1. HPLC Experimental Data for Quantitative Analysis of Transesterification Reaction Mixtures

1.1 Materials. Equipment. and Analytical Conditions

The analysis of reaction mixture components was performed using HPLC with UV detection. The chromatographic system included:

- **HPLC System**: Hitachi LaChrom Elite
    - **Organizer**: Hitachi LaChrom Elite
    - **Pump**: L-2130
    - **UV Detector**: L-2400

Column: Kromasil 100-5-C18 (4.6 × 250 mm)

Elution: Gradient mode with a water/acetonitrile mobile phase. Flow rate: 1 mL/min. Detection wavelength: 254 nm.

The HPLC separation used a gradient of water (A) and acetonitrile (B): 0-10 min 25-55% B, 10-15 min 55-80%, 15-17 min 80-25% B, followed by 3 min re-equilibration.

1.2 Calibration Data

Table 1 summarizes the calibration coefficients (K) and retention times for all N-aryl-O-alkyl carbamates involved in the transesterification reactions.

The calibration coefficients, which relate the molar concentration of a compound in solution to its peak area, were derived using the equation:

$$K = \frac{m}{v * S * M}$$

where:

- K: Calibration coefficient ($mol \cdot s \cdot L^{-1} \cdot mV^{-1}$)
- m: Mass of the sample (g)
- M: Molar mass ($g \cdot mol^{-1}$)
- S: Peak area ($mV \cdot s$)
- V: Sample volume (L)

Table 1. Optimal HPLC Conditions for Analysis

Compound	Retention Time (s)	Molar Extinction Coefficient ($mol \cdot s \cdot L^{-1} \cdot mV^{-1}$)	Correlation Coefficient (R^2)
O-Methyl-N-phenylcarbamate	538±5	(3.14±0.13) ×10⁴	0.995
O-Ethyl-N-phenylcarbamate	837±8	(3.38±0.11) ×10⁴	0.998
O-n-Propyl-N-phenylcarbamate	906±6	(3.78±0.11) ×10⁴	0.997

O-n-Butyl-N-phenylcarbamate	1008±5	(2.58±0.13) ×10^4	0.992
O-Isopropyl-N-phenylcarbamate	767±3	(5.10±0.26) ×10^4	0.993
O-sec-Butyl-N-phenylcarbamate	925±3	(4.45±0.23) ×10^4	0.999
O-n-Pentyl-N-phenylcarbamate	1035±3	(4.01±0.091) ×10^4	0.998
Methyl N-(4-chlorophenyl)carbamate	765±5	(2.06±0.13) ×10^5	0.996
Methyl N-[4-(trifluoromethyl)phenyl]carbamate	941±6	(2.86±0.17) ×10^5	0.996
Methyl N-(4-methoxyphenyl)carbamate	614±5	(2.17±0.078) ×10^5	0.998
Methyl N-(3-chlorophenyl)carbamate	817±4	(5.75±0.13) ×10^4	0.999
Ethyl N-(4-chlorophenyl)carbamate	870±6	(1.42±0.041) ×10^5	0.999
Ethyl N-[4-(trifluoromethyl)phenyl]carbamate	851±4	(3.17±0.071) ×10^5	0.999
Ethyl N-(4-methoxyphenyl)carbamate	600±5	(1.93±0.04) ×10^5	0.999
Isopropyl N-(4-chlorophenyl)carbamate	867±5	(2.74±0.11) ×10^5	0.998
Isopropyl N-[4-(trifluoromethyl)phenyl]carbamate	1093±4	(3.91±0.15) ×10^5	0.999
Isopropyl N-(4-methoxyphenyl)carbamate	864±6	(2.048±0.064) ×10^5	0.9985
Isopropyl N-(3-chlorophenyl)carbamate	997±5	(6.31±0.15) ×10^4	0.9994

The experimental calibration data used to construct the calibration curves are provided in **Tables 2–19**.

Table 2. Methyl phenylcarbamate

Peak area (×10^6 mV·s)	***Concentration (mg/mL)***	***Concentration (mol/L)***
1327.91	*6.00*	*0.0397*
1185.55	*5.00*	*0.0331*
1061.93	*4.50*	*0.0298*
754.02	*3.00*	*0.0199*

407.29	*1.50*	*0.0099*

Table 3. Ethyl phenylcarbamate

Peak area (×10⁶ mV·s)	***Concentration (mg/mL)***	***Concentration (mol/L)***
1138.07	*5.1*	*0.03091*
914.81	*3.8*	*0.02318*
635.38	*2.6*	*0.01546*
305.43	*1*	*0.006061*

Table 4. *n-Propyl phenylcarbamate*

Peak area (×10⁶ mV·s)	***Concentration (mg/mL)***	***Concentration (mol/L)***
593.37	2.7	0.0151
501.49	2.16	0.0121
325.77	1.35	0.0075
185.18	0.675	0.0038
80.06	0.27	0.0015

Table 5. *n-Butyl phenylcarbamate*

Peak area (×10⁶ mV·s)	***Concentration (mg/mL)***	***Concentration (mol/L)***
1803.53	8.4	0.0435
1307.37	4.2	0.0218
1182.26	3.36	0.0174

957.21	2.1	0.0109
822.11	1.05	0.0054

Table 6. *Isopropyl phenylcarbamate*

Peak area (×10⁶ mV·s)	***Concentration (mg/mL)***	***Concentration (mol/L)***
423.66	1.44	0.0080
316.58	0.96	0.0053
252.51	0.816	0.0046
158.49	0.48	0.0027
87.22	0.24	0.0013

Table 7. *sec-Butyl phenylcarbamate*

Peak area (×10⁶ mV·s)	***Concentration (mg/mL)***	***Concentration (mol/L)***
899.80	3.77	0.0196
645.15	2.84	0.0147
466.90	1.89	0.0098
218.77	0.97	0.0051

Table 8. *Pentyl phenylcarbamate*

Peak area (×10⁶ mV·s)	***Concentration (mg/mL)***	***Concentration (mol/L)***
432.11	2	0.0097
329.38	1.5	0.0072

240.05	1	0.0048
147.68	0.5	0.0024
75.78	0.2	0.0010

Table 9. *Methyl N-(4-chlorophenyl)carbamate*

Peak area (×10⁶ mV·s)	***Concentration (mg/mL)***	***Concentration (mol/L)***
198.83	0.1	0.0005
453.03	0.25	0.0013
815.19	0.5	0.0027
1113.04	0.75	0.0040

Table 10. *Methyl N-[4-(trifluoromethyl)phenyl]carbamate*

Peak area (×10⁶ mV·s)	***Concentration (mg/mL)***	***Concentration (mol/L)***
147.19	0.02	9.13E-05
540.31	0.1	0.0005
1073.78	0.25	0.0011
1893.56	0.5	0.0023

Table 11. *Methyl N-(4-methoxyphenyl)carbamate*

Peak area (×10⁶ mV·s)	***Concentration (mg/mL)***	***Concentration (mol/L)***
159.83	0.1	0.00055
366.89	0.25	0.0013

678.25	0.5	0.0028
1002.62	0.8	0.0044

Table 12. *Methyl N-(3-chlorophenyl)carbamate*

Peak area (×10⁶ mV·s)	***Concentration (mg/mL)***	***Concentration (mol/L)***
36.81	0.1	0.0005
82.84	0.25	0.0012
128.70	0.4	0.0019
154.24	0.5	0.0023

Table 13. *Ethyl N-(4-chlorophenyl)carbamate*

Peak area (×10⁶ mV·s)	***Concentration (mg/mL)***	***Concentration (mol/L)***
99.45	0.1	0.0005
225.57	0.25	0.0013
411.09	0.5	0.0025
560.92	0.75	0.0038
749.79	1	0.0050

Table 14. *Ethyl N-[4-(trifluoromethyl)phenyl]carbamate*

Peak area (×10⁶ mV·s)	***Concentration (mg/mL)***	***Concentration (mol/L)***
176.6307	0.1	0.0004
408.4926	0.25	0.0011

724.2213	0.5	0.0021
1070.273	0.75	0.0032

Table 15. *Ethyl N-(4-methoxyphenyl)carbamate*

Peak area (×10⁶ mV·s)	***Concentration (mg/mL)***	***Concentration (mol/L)***
120.50	0.1	0.0005
285.21	0.25	0.0013
518.99	0.5	0.0026
751.75	0.75	0.0038
1026.57	1	0.0051

Table 16. *Isopropyl N-(4-chlorophenyl)carbamate*

Peak area (×10⁶ mV·s)	***Concentration (mg/mL)***	***Concentration (mol/L)***
182.53	0.1	0.0005
414.38	0.25	0.0012
542.89	0.35	0.0016
727.28	0.5	0.0023
893.27	0.65	0.0030

Table 17. *Isopropyl N-[4-(trifluoromethyl)phenyl]carbamate*

Peak area (×10⁶ mV·s)	***Concentration (mg/mL)***	***Concentration (mol/L)***
79.24	0.05	0.0002

188.65	0.1	0.0004
432.27	0.25	0.0010
800.35	0.5	0.0020

Table 18. *Isopropyl N-(4-methoxyphenyl)carbamate*

Peak area (×10⁶ mV·s)	***Concentration (mg/mL)***	***Concentration (mol/L)***
127.73	0.1	0.0005
308.11	0.25	0.0012
566.76	0.5	0.0024
792.84	0.75	0.0036
1016.80	1	0.0048

Table 19. *Isopropyl N-(3-chlorophenyl)carbamate*

Peak area (×10⁶ mV·s)	***Concentration (mg/mL)***	***Concentration (mol/L)***
36.81	0.1	0.0005
82.84	0.25	0.0012
128.7	0.4	0.0019
154.24	0.5	0.0023
36.81	0.1	0.0005

1.3 Determination of O-Alkyl-N-aryl Carbamate Concentrations in Transesterification Reaction Mixtures

Samples of the reaction mixture taken from the reactor were diluted with DMF to achieve a concentration of 1 mg/mL of O-alkyl-N-aryl carbamates. followed by the addition of acetic acid to adjust the pH to a mildly acidic range.

