

## CHAPTER III

### EXPERIMENTS

#### Instruments.

1. Infrared Spectrophotometers:  
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 (500 MHz).
3. Gas chromatograph / Mass spectrometer:  
Varian Star 3400 CX. / Varian Saturn GC/MS/MS 4D.
4. Melting Point Apparatus:  
Buchi capillary melting point apparatus.

#### Chemicals.

Acetic anhydride (AnalaR).  
Benzoic acid (Merck).  
1-Bromopropane (Fluka Chemika).  
N-Bromosuccinimide (Serva feinbiochemica).  
Chloroacetic acid (Fluka Chemika).  
Cuprous chloride (Sigma).  
Dimethylsulphate (Sigma).  
Ethylchloroformate (Wako Pure Chemical Industries, Ltd.).  
Ethyl iodide (Merck).  
Hydrochloric acid, concentrated (Merck).  
Hydroxylamine hydrochloride (Merck).  
Nitric acid (Merck).  
4-Nitrobenzoic acid (Fluka Chemika).

Palladium on activated charcoal (10% Pd) (Merck).  
Phosphorus pentachloride (May & Baker LTD.).  
Sodium metal (Reidel-de Haen).  
Sodium carbonate (Carlo Erba, AG).  
Sodium hydroxide (Merck).  
Sodium valproate (Siegfried Chemie).  
Sulfuric acid, concentrated (Merck).  
Sulfuryl chloride (Aldrich Chemical Company, Inc.).  
Tetrahydrofuran (Merck).  
Thionyl chloride (Laboratory grade).  
Toluene (Merck).  
2-Toluidine (Sigma).  
All solvents used were either B.P. or Laboratory-grade.

### **Benzoyl Chloride.**

#### Method I

Mixed 75 g (0.6 mole) of pure benzoic acid and 126 g (0.6 mole) of pure phosphorus pentachloride in 500-ml round-bottom flask. Fitted the flask with a calcium chloride guard-tube and connected the latter to a gas absorption trap. Heated the flask on a water bath, with occasional shaking, until the reaction commenced and then for a further 30 minutes or until the vigorous evolution of hydrogen chloride has almost ceased: a white homogeneous liquid is formed. Distilled the mixture on an oil bath to remove the phosphorus oxychloride (b.p. 107°C) and the benzoylchloride was passed over as colorless liquid at 195-197°C. The yield was 80 g (95%).

#### Method II

Placed 25 g (0.2 mole) of benzoic acid and 45 g (0.35 mole) of redistilled thionyl chloride to 250 ml round-bottom flask that was fitted with a refluxed condenser and connect at the top to a gas absorption trap. Stirred the mixture and heated the flask on a water bath until the evolution gas, sulfur dioxide and hydrogenchloride, were ceased (about 5 hours). Distilled the mixture on oil bath to remove excess thionyl chloride (b.p. 67°C) and collect the benzoylchloride at 195-

197°C. The yield of the benzoylchloride, colorless liquid, was 18 g (65%).

The structure of benzoyl chloride was confirmed by IR spectrum:  
(See figure 20)

IR	:	3100 - 3000	CM <sup>-1</sup>	(C-H stretch; aromatic)
(NEAT)		2000 - 1667	CM <sup>-1</sup>	(overtone or combination bands; aromatic)
		1775	CM <sup>-1</sup>	(C=O stretch; acyl halide)
		1724	CM <sup>-1</sup>	(fermi resonance band of C=O stretch, and overtone of aromatic of 862 CM <sup>-1</sup> )
		1600, 1452	CM <sup>-1</sup>	(C=C stretch; aromatic)
		862, 765	CM <sup>-1</sup>	(C-H bend; out-of-plane)
		665	CM <sup>-1</sup>	(C=C bend; out-of-plane)

### 2-Chlorotoluene.

Dissolved 35 g (0.35 mole) of cuprous chloride in 170 ml of concentrated hydrochloric acid. Stopped the flask loosely (to prevent oxidation) and cooled it in an ice-salt mixture whilst the diazotisation was being carried out.

Dissolved 36 g (0.33 mole) of 2-toluidine in 85 ml of concentrated hydrochloric acid and 85 ml of water contained in a 750-ml conical flask or beaker. Cooled the mixture to 0°C in an ice-salt bath with vigorous stirring or shaking and a little crushed ice was added. The salt, *O*-toluidine hydrochloride, would separate as a finely divided crystalline precipitate. Added during 10-15 minutes a solution of 24 g (0.35 mole) of sodium nitrite in 50 ml of water; shook or stirred the solution well during the diazotisation, and kept the mixture at a temperature of 0-5°C by the addition of a little crushed ice from time to time. The hydrochloride would dissolve as the very soluble diazonium salt was formed; when all the nitrite solution had been introduced, the solution should contain a trace of free nitrous acid.

Poured the cold diazonium chloride solution slowly and with shaking into the cold copper(I)chloride solution. The mixture became very thick, owing to the separation of an addition product between the diazonium salt and the copper(I)chloride. Allowed the mixture to warm

up to room temperature without external heating, and shook occasionally. When the temperature reached about 15°C, the solid addition complex commences to break down with the liberation of nitrogen and the formation of an oily layer of *O*-chlorotoluene. Warmed the mixture on a water bath to about 60°C to complete the decomposition of the double salt; shook occasionally. When the evolution of nitrogen ceases, steam distilled the mixture until no more oily drops were present in the distillate. Transferred the distillate to a separatory funnel, and remove the layer of *O*-chlorotoluene. Wash successively with 30 ml of 10% sodium hydroxide solution (to remove *O*-cresol which may be present), water, an equal volume of concentrated sulfuric acid (to remove a trace of azo compound that usually colors of the crude product and cannot be removed by distillation) and water (to remove the acid). Dried with 3-4 g of anhydrous calcium chloride, decanted or filter through a small fluted filter-paper and distilled the filtrate under atmosphere. Collected the colorless liquid, *O*-chlorotoluene, at 155-158°C; the yield was 33 g (78%).

The structure of 2-chlorotoluene was confirmed by IR spectrum: (See figure 21)

IR	:	3100 - 3000	CM <sup>-1</sup>	(C-H stretch; aromatic)
(NEAT)		3000 - 2860	CM <sup>-1</sup>	(C-H stretch; aliphatic)
		2000 - 1667	CM <sup>-1</sup>	(overtone or combination bands; aromatic)
		1580 - 1448	CM <sup>-1</sup>	(C=C stretch; aromatic)
		1052	CM <sup>-1</sup>	(C-Cl stretch; aryl chloride)
		1022	CM <sup>-1</sup>	(C-H bend; in plane)
		720	CM <sup>-1</sup>	(=C-H bend; out-of-plane, aromatic)
		429	CM <sup>-1</sup>	(C=C bend; out-of-plane)

#### **$\alpha$ -Bromo-2-chlorotoluene.**

*N*-Bromosuccinimide was purified by recrystallization as rapidly as possible from ten times its weight of hot water or from glacial acetic acid.

Placed 36 g (0.2 mole) of *N*-bromosuccinimide, 25 g (0.2 mole) of *O*-chlorotoluene, and 150 ml of dry, redistilled carbontetrachloride in 250 ml round-bottom flask. Then added about

200 mg of benzoylperoxide. Attached a reflux condenser and allowed the mixture to stand at room temperature when after a short induction period the reaction begins. The reaction mixture became warm and the heavy yellowish. *N*-bromosuccinimide began to be transformed into the light colorless succinimide which became suspended in the reaction mixture. Then heated under reflux until all the *N*-bromosuccinimide had been converted to succinimide (about 12 hours). Cooled the flask, filter under suction and washed the residue with a little dry carbontetrachloride. Distilled the filtrate under reduced pressure and collected the  $\alpha$ -bromo-2-chlorotoluene at 103-104°C / 10 mmHg. The yield was 33 g (82%).

The structure of  $\alpha$ -bromo-2-chlorotoluene was confirmed by IR spectrum: (See figure 22)

IR	:	3100 - 3000 $\text{CM}^{-1}$	(C-H stretch; aromatic)
(NEAT)		3000 - 2860 $\text{CM}^{-1}$	(C-H stretch; aliphatic)
		2000 - 1667 $\text{CM}^{-1}$	(overtone or combination bands; aromatic)
		1601 - 1440 $\text{CM}^{-1}$	(C=C stretch; aromatic)
		1222 $\text{CM}^{-1}$	(CH <sub>2</sub> -wagging; CH <sub>2</sub> -Br)
		1057 $\text{CM}^{-1}$	(C-Cl stretch; aryl chloride)
		1038 $\text{CM}^{-1}$	(C-H bend; in plane)
		744 $\text{CM}^{-1}$	(=C-H bend; out-of-plane, aromatic)

#### 4-Nitro-benzoylchloride.

Mixed 100 g (0.6 mole) of pure *p*-nitrobenzoic acid and 126 g (0.6 mole) of pure phosphorus pentachloride in 500 ml round-bottom flask. Fitted the flask with a calcium chloride guard tube and connect the latter to a gas absorption trap. Heated the flask on water bath, with occasional shaking, until the reaction commenced and then for a further 30 minutes or until the vigorous evolution of hydrogen chloride had almost ceased: a pale yellow homogeneous liquid was formed. Distilled at ordinary atmosphere to remove the phosphorus oxychloride (b.p. 107°C) either by heating in an oil bath gradually to 200-220°C or by heating in an air bath until the temperature was about 150 °C. The mixture was allowed to cool and the excess phosphorus pentachloride was washed with diethyl ether. The yield of *p*-nitrobenzoyl chloride, a

yellow crystalline solid (m.p. 70 °C), was 105 g (95%) and was pure enough for most purposes.

The structure of p-nitro-benzoylchloride was confirmed by IR spectrum: (See figure 23)

IR : 3100 - 3000  $\text{CM}^{-1}$  (C-H stretch; aromatic)  
(Nujol's 2000 - 1667  $\text{CM}^{-1}$  (overtone or combination bands; aromatic)  
mull) 1775  $\text{CM}^{-1}$  (C=O stretch; acid chloride)  
1613, 1580  $\text{CM}^{-1}$  (C=C stretch; aromatic)  
842  $\text{CM}^{-1}$  (=C-H bend; out-of-plane, aromatic)  
3000 - 2860, 1470, and 1383  $\text{CM}^{-1}$  were Nujol's bands.

### **2-Propylpentanoyl Chloride.**

Placed 50 g (0.35 mole) of 2-propylpentanoic acid and 60 g (0.5 mole) of redistilled thionyl chloride to round-bottom flask that was fitted to a reflux condenser and connect at the top to a gas absorption trap. Stirred the mixture, and heated the flask on a water bath until the evolution gases, sulfur dioxide and hydrogen chloride, were ceased (about 3 hours). The excess of thionyl chloride was distilled and residue had been stored in closely bottle.

### **Benzyl Chloride.**

Placed 20 g (0.22 mole) of toluene, 30 g (0.22 mole) of redistilled sulphuryl chloride and about 200 mg of benzoyl peroxide to 250 ml round-bottom flask, and fitted with an efficient reflux condenser. Refluxed gently, when a vigorous reaction take place: the reaction was complete in 30 minutes. Distilled the reaction mixture first under atmospheric pressure until the temperature reached 135-140°C, and continue distillation under reduced pressure. Collected the benzyl chloride at 64-69°C / 120 mmHg. The yield of benzyl chloride was about 21.5 g (79%).

The structure of benzyl chloride was confirmed by IR spectrum:  
(See figure 24)

IR : 3100 - 3000  $\text{CM}^{-1}$  (C-H stretch; aromatic)  
(NEAT) 3000 - 2860  $\text{CM}^{-1}$  (C-H stretch; aliphatic)  
2000 - 1667  $\text{CM}^{-1}$  (overtone or combination bands; aromatic)  
1518, 1452  $\text{CM}^{-1}$  (C=C stretch; aromatic)  
1053  $\text{CM}^{-1}$  ( $\text{CH}_2$ -wagging;  $\text{CH}_2\text{-Cl}$ )  
1084, 1041  $\text{CM}^{-1}$  (C-H bend; in plane)  
690  $\text{CM}^{-1}$  (C-Cl stretch (aliphatic chloride))

### Ethyl- $\alpha$ -chloroacetate.

Placed 50 g of chloroacetic acid to 250 ml of absolute ethanol in 500 ml round-bottom flask, then fitted to a reflux condenser. The 1 ml of concentrated sulfuric acid was added and refluxed for 15 hours. An azeotropic mixture of water and ethanol was distilled at 78°C. The residue was continuously distilled, and collected the ethyl chloroacetate at 144-146°C. The yield of the ethyl chloroacetate, colorless liquid, was 37 g (57%).

The structure of ethyl- $\alpha$ -chloroacetate was confirmed by IR spectrum: (See figure 25)

IR : 3000 - 2860  $\text{CM}^{-1}$  (C-H stretch; aliphatic)  
(NEAT) 1757  $\text{CM}^{-1}$  (C=O stretch)  
1470 - 1370  $\text{CM}^{-1}$  (C-H bend)  
1313 - 1098  $\text{CM}^{-1}$  ( $\text{-(C=O)-O-C-}$  stretch)  
1028  $\text{CM}^{-1}$  (C-O stretch)  
782 - 699  $\text{CM}^{-1}$  (C-Cl stretch)

### 2-Propylpentanohydroxamic Acid.

21 g (0.2 mole) of sodium bicarbonate was added to 10% water in tetrahydrofuran. Added 21 g (0.3 mole) of hydroxylamine hydrochloride and then, stirred vigorously. When carbon dioxide gas ceased, the reaction was stirred continuously for 3 hours. The excess sodium bicarbonate was filtered.

Hydroxylamine solution was cooled to 10°C. Added 21 g (0.2 mole) of sodium bicarbonate with vigorous stir. The 50 g (0.3 mole) of 2-propylpentanoyl chloride was poured to dropping funnel and then, dropwised to the hydroxylamine solution during the course of 4 hours. Stirred vigorously until carbondioxide gas ceased, and the stirring was continued for 4 hours. The mixture was filtered, and the filtrate was evaporated under rotary evaporator until dried. The residue was purified by recrytallization from hexane. The yield of 2-propylpentano hydroxamic acid as white needle, m.p. 124-125°C, was 38 g (78%).

The structure of 2-propylpentanohydroxamic acid was confirmed by:

IR : 3195  $\text{CM}^{-1}$  (N-H stretch)  
 (KBr 3032  $\text{CM}^{-1}$  (O-H stretch)  
 Pellet) 3000 - 2860  $\text{CM}^{-1}$  (C-H stretch; aliphatic)  
 1629  $\text{CM}^{-1}$  (C=O stretch; amide like carbonyl)  
 1466  $\text{CM}^{-1}$  (N-H bend)  
 750 - 600  $\text{CM}^{-1}$  (N-H bend; out-of-plane)  
 (See figure 26)

$^1\text{H-NMR}$  : 0.89 ppm (6H, t)  
 ( $\text{CDCl}_3$ ) 1.19 - 1.36 ppm (4H, multiplet)  
 1.37 - 1.46 ppm (2H, multiplet)  
 1.61 ppm (2H, multiplet)  
 1.94 ppm (1H, dddd)  
 (See figure 27-28)

$^{13}\text{C-NMR}$  : 13.929 ppm (2C;  $\text{C}^5$ ,  $\text{C}^{3'}$ )  
 ( $\text{CDCl}_3$ ) 20.540 ppm (2C;  $\text{C}^4$ ,  $\text{C}^{2'}$ )  
 34.572 ppm (2C;  $\text{C}^3$ ,  $\text{C}^{1'}$ )  
 43.604 ppm (1C;  $\text{C}^2$ )  
 174.292 ppm (1C;  $\text{C}^1$ )  
 (See figure 29)

EIMS : m/z 159 (M), 144, 142, 126, 100, 99, 98, 72, 57, 55, 41.  
 (See figure 30)



### **Sodium-2-propylpentanohydroxamate.**

Placed 50 ml of absolute ethanol to 100 ml round-bottom flask and cooled in the ice-salted bath. Added 2.3 g (0.1 mole) of sliced sodium metal to the absolute ethanol with vigorous stir until the sliced sodium metal were disappeared, and the sodium ethoxide was formed. Poured the solution to a dropping funnel, and connected to anhydrous calcium chloride guard tube.

Dissolved 15 g (0.1 mole) of 2-propylpentanohydroxamic acid in 50 ml of absolute ethanol. Dropwised the sodium ethoxide during the course of 2 hours; white precipitate, water soluble substance, was formed. Added 50 ml of dried diethylether, then filtered the content by using suction filtration. The precipitate, sodium-2-propylpentano hydroxamate, was dried and kept in vacuum desiccator.

### **Ethyl- $\alpha$ -(2-propylpentamidooxy)acetate.**

Dissolved 1.2 g (0.03 mole) of sodium hydroxide with minimum quantity of purified water in 10-ml beaker. Dissolved 5 g (0.03 mole) of 2-propylpentanohydroxamic acid with 25 ml of dried, and redistilled tetrahydrofuran in 100-ml round-bottom flask. Dropwised the sodium hydroxide solution very slowly and stirred vigorously until the clear solution became opaque. Dropwised 3.7 g (0.03 mole) of ethyl chloroacetate and fitted the flask with refluxed condenser that connected anhydrous calcium chloride guard tube at the top. Refluxed the mixture on a water bath for 10 hours. The mixture was evaporated by rotary evaporator, and the residue was extracted with 50 ml of 25% sodium carbonate solution and 50 ml redistilled chloroform. Collected the chloroform layer and washed with three 50 ml portion of purified water. Removed the water layer, and the chloroform layer was dried with anhydrous sodium sulfate. Evaporated the chlorofom on a water bath (rotary evaporator), and then the residue was purified with a silica gel column, eluted with hexane. The yield of Ethyl- $\alpha$ -(2-propylpentamidooxy) acetate was 3.5 g (46%).

The structure of ethyl- $\alpha$ -(2-propylpentamidooxy)acetate was confirmed by:

IR	: 3175	CM <sup>-1</sup>	(N-H stretch)
(KBr Pellet)	3000 - 2860	CM <sup>-1</sup>	(C-H stretch; aliphatic)
	1752	CM <sup>-1</sup>	(C=O stretch; ester like carbonyl)
	1662	CM <sup>-1</sup>	(C=O stretch; amide like carbonyl)
	1462	CM <sup>-1</sup>	(N-H bend)
	1215	CM <sup>-1</sup>	(C-(C=O)-O stretch)
	1075	CM <sup>-1</sup>	(C-O stretch)
	750 - 600	CM <sup>-1</sup>	(N-H bend; out-of-plane)

(See figure 31)

<sup>1</sup> H-NMR	: 0.88 ppm	(3H, t)
(CDCl <sub>3</sub> )	1.31 ppm	(3H, t)
	1.20 - 1.34 ppm	(4H, multiplet)
	1.35 - 1.45 ppm	(2H, multiplet)
	1.56 - 1.68 ppm	(2H, multiplet)
	1.94 ppm	(1H, broad)
	4.26 ppm	(2H, q)
	4.49 ppm	(2H, s)

(See figure 32-33)

<sup>13</sup> C-NMR	: 13.926 ppm	(2C; C <sup>5</sup> , C <sup>3'</sup> )
(CDCl <sub>3</sub> )	14.074 ppm	(1C; C <sup>4''</sup> )
	20.572 ppm	(2C; C <sup>4</sup> , C <sup>2'</sup> )
	34.655 ppm	(2C; C <sup>3</sup> , C <sup>1'</sup> )
	43.703 ppm	(1C; C <sup>2</sup> )
	61.404 ppm	(1C; C <sup>3'</sup> )
	72.130 ppm	(1C; C <sup>1''</sup> )
	169.735 ppm	(1C; C <sup>2''</sup> )
	173.618 ppm	(1C; C <sup>1</sup> )

(See figure 34)

EIMS : m/z 246 (M+1), 230, 216, 203, 202, 174, 142, 126, 100, 99, 98, 72, 57, 55, 41.  
(See figure 35)

### Methyl-2-propylpentanohydroxamate.

Used 1.2 g (0.03 mole) of sodium hydroxide, 1.9 g (0.015 mole) of 2-propylpentanohydroxamic acid, and 5 g (0.03 mole) of dimethylsulfate. Proceed as for ethyl- $\alpha$ -(2-propylpentamidooxy) acetate but heated under reflux for 5 hours. The yield of methyl-2-propylpentanohydroxamate was 3.9 g (73%), after purification by using silica gel column and eluted with ethylacetate : hexane (1 : 4).

The structure of methyl-2-propylpentanohydroxamate was confirmed by:

IR : 3245  $\text{CM}^{-1}$  (N-H stretch)  
 (NEAT) 3000 - 2860  $\text{CM}^{-1}$  (C-H stretch; aliphatic)  
 1689  $\text{CM}^{-1}$  (C=O stretch; amide like carbonyl)  
 1492  $\text{CM}^{-1}$  (N-H bend)  
 1085  $\text{CM}^{-1}$  (C-O stretch)  
 750 - 600  $\text{CM}^{-1}$  (N-H bend; out-of-plane)  
 (See figure 36)

$^1\text{H-NMR}$  : 0.89 ppm (6H, t)  
 ( $\text{CDCl}_3$ ) 1.26 - 1.44 ppm (6H, multiplet)  
 1.55 - 1.68 ppm (2H, multiplet)  
 2.14 ppm (1H, broad)  
 3.76 ppm (3H, s)  
 10.46 ppm ( $\text{NH}$ , broad)  
 (See figure 37-38)

$^{13}\text{C-NMR}$  : 13.926 ppm (2C;  $\text{C}^5, \text{C}^{3'}$ )  
 ( $\text{CDCl}_3$ ) 20.490 ppm (2C;  $\text{C}^4, \text{C}^{2'}$ )  
 34.786 ppm (2C;  $\text{C}^3, \text{C}^{1'}$ )  
 43.143 ppm (1C;  $\text{C}^2$ )  
 63.658 ppm (1C;  $\text{C}^{1''}$ )  
 173.618 ppm (1C;  $\text{C}^1$ )  
 (See figure 39)

EIMS :  $m/z$  174 ( $\text{M}+1$ ), 158, 144, 142, 131, 130, 126, 102, 100, 99, 98,  
 72, 57, 55, 41.  
 (See figure 40)

### Ethyl-2-propylpentanohydroxamate.

Used 1.2 g (0.03 mole) of sodium hydroxide, 5 g (0.03 mole) of 2-propylpentanohydroxamic acid, and 4.7 g (0.03 mole) of ethyl iodide. Proceed as for ethyl- $\alpha$ -(2-propylpentamidooxy) acetate but heated under reflux for 4 hours. The yield of ethyl-2-propylpentanohydroxamate was 4.9 g (84%), after purification by using silica gel column and eluted with ethylacetate : hexane (1 : 4).

The structure of ethyl-2-propylpentanohydroxamate was confirmed by:

IR : 3175  $\text{CM}^{-1}$  (N-H stretch)  
 (NEAT) 3000 - 2860  $\text{CM}^{-1}$  (C-H stretch; aliphatic)  
 1660  $\text{CM}^{-1}$  (C=O stretch; amide like carbonyl)  
 1458  $\text{CM}^{-1}$  (N-H bend)  
 1045  $\text{CM}^{-1}$  (C-O stretch)  
 750 - 600  $\text{CM}^{-1}$  (N-H bend; out-of-plane)  
 (See figure 41)

$^1\text{H-NMR}$  : 0.90 ppm (6H, t)  
 ( $\text{CDCl}_3$ ) 1.27 ppm (3H, t)  
 1.28 - 1.49 ppm (6H, multiplet)  
 1.55 - 1.75 ppm (2H, multiplet)  
 2.03 ppm (1H, broad)  
 3.99 ppm (2H, q)  
 (See figure 42-43)

$^{13}\text{C-NMR}$  : 13.235 ppm (1C;  $\text{C}^{2''}$ )  
 ( $\text{CDCl}_3$ ) 13.860 ppm (2C;  $\text{C}^5$ ,  $\text{C}^{3'}$ )  
 20.424 ppm (2C;  $\text{C}^4$ ,  $\text{C}^{2'}$ )  
 34.803 ppm (2C;  $\text{C}^3$ ,  $\text{C}^{1'}$ )  
 43.045 ppm (1C;  $\text{C}^2$ )  
 71.291 ppm (1C;  $\text{C}^{1''}$ )  
 173.601 ppm (1C;  $\text{C}^1$ )  
 (See figure 44)

EIMS :  $m/z$  188 (M+1), 172, 158, 145, 144, 142, 126, 116, 100, 99, 98, 72, 57, 55, 41.

(See figure 45)

### Propyl-2-propylpentanohydroxamate.

Used 1.2 g (0.03 mole) of sodium hydroxide, 5 g (0.03 mole) of 2-propylpentanohydroxamic acid, and 3.7 g (0.03 mole) of propyl bromide. Proceed as for ethyl- $\alpha$ -(2-propylpentamidooxy) acetate but heated under reflux for 5 hours. The yield of propyl-2-propylpentanohydroxamate was 4.8 g (77%), after purification by using silica gel column and eluted with ethylacetate : hexane (1 : 4).

The structure of propyl-2-propylpentanohydroxamate was confirmed by:

IR : 3185  $\text{CM}^{-1}$  (N-H stretch)  
 (NEAT) 3000 - 2860  $\text{CM}^{-1}$  (C-H stretch; aliphatic)  
 1650  $\text{CM}^{-1}$  (C=O stretch; amide like carbonyl)  
 1467  $\text{CM}^{-1}$  (N-H bend)  
 1075  $\text{CM}^{-1}$  (C-O stretch)  
 750 - 600  $\text{CM}^{-1}$  (N-H bend; out-of-plane)  
 (See figure 46)

$^1\text{H-NMR}$  : 0.82 ppm (6H, t)  
 ( $\text{CDCl}_3$ ) 0.88 ppm (3H, t)  
 1.16 - 1.34 ppm (6H, multiplet)  
 1.49 - 1.56 ppm (2H, multiplet)  
 1.60 ppm (2H,qt)  
 2.01 ppm (1H, broad)  
 3.80 ppm (2H, t)  
 9.56 ppm ( $\text{NH}$ , broad)  
 (See figure 47-48)

$^{13}\text{C-NMR}$  : 10.126 ppm (1C;  $\text{C}^{3''}$ )  
 ( $\text{CDCl}_3$ ) 13.943 ppm (2C;  $\text{C}^5, \text{C}^{3'}$ )  
 20.572 ppm (2C;  $\text{C}^4, \text{C}^{2'}$ )  
 21.198 ppm (1C;  $\text{C}^{2''}$ )  
 34.819 ppm (2C;  $\text{C}^3, \text{C}^{1'}$ )

43.505 ppm (1C; C<sup>2</sup>)  
 77.921 ppm (1C; C<sup>1''</sup>)  
 173.601 ppm (1C; C<sup>1</sup>)  
 (See figure 49)

EIMS : m/z 202 (M+1), 186, 172, 159, 158, 142, 130, 126, 100, 99, 98,  
 72, 57, 55, 41.  
 (See figure 50)

### Benzyl-2-propylpentanohydroxamate.

Used 1.2 g (0.03 mole) of sodium hydroxide, 5 g (0.03 mole) of 2-propylpentanohydroxamic acid, and 3.8 g (0.03 mole) of benzyl chloride. Proceed as for ethyl- $\alpha$ -(2-propylpentamidooxy) acetate but heated under reflux for 3 hours. The yield of benzyl-2-propylpentanohydroxamate as white needle was 5.4 g (69%), m.p. 72-73°C, after recrystallization in hexane.

The structure of benzyl-2-propylpentanohydroxamate was confirmed by:

IR : 3218 CM<sup>-1</sup> (N-H stretch)  
 (KBr 3100 - 3000 CM<sup>-1</sup> (C-H stretch; aromatic)  
 Pellet) 3000 - 2860 CM<sup>-1</sup> (C-H stretch; aliphatic)  
 2000 - 1667 CM<sup>-1</sup> (overtone or combination bands; aromatic)  
 1652 CM<sup>-1</sup> (C=O stretch; amide like carbonyl)  
 1514, 1455 CM<sup>-1</sup> (C=C stretch; aromatic)  
 1045 CM<sup>-1</sup> (C-O stretch)  
 738 CM<sup>-1</sup> (C-H bend; out-of-plane, aromatic)  
 697 CM<sup>-1</sup> (C=C bend; aromatic)  
 750 - 600 CM<sup>-1</sup> (N-H bend; out-of-plane)  
 (See figure 51)

<sup>1</sup>H-NMR : 0.86 ppm (6H, t)  
 (CDCl<sub>3</sub>) 1.15 - 1.40 ppm (6H, multiplet)  
 1.54 - 1.65 ppm (2H, multiplet)  
 1.96 ppm (1H, broad)  
 4.92 ppm (2H, s)  
 7.30 - 7.42 ppm (3H, multiplet and 2H, d)

8.05 ppm (NH, broad)  
(See figure 52-53)

$^{13}\text{C-NMR}$  : 13.992 ppm (2C; C<sup>5</sup>, C<sup>3'</sup>)  
(CDCl<sub>3</sub>) 20.655 ppm (2C; C<sup>4</sup>, C<sup>2'</sup>)  
34.786 ppm (2C; C<sup>3</sup>, C<sup>1'</sup>)  
43.933 ppm (1C; C<sup>2</sup>)  
78.234 ppm (1C; C<sup>1''</sup>)  
173.601 ppm (1C; C<sup>1</sup>)  
128.542 - 135.369 ppm (6C; C<sup>2''</sup>, C<sup>3''</sup>, C<sup>4''</sup>, C<sup>5''</sup>, C<sup>6''</sup>, C<sup>7''</sup>)  
(See figure 54)

EIMS : m/z 250 (M+1), 207, 178, 142, 108, 107, 100, 99, 98, 91, 79, 77,  
72, 65, 57, 55, 41.  
(See figure 55)

### (2-Chlorobenzyl)-2-propylpentanohydroxamate.

Used 1.2 g (0.03 mole) of sodium hydroxide, 5 g (0.03 mole) of 2-propylpentanohydroxamic acid, and 6.2 g (0.03 mole) of 2-chlorobenzyl chloride. Proceed as for ethyl- $\alpha$ -(2-propylpentamidoxy) acetate but heated under reflux for 4 hours. The yield of (2-chlorobenzyl)-2-propylpentanohydroxamate as white needle was 7.4 g (83%), m.p. 104-106°C, after recrystallization in hexane.

The structure of (2-chlorobenzyl)-2-propylpentanohydroxamate was confirmed by:

IR : 3200 CM<sup>-1</sup> (N-H stretch)  
(KBr 3100 - 3000 CM<sup>-1</sup> (C-H stretch; aromatic)  
Pellet) 3000 - 2860 CM<sup>-1</sup> (C-H stretch; aliphatic)  
2000 - 1667 CM<sup>-1</sup> (overtone or combination bands; aromatic)  
1661 CM<sup>-1</sup> (C=O stretch; amide like carbonyl)  
1520, 1450 CM<sup>-1</sup> (C=C stretch; aromatic)  
1055 CM<sup>-1</sup> (C-O stretch)  
758 CM<sup>-1</sup> (C-H bend; out-of-plane, aromatic)  
750 - 600 CM<sup>-1</sup> (N-H bend; out-of-plane)  
(See figure 56)

<sup>1</sup>H-NMR : 0.87 ppm (6H, t)  
 (CDCl<sub>3</sub>) 1.18 - 1.42 ppm (6H, multiplet)  
 1.55 - 1.66 ppm (2H, multiplet)  
 1.90 ppm (1H, broad)  
 5.07 ppm (2H, s)  
 7.27 ppm (2H, multiplet)  
 7.39 ppm (1H, dd)  
 7.50 ppm (1H, broad)  
 8.25 ppm (NH, broad)  
 (See figure 57-58)

<sup>13</sup>C-NMR : 13.992 ppm (2C; C<sup>5</sup>, C<sup>3'</sup>)  
 (CDCl<sub>3</sub>) 20.655 ppm (2C; C<sup>4</sup>, C<sup>2'</sup>)  
 34.770 ppm (2C; C<sup>3</sup>, C<sup>1'</sup>)  
 43.900 ppm (1C, C<sup>2</sup>)  
 75.289 ppm (1C; C<sup>1''</sup>)  
 173.848 ppm (1C; C<sup>1</sup>)  
 126.874 - 134.398 ppm (6C; C<sup>2''</sup>, C<sup>3''</sup>, C<sup>4''</sup>, C<sup>5''</sup>, C<sup>6''</sup>, C<sup>7''</sup>)  
 (See figure 59)

EIMS : m/z 284 (M+1), 241, 212, 142, 141, 125, 113, 100, 99, 98, 89,  
 77, 57, 55, 41.  
 (See figure 60)

### Ethyl-2-propylpentamidooxy Formate.

Added 3.5 g (0.02 mole) of sodium-2-propylpentano hydroxamate to 25 ml of dried and redistilled tetrahydrofuran in 100 ml round-bottom flask. Dropwised 2.2 g (0.02 mole) of ethylchloroformate, and then stirred the mixture at 0-10°C for 15 hours. Subsequently, the mixture was evaporated by using the rotary evaporator (very low temperature was used). The residue was dissolved in 50 ml of chloroform and extracted with three 50 ml portions of purified water. After that, the chloroform layer was dried with anhydrous sodium sulfate. Collected the chloroform layer and removed on a water bath (rotary evaporator) with very low temperature. The residue was purified by recrystallization in diluted methanol. The yield of the compound as white needle, m.p. 82-83°C, was 3.2 g (72 %).



The structure of ethyl-2-propylpentamidooxy formate was confirmed by:

IR	: 3225	CM <sup>-1</sup>	(N-H stretch)
(KBr Pellet)	3000 - 2860	CM <sup>-1</sup>	(C-H stretch; aliphatic)
	1798	CM <sup>-1</sup>	(O-(C=O)-O stretch)
	1667	CM <sup>-1</sup>	(C=O stretch; amide like carbonyl)
	1458	CM <sup>-1</sup>	(N-H bend)
	1245	CM <sup>-1</sup>	(C-O stretch; asym)
	750 - 600	CM <sup>-1</sup>	(N-H bend; out-of-plane)

(See figure 61)

<sup>1</sup> H-NMR	: 0.91 ppm	(6H, t)
(CDCl <sub>3</sub> )	1.37 ppm	(3H, t)
	1.25 - 1.48 ppm	(6H, multiplet)
	1.62 - 1.72 ppm	(2H, multiplet)
	2.12 ppm	(1H, broad)
	4.33 ppm	(2H, q)
	8.52 ppm	(NH, s)

(See figure 62-63)

<sup>13</sup> C-NMR	: 13.943 ppm	(2C; C <sup>5</sup> , C <sup>3'</sup> )
(CDCl <sub>3</sub> )	14.058 ppm	(1C; C <sup>3''</sup> )
	20.490 ppm	(2C; C <sup>4</sup> , C <sup>2'</sup> )
	34.671 ppm	(2C; C <sup>3</sup> , C <sup>1'</sup> )
	43.384 ppm	(1C; C <sup>2</sup> )
	66.142 ppm	(1C; C <sup>2''</sup> )
	154.518 ppm	(1C; C <sup>1''</sup> )
	173.539 ppm	(1C; C <sup>1</sup> )

(See figure 64)

## 2-Propylpentanohydroxamic Acetic Anhydride.

Used 3.5 g (0.02 mole) of sodium-2-propylpentano hydroxamate, and 2 g (0.02 mole) of acetic anhydride. Proceed as for Ethyl-2-propylpentamidooxy formate but stirred at 0-10°C for 24 hours. The yield of 2-propylpentanohydroxamic acetic anhydride as white needle was 2.6 g (67%), m.p. 77-78°C, after recrystallization in hexane.

The structure of 2-propylpentanohydroxamic acetic anhydride was confirmed by:

IR	: 3194	CM <sup>-1</sup>	(N-H stretch)
(KBr Pellet)	3000 - 2860	CM <sup>-1</sup>	(C-H stretch; aliphatic)
	1793	CM <sup>-1</sup>	(C=O stretch; ester like carbonyl)
	1667	CM <sup>-1</sup>	(C=O stretch; amide like carbonyl)
	1458	CM <sup>-1</sup>	(N-H bend)
	1245	CM <sup>-1</sup>	(C-O stretch; asym)
	750 - 600	CM <sup>-1</sup>	(N-H bend; out-of-plane)

(See figure 65)

<sup>1</sup> H-NMR	: 0.91 ppm	(6H, t)
(CDCl <sub>3</sub> )	1.37 ppm	(3H, t)
	1.25 - 1.48 ppm	(6H, multiplet)
	1.58 - 1.70 ppm	(2H, multiplet)
	2.19 ppm	(1H, broad)
	2.22 ppm	(3H, s)
	9.35 ppm	(NH, broad)

(See figure 66-67)

<sup>13</sup> C-NMR	: 13.959 ppm	(2C; C <sup>5</sup> , C <sup>3'</sup> )
(CDCl <sub>3</sub> )	18.236 ppm	(1C; C <sup>2''</sup> )
	20.540 ppm	(2C; C <sup>4</sup> , C <sup>2'</sup> )
	34.753 ppm	(2C; C <sup>3</sup> , C <sup>1'</sup> )
	43.966 ppm	(1C; C <sup>2</sup> )
	168.831 ppm	(1C; C <sup>1''</sup> )
	174.177 ppm	(1C; C <sup>1</sup> )

(See figure 68)

### 2-Propylpentanohydroxamic Benzoic Anhydride.

Used 3.5 g (0.02 mole) of sodium-2-propylpentano hydroxamate, and 2.8 g (0.02 mole) of benzoyl chloride. Proceed as for Ethyl-2-propylpentamidooxy formate but stirred at 0-10°C for 10 hours. The yield of 2-propylpentanohydroxamic benzoic anhydride as white needle was 3.6 g (71%), m.p. 125-126 °C, after recrystallization in hexane.

