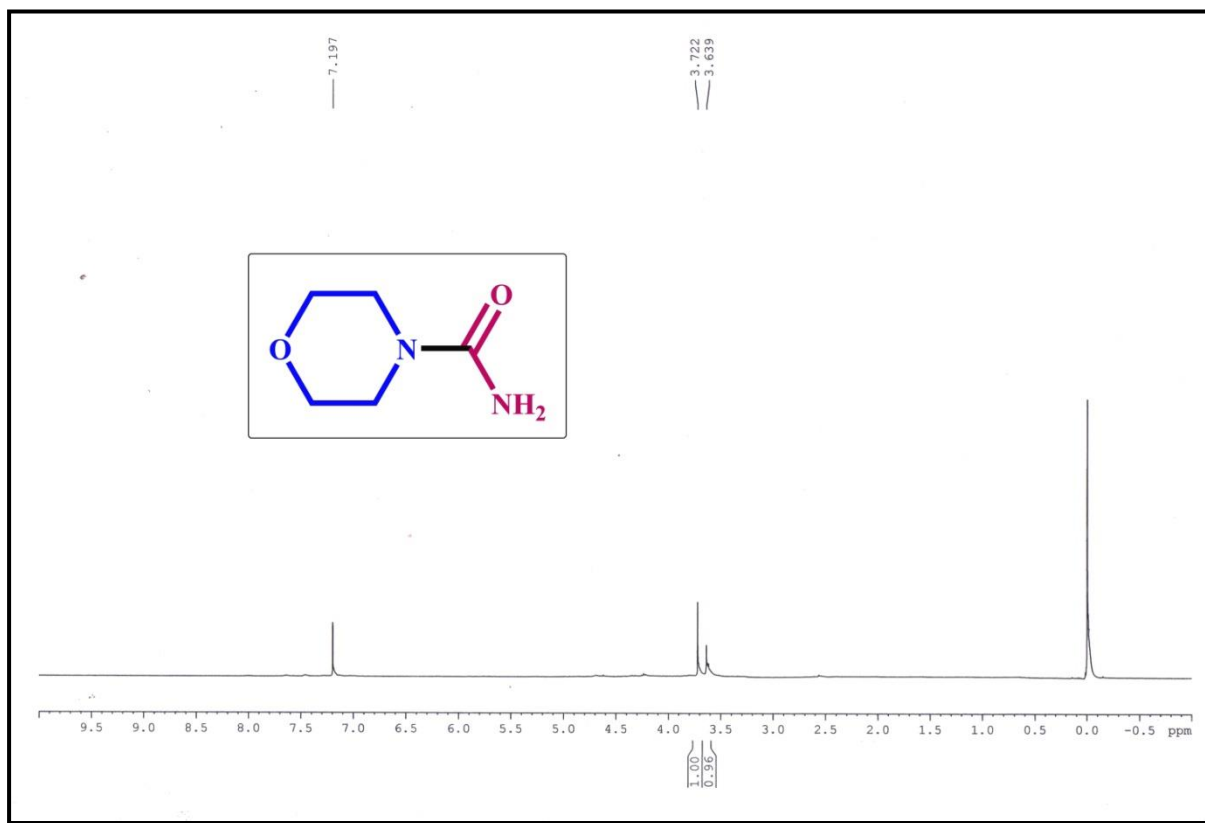
Benzylurea



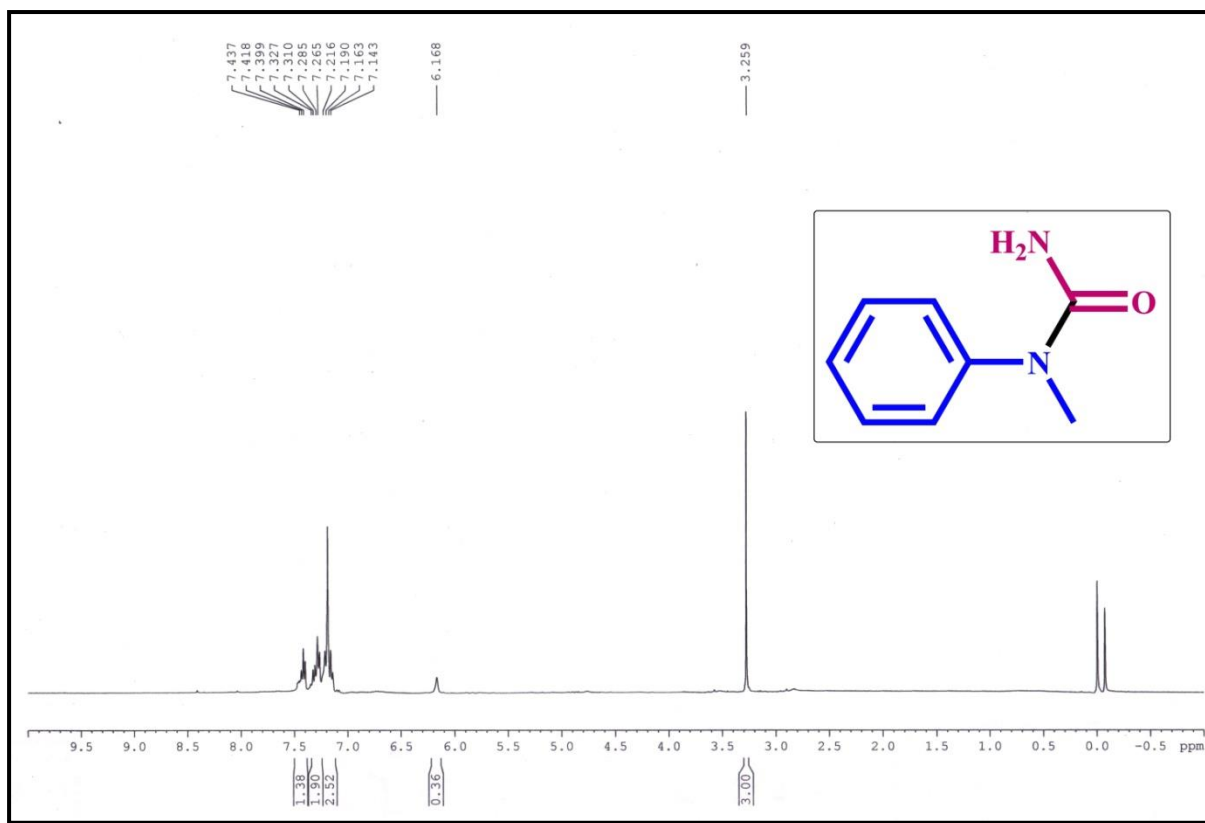
4-methoxyphenylurea



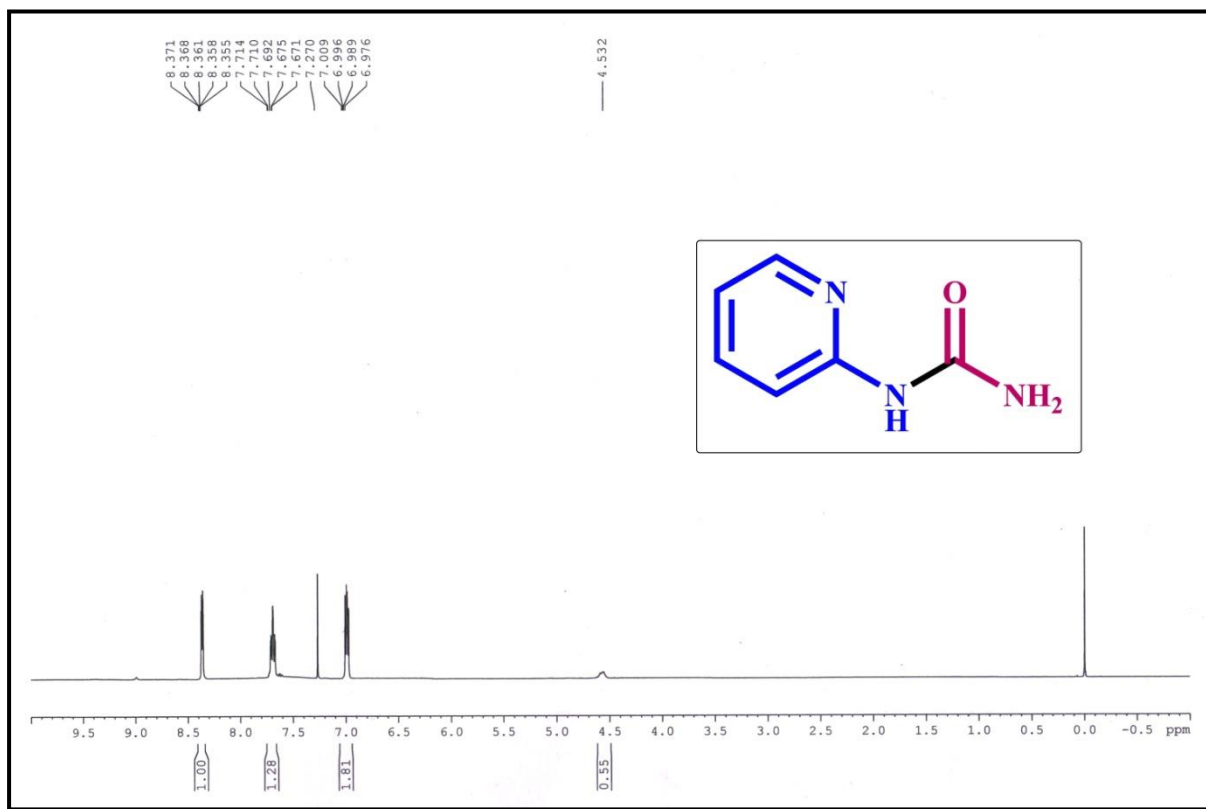
Morpholine-4-carboxamide