The quantification was performed using a calibration coefficient:

$C=K \cdot S$

where:

- ***C*** is the concentration of the O-alkyl-N-aryl carbamate in the reaction mixture (mol/L);
- ***K*** is the calibration coefficient (mol·s/L·mV);
- ***S*** is the chromatographic peak area of O-alkyl-N-aryl carbamate (mV·s).

2. High-Pressure Kinetic Cell for Transesterification Studies

Figure 2 illustrates the high-pressure kinetic cell used for studying the transesterification of O-methyl-N-aryl carbamate

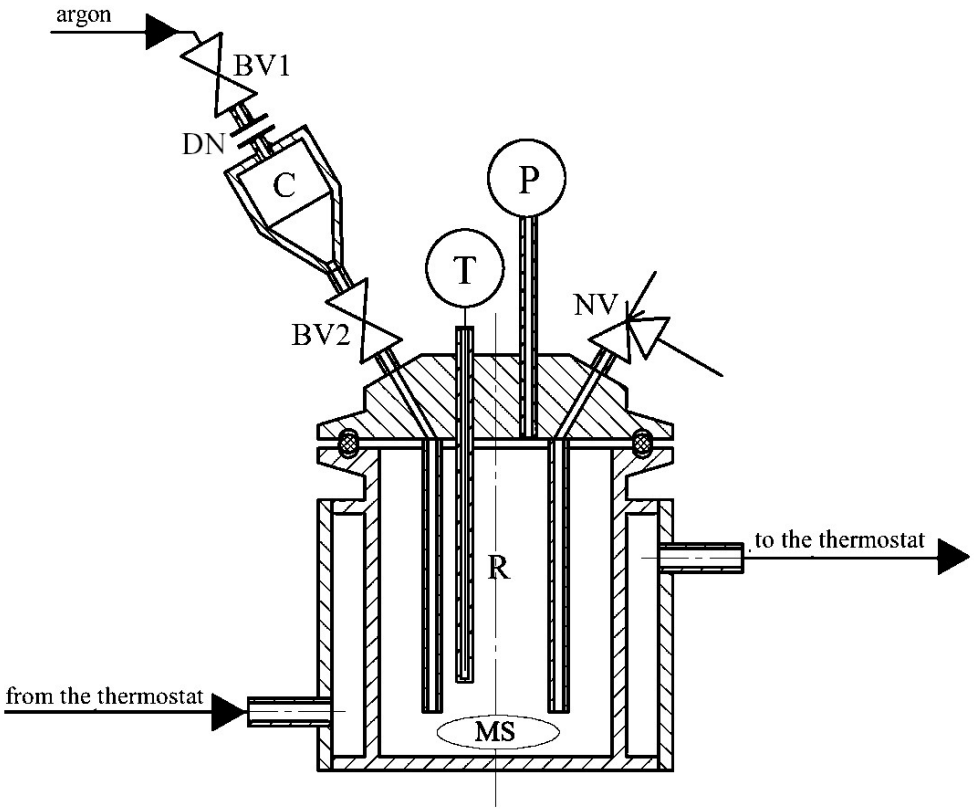

Figure 2. High-pressure kinetic cell: R – reactor with a jacket. C – reagent reservoir. BV1/BV2 – ball valves. NV – needle valve. DN – detachable fitting. MS – magnetic stirrer. T – thermocouple. P – pressure sensor.

Experimental Procedure:

1. Weighed portions of metallic sodium and alcohol were placed into a kinetic cell previously purged with argon and tightly sealed. During this step. valves BV2 and NV were closed. and the DN connector was detached.

2. A solution of O-methyl-N-aryl carbamate in alcohol was introduced into vessel C through the DN connector. The connector was then attached to the argon supply line. Valve BV1 remained closed.
3. The resulting solution of sodium alkoxide in alcohol was thermostated using a high-temperature heat-transfer fluid circulating in the jacket of the kinetic cell between the thermostat and the cell.
4. Valve BV1 was opened to create an overpressure of argon in vessel C1. exceeding the pressure in reactor R by 1–2 atm.
5. Valve BV1 was closed. followed by opening BV2. Due to the pressure differential between vessel C and reactor R. the solution of O-methyl-N-aryl carbamate in alcohol was transferred into the thermostated sodium alkoxide solution. The addition moment was considered the reaction start time. After 30 seconds. BV2 was closed.
6. At fixed time intervals. the needle valve was opened to drain the dead volume. and analytical samples were collected.
7. The concentrations of the starting O-methyl-N-aryl carbamate and the resulting O-alkyl-N-aryl carbamates were determined by HPLC using an external standard method. as described in the referenced section.

3. Kinetic Constants for Transesterification of N-Phenyl-O-methylcarbamate with Various Alcohols

Table 3.1. Rate Constants ($k \times 10^3$ $M^{-1}s^{-1}$) for Transesterification of N-Phenyl-O-methylcarbamate with Different Alcohols

Temperature (K)	EtOH	PrOH	i-PrOH	BuOH	s-BuOH	PeOH
333	1.01 ± 0.03	1.29 ± 0.04	2.16 ± 0.10	1.65 ± 0.07	3.89 ± 0.14	2.65 ± 0.17
343	1.98 ± 0.05	3.23 ± 0.12	5.33 ± 0.18	3.90 ± 0.12	9.40 ± 0.21	5.84 ± 0.19
353	4.59 ± 0.17	6.15 ± 0.18	12.3 ± 0.30	7.70 ± 0.25	22.4 ± 0.15	12.2 ± 0.12
363	7.65 ± 0.11	12.8 ± 0.22	24.8 ± 0.58	17.6 ± 0.28	56.5 ± 0.18	31.4 ± 0.41

Table 3.2. Rate Constants for Transesterification of Substituted N-Phenyl-O-methylcarbamates with Ethanol

Temperature (K)	*p*-MeO ($k \times 10^4$)	H ($k \times 10^3$)	*p*-Cl ($k \times 10^3$)	*p*-CF_3 ($k \times 10^2$)
323	-	-	-	5.15 ± 0.14
333	-	1.01 ± 0.03	2.69 ± 0.07	9.34 ± 0.20

Temperature (K)	*p*-MeO (k×10^4)	H (k×10^3)	*p*-Cl (k×10^3)	*p*-CF_3 (k×10^2)
343	7.56 ± 0.41	1.98 ± 0.05	4.98 ± 0.07	15.3 ± 0.18
353	16.7 ± 0.23	4.59 ± 0.17	8.87 ± 0.16	27.6 ± 0.49
363	31.2 ± 0.65	7.65 ± 0.11	15.4 ± 0.40	-
373	63.3 ± 1.71	-	-	-

Table 3.3. Rate Constants for Transesterification of Substituted N-Phenyl-O-methylcarbamates with Isopropanol

Temperature (K)	*p*-MeO (k×10^3)	H (k×10^3)	*p*-Cl (k×10^3)	*m*-Cl (k×10^3)	*p*-CF_3 (k×10^2)
333	-	2.16 ± 0.10	3.95 ± 0.09	6.08 ± 0.09	1.05 ± 0.01
334	1.14 ± 0.05	-	-	-	-
343	-	5.33 ± 0.18	8.04 ± 0.22	13.0 ± 0.16	1.81 ± 0.04
345	4.33 ± 0.13	-	-	-	-
353	-	12.3 ± 0.30	13.6 ± 0.44	25.3 ± 0.41	3.39 ± 0.04
354	9.86 ± 0.24	-	-	-	-
363	-	24.8 ± 0.58	27.0 ± 0.41	49.5 ± 0.96	5.92 ± 0.08
365	19.2 ± 0.15	-	-	-	-