The structure of 2-propylpentanohydroxamic benzoic anhydride was confirmed by:

IR	: 3174	CM <sup>-1</sup>	(N-H stretch)
(KBr Pellet)	3100 - 3000	CM <sup>-1</sup>	(C-H stretch; aromatic)
	3000 - 2860	CM <sup>-1</sup>	(C-H stretch; aliphatic)
	2000 - 1667	CM <sup>-1</sup>	(overtone or combination bands; aromatic)
	1775	CM <sup>-1</sup>	(C=O stretch; ester like carbonyl)
	1655	CM <sup>-1</sup>	(C=O stretch; amide like carbonyl)
	1600, 1452	CM <sup>-1</sup>	(C=C stretch; aromatic)
	1239	CM <sup>-1</sup>	(C-H bend; in plane)
	697	CM <sup>-1</sup>	(C=C bend; aromatic)
	750 - 600	CM <sup>-1</sup>	(N-H bend; out-of-plane)

(See figure 69)

<sup>1</sup> H-NMR	: 0.92 ppm	(6H, t)
(CDCl <sub>3</sub> )	1.29 - 1.51 ppm	(6H, multiplet)
	1.65 - 1.75 ppm	(2H, multiplet)
	2.25 ppm	(1H, broad)
	7.47 ppm	(2H, dd)
	7.63 ppm	(1H, dddd)
	8.10 ppm	(2H, dd)
	9.22 ppm	(NH, broad)

(See figure 70-71)

<sup>13</sup> C-NMR	: 14.008 ppm	(2C; C <sup>5</sup> , C <sup>3'</sup> )
(CDCl <sub>3</sub> )	20.605 ppm	(2C; C <sup>4</sup> , C <sup>2'</sup> )
	34.836 ppm	(2C; C <sup>3</sup> , C <sup>1'</sup> )
	44.163 ppm	(1C; C <sup>2</sup> )
	164.997 ppm	(1C; C <sup>1''</sup> )
	174.375 ppm	(1C; C <sup>1</sup> )
	126.666 - 134.119 ppm	(1C; C <sup>2''</sup> , C <sup>3''</sup> , C <sup>4''</sup> , C <sup>5''</sup> , C <sup>6''</sup> , C <sup>7''</sup> )

(See figure 72)

### 2-Propylpentanohydroxamic 4-Nitrobenzoic Anhydride.

Used 3.5 g (0.02 mole) of sodium-2-propylpentano hydroxamate, and 3.7 g (0.02 mole) of 4-nitrobenzoyl chloride. Proceed as for Ethyl-2-propylpentamidooxy formate but stirred at 0-10°C for 10 hours. The

yield of 2-propylpentanohydroxamic 4-nitrobenzoic anhydride as pale yellow needle was 4 g (67%), m.p. 138-140°C, after recrystallization in mixed solvent, chloroform and hexane.

The structure of 2-propylpentanohydroxamic 4-nitrobenzoic anhydride was confirmed by:

IR : 3205  $\text{CM}^{-1}$  (N-H stretch)  
 (KBr Pellet) 3100 - 3000  $\text{CM}^{-1}$  (C-H stretch; aromatic)  
 3000 - 2860  $\text{CM}^{-1}$  (C-H stretch; aliphatic)  
 2000 - 1667  $\text{CM}^{-1}$  (overtone or combination bands; aromatic)  
 1770  $\text{CM}^{-1}$  (C=O stretch; ester like carbonyl)  
 1669  $\text{CM}^{-1}$  (C=O stretch; amide like carbonyl)  
 1608, 1464  $\text{CM}^{-1}$  (C=C stretch; aromatic)  
 1526  $\text{CM}^{-1}$  (N-O stretch; asym)  
 1460  $\text{CM}^{-1}$  (N-H bend)  
 1351  $\text{CM}^{-1}$  (N-O stretch; sym)  
 750 - 600  $\text{CM}^{-1}$  (N-H bend; out-of-plane)  
 (See figure 73)

$^1\text{H-NMR}$  : 0.94 ppm (6H, t)  
 ( $\text{CDCl}_3$ ) 1.30 - 1.54 ppm (6H, multiplet)  
 1.66 - 1.76 ppm (2H, multiplet)  
 2.25 ppm (1H, broad)  
 8.29 ppm (2H, dd)  
 8.34 ppm (2H, dd)  
 9.00 ppm (NH, broad)  
 (See figure 74-75)

$^{13}\text{C-NMR}$  : 13.992 ppm (2C;  $\text{C}^5$ ,  $\text{C}^3$ )  
 ( $\text{CDCl}_3$ ) 20.605 ppm (2C;  $\text{C}^4$ ,  $\text{C}^2$ )  
 34.803 ppm (2C;  $\text{C}^3$ ,  $\text{C}^{1'}$ )  
 44.131 ppm (1C;  $\text{C}^2$ )  
 163.286 ppm (1C;  $\text{C}^{1''}$ )  
 174.588 ppm (1C;  $\text{C}^1$ )  
 123.787 - 151.129 ppm (6C;  $\text{C}^{2''}$ ,  $\text{C}^{3''}$ ,  $\text{C}^{4''}$ ,  $\text{C}^{5''}$ ,  $\text{C}^{6''}$ ,  $\text{C}^{7''}$ )  
 (See figure 76)

## 2-Propylpentanohydroxamic 4-Aminobenzoic Anhydride.

Dissolved 3 g (0.01 mole) of 2-propylpentanohydroxamic 4-nitrobenzoic anhydride in 25 ml of absolute ethanol. The solution was added to a Parr hydrogenation bottle. A little amount of catalyst, 10% palladium on activated charcoal was added, and then subjected to low-pressure hydrogenation (45 psi) for 10 hours. The contents were filtered by using filtered-paper, the black precipitate was filtered out. The filtrate was evaporated. Add 25 ml of benzene, then filtered the mixture. The filter, pale orange precipitate, was purified by recrystallization from ethylacetate. The purified product, 2-propylpentanohydroxamic 4-aminobenzoic anhydride, was precipitate as pale yellow crystals. The yield of the final product, m.p. 154-155°C, was 1.8 ml (73%).

The structure of 2-propylpentanohydroxamic 4-aminobenzoic anhydride was confirmed by:

IR	: 3540	CM <sup>-1</sup>	(N-H stretch; sym, primary amine)
(KBr	3460	CM <sup>-1</sup>	(N-H stretch; asym, primary amine)
Pellet)	3248	CM <sup>-1</sup>	(N-H stretch)
	3100 - 3000	CM <sup>-1</sup>	(C-H stretch; aromatic)
	3000 - 2860	CM <sup>-1</sup>	(C-H stretch; aliphatic)
	1774	CM <sup>-1</sup>	(C=O stretch; ester like carbonyl)
	1670	CM <sup>-1</sup>	(C=O stretch; amide like carbonyl)
	1650	CM <sup>-1</sup>	(N-H bend; aromatic amine)
	1622	CM <sup>-1</sup>	(C=C stretch; aromatic)
	1482	CM <sup>-1</sup>	(N-H bend; amide)
	1282	CM <sup>-1</sup>	(C-N stretch; aromatic amine)

(See figure 77)

<sup>1</sup> H-NMR :	0.86 ppm	(6H, t)
(DMSO)	1.23 - 1.37 ppm	(6H, multiplet)
	1.43 - 1.54 ppm	(2H, multiplet)
	2.20 ppm	(1H, dddd)
	6.59 ppm	(2H, d)
	7.67 ppm	(2H, d)
	11.56 ppm	(1H, s)

(See figure 78-79)

$^{13}\text{C-NMR}$ : 13.902 ppm	(2C; C <sup>5</sup> , C <sup>3'</sup> )
(DMDO) 19.956 ppm	(2C; C <sup>4</sup> , C <sup>2'</sup> )
34.499 ppm	(2C; C <sup>3</sup> , C <sup>1'</sup> )
42.182 ppm	(1C; C <sup>2</sup> )
164.151 ppm	(1C; C <sup>1''</sup> )
172.212 ppm	(1C; C <sup>1</sup> )
112.362 - 154.198 ppm	(6C; C <sup>2''</sup> , C <sup>3''</sup> , C <sup>4''</sup> , C <sup>5''</sup> , C <sup>6''</sup> , C <sup>7''</sup> )

(See figure 80)



ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

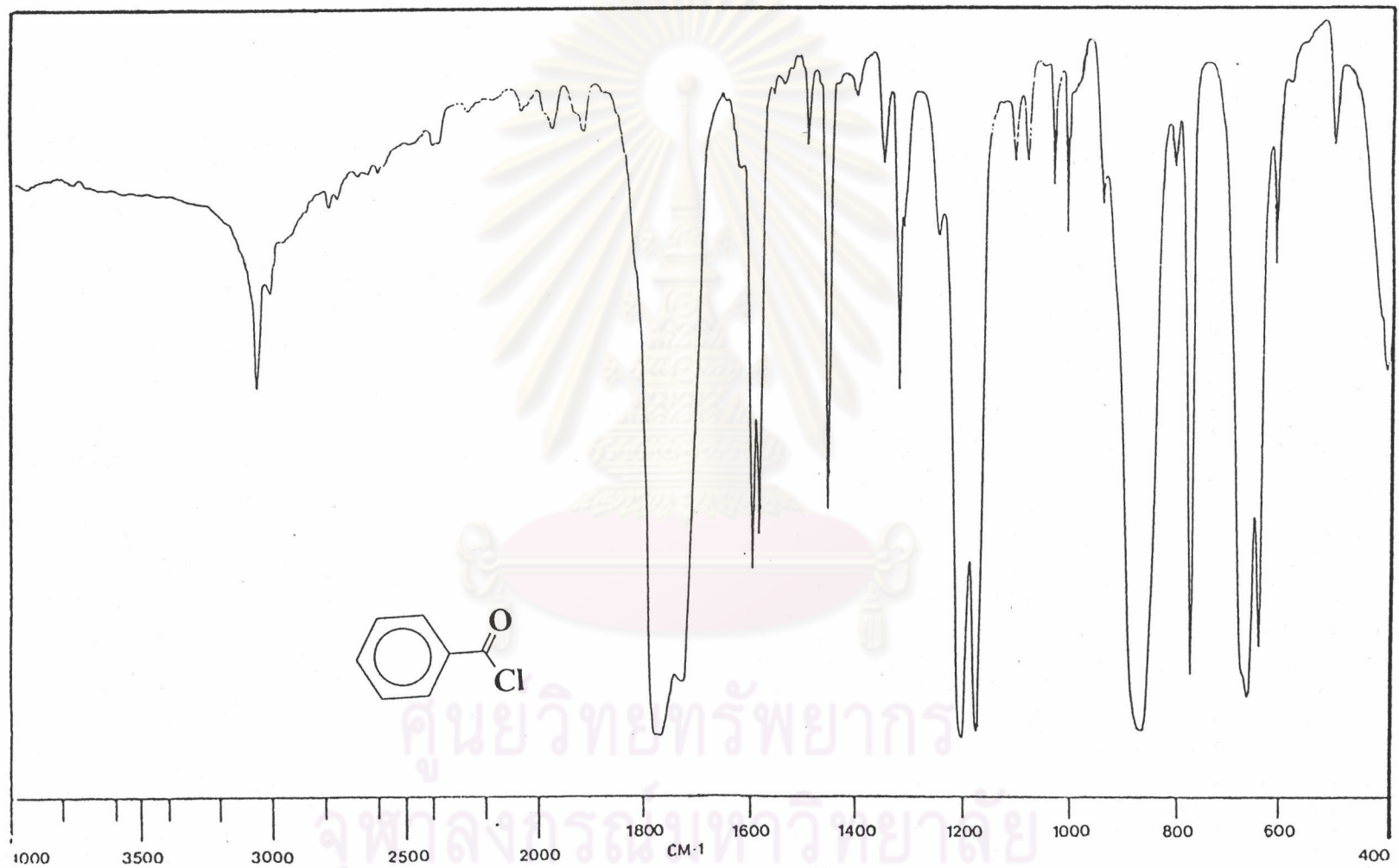


Figure 20. The IR spectrum (NEAT) of benzoyl chloride.

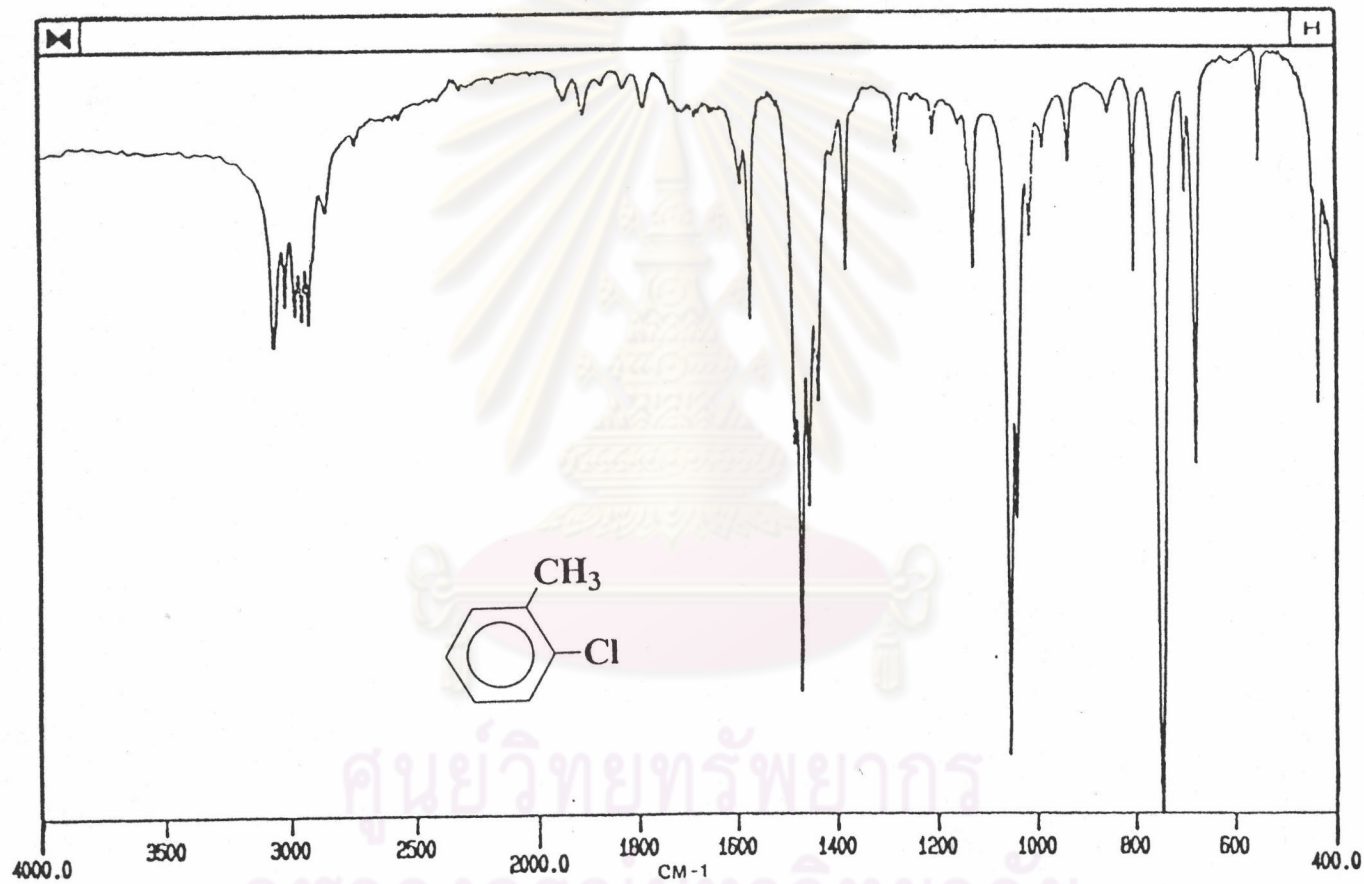


Figure 21. The IR spectrum (NEAT) of 2-chlorotoluene.



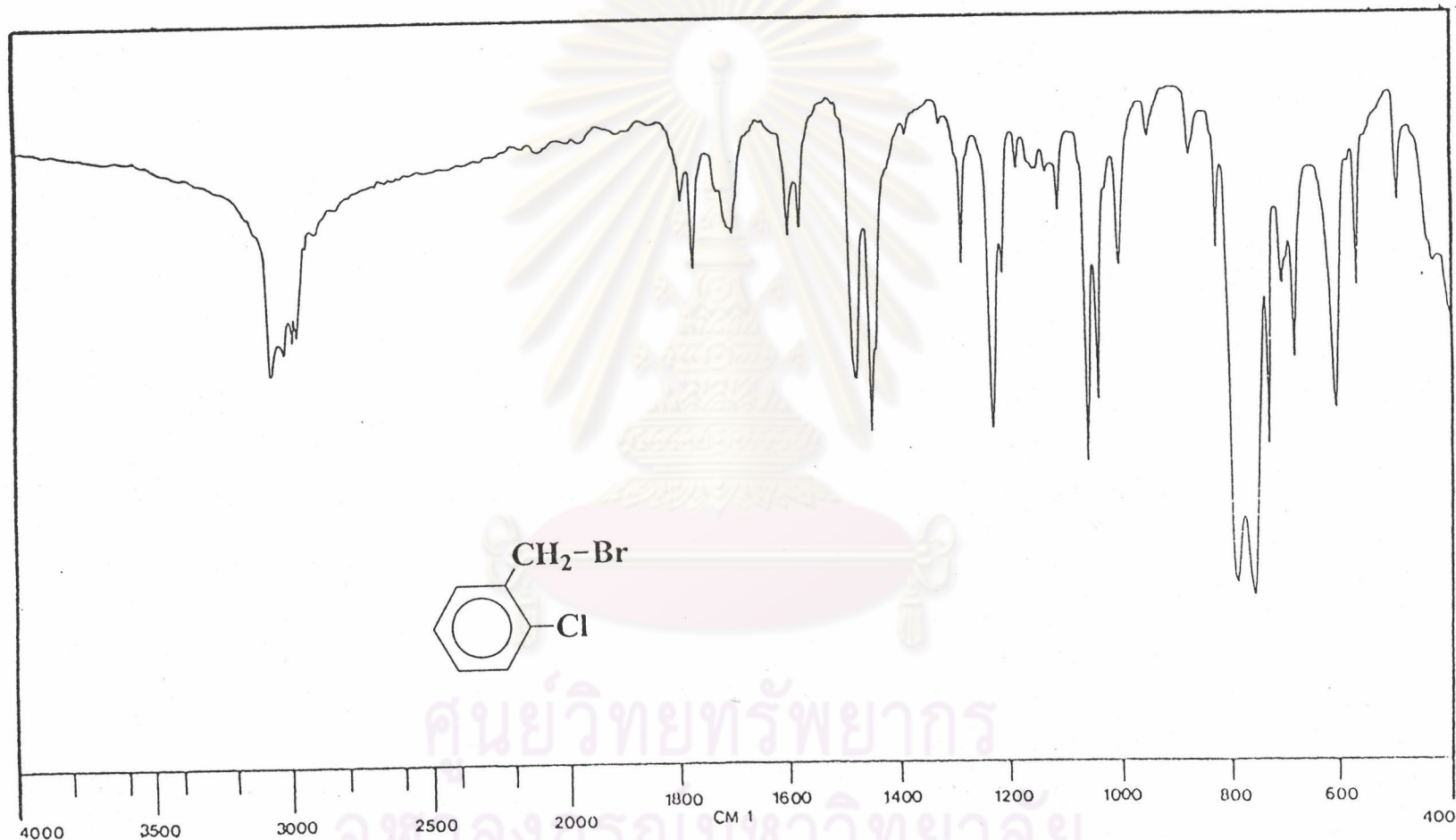


Figure 22. The IR spectrum (NEAT) of  $\alpha$ -bromo-2-chlorotoluene.

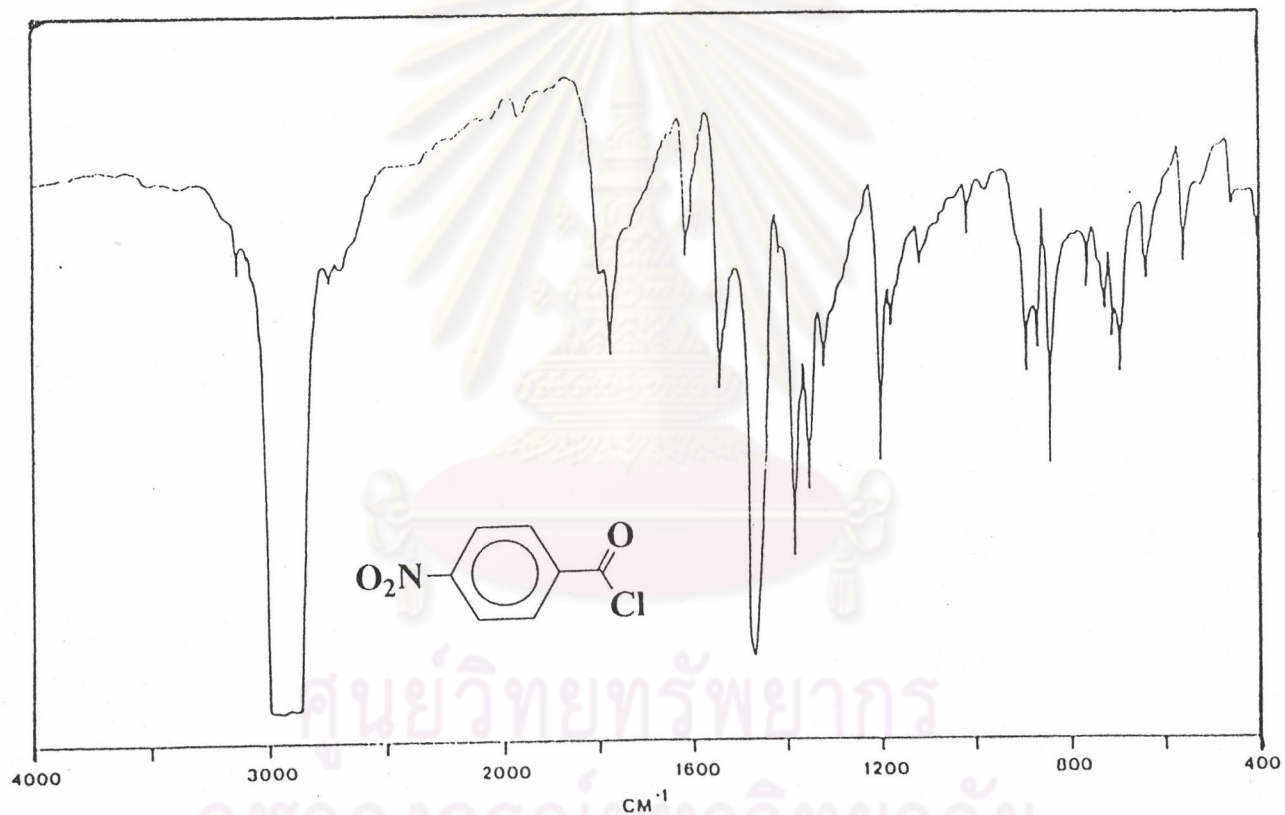


Figure 23. The IR spectrum (Nujol's mull) of p-nitrobenzoylchloride.

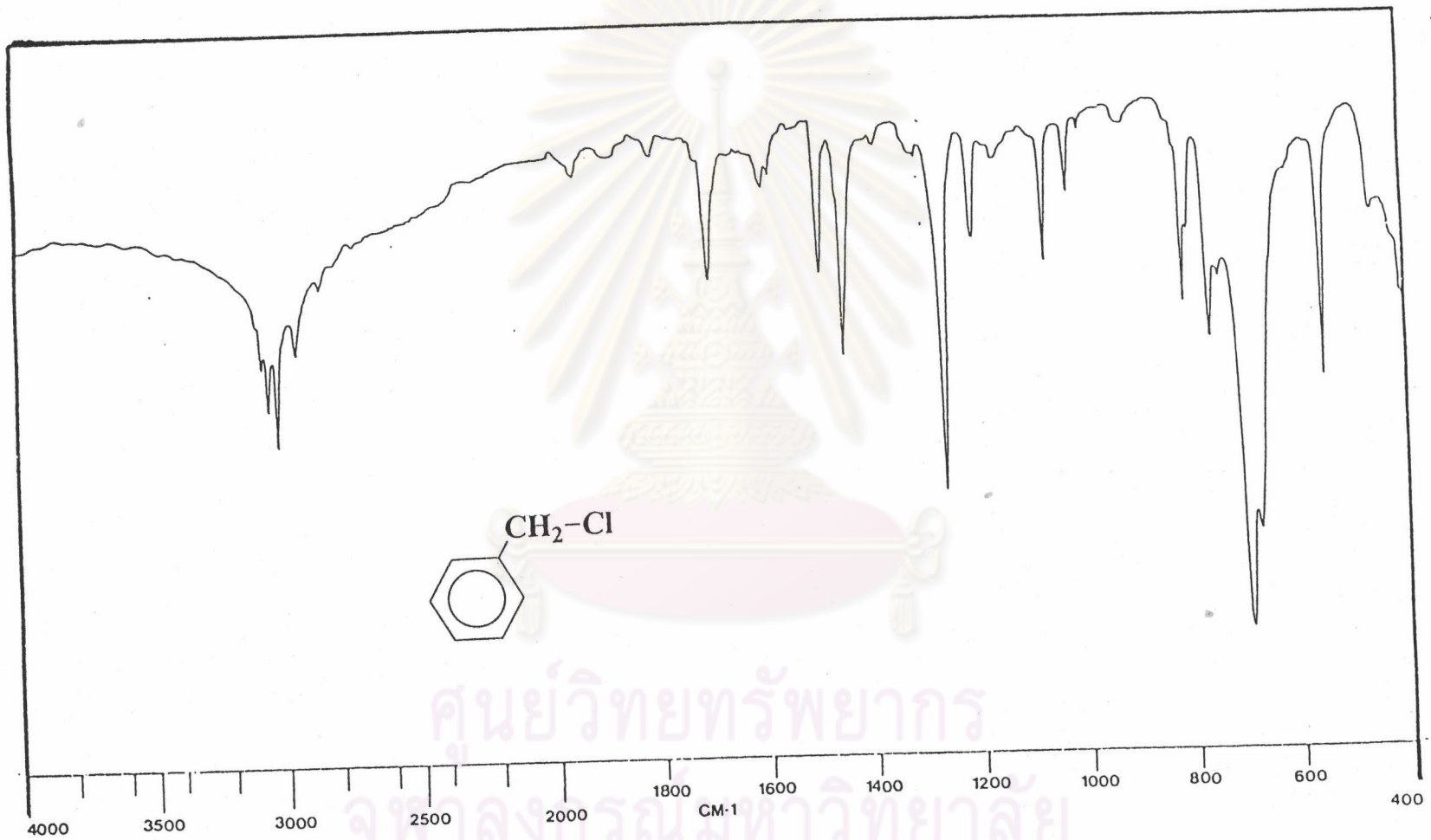


Figure 24. The IR spectrum (NEAT) of benzylchloride.

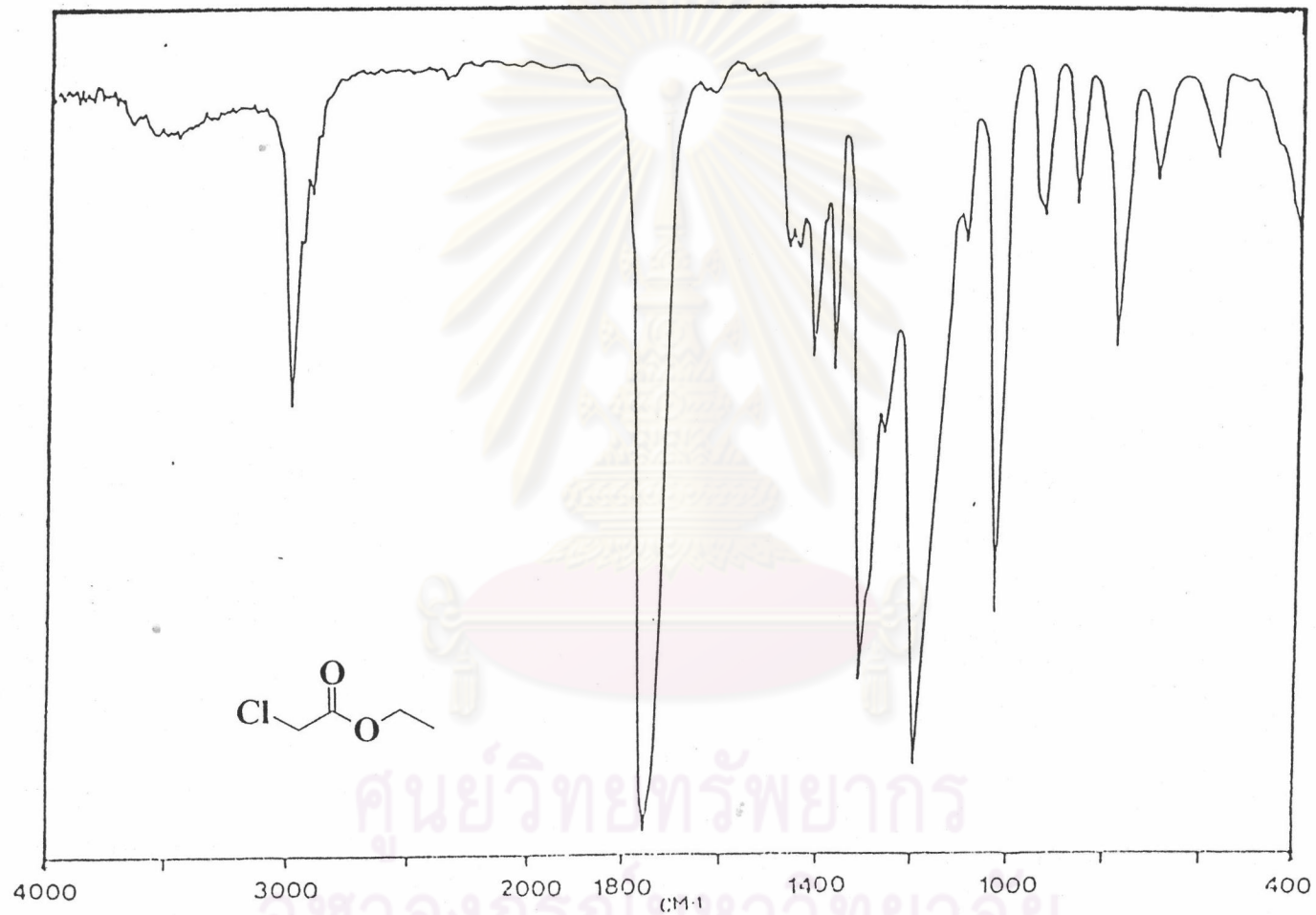


Figure 25. The IR spectrum (NEAT) of ethyl- $\alpha$ -chloroacetate.

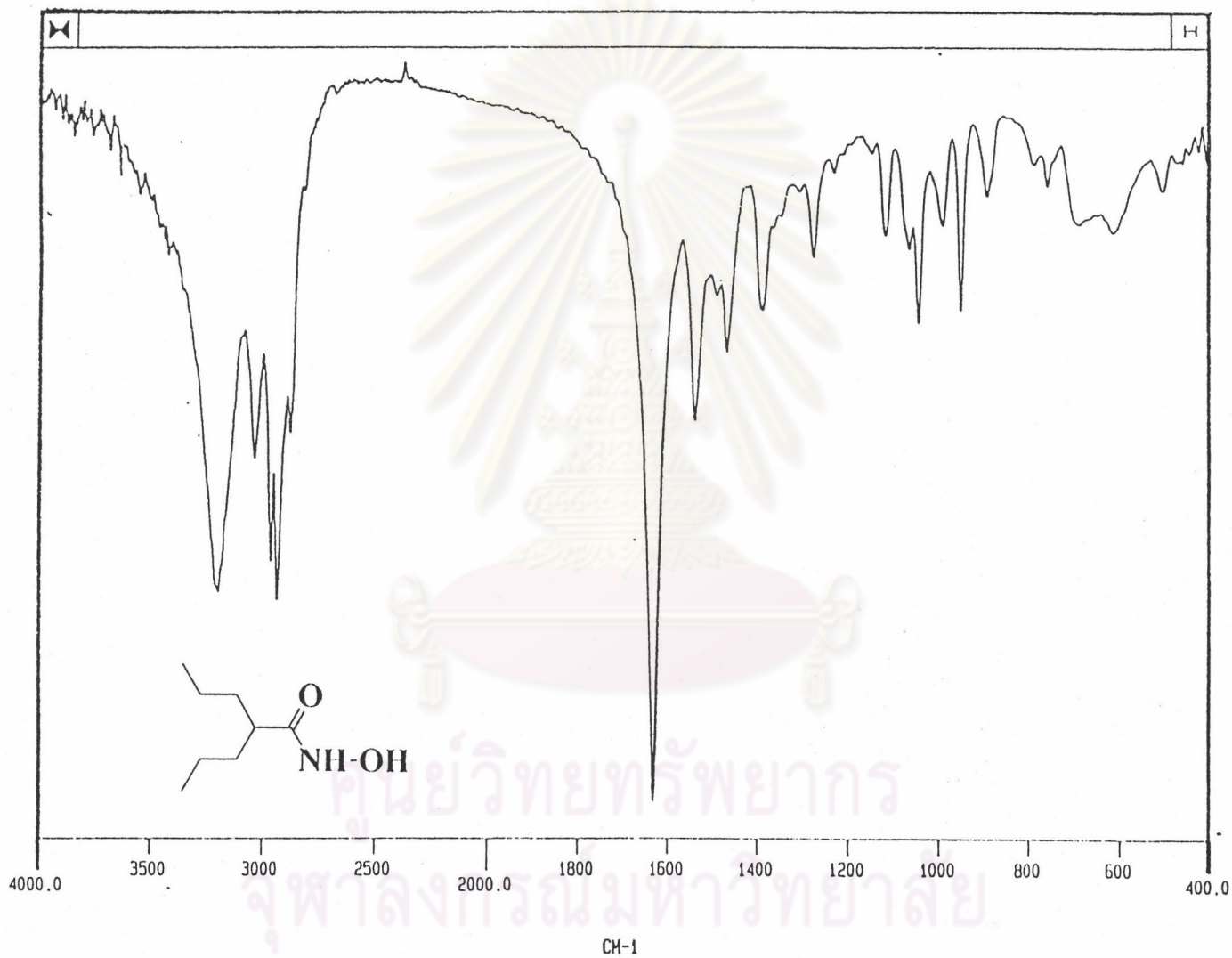


Figure 26. The IR spectrum (KBr pellet) of 2-propylpentanohydroxamic acid.