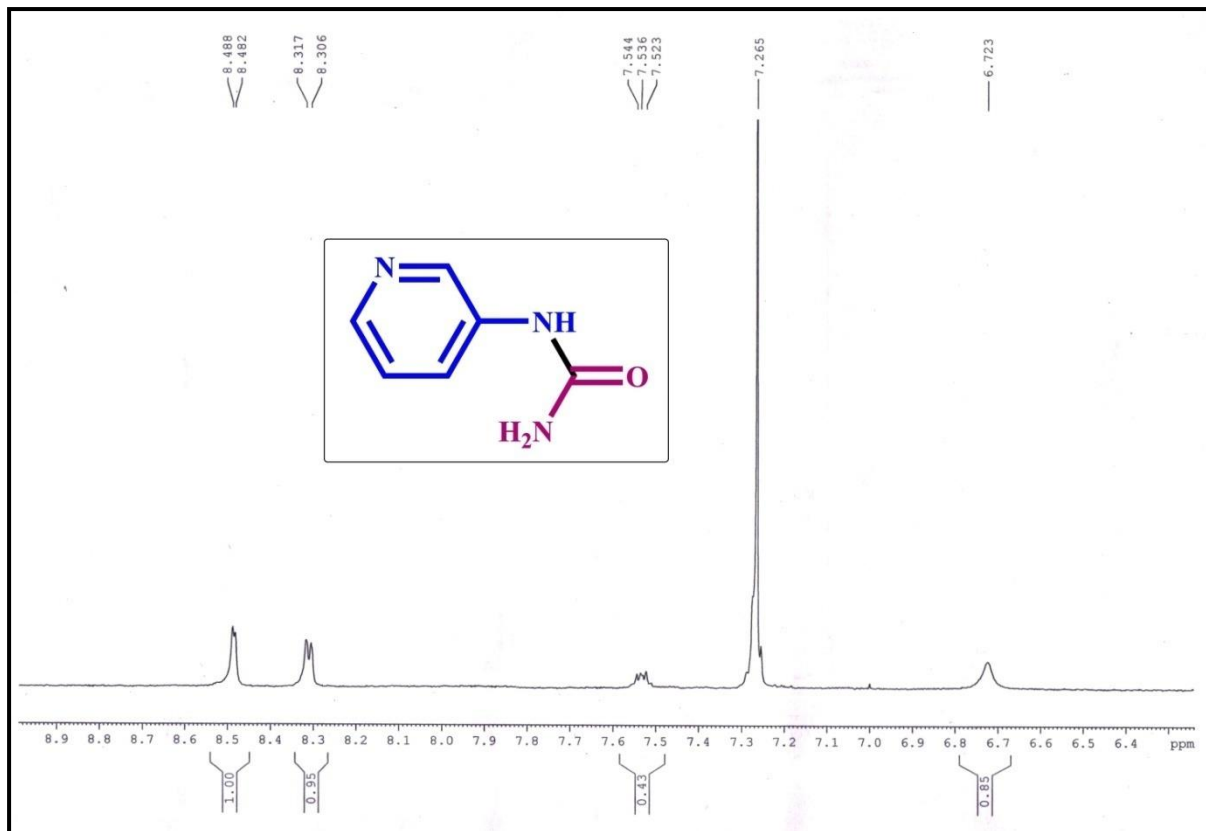
1-methyl-1-phenylurea



Pyridyl urea

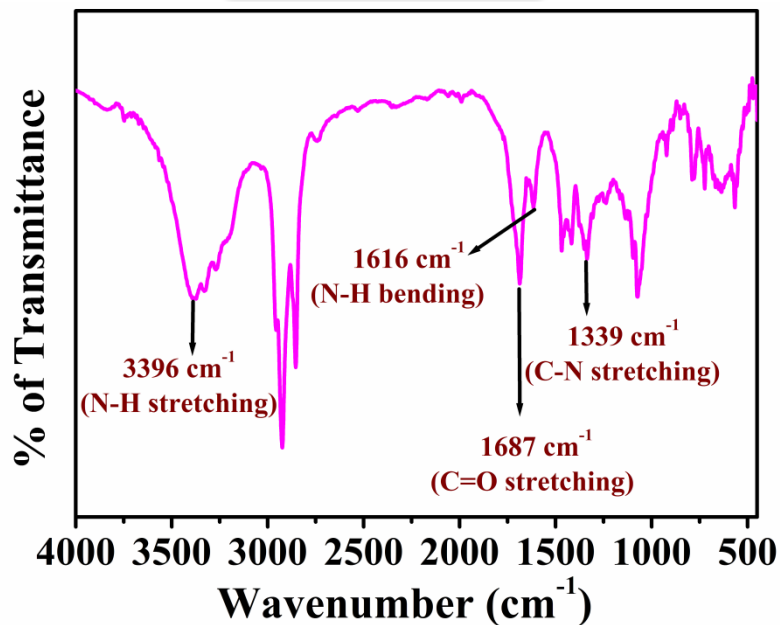
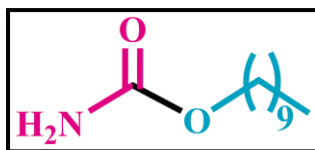