4. NMR Spectra

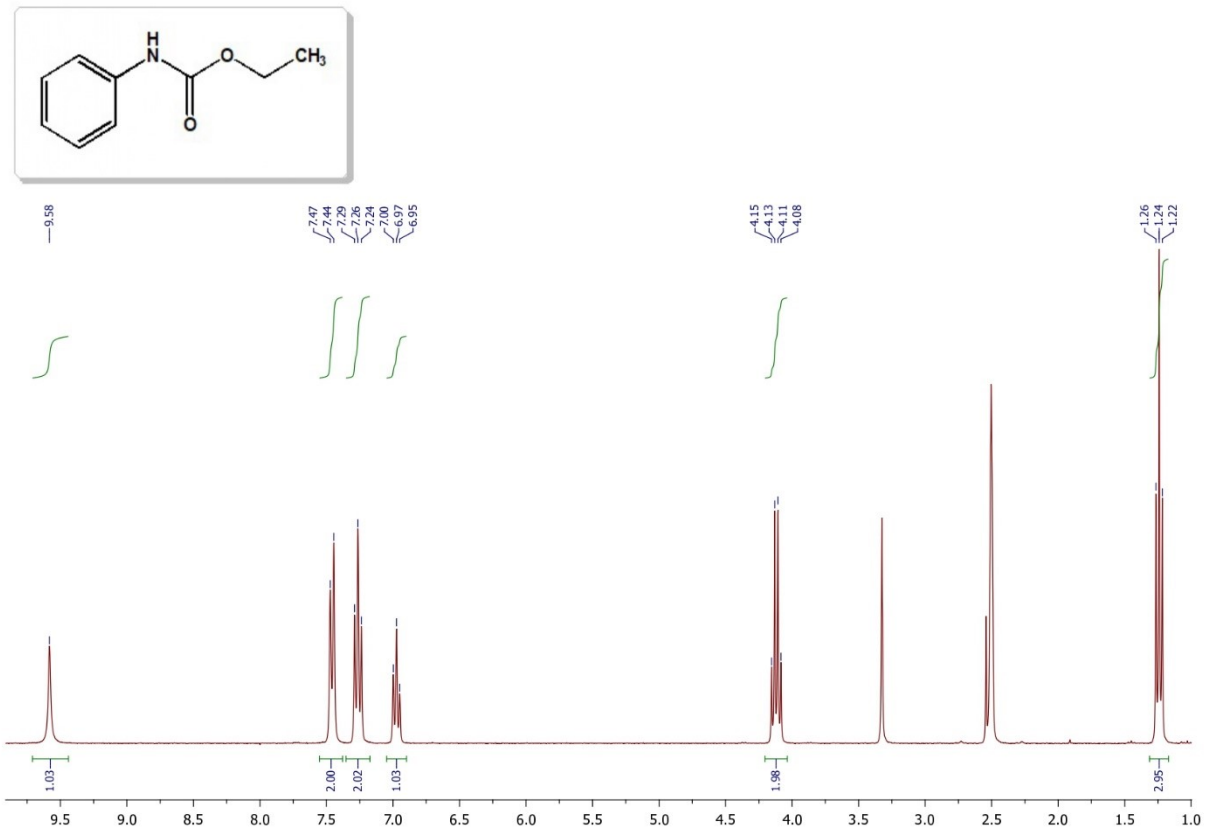

Fig. 3.1. ^{1}H NMR spectrum of Ethyl phenylcarbamate

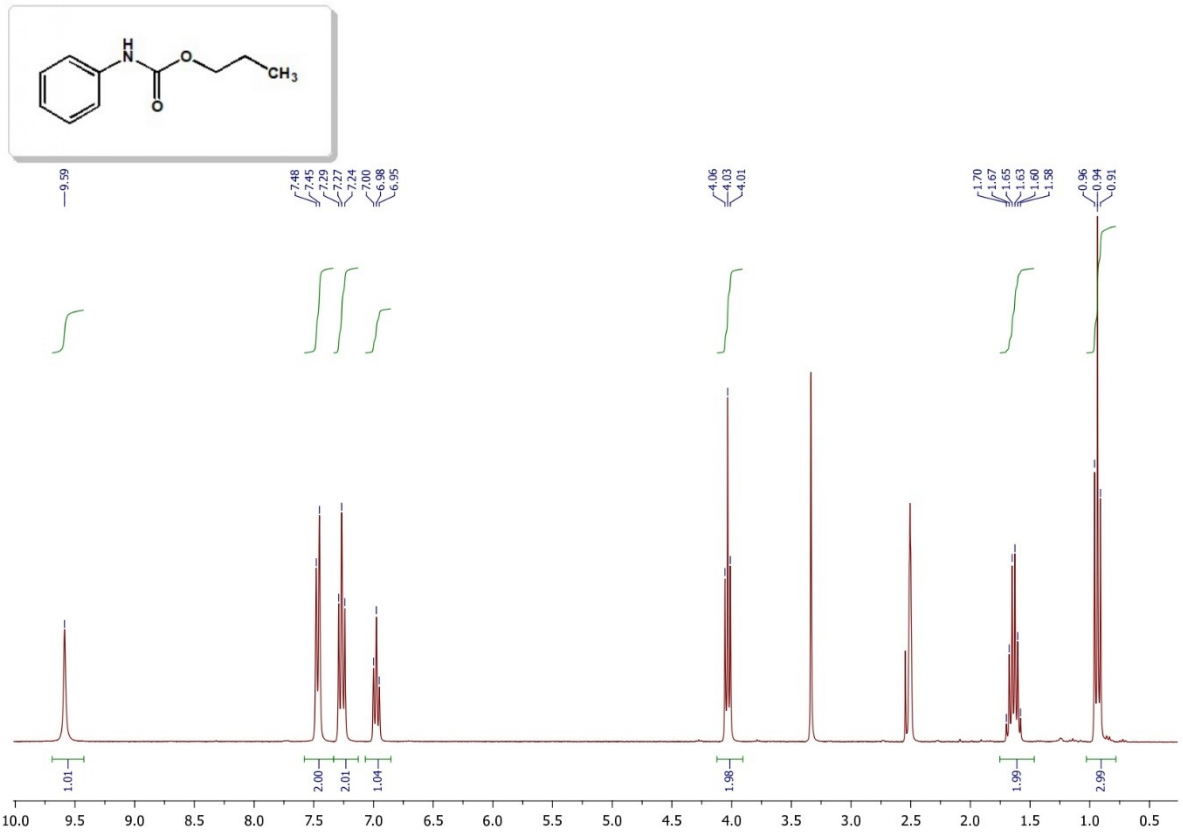

Fig. 3.2. ^{1}H NMR spectrum of n-propyl phenylcarbamate

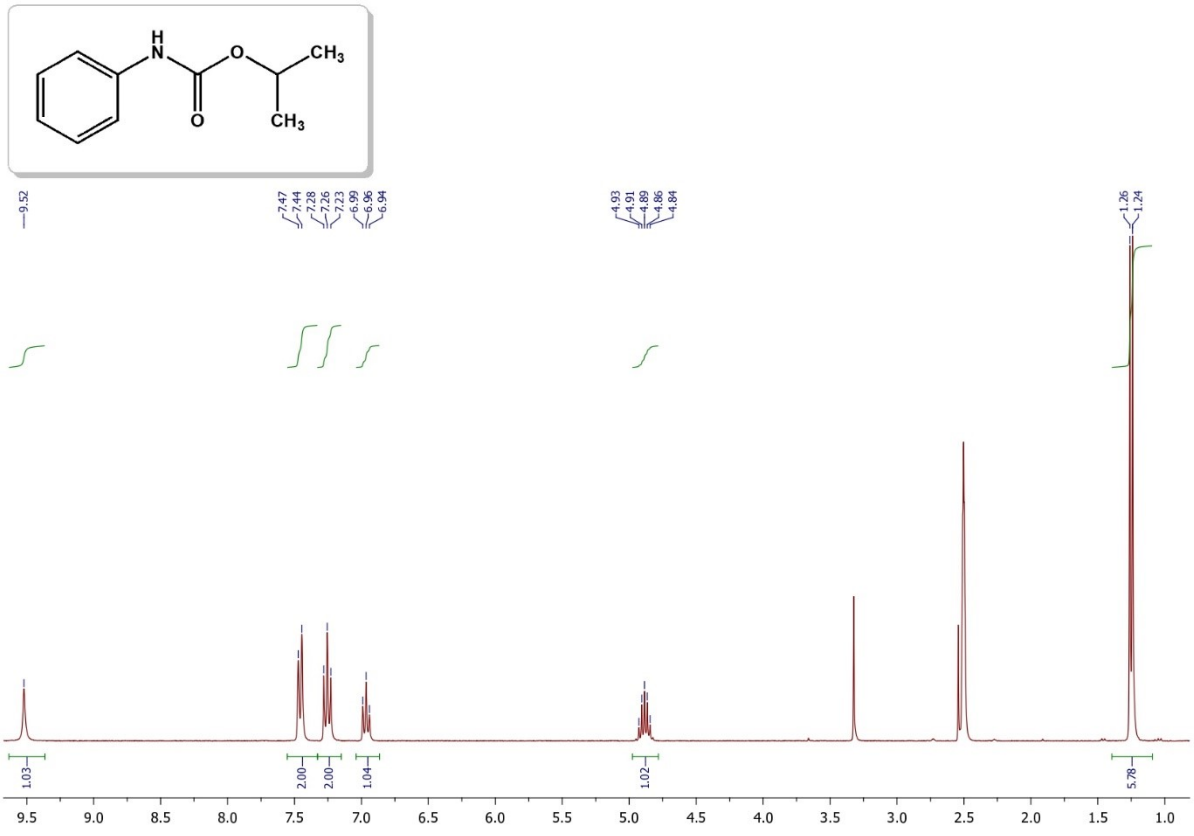

Fig. 3.3. ^{1}H NMR spectrum of isopropyl phenylcarbamate

