

CHAPTER III

EXPERIMENTS

Instruments

1. Infrared Spectrophotometer:

Perkin-Elmer model FT-IR 1760 X.

Perkin-Elmer model FT-IR 16 PC.

Perkin-Elmer model 283

2. Nuclear Magnetic Resonance Spectrometer:

Jeol JNM-A500 (500MHz)

3. Mass Spectrophotometer:

Kratos model Profile.

Varian Star 3400 CX. /Varian Saturn GC/MS/MS 4D.

4. Melting Point Apparatus:

Buchi capillary melting apparatus.

5. CHNS/O Analyser:

Perkin Elmer PE 2400 Series II

Chemicals

Acetone (Merck)

4-Aminopyridine (Nacalia tesque)

Aniline (Merck)

Dioxane (Merck)

Ethanol, Absolute (Merck)

30% Hydrogen peroxide solution

4-Nitroaniline (Fluka)

Potassium cyanate (Wako Pure Chemical Industries)

Potassium thiocyanate (Merck)

2-Propylpentanoic acid (Sigma)

Sodium hydroxide

Sodium sulfate, anhydrous (Merck)

Stannic chloride (Merck)

Thionyl chloride (Laboratory grade)

2-Toluidine (Merck)

4-Toluidine (Merck)

All Solvents used were either B.P. or laboratory grade.

2-Propylpentanoyl chloride

A 6.50 g (0.045 mole) of 2-propylpentanoic acid was dropwisely added to 5.85 g (3.60 ml, 0.050 mole) of thionyl chloride, then the mixture was stirred at room temperature overnight. The excess thionyl

chloride was removed in vacuo to yield crude 2-propylpentanoyl chloride which was not further purified and had been stored in closed bottle.

N-(2-Propylpentanoyl)-N'-phenylthiourea

A 2.90 g (0.018 mole) of 2-propylpentanoyl chloride was dropwisely added into a solution of 1.95 g (0.020 mole) of potassium thiocyanate in dry acetone. After completion of the addition, the mixture was refluxed for 10 minutes. Then, a solution of 1.67 g (0.018 mole) of aniline in dry acetone was added at such a rate that the solution could be refluxed gently. After refluxed for 1 hour, the mixture was evaporated by rotatory evaporator. The residue was washed with adequate water, and filtered through the filtering paper. Recrystallization from hexane gave 3.47 g (69.3 % yield) of pale yellow needles of N-(2-propylpentanoyl)-N'-phenylthiourea, melting point 110.0-111.0°C.

IR :	3200	cm ⁻¹	v N-H	thioimide
(KBr)	3040 - 3000	cm ⁻¹	v C-H	aromatic
	2960 - 2870	cm ⁻¹	v C-H	aliphatic
	1690	cm ⁻¹	v C=O	amide
	1600	cm ⁻¹	v C=C	aromatic
	1535	cm ⁻¹	δ N-H	amide
	1315	cm ⁻¹	v C=S	thiourea
	1240	cm ⁻¹	v C-N	amide
	740	cm ⁻¹	δ C-H	out-of -plane

(Figure 11)

¹ H-NMR	0.93 ppm	(6H, t, $J = 7.3$ Hz, CH_3-CH_2-)
(CDCl ₃)	1.36 ppm	(4H, m, $CH_3-CH_2-CH_2-$)
	1.48 ppm	(2H, m, $CH_3-CH_2-CH_2-$)
	1.66 ppm	(2H, m, $CH_3-CH_2-CH_2-$)
	2.30 ppm	(1H, m, $-CH-$)
	7.26 ppm	(1H, t, $J = 7.6$ Hz, aromatic)
	7.40 ppm	(2H, t, $J = 7.9$ Hz, aromatic)
	7.67 ppm	(2H, d, $J = 8.2$ Hz, aromatic)
	8.96 ppm	(1H, br s, $-NH-CS-NH-$)
	12.54 ppm	(1H, br s, $-CO-NH-CS-$)

(Figures 12-13)

¹³ C-NMR :	14.00 ppm	(2C : C-5', C-3'')
(CDCl ₃)	20.60 ppm	(2C : C-4', C-2'')
	34.66 ppm	(2C : C-3', C-1'')
	43.28 ppm	(1C : C-2')
	124.00 ppm	(2C : C-2''', C-6''')
	126.80 ppm	(1C : C-4''')
	128.80 ppm	(2C : C-3''', C-5''')
	137.48 ppm	(1C : C-1''')
	177.73, 178.22 ppm	(2C : C-2, C-1')

(Figure 14)

EIMS (% relative intensity) : 278 (M^+ , 16), 249 (16), 236 (15), 194 (5),
 153 (46), 135 (35), 93 (41), 77 (28), 57
 (100), 43 (43)
 (Figure 15)

CHN analysis for $C_{15}H_{22}N_2O_1S_1$ % Calcd ; C : 64.75, H : 7.91, N : 10.07
 % Found ; C : 64.75, H : 7.88, N : 9.92

N-(2-Propylpentanoyl)-N'-phenylurea

Four ml of 10 % sodium hydroxide solution and 4 ml of 30 % hydrogen peroxide solution was slowly added to a chilled solution of 2.60 g N-(2-propylpentanoyl)-N'-phenylthiourea in acetone, respectively. The mixture was kept in an ice bath for 30 minutes, then another 4 ml portion of NaOH and H_2O_2 were again added. After left to stand for 30 minutes, acetone was distilled off by rotatory evaporator. The residue was added with 30 ml of water and extracted with 3×30 ml of ethylacetate. The organic fraction was dried over anhydrous sodium sulfate and then evaporated in vacuo. The product was crystallized from aqueous ethanol to afford 1.96 g (80.0 % yield) of white needles of N-(2-propylpentanoyl)-N'-phenylurea, melting point 81.0 - 82.0 °C.

IR :	3220	cm^{-1}	ν N-H	imide
(KBr)	3120	cm^{-1}	ν N-H	amide
	2960 - 2880	cm^{-1}	ν C-H	aliphatic
	1700	cm^{-1}	ν C=O	carbamoyl

1690	cm^{-1}	ν C=O	amide
1600	cm^{-1}	ν C=C	aromatic
1550	cm^{-1}	δ N-H	amide
1230	cm^{-1}	ν C-N	amide
750	cm^{-1}	δ C-H	out-of-plane

(Figure 16)

$^1\text{H-NMR}$	0.93 ppm	(6H, t, $J = 7.3$ Hz, $\text{CH}_3\text{-CH}_2\text{-}$)
(CDCl_3)	1.36 ppm	(4H, m, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$)
	1.50 ppm	(2H, m, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$)
	1.70 ppm	(2H, m, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$)
	2.42 ppm	(1H, m, -CH-)
	7.12 ppm	(1H, t, $J = 8.2$ Hz, aromatic)
	7.33 ppm	(2H, t, $J = 8.2$ Hz, aromatic)
	7.54 ppm	(2H, d, $J = 8.2$ Hz, aromatic)
	9.83 ppm	(1H, br s, -NH-CO-NH-)
	10.81 ppm	(1H, br s, -CO-NH-CO-)

(Figure 17-18)

$^{13}\text{C-NMR}$:	13.94 ppm	(2C : C-5', C-3'')
(CDCl_3)	20.60 ppm	(2C : C-4', C-2'')
	34.55 ppm	(2C : C-3', C-1'')
	47.42 ppm	(1C : C-2')
	120.17 ppm	(2C : C-2''', C-6''')
	124.23 ppm	(1C : C-4''')
	128.92 ppm	(2C : C-3''', C-5''')

137.23 ppm (1C : C-1''')

152.15 ppm (1C : C-2)

179.18 ppm (1C : C-1')

(Figure 19)

EIMS (% relative intensity) : 262 (M^+ , 48), 233 (9), 191 (4), 136 (5),
119 (100), 99 (9), 93 (86), 91 (11), 77
(13), 57 (66), 43 (19)
(figure 20)

CHN analysis of $C_{15}H_{22}N_2O_2$ % Calcd ; C : 68.70, H : 8.40, N : 10.69
% Found ; C : 68.94, H : 8.33, N : 10.57

N-(2-Propylpentanoyl)-N'-(4-methylphenyl)thiourea

A 4.25 g (0.026 mole) of 2-propylpentanoyl chloride was dropwisely added into a solution of 2.72 g (0.028 mole) potassium thiocyanate in dry acetone. After completion of the addition, the mixture was refluxed for 10 minutes. Then, a solution of 2.81 g (0.026 mole) 4-toluidine in dry acetone was added at such a rate that the solution refluxed gently. After refluxed for 2 hour, the mixture was evaporated by rotatory evaporator until the residue became pasty. The mixture was added with 50 ml of water and extracted with 3×30 ml of ethylacetate. The organic fraction was dried over anhydrous sodium sulfat and then evaporated in vacuo. The product was crystallized from aqueous

methanol to afford 4.88 g (64.3 % yield) of pale yellow needles of N-(2-propylpentanoyl)-N'-(4-methylphenyl)thiourea, melting point 96.0-98.0 °C.

IR	:	3232	cm ⁻¹	v N-H thioimide
		2962 - 2871	cm ⁻¹	v C-H aliphatic
		1684	cm ⁻¹	v C=O amide
		1600	cm ⁻¹	v C=C aromatic
		1539	cm ⁻¹	δ N-H amide
		1331	cm ⁻¹	δ N-H thiourea
		1250	cm ⁻¹	v C-N amide
		736	cm ⁻¹	δ C-H out-of -plane

(Figure 21)

¹ H-NMR	0.93 ppm	(6H, t, <i>J</i> = 7.3 Hz, CH ₃ -CH ₂ -)
(CDCl ₃)	1.35 ppm	(4H, m, CH ₃ -CH ₂ -CH ₂ -)
	1.47 ppm	(2H, m, CH ₃ -CH ₂ -CH ₂ -)
	1.66 ppm	(2H, m, CH ₃ -CH ₂ -CH ₂ -)
	2.32 ppm	(1H, m, -CH-)
	2.35 ppm	(3H, s, <i>p</i> -CH ₃)
	7.20 ppm	(2H, d, <i>J</i> = 7.9 Hz , aromatic)
	7.51 ppm	(2H, d, <i>J</i> = 8.6 Hz , aromatic)
	9.18 ppm	(1H, br s, -NH-CS-NH-)
	12.46 pm	(1H, br s, -CO-NH-CS-)

(Figure 22-23)

^{13}C -NMR : 13.96, 14.02 ppm (2C : C-5', C-3'')
 (CDCl₃) 20.57, 21.00 ppm (2C : C-4', C-2'')
 21.05 ppm (1C : *p*-CH₃)
 34.66 ppm (2C : C-3', C-1'')
 43.02 ppm (1C : C-2')
 124.07 ppm (2C : C-2''', C-6''')
 129.38 ppm (2C : C-3''', C-5''')
 134.88 ppm (1C : C-4''')
 136.72 ppm (1C : C-1''')
 177.83, 178.32 ppm (2C : C-2, C-1')
 (Figure 24)

EIMS (% relative intensity) : 186 (3), 149 (14), 127 (20), 106 (40), 91
 (15), 77 (8), 57 (100), 41 (47)
 (Figure 25)

CHN analysis of C₁₆H₂₄N₂O₁S₁% Calcd ; C : 65.75, H : 8.22, N : 9.59
 % Found ; C : 65.90, H : 8.15, N : 9.52

N-(2-Propylpentanoyl)-N'-(4-methylphenyl)urea

Three ml of 10 % sodium hydroxide solution and 3 ml of 30 % hydrogen peroxide solution was added to a chilled solution of 1.55 g N-(2-propylpentanoyl)-N'-(4-methylphenyl)thiourea in acetone, respectively. The mixture was kept in an ice bath for 45 minutes, then another portion of 3 ml NaOH and 3 ml H₂O₂ were again added. After

being left to stand for 45 minutes, the acetone was distilled off by rotatory evaporator. The residue was added with 30 ml of water and extracted with 3 × 30 ml of ethylacetate. The organic fraction was dried over anhydrous sodium sulfate and then evaporated in vacuo. The product was crystallized from aqueous ethanol to afford 1.16 g (79.2 % yield) of white needles of N-(2-propylpentanoyl)-N'-(4-methylphenyl) urea, melting point 90.0 - 91.0 °C.

IR	:	3231	cm ⁻¹	ν N-H imide
		3133	cm ⁻¹	ν N-H amide
		2980 - 2850	cm ⁻¹	ν C-H aliphatic
		1688	cm ⁻¹	ν C=O carbamoyl
		1600	cm ⁻¹	ν C=C aromatic
		1551	cm ⁻¹	δ N-H amide
		1237	cm ⁻¹	δ C-N amide
		816, 759	cm ⁻¹	δ C-H out-of-plane

(figure 26)

¹ H-NMR	0.93 ppm	(6H, t, <i>J</i> = 7.2 Hz, CH ₃ -CH ₂ -)
(CDCl ₃)	1.36 ppm	(4H, m, CH ₃ -CH ₂ -CH ₂ -)
	1.49 ppm	(2H, m, CH ₃ -CH ₂ -CH ₂ -)
	1.67 ppm	(2H, m, CH ₃ -CH ₂ -CH ₂ -)
	2.32 ppm	(3H, s, <i>p</i> -CH ₃)
	2.37 ppm	(1H, m, -CH-)
	7.13 ppm	(2H, d, <i>J</i> = 8.4 Hz, aromatic)
	7.41 ppm	(2H, d, <i>J</i> = 8.4 Hz, aromatic)

9.25 ppm (1H, br s, -NH-CO-NH-)

10.65 ppm (1H, br s, -CO-NH-CO-)

(Figure 27-28)

^{13}C -NMR : 13.96 ppm (2C : C-5', C-3'')

(CDCl₃) 20.61 ppm (2C : C-4', C-2'')

20.80 ppm (1C : *p*-CH₃)

34.57 ppm (2C : C-3', C-1'')

47.68 ppm (1C : C-2')

124.15 ppm (2C : C-2''', C-6''')

129.43 ppm (2C : C-3''', C-5''')

133.79 ppm (1C : C-4''')

134.65 ppm (1C : C-1''')

152.12 ppm (1C : C-2)

179.11 ppm (1C : C-1')

(Figure 29)

EIMS (% relative intensity) : 276 (M⁺,5), 205 (1), 144 (9), 133 (47), 106
(1), 91 (15), 77 (37), 65 (14), 57 (59), 43
(55), 41 (100)

(Figure 30)

CHN analysis of C₁₆H₂₄N₂O₂ % Calcd ; C : 69.56, H : 8.70, N : 10.14

% Found ; C : 69.58, H : 8.62, N : 10.03

N-(2-Propylpentanoyl)-N'-(2-methylphenyl)thiourea

A 3.30 g (0.020 mole) of 2-propylpentanoyl chloride was dropwisely added into a solution of 2.13 g (0.022 mole) potassium thiocyanate in dry acetone. After completion of the addition, the mixture was reflux for 10 minutes. Then, a solution of 2.14 g (0.020 mole) 2-toluidine in dry acetone was added at such a rate that the solution refluxed gently. After refluxed for 3 hour, the mixture was evaporated by rotatory evaporator. The mixture was added with 50 ml of water and extracted with three 30 ml portion of ethylacetate. The organic fraction was dried over anhydrous sodium sulfat and then evaporated in vacuo. The residue was crystallized from aqueous methanol to afford 3.86 g (66.1 % yield) of pale yellow needles of N-(2-propylpentanoyl)-N'-phenylthiourea, melting point 167.0 - 168.0 °C.

IR	3182	cm ⁻¹	ν N-H imide
(KBr)	2990 -2871	cm ⁻¹	ν C-H aliphatic
	1692	cm ⁻¹	ν C=O amide
	1535	cm ⁻¹	δ N-H amide
	1321	cm ⁻¹	δ N-H thiourea
	1247	cm ⁻¹	ν C-N amide
	560	cm ⁻¹	δ C-H out-of -plane

(figure 31)

¹H-NMR (CDCl₃)

- 0.95 ppm (6H, t, $J=7.3$ Hz, CH_3-CH_2-)
- 1.38 ppm (4H, m, $CH_3-CH_2-CH_2-$)
- 1.51 ppm (2H, m, $CH_3-CH_2-CH_2-$)
- 1.68 ppm (2H, m, $CH_3-CH_2-CH_2-$)
- 2.26 ppm (1H, m, $-CH-$)
- 2.31 ppm (3H, s, $o-CH_3$)
- 7.24 ppm (3H, complex , aromatic)
- 7.74 ppm (1H, d, $J = 7.3$ Hz, aromatic)
- 8.75 ppm (1H, br s, $-NH-CS-NH-$)
- 12.14 ppm (1H, br s, $-CO-NH-CS-$)

(Figure 32-33)

¹³C-NMR : (CDCl₃)

- 14.02 ppm (2C : C-5', C-3'')
- 17.89 ppm (1C : $o-CH_3$)
- 20.62 ppm (2C : C-4', C-2'')
- 34.67 ppm (2C : C-3', C-1'')
- 48.18 ppm (1C : C-2')
- 126.09 ppm (1C : C-6''')
- 126.34 ppm (1C : C-4''')
- 127.55 ppm (1C : C-3''')
- 130.70 ppm (1C : C-5''')
- 133.13 ppm (1C : C-2''')
- 136.21 ppm (1C : C-1''')
- 177.81, 179.28 ppm (2C : C-2, C-1')

(Figure 34)

EIMS (% relative intensity) : 186 (3), 149 (20), 127 (23), 106 (49), 99 (6), 72 (13), 57 (100), 41 (54)
(Figure 35)

CHN analysis of $C_{16}H_{22}N_2O_1S_1$ % Calcd ; C : 65.75, H : 8.22, N : 9.59
% Found ; C : 65.77, H : 8.08, N : 9.52

N-(2-Propylpentanoyl)-N'-(2-methylphenyl)urea

Four ml of 10 % sodium hydroxide solution and 4 ml of 30 % hydrogen peroxide solution was added to a chilled solution of 2.00 g of N-(2-propylpentanoyl)-N'-(2-methylphenyl)urea in acetone, respectively. The mixture was kept in an ice bath for 30 minutes, then another 3 ml portion of NaOH and H_2O_2 were again added. After being left to stand for 30 minutes, acetone was distilled off by rotatory evaporator. The residue was added with 30 ml. of water and extracted with 3×30 ml of ethylacetate. The organic fraction was dried over anhydrous sodium sulfate and then evaporated in vacuo. The product was crystallized from aqueous ethanol to afford 1.56 g (82.5 % yield) of white needles of N-(2-propylpentanoyl)-N'-(2-methylphenyl)urea, melting point $90.0 - 91.0$ °C.

IR	:	3227	cm^{-1}	ν N-H imide
(KBr)		3135	cm^{-1}	ν N-H amide
		3000 - 2940	cm^{-1}	ν C-H aliphatic
		1700	cm^{-1}	ν C=O carbamoyl
		1616	cm^{-1}	ν C=C aromatic

1563 cm^{-1} δ N-H amide
 759 cm^{-1} δ C-H out-of-plane

(figure 36)

$^1\text{H-NMR}$ (CDCl₃)
 0.92 ppm (6H, t, $J = 7.3$ Hz, CH₃-CH₂-)
 1.37 ppm (4H, m, CH₃-CH₂-CH₂-)
 1.50 ppm (2H, m, CH₃-CH₂-CH₂-)
 1.71 ppm (2H, m, CH₃-CH₂-CH₂-)
 2.36 ppm (3H, s, *o*-CH₃)
 2.46 ppm (1H, m, -CH-)
 7.05 ppm (1H, dt, $J = 7.5, 0.9$ Hz, aromatic)
 7.20 ppm (2H, complex, aromatic)
 8.06 ppm (1H, dd, $J = 8.5, 0.9$ Hz, aromatic)
 10.14 ppm (1H, br s, -NH-CO-NH-)
 10.77 ppm (1H, br s, -CO-NH-CO-)

(Figure 37-38)

$^{13}\text{C-NMR}$: (CDCl₃)
 13.96 ppm (2C : C-5', C-3'')
 18.06 ppm (*o*-CH₃)
 20.62 ppm (2C : C-4', C-2'')
 34.59 ppm (2C : C-3', C-1'')
 47.90 ppm (1C : C-2')
 121.25 ppm (1C : c-6''')
 124.33 ppm (1C : C-4''')
 126.52 ppm (1C : C-3''')
 128.03 ppm (1C : C-5''')

130.35 ppm (1C : C-2''')

135.76 ppm (1C : C-1''')

151.92 ppm (1C : C-2)

179.08 ppm (1C : C-1')

(Figure 39)

EIMS (% relative intensity) : 276 (M^+ , 19), 144 (30), 133 (100), 107 (42),
91 (19), 79 (13), 77 (28), 72 (48), 65 (13),
57 (80), 41 (73)
(figure 40)

CHN analysis of $C_{16}H_{24}N_2O_2$ % Calcd ; C : 69.56, H : 8.70, N : 10.14
% Found ; C : 69.64, H : 8.66, N : 10.15

N-(2-Propylpentanoyl)-N'-(4-nitrophenyl)thiourea

A 3.60 g (0.022 mole) of 2-propylpentanoyl chloride was dropwisely added into a solution of 2.33 g (0.024 mole) potassium thiocyanate in dry acetone. After completion of the addition, the mixture was refluxed for 10 minutes. Then, a solution of 3.04 g (0.022 mole) 4-nitroaniline in dry acetone was added at such a rate that the solution refluxed gently. After 2 hours of refluxing, the mixture was evaporated by rotatory evaporator until the residue became pasty. The mixture was added with 50 ml of water and extracted with three 30 ml portions of ethylacetate. The organic fraction was dried over anhydrous sodium sulfate and then evaporated in vacuo. The product was recrystallized

from aqueous methanol to afford 4.30 g (60.5 % yield) of pale yellow needles of N-(2-propylpentanoyl)-N'-(4-nitrophenyl)thiourea, melting point 115.0-116.0 °C.

IR :	3369	cm ⁻¹	ν N-H thioimide
(KBr)	2958	cm ⁻¹	ν C-H aliphatic
	1688	cm ⁻¹	ν C=O amide
	1578	cm ⁻¹	δ N-H amide
	1510	cm ⁻¹	ν C-NO ₂ asym
	1305	cm ⁻¹	ν C-NO ₂ sym
	849, 752	cm ⁻¹	δ N-H out-of-plane

(Figure 41)

¹ H-NMR	0.94 ppm	(6H, t, <i>J</i> = 7.3 Hz, CH ₃ -CH ₂ -)
(CDCl ₃)	1.38 ppm	(4H, m, CH ₃ -CH ₂ -CH ₂ -)
	1.52 ppm	(2H, m, CH ₃ -CH ₂ -CH ₂ -)
	1.68 ppm	(2H, m, CH ₃ -CH ₂ -CH ₂ -)
	2.34 ppm	(1H, m, -CH-)
	8.01 ppm	(2H, dd, <i>J</i> = 9.2, 2.1 Hz, aromatic)
	8.27 ppm	(2H, dd, <i>J</i> = 9.2, 2.1 Hz, aromatic)
	9.16 ppm	(1H, br s, -NH-CS-NH-)
	13.07 ppm	(1H, br s, -CO-NH-CS-)

(Figure 42-43)

¹³ C-NMR :	13.91, 13.97 ppm	(2C : C-5', C-3'')
(CDCl ₃)	20.56 ppm	(2 C : C-4', C-2'')

34.55 ppm (2C : C-3', C-1'')
48.21 ppm (1C : C-2')
123.07, 123.15 ppm (2C : C-2''', C-6''')
124.43, 124.51 ppm (2C : C-3''', C-5''')
143.10 ppm (1C : 4')
145.07 ppm (1C : C-1')
178.16, 178.19 ppm (2C : C-2, C-1')
(Figure 44)

EIMS (% relative intensity) : 323 (M^+ , 7), 198 (4), 196 (1), 180 (6), 164
(2), 150 (13), 134 (8), 108 (10), 97 (7), 90
(13), 72 (18), 54 (100), 41 (76)
(Figure 45)

CHN analysis of $C_{15}H_{21}N_3O_3S_1$ % Calcd ; C : 55.73, H : 6.50, N : 13.00
% Found ; C : 55.82, H : 6.54, N : 12.91

N-(2-Propylpentanoyl)-N'-(4-nitrophenyl)urea

Two ml of 10 % sodium hydroxide solution and 2 ml of 30 % hydrogen peroxide solution was added to a chilled solution of 1.25 g N-(2-propylpentanoyl)-N'-(4-nitrophenyl)thiourea, respectively. The mixture was kept in an ice bath for 30 minutes, then another portion of 2 ml. NaOH and 2 ml. H_2O_2 were again added. After left to stand for 30 minutes, the residue was added with 30 ml of water and extracted with three 30-ml portions of ethylacetate. The organic fraction was dried

over anhydrous sodium sulfate and then evaporated in vacuo. The residue was recrystallized from aqueous ethanol to afford 0.68 g (57.28 % yield) of yellow needle of N-(2-propylpentanoyl)-N'-(4-nitrophenyl) urea, melting point 140.0 - 141.5 °C.

IR :	3220	cm ⁻¹	ν N-H imide
	3147	cm ⁻¹	ν N-H amide
	3000 - 2850	cm ⁻¹	ν C-H aliphatic
	1697	cm ⁻¹	ν C=O amide
	1600	cm ⁻¹	ν C=C aromatic
	1513	cm ⁻¹	ν C-NO ₂ asym
	1341	cm ⁻¹	ν C-NO ₂ sym
	784	cm ⁻¹	δ C-H out-of-plane

(Figure 46)

¹ H-NMR	0.95 ppm	(6H, t, <i>J</i> = 7.3 Hz, CH ₃ -CH ₂ -)
(CDCl ₃)	1.38 ppm	(4H, m, CH ₃ -CH ₂ -CH ₂ -)
	1.54 ppm	(2H, m, CH ₃ -CH ₂ -CH ₂ -)
	1.70 ppm	(2H, m, CH ₃ -CH ₂ -CH ₂ -)
	2.40 ppm	(1H, m, -CH-)
	7.71 ppm	(2H, dd, <i>J</i> = 9.2, 2.1 Hz, aromatic)
	8.23 ppm	(2H, dd, <i>J</i> = 9.2, 2.1 Hz, aromatic)
	9.35 ppm	(1H, br s, -NH-CO-NH-)
	11.24 ppm	(1H, br s, -CO-NH-CO-)

(Figure 47-48)

^{13}C -NMR : 13.94 ppm (2C : C-5', C-3'')
 (CDCl_3) 20.64 ppm (2C : C-4', C-2'')
 34.51 ppm (2C : C-3', C-1'')
 48.05 ppm (1C : C-2')
 119.62 ppm (2C : C-2''', C-6''')
 125.02 ppm (2C : C-3''', C-5''')
 143.12 ppm (1C : C-4''')
 143.74 ppm (1C : C-1''')
 151.74 ppm (1C : C-2)
 179.31 ppm (1C : C-1')
 (Figure 49)

EIMS (% relative intensity) : 307 (M^+ ,4), 261 (2), 236 (2), 180 (2), 165
 (6), 148 (3), 134 (16), 108 (11), 99 (7), 91
 (41), 72 (28), 57 (64), 41 (100)
 (figure 50)

CHN analysis of $\text{C}_{15}\text{H}_{21}\text{N}_3\text{O}_4$ % Calcd C : 58.63, H : 6.84, N : 13.68
 % Found C : 58.60, H : 6.93, N : 13.72

N-(2-Propylpentanoyl)-N'-(4-pyridinyl)urea

A 2.50 g (0.015 mole) of 2-propylpentanoyl chloride and 4 drops of stannic chloride (SnCl_4) was dropwisely added to a suspension of 1.38 g (0.017 mole) potassium cyanate in dry dioxane, respectively. The mixture was heated at 120°C for 7 hours, and then added to a

suspension of 4-aminopyridine in dry dioxane. After stirred for half an hour, 50 ml of water was added to the mixture and extracted with chloroform. The organic fraction was dried over anhydrous sodium sulfate and then evaporated in vacuo. The residue was recrystallized from ethyl acetate to afford a 1.24 g (31.4 % yield) of clear, cubic-like crystals of N-(2-propylpentanoly)-N'-(4-pyridinyl)urea, melting point 153.0-154.5 °C.