(3-pyridyl)urea

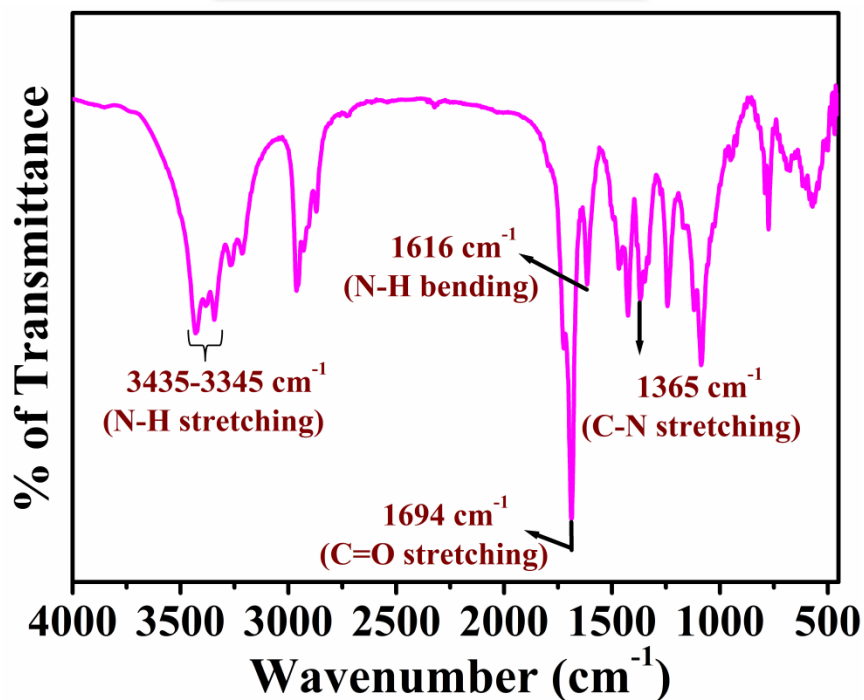
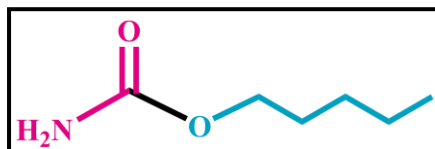


FTIR spectra of Carbamates

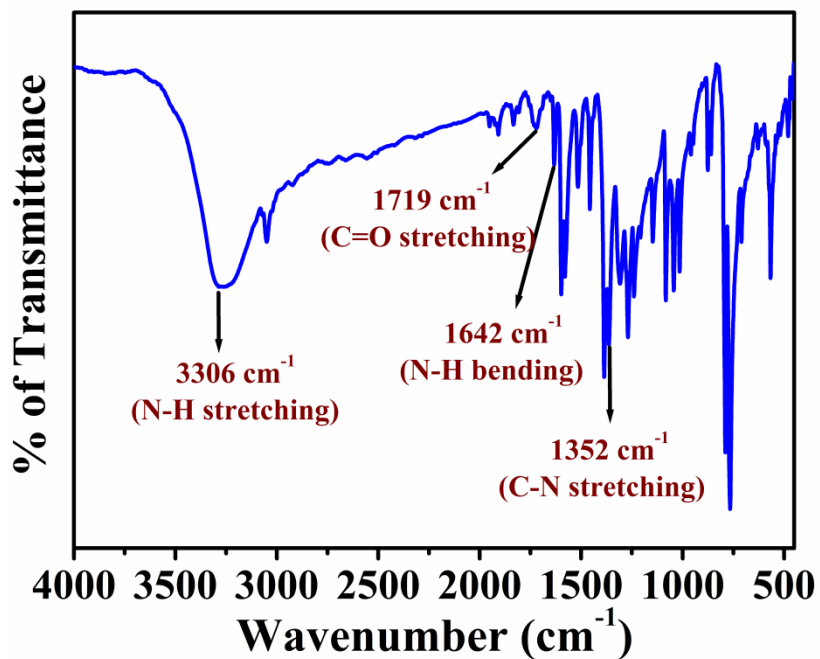
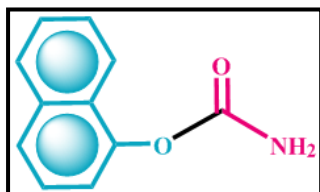
Decyl carbamate



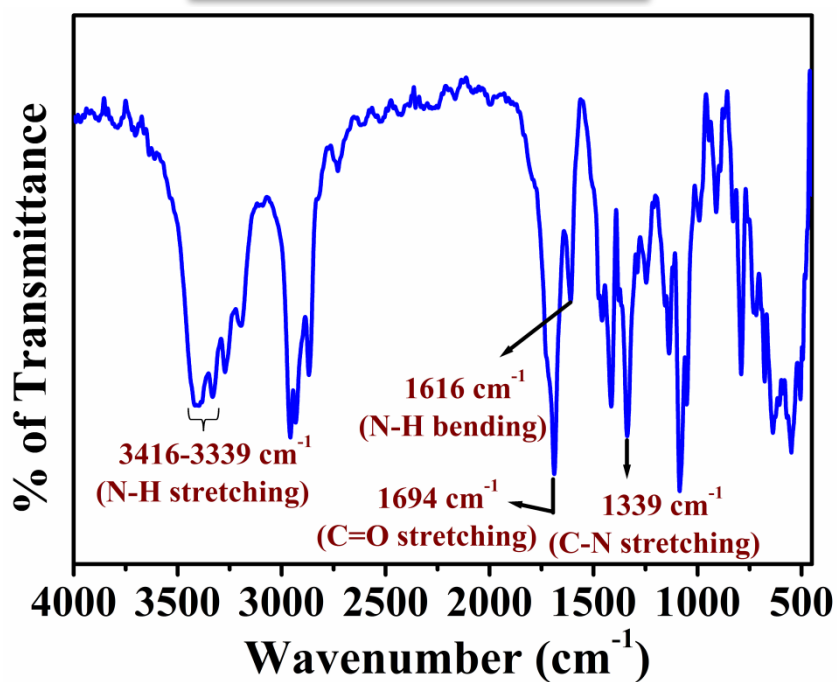
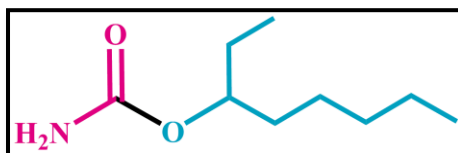
Pentyl carbamate



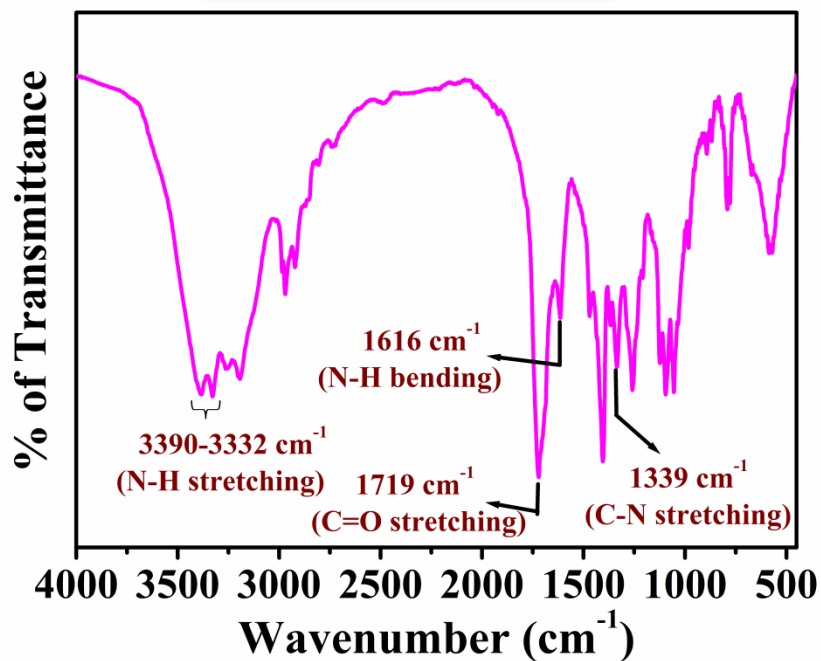
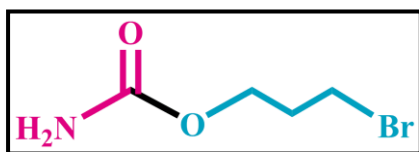
1-naphthyl carbamate