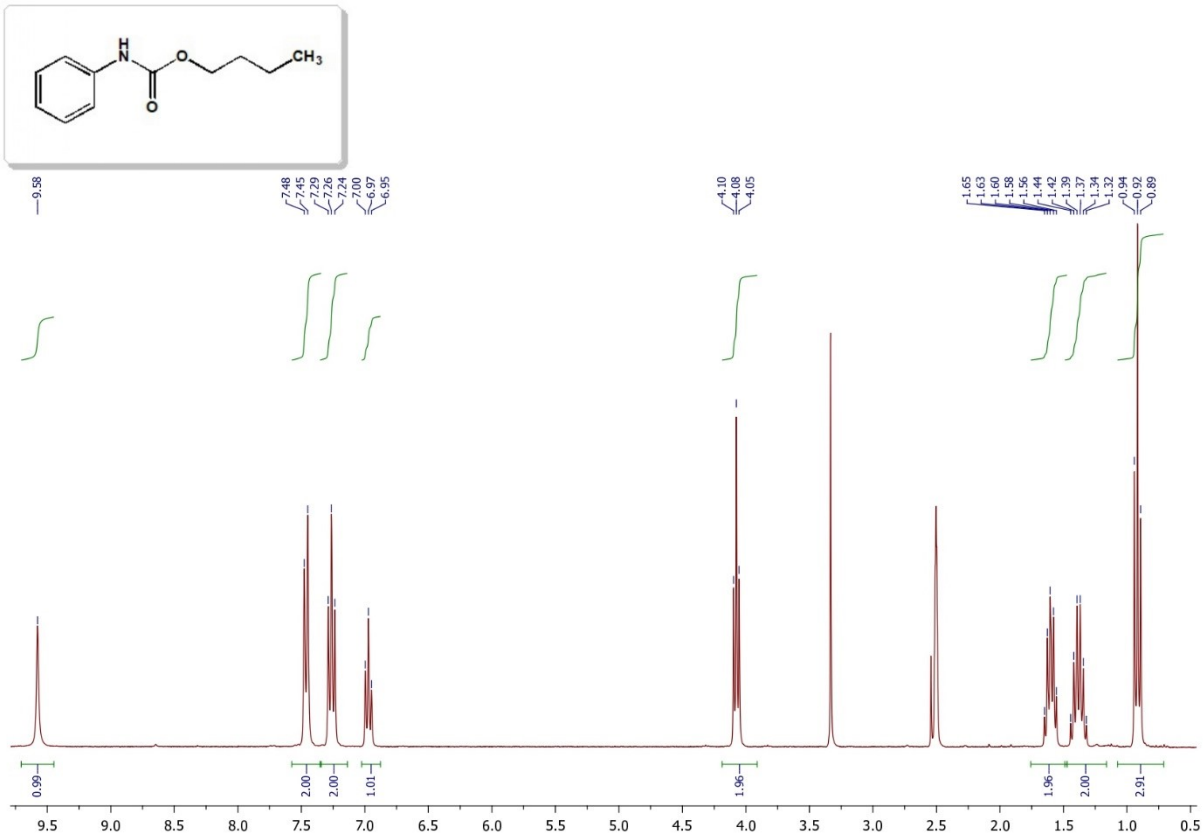

Fig. 3.4. ^{1}H NMR spectrum of n-butyl phenylcarbamate

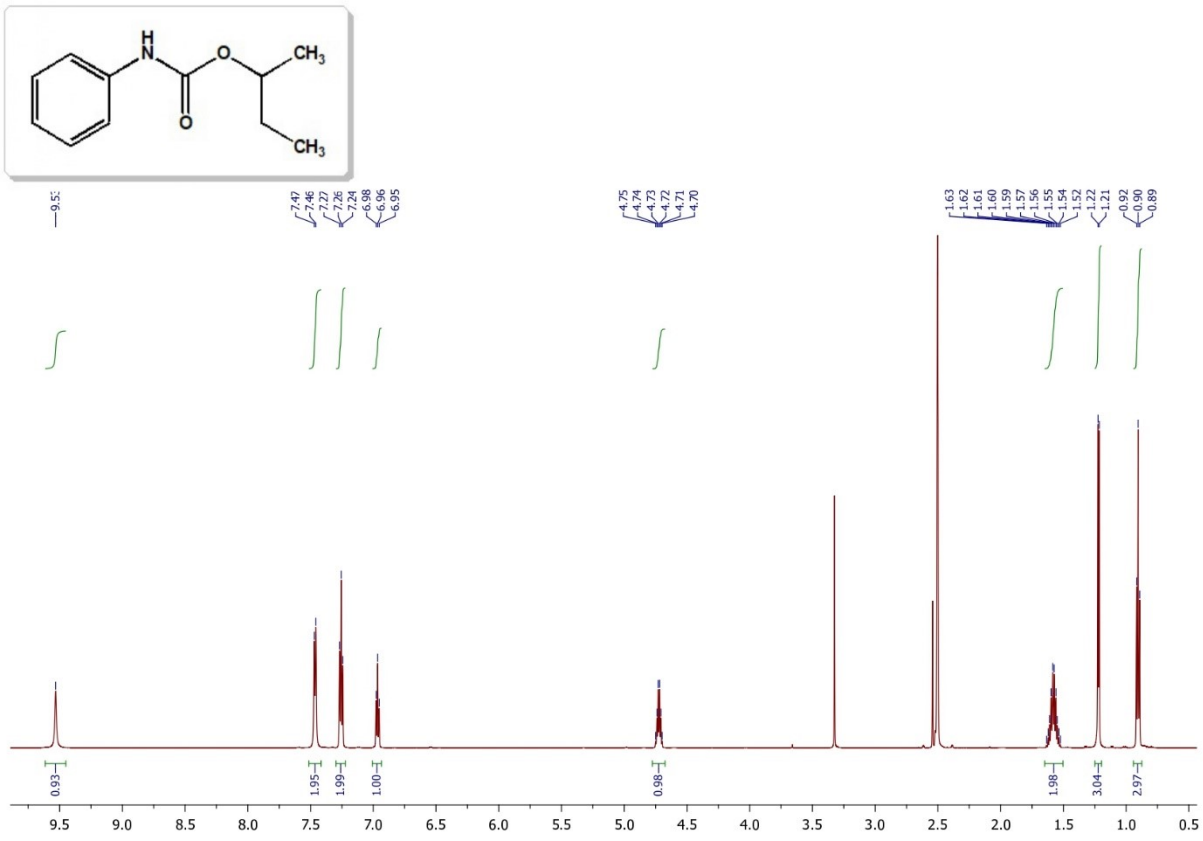

Fig. 3.5. ^{1}H NMR spectrum of sec-Butyl-N-phenylcarbamate

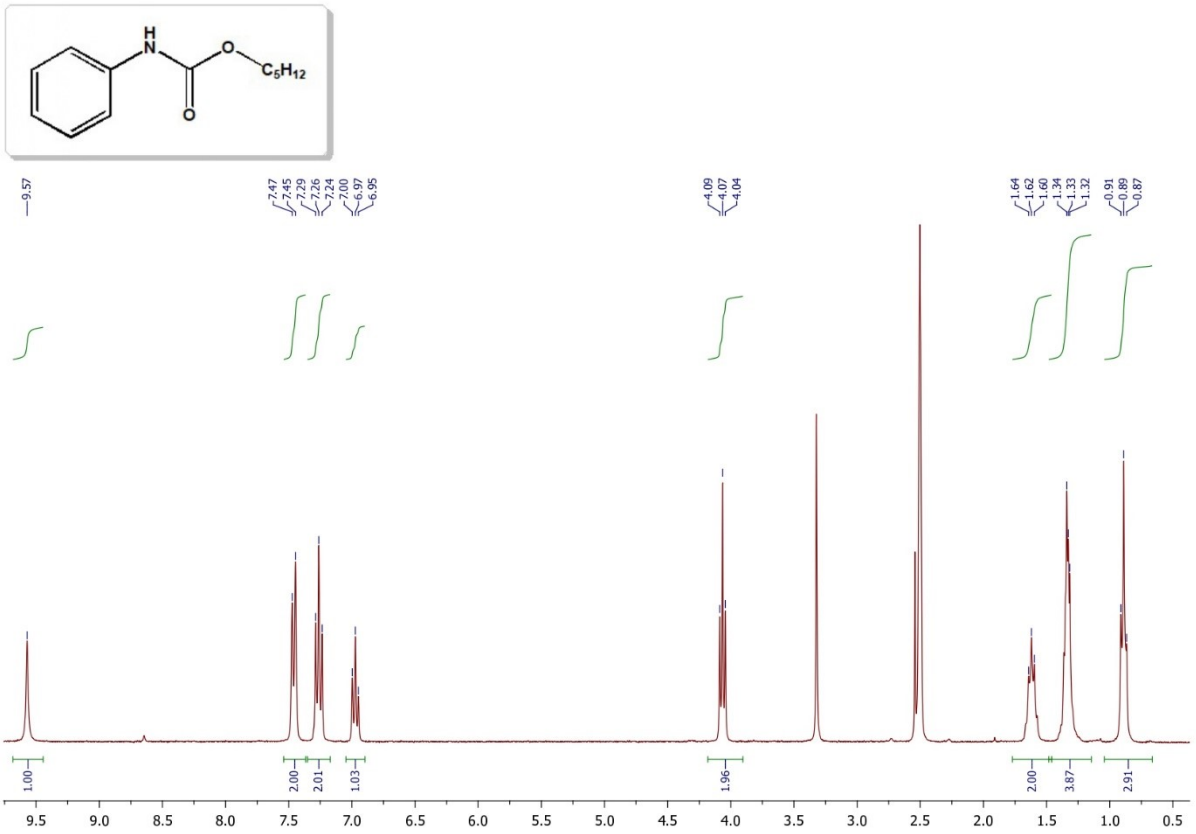

Fig. 3.6. ^{1}H NMR spectrum of Pentyl-N-phenylcarbamate