IR	:	3228	cm ⁻¹	ν N-H imide
(KBr)	:	3148	cm ⁻¹	ν N-H amide
	:	2962 - 2870	cm ⁻¹	ν C-H aliphatic
	:	1734	cm ⁻¹	ν C=O carbamoyl
	:	1688	cm ⁻¹	ν C=O amide
	:	1585	cm ⁻¹	ν C=C pyridine
	:	1385	cm ⁻¹	δ C-H aliphatic

(Figure 51)

¹ H-NMR:	0.94 ppm	(6H, t, <i>J</i> = 7.3 Hz, CH ₃ -CH ₂ -CH ₂)
(CDCl ₃)	1.37 ppm	(4H, m, CH ₃ -CH ₂ -CH ₂ -)
	1.52 ppm	(2H, m, CH ₃ -CH ₂ -CH ₂ -)
	1.70 ppm	(2H, m, CH ₃ -CH ₂ -CH ₂ -)
	2.43 ppm	(1H, m, -CH-)
	7.49 ppm	(2H, dd, <i>J</i> = 5.8, 1.5 Hz, aromatic)
	8.52 ppm	(2H, d, <i>J</i> = 5.8 Hz, aromatic)
	9.73 ppm	(1H, br s, NH-CO-NH-)
	11.06 ppm	(1H, br s, CO-NH-CO)

(Figure 52-53)

^{13}C -NMR : 13.93 ppm (2C : C-5', C-3'')
(CDCl_3) 20.60 ppm (2C : C-4', C-2'')
34.52 ppm (2C : C-3', C-1'')
47.86 ppm (1C : C-2')
114.16 ppm (2C : C-3''', C-5''')
144.58 ppm (2C : C-4''')
150.44 ppm (1C : C-2''', C-6''')
151.95 ppm (1C : C-2)
179.38 ppm (1C : C-1')

(Figure 54)

EIMS (% relative intensity) : 186 (1), 170 (2), 144 (10), 127 (31), 120
(34), 114 (8), 101 (37), 98 (35), 94 (15),
72 (100), 65 (13), 57 (30), 41 (74)

(Figure 55)

CHN analysis of $\text{C}_{14}\text{H}_{21}\text{N}_3\text{O}_2$ % Calcd C : 63.88, H : 7.98, N : 15.97
% Found C : 63.92, H : 8.15, N : 15.70

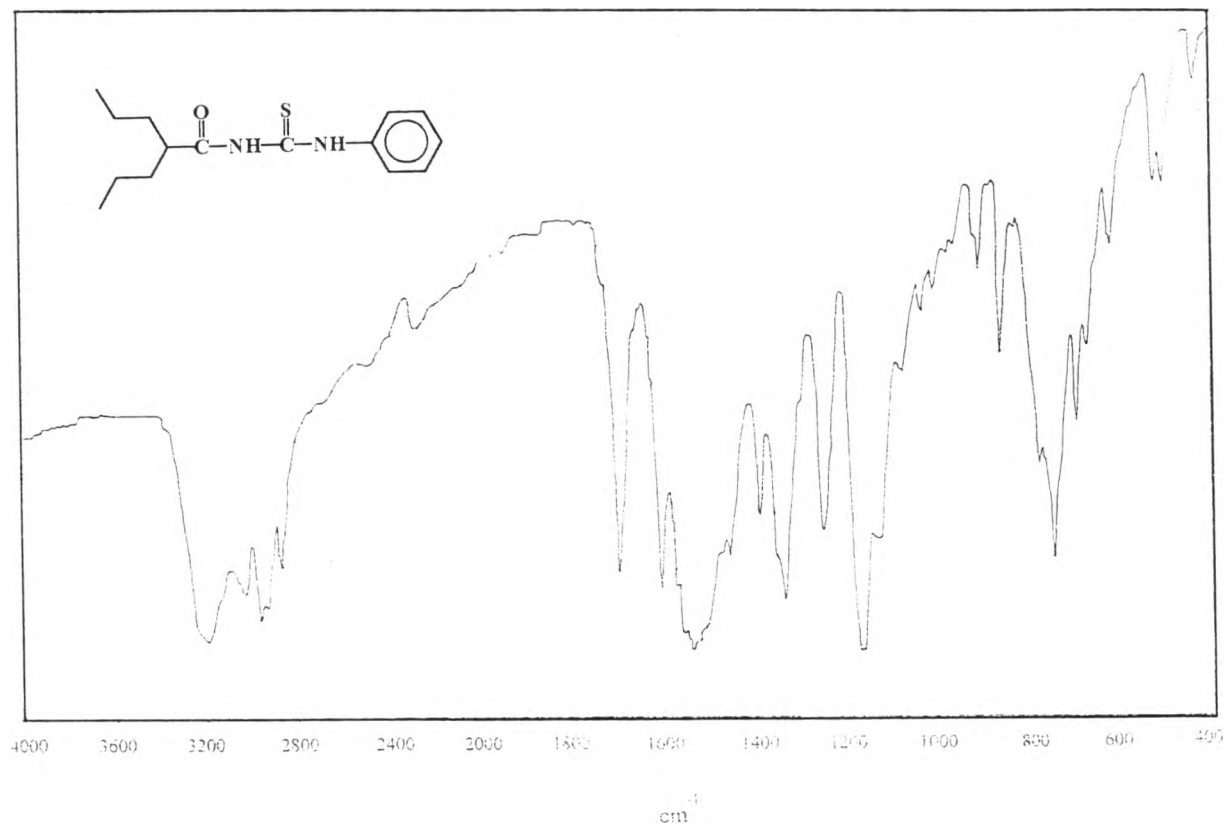


Figure 11. The IR spectrum (KBr) of *N*-(2-propylpentanoyl)-*N'*-phenylthiourea

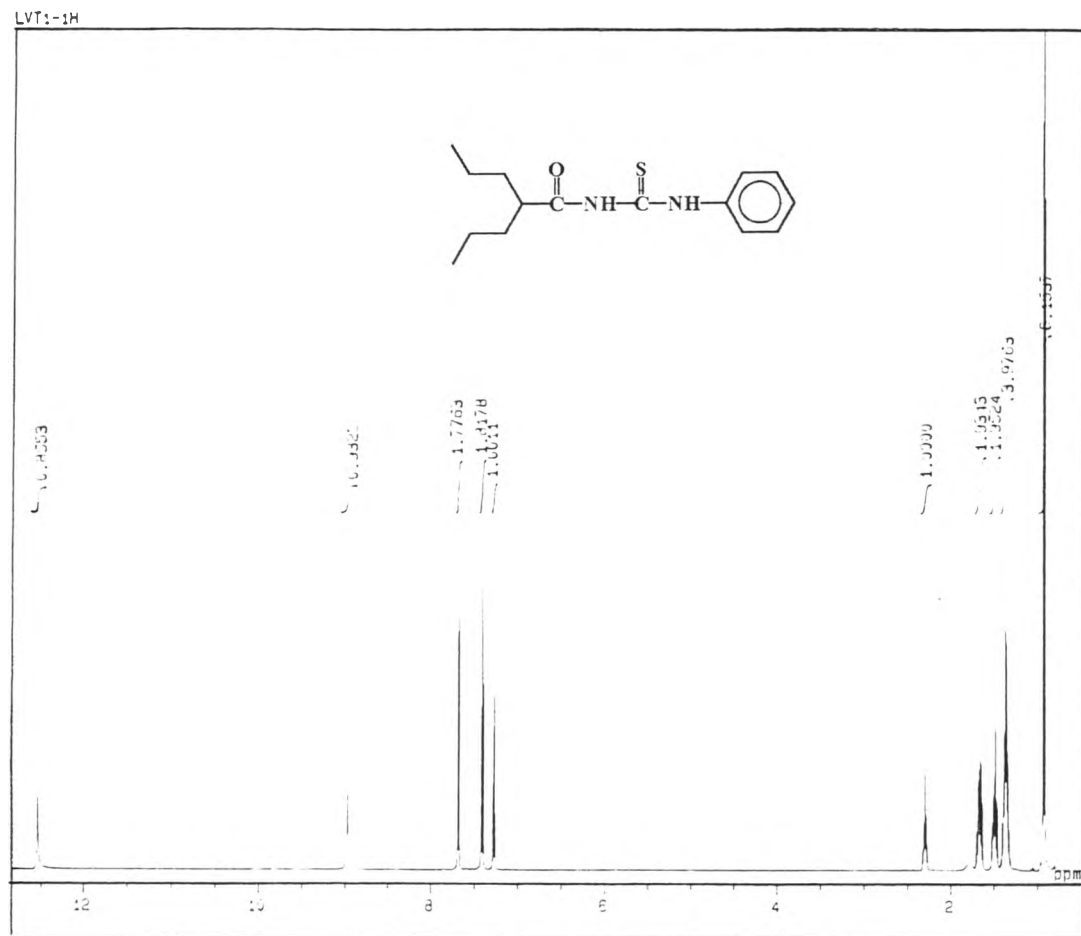


Figure 12. The 500 MHz ^1H -NMR spectrum of N-(2-propylpentanoyl)-N'-phenylthiourea in CDCl_3

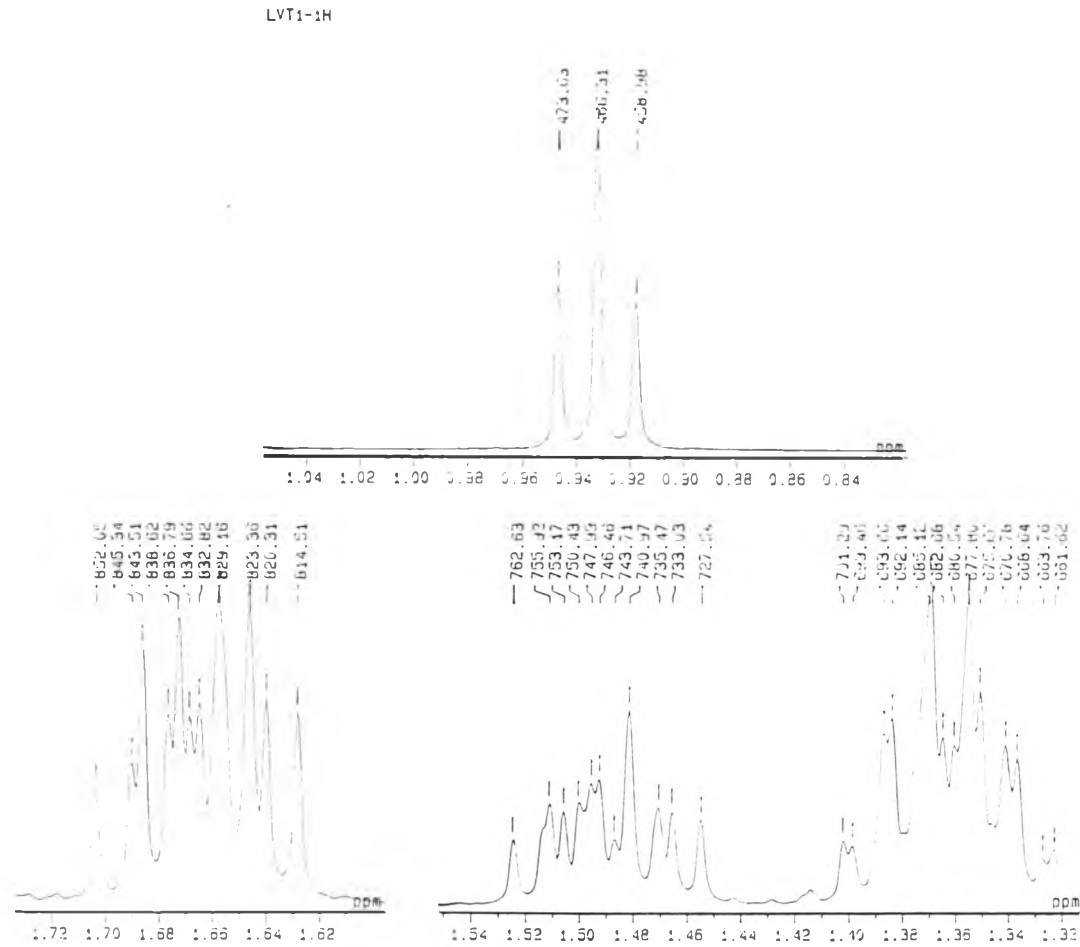


Figure 13. The 500 MHz $^1\text{H-NMR}$ spectrum of of N-(2-propylpentanoyl)-N'-phenylthiourea in CDCl_3 (Enlarged scale)

LVT1-1H

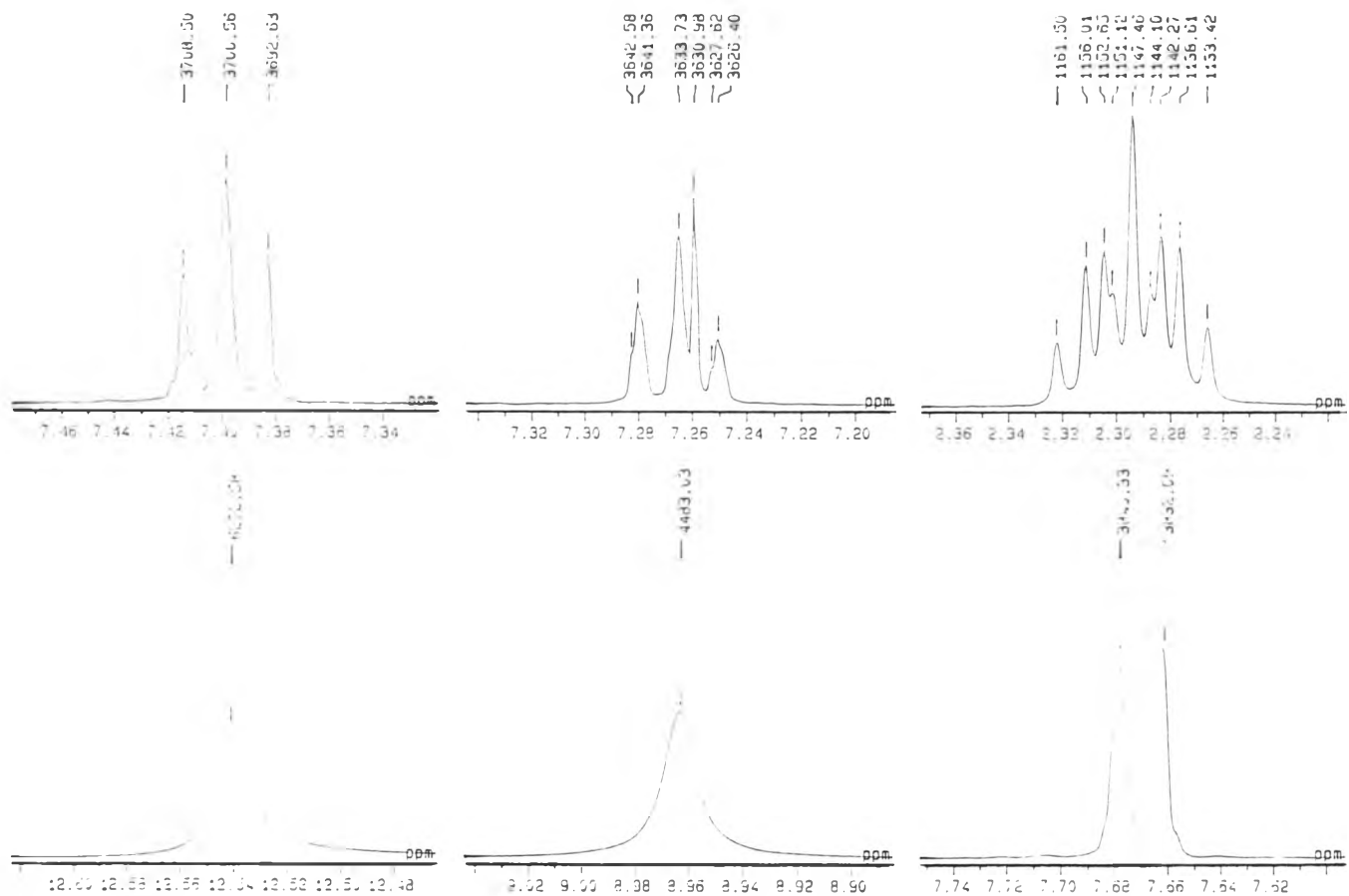


Figure 13.(Cont.) The 500 MHz ^1H -NMR spectrum of of N -(2-propylpentanoyl)- N' -phenylthiourea in CDCl_3 (Enlarged scale)

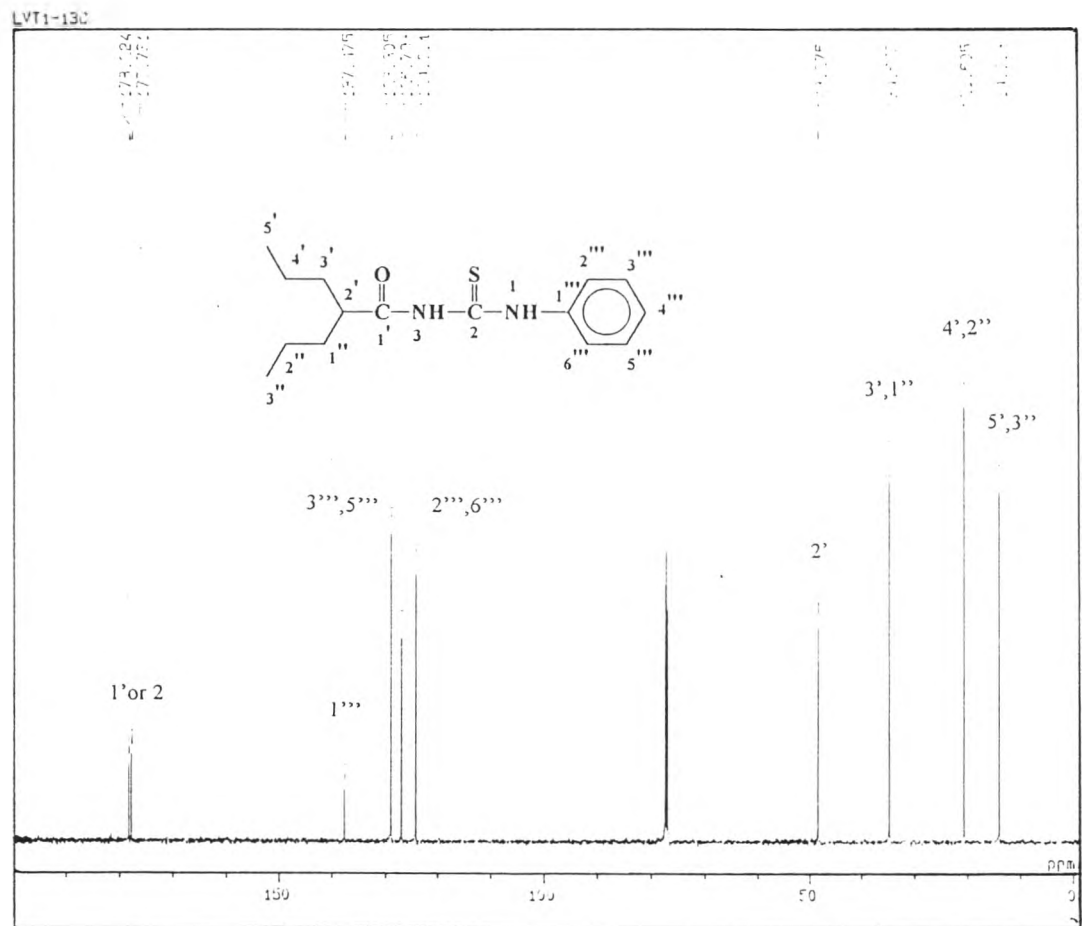


Figure 14. The 500 MHz ^{13}C -NMR spectrum of N-(2-propylpentanoyl)-N'-phenylthiourea in CDCl_3

SM6440002 Scan 337 RT=11:54 100%=130882 mv 15 Dec 95 9:31
LRP +EI LVT1

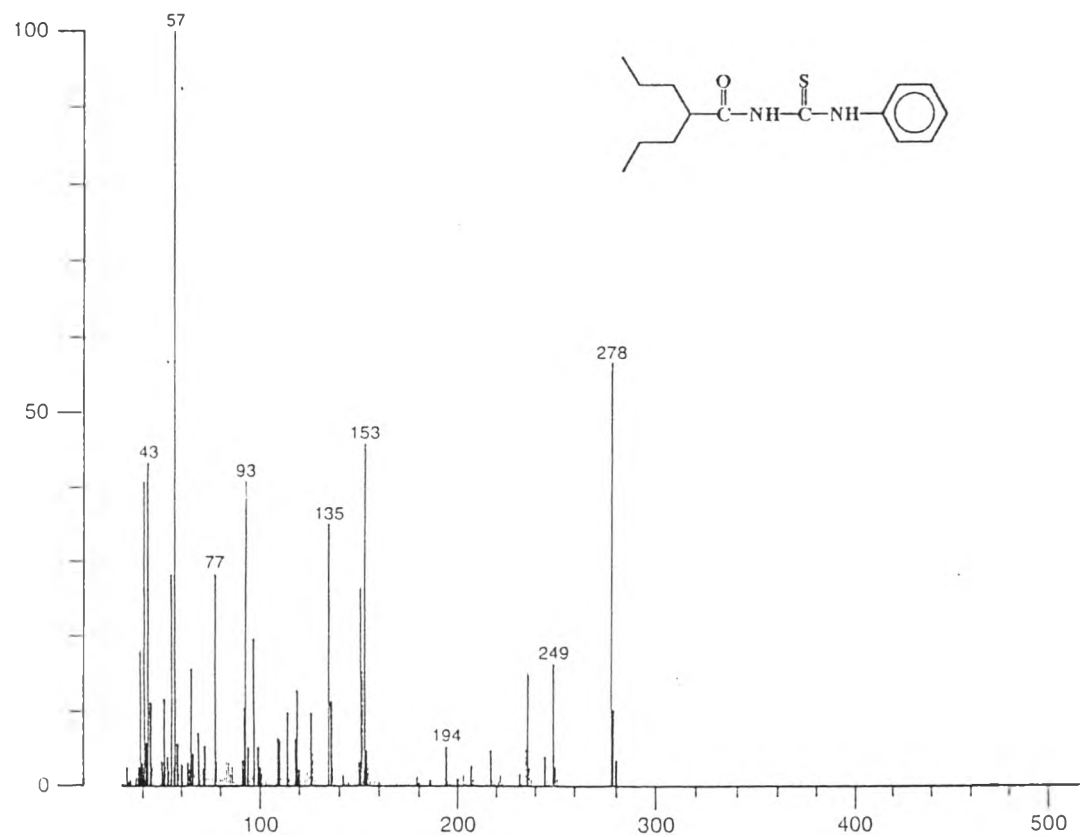


Figure 15 . The EIMS spectrum of *N*-(2-propylpentanoyl)-*N'*-phenylthiourea

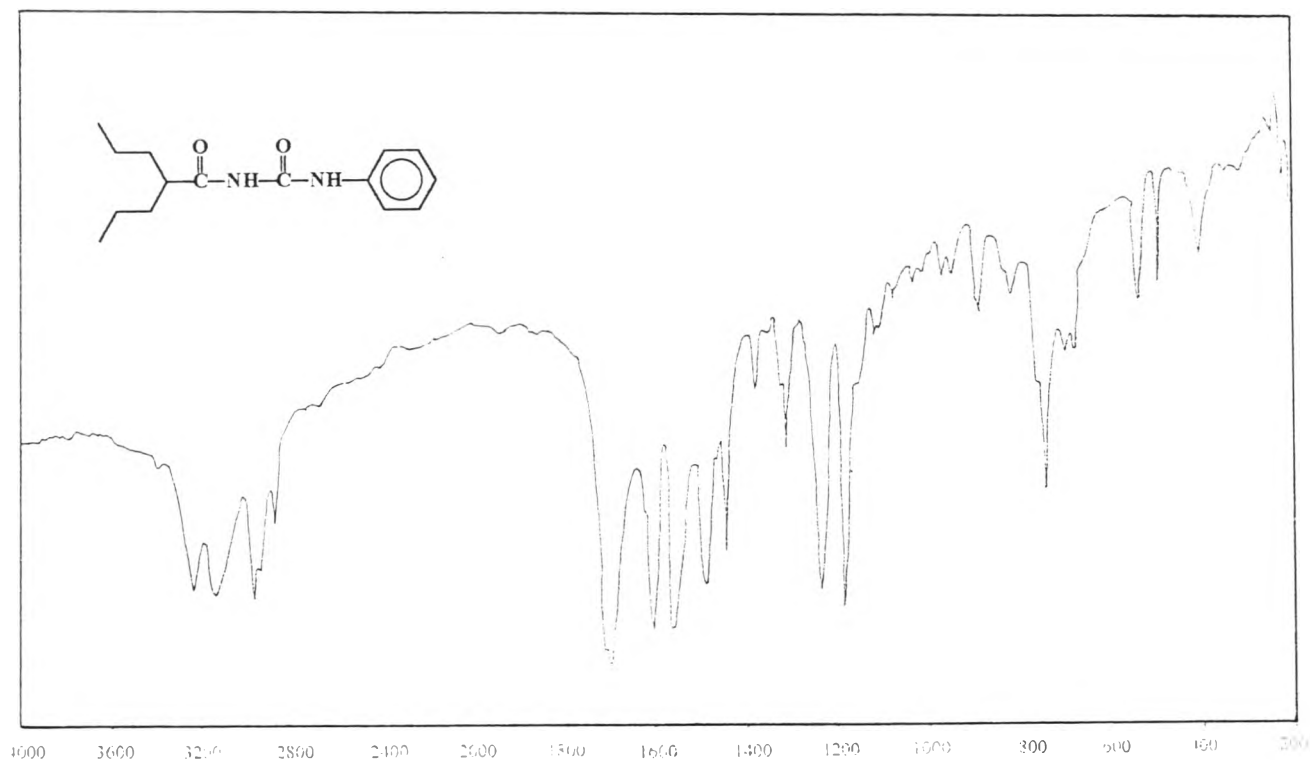


Figure 16. The IR spectrum (KBr) of N-(2-propylpentanoyl)-N'-phenylurea

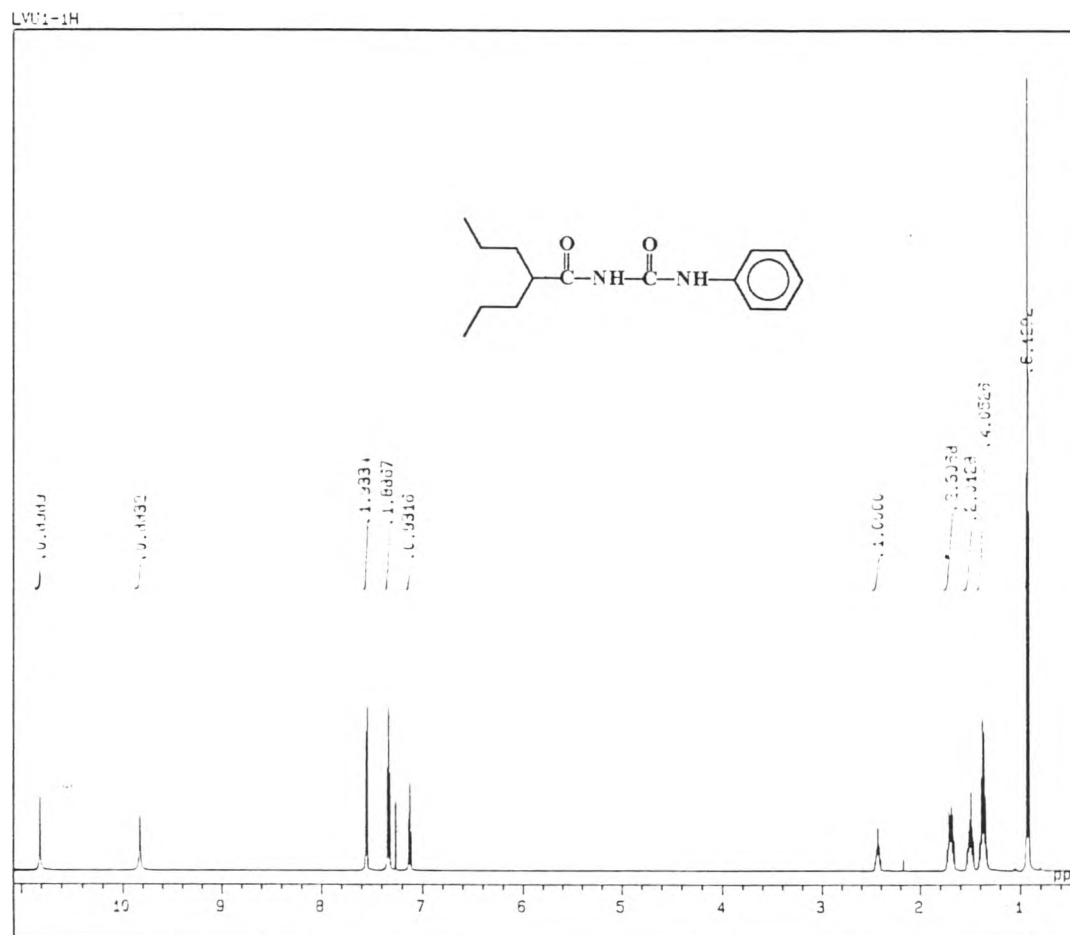


Figure 17. The 500 MHz $^1\text{H-NMR}$ spectrum of N-(2-propylpentanoyl)-N'-phenylurea in CDCl_3