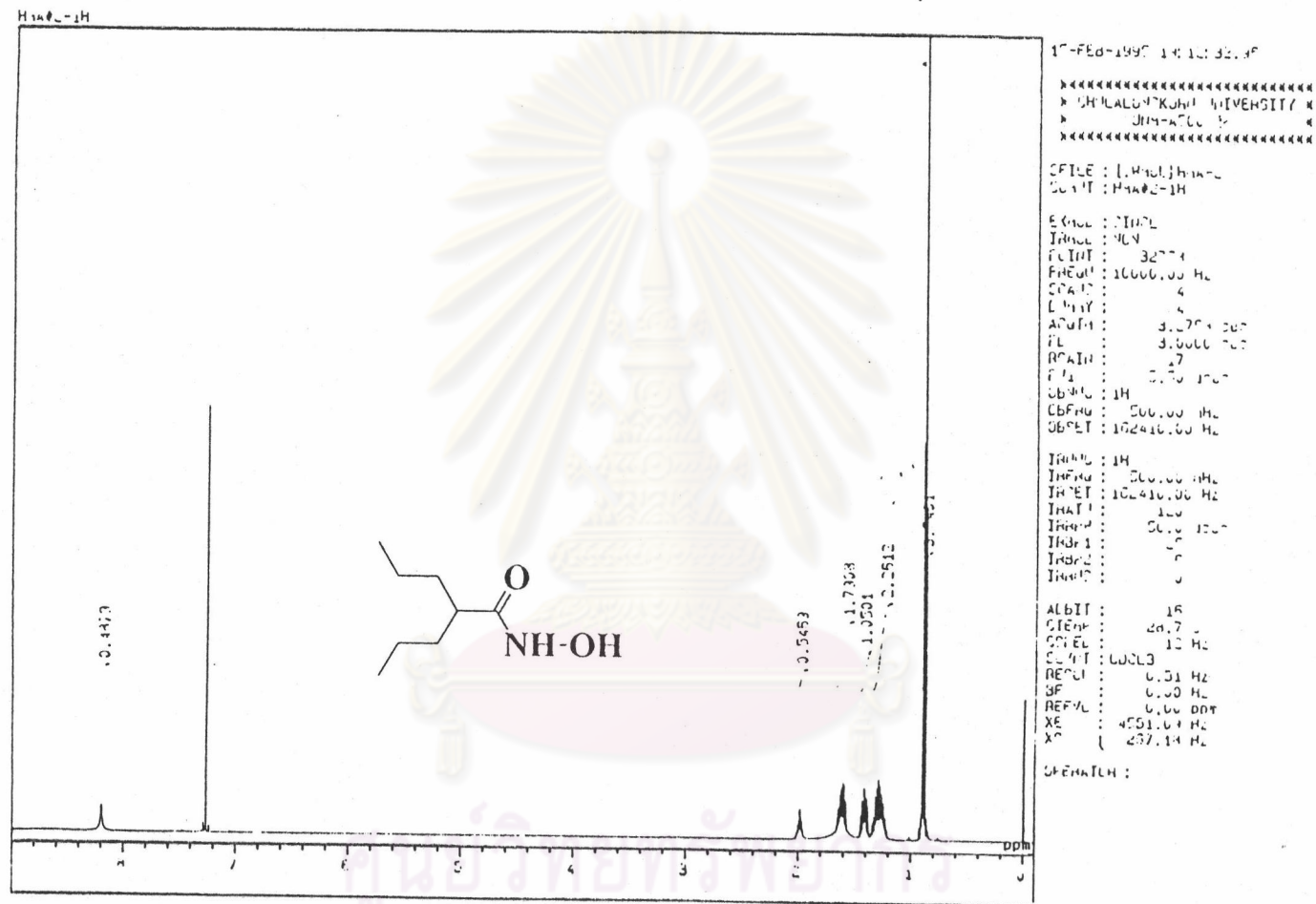


Figure 27. The 500 MHz  $^1\text{H}$ -NMR spectrum of 2-propylpentanohydroxamic acid.

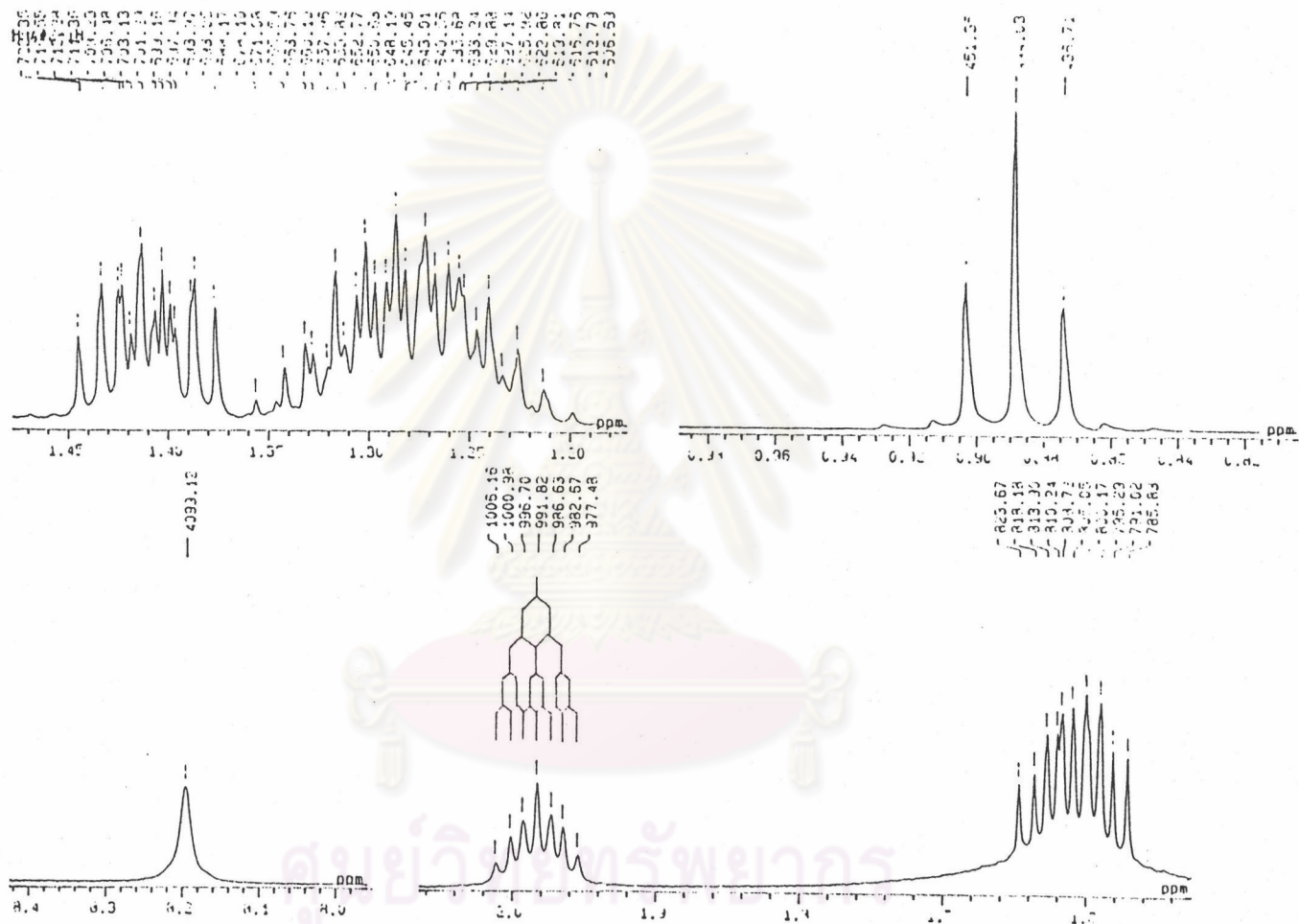


Figure 28. The 500 MHz <sup>1</sup>H-NMR spectrum of 2-propylpentanoic acid. (Enlarge scale : 0.8-8.4 ppm)

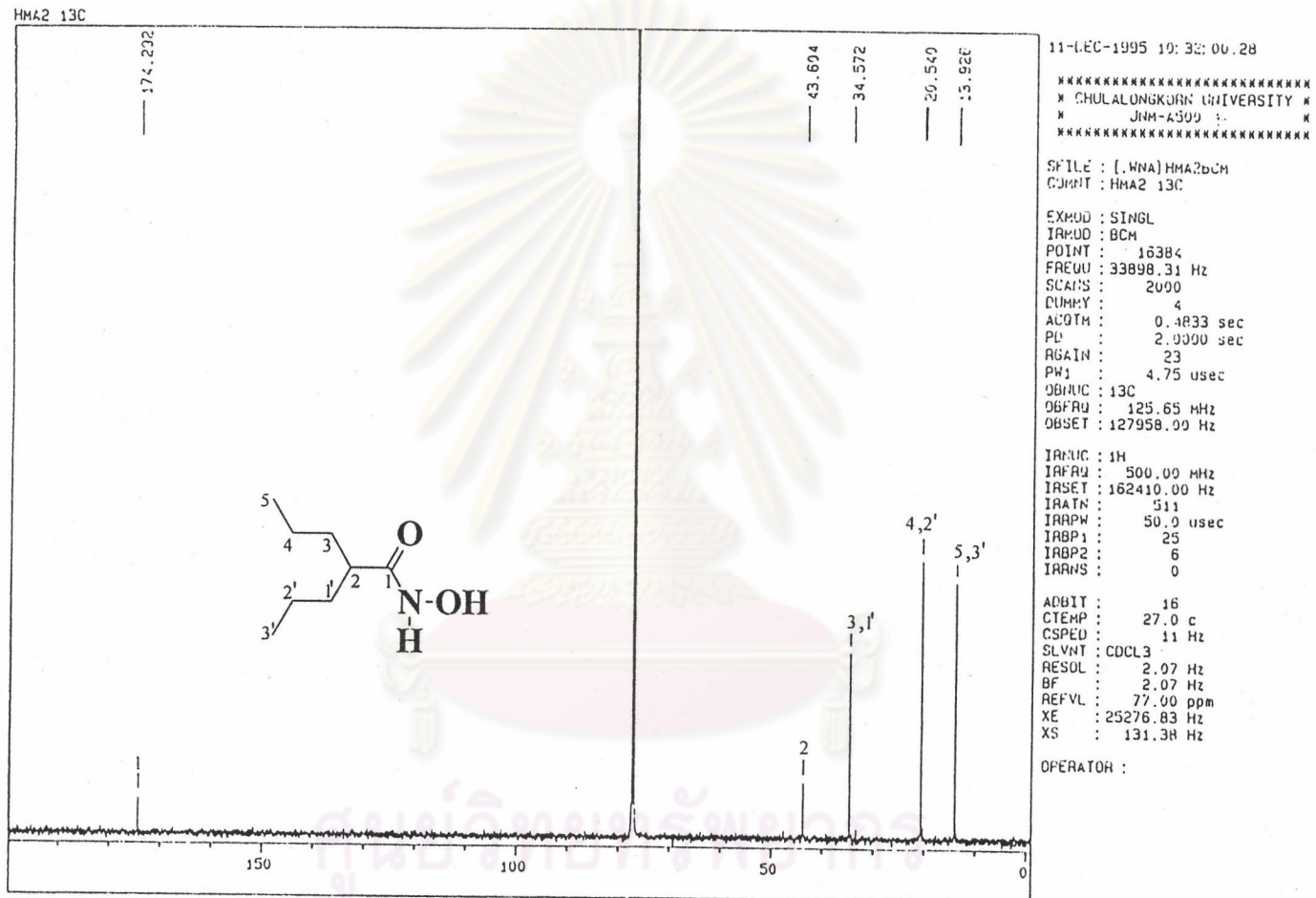


Figure 29. The  $^{13}\text{C}$ -NMR decoupled spectrum of 2-propylpentanohydroxamic acid.



Background Subtract  
Comment: DBS-MS 30X.25MM 17/1/95  
Average of: 359 to 363 Minus: 342 to 346  
100%

C:\SATURN\DATA\HMA2-2

Date: 01/17/96 10:46:22

100% = 9761

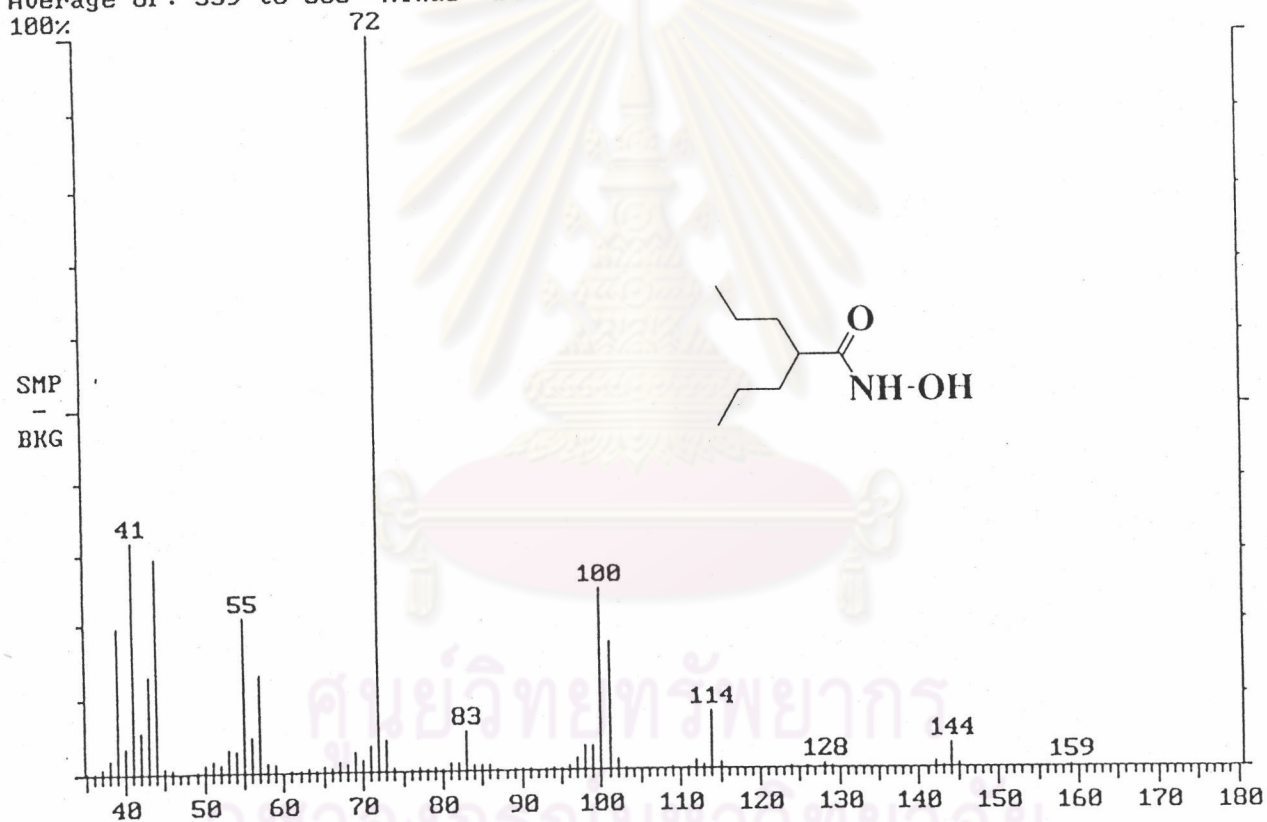


Figure 30. The EIMS spectrum of 2-propylpentanoic acid.

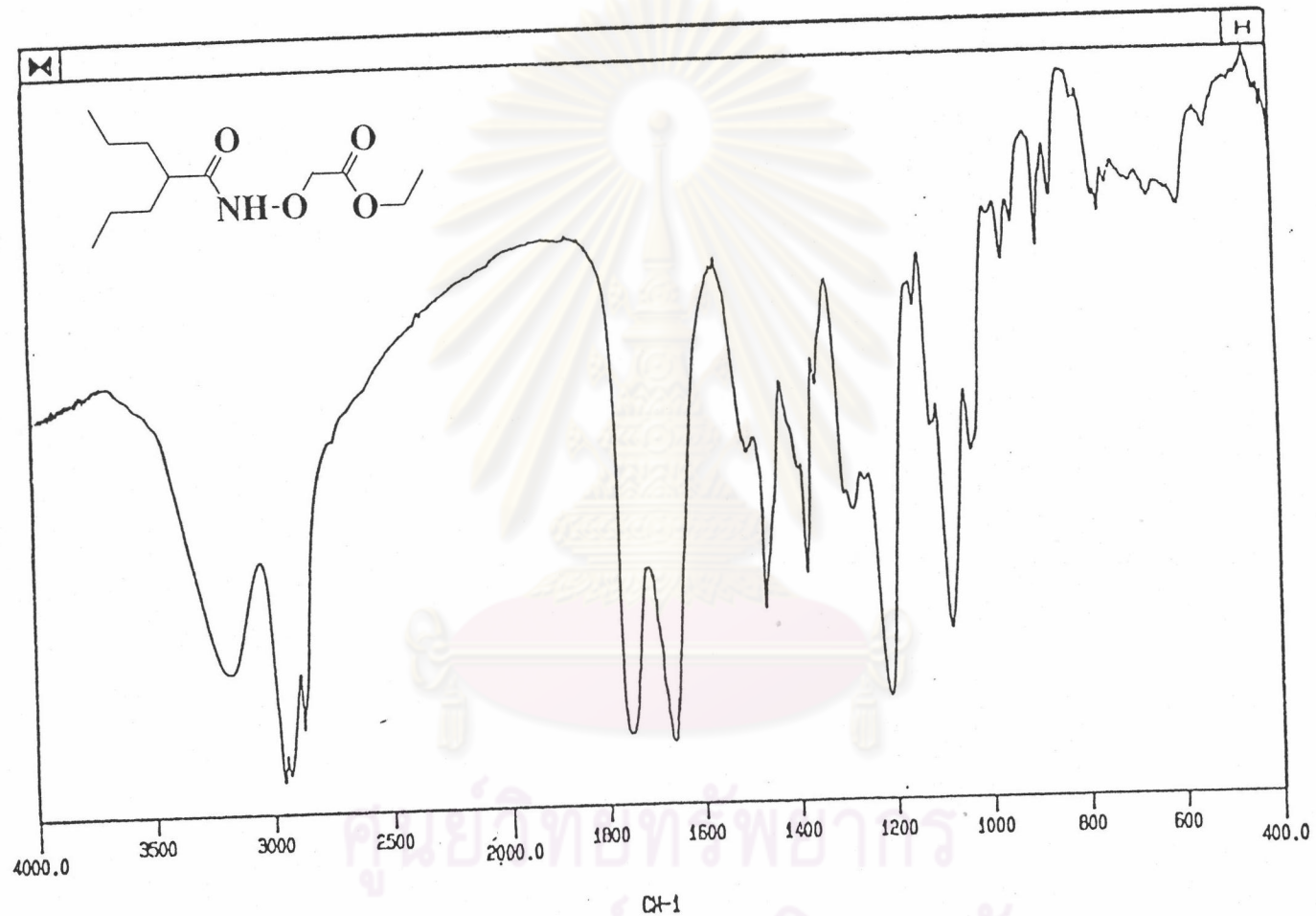


Figure 31. The IR spectrum (KBr pellet) of ethyl- $\alpha$ -(2-propylpentamidoxy) acetate.

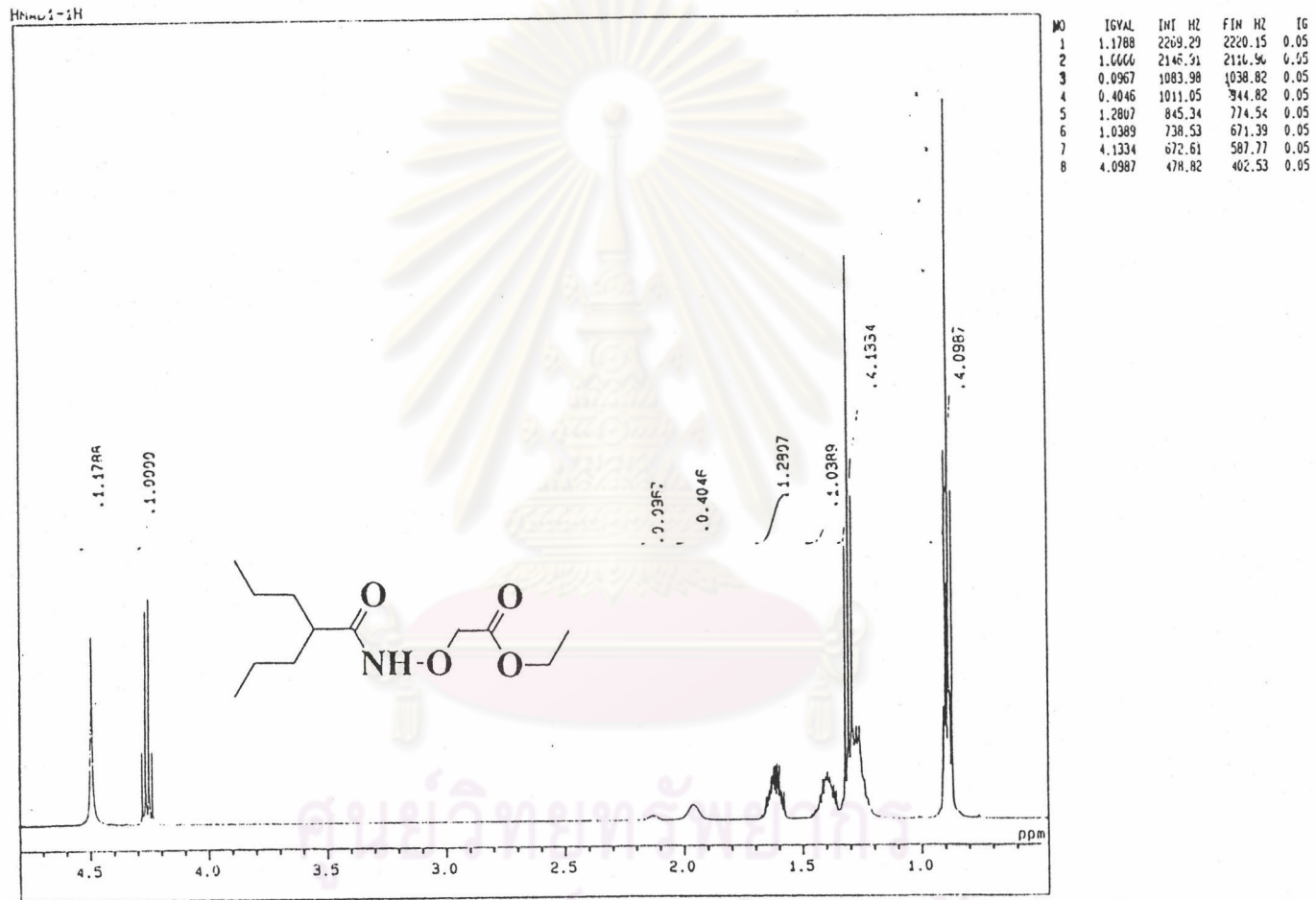


Figure 32. The 500 MHz  $^1\text{H}$ -NMR spectrum of ethyl- $\alpha$ -(2-propyl pentamidoxy)acetate.

HMAD1-1H

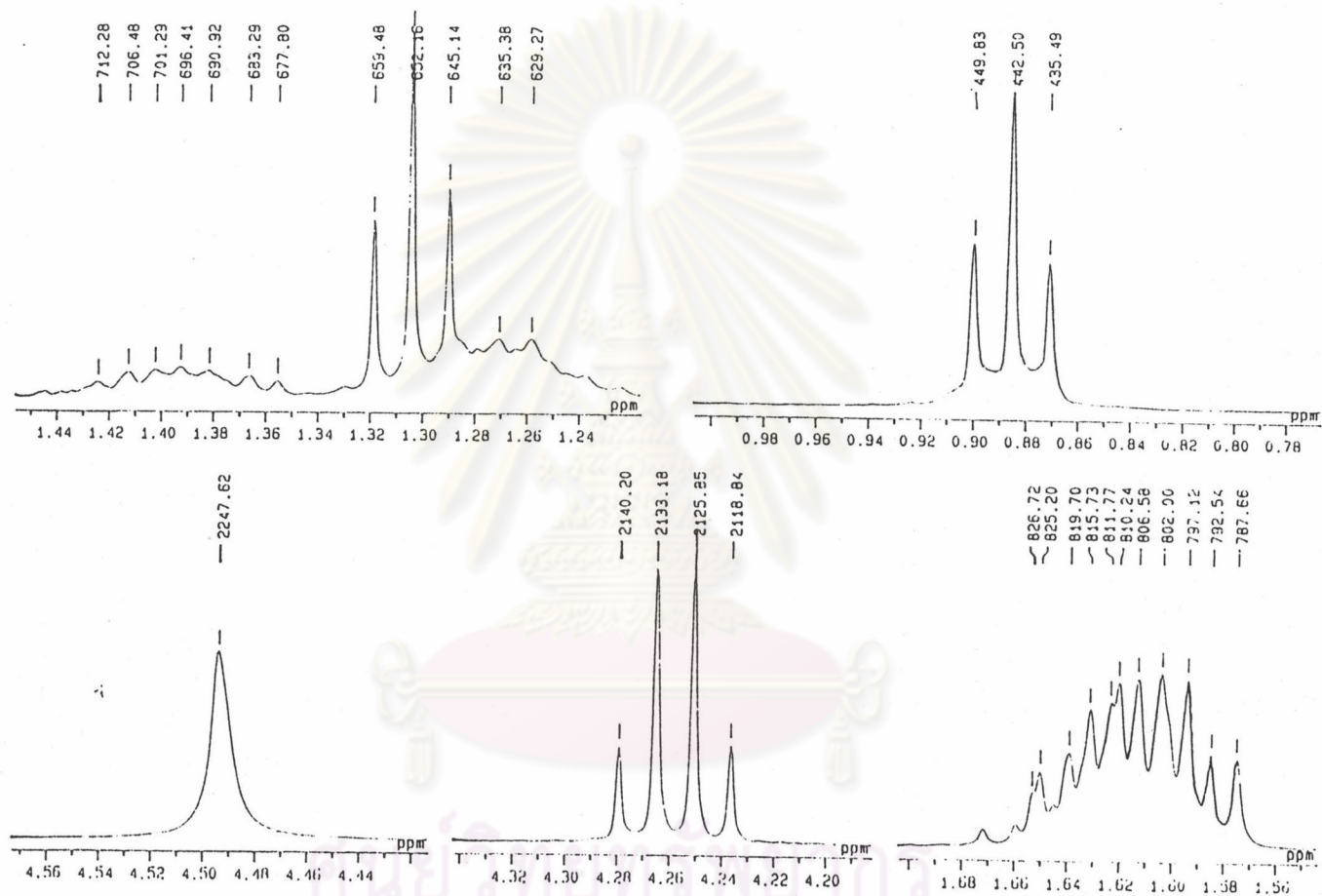


Figure 33. The 500 MHz  $^1\text{H}$ -NMR spectrum of ethyl- $\alpha$ -(2-propyl pentamidoxy)acetate. (Enlarge scale : 0.78-4.56 ppm)

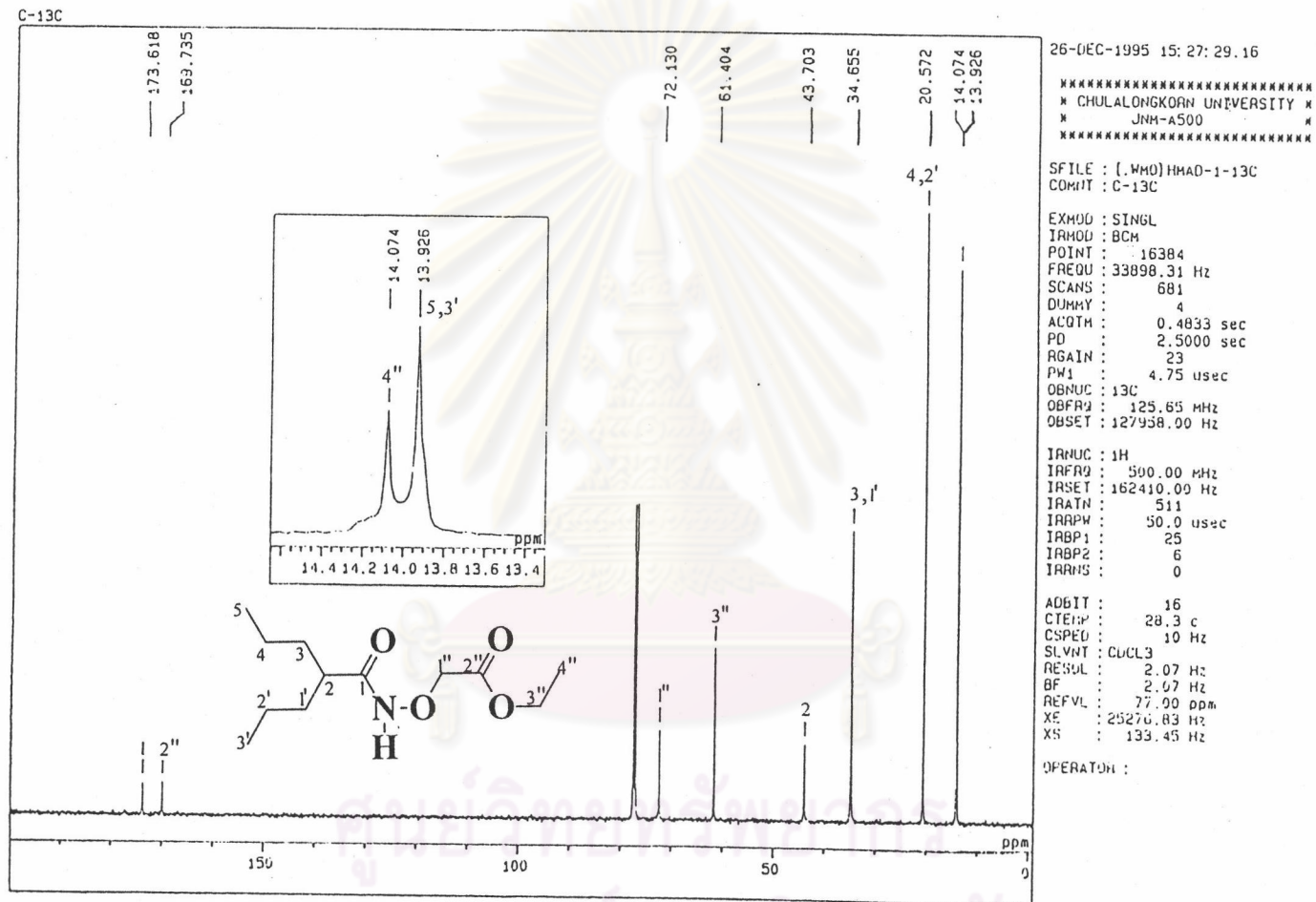


Figure 34. The  $^{13}\text{C}$ -NMR decoupled spectrum of ethyl- $\alpha$ -(2-propyl pentamidoxy)acetate.

Background Subtract

C:\SATURN\DATA\HMAD1

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Comment: DB5-MS 30X.25MM 17/1/95

Average of: 807 to 811 Minus: 619 to 1003

100% = 69726

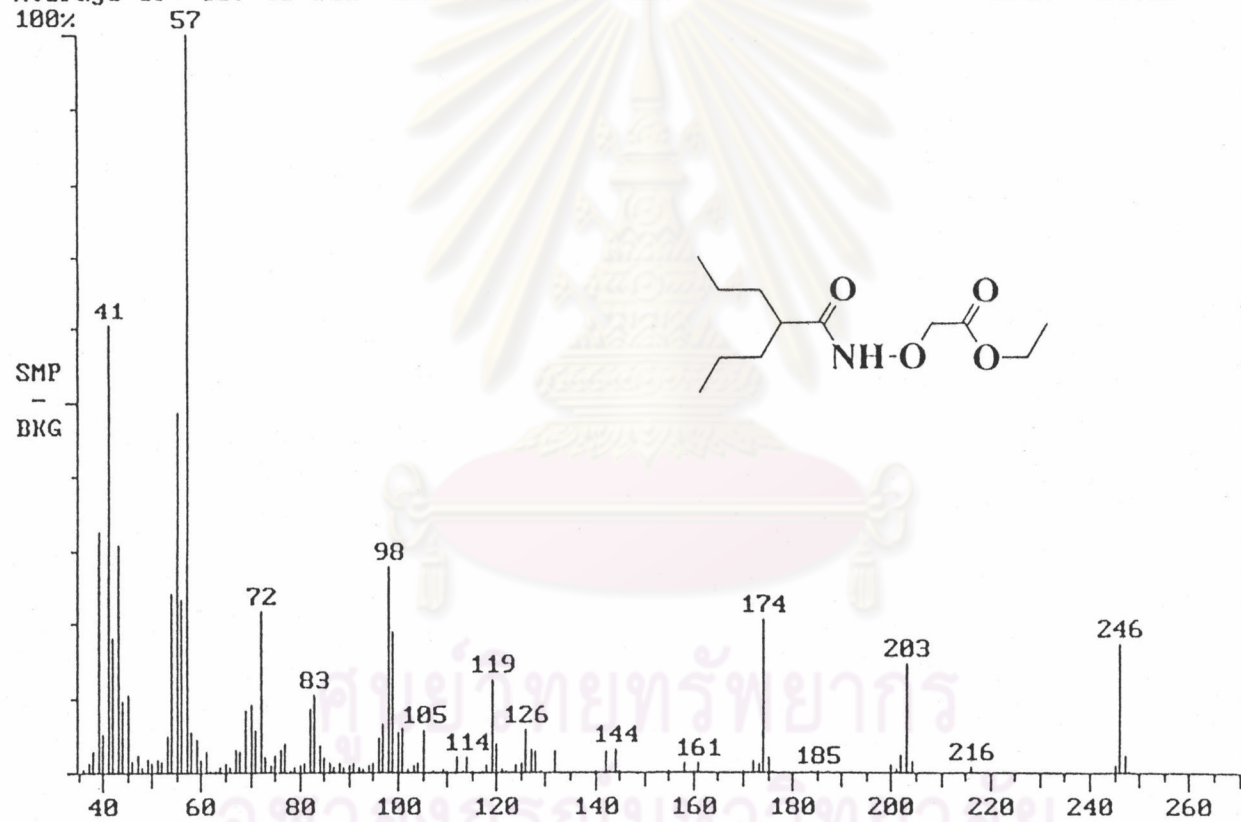


Figure 35. The EIMS spectrum of ethyl- $\alpha$ -(2-propylpentamidoxy)acetate.

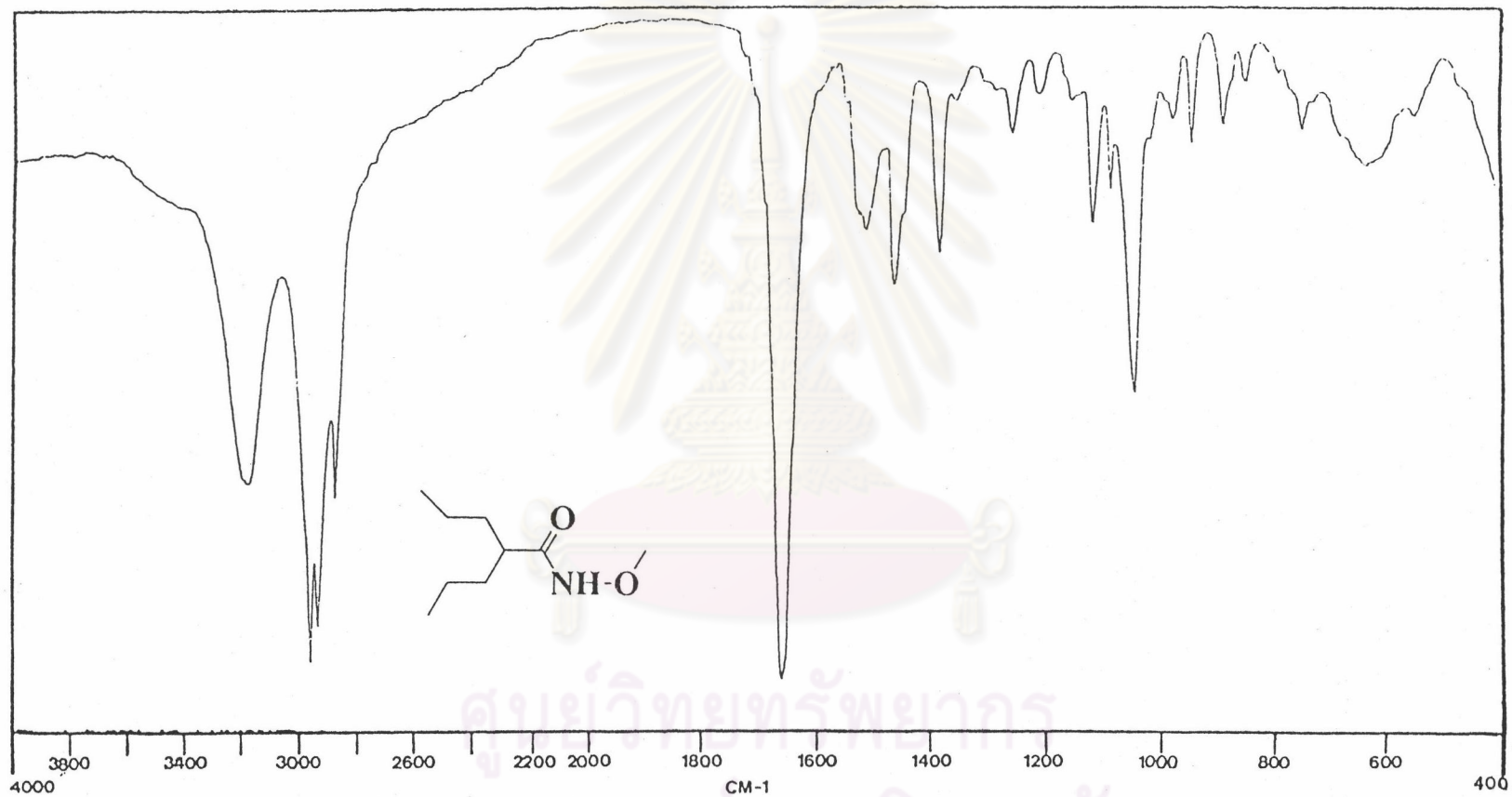


Figure 36. The IR spectrum (NEAT) of methyl-2-propylpentano-hydroxamate.