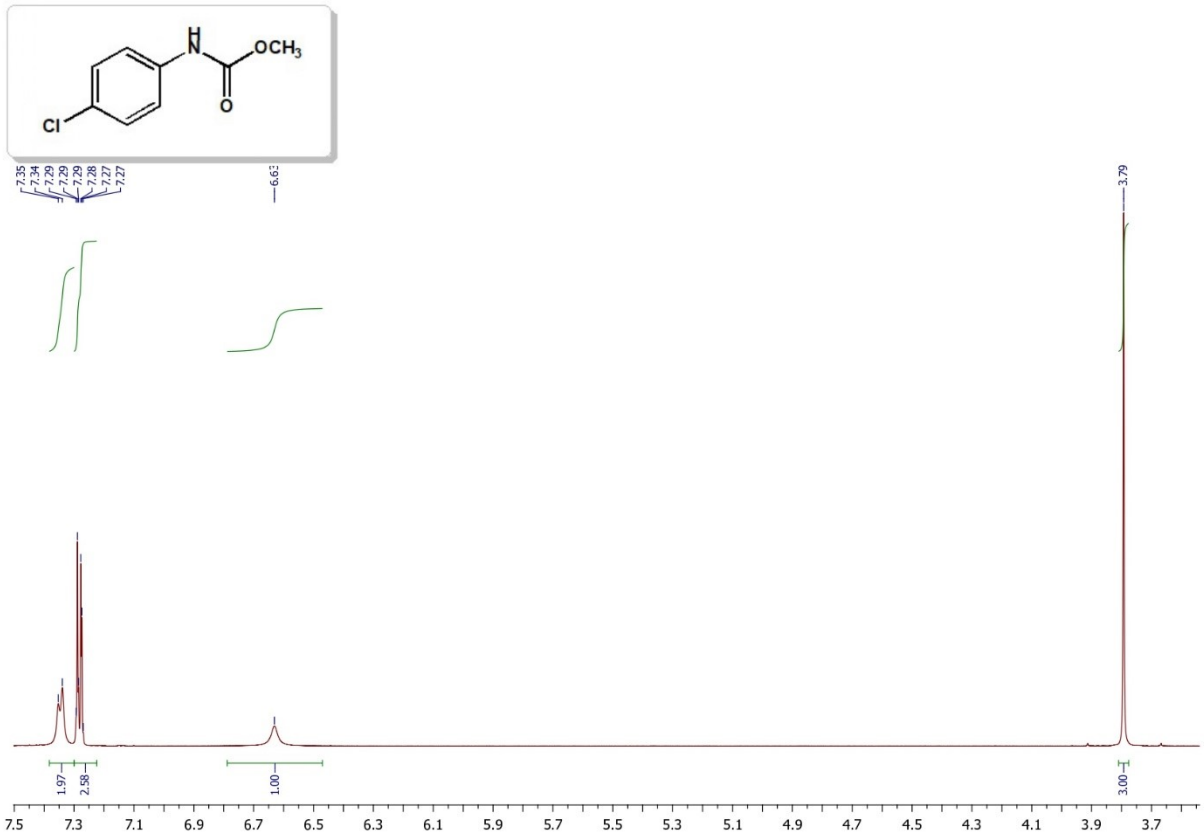

Fig. 3.7. ^{1}H NMR spectrum of Methyl N-(4-chlorophenyl)carbamate

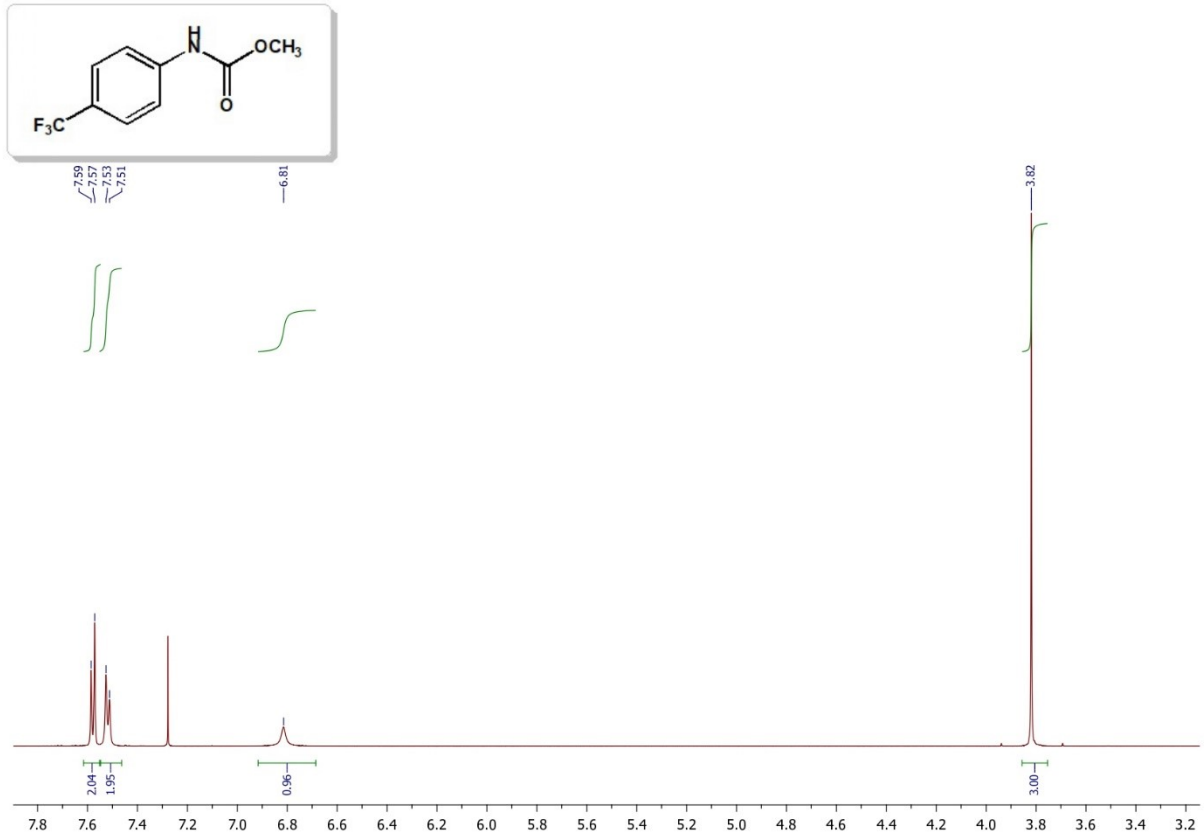

Fig. 3.8. ^{1}H NMR spectrum of Methyl N-[4-(trifluoromethyl)phenyl]carbamate

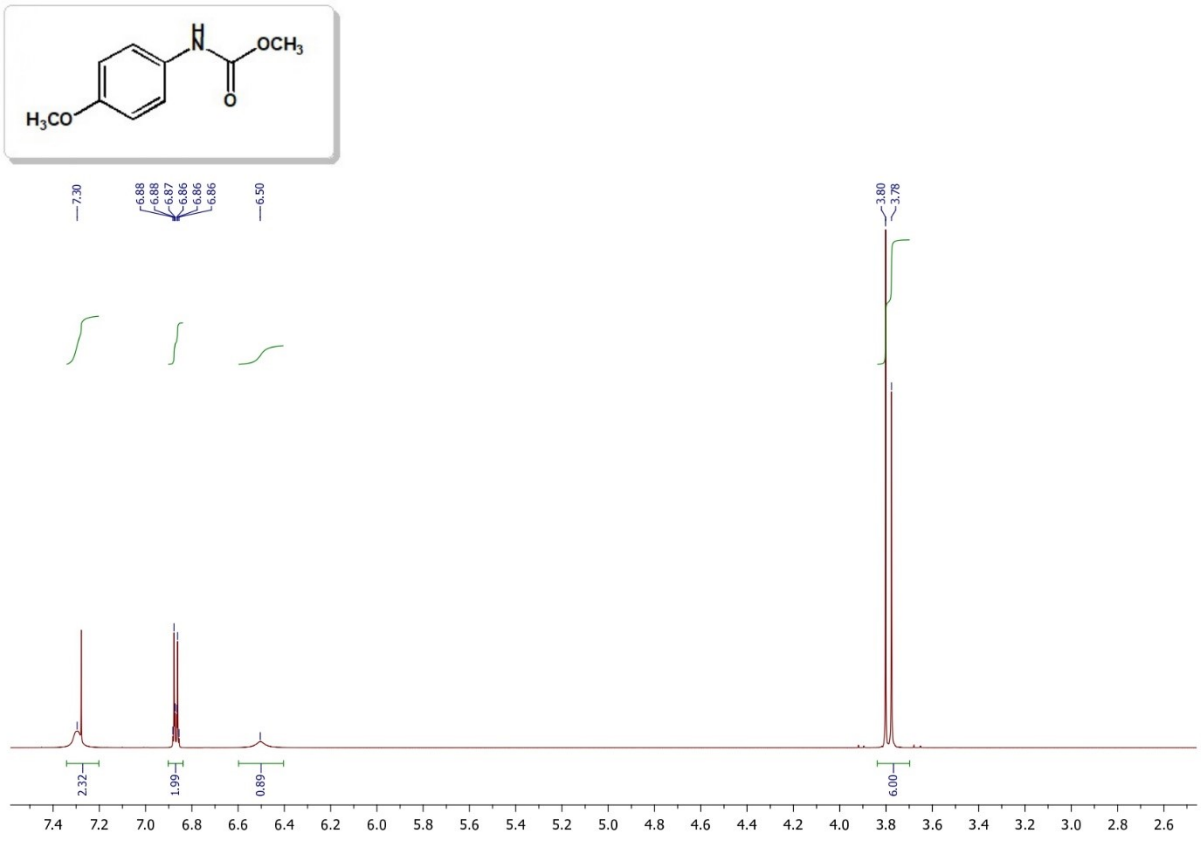