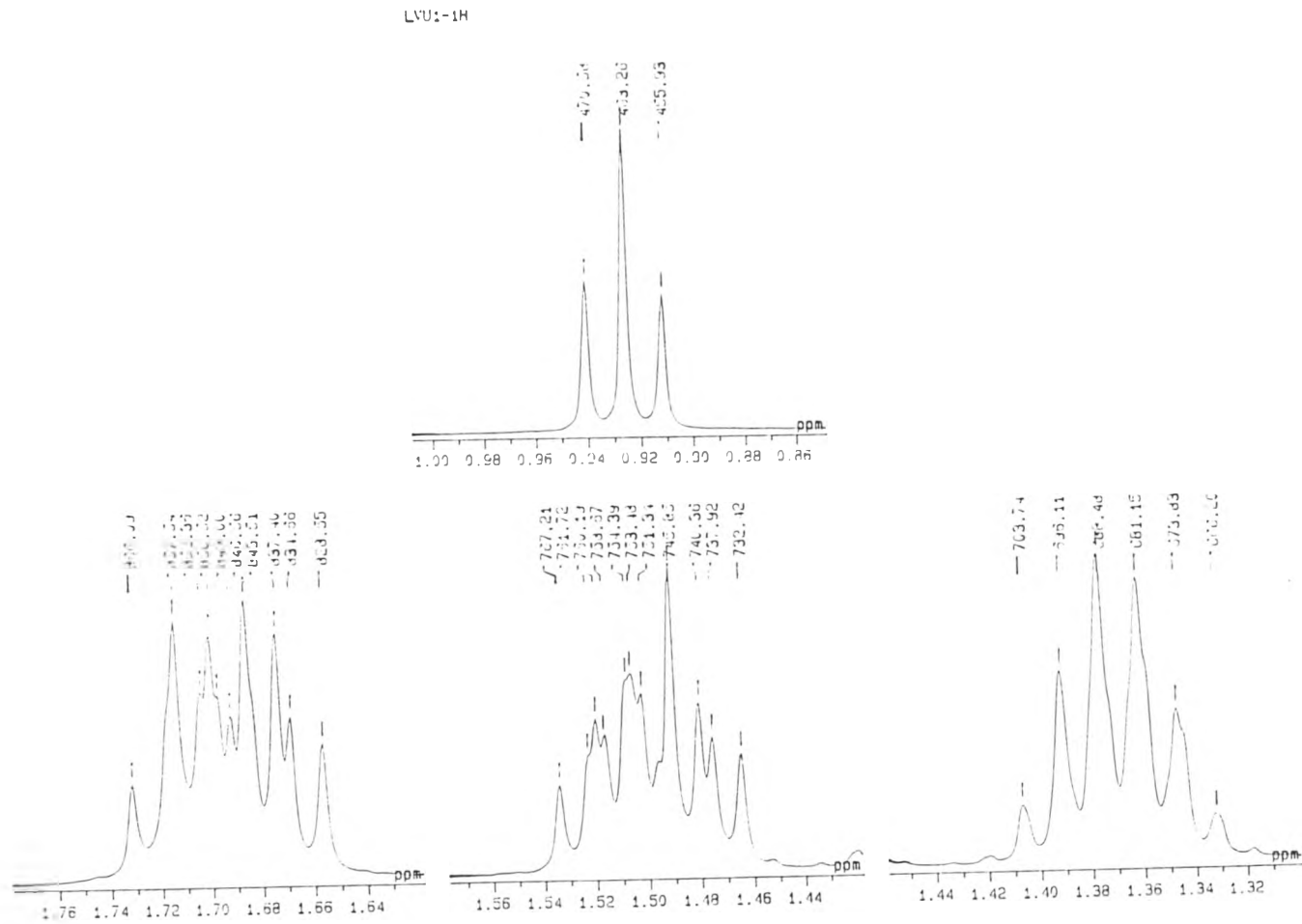


Figure 18. The 500 MHz ^1H -NMR spectrum of of N-(2-propylpentanoyl)-N'-phenylurea in CDCl_3 (Enlarged scale)

LVU1-1H

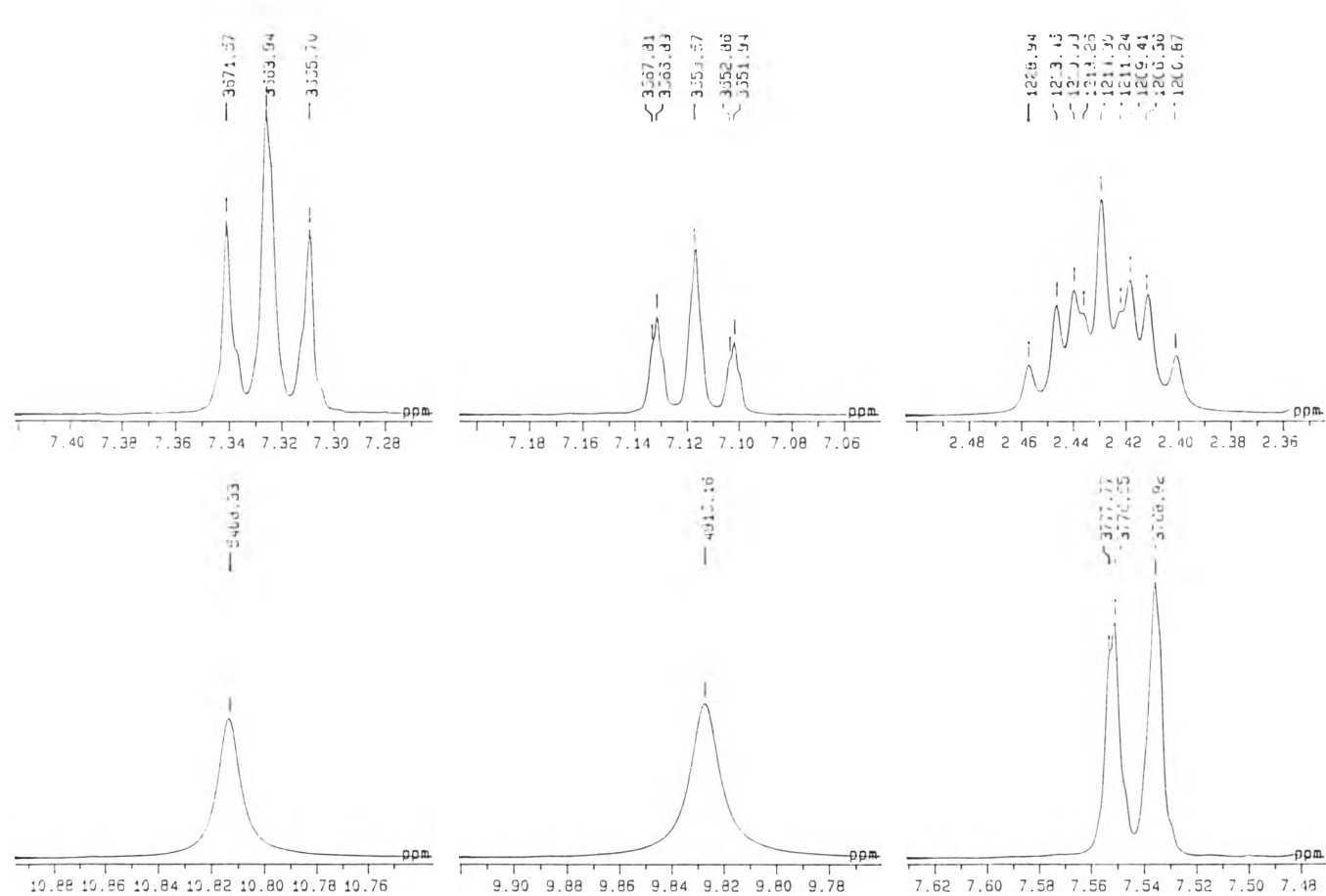


Figure 18.(Cont.) The 500 MHz $^1\text{H-NMR}$ spectrum of of N -(2-propylpentanoyl)- N' -phenylurea in CDCl_3 (Enlarged scale)

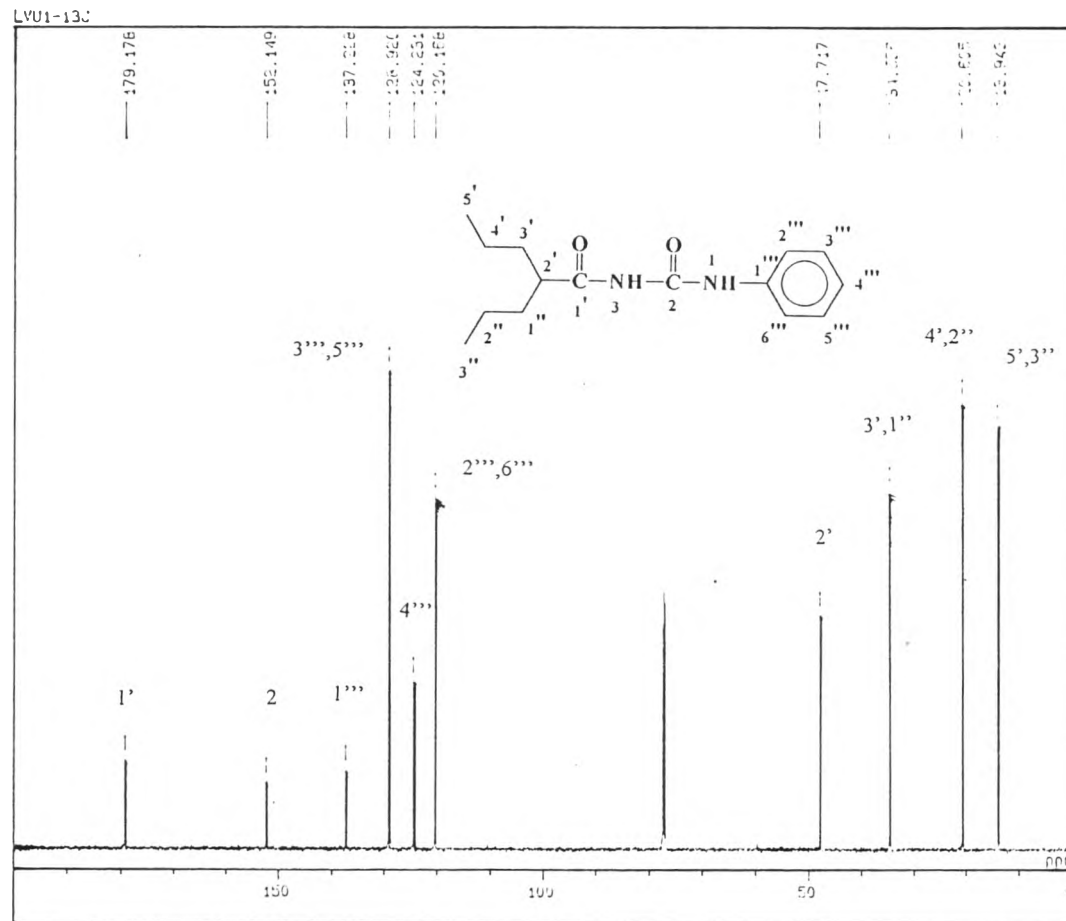


Figure 19. The 500 MHz ^{13}C -NMR spectrum of N-(2-propylpentanoyl)-N'-phenylurea in CDCl_3

SM6450004 Scan 245 RT=8:37 100%=124165 mv 22 Dec 95 10:26
LRP +EI LVU1

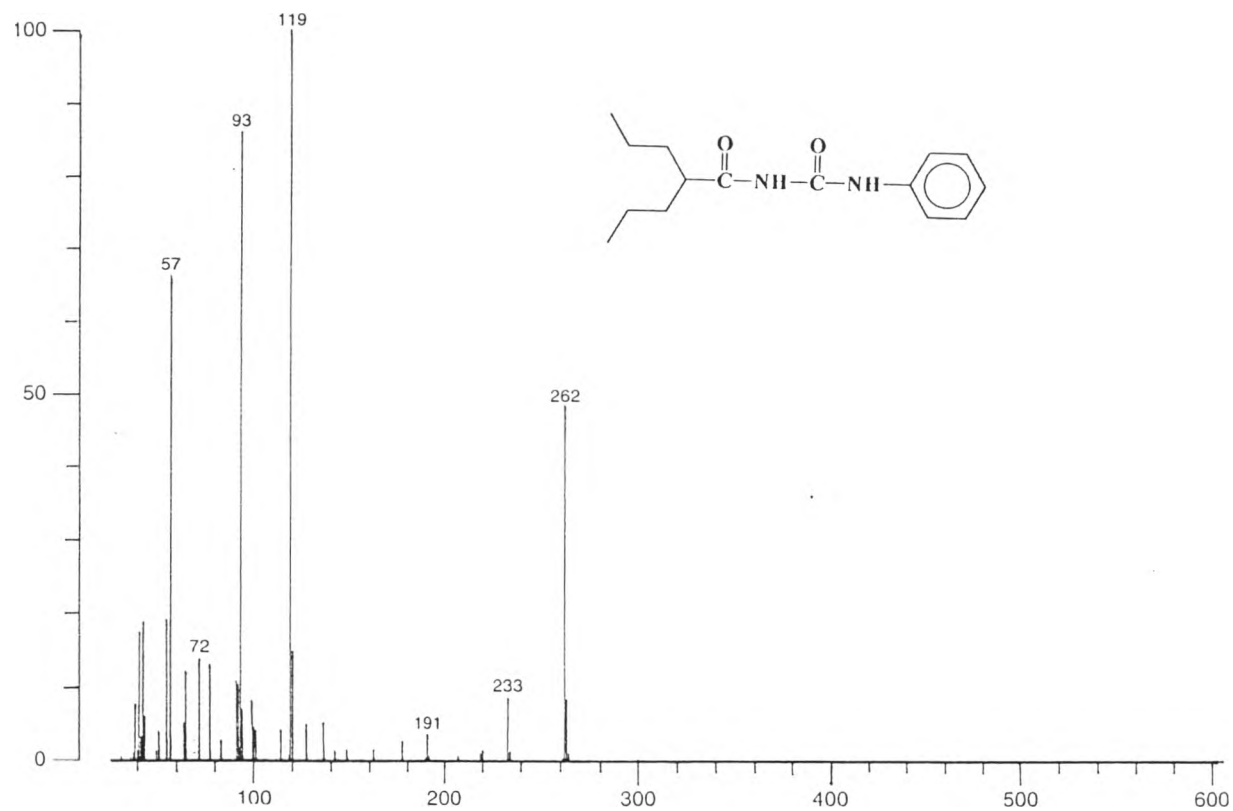


Figure 20. The EIMS spectrum of *N*-(2-propylpentanoyl)-*N'*-phenylurea

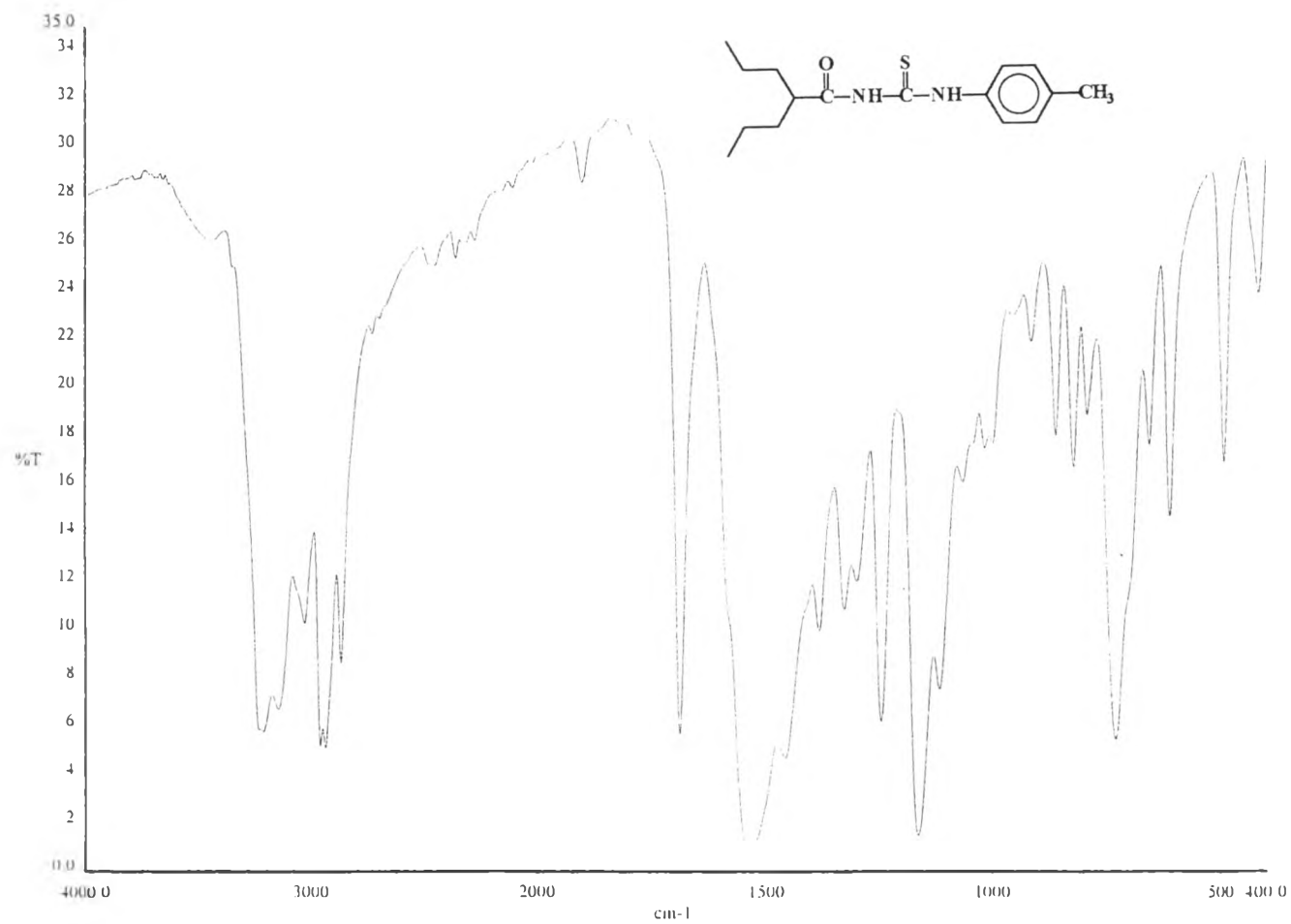


Figure 21. The IR spectrum (KBr) of *N*-(2-propylpentanoyl)-*N'*-(4-methylphenyl)thiourea

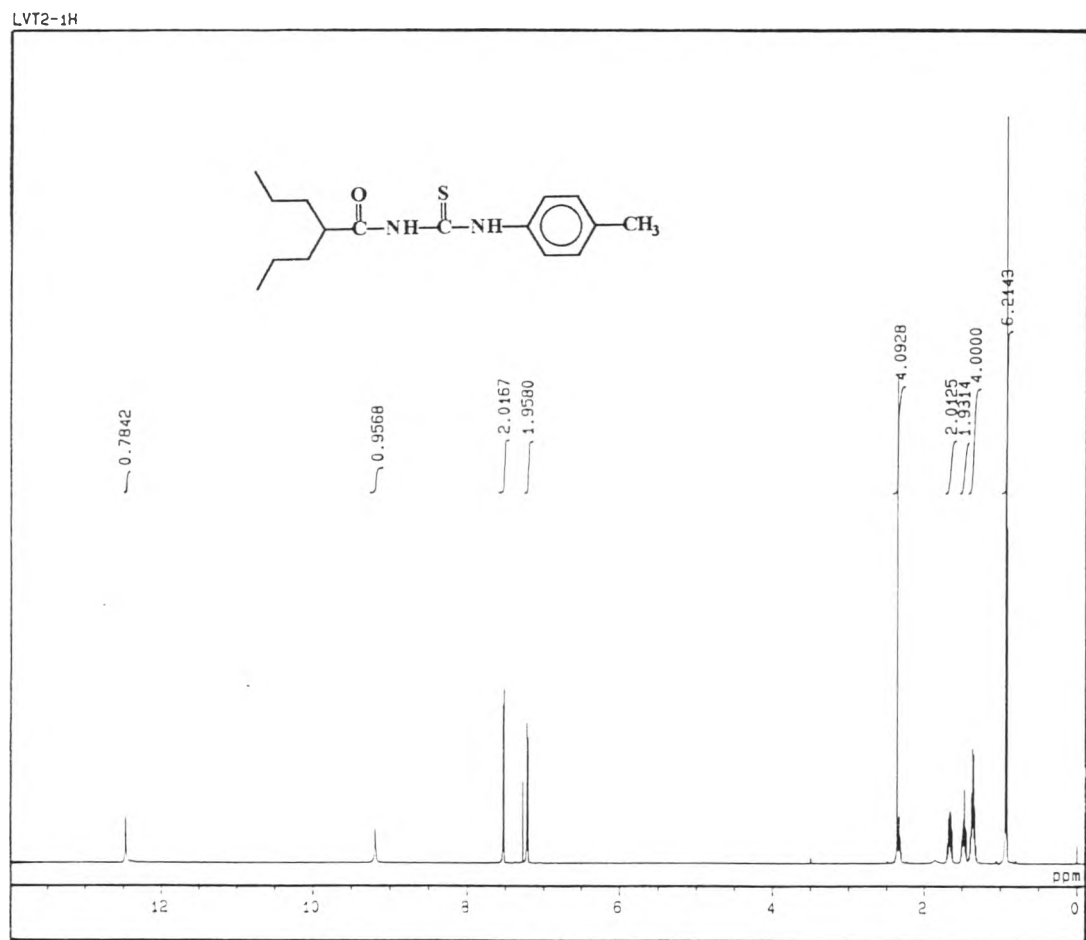


Figure 22. The 500 MHz ^1H -NMR spectrum of *N*-(2-propylpentanoyl)-*N'*-(4-methylphenyl)thiourea in CDCl_3

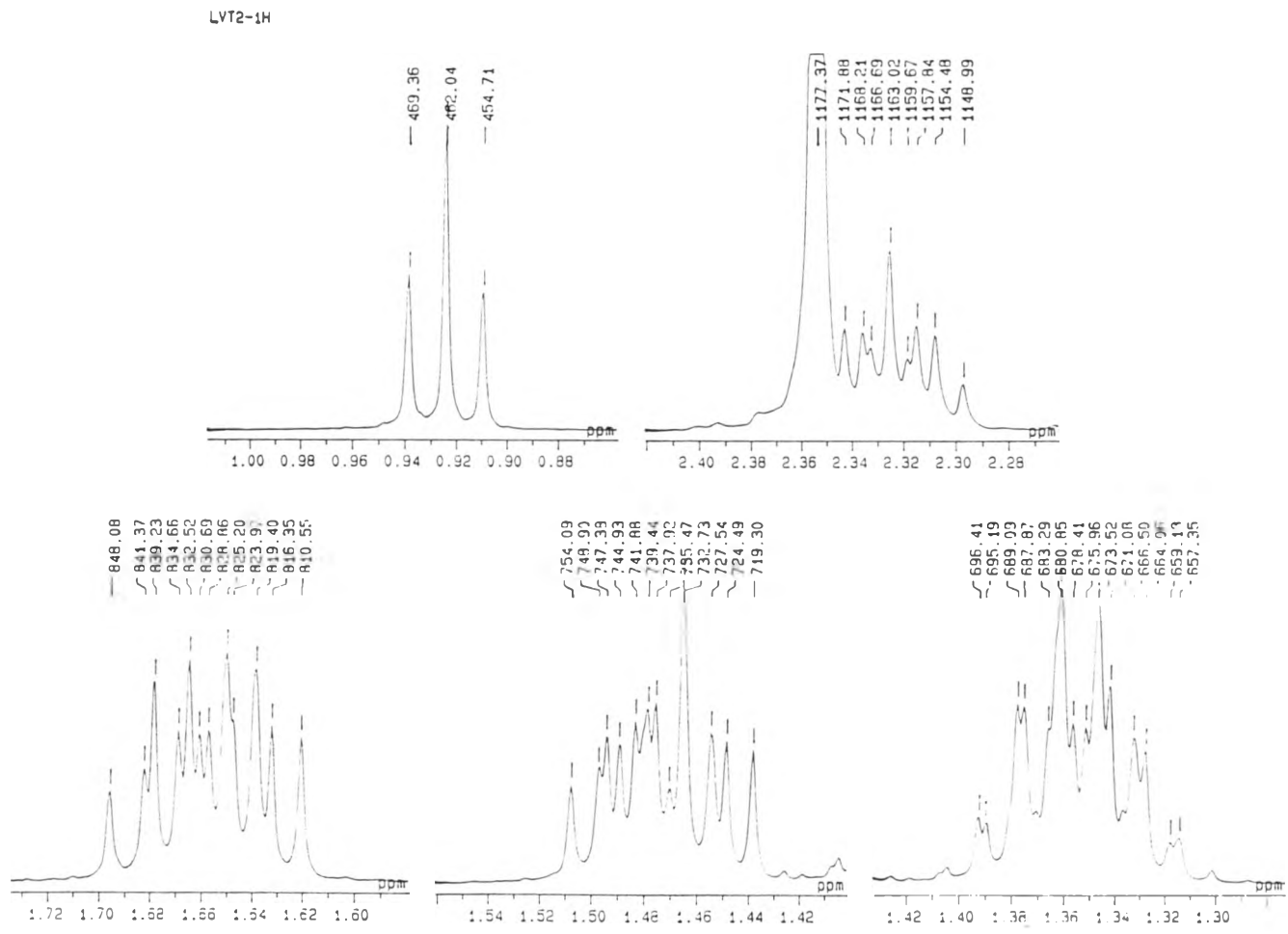


Figure 23. The 500 MHz ^1H -NMR spectrum of of N-(2-propylpentanoyl)-N'-(4-methylphenyl)thiourea in CDCl_3 (Enlarged scale)