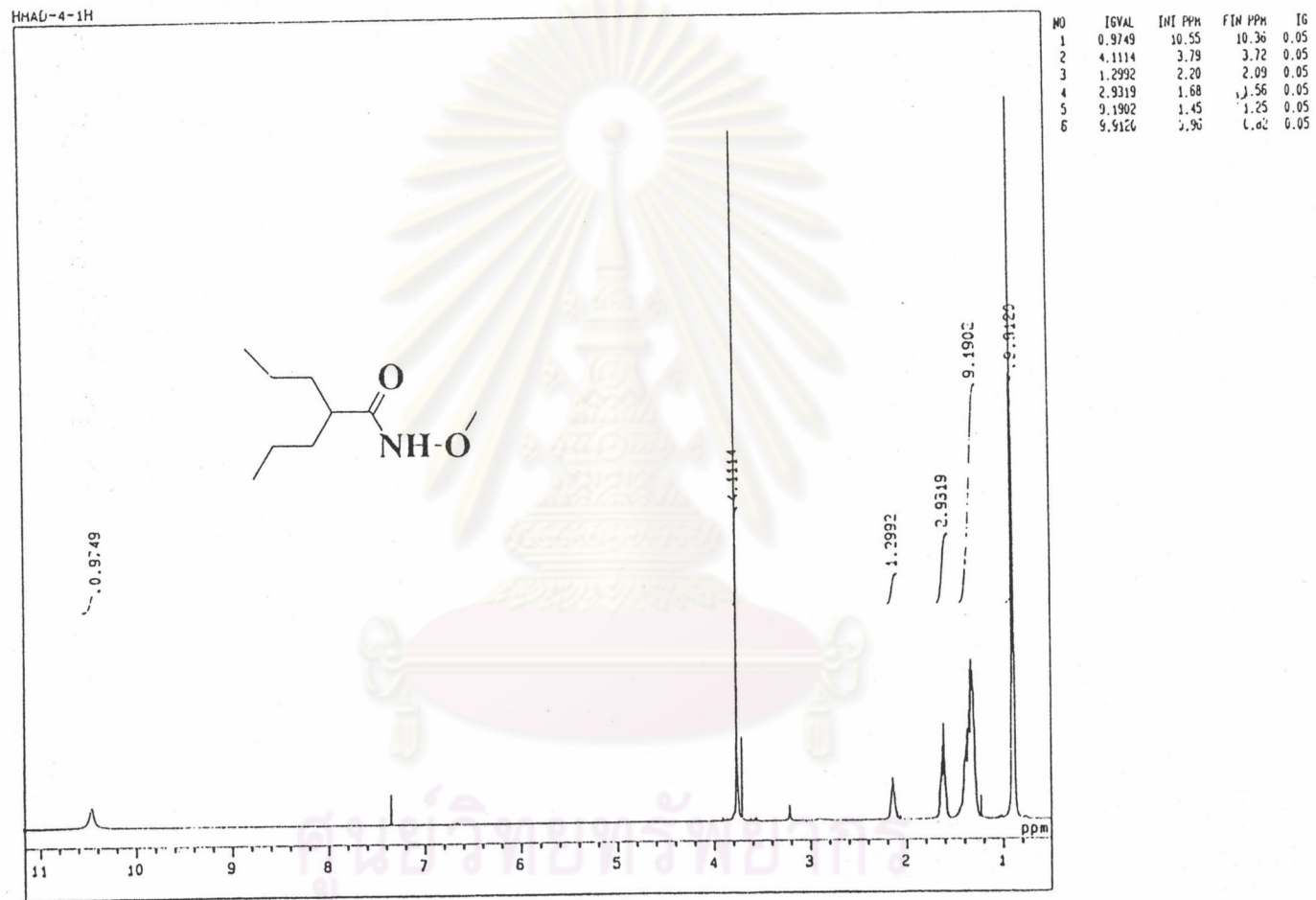


Figure 37. The 500 MHz  $^1\text{H}$ -NMR spectrum of methyl-2-propylpentano hydroxamate.



HMAL-4-1H

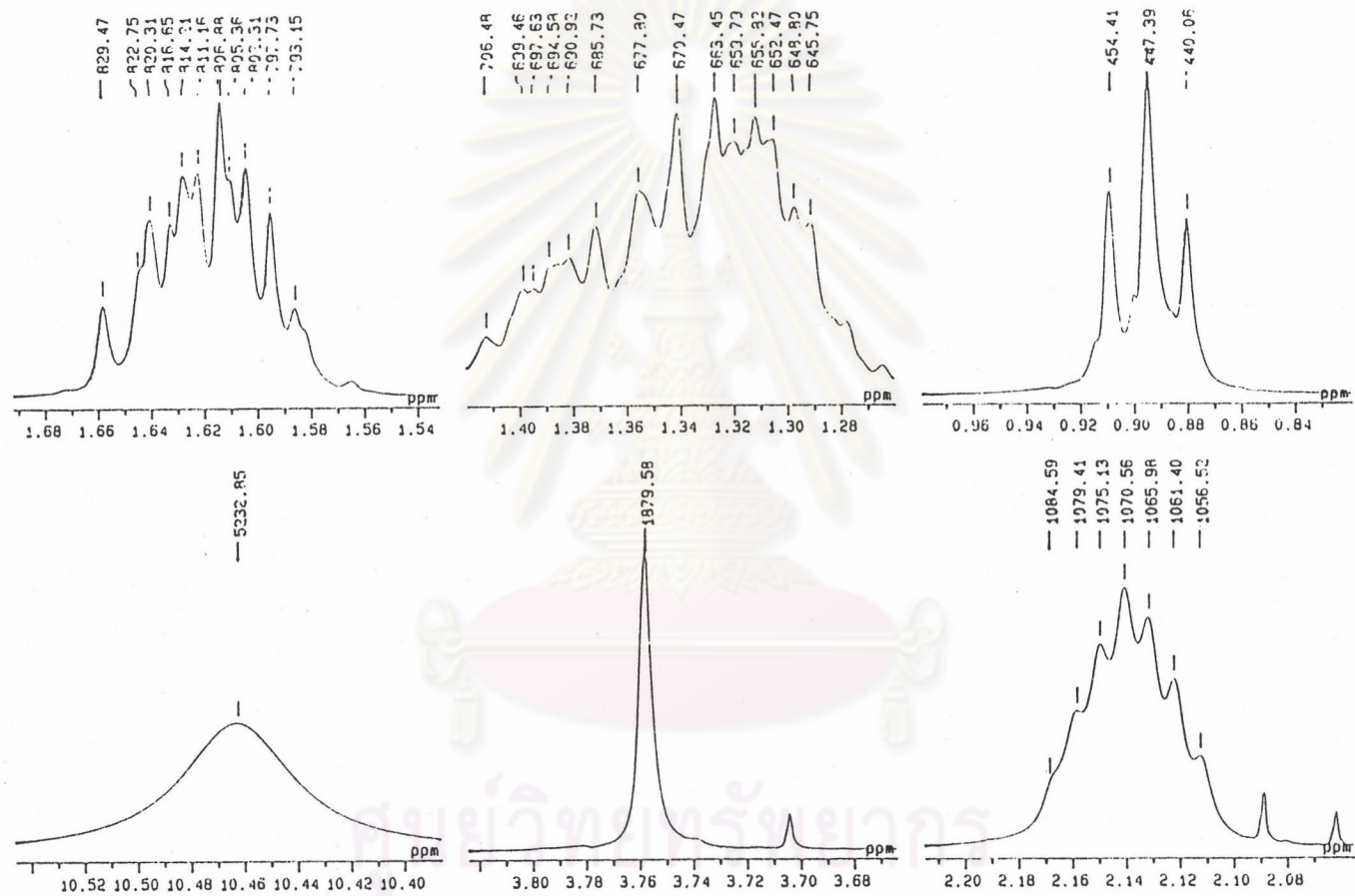


Figure 38. The 500 MHz  $^1\text{H}$ -NMR spectrum of methyl-2-propylpentano hydroxamate. (Enlarge scale : 0.84-10.54 ppm)

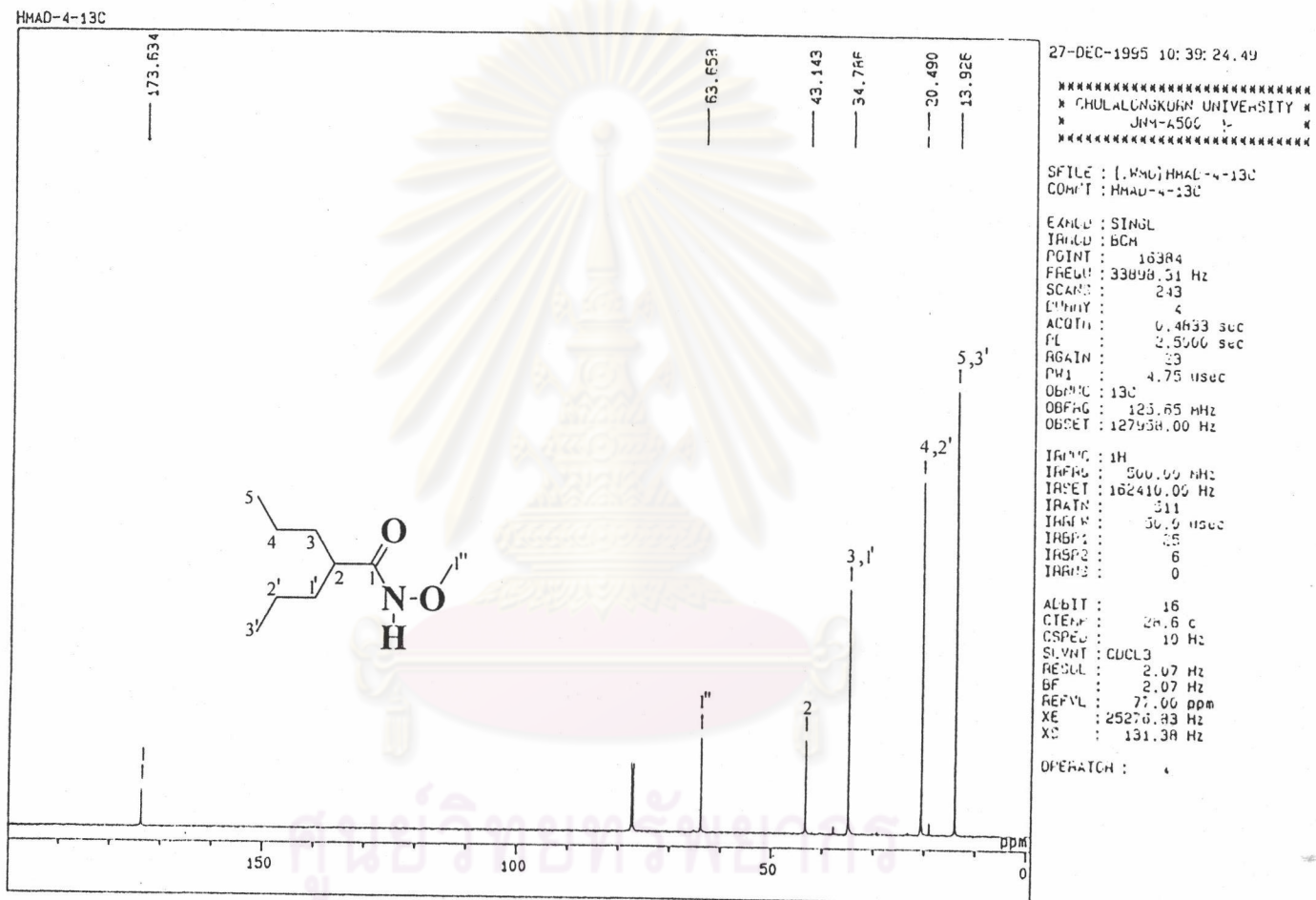


Figure 39. The  $^{13}\text{C}$ -NMR decoupled spectrum of methyl-2-propylpentano hydroxamate.

Background Subtract

C:\SATURN\DATA\HMAD4

Date: 01/18/96 10:30:50

Comment: DB5-MS 30X.25MM 17/1/95

Average of: 954 to 996 Minus: 740 to 1444

100% = 21780

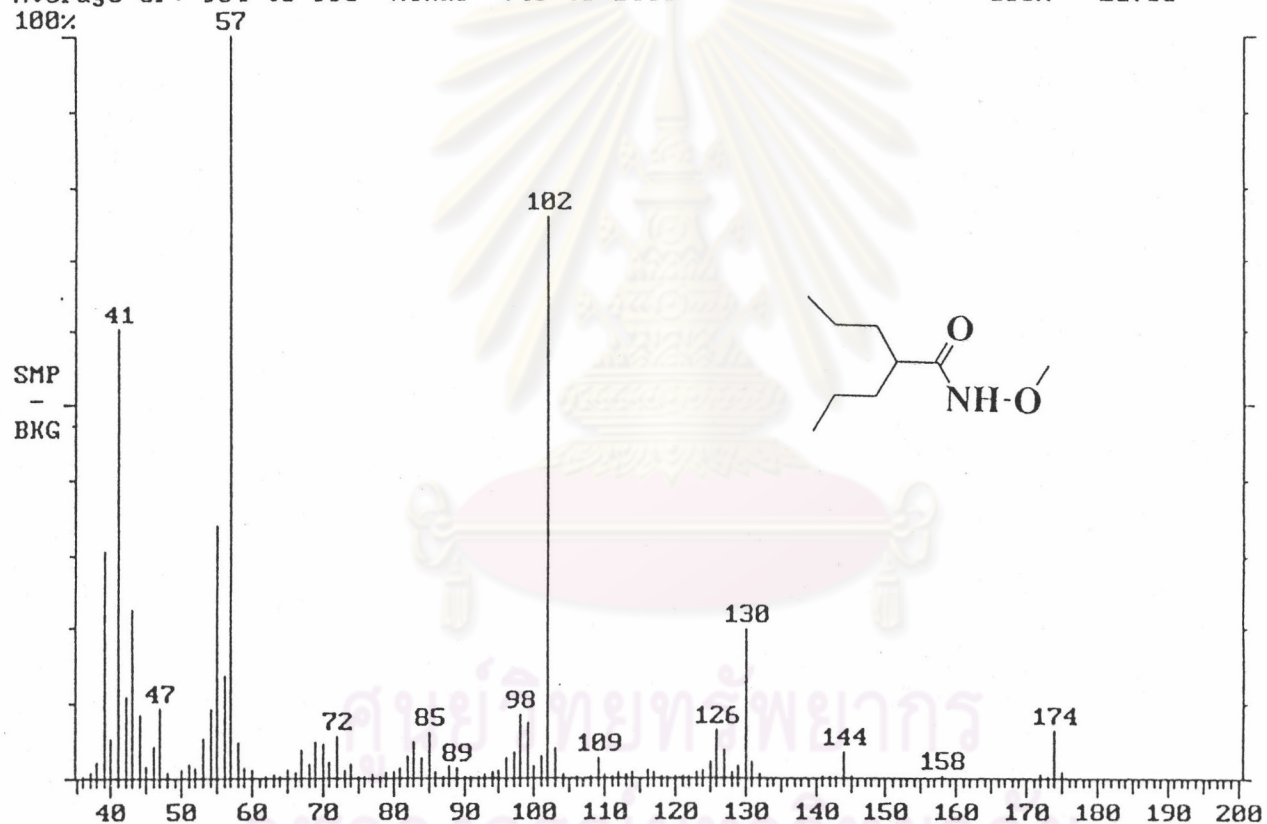


Figure 40. The EIMS spectrum of methyl-2-propylpentanohydroxamate.

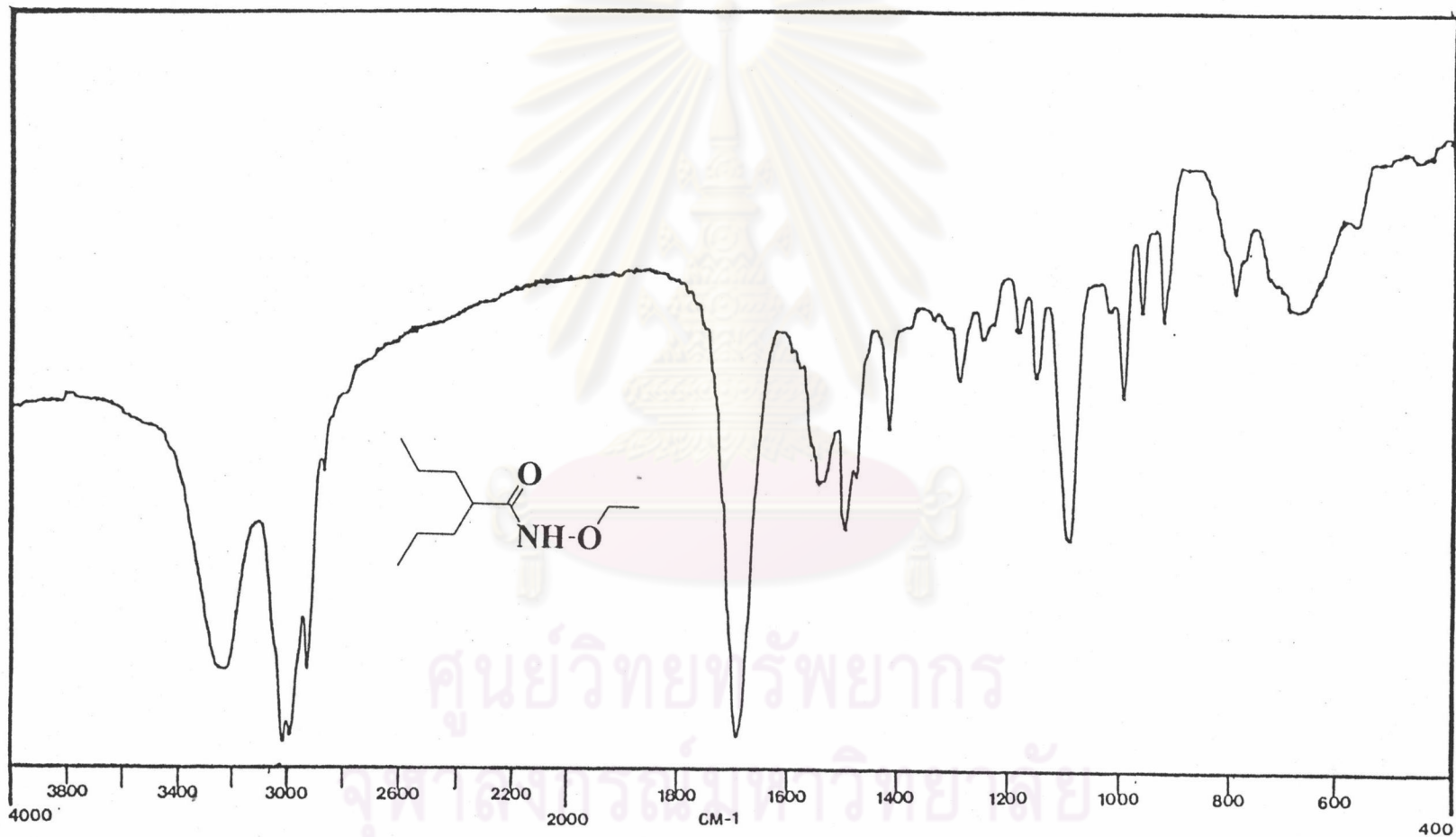


Figure 41. The IR spectrum (NEAT) of ethyl-2-propylpentanohydroxamate.

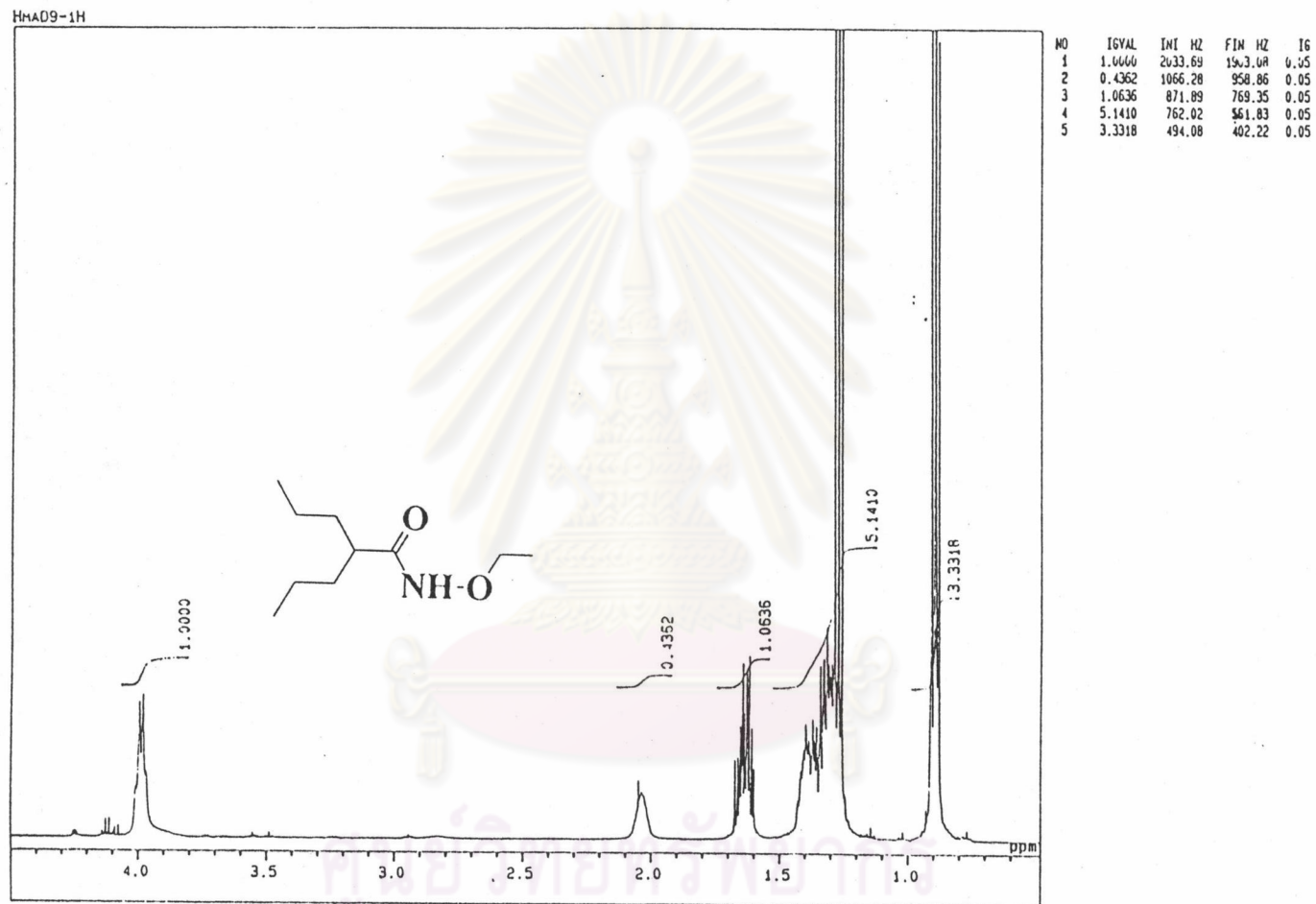


Figure 42. The 500 MHz  $^1\text{H}$ -NMR spectrum of ethyl-2-propylpentano hydroxamate.

H<sub>1</sub>AL9-1H

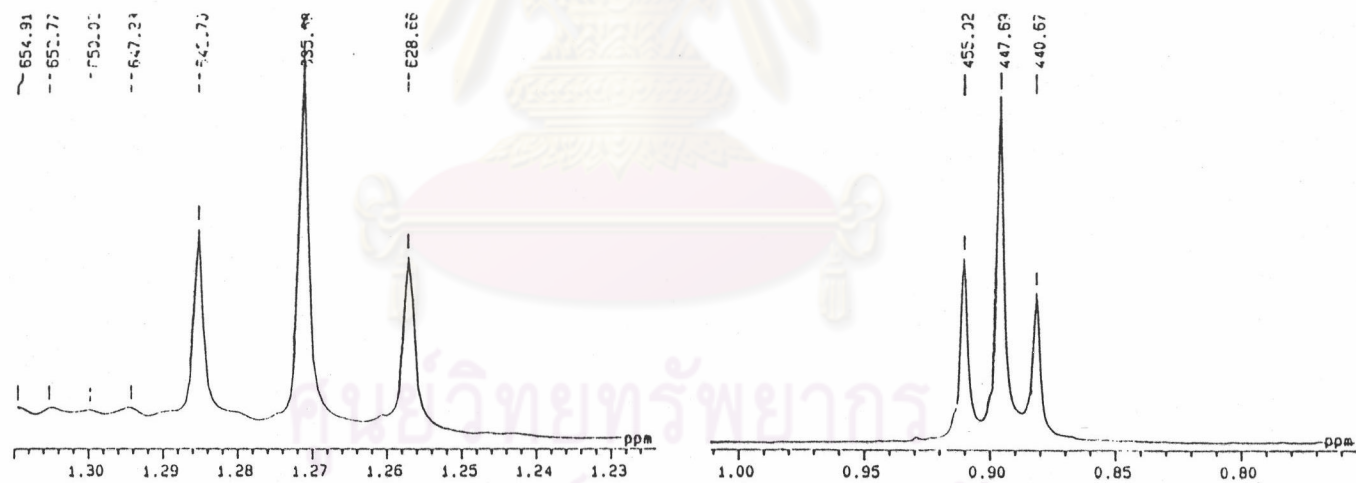


Figure 43. The 500 MHz <sup>1</sup>H-NMR spectrum of ethyl-2-propylpentano hydroxamate. (Enlarge scale : 0.75-1.31 ppm)

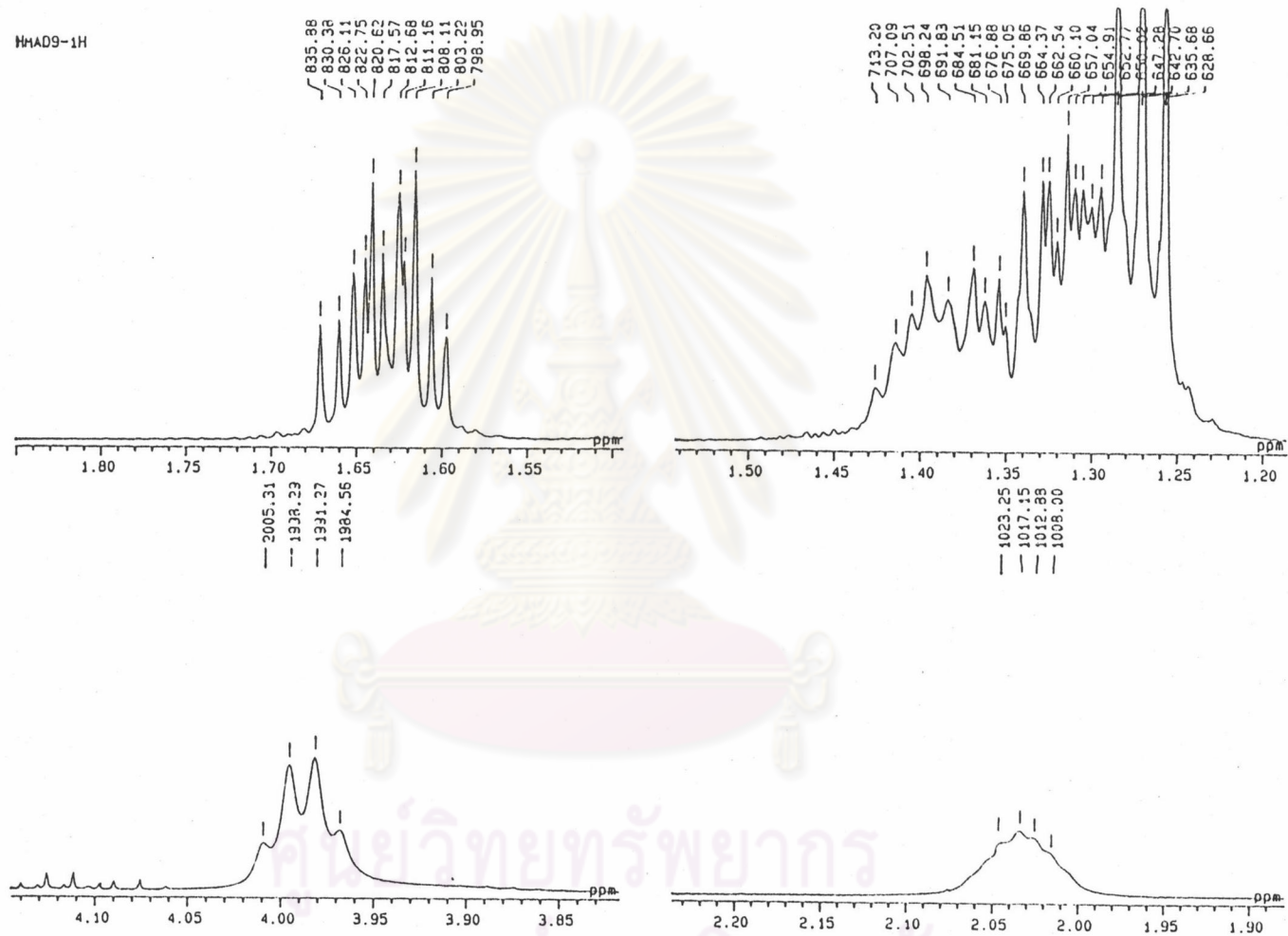
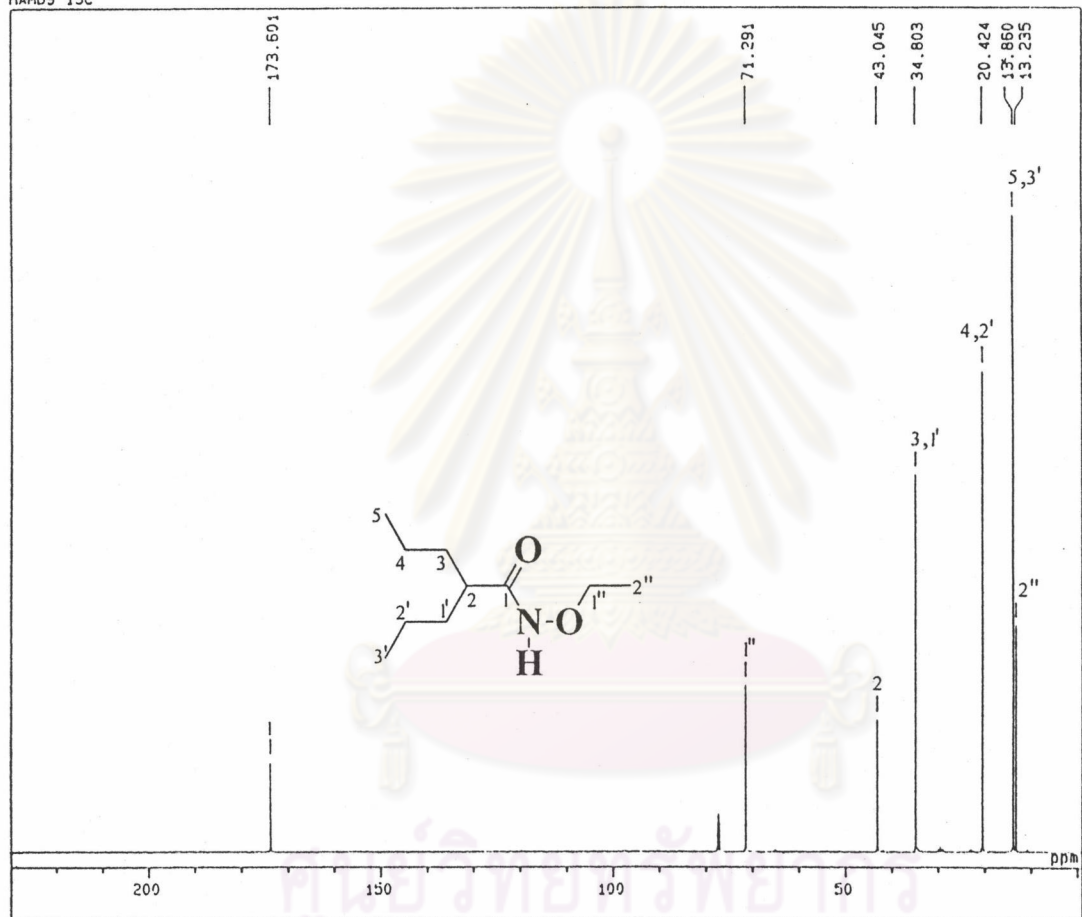


Figure 43. (Continued). The 500 MHz  $^1\text{H}$ -NMR spectrum of ethyl-2-propyl pentanohydroxamate. (Enlarge scale : 1.20-4.15 ppm)

HAM09 13C



8-DEC-1995 16:26:02.15

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 \* JNM-A500 \*  
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SFILE : [ .MVA ] HAM09BCH  
 COMPT : HAM09 13C

EXHD : SINGL  
 IRHD : BCM  
 POINT : 16384  
 FREQ : 33898.31 Hz  
 SCANS : 281  
 DUMY : 4  
 ACQTH : 0.4833 sec  
 PD : 2.0000 sec  
 RGAIN : 23  
 PW1 : 4.75 usec  
 OBNUC : 13C  
 OBFREQ : 125.65 MHz  
 OBSET : 127958.00 Hz

IRNUC : 1H  
 IFRG : 500.00 MHz  
 IRSET : 162410.00 Hz  
 IRATH : 511  
 IRRPW : 50.0 usec  
 IRBP1 : 25  
 IRBP2 : 6  
 IRRNS : 0

ADBIT : 16  
 CTEMP : 27.4 c  
 CSPEU : 13 Hz  
 SLVNT : CDCL3  
 RESOL : 2.07 Hz  
 BF : 2.07 Hz  
 REFVL : 77.00 ppm  
 XE : 29050.67 Hz  
 XS : -1755.54 Hz

OPERATOR :

Figure 44. The  $^{13}\text{C}$ -NMR decoupled spectrum of ethyl-2-propylpentano hydroxamate.



Background Subtract

C:\SATURN\DATA\HMAD9

Date: 01/18/96 10:06:12

Comment: DB5-MS 30X.25MM 17/1/95

Average of: 615 to 647 Minus: 391 to 903

100% = 163074

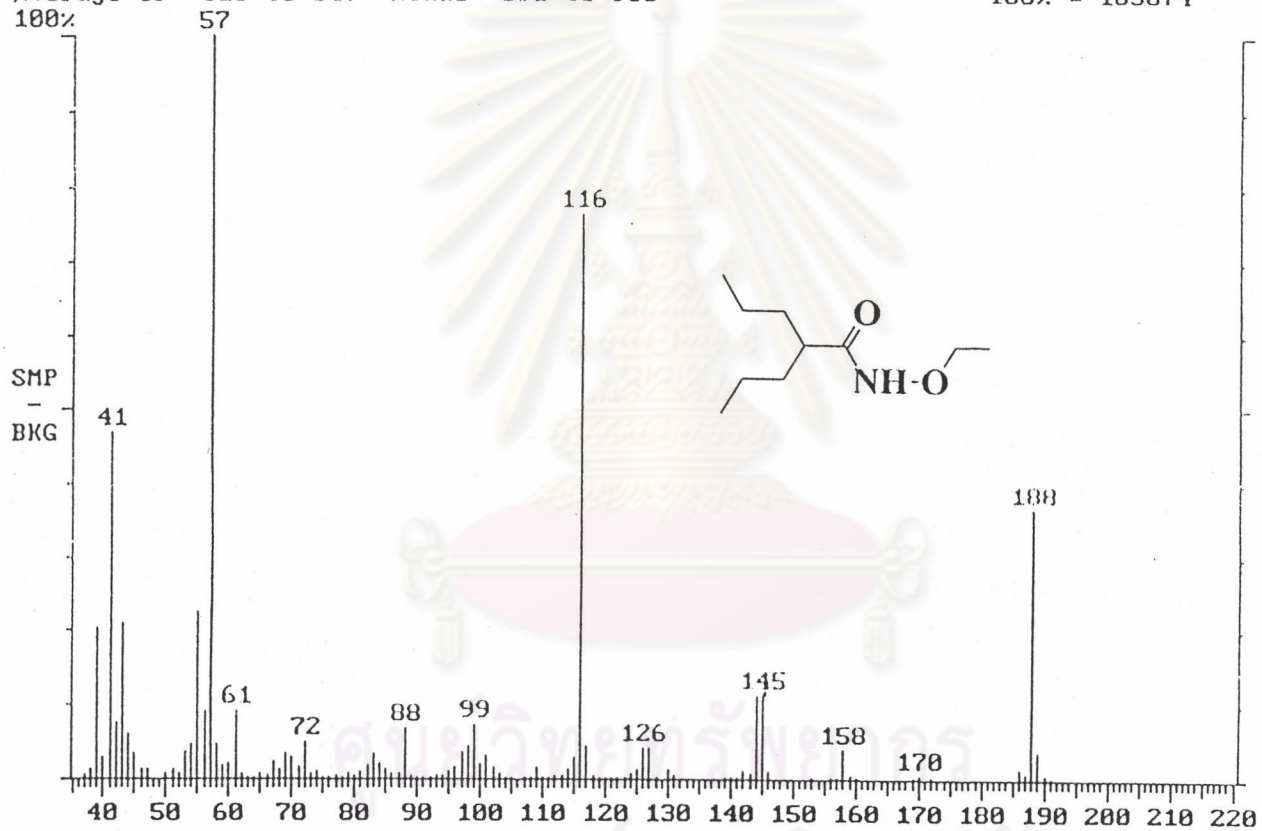


Figure 45. The EIMS spectrum of ethyl-2-propylpentanohydroxamate.