Fig. 3.9. ^{1}H NMR spectrum of Methyl N-(4-methoxyphenyl)carbamate

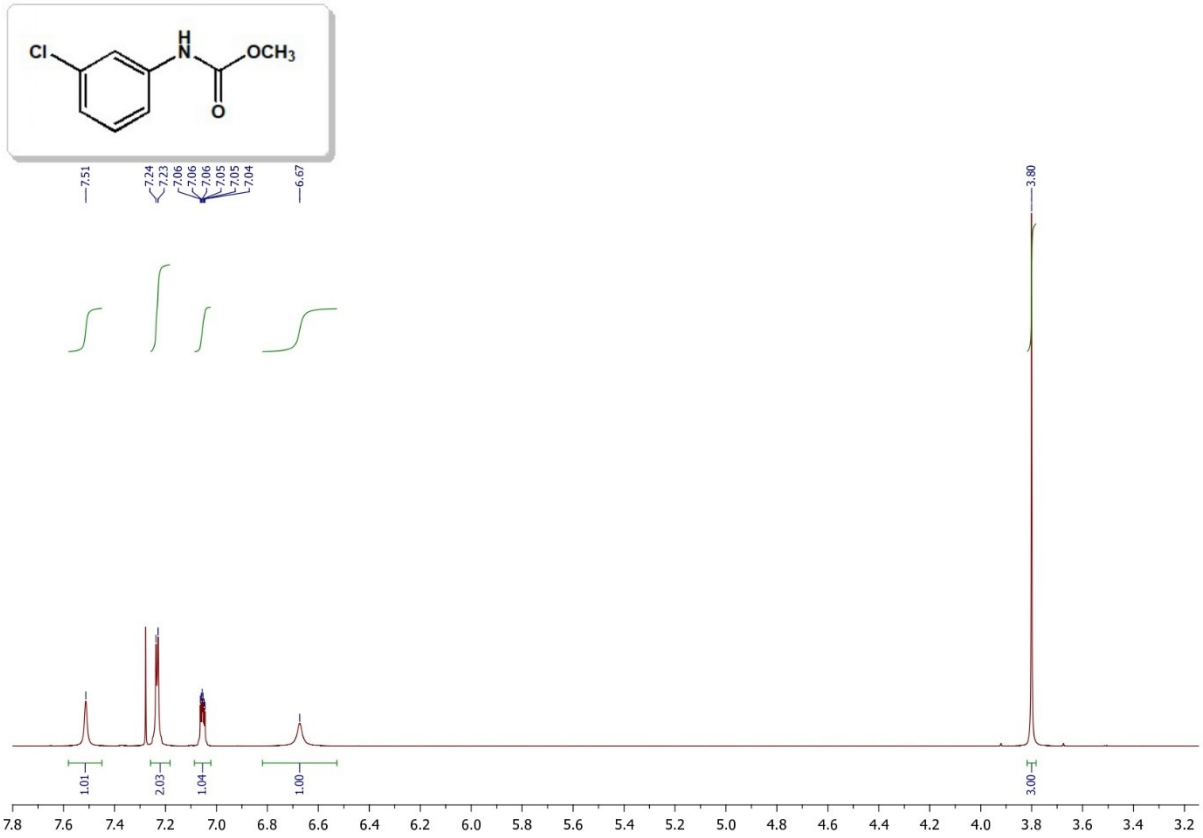

Fig. 3.10. ^{1}H NMR spectrum of Methyl N-(3-chlorophenyl)carbamate

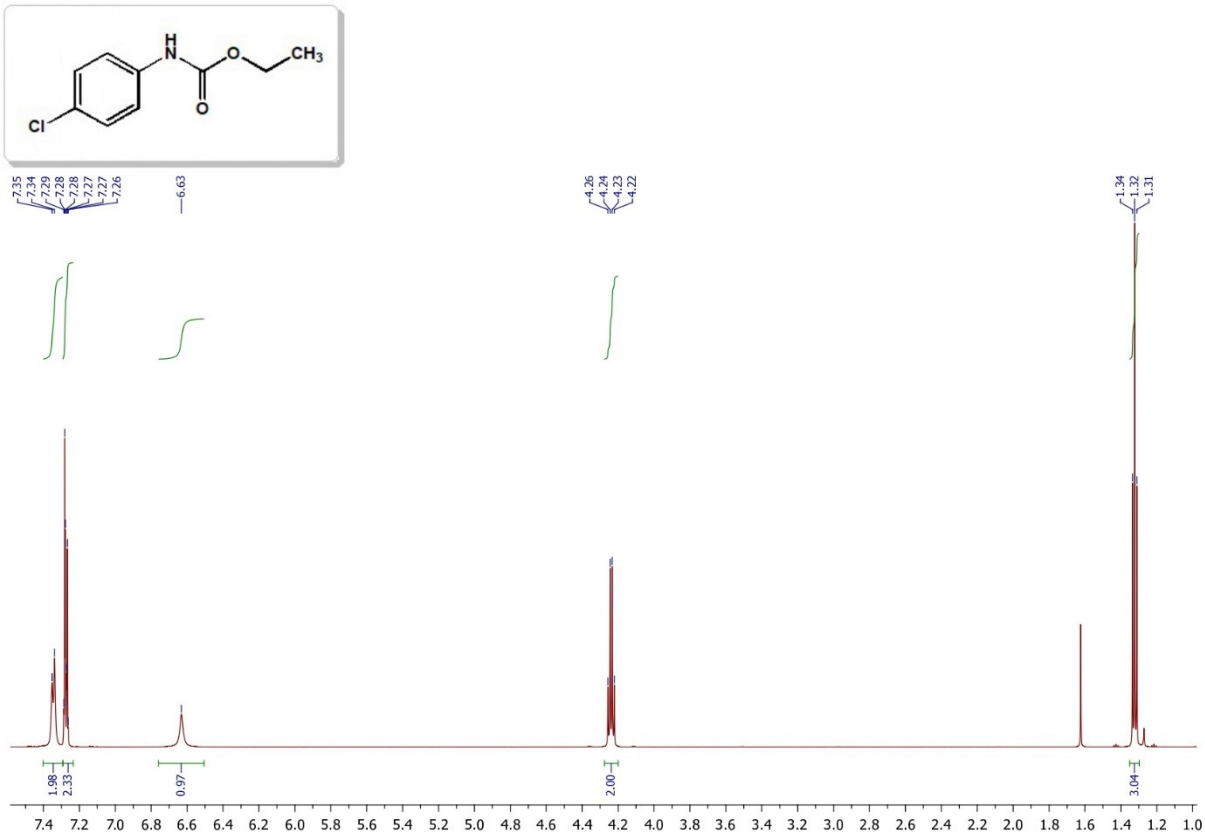

Fig. 3.11. ^{1}H NMR spectrum of Ethyl N-(4-chlorophenyl)carbamate

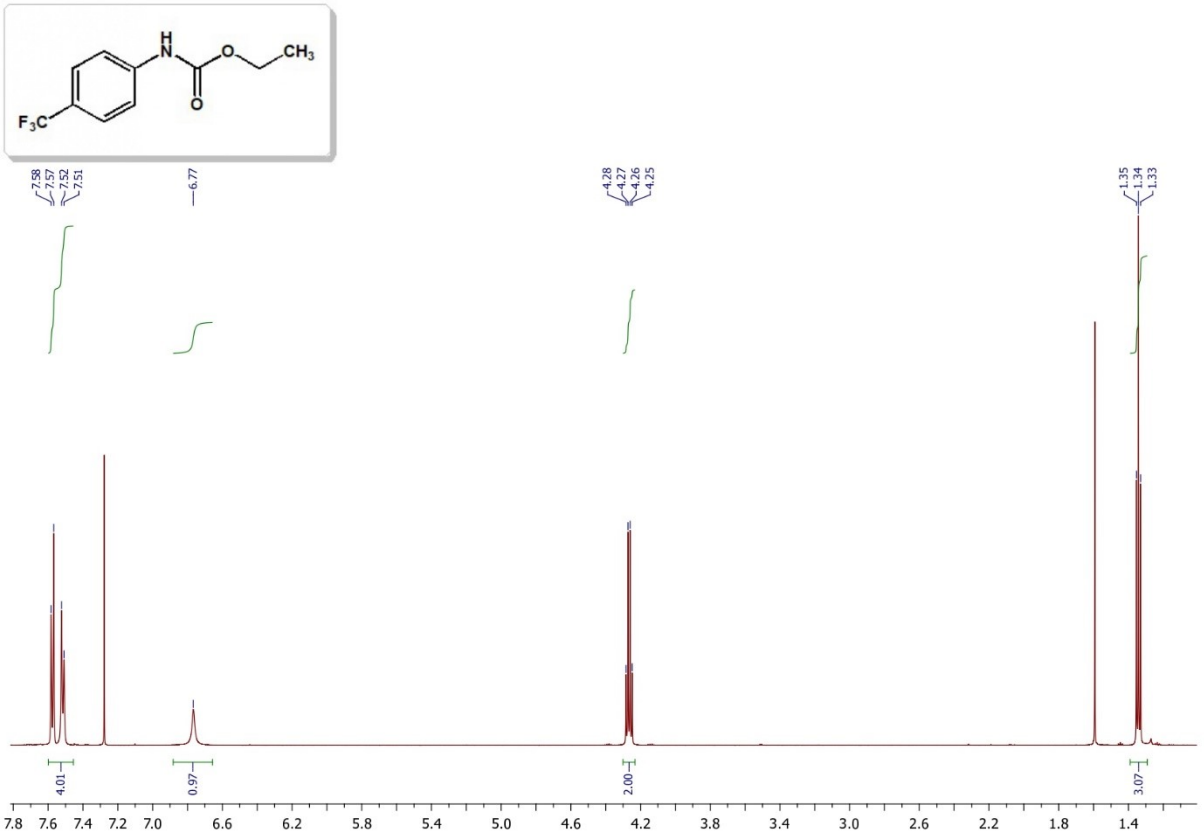