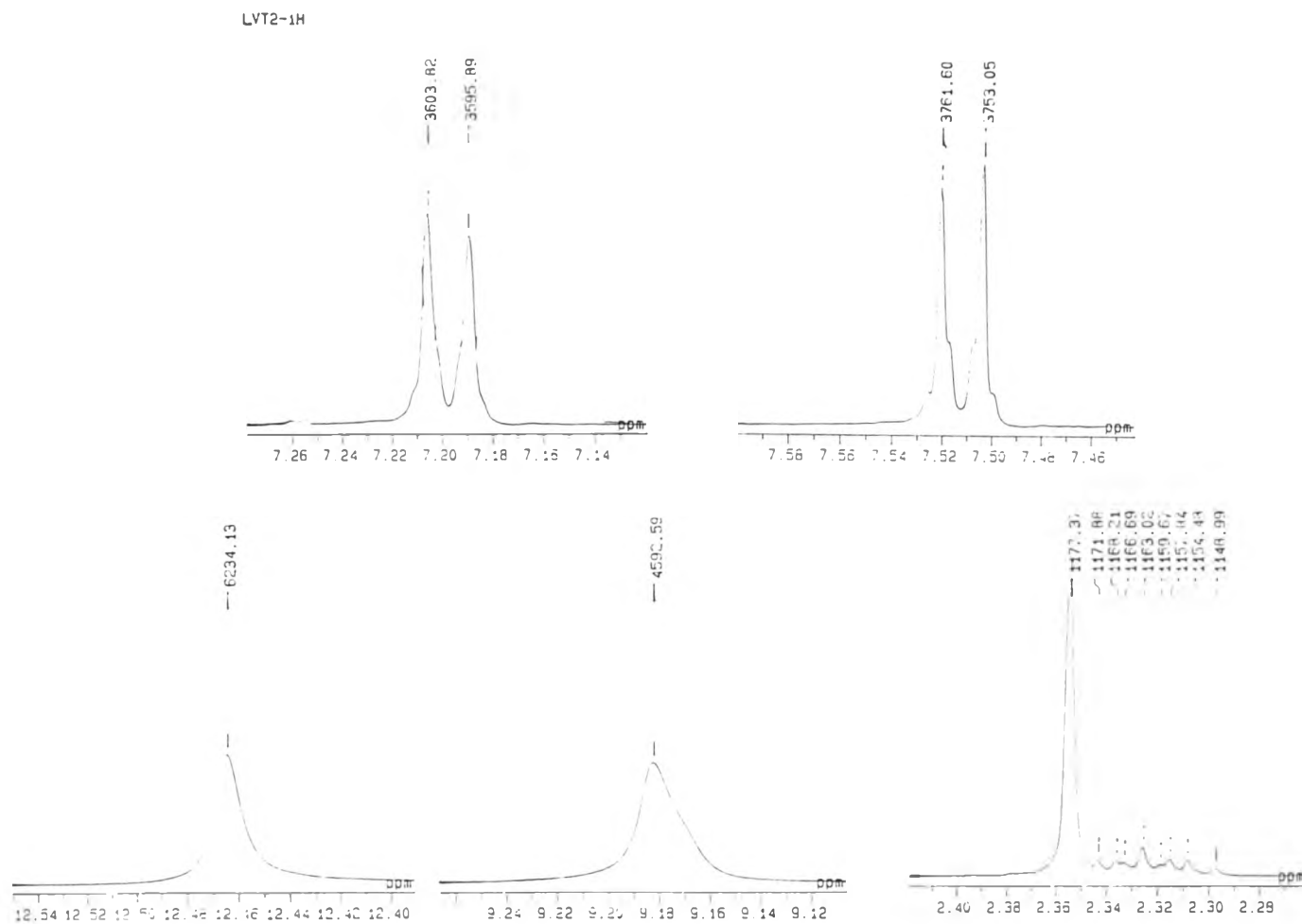


Figure 23.(Cont.) The 500 MHz ^1H -NMR spectrum of of N-(2-propylpentanoyl)-N'-(4-methylphenyl)thiourea in CDCl_3 (Enlarged scale)

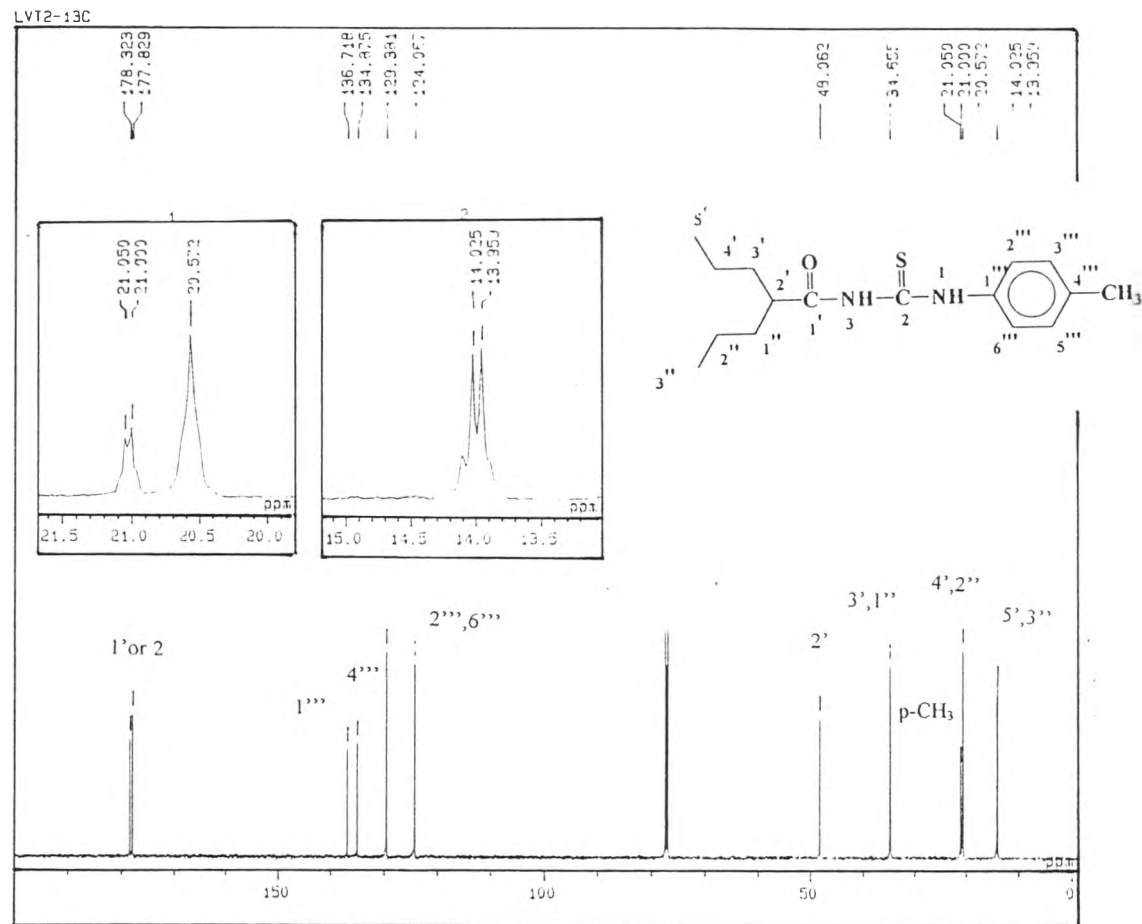


Figure 24. The 500 MHz ^{13}C -NMR spectrum of N-(2-propylpentanoyl)-N'-(4-methylphenyl)thiourea in CDCl_3

Background Subtract

C:\SATURN\DATA\LUT2

Date: 03/17/97 12:23:37

Comment: COL DB-5MS 0.25MMIDX30M

Average of: 572 to 572 Minus: 380 to 764

100% = 3075

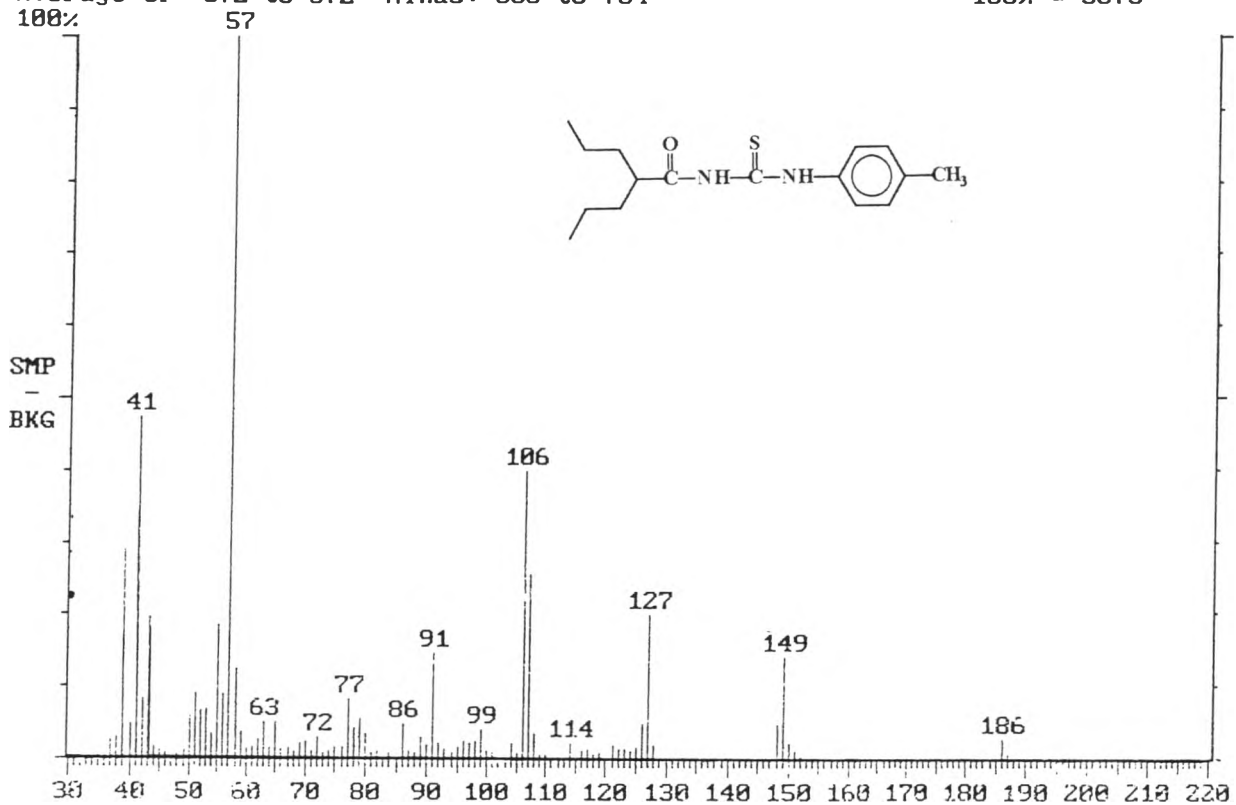


Figure 25. The EIMS spectrum of N-(2-propylpentanoyl)-N'-(4-methylphenyl)thiourea

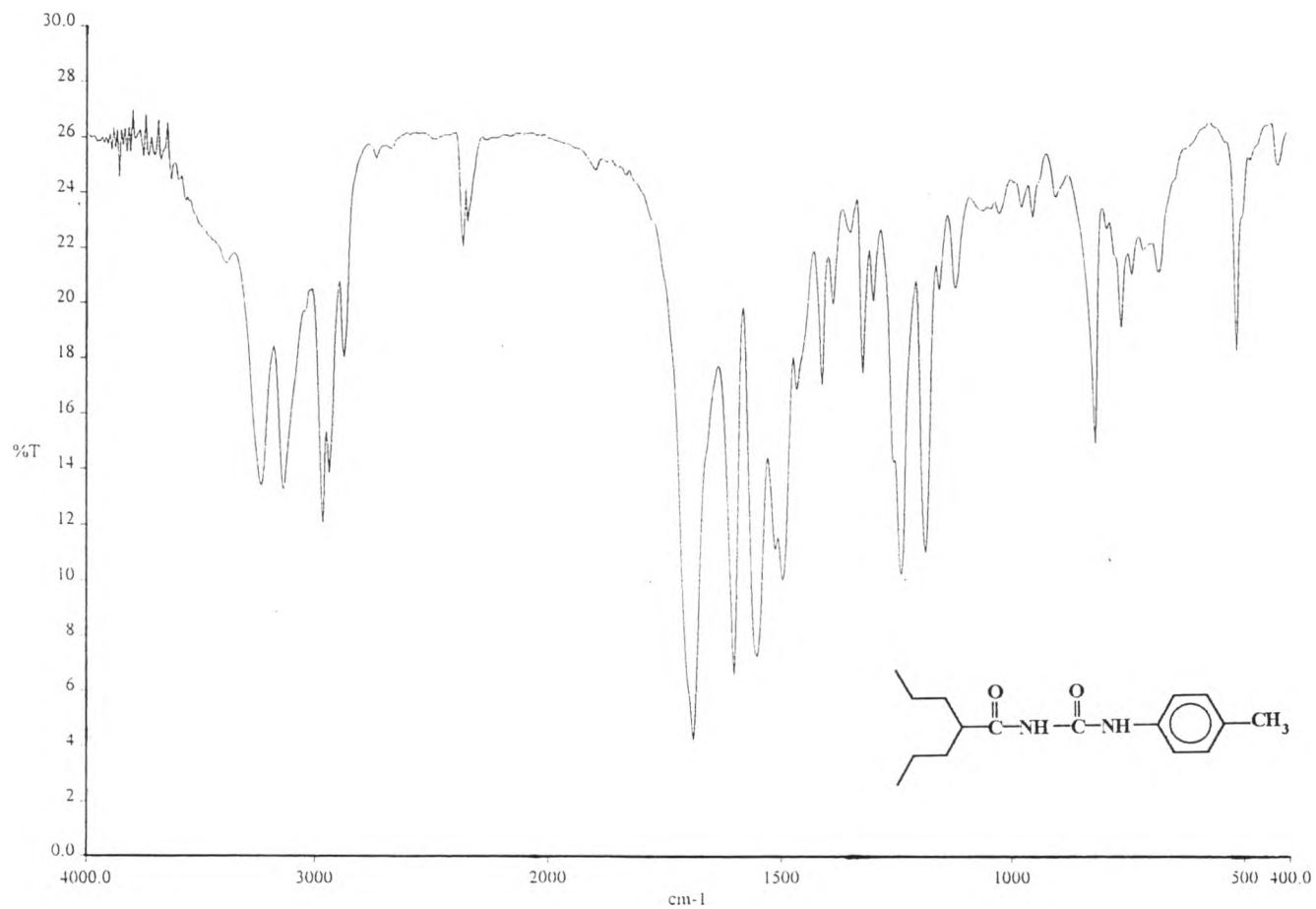


Figure 26. The IR spectrum (KBr) of *N*-(2-propylpentanoyl)-*N'*-(4-methylphenyl)urea

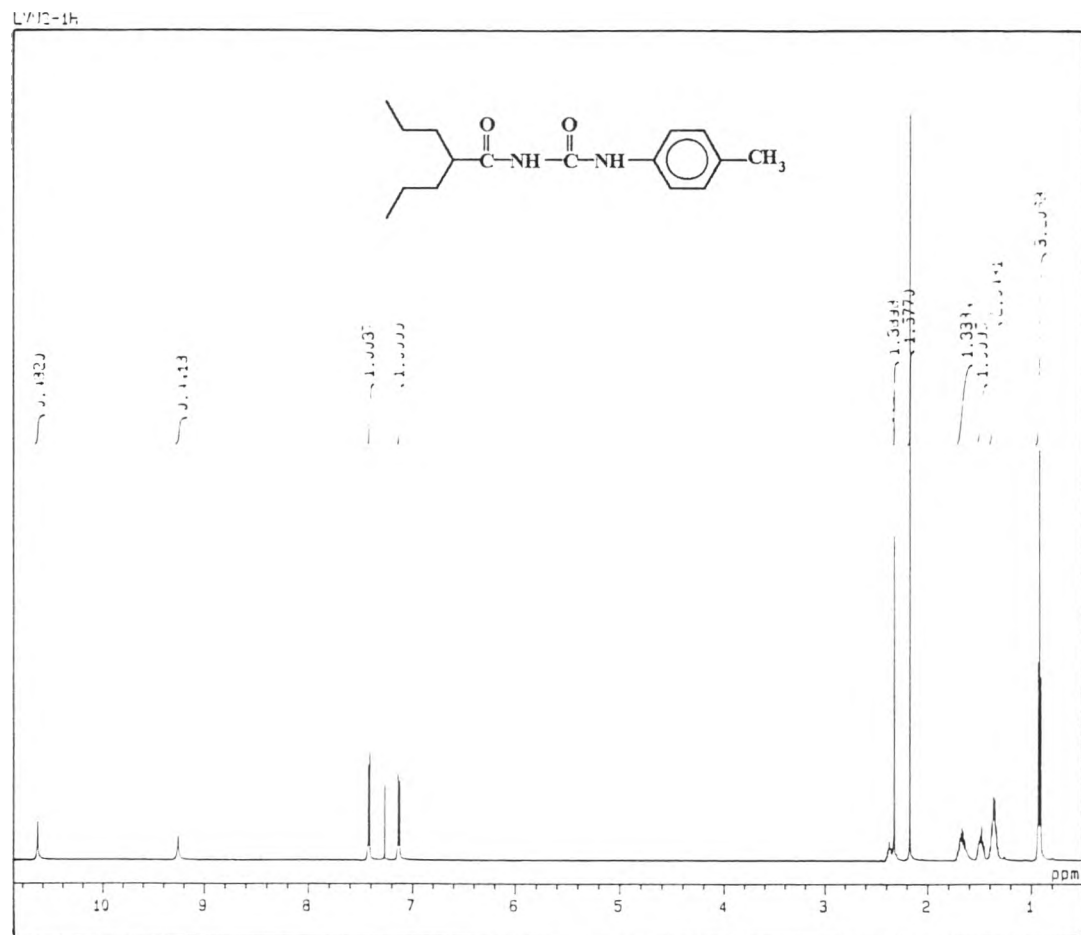


Figure 27. The 500 MHz $^1\text{H-NMR}$ spectrum of N-(2-propylpentanoyl)-N'-(4-methylphenyl)urea in CDCl_3

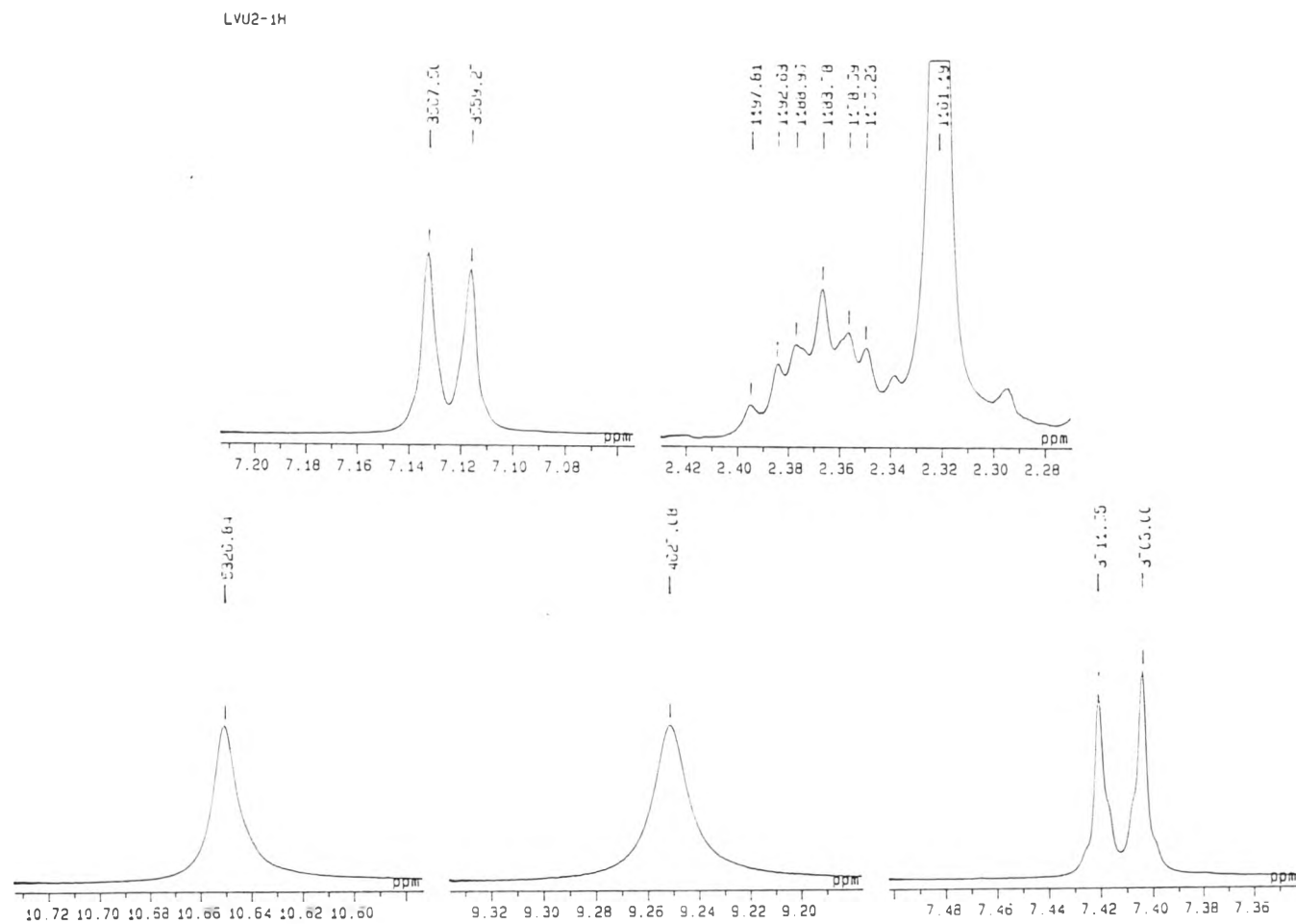


Figure .28 The 500 MHz ^1H -NMR spectrum of of N-(2-propylpentanoyl)-N'-(4-methylphenyl)urea in CDCl_3 (Enlarged scale)

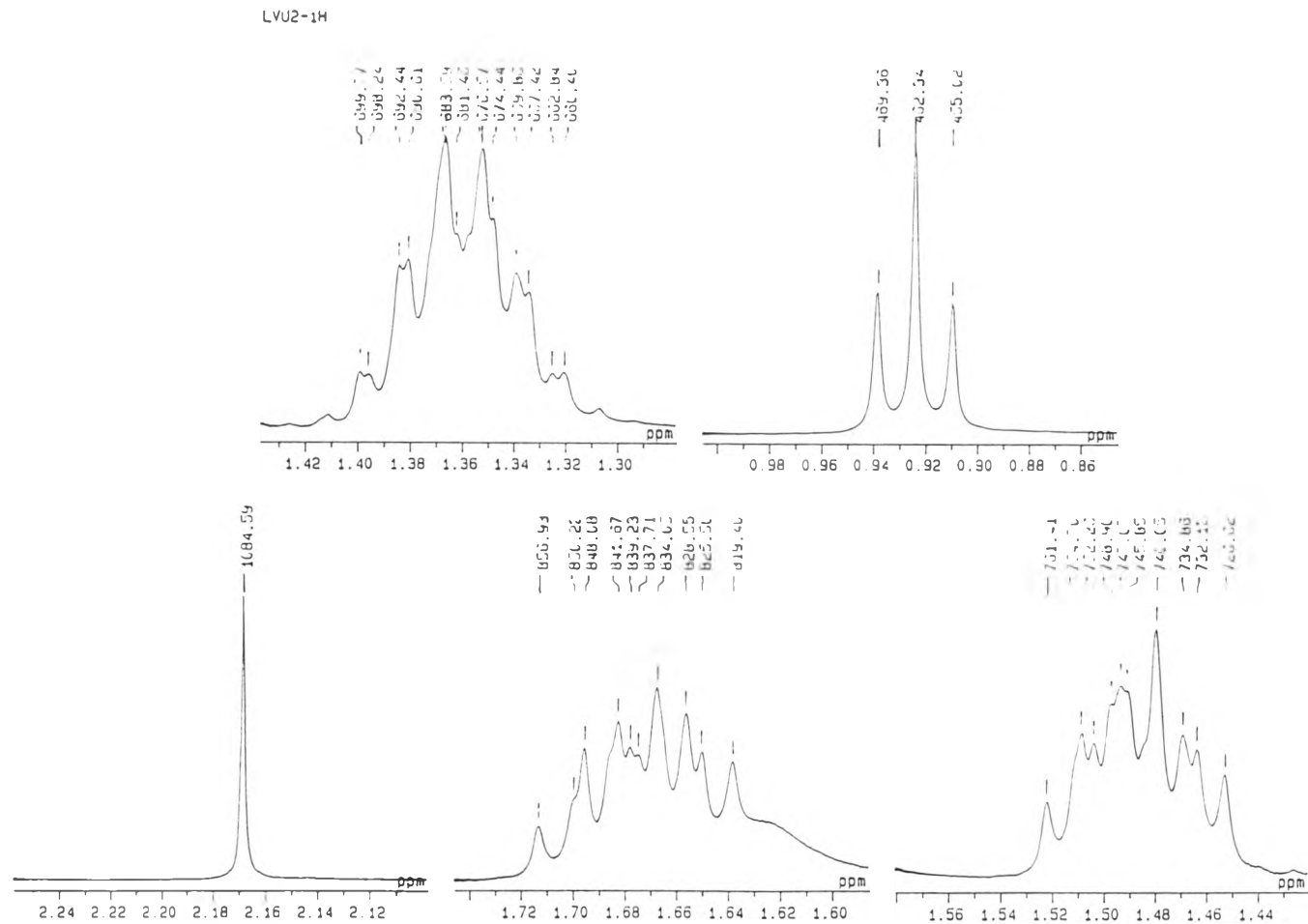


Figure 28.(Cont.) The 500 MHz ^1H -NMR spectrum of of N-(2-propylpentanoyl)-N'-(4-methylphenyl)urea in CDCl_3 (Enlarged scale)