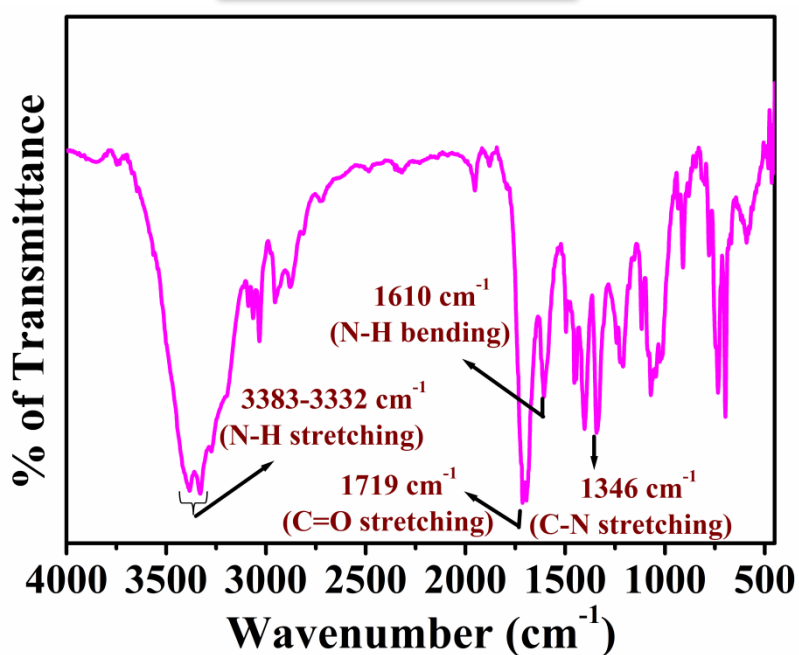
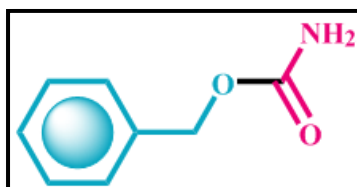
Octan-3-yl carbamate



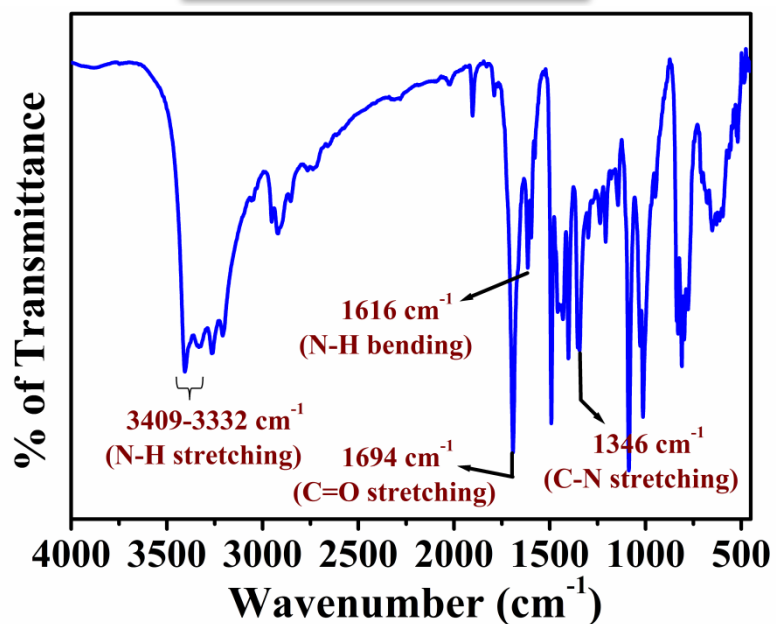
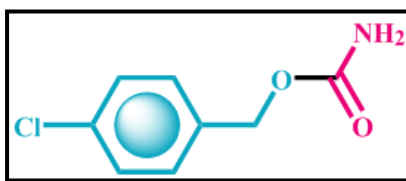
3-bromopropyl carbamate



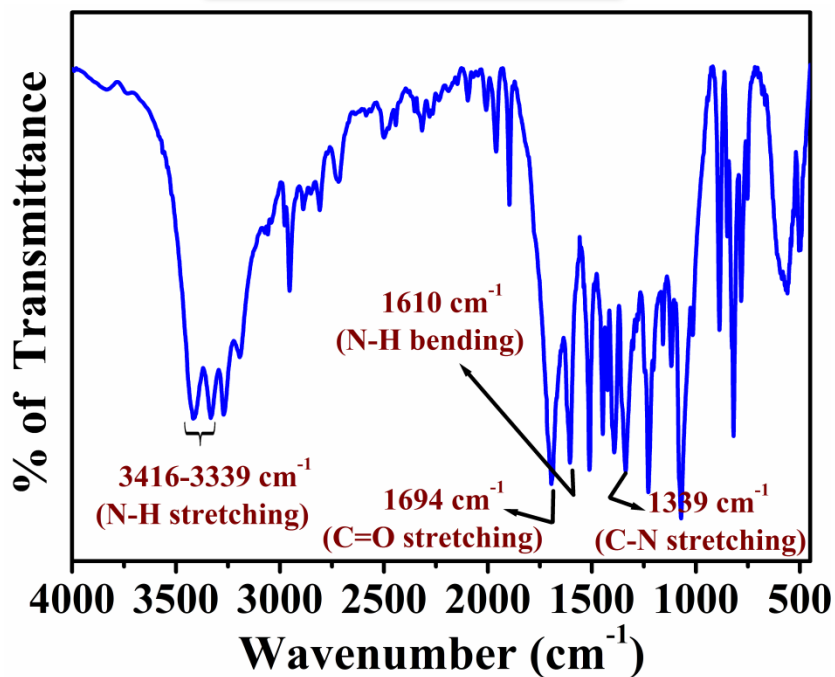
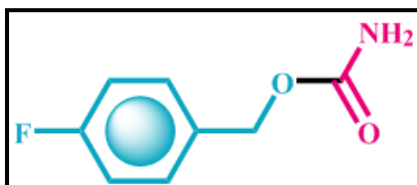
Benzyl carbamate



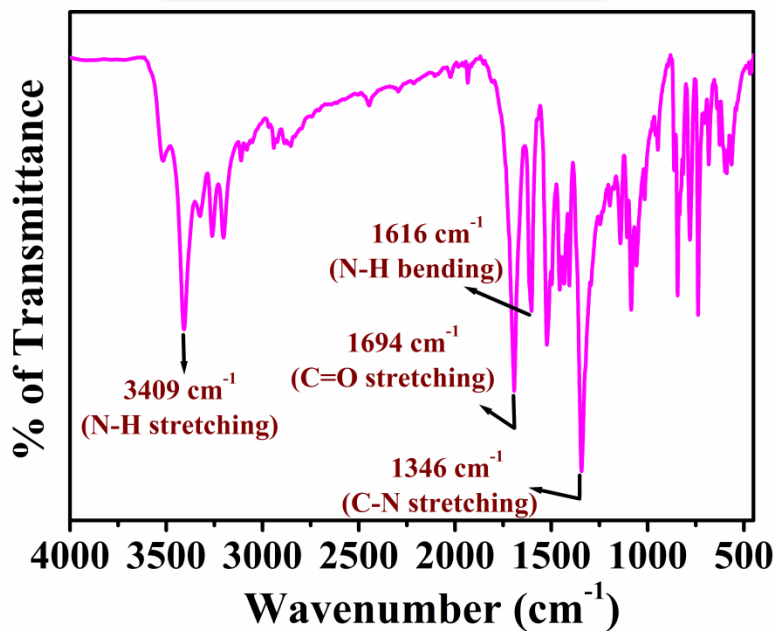
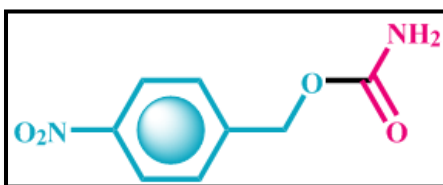
4-chlorobenzyl carbamate