Fig. 3.12. ^{1}H NMR spectrum of Ethyl N-[4-(trifluoromethyl)phenyl]carbamate

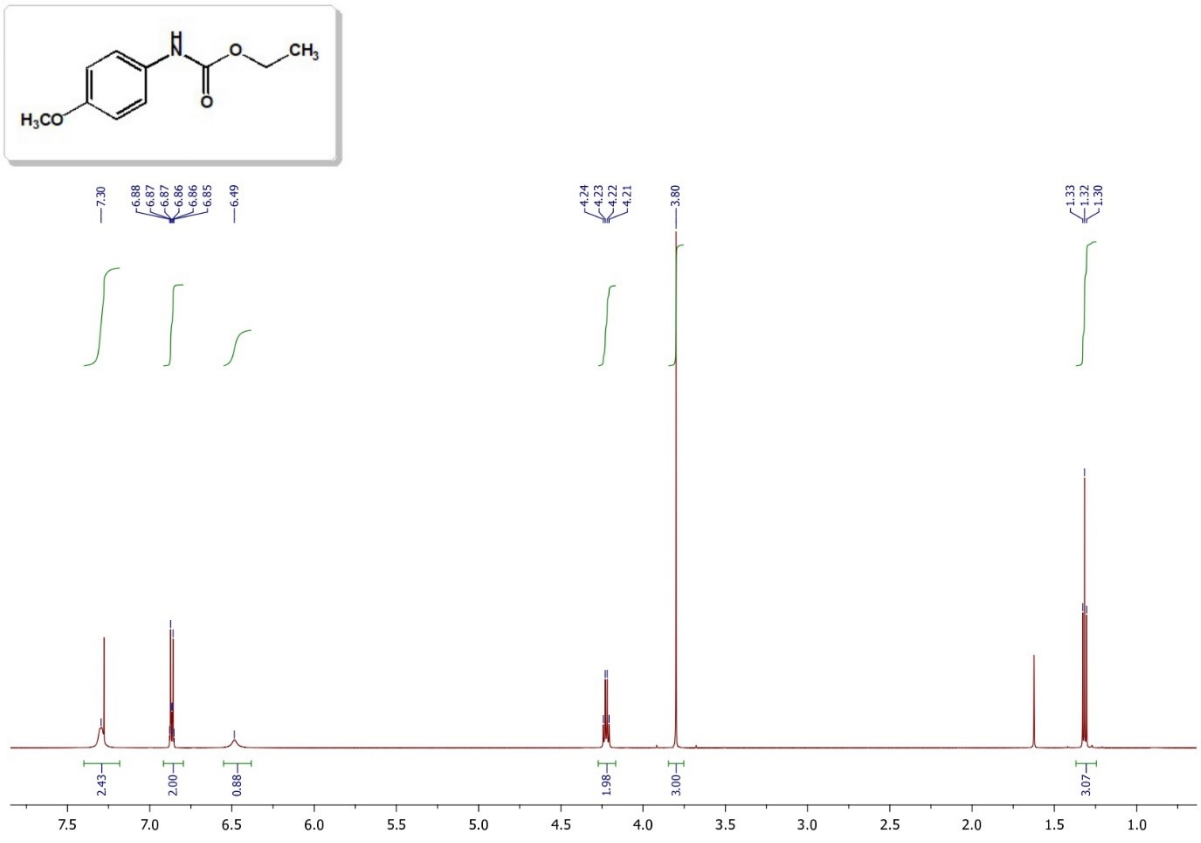

Fig. 3.13. ^{1}H NMR spectrum of Ethyl N-(4-methoxyphenyl)carbamate

Fig. 3.14. ^{1}H NMR spectrum of Isopropyl N-(4-chlorophenyl)carbamate

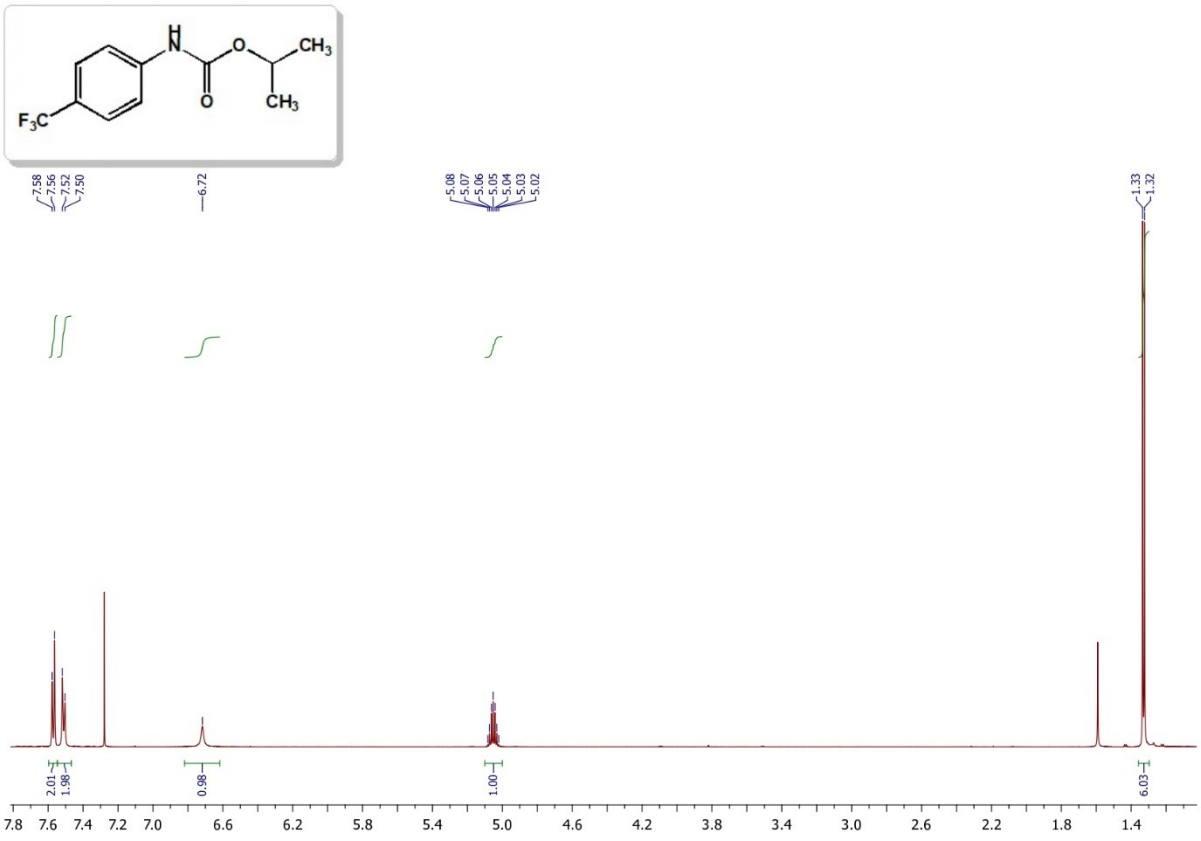