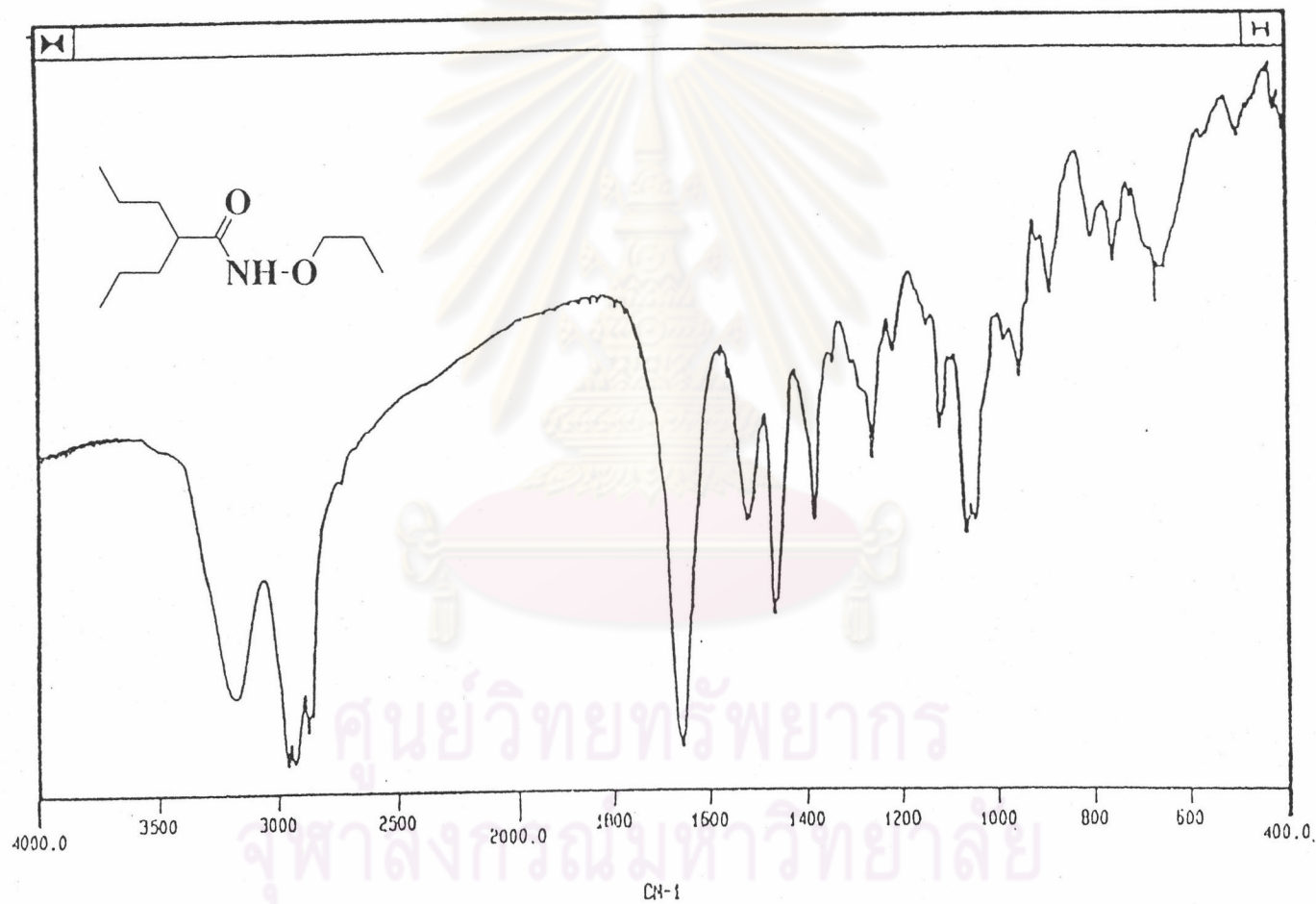


Figure 46. The IR spectrum (NEAT) of propyl-2-propylpentano-hydroxamate.

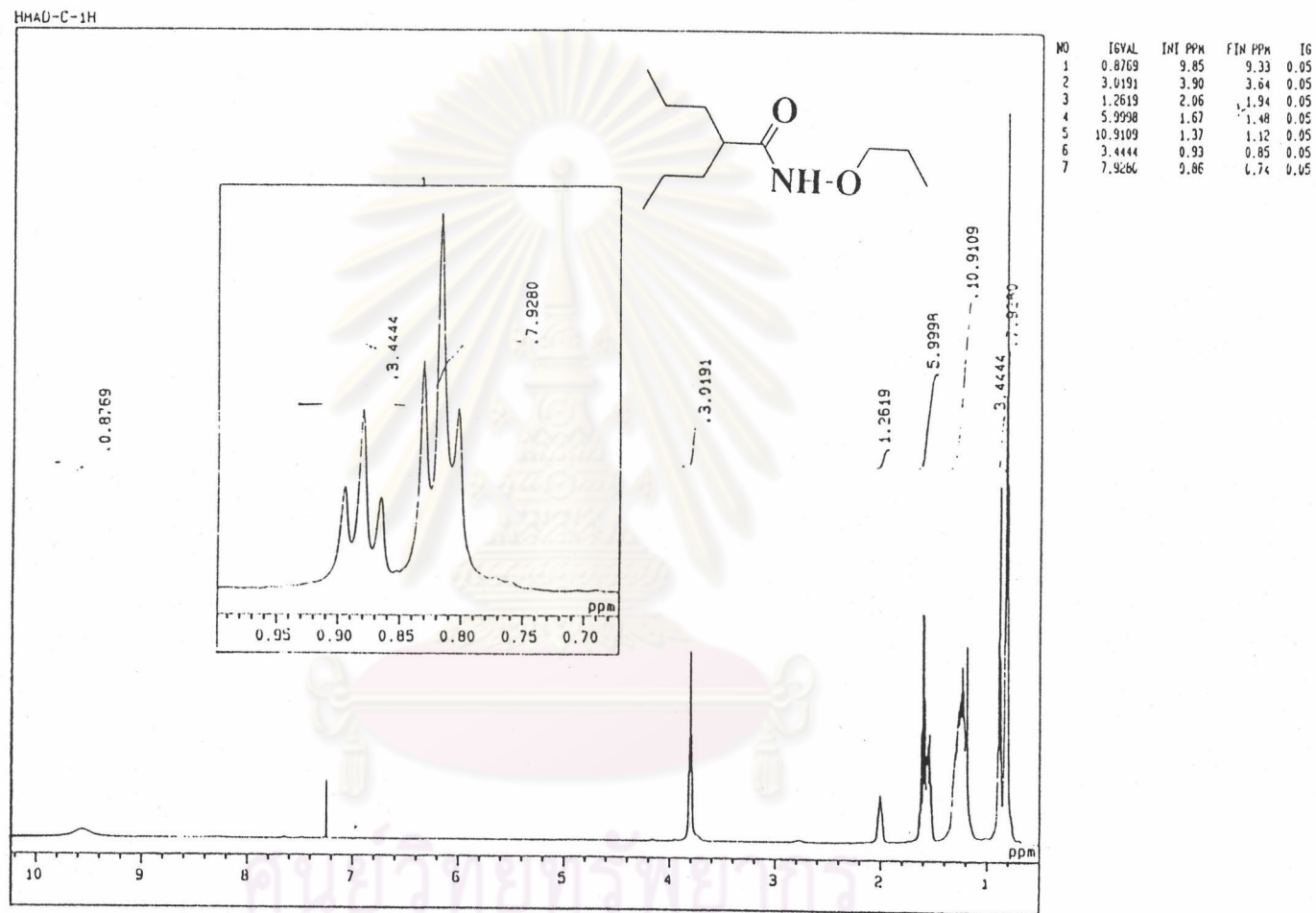


Figure 47. The 500 MHz  $^1\text{H}$ -NMR spectrum of propyl-2-propylpentano hydroxamate.

HMAU-6-1H

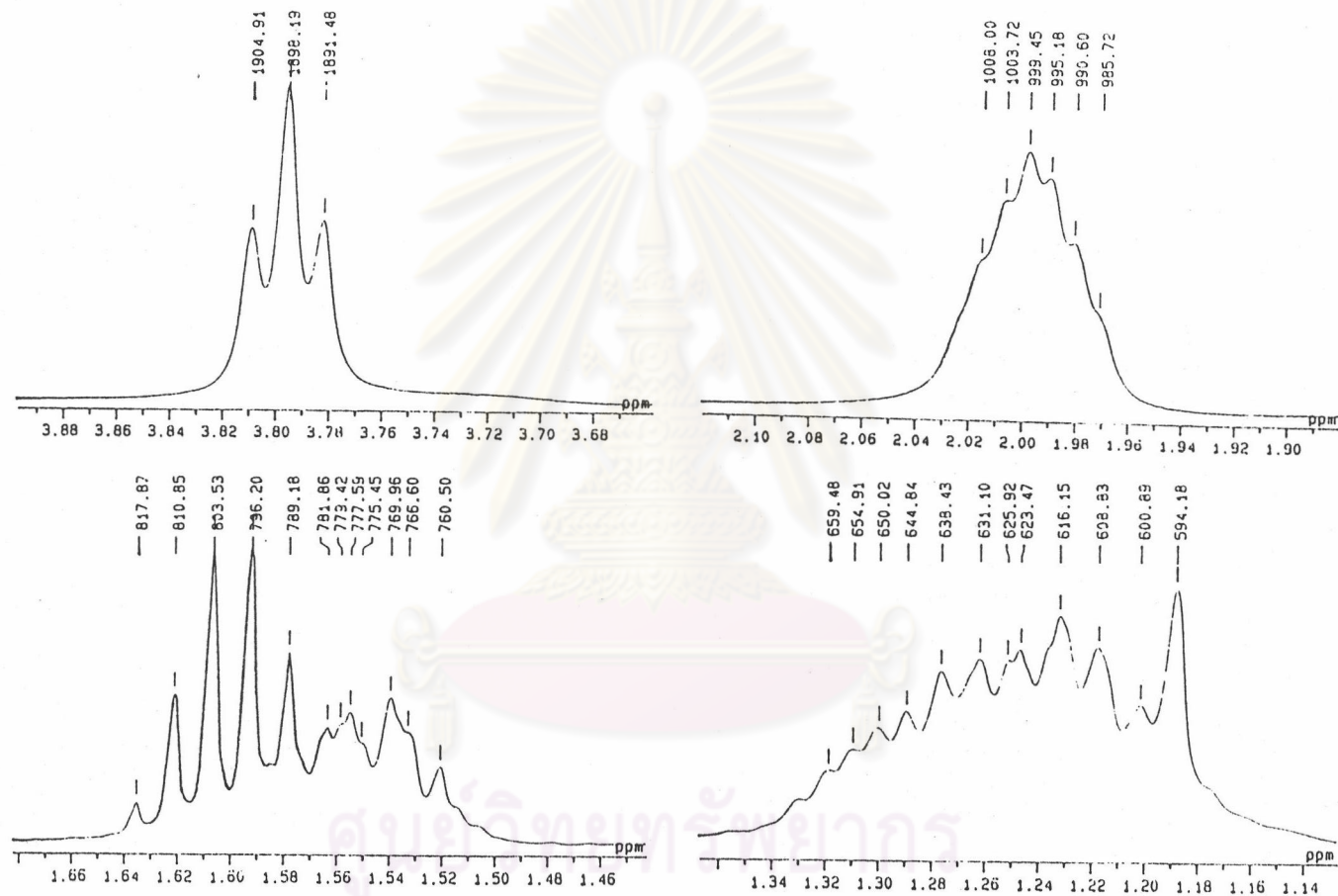


Figure 48. The 500 MHz  $^1\text{H}$ -NMR spectrum of propyl-2-propylpentano hydroxamate. (Enlarge scale : 1.90-1.68 ppm)

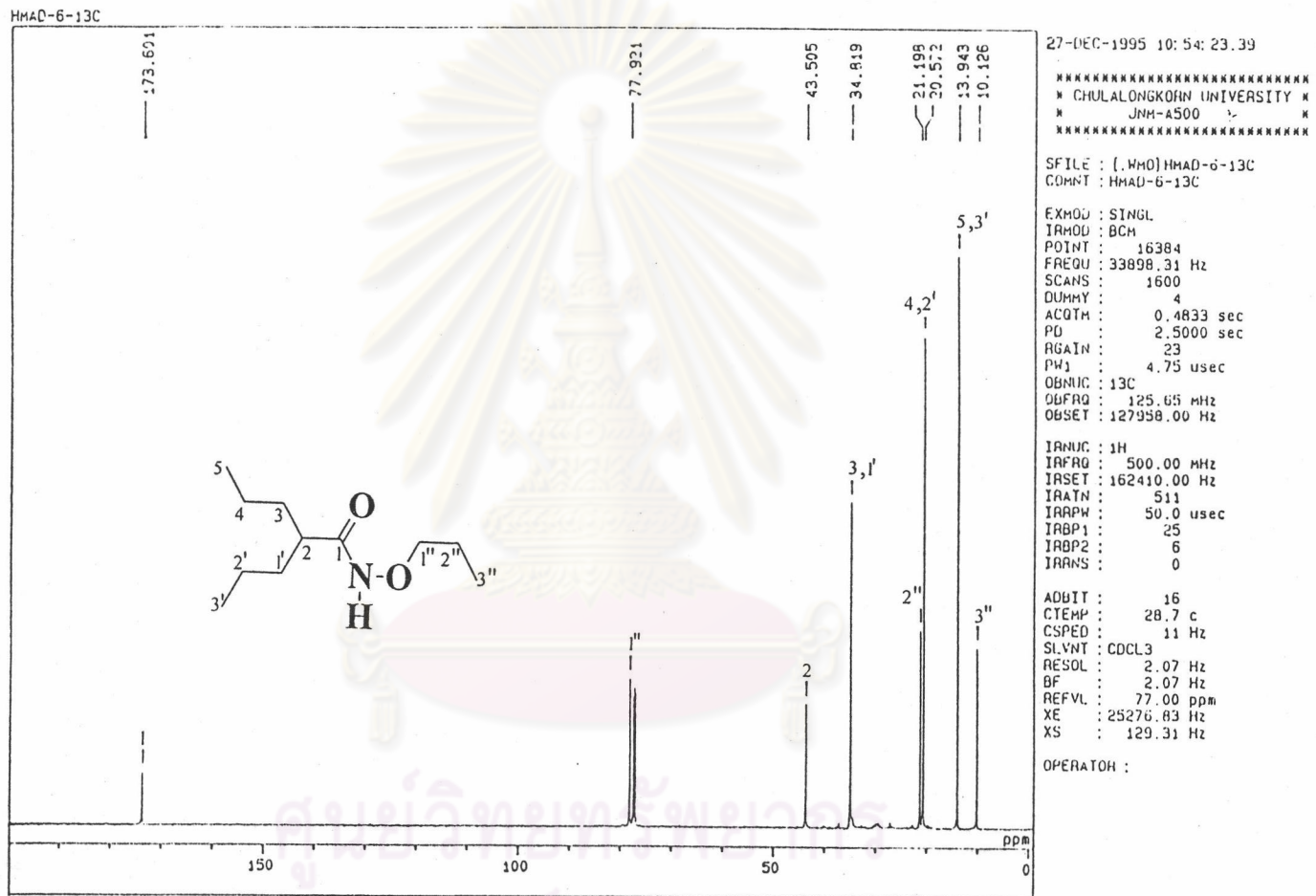


Figure 49. The  $^{13}\text{C}$ -NMR decoupled spectrum of propyl-2-propylpentano hydroxamate.

Background Subtract

C:\SATURN\DATA\HMD6

Date: 01/18/96 09:37:06

Comment: DB5-MS 30X.25MM 17/1/95

Average of: 664 to 699 Minus: 443 to 1083

100% = 109223

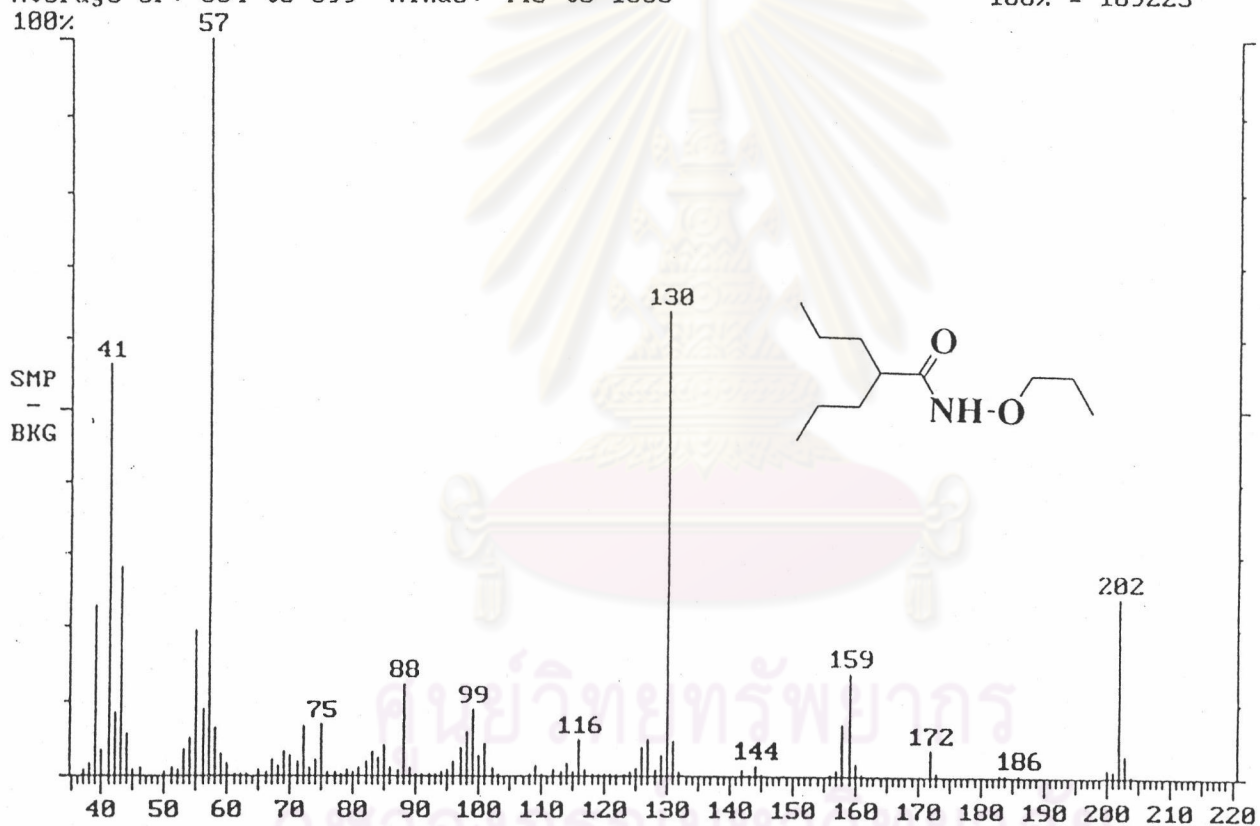


Figure 50. The EIMS spectrum of propyl-2-propylpentanohydroxamate.

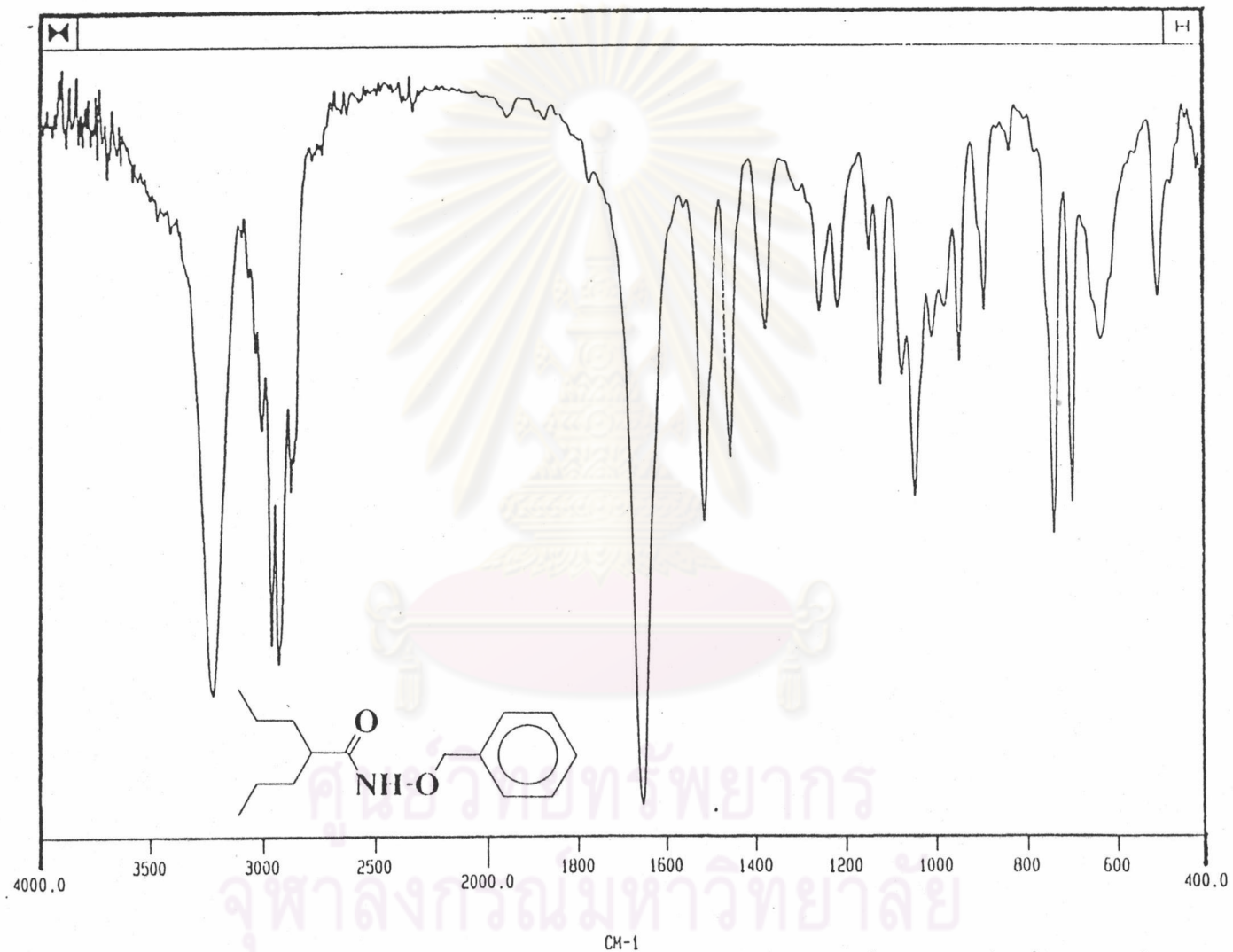


Figure 51. The IR spectrum (KBr pellet) of benzyl-2-propylpentano hydroxamate.

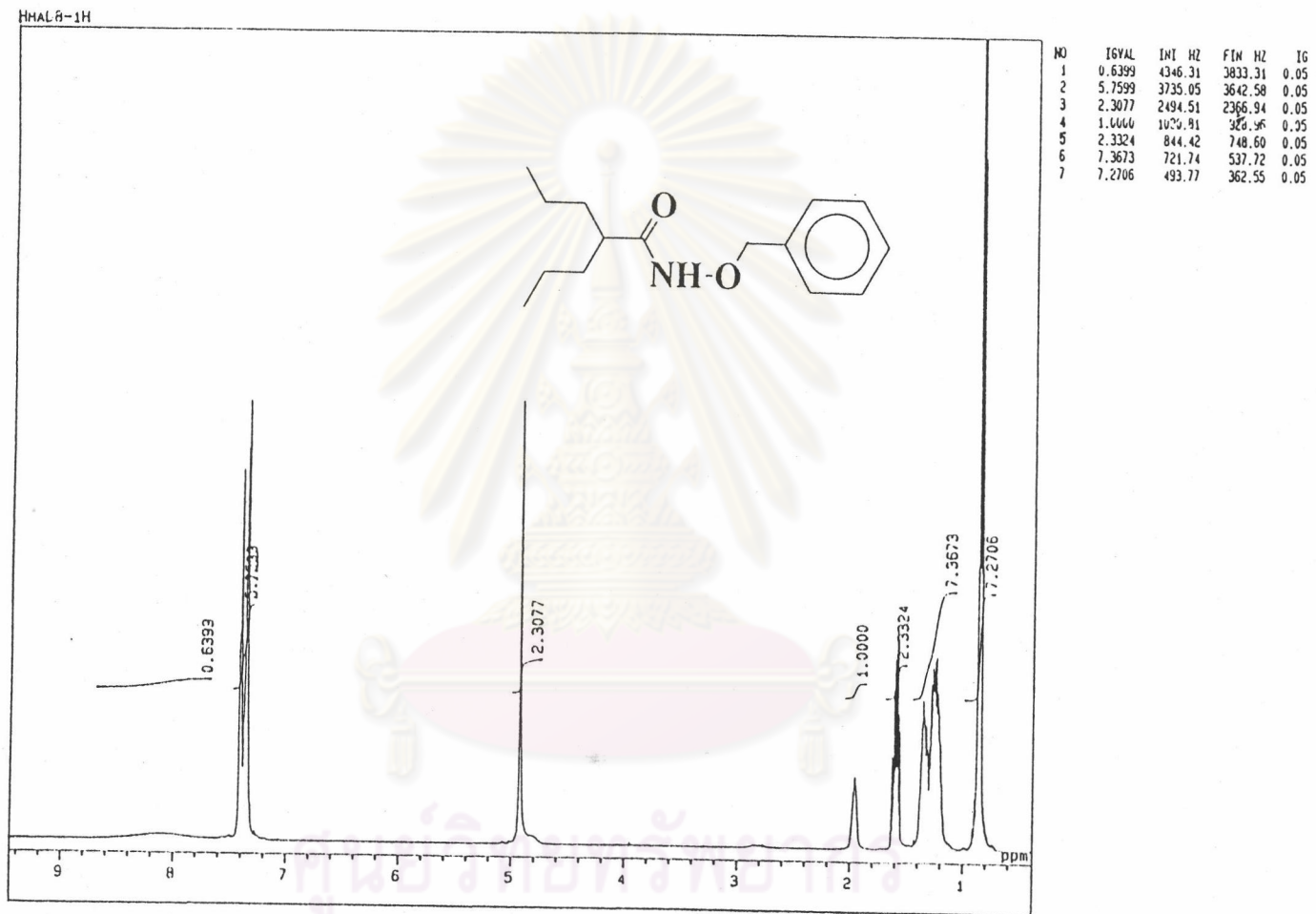


Figure 52. The 500 MHz  $^1\text{H}$ -NMR spectrum of benzyl-2-propylpentano hydroxamate.



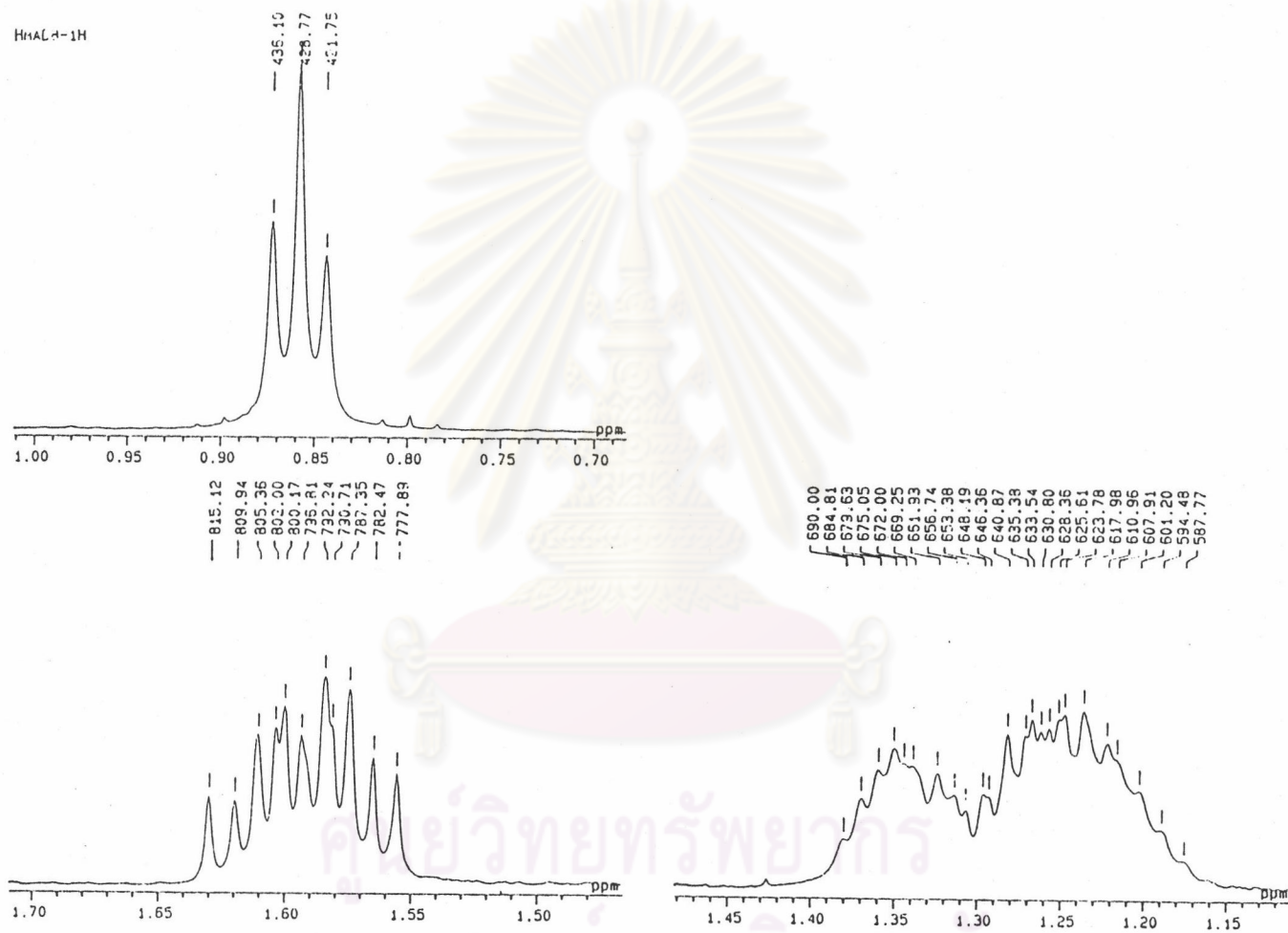


Figure 53. The 500 MHz <sup>1</sup>H-NMR spectrum of benzyl-2-propylpentano hydroxamate. (Enlarge scale : 0.70-1.70 ppm)

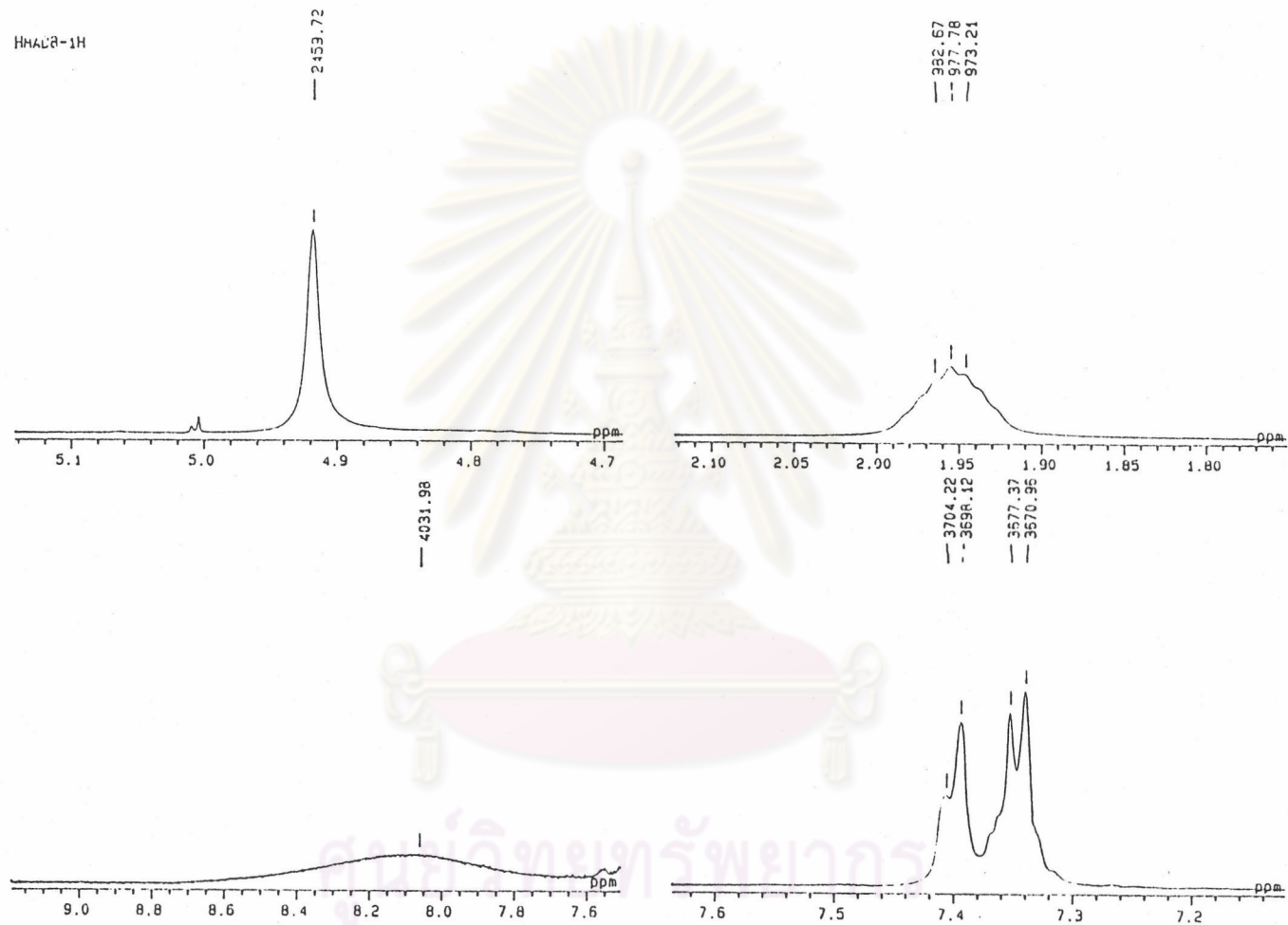


Figure 53. (Continued). The 500 MHz <sup>1</sup>H-NMR spectrum of benzyl-2-propylpentanohydroxamate. (Enlarge scale : 1.80-9.20 ppm)

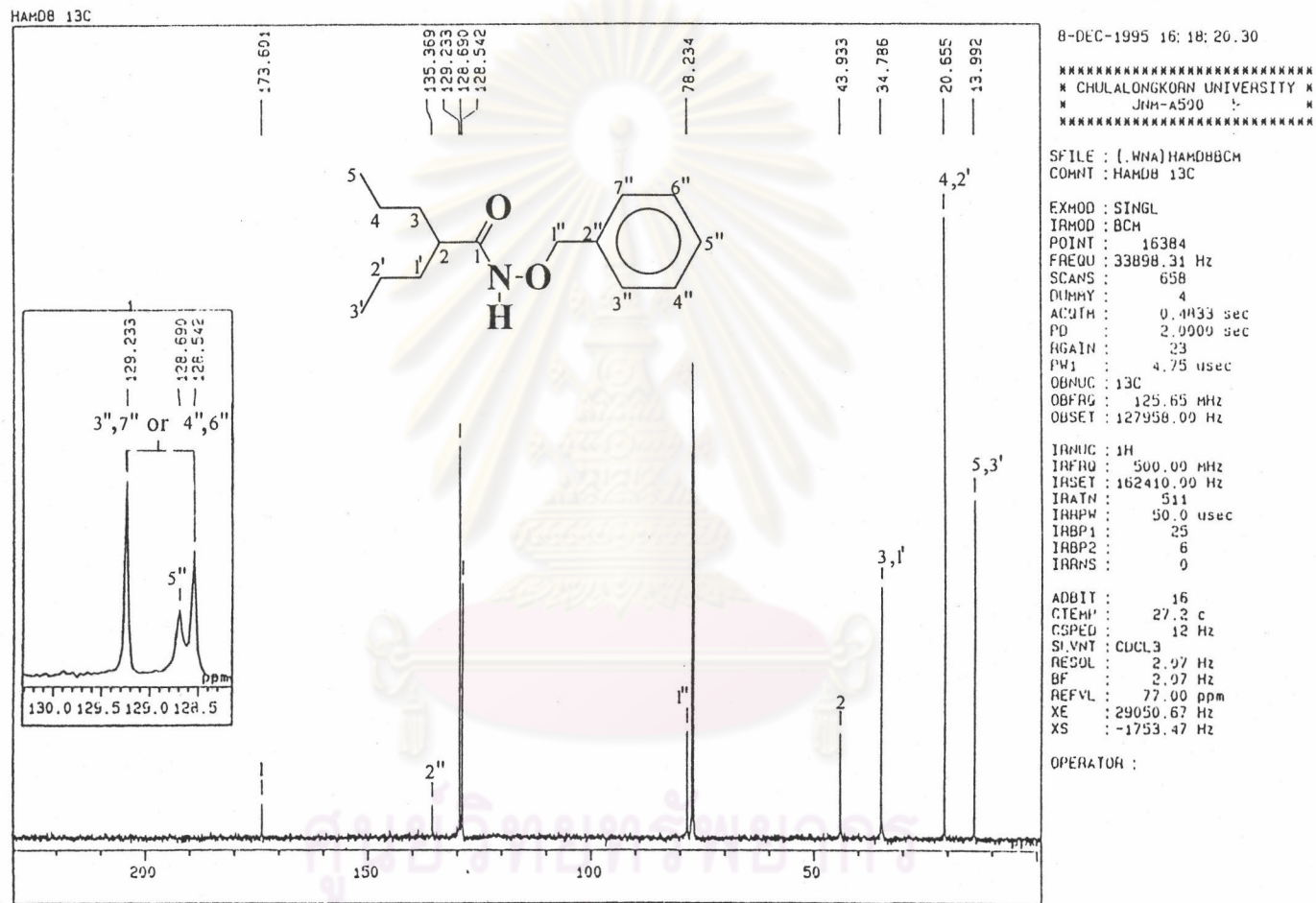


Figure 54. The  $^{13}\text{C}$ -NMR decoupled spectrum of benzyl-2-propylpentano hydroxamate.