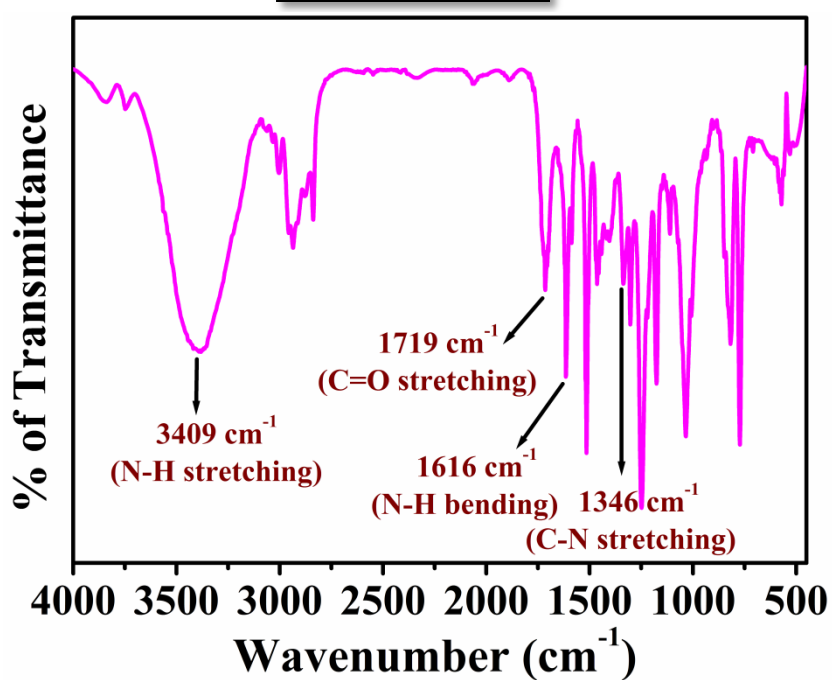
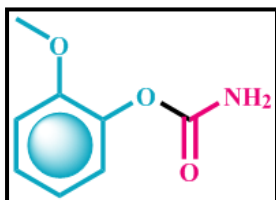
4-fluorobenzyl carbamate



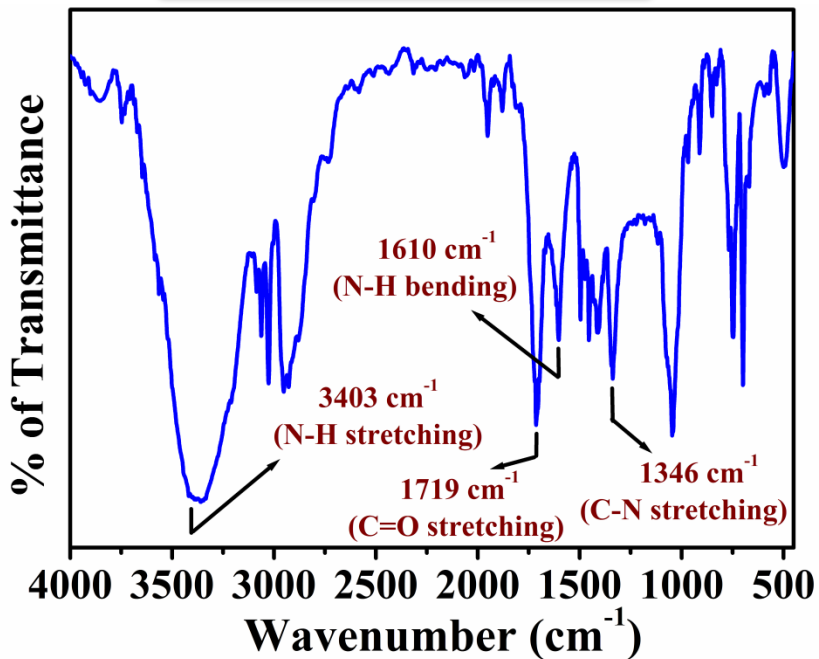
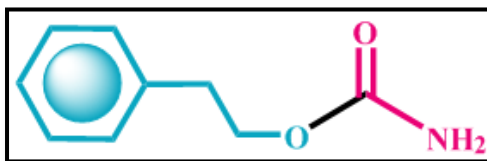
4-nitrobenzyl carbamate



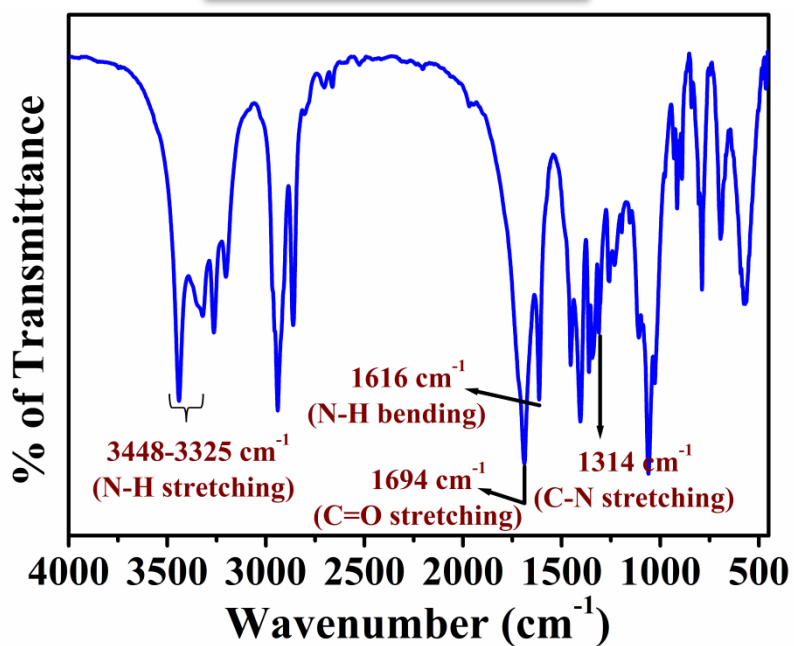
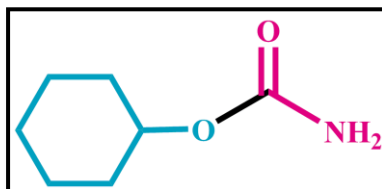
2-methoxyphenyl carbamate



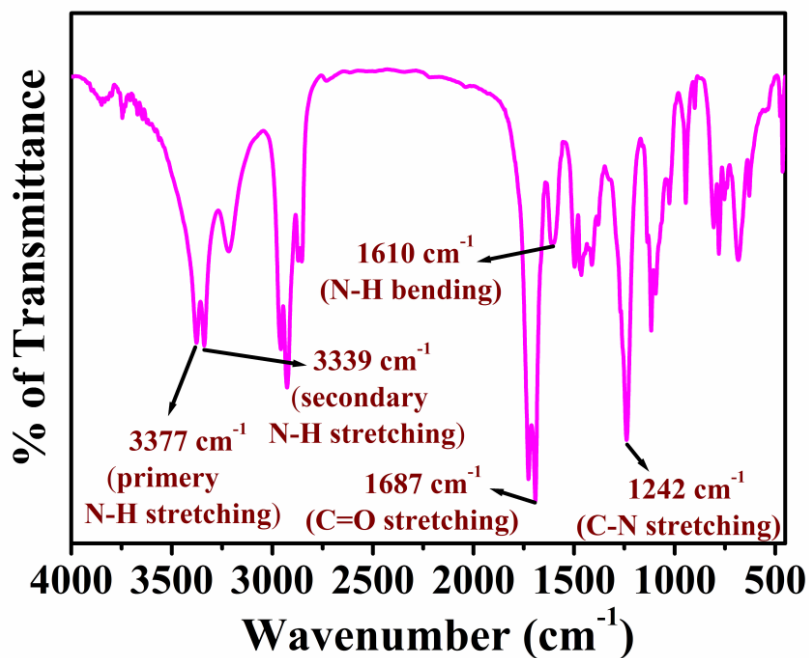
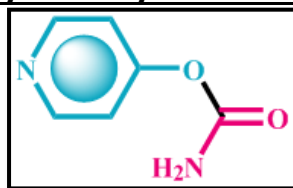
Phenethyl carbamate