Fig. 3.15. ^{1}H NMR spectrum of Isopropyl N-[4-(trifluoromethyl)phenyl]carbamate

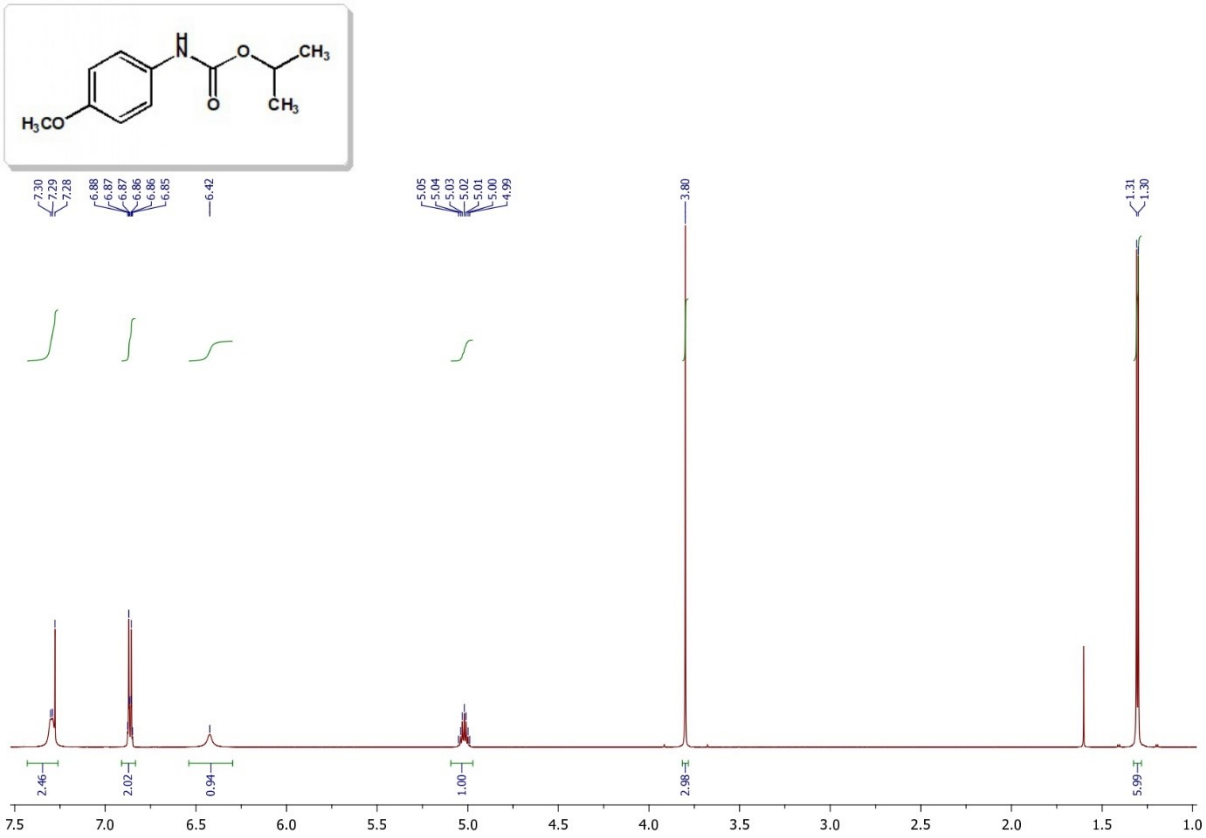

Fig. 3.16. ^{1}H NMR spectrum of Isopropyl N-(4-methoxyphenyl)carbamate

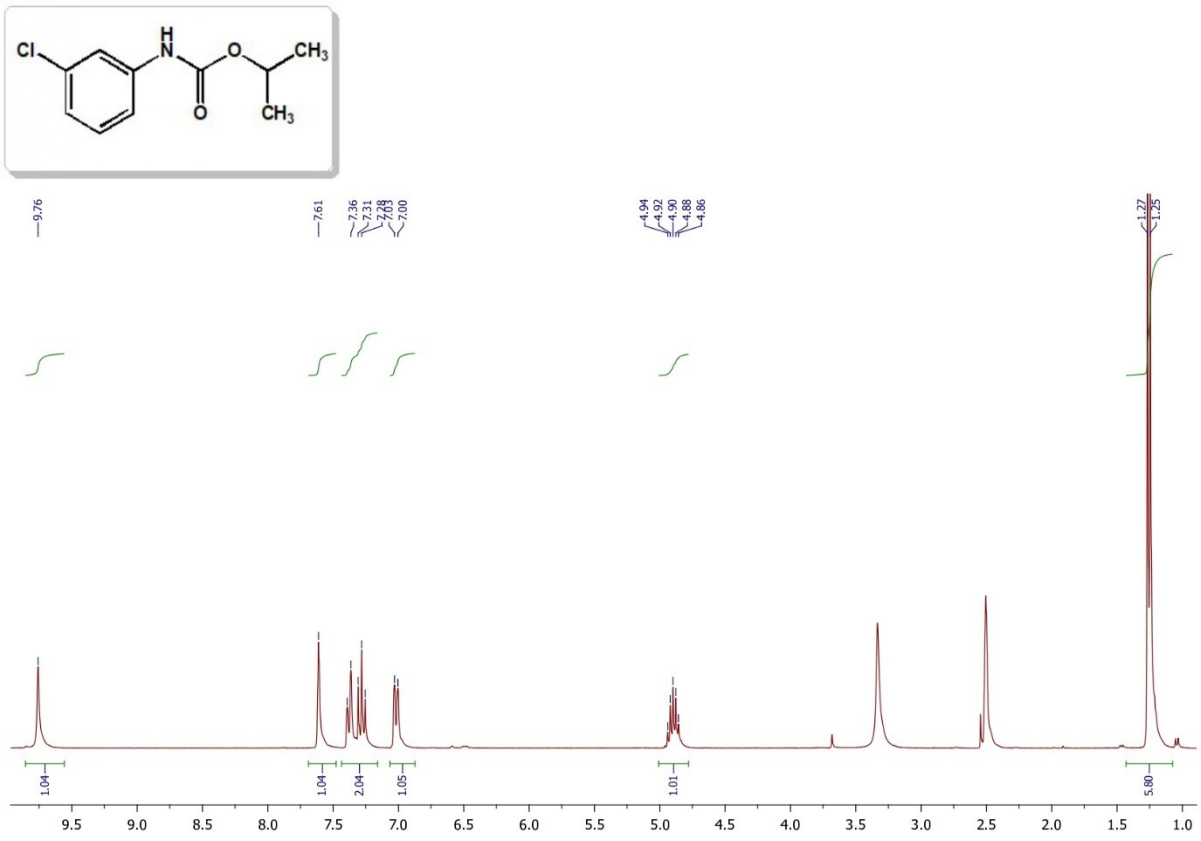

Fig. 3.17. ^{1}H NMR spectrum of Isopropyl N-(3-chlorophenyl)carbamate