Background Subtract

C:\SATURN\DATA\HMA08

Date: 01/24/96 13:09:21

Comment: DB5-MS 30X.25MM 17/1/95

Average of: 712 to 732 Minus: 284 to 1052

100% = 397526

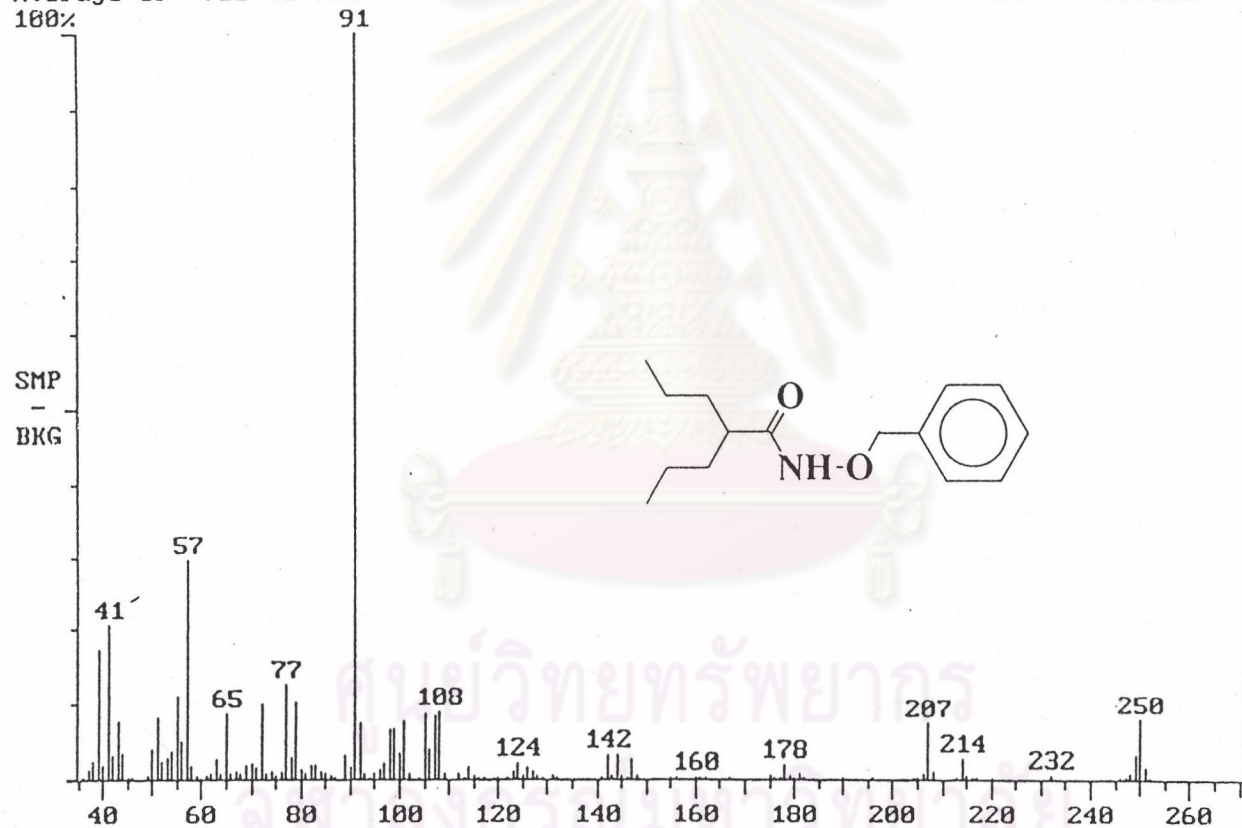


Figure 55. The EIMS spectrum of benzyl-2-propylpentanohydroxamate.

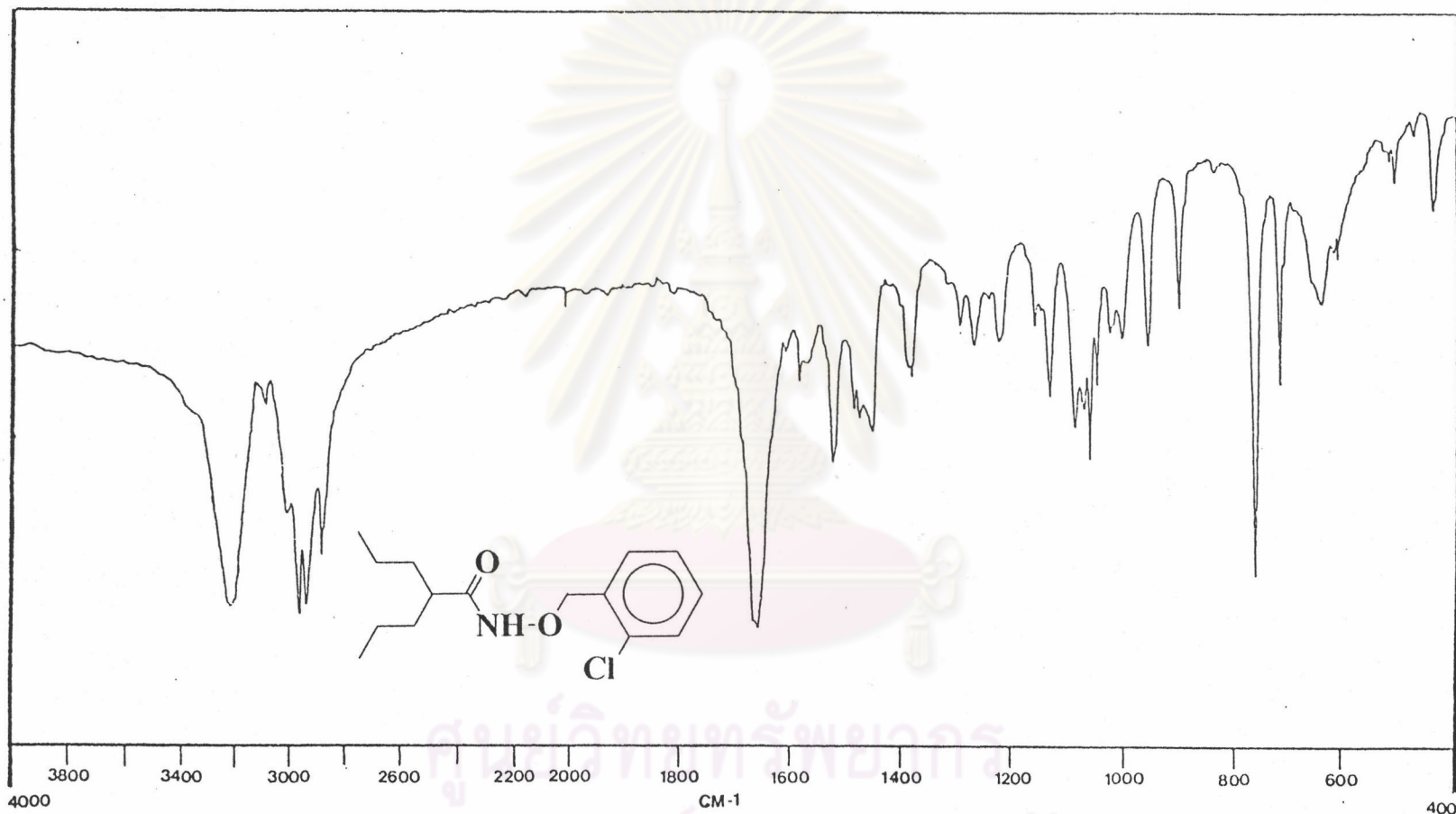


Figure 56. The IR spectrum (KBr pellet) of (2-chlorobenzyl)-2-propyl-pentanohydroxamate.

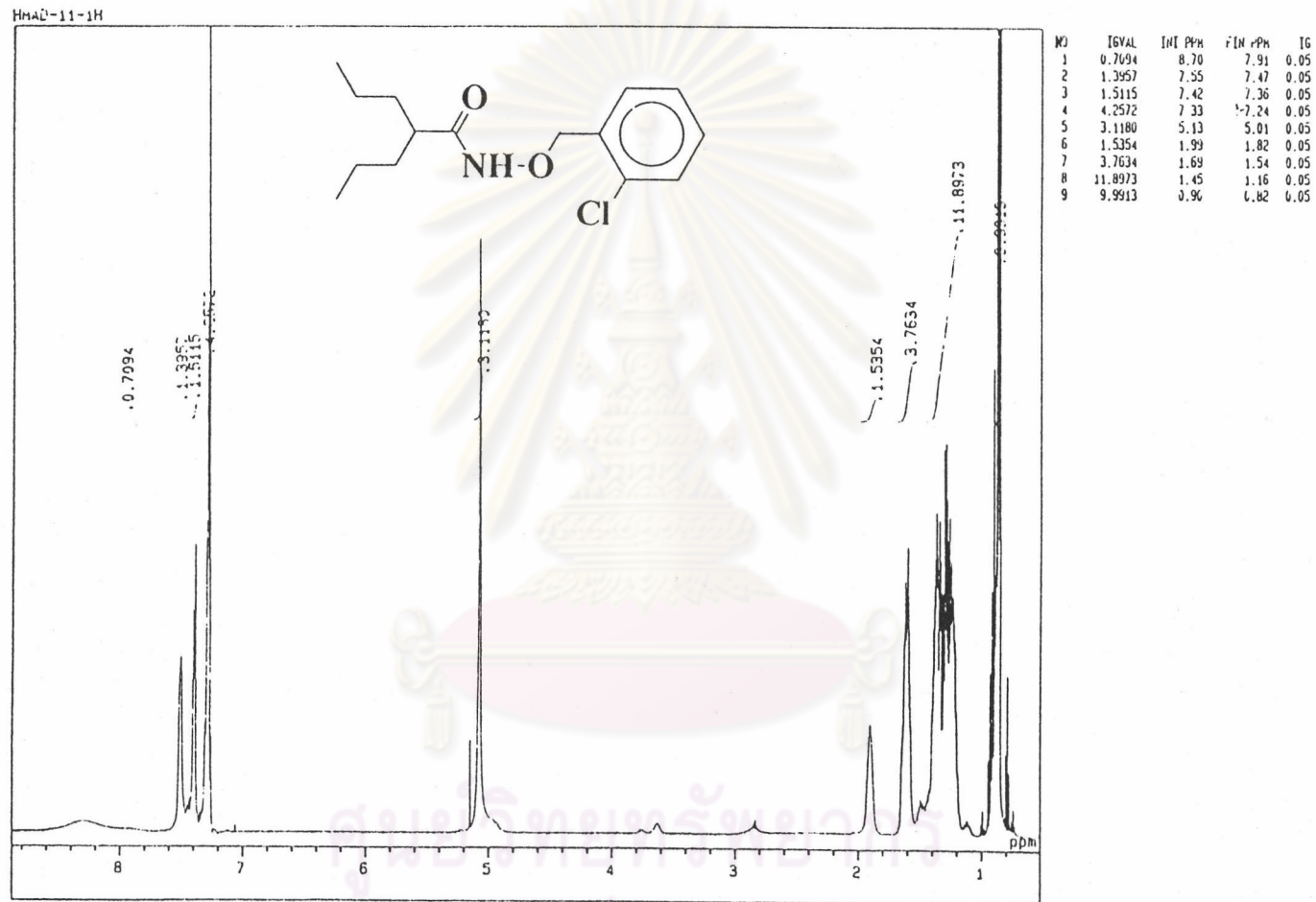


Figure 57. The 500 MHz  $^1\text{H-NMR}$  spectrum of (2-chlorobenzyl)2-propyl pentanohydroxamate.

HM4D-11-1H

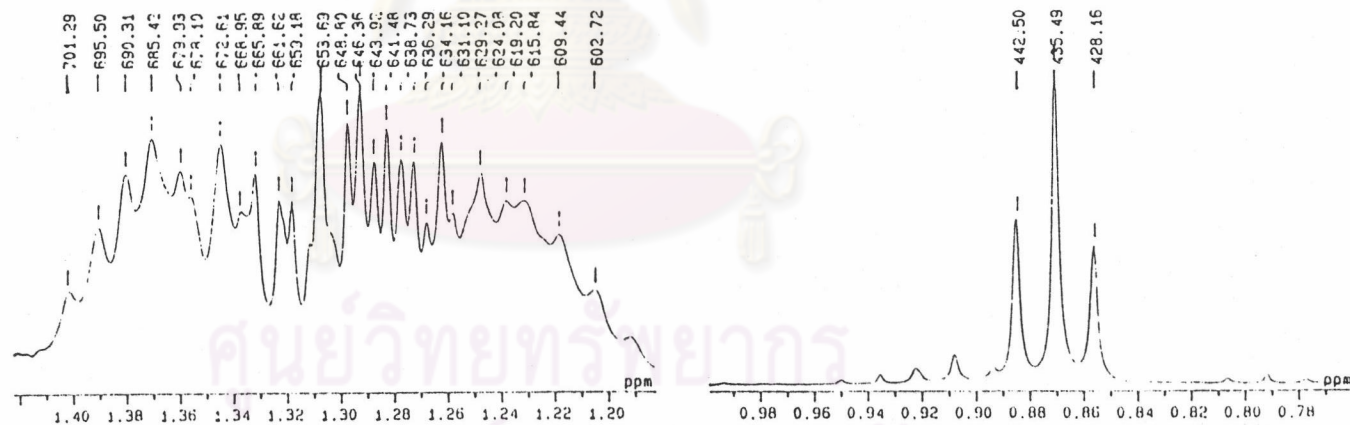


Figure 58. The 500 MHz <sup>1</sup>H-NMR spectrum of (2-chlorobenzyl)2-propyl pentanohydroxamate. (Enlarge scale : 0.78-1.40 ppm)

HHAU-11-1H

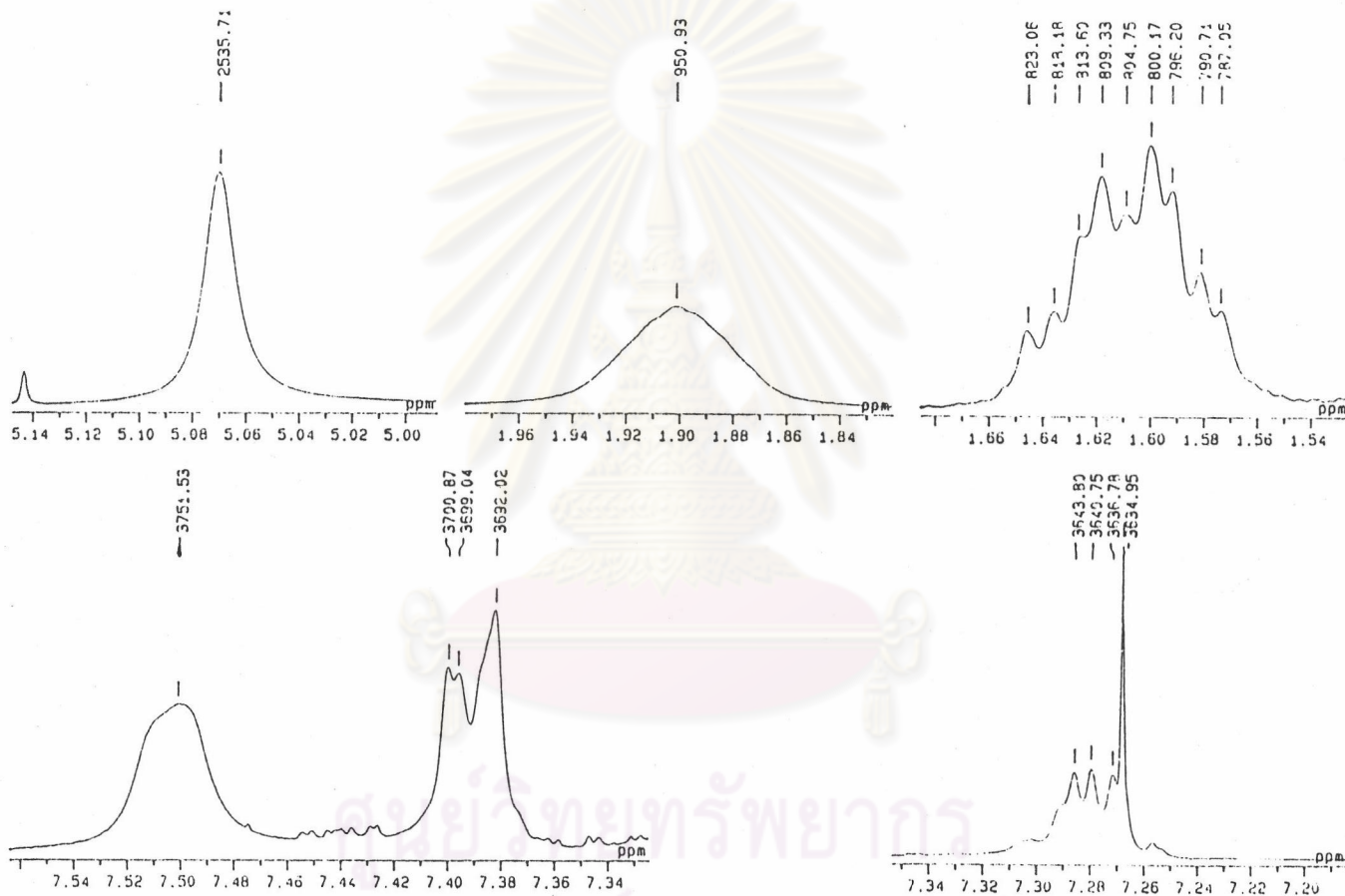
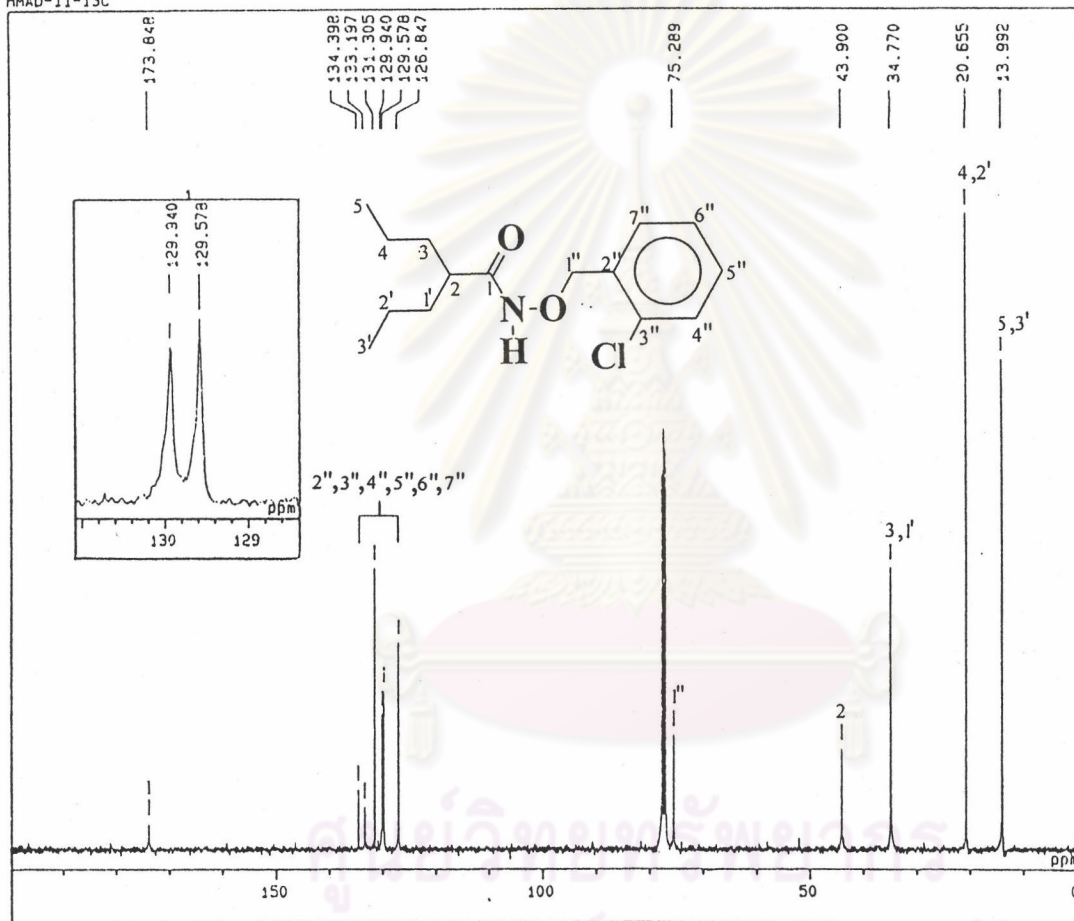


Figure 58. (Continued). The 500 MHz  $^1\text{H}$ -NMR spectrum of (2-chlorobenzyl)2-propylpentanohydroxamate. (Enlarge scale : 1.54-7.56 ppm)



HMAD-11-13C



26-DEC-1995 16:32:54.62

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 \* JNM-A500 \*  
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SFILE : [JNM]HMAD-11-13C  
 COMNT : HMAD-11-13C

EXMOD : SINGL  
 IRMOD : BCM  
 POINT : 16384  
 FREQU : 33898.31 Hz  
 SCANS : 1322  
 DUMMY : 4  
 ACQTH : 0.4833 sec  
 PD : 2.5000 sec  
 RGAIN : 23  
 PW1 : 4.75 usec  
 UBNUC : 13C  
 OBFRO : 125.65 MHz  
 OBSET : 127958.00 Hz

IRNUC : 1H  
 IAFRO : 500.00 MHz  
 IRSET : 162410.00 Hz  
 IRATN : 511  
 IRRPW : 50.0 usec  
 IRBP1 : 25  
 IRBP2 : 6  
 IRANS : 0

ADBIT : 16  
 CTEMP : 28.3 c  
 CSPEU : 11 Hz  
 SLVNT : CDCL3  
 RESOL : 2.07 Hz  
 BF : 2.07 Hz  
 REFVL : 77.00 ppm  
 XE : 25276.83 Hz  
 XS : 133.45 Hz

OPERATOR :

Figure 59. The  $^{13}\text{C}$ -NMR decoupled spectrum of (2-chlorobenzyl)2-propyl pentanohydroxamate.

Background Subtract

C:\SATURN\DATA\HMAD11

Date: 01/18/96 17:16:36

Comment: DB5-MS 30X.25MM 17/1/95

Average of: 784 to 796 Minus: 604 to 1116

100% = 131362

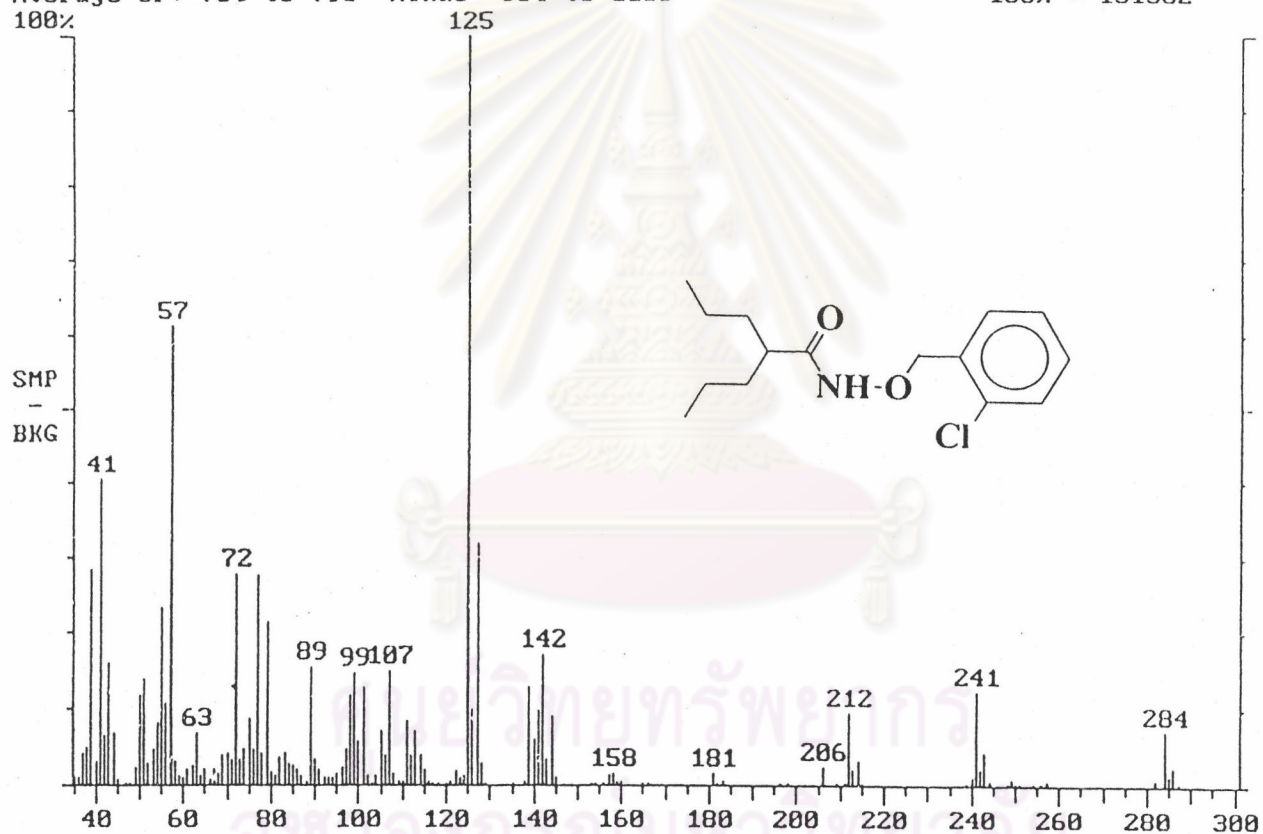


Figure 60. The EIMS spectrum of (2-chlorobenzyl)2-propylpentano-hydroxamate.

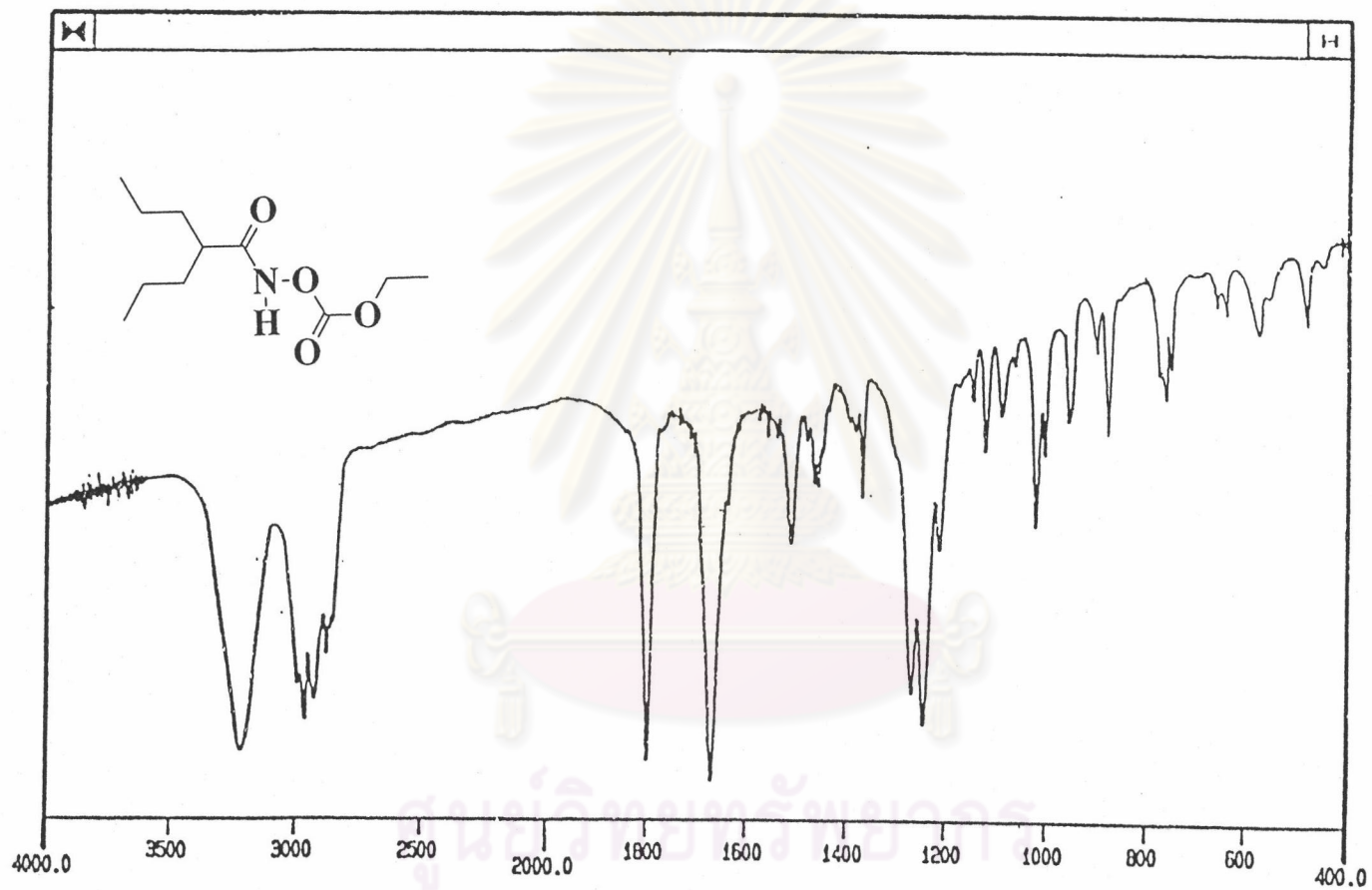


Figure 61. The IR spectrum (KBr pellet) of ethyl-2-propylpentamidoxy formate.

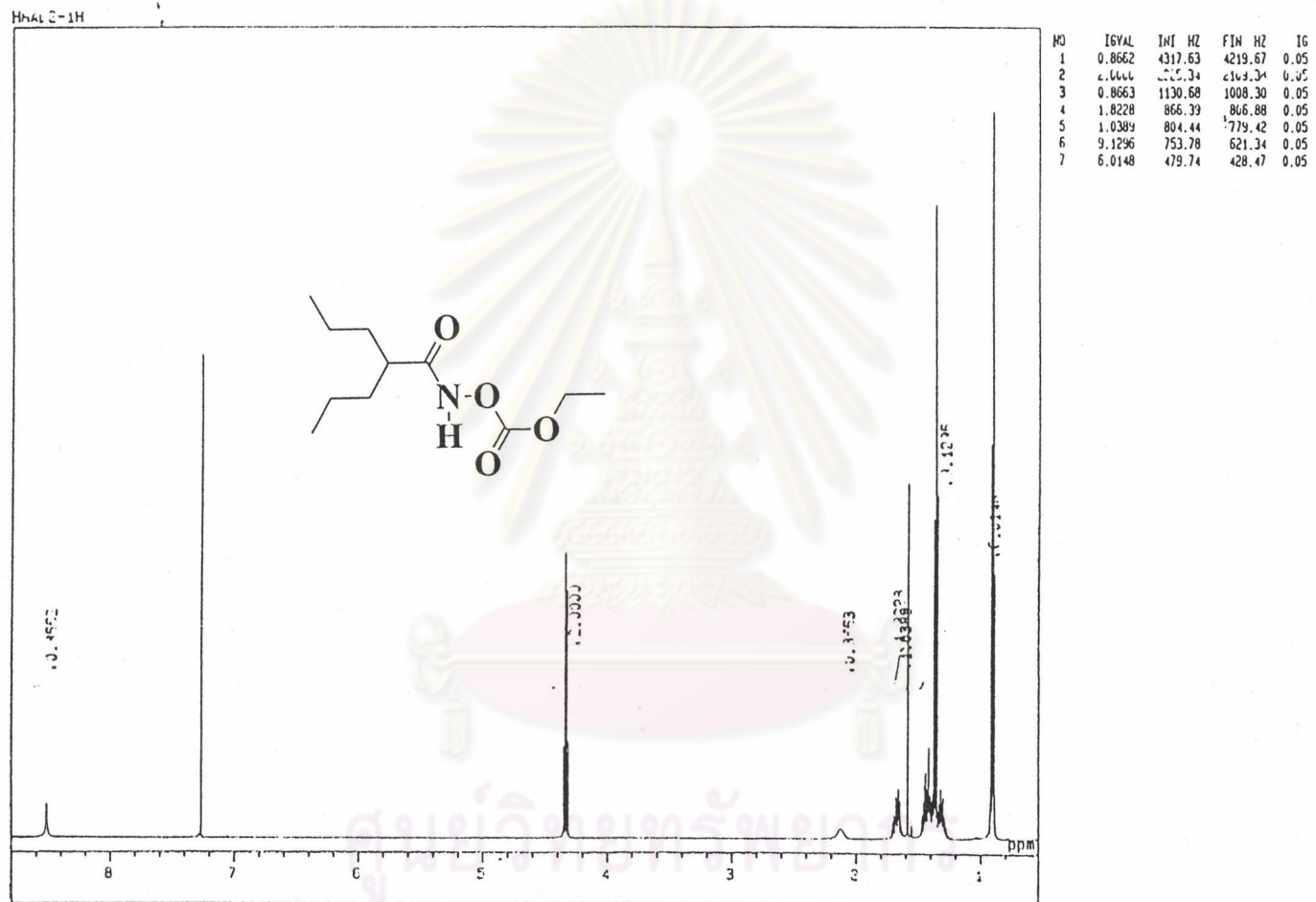


Figure 62. The 500 MHz <sup>1</sup>H-NMR spectrum of ethyl-2-propylpentamidoxy formate.