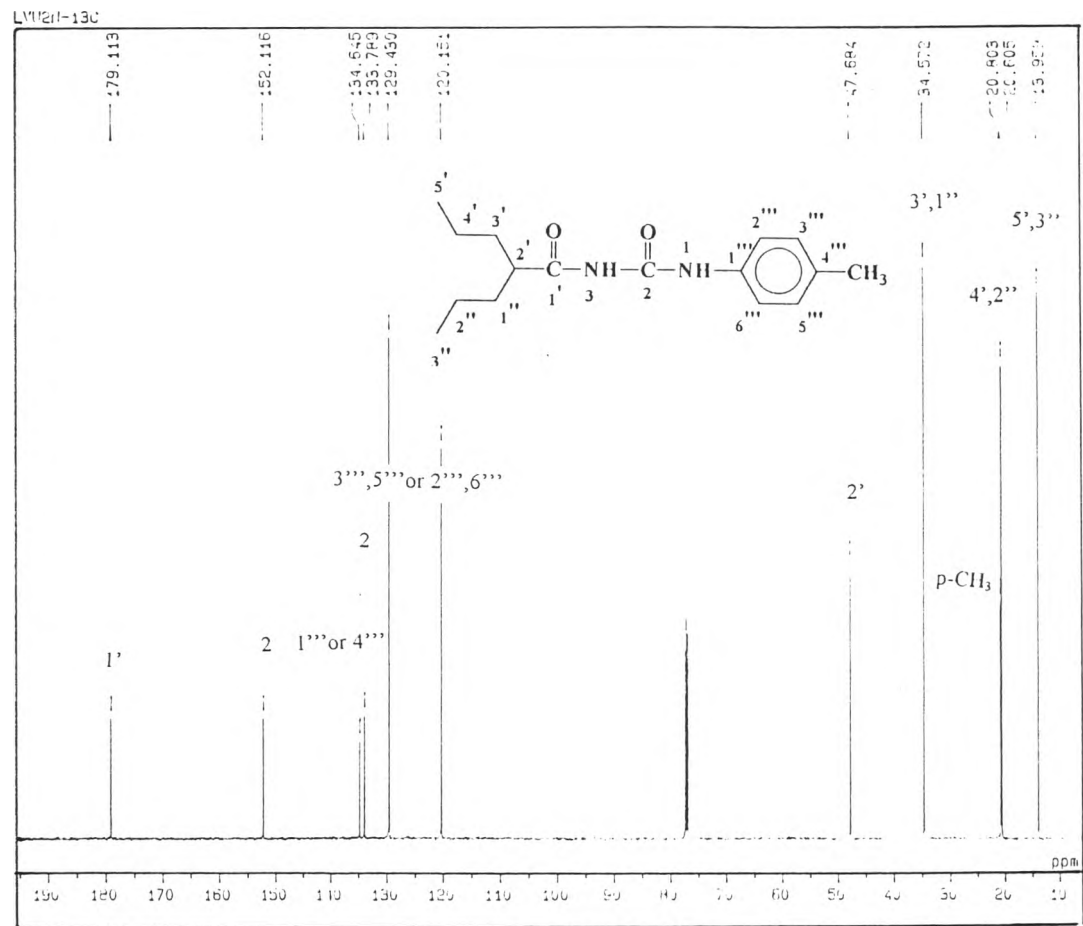


Figure 29. The 500 MHz ^{13}C -NMR spectrum of N-(2-propylpentanoyl)-N'-(4-methylphenyl)urea in CDCl_3

SZ3400001 Scan 302 RT=10:30 100%=37641 mv 20 Dec 96 13:20
LRP +EILVU 2

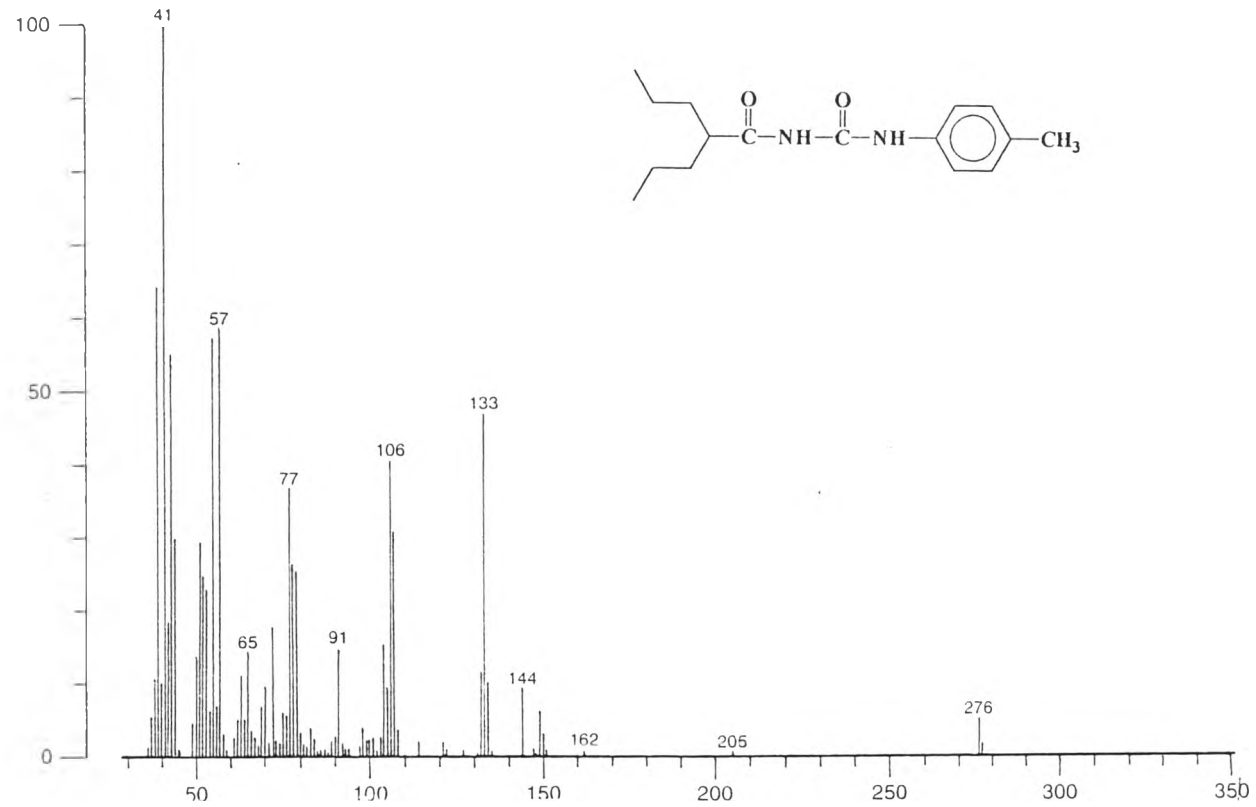


Figure 30. The EIMS spectrum of *N*-(2-propylpentanoyl)-*N'*-(4-methylphenyl)urea

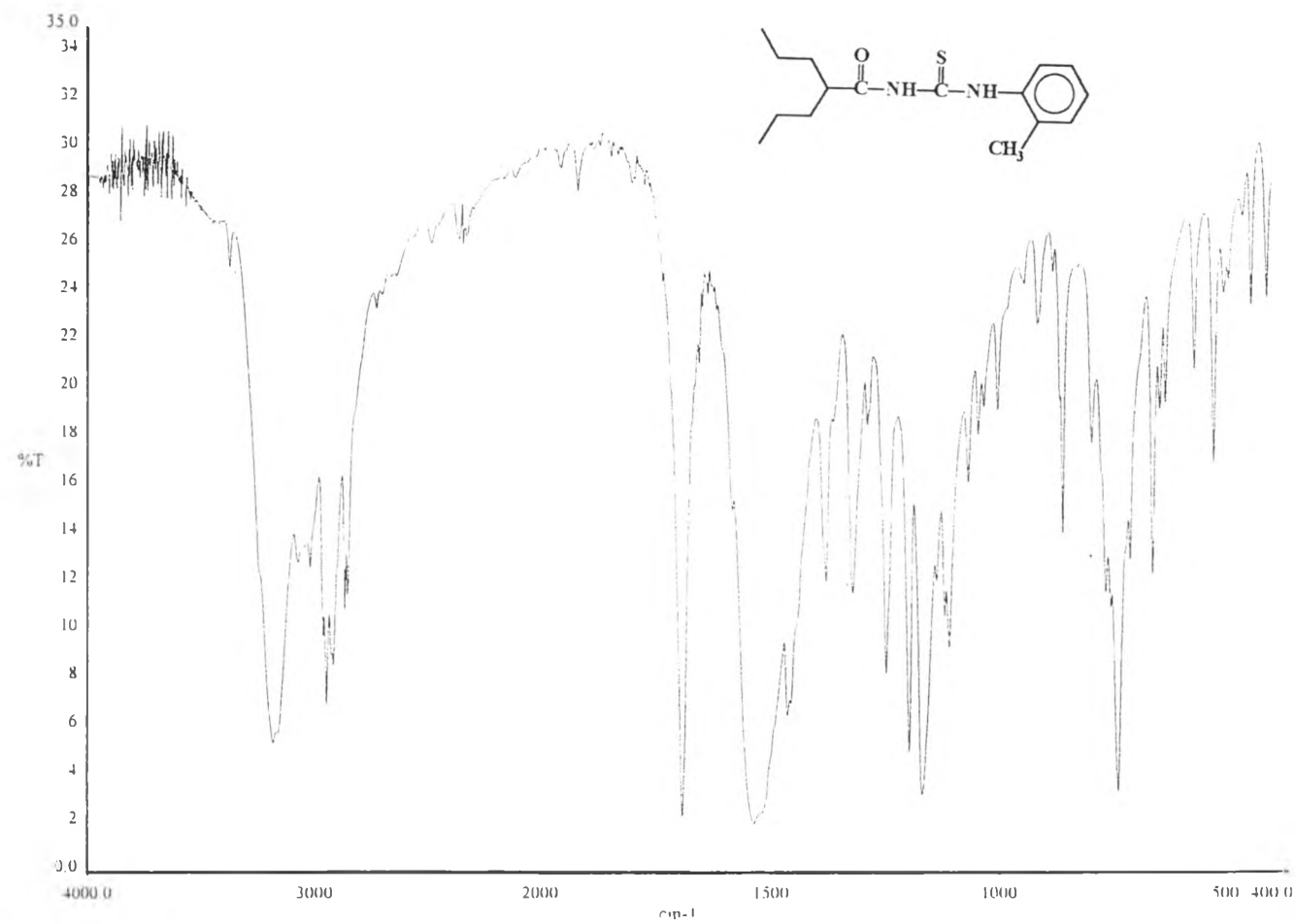


Figure 31. The IR spectrum (KBr) of *N*-(2-propylpentanoyl)-*N'*-(2-methylphenyl)thiourea

LVT3-1H

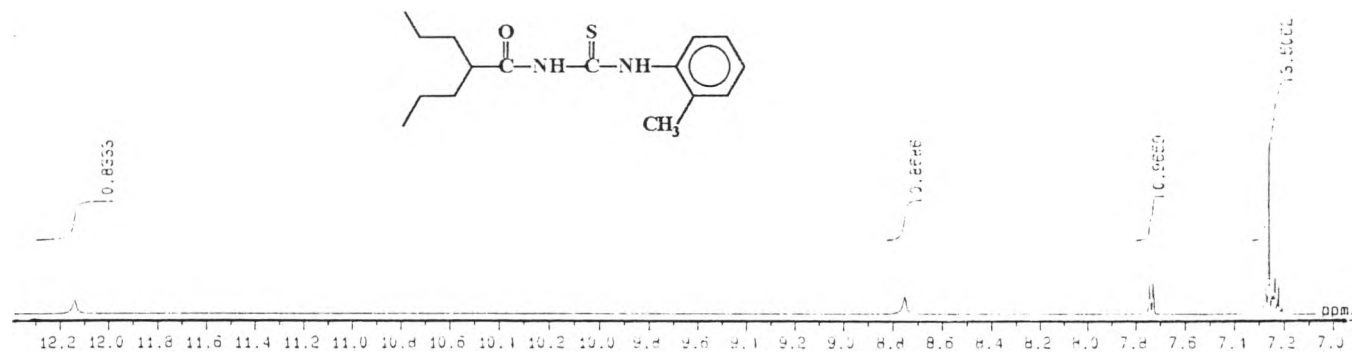
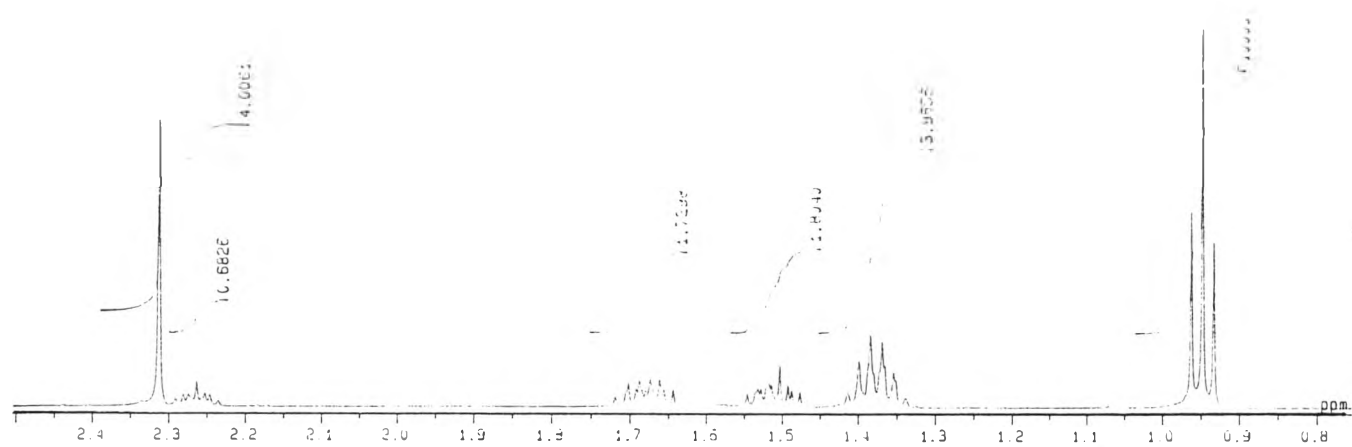


Figure 32. The 500 MHz ^1H -NMR spectrum of N -(2-propylpentanoyl)- N' -(2-methylphenyl)thiourea in CDCl_3

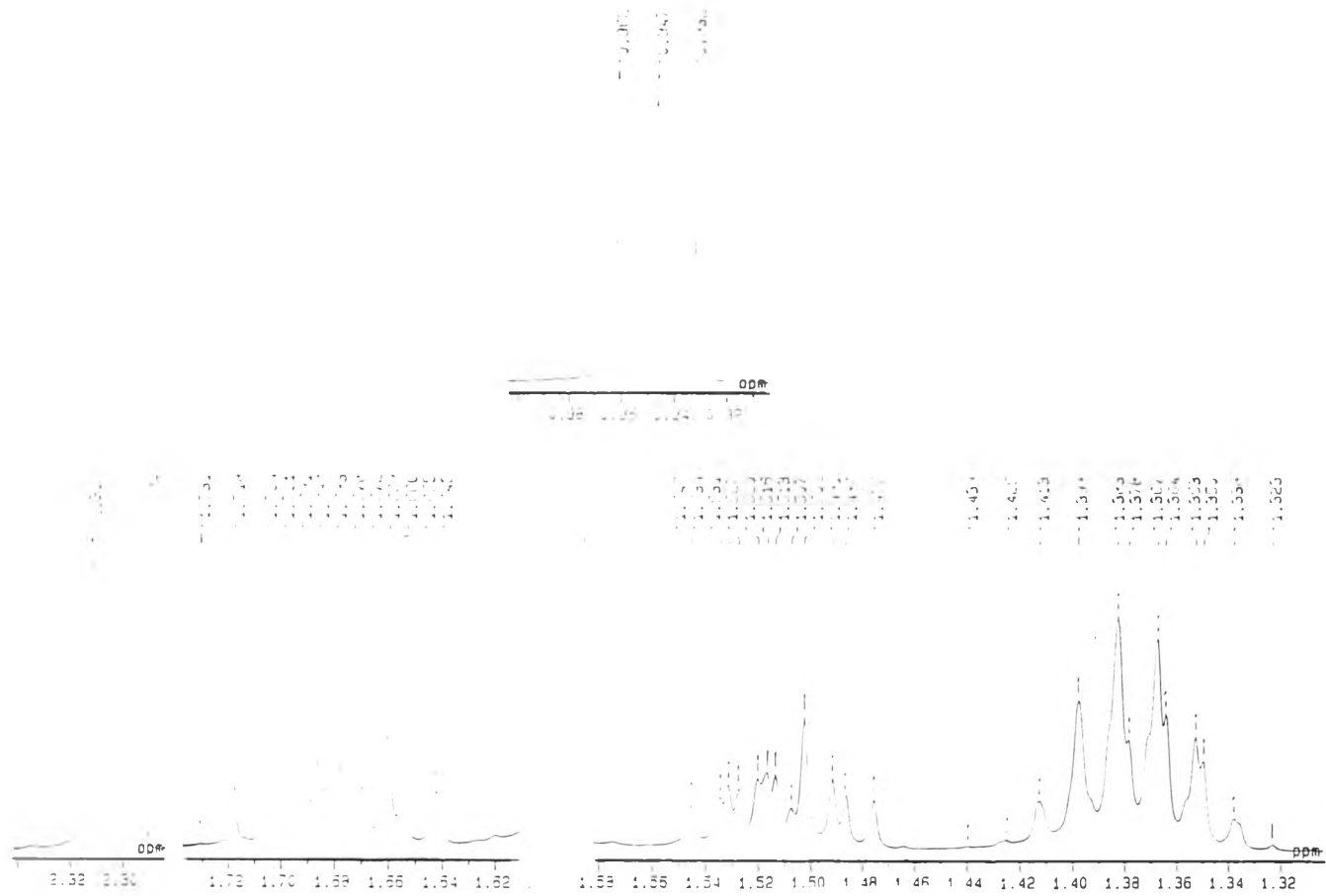


Figure 33. The 500 MHz $^1\text{H-NMR}$ spectrum of N -(2-propylpentanoyl)- N' -(2-methylphenyl)thiourea in CDCl_3 (Enlarged scale)

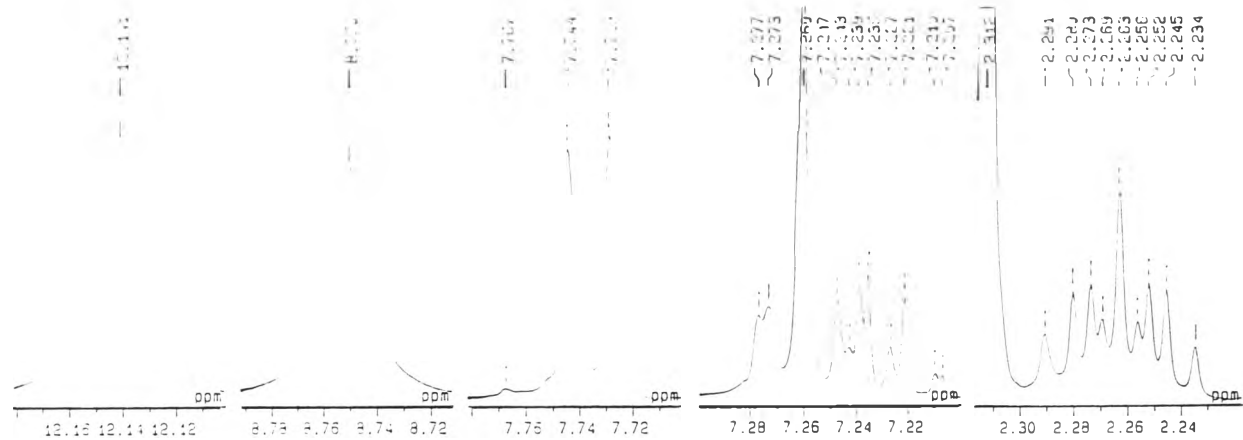


Figure 33.(Cont.) The 500 MHz ¹H-NMR spectrum of of N-(2-propylpentanoyl)-N'-(2-methylphenyl)thiourea in CDCl₃ (Enlarged scale)

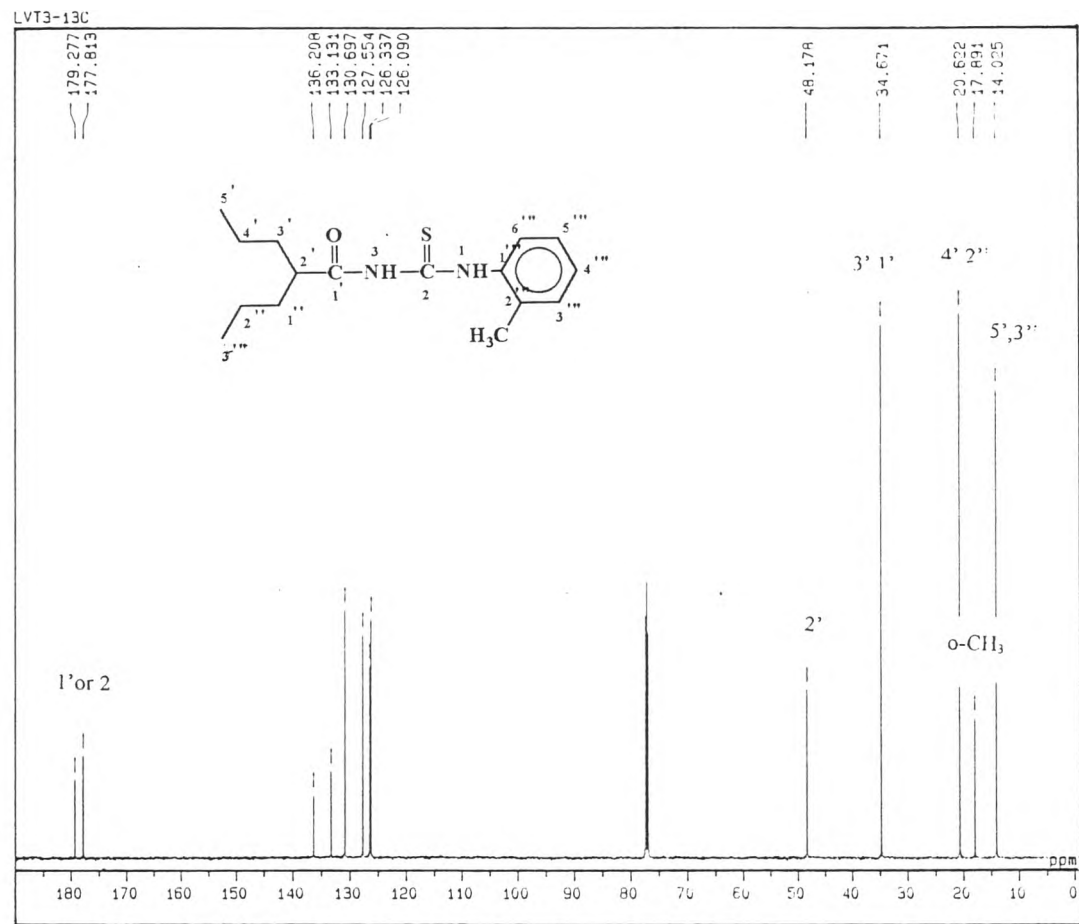


Figure 34. The 500 MHz ¹³C-NMR spectrum of N-(2-propylpentanoyl)-N'-(2-methylphenyl)thiourea in CDCl₃

Background Subtract

C:\SATURN\DATA\LVT3

Date: 03/17/97 13:19:09

Comment: COL DB-5MS 0.25MMIDX30M

Average of: 366 to 370 Minus: 338 to 342

100% = 11271

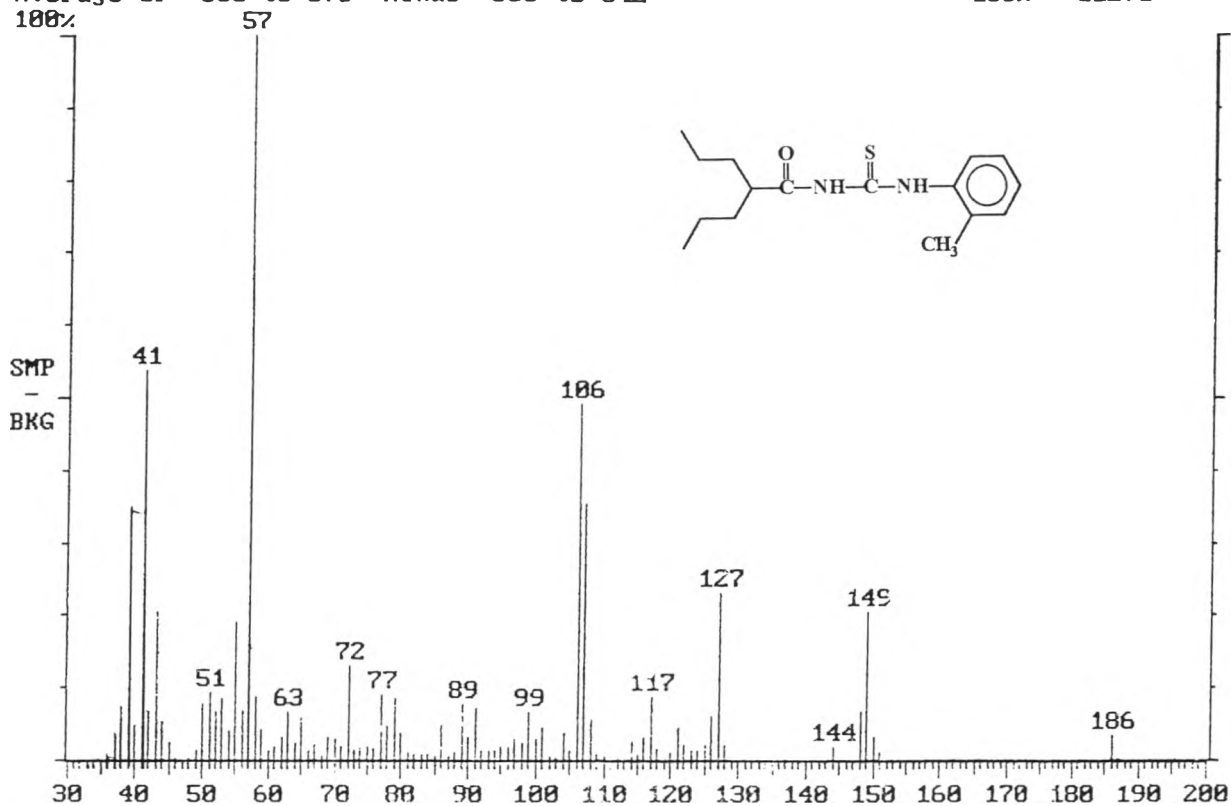


Figure 35. The EIMS spectrum of N-(2-propylpentanoyl)-N'-(2-methylphenyl)thiourea