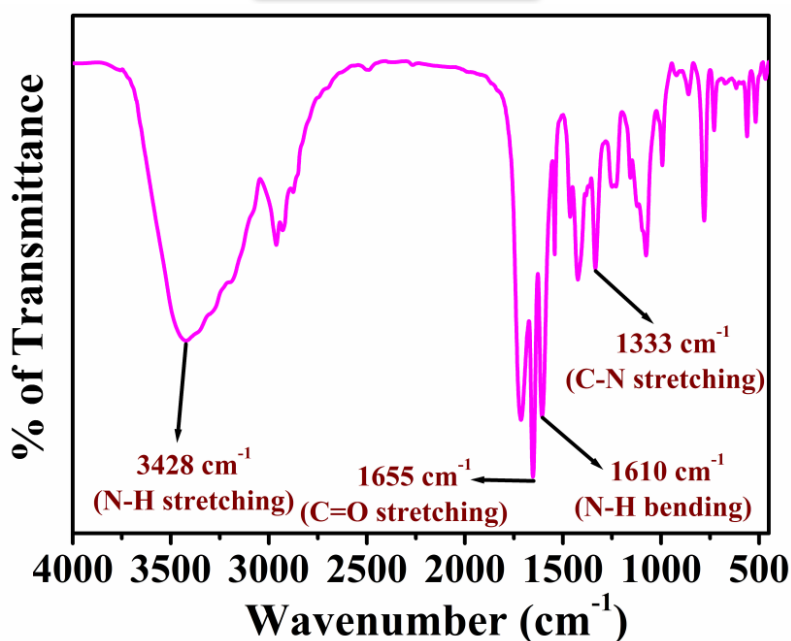
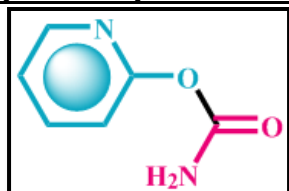
Cyclohexyl carbamate



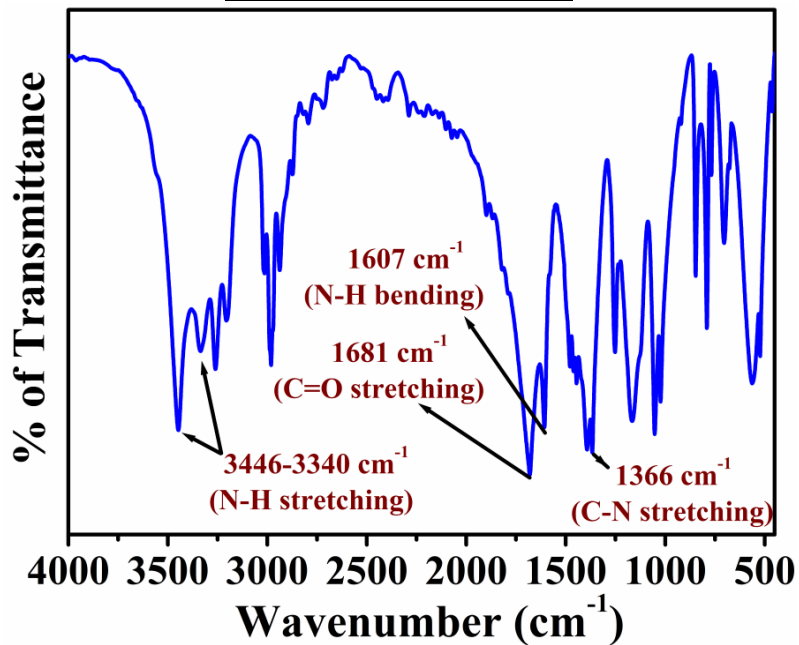
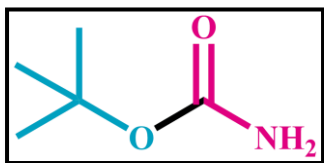
Pyridin-4-yl carbamate



Pyridin-2-yl carbamate

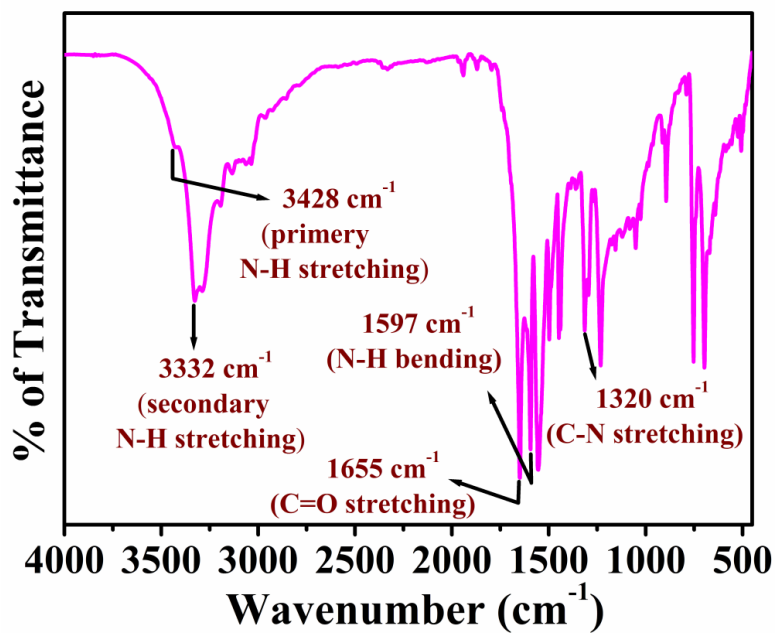
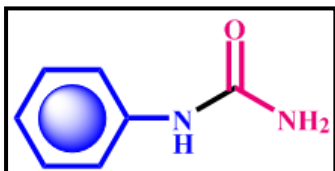


Tert-butyl carbamate

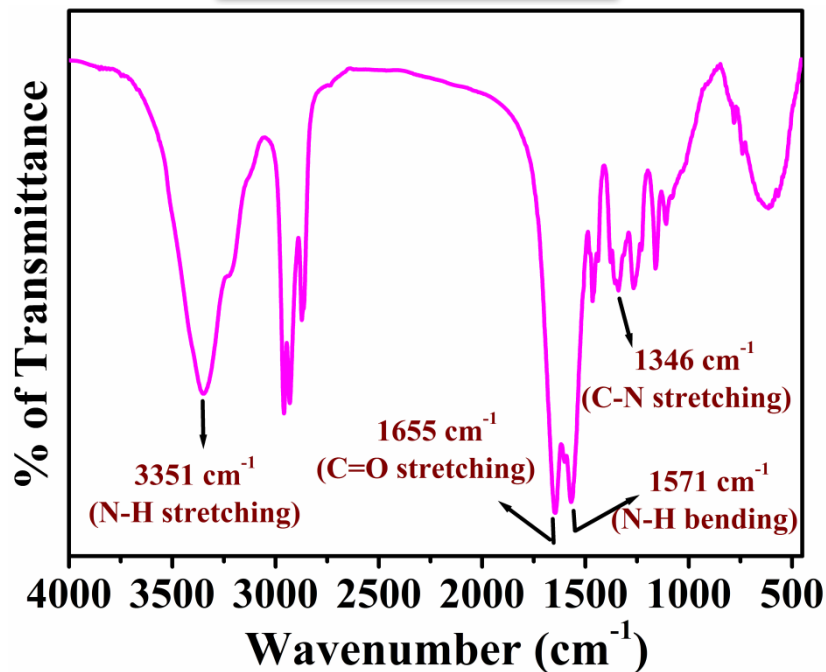
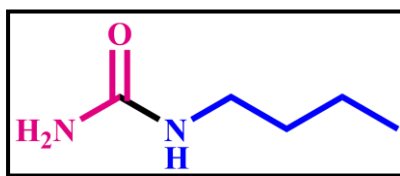