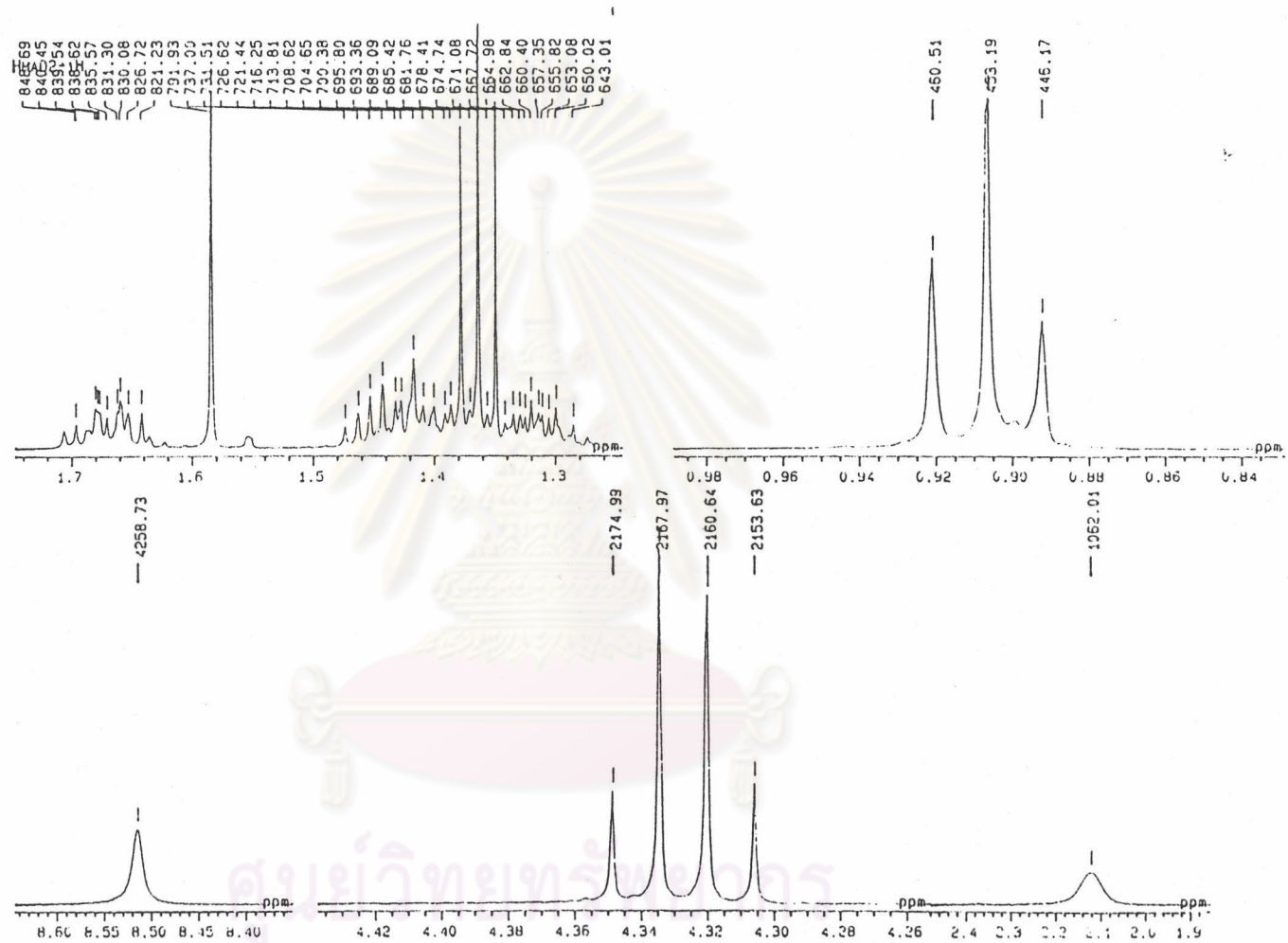


Figure 63. The 500 MHz <sup>1</sup>H-NMR spectrum of ethyl-2-propylpentamidoxy formate. (Enlarge scale : 0.84-8.60 ppm)

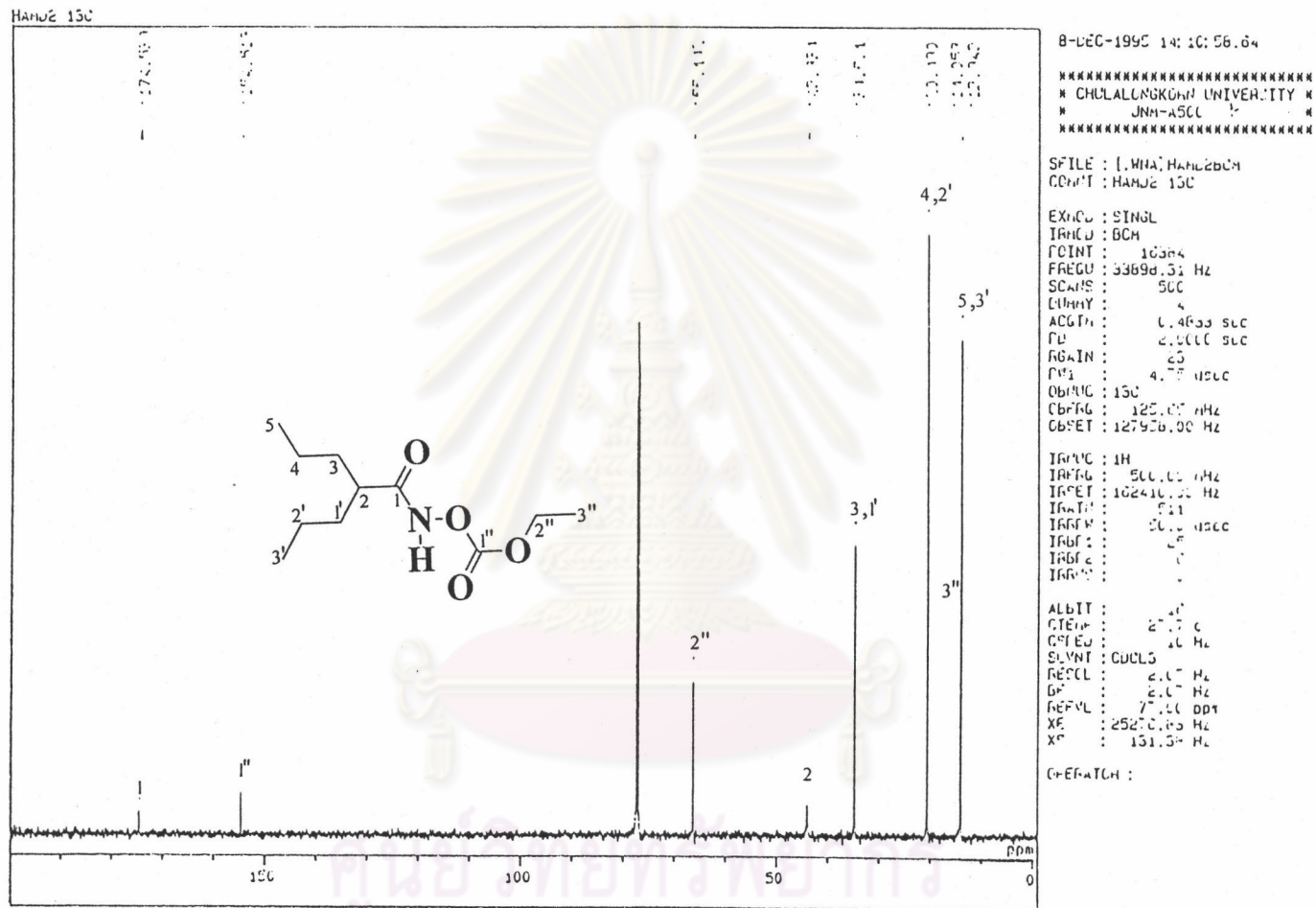


Figure 64. The  $^{13}\text{C}$ -NMR decoupled spectrum of ethyl-2-propylpentamidoxy formate.

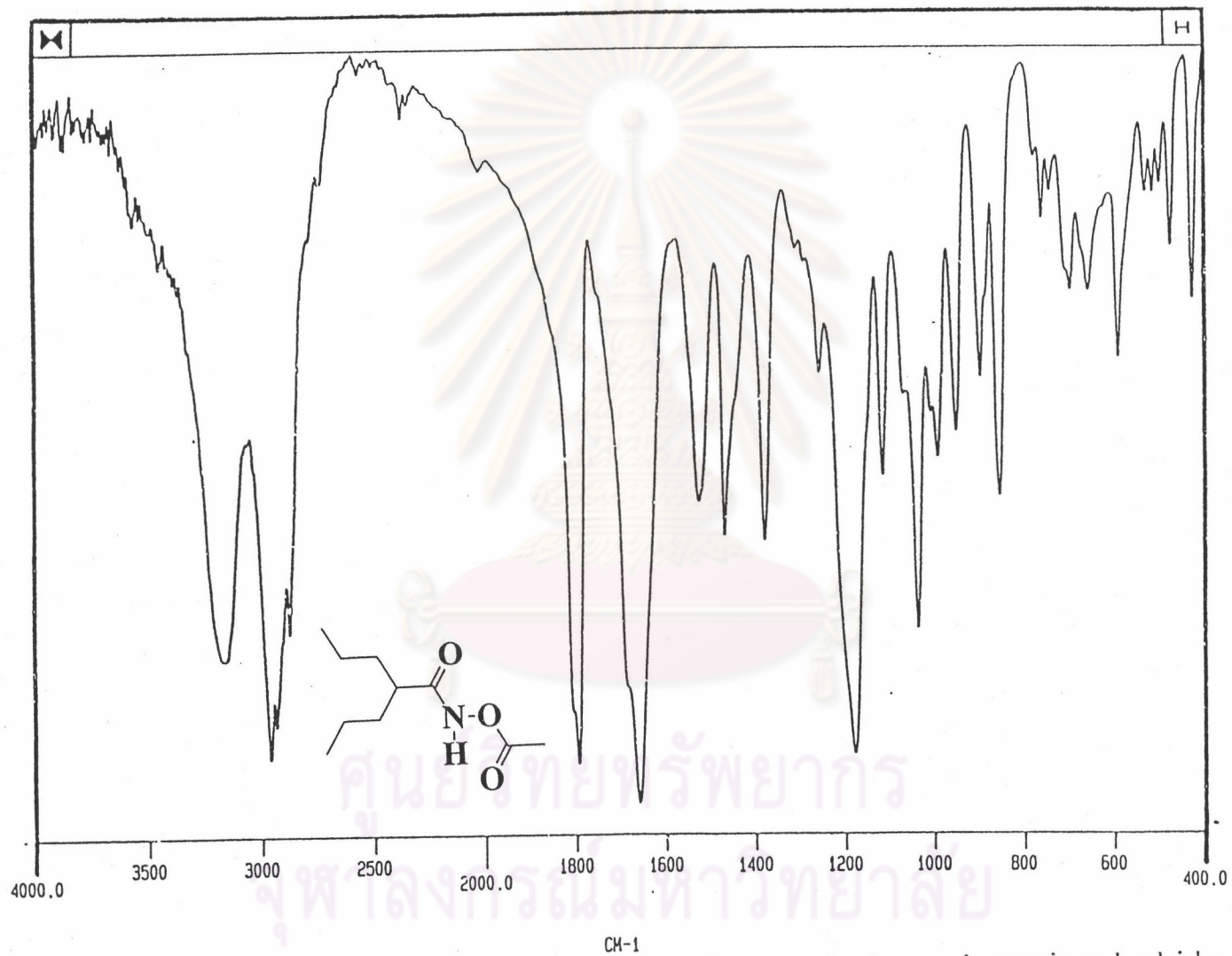


Figure 65. The IR spectrum (KBr pellet) of 2-propylpentanohydroxamic acetic anhydride.

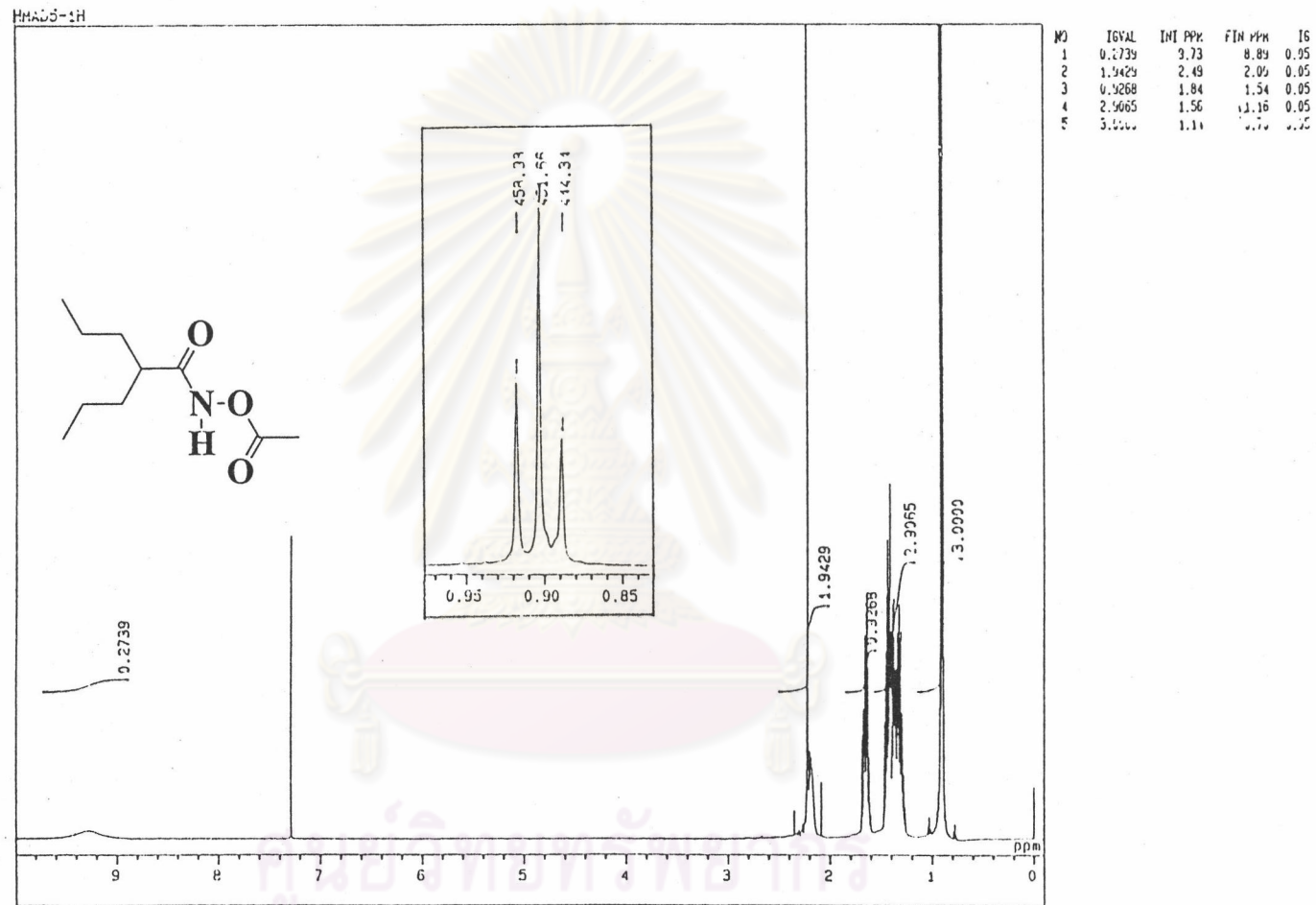


Figure 66. The 500 MHz  $^1\text{H}$ -NMR spectrum of 2-propylpentanohydroxamic acetic anhydride.



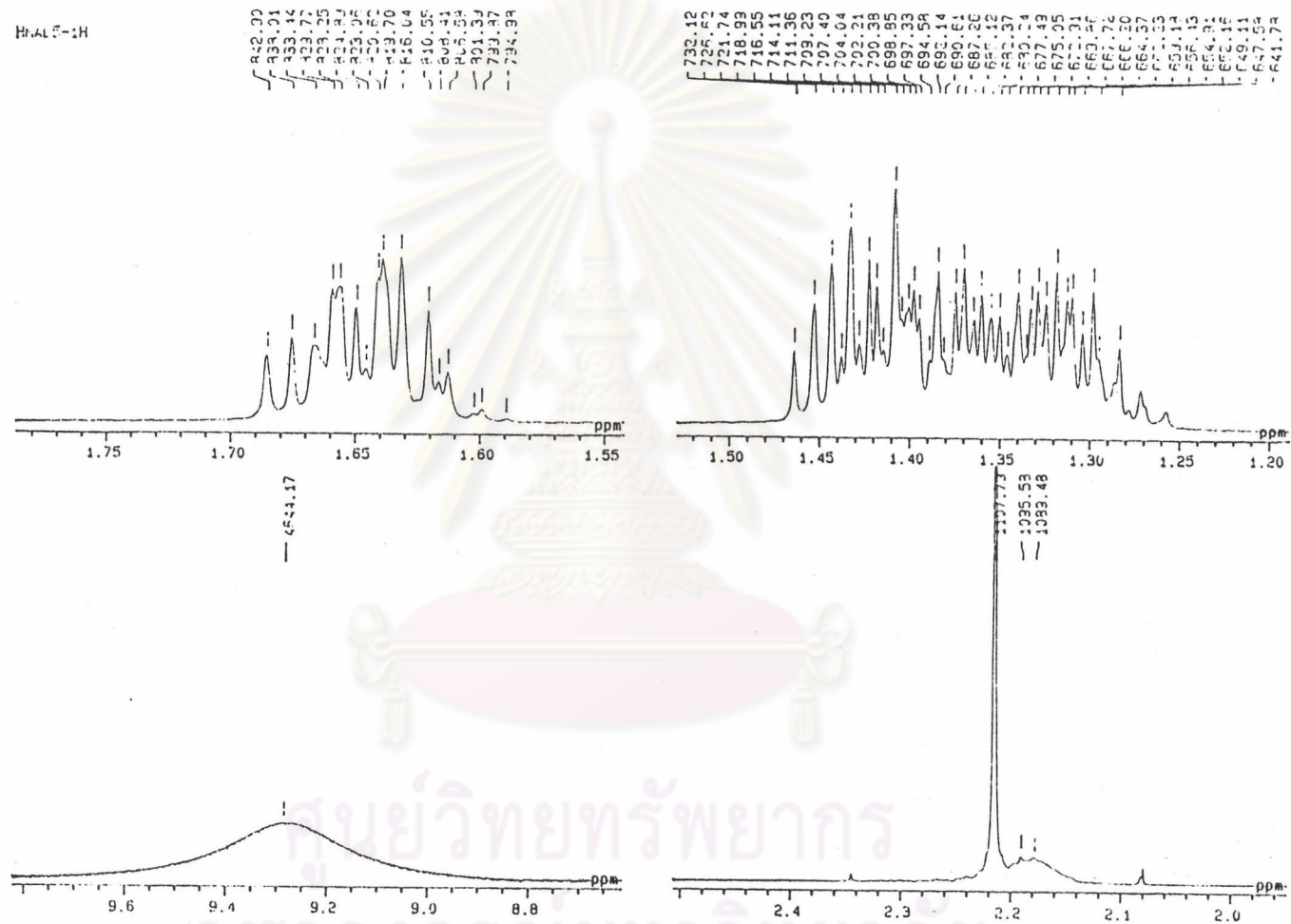


Figure 67. The 500 MHz  $^1\text{H-NMR}$  spectrum of 2-propylpentanohydroxamic acetic anhydride. (Enlarge scale : 1.20-9.80 ppm)

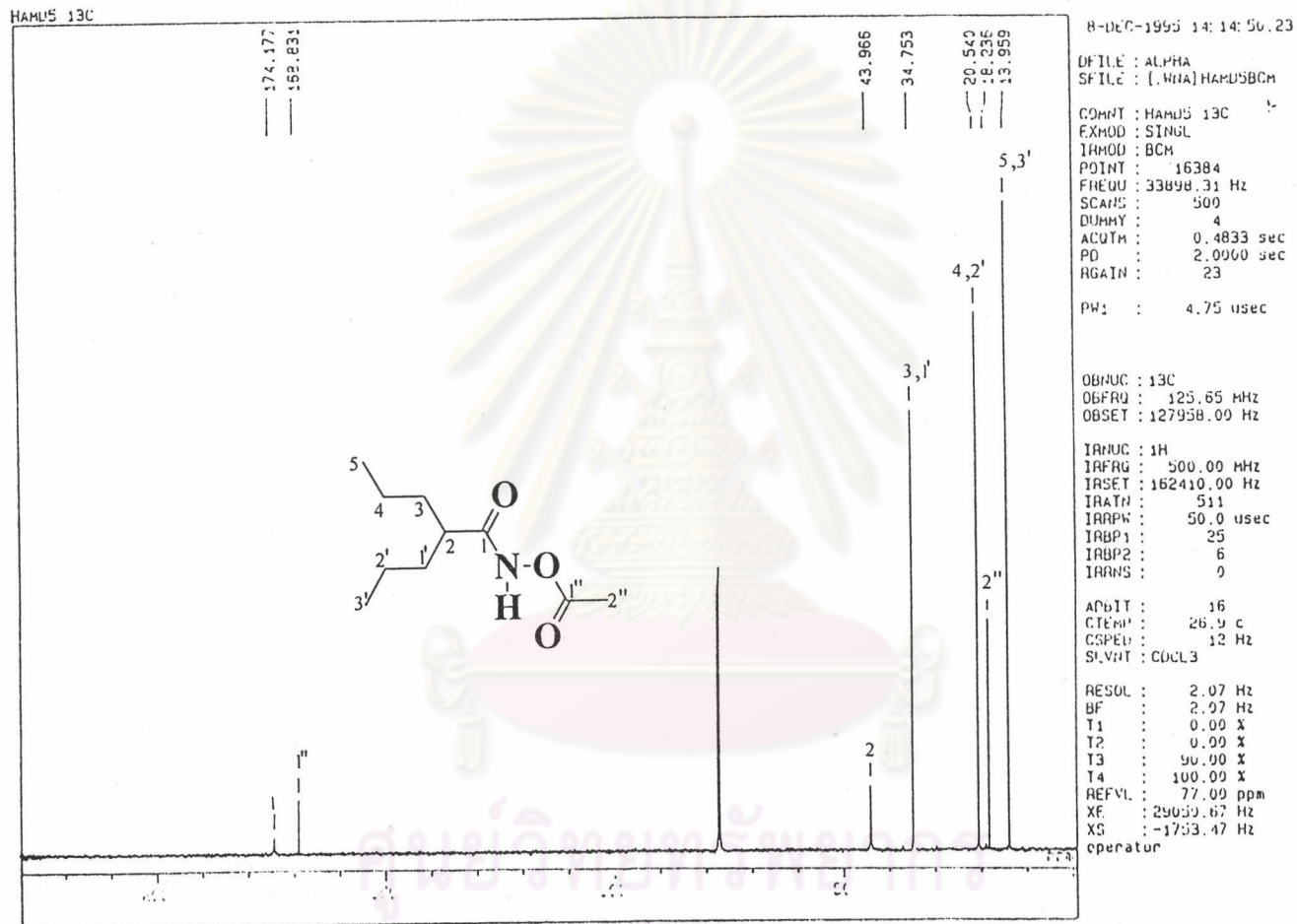


Figure 68. The  $^{13}\text{C}$ -NMR decoupled spectrum of 2-propylpentanohydroxamic acetic anhydride.

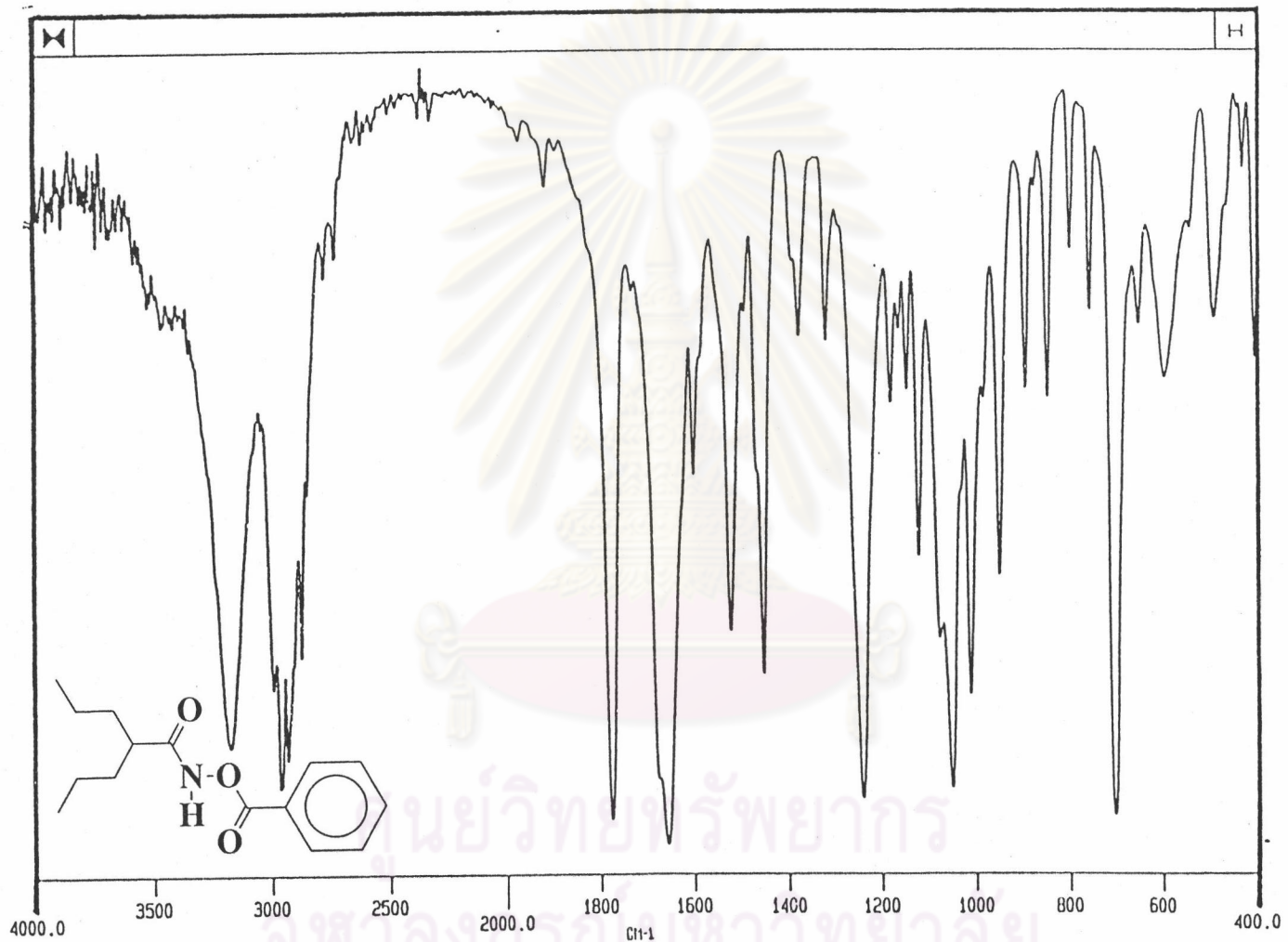


Figure 69. The IR spectrum (KBr pellet) of 2-propylpentanohydroxamic benzoic anhydride.

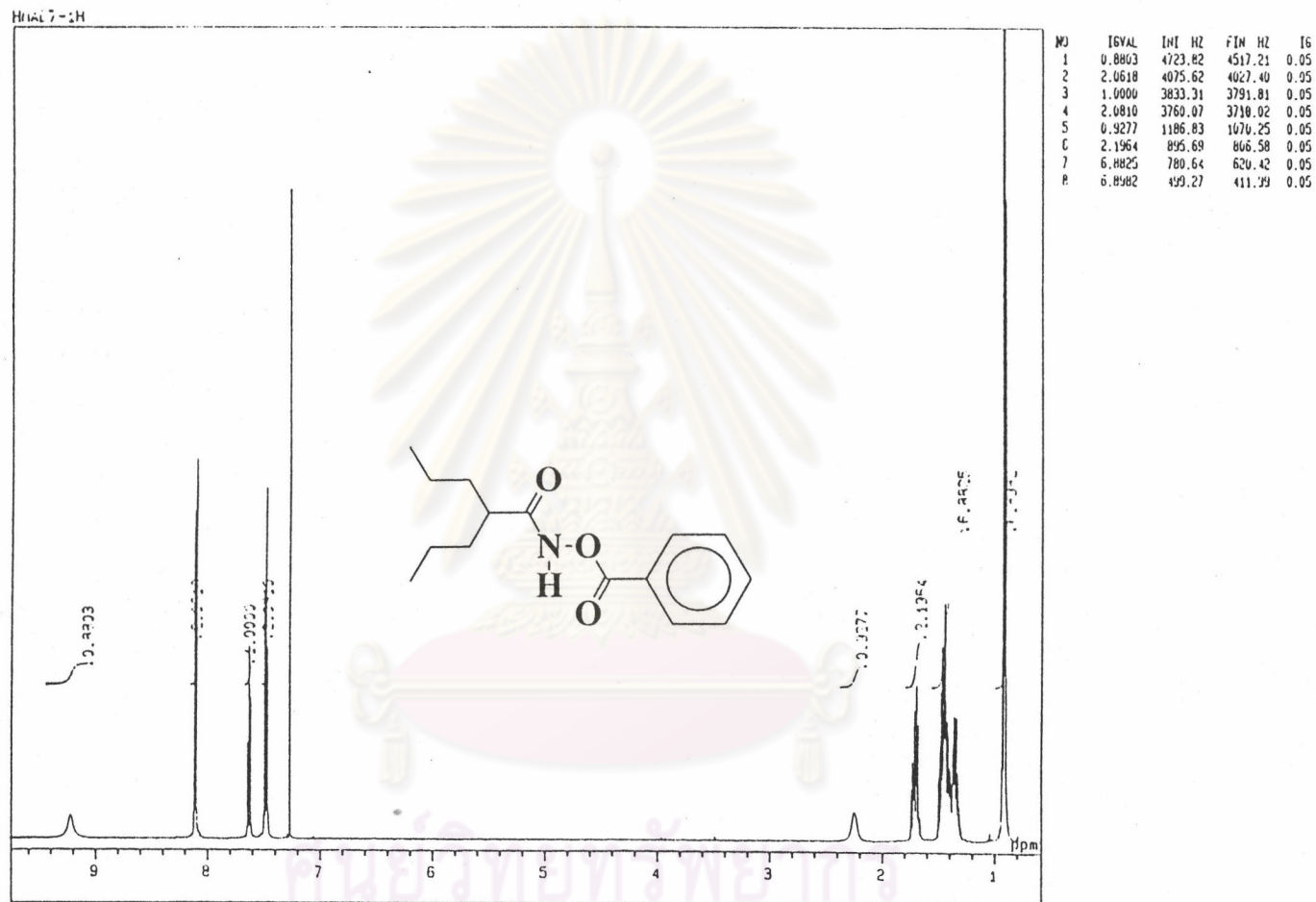


Figure 70. The 500 MHz  $^1\text{H-NMR}$  spectrum of 2-propylpentanohydroxamic benzoic anhydride.

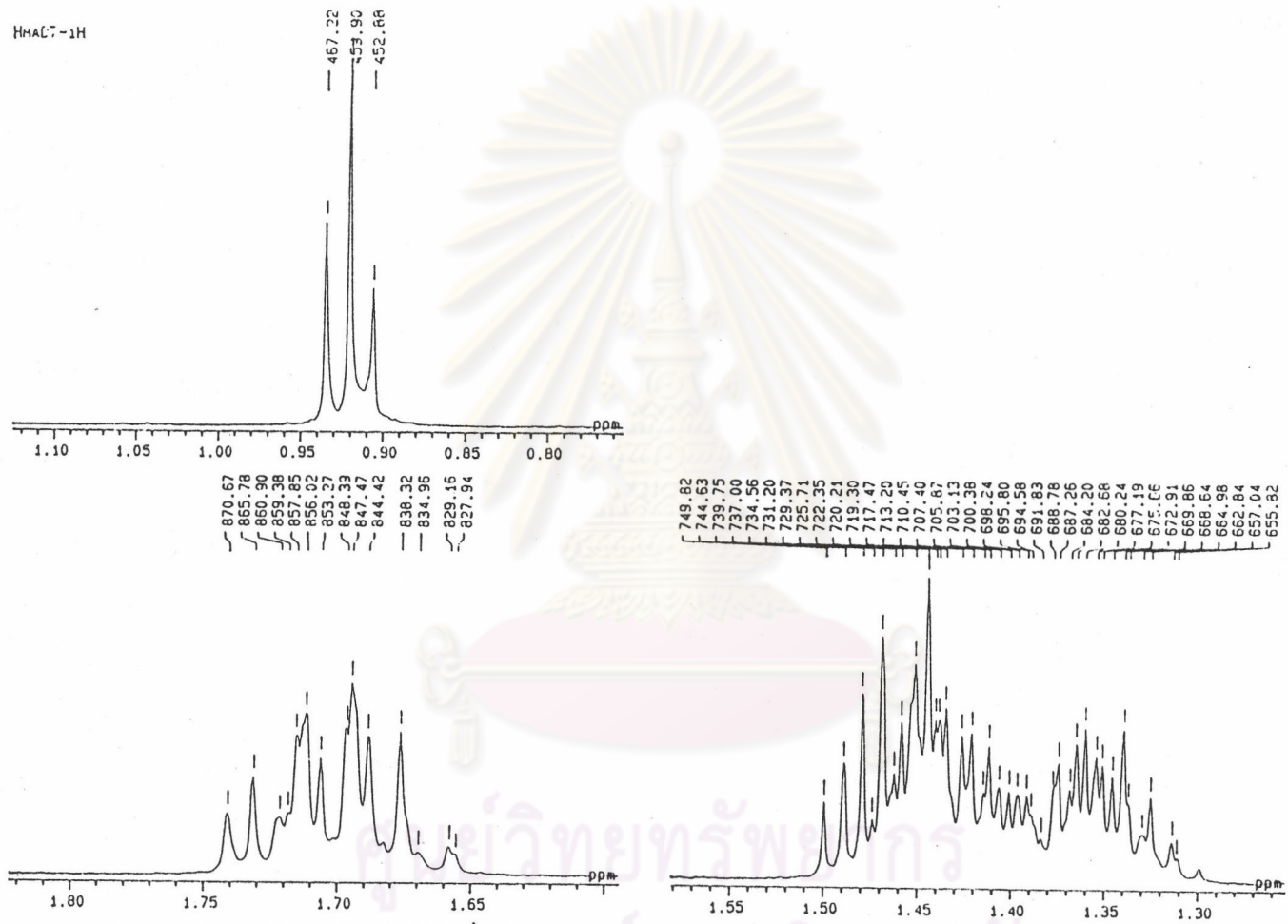


Figure 71. The 500 MHz  $^1\text{H}$ -NMR spectrum of 2-propylpentanohydroxamic benzoic anhydride. (Enlarge scale : 0.80-1.80 ppm)

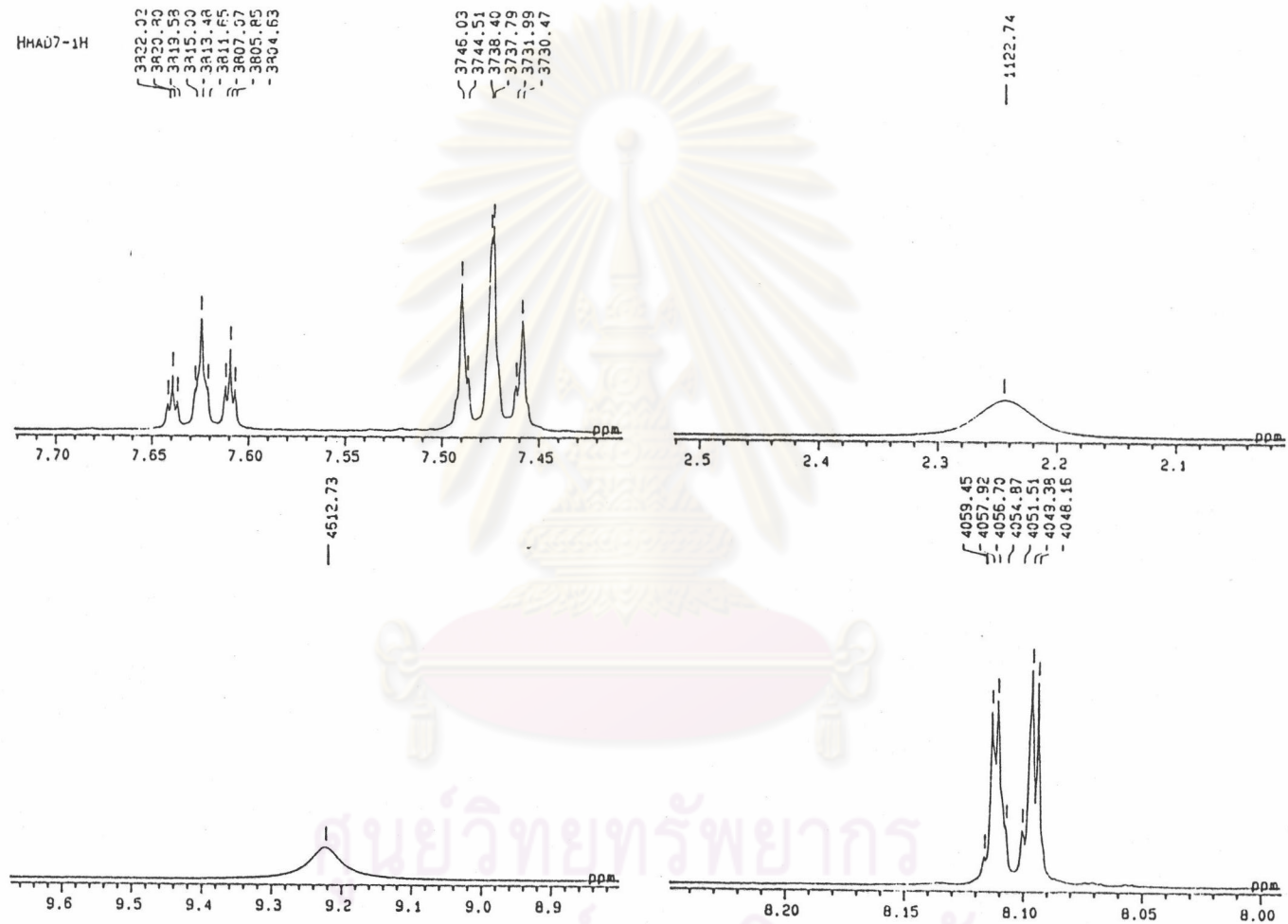
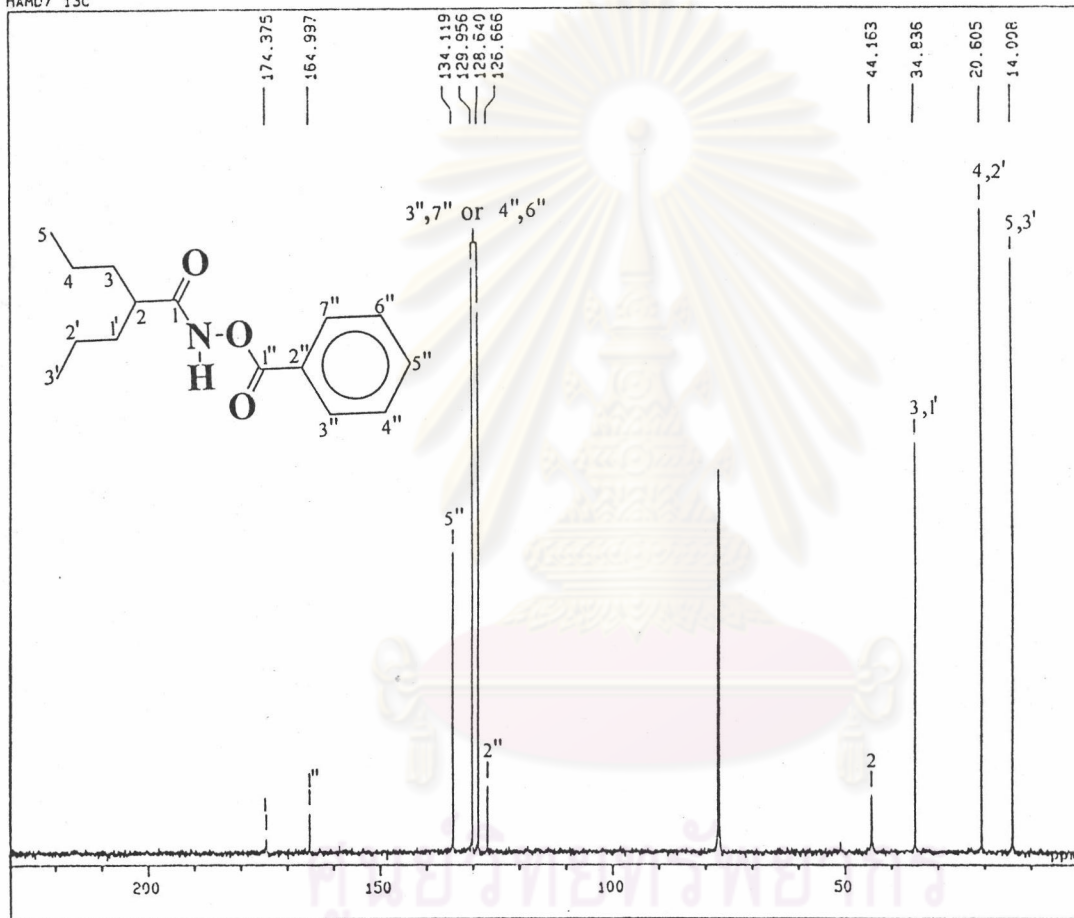


Figure 71. (Continued). The 500 MHz  $^1\text{H}$ -NMR spectrum of 2-propylpentano hydroxamic benzoic anhydride. (Enlarge scale : 2.0-9.6 ppm)

HAMD7 13C



8-DEC-1995 14:16:55.09

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 \* JNM-A500 \*  
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SFILE : (.WNA)HAMD7BCM  
 COMNT : HAMD7 13C

EXMOD : SINGL  
 IRMOD : BCM  
 POINT : 16384  
 FREQU : 33898.31 Hz  
 SCANS : 300  
 DUMMY : 4  
 ACUM : 0.4833 sec  
 PD : 2.0000 sec  
 RGAIN : 23  
 PW1 : 4.75 usec  
 OBHUC : 13C  
 OBFRO : 125.65 MHz  
 OBSET : 127958.00 Hz

IRHUC : 1H  
 IAFRQ : 500.00 MHz  
 IASET : 162410.00 Hz  
 IRATN : 511  
 IRAPW : 50.0 usec  
 IRBP1 : 25  
 IRBP2 : 6  
 IRRNS : 0

AMBIT : 16  
 CTEMP : 26.4 c  
 CSPED : 10 Hz  
 SOLVENT : CDCL3  
 RESOL : 2.07 Hz  
 BF : 2.07 Hz  
 REFVL : 77.00 ppm  
 XE : 29050.67 Hz  
 XS : -1753.47 Hz

OPERATOR :

Figure 72. The  $^{13}\text{C}$ -NMR decoupled spectrum of 2-propylpentano hydroxamic benzoic anhydride.