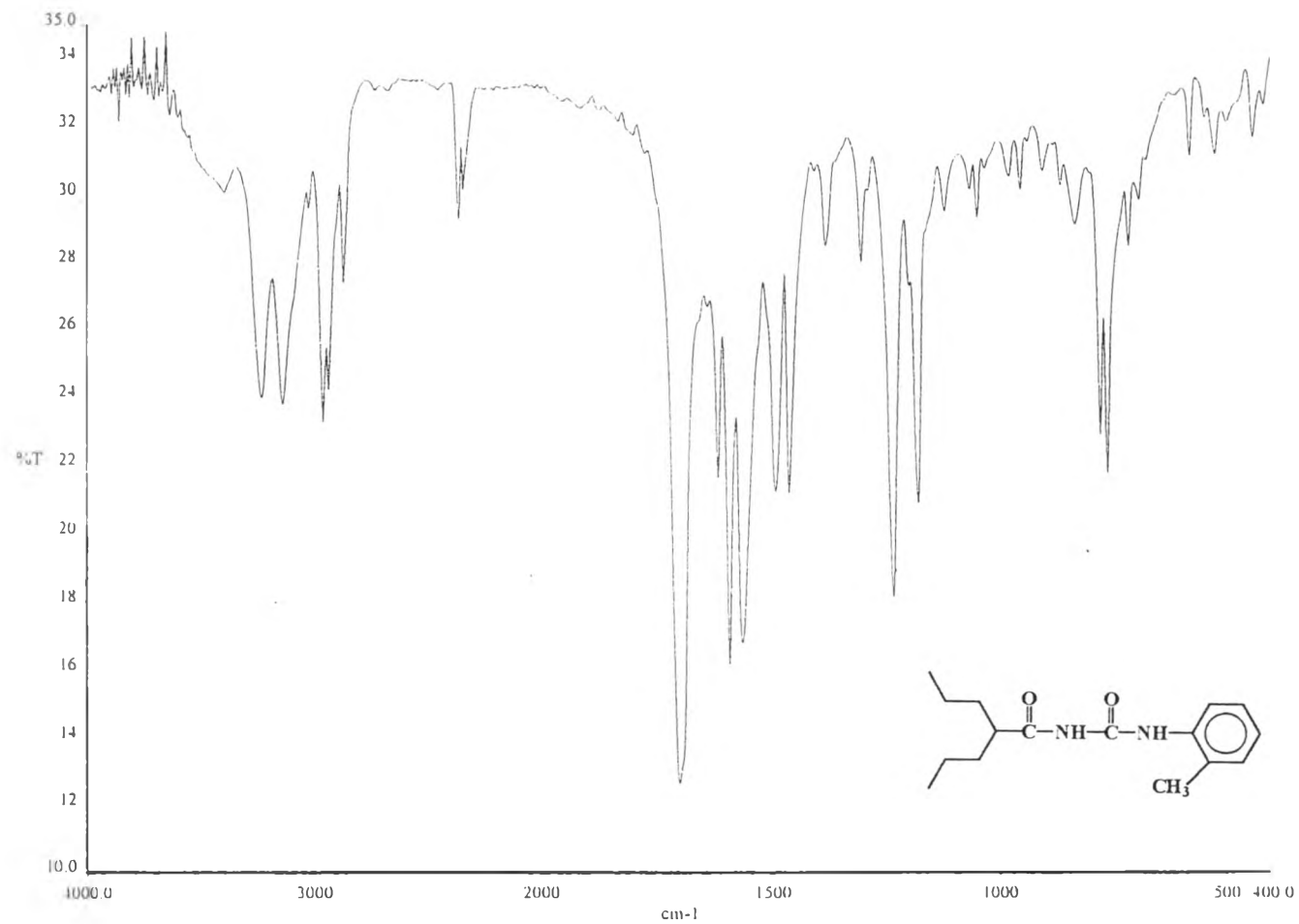


Figure 36. The IR spectrum (KBr) of *N*-(2-propylpentanoyl)-*N'*-(2-methylphenyl)urea

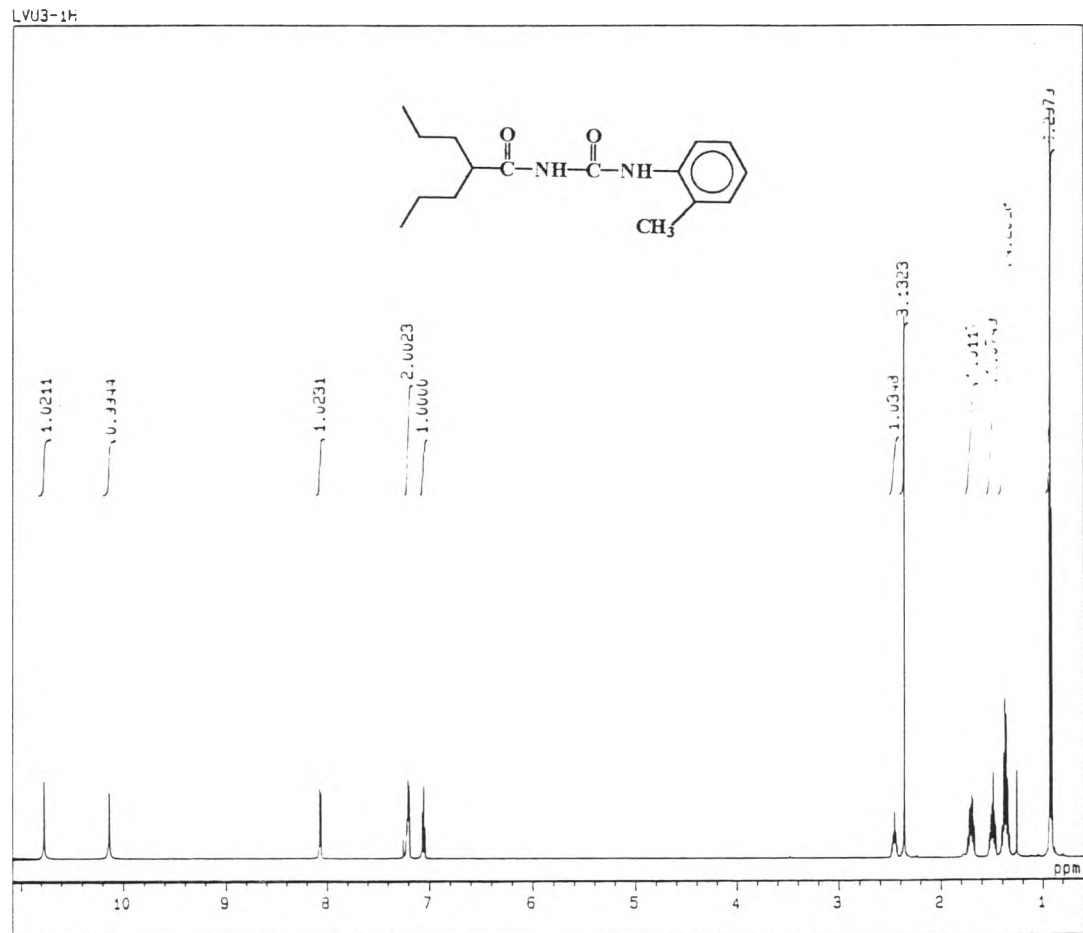


Figure 37. The 500 MHz $^1\text{H-NMR}$ spectrum of *N*-(2-propylpentanoyl)-*N'*-(2-methylphenyl)urea in CDCl_3

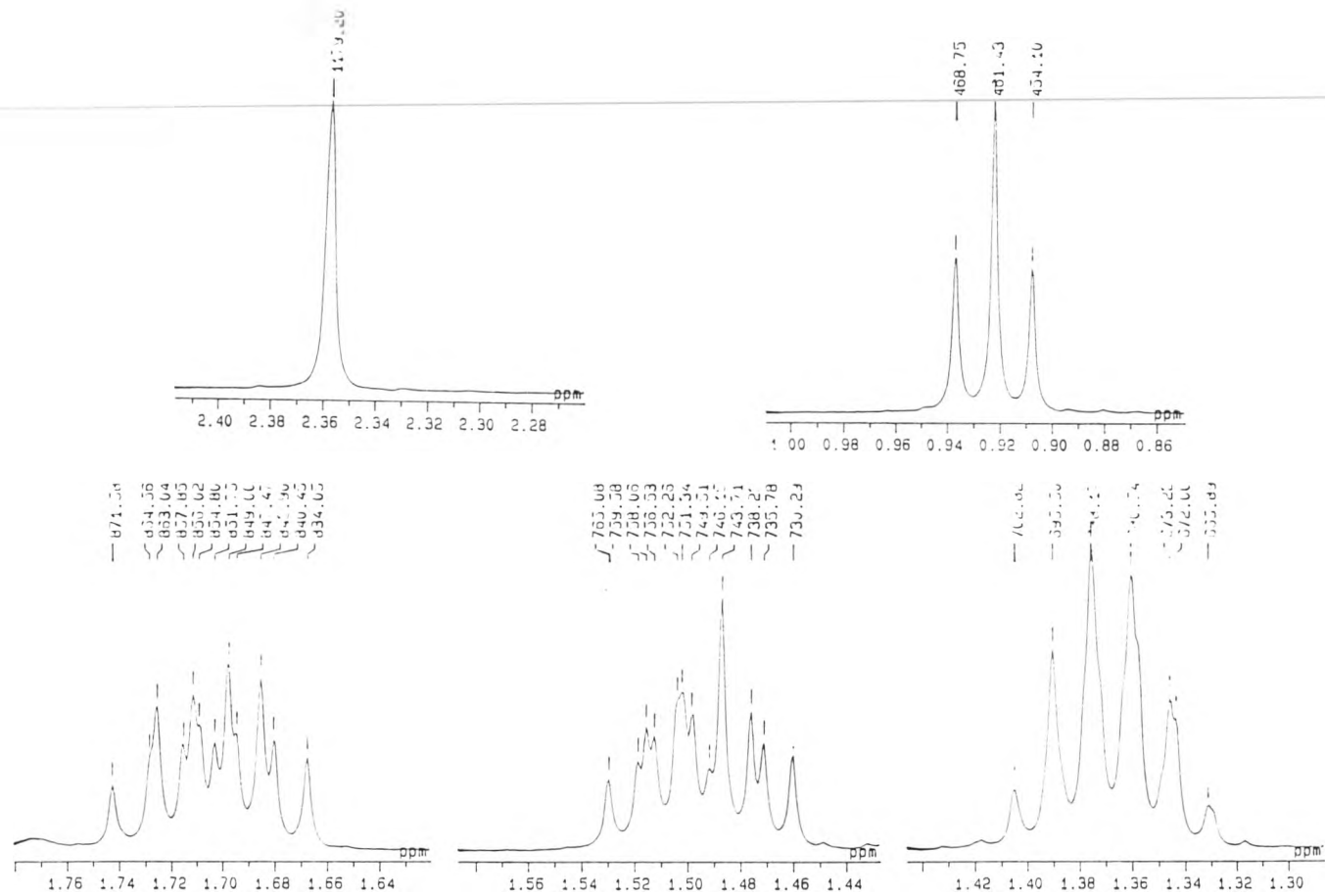


Figure 38. The 500 MHz $^1\text{H-NMR}$ spectrum of of N-(2-propylpentanoyl)-N'-(2-methylphenyl)urea in CDCl_3 (Enlarged scale)

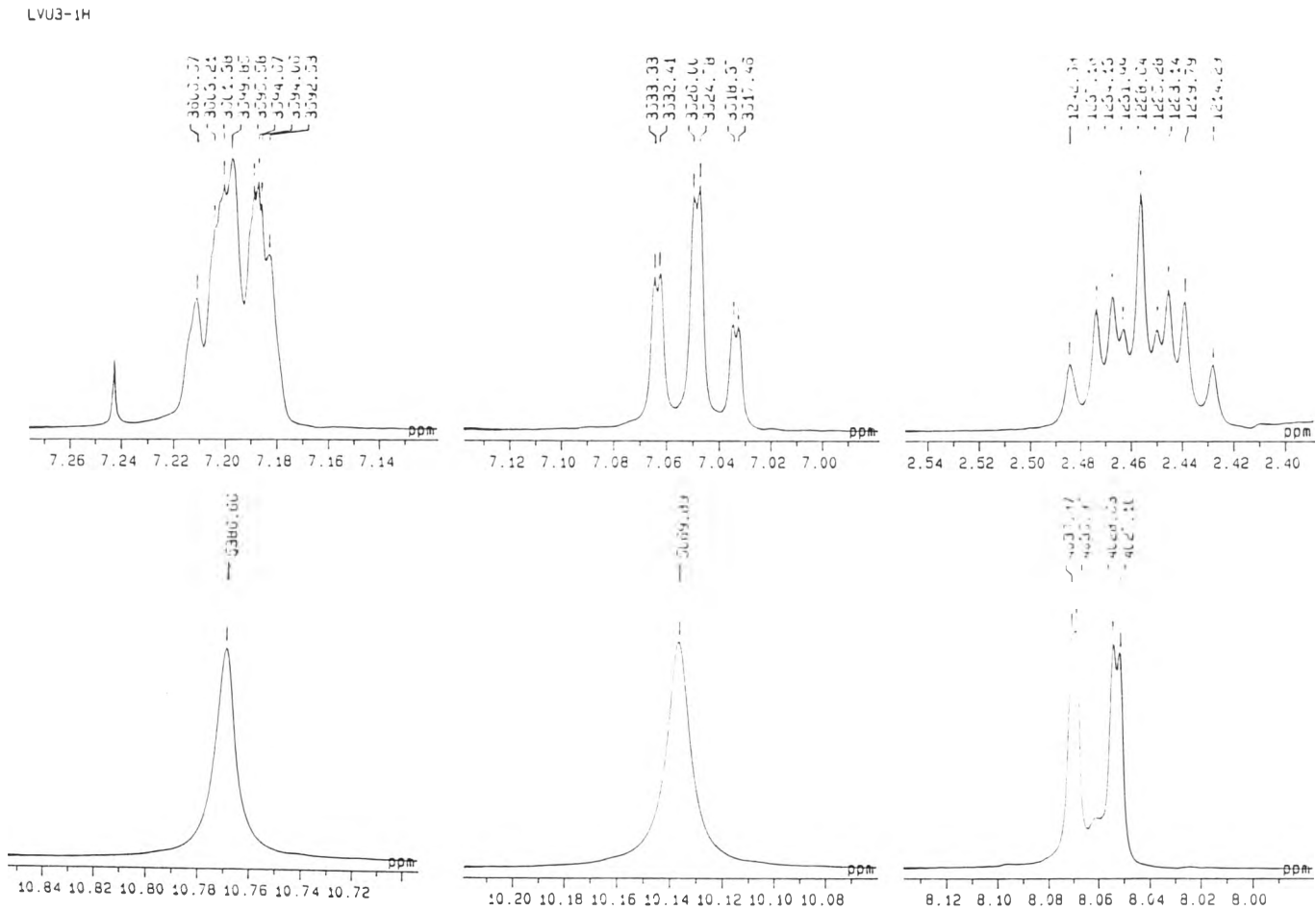


Figure 38.(Cont.) The 500 MHz ^1H -NMR spectrum of of N-(2-propylpentanoyl)-N'-(2-methylphenyl)urea in CDCl_3 (Enlarged scale)

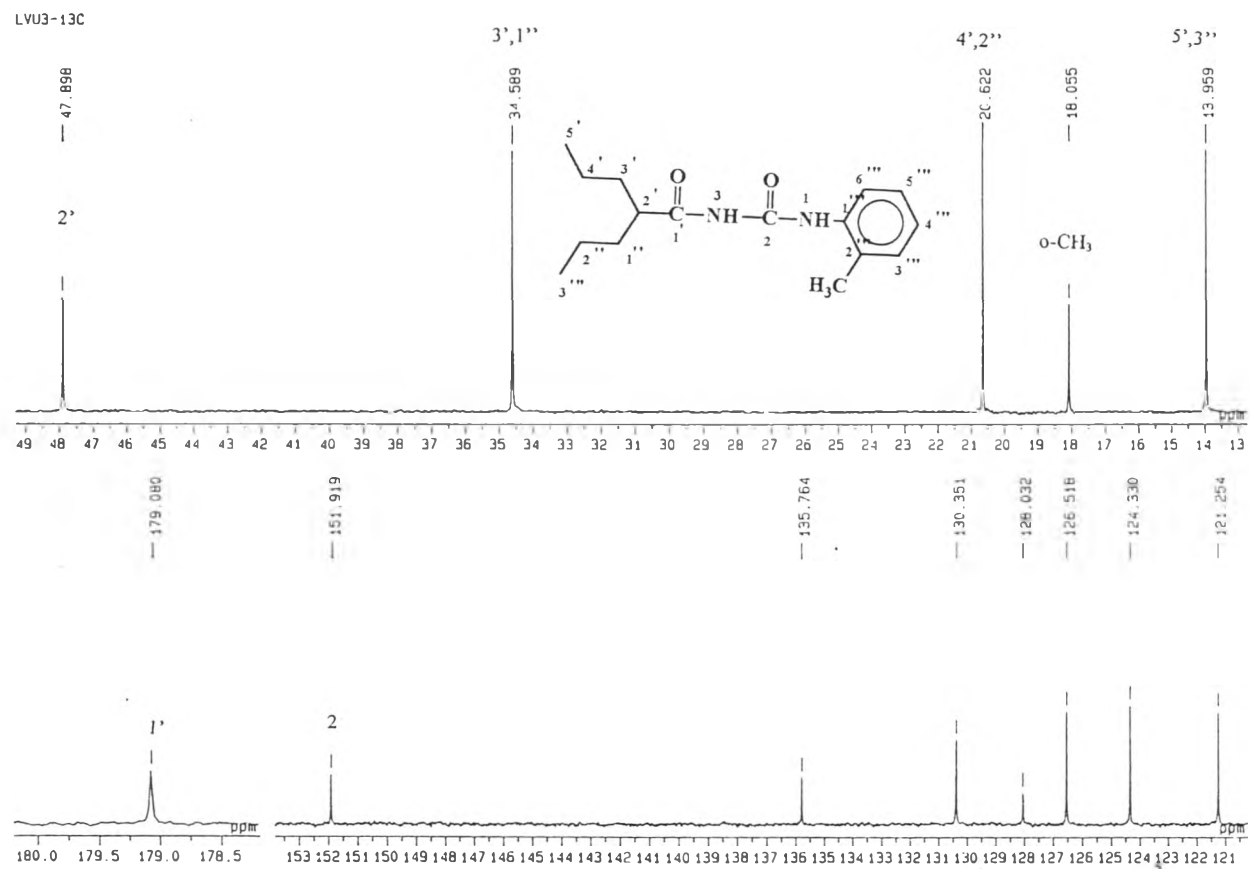


Figure 39. The 500 MHz ¹³C-NMR spectrum of N-(2-propylpentanoyl)-N'-(2-methylphenyl)urea in CDCl₃

SZ3390001 Scan 341 RT=11:51 100%=140471 mv 20 Dec 96 11:44
LRP +EI LVU 3

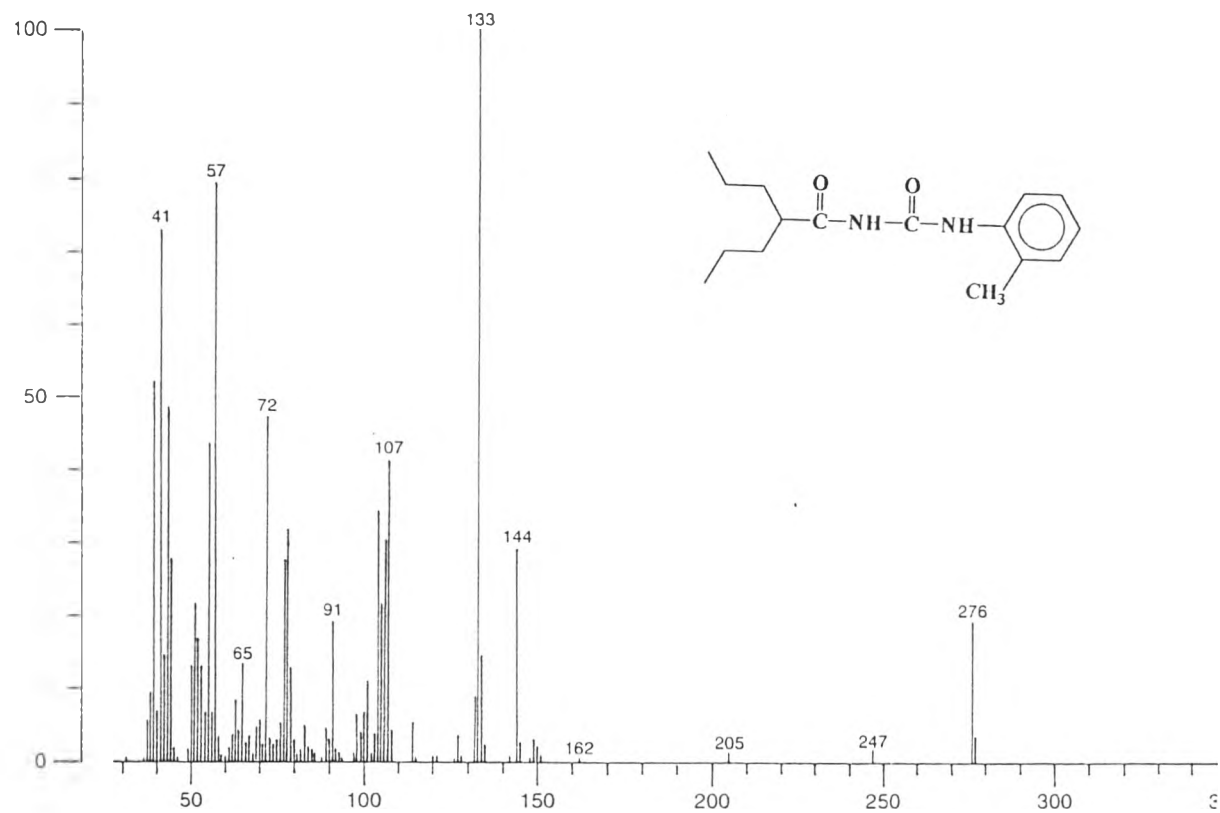


Figure 40. The EIMS spectrum of *N*-(2-propylpentanoyl)-*N'*-(2-methylphenyl)urea

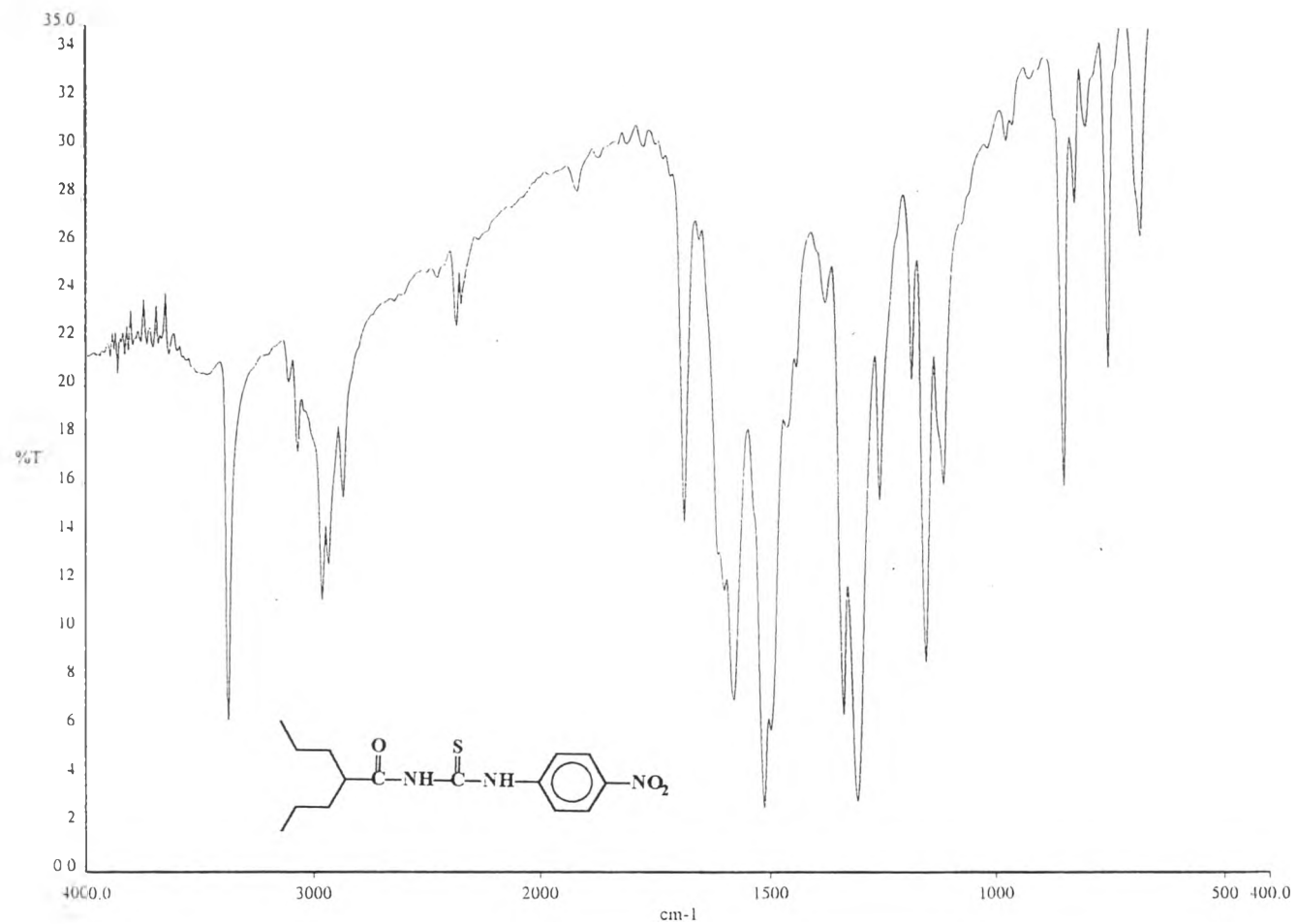


Figure 41. The IR spectrum (KBr) of *N*-(2-propylpentanoyl)-*N'*-(4-nitrophenyl) thiourea