FTIR spectra of N-substituted ureas

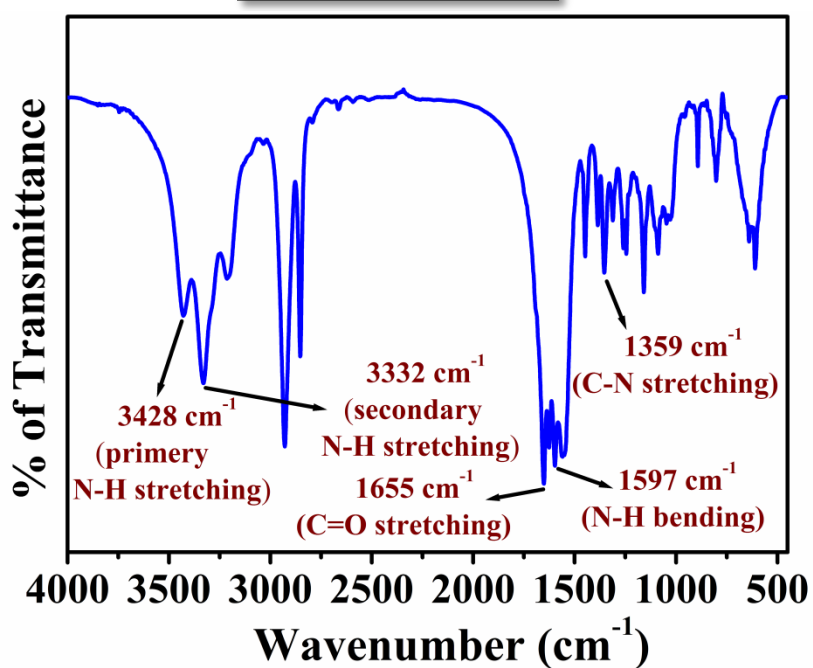
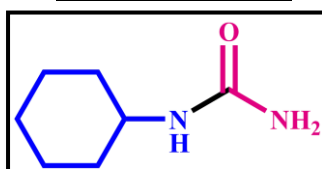
N-phenylurea



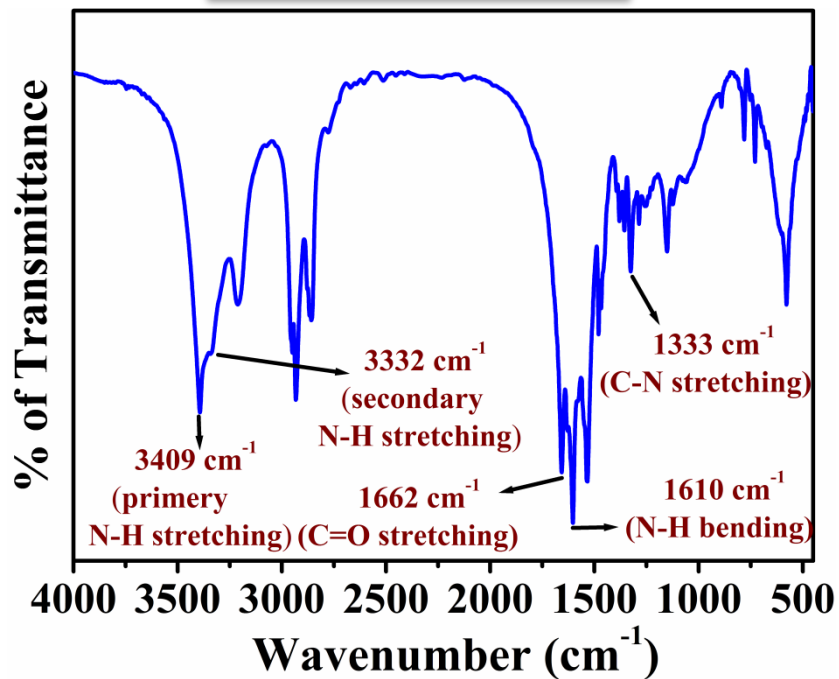
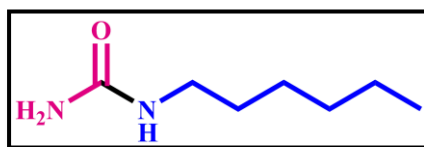
Butylurea



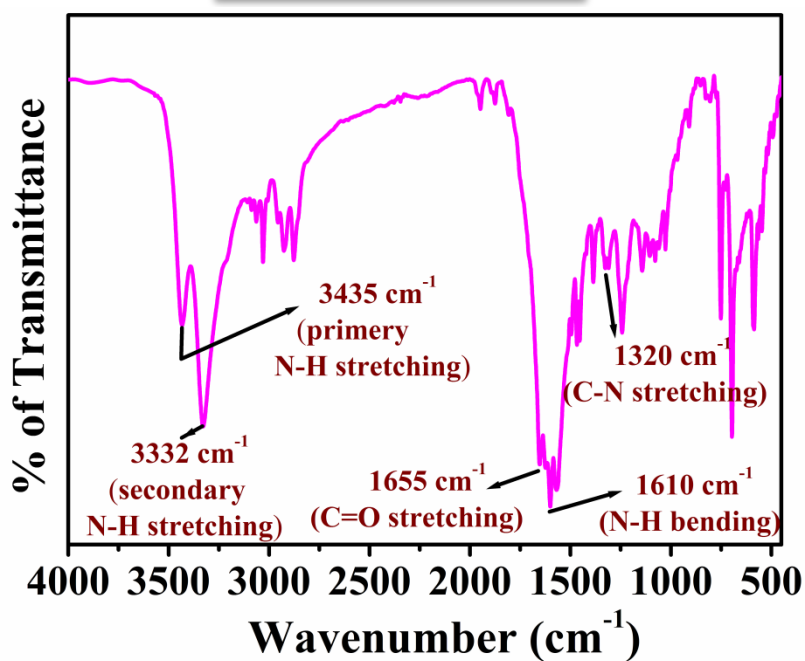
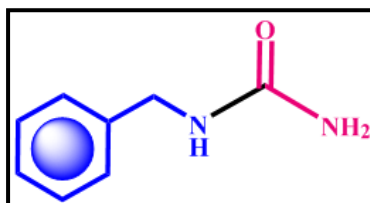
Cyclohexylurea



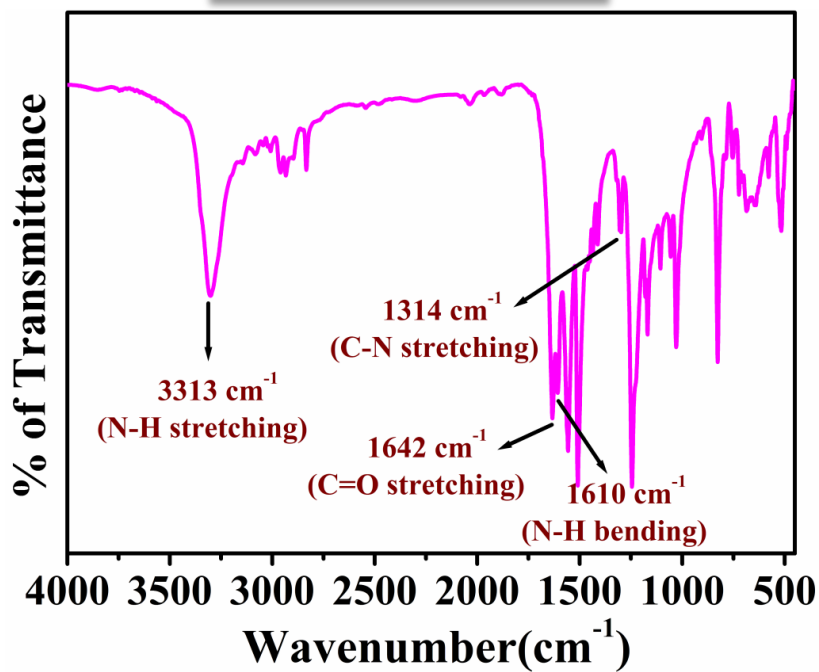
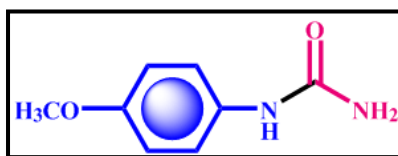
Hexylurea