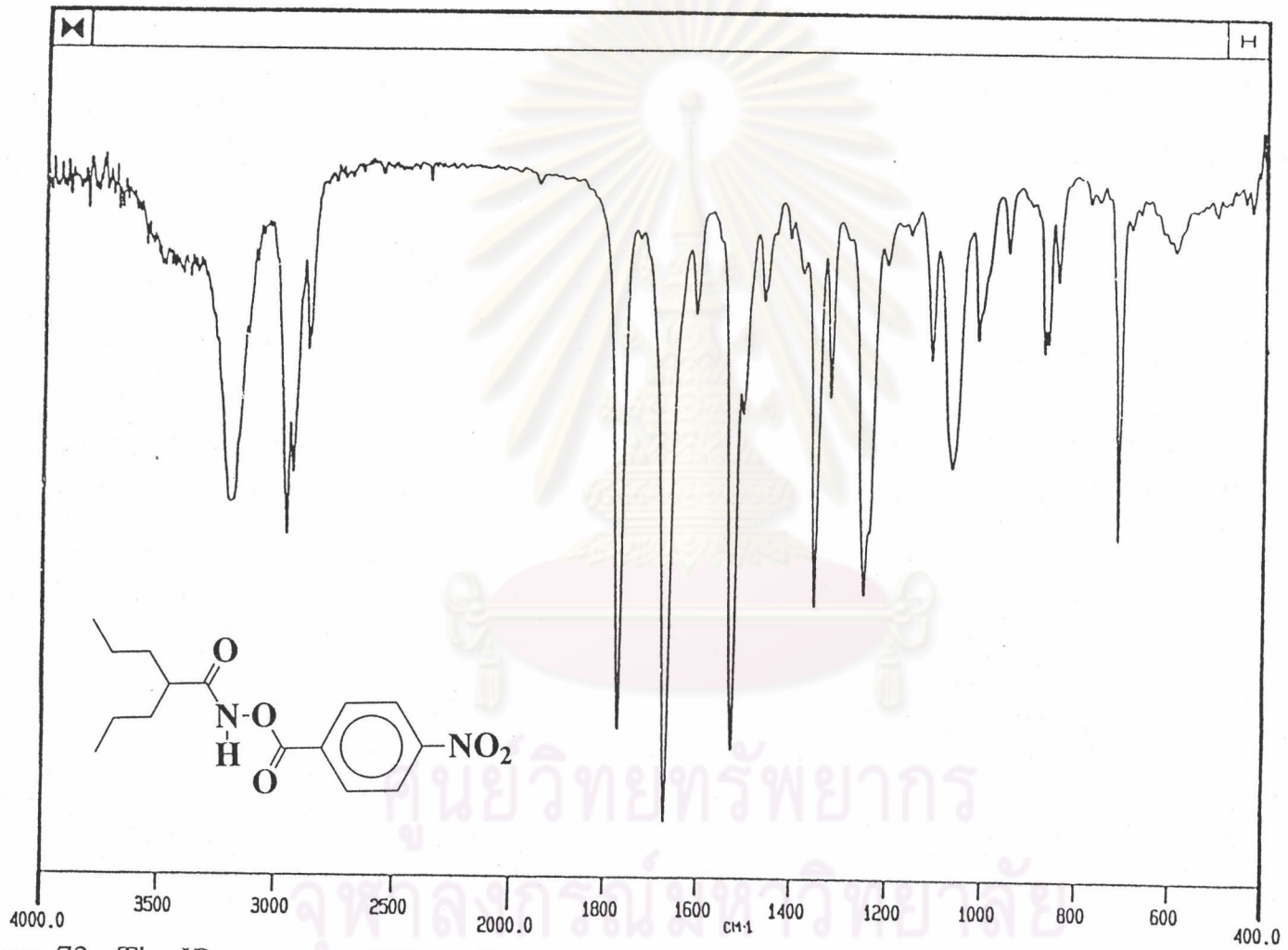


Figure 73. The IR spectrum (KBr pellet) of 2-propylpentanohydroxamic 4-nitrobenzoic anhydride.



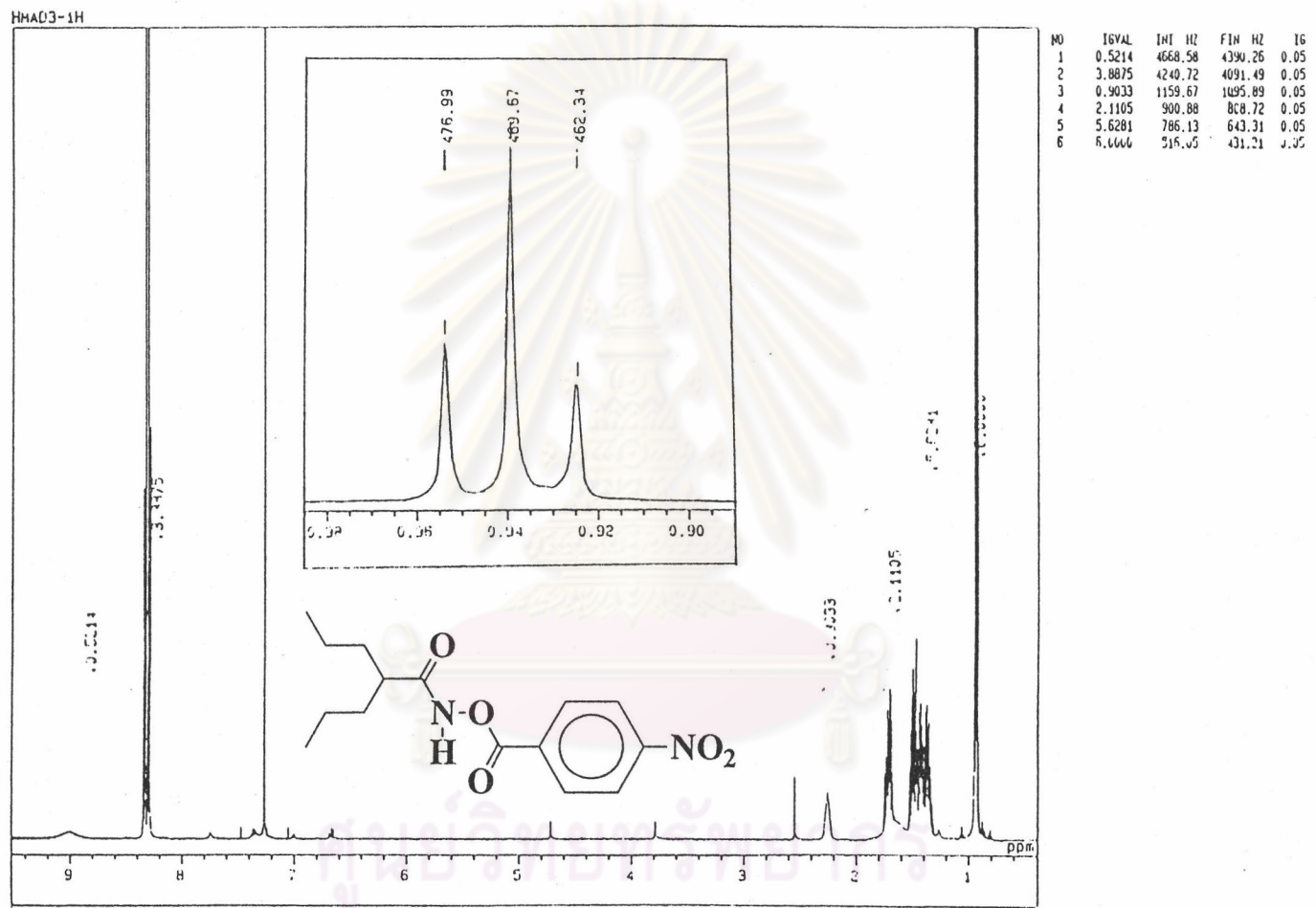


Figure 74. The 500 MHz <sup>1</sup>H-NMR spectrum of 2-propylpentanohydroxamic 4-nitrobenzoic anhydride.

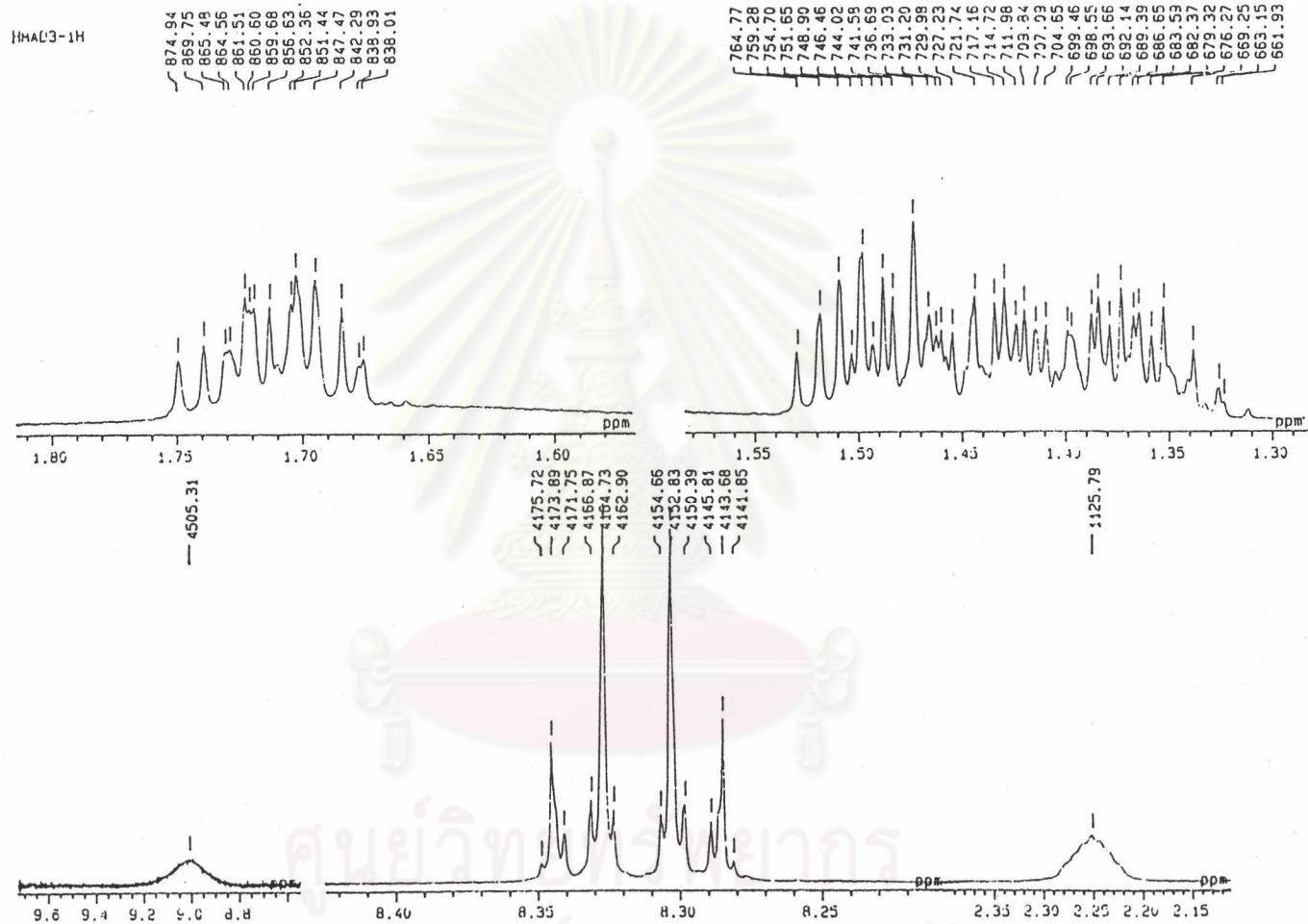


Figure 75. The 500 MHz <sup>1</sup>H-NMR spectrum of 2-propylpentanohydroxamic 4-nitrobenzoic anhydride. (Enlarge scale : 1.30-9.6 ppm)

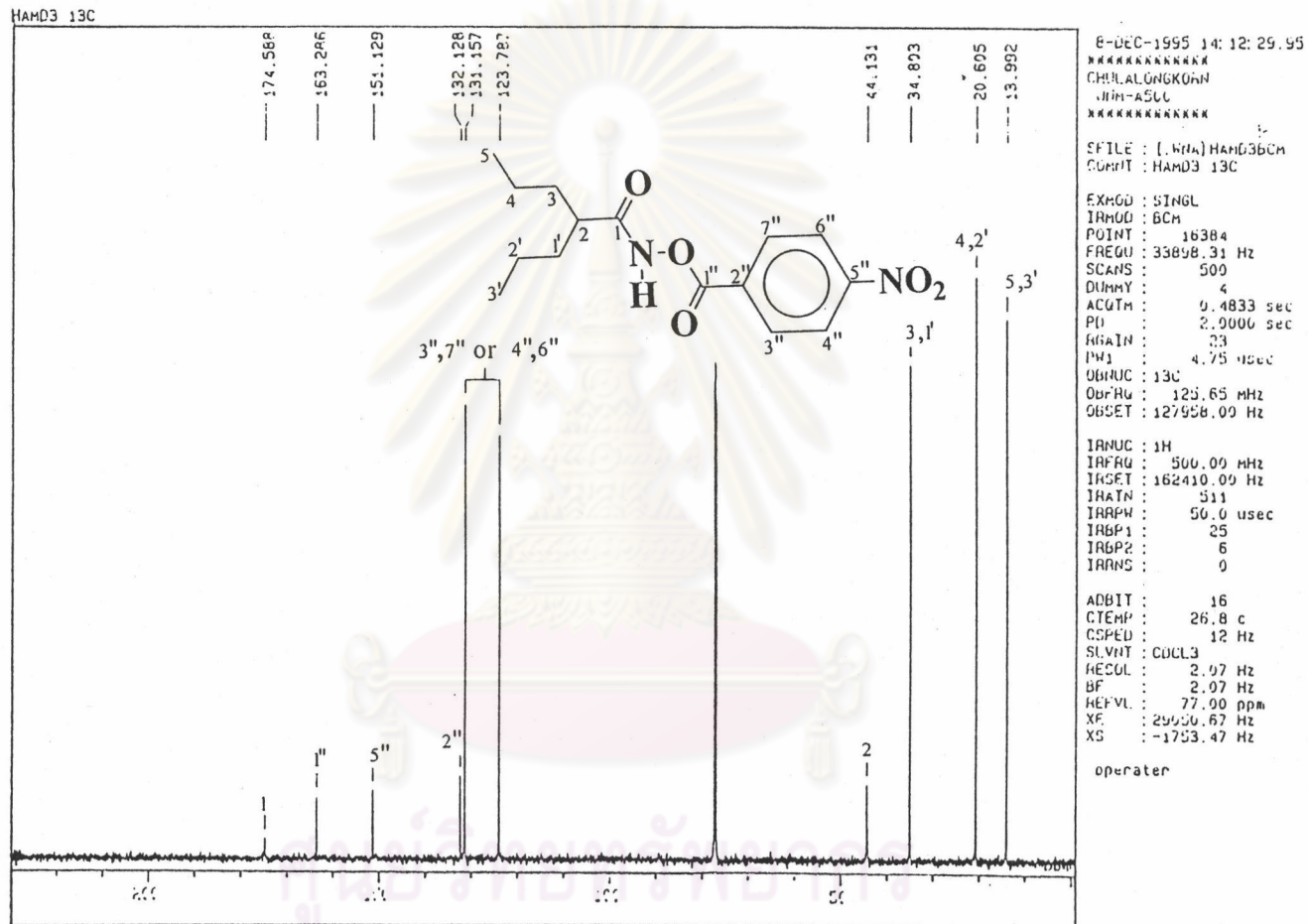


Figure 76. The  $^{13}\text{C}$ -NMR decoupled spectrum of 2-propylpentanohydroxamic 4-nitrobenzoic anhydride.

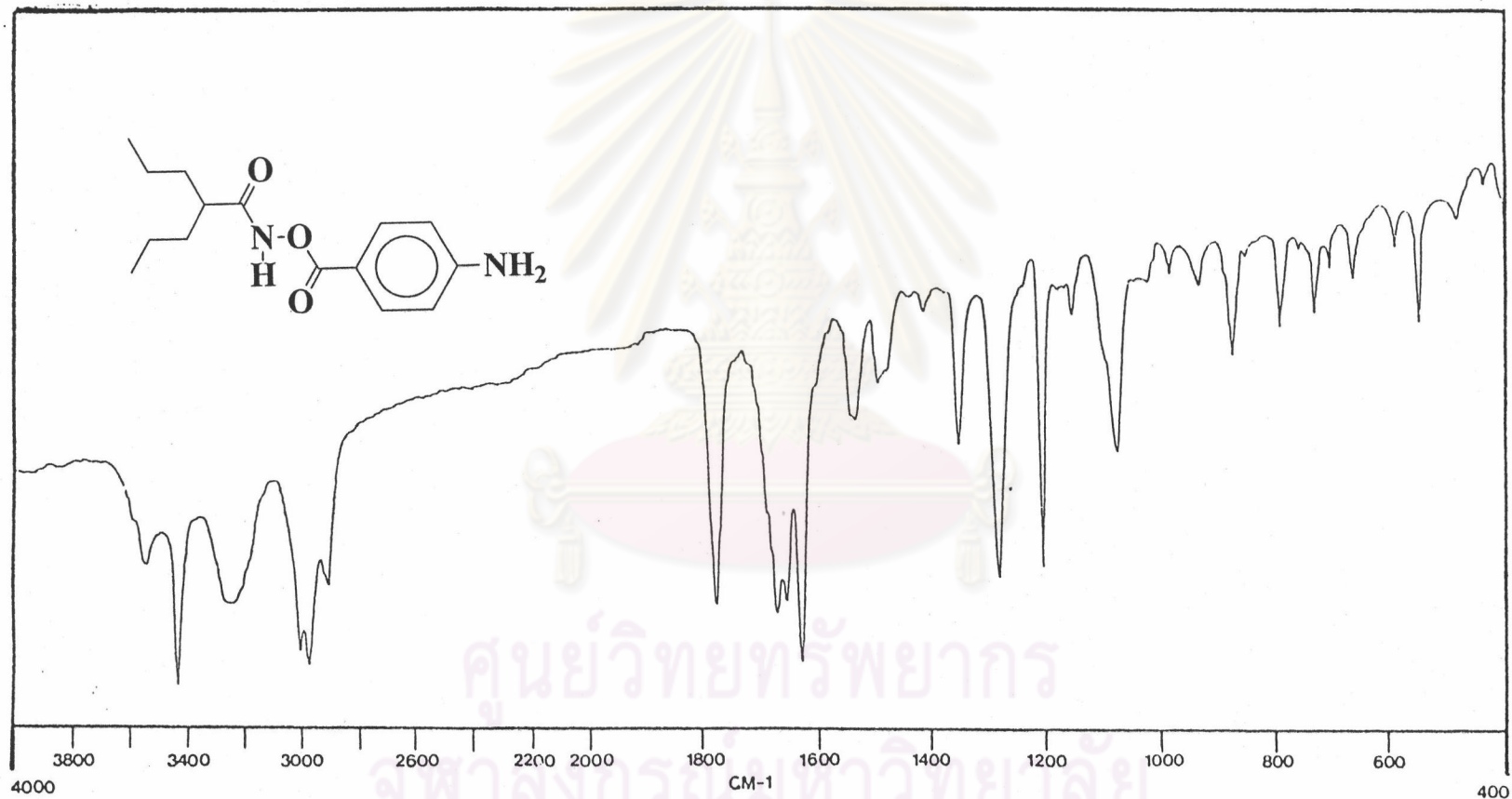


Figure 77. The IR spectrum (KBr pellet) of 2-propylpentanohydroxamic 4-aminobenzoic anhydride.

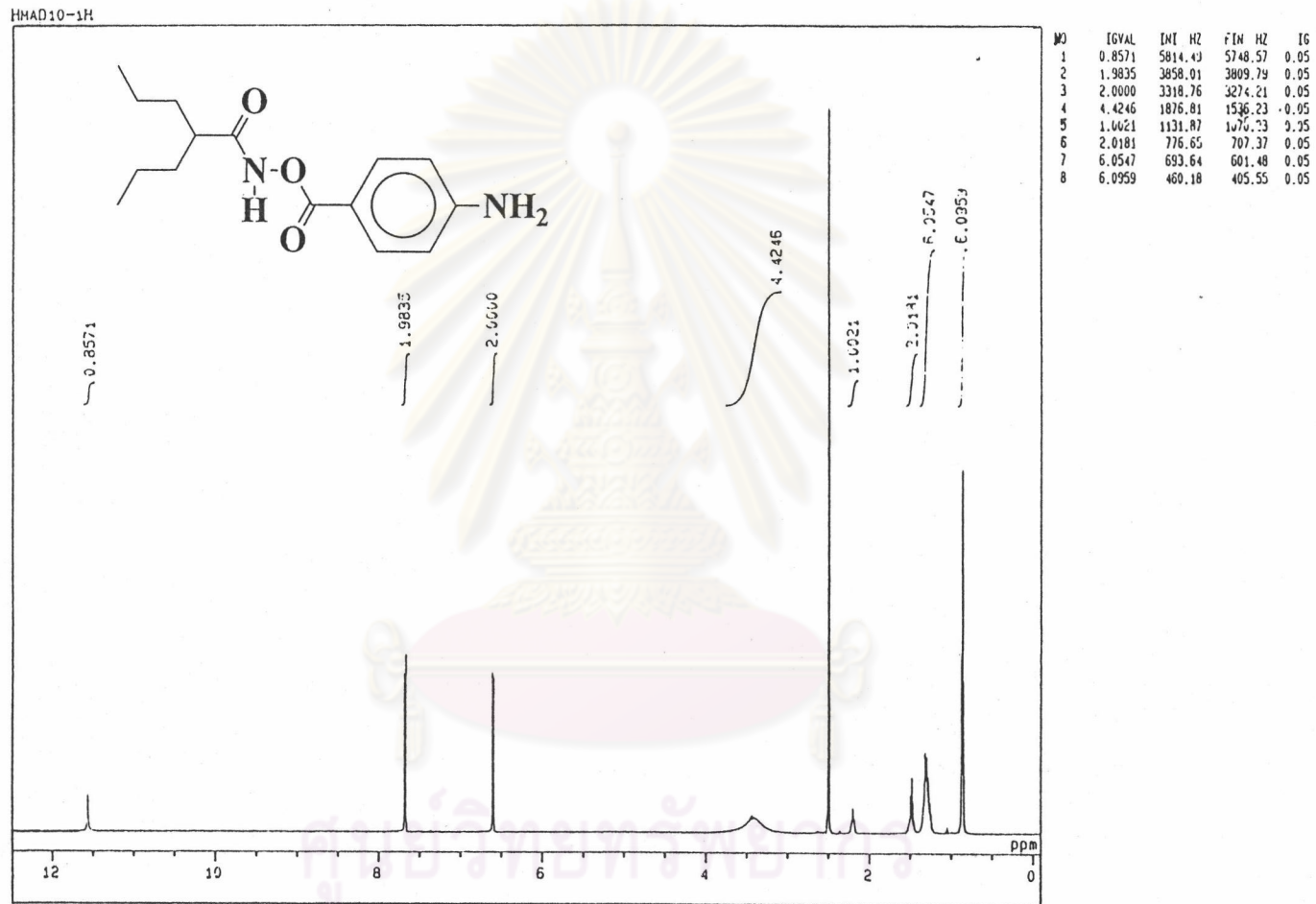


Figure 78. The 500 MHz  $^1\text{H}$ -NMR spectrum of 2-propylpentanohydroxamic 4-aminobenzoic anhydride.

HNAL10-1H

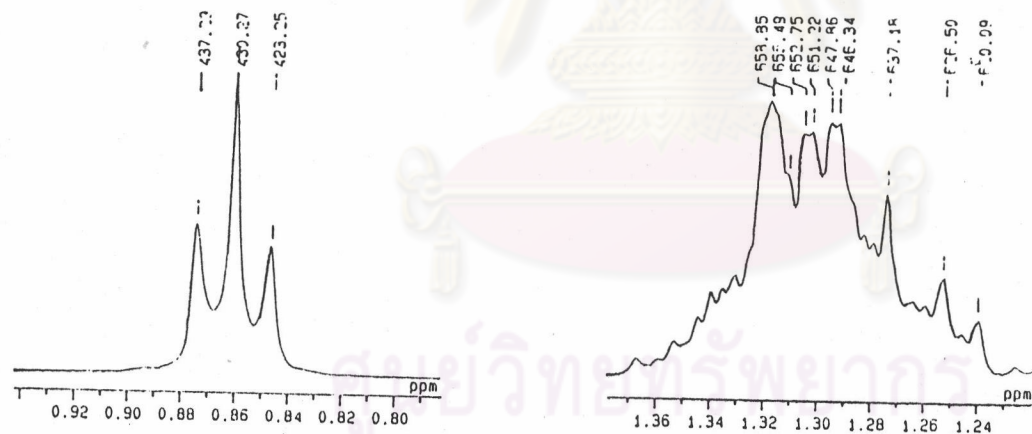


Figure 79. The 500 MHz <sup>1</sup>H-NMR spectrum of 2-propylpentanohydroxamic 4-aminobenzoic anhydride. (Enlarge scale : 0.80-1.38 ppm)

HMAD10-1H

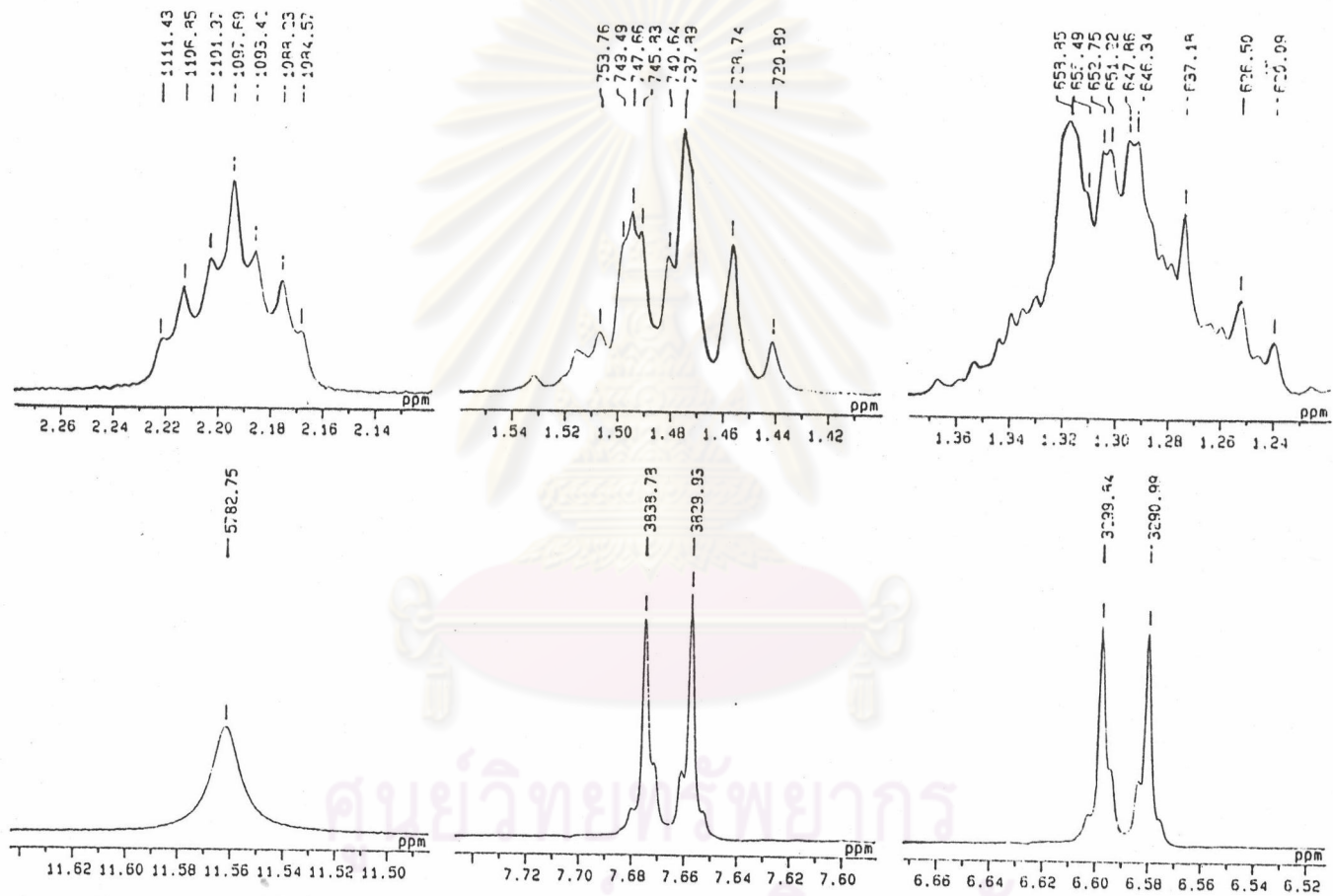


Figure 79. (Continued). The 500 MHz <sup>1</sup>H-NMR spectrum of 2-propyl pentanohydroxamic 4-aminobenzoic anhydride. (Enlarge scale : 1.24-11.63 ppm)

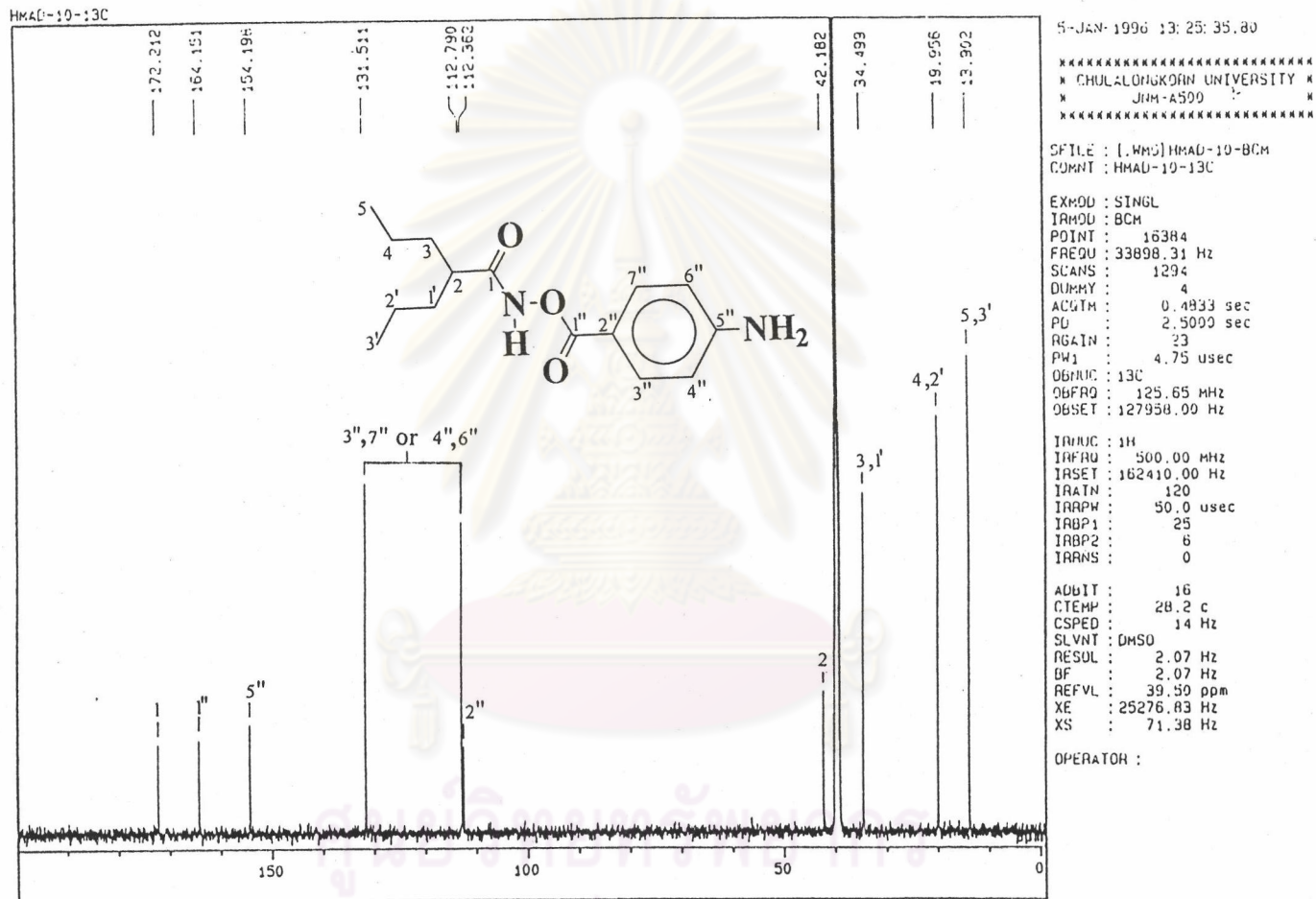


Figure 80. The  $^{13}\text{C}$ -NMR decoupled spectrum of 2-propylpentanohydroxamic 4-aminobenzoic anhydride.