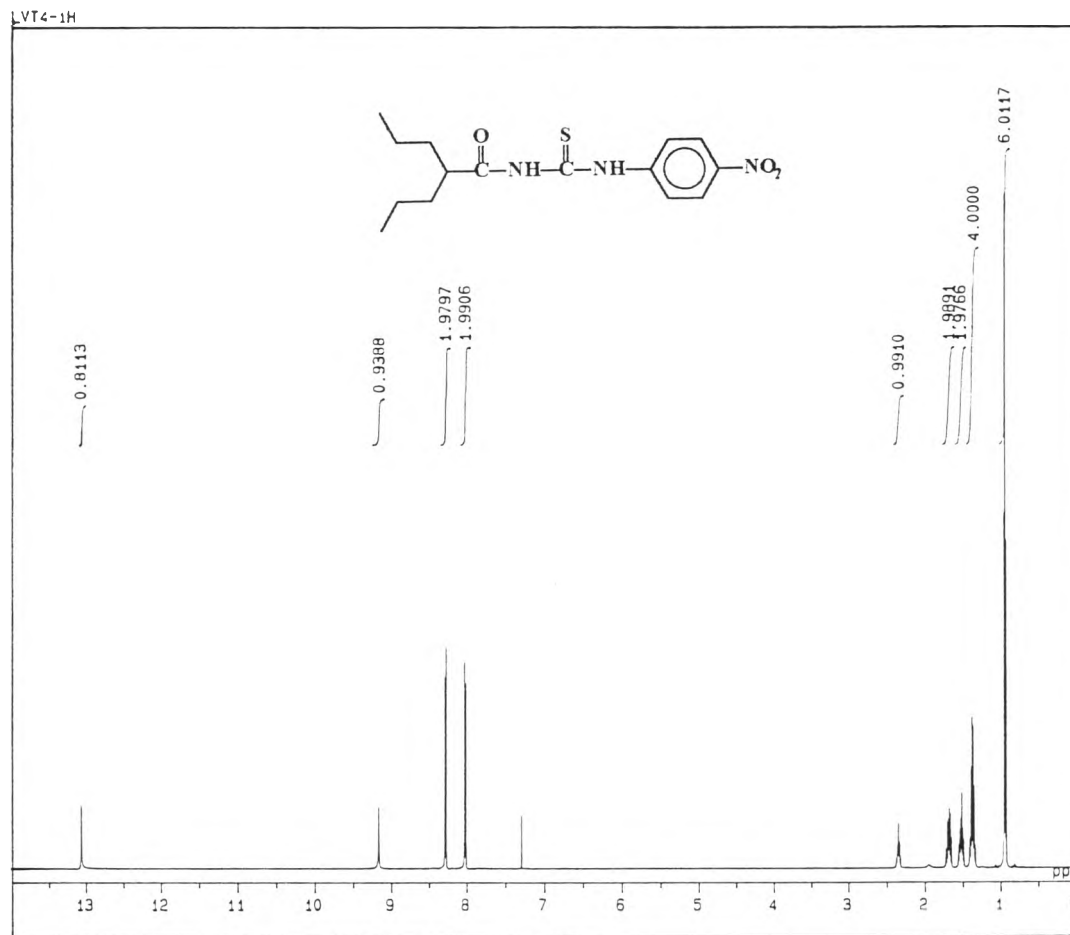


Figure 42. The 500 MHz ^1H -NMR spectrum of N-(2-propylpentanoyl)-N'-(4-nitrophenyl)thiourea in CDCl_3

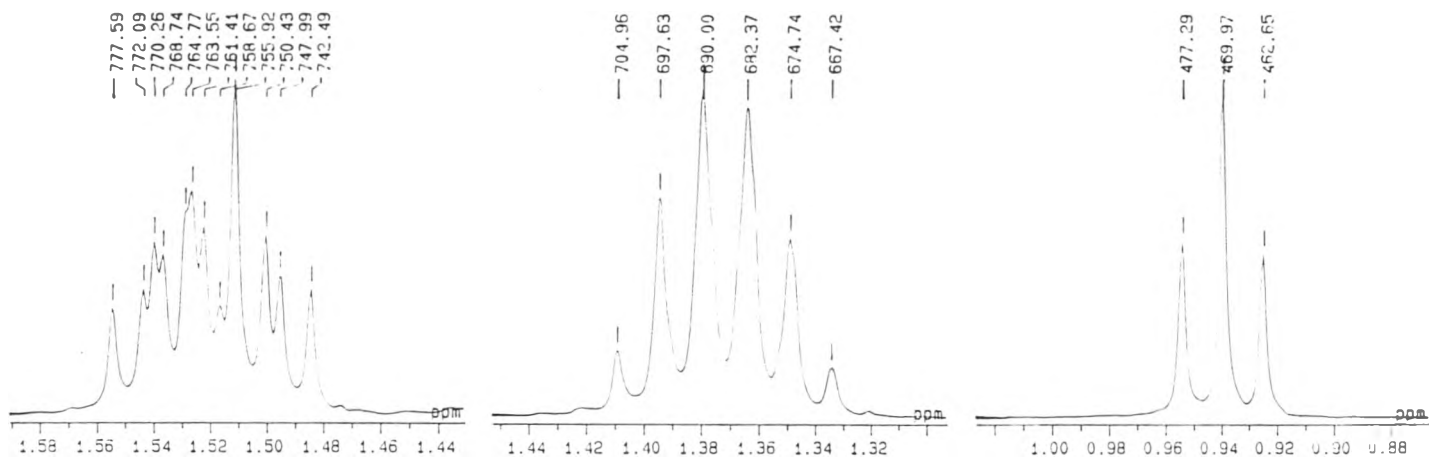


Figure 43. The 500 MHz ¹H-NMR spectrum of N-(2-propylpentanoyl)-N'-(4-nitrophenyl)thiourea in CDCl₃ (Enlarged scale)

LVT4-1H

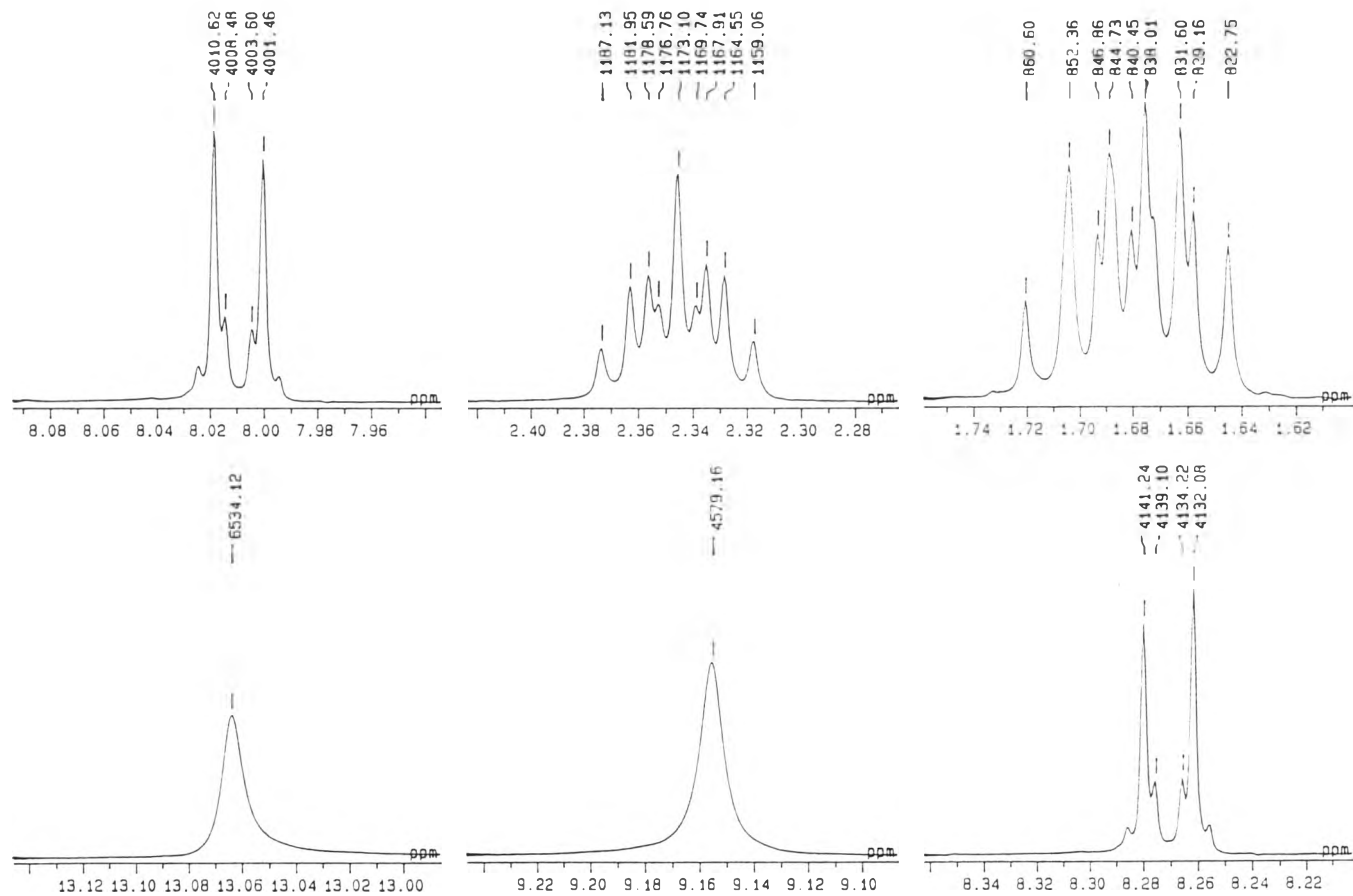


Figure 43.(Cont.) The 500 MHz ^1H -NMR spectrum of of N-(2-propylpentanoyl)-N'-(2-nitrophenyl)thiourea in CDCl_3 (Enlarged scale)

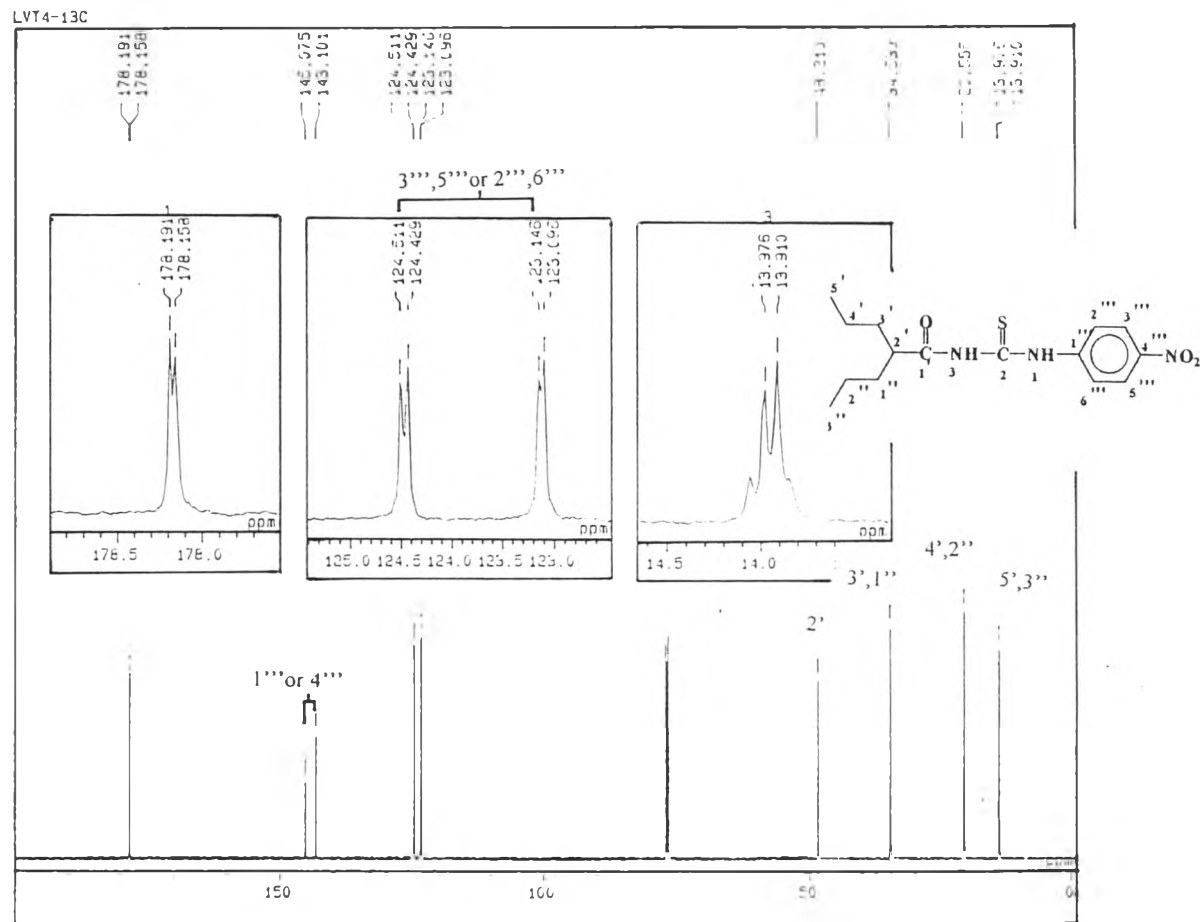


Figure 44. The 500 MHz ¹³C-NMR spectrum of *N*-(2-propylpentanoyl)-*N'*-(4-nitrophenyl)thiourea in CDCl₃

SZ3410001 Scan 384 RT=13:21 100%=113454 mv 20 Dec 96 15:17
LRP +EI LVT 4

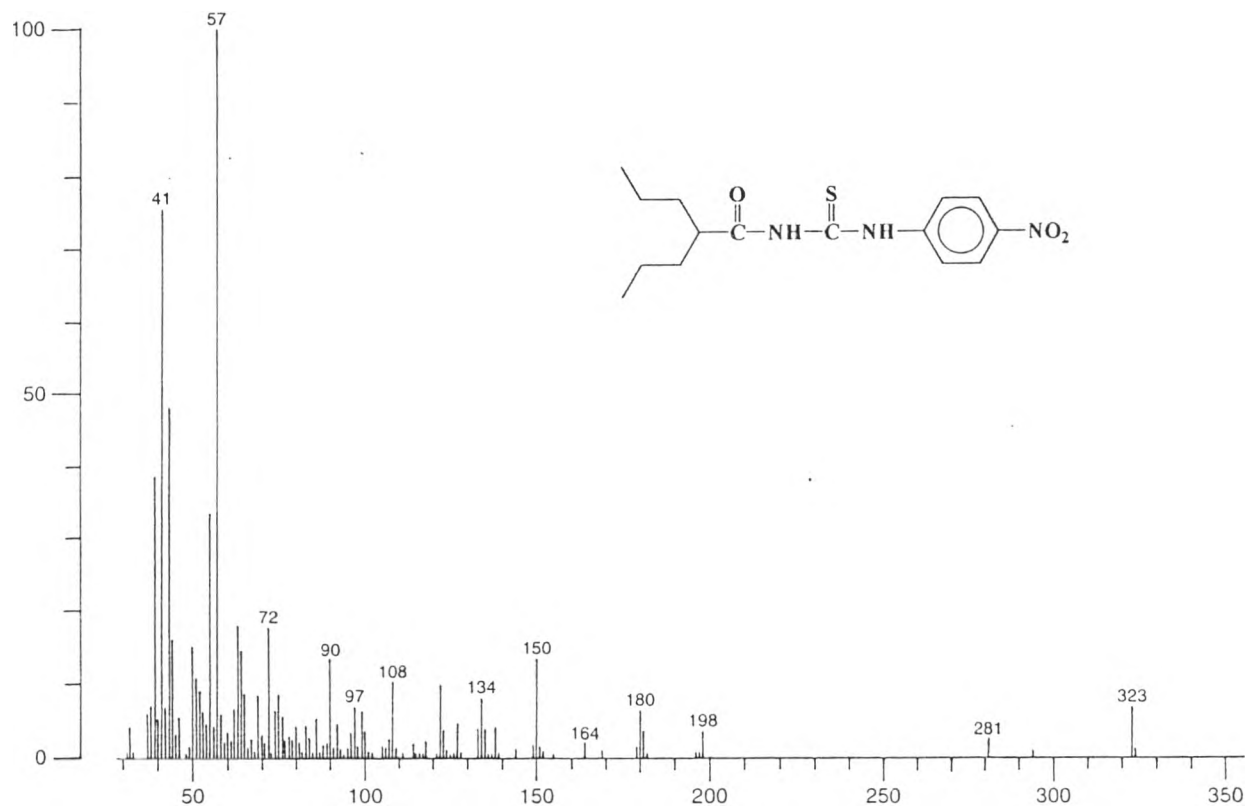


Figure 45. The EIMS spectrum of *N*-(2-propylpentanoyl)-*N'*-(4-nitrophenyl)thiourea

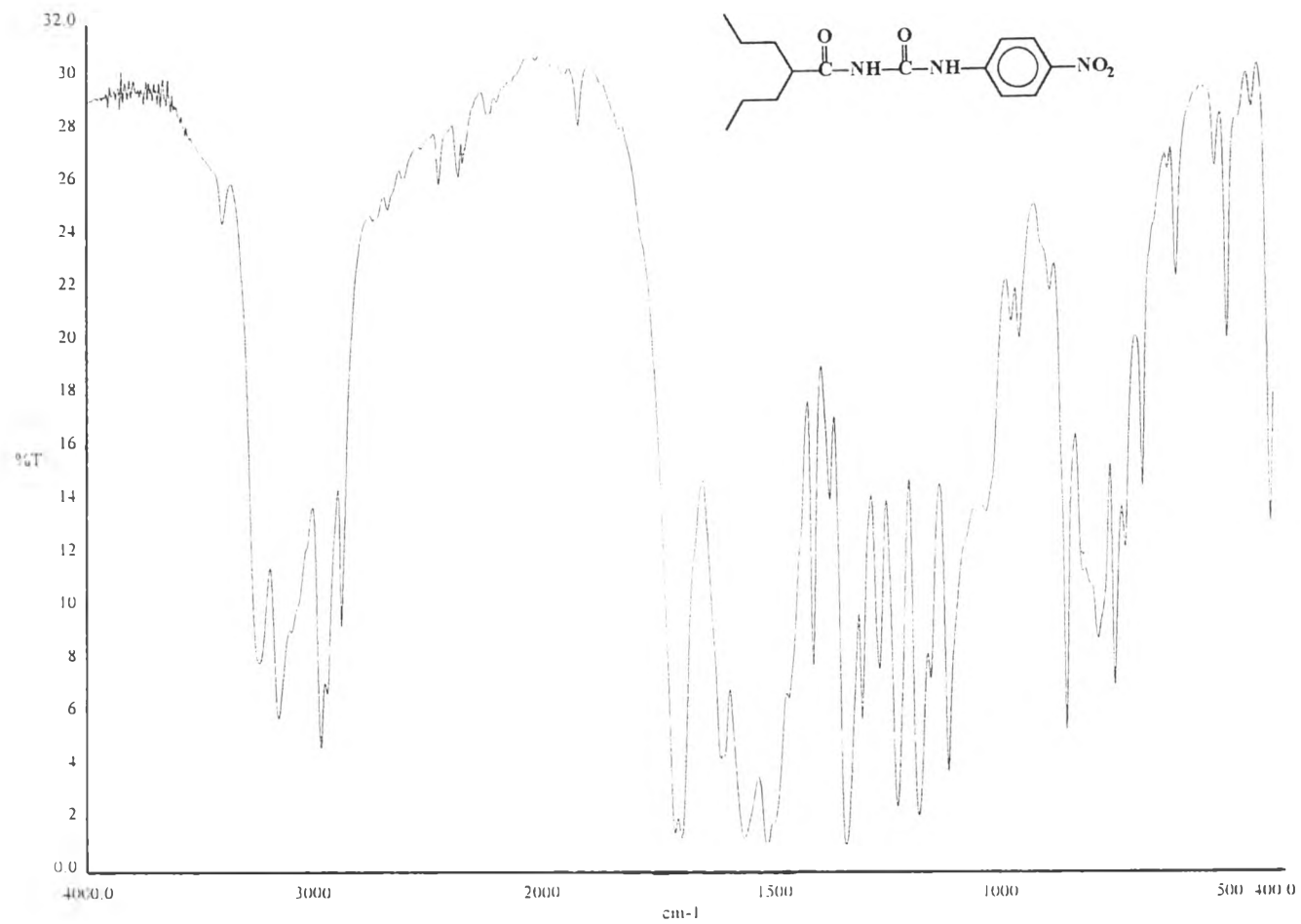


Figure 46. The IR spectrum (KBr) of N-(2-propylpentanoyl)-N'-(4-nitrophenyl)urea

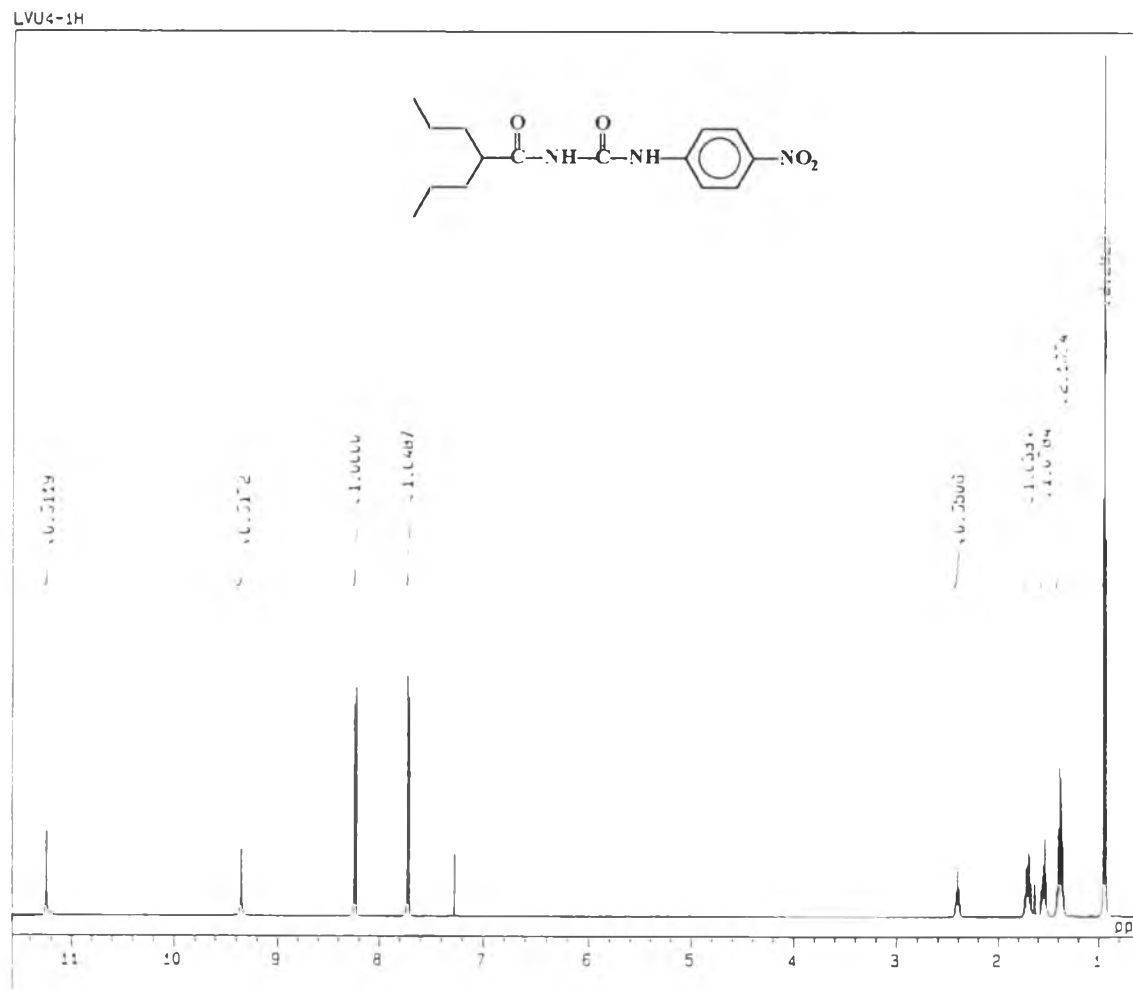


Figure 47. The 500 MHz ^1H -NMR spectrum of N-(2-propylpentanoyl)-N'-(4-nitrophenyl)urea in CDCl_3

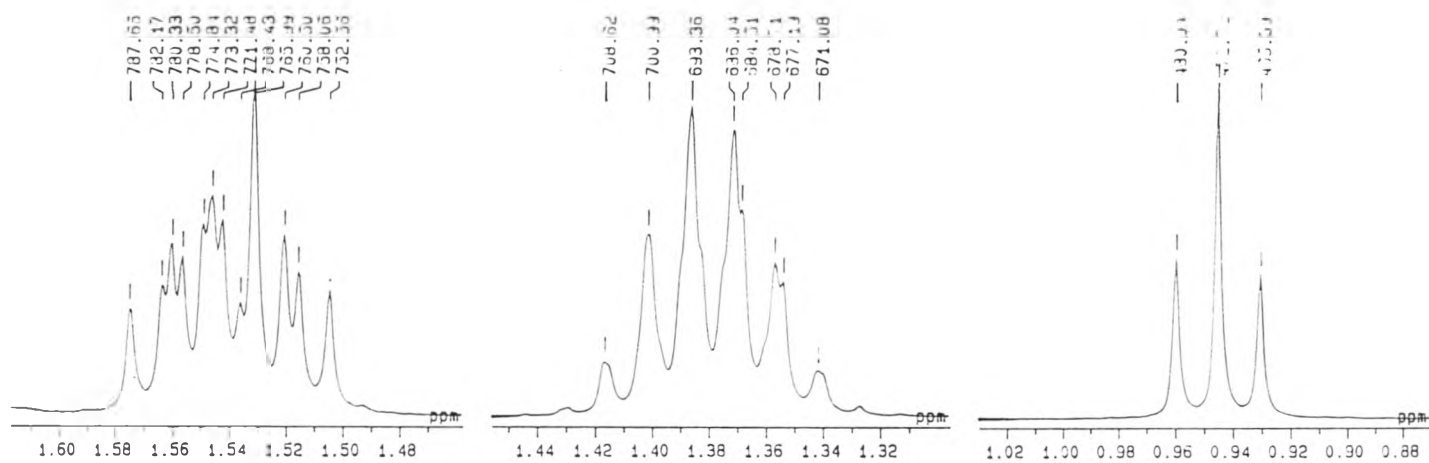


Figure 48. The 500 MHz ¹H-NMR spectrum of of N-(2-propylpentanoyl)-N'-(4-nitrophenyl)urea in CDCl₃ (Enlarged scale)