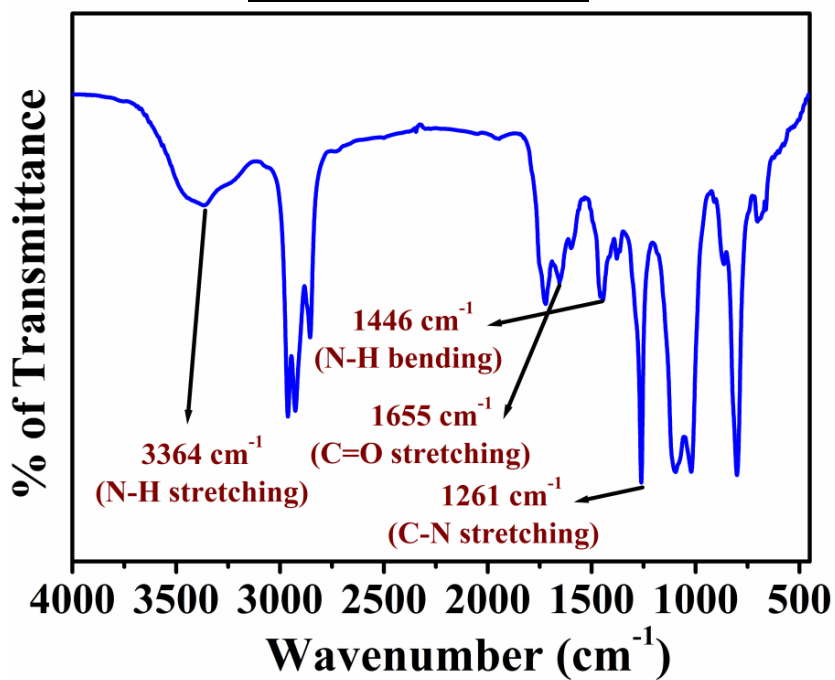
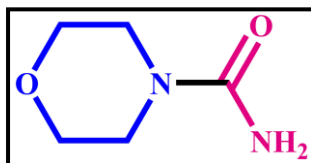
Benzylurea



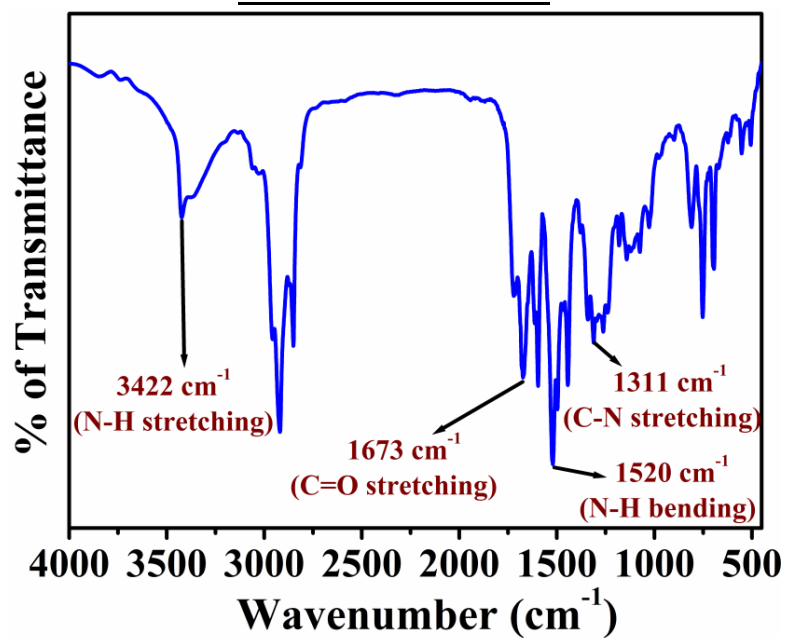
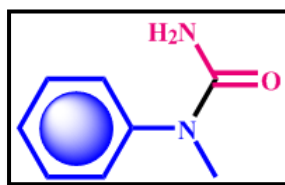
4-methoxyphenylurea



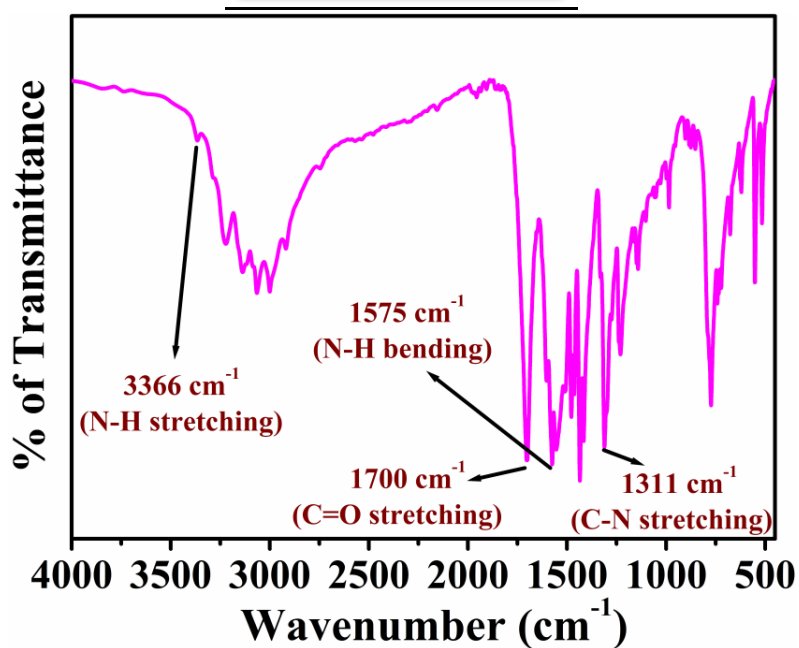
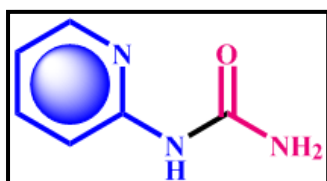
Morpholine-4-carboxamide



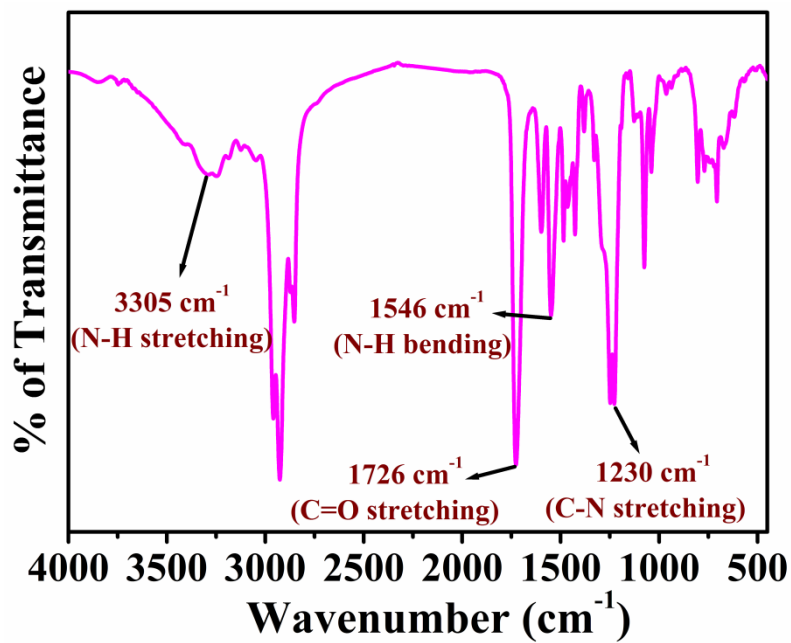
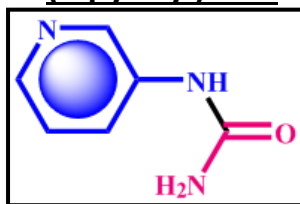
1-methyl-1-phenylurea



Pyridyl urea



(3-pyridyl)urea



Reference

- [1] M. Wang, H. Wang, N. Zhao, W. Wei and Y. Sun, *Ind. Eng. Chem. Res.*, 2007, **46**, 2683.