LVU4-1H

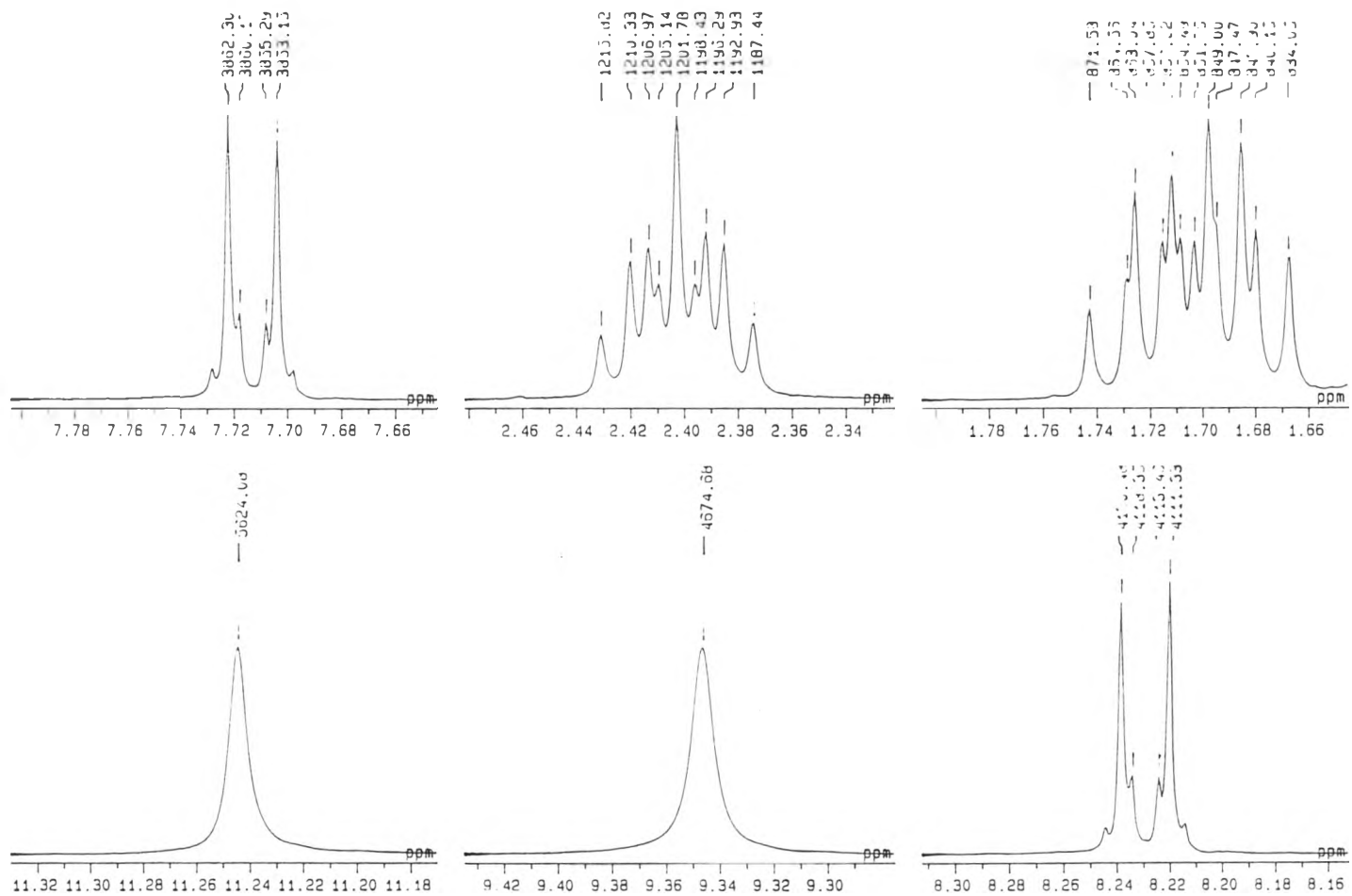


Figure 48.(Cont.) The 500 MHz ^1H -NMR spectrum of of N-(2-propylpentanoyl)-N'-(4-nitrophenyl)urea in CDCl_3 (Enlarged scale)

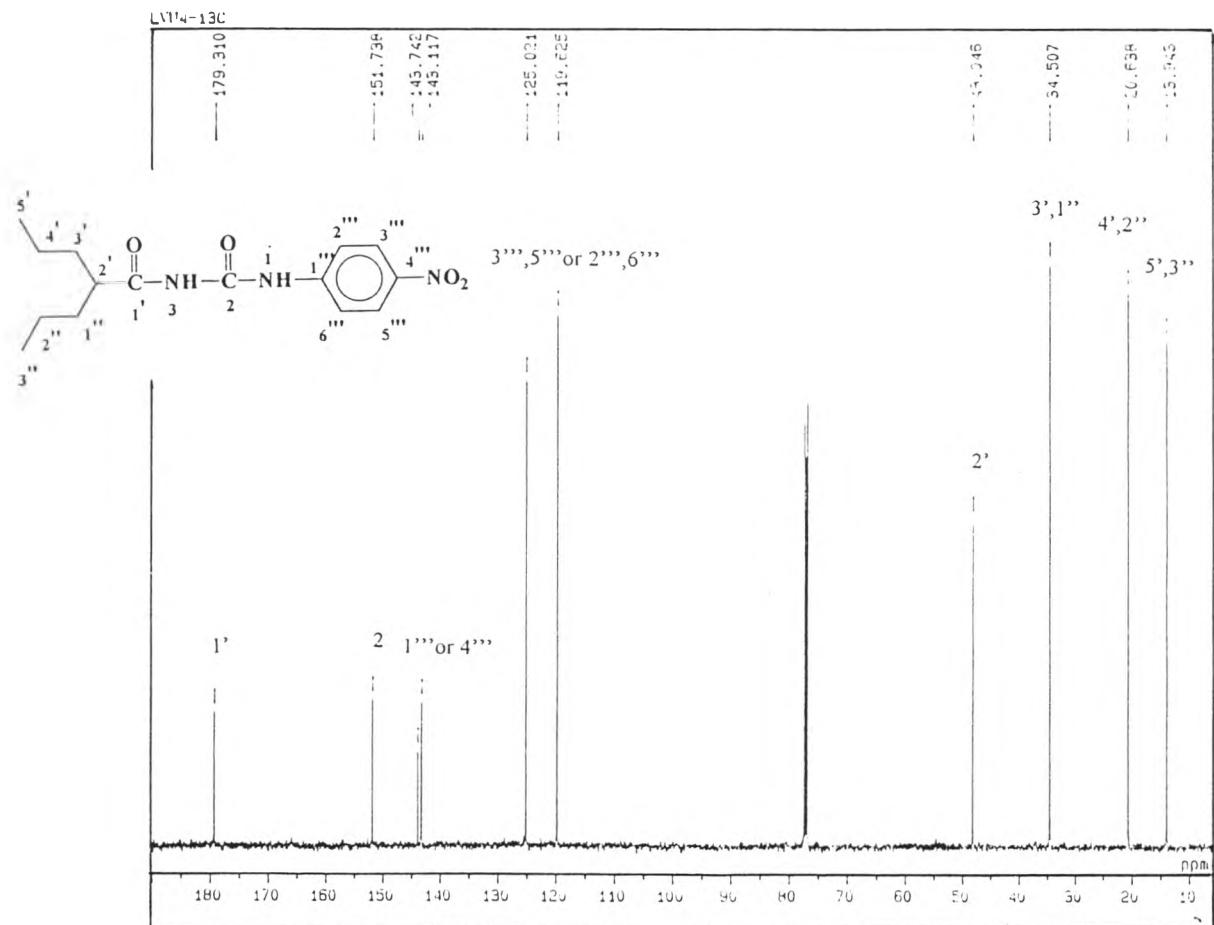


Figure 49. The 500 MHz ^{13}C -NMR spectrum of N-(2-propylpentanoyl)-N'-(4-nitrophenyl)urea in CDCl_3

SZ3380001 Scan 367 RT=12:46 100%=42634 mv 20 Dec 96 11:02
LRP +EI LVU 4

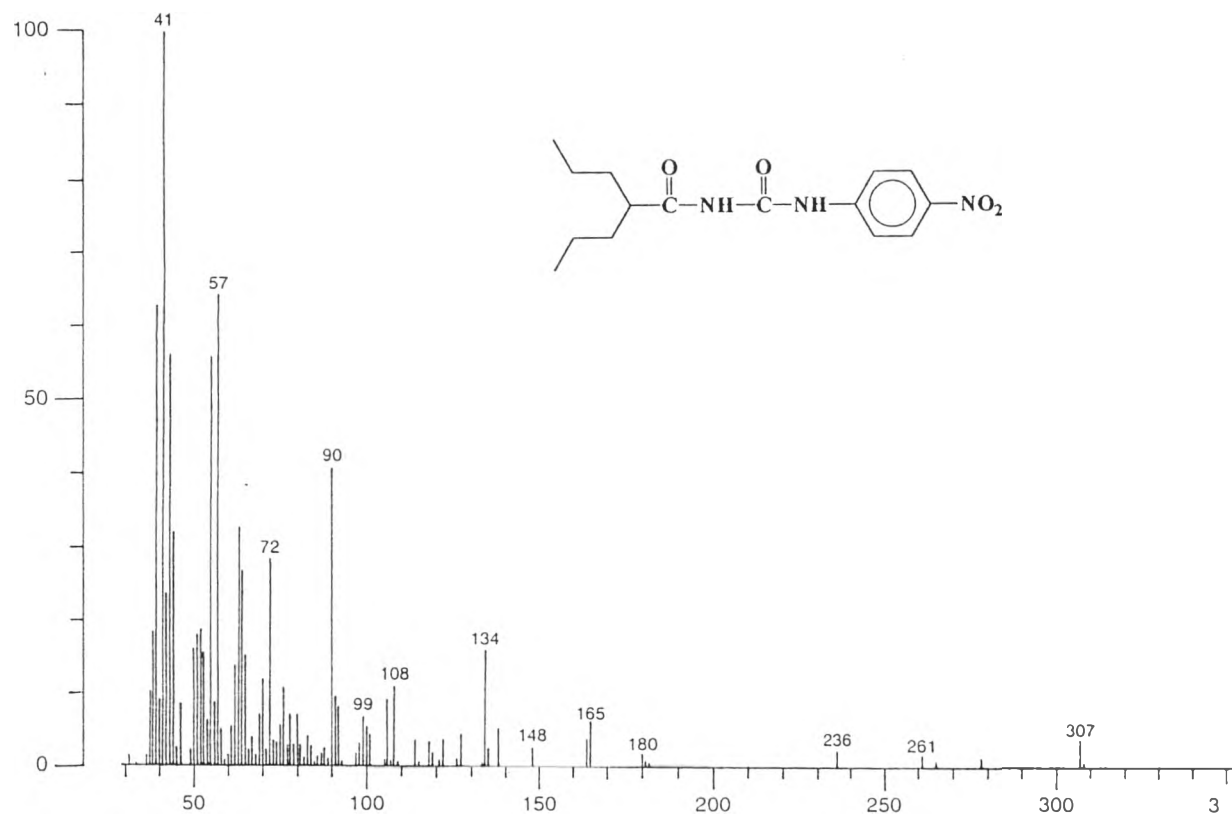


Figure 50. The EIMS spectrum of *N*-(2-propylpentanoyl)-*N'*-(4-nitrophenyl)urea

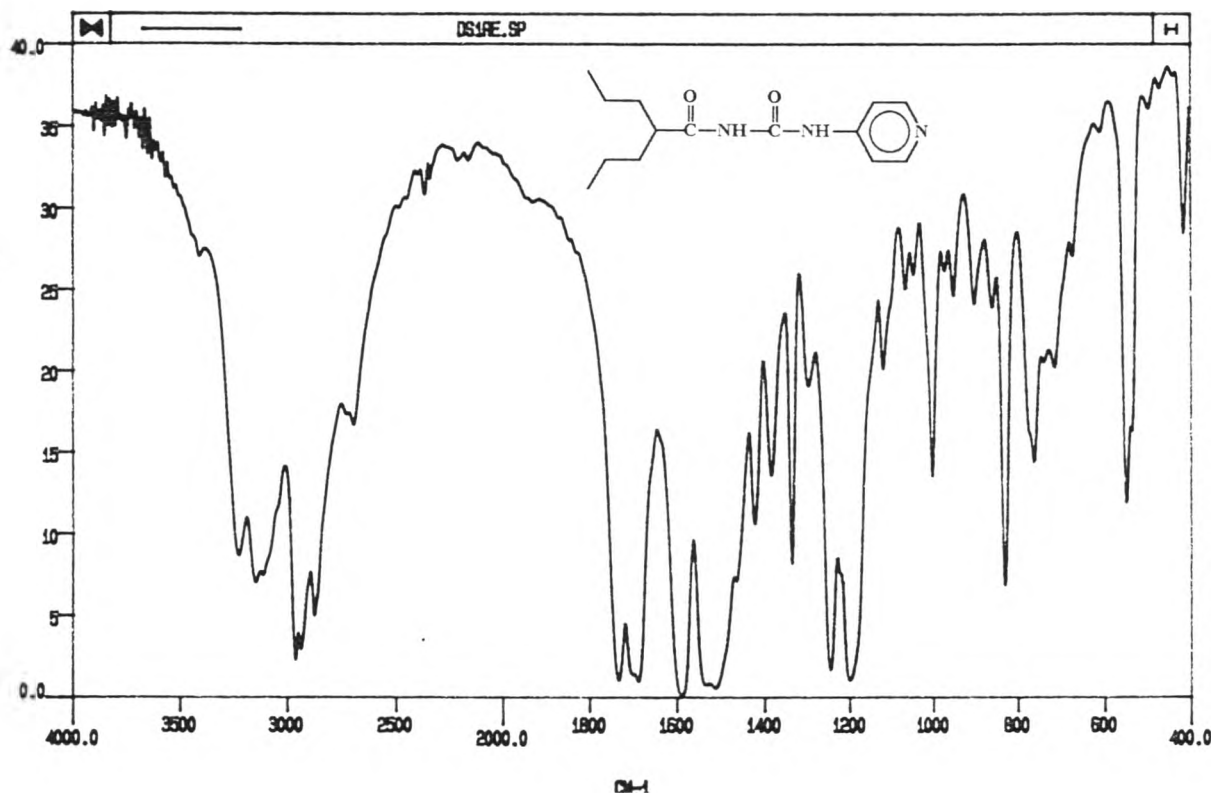


Figure 51 The IR spectrum (KBr) of N-(2-propylpentanoyl)-N'-(4-pyridinyl)urea

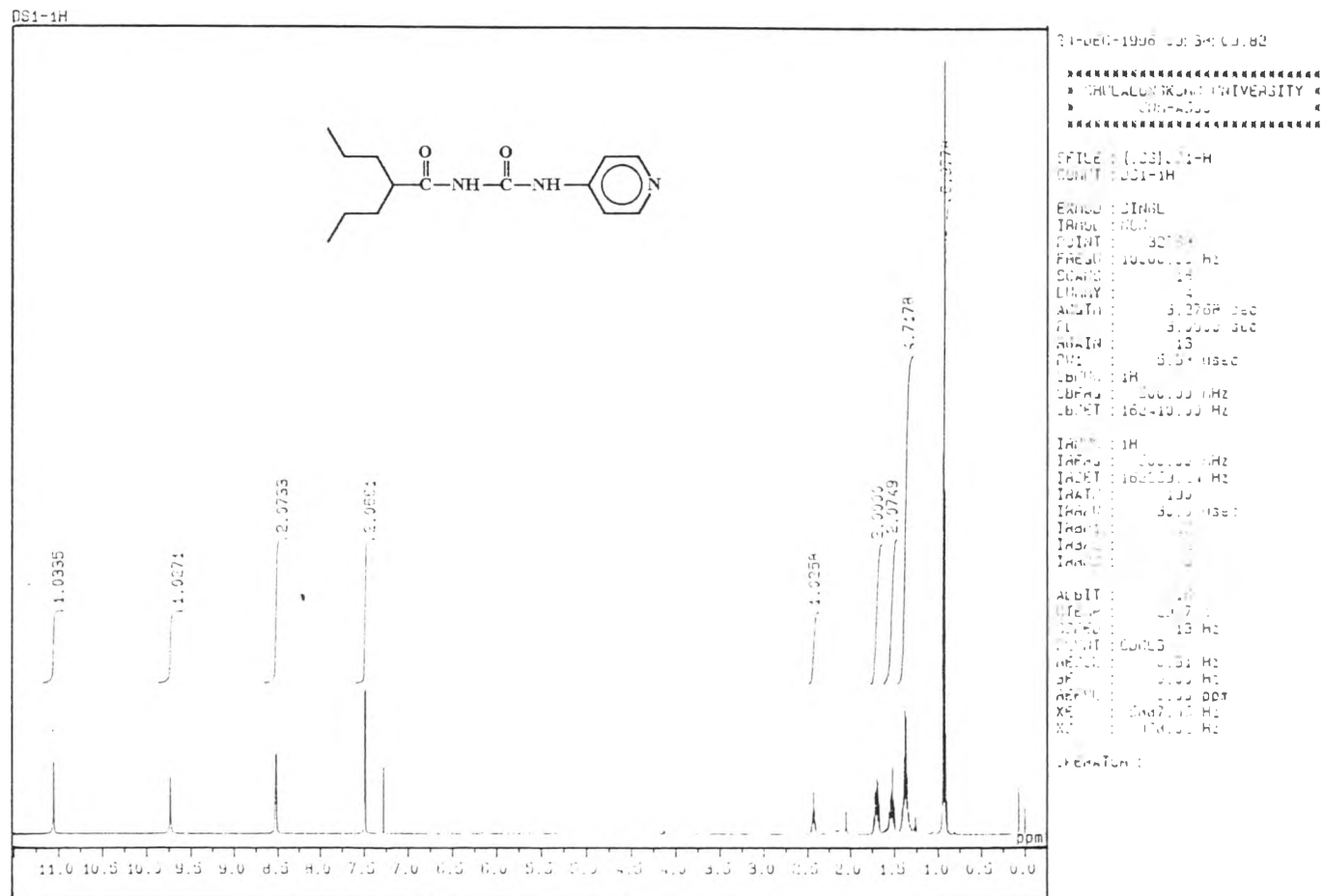


Figure 52. The 500 MHz $^1\text{H-NMR}$ spectrum of N(2-propylpentanoyl)-N'-(4-pyridinyl)urea in CDCl_3

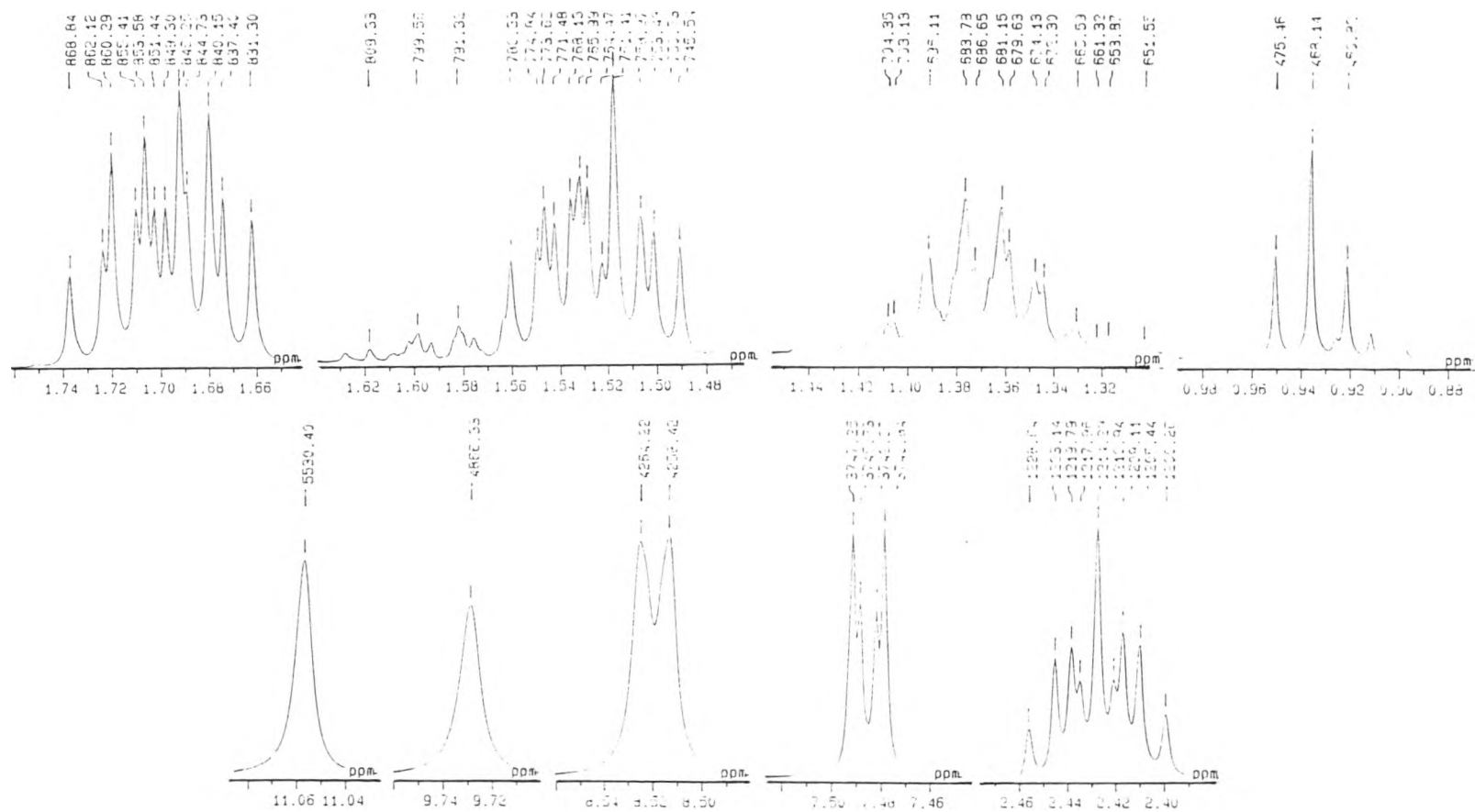


Figure 53. The 500 MHz $^1\text{H-NMR}$ spectrum of N(2-propylpentanoyl)-N'-(4-pyridinyl)urea in CDCl_3 (Enlarged scale)

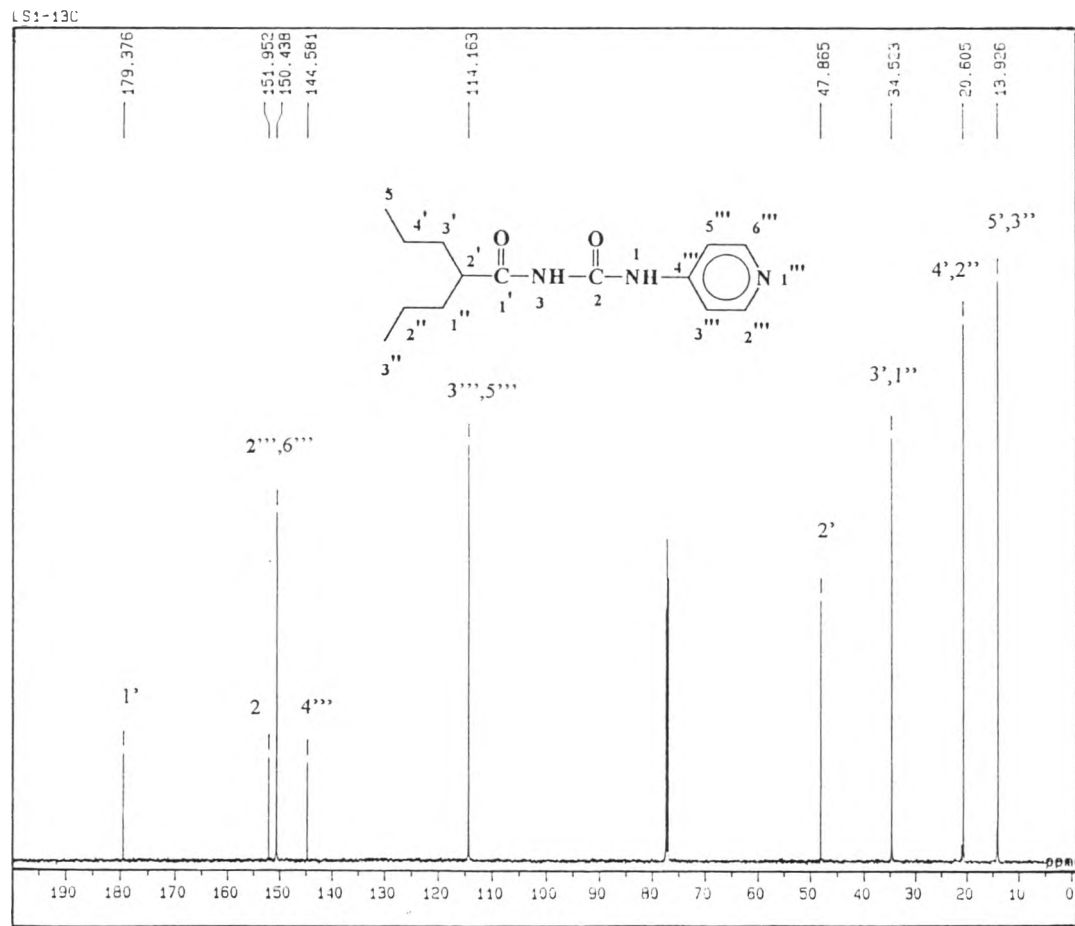


Figure 54. The 500 MHz ^{13}C -NMR spectrum of *N*-(2-propylpentanoyl)-*N'*-(4-pyridinyl)urea in CDCl_3

Background Subtract

C:\SATURN\DATA\DS1

Date: 03/17/97 13:37:44

Comment: COL DB-5MS 0.25MMIDX30M

Average of: 497 to 581 Minus: 523 to 527

100% = 4768

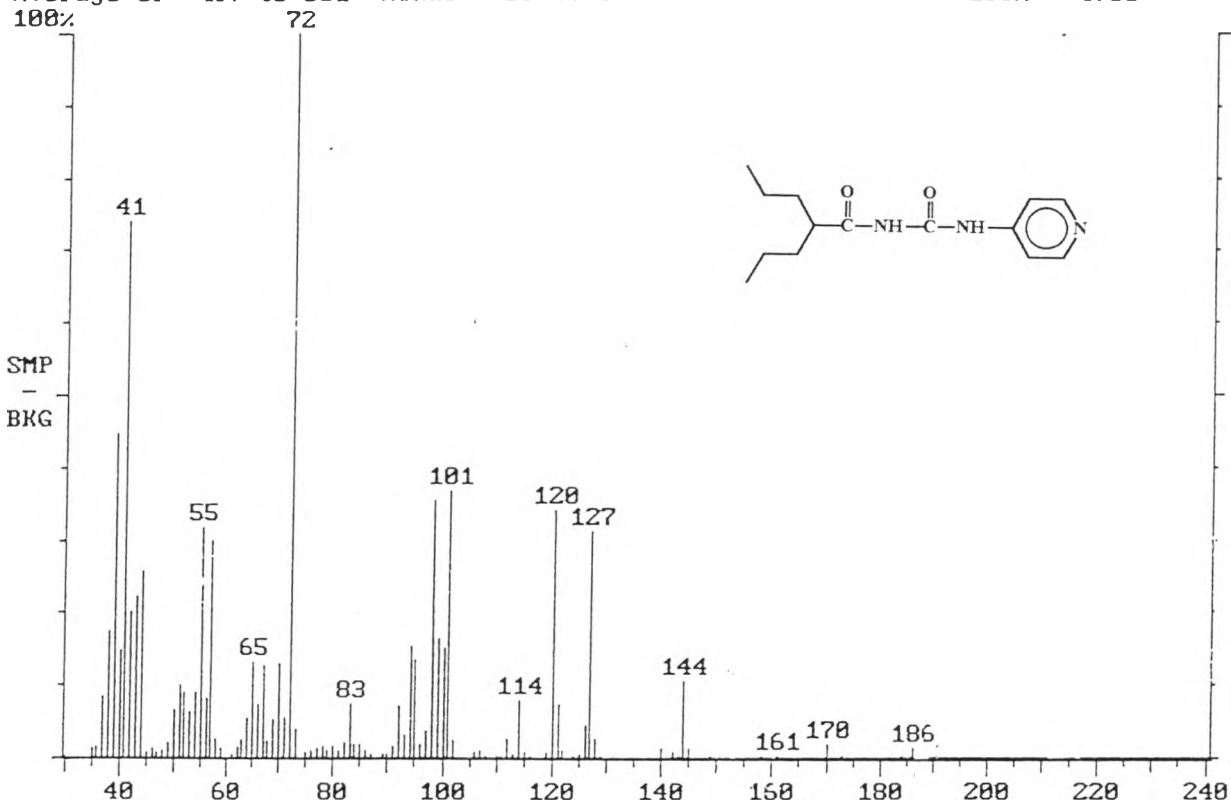


Figure 55. The EIMS Spectrum of N-(2-propylpentanoyl)-N'-(4-pyridinyl)urea